Electronic Supporting Information

Regio- and Stereoselective Divergent Cross-Coupling of Alkynes and Disubstituted Alkenes via Photoredox Cobalt Dual Catalysis

Shi-Qi Zhang,[a,e] Yan-Lin Li,[a] Kun Cui,[a] Chen Chen,[a,e] Zheng-Yang Gu,[c] Hu He*[,d] and Ji-Bao Xia*[,a,b]

[a]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), University of Chinese Academy of Sciences, Chinese Academy of Sciences, Lanzhou 730000, China.

[b]College of Material Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 311121, Zhejiang, China

[c]College of Textiles and Clothing, Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Jiangsu, China

[d]Hangzhou SynRx Therapeutics Biomedical Technology Co., Hangzhou, 311121, China

[e]University of Chinese Academy of Sciences, Beijing, 100049, China

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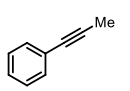
I. General Information

All reactions were carried out under nitrogen (N_2) atmospheric in oven-dried Schlenk tube if otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ^oC). The High Resolution MS analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. GC-MS spectra were recorded on a GCMS-QP2010 SE with helium gas as the carrier gas. NMR spectra were recorded on a 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference and $CDCl_3$ and d_6-DMSO as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of $CDCl_3$ (δ 7.26) and d_6-DMSO (δ 2.50). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet), q (quartet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); qd (quartet of doublets); br (broad). Carbon nuclear magnetic resonance spectra (13C NMR) were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.16) and d_6-DMSO (δ 39.52). The other materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, Bidepharm or other commercial suppliers and used as received unless otherwise noted. The photoreactors used in this research were bought from GeAoChem (Blue LEDs, light intensity = 42 mw/cm^2 , 5 W for every light bulb; every Schlenk tube was irradiated by 1 light bulb from the side).

II. Investigated Substrates

Alkynes



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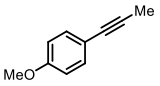

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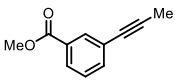

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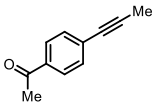

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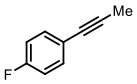

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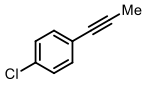

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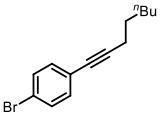

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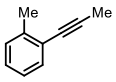

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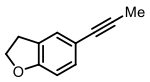

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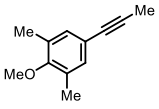

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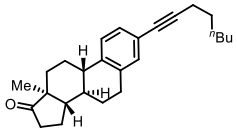

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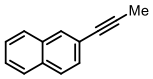

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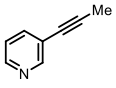

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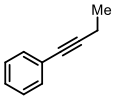

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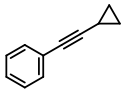

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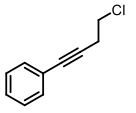

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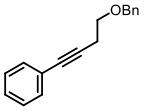

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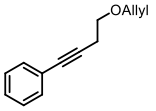

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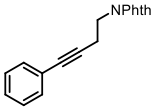

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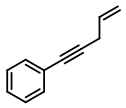

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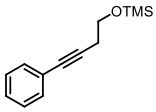

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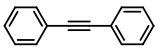

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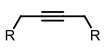
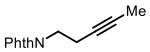


S22, R = Me (for product **26**)
S23, R = H (for product **27**)



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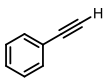
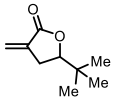


S25 (for product **29**)

Alkenes

2 (for products **3** and **4**)

S26 (for product **30**)



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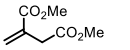

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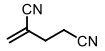

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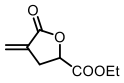


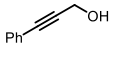
S30 (for products **3** and **40**)

S31 (for product **41**)

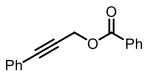
S32 (for product **42**)

S33 (for product **44**)

Unsuccessful Substrates for Ene Type Reaction



N.R.



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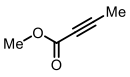

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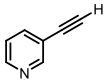


trace

trace

N.R.

N.R.

N.R.

N.R.

Unsuccessful Substrates for Reductive Coupling Reaction

trace

trace

N.R.

N.R.

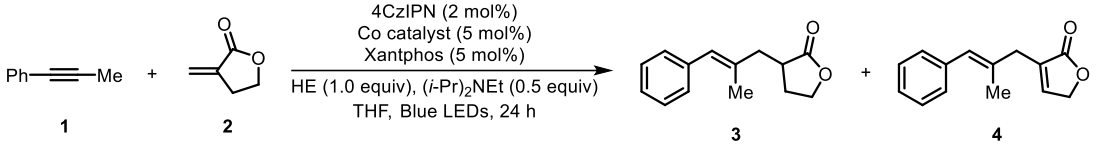
trace

Preparation of Starting Materials

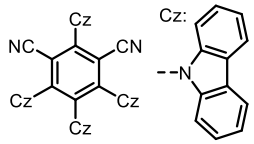
Known alkyne S1,[1] S2-S8,[2] S9,[3] S10,[2] S11,[1] S12,[4] S14,[5] S15,[6] S16-S18,[7] S20,[8] S24,[3] S26-S27, S30[9], S31[10], S33[11] were prepared according to the reported methods. The other alkynes and alkenes are commercially available and used as received from vendors.

III. Optimization of the Reaction Conditions

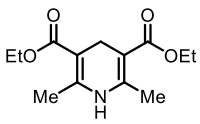
Table S1. The Effect of the Cobalt Catalyst [a]



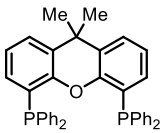
1 2 3 4



4CzIPN



Hantzsch ester (HE)

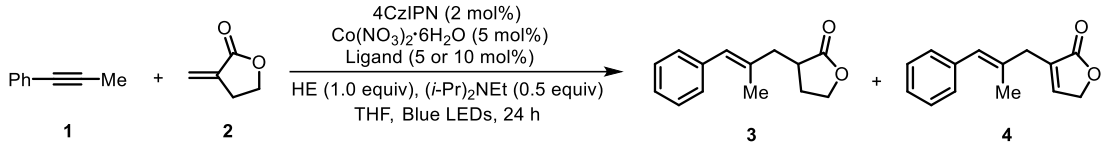


Xantphos

Entry	Co catalyst	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	$CoCl_2$	65	trace
2	$CoBr_2$	54	trace
3	CoI_2	34	0
4	$Co(DME)Br_2$	44	0
5	CoC_2O_4	0	0
6	$Co_2(CO)_8$	0	0
7	$Co(acac)_2$	46	0
8	$Co(OAc)_2$	32	0
9	$Co(BF_4)_2{\cdot}6H_2O$	61	0
10	**$Co(NO_3)_2{\cdot}6H_2O$**	**68 (59)**	**5**

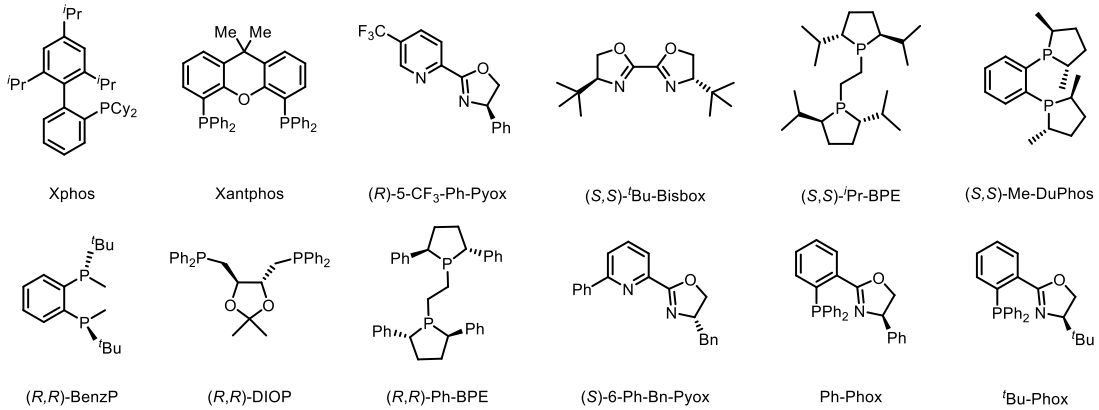
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), 4CzIPN (2 mol%), Co catalyst (5 mol%), Xantphos (5 mol%), HE (1.0 equiv), (*i*-Pr)$_2$NEt (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard and isolated yield in the parenthesis. 4CzIPN: 2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyanobenzene; HE: Hantzsch ester; THF: Tetrahydrofuran; DME: 1,2-dimethoxyethane.

Table S2. The Effect of the Ligands[a]



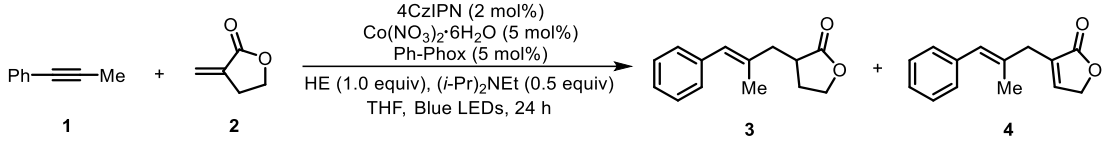
1 2 3 4

Entry	Ligand (x mol %)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	-	44	trace
2	PPh_3 (10)	0	0
3	PCy_3 (10)	0	0
4	Xphos (10)	0	trace
5	dppe (5)	trace	50
6	dppp (5)	trace	62
7	**Xantphos** (5)	**68**	**trace**
8	2,2'-bipyridine (5)	0	0
9	**Ph-Phox** (5)	**5**	**66**
10	^{t}Bu-Phox (5)	0	0
11	(*R*)-5-CF_3-Ph-Pyox (5)	15	0
12	(*S*,*S*)-^{t}Bu-Bisbox (5)	21	0
13	(*S*,*S*)-^{i}Pr-BPE (5)	N.R.	0
14	(*S*,*S*)-Me-DuPhos (5)	N.R.	0
15	(*R*,*R*)-BenzP (5)	N.R.	0
16	(*R*,*R*)-DIOP (5)	N.R.	0
17	(*R*,*R*)-Ph-BPE (5)	17 (5% ee)[c]	<5
18	(*S*)-6-Ph-Bn-Pyox (5)	11 (12% ee)[c]	trace



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), 4CzIPN (2 mol%), $Co(NO_3)_2 \cdot 6H_2O$ (5 mol%), ligand (5 or 10 mol%), HE (1.0 equiv), $(i\text{-Pr})_2NEt$ (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard. [c]Determined by chiral HPLC analysis.

Table S3. The Effect of the Ratio of Substrates[a]

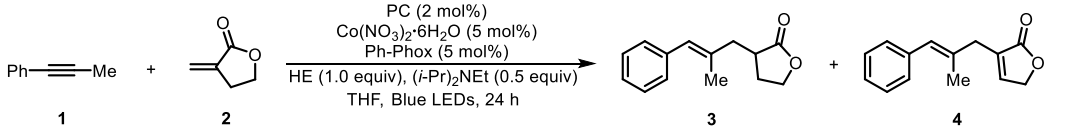


1 2 3 4

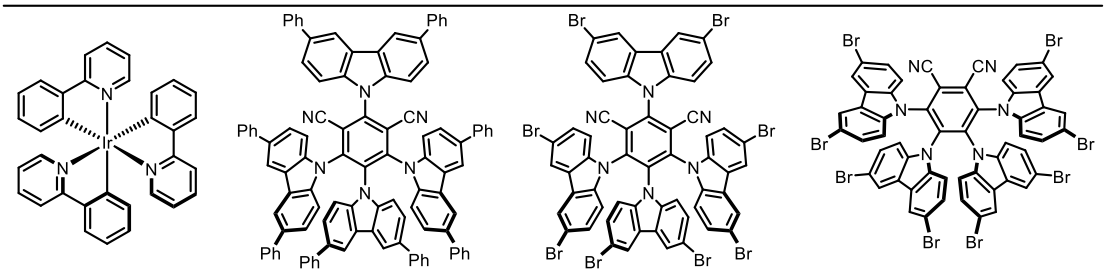
Entry	**2** (x equiv)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	2.0	5	66
2	3.0	5	82 (80)
3	4.0	5	84 (81)

[a]Reaction conditions: **1** (0.2 mmol), **2** (x equiv), 4CzIPN (2 mol%), $Co(NO_3)_2·6H_2O$ (5 mol%), Ph-Phox (5 mol%), HE (1.0 equiv), $(i\text{-Pr})_2$NEt (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard and isolated yield in the parenthesis.

Table S4. The Effect of Photocatalysts[a]



1 2 3 4

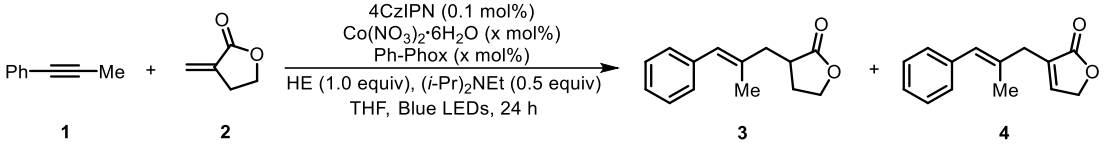


fac-[Ir(ppy)$_3$] 4CzIPN-Ph 4CzIPN-Br 4CzPN-Br

Entry	Photocatalyst (PC)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	4CzIPN	<5	82
2	4CzIPN-Ph	<5	22
3	4CzIPN-Br	<5	82
4	4CzPN-Br	<5	78
5	*fac*-[Ir(ppy)$_3$]	<5	trace
6[d]	4CzIPN	<5	79

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), photocatalyst (PC) (2 mol%), $Co(NO_3)_2·6H_2O$ (5 mol%), Ph-Phox (5 mol%), HE (1.0 equiv), $(i\text{-Pr})_2$NEt (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by ^{1}H NMR analysis with $C_2H_2Cl_4$ as an internal standard. [d]With 4CzIPN (0.1 mol%) was the photocatalyst

Table S5. The Effect of the Catalyst loading[a]

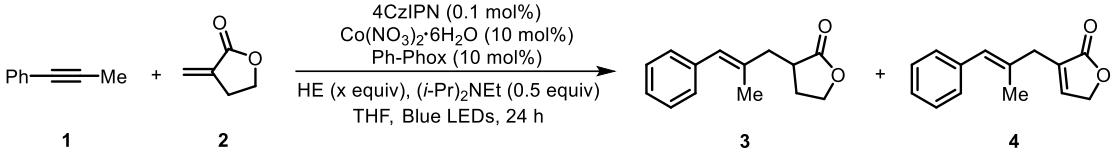


1 2 3 4

Entry	$Co(NO_3)_2$ $6H_2O$ (x mol%)	Ph-Phox (x mol%)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	10	10	<5	86
2	5	5	<5	79
3	1	1	<5	30

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), 4CzIPN (0.1 mol%), $Co(NO_3)_2·6H_2O$ (x mol%), Ph-Phox (x mol%), HE (1.0 equiv), $(i\text{-Pr})_2$NEt (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard.

Table S6. The Effect of the Amount of HE[a]

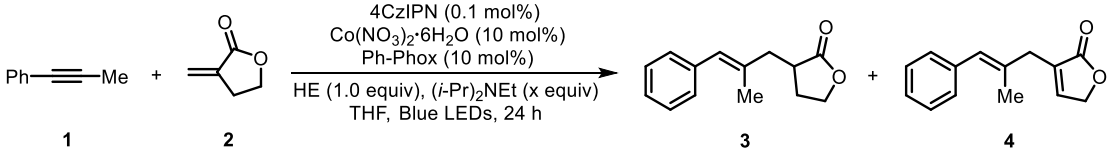


1 2 3 4

Entry	HE (x equiv)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	1.0	<5	86
2	0.5	0	38
3	0.1	0	27

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), 4CzIPN (0.1 mol%), $Co(NO_3)_2·6H_2O$ (10 mol%), Ph-Phox (10 mol%), HE (x equiv), $(i\text{-Pr})_2$NEt (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard.

Table S7. The Effect of the Amount of $(i\text{-Pr})_2$NEt[a]

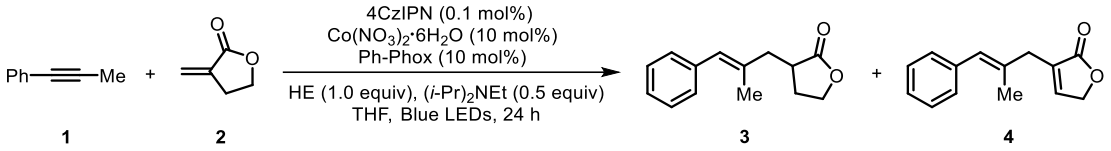


1 2 3 4

Entry	$(i\text{-Pr})_2$NEt (x equiv)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	0.50	<5	86
2	0.12	5.	29
3	1.00	5	70

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), 4CzIPN (0.1 mol%), $Co(NO_3)_2·6H_2O$ (10 mol%), Ph-Phox (10 mol%), HE (1.0 equiv), $(i\text{-Pr})_2$NEt (x equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard.

Table S8. The Control Experiments[a]



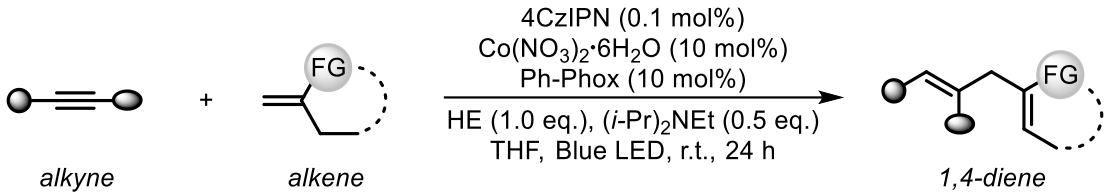
1 2 3 4

Entry	variations from the above conditions	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	none	<5	86
2	no photocatalyst	0	0
3	no Co or ligand	0	0
4	no HE	8	0
5	no $(i\text{-Pr})_2$NEt	0	0
6	no light	0	0

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), 4CzIPN (0.1 mol%), $Co(NO_3)_2 \cdot 6H_2O$ (10 mol%), Ph-Phox (10 mol%), HE (1.0 equiv), $(i\text{-Pr})_2$NEt (0.5 equiv), THF (3 mL), 5 W blue LEDs, r.t., 24 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard.

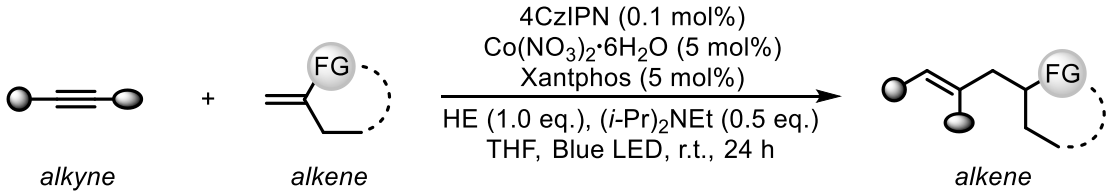
IV. General Procedure and Characterization Data

(1) General Procedure A of the Ene-type Coupling of Alkynes and Disubstituted Alkenes

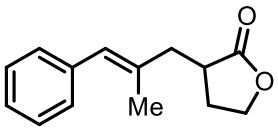


To an oven-dried Schlenk tube (25 mL) was added $Co(NO_3)_2 \cdot 6H_2O$ (0.02 mmol, 5.8 mg) and HE (0.2 mmol, 52.3 mg). The Schlenk tube was transferred into the glovebox. Then Ph-Phox (0.02 mmol, 8.2 mg), THF (3 mL), 4CzIPN (0.0002 mmol, 1 mL, 0.0002M in THF), $(i\text{-Pr})_2$NEt (0.1 mmol, 12.9 mg), alkynes (0.2 mmol, 1.0 equiv) and alkenes (0.6 mmol, 3.0 equiv) were sequentially added into the Schlenk tube. Then, the sealed Schlenk tube was taken out from the glovebox and stirred at room temperature with irradiation of 5 W Blue LED for 24 h. Then, the crude mixture was concentrated under reduced pressure and purified by column chromatography over silica gel (petroleum ether/EtOAc) to give the desired product.

(2) General Procedure B of the Reductive Coupling of Alkynes and Disubstituted Alkenes



To an oven-dried Schlenk tube (25 mL) was added the $Co(NO_3)_2 \cdot 6H_2O$ (0.01 mmol, 2.9 mg) and HE (0.2 mmol, 52.3 mg). The Schlenk tube was transferred into the glovebox. Then Xantphos (0.01 mmol, 5.8 mg), THF (3 mL), 4CzIPN (0.0002 mmol, 1 mL, 0.0002M in THF), $(i\text{-Pr})_2$NEt (0.1 mmol, 12.9 mg), alkynes (0.2 mmol, 1.0 equiv) and alkenes (0.6 mmol, 3.0 equiv) were sequentially added into the Schlenk tube. Then, the sealed Schlenk tube was taken out from the glovebox and stirred at room temperature with irradiation of 5 W Blue LED for 24 h. Then, the crude mixture was concentrated under reduced pressure and purified by column chromatography over silica gel (petroleum ether/EtOAc) to give the desired product.

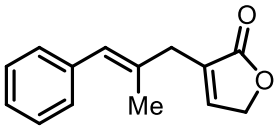


(*E*)-3-(2-Methyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (3). Synthesized according to the **General Procedure B** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **3** as a colorless oil (25.5 mg, 59% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.24 – 7.20 (m, 3H), 6.34 (s, 1H), 4.38 (ddd, *J* = 8.8, 8.8, 3.2 Hz, 1H), 4.24 (ddd, *J* = 9.2, 9.2, 6.8 Hz, 1H), 2.85 – 2.77 (m, 2H), 2.38 – 2.34 (m, 1H), 2.25 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.04 (ddd, *J* = 18.0, 12.8, 9.2 Hz, 1H), 1.89 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 137.8, 135.4, 128.9, 128.3, 127.6, 126.5, 66.7, 41.5, 38.1, 28.4, 17.6.

HRMS (ESI): Calcd for $[C_{14}H_{17}O_2]^+$ $[M+H]^+$ 217.1223, Found 217.1223.

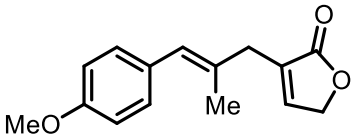


(*E*)-3-(2-Methyl-3-phenylallyl)furan-2(5*H*)-one (4). Synthesized according to the **General Procedure A** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **4** as a colorless oil (34.7 mg, 81% yield, >19:1 rr, >19:1 *E/Z*). The *E*-configuration of the double bond in the product is confirmed by ^{1}H-^{1}H NOESY spectrum.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.26 – 7.19 (m, 4H), 6.40 (s, 1H), 4.85 – 4.78 (m, 2H), 3.16 (s, 2H), 1.89 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 145.8, 137.8, 134.2, 132.7, 128.9, 128.3, 128.1, 126.5, 70.3, 36.1, 18.0.

HRMS (ESI): Calcd for $[C_{14}H_{15}O_2]^+$ $[M+H]^+$ 215.1067, Found 215.1063.

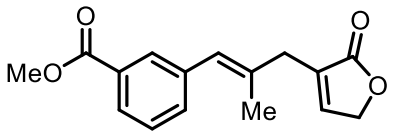


(*E*)-3-(3-(4-Methoxyphenyl)-2-methylallyl)furan-2(5*H*)-one (5). Synthesized according to the **General Procedure A** with 1-(4-methoxy)-phenylpropyne (0.2 mmol, 29.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **5** as a colorless oil (27.3 mg, 56% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.18 (m, 3H), 6.89 – 6.87 (m, 1H), 6.86 – 6.85 (m, 1H), 6.33 (s, 1H), 4.82 (d, *J* = 2.0 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 3.13 (s, 2H), 1.87 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 158.2, 145.7, 132.9, 132.6, 130.4, 130.1, 127.6, 113.7, 70.3, 55.4, 36.2, 17.9.

HRMS (ESI): Calcd for$[C_{15}H_{16}O_3Na]^+$ $[M+Na]^+$ 267.0992, Found 267.0991.

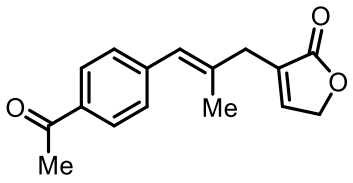


Methyl (*E*)-3-(2-methyl-3-(2-oxo-2,5-dihydrofuran-3-yl)prop-1-en-1-yl)benzoate (6). Synthesized according to the **General Procedure A** with methyl 3-(prop-1-yn-1-yl)benzoate (0.2 mmol, 34.8 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **6** as a colorless oil (48.9 mg, 90% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.89 – 7.86 (m, 1H), 7.43 – 7.38 (m, 2H), 7.22 – 7.21 (m, 1H), 6.40 (s, 1H), 4.83 (d, *J* = 2.0 Hz, 1H), 4.82 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.16 (s, 2H), 1.88 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 167.2, 146.0, 138.1, 135.6, 133.4, 132.4, 130.2, 123.0, 128.3, 127.7, 127.1, 70.3, 52.3, 36.0, 18.0.

HRMS (ESI): Calcd for $[C_{16}H_{16}O_4Na]^+$ $[M+Na]^+$ 295.0941, Found 295.0936.

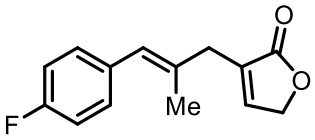


(*E*)-3-(3-(4-Acetylphenyl)-2-methylallyl)furan-2(5*H*)-one (7). Synthesized according to the **General Procedure A** with 1-(4-acetyl)-phenylpropyne (0.2 mmol, 31.6 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **7** as a colorless oil (26.8 mg, 52% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.22 (m, 1H), 6.42 (s, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 3.18 (s, 2H), 2.59 (s, 3H), 1.91 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 174.1, 146.1, 142.8, 136.9, 135.2, 132.3, 129.1, 128.4, 127.3, 70.3, 36.2, 26.7, 18.2.

HRMS (ESI): Calcd for $[C_{16}H_{16}O_3Na]^+$ $[M+Na]^+$ 279.0992, Found 279.0996.



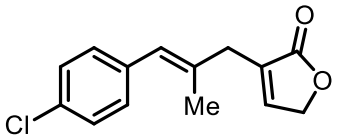
(*E*)-3-(3-(4-Fluorophenyl)-2-methylallyl)furan-2(5*H*)-one (8). Synthesized according to the **General Procedure A** with 1-(4-fluoro)-phenylpropyne (0.2 mmol, 26.8 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **8** as a colorless oil (36.6 mg, 79% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 3H), 7.01 – 6.98 (m, 2H), 6.35 (s, 1H), 4.83 (d, J = 1.6 Hz, 1H), 4.82 (d, J = 2.0 Hz, 1H), 3.14 (s, 2H), 1.85 (d, J = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 161.5 (d, J_F = 244.1 Hz), 145.9, 134.2, 133.8 (d, J_F = 3.4 Hz), 132.6, 130.5 (d, J_F = 17.9 Hz), 127.0, 115.1 (d, J_F = 21.2 Hz), 70.3, 36.0, 17.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ –115.8.

HRMS (ESI): Calcd for $[C_{14}H_{14}FO_2]^+$ $[M+H]^+$ 233.0972, Found 233.0974.

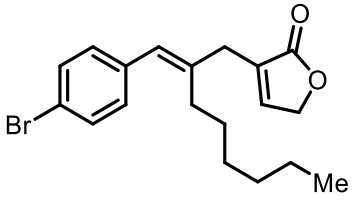


(*E*)-3-(3-(4-Chlorophenyl)-2-methylallyl)furan-2(5*H*)-one (9). Synthesized according to the **General Procedure A** with 1-(4-chloro)-phenylpropyne (0.2 mmol, 30.0 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **9** as a colorless oil (34.1 mg, 69% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.21 – 7.16 (m, 3H), 6.34 (s, 1H), 4.89 – 4.78 (m, 2H), 3.15 (s, 2H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 146.0, 136.2, 135.0, 132.4, 132.2, 130.2, 128.4, 126.9, 70.3, 36.0, 17.9.

HRMS (ESI): Calcd for $[C_{14}H_{13}ClO_2Na]^+$ $[M+Na]^+$ 271.0496, Found 271.0490.

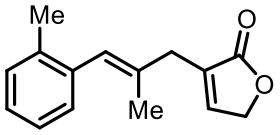


(*E*)-3-(2-(4-Bromobenzylidene)octyl)furan-2(5*H*)-one (10). Synthesized according to the **General Procedure A** with 1-bromo-4-(oct-1-yn-1-yl)benzene (0.2 mmol, 52.8 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **10** as a colorless oil (39.8 mg, 55% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.16 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 4.86 – 4.79 (m, 2H), 3.14 (s, 2H), 2.20 – 2.16 (m, 2H), 1.48 – 1.42 (m, 2H), 1.38 – 1.16 (m, 6H), 0.86 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 145.9, 140.1, 136.7, 132.9, 131.4, 130.4, 127.0, 120.4, 70.3, 32.9, 31.7, 30.9, 29.4, 28.3, 22.7, 14.2.

HRMS (ESI): Calcd for $[C_{19}H_{23}BrO_2Na]^+$ $[M+Na]^+$ 385.0774, Found 385.0789.

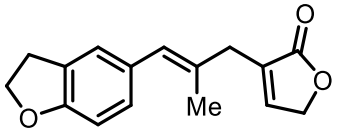


(*E*)-3-(2-Methyl-3-(*o*-tolyl)allyl)furan-2(5*H*)-one (11). Synthesized according to the **General Procedure A** with 1-(2-methyl)-phenylpropyne (0.2 mmol, 26.0 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **11** as a colorless oil (27.8 mg, 61% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.21 (m, 1H), 7.18 – 7.11 (m, 4H), 6.38 (s, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.82 (d, *J* = 1.2 Hz, 1H), 3.18 (s, 2H), 2.24 (s, 3H), 1.72 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 145.6, 137.0, 136.5, 134.1, 132.8, 129.9, 129.3, 127.3, 126.9, 125.4, 70.3, 35.4, 20.0, 17.6.

HRMS (ESI): Calcd for $[C_{15}H_{16}O_2Na]^+$ $[M+Na]^+$ 251.1043, Found 251.1036.

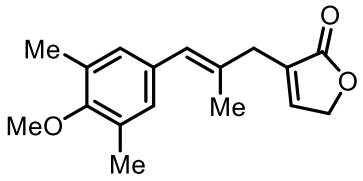


(*E*)-3-(3-(2,3-Dihydrobenzofuran-5-yl)-2-methylallyl)furan-2(5*H*)-one (12). Synthesized according to the **General Procedure A** with methyl 5-(prop-1-yn-1-yl)-2,3-dihydrobenzofuran (0.2 mmol, 31.6 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **12** as a colorless oil (40.8 mg, 80% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.10 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.33 (s, 1H), 4.82 (d, *J* = 2.0 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 4.57 (t, *J* = 8.8 Hz, 2H), 3.20 (t, *J* = 8.8 Hz, 2H), 3.12 (s, 2H), 1.87 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 158.8, 145.6, 133.0, 132.1, 130.4, 128.9, 128.0, 127.0, 125.5, 109.0, 71.4, 70.3, 36.2, 29.8, 18.0.

HRMS (ESI): Calcd for $[C_{16}H_{16}O_3Na]^+$ [M+Na]$^+$ 279.0992, Found 279.0986.

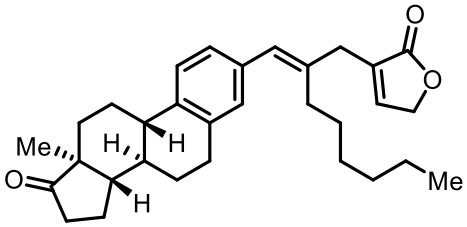


(*E*)-3-(3-(4-Methoxy-3,5-dimethylphenyl)-2-methylallyl)furan-2(5*H*)-one (13). Synthesized according to the **General Procedure A** with 2-methoxy-1,3-dimethyl-5-(prop-1-yn-1-yl)benzene (0.2 mmol, 34.8 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **13** as a colorless oil (36.4 mg, 67% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.17 (m, 1H), 6.90 (s, 2H), 6.28 (s, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 4.80 (d, *J* = 2.0 Hz, 1H), 3.71 (s, 3H), 3.12 (s, 2H), 2.27 (s, 6H), 1.87 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 155.6, 145.7, 133.4, 133.2, 132.8, 130.5, 129.4, 127.7, 70.3, 59.8, 36.1, 18.0, 16.2.

HRMS (ESI): Calcd for $[C_{17}H_{20}O_3Na]^+$ [M+Na]$^+$ 295.1305, Found 295.1297.

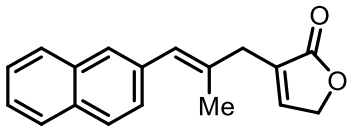


3-((*E*)-2-(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclo-penta[*a*]phenanthren-3-yl)methylene)octyl)furan-2(5*H*)-one (14). Synthesized according to the **General Procedure A** with methyl (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(oct-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17 H-cyclopenta[*a*]phenanthren-17-one (0.2 mmol, 72.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **14** as a colorless oil (44.6 mg, 48% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 1H), 6.30 (s, 1H), 4.84 – 4.76 (m, 2H), 3.13 (s, 2H), 2.91 – 2.89 (m, 2H), 2.54 – 2.48 (m, 1H), 2.24 – 1.95 (m, 4H), 1.63 – 1.46 (m, 8H), 1.27 – 1.26 (m, 7H), 0.92 – 0.86 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.1, 174.3, 145.7, 138.7, 138.2, 136.3, 135.3, 133.2, 129.3, 128.0, 126.1, 125.3, 70.3, 50.6, 48.1, 44.5, 38.3, 36.0, 33.0, 31.7, 31.0, 29.6, 29.5, 28.4, 26.7, 25.8, 22.7, 21.7, 14.2, 14.0.

HRMS (ESI): Calcd for $[C_{31}H_{41}O_3]^+$ $[M+H]^+$ 461.3050, Found 461.3044.

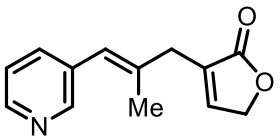


(*E*)-3-(2-Methyl-3-(naphthalen-2-yl)allyl)furan-2(5*H*)-one (15). Synthesized according to the **General Procedure A** with 2-(prop-1-yn-1-yl)naphthalene (0.2 mmol, 33.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **15** as a colorless oil (45.1 mg, 85% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 3H), 7.70 (s, 1H), 7.49 – 7.43 (m, 2H), 7.39 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.24 – 7.23 (m, 1H), 6.55 (s, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 3.21 (s, 2H), 1.97 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 145.9, 135.6, 134.8, 133.4, 132.7, 132.2, 128.1, 128.0, 127.7, 127.7, 127.6, 127.4, 126.2, 125.8, 70.3, 36.2, 18.1.

HRMS (ESI): Calcd for $[C_{18}H_{16}O_2Na]^+$ $[M+Na]^+$ 287.1043, Found 287.1044.

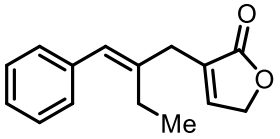


(*E*)-3-(2-Methyl-3-(pyridin-3-yl)allyl)furan-2(5*H*)-one (16). Synthesized according to the **General Procedure A** with 3-(prop-1-yn-1-yl)pyridine (0.2 mmol, 23.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **16** as a colorless oil (32.0 mg, 74% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.45 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 6.35 (s, 1H), 4.88 – 4.83 (m, 2H), 3.20 (s, 2H), 1.89 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 145.0, 147.5, 146.1, 137.0, 136.0, 133.5, 132.2, 124.4, 123.2, 70.3, 36.0, 18.0.

HRMS (ESI): Calcd for $[C_{13}H_{13}NO_2Na]^+$ $[M+Na]^+$ 238.0838, Found 238.0847.



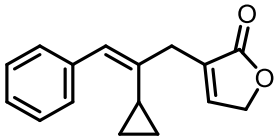
(*E*)-3-(2-Benzylidenebutyl)furan-2(5*H*)-one (17). Synthesized according to the **General Procedure A** with 1-phenyl-1-butyne (0.2 mmol, 26.0 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN

(0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **17** as a colorless oil (30.2 mg, 66% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.16 (m, 4H), 6.35 (s, 1H), 4.82 (d, *J* = 1.6 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 3.17 – 3.15 (m, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 1.10 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 145.9, 140.2, 137.7, 132.9, 128.6, 128.3, 127.8, 126.6, 70.3, 32.3, 23.9, 13.1.

HRMS (ESI): Calcd for $[C_{15}H_{16}O_2Na]^+$ $[M+Na]^+$ 251.1043, Found 251.1052.

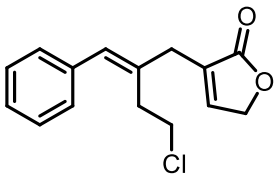


(*Z*)-3-(2-Cyclopropyl-3-phenylallyl)furan-2(5*H*)-one (18). Synthesized according to the **General Procedure A** with (cyclopropylethynyl)benzene (0.2 mmol, 28.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **18** as a colorless oil (30.0 mg, 63% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.41 (m, 2H), 7.35 – 7.31 (m, 2H), 7.25 – 7.18 (m, 2H), 6.40 (s, 1H), 4.82 (d, *J* = 2.0 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 2.86 (s, 2H), 1.91 – 1.84 (m, 1H), 0.76 – 0.72 (m, 2H), 0.53 – 0.48 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 146.0, 138.2, 137.6, 133.5, 129.2, 129.2, 128.1, 126.5, 70.4, 29.8, 13.1, 7.0.

HRMS (ESI): Calcd for $[C_{16}H_{16}O_2Na]^+$ $[M+Na]^+$ 263.1043, Found 263.1051.

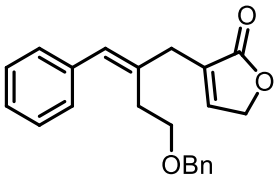


(*Z*)-3-(2-Benzylidene-4-chlorobutyl)furan-2(5*H*)-one (19). Synthesized according to the **General Procedure A** with 1-phenyl-4-chloro-1-butyne (0.2 mmol, 32.8 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **19** as a colorless oil (35.4 mg, 68% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.28 – 7.23 (m, 4H), 6.55 (s, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.24 – 3.16 (m, 2H), 2.73 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 146.4, 136.9, 134.3, 132.4, 131.6, 128.6, 128.5, 127.2, 70.4, 42.3, 33.9, 32.6.

HRMS (ESI): Calcd for $[C_{15}H_{15}ClO_2Na]^+$ $[M+Na]^+$ 285.0653, Found 285.0661.

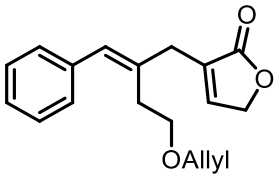


(*Z*)-3-(2-Benzylidene-4-(benzyloxy)butyl)furan-2(5*H*)-one (20). Synthesized according to the **General Procedure A** with 1-phenyl-4-benzyloxy-1-butyne (0.2 mmol, 47.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **20** as a colorless oil (28.9 mg, 43% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 9H), 7.24 – 7.20 (m, 1H), 7.19 – 7.18 (m, 1H), 6.48 (s, 1H), 4.77 (d, *J* = 2.0 Hz, 1H), 4.76 (d, *J* = 2.0 Hz, 1H), 4.48 (s, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.19 (s, 2H), 2.59 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 146.0, 138.4, 137.4, 135.4, 132.8, 130.4, 128.8, 128.5, 128.4, 127.7, 127.7, 126.8, 73.1, 70.3, 68.6, 33.3, 31.3.

HRMS (ESI): Calcd for $[C_{22}H_{23}O_3]^+$ $[M+H]^+$ 335.1642, Found 335.1647.

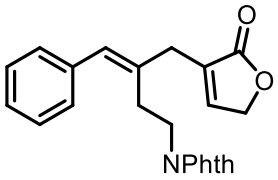


(*Z*)-3-(4-(Allyloxy)-2-benzylidenebutyl)furan-2(5*H*)-one (21). Synthesized according to the **General Procedure A** with (4-(allyloxy)but-1-yn-1-yl)benzene (0.2 mmol, 37.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **21** as a colorless oil (28.5 mg, 50% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, CDCl3) δ 7.34 – 7.06 (m, 4H), 7.23 – 7.21 (m, 2H), 6.49 (s, 1H), 5.89 (ddd, *J* = 22.8, 11.2, 6.4 Hz, 1H), 5.36 – 5.21 (m, 1H), 5.16 (d, *J* = 10.0 Hz, 1H), 4.86 – 4.77 (m, 1H), 3.94 (d, *J* = 5.6 Hz, 2H), 3.57 (t, *J* = 7.2 Hz, 2H), 3.20 (s, 2H), 2.56 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 146.0, 137.4, 135.4, 134.8, 132.9, 130.4, 128.8, 128.4, 126.8, 117.0, 72.0, 70.4, 68.6, 33.3, 31.3.

HRMS (ESI): Calcd for $[C_{18}H_{20}O_3Na]^+$ $[M+Na]^+$ 307.1305, Found 307.1297.



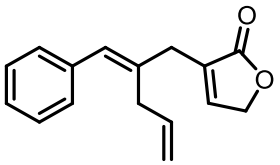
(*Z*)-2-(3-((2-Oxo-2,5-dihydrofuran-3-yl)methyl)-4-phenylbut-3-en-1-yl)isoindoline-1,3-dione (22).

Synthesized according to the **General Procedure A** with 2-(4-phenylbut-3-yn-1-yl)isoindoline-1,3-dione (0.2 mmol, 55.0 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 2:1) to give **22** as a colorless oil (34.9 mg, 47% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.70 – 7.66 (m, 2H), 7.35 (s, 1H), 7.17 – 7.07 (m, 5H), 6.46 (s, 1H), 4.90 – 4.77 (m, 2H), 3.79 (t, *J* = 7.2 Hz, 2H), 3.30 (s, 2H), 2.62 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 168.1, 146.7, 136.8, 134.3, 133.9, 132.2, 132.1, 131.1, 128.4, 128.3, 126.8, 123.2, 70.3, 36.1, 33.0, 29.4.

HRMS (ESI): Calcd for $[C_{23}H_{19}NO_4Na]^+$ $[M+Na]^+$ 396.1206, Found 396.1197.

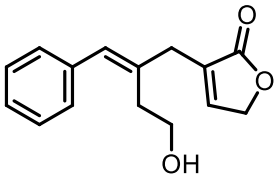


(*E*)-3-(2-Benzylidenepent-4-en-1-yl)furan-2(5*H*)-one (23). Synthesized according to the **General Procedure A** with pent-4-en-1-yn-1-ylbenzene (0.2 mmol, 28.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **23** as a colorless oil (33.2 mg, 69% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.14 (m, 4H), 6.49 (s, 1H), 5.91 – 5.81 (m, 1H), 5.16 – 5.15 (m, 1H), 5.12 – 5.11 (m, 1H), 4.81 (d, *J* = 1.6 Hz, 1H), 4.80 (d, *J* = 1.6 Hz, 1H), 3.16 (s, 2H), 2.99 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 146.1, 137.3, 135.8, 135.4, 132.7, 129.5, 128.5, 128.3, 126.8, 116.9, 70.3, 35.4, 32.8.

HRMS (ESI): Calcd for $[C_{16}H_{16}O_2Na]^+$ $[M+Na]^+$ 263.1043, Found 263.1053.

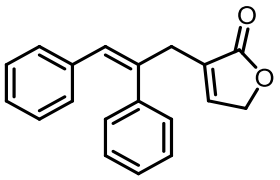


(*Z*)-3-(2-Benzylidene-4-hydroxybutyl)furan-2(5*H*)-one (24). Synthesized according to the **General Procedure A** with trimethyl((4-phenylbut-3-yn-1-yl)oxy)silane (0.2 mmol, 43.6 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **24** as a colorless oil (20.1 mg, 41% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 7.24 – 7.19 (m, 1H), 6.45 (s, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 3.84 (t, *J* = 6.4 Hz, 2H), 3.26 – 3.17 (m, 2H), 2.54 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 146.5, 137.3, 135.3, 132.8, 130.6, 128.8, 128.4, 126.9, 70.6, 60.9, 34.3, 32.4.

HRMS (ESI): Calcd for $[C_{15}H_{16}O_3Na]^+$ $[M+Na]^+$ 267.0992, Found 267.1000.

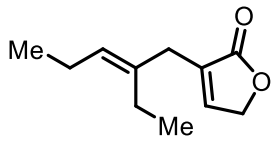


(*Z*)-3-(2,3-Diphenylallyl)furan-2(5*H*)-one (25). Synthesized according to the **General Procedure A** with 1,2-diphenylethyne (0.2 mmol, 35.6 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **25** as a colorless oil (24.1 mg, 44% yield, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 3H), 7.19 – 7.17 (m, 2H), 7.12 – 7.10 (m, 3H), 6.98 – 6.96 (m, 3H), 6.60 (s, 1H), 4.73 – 4.65 (m, 2H), 3.51 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 146.1, 139.9, 137.7, 136.8, 132.0, 129.4, 129.3, 128.9, 128.8, 128.1, 127.6, 126.9, 70.3, 35.9.

HRMS (ESI): Calcd for $[C_{19}H_{17}O_2]^+$ $[M+H]^+$ 277.1223, Found 277.1227.

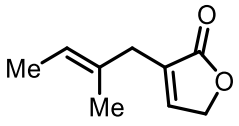


(*E*)-3-(2-Ethylpent-2-en-1-yl)furan-2(5*H*)-one (26). Synthesized according to the **General Procedure A** with 3-hexyne (0.2 mmol, 16.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **26** as a colorless oil (17.8 mg, 49% yield, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 1H), 5.20 (t, J = 7.2 Hz, 1H), 4.80– 4.73 (m, 2H), 2.95 (s, 2H), 2.07 – 2.00 (m, 4H), 0.96 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 145.5, 136.1, 133.5, 129.7, 70.2, 32.1, 23.1, 21.1, 14.7, 13.3.

HRMS (ESI): Calcd for $[C_{11}H_{16}O_2K]^+$ $[M+K]^+$ 219.0782, Found 219.0781.



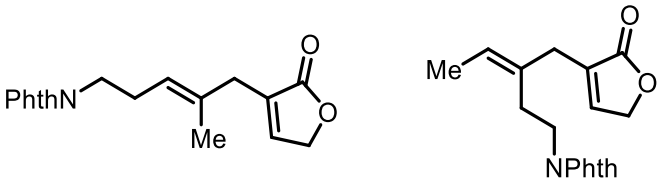
(*E*)-3-(2-Methylbut-2-en-1-yl)furan-2(5*H*)-one (27). Synthesized according to the **General Procedure A** with 2-butyne (10.0 mmol, 1.0 mL, 10 M in THF) and Tulipalin A (0.2 mmol, 19.6 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **27** as a colorless oil (11.5 mg, 38%

yield, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.08 (m, 1H), 5.35 – 5.30 (m, 1H), 4.77 (d, *J* = 1.6 Hz, 1H), 4.76 (d, *J* = 2.0 Hz, 1H), 2.93 – 2.92 (m, 2H), 1.60 – 1.57 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 145.5, 133.0, 131.3, 122.1, 70.3, 35.2, 15.9, 13.6.

HRMS (ESI): Calcd for $[C_9H_{12}O_2K]^+$ $[M+K]^+$ 191.0469, Found 191.0474.



(*E*)-2-(4-Methyl-5-(2-oxo-2,5-dihydrofuran-3-yl)pent-3-en-1-yl)isoindoline-1,3-dione (28). Synthesized according to the General Procedure A with 2-(pent-3-yn-1-yl)isoindoline-1,3-dione (0.2 mmol, 42.6 mg) and Tulipalin A (0.6 mmol, 58.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **28** as a colorless oil (44.8 mg, 78% yield, 2:1 rr, >19:1 *E/Z*).

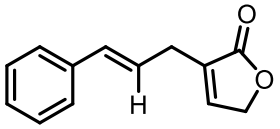
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 3H), 7.73 – 7.68 (m, 3H), 7.05 – 7.04 (m, 1H), 5.26 (t, *J* = 6.8 Hz, 1H), 4.82 – 4.76 (m, 2H), 3.75 – 3.69 (m, 2H), 2.91 (s, 2H), 2.45 – 2.39 (m, 2H), 1.58 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 168.5, 145.7, 134.1,132.6, 132.2, 125.6, 123.3, 70.2, 37.6, 35.0, 27.3, 16.2.

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 3H), 7.73 – 7.68 (m, 3H), 7.21 – 7.20 (m, 1H), 5.42 (q, *J* = 6.8 Hz, 1H), 4.76 – 4.70 (m, 2H), 3.75 – 3.69 (m, 2H), 3.09 (s, 2H), 2.45 – 2.39 (m, 2H), 1.54 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 168.4, 146.2, 134.4, 132.5, 131.7, 125.6, 123.3, 70.2, 36.0, 32.6, 28.6, 13.6.

HRMS (ESI): Calcd for $[C_{18}H_{17}NO_4Na]^+$ $[M+Na]^+$ 334.1050, Found 334.1060.

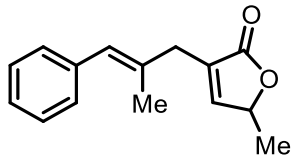


3-Cinnamylfuran-2(5*H*)-one (29). Synthesized according to the **General Procedure A** with phenylacetylene (0.2 mmol, 20.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **29** as a colorless oil (35.2 mg, 88% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.27 (dt, *J* = 15.6, 6.8 Hz, 1H), 4.81 (d, *J* = 2.0 Hz, 1H), 4.80 (d, *J* = 2.0 Hz, 1H), 3.22 – 3.20 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 145.3, 137.0, 133.2, 133.1, 128.7, 127.7, 126.3, 124.6, 70.5, 29.0.

HRMS (ESI): Calcd for $[C_{13}H_{12}O_2Na]^+$ $[M+Na]^+$ 223.0730, Found 223.0725.

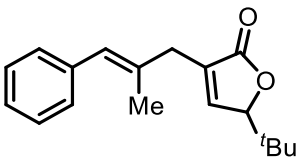


(*E*)-5-Methyl-3-(2-methyl-3-phenylallyl)furan-2(5*H*)-one (30). Synthesized according to the **General Procedure A** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and 5-methyl-3-methylenedihydrofuran-2(3H)-one (0.6 mmol, 67.2 mg) using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst and DMF as the solvent. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **30** as a colorless oil (20.1 mg, 44% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 7.6 Hz 2H), 7.24 – 7.20 (m, 3H), 7.09 – 7.08 (m, 1H), 6.39 (s, 1H), 5.05 (dq, *J* = 1.6, 6.8 Hz 1H), 3.14 (s, 2H), 1.89 (s, 3H), 1.44 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 150.6, 137.9, 134.3, 132.5, 128.9, 128.3, 128.1, 126.5, 77.7, 36.0, 19.3, 17.9.

HRMS (ESI): Calcd for $[C_{15}H_{17}O_2]^+$ $[M+H]^+$ 229.1223, Found 229.1221.

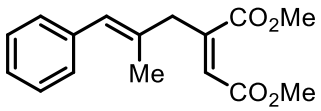


(*E*)-5-(*tert*-Butyl)-3-(2-methyl-3-phenylallyl)furan-2(5*H*)-one (31). Synthesized according to the **General Procedure A** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and 5-(tert-butyl)-3-methylenedihydrofuran-2(3H)-one (0.6 mmol, 92.4 mg) using 2 mol% 4CzIPN-Br (0.004 mmol, 5.7 mg) as the photocatalyst and DMF as the solvent. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **31** as a colorless oil (26.5 mg, 49% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.23 – 7.16 (m, 3H), 7.01 – 7.00 (m, 1H), 6.51 (s, 1H), 4.63 – 4.62 (m, 1H), 3.20 (d, *J* = 1.6 Hz, 2H), 1.90 (d, *J* = 1.2 Hz, 3H), 0.97 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 147.1, 137.6, 134.1, 133.7, 128.6, 128.5, 128.2, 126.8, 89.1, 35.2, 29.2, 25.6, 24.5.

HRMS (ESI): Calcd for $[C_{18}H_{23}O_2]^+$ $[M+H]^+$ 271.1693, Found 271.1688.

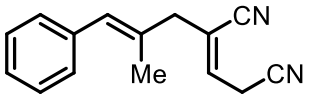


Dimethyl 2-((*E*)-2-methyl-3-phenylallyl)maleate (32). Synthesized according to the **General Procedure A** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and dimethyl 2-methylenesuccinate (0.6 mmol, 94.8 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **32** as a colorless oil (25.8 mg, 47% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.20 – 7.16 (m, 3H), 6.88 (s, 1H), 6.22 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.74 (s, 2H), 1.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.2, 145.7, 138.3, 135.4, 129.0, 128.1, 127.5, 126.6, 126.2, 52.7, 52.0, 37.1, 18.3.

HRMS (ESI): Calcd for $[C_{16}H_{19}O_4]^+$ $[M+H]^+$ 275.1278, Found 275.1288.

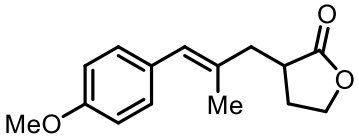


(*Z*)-2-((*E*)-2-Methyl-3-phenylallyl)pent-2-enedinitrile (33). Synthesized according to the General Procedure A with 1-phenylpropyne (0.2 mmol, 23.2 mg) and 2-methylenesuccinonitrile (0.6 mmol, 55.2 mg), using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst and DMF as the solvent. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **33** as a colorless oil (20.4 mg, 46% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.27 – 7.22 (m, 3H), 6.44 (s, 1H), 6.22 (t, *J* = 7.2 Hz, 1H), 3.49 (d, *J* = 7.2 Hz, 2H), 3.11 (s, 2H), 1.86 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.5, 131.9, 130.2, 129.0, 128.4, 127.0, 119.7, 115.6, 115.5, 44.9, 19.8, 17.5.

HRMS (ESI): Calcd for $[C_{15}H_{15}N_2]^+$ $[M+H]^+$ 223.1230, Found 223.1235.



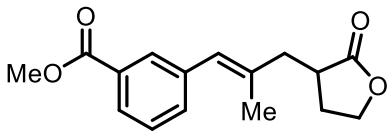
(*E*)-3-(3-(4-Methoxyphenyl)-2-methylallyl)dihydrofuran-2(3*H*)-one (34). Synthesized according to the **General Procedure B** with 1-(4-methoxy)-phenylpropyne (0.2 mmol, 29.2 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **34** as a colorless oil (21.6 mg, 44% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.27 (s, 1H), 4.37 (ddd,

J = 9.2, 9.2, 3.6 Hz, 1H), 4.23 (ddd, *J* = 9.2, 9.2, 6.8 Hz, 1H), 3.81 (s, 3H), 2.85 – 2.75 (m, 2H), 2.41 – 2.33 (m, 1H), 2.23 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.03 (ddd, *J* = 18.0, 12.8, 9.2 Hz, 1H), 1.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 158.2, 133.8, 130.4, 130.1, 127.1, 113.7, 66.7, 55.4, 41.5, 38.2, 28.3, 17.5.

HRMS (ESI): Calcd for $[C_{15}H_{19}O_3]^+$ $[M+H]^+$ 247.1329, Found 247.1340.

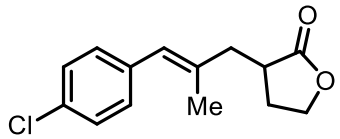


Methyl (*E*)-3-(2-methyl-3-(2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl)benzoate (35). Synthesized according to the **General Procedure B** with methyl 3-(prop-1-yn-1-yl)benzoate (0.2 mmol, 34.8 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **35** as a colorless oil (29.0 mg, 53% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.41– 7.40 (m, 2H), 6.36 (s, 1H), 4.39 (ddd, *J* = 8.8, 8.8, 3.2 Hz, 1H), 4.25 (ddd, *J* = 9.2, 9.2, 6.8 Hz, 1H), 3.92 (s, 3H), 2.87 – 2.78 (m, 2H), 2.44 – 2.36 (m, 1H), 2.27 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.04 (ddd, *J* = 18.8, 12.8, 9.6 Hz, 1H), 1.88 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 167.3, 138.1, 136.8, 133.4, 130.2, 130.0, 128.4, 127.7, 126.7, 66.7, 52.3, 41.4, 38.1, 28.5, 17.6.

HRMS (ESI): Calcd for $[C_{16}H_{18}O_4Na]^+$ $[M+Na]^+$ 297.1097, Found 297.1094.

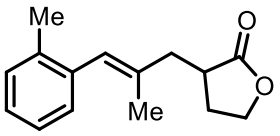


(*E*)-3-(3-(4-Chlorophenyl)-2-methylallyl)dihydrofuran-2(3*H*)-one (36). Synthesized according to the **General Procedure B** with 1-(4-chloro)-phenylpropyne (0.2 mmol, 30.0 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **36** as a colorless oil (29.6 mg, 59% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 7.16 – 7.14 (m, 2H), 6.28 (s, 1H), 4.38 (ddd, *J* = 8.8, 8.8, 3.2 Hz, 1H), 4.24 (ddd, *J* = 9.2, 9.2, 6.8 Hz, 1H), 2.84 – 2.76 (m, 2H), 2.41 – 2.34 (m, 1H), 2.25 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.01 (ddd, *J* = 18.0, 12.8, 9.6 Hz, 1H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 136.2, 132.2, 130.2, 128.4, 126.5, 66.7, 41.5, 38.1, 28.4, 17.6.

HRMS (ESI): Calcd for $[C_{14}H_{15}ClO_2Na]^+$ $[M+Na]^+$ 273.0653, Found 273.0645.

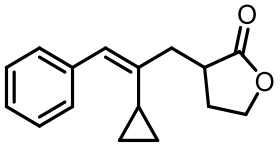


(*E*)-3-(2-Methyl-3-(*o*-tolyl)allyl)dihydrofuran-2(3*H*)-one (37). Synthesized according to the **General Procedure B** with 1-(2-methyl)-phenylpropyne (0.2 mmol, 26.0 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **37** as a colorless oil (17.9 mg, 39% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 3H), 7.13 – 7.10 (m, 1H), 6.31 (s, 1H), 4.40 (ddd, *J* = 8.8, 8.8, 3.2 Hz, 1H), 4.26 (ddd, *J* = 9.2, 9.2, 7.2 Hz, 1H), 2.86 – 2.80 (m, 2H), 2.43 – 2.38 (m, 1H), 2.28 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.23 (s, 3H), 2.07 (ddd, *J* = 18.4, 12.8, 9.6 Hz, 1H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 137.1, 136.4, 135.2, 129.9, 129.4, 126.9, 126.8, 125.5, 66.7, 40.8, 38.1, 28.4, 20.1, 17.2.

HRMS (ESI): Calcd for $[C_{15}H_{18}O_2Na]^+$ $[M+Na]^+$ 253.1199, Found 253.1191.

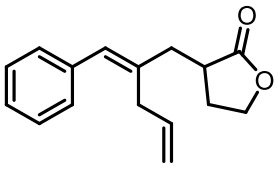


(*Z*)-3-(2-Cyclopropyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (38). Synthesized according to the **General Procedure B** with (cyclopropylethynyl)benzene (0.2 mmol, 28.4 mg) and Tulipalin A (0.6 mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **38** as a colorless oil (24.7 mg, 51% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.35 – 7.31 (m, 2H), 7.23 – 7.19 (m, 1H), 6.36 (s, 1H), 4.38 (ddd, *J* = 8.8, 8.8, 3.2 Hz, 1H), 4.23 (ddd, *J* =9.2, 9.2, 6.4 Hz, 1H), 2.89 – 2.80 (m, 1H), 2.63 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.11 – 1.98 (m, 2H), 1.76 – 1.70 (m, 1H), 0.84 – 0.71 (m, 2H), 0.63 – 0.57 (m, 1H), 0.50 – 0.44 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 139.0, 137.6, 129.2, 128.6, 128.1, 126.5, 66.7, 38.8, 36.2, 28.9, 12.9, 7.3, 6.7.

HRMS (ESI): Calcd for $[C_{16}H_{18}O_2Na]^+$ $[M+Na]^+$ 265.1199, Found 265.1189.



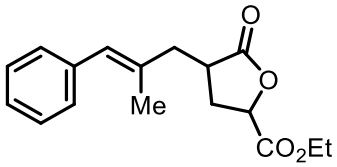
(*E*)-3-(2-Benzylidenepent-4-en-1-yl)dihydrofuran-2(3*H*)-one (39). Synthesized according to the **General Procedure B** with (cyclopropylethynyl)benzene (0.2 mmol, 28.4 mg) and Tulipalin A (0.6

mmol, 58.8 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **39** as a colorless oil (16.5 mg, 34% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.25 – 7.21 (m, 3H), 6.44 (s, 1H), 5.92 – 5.82 (m, 1H), 5.17 – 5.15 (m, 1H), 5.13 (s, 1H), 4.38 (ddd, *J* = 8.8, 8.8, 2.8 Hz, 1H), 4.23 (ddd, *J* = 9.2, 9.2, 6.8 Hz, 1H), 3.13 – 3.07 (dd, *J* = 15.6, 5.6 Hz, 1H), 2.94 – 2.78 (m, 3H), 2.45 – 2.37 (m, 1H), 2.20 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.04 (ddd, *J* = 18.4, 12.8, 9.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 137.4, 137.0, 135.5, 128.8, 128.6, 128.4, 126.8, 116.9, 66.7, 38.3, 38.1, 35.3, 28.8.

HRMS (ESI): Calcd for $[C_{16}H_{18}O_2Na]^+$ $[M+Na]^+$ 265.1199, Found 265.1190.

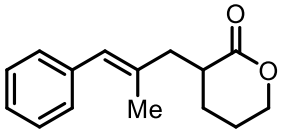


Ethyl (*E*)-4-(2-methyl-3-phenylallyl)-5-oxotetrahydrofuran-2-carboxylate (40). Synthesized according to the **General Procedure B** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and ethyl 4-methylene-5-oxotetrahydrofuran-2-carboxylate (0.6 mmol, 102.0 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **40** as a colorless oil (33.4 mg, 58% yield, >19:1 rr, >19:1 *E/Z*, >19:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.23 – 7.20 (m, 3H), 6.31 (s, 1H), 4.85 (dd, *J* = 8.4, 8.0 Hz, 1H), 4.28 (qd, *J* = 7.2, 2.4 Hz, 2H), 2.95 – 2.82 (m, 2H), 2.70 (ddd, *J* = 13.2, 9.2, 7.6 Hz, 1H), 2.31 (dd, *J* = 14.0, 11.2 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 169.8, 137.7, 134.9, 129.0, 128.3, 128.1, 126.6, 74.4, 62.2, 41.7, 38.3, 31.6, 17.5, 14.2.

HRMS (ESI): Calcd for $[C_{17}H_{20}O_4Na]^+$ $[M+Na]^+$ 311.1254, Found 311.1257.

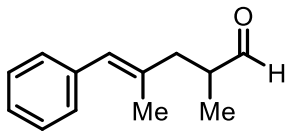


(*E*)-3-(2-Methyl-3-phenylallyl)tetrahydro-2H-pyran-2-one (41). Synthesized according to the **General Procedure B** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and 3-methylenetetrahydro-2H-pyran-2-one (0.6 mmol, 67.2 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **41** as a colorless oil (27.1 mg, 59% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.25 – 7.19 (m, 3H), 6.32 (s, 1H), 4.41 – 4.30 (m, 2H), 2.93 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.30 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.06 (ddd, *J* = 12.8, 12.8, 6.4 Hz, 1H), 2.00 – 1.88 (m, 2H), 1.85 (s, 3H), 1.64 – 1.54 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 138.0, 135.3, 128.9, 128.2, 128.0, 126.4, 68.9, 42.5, 38.1, 24.3, 22.0, 17.4.

HRMS (ESI): Calcd for $[C_{15}H_{18}O_2Na]^+$ [M+Na]$^+$ 253.1199, Found 253.1188.

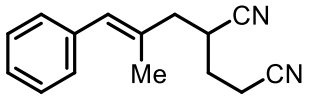


(*E*)-2,4-Dimethyl-5-phenylpent-4-enal (42). Synthesized according to the **General Procedure B** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and methacrylaldehyde (0.6 mmol, 42.0 mg). Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **42** as a colorless oil (15.8 mg, 42% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 7.8, 7.8 Hz 2H), 7.23 – 7.19 (m, 3H), 6.32 (s, 1H), 2.67 – 2.61 (m, 2H), 2.17 (dd, *J* = 16.0, 10.8 Hz, 1H), 1.86 (d, *J* = 0.8 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 138.0, 135.3, 129.0, 128.2, 127.8, 126.4, 44.7, 41.8, 17.8, 13.3.

HRMS (ESI): Calcd for $[C_{13}H_{16}ONa]^+$ [M+Na]$^+$ 211.1093, Found 211.1083.

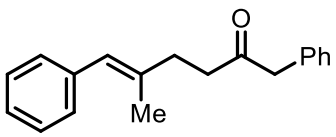


(*E*)-2-(2-Methyl-3-phenylallyl)pentanedinitrile (43). Synthesized according to the **General Procedure B** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and 2-methylenepentanedinitrile (0.6 mmol, 63.6 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **43** as a colorless oil (25.5 mg, 57% yield, >19:1 rr, >19:1 *E/Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.18 – 7.15 (m, 3H), 6.37 (s, 1H), 2.95 – 2.87 (m, 1H), 2.62 – 2.48 (m, 3H), 2.39 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.00 – 1.89 (m, 2H), 1.84 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 132.4, 130.0, 129.0, 128.4, 127.0, 120.2, 118.1, 42.8, 29.7, 28.0, 17.6, 15.5.

HRMS (ESI): Calcd for $[C_{15}H_{16}N_2Na]^+$ [M+ Na]$^+$ 247.1206, Found 247.1202.



(*E*)-5-Methyl-1,6-diphenylhex-5-en-2-one (44). Synthesized according to the **General Procedure B** with 1-phenylpropyne (0.2 mmol, 23.2 mg) and 1-phenylbut-3-en-2-one (0.6 mmol, 87.6 mg). Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **44** as a colorless oil (28.0 mg, 53% yield, >19:1 rr, >19:1 *E/Z*).

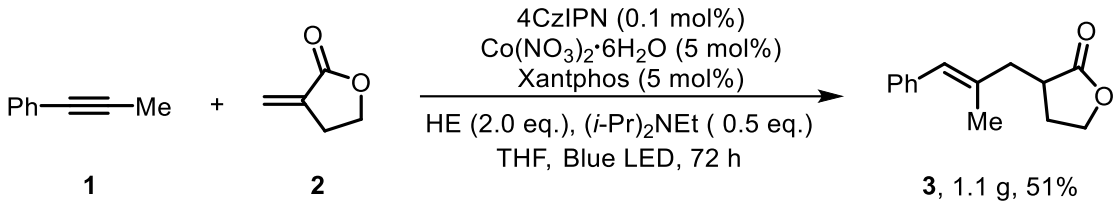
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 7.23 – 7.16 (m, 5H), 6.21 (s, 1H), 3.73 (s, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 8.0 Hz, 2H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 138.3, 137.4, 134.3, 129.6, 128.9, 128.9, 128.2, 127.2, 126.2, 125.6, 50.5, 40.6, 34.5, 17.9.

HRMS (ESI): Calcd for $[C_{19}H_{20}ONa]^+$ $[M+Na]^+$ 287.1406, Found 287.1399.

V. Synthetic Applications

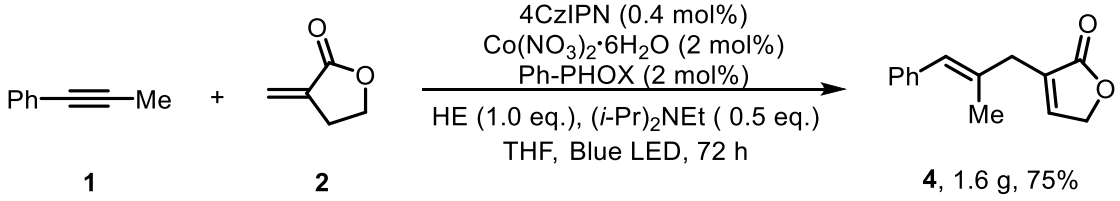
(1) Scale-up Reaction to Produce Alkene 3.



1 **2** **3**, 1.1 g, 51%

To an oven-dried Schlenk tube (250 mL) was added the $Co(NO_3)_2$ $6H_2O$ (0.5 mmol, 146.0 mg) and HE (10 mmol, 5.06 g). Then the Schlenk tube was transferred into the glovebox. The Xantphos (0.5 mmol, 289.3 mg), THF (150 mL), 4CzIPN (0.01 mmol, 8.0 mg), $(i\text{-Pr})_2$NEt (5 mmol, 646.2 mg), 1-phenylpropyne (**1**, 10 mmol, 1.16 g) and 3-methylenedihydrofuran-2(3*H*)-one (**2**, 30 mmol, 2.94 g) were added into the Schlenk tube. Then, the sealed Schlenk tube was taken out from the glovebox and stirred under 20 W Blue LEDs at room temperature for 72 h. Then, the crude mixture was concentrated under reduced pressure and purified by column chromatography over silica gel (PE/EA 5:1) to give the desired product **3** (1.1 g, 51% yield).

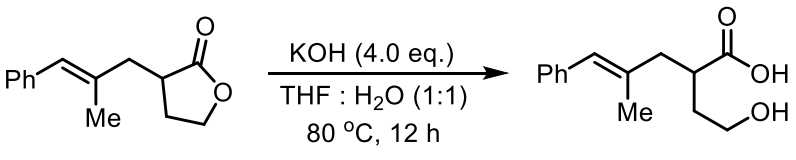
(2) Scale-up Reaction to Produce 1,4-Diene 4.



1 **2** **4**, 1.6 g, 75%

To an oven-dried Schlenk tube (250 mL) was added the $Co(NO_3)_2$ $6H_2O$ (0.2 mmol, 58.0 mg) and HE (10 mmol, 2.53 g). Then the Schlenk tube was transferred into the glovebox. The Ph-Phox (0.2 mmol, 82.0 mg), THF (150 mL), 4CzIPN (0.04 mmol, 31.6 mg), $(i\text{-Pr})_2$NEt (5 mmol, 646.2 mg), 1-phenylpropyne (**1**, 10 mmol, 1.16 g) and 3-methylenedihydrofuran-2(3*H*)-one (**2**, 30 mmol, 2.94 g) were added sequentially into the Schlenk tube. Then, the sealed Schlenk tube was taken out from the glovebox and stirred under 30 W Blue LEDs at room temperature for 72 h. Then, the crude mixture was concentrated under reduced pressure and purified by column chromatography over silica gel (PE/EA 5:1) to give the desired product **4** (1.6 g, 75% yield).

(6) Aminolysis of Aalkene 3 with 4-Methoxybenzylamine to Produce γ-Hydroxy amide 45.



3 **45**, 87%

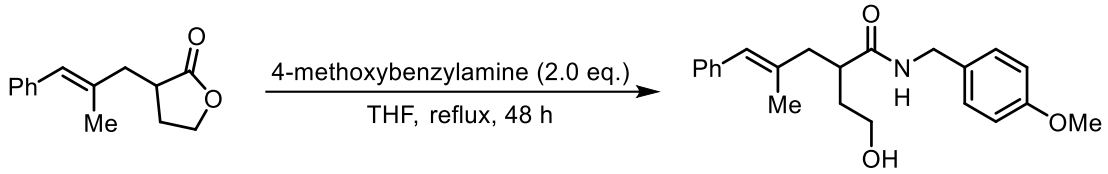
A 25 mL Schlenk tube was charged with alkene **3** (0.2 mmol, 43.2 mg), KOH (0.8 mmol, 44.8 mg,), THF (1.0 mL) and H_2O (1.0 mL). Then the mixture was heated to 80 ℃ for 12 h. After the reaction completed, the solution was quenched by 1M HCl aqueous solution (2.0 mL), and the resulted mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water and brine, dried by anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purification by flash column chromatography on silica gel (PE/EA = 1:1) afforded **45** (40.7 mg, 87% yield) as colorless jelly.

^{1}H NMR (400 MHz, d_6-DMSO) δ 7.31 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.19 (m, 3H), 6.25 (s, 1H), 4.84 (brs, 2H), 3.47 – 3.40 (m, 2H), 2.59 – 2.53 (m, 1H), 2.45 (dd, *J* = 13.4, 7.2 Hz, 1H), 2.17 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.80 (d, *J* = 0.8 Hz, 3H), 1.67 – 1.62 (m, 1H), 1.57 – 1.49 (m, 1H).

^{13}C NMR (100 MHz, d_6-DMSO) δ 178.0, 137.9, 137.2, 128.6, 128.1, 125.9, 125.9, 59.4, 43.8, 41.7, 34.8, 17.5

HRMS (ESI): Calcd for $[C_{14}H_{19}O_3]^+$ $[M+H]^+$ 253.1329, Found 253.1319.

(7) Hydrolysis of Alkene 3 to Produce γ-Hydroxy Carboxylic Acid 46.



3 **46**, 52%

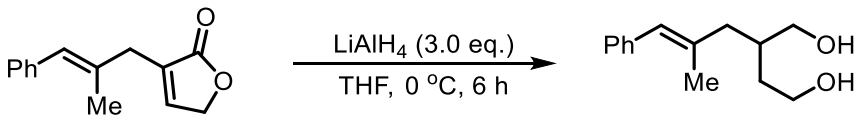
A 25 mL Schlenk tube was charged with alkene **3** (0.2 mmol, 43.2 mg), 4-methoxybenzylamine (0.4 mmol, 54.8 mg,) and THF (2 mL) under N_2 atmosphere. The mixture was heated to reflux for 48 h. After the reaction completed, the solution was then concentrated in vacuum. The residue was purification by flash column chromatography on silica gel (PE/EA = 1:1) afforded **46** (36.7 mg, 52% yield) as a colorless jelly.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 9.2, 7.6 Hz, 2H), 7.21 – 7.11 (m, 5H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.33 (s, 1H), 5.99 (brs, 1H), 4.44 (dd, *J* = 14.4, 6.0 Hz, 1H), 4.28 (dd, *J* = 14.4, 5.2 Hz, 0H), 3.74 (s, 1H), 3.70 (t, *J* = 5.2 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.31 (dd, *J* = 12.4, 4.8 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.85 (s, 3H), 1.81 – 1.75 (m, 1H), 1.68 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 159.1, 138.1, 135.8, 130.3, 129.3, 129.0, 128.2, 127.8, 126.3, 114.2, 60.6, 55.4, 43.9, 43.2, 43.0, 35.2, 18.0.

HRMS (ESI): Calcd for $[C_{22}H_{28}NO_3]^+$ $[M+H]^+$ 354.2064, Found 354.2063.

(3) Selective Reduction of 1,4-Diene 4 to Produce Diol and Furan Derivatives.



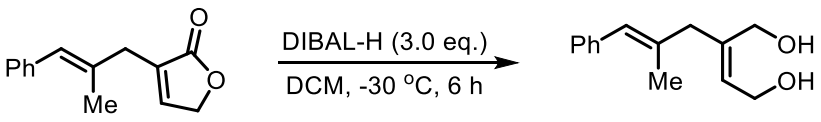
4 **47**, 61%

To a solution of 1,4-diene **4** (0.2 mmol, 42.3 mg) in THF (5 mL) was added $LiAlH_4$ (0.6 mmol, 0.6 mL, 1.0 M in THF), and the resulting mixture was stirred for 6 h at 0 ºC. The reaction was quenched with H_2O (2 mL). Ethyl acetate (10 mL) was added to the resulting mixture. After separation, the aqueous layer was extracted with ethyl acetate for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA = 2:1) to give **47** (26.8 mg, 61% yield) as a white jelly.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.25 – 7.16 (m, 3H), 6.29 (s, 1H), 3.86 – 3.80 (m, 1H), 3.73 – 3.67 (m, 2H), 3.53 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.87 (brs, 2H), 2.23 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.11 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.02 – 1.94 (m, 1H), 1.87 (d, *J* = 0.8 Hz, 3H), 1.79 – 1.73 (m, 1H), 1.64 – 1.57 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.0, 128.9, 128.2, 127.3, 126.2, 66.4, 61.4, 43.7, 37.5, 35.7, 17.9.

HRMS (ESI): Calcd for $[C_{14}H_{21}O_2]^+$ $[M+H]^+$ 221.1536, Found 221.1532.



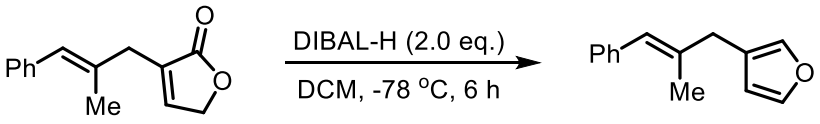
4 **48**, 52%

To a solution of 1,4-diene **4** (0.2 mmol, 42.3 mg) in DCM (5 mL) was added DIBAL-H (0.6 mmol, 0.3 mL, 2.0 M in THF) under –30 ºC, and the resulting mixture was stirred for 6 h at –30 ºC. Then the reaction was quenched with H_2O (2 mL). DCM (10 mL) was added to the resulting mixture. After separation, the aqueous layer was extracted with DCM for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA = 2:1) to give **48** (22.7 mg, 52% yield) as a white jelly.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.27 – 7.16 (m, 3H), 6.37 (s, 1H), 5.74 (t, *J* = 6.8 Hz, 1H), 4.27 (d, *J* = 7.2 Hz, 2H), 4.20 (s, 2H), 3.00 (s, 2H), 1.92 (brs, 2H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 141.2, 138.2, 136.4, 128.9, 128.3, 127.6, 126.4, 60.6, 58.8, 47.4, 17.7.

HRMS (ESI): Calcd for $[C_{14}H_{18}O_2Na]^+$ $[M+Na]^+$ 241.1199, Found 241.1193.



4 **49**, 56%

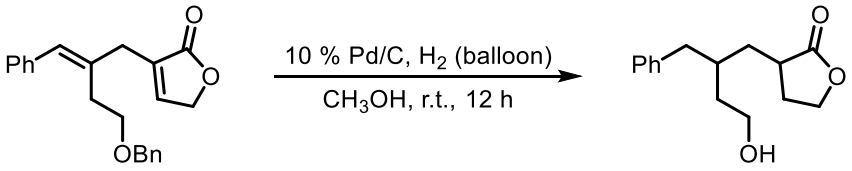
To a solution of 1,4-diene **4** (0.2 mmol, 42.3 mg) in DCM (5 mL) was added DIBAL-H (0.4 mmol, 0.2 mL, 2.0 M in THF) under –78 ºC, and the resulting mixture was stirred for 6 h at –78 ºC. Then the reaction was quenched with H_2O (2 mL). DCM (10 mL) was added sequentially to the resulting mixture. After separation, the aqueous layer was extracted with DCM for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **49** (22.2 mg, 56% yield) as a white jelly.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.6, 1.2 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.25 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 6.36 (s, 1H), 6.31 (d, *J* = 0.8 Hz, 1H), 3.27 (s, 2H), 1.84 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 139.9, 138.4, 137.5, 129.0, 128.2, 126.2, 123.0, 111.5, 36.1, 17.8.

HRMS (ESI): Calcd for $[C_{14}H_{15}O]^+$ $[M+H]^+$ 199.1117, Found 119.1125.

(4) Pd/C Catalyzed Hydrogenation of 1,4-Diene 21 to Produce Dihydro-2-furanone 52.



20 **52**, 85%, 1.4:1 d.r.

A 25 mL Schlenk tube was charged with 1,4-diene **20** (0.1 mmol, 33.4 mg), 10% wet Pd/C (0.01 mmol, 10.6 mg) and CH_3OH (2 mL) under an N_2 atmosphere. The mixture was then connected to a hydrogen balloon, and the atmosphere in the tube is replaced by hydrogen gas for three times. After stirring at room temperature overnight, the solution was filtered through celite and then concentrated in vacuum. The residue was purified by flash chromatography (PE/EA 5:1) to afford **52** as a colorless oil. (21.0 mg, 85% yield, 1.4:1 d.r.).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.15 – 7.09 (m, 3H), 4.25 (td, *J* = 8.8, 2.8 Hz, 1H), 4.07 (td, *J* = 9.2, 6.8 Hz, 1H), 3.71 – 3.54 (m, 2H), 2.69 – 2.56 (m, 1H), 2.55 – 2.39 (m, 2H), 2.32 – 2.20 (m, 1H), 2.02 – 1.72 (m, 3H), 1.69 – 1.40 (m, 4H).

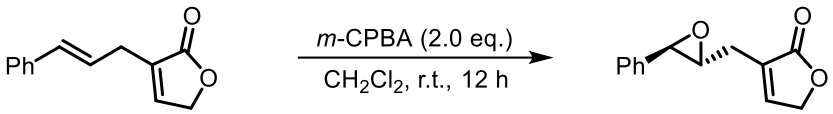
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 140.3, 129.2, 128.6, 126.3, 66.6, 60.6, 40.6, 37.3, 36.9, 35.3, 34.4, 29.4.

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.15 – 7.09 (m, 3H), 4.17 (td, *J* = 8.8, 2.8 Hz, 1H), 4.03 (td, *J* = 9.2, 6.8 Hz, 1H), 3.71 – 3.54 (m, 2H), 2.69 – 2.56 (m, 1H), 2.55 – 2.39 (m, 2H), 2.32 – 2.20 (m, 1H), 2.02 – 1.72 (m, 3H), 1.69 – 1.40 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 140.4, 129.3, 128.5, 126.3, 66.6, 60.3, 41.5, 37.5, 36.3, 34.9, 34.4, 29.4.

HRMS (ESI): Calcd for $[C_{15}H_{20}O_3Na]^+$ $[M+Na]^+$ 271.1305, Found 271.1292.

(5) Selective Epoxidation of 1,4-Diene 29 to Produce Epoxide 53.



29 **53**, 74%

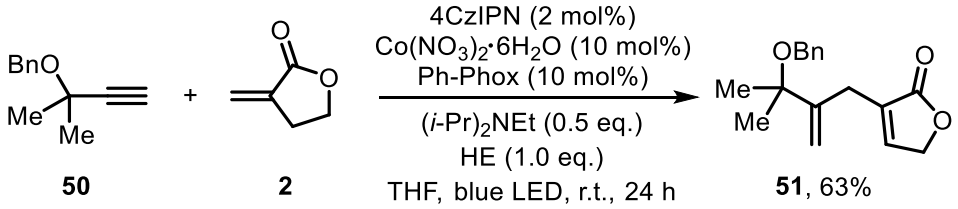
A 25 mL Schlenk tube was charged with 1,4-diene **29** (0.2 mmol, 40.0 mg), *m*-CPBA (0.4 mmol, 69.0 mg,) and DCM (2 mL) under N_2 atmosphere. After stirring at room temperature overnight, the reaction was quenched by $Na_2S_2O_3$ (10 mL, 5% aqueous solution). Then, the solution was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water and brine, dried by anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purification by flash column chromatography on silica gel (PE/EA 5:1) afforded **53** (31.9 mg, 74% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.38 (m, 1H), 7.37 – 7.31 (m, 3H), 7.28 – 7.26 (m, 2H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 3.74 (d, *J* = 1.6 Hz, 1H), 3.22 – 3.19 (m, 1H), 2.81 – 2.75 (m, 1H), 2.68 – 2.62 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 147.0, 136.8, 129.8, 128.7, 128.5, 125.7, 70.6, 60.0, 58.6, 28.6.

HRMS (ESI): Calcd for $[C_{13}H_{12}O_3Na]^+$ $[M+Na]^+$ 239.0679, Found 239.0684.

(8) Study to Access Natural Product Sibiscolacton.



50 **2** **51**, 63%

(((2-Methylbut-3-yn-2-yl)oxy)methyl)benzene (**50**) was synthesized according to the reported literature.[12] The **51** was synthesized according to the General Procedure A with (((2-methylbut-3-yn-2-yl)oxy)methyl)benzene (**50**) (0.2 mmol, 34.8 mg), Tulipalin A (0.6 mmol, 58.8 mg) and using 2 mol% 4CzIPN (0.004 mmol, 3.2 mg) as the photocatalyst. After the reaction completed, the reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA = 5:1)0 to give **51** (34.3 mg, 63%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.24 – 7.23 (m, 1H), 7.14 (s, 1H), 5.23 (s, 1H), 4.94

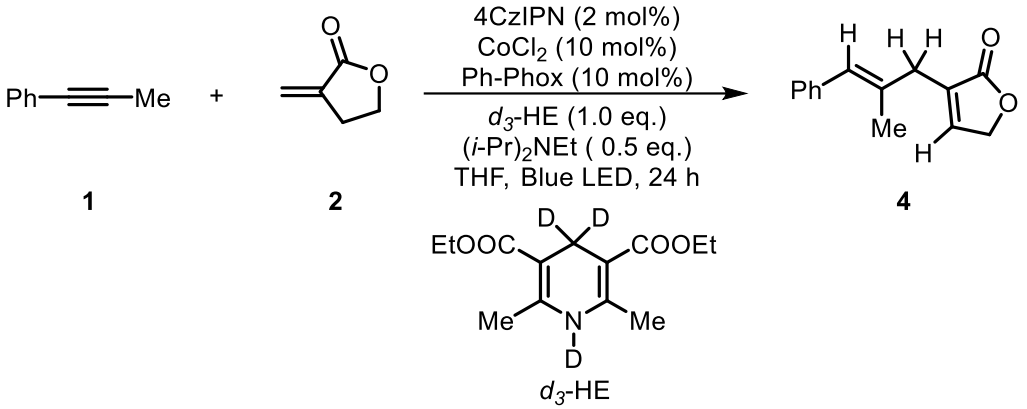
(s, 1H), 4.80 – 4.68 (m, 2H), 4.33 (s, 1H), 3.17 (s, 2H), 1.44 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 149.1, 146.5, 139.4, 133.2, 128.5, 127.5, 127.3, 113.4, 77.6, 70.2, 64.9, 26.6, 26.1.

HRMS (ESI): Calcd for $[C_{17}H_{20}O_3Na]^+$ $[M+Na]^+$ 295.1305, Found 295.1306.

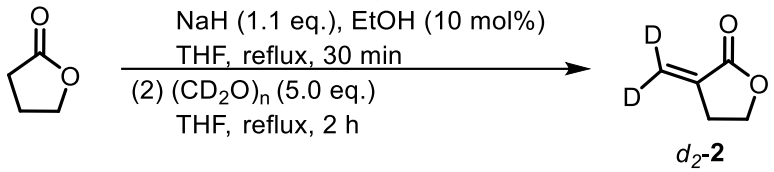
VI. Control Experiments and Mechanistic Studies

(1) Deuterium Labelling Experiment with *d*$_3$-HE



According to the General Procedure A with *d*$_3$-HE (0.2 mmol, 51 mg) and $CoCl_2$ (0.02 mmol, 2.6 mg) as the metal catalyst. After the reaction completed, the reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give **4** in 70% (30.0 mg) isolated yield. ^{1}H NMR analysis revealed that there is no deuterium in the 1,4-diene product.

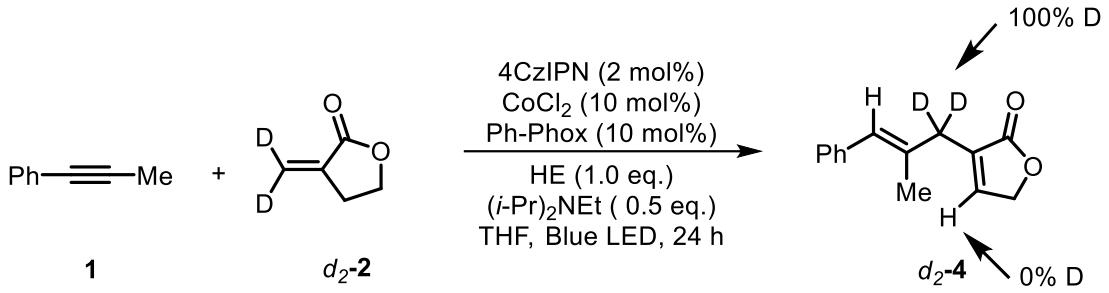
(2) Deuterium Labelling Experiment with *d*$_2$-**2**



Deuterium 3-methylenedihydrofuran-2(3*H*)-one (*d*$_2$-**2**) was prepared according to reported procedure. [10] To a stirred suspension of NaH (4 mmol, 96.0 mg) in 10 mL of diethyl ether under N_2, absolute ethanol was slowly added (0.4 mmol, 24 μL), then a mixture of 1,4-butyrolactone (3.6 mmol, 326.0 mg) and ethyl formate (4.4 mmol, 326.0 mg) was added over 0.5 h. After the addition was completed, the suspension was heated to reflux for additional 0.5 h with evolution of H_2. After cooling to room temperature, the resulting solid was filtered and washed with diethyl ether three times and dried in vacuum. To the resulted solid in 30 mL dry THF, deuterium-paraformaldehyde (18 mmol, 546.0 mg) was added under N_2. The suspension was heated to reflux for 2 h. Then the suspension was cooled down using an ice-water bath and quenched with aqueous K_2CO_3 solution (30 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA = 5:1) to yield deuterium 3-

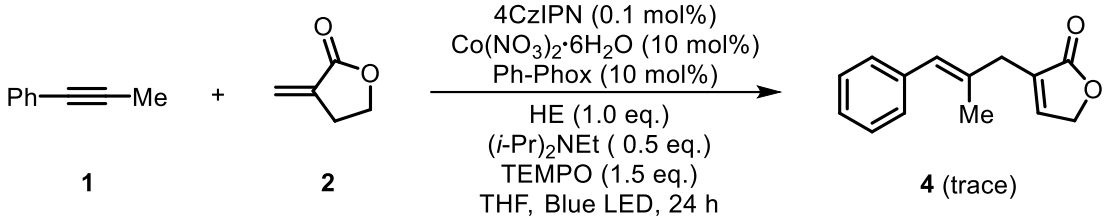
methylenedihydrofuran-2(3*H*)-one (*d*$_2$-**2**) (30%, 108.0 mg) as colorless liquid.

^{1}H NMR (400 MHz, CDCl3) δ 4.38 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H).



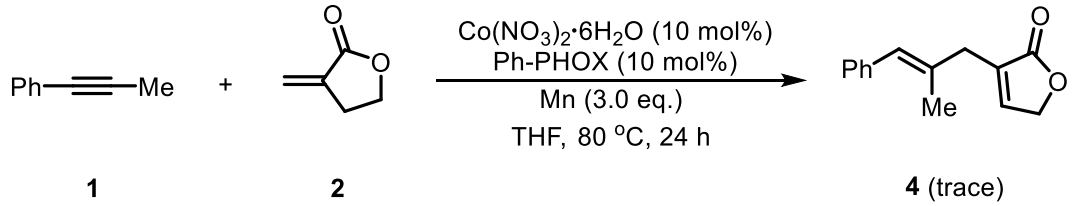
According to the General Procedure A with deuterated 3-Methylenedihydrofuran-2(3H)-one (0.6 mmol, 60.0 mg) as the substrate and $CoCl_2$ (0.02 mmol, 2.6 mg) as the metal catalyst. After the reaction completed, the reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA = 5:1) to give ***d*$_2$-4** in 44% (18.8 mg) isolated yield. ^{1}H NMR analysis revealed that 100% deuterium is reserved in the sp^3-hybridized carbon. The result indicates exocyclic *β*-H elimination is much faster than *β*-H elimination, leading to the 1,4-diene product.

(3) Radical Inhibition Experiment



According to the General Procedure A but with TEMPO (1.5 equiv). After the reaction completed, a trace amount of **4** was detected. The ene-type reaction was inhibited, suggesting that some free radical intermediates might exist during the reaction.

(4) Alder-ene Reaction Using Stoichiometric Metal Reductant



A 25 mL Schlenk tube was charged with 1-phenylpropyne (0.2 mmol, 23.2 mg), Tulipalin A (0.6 mmol, 58.8 mg), Mn powder (3.0 equiv) as the reductant and THF (3 mL) under N_2 atmosphere. Then the mixture was stirring at 80 ℃ for 24 h. After the reaction completed, a trace amount of **4** was detected. The result indicates the high efficiency of the photoredox catalytic system.

VII. References

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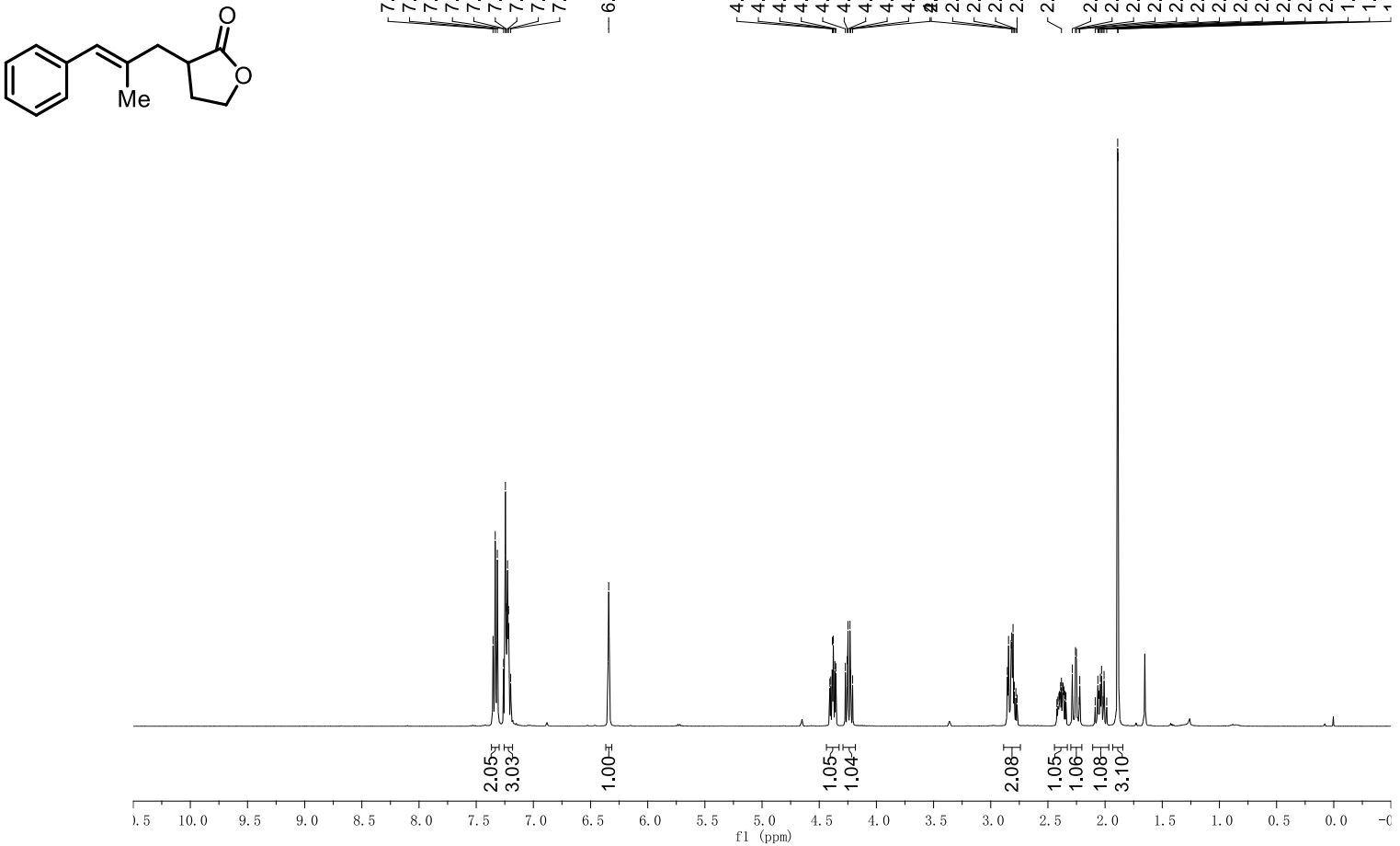
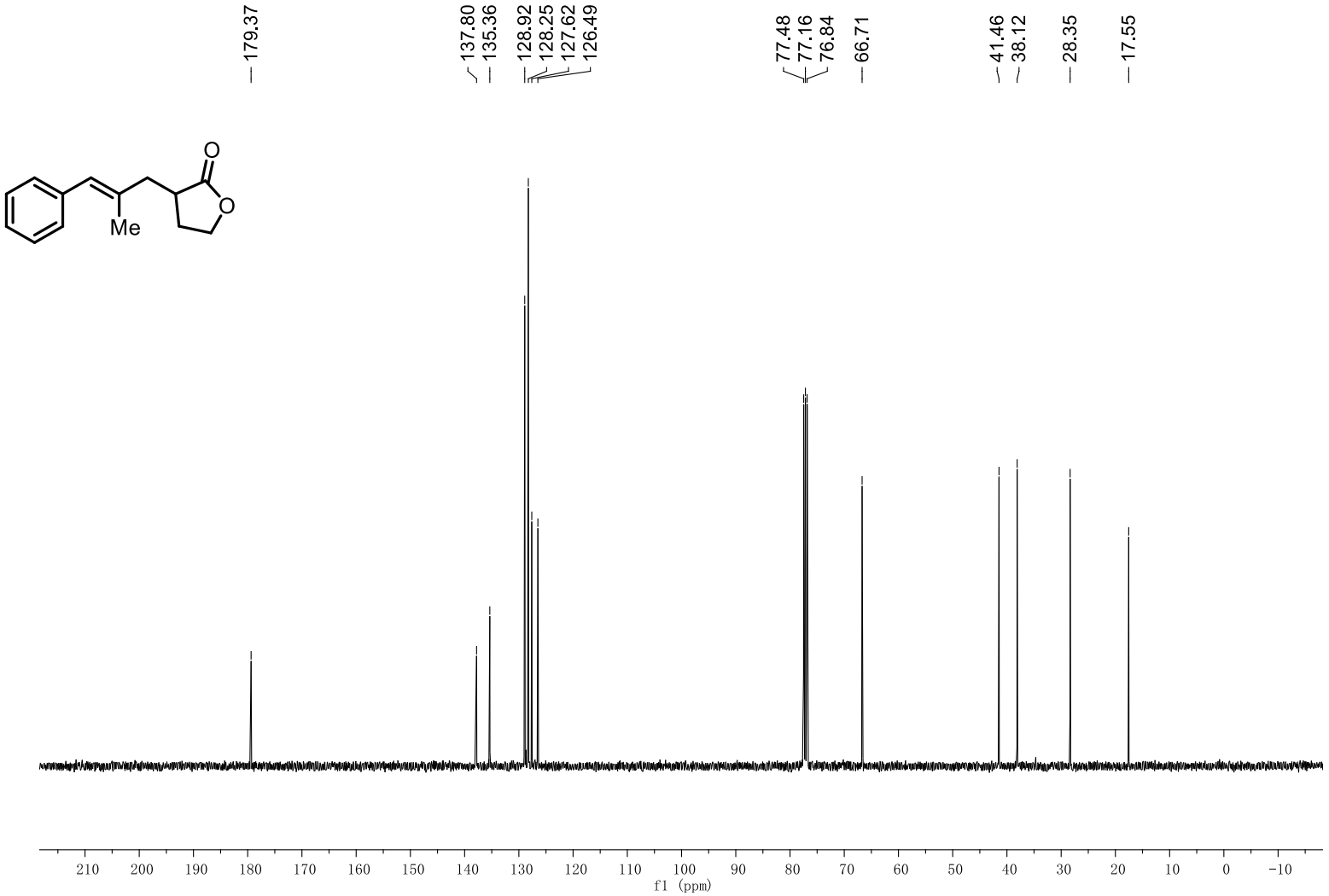
VIII. NMR Spectra

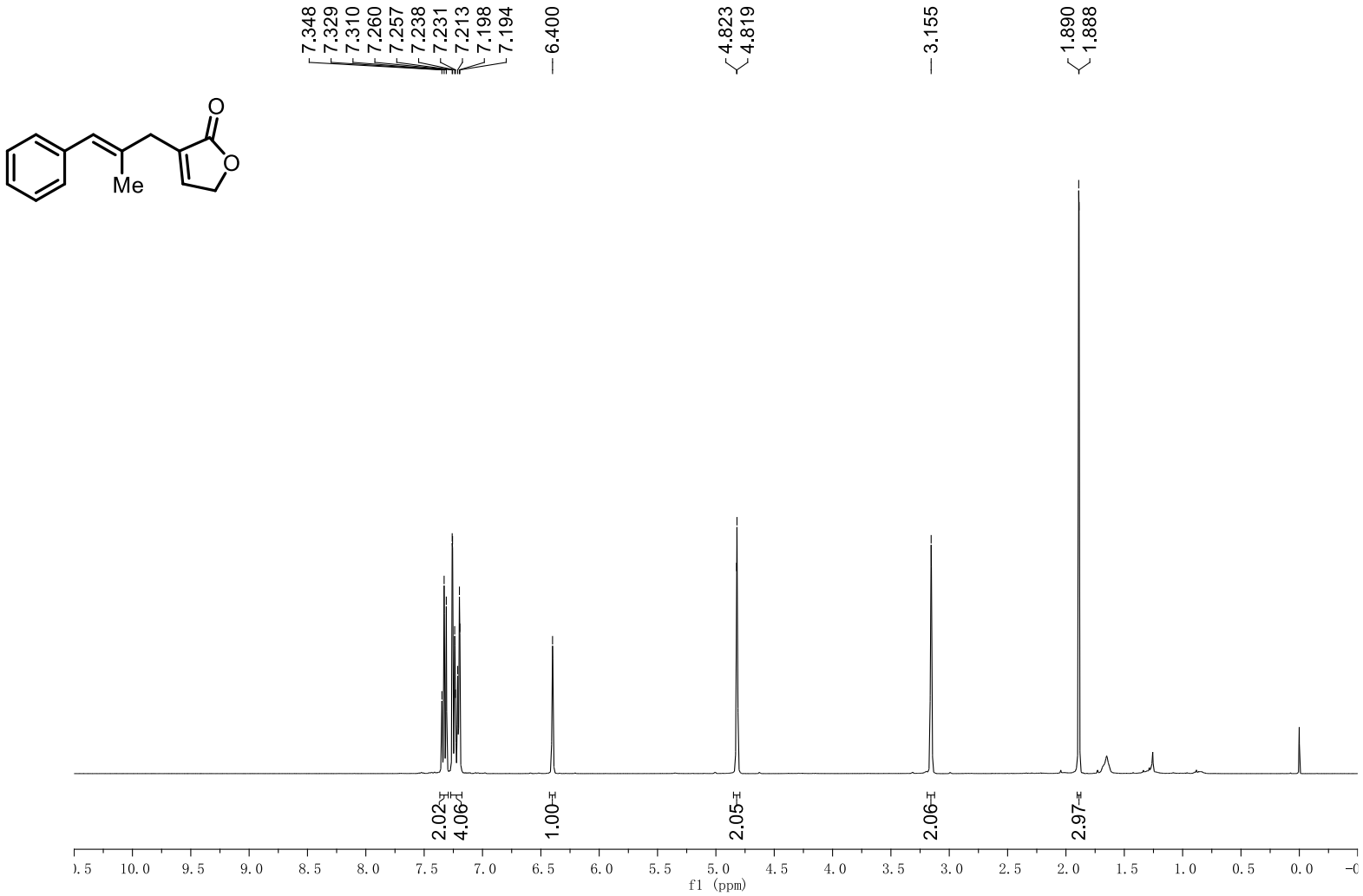
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (3)



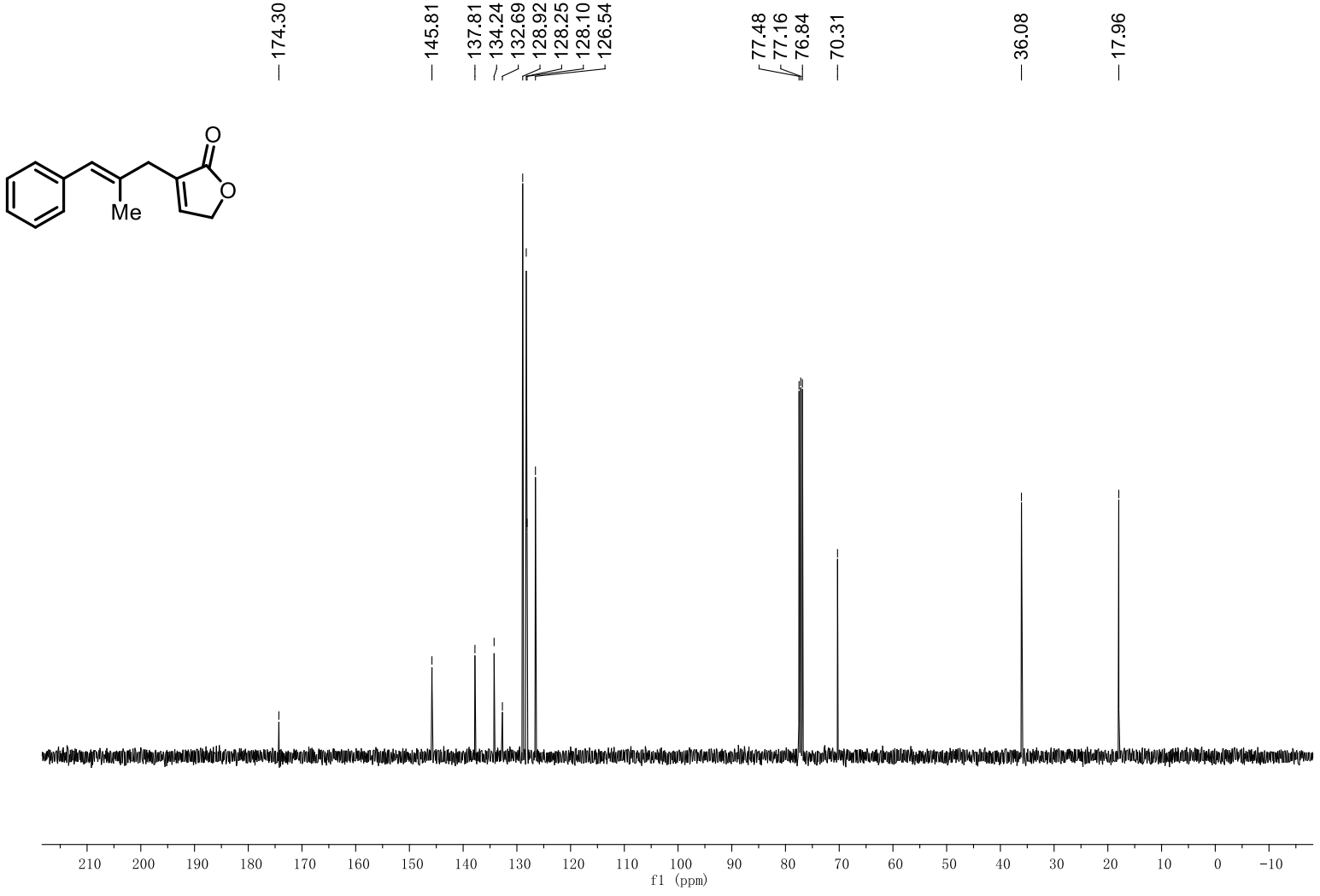
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (3)



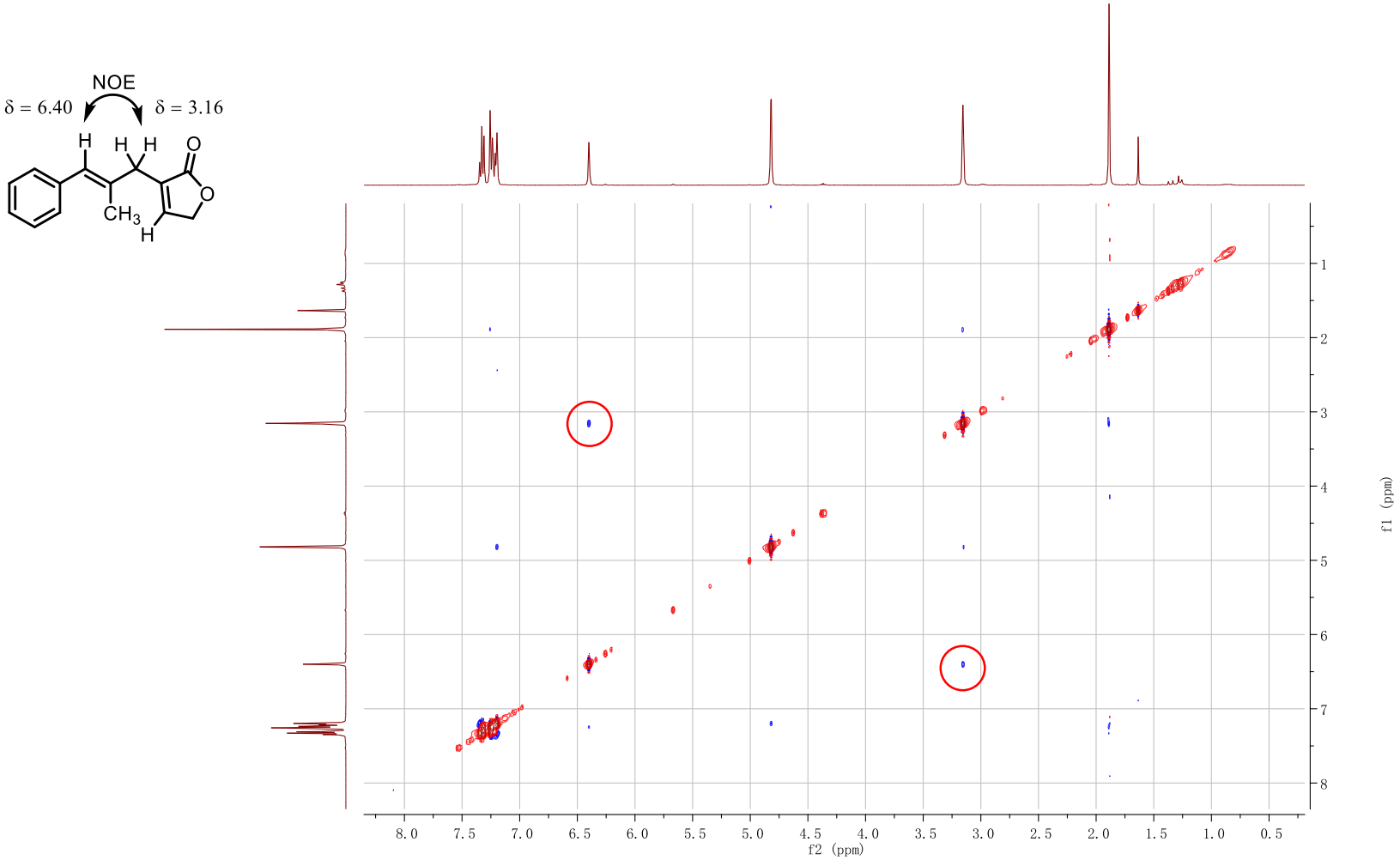
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)furan-2(5*H*)-one (4)



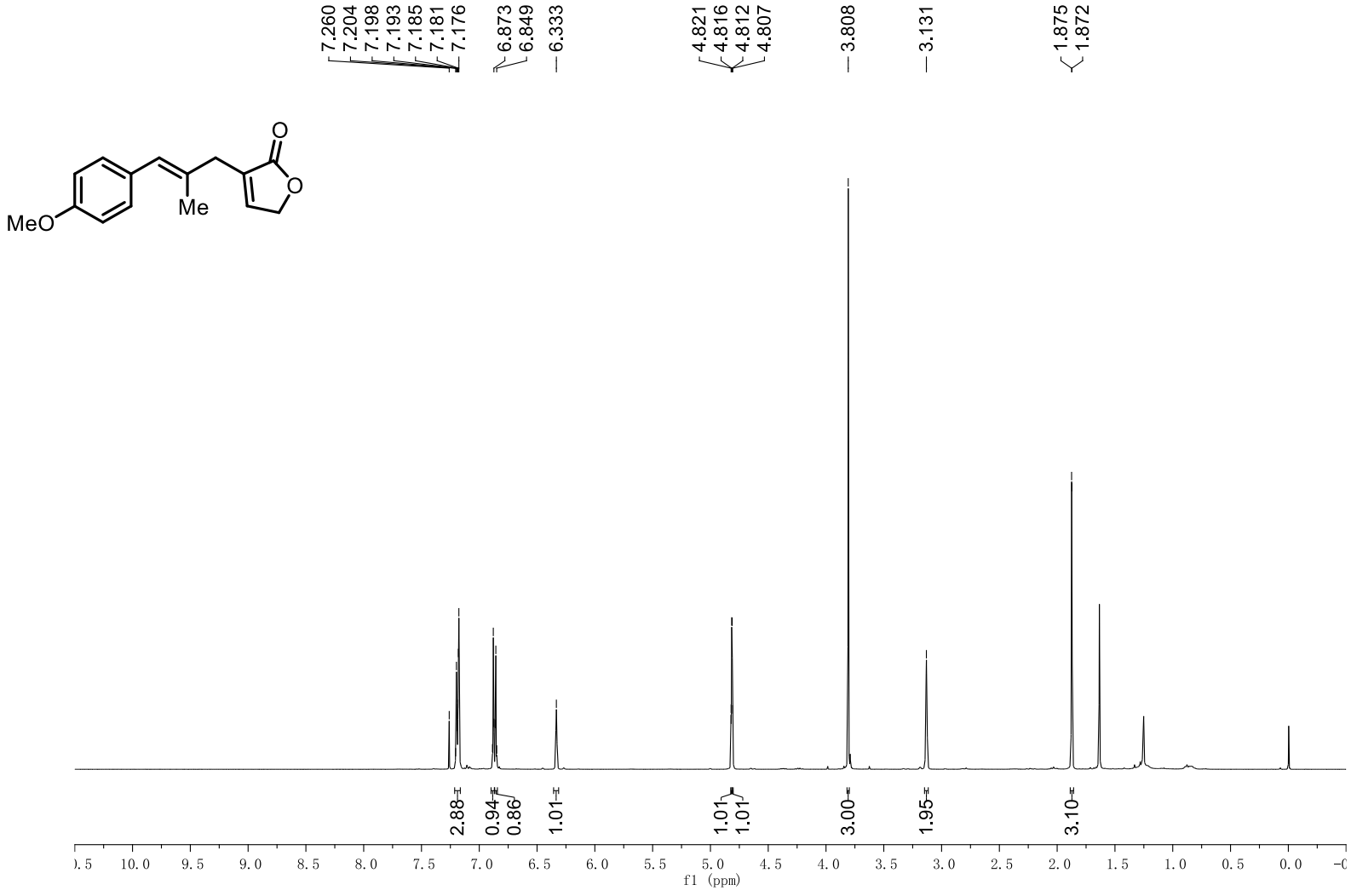
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)furan-2(5*H*)-one (4)



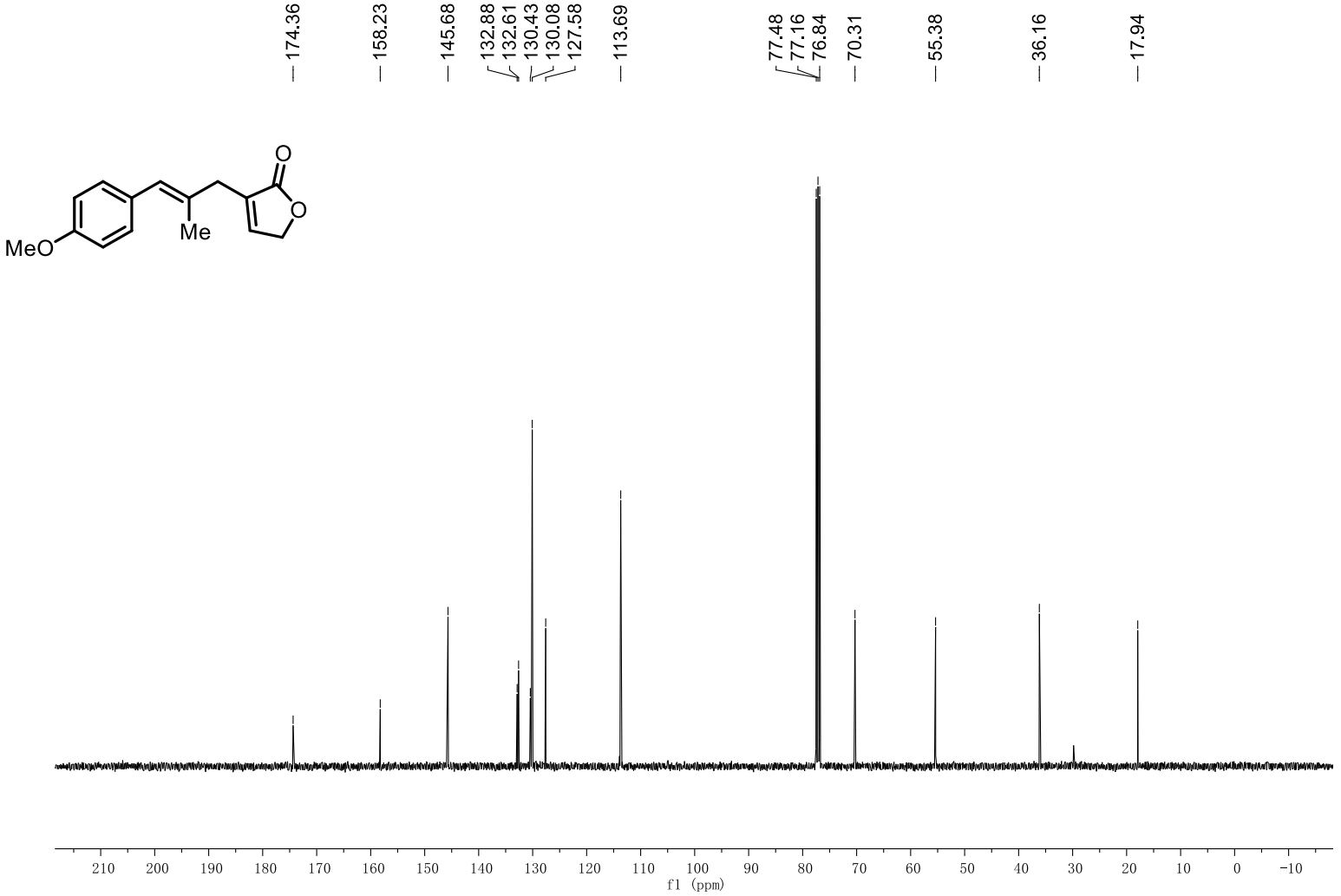
^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)furan-2(5*H*)-one (4)



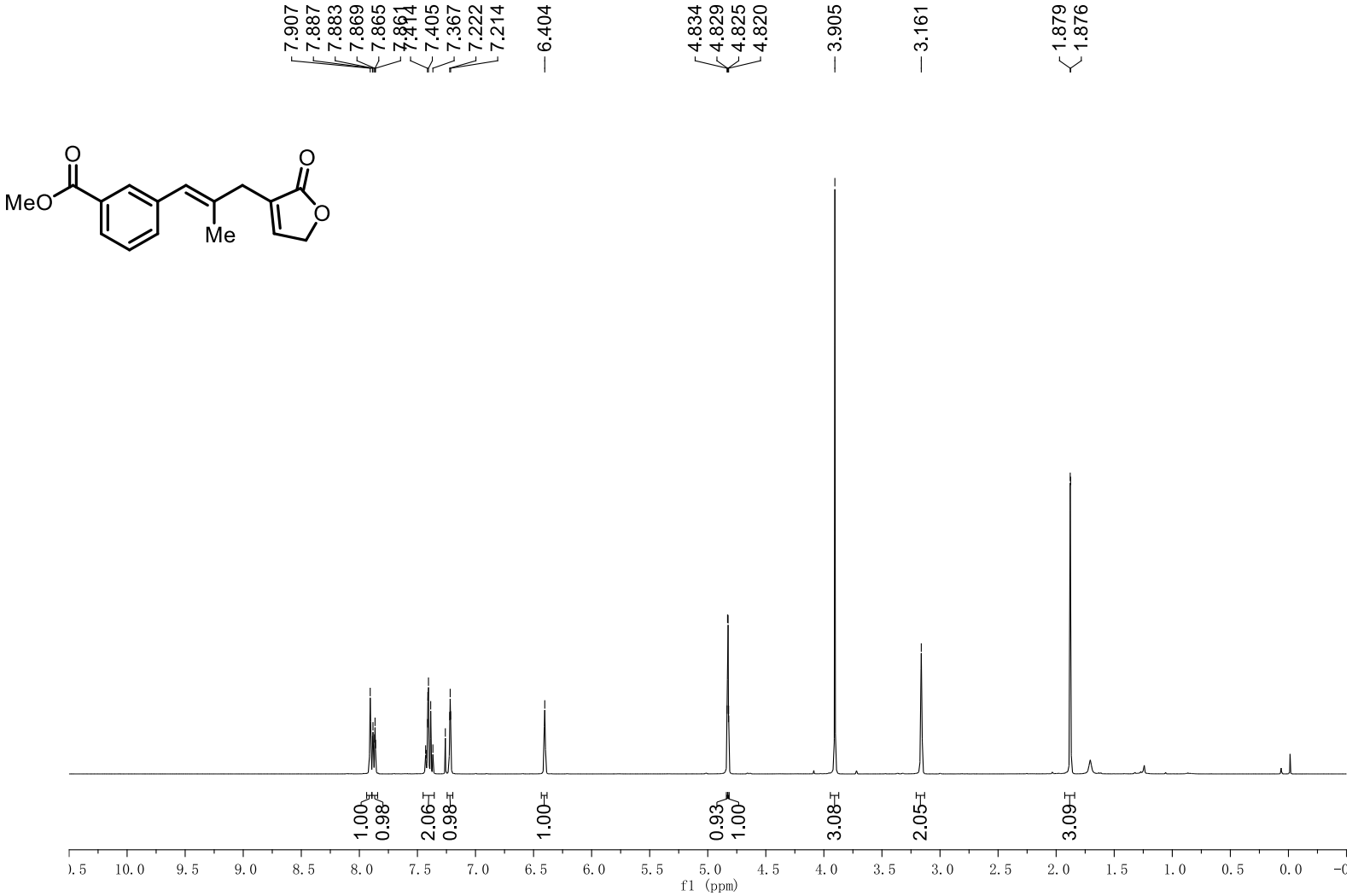
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Methoxyphenyl)-2-methylallyl)furan-2(5*H*)-one (5)



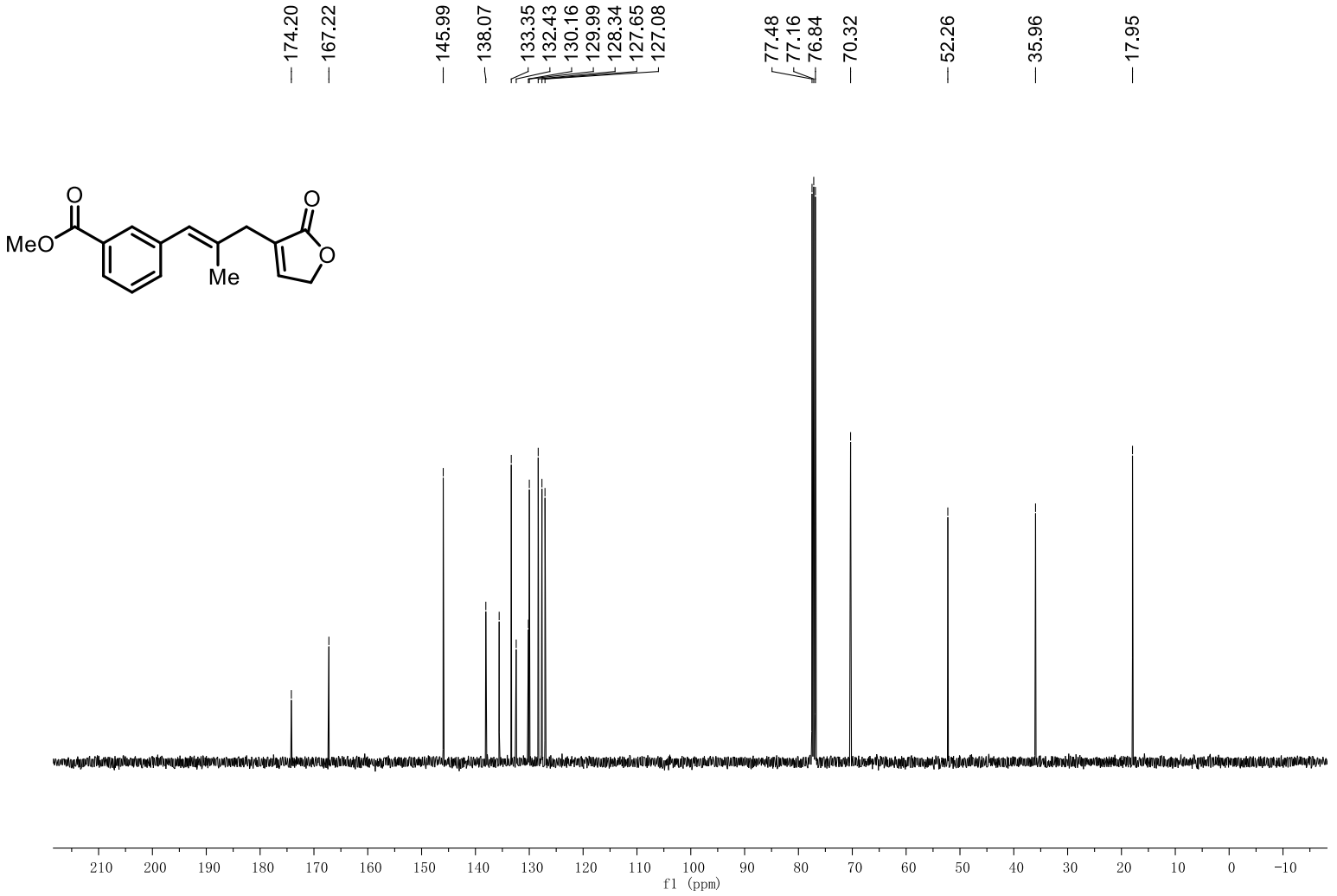
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Methoxyphenyl)-2-methylallyl)furan-2(5*H*)-one (5)



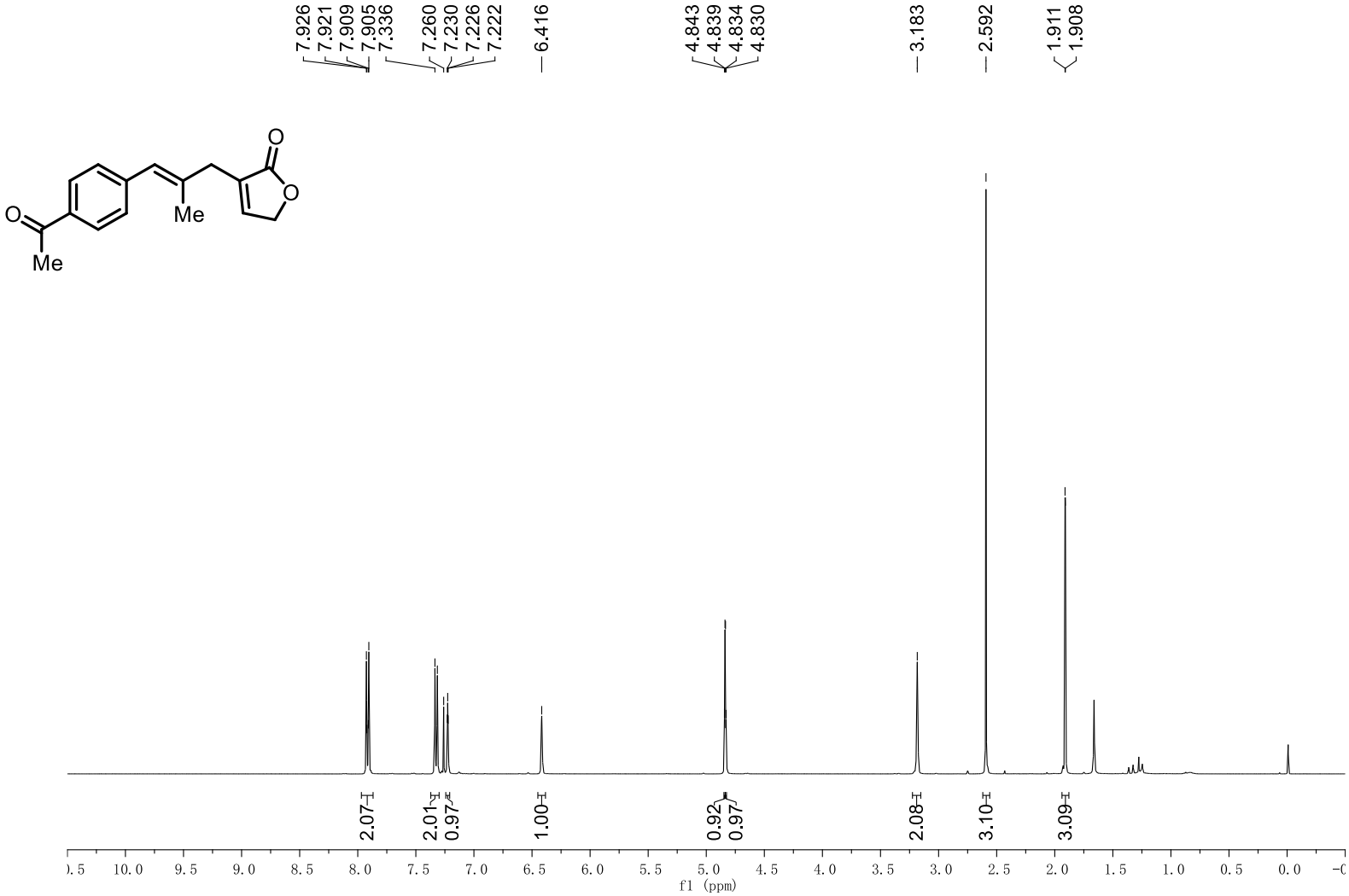
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Methyl (*E*)-3-(2-methyl-3-(2-oxo-2,5-dihydrofuran-3-yl)prop-1-en-1-yl)benzoate (6)



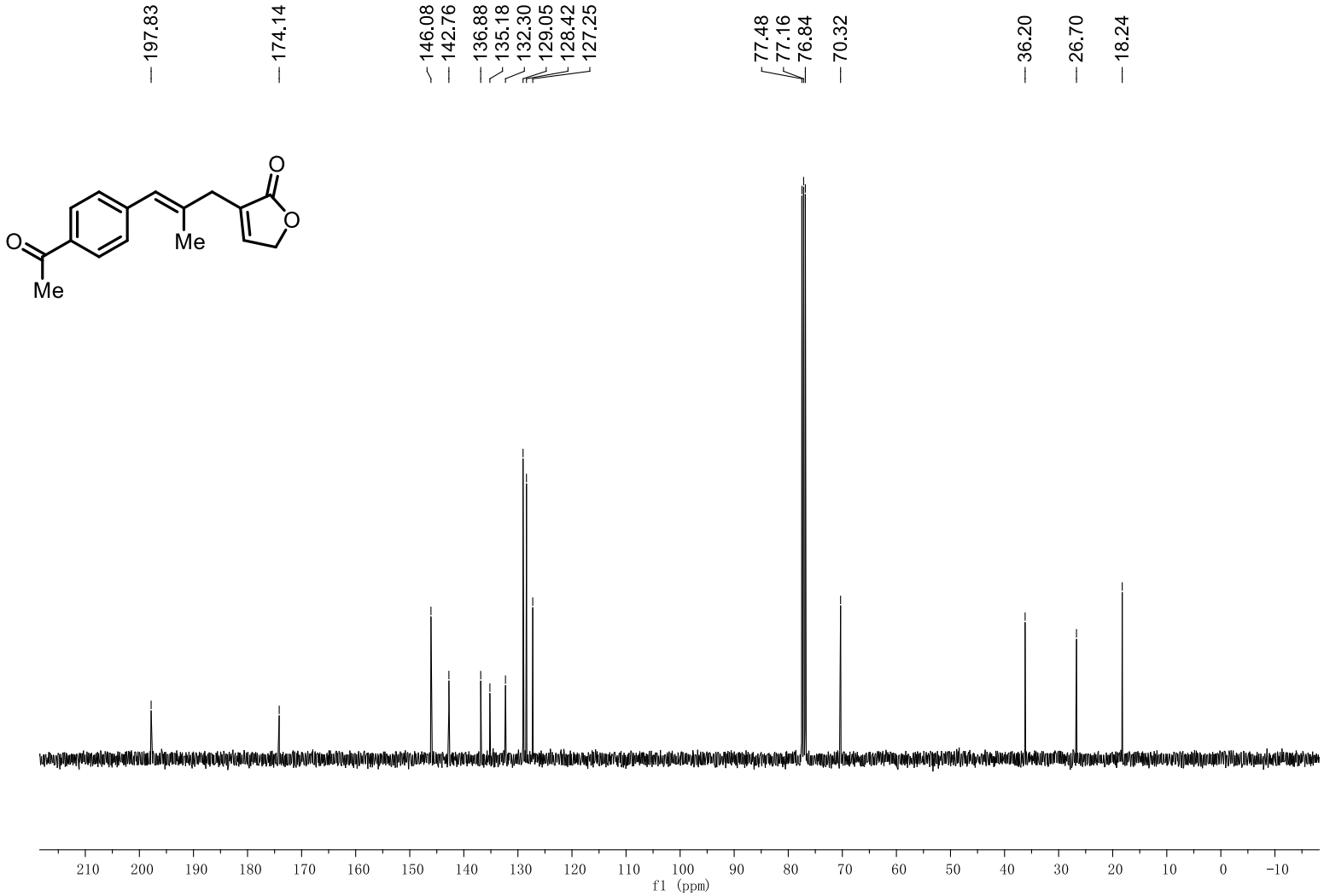
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Methyl (*E*)-3-(2-methyl-3-(2-oxo-2,5-dihydrofuran-3-yl)prop-1-en-1-yl)benzoate (6)



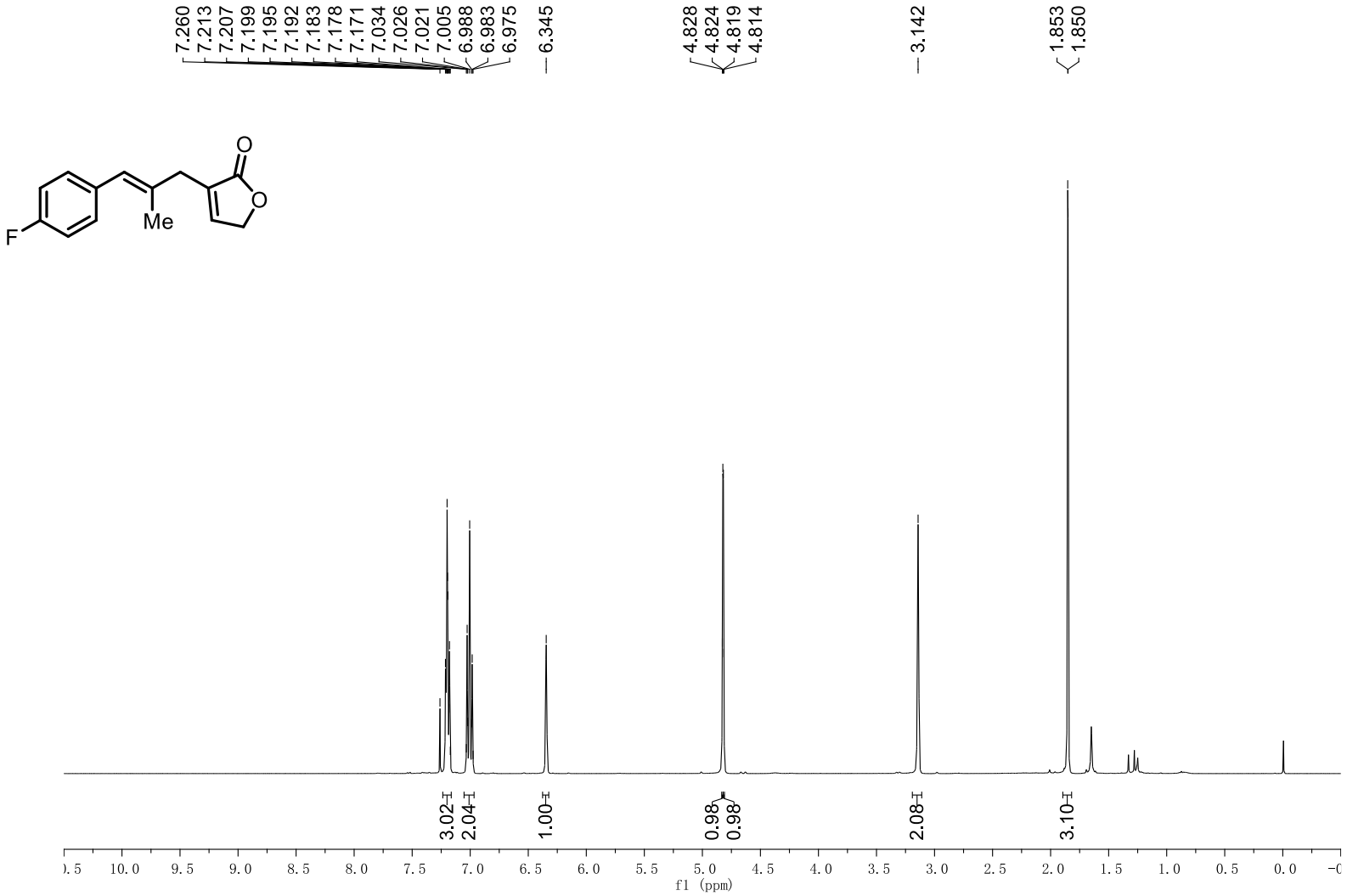
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Acetylphenyl)-2-methylallyl)furan-2(5*H*)-one (7)



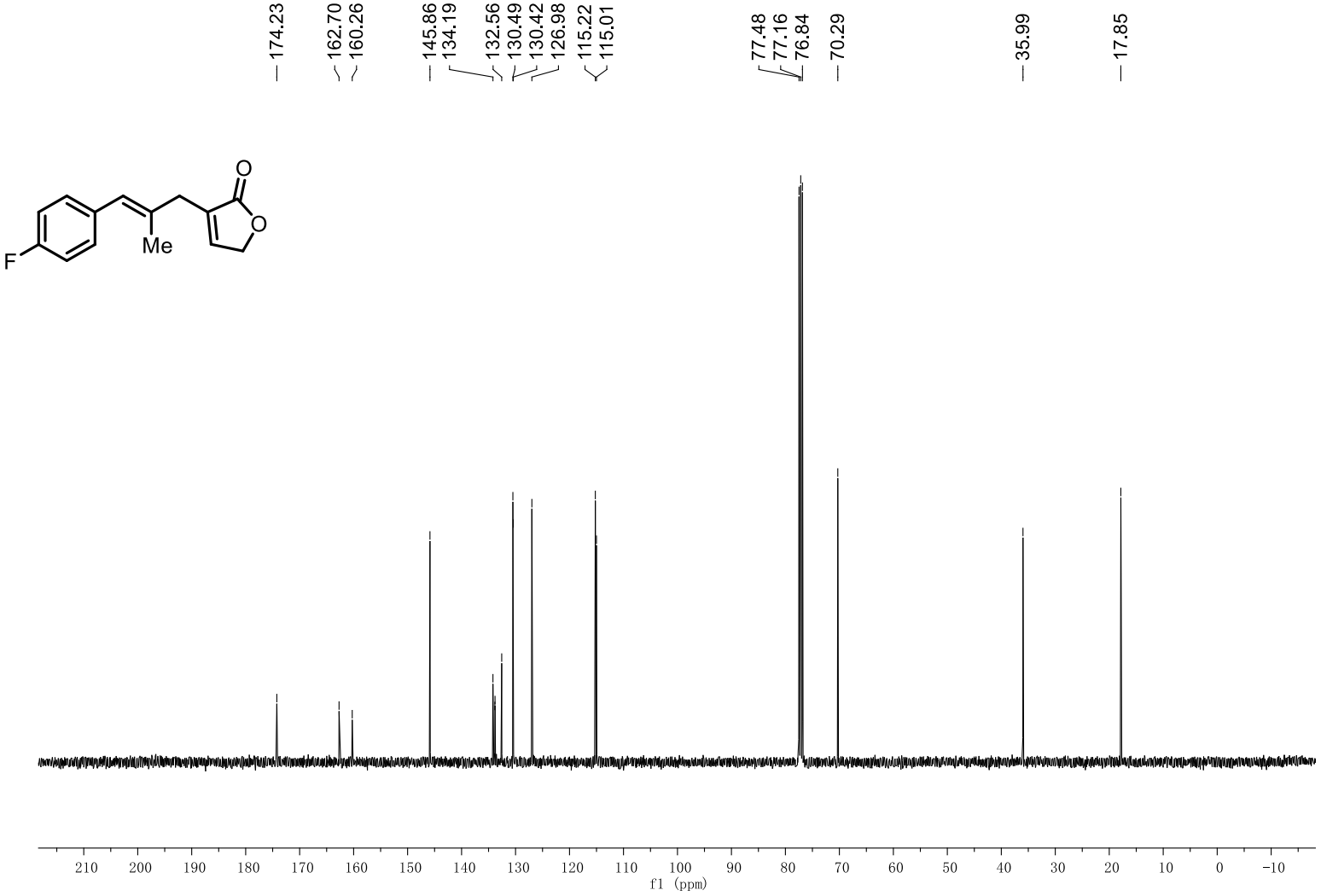
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Acetylphenyl)-2-methylallyl)furan-2(5*H*)-one (7)



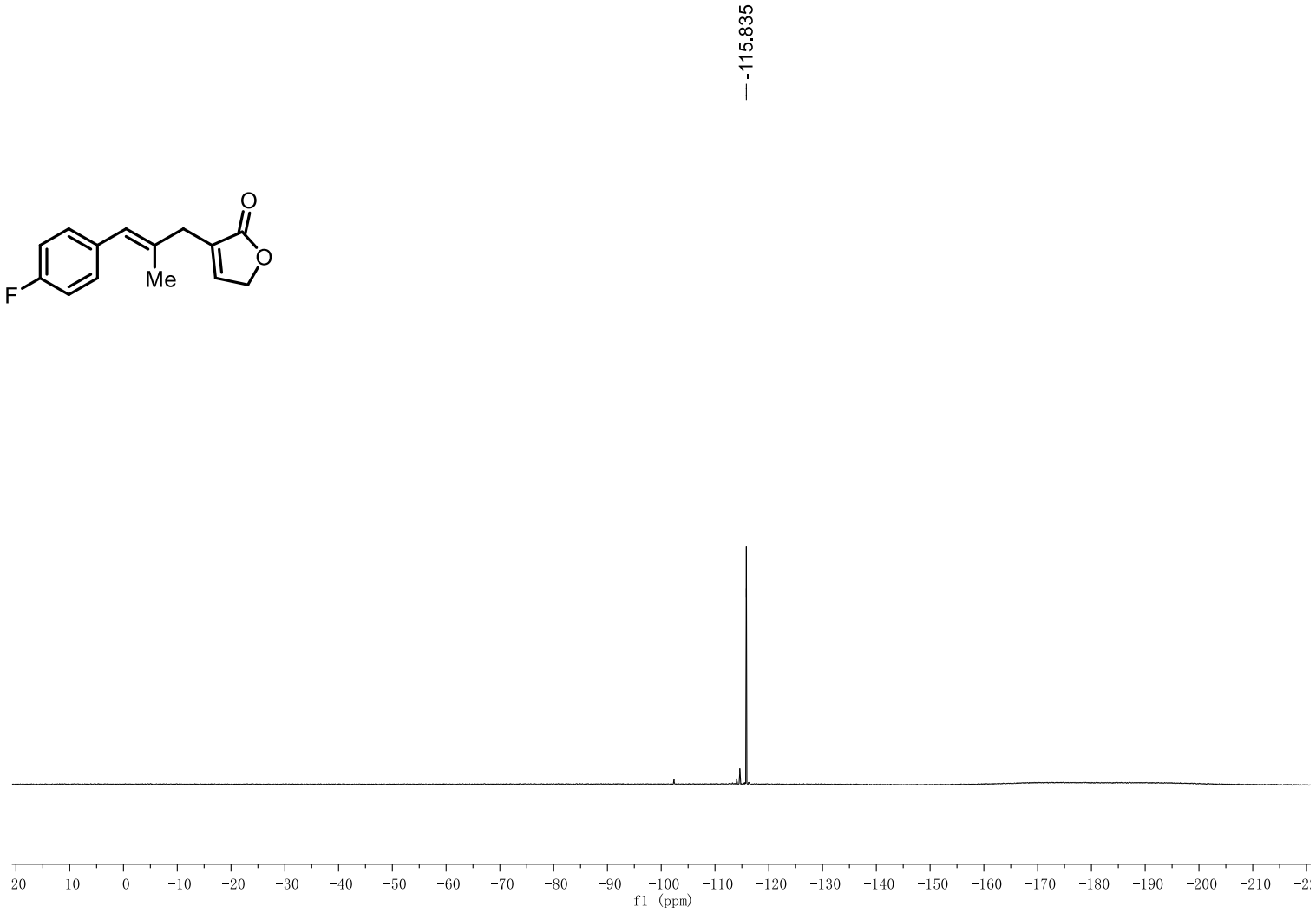
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Fluorophenyl)-2-methylallyl)furan-2(5*H*)-one (8)



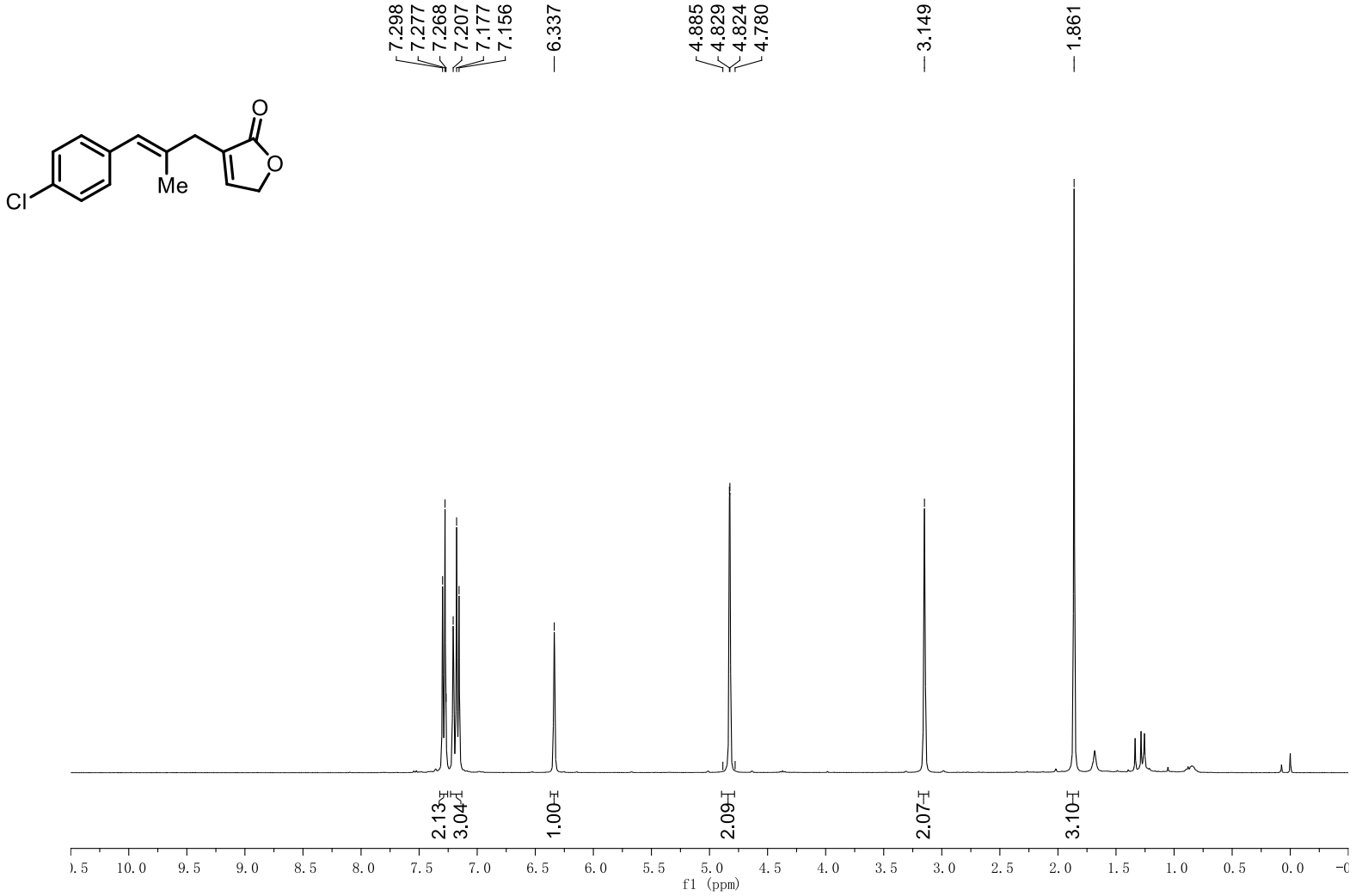
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Fluorophenyl)-2-methylallyl)furan-2(5*H*)-one (8)



^{19}F NMR (377 MHz, CDCl3) spectrum of (*E*)-3-(3-(4-Fluorophenyl)-2-methylallyl)furan-2(5*H*)-one (8)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Chlorophenyl)-2-methylallyl)furan-2(5*H*)-one (9)



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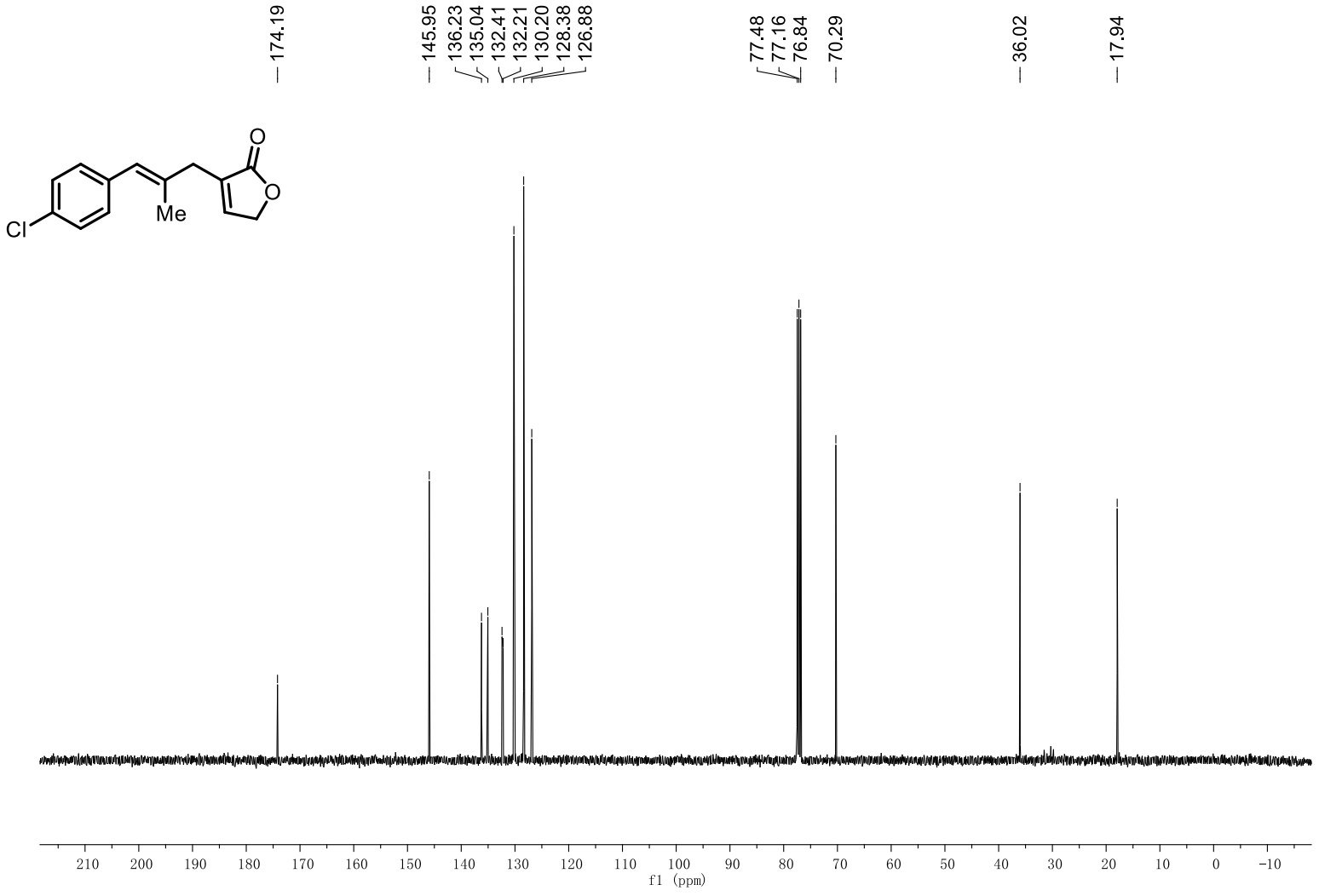
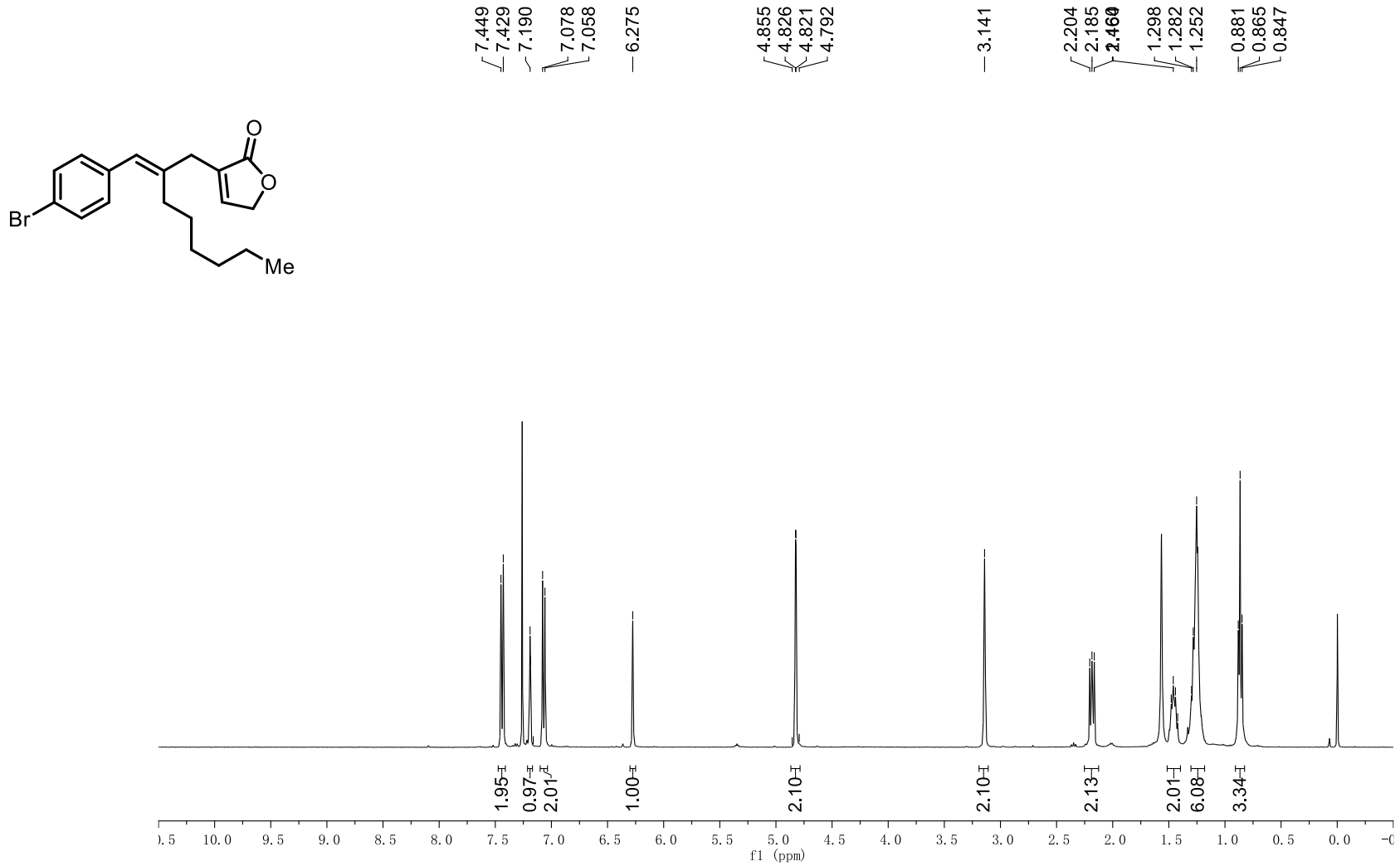


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-(4-Bromobenzylidene)octyl)furan-2(5*H*)-one (10)



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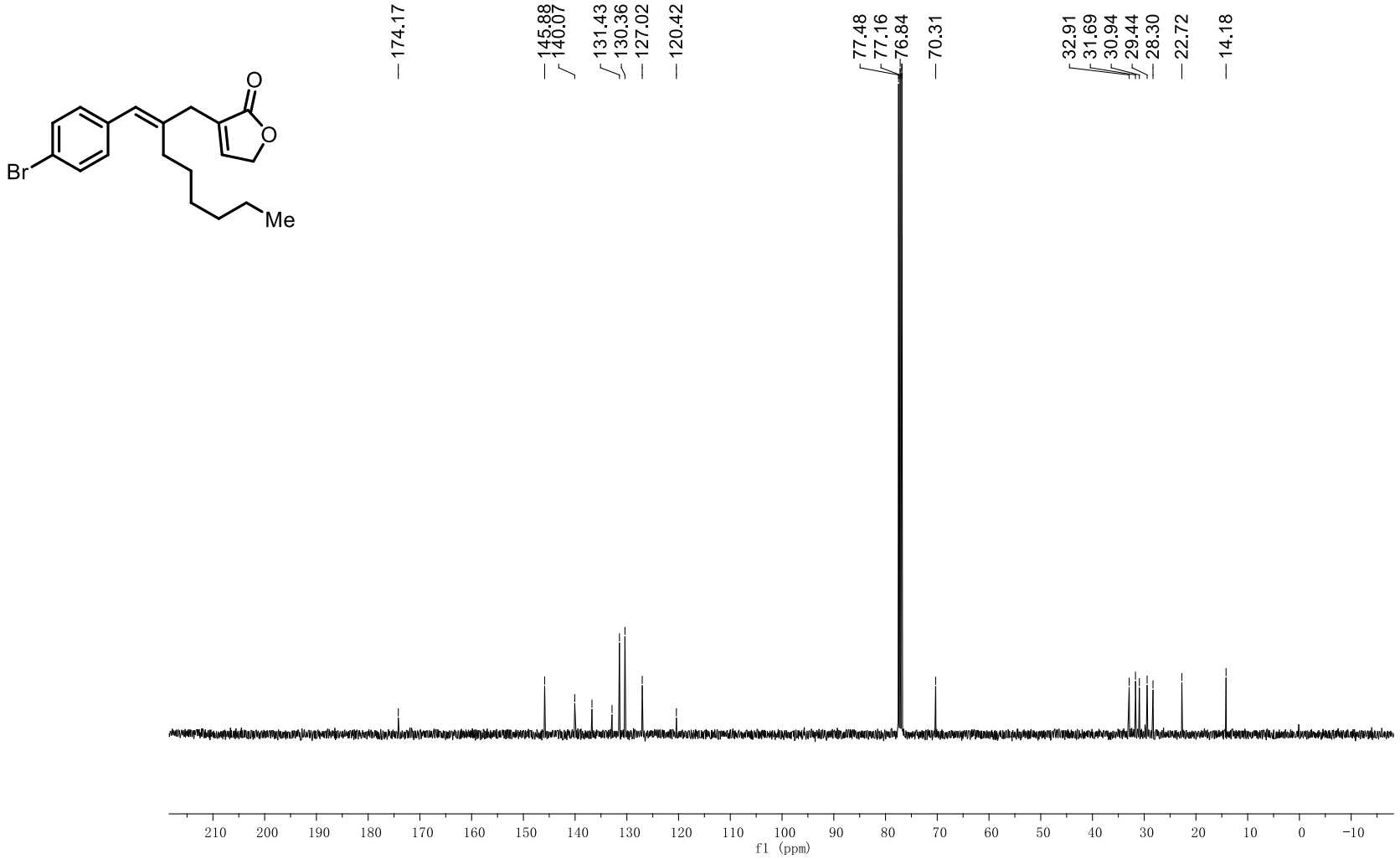
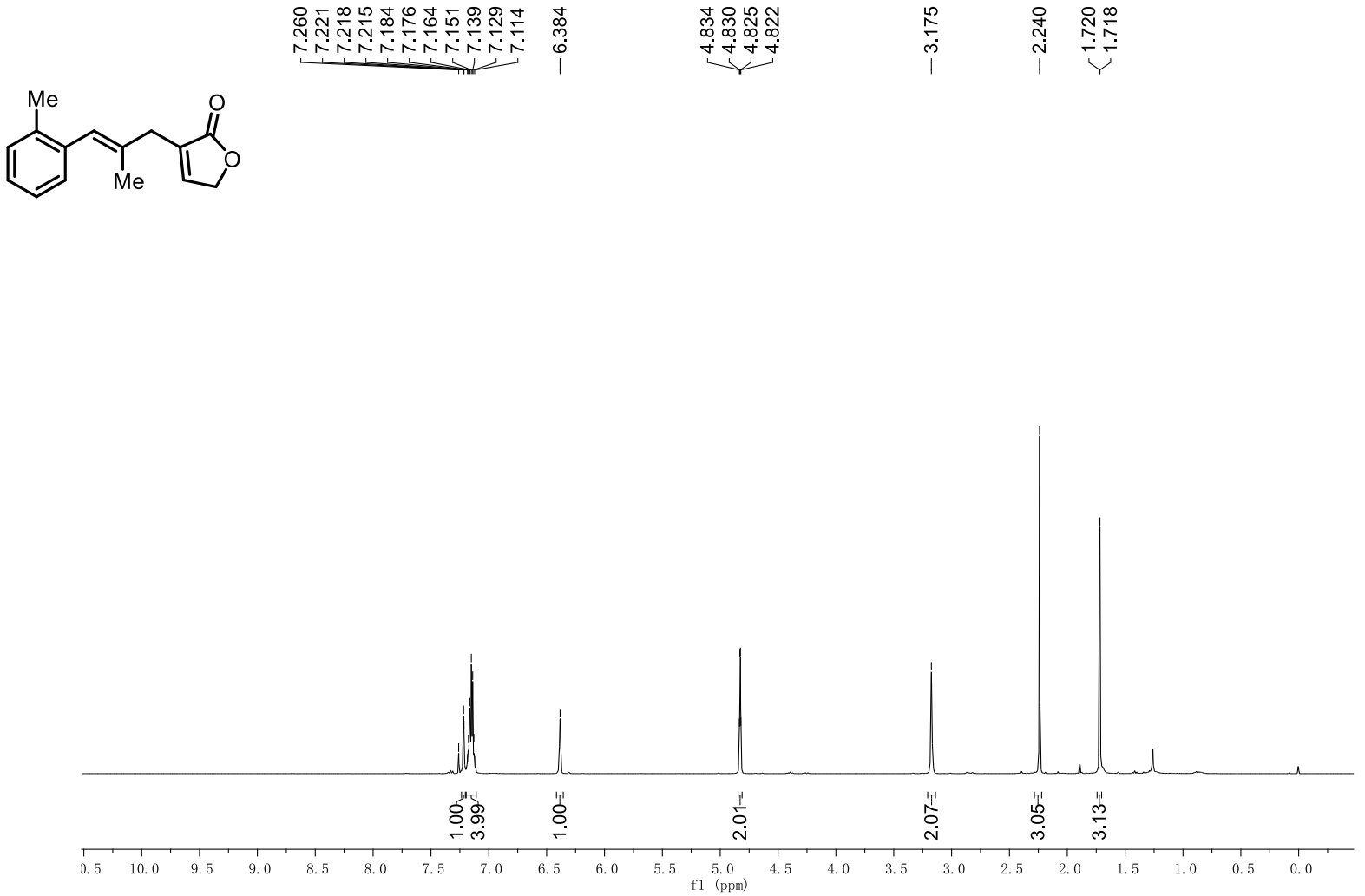
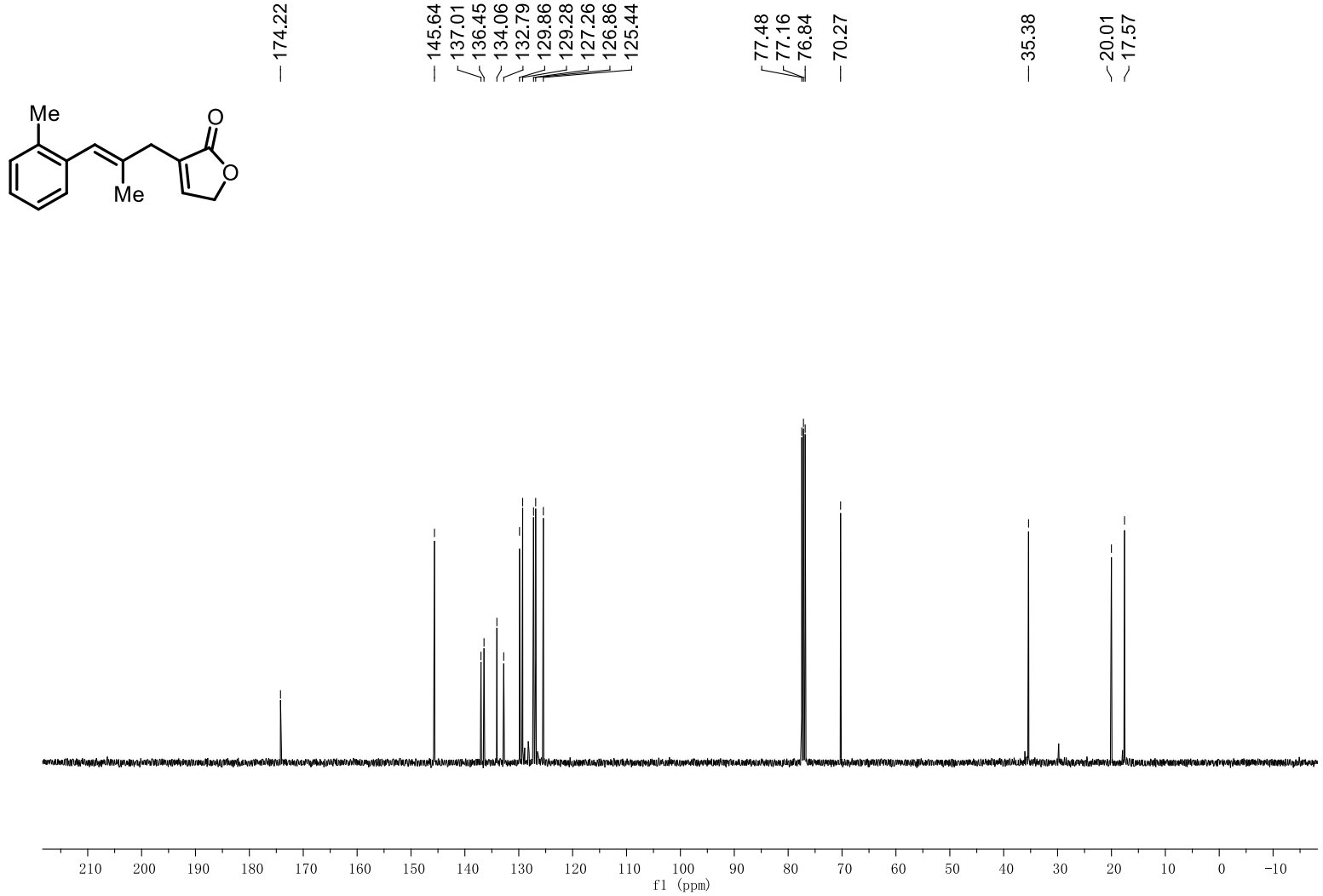


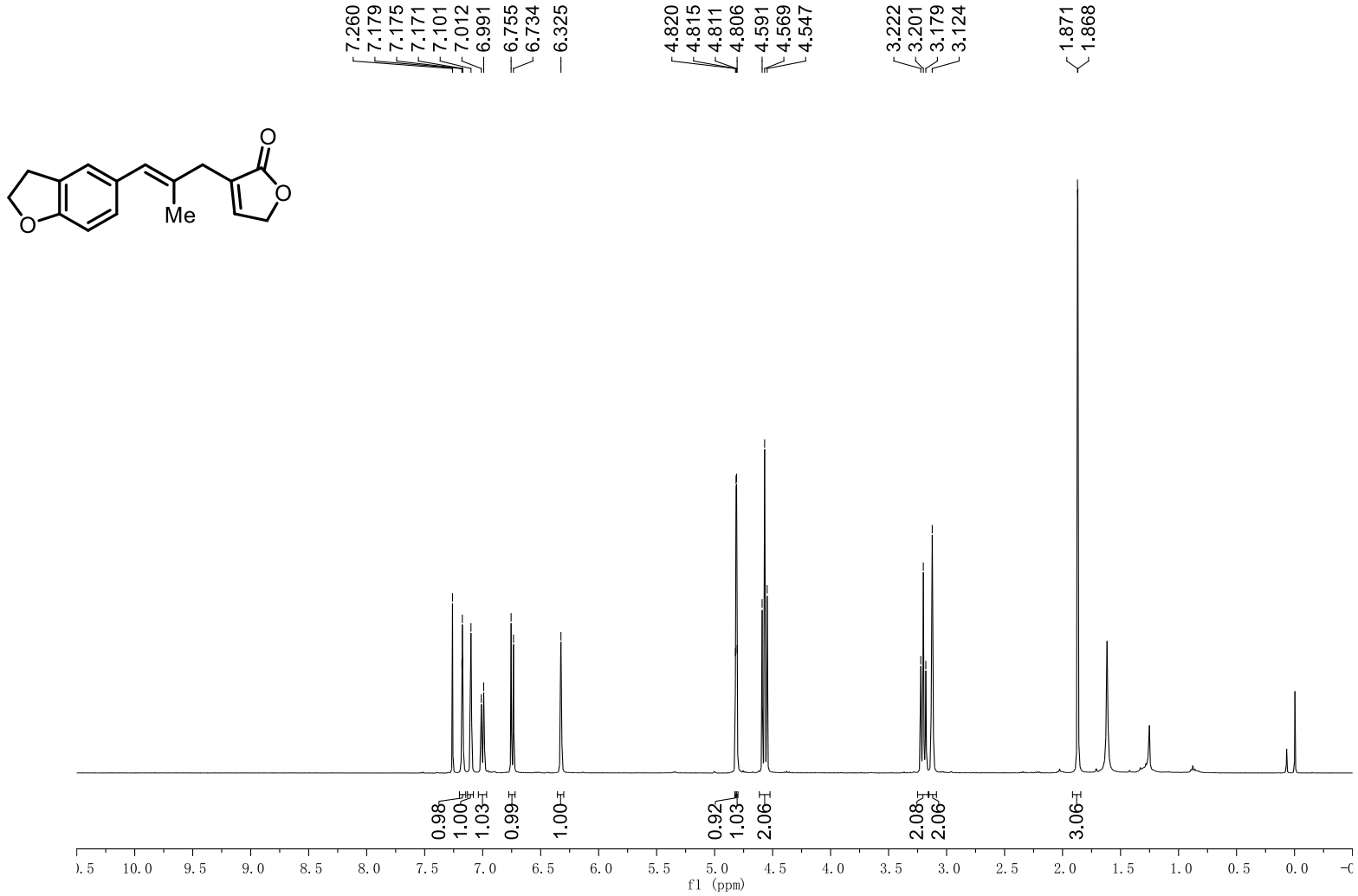
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(*o*-tolyl)allyl)furan-2(5*H*)-one (11)



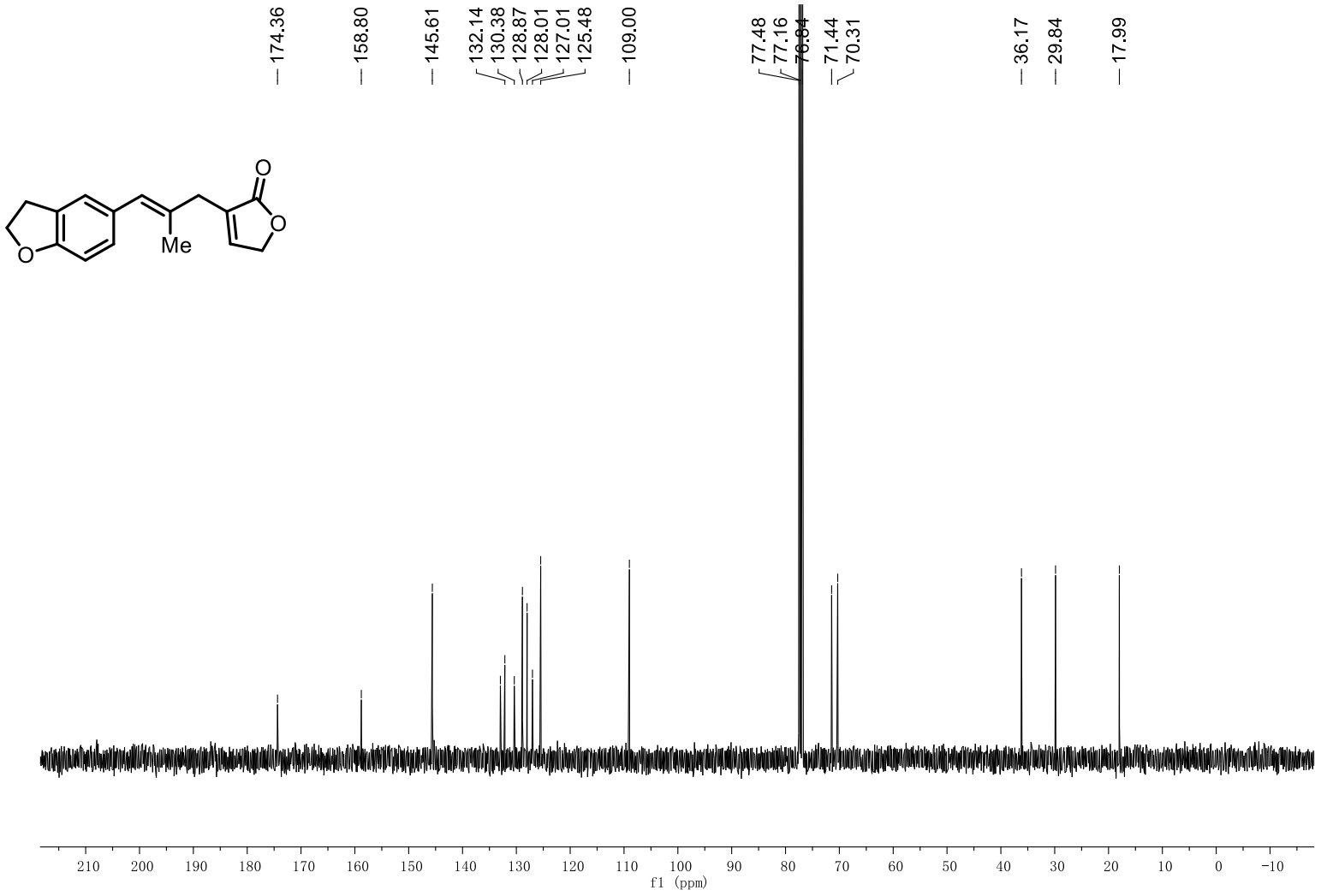
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(*o*-tolyl)allyl)furan-2(5*H*)-one (11)



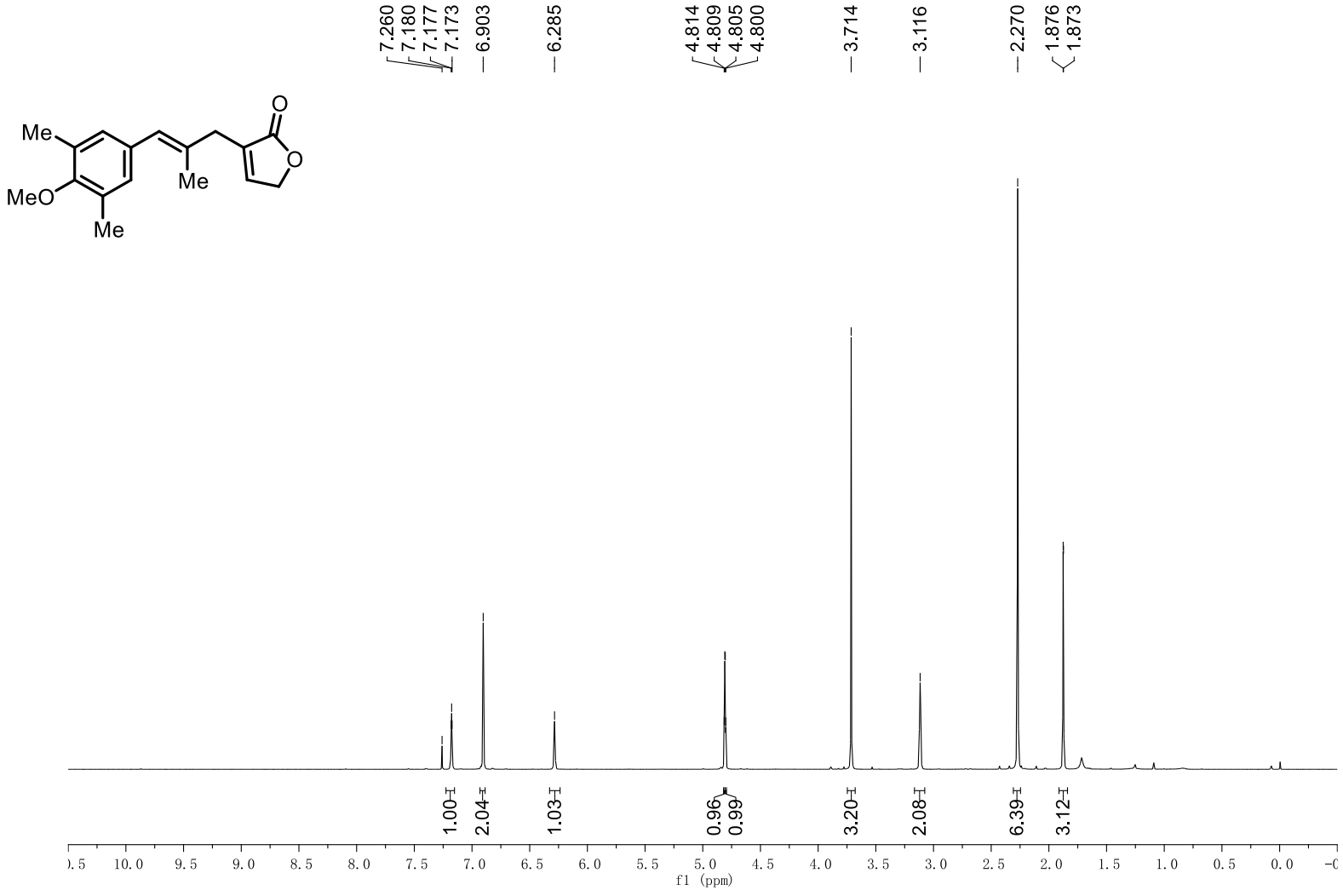
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(2,3-Dihydrobenzofuran-5-yl)-2-methylallyl)furan-2(5*H*)-one (12)



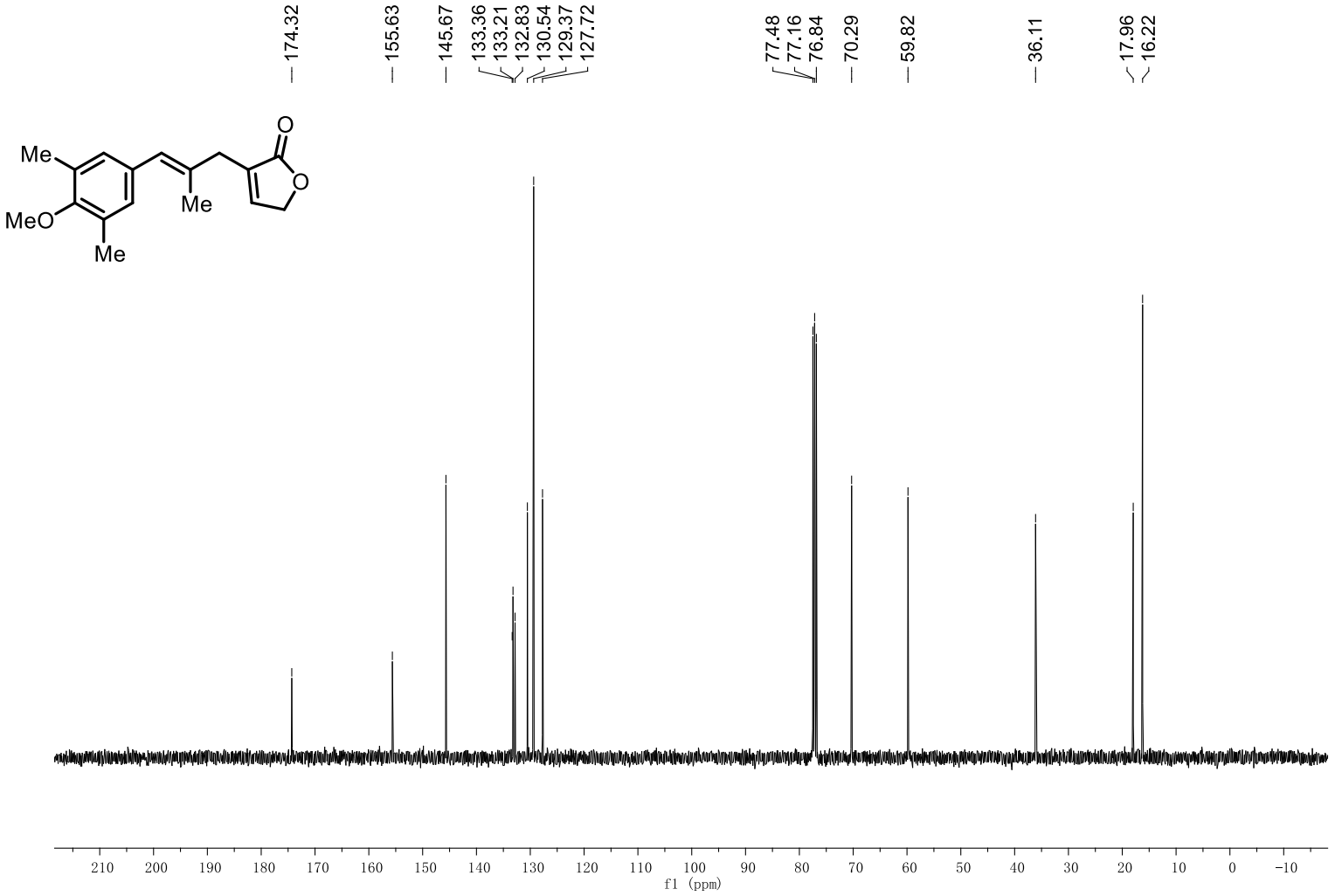
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(2,3-Dihydrobenzofuran-5-yl)-2-methylallyl)furan-2(5*H*)-one (12)



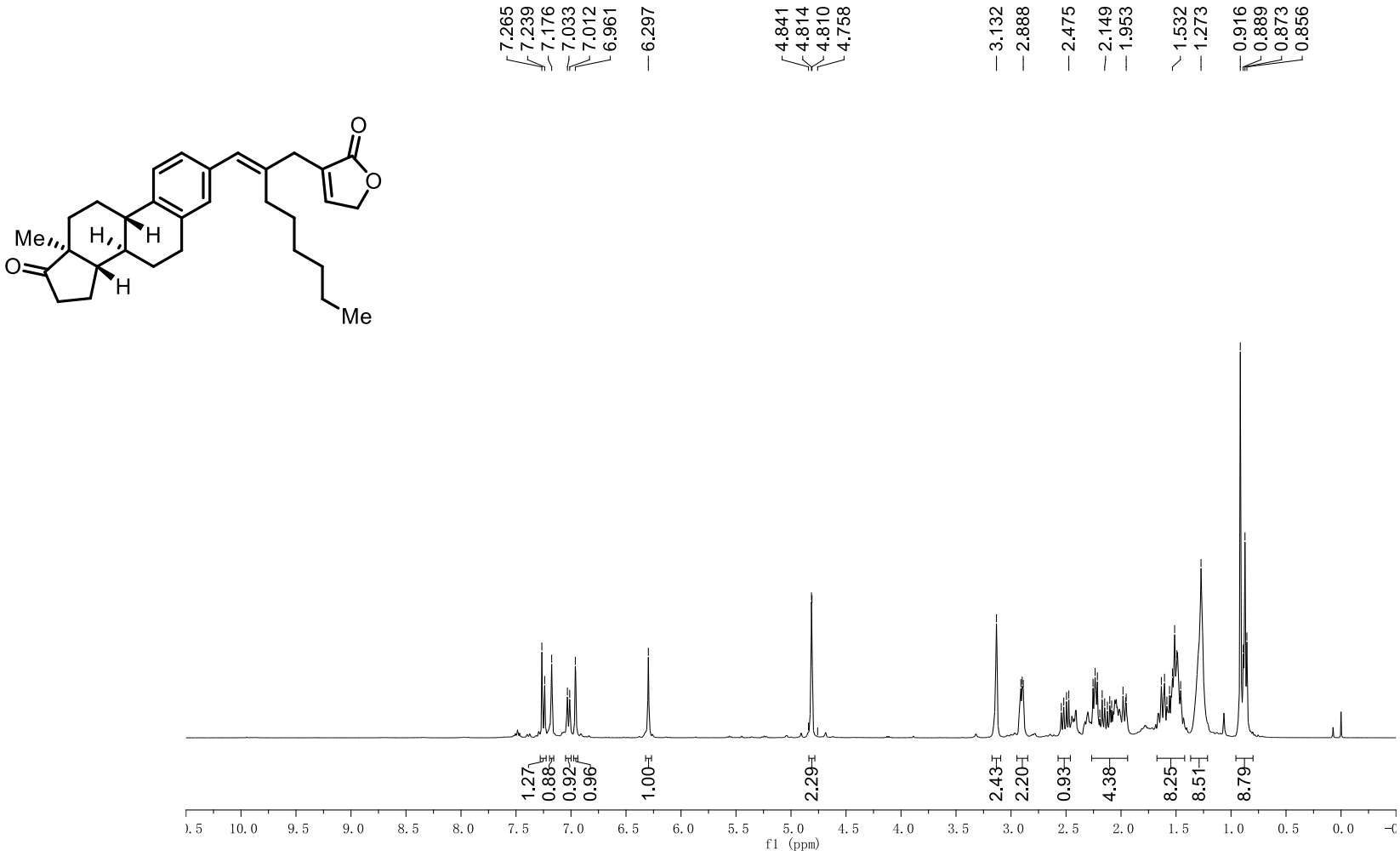
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Methoxy-3,5-dimethylphenyl)-2-methylallyl)furan-2(5*H*)-one (13)



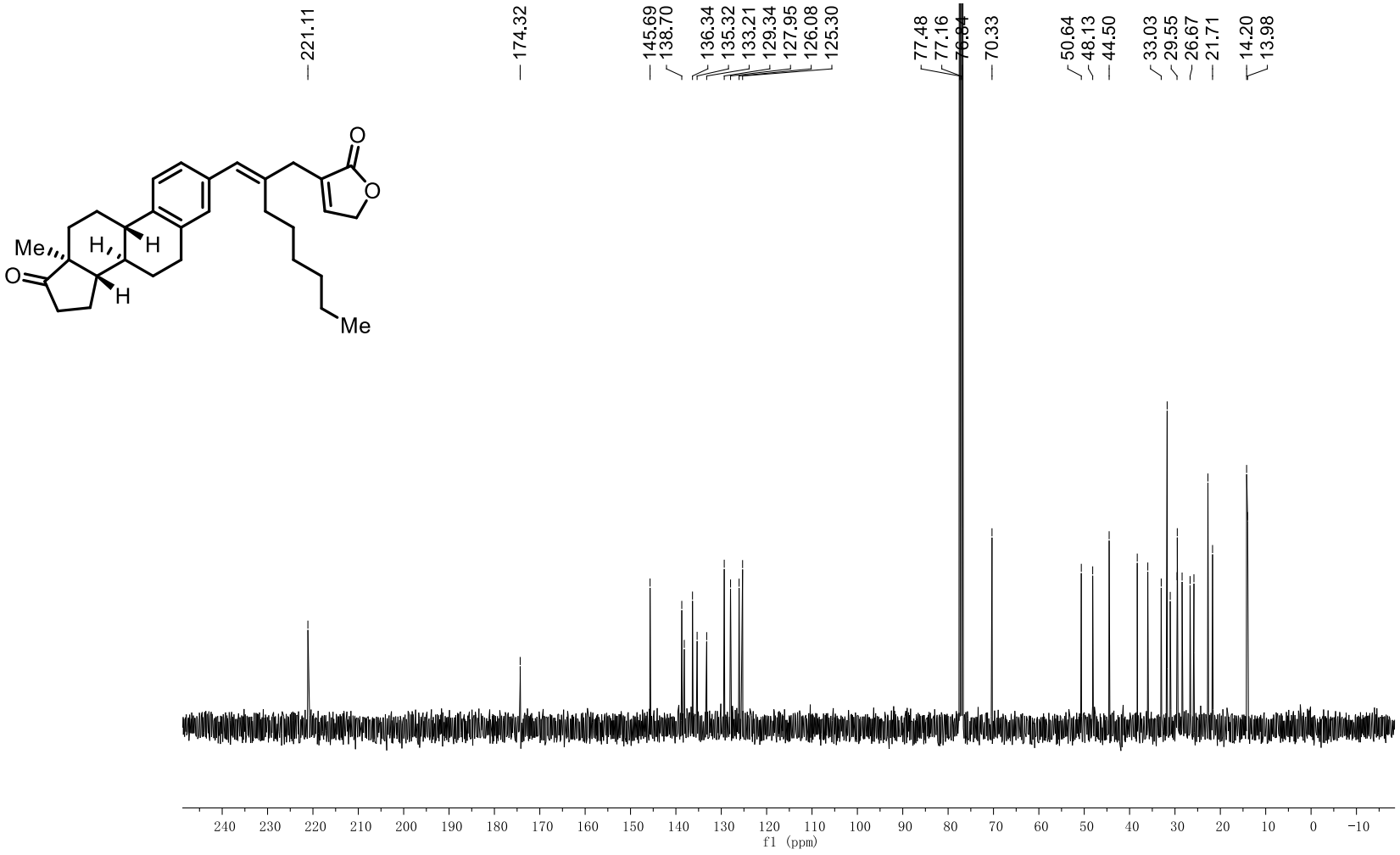
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Methoxy-3,5-dimethylphenyl)-2-methylallyl)furan-2(5*H*)-one (13)



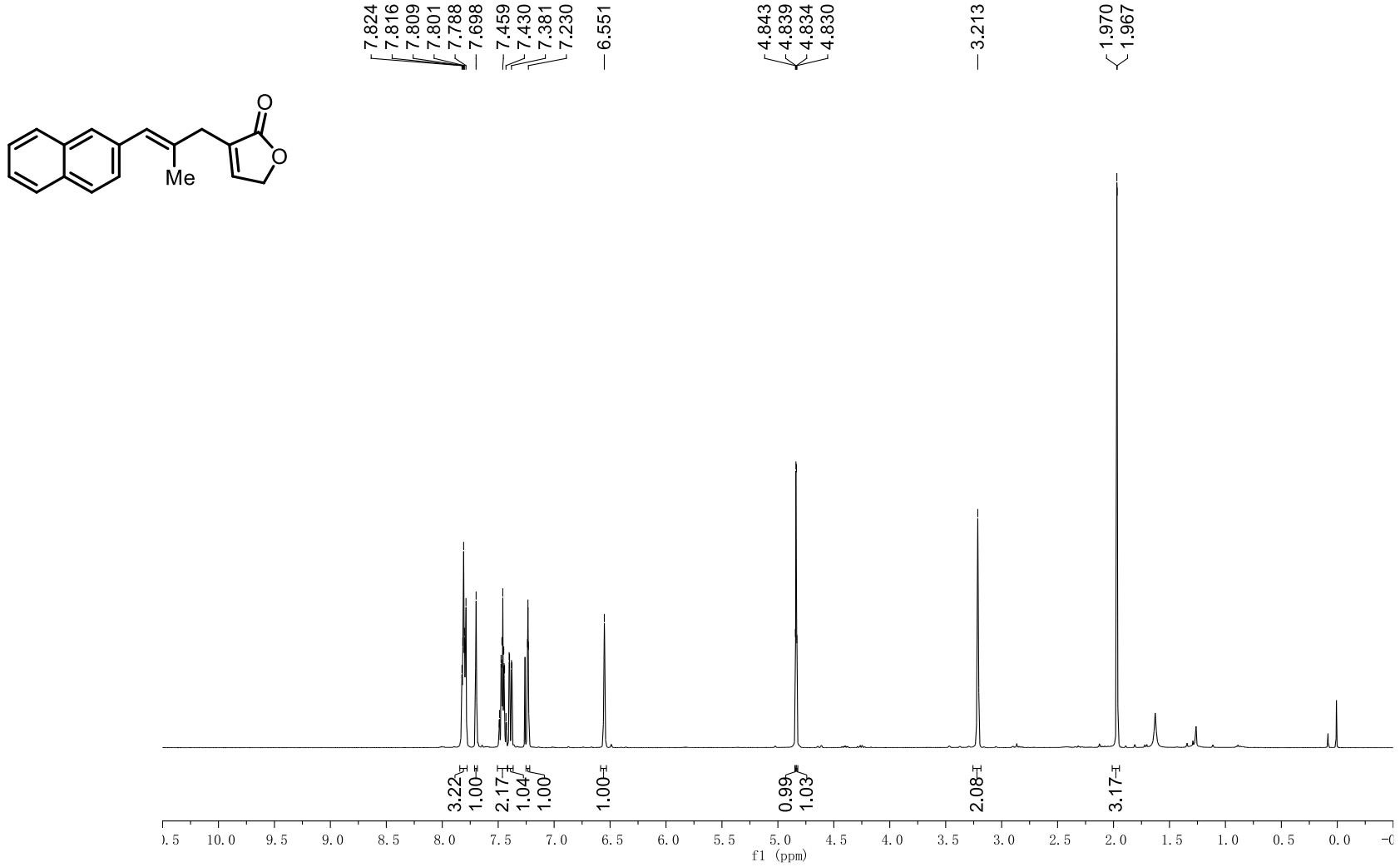
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((*E*)-2-(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclo-penta[a]phenanthren-3-yl)methylene)octyl)furan-2(5*H*)-one (14)



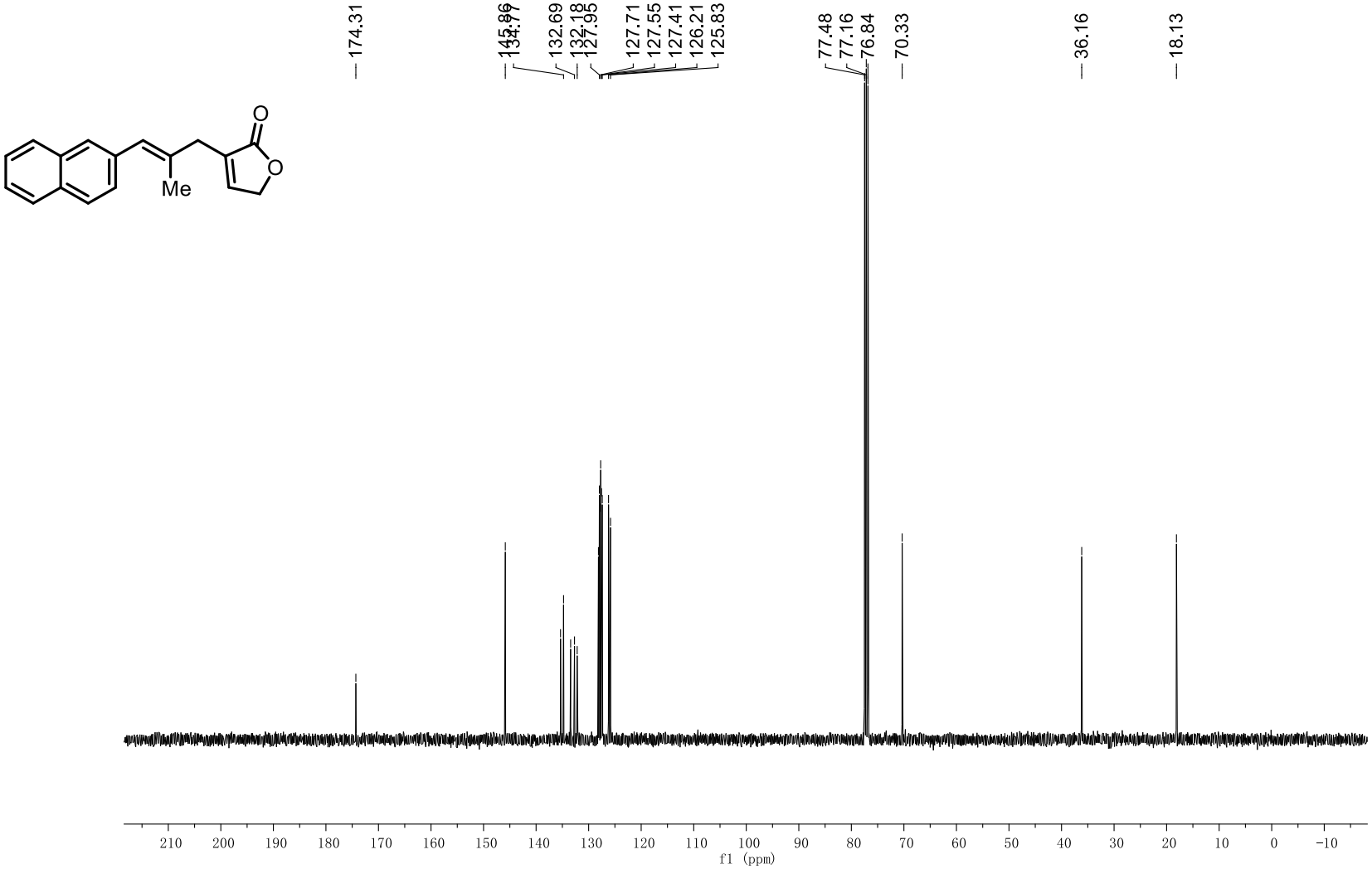
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-((*E*)-2-(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclo-penta[a]phenanthren-3-yl)methylene)octyl)furan-2(5*H*)-one (14)



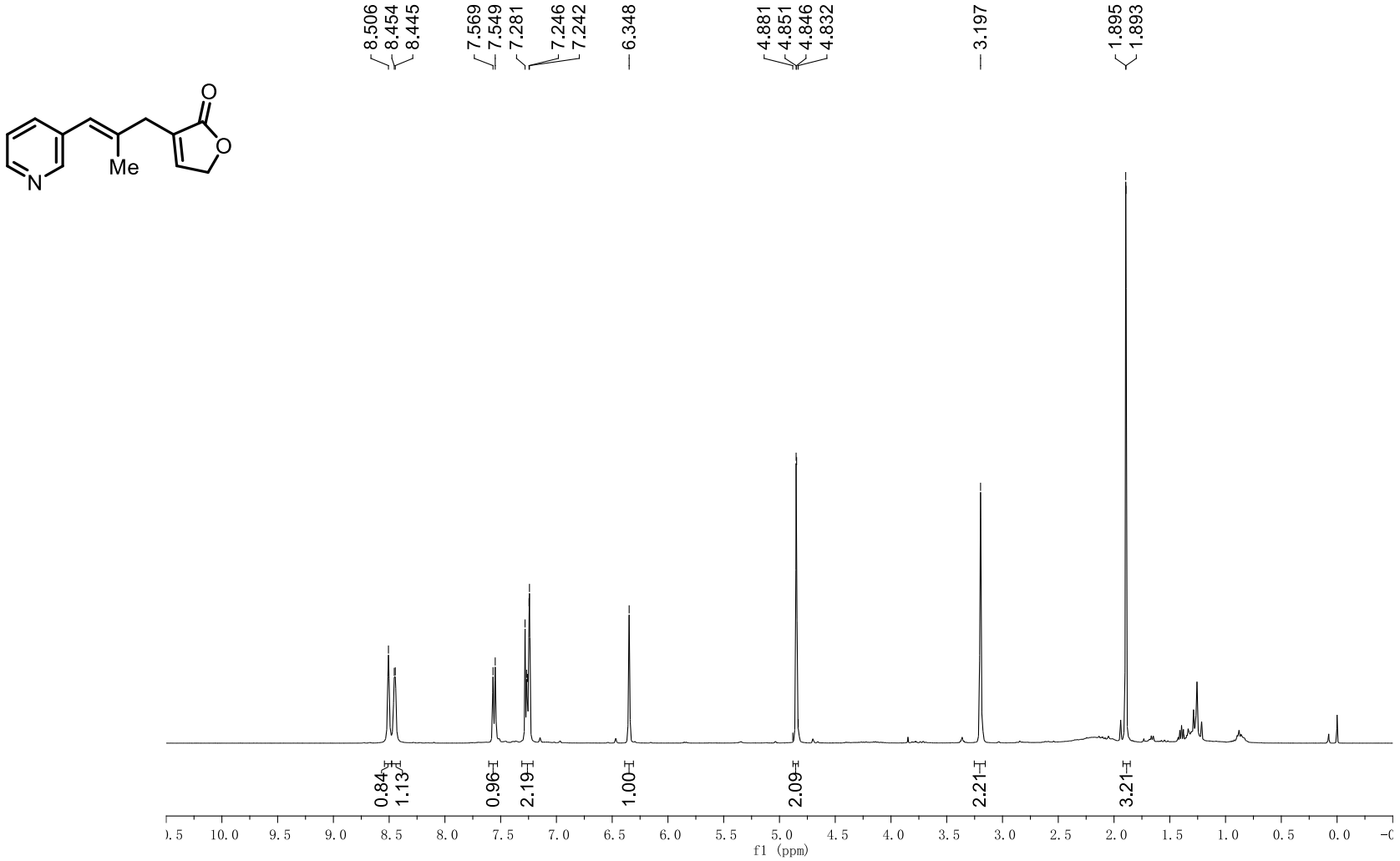
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(naphthalen-2-yl)allyl)furan-2(5*H*)-one (15)



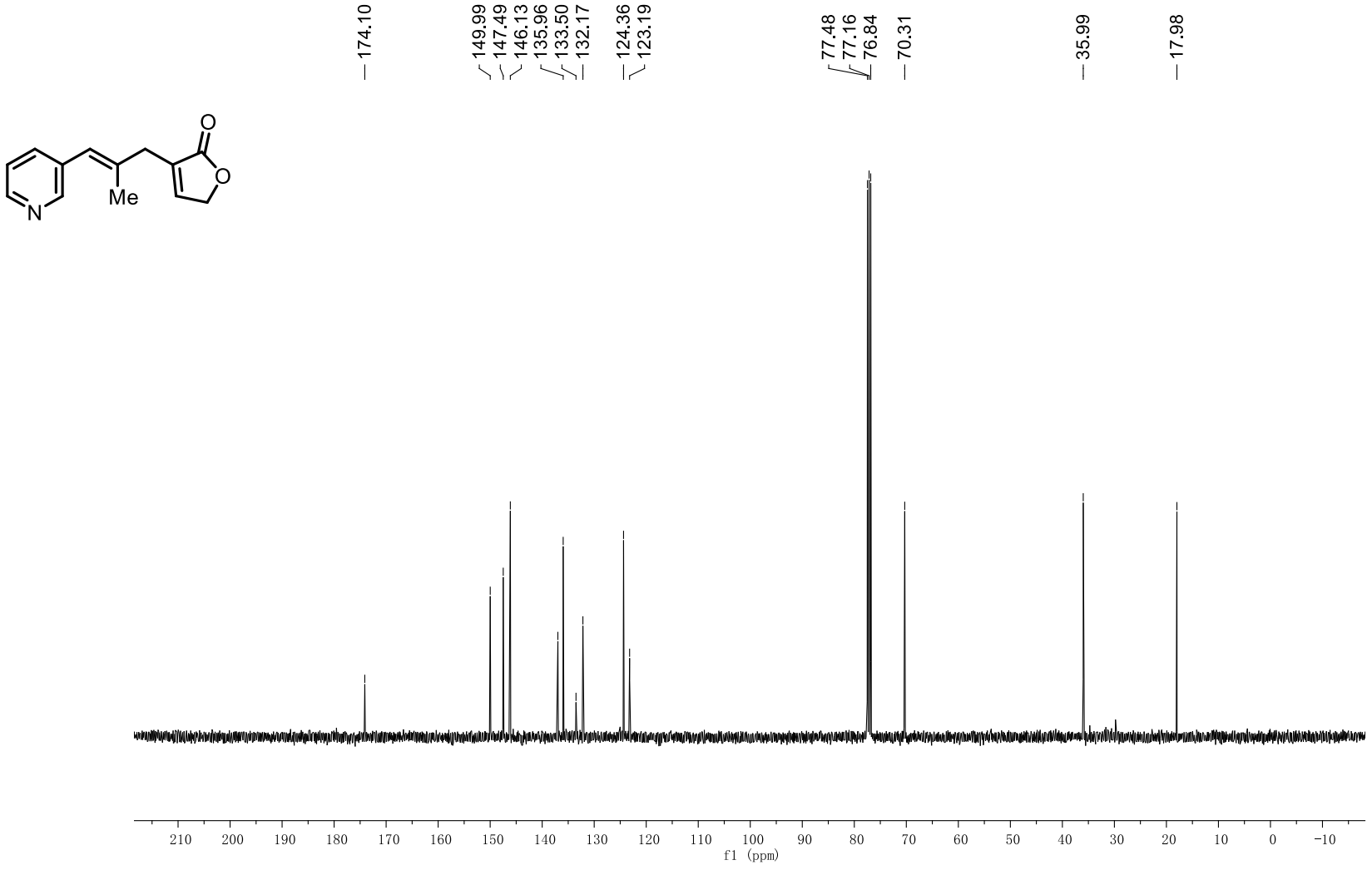
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(naphthalen-2-yl)allyl)furan-2(5*H*)-one (15)



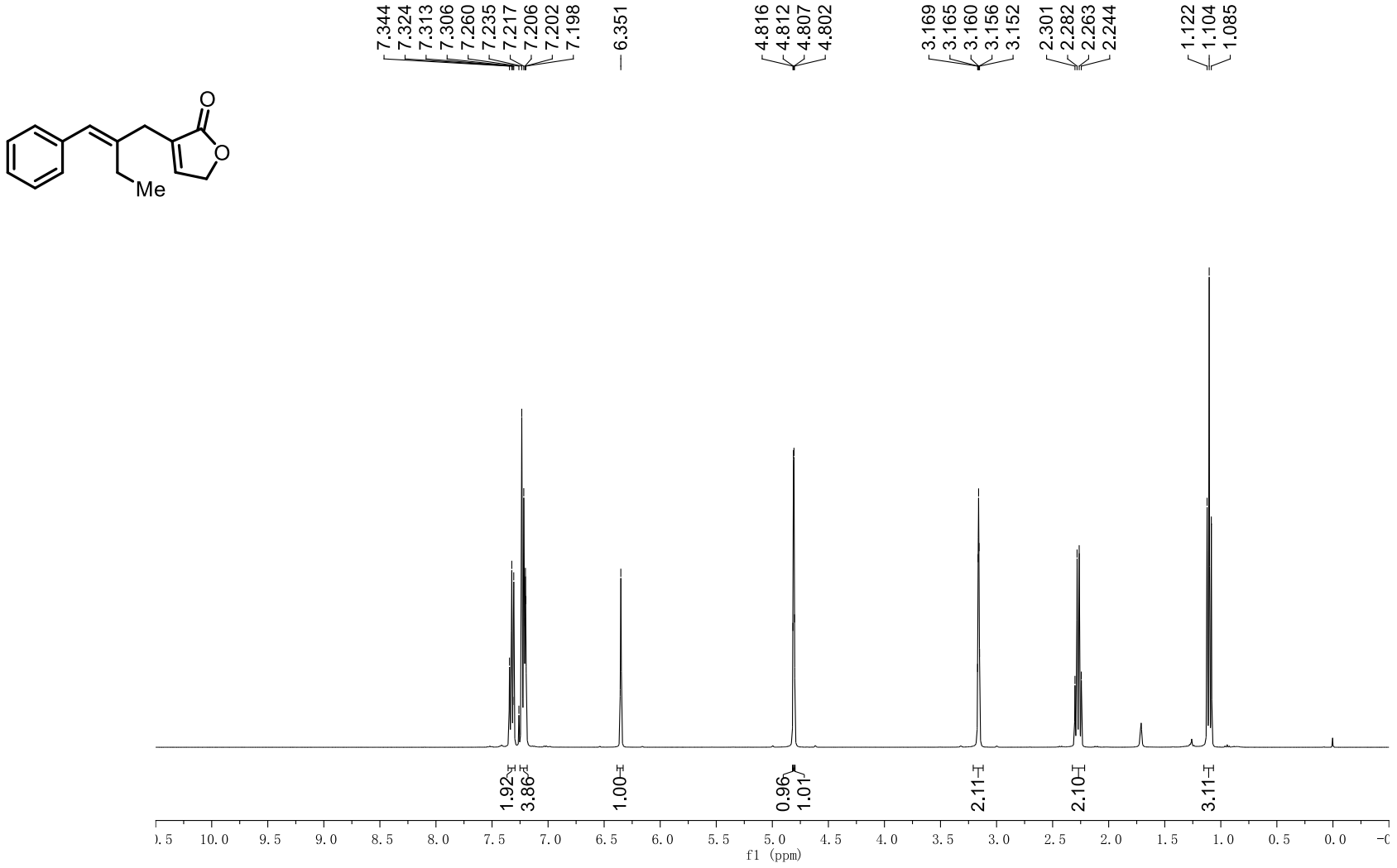
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(pyridin-3-yl)allyl)furan-2(5*H*)-one (16)



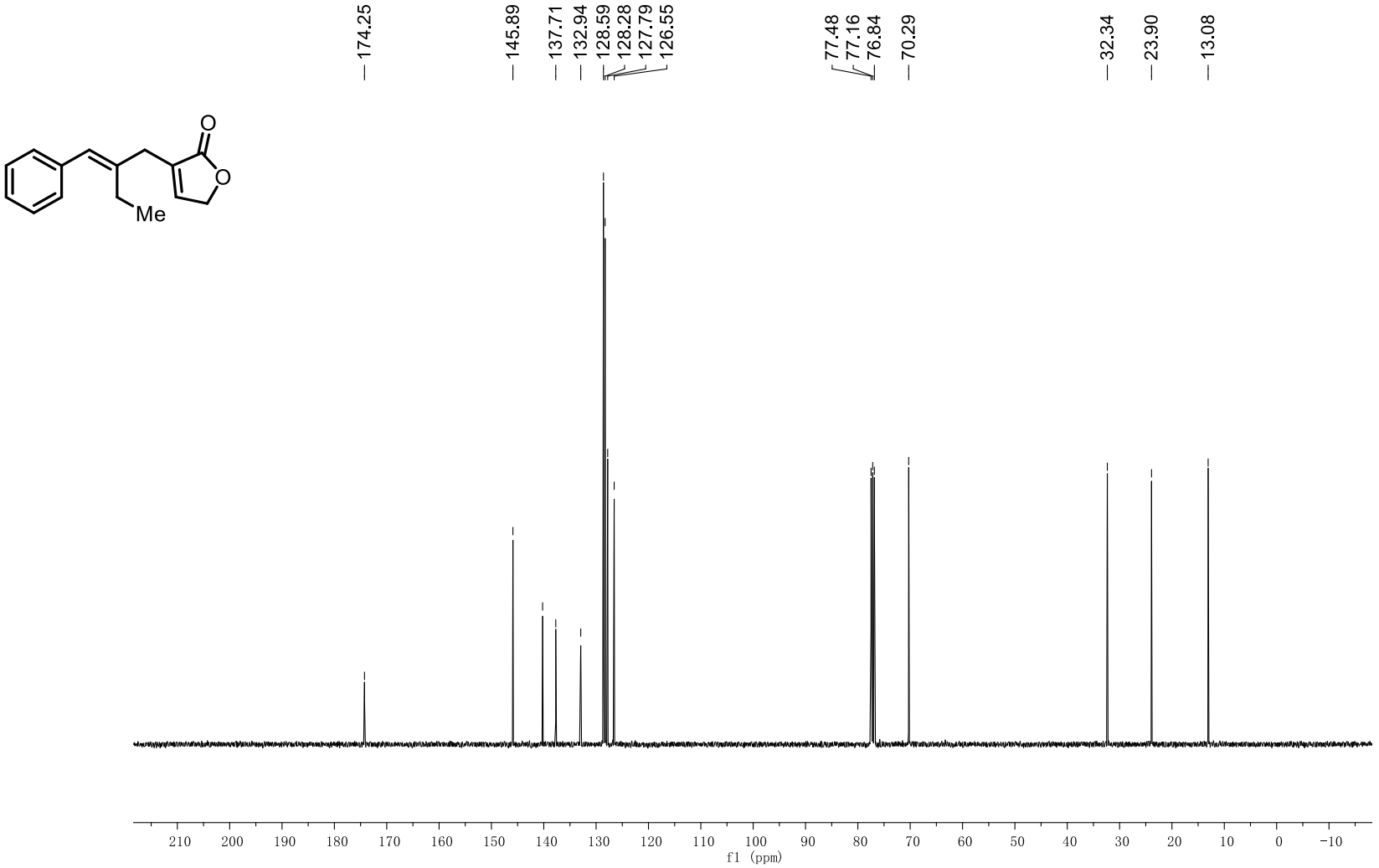
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(pyridin-3-yl)allyl)furan-2(5*H*)-one (16)



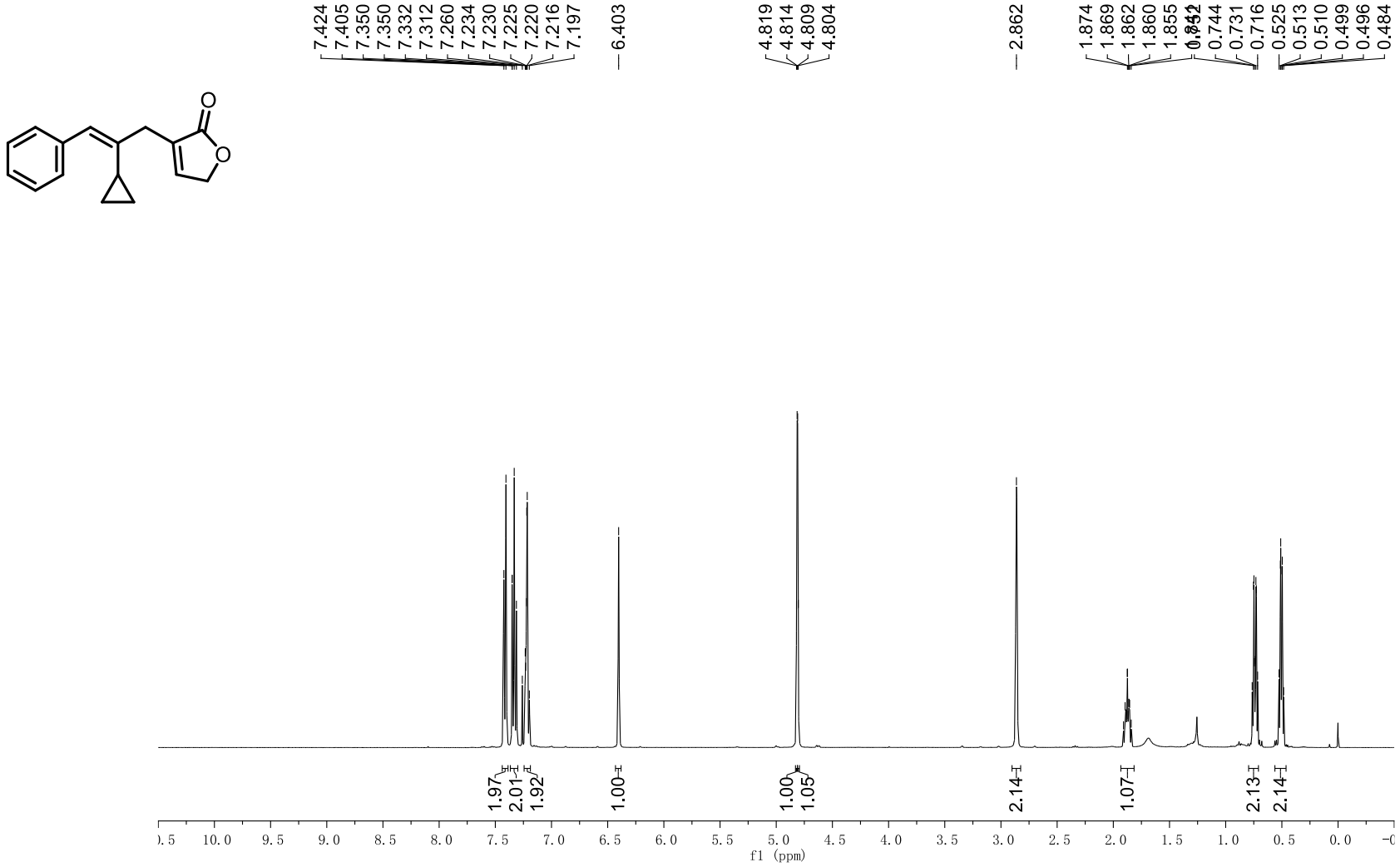
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Benzylidenebutyl)furan-2(5H)-one (17)



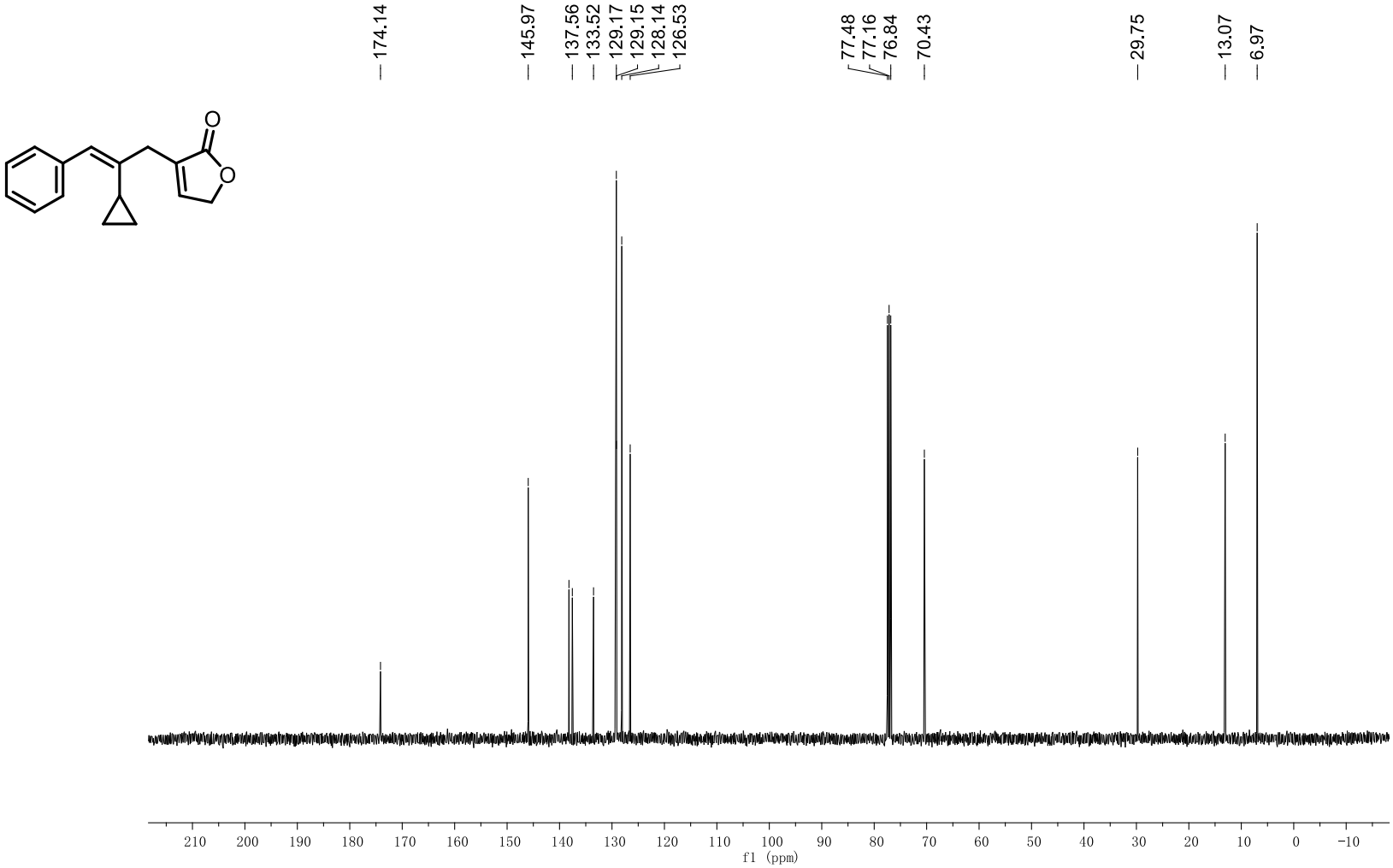
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Benzylidenebutyl)furan-2(5*H*)-one (17)



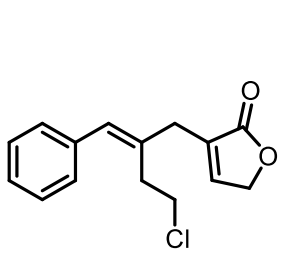
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Cyclopropyl-3-phenylallyl)furan-2(5*H*)-one (18)

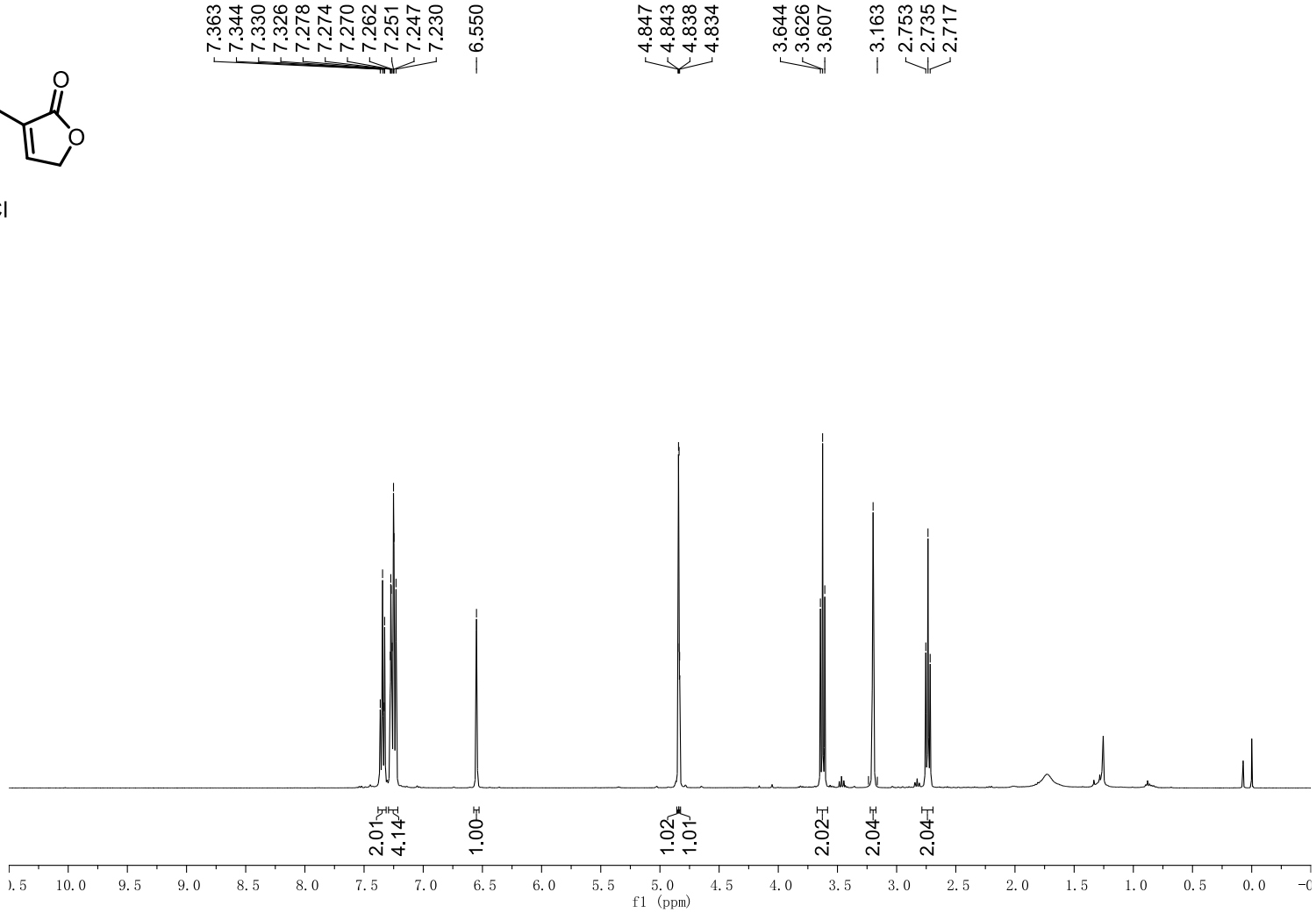


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Cyclopropyl-3-phenylallyl)furan-2(5*H*)-one (18)

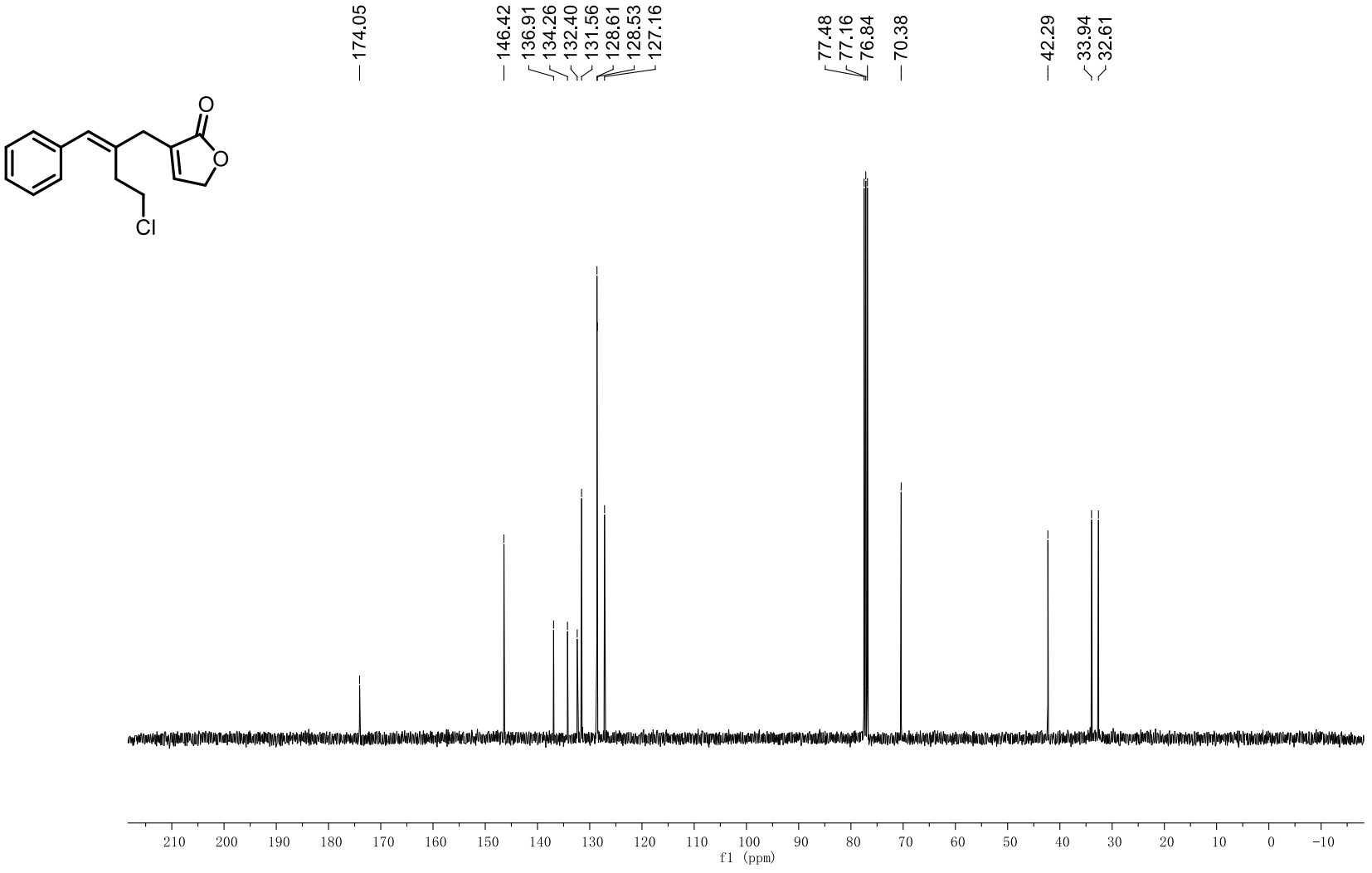


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Benzylidene-4-chlorobutyl)furan-2(5*H*)-one (19)

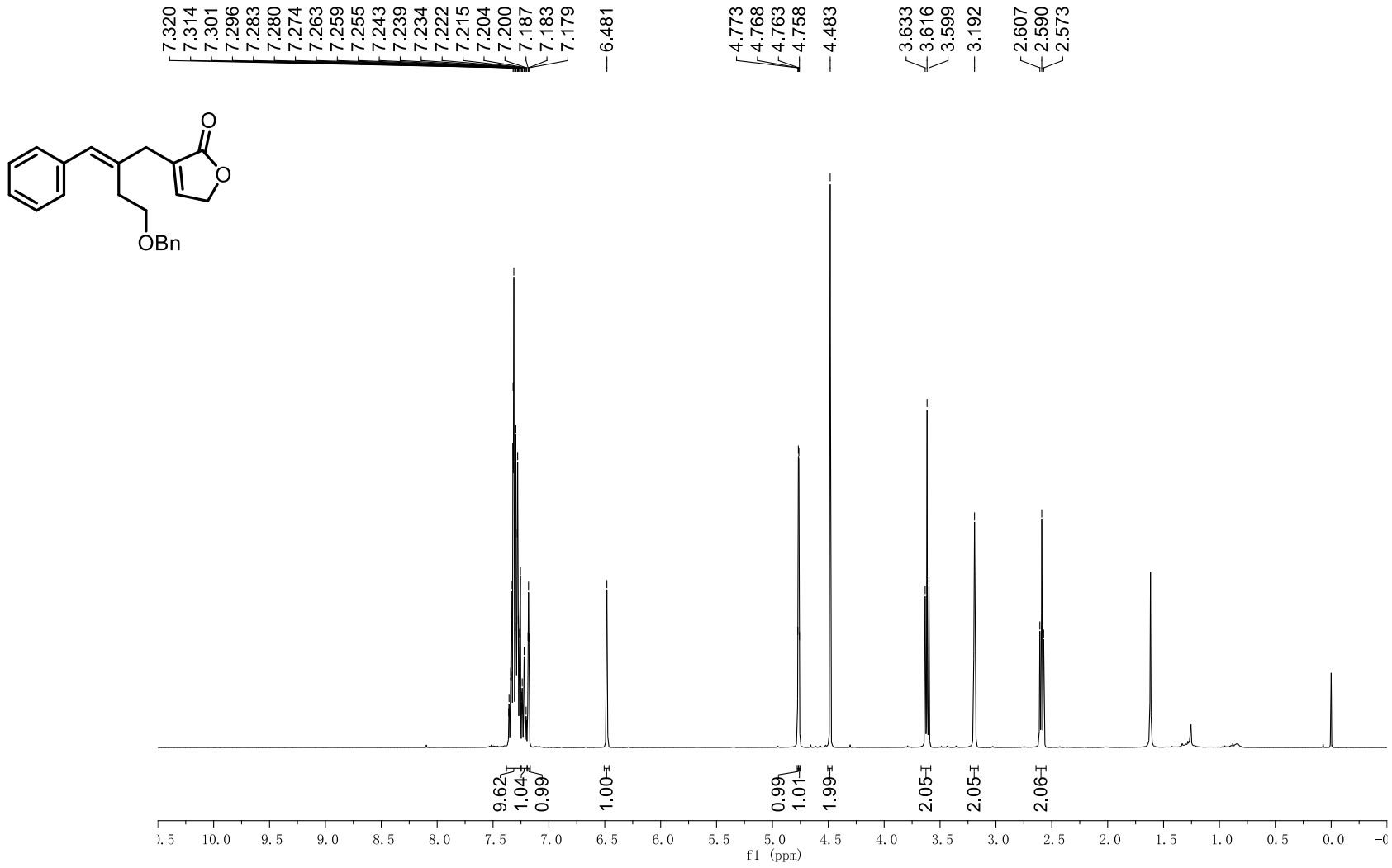




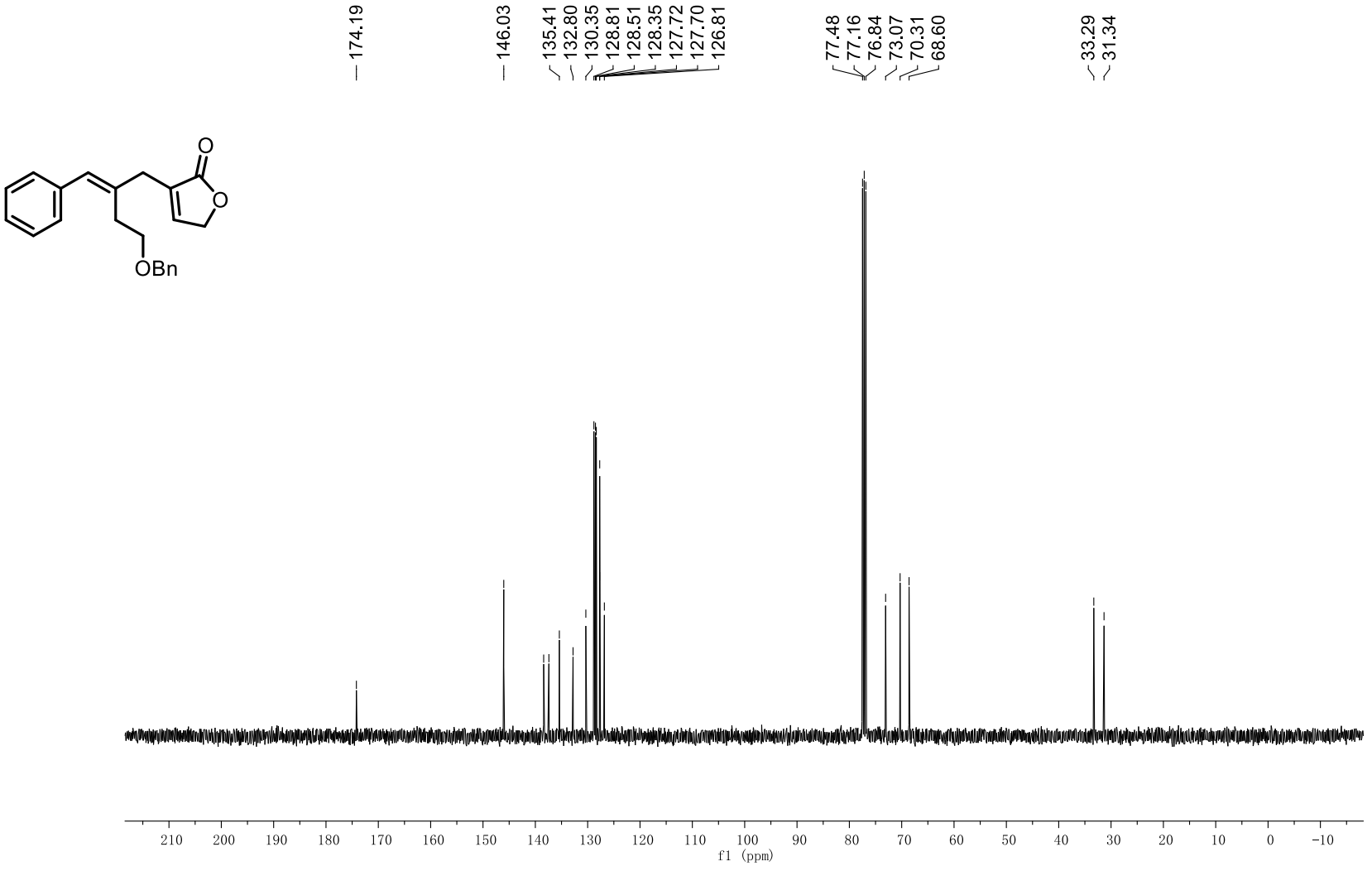
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Benzylidene-4-chlorobutyl)furan-2(5*H*)-one (19)



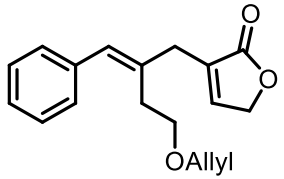
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Benzylidene-4-(benzyloxy)butyl)furan-2(5*H*)-one (20)

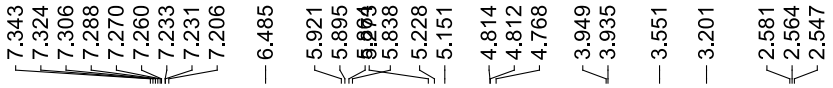


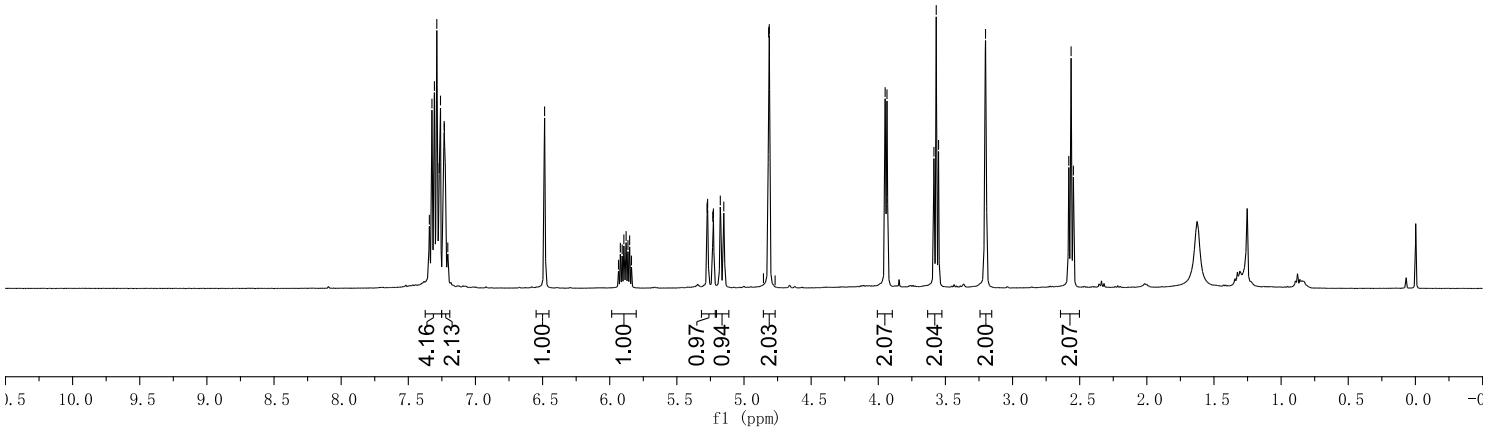
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Benzylidene-4-(benzyloxy)butyl)furan-2(5*H*)-one (20)



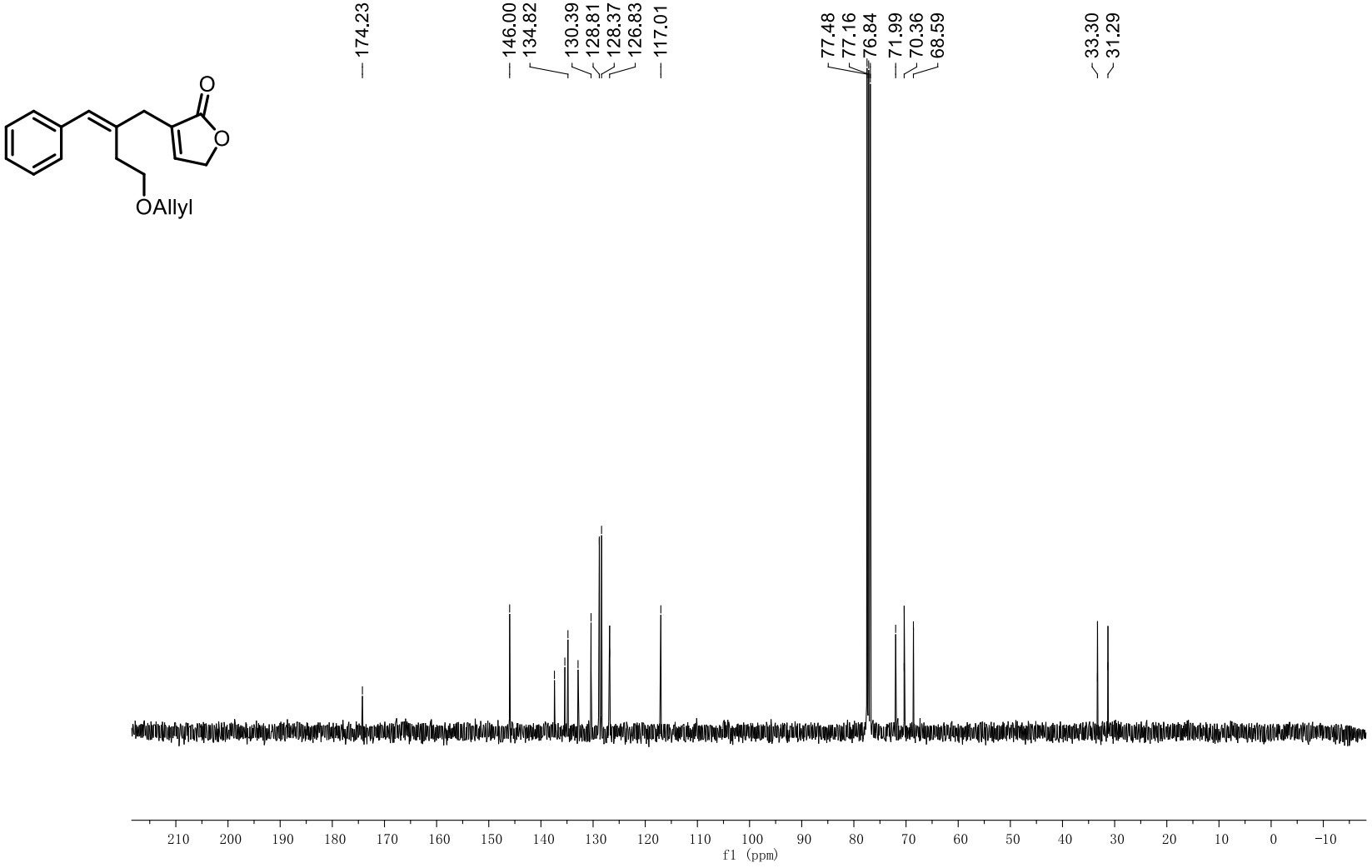
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-3-(4-(Allyloxy)-2-benzylidenebutyl)furan-2(5*H*)-one (21)



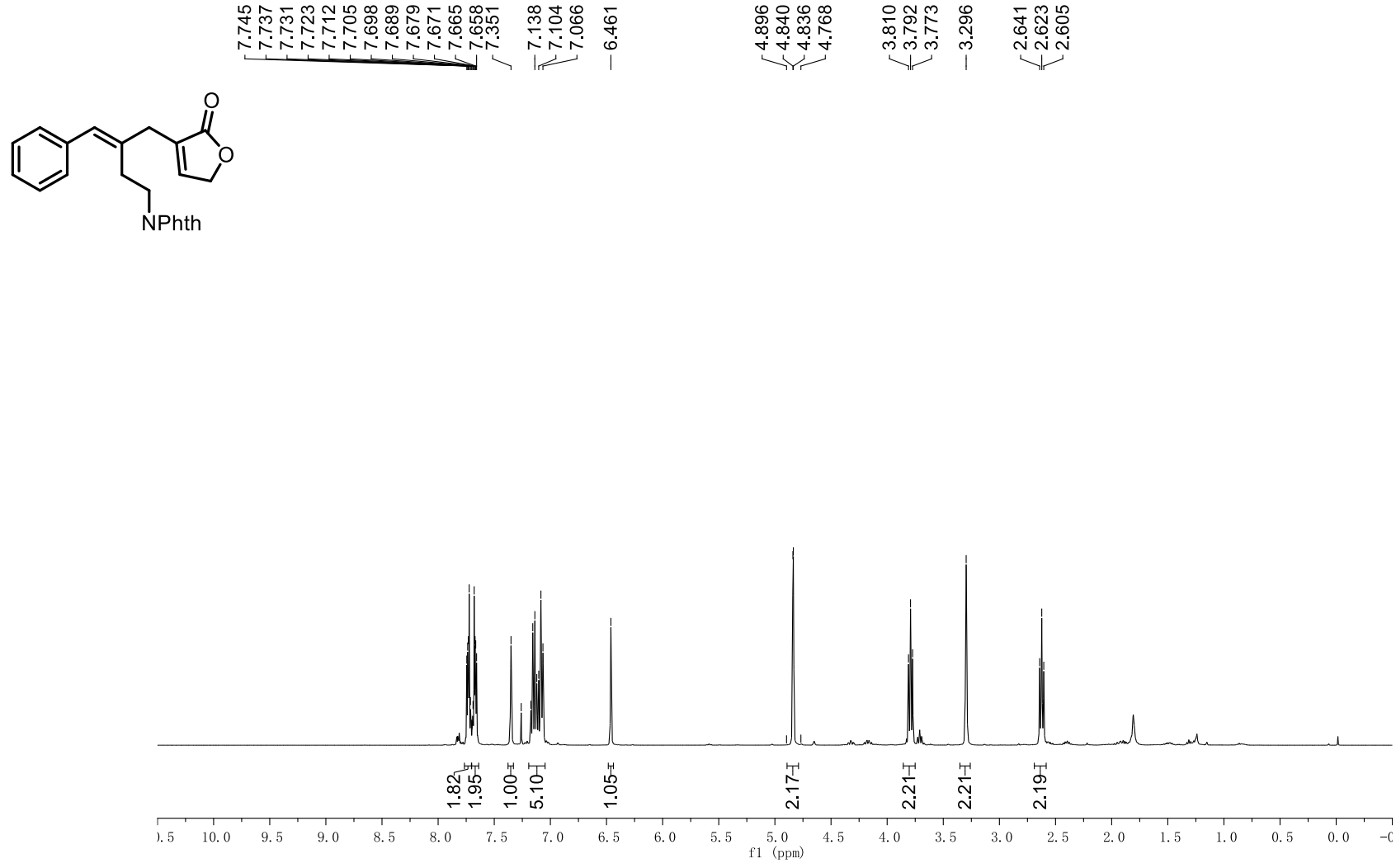




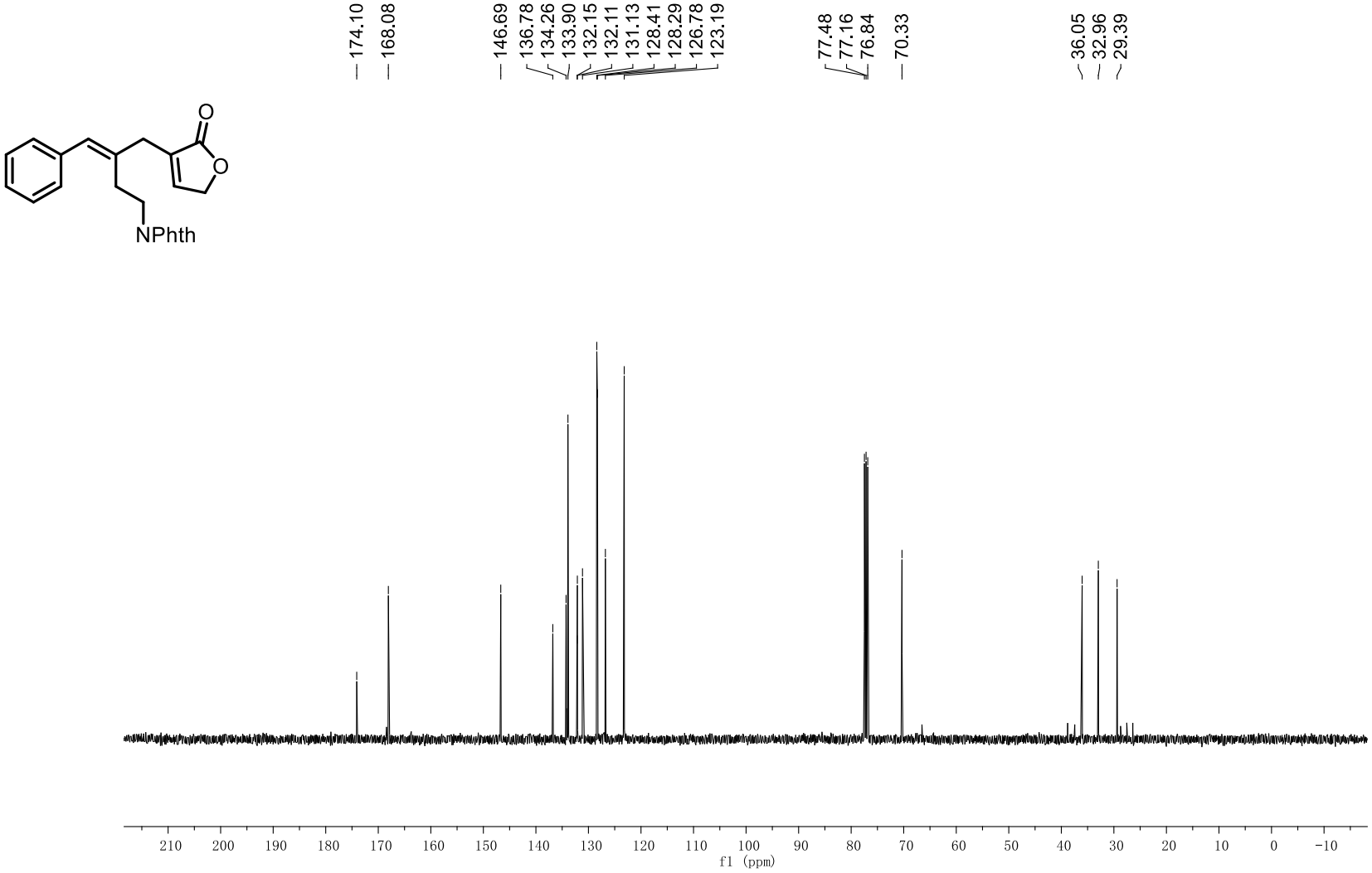
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-3-(4-(Allyloxy)-2-benzylidenebutyl)furan-2(5*H*)-one (21)



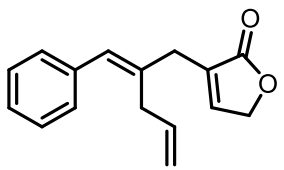
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-2-(3-((2-Oxo-2,5-dihydrofuran-3-yl)methyl)-4-phenylbut-3-en-1-yl)isoindoline-1,3-dione (22)

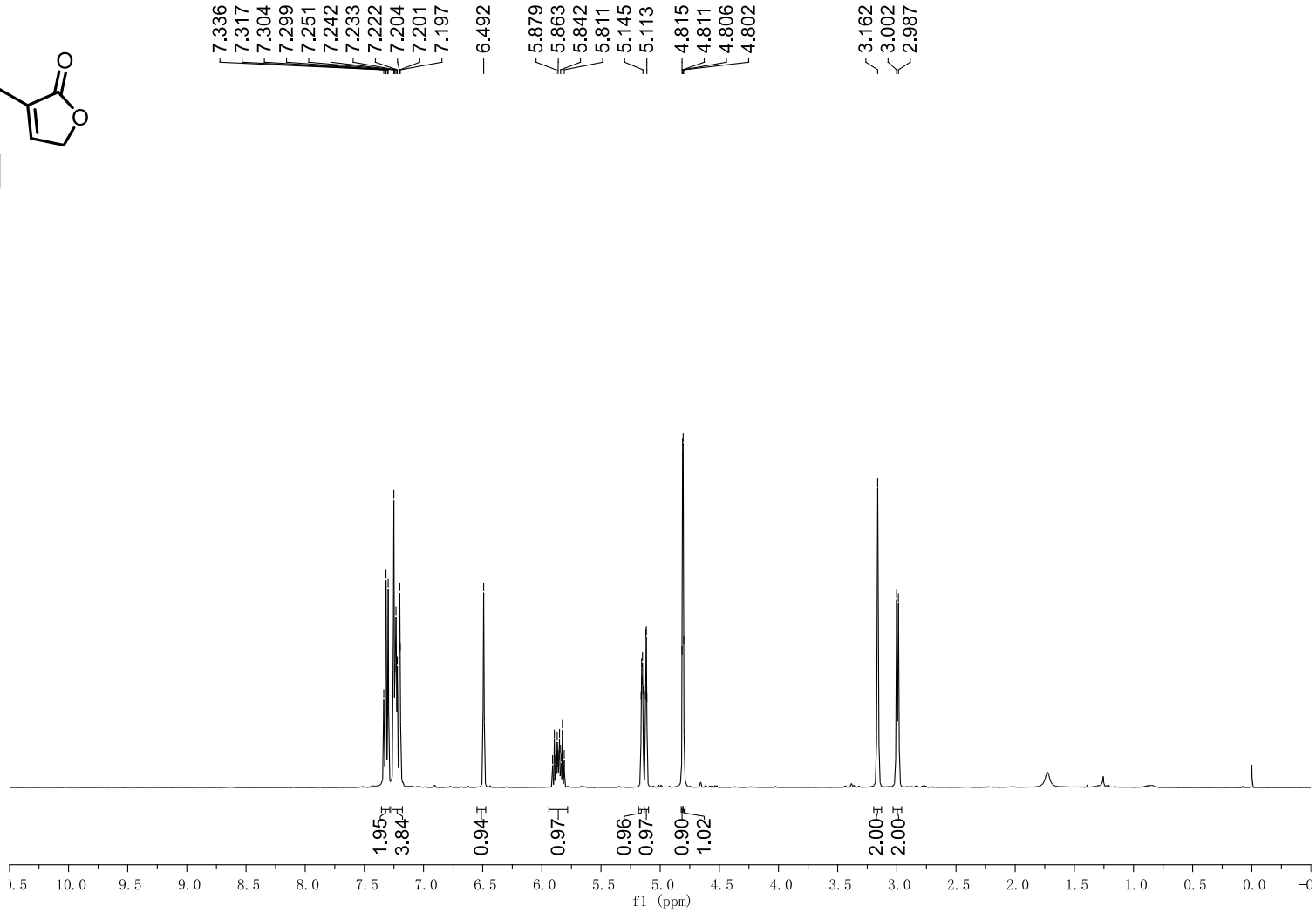


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-2-(3-((2-Oxo-2,5-dihydrofuran-3-yl)methyl)-4-phenylbut-3-en-1-yl)isoindoline-1,3-dione (22)

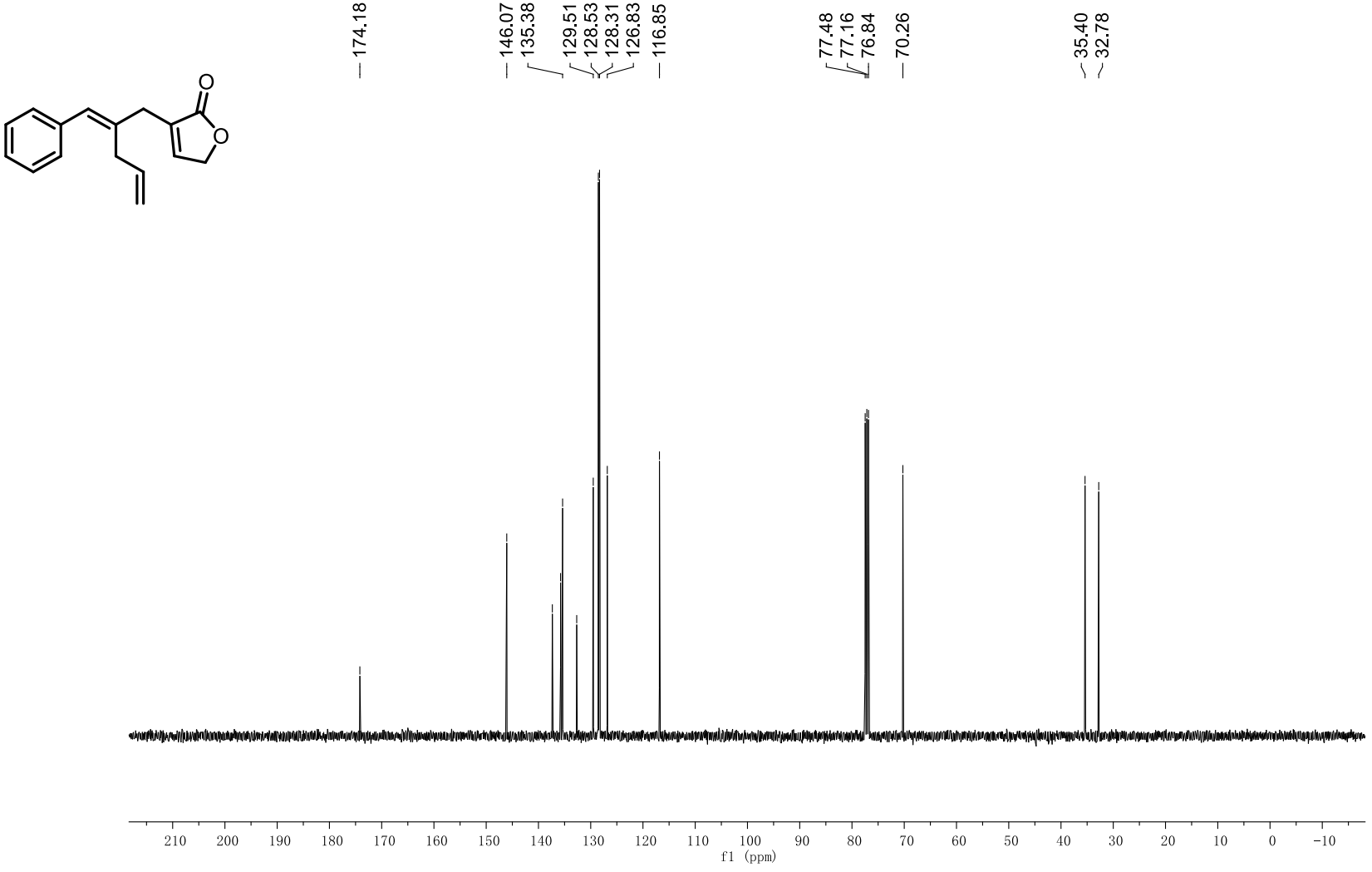


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Benzylidenepent-4-en-1-yl)furan-2(5*H*)-one (23)

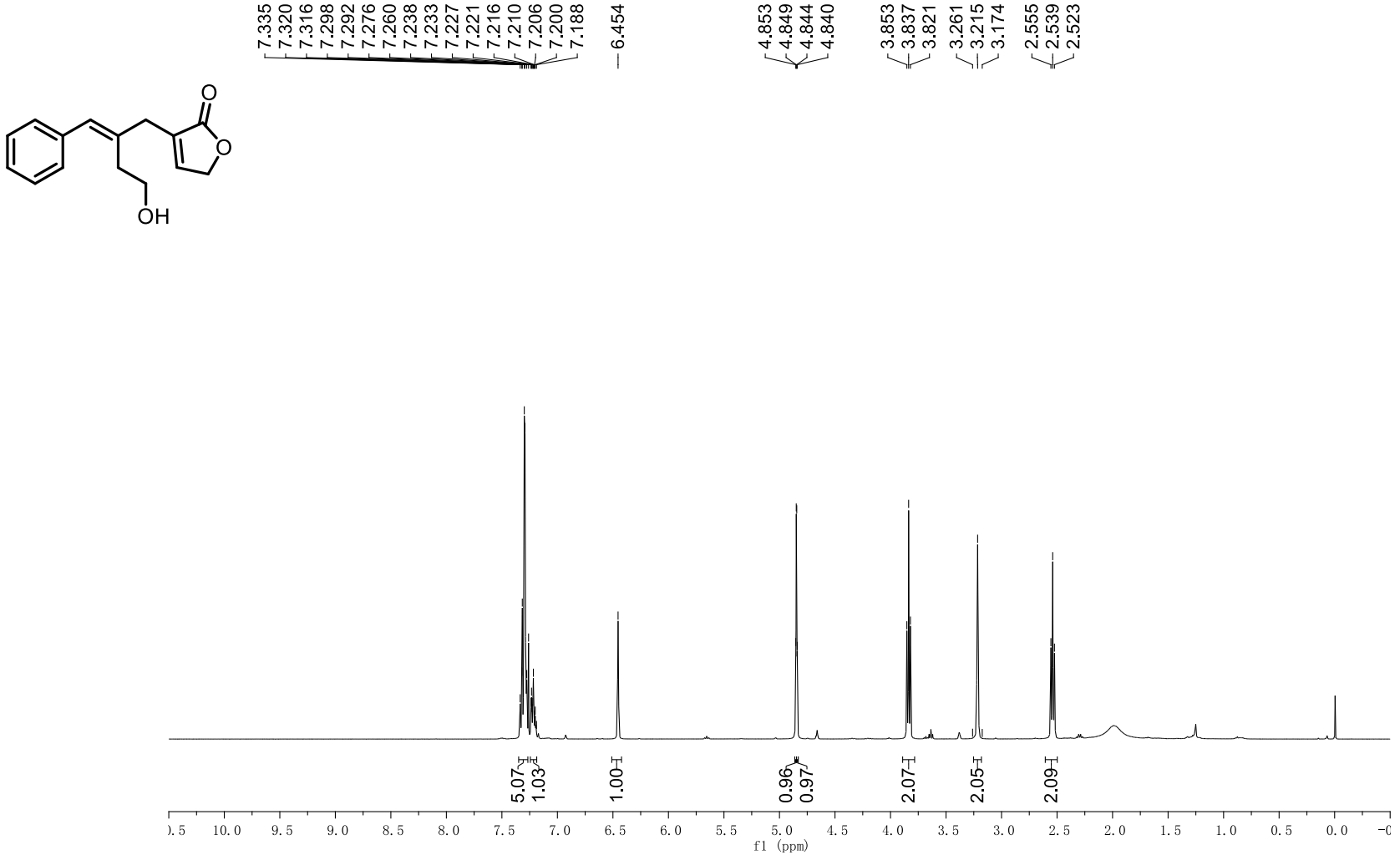




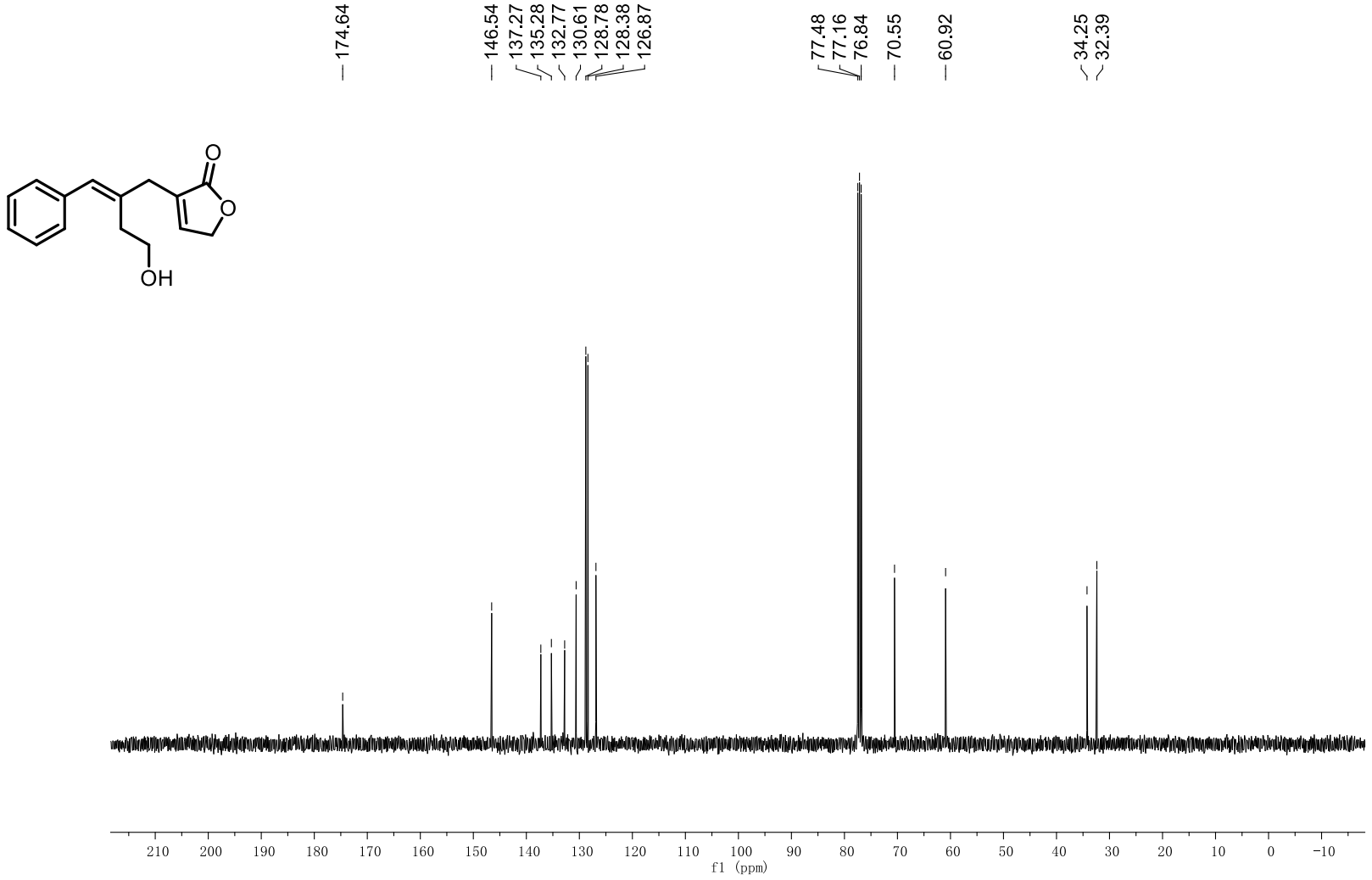
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Benzylidenepent-4-en-1-yl)furan-2(5*H*)-one (23)



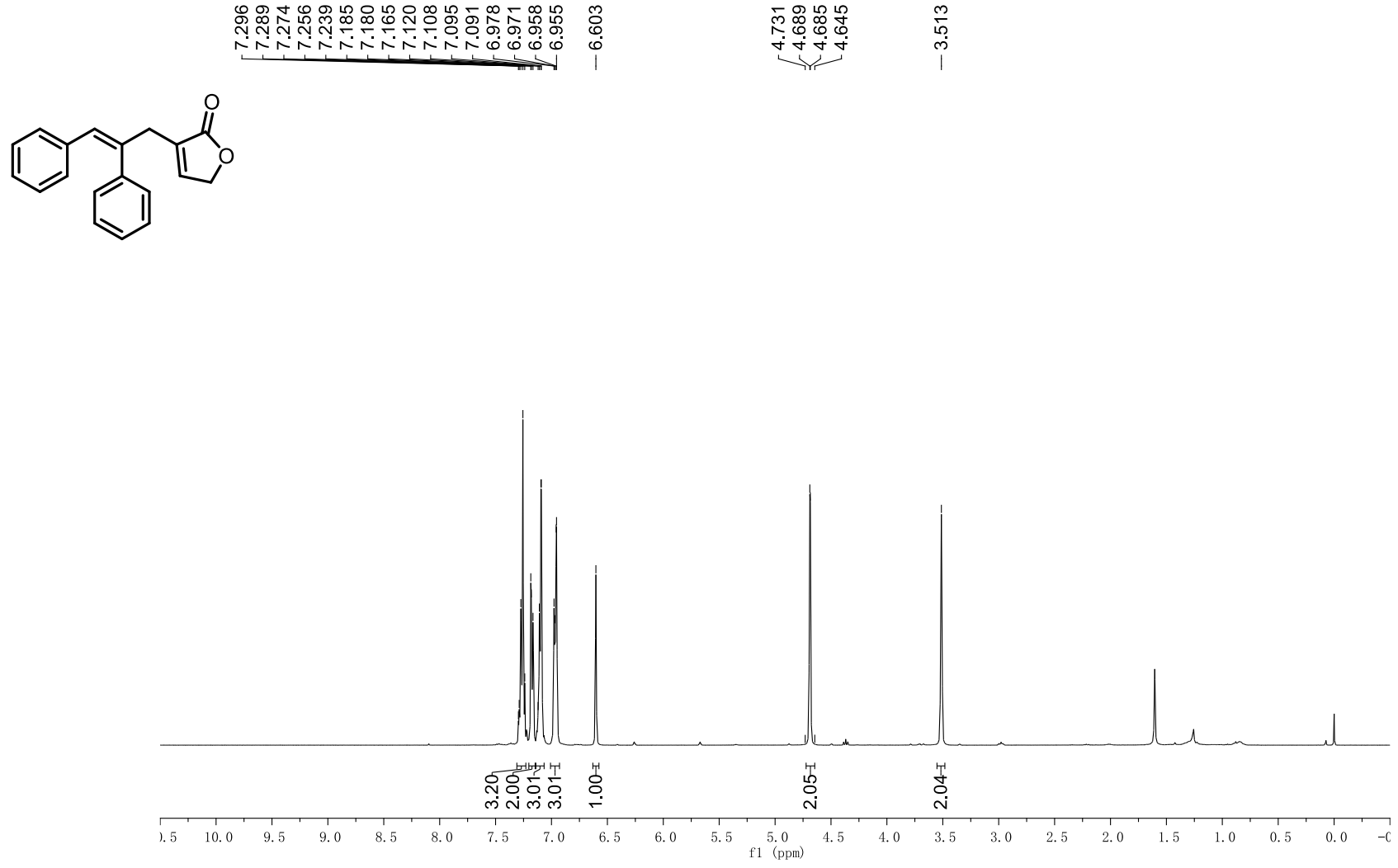
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Benzylidene-4-hydroxybutyl)furan-2(5*H*)-one (24)



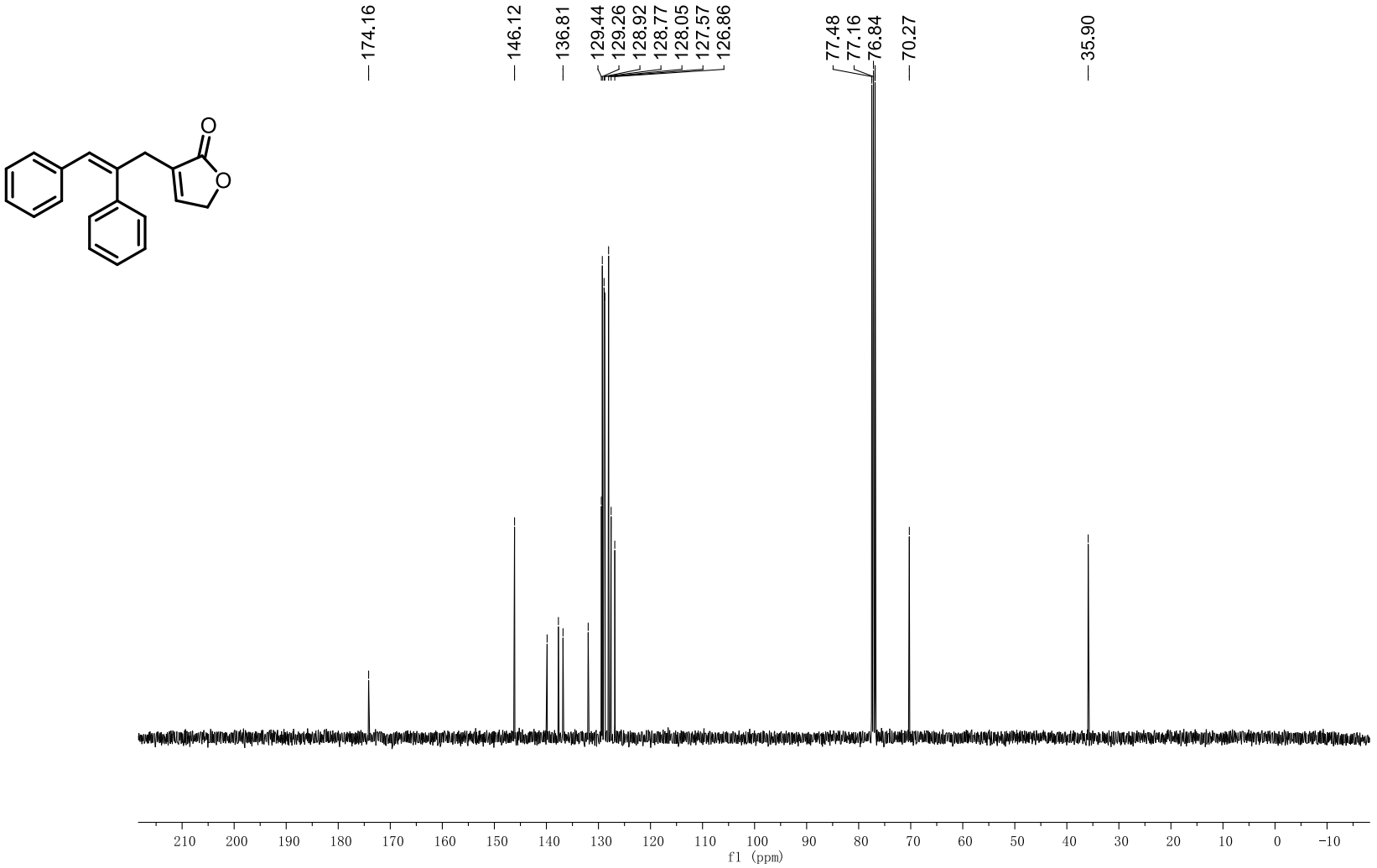
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2-Benzylidene-4-hydroxybutyl)furan-2(5*H*)-one (24)



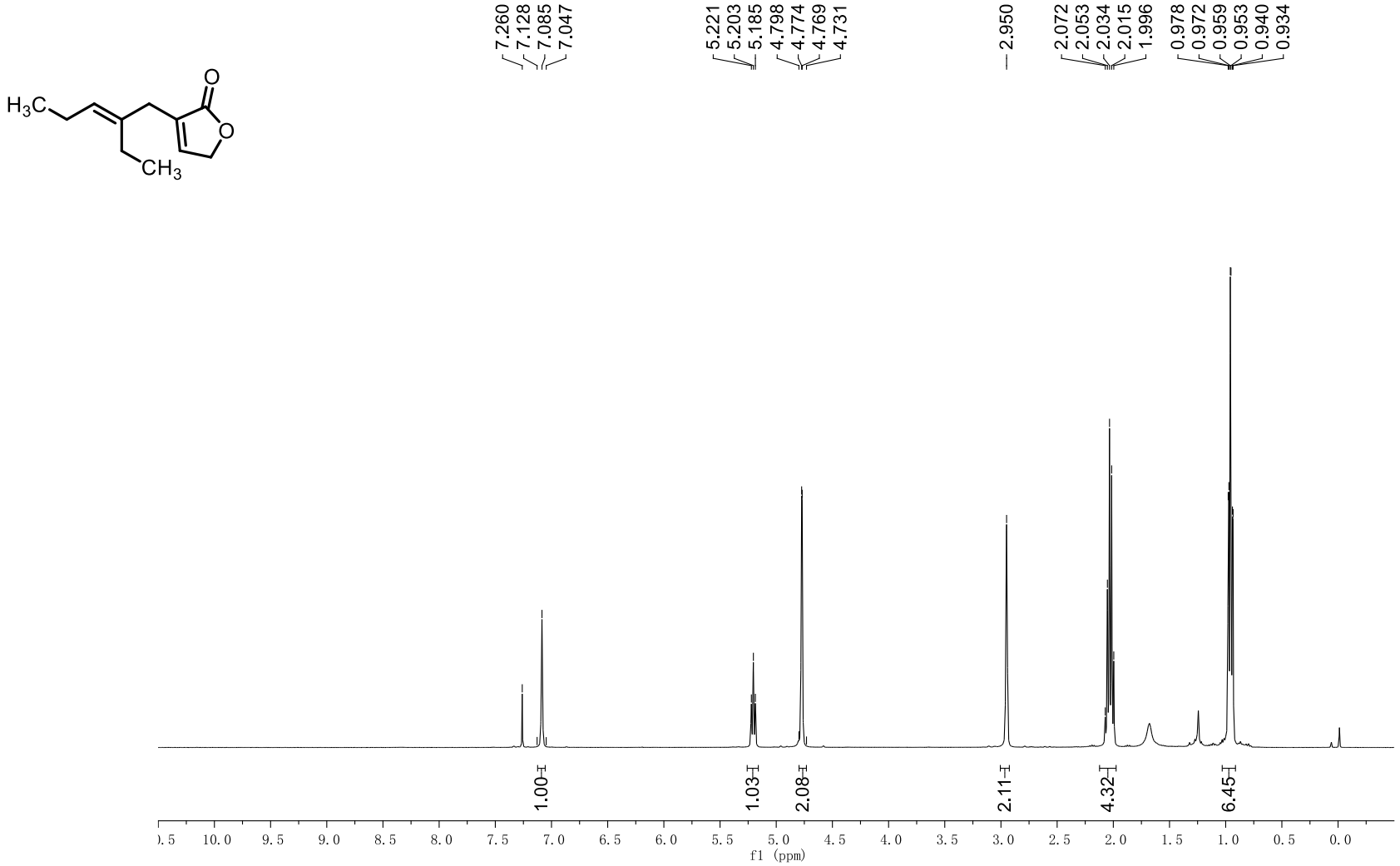
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2,3-Diphenylallyl)furan-2(5*H*)-one (25)



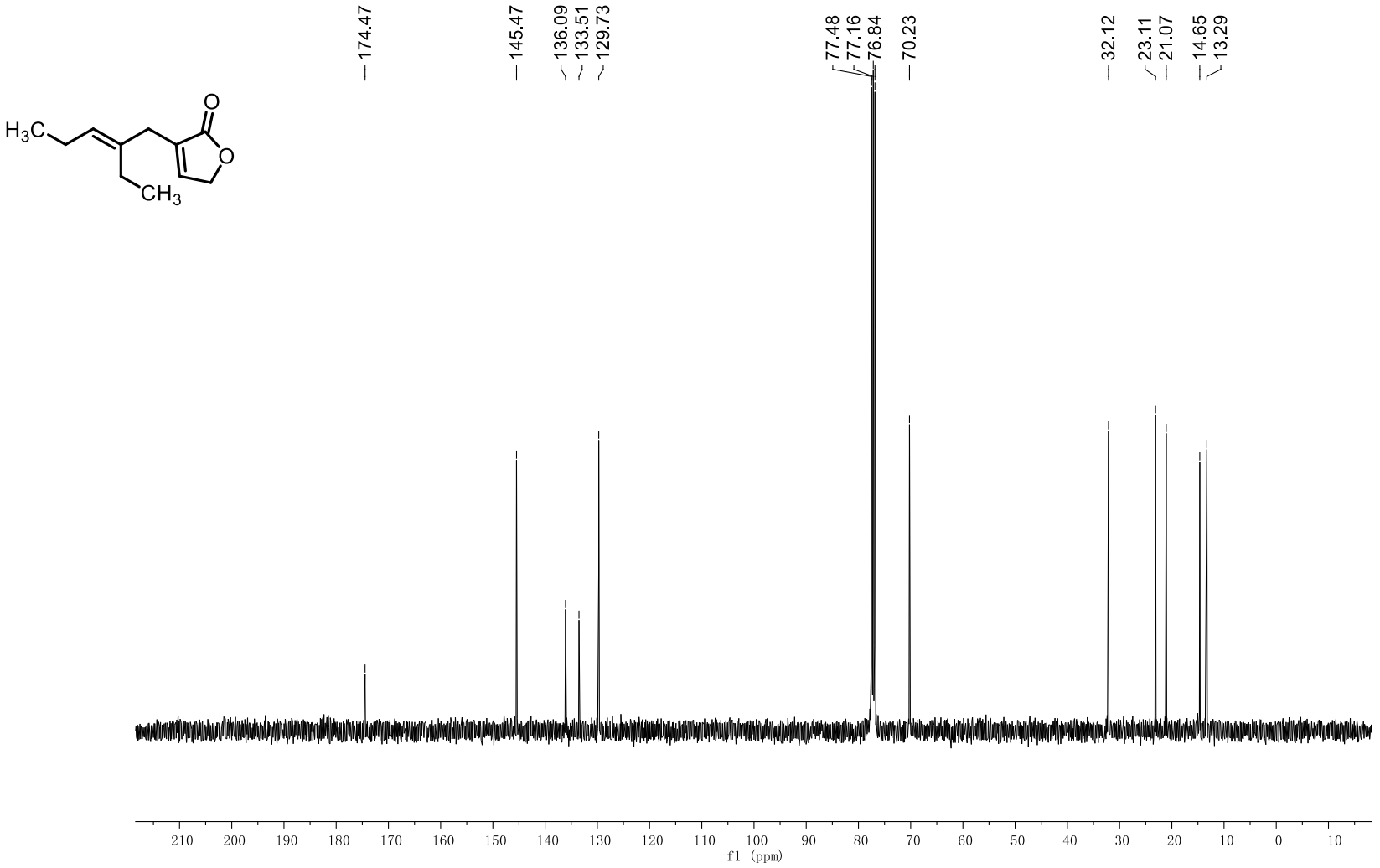
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-3-(2,3-Diphenylallyl)furan-2(5*H*)-one (25)



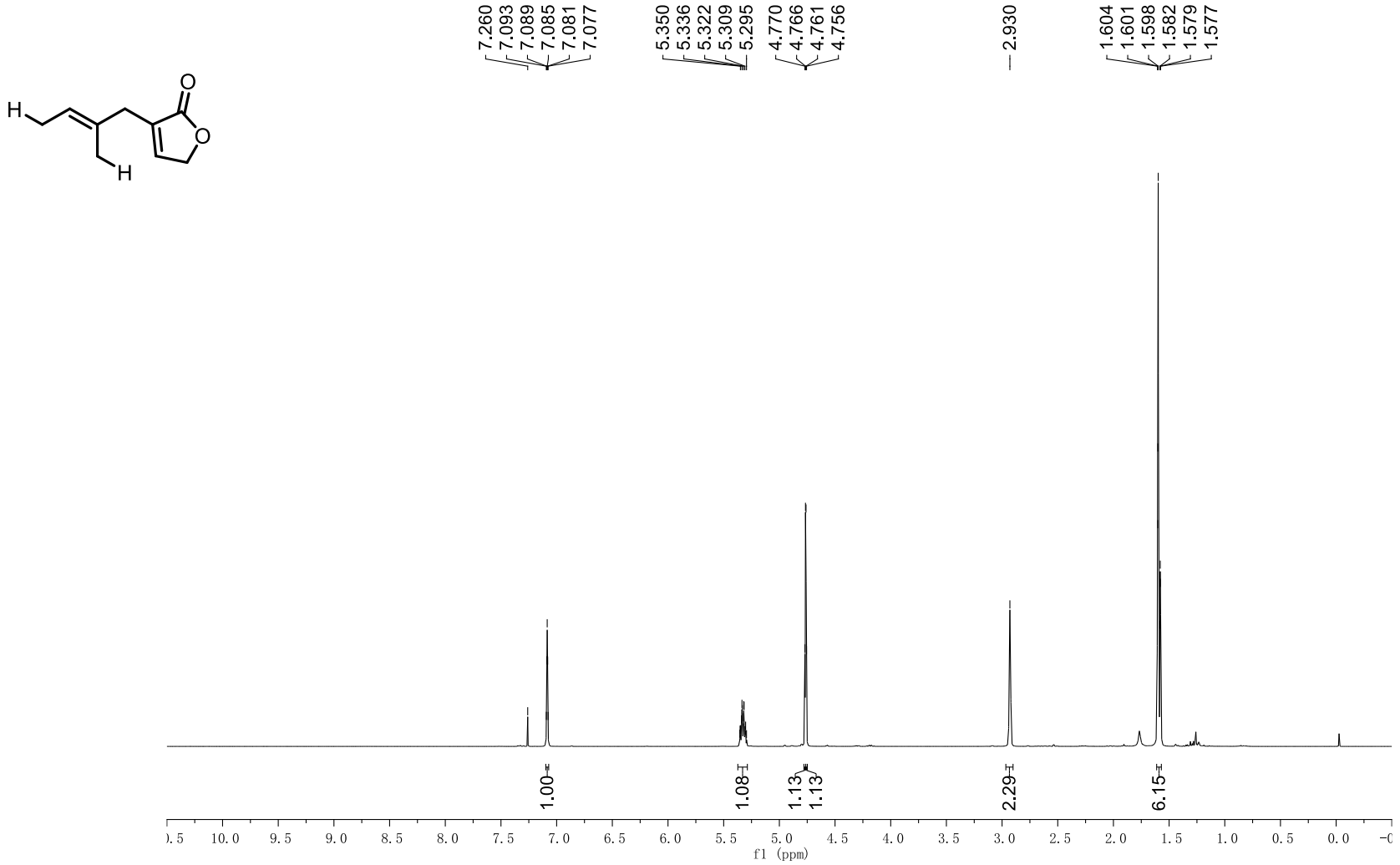
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Ethylpent-2-en-1-yl)furan-2(5*H*)-one (26)



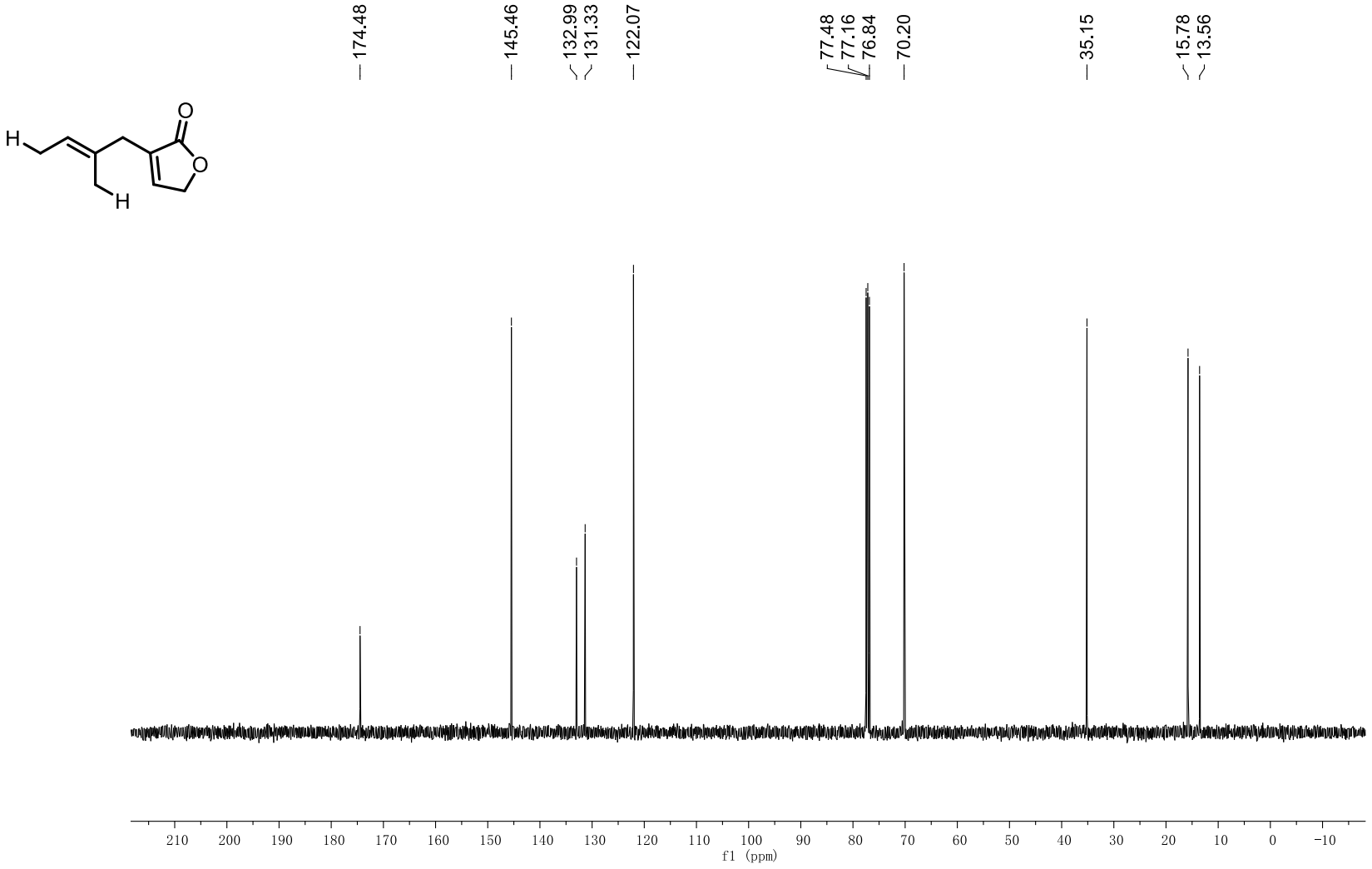
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Ethylpent-2-en-1-yl)furan-2(5*H*)-one (26)



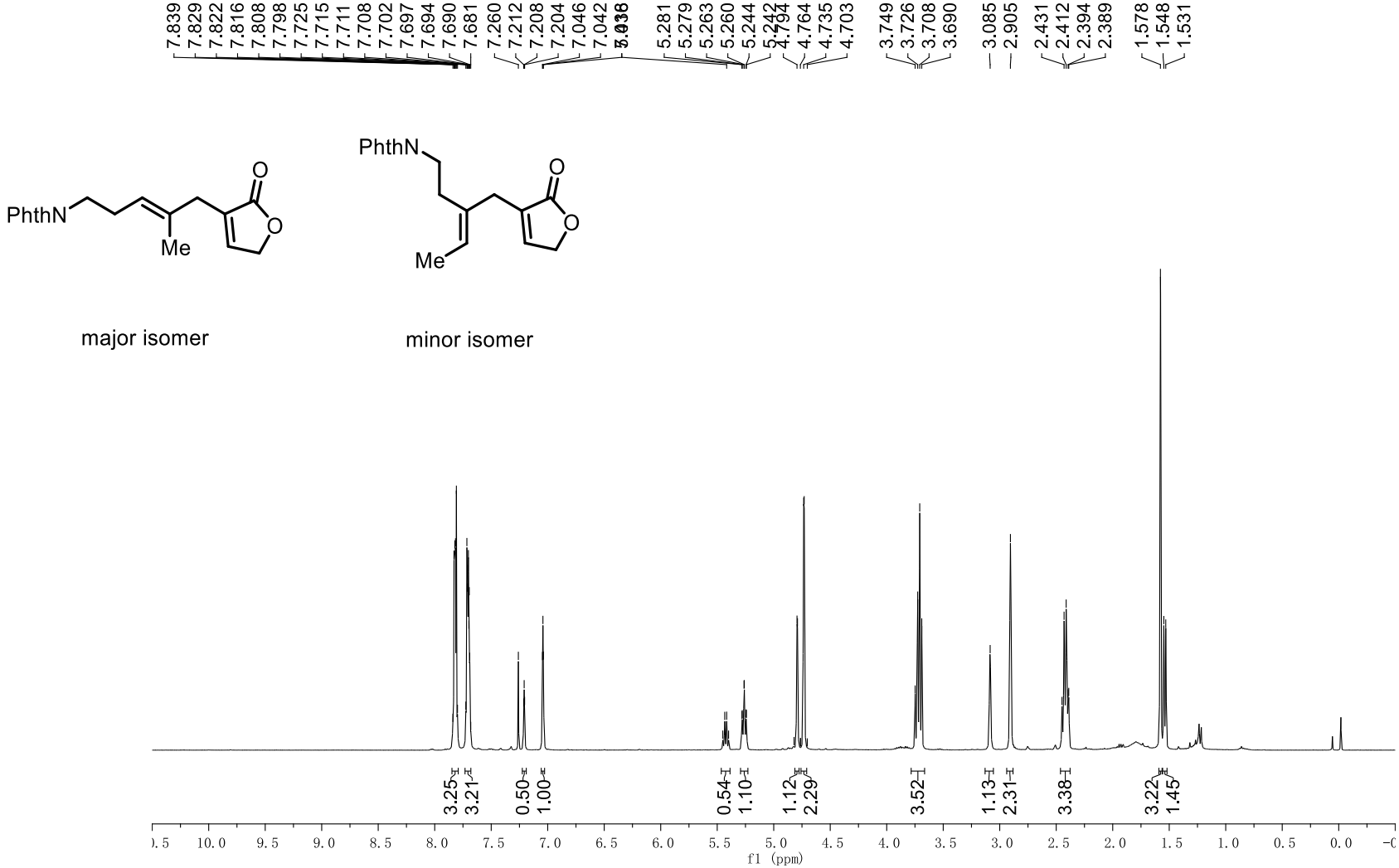
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methylbut-2-en-1-yl)furan-2(5*H*)-one (27)



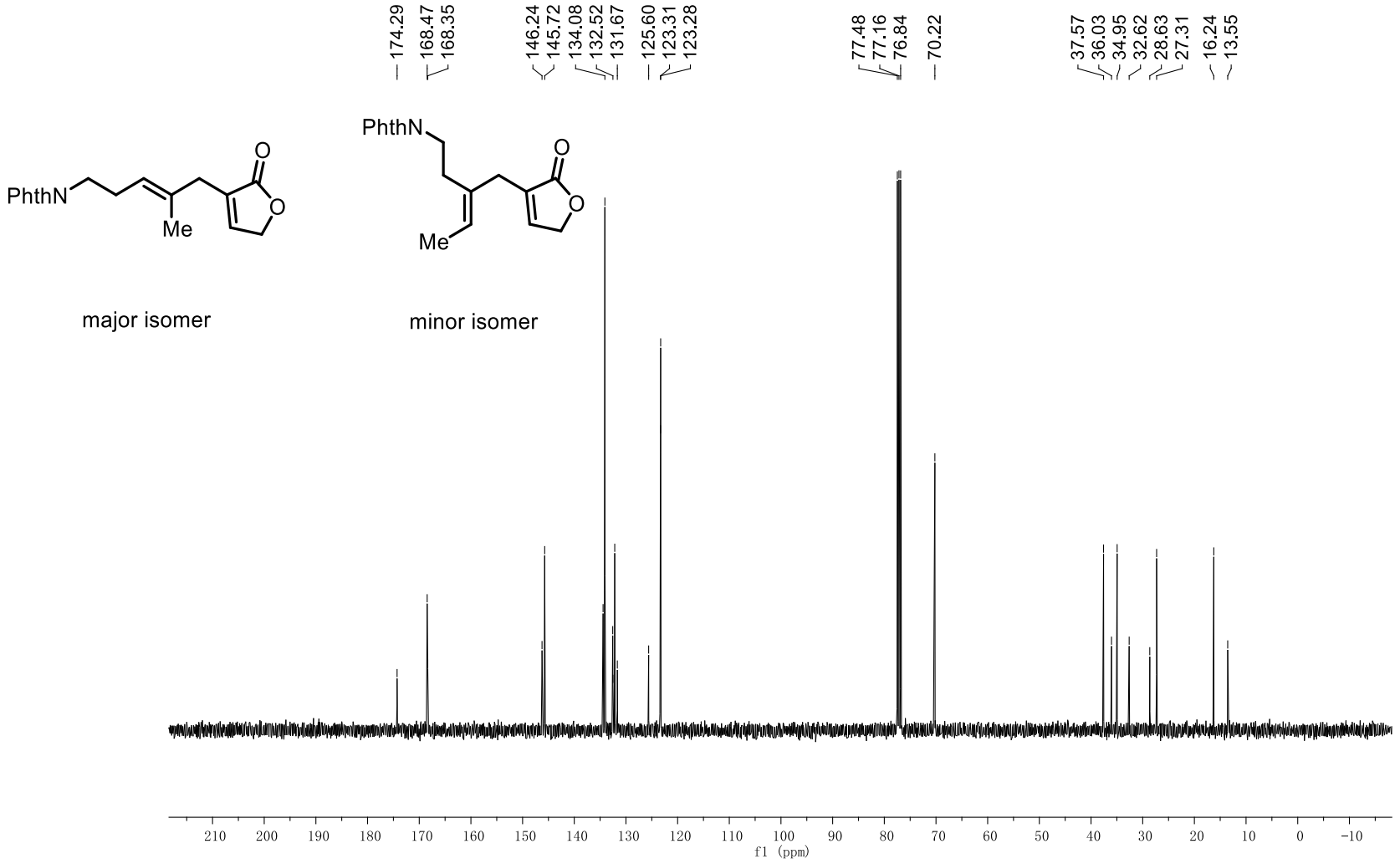
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methylbut-2-en-1-yl)furan-2(5*H*)-one (27)



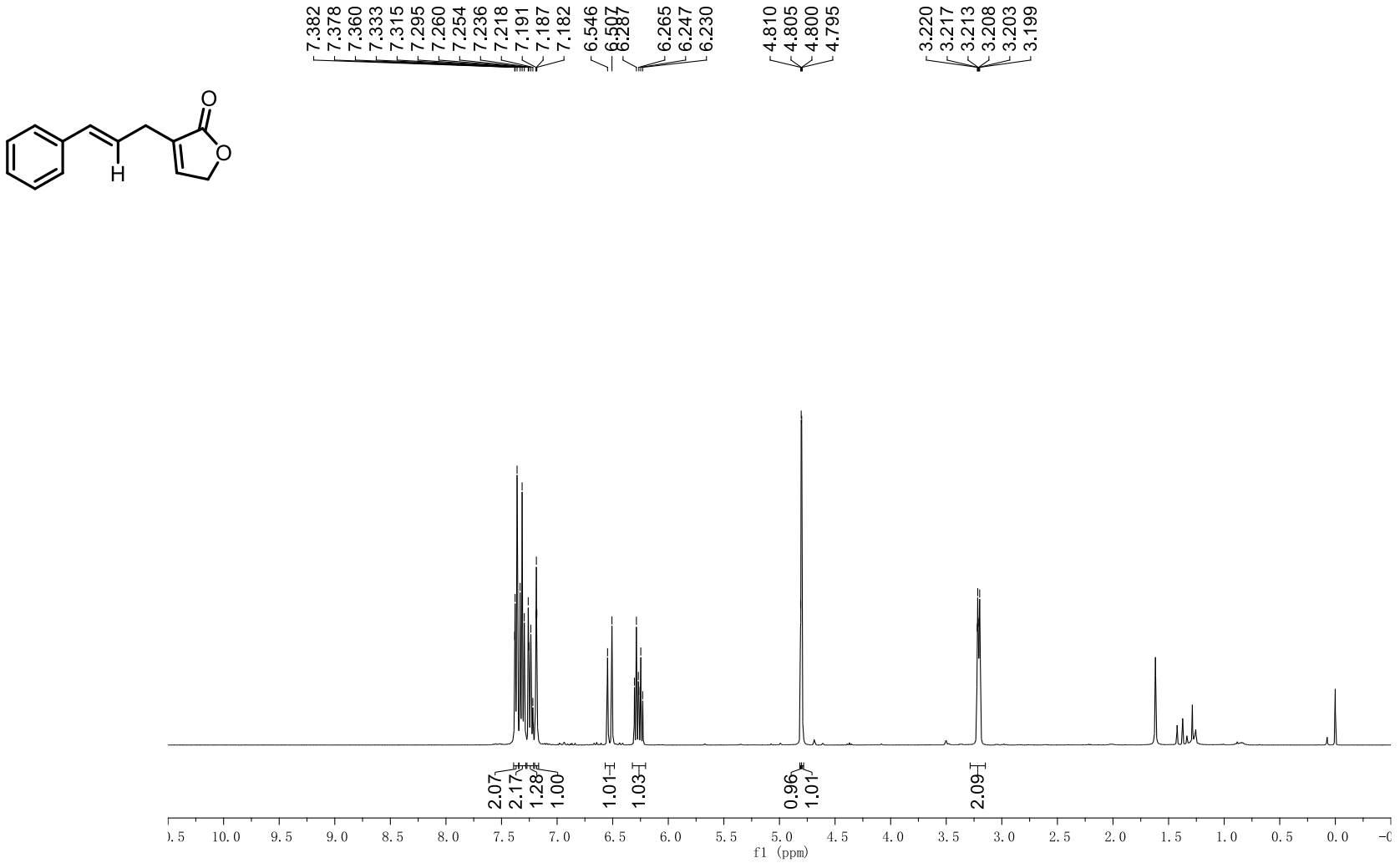
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-2-(4-Methyl-5-(2-oxo-2,5-dihydrofuran-3-yl)pent-3-en-1-yl)isoindoline-1,3-dione (28)



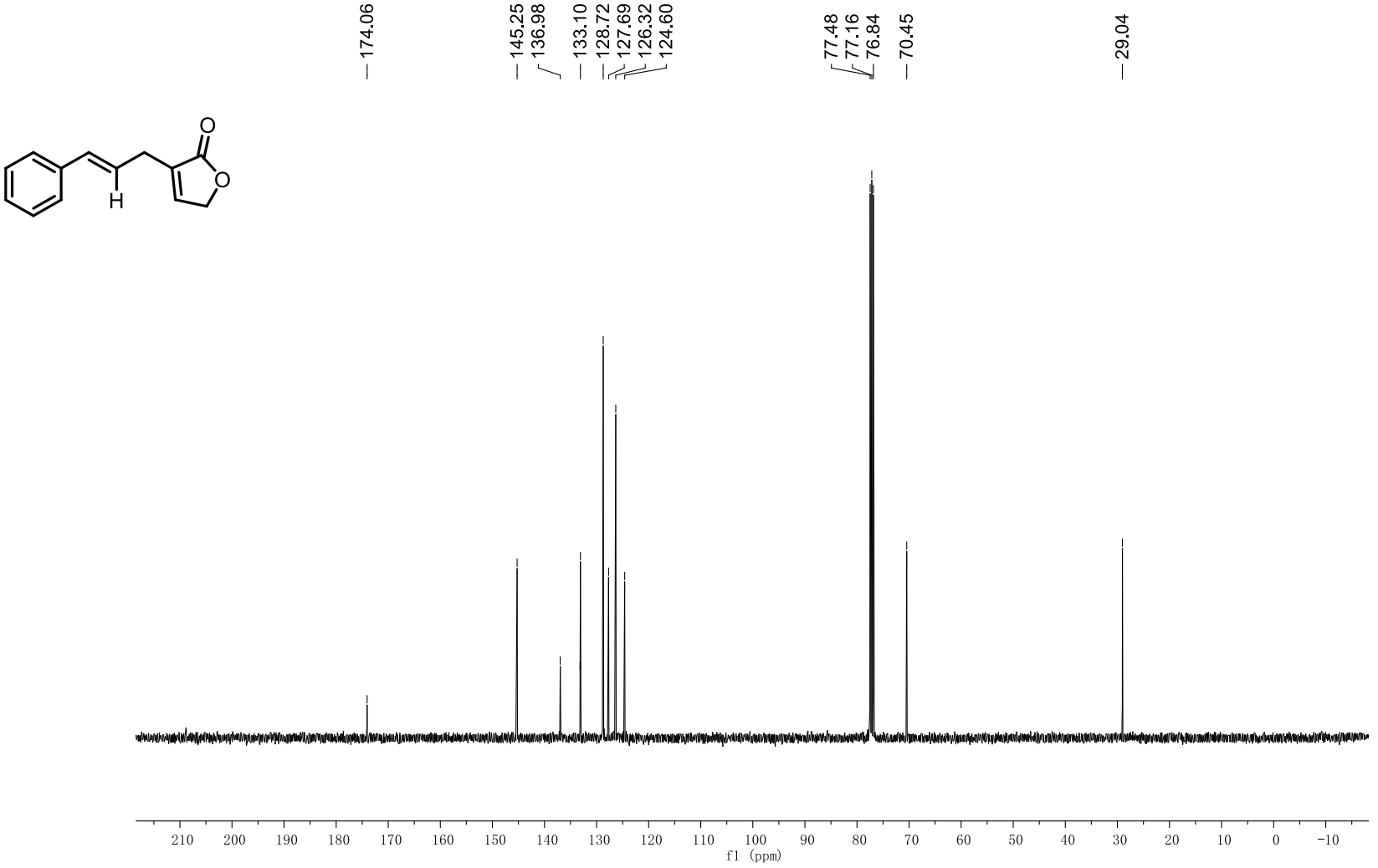
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-2-(4-Methyl-5-(2-oxo-2,5-dihydrofuran-3-yl)pent-3-en-1-yl)isoindoline-1,3-dione (28)



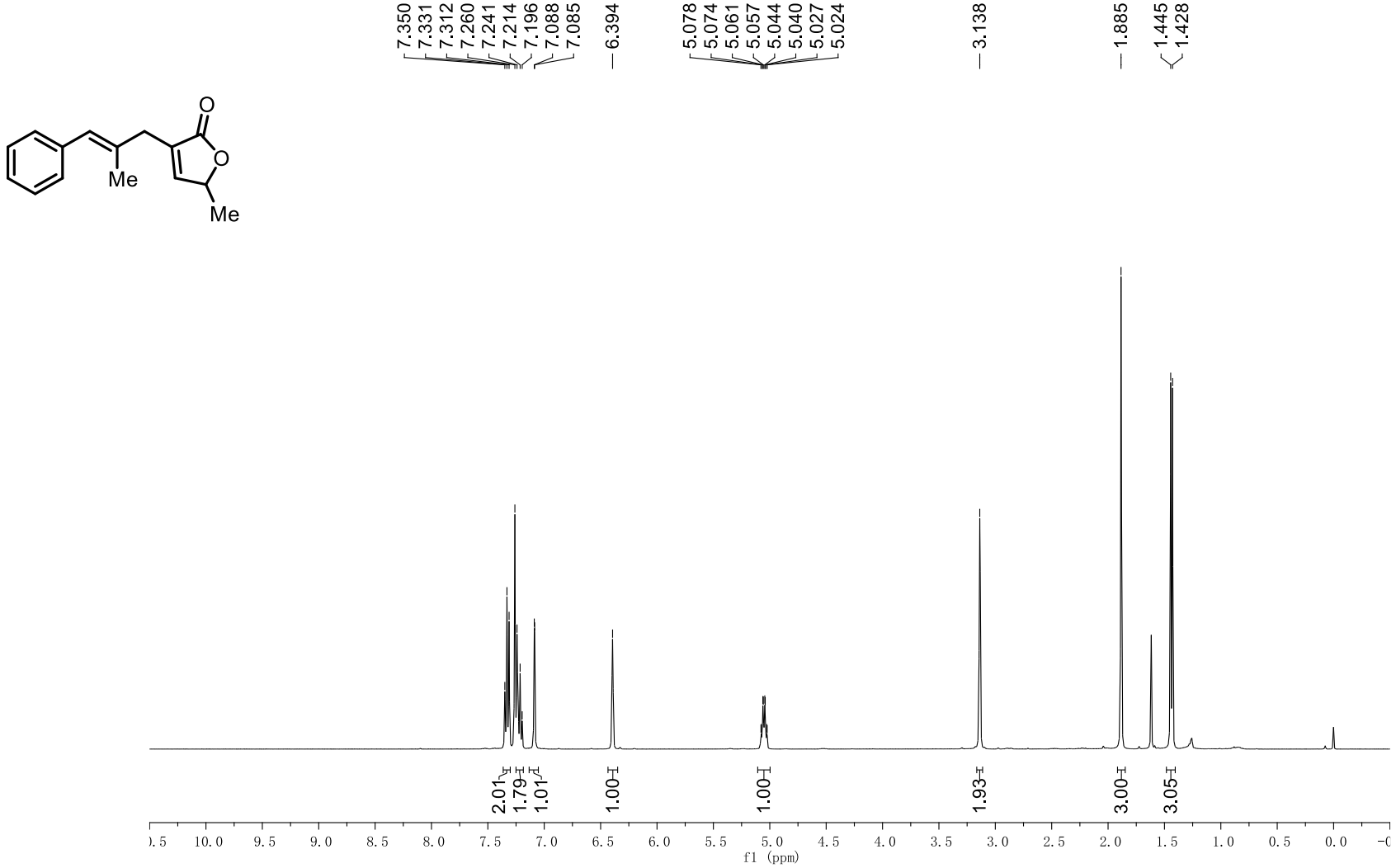
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-Cinnamylfuran-2(5*H*)-one (29)



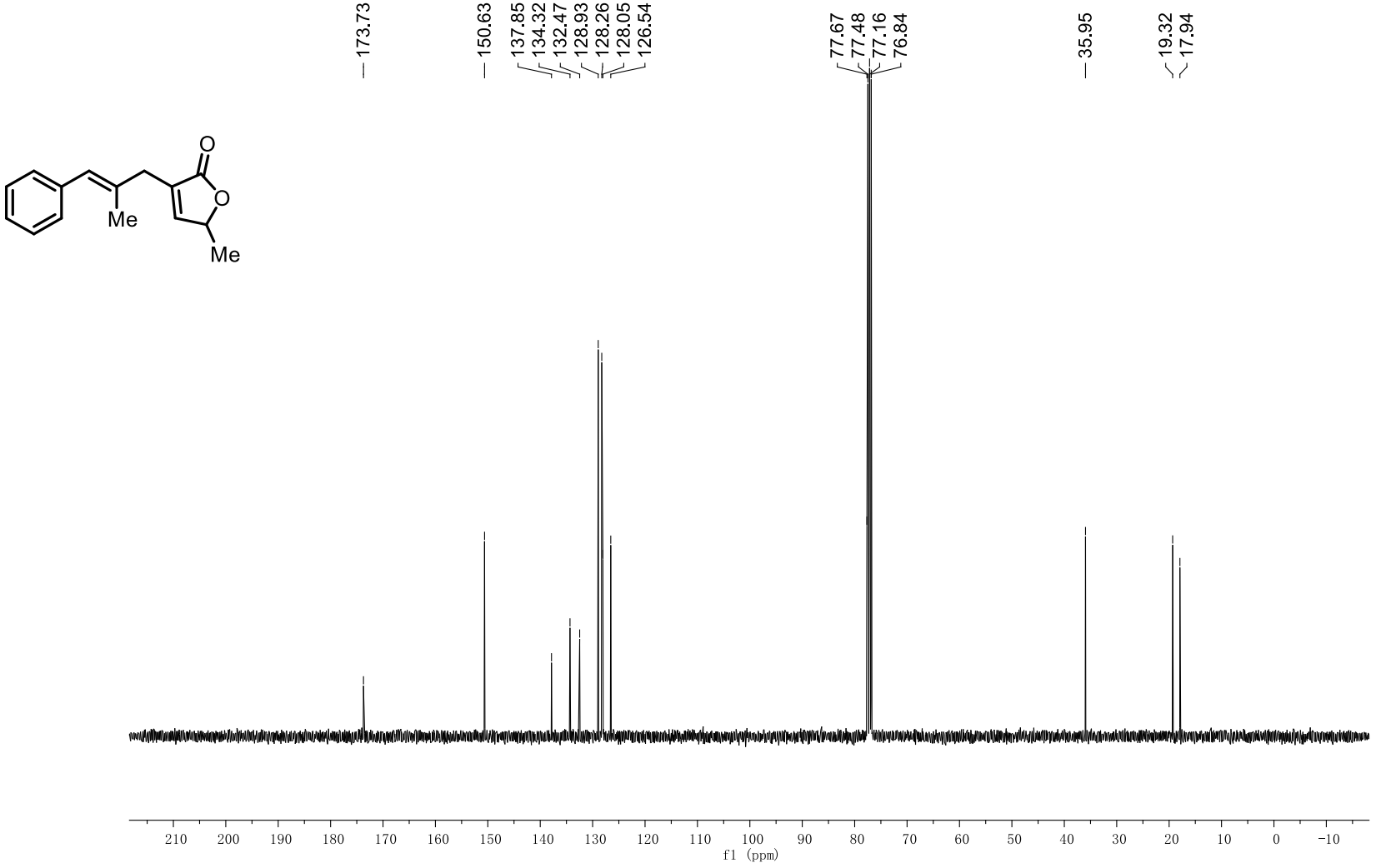
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-Cinnamylfuran-2(5*H*)-one (29)



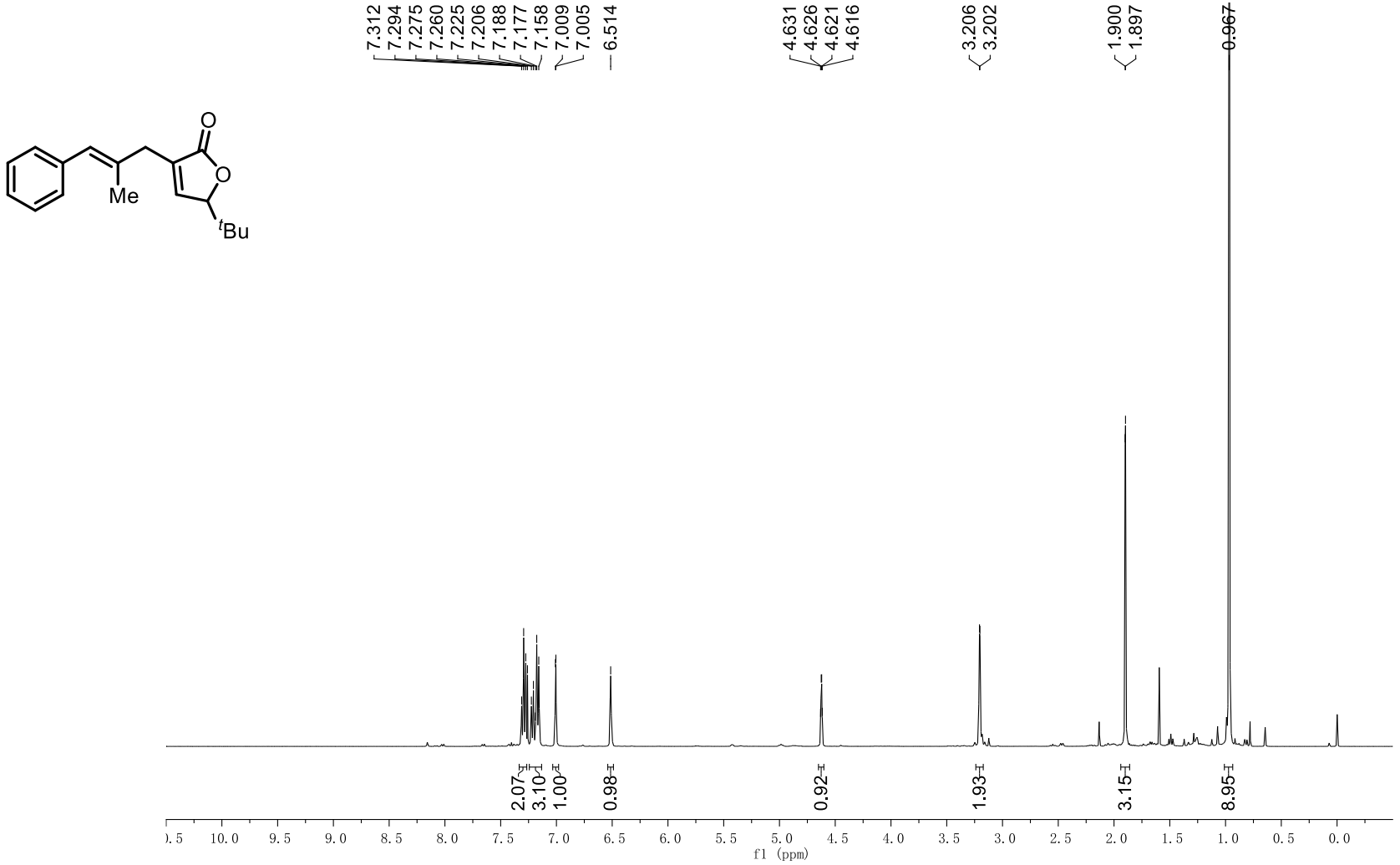
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-5-methyl-3-(2-Methyl-3-phenylallyl)furan-2(5*H*)-one (30)



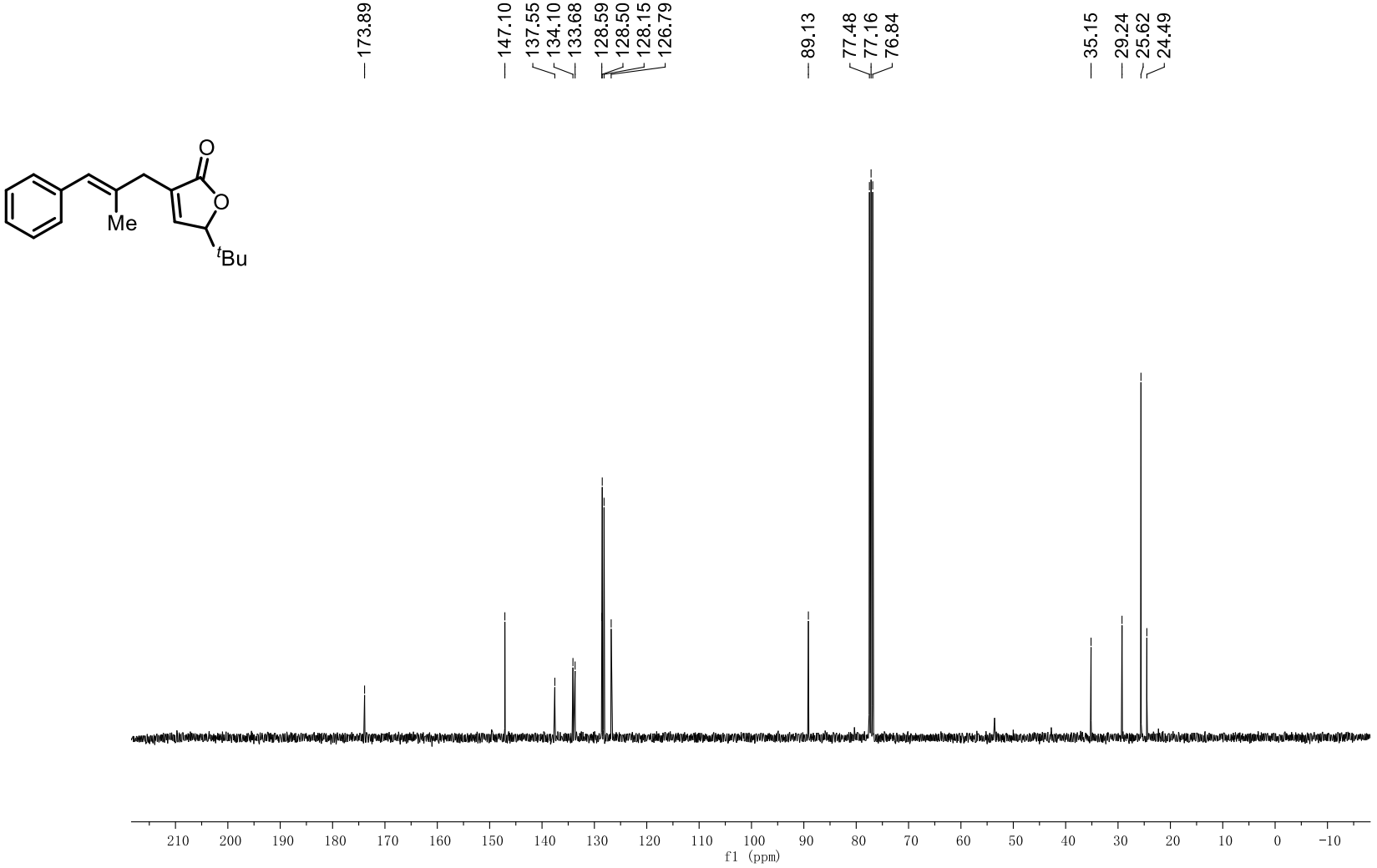
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of(*E*)-5-methyl-3-(2-Methyl-3-phenylallyl)furan-2(5*H*)-one (30)



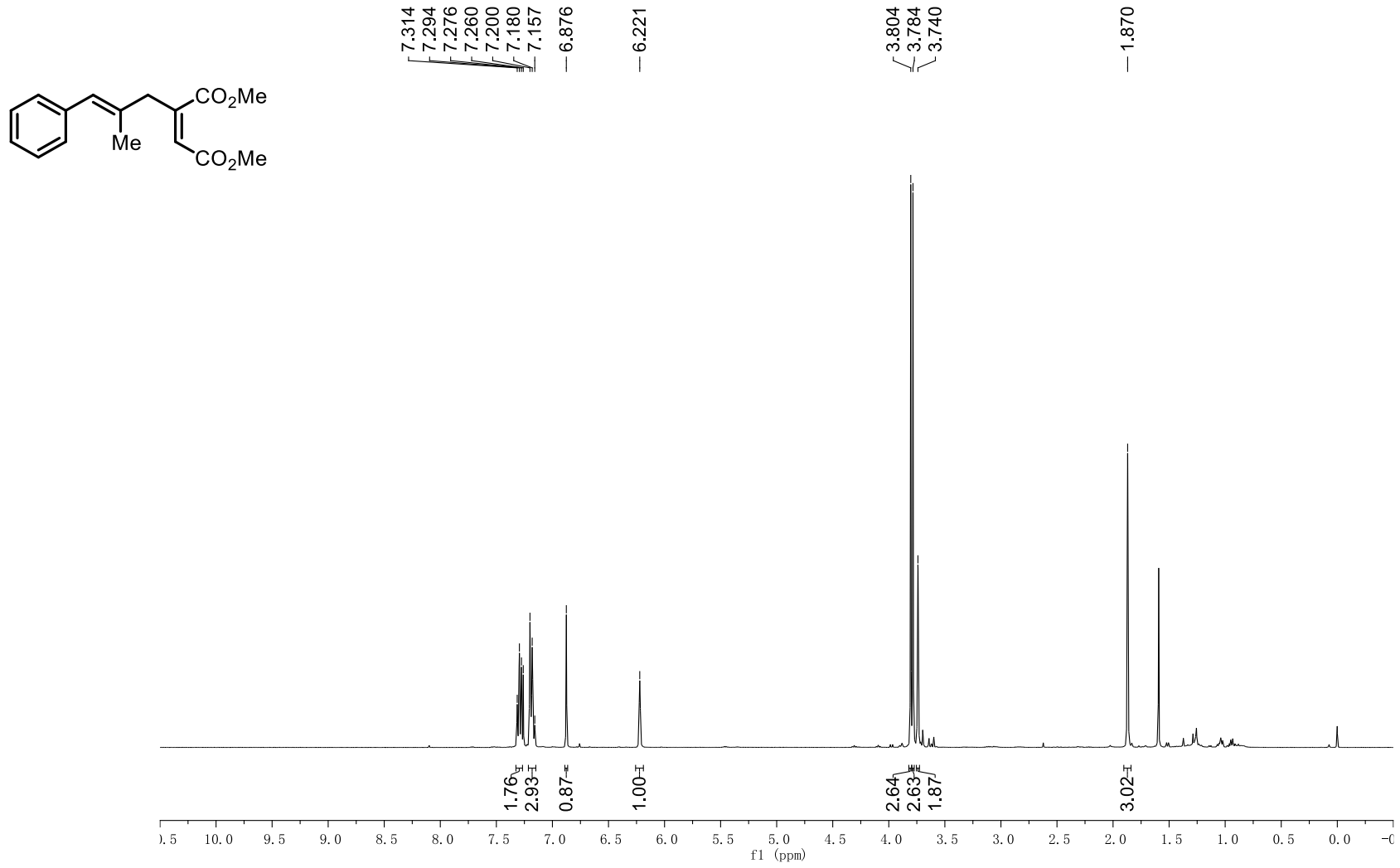
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-5-(*tert*-Butyl)-3-(2-methyl-3-phenylallyl)furan-2(5H)-one (31)



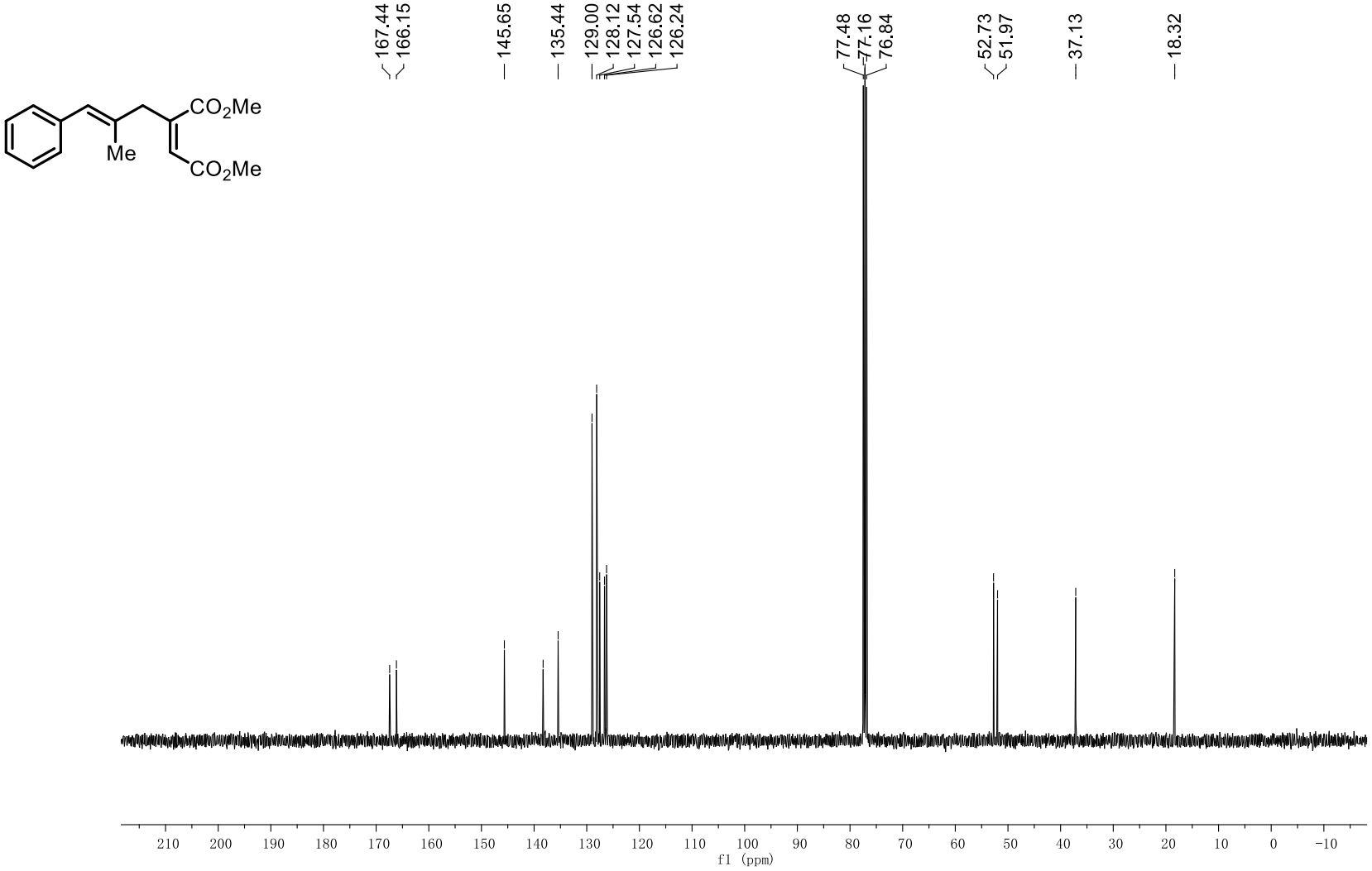
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-5-(*tert*-Butyl)-3-(2-methyl-3-phenylallyl)furan-2(5*H*)-one (31)



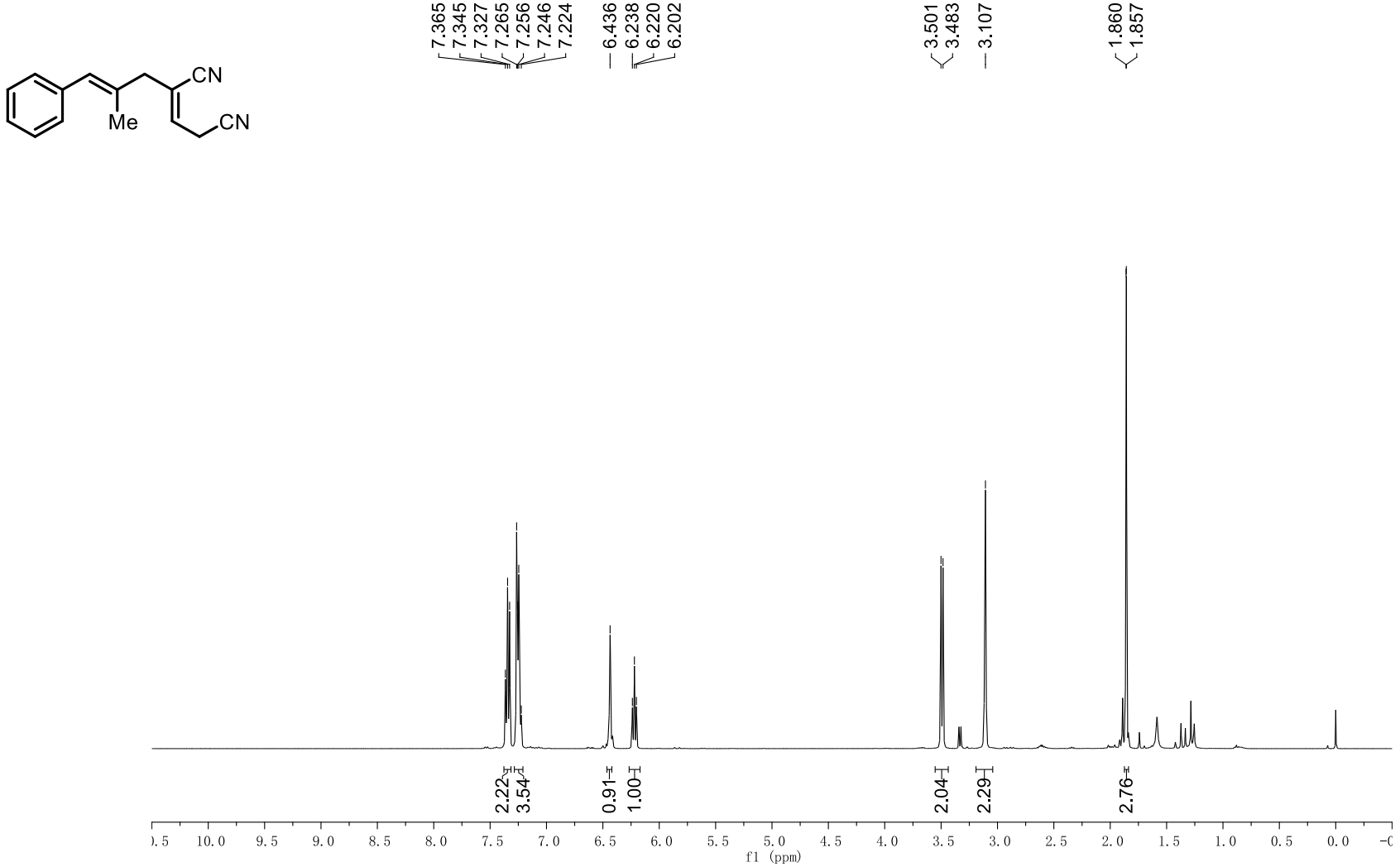
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Dimethyl 2-((*E*)-2-methyl-3-phenylallyl)maleate (32)



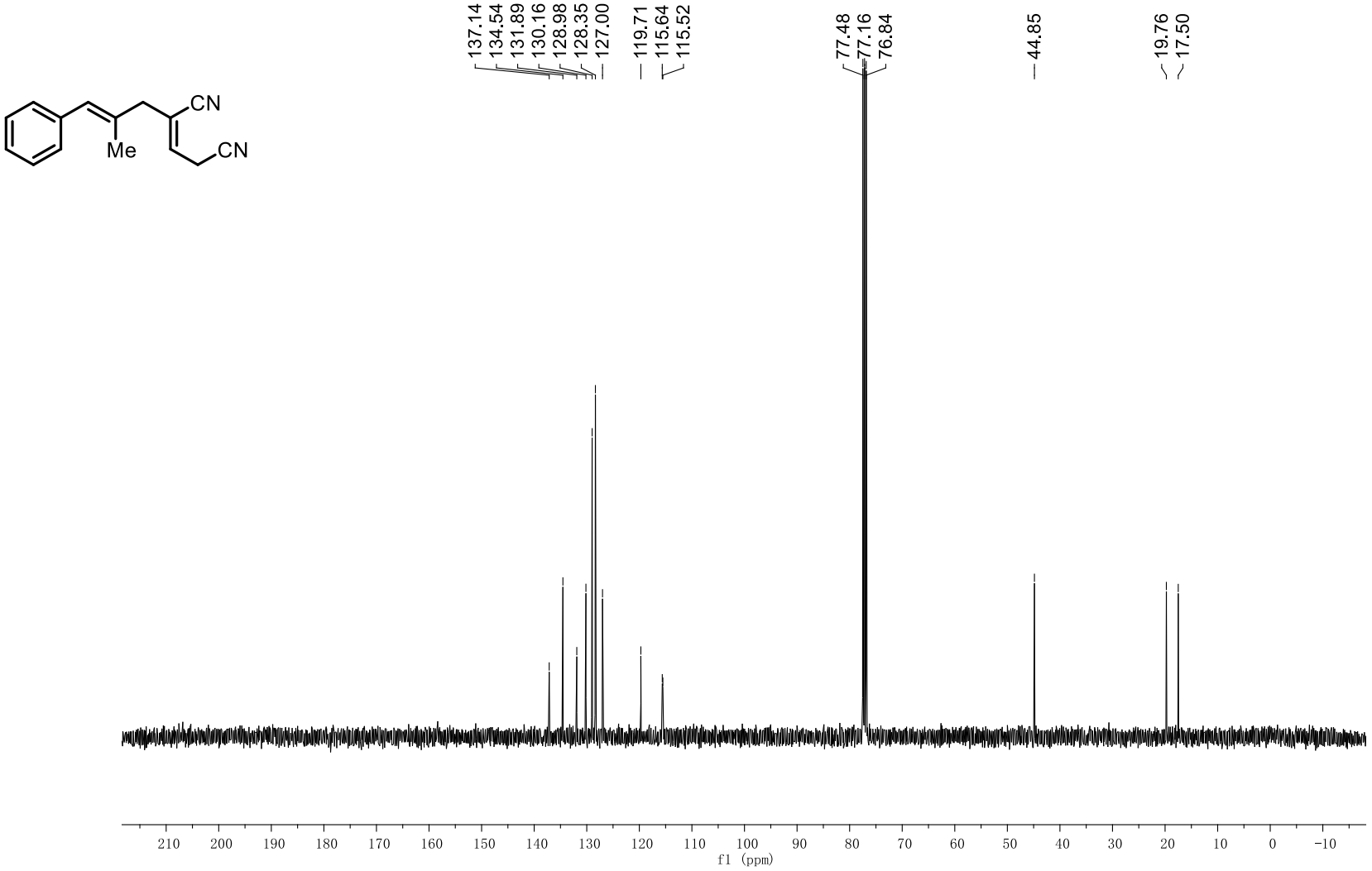
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Dimethyl 2-((*E*)-2-methyl-3-phenylallyl)maleate (32)



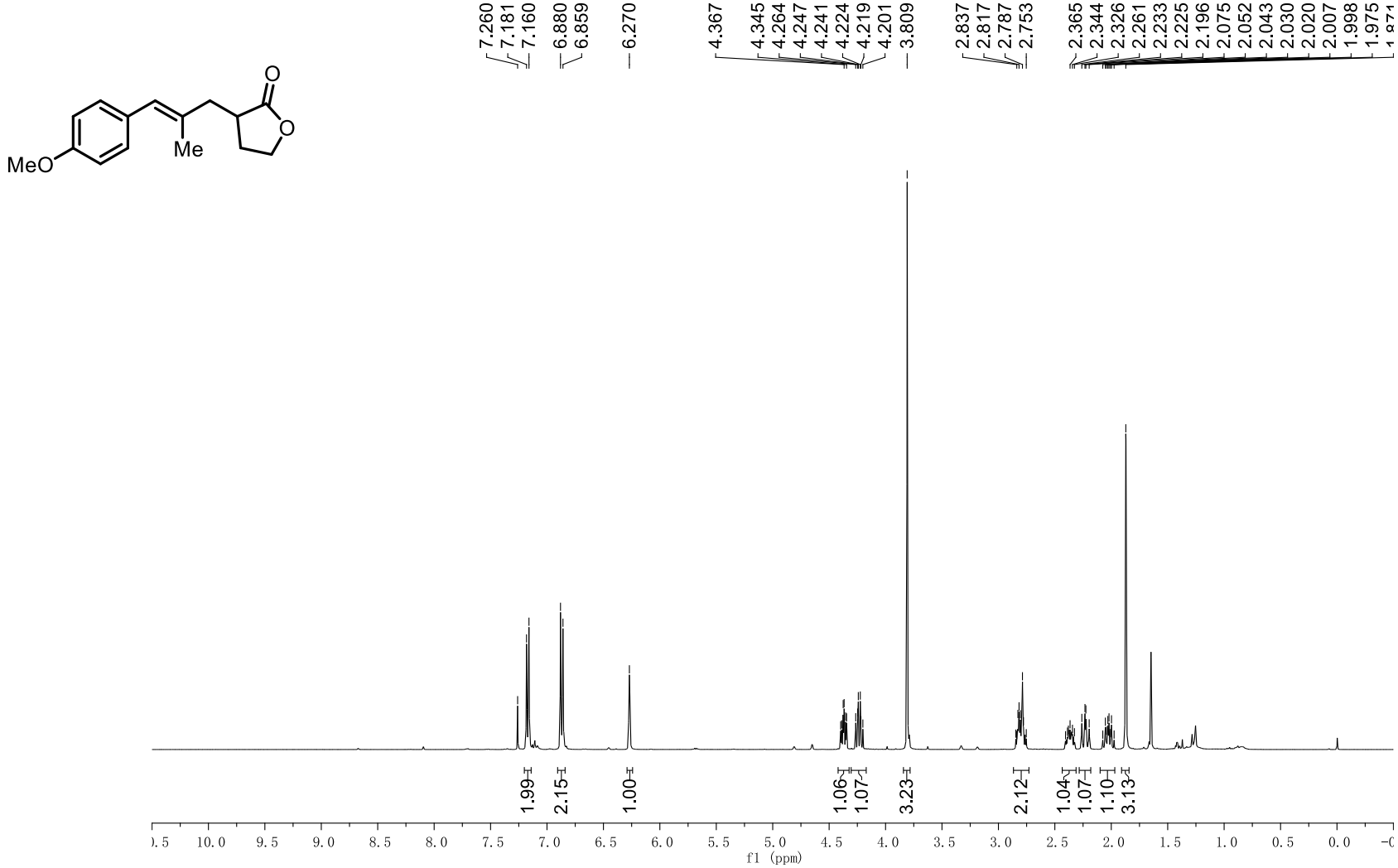
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-2-((*E*)-2-Methyl-3-phenylallyl)pent-2-enedinitrile (33)



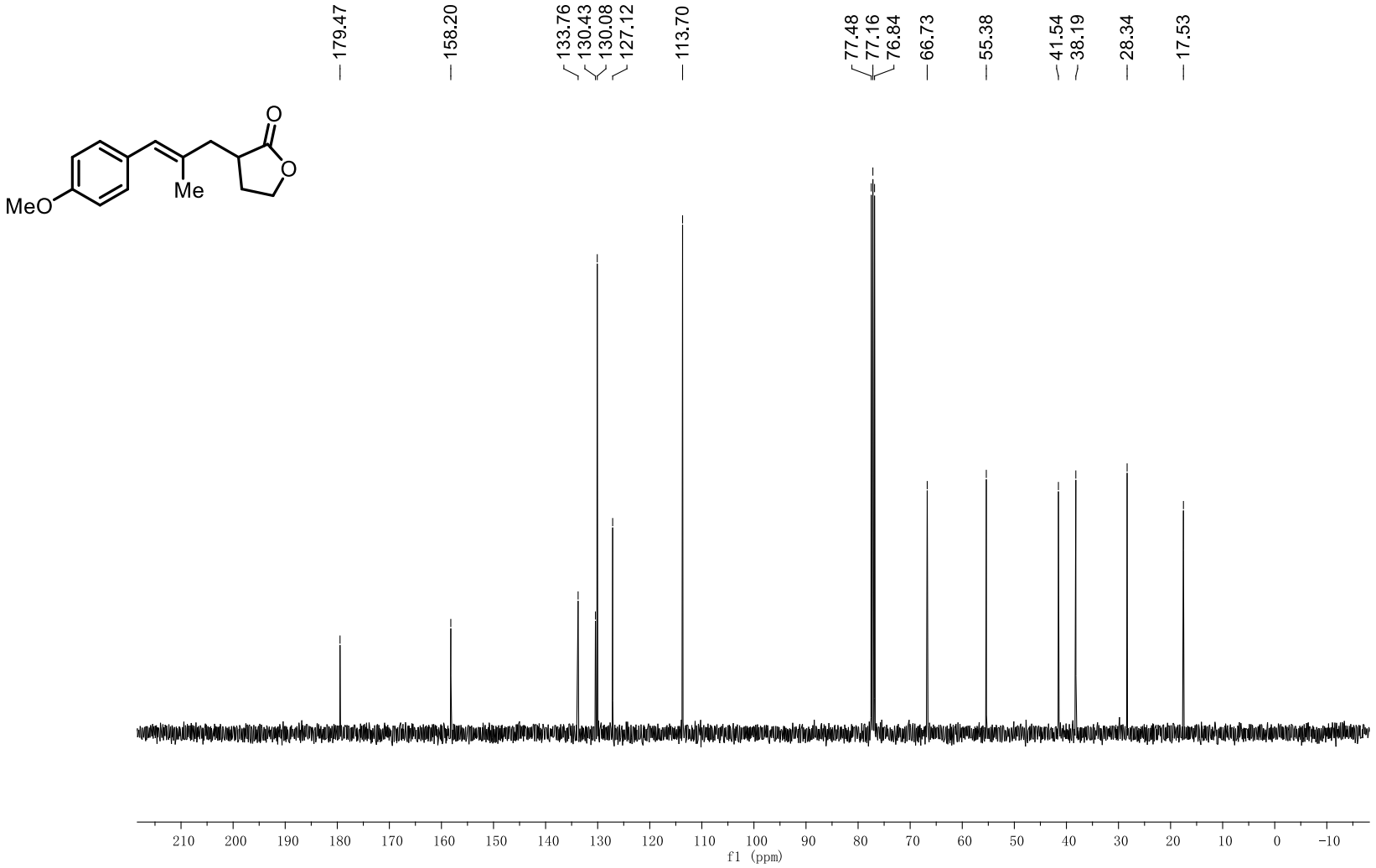
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-2-((*E*)-2-Methyl-3-phenylallyl)pent-2-enedinitrile (33)



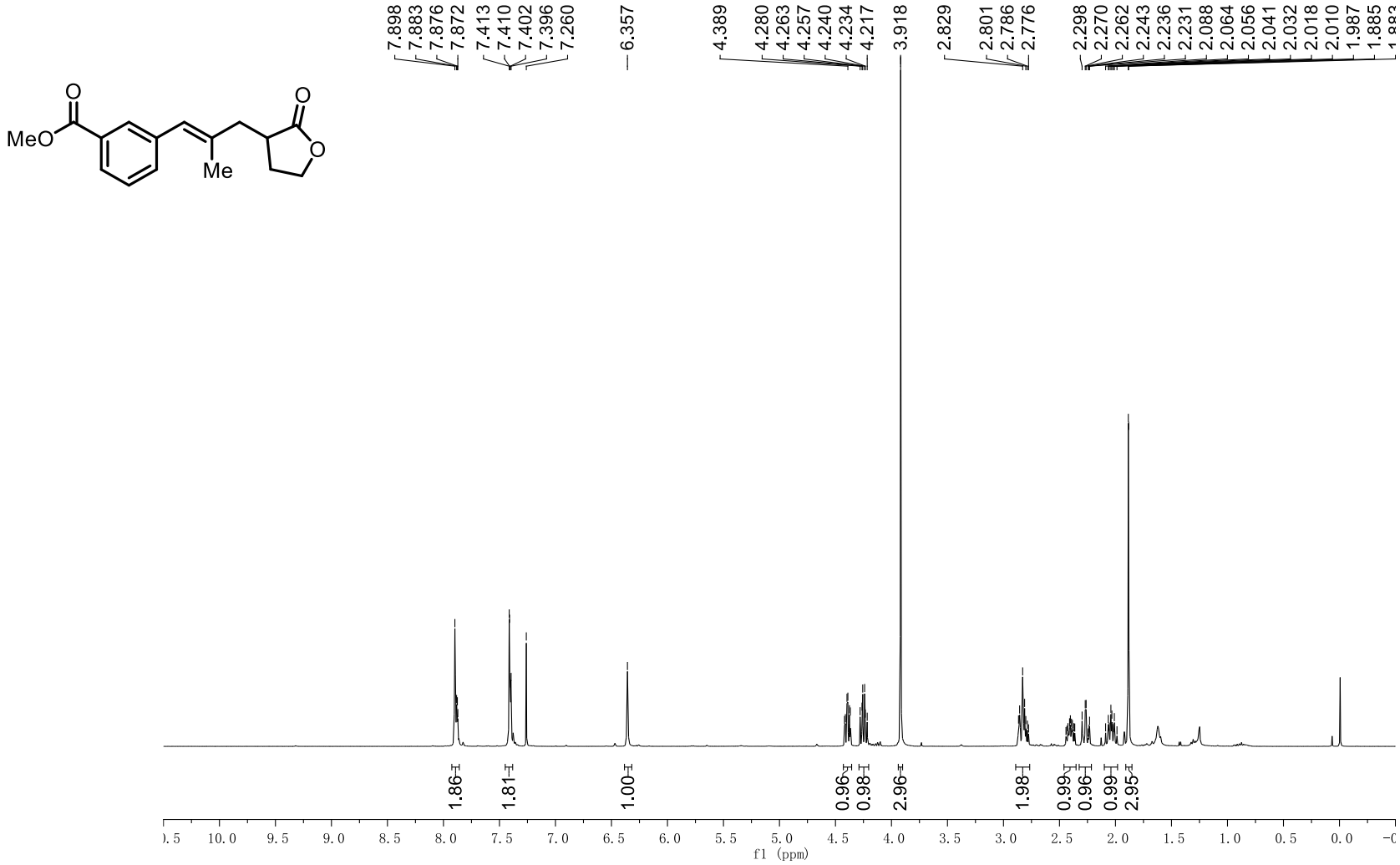
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Methoxyphenyl)-2-methylallyl)dihydrofuran-2(3*H*)-one (34)



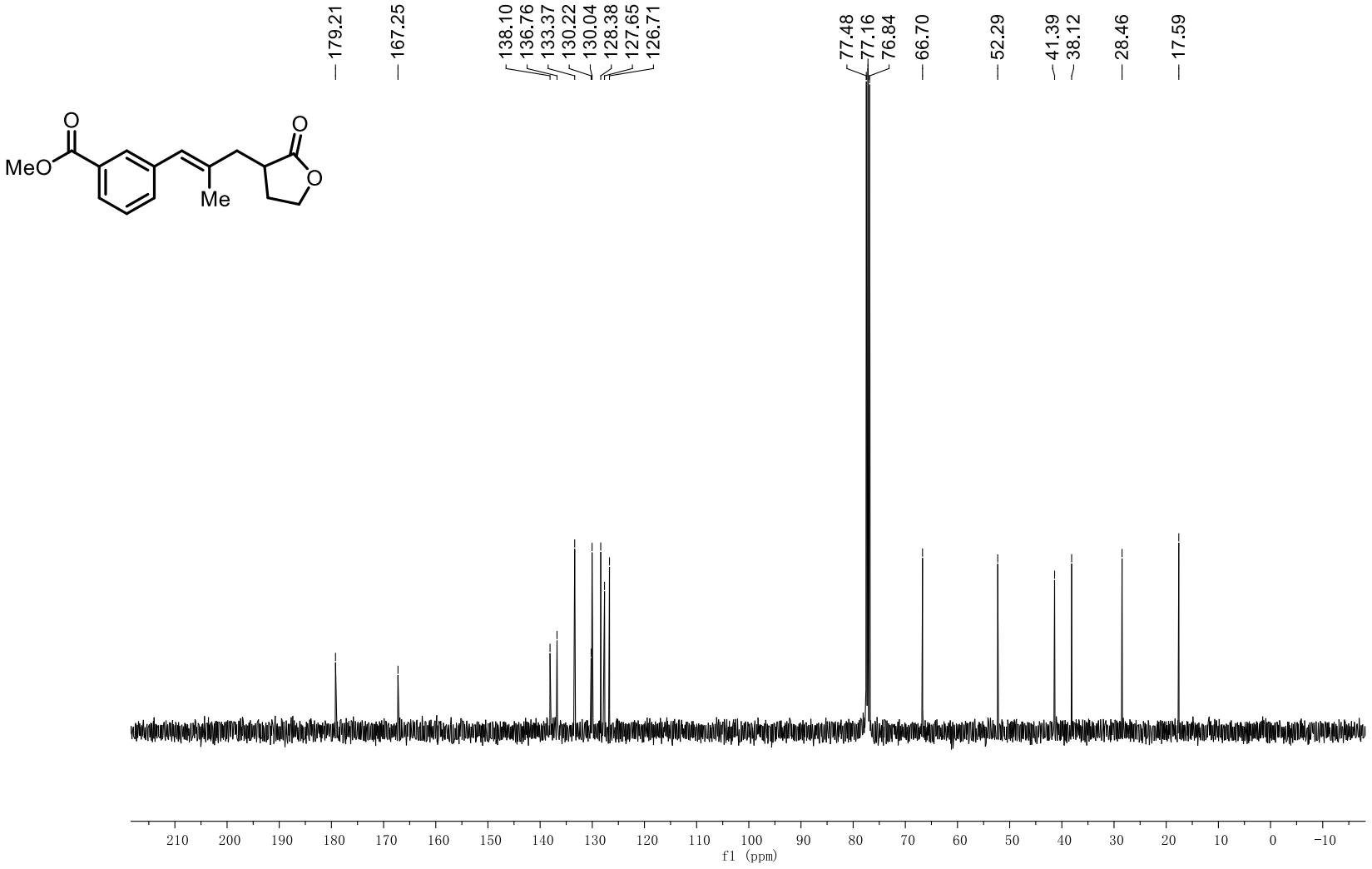
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Methoxyphenyl)-2-methylallyl)dihydrofuran-2(3*H*)-one (34)



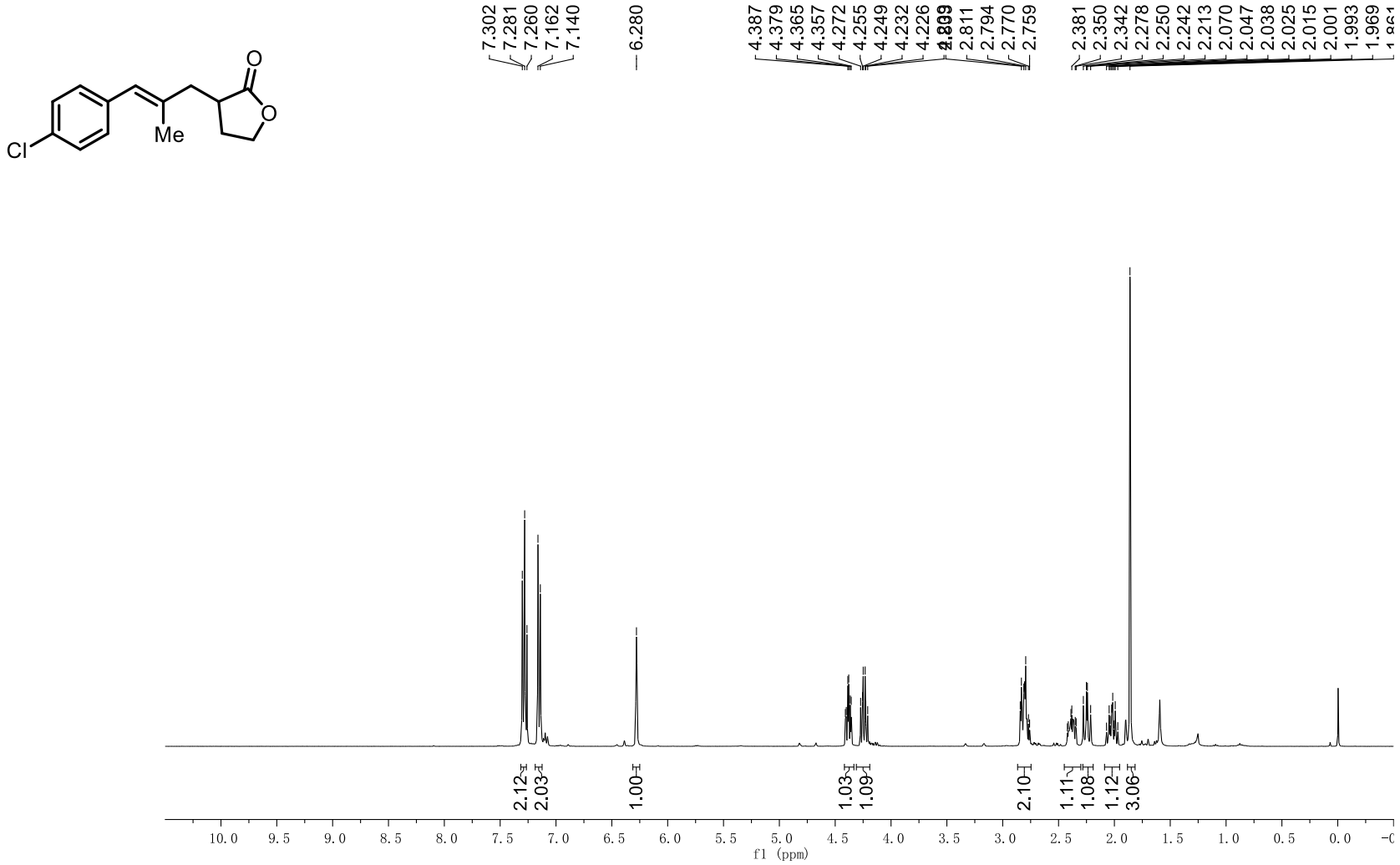
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Methyl (*E*)-3-(2-methyl-3-(2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl)benzoate (35)



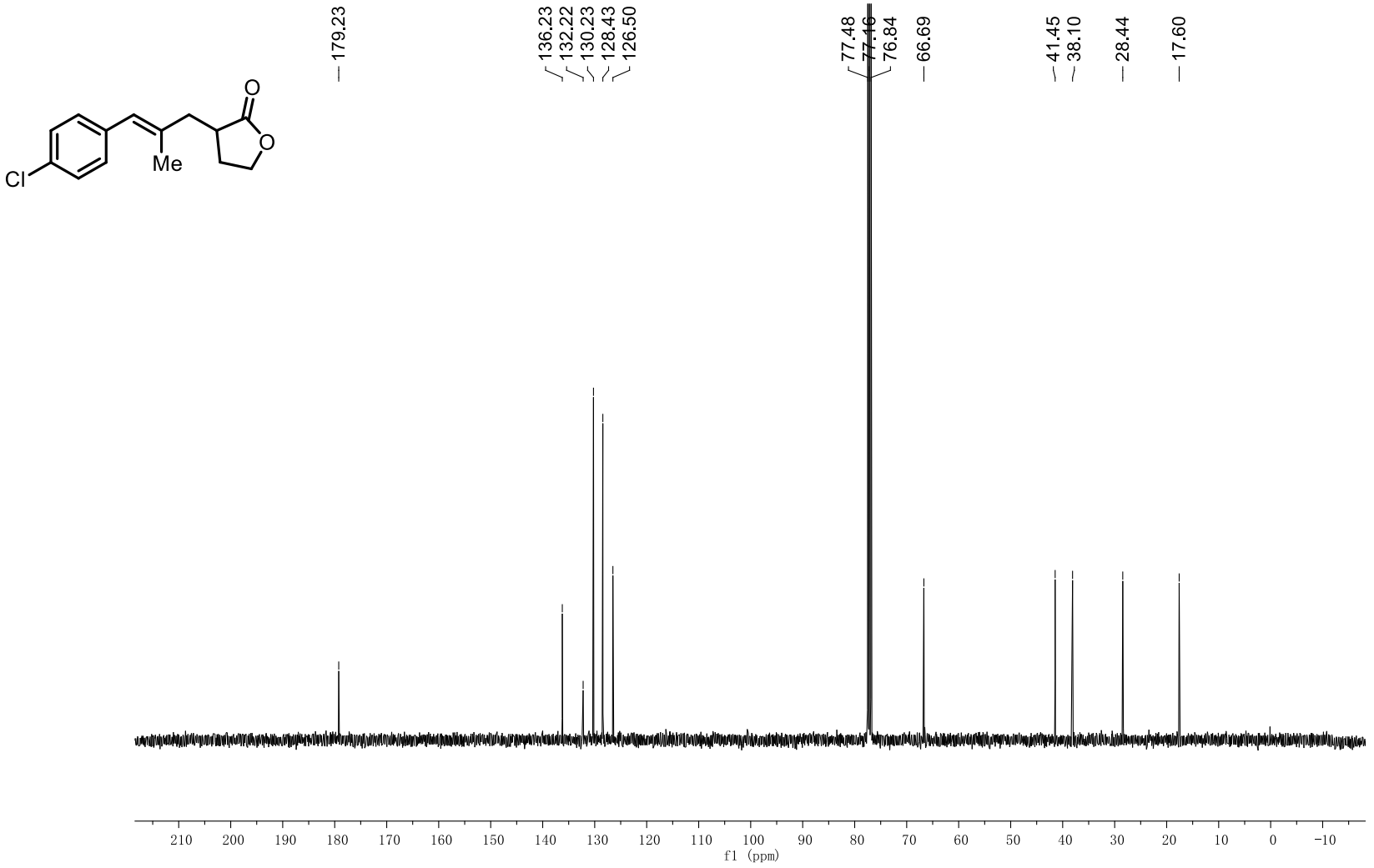
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Methyl (*E*)-3-(2-methyl-3-(2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl)benzoate (35)



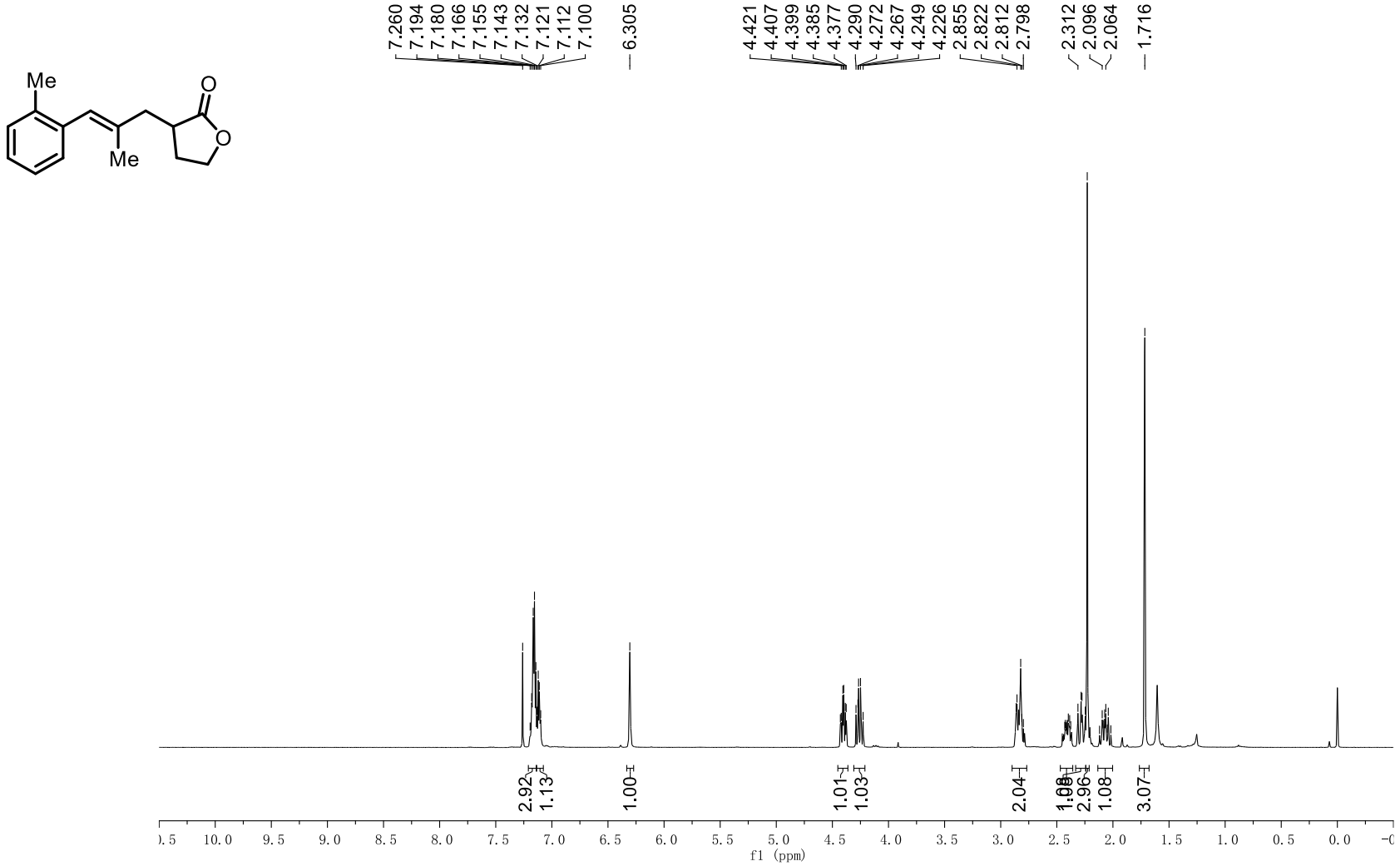
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Chlorophenyl)-2-methylallyl)dihydrofuran-2(3*H*)-one (36)



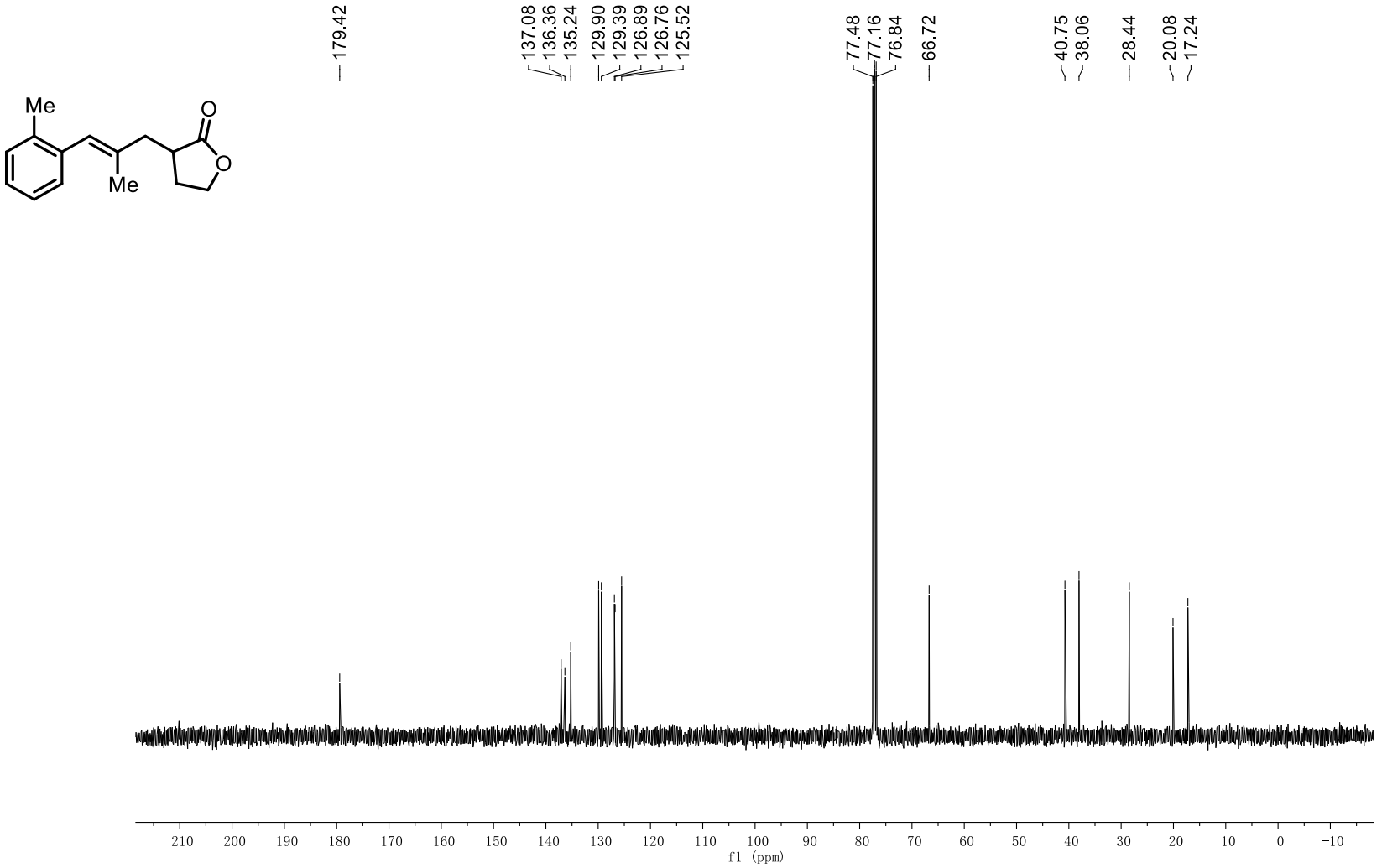
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(3-(4-Chlorophenyl)-2-methylallyl)dihydrofuran-2(3*H*)-one (36)



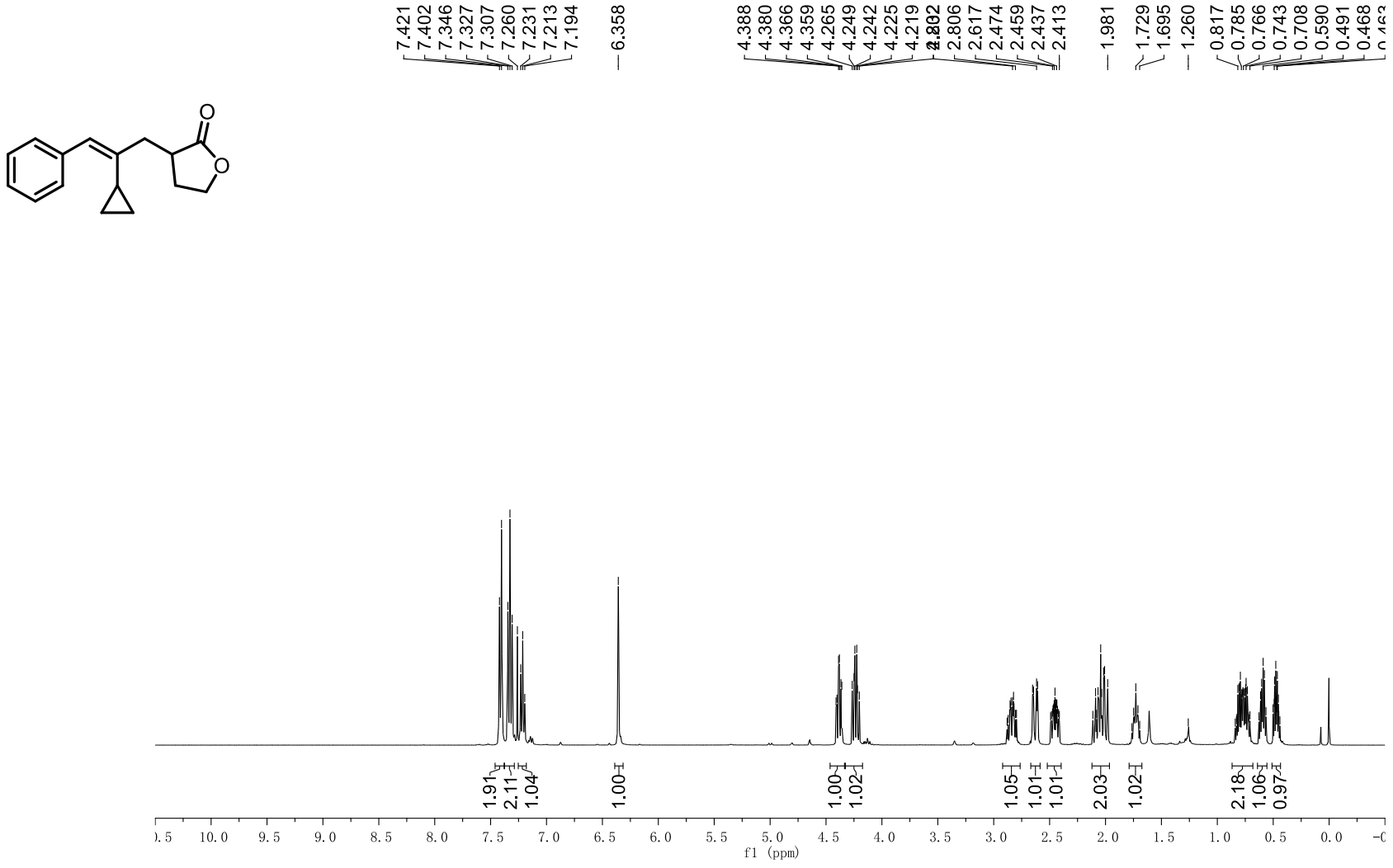
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(*o*-tolyl)allyl)dihydrofuran-2(3*H*)-one (37)



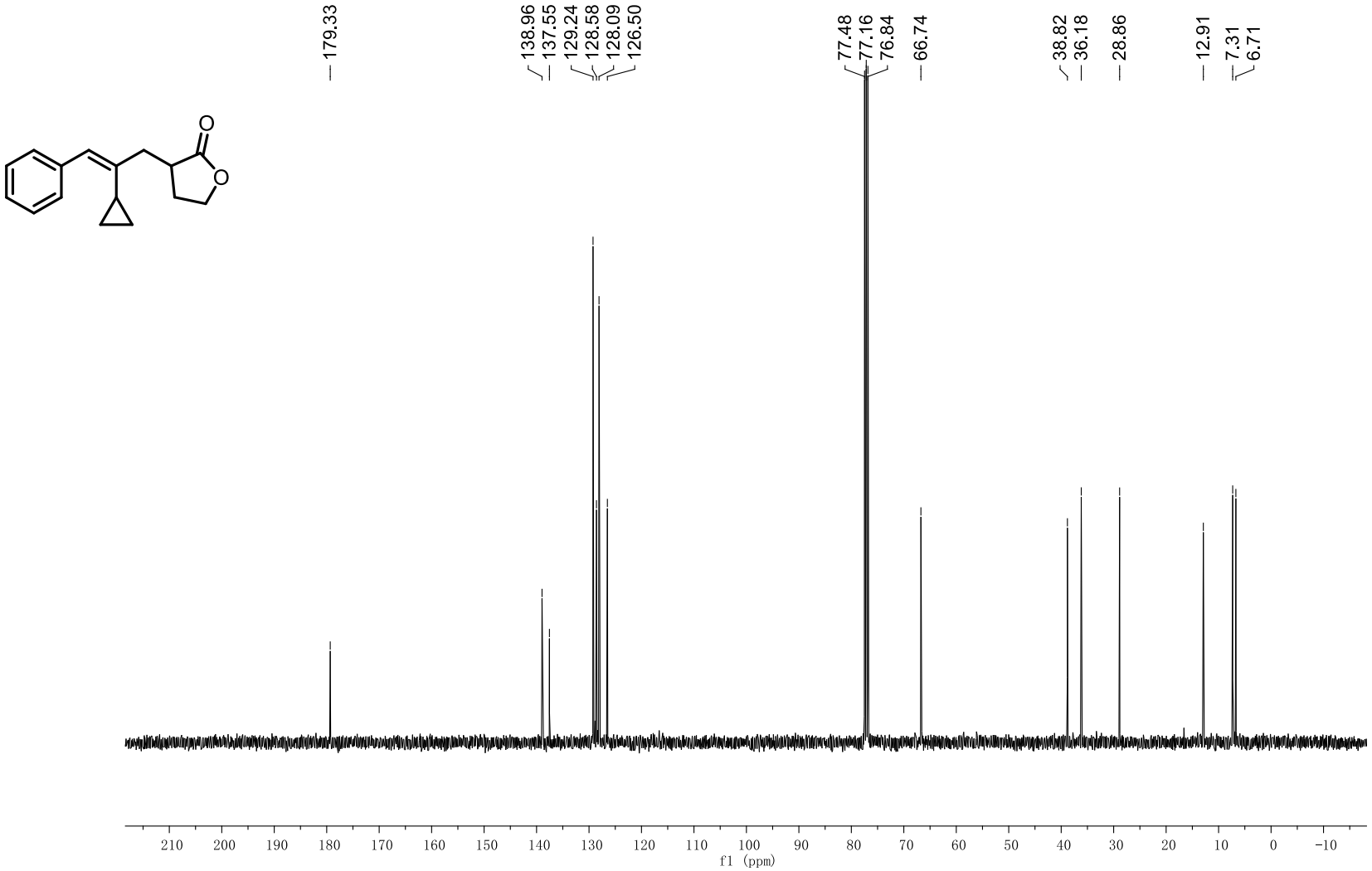
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-(*o*-tolyl)allyl)dihydrofuran-2(3*H*)-one (37)



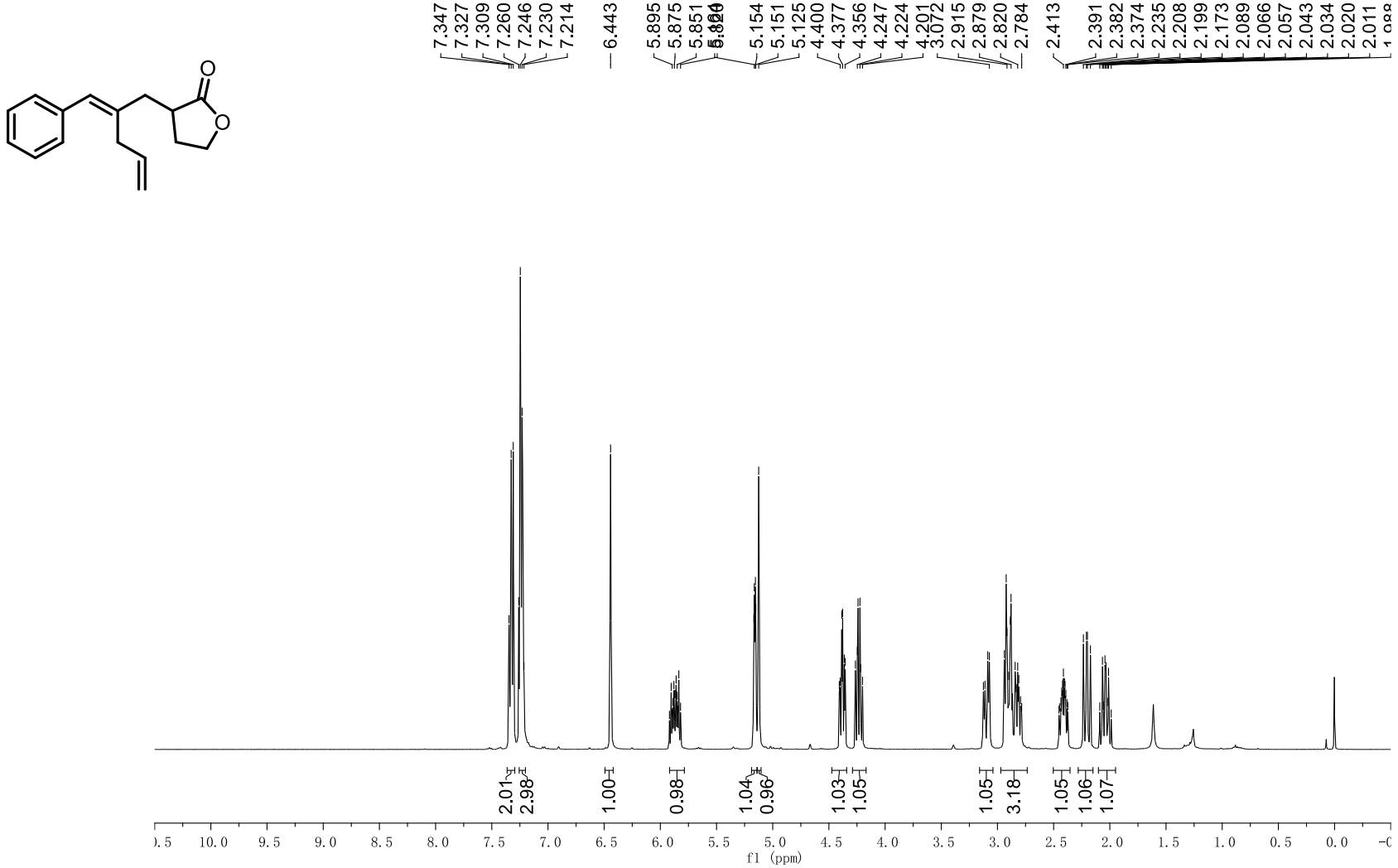
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (Z)-3-(2-Cyclopropyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (38)



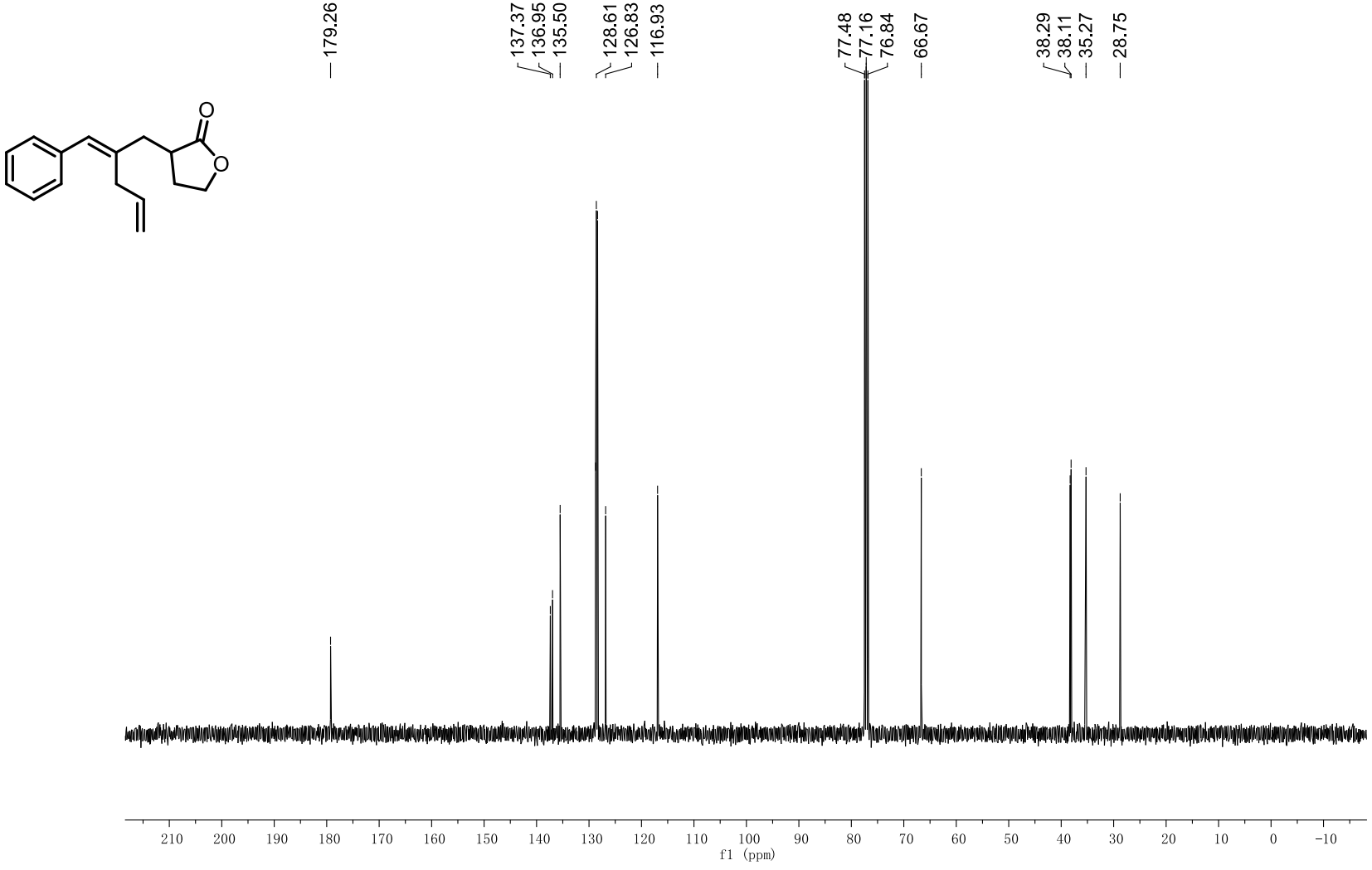
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (Z)-3-(2-Cyclopropyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (38)



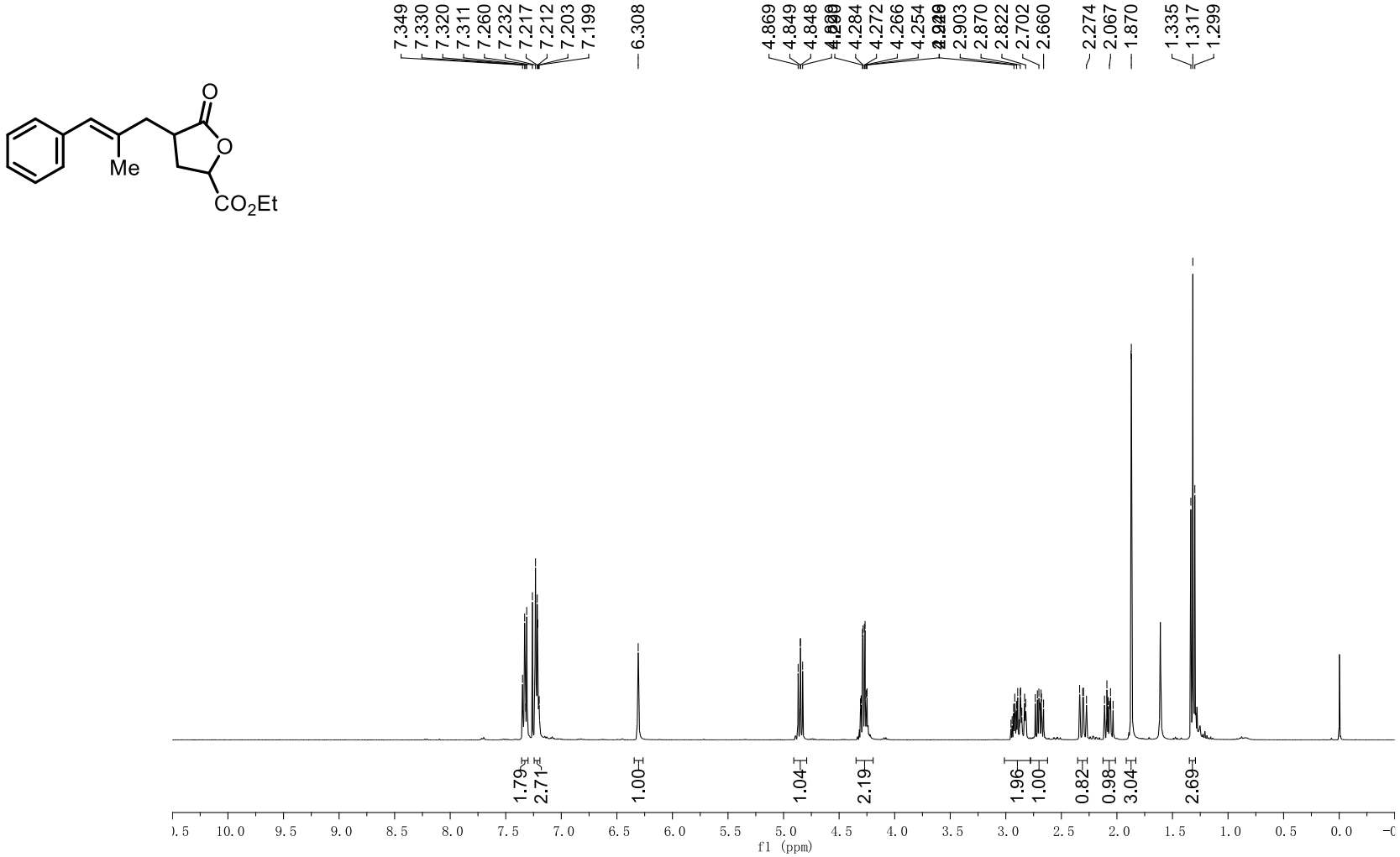
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Benzylidenepent-4-en-1-yl)dihydrofuran-2(3*H*)-one (39)



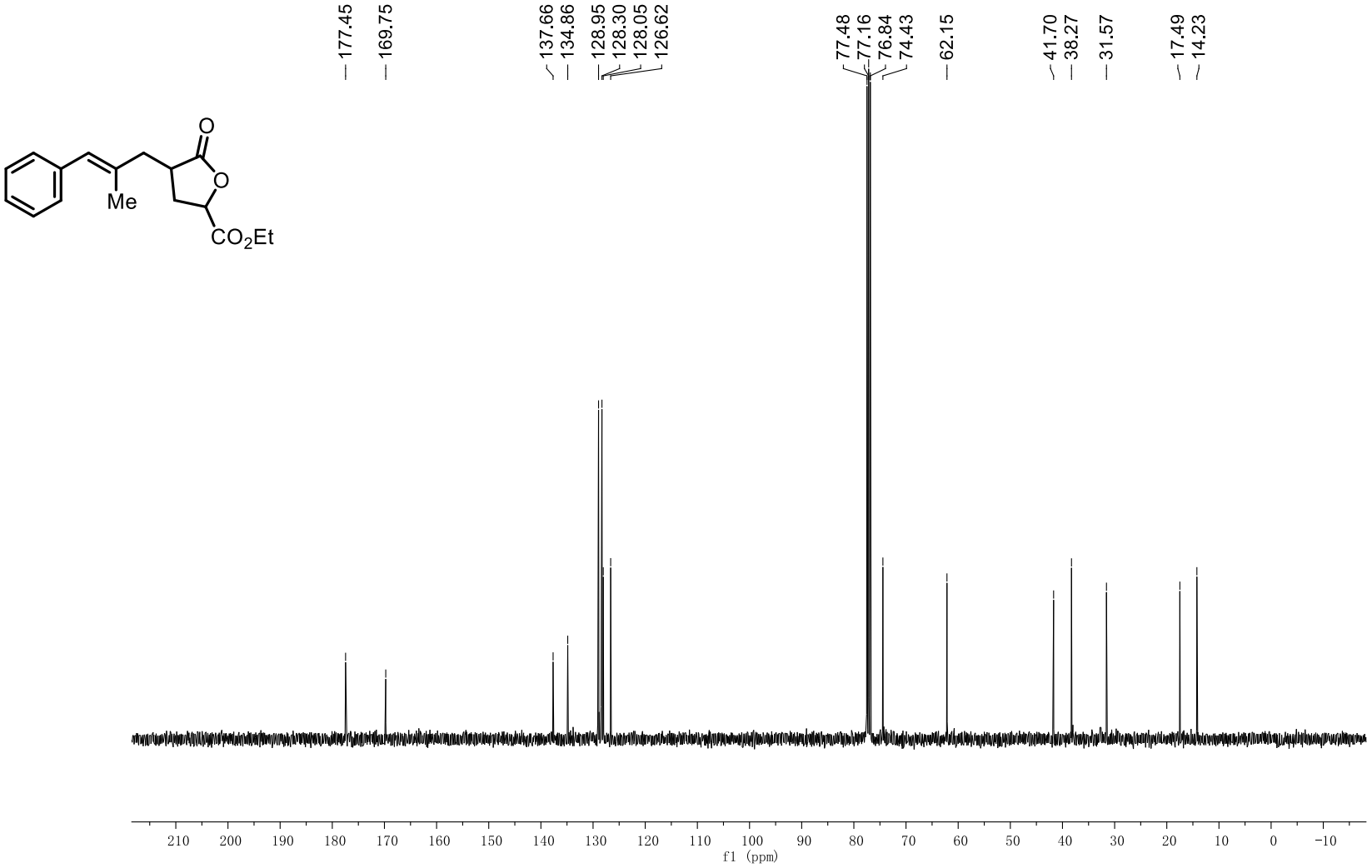
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Benzylidenepent-4-en-1-yl)dihydrofuran-2(3*H*)-one (39)



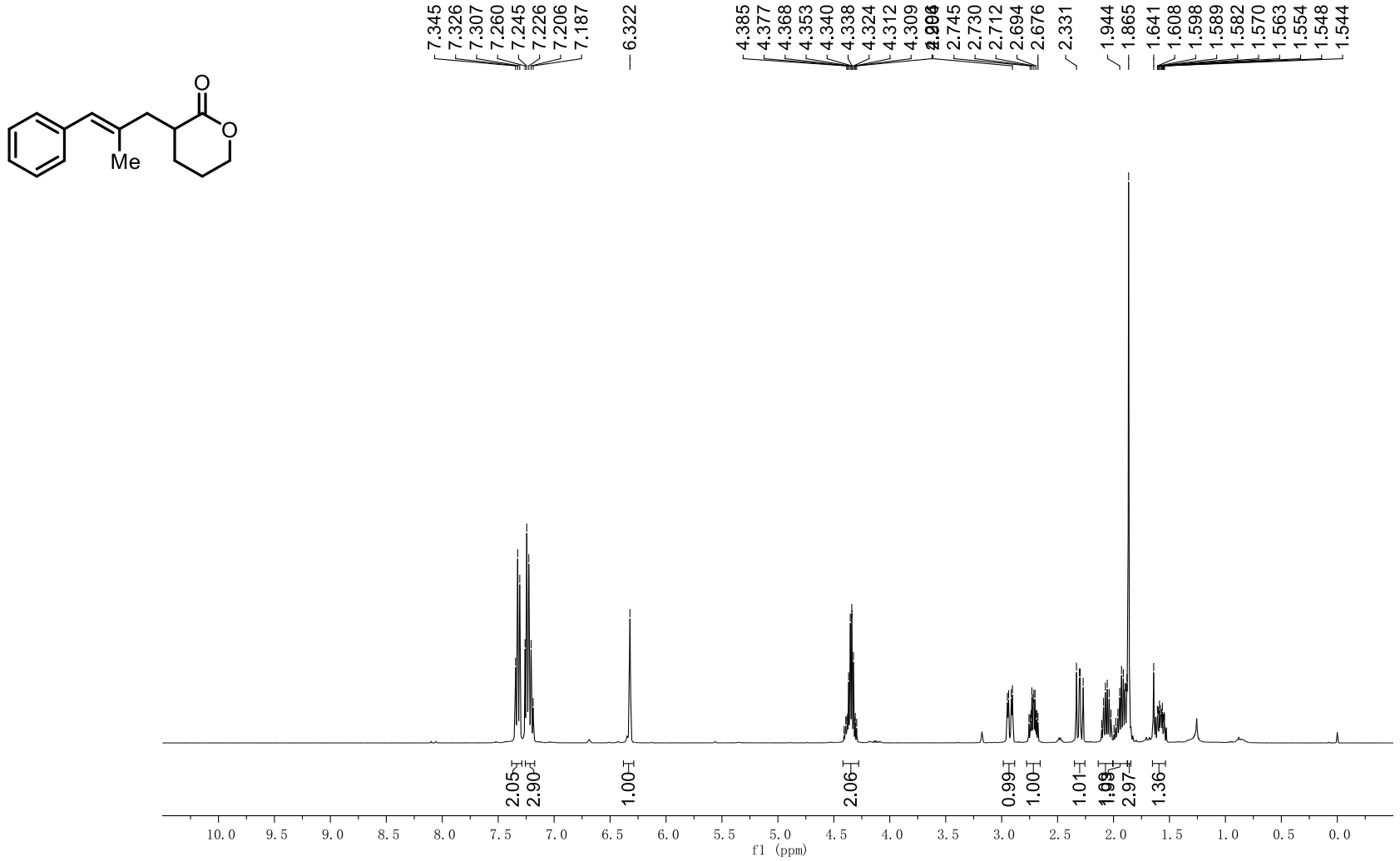
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Ethyl (*E*)-4-(2-Methyl-3-phenylallyl)-5-oxotetrahydrofuran-2-carboxylate (40)



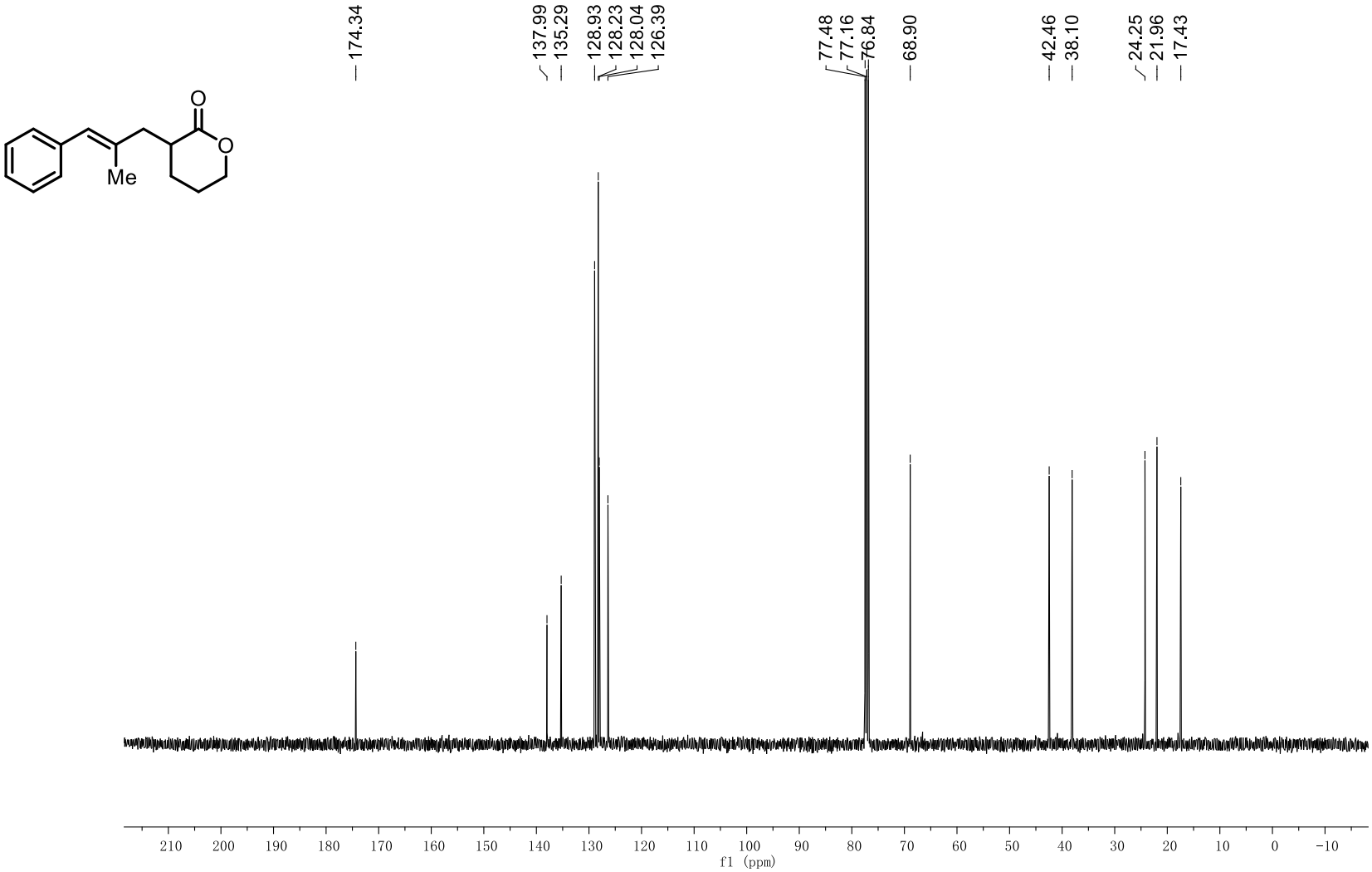
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Ethyl (*E*)-4-(2-Methyl-3-phenylallyl)-5-oxotetrahydrofuran-2-carboxylate (40)



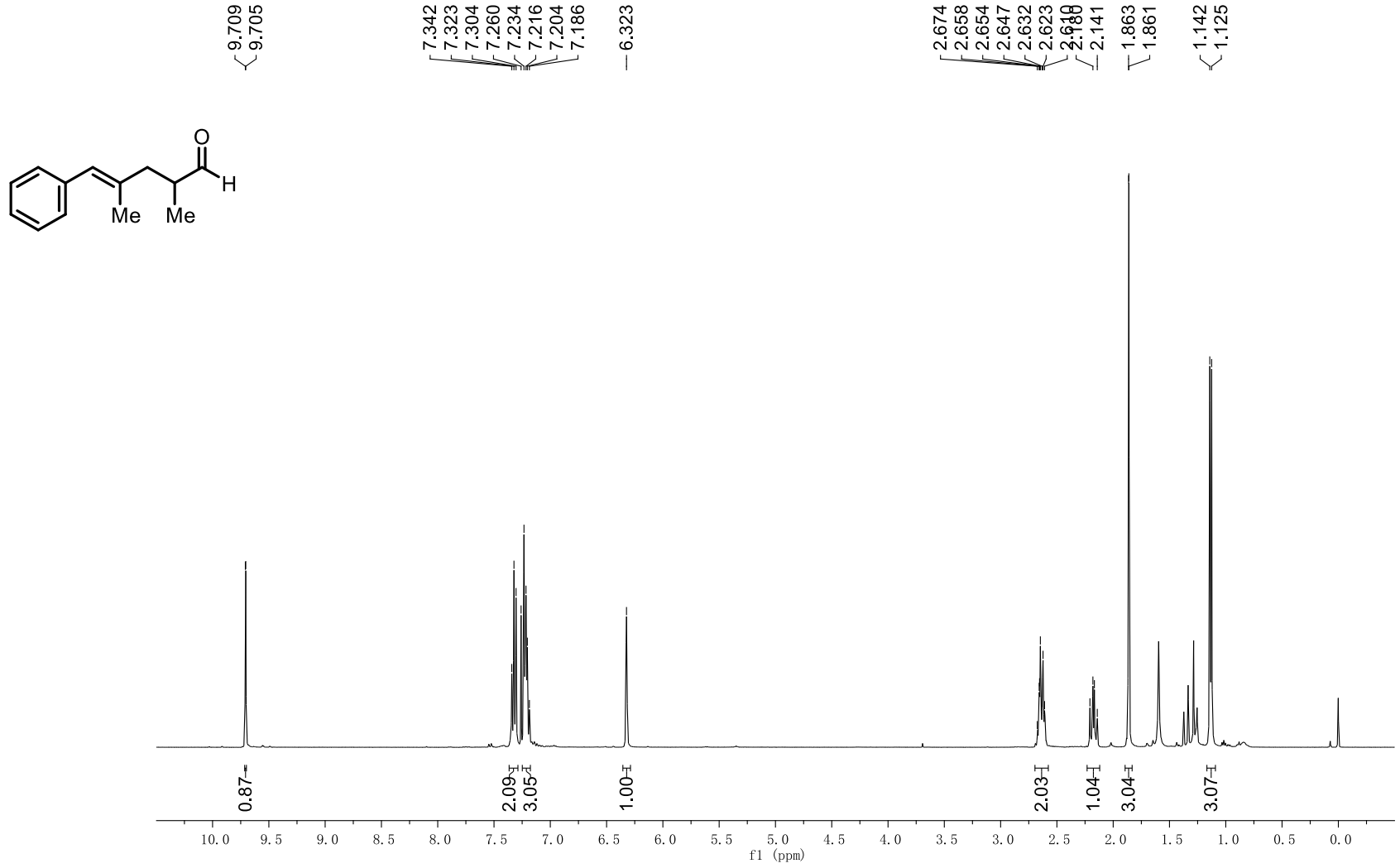
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)tetrahydro-2H-pyran-2-one (41)



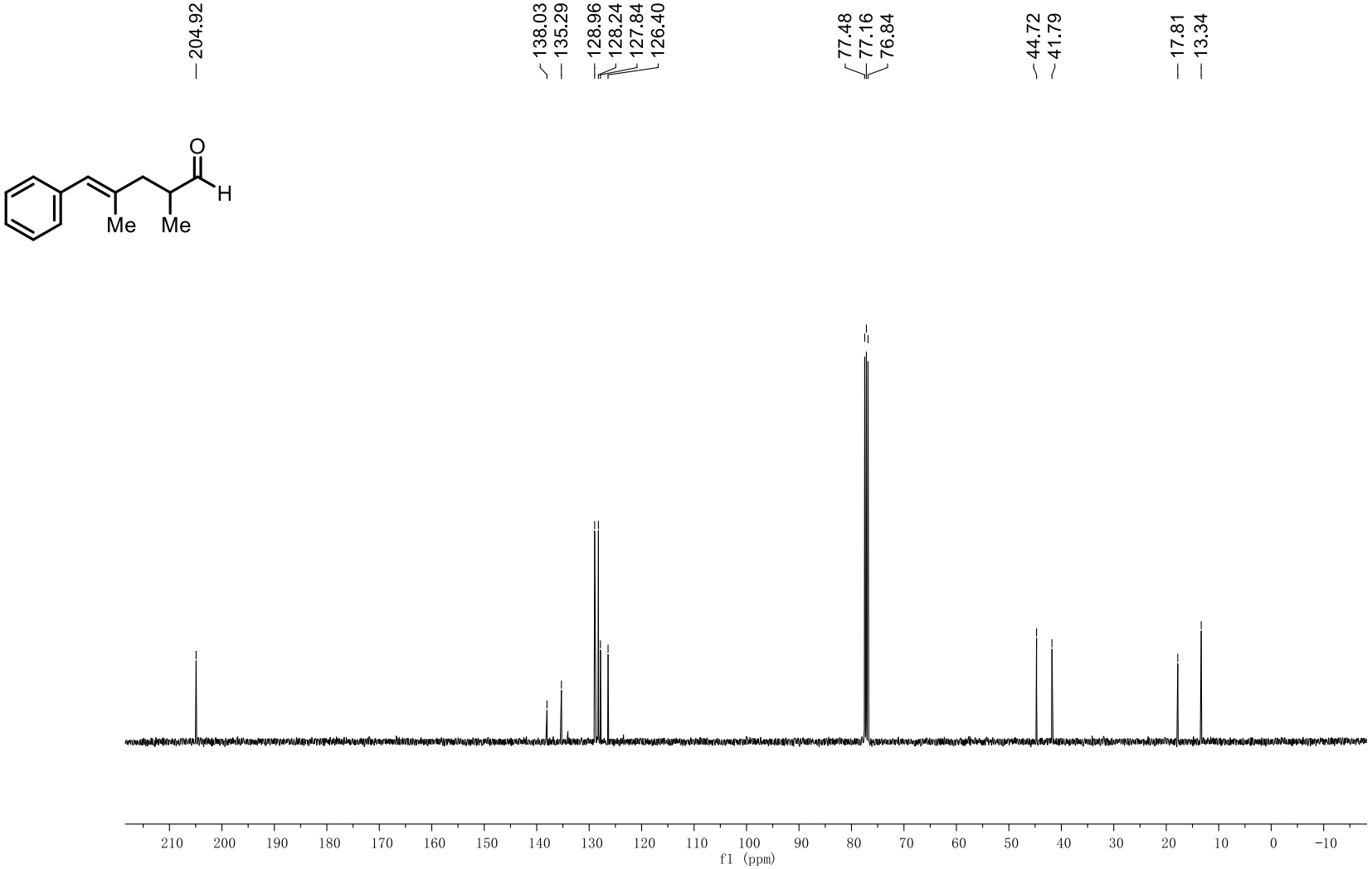
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)tetrahydro-2H-pyran-2-one (41)



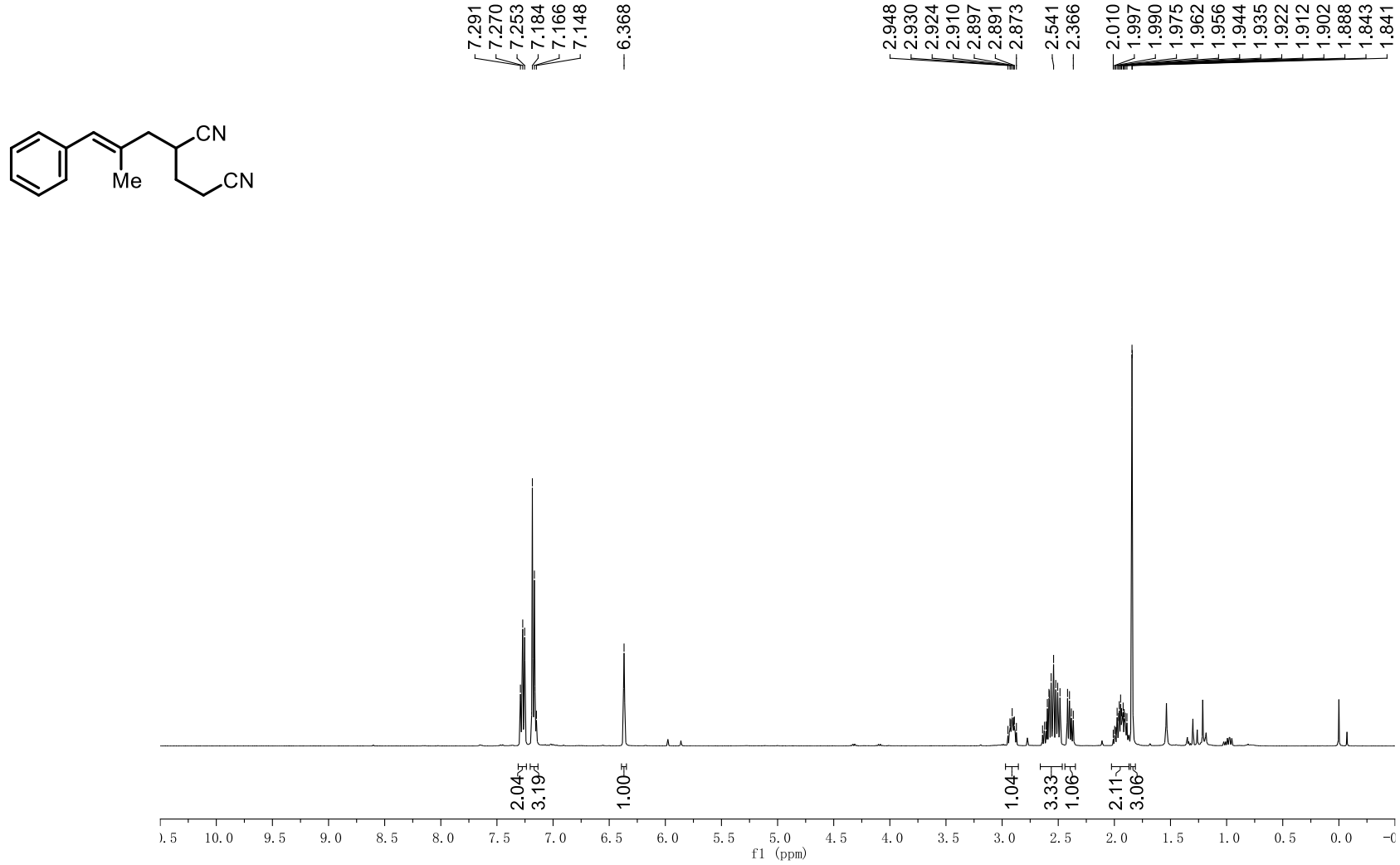
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-2,4-Dimethyl-5-phenylpent-4-enal (42)



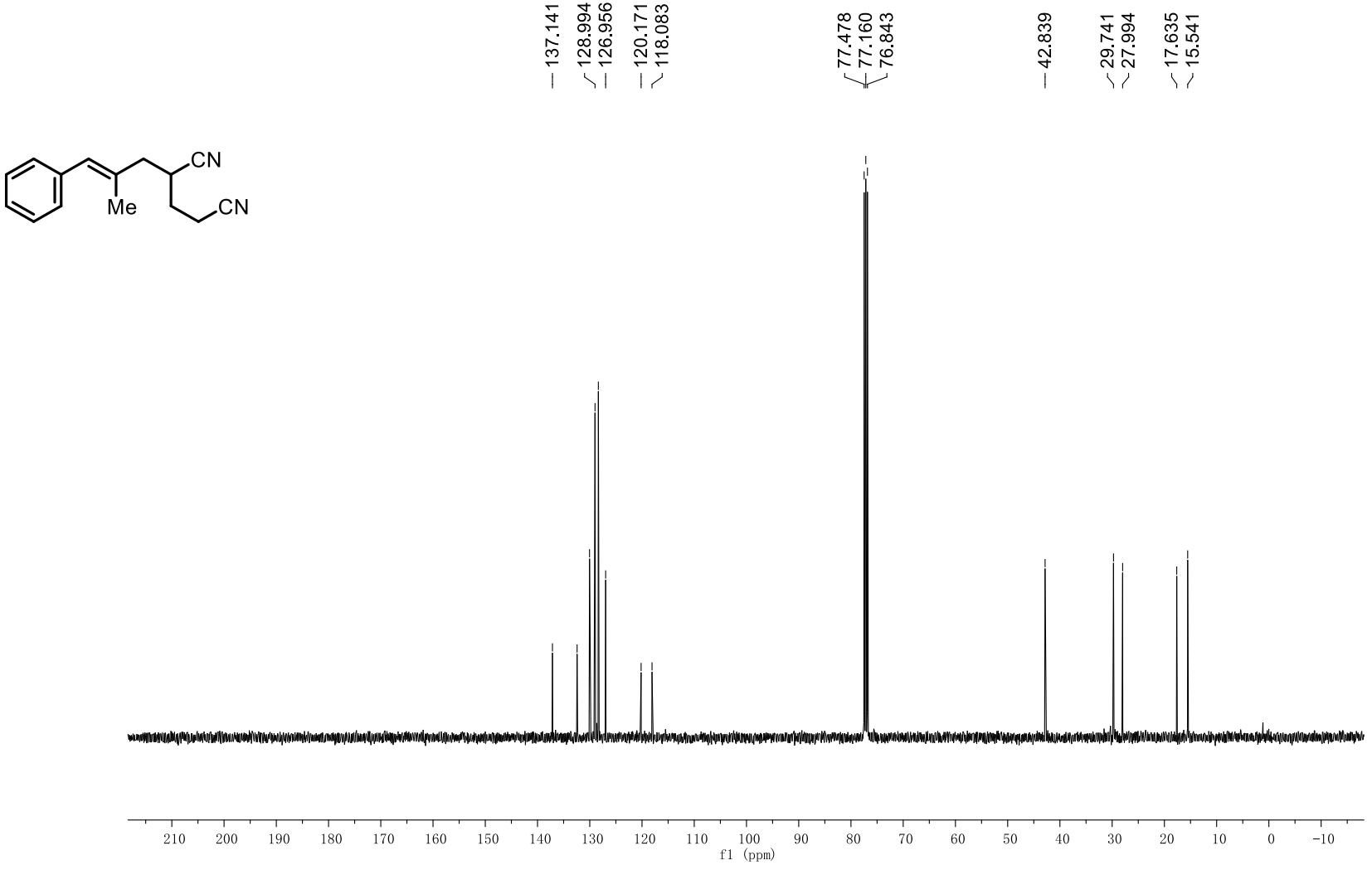
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-2,4-Dimethyl-5-phenylpent-4-enal (42)



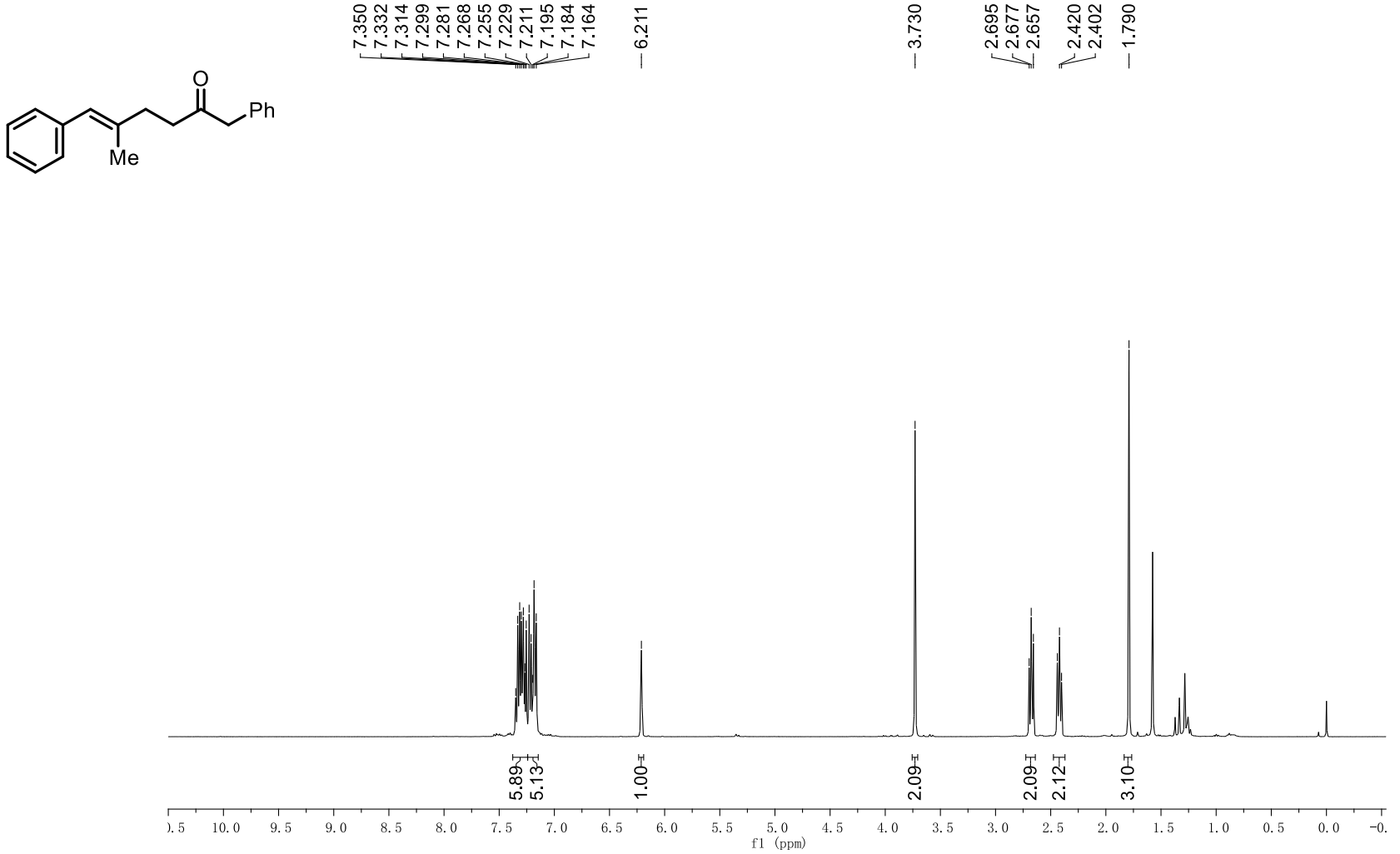
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-2-(2-Methyl-3-phenylallyl)pentanedinitrile (43)



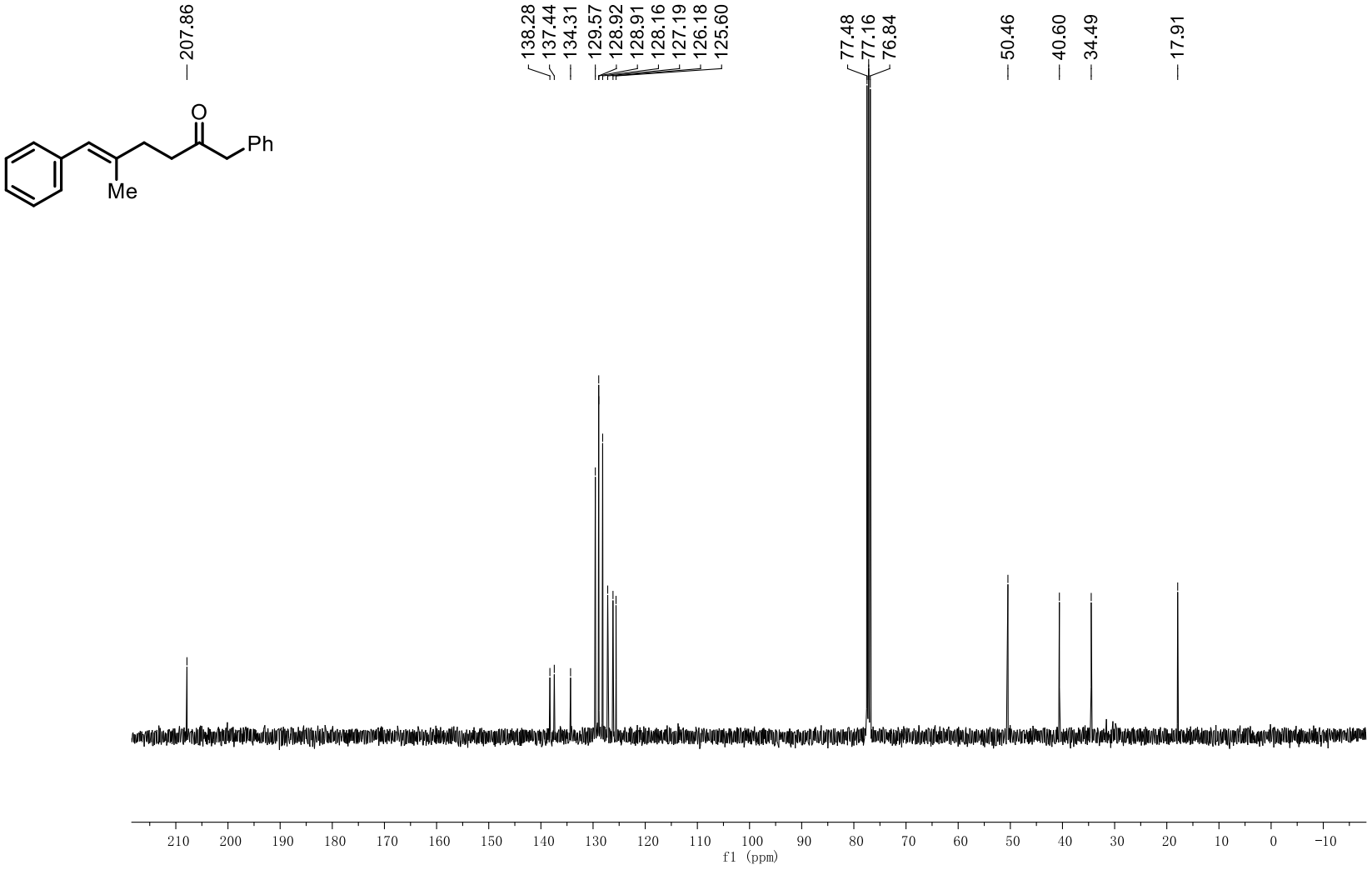
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-2-(2-Methyl-3-phenylallyl)pentanedinitrile (43)



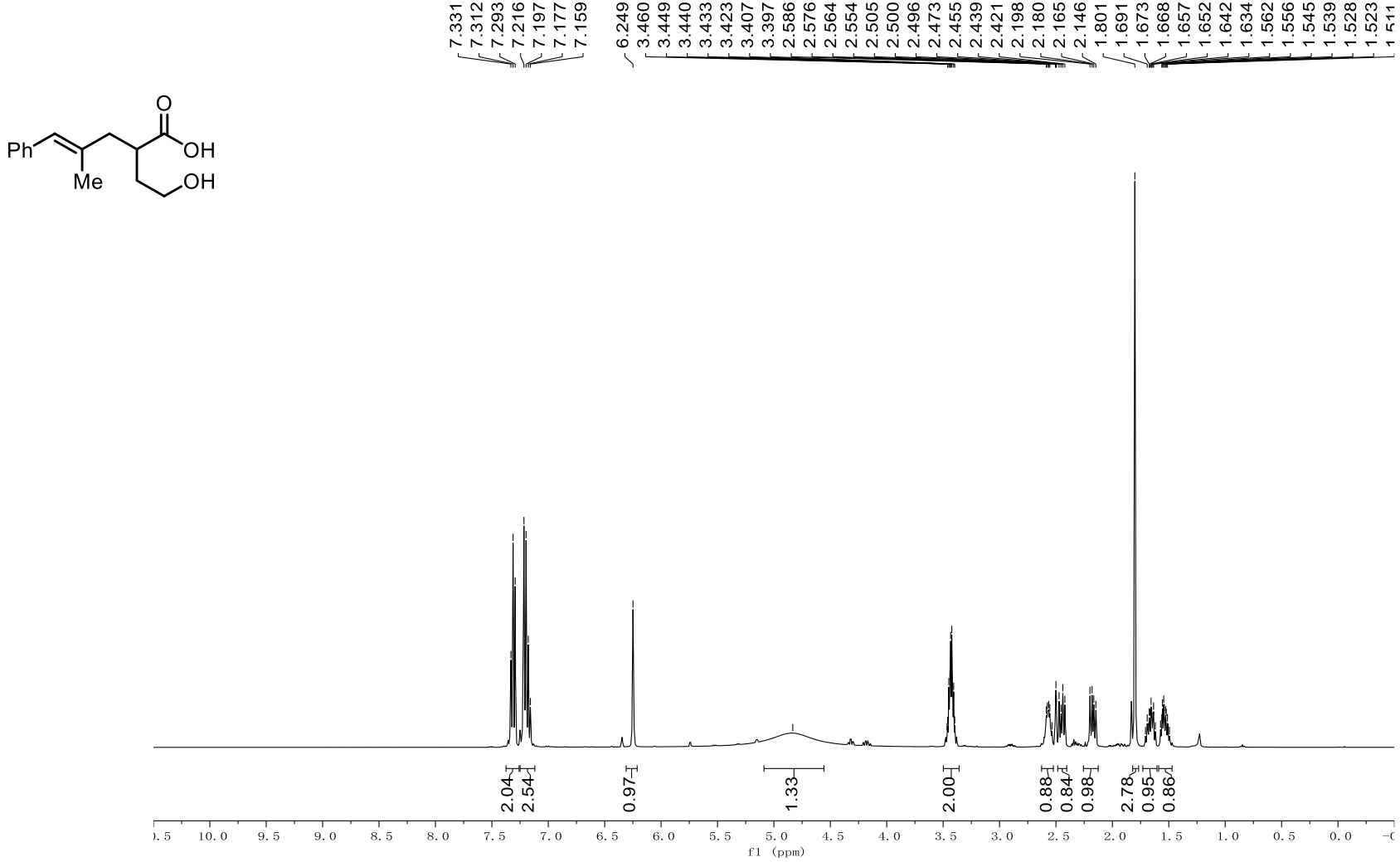
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-5-Methyl-1,6-diphenylhex-5-en-2-one (44)



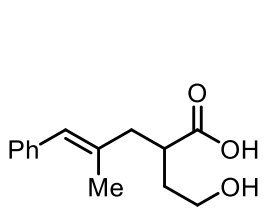
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-5-Methyl-1,6-diphenylhex-5-en-2-one (44)

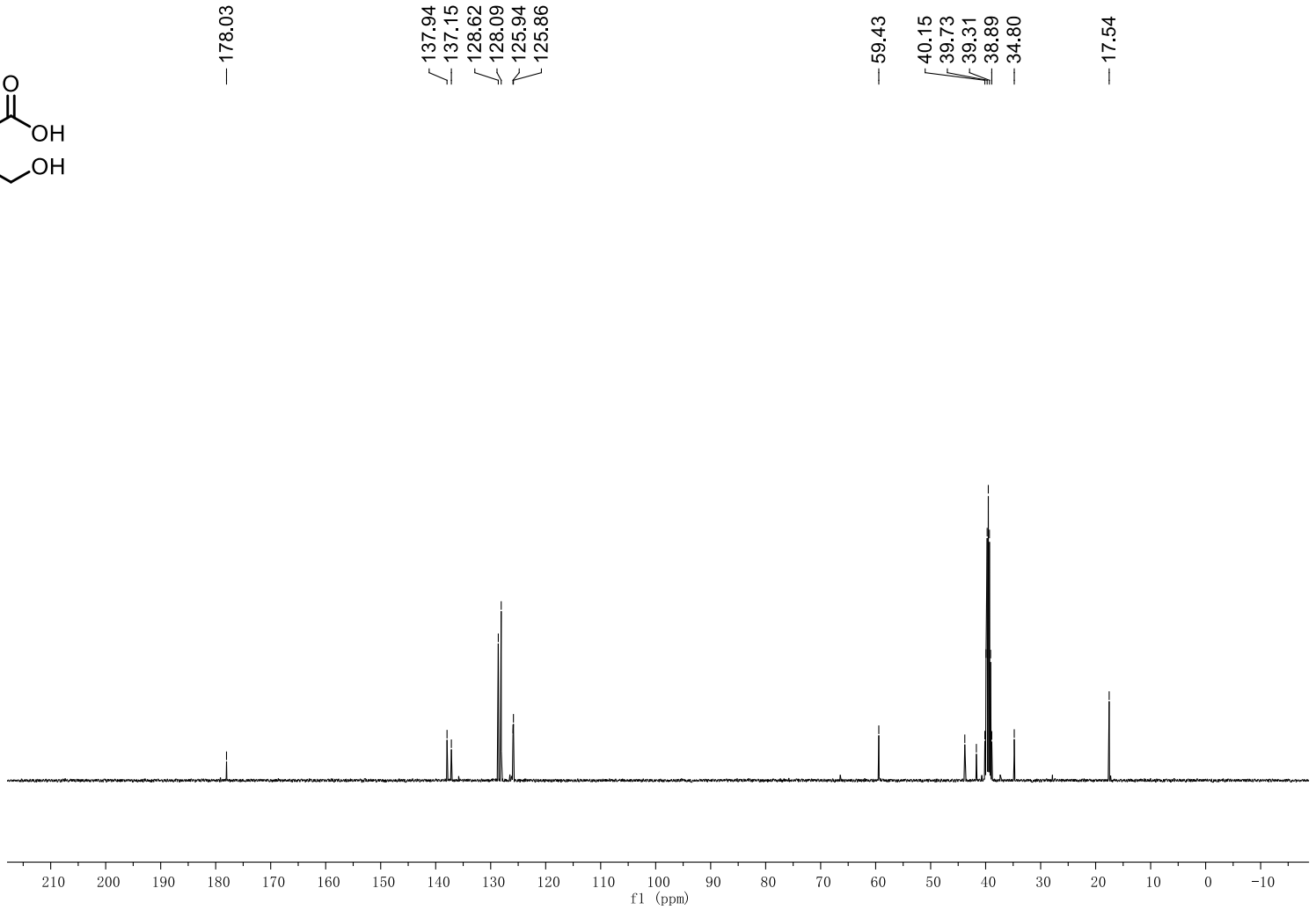


^{1}H NMR (400 MHz, d_6-DMSO) spectrum of (*E*)-2-(2-Hydroxyethyl)-4-methyl-5-phenylpent-4-enoic acid (45)

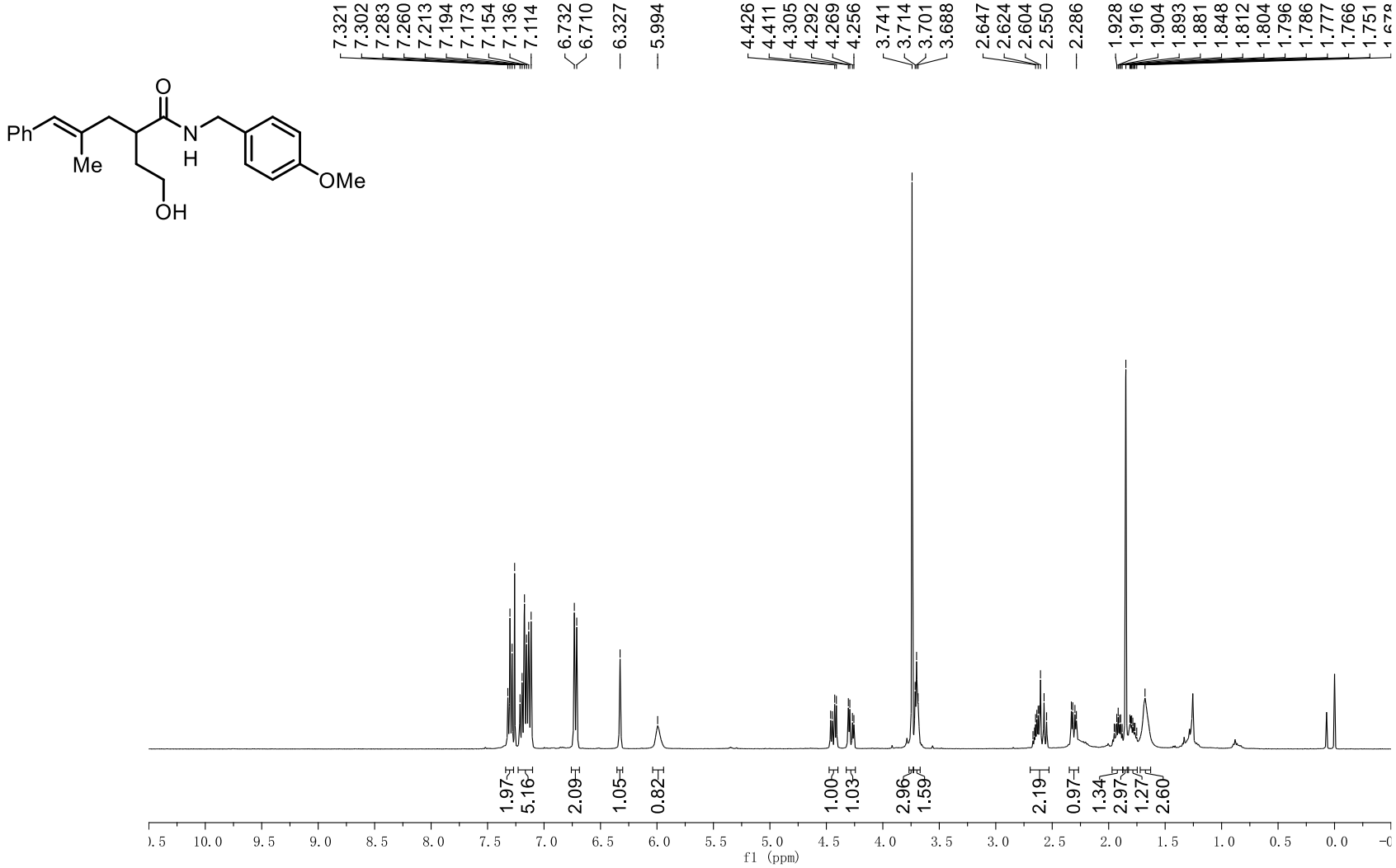


^{13}C NMR (100 MHz, d_6-DMSO) spectrum of (*E*)-2-(2-Hydroxyethyl)-4-methyl-5-phenylpent-4-enoic acid (45)

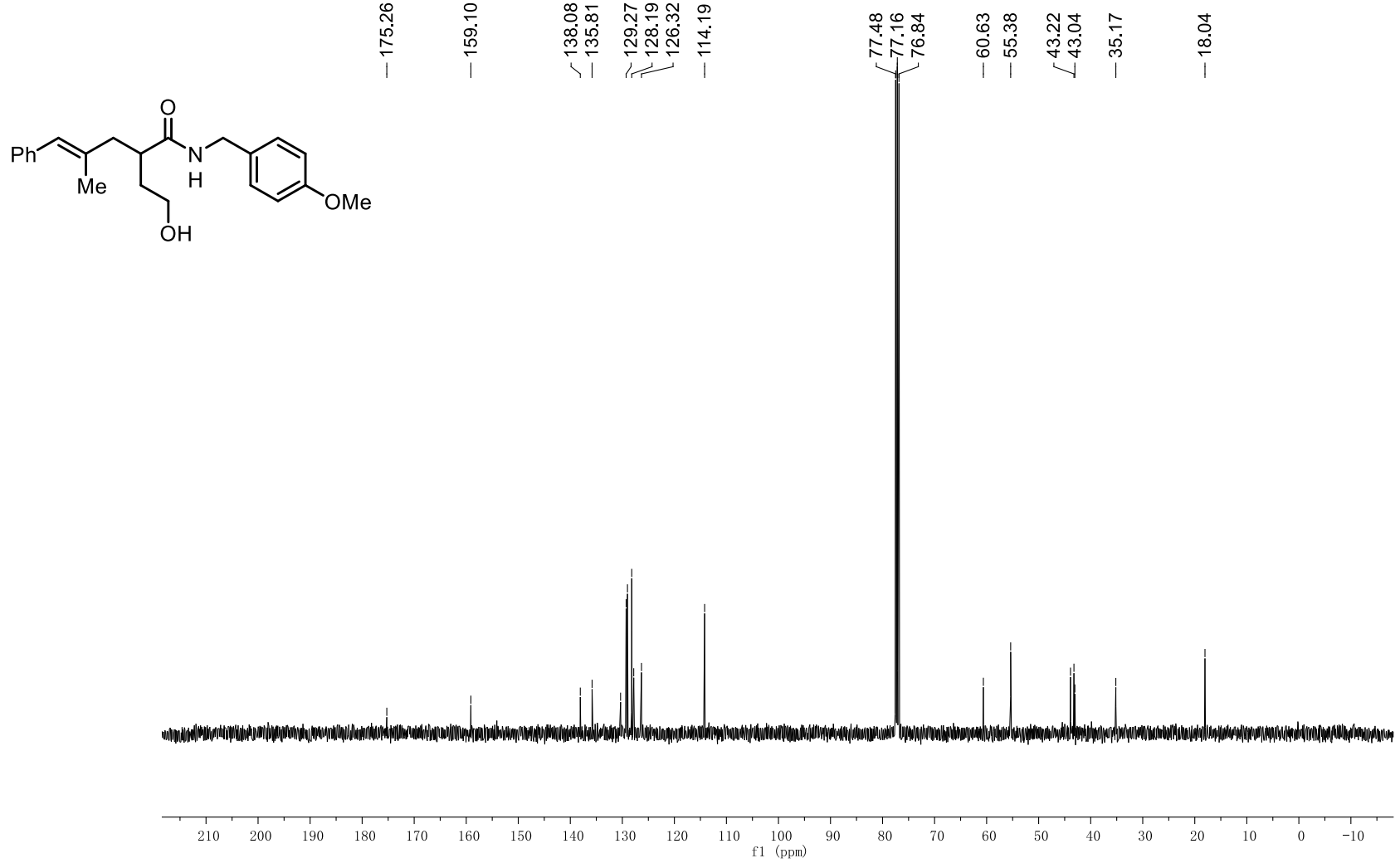




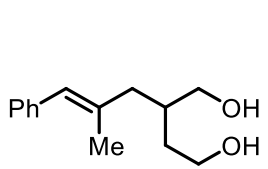
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-2-(2-Hydroxyethyl)-N-(4-methoxybenzyl)-4-methyl-5-phenylpent-4-enamide (46)

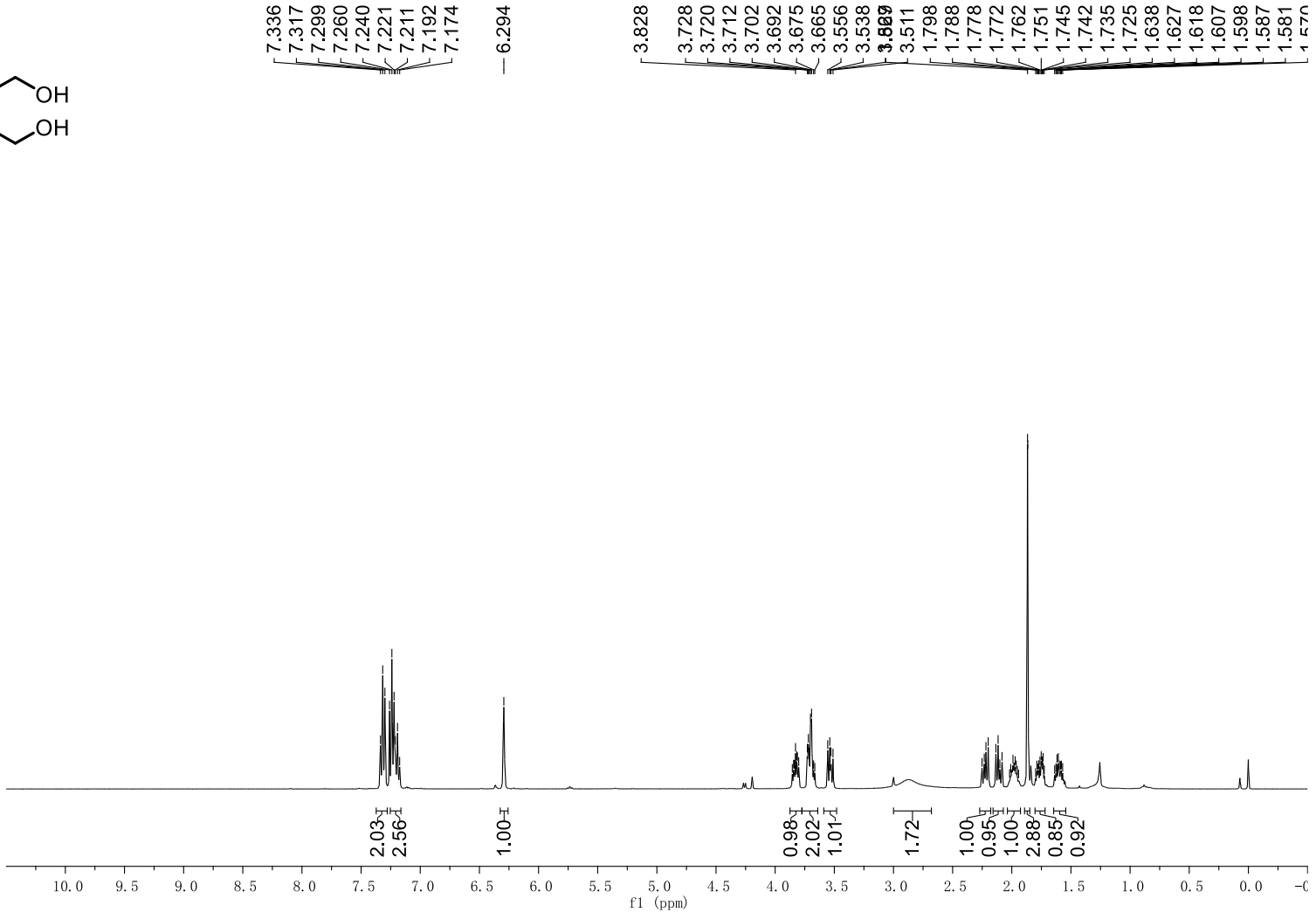


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-2-(2-Hydroxyethyl)-N-(4-methoxybenzyl)-4-methyl-5-phenylpent-4-enamide (46)

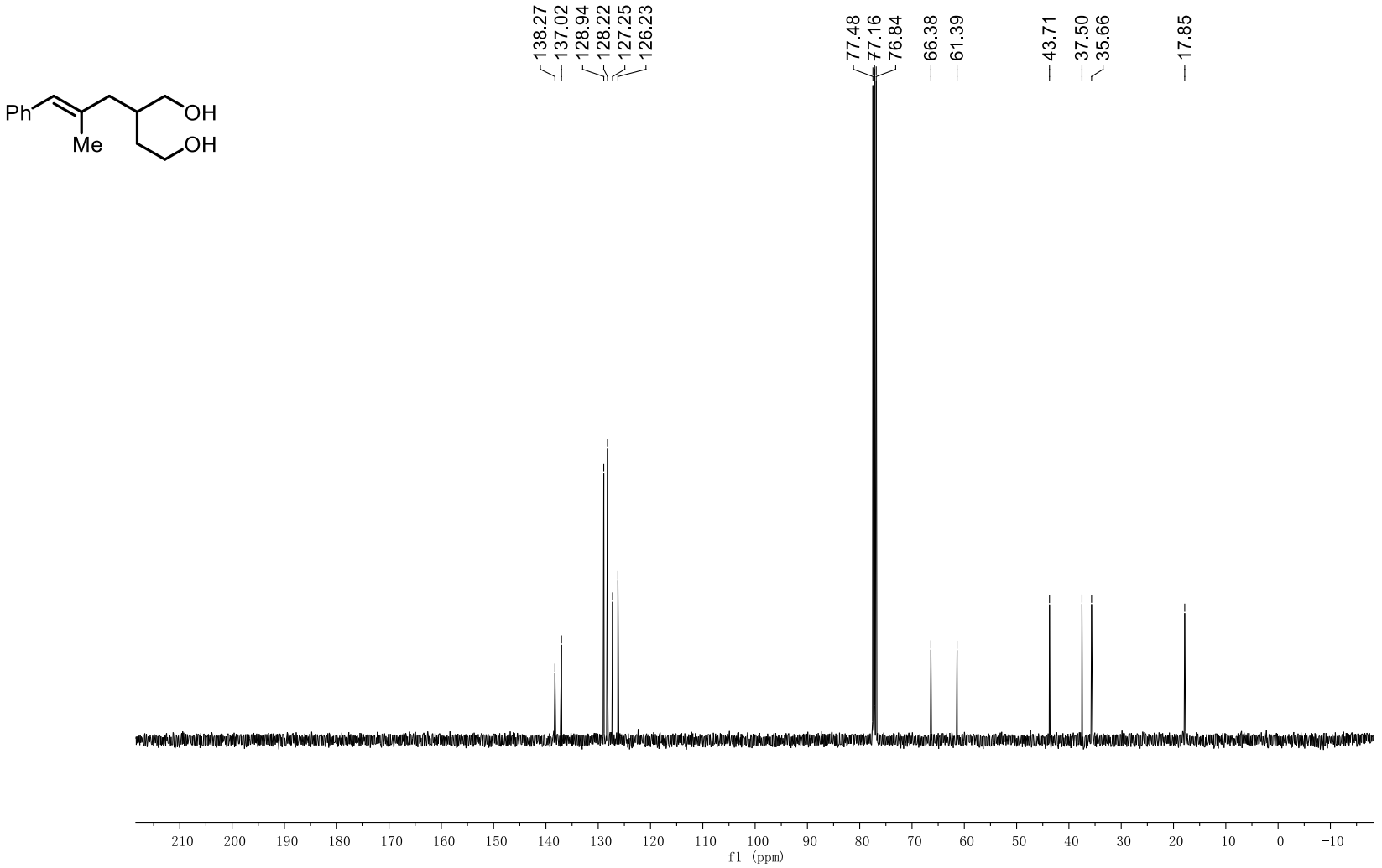


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-2-(2-Methyl-3-phenylallyl)butane-1,4-diol (47)

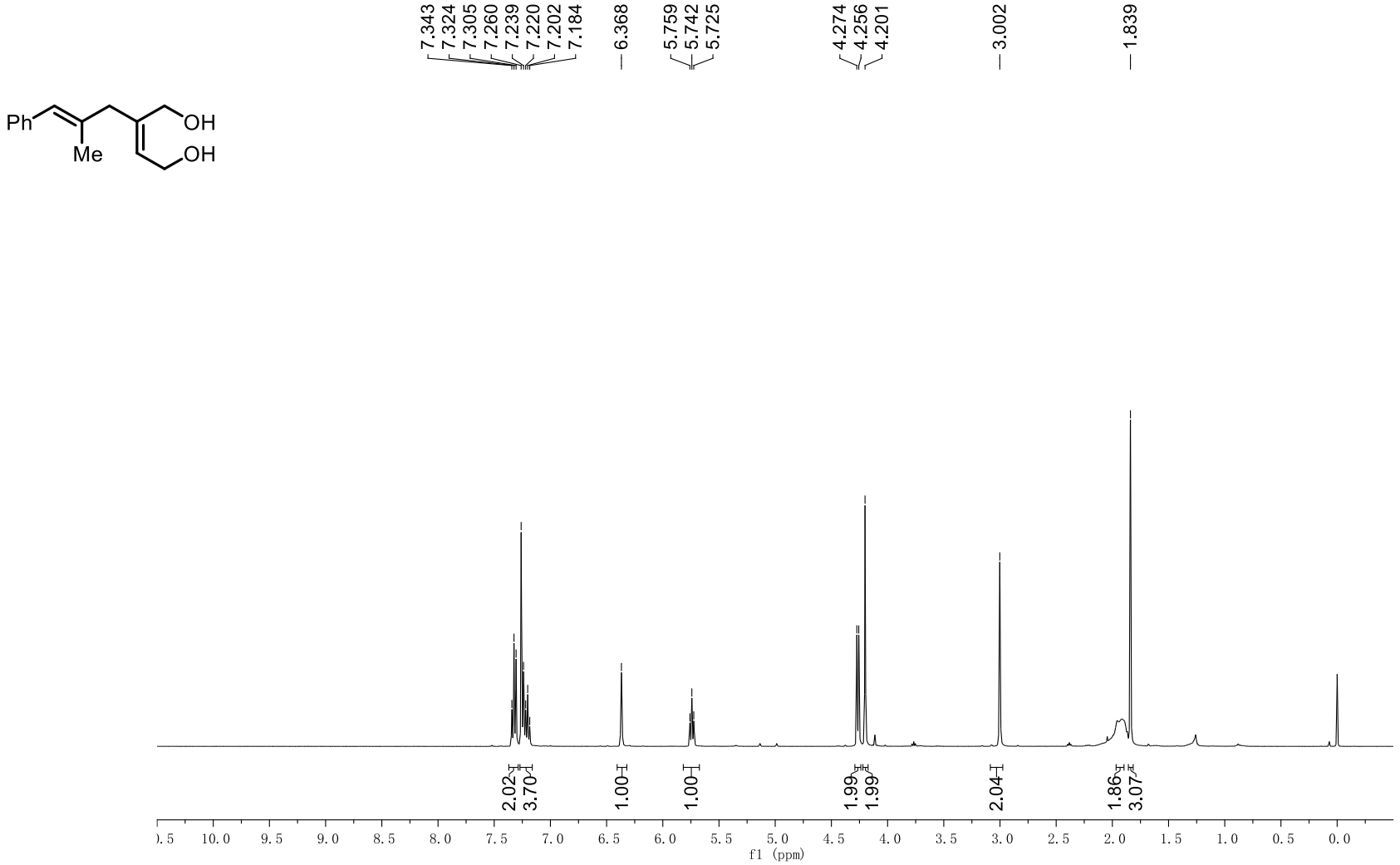




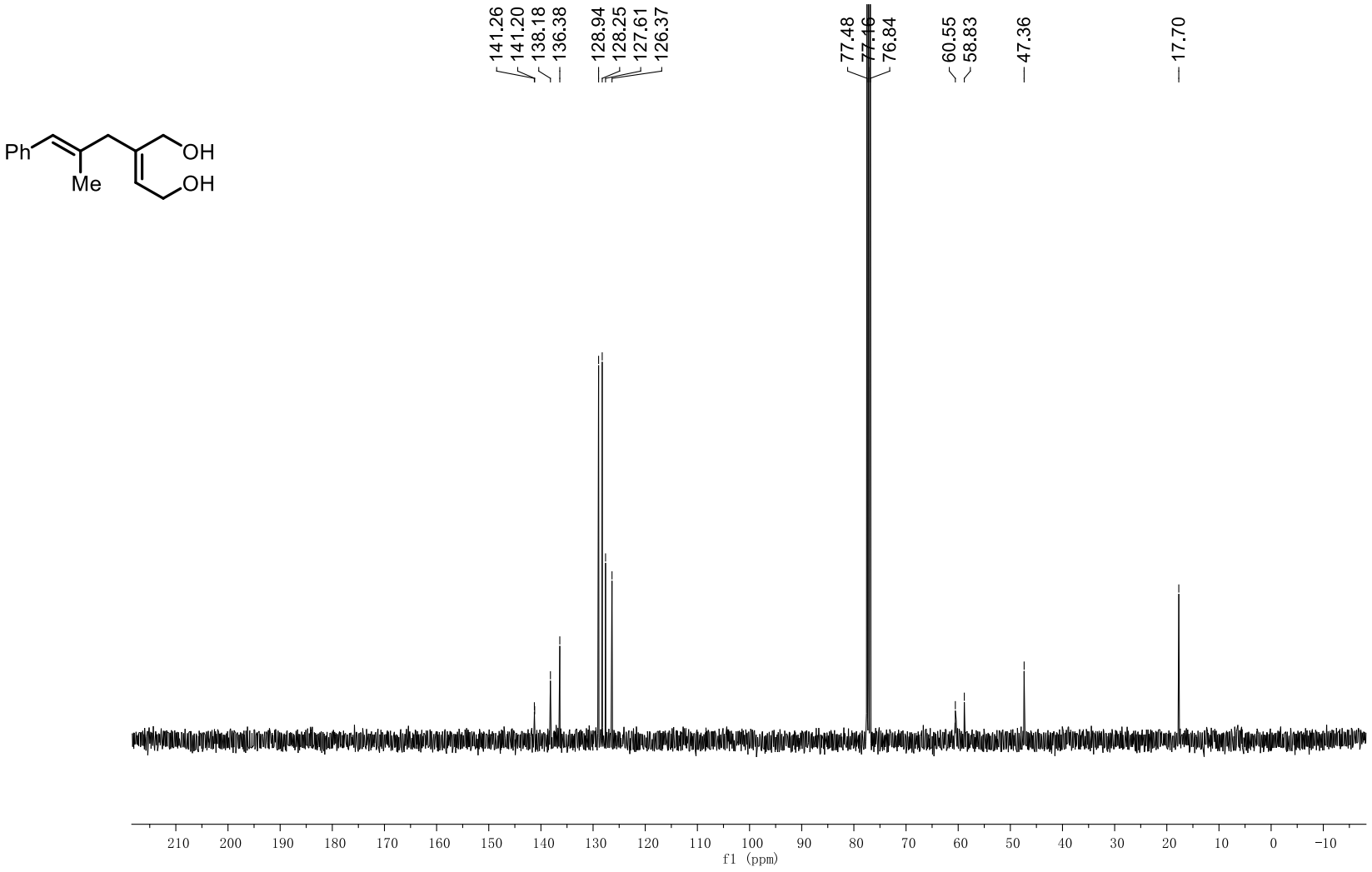
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-2-(2-Methyl-3-phenylallyl)butane-1,4-diol (47)



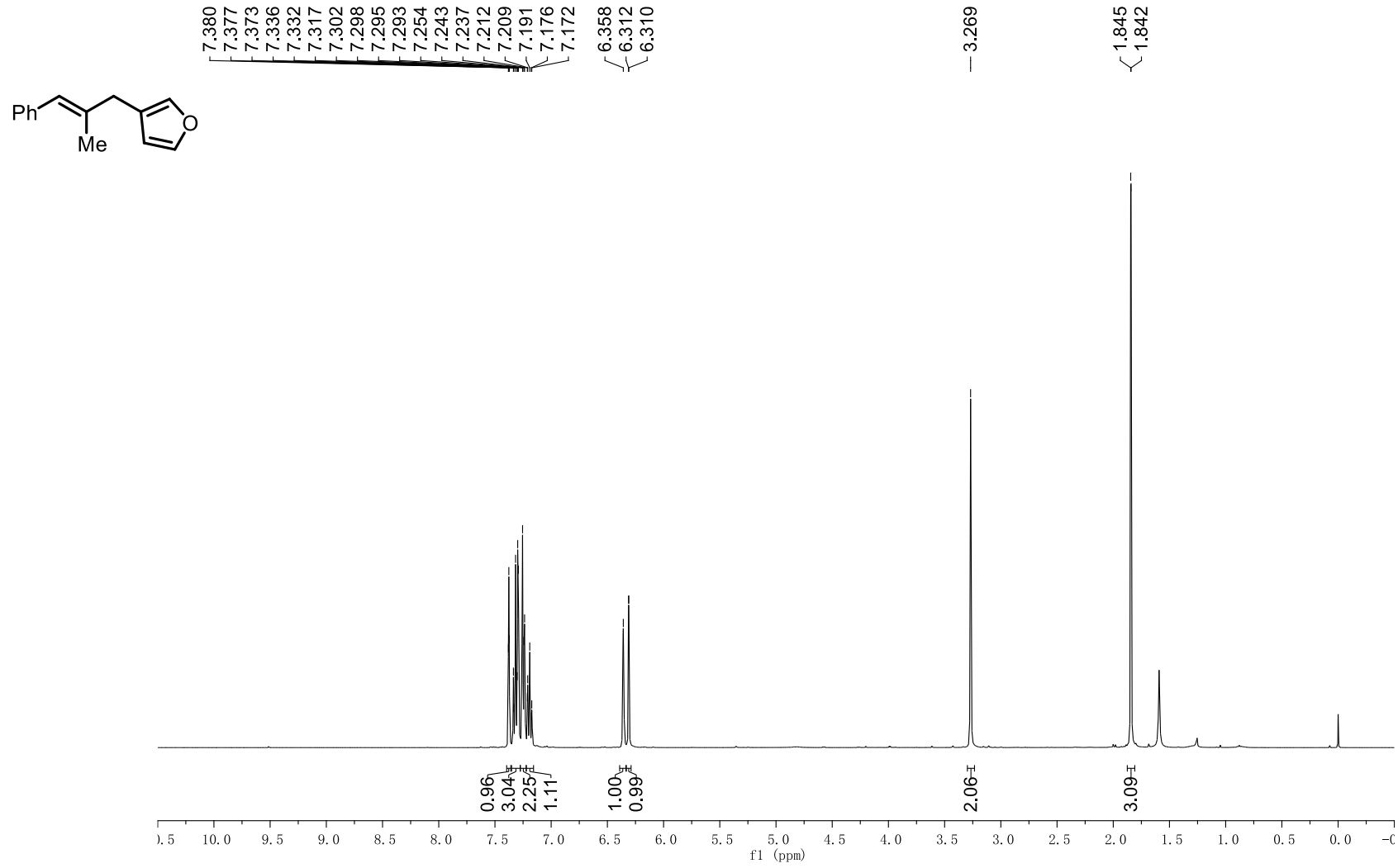
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-2-((*E*)-2-Methyl-3-phenylallyl)but-2-ene-1,4-diol (48)



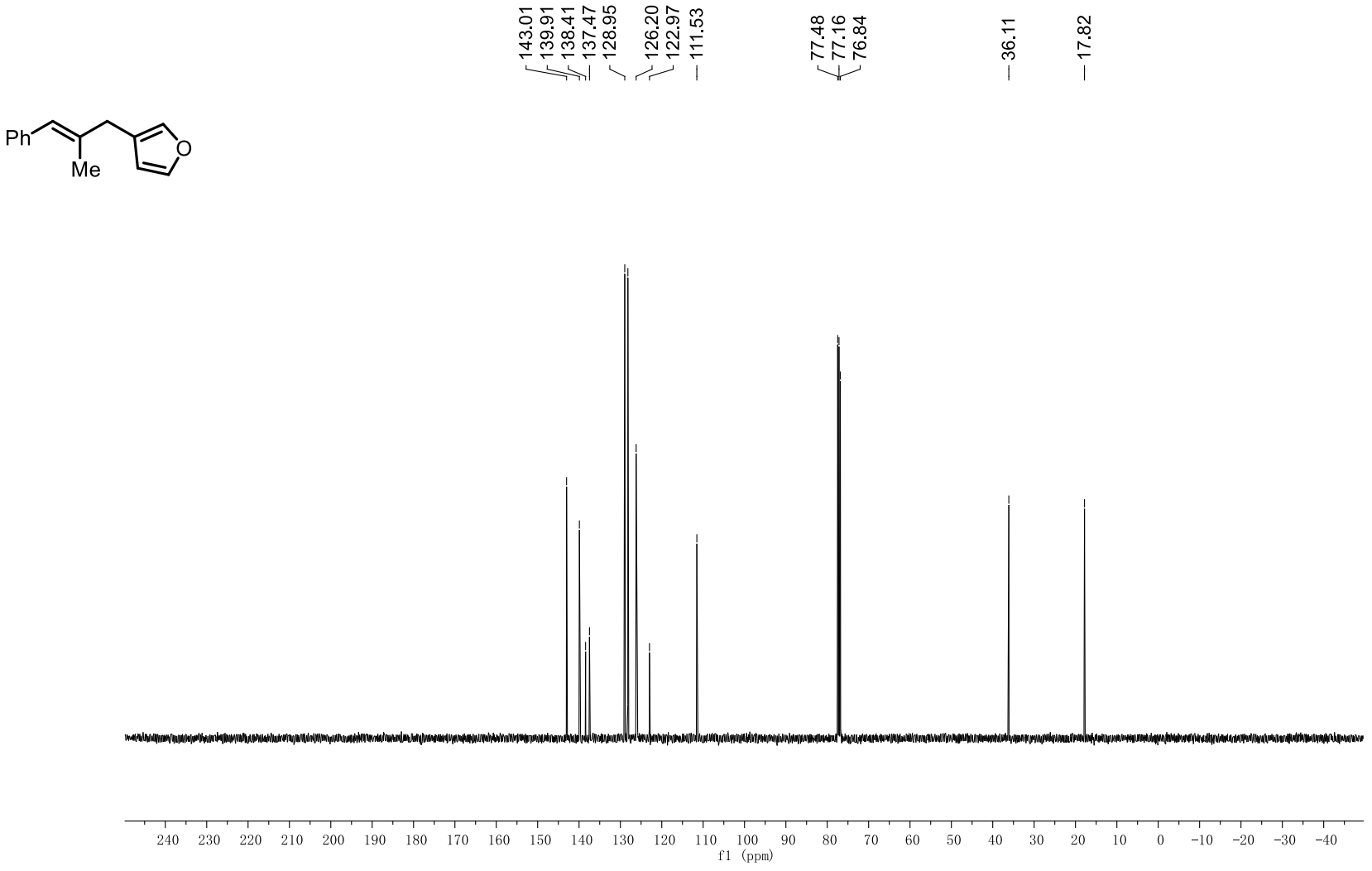
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-2-((*E*)-2-Methyl-3-phenylallyl)but-2-ene-1,4-diol (48)



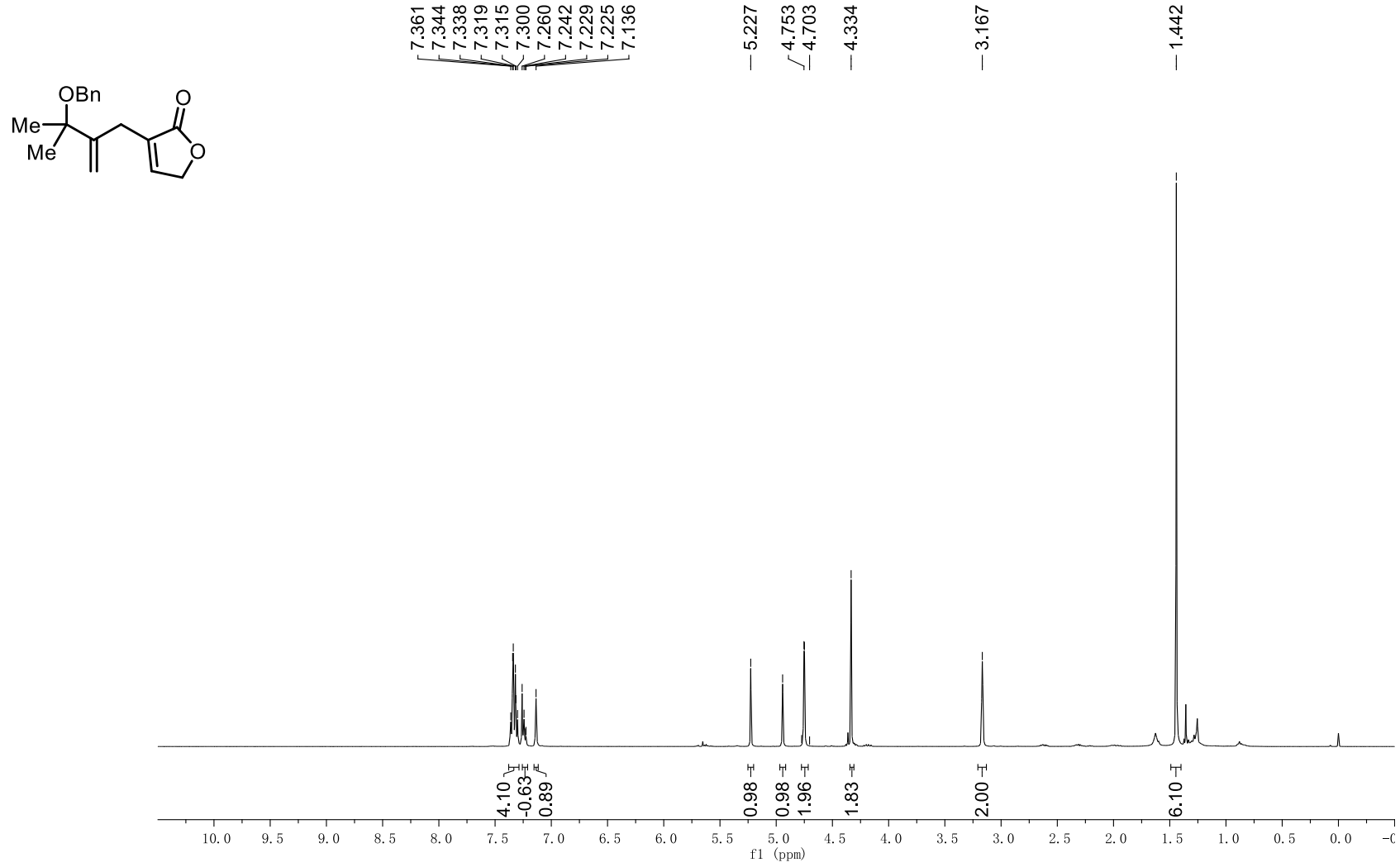
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)furan (49)



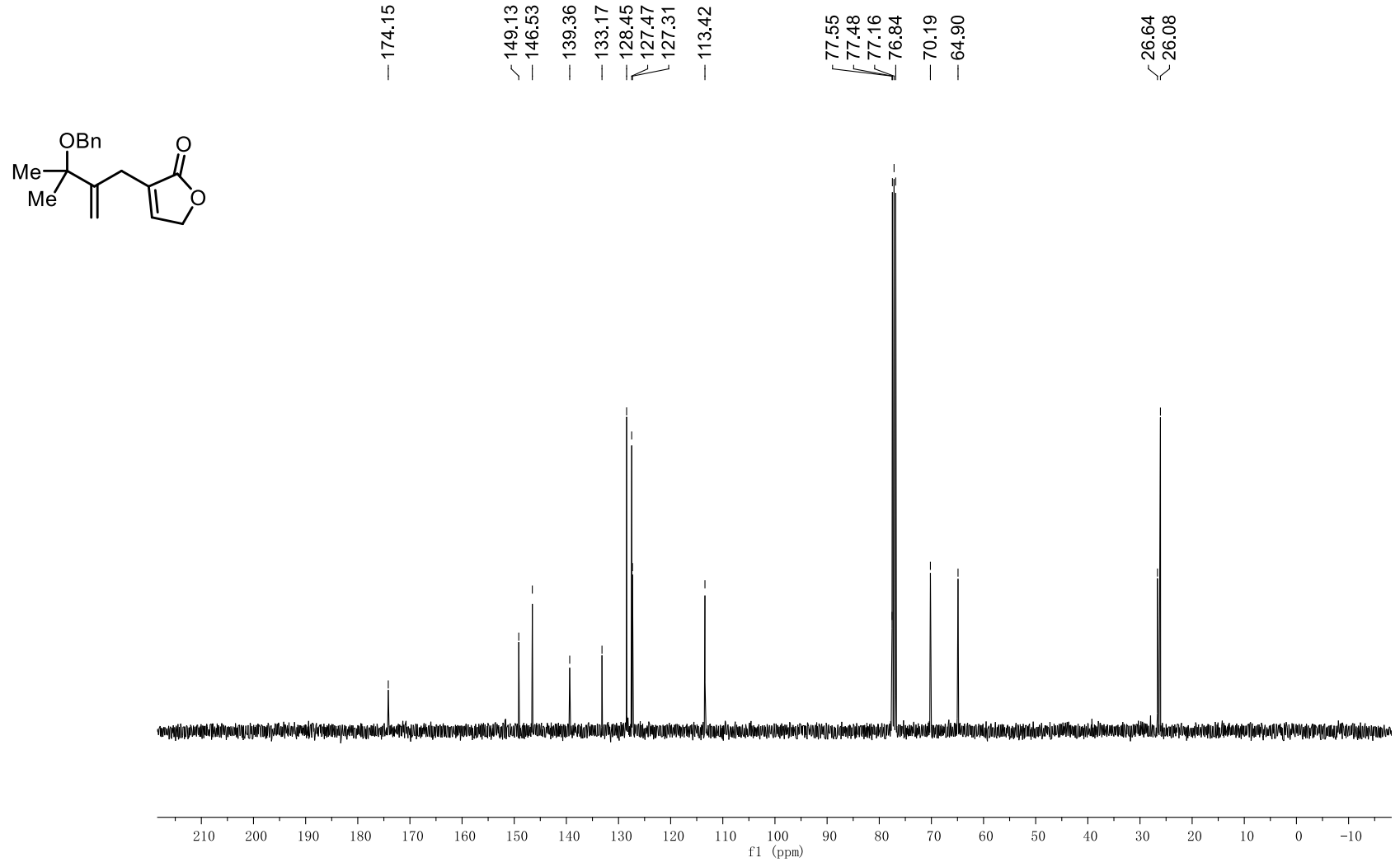
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-3-(2-Methyl-3-phenylallyl)furan (49)



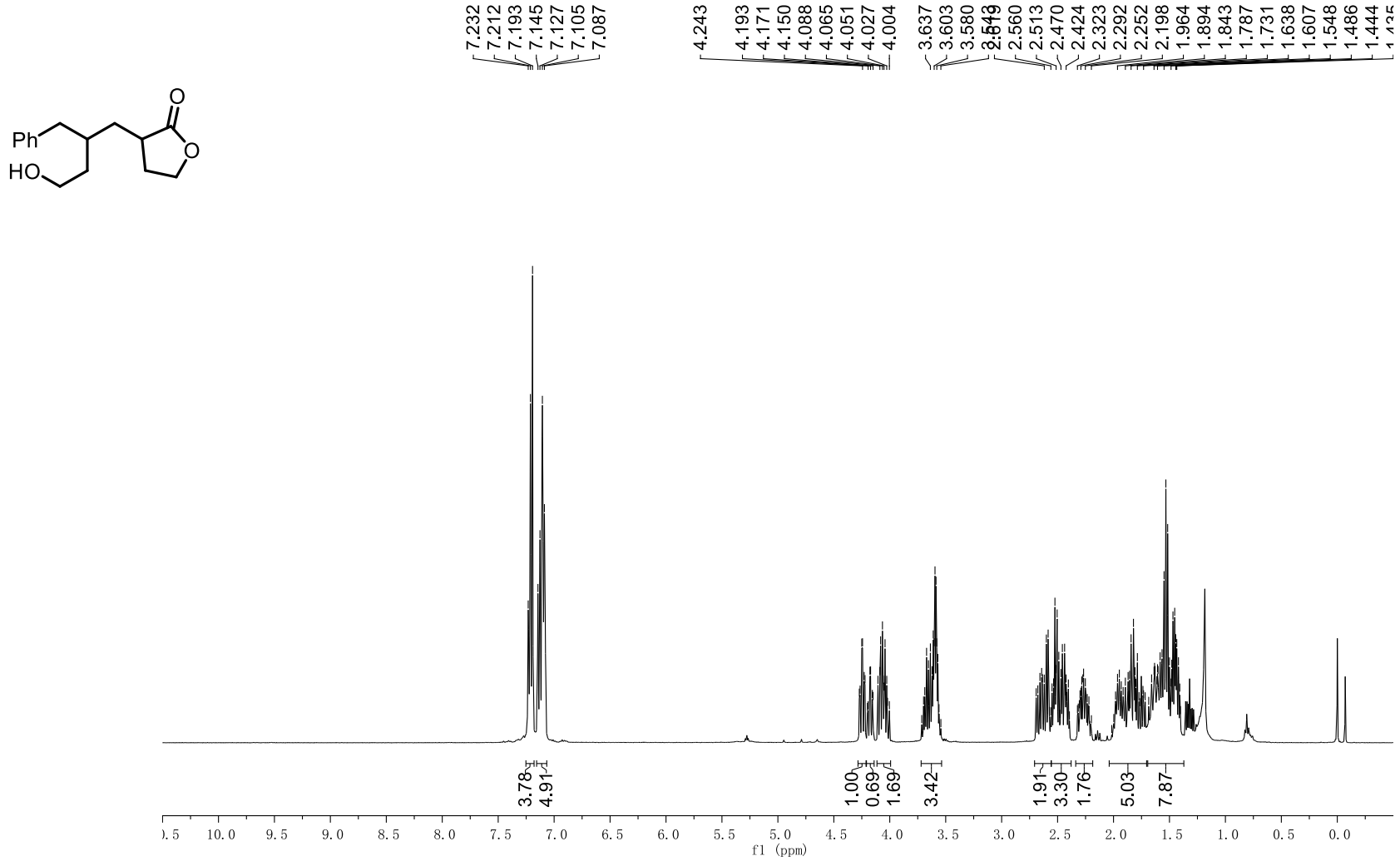
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(3-(Benzyloxy)-3-methyl-2-methylenebutyl)furan-2(5*H*)-one (51)



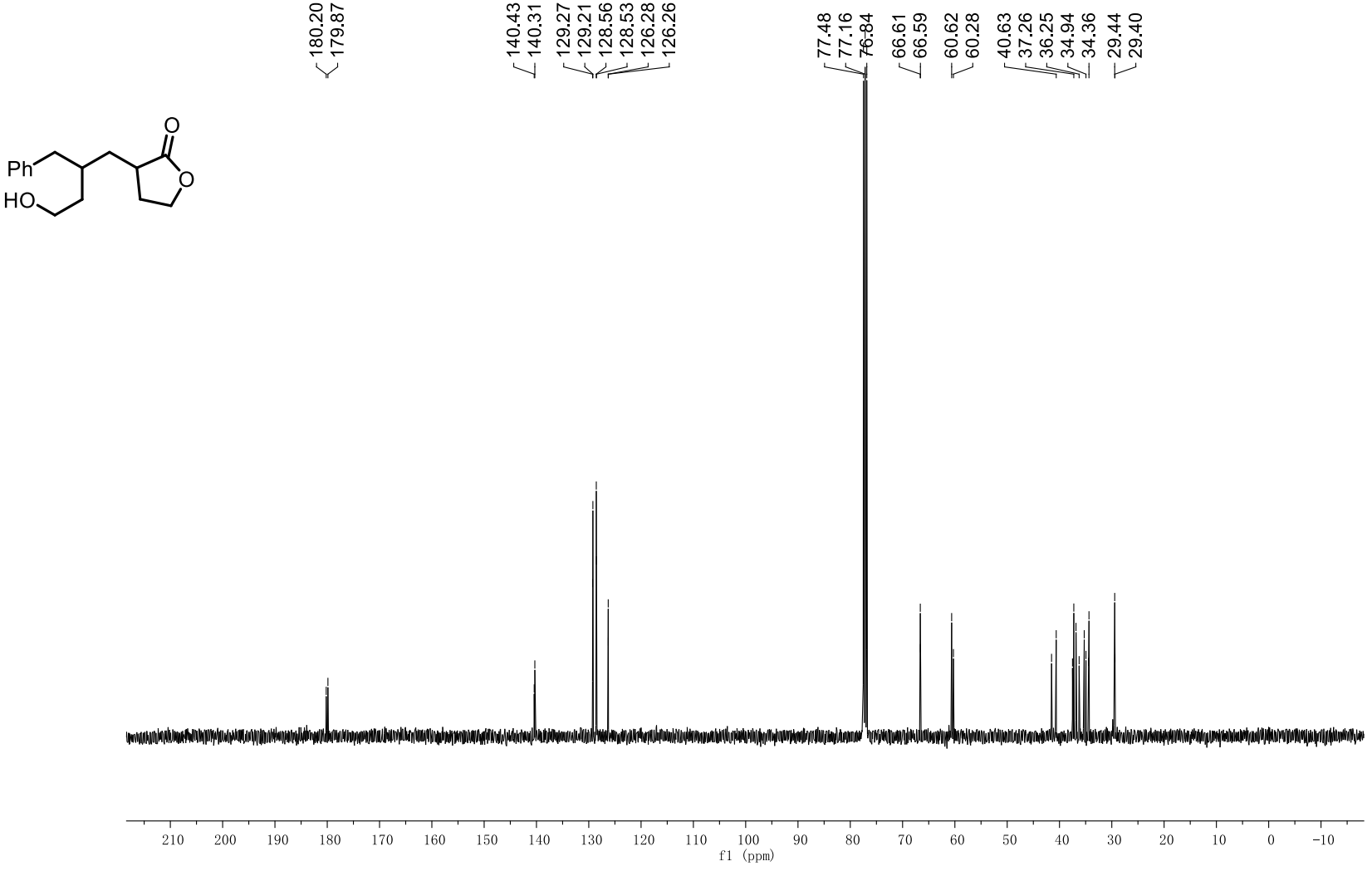
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(3-(Benzyloxy)-3-methyl-2-methylenebutyl)furan-2(5*H*)-one (51)



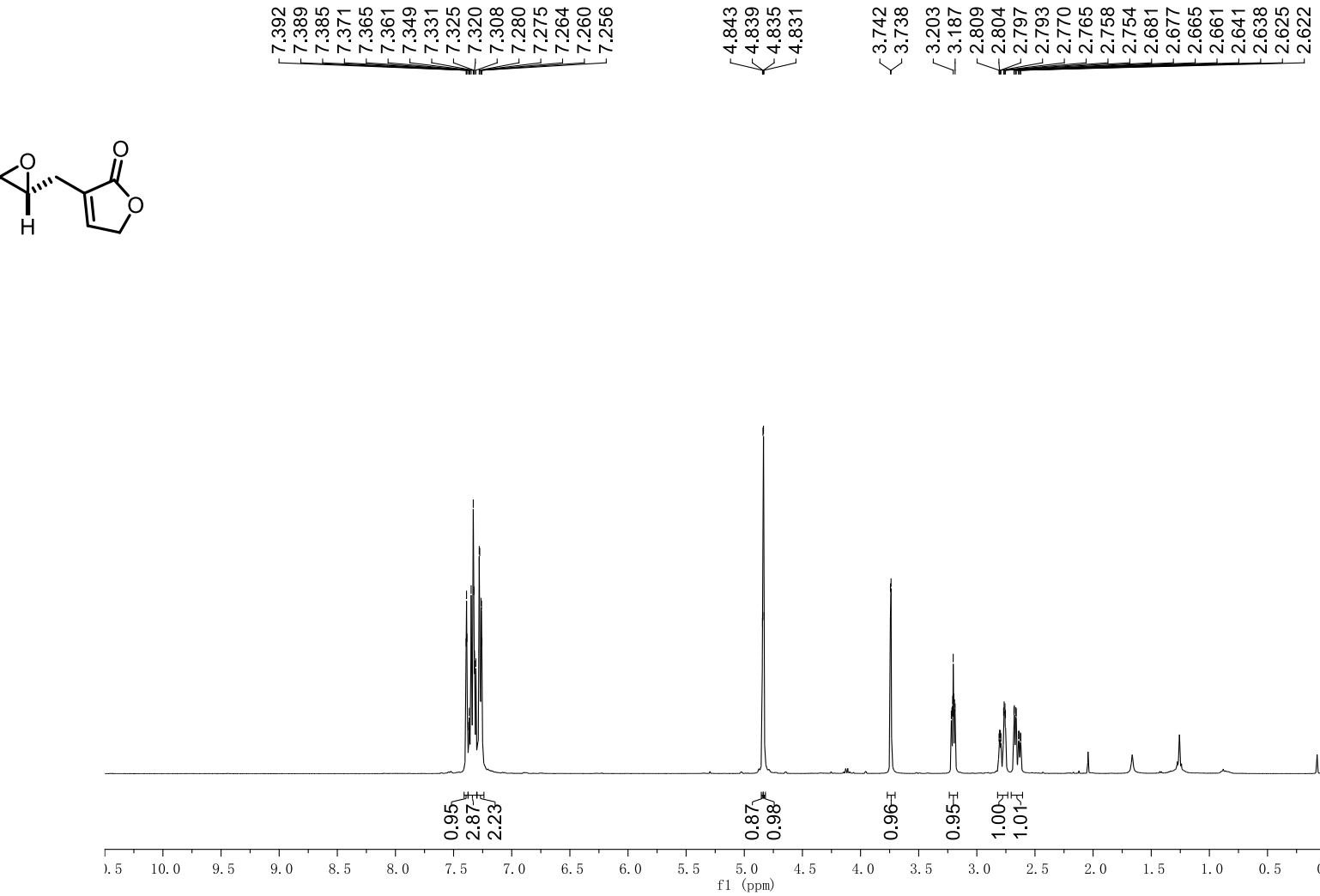
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(2-Benzyl-4-hydroxybutyl)dihydrofuran-2(3*H*)-one (52)



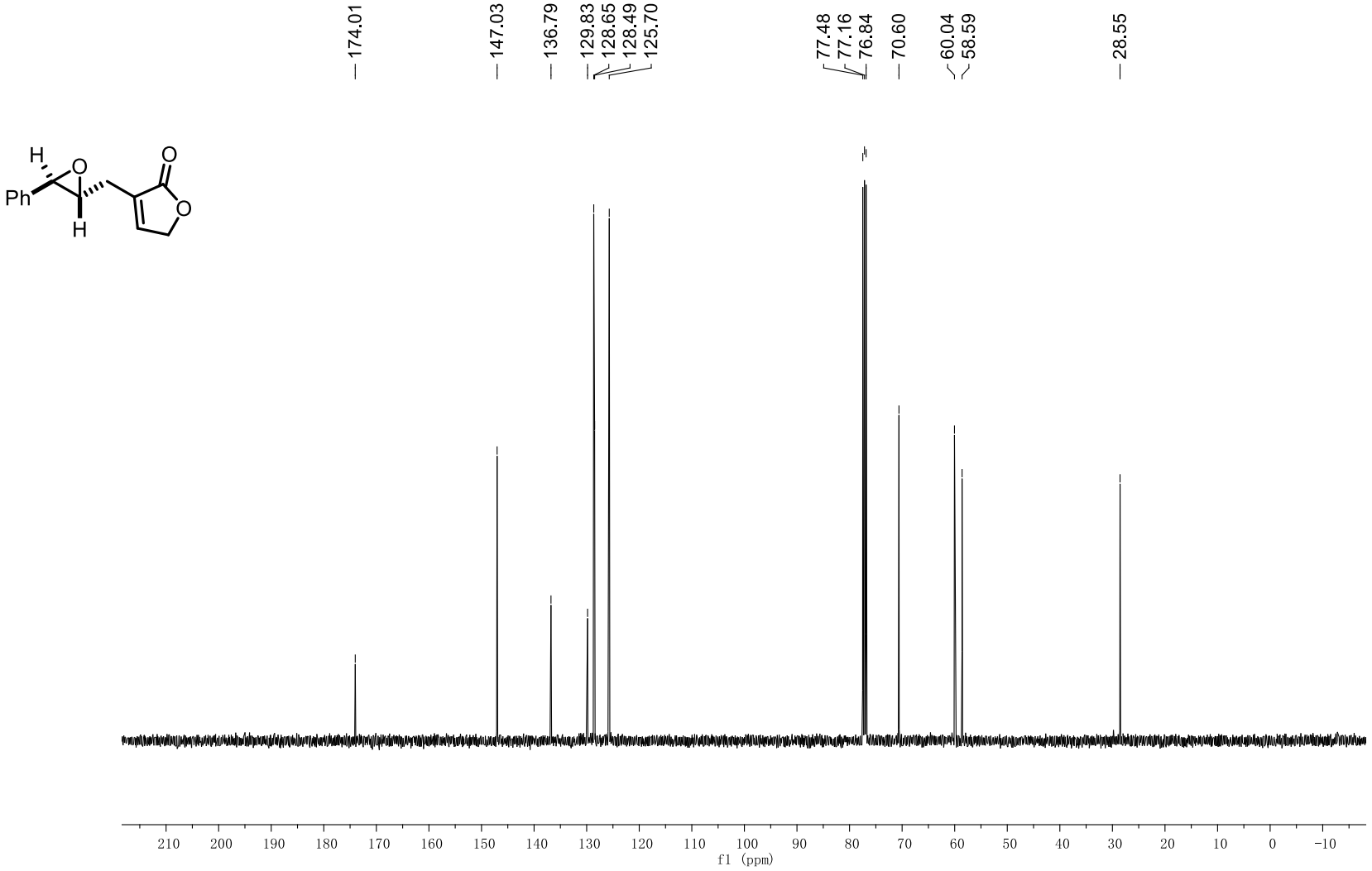
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(2-Benzyl-4-hydroxybutyl)dihydrofuran-2(3*H*)-one (52)



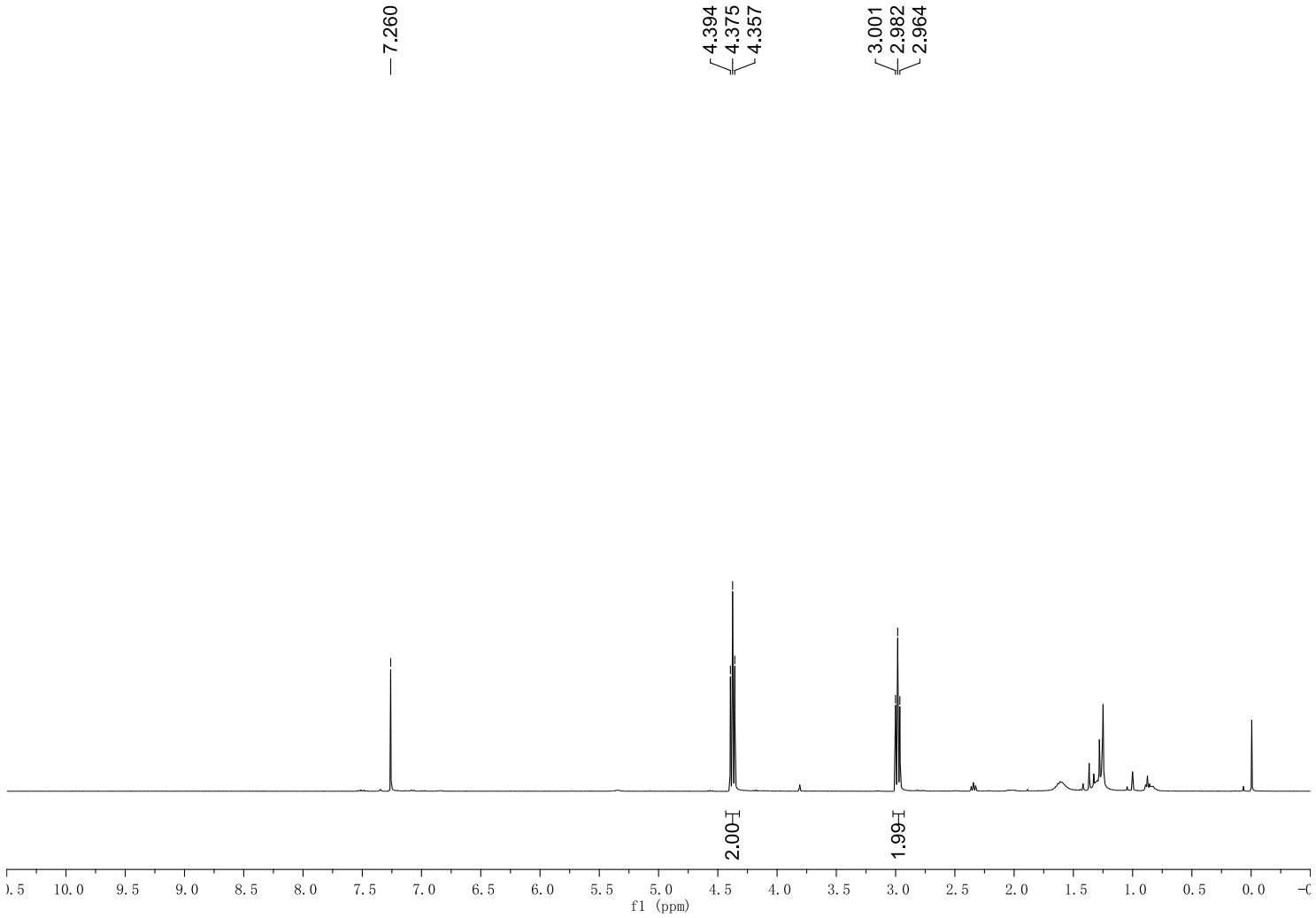
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((3-Phenyloxiran-2-yl)methyl)furan-2(5*H*)-one (53)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-((3-Phenyloxiran-2-yl)methyl)furan-2(5*H*)-one (53)



^{1}H NMR (400 MHz, CDCl3) spectrum of *d*$_2$-2.



^{1}H NMR (400 MHz, d_6-DMSO) spectrum of d_2-4.