Supporting Information

A novel copper-catalyzed multicomponent reaction for the synthesis of γ-butenolides via the interception of carbonyl ylides with iminium ions

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Table of Contents

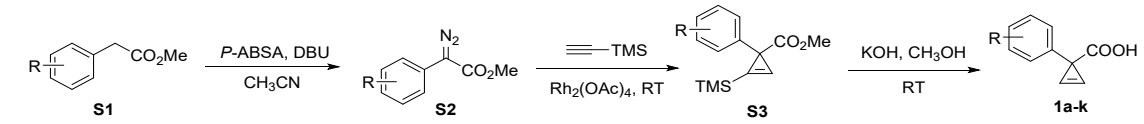
1. General information & materials

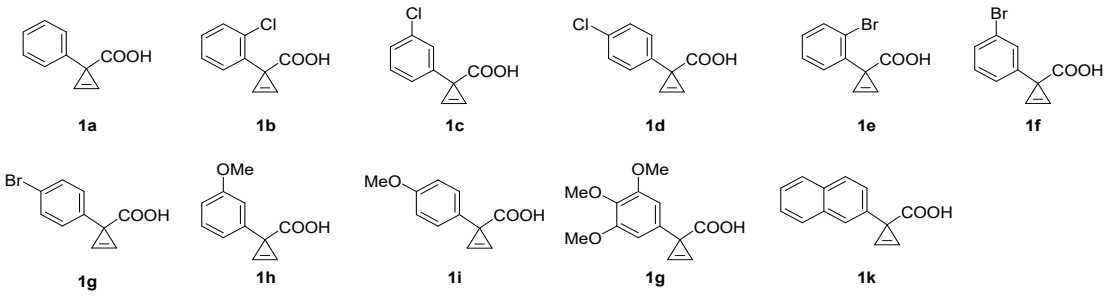
General: All reactions were carried out in oven-dried glassware with magnetic stirring. Melting points were uncorrected. All ^{1}H NMR and ^{13}C NMR spectra were recorded using a Brucker-300 MHz, 400 MHz or 500 MHz spectrometer in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br =broad). High-resolution mass spectrometry (HRMS) data were collected on Waters Micromass Q-TOF micro Synapt High Definition Mass Spectrometer. Single crystal X-ray diffraction data (*anti*-**4a**/ *anti*-**4b** / *anti*-**4x**) were recorded on Bruker-AXS SMART APEX II single crystal X-ray diffractometer. Yields for all compounds were isolated yields for all isomers.

2. Preparation of starting materials

(1) Typical procedure for cyclopropene carboxylic acids

The cyclopropene carboxylic acids **1a-k** were known compounds and prepared by the similar procedure in the literatures.[1-3]





General procedure: Methyl 2-phenylacetate **S1** (1.0 equiv., 0.10 mol), *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.2 equiv., 0.12 mol) and acetonitrile (100 mL) were added to a 250 mL oven-dried flask. The mixture was cooled with an ice-bath and a solution of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (1.5 equiv., 0.15 mol) in acetonitrile (40 mL) was added dropwise over 0.5 h. Then the ice-bath was removed and the mixture was stirred at room temperature (RT) overnight. The reaction was then quenched with saturated aqueous NH_4Cl and the mixture was extracted with diethyl ether (3 × 25 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure (temperature 24 °C). The crude material was purified by diatomite and silica gel through a sand

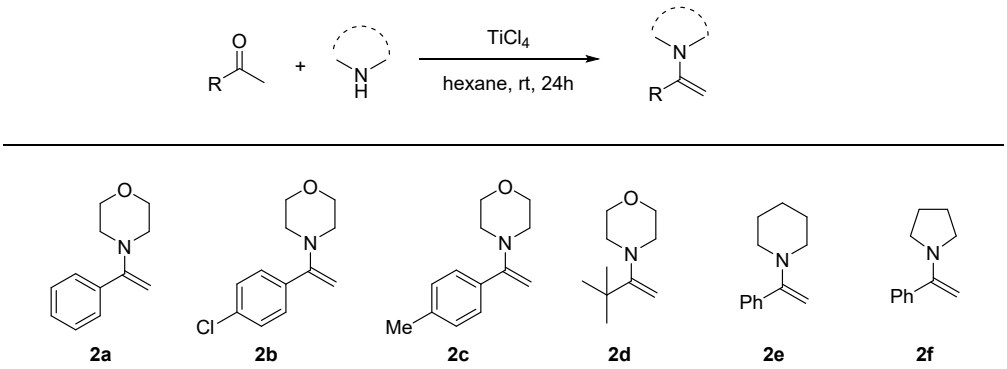
funnel with EtOAc as eluent. Then the filtrate was evaporated and purified by silica gel chromatography (petroleum ether/ethyl acetate=100/1~50/1) to provide **S2**.

A solution of **S2** (1.0 equiv.) in trimethylsilylacetylene (20 mL) was added using syringe pump over 10 h to a stirred suspension of $Rh_2(OAc)_4$ (0.5 mol%) in trimethylsilylacetylene (30 mL) under argon. After the addition was complete, the syringe was washed with anhydrous CH_2Cl_2 (4 mL). The mixture was stirred until the Thin layer chromatography (TLC) shown the reaction was complete. After concentrated under reduced pressure, the crude residue was purified by silica gel chromatography (petroleum ether/ethyl acetate=100/1~50/1) to provide **S3**.

To a clean 250 mL round bottomed flask was added **S3** (1.0 equiv.) and methanol (50 mL). The mixture was cooled in an ice bath and allowed to stir. A solution of 1.5 M aqueous KOH (50mL) was added. The ice bath was removed. After the mixture had stirred overnight at RT, the methanol was removed under reduced pressure. HCl (conc. aq) was added to render the solution acidic (pH =1~2), and the mixture was extracted three times with CH_2Cl_2. The combined organics were dried (Na_2SO_4), filtered, and concentrated. The crude residue was chromatographed on silica gel (petroleum ether/ethyl acetate=10/1~1/1) and recrystallized to provide **1a-k**.

(2) Typical procedure for functionalized enamines

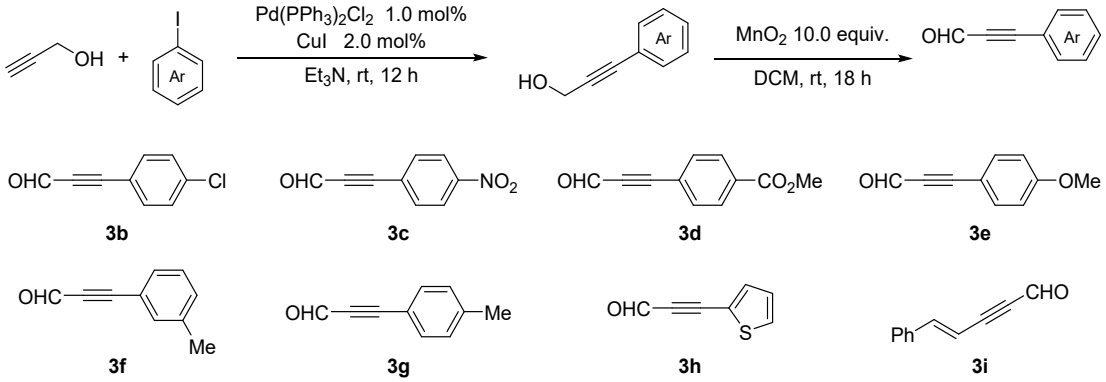
The functionalized enamines **2a-f** were known compounds and prepared by the similar procedure in the literatures.[4,5]



General procedure: To a dried 100-mL round-bottom flask with a magnetic stir bar was added amine (12 mL) and dry hexanes (10 mL), and the solution was cooled in an ice-water bath. Titanium tetrachloride (1.7 mL) was dissolved in hexanes (10 mL) and the solution was added dropwise to the cold amine solution, after which acetophenone (2.5 mL) was added slowly. The reaction mixture was allowed to warm up to room temperature and was stirred for an additional 8 hours. Then the reaction mixture (with solids inside) was filtered and the solvent was removed under reduced pressure. The crude product was further purified by distillation using a Buchi Kugelrohr apparatus. Moreover, enamines **2a-f** were stored protected from light at drying oven.

(3) Typical procedure for alkynaldehydes preparation

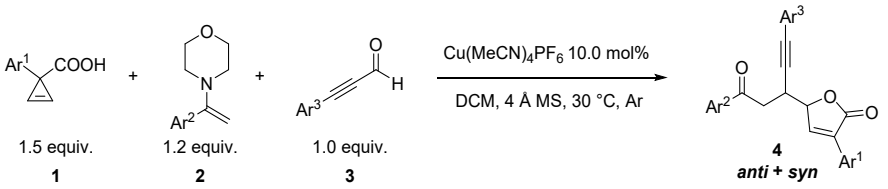
The alkynaldehydes **3b-i** were known compounds. The procedure for the synthesis of alkynaldehydes were adapted from literatures.[6,7]



General procedure: To a solution of iodoarene (1.2 equiv., 9.8 mmol) in trimethylamine (0.34 M, 26 mL) was added $Pd(PPh_3)_2Cl_2$ (1 mol %, 0.9 mmol) and CuI (2 mol %, 0.18 mmol). The reaction was stirred for 5 min before the addition of propargyl alcohol (1.0 equiv., 8.9 mmol). The resulting mixture was stirred for 12 h. Then, the reaction was treated with a saturated $NaHCO_3$ solution. The solution was extracted with ethyl acetate (3 × 20 mL), washed with a saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the product was purified by column chromatography (petroleum ether/ethyl acetate=10/1~2/1).

Manganese (IV) oxide (10 equiv.) was added to a stirred solution of corresponding propargyl alcohol (1.0 equiv.) in DCM (0.25 M). The mixture was stirred at the room temperature for 18 h, then filtered through silica gel and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=10/1~5/1) to afford the desired product.

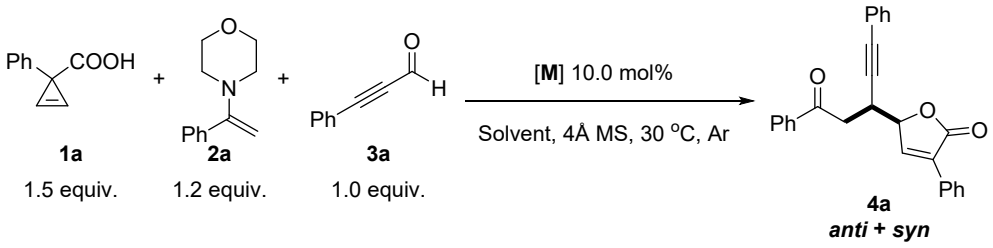
3. General procedure for the three-component reactions



To a 10 mL oven-dried test tube equipped with a stirring bar was added $Cu(MeCN)_4PF_6$ (10.0 mol%), alkynal **3** (0.2 mmol, 1.0 equiv.), 4Å molecular sieve (100 mg) and anhydrous DCM (1.0 mL), which later stirred under argon atmosphere at room temperature. Then the cyclopropene carboxylic acid **1** (0.3 mmol, 1.5 equiv.) and enamine **2** (0.24 mmol, 1.2 equiv.) respectively dissolved in anhydrous DCM (0.75 mL) were introduced to the suspension over 3 h via a syringe pump. After completion of the addition, the stir was continued at room temperature for 2h. Then the mixture went through filtration, hydrolysis, dried by anhydrous Na_2SO_4 and concentrated to give a residue which was subjected to ^1H NMR spectroscopy analysis for the determination of

diastereoselectivity. Purification of the crude products by flash chromatography on silica gel (eluent: EtOAc/ petroleum ether = 1/20~1/5) afforded desired products.

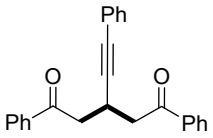
More details for the optimization of three-component reaction



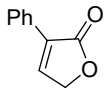
1a 1.5 equiv. **2a** 1.2 equiv. **3a** 1.0 equiv.

4a
anti* + *syn

major side products:



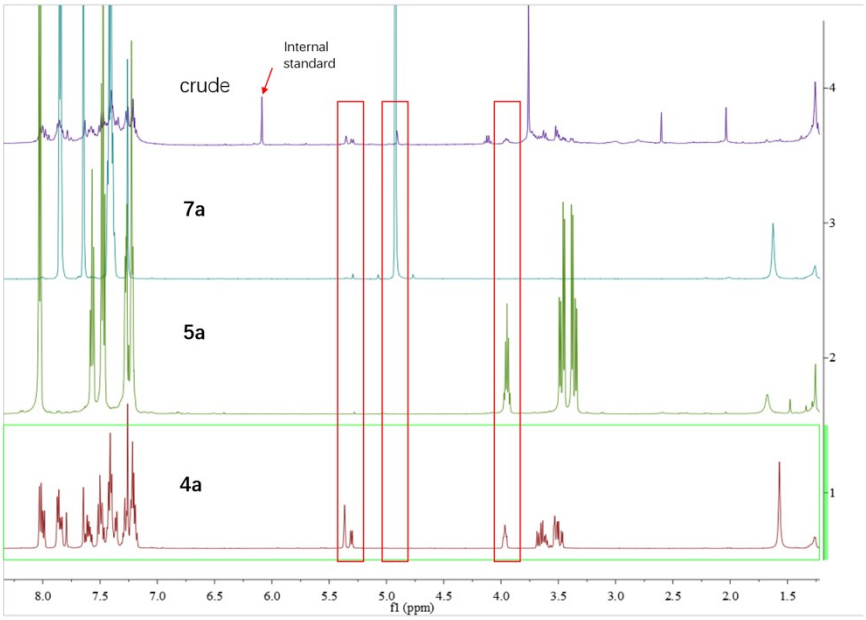
5a



7a

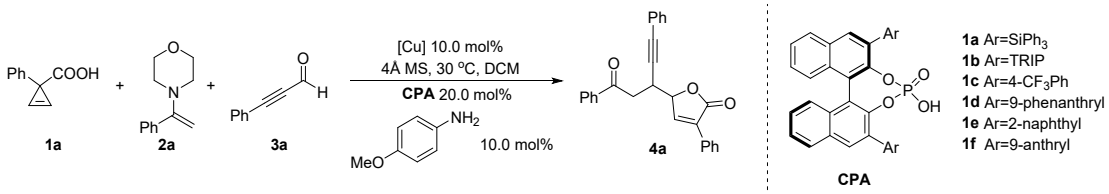
entry	[M]	Solvent	NMR yield of 4a [%]	*anti* : *syn* [b]	NMR yield of 5a [%]	NMR yield of 7a [%]
1	$[PdCl(cinnyl)]_2$	DCM	<5	/	32	Trace
2	JohnPhosAu(I)	DCM	<5	/	50	18
3	AgOTf	DCM	<5	/	31	4
4	$Rh_2(OAc)_4$	DCM	15	56:44	70	7
5	$Rh_2(esp)_2$	DCM	34	58:42	57	36
6	$Cu(OTf)_2$	DCM	44	47:53	51	5
7	$CuBr_2$	DCM	40	52:48	40	3
8	CuI	DCM	31	53:47	51	3
9	CuTC	DCM	38	40:60	31	5
10	$Cu(MeCN)_4BF_4$	DCM	19	52:48	40	43
11	$Cu(MeCN)_4PF_6$	DCM	70(65 [c])	55:45	30	Trace
12	$Cu(MeCN)_4PF_6$	DCE	52	52:48	37	Trace
13	$Cu(MeCN)_4PF_6$	PhCl	43	52:48	46	Trace
14	$Cu(MeCN)_4PF_6$	EA	23	53:47	53	32
15	$Cu(MeCN)_4PF_6$	MTBE	21	48:52	52	11
16[d]	$Cu(MeCN)_4PF_6$	DCM	41	53:47	40	13

[a] Reaction Conditions: 0.1 mmol scale, **1a**/**2a**/**3a**/**[M]** = 1.5/1.2/1.0/0.1. **1a** and **2a** were added to the system over 3h via a syringe pump respectively. Yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b] Determined by crude ^{1}H NMR. [c] Isolated yield. [d] Reaction was performed at -20 °C.



More details for the asymmetric attempts for the three-component reaction

(1) Cooperative catalysis

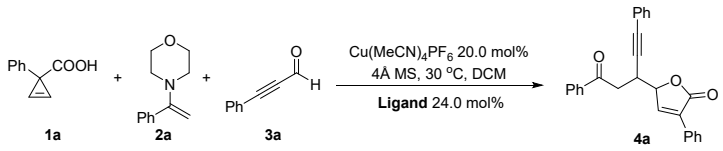


entry	[Cu]	CPA	Yield%	*dr*	*ee* %
1	$Cu(MeCN)_4PF_6$	**1a**	50	1:1	0/0
2*	$Cu(MeCN)_4PF_6$	**1a**	34	1:1	0/0
3	CuOTf	**1a**	47	1:1	0/0
4	CuCl	**1a**	38	1:1	0/0
5	CuOAc	**1a**	15	2:1	0/0
6	CuO	**1a**	<5	/	/
7	$Cu(MeCN)_4PF_6$	**1b**	<5	/	/
8	$Cu(MeCN)_4PF_6$	**1c**	46	1:1	0/0
9	$Cu(MeCN)_4PF_6$	**1d**	54	1:1	0/0
10	$Cu(MeCN)_4PF_6$	**1e**	54	1:1	0/0
11	$Cu(MeCN)_4PF_6$	**1f**	15	2:1	0/0

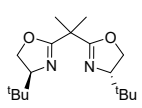
[a] Reaction Conditions: 0.05 mmol scale, **1a**/**2a**/**3a**/**[Cu]**/**CPA**/**Amine** = 1.5/1.2/1.0/0.1/0.2/0.1. **1a**

and **2a** were added to the system over 3h via a syringe pump respectively. Yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. *dr* was determined by crude ^{1}H NMR. *ee* was determined by HPLC using a Chiralpak IC column.

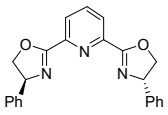
(2) Organo-catalysis



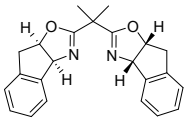
Ligand



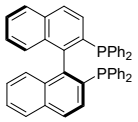
L1



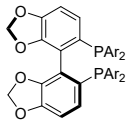
L2



L3



L4

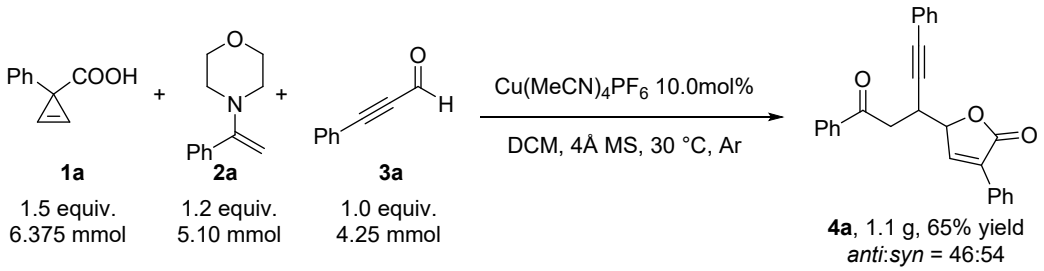


L5 Ar=Ph
L6 Ar=3,5-*t*Bu-4-MeOC$_6$H$_2$

entry	Ligand	Yield %	*dr*	*ee* %
1	**L1**	43	1:1	0/0
2	**L2**	51	1:1	0/0
3	**L3**	28	5:1	0/0
4	**L4**	59	1:1	0/0
5	**L5**	27	2:1	0/0
6	**L6**	20	2:1	0/0

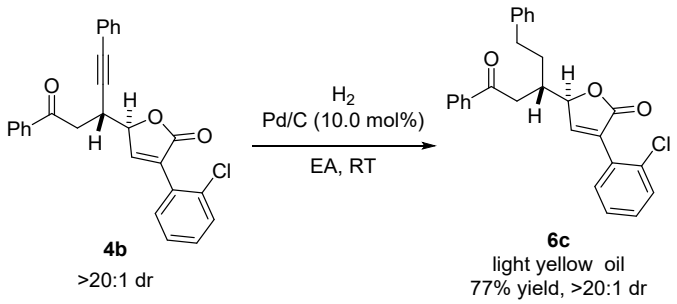
[a] Reaction Conditions: 0.05 mmol scale, **1a**/**2a**/**3a**/**[Cu]**/**Ligand** = 1.5/1.2/1.0/0.2/0.24. **1a** and **2a** were added to the system over 3h via a syringe pump respectively. Yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. *dr* was determined by crude ^{1}H NMR. *ee* was determined by HPLC using a Chiralpak IC column.

General Procedure for the Scale Up



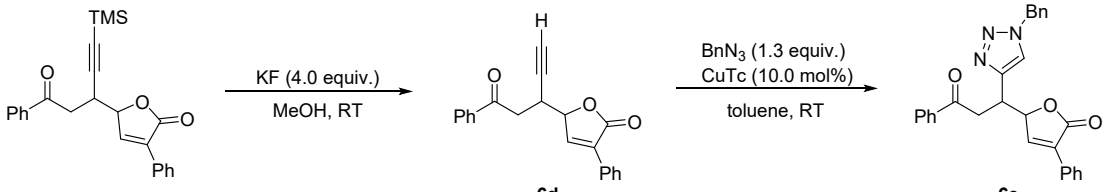
To a 100 mL oven-dried test tube equipped with a stirring bar was added $Cu(MeCN)_4PF_6$ (157.3 mg, 10.0 mol%), alkynal **3a** (552.5 mg, 4.25 mmol, 1.0 equiv.), 4Å molecular sieve (1.0 g) and anhydrous DCM (25.0 mL), which later stirred under argon atmosphere at room temperature. Then the cyclopropene carboxylic acid **1a** (1.02 g, 6.375 mmol, 1.5 equiv.) and enamine **2a** (963.9 mg, 5.10 mmol, 1.2 equiv.) respectively dissolved in anhydrous DCM (9 mL) were introduced to the suspension over 3 h via a syringe pump. After completion of the addition, the stir was continued at room temperature for 2h. Then the mixture went through filtration, hydrolysis, dried by anhydrous Na_2SO_4 and concentrated to give a residue which was subjected to ^1H NMR spectroscopy analysis for the determination of diastereoselectivity. Purification of the crude products by flash chromatography on silica gel (eluent: EtOAc/ petroleum ether = 1/20~1/5) afforded 1.1g of **4a** in 65% yield with *anti*/*syn* = 46:54.

Procedure for synthesis of 6c



To a 25-mL hydrogenation reactor containing a magnetic stirring bar, **4b** (85.2 mg, 0.2 mmol) in 5 mL of EA, was added wet 10% Pd/C (5 mg, 10.0 mol%). The heterogeneous mixture was placed under 40-60 psi H_2 atmosphere and stirred overnight at room temperature. After the hydrogenolysis was complete, as indicated by TLC analysis. The mixture was filtered through a pad of Celite to remove Pd/C, and the combined filtrate was concentrated under vacuum. The residue was purified by flash chromatography (eluent: EtOAc/ petroleum ether = 1/20~1/10) to give 66.2 mg **6c** in 77% yield as light yellow oil.

Procedure for synthesis of 6d, 6e[8]



Synthesis of 6d: To a flame-dried 10-mL test tube charged with a magnetic stirring bar, **4w** (*anti* : *syn* = 68:32, 77.6 mg, 0.20 mmol) and anhydrous KF (46.4 mg, 0.80 mmol) were dissolved in 5.0 mL dry MeOH at room temperature overnight. The reaction was then slowly quenched with saturated aqueous NH_4Cl and the mixture was extracted with EtOAc (3 x 10 mL). The organic layers were washed with brine. After drying over anhydrous Na_2SO_4 and concentration in vacuo, the crude product was purified by flash chromatography on silica gel (30:1 to 10:1 gradient of petroleum : ethyl acetate as eluents) to afford the pure product **6d** in 90% yield (56.9 mg, *anti* : *syn* = 68:32).

Synthesis of 6e: To a 25 mL flask charged with 10.0 mol% CuTC, **6d** (31.6 mg, 0.1 mmol) in 2.0 mL of dry toluene under an argon atmosphere was stirred at room temperature. BnN_3 (17.3 mg, 0.13 mmol) in dry toluene (1.0 mL) was added slowly into the aboved mixture over 10.0 minutes and the reaction mixture was stirred for another 1.0 hour. After completion of the reaction, the mixture was concentrated in vacuo and the crude product was purified by flash chromatography on silica gel (eluent: PE/EA = 10:1 ~ 3:1, v/v) to afford the pure product **6e** in 84% yield (37.7 mg, *anti* : *syn* = 68:32).

4. References

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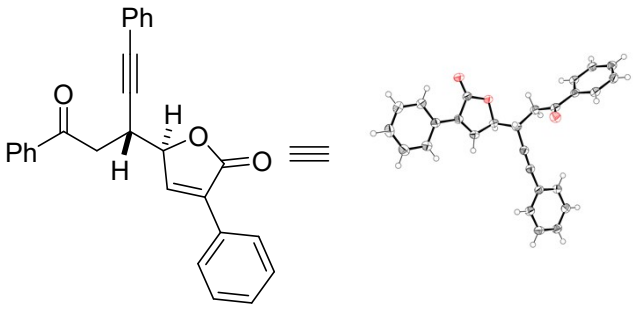
5. Single Crystal X-ray Diffraction Data

Single crystal X-ray diffraction data of *anti*-4a (CCDC NO.: 2101905)



***anti* - 4a** CCDC **2101905**

```
Bond precision:  C-C = 0.0024 A          Wavelength=1.54184

Cell:            a=23.3680(5)     b=13.3744(3)       c=12.7991(3)
                 alpha=90         beta=95.115(2)     gamma=90
Temperature:     100 K

                 Calculated                Reported
Volume           3984.21(16)               3984.21(16)
Space group      C 2/c                     C 1 2/c 1
Hall group       -C 2yc                    -C 2yc
Moiety formula   C27 H20 O3                C27 H20 O3
Sum formula      C27 H20 O3                C27 H20 O3
Mr               392.43                    392.43
Dx,g cm-3        1.309                     1.308
Z                8                         8
Mu (mm-1)        0.673                     0.673
F000             1648.0                    1648.0
F000'            1652.90
h,k,lmax         29,16,16                  29,16,15
Nref             4210                      4057
Tmin,Tmax        0.949,0.967               0.957,1.000
Tmin'            0.929

Correction method= # Reported T Limits: Tmin=0.957 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.964          Theta(max)= 76.816

R(reflections)= 0.0452( 3074)     wR2(reflections)= 0.1259( 4057)

S = 1.045                 Npar= 272
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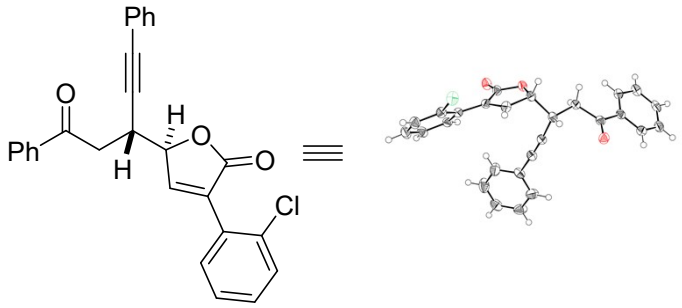
Single crystal X-ray diffraction data of *anti*-4b (CCDC NO.: 2101411)



***anti* - 4b** CCDC **2101411**

Bond precision: C-C = 0.0035 A Wavelength=1.54184

Cell: a=9.4913(2) b=11.5055(2) c=19.8764(4)
alpha=90 beta=95.697(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2159.83(7)	2159.82(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C27 H19 Cl O3	C27 H19 Cl O3
Sum formula	C27 H19 Cl O3	C27 H19 Cl O3
Mr	426.87	426.87
Dx,g cm-3	1.313	1.313
Z	4	4
Mu (mm-1)	1.776	1.776
F000	888.0	888.0
F000'	891.92	
h,k,lmax	11,14,25	11,14,25
Nref	4510	4305
Tmin,Tmax	0.686,0.701	0.779,1.000
Tmin'	0.559	

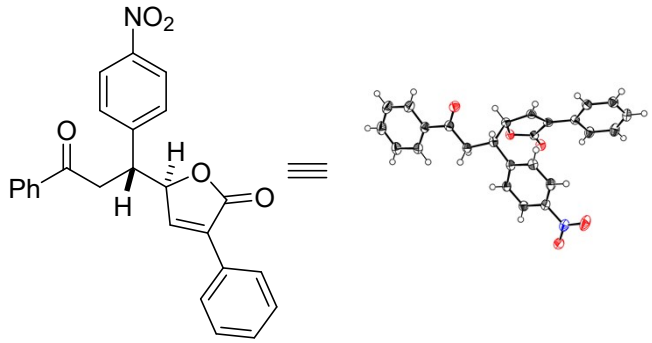
Correction method= # Reported T Limits: Tmin=0.779 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.955 Theta(max)= 76.100

R(reflections)= 0.0635(3698) wR2(reflections)= 0.1844(4305)

S = 1.051 Npar= 280

Single crystal X-ray diffraction data of *anti*-4x (CCDC NO.: 2104320)



***anti* - 4x** CCDC **2104320**

```
Bond precision:  C-C = 0.0022 A          Wavelength=1.54184

Cell:          a=7.6080(3)        b=10.7491(3)      c=13.6882(4)
               alpha=104.255(2)   beta=103.185(3)   gamma=102.624(3)
Temperature:   100 K
```

	Calculated	Reported
Volume	1010.59(6)	1010.58(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C25 H19 N O5	C25 H19 N O5
Sum formula	C25 H19 N O5	C25 H19 N O5
Mr	413.41	413.41
Dx,g cm-3	1.359	1.359
Z	2	2
Mu (mm-1)	0.782	0.782
F000	432.0	432.0
F000'	433.40	
h,k,lmax	9,13,17	9,13,16
Nref	4233	4008
Tmin,Tmax	0.869,0.925	0.902,1.000
Tmin'	0.822	

```
Correction method= # Reported T Limits: Tmin=0.902 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.947          Theta(max)= 76.086

R(reflections)= 0.0412( 3357)     wR2(reflections)= 0.1224( 4008)

S = 1.099                 Npar= 281
```

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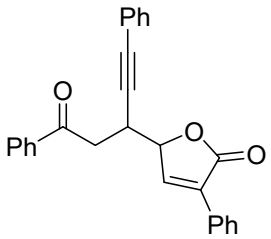
6. Analytical data of Products

5-(5-Oxo-1,5-diphenylpent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4a)



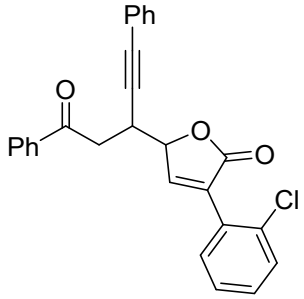
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (51.0 mg, 65%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 55:45 as determined by crude ^{1}H spectroscopy, but 63:37 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.04 – 7.97 (m, 4H), 7.89 – 7.82 (m, 4H), 7.80 – 7.78 (m, 1H), 7.66 – 7.64 (m, 1H), 7.63 – 7.56 (m, 2H), 7.53 – 7.46 (m, 4H), 7.45 – 7.38 (m, 6H), 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.17 (m, 6H), 5.38 – 5.34 (m, 1H), 5.33 – 5.28 (m, 1H), 3.99 – 3.94 (m, 1H), 3.69 – 3.59 (m, 2H), 3.55 – 3.45 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.7, 171.6, 171.1, 146.5, 146.4, 136.6, 136.4, 133.8, 133.7, 133.2, 132.8, 131.9, 131.8, 129.7, 129.6, 129.5, 129.3, 128.91, 128.87, 128.82, 128.80, 128.6, 128.38, 128.38, 128.32, 128.31, 128.3, 127.32, 127.27, 122.6, 122.5, 86.5, 85.6, 85.1, 84.7, 80.8, 79.8, 40.2, 40.1, 33.1, 31.9.

HRMS: calcd for $C_{27}H_{21}O_3$ $[M+H]^+$: 393.1485; found: 393.1493.

3-(2-Chlorophenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4b)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1b** (58.2 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (60.0 mg, 70%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 73:27 as determined by crude ^{1}H spectroscopy, but 62:38 after recrystallization.

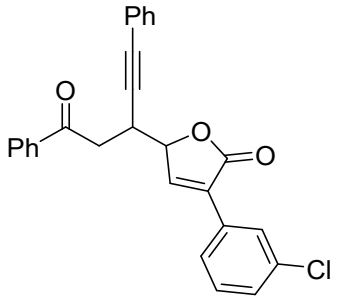
^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.06 – 7.99 (m, 3H), 7.97 – 7.94 (m, 1H), 7.87 – 7.82 (m, 2H), 7.69 – 7.66 (m, 1H), 7.64 – 7.57 (m, 4H), 7.53 – 7.43 (m, 5H), 7.37 – 7.20 (m, 14H), 5.45 (dd, J = 2.7, 1.6 Hz, 1H), 5.40 (dd, J = 7.5, 1.5 Hz, 1H), 5.02 – 4.99 (m, 1H), 4.03 – 3.97 (m, 1H), 3.74 – 3.63 (m, 2H), 3.56 – 3.48 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.5, 171.5, 171.1, 151.7, 149.9, 136.6,

136.4, 133.9, 133.7, 133.41, 133.35, 131.90, 131.85, 131.4, 131.2, 131.0, 130.92, 130.86, 130.4, 130.32, 130.29, 130.2, 128.93, 128.90, 128.5, 128.44, 128.36, 128.32, 128.32, 128.31,127.02, 126.99, 126.97, 122.6, 86.3, 85.6, 85.0, 84.8, 81.3, 80.4, 70.1, 40.14, 40.09, 32.8, 31.7.
HRMS: calcd for $C_{27}H_{20}O_3Cl$ $[M+H]^+$: 427.1095; found: 427.1085.

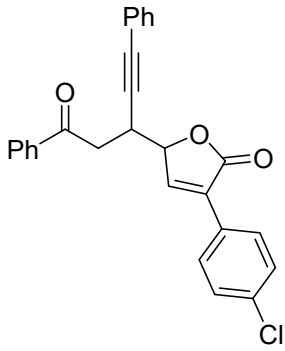
After recrystallization, the major *anti* diastereomer can be serparared.
^{1}H NMR (500 MHz, $CDCl_3$) δ: ***anti*:** 8.05 – 8.01 (m, 2H), 7.84 – 7.81 (m, 1H), 7.63 – 7.58 (m, 2H), 7.52 – 7.45 (m, 3H), 7.32 – 7.28 (m, 4H), 7.26 – 7.21 (m, 3H), 5.47 – 5.43 (m, 1H), 4.03 – 3.98 (m, 1H), 3.71 – 3.64 (m, 1H), 3.55 – 3.49 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ: ***anti*:** 197.1, 171.4, 151.6, 136.3, 133.8, 133.3, 131.7, 131.3, 130.9, 130.21, 130.19, 128.8, 128.4, 128.30, 128.30, 128.2, 126.9, 122.5, 85.5, 84.9, 80.3, 40.0, 31.6.

3-(3-Chlorophenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4c)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1c** (58.2 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (60.5 mg, 71%) as a brownish purble solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 60:40 as determined by crude ^{1}H spectroscopy, but 58:42 after recrystallization.
^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.04 – 7.97 (m, 4H), 7.89 – 7.86 (m, 1H), 7.84 – 7.80 (m, 2H), 7.79 – 7.73 (m, 2H), 7.69 – 7.66 (m, 1H), 7.64 – 7.56 (m, 2H), 7.53 – 7.46 (m, 4H), 7.39 – 7.32 (m, 5H), 7.31 – 7.27 (m, 3H), 7.25 – 7.18 (m, 6H), 5.40 – 5.37 (m, 1H), 5.33 (dd, J = 7.8, 1.7 Hz, 1H), 3.98 – 3.94 (m, 1H), 3.70 – 3.61 (m, 2H), 3.57 – 3.46 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.1, 196.6, 171.1, 170.6, 147.6, 147.5, 136.5, 136.3, 134.84, 134.81, 133.9, 133.7, 132.0, 131.9, 131.7, 131.6, 131.2, 130.9, 130.10, 130.07, 129.74, 129.67, 128.91, 128.88, 128.6, 128.5, 128.39, 128.35, 128.30, 128.25, 127.34, 127.29, 125.41, 125.38, 122.44, 122.37, 86.2, 85.8, 84.87, 84.85, 80.8, 79.9, 40.09, 40.07, 33.0, 31.9.
HRMS: calcd for $C_{27}H_{20}O_3Cl$ $[M+H]^+$: 427.1095; found: 427.1083.

3-(4-Chlorophenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4d)



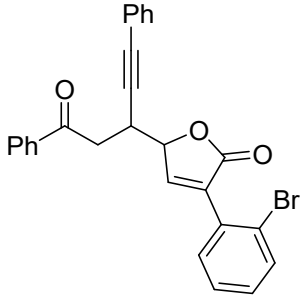
According to the general procedure, the reaction of cyclopropene carboxylic acid **1d** (58.2 mg, 0.3 mmol, 1.5 equiv.), enamine **2** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (47.8 mg, 56%) as a brownish purble solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 52:48 as determined by crude ^{1}H spectroscopy, but 57:43 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.03 – 7.96 (m, 4H), 7.85 – 7.77 (m, 5H), 7.65 – 7.56 (m, 3H), 7.52 – 7.45 (m, 4H), 7.40 – 7.33 (m, 5H), 7.31 – 7.26 (m, 3H), 7.25 – 7.17 (m, 6H), 5.38 – 5.34 (m, 1H), 5.31 (dd, J = 7.8, 1.5 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.70 – 3.59 (m, 2H), 3.56 – 3.45 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.6, 171.3, 170.8, 146.7, 146.6, 136.6, 136.4, 135.8, 135.7, 133.9, 133.7, 132.1, 131.9, 131.70, 131.65, 129.08, 129.06, 128.93, 128.89, 128.62, 128.60, 128.56, 128.5, 128.40, 128.35, 128.31, 128.26, 127.9, 127.7, 122.5, 122.4, 86.3, 85.7, 84.9, 84.8, 80.8, 79.8, 40.13, 40.13, 33.1, 32.0.

HRMS: calcd for $C_{27}H_{20}O_3Cl$ $[M+H]^+$: 427.1095; found: 427.1079.

3-(2-Bromophenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4e)



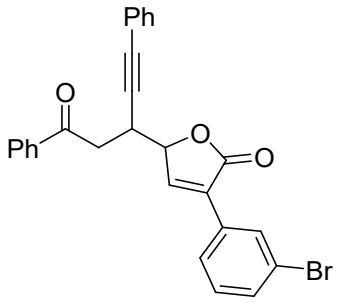
According to the general procedure, the reaction of cyclopropene carboxylic acid **1e** (71.4 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (61.1 mg, 65%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 75:25 as determined by crude ^{1}H spectroscopy, but 92:8 after recrystallization.

^{1}H NMR (400 MHz, $CDCl_3$): (major) δ 8.07 – 8.00 (m, 2H), 7.82 – 7.77 (m, 1H), 7.66 – 7.58 (m, 2H), 7.52 – 7.46 (m, 3H), 7.35 – 7.29 (m, 3H), 7.26 – 7.19 (m, 4H), 5.48 – 5.41 (m, 1H), 4.05 – 3.95 (m, 1H), 3.67 (dd, J = 17.9, 7.8 Hz, 1H), 3.52 (dd, J = 17.9, 5.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): (major) δ 197.1, 171.3, 151.7 136.4, 133.8, 133.5, 133.4, 131.9, 131.1, 130.6, 130.5, 128.9, 128.4, 128.32, 128.30, 127.5, 123.0, 122.6, 85.5, 85.1, 80.3, 40.1, 31.6.

HRMS: calcd for $C_{27}H_{20}O_3Br$ $[M+H]^+$: 471.0590; found: 471.0593.

3-(3-Bromophenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4f)



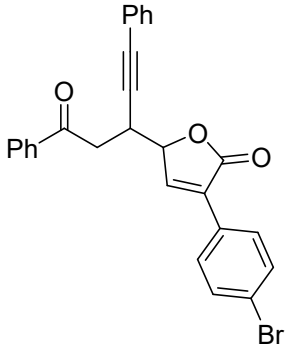
According to the general procedure, the reaction of cyclopropene carboxylic acid **1f** (71.4 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (56.4 mg, 60%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 60:40 as determined by crude ^{1}H spectroscopy, but 61:39 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.04 – 8.00 (m, 4H), 8.00 – 7.94 (m, 2H), 7.84 – 7.78 (m, 3H), 7.69 – 7.66 (m, 1H), 7.64 – 7.56 (m, 2H), 7.54 – 7.45 (m, 6H), 7.38 – 7.34 (m, 2H), 7.31 – 7.27 (m, 5H), 7.25 – 7.19 (m, 5H), 5.38 (dd, *J* = 2.6, 1.6 Hz, 1H), 5.33 (dd, *J* = 7.8, 1.5 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.74 – 3.60 (m, 2H), 3.57 – 3.45 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.6, 171.0, 170.6, 147.6, 147.5, 136.5, 136.4, 133.9, 133.7, 132.7, 132.6, 131.94, 131.90, 131.7, 131.5, 131.4, 131.2, 130.4, 130.3, 130.23, 130.17, 128.94, 128.90, 128.6, 128.5, 128.41, 128.37, 128.32, 128.27, 125.89, 125.86, 122.94, 122.91, 122.5, 122.4, 86.2, 85.8, 84.86, 84.86, 80.8, 79.9, 40.1, 33.0, 31.9, 29.8.

HRMS: calcd for $C_{27}H_{20}O_3Br$ $[M+H]^+$: 471.0590; found: 471.0613.

3-(4-Bromophenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4g)



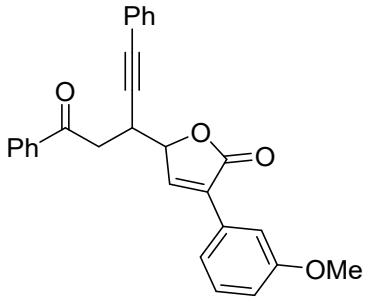
According to the general procedure, the reaction of cyclopropene carboxylic acid **1g** (71.4 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (58.3 mg, 62%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 59:41 as determined by crude ^{1}H spectroscopy, but 68:32 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.97 (m, 4H), 7.83 – 7.80 (m, 1H), 7.79 – 7.70 (m, 4H), 7.67 – 7.65 (m, 1H), 7.64 – 7.57 (m, 3H), 7.57 – 7.45 (m, 6H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.16 (m, 6H), 5.38 – 5.34 (m, 1H), 5.30 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.70 – 3.59 (m, 2H), 3.54 – 3.45 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.6, 171.2, 170.8, 146.8, 146.7, 136.6, 136.4, 133.9, 133.7, 132.2, 132.1, 132.0, 131.9, 131.71, 131.71, 128.94, 128.91, 128.84, 128.80, 128.6, 128.5, 128.42, 128.37, 128.37, 128.32, 128.27, 128.2, 124.1, 124.0, 122.5, 122.4, 86.3, 85.7, 84.9, 84.8, 80.8, 79.8, 40.13, 40.13, 33.0, 31.9.

HRMS: calcd for $C_{27}H_{20}O_3Br$ $[M+H]^+$: 471.0590; found: 471.0567.

3-(3-Methoxyphenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4h)



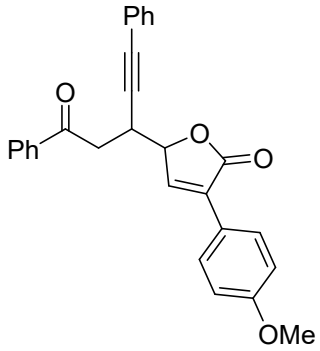
According to the general procedure, the reaction of cyclopropene carboxylic acid **1h** (57.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (47.3 mg, 56%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 62:38 as determined by crude ^{1}H spectroscopy, but 64:36 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.04 – 7.96 (m, 4H), 7.79 – 7.77 (m, 1H), 7.65 – 7.55 (m, 4H), 7.52 – 7.38 (m, 8H), 7.37 – 7.16 (m, 11H), 6.96 – 6.91 (m, 2H), 5.37 – 5.33 (m, 1H), 5.29 (dd, J = 7.8, 1.4 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.85 – 3.78 (m, 6H), 3.68 – 3.59 (m, 2H), 3.56 – 3.44 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.6, 171.5, 171.0, 159.9, 159.8, 146.7, 146.6, 136.6, 136.4, 133.8, 133.7, 133.1, 132.6, 131.9, 131.8, 130.8, 130.6, 129.84, 129.82, 128.90, 128.86, 128.6, 128.39, 128.38, 128.31, 128.30, 128.27, 122.4, 122.5, 119.7, 119.7, 115.6, 115.6, 112.54, 112.53, 86.4, 85.6, 85.1, 84.7, 80.7, 79.7, 55.5, 55.4, 40.2, 40.1, 33.1, 31.9.

HRMS: calcd for $C_{28}H_{23}O_4$ $[M+H]^+$: 423.1591; found: 423.1594.

3-(4-Methoxyphenyl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4i)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1f** (57.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (52.3 mg, 62%) as a brownish purble solid consisting of two

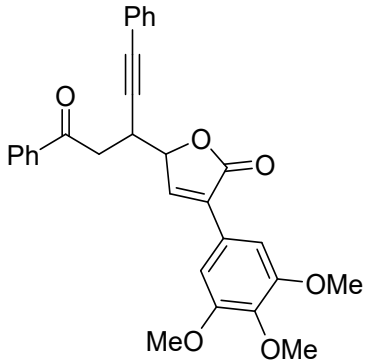
diastereomers. The *anti*/*syn* of diastereomers was 50:50 as determined by crude ^{1}H spectroscopy, but 65:35 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.97 (m, 4H), 7.88 – 7.80 (m, 4H), 7.68 – 7.65 (m, 1H), 7.64 – 7.56 (m, 2H), 7.54 – 7.45 (m, 5H), 7.38 – 7.33 (m, 2H), 7.30 – 7.26 (m, 3H), 7.24 – 7.17 (m, 6H), 6.97 – 6.90 (m, 3H), 5.36 – 5.31 (m, 1H), 5.27 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.84 (m, 6H), 3.66 – 3.56 (m, 2H), 3.56 – 3.44 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.7, 171.9, 171.4, 160.72, 160.66, 144.03, 143.97, 136.6, 136.4, 133.8, 133.6, 132.5, 132.1, 131.9, 131.7, 128.9, 128.8, 128.69, 128.67, 128.5, 128.4, 128.33, 128.30, 128.28, 128.25, 122.60, 122.55, 122.1, 121.9, 114.20, 114.17, 86.6, 85.5, 85.3, 84.6, 80.7, 79.7, 55.43, 55.43, 40.2, 40.0, 33.2, 32.0.

HRMS: calcd for $C_{28}H_{23}O_4$ $[M+H]^+$: 423.1591; found: 423.1585.

5-(5-Oxo-1,5-diphenylpent-1-yn-3-yl)-3-(3,4,5-trimethoxyphenyl)furan-2(5*H*)-one (4j)



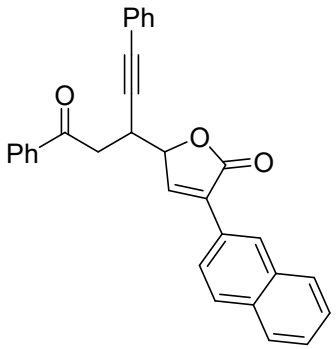
According to the general procedure, the reaction of cyclopropene carboxylic acid **1g** (75.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (57.8 mg, 60%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 46:54 as determined by crude ^{1}H spectroscopy, but 60:40 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.06 – 7.96 (m, 4H), 7.71 – 7.67 (m, 2H), 7.64 – 7.55 (m, 3H), 7.54 – 7.46 (m, 4H), 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 7.12 – 7.06 (m, 4H), 5.38 – 5.33 (m, 1H), 5.33 – 5.28 (m, 1H), 3.98 – 3.93 (m, 1H), 3.91 – 3.85 (m, 18H), 3.75 – 3.62 (m, 2H), 3.57 – 3.46 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.7, 171.5, 171.1, 153.46, 153.45, 145.8, 145.7, 139.5, 139.4, 136.6, 136.4, 133.9, 133.7, 133.0, 132.4, 131.9, 131.8, 128.92, 128.89, 128.6, 128.5, 128.4, 128.32, 128.27, 125.1, 124.8, 122.6, 122.5, 104.7, 104.6, 86.5, 85.7, 85.2, 84.7, 80.6, 79.6, 61.05, 61.05, 56.4, 56.3, 40.10, 40.09, 33.0, 32.0, 31.7.

HRMS: calcd for $C_{30}H_{27}O_6$ $[M+H]^+$: 483.1802; found: 483.1791.

3-(Naphthalen-2-yl)-5-(5-oxo-1,5-diphenylpent-1-yn-3-yl)furan-2(5*H*)-one (4k)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1k** (63.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (47.7 mg, 54%) as a brownish purble solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 56:44 as determined by crude ^{1}H spectroscopy, but 59:41 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.62 – 8.54 (m, 2H), 8.06 – 7.97 (m, 4H), 7.94 – 7.73 (m, 9H), 7.64 – 7.55 (m, 3H), 7.53 – 7.44 (m, 7H), 7.39 – 7.35 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.12 (m, 6H), 5.44 – 5.39 (m, 1H), 5.38 – 5.33 (m, 1H), 4.03 – 3.97 (m, 1H), 3.72 – 3.64 (m, 2H), 3.61 – 3.48 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.7, 171.6, 171.2, 146.40, 146.34, 136.6, 136.4, 133.8, 133.68, 133.67, 133.6, 133.3, 133.2, 132.9, 132.5, 131.9, 131.7, 130.0, 129.0, 128.90, 128.86, 128.6, 128.54, 128.52, 128.38, 128.37, 128.32, 128.30, 128.27, 127.76, 127.76, 127.19, 127.15, 127.14, 127.10, 126.70, 126.69, 126.67, 126.5, 124.4, 124.3, 122.6, 122.5, 86.5, 85.6, 85.1, 84.8, 80.8, 79.9, 40.2, 40.1, 33.1, 32.0.

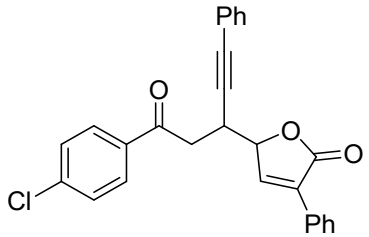
HRMS: calcd for $C_{31}H_{23}O_3$ $[M+H]^+$: 443.1642; found: 443.1623.

After recrystallization, the major *anti* diastereomer can be serparared.

^{1}H NMR (500 MHz, $CDCl_3$) δ: ***anti***: 8.63 – 8.58 (m, 1H), 8.07 – 8.00 (m, 2H), 7.95 – 7.80 (m, 4H), 7.79 – 7.74 (m, 1H), 7.65 – 7.59 (m, 1H), 7.55 – 7.46 (m, 4H), 7.25 – 7.12 (m, 5H), 5.45 – 5.38 (m, 1H), 4.04 – 3.96 (m, 1H), 3.69 (dd, *J* = 17.8, 8.0 Hz, 1H), 3.51 (dd, *J* = 17.9, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ: ***anti***: 197.3, 171.7, 146.3, 136.5, 133.9, 133.7, 133.3, 133.0, 131.8, 129.0, 128.9, 128.6, 128.40, 128.36, 128.3, 127.8, 127.2, 127.1, 126.72, 126.70, 124.4, 122.5, 85.7, 85.1, 79.9, 40.1, 32.0.

5-(5-(4-Chlorophenyl)-5-oxo-1-phenylpent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4l)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2b** (51.1 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (56.8 mg, 60%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 69:31 as determined by crude ^{1}H spectroscopy,

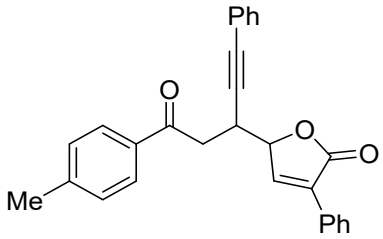
but 84:16 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 7.98 – 7.91 (m, 4H), 7.88 – 7.82 (m, 4H), 7.80 – 7.77 (m, 2H), 7.65 – 7.62 (m, 2H), 7.49 – 7.45 (m, 3H), 7.44 – 7.39 (m, 5H), 7.37 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.16 (m, 6H), 5.36 – 5.33 (m, 1H), 5.28 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.63 – 3.52 (m, 2H), 3.51 – 3.41 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 196.0, 195.5, 171.5, 171.0, 146.4, 146.2, 140.4, 140.2, 134.9, 134.7, 133.3, 132.8, 131.9, 131.8, 129.74, 129.74, 129.69, 129.67, 129.47, 129.47, 129.3, 129.2, 128.84, 128.84, 128.7, 128.5, 128.4, 128.3, 127.32, 127.27, 122.5, 122.4, 86.3, 85.7, 84.9, 84.8, 80.7, 79.7, 40.2, 40.1, 33.2, 31.9.

HRMS: calcd for $C_{27}H_{20}O_3Cl$ $[M+H]^+$: 427.1095; found: 427.1113.

5-(5-Oxo-1-phenyl-5-(p-tolyl)pent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4m)



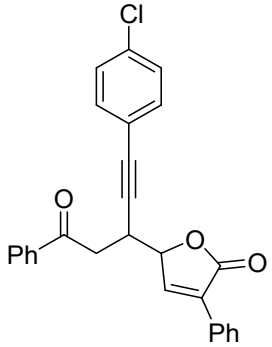
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2c** (48.7 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3a** (26.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (52.9 mg, 65%) as a brownish purble solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 52:48 as determined by crude ^{1}H spectroscopy, but 65:35 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 7.94 – 7.81 (m, 8H), 7.79 – 7.76 (m, 1H), 7.65 – 7.62 (m, 1H), 7.45 – 7.37 (m, 6H), 7.37 – 7.33 (m, 2H), 7.31 – 7.26 (m, 6H), 7.24 – 7.16 (m, 6H), 5.38 – 5.33 (m, 1H), 5.30 (dd, *J* = 7.7, 1.6 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.68 – 3.59 (m, 2H), 3.53 – 3.41 (m, 3H), 2.42 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 196.8, 196.3, 171.6, 171.2, 146.5, 146.4, 144.8, 144.6, 134.2, 134.0, 133.2, 132.8, 131.9, 131.8, 129.7, 129.59, 129.59, 129.56, 129.55, 129.3, 128.82, 128.79, 128.52, 128.45, 128.40, 128.36, 128.36, 128.3, 127.33, 127.28, 122.61, 122.55, 86.6, 85.5, 85.2, 84.7, 80.8, 79.8, 39.99, 39.97, 33.1, 32.0, 21.84, 21.81.

HRMS: calcd for $C_{28}H_{23}O_3$ $[M+H]^+$: 407.1642; found: 407.1637.

5-(1-(4-Chlorophenyl)-5-oxo-5-phenylpent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4n)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3

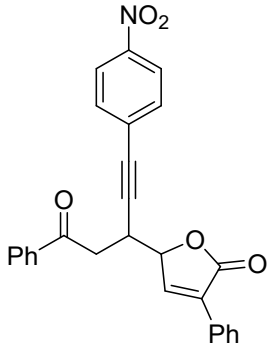
mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3b** (32.8 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (64.8 mg, 76%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 53:47 as determined by crude ^{1}H spectroscopy, but 59:41 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.97 (m, 4H), 7.89 – 7.81 (m, 4H), 7.77 – 7.74 (m, 1H), 7.64 – 7.56 (m, 3H), 7.53 – 7.46 (m, 4H), 7.45 – 7.38 (m, 6H), 7.29 – 7.26 (m, 2H), 7.26 – 7.22 (m, 2H), 7.19 – 7.10 (m, 4H), 5.37 – 5.34 (m, 1H), 5.31 (dd, J = 7.6, 1.7 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.73 – 3.60 (m, 2H), 3.55 – 3.45 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.1, 196.5, 171.5, 171.2, 146.2, 146.1, 136.5, 136.3, 134.6, 134.4, 133.9, 133.7, 133.2, 133.1, 133.0, 132.9, 129.8, 129.7, 129.4, 129.2, 128.92, 128.89, 128.85, 128.8, 128.7, 128.6, 128.30, 128.25, 127.27, 127.25, 121.02, 120.95, 87.5, 86.2, 84.5, 83.6, 80.6, 79.7, 40.1, 39.9, 33.0, 32.0.

HRMS: calcd for $C_{27}H_{20}O_3Cl$ $[M+H]^+$: 427.1095; found: 427.1080.

5-(1-(4-Nitrophenyl)-5-oxo-5-phenylpent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4o)



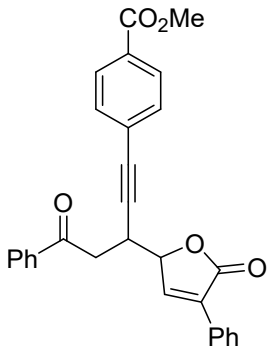
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3c** (35.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (43.7 mg, 50%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 73:27 as determined by crude ^{1}H spectroscopy, but 58:42 after recrystallization.

^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.16 – 8.10 (m, 3H), 8.08 – 8.01 (m, 2H), 8.00 – 7.97 (m, 3H), 7.90 – 7.85 (m, 1H), 7.85 – 7.80 (m, 3H), 7.75 – 7.70 (m, 2H), 7.66 – 7.57 (m, 2H), 7.54 – 7.46 (m, 7H), 7.44 – 7.31 (m, 7H), 5.38 – 5.36 (m, 1H), 5.36 – 5.34 (m, 1H), 4.02 – 3.96 (m, 1H), 3.78 – 3.71 (m, 2H), 3.69 – 3.66 (m, 1H), 3.58 – 3.55 (m, 1H), 3.54 – 3.49 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 196.8, 196.2, 171.4, 170.9, 147.3, 147.2, 145.9, 145.6, 136.3, 136.2, 134.0, 133.9, 133.4, 133.2, 132.7, 132.5, 129.89, 129.87, 129.4, 129.31, 129.26, 129.1, 128.99, 128.96, 128.94, 128.86, 128.31, 128.25, 127.23, 127.23, 123.63, 123.59, 92.2, 90.9, 83.9, 82.9, 80.2, 79.5, 40.0, 39.5, 33.0, 32.2.

HRMS: calcd for $C_{27}H_{18}NO_5$ $[M-H]^-$: 436.1190; found: 436.1196.

Methyl 4-(5-oxo-3-(5-oxo-4-phenyl-2,5-dihydrofuran-2-yl)-5-phenylpent-1-yn-1-yl)benzoate (4p)



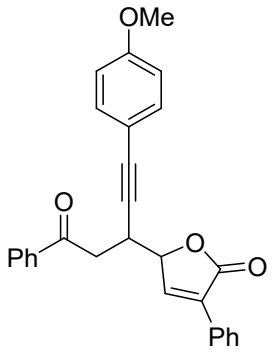
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3d** (37.6 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (46.8 mg, 52%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 53:47 as determined by crude ^{1}H spectroscopy, but 63:37 after recrystallization.

^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.07 – 7.92 (m, 6H), 7.90 – 7.81 (m, 6H), 7.78 – 7.73 (m, 1H), 7.66 – 7.56 (m, 3H), 7.54 – 7.47 (m, 4H), 7.47 – 7.37 (m, 8H), 7.30 – 7.26 (m, 2H), 5.39 – 5.35 (m, 1H), 5.35 – 5.30 (m, 1H), 4.02 – 3.95 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.73 – 3.63 (m, 2H), 3.56 – 3.46 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 196.9, 196.4, 171.4, 171.0, 166.48, 166.48, 146.1, 146.0, 136.4, 136.3, 133.9, 133.7, 133.2, 132.9, 131.8, 131.6, 129.8, 129.72, 129.67, 129.65, 129.5, 129.43, 129.35, 129.2, 128.89, 128.85, 128.82, 128.77, 128.3, 128.2, 127.23, 127.21, 127.21, 127.1, 89.6, 88.3, 84.8, 83.9, 80.5, 79.6, 52.30, 52.26, 40.0, 39.8, 33.0, 32.0.

HRMS: calcd for $C_{29}H_{23}O_5$ $[M+H]^+$: 451.1540; found: 451.1550.

5-(1-(4-Methoxyphenyl)-5-oxo-5-phenylpent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4q)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3e** (32.0 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (58.2 mg, 69%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 54:46 as determined by crude ^{1}H spectroscopy, but 57:43 after recrystallization.

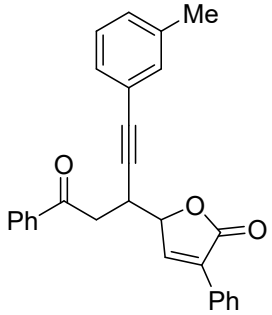
^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.04 – 7.95 (m, 4H), 7.88 – 7.81 (m, 4H), 7.80 – 7.77 (m, 1H), 7.65 – 7.54 (m, 3H), 7.52 – 7.35 (m, 10H), 7.31 – 7.24 (m, 3H), 7.18 – 7.13 (m, 2H), 6.81 – 6.76 (m, 1H), 6.74 – 6.68 (m, 2H), 5.36 – 5.32 (m, 1H), 5.30 – 5.25 (m, 1H), 3.97 – 3.90 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.67 – 3.55 (m, 2H), 3.53 – 3.41 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.3, 196.8, 171.6, 171.2, 159.8, 159.6, 146.6,

146.5, 136.6, 136.5, 133.8, 133.6, 133.3, 133.2, 132.67, 132.67, 129.7, 129.6, 129.34, 129.34, 128.9, 128.84, 128.80, 128.78, 128.31, 128.27, 127.31, 127.26, 114.63, 114.60, 114.0, 113.9, 85.5, 85.0, 84.6, 83.6, 80.9, 79.9, 55.4, 55.3, 40.3, 40.2, 33.2, 32.0.

HRMS: calcd for $C_{28}H_{23}O_4$ $[M+H]^+$: 423.1591; found: 423.1591

5-(5-Oxo-5-phenyl-1-(*m*-tolyl)pent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4r)



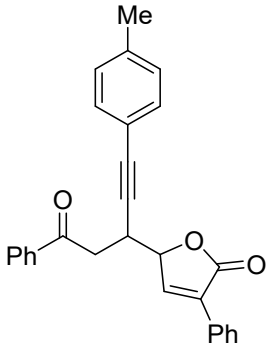
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3f** (28.8 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (51.2 mg, 63%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 46:54 as determined by crude ^{1}H spectroscopy, but 57:43 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.96 (m, 4H), 7.91 – 7.82 (m, 4H), 7.80 – 7.77 (m, 1H), 7.65 – 7.63 (m, 1H), 7.63 – 7.55 (m, 2H), 7.52 – 7.45 (m, 4H), 7.44 – 7.36 (m, 6H), 7.18 – 7.12 (m, 3H), 7.11 – 7.05 (m, 2H), 7.05 – 7.00 (m, 3H), 5.38 – 5.33 (m, 1H), 5.32 – 5.26 (m, 1H), 3.98 – 3.91 (m, 1H), 3.68 – 3.57 (m, 2H), 3.54 – 3.43 (m, 3H), 2.28 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.3, 196.7, 171.6, 171.1, 146.5, 146.4, 138.1, 138.0, 136.6, 136.4, 133.8, 133.6, 133.2, 132.7, 132.5, 132.4, 129.7, 129.59, 129.55, 129.4, 129.32, 129.26, 128.89, 128.89, 128.85, 128.79, 128.79, 128.7, 128.32, 128.27, 128.27, 128.2, 127.33, 127.27, 122.33, 122.27, 86.0, 85.8, 84.9, 84.7, 80.8, 79.8, 40.2, 40.1, 33.1, 32.0, 21.3, 21.2.

HRMS: calcd for $C_{28}H_{23}O_3$ $[M+H]^+$: 407.1642; found: 407.1640.

5-(5-Oxo-5-phenyl-1-(*p*-tolyl)pent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4s)



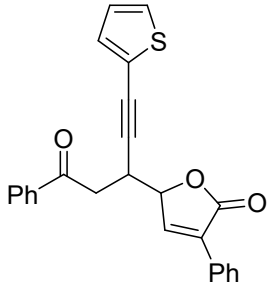
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3g** (28.8 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (46.3 mg, 57%) as a brownish purple solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 50:50 as determined by crude ^{1}H spectroscopy, but 66:34 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.96 (m, 3H), 7.89 – 7.81 (m, 4H), 7.81 – 7.77 (m, 1H), 7.66 – 7.55 (m, 4H), 7.52 – 7.45 (m, 4H), 7.44 – 7.36 (m, 6H), 7.24 – 7.22 (m, 2H), 7.14 – 7.09 (m, 2H), 7.09 – 7.05 (m, 2H), 7.02 – 6.97 (m, 2H), 5.39 – 5.32 (m, 1H), 5.31 – 5.26 (m, 1H), 3.98 – 3.91 (m, 1H), 3.68 – 3.57 (m, 2H), 3.56 – 3.43 (m, 3H), 2.32 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.3, 196.7, 171.6, 171.2, 146.6, 146.4, 138.7, 138.5, 136.6, 136.5, 133.8, 133.6, 133.2, 132.7, 131.8, 131.6, 129.7, 129.57, 129.57,129.3, 129.13, 129.05, 128.90, 128.86, 128.81, 128.80, 128.32, 128.28, 127.33, 127.28, 119.5, 119.4, 85.7, 84.9, 84.3, 80.8, 79.84, 79.84, 40.3, 40.1, 33.2, 31.9, 21.6, 21.5.

HRMS: calcd for $C_{28}H_{23}O_3$ $[M+H]^+$: 407.1642; found: 407.1651.

5-(5-Oxo-5-phenyl-1-(thiophen-2-yl)pent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4t)



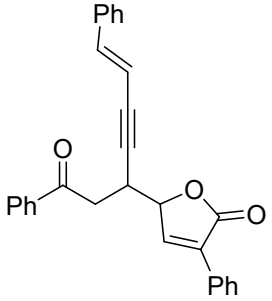
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3h** (27.2 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (39.8 mg, 50%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 51:49 as determined by crude ^{1}H spectroscopy, but 58:42 after recrystallization.

^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.95 (m, 4H), 7.89 – 7.80 (m, 4H), 7.78 – 7.74 (m, 1H), 7.65 – 7.55 (m, 3H), 7.53 – 7.36 (m, 9H), 7.24 – 7.19 (m, 2H), 7.17 – 7.12 (m, 2H), 7.03 – 6.98 (m, 1H), 6.96 – 6.91 (m, 1H), 6.89 – 6.82 (m, 1H), 5.38 – 5.33 (m, 1H), 5.32 – 5.26 (m, 1H), 4.02 – 3.94 (m, 1H), 3.70 – 3.59 (m, 2H), 3.58 – 3.42 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.1, 196.5, 171.4, 171.1, 146.3, 146.2, 136.5, 136.3, 133.9, 133.7, 133.3, 132.8, 132.5, 132.3, 129.7, 129.6, 129.5, 129.3, 128.91, 128.87, 128.79, 128.79, 128.31, 128.26, 127.4, 127.3, 127.1, 127.0, 126.93, 126.93, 122.5, 122.4, 90.5, 89.1, 80.6, 79.7, 78.8, 77.9, 39.94, 39.85, 33.3, 32.1.

HRMS: calcd for $C_{25}H_{19}O_3S$ $[M+H]^+$: 399.1049; found: 399.1056.

(*E*)-5-(1-Oxo-1,7-diphenylhept-6-en-4-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4u)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and alkynal **3i** (31.2 mg, 0.2 mmol,

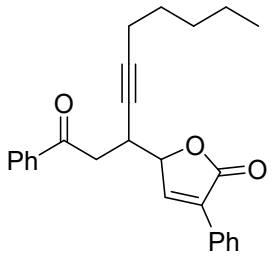
1.0 equiv.) gave the title compound (46.8 mg, 56%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 48:52 as determined by crude ^{1}H spectroscopy, but 92:8 after recrystallization.

^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.05 – 7.97 (m, 2H), 7.92 – 7.86 (m, 2H), 7.64 – 7.57 (m, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.38 (m, 3H), 7.30 – 7.21 (m, 5H), 6.72 (d, *J* = 16.3 Hz, 1H), 5.99 (d, *J* = 16.3 Hz, 1H), 5.34 – 5.30 (m, 1H), 3.96 – 3.86 (m, 1H), 3.59 (dd, *J* = 17.9, 7.7 Hz, 1H), 3.43 (dd, *J* = 17.9, 5.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 171.5, 146.3, 142.1, 136.4, 136.1, 133.9, 133.2, 129.7, 129.6, 128.92, 128.86, 128.76, 128.76, 128.3, 127.4, 126.3, 107.4, 87.2, 84.7, 79.8, 40.0, 32.1.

HRMS: calcd for $C_{29}H_{23}O_3$ $[M+H]^+$: 419.1642; found: 419.1632.

5-(1-Oxo-1-phenyldec-4-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4v)



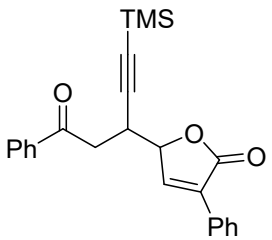
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and oct-2-ynal (24.8 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (44.8 mg, 58%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 58:42 as determined by crude ^{1}H spectroscopy, but 84:16 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.02 – 7.95 (m, 4H), 7.91 – 7.86 (m, 2H), 7.85 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.62 – 7.55 (m, 2H), 7.51 – 7.36 (m, 10H), 5.28 – 5.22 (m, 1H), 5.18 – 5.13 (m, 1H), 3.77 – 3.65 (m, 1H), 3.57 – 3.46 (m, 2H), 3.44 – 3.29 (m, 3H), 2.12 (t, *J* = 6.3 Hz, 2H), 2.02 (t, *J* = 6.2 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.47 – 1.37 (m, 3H), 1.35 – 1.23 (m, 3H), 1.20 – 1.07 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.75 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.5, 197.0, 171.6, 171.2, 146.8, 146.5, 136.8, 136.5, 133.7, 133.5, 132.86, 132.86, 129.62, 129.60, 129.5, 129.4, 128.83, 128.80, 128.76, 128.76, 128.29, 128.25, 127.24, 127.22, 86.1, 85.4, 81.1, 80.1, 75.52, 75.52, 40.6, 40.4, 32.7, 31.4, 31.1, 31.0, 28.48, 28.48, 22.24, 22.15, 18.8, 18.6, 14.1, 13.9.

HRMS: calcd for $C_{26}H_{27}O_3$ $[M+H]^+$: 387.1955; found: 387.1958.

5-(5-Oxo-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (4w)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3

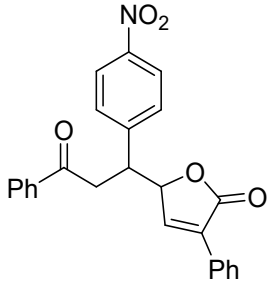
mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and 3-(trimethylsilyl)-propiolaldehyde (25.2 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (46.6 mg, 60%) as a light yellow solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 60:40 as determined by crude ^{1}H spectroscopy, but 74:26 after recrystallization.

^{1}H NMR (400 MHz, $CDCl_3$): (two diastereomers) δ 8.04 – 7.96 (m, 3H), 7.91 – 7.82 (m, 4H), 7.71 – 7.68 (m, 1H), 7.64 – 7.55 (m, 4H), 7.53 – 7.48 (m, 4H), 7.47 – 7.38 (m, 6H), 5.29 – 5.25 (m, 1H), 5.24 – 5.20 (m, 1H), 3.77 – 3.72 (m, 1H), 3.66 – 3.57 (m, 2H), 3.50 – 3.35 (m, 3H), 0.11 (s, 9H), -0.00 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 197.2, 196.6, 171.5, 171.1, 146.19, 146.19, 136.6, 136.4, 133.8, 133.6, 133.0, 132.8, 129.7, 129.6, 129.5, 129.3, 128.9, 128.83, 128.77, 128.75, 128.31, 128.27, 127.29, 127.25, 103.0, 101.6, 90.5, 89.7, 80.5, 79.4, 40.03, 39.96, 33.32, 32.27, -0.0, -0.2.

HRMS: calcd for $C_{24}H_{25}O_3Si$ $[M+H]^+$: 389.1567; found: 389.1557.

5-(1-(4-Nitrophenyl)-3-oxo-3-phenylpropyl)-3-phenylfuran-2(5*H*)-one (4x)



According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48.0 mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and 4-nitrobenzaldehyde (30.2 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (40.5 mg, 49%) as a white solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 73:47 as determined by crude ^{1}H spectroscopy, and they could separate after column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): ***anti***: δ 8.26 – 8.20 (m, 2H), 7.89 – 7.83 (m, 2H), 7.77 – 7.71 (m, 2H), 7.66 – 7.60 (m, 2H), 7.58 – 7.51 (m, 1H), 7.45 – 7.34 (m, 6H), 5.35 – 5.29 (m, 1H), 4.04 – 3.96 (m, 1H), 3.59 (dd, *J* = 17.8, 5.1 Hz, 1H), 3.46 (dd, *J* = 17.8, 8.1 Hz, 1H).

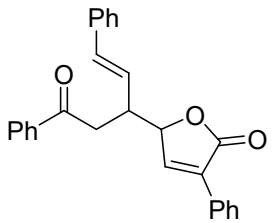
^{13}C NMR (125 MHz, $CDCl_3$): ***anti***: δ 196.9, 171.1, 147.8, 147.5, 145.9, 136.3, 133.9, 133.0, 129.9, 129.5, 128.92, 128.92, 128.86, 128.1, 127.2, 124.3, 82.2, 44.3, 39.1.

^{1}H NMR (500 MHz, $CDCl_3$) : ***syn***: δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.52 – 7.44 (m, 5H), 7.37 – 7.32 (m, 3H), 5.50 – 5.44 (m, 1H), 4.19 – 4.12 (m, 1H), 3.88 (dd, *J* = 18.1, 7.3 Hz, 1H), 3.61 (dd, *J* = 18.1, 6.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): ***syn***: δ 197.1, 171.1, 147.5, 145.9, 145.1, 136.4, 134.0, 133.2, 129.8, 129.6, 129.0, 128.9, 128.8, 128.2, 127.0, 124.0, 81.2, 43.5, 40.4.

HRMS: calcd for $C_{25}H_{20}NO_5$ $[M+H]^+$: 414.1336; found: 414.1345.

(*E*)-5-(5-Oxo-1,5-diphenylpent-1-en-3-yl)-3-phenylfuran-2(5*H*)-one (4y)



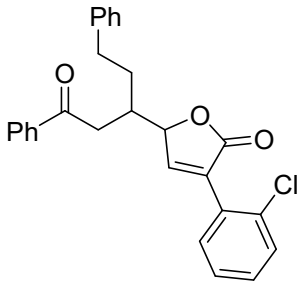
According to the general procedure, the reaction of cyclopropene carboxylic acid **1a** (48mg, 0.3 mmol, 1.5 equiv.), enamine **2a** (45.4 mg, 0.24 mmol, 1.2 equiv.) and cinnamaldehyde (26.4 mg, 0.2 mmol, 1.0 equiv.) gave the title compound (33.1 mg, 42%) as an off-white solid consisting of two diastereomers. The *anti*/*syn* of diastereomers was 56:44 as determined by crude ^{1}H spectroscopy, but 66:34 after recrystallization.

^{1}H NMR (500 MHz, $CDCl_3$): (two diastereomers) δ 8.02 – 7.96 (m, 3H), 7.93 – 7.88 (m, 1H), 7.82 – 7.75 (m, 4H), 7.62 – 7.56 (m, 3H), 7.55 – 7.46 (m, 4H), 7.44 – 7.34 (m, 8H), 7.33 – 7.28 (m, 2H), 7.27 – 7.16 (m, 7H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 15.9, 8.8 Hz, 1H), 6.02 (dd, *J* = 15.9, 8.8 Hz, 1H), 5.38 – 5.33 (m, 1H), 5.30 – 5.26 (m, 1H), 3.67 – 3.59 (m, 1H), 3.58 – 3.51 (m, 1H), 3.43 – 3.34 (m, 1H), 3.34 – 3.30 (m, 1H), 3.29 – 3.25 (m, 1H), 3.24 – 3.20 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): (two diastereomers) δ 198.1, 198.0, 171.8, 171.5, 147.2, 147.1, 136.88, 136.86, 136.54, 136.51, 134.3, 133.8, 133.7, 133.5, 132.8, 132.4, 129.58, 129.56, 129.5, 129.4, 128.9, 128.83, 128.80, 128.76, 128.73, 128.69, 128.3, 128.2, 128.1, 128.0, 127.4, 127.24, 127.19, 126.6, 126.5, 125.0, 82.3, 82.0, 42.8, 41.1, 40.1, 39.0.

HRMS: calcd for $C_{27}H_{23}O_3$ $[M+H]^+$: 395.1642; found: 395.1661.

3-(2-Chlorophenyl)-5-(1-oxo-1,5-diphenylpentan-3-yl)furan-2(5*H*)-one (6c)



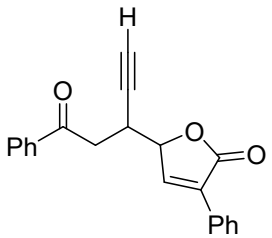
Light yellow oli, combined in 75% yield, 64.5 mg, dr > 20:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.72 – 7.66 (m, 1H), 7.65 – 7.56 (m, 2H), 7.52 – 7.43 (m, 3H), 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 5.34 (dd, *J* = 3.3, 1.6 Hz, 1H), 3.38 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.11 (dd, *J* = 17.7, 5.2 Hz, 1H), 2.86 – 2.59 (m, 3H), 1.83 – 1.66 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 171.7, 152.5, 141.2, 136.9, 133.6, 133.3, 130.9, 130.7, 130.3, 128.9, 128.6, 128.4, 128.2, 127.0, 126.3, 82.9, 39.3, 36.3, 33.7, 30.2.

HRMS: calcd for $C_{27}H_{24}O_3Cl$ $[M+H]^+$: 431.1408; found: 431.1408.

5-(5-Oxo-5-phenylpent-1-yn-3-yl)-3-phenylfuran-2(5*H*)-one (6d)



Yellow solid, combined in 88% yield, 56.9 mg (*anti*: *syn* = 67 : 33)

The *anti*/*syn* of diastereomers was 61:39 as determined by crude ^{1}H spectroscopy, but 73:27 after recrystallization.

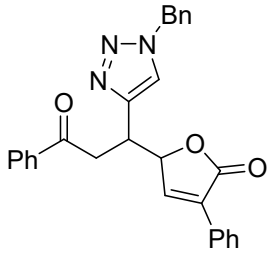
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 4H), 7.91 – 7.81 (m, 4H), 7.78 – 7.74 (m, 1H), 7.64 – 7.56 (m, 4H), 7.53 – 7.37 (m, 9H), 5.29 – 5.25 (m, 1H), 5.24 – 5.20 (m, 1H), 3.79 – 3.73 (m, 1H), 3.62 – 3.50

(m, 2H), 3.49 – 3.33 (m, 3H), 2.25 (s, 1H), 2.11 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 196.4, 171.4, 171.0, 146.1, 145.8, 136.4, 136.3, 133.9, 133.7, 133.2, 132.8, 129.8, 129.7, 129.4, 129.2, 128.92, 128.89, 128.84, 128.82, 128.3, 128.2, 127.33, 127.27, 81.3, 80.4, 79.9, 79.41, 73.37, 72.8, 39.94, 39.85, 32.2, 30.9.

HRMS: calcd for $C_{21}H_{17}O_3$ $[M+H]^+$: 317.1172; found: 317.1176.

5-(1-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-3-oxo-3-phenylpropyl)-3-phenylfuran-2(5*H*)-one (6e)



White solid, combined in 84% yield, 75.4 mg (*anti*: *syn* = 57 : 43)

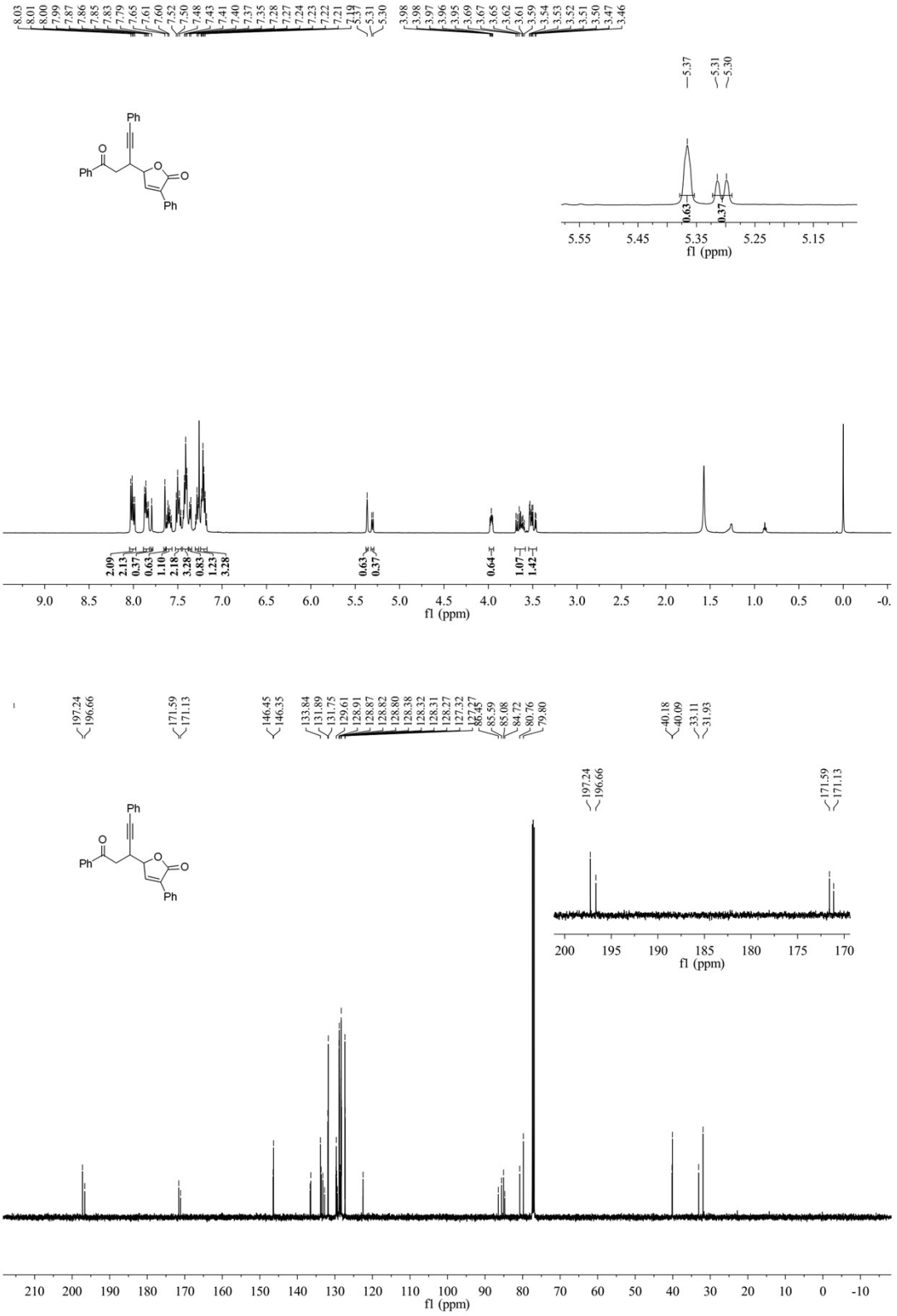
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 4H), 7.82 – 7.77 (m, 2H), 7.77 – 7.66 (m, 4H), 7.59 – 7.51 (m, 3H), 7.50 – 7.42 (m, 6H), 7.41 – 7.27 (m, 9H), 7.25 – 7.14 (m, 4H), 7.12 – 7.05 (m, 2H), 5.58 – 5.51 (m, 1H), 5.49 – 5.40 (m, 5H), 4.39 – 4.29 (m, 1H), 4.06 – 3.98 (m, 1H), 3.79 – 3.69 (m, 1H), 3.66 – 3.54 (m, 1H), 3.53 – 3.41 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 197.5, 171.5, 171.3, 147.4, 146.8, 145.8, 145.1, 136.57, 136.55, 134.6, 134.5, 133.7, 133.6, 132.5, 132.4, 129.53, 129.52, 129.34, 129.33, 129.24, 129.19, 128.84, 128.83, 128.81, 128.77, 128.75, 128.7, 128.19, 128.15, 128.0, 127.8, 127.22, 127.18, 122.9, 122.5, 81.3, 80.9, 54.29, 54.26, 39.3, 39.0, 36.3, 35.5.

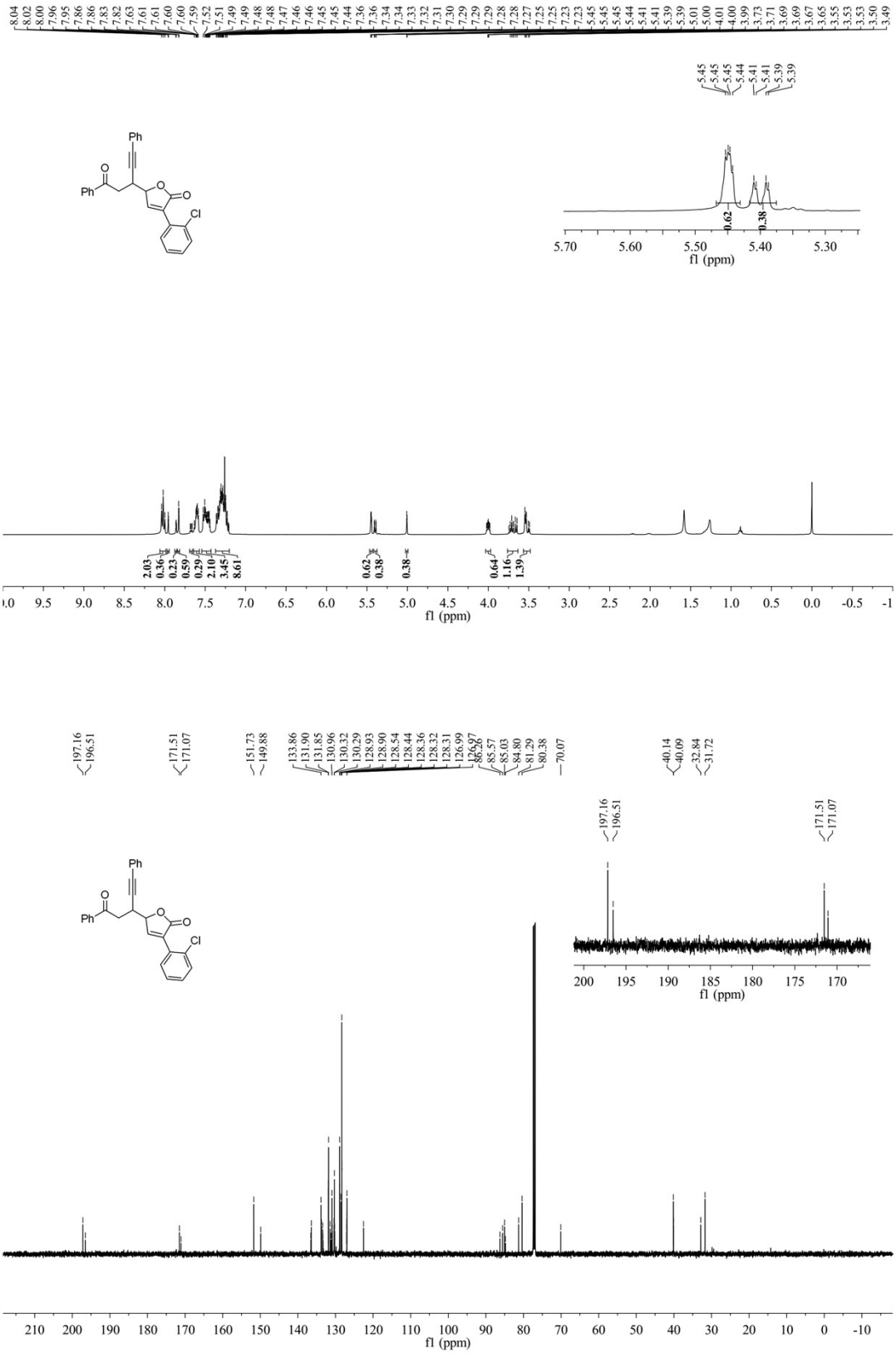
HRMS: calcd for $C_{28}H_{24}N_3O_3$ $[M+H]^+$: 450.1812; found: 450.1825.

7. NMR Spectra of Products

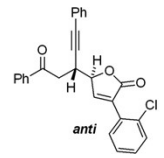
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4a**

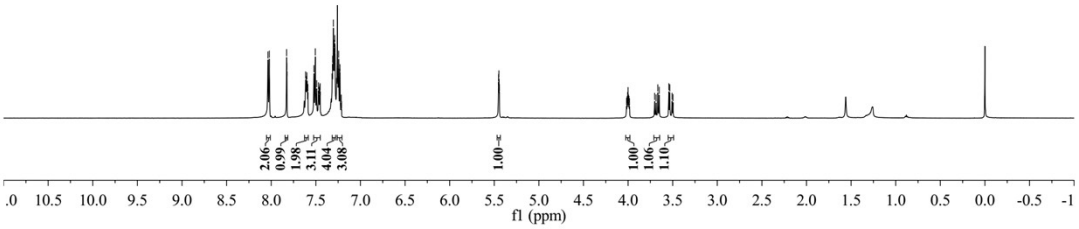


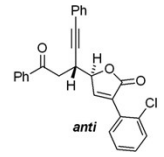
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4b**



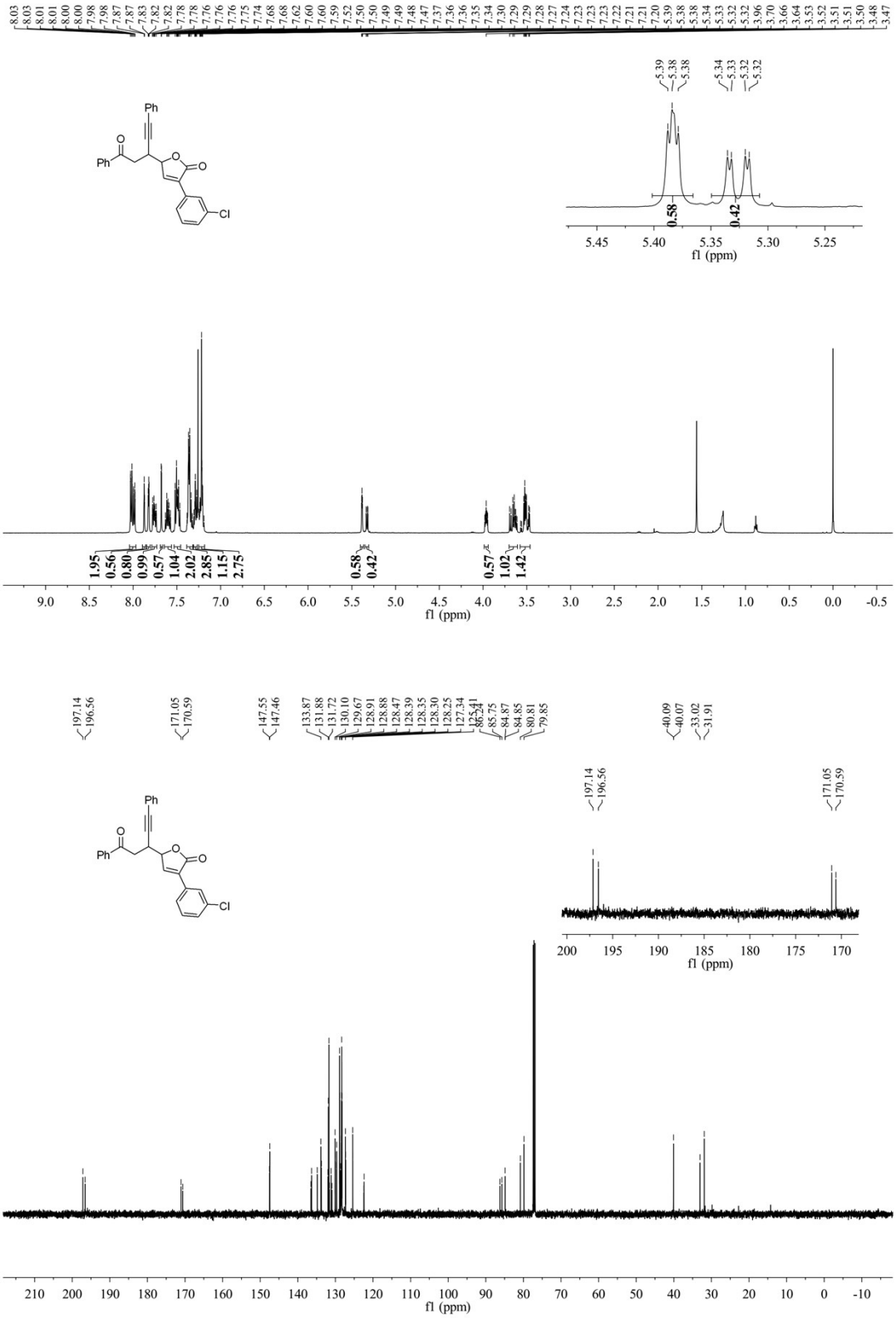
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for *anti*-**4b**



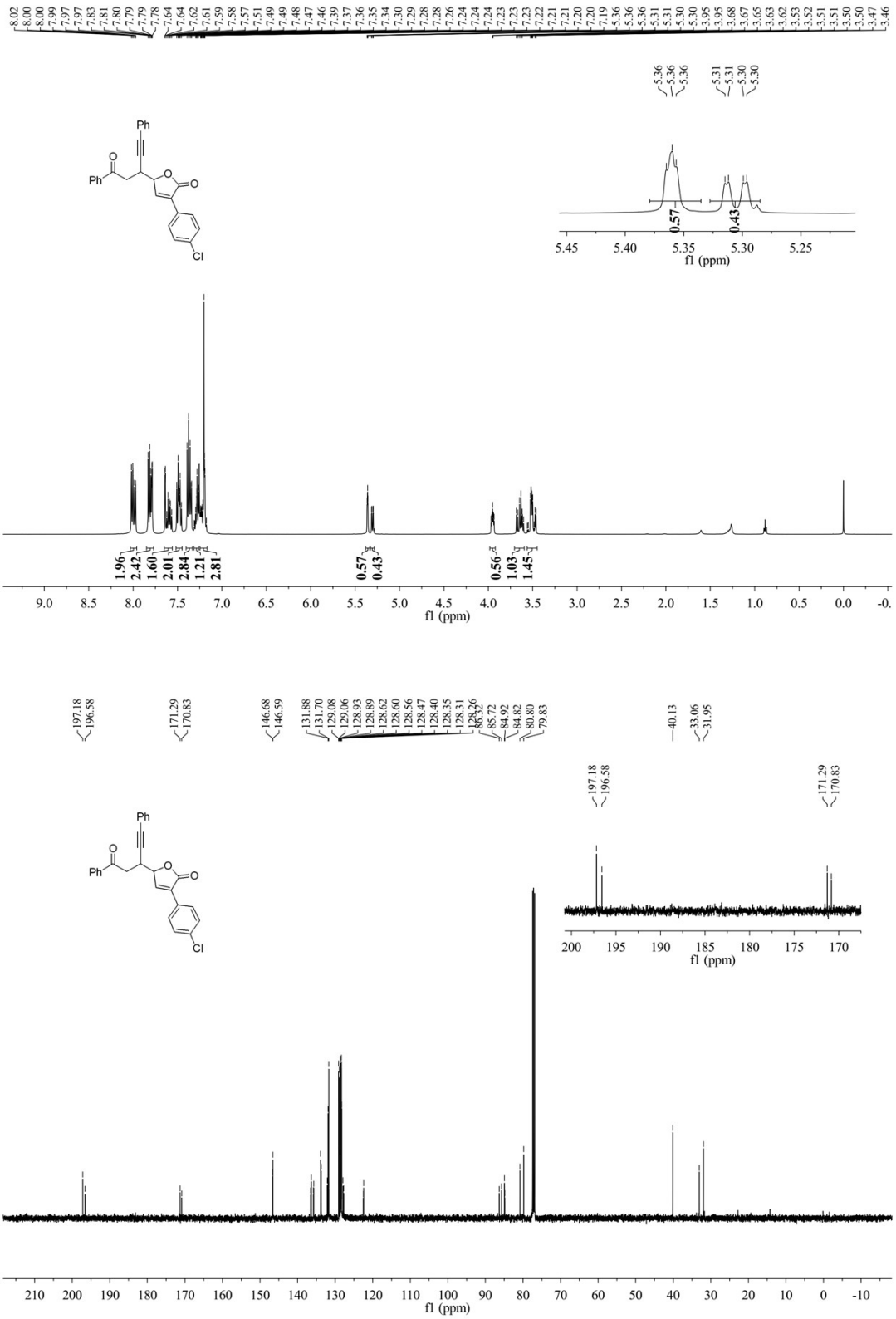




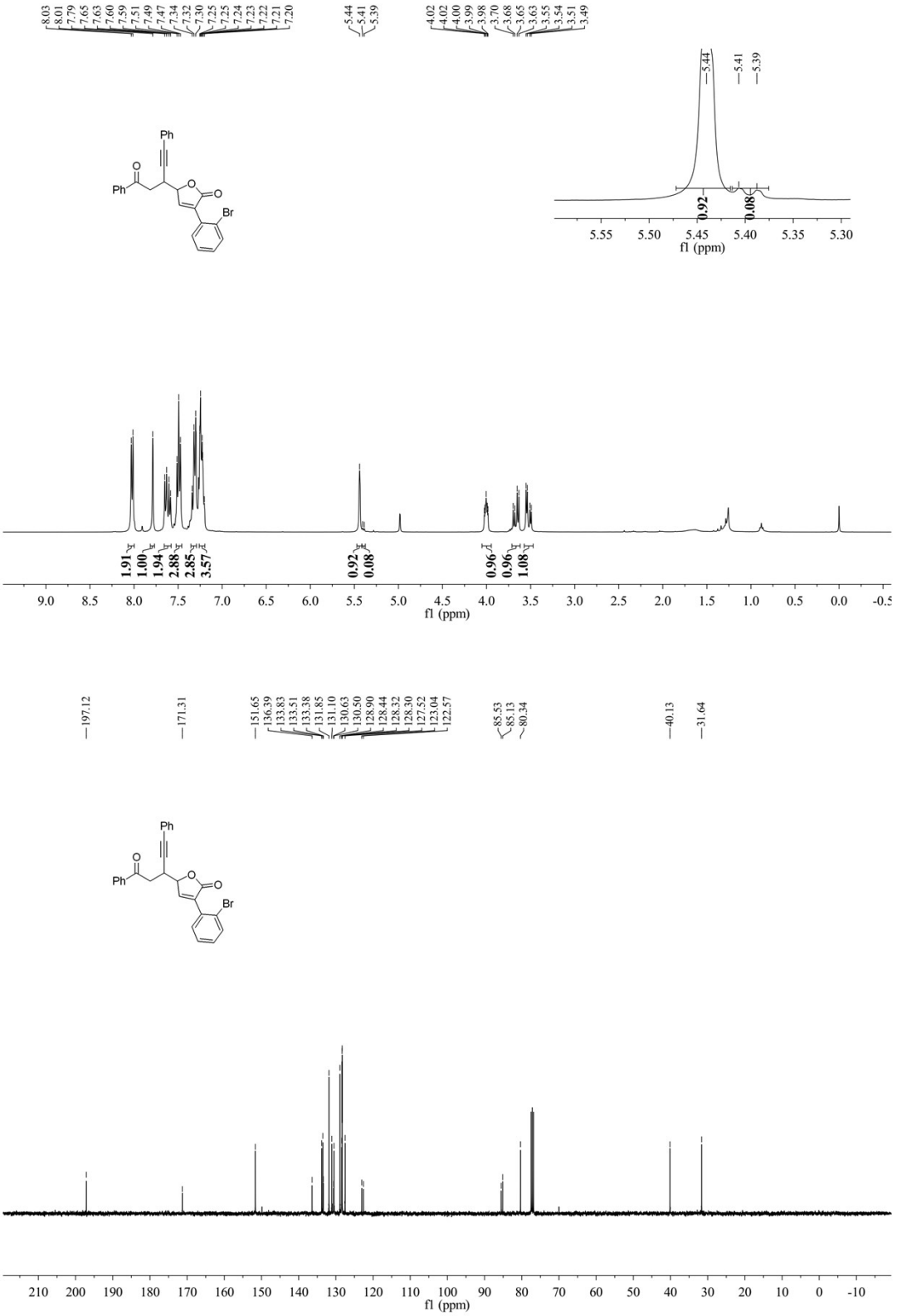
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4c**



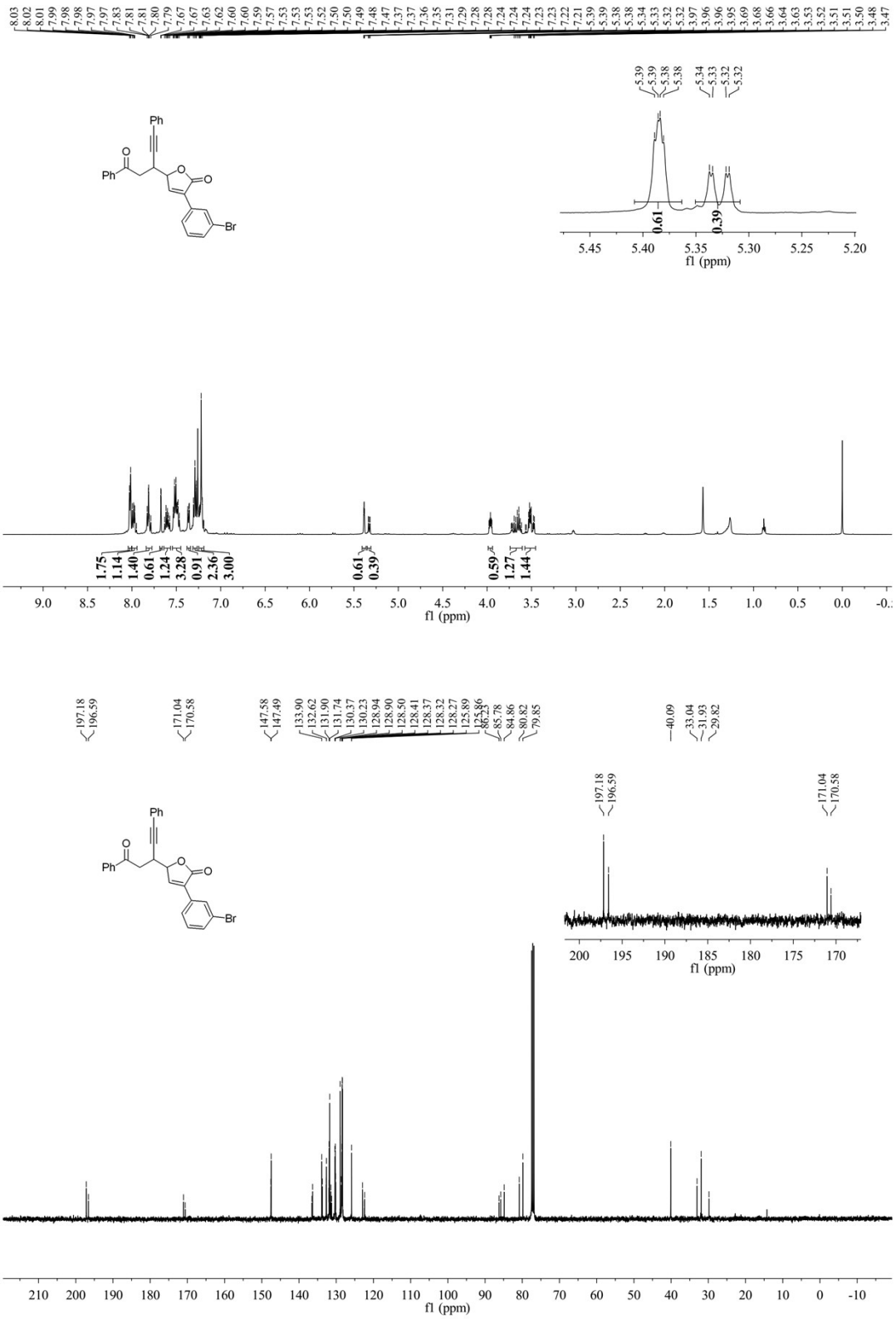
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4d**



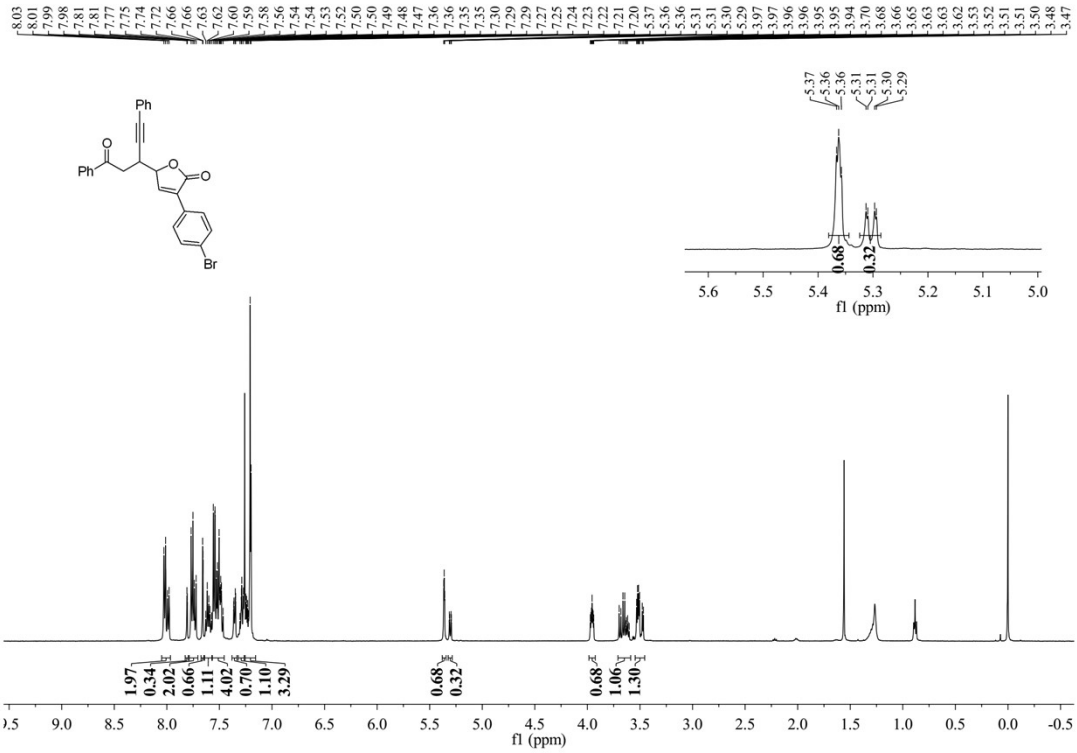
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **4e**

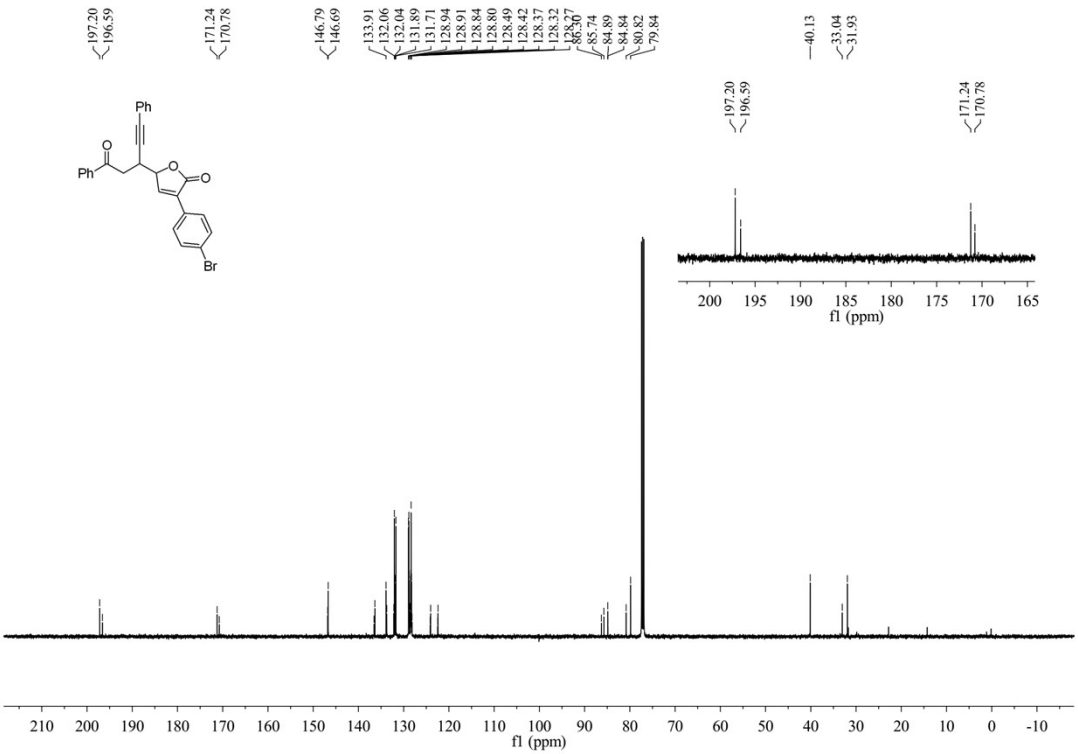


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for **4f**

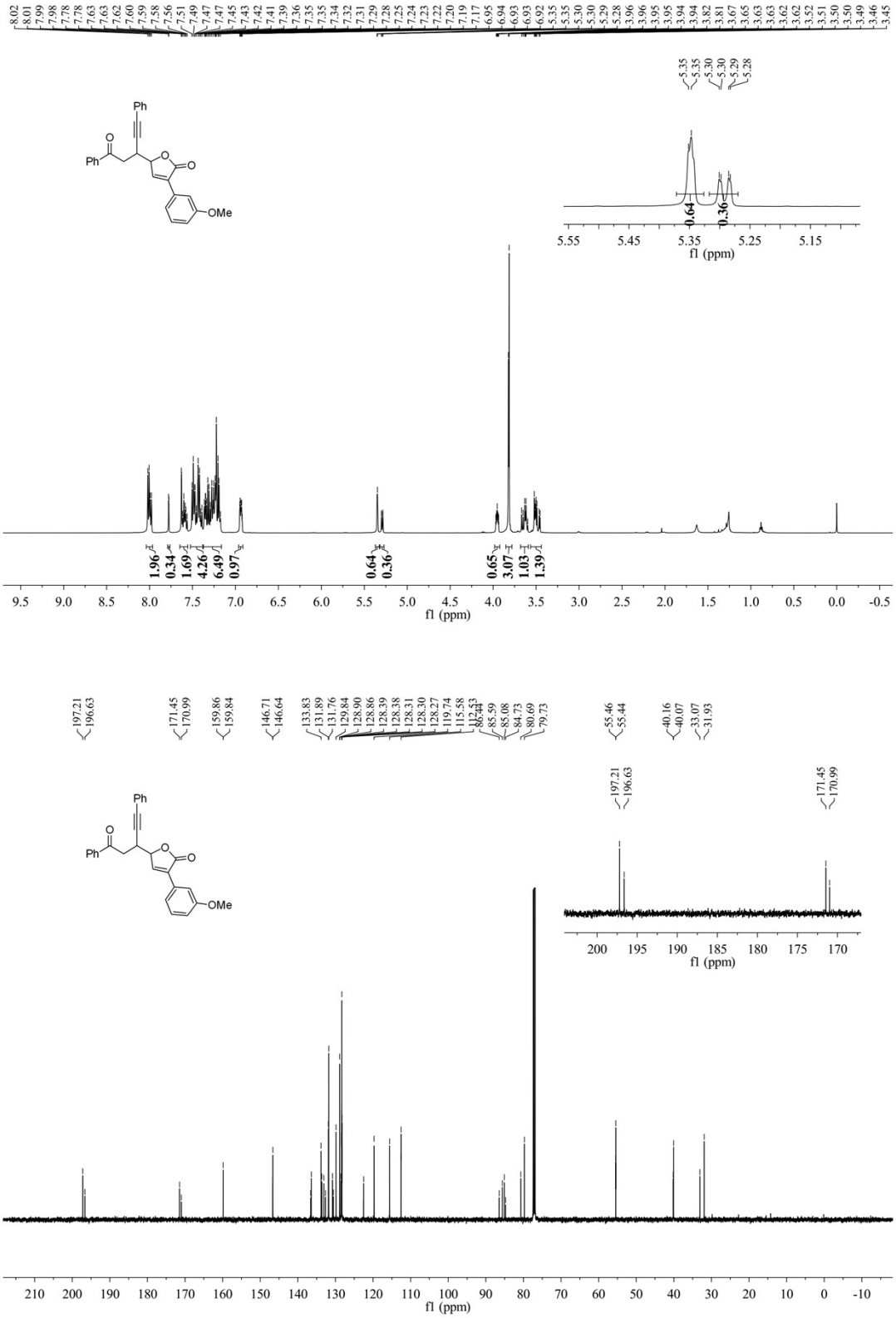


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4g**

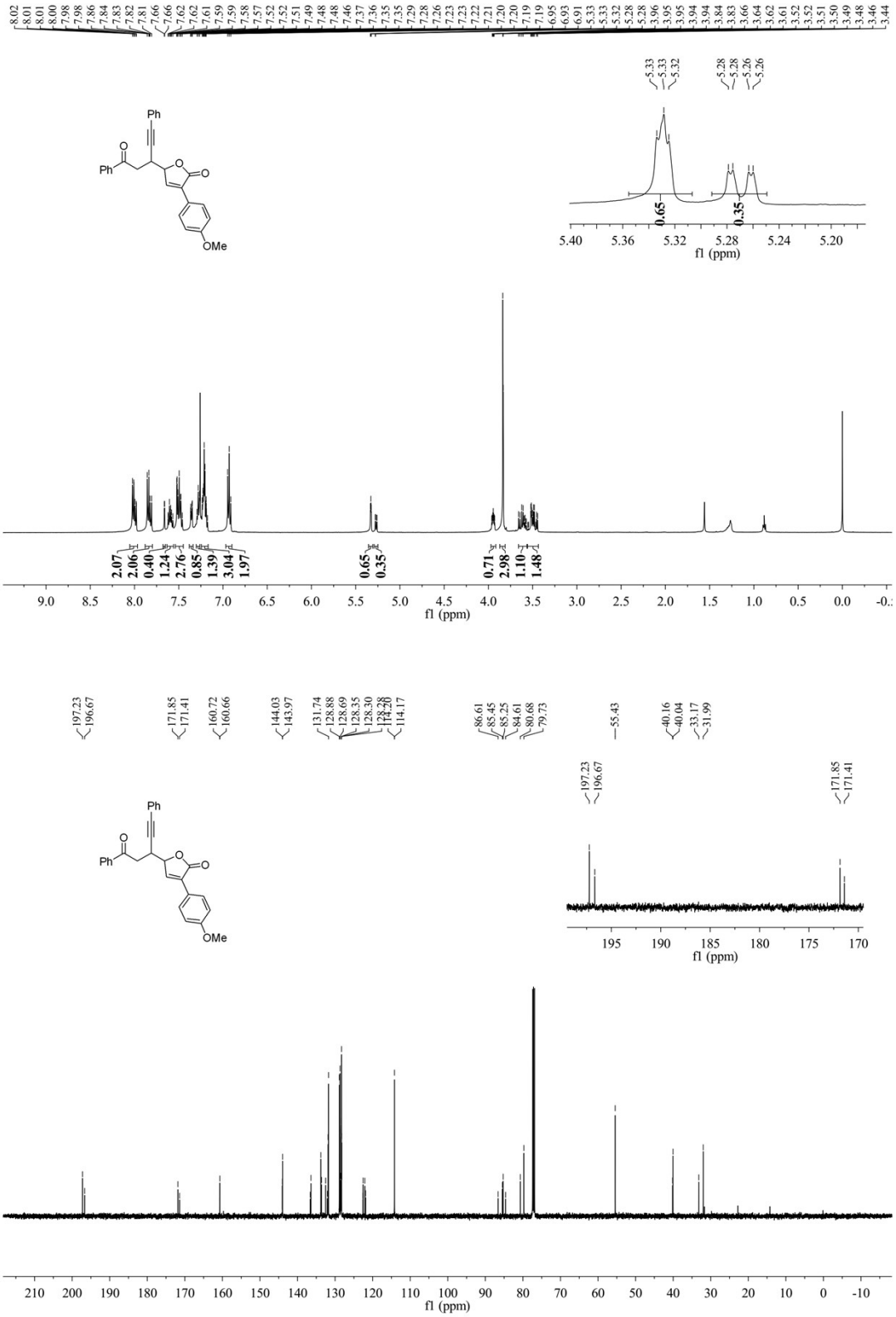




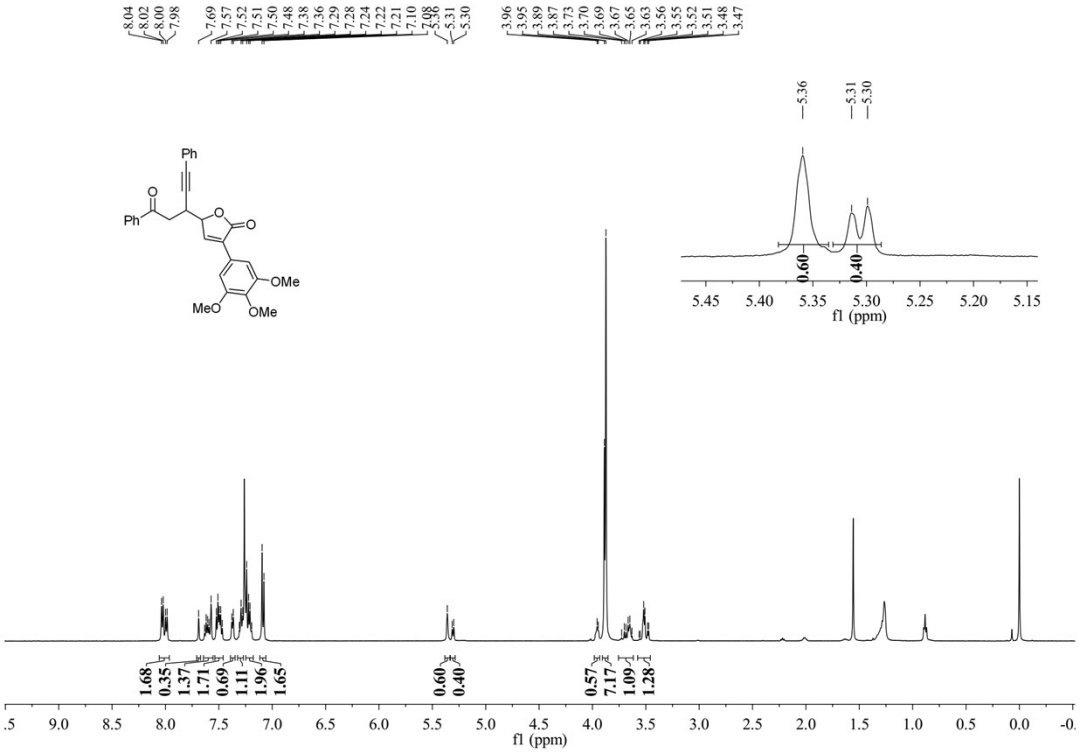
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4h**

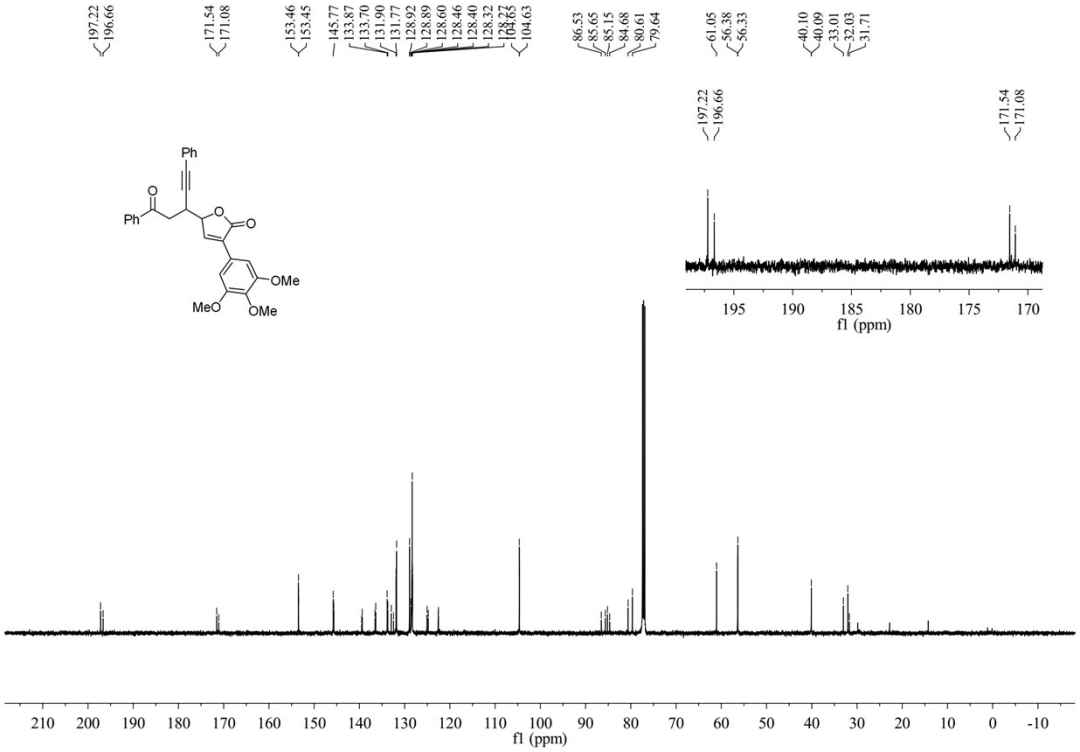


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4i**

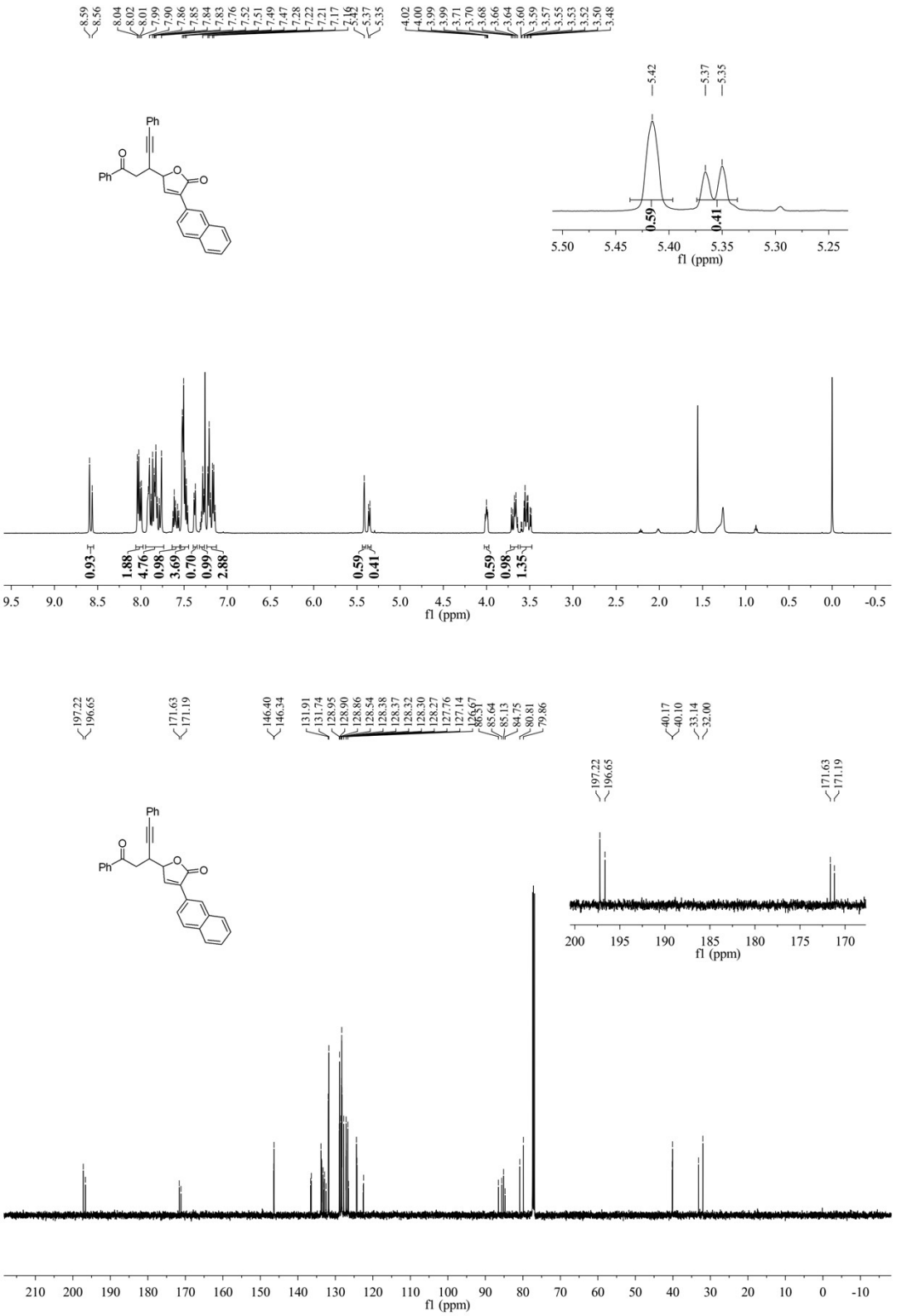


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4j**

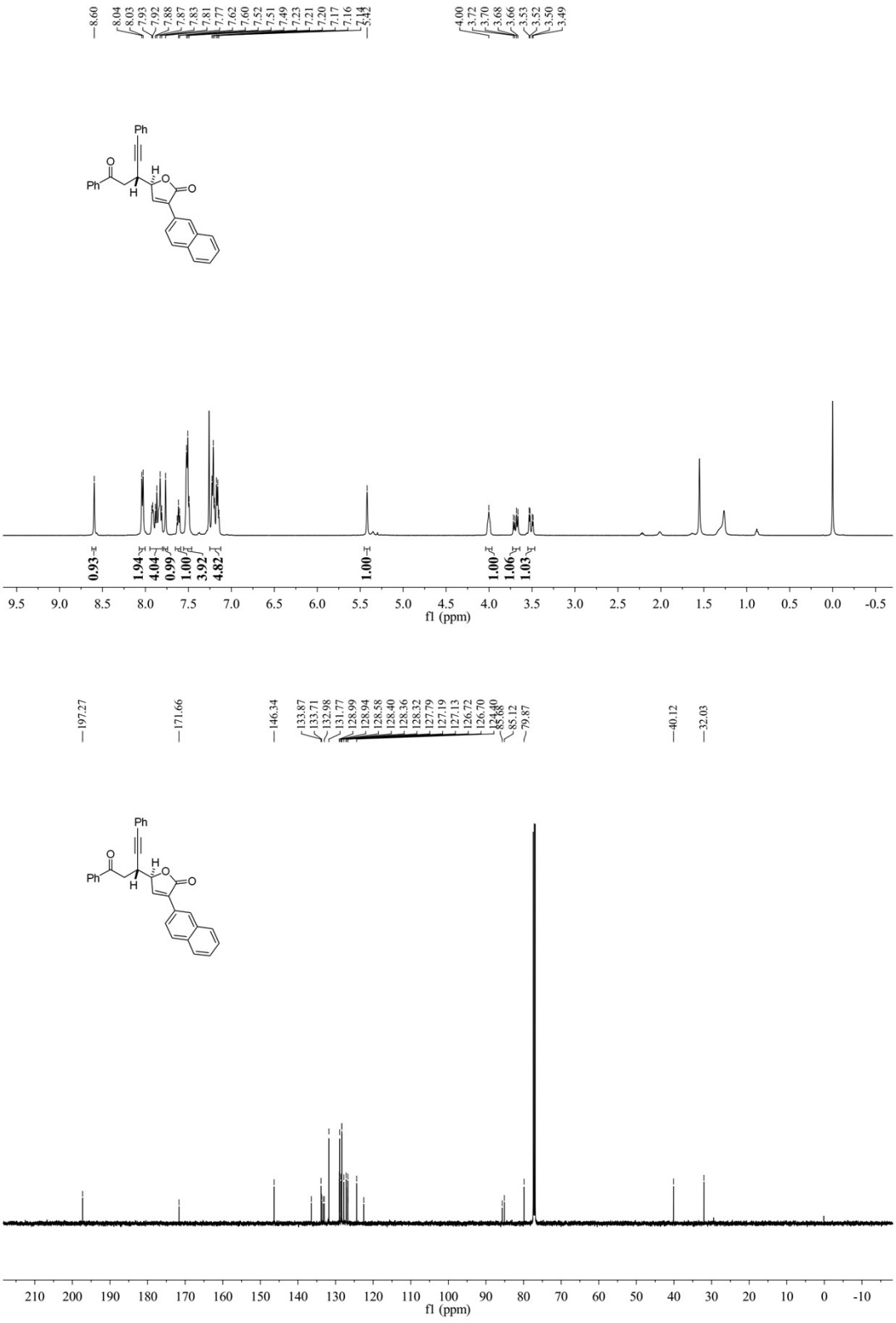




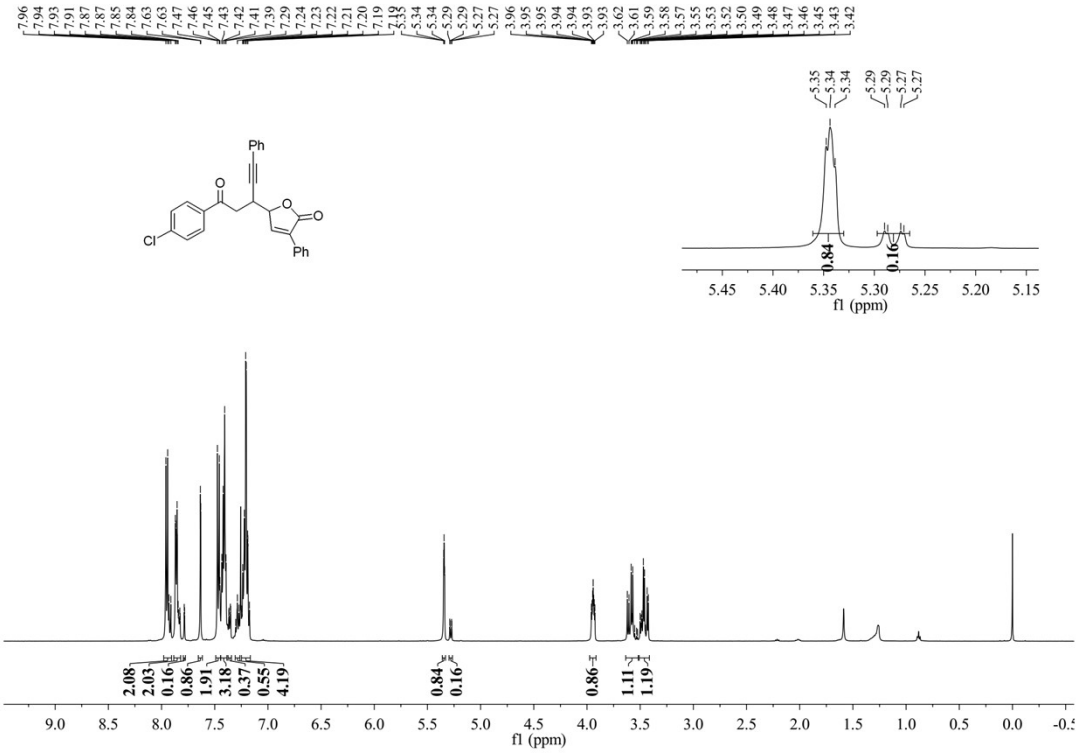
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4k**

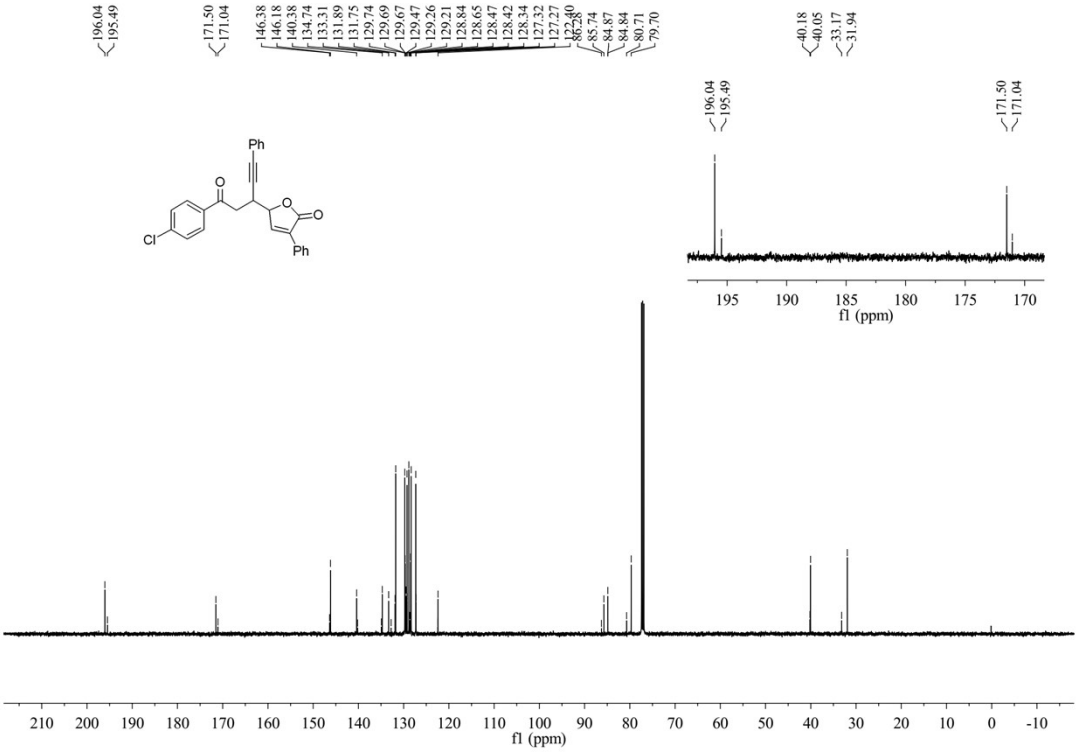


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for *anti*-**4k**

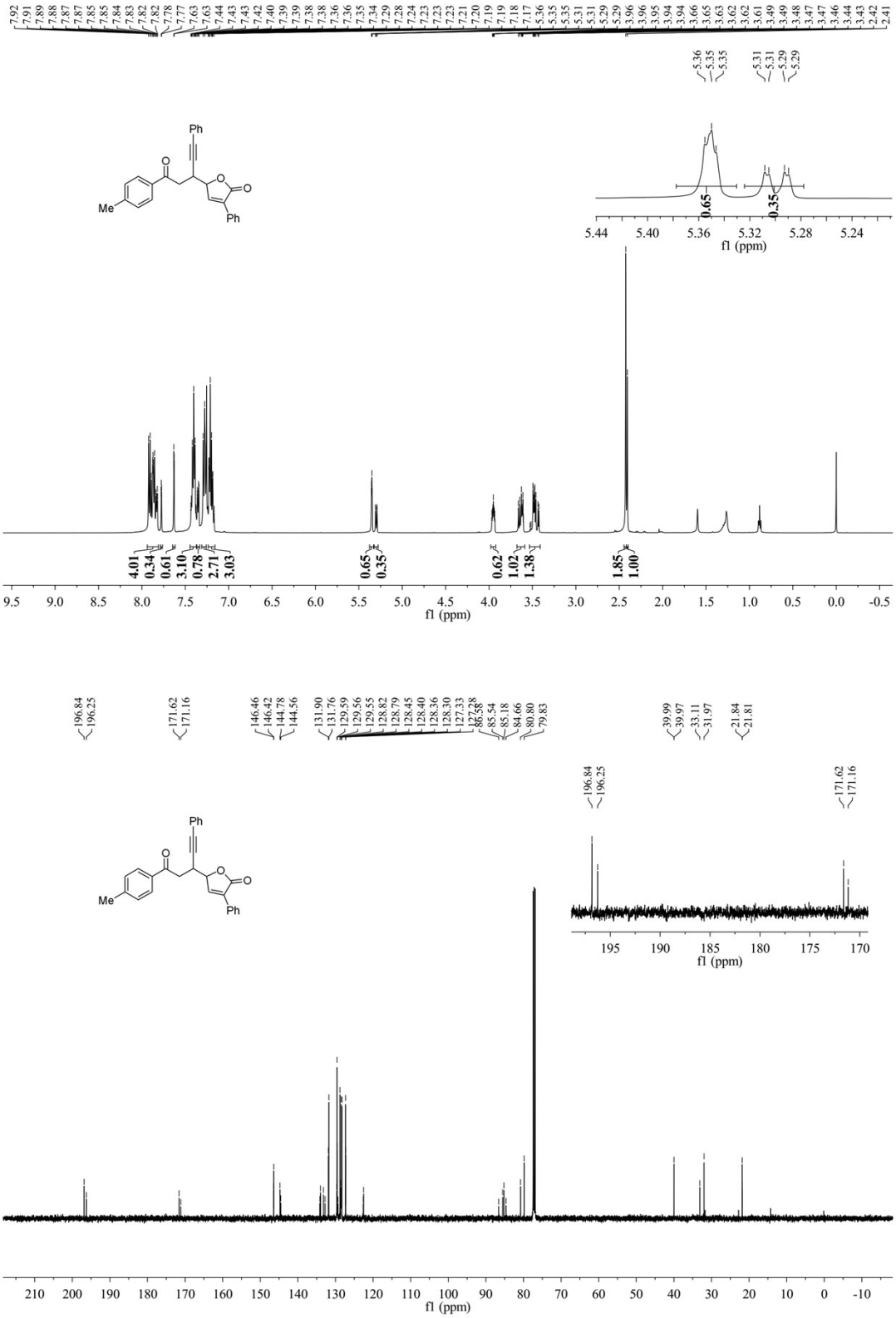


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4l**

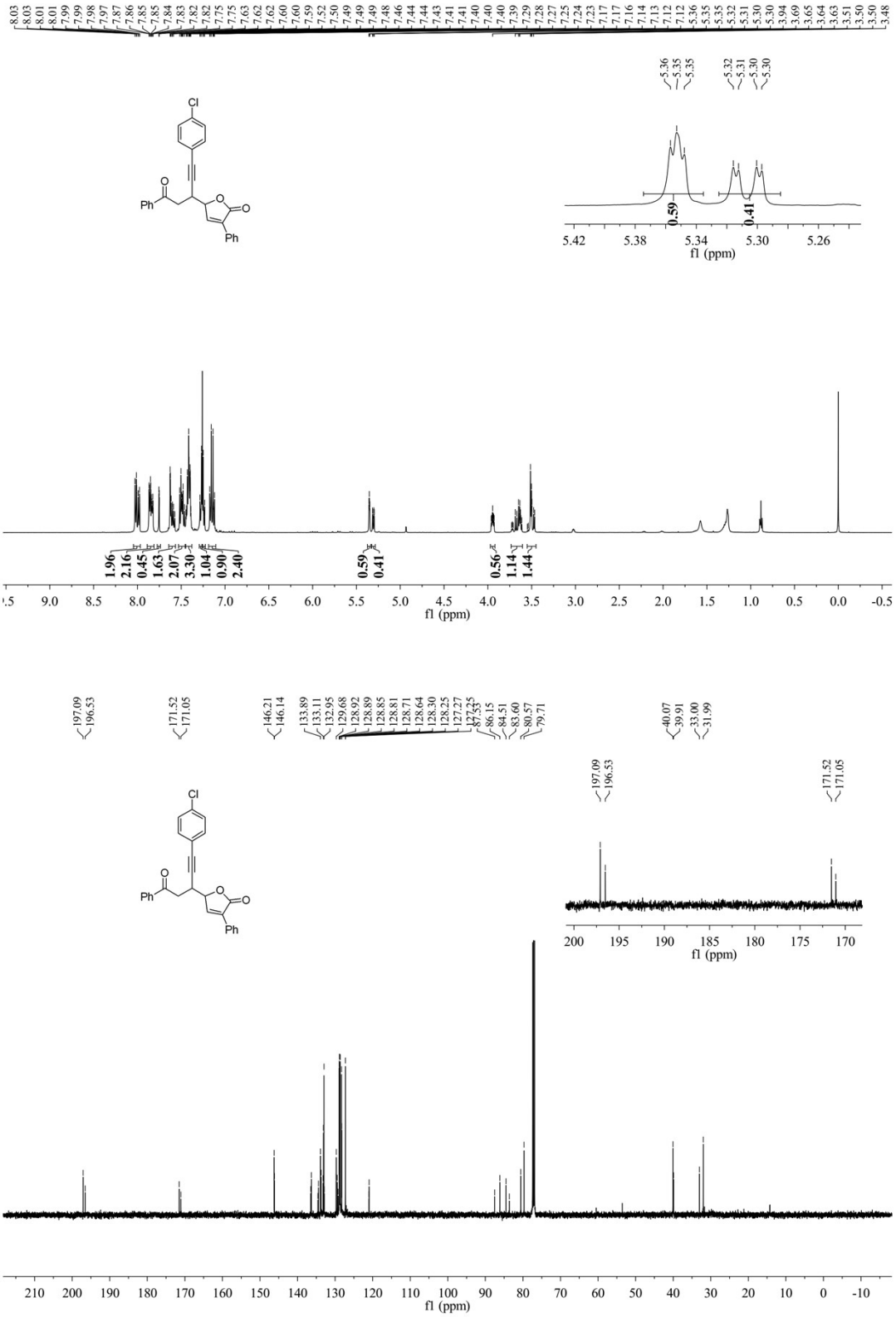




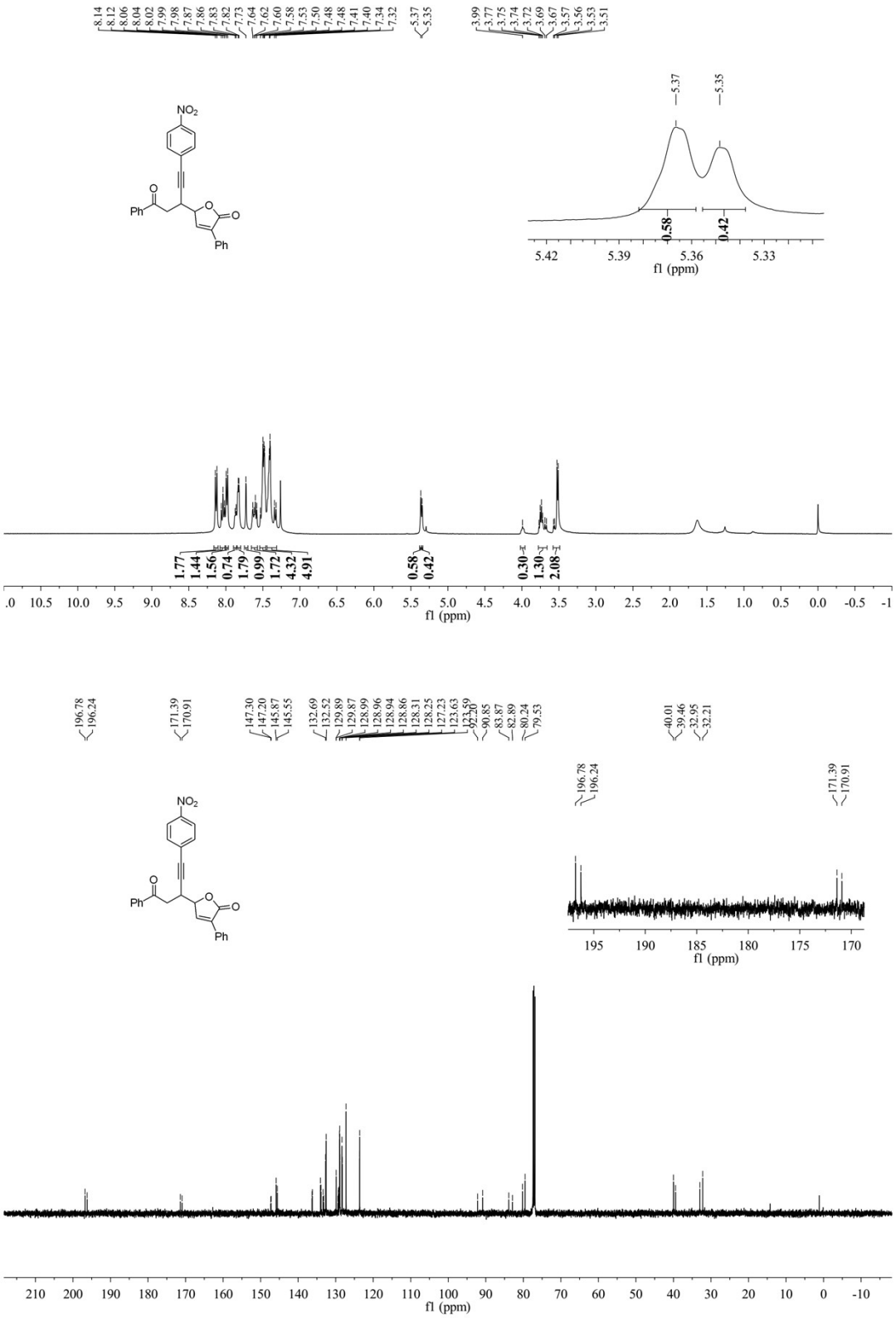
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4m**



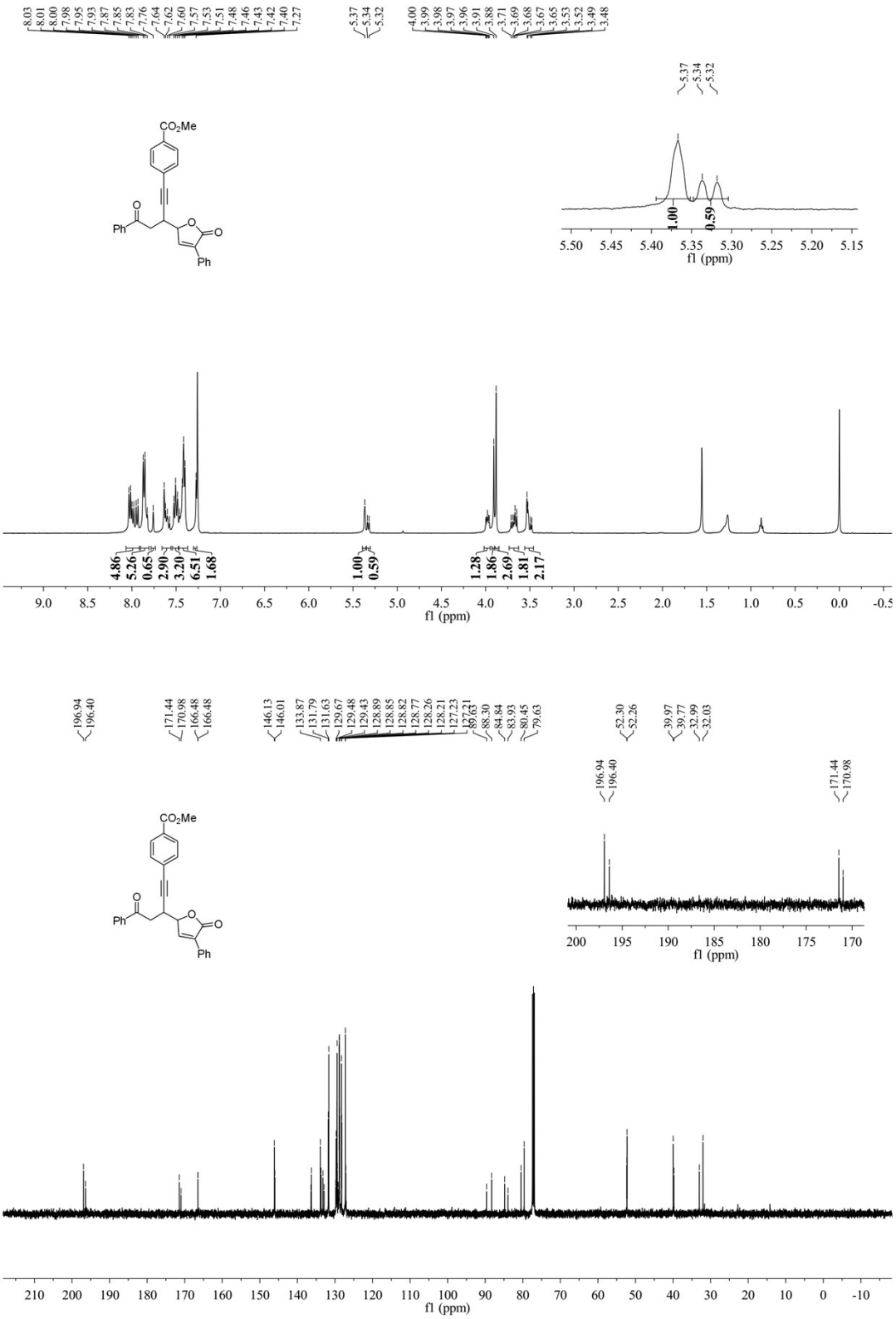
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4n**



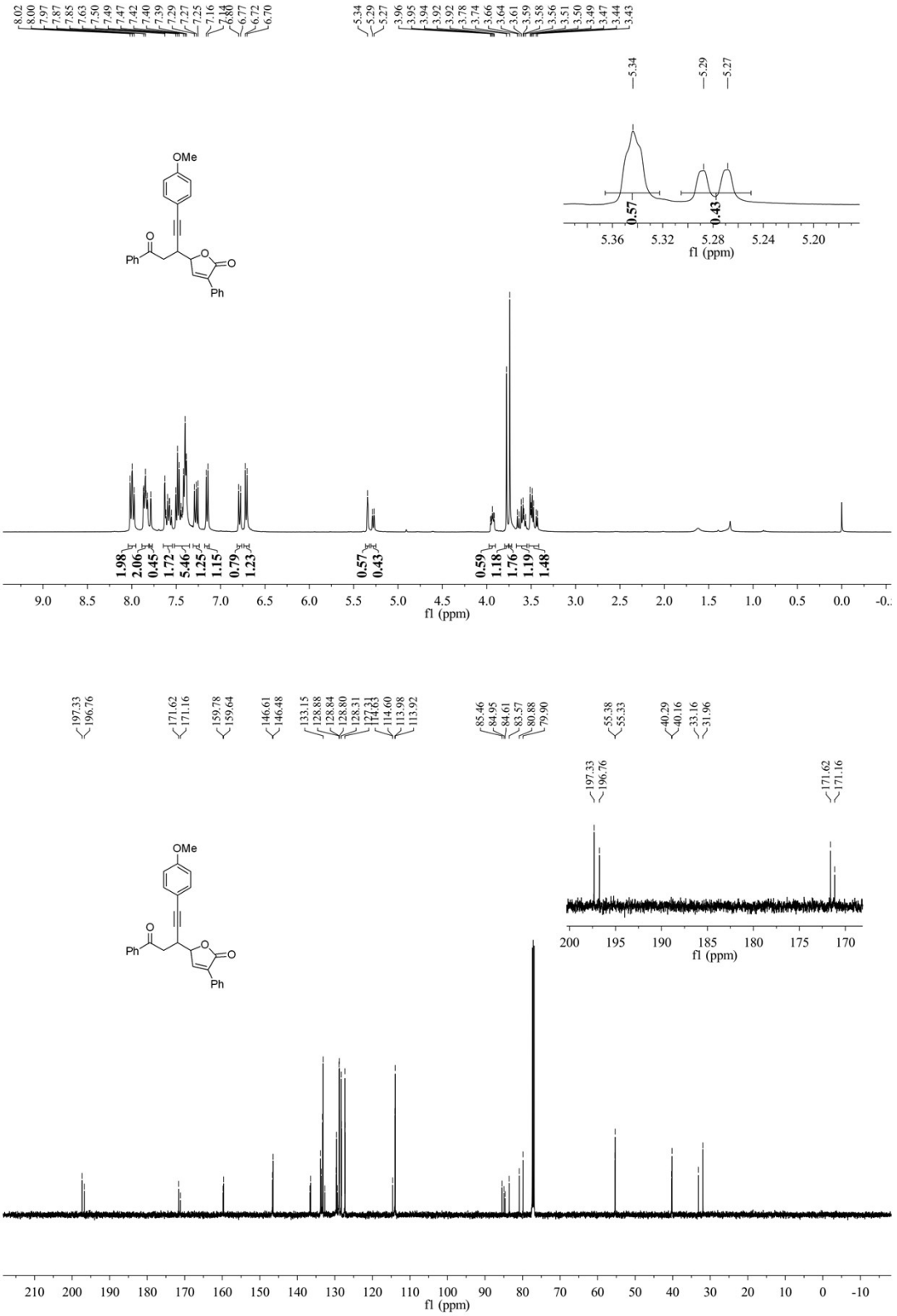
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4o**



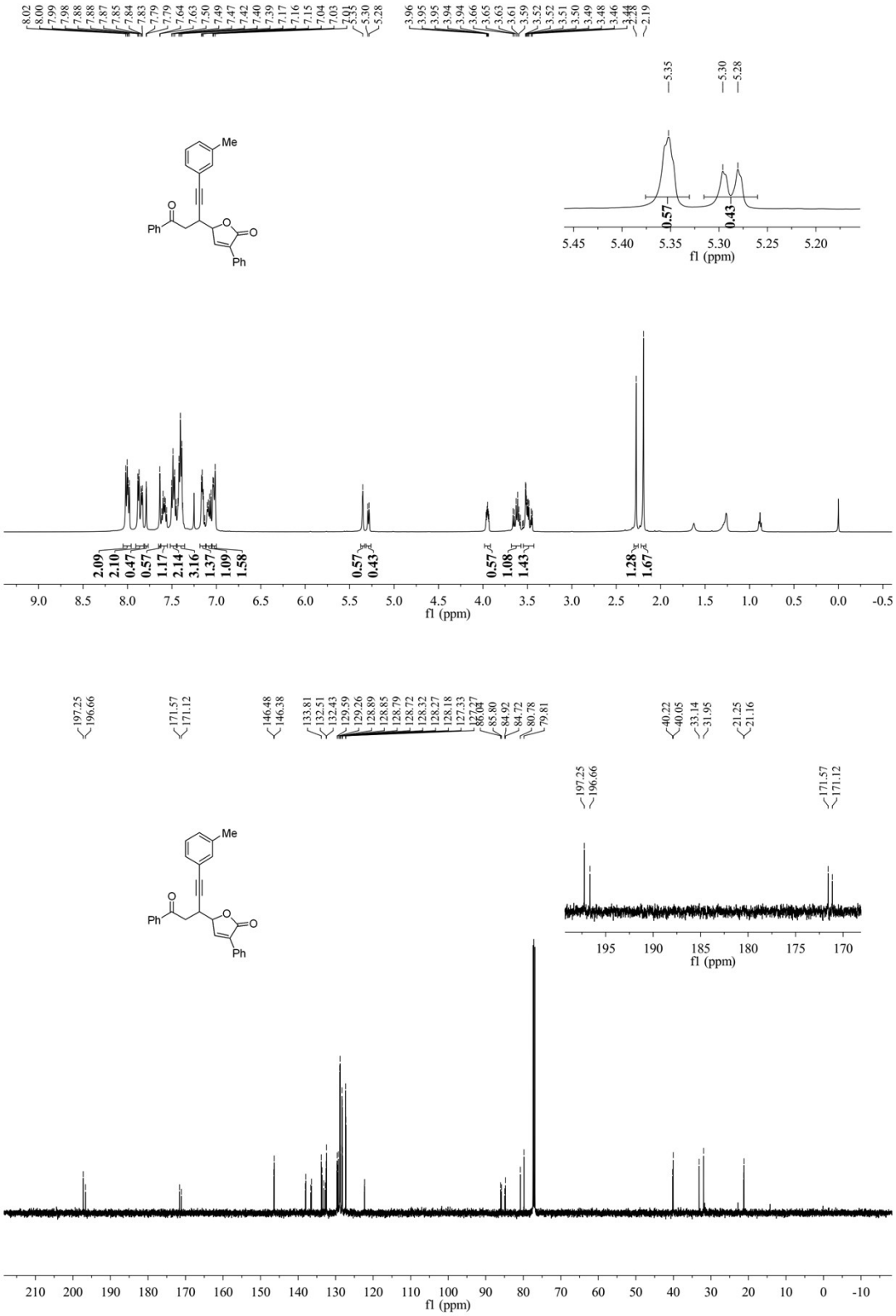
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4p**



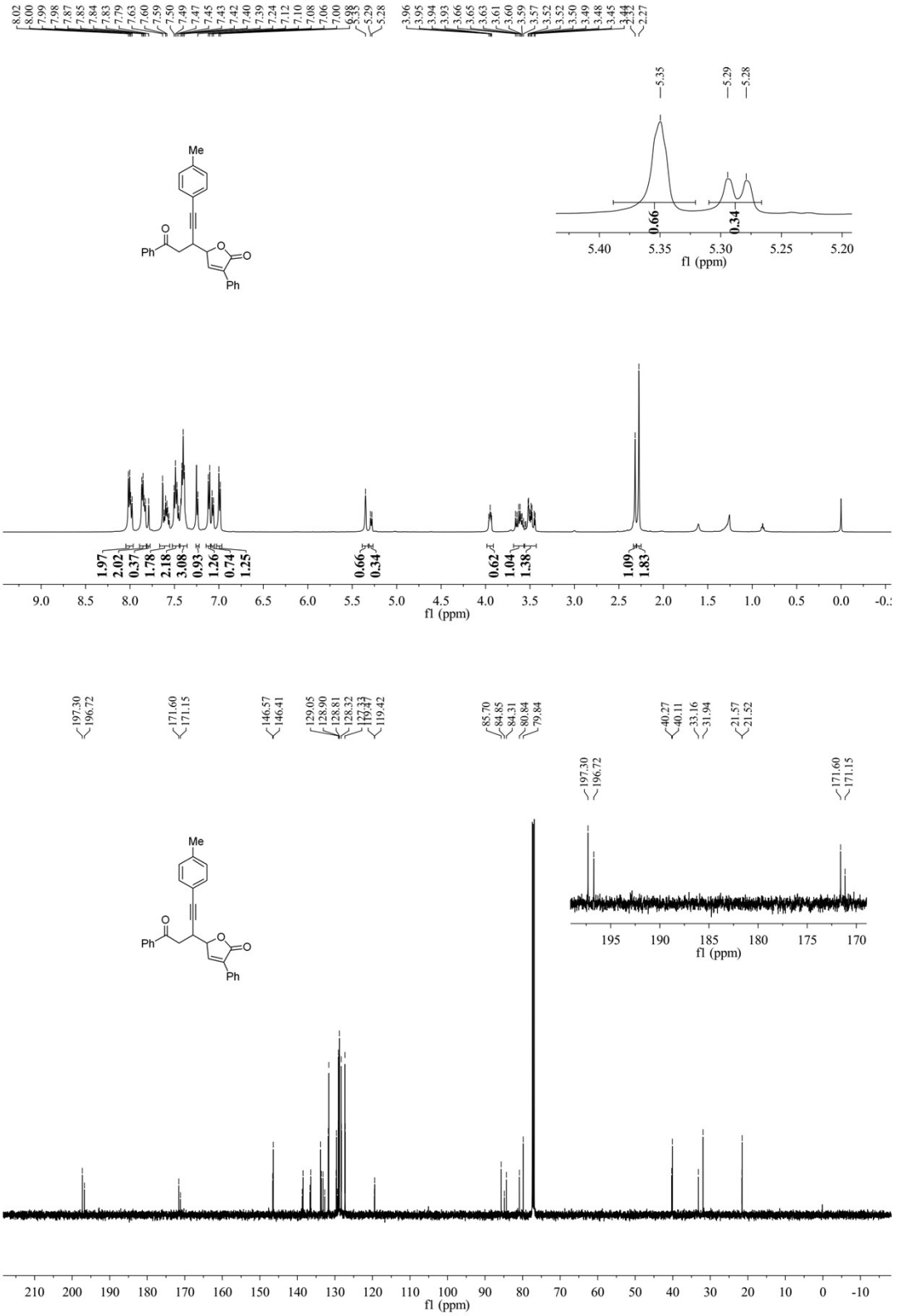
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4q**



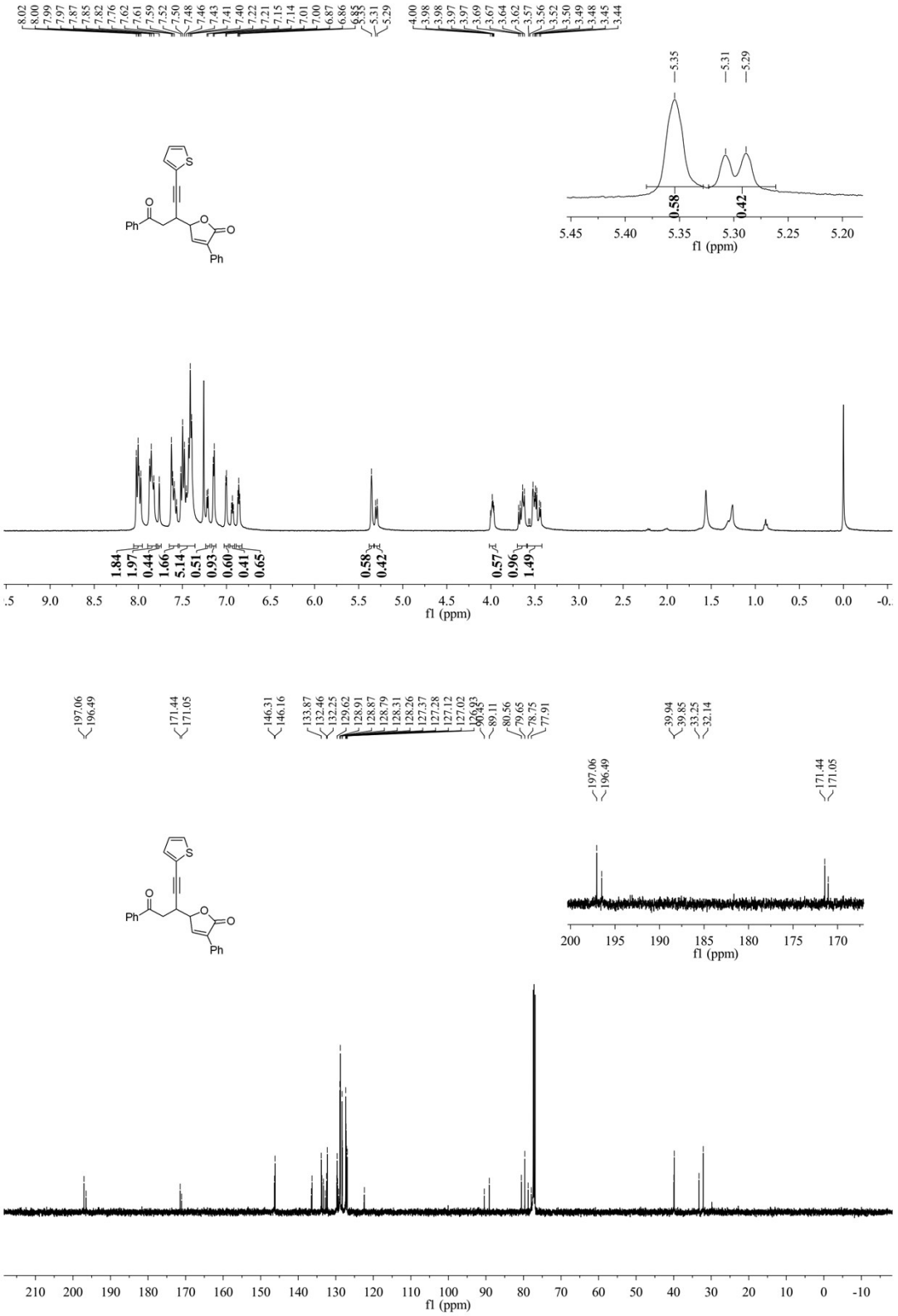
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4r**



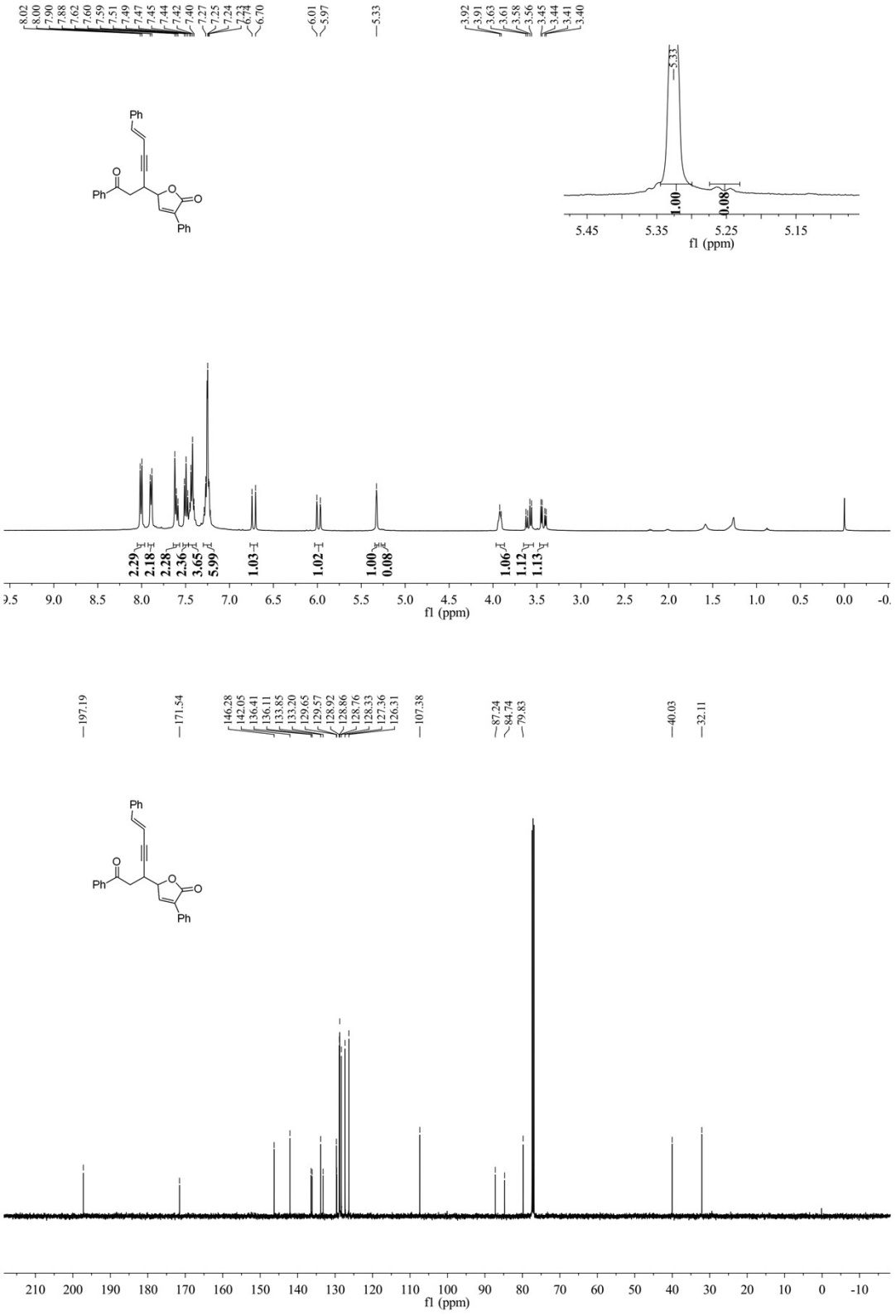
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4s**



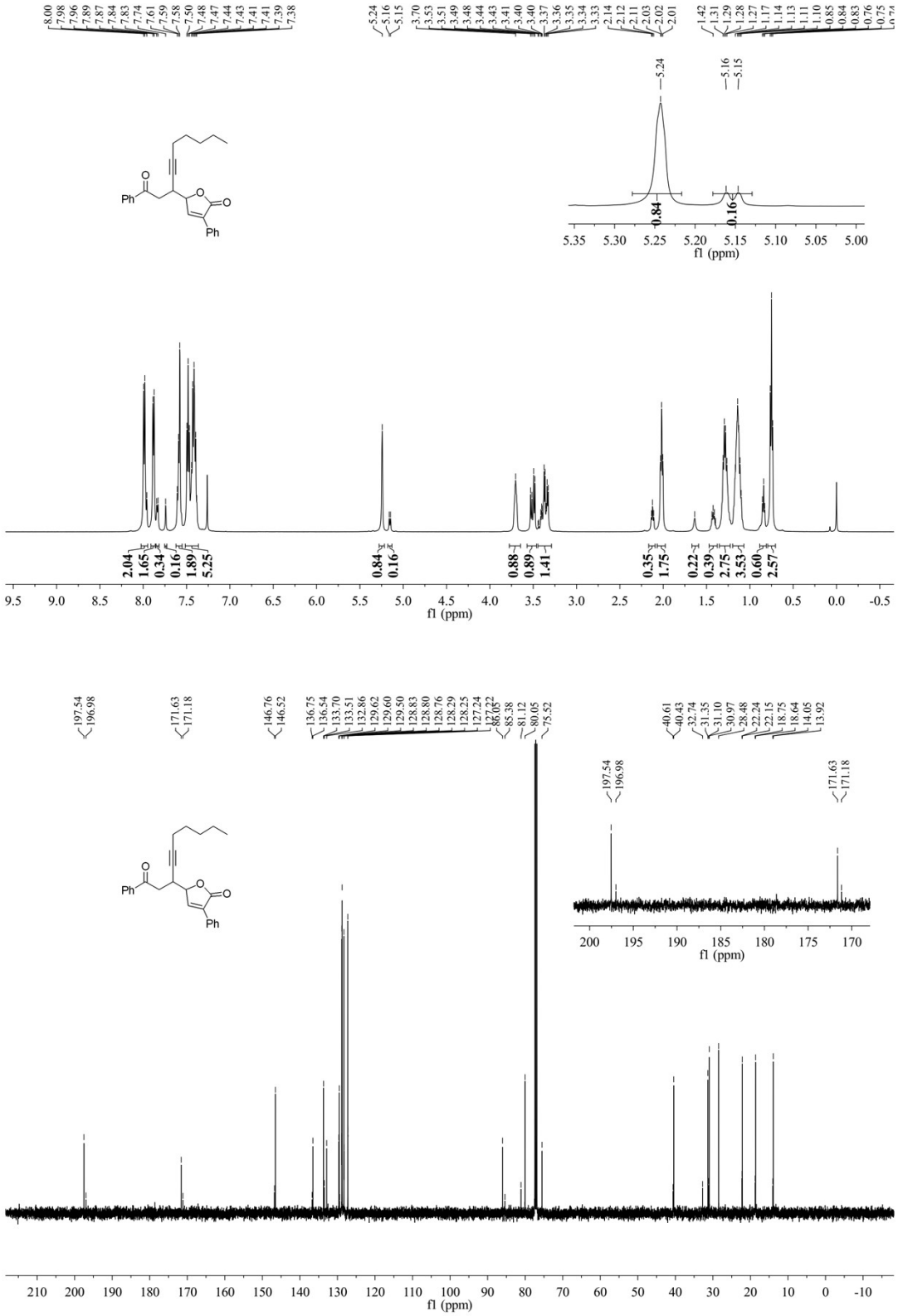
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4t**



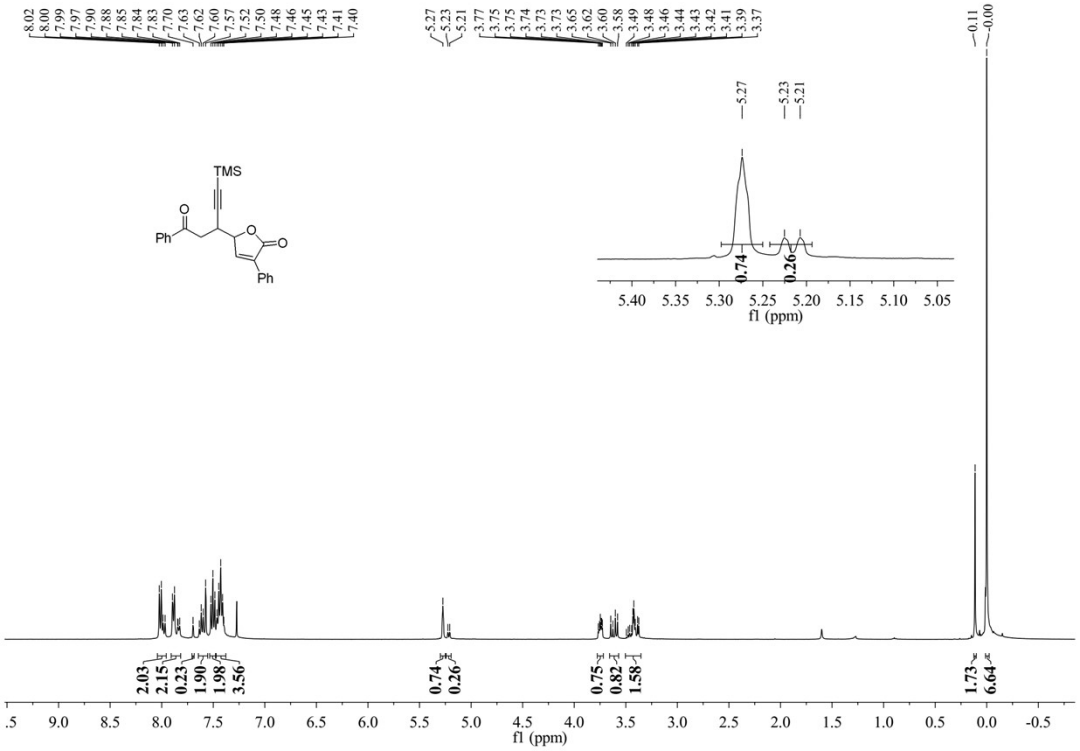
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4u**

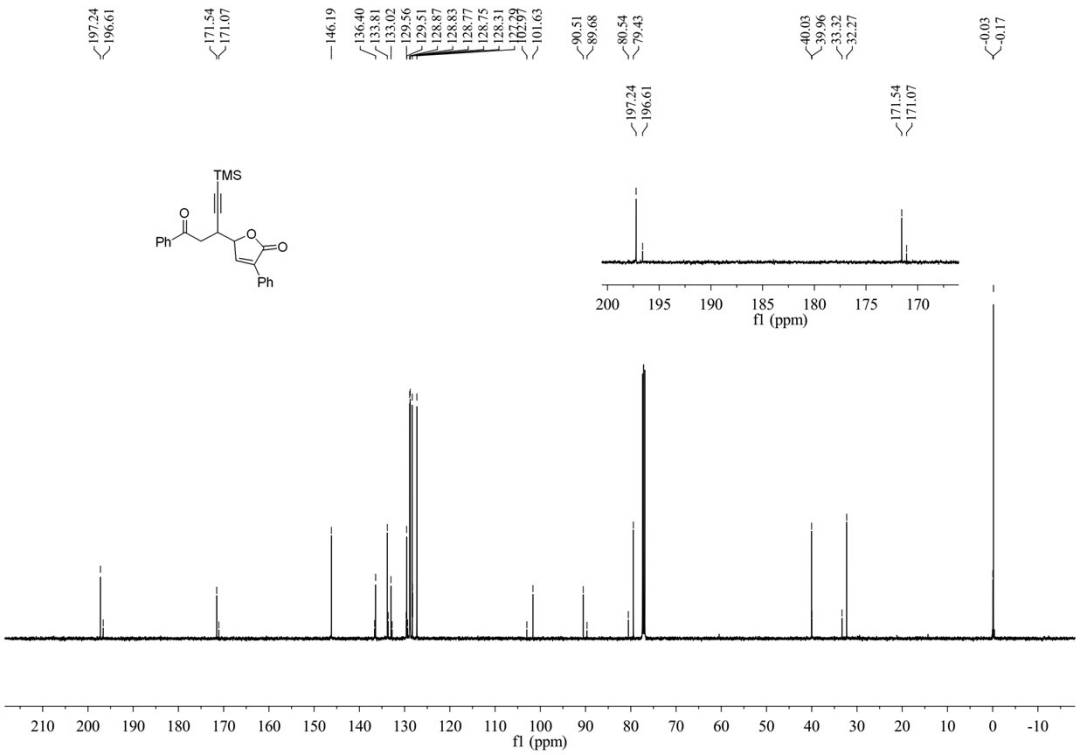


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4v**

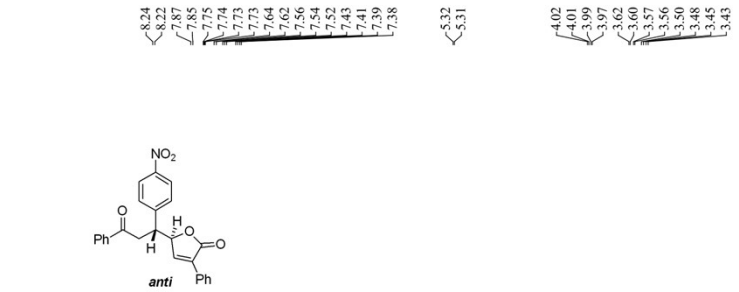


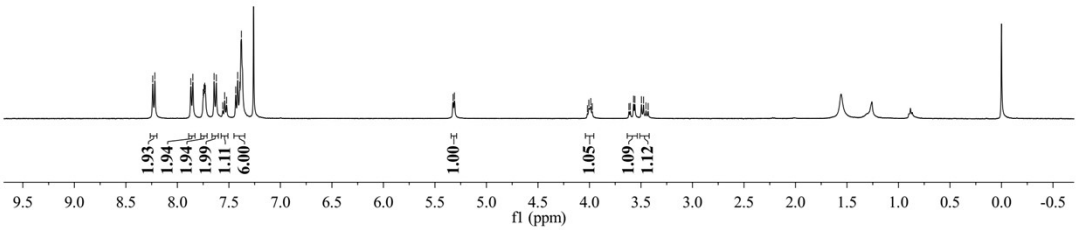
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4w**

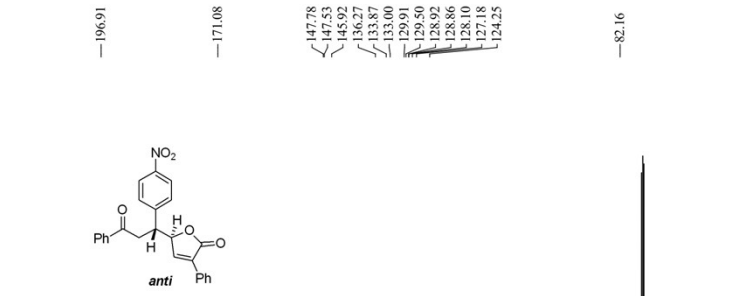


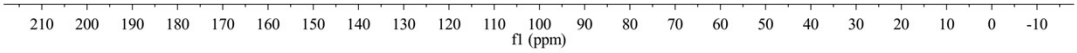


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for *anti*-**4x**

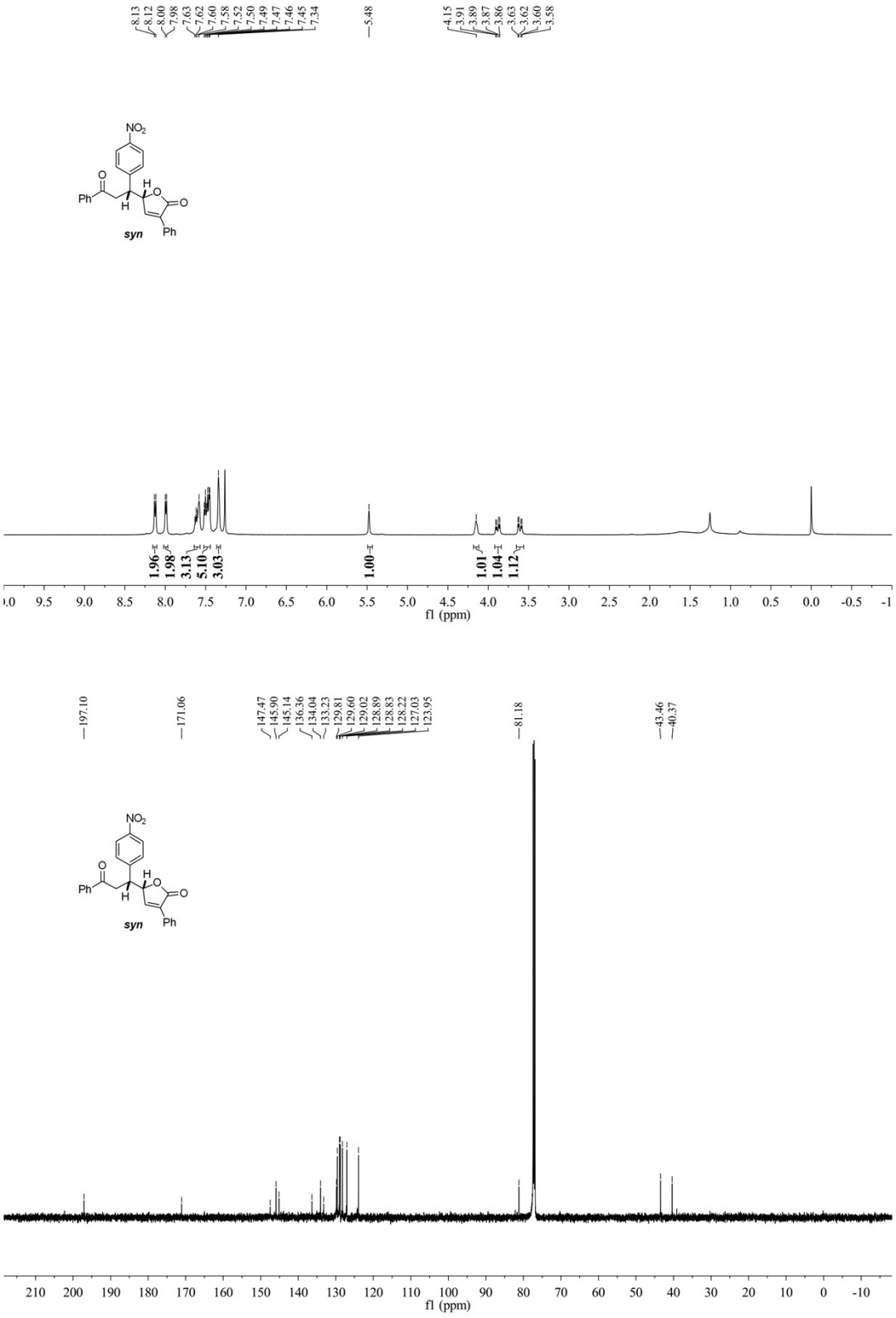




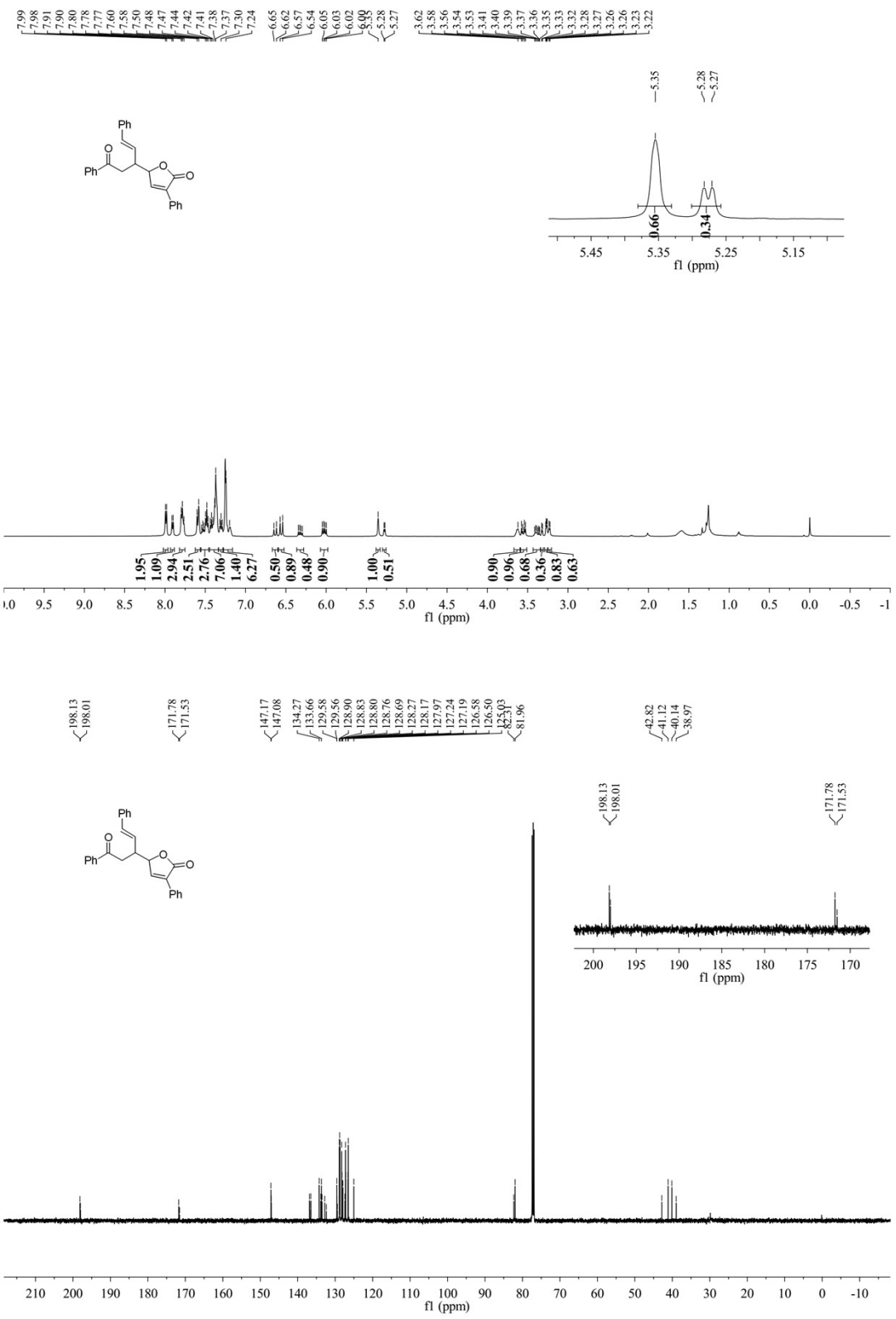




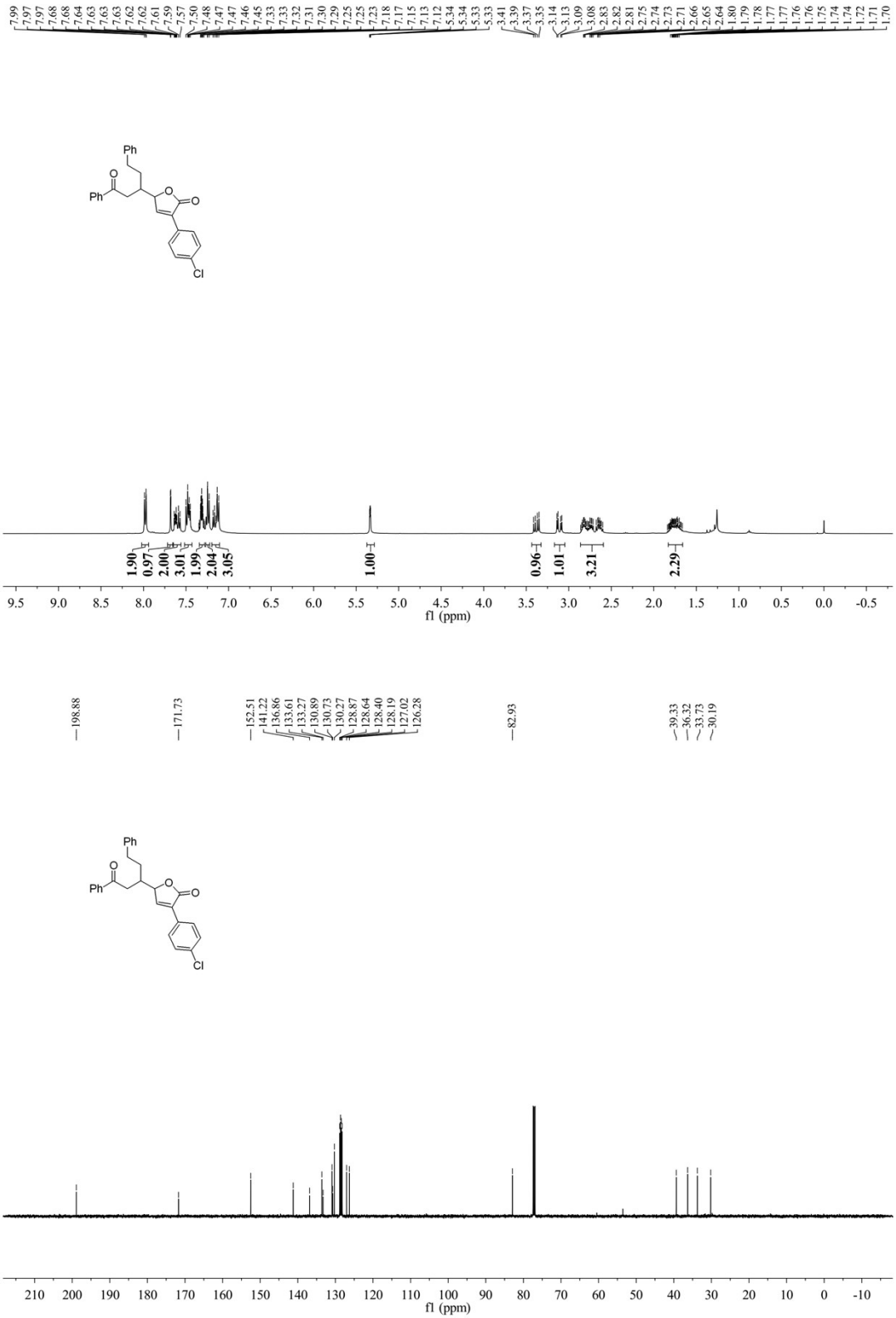
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for *syn*-**4x**



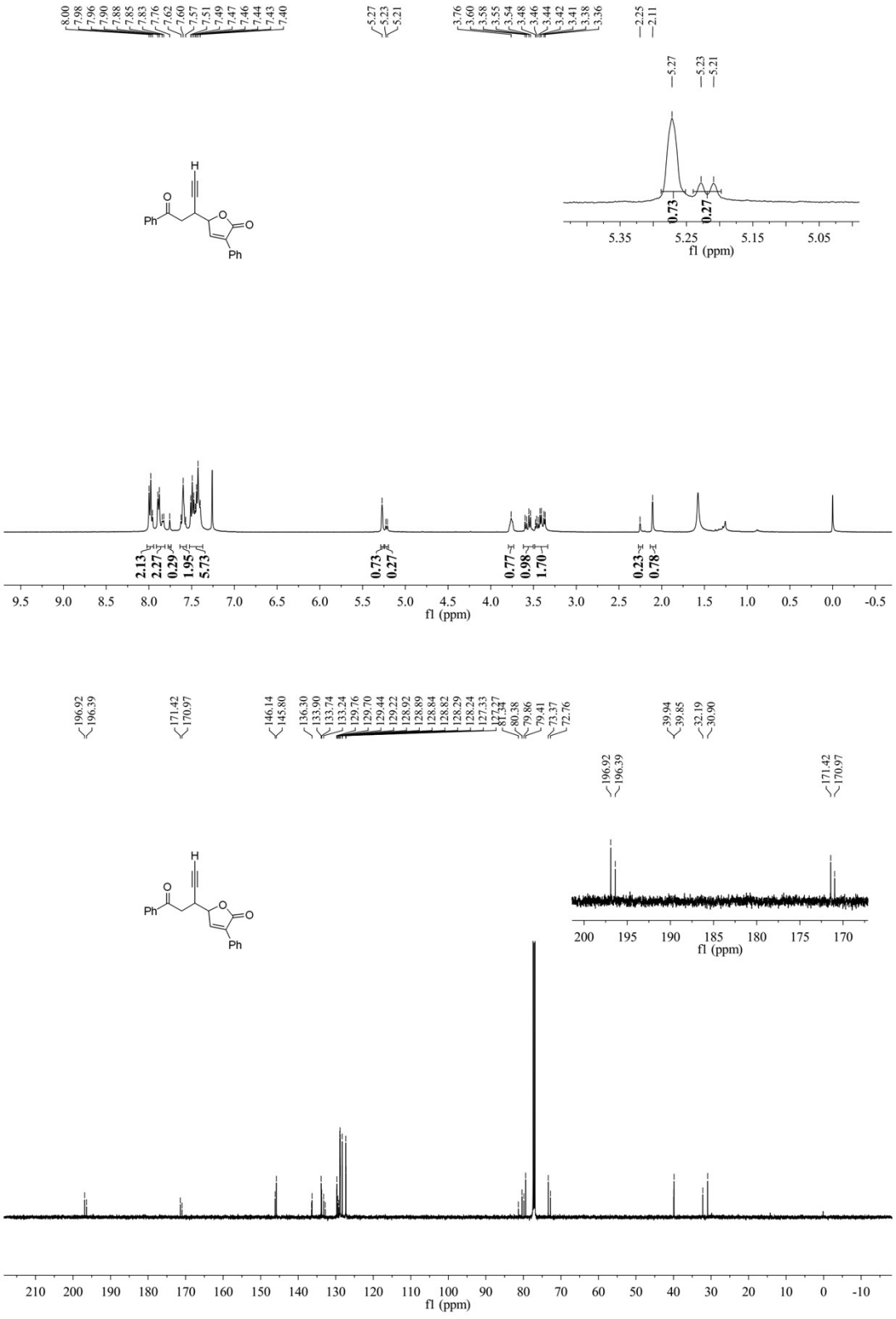
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **4y**



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **6c**



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **6d**



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for **6e**