Supporting Information

Copper-catalyzed 1,2-dioxygenation of 1,3-dienes with tert-butyl benzoperoxoate at room temperature

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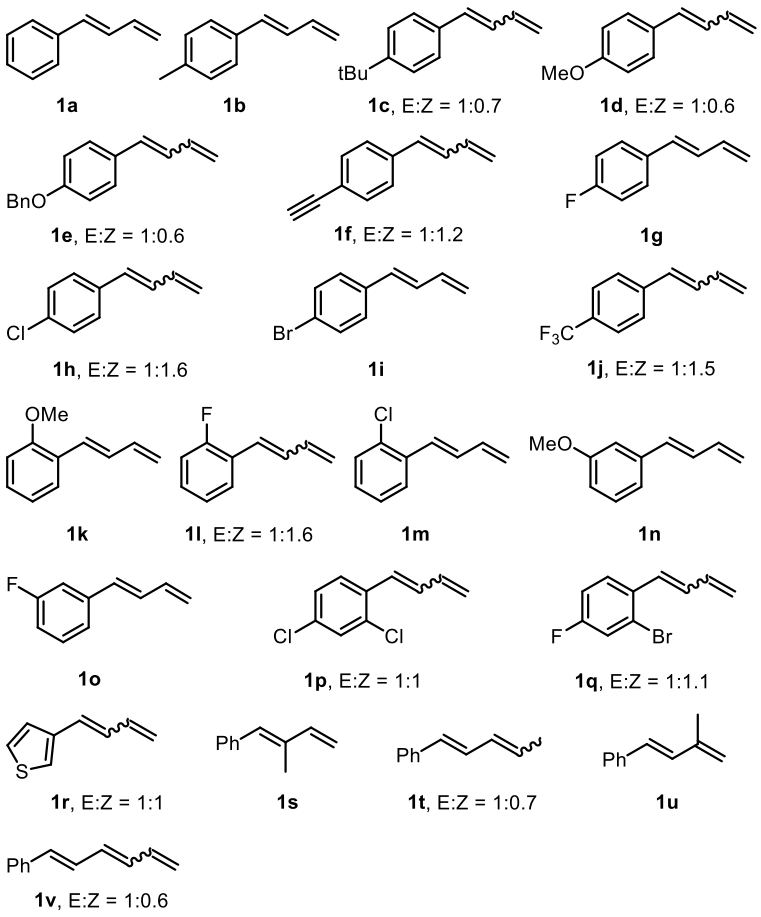
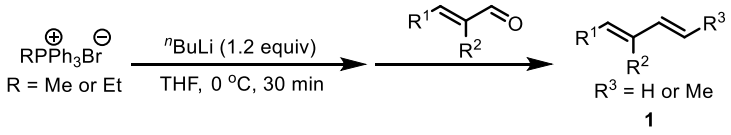
1. General information

Reactions via general procedure were carried out under an air atmosphere unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker-AV (400, 100, 162 MHz, respectively) instrument using $CDCl_3$ or Dimethyl Sulfoxide-d_6 as solvent, Chemical shifts are given in ppm and coupling constants in 400Hz. Chemical shift values are reported in δ (ppm) relative to $CDCl_3$ (^{1}H NMR, δ = 7.26; ^{13}C NMR, δ = 77.00), respectively. In order to indicate the signal multiplicity, the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected.

2. General procedure for the synthesis of 1,3-dienes (1)[1-4]

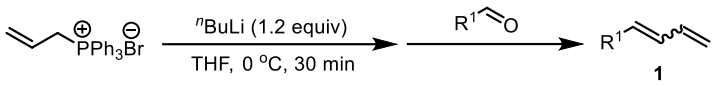


Method A:



^{n}BuLi (6 mmol, 2.5 M in hexane) was added dropwise to a stirred suspension of $MePPh_3Br$ (6 mmol, 1.2 equiv.) in anhydrous THF (30 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 30 min. Then cinnamaldehydes (5 mmol, 1.0 equiv.) was added, and the reaction was kept stirring for 4-8 h with TLC detection. After the complete consumption of cinnamaldehyde, the mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and then concentrated. The product was purified by column chromatography on silica gel to afford desired 1,3-dienes. **1a**, **1b**, **1g**, **1i**, **1k**, **1m-1o**, **1s-1u** were prepared according to method A.

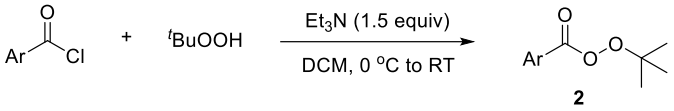
Method B:



nBuLi (6 mmol, 2.5 M in hexane) was added dropwise to a stirred suspension of allylPPh_3Br (6 mmol, 1.2 equiv.) in anhydrous THF (30 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 30 min. Then the aldehyde (5 mmol, 1.0 equiv.) was added, and the reaction was kept stirring for 4-8 h with TLC detection. After the complete consumption of cinnamaldehyde, the mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and then concentrated. The product was purified by column chromatography on silica gel to afford desired 1,3-dienes. All spectroscopic data are in agreement with the literature. **1c-1f**, **1h**, **1j**, **1l**, **1p-1r**, **1v** were prepared according to method B.

3. General procedure for the synthesis of peroxides (2)[2]

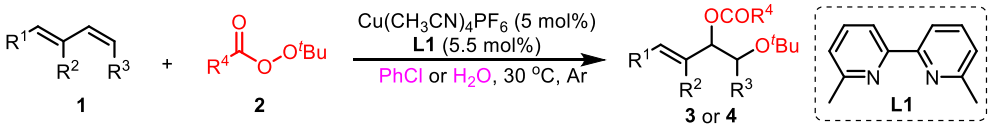
Method C:



2

To a solution of TBHP (5 mmol, 5.5 M in decane) in DCM (20 mL) at 0 °C was added acyl chloride (5 mmol) dropwise. Then Et_3N (7.5 mmol) was slowly added. After being stirred for 8 h at room temperature, the solution was concentrated on a rotary evaporator under vacuum at 25 °C and then purified by flash column chromatography on silica gel to afford the peroxides **2**.

4. General procedures for the synthesis of 3 or 4.



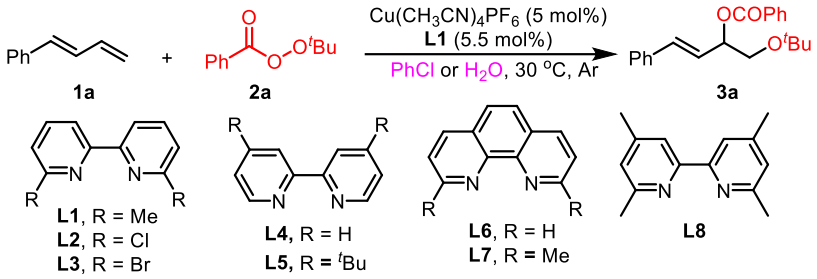
Standard conditions: A 10 mL reaction vessel was charged with 1,3-butadienes **1** (0.2 mmol), peroxides **2** (2.0 equiv, 0.24 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L1** (5.5 mol %,) and PhCl or H_2O (2 mL) at 30 °C for 24 h under an argon atmosphere. Until complete consumption of the starting material was observed by TLC and/or GC-MS analysis. The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. The reaction yield was quantified by separation, and then column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **3** or **4** (petroleum ether/ethyl acetate, 20 : 1 to 50 : 1).

Gram-scale experiment: A 100 mL reaction vessel was charged with 1-phenylbutadiene **1a** (0.78 g, 6 mmol), *tert*-butyl 4-(*tert*-butyl)benzoperoxoate **2c** (2 equiv, 12 mmol, 3.00 g), $Cu(CH_3CN)_4PF_6$ (5 mol %, 111.6 mg), **L1** (5.5 mol %, 60.7 mg) and PhCl or H_2O (60 mL) at 30 °C for 60 h under an argon atmosphere gave the target product **4c** in 65% (1.48 g) or 50% (1.14 g)yield.

5. Optimization of reaction conditions.

5.1 Optimization of the reaction conditions for the synthesis of 3a

Table S1: [a]

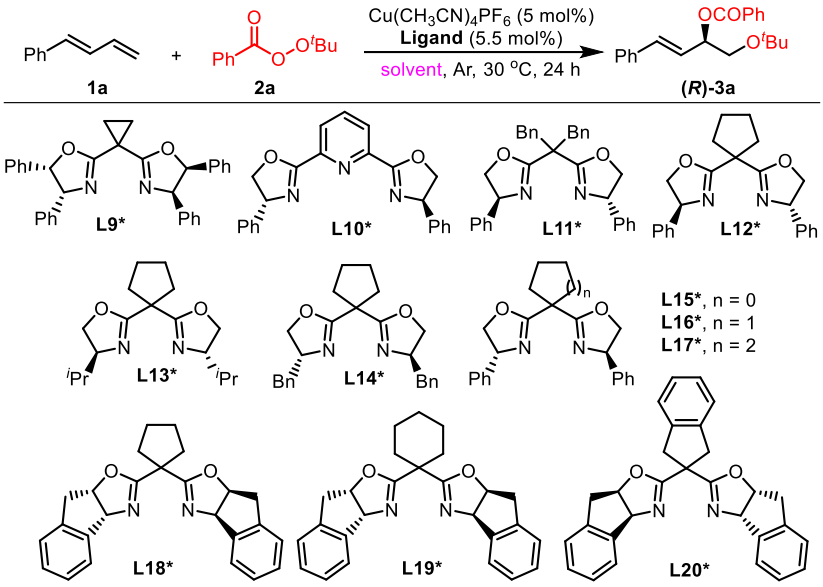


Entry	Cat.[Cu] (5.0	Ligand (5.5	Solvent	Yield (%)[b]
1	**Cu(CH$_3$CN)$_4$PF$_6$**	**L1**	**PhCl**	**65%**
2	Cu(CH$_3$CN)$_4$BF$_4$	**L1**	PhCl	41%
3	CuBr	**L1**	PhCl	21%
4	CuCN	**L1**	PhCl	27%
5	Cu(OAc)$_2$	**L1**	PhCl	n.r
6	Cu(OTf)$_2$	**L1**	PhCl	trace
7	Cu(CH$_3$CN)$_4$PF$_6$	**L2**	PhCl	34%
8	Cu(CH$_3$CN)$_4$PF$_6$	**L3**	PhCl	10%
9	Cu(CH$_3$CN)$_4$PF$_6$	**L4**	PhCl	trace
10	Cu(CH$_3$CN)$_4$PF$_6$	**L5**	PhCl	trace
11	Cu(CH$_3$CN)$_4$PF$_6$	**L6**	PhCl	trace
12	Cu(CH$_3$CN)$_4$PF$_6$	**L7**	PhCl	42%
13	Cu(CH$_3$CN)$_4$PF$_6$	**L8**	PhCl	55%
14	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	CH$_3$CN	47%
15	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	DCE	21%
16	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	acetone	24%
17	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	THF	n.r
18c	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	toluene	trace
19	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	DMF	n.r
20	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	1,2-dichlorobenz	61%
21	**Cu(CH$_3$CN)$_4$PF$_6$**	**L1**	**H$_2$O**	**58%**
22	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	H$_2$O:PhCl = 9:1	61%
23	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	H$_2$O:CH3CN =	52%
24	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	H$_2$O:DCE = 9:1	48%
25	Cu(CH$_3$CN)$_4$PF$_6$	**L1**	---	35%
26	---	**L1**	PhCl	n.r
27	Cu(CH$_3$CN)$_4$PF$_6$	---	PhCl	n.r

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), Cu(CH$_3$CN$_4$)PF$_6$ (5 mol%), ligand (5.5 mol%), solvent (0.1 mol/L) under Ar at 30 °C for 24 h. [b] Isolated yield.

5.2 Optimization of the reaction conditions for the synthesis of (*R*)-3a.

Table S2: [a]



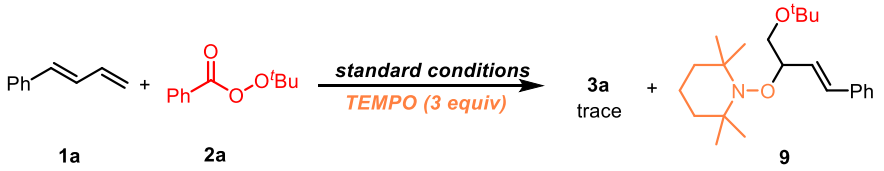
Entry	Cat.[Cu] (5.0 mol%)	Ligand (5.5	Solvent	Yield (%)[b]	e.e
1	$Cu(CH_3CN)_4PF_6$	**L9***	H_2O	45%	-50%
2	$Cu(CH_3CN)_4PF_6$	**L10***	H_2O	32%	-5%
3	$Cu(CH_3CN)_4PF_6$	**L11***	H_2O	43%	0
4	$Cu(CH_3CN)_4PF_6$	**L12***	**H_2O**	**55%**	**79%**
5	$Cu(CH_3CN)_4PF_6$	**L13***	H_2O	12%	3%
6	$Cu(CH_3CN)_4PF_6$	**L14***	H_2O	15%	-13%
7	$Cu(CH_3CN)_4PF_6$	**L15***	H_2O	50%	-71%
8	$Cu(CH_3CN)_4PF_6$	**L16***	**H_2O**	**54%**	**-79%**
9	$Cu(CH_3CN)_4PF_6$	**L17***	H_2O	45%	-16%
10	$Cu(CH_3CN)_4PF_6$	**L18***	H_2O	54%	-31%
11	$Cu(CH_3CN)_4PF_6$	**L19***	H_2O	trace	---
12	$Cu(CH_3CN)_4PF_6$	**L20***	H_2O	16%	65%
13	$Cu(OTf)_2$	**L12***	H_2O	27%	62%
14	$Cu(CH_3CN)_4BF_4$	**L12***	H_2O	34%	70%
15	$Cu(CH_3CN)_4PF_6$	**L12***	CH_3CN	50%	67%
16	$Cu(CH_3CN)_4PF_6$	**L12***	PhCl	44%	74%
17	$Cu(CH_3CN)_4PF_6$	**L12***	acetone	37%	74%
18	$Cu(CH_3CN)_4PF_6$	**L12***	DCM	trace	---
19[c]	$Cu(CH_3CN)_4PF_6$	**L12***	H_2O	50%	**79%**

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), [Cu] (5 mol%), ligand (5.5 mol%), solvent (0.1 mol/L) under Ar at 30 °C for 24 h. [b] R/S total isolated yield. [c] At 0 °C with ice-water bath.

6. Mechanistic investigations

6.1 Free radical trapping experiments

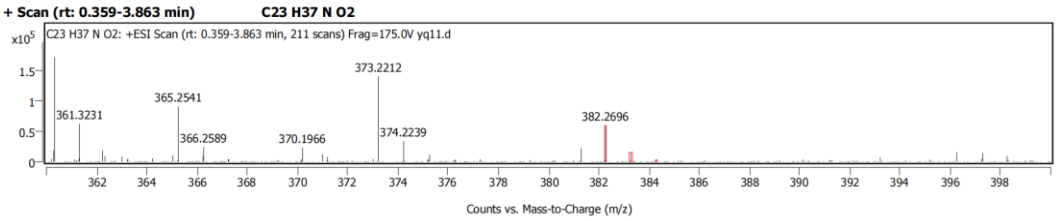
The following reaction was carried out under standard condition: A 10 mL reaction vessel was charged with 1-phenylbutadiene **1a** (0.2 mmol), *tert*-butyl benzoperoxoate **2a** (2.0 equiv, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L1** (5.5 mol %), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (3.0 equiv), 1,1-Diphenylethylene (3.0 equiv) or 2,6-di-tert-butyl-4-methylphenol (3.0 equiv) and PhCl (2 mL) at 30 °C for 24 h under an argon atmosphere. After completion, the consequence was detected by HRMS and/or GC-MS analysis.

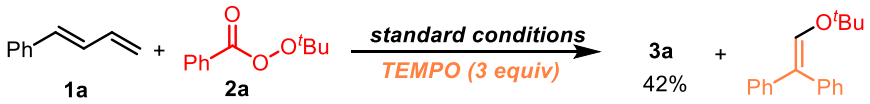


1a **2a** **9**

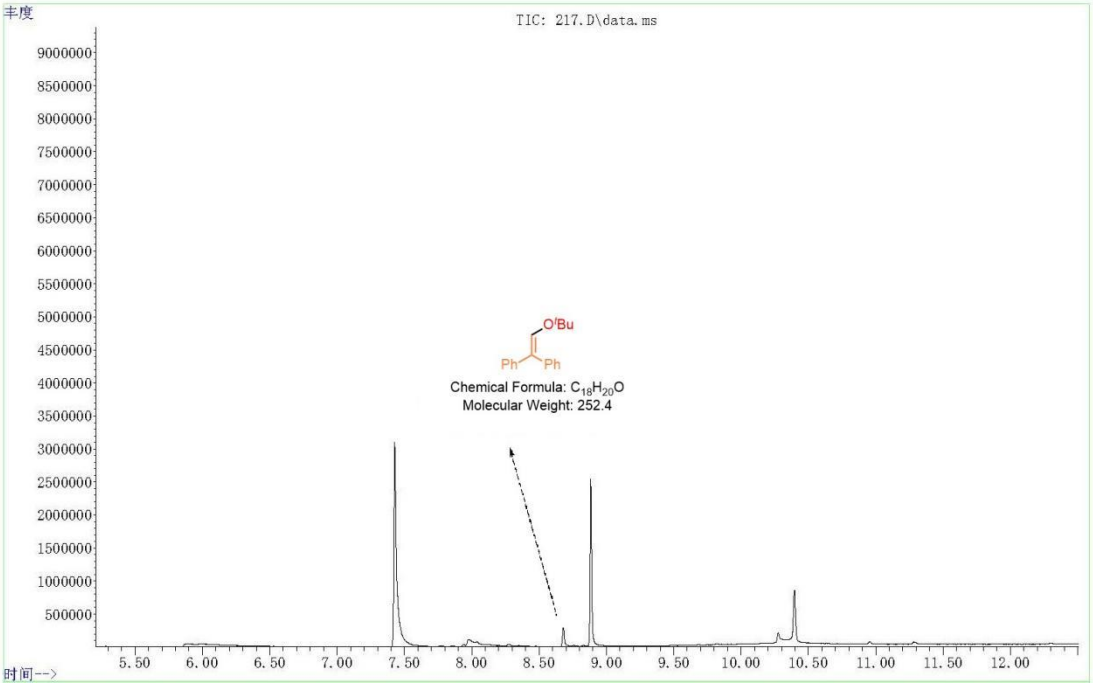
Chemical Formula $[M+Na]^+$: $C_{23}H_{37}NNaO_2^+$
Exact Mass: 382.2716, Found: 382.2696

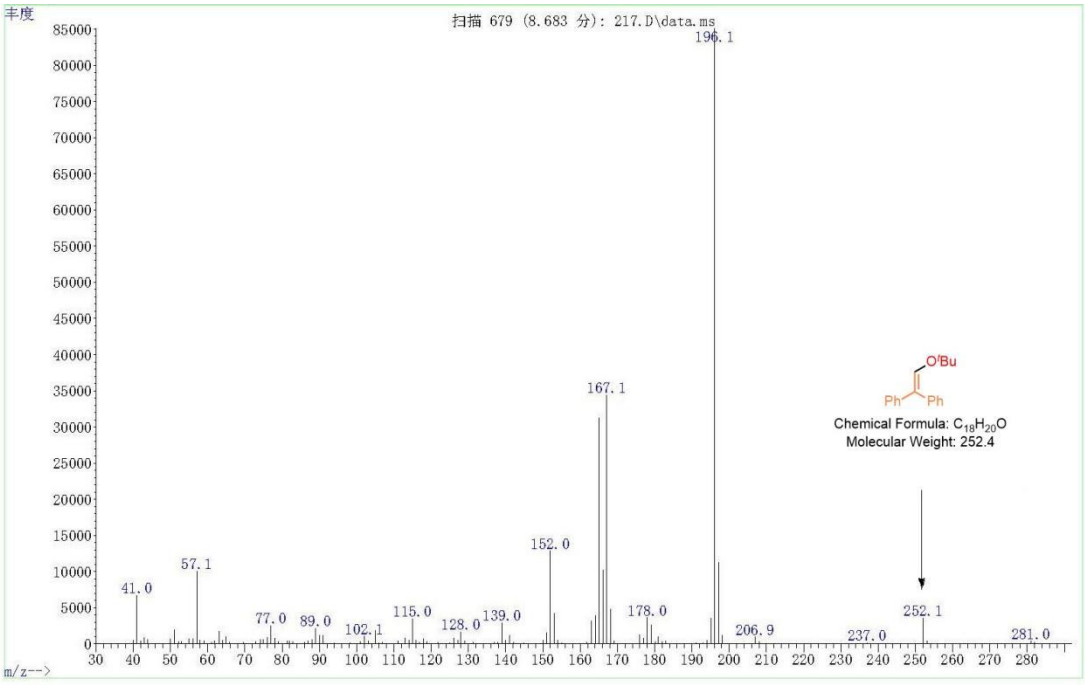
Sample Spectra

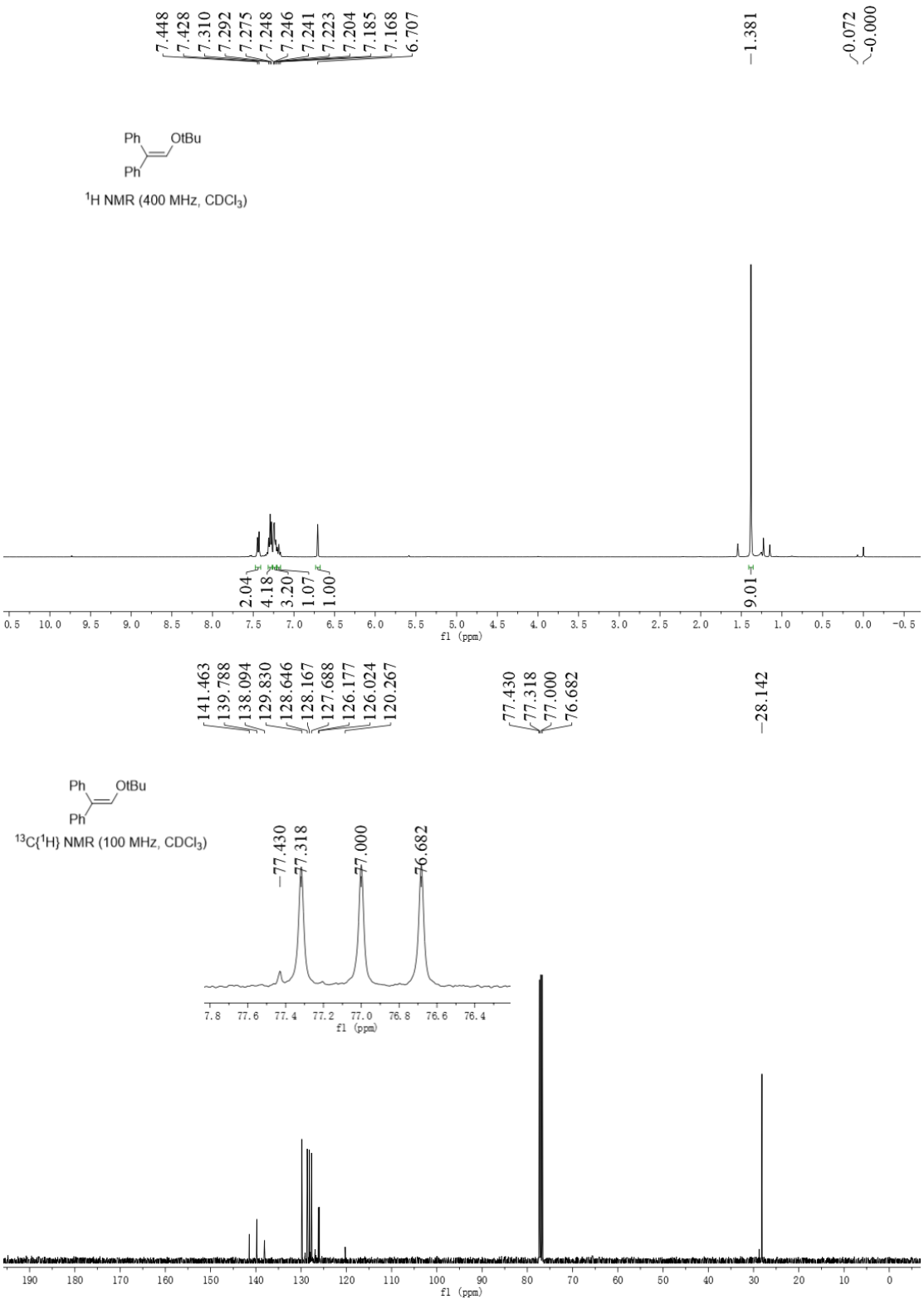




Chemical Formula: $C_{18}H_{20}O$
Exact Mass: 252.1514
detected by GC-MS






7.448
7.428
7.310
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7.275
7.248
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7.204
7.185
7.168
6.707
1.381
0.072
-0.000
Ph
OtBu
Ph
1H NMR (400 MHz, CDCl3)
2.04
4.18
3.20
1.07
1.00
9.01
f1 (ppm)
141.463
139.788
138.094
129.830
128.646
128.167
127.688
126.177
126.024
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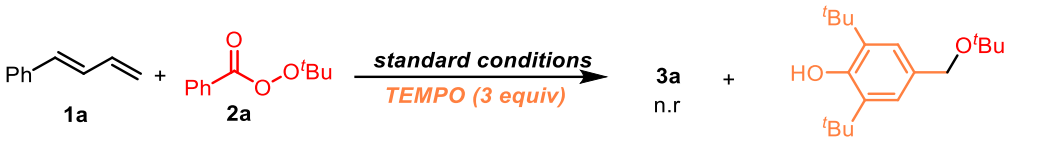
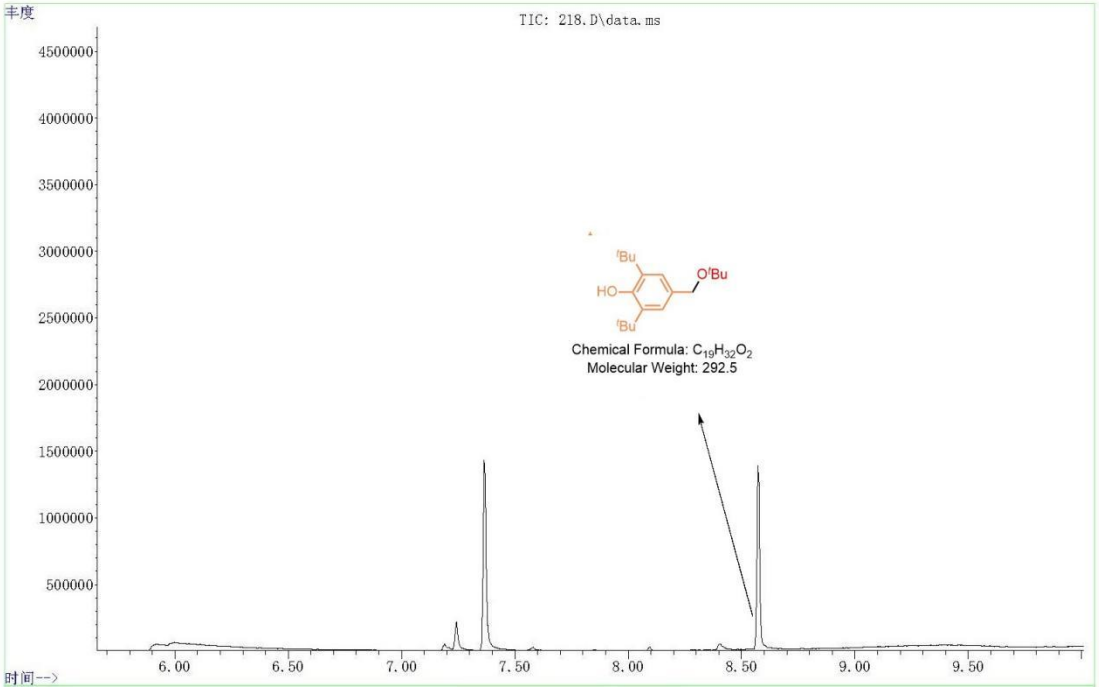
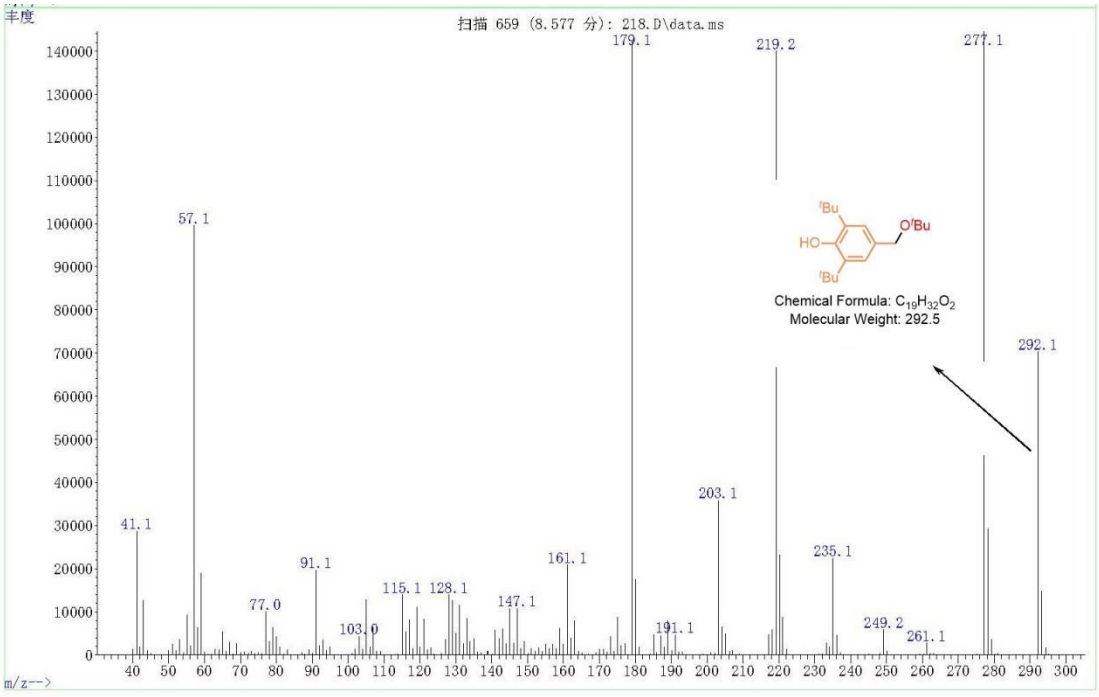
77.000
76.682
28.142
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



Chemical Formula: $C_{19}H_{32}O_2$
Exact Mass: 292.2402
detected by GC-MS

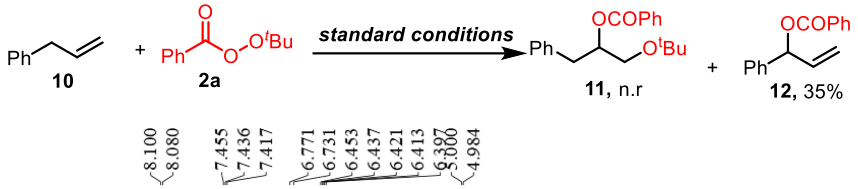


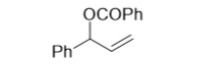


6.2 Reaction with allyl benzene and naphthalene ethylene

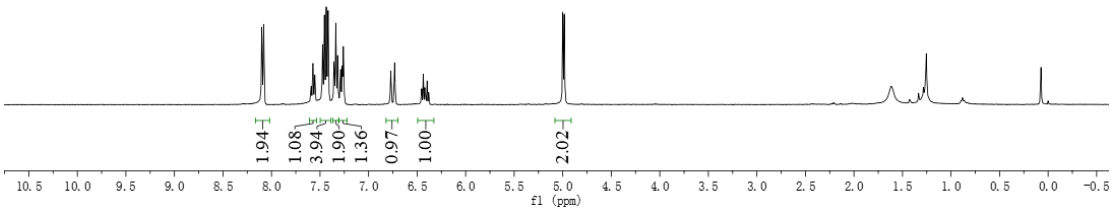
The following reaction was carried out under standard condition: A 10 mL reaction vessel was charged with alkenes (0.2 mmol), *tert*-butyl benzoperoxoate **2a** (2.0 equiv, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L1** (5.5 mol %), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L1** (5.5 mol %) and PhCl (2 mL) at 30 °C for 24 h under an argon atmosphere. After completion, the consequence was detected by TLC and/or GC-MS analysis. Then, separated by column chromatography was performed using silica gel (200-300 mesh).

Reaction with allyl benzene **10**: column chromatography was performed using silica gel (200-300 mesh) to give products **12** in 35% yield (petroleum ether/ethyl acetate, 40 :1) and NMR was performed.

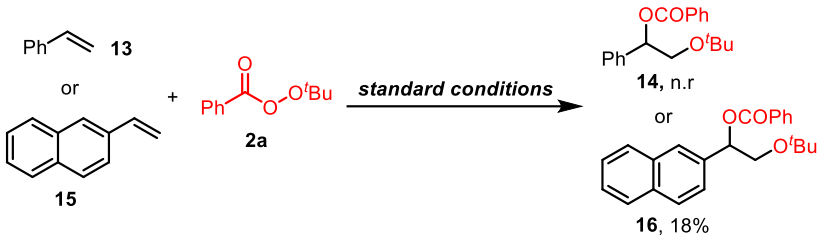




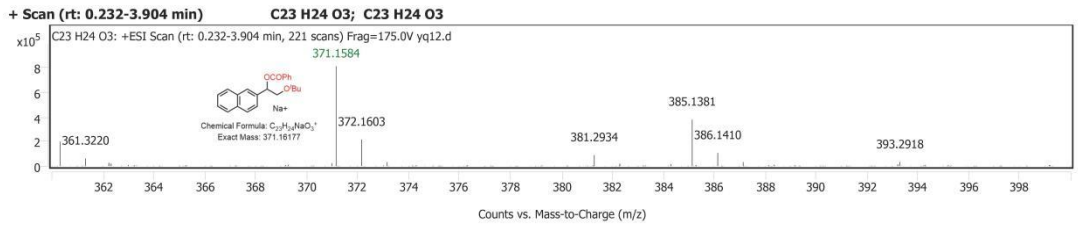
^{1}HNMR (400 MHz, $CDCl_3$)

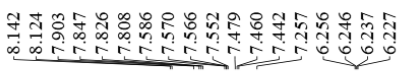


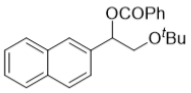
Reaction with alkenes **13** or **15**: column chromatography was performed using silica gel (200-300 mesh) to give products **16** in 18% yield (petroleum ether/ethyl acetate, 20 :1) and NMR was performed.



Sample Spectra



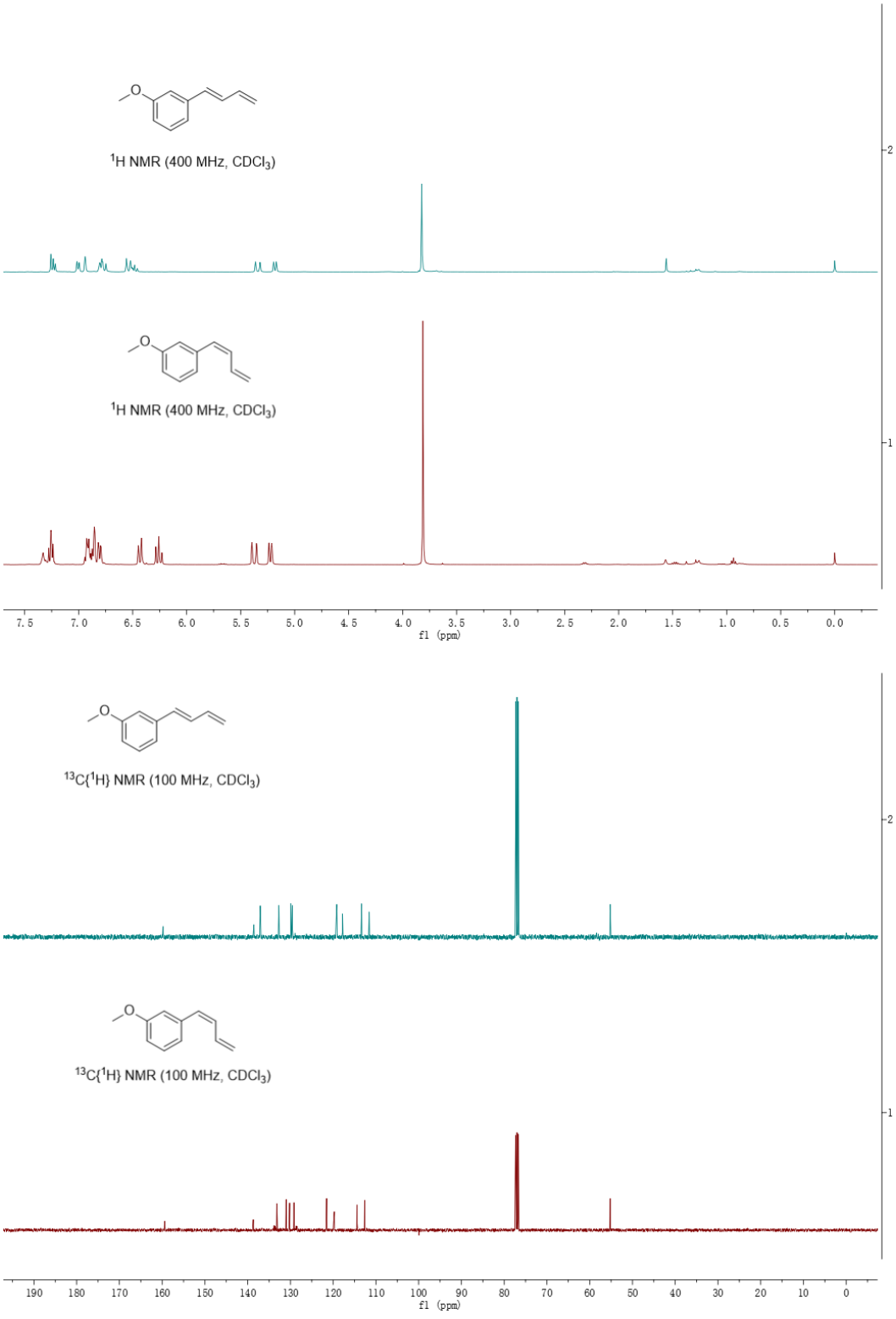




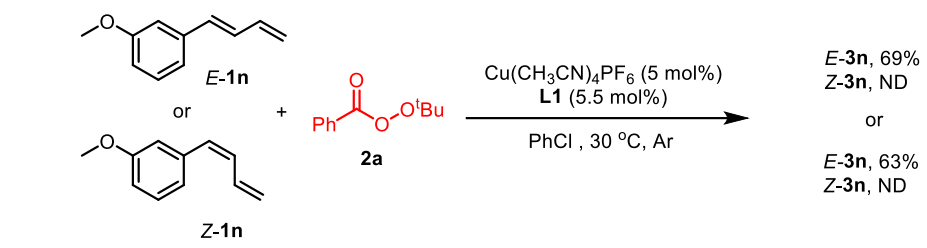
^{1}HNMR (400 MHz, $CDCl_3$)

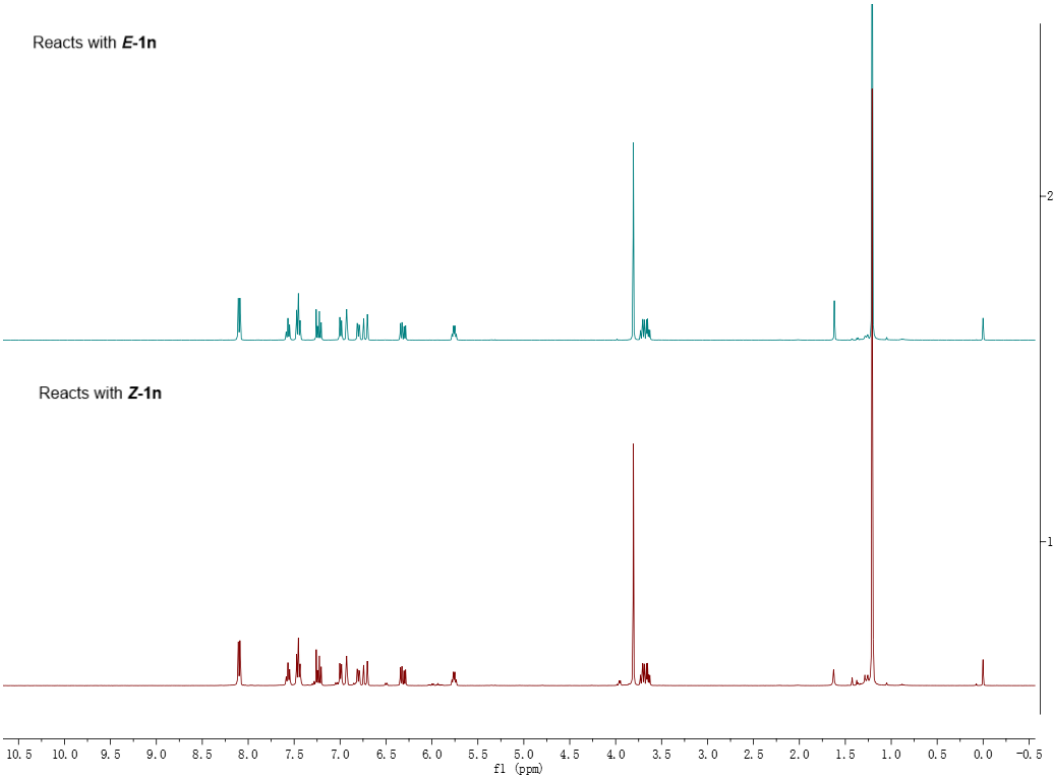
6.3 Z/E configuration control experiment

NMR data for ***E*-1n** and ***Z*-1n**:

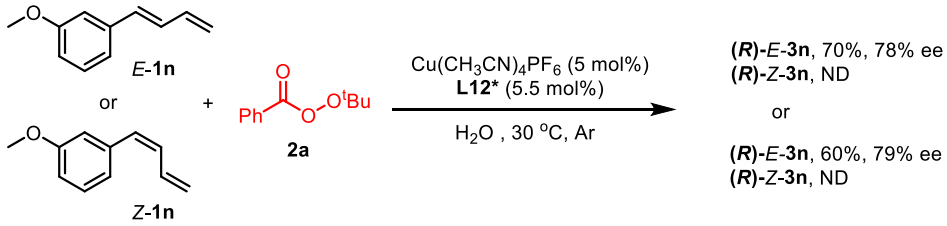


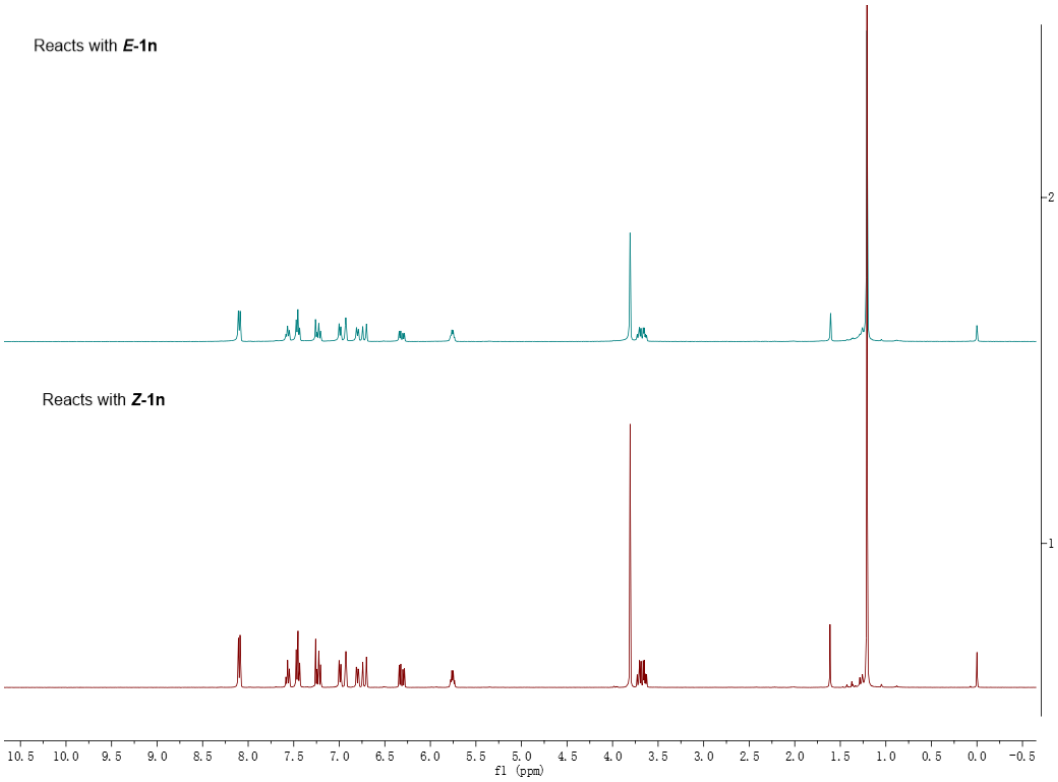
The following reaction was carried out under standard condition: A 10 mL reaction vessel was charged with ***E*-1n** or ***Z*-1n** (0.2 mmol), *tert*-butyl benzoperoxoate **2a** (2.0 equiv, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L1** (5.5 mol %) and PhCl (2 mL) at 30 °C for 24 h under an argon atmosphere.



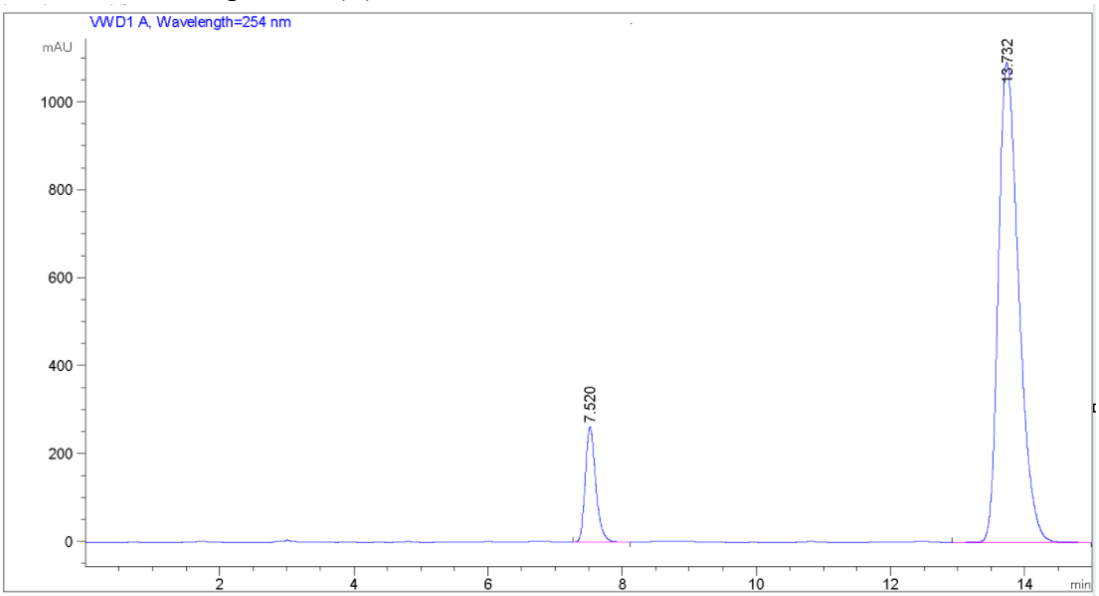


The following reaction was carried out under standard condition: A 10 mL reaction vessel was charged with ***E*-1n** or ***Z*-1n** (0.2 mmol), *tert*-butyl benzoperoxoate **2a** (2.0 equiv, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L12*** (5.5 mol %) and H_2O (2 mL) at 30 °C for 24 h under an argon atmosphere.



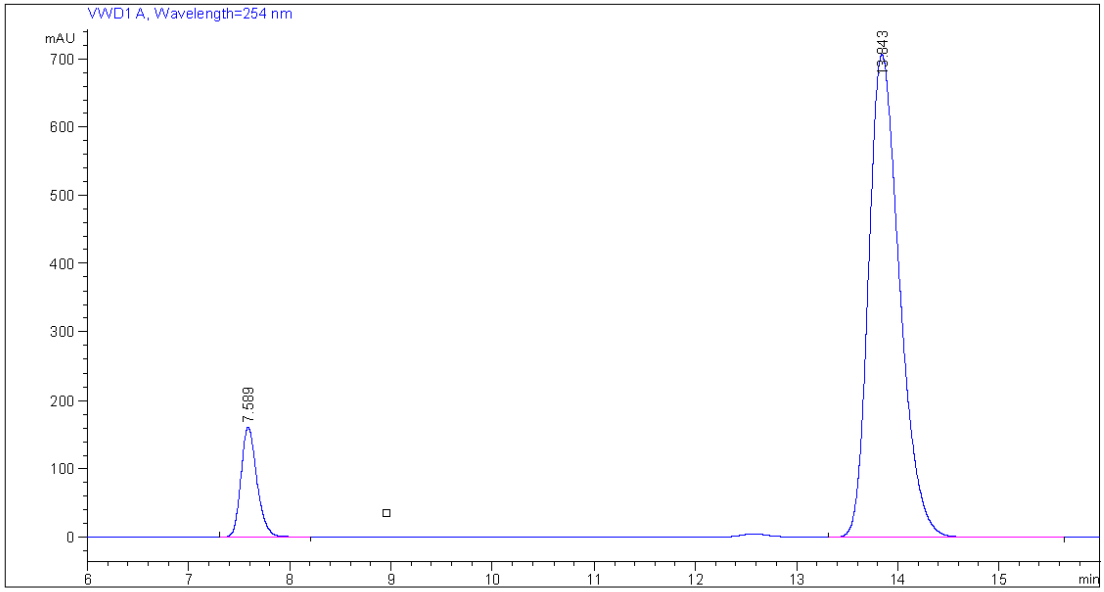


Reacts with ***E*-1n,** product **(*R*)-*E*-3n**:



	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.520	BB	0.1656	2842.58545	261.90549	11.0145
2	13.732	BBA	0.3245	2.29651e4	1091.42493	88.9855

Reacts with ***Z*-1n**, product **(*R*)-*E*-3n**:



	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.589	BB	0.1663	1758.97339	161.15710	10.5292
2	13.843	BB	0.3244	1.49467e4	707.56683	89.4708

7. Metrics calculations

E-factor were calculated using Waste Mass/Product Mass.

(a) J. Org. Chem. 2024, 89, 16865

E-factor: [2.098 (sol.)+0.065 (SM1) +0.318 (SM2)+0.156 (SM3)-0.136 (Pro)]/0.136 = 24.9

(b) Org. Lett. 2023, 25, 4313

E-factor: [31.2 (sol.)+0.320 (SM1) +0.630 (SM2)+0.222 (Cat)-0.404 (Pro)]/0.404 = 79.1

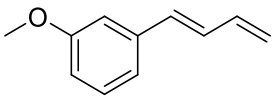
(c) Chem. Commun. 2023, 59, 9481

E-factor: [0.742 (sol.)+0.065 (SM1) +0.180 (SM2)+0.106 (additive)-0.079 (Pro)]/0.079 = 12.8

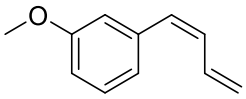
(d) **Our system in water:**

E-factor: [0.780 (SM1)+3.000 (SM2)+0.111 (Cat)+0.061 (Ligand)-1.140]/1.140 = 2.5

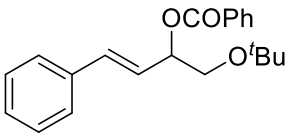
8. Characterization data of products



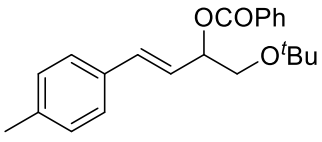
(*E*)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (*E*-1n), by silica gel column chromatography (hexane/ethyl acetate = 80:1), colorless oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.26 (dd, *J* = 9.1, 6.7 Hz, 1H), 6.99 – 6.72 (m, 4H), 6.43 (d, *J* = 11.5 Hz, 1H), 6.26 (t, *J* = 11.3 Hz, 1H), 5.37 (d, *J* = 16.9 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 159.4, 138.7, 133.2, 131.0, 130.2, 129.2, 121.5, 119.7, 114.4, 112.6, 55.2.



(*Z*)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (*Z*-1n), by silica gel column chromatography (hexane/ethyl acetate = 80:1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.30 – 7.16 (m, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.94 (s, 1H), 6.84 – 6.72 (m, 2H), 6.58 – 6.42 (m, 2H), 5.34 (d, *J* = 16.5 Hz, 1H), 5.18 (d, *J* = 9.7 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 159.8, 138.5, 137.1, 132.7, 129.9, 129.5, 119.2, 117.8, 113.3, 111.6, 55.2.

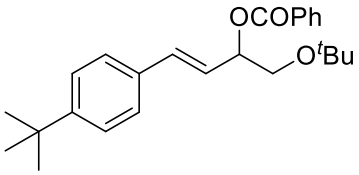


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl benzoate (3a), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 44.1 mg, 65% yield, colorless oil, HPLC: 79% ee, t_R = 6.308 min (minor), t_R = 9.397 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.14 – 8.06 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.37 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.80 – 5.73 (m, 1H), 3.68 (ddd, *J* = 14.7, 10.0, 5.7 Hz, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.9, 136.3, 133.2, 132.9, 130.5, 129.7, 128.5, 128.3, 127.9, 126.6, 125.0, 74.6, 73.4, 63.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{24}NaO_3$ $(M + Na)^+$ calcd for 347.1618, found 347.1632.

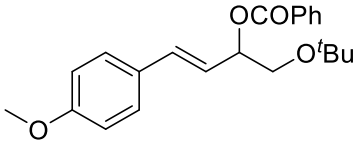


(*E*)-1-(*tert*-butoxy)-4-(*p*-tolyl)but-3-en-2-yl benzoate (3b), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 50.7 mg, 75% yield, white solid (mp 88-90 °C), HPLC: 64% ee, t_R = 6.792 min (minor), t_R = 9.007 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 15.9, 6.9 Hz,

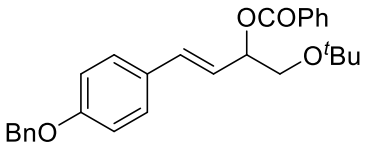
1H), 5.83 – 5.67 (m, 1H), 3.79 – 3.54 (m, 2H), 2.33 (s, 3H), 1.20 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.9, 137.8, 133.6, 133.2, 132.8, 130.6, 129.7, 129.2, 128.3, 126.5, 124.0, 74.7, 73.4, 64.0, 27.5, 21.2; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1794.



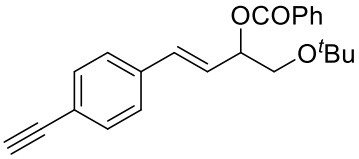
((*E*)-1-(*tert*-butoxy)-4-(4-(*tert*-butyl)phenyl)but-3-en-2-yl benzoate (3c), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 53.9 mg, 78% yield, white solid (mp 75-77 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.10 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (s, 4H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.77 (q, *J* = 6.3 Hz, 1H), 3.68 (ddd, *J* = 25.0, 10.0, 5.8 Hz, 2H), 1.31 (s, 9H), 1.22 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.8, 151.1, 133.6, 133.1, 132.8, 130.6, 129.6, 128.3, 126.3, 125.4, 124.2, 74.7, 73.4, 64.0, 34.6, 31.2, 27.5; HRMS (ESI-TOF) *m/z*: $C_{25}H_{32}NaO_3$ $(M + Na)^+$ calcd for 403.2244, found 403.2266.



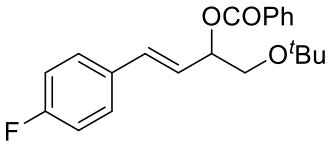
(*E*)-1-(*tert*-butoxy)-4-(4-methoxyphenyl)but-3-en-2-yl benzoate (**3d**), by silica gel column chromatography (hexane/ethyl acetate = 20:1), 30.5 mg, 43% yield, yellow solid (mp 101-103 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.09 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.46-7.43 (m, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.74 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.73 – 3.57 (m, 2H), 1.20 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.9, 159.5, 132.9, 132.8, 130.7, 129.7, 129.2, 128.3, 127.9, 122.8, 113.9, 74.9, 73.4, 64.0, 55.3, 27.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_4$ $(M + Na)^+$ calcd for 377.1723, found 377.1738.



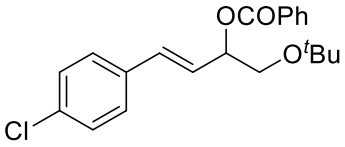
(*E*)-4-(4-(benzyloxy)phenyl)-1-(*tert*-butoxy)but-3-en-2-yl benzoate (**3e**), by silica gel column chromatography (hexane/ethyl acetate = 20:1), 33.6 mg, 39% yield, yellow solid (mp 112-114 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.09 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46-7.39 (m, 5H), 7.38-7.31 (m, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.74 (q, *J* = 6.5 Hz, 1H), 5.06 (s, 2H), 3.76 – 3.57 (m, 2H), 1.20 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.9, 158.6, 136.8, 132.9, 132.8, 130.6, 129.6, 129.4, 128.6, 128.3, 128.0, 127.9, 127.4, 122.8, 114.9, 74.8, 73.4, 70.0, 64.0, 27.5; HRMS (ESI-TOF) *m/z*: $C_{28}H_{30}NaO_4$ $(M + Na)^+$ calcd for 453.2036, found 386.9998.



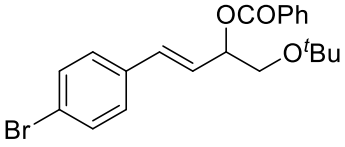
(*E*)-1-(*tert*-butoxy)-4-(4-ethynylphenyl)but-3-en-2-yl benzoate (**3f**), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 44.6 mg, 65% yield, white solid (mp 92-94 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.10 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 13.1, 7.9 Hz, 4H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.75 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.73-3.63 (m, 2H), 3.11 (s, 1H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 136.8, 132.9, 132.3, 132.2, 130.4, 129.7, 128.3, 126.5, 126.4, 121.4, 83.6, 77.9, 74.3, 73.5, 63.8, 27.5; HRMS (ESI-TOF) *m/z*: $C_{23}H_{24}NaO_3$ $(M + Na)^+$ calcd for 371.1618, found 371.1632.



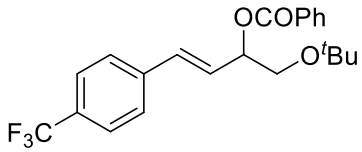
(***E*)-1-(*tert*-butoxy)-4-(4-fluorophenyl)but-3-en-2-yl benzoate** (**3g**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 48.6 mg, 71% yield, yellow solid (mp 107-109 °C), HPLC: 71% ee, t_R = 6.711 min (minor), t_R = 9.043 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.09 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.74 (q, *J* = 5.9 Hz, 1H), 3.74 – 3.60 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 162.5 (d, *J* = 245.7 Hz, 1C), 132.9, 132.5 (d, *J* = 3.2 Hz, 1C), 132.1, 130.5, 129.7, 128.3, 128.2 (d, *J* = 8.0 Hz, 1C), 124.9, 115.4 (d, *J* = 21.5 Hz, 1C), 74.5, 73.4, 63.9, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9 (s, 1F); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}FNaO_3$ $(M + Na)^+$ calcd for 365.1523, found 365.1546.



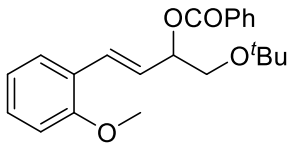
(*E*)-1-(*tert*-butoxy)-4-(4-chlorophenyl)but-3-en-2-yl benzoate (**3h**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 45.1 mg, 63% yield, white solid (mp 100-102 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.23 (m, 4H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.74 (q, *J* = 6.1 Hz, 1H), 3.77 – 3.56 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 134.9, 133.5, 132.9, 131.9, 130.4, 129.7, 128.7, 128.3, 127.8, 125.8, 74.3, 73.5, 63.8, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}ClNaO_3$ $(M + Na)^+$ calcd for 381.1228, found 381.1250.



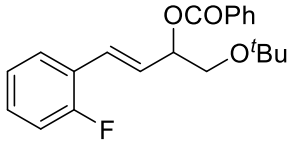
(*E*)-4-(4-bromophenyl)-1-(*tert*-butoxy)but-3-en-2-yl benzoate (**3i**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 48.2 mg, 60% yield, yellow solid (mp 85-87 °C), HPLC: 79% ee, t_R = 7.550 min (minor), t_R = 10.490 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 15.4, 8.1 Hz, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.74 (dd, *J* = 11.8, 5.8 Hz, 1H), 3.72-3.62 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 135.3, 132.9, 131.9, 131.6, 130.3, 129.6, 128.3, 128.1, 125.9, 121.7, 74.3, 73.5, 63.8, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}BrNaO_3$ (M + Na)$^+$ calcd for 425.0723, found 425.0745.



(*E*)-1-(*tert*-butoxy)-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl benzoate (**3j**), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 45.5 mg, 58% yield, yellow solid (mp 123-125 °C), HPLC: 77% ee, t_R = 6.627 min (minor), t_R = 9.179 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.18 – 8.04 (m, 2H), 7.60-7.55 (m, 3H), 7.51 – 7.42 (m, 4H), 6.77 (d, *J* = 16.1 Hz, 1H), 6.43 (dd, *J* = 16.1, 6.5 Hz, 1H), 5.77 (q, *J* = 5.5 Hz, 1H), 3.78 – 3.58 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 139.9, 133.0, 130.3, 129.9 (q, *J* = 44.6 Hz, 1C), 129.8, 128.4, 128.1, 126.8, 125.5 (q, *J* = 3,8 Hz, 1C), 121.5 (q, *J* = 270.8 Hz, 1C), 74.1, 73.5, 63.7, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 (s, 3F); HRMS (ESI-TOF) *m/z*: $C_{22}H_{23}F_3NaO_3$ (M + Na)$^+$ calcd for 415.1492, found 415.1511.

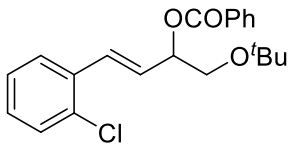


(*E*)-1-(*tert*-butoxy)-4-(2-methoxyphenyl)but-3-en-2-yl benzoate (**3k**), by silica gel column chromatography (hexane/ethyl acetate = 30:1), 40.4 mg, 57% yield, white solid (mp 98-91 °C), HPLC: 68% ee, t_R = 6.670 min (minor), t_R = 10.498 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 3H), 7.23 (dd, *J* = 14.1, 5.9 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.35 (dd, *J* = 16.2, 7.0 Hz, 1H), 5.78 (m, 1H), 3.82 (s, 3H), 3.76 – 3.61 (m, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.9, 156.9, 132.7, 130.7, 129.7, 129.0, 128.3, 128.2, 127.1, 125.5, 125.3, 120.5, 110.8, 75.1, 73.3, 64.0, 55.4, 27.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_4$ (M + Na)$^+$ calcd for 377.1723, found 377.1744.

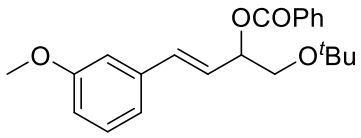


(*E*)-1-(*tert*-butoxy)-4-(2-fluorophenyl)but-3-en-2-yl benzoate (**3l**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 45.2 mg, 66% yield, white solid (mp 101-103 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ:

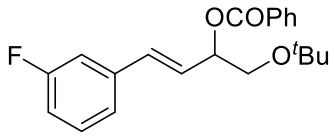
8.13 – 8.06 (m, 2H), 7.60 – 7.53 (m, 1H), 7.45 (td, *J* = 7.7, 1.9 Hz, 3H), 7.23 – 7.17 (m, 1H), 7.11 – 6.98 (m, 2H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.43 (dd, *J* = 16.2, 6.6 Hz, 1H), 5.77 (q, *J* = 5.6 Hz, 1H), 3.79 – 3.59 (m, 2H), 1.21 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.8, 160.3 (d, *J* = 247.5 Hz, 1C), 132.9, 130.5 (2C), 129.7, 129.2 (d, *J* = 8.5 Hz, 1C), 128.3, 127.9 (d, *J* = 5.3 Hz, 1C), 127.7 (d, *J* = 3.6 Hz, 1C), 125.5 (d, *J* = 3.5 Hz, 1C), 124.0 (d, *J* = 3.5 Hz, 1C), 115.7 (d, *J* = 21.9 Hz, 1C), 74.5, 73.4, 63.8, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}FNaO_3$ $(M + Na)^+$ calcd for 365.1523, found 365.1544.



(*E*)-1-(*tert*-butoxy)-4-(2-chlorophenyl)but-3-en-2-yl benzoate (**3m**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 42.3 mg, 59% yield, white solid (mp 78-80 °C), $^{1}HNMR$ (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 7.4 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.23-7.13 (m, 3H), 6.34 (dd, *J* = 16.1, 6.4 Hz, 1H), 5.79 (dd, *J* = 11.5, 5.6 Hz, 1H), 3.75-3.65 (m, 2H), 1.21 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.8, 134.6, 133.3, 132.9, 130.4, 129.7 (2C), 129.0, 128.8, 128.3, 128.1, 126.9, 126.8, 74.2, 73.4, 63.8, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}ClNaO_3$ $(M + Na)^+$ calcd for 381.1228, found 381.1245.

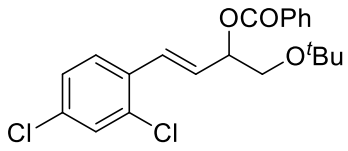


(*E*)-1-(*tert*-butoxy)-4-(3-methoxyphenyl)but-3-en-2-yl benzoate (**3n**), by silica gel column chromatography (hexane/ethyl acetate = 20:1), 50.3 mg, 71% yield: white solid (mp 98-100 °C), HPLC: 79% ee, t_R = 7.520 min (minor), t_R = 13.732 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). $^{1}HNMR$ (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.18 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.80 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.76 (q, *J* = 5.8 Hz, 1H), 3.80 (s, 3H), 3.75 – 3.59 (m, 2H), 1.21 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.8, 159.7, 137.8, 133.1, 132.9, 130.5, 129.6, 129.5, 128.3, 125.4, 119.3, 113.7, 111.8, 74.5, 73.4, 63.9, 55.2, 27.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_4$ $(M + Na)^+$ calcd for 377.1723, found 377.1738.

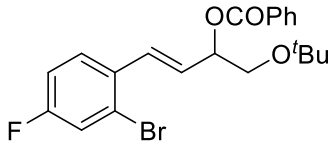


(*E*)-1-(*tert*-butoxy)-4-(3-fluorophenyl)but-3-en-2-yl benzoate (**3o**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 28.7 mg, 42% yield, yellow solid (mp 92-94 °C), $^{1}HNMR$ (400 MHz, $CDCl_3$) δ: 8.14 – 8.07 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 3.9 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 10.1 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.75 (q, *J* = 5.4 Hz, 1H), 3.77 – 3.57 (m, 2H), 1.21 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.8, 163.0 (d, *J* = 244.3 Hz, 1C), 138.8 (d, *J* = 8.9 Hz, 1C), 132.9, 131.9, 130.4, 130.0 (d, *J* = 8.6 Hz, 1C), 129.7, 128.3, 126.7,

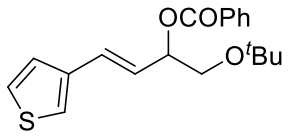
122.6, 114.7 (d, J = 21.3 Hz, 1C), 113.0 (d, J = 21.6 Hz, 1C), 74.2, 73.5, 63.8, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}FNaO_3$ $(M + Na)^+$ calcd for 365.1523, found 365.1541.



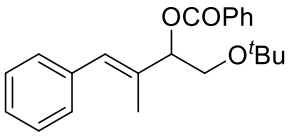
(*E*)-1-(*tert*-butoxy)-4-(2,4-dichlorophenyl)but-3-en-2-yl benzoate (**3p**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 40.8 mg, 52% yield, yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.09 (t, J = 6.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.36 (d, J = 2.0 Hz, 1H), 7.19 (dd, J = 8.4, 1.9 Hz, 1H), 7.08 (d, J = 16.1 Hz, 1H), 6.33 (dd, J = 16.0, 6.4 Hz, 1H), 5.79-5.75 (m, 1H), 3.74-3.64 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 133.8, 133.8, 133.2, 133.0, 130.3, 129.7, 129.4, 128.7, 128.4, 127.9, 127.7, 127.2, 74.1, 73.5, 63.7, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}Cl_2NaO_3$ $(M + Na)^+$ calcd for 415.0838, found 415.0857.



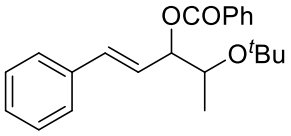
(*E*)-4-(2-bromo-4-fluorophenyl)-1-(*tert*-butoxy)but-3-en-2-yl benzoate (**3q**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 27.7 mg, 33% yield, yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.33 – 7.21 (m, 1H), 7.01 (dd, J = 20.6, 11.9 Hz, 2H), 6.24 (dd, J = 16.0, 6.4 Hz, 1H), 5.77 (d, J = 5.7 Hz, 1H), 3.77 – 3.61 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 161.8 (d, J = 250.0 Hz, 1C), 133.0, 132.7 (d, J = 3.6 Hz, 1C), 130.5, 130.4, 129.7, 128.4, 128.2, 128.1 (d, J = 8.4 Hz, 1C), 123.7 (d, J = 9.4 Hz, 1C), 120.0 (d, J = 24.2 Hz, 1C), 114.9 (d, J = 21.1 Hz, 1C), 74.1, 73.5, 63.8, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}BrFNaO_3$ $(M + H)^+$ calcd for 443.0629, found 443.0616.



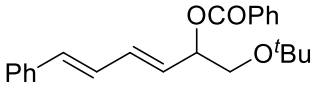
(*E*)-1-(*tert*-butoxy)-4-(thiophen-3-yl)but-3-en-2-yl benzoate (**3r**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 36.3 mg, 55% yield: yellow solid (mp 77-79 ^{o}C), HPLC: 57% ee, t_R = 7.540 min (minor), t_R = 16.135 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.12 – 8.06 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 3.9 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.18 (d, J = 2.2 Hz, 1H), 6.76 (d, J = 15.9 Hz, 1H), 6.16 (dd, J = 16.0, 7.0 Hz, 1H), 5.72 (q, J = 6.0 Hz, 1H), 3.74 – 3.58 (m, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 139.0, 132.8, 130.5, 129.6, 128.3, 127.5, 126.0, 124.9, 124.8, 123.0, 74.5, 73.4, 63.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{19}H_{22}NaO_3S$ $(M + Na)^+$ calcd for 353.1182, found 353.1198.



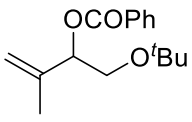
(*E*)-1-(*tert*-butoxy)-3-methyl-4-phenylbut-3-en-2-yl benzoate (**3s**), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 25.7 mg, 38% yield, yellow oil, HPLC: 90% ee, t_R = 4.720 min (minor), t_R = 7.114 min (major) (Chiralcel AD-H column, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.10 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.24 (m, 4H), 7.21 (t, *J* = 7.1 Hz, 1H), 6.65 (s, 1H), 5.69 – 5.54 (m, 1H), 3.82 – 3.60 (m, 2H), 1.98 (s, 3H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.7, 137.2, 134.4, 132.8, 130.6, 129.6, 129.0, 128.3, 128.0 (2C), 126.6, 78.9, 73.3, 63.2, 27.5, 14.8.; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1792.



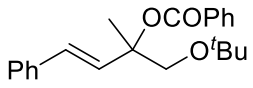
(*E*)-4-(*tert*-butoxy)-1-phenylpent-1-en-3-yl benzoate (3t), d.r 1:1.2, by silica gel column chromatography (hexane/ethyl acetate = 50:1), 44.6 mg, 66% yield, colorless oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.20 – 8.02 (m, 2H), 7.57 (dd, *J* = 15.0, 7.4 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.19 (m, 1H), 6.70 (dd, *J* = 16.0, 9.3 Hz, 1H), 6.39 – 6.28 (m, 1H), 5.64 (t, *J* = 5.7 Hz, 0.55H), 5.55 (dd, *J* = 7.5, 3.8 Hz, 0.45H), 3.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.25 (d, *J* = 5.2 Hz, 6.6H), 1.20 (d, *J* = 6.9 Hz, 5.4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.9, 165.6, 136.6, 136.5, 133.8, 133.0, 132.9 (2C), 130.6, 130.5, 129.7 (2C), 128.5 (2C), 128.4, 128.3, 127.8, 127.7, 126.7, 126.6, 124.8, 124.4, 79.0, 77.4, 74.2, 74.0, 68.8, 68.0, 28.5 (2C), 19.3, 18.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1794.



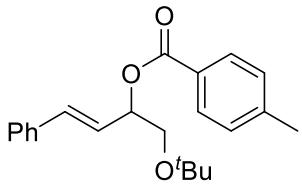
(3*E*,5*E*)-1-(*tert*-butoxy)-6-phenylhexa-3,5-dien-2-yl benzoate (**3u**), by silica gel column chromatography (hexane/ethyl acetate = 30:1), 18.9 mg, 27% yield, white solid (mp 90-92 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.19 (m, 1H), 6.78 (dd, *J* = 15.4, 10.7 Hz, 1H), 6.57 (dd, *J* = 15.6, 5.9 Hz, 2H), 5.92 (dd, *J* = 15.3, 6.8 Hz, 1H), 5.69 (q, *J* = 6.2 Hz, 1H), 3.76 – 3.53 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.8, 137.0, 133.6, 133.5, 132.9, 130.6, 129.7, 129.0, 128.6, 128.3, 128.0, 127.7, 126.4, 74.3, 73.4, 63.8, 27.5; HRMS (ESI-TOF) *m/z*: $C_{23}H_{26}NaO_3$ $(M + Na)^+$ calcd for 373.1774, found 373.1791.



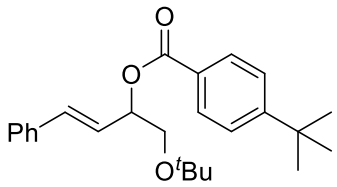
1-(*tert*-butoxy)-3-methylbut-3-en-2-yl benzoate (**3v**), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 25.7 mg, 49% yield: colorless oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.02 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.18 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.26 (dd, *J* = 30.4, 14.3 Hz, 2H), 3.71 (d, *J* = 9.1 Hz, 1H), 3.59 (d, *J* = 9.1 Hz, 1H), 1.69 (s, 3H), 1.19 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.4, 139.8, 132.5, 131.5, 129.5, 128.2, 114.4, 82.7, 72.9, 67.1, 27.5, 21.3; HRMS (ESI-TOF) *m/z*: $C_{16}H_{22}NaO_3$ $(M + Na)^+$ calcd for 285.1461, found 285.1476.



(*E*)-1-(*tert*-butoxy)-2-methyl-4-phenylbut-3-en-2-yl benzoate (3w), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 39.9 mg, 59% yield: Colorless oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.04 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 13.0, 7.5 Hz, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (dd, *J* = 13.4, 5.9 Hz, 1H), 6.62 (q, *J* = 16.4 Hz, 2H), 3.81 (d, *J* = 9.1 Hz, 1H), 3.68 (d, *J* = 9.1 Hz, 1H), 1.79 (s, 3H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.3, 136.8, 132.6, 131.6, 131.3, 129.6 (2C), 128.5, 128.2, 127.6, 126.6, 82.7, 73.0, 67.2, 27.5, 21.8; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1793.

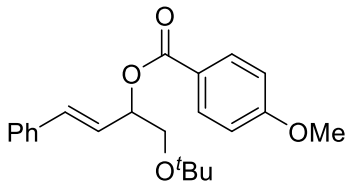


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-methylbenzoate (**4b**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 52.8 mg, 78% yield, yellow oil, HPLC: 77% ee, t_R = 4.882 min (minor), t_R = 17.292 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm). ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.98 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 3H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.75 (q, *J* = 5.8 Hz, 1H), 3.77 – 3.57 (m, 2H), 2.41 (s, 3H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.9, 143.5, 136.4, 133.0, 129.7, 129.0, 128.5, 127.8, 127.8, 126.6, 125.3, 74.3, 73.4, 63.9, 27.5, 21.6; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1793.

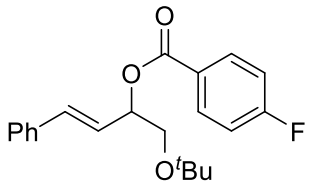


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-(*tert*-butyl)benzoate (**4c**), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 60.8 mg, 80% yield: yellow solid (mp 75-77 °C), HPLC: 71% ee, t_R = 5.131 min (minor), t_R = 12.052 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.19 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.75 (q, *J* = 5.9 Hz, 1H), 3.83 – 3.49 (m, 2H), 1.34 (s, 9H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz,

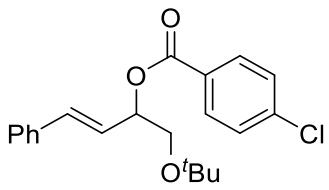
$CDCl_3$) δ: 165.8, 156.5, 136.4, 132.9, 129.6, 129.5, 128.5, 127.8, 127.7, 126.6, 125.3, 74.2, 73.4, 63.9, 35.0, 31.1, 27.5; HRMS (ESI-TOF) *m/z*: $C_{25}H_{32}NaO_3$ $(M + Na)^+$ calcd for 403.2244, found 403.2264.



(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-methoxybenzoate (**4d**), by silica gel column chromatography (hexane/ethyl acetate = 30:1), 29.8 mg, 42% yield, yellow oil, HPLC: 75% ee, t_R = 6.681 min (minor), t_R = 23.375 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.05 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.19 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.73 (q, *J* = 5.9 Hz, 1H), 3.86 (s, 3H), 3.75 – 3.59 (m, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.6, 163.3, 136.4, 132.9, 131.7, 128.5, 127.8, 126.6, 125.3, 122.9, 113.5, 74.2, 73.4, 64.0, 55.4, 27.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_4$ $(M + Na)^+$ calcd for 377.1723, found 377.1747.

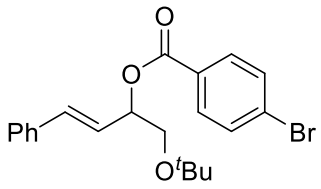


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-fluorobenzoate (**4e**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 44.5 mg, 65% yield, yellow oil, HPLC: 59% ee, t_R = 4.671 min (minor), t_R = 6.830 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.11 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.74 (q, *J* = 6.0 Hz, 1H), 3.76 – 3.57 (m, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.7 (d, *J* = 252.1 Hz, 1C), 164.9, 136.3, 133.4, 132.2 (d, *J* = 9.3 Hz, 1C), 128.5, 128.0, 126.8 (d, *J* = 2.5 Hz, 1C), 126.6, 124.9, 115.5 (d, *J* = 21.8 Hz, 1C), 74.8, 73.4, 63.9, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.8 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}FNaO_3$ $(M + Na)^+$ calcd for 365.1523, found 365.1545.

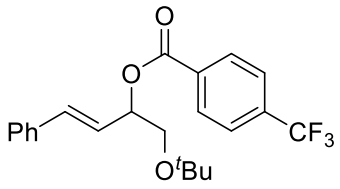


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-chlorobenzoate (**4f**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 52.3 mg, 73% yield, yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.02 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.75 (q, *J* = 6.3 Hz, 1H), 3.67 (qd, *J* = 10.1, 5.7 Hz, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz,

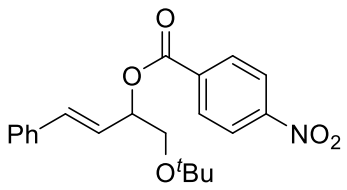
$CDCl_3$) δ: 165.0, 139.3, 136.2, 133.5, 131.0, 129.0, 128.6, 128.5, 128.0, 126.6, 124.7, 74.9, 73.4, 63.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}ClNaO_3$ $(M + Na)^+$ calcd for 381.1228, found 381.1249.



(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-bromobenzoate (**4g**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 48.2 mg, 60% yield, yellow oil, HPLC: 59% ee, t_R = 5.172 min (minor), t_R = 14.332 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.95 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.20 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.74 (q, *J* = 6.1 Hz, 1H), 3.67 (qd, *J* = 10.1, 5.7 Hz, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.1, 136.2, 133.5, 131.6, 131.2, 129.5, 128.5, 128.0, 127.9, 126.6, 124.7, 75.0, 73.4, 63.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}BrNaO_3$ $(M + Na)^+$ calcd for 425.0723, found 425.0741.

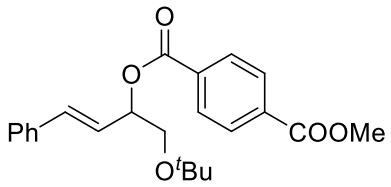


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-(trifluoromethyl)benzoate (**4h**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 45.5 mg, 58% yield, colorless oil, HPLC: 77% ee, t_R = 5.462 min (minor), t_R = 7.003 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.20 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.79 (q, *J* = 6.5 Hz, 1H), 3.69 (qd, *J* = 10.1, 5.6 Hz, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 164.7, 136.1, 134.3 (q, *J* = 32.4 Hz, 1C), 133.8, 130.0, 128.6, 128.1, 126.6 (2C), 125.4 (q, *J* = 3.7 Hz, 1C), 124.4, 123.6 (q, *J* = 271.1 Hz, 1C), 75.4, 73.5, 63.8, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1 (s, 3F); HRMS (ESI-TOF) *m/z*: $C_{22}H_{23}F_3NaO_3$ $(M + Na)^+$ calcd for 415.1492, found 415.1515.

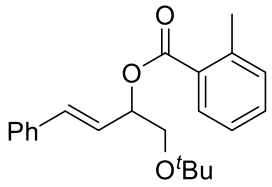


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-nitrobenzoate (**4i**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 20.7 mg, 28% yield, yellow solid (mp 102-104°C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.28 (q, *J* = 8.7 Hz, 4H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.79 (d, *J* = 4.4 Hz, 1H), 3.79 – 3.61 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H}

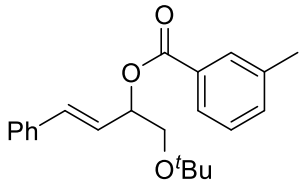
NMR (100 MHz, $CDCl_3$) δ: 164.0, 150.5, 136.0, 134.2, 130.7, 128.6 (2C), 128.2, 126.7, 124.0, 123.5, 75.9, 73.5, 63.8, 27.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}NNaO_5$ $(M + Na)^+$ calcd for 392.1468, found 392.1496.



(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl methyl terephthalate (**4j**), by silica gel column chromatography (hexane/ethyl acetate = 20:1), 48.2 mg, 63% yield, white solid (mp 121-123 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.13 (q, *J* = 8.4 Hz, 4H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.20 (m, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.77 (q, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 3.69 (ddt, *J* = 14.6, 10.1, 5.7 Hz, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 166.3, 165.0, 136.2, 134.4, 133.8, 133.7, 129.6, 129.5, 128.5, 128.0, 126.6, 124.6, 75.2, 73.4, 63.9, 52.4, 27.4; HRMS (ESI-TOF) *m/z*: $C_{23}H_{26}NaO_5$ $(M + Na)^+$ calcd for 405.1673, found 405.1698.

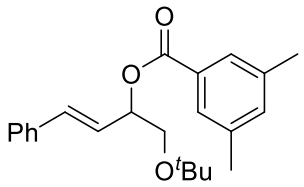


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 2-methylbenzoate (**4k**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 38.6 mg, 57% yield, yellow oil, HPLC: 69% ee, t_R = 4.119 min (minor), t_R = 5.259 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.96 (d, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 3H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.75 (q, *J* = 6.1 Hz, 1H), 3.66 (qd, *J* = 9.9, 5.7 Hz, 2H), 2.62 (s, 3H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 166.9, 140.1, 136.4, 133.2, 131.8, 131.6, 130.5, 130.1, 128.5, 127.9, 126.6, 125.6, 125.2, 74.5, 73.3, 63.9, 27.5, 21.7; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1798.

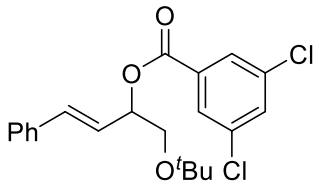


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 3-methylbenzoate (**4l**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 42.6 mg, 63% yield: yellow oil, HPLC: 71% ee, t_R = 4.485 min (minor), t_R = 6.196 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.89 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.6 Hz, 3H), 7.35 – 7.27 (m, 3H), 7.24 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.75 (q, *J* = 6.1 Hz, 1H), 3.75 – 3.60 (m, 2H), 2.41 (s, 3H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 166.0, 138.1, 136.4, 133.6, 133.1, 130.5,

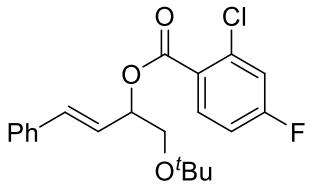
130.2, 128.5, 128.2, 127.9, 126.8, 126.6, 125.2, 74.5, 73.4, 63.9, 27.5, 21.3; HRMS (ESI-TOF) *m/z*: $C_{22}H_{26}NaO_3$ $(M + Na)^+$ calcd for 361.1774, found 361.1800.



(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 3,5-dimethylbenzoate (4m), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 34.5 mg, 49% yield, colorless oil, HPLC: 57% ee, t_R = 4.547 min (minor), t_R = 5,437 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.70 (s, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.19 (s, 1H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.75 (q, *J* = 6.1 Hz, 1H), 3.79 – 3.55 (m, 2H), 2.36 (s, 6H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 166.2, 137.9, 136.4, 134.5, 133.1, 130.4, 128.5, 127.9, 127.4, 126.6, 125.2, 74.3, 73.4, 63.9, 27.5, 21.2; HRMS (ESI-TOF) *m/z*: $C_{23}H_{28}NaO_3$ $(M + Na)^+$ calcd for 375.1931, found 375.1956.

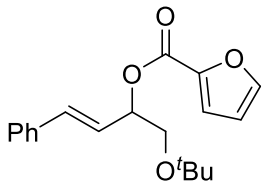


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 3,5-dichlorobenzoate (**4n**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 32.9 mg, 42% yield, yellow oil, HPLC: 49% ee, t_R = 3.793 min (minor), t_R = 4.152 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.94 (d, *J* = 1.6 Hz, 2H), 7.54 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 6.7 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.28 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.74 (q, *J* = 6.7 Hz, 1H), 3.75 – 3.59 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 163.6, 136.0, 135.2, 134.1, 133.4, 132.7, 128.6, 128.1, 128.1, 126.7, 124.1, 75.7, 73.5, 63.8, 27.4; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}Cl_2NaO_3$ $(M + Na)^+$ calcd for 415.0838, found 415.0865.

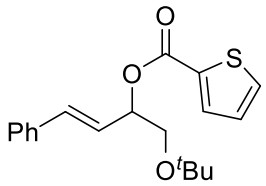


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 2-chloro-4-fluorobenzoate (4o), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 33.8 mg, 45% yield, white solid (mp 90-92 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.01 – 7.86 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.16 (m, 1H), 7.07 – 6.98 (m, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.76 (q, *J* = 6.3 Hz, 1H), 3.66 (dt, *J* = 10.0, 6.1 Hz, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 164.0, 164.0 (d, *J* = 254.3 Hz, 1C), 136.2, 135.7 (d, *J* = 10.6 Hz, 1C), 133.9, 133.5 (d, *J* = 9.5 Hz, 1C), 128.5, 128.0, 126.7, 126.6 (d, *J* = 3.5 Hz,

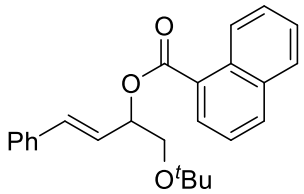
1C), 124.4, 118.5 (d, J = 24.6 Hz, 1C), 114.0 (d, J = 21.2 Hz, 1C), 75.6, 73.4, 63.7, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.7 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}ClFNaO_3$ $(M + Na)^+$ calcd for 399.1134, found 399.1160.



(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl furan-2-carboxylate (4p), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 27.0 mg, 43% yield, colorless oil, HPLC: 70% ee, t_R = 6.750 min (minor), t_R = 8.378 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.62 – 7.54 (m, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.23 (dd, J = 12.7, 5.3 Hz, 2H), 6.75 (d, J = 16.0 Hz, 1H), 6.51 (dd, J = 3.4, 1.6 Hz, 1H), 6.29 (dd, J = 16.0, 7.0 Hz, 1H), 5.74 (q, J = 6.1 Hz, 1H), 3.66 (qd, J = 10.1, 5.7 Hz, 2H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 158.0, 146.2, 144.8, 136.2, 133.7, 128.5, 128.0, 126.6, 124.6, 117.9, 111.8, 74.6, 73.5, 63.8, 27.4; HRMS (ESI-TOF) *m/z*: $C_{19}H_{22}NaO_4$ $(M + Na)^+$ calcd for 337.1410, found 337.1435.

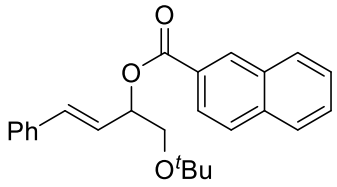


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl thiophene-2-carboxylate (**4q**), by silica gel column chromatography (hexane/ethyl acetate = 40:1), 35.7 mg, 54% yield, yellow oil, HPLC: 71% ee, t_R = 5.487 min (minor), t_R = 7.711 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:7.84 (dd, J = 3.7, 1.1 Hz, 1H), 7.55 (dd, J = 5.0, 1.1 Hz, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.10 (dd, J = 4.9, 3.8 Hz, 1H), 6.75 (d, J = 16.0 Hz, 1H), 6.29 (dd, J = 16.0, 6.9 Hz, 1H), 5.71 (q, J = 5.8 Hz, 1H), 3.75 – 3.54 (m, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 161.5, 136.3, 134.1 (2C), 133.4, 132.3, 128.5, 127.9, 127.7, 126.6, 124.8, 74.8, 73.4, 63.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{19}H_{22}NaO_3S$ $(M + Na)^+$ calcd for 353.1182, found 353.1106.

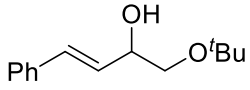


(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 1-naphthoate (4r), by silica gel column chromatography (hexane/ethyl acetate = 30:1), 34.4 mg, 46% yield, yellow oil, HPLC: 69% ee, t_R = 5.185 min (minor), t_R = 6.579 min (major) (Chiralcel AD-H column, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 28°C, 254 nm), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.95 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.52 (q, J = 7.2 Hz, 2H), 7.41 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.25 (d, J = 7.0 Hz, 1H), 6.82 (d, J = 16.0 Hz, 1H), 6.37 (dd, J = 16.0, 7.0 Hz, 1H), 5.89 (q, J = 6.4 Hz, 1H), 3.83 –

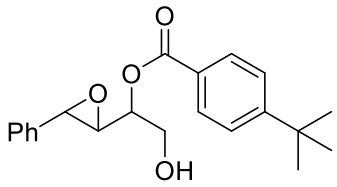
3.61 (m, 2H), 1.25 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 167.1, 136.4, 133.8, 133.5, 133.1, 131.3, 130.0, 128.5, 128.4, 127.9, 127.6, 126.6 (2C), 126.1 (2C), 125.0, 124.5, 74.9, 73.4, 63.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{25}H_{26}NaO_3$ $(M + Na)^+$ calcd for 397.1774, found 397.1802.



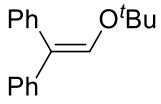
(*E*)-1-(tert-butoxy)-4-phenylbut-3-en-2-yl 2-naphthoate (4s), by silica gel column chromatography (hexane/ethyl acetate = 30:1), 39.7 mg, 53% yield, white solid (mp 95-97 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ:8.66 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.89 (dd, *J* = 8.2, 3.2 Hz, 2H), 7.56 (dq, *J* = 14.6, 6.9 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.20 (m, 1H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.83 (q, *J* = 6.0 Hz, 1H), 3.84 – 3.61 (m, 2H), 1.22 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 166.0, 136.4, 135.5, 133.3, 132.5, 131.1, 129.4, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 126.6 (2v), 125.4, 125.1, 74.7, 73.4, 64.0, 27.5; HRMS (ESI-TOF) *m/z*: $C_{25}H_{26}NaO_3$ $(M + Na)^+$ calcd for 397.1774, found 397.1801.



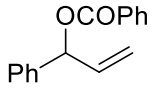
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-ol (**7**), by silica gel column chromatography (hexane/ethyl acetate = 20:1), 34.3 mg, 78% yield, yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.2 Hz, 1H), 4.41 (s, 1H), 3.49 (dd, *J* = 9.0, 3.3 Hz, 1H), 3.30 (t, *J* = 8.7 Hz, 1H), 2.81 (s, 1H), 1.23 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 136.7, 131.5, 128.5, 127.9, 127.6, 126.4, 73.5, 71.6, 65.9, 27.5; HRMS (ESI-TOF) *m/z*: $C_{14}H_{20}NaO_2$ $(M + Na)^+$ calcd for 243.1356, found 243.1376.



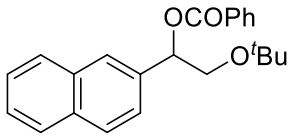
2-hydroxy-1-(3-phenyloxiran-2-yl)ethyl 4-(*tert*-butyl)benzoate (**8**), by silica gel column chromatography (hexane/ethyl acetate = 10:1), 41.2 mg, 52% yield, white solid (mp 98-100 °C), ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 5.31 – 5.21 (m, 1H), 4.77 (d, *J* = 6.2 Hz, 1H), 4.35 (t, *J* = 4.1 Hz, 2H), 4.22 (d, *J* = 4.2 Hz, 1H), 3.30 (s, 1H), 1.34 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 167.4, 157.3, 139.1, 129.6, 128.4, 127.9 (2C), 126.4, 125.9, 125.4, 99.9, 85.8, 84.0, 83.0, 71.1, 35.1, 31.1; HRMS (ESI-TOF) *m/z*: $C_{21}H_{24}NaO_4$ $(M + Na)^+$ calcd for 363.1567, found 363.1599.



(2-(*tert*-butoxy)ethene-1,1-diyl)dibenzene (**10**), by silica gel column chromatography (hexane/ethyl acetate = 50:1), 9.1 mg, 52% yield, Colorless oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 4H), 7.24 (dd, *J* = 6.1, 4.0 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.71 (s, 1H), 1.38 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 141.5, 139.8, 138.1, 129.8, 128.7, 128.2, 127.7, 126.2, 126.0, 120.3, 77.4, 28.1; HRMS (ESI-TOF) *m/z*: $C_{18}H_{20}NaO$ $(M + Na)^+$ calcd for 275.1406, found 275.1415.



1-phenylallyl benzoate (**13**)[5], by silica gel column chromatography (hexane/ethyl acetate = 30:1), 16.7 mg, 35% yield: Yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 15.3, 7.6 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.22 (m, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.42 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.99 (d, *J* = 6.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 166.4, 136.2, 134.3, 133.0, 130.2, 129.6, 128.6, 128.4, 128.1, 126.6, 123.2, 65.5.



2-(*tert*-butoxy)-1-(naphthalen-2-yl)ethyl benzoate (**17**), by silica gel column chromatography (hexane/ethyl acetate = 30:1), 20.5 mg, 18% yield: Yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 7.3 Hz, 2H), 7.90 (s, 1H), 7.83 (t, *J* = 7.9 Hz, 3H), 7.57 (dd, *J* = 7.7, 5.9 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 4H), 6.24 (dd, *J* = 7.7, 4.2 Hz, 1H), 3.90 (dd, *J* = 10.2, 8.0 Hz, 1H), 3.75 (dd, *J* = 10.3, 4.2 Hz, 1H), 1.18 (s, 9H); HRMS (ESI-TOF) *m/z*: $C_{23}H_{24}NaO_3$ $(M + Na)^+$ calcd for 371.1618, found 371.1584.

9. References

[1] P.-Z. Wang, X. Wu, Y. Cheng, M. Jiang, W.-J. Xiao, J.-R. Chen, *Angew. Chem. Int. Ed.* **2021**, *60*, 22956-22962

[2] L.-F. Fan, R. Liu, X.-Y. Ruan, P.-S. Wang, L.-Z. Gong, *Nat. Synth.* **2022**, *1*, 946-955.

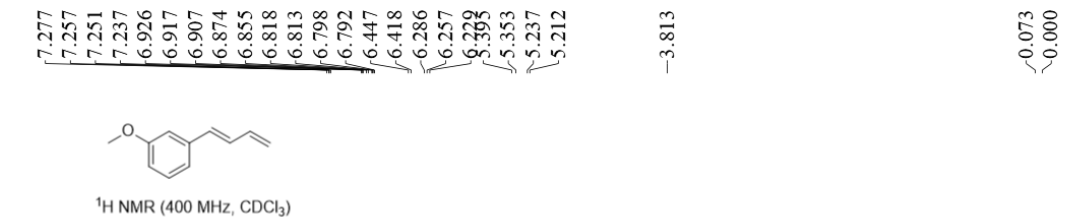
[3] A. Lishchynskyi, K. Muñiz, *Chem. Eur. J.* **2012**, *18*, 2212-2216.

[4] A. Tortajada, O. Ninokata, R. Martin, *J. Am. Chem. Soc.* **2018**, *140*, 2050-2053.

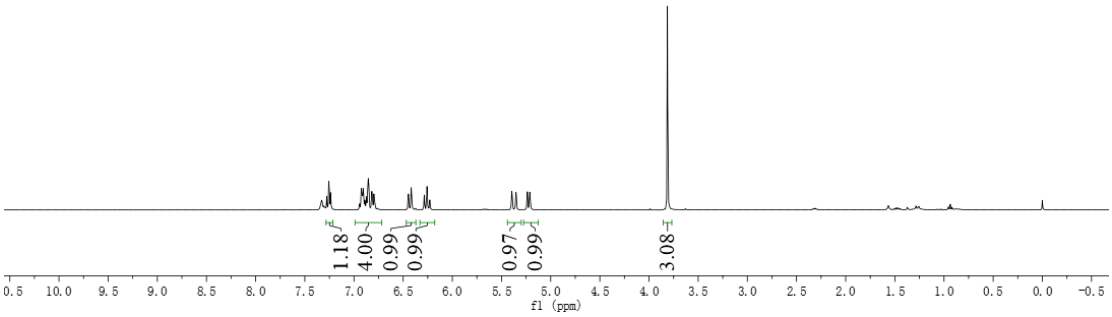
[5] H. Mo, D. Chen, L. Xu , D. Chen, F. Pan , J. Yang, Synthesis, **2015**, 47, 209-215.

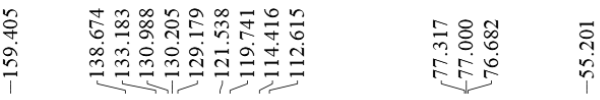
10. NMR Spectra

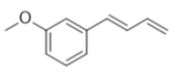
(*E*)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (*E*-1n)



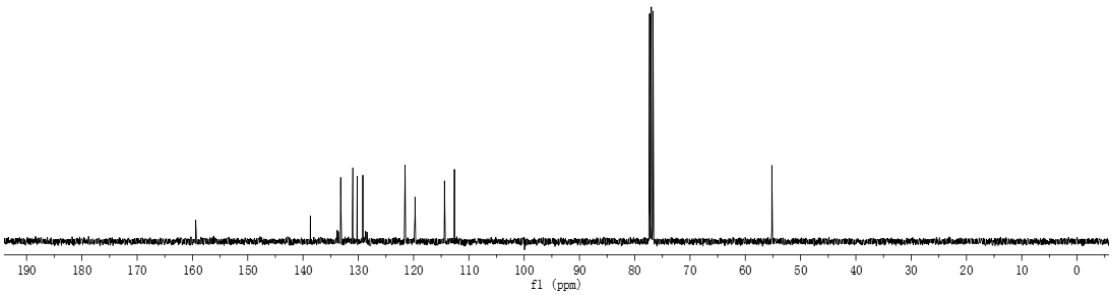
^{1}H NMR (400 MHz, $CDCl_3$)



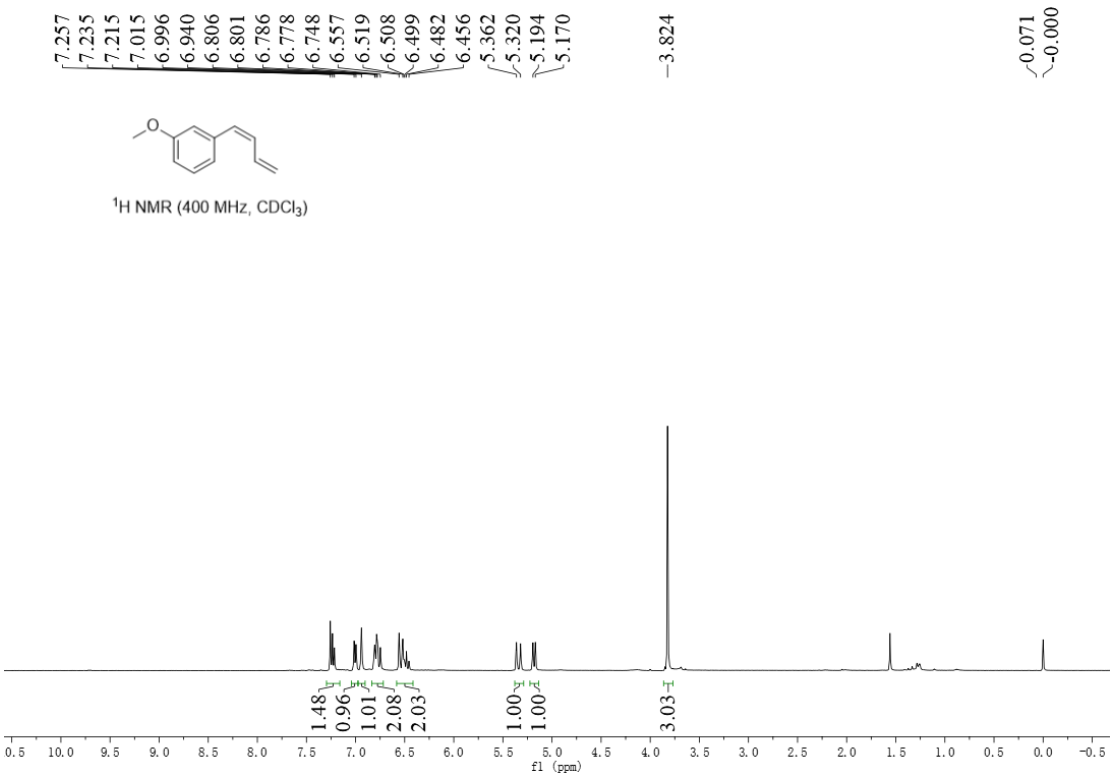




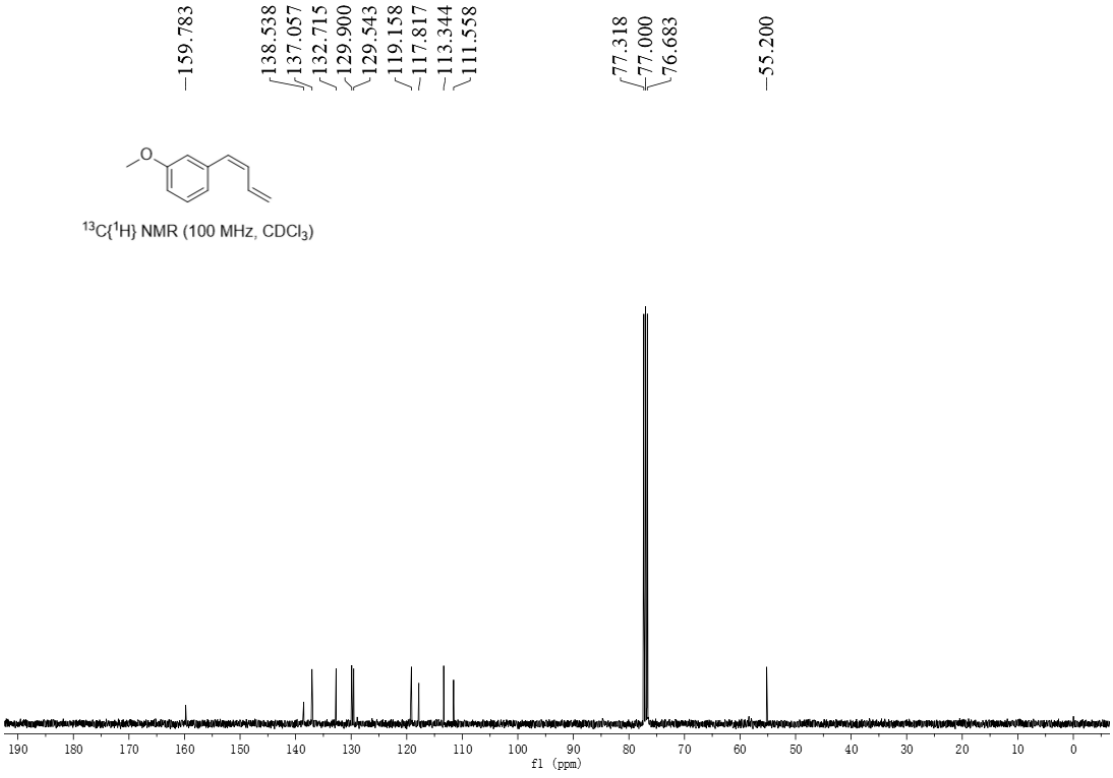
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



(*E*)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (*E*-1n)

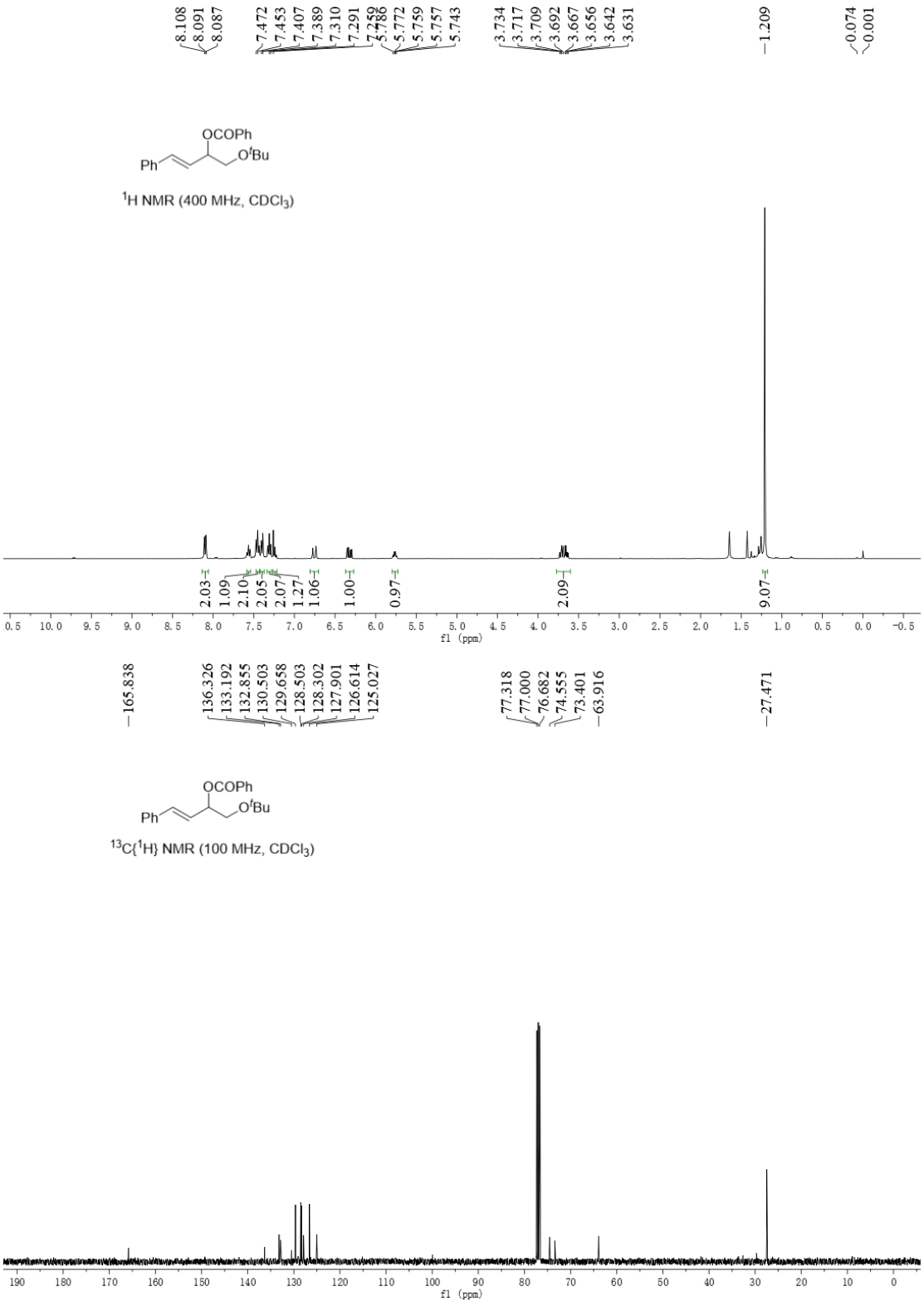


^{1}H NMR (400 MHz, $CDCl_3$)

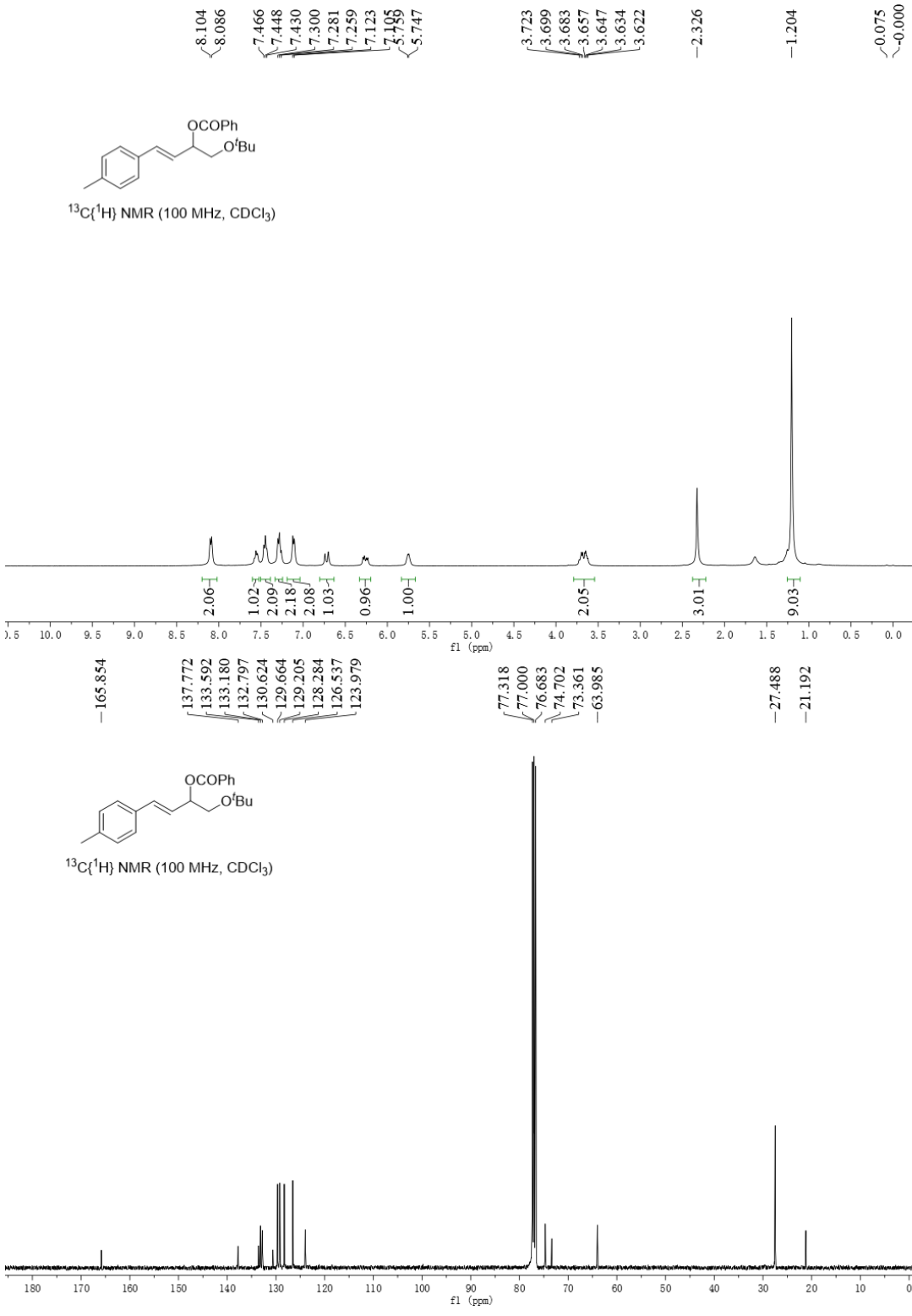


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

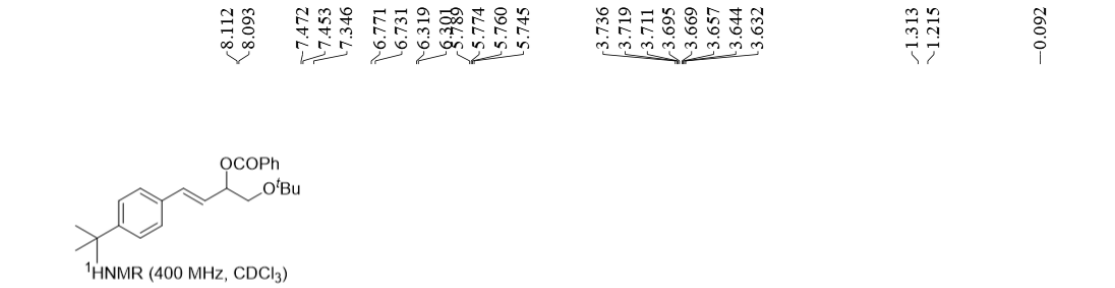
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl benzoate (3a)



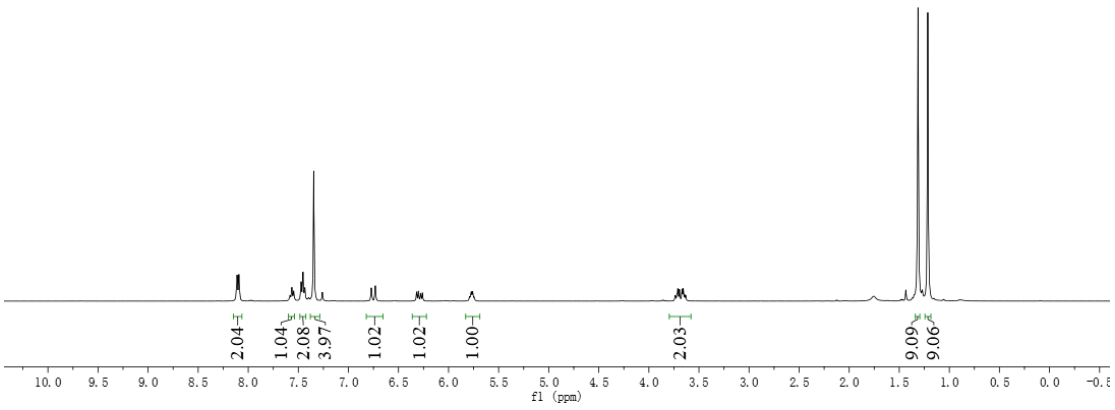
(*E*)-1-(*tert*-butoxy)-4-(p-tolyl)but-3-en-2-yl benzoate (3b)

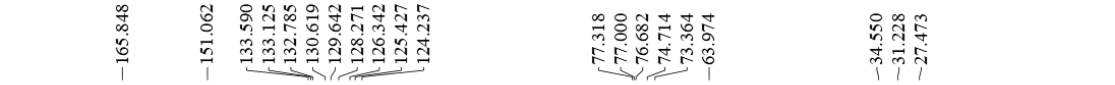


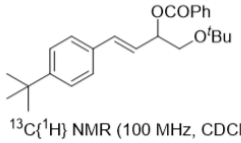
((*E*)-1-(*tert*-butoxy)-4-(4-(*tert*-butyl)phenyl)but-3-en-2-yl benzoate (3c)



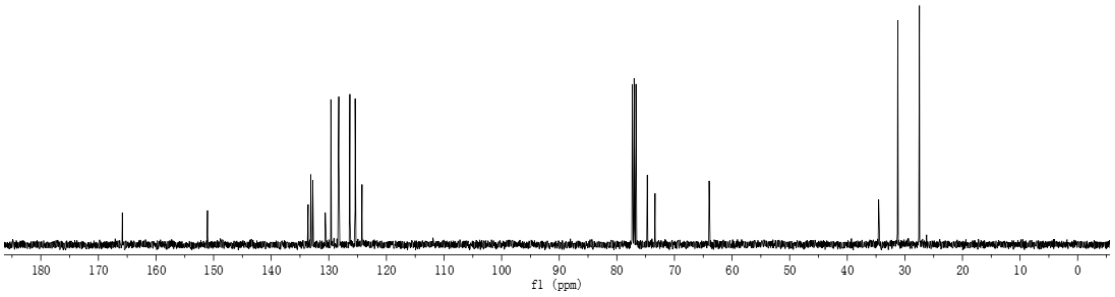
^{1}HNMR (400 MHz, $CDCl_3$)



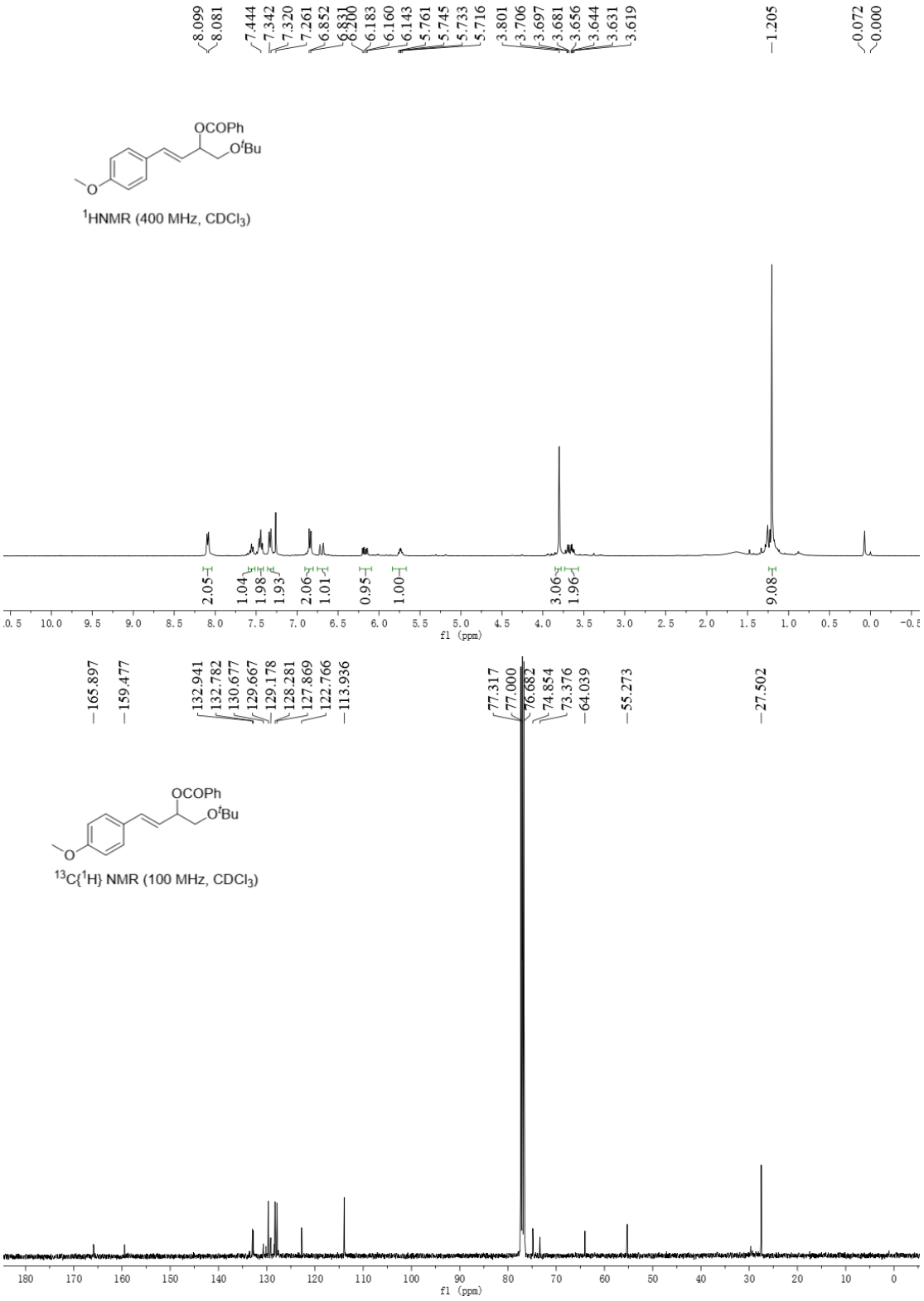




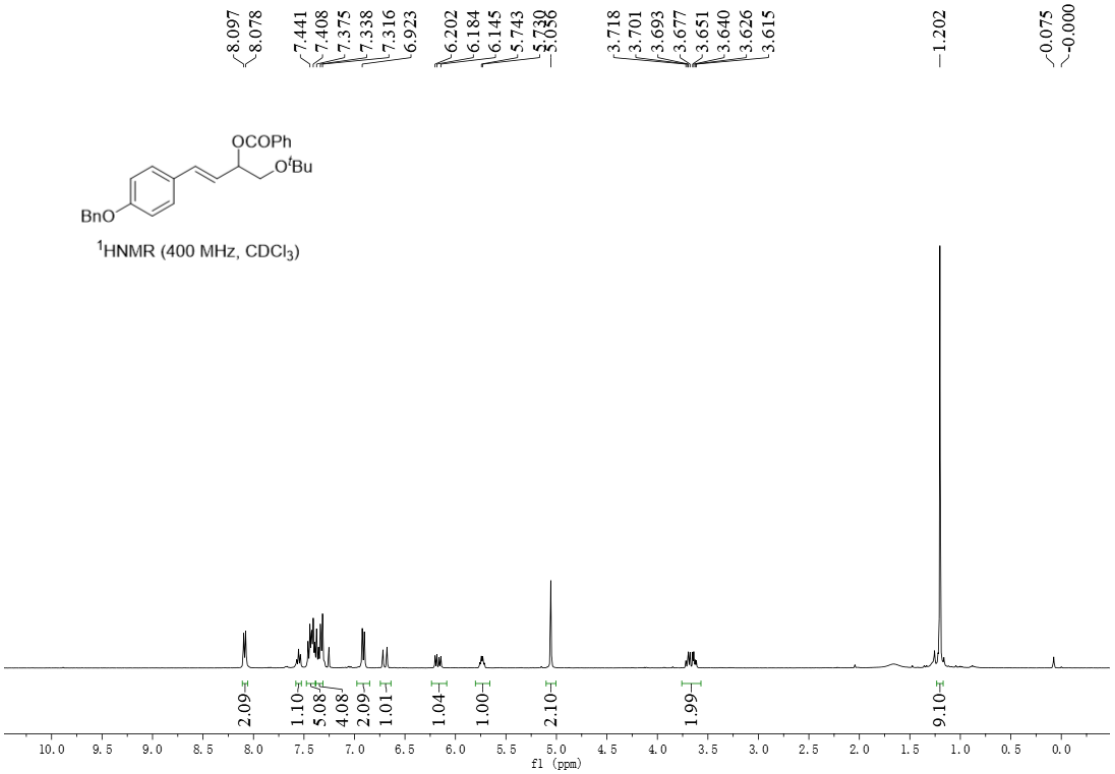
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

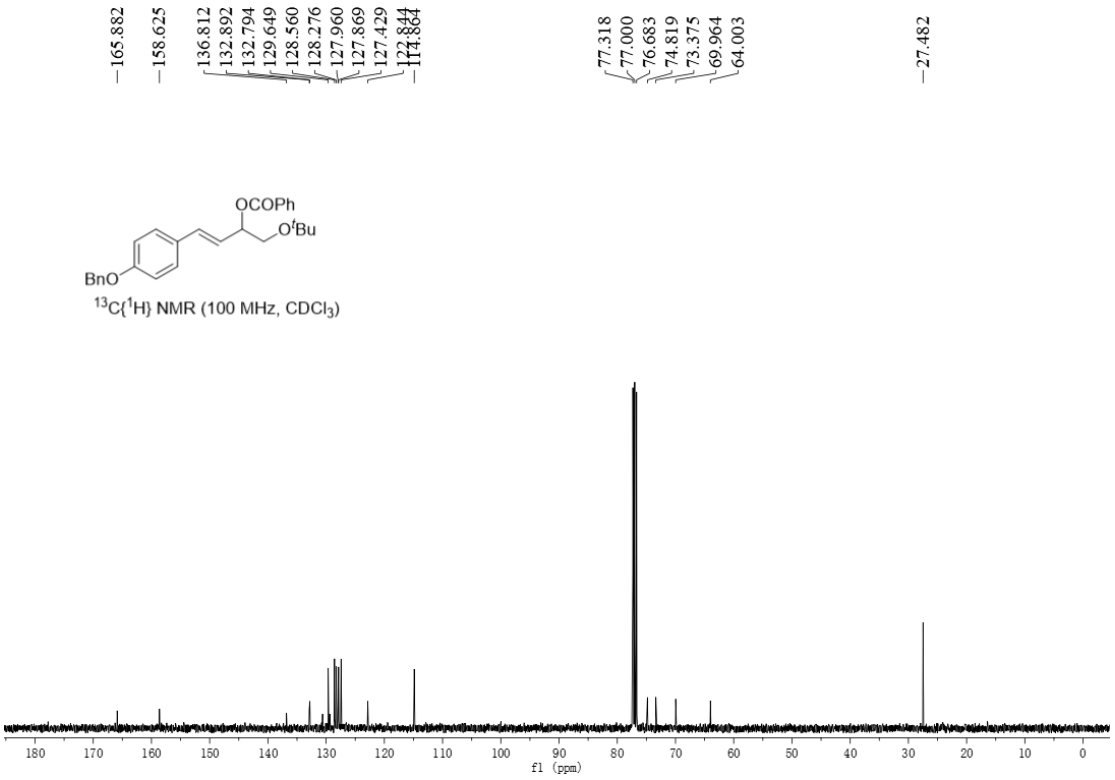


(*E*)-1-(*tert*-butoxy)-4-(4-methoxyphenyl)but-3-en-2-yl benzoate (3d)

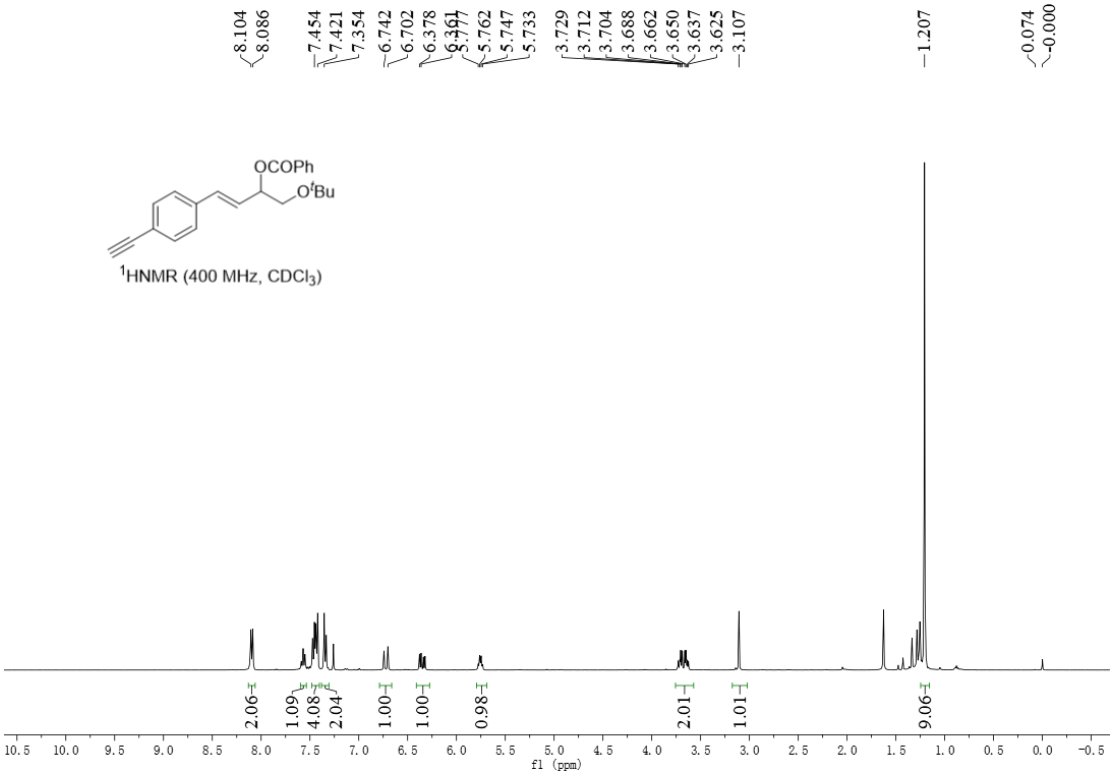


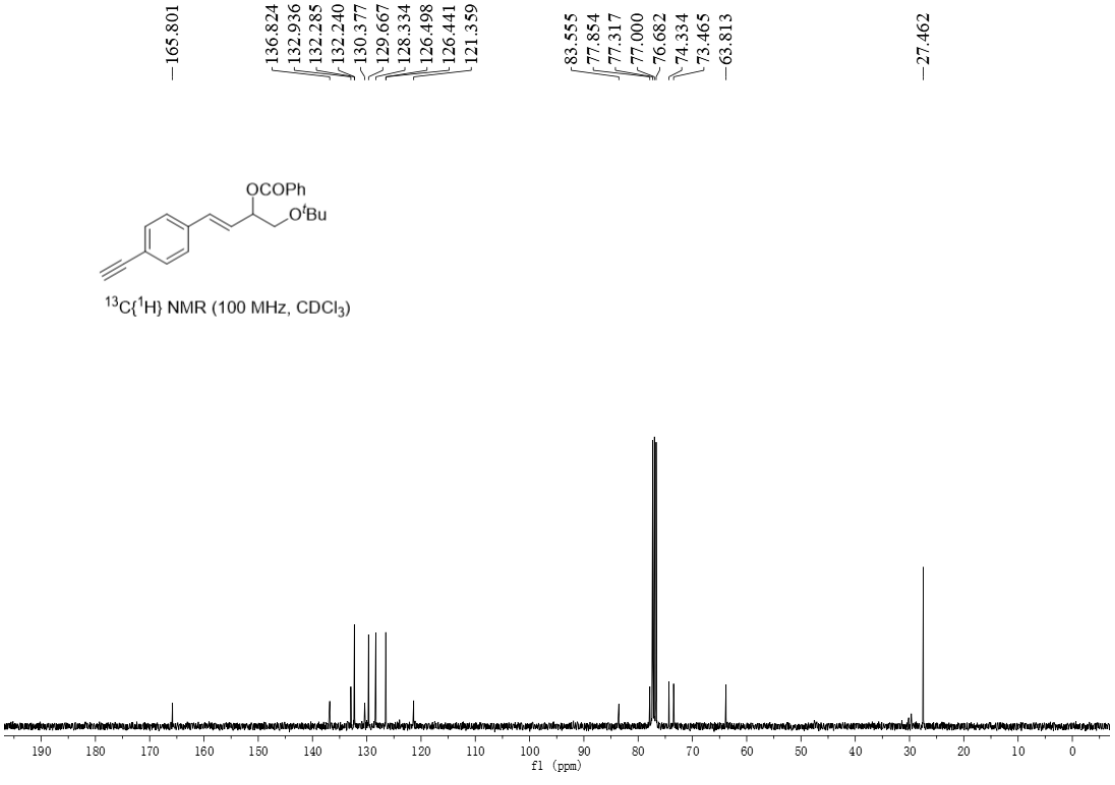
(*E*)-4-(4-(benzyloxy)phenyl)-1-(*tert*-butoxy)but-3-en-2-yl benzoate (3e)



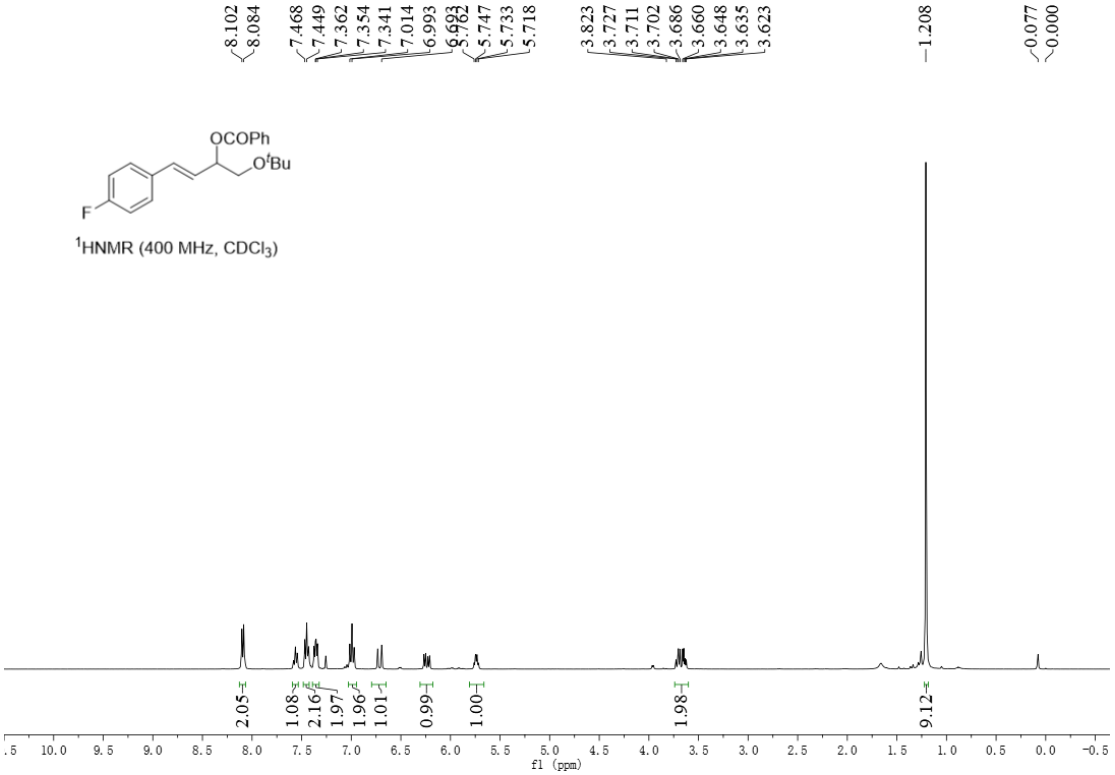


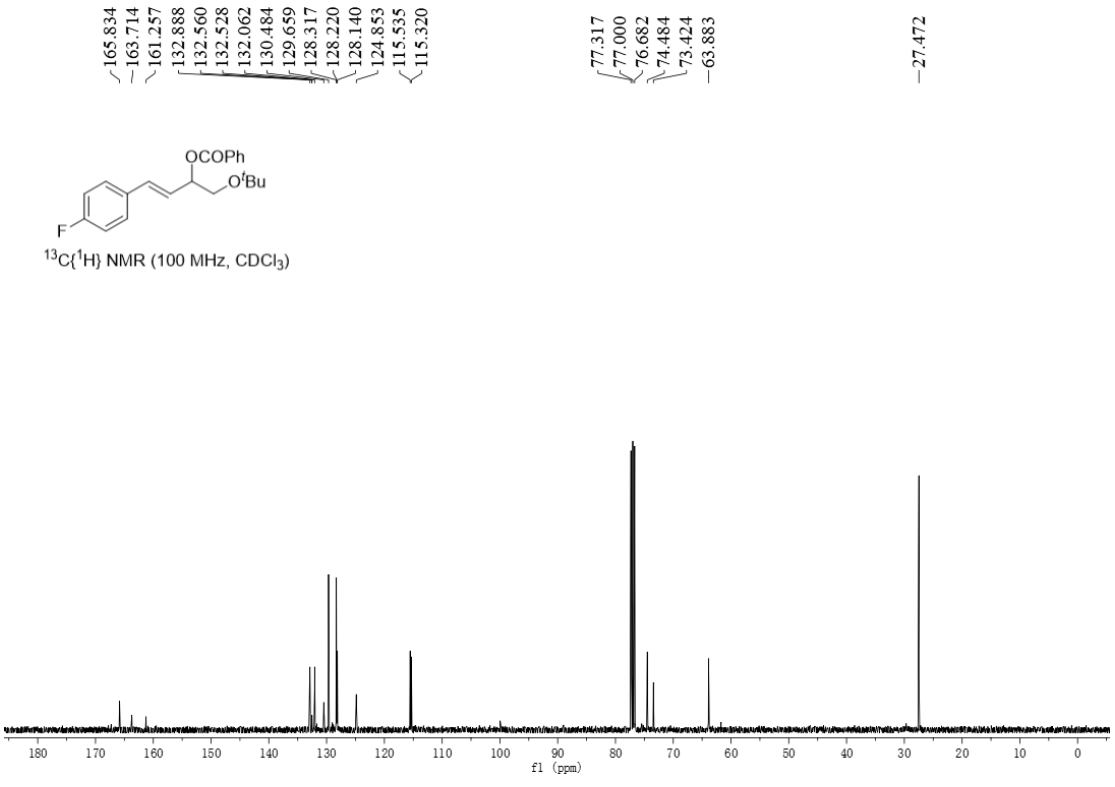
(*E*)-1-(*tert*-butoxy)-4-(4-ethynylphenyl)but-3-en-2-yl benzoate (3f)

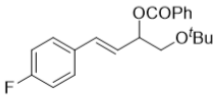




(*E*)-1-(*tert*-butoxy)-4-(4-fluorophenyl)but-3-en-2-yl benzoate (3g)

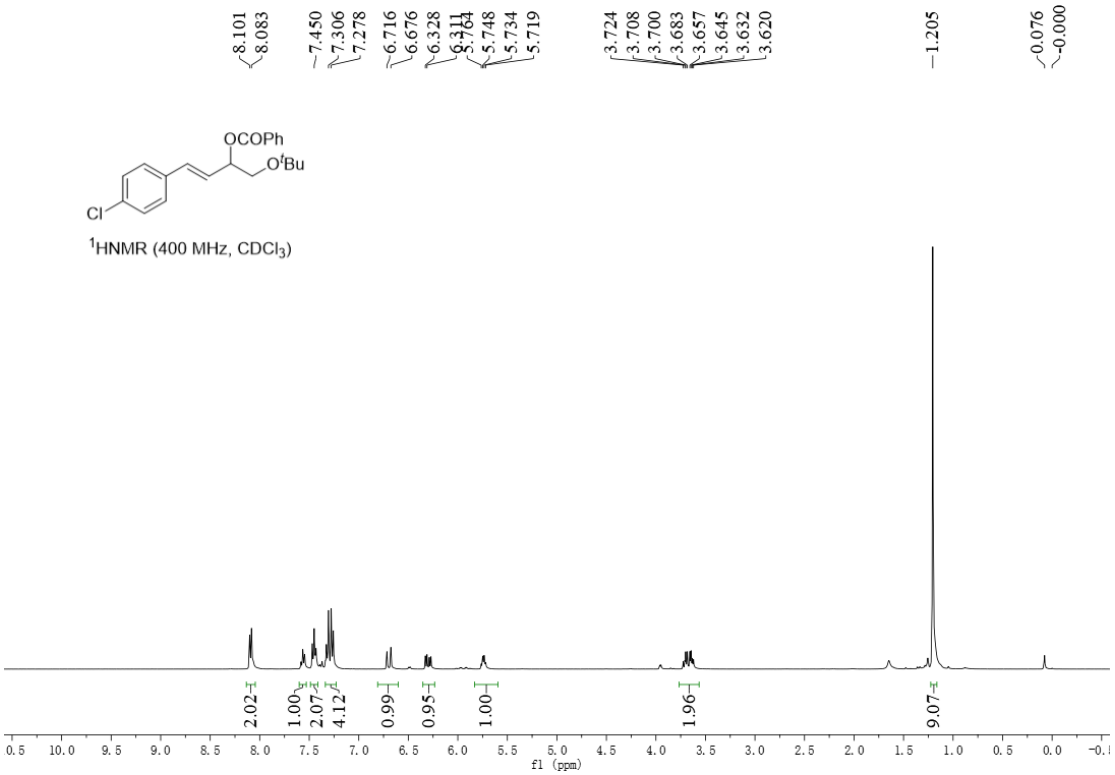


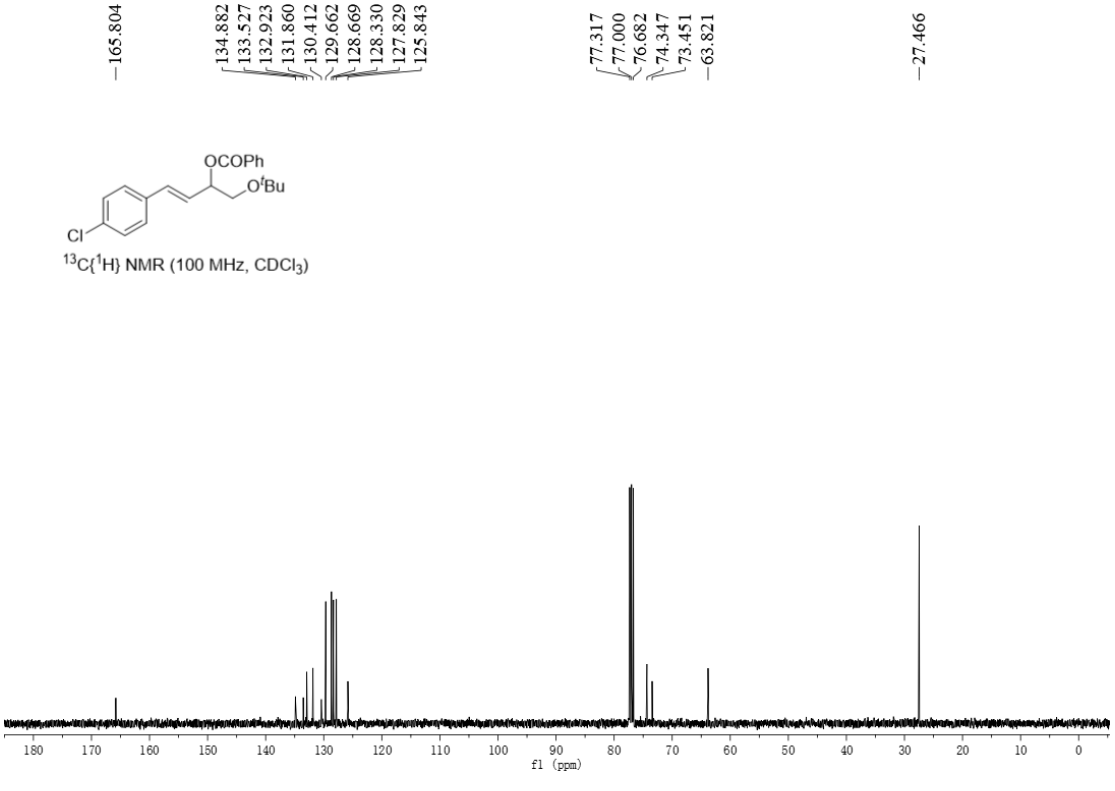




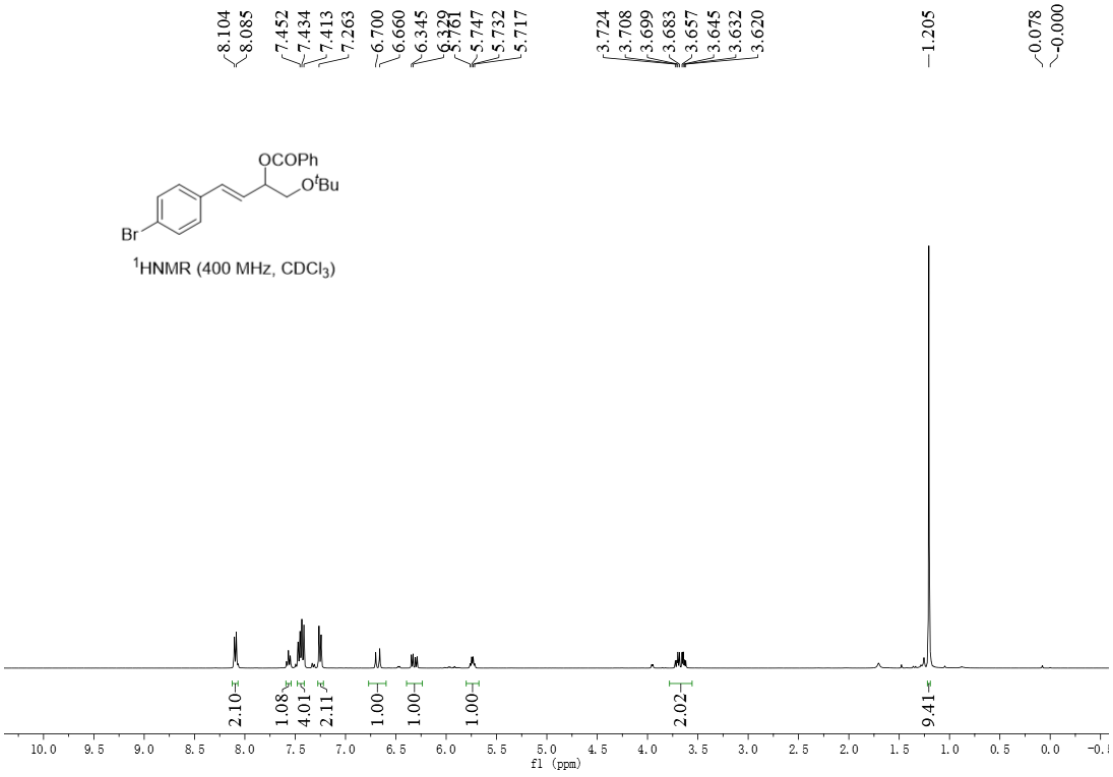
^{19}F NMR (376 MHz, $CDCl_3$)

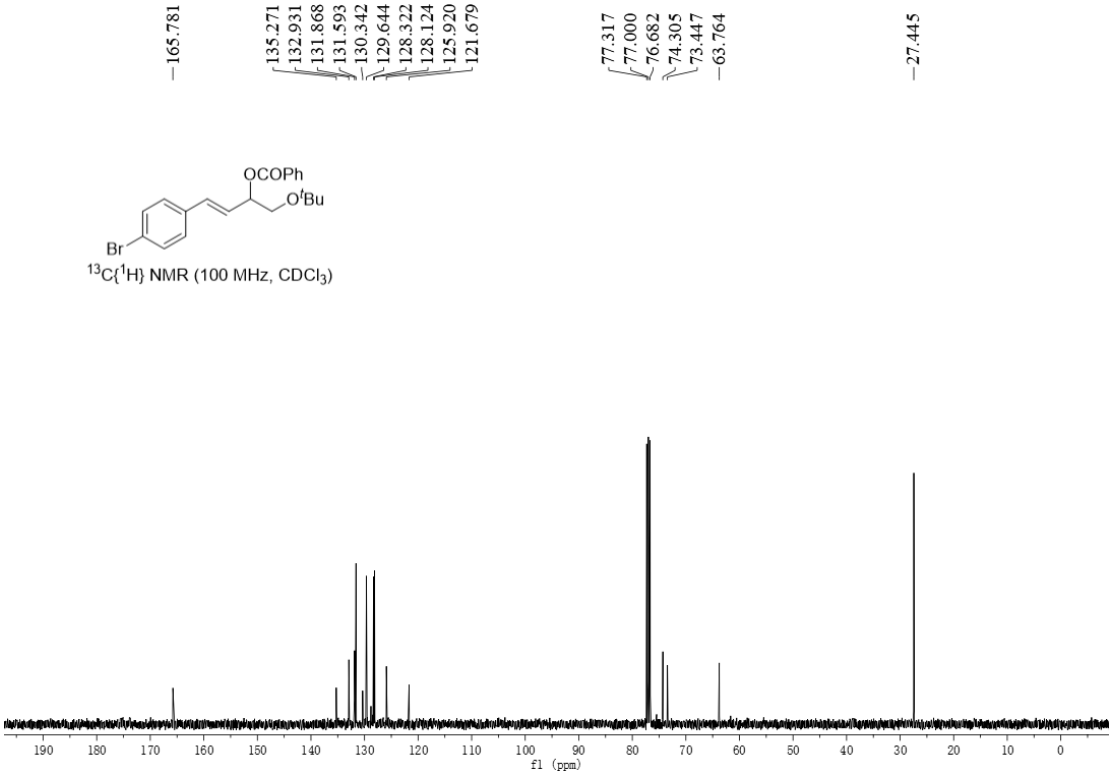
(*E*)-1-(*tert*-butoxy)-4-(4-chlorophenyl)but-3-en-2-yl benzoate (3h)



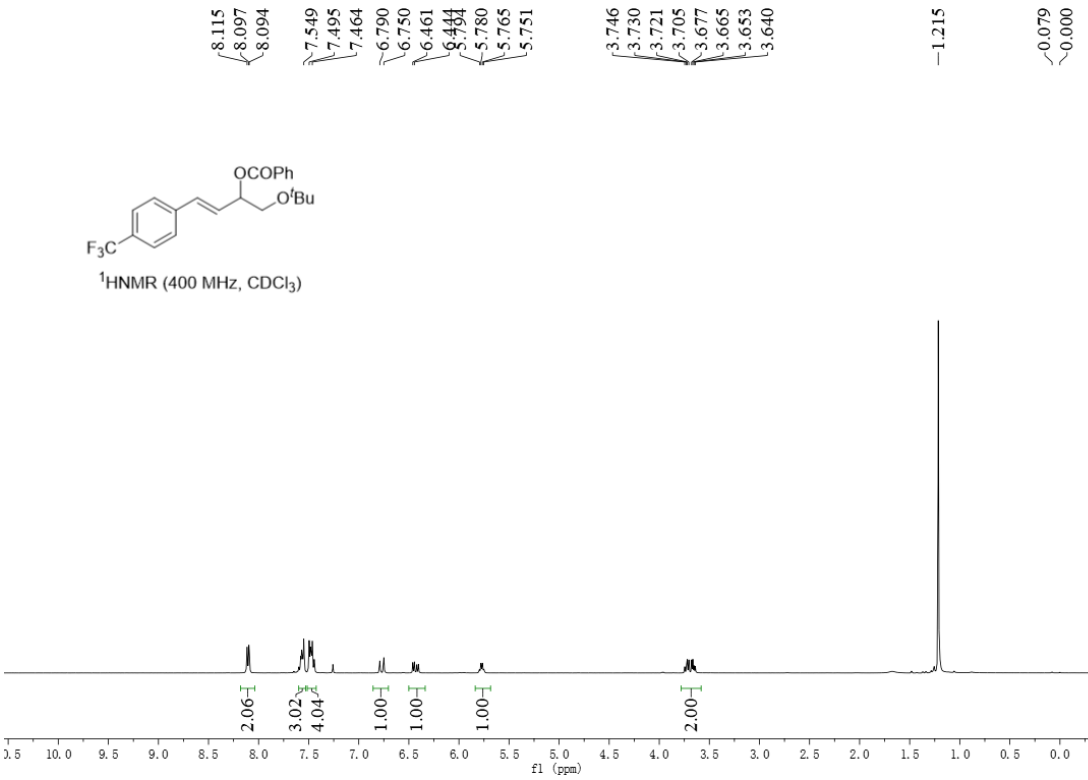


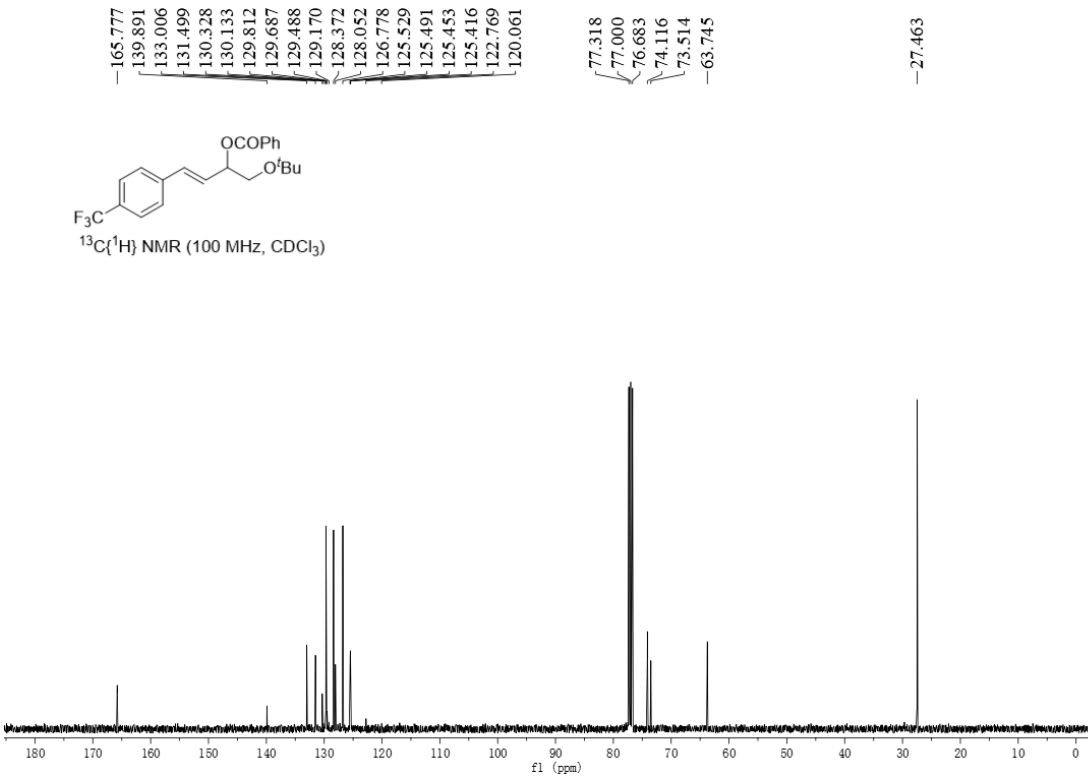
(*E*)-4-(4-bromophenyl)-1-(*tert*-butoxy)but-3-en-2-yl benzoate (3i)

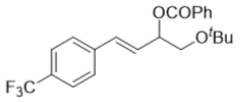




(*E*)-1-(*tert*-butoxy)-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl benzoate (3j)

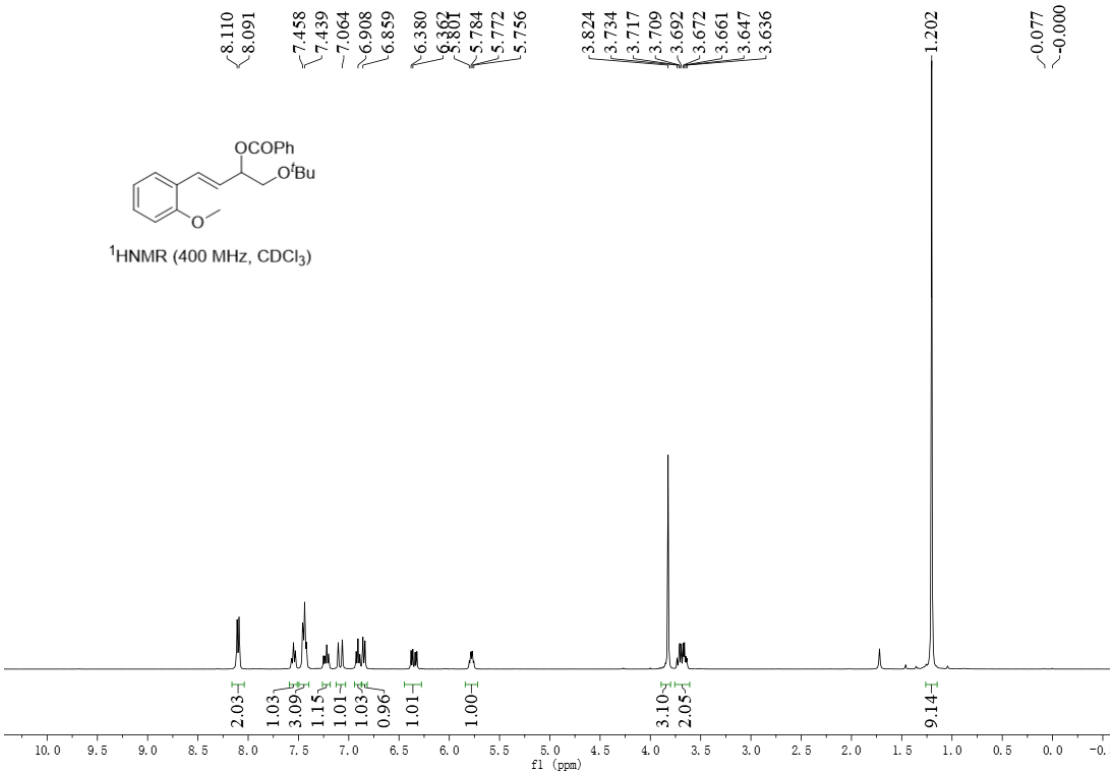


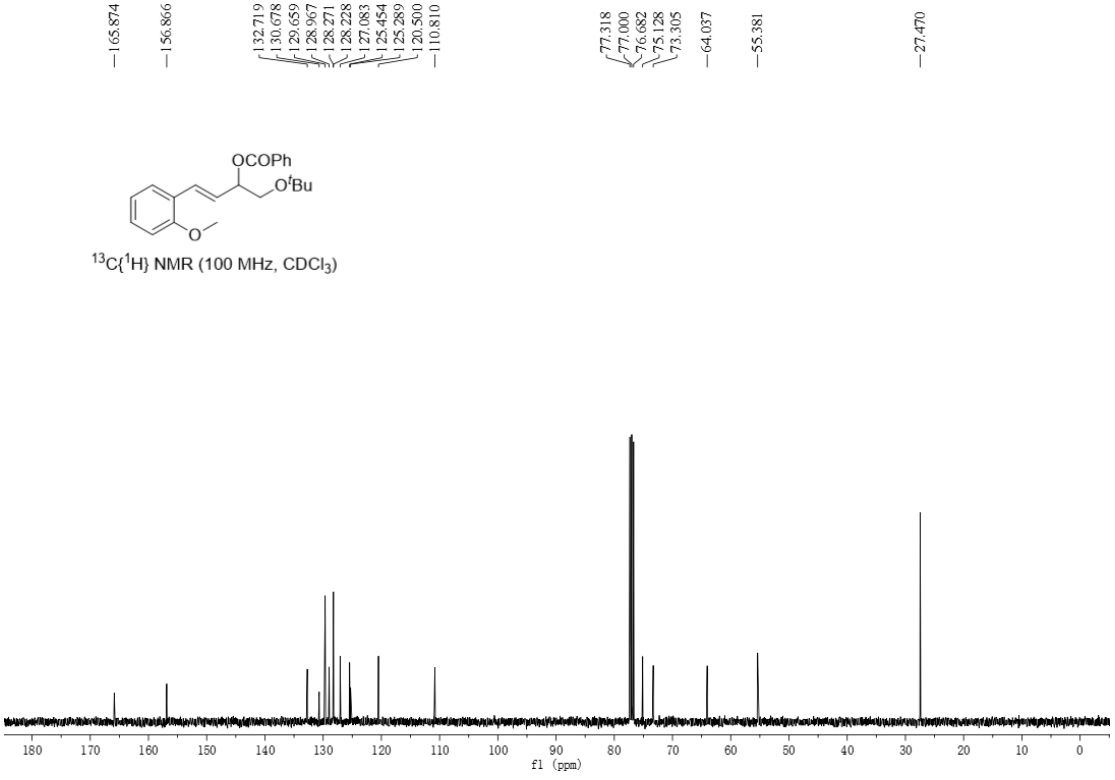




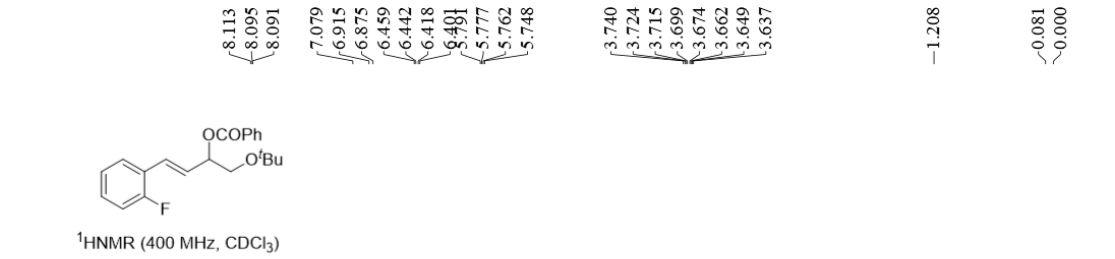
^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-1-(*tert*-butoxy)-4-(2-methoxyphenyl)but-3-en-2-yl benzoate (3k)

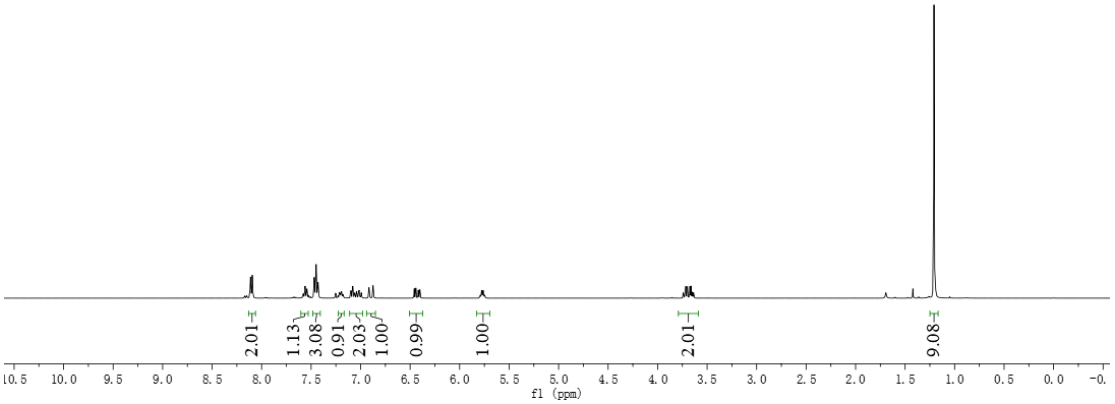


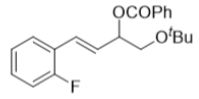


(*E*)-1-(*tert*-butoxy)-4-(2-fluorophenyl)but-3-en-2-yl benzoate (3l)

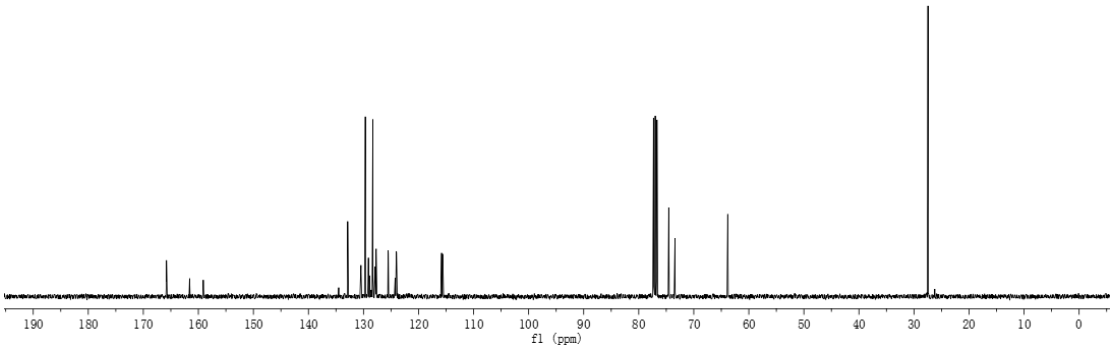


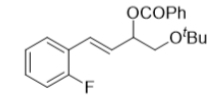
^{1}HNMR (400 MHz, $CDCl_3$)





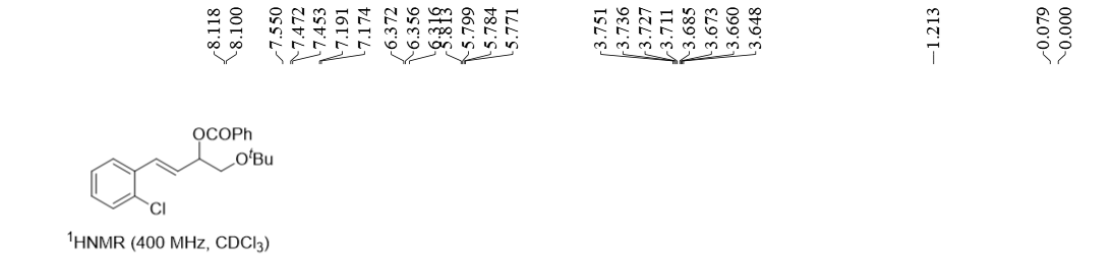
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



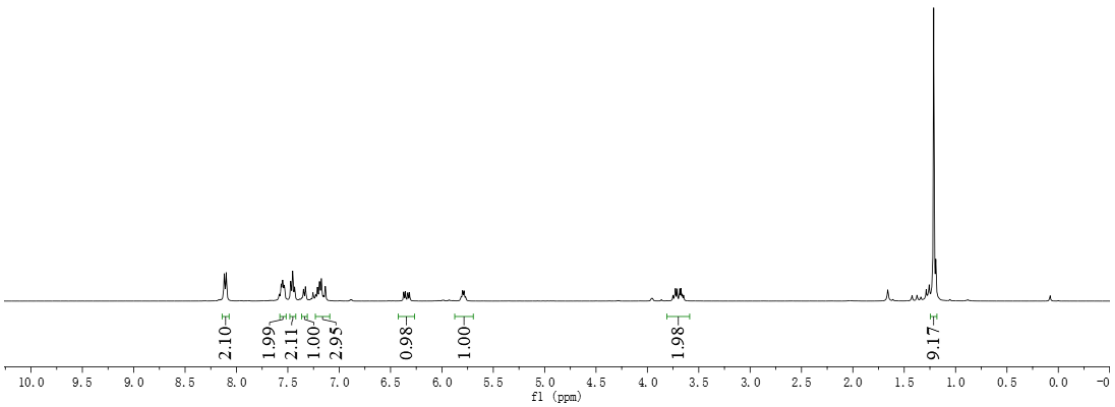


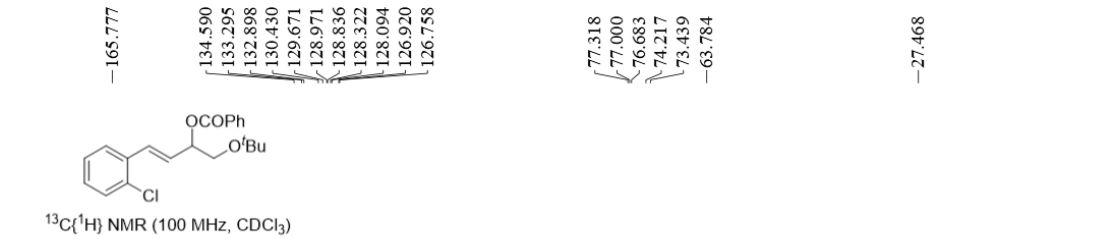
^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-1-(*tert*-butoxy)-4-(2-chlorophenyl)but-3-en-2-yl benzoate (3m)

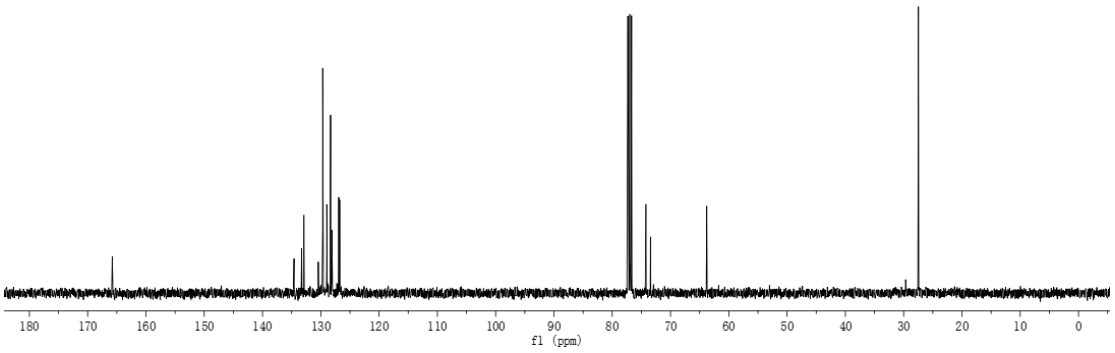


^{1}HNMR (400 MHz, $CDCl_3$)

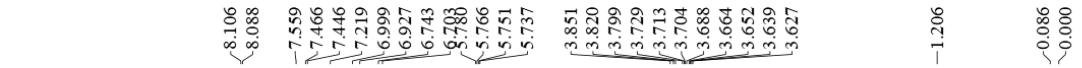


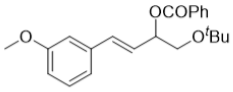


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

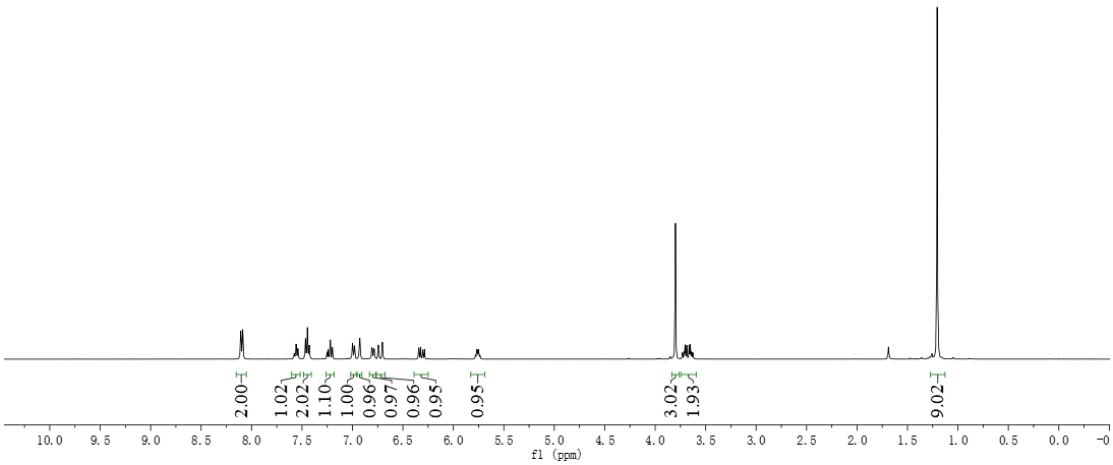


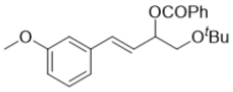
(*E*)-1-(*tert*-butoxy)-4-(3-methoxyphenyl)but-3-en-2-yl benzoate (3n)



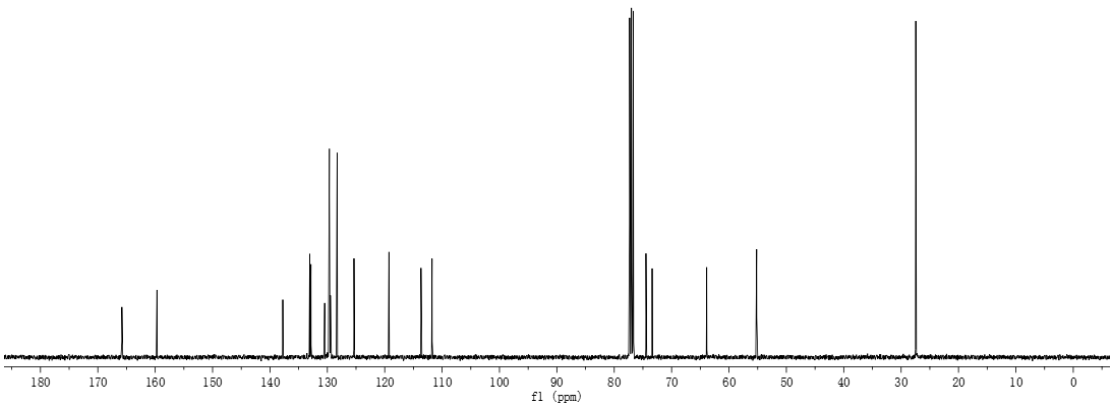


^{1}HNMR (400 MHz, $CDCl_3$)

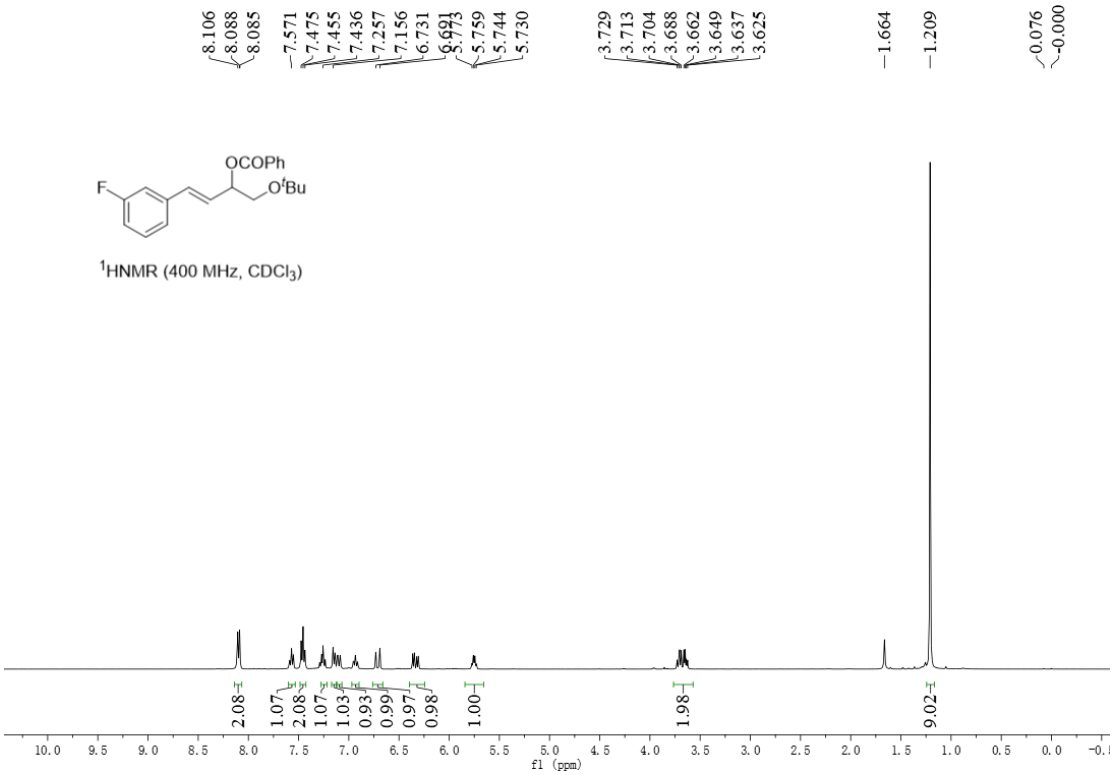


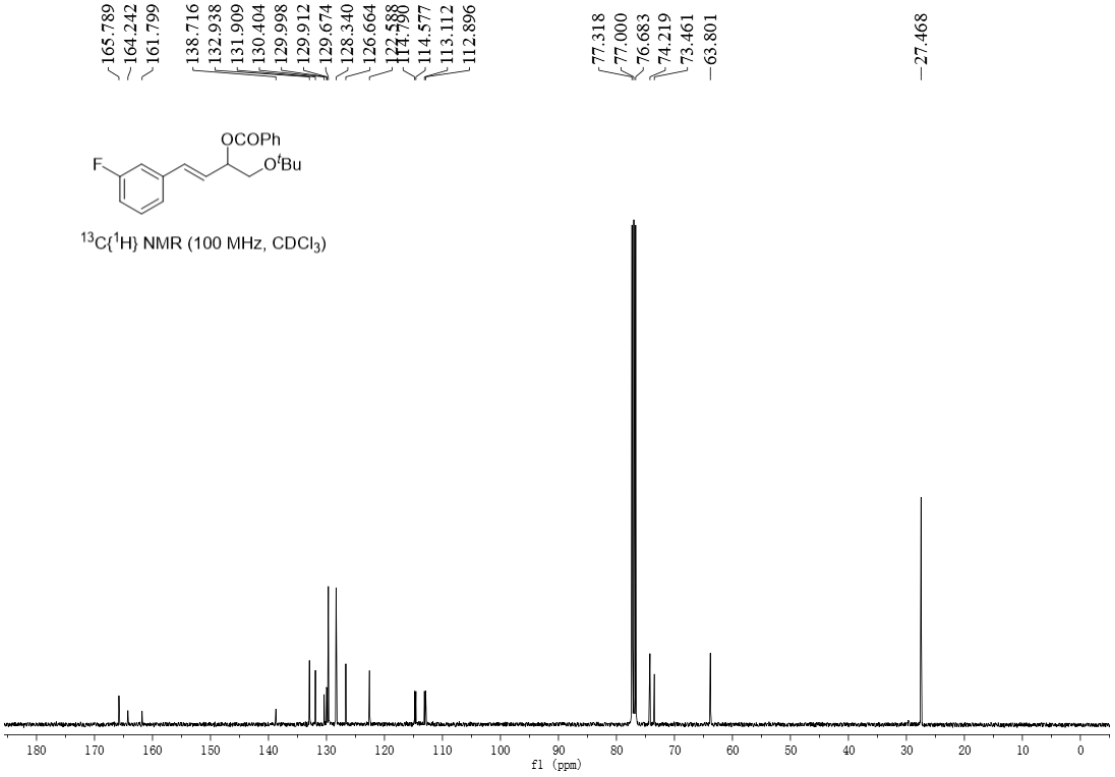


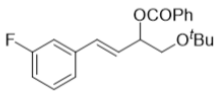
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



(*E*)-1-(*tert*-butoxy)-4-(3-fluorophenyl)but-3-en-2-yl benzoate (3o)



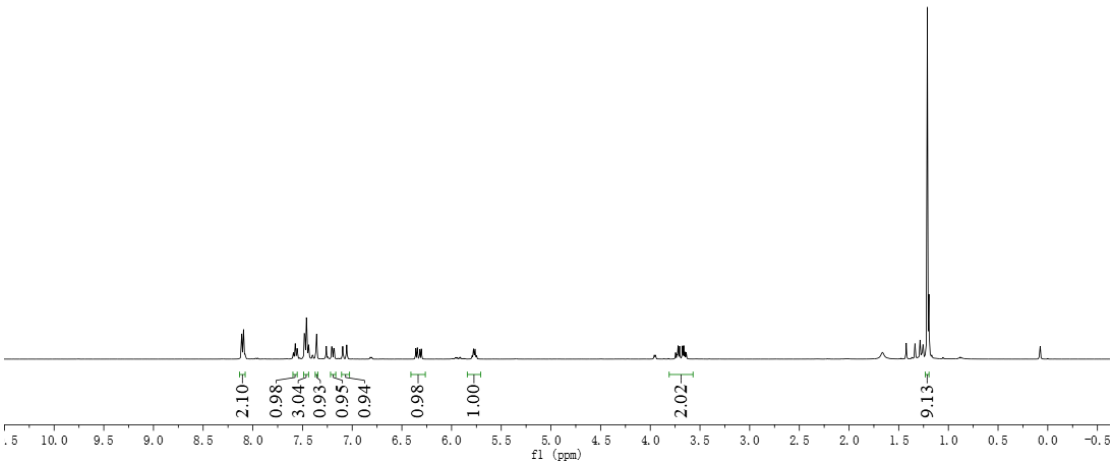


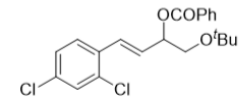


^{19}F NMR (376 MHz, $CDCl_3$)

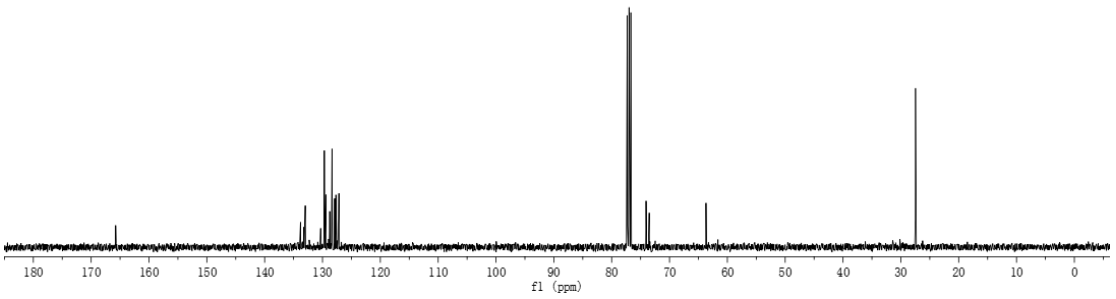
(*E*)-1-(*tert*-butoxy)-4-(2,4-dichlorophenyl)but-3-en-2-yl benzoate (3p)

^{1}HNMR (400 MHz, $CDCl_3$)

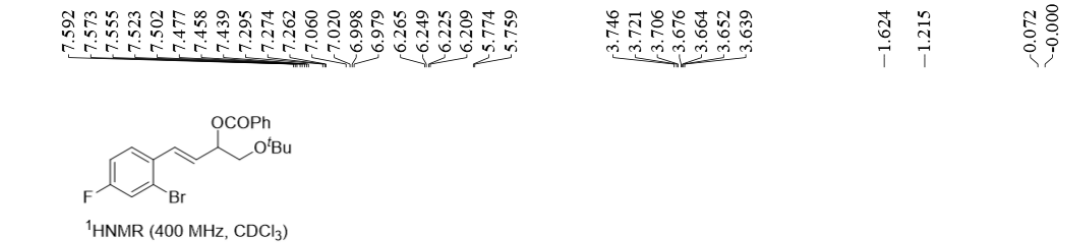




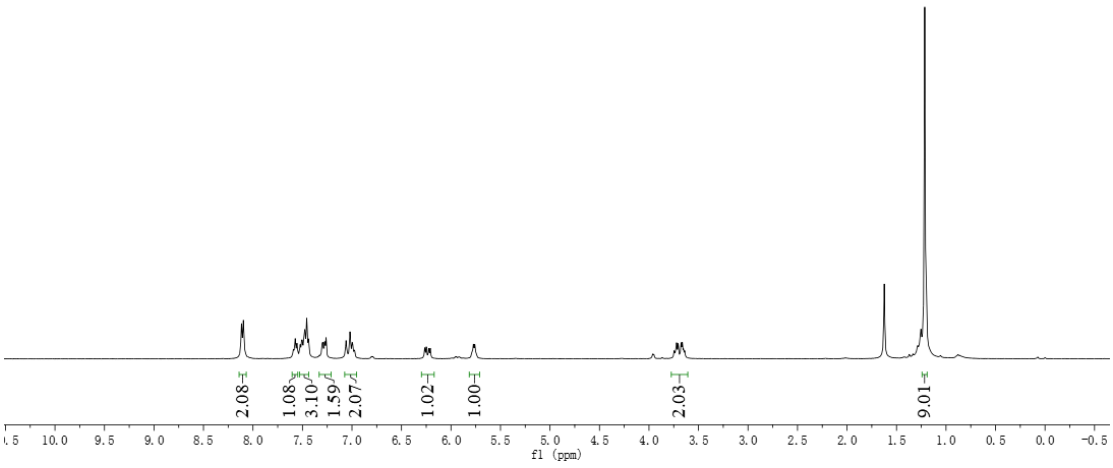
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

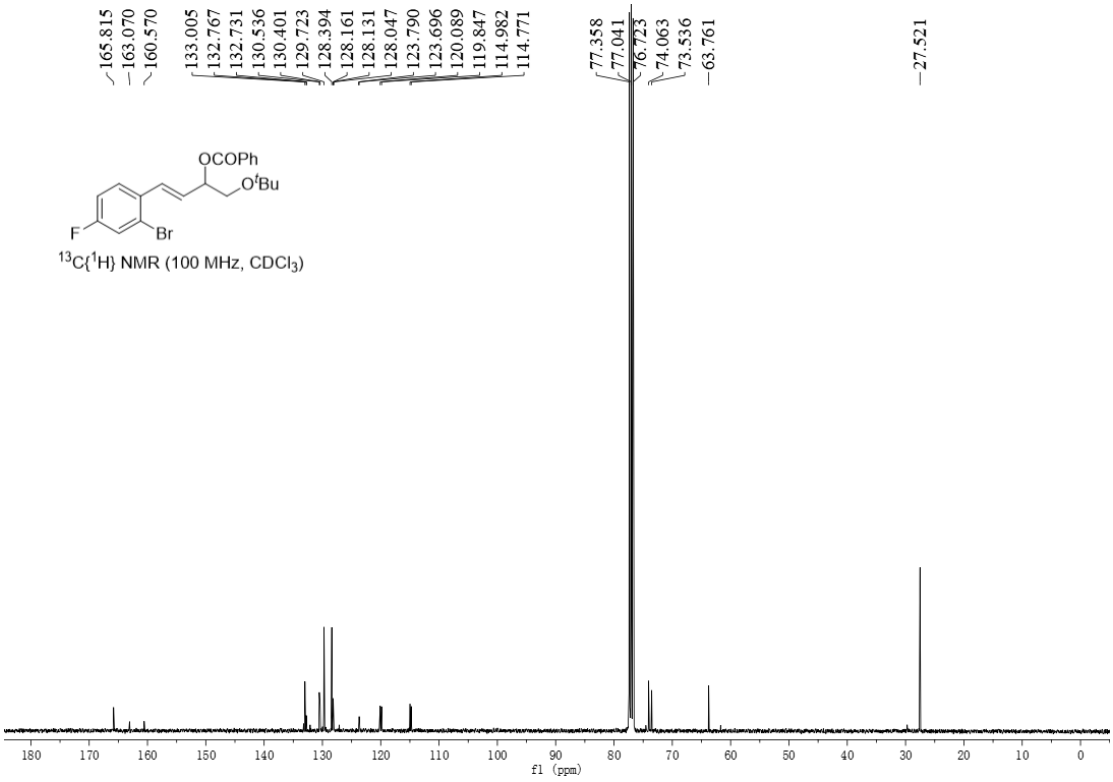


(*E*)-4-(2-bromo-4-fluorophenyl)-1-(*tert*-butoxy)but-3-en-2-yl benzoate (3q)

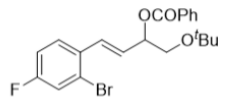


^{1}HNMR (400 MHz, $CDCl_3$)



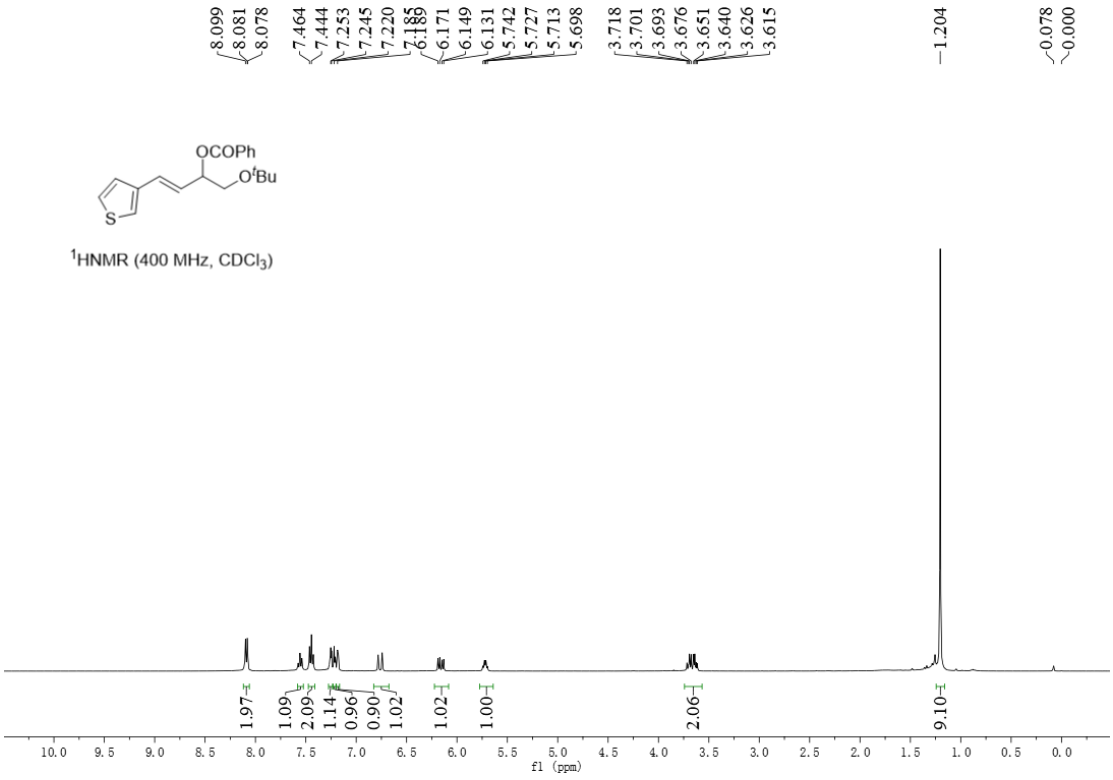


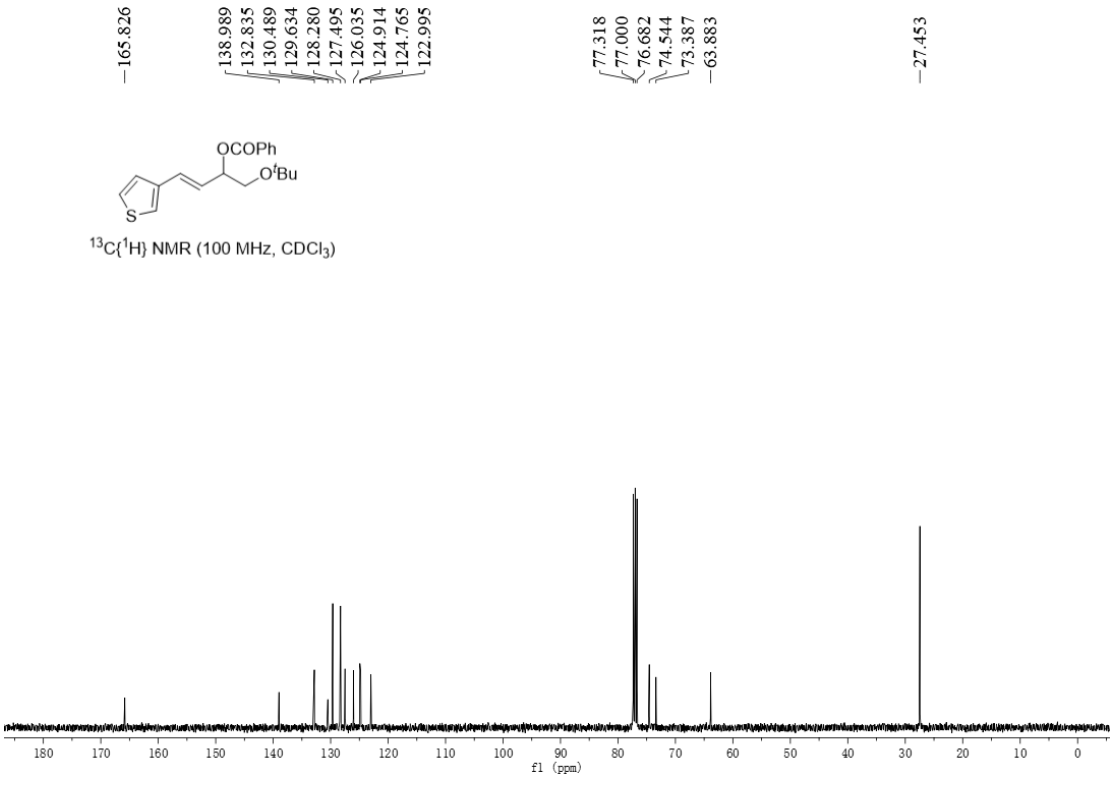
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



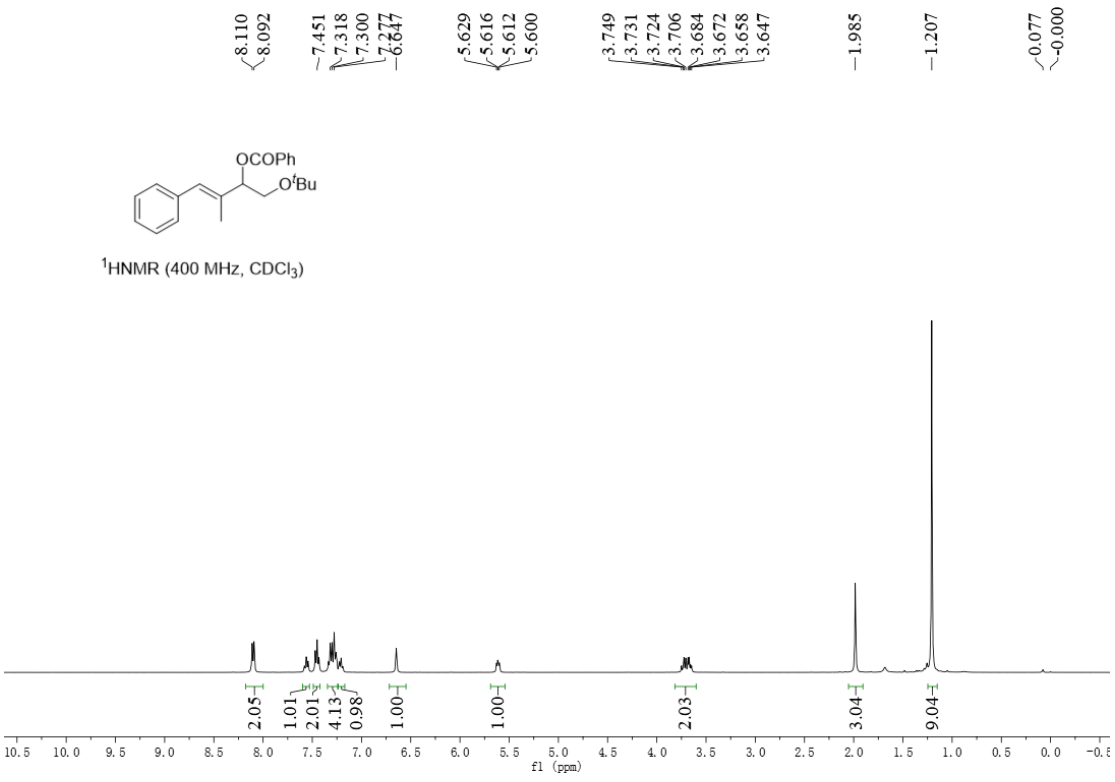
^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-1-(*tert*-butoxy)-4-(thiophen-3-yl)but-3-en-2-yl benzoate (3r)

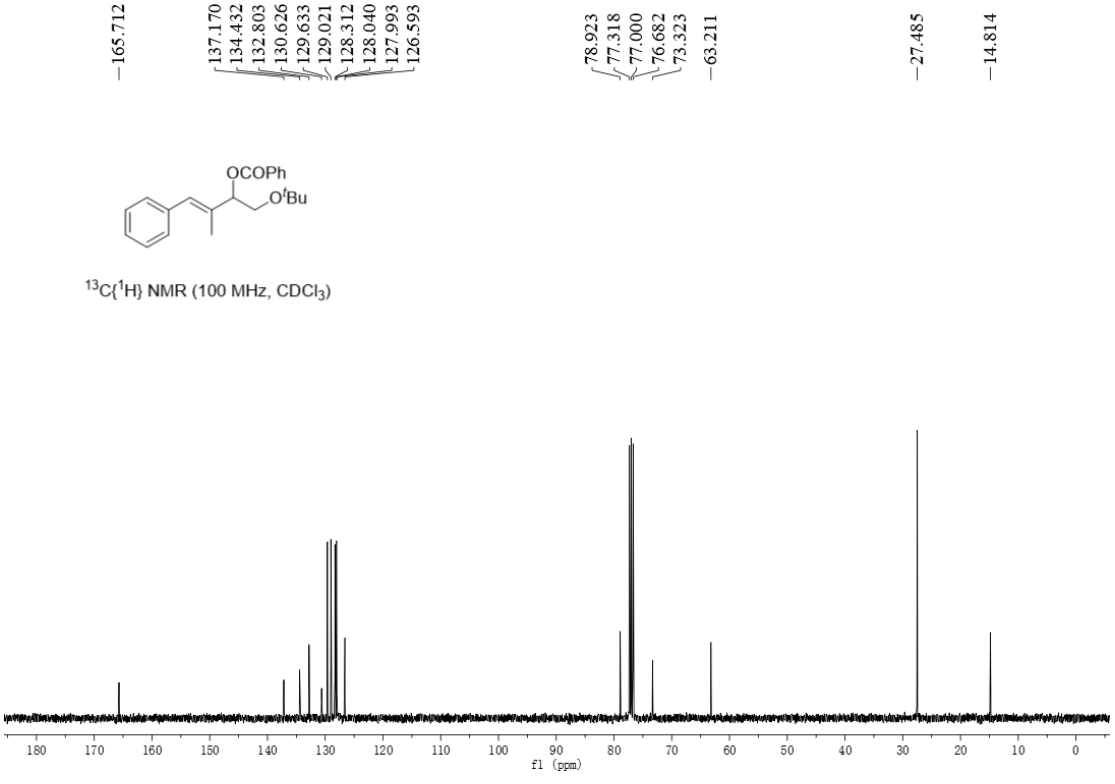




(*E*)-1-(*tert*-butoxy)-3-methyl-4-phenylbut-3-en-2-yl benzoate (3s)

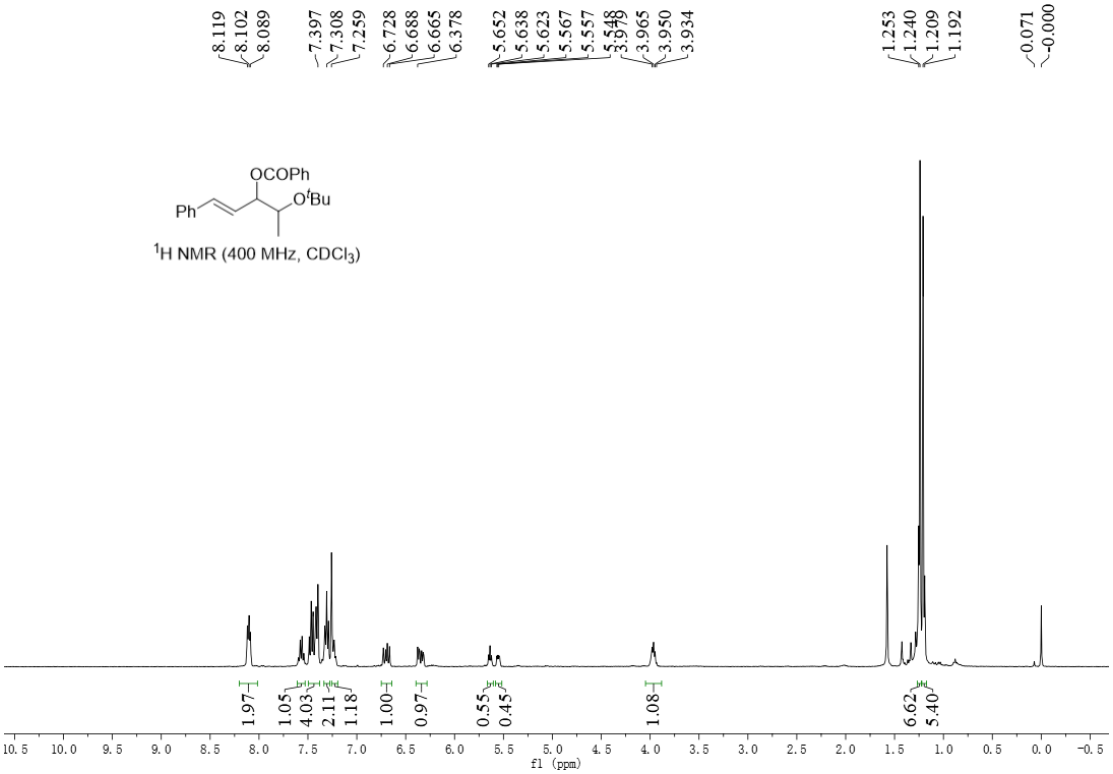


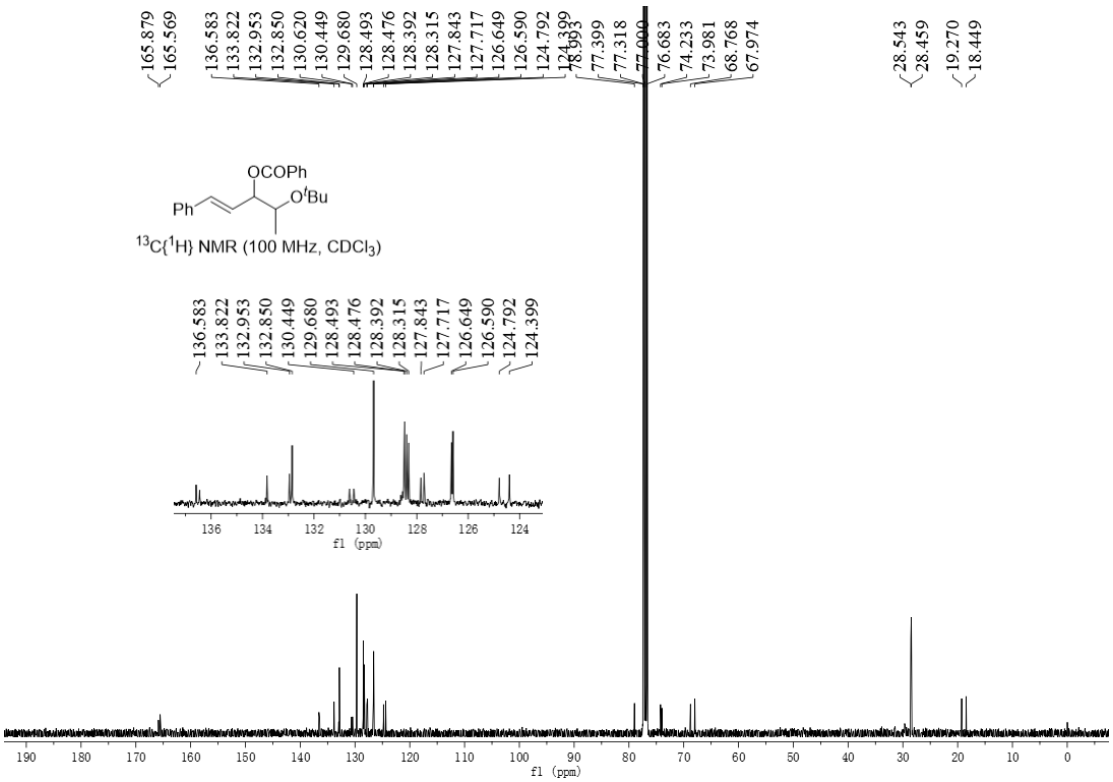
^{1}HNMR (400 MHz, $CDCl_3$)



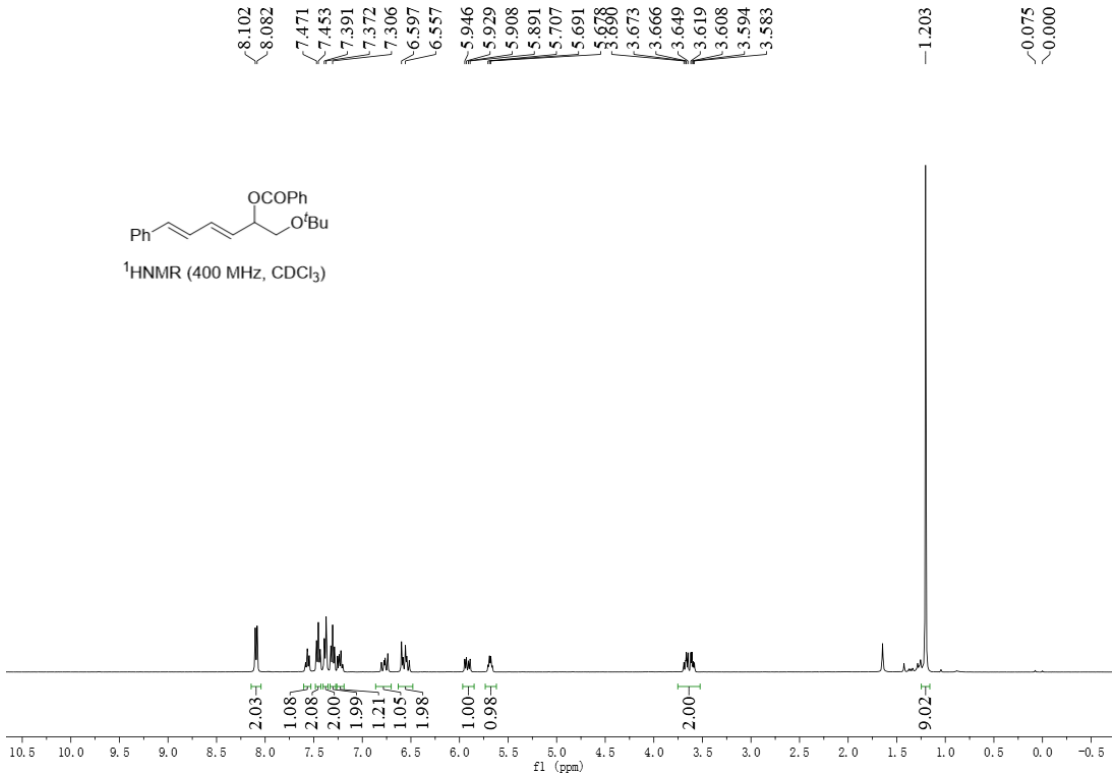
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

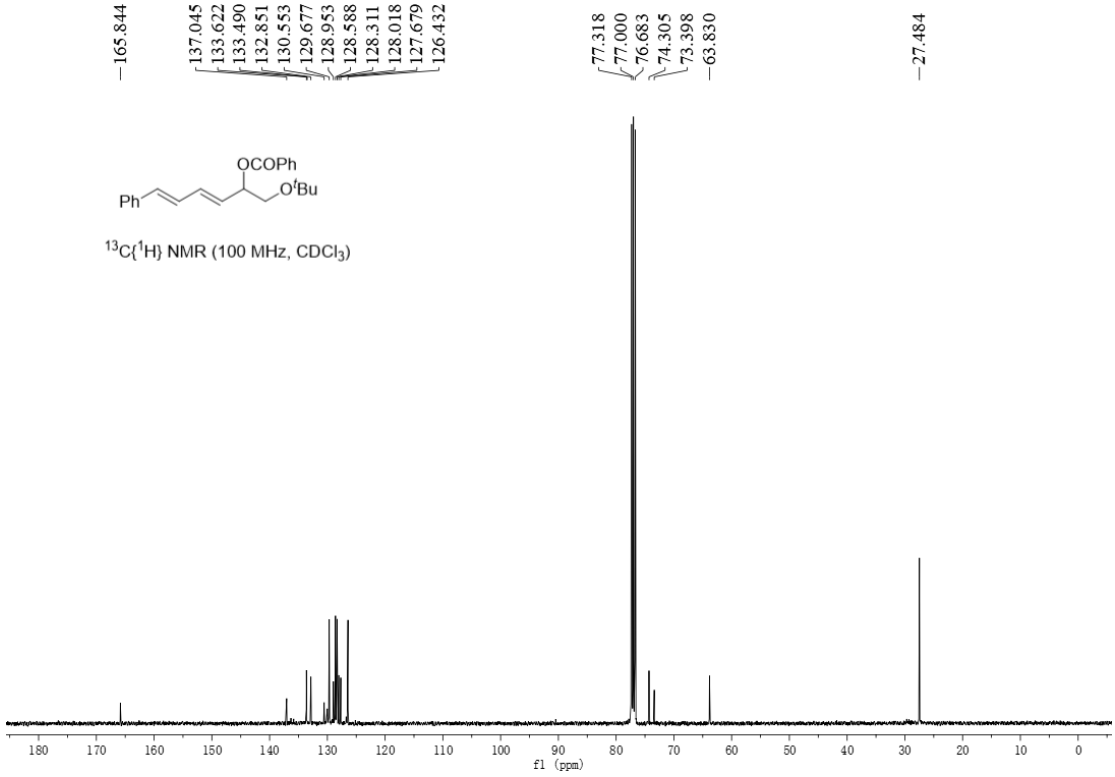
(*E*)-4-(*tert*-butoxy)-1-phenylpent-1-en-3-yl benzoate (3t)



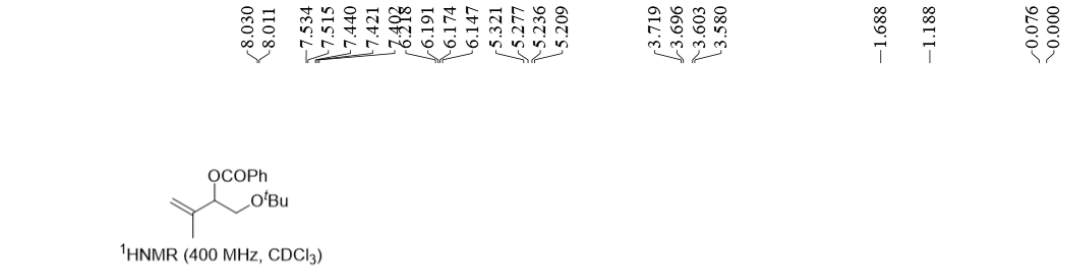


(3*E*,5*E*)-1-(*tert*-butoxy)-6-phenylhexa-3,5-dien-2-yl benzoate (3u)

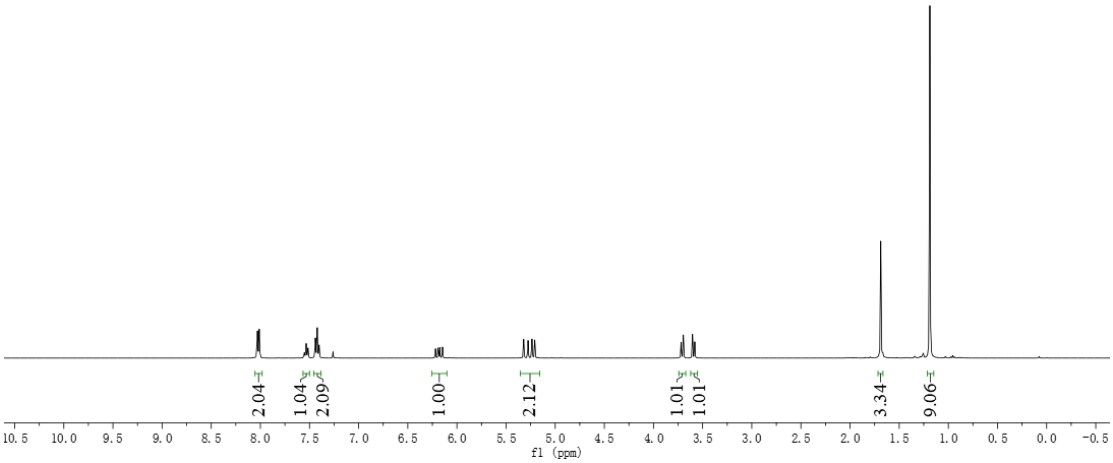


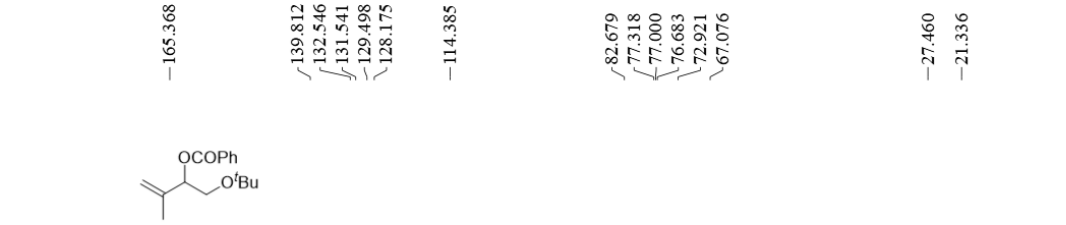


1-(*tert*-butoxy)-3-methylbut-3-en-2-yl benzoate (3v)

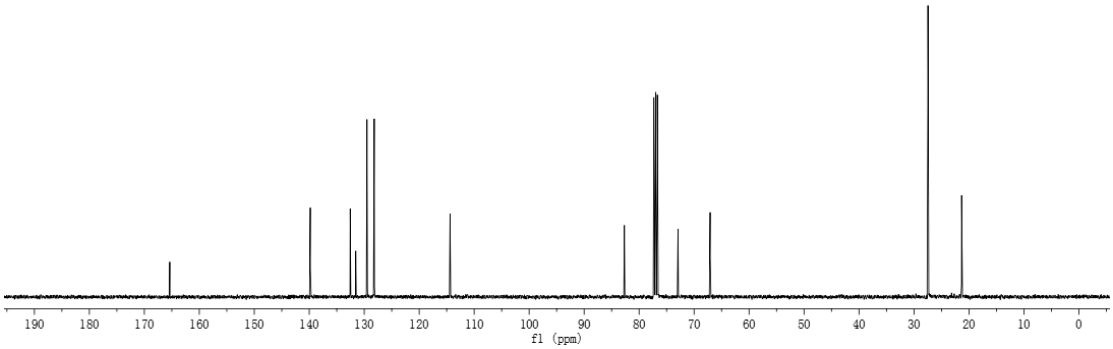


^{1}HNMR (400 MHz, $CDCl_3$)

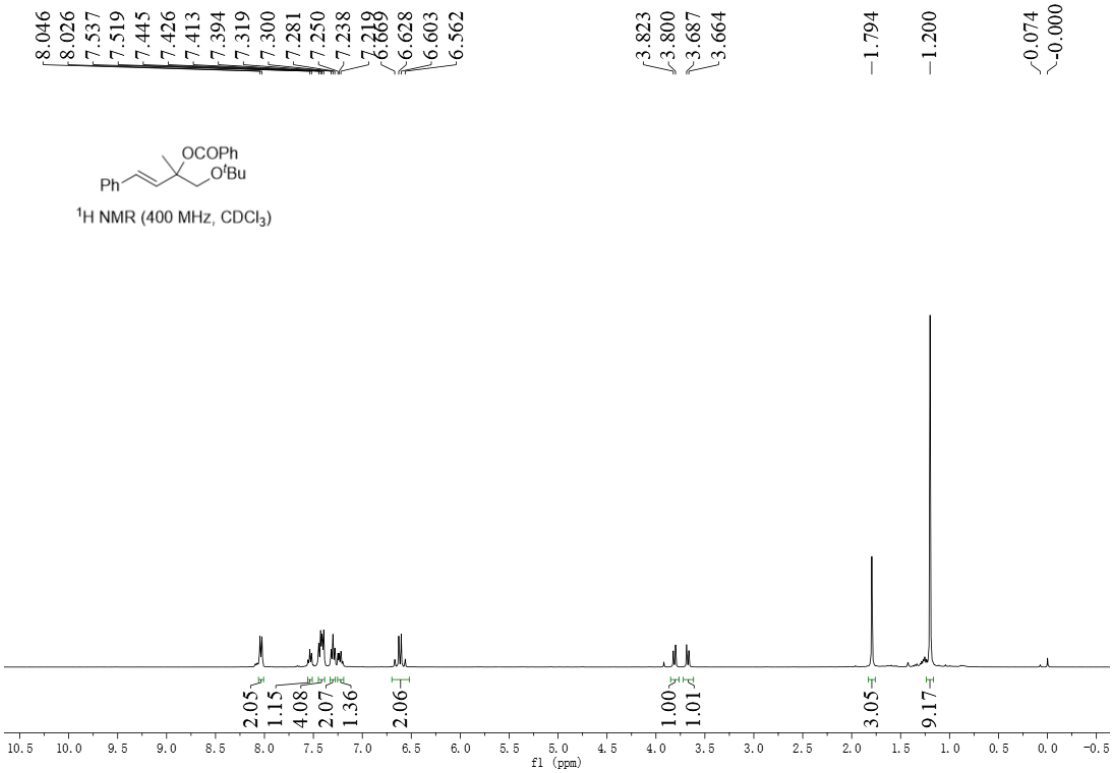




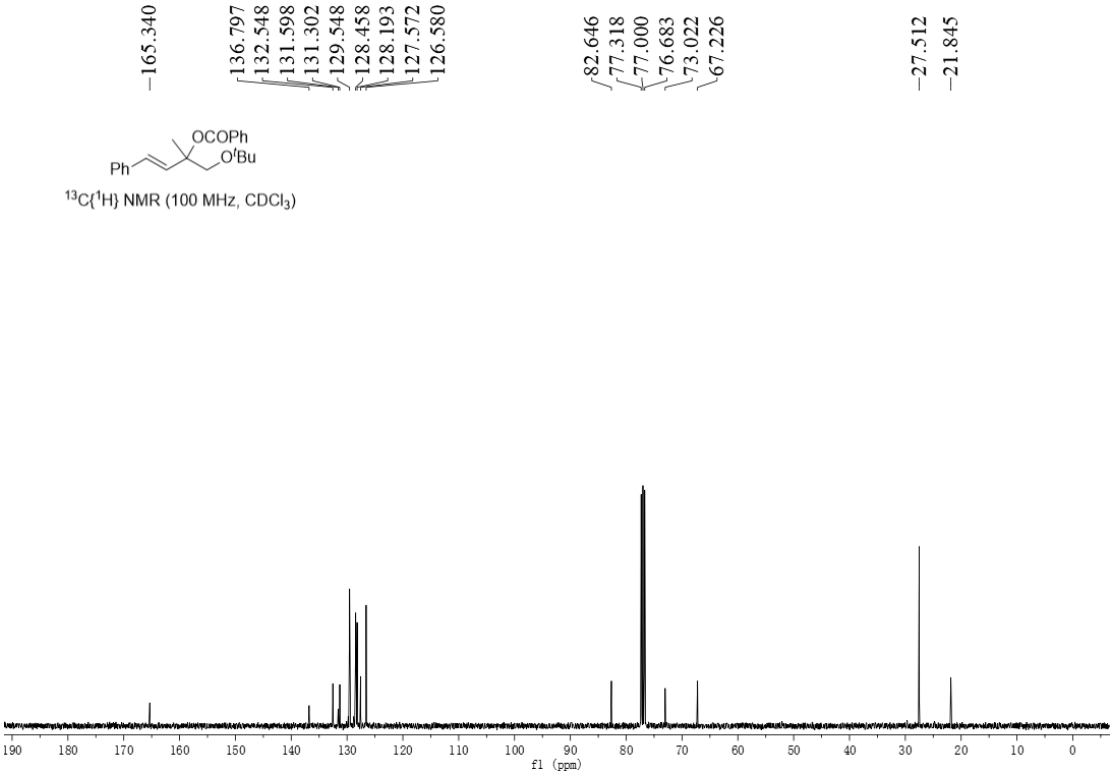
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



(*E*)-1-(*tert*-butoxy)-2-methyl-4-phenylbut-3-en-2-yl benzoate (3w)

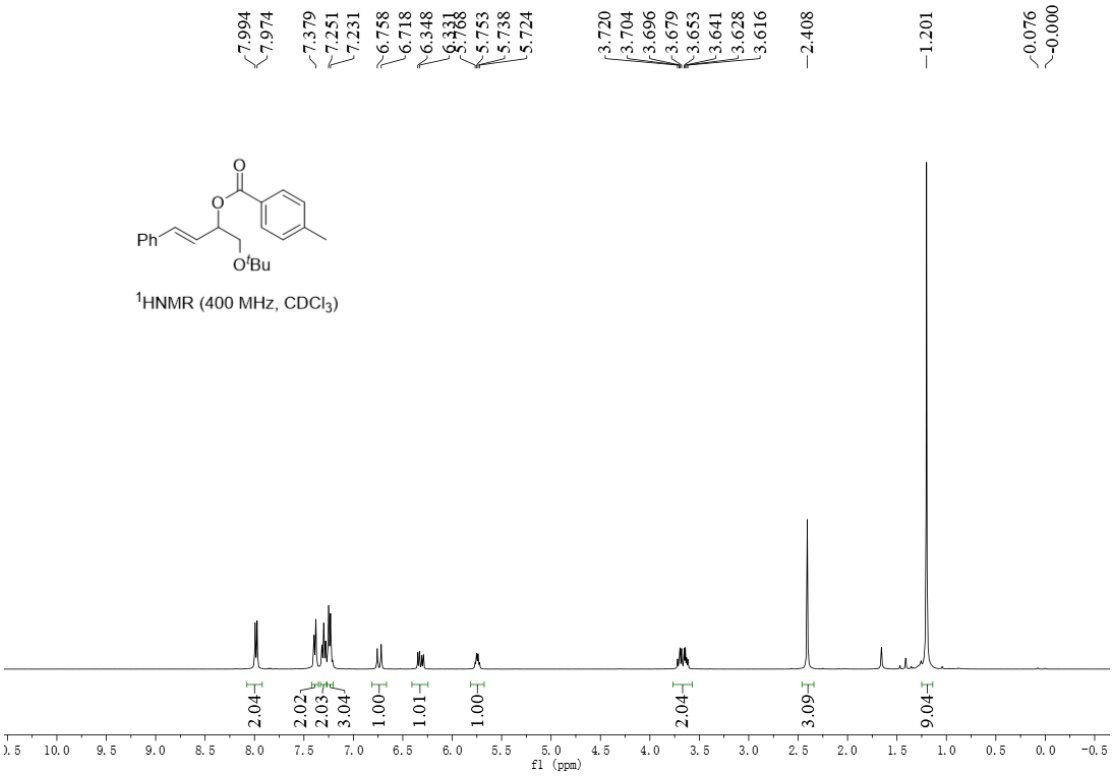


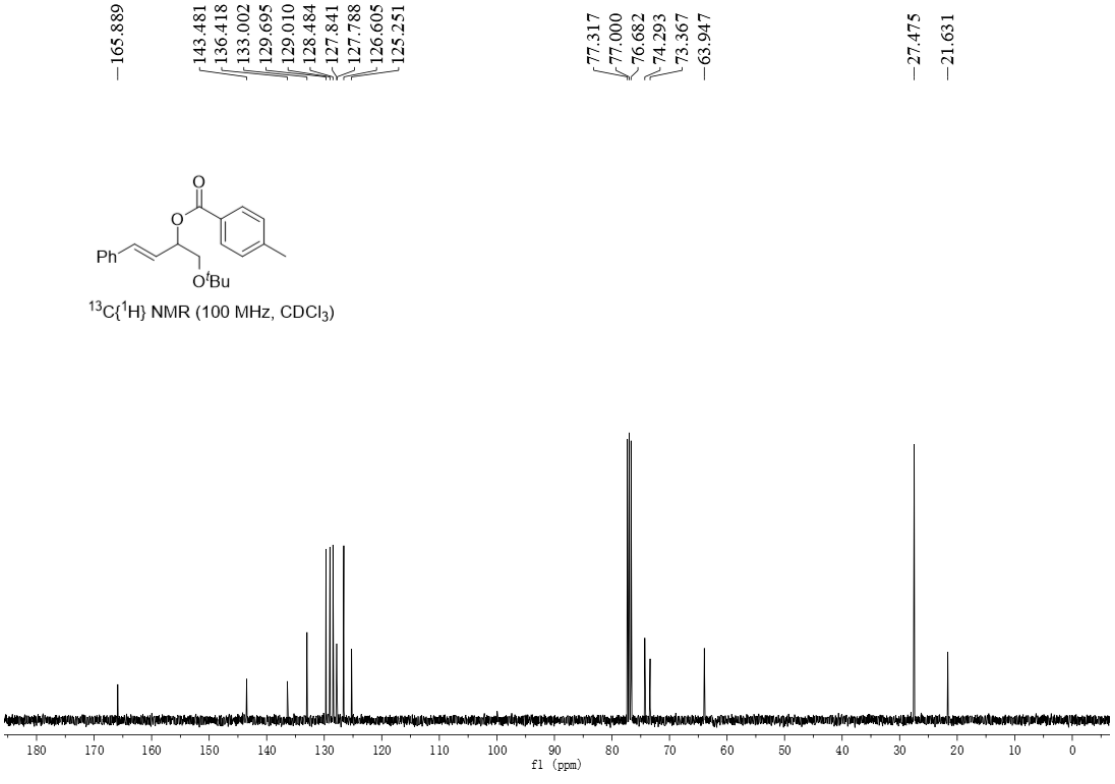
^{1}H NMR (400 MHz, $CDCl_3$)



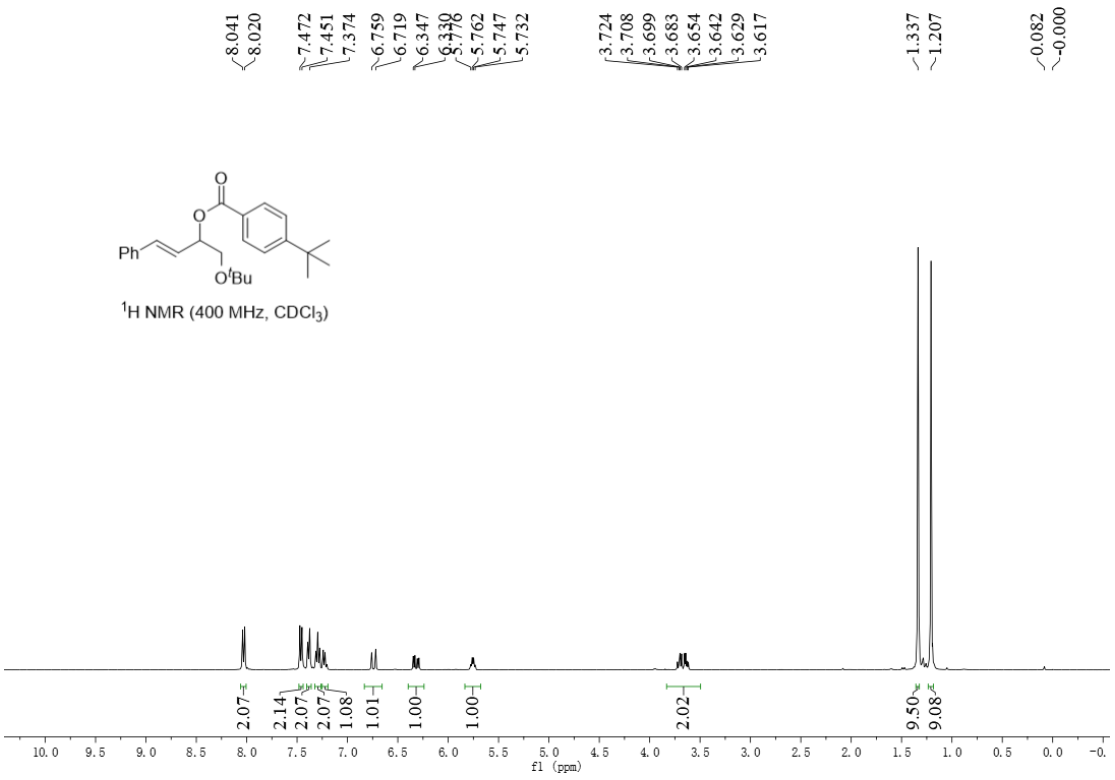
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

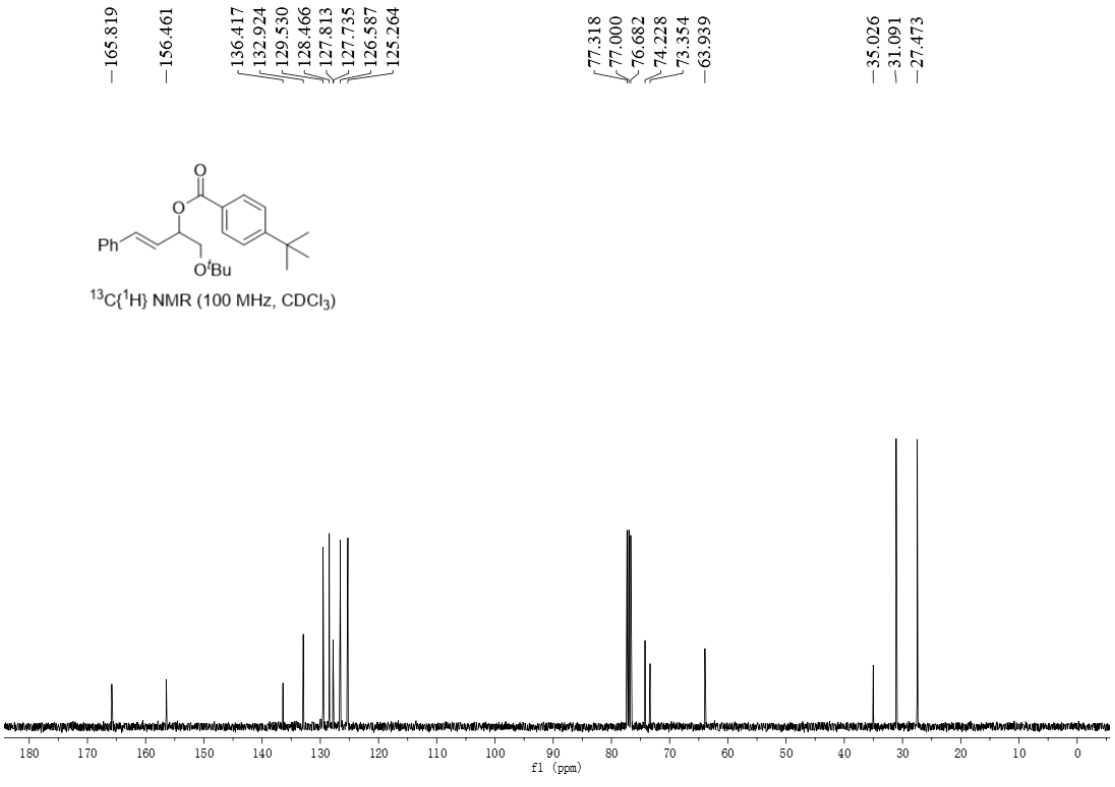
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-methylbenzoate (4b)



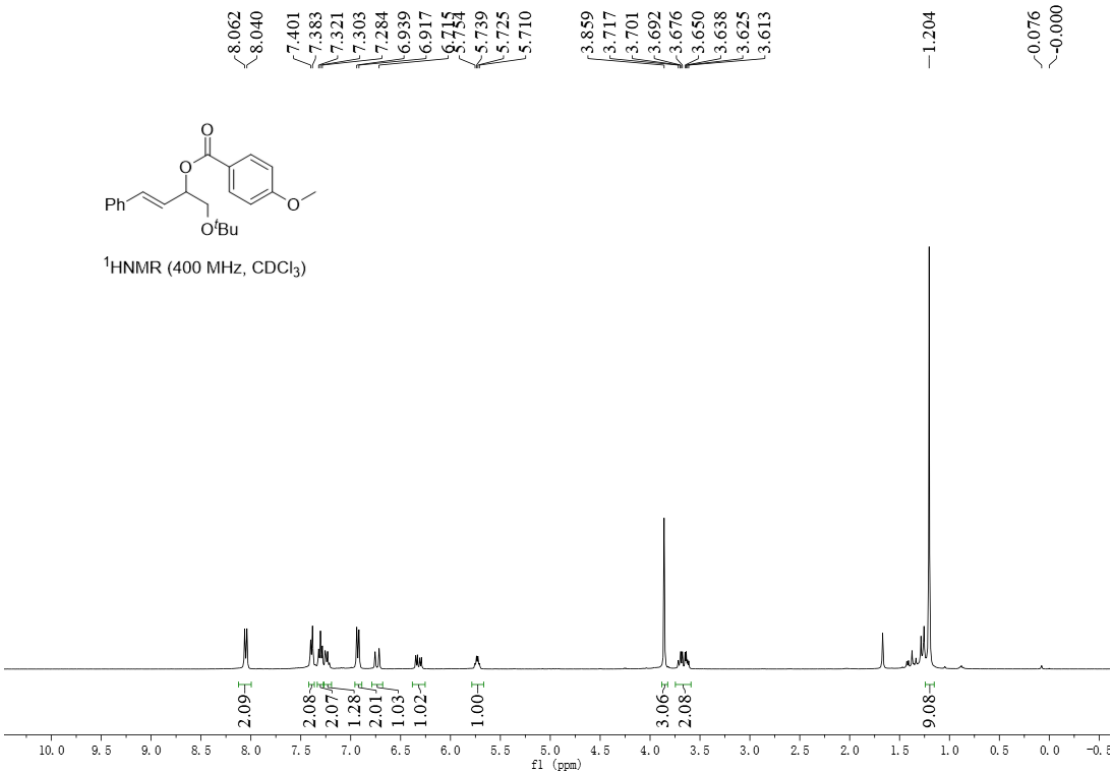


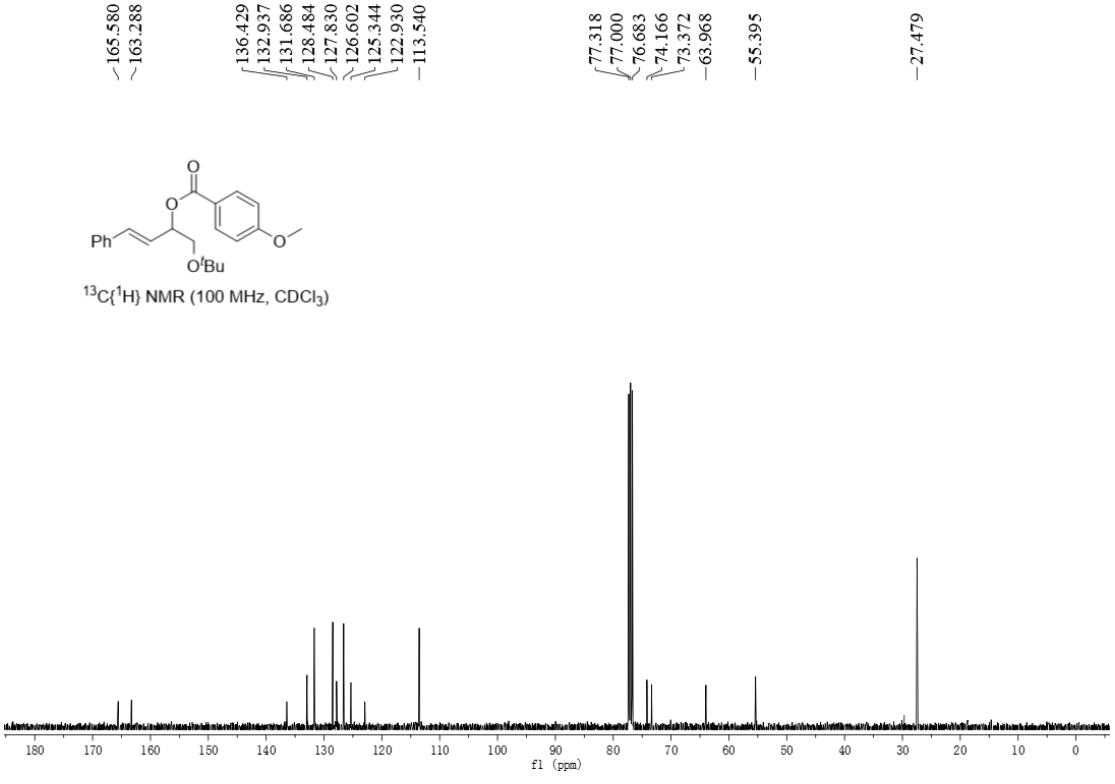
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-(*tert*-butyl)benzoate (4c)



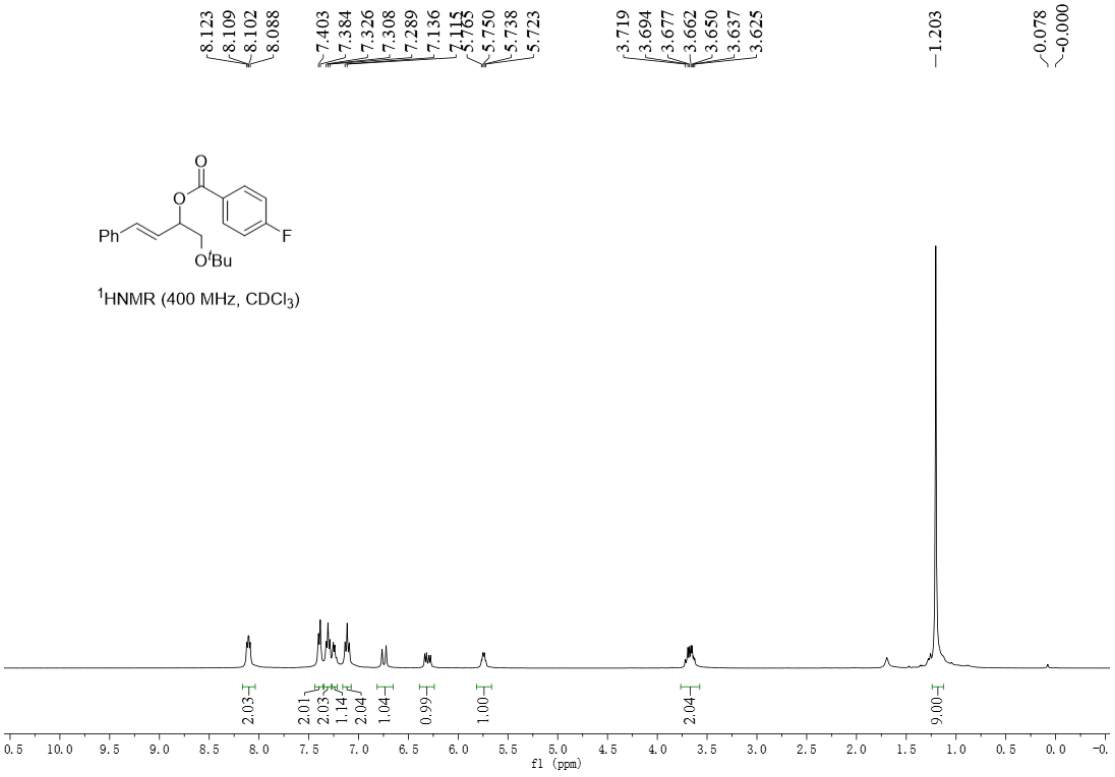


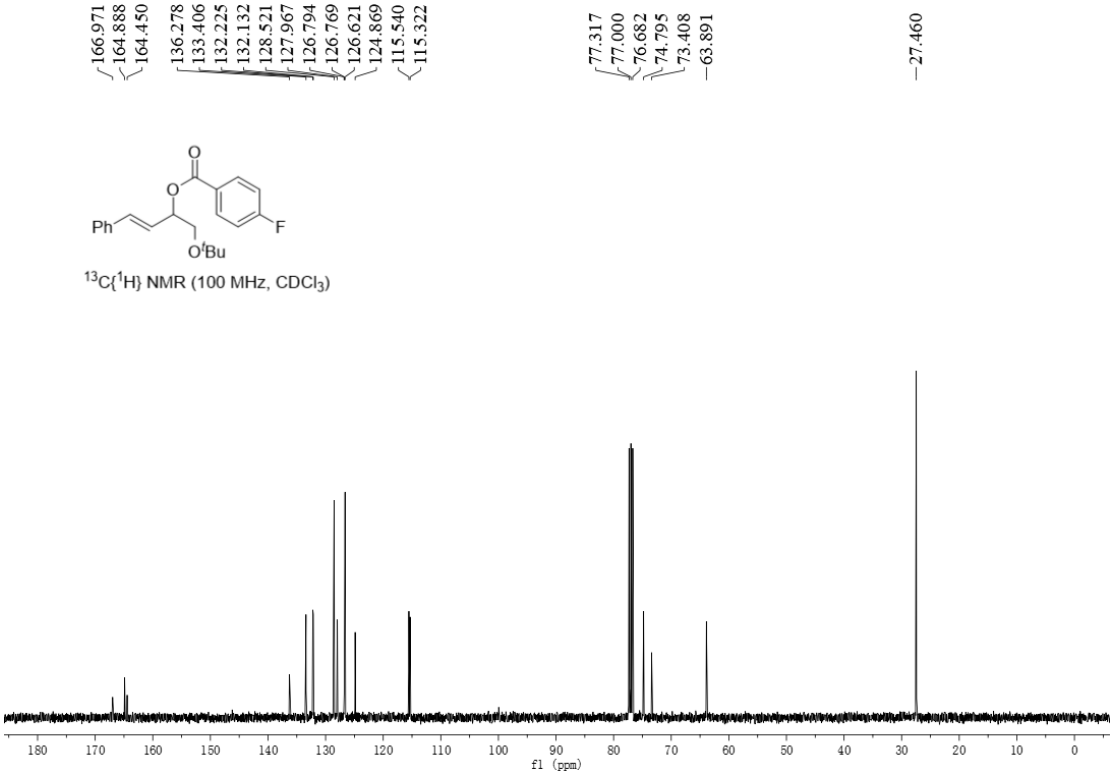
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-methoxybenzoate (4d)

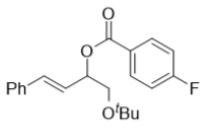




(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-fluorobenzoate (4e)

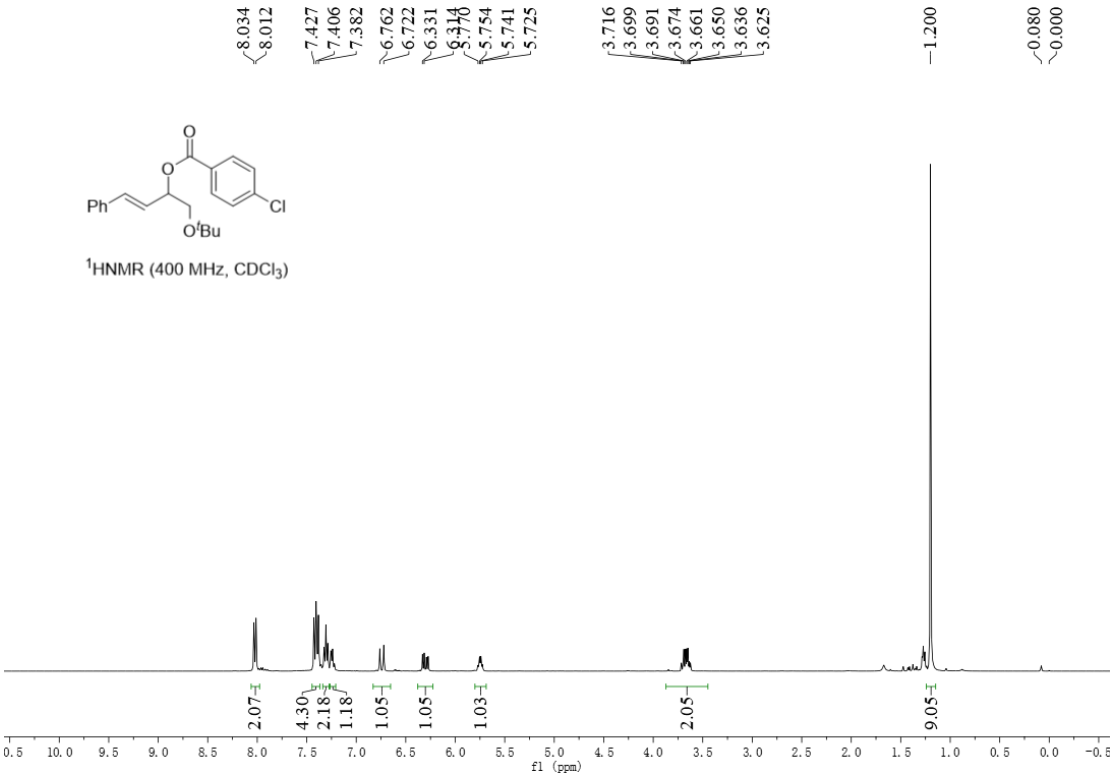


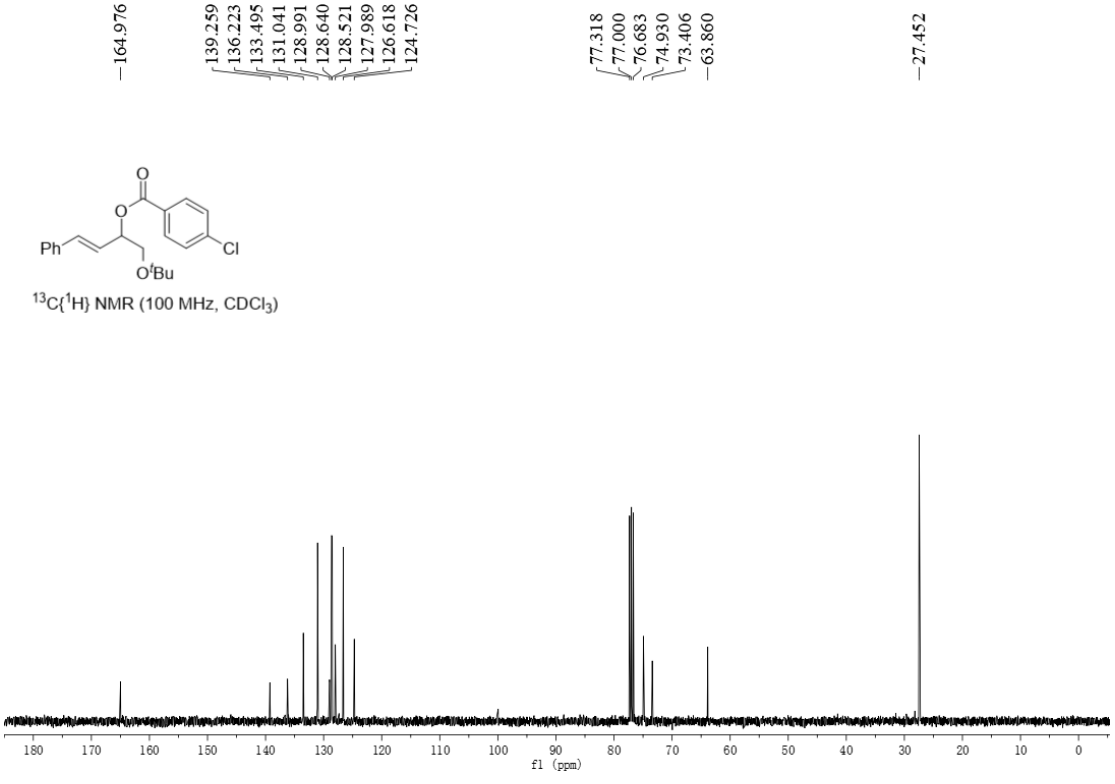




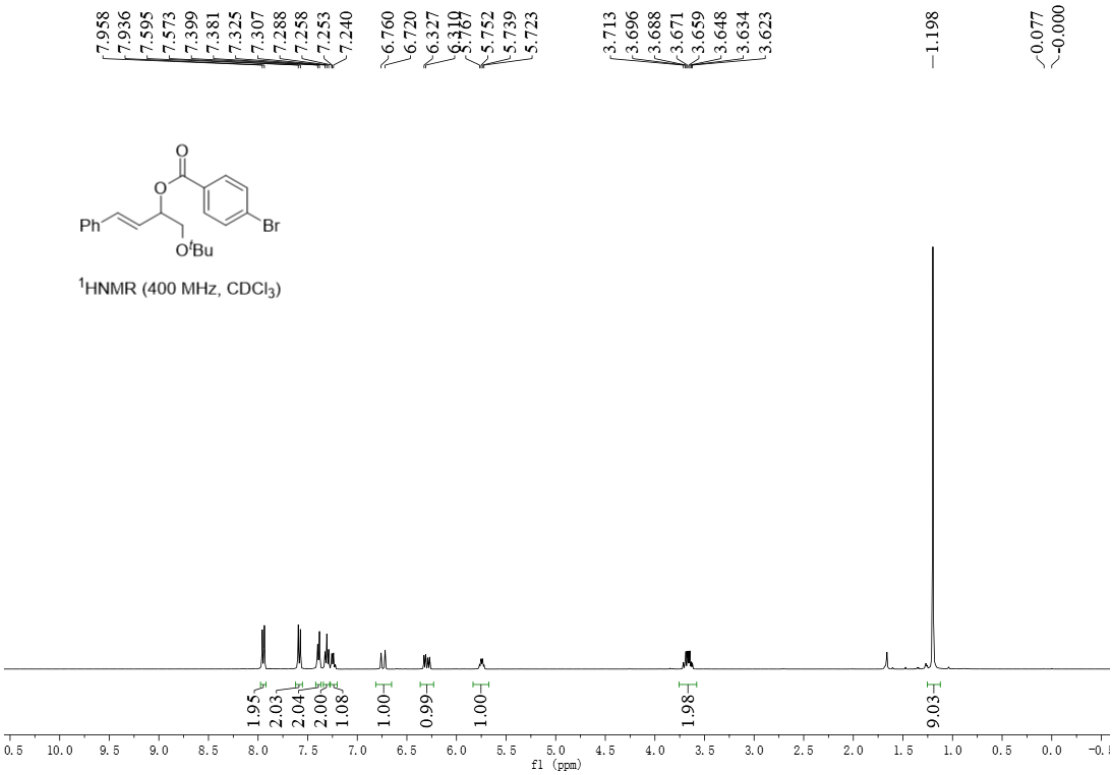
^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-chlorobenzoate (4f)

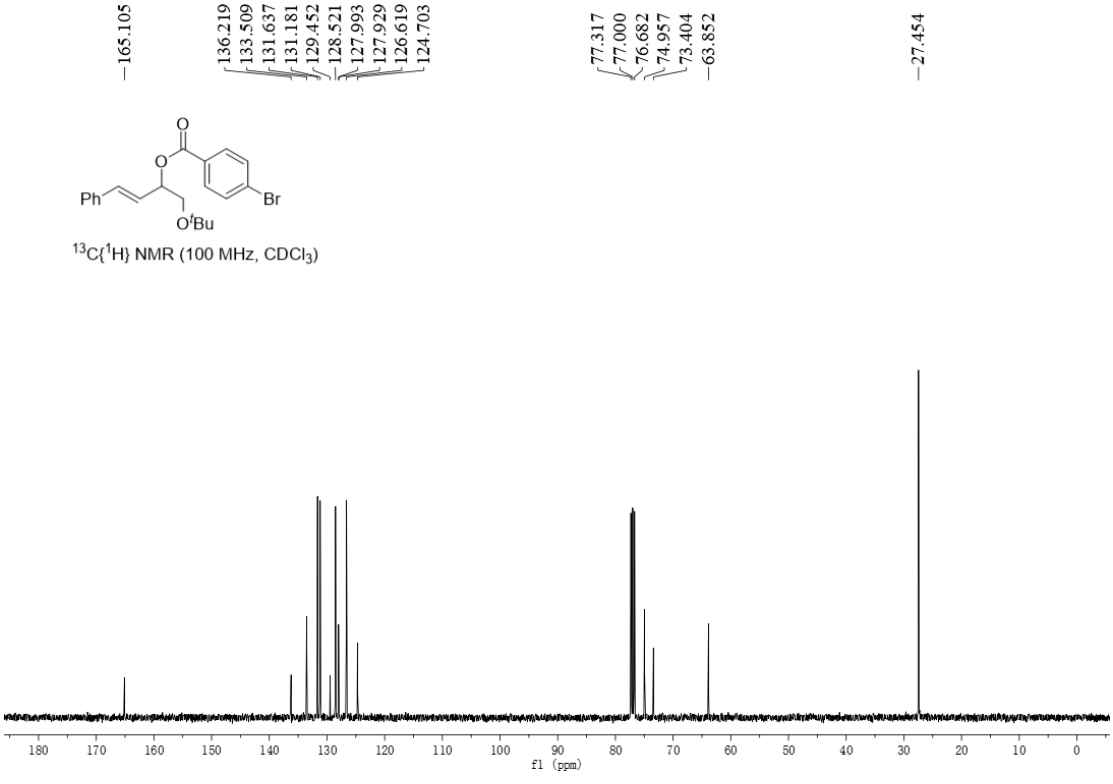




(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-bromobenzoate (4g)

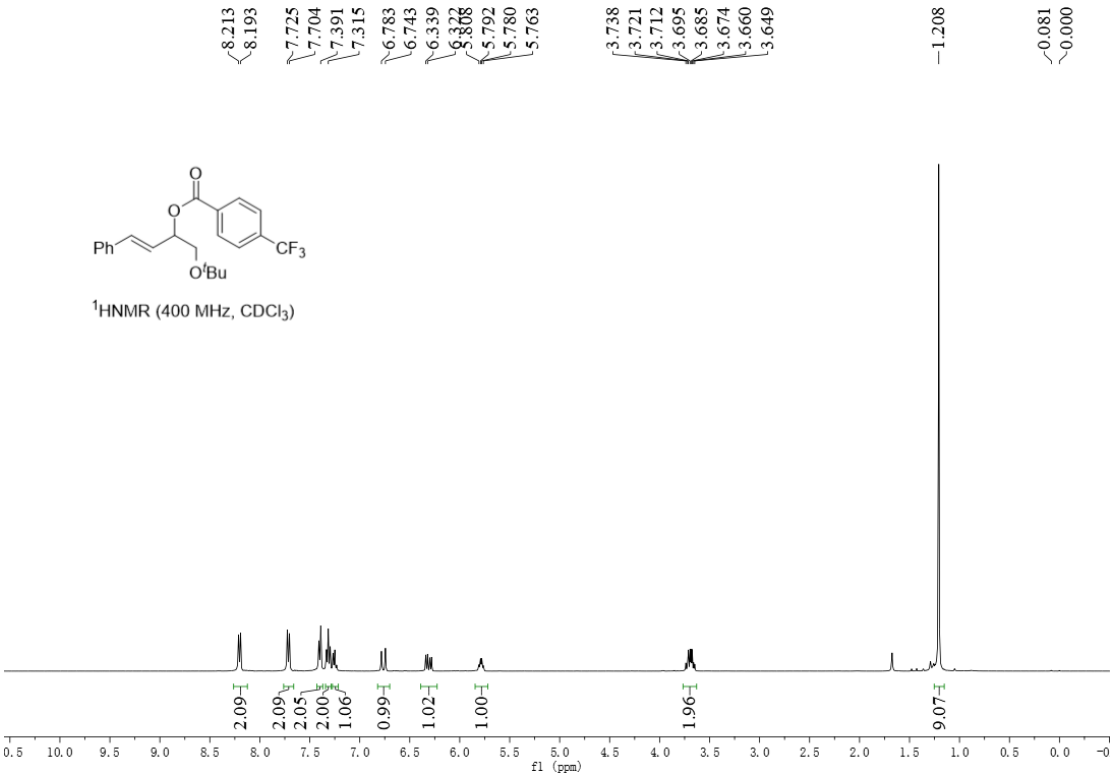


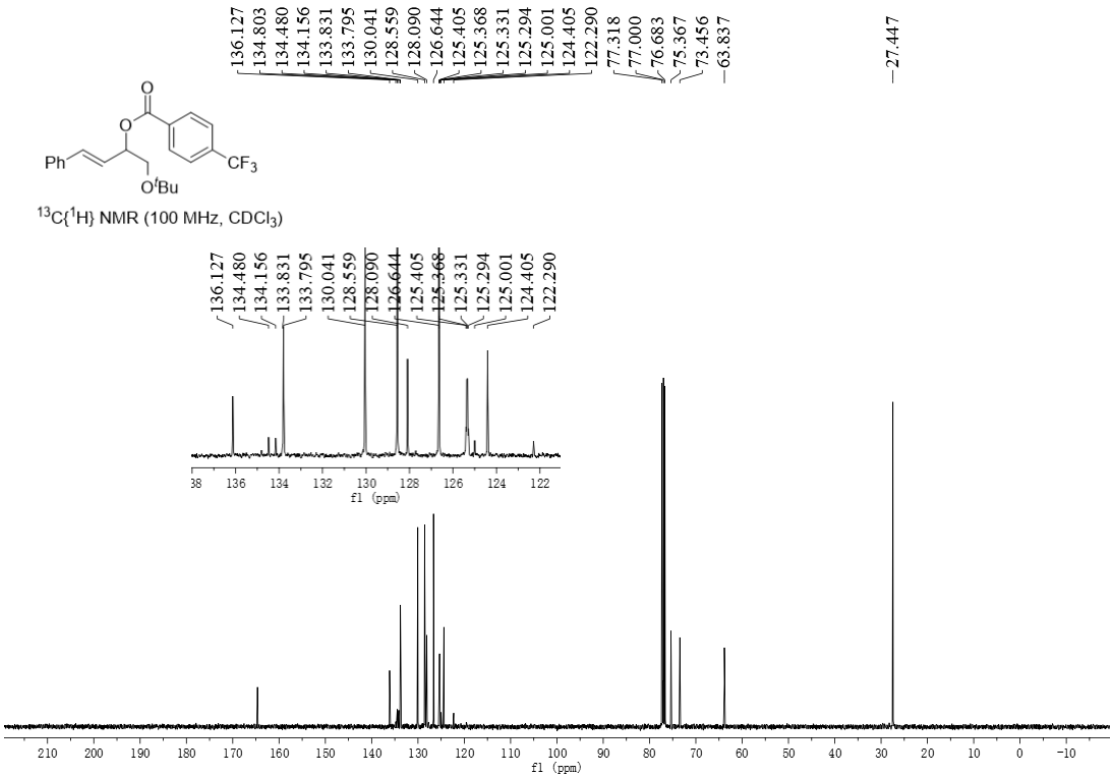
^{1}HNMR (400 MHz, $CDCl_3$)

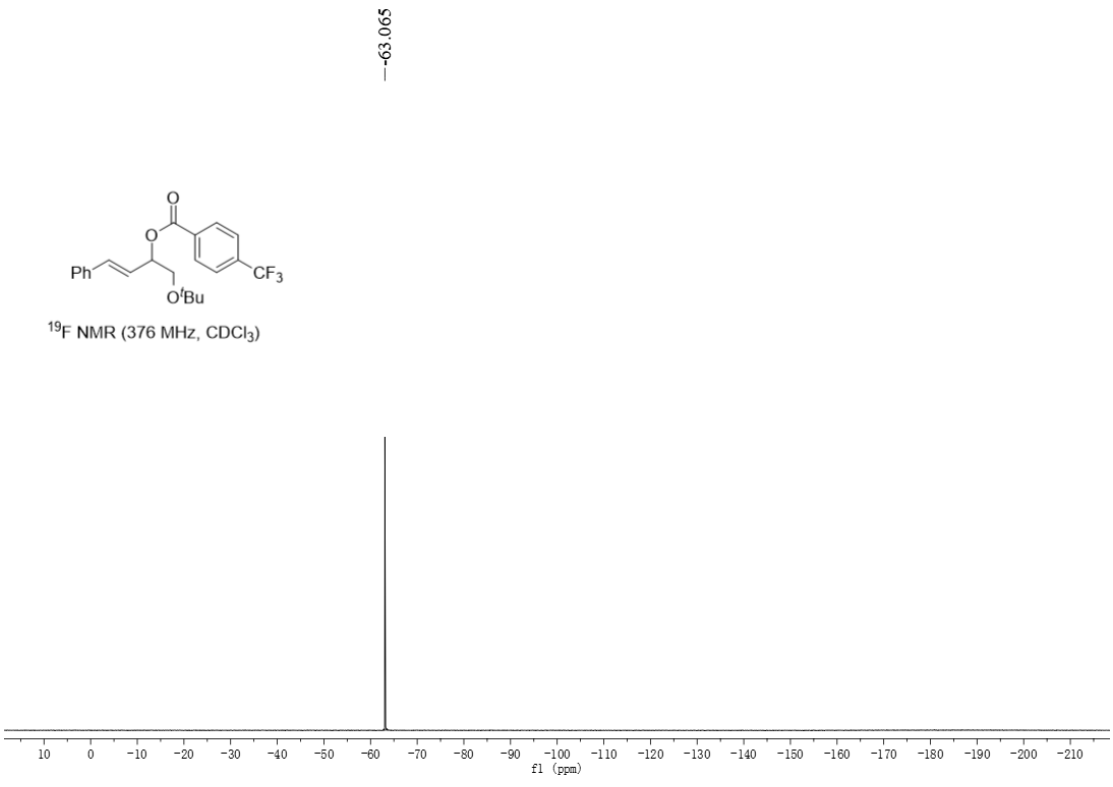


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

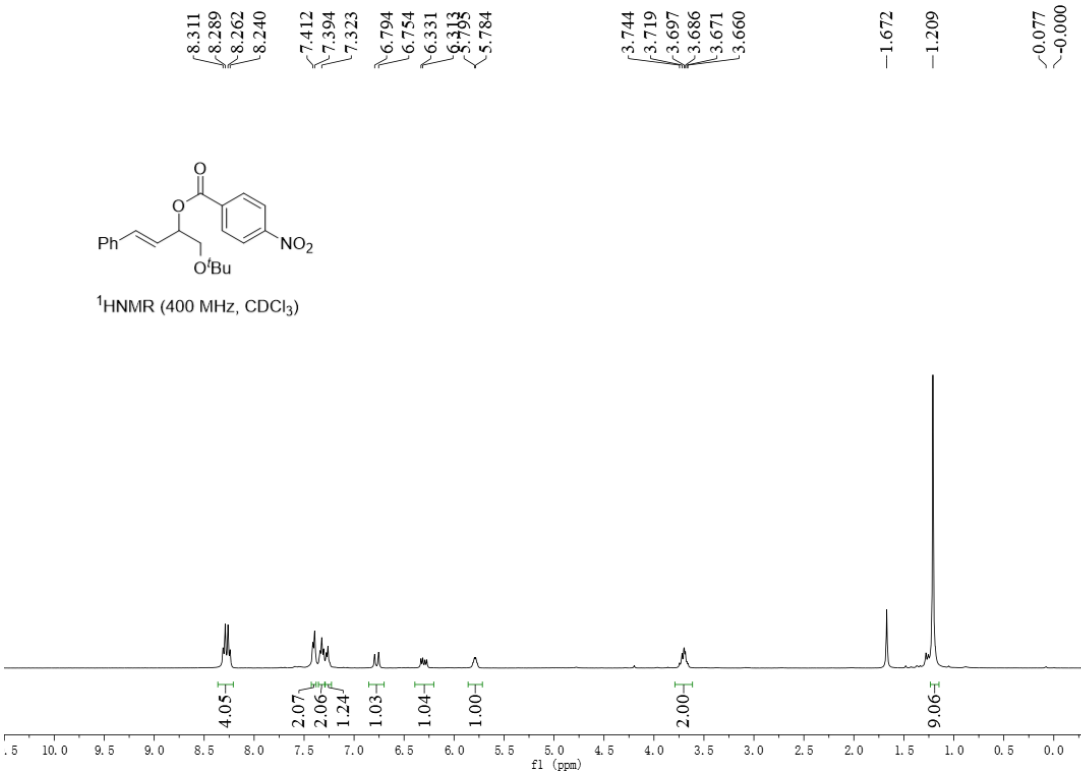
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-(trifluoromethyl)benzoate (4h)

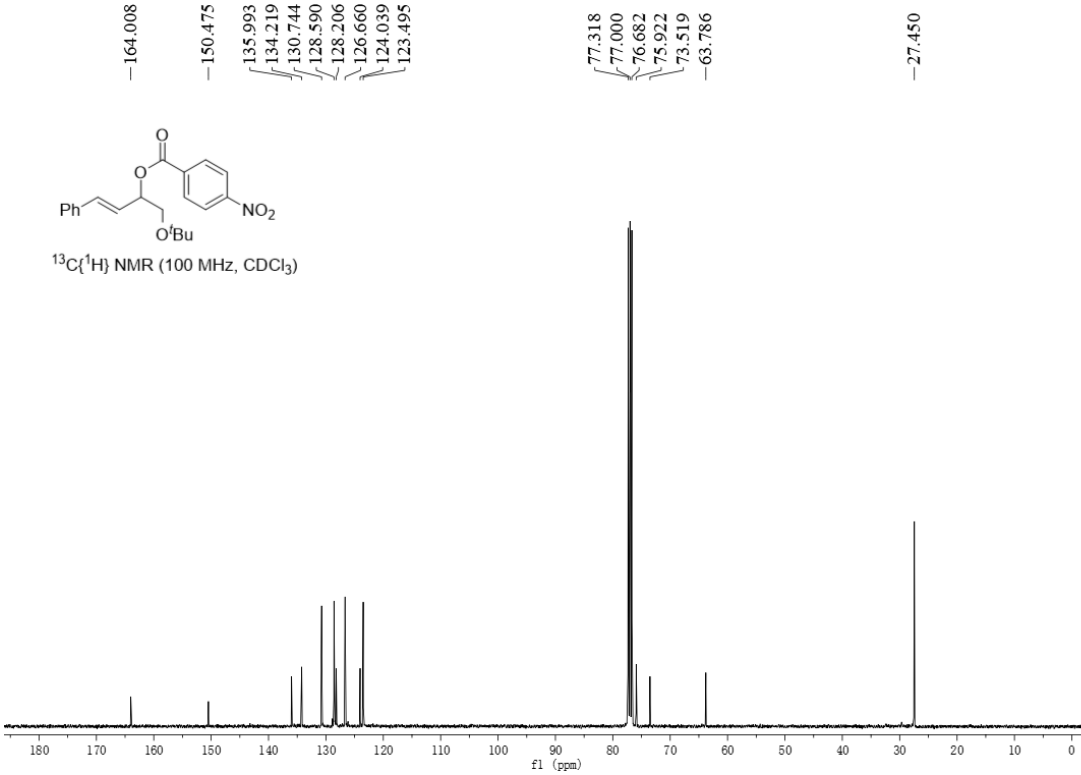




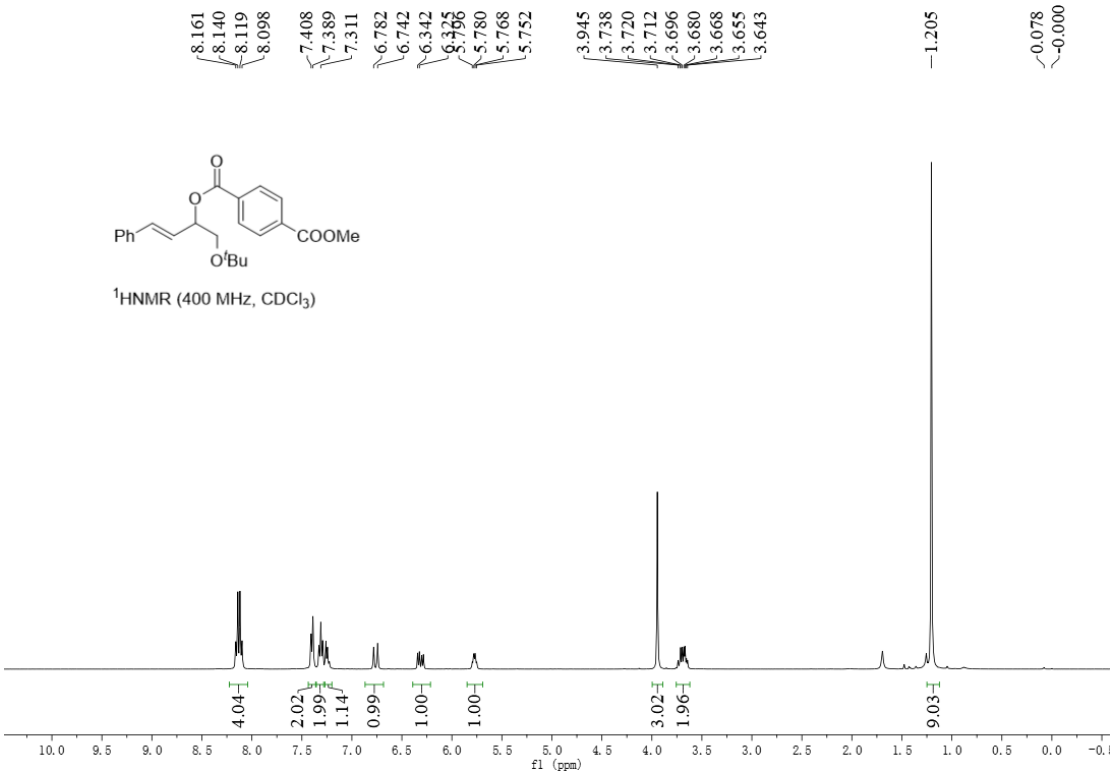

-63.065
O
O
Ph
CF3
OtBu
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 4-nitrobenzoate (4i)

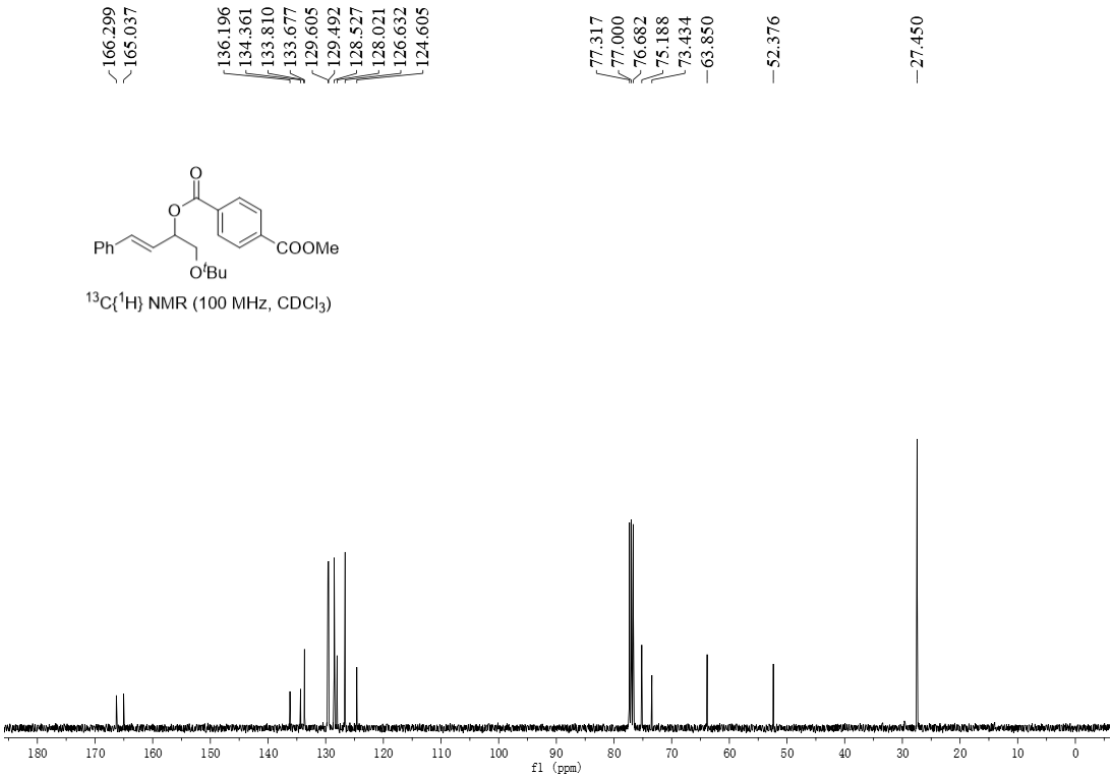




(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl methyl terephthalate (4j)

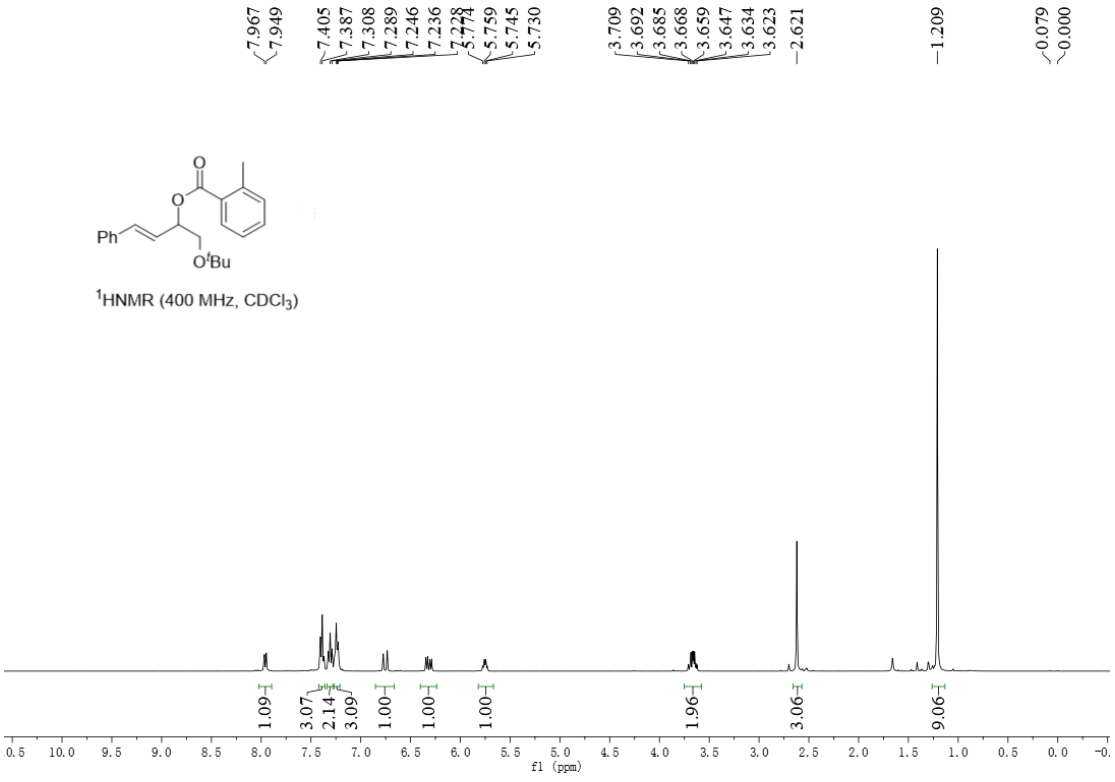


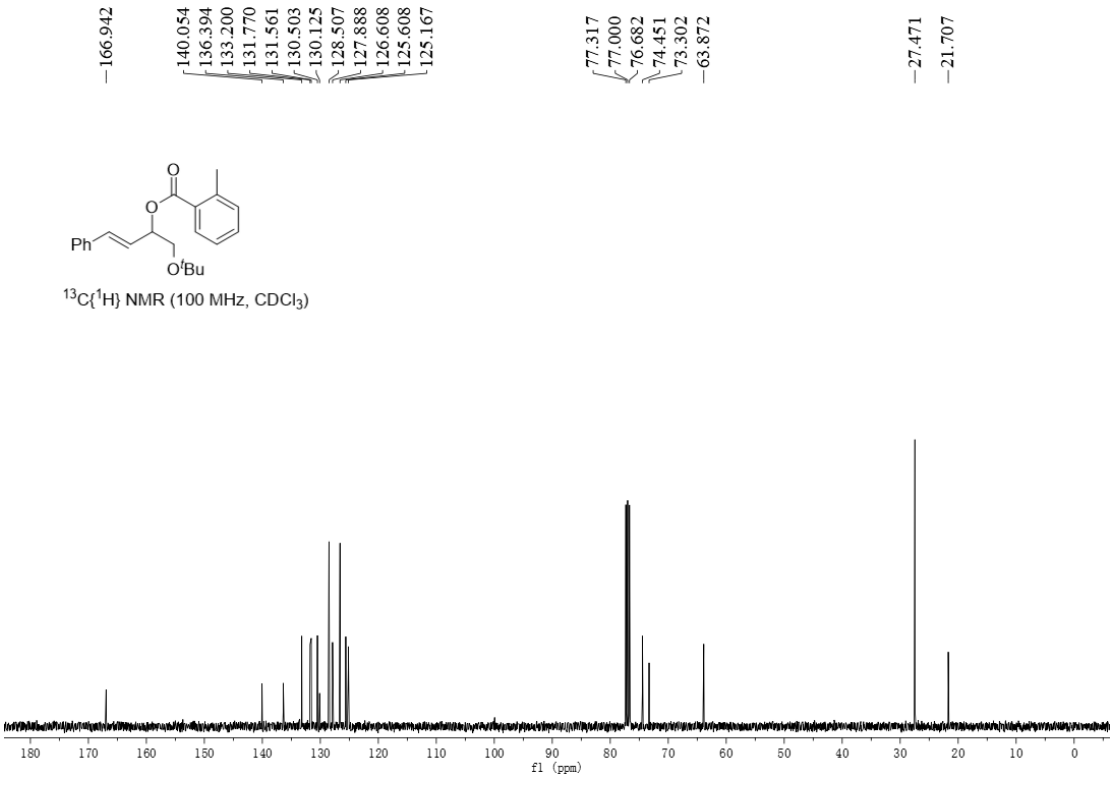
^{1}HNMR (400 MHz, $CDCl_3$)



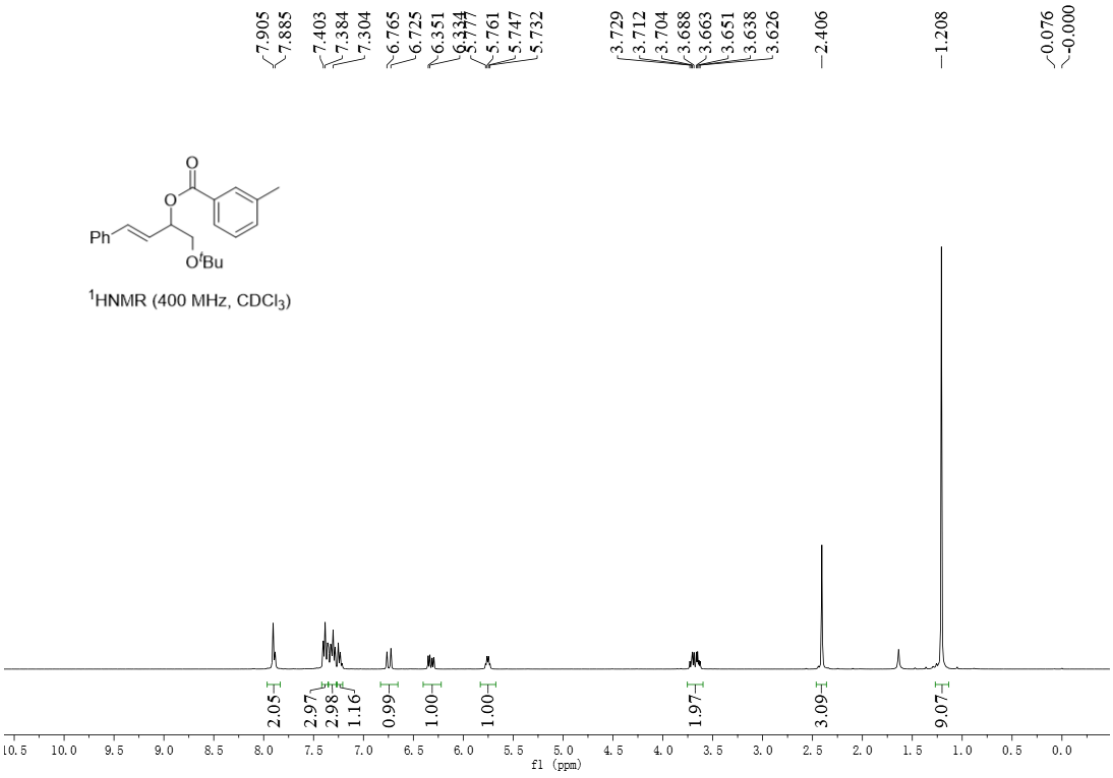
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 2-methylbenzoate (4k)

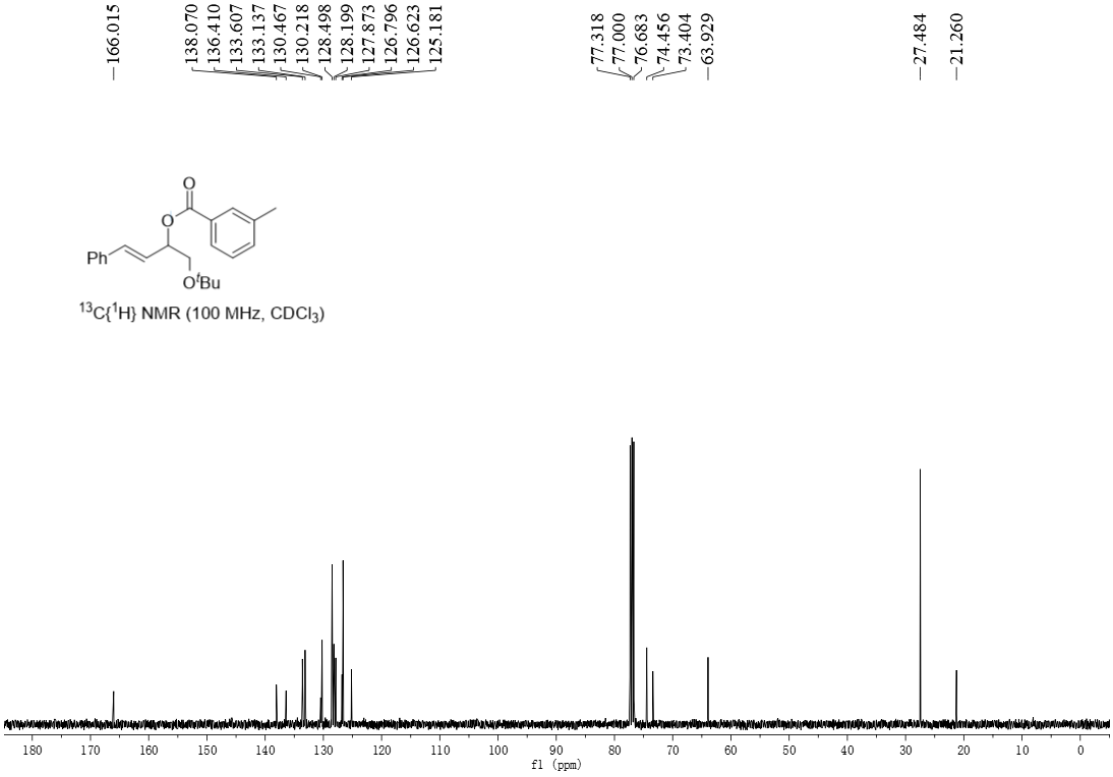




(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 3-methylbenzoate (4l)

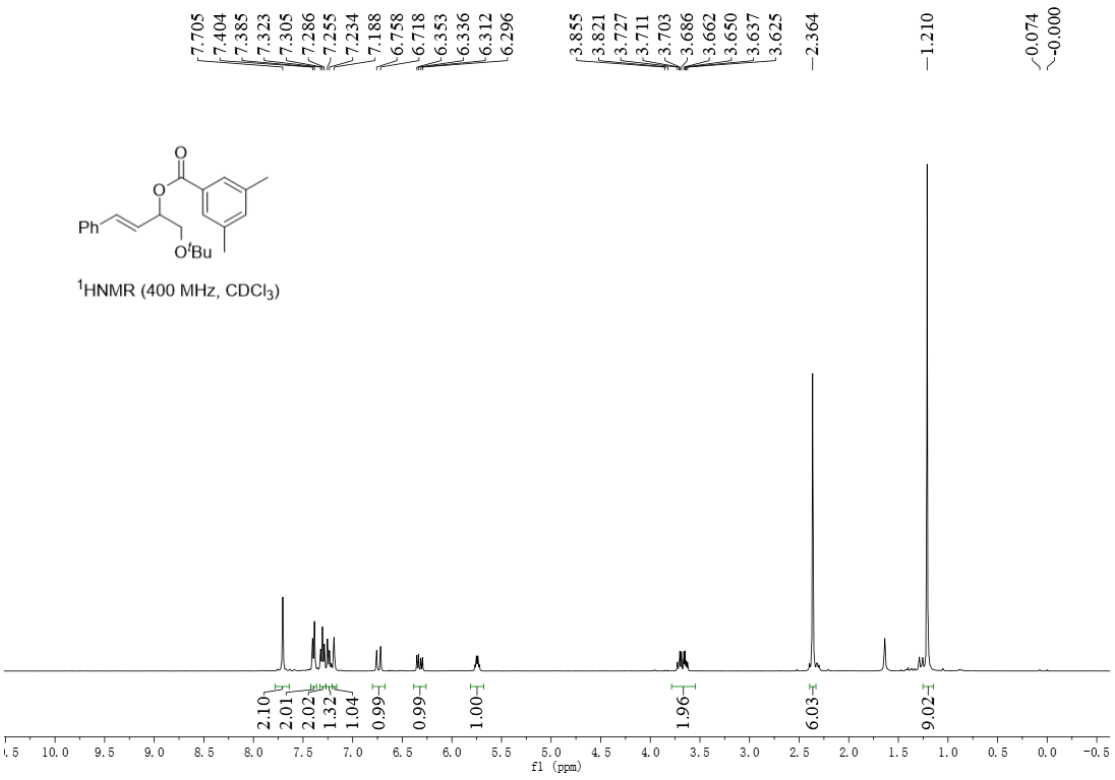


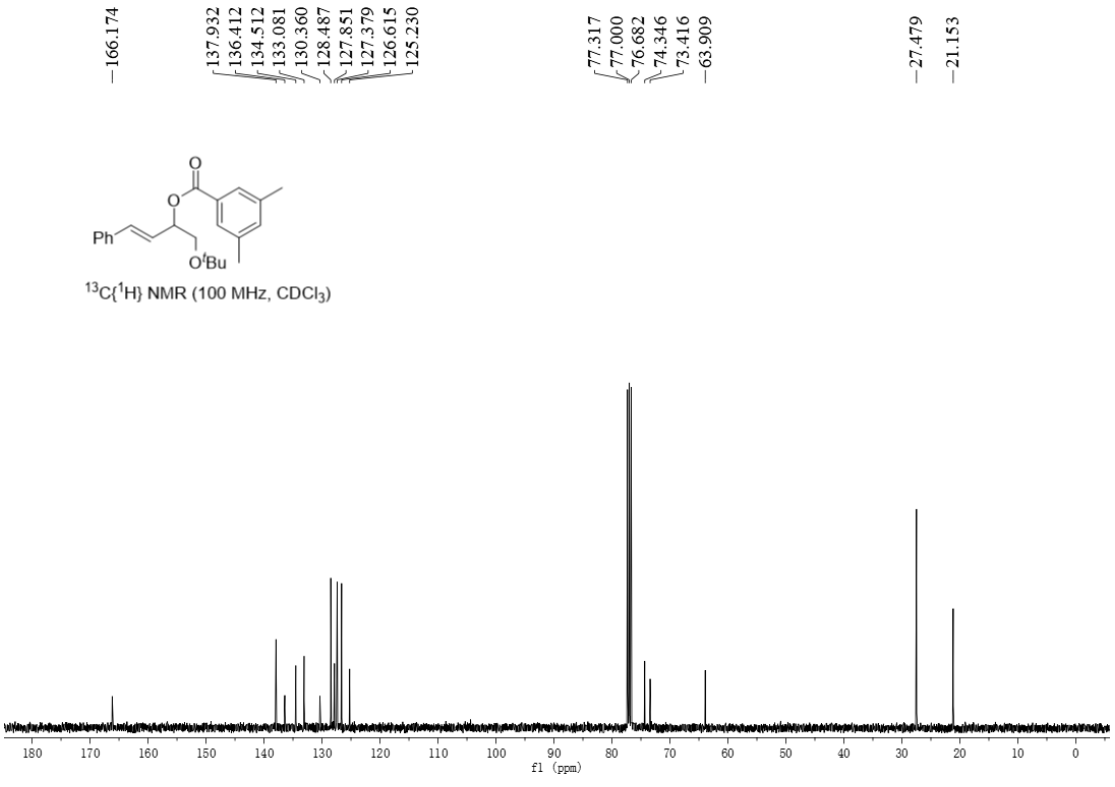
^{1}HNMR (400 MHz, $CDCl_3$)



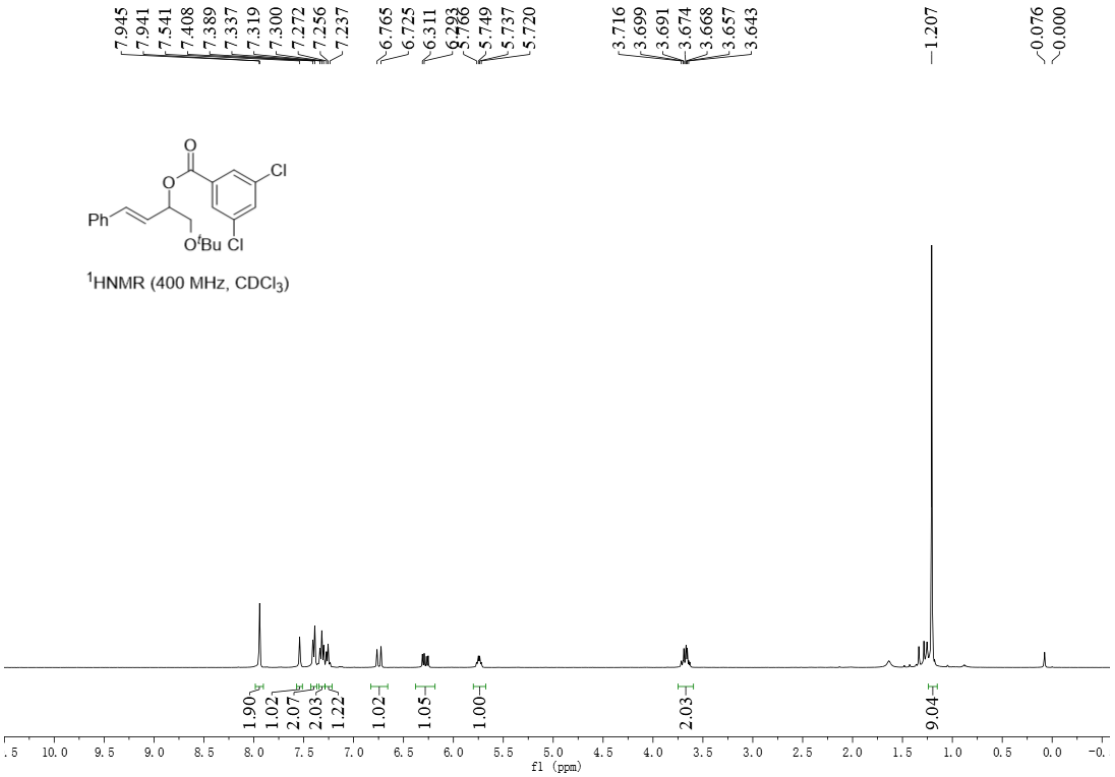
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

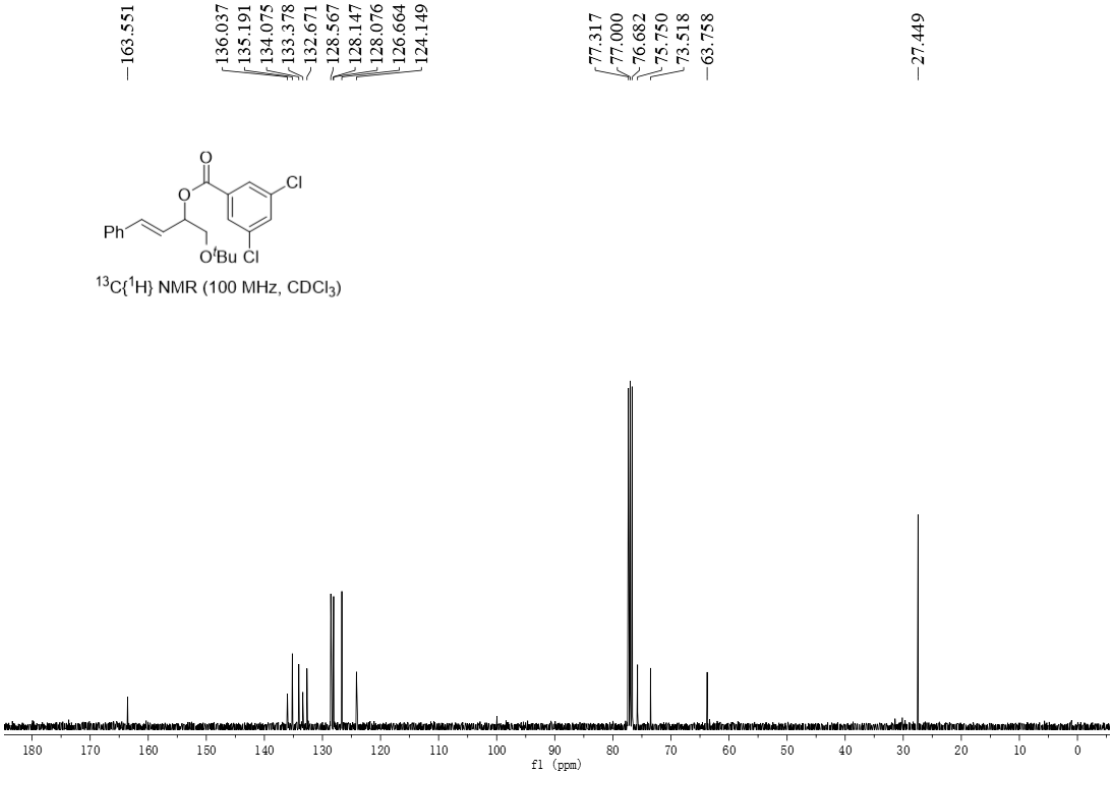
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 3,5-dimethylbenzoate (4m)



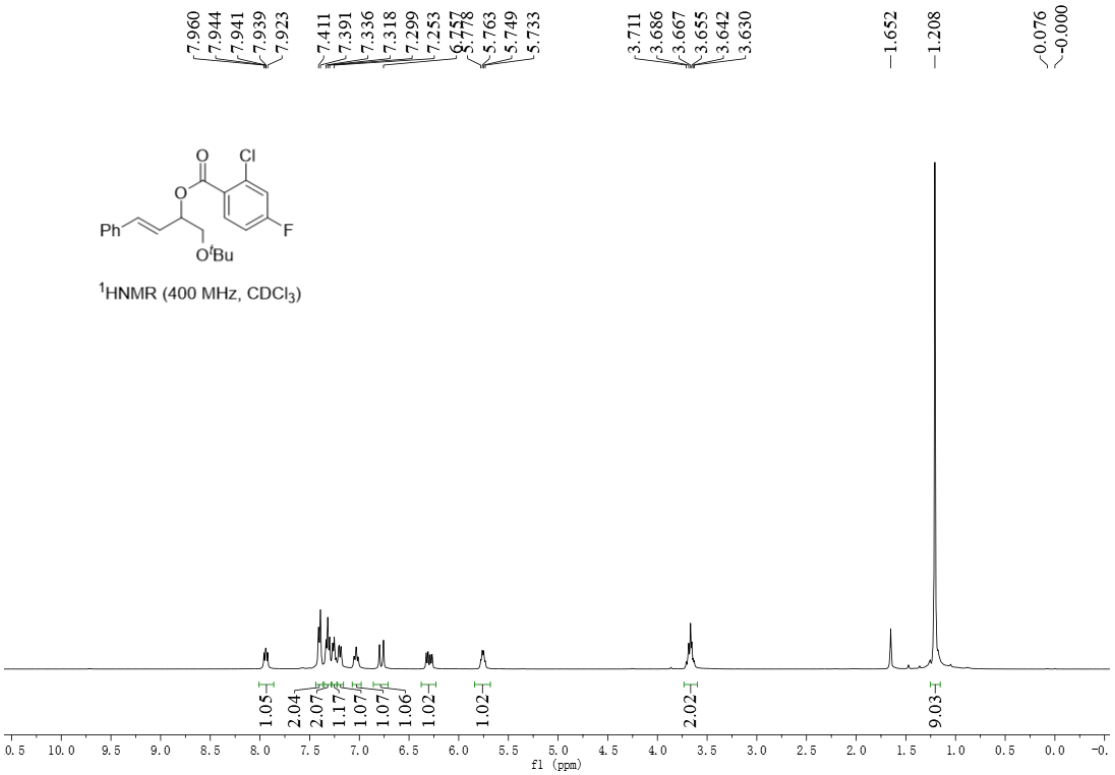


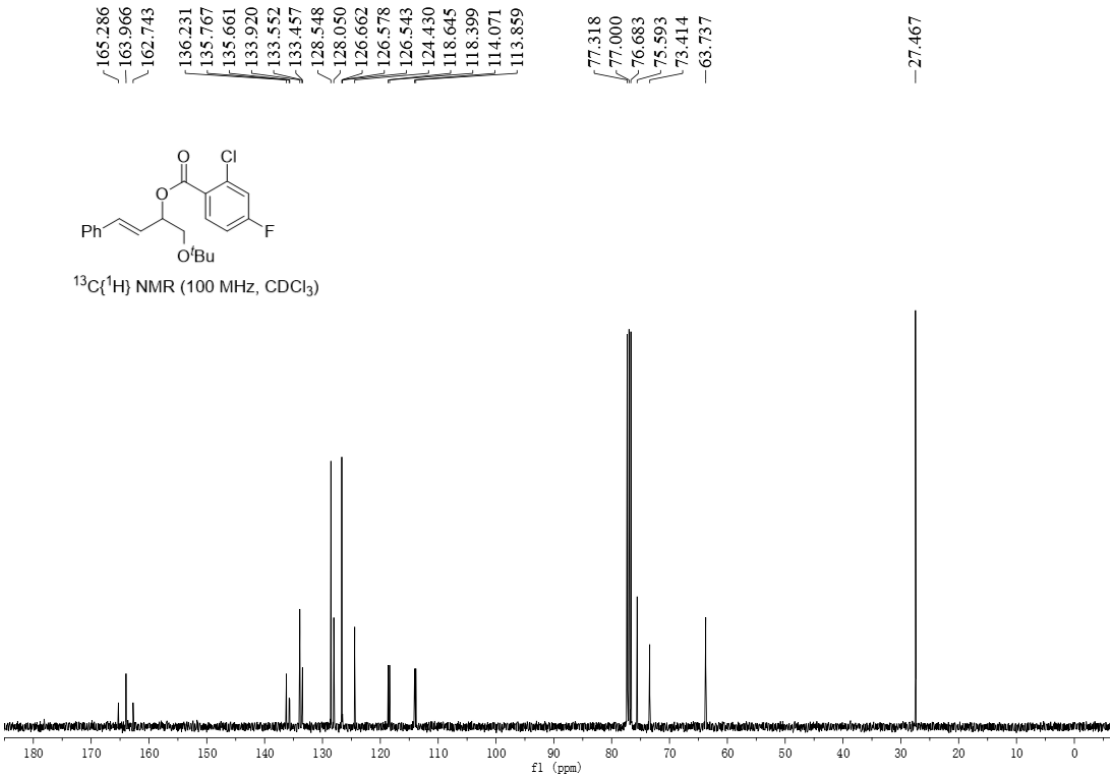
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 3,5-dichlorobenzoate (4n)

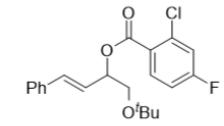




(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 2-chloro-4-fluorobenzoate (4o)

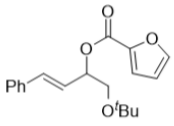




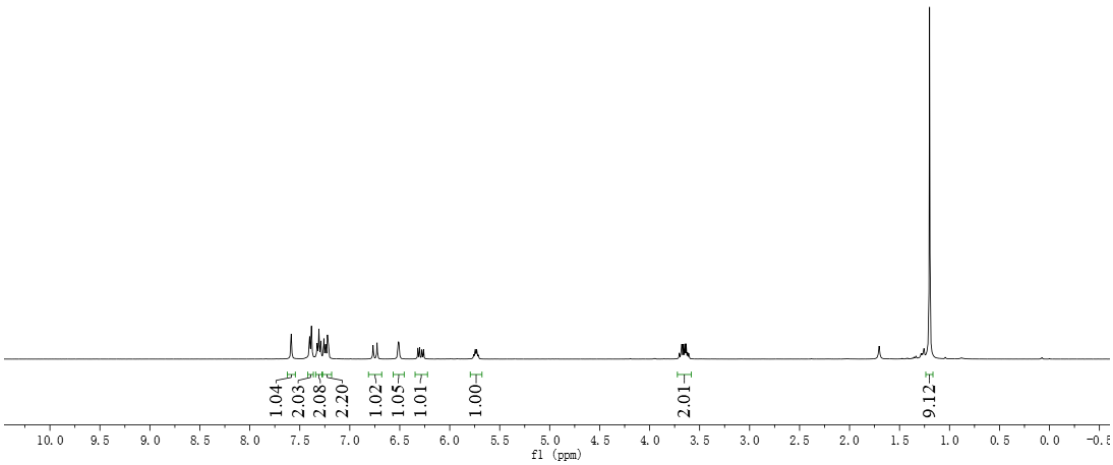


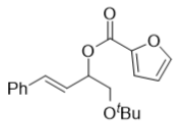
^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl furan-2-carboxylate (4p)

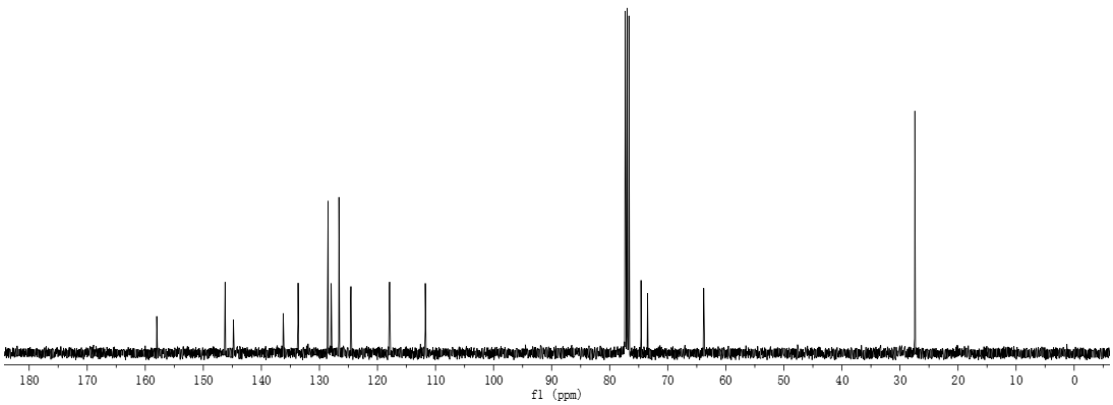


^{1}HNMR (400 MHz, $CDCl_3$)

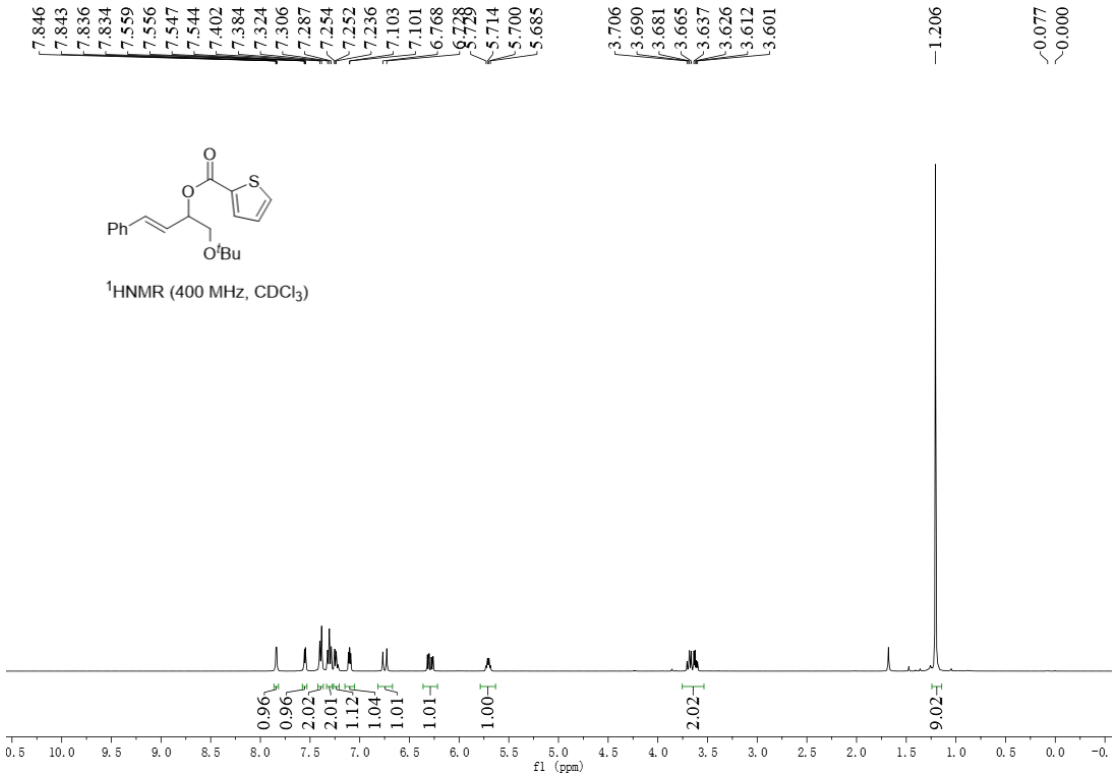


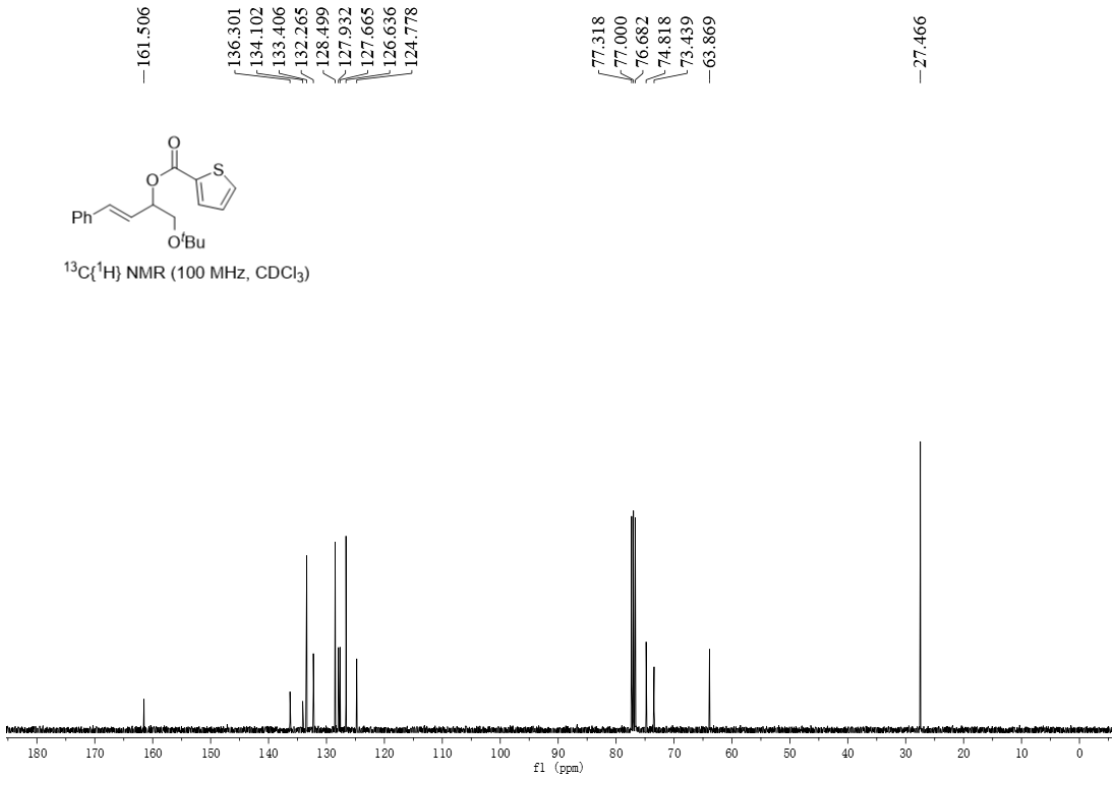


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

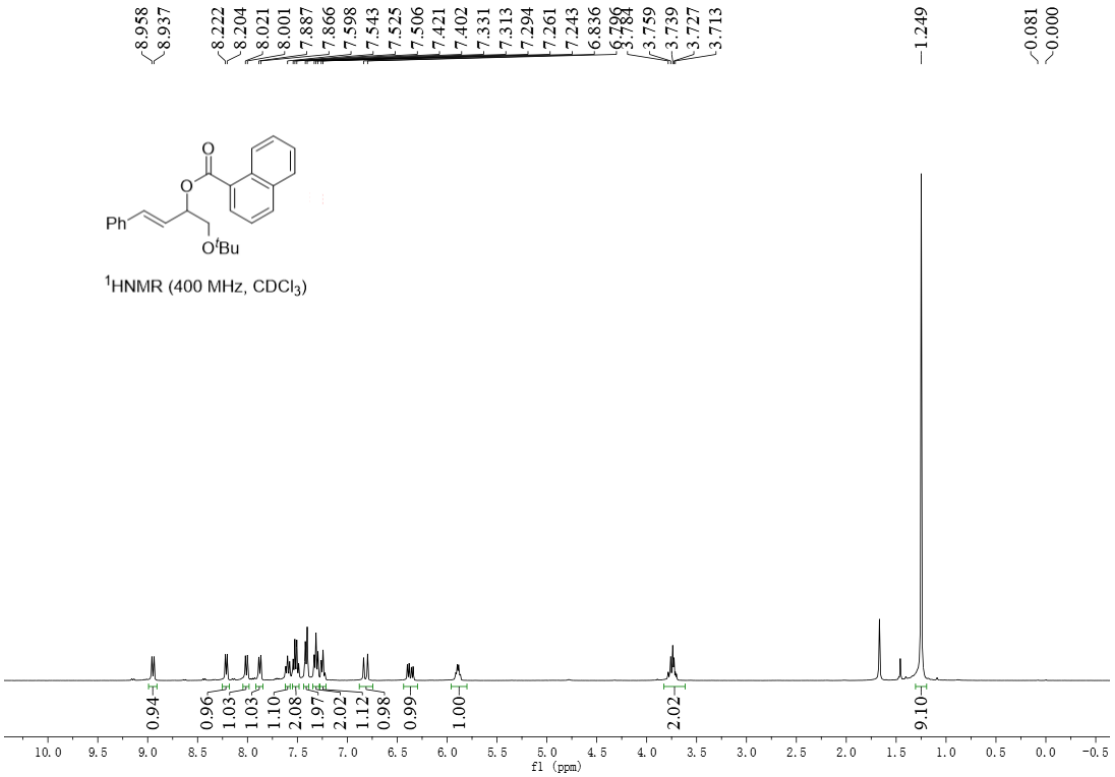


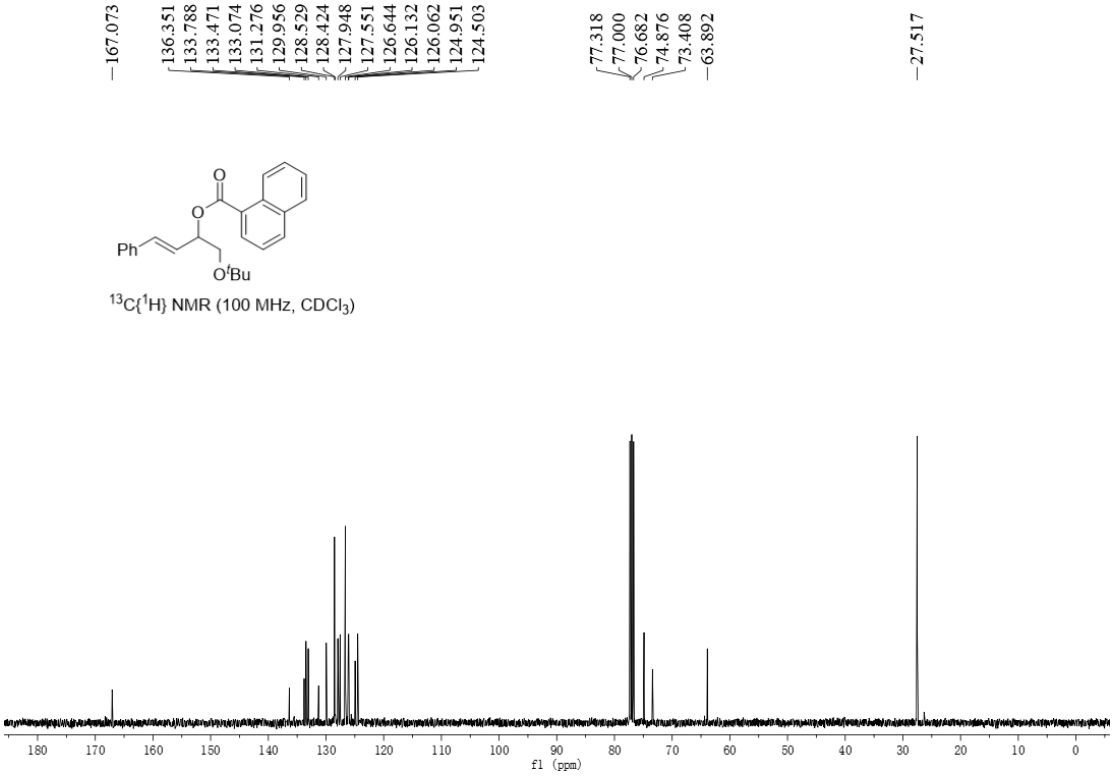
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl thiophene-2-carboxylate (4q)



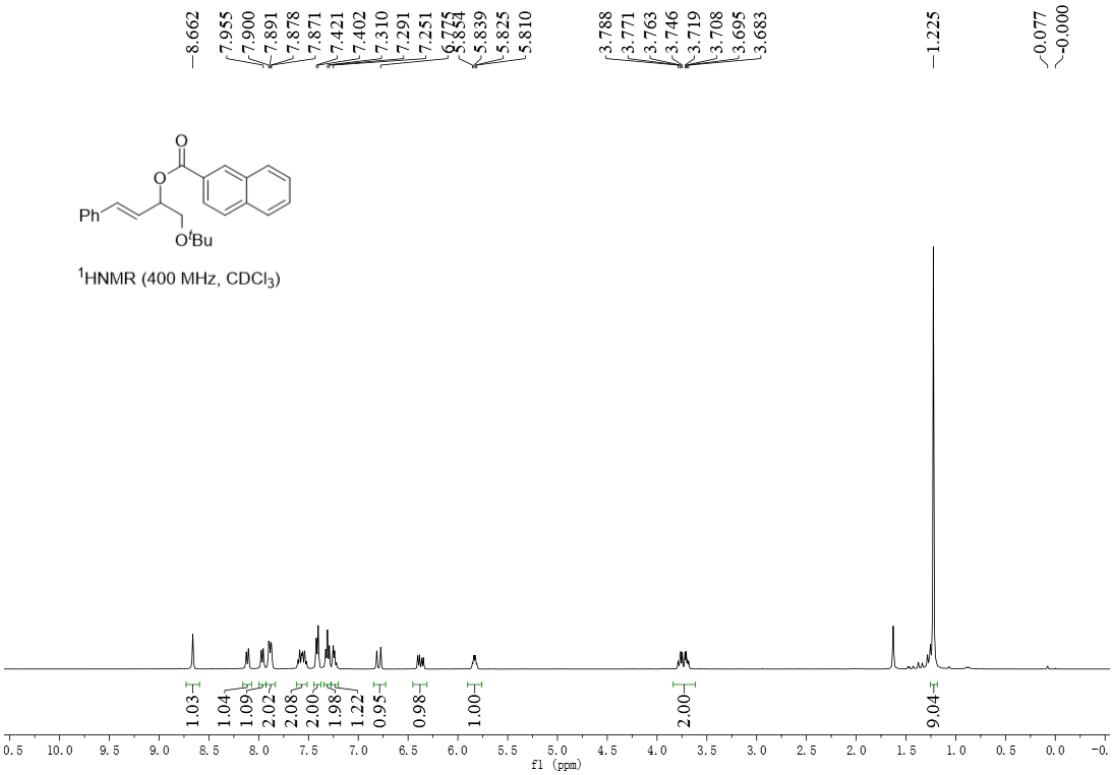


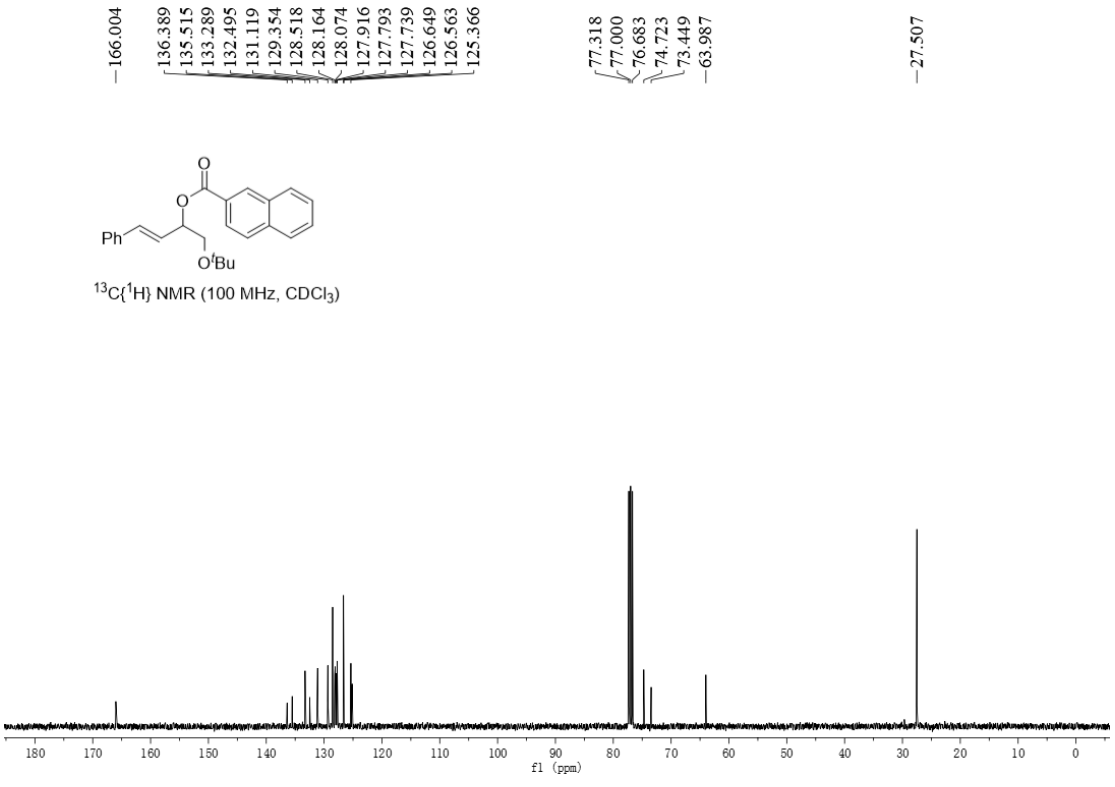
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-yl 1-naphthoate (4r)



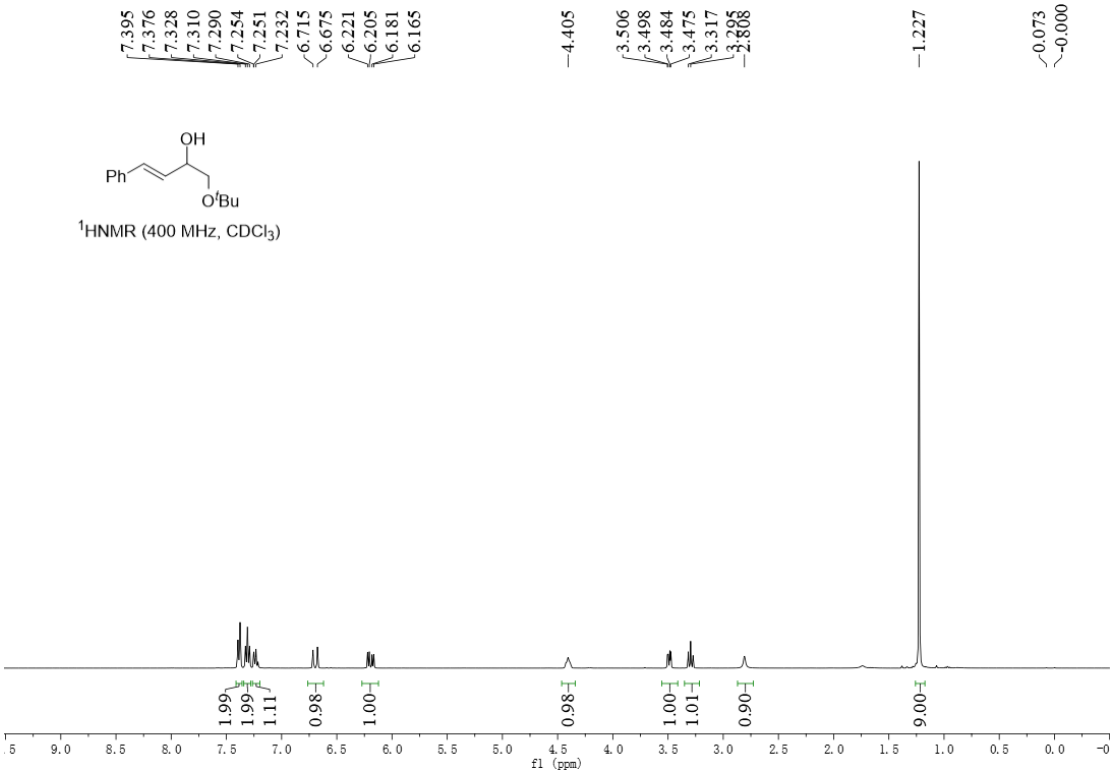


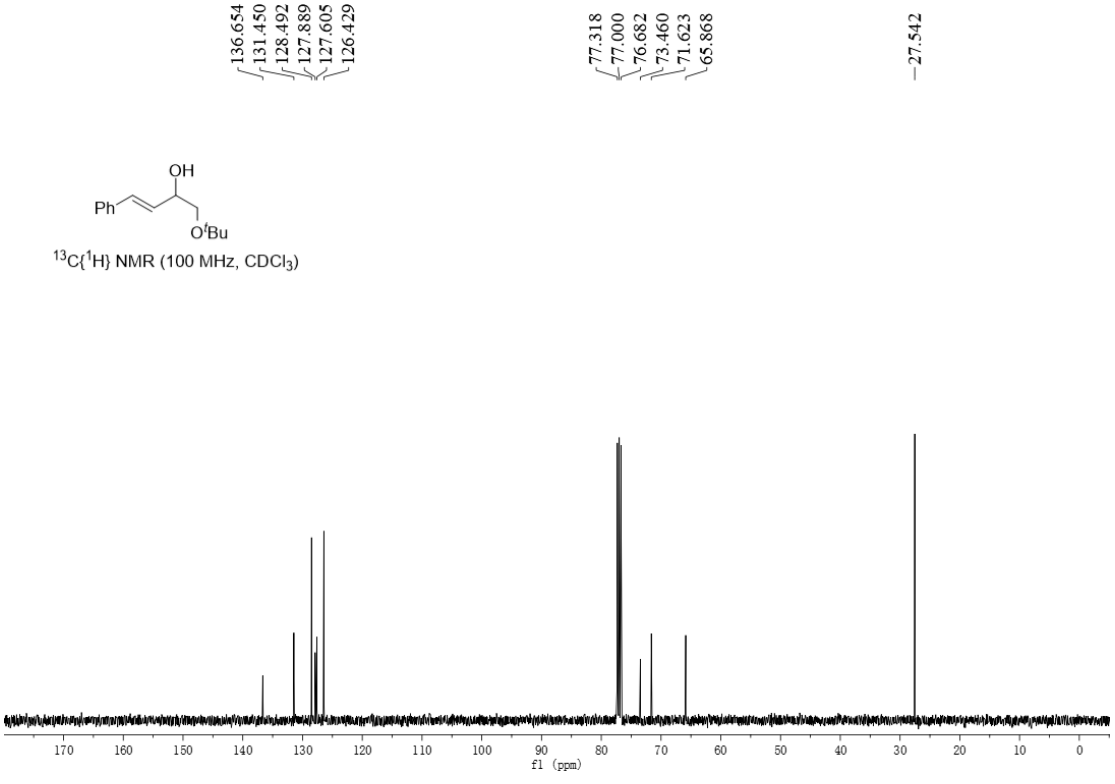
(*E*)-1-(tert-butoxy)-4-phenylbut-3-en-2-yl 2-naphthoate (4s)



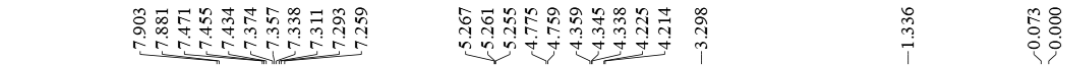


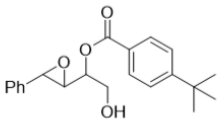
(*E*)-1-(*tert*-butoxy)-4-phenylbut-3-en-2-ol (7)



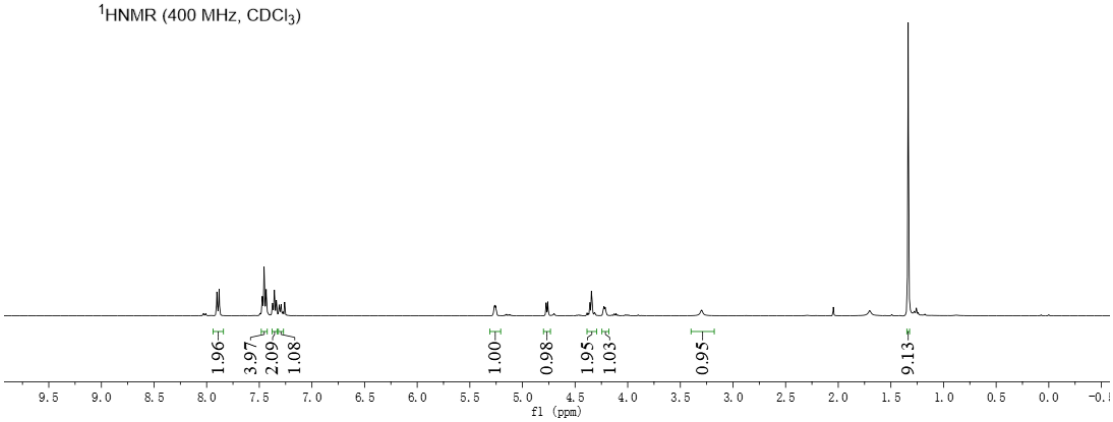


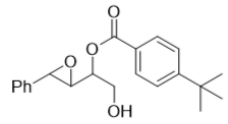
2-hydroxy-1-(3-phenyloxiran-2-yl)ethyl 4-(*tert*-butyl)benzoate (8)



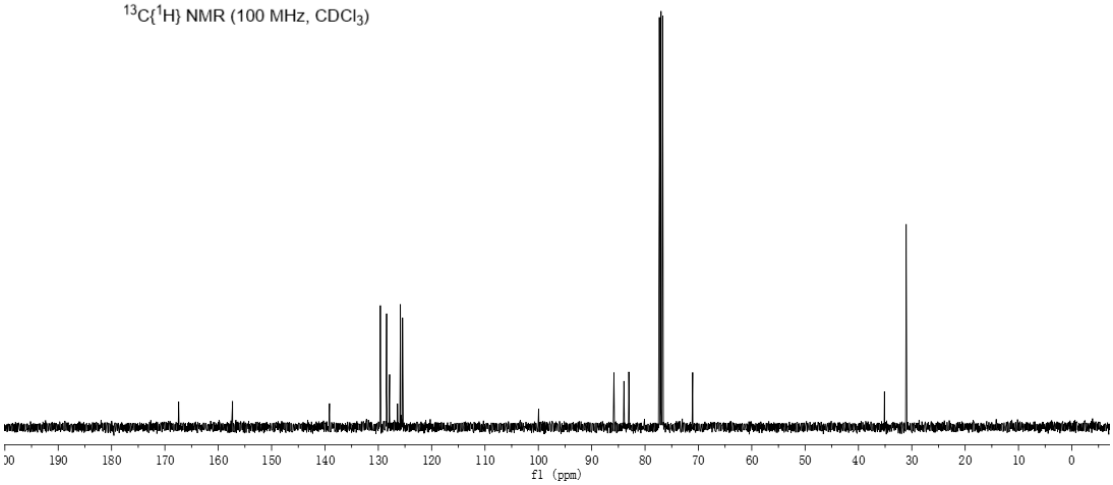


^{1}HNMR (400 MHz, $CDCl_3$)

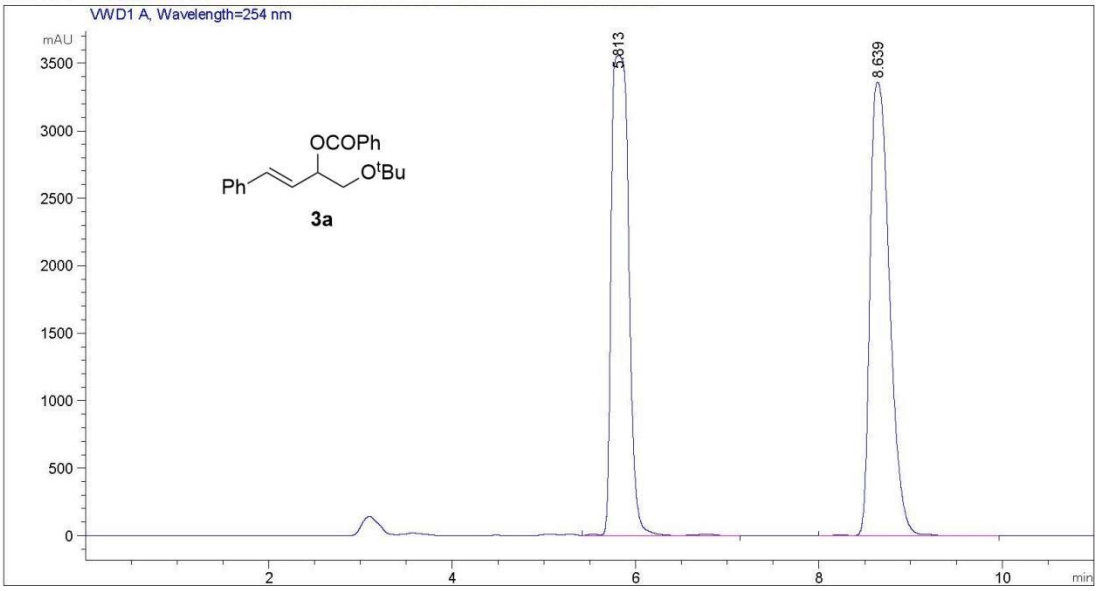




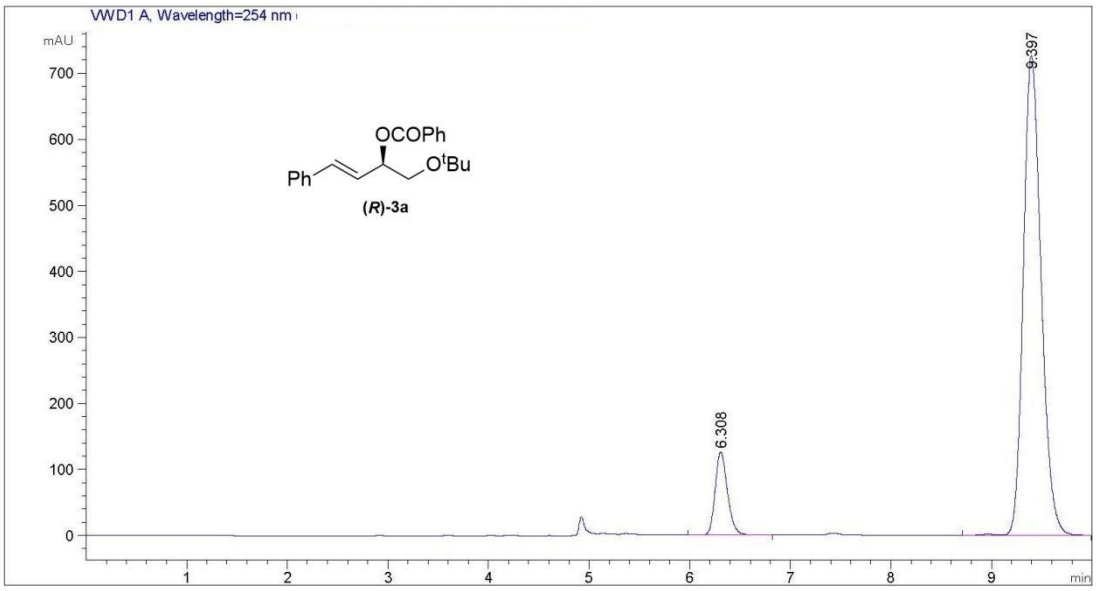
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



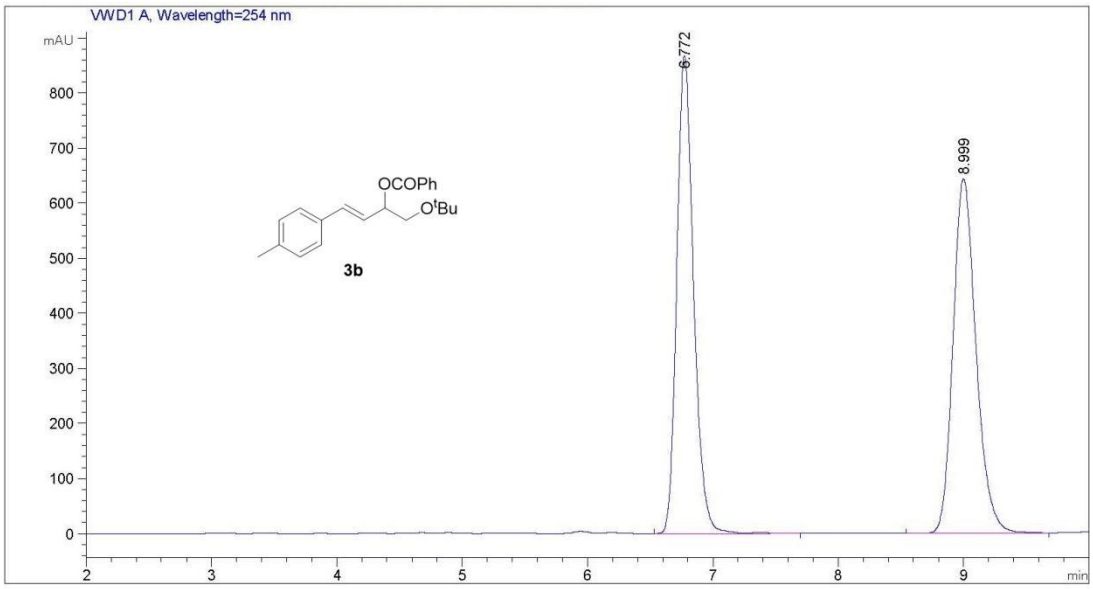
11. HPLC trace



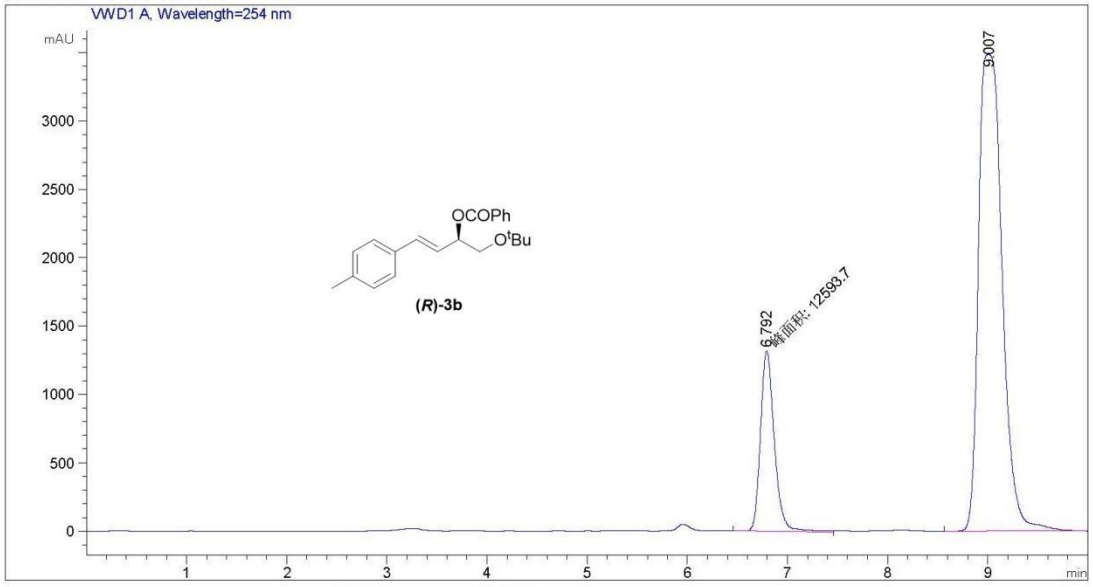
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.813	VV R	0.2110	4.68231e4	3555.77075	48.6727
2	8.639	VV R	0.2293	4.93767e4	3358.34009	51.3273



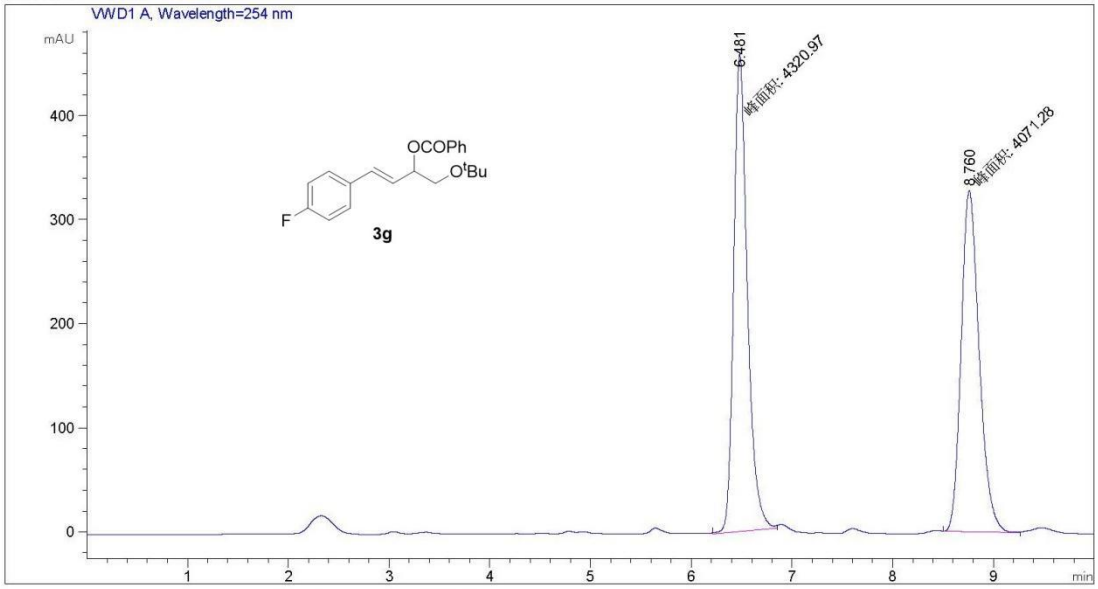
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.308	BB	0.1296	1065.37830	126.00104	10.6624
2	9.397	VBAR	0.1900	8926.51367	726.39166	89.3376



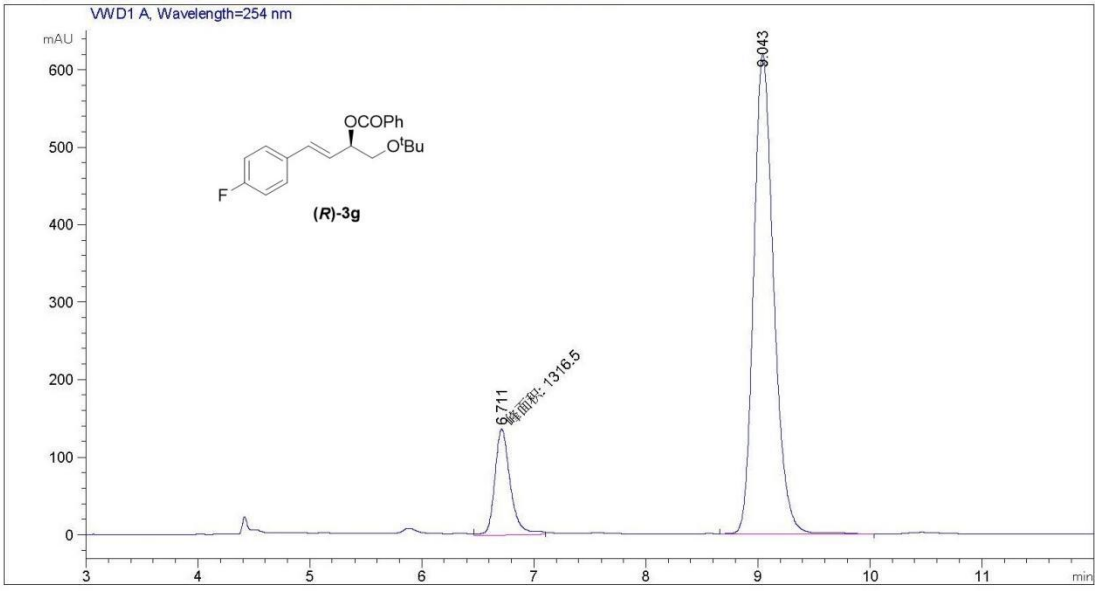
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.772	BV R	0.1423	8074.92627	867.73401	49.6747
2	8.999	BB	0.1943	8180.69482	643.54425	50.3253



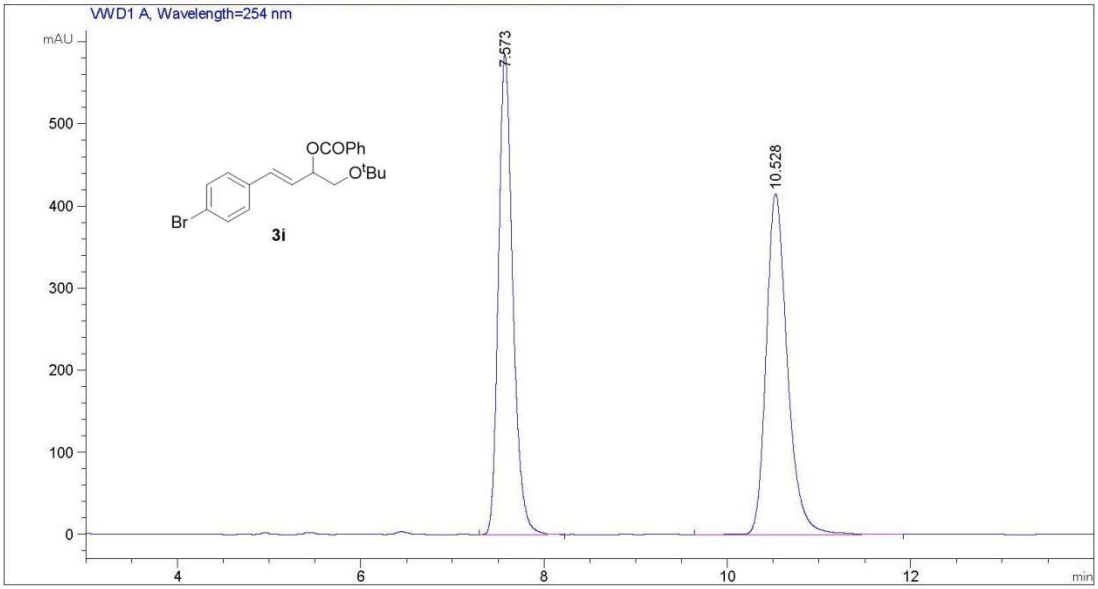
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.792	MM	0.1595	1.25937e4	1316.03674	18.0560
2	9.007	BBA	0.2562	5.71544e4	3487.61133	81.9440



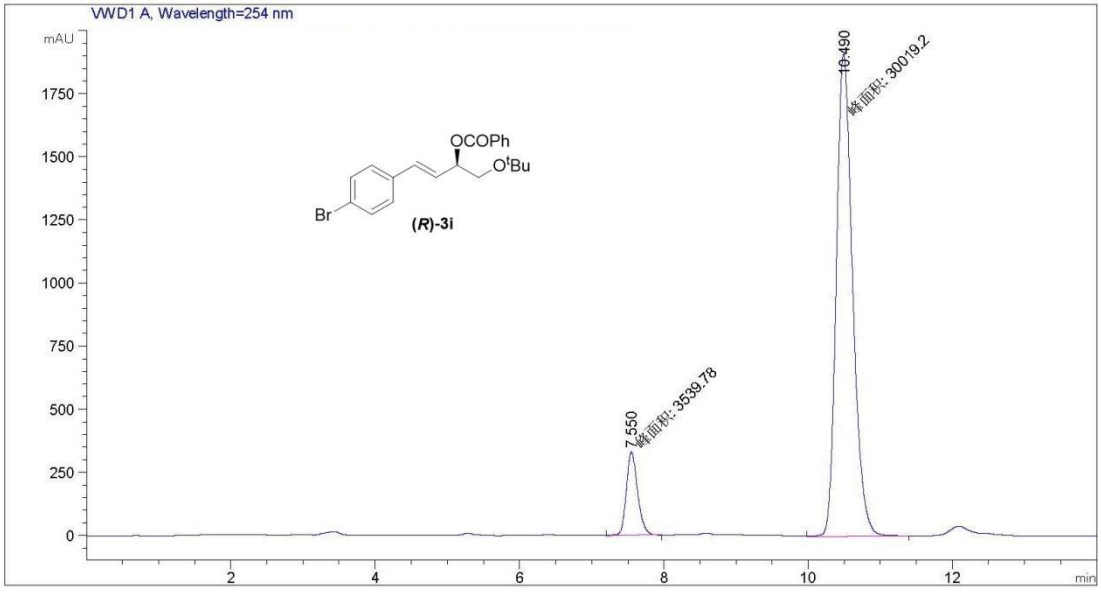
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.481	MM	0.1570	4320.96875	458.62671	51.4876
2	8.760	MM	0.2071	4071.28198	327.64420	48.5124



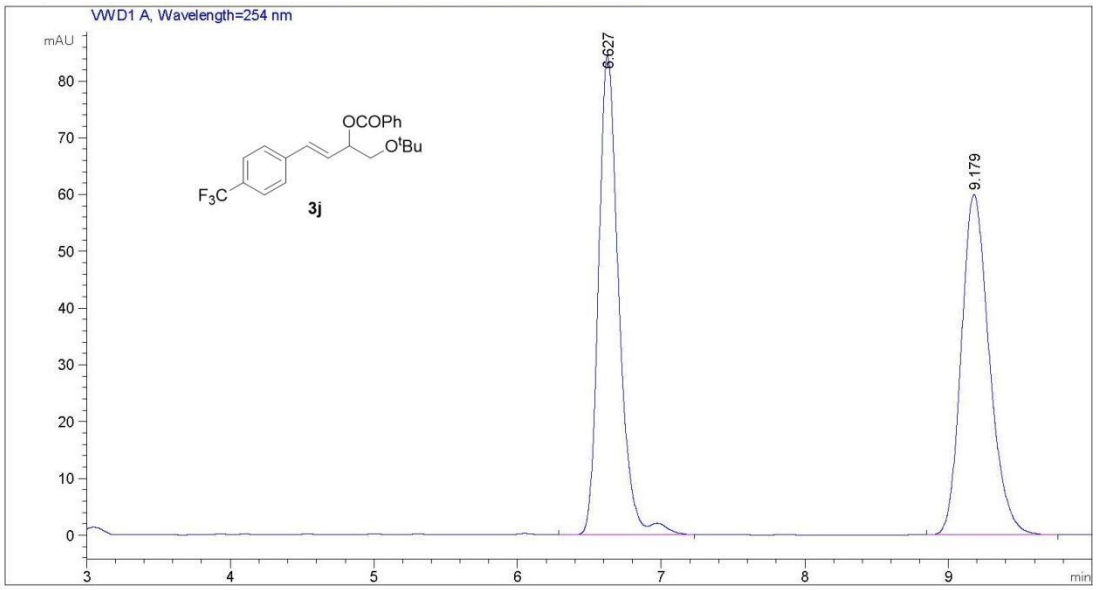
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.711	MM	0.1604	1316.50232	136.83461	14.6524
2	9.043	BV R	0.1896	7668.40039	618.53088	85.3476



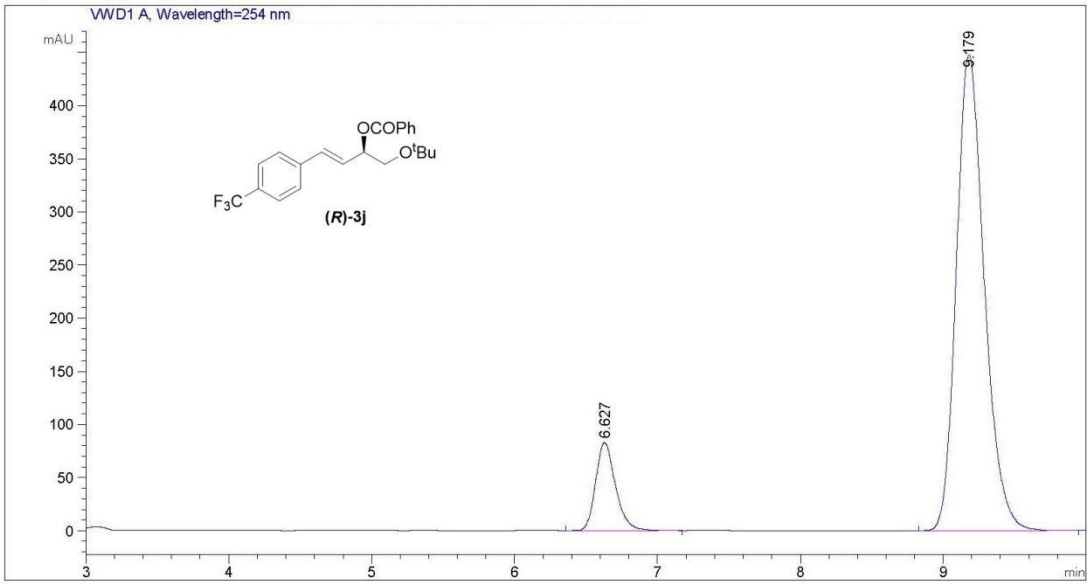
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.573	BB	0.1653	6382.49854	584.73853	48.9188
2	10.528	BB	0.2432	6664.63379	415.27417	51.0812



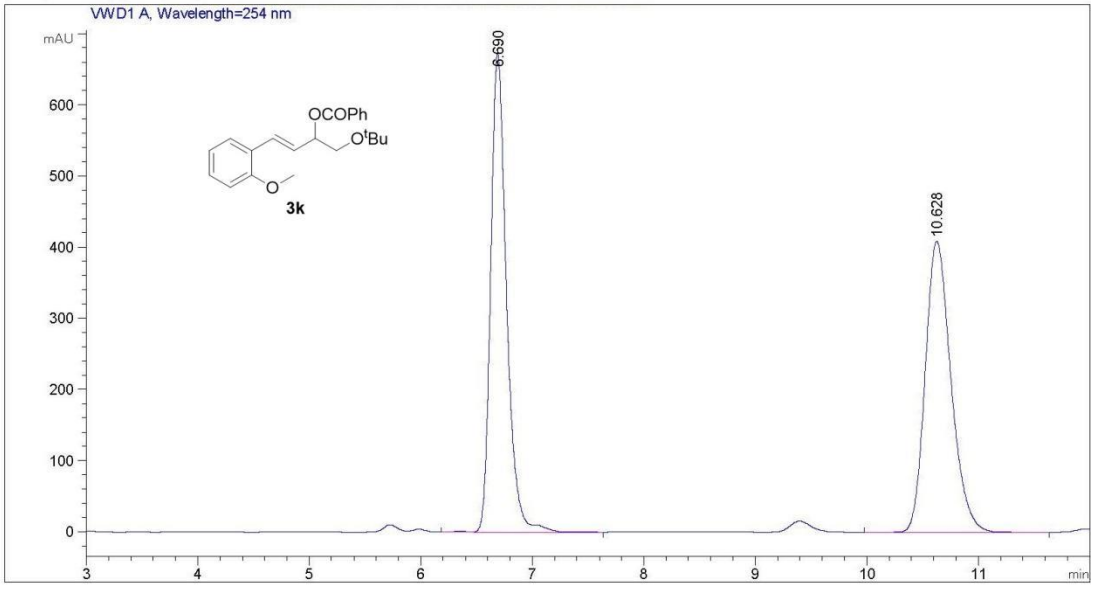
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.550	MM	0.1789	3539.77832	329.82367	10.5479
2	10.490	MM	0.2618	3.00192e4	1910.75354	89.4521



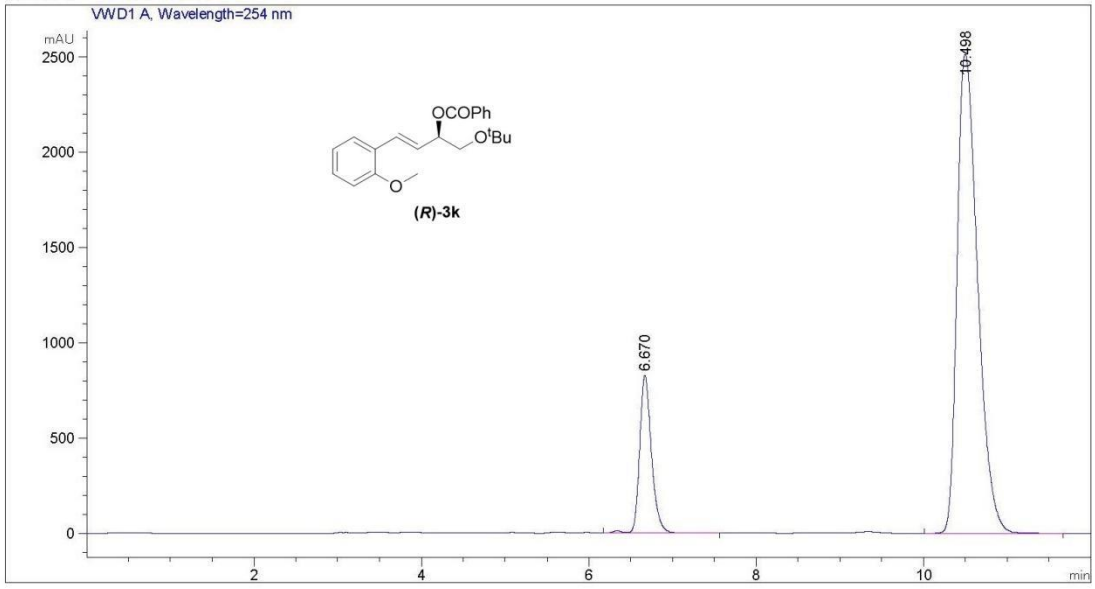
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.627	BV R	0.1462	827.05658	84.37080	50.4202
2	9.179	BB	0.2071	813.27063	60.00721	49.5798



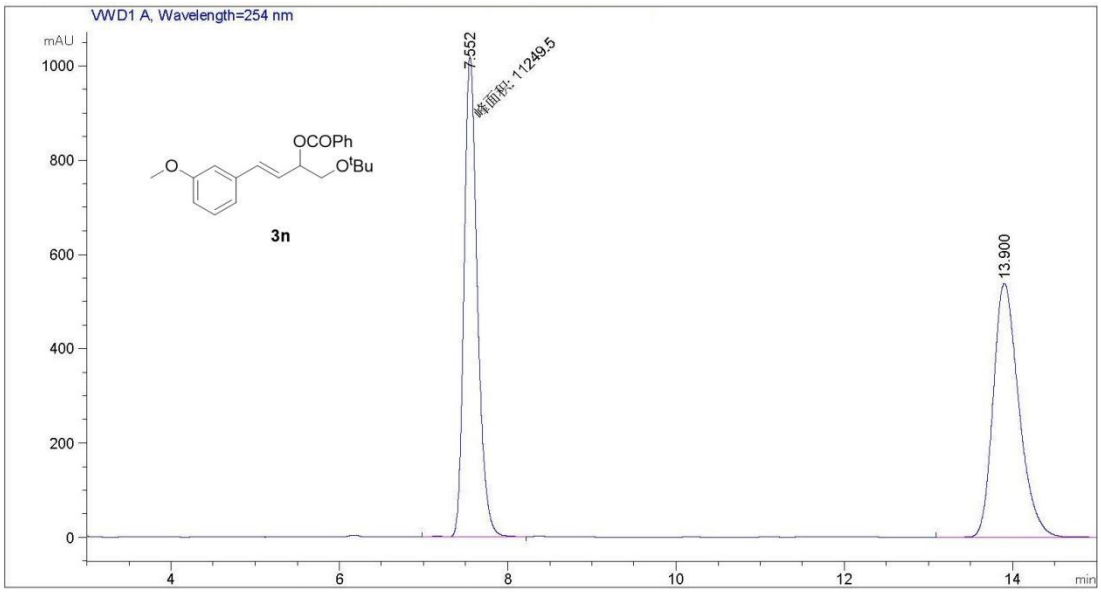
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.627	BB	0.1468	801.37408	82.90154	11.6282
2	9.179	BB	0.2077	6090.25244	447.78754	88.3718



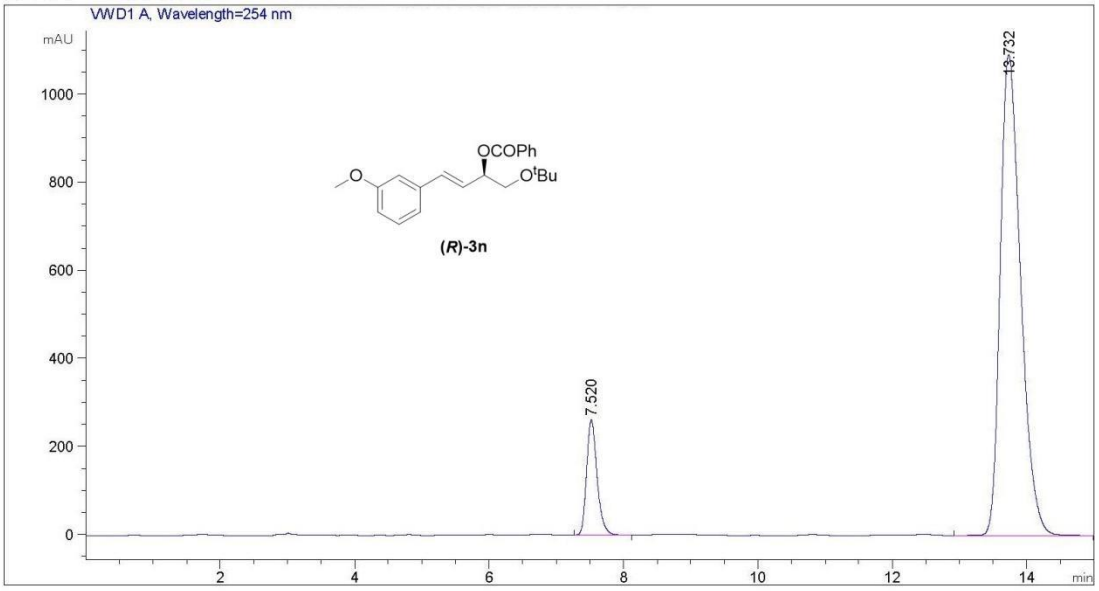
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.690	VV R	0.1493	6656.41064	671.85382	50.3839
2	10.628	BB	0.2459	6554.97998	409.25833	49.6161



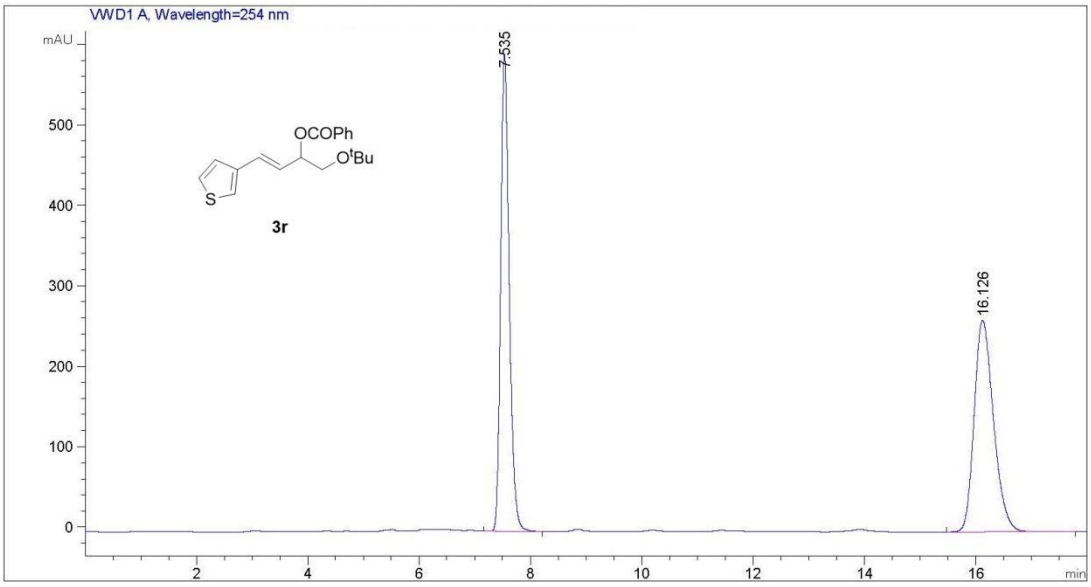
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.670	VV R	0.1470	8118.80176	828.90771	15.9432
2	10.498	BB	0.2627	4.28044e4	2512.91187	84.0568



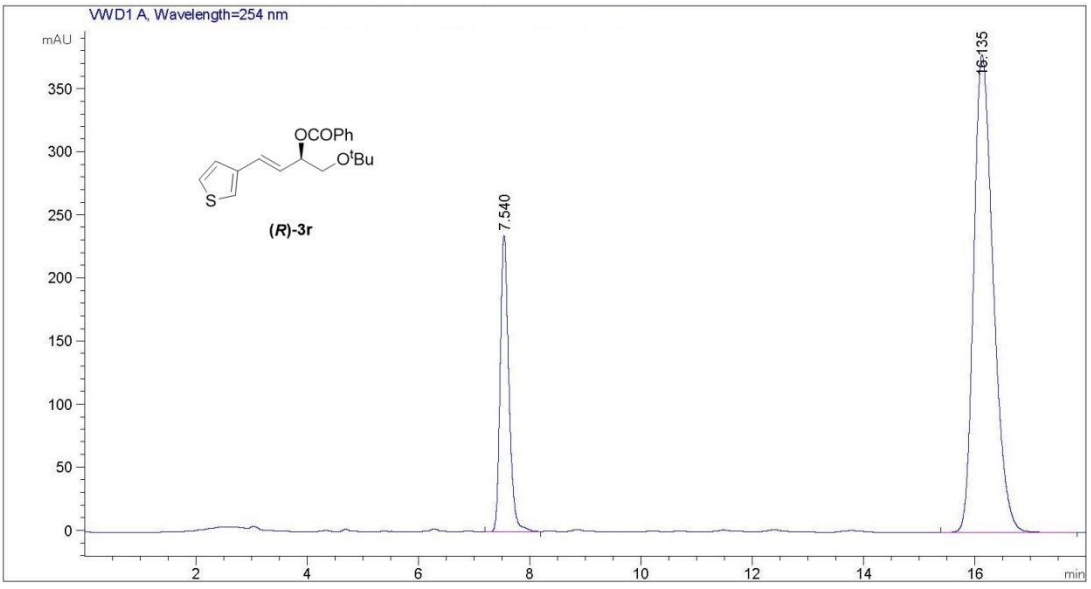
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.552	MF	0.1838	1.12495e4	1020.20410	49.6358
2	13.900	BBA	0.3241	1.14146e4	538.89807	50.3642



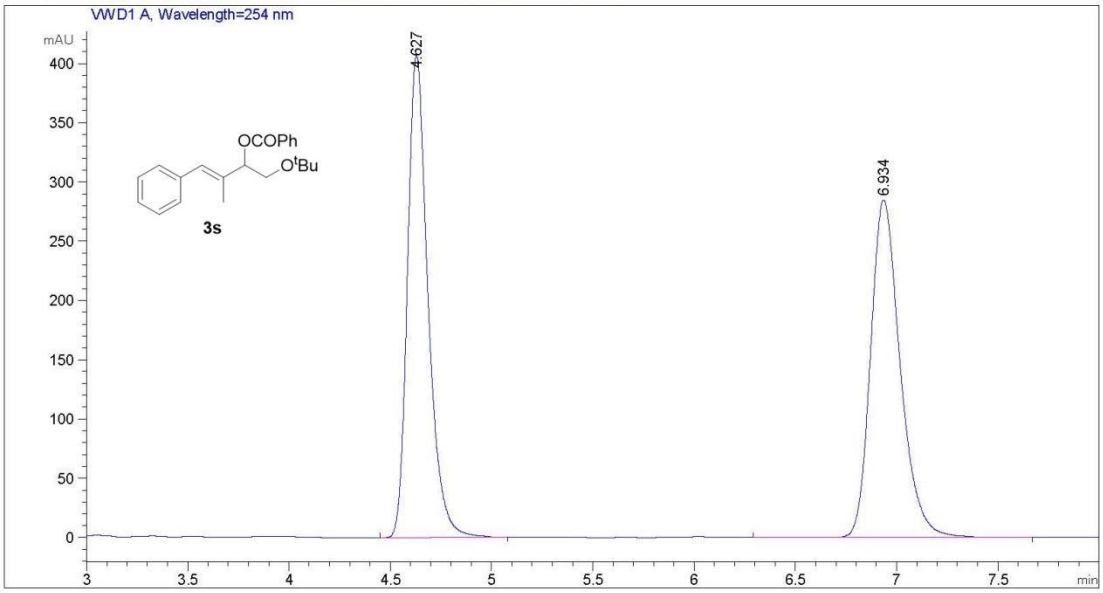
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.520	BB	0.1656	2842.58545	261.90549	11.0145
2	13.732	BBA	0.3245	2.29651e4	1091.42493	88.9855



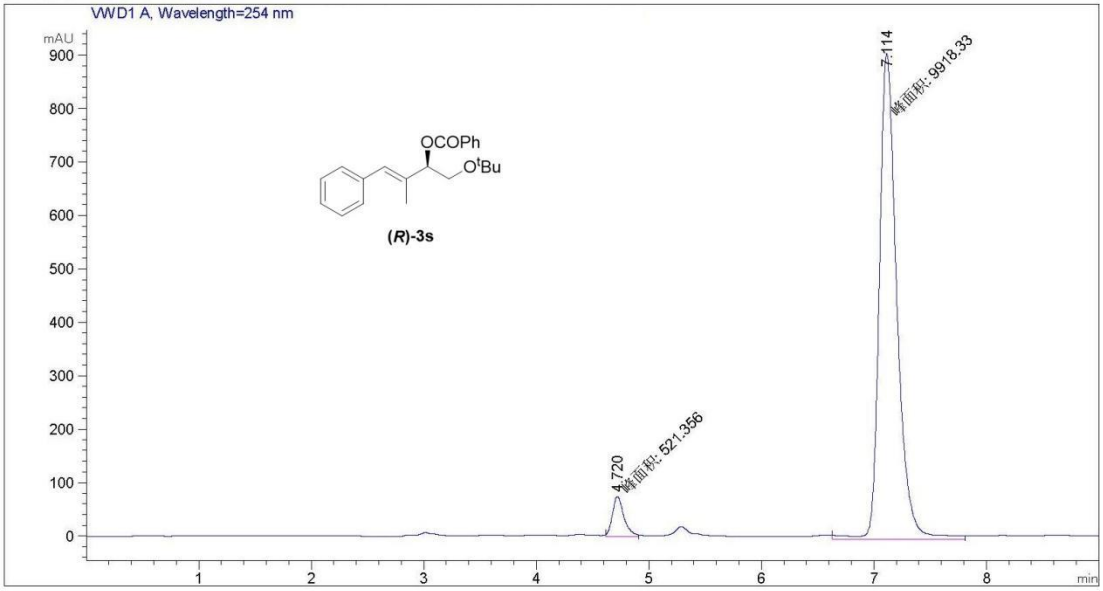
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.535	BB	0.1625	6321.35742	592.29150	49.9438
2	16.126	BB	0.3715	6335.58350	262.57666	50.0562



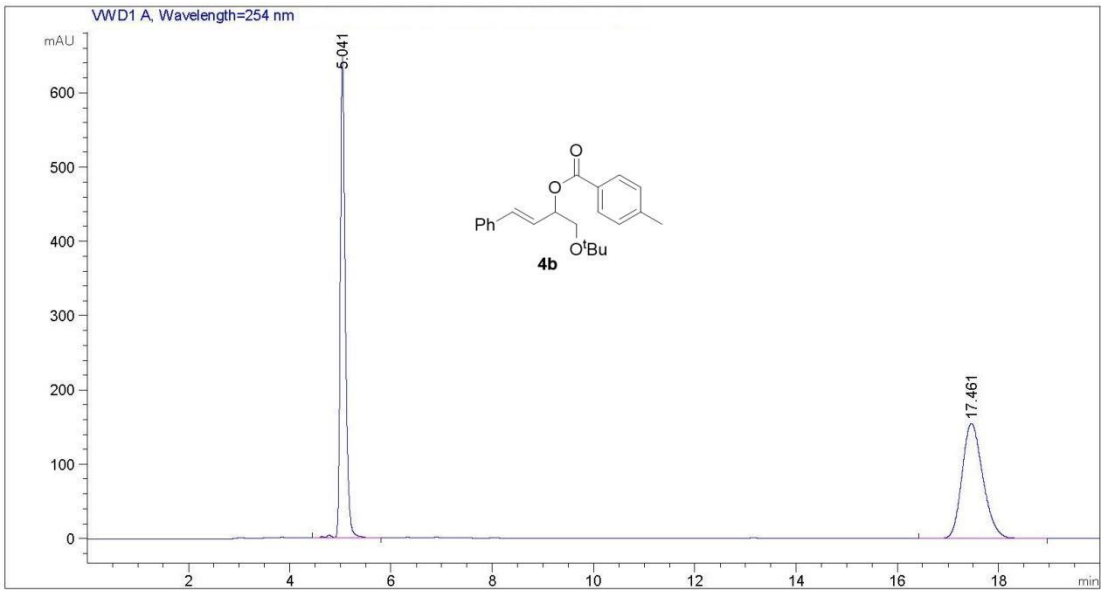
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.540	BB	0.1639	2540.88159	235.44618	21.6433
2	16.135	BB	0.3747	9198.93848	378.23102	78.3567



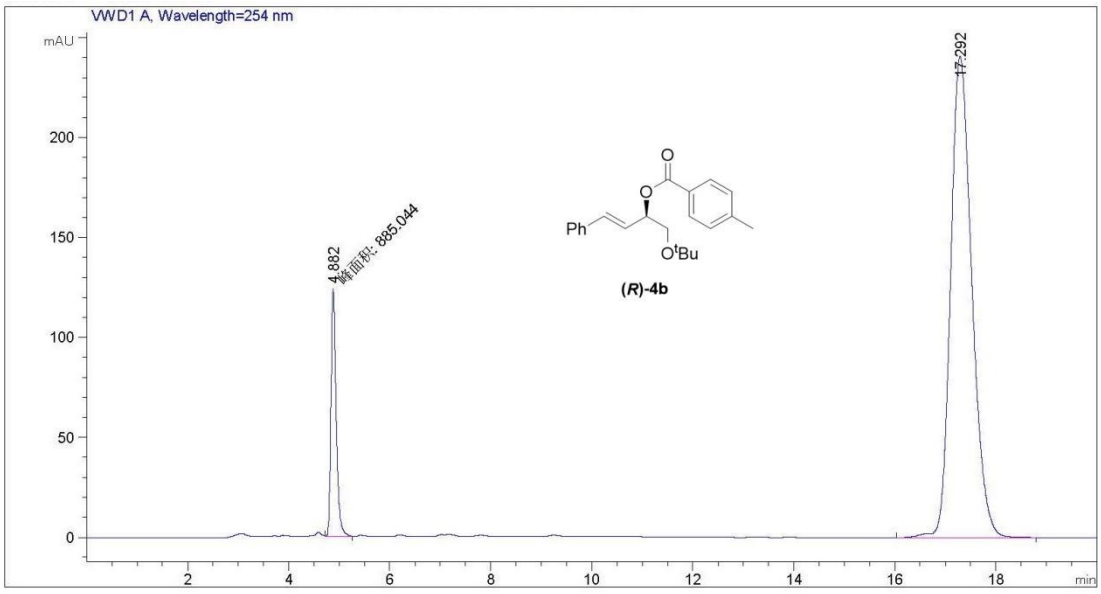
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.627	BB	0.1059	2855.33765	406.86047	49.6960
2	6.934	BB	0.1545	2890.26929	284.60648	50.3040



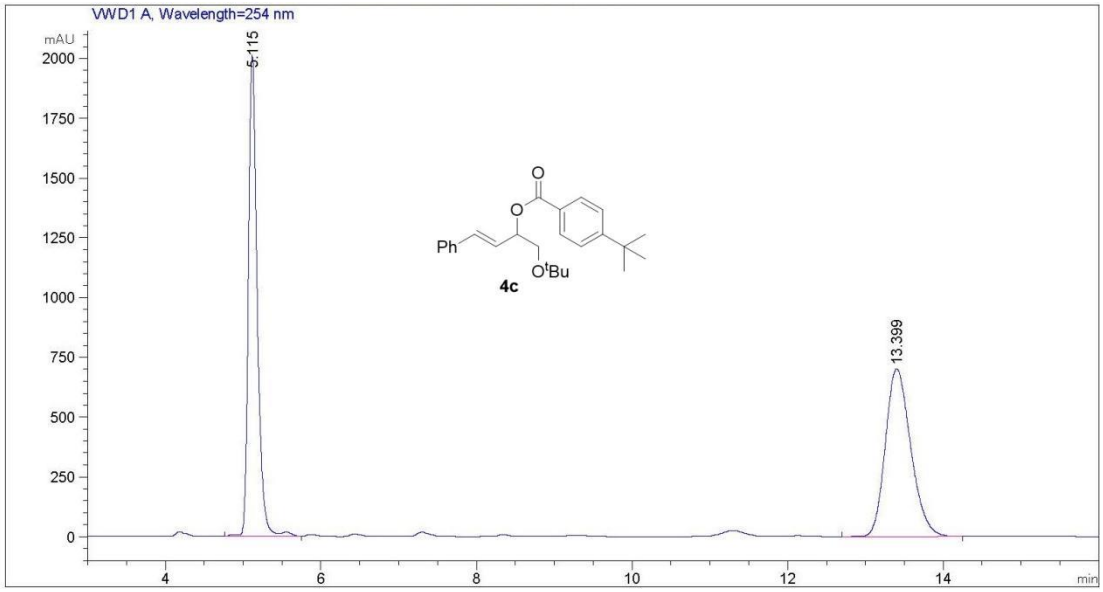
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.720	MM	0.1173	521.35614	74.07644	4.9940
2	7.114	MM	0.1818	9918.32910	909.19489	95.0060



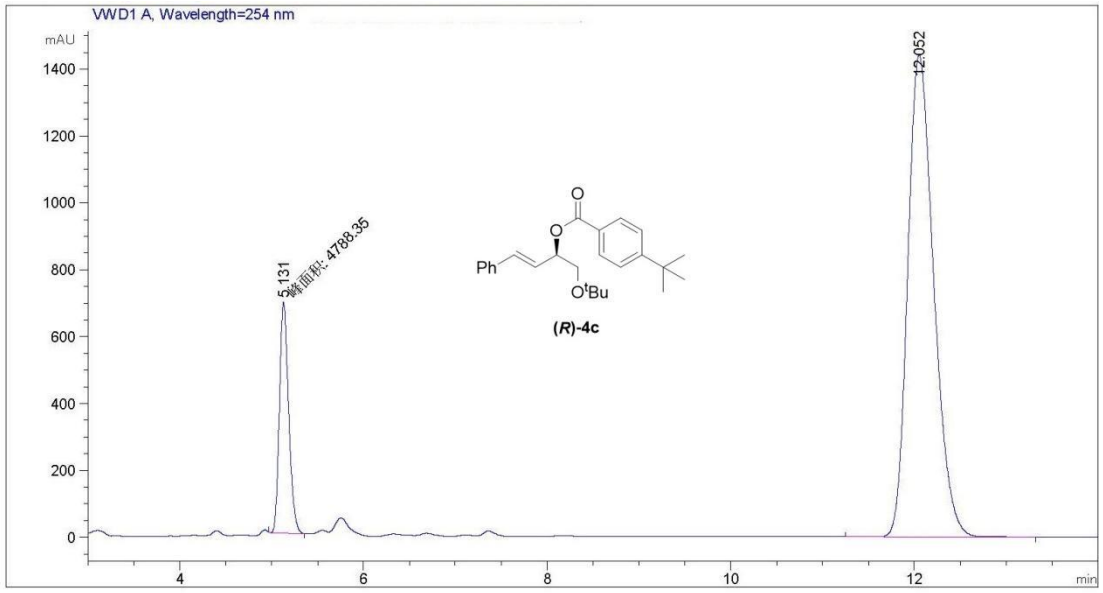
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.041	VV R	0.1028	4459.57813	648.51489	50.1110
2	17.461	BB	0.4422	4439.81445	155.00603	49.8890



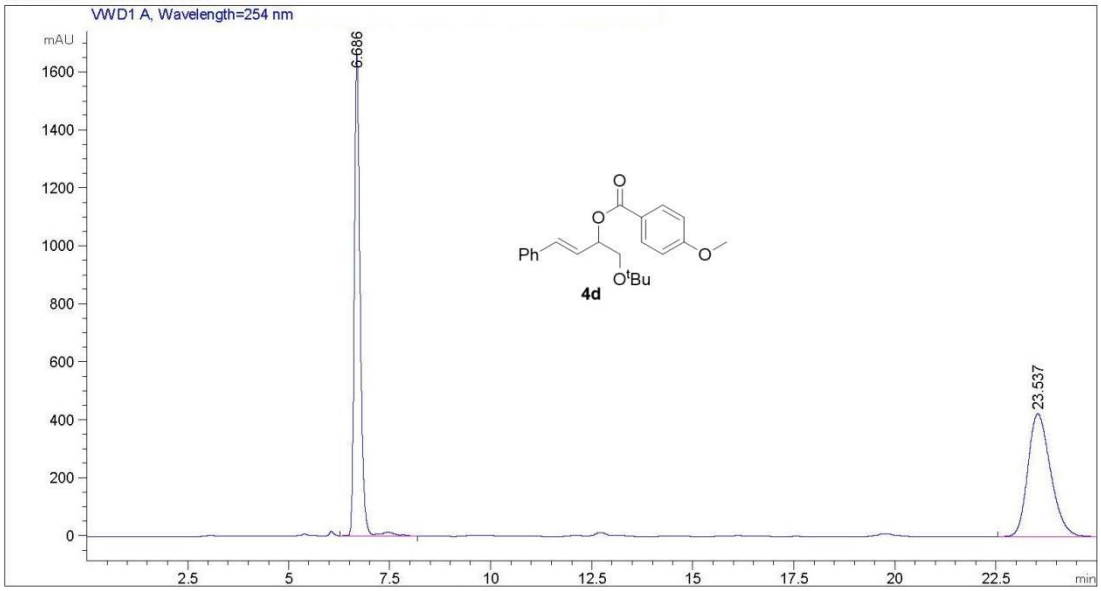
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.882	MF	0.1186	885.04376	124.33823	11.2222
2	17.292	BB	0.4485	7001.51025	240.58299	88.7778



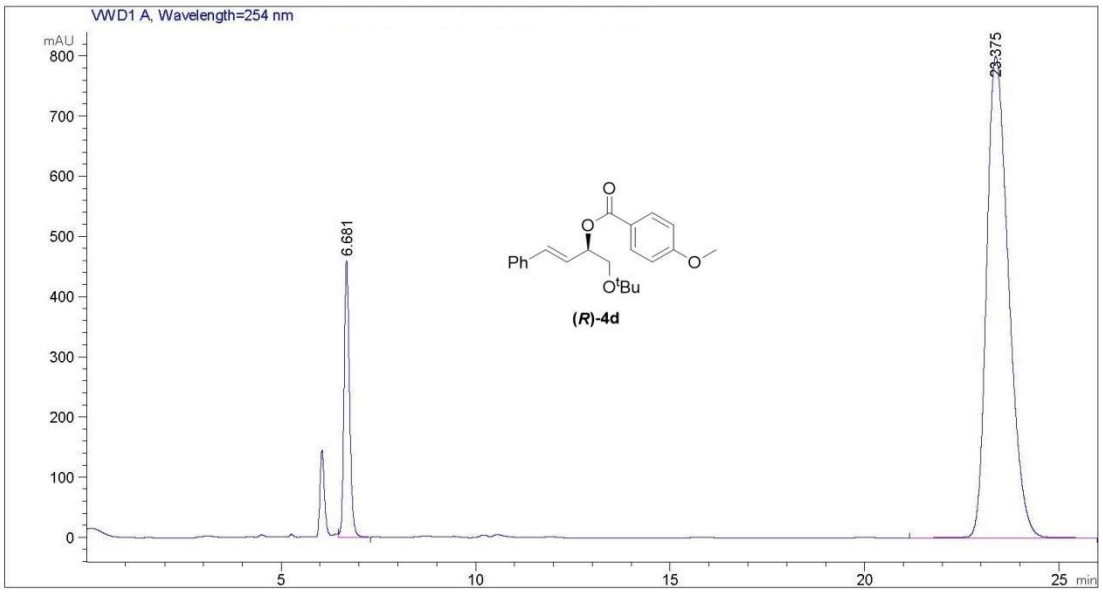
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.115	VV R	0.1172	1.58334e4	2012.98816	49.9647
2	13.399	BB	0.3496	1.58557e4	701.73688	50.0353



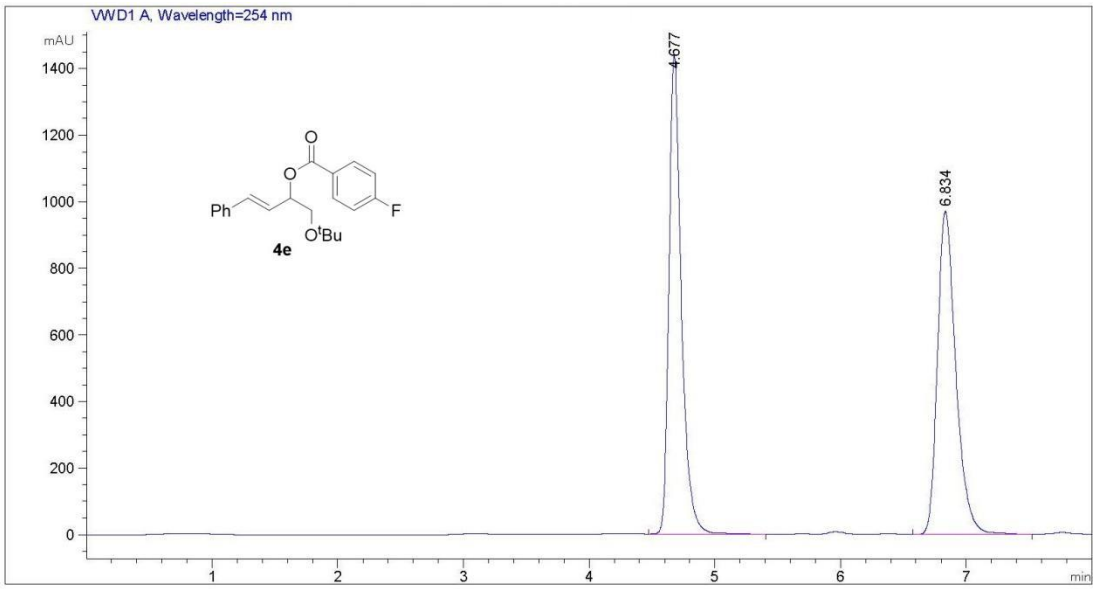
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.131	MM	0.1155	4788.35498	690.84058	14.5050
2	12.052	VB R	0.3027	2.82233e4	1439.90344	85.4950



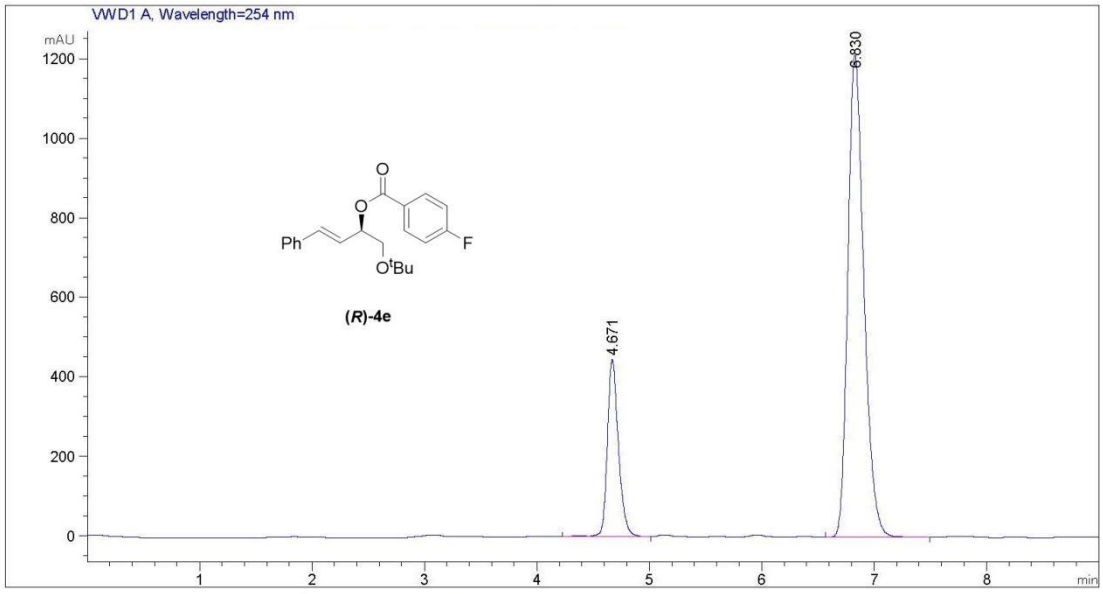
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.686	VV R	0.1507	1.68754e4	1660.15088	50.6019
2	23.537	BBA	0.6009	1.64739e4	423.43280	49.3981



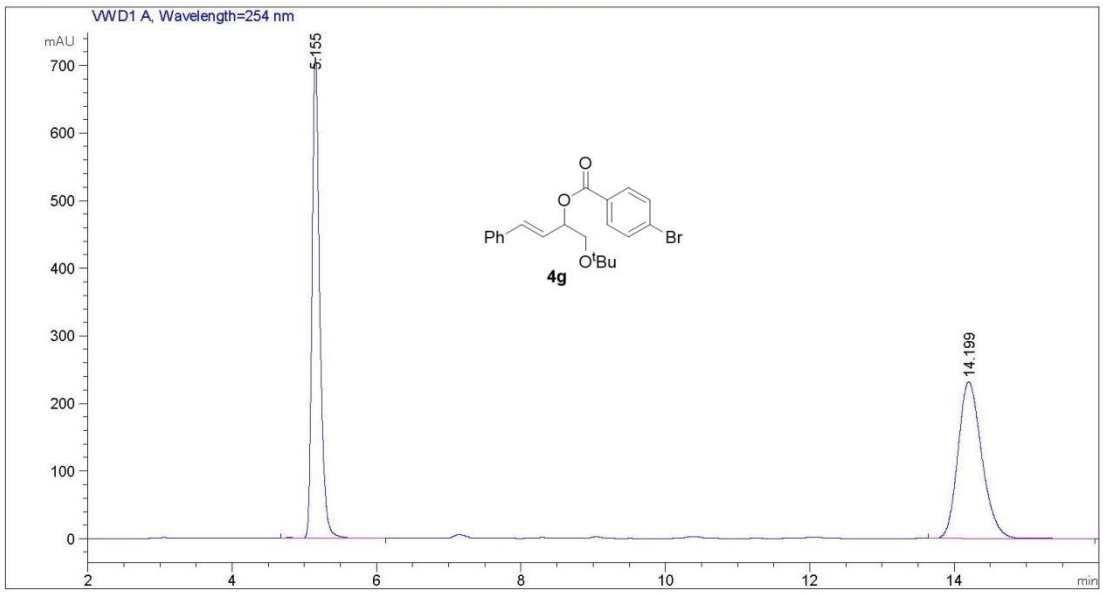
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.681	VB	0.1487	4483.84033	460.16760	12.5192
2	23.375	BBA	0.6055	3.13320e4	800.77441	87.4808



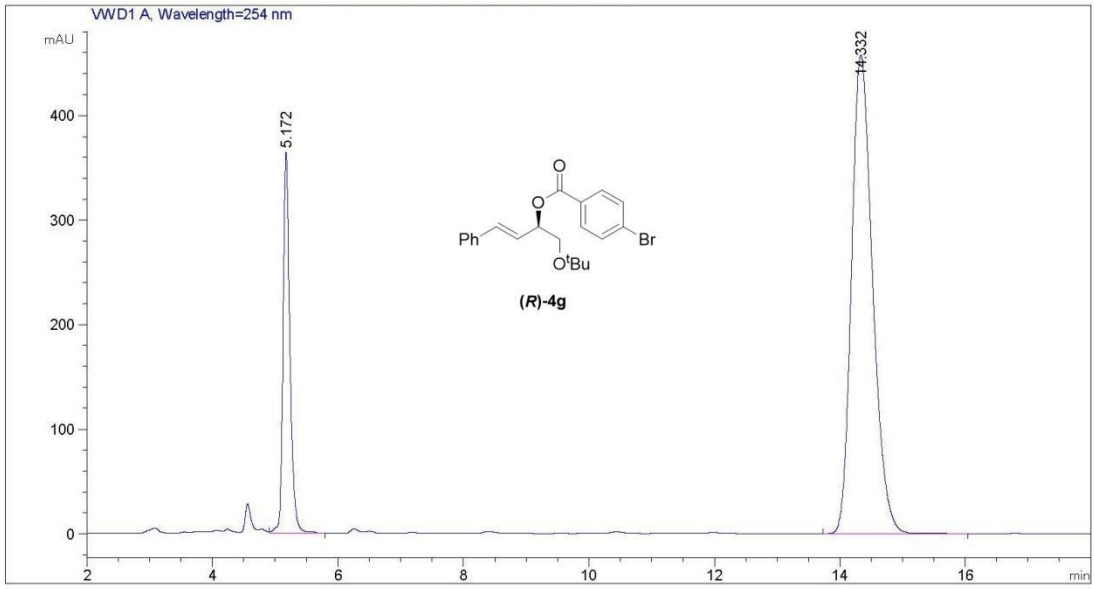
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.677	BV R	0.1028	9880.61230	1437.16345	49.9497
2	6.834	BV	0.1548	9900.50293	972.35327	50.0503



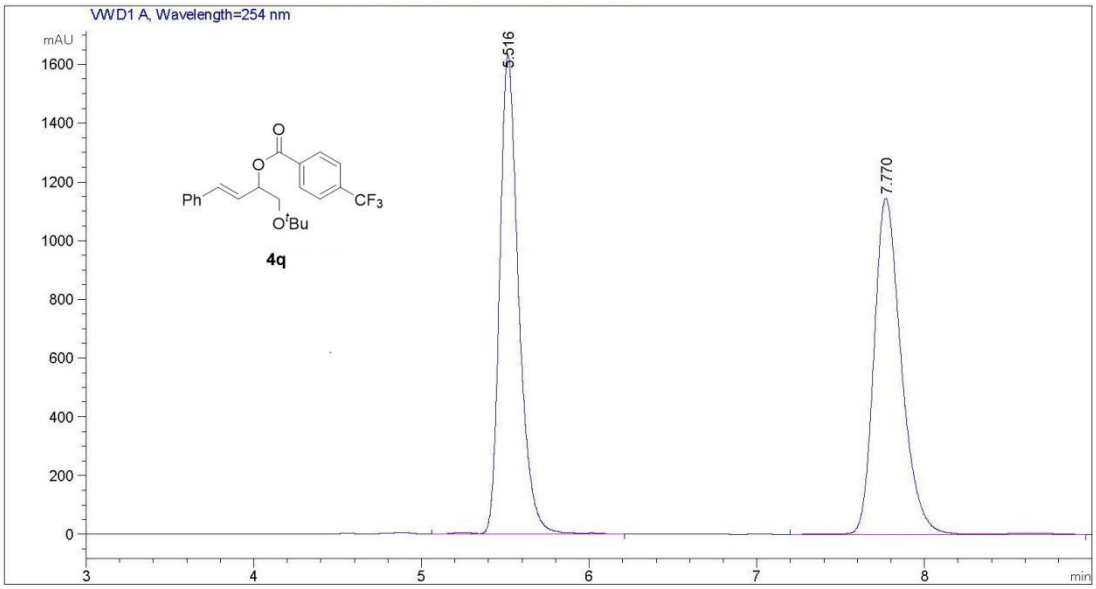
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.671	VB R	0.1021	3045.07178	445.29373	20.2592
2	6.830	VB	0.1524	1.19855e4	1211.90222	79.7408



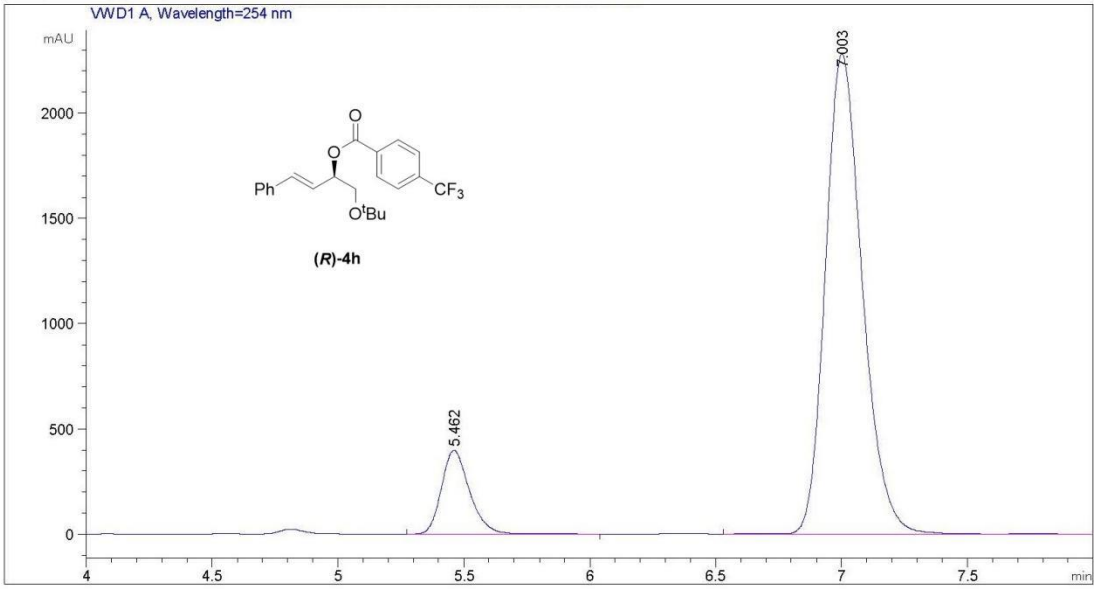
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.155	VV R	0.1121	5317.76270	712.40240	50.1101
2	14.199	BB	0.3514	5294.40234	231.83969	49.8899



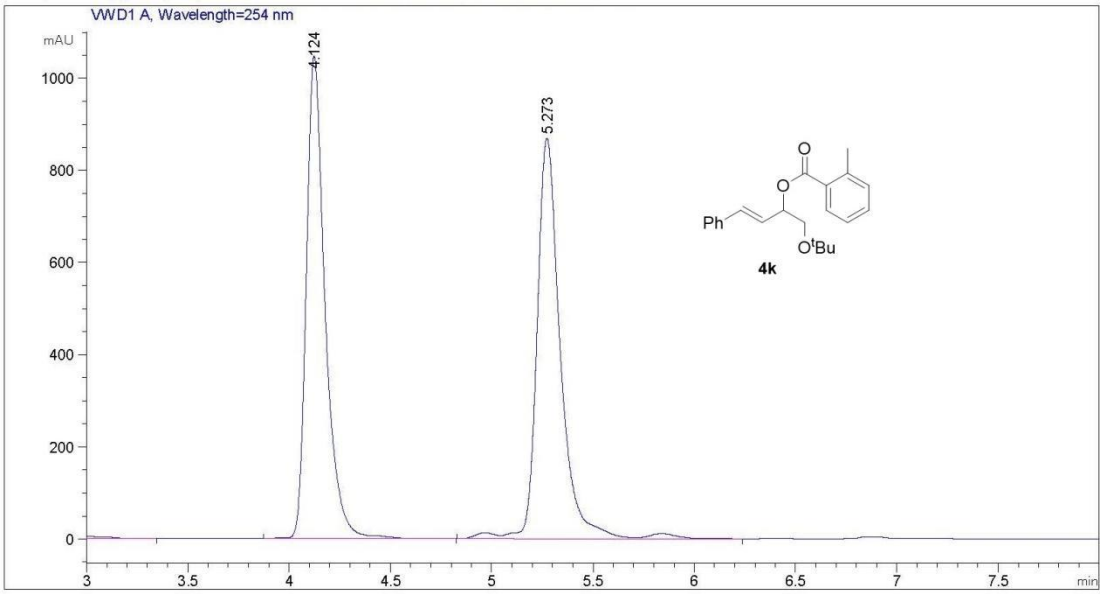
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.172	VB	0.1144	2757.47559	363.98138	20.5516
2	14.332	BB	0.3597	1.06598e4	457.80057	79.4484



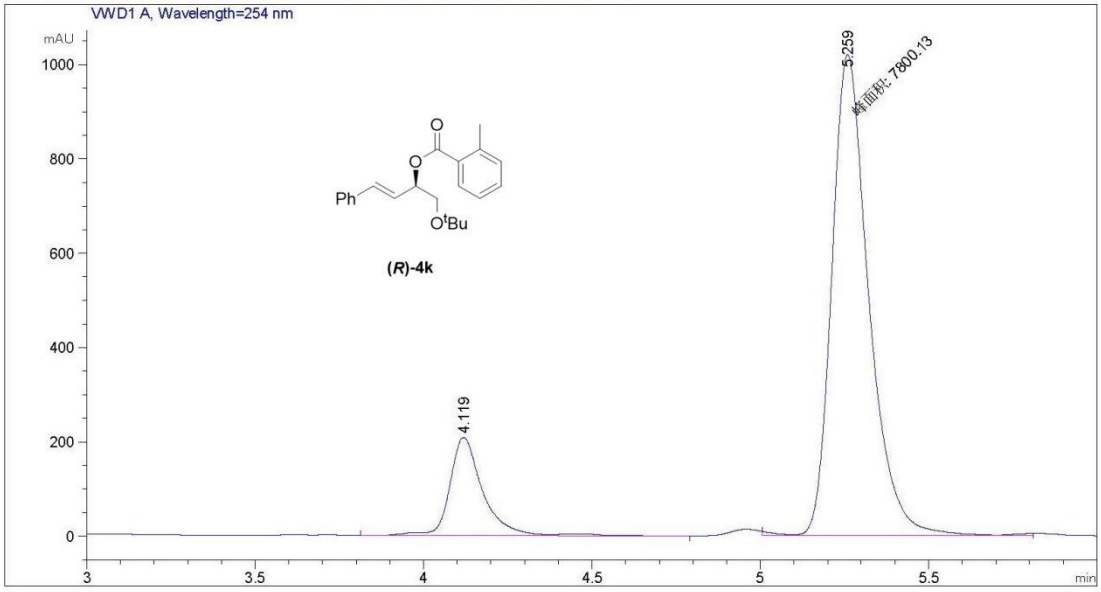
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.516	VV R	0.1187	1.28868e4	1630.63220	49.7623
2	7.770	BV R	0.1714	1.30099e4	1145.01086	50.2377



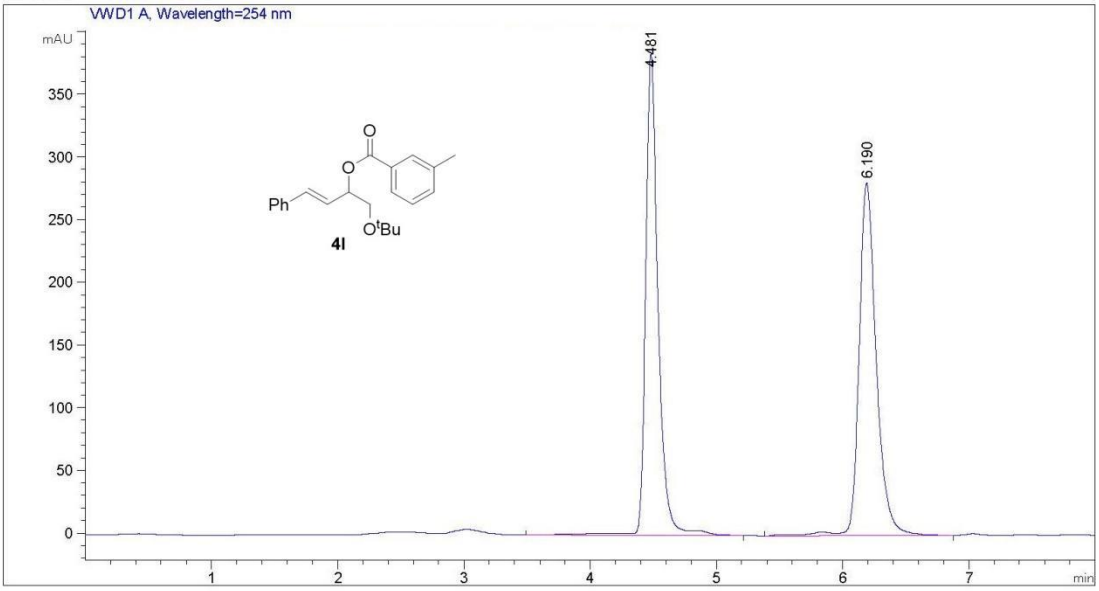
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.462	BB	0.1180	3101.45068	397.69455	11.7821
2	7.003	VV R	0.1567	2.32219e4	2280.35010	88.2179



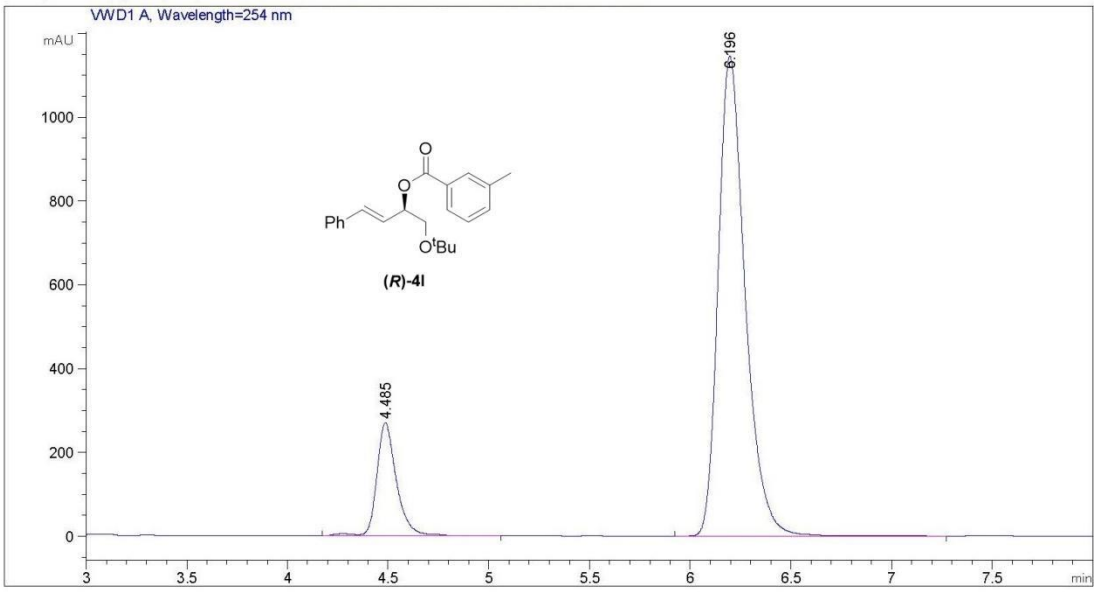
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.124	VV R	0.0958	6727.58545	1047.76965	49.1409
2	5.273	VV R	0.1184	7049.00098	869.52899	50.8591



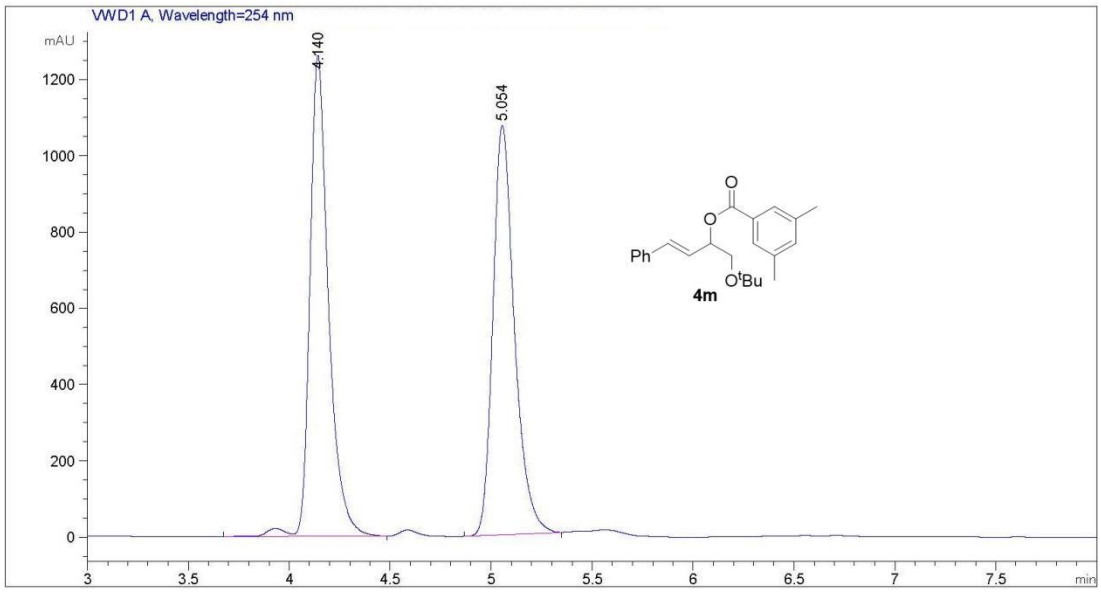
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.119	BV R	0.0988	1414.96643	207.68640	15.3549
2	5.259	MM	0.1273	7800.13477	1021.08417	84.6451



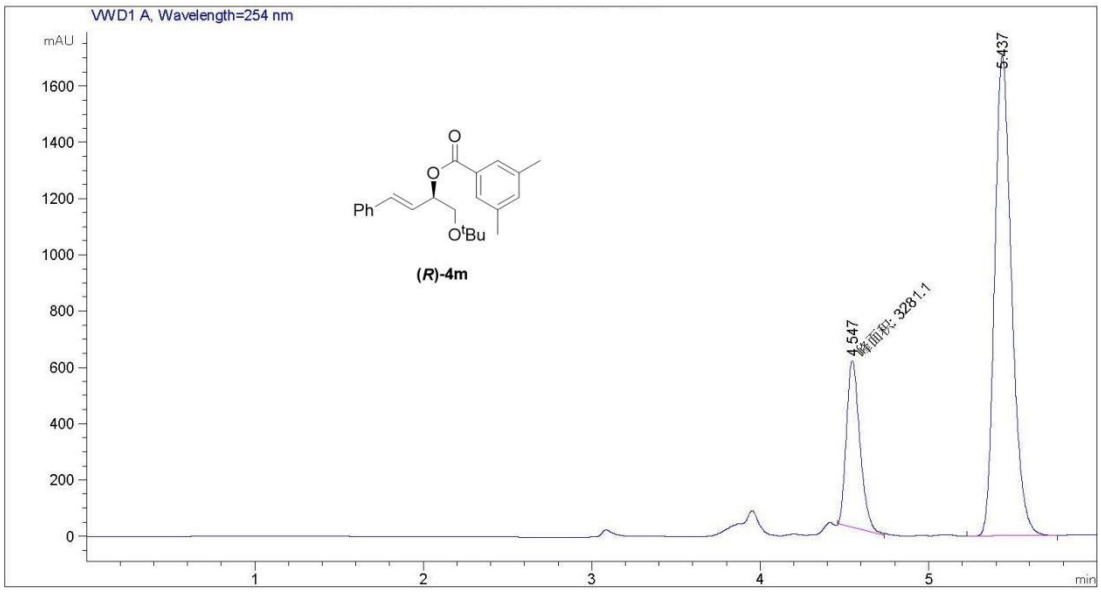
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.481	VV R	0.1017	2640.53735	383.57205	49.7231
2	6.190	VB R	0.1407	2669.94458	281.57007	50.2769



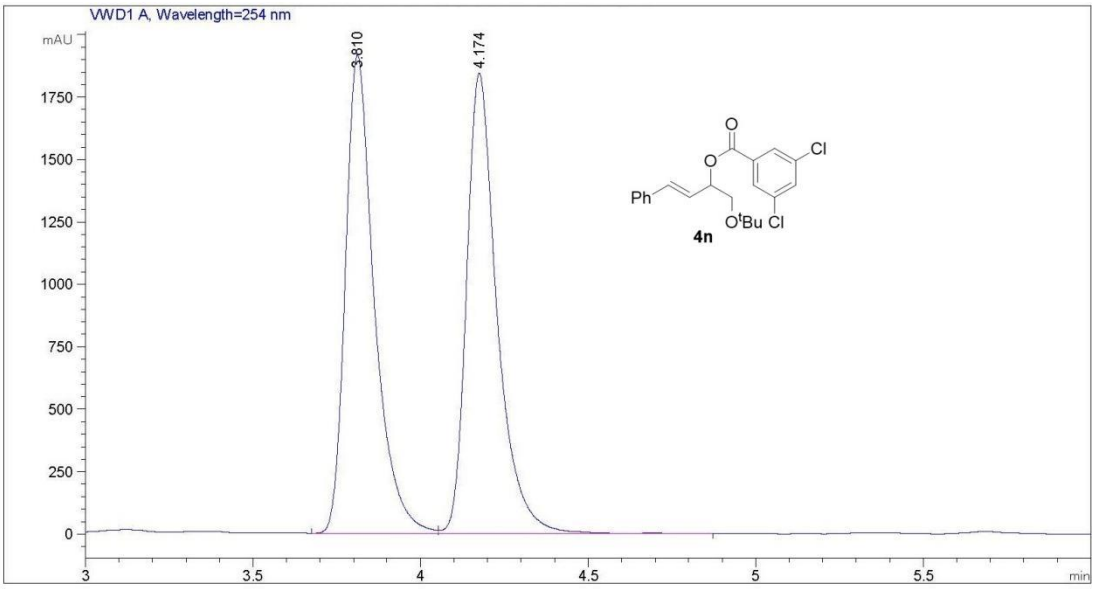
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.485	VB R	0.0998	1824.71594	269.32129	14.6137
2	6.196	BV R	0.1405	1.06617e4	1146.39880	85.3863



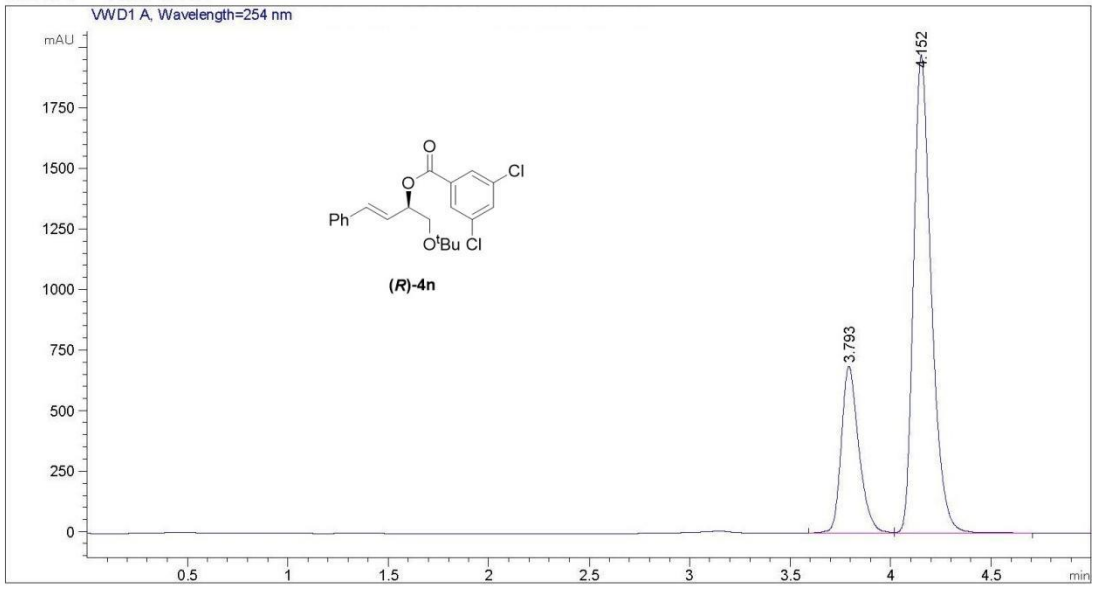
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.140	VB R	0.0946	8088.41504	1260.98608	50.3598
2	5.054	BB	0.1126	7972.83057	1074.16833	49.6402



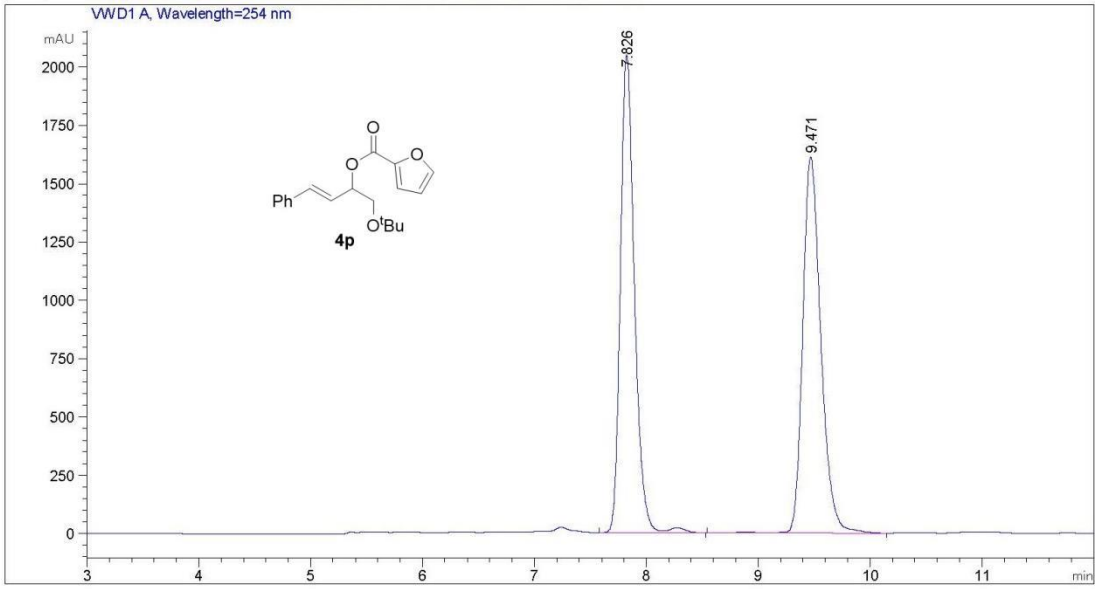
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	4.547	MM	0.0923	3281.09692	592.27863	21.5093
2	5.437	BB	0.1079	1.19732e4	1706.19910	78.4907



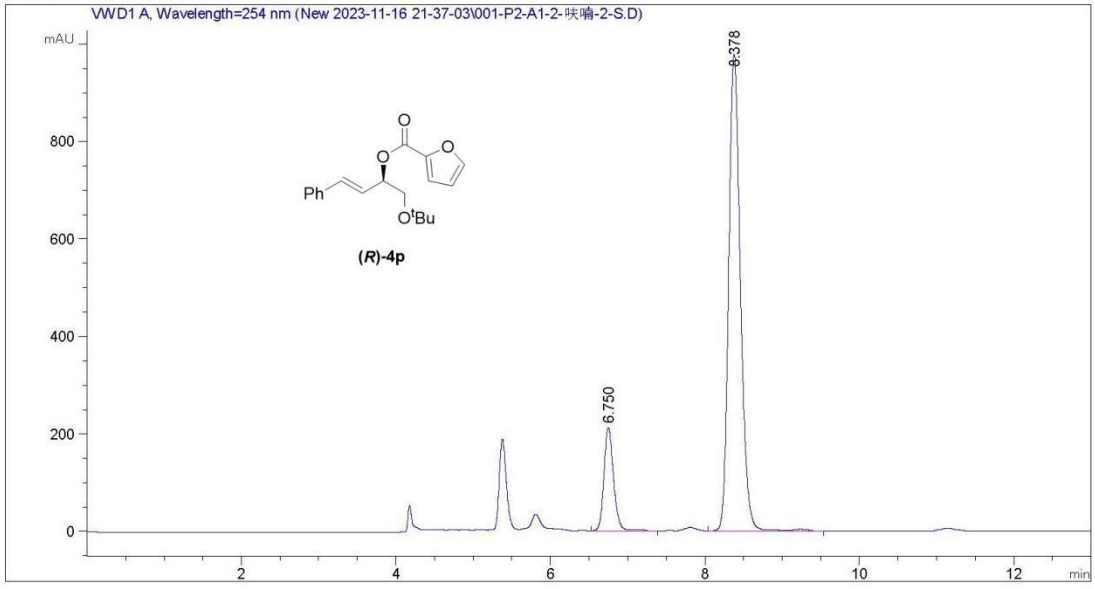
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	3.810	BV	0.0889	1.14955e4	1917.83740	49.6953
2	4.174	VV R	0.0946	1.16364e4	1845.45142	50.3047



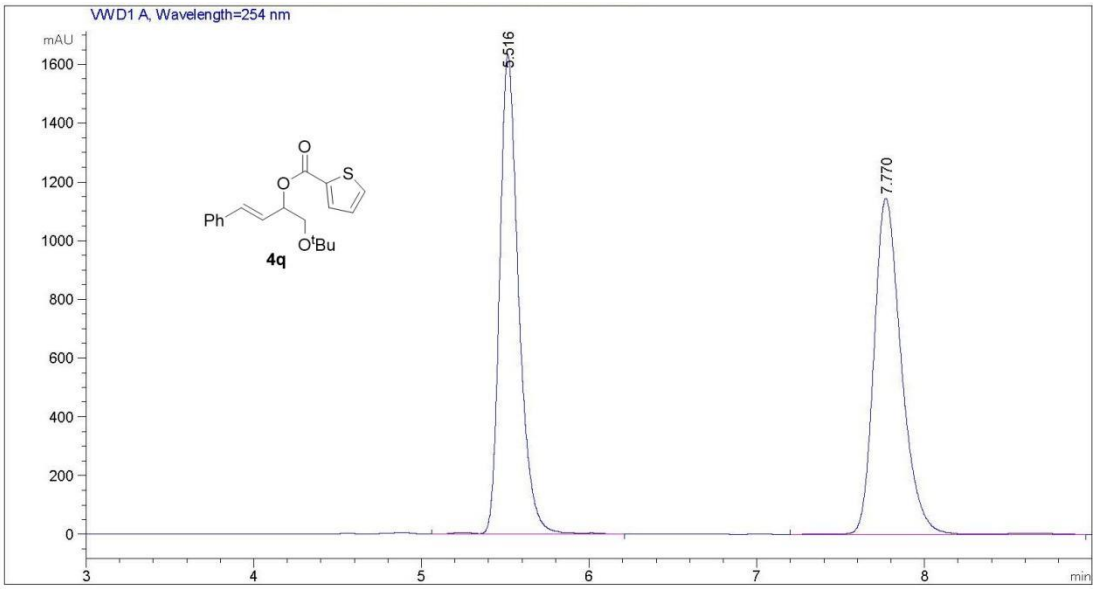
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	3.793	BV	0.0903	4148.11328	687.98175	25.5051
2	4.152	VV R	0.0936	1.21157e4	1974.86670	74.4949



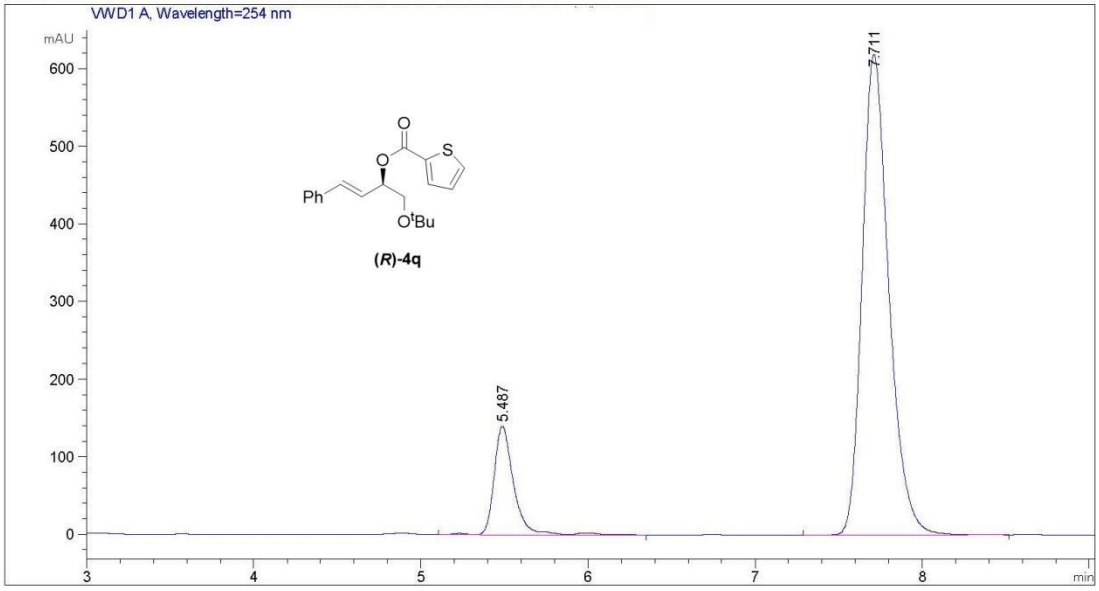
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	7.826	BV R	0.1316	1.79116e4	2051.22144	49.8191
2	9.471	VB R	0.1704	1.80416e4	1611.41040	50.1809



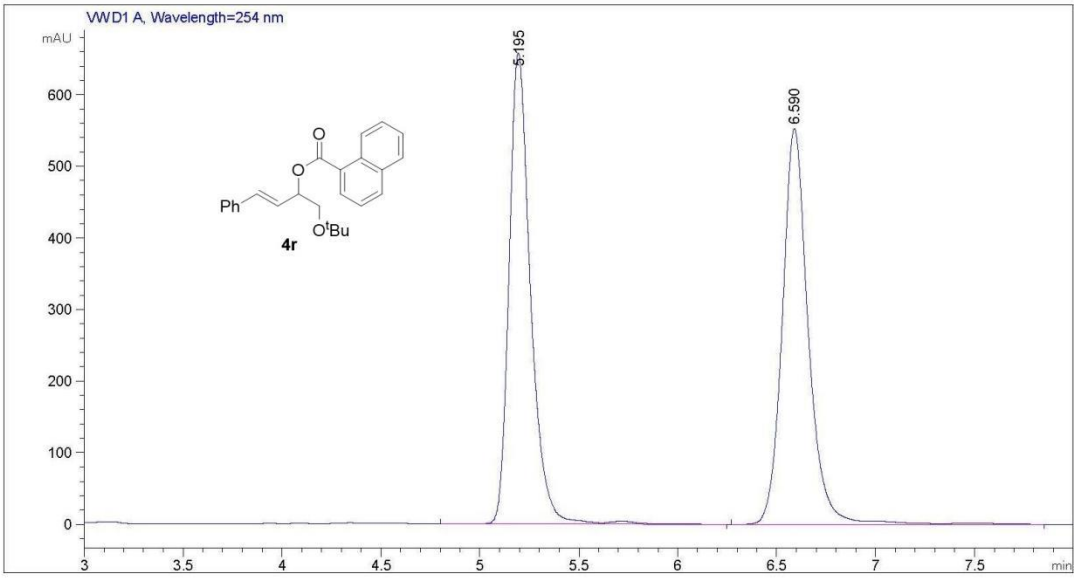
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	6.750	BV R	0.1299	1840.58838	212.39830	15.1209
2	8.378	BV R	0.1612	1.03319e4	978.55756	84.8791



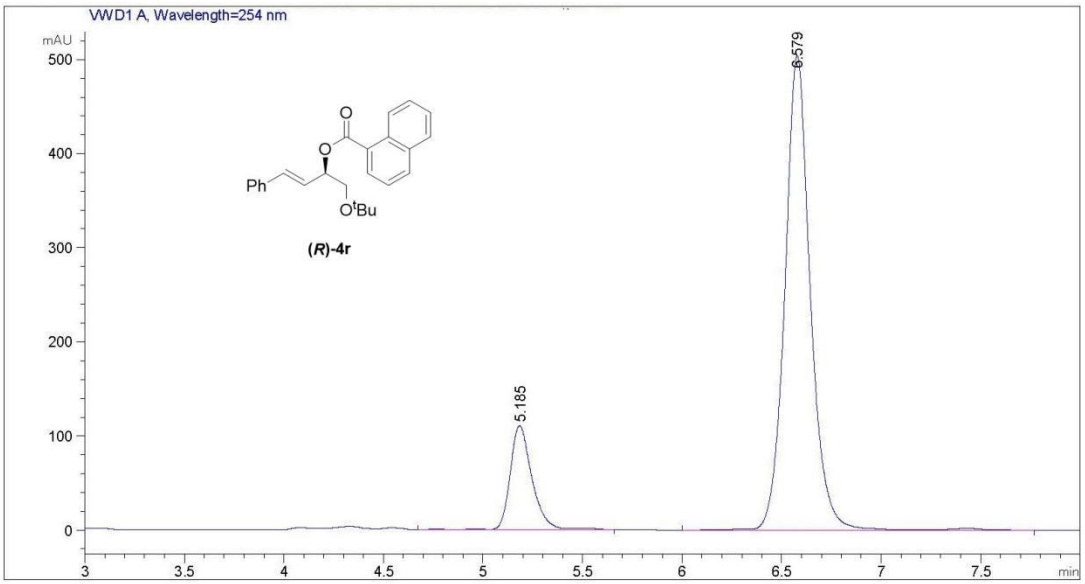
	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.516	VV R	0.1187	1.28868e4	1630.63220	49.7623
2	7.770	BV R	0.1714	1.30099e4	1145.01086	50.2377



	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.487	VV R	0.1200	1138.38318	140.15034	14.2310
2	7.711	BB	0.1682	6860.93018	619.58044	85.7690



	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.195	VV R	0.1126	4969.83740	657.97791	50.0113
2	6.590	BV R	0.1351	5040.73975	552.50934	49.9887



	Time/ [min]	Type	Width/ [min]	Area/mAU*s	Height/mAU	Area%
1	5.185	VV R	0.1149	840.35992	110.23548	15.7824
2	6.579	VV R	0.1312	4484.29102	504.35605	84.2176