Supplementary Information

Photoinduced umpolung addition of carbonyl compounds with α,β-unsaturated esters enables the polysubstituted γ-lactone formation

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Contents

1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All air- and moisture-sensitive reactions were performed using oven-dried glassware, including standard Schlenk techniques under an argon atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light, phosphomolybdic acid and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 300–400 mesh silica gel at increased pressure. ^{1}H NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz and 150 MHz NMR or 400 MHz and 101 MHz Bruker spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants (J) were reported in Hz. High-resolution mass spectra (HRMS) were obtained by using ESI ionization sources (Varian 7.0 T FTICR-MS) and ESI-TOF. Melting points were taken on a WPX-4 apparatus (Yice instrument equipment Co Ltd, Shanghai) and were uncorrected. Single-crystal X-ray diffraction measurements were carried out on an Agilent SuperNova EosS2 diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54184 Å) or Mo Kα radiation (λ = 0.710 Å). The crystals were kept at 150 (10) K during data collection. The structures were solved by the Superflip[3] or ShelXT[4] structure solution program in Olex2[5] and refined using Full-matrix Least Squares based on F^2 with program SHELXL-2018[6] within Olex2. Disorder was modelled using standard crystallographic methods including constraints and restraints S16S17 where necessary.

2. Setup of the Photoredox Reaction

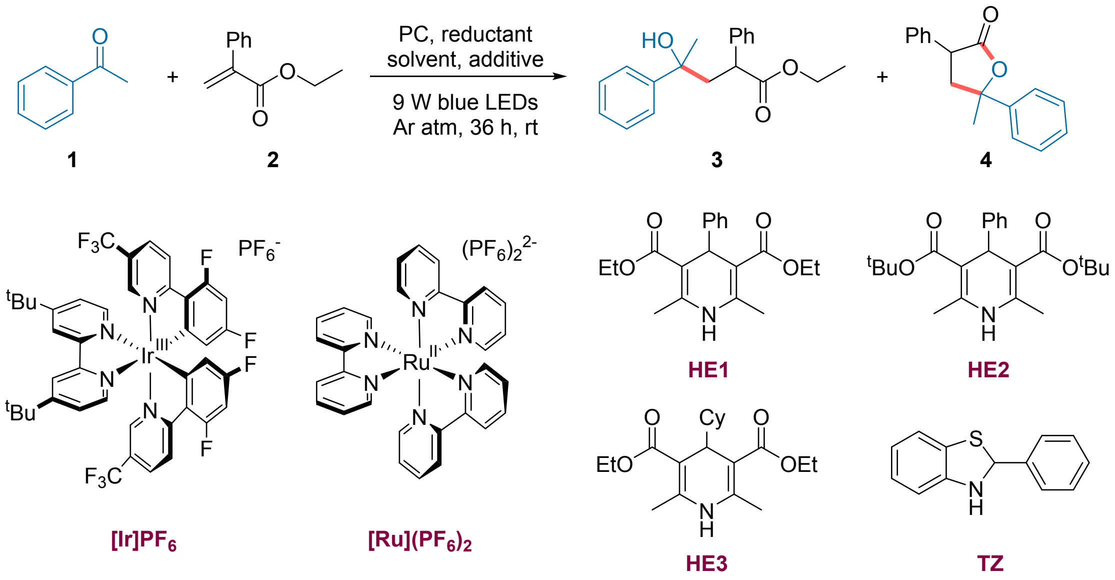
Figure S1. Reaction setup

As depicted in the picture, reactions were carried out in oven-dried schlenk tubes with an argon balloon. The distance between light sources and the reactor is about 5 cm.

3. Optimization studies

Optimization reactions for coupling between ketone and alkene

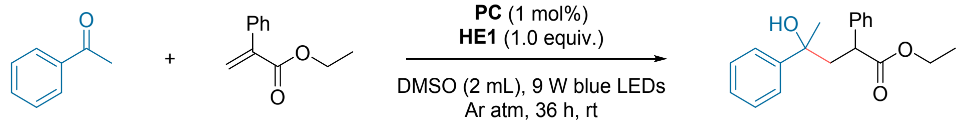
Table S1. Selected Optimization Experiments [a]



entry	PC	solvent	reductant	additive (10 mol%)	yield **3** (%)[b]	yield **4** (%)[b]
1	**[Ir]PF$_6$**	DMSO	**HE1**	-	42	trace
2	**[Ru](PF$_6$)$_2$**	DMSO	**HE1**	-	NR[c]	-
3	4CzIPN	DMSO	**HE1**	-	32	trace
4	Eosin Y	DMSO	**HE1**	-	NR	-
5	**[Ir]PF$_6$**	CH_2Cl_2	**HE1**	-	28	-
6	**[Ir]PF$_6$**	DMF	**HE1**	-	32	-
7	**[Ir]PF$_6$**	CH_3CN	**HE1**	-	trace	-
8	**[Ir]PF$_6$**	DMSO	**HE1**	$B(C_6F_5)_3$	67	trace
9	**[Ir]PF$_6$**	DMSO	**HE2**	$B(C_6F_5)_3$	43	trace
10	**[Ir]PF$_6$**	DMSO	**HE3**	$B(C_6F_5)_3$	41	trace
11	**[Ir]PF$_6$**	DMSO	**TZ**	$B(C_6F_5)_3$	61	trace
12 [d]	**[Ir]PF$_6$**	DMSO	**HE1**	$B(C_6F_5)_3$	95	trace
13 [e]	**[Ir]PF$_6$**	DMSO	**HE1**	$B(C_6F_5)_3$	trace	97

[a] Unless otherwise noted, reaction conditions: a mixture of **1** (0.25 mmol), **2** (0.50 mmol), **HE** (1.0 equiv.), **PC** (1 mol%) and additive (if any) in DMSO (2 mL) was irradiated with 9 W blue LEDs under argon atmosphere at room temperature for 36 hours. [b] Isolated yield. [c] No reaction. [d] 2.0 equiv. of **HE1**. [e] After full consumption of initial reactants, pTSA was added and stirred for 24 hours without light irradiation, **HE1** (2.0 equiv.).

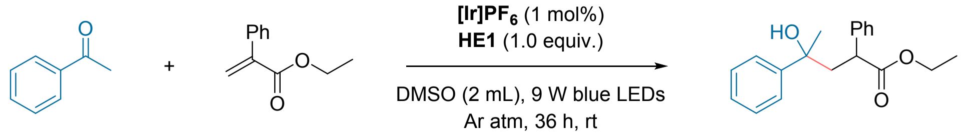
Table S2. Photocatalyst screening



1 (0.25 mmol, 1.0 eq.) **2** (0.50 mmol, 2.0 eq.) **3**

entry	PC	isolated yield of **3** (%)
1	**[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ ([Ir]PF$_6$)**	**42**
2	[Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$	32
3	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	trace
4	*fac*-Ir(ppy)$_3$	trace
5	4CzIPN	32
6	Ru[(bpy)$_3$](PF$_6$)$_2$ (**[Ru](PF$_6$)$_2$**)	NR
7	Eosin Y	NR

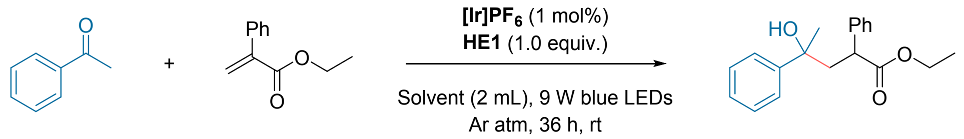
Table S3. Effect of substrate molar ratio on the reaction



1 (X mmol) **2** (Y mmol) **3**

entry	X (mmol)	Y (mmol)	isolated yield of **3** (%)
1	0.75	0.25	43
2	**0.25**	**0.50**	**42**
3	0.50	0.25	41
4	0.25	0.25	37

Table S4. Solvent screening

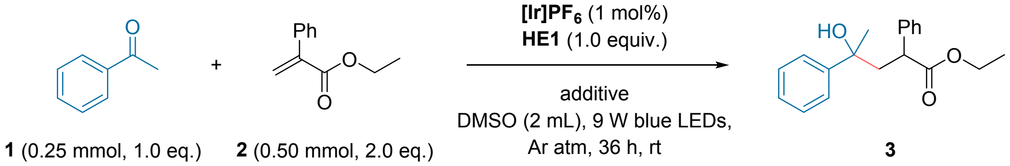


1 (0.25 mmol, 1.0 eq.) **2** (0.50 mmol, 2.0 eq.) **3**

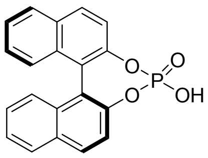
entry	solvent	isolated yield of **3** (%)
1	**DMSO**	**42**
2	DMF	32
3	CH$_2$Cl$_2$	28
4	1,4-dioxane	trace

5	CH_3CN	trace
6	MeOH/DMSO (3:2)	27

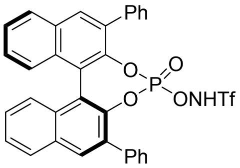
Table S5. Additive screening



entry	additive	equiv.	isolated yield of **3** (%)
1	^{i}Pr$_2$NEt	2	trace
2	Sc(OTf)$_3$	0.2	45
3	In(OTf)$_3$	0.2	34
4	La(OTf)$_3$ + bpy	0.2 + 0.4	22
5	$BF_3 \cdot Et_2O$ (48%)	0.2	62
6	$BF_3 \cdot Et_2O$ (48%)	0.5	60
7	$BF_3 \cdot Et_2O$ (48%)	1.0	46
8	$B(C_6F_5)_3$	0.05	51
9	**$B(C_6F_5)_3$**	**0.1**	**67**
10	$B(C_6F_5)_3$	0.2	64
11	$B(C_6F_5)_3$	0.5	58
12	L-proline	0.2	33
13	**phosphoric acid Ⅰ**	0.2	57
14	(PhO)$_2$POH	0.2	52
15	**phosphoric acid Ⅱ**	0.1	46
16	**phosphoric acid Ⅰ**	1.0	26
17	*p*TSA·H$_2$O	0.2	23

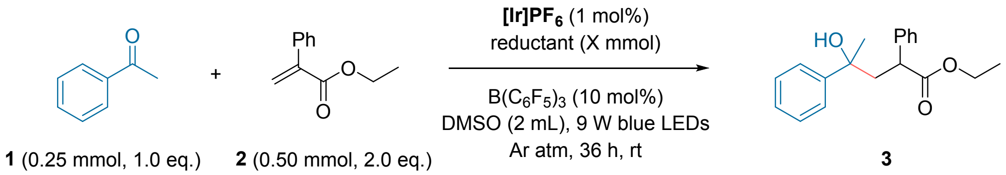


phosphoric acid I



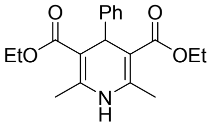
phosphoric acid II

Table S6. Reductant screening

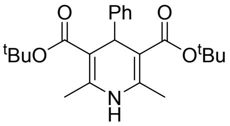


entry	reductant	X (mmol)	isolated yield of **3** (%)
1	**HE1**	**0.50**	**95**
2	**HE1**	0.375	88
3	**HE1**	0.25	67
4	**TZ**	0.25	61

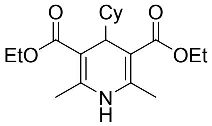
5	**HE2**	0.25	43
6	**HE3**	0.25	41



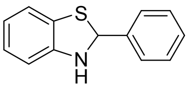
HE1



HE2

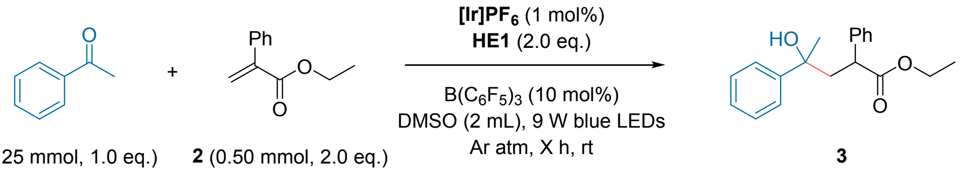


HE3



TZ

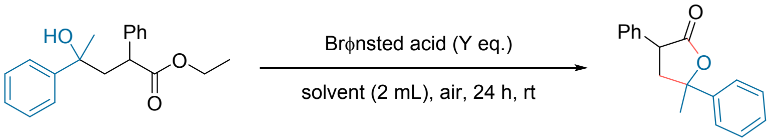
Table S7. Time course of the reaction



1 (0.25 mmol, 1.0 eq.) **2** (0.50 mmol, 2.0 eq.) **3**

entry	time (h)	isolated yield of **3** (%)
1	16	85
2	24	89
3	**36**	**92**

Table S8. Reaction conditions for acid catalyzed intramolecular transesterification

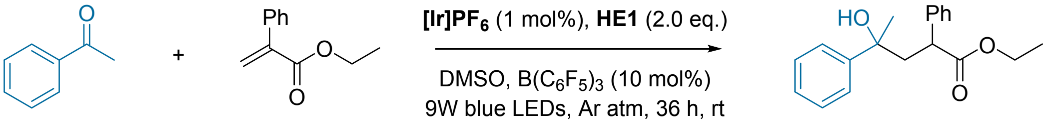


3 (X mmol, 1.0 eq.) **4**

entry	acid	X (mmol)	Y (eq.)	solvent	time (h)	isolated yield of **4** (%)
1	*p*TSA	0.20	2.0	CH_2Cl_2	10	97
2	CF_3COOH	0.20	2.0	CH_2Cl_2	10	75
3	*p*TSA	0.25	0.1	DMSO	24	79
4	*p*TSA	0.25	0.5	DMSO	24	95
5	***p*TSA**	**0.25**	**1.0**	**DMSO**	**24**	**97**
6	*p*TSA	0.25	2.0	DMSO	12	98

It should be noted that after reacting for 10 hours in CH_2Cl_2 with CF_3COOH, the initial reactant **3** was completely consumed, which afforded product **4** in 75% yield with some complex by-products.

Table S9. Control experiments



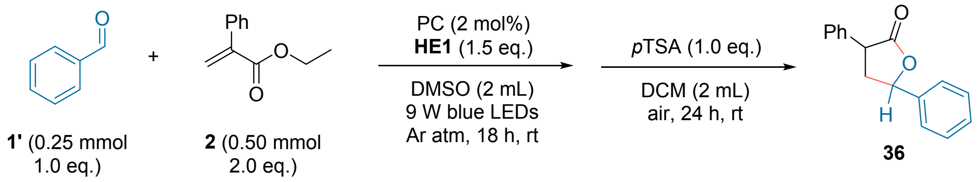
1 (0.25 mmol, 1.0 eq.) **2** (0.50 mmol, 2.0 eq.) **3**

entry	deviations	**3** (%)

1	no light	NR
2	air atm	NR
3	no PC	NR
4	no reductant	NR

Optimization of coupling reaction between aldehyde and alkene

Table S10. Photocatalyst screening



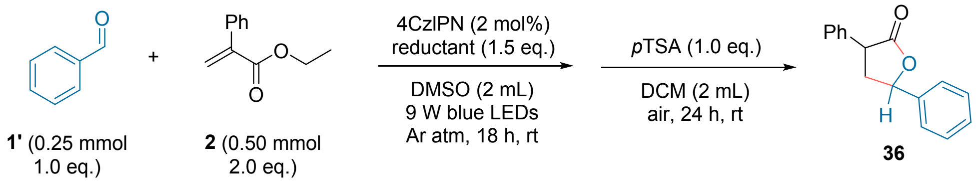
entry	PC	isolated yield of **36** (%)
1	**4CzIPN**	**97**
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**[Ir]PF$_6$**)	59
3	Eosin Y	NR

$E_{1/2}$ (4CzIPN/4CzIPN$^{\cdot -}$) = - 1.21 V vs SCE in MeCN
$E_{1/2}$ = - 1.93 V vs SCE in MeCN for benzaldehyde

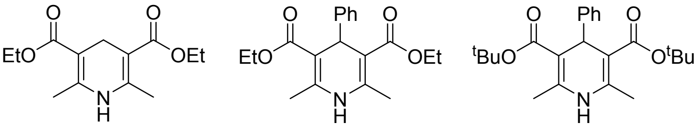
$E_{1/2}$ (Ir^{III}/Ir^{II}) = - 1.37 V vs SCE in MeCN
$E_{1/2}$ = - 2.11 V vs SCE in MeCN for acetophenone

From the standard electrode potentials listed above, we can conclude that aromatic ketones are harder to be reduced, so the usage of **[Ir]PF$_6$** with a stronger reducing ability seems to be essential in terms of aromatic ketones. In other words, 4CzIPN is an adequate photoredox catalyst for aldehyde substrates. Additionally, now that we have got a satisfactory yield of **36**, there is no need to add the Lewis acid catalyst any more.

Table S11. Reductant screening



entry	reductant	isolated yield of **36** (%)
1	**HE**	89
2	**HE1**	**97**
3	**HE2**	98

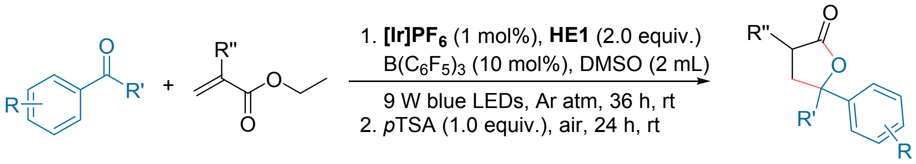


HE **HE1** **HE2**

HE1 was finally chosen to be the optimal reductant instead of **HE2**, partly because of the cheaper price of the starting materials and higher synthetic efficiency.

4. General procedures

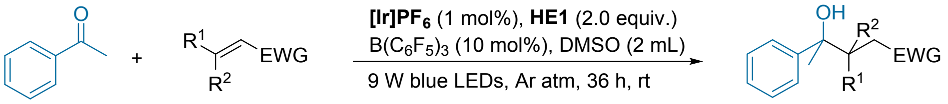
General procedure A: addition of ketones to α,β-unsaturated esters (synthesis of products 4 - 38 in Scheme 2)



A 10 mL two-necked schlenk tube containing a stirring bar was charged with ketone (0.25 mmol), if soild, $B(C_6F_5)_3$ (10 mol%), Hantzsch ester (0.50 mmol) and $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (1 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. Then, liquid α,β-unsaturated ester (0.50 mmol) and dry DMSO (2 mL) were added via syringe. The resulting mixture was stirred under irradiation of 9 W blue LEDs for 36 hours. *p*-Toluenesulfonic acid (0.25 mmol) was added to the reaction mixture, the resulting mixture was stirred for 24 hours under air atmosphere without light irradiation. Distilled water (30 mL) was added, the mixture was extracted 3 times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Products were purified via silica gel chromatography with ethyl acetate, petroleum ether and dichloromethane as eluents.

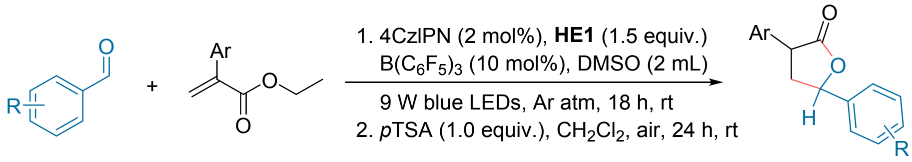
Note： For products **29**, **30** and **38**, the acid catalyzed transesterification was carried out in CH_2Cl_2 instead of DMSO, as described below: After the reactants were stirred under irradiation of 9 W blue LEDs for 36 hours, distilled water (30 mL) was added into the reaction mixture, which was then extracted 3 times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. CH_2Cl_2 (2 mL) and *p*-toluenesulfonic acid (0.25 mmol) were added in this concentrated mixture which was further stirred for 24 h. The reaction mixture was concentrated in vacuo, and products were purified via silica gel chromatography with ethyl acetate, petroleum ether and dichloromethane as eluents.

General procedure B：addition of ketones to other electron-deficient alkenes (synthesis of products 39 - 42 in Scheme 2)



A 10 mL two-necked schlenk tube containing a stirring bar was charged with ketone (0.25 mmol), if soild, $B(C_6F_5)_3$ (10 mol%), Hantzsch ester (0.50 mmol) and $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (1 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. Then, liquid alkene (0.50 mmol) and dry DMSO (2 mL) were added via syringe. The resulting mixture was stirred under irradiation of 9 W blue LEDs for 36 hours. Distilled water (30 mL) was added, the mixture was extracted 3 times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Products were purified via silica gel chromatography with ethyl acetate, petroleum ether and dichloromethane as eluents.

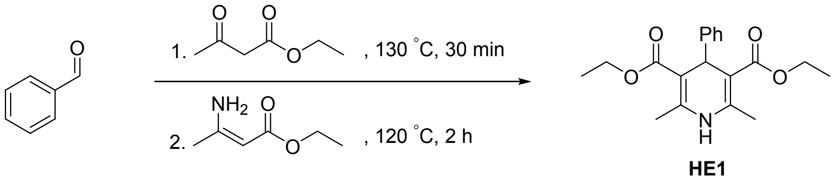
General procedure C: addition of aldehydes to α,β-unsaturated esters (synthesis of products 43 - 48 in Scheme 3)



A 10 mL two-necked schlenk tube containing a stirring bar was charged with aldehyde (0.25 mmol), if soild, Hantzsch ester (0.375 mmol) and 4CzIPN (2 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. Then, liquid α,β-unsaturated ester (0.50 mmol) and dry DMSO (2 mL) were added via syringe. The resulting mixture was stirred under irradiation of 9 W blue LEDs for 18 hours. Distilled water (30 mL) was added to the reaction mixture, which was then extracted 3 times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Dichloromethane (2 mL) and *p*-toluenesulfonic acid (0.25 mmol) were added to this concentrated mixture which was further stirred for 24 h, the reaction mixture was concentrated in vacuo, and products were purified via silica gel chromatography with ethyl acetate, petroleum ether and dichloromethane as eluents.

5. Starting materials

Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (HE1) [1]



HE1

Ethyl acetoacetate (5 mL, 1.0 equiv.) and the benzaldehyde (5 mL, 1.0 equiv.) were added to a 50 mL round bottom flask equipped with a magnetic stirrer. The mixture was heated to 130 °C and kept under stirring for 30 minutes. The solution was then cooled to about 80 °C. Ethyl 3-aminocrotonate (4.9 g, 1.0 equiv.) was slowly added, and the mixture was heated at 120 °C for 3 hours. After that time, the reaction mixture was cooled to ambient temperature and the crude product (orange solid) was filtered off. The crude product was purified by recrystallization from petroleum ether/ethyl acetate, the anticipated product was obtained as a white to palegreen crystalline solid.

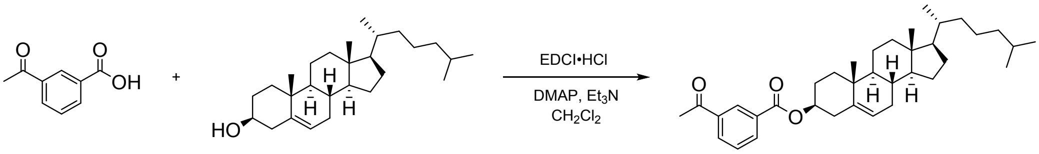
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.30 – 7.25 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.15 – 7.09 (m, 1H), 5.94 (s, 1H), 4.99 (s, 1H), 4.13 – 4.04 (m, 4H), 2.30 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 167.73, 167.71, 147.8, 144.01, 143.99, 128.0, 127.8, 126.1, 104.1, 59.7, 39.7, 19.4, 14.2.

2-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 3-acetylbenzoate (a) [2]

N-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (1.20 equiv) was added to a suspension of 3-acetylbenzoic acid (0.5 g, 1.00 equiv), 2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethan-1-ol (1.00 equiv), 4-dimethylaminopyridine (0.30 equiv.) and triethylamine (1.00 equiv.) in CH$_2$Cl$_2$ (10 mL), and the reaction mixture was stirred at 25 °C for 12 hours. The reaction mixture was then concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with petroleum ether and EtOAc, to afford the title compound as a brown clear liquid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.58 (s, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 5.38 (s, 1H), 4.42 – 4.33 (m, 2H), 2.64 (s, 3H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.41 – 2.38 (m, 1H), 2.25 (q, *J* = 17.6 Hz, 2H), 2.16 – 2.08 (m, 2H), 1.28 (s, 3H), 1.18 (d, *J* = 8.6 Hz, 1H), 0.85 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 197.0, 165.6, 144.1, 137.3, 133.8, 132.1, 131.0, 129.5, 128.8, 119.0, 63.6, 45.8, 40.7, 38.0, 36.0, 31.7, 31.4, 26.6, 26.2, 21.1.

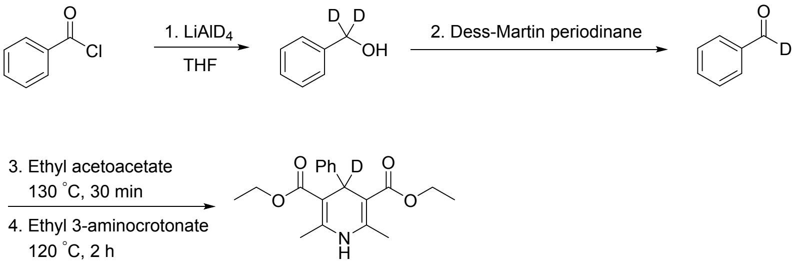
(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 3-acetylbenzoate (b) [2]



N-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (1.20 equiv) was added to a suspension of 3-acetylbenzoic acid (0.5 g, 1.00 equiv), (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (1.00 equiv), 4-dimethylaminopyridine (0.30 equiv.) and triethylamine (1.00 equiv.) in CH$_2$Cl$_2$ (10 mL), and the reaction mixture was stirred at 25 °C for 12 hours. The reaction mixture was then concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with petroleum ether and EtOAc, to afford the title compound as a white solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.58 (s, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 5.43 (s, 1H), 4.92 – 4.87 (m, 1H), 2.65 (s, 3H), 2.52 – 2.45 (m, 2H), 2.05 – 1.91 (m, 4H), 1.87 – 1.73 (m, 2H), 1.62 – 1.12 (m, 16H), 1.08 (s, 3H), 1.04 – 0.97 (m, 4H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.87 (s, 3H), 0.87 (s, 3H), 0.69 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 197.2, 165.1, 139.5, 137.3, 133.9, 132.1, 131.5, 129.4, 128.7, 122.9, 75.2, 56.7, 56.2, 50.1, 42.4, 39.8, 39.5, 38.2, 37.1, 36.7, 36.2, 35.0, 32.0, 31.9, 28.2, 28.0, 27.9, 26.7, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9.

Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate-4-d (HE4) [3]



1. To a stirring suspension of lithium aluminum deuteride (0.5 g, 13 mmol) in dry THF (15 mL), a THF solution (20 mL) of benzoyl chloride (3 g, 21 mmol) was added at 0 °C under argon atmosphere. When addition was completed, the solution was refluxed for 2 hours and then was re-cooled to 0 °C. The mixture was carefully quenched by water, and the resulting mixture was acidified with 1 M aqueous HCl, and then extracted with Et$_2$O (3 × 20 mL). The combined organic fraction was washed with 10% aqueous Na$_2$CO$_3$ and saturated brine, dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated to give a paleyellow oil as the alcohol product. This compound was directly used for the next step without further purification.

2. To a solution of alcohol compound (1.0 equiv.) in DMSO was added Dess-Martin periodinane (1.2 equiv.). The reaction mixture was stirred at room temperature for 4 hours and a solution of NaHCO$_3$ added to quench the reaction. The two phases were separated and the aqueous phase was washed 3 times with CH$_2$Cl$_2$ (20 mL). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the deuterated benzaldehyde as colourless oil.

3. Ethyl acetoacetate (1.0 equiv.) and the deuterated benzaldehyde (1.0 equiv.) were added to a 50 mL round bottom flask equipped with a magnetic stirrer. The mixture was heated to 130 °C and kept under stirring for 30 minutes. The solution was then cooled to about 80 °C.

4. Ethyl 3-aminocrotonate (1.0 equiv.) was slowly added, and then the mixture was heated at 120 °C for 30 minutes. After that time, the reaction mixture was cooled to ambient temperature and the crude product (orange solid) was filtered. The crude product was purified by recrystallization from petroleum ether/ethyl acetate, the desired product was attained as colourless to white crystals.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.30 – 7.25 (m, 2H), 7.20 (t, J = 7.7 Hz, 2H), 7.15 – 7.08 (m, 1H), 5.91 (s, 1H), 4.13 – 4.04 (m, 4H), 2.31 (s, 6H), 1.22 (t, J = 7.1 Hz, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 167.7, 147.8, 144.0, 128.0, 127.8, 126.1, 104.0, 59.7, 19.5, 14.3.

6. Mechanistic Studies

6.1 Stern-Volmer luminescence quenching experiments

The measurements were performed using a 0.1 mM solution of [Ir(dF(CF$_3$)ppy)$_2$dtbbpy]PF$_6$ in degassed DMSO with varying concentration of a quencher. The samples were excited at 316 nm and emission intensity was recorded at 484 nm.

The quenching of the excited state Ir(III)* by the acetophenone **1**, ethyl 2-phenylacrylate **2**, Hantzsch ester **HE1** and Lewis acid B(C$_6$F$_5$)$_3$ was carried out in DMSO separately (**Figures S1-S8**). The results revealed that **HE1** could significantly quench Ir(III)*, and the other components did not display obvious quenching ability to Ir(III)*.

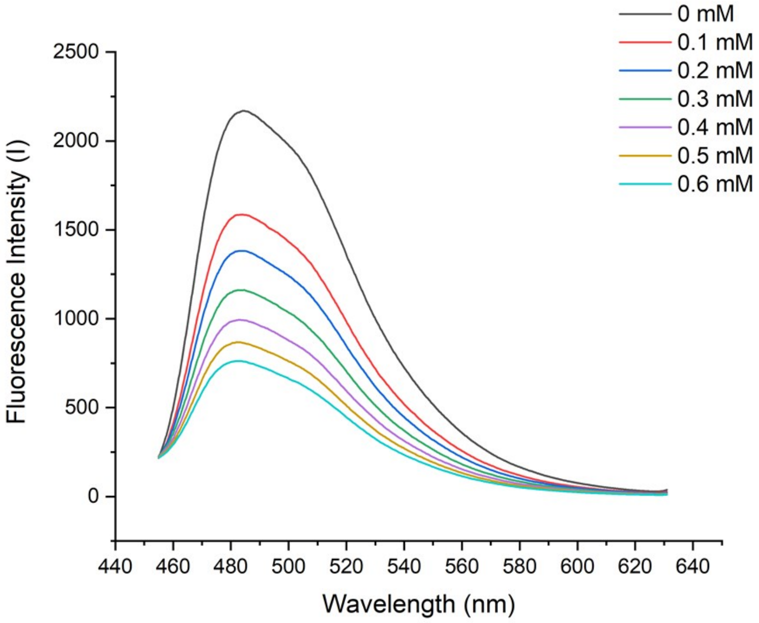


Figure S2. Emission quenching experiments of Ir(III)* with **HE1** in DMSO (Curve graph).

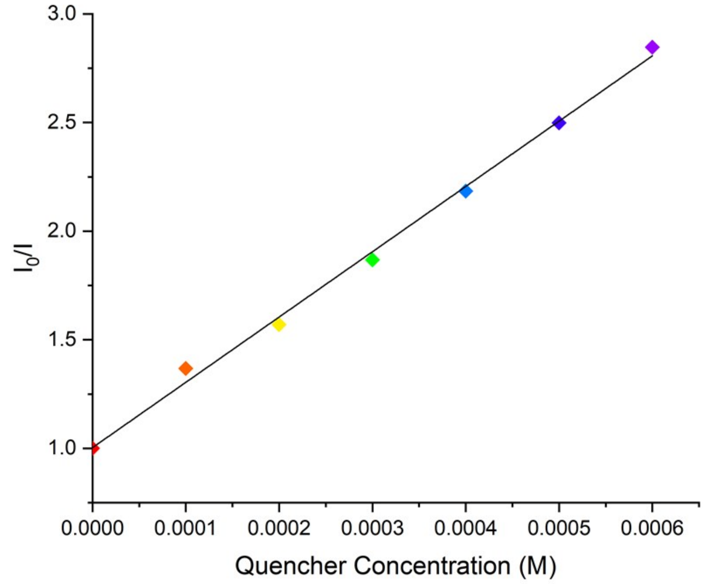


Figure S3. Emission quenching experiments of Ir(III)* with **HE1** in DMSO (Scatter diagram).

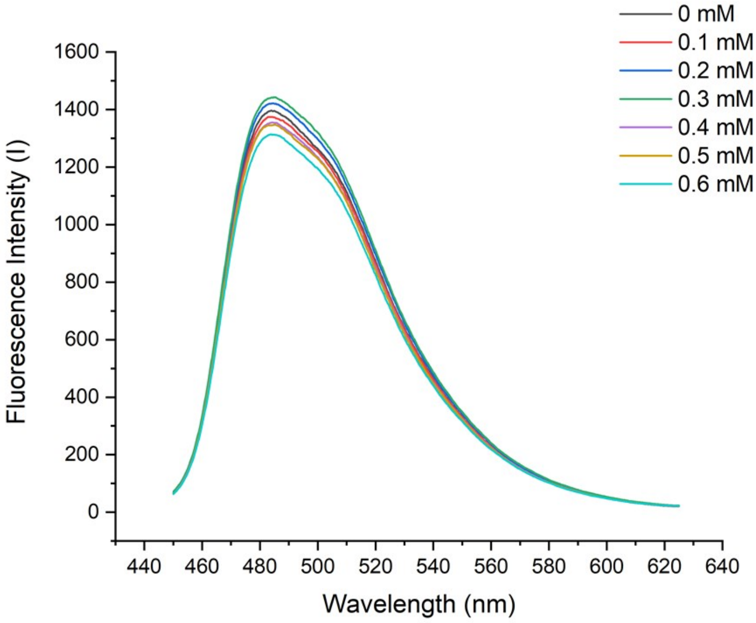
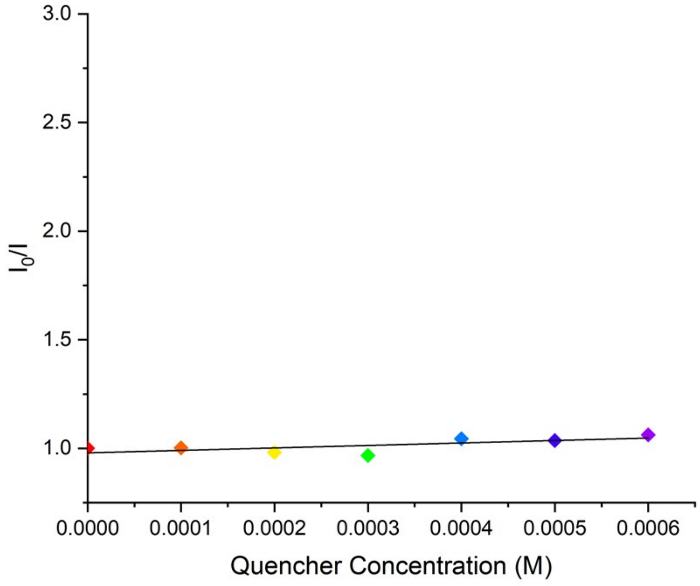


Figure S4. Emission quenching experiments of Ir(III)* with acetophenone **1** in DMSO (Curve graph).



(No obvious luminescence quenching)

Figure S5. Emission quenching experiments of Ir(III)* with acetophenone **1** in DMSO (Scatter diagram).

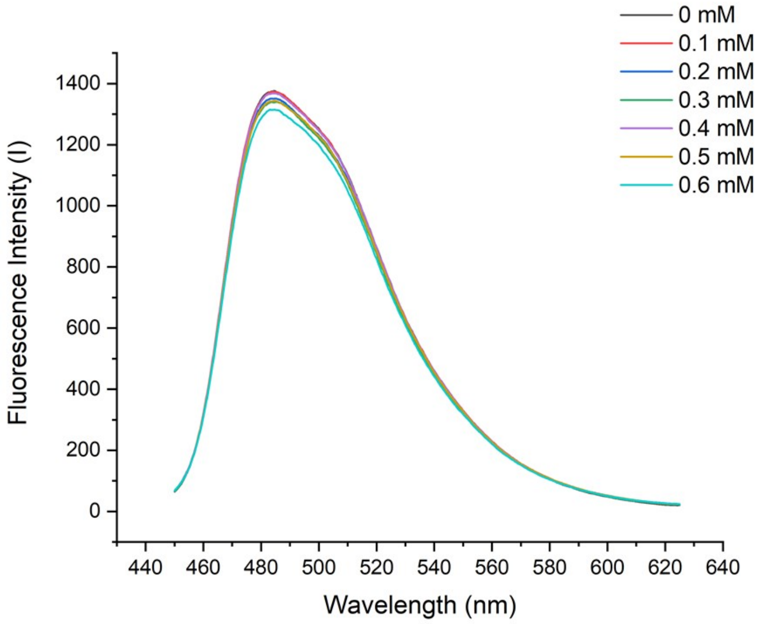
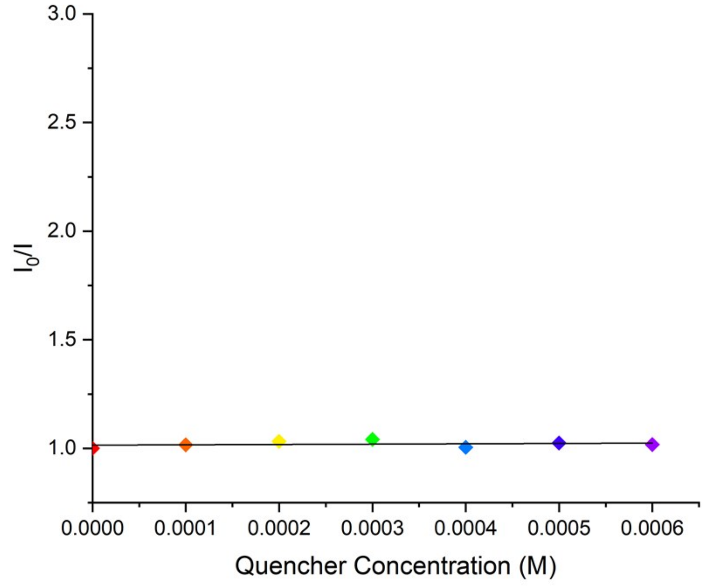


Figure S6. Emission quenching experiments of Ir(III)* with ethyl 2-phenylacrylate **2** in DMSO (Curve graph).



(No obvious luminescence quenching)

Figure S7. Emission quenching experiments of Ir(III)* with ethyl 2-phenylacrylate **2** in DMSO (Scatter diagram).

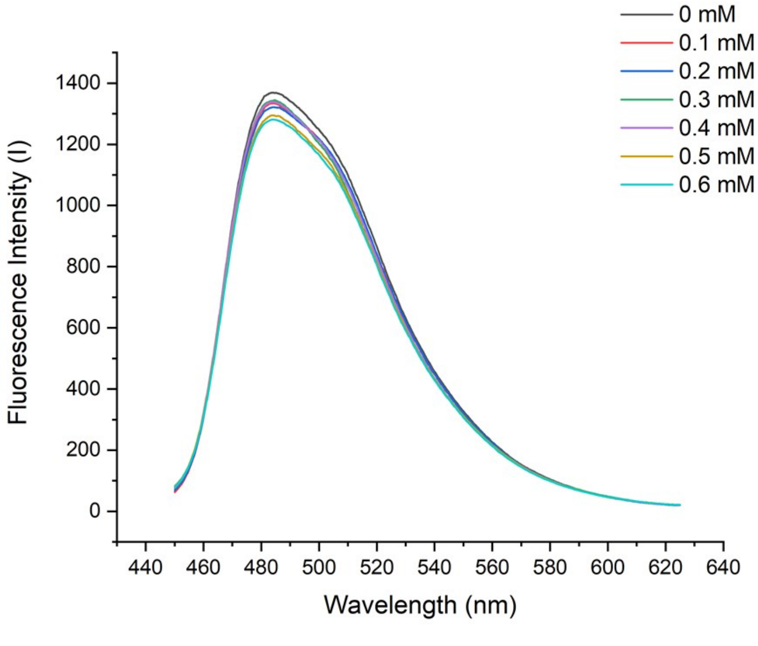
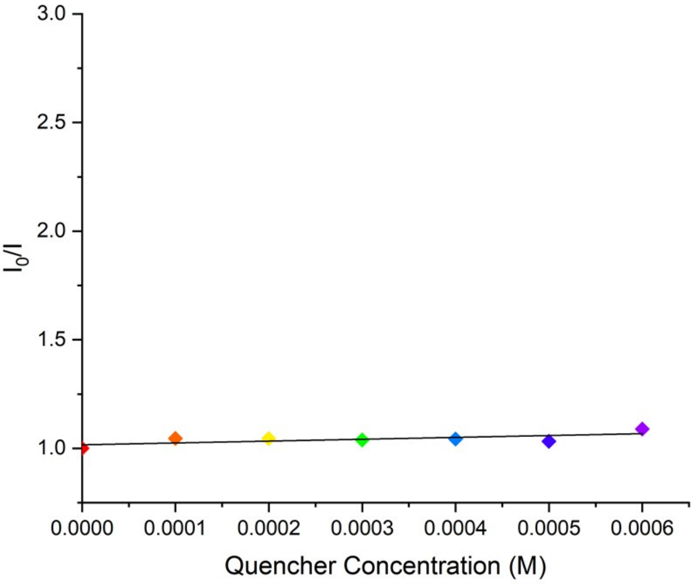


Figure S8. Emission quenching experiments of Ir(III)* with $B(C_6F_5)_3$ in DMSO (Curve graph).



(No obvious luminescence quenching)

Figure S9. Emission quenching experiments of Ir(III)* with $B(C_6F_5)_3$ in DMSO (Scatter diagram).

6.2 Cyclic voltammetry measurement

The cyclic voltammetry experiments were performed, and the oxidation potentials of **HE1** was determined as: **HE1** (E_{ox} = +0.85 V vs SCE in MeCN) (**Figure S9**). The data indicated that **HE1** can be oxidized by the excited Ir(III)* ($E_{1/2}^{*III/II}$ = +1.21 V vs SCE in MeCN). The electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Cyclic voltammetry was performed in a three-electrode cell (volume 10 mL; acetonitrile as solvent, $^{n}Bu_4N^+ClO_4^-$ 0.05 M as the supporting electrolyte, **HE1** (2 mM) as the tested compound) with glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (3 M KCl) as the reference electrode. The scan speed was 100 mV·s^{-1}. The potential ranges investigated for oxidations were 0 to +1.5 V vs Ag/AgCl (3 M KCl) for **HE1** and blank. As shown below, E_{ox} of **HE1** was determined to be 0.90 V vs Ag/AgCl (3 M KCl), which suggest that single electron oxidation of **HE1** by the excited Ir(III)* is feasible. (Referenced to SCE by subtracting 0.047 V from the relative value.)

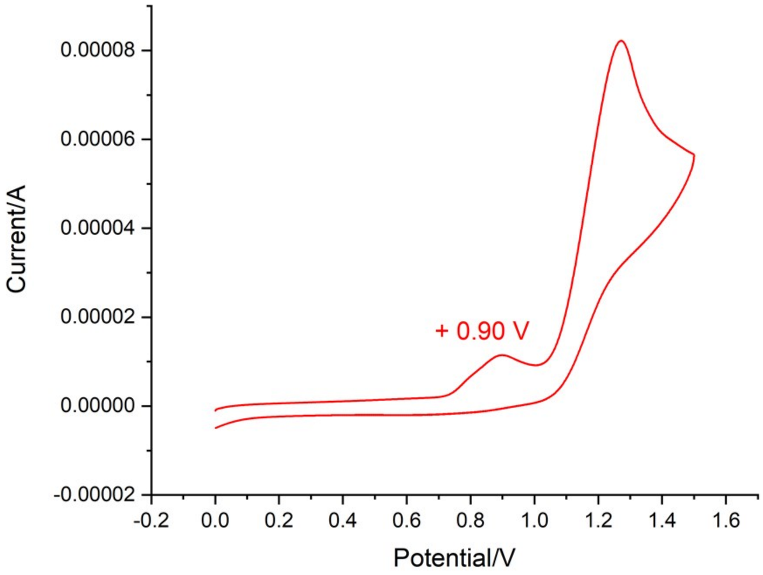


Figure S10. Cyclic voltammetry (CV) of **HE1** in MeCN.

6.3 UV-vis absorption spectroscopy

UV-vis absorption spectroscopy was performed using a spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in a 1.5 mL quartz cuvette fitted with a PTFE stopper. Acetophenone, ethyl 2-phenylacrylate, $B(C_6F_5)_3$, and **HE1** were prepared as a 2.5 mM, 2.5 mM, 3.5 mM, and 0.3 mM solution respectively. $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ was prepared as a 0.05 mM solution in DMSO for measurement.

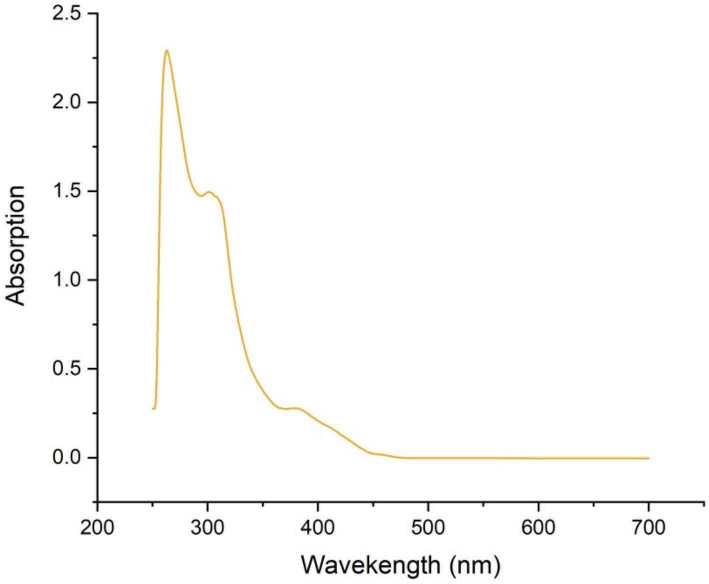


Figure S11. UV-Vis of [Ir(dF(CF$_3$)ppy)$_2$dtbbpy]PF$_6$ in DMSO.

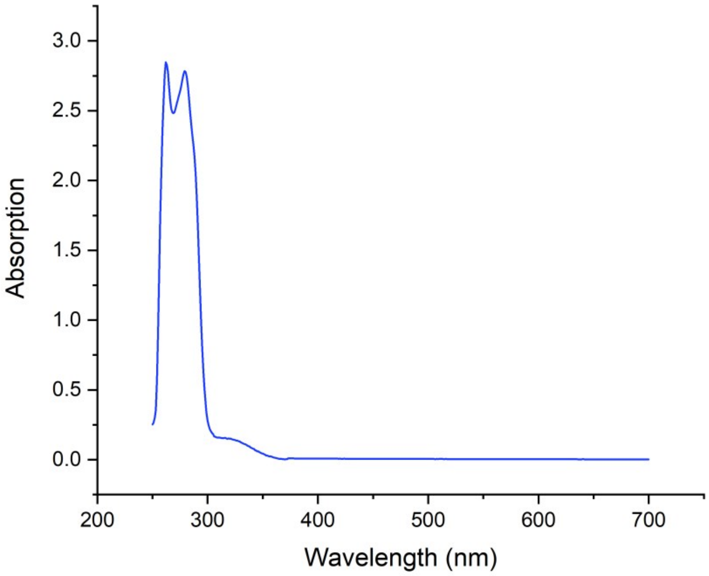


Figure S12. UV-Vis of acetophenone **1** in DMSO.

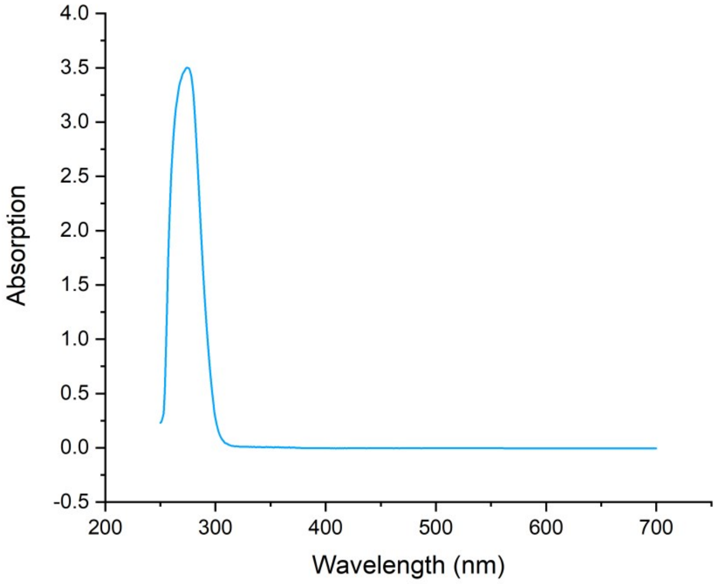


Figure S13. UV-Vis of ethyl 2-phenylacrylate **2** in DMSO.

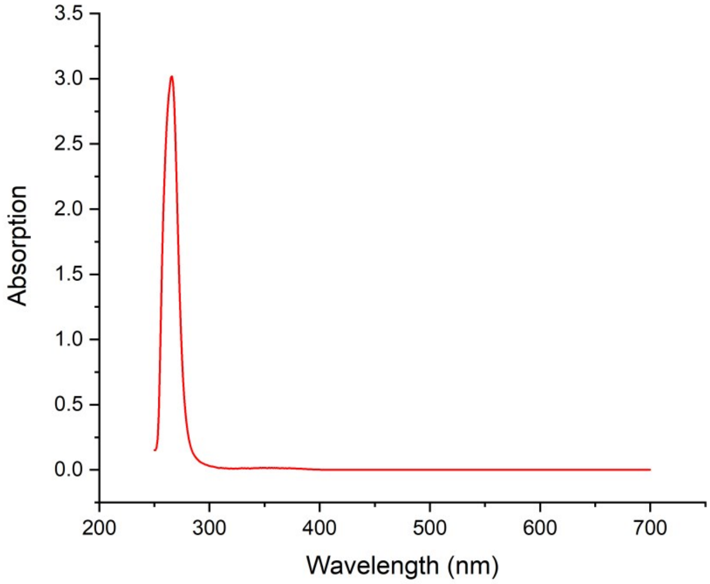


Figure S14. UV-Vis of $B(C_6F_5)_3$ in DMSO.

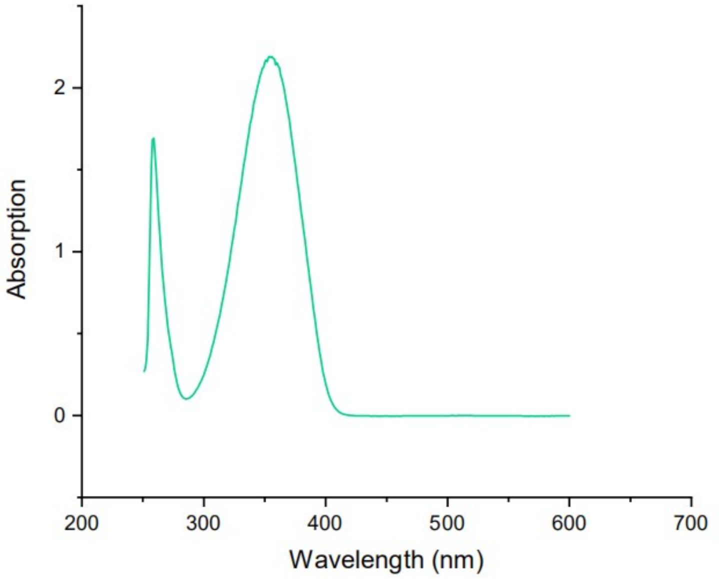


Figure S15. UV-Vis of **HE1** in DMSO.

6.4 Emission spectrum of the LED light

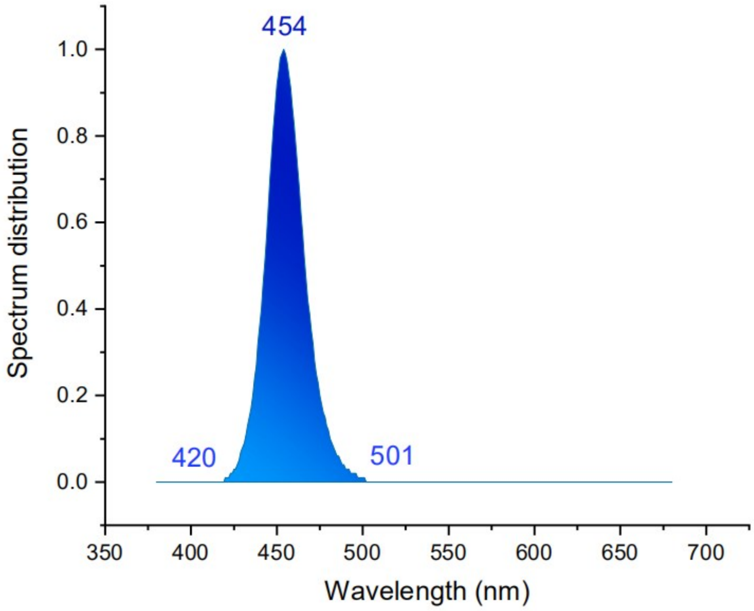
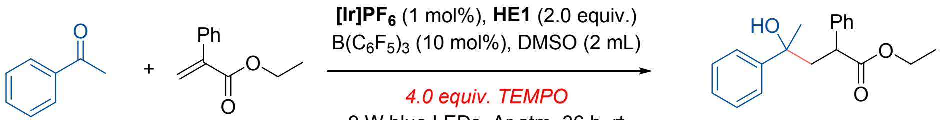


Figure S16. Spectrum distribution of light sources.

Chromaticity Coordinates	x=0.1476 y=0.0323 u=0.1910 v=0.0941		
Temperature	>25000K	Peak Wavelength	454nm
SDCM	0	Main Wavelength	458nm
Color Shift	0.000000 duv	Wavelength Width	0nm
Red Ratio	0	Color Purty	98.00%
Luminous Flux	1.241e3lux	Radiant Flux	2.959e4w/m2
Rendering Flux	Ra=54.0 R1=21.0 R2=57.0 R3=99.0 R4=90.0 R5=3.0 R6=68.0 R7=56.0 R8=41.0 R9=99.0 R10=99.0 R11=99.0 R12=99.0 R13=44.0 R14=36.0		

6.5 Radical trapping experiments

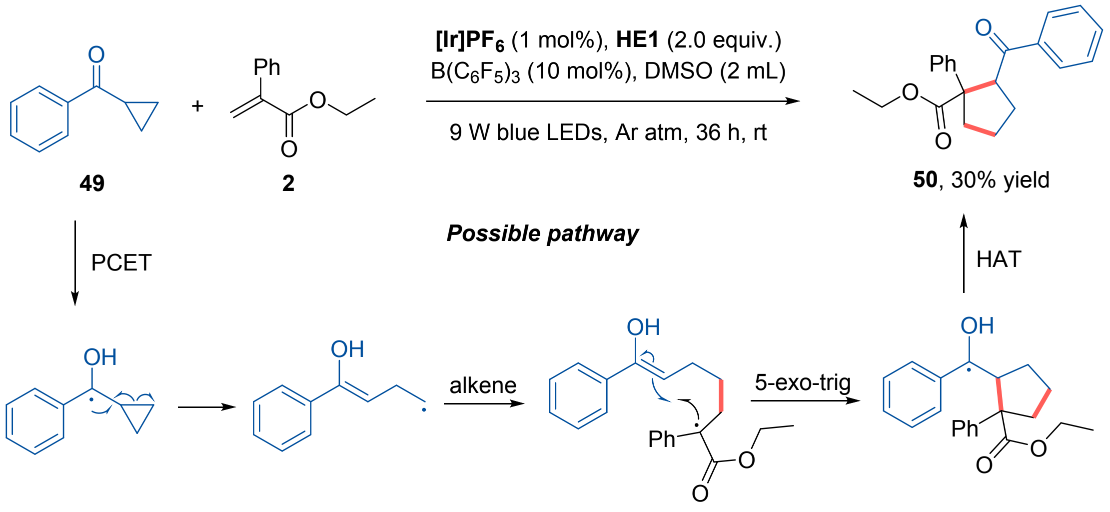
In order to confirm if the reaction undergoes a radical mechanism, common radical scavenger, 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was employed for the radical trapping and inhibition experiment. TEMPO (4.0 equivalents) was added into the reaction system at the beginning of the reaction under the standard conditions. No reaction was detected even after 36 hours when using TEMPO. The experiment suggested that the reaction might go through a radical pathway.



3, 0% yield

6.6 Radical clock study

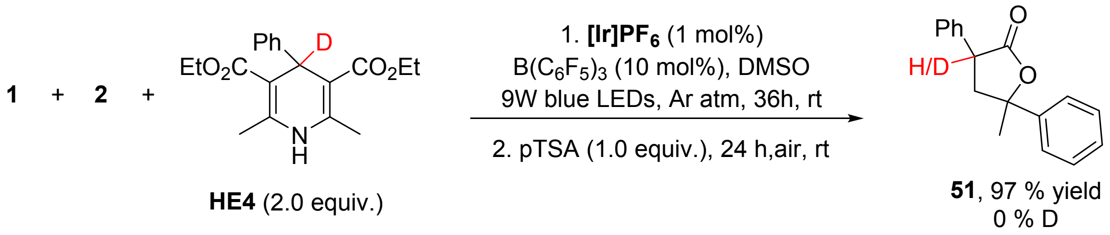
Radical clock reaction was carried out following the general procedure A.



A 10 mL two-necked schlenk tube containing a stirring bar was charged with cyclopropyl(phenyl)methanone (34.5 µL, 0.25 mmol), $B(C_6F_5)_3$ (10 mol%), **HE1** (0.50 mmol) and $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (1 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. Then, ethyl 2-phenylacrylate (89 µL 0.50 mmol) and dry DMSO (2 mL) were added via syringe. The resulting mixture was stirred under irradiation of 9 W blue LEDs for 36 hours. After that time, distilled water (30 mL) was added, the mixture was extracted 3 times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Products were purified via silica gel chromatography with ethyl acetate, petroleum ether and dichloromethane as eluents, product **46** was obtained as a paleyellow liquid (24.0 mg, 30% yield).[4] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.99 (d, J = 7.7 Hz, 2H), 7.56 – 7.52 (m , 3H), 7.48– 7.45 (m, 2H), 7.38 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 4.47 (d, J = 9.3 Hz, 1H), 4.03 – 3.97 (m, 2H), 2.94 – 2.88 (m, 1H), 2.46 – 2.43 (m, 1H), 2.14 – 2.10 (m, 1H), 1.89 – 1.81 (m, 2H), 1.75 – 1.68 (m, 1H), 1.02 (t, J = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 201.8, 174.5, 142.2, 136.7, 132.8, 128.6, 128.6, 128.5, 127.1, 126.2, 61.7, 60.7, 54.2, 34.4, 29.2, 22.4, 13.8. **HRMS (ESI)** calcd. for $C_{21}H_{22}NaO_3$ $[M+Na]^+$: 345.1461, found 345.1461

6.7 Deuterium labeling experiment

The reaction was carried out following the general procedure A.



A 10 mL two-necked schlenk tube containing a stirring bar was charged with acetophenone (29.1 µL, 0.25 mmol), $B(C_6F_5)_3$ (10 mol%), **HE4** (165.1 mg, 0.50 mmol) and $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (1 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. Then, ethyl 2-phenylacrylate (89 µL 0.50 mmol) and dry DMSO (2 mL) were added via syringe. The resulting mixture was stirred under irradiation of 9 W blue LEDs for 36 hours. *p*-Toluenesulfonic acid (0.25 mmol) was added to the reaction mixture, the resulting mixture was stirred for 24 hours under air atmosphere without light irradiation. After that time, distilled water (30 mL) was added, the mixture was extracted 3 times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Products were purified via silica gel chromatography with ethyl acetate, petroleum ether and dichloromethane as eluents, the desired product **51** was afforded as a yellowish oil (62.9 mg, 97% yield).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.44 – 7.36 (m, 4H), 7.34 – 7.30 (m, 3H), 7.27 – 7.21 (m, 3H), 4.13 (dd, J = 11.9, 8.9 Hz, 0.56H), 3.68 (dd, *J* = 12.7, 8.3 Hz, 0.44H), 3.01 (dd, *J* = 12.6, 8.4 Hz, 0.47H), 2.96 (dd, J = 12.8, 9.0 Hz, 0.53H), 2.59 – 2.56 (m, 1H), 1.78 (d, J = 15.1 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.5, 176.1, 145.1, 143.6, 136.6, 136.3, 128.88, 128.86, 128.8, 128.7, 128.18, 128.17, 127.9, 127.73, 127.65, 124.3, 124.0, 84.6, 84.5, 46.7, 46.3, 45.6, 44.8, 30.3, 28.7.

6.8 Effective "BDFE" calculations

The O-H bond of acetophenone ketyl is extremely weak, therefore, formation of these intermediates entails H atom from a similar weak bond. While most of the H atom donors, whose bond strength is generally too large, fall short of this standard. Fortunately, concerted PECT processes bypass the direct HAT from a H atom donor to the acceptor, which largely facilitate these transformations with energetic limitations. According to Knowles's work, a suitable catalyst combination with effective "BDFE" close to/less than 26 kcal/mol (O-H BDFE for acetophenone ketyl) enables efficient ketyl formation. Thus, effective "BDFE" of the reductant/acid pair in our conditions was first calculated:

- *pKa* of **HE1**$^{\cdot+}$ (denoted as HA$^{\cdot+}$)

$$pKa_{HA^{\cdot+}} = pKa_{HA} + \frac{\left[E_{ox}(A^-) - E_{ox}(HA)\right] \times 23.06}{1.37}$$

$$= 19.1 + \frac{(-0.384 - 0.662) \times 23.06}{1.37}$$

$$= 1.5$$

pKa calculation method ref. *Acc. Chem. Res. 1988, 21, 456*

pKa$_{HA}$, *E$_{ox}$(A$^-$)*, *E$_{ox}$(HA)* values ref. *J. Org. Chem. 2000, 65, 3853-3857*

- redox potential of Ir^{II} against Fc$^+$/Fc

$$E_{1/2}^{Ir^{III}/Ir^{II}} = -1.37\ V\ vs.\ SCE$$

referenced to Fc$^+$/Fc by subtracting 0.380 V from the value relative to SCE.

$$E_{1/2}^{Ir^{III}/Ir^{II}} = -1.75\ V\ vs.\ Fc^+/Fc$$

conversion method ref. *Inorganica Chimica Acta 298 (2000) 97–102*

- effective BDFE of Ir^{II}/**HE1**$^{\cdot+}$ pair

$$BDFE = 2.3RT \times pKa_{HA^{\cdot +}} + 23.06 \times E_{1/2}^{Ir^{III}/Ir^{II}} + 54.9$$

$$= 2.3 \times 1.987 \times 10^{-3} \times 298.15 \times 1.5 + 23.06 \times (-1.75) + 54.9$$

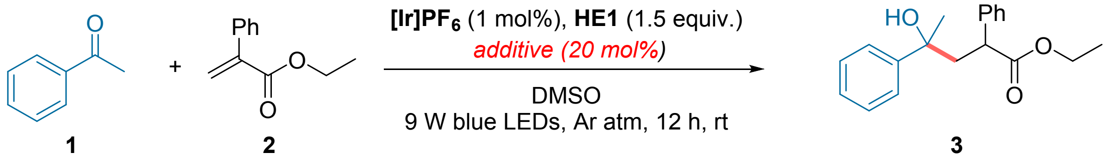
$$= 16.59\ kcal/mol$$

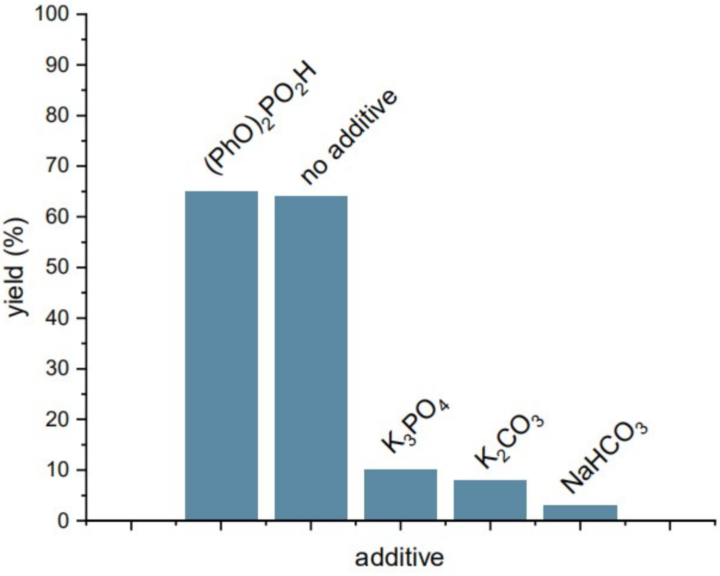
calculation method ref. *Acc. Chem. Res. 2016, 49, 1546-1556*

With effective “BDFE” lower than the 26 kcal/mol threshold, high yields of anticipated products were observed, which indicates the feasibility of a PCET process.

6.9 Acid/base adding experiments

As shown in the graph below, when diphenyl phosphoric acid was added, the reaction efficacy was slightly enhanced, probably because its weak acidity (pKa ~ 13) can hardly promote the reaction any further. On the contrary, the presence of several inorganic bases largely inhibited the reaction, which verified the important role of the Brønsted acidic **HE1**$^{\cdot+}$.





7. Determination of the configurations

7.1 2D ^{1}H-^{13}C HMQC and NOESY spectra

The mixing time for NOESY experiment was adjusted to 500 ms, and the spin-lock for ROESY was adjusted to 400 ms. The 2D ^{1}H-^{13}C HMQC and NOESY spectrum was measured at resonance frequencies of 600 MHz (^{1}H) and 151 MHz (^{13}C). The HMQC step was adjusted for $^{1}J_{H\text{-}C}$ = 145 Hz with a subsequent NOE transfer of 700 ms. The spectrum was recorded in phase-sensitive mode using the echo-antiecho protocol. The relative configuration of product **4** was determined. The relative configuration of other substrates were assigned by analogy.

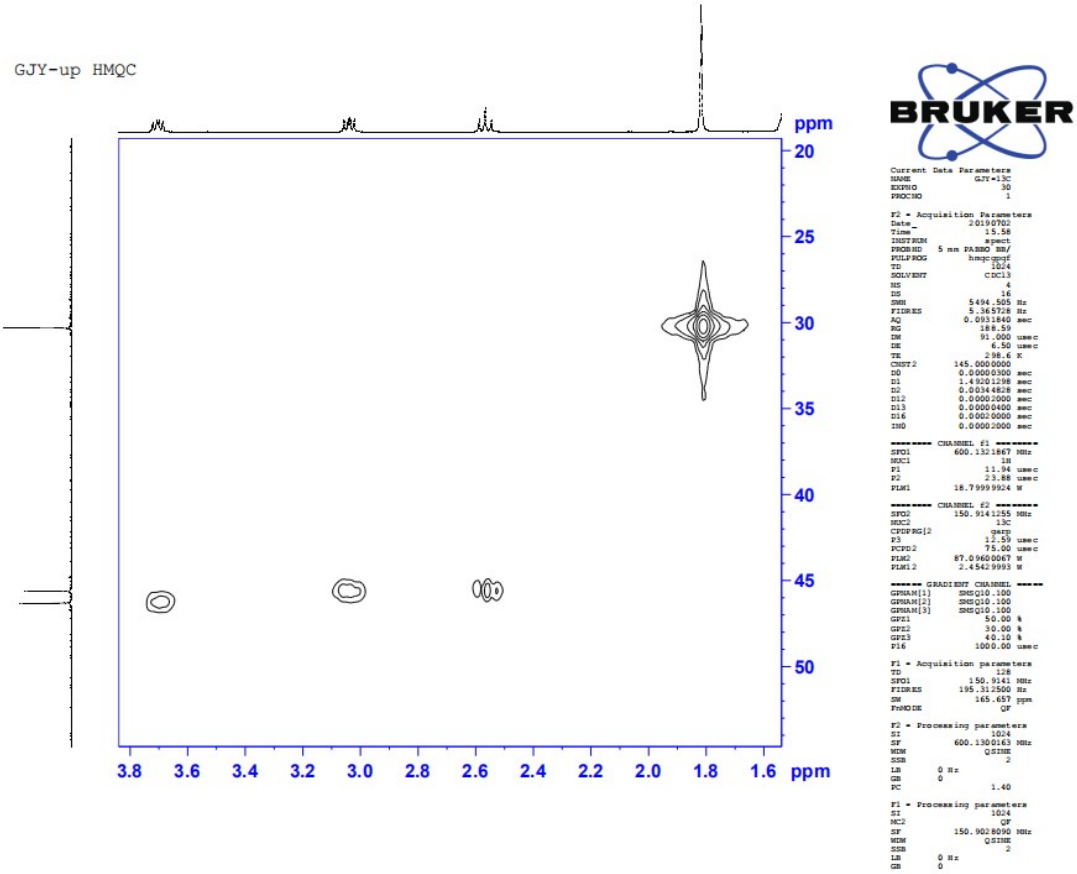


Figure S17. HMQC spectrum of **4** (the *anti*-diastereomer).

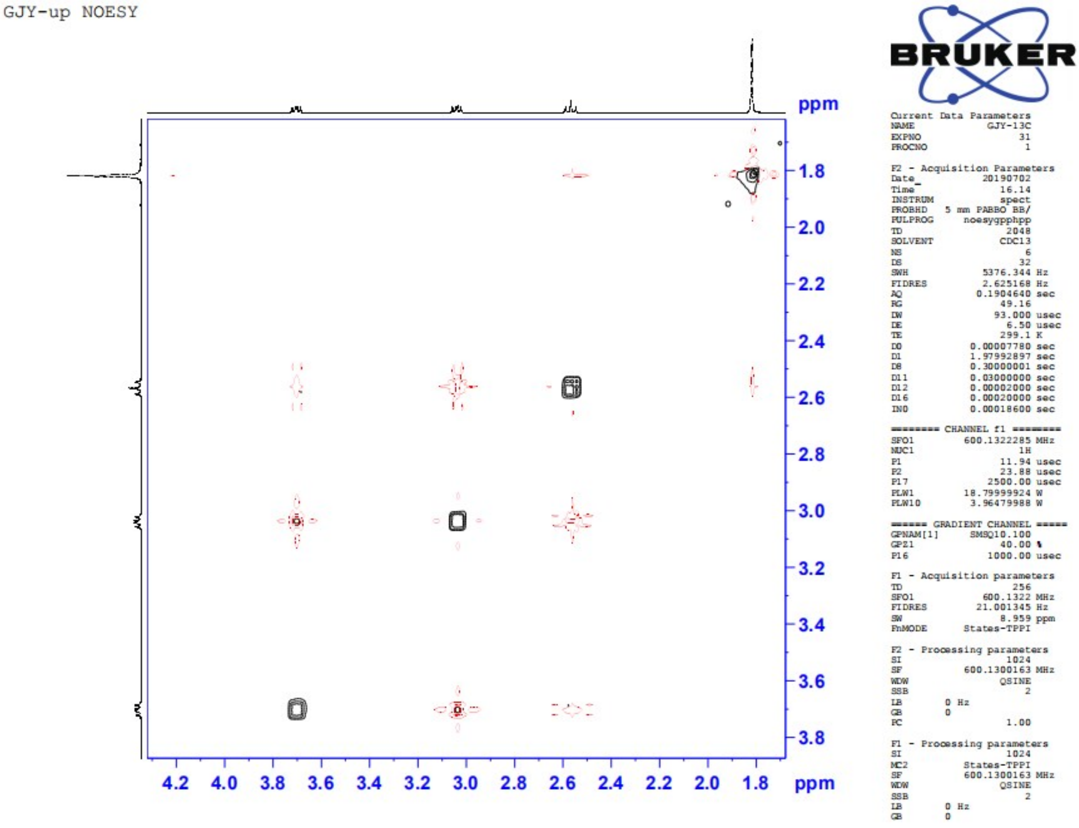


Figure S18. NOESY spectrum of **4** (the *anti*-diastereomer).

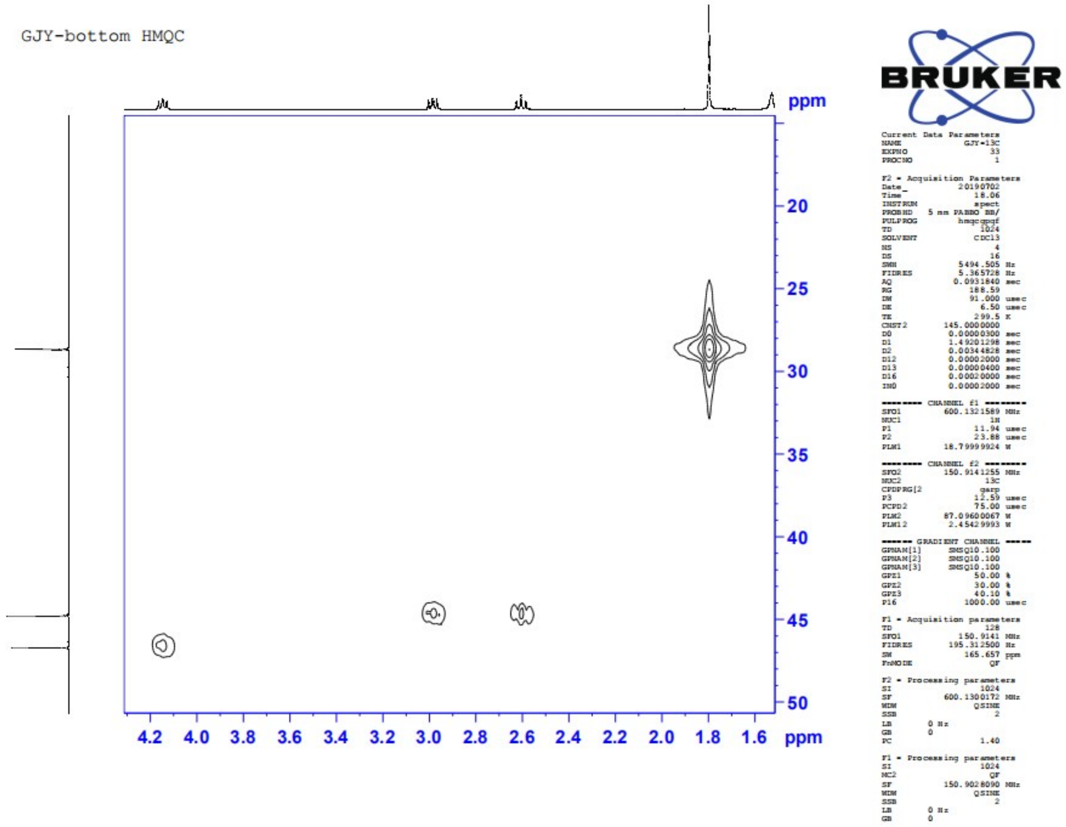
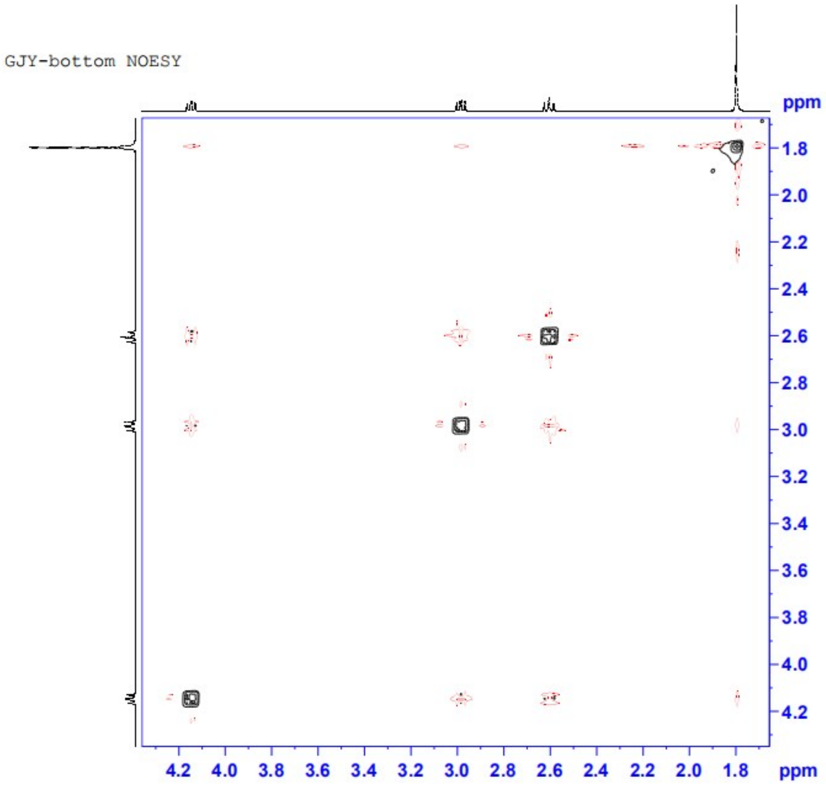


Figure S19. HMQC spectrum of **4** (the *syn*-diastereomer).



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PROCNO                    1

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DS                       32
SWH                5494.505 Hz
FIDRES             1.341432 Hz
AQ                0.3727360 sec
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DE                     6.50 usec
TE                    299.4 K
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D1               1.96805096 sec
D8               0.30000001 sec
D11              0.03000000 sec
D12              0.00002000 sec
D16              0.00020000 sec
IN0              0.00018200 sec

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NUC1                     1H
P1                    11.94 usec
P2                    23.88 usec
P17                 2500.00 usec
PLW1            18.79999924 W
PLW10            3.96479988 W

====== GRADIENT CHANNEL =====
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GPZ1                  40.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
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FIDRES            21.462912 Hz
SW                    9.155 ppm
FnMODE          States-TPPI

F2 - Processing parameters
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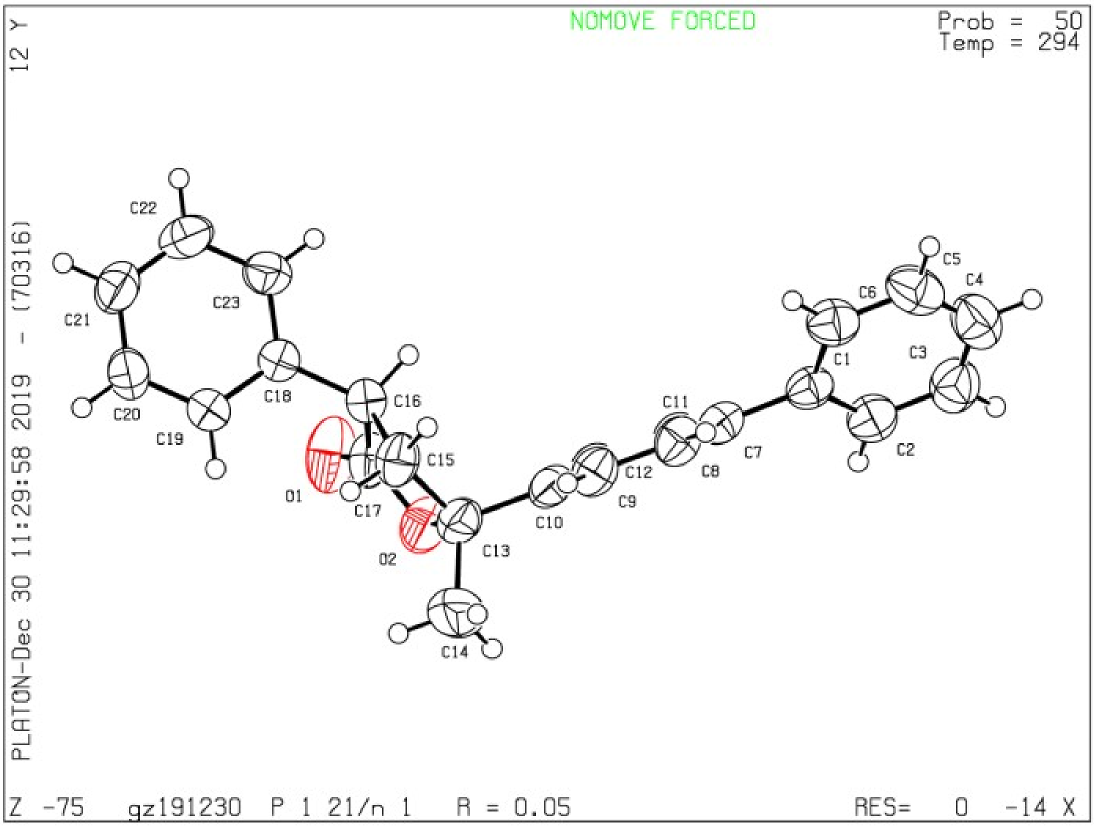
SSB                       2
LB             0 Hz
GB             0
PC                     1.00

F1 - Processing parameters
SI                     1024
MC2             States-TPPI
SF              600.1300172 MHz
WDW                   QSINE
SSB                       2
LB             0 Hz
GB             0
```

Figure S20. NOESY spectrum of **4** (the *syn*-diastereomer).

7.2 Crystallographic data

X-ray crystal structure analysis of 13a

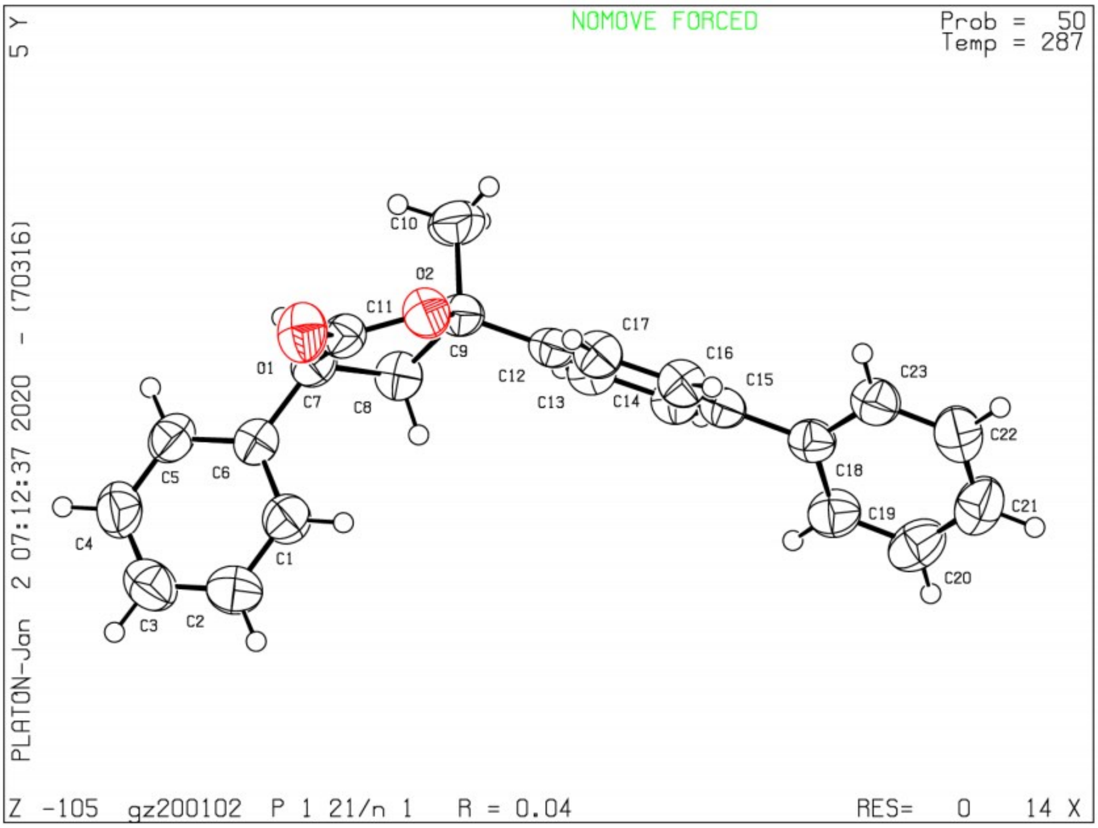


Identification code	gz191230
Empirical formula	$C_{23}H_{20}O_2$
Formula weight	328.39
Temperature/K	293.9(4)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.97592(10)
b/Å	22.3752(5)
c/Å	13.3264(3)
α/°	90
β/°	97.3628(17)
γ/°	90
Volume/Å^3	1767.21(6)
Z	4
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.609
F(000)	696.0
Crystal size/mm^3	0.2 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.77 to 143.518
Index ranges	$-4 \le h \le 7$, $-26 \le k \le 27$, $-16 \le l \le 15$

Reflections collected	9939
Independent reflections	3393 [R_{int} = 0.0143, R_{sigma} = 0.0153]
Data/restraints/parameters	3393/0/227
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1309
Final R indexes [all data]	R_1 = 0.0516, wR_2 = 0.1353
Largest diff. peak/hole / e Å^{-3}	0.21/-0.18

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1985254. Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB21EZ, UK (fax:+ 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

X-ray crystal structure analysis of 13b



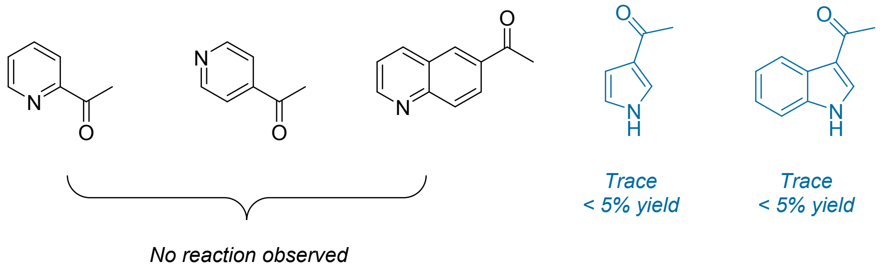
Identification code	gz200102
Empirical formula	$C_{23}H_{20}O_2$
Formula weight	328.39
Temperature/K	287(7)
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	6.11677(9)
b/Å	21.9208(3)
c/Å	13.21139(19)
α/°	90
β/°	96.7434(14)
γ/°	90
Volume/Å^3	1759.19(5)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	0.611
F(000)	696.0
Crystal size/mm^3	0.2 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.854 to 143.824
Index ranges	$-7 \leq h \leq 5$, $-26 \leq k \leq 26$, $-16 \leq l \leq 16$
Reflections collected	13071
Independent reflections	3412 [R_{int} = 0.0199, R_{sigma} = 0.0165]
Data/restraints/parameters	3412/0/227
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.1121
Largest diff. peak/hole / e Å^{-3}	0.12/-0.20

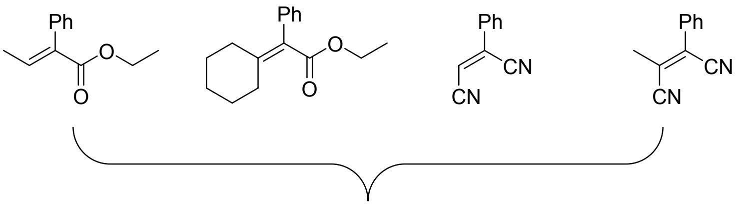
Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1985255. Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB21EZ, UK (fax:+ 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

8. Unsuccessful substrates

Ketones:



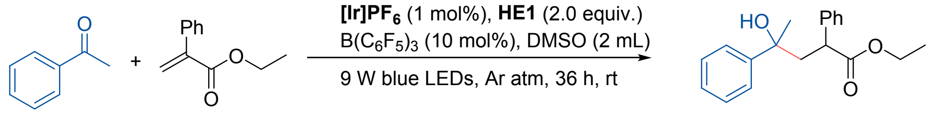
Alkenes:



Product not detected

9. Characterization of products

Ethyl 4-hydroxy-2,4-diphenylpentanoate (3)

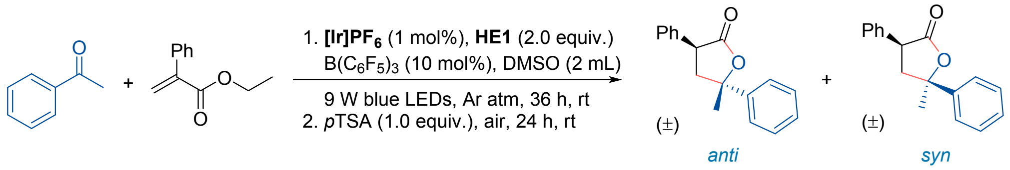


Following the general procedure A without acid treatment, the product ethyl 4-hydroxy-2,4-diphenylpentanoate (**3**) was formed in 95% yield (70.5 mg, 1.1:1 dr).

Mixture of diastereomers: Colourless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.47 – 7.39 (m, 2H), 7.35 (dd, J = 15.0, 7.4 Hz, 2H), 7.32 – 7.17 (m, 5H), 7.10 (d, J=7.4Hz, 1H), 4.17 – 4.12 (m, 0.49H), 4.08 – 3.97 (m, 0.48H), 3.89 – 3.92 (m, 1H), 3.80 – 3.72 (m, 0.52H), 3.41 (d, J = 10.6 Hz, 0.48H), 2.88 – 2.82 (m, 1H), 2.42 (s, 0.42H), 2.24 – 2.04 (m, 1H), 1.91 (s, 0.50H), 1.56 (d, J = 6.8 Hz, 3H), 1.17 (t, J = 7.1 Hz, 1.37H), 1.10 (t, J = 7.1 Hz, 1.61H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 175.4, 174.4, 147.6, 146.6, 140.3, 140.1, 128.8, 128.7, 128.3, 128.2, 127.9, 127.5, 127.3, 127.0, 126.8, 126.7, 125.0, 124.8, 74.5, 74.3, 61.0, 60.9, 47.9, 47.6, 47.4, 47.2, 31.9, 30.1, 14.0, 13.9. **HRMS (ESI)** calcd. for $C_{19}H_{22}NaO_3$ [M+Na]$^+$: 321.1461, found 321.1457.

5-Methyl-3,5-diphenyldihydrofuran-2(3H)-one (4)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-methyl-3,5-diphenyldihydrofuran-2(3H)-one (**4**) was formed in 97% yield (62.0 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

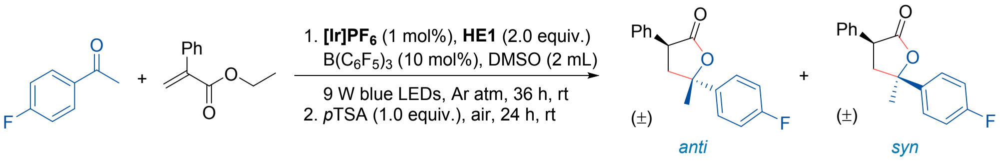


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 – 7.35 (m, 4H), 7.33 – 7.20 (m, 6H), 4.13 (dd, *J* = 11.8, 9.1 Hz, 1H), 2.96 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.57 (t, *J* = 12.4 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.1, 145.1, 136.6, 128.9, 128.7, 128.2, 127.7, 127.7, 124.0, 84.5, 46.7, 44.8, 28.7.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 – 7.33 (m, 4H), 7.32 – 7.18 (m, 6H), 4.12 (dd, *J* = 11.8, 9.1 Hz, 1H), 2.95 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.55 (t, *J* = 12.4 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.1, 145.1, 136.6, 128.9, 128.7, 128.2, 127.7, 127.6, 124.0, 84.5, 46.7, 44.8, 28.7.

5-(4-Fluorophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (5)

Following the general procedure A, the reaction was carried out with 1-(4-fluorophenyl)ethan-1-one (0.25 mmol, 30.2 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(4-fluorophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**5**) was formed in 89% yield (60.0 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

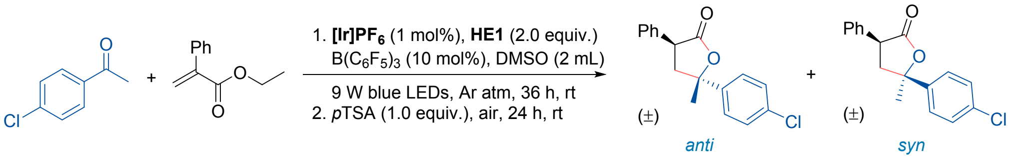


anti-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 8.4, 5.1 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.30 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 7.10 (t, *J* = 8.3 Hz, 2H), 3.69 (dd, *J* = 12.6, 8.3 Hz, 1H), 3.00 (dd, *J* = 12.6, 8.5 Hz, 1H), 2.56 (t, *J* = 12.7 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.2, 163.1, 161.5, 139.42, 139.40, 136.1, 128.9, 128.1, 127.7, 126.2, 126.1, 115.7, 115.6, 84.2, 46.3, 45.5, 30.5. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaFO_2$ $[M+Na]^+$: 293.0948, found 293.0946.

syn-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.21 (m, 2H), 7.10 – 7.04 (m, 2H), 4.18 – 4.10 (m, 1H), 2.97 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.56 (t, *J* = 12.3 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.8, 163.0, 161.4, 140.92, 140.90, 136.4, 128.9, 128.1, 127.7, 125.9, 125.8, 115.6, 115.5, 84.0, 46.7, 44.9, 28.8.

5-(4-Chlorophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (6)

Following the general procedure A, the reaction was carried out with 1-(4-chlorophenyl)ethan-1-one (0.25 mmol, 32.2 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(4-chlorophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**6**) was formed in 72% yield (62.0 mg, 1:1.6 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

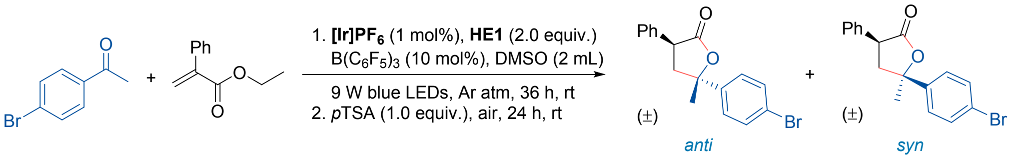


anti-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 – 7.32 (m, 6H), 7.32 – 7.28 (m, 1H), 7.25 (d, *J* = 1.9 Hz, 2H), 3.68 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.99 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.57 (t, *J* = 12.7 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.1, 142.2, 136.0, 133.9, 129.0, 128.9, 128.1, 127.7, 125.8, 84.1, 46.2, 45.5, 30.3. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaClO_2$ $[M+Na]^+$: 309.0653, found 309.0650.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.42 – 7.30 (m, 6H), 7.30 – 7.26 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 4.14 (dd, *J* = 11.8, 9.0 Hz, 1H), 2.97 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.55 (t, *J* = 12.3 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 175.7, 143.6, 136.3, 133.7, 128.9, 128.9, 128.1, 127.7, 125.5, 83.9, 46.6, 44.7, 28.7.

5-(4-Bromophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (7)

Following the general procedure A, the reaction was carried out with 1-(4-bromophenyl)ethan-1-one (0.25 mmol, 49.5 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(4-bromophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**7**) was formed in 65% yield (53.9 mg, 1:1.6 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.



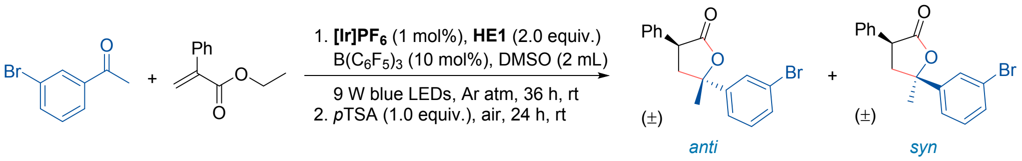
anti-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.57 – 7.51 (m, 2H), 7.37 – 7.28 (m, 5H), 7.25 (d, *J* = 5.8 Hz, 2H), 3.68 (dd, *J* = 11.7, 9.2 Hz, 1H), 2.98 (dd, *J* = 12.2, 8.8 Hz, 1H), 2.56 (t, *J* = 12.2 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.0, 142.7, 136.0, 131.9, 128.9, 128.1, 127.7, 126.2, 121.9, 84.1, 46.2, 45.5, 30.2. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaBrO_2$ $[M+Na]^+$: 353.0148, found 353.0149.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.56 – 7.49 (m, 2H), 7.36 – 7.26 (m, 5H), 7.25 – 7.19 (m, 2H), 4.14 (dd, *J* = 11.8, 9.1 Hz, 1H), 2.97 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.54 (t, *J* = 12.4 Hz, 1H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 175.7, 144.1, 136.3, 131.8, 128.9, 128.1, 127.7, 125.8, 121.7, 83.9, 46.6, 44.7, 28.6.

5-(3-Bromophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (8)

Following the general procedure A, the reaction was carried out with 1-(3-bromophenyl)ethan-1-one (0.25 mmol, 33.1 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(3-bromophenyl)-5-methyl-3-

phenyldihydrofuran-2(3H)-one (**8**) was formed in 72% yield (59.6 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

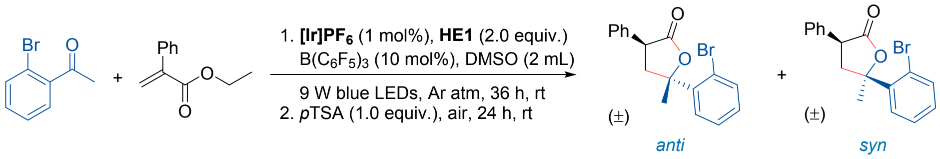


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.60 (t, *J* = 1.9 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.40 – 7.32 (m, 3H), 7.31 – 7.24 (m, 4H), 3.69 (dd, *J* = 12.6, 8.4 Hz, 1H), 3.00 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.56 (t, *J* = 12.7 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.0, 146.0, 136.0, 131.1, 130.4, 128.9, 128.1, 127.7, 127.6, 123.1, 123.0, 83.8, 46.2, 45.4, 30.3. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaBrO_2$ $[M+Na]^+$: 353.0148, found 353.1046.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 (s, 1H), 7.48 – 7.42 (m, 1H), 7.38 – 7.19 (m, 7H), 4.14 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.97 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.55 (t, *J* = 12.4 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.6, 147.2, 136.2, 130.9, 130.3, 128.9, 128.1, 127.8, 127.3, 122.9, 122.7, 83.6, 46.5, 44.6, 28.6.

5-(2-Bromophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (9)

Following the general procedure A, the reaction was carried out with 1-(2-bromophenyl)ethan-1-one (0.25 mmol, 33.5 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(2-bromophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**9**) was formed in 87% yield (74.2 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.



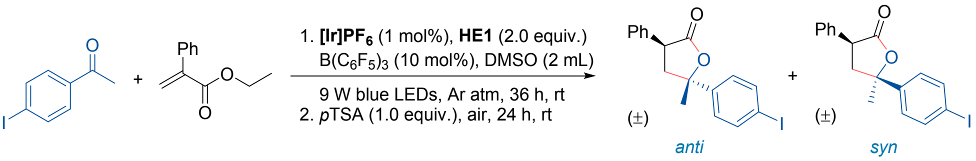
anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.40 – 7.26 (m, 4H), 7.25 – 7.15 (m, 3H), 4.13 (dd, *J* = 11.5, 9.5 Hz, 1H), 3.57 (dd, *J* = 13.3, 9.5 Hz, 1H), 2.68 – 2.59 (t, *J* = 11.3 Hz, 1H), 1.93 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.4, 143.6, 136.4, 134.8, 129.3, 128.9, 128.1, 127.8, 127.6, 126.9, 118.8, 46.2, 43.6, 26.3. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaBrO_2$ $[M+Na]^+$:353.0148, found 353.1048.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 – 7.69 (m, 1H), 7.65 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.30 – 7.25 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 3.68 – 3.61 (m, 2H), 2.60 – 2.51 (m, 1H), 2.01 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.2, 141.9, 136.3, 135.4, 129.7, 128.9, 128.1, 128.0, 127.7, 126.9, 119.5, 85.4, 46.2, 43.2, 27.6.

5-(4-Iodophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (10)

Following the general procedure A, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (0.25 mmol, 61.5 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0

mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(4-iodophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**10**) was formed in 61% yield (58.1 mg, 1:1.1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

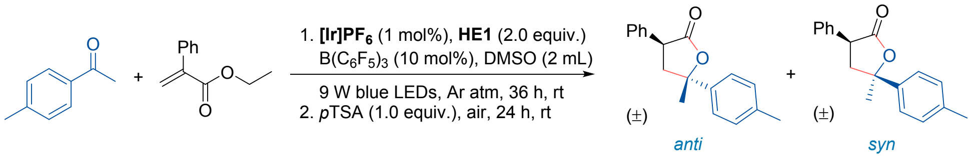


anti-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.78 – 7.71 (m, 2H), 7.38 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 3.68 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.97 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.55 (t, *J* = 12.7 Hz, 1H), 1.78 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.0, 143.4, 137.9, 136.0, 128.9, 128.1, 127.7, 126.4, 93.4, 84.1, 46.2, 45.4, 30.1. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaIO_2$ $[M+Na]^+$: 401.0009, found 401.0007.

syn-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 – 7.68 (m, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.15 (m, 4H), 4.13 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.96 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.53 (t, *J* = 12.3 Hz, 1H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.7, 144.8, 137.8, 136.2, 128.9, 128.1, 127.7, 126.0, 93.2, 83.9, 46.6, 44.6, 28.6.

5-Methyl-3-phenyl-5-(p-tolyl)dihydrofuran-2(3H)-one (11)

Following the general procedure A, the reaction was carried out with 1-(p-tolyl)ethan-1-one (0.25 mmol, 33.3 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). After acid work up, the desired product 5-(4-fluorophenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**11**) was formed in 67% yield (44.8 mg, 1:1.3 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

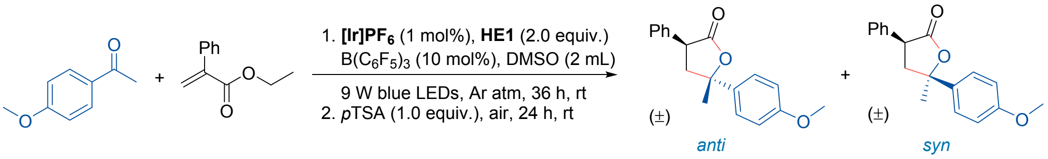


anti-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 4H), 7.30 – 7.20 (m, 5H), 3.70 (dd, *J* = 12.7, 8.3 Hz, 1H), 3.01 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.53 (t, *J* = 12.7 Hz, 1H), 2.37 (s, 3H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.5, 140.62, 137.61, 136.3, 129.4, 128.8, 128.1, 127.6, 124.3, 84.6, 46.4, 45.7, 30.4, 21.0. **HRMS (ESI)** calcd. for $C_{18}H_{18}NaO_2$ $[M+Na]^+$: 289.1199, found 289.1198.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36 – 7.21 (m, 7H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.13 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.95 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.58 (t, *J* = 12.4 Hz, 1H), 2.36 (s, 3H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.5, 140.6, 137.6, 136.3, 129.4, 128.8, 128.1, 127.6, 124.3, 84.6, 46.4, 45.7, 30.4, 21.0.

5-(4-Methoxyphenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (12)

Following the general procedure A, the reaction was carried out with 1-(4-methoxyphenyl)ethan-1-one (0.25 mmol, 37.5 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(4-methoxyphenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**12**) was formed in 80% yield (56.2 mg, 1:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

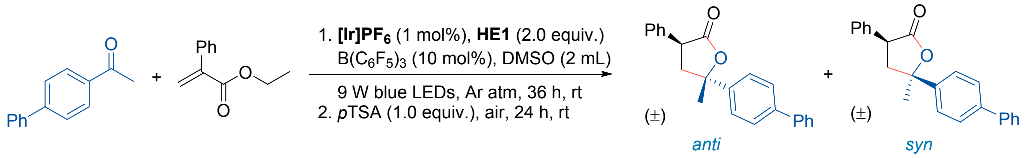


anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38 – 7.32 (m, 4H), 7.30 – 7.24 (m, 3H), 6.97 – 6.89 (m, 2H), 3.82 (s, 3H), 3.70 (dd, *J* = 12.7, 8.3 Hz, 1H), 3.00 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.53 (t, *J* = 12.6 Hz, 1H), 1.78 (s, 3H). **^{13}C NMR (151 MHz, (CD$_3$)$_2$SO)** δ 176.0, 146.0, 136.0, 131.1, 130.4, 128.9, 128.1, 127.7, 127.6, 123.1, 123.0, 83.8, 46.2, 45.4, 30.3. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaBrO_2$ [M+Na]$^+$: 305.1148, found 305.1147.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.38 – 7.19 (m, 7H), 4.14 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.97 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.55 (t, *J* = 12.4 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, (CD$_3$)$_2$SO)** δ 175.6, 147.2, 136.2, 130.9, 130.3, 128.9, 128.1, 127.8, 127.3, 122.9, 122.7, 83.6, 46.5, 44.6, 28.6.

5-([1,1'-Biphenyl]-4-yl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (13)

Following the general procedure A, the reaction was carried out with 1-([1,1'-biphenyl]-4-yl)ethan-1-one (0.25 mmol, 49.0 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-([1,1'-biphenyl]-4-yl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**13**) was formed in 80% yield (65.3 mg, 1.4:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

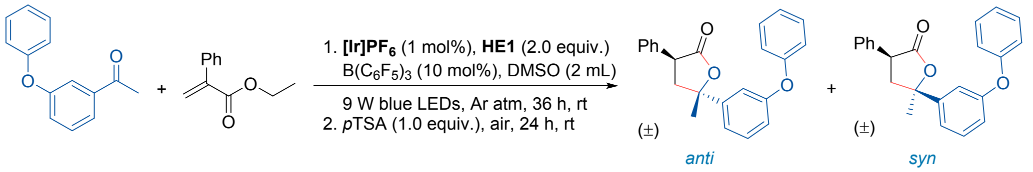


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.67 – 7.57 (m, 4H), 7.54 – 7.48 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.31 – 7.27 (m, 2H), 7.24 (s, 1H), 3.75 (dd, *J* = 12.6, 8.3 Hz, 1H), 3.07 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.59 (t, *J* = 12.7 Hz, 1H), 1.84 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.4, 142.6, 140.9, 140.4, 136.3, 128.88, 128.85, 128.1, 127.7, 127.6, 127.5, 127.1, 124.8, 84.5, 46.4, 45.6, 30.3. **HRMS (ESI)** calcd. for $C_{23}H_{20}NaO_2$ [M+Na]$^+$: 351.1356, found 351.1355.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.64 – 7.55 (m, 4H), 7.53 – 7.42 (m, 4H), 7.38 – 7.28 (m, 3H), 7.27 – 7.22 (m, 3H), 4.16 (dd, *J* = 11.9, 9.0 Hz, 1H), 3.01 (dd, *J* = 12.9, 9.0 Hz, 1H), 2.64 (t, *J* = 12.3 Hz, 1H), 1.83 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.0, 144.0, 140.7, 140.5, 136.5, 128.89, 128.85, 128.2, 127.7, 127.52, 127.4, 127.1, 124.5, 84.3, 46.8, 44.9, 28.7.

5-Methyl-5-(3-phenoxyphenyl)-3-phenyldihydrofuran-2(3H)-one (14)

Following the general procedure A, the reaction was carried out with 1-(3-phenoxyphenyl)ethan-1-one (0.25 mmol, 44.5 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-methyl-5-(3-phenoxyphenyl)-3-phenyldihydrofuran-2(3H)-one (**14**) was formed in 46% yield (39.3 mg, 1:1.1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

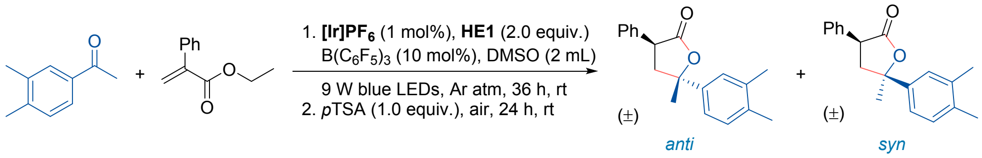


anti-diastereomer: yellowish oil; ^{1}**H NMR (600 MHz, CDCl$_3$)** δ 7.39 – 7.25 (m, 8H), 7.21 – 7.10 (m, 3H), 7.03 (d, J = 8.1 Hz, 2H), 6.93 (dd, J = 8.1, 2.4 Hz, 1H), 3.73 (dd, J = 12.7, 8.5 Hz, 1H), 3.01 (dd, J = 12.7, 8.4 Hz, 1H), 2.54 (t, J = 12.6 Hz, 1H), 1.80 (s, 3H). ^{13}**C NMR (151 MHz, CDCl$_3$)** δ 176.2, 157.9, 156.8, 145.9, 136.2, 130.1, 129.9, 128.9, 128.1, 127.7, 123.7, 119.1, 119.0, 117.7, 115.1, 84.2, 46.3, 45.5, 30.2. **HRMS (ESI)** calcd. for $C_{23}H_{20}NaO_3$ [M+Na]$^+$: 367.1305, found 367.1303.

syn-diastereomer: yellowish oil; ^{1}**H NMR (600 MHz, CDCl$_3$)** δ 7.38 – 7.26 (m, 6H), 7.23 (d, J = 6.8 Hz, 2H), 7.18 – 7.09 (m, 3H), 7.00 (d, J = 8.0 Hz, 2H), 6.92 (dd, J = 8.2, 2.4 Hz, 1H), 4.12 (dd, J = 11.7, 9.0 Hz, 1H), 2.94 (dd, J = 12.8, 9.0 Hz, 1H), 2.59 (t, J = 12.3 Hz, 1H), 1.77 (s, 3H). ^{13}**C NMR (151 MHz, CDCl$_3$)** δ 175.8, 157.6, 156.9, 147.1, 136.4, 130.1, 129.8, 128.9, 128.1, 127.7, 123.5, 119.0, 118.7, 117.8, 114.8, 84.1, 46.6, 44.7, 28.6.

5-(3,4-Dimethylphenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (15)

Following the general procedure A, the reaction was carried out with 1-(3,4-dimethylphenyl)ethan-1-one (0.25 mmol, 37.1 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(3,4-dimethylphenyl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**15**) was formed in 91% yield (63.7 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.



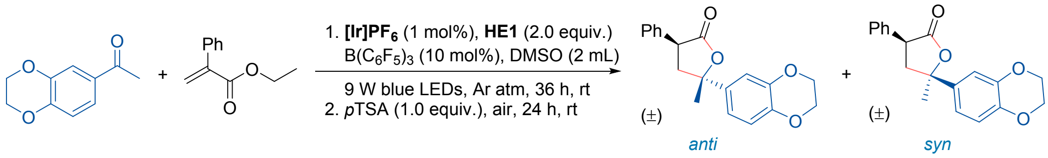
anti-diastereomer: yellowish oil; ^{1}**H NMR (600 MHz, CDCl$_3$)** δ 7.35 – 7.32 (m, 2H), 7.29 – 7.20 (m, 4H), 7.17 – 7.14 (m, 2H), 3.70 (dd, J = 12.7, 8.3 Hz, 1H), 3.01 (dd, J = 12.6, 8.3 Hz, 1H), 2.52

(t, J = 12.6 Hz, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 1.78 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.6, 141.1, 137.1, 136.4, 136.2, 130.0, 128.8, 128.2, 127.6, 125.6, 121.7, 84.6, 46.41 45.6, 30.4, 20.0, 19.3. **HRMS (ESI)** calcd. for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1356, found 303.1357.

syn-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 – 7.30 (m, 2H), 7.28 – 7.20 (m, 4H), 7.15 – 7.12 (m, 2H), 4.12 (dd, J = 12.0, 9.0 Hz, 1H), 2.95 (dd, J = 12.8, 9.0 Hz, 1H), 2.57 (t, J = 12.4 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (151 MHz, $(CD_3)_2SO$)** δ 181.3, 147.9, 142.7, 141.5, 140.6, 134.7, 133.8, 133.6, 132.4, 130.4, 126.7, 89.3, 51.0, 49.5, 32.9, 24.7, 24.2.

5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (16)

Following the general procedure A, the reaction was carried out with 1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (0.25 mmol, 44.5 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methyl-3-phenyldihydrofuran-2(3H)- one (**16**) was formed in 78% yield (60.8 mg, 1:1.5 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

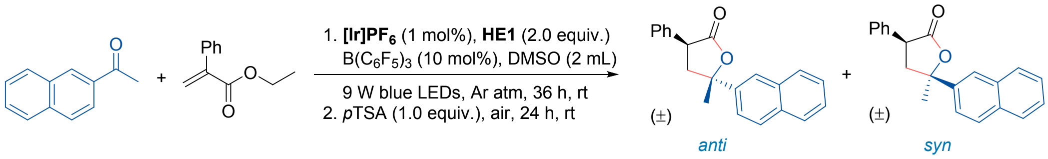


anti-diastereomer: white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.26 (m, 4H), 7.24 (s, 1H), 6.98 – 6.86 (m, 3H), 4.27 (s, 4H), 3.73 (dd, J = 12.7, 8.2 Hz, 1H), 2.98 (dd, J = 12.6, 8.2 Hz, 1H), 2.50 (t, J = 12.6 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.5, 143.6, 143.1, 136.8, 136.3, 128.8, 128.2, 127.6, 117.5, 117.3, 113.7, 84.3, 64.4, 64.4, 46.4, 45.6, 30.4. **HRMS (ESI)** calcd. for $C_{19}H_{18}NaO_4$ $[M+Na]^+$: 333.1097, found 333.1097.

syn-diastereomer: yellowish solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.26 (m, 3H), 7.25 – 7.23 (m, 2H), 6.99 – 6.81 (m, 3H), 4.26 (s, 4H), 4.12 (dd, J = 12.0, 9.0 Hz, 1H), 2.91 (dd, J = 12.8, 9.0 Hz, 1H), 2.56 (t, J = 12.4 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.1, 143.5, 143.0, 138.3, 136.6, 128.9, 128.2, 127.6, 117.4, 117.1, 113.4, 84.1, 64.4, 64.4, 46.9, 44.9, 28.5.

5-Methyl-5-(naphthalen-2-yl)-3-phenyldihydrofuran-2(3H)-one (17)

Following the general procedure A, the reaction was carried out with 1-(naphthalen-2-yl)ethan-1-one (0.25 mmol, 42.6 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-methyl-5-(naphthalen-2-yl)-3-phenyldihydrofuran-2(3H)-one (**17**) was formed in 84% yield (63.2 mg, 1.2:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

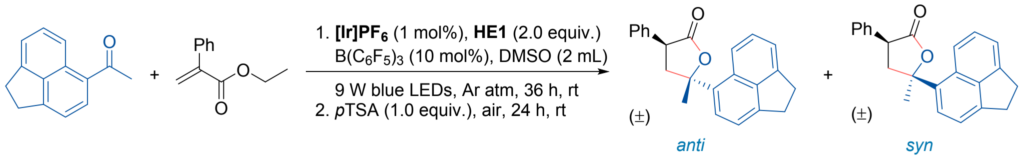


anti-diastereomer: yellowish solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.84 (m, 4H), 7.56 – 7.46 (m, 3H), 7.38 – 7.28 (m, 3H), 7.25 – 7.23 (m, 2H), 3.73 (dd, *J* = 12.7, 8.3 Hz, 1H), 3.14 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.62 (t, *J* = 12.7 Hz, 1H), 1.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.6, 140.7, 136.2, 133.0, 132.7, 128.9, 128.3, 128.2, 127.7, 127.6, 126.8, 126.5, 122.9, 122.5, 84.7, 46.3, 45.5, 30.1. **HRMS** (ESI) calcd. for $C_{21}H_{18}NaO_2$ $[M+Na]^+$: 325.1199, found 325.1200.

syn-diastereomer: yellowish solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.80 (m, 4H), 7.56 – 7.46 (m, 3H), 7.37 – 7.20 (m, 5H), 4.20 (dd, *J* = 11.9, 9.0 Hz, 1H), 3.08 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.69 (t, *J* = 12.4 Hz, 1H), 1.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.2, 142.2, 136.5, 133.1, 132.7, 128.9, 128.7, 128.3, 128.2, 127.70, 127.65, 126.6, 126.4, 122.6 122.3, 84.6, 46.8, 44.8, 28.6.

5-(1,2-Dihydroacenaphthylen-4-yl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (18)

Following the general procedure A, the reaction was carried out with 1-(1,2-dihydroacenaphthylen-5-yl)ethan-1-one (0.25 mmol, 49.0 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(1,2-dihydroacenaphthylen-4-yl)-5-methyl-3-phenyldihy1drofuran-2(3H)-one (**18**) was formed in 49% yield (40.4 mg, 1.3:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.



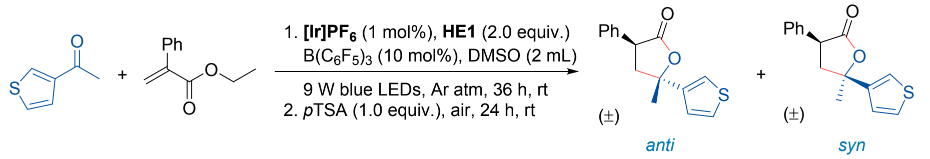
anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.49 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.34 – 7.22 (m, 7H), 3.69 (dd, *J* = 12.4, 8.5 Hz, 1H), 3.53 (dd, *J* = 12.6, 8.5 Hz, 1H), 3.44 – 3.35 (m, 4H), 2.67 (t, *J* = 12.5 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.5, 147.3, 147.0, 140.4, 136.5, 134.5 128.8, 128.2, 128.0, 127.7, 127.6, 124.0, 120.4, 119.5, 118.8, 85.4, 46.7, 44.5, 30.6, 29.7, 29.5. **HRMS (ESI)** calcd. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$: 351.1356, found 351.1356.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 4.21 (dd, *J* = 11.6, 9.3 Hz, 1H), 3.42 – 3.31 (m, 5H), 2.85 (t, *J* = 12.2 Hz, 1H), 1.99 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.9, 147.0, 146.7, 140.2, 136.8, 136.4, 128.9, 128.2, 128.0, 127.7, 127.6, 123.8, 120.8, 119.5, 118.7, 85.6, 46.5, 44.8, 30.5, 29.8, 28.3.

5-Methyl-3-phenyl-5-(thiophen-3-yl)dihydrofuran-2(3H)-one (19)

Following the general procedure A, the reaction was carried out with 1-(thiophen-3-yl)ethan-1-one (0.25 mmol, 31.5 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-

1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-methyl-3-phenyl-5-(thiophen-3-yl)dihydrofuran-2(3H)-one (**19**) was formed in 77% yield (49.9 mg, 1:1.3 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

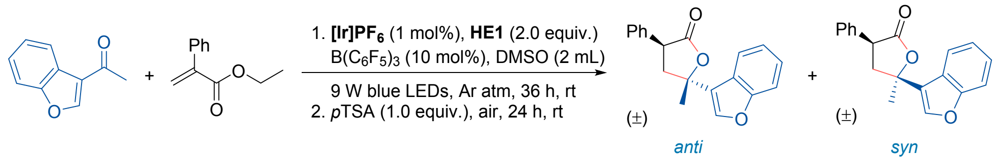


anti-diastereomer: yellowish oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.35 – 7.23 (m, 7H), 7.13 – 7.05 (m, 1H), 4.13 (dd, *J* = 11.6, 9.2 Hz, 1H), 2.89 (dd, *J* = 12.7, 9.2 Hz, 1H), 2.61 (t, *J* = 12.2 Hz, 1H), 1.80 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.1, 145.9, 136.5, 128.9, 128.1, 127.7, 126.9, 124.7, 120.1, 83.0, 46.7, 44.64, 27.9. **HRMS (ESI)** calcd. for $C_{15}H_{14}NaO_2S$ [M+Na]$^+$: 281.0607, found 281.0607.

syn-diastereomer: yellowish oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.23 (m, 7H), 7.07 (dd, *J* = 5.1, 1.4 Hz, 1H), 3.82 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.97 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.50 (t, *J* = 12.6 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.5, 145.0, 136.3, 128.9, 128.2, 127.7, 127.3, 124.9, 120.3, 83.4, 46.6, 45.3, 29.7.

5-(Benzofuran-3-yl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (20)

Following the general procedure A, the reaction was carried out with 1-(benzofuran-3-yl)ethan-1-one (0.25 mmol, 40.0 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(benzofuran-3-yl)-5-methyl-3-phenyldihydrofuran-2(3H)-one (**20**) was formed in 49% yield (36.0 mg, 1.6:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

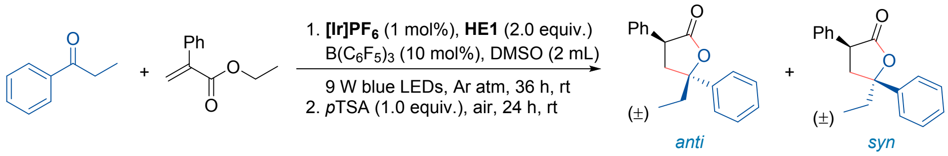


anti-diastereomer: yellowish oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 – 7.64 (m, 2H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.26 (m, 7H), 3.92 (dd, *J* = 12.4, 8.6 Hz, 1H), 3.16 (dd, *J* = 12.8, 8.6 Hz, 1H), 2.55 (t, *J* = 12.6 Hz, 1H), 1.97 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.2, 156.2, 140.6, 136.1, 128.9, 128.1, 127.7, 125.0, 124.9, 123.8, 123.1, 120.2, 112.1, 81.2, 46.6, 43.5, 28.5. **HRMS (ESI)** calcd. for $C_{19}H_{16}NaO_3$ [M+Na]$^+$: 315.0992, found 315.0991.

syn-diastereomer:yellowish solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 (t, *J* = 3.9 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.27 (m, 7H), 4.20 (dd, *J* = 11.7, 9.2 Hz, 1H), 3.00 (dd, *J* = 12.9, 9.2 Hz, 1H), 2.79 (t, *J* = 12.3 Hz, 1H), 1.93 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 175.8, 155.9, 140.4, 136.3, 129.0, 128.1, 127.8, 125.0, 124.9, 124.7, 123.1, 120.5, 112.0, 80.9, 46.2, 43.4, 27.0

5-Ethyl-3,5-diphenyldihydrofuran-2(3H)-one (21)

Following the general procedure A, the reaction was carried out with propiophenone (0.25 mmol, 33.2 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-ethyl-3,5-diphenyldihydrofuran-2(3H)-one (**21**) was formed in 96% yield (63.7 mg, 1:1.1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

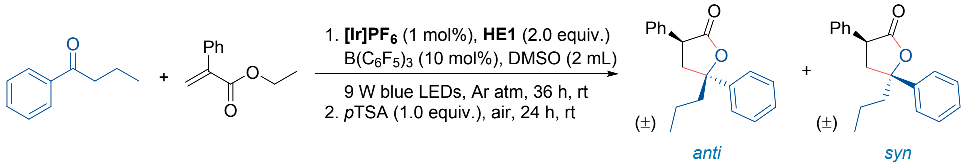


anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 – 7.37 (m, 4H), 7.34 – 7.32 (m, 3H), 7.29 – 7.21 (m, 3H), 3.66 (dd, *J* = 12.7, 8.4 Hz, 1H), 2.96 (dd, *J* = 12.7, 8.4 Hz, 1H), 2.55 (t, *J* = 12.7 Hz, 1H), 2.12 – 2.02 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.5, 142.0, 136.5, 128.9, 128.7, 128.2, 127.8, 127.6, 125.0, 87.4, 46.0, 43.9, 35.7, 8.3. **HRMS (ESI)** calcd. for $C_{18}H_{18}NaO_2$ [M+Na]$^+$: 289.1199, found 289.1197.

syn-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.37 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.27 (m, 3H), 7.25 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 4.10 (dd, *J* = 11.2, 9.5 Hz, 1H), 3.04 (dd, *J* = 13.0, 9.5 Hz, 1H), 2.57 (dd, *J* = 13.0, 11.2 Hz, 1H), 2.14 – 2.08 (m, 1H), 2.05 – 1.99 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.3, 143.5, 136.9, 128.8, 128.5, 128.1, 127.6, 127.5, 124.5, 87.4, 46.7, 43.5, 34.7, 8.3.

3,5-Diphenyl-5-propyldihydrofuran-2(3H)-one (22)

Following the general procedure A, the reaction was carried out with 1-phenylbutan-1-one (0.25 mmol, 36.3 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3,5-diphenyl-5-propyldihydrofuran-2(3H)-one (**22**) was formed in 95% yield (66.4 mg, 1.3:1dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.



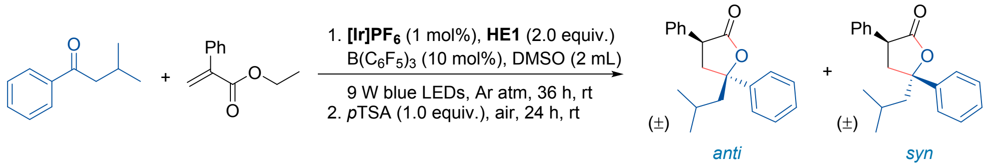
anti-diastereomer: yellowish solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46 – 7.27 (m, 8H), 7.25 – 7.23 (m, 2H), 3.65 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.98 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.56 (t, *J* = 12.7 Hz, 1H), 2.11 – 1.92 (m, 2H), 1.50 – 1.36 (m, 1H), 1.21 – 1.06 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.7, 142.2, 136.4, 128.9, 128.7, 128.2, 127.8, 127.6, 124.9, 87.2, 45.9, 45.0, 44.5, 17.3, 14.1. **HRMS (ESI)** calcd. for $C_{19}H_{20}NaO_2$ [M+Na]$^+$: 303.1356, found 303.1355.

syn-diastereomer: yellowish oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.27 (m, 7H), 7.26 – 7.17 (m, 3H), 4.12 (dd, *J* = 11.3, 9.4 Hz, 1H), 3.04 (dd, *J* = 13.0, 9.4 Hz, 1H), 2.57 (dd, *J* = 13.0, 11.3

Hz, 1H), 2.10 – 1.90 (m, 2H), 1.50 – 1.34 (m, 1H), 1.23 – 1.11 (m, 1H), 0.87 (t, J = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.4, 143.8, 136.8, 128.9, 128.5, 128.1, 127.6, 127.5, 124.4, 87.1, 46.7, 44.1, 44.0, 17.3, 14.1.

5-Isobutyl-3,5-diphenyldihydrofuran-2(3H)-one (23)

Following the general procedure A, the reaction was carried out with 3-methyl-1-phenylbutan-1-one (0.25 mmol, 42.0 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-isobutyl-3,5-diphenyldihydrofuran-2(3H)-one (**23**) was formed in 91% yield (66.0 mg, 1.2:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

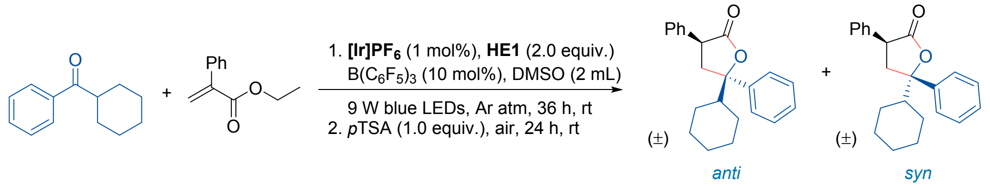


anti-diastereomer: yellowish oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 (d, J = 4.3 Hz, 4H), 7.37 – 7.21 (m, 6H), 3.60 (dd, J = 12.9, 8.2 Hz, 1H), 2.95 (dd, J = 12.5, 8.3 Hz, 1H), 2.54 (t, J = 12.7 Hz, 1H), 2.09 (dd, J = 14.7, 5.1 Hz, 1H), 1.90 (dd, J = 14.7, 7.5 Hz, 1H), 1.58 – 1.45 (m, 1H), 0.93 (d, J = 6.7 Hz, 3H), 0.77 (d, J = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.8, 142.2, 136.4, 128.9, 128.7, 128.2, 127.7, 127.6, 125.0, 87.4, 51.3, 46.1, 45.5, 24.6, 24.1, 23.5. **HRMS (ESI)** calcd. for $C_{20}H_{22}NaO_2$ [M+Na]$^+$: 317.1512, found 317.1509.

syn-diastereomer: white solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 – 7.35 (m, 4H), 7.32 – 7.23 (m, 4H), 7.20 – 7.14 (m, 2H), 4.09 (dd, J = 11.3, 9.3 Hz, 1H), 2.98 (dd, J = 13.0, 9.4 Hz, 1H), 2.54 (dd, J = 13.0, 11.3 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.65 – 1.56 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H), 0.72 (d, J = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 176.3, 143.9, 136.8, 128.8, 128.6, 128.1, 127.6, 127.5, 124.4, 87.3, 50.1, 46.6, 45.5, 24.5, 24.3, 23.8.

5-Cyclohexyl-3,5-diphenyldihydrofuran-2(3H)-one (24)

Following the general procedure A, the reaction was carried out with cyclohexyl(phenyl)methanone (0.25 mmol, 48.7 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-cyclohexyl-3,5-diphenyldihydrofuran-2(3H)-one (**24**) was formed in 92% yield (73.7 mg, 1:1.4 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

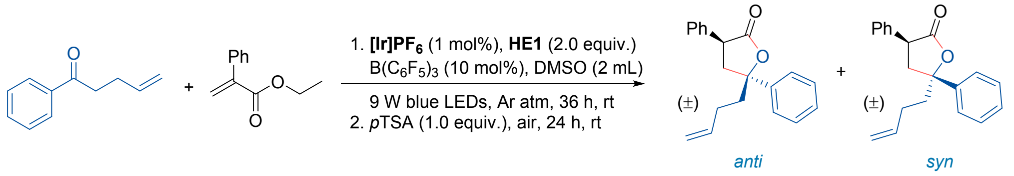


anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.38 – 7.31 (m, 4H), 7.30 – 7.20 (m, 4H), 7.13 – 7.11 (m, 2H), 4.06 (t, *J* = 10.2 Hz, 1H), 3.24 (dd, *J* = 13.4, 10.2 Hz, 1H), 2.55 (dd, *J* = 13.4, 10.2 Hz, 1H), 1.97 (dt, *J* = 12.2, 3.4 Hz, 1H), 1.84 – 1.80 (m, 2H), 1.76 – 1.70 (m, 1H), 1.66 – 1.58 (m, 2H), 1.30 – 1.12 (m, 2H), 1.11 – 0.97 (m, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.3, 140.7, 136.6, 128.8, 128.3, 128.2, 127.8, 127.6, 126.0, 89.4, 48.3, 46.2, 41.5, 27.3, 26.4, 26.13, 26.08. **HRMS (ESI)** calcd. for $C_{22}H_{24}NaO_2$ $[M+Na]^+$: 343.1669, found 343.1664.

syn-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 – 7.37 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 3H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 3.57 (dd, *J* = 12.9, 8.3 Hz, 1H), 2.99 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.63 (t, *J* = 12.8 Hz, 1H), 1.94 (d, *J* = 12.3 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.75 (d, *J* = 13.2 Hz, 2H), 1.68 (d, *J* = 12.2 Hz, 1H), 1.63 (d, *J* = 12.6 Hz, 1H), 1.25 – 1.17 (m, 2H), 1.08 – 1.02 (m, 2H), 0.88 (qd, *J* = 12.6, 3.6 Hz, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.6, 143.5, 137.7, 128.8, 128.1, 128.0, 127.5, 127.4, 127.3, 125.3, 89.5, 48.4, 47.0, 41.6, 27.8, 26.9, 26.4, 26.2, 26.0.

5-(But-3-en-1-yl)-3,5-diphenyldihydrofuran-2(3H)-one (25)

Following the general procedure A, the reaction was carried out with 1-phenylpent-4-en-1-one (0.25 mmol, 41.4 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(but-3-en-1-yl)-3,5-diphenyldihydrofuran-2(3H)-one (**25**) was formed in 59% yield (42.9 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.



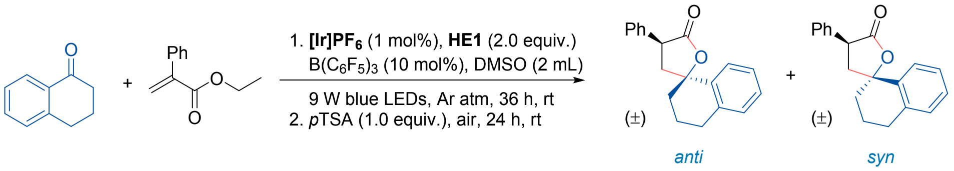
anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43 – 7.42 (m, 4H), 7.35 (t, *J* = 7.2 Hz, 3H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.24 (m, 2H), 5.80 – 5.66 (m, 1H), 5.02 – 4.87 (m, 2H), 3.67 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.99 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.59 (t, *J* = 12.7 Hz, 1H), 2.23 – 2.08 (m, 3H), 1.88 – 1.83 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.3, 141.9, 137.4, 136.3, 128.9, 128.8, 128.1, 127.9, 127.7, 124.9, 115.0, 86.6, 45.8, 44.6, 42.0, 28.3. **HRMS (ESI)** calcd. for $C_{20}H_{20}NaO_2$ $[M+Na]^+$: 315.1356, found 315.1355.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.42 – 7.25 (m, 8H), 7.21 – 7.16 (m, 2H), 5.77 – 5.71 (m, 1H), 5.09 – 4.86 (m, 2H), 4.12 (dd, *J* = 11.3, 9.4 Hz, 1H), 3.06 (dd, *J* = 13.1, 9.5 Hz, 1H), 2.59 (dd, *J* = 13.1, 11.3 Hz, 1H), 2.22 – 2.06 (m, 3H), 1.93 – 1.82 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.1, 143.4, 137.3, 136.7, 128.9, 128.6, 128.1, 127.63, 127.61, 124.4, 115.1, 86.6, 46.6, 44.1, 41.0, 28.1.

4-Phenyl-3,3',4,4'-tetrahydro-2'H,5H-spiro[furan-2,1'-naphthalen]-5-one (26)

Following the general procedure A, the reaction was carried out with 3,4-dihydronaphthalen-1(2H)-one (0.25 mmol, 33.3 μL), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-

phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-cyclohexyl-3,5-diphenyldihydrofuran-2(3H)-one (**26**) was formed in 50% yield (34.7 mg, 2.1:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

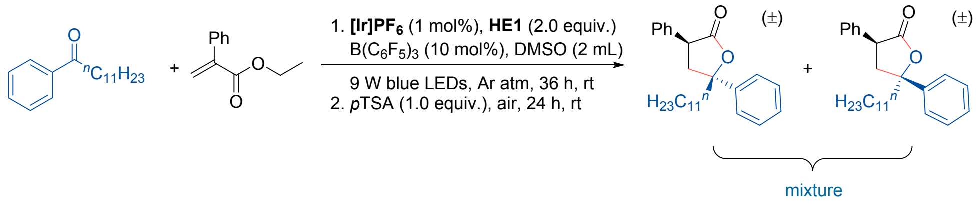


anti-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 – 7.27 (m, 6H), 7.26 – 7.22 (m, 2H), 7.16 – 7.14 (m, 1H), 4.27 (t, *J* = 10.2 Hz, 1H), 2.96 (dd, *J* = 13.4, 10.3 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.47 (dd, *J* = 13.4, 10.2 Hz, 1H), 2.30 – 2.26 (m, 1H), 2.09 – 2.03 (m, 2H), 1.93 – 1.84 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 177.0, 138.8, 137.7, 136.6, 129.5, 129.0, 128.2, 128.0, 127.6, 126.5, 124.7, 83.8, 46.6, 45.7, 37.7, 28.6, 19.3. **HRMS (ESI)** calcd. for $C_{19}H_{18}NaO_2$ $[M+Na]^+$: 301.1199, found 301.1197.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 – 7.27 (m, 6H), 7.26 – 7.23 (m, 2H), 7.16 – 7.14 (m, 1H), 4.27 (t, *J* = 10.2 Hz, 1H), 2.96 (dd, *J* = 13.4, 10.3 Hz, 1H), 2.93 – 2.80 (m, 2H), 2.47 (dd, *J* = 13.3, 10.2 Hz, 1H), 2.32 – 2.25 (m, 1H), 2.10 – 2.02 (m, 2H), 1.94 – 1.85 (m, 1H). **^{13}C NMR (151 MHz, (CD$_3$)$_2$SO)** δ 181.7, 143.3, 142.9, 142.8, 134.0, 133.9, 133.8, 133.2, 132.5, 132.0, 131.8, 88.5, 51.0, 50.4, 38.5, 33.8, 25.1.

3,5-Diphenyl-5-undecyldihydrofuran-2(3H)-one (27)

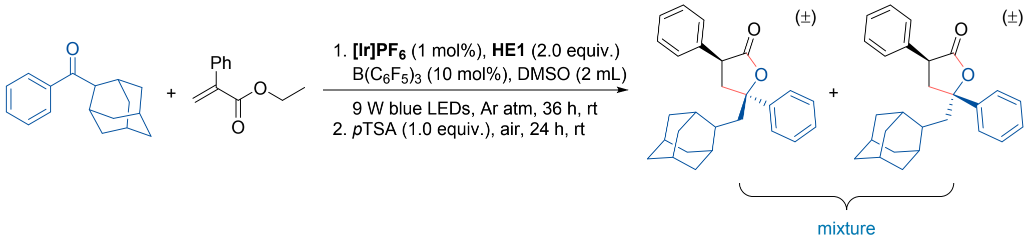
Following the general procedure A, the reaction was carried out with 1-phenyldodecan-1-one (0.25 mmol, 65.1 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3,5-Diphenyl-5-undecyldihydrofuran-2(3H)-one (**27**) was formed in 63% yield (62.0 mg, 1.1:1 dr). The diastereomers seems inseparable by column chromatography.



mixture of diastereomers: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.41 – 7.36 (m, 4H), 7.34 – 7.20 (m, 5H), 7.18 (d, *J* = 7.1 Hz, 1H), 4.10 (dd, *J* = 11.2, 9.4Hz, 0.48H), 3.64 (dd, *J* = 12.7, 8.4Hz, 0.45H), 3.03 (dd, *J* = 13.0, 9.5Hz, 0.48H), 2.96 (dd, *J* = 12.6, 8.3Hz, 0.46H), 2.63 – 2.48 (m, 1H), 2.12 – 1.88 (m, 2H), 1.42 – 1.35 (m, 1H), 1.30 – 1.20 (m, 16H), 1.14 – 1.09 (m, 1H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.5, 176.3, 143.9, 142.3, 137.0, 136.4, 128.8, 128.7, 128.5, 128.2, 128.1, 127.8, 127.6, 127.6, 127.5, 124.9, 124.4, 87.13, 87.07, 46.7, 46.0, 44.4, 44.0, 42.9, 42.0, 31.9, 29.7, 29.6, 29.52, 29.51, 29.40, 29.37, 29.3, 23.9, 22.7, 14.1. **HRMS (ESI)** calcd. for $C_{27}H_{36}NaO_2$ $[M+Na]^+$: 415.2608, found 415.2609.

5-(((1r,3r,5r,7r)-Adamantan-2-yl)methyl)-3,5-diphenyldihydrofuran-2(3H)-one (28)

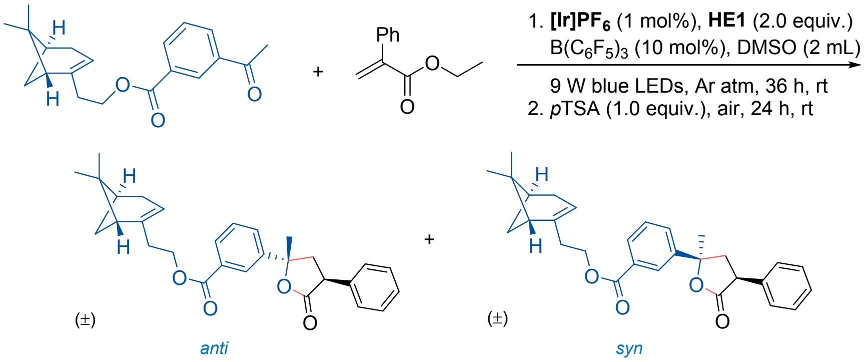
Following the general procedure A, the reaction was carried out with 2-((1r,3r,5r,7r)-adamantan-2-yl)-1-phenylethan-1-one (0.25 mmol, 63.5 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-(((1r,3r,5r,7r)-adamantan-2-yl)methyl)-3,5-diphenyldihydrofuran-2(3H)-one (28) was formed in 58% yield (56.3 mg, 1.4:1 dr). The diastereomers seems inseparable by column chromatography.



mixture of diastereomers : white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.48 – 7.29 (m, 6H), 7.28 – 7.15 (m, 4H), 4.07 (dd, J = 9.4, 9.0 Hz, 0.40H), 3.54 (dd, J = 12.9, 8.2 Hz, 0.56H), 2.95 – 2.90 (m, 1H), 2.52 (t, J = 12.7 Hz, 0.58H), 2.37 (t, J = 12.2 Hz, 0.42H), 2.11 – 1.88 (m, 2H), 1.80 – 1.78 (m, 3H), 1.60 – 1.41 (m, 9H), 1.31 (t, J = 14.7 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.9, 176.1, 145.2, 142.8, 136.7, 136.4, 128.8, 128.44, 128.42, 128.2, 128.1, 127.7, 127.5, 127.2, 125.4, 124.2, 86.92, 86.89, 56.7, 54.5, 48.5, 48.2, 46.4, 45.0, 43.5, 43.4, 36.77, 36.75, 34.1, 34.0, 28.6. **HRMS (ESI)** calcd. for $C_{27}H_{30}NaO_2$ [M+Na]$^+$: 409.2138, found 409.2139.

2-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 3-(2-methyl-5-oxo-4-phenyltetra hydrofuran-2-yl)benzoate (29)

Following the general procedure A, the reaction was carried out with 2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 3-acetylbenzoate (0.25 mmol, 78.04 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF_3)ppy]$_2$]PF_6 (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 3-(2-methyl-5-oxo-4-phenyltetrahydro furan-2-yl)benzoate (**42**) was formed in 58% yield (64.4mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

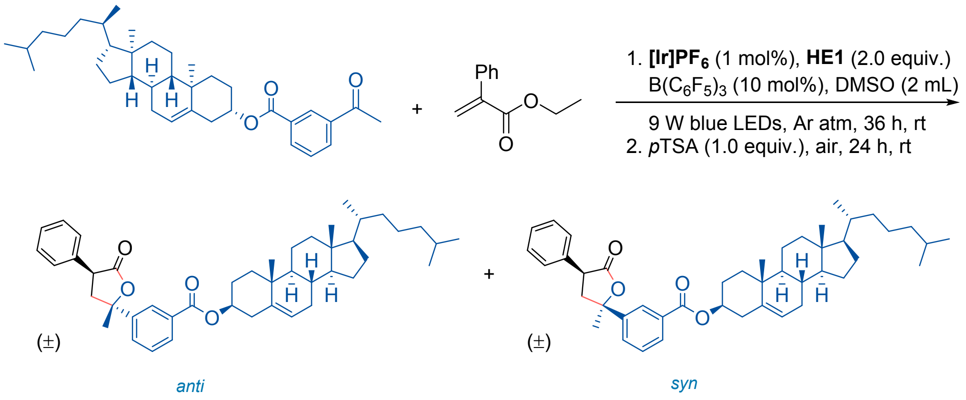


anti-diastereomer: Yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.09 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 5.38 (s, 1H), 4.48 – 4.25 (m, 2H), 3.67 (dd, *J* = 12.6, 8.5 Hz, 1H), 3.07 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.60 (t, *J* = 12.7 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.41 – 2.36 (m, 1H), 2.24 (q, *J* = 18.0 Hz, 2H), 2.16 – 2.05 (m, 2H), 1.82 (s, 3H), 1.27 (s, 3H), 1.18 (d, *J* = 8.6 Hz, 1H), 0.84 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.0, 166.1, 144.2, 144.1, 136.0, 131.2, 129.1, 129.0, 128.9, 128.7, 128.1, 127.7, 125.5, 119.1, 84.2, 63.5, 46.2, 45.8, 45.4, 40.8, 38.0, 36.1, 31.7, 31.4, 30.4, 26.3, 21.2. **HRMS (ESI)** calcd. for $C_{29}H_{32}NaO_4$ $[M+Na]^+$: 467.2193, found 467.2195.

syn-diastereomer: Yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.06 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.29 – 7.23 (m, 3H), 5.37 – 5.36 (m, 1H), 4.43 – 4.27 (m, 2H), 4.16 (dd, *J* = 11.9, 9.0 Hz, 1H), 3.02 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.59 (t, *J* = 12.3 Hz, 1H), 2.47 – 2.41 (m, 2H), 2.40 – 2.36 (m, 1H), 2.29 – 2.16 (m, 2H), 2.15 – 2.06 (m, 2H), 1.80 (s, 3H), 1.27 (s, 3H), 1.17 (d, *J* = 8.6 Hz, 1H), 0.84 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 175.7, 166.1, 145.4, 144.2, 136.3, 131.0, 128.9, 128.88, 128.85, 128.5, 128.1, 127.7, 125.2, 119.0, 84.0, 63.5, 46.6, 45.8, 44.7, 40.8, 38.0, 36.1, 31.7, 31.4, 28.7, 26.3, 21.2.

(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-(2-methyl-5-oxo-4-phenyltetrahydrofuran-2-yl)benzoate (30)

Following the general procedure A, the reaction was carried out with (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-acetylbenzoate (0.25 mmol, 133.1 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-(2-methyl-5-oxo-4-phenyltetrahydrofuran-2-yl)benzoate (**43**) was formed in 37% yield (61.7 mg, 1.2:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

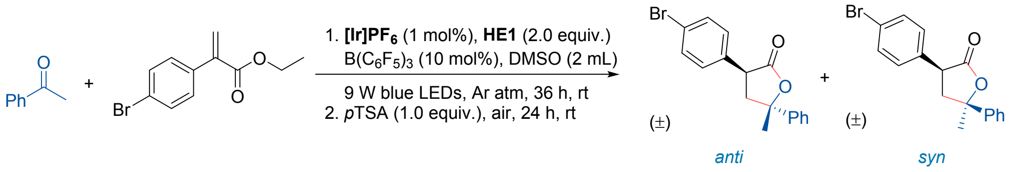


anti-diastereomer: White solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.08 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.31 – 7.26 (m, 3H), 5.43 (d, *J* = 4.9 Hz, 1H), 4.91 – 4.86 (m, 1H), 3.68 (dd, *J* = 13.9, 7.1 Hz, 1H), 3.10 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.60 (t, *J* = 12.7 Hz, 1H), 2.52 – 2.45 (m, 2H), 2.07 – 1.96 (m, 3H), 1.93 (dt, *J* = 13.4, 3.6 Hz, 1H), 1.88 – 1.83 (m, 1H), 1.82 (s, 3H), 1.76 (dd, *J* = 13.6, 10.1 Hz, 1H), 1.64 – 1.47 (m, 7H), 1.42 – 1.10 (m, 11H), 1.08 (s, 3H), 1.07 – 0.95 (m, 4H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.8 Hz, 3H), 0.69 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.1, 165.6, 144.0, 139.6, 136.0, 131.6, 129.1, 128.88, 128.86, 128.6, 128.1, 127.7, 125.4, 122.9, 84.3, 75.1, 56.7, 56.2, 50.1, 46.2, 45.4, 42.4, 39.8, 39.5, 38.2, 37.1, 36.7, 36.2, 35.8, 32.0, 31.9, 30.4, 28.2, 28.0, 27.9, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9. **HRMS (ESI)** calcd. for $C_{45}H_{60}NaO_4$ $[M+Na]^+$: 687.4384, found 687.4381.

syn-diastereomer: White solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.23 (m, 2H), 5.47 – 5.38 (m, 1H), 4.91 – 4.85 (m, 1H), 4.17 (dd, *J* = 11.9, 8.9 Hz, 1H), 3.04 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.60 (t, *J* = 12.4 Hz, 1H), 2.54 – 2.42 (m, 2H), 2.07 – 1.96 (m, 3H), 1.92 (dt, *J* = 13.4, 3.6 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.81 (s, 3H), 1.79 – 1.72 (m, 1H), 1.61 – 1.46 (m, 7H), 1.41 – 1.09 (m, 11H), 1.08 (s, 3H), 1.07 – 0.95 (m, 4H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.7 Hz, 3H), 0.69 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.8, 165.6, 145.4, 139.7, 136.3, 131.4, 129.0, 128.9, 128.8, 128.3, 128.1, 127.7, 125.1, 122.8, 84.1, 75.0, 56.7, 56.2, 50.1, 46.6, 44.7, 42.4, 39.8, 39.5, 38.2, 37.1, 36.7, 36.2, 35.8, 32.0, 31.9, 28.8, 28.2, 28.0, 27.9, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.7, 11.8.

3-(4-Bromophenyl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (31)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 μL), ethyl 2-(4-bromophenyl)acrylate (0.50 mmol, 127.0 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3-(4-bromophenyl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (**29**) was formed in 81% yield (67.0 mg, 1.2:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

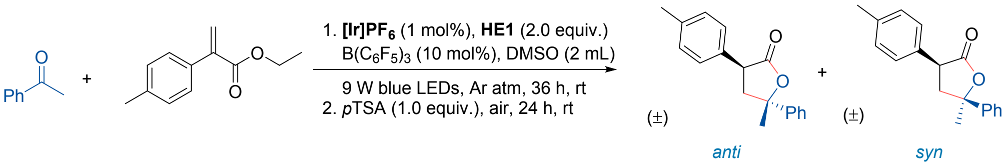


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.51 – 7.40 (m, 6H), 7.37 – 7.32 (m, 1H), 7.18 – 7.10 (m, 2H), 3.66 (dd, *J* = 12.8, 8.2 Hz, 1H), 3.03 (dd, *J* = 12.6, 8.2 Hz, 1H), 2.51 (t, *J* = 12.7 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.8, 143.3, 135.1, 132.0, 129.8, 128.8, 127.9, 124.3, 121.7, 84.7, 45.7, 45.3, 30.2. **HRMS (ESI)** calcd. for $C_{17}H_{15}NaBrO_2$ $[M+Na]^+$: 353.0148, found 353.0145.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.50 – 7.36 (m, 6H), 7.34 – 7.30 (m, 1H), 7.16 – 7.08 (m, 2H), 4.11 (dd, *J* = 11.8, 9.0 Hz, 1H), 2.98 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.56 (t, *J* = 12.3 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.4, 144.8, 135.4, 132.0, 129.8, 128.7, 127.8, 123.9, 121.7, 84.5, 46.1, 44.4, 28.7.

5-Methyl-5-phenyl-3-(p-tolyl)dihydrofuran-2(3H)-one (32)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), ethyl 2-(p-tolyl)acrylate (0.50 mmol, 95.1 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-methyl-5-phenyl-3-(p-tolyl)dihydrofuran-2(3H)-one (**30**) was formed in 86% yield (57.0 mg, 1.2:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

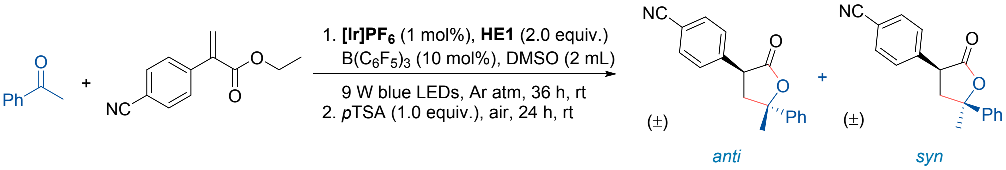


anti-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.48 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 7.21 – 7.10 (m, 4H), 3.66 (dd, *J* = 12.7, 8.3 Hz, 1H), 3.01 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.54 (t, *J* = 12.7 Hz, 1H), 2.33 (s, 3H), 1.80 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.6, 143.7, 137.4, 133.2, 129.5, 128.8, 128.0, 127.8, 124.3, 84.5, 46.0, 45.7, 30.3, 21.0. **HRMS (ESI)** calcd. for $C_{19}H_{18}NaO_2$ [M+Na]$^+$: 289.1199, found 289.1198.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.48 – 7.34 (m, 4H), 7.33 – 7.30 (m, 1H), 7.14 – 7.11 (m, 4H), 4.11 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.96 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.58 (t, *J* = 12.4 Hz, 1H), 2.31 (s, 3H), 1.78 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.2, 145.1, 137.4, 133.5, 129.5, 128.7, 128.0, 127.7, 124.0, 84.3, 46.4, 44.8, 28.7, 21.0.

4-(5-Methyl-2-oxo-5-phenyltetrahydrofuran-3-yl)benzonitrile (33)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), ethyl 2-(4-cyanophenyl)acrylate (0.50 mmol, 100.5 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 4-(5-methyl-2-oxo-5-phenyltetrahydrofuran-3-yl)benzonitrile (**31**) was formed in 93% yield (64.5 mg, 1.5:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

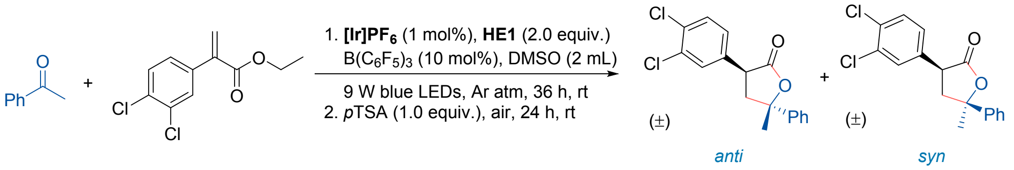


anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.67 – 7.62 (m, 2H), 7.46 – 7.37 (m, 7H), 3.76 (dd, *J* = 12.8, 8.2 Hz, 1H), 3.07 (dd, *J* = 12.5, 8.2 Hz, 1H), 2.55 (t, *J* = 12.7 Hz, 1H), 1.83 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 175.0, 143.0, 141.4, 132.5, 129.0, 128.9, 128.1, 124.2, 118.4, 111.7, 84.9, 46.1, 45.0, 30.2. **HRMS (ESI)** calcd. for $C_{18}H_{15}NaNO_2$ [M+Na]$^+$: 300.0995, found 300.0997.

syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.62 – 7.60 (m, 2H), 7.45 – 7.34 (m, 7H), 4.21 (dd, *J* = 11.6, 9.0 Hz, 1H), 3.02 (dd, *J* = 12.9, 9.0 Hz, 1H), 2.60 (t, *J* = 12.5 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 174.6, 144.5, 141.6, 132.6, 129.0, 128.8, 128.0, 123.9, 118.4, 111.7, 84.8, 46.5, 44.1, 28.7.

3-(3,4-Dichlorophenyl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (34)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 μL), ethyl 2-(3,4-dichlorophenyl)acrylate (0.50 mmol, 122.0 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3-(3,4-dichlorophenyl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (**32**) was formed in 89% yield (71.3 mg, 1.4:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

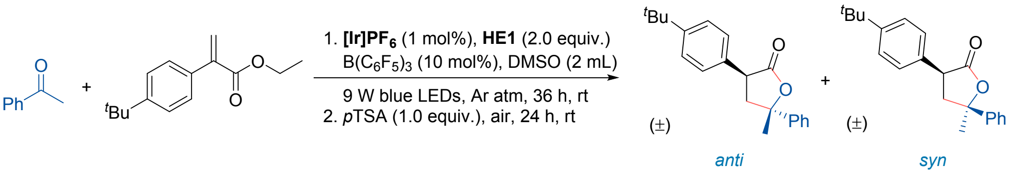


anti-diastereomer: white solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 – 7.36 (m, 7H), 7.17 – 7.10 (m, 1H), 3.65 (dd, J = 12.8, 8.4 Hz, 1H), 3.04 (dd, J = 12.2, 8.6 Hz, 1H), 2.51 (t, J = 12.7 Hz, 1H), 1.82 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 175.4, 143.0, 136.1, 132.9, 131.9, 130.7, 130.2, 128.9, 128.1, 127.6, 124.2, 84.8, 45.3, 45.1, 30.2. **HRMS (ESI)** calcd. for $C_{17}H_{14}NaCl_2O_2$ [M+Na]$^+$: 343.0263, found 343.0264.

syn-diastereomer: white solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46 – 7.26 (m, 7H), 7.10 (dd, J = 8.3, 2.2 Hz, 1H), 4.11 (dd, J = 11.7, 9.0 Hz, 1H), 2.99 (dd, J = 12.8, 9.0 Hz, 1H), 2.56 (t, J = 12.3 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 175.0, 144.6, 136.4, 132.9, 131.9, 130.8, 130.2, 128.8, 127.9, 127.5, 123.9, 84.7, 45.7, 44.2, 28.7.

3-(4-(tert-Butyl)phenyl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (35)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 μL), ethyl 2-(4-(tert-butyl)phenyl)acrylate (0.50 mmol, 116.1 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3-(4-(tert-butyl)phenyl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (**33**) was formed in 89% yield (68.4 mg, 1.2:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

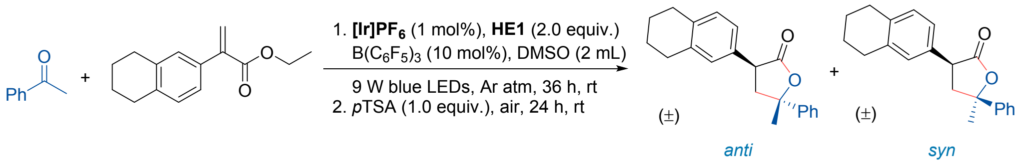


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.47 – 7.31 (m, 7H), 7.18 (d, J = 8.2 Hz, 2H), 3.67 (dd, J = 12.7, 8.3 Hz, 1H), 3.01 (dd, J = 12.7, 8.3 Hz, 1H), 2.55 (t, J = 12.7 Hz, 1H), 1.80 (s, 3H), 1.30 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.7, 150.6, 143.7, 133.2, 128.8, 127.80, 127.77, 125.8, 124.3, 84.5, 45.9, 45.6, 34.5, 31.3, 30.4. **HRMS (ESI)** calcd. for $C_{21}H_{24}NaO_2$ $[M+Na]^+$: 331.1669, found 331.1669.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 – 7.29 (m, 7H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.12 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.95 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.59 (t, *J* = 12.4 Hz, 1H), 1.78 (s, 3H), 1.28 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.3, 150.6, 145.1, 133.5, 128.7, 127.8, 127.7, 125.8, 124.0, 84.4, 46.3, 44.8, 34.5, 31.3, 28.7.

5-Methyl-5-phenyl-3-(5,6,7,8-tetrahydronaphthalen-2-yl)dihydrofuran-2(3H)-one (36)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), 2-(5,6,7,8-tetrahydronaphthalen-2-yl)hex-1-en-3-one (0.50 mmol, 115.0 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 5-methyl-5-phenyl-3-(5,6,7,8-tetrahydronaphthalen-2-yl)dihydrofuran-2(3H)-one (**34**) was formed in 52% yield (39.8 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

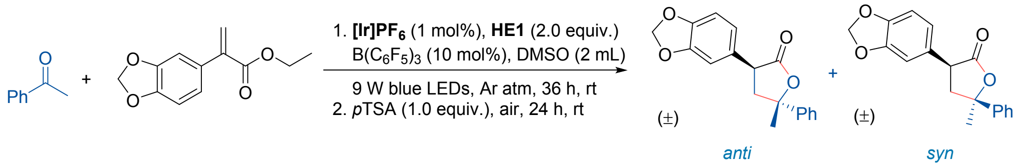


anti-diastereomer: yellowish oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.29 (m, 5H), 7.07 – 6.91 (m, 3H), 3.61 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.99 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.77 – 2.70 (m, 4H), 2.54 (t, *J* = 12.7 Hz, 1H), 1.80 (s, 3H), 1.79 – 1.75 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.8, 143.7, 137.7, 136.7, 133.3, 129.6, 128.8, 128.7, 127.8, 125.2, 124.3, 84.5, 46.1, 45.8, 30.3, 29.4, 29.1, 23.1, 23.1. **HRMS (ESI)** calcd. for $C_{21}H_{22}NaO_2$ $[M+Na]^+$: 329.1512, found 329.1512.

syn-diastereomer: white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.35 (m, 4H), 7.33 – 7.30 (m, 1H), 7.03 – 6.88 (m, 3H), 4.06 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.94 (dd, *J* = 12.8, 9.0 Hz, 1H), 2.71 – 2.69 (m, 4H), 2.58 (t, *J* = 12.3 Hz, 1H), 1.77 (s, 3H), 1.77 – 1.73 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.4, 145.2, 137.7, 136.7, 133.5, 129.6, 128.8, 128.6, 127.6, 125.2, 124.0, 84.3, 46.5, 44.9, 29.4, 29.1, 28.7, 23.1, 23.1.

3-(Benzo[d][1,3]dioxol-5-yl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (37)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), ethyl 2-(benzo[d][1,3]dioxol-5-yl)acrylate (0.50 mmol, 110.0 mg), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), $[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3-(benzo[d][1,3]dioxol-5-yl)-5-methyl-5-phenyldihydrofuran-2(3H)-one (**35** was formed in 42% yield (30.8 mg, 1.1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

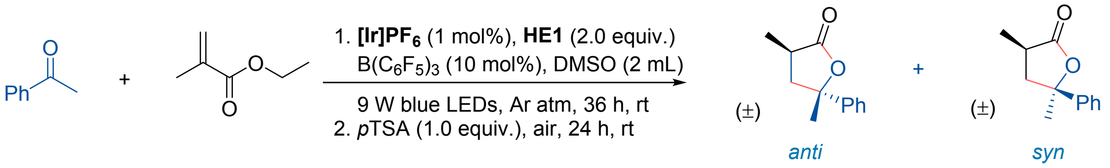


anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.57 – 7.29 (m, 5H), 6.91 – 6.61 (m, 3H), 5.94 (d, *J* = 1.4 Hz, 2H), 3.61 (dd, *J* = 12.7, 8.3 Hz, 1H), 3.00 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.50 (t, *J* = 12.7 Hz, 1H), 1.80 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.4, 148.1, 147.1, 143.5, 129.8, 128.8, 127.8, 124.3, 121.5, 108.46, 108.45, 101.2, 84.5, 46.1, 45.7, 30.3. **HRMS (ESI)** calcd. for $C_{18}H_{16}NaO_4$ [M+Na]$^+$: 319.0941, found 319.0940.

syn-diastereomer: yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.50 – 7.28 (m, 5H), 6.82 – 6.62 (m, 3H), 5.92 (s, 2H), 4.06 (dd, *J* = 11.9, 9.0 Hz, 1H), 2.95 (dd, *J* = 12.9, 9.0 Hz, 1H), 2.54 (t, *J* = 12.4 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.1, 148.1, 147.1, 145.0, 130.1, 128.7, 127.7, 123.9, 121.6, 108.5, 108.4, 101.2, 84.3, 46.5, 44.9, 28.6.

3,5-dimethyl-5-phenyldihydrofuran-2(3H)-one (38)

Following the general procedure A, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), ethyl methacrylate (0.50 mmol, 62.3 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3,5-dimethyl-5-phenyldihydrofuran-2(3H)-one (**38**) was formed in 35% yield (16.8 mg, 1.6:1 dr). The diastereomers were separated by column chromatography (SiO$_2$) for analytical purposes.

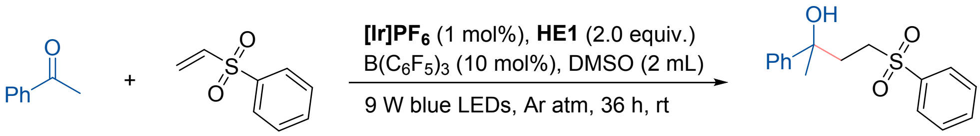


anti-diastereomer: colourless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.37 (m, 4H), 7.29 (m, 1H), 2.77 (dd, *J* = 12.5, 8.2 Hz, 1H), 2.51 (m, 1H), 2.03 (t, *J* = 12.3 Hz, 1H), 1.73 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 179.1, 144.0, 128.6, 127.6, 124.2, 84.5, 45.1, 35.0, 30.3, 14.7.

syn-diastereomer: colourless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.43 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 2.93 (m, 1H), 2.70 (dd, *J* = 12.6, 8.8 Hz, 1H), 2.14 – 2.04 (t, *J* = 10.9 Hz, 1H), 1.67 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 178.7, 145.4, 128.6, 127.5, 123.9, 84.4, 44.1, 35.3, 28.8, 15.4.

2-Phenyl-4-(phenylsulfonyl)butan-2-ol (39)

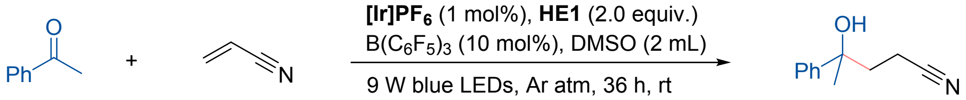
Following the general procedure B, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), (vinylsulfonyl)benzene (0.50 mmol, 66.4 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 2-phenyl-4-(phenylsulfonyl)butan-2-ol (**39**) was formed in 34% yield (24.5 mg).



Yellowish solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.89 – 7.77 (m, 2H), 7.67 – 7.61 (m, 1H), 7.55 – 7.52 (m, 2H), 7.39 – 7.28 (m, 4H), 7.25 – 7.23 (m, 1H), 3.27 – 3.14 (m, 1H), 2.89 – 2.84 (m, 1H), 2.26 – 2.18 (m, 2H), 1.83 (s, 1H), 1.57 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 145.7, 139.2, 133.6, 129.3, 128.5, 128.0, 127.1, 124.5, 73.4, 52.0, 36.3, 31.1. **HRMS (ESI)** calcd. for $C_{16}H_{18}NaO_3S$ [M+Na]$^+$: 313.0869, found 313.0870.

4-Hydroxy-4-phenylpentanenitrile (40)

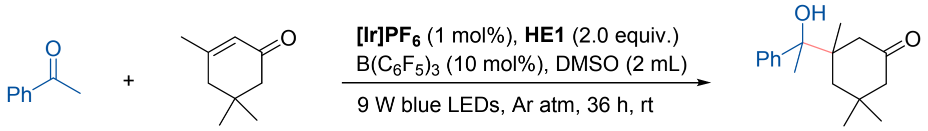
Following the general procedure B, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), acrylonitrile (0.50 mmol, 32.9 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 4-hydroxy-4-phenylpentanenitrile (**40**) was formed in 49% yield (21.3 mg).



Colourless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 2.45 – 2.34 (m, 1H), 2.16 – 2.13 (m, 2H), 2.10 – 2.04 (m, 1H), 2.00 (s, 1H), 1.61 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 145.6, 128.6, 127.3, 124.6, 120.2, 73.5, 39.6, 30.6, 12.1. **HRMS (ESI)** calcd. for $C_{11}H_{14}NO_4$ [M+H]$^+$: 176.1070, found 176.1073.

3-(1-Hydroxy-1-phenylethyl)-3,5,5-trimethylcyclohexan-1-one (41)

Following the general procedure B, the reaction was carried out with acetophenone (0.25 mmol, 29.1 µL), 3,5,5-trimethylcyclohex-2-en-1-one (0.50 mmol, 74.9 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.50 mmol, 164.6 mg), tris(pentafluorophenyl)boron (10.0 mol%, 12.8 mg), [Ir(dtbbpy)[dF(CF$_3$)ppy]$_2$]PF$_6$ (1.0 mol%, 2.8 mg) and DMSO (2.0 mL). The desired product 3-(1-Hydroxy-1-phenylethyl)-3,5,5-trimethylcyclohexan-1-one (**41**) was formed in 72 % yield (47.0 mg).

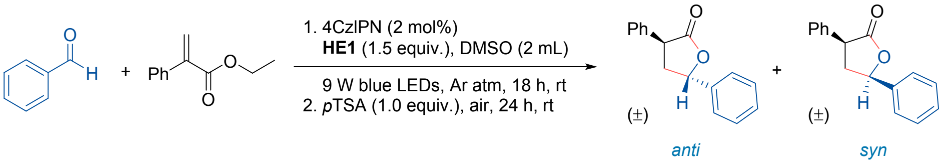


diastereomer-1: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.39 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 2.83 (d, J = 13.6 Hz, 1H), 2.24 (dd, J = 14.1, 4.5 Hz, 2H), 2.06 (d, J = 13.6 Hz, 1H), 1.71 (d, J = 13.7 Hz, 1H), 1.64 (s, 3H), 1.50 (d, J = 13.9 Hz, 1H), 1.10 (s, 3H), 1.03 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 213.7, 144.9, 127.4, 127.0, 78.6, 53.3, 46.8, 45.2, 43.3, 35.0, 34.6, 29.3, 24.7, 23.4. **HRMS (ESI)** calcd. for $C_{17}H_{24}NaO_2$ [M+Na]$^+$: 283.1669, found 283.1665.

diastereomer-2: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.29 – 7.26 (m, 1H), 2.76 (d, J = 13.5 Hz, 1H), 2.22 (d, J = 13.5 Hz, 1H), 2.17 (d, J = 13.5 Hz, 2H), 2.04 (d, J = 13.4 Hz, 1H), 1.69 (s, 1H), 1.58 (s, 3H), 1.09 – 1.05 (m, 1H), 1.04 (s, 3H), 1.00 (s, 3H), 0.92 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 213.5, 145.2, 127.4, 127.3, 126.9, 78.5, 53.5, 47.1, 45.5, 43.1, 35.0, 34.6, 28.9, 24.9, 23.3.

3,5-Diphenyldihydrofuran-2(3H)-one (43)

Following the general procedure C, the reaction was carried out with benzaldehyde (0.25 mmol, 25.4 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.375 mmol, 123.4 mg), 4CzIPN (5.0 mol%, 3.9 mg) and DMSO (2.0 mL). The desired product 3,5-diphenyldihydrofuran-2(3H)-one (**43**) was formed in 97% yield (57.7 mg, 1.6:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

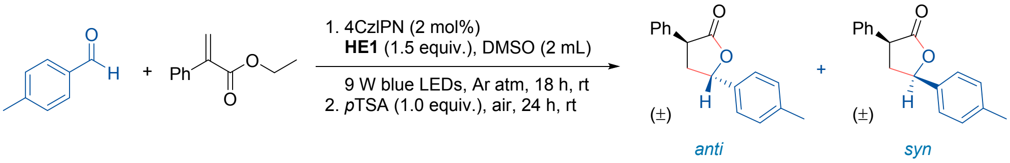


anti-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 – 7.35 (m, 7H), 7.35 – 7.29 (m, 3H), 5.69 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.95 (t, *J* = 8.4 Hz, 1H), 2.88 – 2.83 (m, 1H), 2.74 – 2.69 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 177.0, 139.4, 136.6, 129.1, 128.9, 128.4, 127.7, 125.1, 78.8, 45.2, 39.3. **HRMS (ESI)** calcd. for $C_{16}H_{14}NaO_2$ $[M+Na]^+$: 261.0886, found 261.0884.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 – 7.36 (m, 6H), 7.35 – 7.28 (m, 3H), 7.25 (s, 1H), 5.51 (dd, *J* = 10.8, 5.5 Hz, 1H), 4.04 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.09 – 3.05 (m, 1H), 2.42 – 2.36 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.3, 138.7, 136.1, 128.9, 128.9, 128.7, 128.1, 127.8, 125.6, 79.1, 47.6, 40.5.

3-Phenyl-5-(p-tolyl)dihydrofuran-2(3H)-one (44)

Following the general procedure C, the reaction was carried out with 4-methylbenzaldehyde (0.25 mmol, 29.5 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.375 mmol, 123.4 mg), 4CzIPN (5.0 mol%, 3.9 mg) and DMSO (2.0 mL). The desired product 3-phenyl-5-(p-tolyl)dihydrofuran-2(3H)-one (**44**) was formed in 94% yield (59.3 mg, 1.4:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

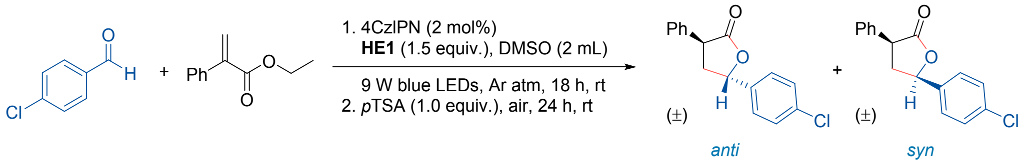


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.35 (m, 2H), 7.31 – 7.29 (m, 3H), 7.26 – 7.20 (m, 4H), 5.65 (dd, *J* = 7.4, 5.3 Hz, 1H), 3.94 (t, *J* = 8.3 Hz, 1H), 2.83 – 2.79 (m, 1H), 2.71 – 2.67 (m, 1H), 2.37 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 177.1, 138.3, 136.7, 136.4, 129.5, 129.0, 127.8, 127.7, 125.2, 78.9, 45.3, 39.3, 21.1. **HRMS (ESI)** calcd. for $C_{17}H_{16}NaO_2$ $[M+Na]^+$: 275.1043, found 275.1042.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 – 7.36 (m, 2H), 7.33 – 7.29 (m, 5H), 7.22 (d, *J* = 7.7 Hz, 2H), 5.47 (dd, *J* = 10.8, 5.5 Hz, 1H), 4.02 (dd, *J* = 12.9, 8.4 Hz, 1H), 3.05 – 3.01 (m, 1H), 2.41 – 2.35 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.4, 138.6, 136.2, 135.7, 129.5, 128.9, 128.1, 127.7, 125.7, 79.2, 47.7, 40.5, 21.2.

5-(4-Chlorophenyl)-3-phenyldihydrofuran-2(3H)-one (45)

Following the general procedure C, the reaction was carried out with 4-chlorobenzaldehyde (0.25 mmol, 35.1 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.375 mmol, 123.4 mg), 4CzIPN (5.0 mol%, 3.9 mg) and DMSO (2.0 mL). The desired product 5-(4-chlorophenyl)-3-phenyldihydrofuran-2(3H)-one (**45**) was formed in 90% yield (61.2 mg, 1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

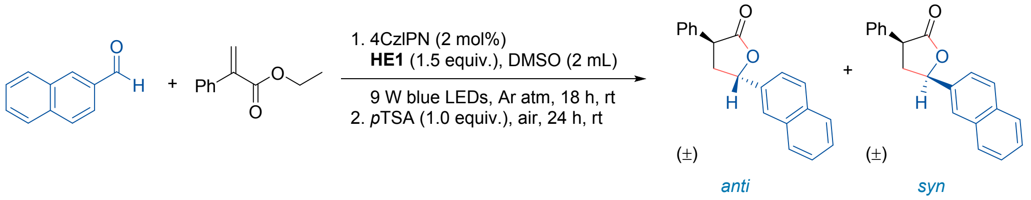


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 – 7.38 (m, 4H), 7.34 – 7.30 (m, 5H), 5.65 (t, J = 6.6 Hz, 1H), 3.93 (t, J = 8.2 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.69 – 2.64 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.6, 137.9, 136.3, 134.4, 129.1, 129.1, 127.8, 127.7, 126.5, 78.1, 45.2, 39.2. **HRMS (ESI)** calcd. for $C_{16}H_{13}NaClO_2$ $[M+Na]^+$: 295.0496, found 295.0495.

syn-diastereomer: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.44 – 7.29 (m, 8H), 7.26 (s, 1H), 5.48 (dd, J = 10.7, 5.6 Hz, 1H), 4.04 (dd, J = 12.6, 8.3 Hz, 1H), 3.09 – 3.04 (m, 1H), 2.34 (q, J = 12.5, 11.8 Hz, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.0, 137.3, 135.9, 134.6, 129.1, 129.0, 128.1, 127.9, 126.9, 78.3, 47.5, 40.4.

5-(Naphthalen-2-yl)-3-phenyldihydrofuran-2(3H)-one (46)

Following the general procedure C, the reaction was carried out with 2-naphthaldehyde (0.25 mmol, 39.0 mg), ethyl 2-phenylacrylate (0.50 mmol, 89 μL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.375 mmol, 123.4 mg), 4CzIPN (5.0 mol%, 3.9 mg) and DMSO (2.0 mL). The desired product 5-(naphthalen-2-yl)-3-phenyldihydrofuran-2(3H)-one (**46**) was formed in 91% yield (65.5) mg, 1:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

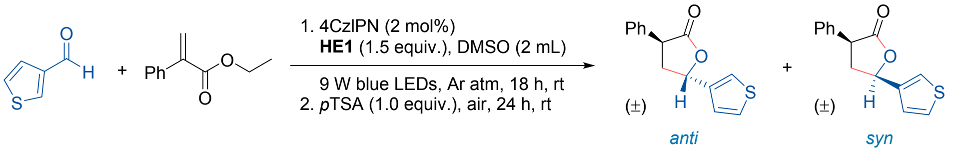


anti-diastereomer: gray solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.96 – 7.82 (m, 4H), 7.53 – 7.49 (m, 2H), 7.46 – 7.27 (m, 6H), 5.83 (dd, J = 7.5, 5.2 Hz, 1H), 3.97 (t, J = 8.4 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.80 – 2.76 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 177.1, 136.7, 136.6, 133.2, 133.1, 129.1, 129.0, 128.1, 127.8, 127.8, 126.7, 126.5, 124.0, 122.8, 78.9, 45.1, 39.2. **HRMS (ESI)** calcd. for $C_{14}H_{12}NaO_3$ $[M+Na]^+$: 311.1043, found 311.1041.

syn-diastereomer: Colourless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.96 – 7.78 (m, 4H), 7.55 – 7.45 (m, 3H), 7.35 (m, 5H), 5.66 (dd, J = 10.8, 5.7 Hz, 1H), 4.07 (dd, J = 12.8, 8.5 Hz, 1H), 3.12 (m, 1H), 2.54 – 2.40 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 176.4, 136.1, 136.1, 133.4, 133.2, 128.9, 128.9, 128.2, 128.1, 127.8, 127.8, 126.7, 126.6, 124.8, 123.0, 79.3, 47.6, 40.5.

3-Phenyl-5-(thiophen-3-yl)dihydrofuran-2(3H)-one (47)

Following the general procedure C, the reaction was carried out with thiophene-3-carbaldehyde (0.25 mmol, 21.9 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.375 mmol, 123.4 mg), 4CzlPN (5.0 mol%, 3.9 mg) and DMSO (2.0 mL). The desired product 3-phenyl-5-(thiophen-3-yl)dihydrofuran-2(3H)-one (**47**) was formed in 61% yield (37.4 mg, 1.4:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

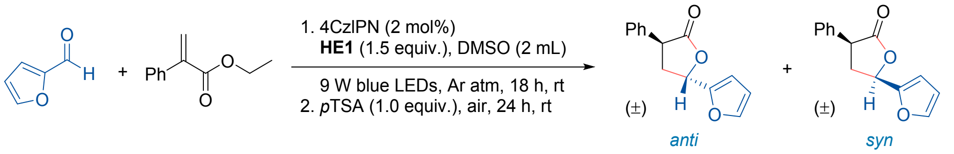


anti-diastereomer: white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47 – 7.36 (m, 3H), 7.36 – 7.19 (m, 5H), 7.10 (dd, J = 5.0, 1.4 Hz, 1H), 5.74 (dd, J = 7.3, 4.9 Hz, 1H), 3.95 (t, J = 8.7 Hz, 1H), 2.84 – 2.75 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.7, 140.5, 136.5, 129.0, 127.8, 127.7, 127.3, 125.1, 121.7, 75.9, 45.2, 38.3. **HRMS (ESI)** calcd. for $C_{14}H_{12}NaO_2S$ $[M+Na]^+$: 267.0450, found 267.0448.

syn-diastereomer: yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.29 (m, 6H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.16 – 7.10 (m, 1H), 5.65 – 5.53 (m, 1H), 4.04 – 4.00 (m, 1H), 3.10 – 3.01 (m, 1H), 2.51 – 2.39 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.1, 139.6, 136.1, 128.9, 128.1, 127.8, 127.1, 125.2, 122.4, 75.7, 47.4, 39.5.

5-(Furan-3-yl)-3-phenyldihydrofuran-2(3H)-one (48)

Following the general procedure C, the reaction was carried out with furan-2-carbaldehyde (0.25 mmol, 20.7 µL), ethyl 2-phenylacrylate (0.50 mmol, 89 µL), diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (0.375 mmol, 123.4 mg), 4CzlPN (5.0 mol%, 3.9 mg) and DMSO (2.0 mL). The desired product 5-(furan-3-yl)-3-phenyldihydrofuran-2(3H)-one (**48**) was formed in 72% yield (41.1 mg, 1.4:1 dr). The diastereomers were separated by column chromatography (SiO_2) for analytical purposes.

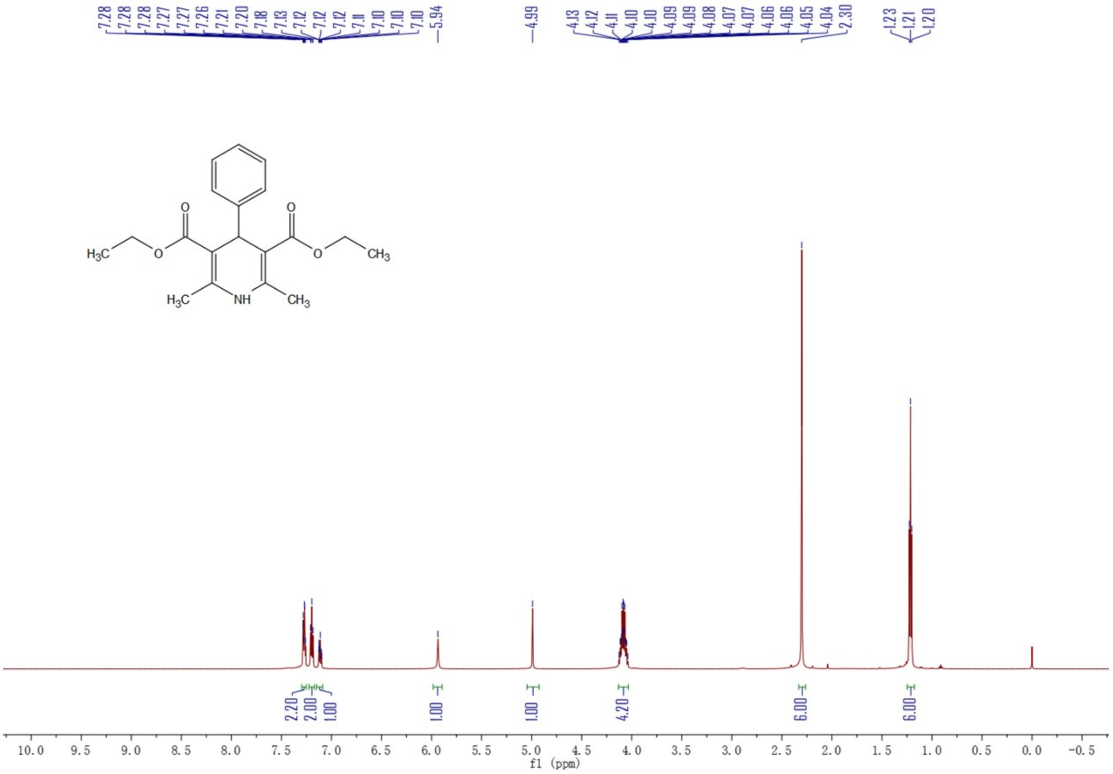


anti-diastereomer: Colourless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 1.8 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.30 (m, 3H), 6.45 (d, *J* = 3.3 Hz, 1H), 6.40 – 6.39 (m, 1H), 5.62 (dd, *J* = 8.0, 4.1 Hz, 1H), 4.17 (t, *J* = 9.2 Hz, 1H), 2.89 – 2.93 (m, 1H), 2.76 – 2.69 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.6, 151.2, 143.5, 136.7, 129.0, 127.8, 127.7, 110.6, 109.3, 72.4, 45.4, 35.5. **HRMS (ESI)** calcd. for $C_{14}H_{12}NaO_3$ $[M+Na]^+$: 251.0679, found 251.0678.

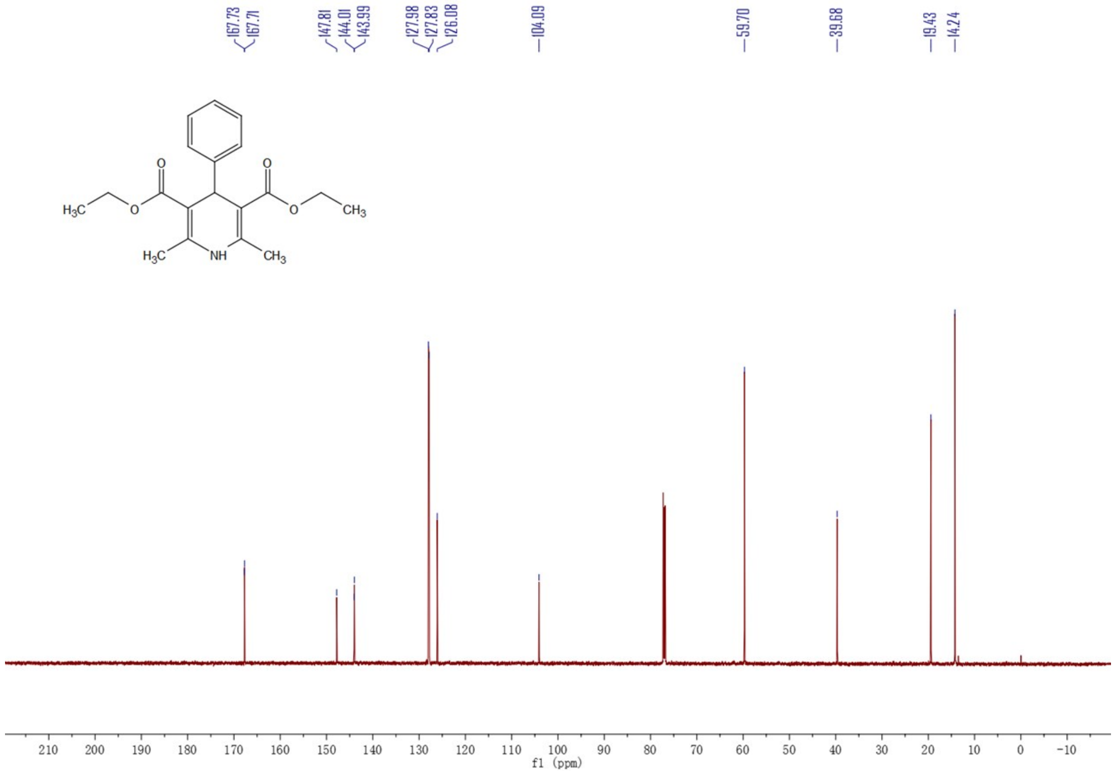
syn-diastereomer: yellowish oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.49 (d, J = 1.8 Hz, 1H), 7.44 – 7.27 (m, 5H), 6.50 (d, J = 3.3 Hz, 1H), 6.41 (dd, J = 3.3, 1.8 Hz, 1H), 5.50 (dd, J = 10.7, 5.9 Hz, 1H), 3.99 (dd, J = 12.5, 8.8 Hz, 1H), 2.94 (m, 1H), 2.80 – 2.74 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.7, 150.0, 143.8, 136.2, 128.9, 128.2, 127.8, 110.6, 110.2, 72.3, 47.1, 35.8.

10. NMR Spectra

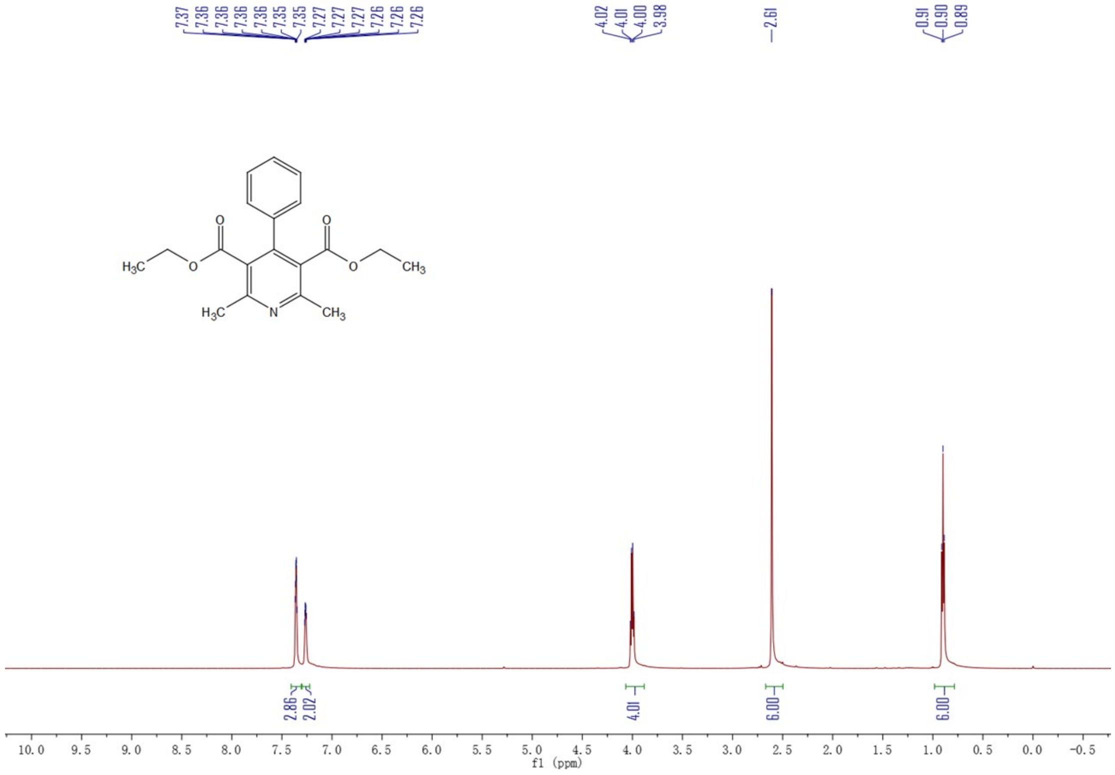
^{1}H NMR (600 MHz, $CDCl_3$) of **HE1**



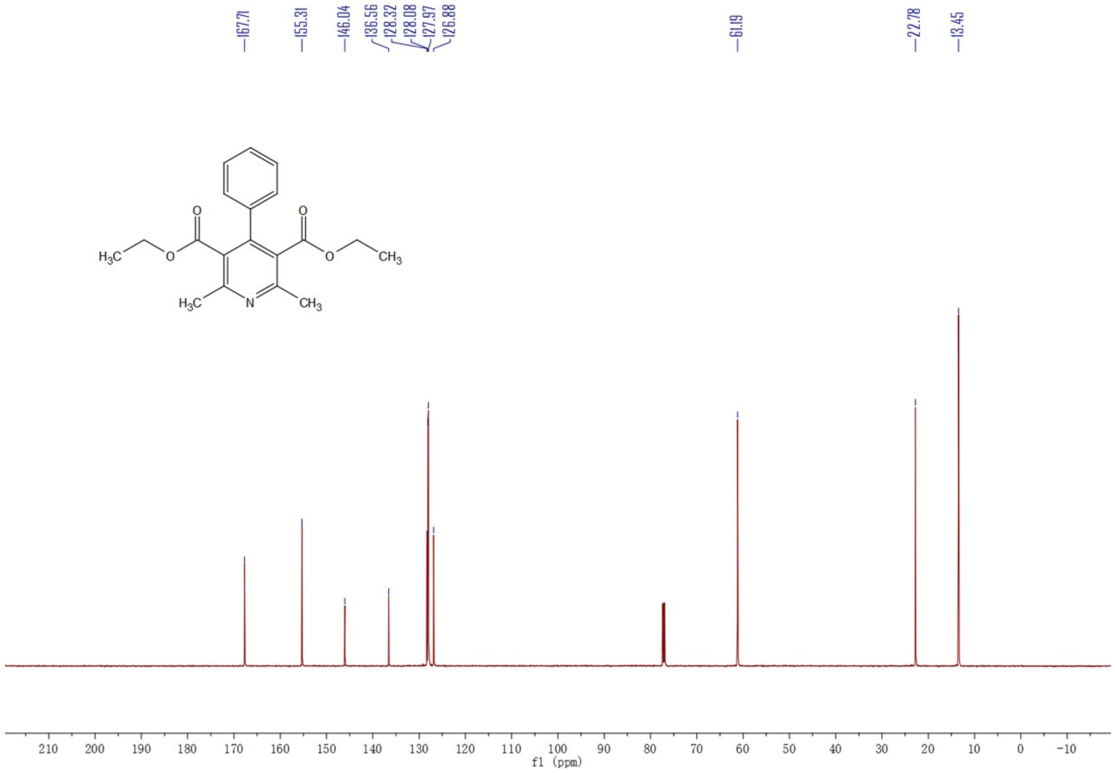
^{13}C NMR (151 MHz, $CDCl_3$) of **HE1**



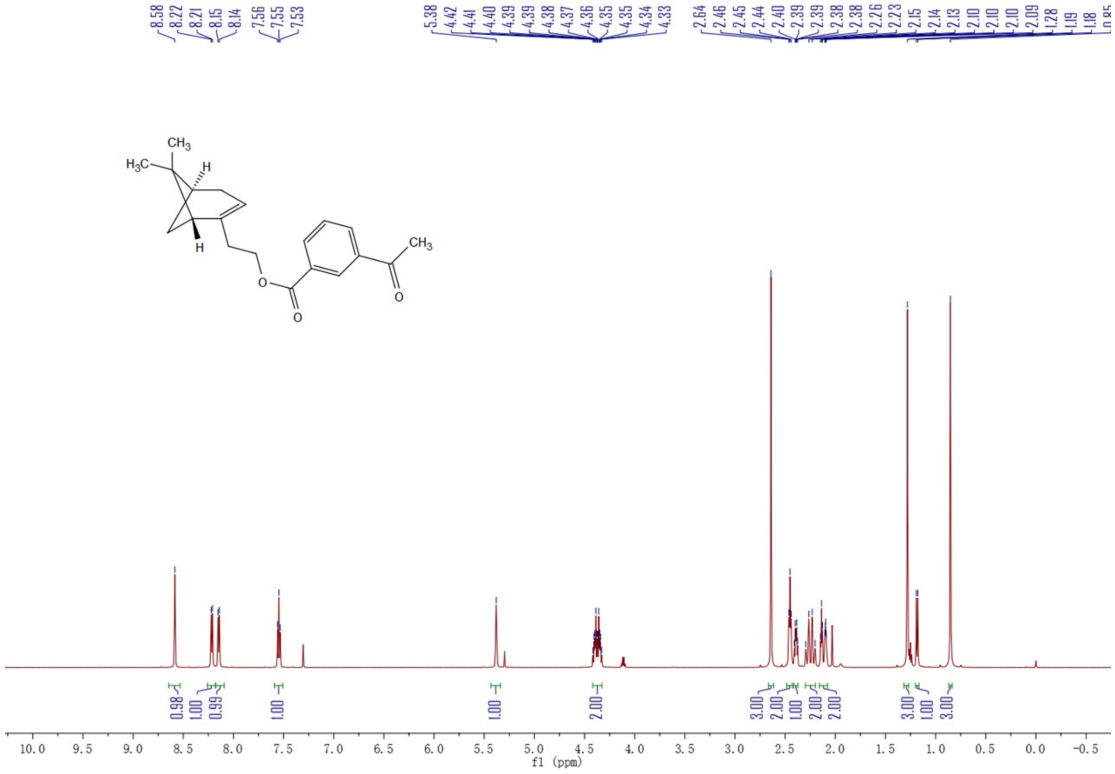
^{1}H NMR (600 MHz, $CDCl_3$) of **OxHE1**



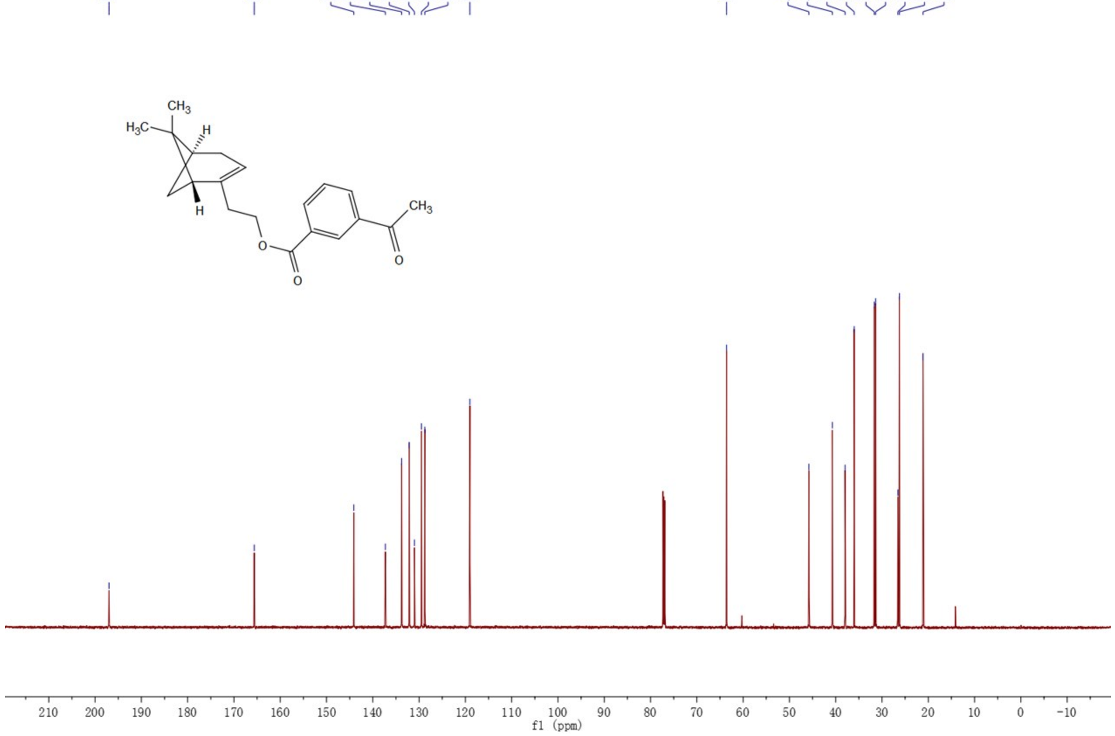
^{13}C NMR (151 MHz, $CDCl_3$) of **OxHE1**



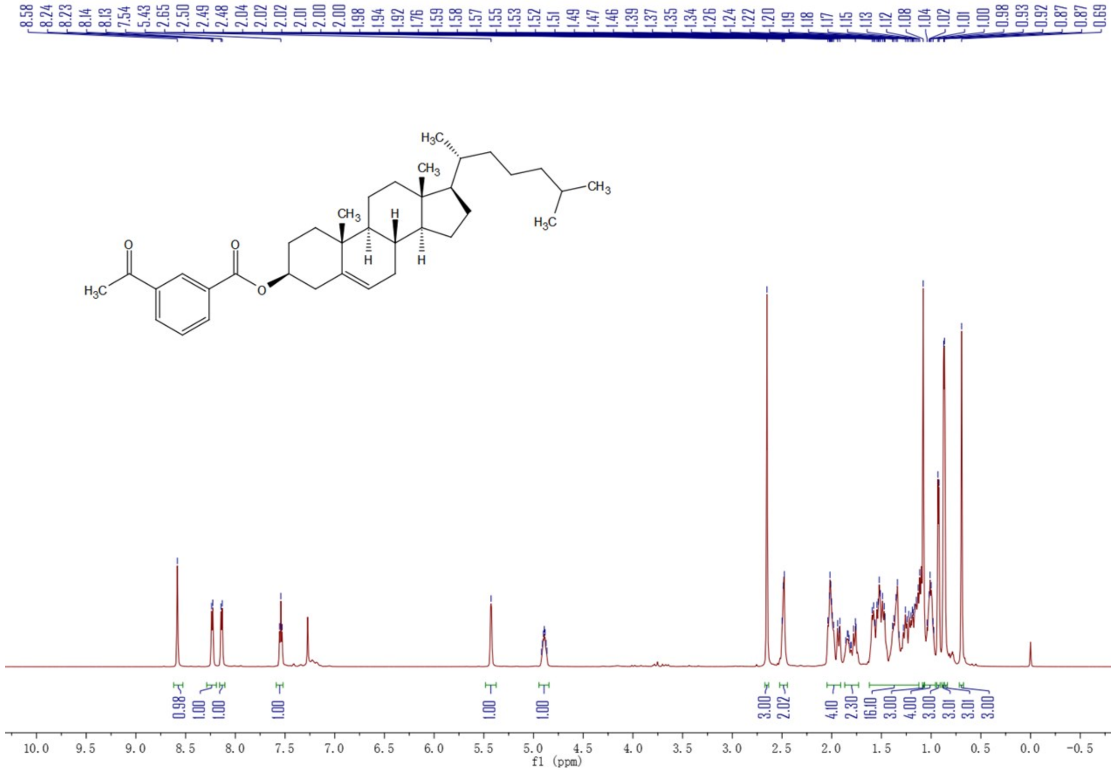
^{1}H NMR (600 MHz, CDCl$_3$) of **a**



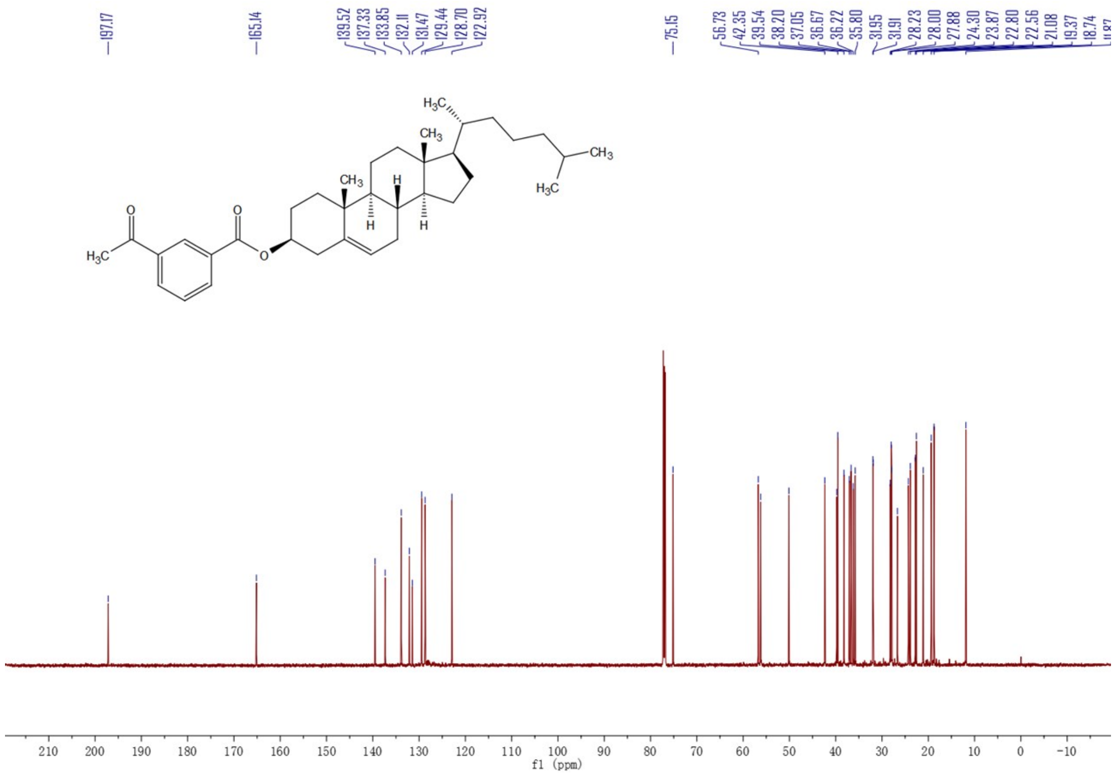
^{13}C NMR (151 MHz, CDCl$_3$) of **a**



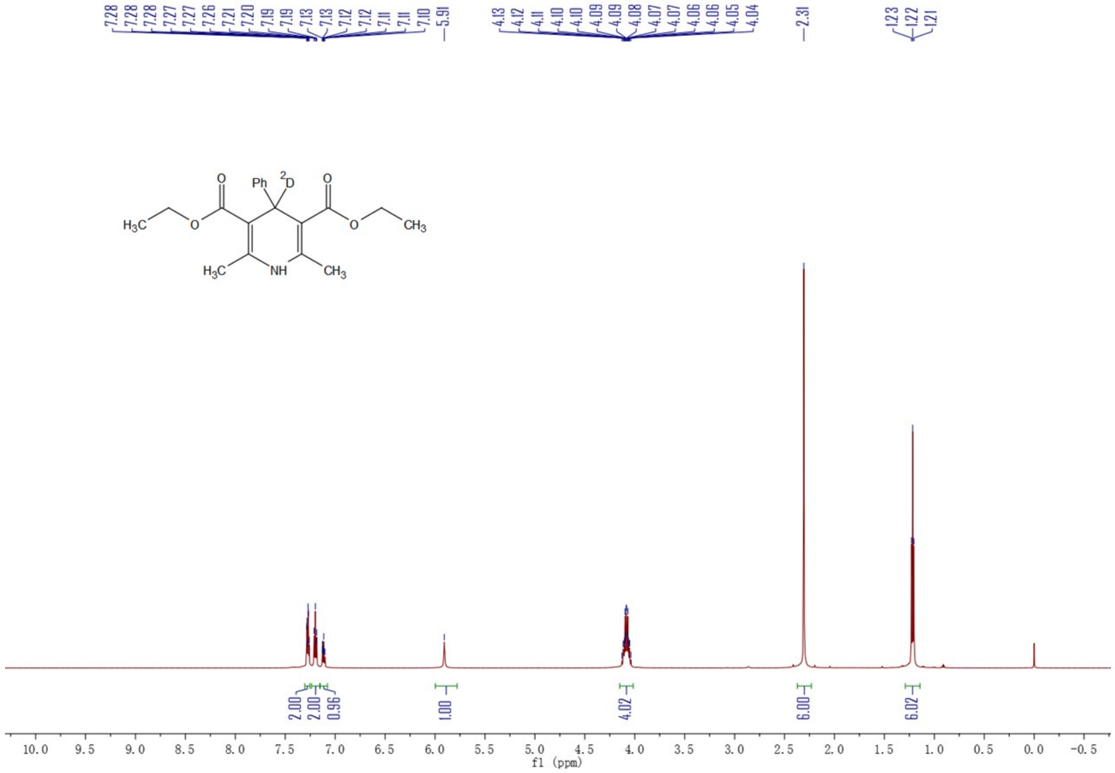
^{1}H NMR (600 MHz, CDCl$_3$) of **b**



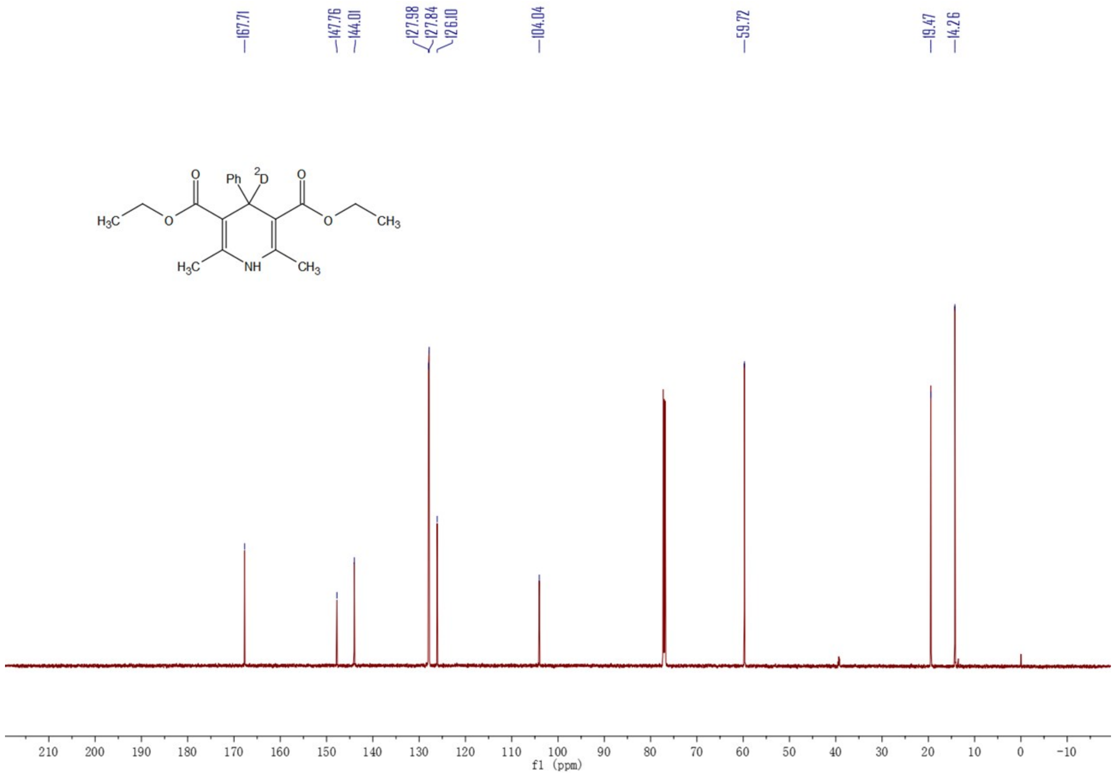
^{13}C NMR (151 MHz, CDCl$_3$) of **b**



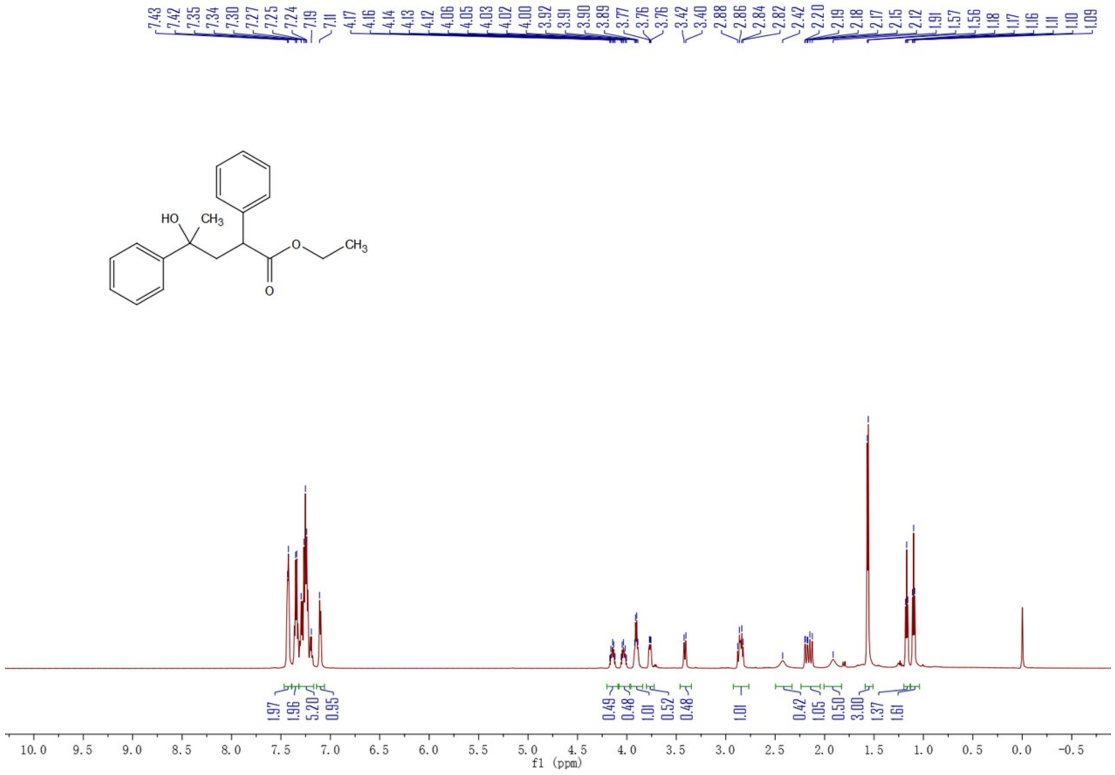
^{1}H NMR (600 MHz, CDCl$_3$) of **HE4**



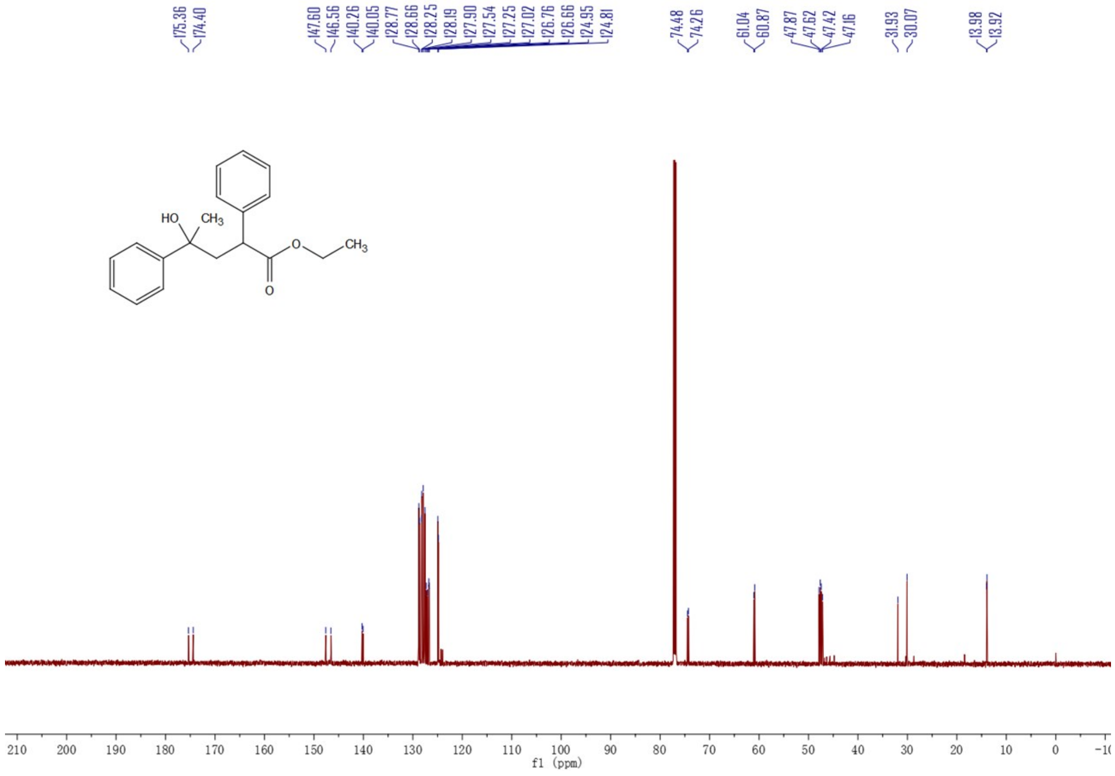
^{13}C NMR (151 MHz, CDCl$_3$) of **HE4**



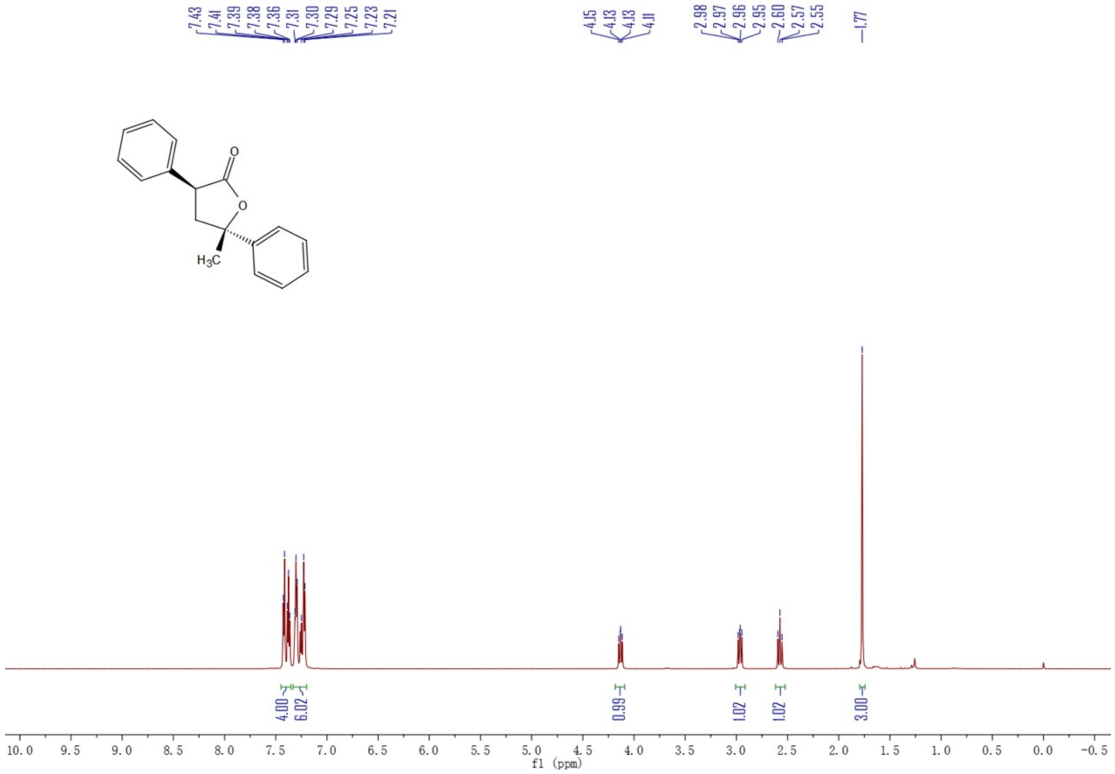
^{1}H NMR (600 MHz, $CDCl_3$) of **3**



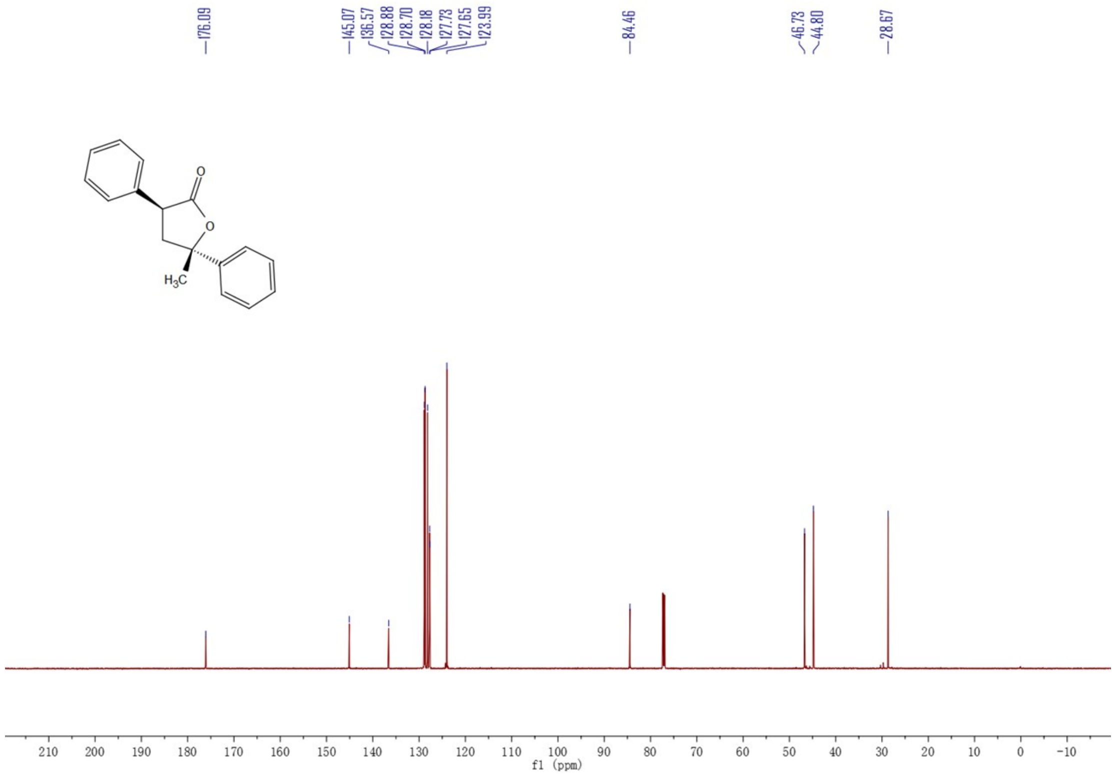
^{13}C NMR (151 MHz, $CDCl_3$) of **3**



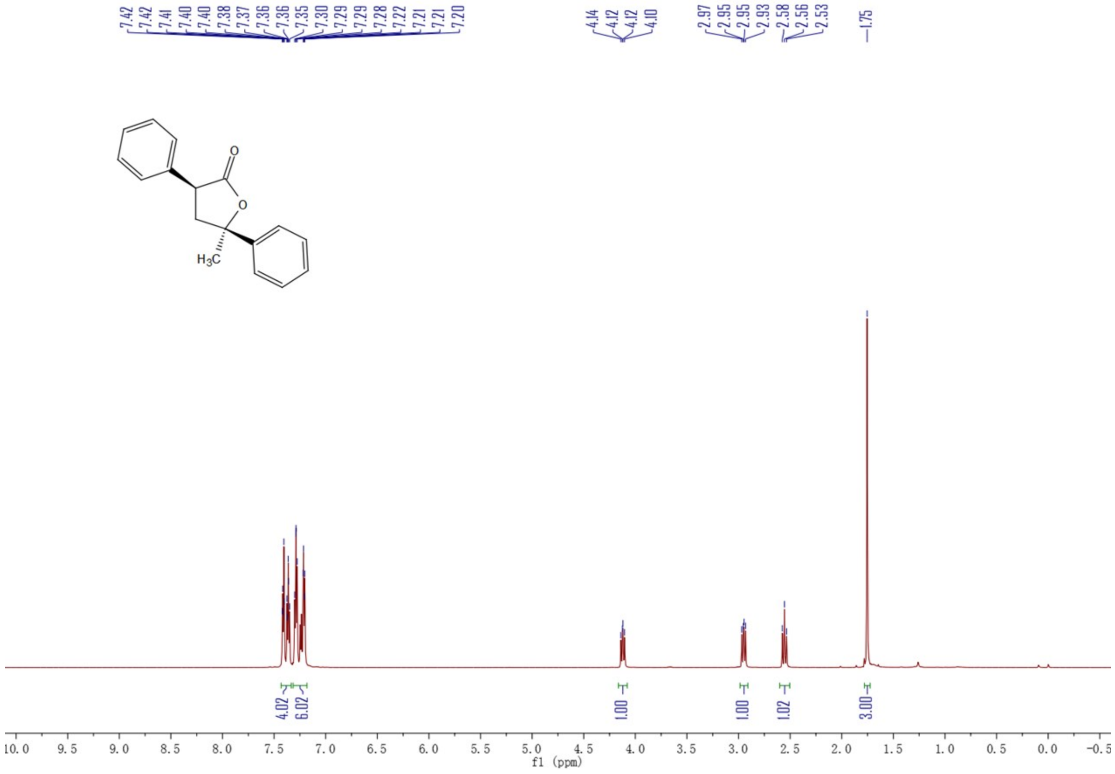
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**4**



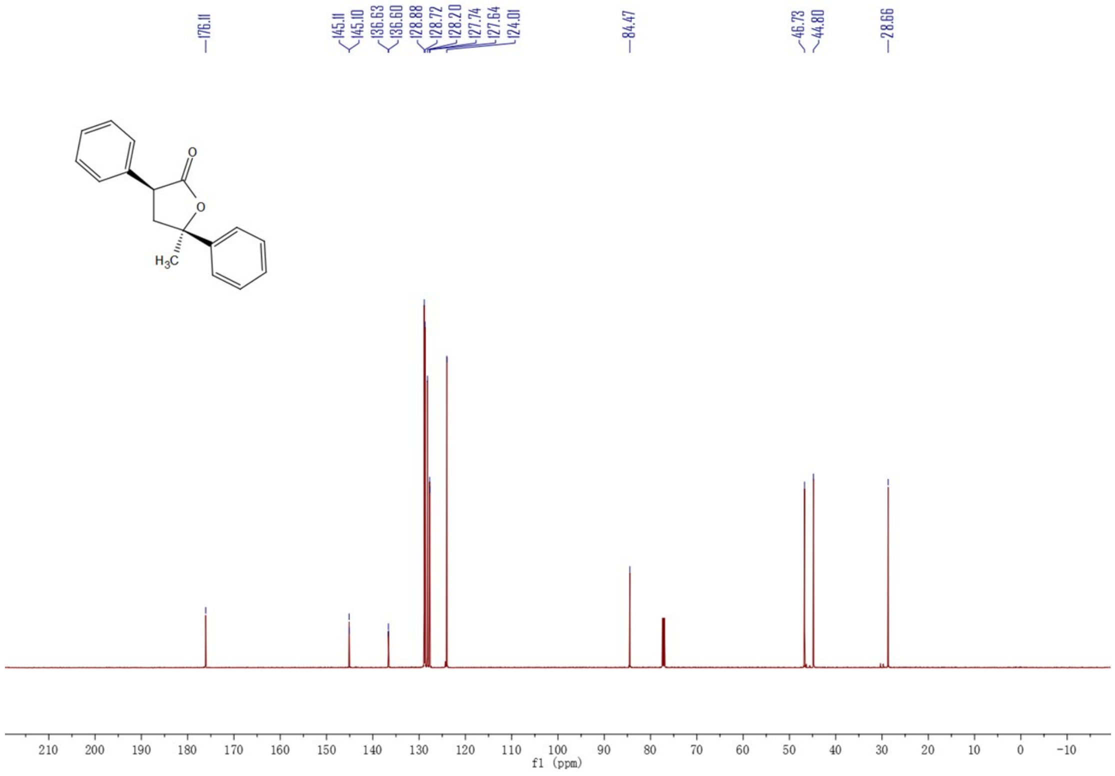
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**4**



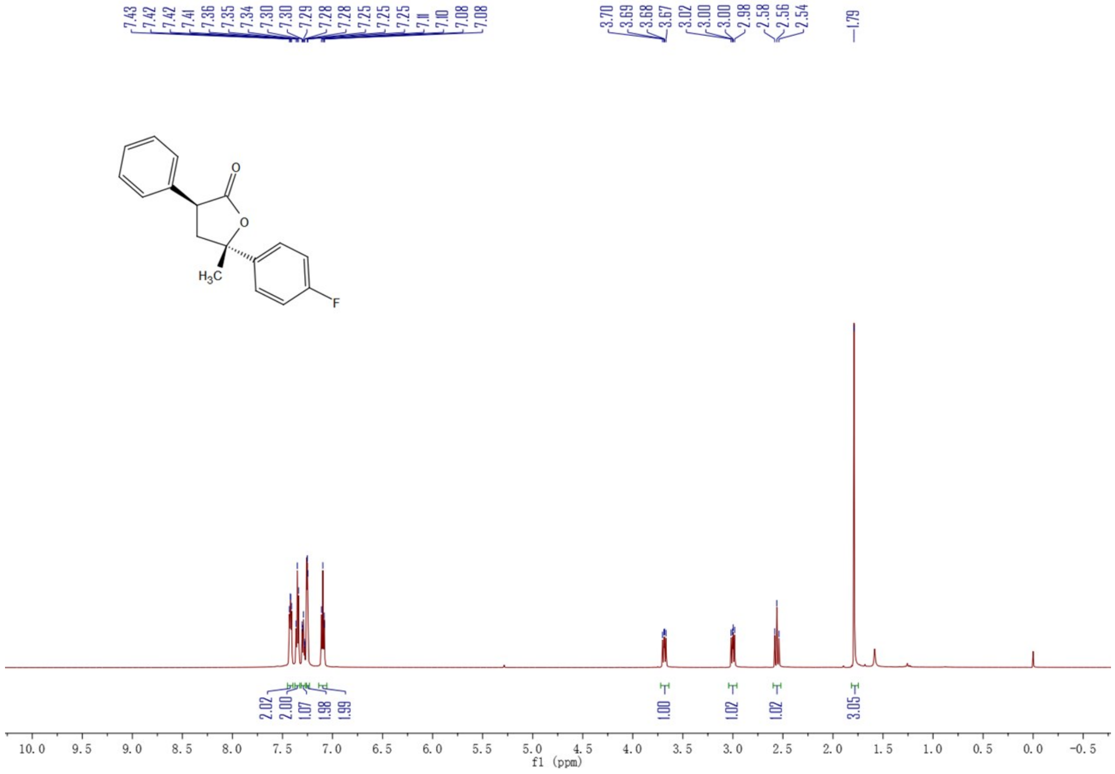
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**4**



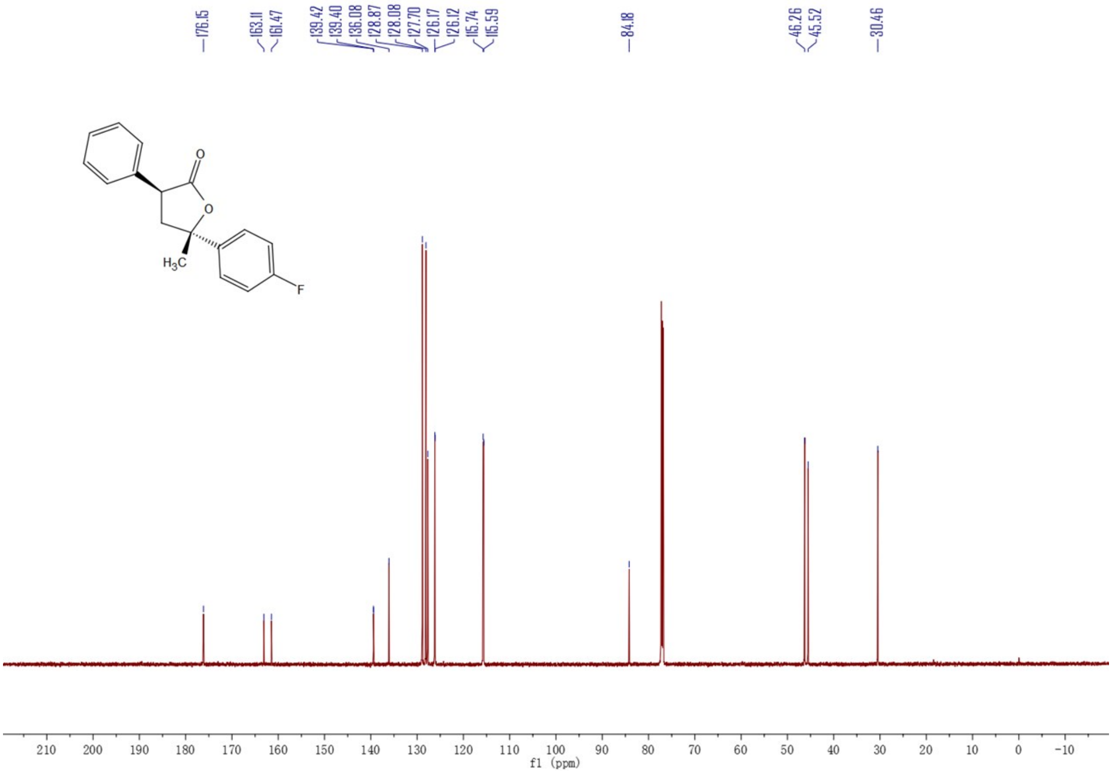
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**4**



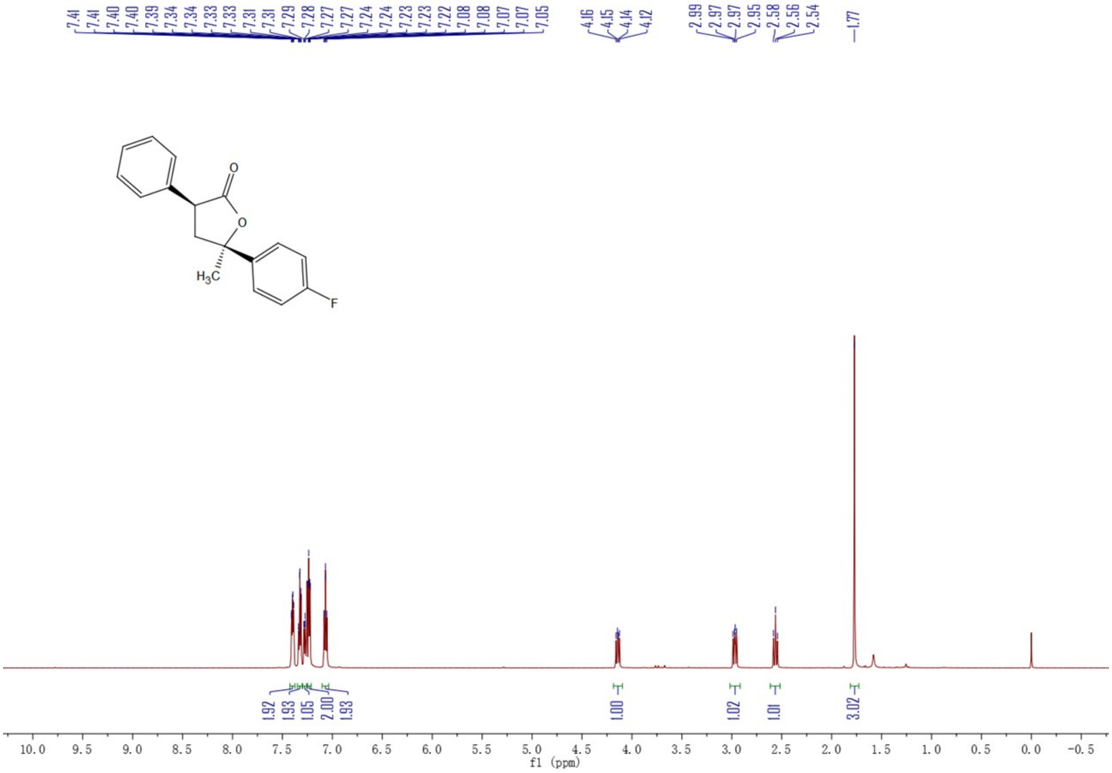
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**5**



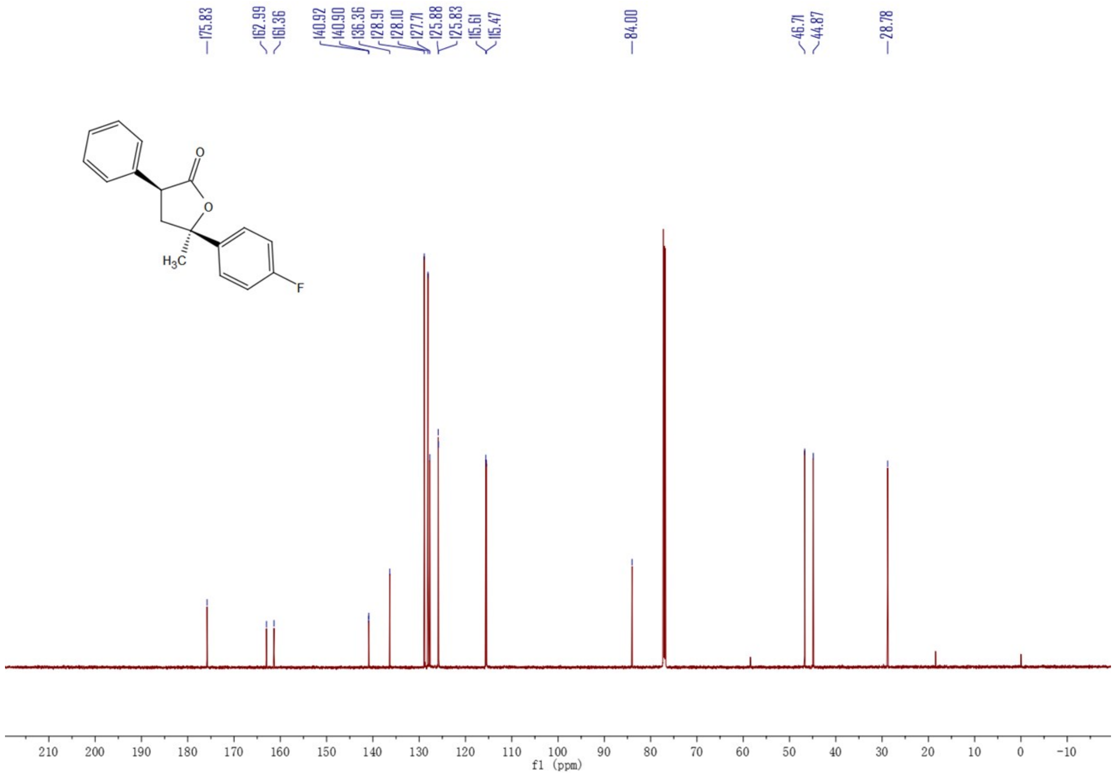
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**5**



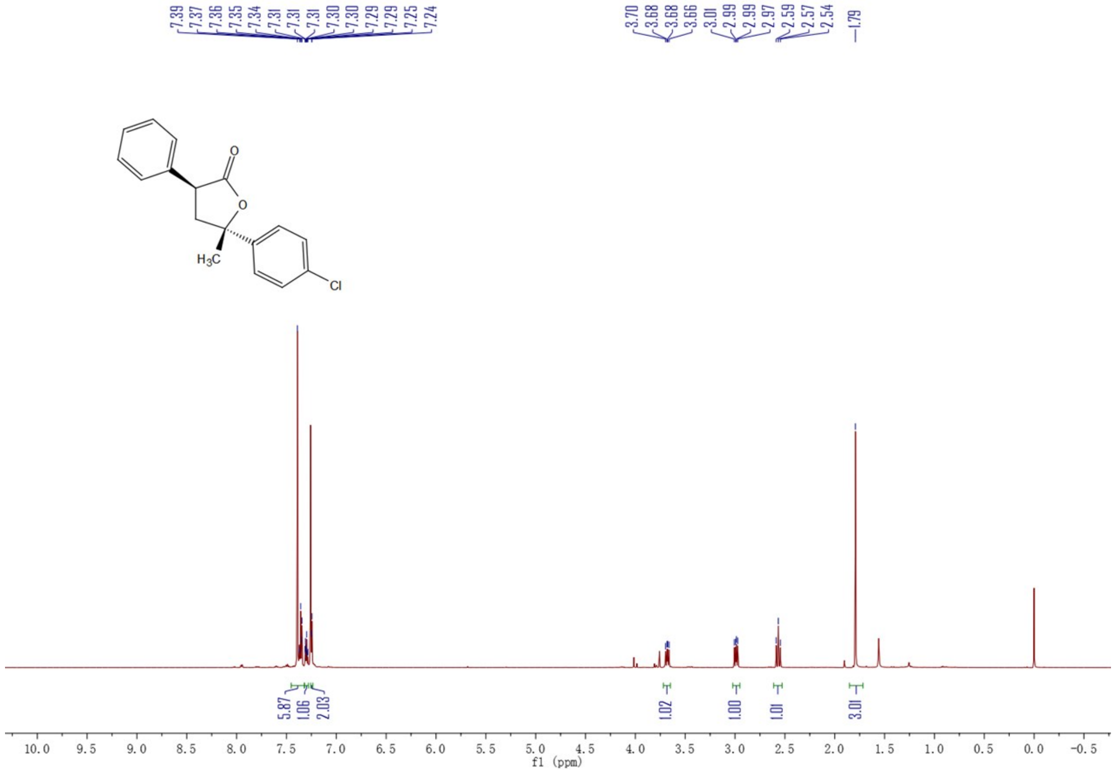
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**5**



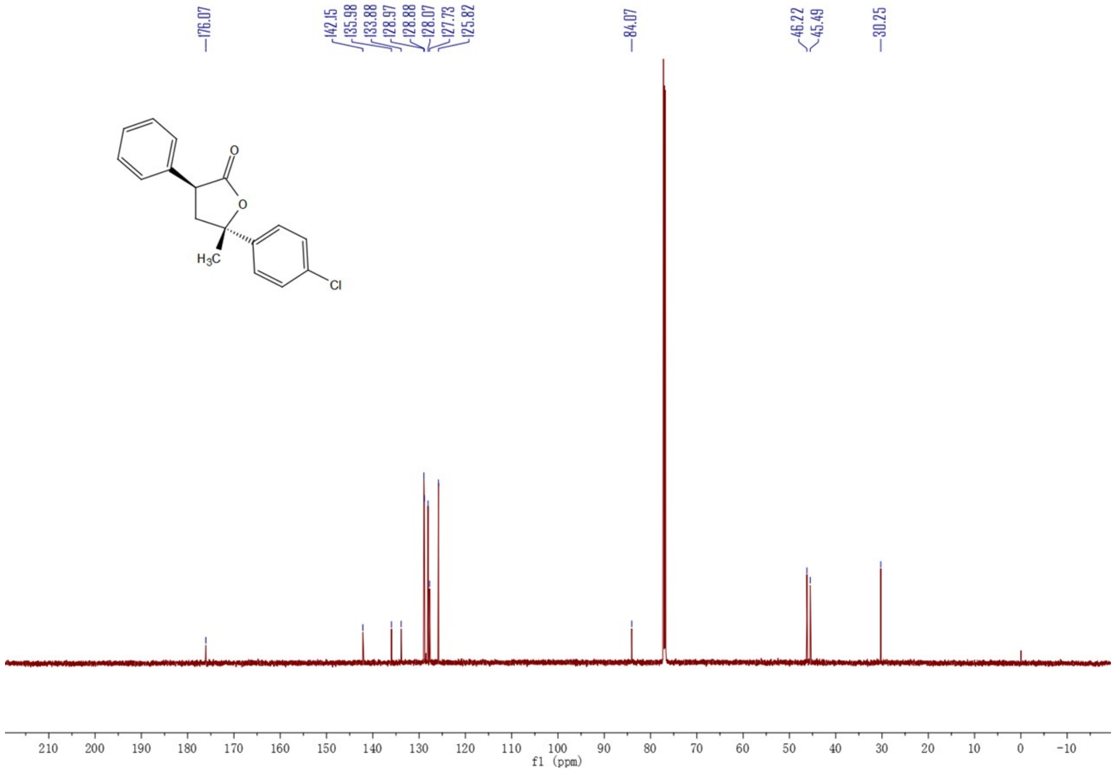
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**5**



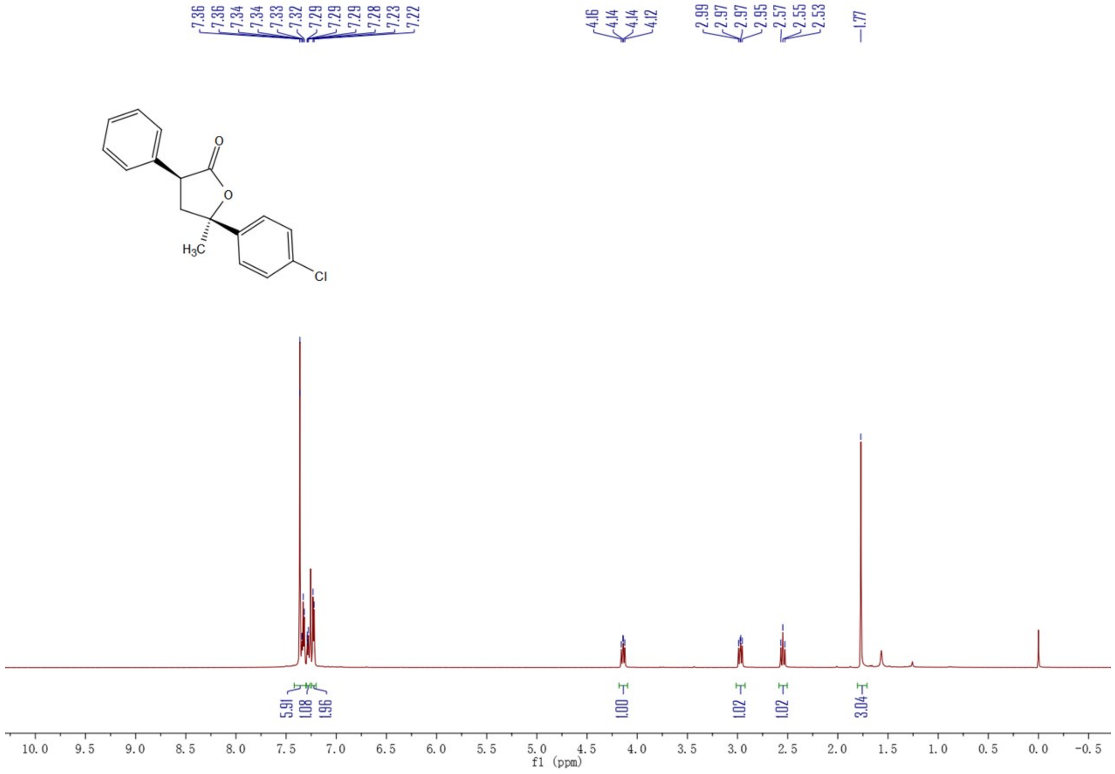
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**6**



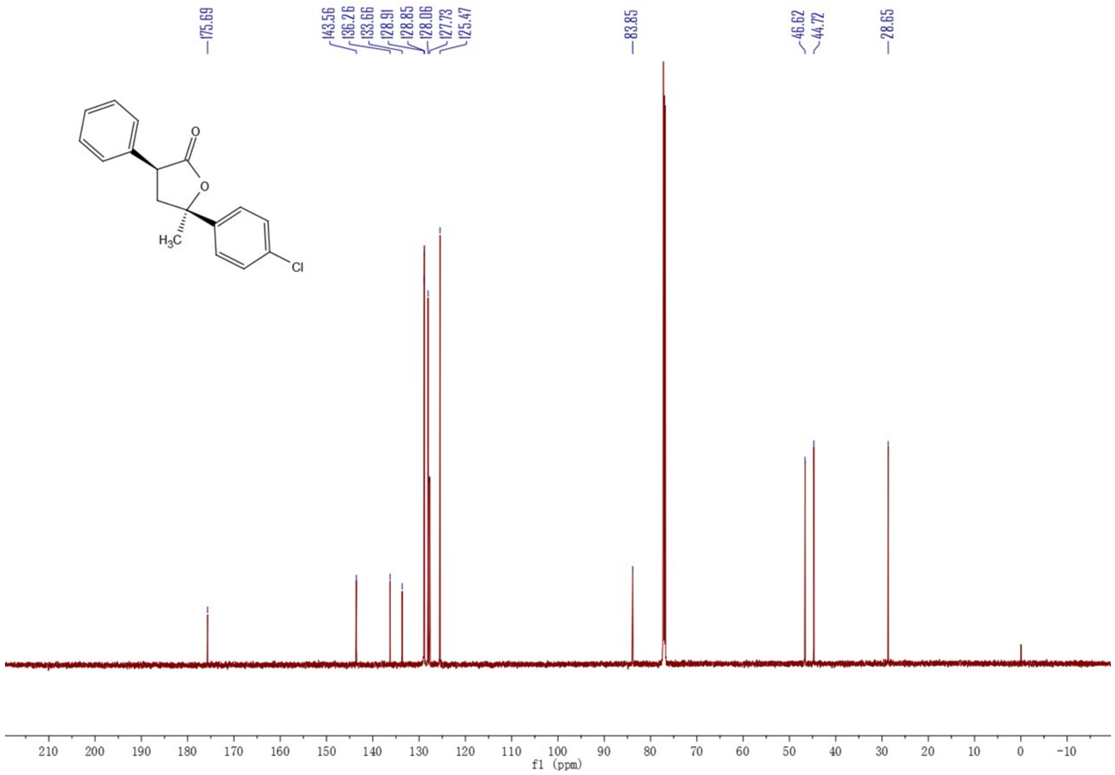
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**6**



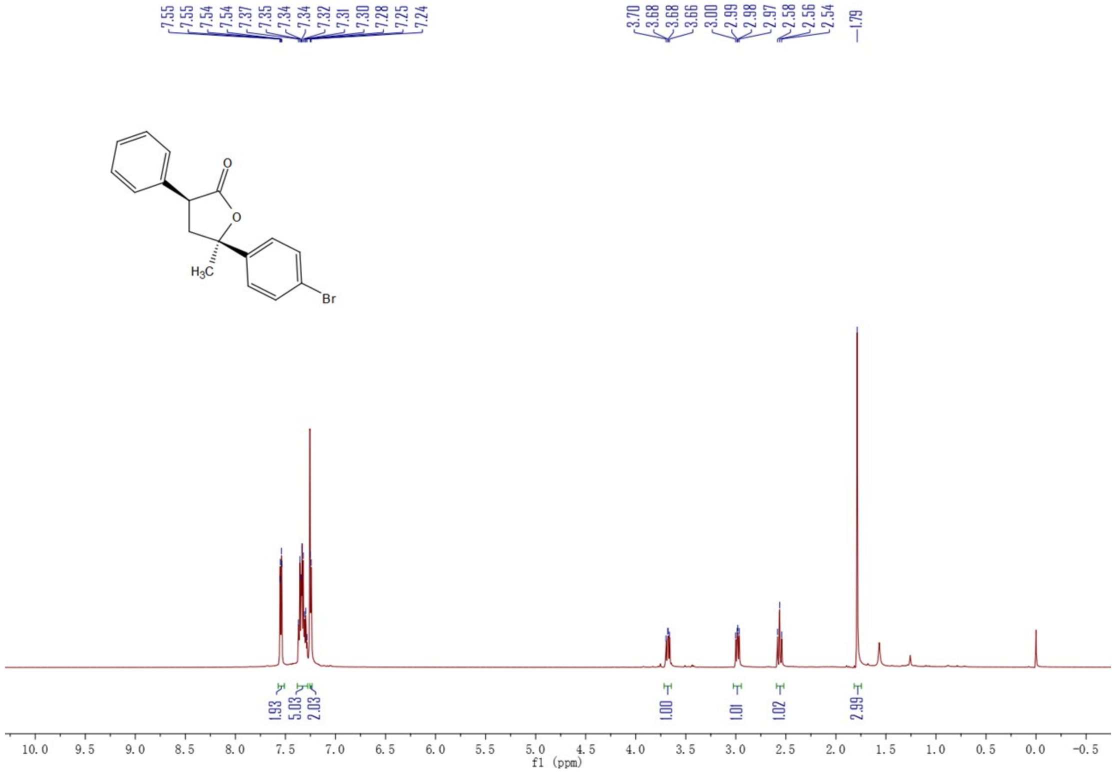
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**6**



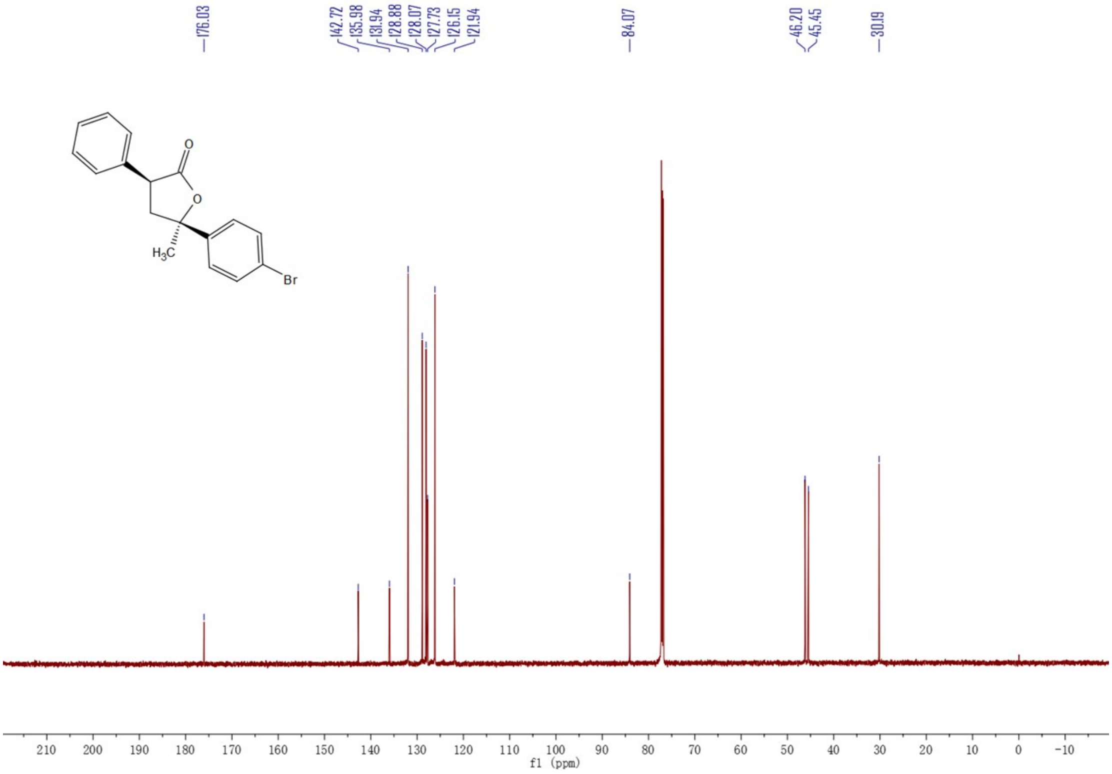
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**6**



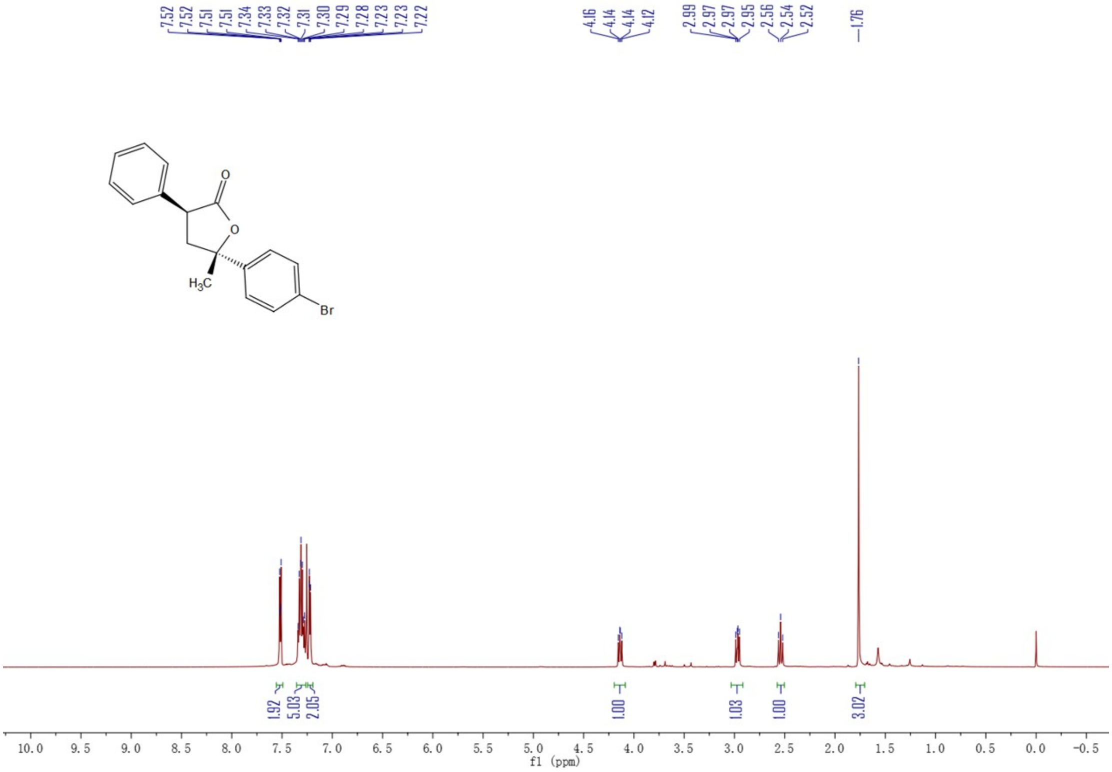
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**7**



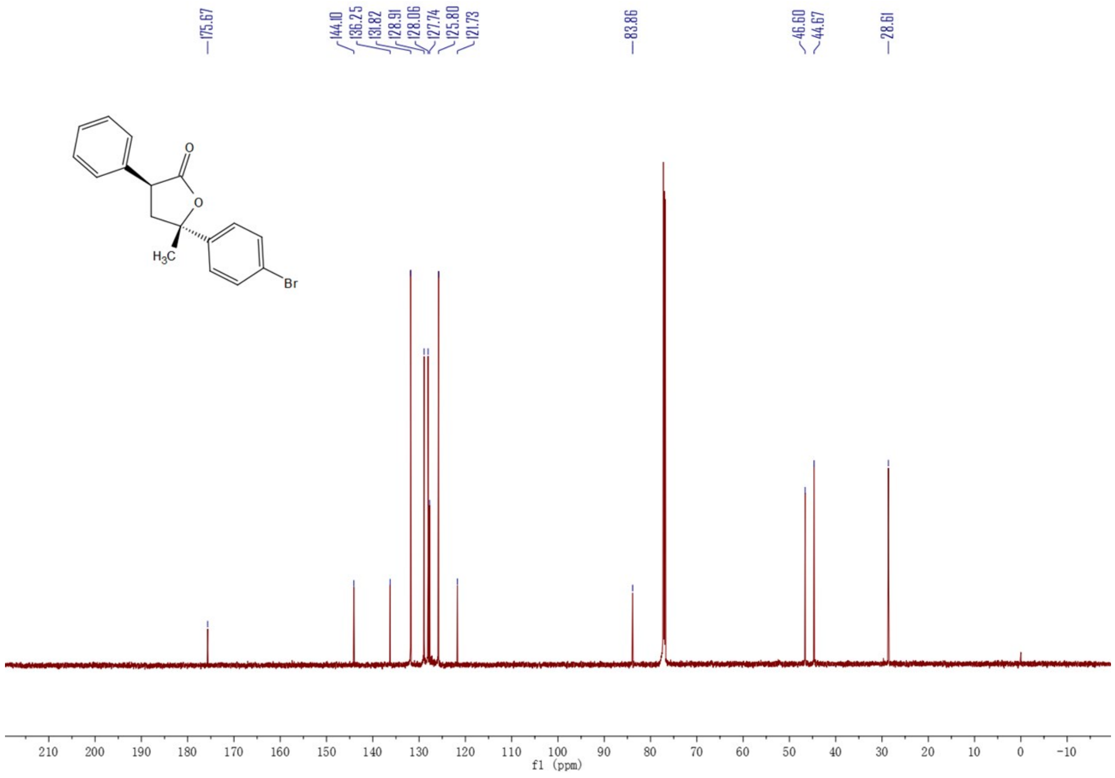
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**7**



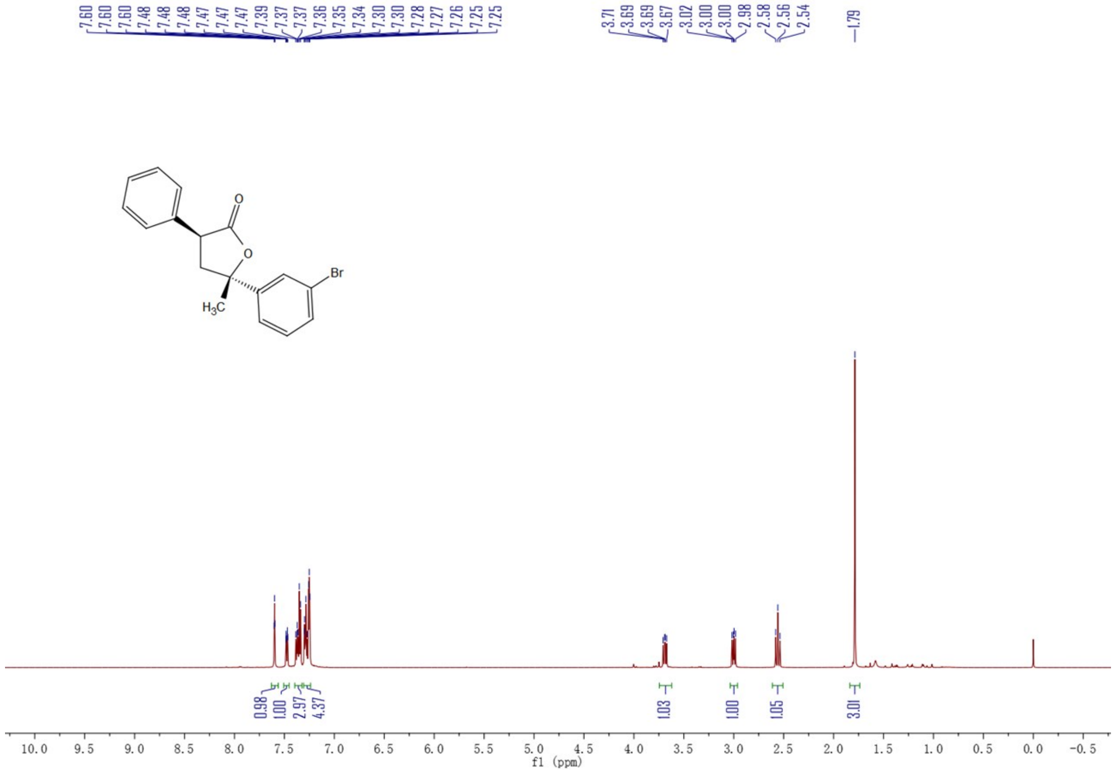
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**7**



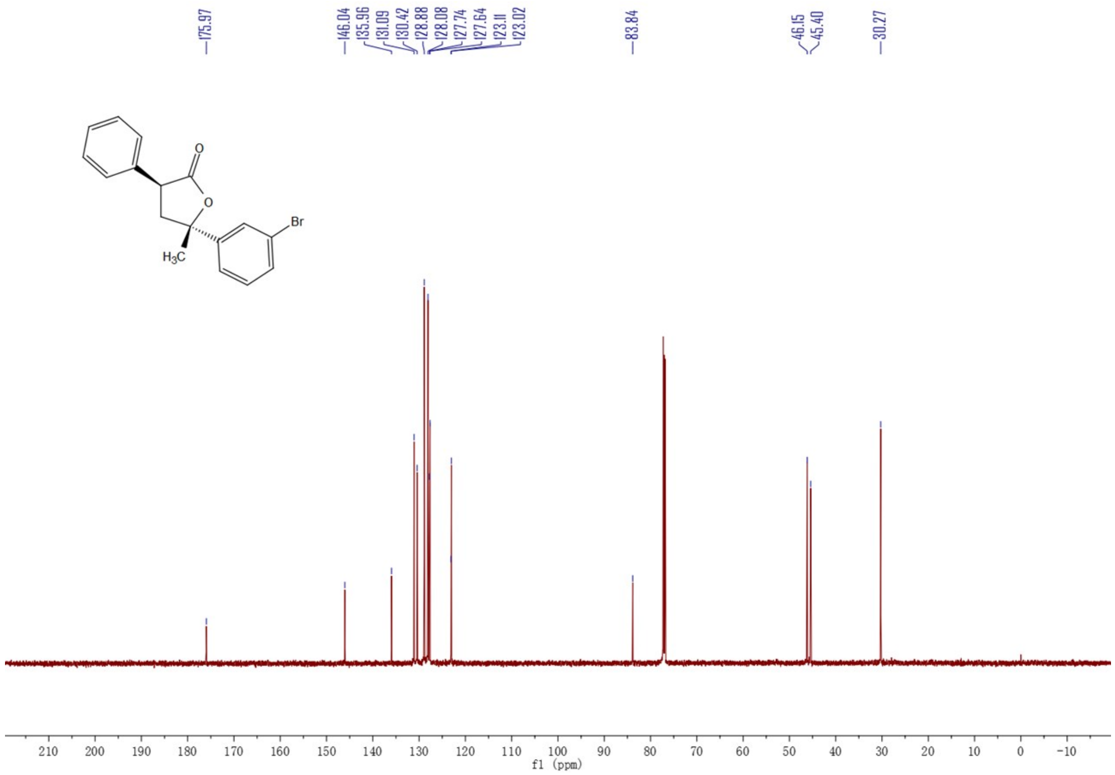
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**7**



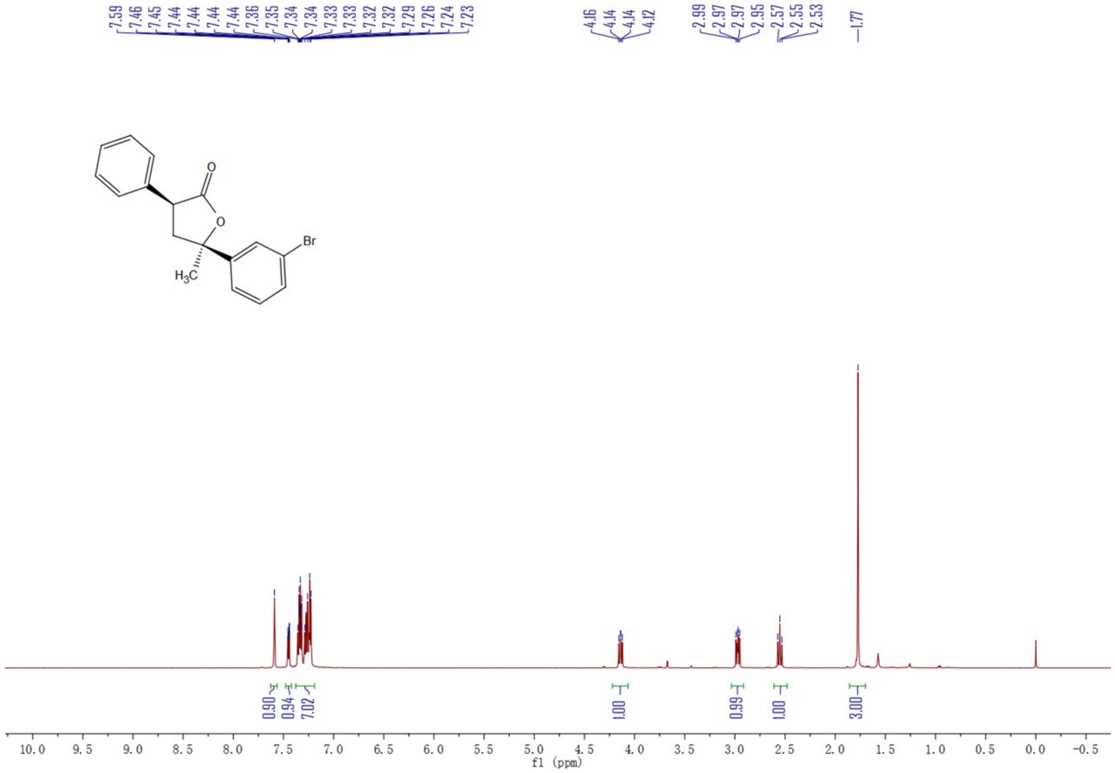
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**8**



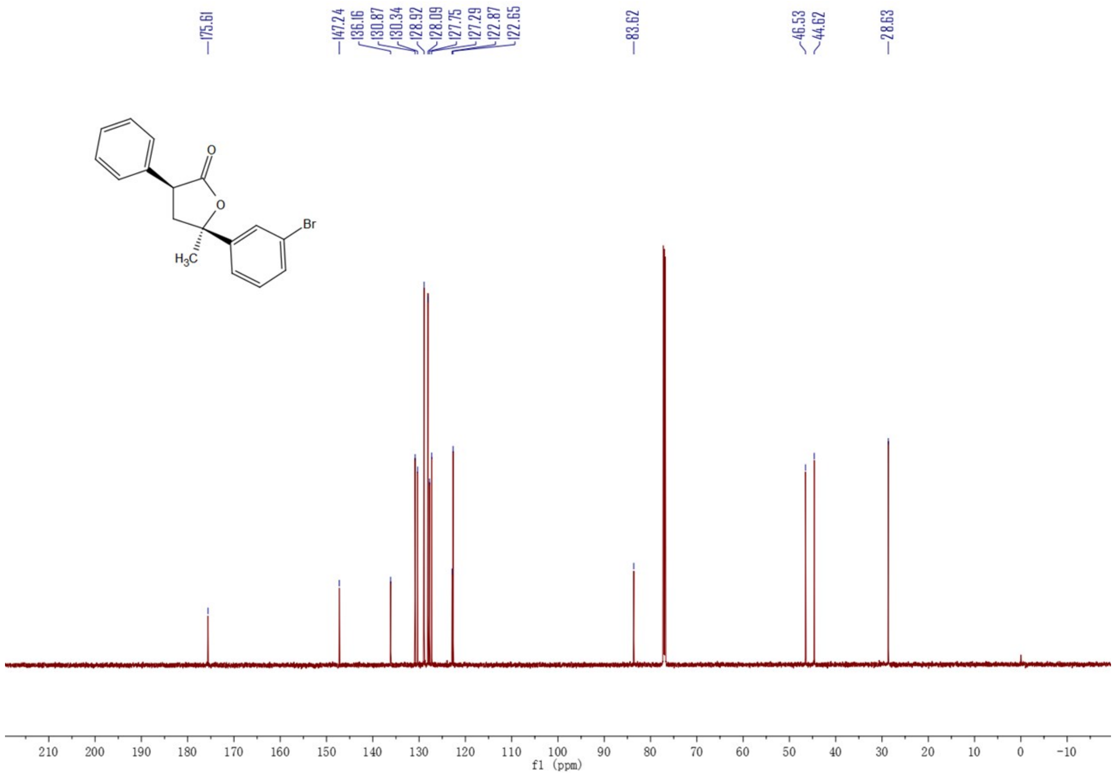
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**8**



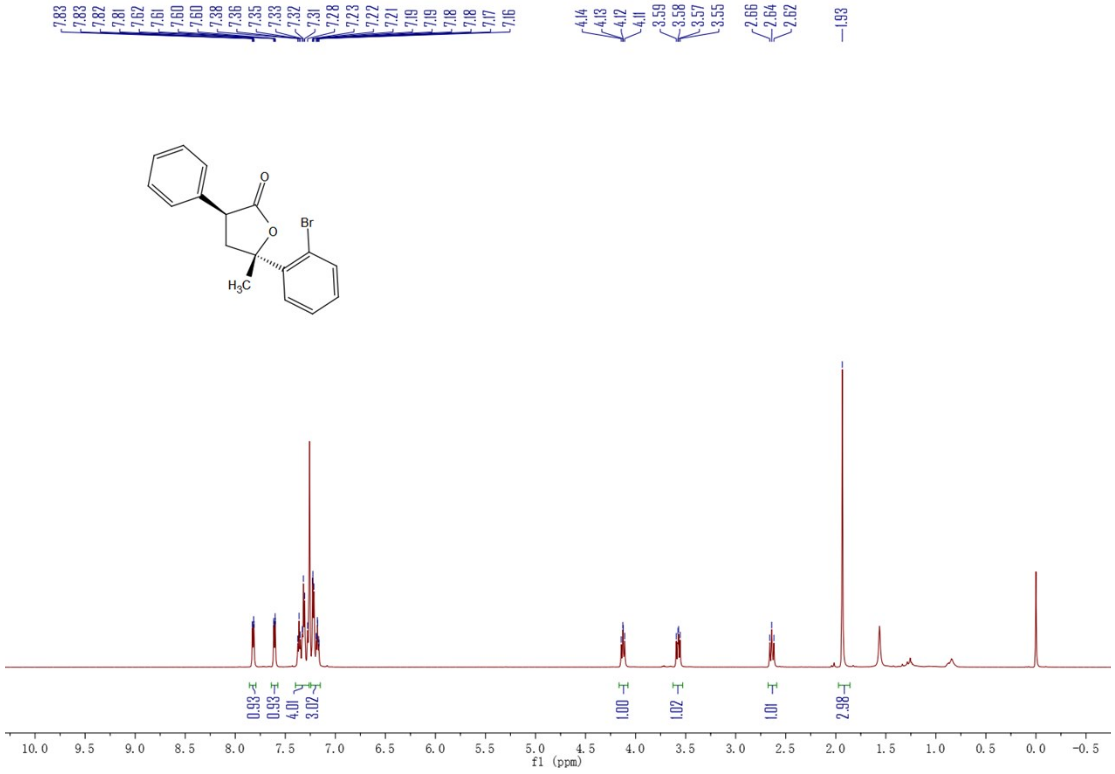
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**8**



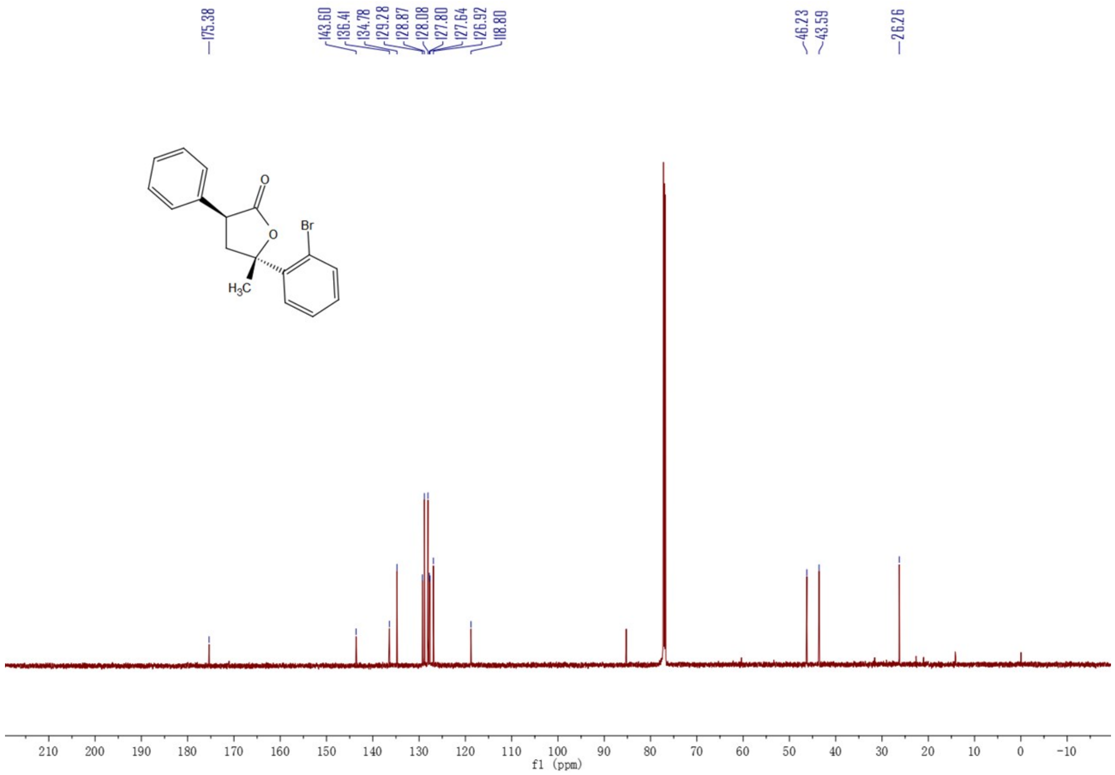
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**8**



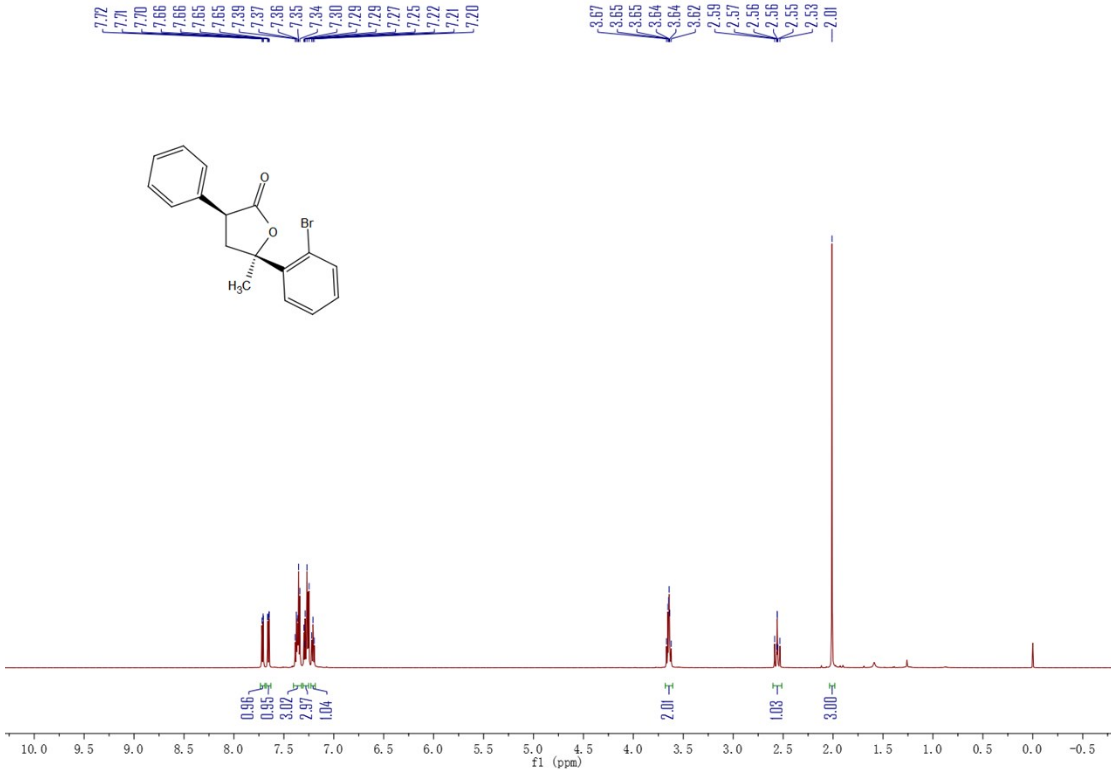
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**9**



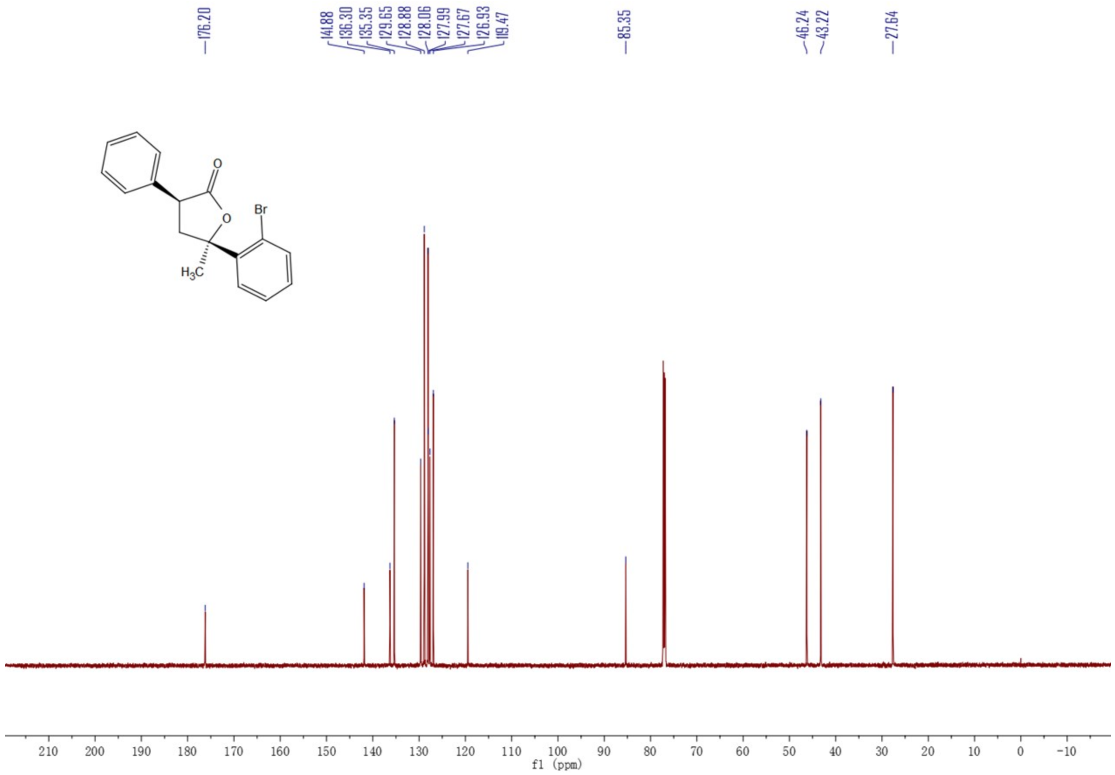
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**9**



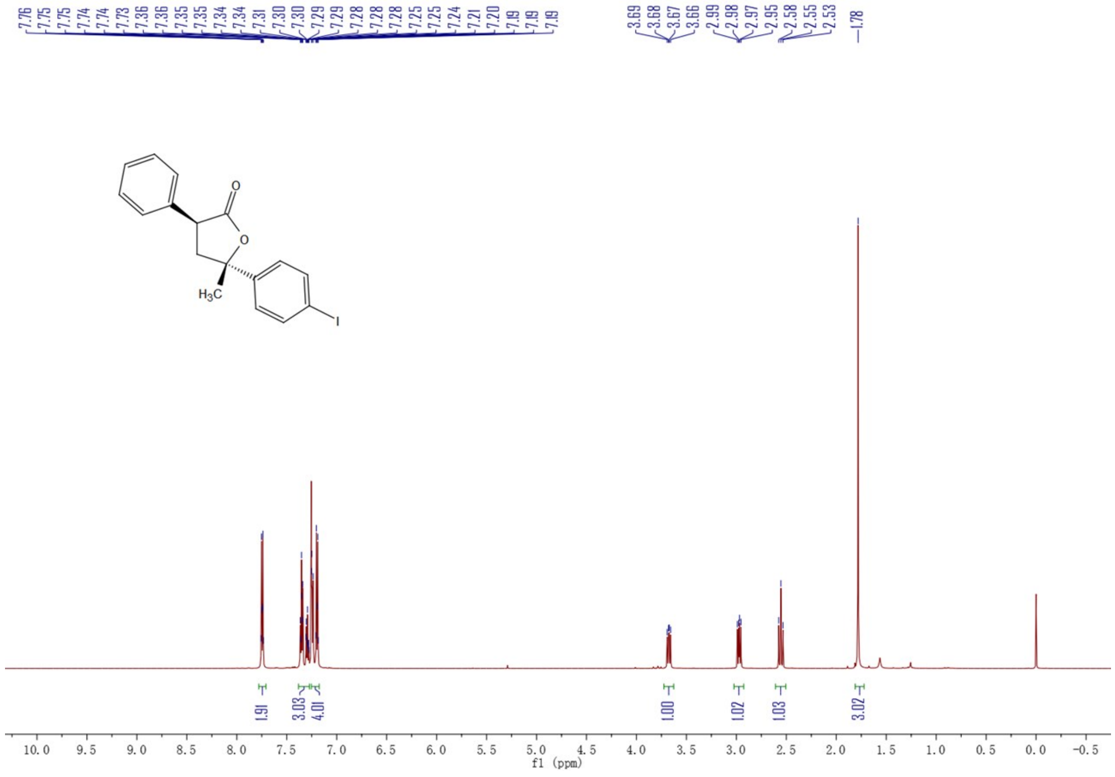
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**9**



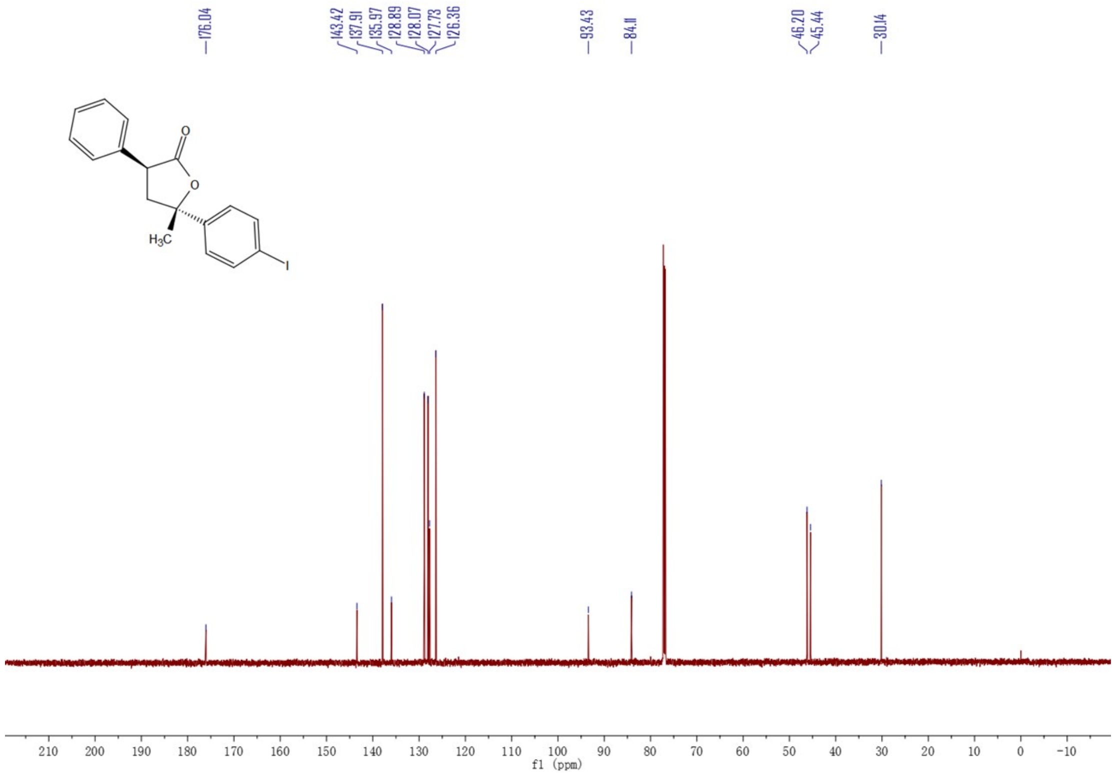
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**9**



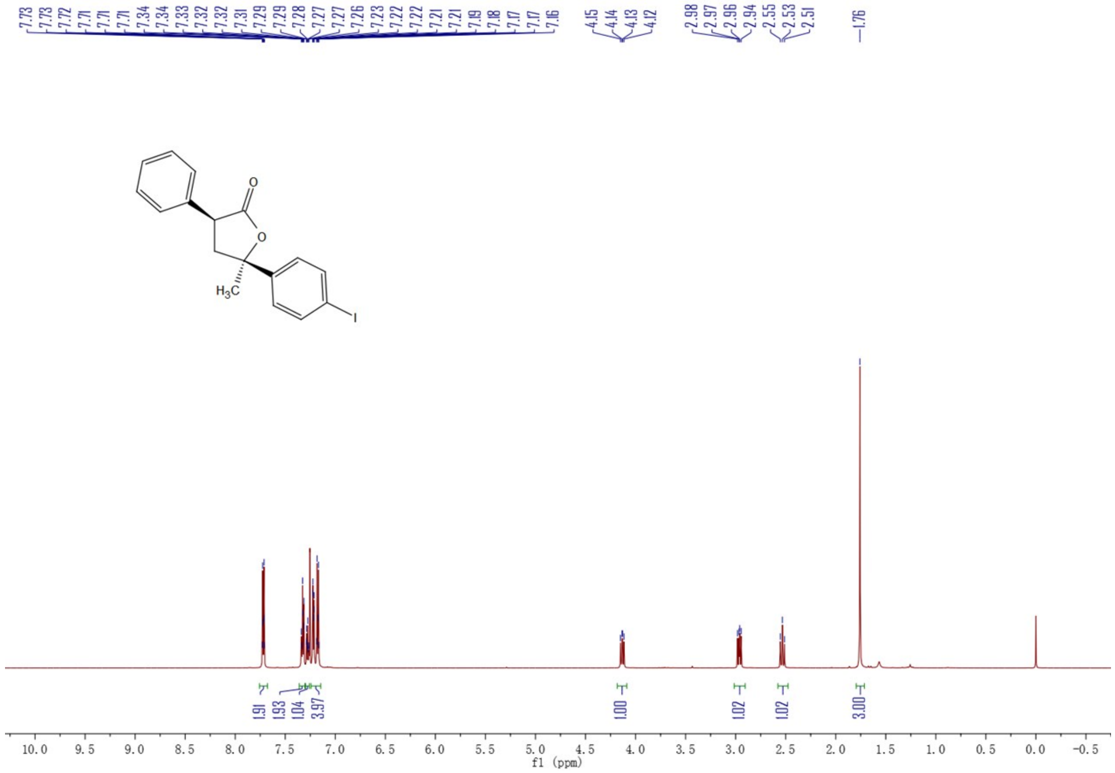
^1H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**10**



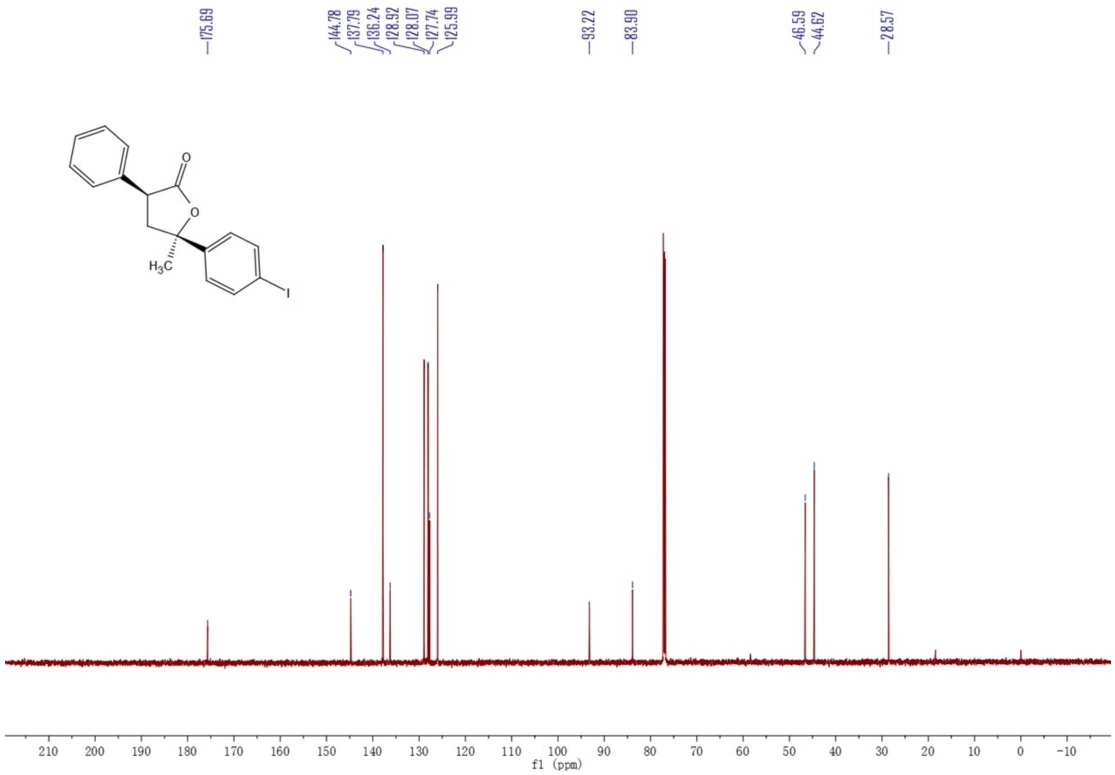
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**10**



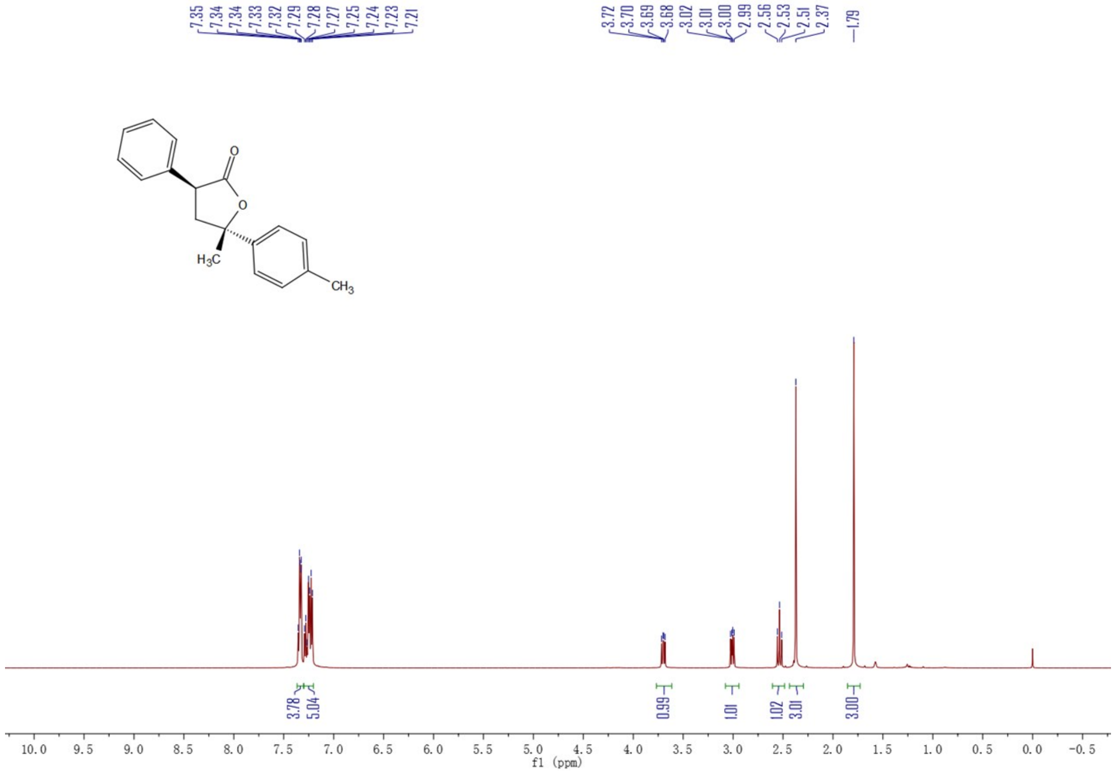
^1H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**10**



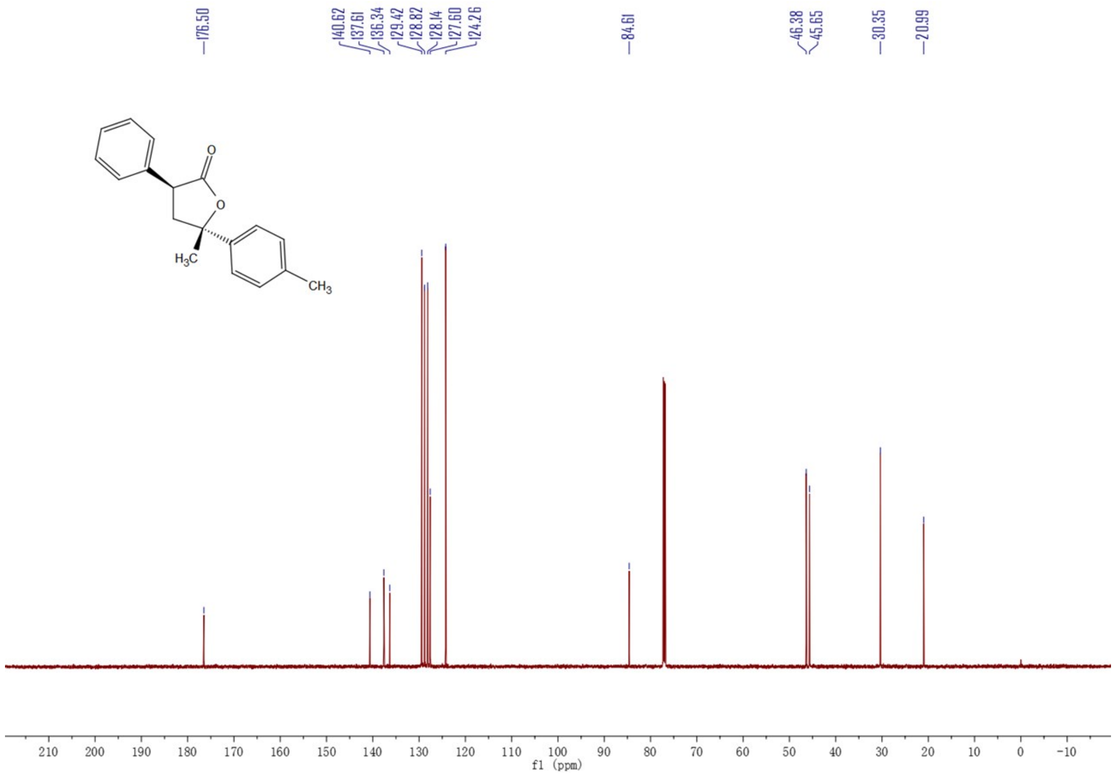
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*syn*-**10**



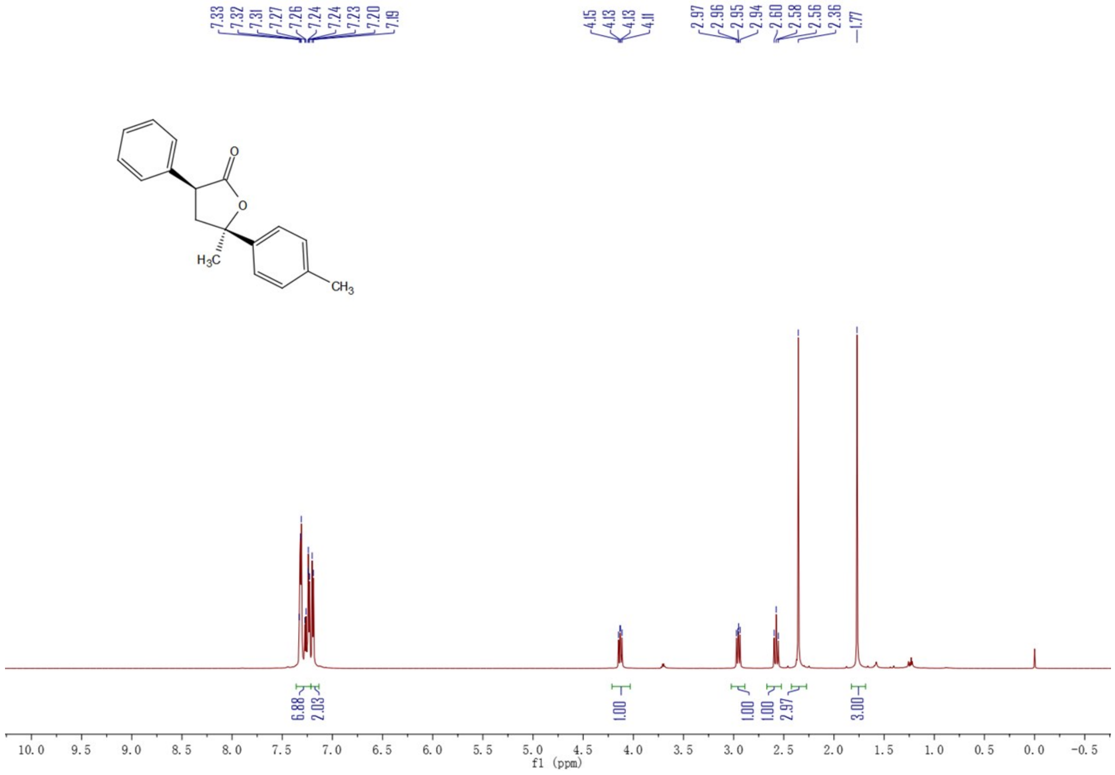
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**11**



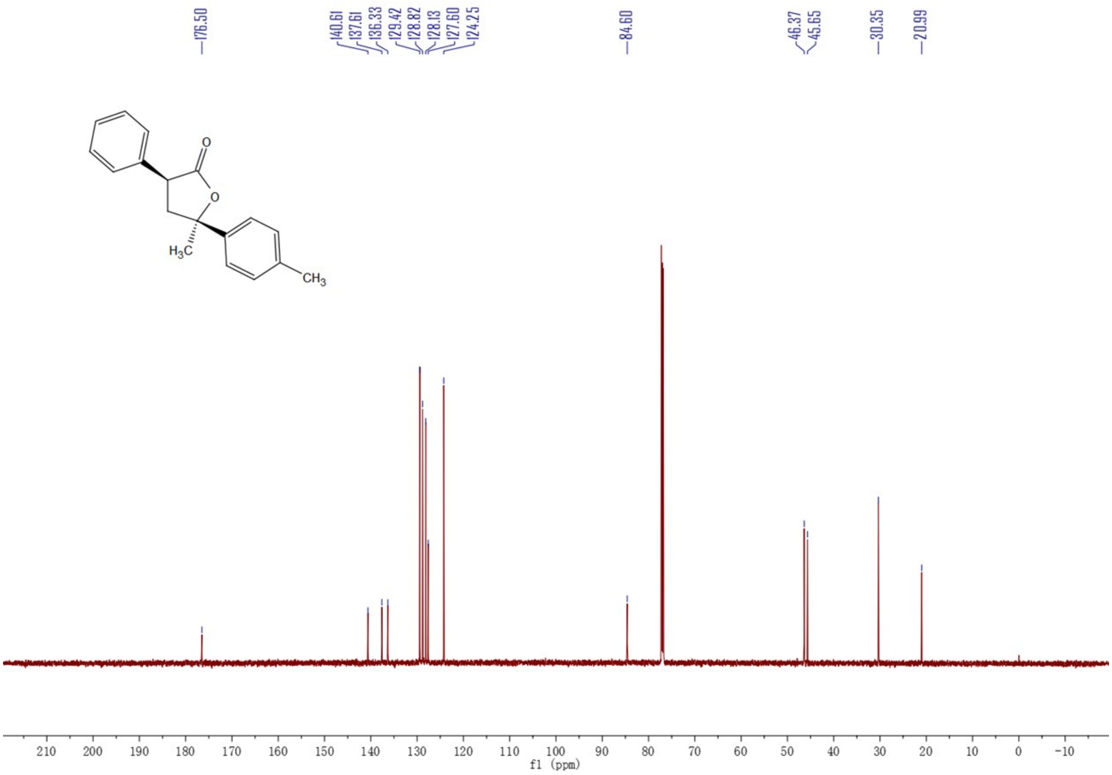
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**11**



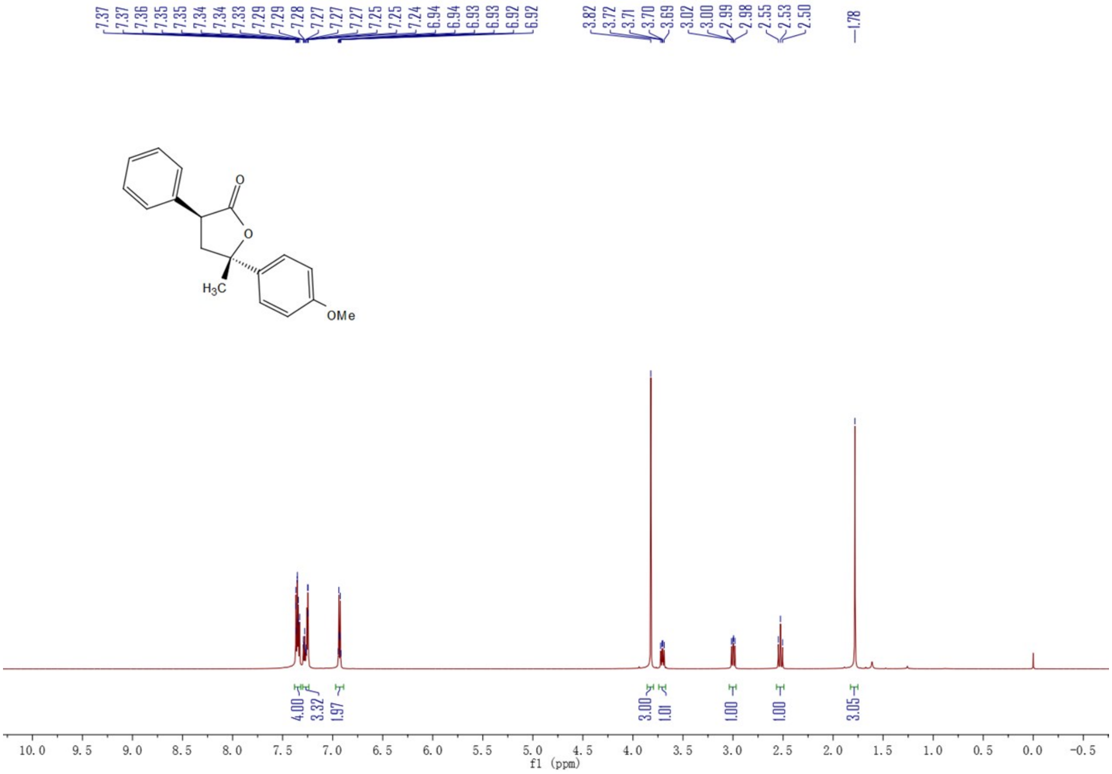
^1H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**11**



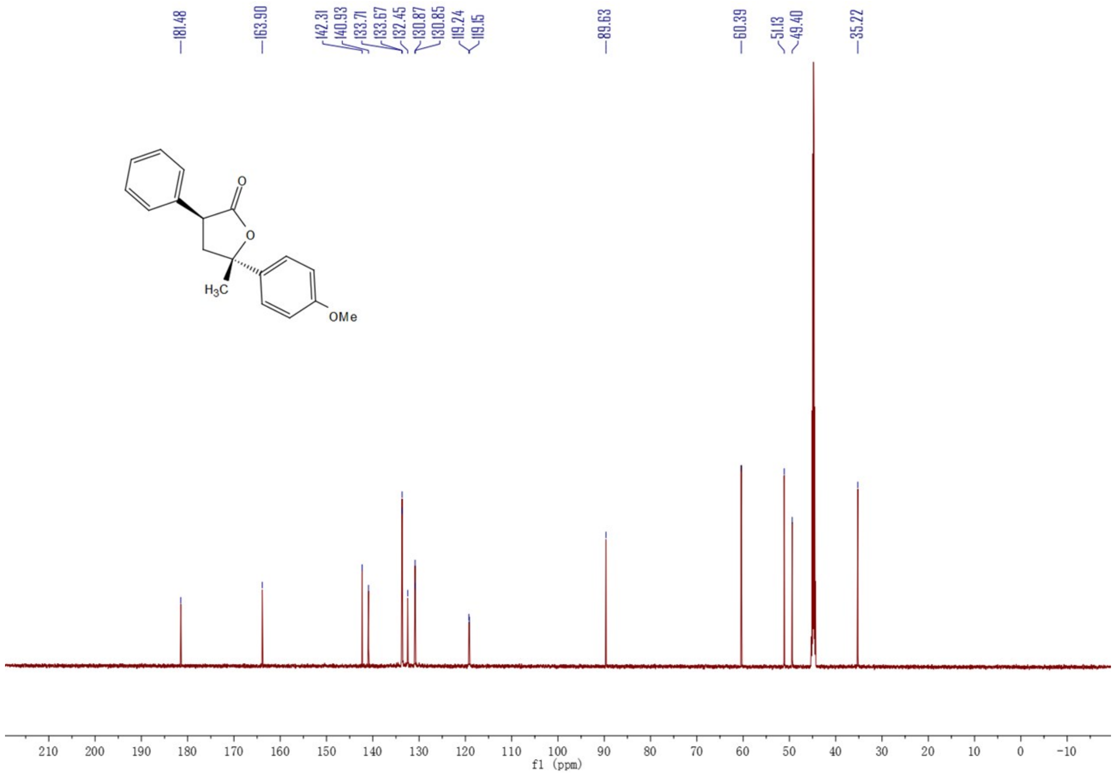
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*syn*-**11**



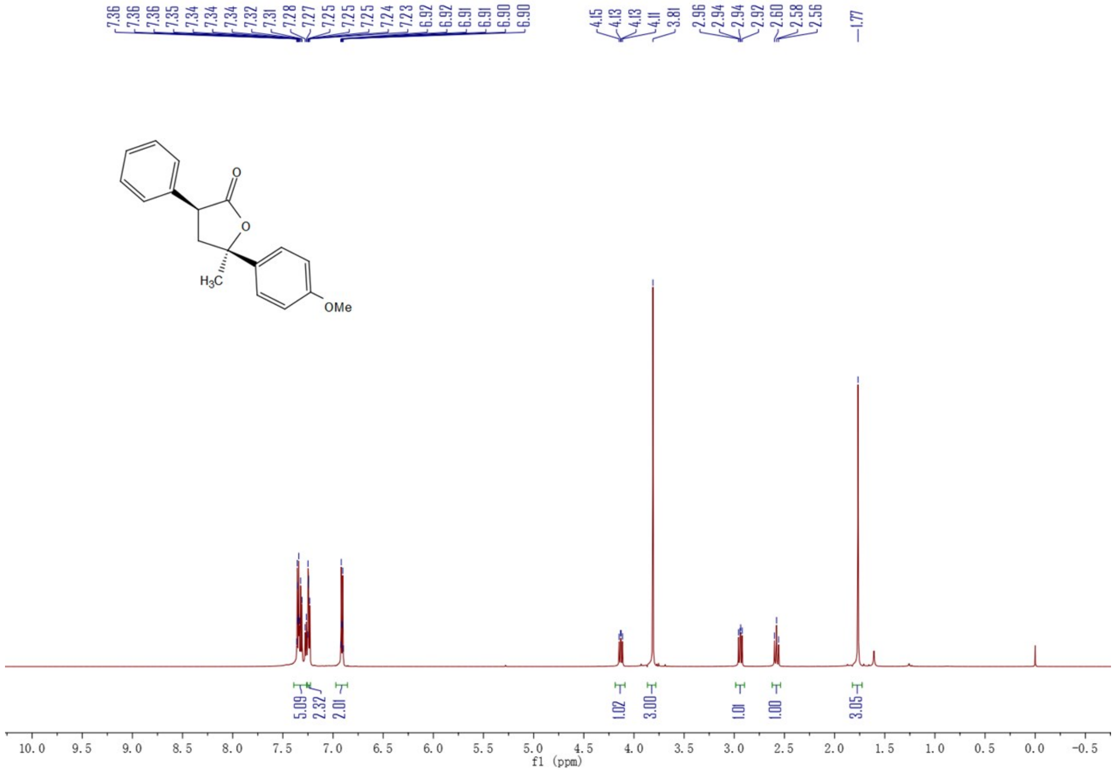
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**12**



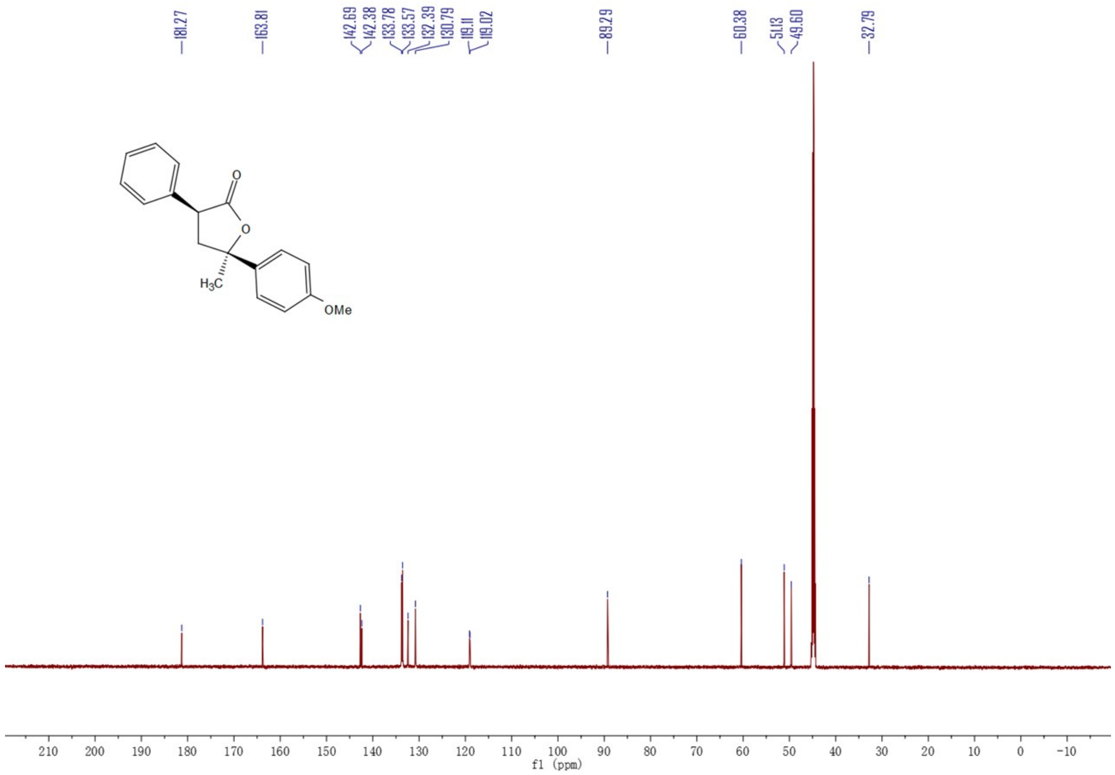
^{13}C NMR (151 MHz, $(CD_3)_2SO$) of (±)-*anti*-**12**



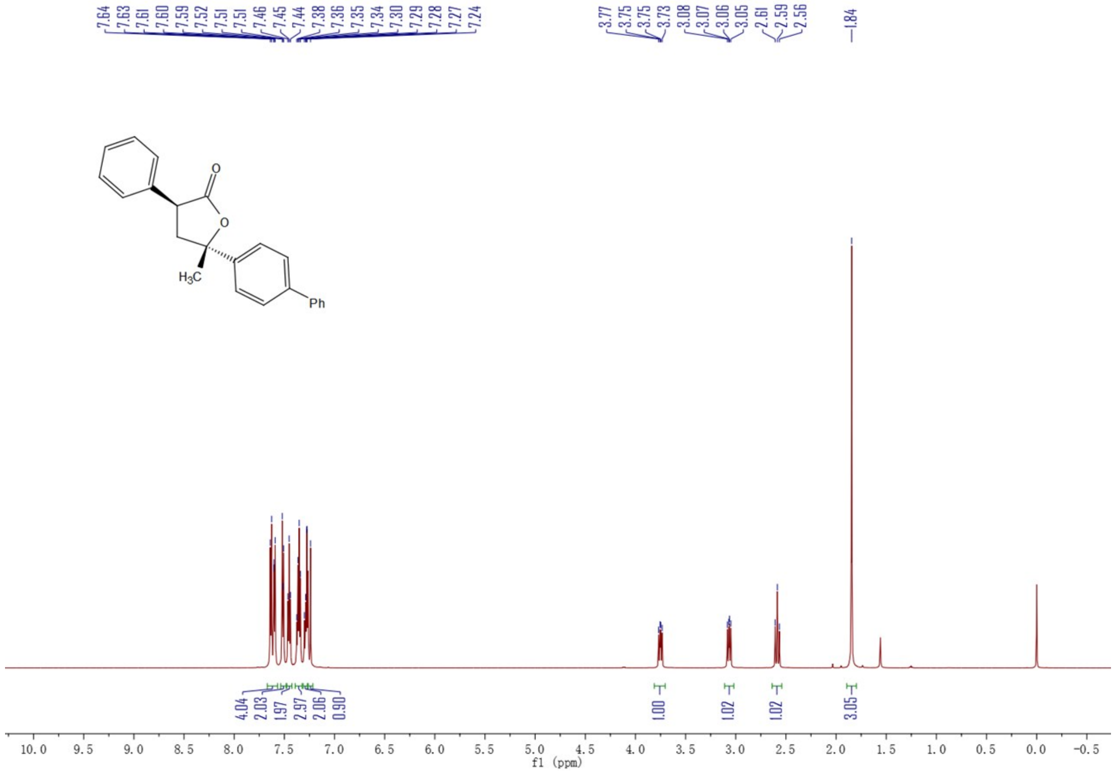
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**12**



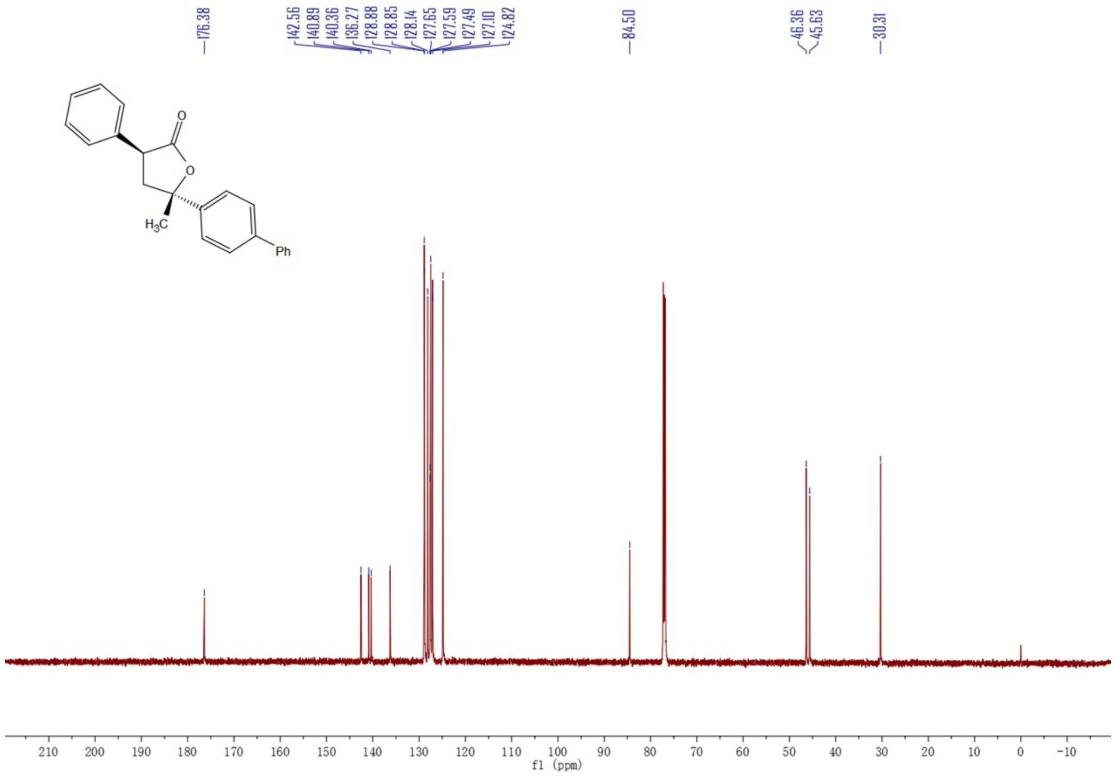
^{13}C NMR (151 MHz, (CD$_3$)$_2$SO) of (±)-*syn*-**12**



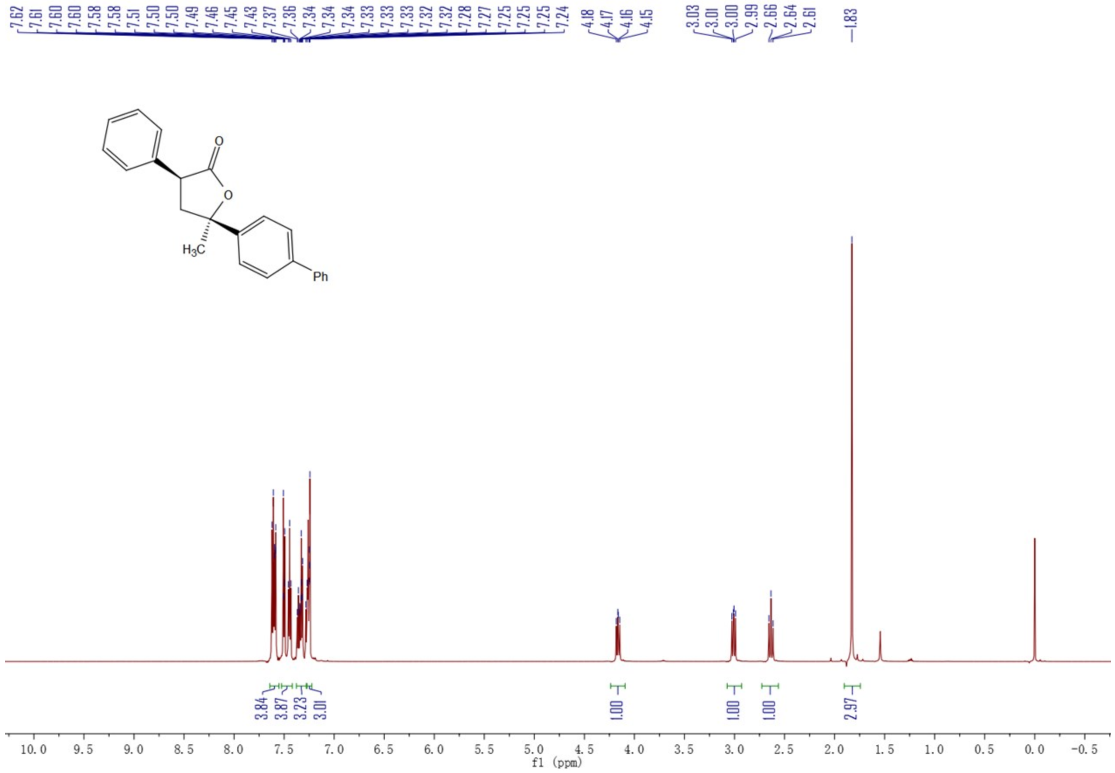
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**13**



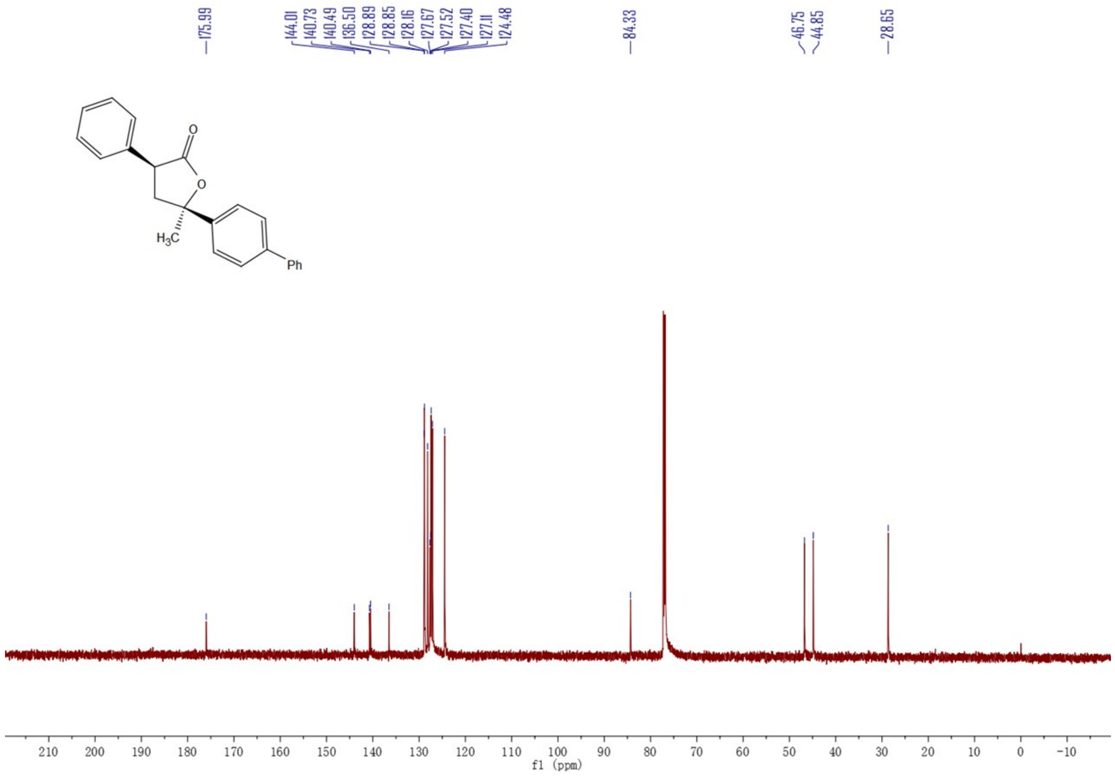
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**13**



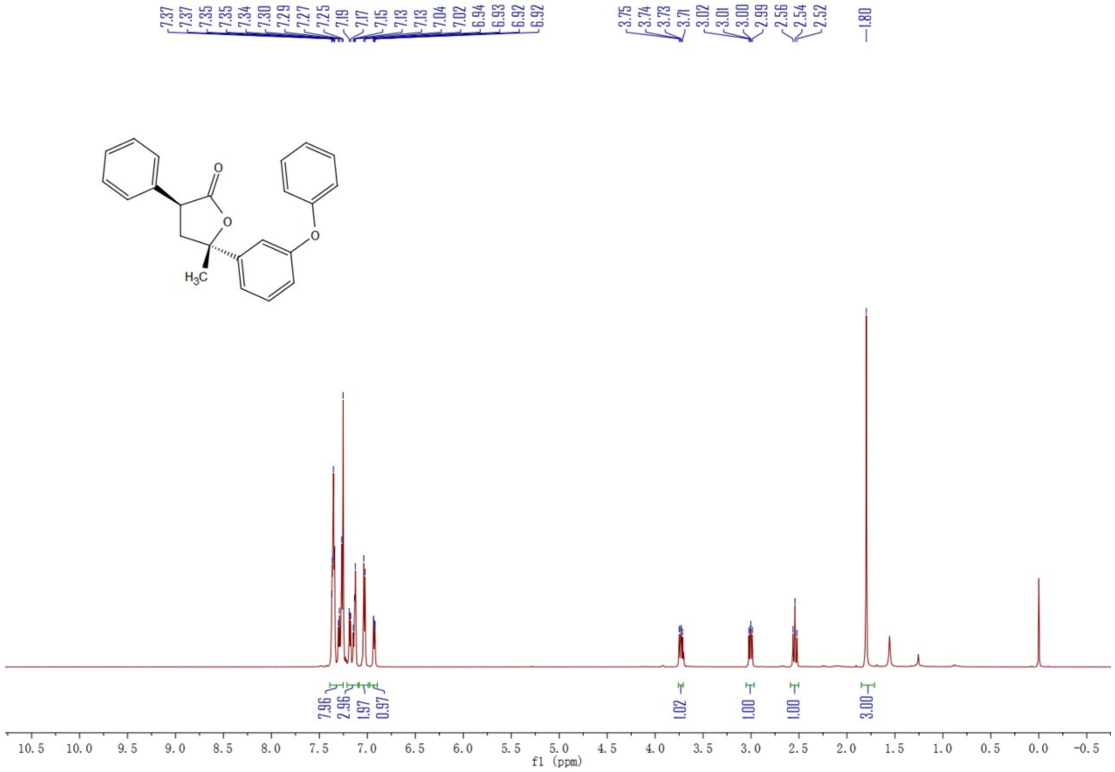
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**13**



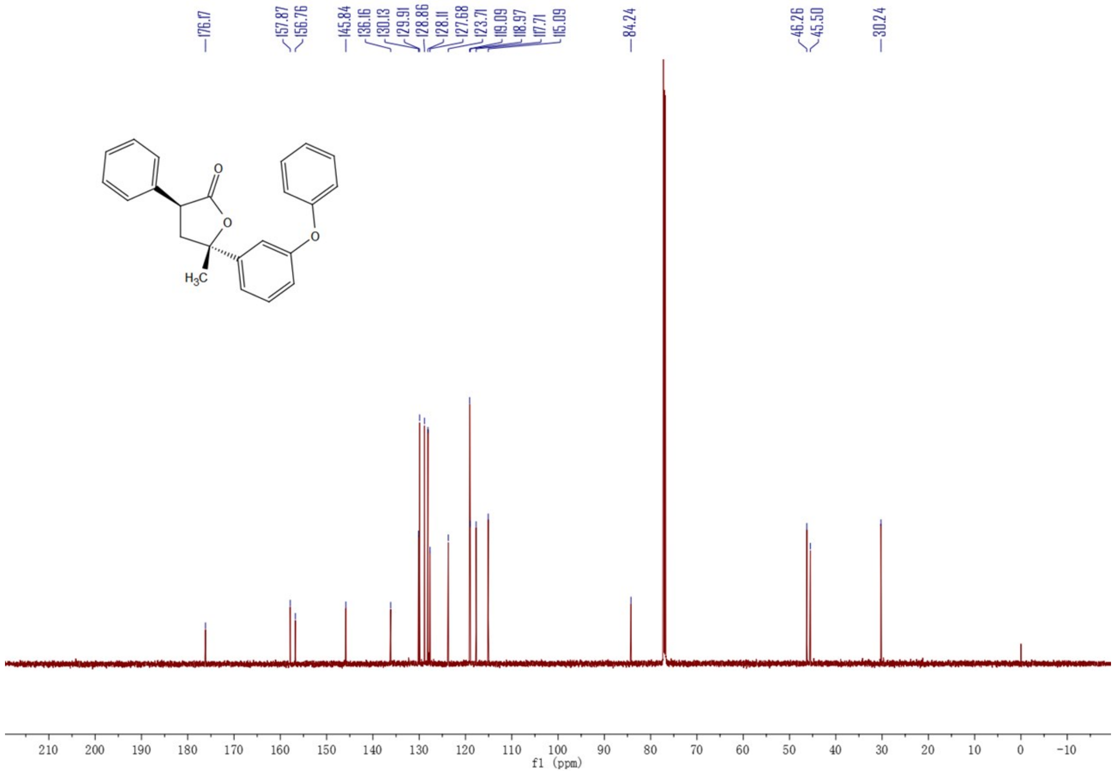
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*syn*-**13**



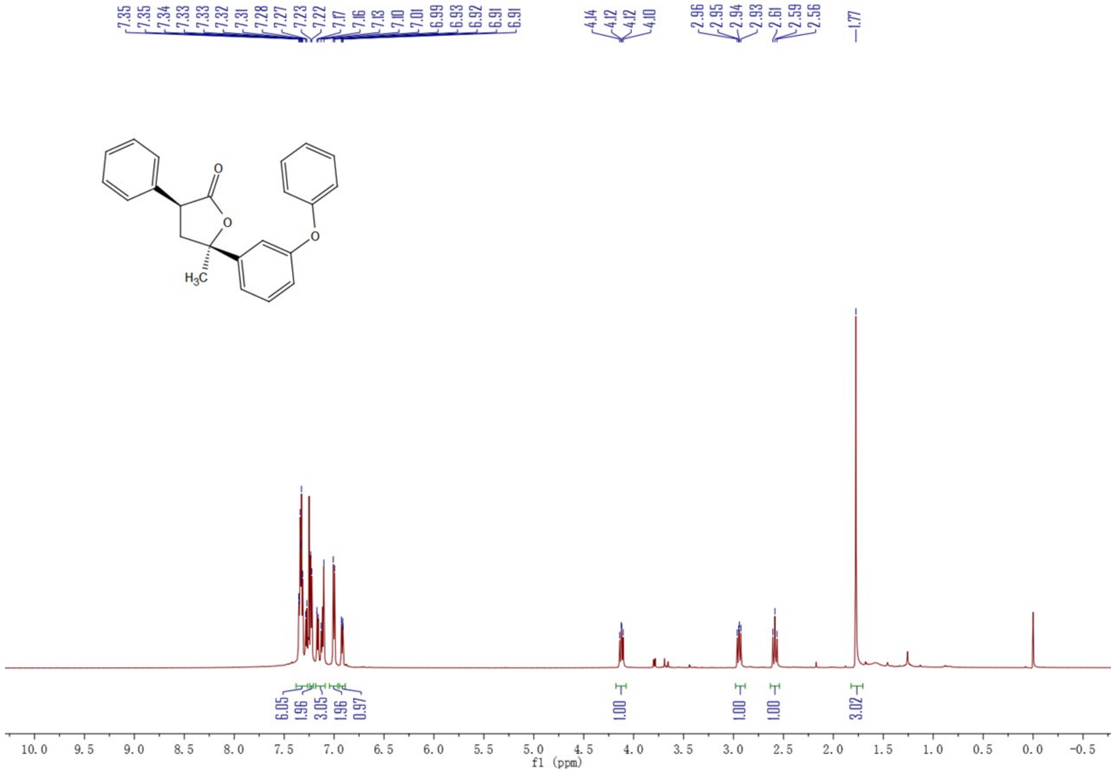
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**14**



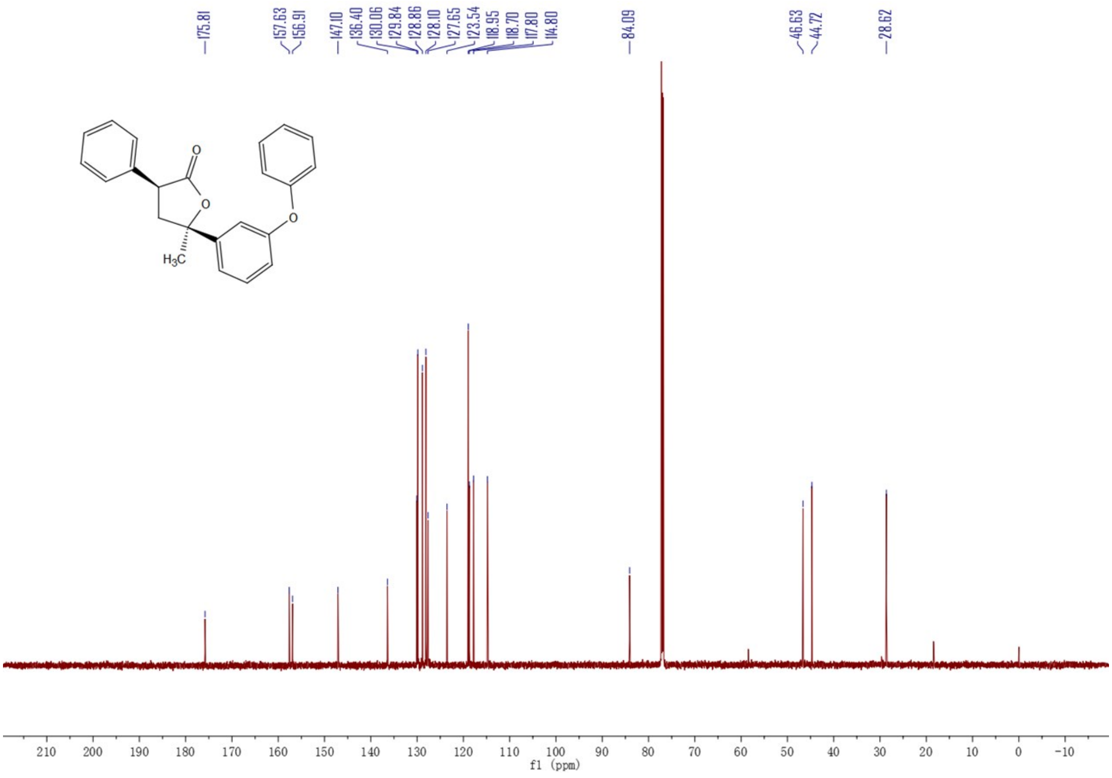
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**14**



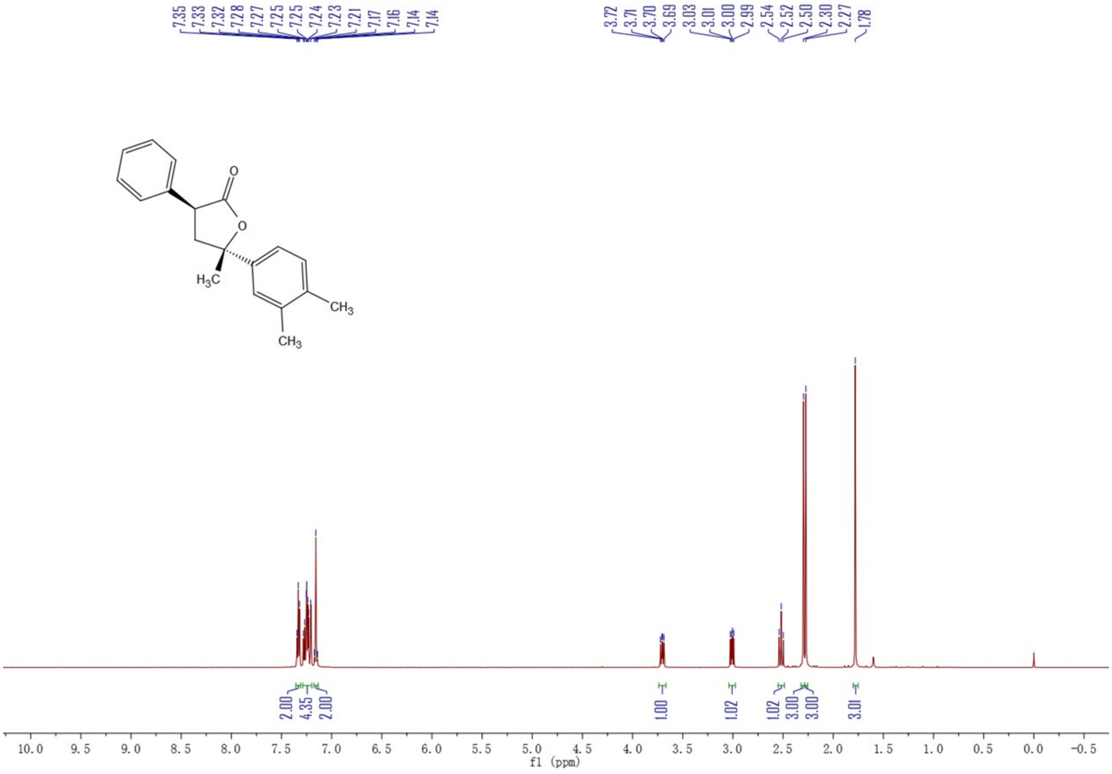
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**14**



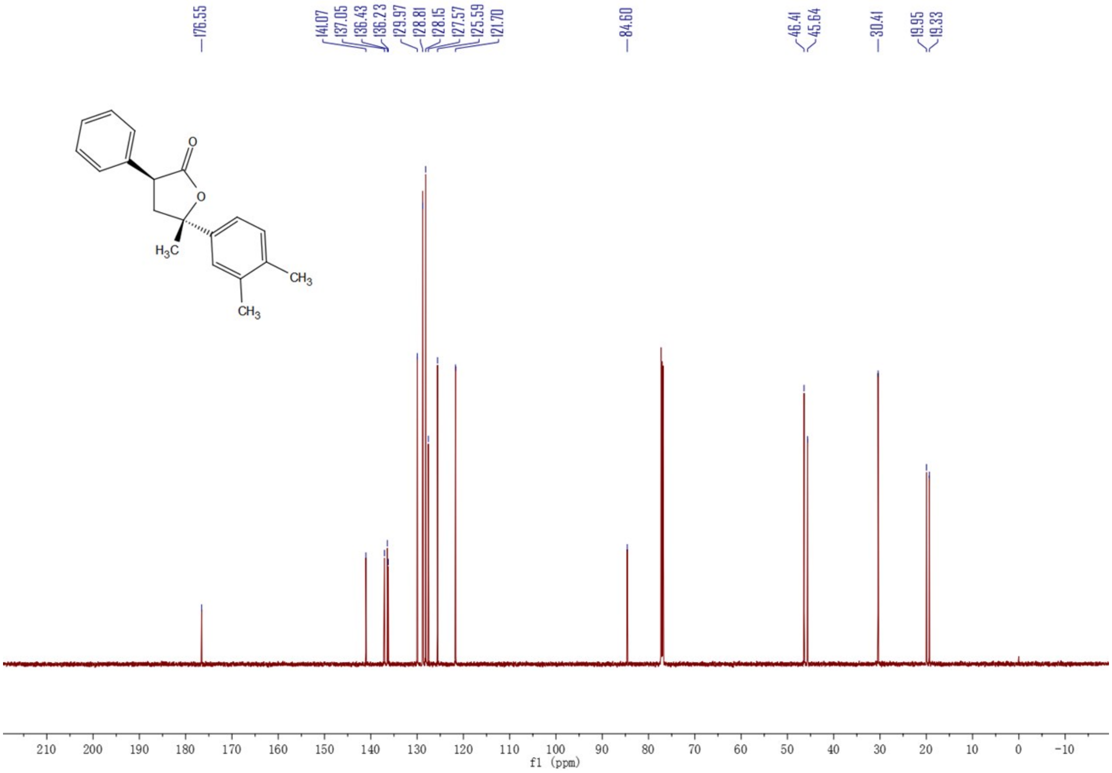
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**14**



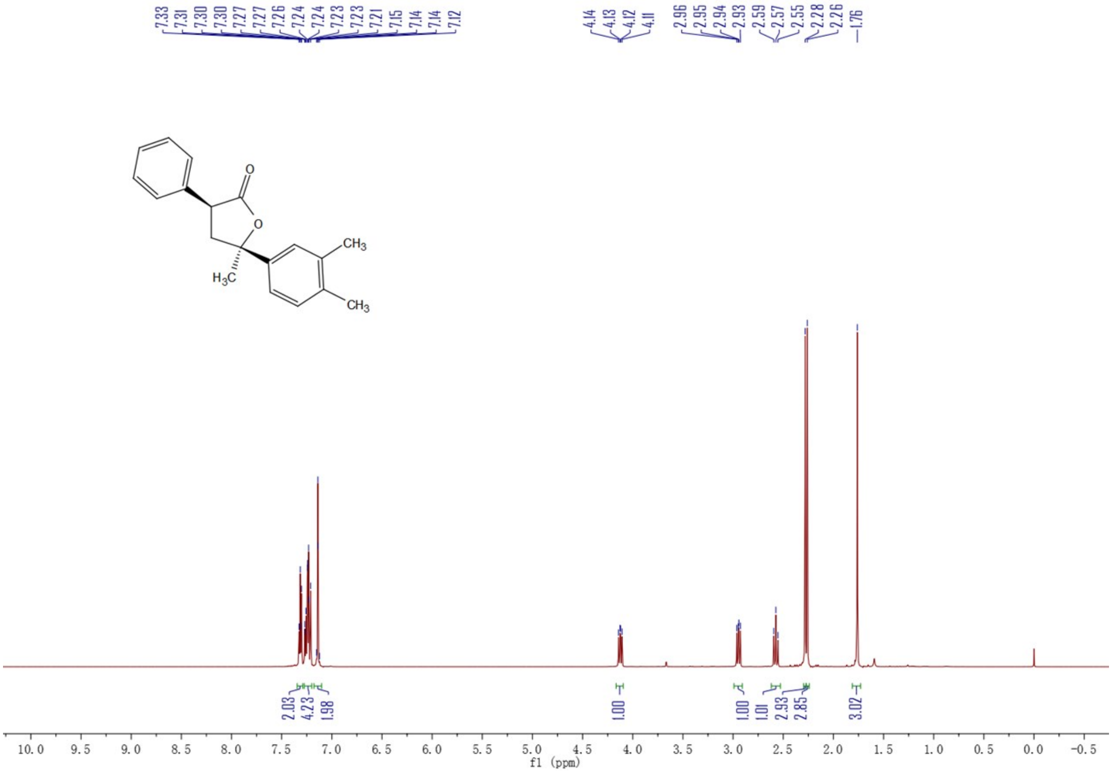
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**15**



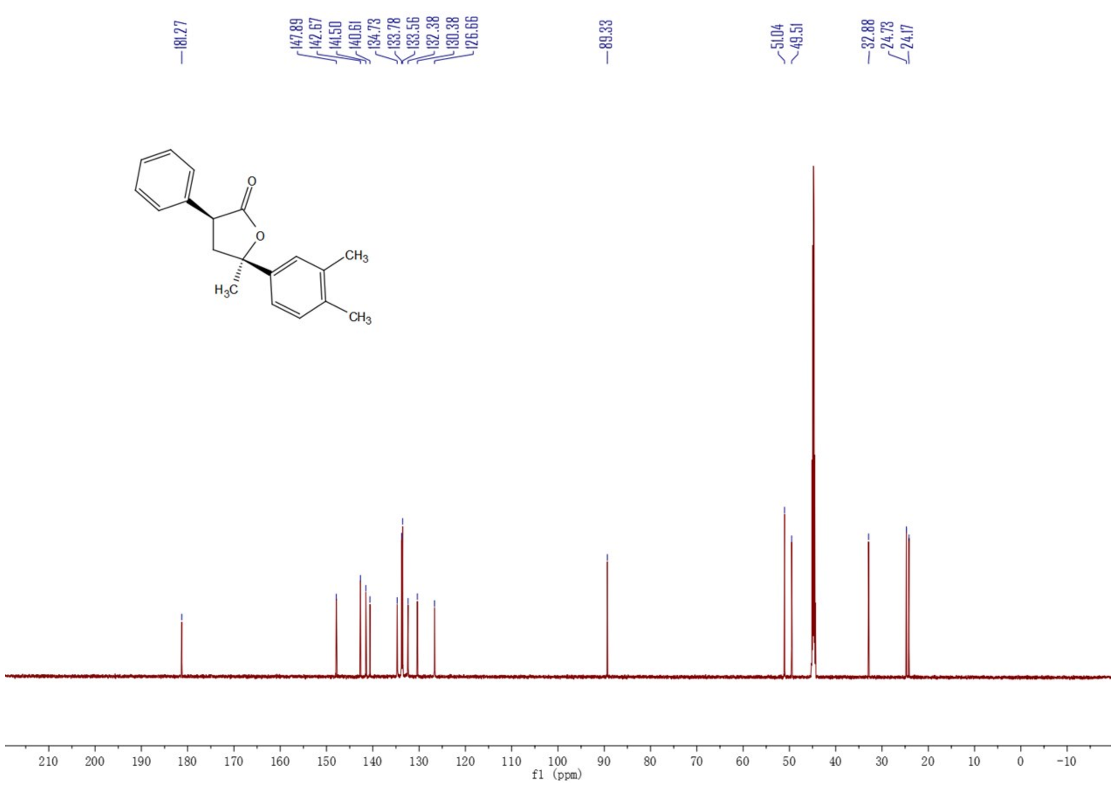
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**15**



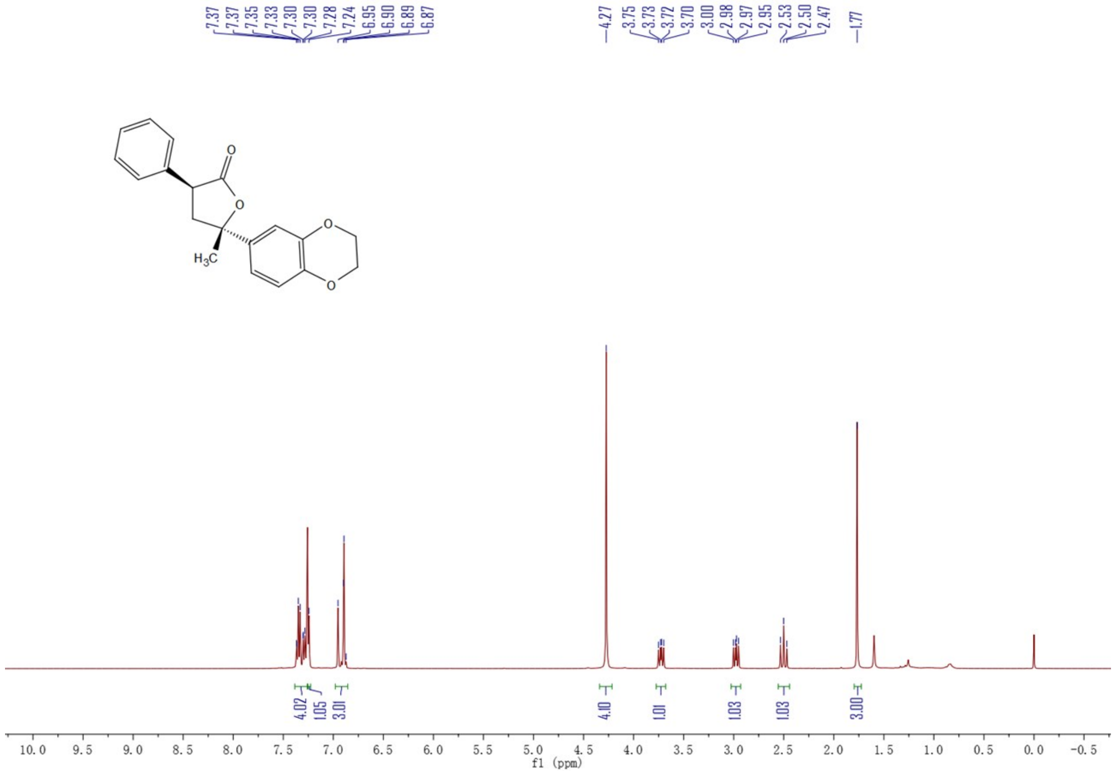
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**15**



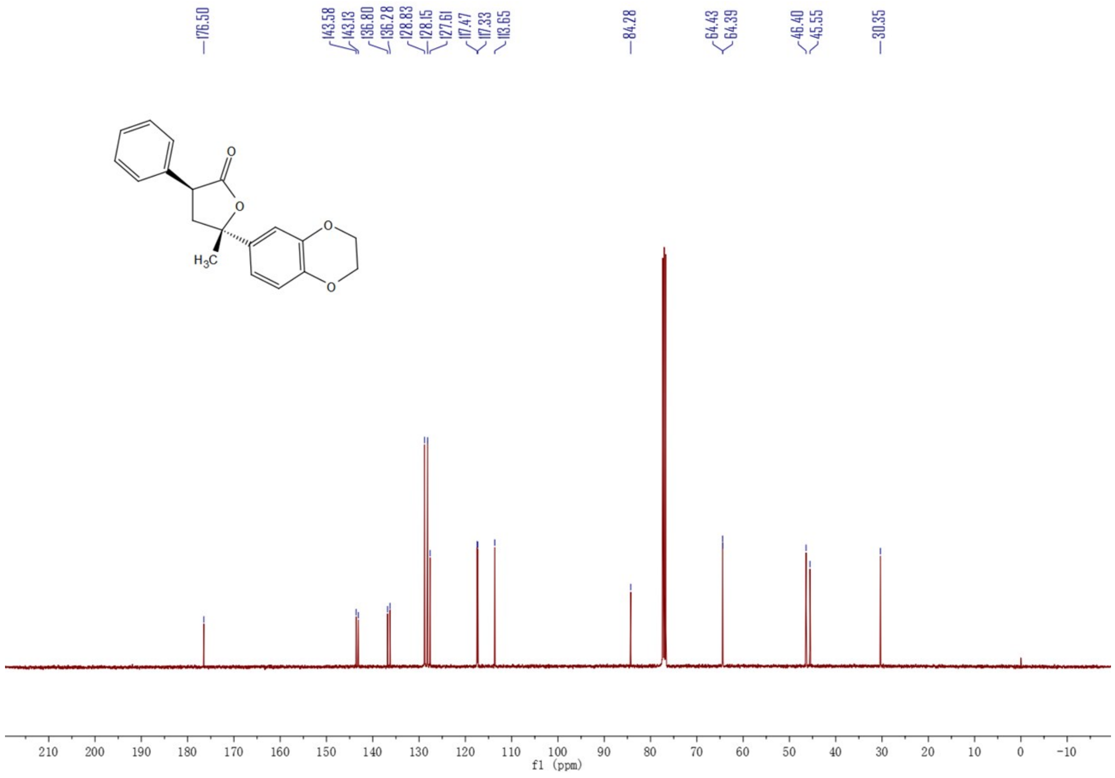
^{13}C NMR (151 MHz, (CD$_3$)$_2$SO) of (±)-*syn*-**15**



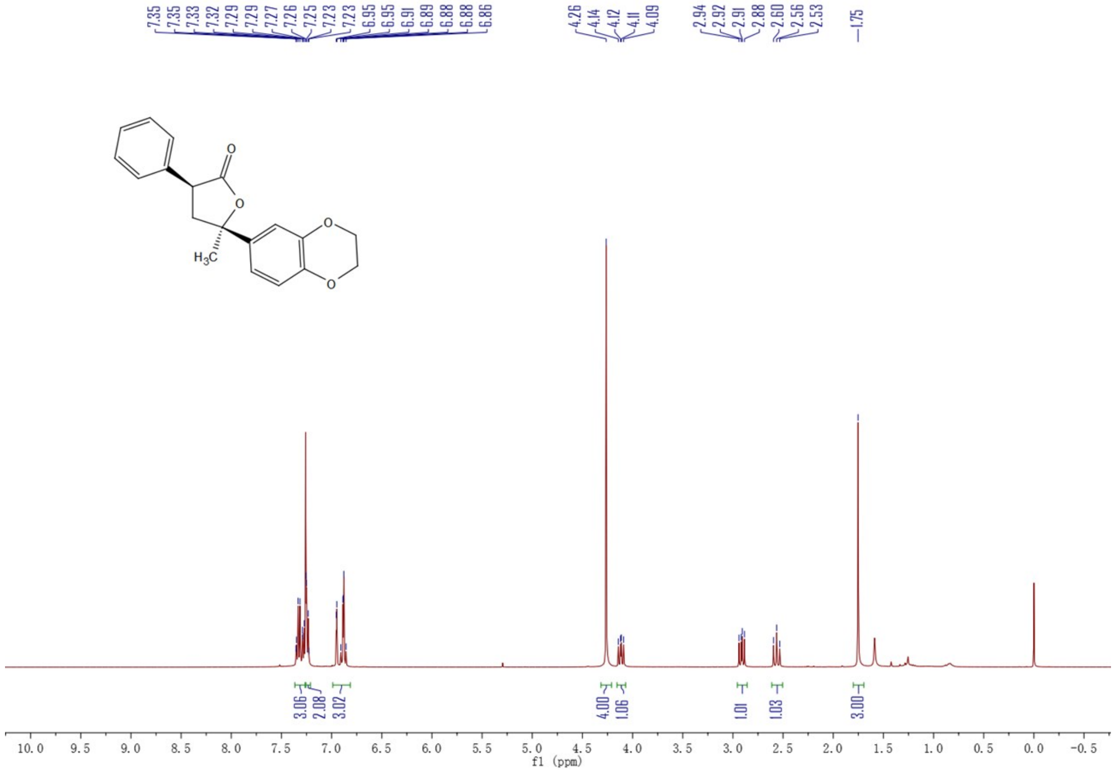
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**16**



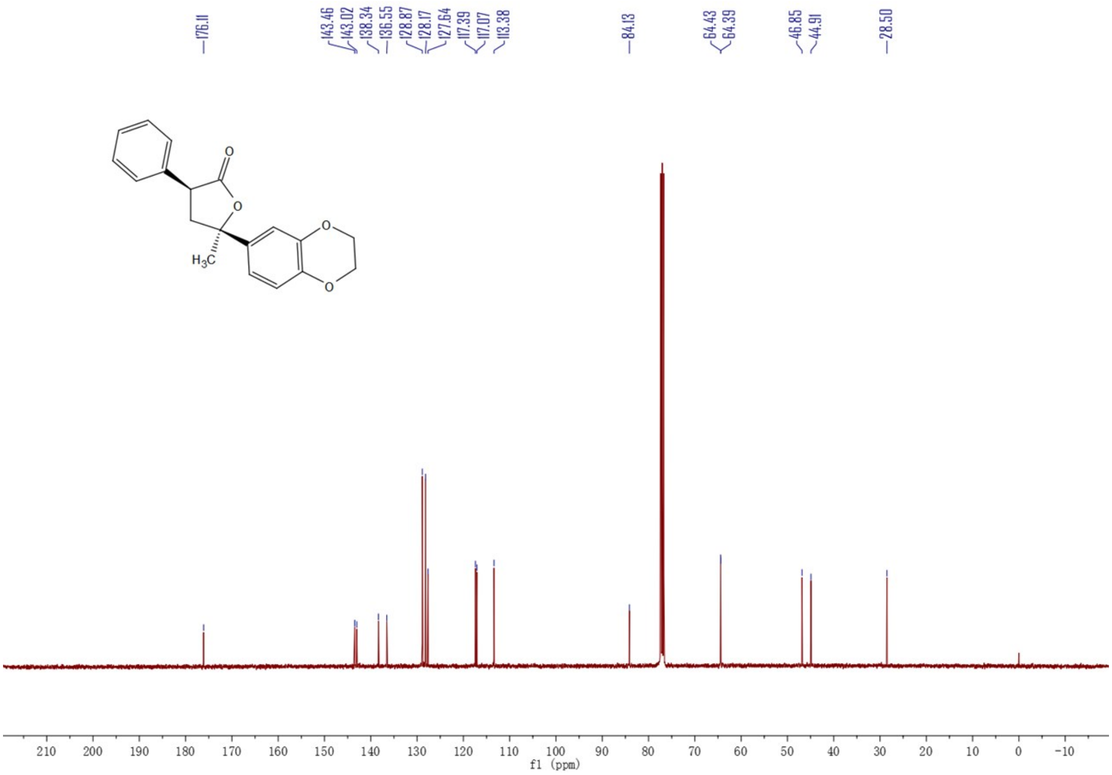
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**16**



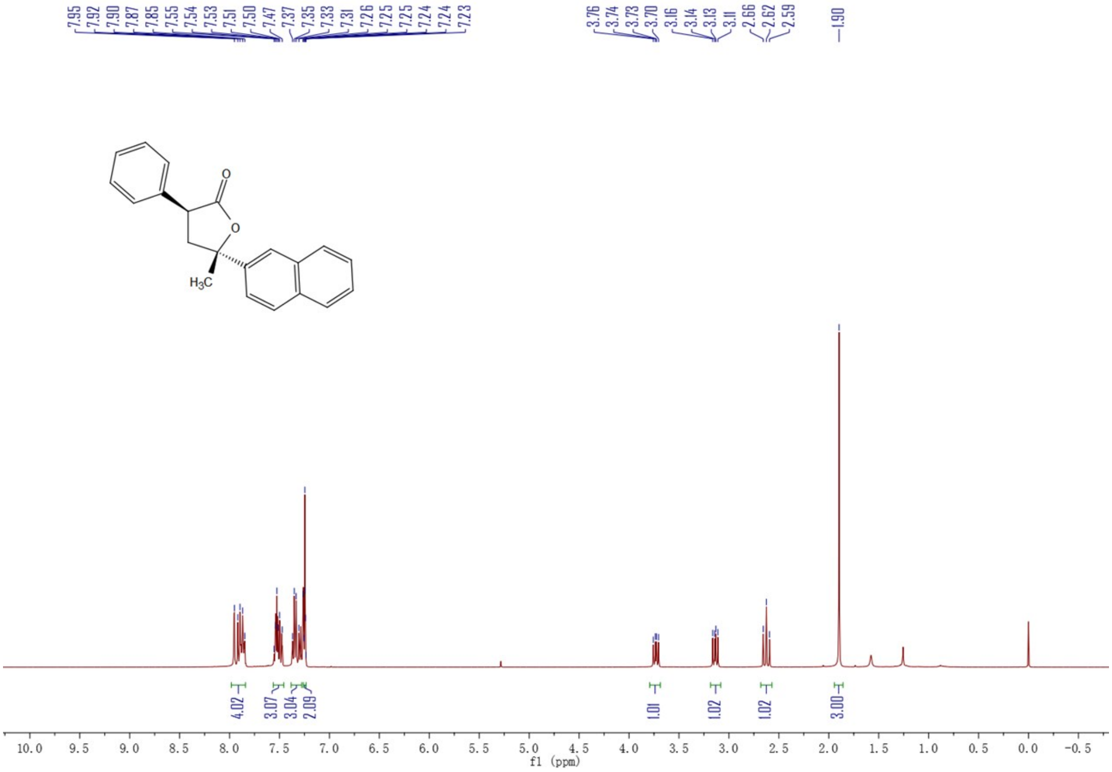
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**16**



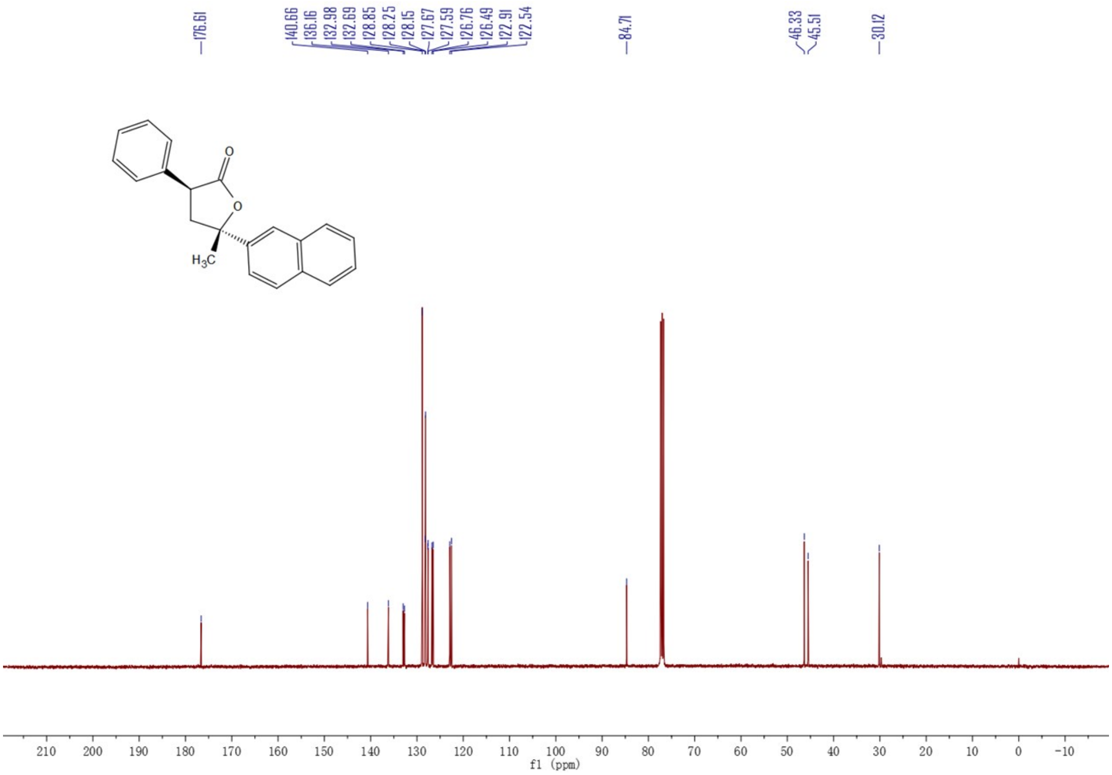
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**16**



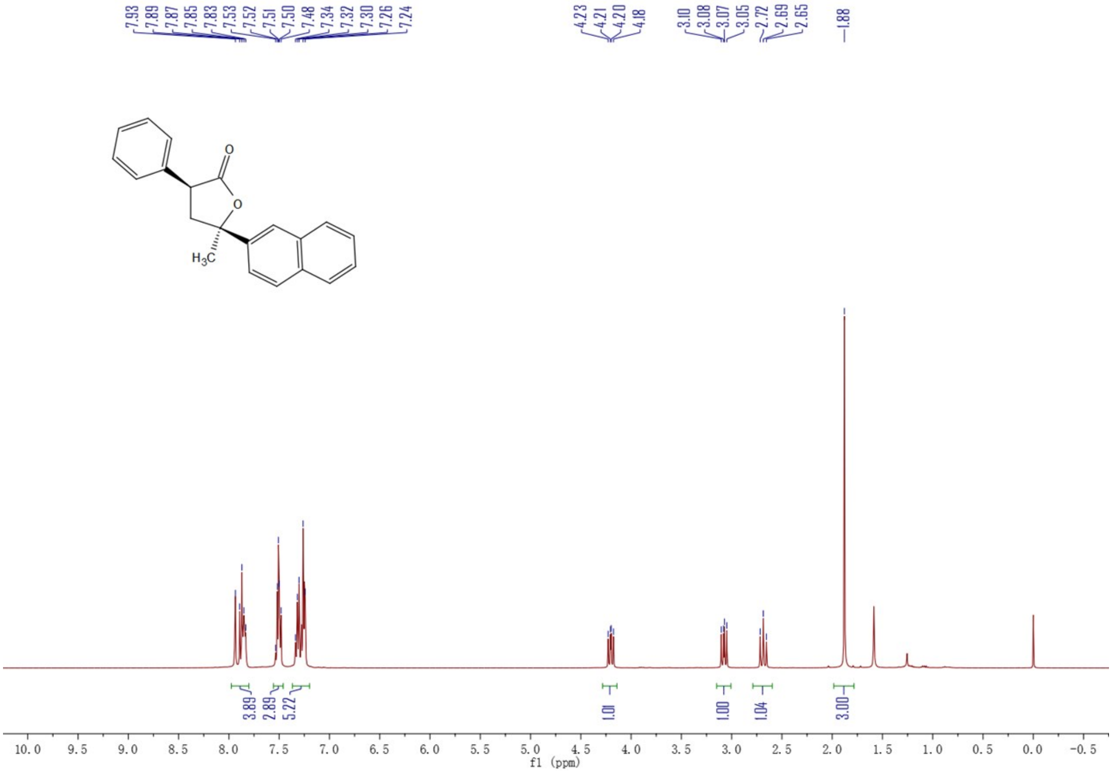
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**17**



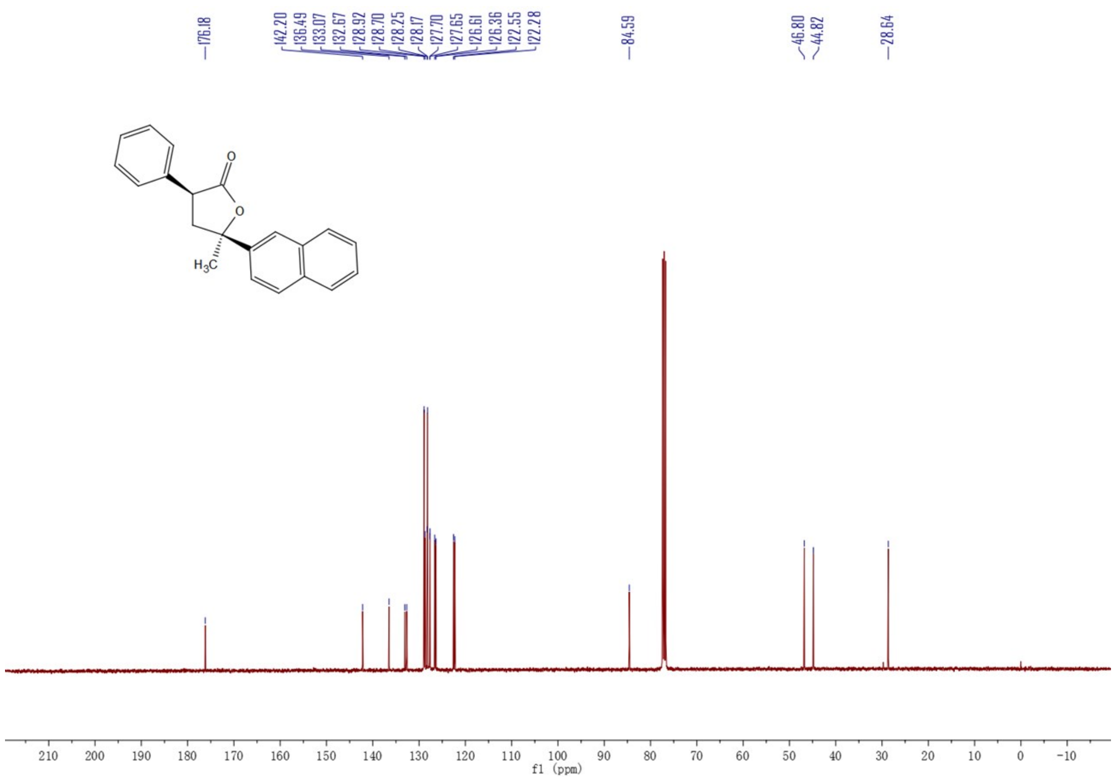
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**17**



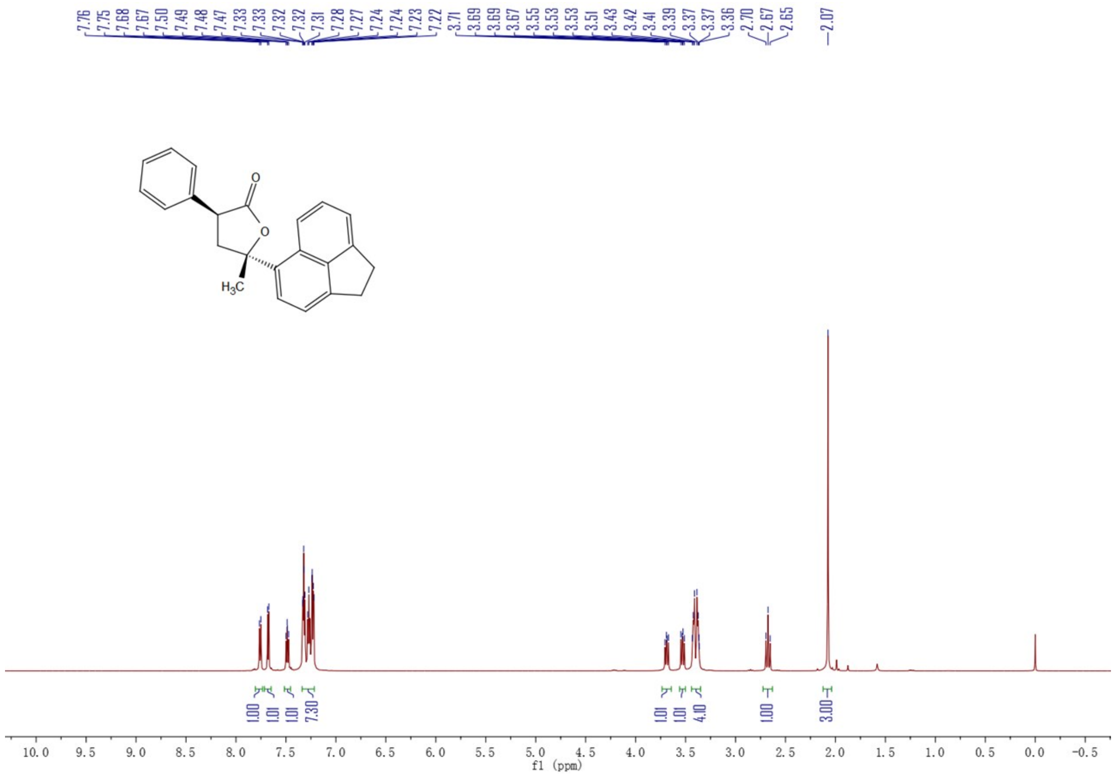
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**17**



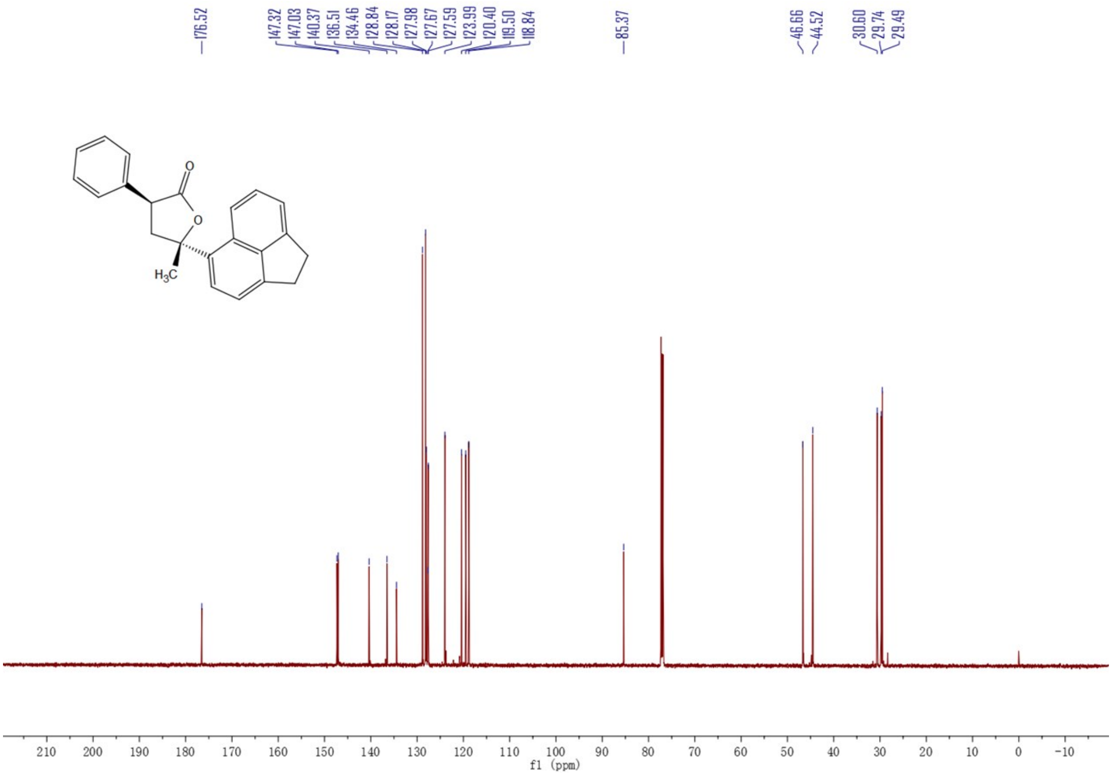
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**17**



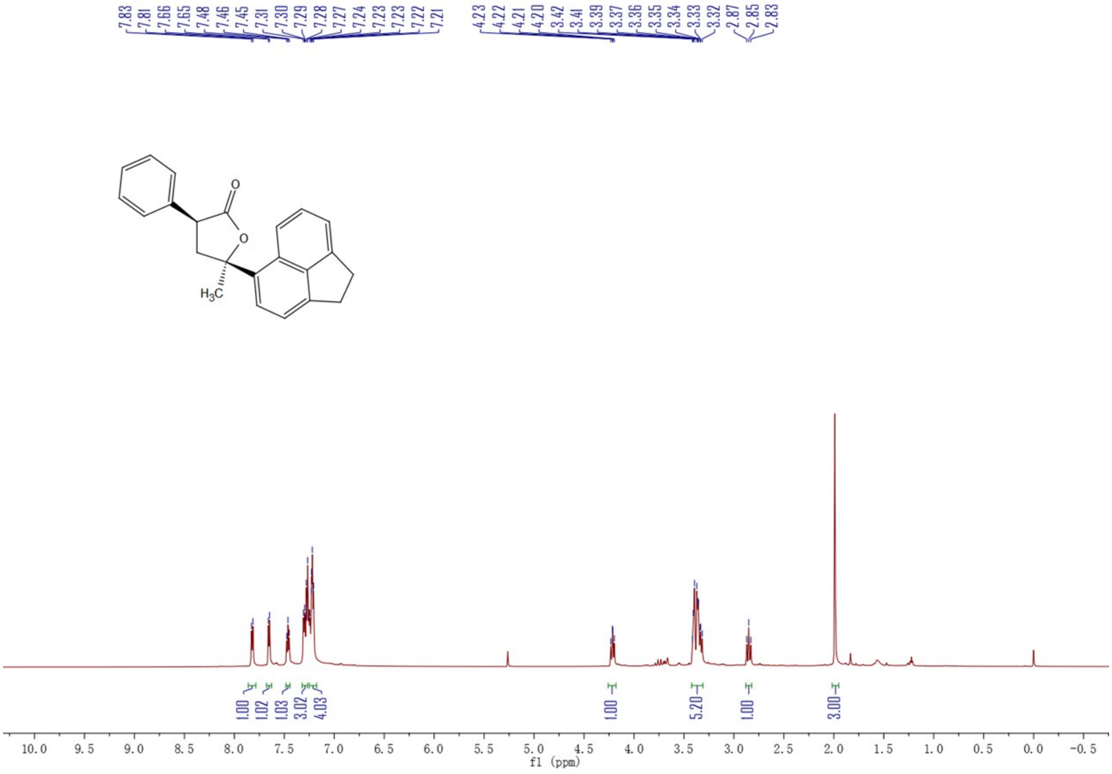
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**18**



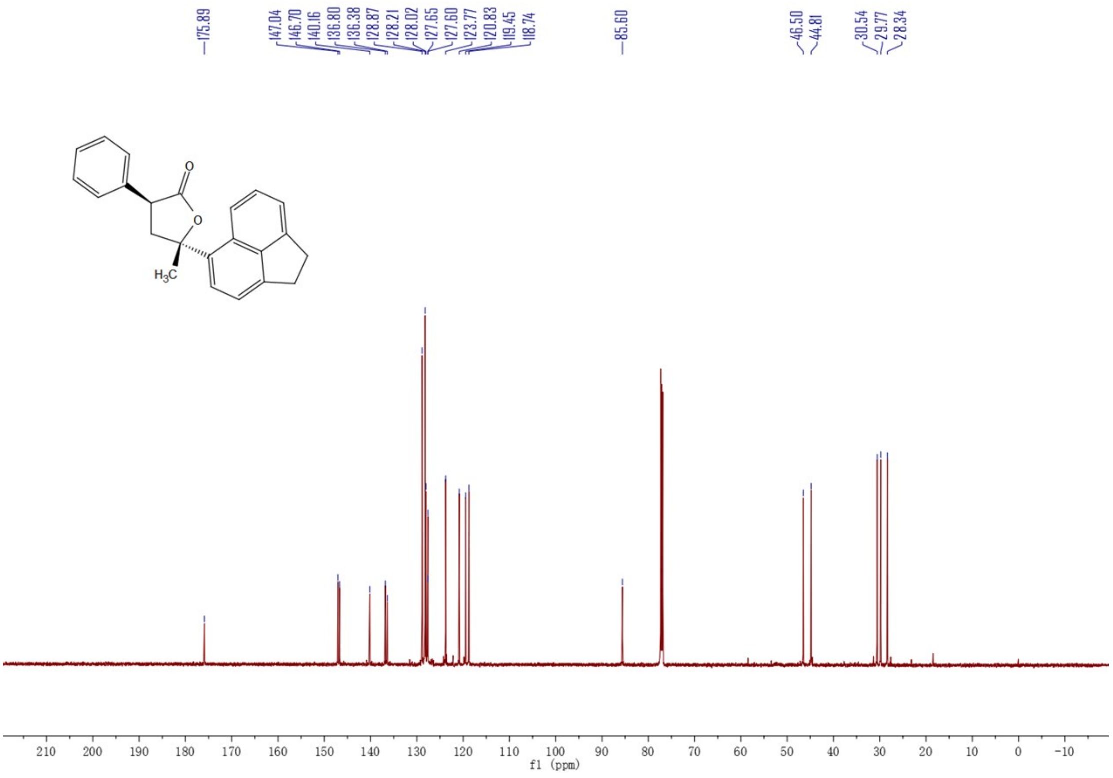
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**18**



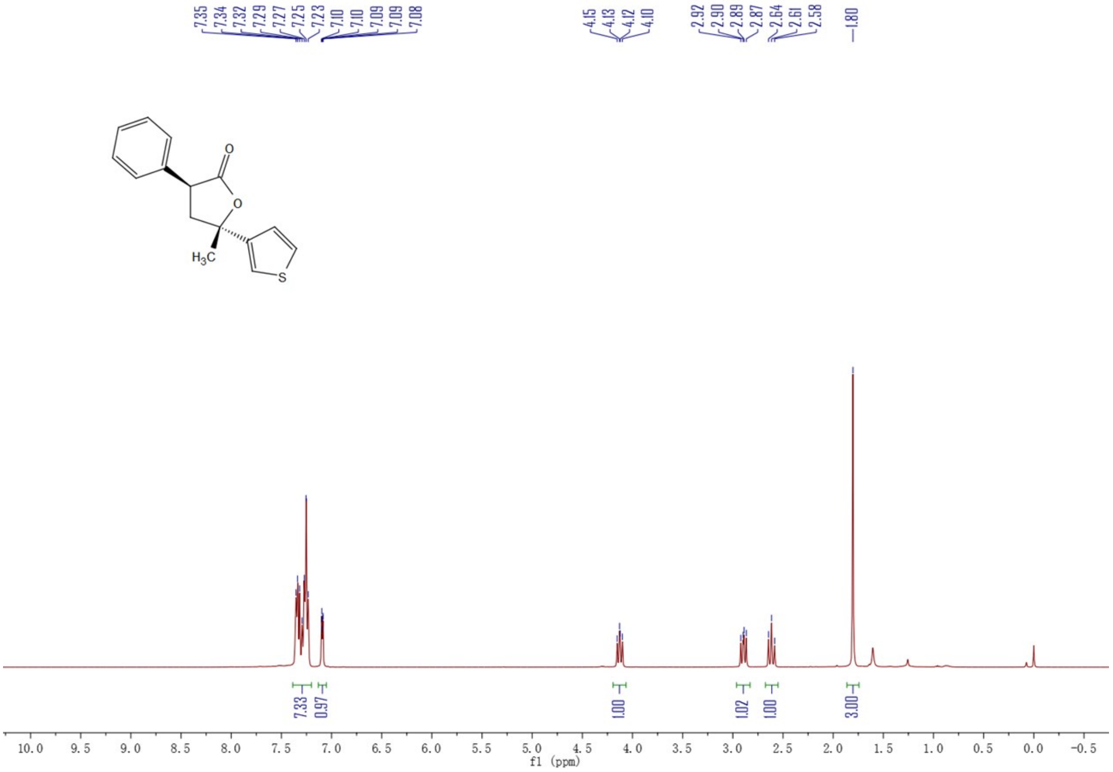
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**18**



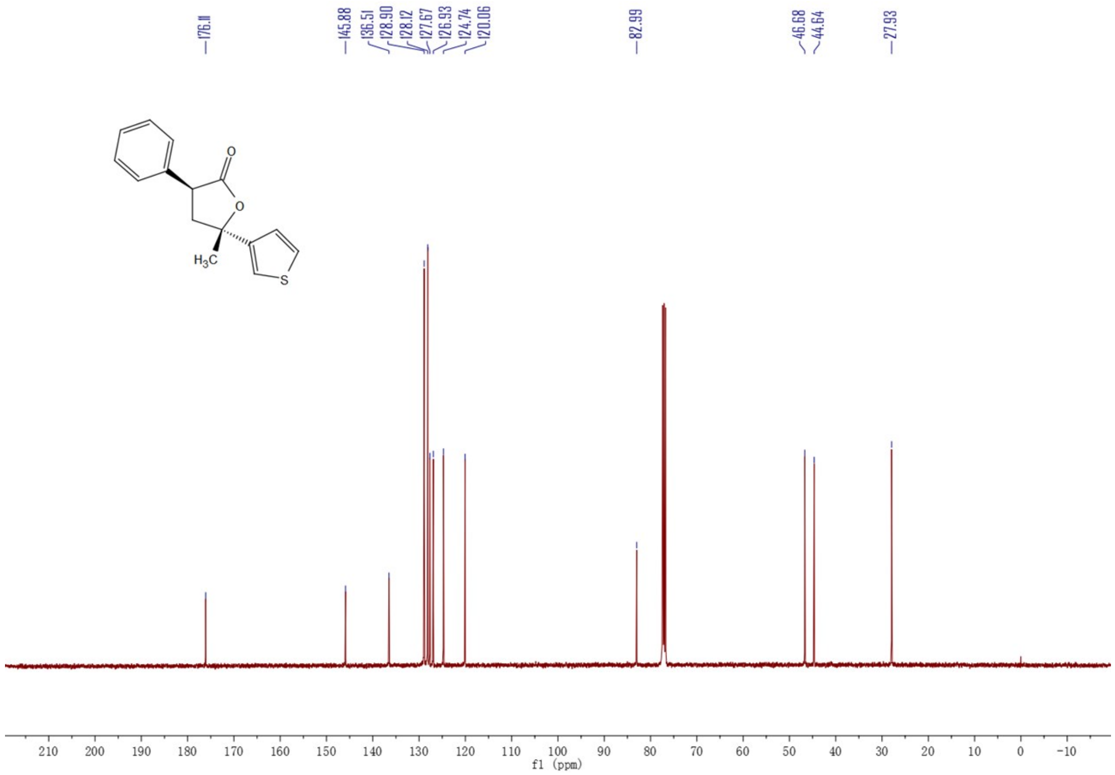
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**18**



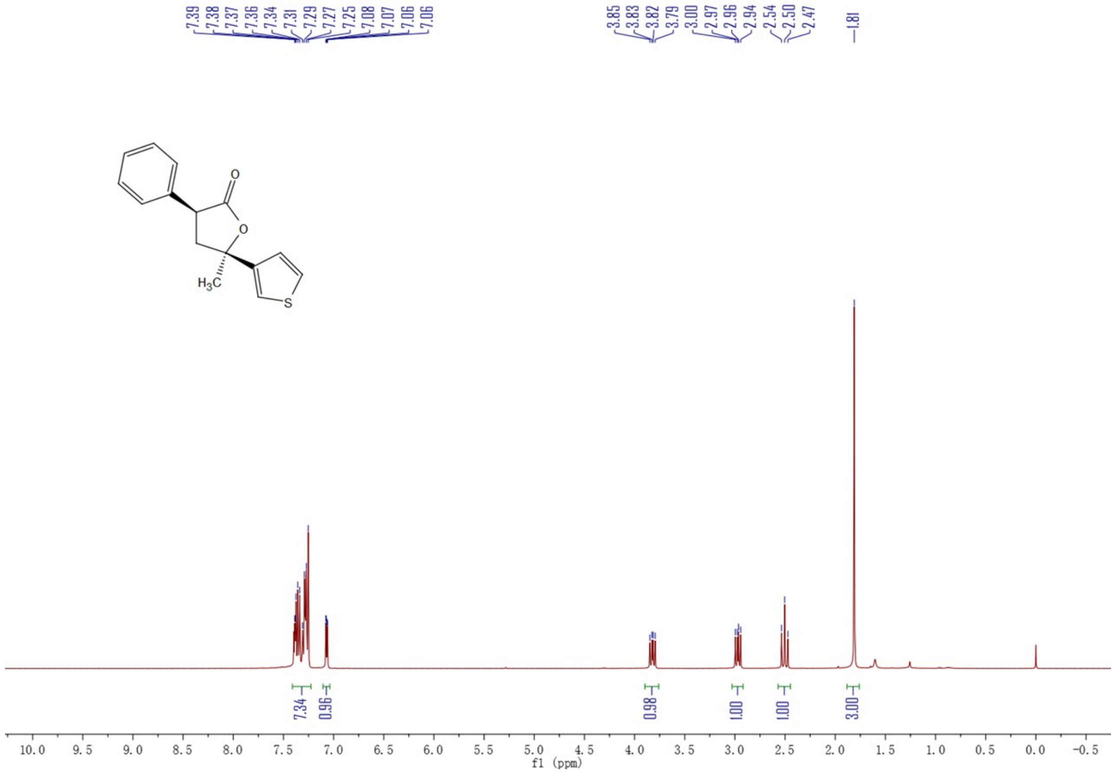
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**19**



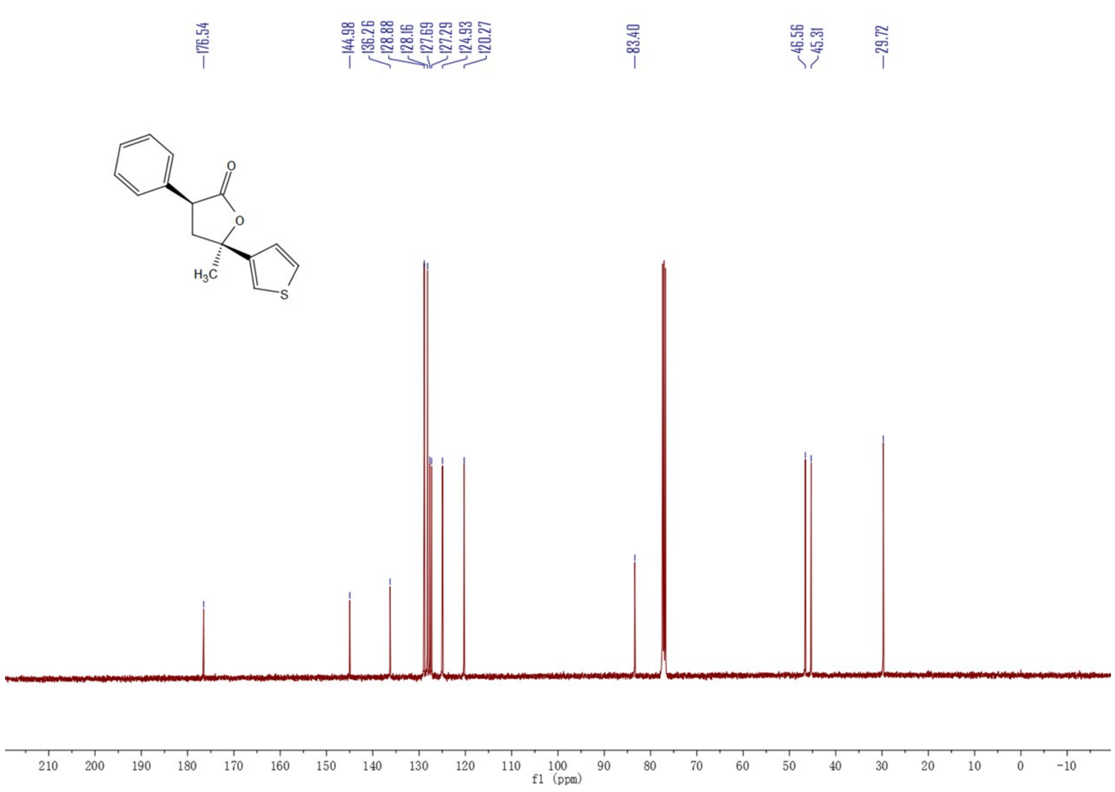
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**19**



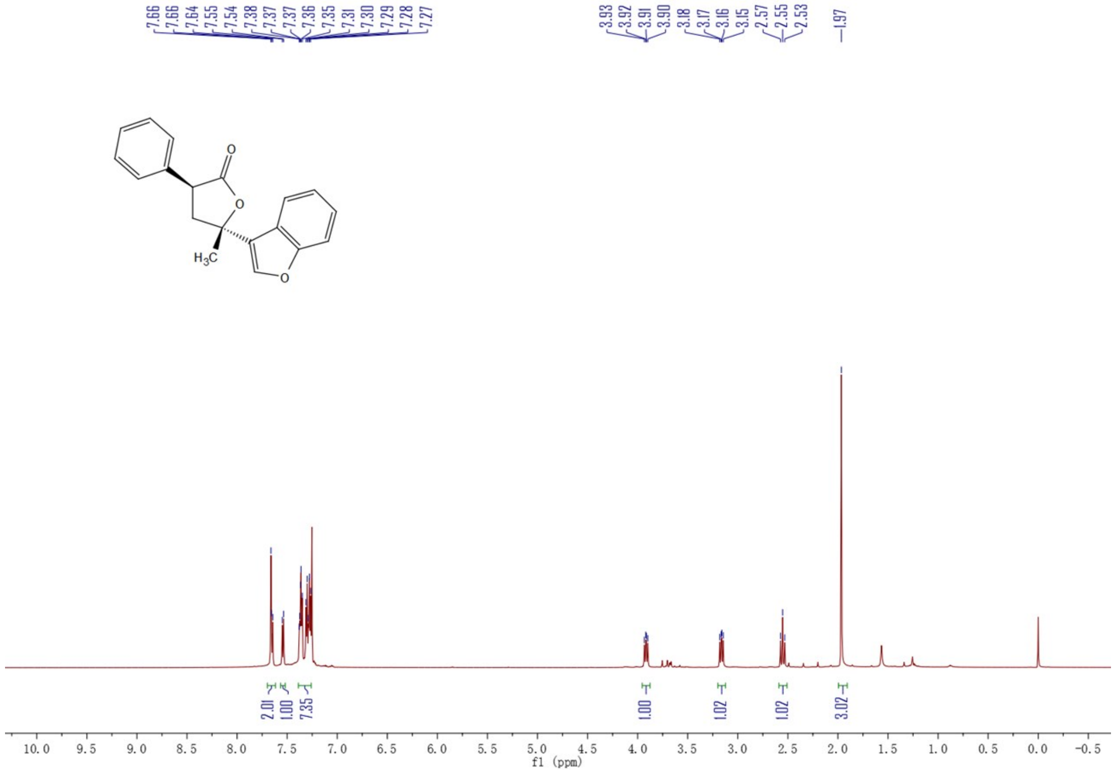
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**19**



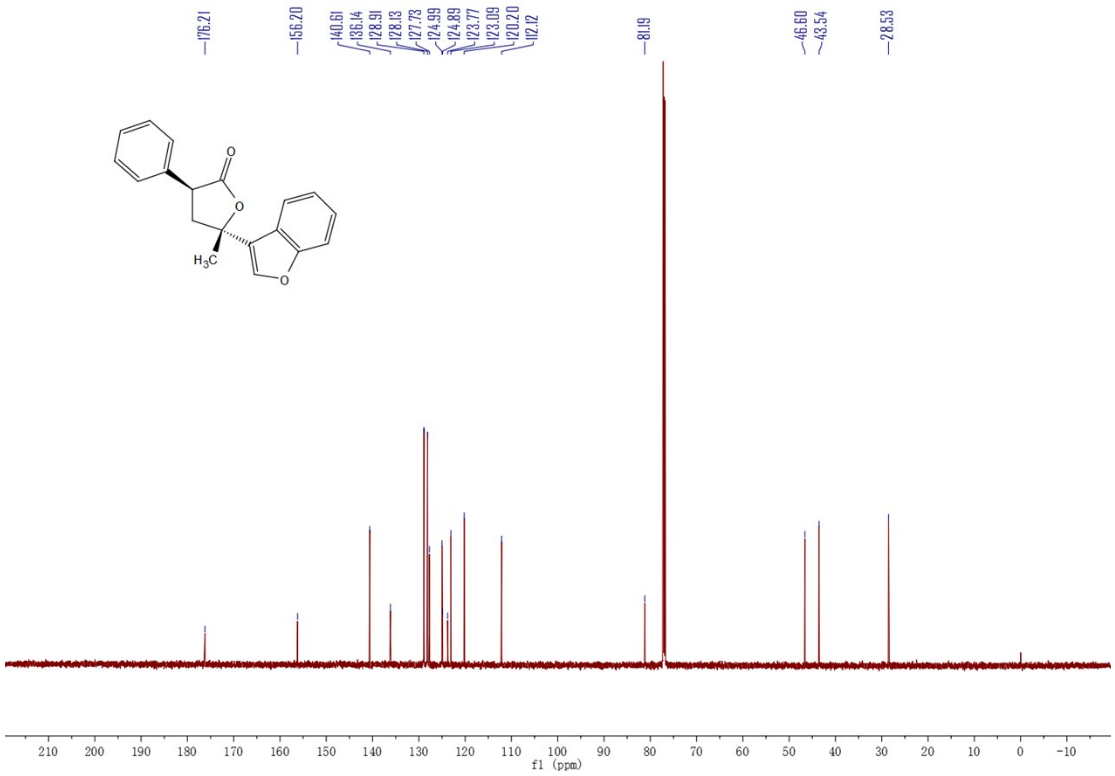
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**19**



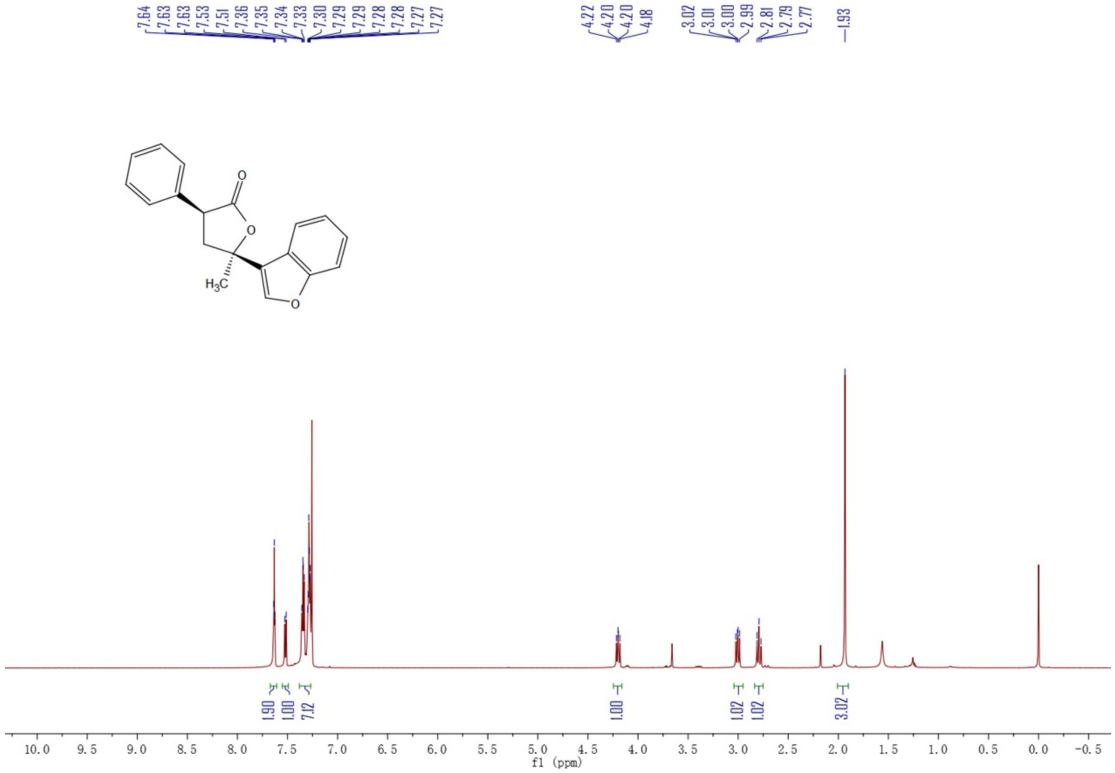
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**20**



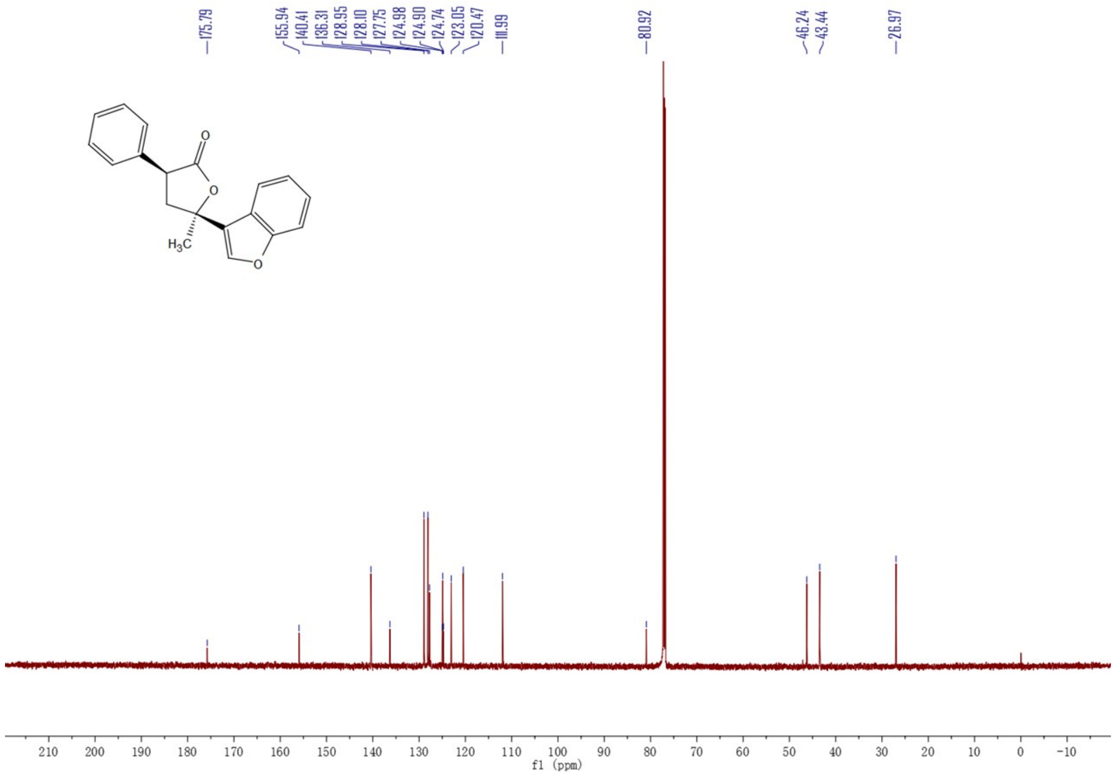
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**20**



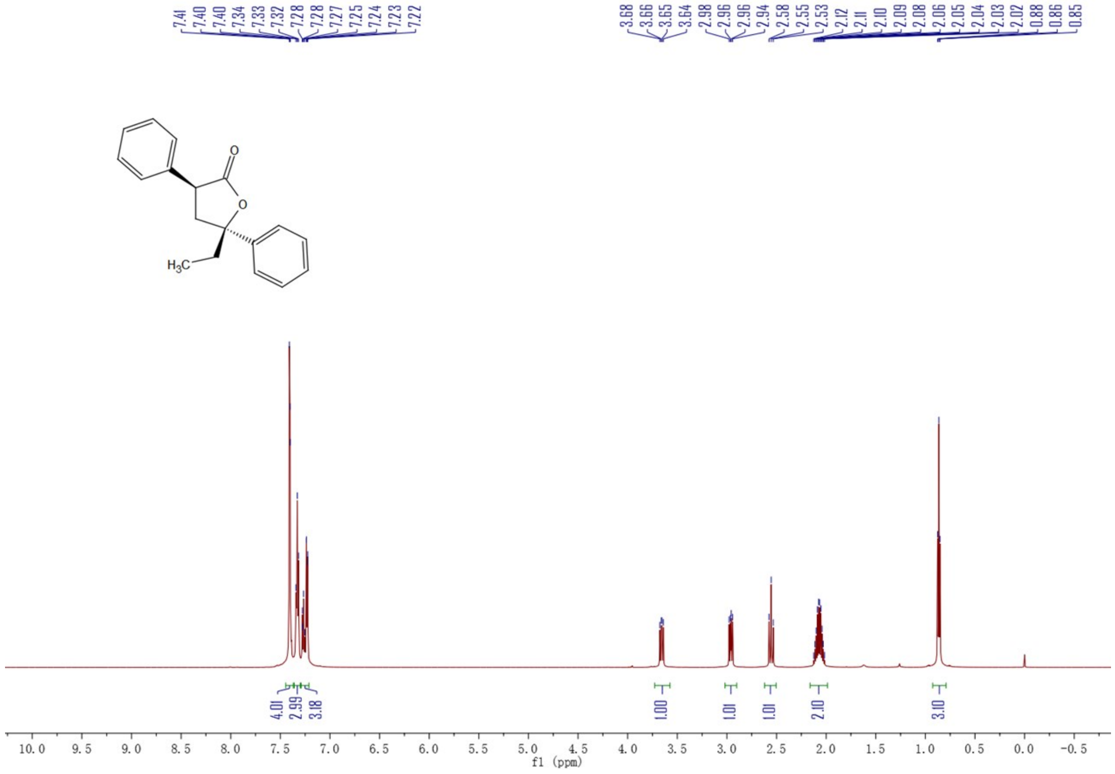
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**20**



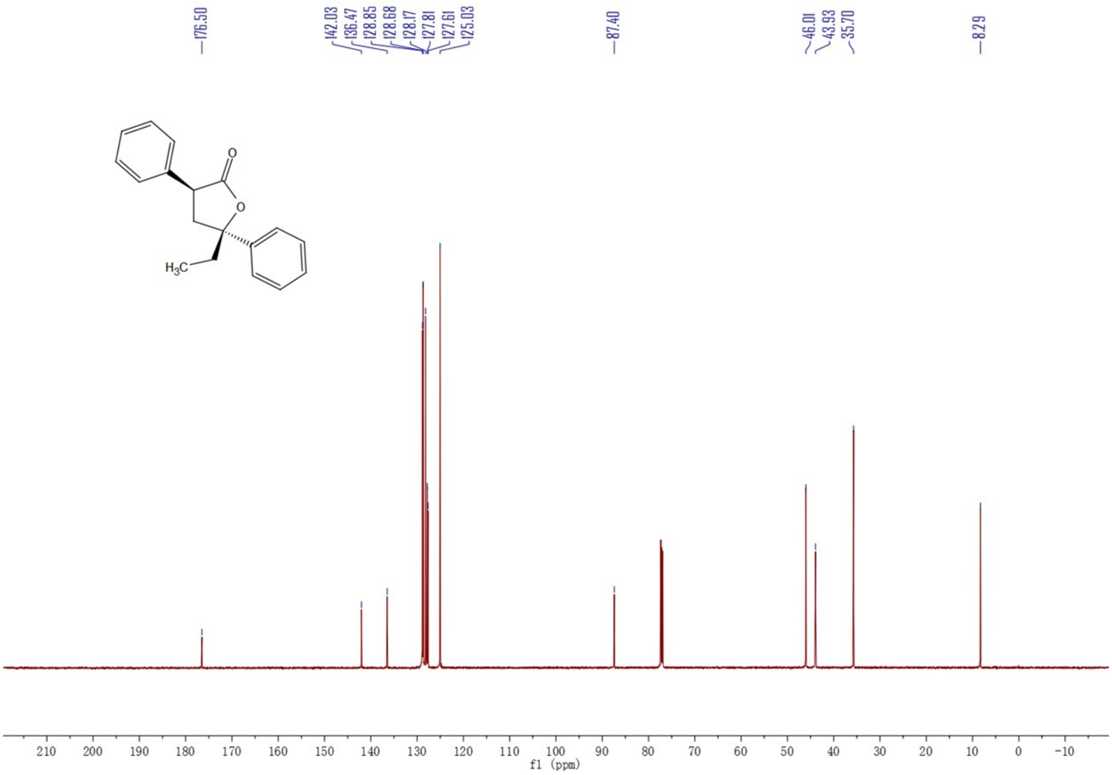
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**20**



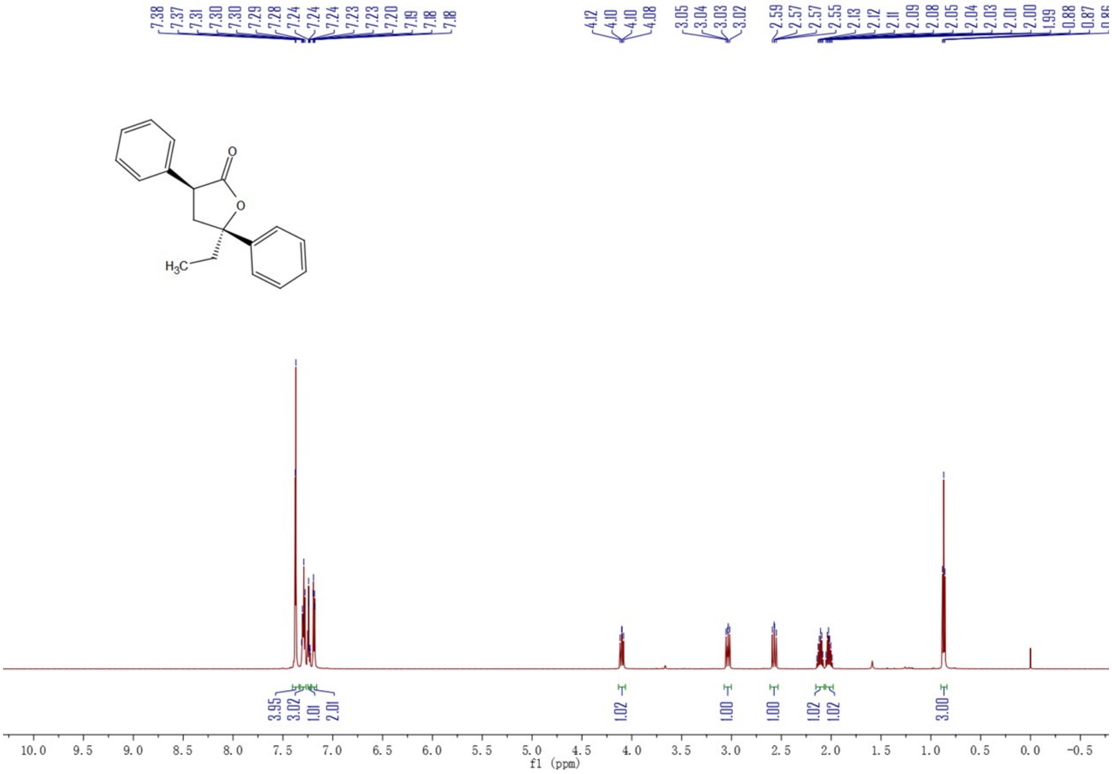
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**21**



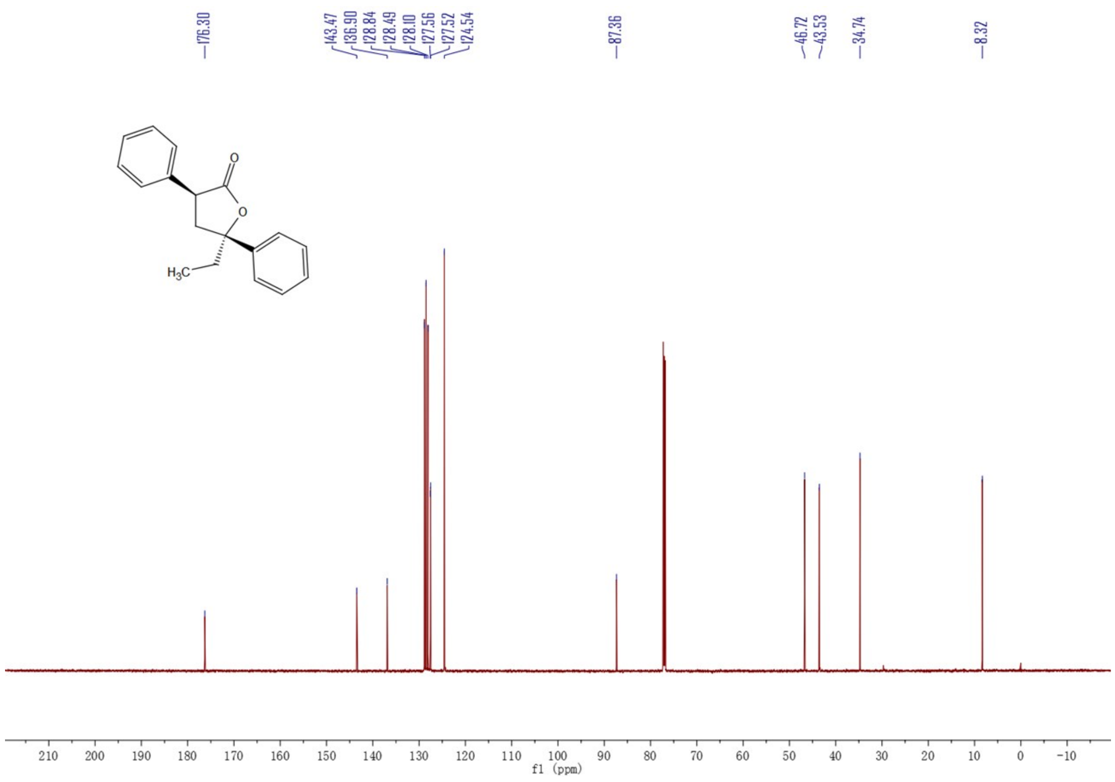
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**21**



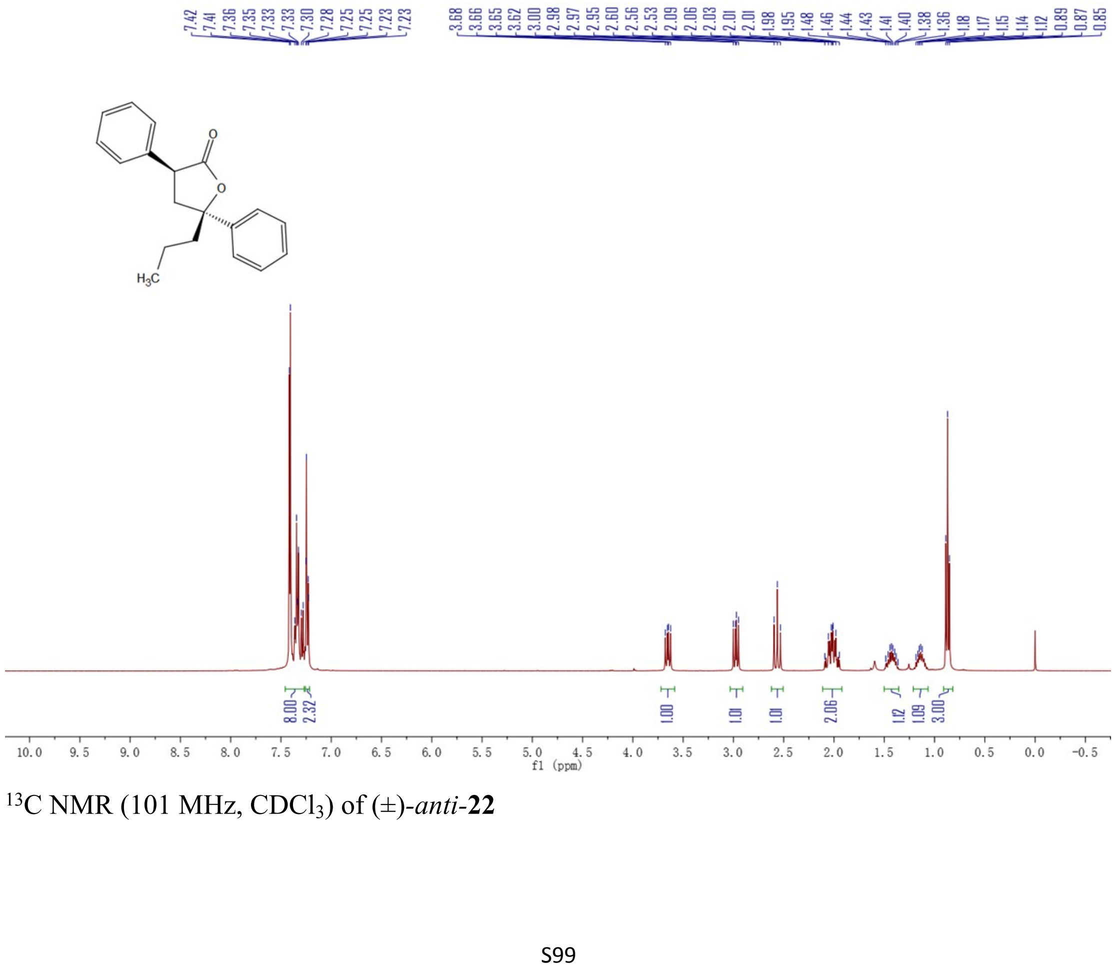
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**21**



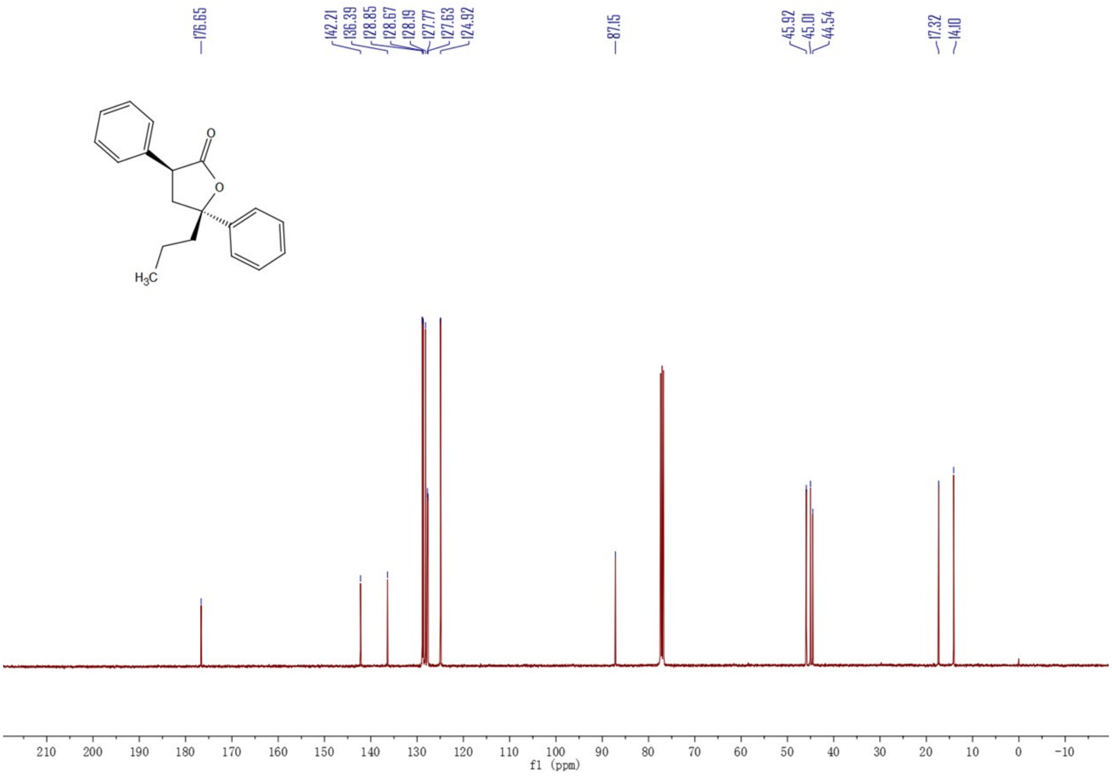
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**21**



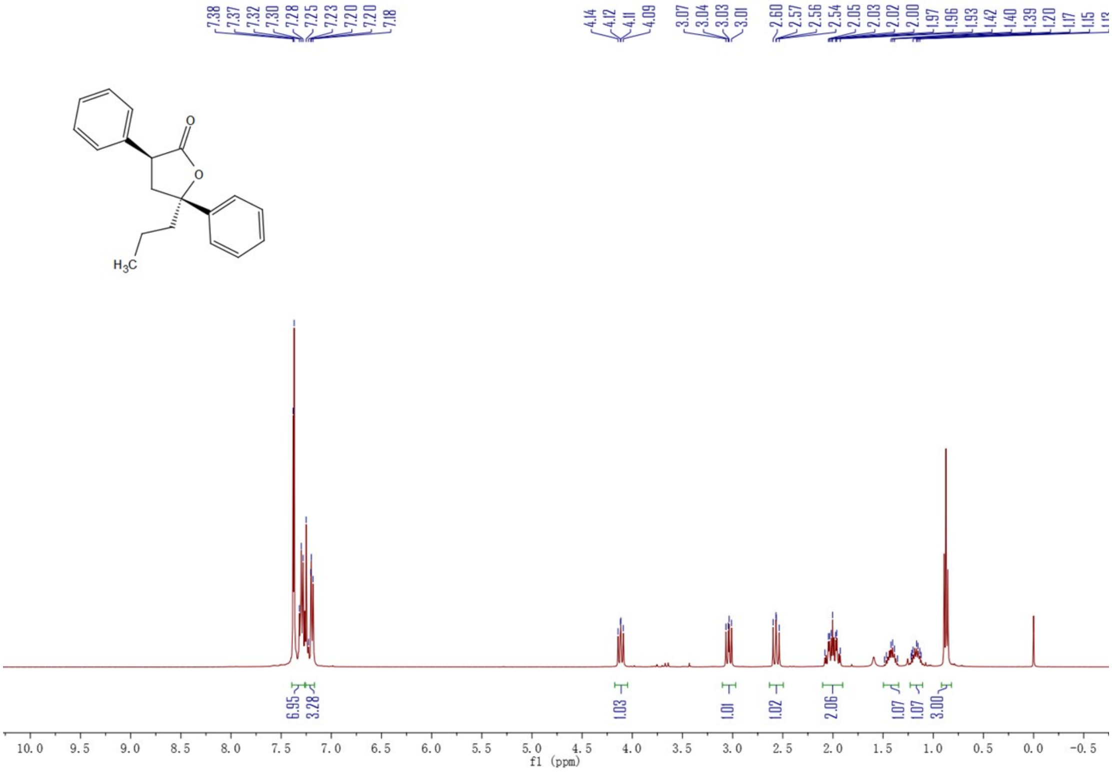
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**22**



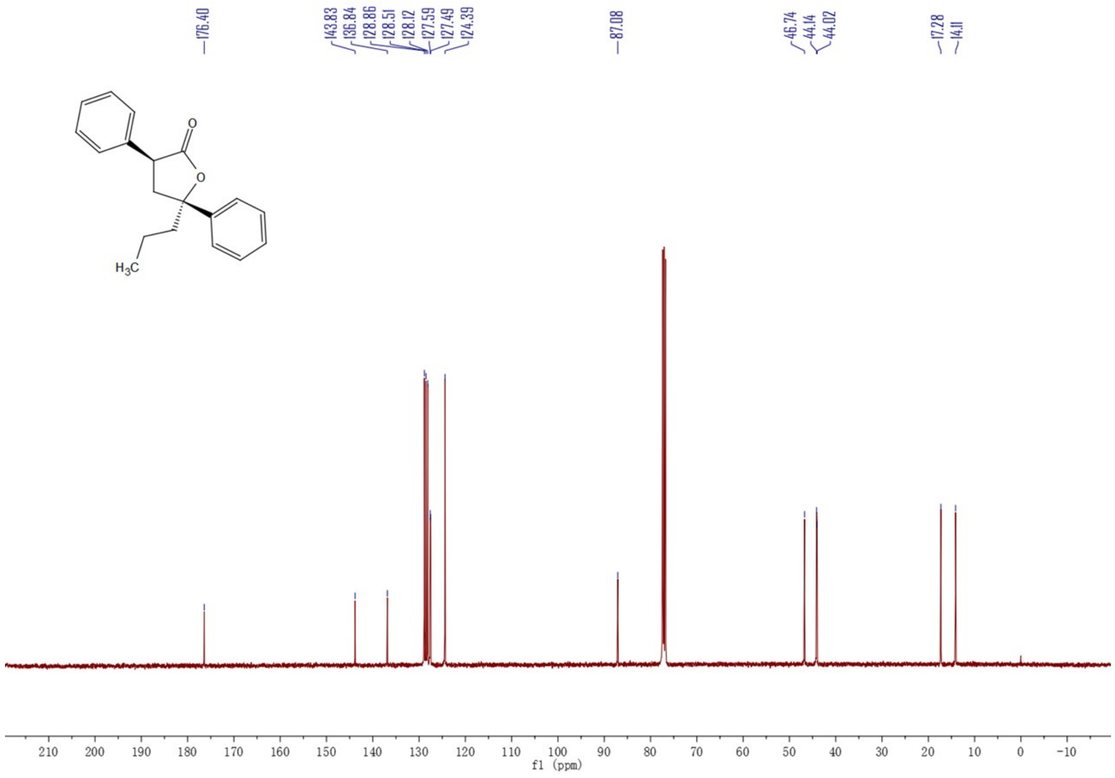
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**22**



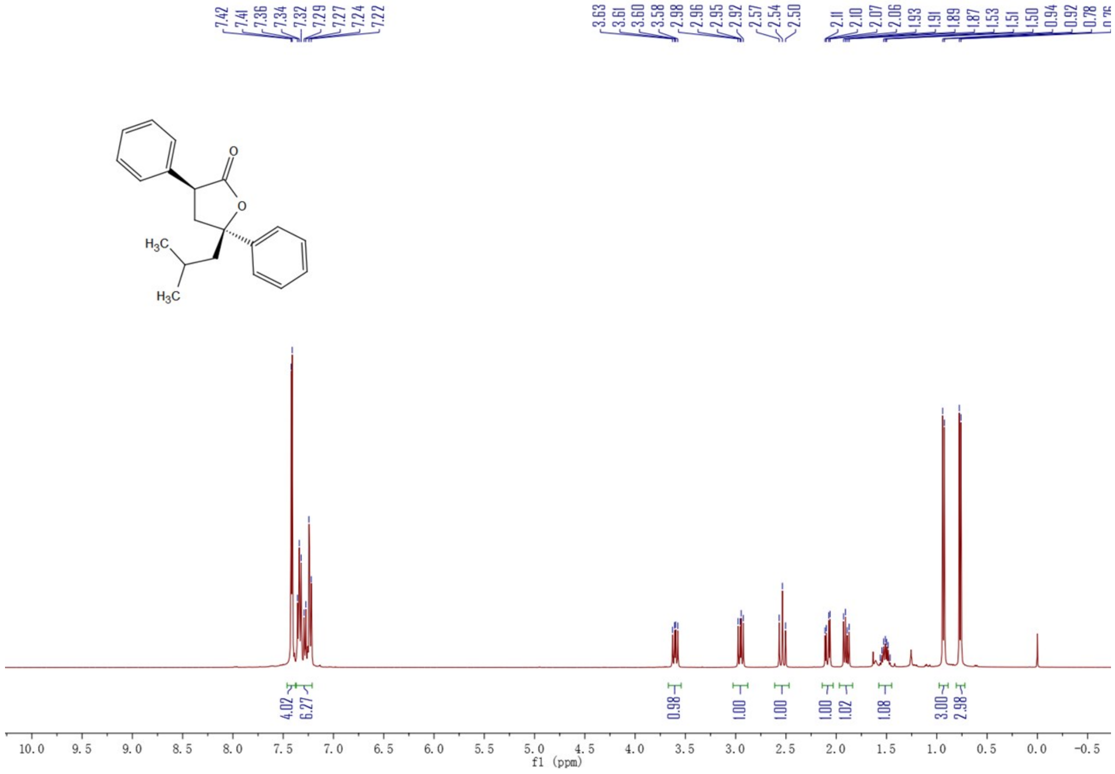
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**22**



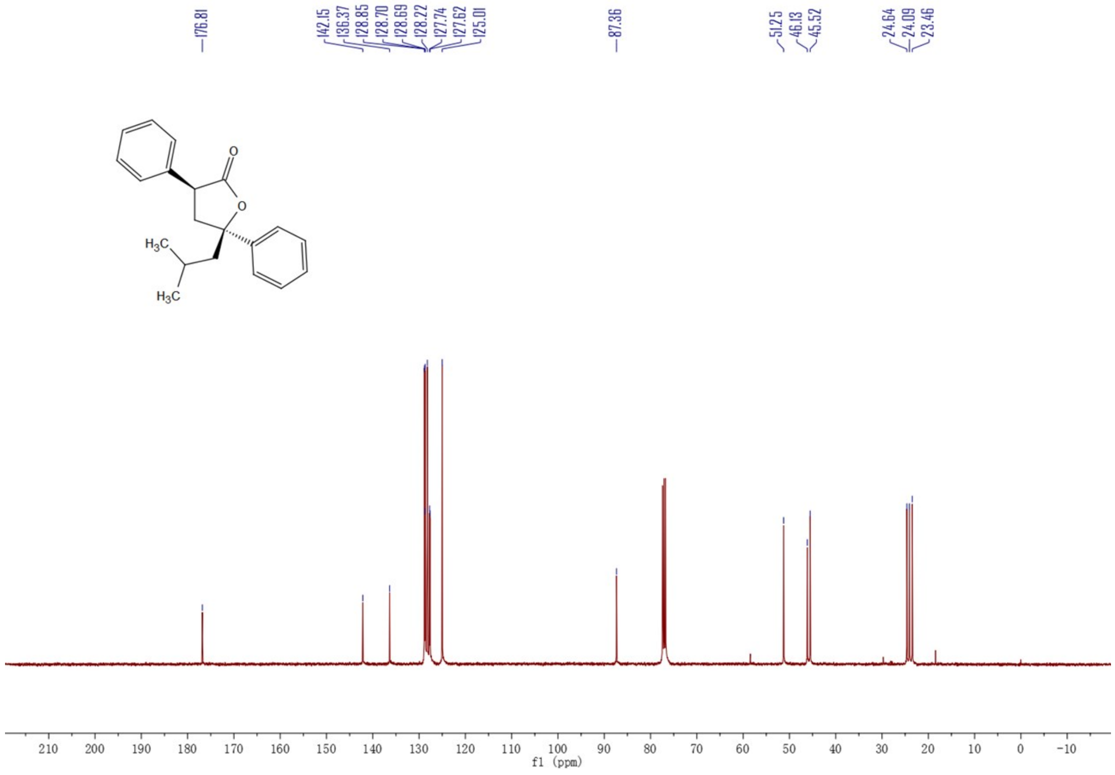
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**22**



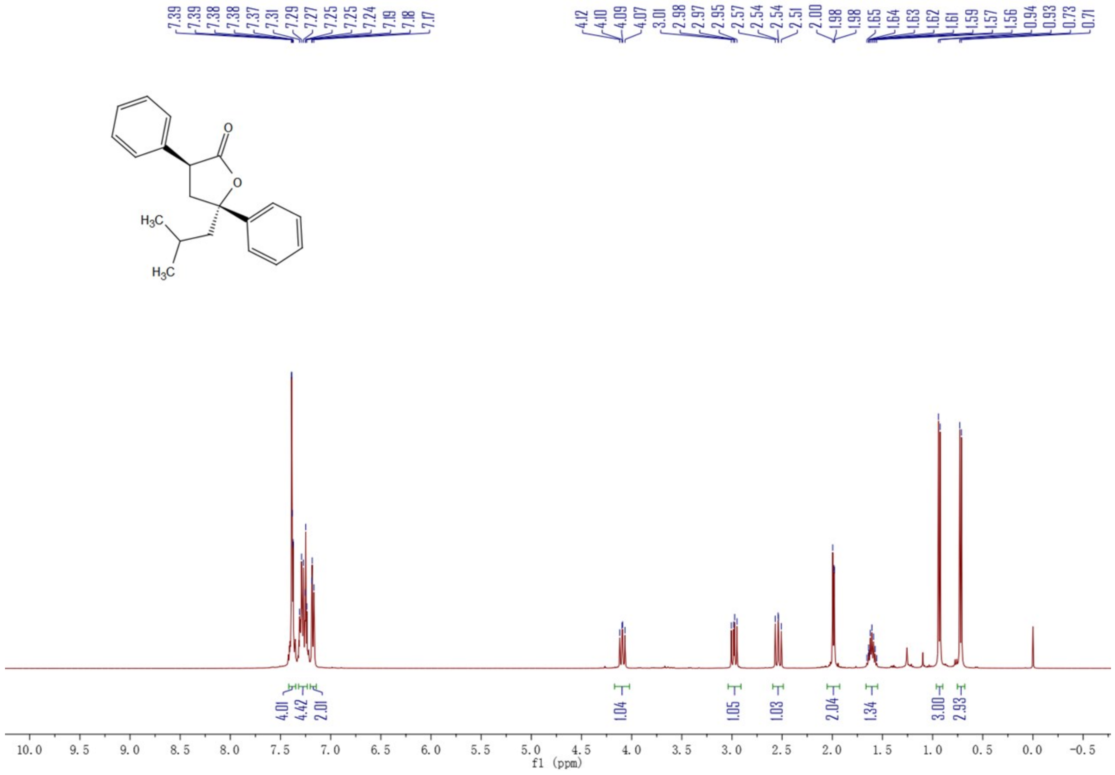
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**23**



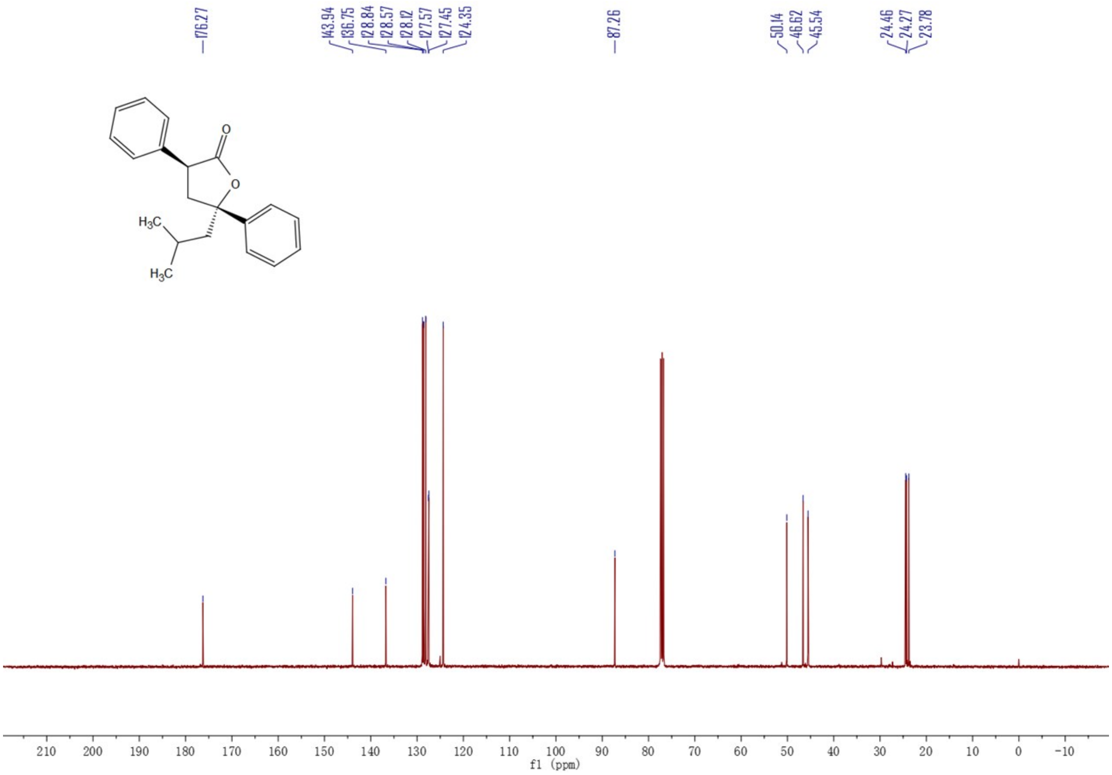
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**23**



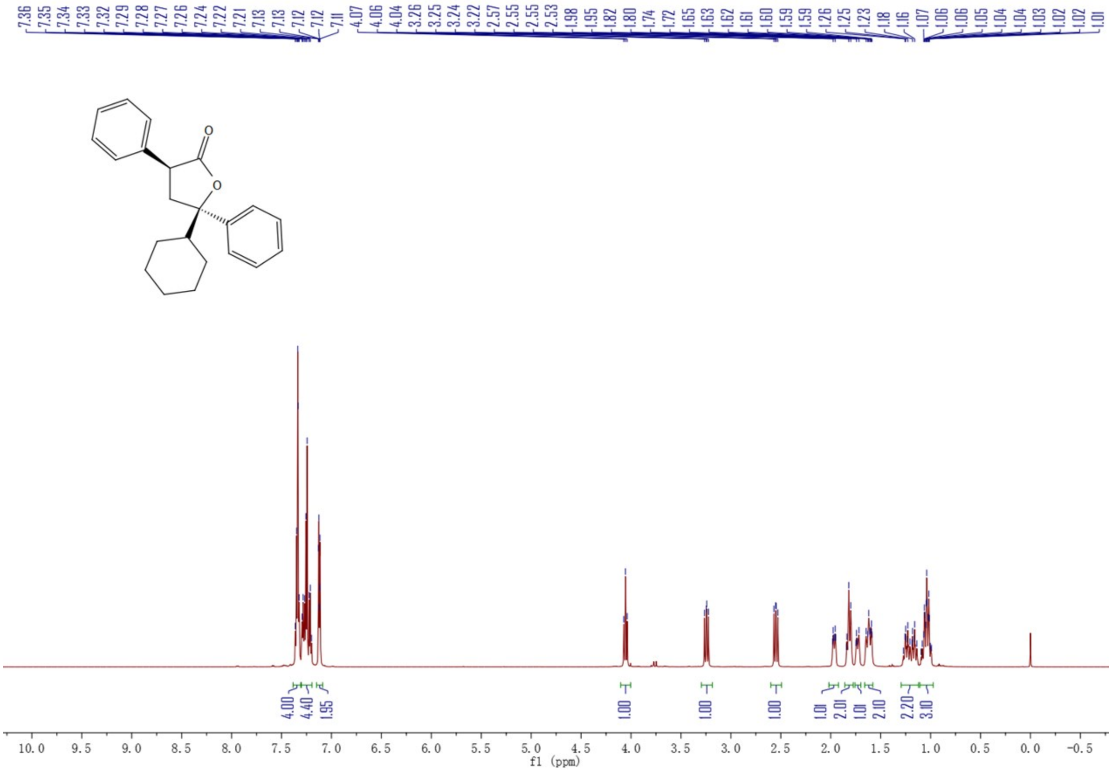
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**23**



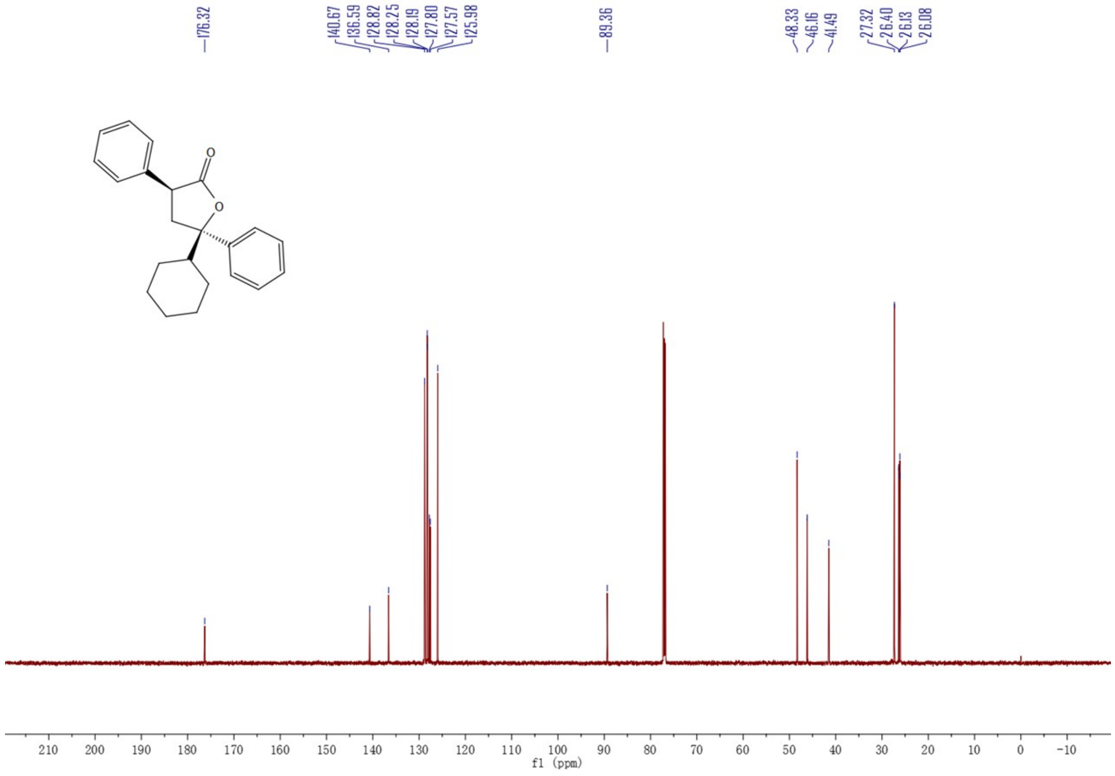
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**23**



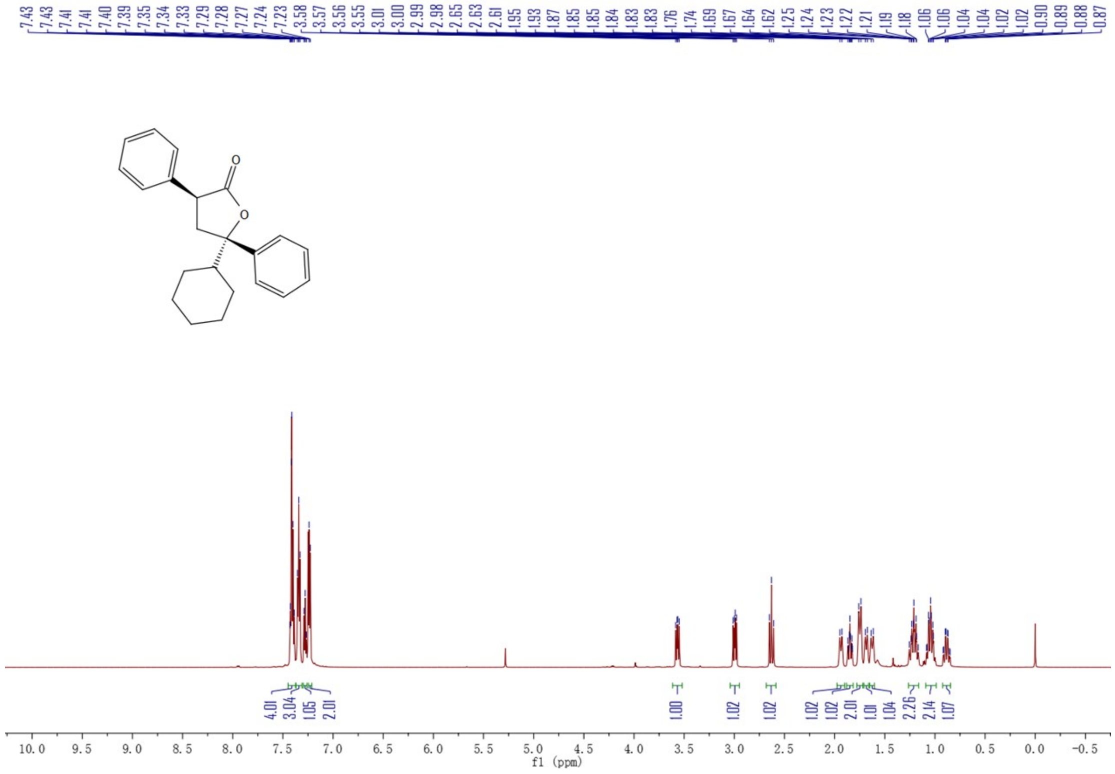
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**24**



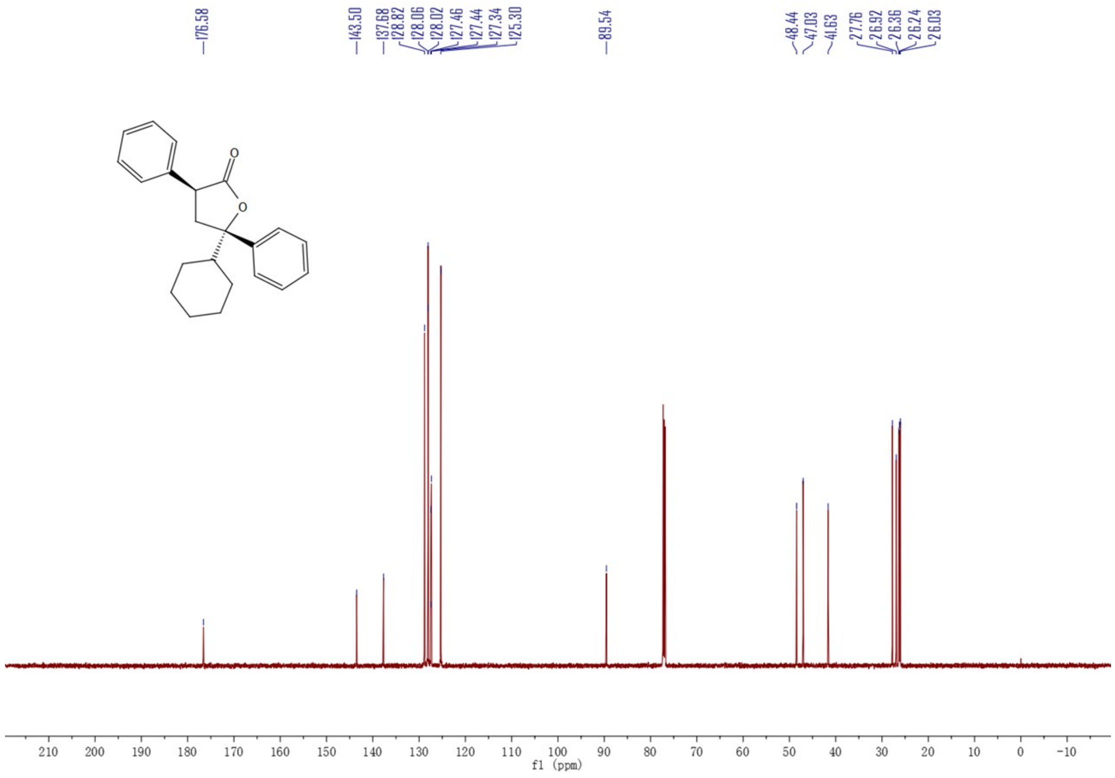
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**24**



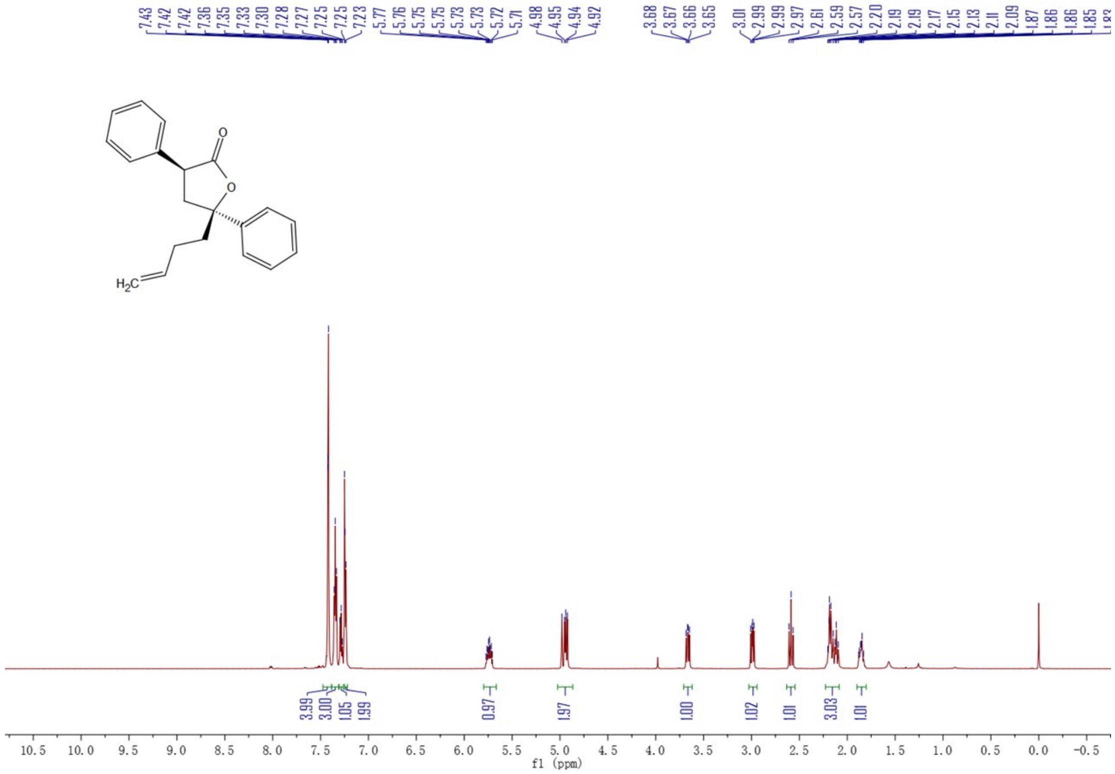
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**24**



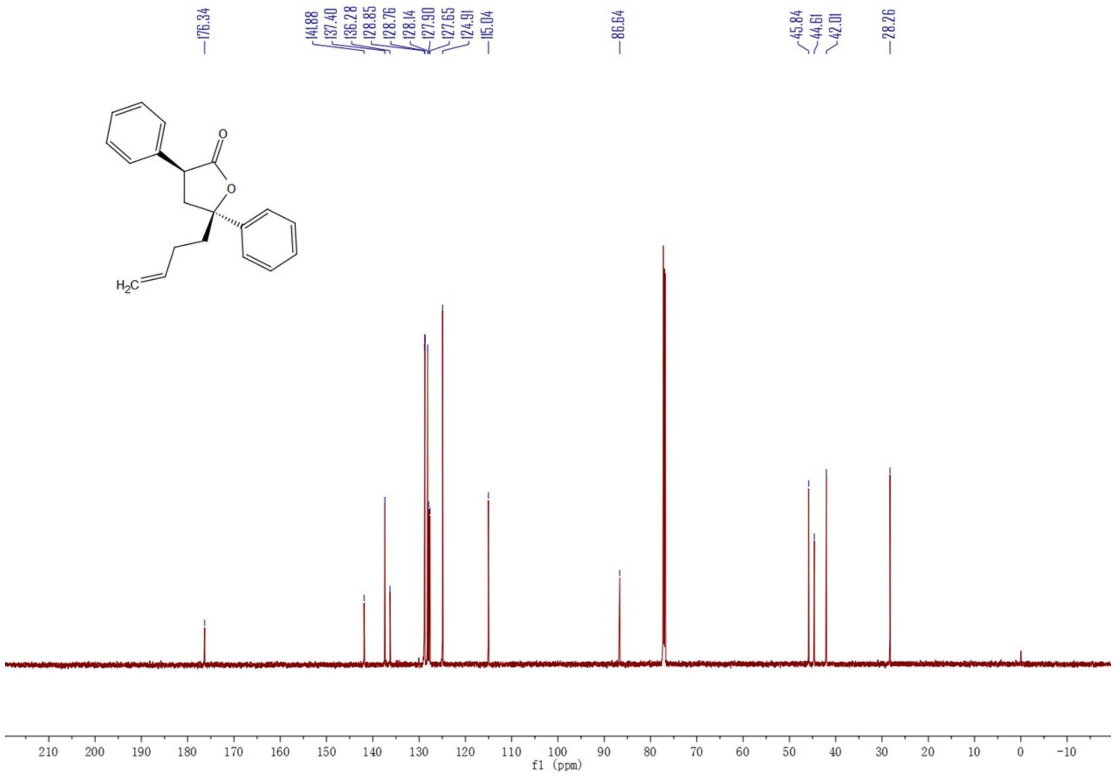
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**24**



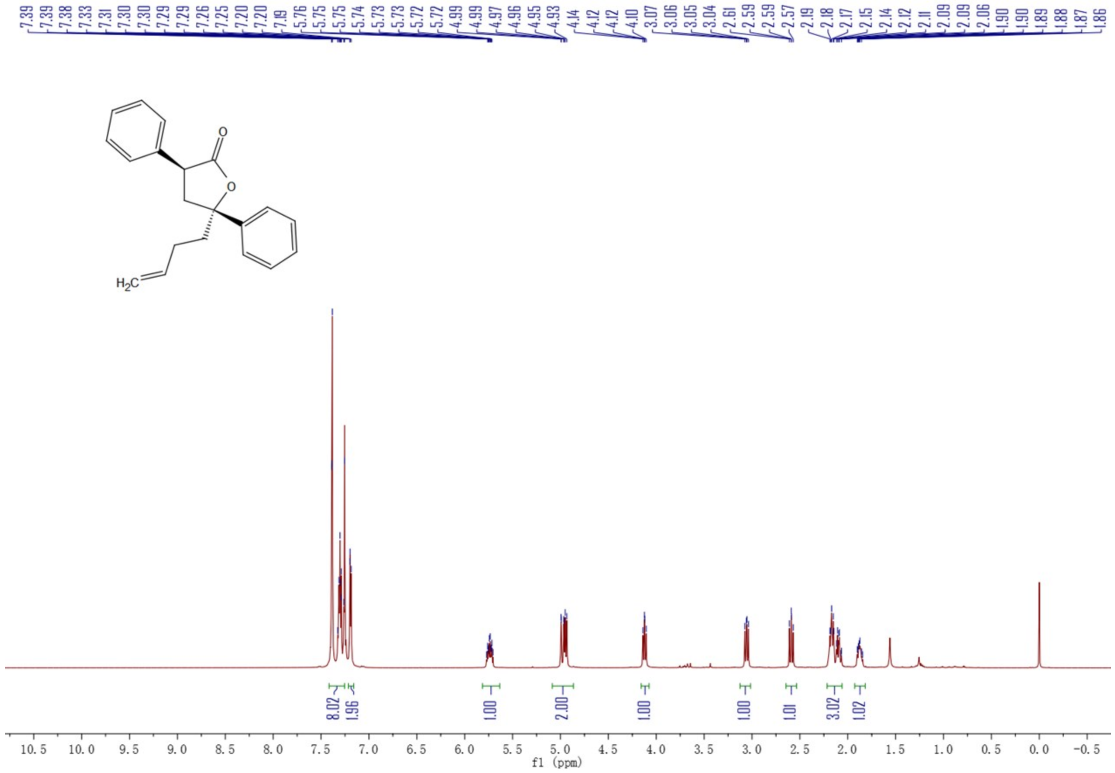
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**25**



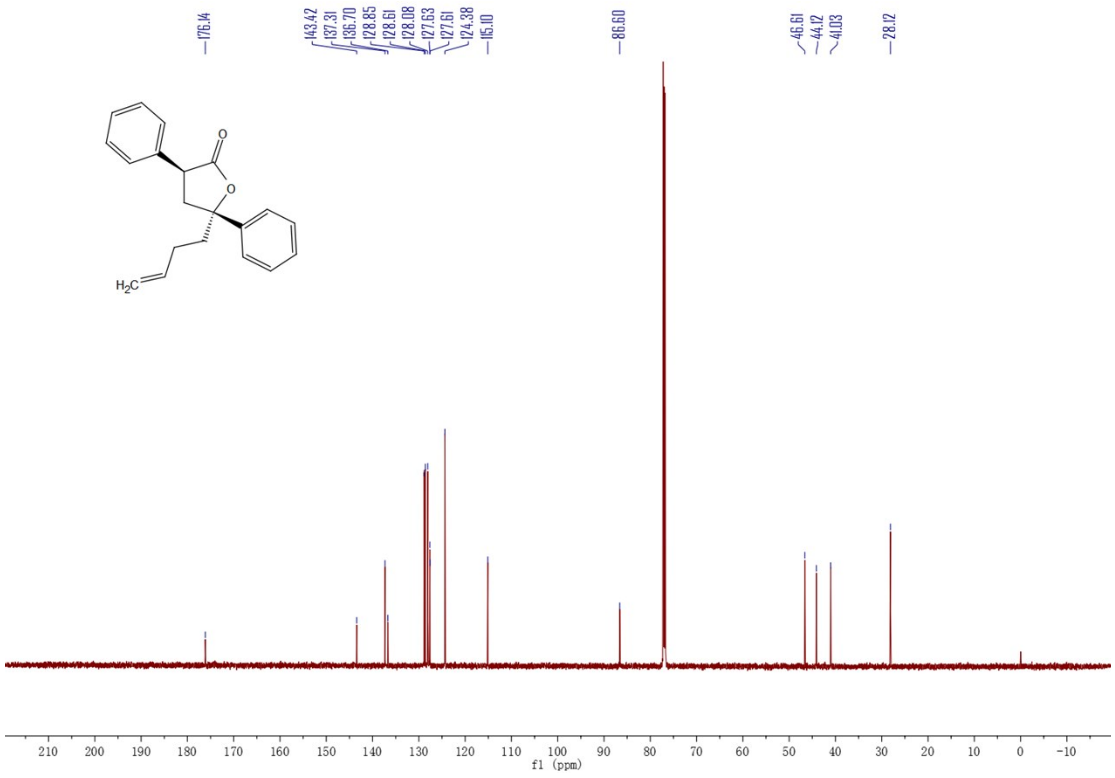
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**25**



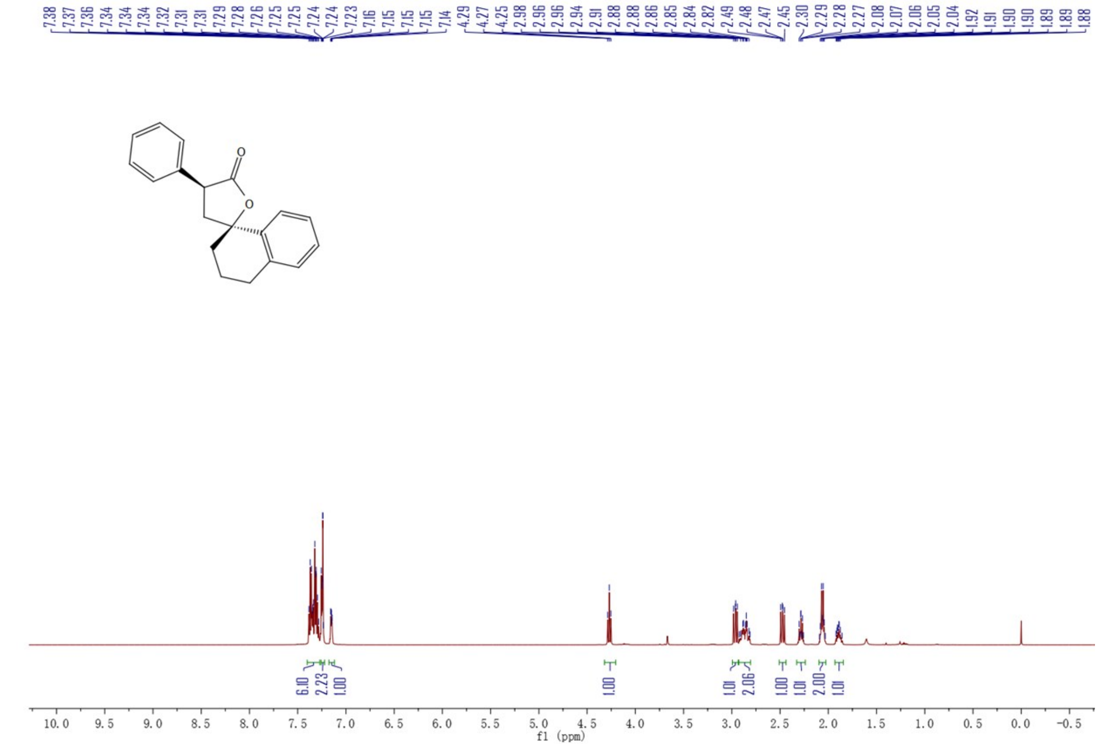
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**25**



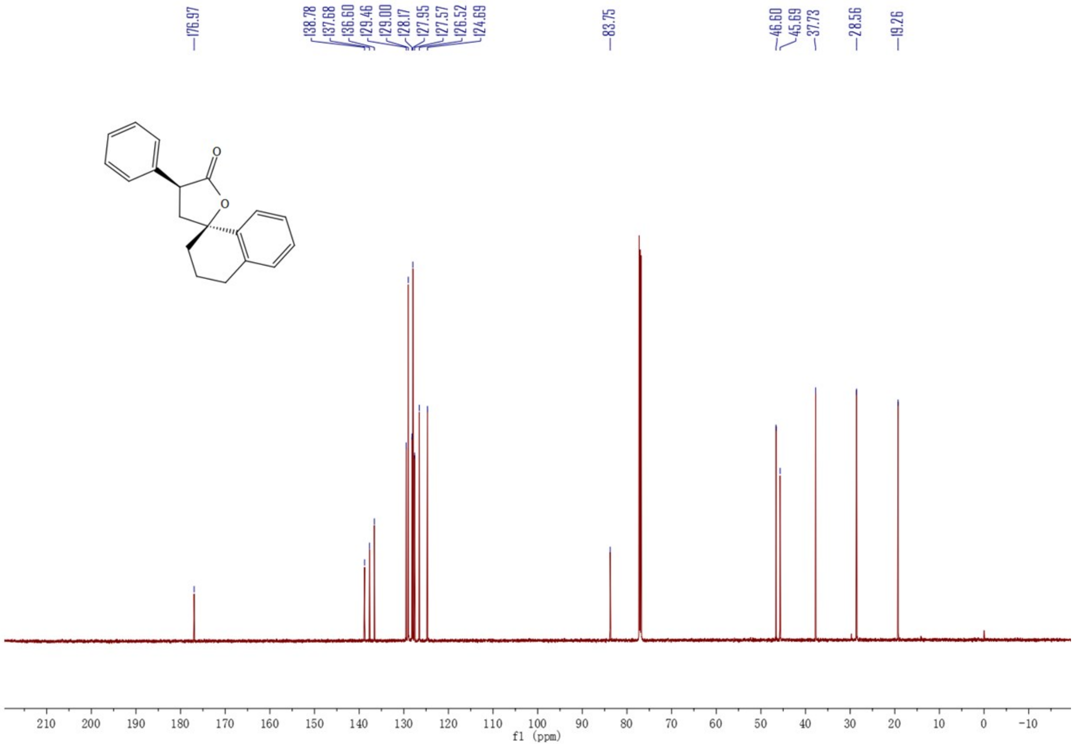
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**25**



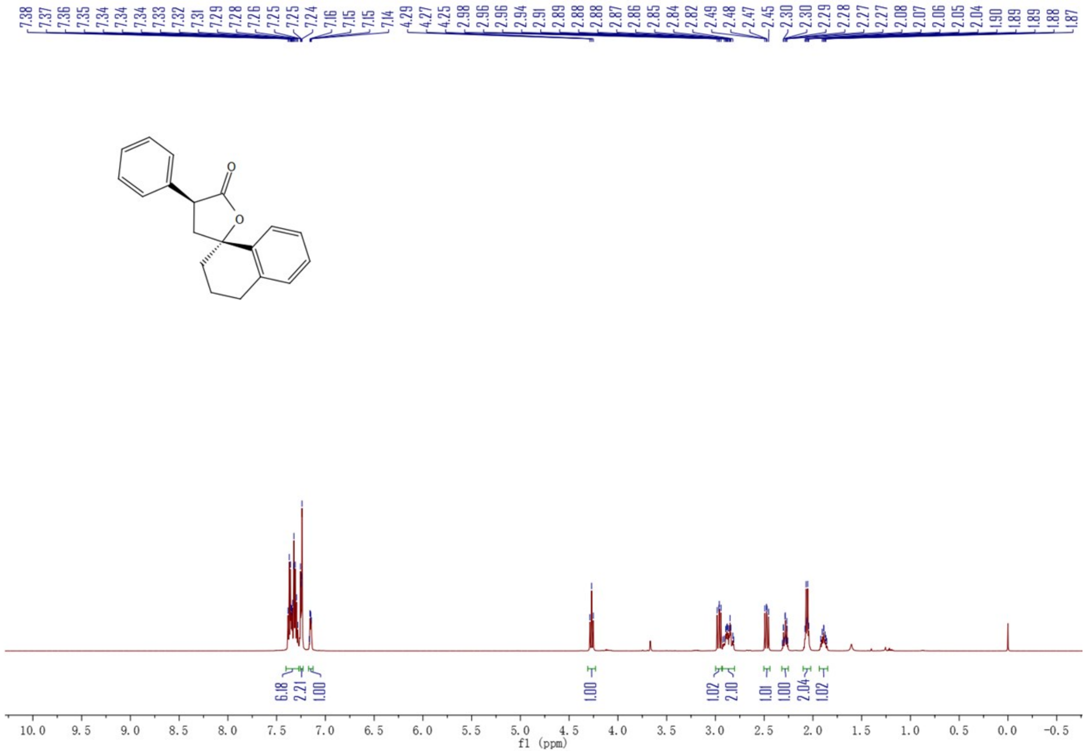
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**26**



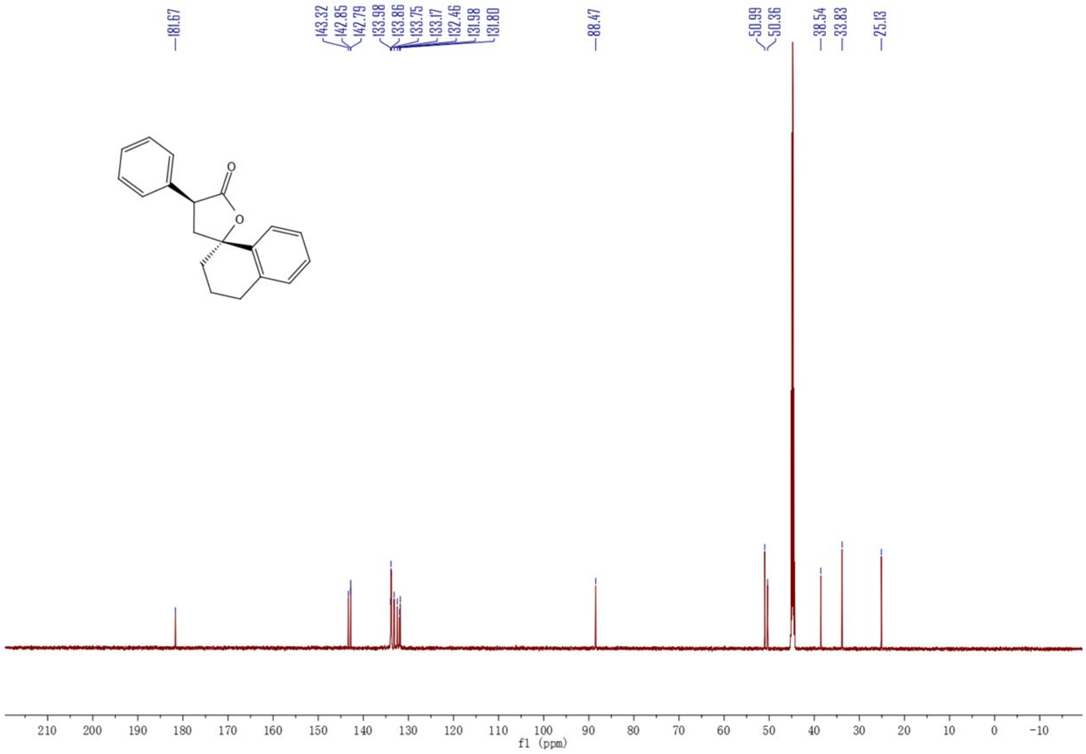
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**26**



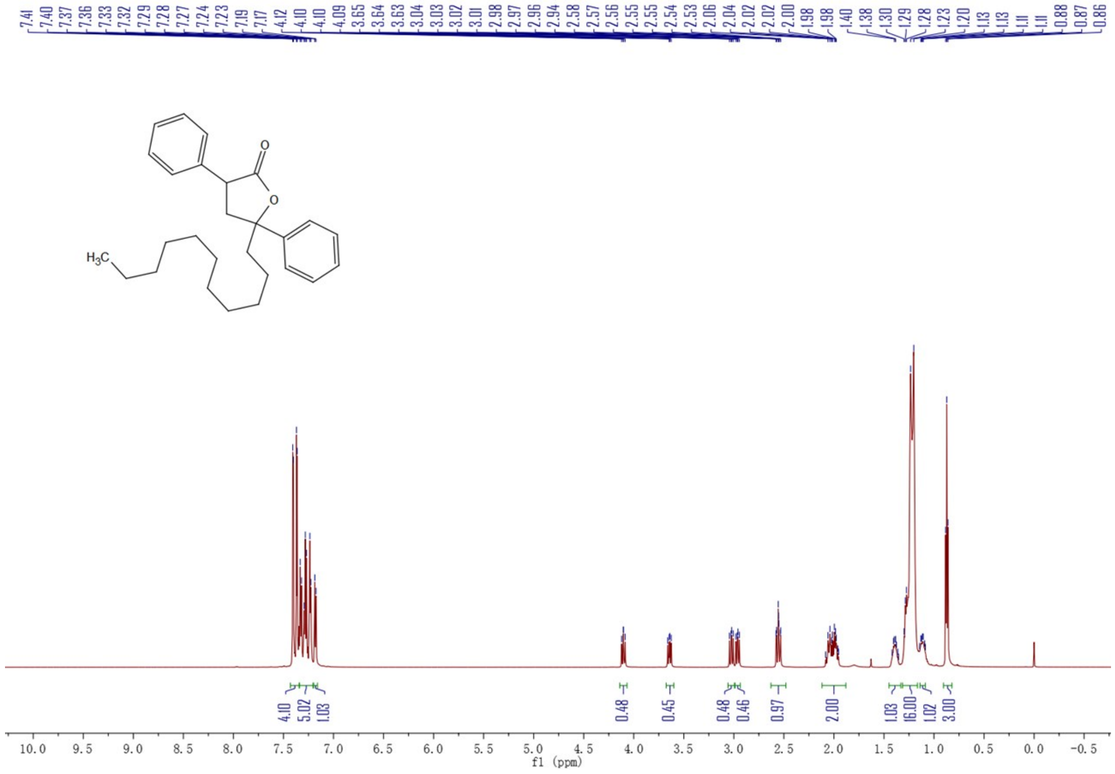
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**26**



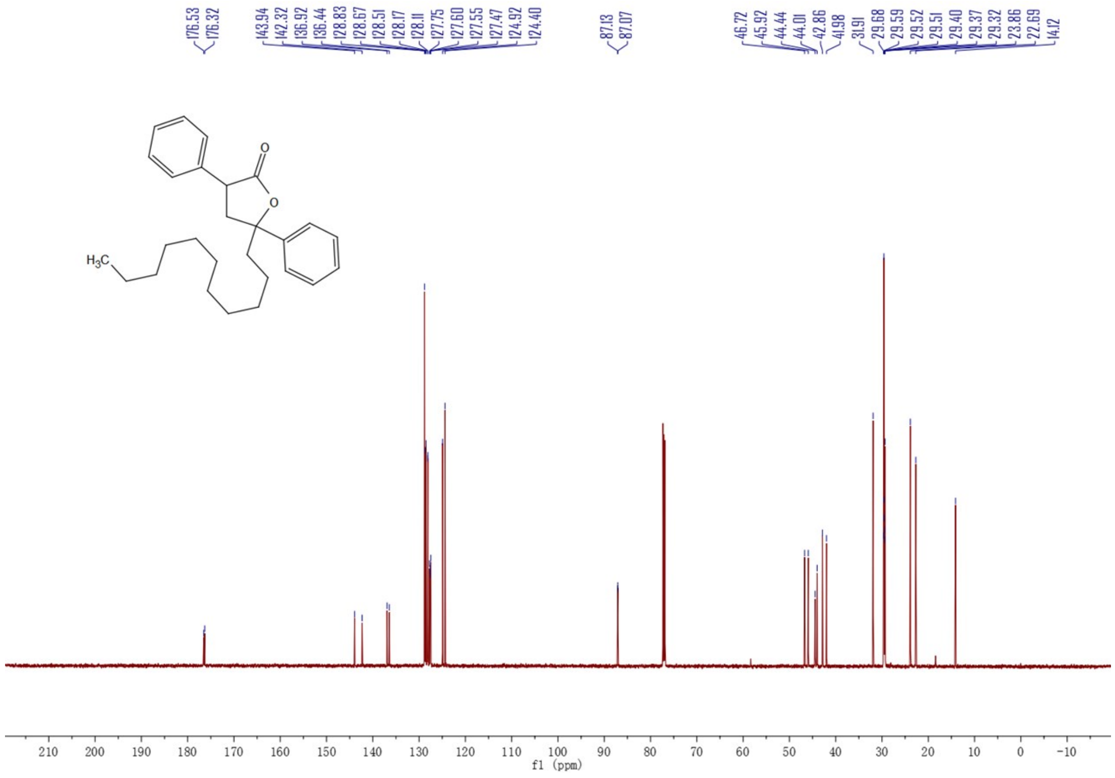
^{13}C NMR (151 MHz, $(CD_3)_2SO$) of (±)-*syn*-**26**



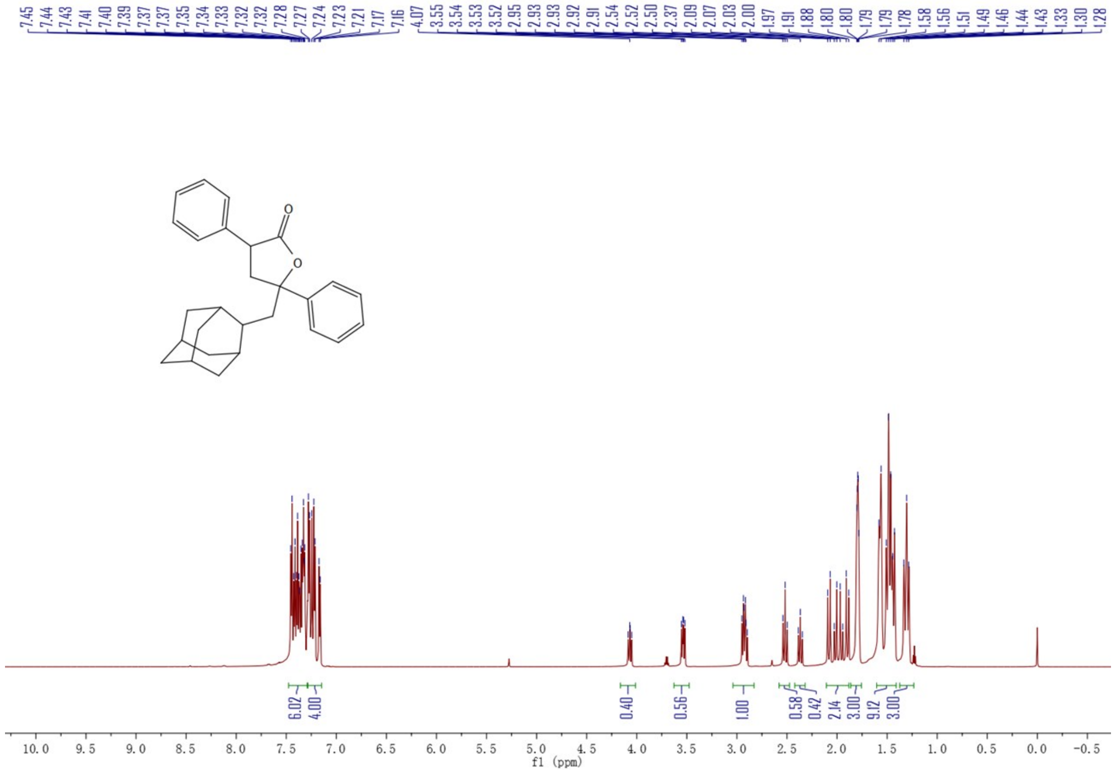
^{1}H NMR (600 MHz, CDCl$_3$) of **27**



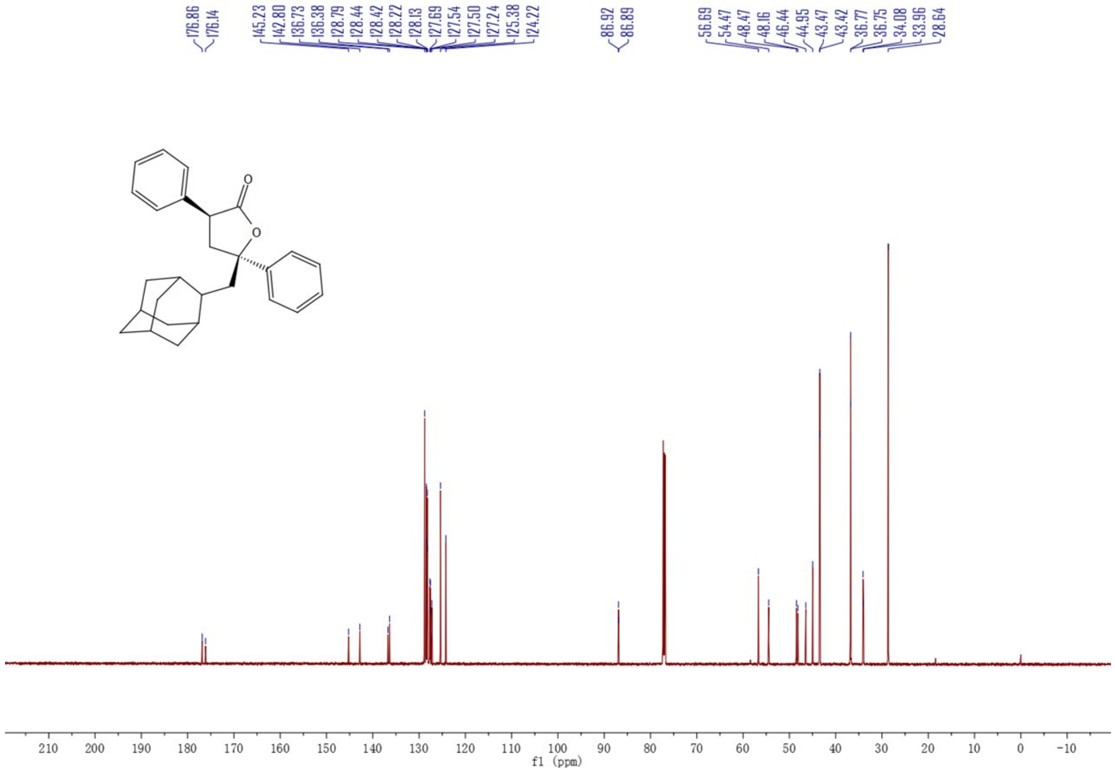
^{13}C NMR (151 MHz, CDCl$_3$) of **27**



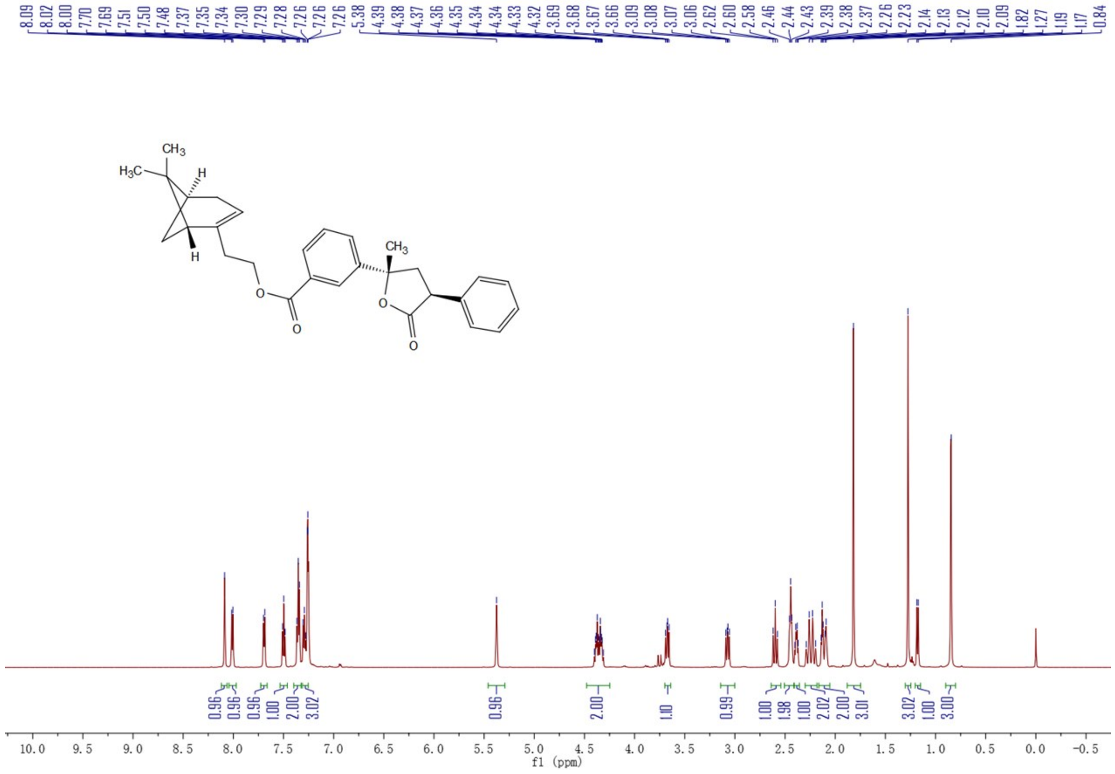
^{1}H NMR (600 MHz, CDCl$_3$) of **28**



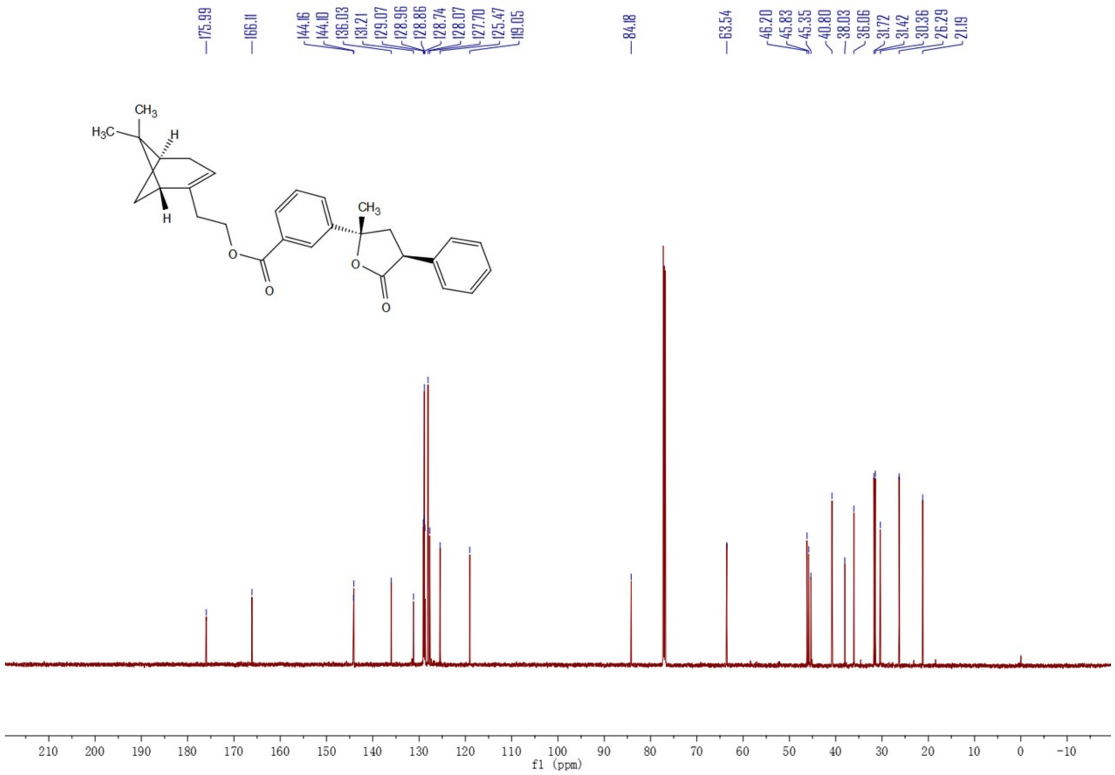
^{13}C NMR (151 MHz, CDCl$_3$) of **28**



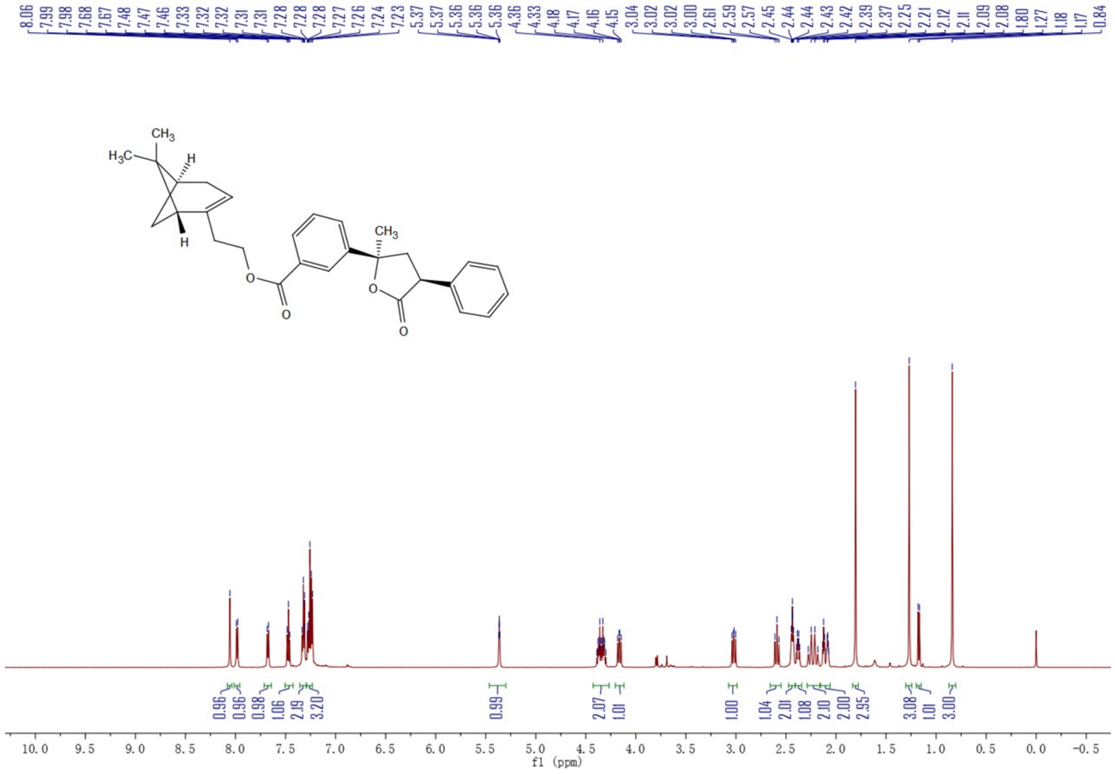
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**29**



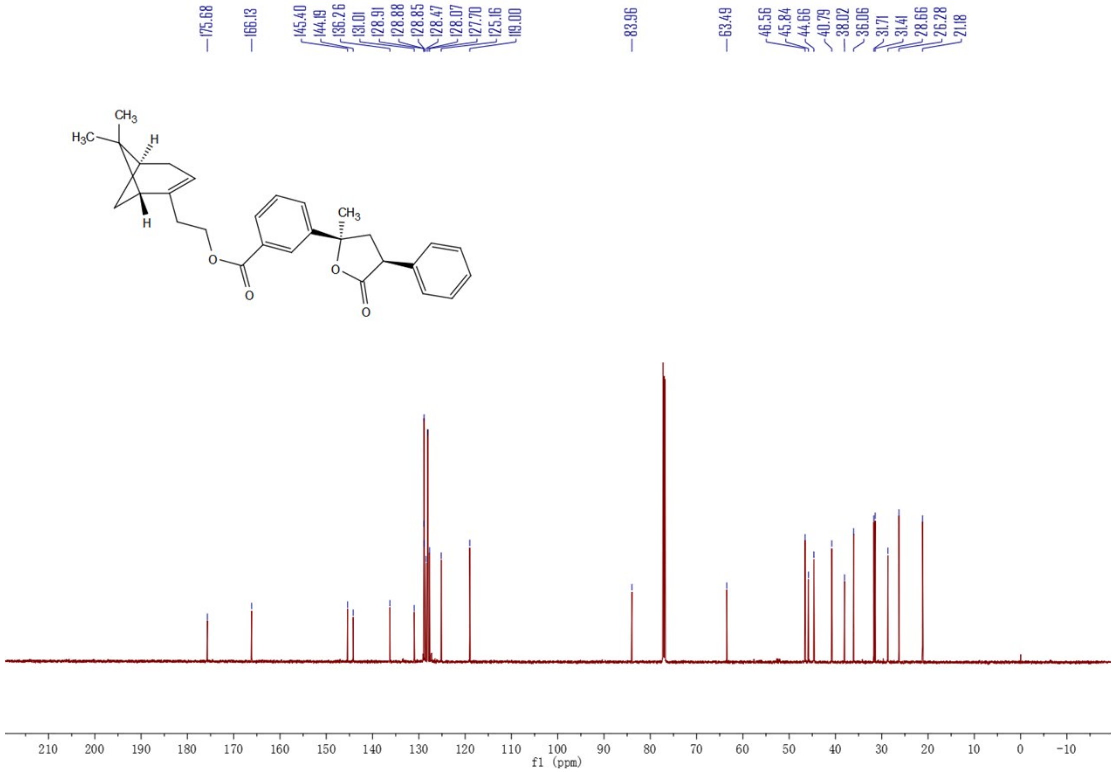
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**29**



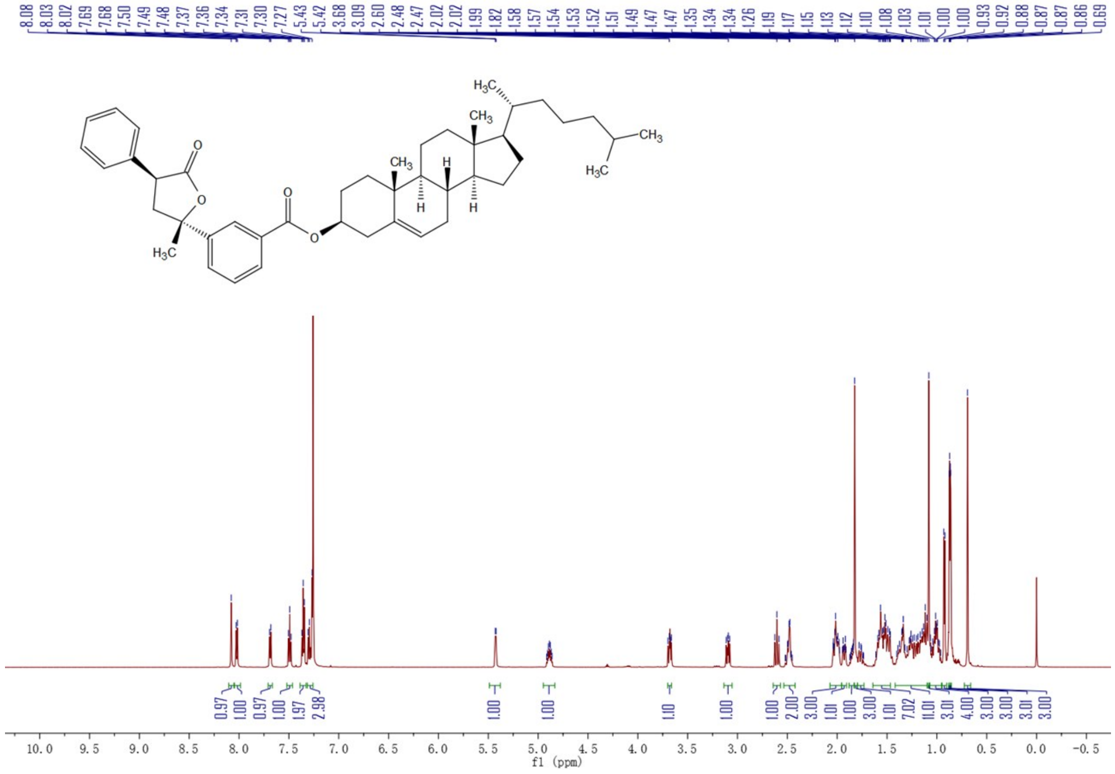
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**29**



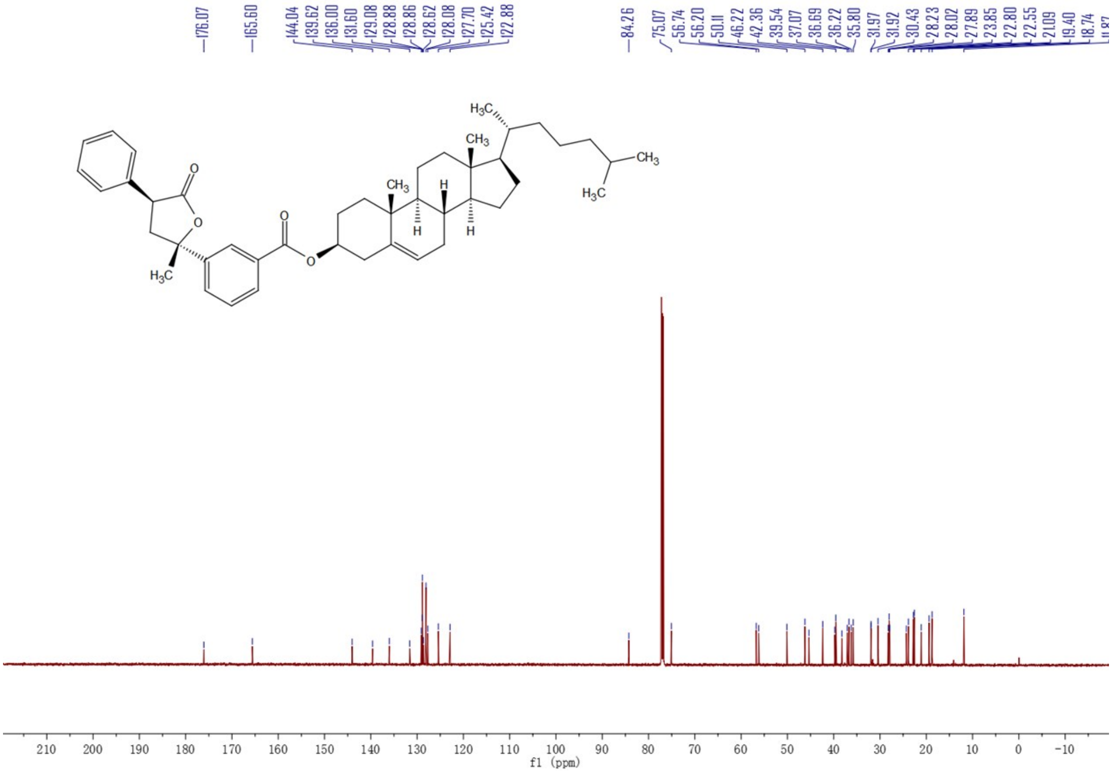
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**29**



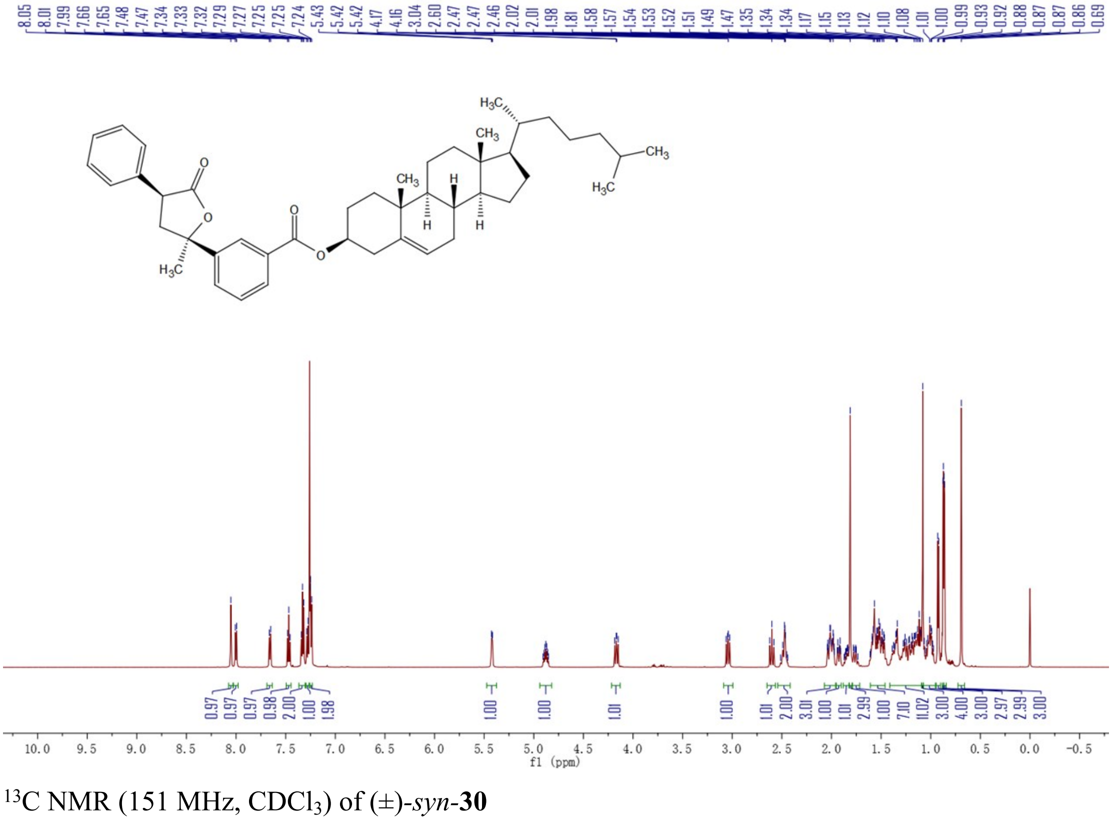
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**30**



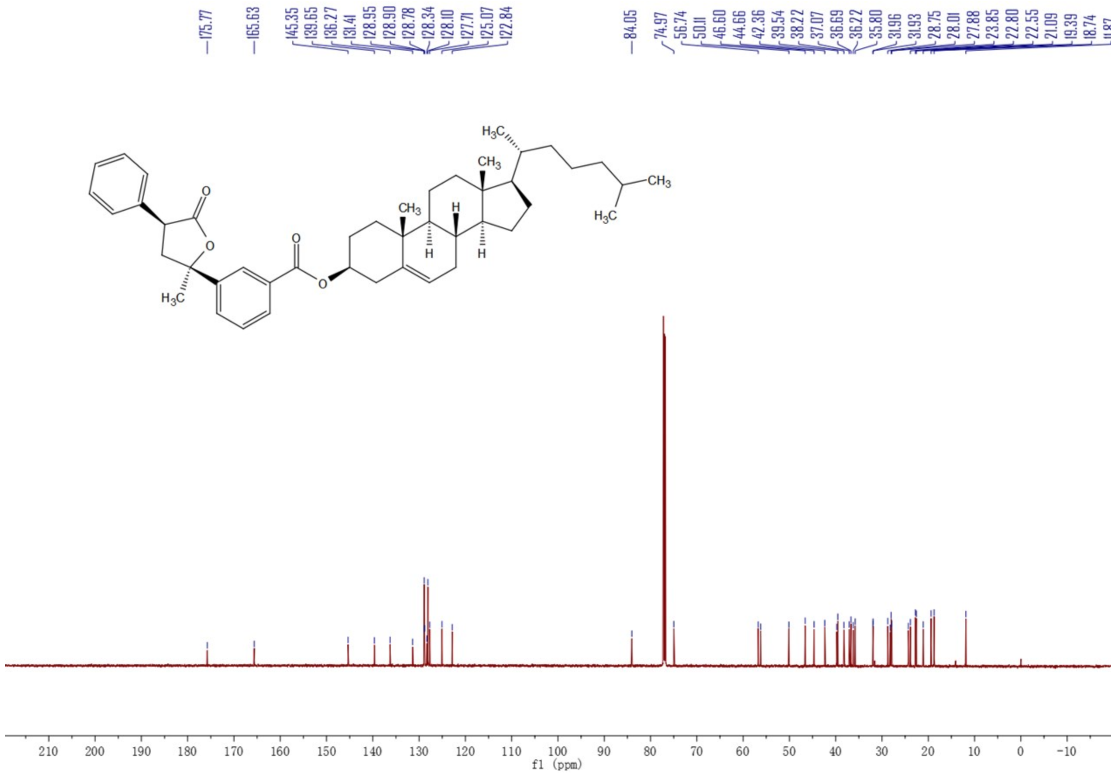
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**30**



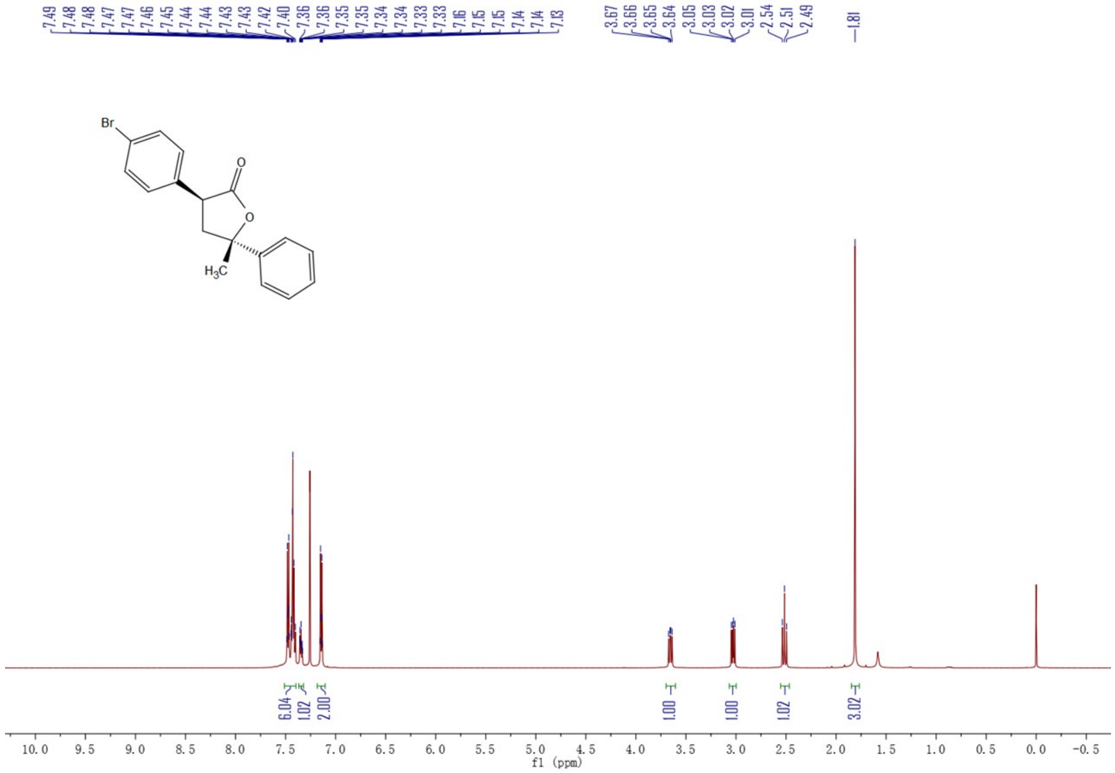
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**30**



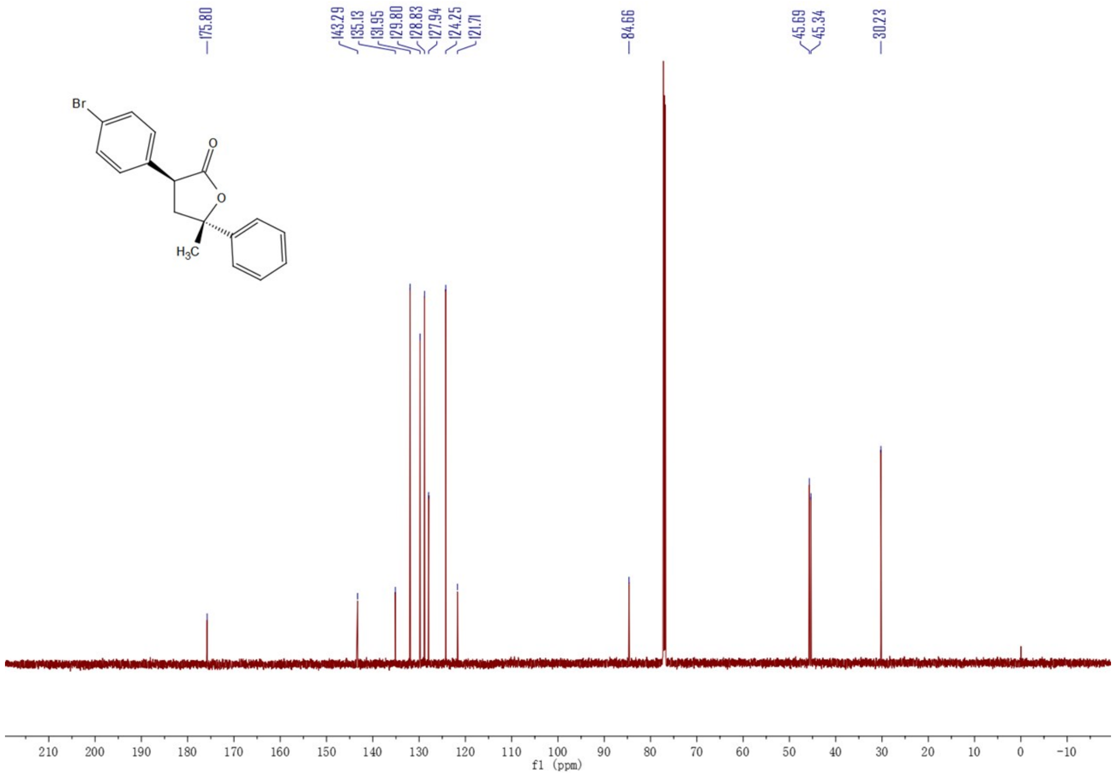
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**30**



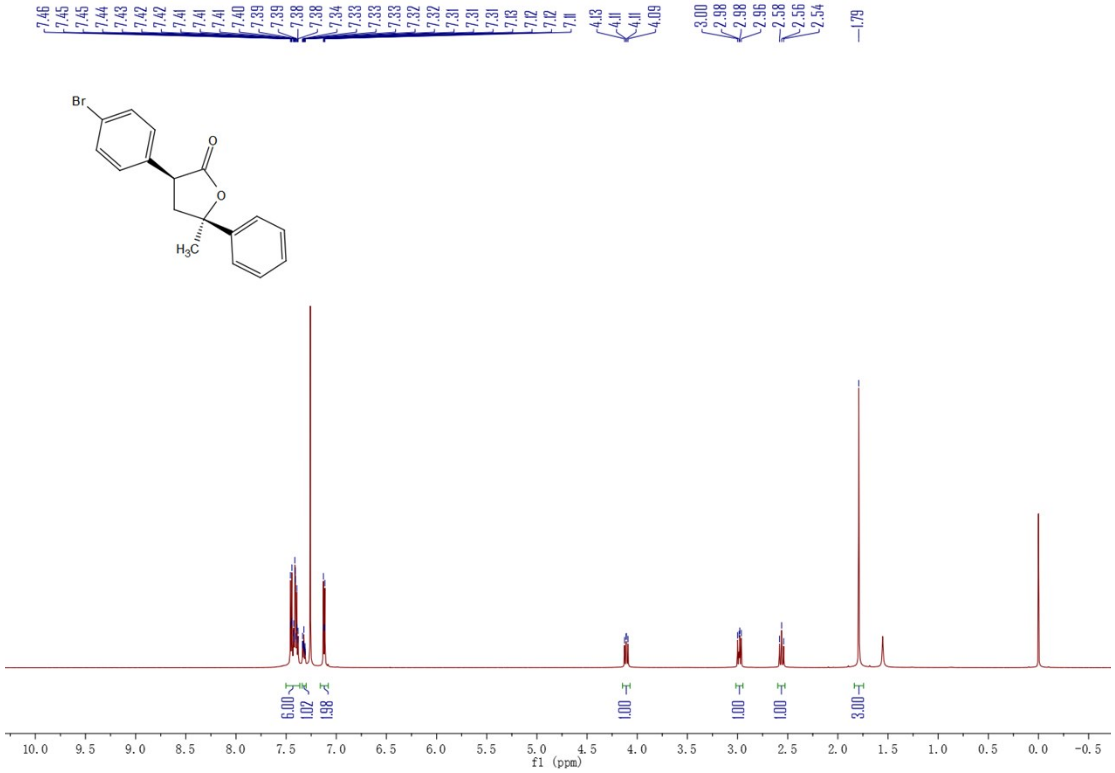
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**31**



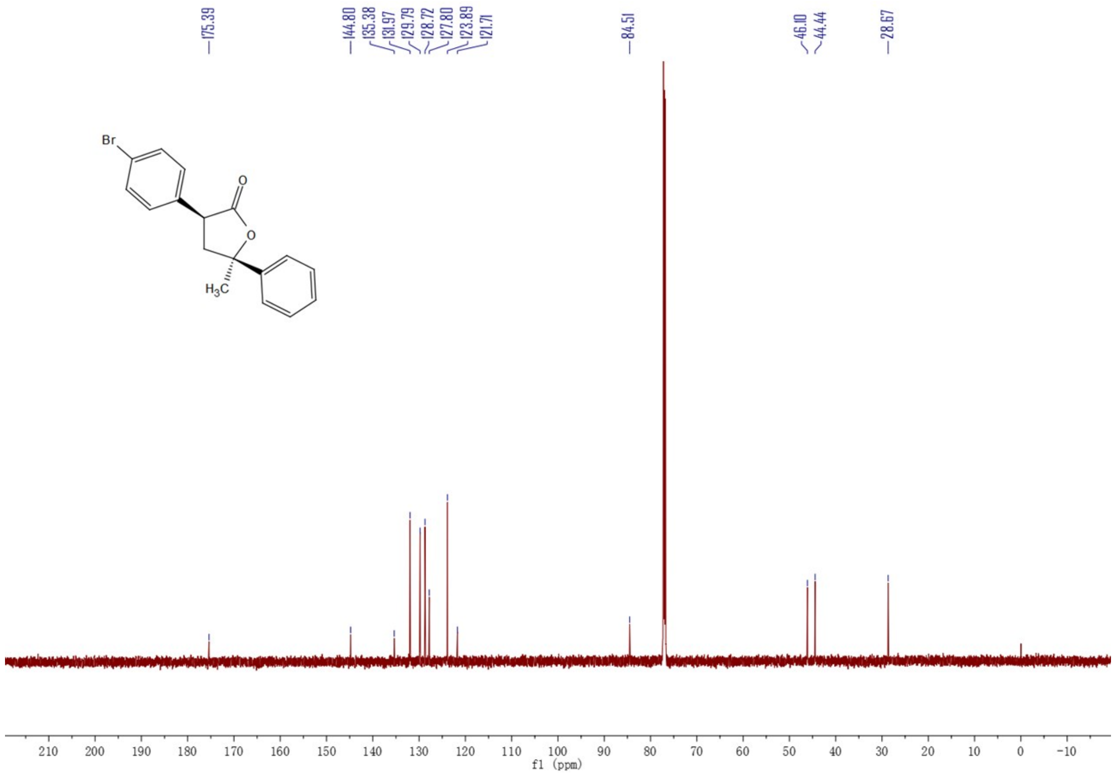
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**31**



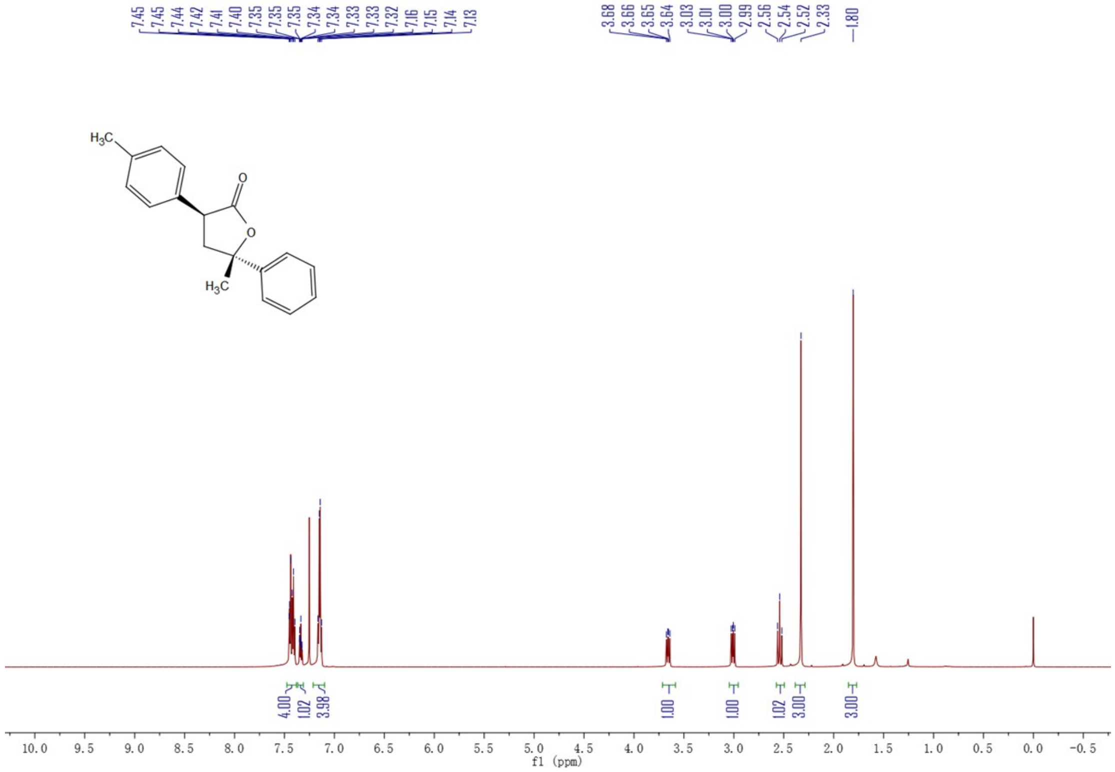
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**31**



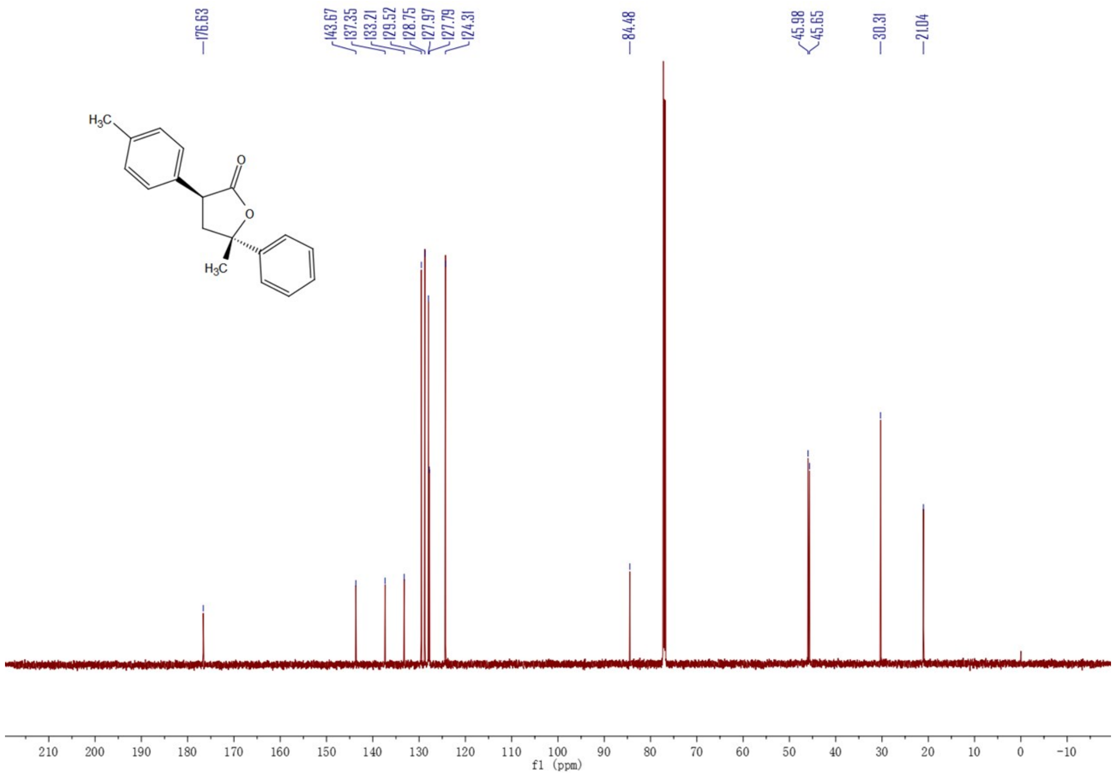
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**31**



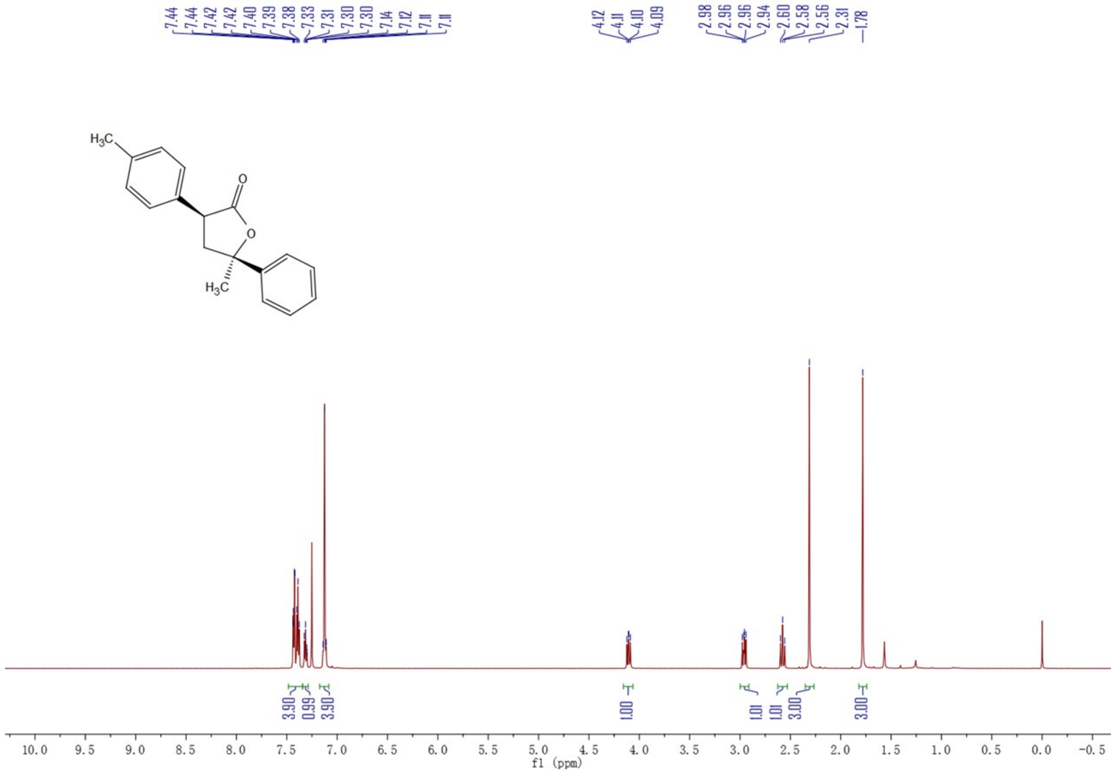
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**32**



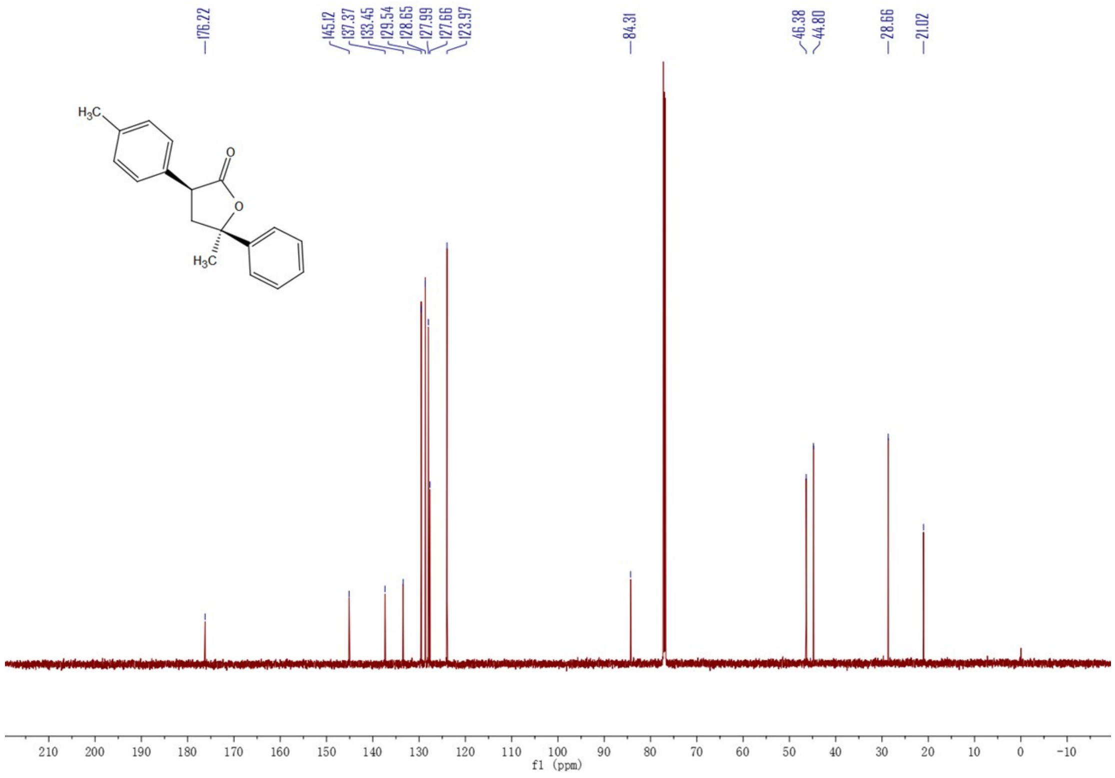
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**32**



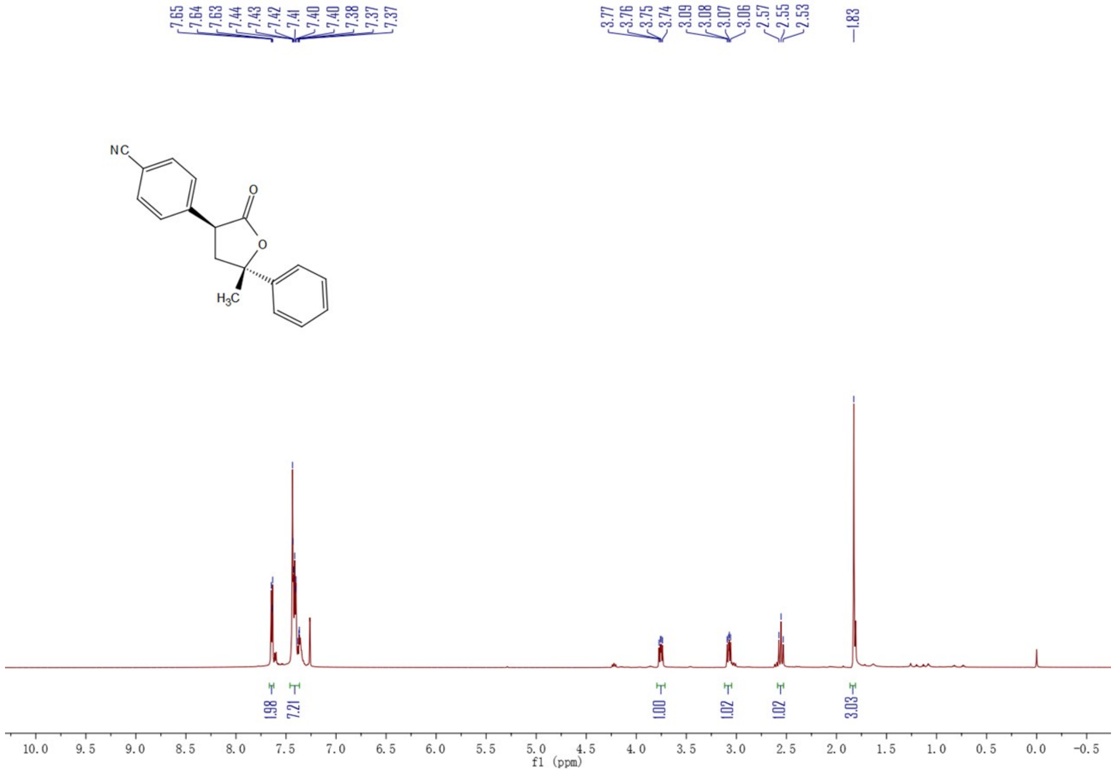
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**32**



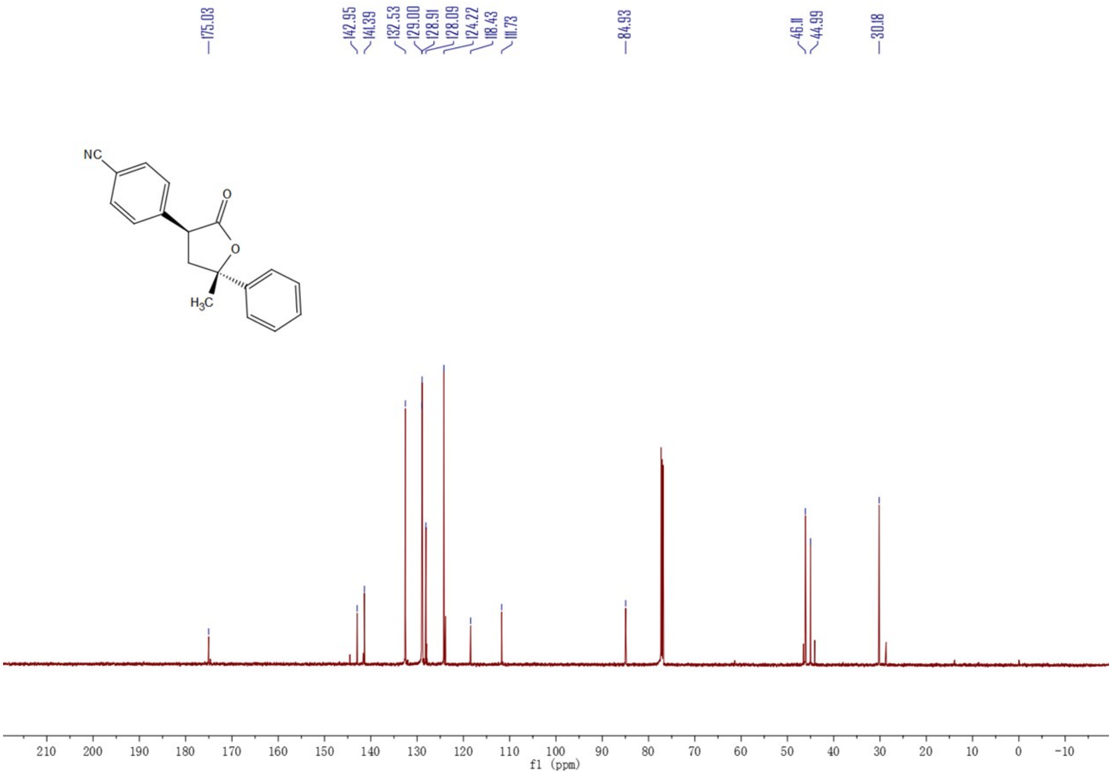
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*syn*-**32**



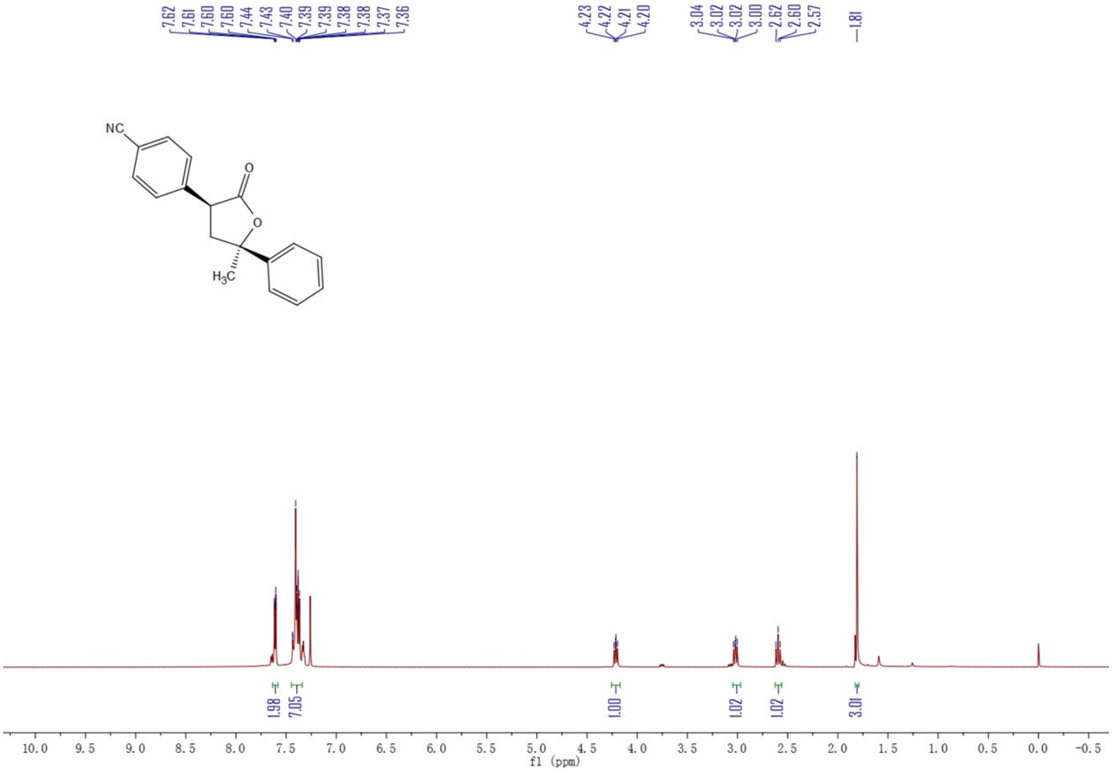
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**33**



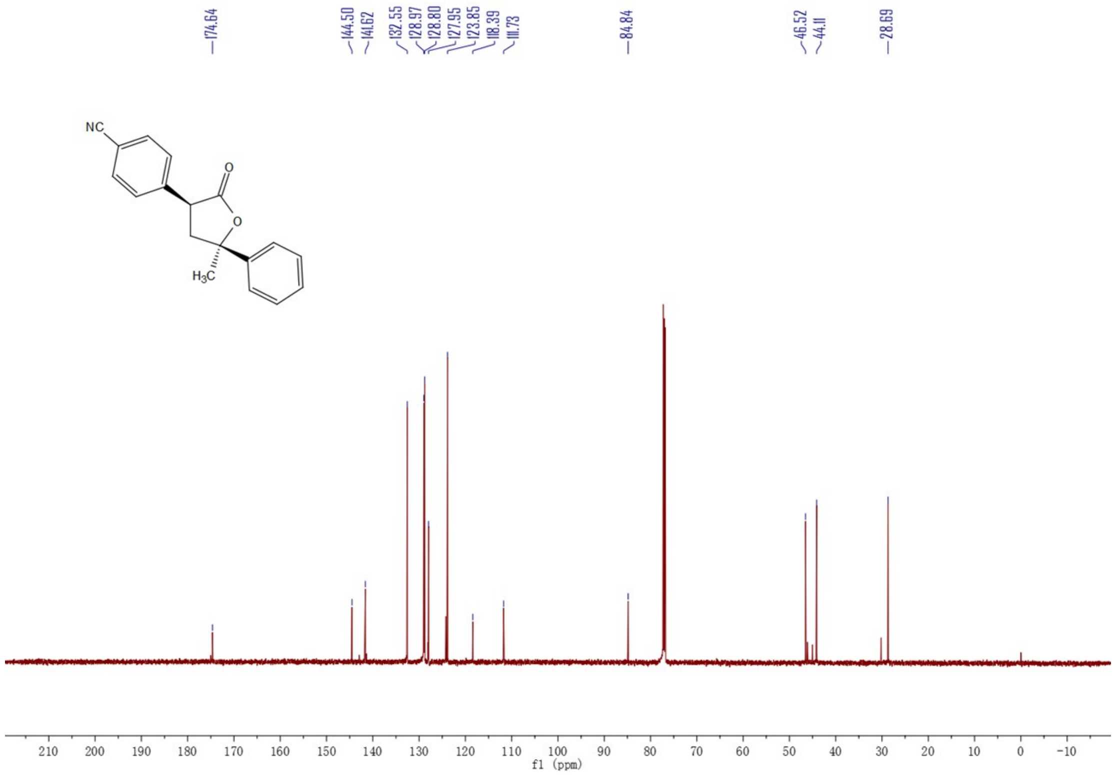
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**33**



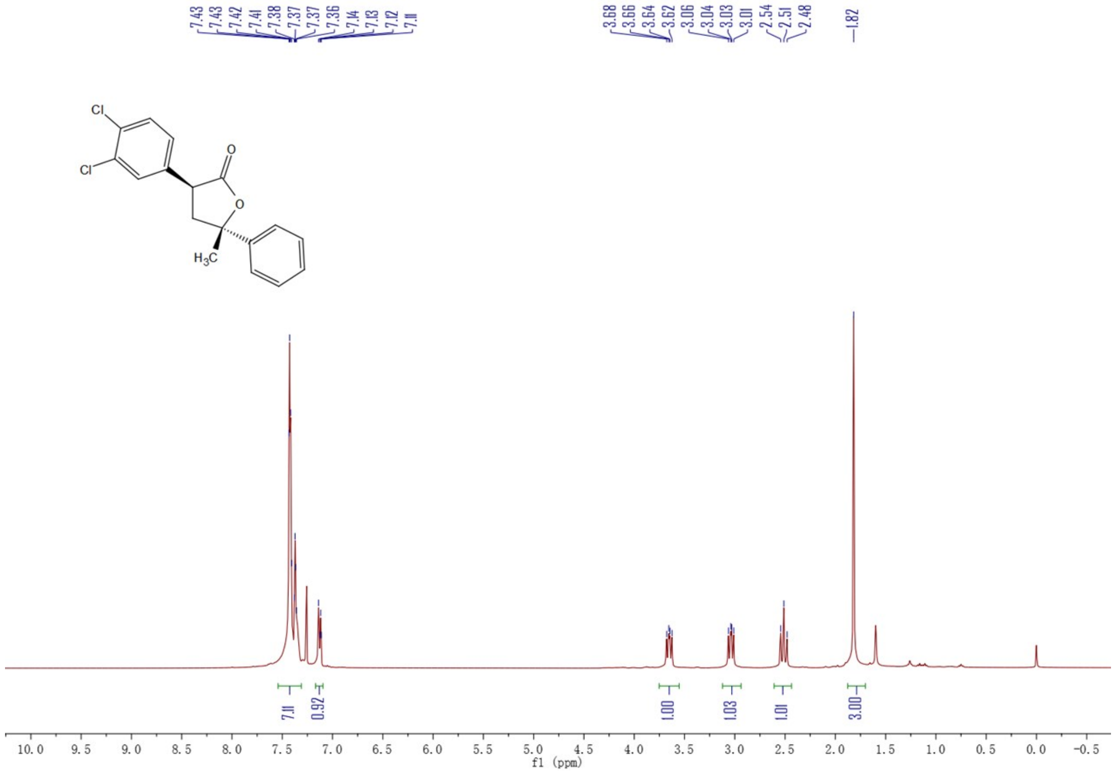
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**33**



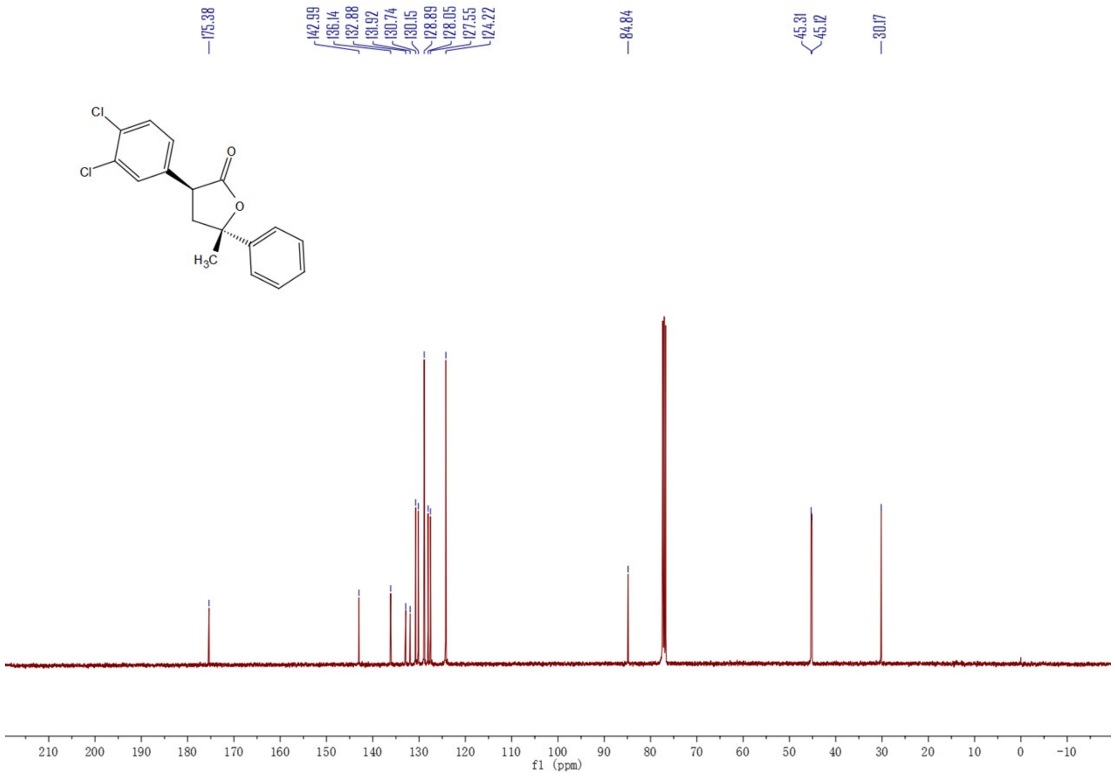
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**33**



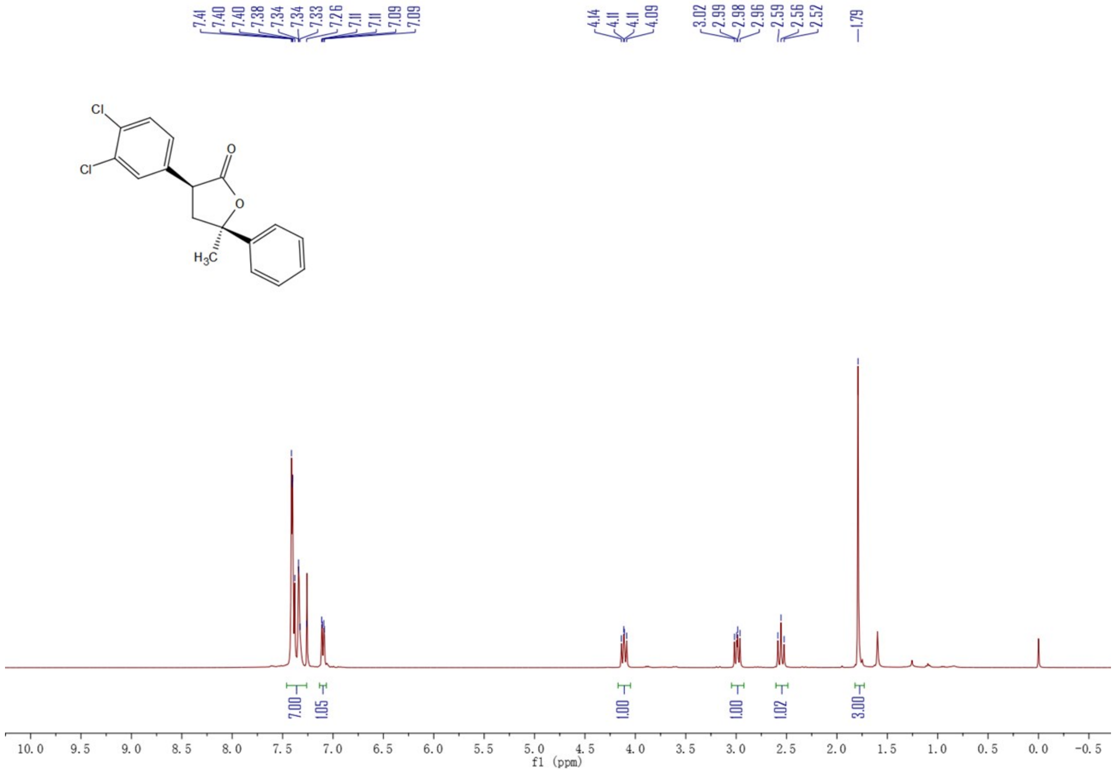
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**34**



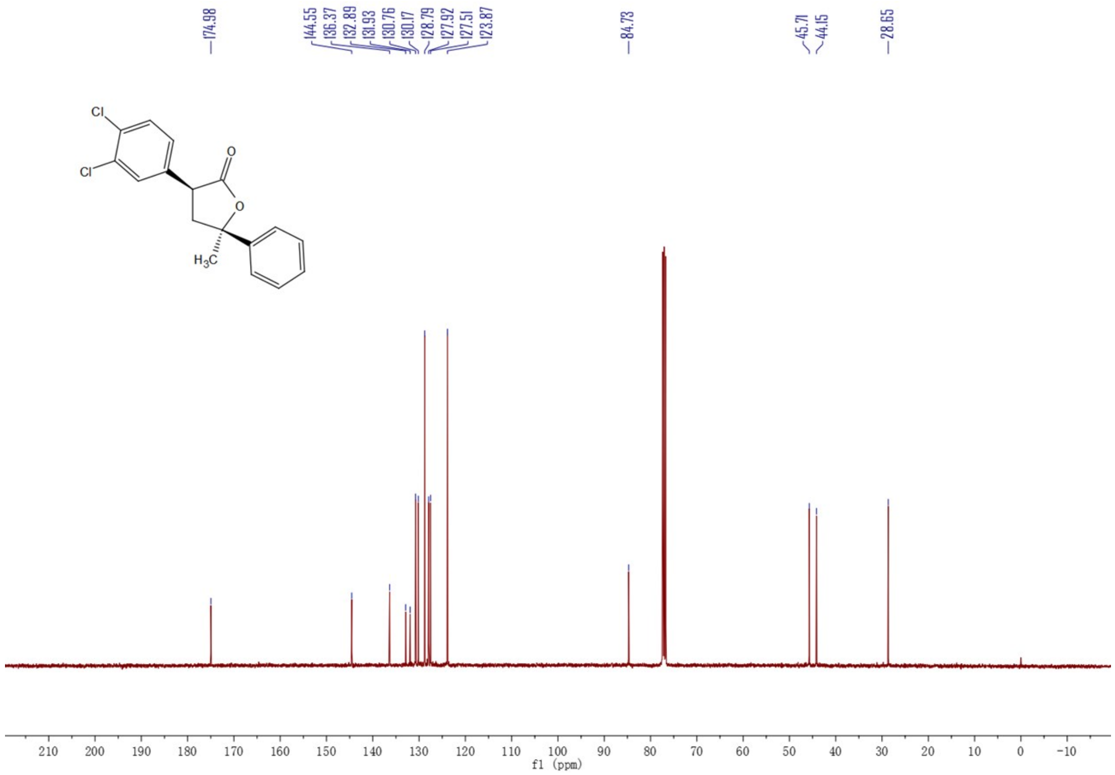
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**34**



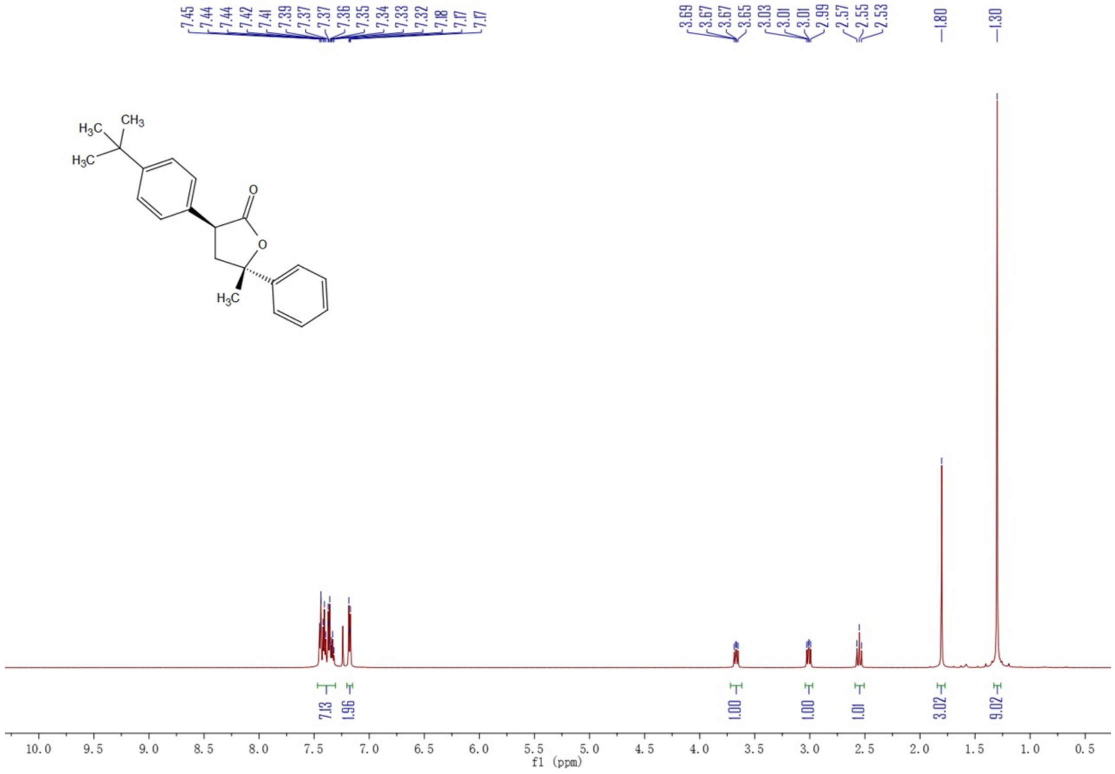
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**34**



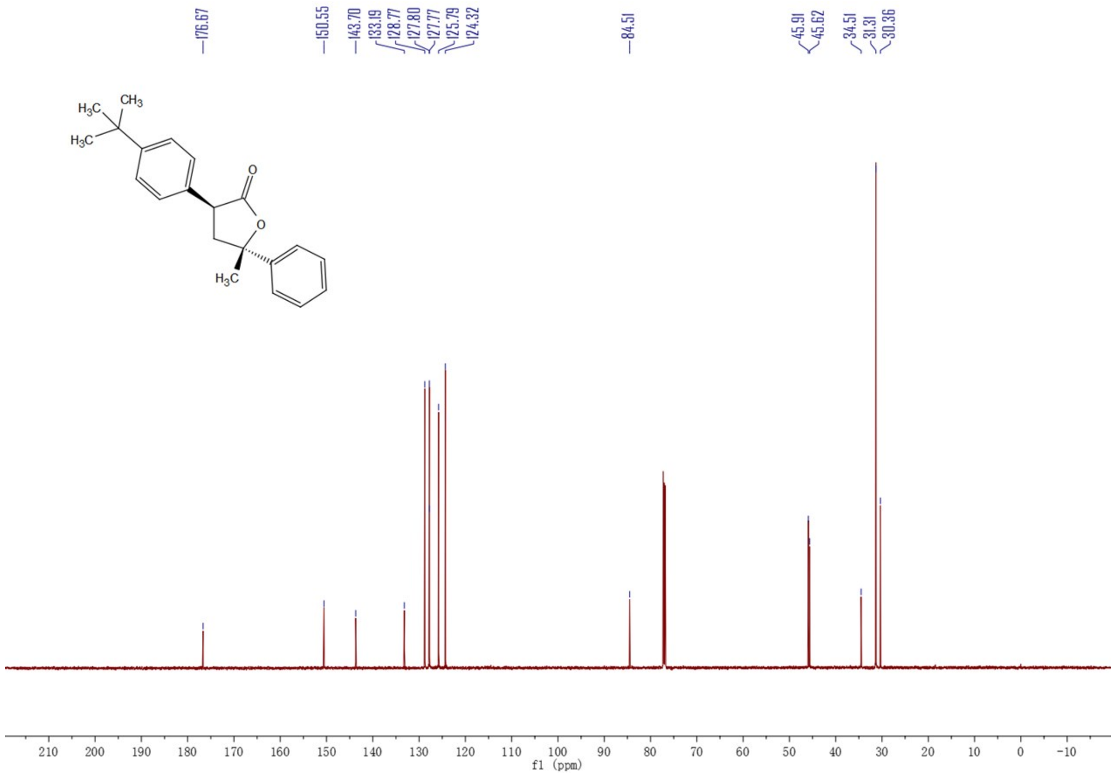
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**34**



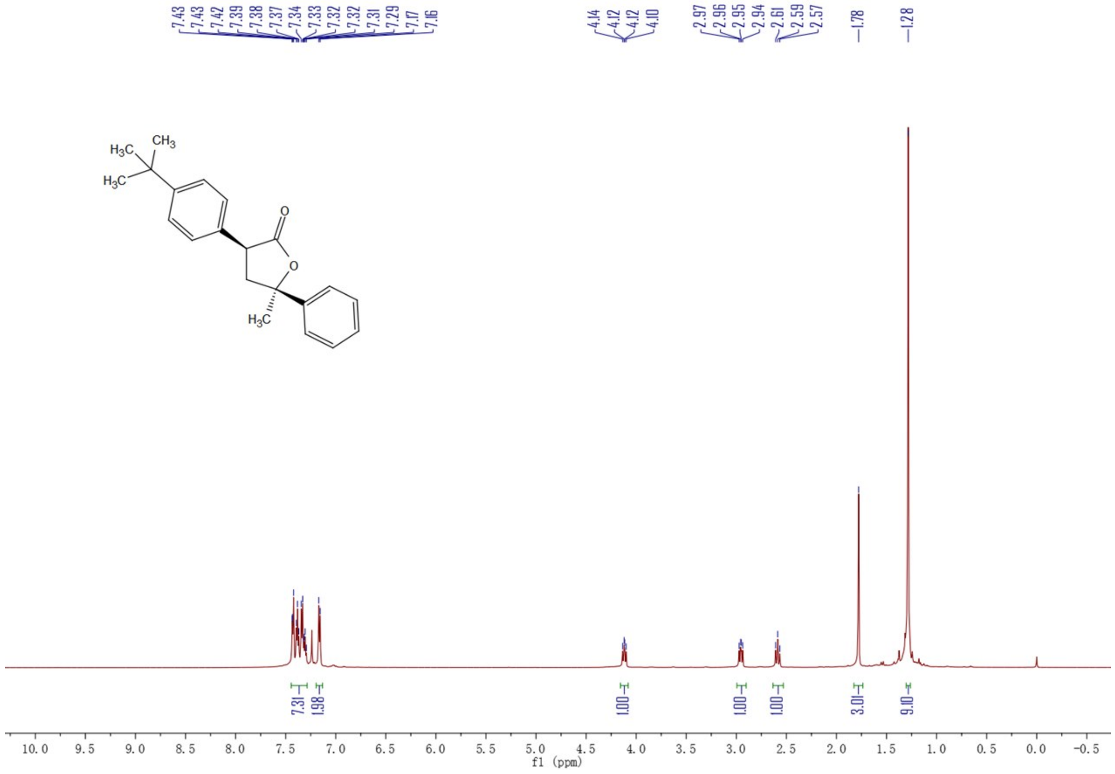
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**35**



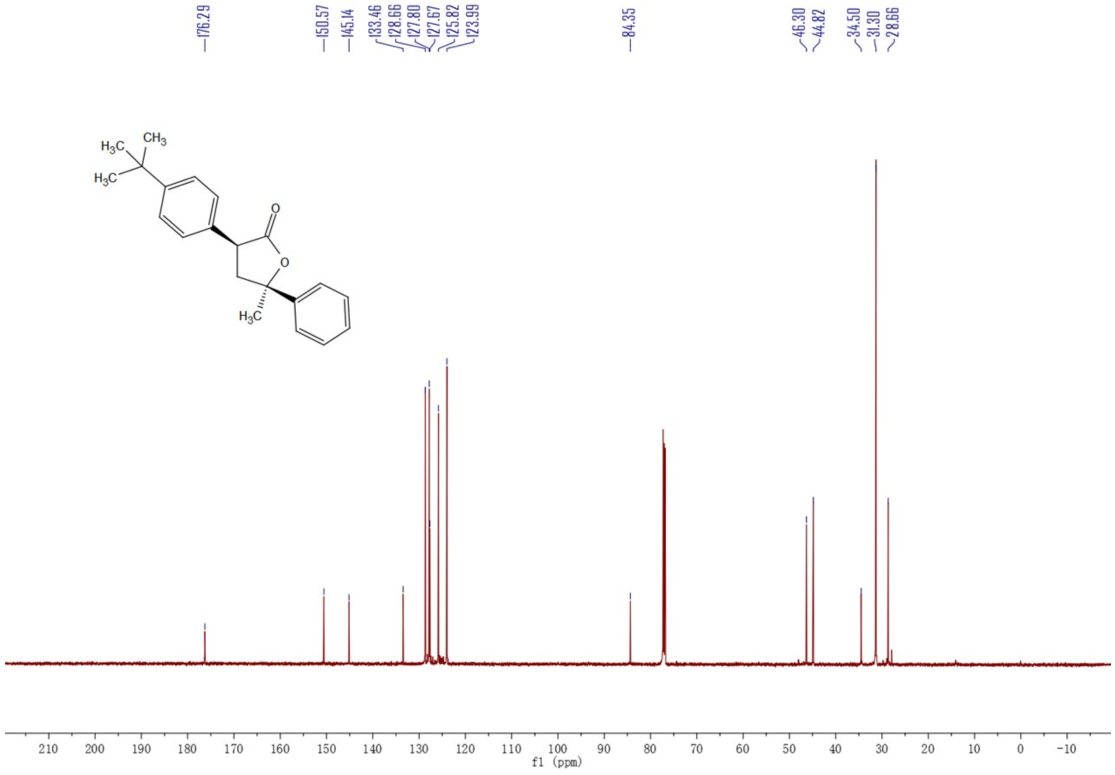
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**35**



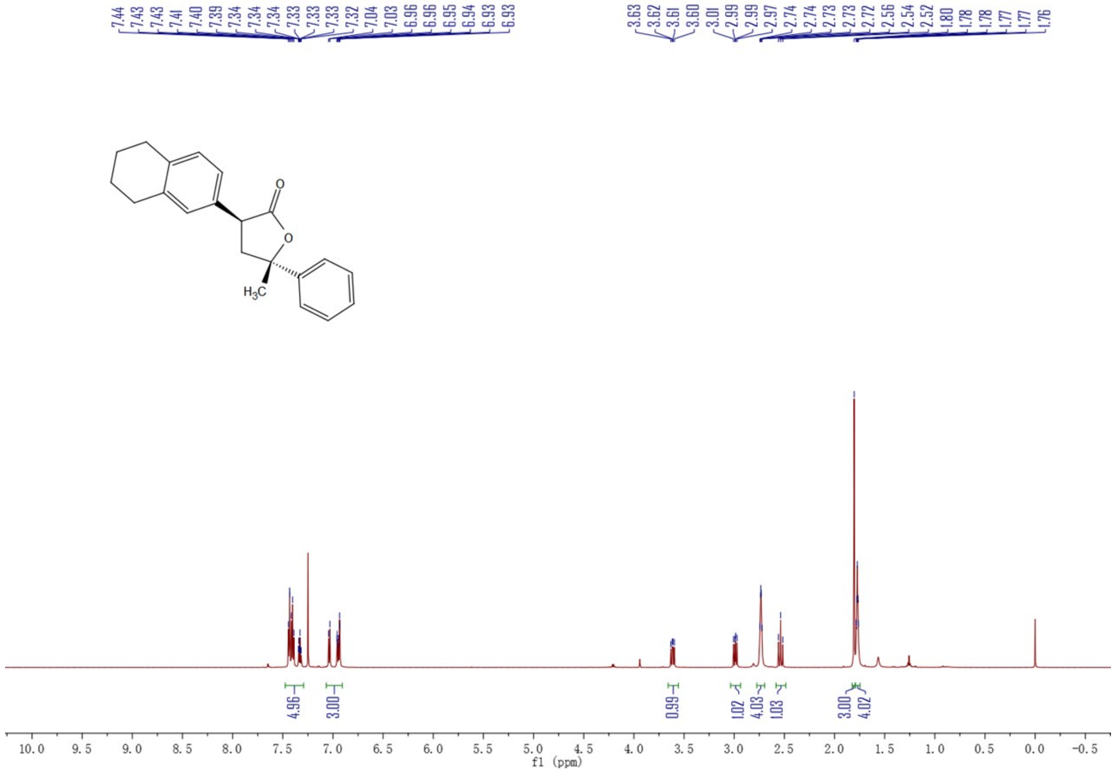
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**35**



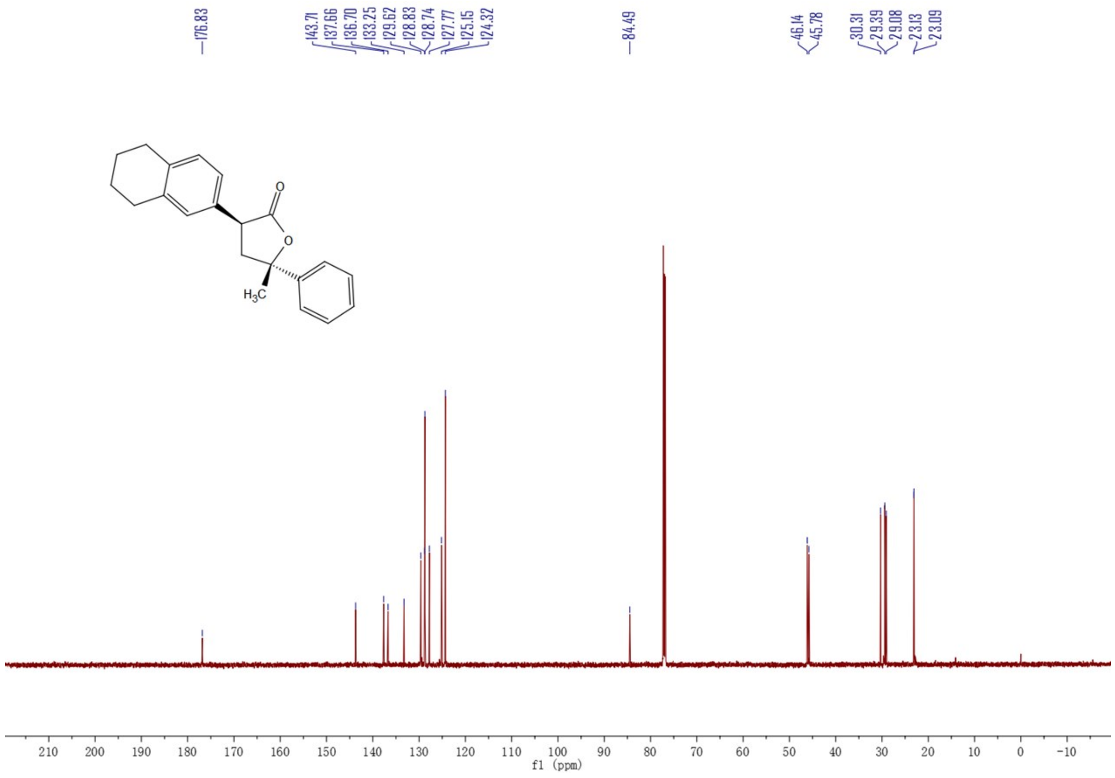
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*syn*-**35**



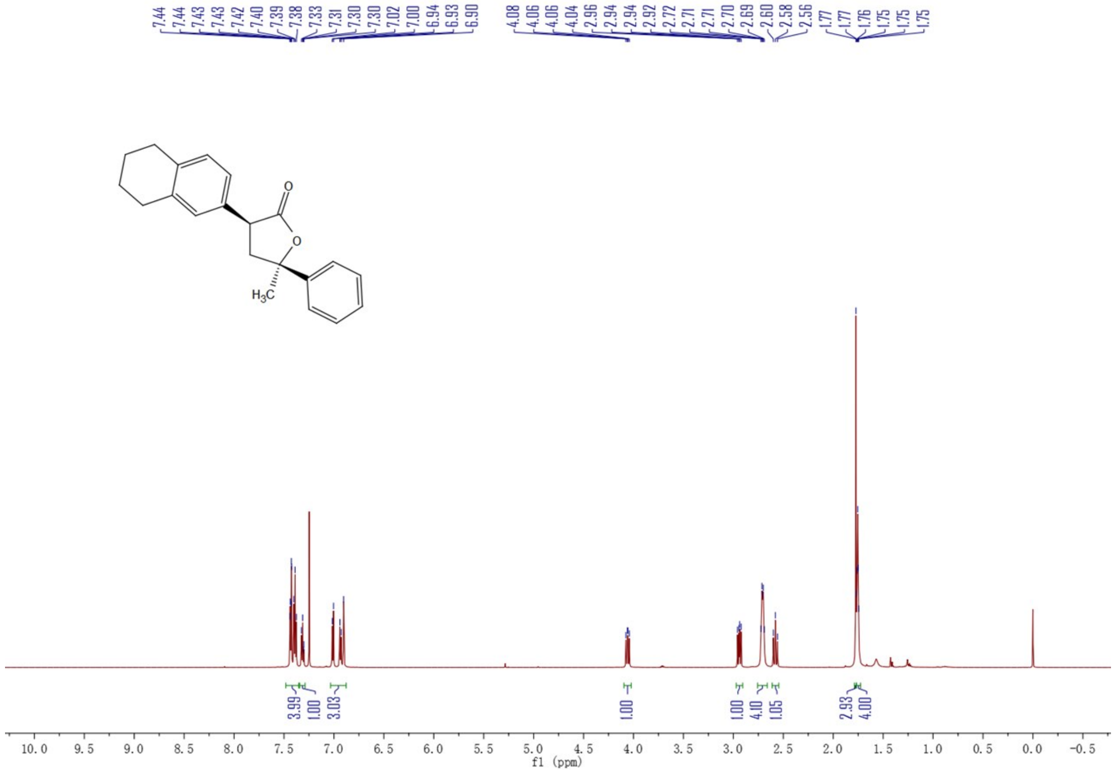
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*anti*-**36**



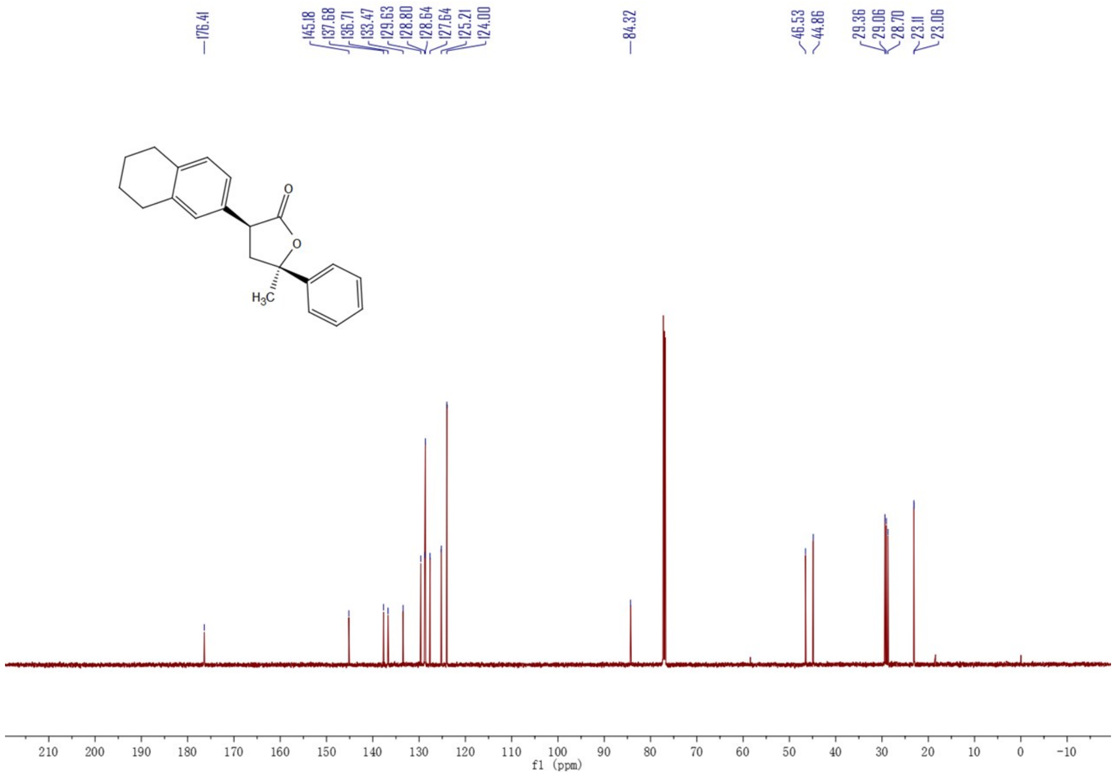
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*anti*-**36**



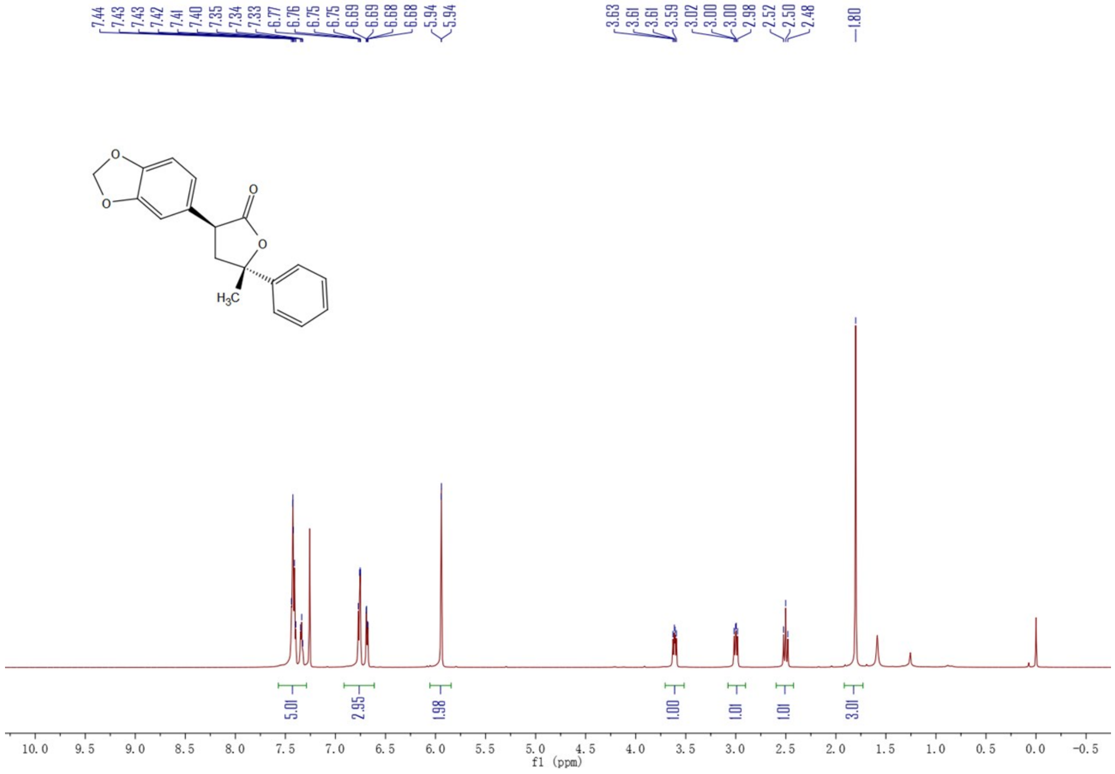
^{1}H NMR (400 MHz, CDCl$_3$) of (±)-*syn*-**36**



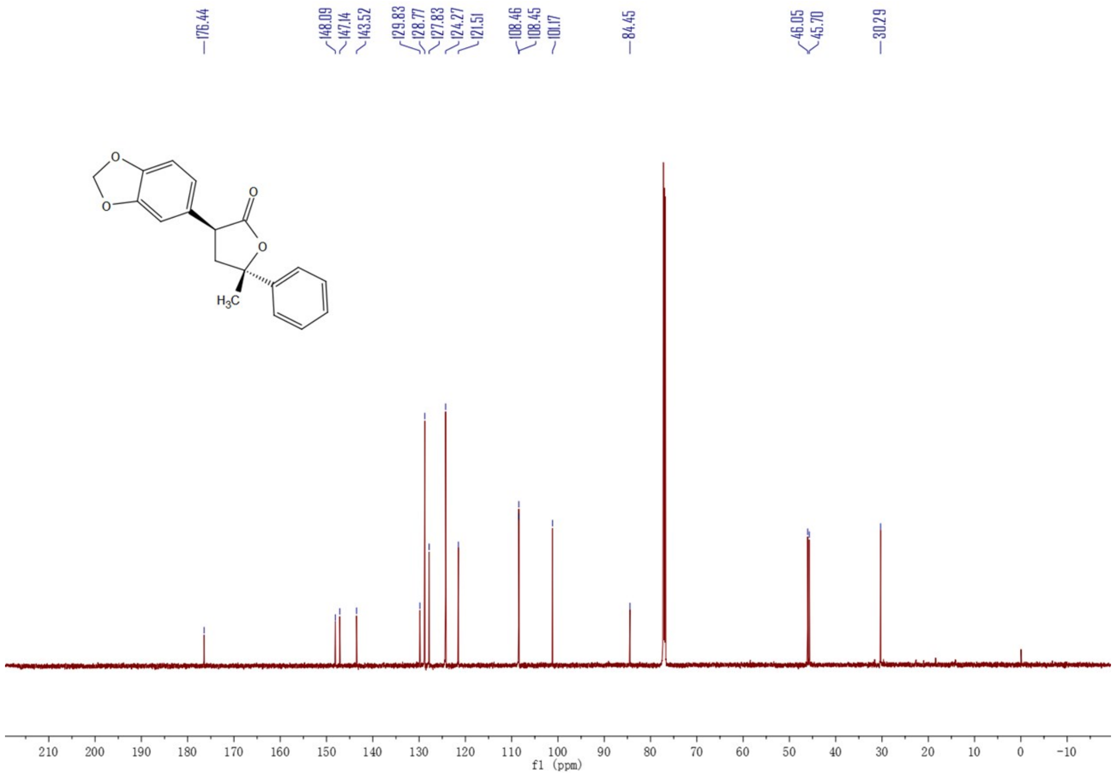
^{13}C NMR (101 MHz, CDCl$_3$) of (±)-*syn*-**36**



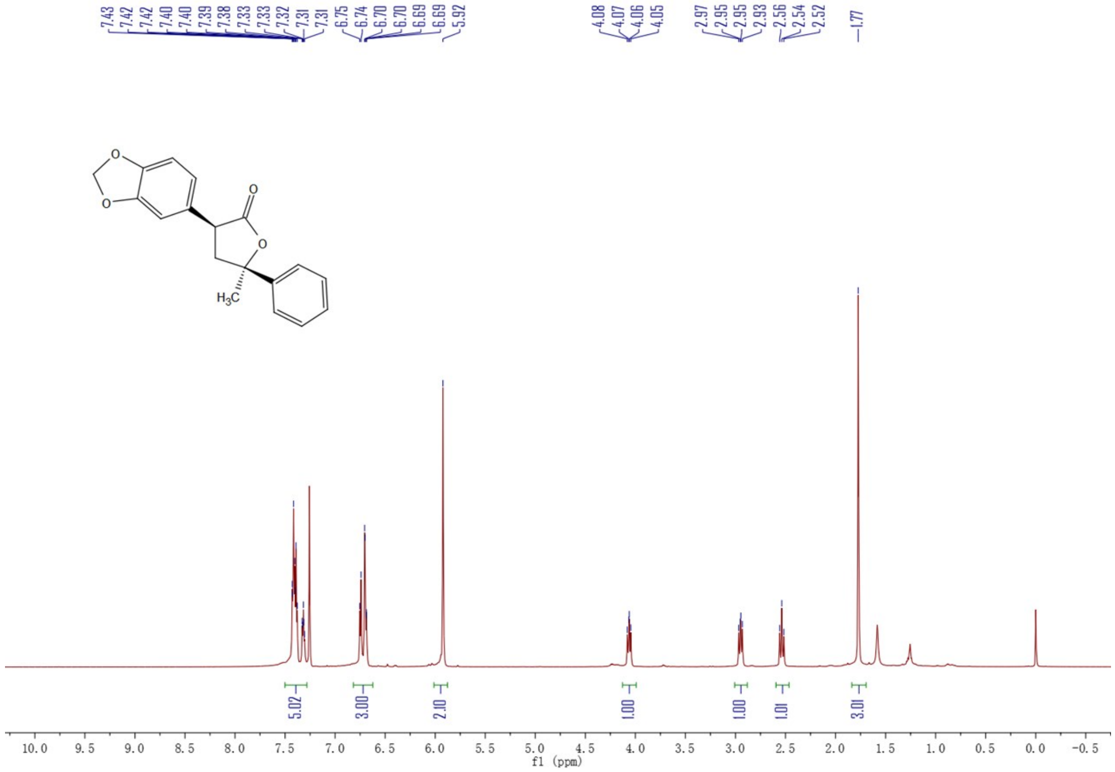
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**37**



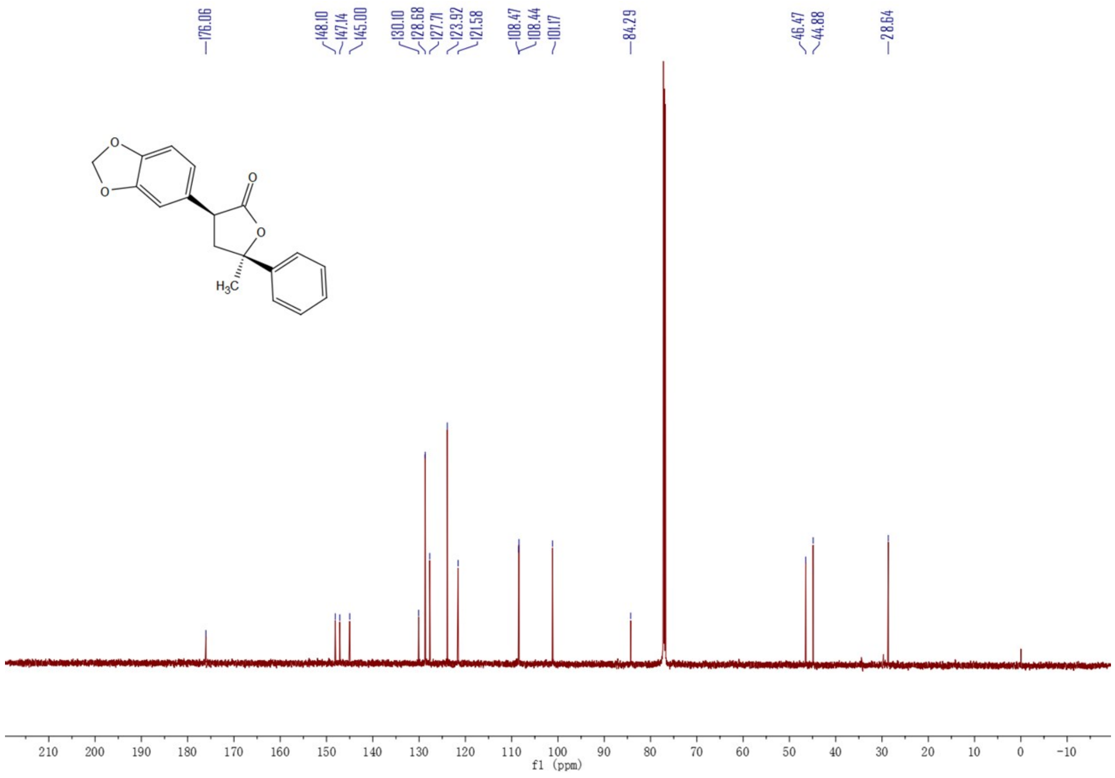
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**37**



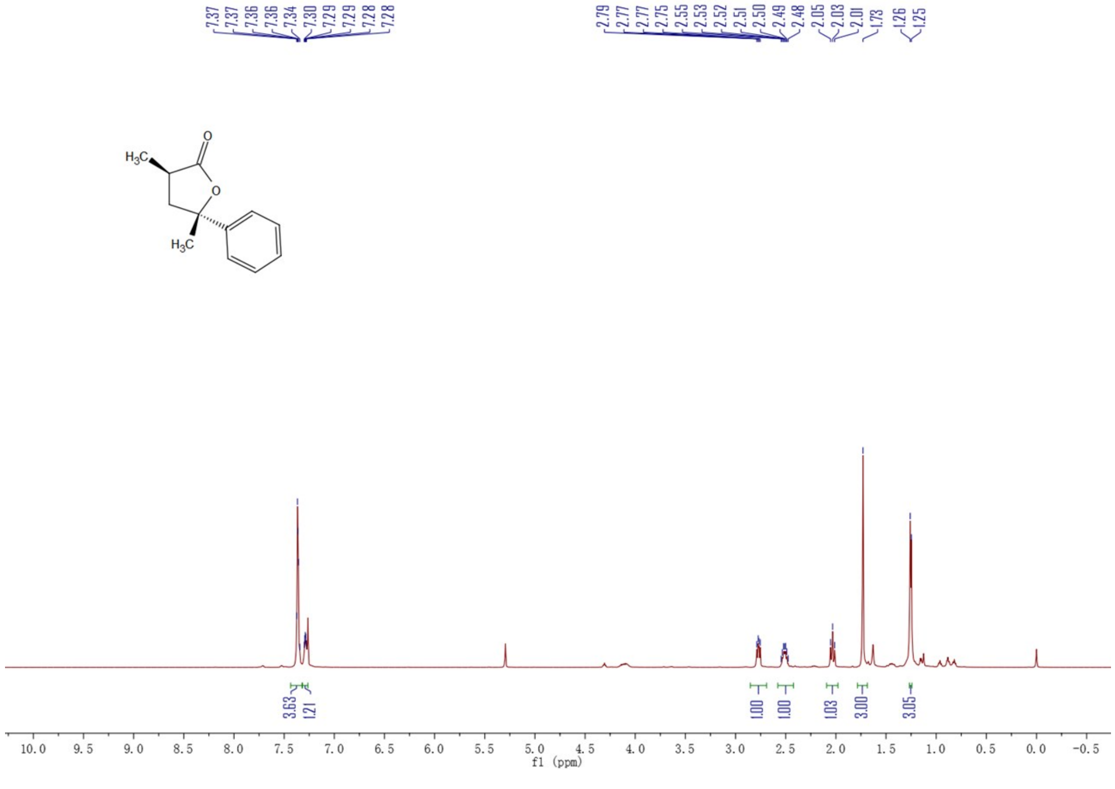
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*syn*-**37**



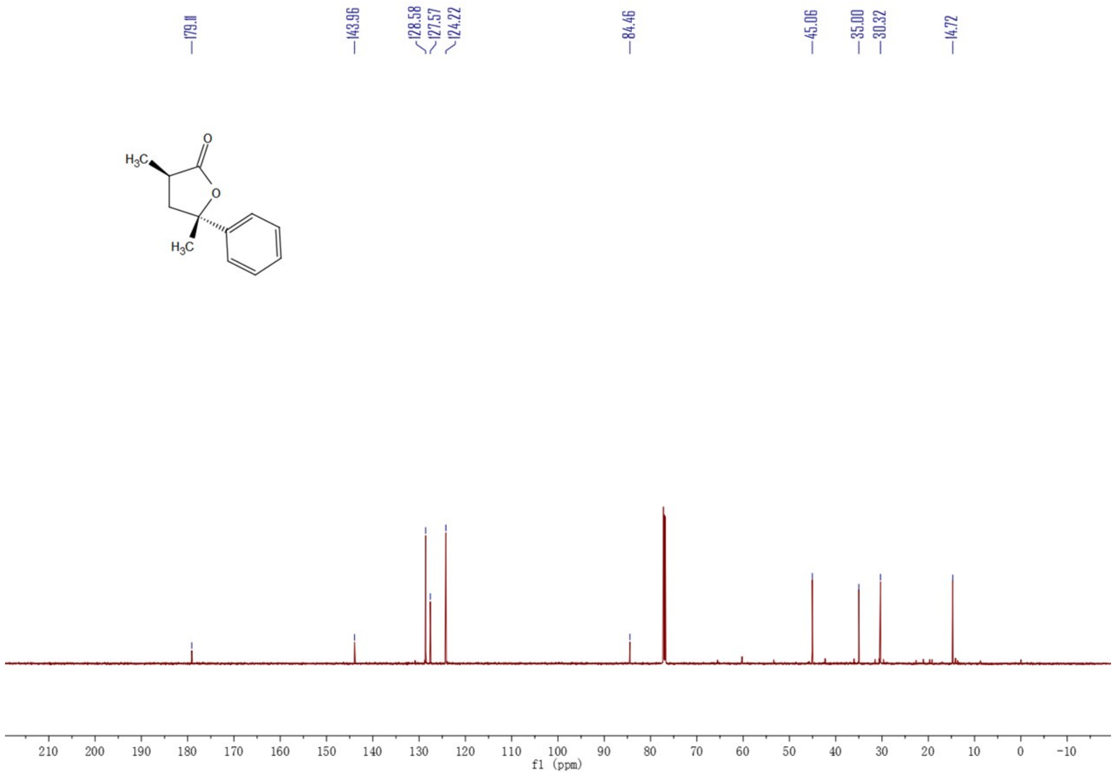
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*syn*-**37**



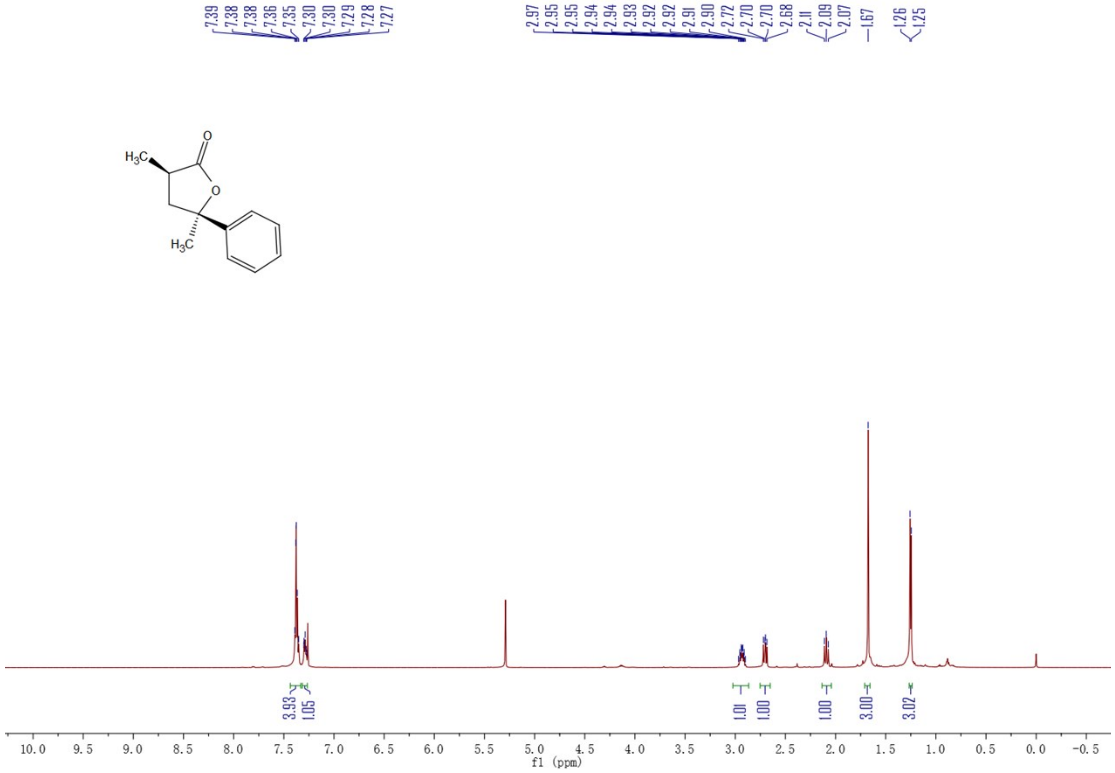
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-*anti*-**38**



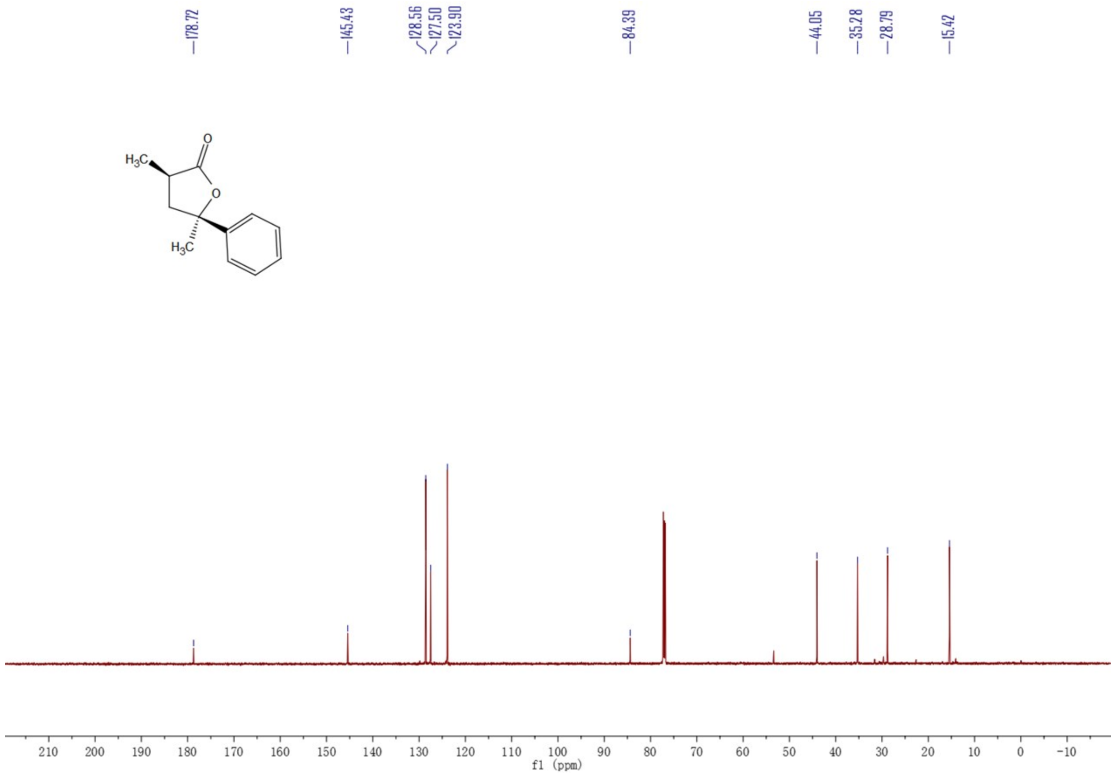
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-*anti*-**38**



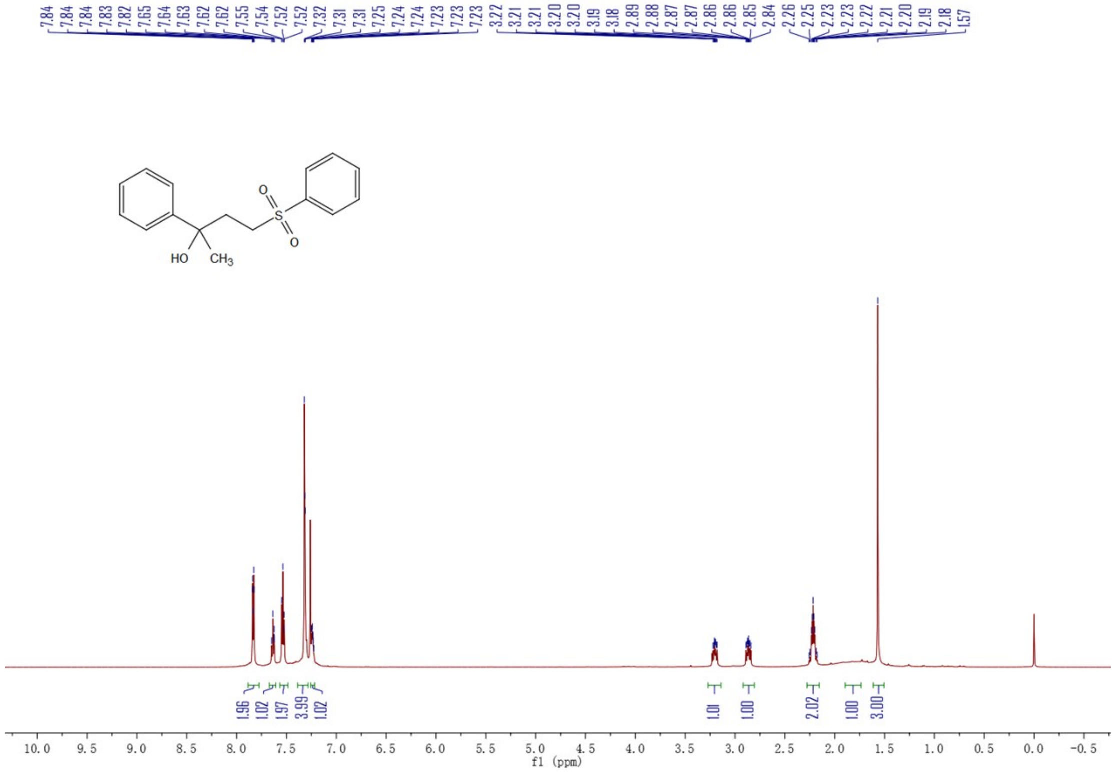
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**38**



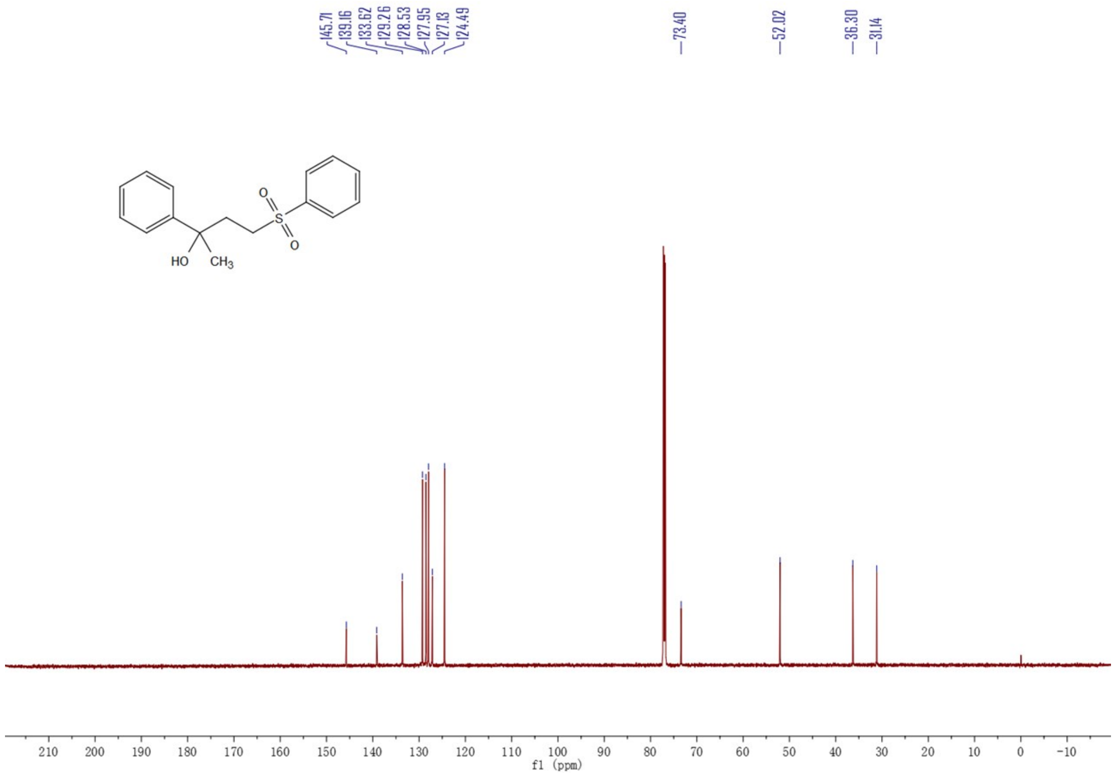
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**38**



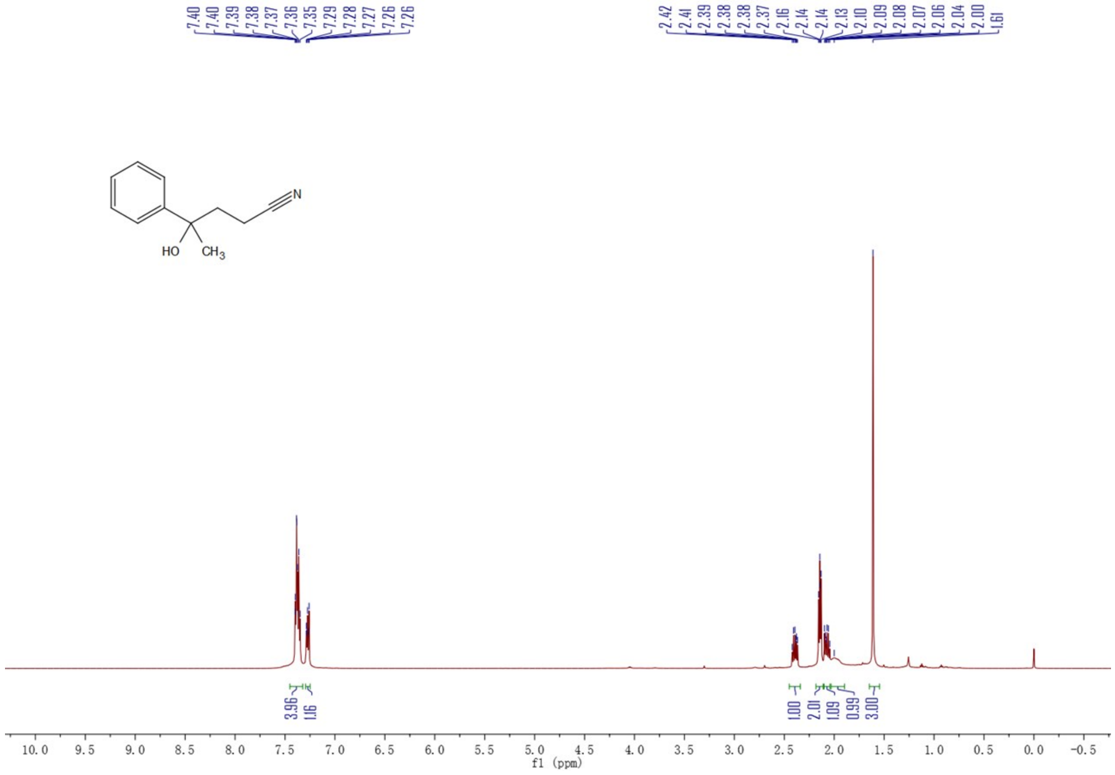
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-**39**



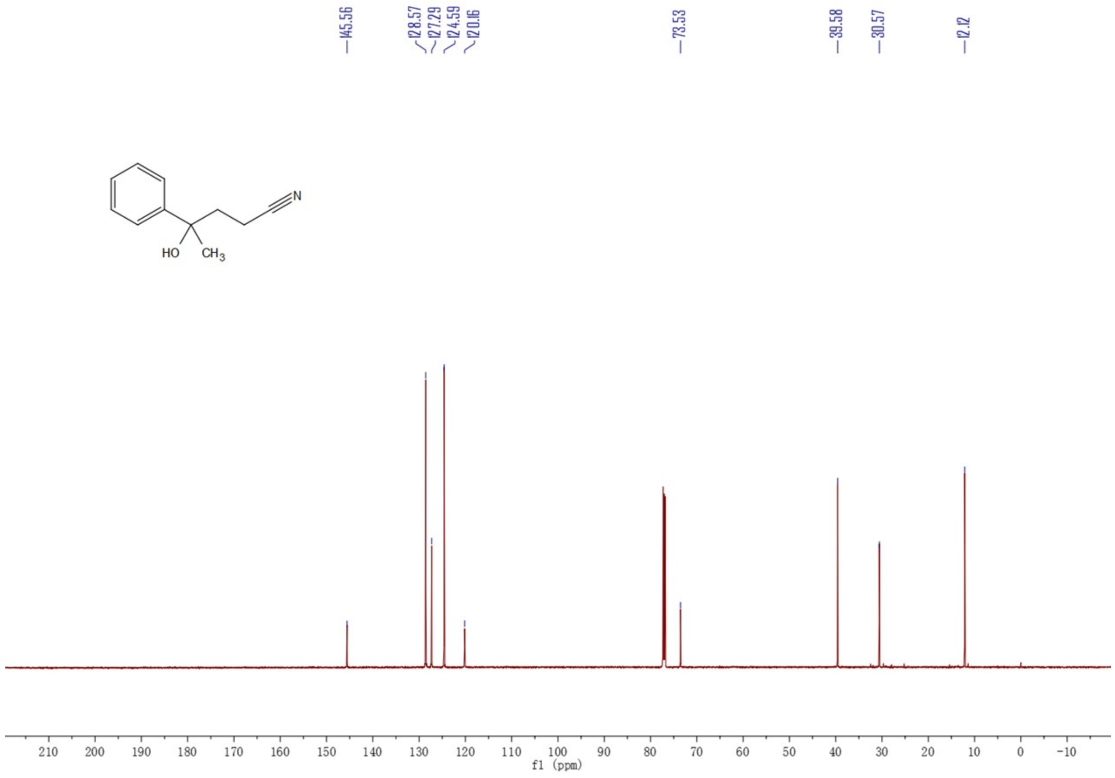
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-**39**



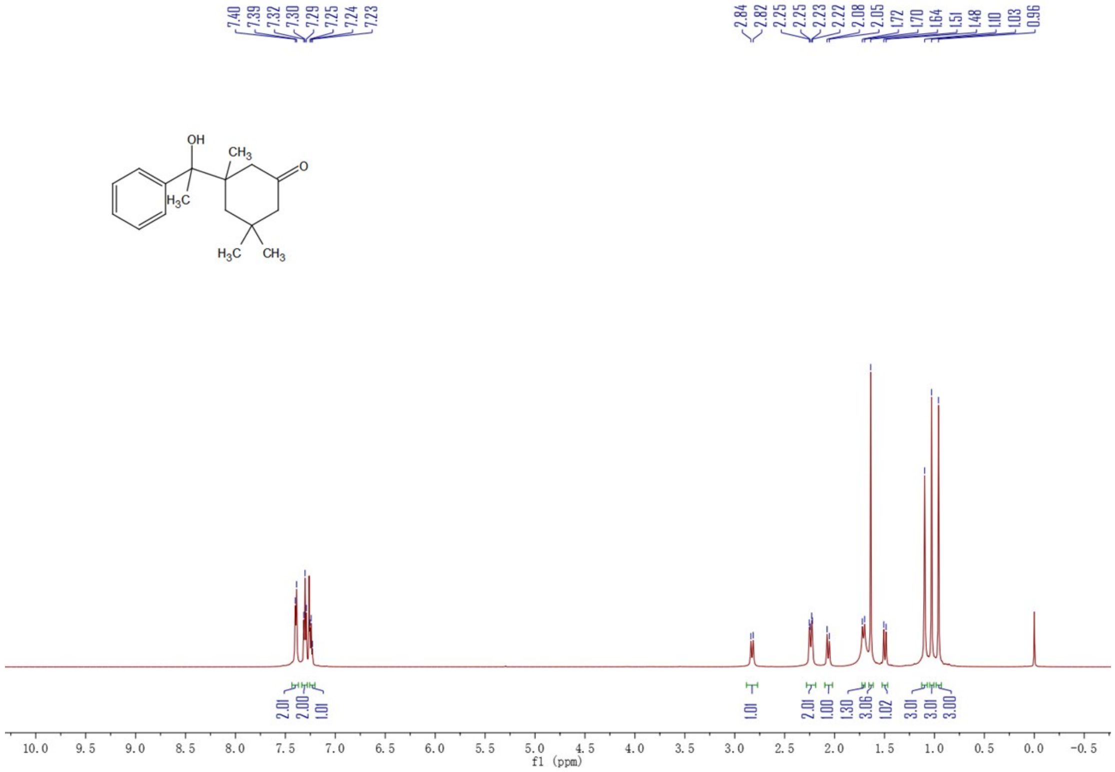
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-**40**



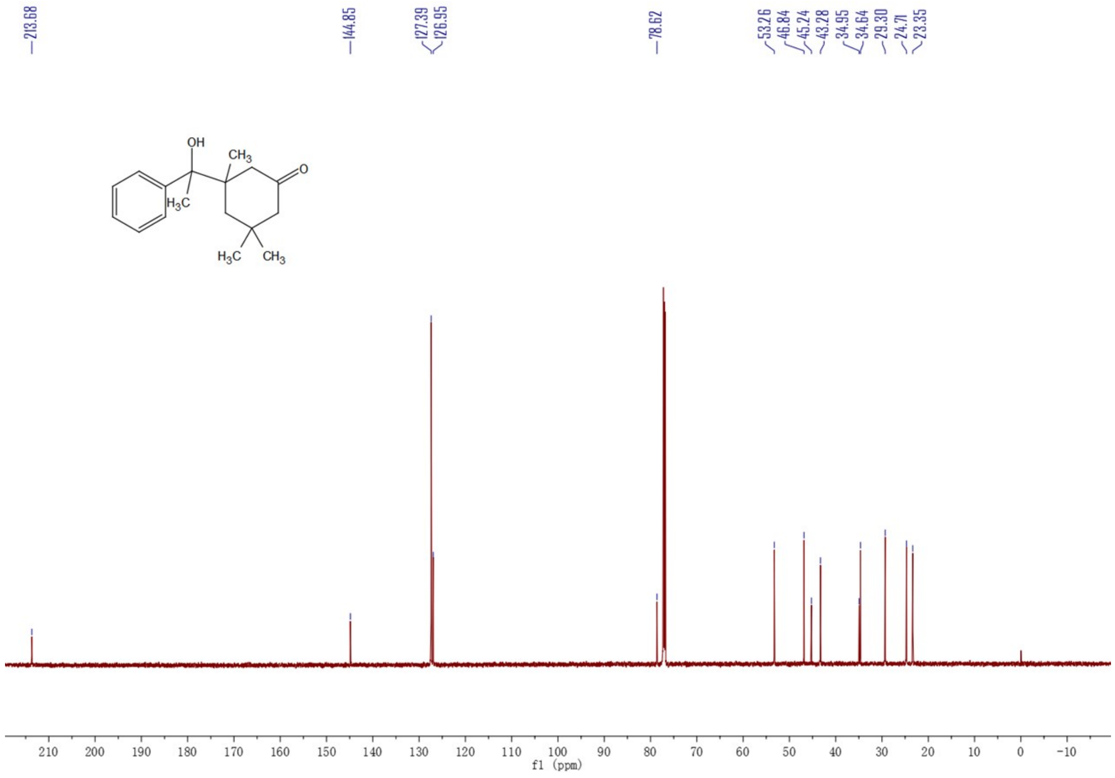
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-**40**



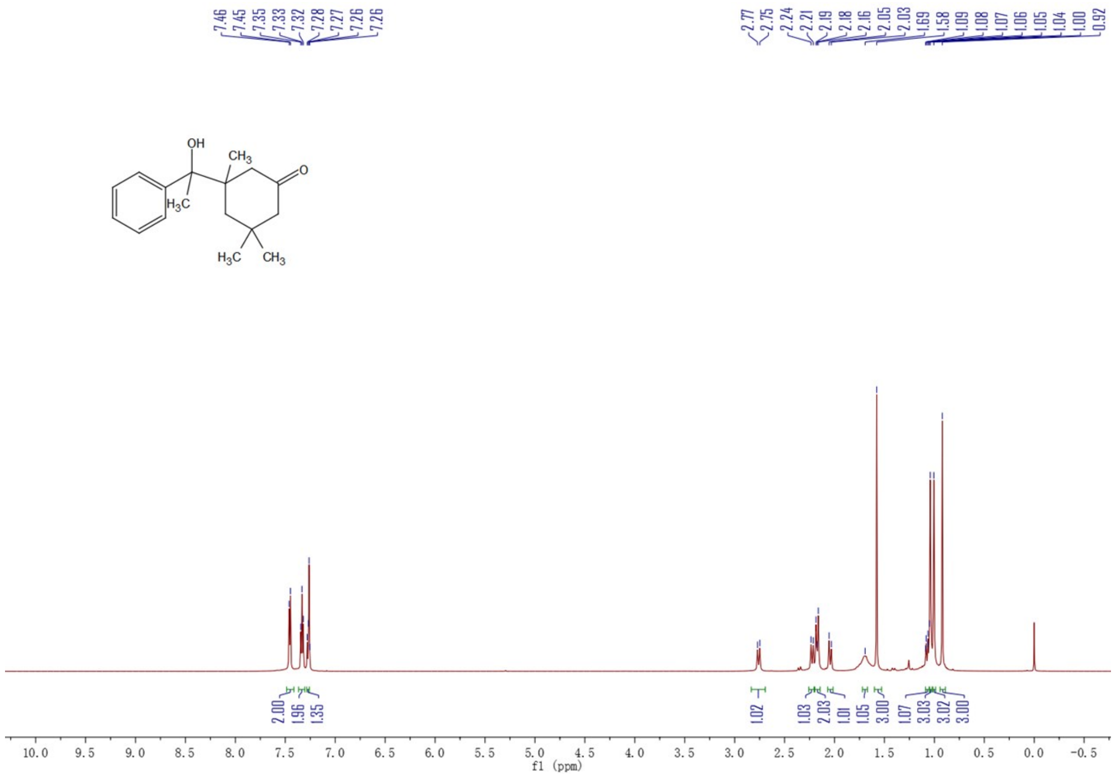
^{1}H NMR (600 MHz, $CDCl_3$) of (±)-1-**41**



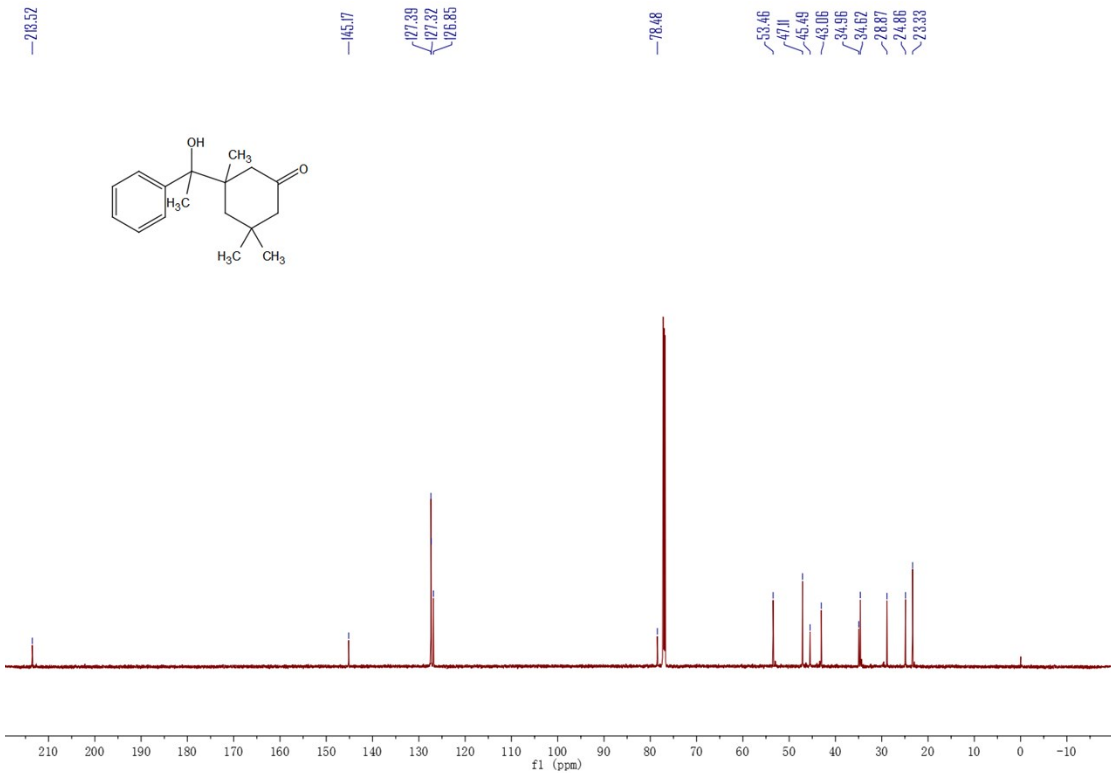
^{13}C NMR (151 MHz, $CDCl_3$) of (±)-1-**41**



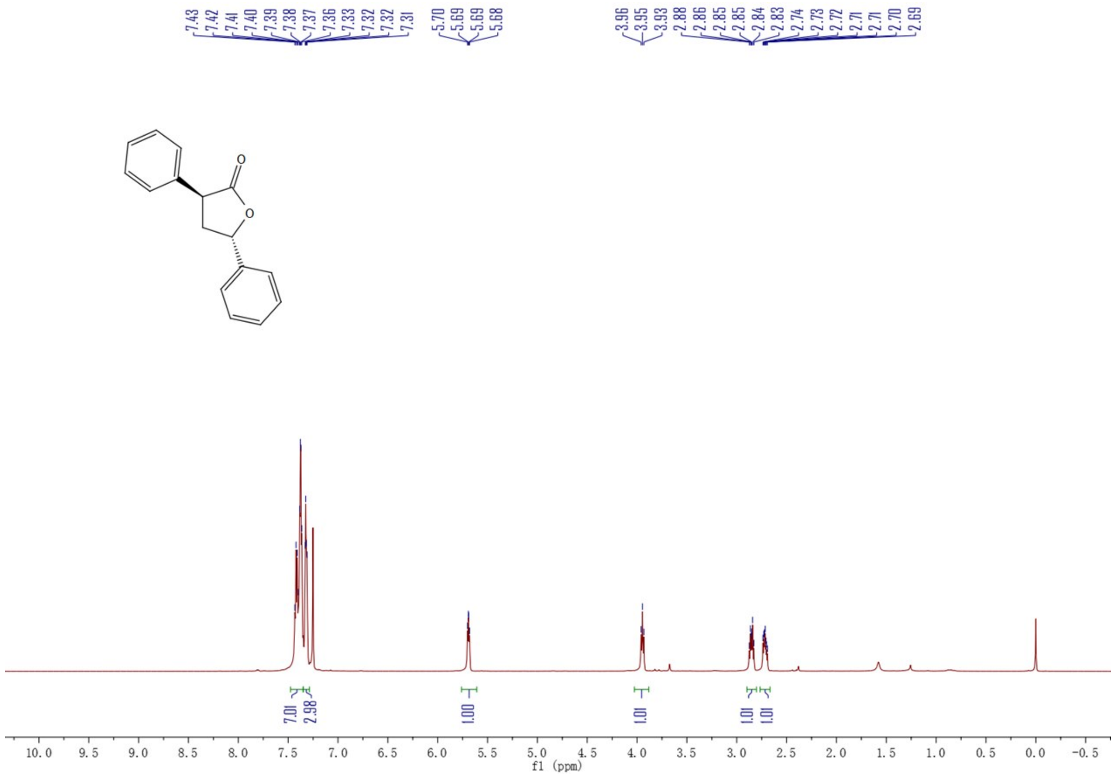
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-2-**41**



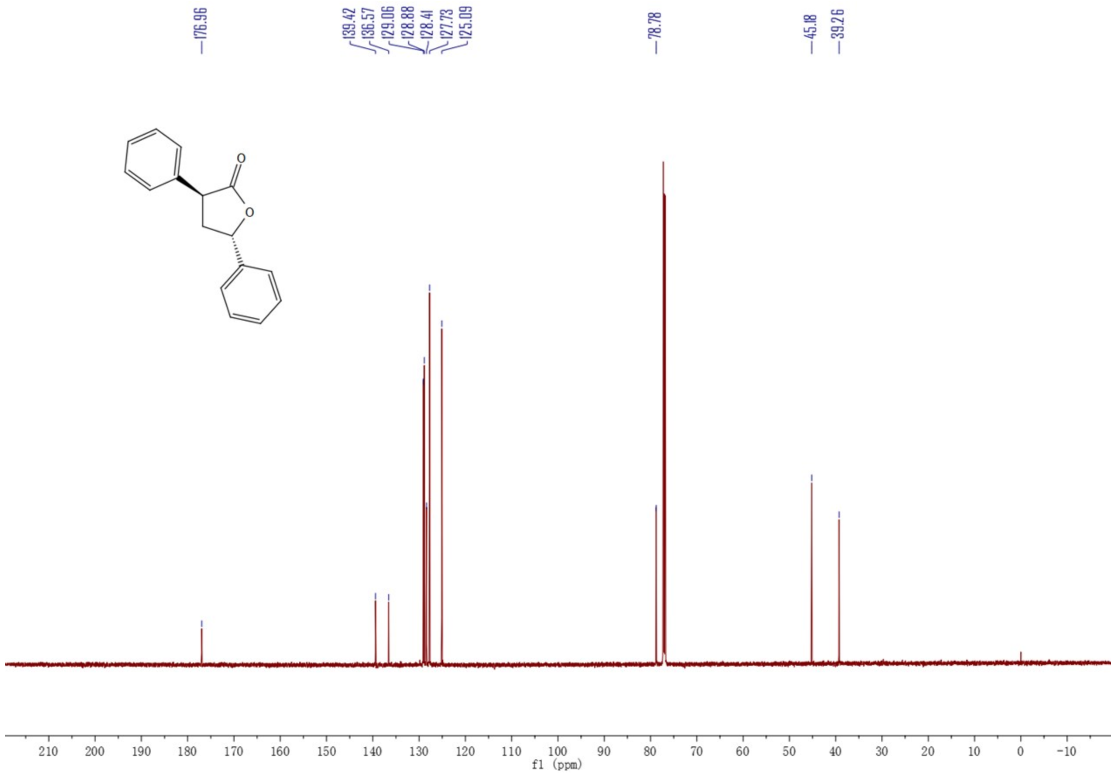
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-2-**41**



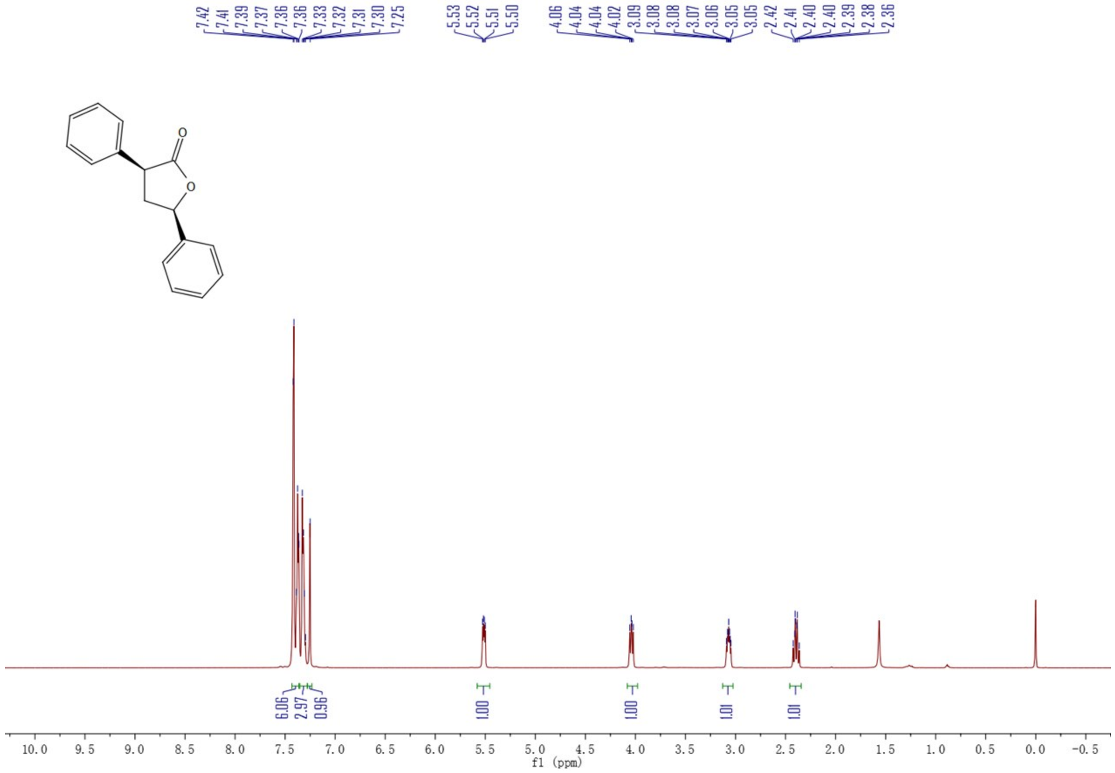
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**43**



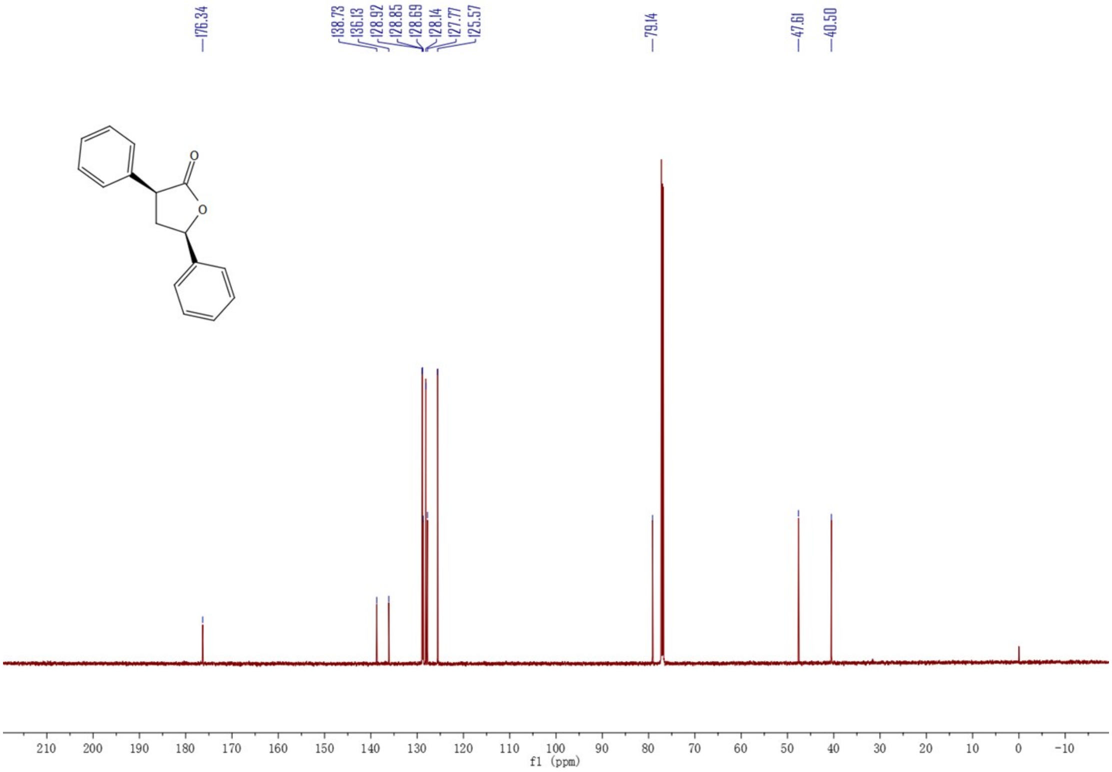
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**43**



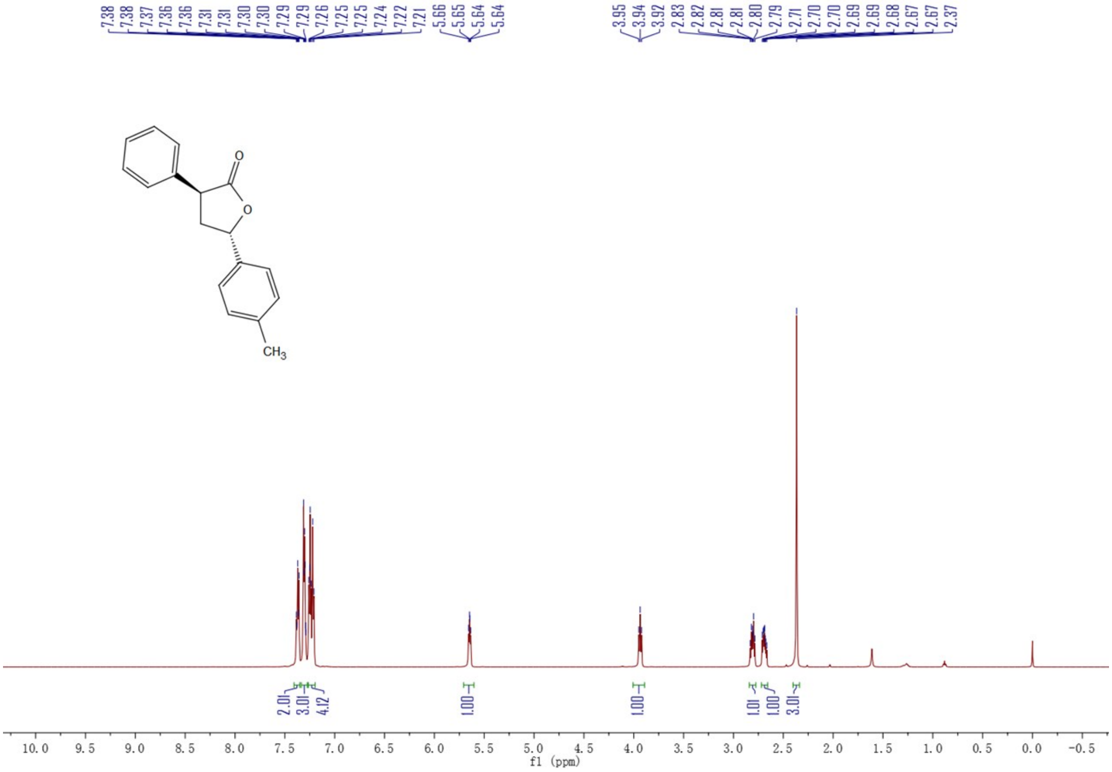
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**43**



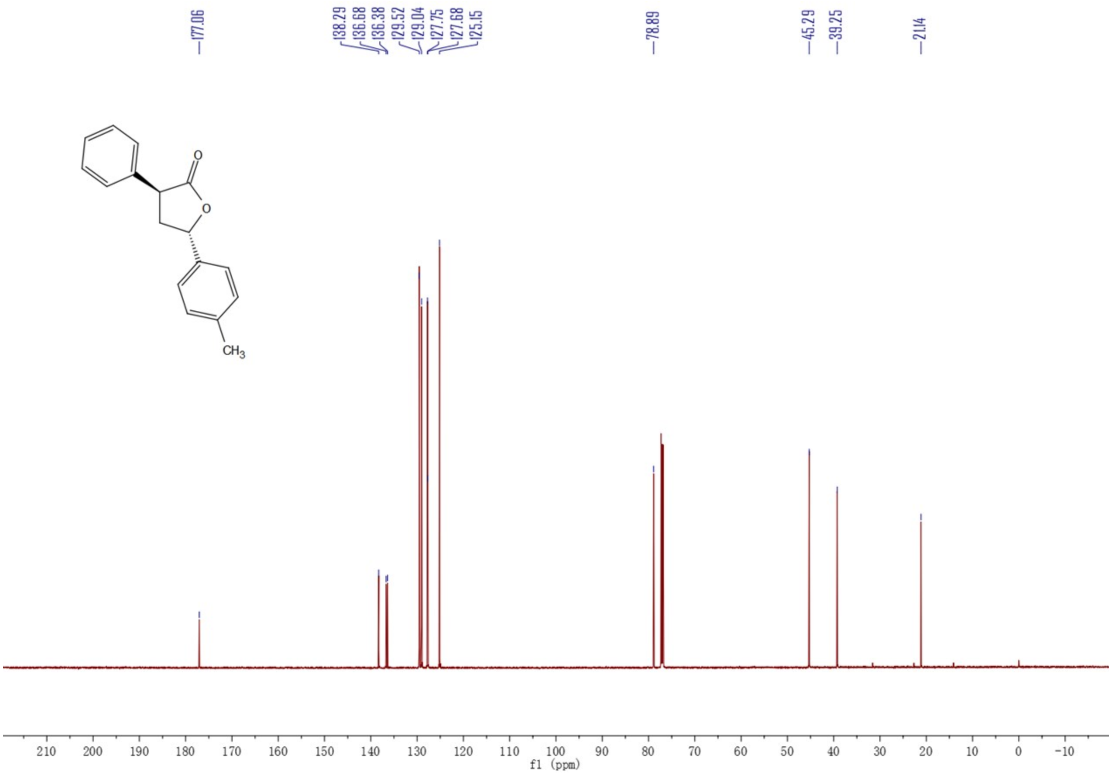
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**43**



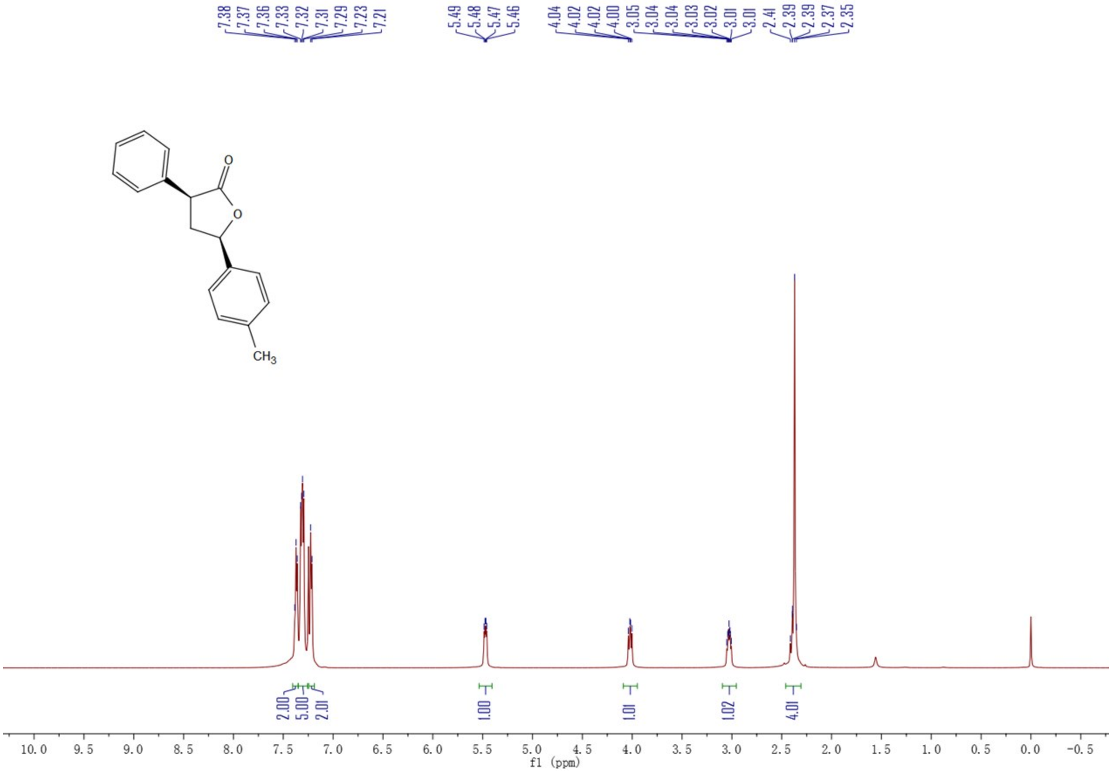
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**44**



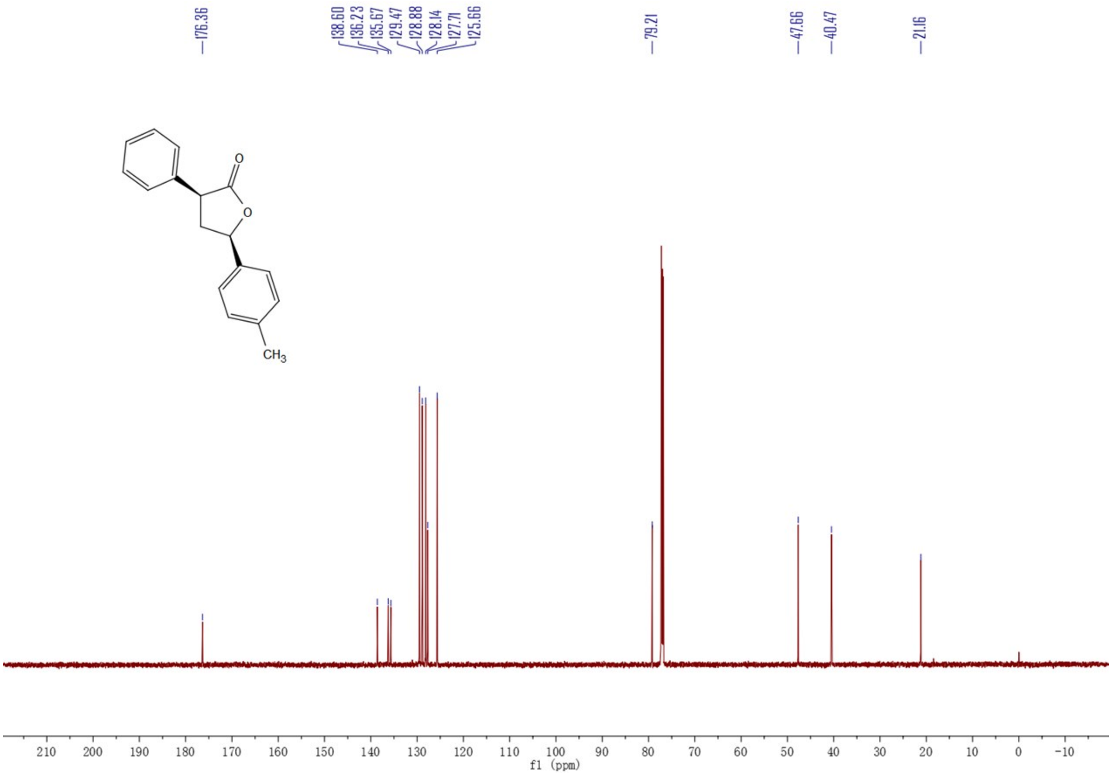
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**44**



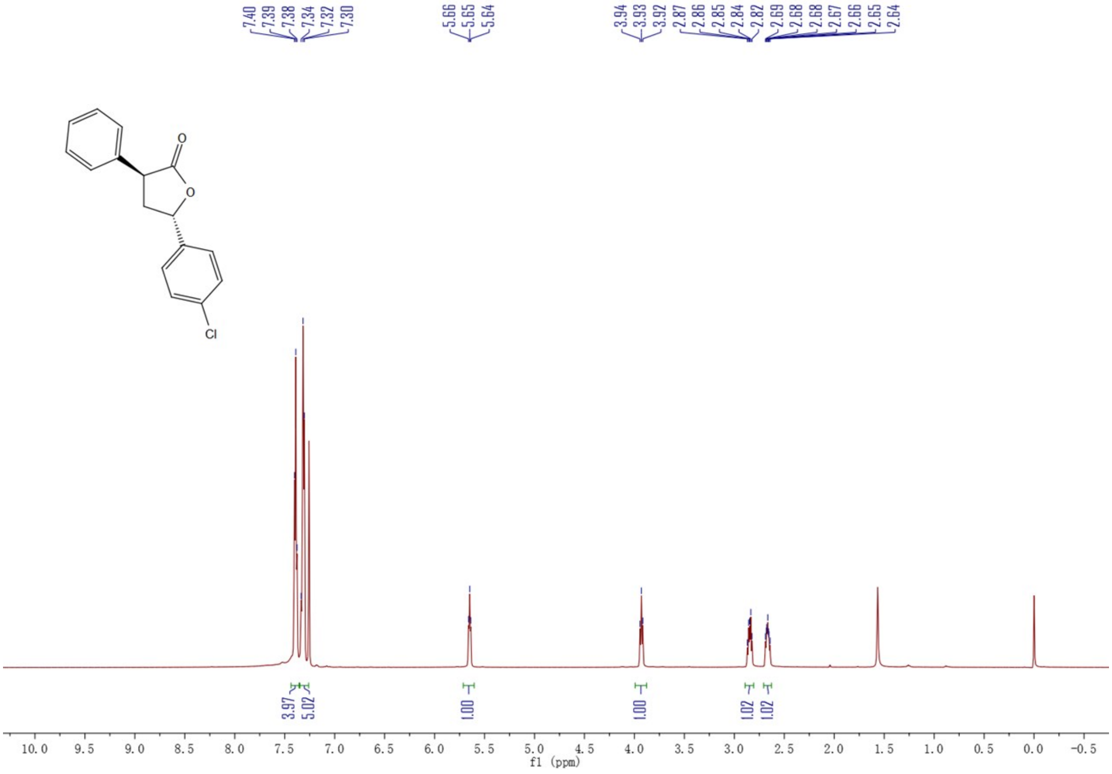
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**44**



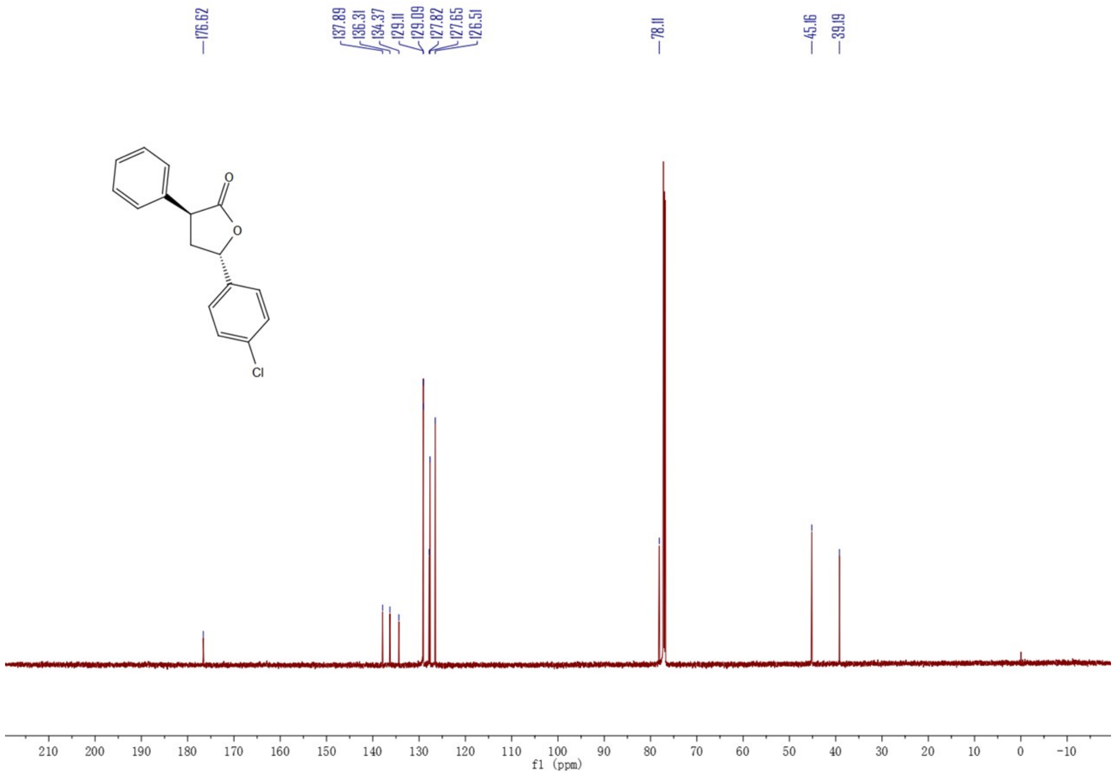
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**44**



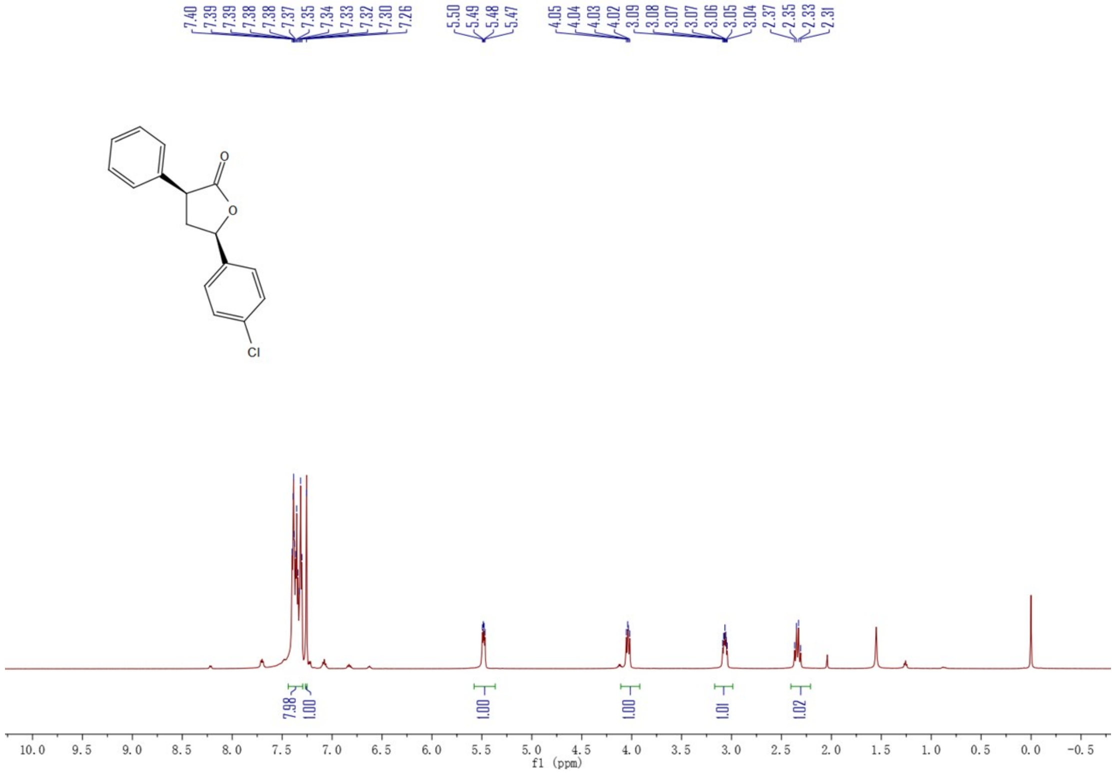
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**45**



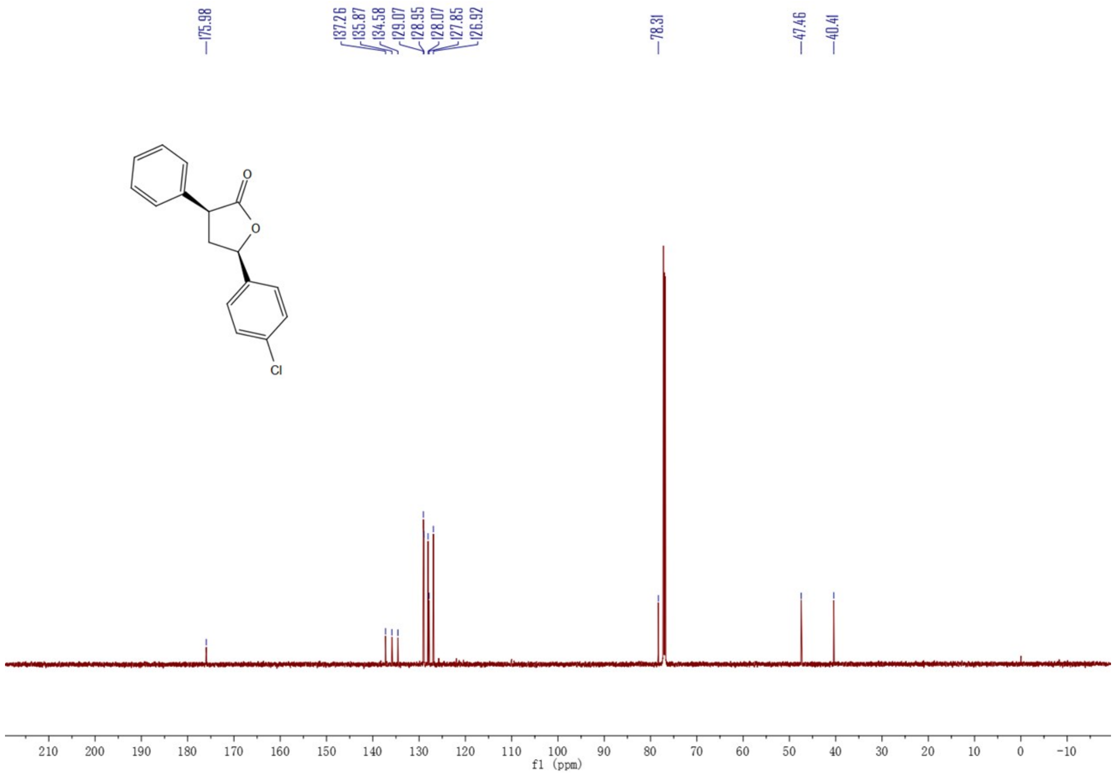
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**45**



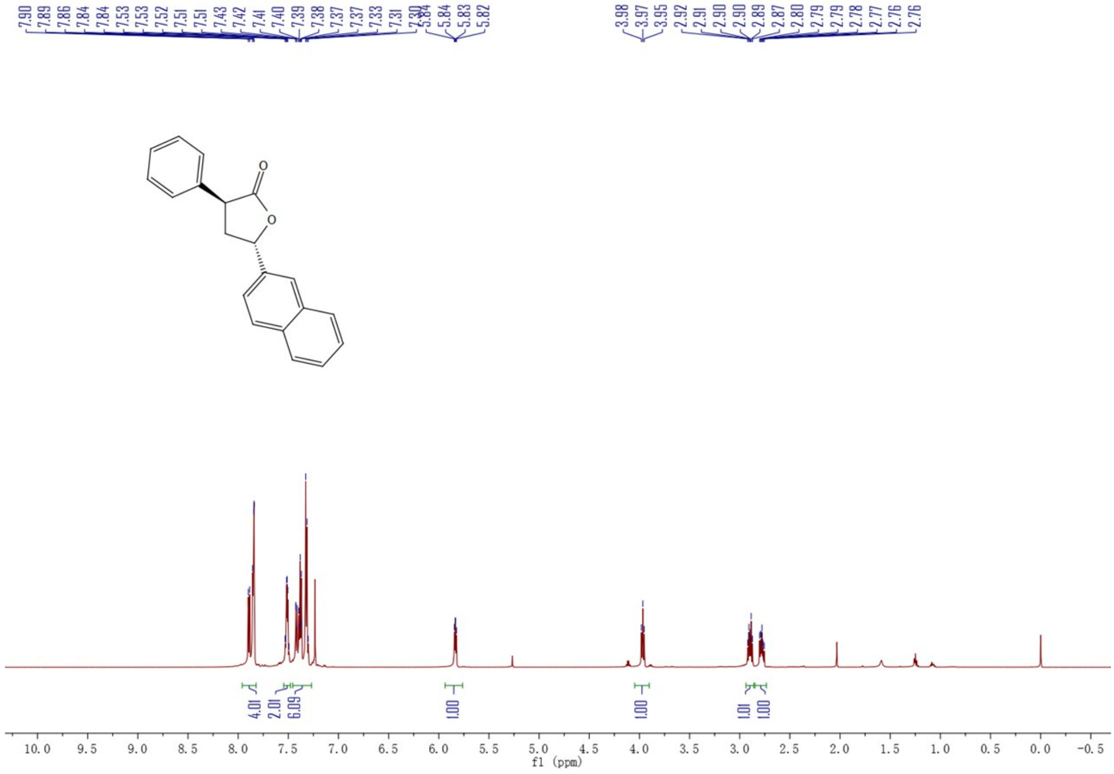
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**45**



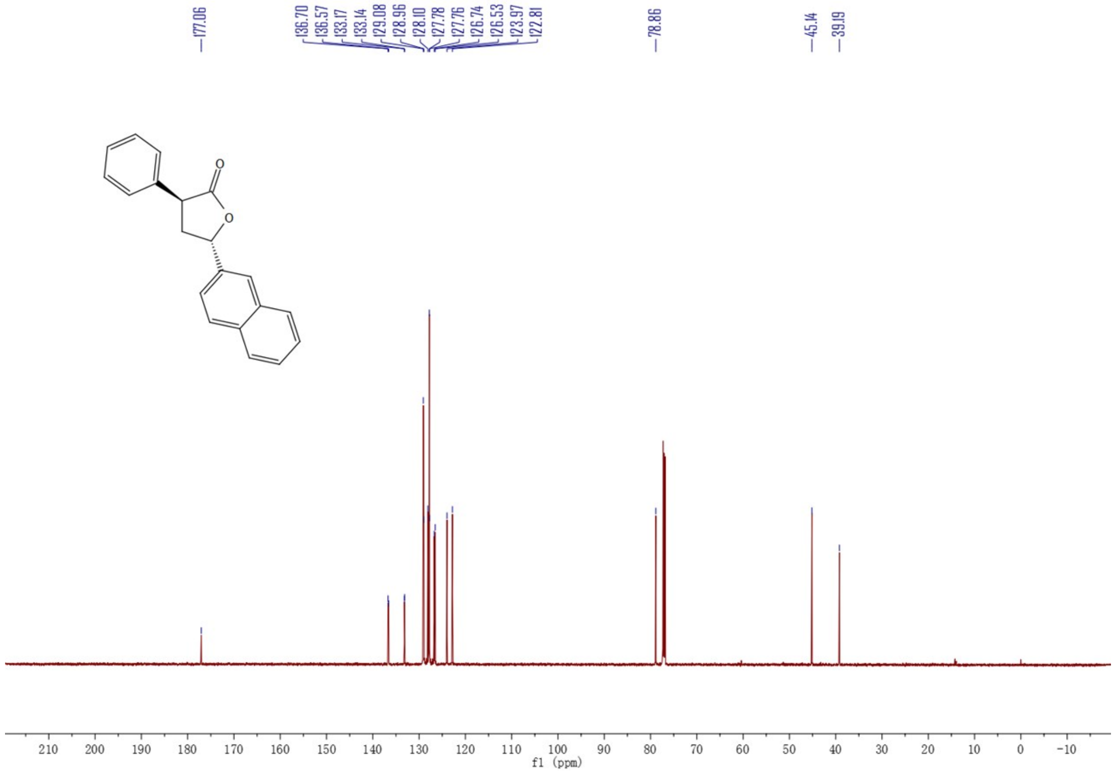
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**45**



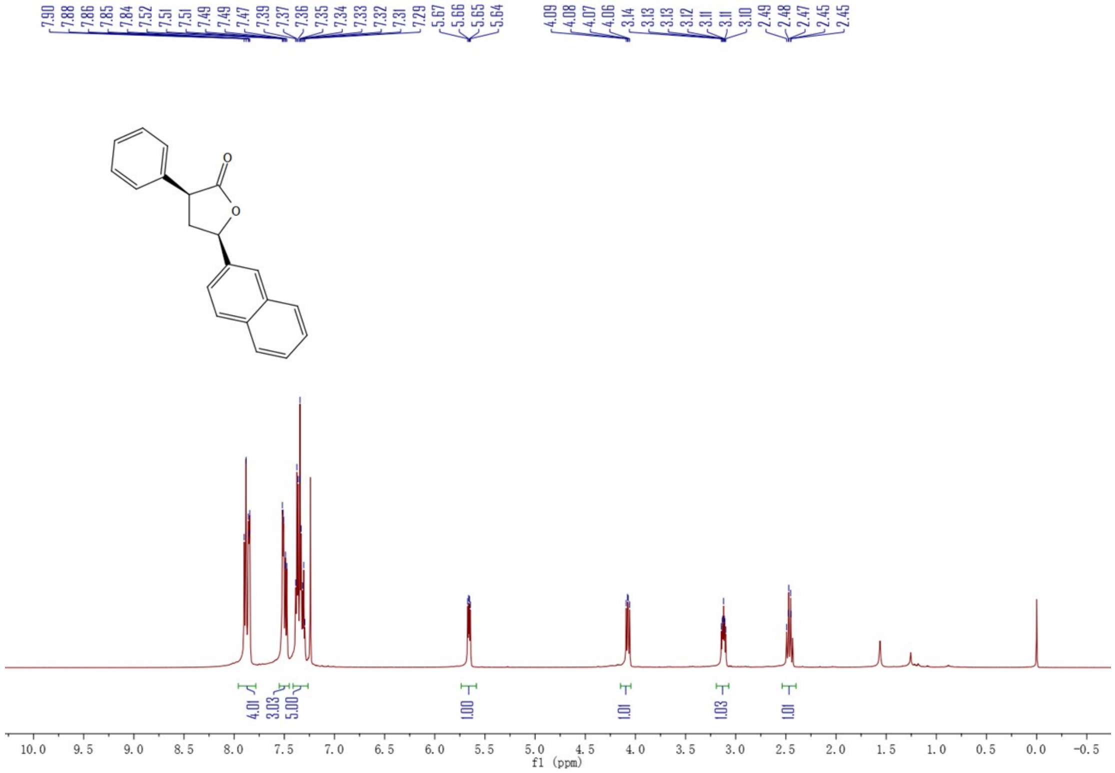
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**46**



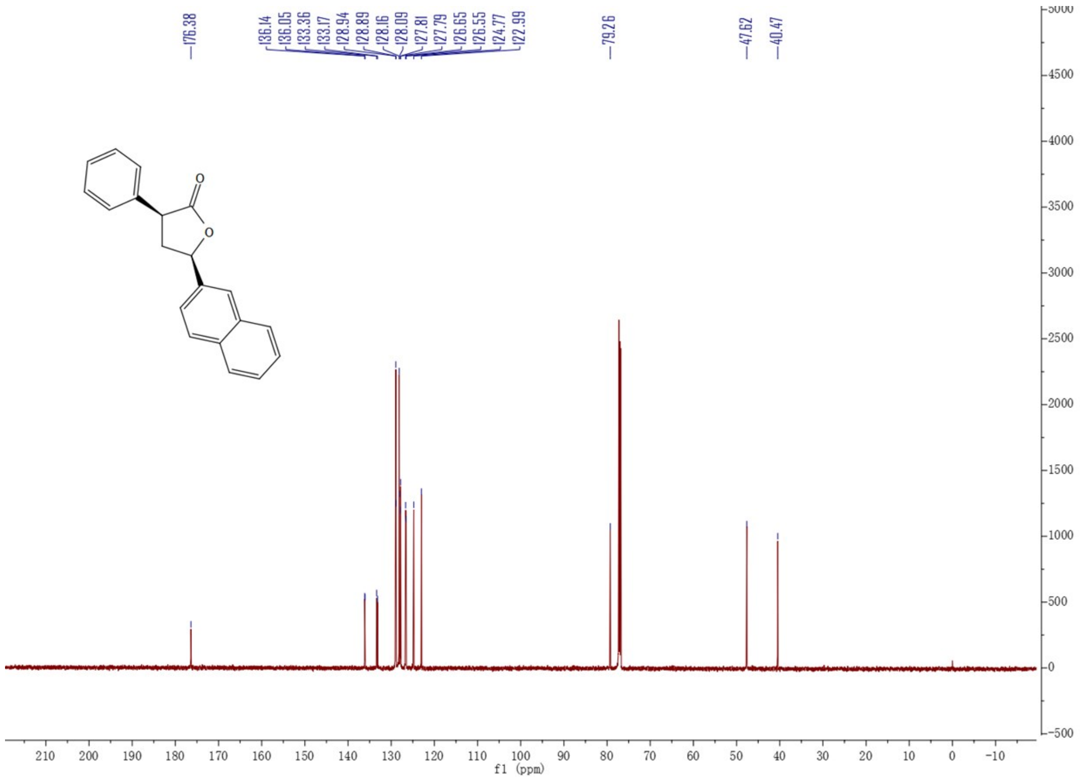
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**46**



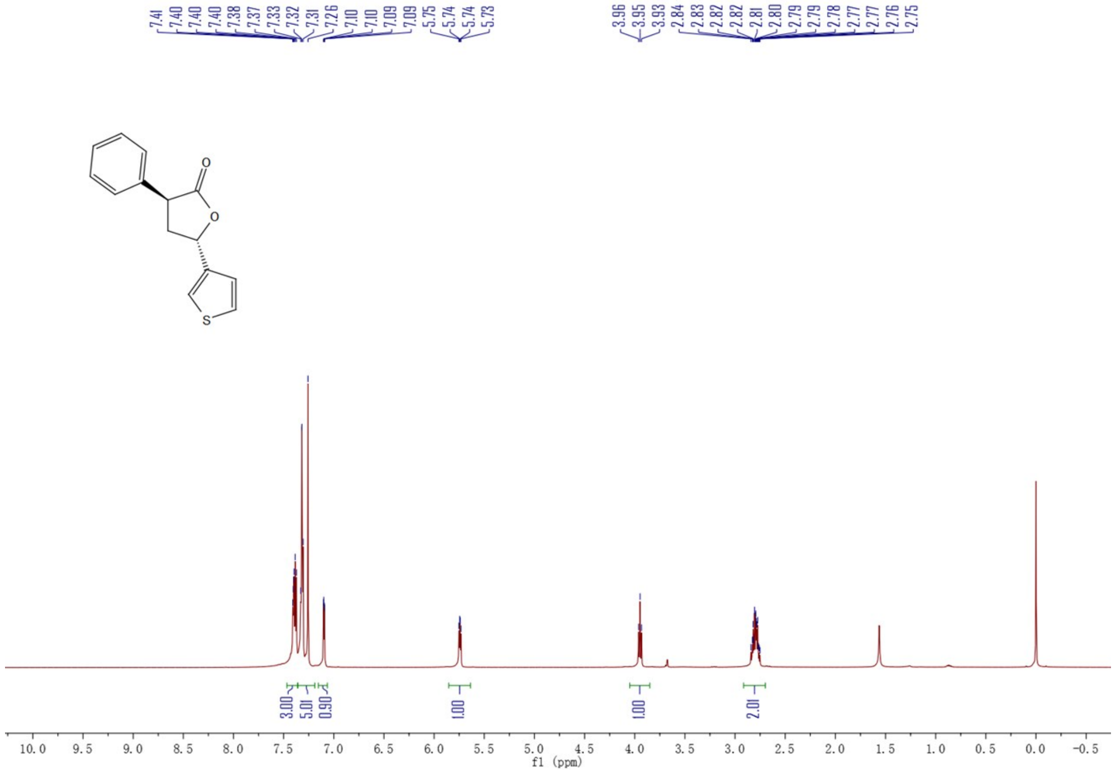
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**46**



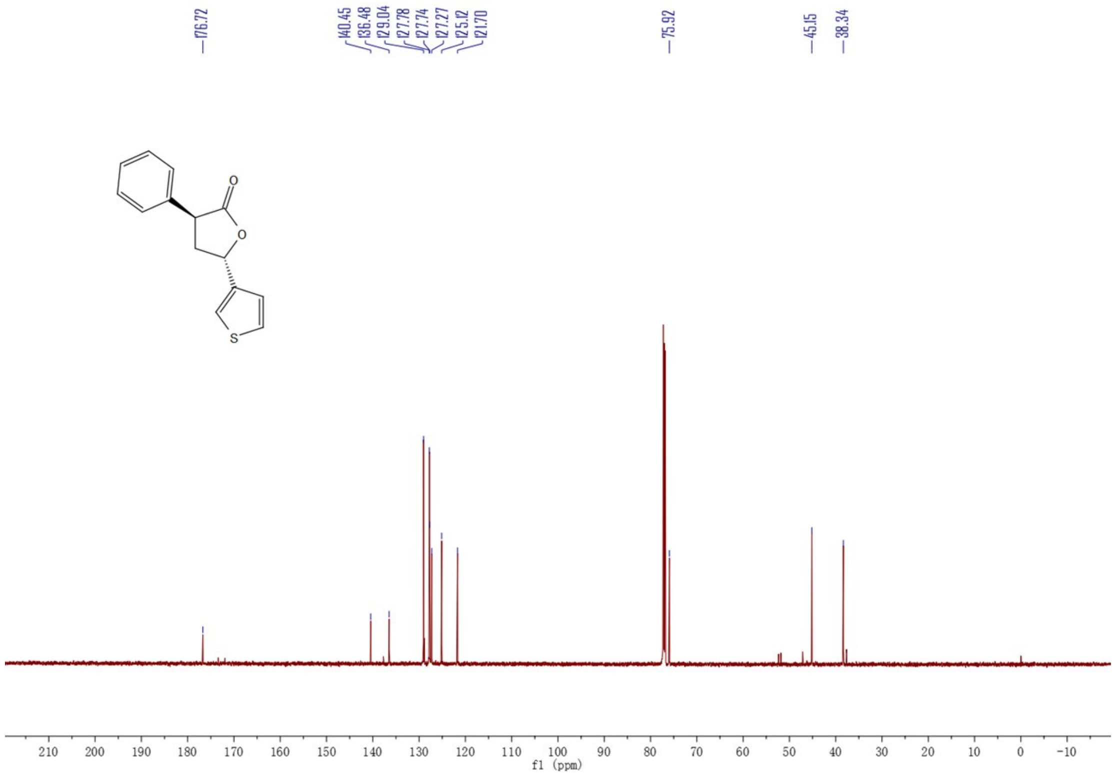
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**46**



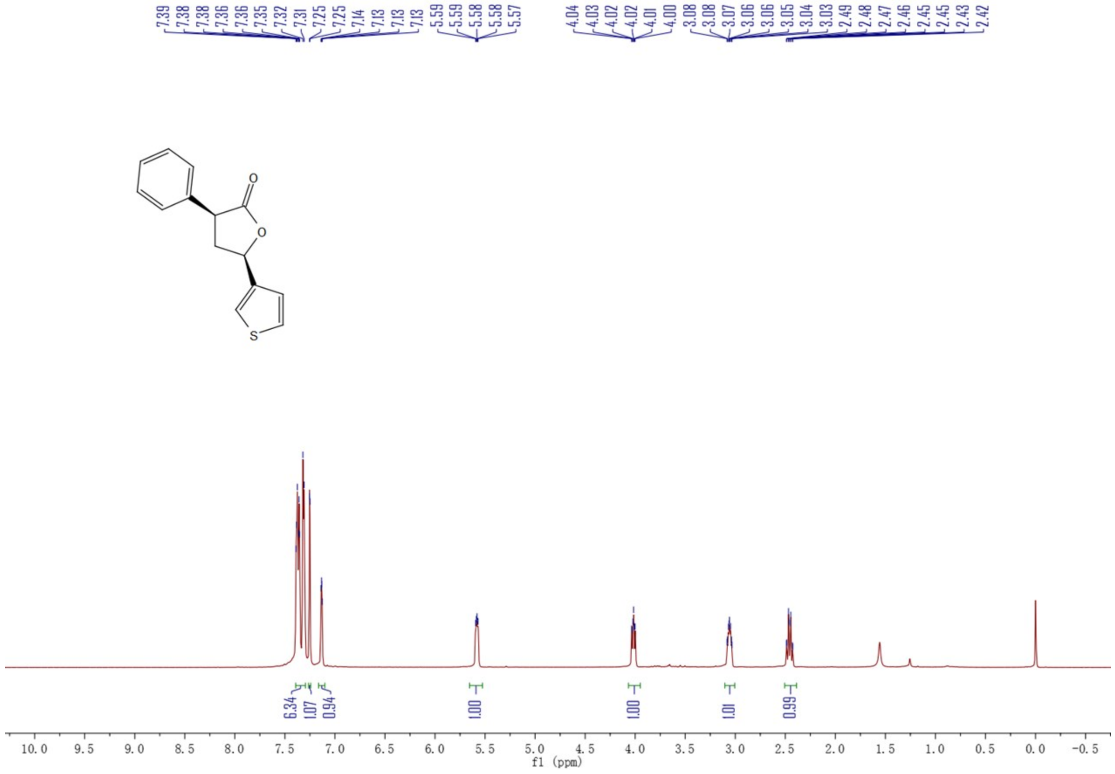
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**47**



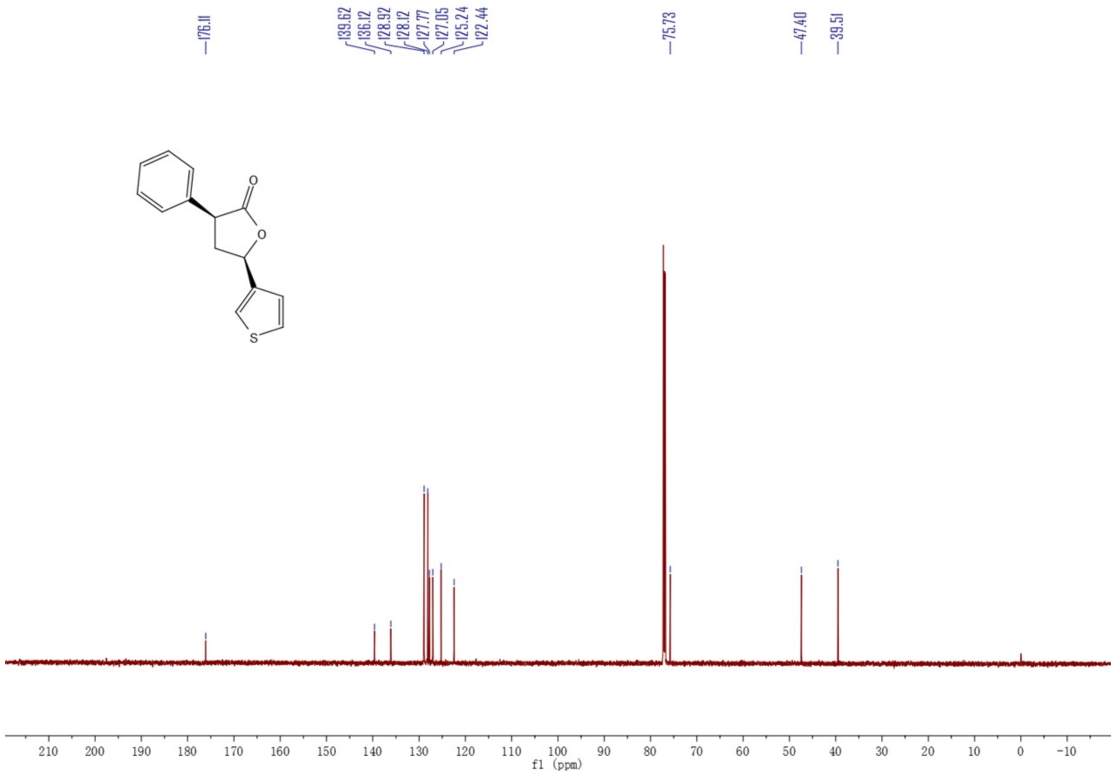
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**47**



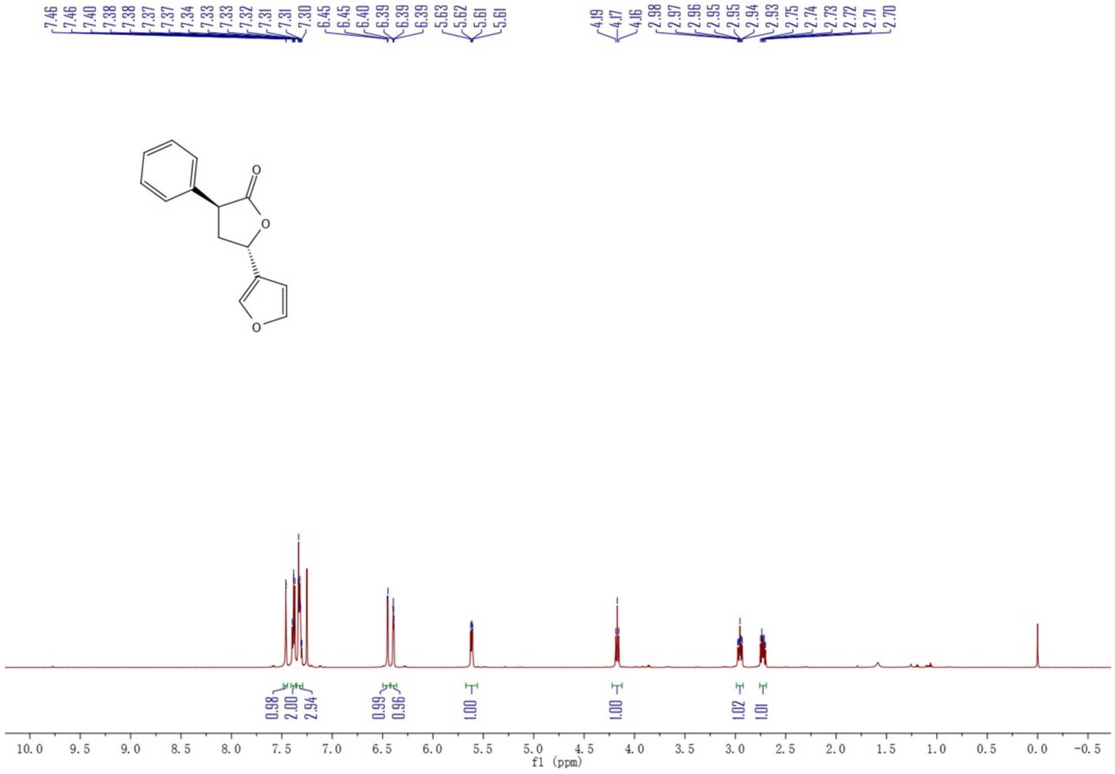
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**47**



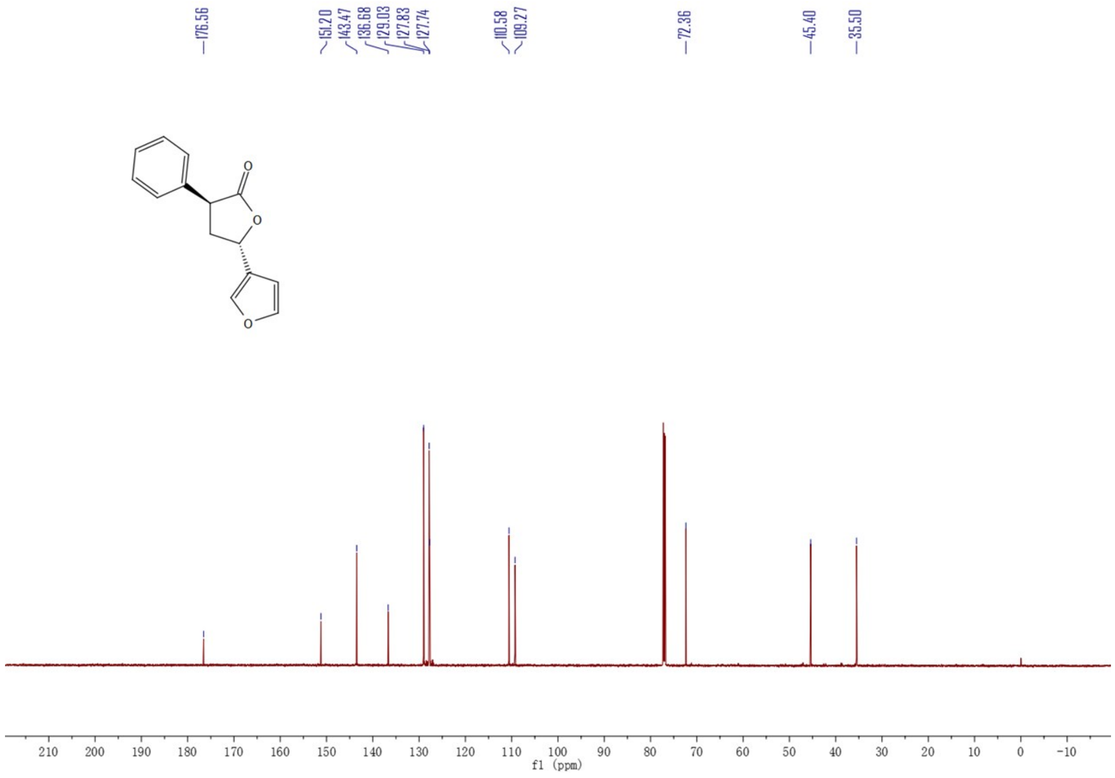
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**47**



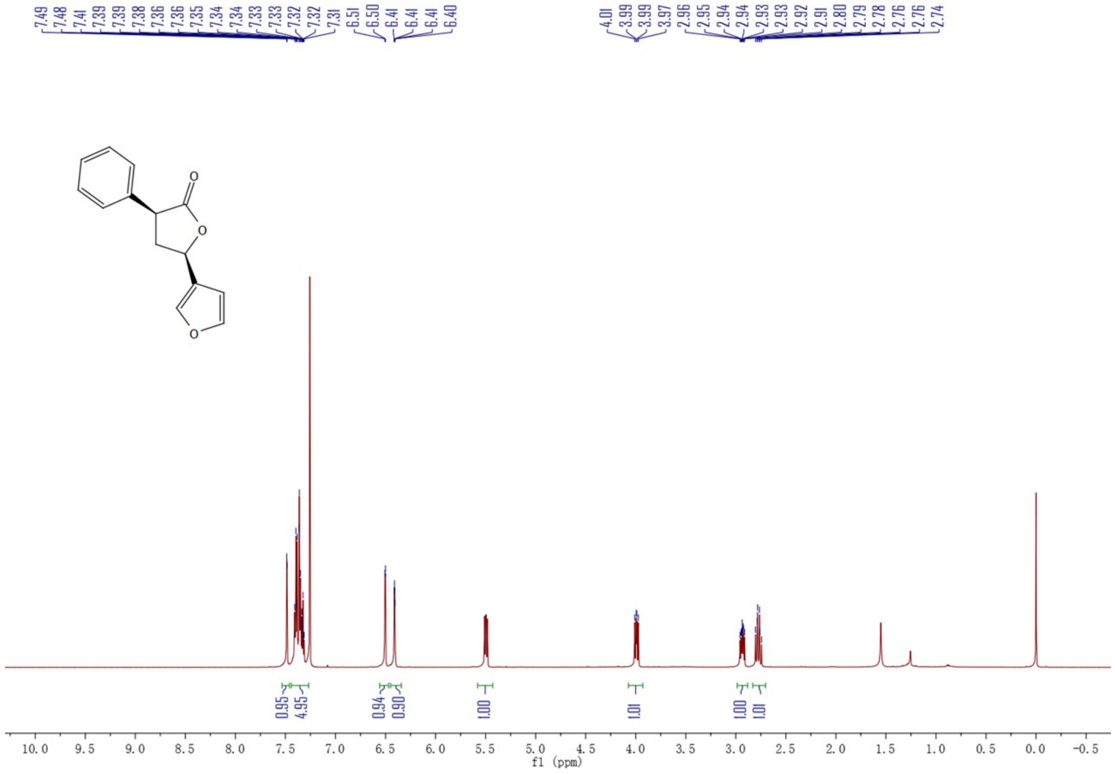
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*anti*-**48**



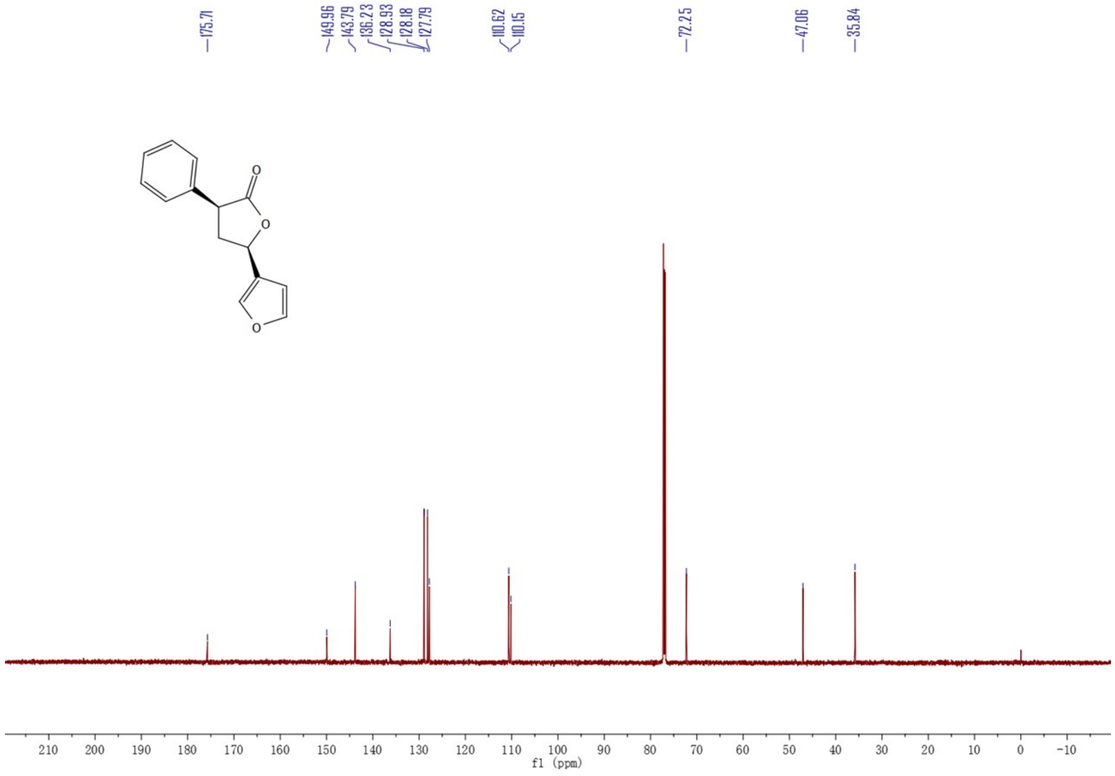
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*anti*-**48**



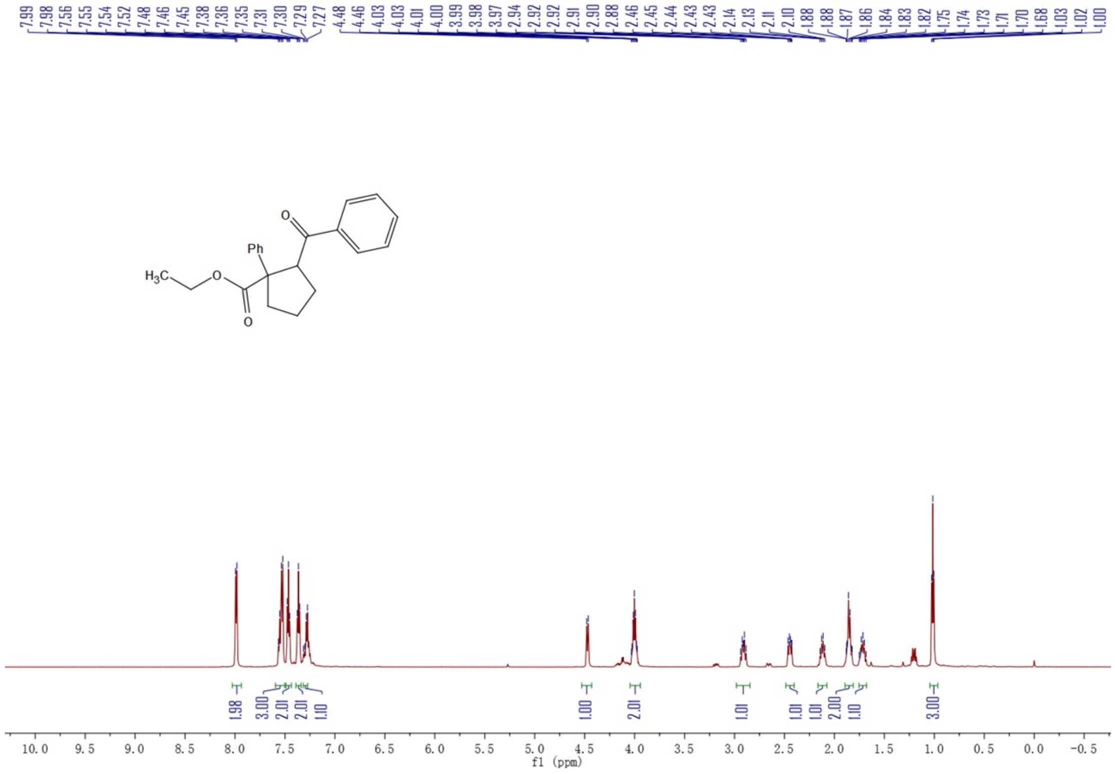
^{1}H NMR (600 MHz, CDCl$_3$) of (±)-*syn*-**48**



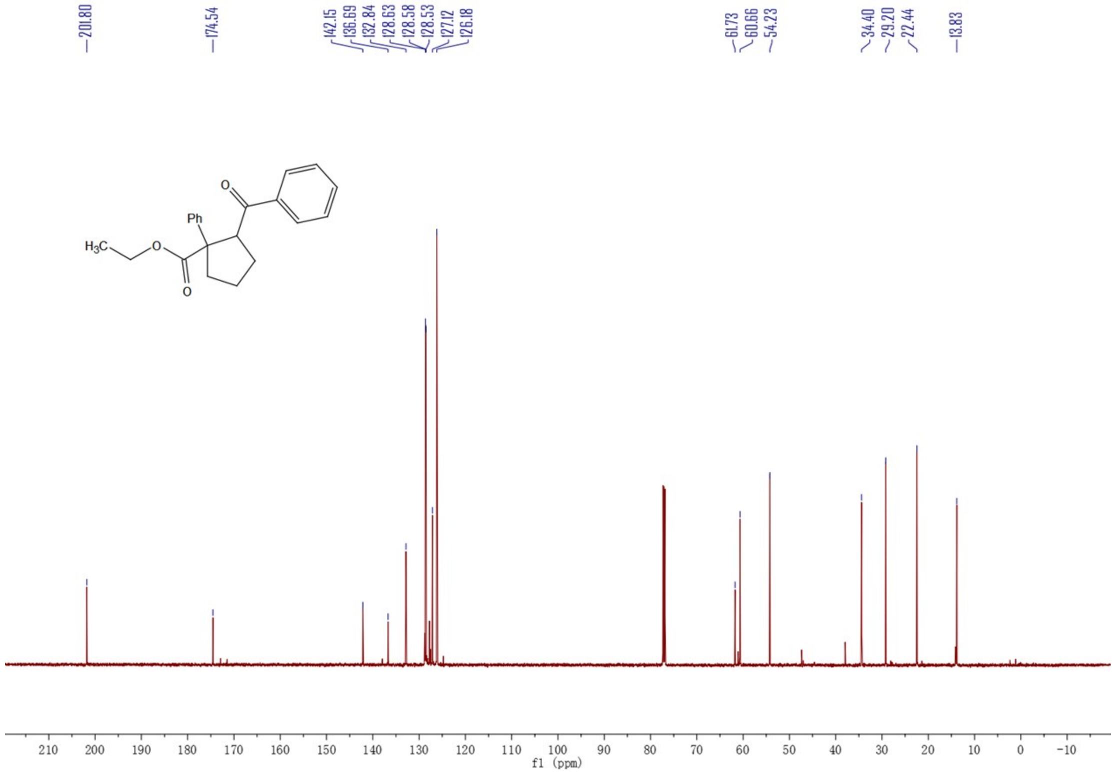
^{13}C NMR (151 MHz, CDCl$_3$) of (±)-*syn*-**48**



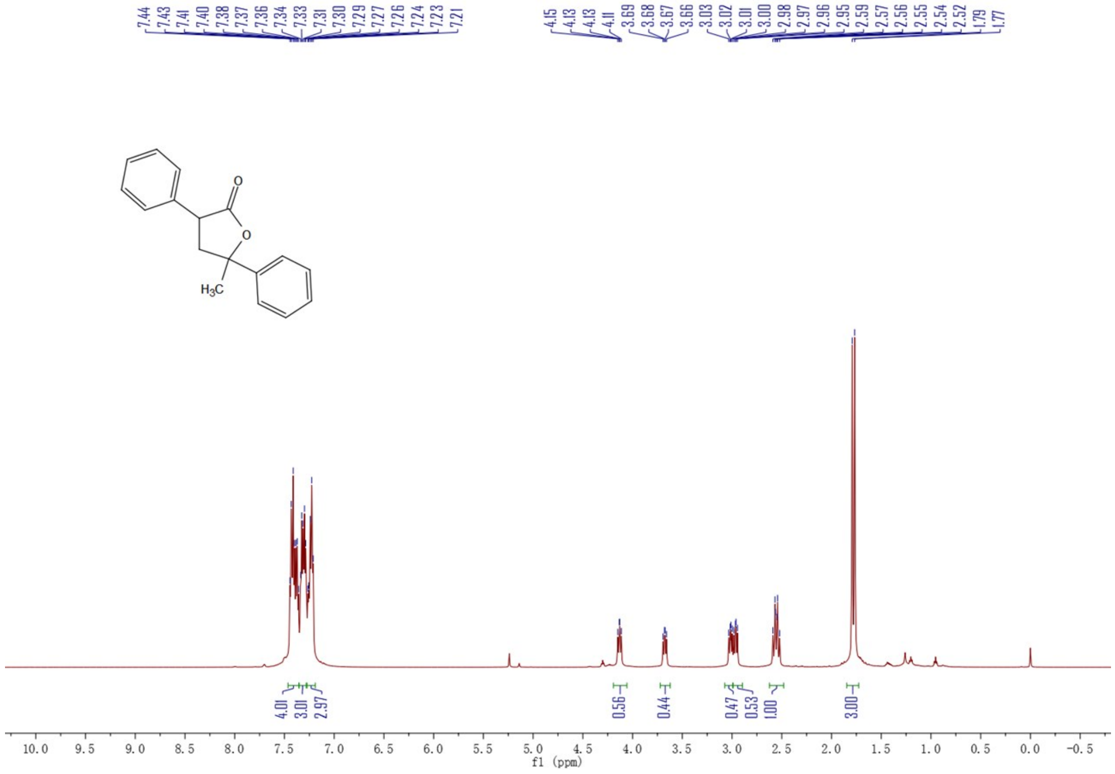
^{1}H NMR (600 MHz, CDCl$_3$) of **50**



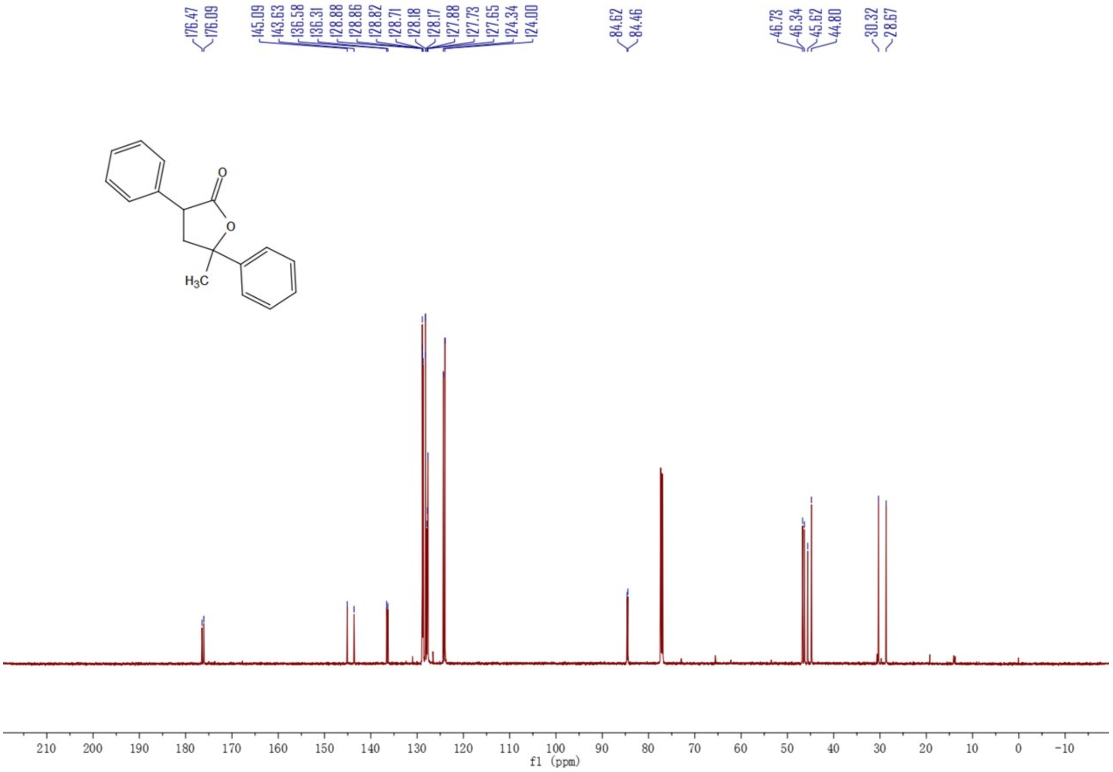
^{13}C NMR (151 MHz, CDCl$_3$) of **50**



^{1}H NMR (600 MHz, CDCl$_3$) of **51**



^{13}C NMR (151 MHz, CDCl$_3$) of **51**



11. References

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