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Supporting Information

Asymmetric binary-acid catalysis: a diastereo- and enantioselective oxa-Nazarov-cyclization Michael addition of conjugated 1,2-diketones

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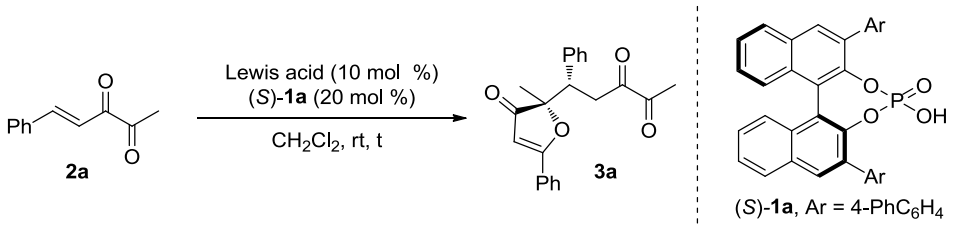
I. General Experimental Information and Materials

All commercial reagents were used without further purification unless otherwise noted. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker Avance 500MHz spectrometer. Tetramethylsilane (TMS) served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR. ^{1}H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet is10. High resolution mass spectra were obtained on an Ultima Global spectrometer with an ESI source. The enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) analysis using as Shimadzu SPD-20A on Chiral Diacel Chiralpak AD-H, and OD-H columns. Optical rotations were measured on an INESA WZZ-2S. According to the known reference, compounds **2a-s**,[1] **2t-v**,[2] and **2w-x**[3] were prepared.

II. Optimization

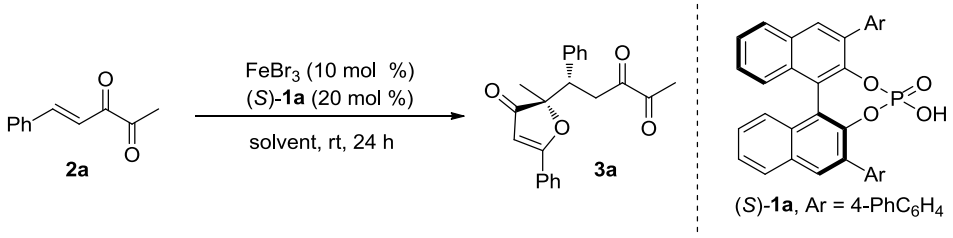
Table S1. Screening of Different Lewis Acids[a]



Entry	Lewis acid	t (h)	Yield [%][b]	ee [%][c]
1	$InBr_3$	24	94 (75:25)	23
2	$InCl_3$	24	93 (67:33)	18
3	InI_3	24	94 (75:25)	27
4	$In(OTf)_3$	24	91 (80:20)	13
5	$Sc(OTf)_3$	24	94 (90:10)	25
6	$Bi(OTf)_3$	6	93 (75:25)	3
7	**$FeBr_3$**	**24**	**96 (80:20)**	**56**
8	$FeCl_3$	24	95 (75:25)	56
9	$HfCl_4$	48	91 (71:29)	5
10	$Hf(OTf)_4$	48	21 (67:33)	37
11	$Ni(OTf)_2$	48	32 (83:17)	63
12	$Cu(OTf)_2$	24	94 (75:25)	27
13	$Zn(OTf)_2$	48	93 (75:25)	38
14	$AgBF_4$	48	64 (67:33)	17
15	Ph_3CBF_4	48	92 (60:40)	34

[a] Reaction conditions: **2a** (0.1 mmol), **1a** (20 mol %), Lewis acid (10 mol %) at room temperature in CH_2Cl_2 (0.5 mL). [b] Isolated yield, diastereomeric ratio (in parenthesis) was determined by ^1H NMR. [c] Enantiomeric excess determined by chiral HPLC analysis.

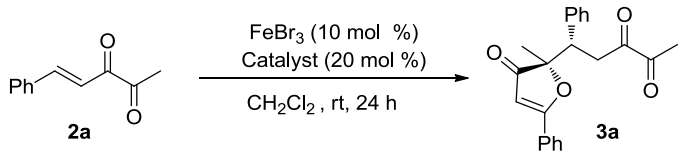
Table S2. Screening of Other Different Lewis Acids[a]

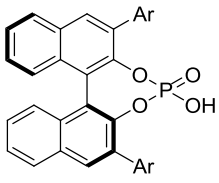


Entry	Solvent	Yield [%][b]	ee [%][c]
1	**CH_2Cl_2**	**96 (80:20)**	**56**
2	$CHCl_3$	67 (60:40)	11
3	$CH_3CO_2C_2H_5$	48 (67:33)	33
4	THF	NR	–
5	1,4-dioxane	NR	–
6	Et_2O	Trace	–
7	MeCN	37 (67:33)	–
8	n-Hexane	14 (67:33)	27
9	DMSO	NR	–
10	CH_3OH	NR	–
11	DMF	NR	–
12	Acetone	NR	–

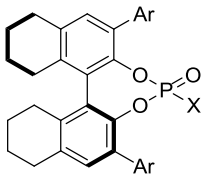
[a] Reaction conditions: **2a** (0.1 mmol), **1a** (20 mol %), $FeBr_3$ (10 mol %) at room temperature in solvent (0.5 mL) for 24 h. [b] Isolated yield, diastereomeric ratio (in parenthesis) was determined by ^1H NMR. [c] Enantiomeric excess determined by chiral HPLC analysis.

Table S3. Screening of Different Chiral Phosphoric Acid[a]





(*S*)-**1a**, Ar = 4-PhC_6H_4
(*S*)-**1b**, Ar = 4-(2-Nap)C_6H_4
(*S*)-**1c**, Ar = 4-$CH_3C_6H_4$
(*S*)-**1d**, Ar = 1-Pyren
(*S*)-**1f**, Ar = 4-$NO_2C_6H_4$
(*S*)-**1g**, Ar = 2,4,6-$Me_3C_6H_2$
(*S*)-**1h**, Ar = 9-Anthryl



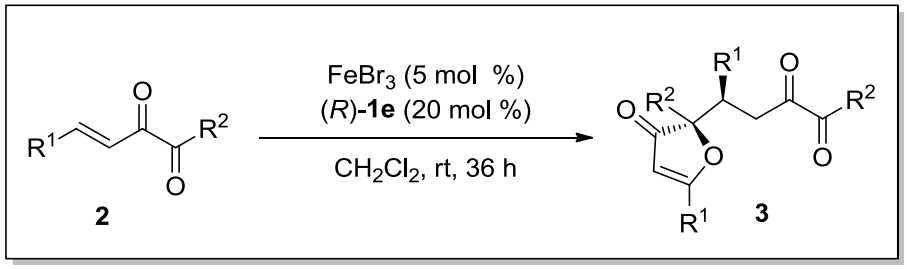
X = OH:
(*S*)-**1e**, Ar = 1-Pyren
(*S*)-**1i**, Ar = 4-PhC_6H_4
(*S*)-**1j**, Ar = 4-(2-Nap)C_6H_4
(*S*)-**1k**, Ar = 9-Anthryl
X = NHTf:
(*S*)-**1l** Ar = 1-Pyren

Entry	Catalyst	Yield [%][b]	ee [%][c]
1	(*S*)-**1a**	96 (80:20)	56
2	(*S*)-**1b**	92 (89:11)	71
3	(*S*)-**1c**	92 (85:15)	53
4	(*S*)-**1d**	90 (83:17)	73
5	**(*S*)-1e**	**89 (96:4)**	**81**
6	(*S*)-**1f**	90 (83:17)	73
7	(*S*)-**1g**	83 (80:20)	7
8	(*S*)-**1h**	81 (80:20)	70
9	(*S*)-**1i**	87 (86:14)	68
10	(*S*)-**1j**	87 (88:12)	66
11	(*S*)-**1k**	88 (88:12)	70
12	(*S*)-**1l**	95 (80:20)	7

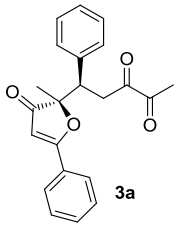
[a] Reaction conditions: **2a** (0.1 mmol), catalyst (*S*)-**1** (20 mol %), $FeBr_3$ (10 mol %) at room temperature in CH_2Cl_2 (0.5 mL) for 24 h. [b] Isolated yield, diastereomeric ratio (in parenthesis) was determined by ^1H NMR. [c] Enantiomeric excess determined by chiral HPLC analysis.

III. Experimental Procedures and Characterization Data

A) Synthesis of chiral *syn*-3(*2H*)-furanones:

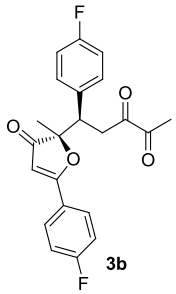


General procedure I: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (0.005 mmol, 5 mol %) and chiral phosphoric acid (*R*)-**1e** (0.02 mmol, 20 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketones **2** (0.2 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 36 h. After reaction, the mixture was directly loaded onto silica gel column and eluted with PE/EA (5:1) to give the chiral target product.



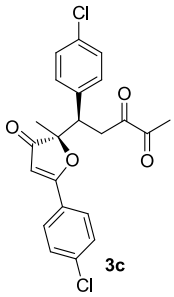
(R)-5-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-5-phenylpentane-2,3-dione 3a: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (34.5 mg, 99% yield, 90:10 dr, 96% ee for *syn*-**3a**); $[\alpha]_D^{30}$ = +139.1 (c = 0.33 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 0.22 H), 7.63–7.60 (m, 1H), 7.56–7.53 (m, 2H), 7.49-7.47 (m, 0.33H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.28 – 7.27 (m, 1H), 7.18 – 7.14 (m, 0.55H), 6.07 (s, 1H), 5.71 (s, 0.11H), 3.77 – 3.75 (m, 0.11H), 3.69 – 3.67 (m, 1H), 3.53–3.51 (m, 0.11H), 3.47–3.41 (m, 1.11H), 2.78-2.74 (m, 1H), 2.12 (s, 0.33H), 2.06 (s, 3H), 1.49 (s, 0.33H),

1.25 (s, 3H) ppm; major isomer *syn*-**3a**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 197.0, 196.7, 184.8, 138.4, 133.1, 129.5, 129.1, 128.5, 127.6, 127.3, 127.0, 100.6, 92.4, 46.2, 36.3, 23.4, 21.6, ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{20}NaO_4$ 371.1254, found 371.1259; HPLC analysis (*syn*-**3a**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 8.4 min (major), 9.0 min (minor).



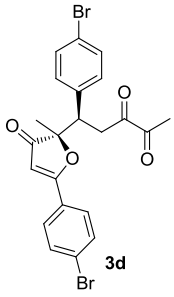
3b

(R)-5-(4-fluorophenyl)-5-((S)-5-(4-fluorophenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3b: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (37.3 mg, 97% yield, 90:10 dr, 95% ee for *syn*-**3b**); $[\alpha]_D^{30}$ = +162.7 (c = 0.36 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 5.5 Hz, 2H), 7.78 – 7.76 (m, 0.33H), 7.35 (dd, *J* = 8.0, 6.0 Hz, 2H), 7.28-7.13 (m, 2.55H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.83 (t, *J* = 8.5 Hz, 0.22H), 6.01 (s, 1H), 5.67 (s, 0.11H), 3.75 (dd, *J* = 9.5, 5.5 Hz, 0.11H), 3.69 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.53 (dd, *J* = 17.5, 9.5 Hz, 0.11H), 3.46 – 3.40 (m, 1.11H), 2.77 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.17 (s, 0.33H), 2.12 (s, 3H), 1.48 (s, 0.33H), 1.25 (s, 3H) ppm; major isomer *syn*-**3b**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 196.8, 196.3, 183.5, 165.6 (d, $^1J_{C\text{-}F}$ = 254.1 Hz), 162.1 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 134.0 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 130.9 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 129.6 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 124.8 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 116.4 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 100.4, 92.4, 45.4, 36.4, 23.4, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}F_2NaO_4$ 407.1065, found 407.1064; HPLC analysis (*syn*-**3b**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 9.3 min (major), 10.7 min (minor).



3c

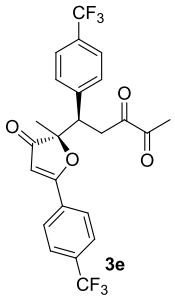
(R)-5-(4-chlorophenyl)-5-((S)-5-(4-chlorophenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3c: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (38.4 mg, 92% yield, 90:10 dr, 96% ee for *syn*-**3c**); $[\alpha]_D^{30}$ = +163.4 (c = 0.45 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 0.22H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 0.22H), 7.31 (s, 4H), 7.11 (s, 0.44H), 6.04 (s, 1H), 5.71 (s, 0.11H), 3.73 (dd, *J* = 9.5, 5.0 Hz, 0.11H), 3.67 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.52 (dd, *J* = 18.0, 10.0 Hz, 1H), 3.45 – 3.39 (m, 1.11H), 2.77 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.19 (s, 0.33H), 2.13 (s, 3H), 1.48 (s, 0.33H), 1.25 (s, 3H) ppm; major isomer *syn*-**3c**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 196.7, 196.1, 183.4, 139.5, 136.8, 133.5, 130.7, 129.5, 128.7, 128.5, 126.9, 100.9, 92.3, 45.5, 44.7, 36.1, 26.9, 23.5, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}Cl_2NaO_4$ 439.0474, found 439.0474; HPLC analysis (*syn*-**3c**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 10.4 min (major), 13.6 min (minor).



3d

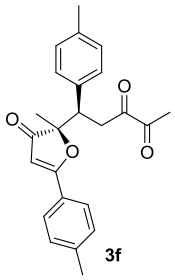
(R)-5-(4-bromophenyl)-5-((S)-5-(4-bromophenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3d: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (47.9 mg, 95% yield, 84:16 dr, 96% ee for *syn*-**3d**); $[\alpha]_D^{30}$ = +153.3 (c = 0.62 in $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.62 (m, 1.19H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 1.95H), 7.07 (d, *J* = 8.0 Hz, 0.38H), 6.06 (s, 1H), 5.74 (s, 0.19H), 3.74 (dd, *J* = 9.5, 5.0 Hz, 0.19H), 3.67 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.53 (dd, *J* = 17.5, 9.5 Hz, 0.19H), 3.46 – 3.41 (m, 1.19H), 2.78 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.22 (s, 0.57H), 2.15 (s, 3H), 1.49 (s, 0.57H), 1.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 204.8, 197.0, 196.7, 196.4, 196.1, 183.5, 182.5, 137.3, 136.6, 132.5, 132.4, 131.7, 131.3, 131.1, 130.7, 128.5, 128.4, 128.0, 127.4, 121.66, 121.65, 101.0, 100.6, 92.2, 91.2, 45.6, 44.8, 36.1, 35.6, 23.5, 23.4, 21.6,19.9 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}NaBr_2O_4$ 526.9464, found 526.9473; HPLC analysis (*syn*-**3d**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 9.6 min (major), 12.1 min (minor).



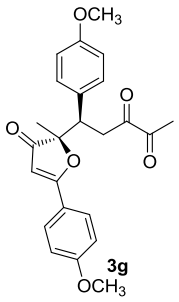
(R)-5-((S)-2-methyl-3-oxo-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrofuran-2-yl)-5-(4-(trifluoromethyl)phenyl)pentane-2,3-dione 3e: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (45.1 mg, 93% yield, 84:16 dr, 90% ee for *syn*-**3e**); $[\alpha]_D^{30}$ = +186.8 (c = 0.54 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 0.38H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 0.38H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 0.38H), 7.34 (d, *J* = 8.0 Hz, 0.38H), 6.18 (s, 1H), 5.84 (s, 0.19H), 3.86 (dd, *J* = 9.5, 5.0 Hz, 0.19H), 3.80 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.60 (dd, *J* = 18.0, 9.0 Hz, 0.19H), 3.55 – 3.48 (m, 1.19H), 2.85 (dd, *J* = 18.5, 3.5 Hz, 1H), 2.24 (s, 0.57H), 2.17 (s, 3H), 1.53 (s, 0.57H), 1.30 (s, 3H) ppm; major isomer *syn*-**3e** ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 196.6, 195.7, 182.8, 142.3, 134.5 (q, $^2J_{C\text{-}F}$ =

32.5 Hz), 131.7, 129.8, 127.5, 126.1 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.5 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 102.1, 92.3, 45.9, 36.0, 23.4, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^{+}$ calcd for $C_{22}H_{18}F_6NaO_4$ 507.1001, found 507.1002; HPLC analysis (*syn*-**3e**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 14.0 min (major), 15.2 min (minor).

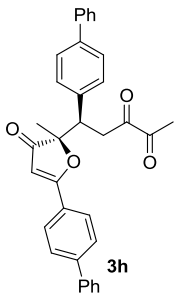


3f

(R)-5-((S)-2-methyl-3-oxo-5-(p-tolyl)-2,3-dihydrofuran-2-yl)-5-(p-tolyl)pentane-2,3-dione 3f: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (32.7 mg, 87% yield, 86:14 dr, 96% ee for *syn*-**3f**); $[\alpha]_D^{30}$ = +127.9 (c = 0.31 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 0.32H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 2.32H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 0.32H), 6.87 (d, *J* = 7.8 Hz, 0.32H), 5.94 (s, 1H), 5.60 (s, 0.16H), 3.63 (dd, *J* = 9.0, 6.0 Hz, 0.16H), 3.55 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.44 – 3.37 (m, 0.32H), 3.32 (dd, *J* = 17.5, 11.0 Hz, 1H), 2.65 (dd, *J* = 17.5, 3.5 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 0.48H), 2.25 (s, 3H), 2.14 (s, 0.48H), 2.04 (s, 0.48H), 1.98 (s, 3H), 1.39 (s, 0.48H), 1.15 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 205.4, 197.5, 197.2, 197.1, 196.8, 184.9, 183.9, 144.0, 143.6, 137.2, 137.0, 135.3, 134.6, 129.8, 129.6, 129.4, 129.2, 129.0, 128.9, 127.3, 127.1, 126.0, 125.9, 100.0, 99.7, 92.4, 91.2, 45.8, 45.1, 36.4, 36.0, 23.5, 23.4, 21.81, 21.76, 21.6, 21.1, 21.0, 19.8 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^{+}$ calcd for $C_{24}H_{24}NaO_4$ 399.1567, found 399.1568; HPLC analysis (*syn*-**3f**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 8.5 min (major), 10.3 min (minor).

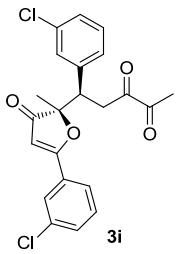


(R)-5-(4-methoxyphenyl)-5-((S)-5-(4-methoxyphenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3g: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (2:1) as the eluent. Yellow oil (21.5 mg, 53% yield, 75:25 dr, 84% ee for *syn*-**3g**); $[\alpha]_D^{30}$ = +117.9 (c = 0.37 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 0.66H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 0.66H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 0.66H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 0.66H), 5.95 (s, 1H), 5.61 (s, 0.33H), 3.91 (s, 3H), 3.89 (s, 0.99H), 3.80 (s, 3H), 3.70 (s, 0.99H), 3.62 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.49 (dd, *J* = 17.5, 10.0 Hz, 0.33H), 3.43 – 3.35 (m, 1.33H), 2.73 (dd, *J* = 17.5, 4.0 Hz, 1H), 2.11 (s, 0.99H), 2.06 (s, 3H), 1.47 (s, 1H), 1.23 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 205.1, 197.5, 197.4, 197.1, 197.0, 184.5, 183.6, 163.5, 158.9, 158.7, 130.6, 130.4, 130.2, 129.6, 129.3, 129.1, 121.2, 121.1, 114.5, 114.3, 113.8, 113.5, 99.0, 98.8, 92.5, 91.3, 55.6, 55.5, 55.2, 55.1, 45.5, 44.8, 36.5, 36.1, 23.5, 23.4, 21.6, 19.9 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{24}H_{24}NaO_6$ 431.1465, found 431.1467; HPLC analysis (*syn*-**3g**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 16.2 min (major), 22.3 min (minor).



(R)-5-([1,1'-biphenyl]-4-yl)-5-((S)-5-([1,1'-biphenyl]-4-yl)-2-methyl-3-oxo-2,3-dihydr

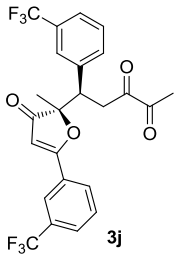
ofuran-2-yl)pentane-2,3-dione 3h: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (49.1 mg, 98% yield, 83:17 dr, 92% ee for *syn*-**3h**); $[\alpha]_D^{30}$ = +195.4 (c = 0.45 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 0.40H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 0.40H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.60-7.58 (m, 4H), 7.52-7.42 (m, 5H), 7.45-7.42 (m, 4H), 7.37-7.27 (m, 1.80H), 6.11 (s, 1H), 5.77 (s, 0.2H), 3.82 (dd, *J* = 9.5, 5.5 Hz, 0.2H), 3.76 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.59 (dd, *J* = 17.5, 9.0 Hz, 0.2H), 3.53 – 3.48 (m, 1.2H), 2.82 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.16 (s, 0.6H), 2.10 (s, 3H), 1.53 (s, 0.6H), 1.32 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 205.3, 197.4, 197.0, 196.6, 184.5, 183.5, 145.9, 145.6, 140.5, 140.4, 140.3, 140.1, 139.72, 139.70, 137.5, 136.8, 130.0, 129.6, 129.09, 129.05, 128.8, 128.7, 128.5, 128.4, 127.8, 127.7, 127.64, 127.55, 127.44, 127.40, 127.3, 127.22, 127.15, 127.0, 126.9, 126.8, 100.6, 100.3, 92.5, 91.3, 45.9, 45.2, 36.4, 36.0, 23.52, 23.45, 21.8, 20.0 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{34}H_{28}NaO_4$ 523.1880, found 523.1880; HPLC analysis (*syn*-**3h**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 14.0 min (major), 23.2 min (minor).



3i

(R)-5-(3-chlorophenyl)-5-((S)-5-(3-chlorophenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3i: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (37.2 mg, 89% yield, 87:13 dr, 91% ee for *syn*-**3i**); $[\alpha]_D^{30}$ = +70.2 (c = 0.40 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 0.15H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 6.5 Hz, 0.15H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 0.15H), 7.38 (s, 1H), 7.29 – 7.25 (m, 3H), 7.18 (s, 0.15H), 7.15-7.07 (m,

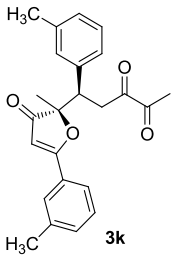
0.45H), 6.07 (s, 1H), 5.74 (s, 0.15H), 3.76 – 3.71 (m, 0.15H), 3.67 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.51 – 3.47 (m, 0.30H), 3.42 (dd, *J* = 18.0, 11.0 Hz, 1H), 2.79 (dd, *J* = 18.5, 3.5 Hz, 1H), 2.22 (s, 0.45H), 2.16 (s, 3H), 1.48 (s, 0.45H), 1.27 (s, 3H) ppm; major isomer *syn*-**3i**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 196.7, 195.9, 183.1, 140.3, 135.3, 134.3, 133.0, 130.4, 130.2, 129.8, 129.5, 127.9, 127.6, 127.1, 125.3, 101.5, 101.1, 92.3, 45.8, 36.1, 23.5, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}Cl_2NaO_4$ 439.0474, found 439.0474; HPLC analysis (*syn*-**3i**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 17.6 min (major), 23.3 min (minor).



3j

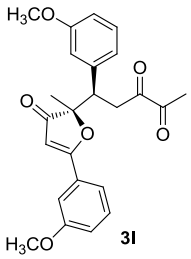
(R)-5-((S)-2-methyl-3-oxo-5-(3-(trifluoromethyl)phenyl)-2,3-dihydrofuran-2-yl)-5-(3-(trifluoromethyl)phenyl)pentane-2,3-dione 3j: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (41.1 mg, 85% yield, 86:14 dr, 91% ee for *syn*-**3j**); $[\alpha]_D^{30}$ = +147.1 (c = 0.39 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 0.16H), 7.92 (d, *J* = 8.0 Hz, 0.16H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 0.16H), 7.73-7.70 (m, 2H), 7.68 – 7.63 (m, 0.32H), 7.6 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 1H), 7.45-7.40 (m, 0.32H), 7.36-7.33 (m, 0.16H), 6.14 (s, 1H), 5.81 (s, 0.16H), 3.87 (dd, *J* = 8.5, 5.5 Hz, 0.16H), 3.81 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.63 – 3.55 (m, 0.32H), 3.50 (dd, *J* = 10.5, 19.0 Hz 1H), 2.92 (dd, *J* = 18.5, 3.5 Hz, 1H), 2.25 (s, 0.48H), 2.18 (s, 3H), 1.52 (s, 0.48H), 1.32 (s, 3H) ppm; major isomer *syn*-**3j**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 196.6, 195.8, 182.7, 139.2, 132.9, 131.9 (q, $^1J_{C\text{-}F}$ = 32.5 Hz), 130.9 (q, $^1J_{C\text{-}F}$ = 32.5 Hz), 129.8, 129.5 (q, $^2J_{C\text{-}F}$ = 3.75 Hz), 129.2, 129.0, 125.9, 124.5 ($^2J_{C\text{-}F}$ = 3.75 Hz), 123.7 ($^2J_{C\text{-}F}$ = 3.75 Hz), 122.8, 122.4, 101.7, 92.1, 45.9, 36.1, 23.4, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}F_6NaO_4$

507.1001, found 507.1002; HPLC analysis (*syn*-**3j**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 13.3 min (major), 14.6 min (minor).



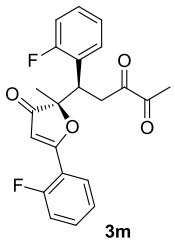
3k

(R)-5-((S)-2-methyl-3-oxo-5-(m-tolyl)-2,3-dihydrofuran-2-yl)-5-(m-tolyl)pentane-2,3-dione 3k: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (29.8 mg, 74% yield, 86:14 dr, 91% ee for *syn*-**3k**); $[\alpha]_D^{30}$ = +197.7 (c = 0.27 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.70 (m, 2H), 7.59 – 7.57 (m, 0.32H), 7.48 – 7.41 (m, 2H), 7.39 (d, *J* = 5.0 Hz, 0.32H), 7.29 – 7.21 (m, 3H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.07 – 6.96 (m, 0.64H), 6.07 (s, 1H), 5.71 (s, 0.16H), 3.73 (dd, *J* = 8.5, 5.5 Hz, 0.16H), 3.67 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.57 – 3.50 (m, 0.32H), 3.45 (dd, *J* = 17.5, 10.5 Hz, 1H), 2.77 (dd, *J* = 17.5, 3.5 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 0.48H), 2.38 (s, 3H), 2.18 (s, 0.48H), 2.15 (s, 0.48H), 2.09 (s, 3H), 1.50 (s, 0.48H), 1.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 205.4, 197.5, 197.2, 197.1, 196.8, 185.0, 184.0, 138.9, 138.7, 138.3, 137.9, 137.6, 137.5, 133.8, 133.5, 130.5, 130.0, 128.9, 128.8, 128.7, 128.6, 128.34, 128.27, 128.2, 128.0, 127.7, 127.5, 126.4, 126.2, 124.5, 124.3, 100.6, 100.2, 92.3, 91.2, 46.2, 45.5, 36.4, 36.0, 23.5, 23.4, 21.6, 21.5, 21.42, 21.36, 21.2, 19.7 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{24}H_{24}NaO_4$ 399.1567, found 399.1568; HPLC analysis (*syn*-**3k**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 11.0 min (major), 19.7 min (minor).



3l

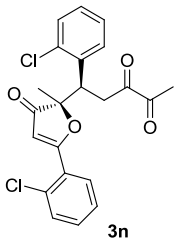
(R)-5-(3-methoxyphenyl)-5-((S)-5-(3-methoxyphenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3l: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (3:1) as the eluent. Yellow oil (27.5 mg, 68% yield, 90:10 dr, 85% ee for *syn*-**3l**); $[\alpha]_D^{30}$ = +145.5 (c = 0.45 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.38 (s, 1H), 7.38-7.35 (m, 0.11H), 7.27-7.23 (m, 1H), 7.15-7.13 (m, 1H), 7.10-7.07 (m, 0.33H), 6.97 (d, *J* = 7.5 Hz 1H), 6.94 (s, 1H), 6.82-6.80 (m, 1H), 6.78-6.68 (m, 0.44H), 6.05 (s, 1H), 5.73 (s, 0.11H), 3.90 (s, 3H), 3.89 (s, 0.33H), 3.81 (s, 3H), 3.72 (dd, *J* = 9.0, 5.5 Hz), 3.65 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.61 (s, 0.33H), 3.54-3.46 (m, 0.22H), 3.42 (dd, *J* = 17.5, 11.0 Hz, 1H), 2.73 (dd, *J* = 17.5, 3.5 Hz 1H), 2.14 (s, 0.33H), 2.08 (s, 3H), 1.48 (s, 0.33H), 1.26 (s, 3H) ppm; major isomer *syn*-**3l**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 197.0, 196.6, 184.6, 160.0, 159.5, 139.9, 130.1, 129.9, 129.4, 121.9, 119.8, 119.7, 115.3, 112.9, 112.3, 100.9, 100.6, 92.4, 55.5, 55.1, 46.3, 36.3, 23.4, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{24}H_{24}NaO_6$ 431.1465, found 431.1467; HPLC analysis (*syn*-**3l**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 9.9 min (major), 13.1 min (minor).



3m

(R)-5-(2-fluorophenyl)-5-((S)-5-(2-fluorophenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3m: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (8:1) as the eluent. Yellow oil (29.6 mg, 77% yield, 88:12 dr, 92% ee for *syn*-**3m**); $[\alpha]_D^{30}$ = +127.6 (c = 0.33 in $CHCl_3$);

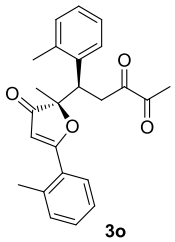
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 1H), 7.90 – 7.87 (m, 0.13H), 7.64 –7.54 (m, 1.13H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31-7.29 (m, 0.26H), 7.27-7.20 (m, 2H), 7.20-7.18 (m, 0.26H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 9.0 Hz, 1H), 7.03-6.99 (m, 0.26H), 6.24 (d, *J* = 3.5 Hz, 1H), 6.03 (d, *J* = 3.5 Hz, 0.13H), 4.17 – 4.13 (m, 1H), 3.61 – 3.56 (m, 0.13H), 3.52 – 3.42 (m, 1.13H), 2.87 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.22 (s, 0.39H), 2.14 (s, 3H), 1.48 (s, 0.39H), 1.31 (s, 3H) ppm; major isomer *syn*-**3m**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 195.8, 195.5, 177.6 (d, $^3J_{C\text{-}F}$ = 2.5 HZ), 160.7 (d, $^1J_{C\text{-}H}$ = 256.3 Hz), 160.3 (d, $^1J_{C\text{-}H}$ = 245.0 Hz), 133.6 (d, $J_{C\text{-}H}$ = 8.8 Hz), 128.2 (d, $J_{C\text{-}H}$ = 8.8 Hz), 126.9, 124.3 (d, $J_{C\text{-}H}$ = 13.8 Hz), 123.7 (d, $J_{C\text{-}H}$ = 3.8 Hz), 123.3 (d, $J_{C\text{-}H}$ = 3.8 Hz), 116.2 (d, *J* = 10.0 Hz), 115.7 (d, *J* = 22.5 Hz), 114.5 (d, *J* = 22.5 H), 104.4 (d, *J* = 12.5 Hz), 89.2, 36.8, 34.4, 22.4, 20.1 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}F_2NaO_4$ 407.1065, found 407.1064; HPLC analysis (*syn*-**3m**): Daicel Chiralpak OD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 10.9 min (major), 12.0 min (minor).



3n

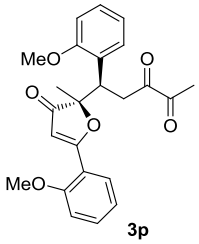
(R)-5-(2-chlorophenyl)-5-((S)-5-(2-chlorophenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3n: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (8:1) as the eluent. Yellow oil (31.6 mg, 76% yield, 90:10 dr, 90% ee for *syn*-**3n**); $[\alpha]_D^{30}$ = +159.9 (c = 0.44 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.88 – 7.83 (m, 0.11H), 7.59 – 7.57 (m, 1H), 7.54 – 7.51 (m, 1H), 7.48 – 7.43 (m, 3.22H), 7.41– 7.36 (m, 0.33H), 7.29 – 7.26 (m, 1H), 7.23-7.20 (m, 1H), 7.20 – 7.17 (m, 0.22H), 6.44 (s, 1H), 6.30 (s, 0.11H), 4.51-4.48 (m, 1.11H), 3.57-3.51 (m, 1.11H), 3.46-3.41 (m, 0.11H), 2.22 (s, 0.33H), 2.16 (s, 3H), 1.54 (s, 0.33H), 1.34 (s, 3H) ppm; major isomer *syn*-**3n**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 196.8, 196.2, 181.5, 136.2, 135.9, 134.0, 133.0, 131.4, 129.7, 129.5, 129.0, 128.7, 127.9, 127.2, 127.1, 106.4, 91.0, 40.9, 36.3, 23.4, 20.9

ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{18}Cl_2NaO_4$ 439.0474, found 439.0474; HPLC analysis (*syn*-**3n**): Daicel Chiralpak OD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 5.4 min (major), 5.9 min (minor).



3o

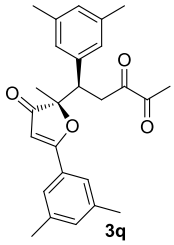
(R)-5-((S)-2-methyl-3-oxo-5-(o-tolyl)-2,3-dihydrofuran-2-yl)-5-(o-tolyl)pentane-2,3-dione 3o: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (8:1) as the eluent. Yellow oil (25.2 mg, 67% yield, >95:5 dr, 91% ee for *syn*-**3o**); $[\alpha]_D^{30}$ = +121.6 (c = 0.64 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.16 – 7.12 (m, 3H), 5.93 (s, 1H), 4.04 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.54 (dd, *J* = 17.5, 10.5 Hz, 1H), 2.80 (dd, *J* = 17.5, 4.0 Hz, 1H), 2.53 (s, 3H), 2.52 (s, 3H), 2.04 (s, 3H), 1.25 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 196.9, 196.9, 185.8, 137.93, 137.92, 137.1, 132.0, 131.9, 130.4, 128.8, 128.6, 127.7, 127.3, 126.4, 126.3, 104.9, 92.0, 40.3, 37.0, 23.3, 21.9, 21.1, 20.3 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{24}H_{24}NaO_4$ 399.1567, found 399.1568; HPLC analysis (*syn*-**3o**): Daicel Chiralpak OD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 8.2 min (major), 8.7 min (minor).



3p

(R)-5-(2-methoxyphenyl)-5-((S)-5-(2-methoxyphenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3p: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (3:1) as the eluent. Yellow

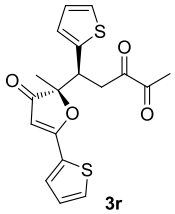
oil (25.7 mg, 63% yield, 83:17 dr, 83% ee for *syn*-**3p**); $[\alpha]_D^{30}$ = +134.6 (c = 0.27 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 0.21H), 7.59 – 7.56 (m, 1H), 7.55 – 7.51 (m, 0.21H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.26 (m, 1.21H), 7.20 (t, *J* = 8.0 Hz, 0.21H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.08 – 7.06 (m, 1.21H), 7.02 – 6.99. (m, 1.21H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.85-6.83 (m, 0.42H), 6.44 (s, 1H), 6.23 (s, 0.21H), 4.53 – 4.31 (m, 1.21H), 3.99 (s, 3H), 3.92 (s, 0.63H), 3.92 (s, 3H), 3.74 (s, 0.63H), 3.52 (m 0.21H), 3.38 – 3.33 (m, 1.21H), 2.81 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.14 (s, 0.63H), 2.05 (s, 3H), 1.47 (s, 0.64H), 1.24 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.5, 207.1, 197.5, 197.34, 197.29, 197.2, 180.6, 179.4, 159.4, 159.2, 158.0, 157.6, 134.1, 133.8, 128.44, 128.38, 128.2, 128.1, 120.71, 120.70, 120.5, 120.3, 117.8, 117.7, 111.5, 111.3, 110.9, 110.8, 105.6, 105.0, 90.1, 88.7, 60.4, 55.7, 55.6, 55.5, 36.6, 36.4, 36.1, 36.0, 23.43, 23.38, 20.8, 19.4 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{24}H_{24}NaO_6$ 431.1465, found 431.1467; HPLC analysis (*syn*-**3p**): Daicel Chiralpak OD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 15.7 min (major), 18.2 min (minor).



3q

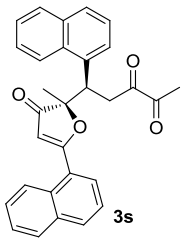
(R)-5-(3,5-dimethylphenyl)-5-((S)-5-(3,5-dimethylphenyl)-2-methyl-3-oxo-2,3-dihydrofuran-2-yl)pentane-2,3-dione 3q: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (38.4 mg, 95% yield, 86:14 dr, 93% ee for *syn*-**3q**); $[\alpha]_D^{30}$ = +220.8 (c = 0.62 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.36 (s, 0.32H), 7.24 (s, 1H), 7.18 (s, 0.16H), 6.99 (s, 2H), 6.90 (s, 1H), 6.80 (s, 0.32H), 6.77 (s, 0.16H), 6.01 (s, 1H), 5.70 (s, 0.16H), 3.65 (t, *J* = 7.5 Hz, 0.16H), 3.59 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.47 (d, *J* = 7.5 Hz, 0.32H), 3.39 (dd, *J* = 17.5, 10.5 Hz, 1H), 2.73 (dd, *J* = 17.5, 3.5 Hz, 1H), 2.42 (s, 6H), 2.41 (s, 0.96H), 2.35 (s, 6H), 2.17 (s, 0.48H), 2.16 (s, 0.96H), 2.10 (s, 3H), 1.49 (s, 0.48H), 1.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 205.5, 197.6, 197.19,

197.15, 196.9, 185.2, 184.3, 138.7, 138.5, 138.2, 137.7, 137.5, 137.4, 134.7, 134.4, 129.2, 129.0, 128.7, 128.6, 127.5, 127.1, 125.0, 124.8, 100.4, 100.2, 92.2, 91.0, 46.0, 45.4, 36.4, 35.9, 23.50, 23.45, 21.7, 21.4, 21.3, 21.2, 21.1, 19.5 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{26}H_{28}NaO_4$ 427.1880, found 427.1880; HPLC analysis (*syn*-**3q**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 15.0 min (major), 16.0 min (minor).



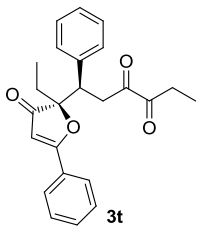
3r

(S)-5-((S)-2-methyl-3-oxo-5-(thiophen-2-yl)-2,3-dihydrofuran-2-yl)-5-(thiophen-2-yl) pentane-2,3-dione 3r: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (25.9 mg, 72% yield, 87:13 dr, 91% ee for *syn*-**3r**); $[\alpha]_D^{30}$ = +194.0 (c = 0.31 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.5 Hz, 1H), 7.98 (d, *J* = 2.5 Hz, 0.15H), 7.49 – 7.47 (m, 1H), 7.45 – 7.42 (m, 1.15H), 7.33 (d, *J* = 5.5 Hz, 0.15H), 7.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.19 – 7.18 (m, 1H), 7.13 – 7.10 (m, 1.15H), 7.02 (d, *J* = 3.0 Hz, 0.15H), 6.91 (d, *J* = 5.0 Hz, 0.15H), 5.86 (s, 1H), 5.56 (s, 0.15H), 3.88 (dd, *J* = 9.5, 5.0 Hz, 0.15H), 3.84 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.45 (dd, *J* = 17.0, 9.5 Hz, 0.15H), 3.38 – 3.32 (m, 1.15H), 2.69 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.15 (s, 0.45H), 2.10 (s, 3H), 1.45 (s, 0.45H), 1.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 205.3, 197.3, 197.0, 196.7, 180.0, 179.1, 138.8, 138.2, 131.41, 131.35, 129.2, 128.8, 128.2, 128.1, 127.6, 127.4, 126.1, 126.0, 125.8, 125.2, 123.8, 123.3, 100.4, 100.0, 91.9, 90.8, 41.6, 41.2, 36.5, 26.2, 23.5, 23.4, 21.5, 19.7 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{18}H_{16}NaO_4S_2$ 383.0382, found 383.0386; HPLC analysis (*syn*-**3r**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 5.1 min (major), 6.4 min (minor).



3s

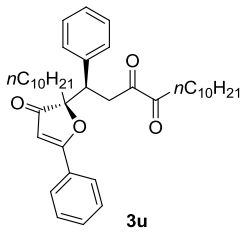
(R)-5-((S)-2-methyl-5-(naphthalen-1-yl)-3-oxo-2,3-dihydrofuran-2-yl)-5-(naphthalen-1-yl)pentane-2,3-dione 3s: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (10:1) as the eluent. Yellow oil (28.7 mg, 64% yield, 85:15 dr, 90% ee for *syn*-**3s**); $[\alpha]_D^{30}$ = +181.5 (c = 0.34 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 0.18H), 8.24 – 8.21 (m, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 0.18H), 7.96 – 7.90 (m, 1.36H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 0.18H), 7.66 – 7.62 (m, 2.18H), 7.58 – 7.52 (m, 4H), 7.50 (s, 0.36H), 7.48 (s, 0.36H), 7.46 (s, 0.18H), 7.44 – 7.40 (m, 1.18H), 7.20-7.15 (m, 0.18), 6.12 (s, 1H), 5.66 (s, 0.18H), 4.89 – 4.83 (m, 1.18H), 3.76 (dd, *J* = 17.6, 10.4 Hz, 1H), 3.66 (dd, *J* = 8.8, 7.6 Hz, 0.36H), 3.11 (dd, *J* = 17.2, 4.4 Hz, 1H), 1.95 (s, 3H), 1.93 (s, 0.54H), 1.42 (s, 0.54H), 1.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 205.0, 197.3, 197.1, 197.0, 196.8, 186.2, 184.7, 135.2, 134.5, 133.83, 133.78, 133.72, 133.7, 132.93, 132.90, 132.7, 132.2, 130.22, 130.15, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 127.9, 127.8, 127.62, 127.57, 127.5, 127.0, 126.68, 126.65, 126.5, 126.3, 125.84, 125.80, 125.75, 125.7, 125.4, 125.0, 124.9, 124.8, 124.71, 124.68, 124.2, 123.7, 105.9, 105.7, 92.6, 91.0, 105.9, 105.7, 92.6, 90.9, 39.1, 37.9, 37.8, 37.4, 29.7, 26.9, 23.4, 21.8 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{30}H_{24}NaO_4$ 448.1675, found 448.1667; HPLC analysis (*syn*-**3s**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 10.3 min (major), 15.3 min (minor).



3t

(R)-1-((S)-2-ethyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-1-phenylhexane-3,4-dione

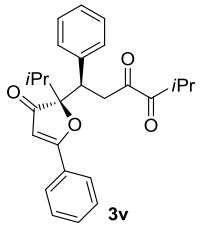
3t: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Yellow oil (37.3 mg, 99% yield, 94:6 dr, 93% ee for *syn*-**3t**); $[\alpha]_D^{30}$ = +164.8 (c = 0.56 in $CHCl_3$); major isomer *syn*-**3t**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26-7.23 (m, 1H), 7.12 (d, *J* = 8.0H, 3H), 6.09 (s, 1H), 3.69 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.45 (dd, *J* = 17.0, 10.5 Hz, 1H), 2.79 (dd, 17.0, 3.5 Hz, 1H), 2.45 – 2.41 (m, 2H), 1.83 – 1.75 (m, 1H), 1.62 – 1.53 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.4 Hz, 3H) ppm; major isomer *syn*-**3t**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 199.9, 197.3, 185.7, 138.4, 133.0, 129.6, 129.1, 128.5, 128.4, 127.5, 127.2, 102.7, 95.5, 46.4, 36.7, 29.2, 28.7, 7.0, 6.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{24}H_{24}NaO_4$ 399.1567, found 399.1572; HPLC analysis (*syn*-**3t**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 15.9 min (major), 20.6 min (minor).



3u

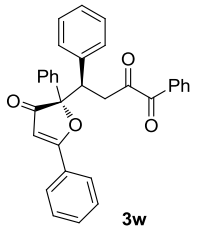
(R)-1-((S)-2-decyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-1-phenyltetradecane-3,4-dione 3u: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (20:1) as the eluent. Yellow oil (52.2 mg, 87% yield, 90:10 dr, 88% ee for *syn*-**3u**); $[\alpha]_D^{30}$ = +126.8 (c = 0.64 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.07 (s, 1H), 3.68 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.44 (dd, *J* = 17.0, 11.0 Hz, 1H), 2.76 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.41 – 2.37 (m, 2H), 1.81 – 1.72 (m, 1H), 1.51 – 1.46 (m, 1H), 1.27 – 1.11 (m, 32H), 0.88 – 0.83 (m, 6H) ppm; major isomer **3u**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 199.5, 197.4, 185.5, 138.3, 133.0, 129.6, 129.0, 128.6, 128.4, 127.5, 127.2, 102.6, 95.2, 46.6, 36.5, 35.7, 35.6, 31.9, 31.8, 29.6, 29.5, 29.42, 29.35, 29.3, 29.2, 29.0, 22.8,

22.64, 22.62, 14.1 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{40}H_{56}NaO_4$ 623.4071, found 623.4079; HPLC analysis (*syn*-**3u**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 25.1 min (major), 31.7 min (minor).



3v

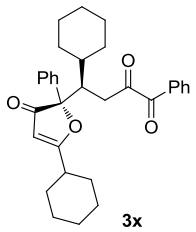
(R)-1-((S)-2-isopropyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-5-methyl-1-phenylhexane-3,4-dione 3v: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (15:1) as the eluent. Yellow oil (33.1 mg, 82% yield, 93:7 dr, 85% ee for *syn*-**3v**); $[\alpha]_D^{30}$ = +398.8 (c = 1.31 in $CHCl_3$); major isomer *syn*-**3v** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.60 – 7.55 (m, 1H), 7.53 – 7.48 (m, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.25 – 7.16 (m, 3H), 5.94 (s, 1H), 3.96 (dd, *J* = 14.5, 4.0Hz, 1H), 3.60 (dd, *J* = 21.5, 13.0Hz, 1H), 3.13-3.03 (m, 1H), 2.80 (dd, *J* = 21.5, 4.0 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.03 (d, *J* = 8.5 Hz, 3H), 0.93 (d, *J* = 8.5 Hz, 3H), 0.86 (d, *J* = 9.0Hz, 3H), 0.75 (d, *J* = 9.0 Hz, 3H) ppm; major isomer *syn*-**3v**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 202.5, 197.9, 185.1, 137.9, 132.8, 129.7, 128.9, 128.5, 128.2, 127.4, 127.1, 103.3, 96.6, 44.2, 36.9, 33.5, 32.5, 29.7, 17.1, 17.0., 16.4, 15.3 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{26}H_{28}NaO_4$ 427.1885, found 427.1880; HPLC analysis (*syn*-**3v**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 16.5 min (major), 33.8 min (minor).



3w

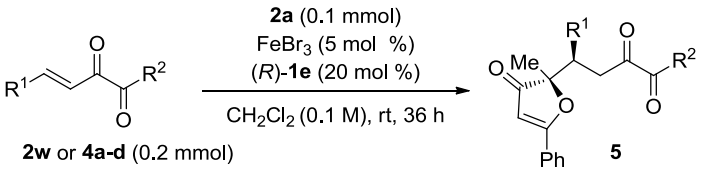
(R)-4-((S)-3-oxo-2,5-diphenyl-2,3-dihydrofuran-2-yl)-1,4-diphenylbutane-1,2-dione

3w: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (6:1) as the eluent. Yellow oil (41.2 mg, 87% yield, <5:95 dr, 42% ee for *anti*-**3w**); $[\alpha]_D^{30}$ = +93.6 (c = 0.28 in $CHCl_3$); major isomer *anti*-**3w**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 9.5 Hz, 2H), 7.59 (t, *J* = 9.0 Hz, 1H), 7.53 – 7.40 (m, 7H), 7.36 – 7.25 (m, 5H), 7.07 (m, 3H), 5.58 (s, 1H), 4.38 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.72 (dd, *J* = 21.5, 14.5 Hz, 1H), 3.10 (dd, *J* = 21.5, 5.0 Hz, 1H) ppm; major isomer **3w**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.1, 200.6, 191.5, 184.0, 136.3, 136.1, 134.4, 133.0, 131.6, 130.2, 129.6, 129.2, 129.0, 128.64, 128.57, 128.5, 128.4, 127.8, 127.1, 125.0, 100.8, 93.7, 48.0, 39.4 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{32}H_{24}NaO_4$ 495.1567, found 495.1568; HPLC analysis (*anti*-**3w**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 10.4 min (major), 17.0 min (minor).

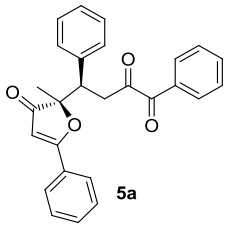


3x

(R)-4-cyclohexyl-4-((S)-5-cyclohexyl-3-oxo-2-phenyl-2,3-dihydrofuran-2-yl)-1-phenylbutane-1,2-dione 3x: Prepared according to the general procedure I above and purified by flash chromatography column with PE/EA (20:1) as the eluent. Yellow oil as (13.1 mg, 27% yield, <5:95 dr, 64% ee for known compound *anti*-**3x**); $[\alpha]_D^{30}$ = +53.0 (c = 0.34 in $CHCl_3$); major isomer *anti*-**3x**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.4Hz, 4H), 7.41 – 7.33 (m, 2H), 7.28 – 7.17 (m, 4H), 5.39 (s, 1H), 3.25 – 3.13 (m, 1H), 3.08 (s, 1H), 3.03 (d, J = 8.4Hz , 1H), 2.97 – 2.86 (m, 1H), 2.61 – 2.48 (m, 1H), 2.03 (d, J = 11.5Hz, 2H), 1.88 – 1.85 (m, 2H), 1.78 –1.60 (m, 8H), 1.53 – 1.35 (m, 5H), 1.14 – 0.97 (m, 4H) ppm; major isomer **3x**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 200.6, 196.3, 191.4, 137.5, 134.4, 131.7, 130.3, 128.6, 128.1, 125.0, 101.9, 95.2, 45.1, 40.0, 38.9, 35.0, 33.4, 30.0, 29.8, 29.2, 26.8, 26.5, 26.21, 25.7, 25.7, 25.6 ppm; HPLC analysis (*anti*-**3x**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 10.2 min (minor), 13.7 min (major).

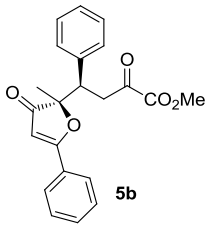


General procedure II: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (0.005 mmol, 5 mol %) and chiral phosphoric acid (*R*)-**1e** (0.02 mmol, 20 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketones **2a** (0.1 mmol) and **2w** or **4a-d** (0.2 mmol) were added under nitrogen. The reaction mixture was stirred at room temperature for 36 h. After reaction, the mixture was directly loaded onto silica gel column and eluted with PE/EA (3:1) to give the chiral target product.



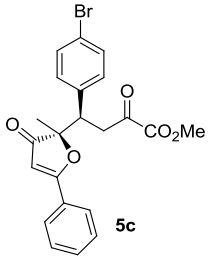
(R)-4-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-1,4-diphenylbutane-1,2-dione 5a: Prepared according to the general procedure II above and purified by flash chromatography column with PE/EA (3:1) as the eluent. Yellow oil (28.4 mg, 77% yield, 82:18 dr, 87% ee for *syn*-**5a**); $[\alpha]_D^{30}$ = +143.7 (c = 0.34 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 0.44H), 7.60 (t, *J* = 7.0 Hz, 1.22H), 7.57 – 7.45 (m, 6.32H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 – 7.28 (m, 4H), 7.25-7.22 (m, 1.22H), 7.20 – 7.15 (m, 0.44H), 7.07-7.04 (m, 0.66H), 6.07 (s, 1H), 5.69 (s, 0.22H), 3.86 (dd, *J* = 10.0, 5.5 Hz, 0.22H), 3.81 (dd, *J* = 11.0, 3.0Hz, 1H), 3.71 – 3.62 (m, 0.44H), 3.49 (dd, *J* = 17.5, 11.5 Hz, 1H), 3.04 (dd, *J* = 17.5, 3.5 Hz, 1H), 1.57 (s, 0.66H), 1.29 (s, 3H) ppm; major isomer *syn*-**5a**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.6, 204.2, 199.6, 199.1, 190.6, 190.3, 183.7, 182.9, 137.1, 136.2, 133.4, 132.1, 131.8, 130.6, 129.2, 129.1, 128.7, 128.36, 128.1, 128.0, 127.7, 127.6, 127.3, 126.7, 126.6, 126.3, 126.1, 99.8, 99.4, 91.3, 90.4, 45.3, 44.5, 37.9, 37.8, 20.6, 19.2 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{27}H_{22}NaO_4$ 433.1416, found 433.1414; HPLC analysis (*syn*-**5a**):

Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 75:25, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 14.5 min (major), 18.6 min (minor).



5b

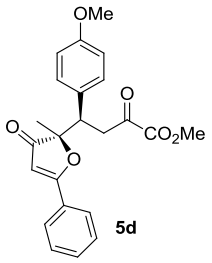
(R)-methyl 4-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-2-oxo-4-phenylbutanoate 5b: Prepared according to the general procedure II above and purified by flash chromatography column with PE/EA (3:1) as the eluent. Yellow oil (25.1 mg, 72% yield, >95:5 dr, 84% ee for *syn*-**5b**); $[\alpha]_D^{30}$ = +372.5 (c = 1.21 in $CHCl_3$); major isomer *syn*-**5b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.07 (s, 1H), 3.77 – 3.69 (m, 4H), 3.46 (dd, *J* = 18.5, 11.0 Hz, 1H), 2.97 (dd, *J* = 18.5, 3.0 Hz, 1H), 1.27 (s, 3H) ppm; major isomer *syn*-**5b**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 191.1, 184.7, 160.9, 138.0, 133.1, 129.5, 129.1, 128.6, 128.5, 127.6, 127.2, 100.7, 92.3, 52.9, 46.1, 39.7, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{20}NaO_5$ 387.1208, found 387.1210; HPLC analysis (*syn*-**5b**): Daicel Chiralpak OD-H column, hexane/*i*-PrOH = 85:15, flow rate = 0.8 mL/min, λ = 210 nm, 35 °C, retention time: 13.8 min (major), 14.8 min (minor).



5c

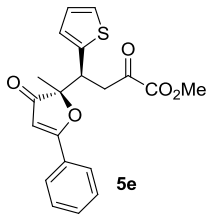
(R)-methyl 4-(4-bromophenyl)-4-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-2-oxobutanoate 5c: Prepared according to the general procedure II above and purified by flash chromatography column with PE/EA (3:1) as the eluent. Yellow oil (36.3 mg, 76% yield, 91:9 dr, 88% ee for *syn*-**5c**); $[\alpha]_D^{30}$ = +104.5 (c = 0.87 in $CHCl_3$);

major isomer *syn*-**5c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.24 (m, 1H), 6.08 (s, 1H), 3.75 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.71 (s, 3H), 3.50 (dd, *J* = 18.0, 11.0 Hz, 1H), 2.97 (dd, *J* = 18.0, 3.5 Hz, 1H), 1.26 (s, 3H) ppm; major isomer *syn*-**5c**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 190.9, 184.7, 160.8, 137.1, 133.2, 131.6, 131.1, 129.1, 128.5, 127.2, 121.7, 100.7, 91.9, 53.0, 45.5, 39.6, 21.6 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{22}H_{19}BrNaO_5$ 465.0314, found 465.0313; HPLC analysis (*syn*-**5c**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 13.4 min (major), 19.9 min (minor).



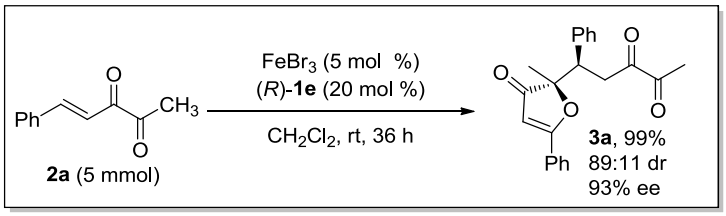
5d

(R)-methyl 4-(4-methoxyphenyl)-4-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydro furan-2-yl)-2-oxobutanoate 5d: Prepared according to the general procedure II above and purified by flash chromatography column with PE/EA (2:1) as the eluent. Yellow oil (14.0 mg, 34% yield, 89:11 dr, 90% ee for *syn*-**5d**); $[\alpha]_D^{30}$ = +124.4 (c = 0.27 in $CHCl_3$); major isomer *syn*-**5d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.07 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3,70-3.69 (m, 1H), 3.75 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.71 (s, 3H), 3.45 (dd, *J* = 18.0, 11.0 Hz, 1H), 2.93 (dd, *J* = 18.0, 3.5 Hz, 1H), 1.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 205.3, 191.7, 191.3, 184.6, 183.7, 161.1, 160.9, 158.9, 158.8, 133.0, 132.7, 130.5, 130.2, 130.1, 129.9, 129.03, 128.9, 128.7, 127.21, 127.1, 113.8, 113.51, 100.7, 100.4, 92.6, 91.4, 55.2, 55.1, 53.0, 52.9, 45.4, 44.5, 39.8, 39.4, 21.6, 20.1, 14.2, 14.1 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{23}H_{22}NaO_6$ 417.1314, found 417.1311; HPLC analysis (*syn*-**5d**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 26.4 min (major), 30.7 min (minor).



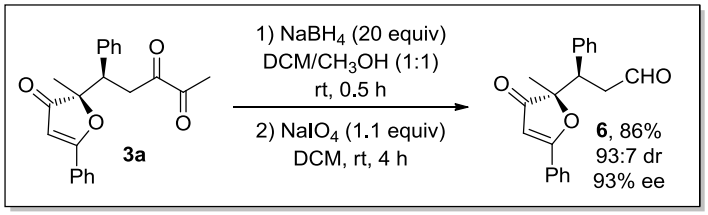
(S)-methyl 4-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-2-oxo-4-(thiophen-2-yl)butanoate 5e: Prepared according to the general procedure II above and purified by flash chromatography column with PE/EA (3:1) as the eluent. Yellow oil (24.9 mg, 67% yield, 93:7 dr, 85% ee for *syn*-**5e**); $[\alpha]_D^{30}$ = +89.8 (c = 0.26 in $CHCl_3$); major isomer *syn*-**5e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5k Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.28-7.27 (m, 1H), 7.23 (br, 1H), 7.15 (d, *J* = 5.0 Hz, 1H), 6.06 (s, 1H), 3.93 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.73 (s, 3H), 3.40 (dd, *J* = 17.5, 11.0 Hz, 1H), 2.92 (dd, *J* = 17.5, 3.5 Hz, 1H), 1.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4 191.1, 184.6, 160.9 138.4 133.1 129.1 128.6, 128.0, 127.2, 125.8 123.9, 100.7, 92.1, 52.9, 41.5, 39.8, 21.5 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{20}H_{18}NaO_5S$ 393.0773, found 393.0770; HPLC analysis (*syn*-**5e**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time:16.6 min (minor), 22.5 min (major).

B) Gram-scale reaction:

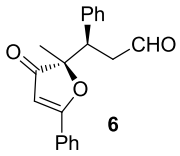


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (36.5 mg, 0.125 mmol, 5 mol %) and chiral phosphoric acid (*R*)-**1e** (379 mg, 0.5 mmol, 20 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (25 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketone **2a** (870 mg, 5 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 36 h. After reaction, the mixture was directly loaded onto silica gel column and eluted with PE/EA (5:1) to give the chiral target product **3a** (861 mg, 99% yield, 89:11 dr, 93% ee for *syn*-**3a**).

C) Transformation of chiral *syn*-3(*2H*)-furanone 3a:



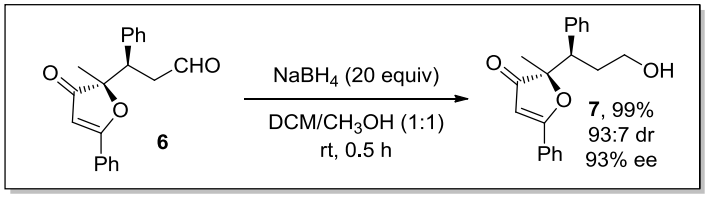
Reaction procedure I: $NaBH_4$ (378 mg, 10 mmol) was added to a solution of **3a** (174 mg, 0.5 mmol) in CH_3OH/CH_2Cl_2 (1:1, 5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and then quenched with HCl (1.0 M). NaCl followed by extraction with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4, filtered, and the solvent was concentrated under vacuum to give the crude diol, which was used for next step without further purification. To a solution of the crude diol in DCM (5 mL), was added $NaIO_4$ (118 mg, 0.55 mmol) at room temperature in an oven-dried round flask. The reaction mixture was stirred at room temperature for 4 h and then NaCl followed by extraction with CH_2Cl_2. The organic phase was washed with brine and dried over Na_2SO_4, the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluted with PE/EA = 50:1) to afford a product **6** as a colorless oil (131.6 mg, 86% yield, 93:7 dr, 93% ee for *syn*-**6**).



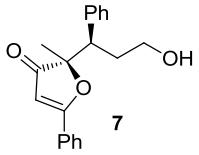
6

(R)-3-((S)-2-methyl-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)-3-phenylpropanal 6: Prepared according to the reaction procedure I above and purified by flash chromatography column with PE/EA (50:1) as the eluent. Colorless oil, 131.6 mg, 86% yield, 93:7 dr, 94% ee for *syn*-**6**); $[\alpha]_D^{30}$ = +279.3 (c = 1.27 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 0.08H), 9.48 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 0.16H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 0.16H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 –7.27 (m, 1H), 7.24 (d, *J* = 5.0 Hz, 0.24 H), 7.18 (d, *J* = 4.0 Hz, 0.24H), 6.07 (s, 1H), 5.73 (s, 0.08H), 3.78 (dd, *J* = 10.0, 5.0 Hz, 0.08H), 3.70 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.20 – 3.13 (m, 0.16H), 2.90 – 2.85 (m, 1H),

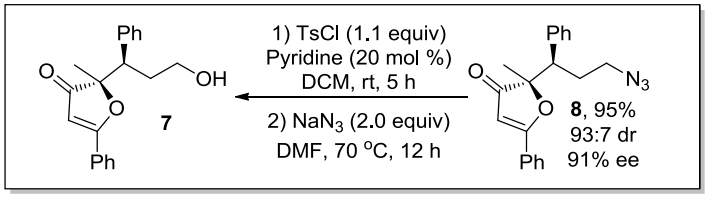
2.63 (d, *J* = 17.0, 4.0 Hz, 1H), 1.51 (s, 0.24H), 1.30 (s, 3H) ppm; major isomer *syn*-**6**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 199.9, 184.7, 138.1, 133.1, 129.3, 129.1, 128.7, 128.6, 127.7, 127.2, 100.7, 92.2, 45.9, 43.6, 21.5 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{20}H_{18}NaO_3$ 329.1148, found 329.1147; HPLC analysis (*syn*-**6**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 6.8 min (major), 7.9 min (minor).



Reaction procedure II: $NaBH_4$ (226.8 mg, 6.0 mmol) was added to a solution of **6** (91.8 mg, 0.3 mmol) in CH_3OH/CH_2Cl_2 (1:1, 3 mL) at 0 ^oC. The reaction mixture was stirred at room temperature for 30 min and then quenched with HCl (1.0 M). NaCl followed by extraction with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4, filtered, and the solvent was concentrated under vacuum to give the crude alcohol. The crude product was purified by column chromatography on silica gel (eluted with PE/EA = 1:1) to afford a product **7** as a white solid (91.8 mg, 99% yield, 94:6 dr, 91% ee for *syn*-**7**).

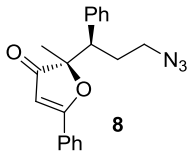


(S)-2-((R)-3-hydroxy-1-phenylpropyl)-2-methyl-5-phenylfuran-3(2H)-one 7: Prepared according to the reaction procedure II above and purified by flash chromatography column with PE/EA (1:1) as the eluent. Colorless oil, 91.8 mg, 99% yield, 93:7 dr, 92% ee for *syn*-**7**; $[\alpha]_D^{30}$ = +163.9 (c = 0.38 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 0.16H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 0.16H), 7.39 (m, 4H), 7.312(m, 1.08H), 7.18 – 7.14 (m, 0.40H), 6.09 (s, 1H), 5.65 (s, 0.08H), 3.25-3.20 (m, 0.16H), 3.16 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.08 – 3.03 (m, 1H), 2.95 – 2.90 (m, 1.08), 2.38 – 2.30 (m, 0.08H), 2.28 – 2.21 (m, 0.08H), 1.96 – 1.90 (m, 1H), 1.82 – 1.80 (m, 1H), 1.55 (s, 0.24H), 1.22 (s, 3H) ppm; major isomer *syn*-**7**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 184.6, 138.1, 132.9, 129.4, 129.0, 128.8, 128.7, 127.6, 127.2, 100.6, 92.9, 49.4, 49.3, 28.8, 21.8 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{20}H_{20}NaO_3$ 331.1305, found 331.1305; HPLC analysis (*syn*-**5**): Daicel Chiralpak AD-H column, hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 8.5 min (major), 9.4 min (minor).



Reaction procedure III: TsCl (83.6 mg, 0.44 mmol) was added to a solution of **7** (125.3 mg, 0.4 mmol) in and pyridine (80 uL, 20 mol %) in DCM (5 mL) at 0 °C. The reaction mixture was stirred for 5 hours at room temperature. After the reaction completed, it was poured into ice water. The organic layer was washed with 1 M HCl solution (10 mL × 2) and saturated aqueous Na_2CO_3 (10 mL × 2). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to give the crude product, which was used directly in the next step without further purification.

Sodium azide (52 mg, 0.8 mmol) was added to a solution of the crude from the previous step in DMF (5 mL) under nitrogen atmosphere. The resulting mixture was stirred at 70 °C for 12 hours. Then the reaction was allowed to cool to room temperature and diluted with water (20 mL). The aqueous layer was extracted by EtOAc (20 mL x 3) and the combined organic layers were dried over Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford product **8** (126.5 mg, 95% yield, 94:6 dr, 91% ee for *syn*-**8**).

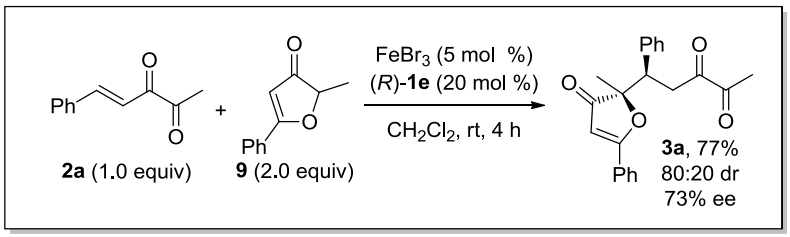


8

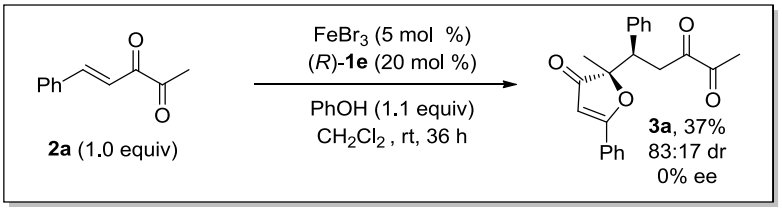
(S)-2-((R)-3-azido-1-phenylpropyl)-2-methyl-5-phenylfuran-3(2H)-one 8: Prepared according to the reaction procedure III above and purified by flash chromatography column with PE/EA (5:1) as the eluent. Colorless oil, 126.5 mg, 95% yield, 93:7 dr, 91% ee for *syn*-**8**; $[\alpha]_D^{30}$ = +200.4 (c = 1.35 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 7.0 Hz, 0.16H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 – 7.45 (m, 0.24H), 7.42 – 7.35 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.17 (m, 0.16H), 7.14 – 7.09 (m, 0.24H), 6.08 (s, 1H), 5.64 (s, 0.08H), 3.67 – 3.63 (m, 0.08H), 3.55 – 3.53 (m, 0.08H), 3.48 (dd, *J* = 9.1, 4.7 Hz, 0.08H), 3.40 – 3.37 (m, 1H), 3.32 –

3.27 (m, 1H), 3.23 (dd, *J* = 12.0, 3.5 Hz, 1H), 2.45 – 2.35 (m, 2H), 2.00 – 1.77 (m, 2H), 1.21 (s, 3H), 1.18 (s, 0.24H) ppm; major isomer *syn*-**8**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 184.6, 138.0, 132.9, 129.4, 129.0, 128.8, 128.7, 127.6, 127.2, 100.7, 92.9, 49.4, 49.3, 28.8, 21.8 ppm; HRMS (ESI, quarupole) m/z: $(M+Na)^+$ calcd for $C_{20}H_{19}N_3NaO_2$ 356.1369, found 356.1375; HPLC analysis (*syn*-**8**): Daicel Chiralpak OD-H column, hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, λ = 210 nm, 35 °C, retention time: 9.5 min (major), 10.5 min (minor).

IV. Control Experiments



A) Fe(III)/(*R*)-1e catalyzed Michael Addition of 2a with 9: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (1.5 mg, 0.005 mmol, 5 mol %) and chiral phosphoric acid (*R*)-**1e** (11.5 mg, 0.02 mmol, 20 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketones **2a** (0.1 mmol) and **9** (0.2 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 4 h. After reaction, the mixture was directly loaded onto silica gel column and eluted with PE/EA (5:1) to give the chiral target product **3a** (26.8 mg, 77% yield, 80:20 dr, 73% ee for *syn*-**3a**).



B) Phenol as an acidic additive: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (1.5 mg, 0.005 mmol, 5 mol %) and chiral phosphoric acid (*R*)-**1e** (11.5 mg, 0.02 mmol, 20 mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketones **2a** (34.8 mg, 0.2 mmol) and PhOH (20.7 mg, 0.22 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 36 h. After reaction, the mixture was directly loaded onto silica gel column and eluted with PE/EA (5:1) to give the chiral target product **3a** (12.9 mg, 37% yield, 83:17 dr, 0% ee for *syn*-**3a**). Compound **9** couldn't be observed.

C) Non-linear Effect:

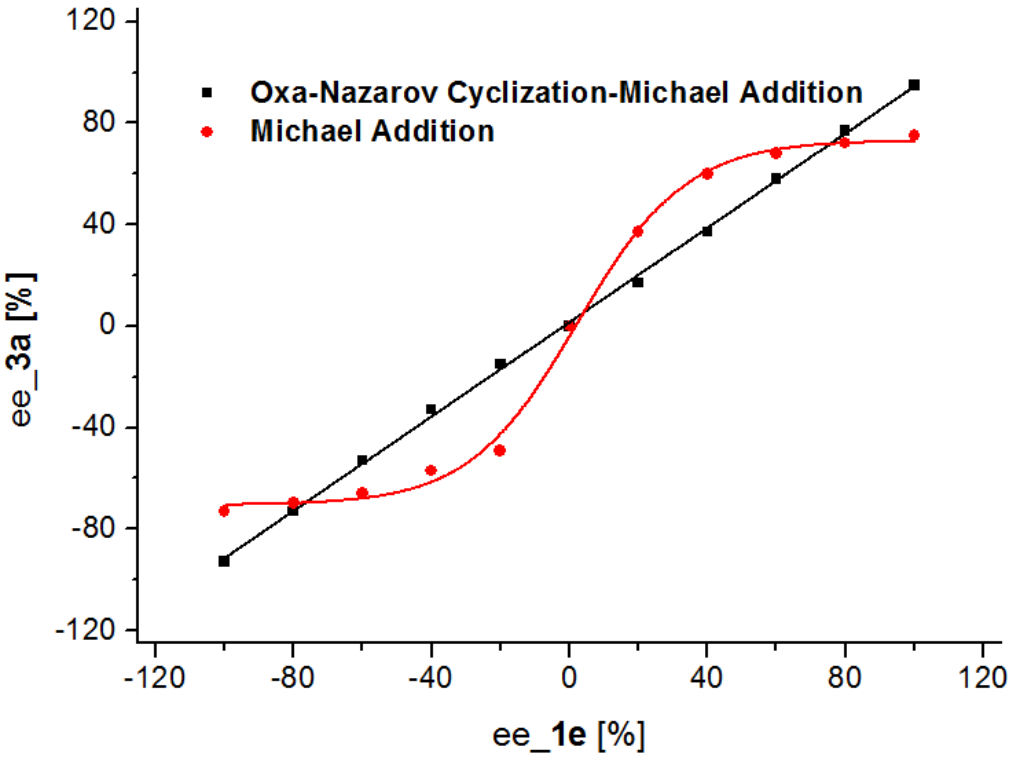


Fig. S1. Nonlinear effect in Oxa-Nazarov Cyclization-Michael Addition and direct Michael Addition.

D) **ESI-MS Experiment**

[(*R*)-**1e**]-$FeBr_3$-**2a** system: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (1.5 mg, 0.005 mmol) and chiral phosphoric acid (*R*)-**1e** (15.2 mg, 0.02 mmol). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketone **2a** (17.4 mg, 0.1 mmol) was added under nitrogen. After stirring for 1 h, an aliquot was diluted with CH_3CN (CH_3CN/CH_2Cl_2 = 20:1) and subjected to analysis by ESI-MS.

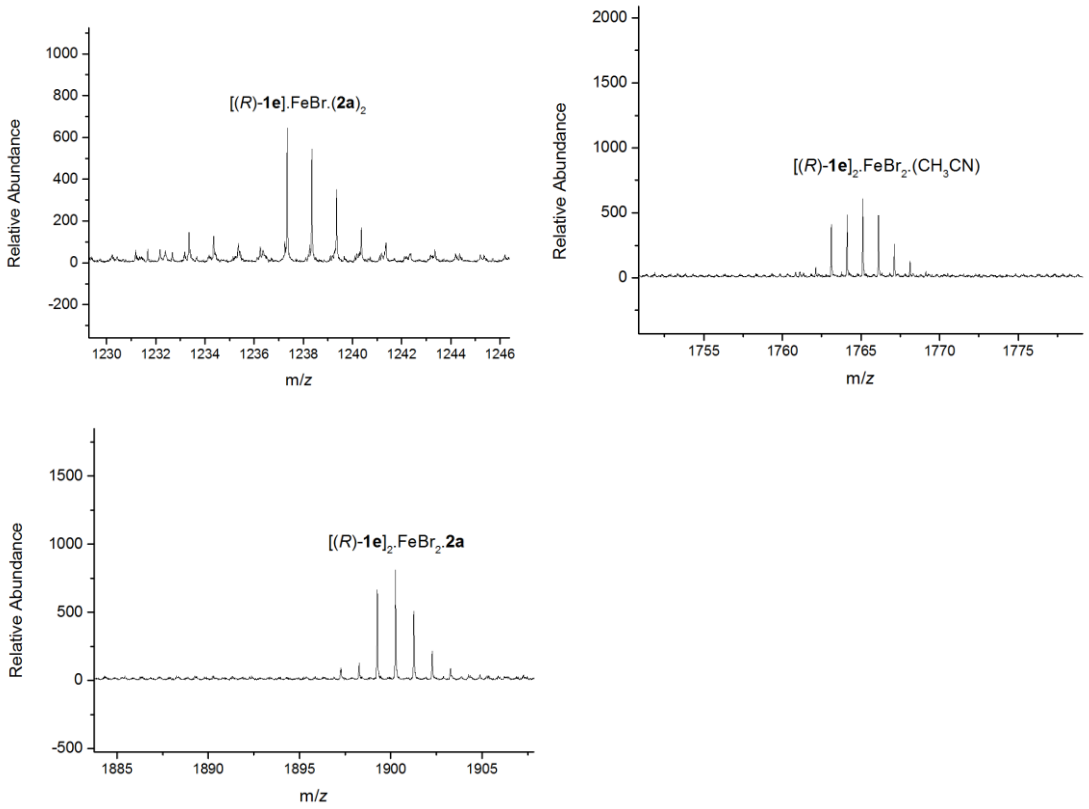
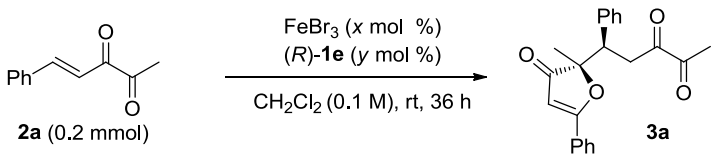


Fig. S2. ESI-MS analysis of a solution of [(*R*)-**1e**]-$FeBr_3$-**2a** (4:1:20)

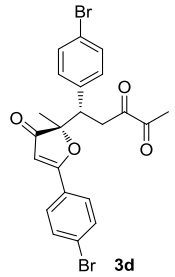


entry	*x*	*y*	yield (%, dr)	ee (%)
1	5	20	99 (95:5)	96
2	5	15	90 (90:10)	87
3	5	10	82 (89:11)	73
4	5	5	71 (85:15)	53
5	10	10	86 (89:11)	73
6[a]	20	20	99 (92:8)	83
7[b]	30	30	99 (94:6)	87

[a] t = 12 h, [b] t = 5 h

E) Impact of the ratio of two acids: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $FeBr_3$ (x mol %) and chiral phosphoric acid (*R*)-**1e** (y mol %). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DCM (1.0 mL) was added. After stirring for 0.5 h, conjugated 1,2-diketones **2a** (34.8 mg, 0.2 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 36 h. After reaction, the mixture was directly loaded onto silica gel column and eluted with PE/EA (5:1) to give the chiral target product **3a**.

V. X-ray structure of 3d



3d

The crystal was cultivated from petrol ether/DCM (20:1) with volatilization method.

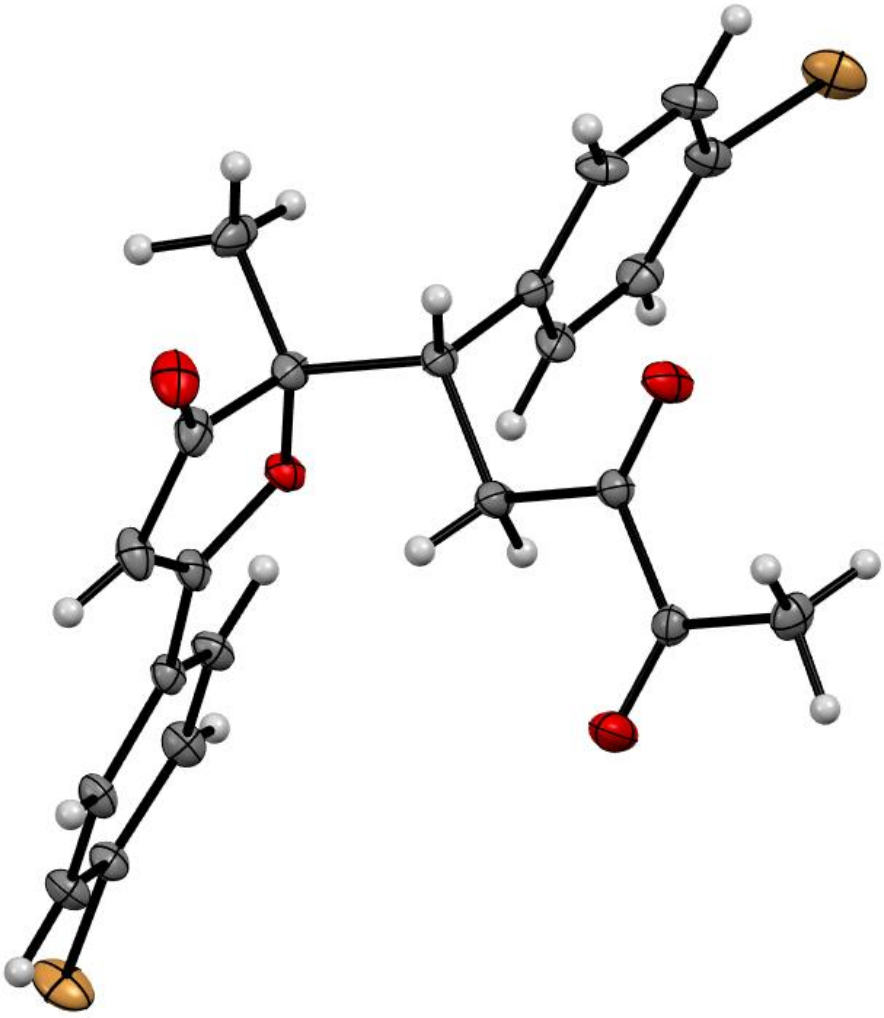


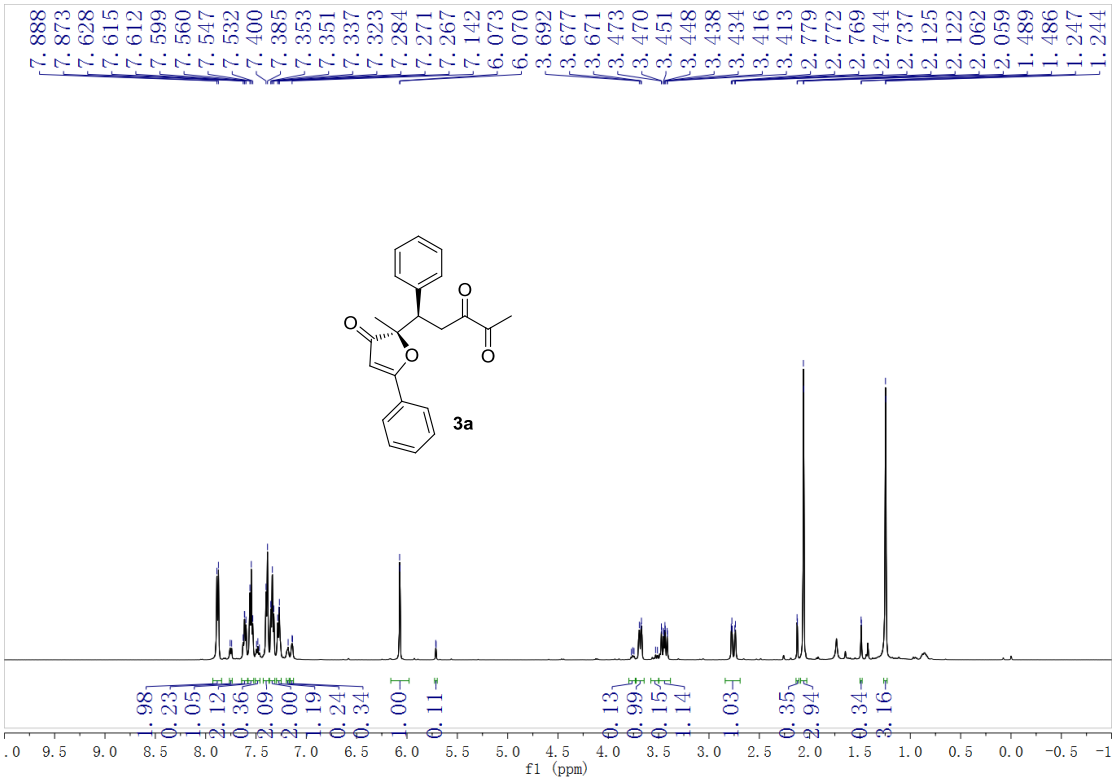
Fig. S3. ORTEP drawing of **3d** delated one CH_2Cl_2 molecule at 30% ellipsoid probability (CCDC 2233765)

Table S4. Crystal data and structure refinement for **3d**

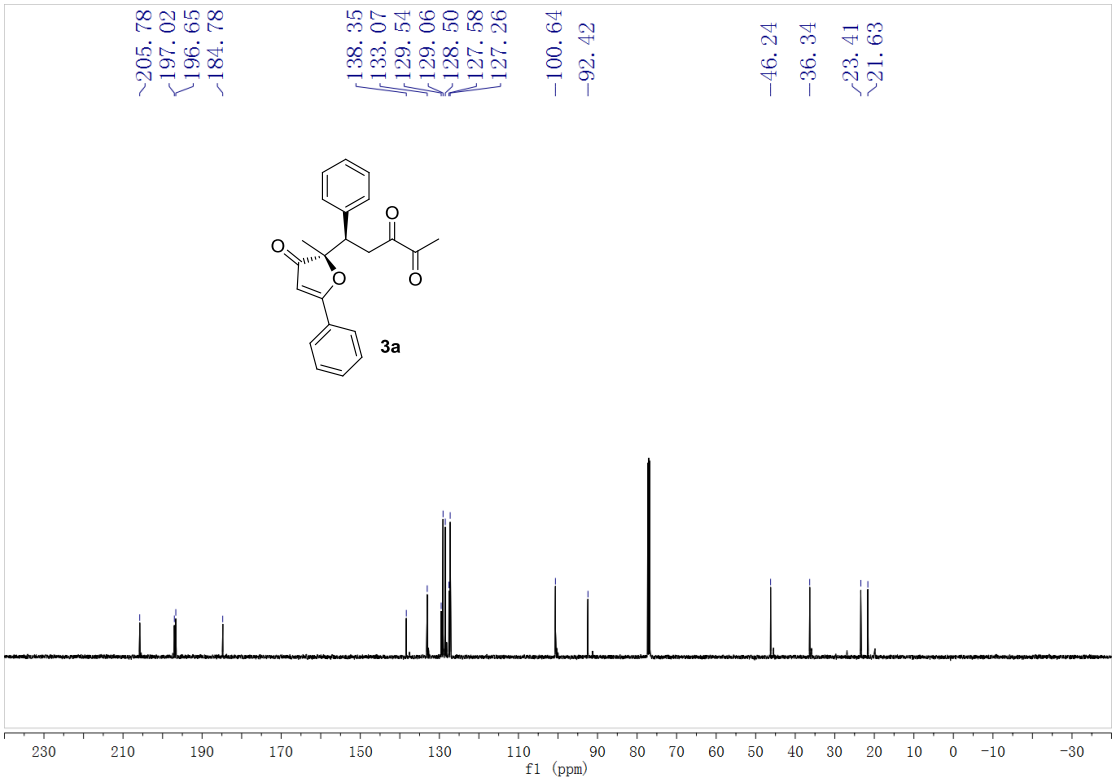
Empirical formula	$C_{45}H_{38}Br_4Cl_2O_8$
Formula weight	1097.29
Temperature/K	169.95(10)
Crystal system	monoclinic
Space group	I2
a/Å	12.52272(12)
b/Å	7.55112(7)
c/Å	23.7108(2)
α/°	90
β/°	101.6582(9)
γ/°	90
Volume/Å^3	2195.85(4)
Z	2
ρ_{calc}g/cm^3	1.660
μ/mm^{-1}	6.028
F(000)	1092.0
Crystal size/mm^3	0.26 × 0.25 × 0.21
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.44 to 153.974
Index ranges	-15 ≤ h ≤ 15, -9 ≤ k ≤ 9, -29 ≤ l ≤ 27
Reflections collected	12625
Independent reflections	4439 [R_{int} = 0.0231, R_{sigma} = 0.0196]
Data/restraints/parameters	4439/21/283
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0619
Final R indexes [all data]	R_1 = 0.0238, wR_2 = 0.0621
Largest diff. peak/hole / e Å^{-3}	0.47/-0.32
Flack parameter	-0.011(7)

VI. NMR Spectrum

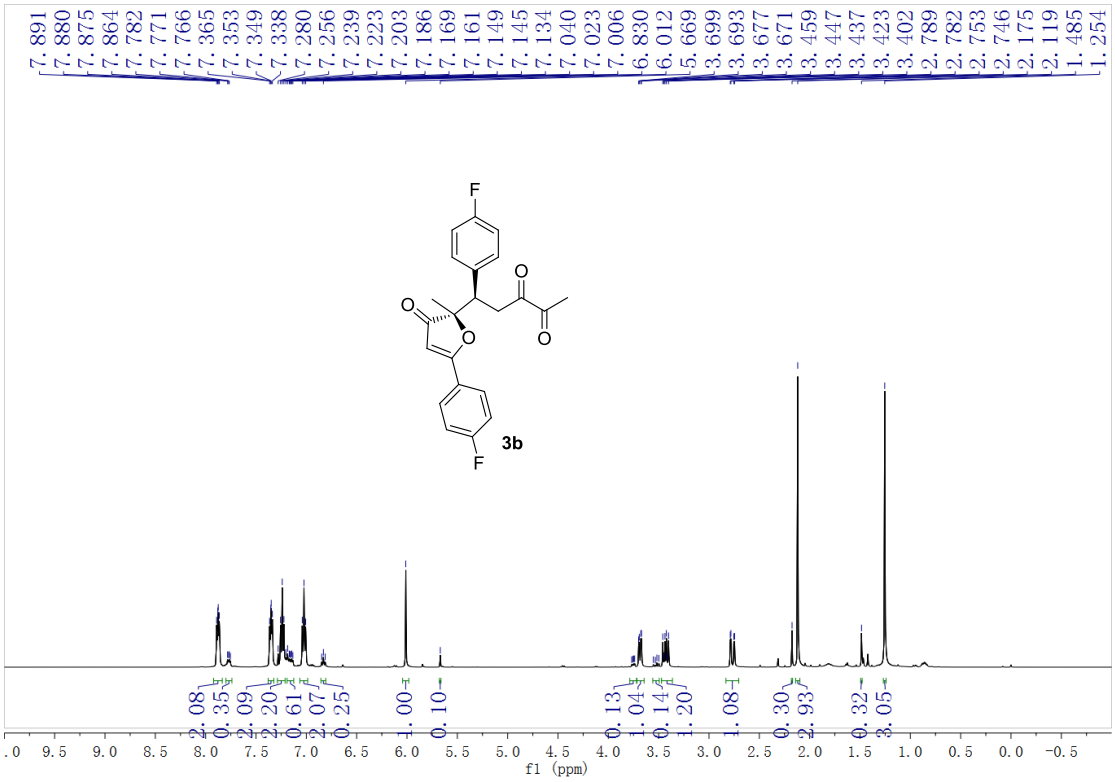
^{1}H NMR (500 MHz, $CDCl_3$)



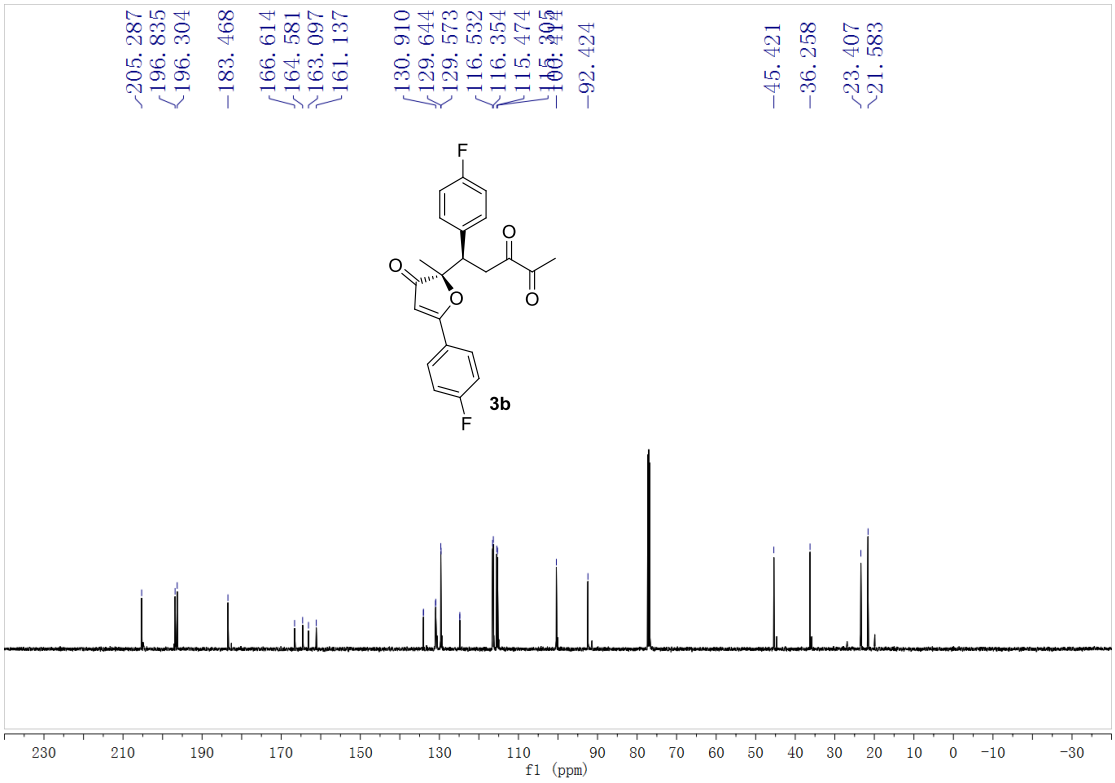
^{13}C NMR (125 MHz, $CDCl_3$)



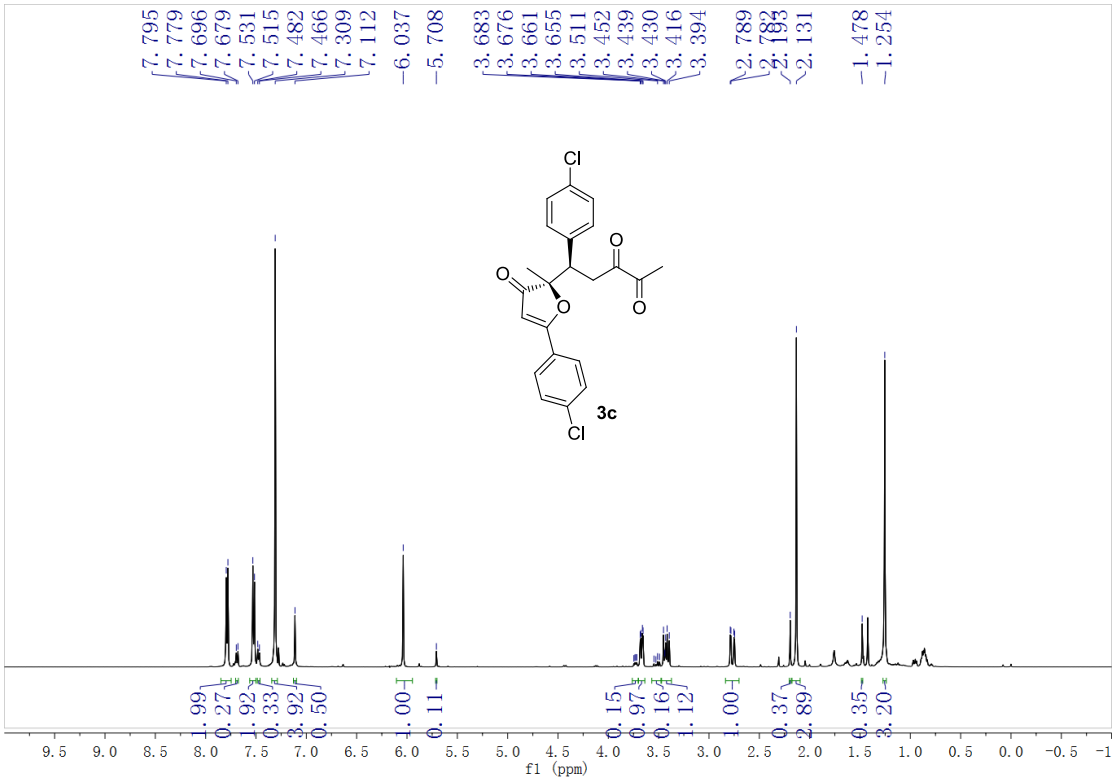
^{1}H NMR (500 MHz, $CDCl_3$)



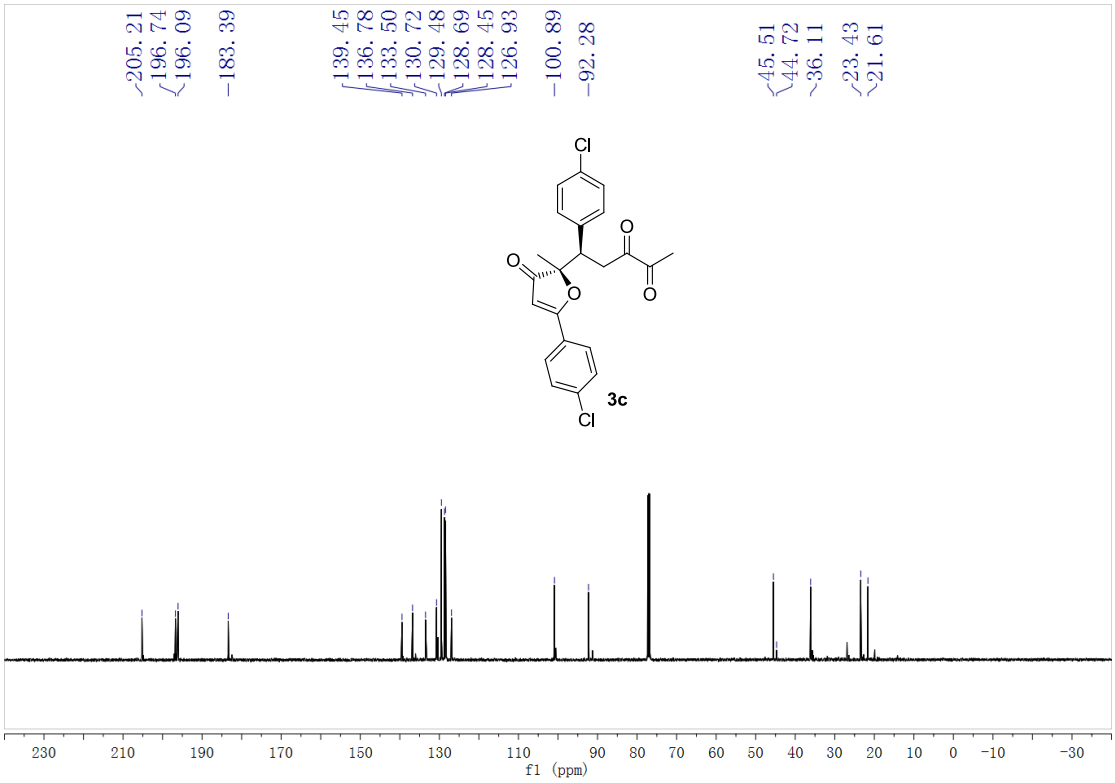
^{13}C NMR (125 MHz, $CDCl_3$)



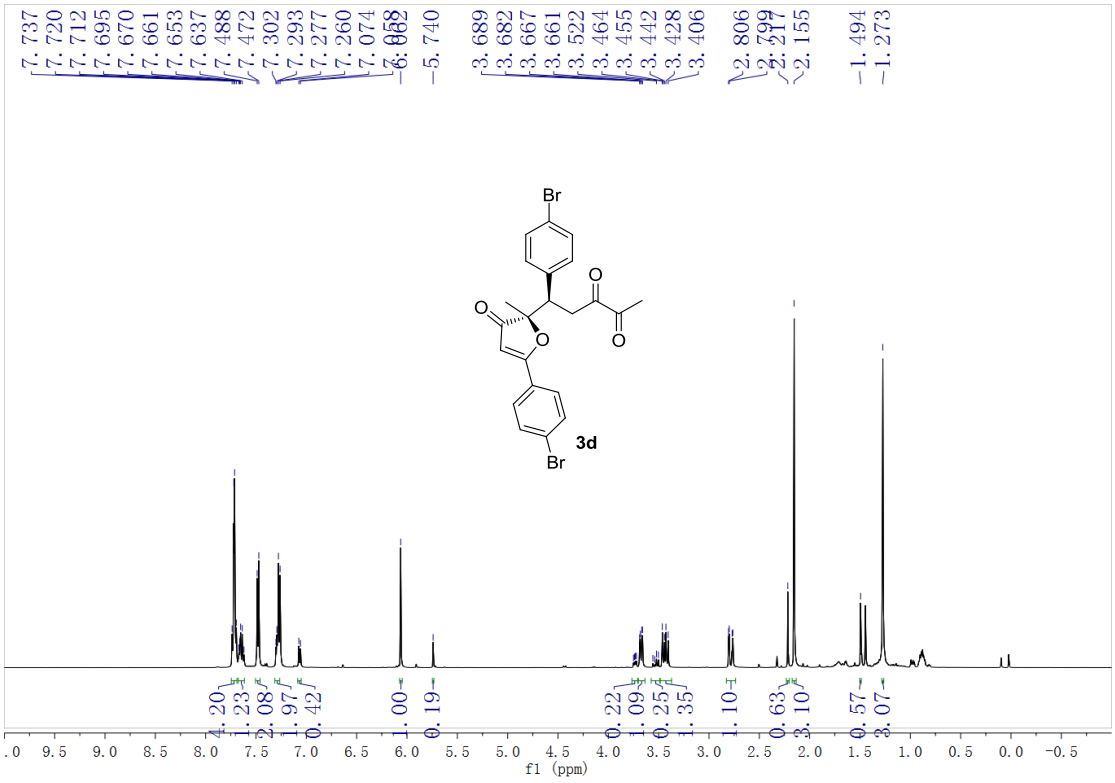
^{1}H NMR (500 MHz, $CDCl_3$)



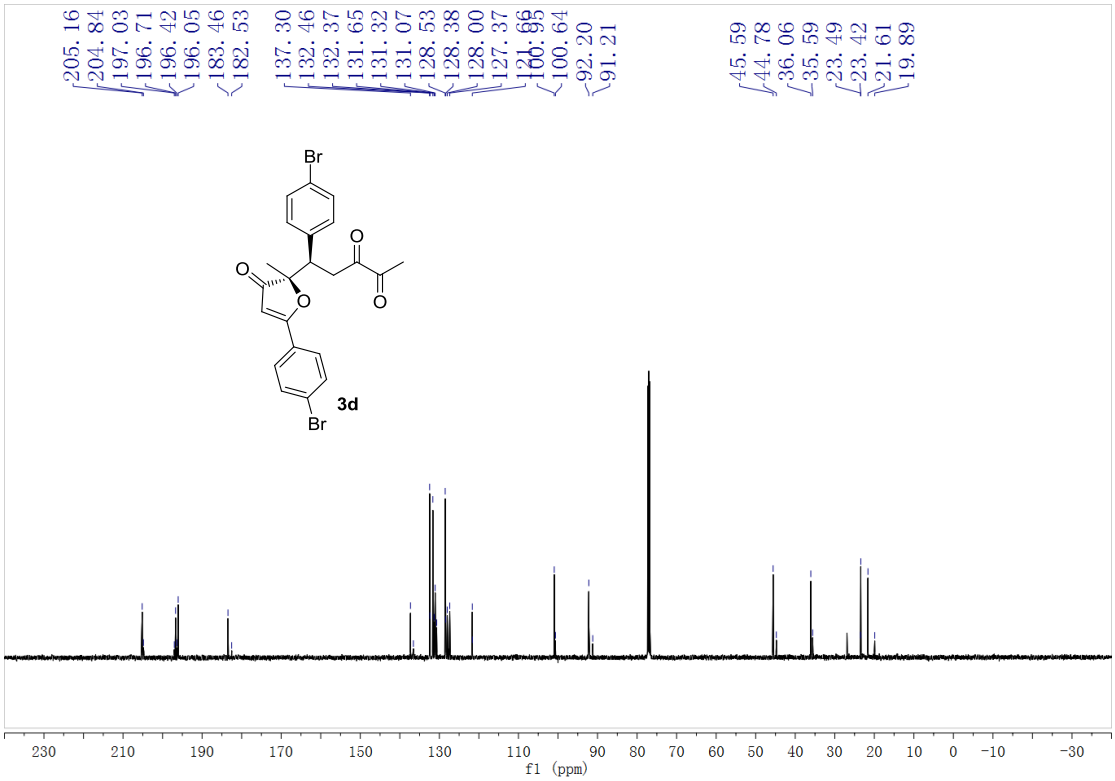
^{13}C NMR (125 MHz, $CDCl_3$)



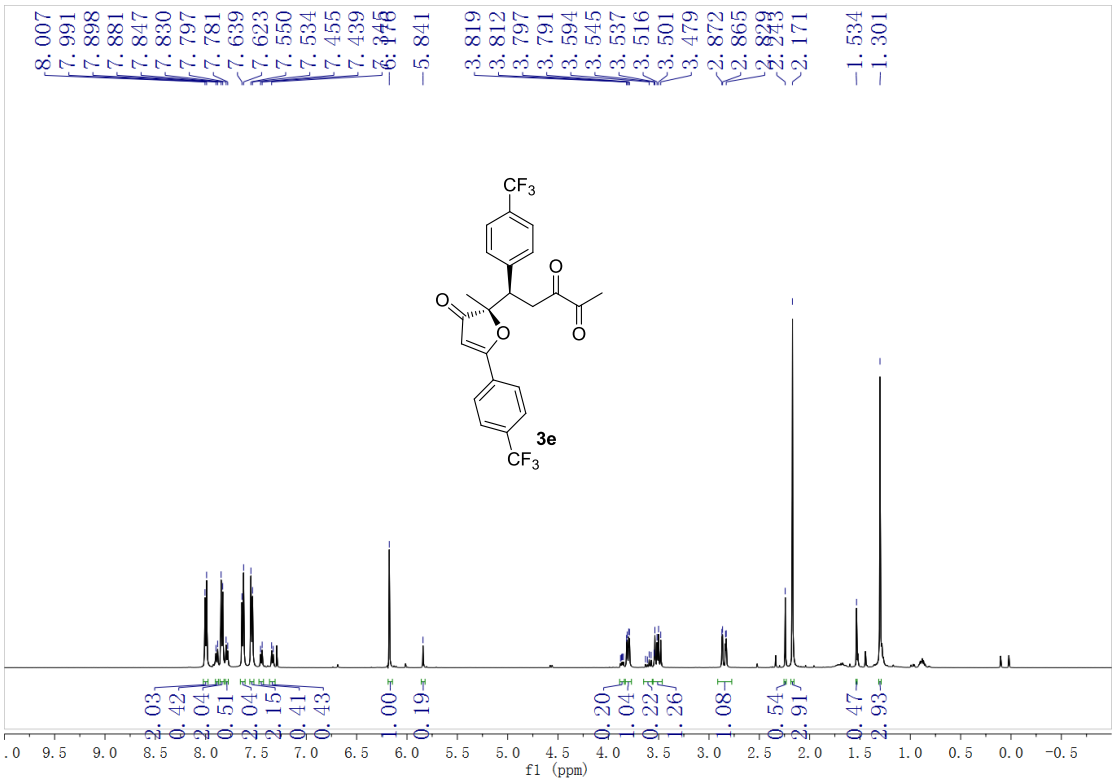
^{1}H NMR (500 MHz, $CDCl_3$)



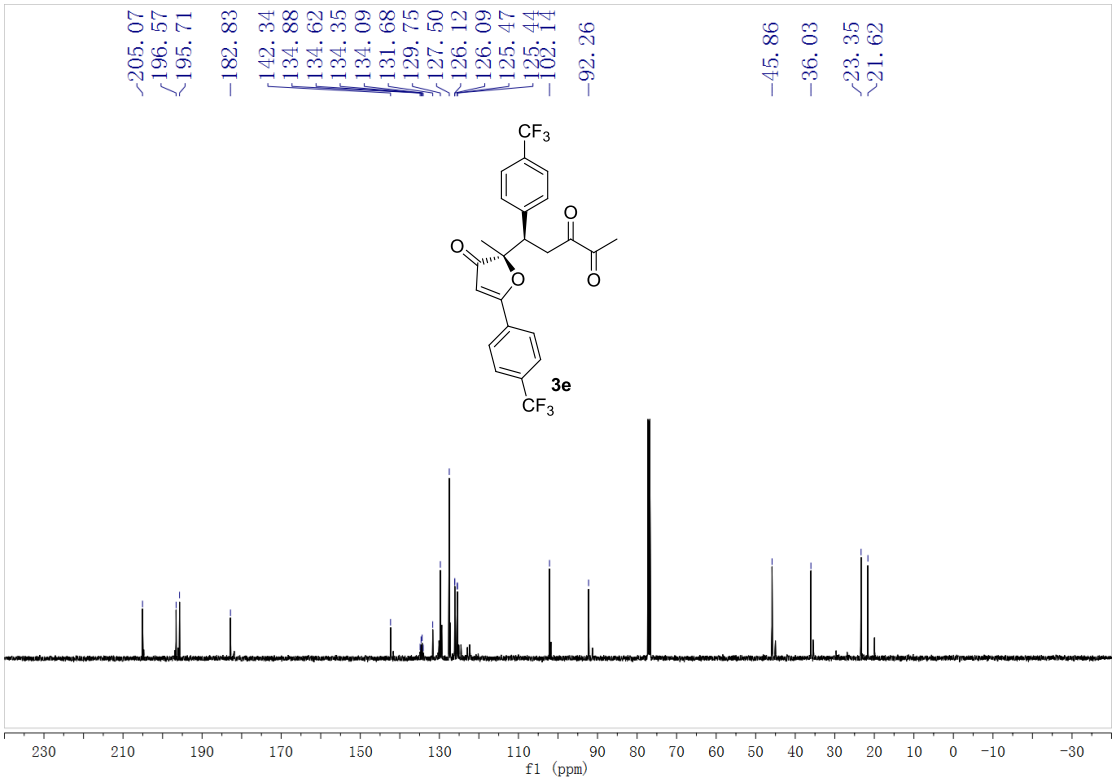
^{13}C NMR (125 MHz, $CDCl_3$)



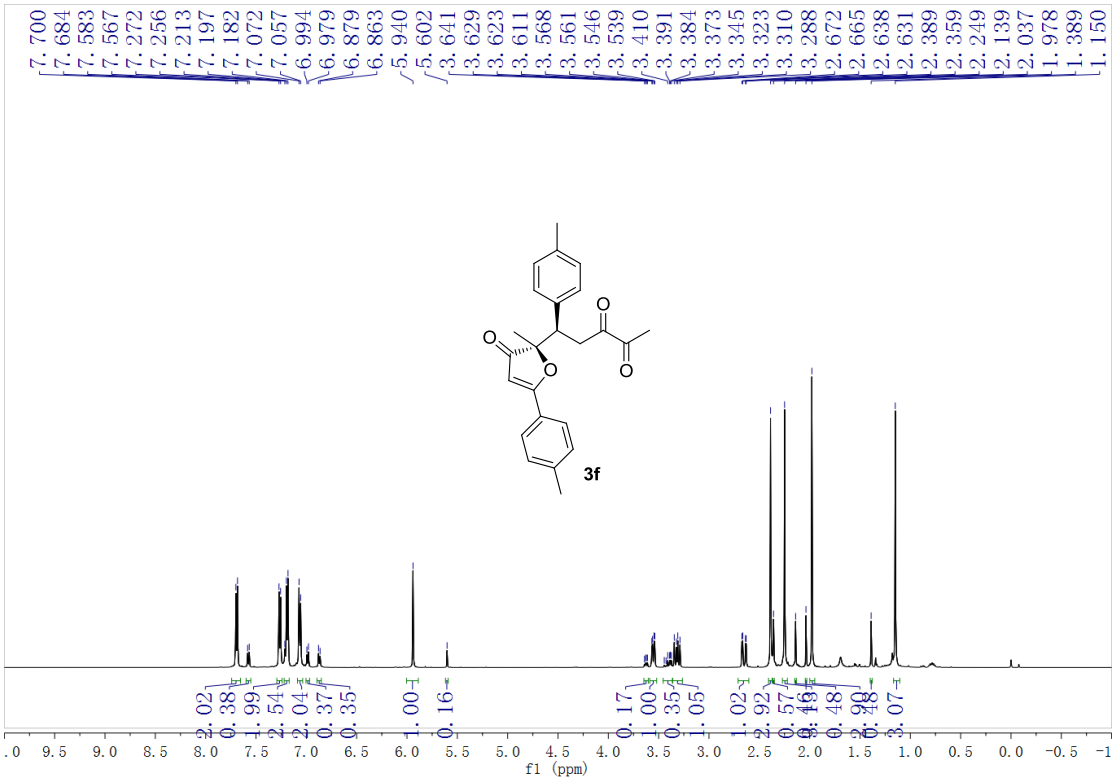
^{1}H NMR (500 MHz, $CDCl_3$)



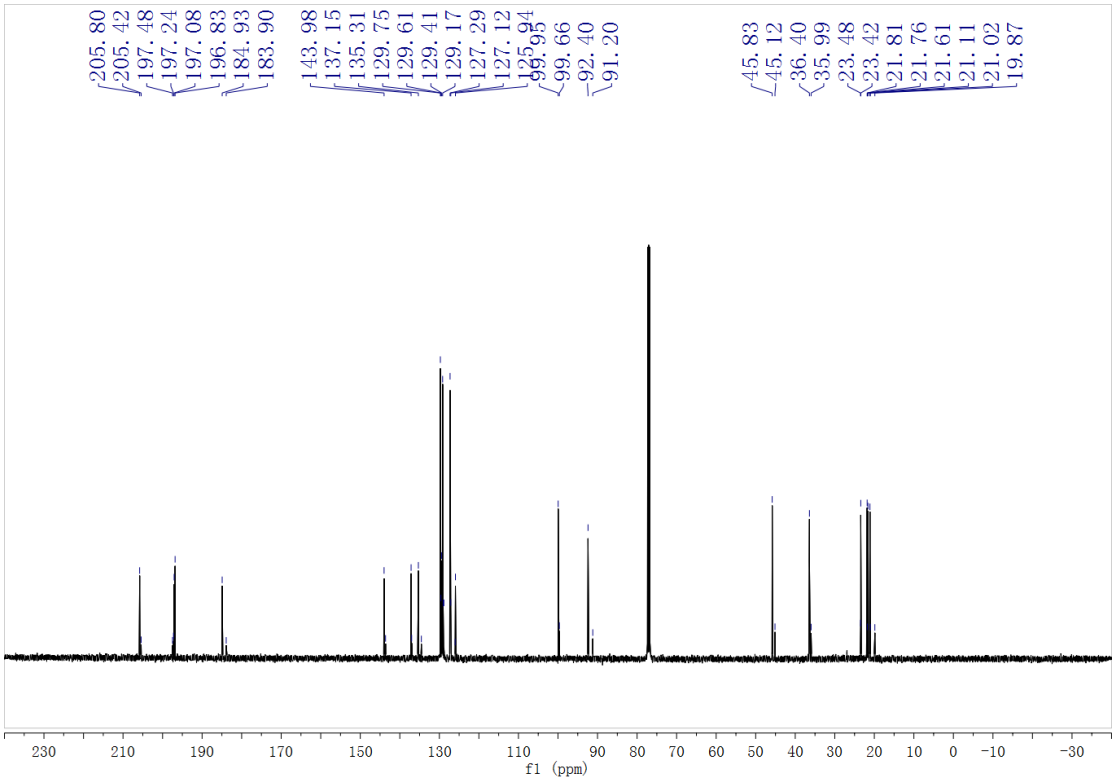
^{13}C NMR (125 MHz, $CDCl_3$)



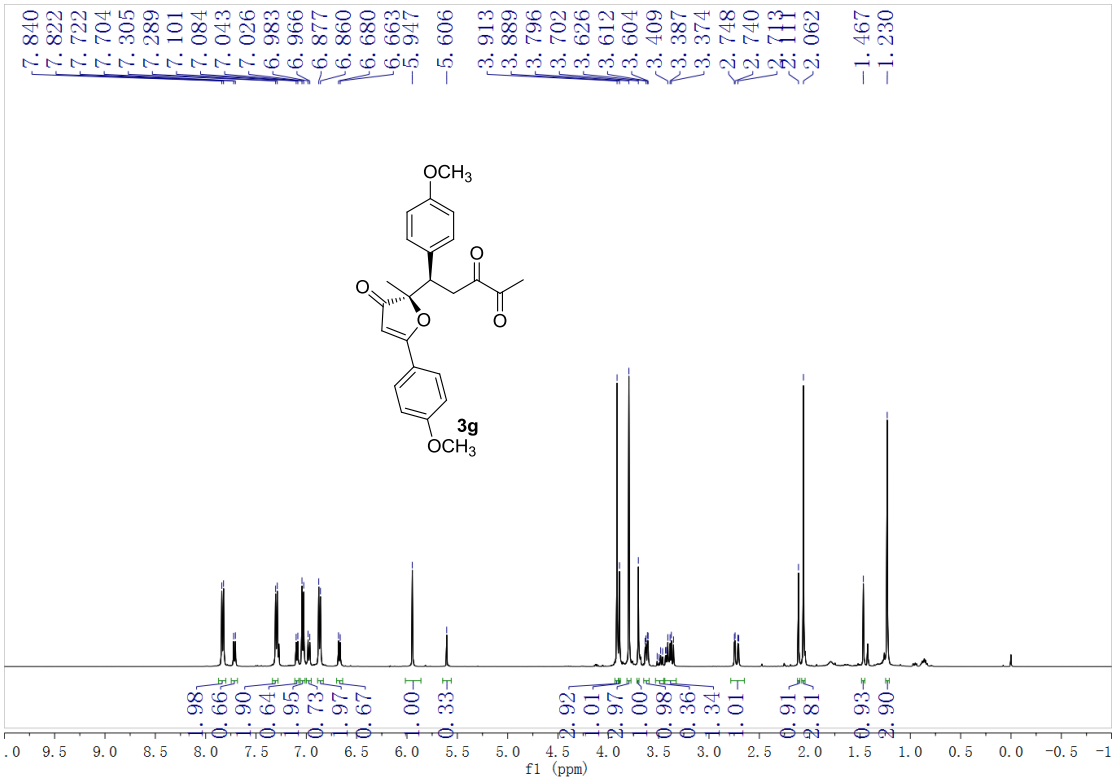
^{1}H NMR (500 MHz, $CDCl_3$)



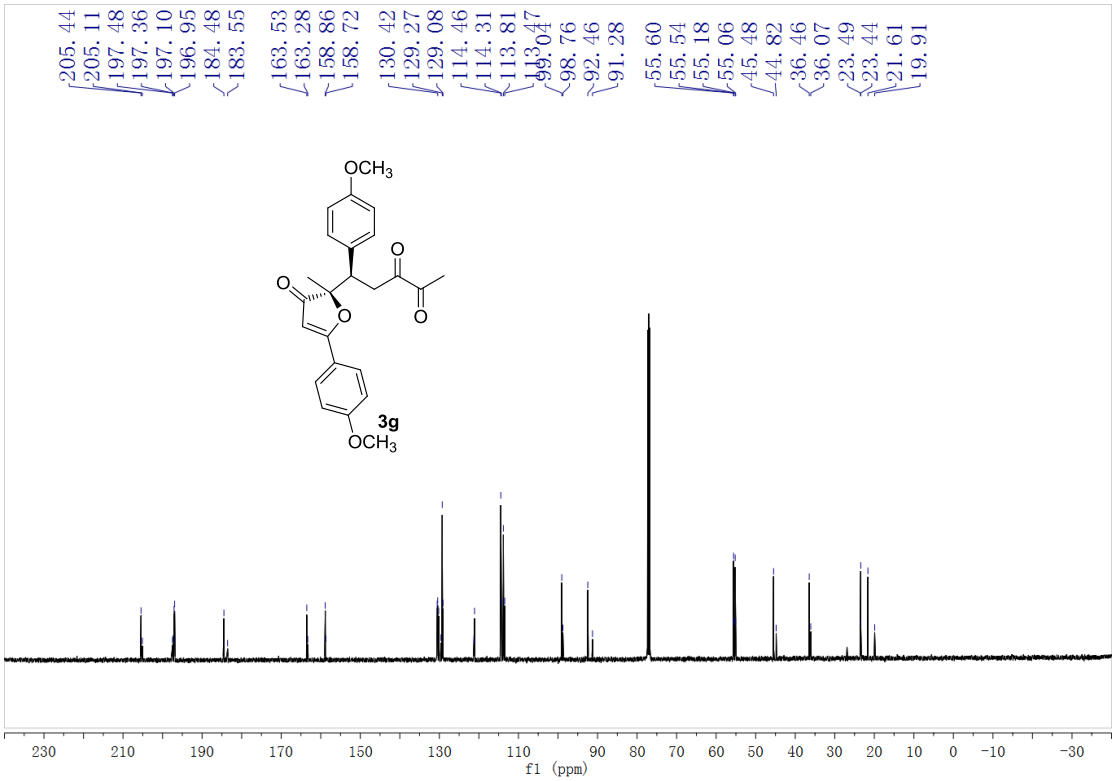
^{13}C NMR (125 MHz, $CDCl_3$)



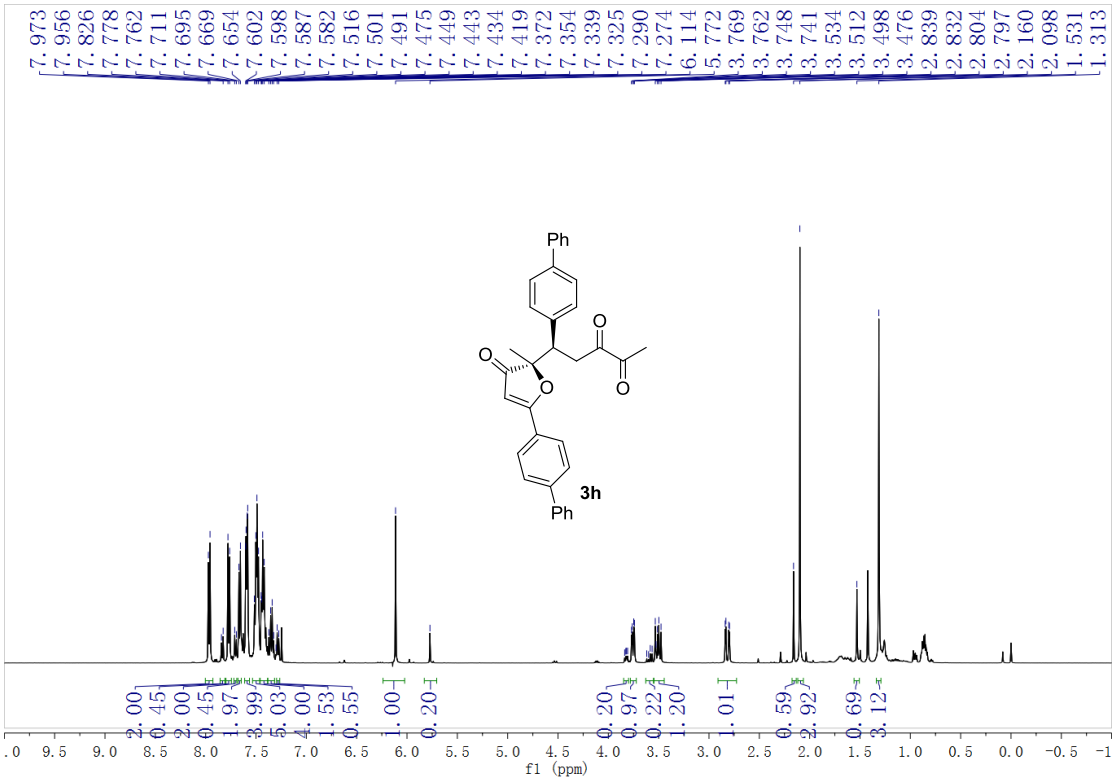
^{1}H NMR (500 MHz, $CDCl_3$)



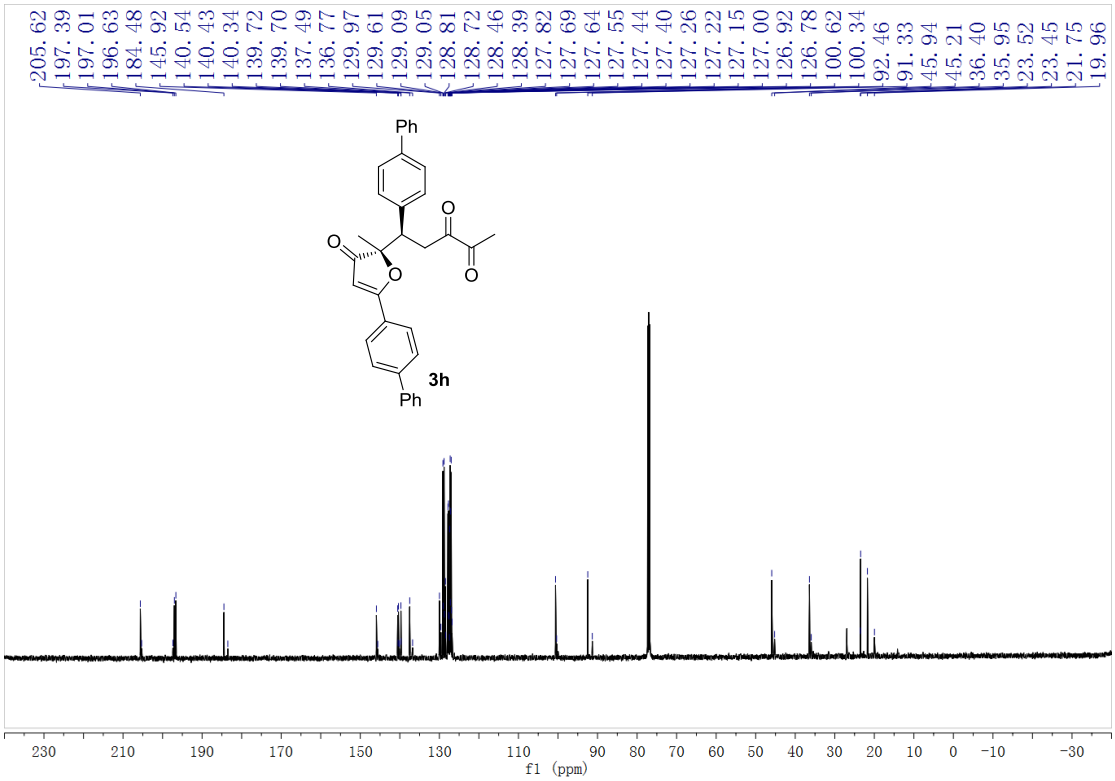
^{13}C NMR (125 MHz, $CDCl_3$)



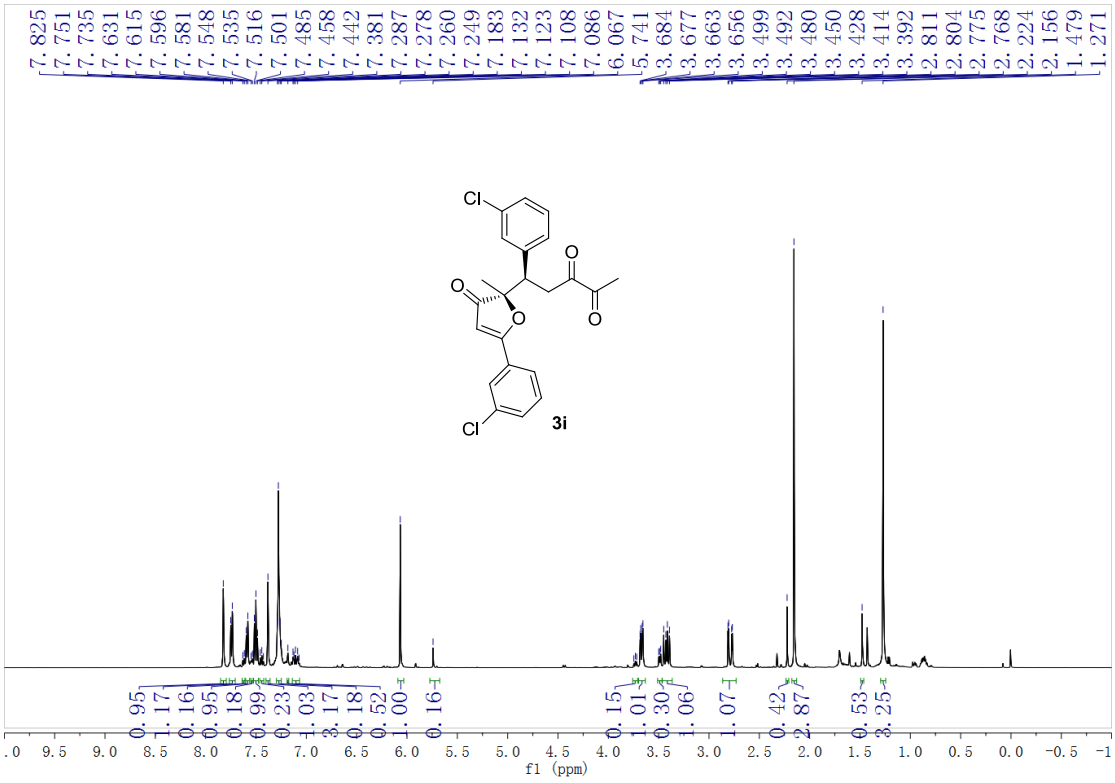
^{1}H NMR (500 MHz, $CDCl_3$)



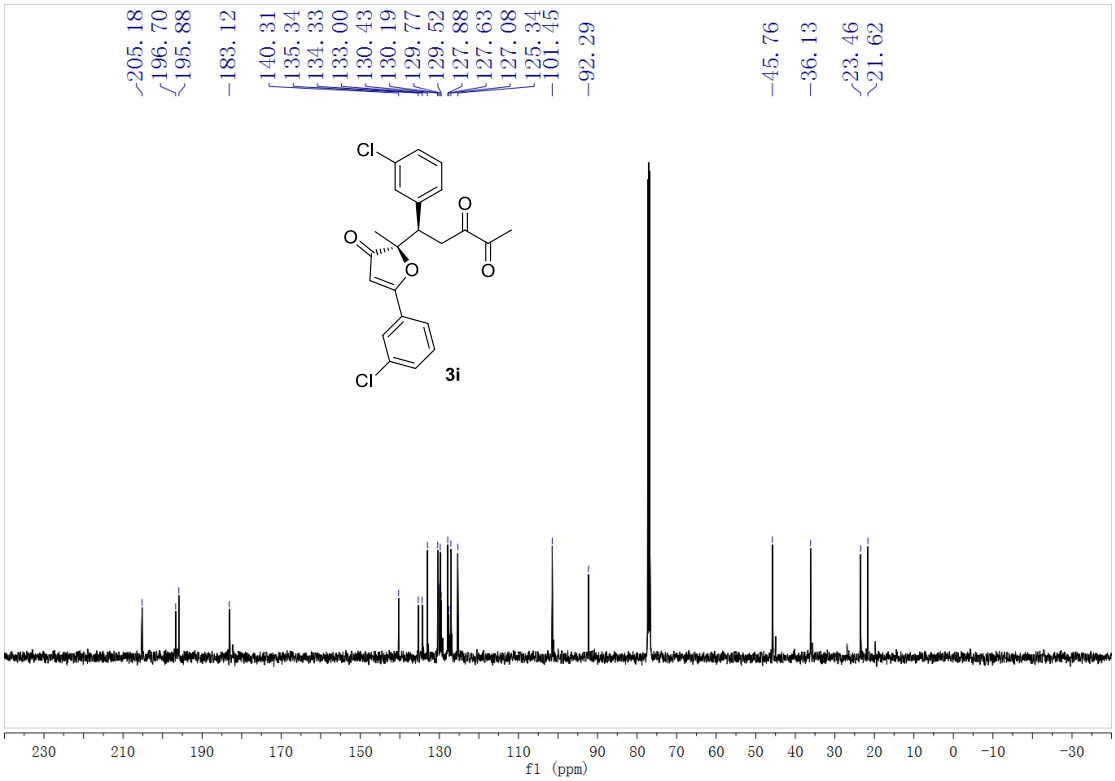
^{13}C NMR (125 MHz, $CDCl_3$)



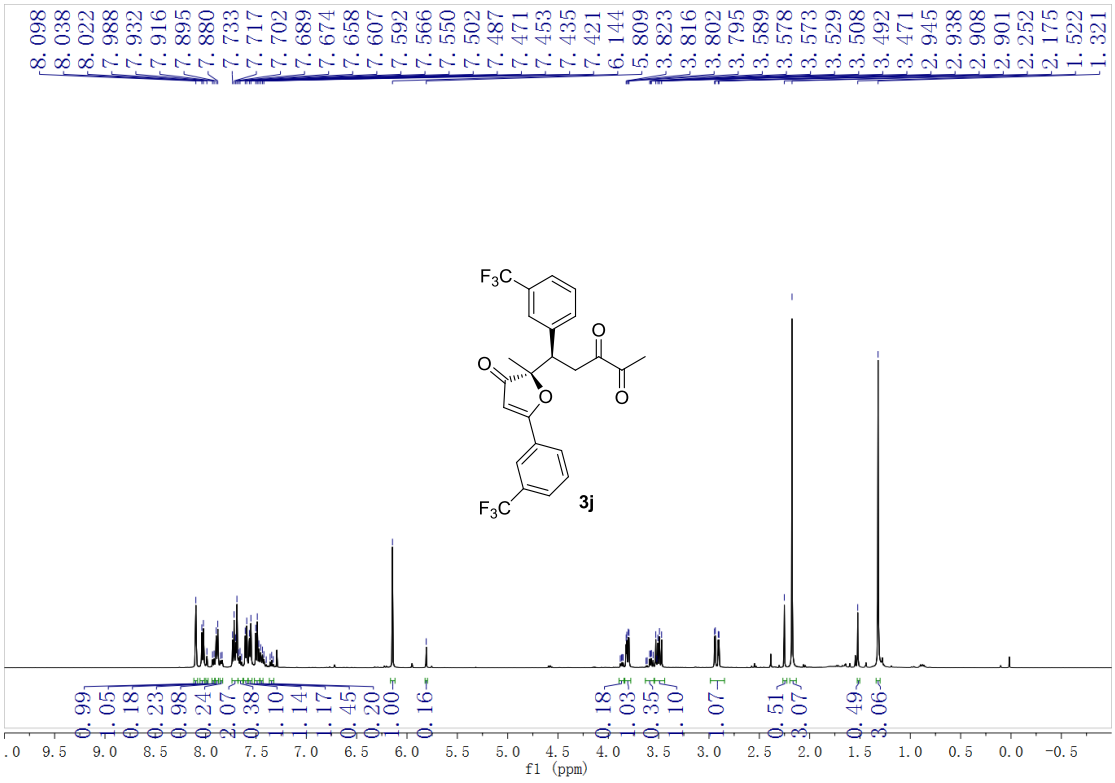
^{1}H NMR (500 MHz, $CDCl_3$)



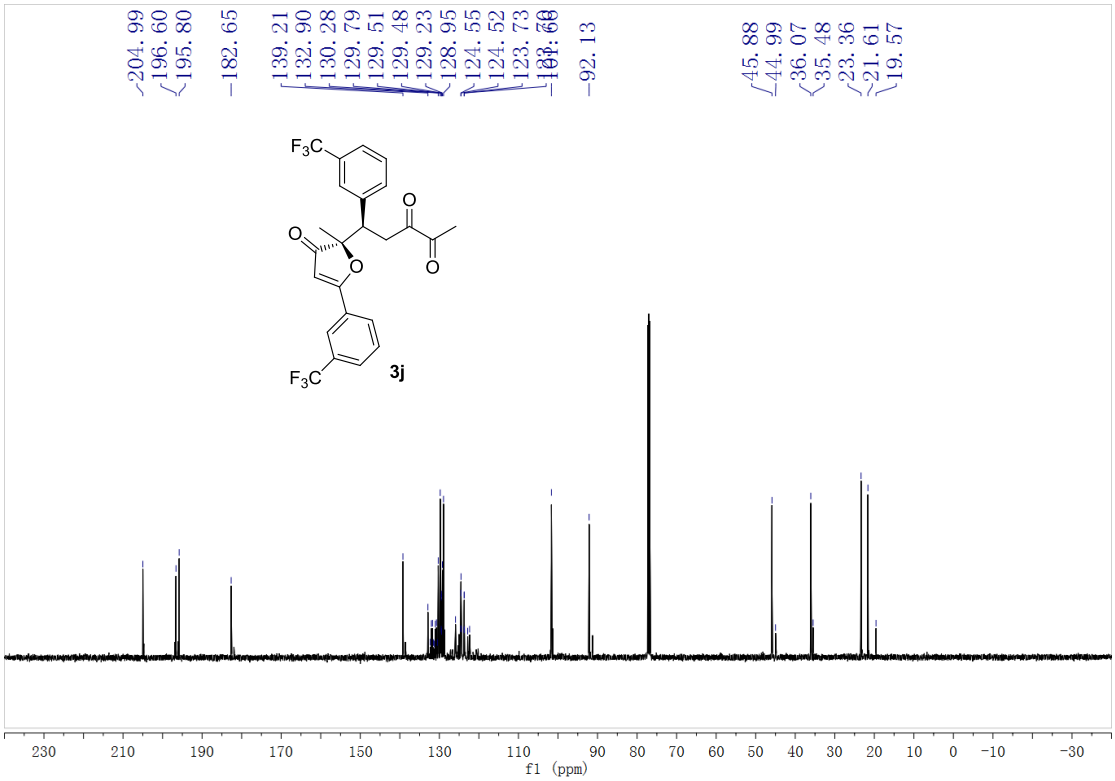
^{13}C NMR (125 MHz, $CDCl_3$)



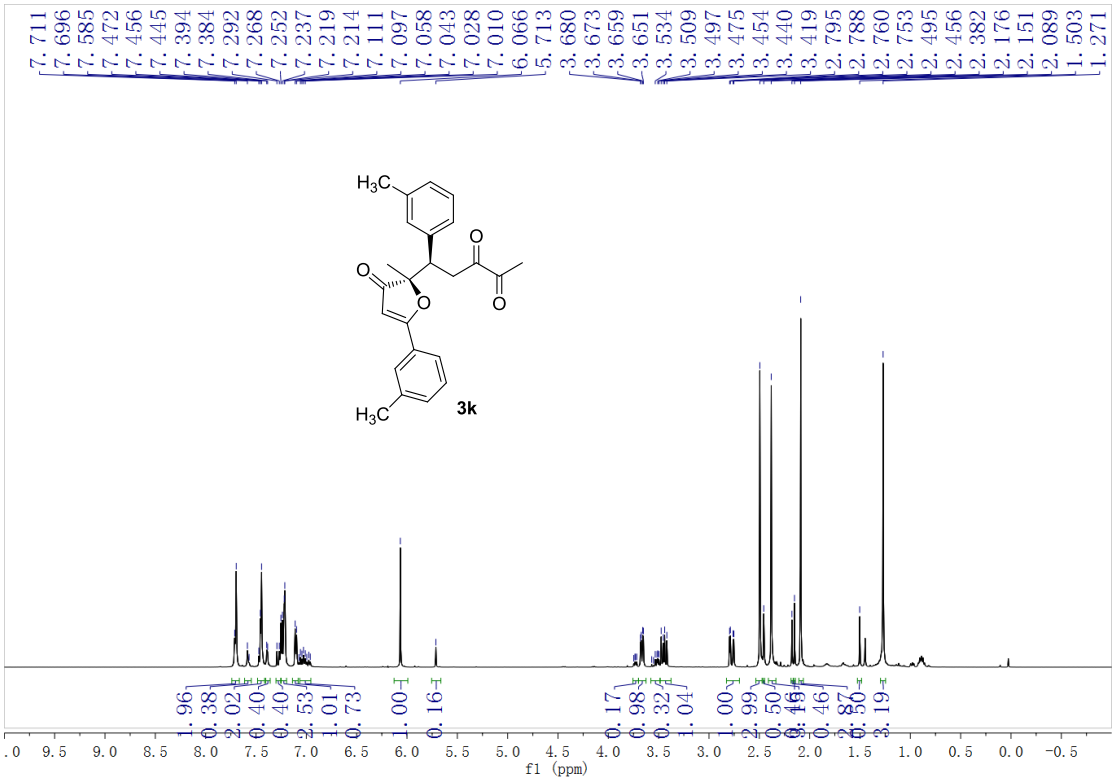
^{1}H NMR (500 MHz, $CDCl_3$)



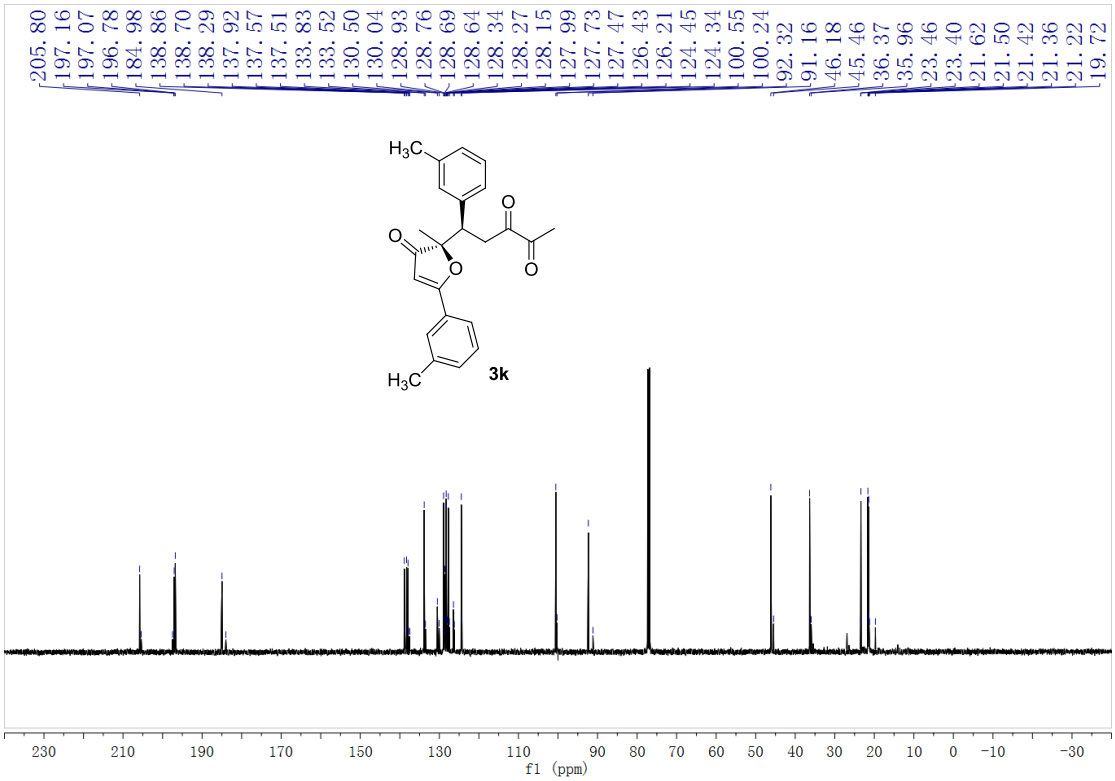
^{13}C NMR (125 MHz, $CDCl_3$)



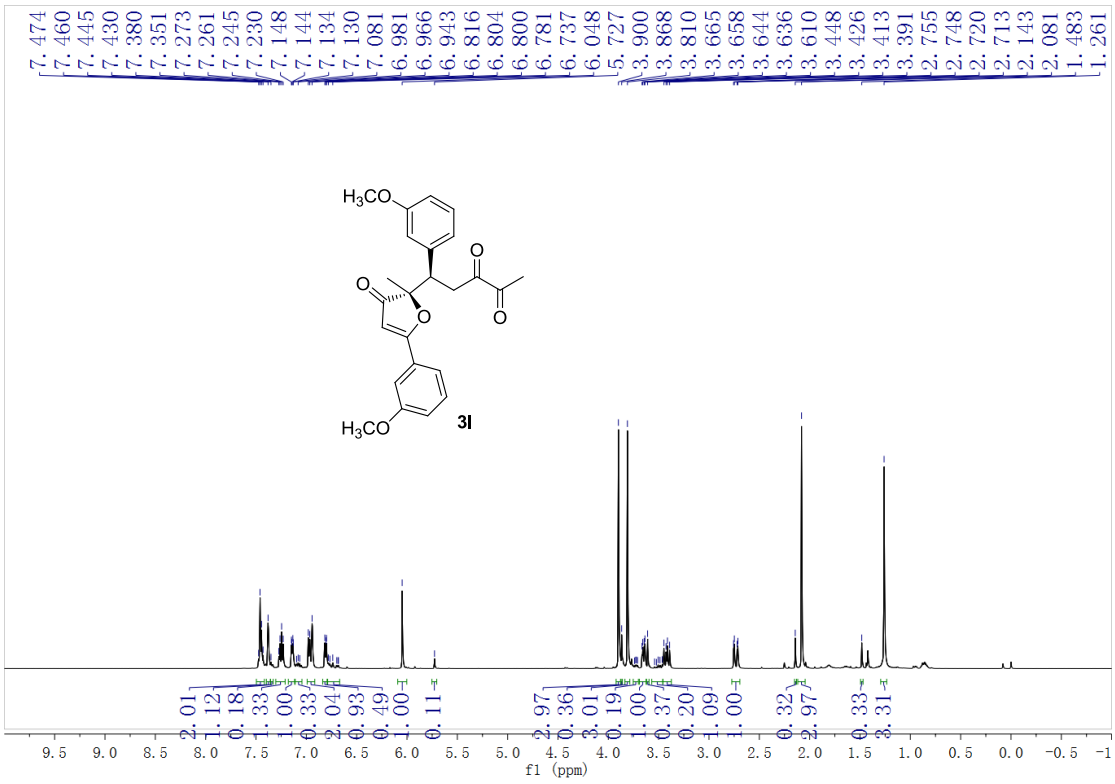
^{1}HNMR (500 MHz, $CDCl_3$)



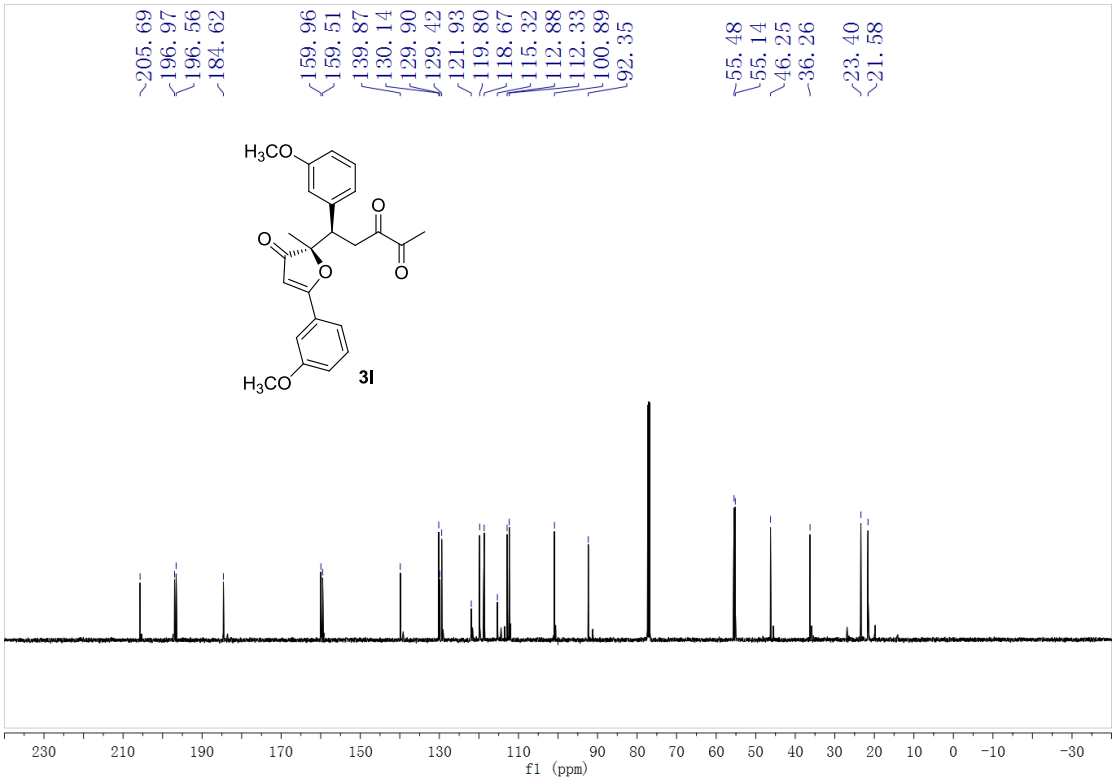
^{13}C NMR (125 MHz, $CDCl_3$)



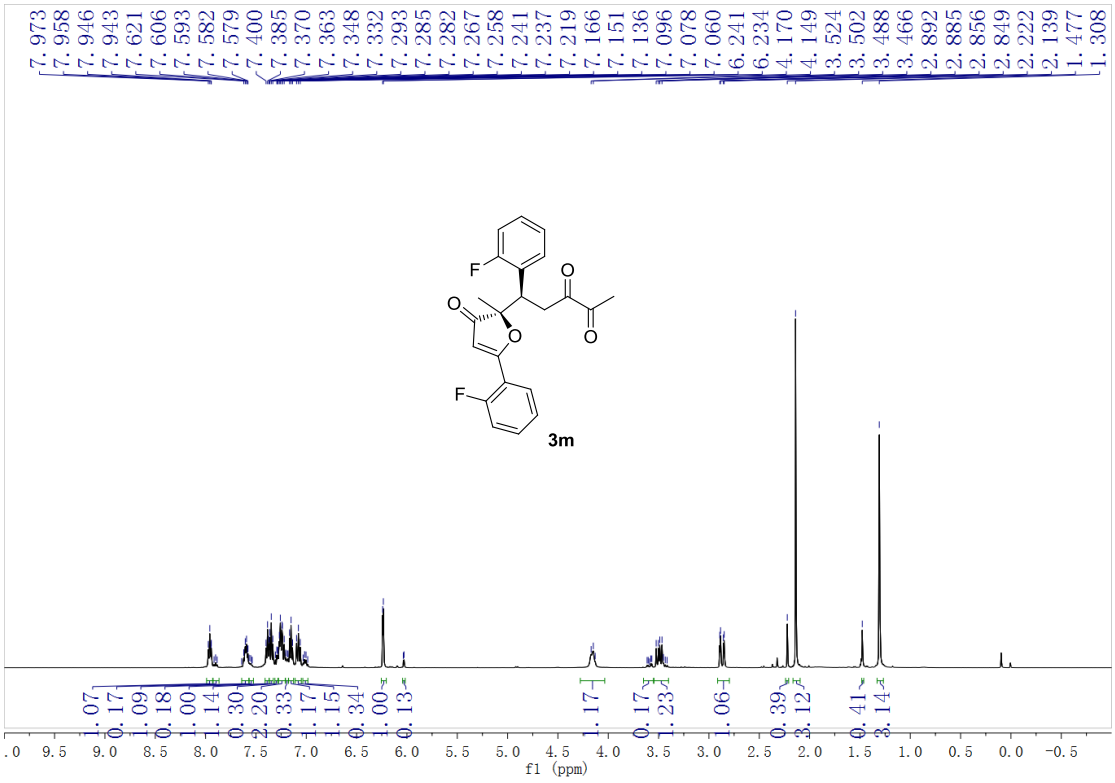
^{1}H NMR (500 MHz, $CDCl_3$)



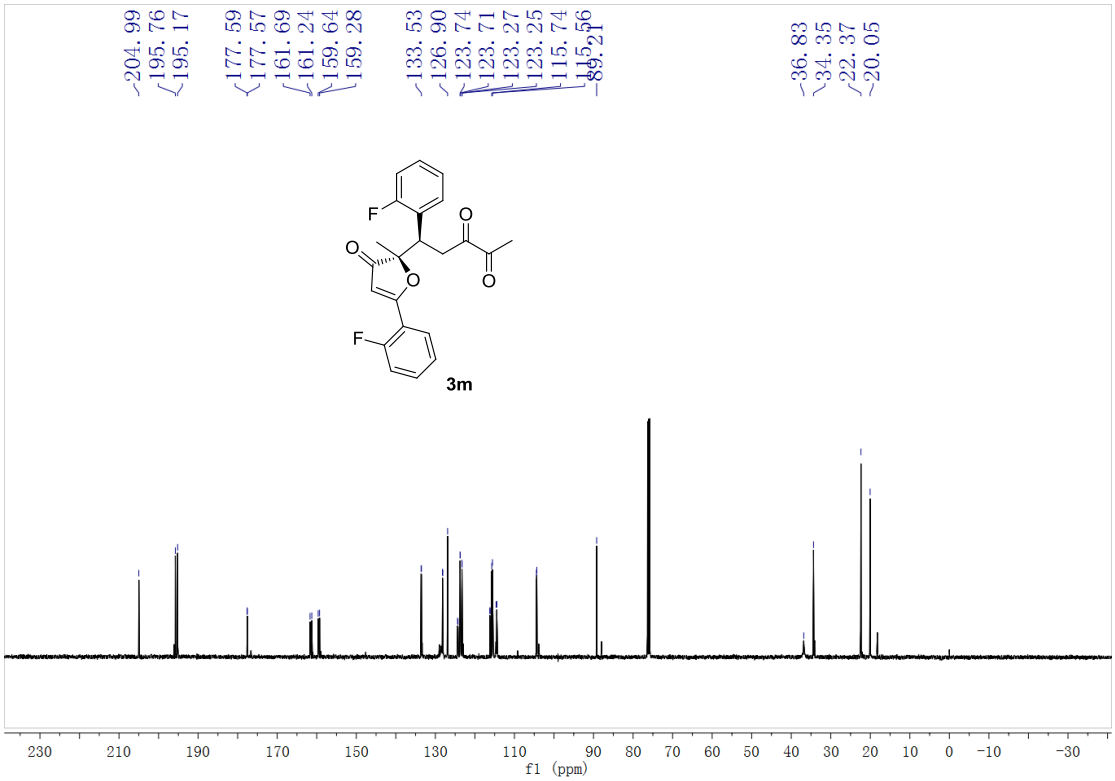
^{13}C NMR (125 MHz, $CDCl_3$)



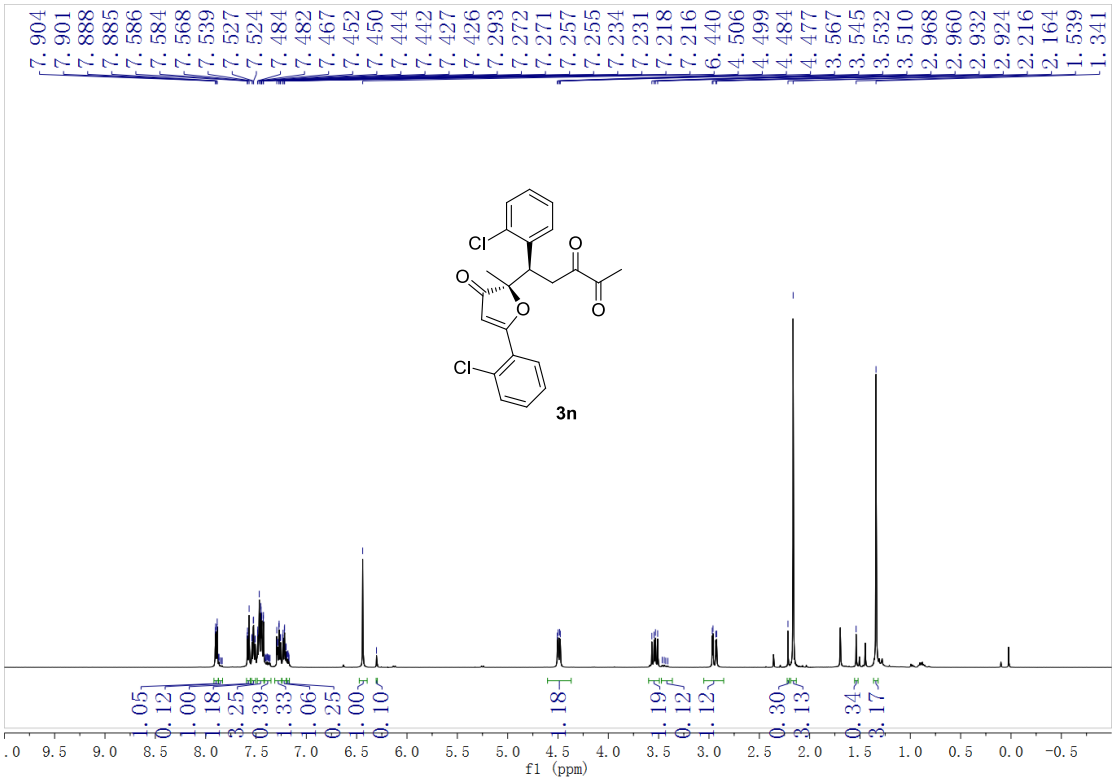
^{1}H NMR (500 MHz, $CDCl_3$)



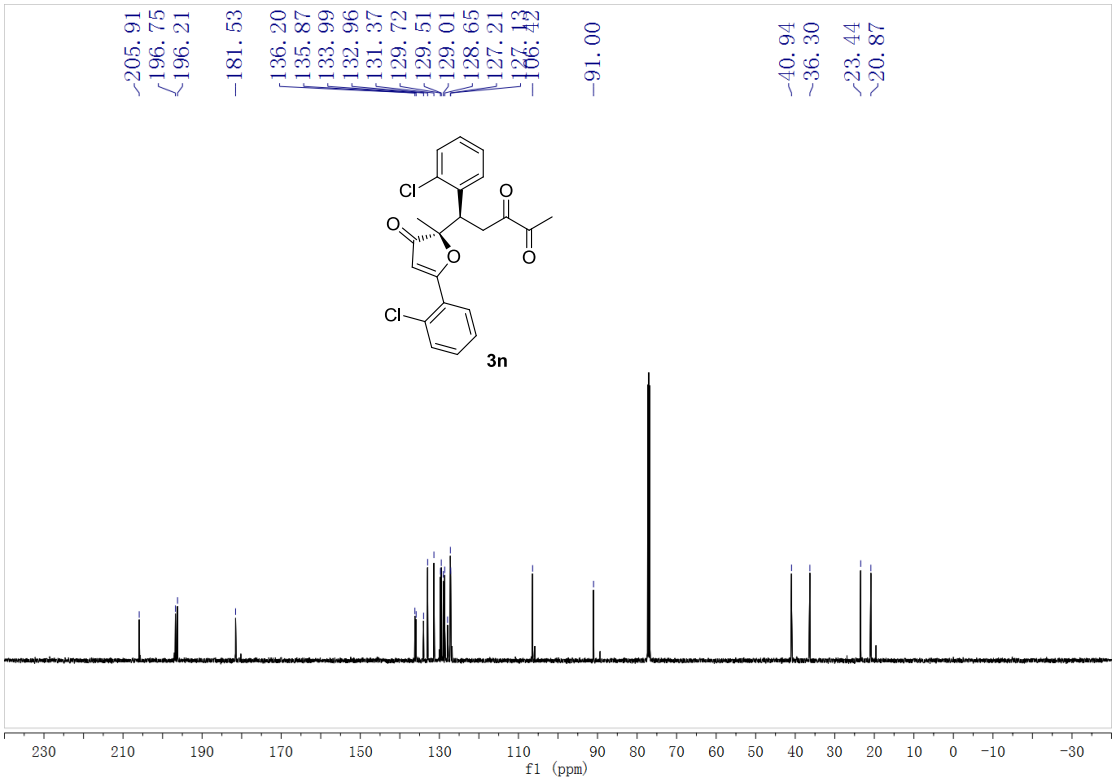
^{13}C NMR (125 MHz, $CDCl_3$)



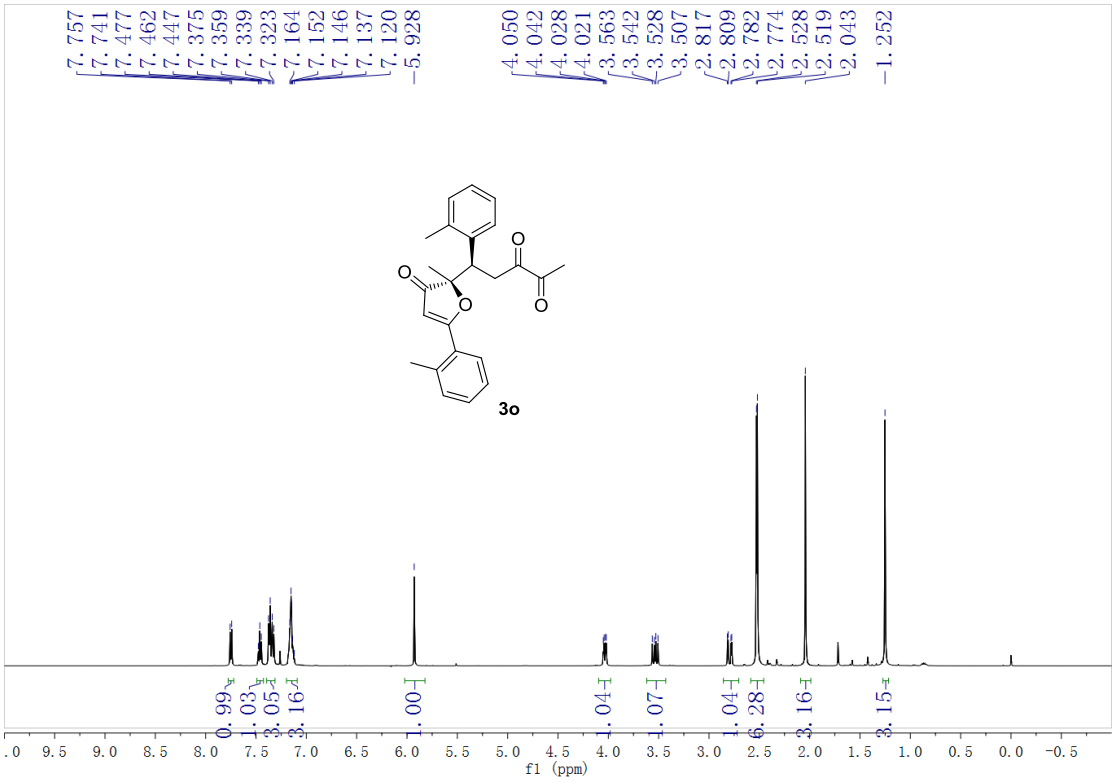
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}NMR (125 MHz, $CDCl_3$)

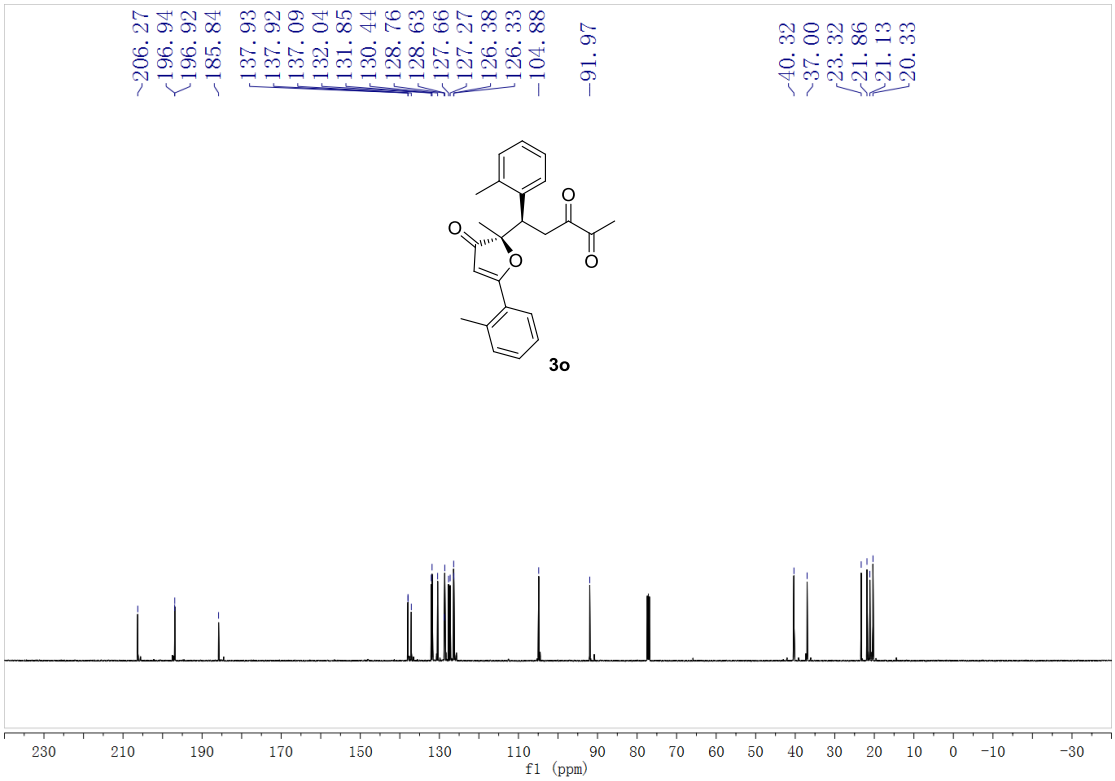


^{1}H NMR (500 MHz, $CDCl_3$)



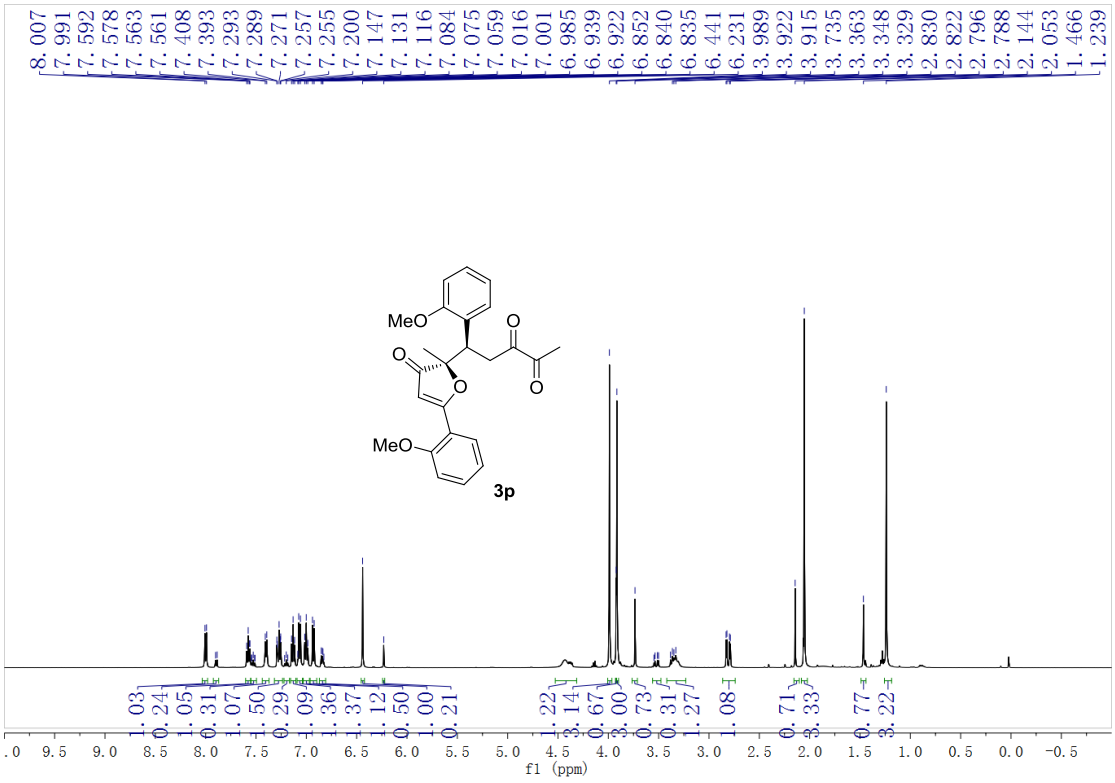
3o

^{13}C NMR (125 MHz, $CDCl_3$)

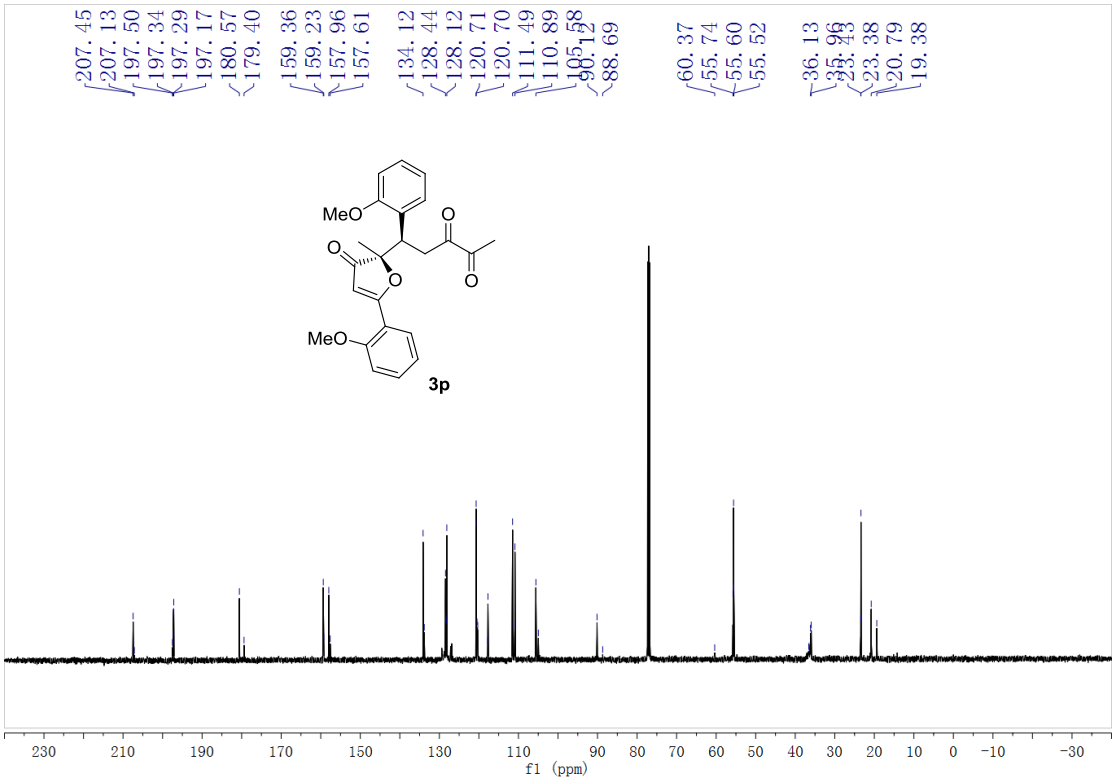


3o

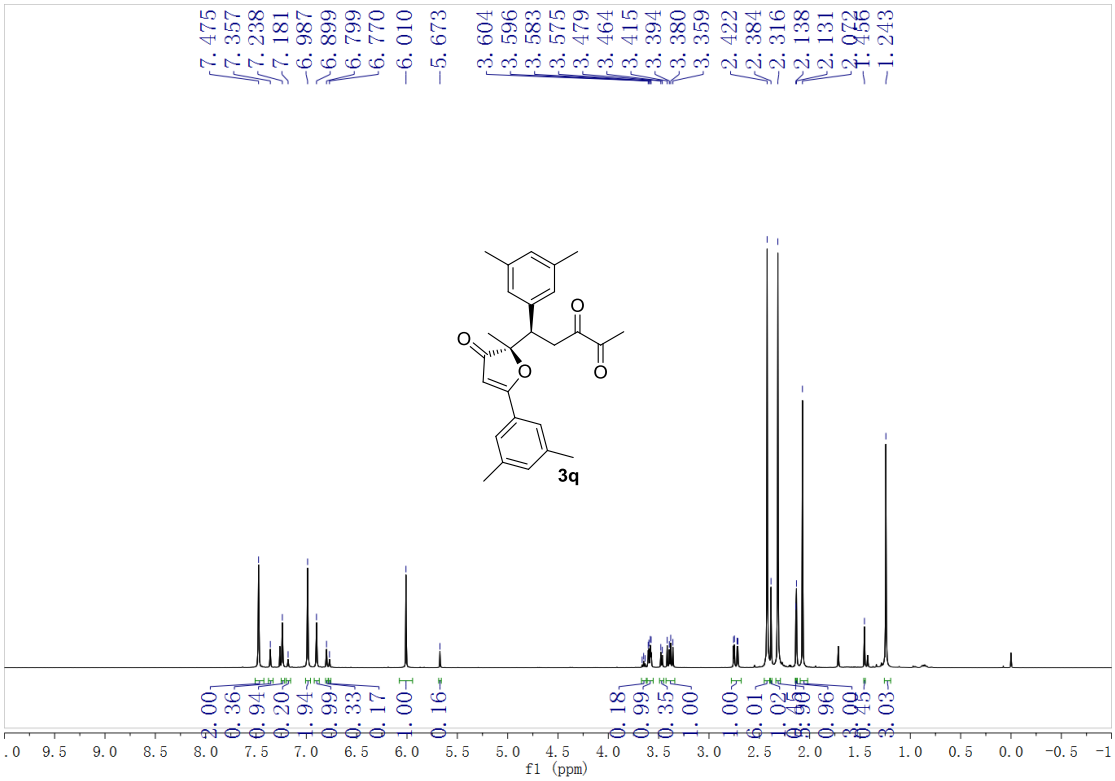
^{1}H NMR (500 MHz, $CDCl_3$)



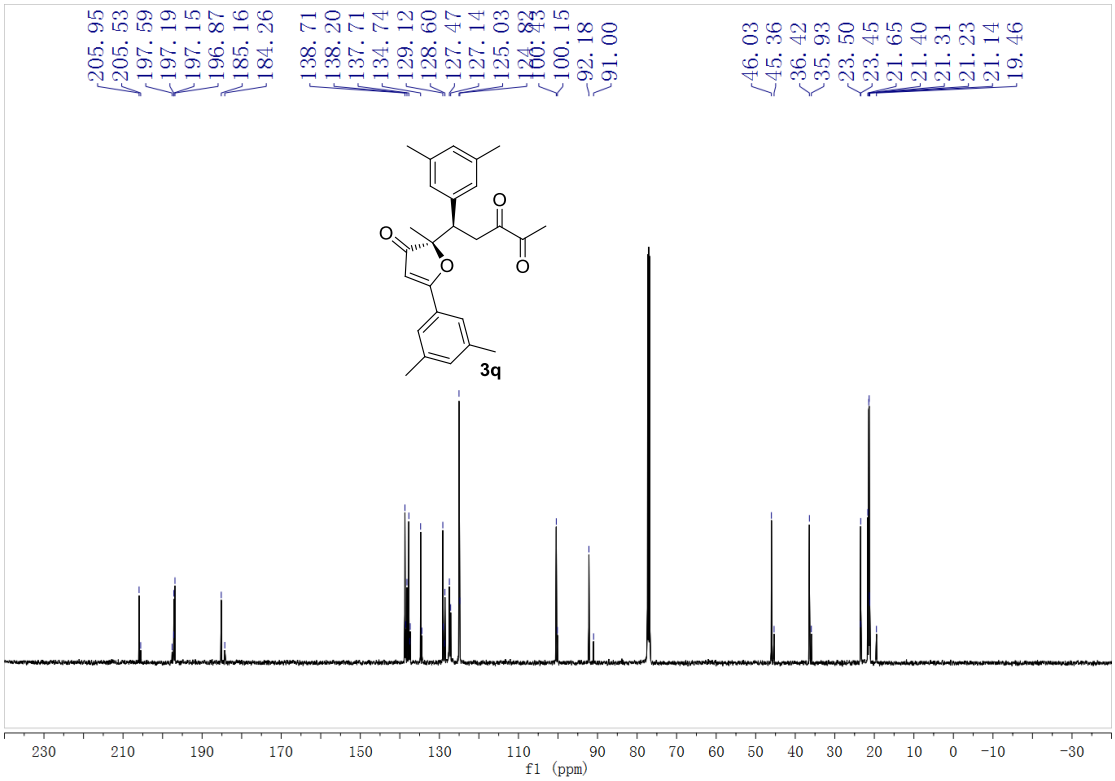
^{13}C NMR (125 MHz, $CDCl_3$)



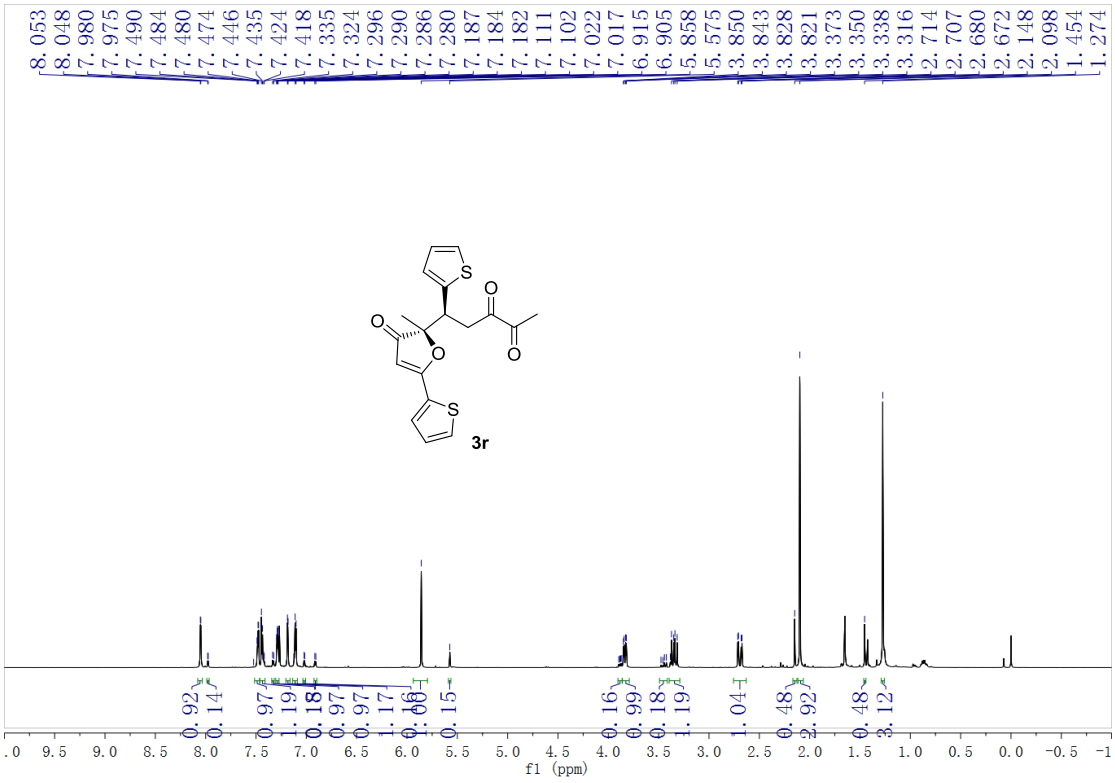
^{1}H NMR (500 MHz, $CDCl_3$)



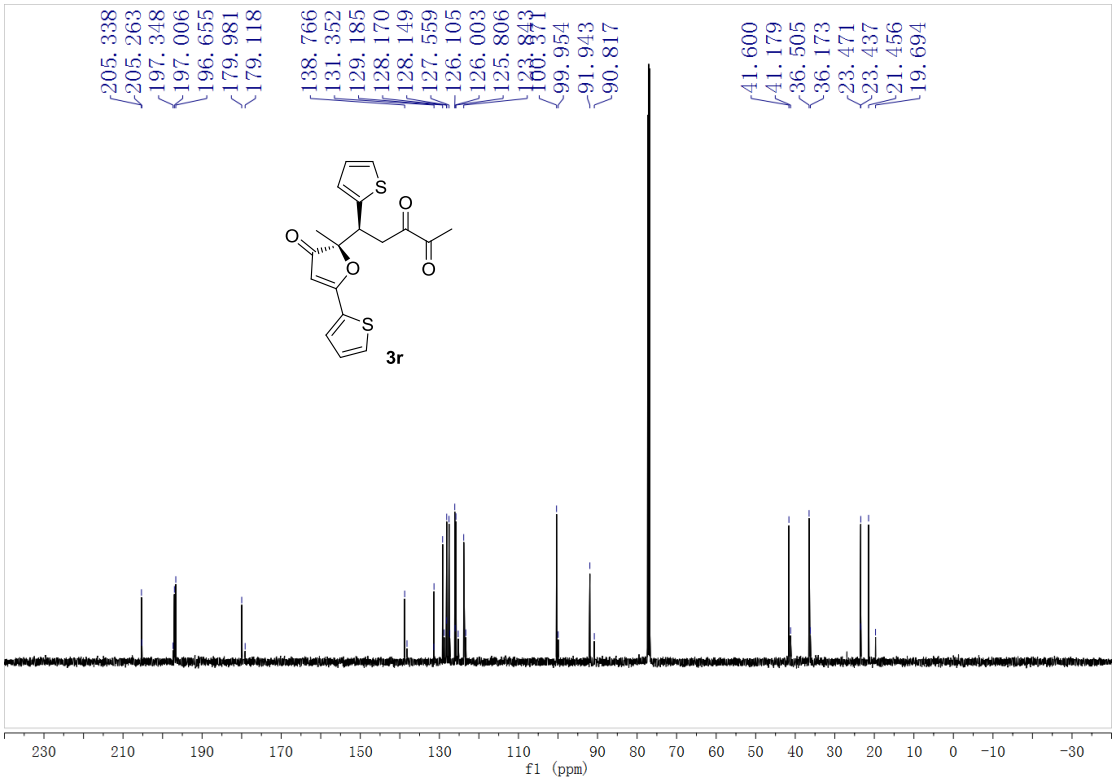
^{13}C NMR (125 MHz, $CDCl_3$)



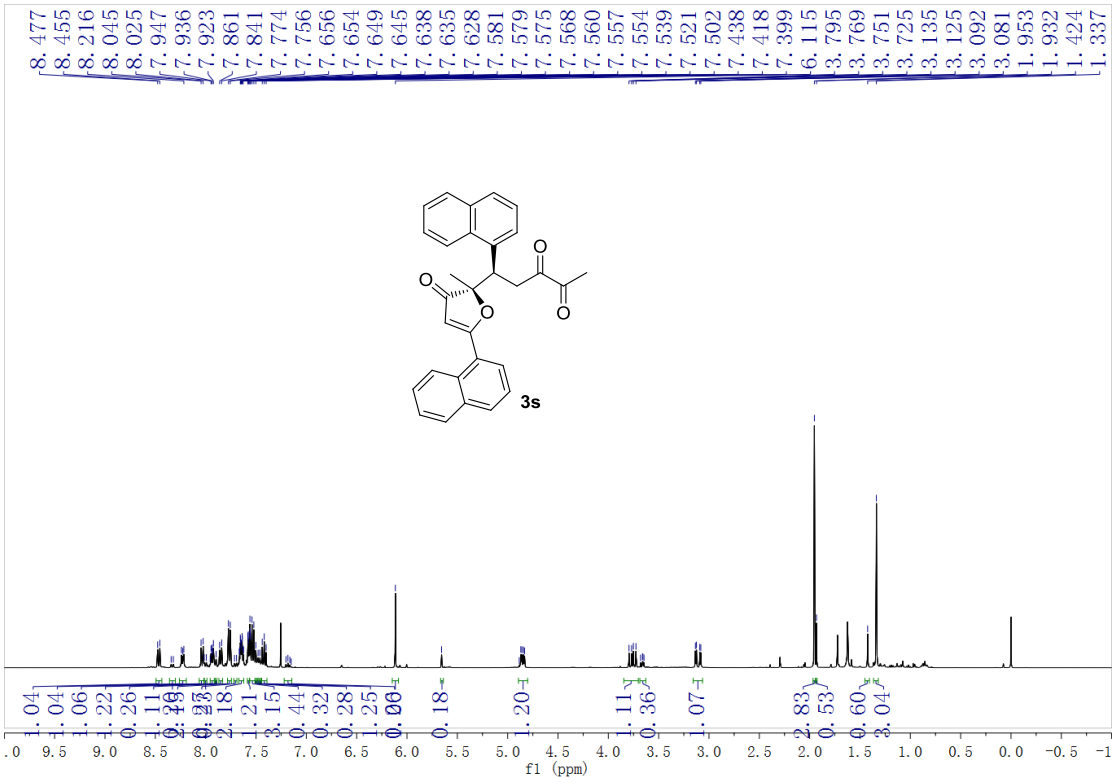
^{1}H NMR (500 MHz, $CDCl_3$)



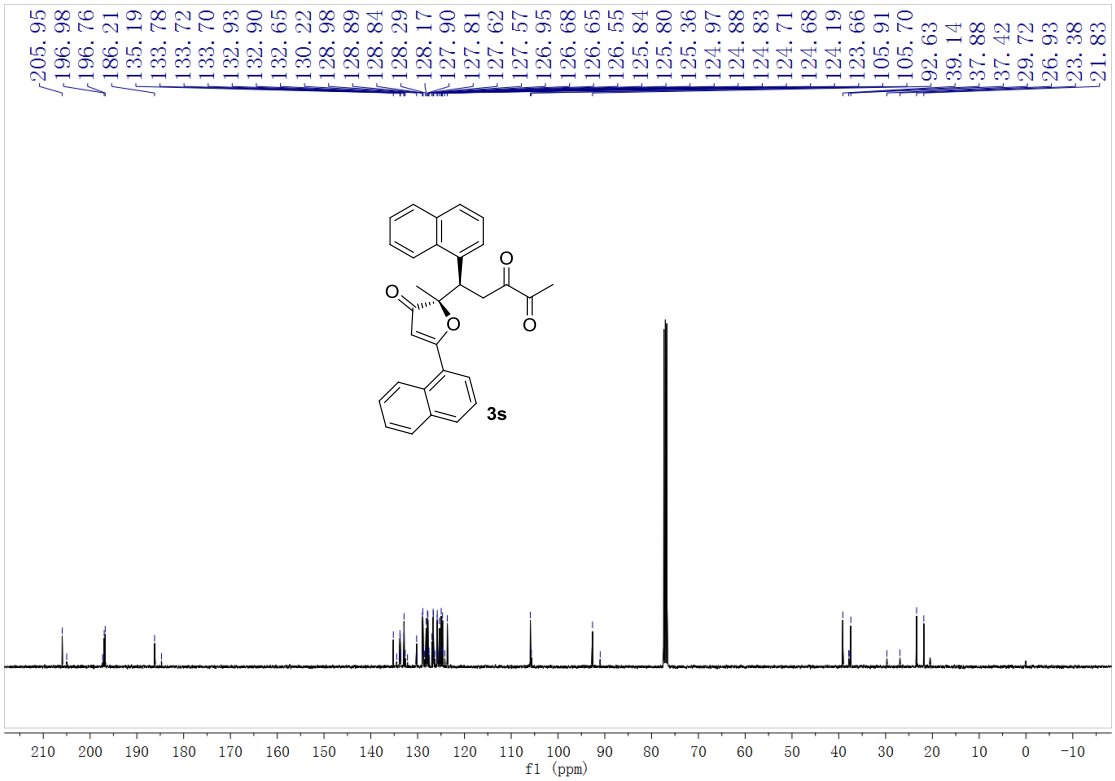
^{13}C NMR (125 MHz, $CDCl_3$)



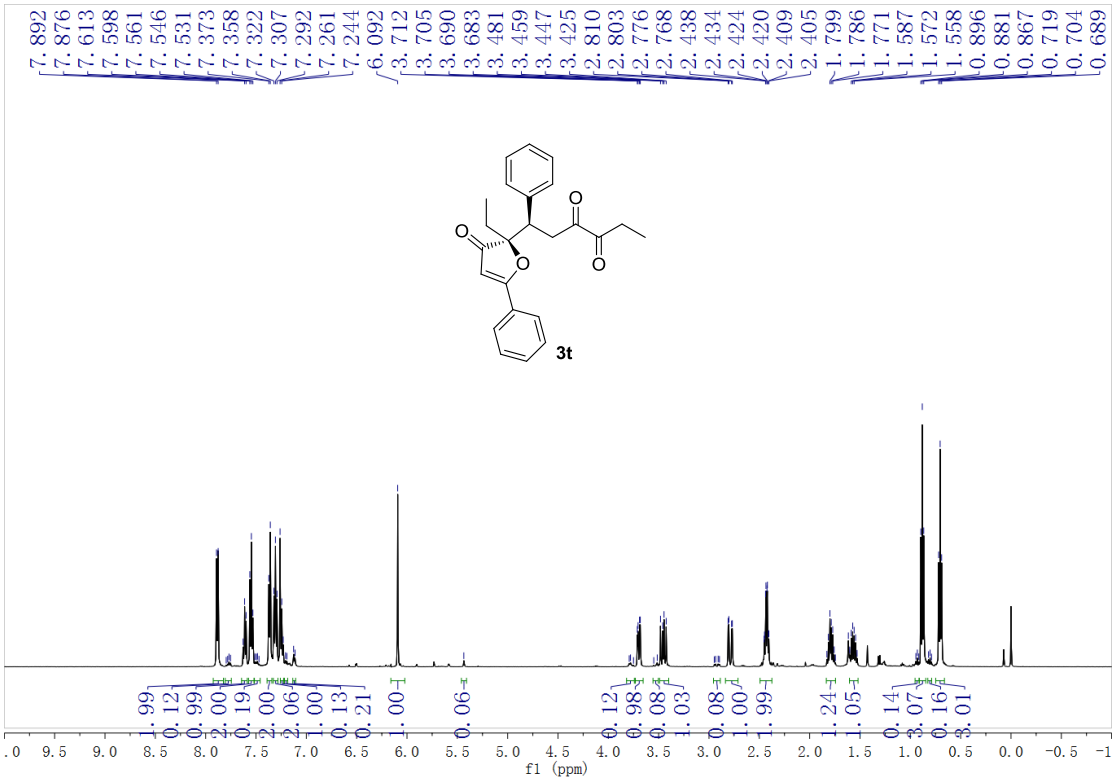
^{1}H NMR (500 MHz, $CDCl_3$)



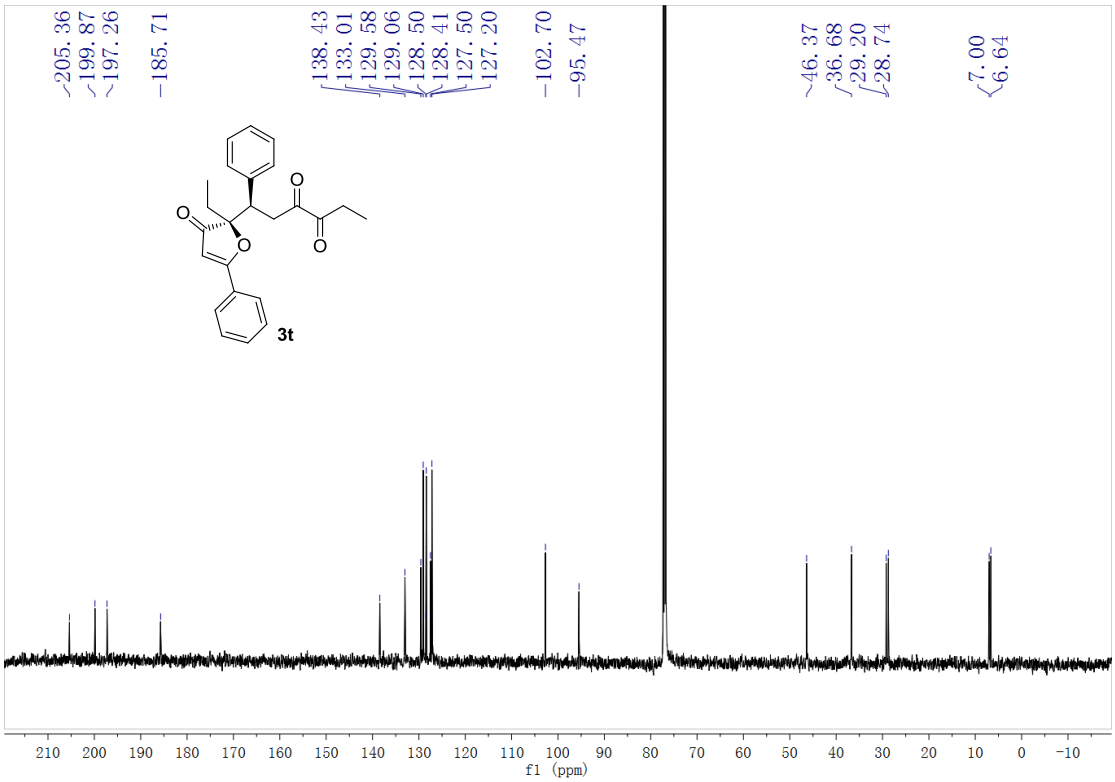
^{13}C NMR (100 MHz, $CDCl_3$)



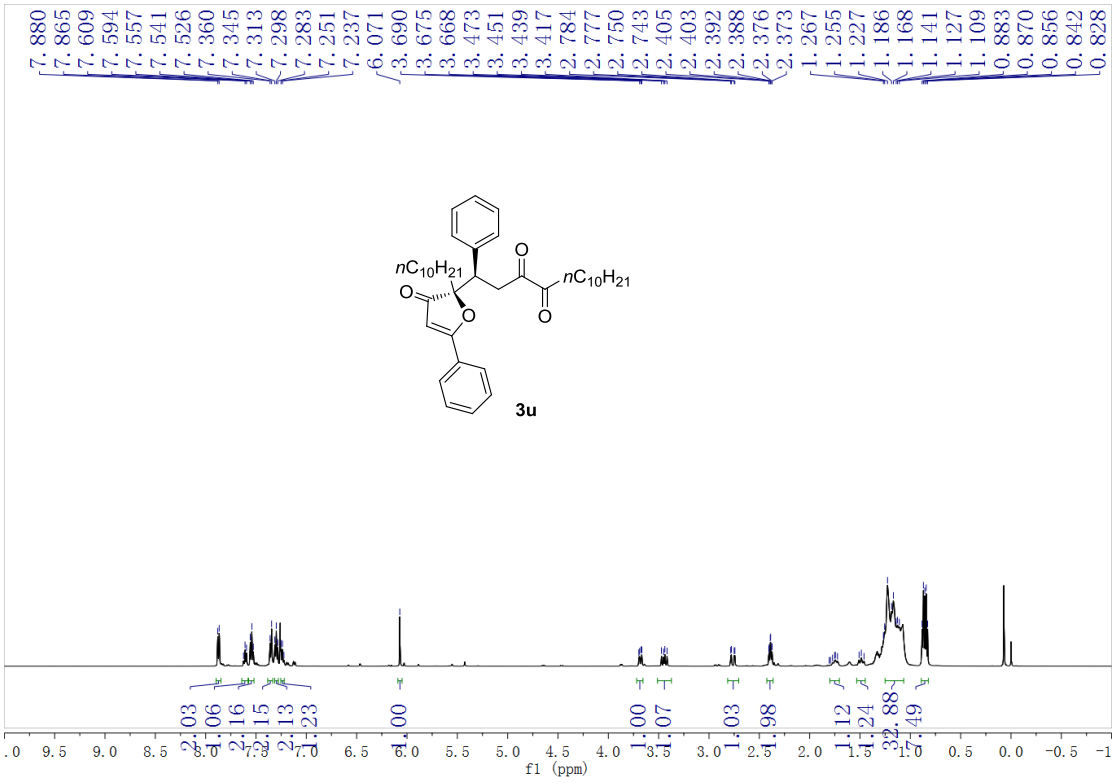
^{1}H NMR (500 MHz, $CDCl_3$)



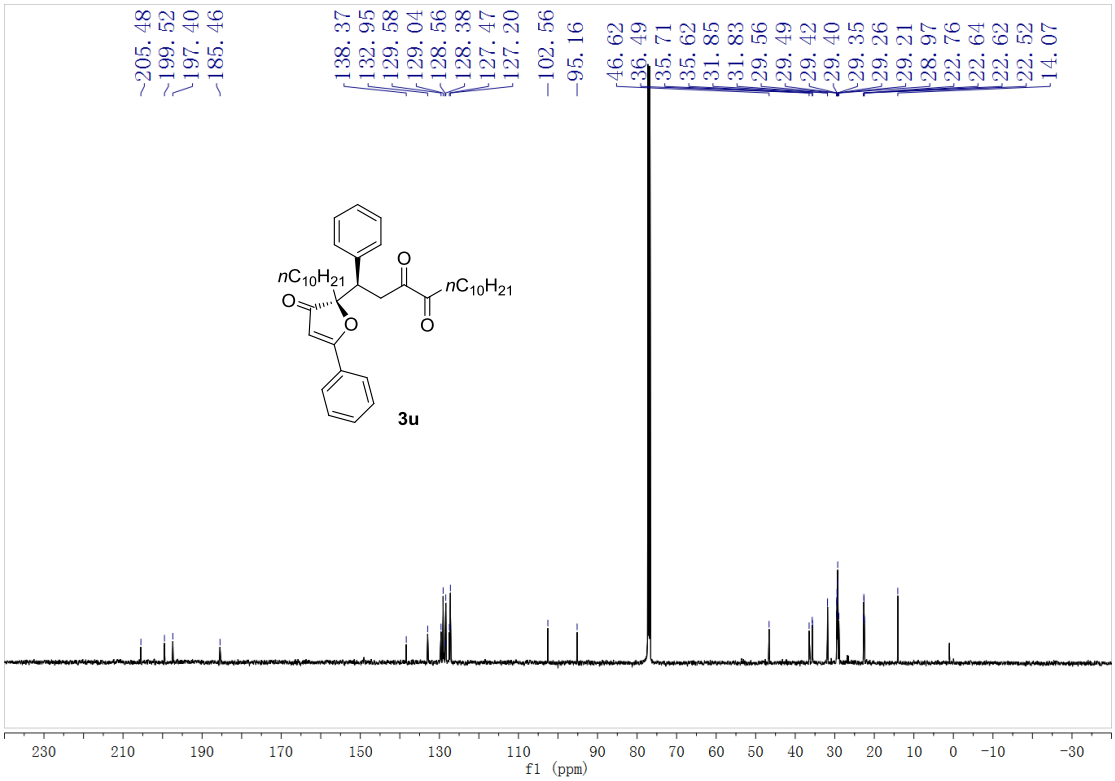
^{13}C NMR (125 MHz, $CDCl_3$)



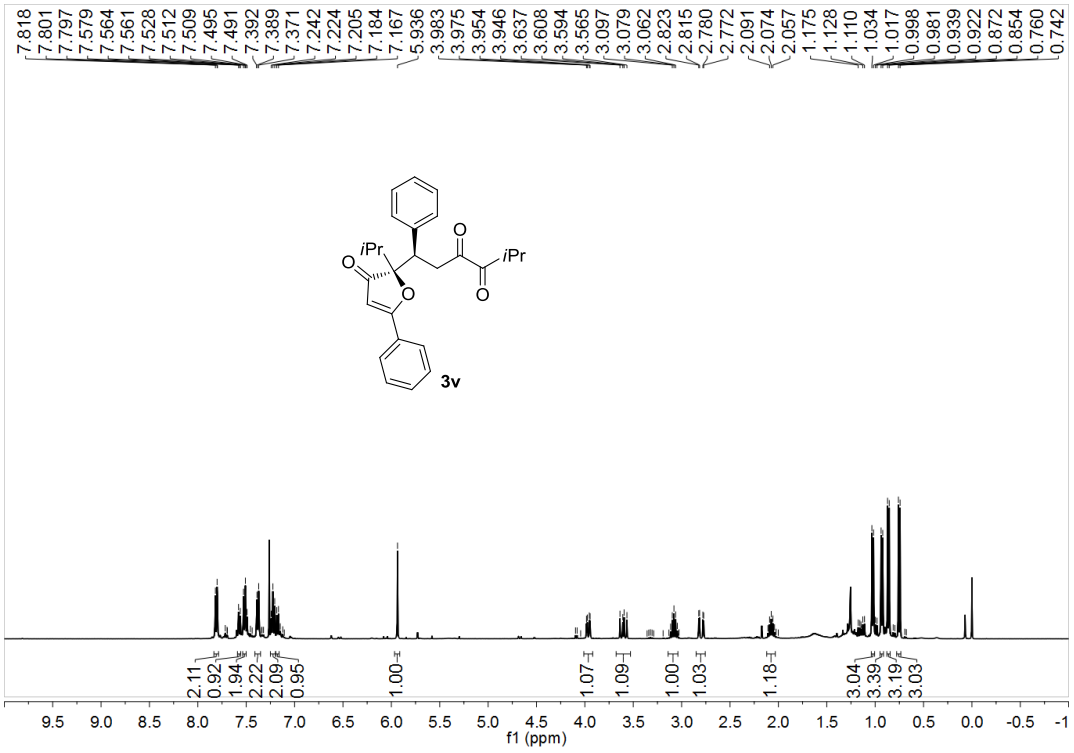
^{1}H NMR (500 MHz, $CDCl_3$)



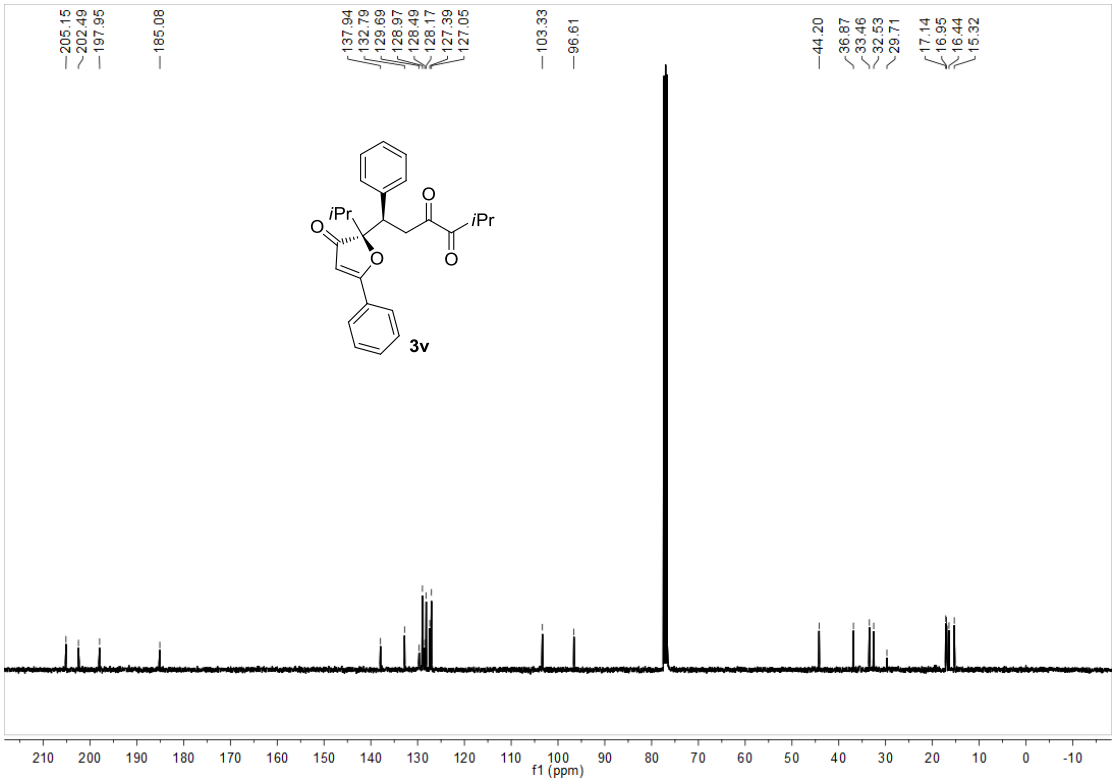
^{13}C NMR (125 MHz, $CDCl_3$)



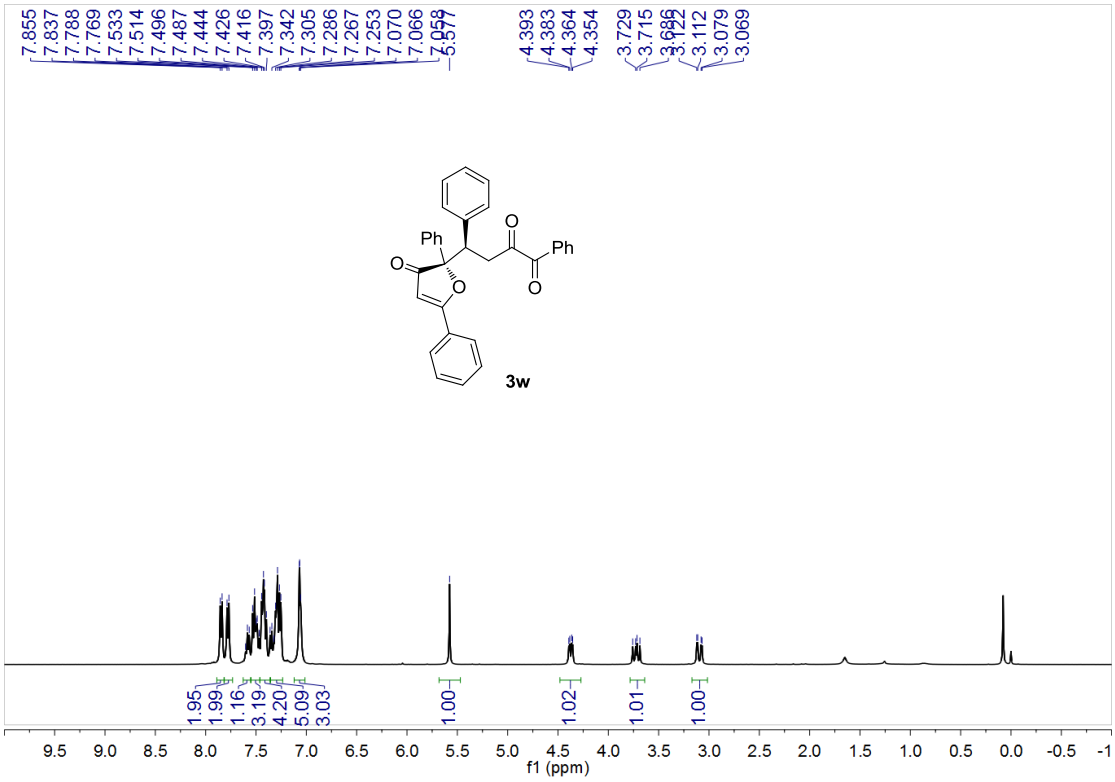
^{1}H NMR (500 MHz, $CDCl_3$)



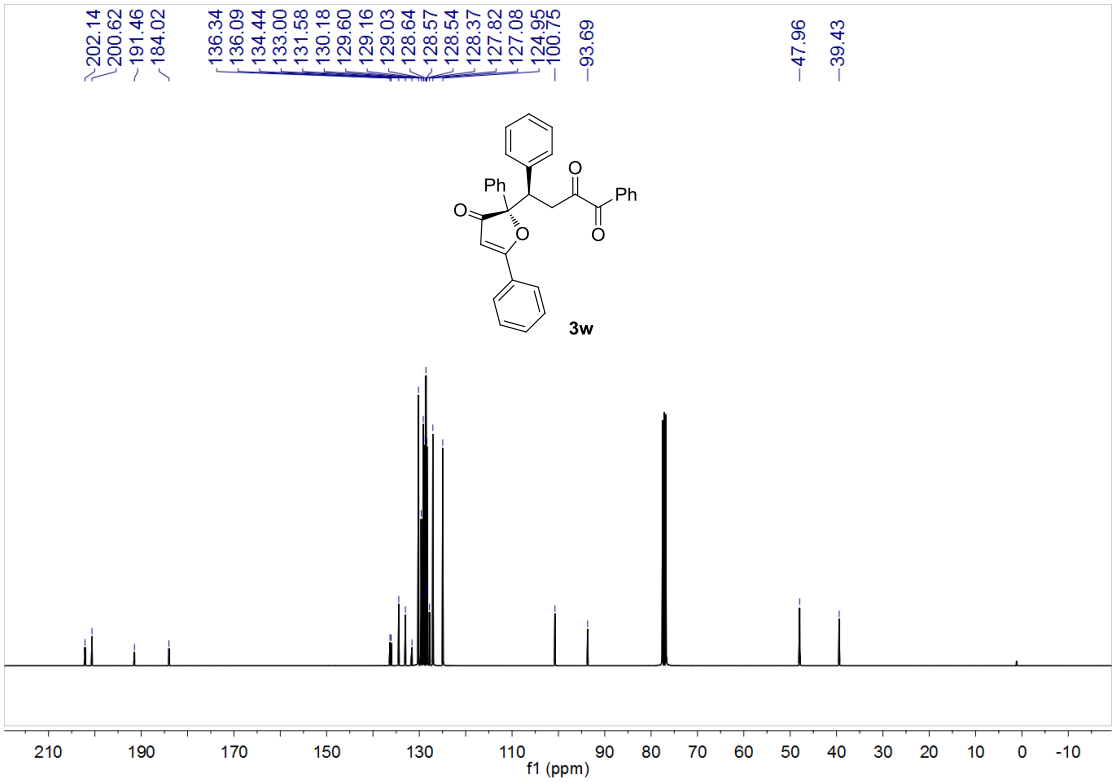
^{13}C NMR (125 MHz, $CDCl_3$)



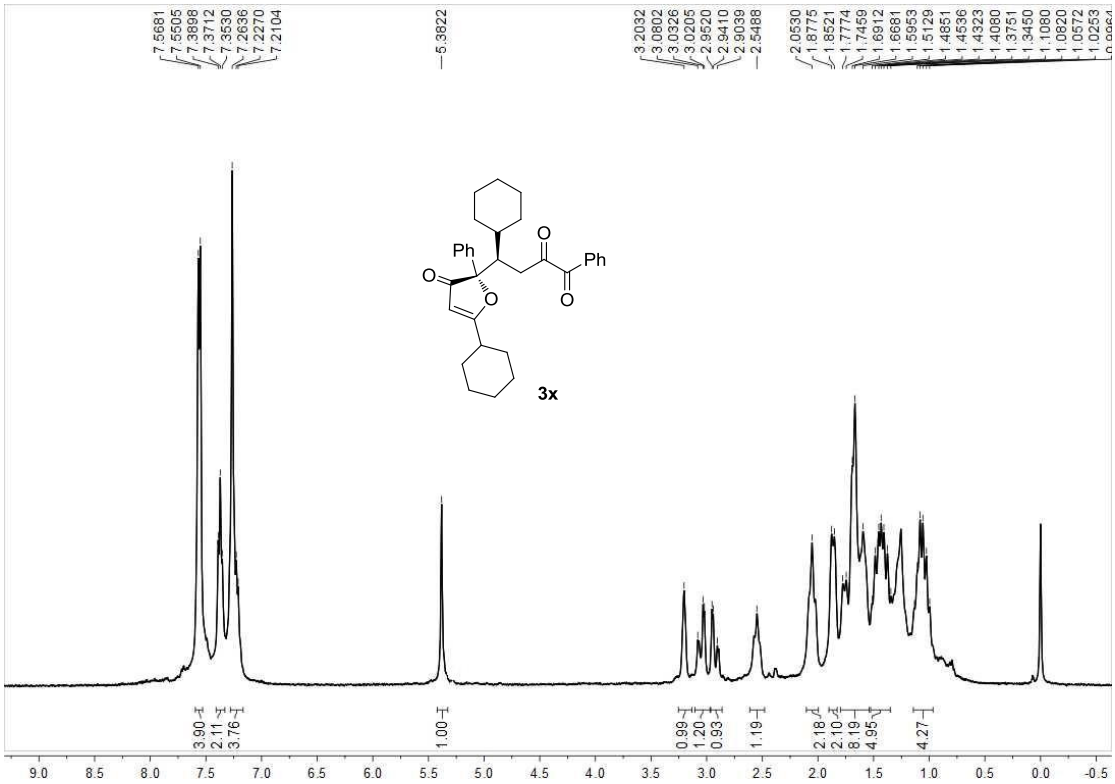
^{1}H NMR (500 MHz, $CDCl_3$)



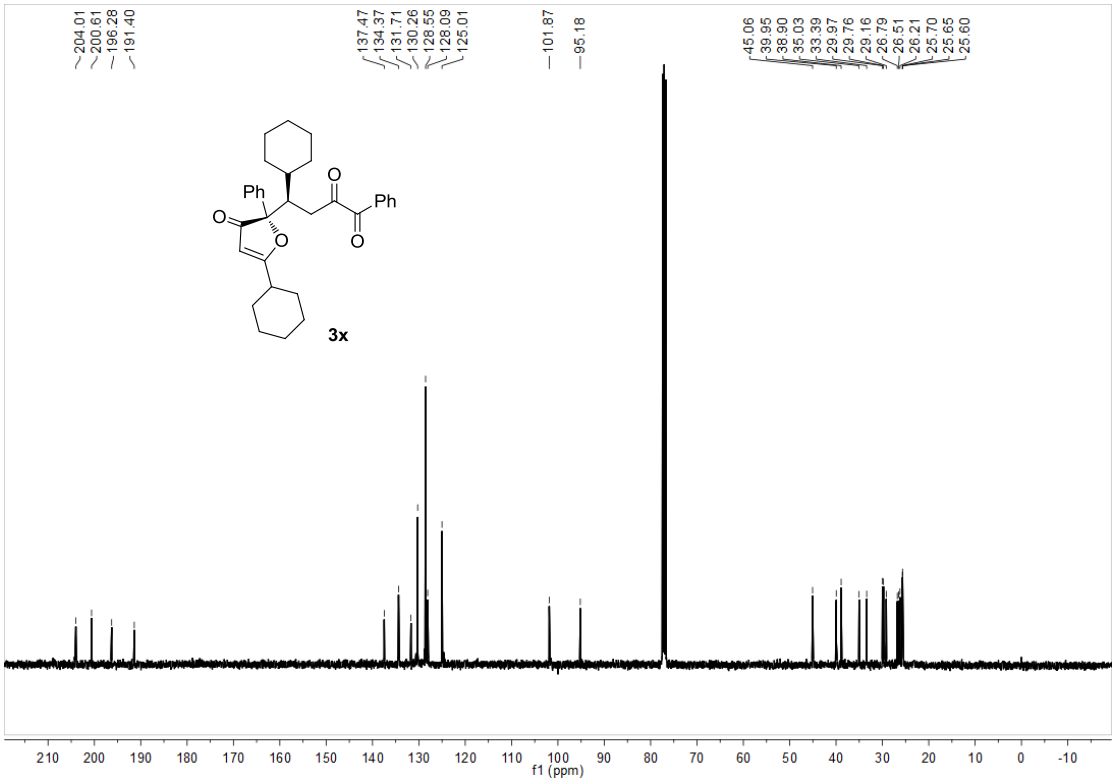
^{13}C NMR (125 MHz, $CDCl_3$)



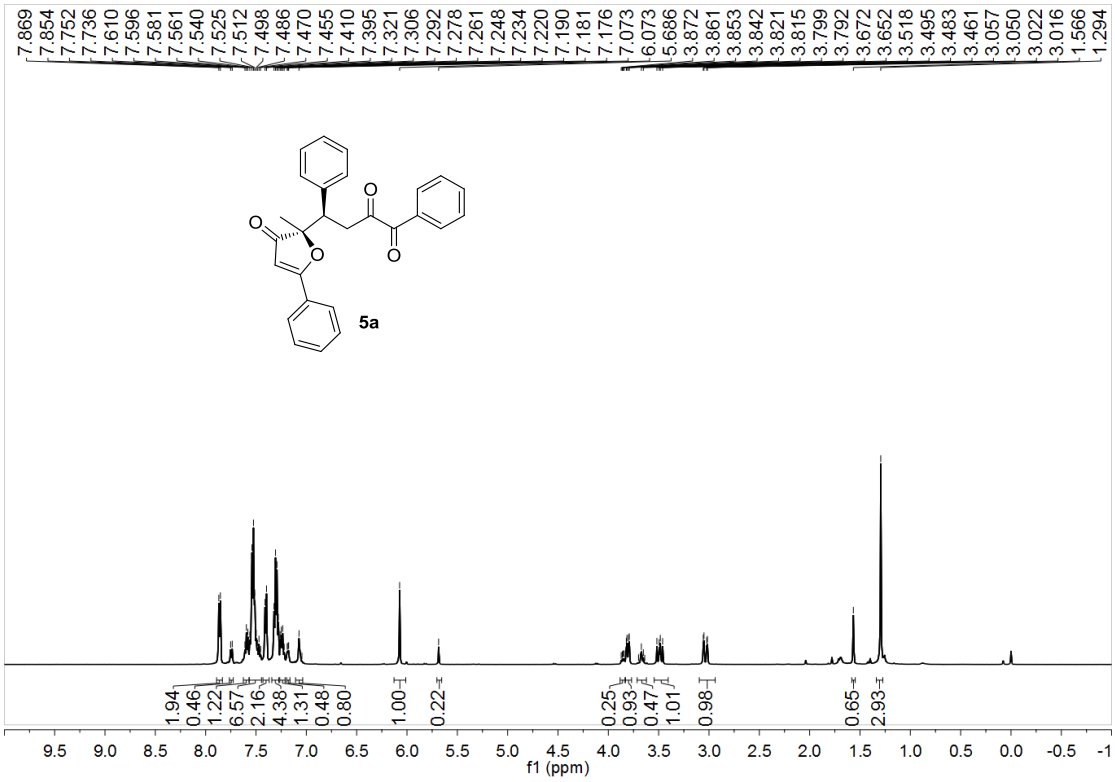
^{1}H NMR (500 MHz, $CDCl_3$)



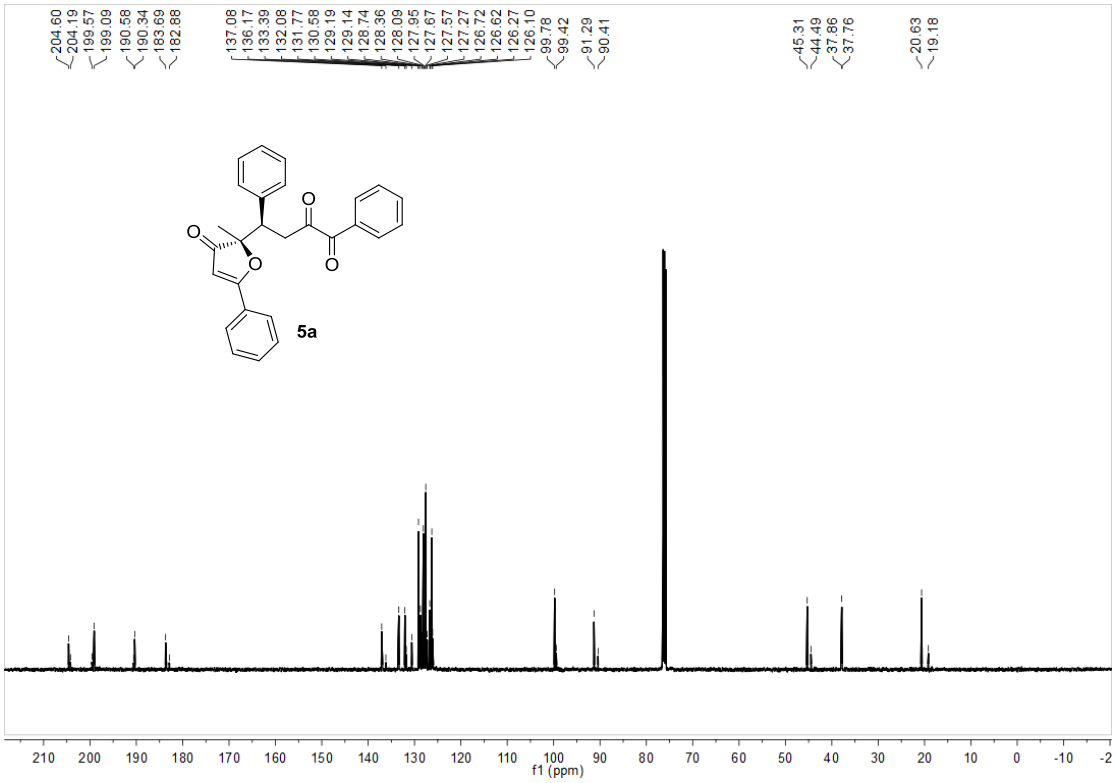
^{13}C NMR (125 MHz, $CDCl_3$)



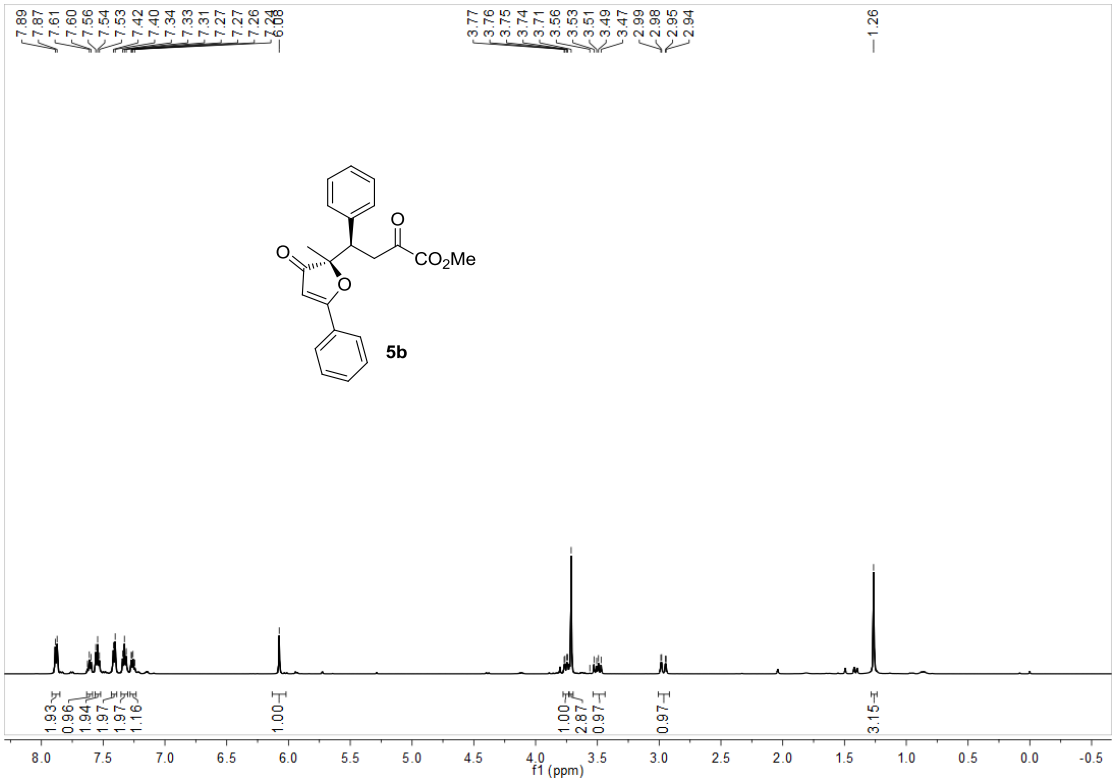
^{1}H NMR (500 MHz, $CDCl_3$)



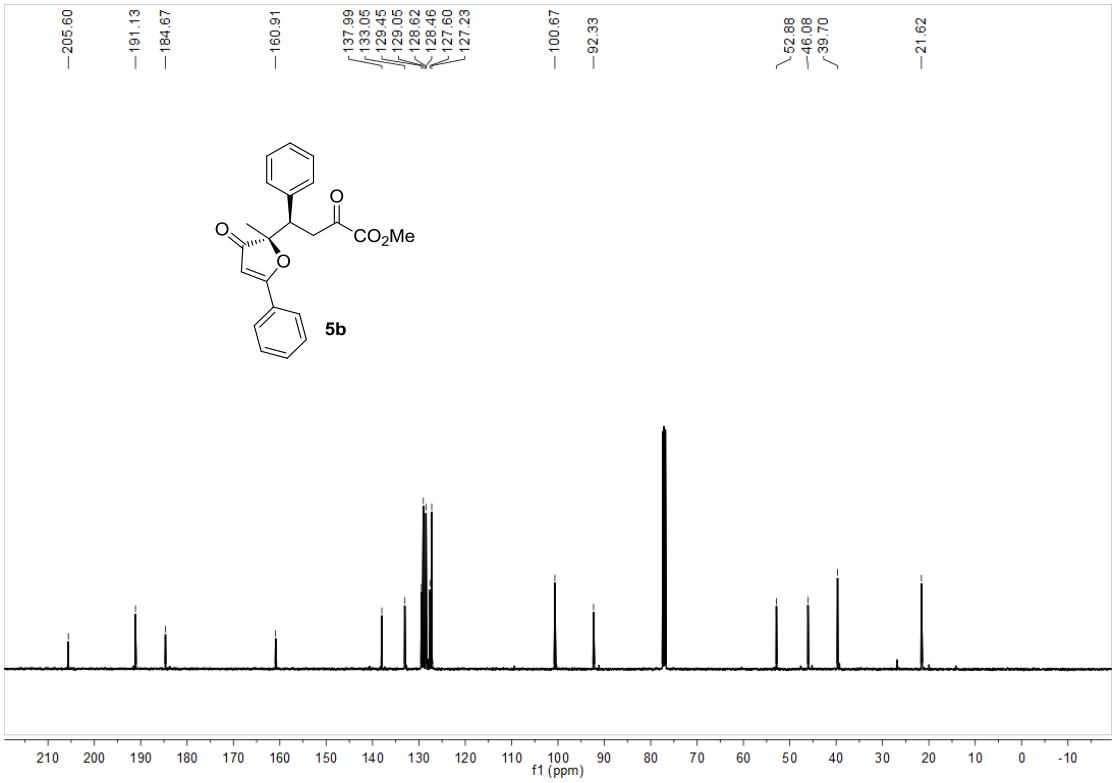
^{13}C NMR (125 MHz, $CDCl_3$)



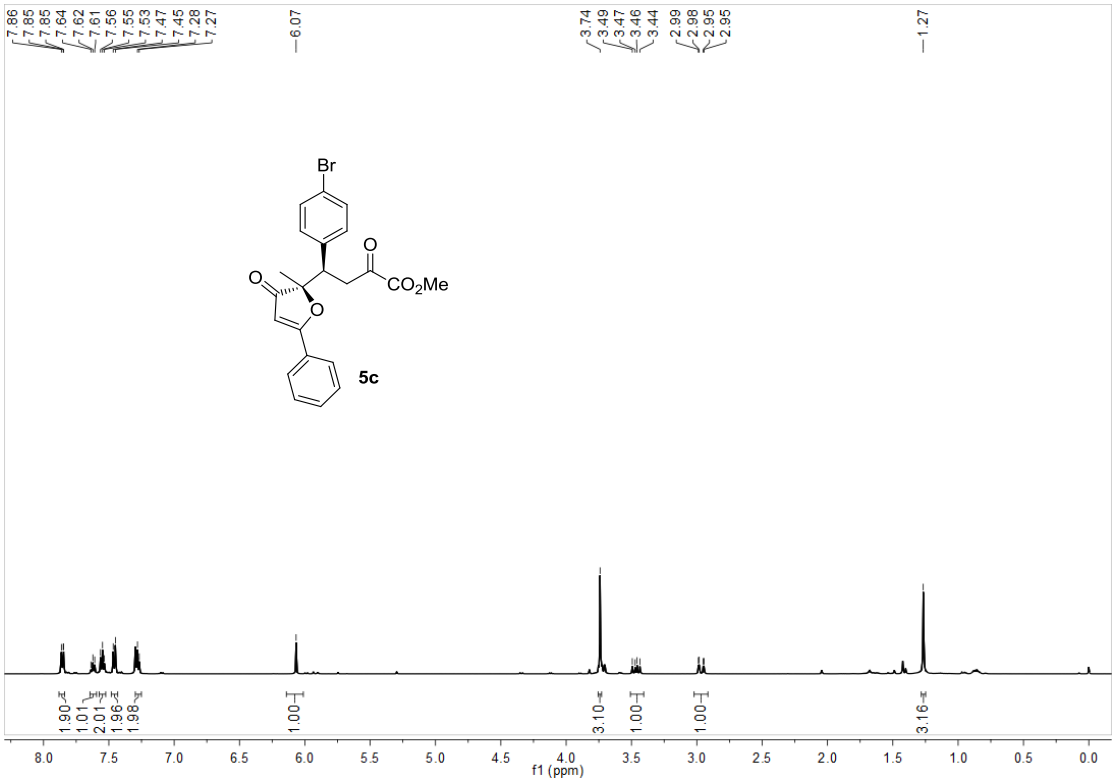
^{1}H NMR (500 MHz, $CDCl_3$)



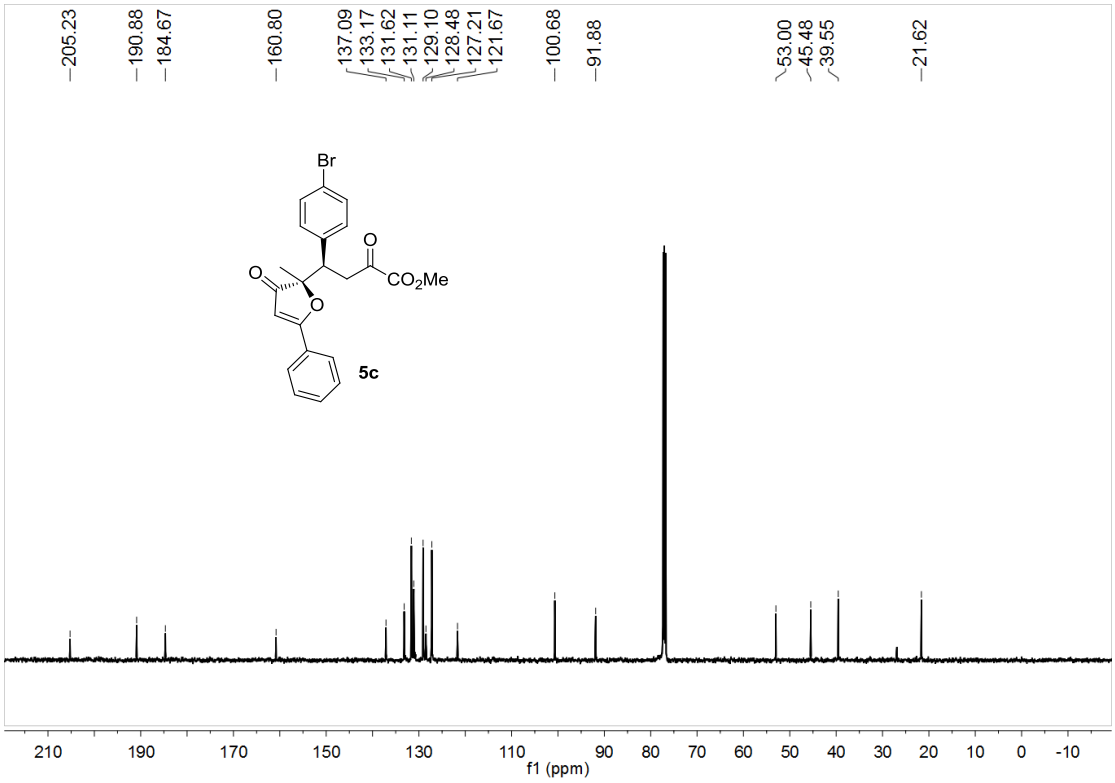
^{13}C NMR (125 MHz, $CDCl_3$)



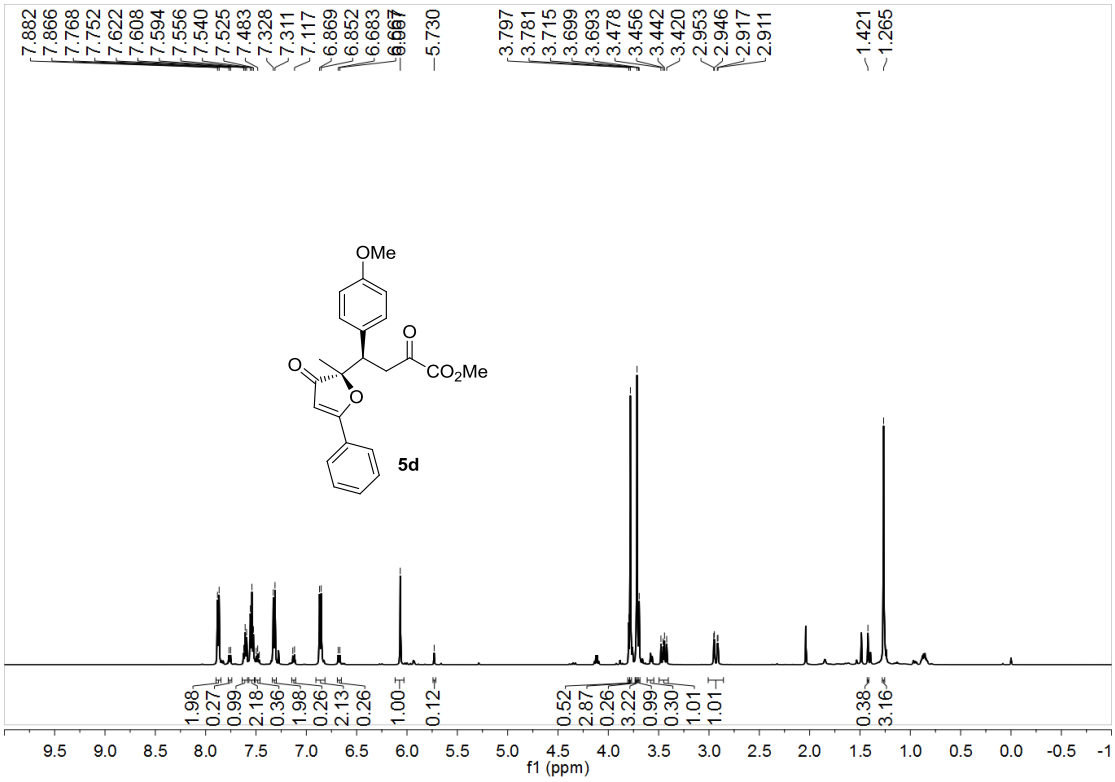
^{1}H NMR (500 MHz, $CDCl_3$)



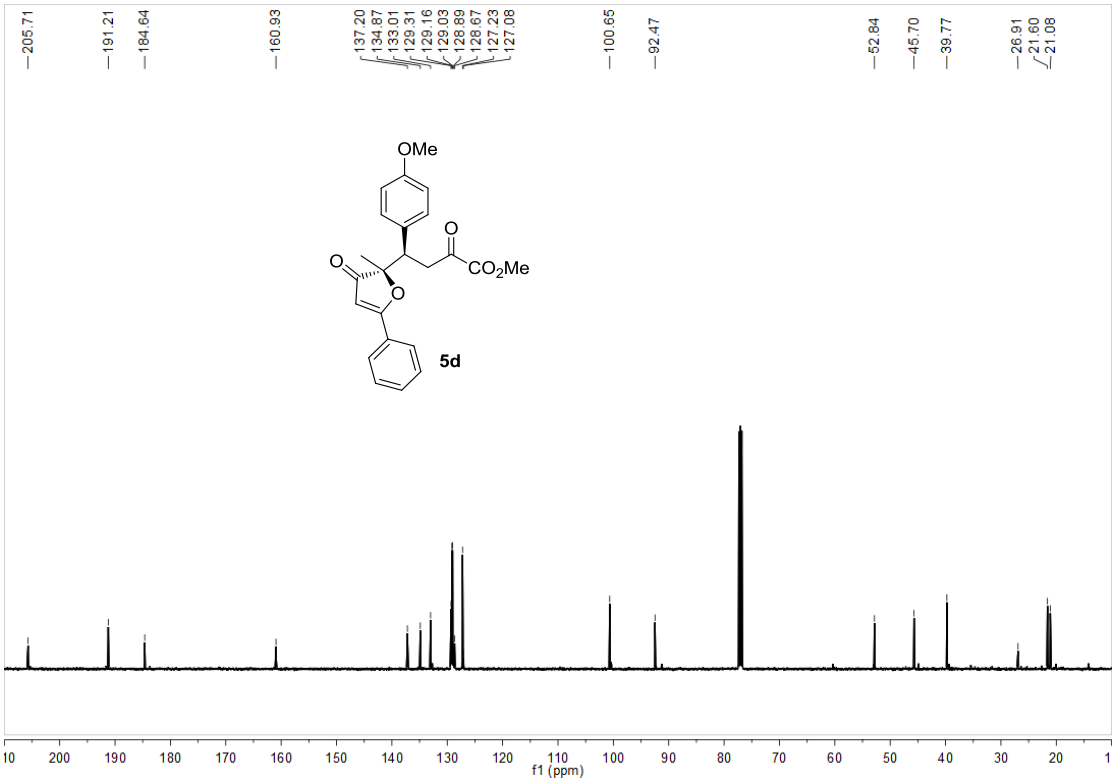
^{13}C NMR (125 MHz, $CDCl_3$)



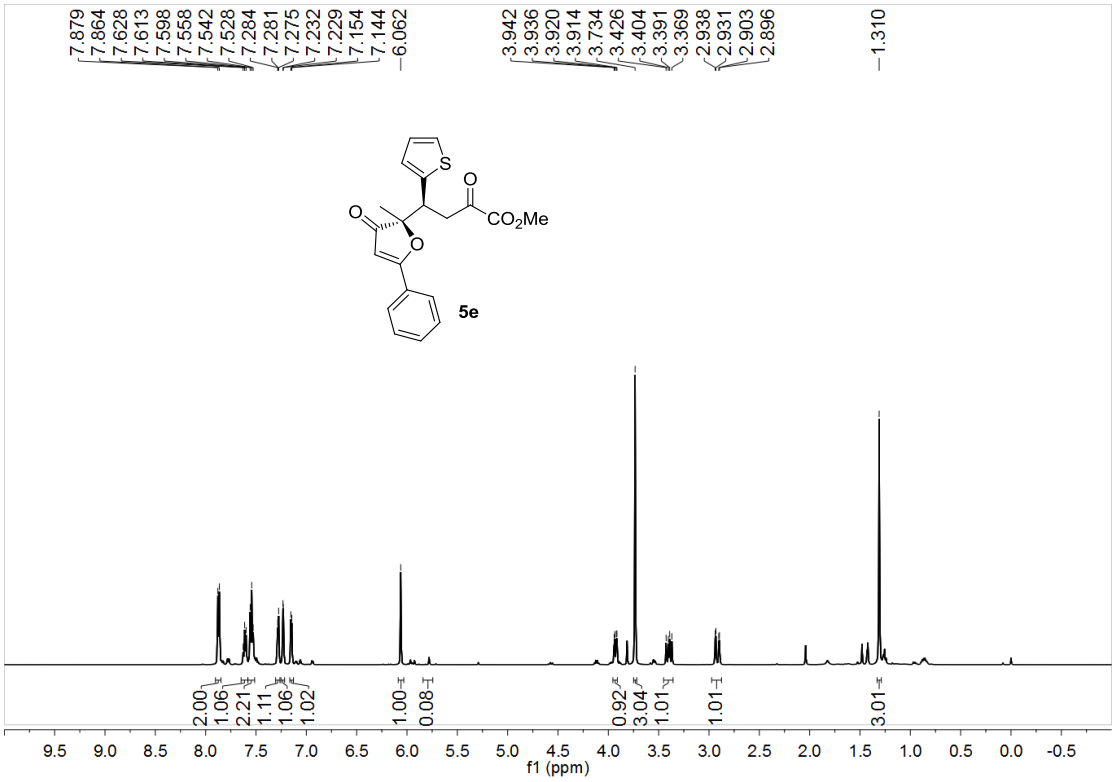
^{1}H NMR (500 MHz, $CDCl_3$)



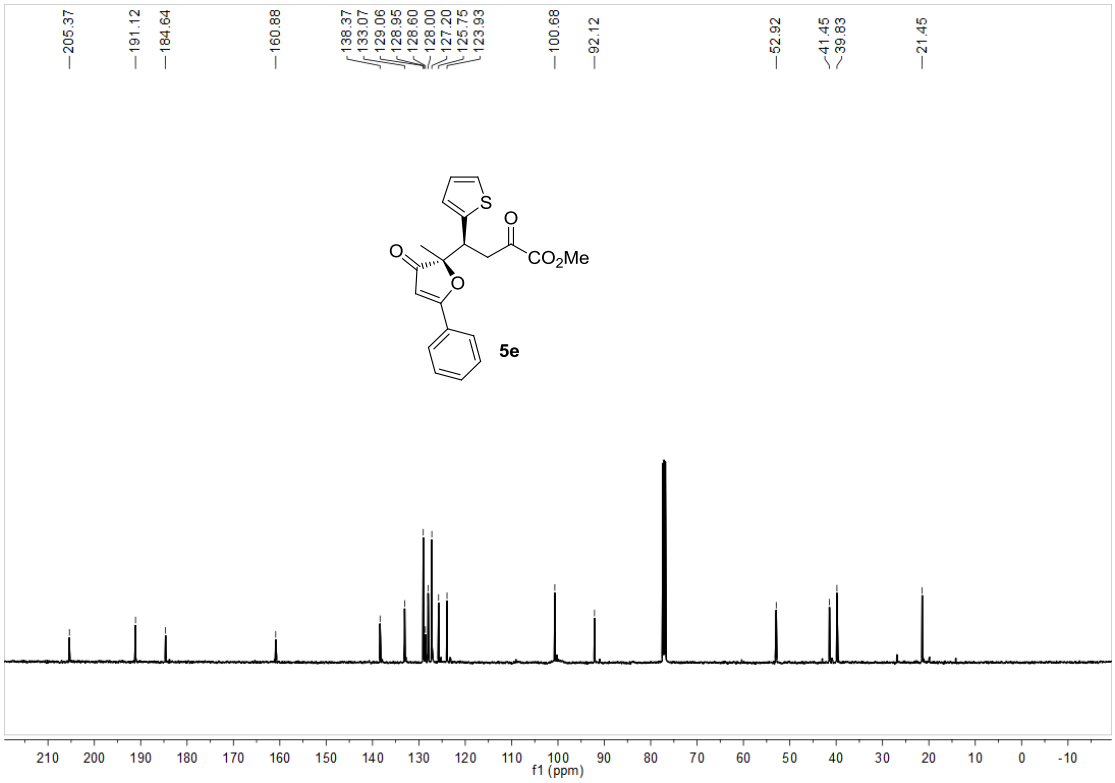
^{13}C NMR (125 MHz, $CDCl_3$)



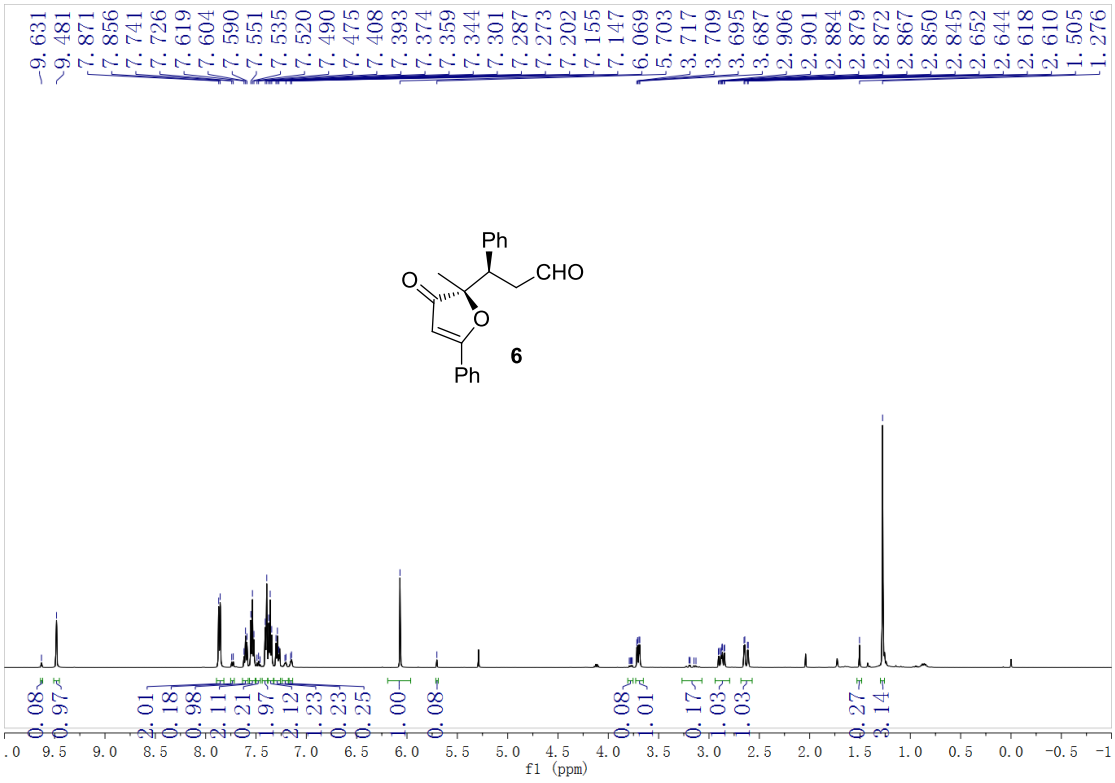
^{1}H NMR (500 MHz, $CDCl_3$)



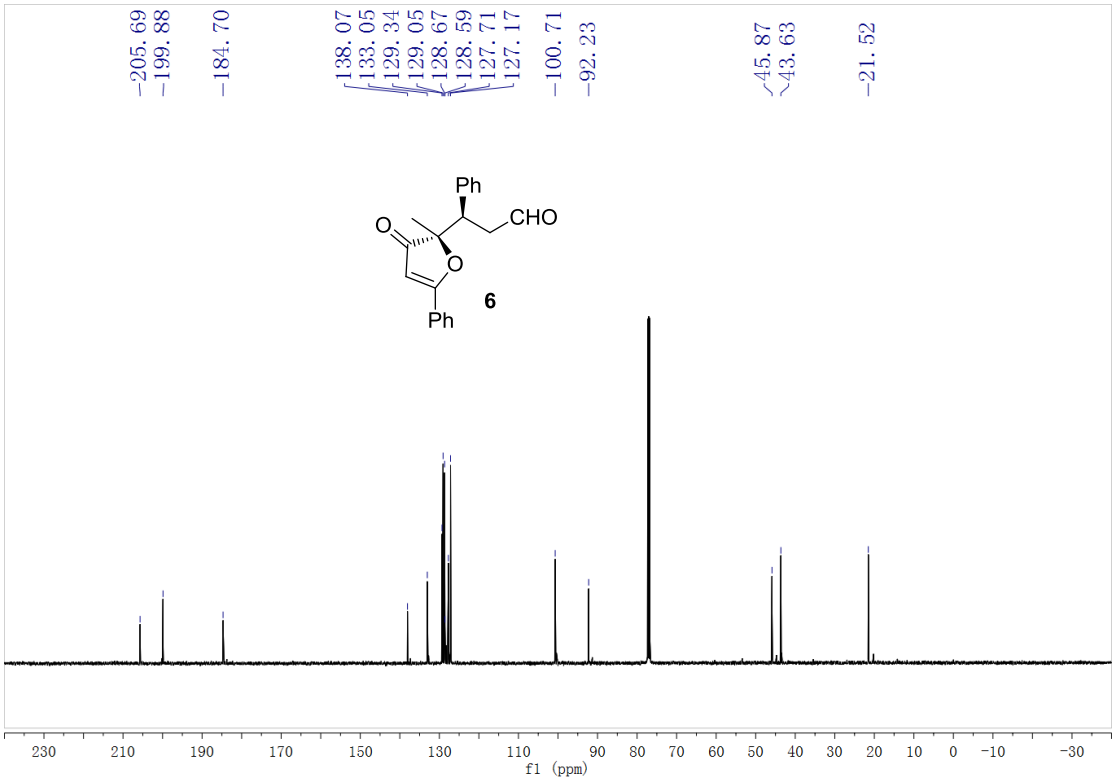
^{13}C NMR (125 MHz, $CDCl_3$)



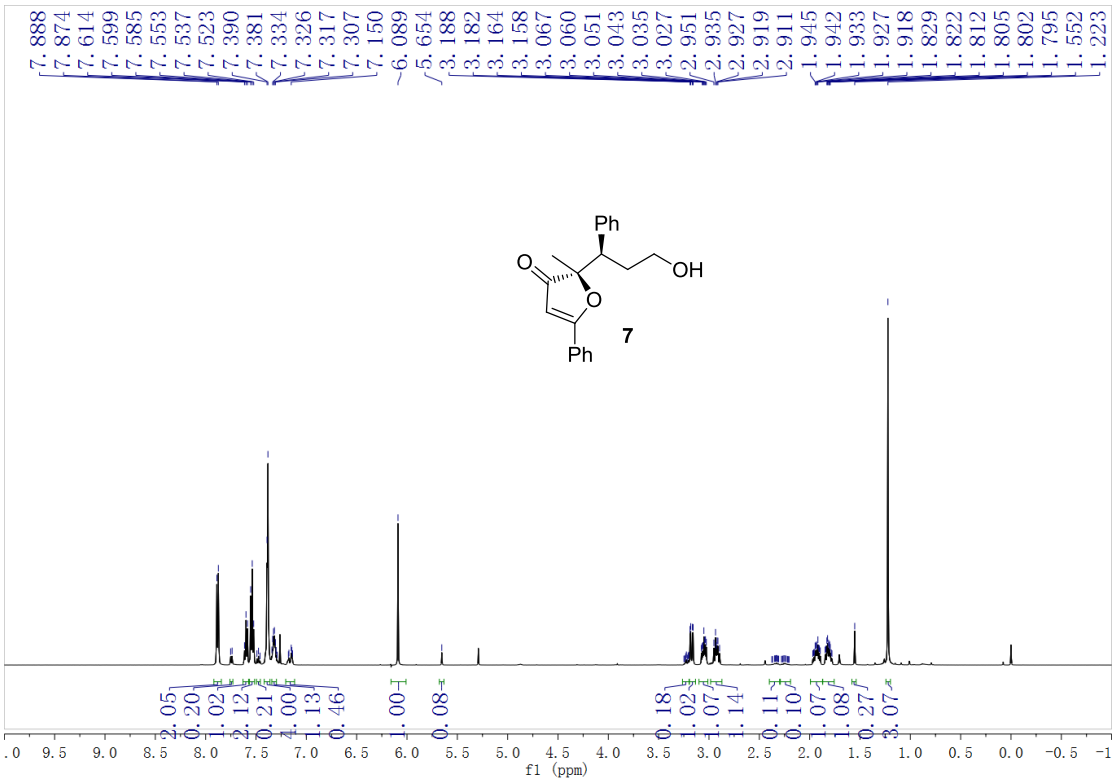
^{1}H NMR (500 MHz, $CDCl_3$)



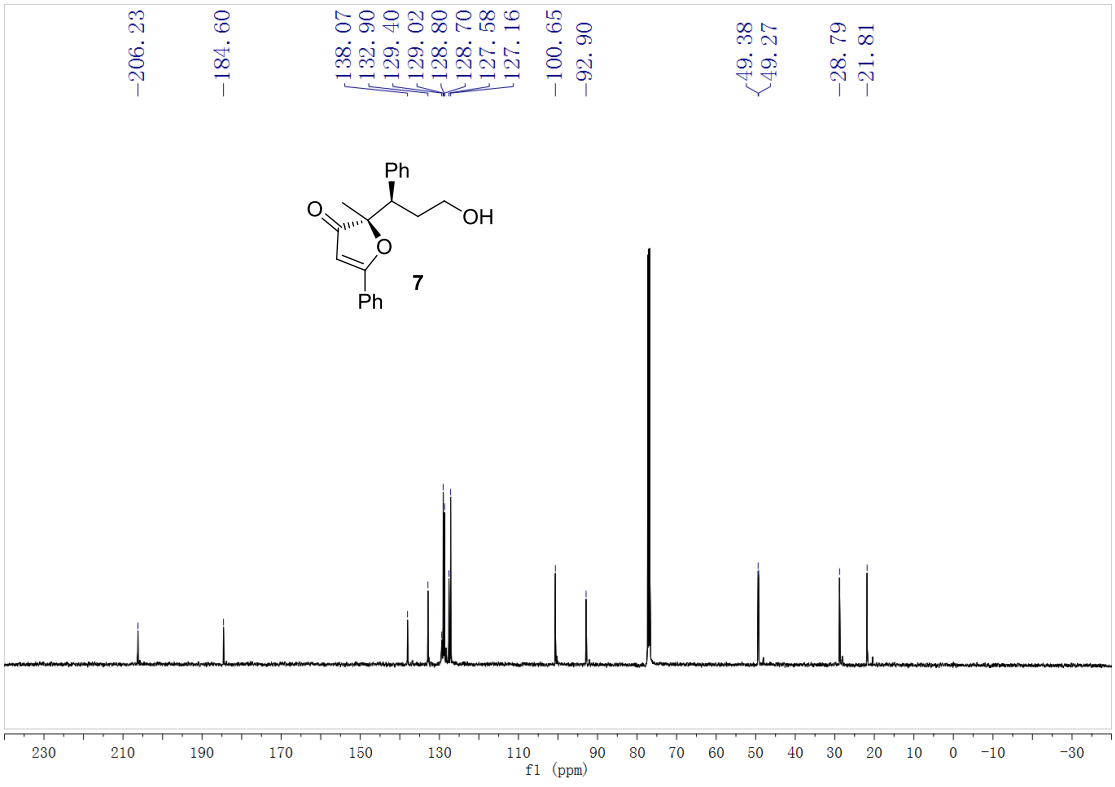
^{13}C NMR (125 MHz, $CDCl_3$)



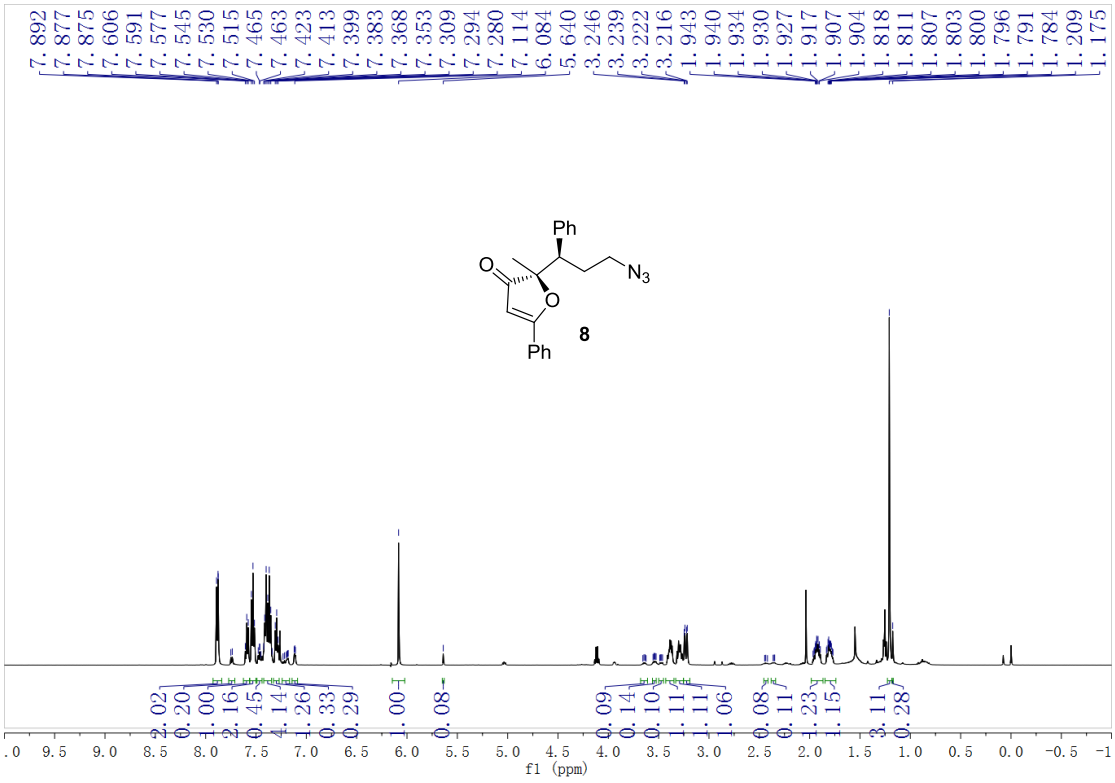
^{1}H NMR (500 MHz, $CDCl_3$)



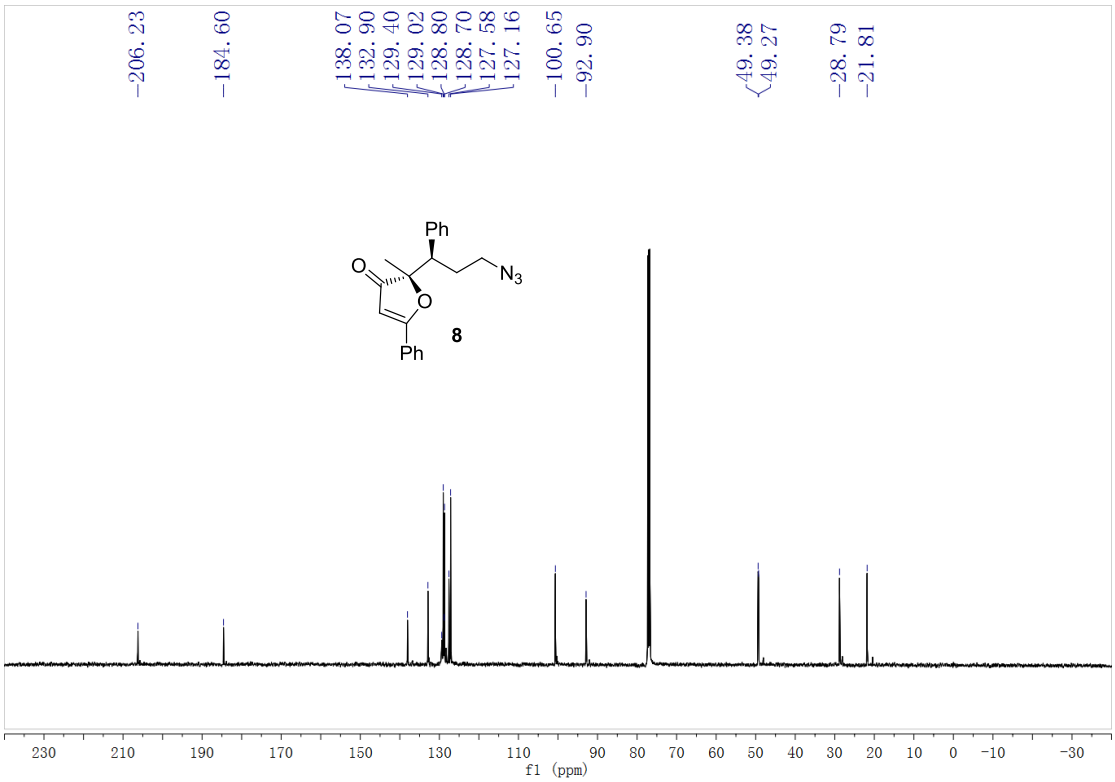
^{13}C NMR (125 MHz, $CDCl_3$)



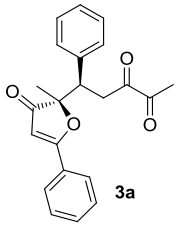
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

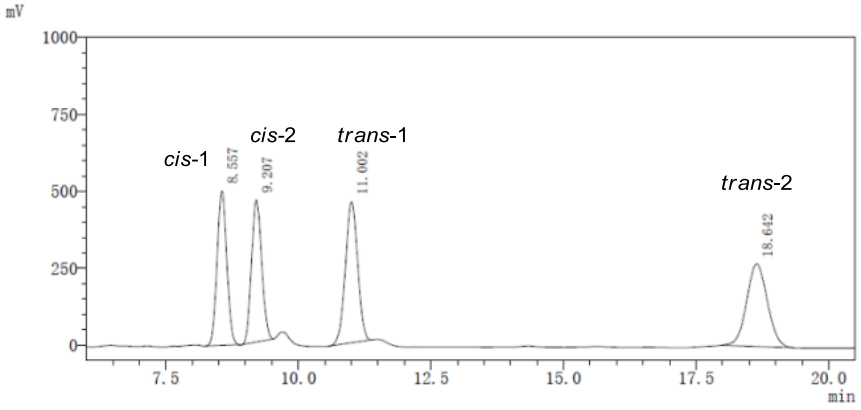


VII. HPLC Charts



3a

*Chiral HPLC spectrum of racemic **3a***

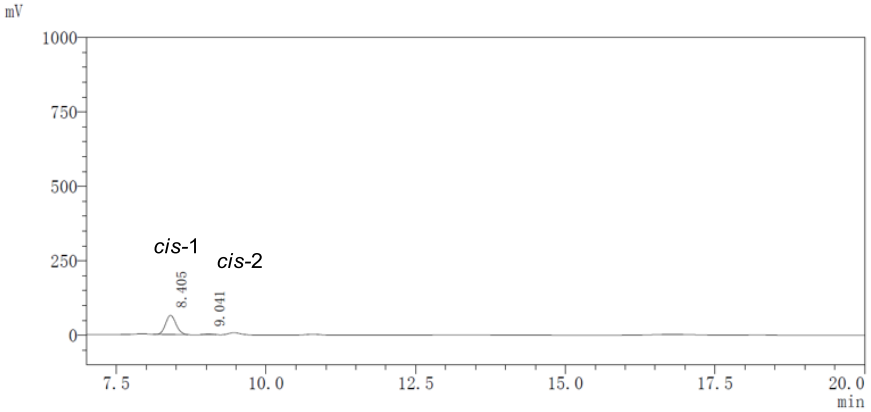


〈Peak Results〉

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	8.557	6403115	23.466	501620	29.707
2	9.207	6190060	22.685	461214	27.315
3	11.002	7394346	27.098	457939	27.121
4	18.642	7299421	26.751	267757	15.857

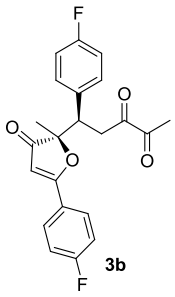
*Chiral HPLC spectrum of chiral **3a***



〈Peak Results〉

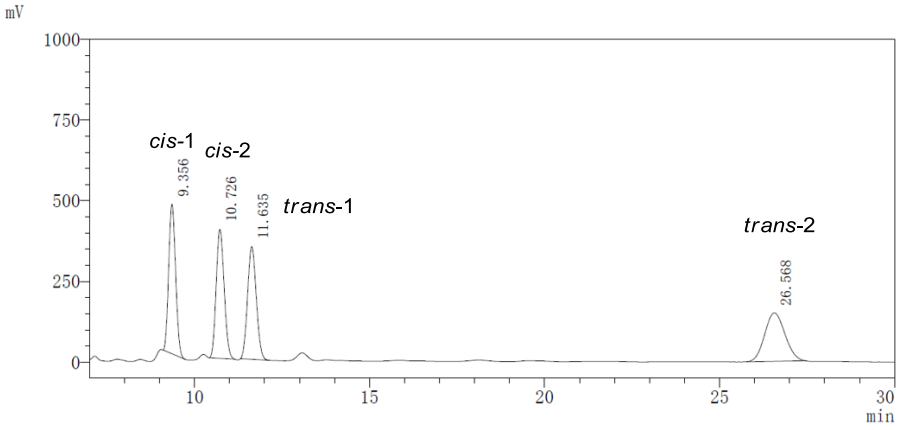
Ch2 254nm

Index	Time	Area	Area%	Height	Height%
1	8.405	777519	97.716	64390	96.927
2	9.041	18174	2.284	2042	3.073



3b

*Chiral HPLC spectrum of racemic **3b***

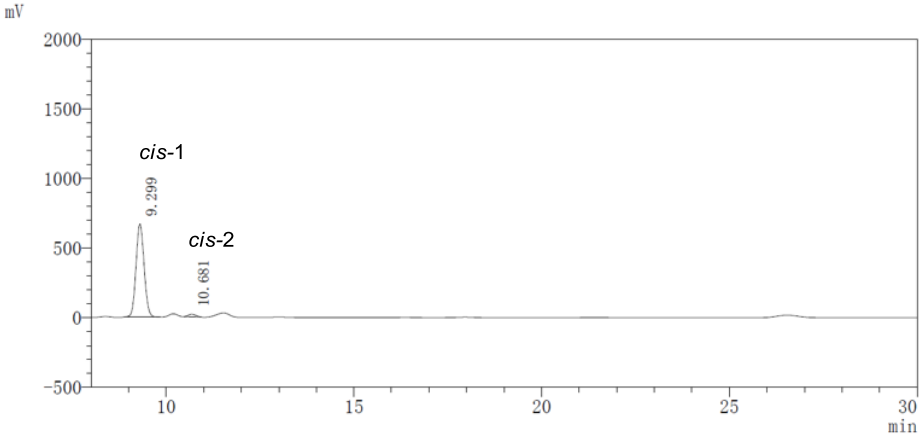


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.356	6367434	25.703	463826	34.028
2	10.726	6334748	25.571	399928	29.341
3	11.635	6054064	24.438	349248	25.622
4	26.568	6017321	24.289	150052	11.009

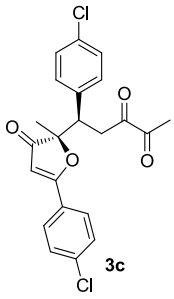
*Chiral HPLC spectrum of chiral **3b***



<Peak Results>

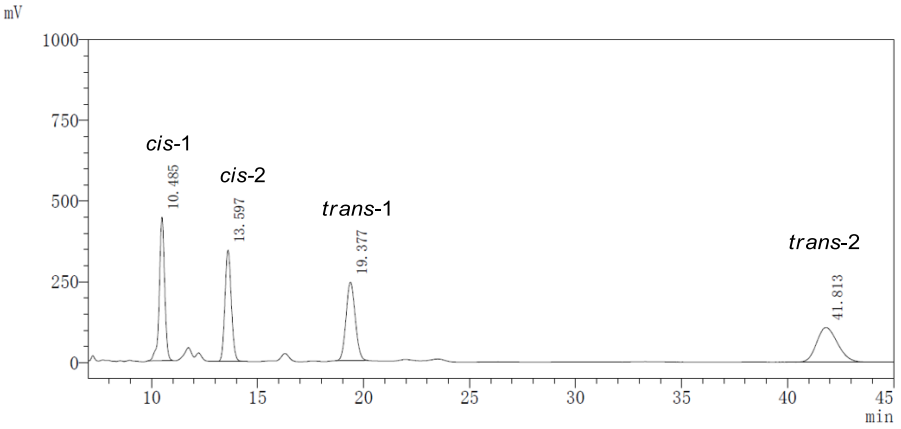
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.299	10029723	97.557	668620	97.372
2	10.681	251149	2.443	18048	2.628



3c

Chiral HPLC spectrum of racemic ***3c***

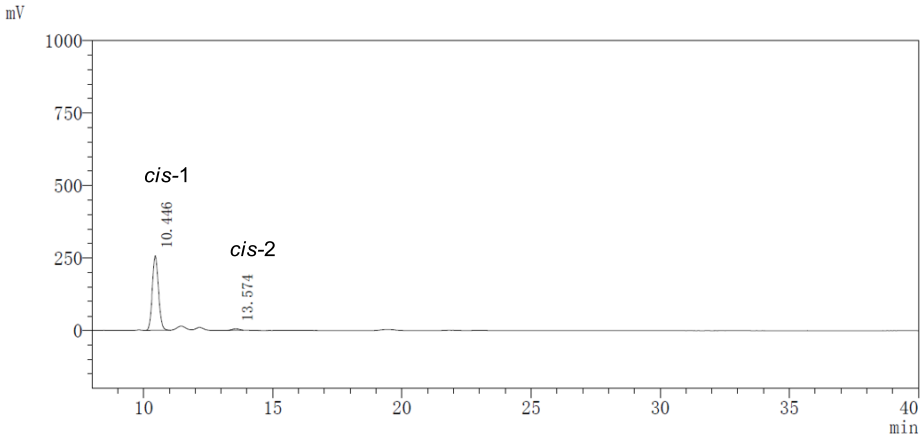


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.485	7746096	26.221	444708	39.064
2	13.597	7201431	24.378	343912	30.210
3	19.377	7323305	24.790	242811	21.329
4	41.813	7270277	24.611	106967	9.396

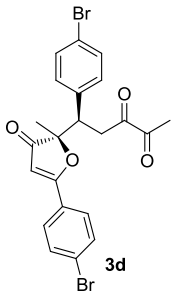
Chiral HPLC spectrum of chiral ***3c***



<Peak Results>

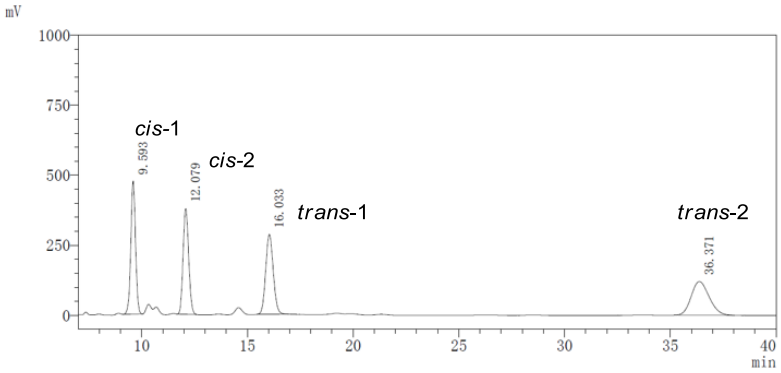
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.446	4247449	97.969	256849	98.159
2	13.574	88061	2.031	4817	1.841



3d

*Chiral HPLC spectrum of racemic **3d***

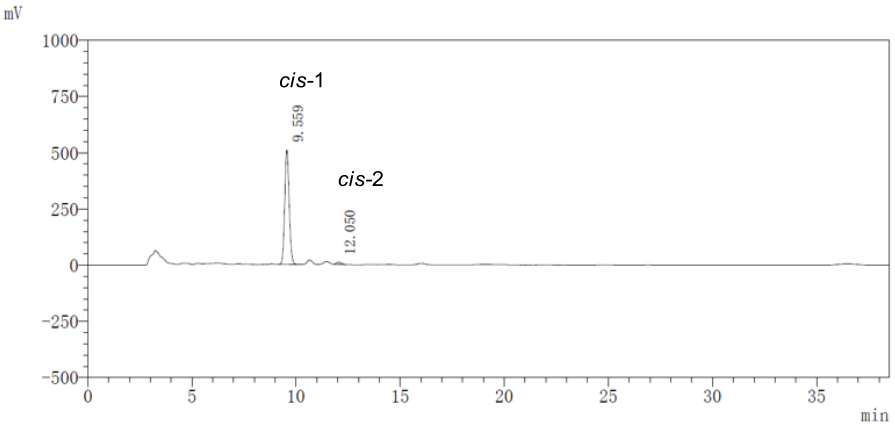


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.593	7381119	25.934	475466	37.822
2	12.079	6938466	24.379	376738	29.968
3	16.033	7073087	24.852	284930	22.665
4	36.371	7068432	24.835	119991	9.545

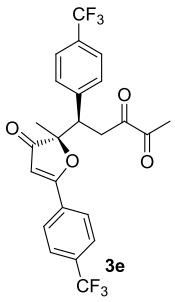
*Chiral HPLC spectrum of chiral **3d***



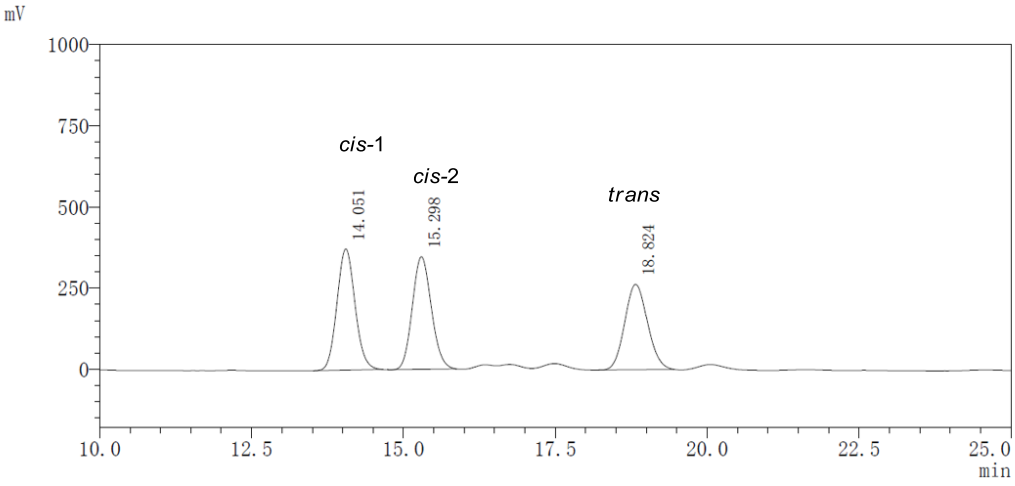
<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.559	7591137	97.904	508877	98.070
2	12.050	162530	2.096	10012	1.930



*Chiral HPLC spectrum of racemic **3e***

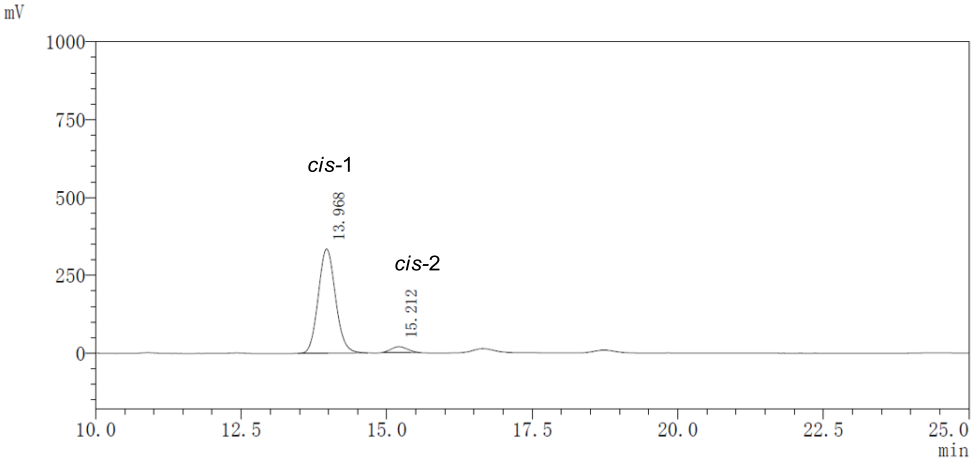


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	14.051	7759852	34.983	373636	37.973
2	15.298	7587269	34.205	347244	35.291
3	18.824	6834636	30.812	263067	26.736

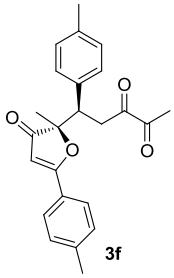
*Chiral HPLC spectrum of chiral **3e***



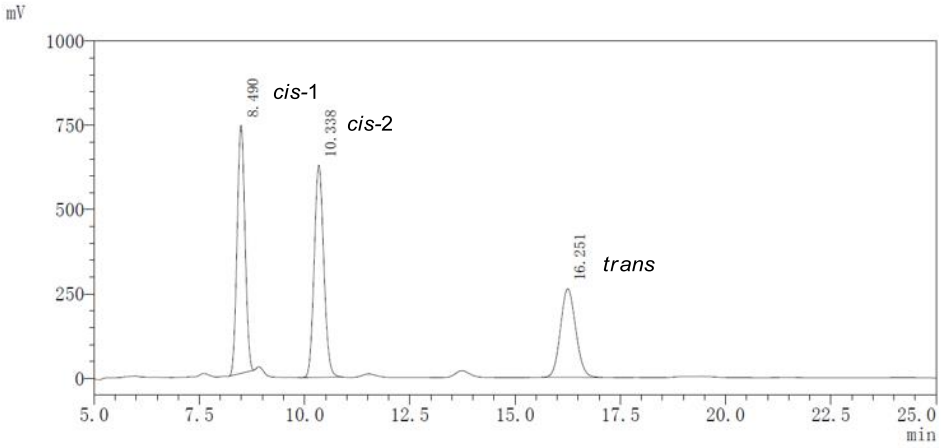
<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	13.968	6906835	95.030	334924	94.730
2	15.212	361236	4.970	18633	5.270



*Chiral HPLC spectrum of racemic **3f***

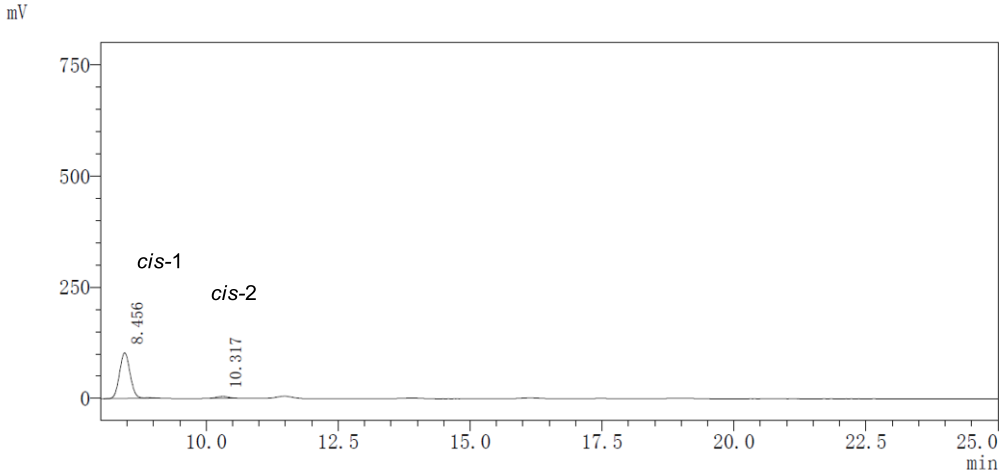


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	8.490	9592665	36.585	734949	45.177
2	10.338	10000330	38.140	629060	38.668
3	16.251	6627392	25.276	262813	16.155

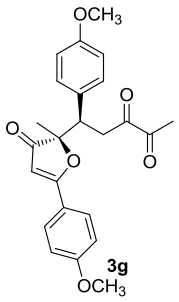
*Chiral HPLC spectrum of chiral **3f***



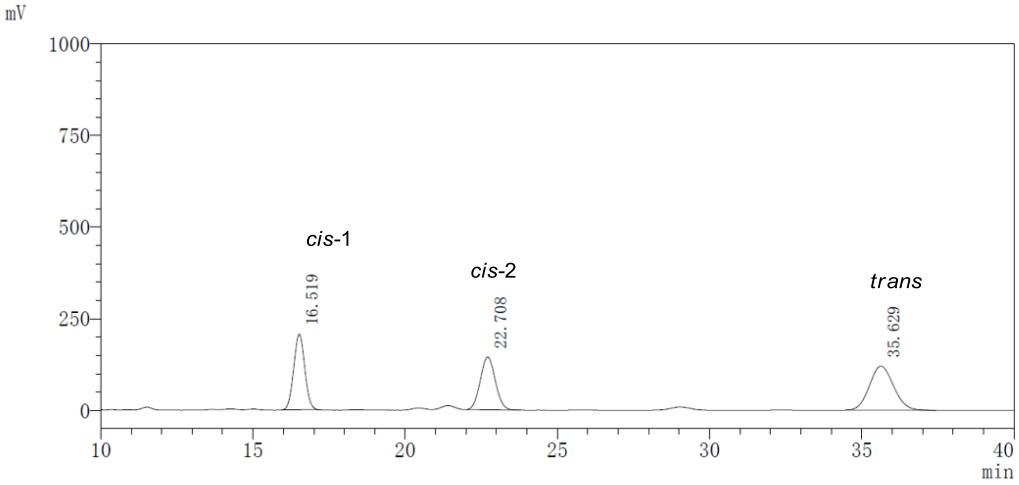
<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	8.456	1435251	97.952	102615	96.192
2	10.317	60554	2.048	4063	3.808



*Chiral HPLC spectrum of racemic **3g***

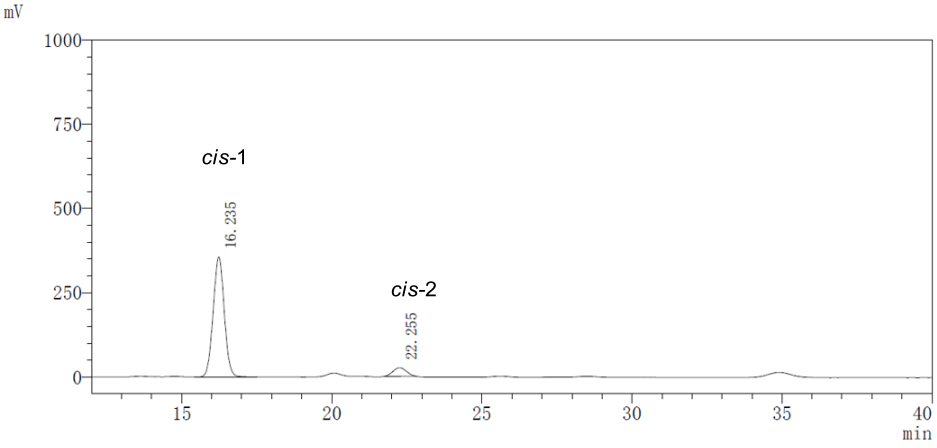


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	16.519	5186216	30.911	205866	43.792
2	22.708	4945989	29.479	143876	30.606
3	35.629	6645726	39.610	120356	25.602

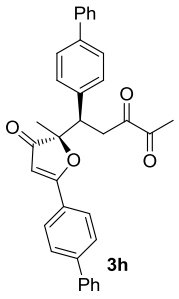
*Chiral HPLC spectrum of chiral **3g***



<Peak Results>

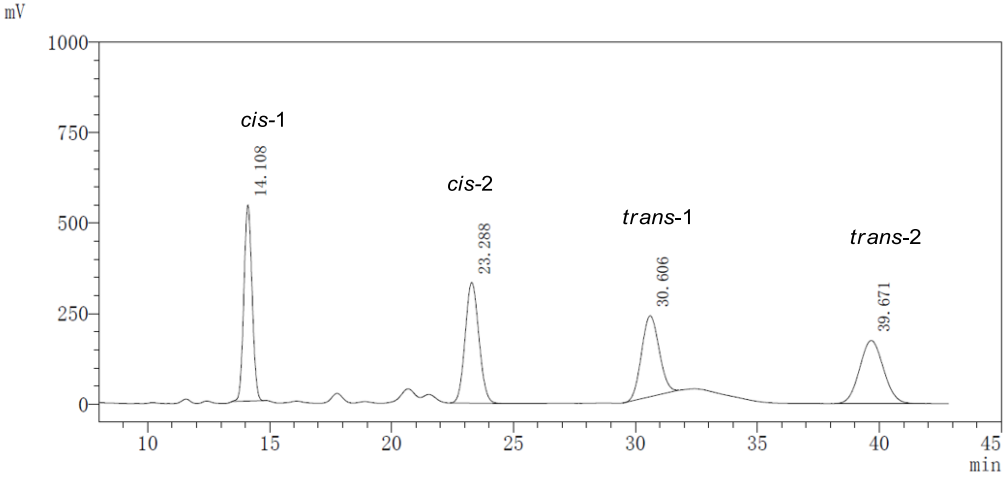
Ch2 210nm

Index	Times	Area	Area%	Height	Height%
1	16.235	9166941	91.995	356267	93.298
2	22.255	797660	8.005	25593	6.702



3h

*Chiral HPLC spectrum of racemic **3h***

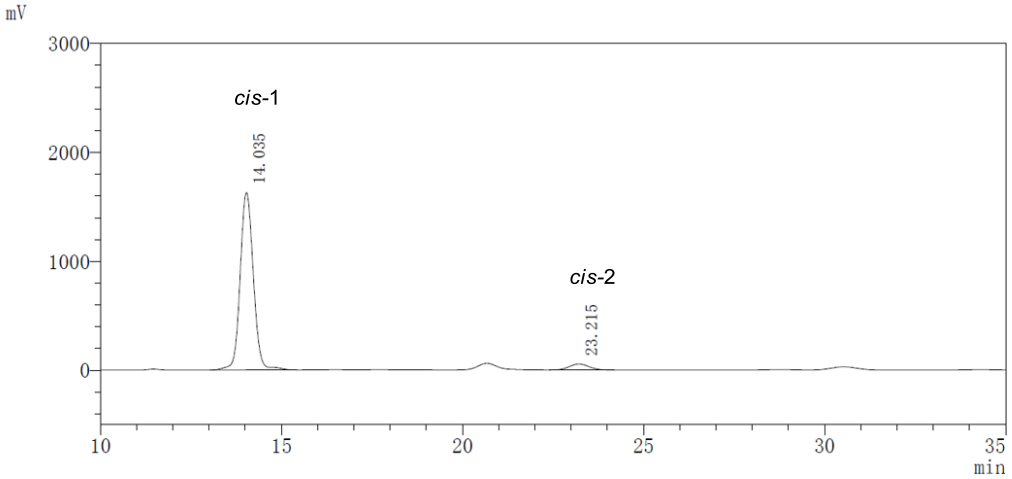


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	14.108	12713579	26.009	541701	42.546
2	23.288	13079870	26.758	333574	26.200
3	30.606	11216319	22.946	223599	17.562
4	39.671	11872278	24.288	174326	13.692

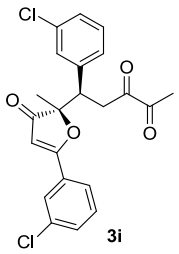
*Chiral HPLC spectrum of chiral **3h***



<Peak Results>

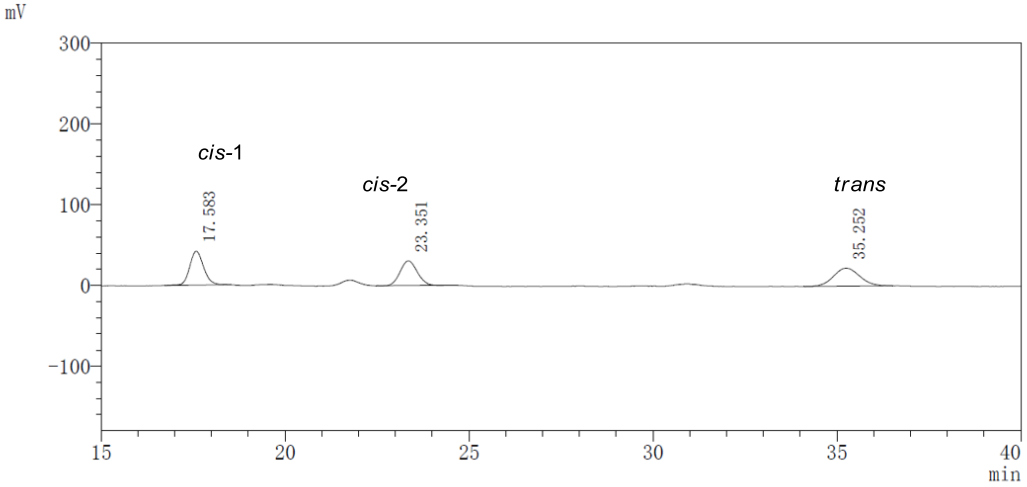
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	14.035	41200571	95.791	1628939	96.760
2	23.215	2081516	4.209	54541	3.240



3i

*Chiral HPLC spectrum of racemic **3i***

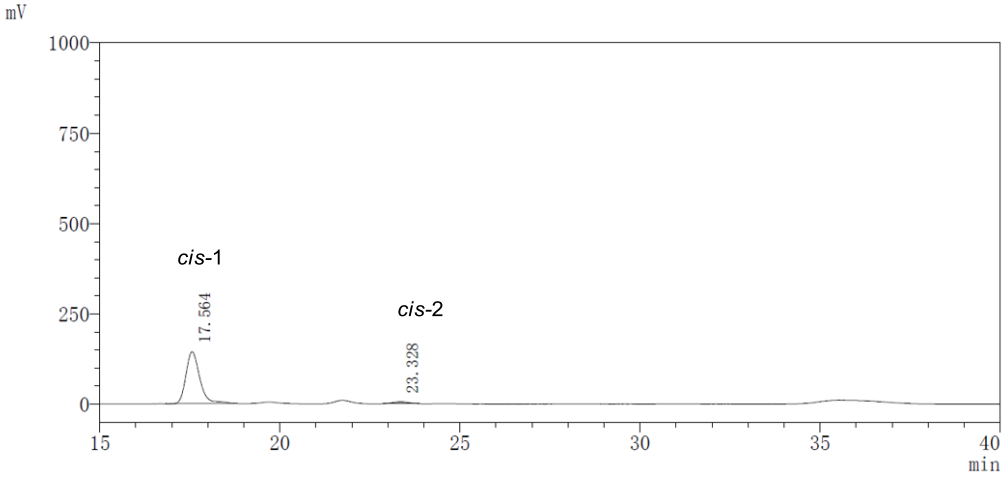


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	17.583	1110164	34.751	41969	44.237
2	23.351	988345	30.938	30663	32.320
3	35.252	1096086	34.311	22241	23.443

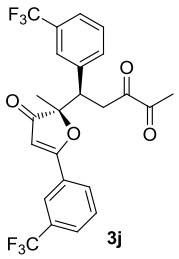
*Chiral HPLC spectrum of chiral **3i***



<Peak Results>

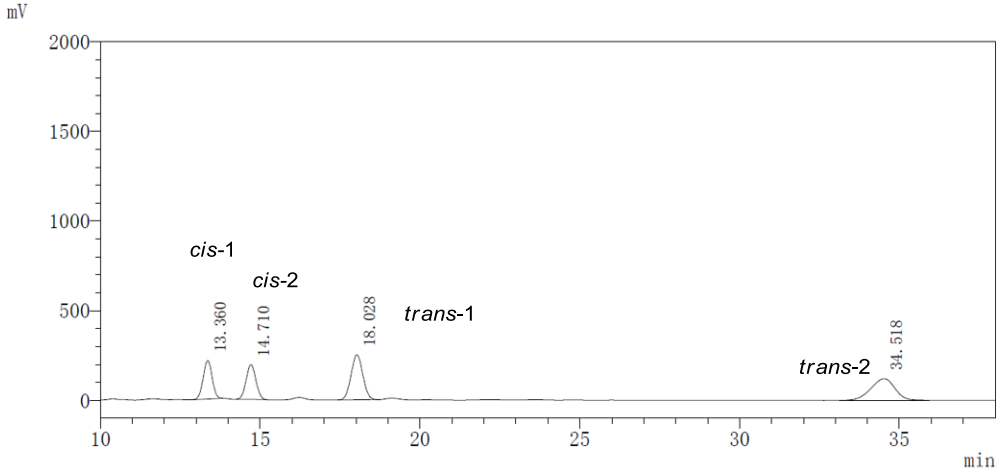
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	17.564	3862985	95.691	143823	96.160
2	23.328	173943	4.309	5744	3.840



3j

*Chiral HPLC spectrum of racemic **3j***

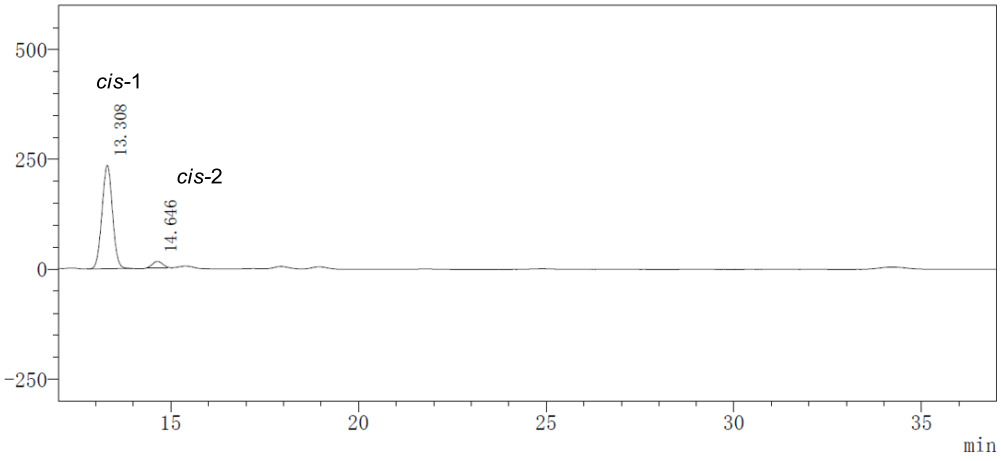


〈Peak Results〉

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	13.360	4179307	19.925	214405	27.497
2	14.710	4100207	19.548	193608	24.830
3	18.028	6418067	30.598	251040	32.195
4	34.518	6278009	29.930	120693	15.479

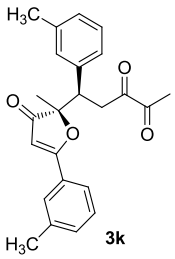
*Chiral HPLC spectrum of chiral **3j***



〈Peak Results〉

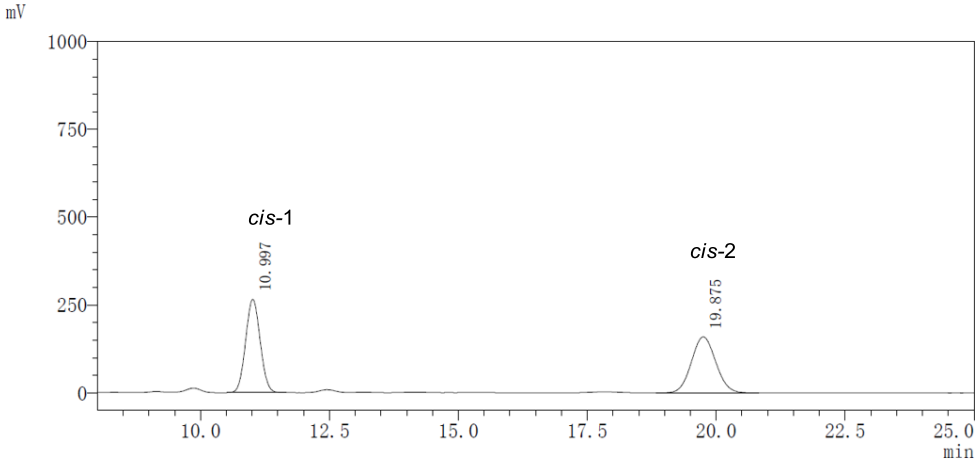
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	13.308	4602469	95.215	235837	94.603
2	14.646	231276	4.785	13454	5.397



3k

*Chiral HPLC spectrum of racemic **3k***

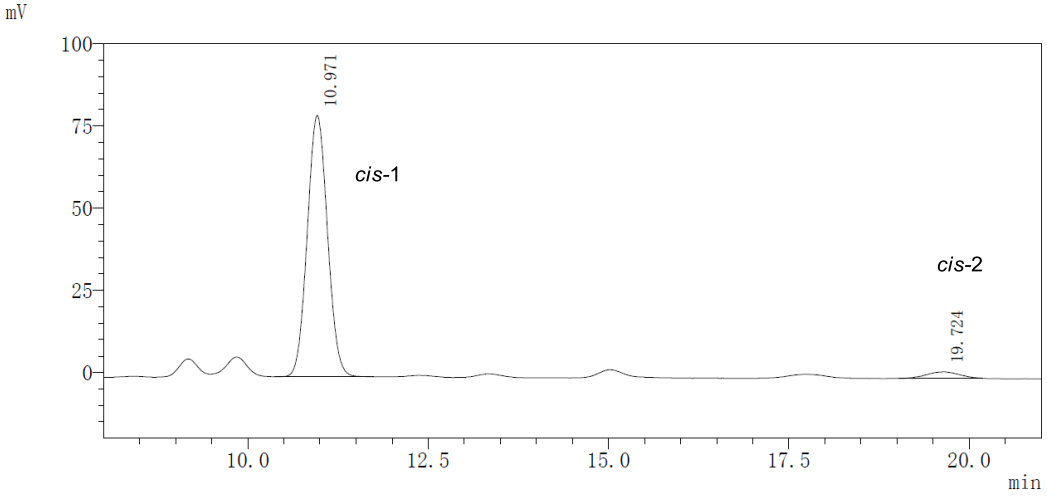


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.997	7261293	49.281	192812	56.272
2	19.875	7392891	50.719	121293	43.728

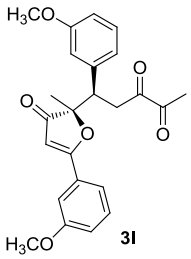
*Chiral HPLC spectrum of chiral **3k***



<Peak Results>

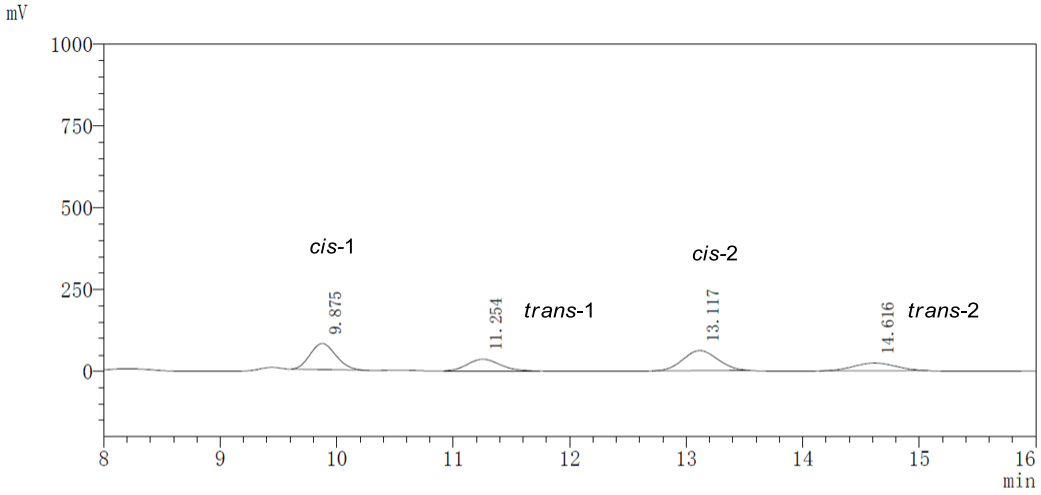
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.971	1671293	95.368	62992	97.722
2	19.724	72182	4.632	1762	2.278



3l

*Chiral HPLC spectrum of racemic **3l***

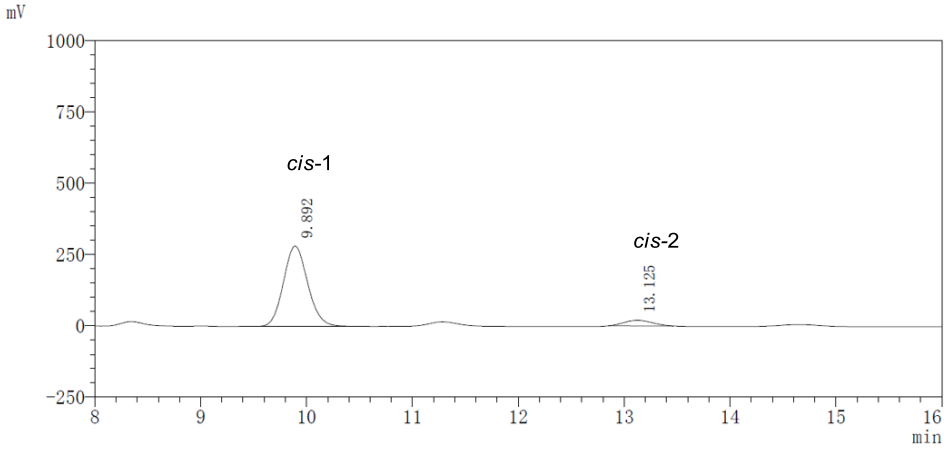


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.875	1222366	32.312	79575	39.671
2	11.254	689699	18.232	35706	17.801
3	13.117	1272434	33.636	61518	30.669
4	14.616	598470	15.820	23788	11.859

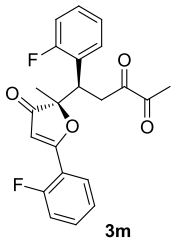
*Chiral HPLC spectrum of chiral **3l***



<Peak Results>

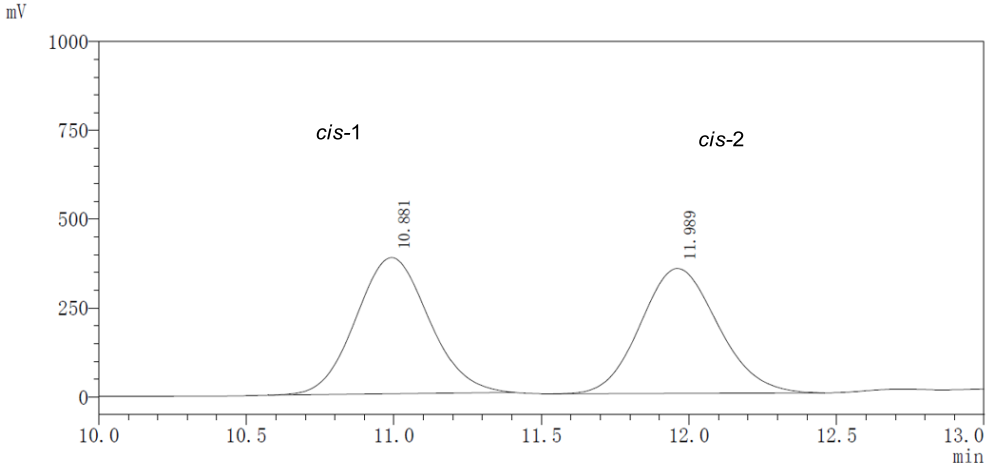
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.892	4468641	92.510	281526	93.522
2	13.125	361800	7.490	19501	6.478



3m

*Chiral HPLC spectrum of racemic **3m***

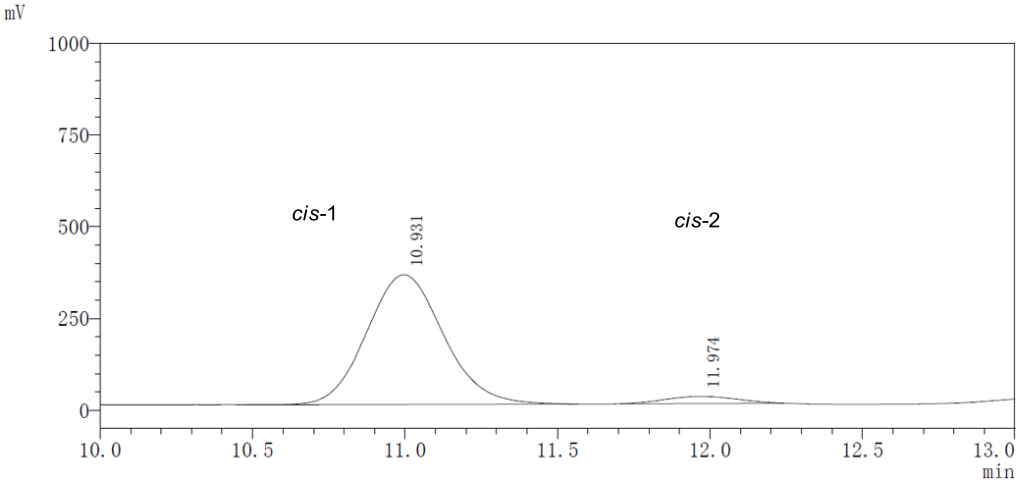


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.881	6809127	50.251	446765	52.328
2	11.989	6436972	49.749	451721	47.672

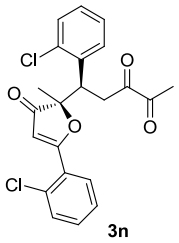
*Chiral HPLC spectrum of chiral **3m***



<Peak Results>

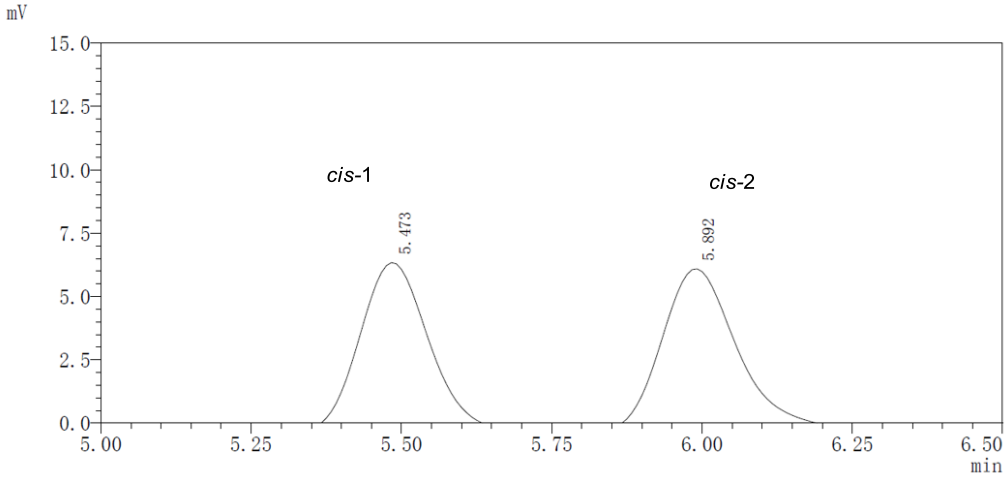
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.931	7219283	95.741	353500	97.758
2	11.974	428712	4.259	19482	2.242



3n

*Chiral HPLC spectrum of racemic **3n***

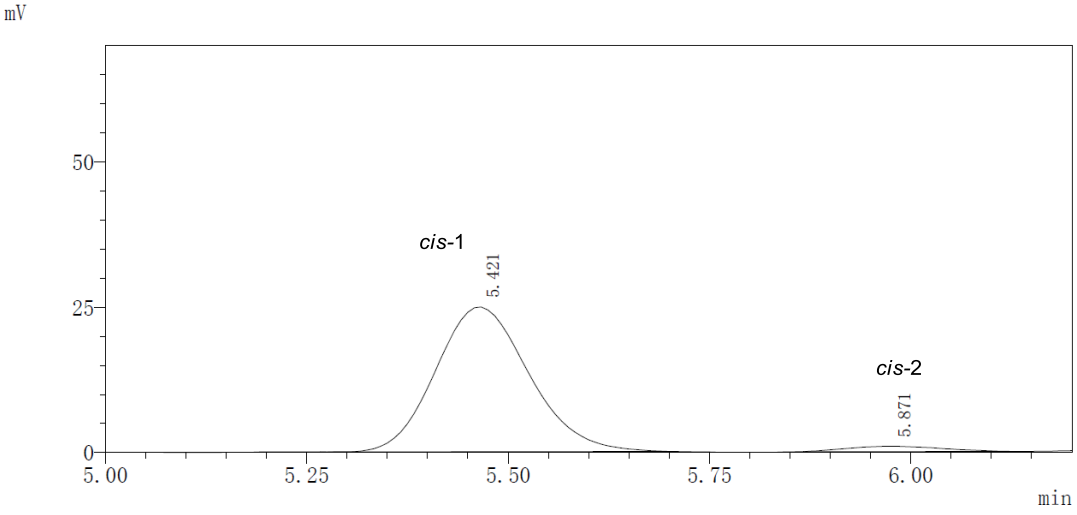


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	5.473	55499	49.874	6192	51.441
2	5.892	57232	50.126	6216	48.559

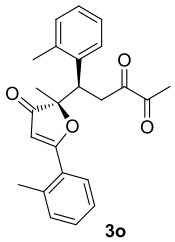
*Chiral HPLC spectrum of chiral **3n***



<Peak Results>

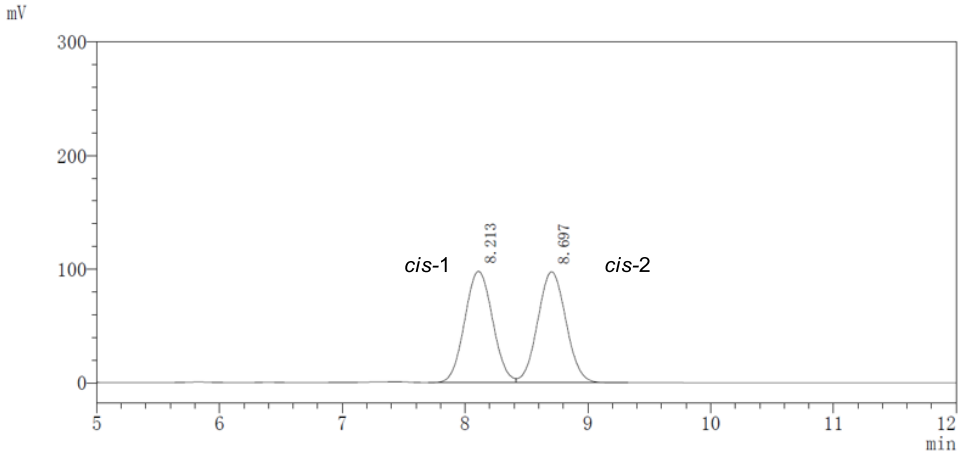
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	5.421	343257	95.185	23406	97.553
2	5.871	5215	4.815	694	2.447



3o

Chiral HPLC spectrum of racemic ***3o***

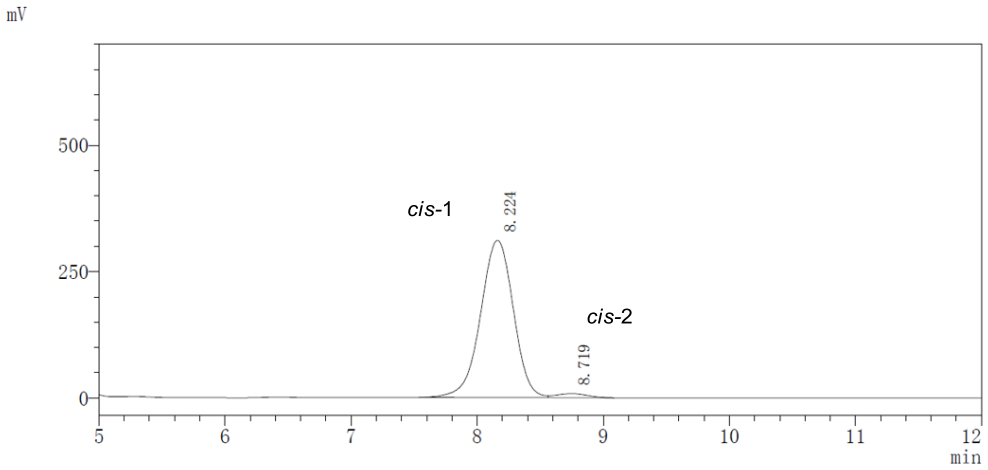


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	8.213	1466283	49.818	97157	50.315
2	8.697	1443887	50.182	97254	49.685

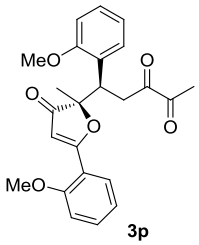
Chiral HPLC spectrum of chiral ***3o***



<Peak Results>

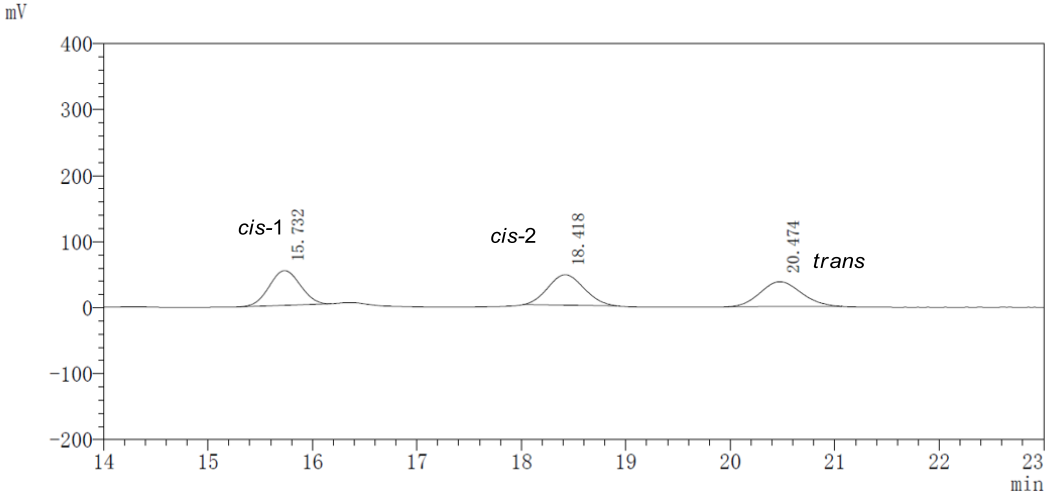
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	8.224	5667149	95.643	31384	97.207
2	8.719	326252	4.357	9011	2.793



3p

*Chiral HPLC spectrum of racemic **3p***

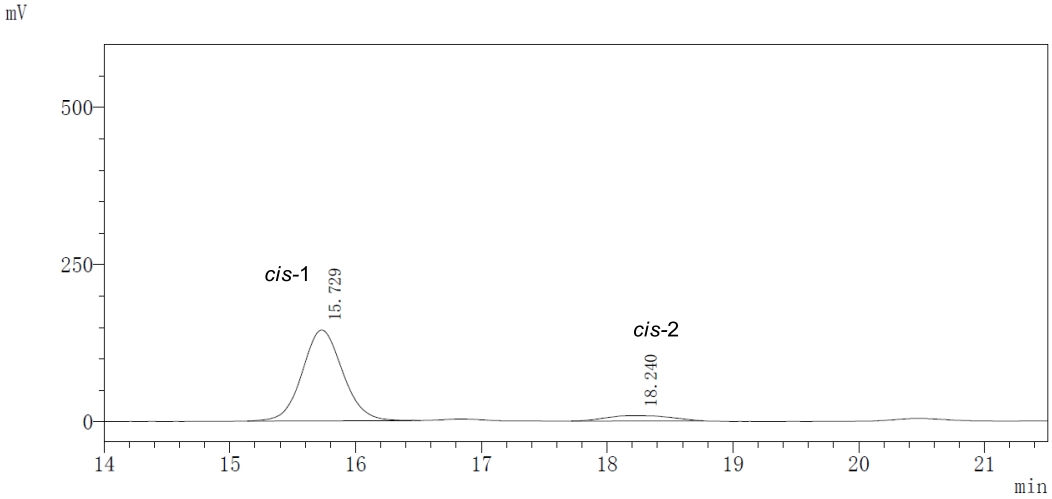


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	15.732	1087537	33.717	52693	38.609
2	18.418	1107135	34.325	46101	33.779
3	20.474	1030790	31.958	37684	27.612

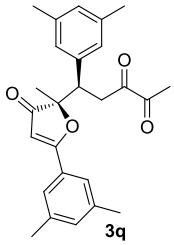
*Chiral HPLC spectrum of chiral **3p***



<Peak Results>

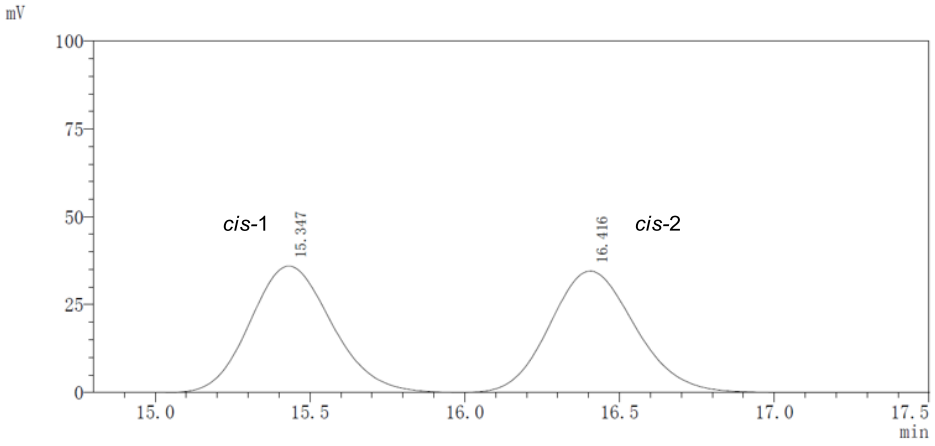
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	15.729	3226528	91.521	144442	94.390
2	18.240	298911	8.479	8585	5.610



3q

*Chiral HPLC spectrum of racemic **3q***

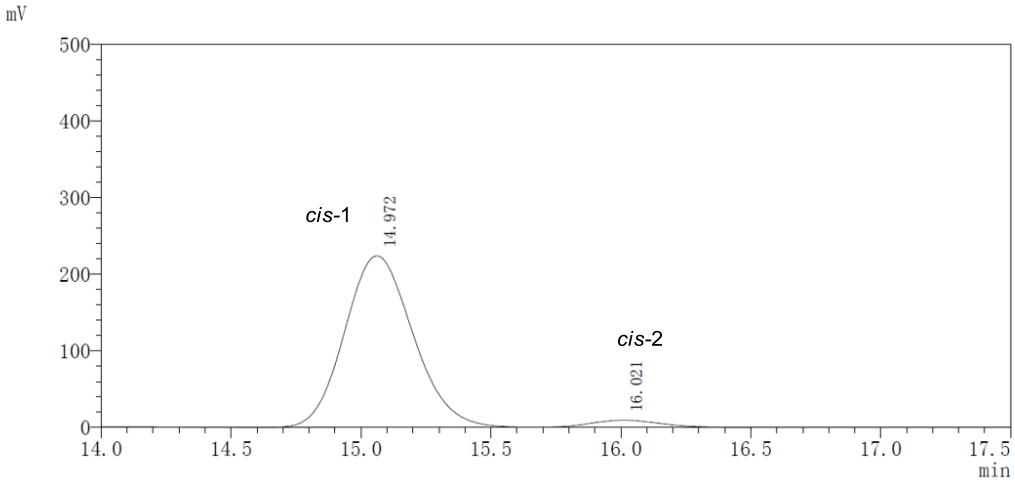


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	15.347	667524	49.548	32356	51.154
2	16.416	683831	50.452	34447	48.846

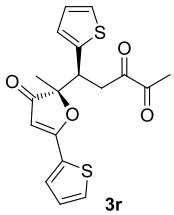
*Chiral HPLC spectrum of chiral **3q***



<Peak Results>

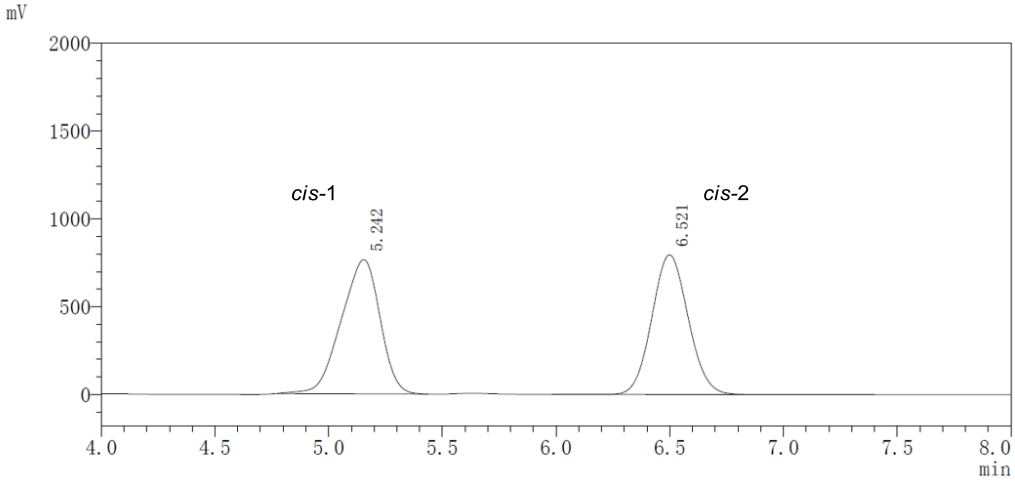
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	14.972	4056211	96.227	512062	97.348
2	16.021	265927	3.773	9761	2.652



3r

*Chiral HPLC spectrum of racemic **3r***

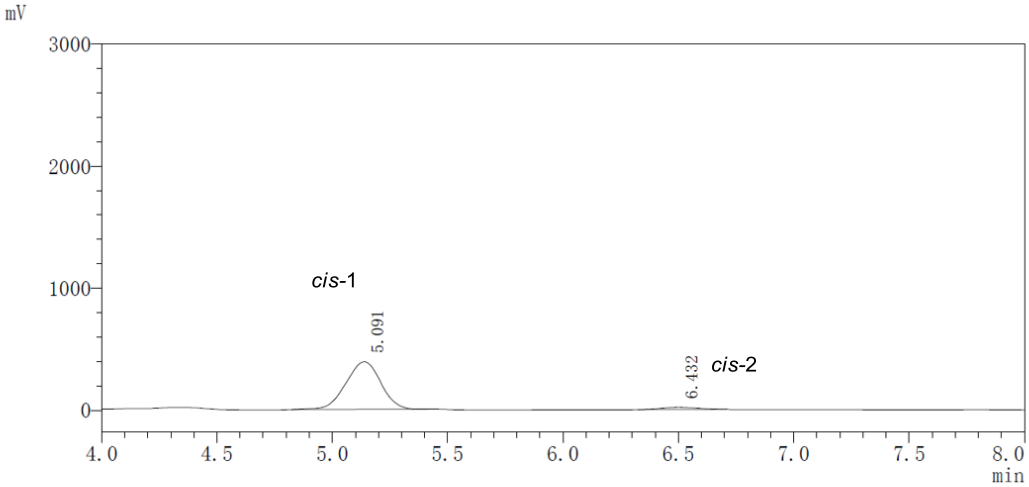


<Peak Results>

Ch2 210nm

Index	Time	Area	Area/%	Height	Height/%
1	5.242	8982132	50.261	621321	49.721
2	6.521	8827326	49.739	638734	50.279

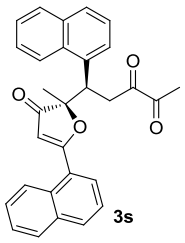
*Chiral HPLC spectrum of chiral **3r***



<Peak Results>

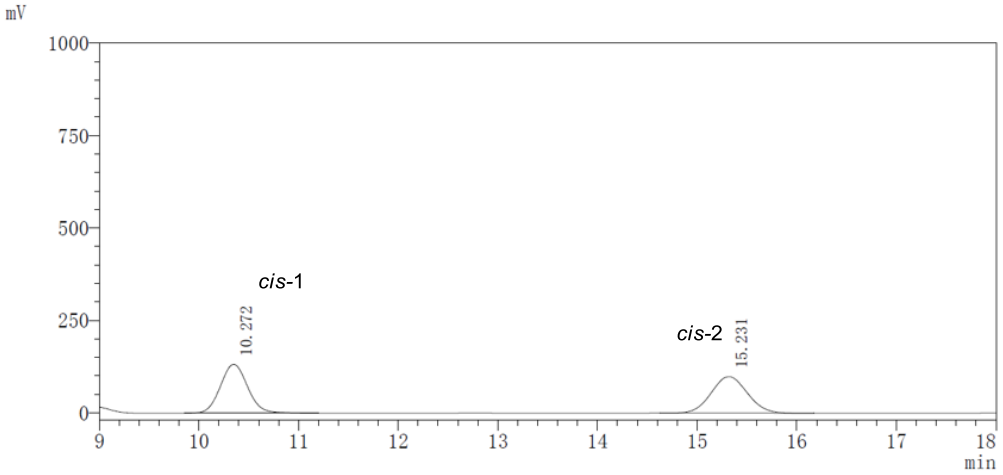
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	5.091	3292812	95.231	389744	95.662
2	6.432	219239	4.769	17674	4.338



3s

*Chiral HPLC spectrum of racemic **3s***

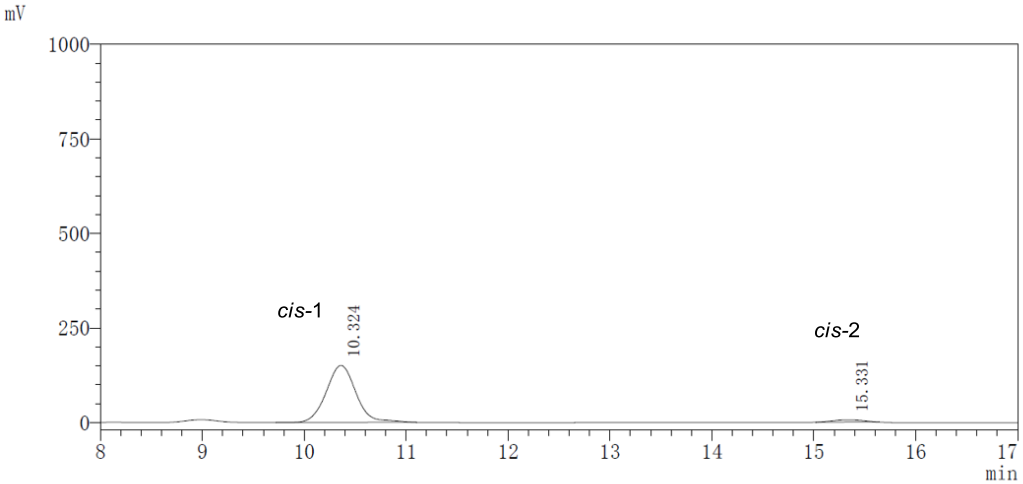


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.272	2513053	50.245	133183	55.212
2	15.231	2491873	49.755	94857	44.788

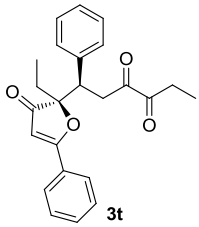
*Chiral HPLC spectrum of chiral **3s***



<Peak Results>

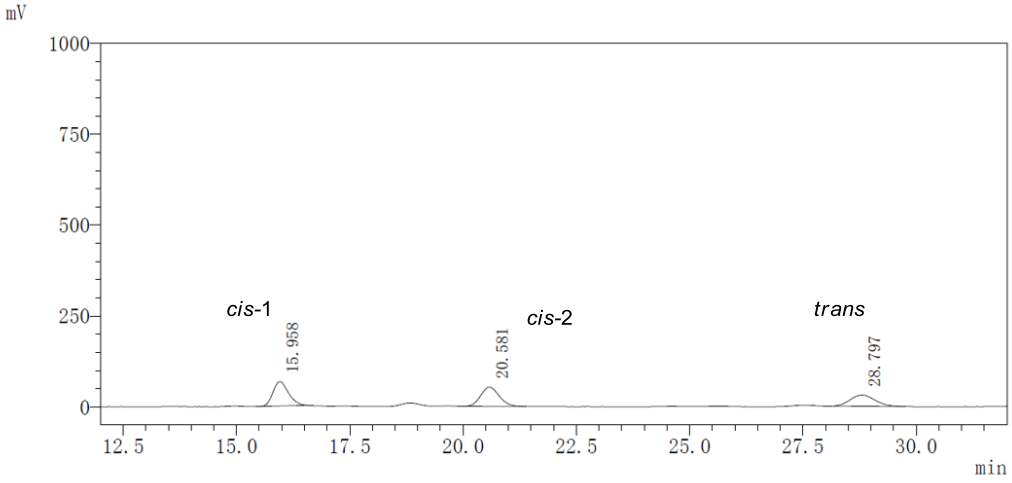
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.324	3058608	95.058	159613	96.095
2	15.331	145161	4.942	6523	3.905



3t

*Chiral HPLC spectrum of racemic **3t***

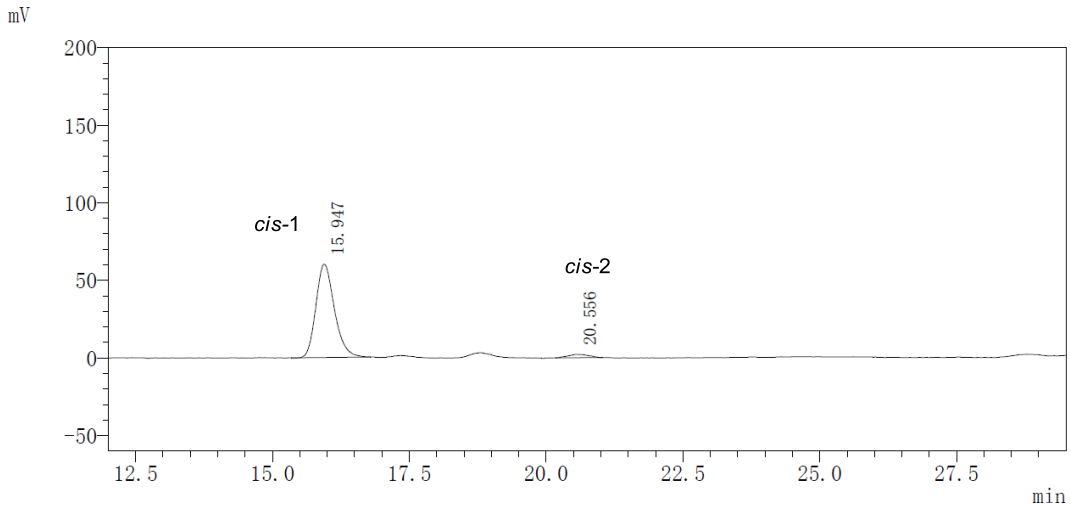


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	15.958	1590569	37.349	67227	44.584
2	20.581	1495843	35.125	52802	35.018
3	28.797	1172238	27.526	30757	20.398

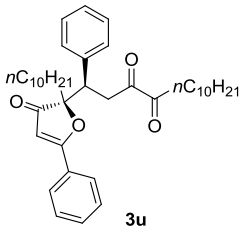
*Chiral HPLC spectrum of chiral **3t***



<Peak Results>

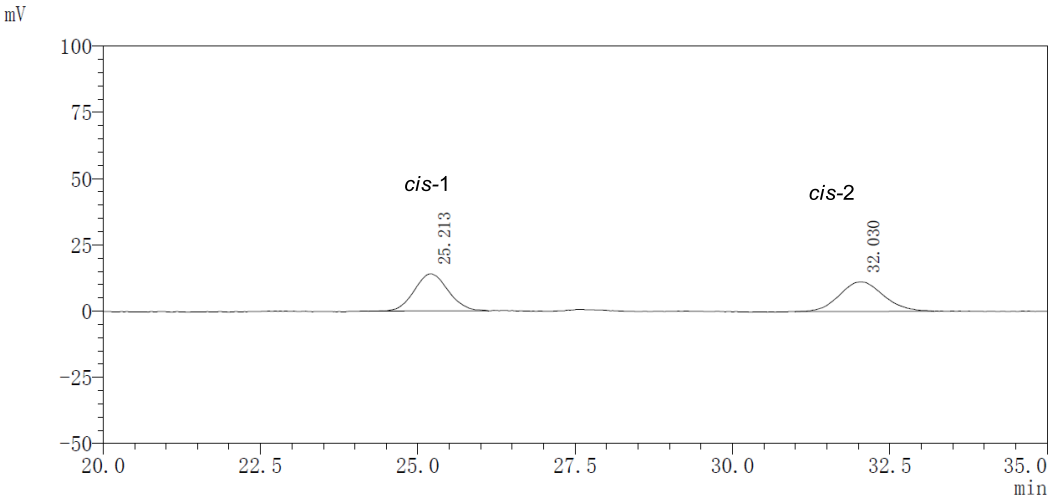
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	15.947	1417610	96.271	60218	96.538
2	20.556	54905	3.729	2159	3.462



3u

*Chiral HPLC spectrum of racemic **3u***

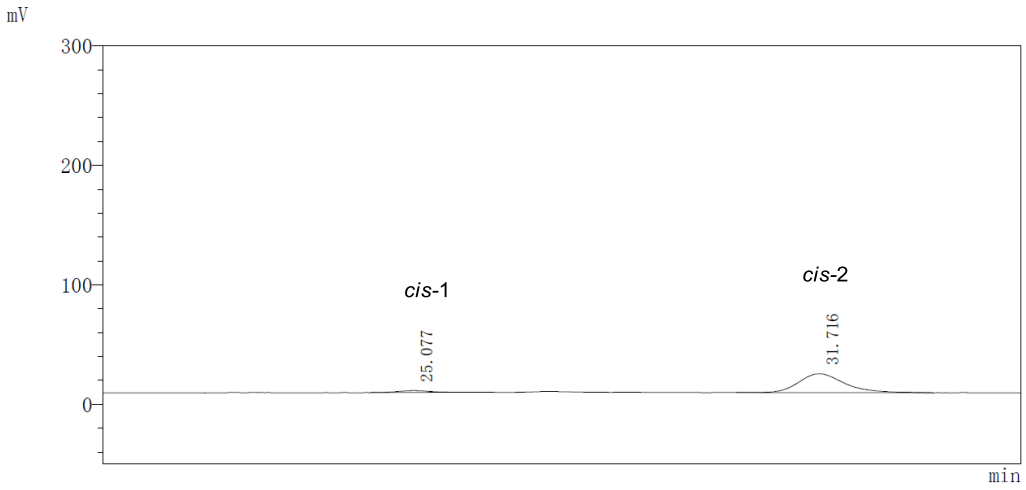


〈Peak Results〉

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	25.213	524324	49.358	14007	55.759
2	32.030	537958	50.642	11114	44.241

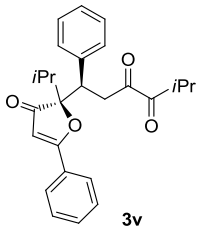
*Chiral HPLC spectrum of chiral **3u***



〈Peak Results〉

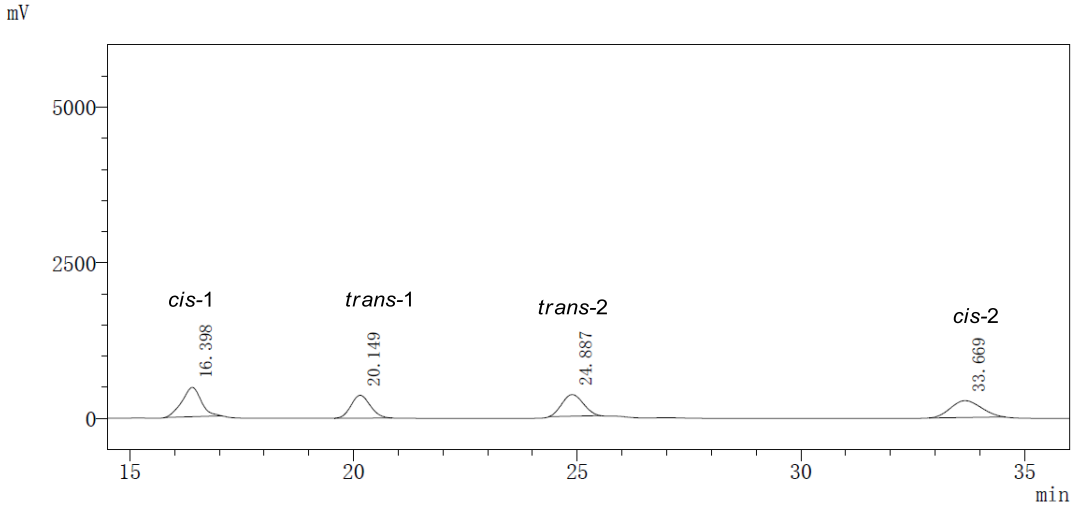
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	25.077	52298	6.005	1560	8.983
2	31.716	818682	93.995	15805	91.017



3v

*Chiral HPLC spectrum of racemic **3u***

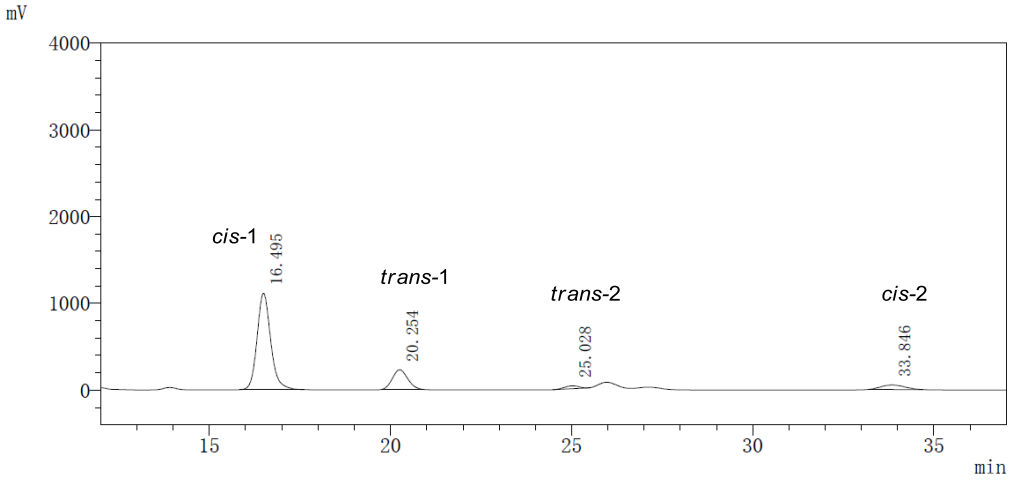


〈Peak Results〉

Ch2 254nm

Index	Time	Area	Area%	Height	Height%
1	16.398	14079940	28.461	470087	32.303
2	20.149	10924125	22.082	366408	25.179
3	24.887	11543529	23.334	347842	23.903
4	33.669	12923700	26.124	270900	18.616

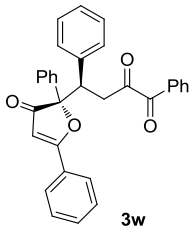
*Chiral HPLC spectrum of chiral **3v***



〈Peak Results〉

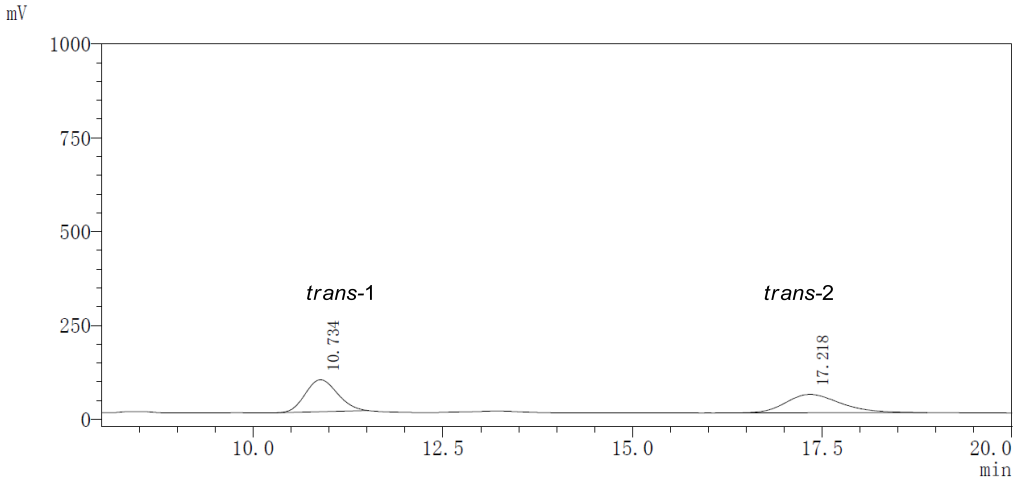
Ch2 254nm

Index	Time	Area	Area%	Height	Height%
1	16.495	29180125	74.717	1113082	78.147
2	20.254	6570691	16.824	225631	15.841
3	25.028	936715	2.398	33247	2.334
4	33.846	2366867	6.060	52388	3.678



3w

*Chiral HPLC spectrum of racemic **3w***

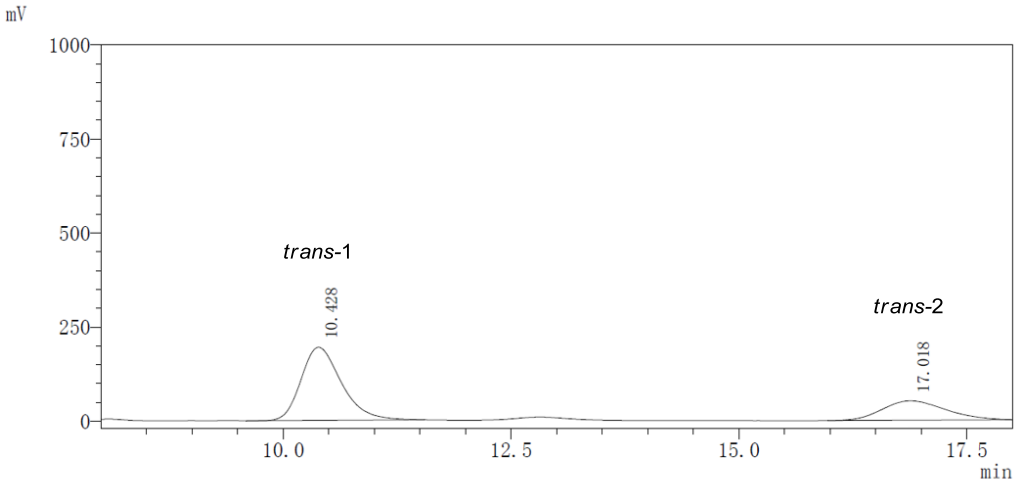


〈Peak Results〉

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.734	2814924	50.721	92741	68.821
2	17.218	2389156	49.279	68194	31.179

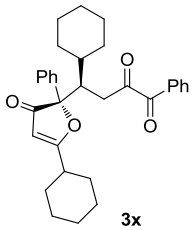
*Chiral HPLC spectrum of chiral **3w***



〈Peak Results〉

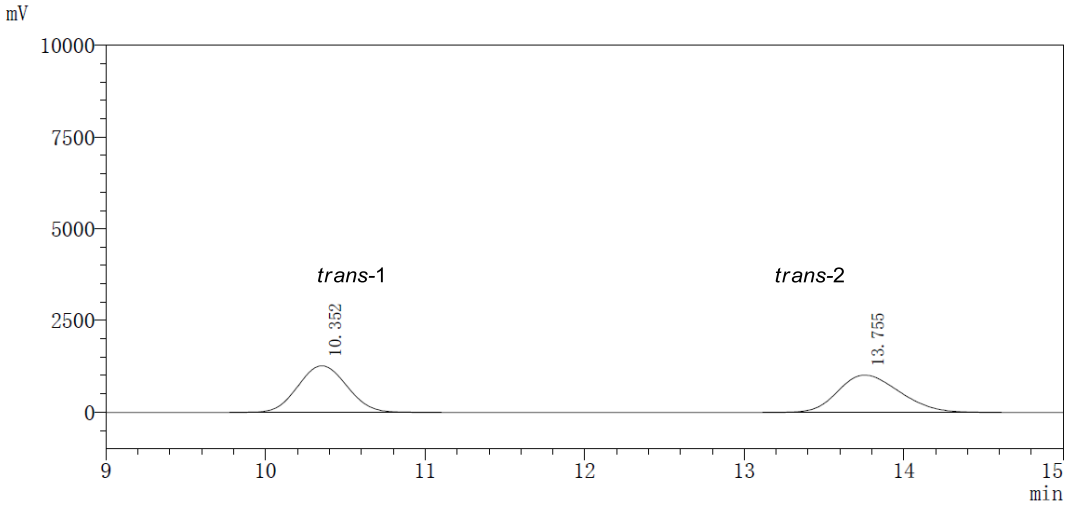
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.428	8912815	70.664	194379	79.036
2	17.018	4893150	29.336	51559	20.964



3x

*Chiral HPLC spectrum of racemic **3x***

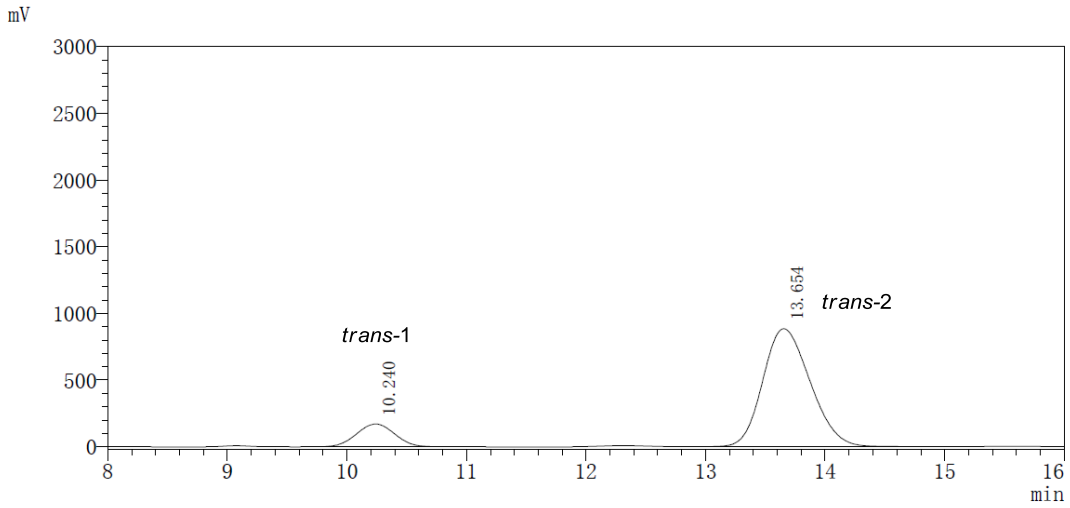


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.352	27048935	49.750	1270697	55.517
2	13.755	27320326	50.250	1018164	44.483

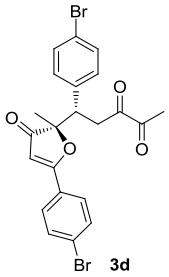
*Chiral HPLC spectrum of chiral **3x***



<Peak Results>

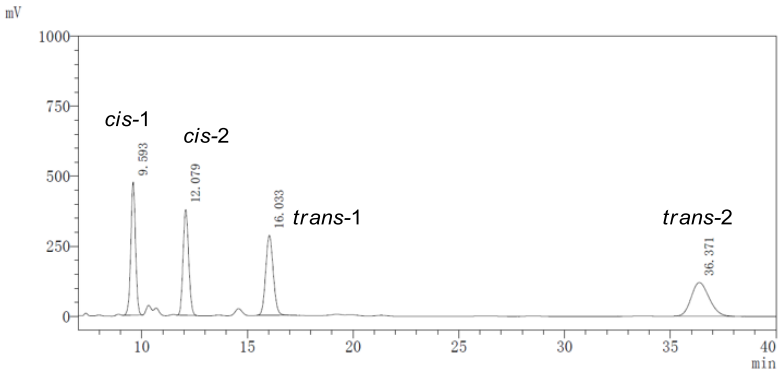
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	10.240	3718972	18.256	169191	16.060
2	13.654	24335409	81.744	884311	83.940



3d

*Chiral HPLC spectrum of racemic **3d***

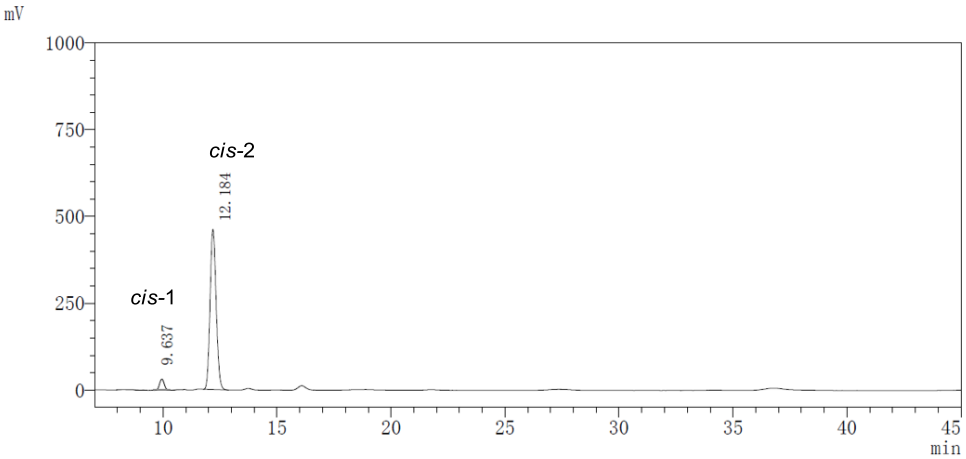


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.593	7381119	25.934	475466	37.822
2	12.079	6938466	24.379	376738	29.968
3	16.033	7073087	24.852	284930	22.665
4	36.371	7068432	24.835	119991	9.545

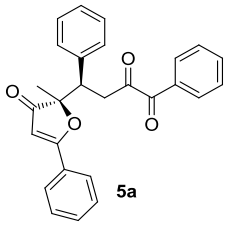
*Chiral HPLC spectrum of chiral **3d***



<Peak Results>

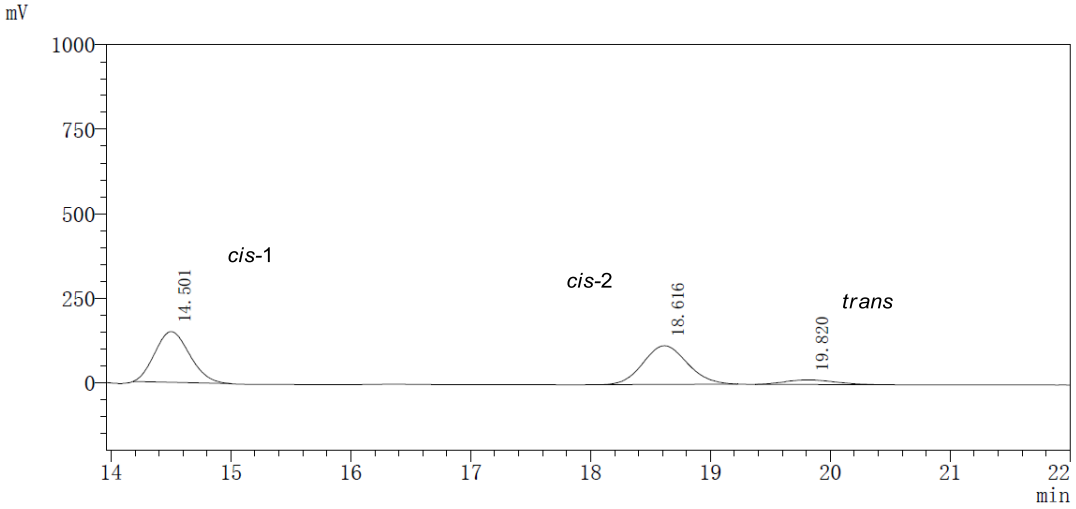
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	9.637	918154	7.306	48686	7.548
2	12.184	8553347	92.694	461226	92.452



5a

*Chiral HPLC spectrum of racemic **5a***

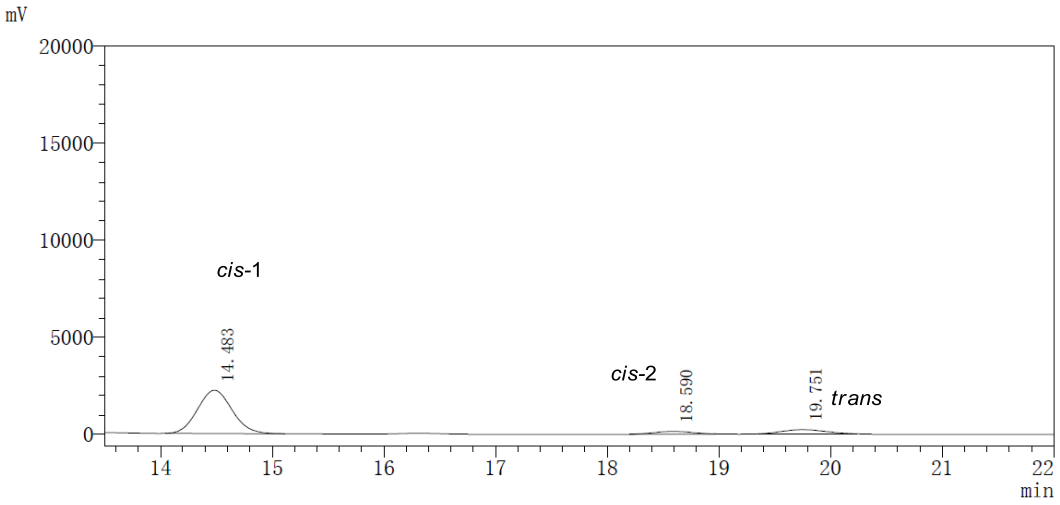


〈Peak Results〉

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	14.501	3028051	47.574	149826	53.868
2	18.616	2938899	46.173	114424	41.140
3	19.820	397987	6.253	13886	4.993

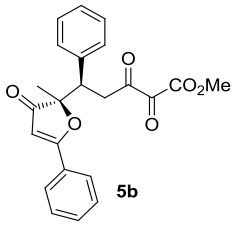
*Chiral HPLC spectrum of chiral **5a***



〈Peak Results〉

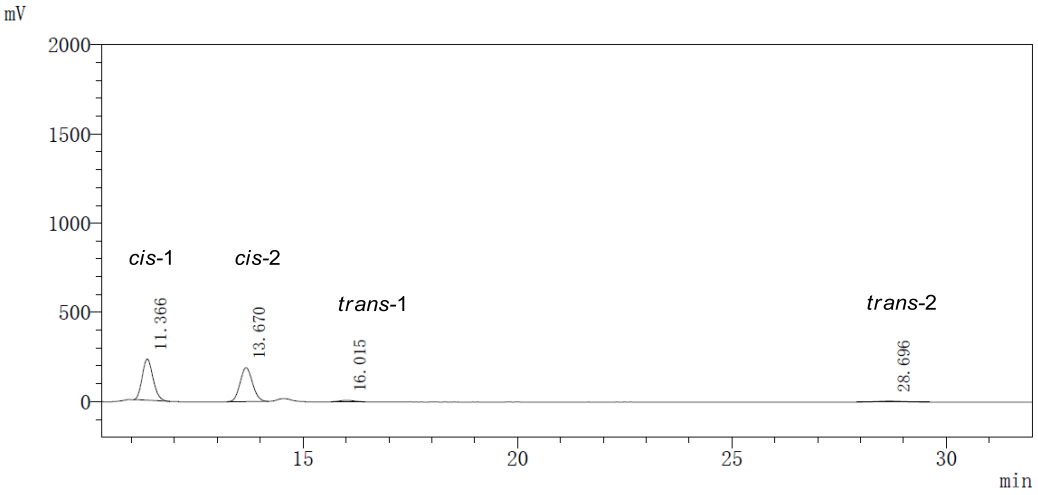
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	14.483	47816122	83.957	2227712	86.230
2	18.590	3333800	5.854	139727	5.409
3	19.751	5803097	10.189	216019	8.362



5b

*Chiral HPLC spectrum of racemic **5b***

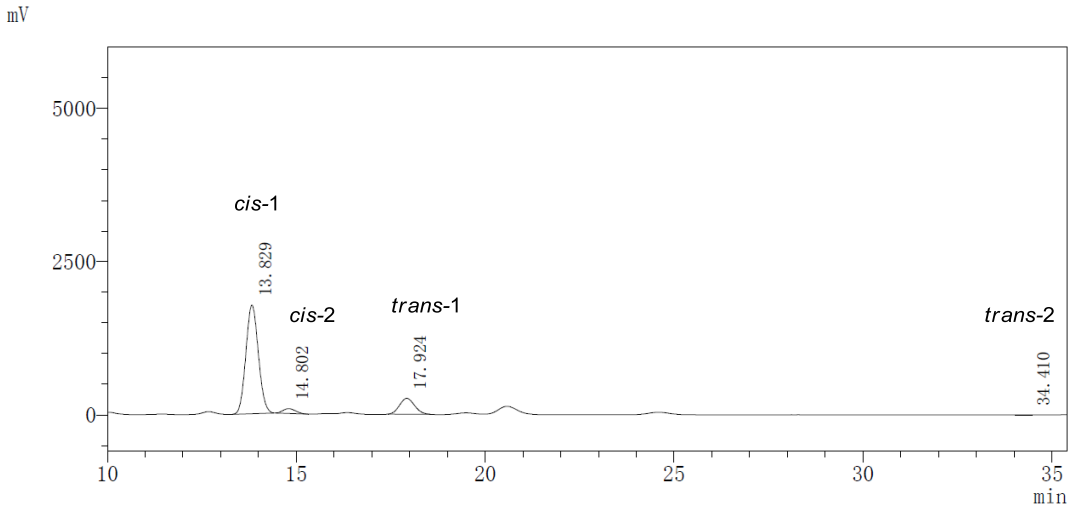


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	11.366	4051154	48.965	230886	53.076
2	13.670	3836399	46.370	190496	43.792
3	16.015	190791	2.306	8783	2.019
4	28.696	195152	2.359	4842	1.113

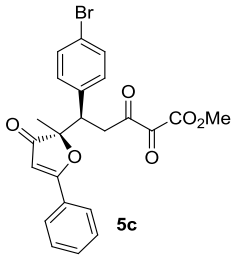
*Chiral HPLC spectrum of chiral **5b***



<Peak Results>

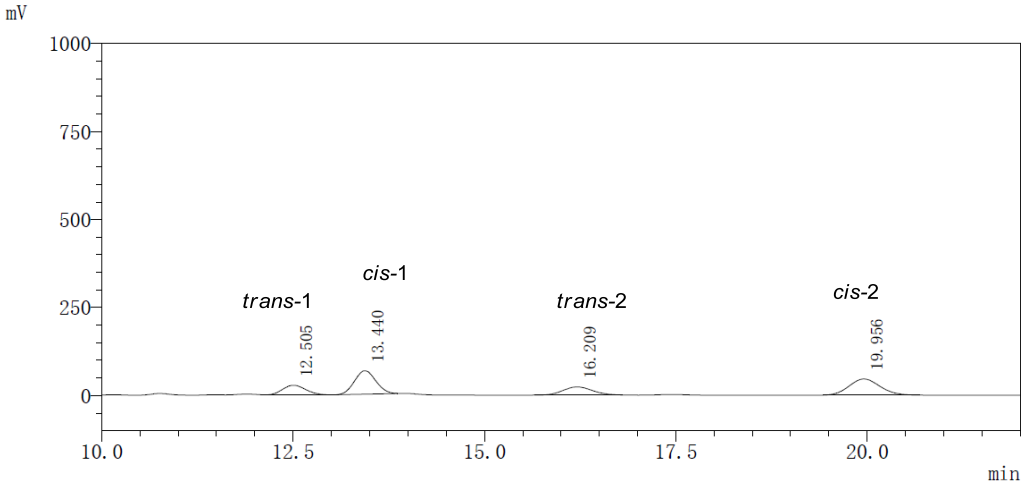
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	13.829	40906838	81.961	1774221	84.011
2	14.802	1849754	3.706	78211	3.703
3	17.924	7153438	14.146	259372	12.282
4	34.410	283	0.187	79	0.004



5c

Chiral HPLC spectrum of racemic ***5c***

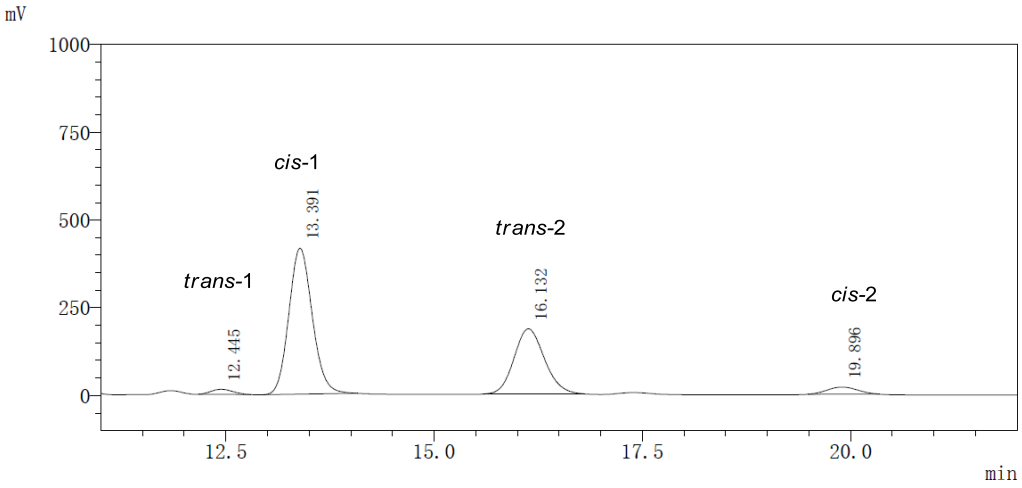


<Peak Results>

Ch2 254nm

Index	Time	Area	Area%	Height	Height%
1	12.505	554136	14.751	27066	16.626
2	13.440	1285426	34.218	66524	40.864
3	16.209	622419	16.569	23331	14.332
4	19.956	1294634	34.463	45873	28.178

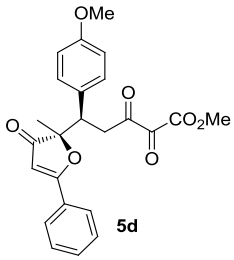
Chiral HPLC spectrum of chiral ***5c***



<Peak Results>

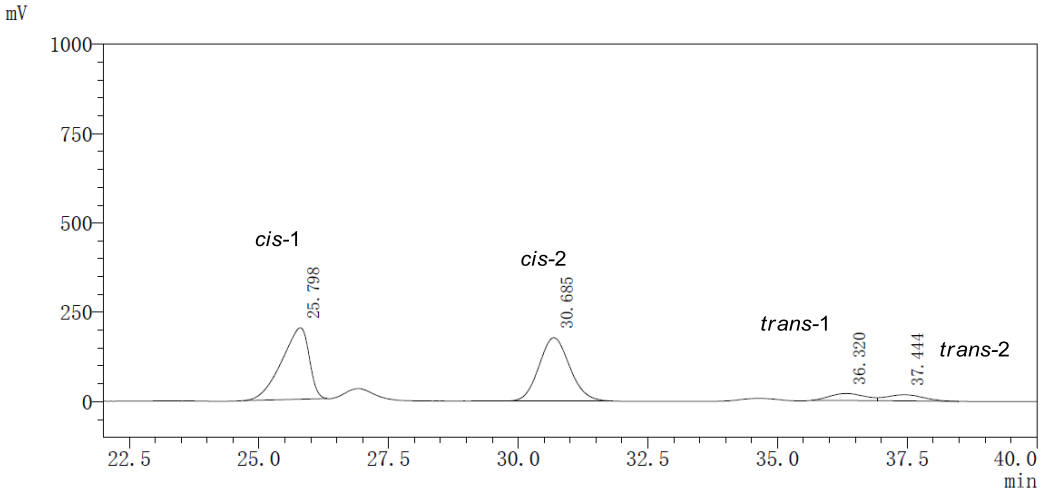
Ch2 254nm

Index	Time	Area	Area%	Height	Height%
1	12.445	259934	1.905	14439	2.268
2	13.391	8158159	59.802	416254	65.378
3	16.132	4712323	34.543	185650	29.159
4	19.896	511612	3.750	20345	3.195



5d

*Chiral HPLC spectrum of racemic **5d***

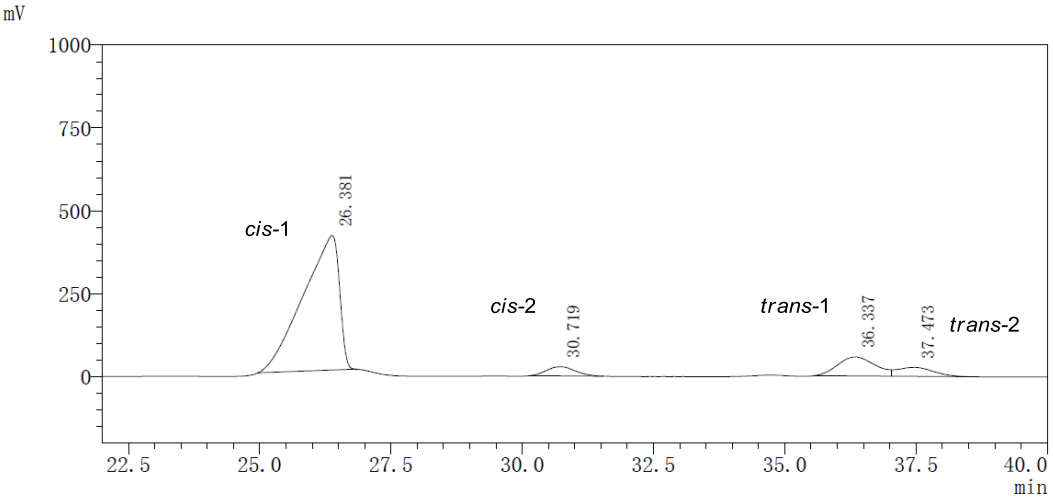


<Peak Results>

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	25.798	7375602	45.004	200210	48.341
2	30.685	7242771	44.193	176758	42.679
3	36.320	915828	5.588	19631	4.740
4	37.444	854683	5.215	17561	4.240

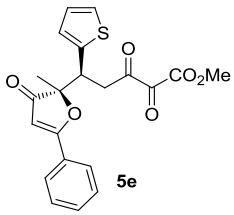
*Chiral HPLC spectrum of chiral **5d***



<Peak Results>

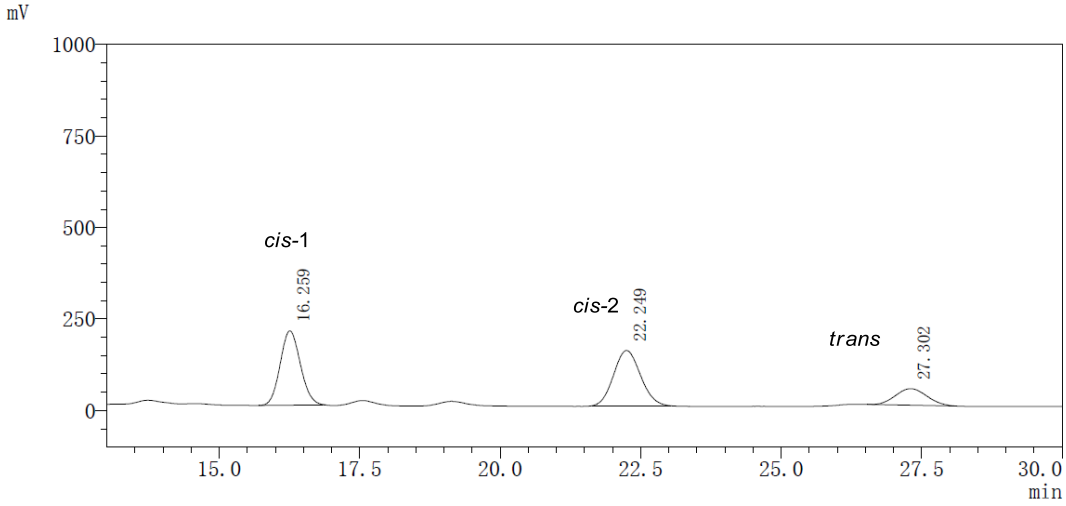
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	26.381	19562858	78.901	405787	78.273
2	30.719	1050891	4.238	27843	5.371
3	36.337	2871367	11.581	57568	11.104
4	37.473	1309104	5.280	27230	5.252



5e

*Chiral HPLC spectrum of racemic **5e***

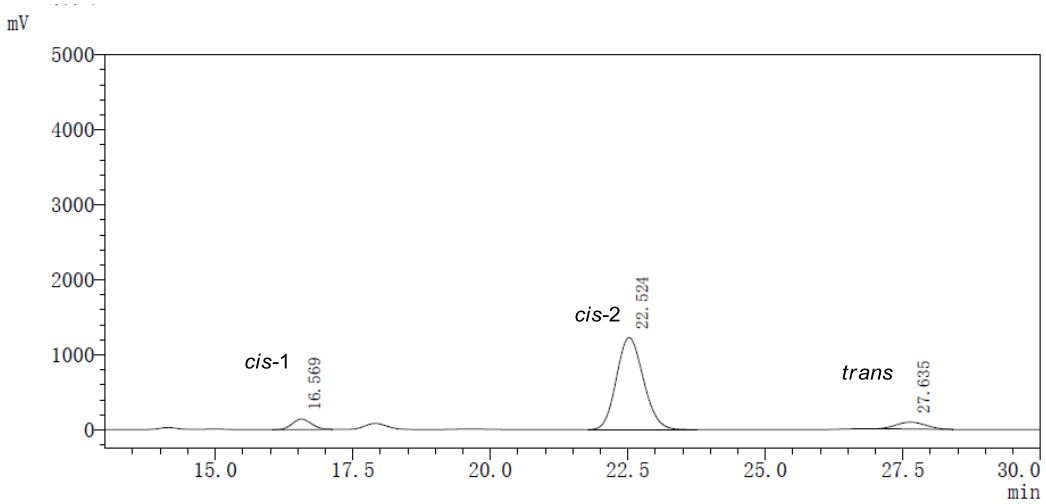


〈Peak Results〉

Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	16.259	5071184	42.900	203312	50.904
2	22.249	4996822	42.270	150874	37.775
3	27.302	1753061	14.830	45218	11.321

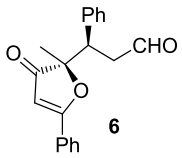
*Chiral HPLC spectrum of chiral **5e***



〈Peak Results〉

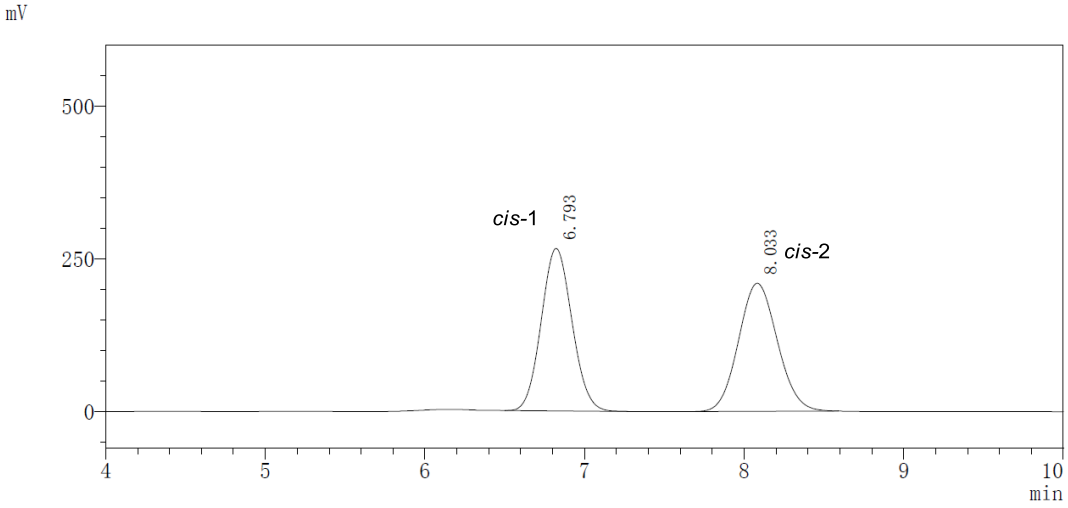
Ch2 210nm

Index	Time	Area	Area%	Height	Height%
1	16.569	3387318	6.944	139681	9.564
2	22.524	41959294	86.015	1228905	84.141
3	27.635	3434730	7.041	91941	6.295



6

*Chiral HPLC spectrum of racemic **6***

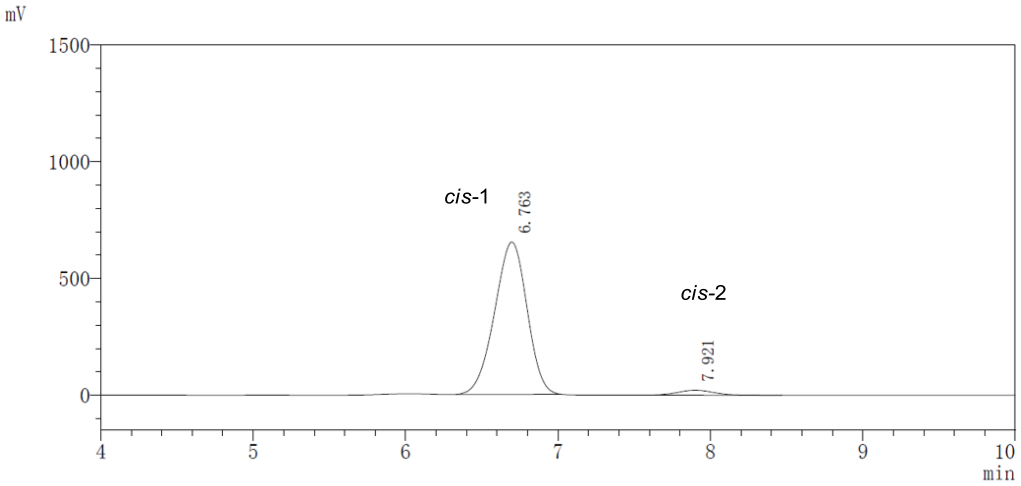


<Peak Results>

Ch2 210nm

Index	Time	Area	Area/%	Height	Height/%
1	6.793	4821234	50.572	265746	57.368
2	8.033	4813213	49.428	209642	42.632

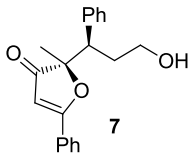
*Chiral HPLC spectrum of chiral **6***



<Peak Results>

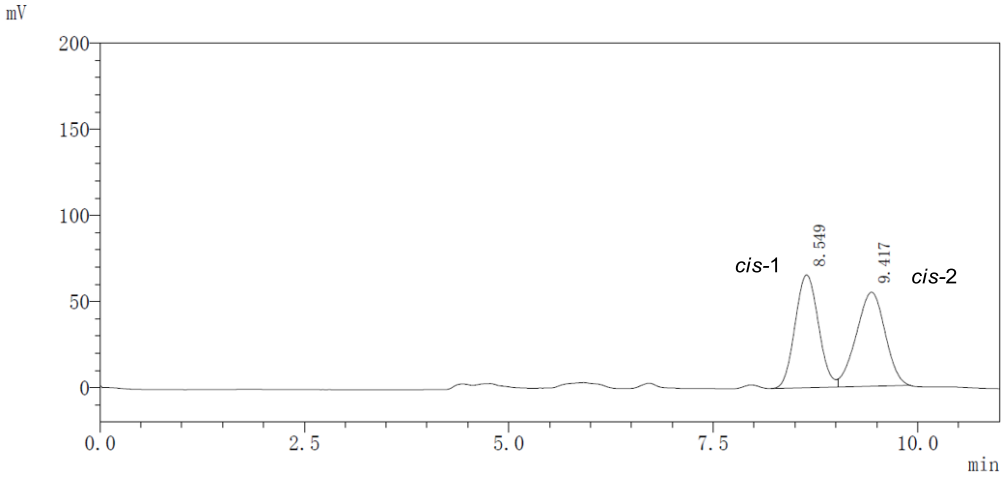
Ch2 210nm

Index	Time	Area	Area/%	Height	Height/%
1	6.763	9428325	96.731	729316	96.352
2	7.921	281938	3.269	34291	3.648



7

*Chiral HPLC spectrum of racemic **7***

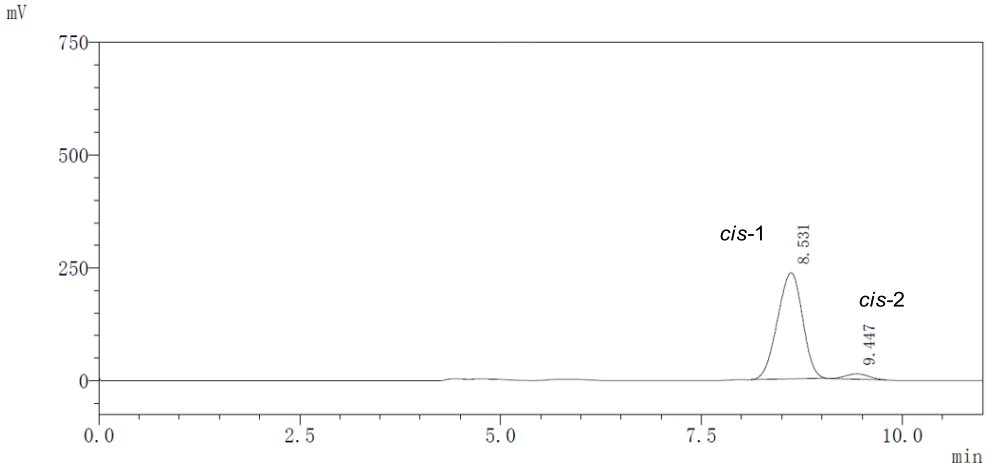


<Peak Results>

Ch2 210nm

Index	Time	Area	Area/%	Height	Height/%
1	8.549	1582146	49.195	67219	51.846
2	9.417	1698214	50.905	62194	48.154

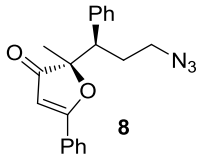
*Chiral HPLC spectrum of chiral **7***



<Peak Results >

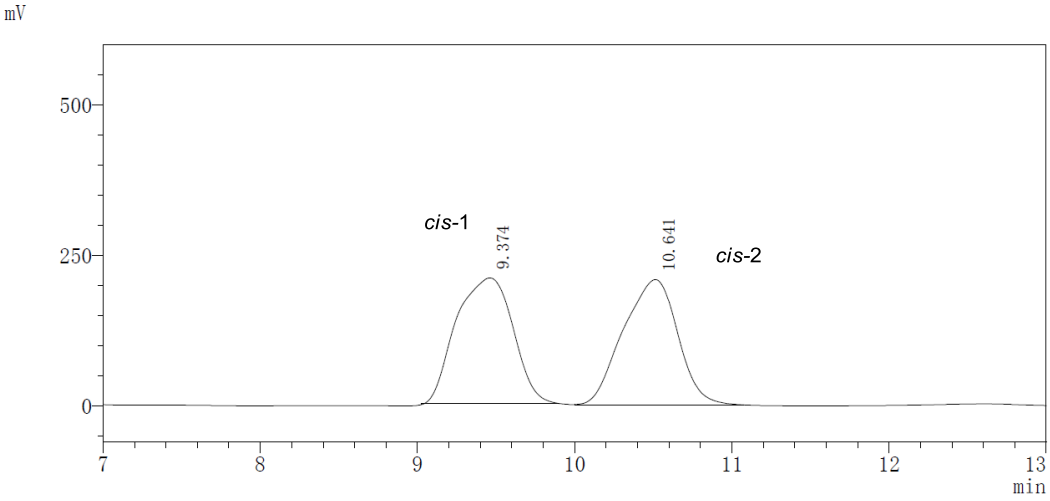
Ch2 210nm

Index	Time	Area	Area/%	Height	Height/%
1	8.531	5319234	95.827	381345	95.539
2	9.447	221741	4.173	27921	4.461



8

*Chiral HPLC spectrum of racemic **8***

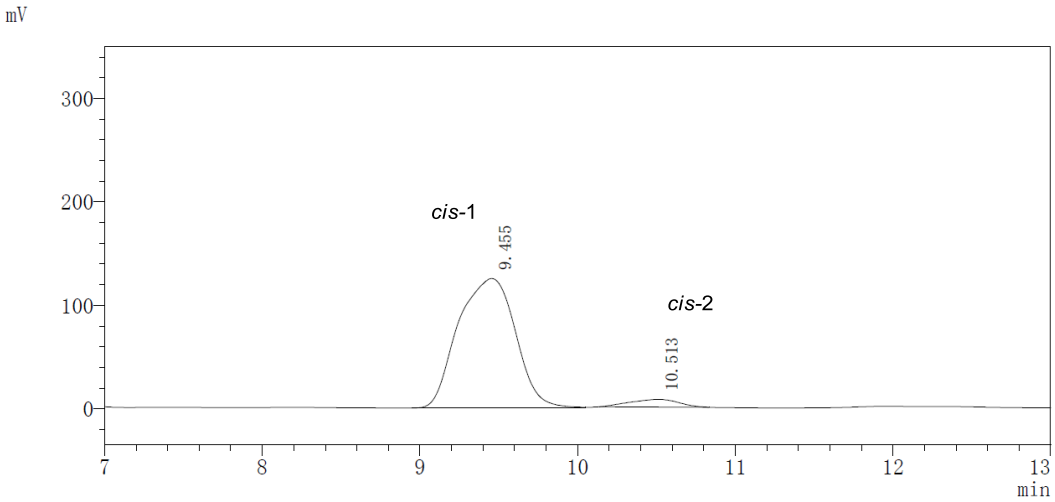


<Peak Results>

Ch2 210nm

Index	Time	Area	Area/%	Height	Height/%
1	9.374	4928729	50.243	173492	50.428
2	10.641	4942814	49.757	172593	49.572

*Chiral HPLC spectrum of chiral **8***



<Peak Results>

Ch2 210nm

Index	Time	Area	Area/%	Height/mV	Height/%
1	9.455	3791235	95.428	174924	94.451
2	10.513	238524	4.572	8795	5.549

VIII. Reference

1. J. Liu, D. K. Das, G. Zhang, S. Yang, H. Zhang, X. Fang, *Org. Lett.*, 2018, **20**, 64.

2. S. Fredrich, R. Göstl, M. Herder, L. Grubert, S. Hecht, *Angew. Chem., Int. Ed.,* 2016, **55**, 1208.

3. S. Chen, X. Li, H. Zhao, B. Li, B. *J. Org. Chem.,* 2014, **79**, 4137.