Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cobalt-Catalysed Regiodivergent Hydrofunctionalization of Allenes

*Jia-Feng Chen, Sajid Ur Rehman, Changkun Li**

Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering Shanghai Jiao Tong University, China

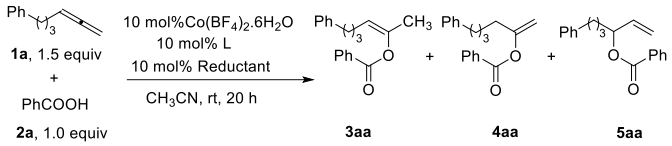
E-mail: chkli@sjtu.edu.cn

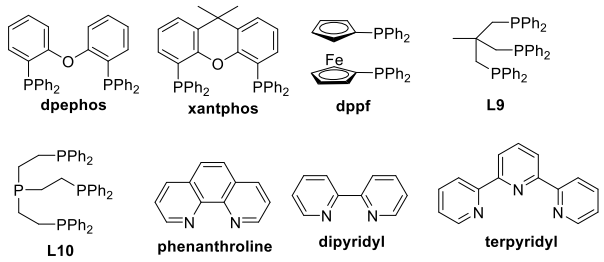
1. General information

All air and moisture sensitive manipulations were carried out in a nitrogen-filled glove box. Most solvents used were dried and remove of oxygen over solvent purification system (Vigor YJC-7). Column chromatography was performed using 200-300 mesh silica gels. The NMR spectra were recorded on a Bruker-400 instrument (400 MHz, ^{1}H; 101 MHz, ^{13}C) with chemical shifts reported in ppm relative to the residual deuterated solvents. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. The *ee* values were determined by Shimadzu HPLC system. $Co(BF_4)_2 \cdot 6H_2O$ was purchased from Alfa Aesar. Other cobalt salts were purchased from Strem Chemicals, Inc. Manganese (-325 mesh, 99.95%) and indium (-325 mesh, 99.99%) were purchased from Alfa Aesar. Zinc (-600 mesh, 99.99%) was purchased from Aladdin and was washed successively with 1 M HCl, diethyl ether, and acetone, dried under vacuum, and stored under argon. Other cobalt salts were purchased from Strem Chemicals, Inc. Substrates were purchased from TCI, Energy Chemical or Alfa Aesar and used as received. Most of ligands were purchased from TCI or Strem company and **L1** was purchased from Acros Organics.

2. Optimizations of the Cobalt-Catalysed addition of Carboxylic Acids to Allenes

Table S1. Optimization of the Cobalt-Catalysed addition of Carboxylic Acids to Allenes





Entry[a]	catalyst precursor	Ligand	Reductant	solvent	Yield [%][b]	**3aa / (4aa+5aa)[c]**
1	-	-	-	CH_3CN	<1	-
2	$Co(BF_4)_2{\cdot}6H_2O$	-	-	CH_3CN	<1	-
3	$Co(BF_4)_2{\cdot}6H_2O$	**L3**	-	CH_3CN	<1	-
4	$Co(BF_4)_2{\cdot}6H_2O$	-	Zn	CH_3CN	<1	
5	$Zn(BF_4)_2$	-	-	CH_3CN	<1	-
6	$Co(BF_4)_2{\cdot}6H_2O$	**PPh_3[d]**	Zn	CH_3CN	<1	-
7	$Co(BF_4)_2{\cdot}6H_2O$	**PCy_3[d]**	Zn	CH_3CN	<1	-
8	$Co(BF_4)_2{\cdot}6H_2O$	**dpephos**	Zn	CH_3CN	<1	-
9	$Co(BF_4)_2{\cdot}6H_2O$	**Xantphos**	Zn	CH_3CN	<1	-
10	$Co(BF_4)_2{\cdot}6H_2O$	**dppf**	Zn	CH_3CN	<1	-
11	$Co(BF_4)_2{\cdot}6H_2O$	**L9**	Zn	CH_3CN	<1	-
12	$Co(BF_4)_2{\cdot}6H_2O$	**L10**	Zn	CH_3CN	<1	-
13	$Co(BF_4)_2{\cdot}6H_2O$	**phenanthrol**	Zn	CH_3CN	<1	-
14	$Co(BF_4)_2{\cdot}6H_2O$	**dipyridyl**	Zn	CH_3CN	<1	-
15	$Co(BF_4)_2{\cdot}6H_2O$	**terpyridyl**	Zn	CH_3CN	<1	-
16	CoF_2	**L3**	Zn	CH_3CN	<5	-
17	$CoCl_2$	**L3**	Zn	CH_3CN	39	30/1
18	$CoBr_2$	**L3**	Zn	CH_3CN	36	20/1
19	CoI_2	**L3**	Zn	CH_3CN	57	22/1
20	$Co(BF_4)_2{\cdot}6H_2O$	**L3**	Zn	THF	<5	-
21	$Co(BF_4)_2{\cdot}6H_2O$	**L3**	Zn	DCM	<1	-
22	$Co(BF_4)_2{\cdot}6H_2O$	**L3**	Zn	DMSO	<1	-
23	$Co(BF_4)_2{\cdot}6H_2O$	**L3**	Zn	DMF	<1	-
24	$Co(BF_4)_2{\cdot}6H_2O$	**L3**	Zn	toluene	<1	-

[a]Conditions: **1a** (0.375 mmol, 1.5 equiv), benzoic acid **2a** (0.25 mmol, 1.0 equiv), catalyst precursor (0.025 mmol), ligand (0.025 mmol), reductant (0.025 mmol), solvent (1.5 mL), r.t., 20 h. [b]Isolate yield. [c]the ratios of **3aa** / (**4aa**+**5aa**) were determined with crude ^1H NMR analysis. [d]20 mol %.

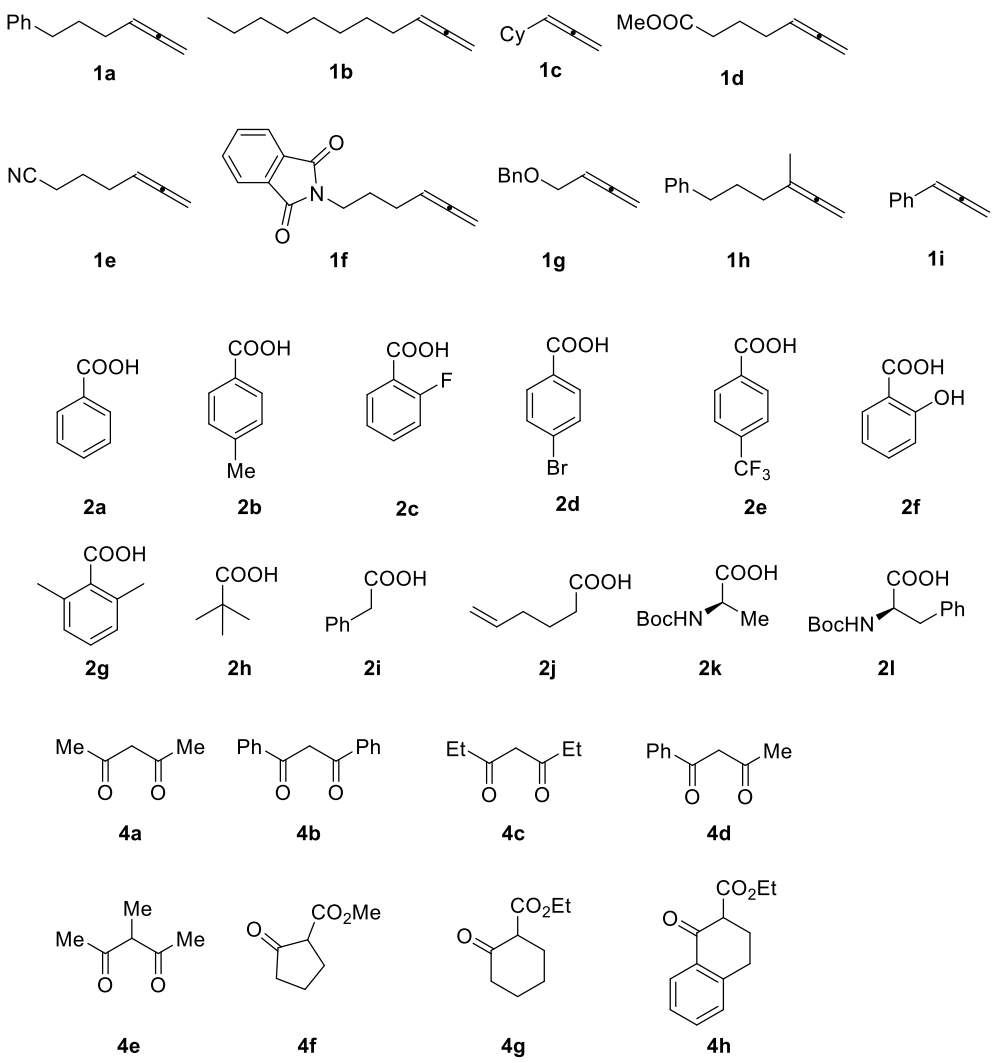
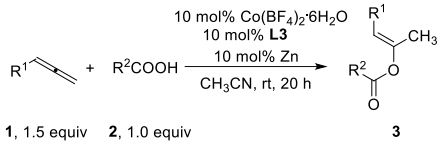


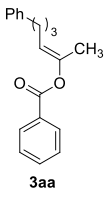
Figure S1. substrates of the reaction

All the allenes were sythesized according to the corresponding literature: **1a**[1], **1b**[2], **1c**[1], **1d**[3], **1e**[3], **1f**[3], **1g**[4], **1h**[5], **1i**[2].

3. Cobalt-catalysed enol ester formation from carboxylic acids and allenes

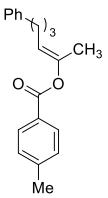


In a nitrogen-filled glove box, $Co(BF_4)_2 \cdot 6H_2O$ (8.5 mg, 0.025 mmol), **L3** (10.0 mg, 0.025 mmol), Zn (1.6 mg, 0.025 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, allene (0.375 mmol) and carboxylic acid (0.25 mmol) were added. Then stirring the solution at room temperature for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get the corresponding product.



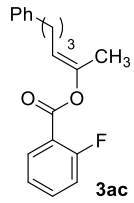
3aa

(E)-6-phenylhex-2-en-2-yl benzoate (**3aa**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 60 mg (86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.16 (m, 3H), 5.29 (t, *J* = 7.7 Hz, 1H), 2.73 – 2.66 (m, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.96 (s, 3H), 1.83 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.33, 145.91, 142.16, 133.15, 130.15, 129.89, 128.49, 128.41, 128.31, 125.76, 117.42, 35.21, 31.12, 26.12, 15.40. HRMS (ESI-MS): Calcd. For $C_{19}H_{20}NaO_2^+$ $[M+Na]^+$: 303.1361, Found: 303.1358.



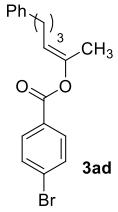
3ab

(E)-6-phenylhex-2-en-2-yl 4-methylbenzoate (**3ab**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 70 mg (95 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.19 (m, 7H), 5.30 (td, *J* = 7.7, 0.8 Hz, 1H), 2.74 – 2.68 (m, 2H), 2.46 (s, 3H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.98 (s, 3H), 1.85 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.42, 145.93, 143.88, 142.18, 129.93, 129.14, 128.50, 128.31, 127.38, 125.75, 117.33, 35.22, 31.15, 26.13, 21.71, 15.44. HRMS (ESI-MS): Calcd. For $C_{20}H_{22}NaO_2^+$ $[M+Na]^+$: 317.1517, Found: 317.1519.



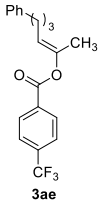
3ac

(E)-6-phenylhex-2-en-2-yl 2-fluorobenzoate (**3ac**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 56 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 7.1 Hz, 1H), 7.47 (dd, *J* = 12.3, 6.6 Hz, 1H), 7.23 – 7.15 (m, 3H), 7.16 – 7.07 (m, 4H), 5.22 (t, *J* = 7.6 Hz, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.05 (q, *J* = 7.3 Hz, 2H), 1.88 (s, 3H), 1.73 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 163.0, 160.8, 145.7, 142.1, 134.8, 134.7, 132.3, 128.5, 128.3, 125.8, 124.0, 117.6, 117.2, 117.0, 35.2, 31.0, 26.1, 15.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{19}H_{19}FO_2Na^+$ 321.1261; found 321.1269.



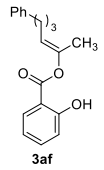
3ad

(E)-6-phenylhex-2-en-2-yl 4-bromobenzoate (**3ad**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 75 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 5.29 (t, *J* = 7.7 Hz, 1H), 2.73 – 2.66 (m, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.96 (s, 3H), 1.82 – 1.77 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ164.6, 145.8, 142.1, 131.8, 131.4, 128.5, 128.3, 125.8, 117.6, 35.2, 31.1, 26.1, 15.4. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{19}H_{19}BrO_2Na^+$ 321.1261; found 321.1269.



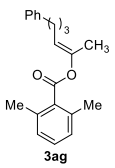
3ae

(E)-6-phenylhex-2-en-2-yl 4-(trifluoromethyl)benzoate (**3ae**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 70 mg (80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 5.30 (td, *J* = 7.7, 0.9 Hz, 1H), 2.72 – 2.65 (m, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.96 (d, *J* = 0.8 Hz, 3H), 1.83 – 1.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.10, 145.76, 142.05, 134.63 (q, *J* = 32.7 Hz), 133.36, 130.28, 128.48, 128.33, 125.80, 125.45 (q, *J* = 3.7 Hz), δ 123.62 (q, *J* = 272.8 Hz), 117.79, 35.18, 31.06, 26.07, 15.32. HRMS (ESI-MS): Calcd. For $C_{20}H_{19}F_3NaO_2^+$ [M+Na]$^+$: 371.1235, Found: 371.1234.



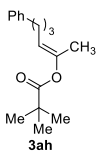
3af

(E)-6-phenylhex-2-en-2-yl 2-hydroxybenzoate (**3af**). (Petroleum ether : ethyl acetate = 30 : 1), colorless oil, 53 mg (72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.21 (m, 5H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.34 (t, *J* = 7.6 Hz, 1H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.20 – 2.14 (m, 2H), 1.99 (s, 3H), 1.85 – 1.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.12, 161.98, 145.34, 142.02, 136.00, 130.24, 128.48, 128.35, 125.82, 119.23, 118.12, 117.67, 112.30, 35.18, 31.05, 26.07, 15.35. HRMS (ESI-MS): Calcd. For $C_{19}H_{20}NaO_3^+$ [M+Na]$^+$: 319.1310, Found: 319.1318.



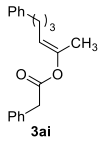
3ag

(E)-6-phenylhex-2-en-2-yl 2,6-dimethylbenzoate (**3ag**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 53 mg (58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 4H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.28 (td, *J* = 7.7, 1.0 Hz, 1H), 2.71 – 2.64 (m, 2H), 2.39 (s, 6H), 2.14 (q, *J* = 7.4 Hz, 2H), 2.00 (d, *J* = 0.8 Hz, 3H), 1.82 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.62, 145.71, 142.10, 134.80, 133.56, 129.42, 128.47, 128.32, 127.59, 125.78, 117.62, 35.25, 31.13, 26.11, 19.69, 15.43. HRMS (ESI-MS): Calcd. For $C_{21}H_{24}NaO_2^+$ [M+Na]$^+$: 331.1674, Found: 331.1671.

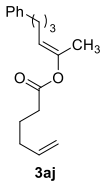


3ah

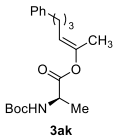
(E)-6-phenylhex-2-en-2-yl pivalate (**3ah**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 51 mg (78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 5.08 (t, *J* = 7.6 Hz, 1H), 2.67 – 2.62 (m, 2H), 2.05 (q, *J* = 7.4 Hz, 2H), 1.80 (s, 3H), 1.77 – 1.68 (m, 2H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.31, 145.81, 142.17, 128.47, 128.27, 125.71, 116.70, 38.72, 35.18, 31.08, 27.10, 26.06, 15.07. HRMS (ESI-MS): Calcd. For $C_{17}H_{24}NaO_2^+$ [M+Na]$^+$: 283.1674, Found: 283.1679.



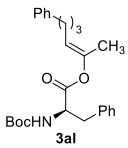
(E)-6-phenylhex-2-en-2-yl 2-phenylacetate (**3ai**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 56 mg (76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 10H), 5.16 (t, *J* = 7.6 Hz, 1H), 3.69 (s, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.10 – 2.05 (m, 2H), 1.83 (s, 3H), 1.74 (dt, *J* = 14.6, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.22, 145.74, 142.11, 133.83, 129.23, 128.64, 128.46, 128.29, 127.17, 125.74, 117.22, 41.39, 35.15, 31.03, 26.00, 15.16. HRMS (ESI-MS): Calcd. For $C_{20}H_{22}NaO_2^+$ $[M+Na]^+$: 317.1517, Found: 317.1516.



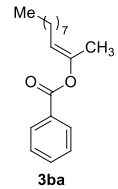
(E)-6-phenylhex-2-en-2-yl hex-5-enoate (**3aj**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 45 mg (66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 5H), 5.88 – 5.76 (m, 1H), 5.20 – 5.02 (m, 3H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.18 – 2.06 (m, 4H), 1.88 – 1.66 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.27, 145.65, 142.14, 137.62, 128.46, 128.29, 125.74, 117.07, 115.48, 35.17, 33.56, 33.03, 31.10, 26.03, 24.07, 15.29. HRMS (ESI-MS): Calcd. For $C_{18}H_{24}NaO_2^+$ $[M+Na]^+$: 295.1674, Found: 295.1670.



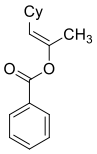
(R, E)-6-phenylhex-2-en-2-yl 2-((tert-butoxycarbonyl)amino)propanoate (**3ak**). (Petroleum ether : ethyl acetate = 10 : 1), colorless oil, 67 mg (77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.18 (dd, *J* = 7.7, 7.1 Hz, 1H), 5.08 (s, 1H), 4.40 – 4.36 (m, 1H), 2.69 – 2.62 (m, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.85 (d, *J* = 0.7 Hz, 3H), 1.79 – 1.72 (m, 2H), 1.49 – 1.44 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.08, 155.10, 145.48, 142.05, 128.45, 128.30, 125.77, 117.40, 79.90, 49.27, 35.13, 30.98, 28.33, 25.96, 18.60, 15.03. HRMS (ESI-MS): Calcd. For $C_{20}H_{29}NNaO_2^+$ $[M+Na]^+$: 370.1994, Found: 370.1992.



(R, E)-6-phenylhex-2-en-2-yl 2-((tert-butoxycarbonyl)amino)-3-phenylpropanoate (**3al**). (Petroleum ether : ethyl acetate = 10 : 1), colorless oil, 79 mg (75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 10H), 5.14 – 4.98 (m, 2H), 4.66 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.25 – 3.08 (m, 2H), 2.70 – 2.62 (m, 2H), 2.07 (q, *J* = 7.4 Hz, 2H), 1.84 – 1.69 (m, 5H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.64, 155.08, 145.53, 142.05, 135.92, 129.50, 128.56, 128.47, 128.32, 127.10, 125.79, 117.48, 79.98, 54.44, 38.35, 35.12, 31.00, 28.32, 25.92, 15.11. HRMS (ESI-MS): Calcd. For $C_{26}H_{33}NNaO_4^+$ $[M+Na]^+$: 446.2307, Found: 446.2302.

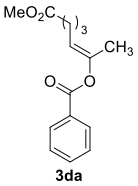


(E)-undec-2-en-2-yl benzoate (**3ba**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 60 mg (88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.25 (t, *J* = 7.7 Hz, 1H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.97 (s, 3H), 1.44 – 1.26 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.35, 145.41, 133.10, 130.17, 129.86, 128.38, 117.93, 31.91, 29.56, 29.47, 29.30, 29.20, 26.68, 22.69, 15.30, 14.13. HRMS (ESI-MS): Calcd. For $C_{18}H_{26}NaO_2^+$ $[M+Na]^+$: 297.1830, Found: 297.1826.



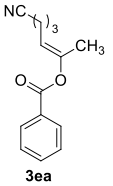
3ca

(E)-1-cyclohexylprop-1-en-2-yl benzoate (**3ca**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 52 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.11 (d, *J* = 9.7 Hz, 1H), 2.23 – 2.11 (m, 1H), 1.99 (s, 3H), 1.78 – 1.70 (m, 4H), 1.37 – 1.06 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.31, 144.40, 133.09, 130.19, 129.85, 128.38, 123.55, 36.17, 33.24, 25.94, 25.89, 15.50. HRMS (ESI-MS): Calcd. For $C_{16}H_{20}NaO_2^+$ $[M+Na]^+$: 267.1361, Found: 267.1362.



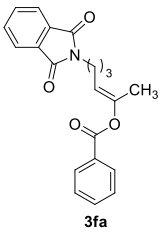
3da

(E)-7-methoxy-7-oxohept-2-en-2-yl benzoate (**3da**). (Petroleum ether : ethyl acetate = 30 : 1), colorless oil, 63 mg (96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.24 (t, *J* = 7.8 Hz, 1H), 3.70 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.99 (s, 3H), 1.79 (p, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.95, 165.25, 146.45, 133.19, 130.01, 129.86, 128.41, 116.66, 51.54, 33.18, 25.97, 24.69, 15.33. HRMS (ESI-MS): Calcd. For $C_{15}H_{18}NaO_4^+$ $[M+Na]^+$: 285.1103, Found: 285.1104.



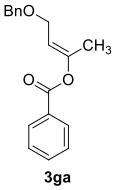
3ea

(E)-6-cyanohex-2-en-2-yl benzoate (**3ea**). (Petroleum ether : ethyl acetate = 30 : 1), colorless oil, 62 mg (82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.51 – 7.46 (m, 2H), 5.20 (td, *J* = 7.9, 1.0 Hz, 1H), 2.47 (t, *J* = 7.1 Hz, 2H), 2.31 (q, *J* = 7.3 Hz, 2H), 2.03 (d, *J* = 0.8 Hz, 3H), 1.83 (p, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.23, 147.51, 133.34, 129.88, 129.81, 128.47, 119.57, 115.34, 25.39, 25.23, 16.27, 15.51. HRMS (ESI-MS): Calcd. For $C_{14}H_{15}NNaO_2^+$ $[M+Na]^+$: 252.1000, Found: 252.0997.



3fa

(E)-6-(1,3-dioxoisoindolin-2-yl)hex-2-en-2-yl benzoate (**3fa**). (Petroleum ether : ethyl acetate = 25 : 1), white solid, melting point: 103.5-104.8 °C, 71 mg (81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H), 7.87 – 7.81 (m, 2H), 7.74 – 7.67 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.26 (t, *J* = 7.5 Hz, 1H), 3.77 – 3.71 (m, 2H), 2.17 (q, *J* = 7.5 Hz, 2H), 1.97 (s, 3H), 1.87 – 1.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.38, 165.19, 146.37, 133.91, 133.16, 132.13, 129.99, 129.61, 128.38, 123.22, 116.44, 37.58, 28.34, 24.21, 15.43. HRMS (ESI-MS): Calcd. For $C_{21}H_{19}NNaO_4^+$ $[M+Na]^+$: 372.1212, Found: 372.1212.

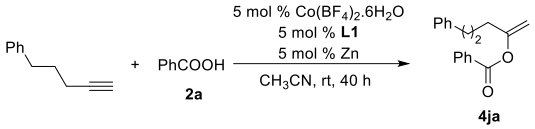


3ga

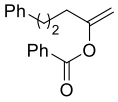
(E)-4-(benzyloxy)but-2-en-2-yl benzoate (**3ga**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 53 mg (75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.27 (m, 5H), 5.52 (td, *J* = 7.3, 0.7 Hz, 1H), 4.57 (s, 2H), 4.14 (d, *J* = 7.4 Hz, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.96, 149.82, 138.11, 129.95, 129.75, 128.48, 128.43, 127.91, 127.70, 114.53, 71.84, 65.03, 15.88. HRMS (ESI-MS): Calcd. For $C_{18}H_{18}NaO_3^+$ $[M+Na]^+$: 305.1154, Found: 305.1157.

4. Mechanism study on the formation of enol ester.

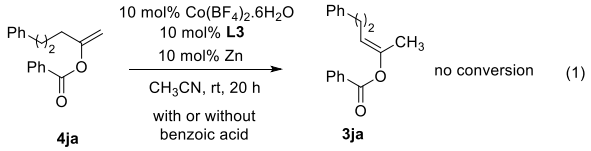
Synthesis of **4ja**:



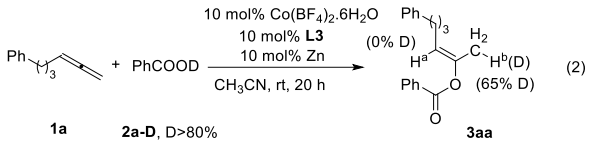
According to previous reported[6], $Co(BF_4)_2 \cdot 6H_2O$ (8.5 mg, 0.025 mmol), **L1** (13.4 mg, 0.025 mmol), Zn (1.6 mg, 0.025 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 1 h, 5-phenyl-1-pentyne (0.5 mmol) and **2a** (0.65 mmol) were added. Then stirring the solution at room temperature for 40 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **4ja**.


4ja

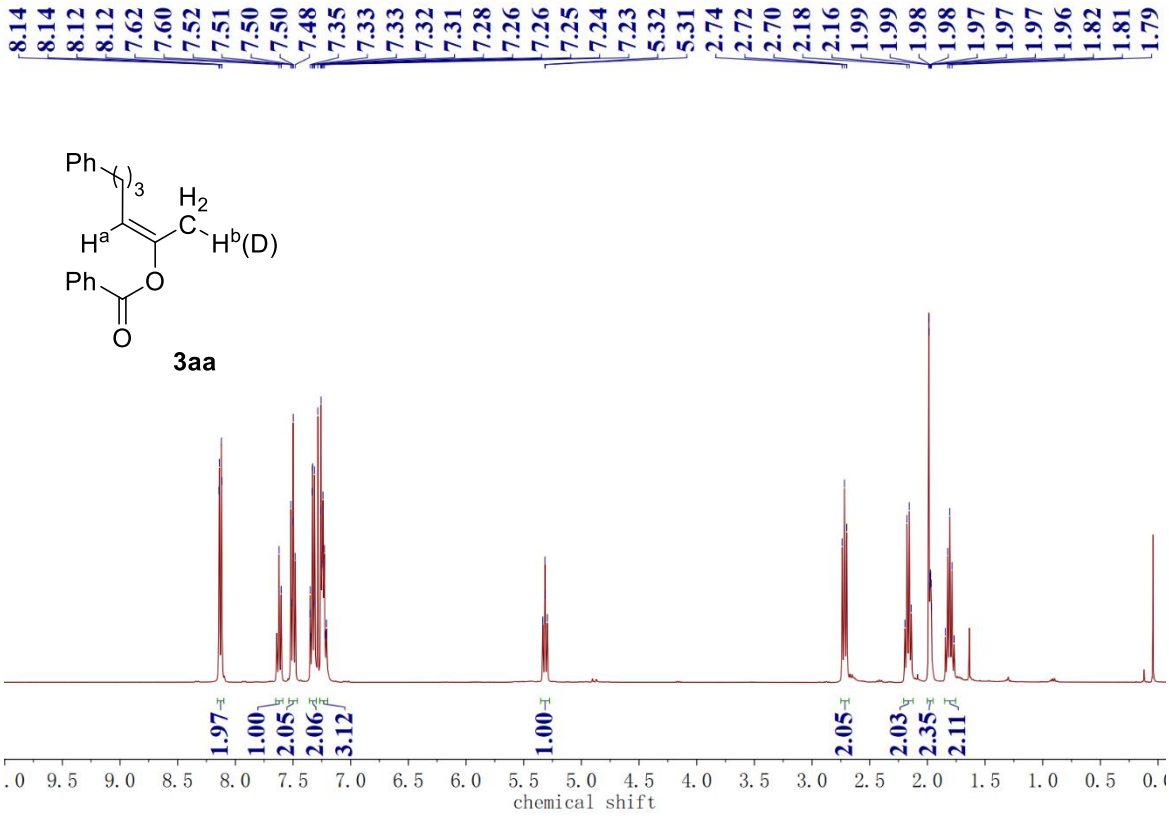
5-Phenylpent-1-en-2-yl benzoate (**4ja**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 109 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.61 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 4.91 (d, *J* = 15.3 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.95 – 1.84 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.80, 156.27, 141.87, 133.38, 129.98, 129.85, 128.53, 128.50, 128.41, 125.93, 101.89, 35.17, 33.06, 28.28. HRMS (ESI-MS): Calcd. For $C_{18}H_{18}NaO_2^+$ $[M+Na]^+$: 289.1204, Found: 289.1201.



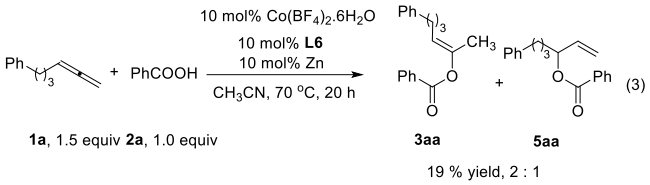
In a nitrogen-filled glove box, $Co(BF_4)_2 \cdot 6H_2O$ (8.5 mg, 0.025 mmol), **L3** (10.0 mg, 0.025 mmol), Zn (1.6 mg, 0.025 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, **4ja** (0.25 mmol) and benzoic acid (0.25 mmol) were added (or only **4ja**). After stirring the solution at room temperature for 20 h, the solvent was removed under reduced pressure. The residue was test ^{1}H NMR directly.



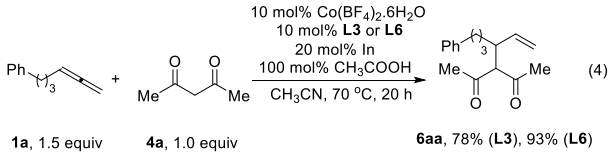
In a nitrogen-filled glove box, $Co(BF_4)_2 \cdot 6H_2O$ (8.5 mg, 0.025 mmol), **L3** (10.0 mg, 0.025 mmol), Zn (1.6 mg, 0.025 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, **1a** (0.375 mmol) and **2a-D**[7] (0.25 mmol) were added. Then stirring the solution at room temperature for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **3aa**.



5. The competing enol ester and allylic product formation.

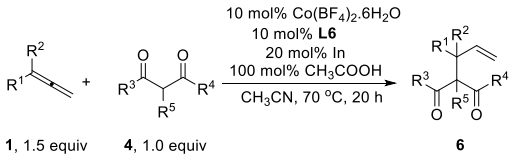


In a nitrogen-filled glove box, $Co(BF_4)_2{\cdot}6H_2O$ (8.5 mg, 0.025 mmol), **L6** (11.2 mg, 0.025 mmol), Zn (1.6 mg, 0.025 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, **1a** (0.375 mmol) and **2a** (0.25 mmol) were added. Then stirring the solution at 70 °C for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **3aa** and **5aa** (13 mg, 19 %, 2:1).

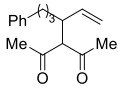


In a nitrogen-filled glove box, $Co(BF_4)_2{\cdot}6H_2O$ (8.5 mg, 0.025 mmol), **L3** (10.0 mg, 0.025 mmol) or **L6** (11.2 mg, 0.025 mmol), indium (5.8 mg, 0.05 mmol) (using Zn as reductant the yield is moderate) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, **1a** (0.375 mmol), **2a** (0.25 mmol) and acetic acid (0.25 mmol) were added. Then stirring the solution at 70 °C for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **6aa** (50 mg, 78 %, **L3**) (60 mg, 93 %, **L6**).

6. Cobalt-catalyzed addition of carbon nucleophiles to allenes.

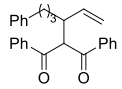


In a nitrogen-filled glove box, $Co(BF_4)_2{\cdot}6H_2O$ (8.5 mg, 0.025 mmol), **L6** (11.2 mg, 0.025 mmol), indium (5.8 mg, 0.05 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, allene **1**(0.375 mmol), 1,3-dicarbonyl compounds **4** (0.25 mmol) and acetic acid (0.25 mmol) were added. Then stirring the solution at 70 °C for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give the corresponding product.



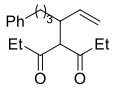
6aa

3-(6-Phenylhex-1-en-3-yl)pentane-2,4-dione (**6aa**)[8]. (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 60 mg (93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 5.54 – 5.42 (m, 1H), 5.13 – 5.06 (m, 2H), 3.68 (d, *J* = 10.6 Hz, 1H), 2.92 (qd, *J* = 10.2, 3.2 Hz, 1H), 2.65 (ddd, *J* = 14.9, 9.4, 5.9 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 1.70 – 1.49 (m, 2H), 1.42 – 1.33 (m, 1H), 1.29 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.60, 203.47, 142.07, 137.67, 128.33, 128.32, 125.79, 117.91, 74.66, 44.31, 35.51, 32.05, 30.16, 29.53, 28.63.



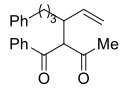
6ab

1,3-Diphenyl-2-(6-phenylhex-1-en-3-yl)propane-1,3-dione (**6ab**)[8]. (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 82 mg (86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 4H), 7.60 – 7.53 (m, 2H), 7.49 – 7.43 (m, 4H), 7.29 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 5.66 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.36 (d, *J* = 9.0 Hz, 1H), 4.98 (dd, *J* = 19.5, 9.3 Hz, 2H), 3.34 (qd, *J* = 9.9, 2.8 Hz, 1H), 2.71 – 2.44 (m, 2H), 1.76 – 1.66 (m, 1H), 1.64 – 1.55 (m, 2H), 1.51 – 1.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.91, 194.87, 142.40, 138.31, 137.08, 136.99, 133.52, 133.33, 128.86, 128.78, 128.72, 128.68, 128.38, 128.26, 125.66, 117.88, 62.14, 45.37, 35.62, 32.63, 29.21.



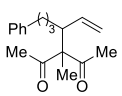
6ac

4-(6-Phenylhex-1-en-3-yl)heptane-3,5-dione (**6ac**)[8]. (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 61 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.51 – 5.41 (m, 1H), 5.10 – 5.03 (m, 2H), 3.72 – 3.67 (m, 1H), 2.95 (qd, *J* = 10.3, 3.2 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.56 – 2.33 (m, 5H), 1.73 – 1.48 (m, 2H), 1.37 – 1.13 (m, 2H), 0.99 (dt, *J* = 16.3, 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.19, 205.96, 142.11, 137.97, 128.35, 128.30, 125.76, 117.73, 73.18, 44.49, 36.27, 35.72, 35.47, 32.14, 28.64, 7.47, 7.30.



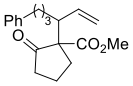
6ad

1-Phenyl-2-(6-phenylhex-1-en-3-yl)butane-1,3-dione (**6ad**)[8]. (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 70 mg (88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.94 (m, 2H), 7.61 (dt, *J* = 11.9, 7.4 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.32 – 7.24 (m, 2H), 7.17 (dt, *J* = 15.1, 8.3 Hz, 3H), 5.65 – 5.41 (m, 1H), 5.20 – 4.95 (m, 2H), 4.52 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.17 (pd, *J* = 10.0, 3.3 Hz, 1H), 2.72 – 2.43 (m, 2H), 2.14 (d, *J* = 19.1 Hz, 3H), 1.81 – 1.65 (m, 1H), 1.62 – 1.52 (m, 1H), 1.50 – 1.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.75, 203.61, 195.44, 195.36, 142.24, 142.10, 137.98, 137.83, 137.36, 137.18, 133.85, 133.60, 128.88, 128.81, 128.78, 128.75, 128.65, 128.37, 128.33, 128.26, 125.79, 125.69, 117.96, 117.82, 69.57, 68.58, 44.84, 44.57, 35.56, 35.52, 32.74, 31.73, 28.90, 28.58, 27.95, 27.51.



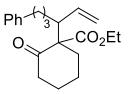
6ae

3-Methyl-3-(6-phenylhex-1-en-3-yl)pentane-2,4-dione (**6ae**)[8]. (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 61 mg (90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 5.45 (dt, *J* = 16.7, 10.1 Hz, 1H), 5.14 – 5.06 (m, 2H), 3.08 (td, *J* = 9.9, 3.0 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.60 – 2.50 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 1.76 – 1.65 (m, 1H), 1.62 – 1.50 (m, 1H), 1.36 (s, 3H), 1.29 – 1.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.83, 206.04, 142.34, 136.40, 128.33, 128.28, 125.71, 118.65, 71.32, 47.25, 35.69, 29.58, 29.53, 27.31, 26.89, 13.86.



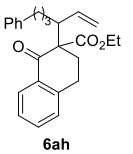
6af

Methyl 2-oxo-1-(6-phenylhex-1-en-3-yl)cyclopentanecarboxylate (**6af**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 60 mg (80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.14 (m, 3H), 5.59 – 5.40 (m, 1H), 5.15 – 5.05 (m, 2H), 3.69 (s, 3H), 2.92 (qd, *J* = 10.8, 2.6 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.58 – 2.31 (m, 3H), 2.20 – 2.04 (m, 1H), 2.04 – 1.84 (m, 3H), 1.72 – 1.64 (m, 1H), 1.57 – 1.17 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.19, 213.79, 170.35, 170.18, 142.35, 137.26, 136.44, 128.36, 128.33, 128.26, 125.68, 119.63, 118.32, 65.50, 52.65, 48.42, 47.47, 39.17, 38.96, 35.62, 35.43, 29.66, 29.61, 29.47, 29.11, 28.87, 28.47, 19.89, 19.65. HRMS (ESI-MS): Calcd. For $C_{19}H_{24}NaO_3^+$ $[M+Na]^+$: 323.1623, Found: 323.1620.



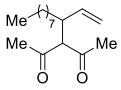
6ag

Ethyl 2-oxo-1-(6-phenylhex-1-en-3-yl)cyclohexanecarboxylate (**6ag**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 58 mg (71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 5.71 – 5.57 (m, 1H), 5.13 – 4.96 (m, 2H), 4.25 – 4.09 (m, 2H), 2.71 – 2.33 (m, 6H), 2.05 – 1.93 (m, 1H), 1.82 – 1.34 (m, 8H), 1.30 – 1.22 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.72, 206.68, 171.49, 171.17, 142.69, 142.66, 137.74, 137.47, 128.37, 128.21, 128.20, 125.58, 118.01, 117.88, 64.71, 63.73, 61.22, 61.05, 48.71, 48.35, 41.80, 41.74, 35.86, 35.76, 31.62, 30.02, 29.91, 29.82, 29.80, 27.62, 26.75, 22.79, 22.40, 14.20, 14.15. HRMS (ESI-MS): Calcd. For $C_{21}H_{28}NaO_3^+$ $[M+Na]^+$: 351.1936, Found: 351.1937.



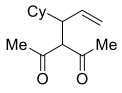
6ah

Ethyl 2-oxo-1-(6-phenylhex-1-en-3-yl)cyclohexanecarboxylate (**6ah**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 60 mg (64 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 7.50 – 7.45 (m, 1H), 7.35 – 7.26 (m, 3H), 7.23 – 7.16 (m, 4H), 5.98 – 5.67 (m, 1H), 5.16 – 5.04 (m, 2H), 4.17 – 4.03 (m, 2H), 3.25 – 3.06 (m, 1H), 2.96 – 2.43 (m, 5H), 2.31 – 2.16 (m, 1H), 1.78 – 1.40 (m, 4H), 1.18 – 1.12 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.80, 194.26, 170.90, 170.55, 143.07, 142.73, 142.63, 142.57, 138.23, 137.21, 133.37, 133.24, 132.91, 132.87, 128.71, 128.56, 128.39, 128.37, 128.24, 128.23, 128.00, 127.96, 126.68, 126.60, 125.63, 125.60, 118.51, 118.26, 61.33, 61.32, 61.20, 61.13, 49.88, 49.24, 35.72, 30.39, 30.09, 29.89, 29.87, 28.97, 28.54, 26.32, 26.27, 14.10, 14.06. HRMS (ESI-MS): Calcd. For $C_{25}H_{28}NaO_3^+$ $[M+Na]^+$: 399.1936, Found: 399.1939.

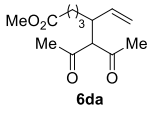


6ba

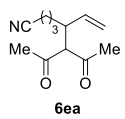
3-(Undec-1-en-3-yl)pentane-2,4-dione (**6ba**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 55 mg (87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 – 5.40 (m, 1H), 5.14 – 5.02 (m, 2H), 3.68 (d, *J* = 10.7 Hz, 1H), 2.87 (q, *J* = 9.6 Hz, 1H), 2.21 (s, 3H), 2.11 (s, 3H), 1.34 – 1.17 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.73, 203.63, 137.93, 117.61, 74.77, 44.48, 32.52, 31.82, 30.19, 29.52, 29.44, 29.32, 29.22, 26.77, 22.64, 14.09. HRMS (ESI-MS): Calcd. For $C_{16}H_{28}NaO_2^+$ $[M+Na]^+$: 275.1987, Found: 275.1982.



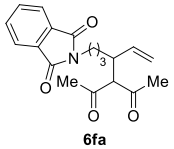
3-(1-Cyclohexylallyl)pentane-2,4-dione (**6ca**)[8]. (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 52 mg (93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dt, *J* = 17.1, 10.1 Hz, 1H), 5.10 – 4.98 (m, 2H), 3.93 (d, *J* = 11.0 Hz, 1H), 2.78 (td, *J* = 10.5, 3.7 Hz, 1H), 2.19 (s, 3H), 2.07 (s, 3H), 1.74 – 1.58 (m, 4H), 1.50 – 1.42 (m, 1H), 1.27 – 1.00 (m, 5H), 0.96 – 0.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.03, 203.91, 135.20, 118.57, 71.79, 49.99, 39.39, 32.02, 30.18, 29.29, 27.55, 26.46, 26.41, 26.35.



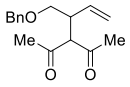
Methyl 6-acetyl-7-oxo-5-vinyloctanoate (**6da**). (Petroleum ether : ethyl acetate = 30 : 1), colorless oil, 58 mg (96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 – 5.40 (m, 1H), 5.12 – 5.05 (m, 2H), 3.68 – 3.62 (m, 4H), 2.85 (qd, *J* = 10.2, 3.2 Hz, 1H), 2.34 – 2.20 (m, 2H), 2.17 (s, 3H), 2.08 (s, 3H), 1.73 – 1.59 (m, 1H), 1.56 – 1.41 (m, 1H), 1.35 – 1.25 (m, 1H), 1.24 – 1.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.42, 203.30, 173.69, 137.32, 118.22, 74.45, 51.53, 44.04, 33.52, 31.74, 30.14, 29.53, 22.18. HRMS (ESI-MS): Calcd. For $C_{13}H_{20}NaO_4^+$ $[M+Na]^+$: 263.1259, Found: 263.1261.



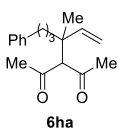
6-Acetyl-7-oxo-5-vinyloctanenitrile (**6ea**)[8]. (Petroleum ether : ethyl acetate = 30 : 1), colorless oil, 49 mg (95 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 – 5.43 (m, 1H), 5.18 – 5.10 (m, 2H), 3.70 (d, *J* = 10.4 Hz, 1H), 2.88 (qd, *J* = 10.3, 3.1 Hz, 1H), 2.42 – 2.25 (m, 2H), 2.22 (s, 3H), 2.12 (s, 3H), 1.79 – 1.68 (m, 1H), 1.64 – 1.52 (m, 1H), 1.51 – 1.42 (m, 1H), 1.38 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.02, 202.84, 136.87, 119.32, 118.82, 74.23, 43.49, 31.26, 30.38, 29.47, 22.95, 16.89.



2-(5-Acetyl-6-oxo-4-vinylheptyl)isoindoline-1,3-dione (**6fa**)[8]. (Petroleum ether : ethyl acetate = 20 : 1), white solid, melting point: 71.1-72.6 °C, 74 mg (91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.75 – 7.69 (m, 2H), 5.46 (dt, *J* = 17.4, 9.6 Hz, 1H), 5.14 – 5.07 (m, 2H), 3.73 – 3.56 (m, 3H), 2.90 (qd, *J* = 10.2, 3.2 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 1.79 – 1.67 (m, 1H), 1.64 – 1.52 (m, 1H), 1.45 – 1.34 (m, 1H), 1.29 – 1.17 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.36, 203.24, 168.32, 137.16, 133.93, 132.06, 123.20, 118.43, 74.45, 43.92, 37.59, 30.38, 29.63, 29.33, 26.04.

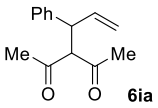


3-(1-(Benzyloxy)but-3-en-2-yl)pentane-2,4-dione (**6ga**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 55 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 5.77 – 5.66 (m, 1H), 5.22 – 5.09 (m, 2H), 4.44 (s, 2H), 3.94 (d, *J* = 10.1 Hz, 1H), 3.51 (dd, *J* = 9.5, 4.8 Hz, 1H), 3.39 (dd, *J* = 9.5, 6.8 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.16 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.59, 203.16, 137.76, 135.42, 128.39, 127.73, 127.69, 118.38, 73.18, 71.91, 71.05, 44.44, 30.40, 29.51. HRMS (ESI-MS): Calcd. For $C_{16}H_{20}NaO_3^+$ $[M+Na]^+$: 283.1310, Found: 283.1310.



3-(3-Methyl-6-phenylhex-1-en-3-yl)pentane-2,4-dione (**6ha**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 49 mg (72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.23 – 7.14 (m, 3H), 6.01 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.17 – 5.12 (m, 1H), 5.02 – 4.94 (m, 1H), 3.79 (s, 1H), 2.59 (d, *J* = 18.7 Hz, 2H), 2.19 (s, 6H), 1.58 – 1.48 (m, 4H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

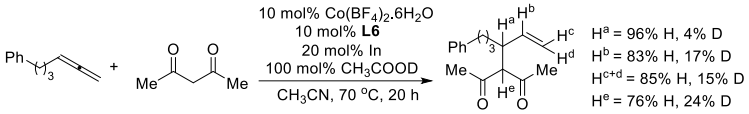
204.18, 203.74, 143.07, 142.19, 128.33, 125.83, 114.44, 76.13, 43.64, 39.00, 36.29, 33.08, 31.96, 26.01, 19.61. HRMS (ESI-MS): Calcd. For $C_{18}H_{24}NaO_2^+$ $[M+Na]^+$: 295.1674, Found: 295.1671.



6ia

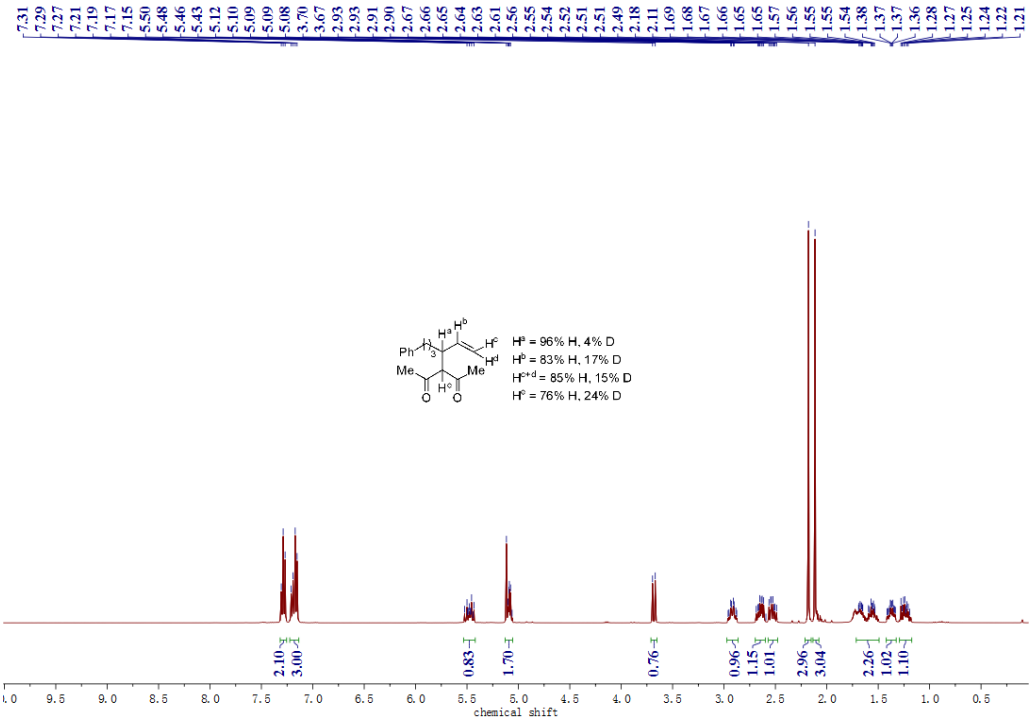
3-(1-phenylallyl)pentane-2,4-dione (**6ia**). (Petroleum ether : ethyl acetate = 50 : 1), colorless oil, 39.5 mg (73 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.23 (t, J = 7.4 Hz, 2H), 7.13 (dd, J = 8.4, 7.1 Hz, 3H), 5.82 – 5.75 (m, 1H), 5.03 – 4.98 (m, 2H), 4.19 (d, J = 11.7 Hz, 1H), 4.10 (dd, J = 11.6, 7.7 Hz, 1H), 2.18 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ202.9, 202.8, 139.8, 138.0, 128.9, 127.9, 127.2, 116.5, 74.3, 49.8, 30.1, 29.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{14}H_{16}O_2Na^+$ 239.1043; found 239.1044.

7. Mechanism study on the formation of allylic products.

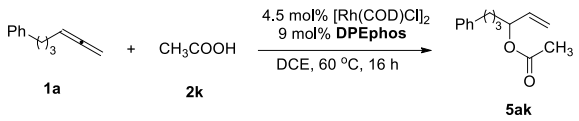


1a, 1.5 equiv **4a**, 1.0 equiv **6aa**, 93% (5)

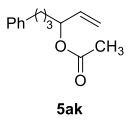
In a nitrogen-filled glove box, $Co(BF_4)_2{\cdot}6H_2O$ (8.5 mg, 0.025 mmol), **L3** (10.0 mg, 0.025 mmol) or **L6** (11.2 mg, 0.025 mmol), indium (5.8 mg, 0.05 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, **1a** (0.375 mmol), **2a** (0.25 mmol) and CH_3COOD (0.25 mmol, D > 95 %) were added. Then stirring the solution at 70 °C for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **6aa** (60 mg, 93 %).



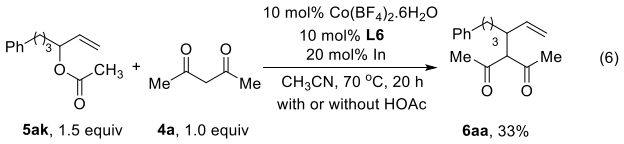
Synthesis of **5ak**:



According to previous reported[9], In a nitrogen-filled glove box, $[Rh(COD)Cl]_2$ (0.020 mmol), **DPEphos** (0.04 mmol) and DCE (4.4 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 10 min, **1a** (0.53 mmol) and **2k** (0.44 mmol) were added. Then stirring the solution at 60 °C for 16 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **5ak** (60 mg, 93 %).



6-Phenylhex-1-en-3-yl acetate (**5ak**). (Petroleum ether : ethyl acetate = 100 : 1), colorless oil, 60 mg (93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 5.79 (ddd, *J* = 17.1, 10.5, 6.5 Hz, 1H), 5.34 – 5.16 (m, 3H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.09 (s, 3H), 1.77 – 1.60 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.39, 142.05, 136.44, 128.42, 128.37, 125.87, 116.77, 74.65, 35.59, 33.75, 26.94, 21.29. HRMS (ESI-MS): Calcd. For $C_{14}H_{18}NaO_2^+$ $[M+Na]^+$: 241.1204, Found: 241.1210.



(6)

In a nitrogen-filled glove box, $Co(BF_4)_2{\cdot}6H_2O$ (8.5 mg, 0.025 mmol), **L6** (11.2 mg, 0.025 mmol), indium (5.8 mg, 0.05 mmol) and CH_3CN (1.5 ml) were put into a 10 mL flame-dried Schlenk flask. After stirring the mixture at room temperature for 30 min, **5ak** (0.375 mmol), **4a** (0.25 mmol) and CH_3COOH (0.25 mmol) were added (or without CH_3COOH). Then stirring the solution at 70 °C for 20 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to get **6aa** (19 mg, 30 %) (21 mg, 33 %, without CH_3COOH).

8. Attempt on asymmetric catalysis.

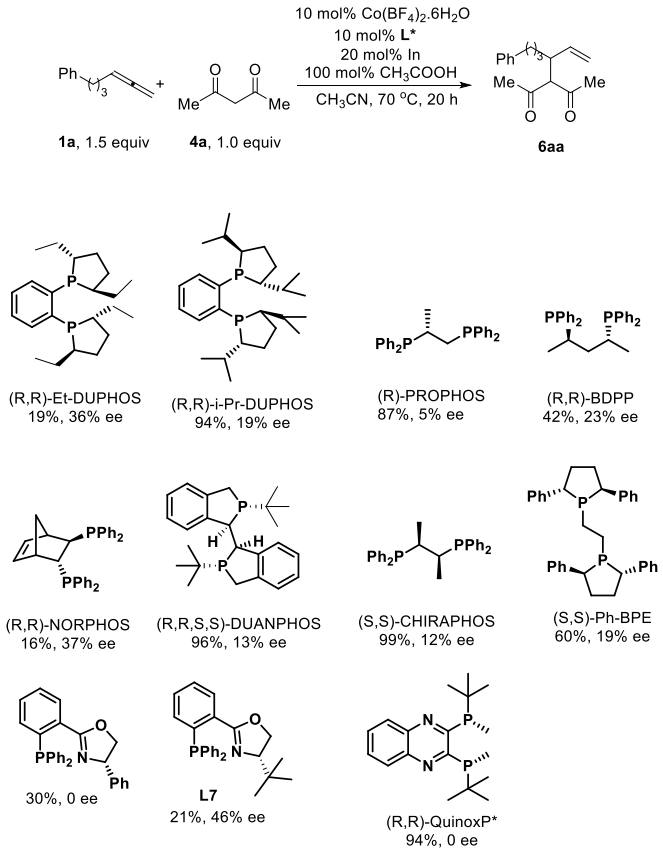


Figure S2. Chiral ligand screening

9. References:

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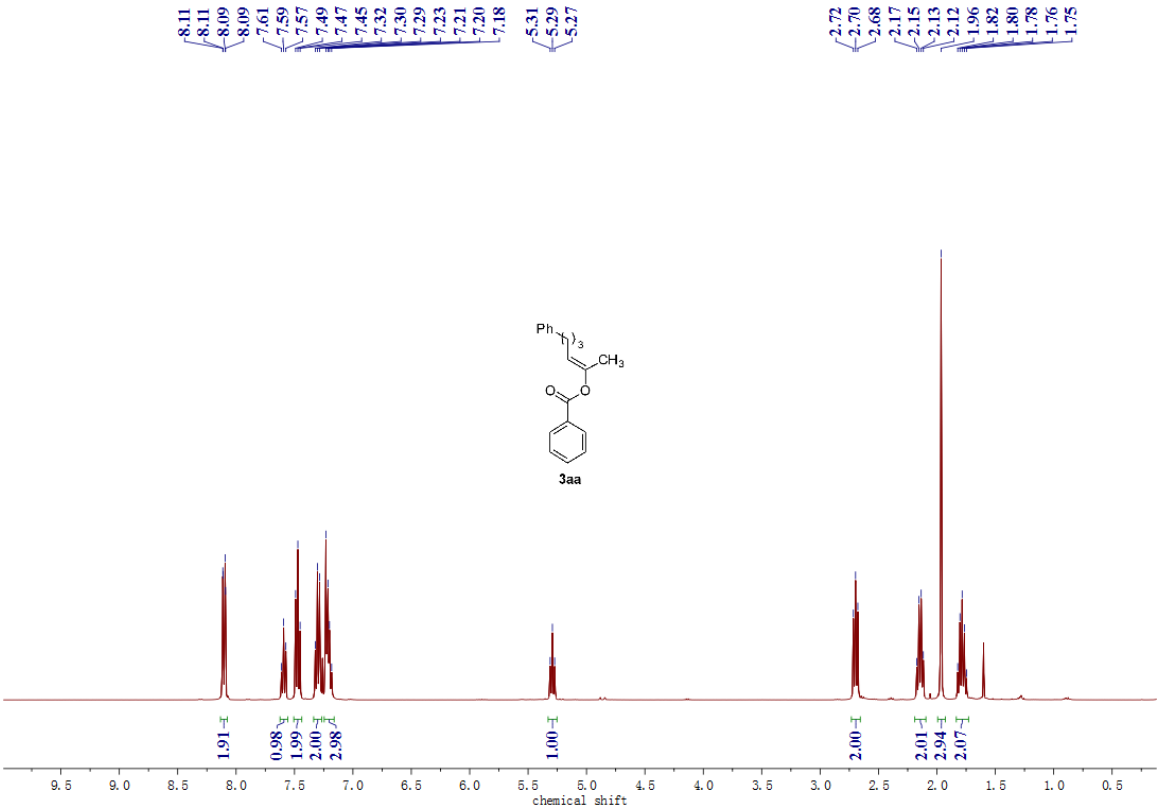
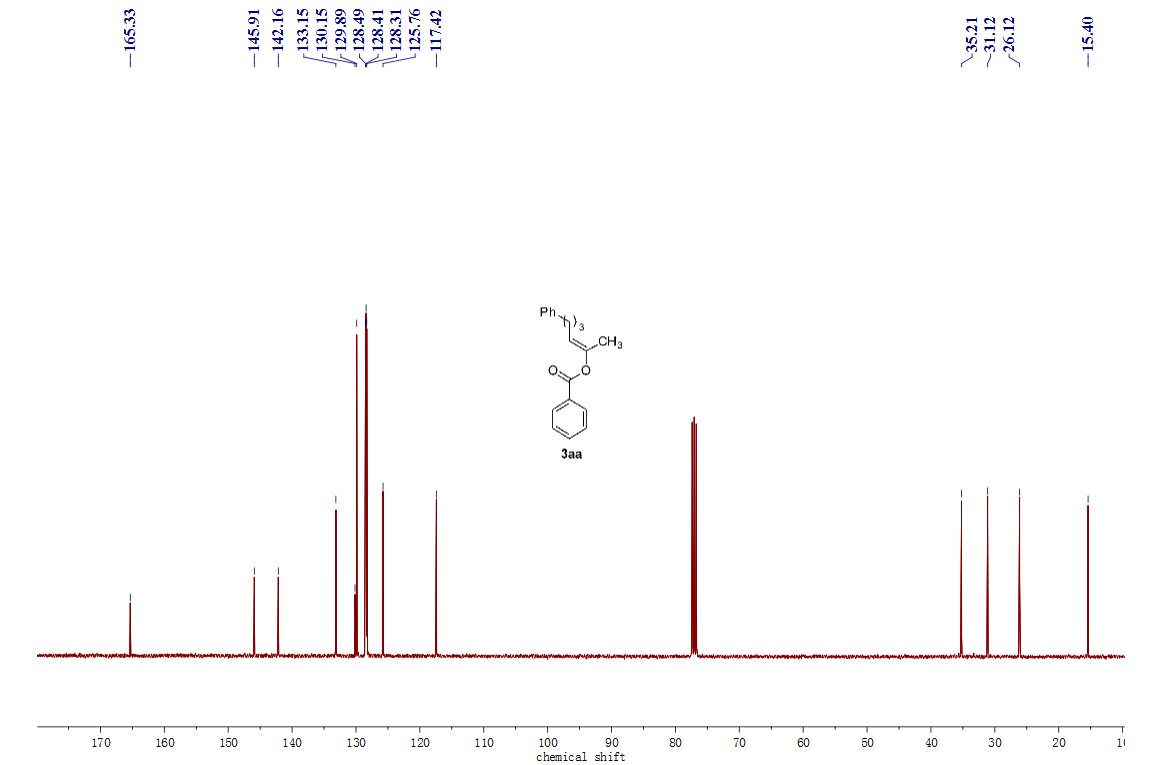
(9) P. Koschker, A. Lumbroso, B. Breit, Enantioselective synthesis of branched allylic esters via rhodium-catalyzed coupling of allenes with carboxylic acids, *J. Am. Chem. Soc.*, 2011, **133**, 20746-20749.

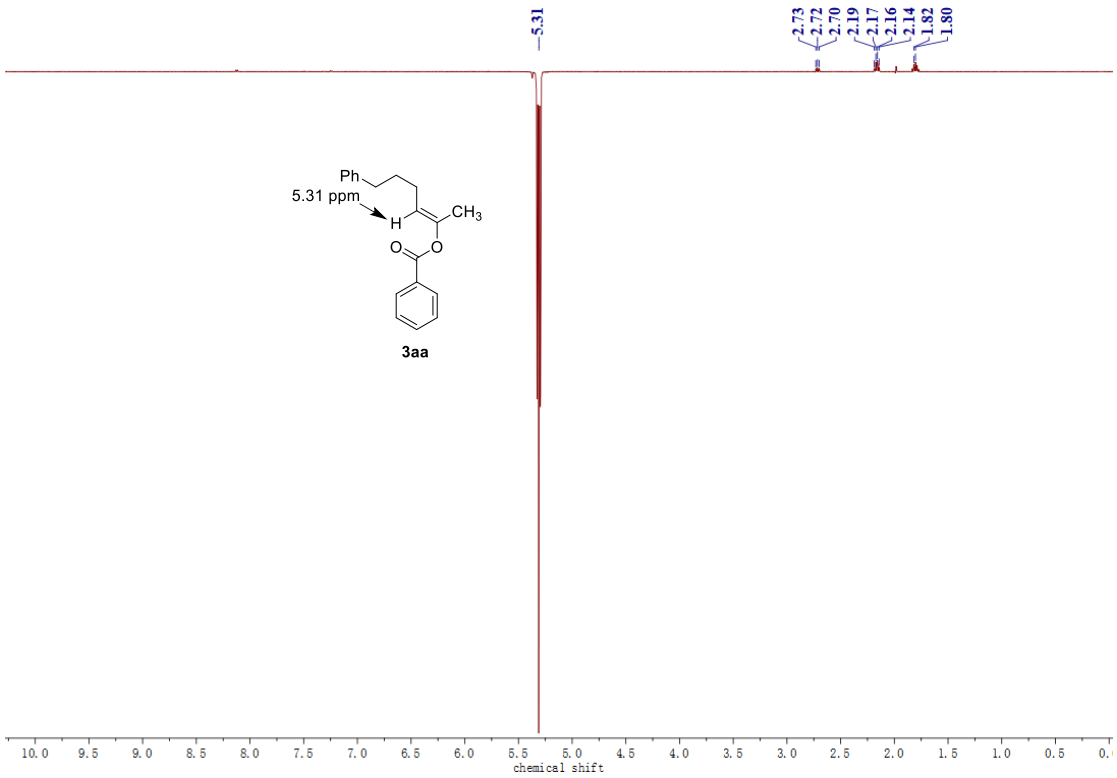
10. NMR Spectra of novel compounds

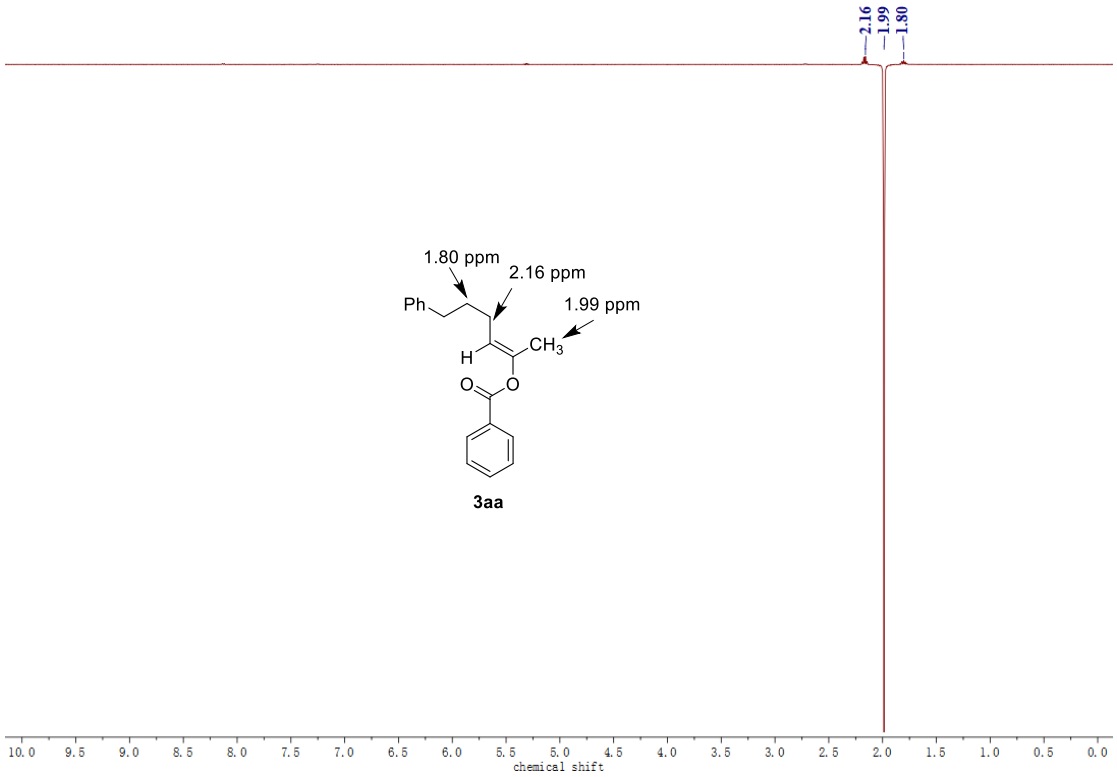
(E)-6-phenylhex-2-en-2-yl benzoate (**3aa**).



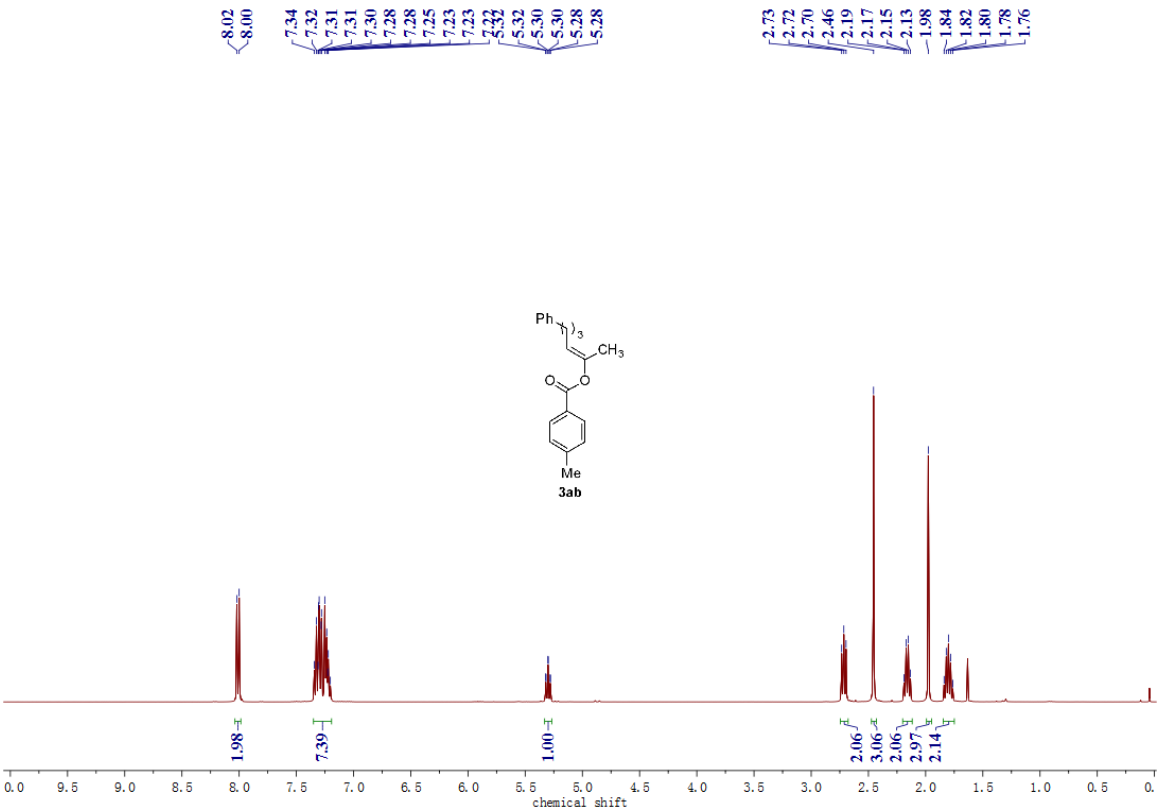


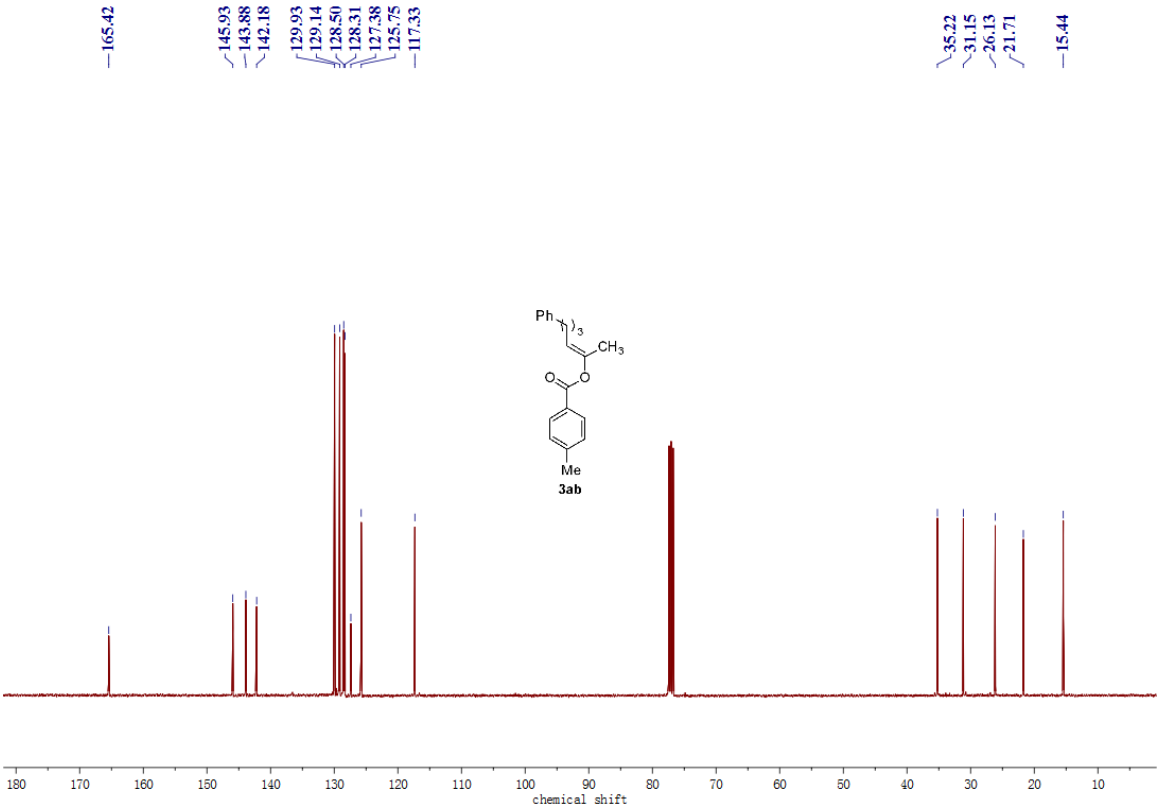
1D NOE of **3aa**


5.31
2.73
2.72
2.70
2.19
2.17
2.16
2.14
1.82
1.80
Ph
5.31 ppm
H
CH3
O
O
3aa
chemical shift

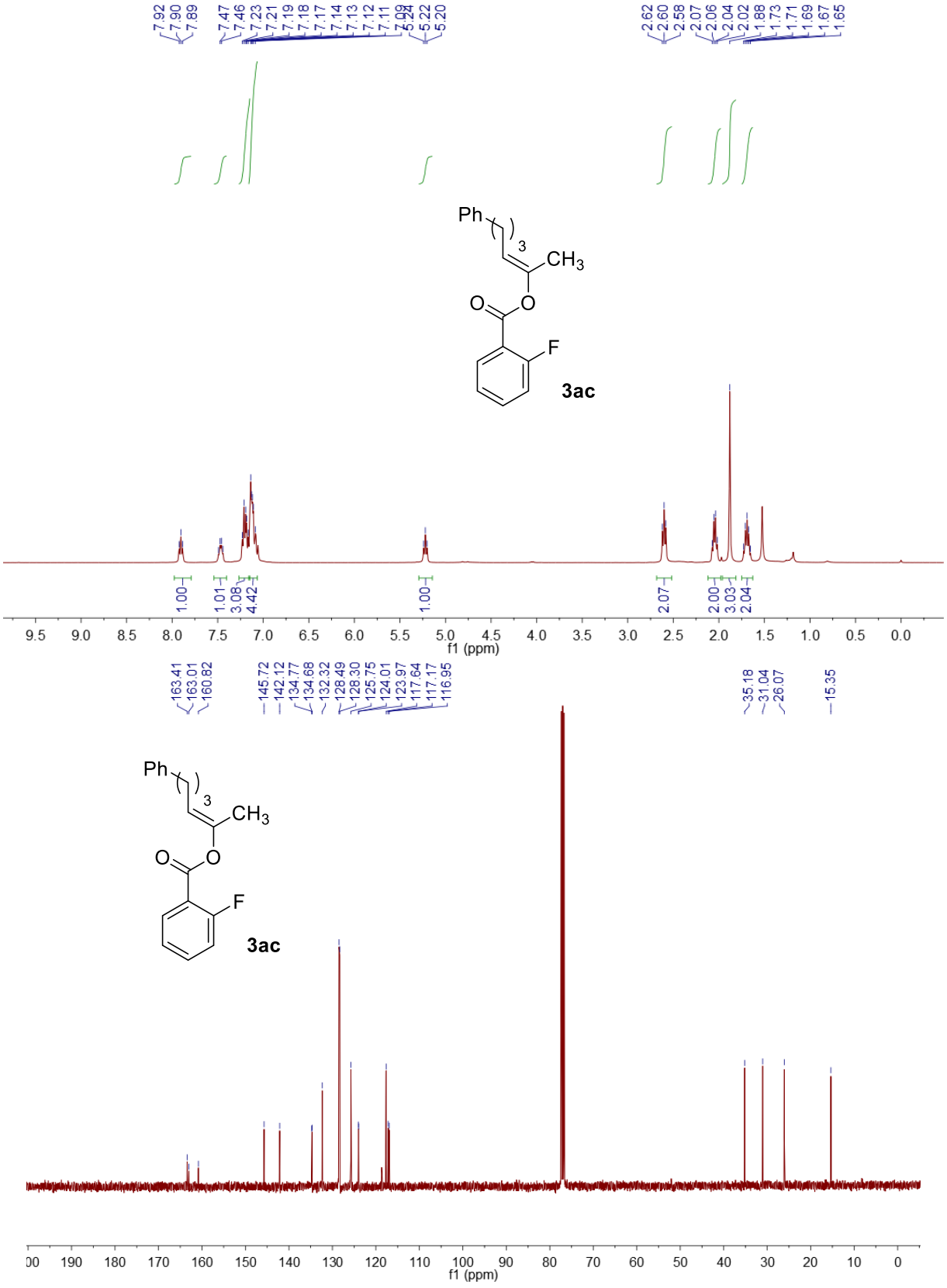

2.16
1.99
1.80
1.80 ppm
2.16 ppm
1.99 ppm
Ph
H
CH3
O
O
3aa
chemical shift

(E) -6-phenylhex-2-en-2-yl 4-methylbenzoate (**3ab**).

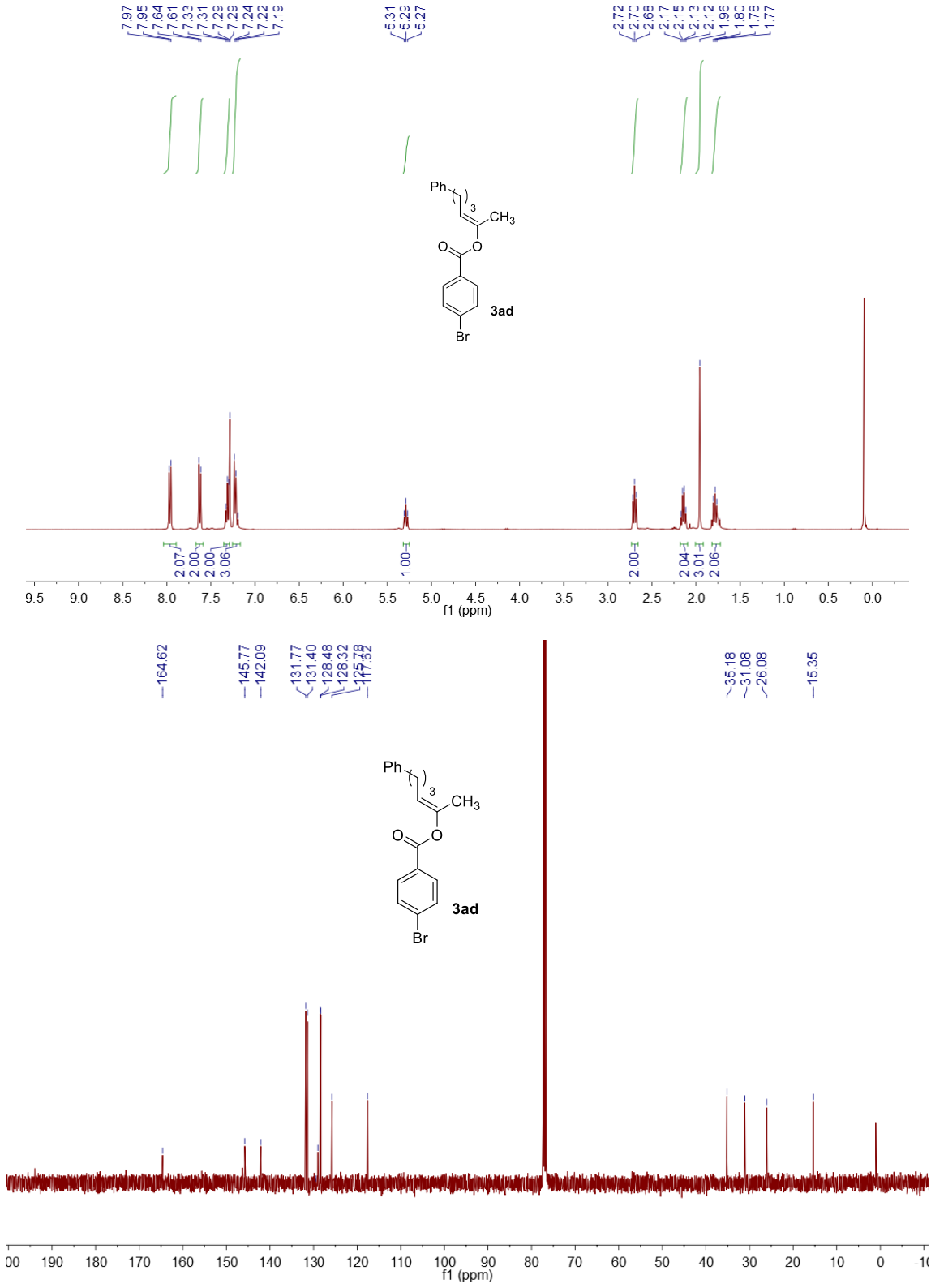




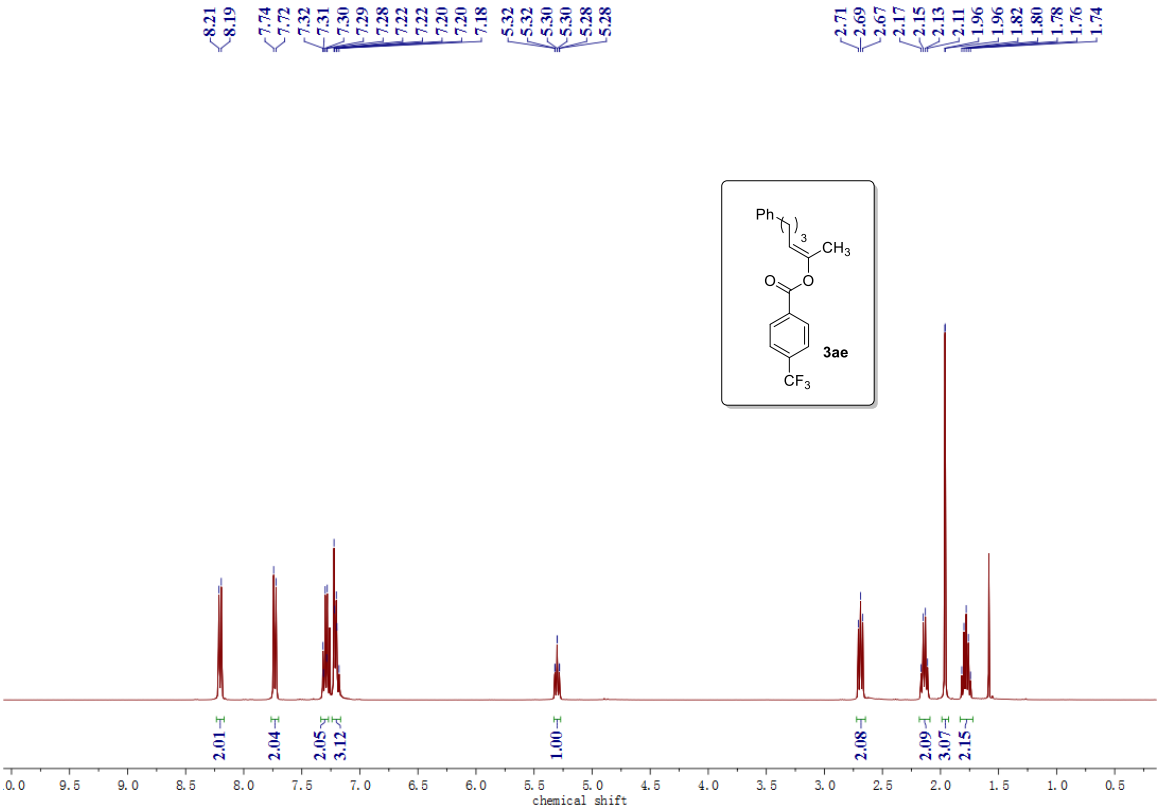
(E)-6-phenylhex-2-en-2-yl 2-fluorobenzoate (**3ac**).

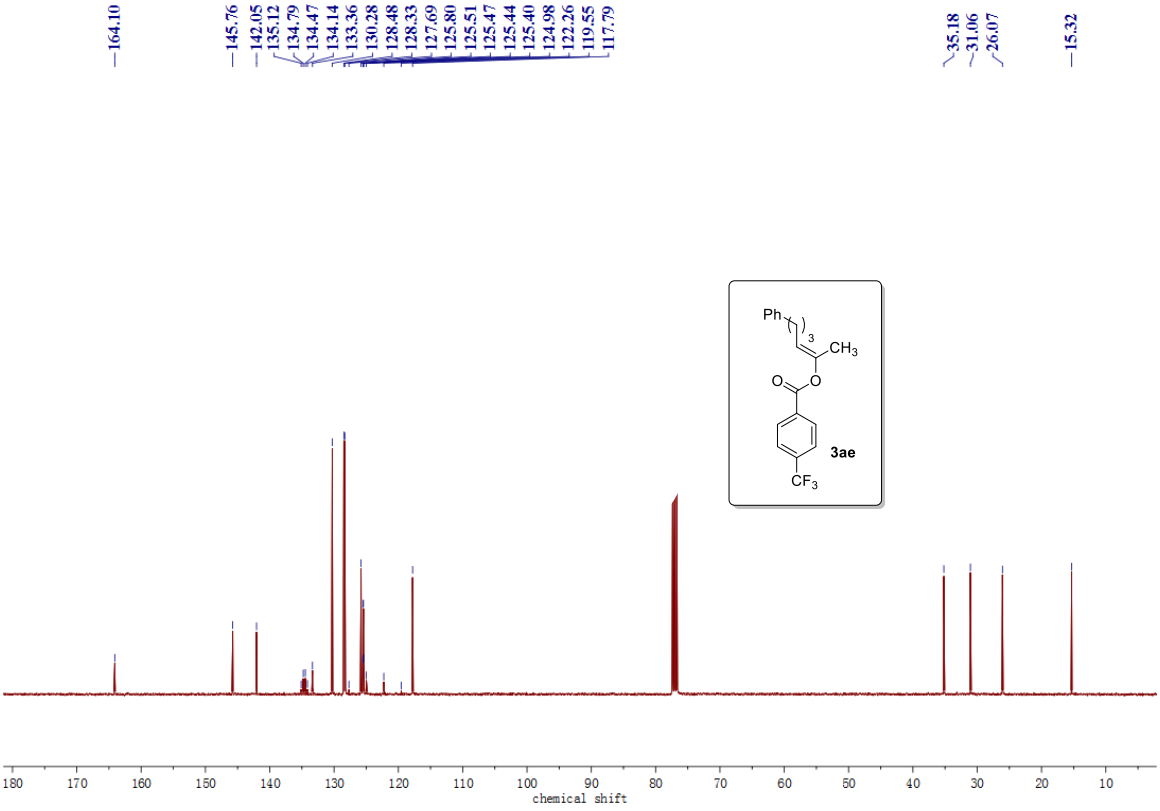


(E)-6-phenylhex-2-en-2-yl 4-bromobenzoate (**3ad**)

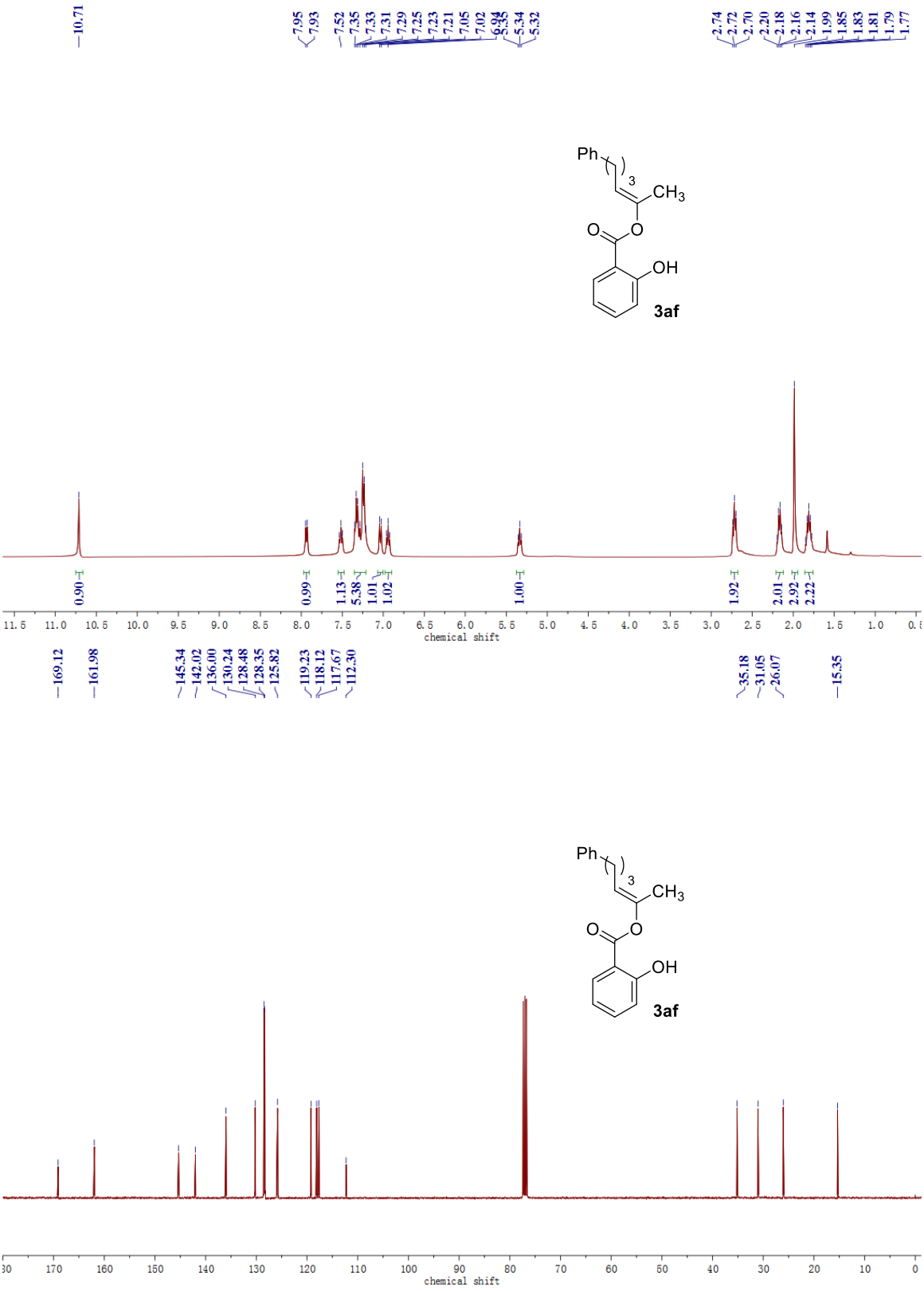


(E)-6-phenylhex-2-en-2-yl 4-(trifluoromethyl)benzoate (**3ae**).

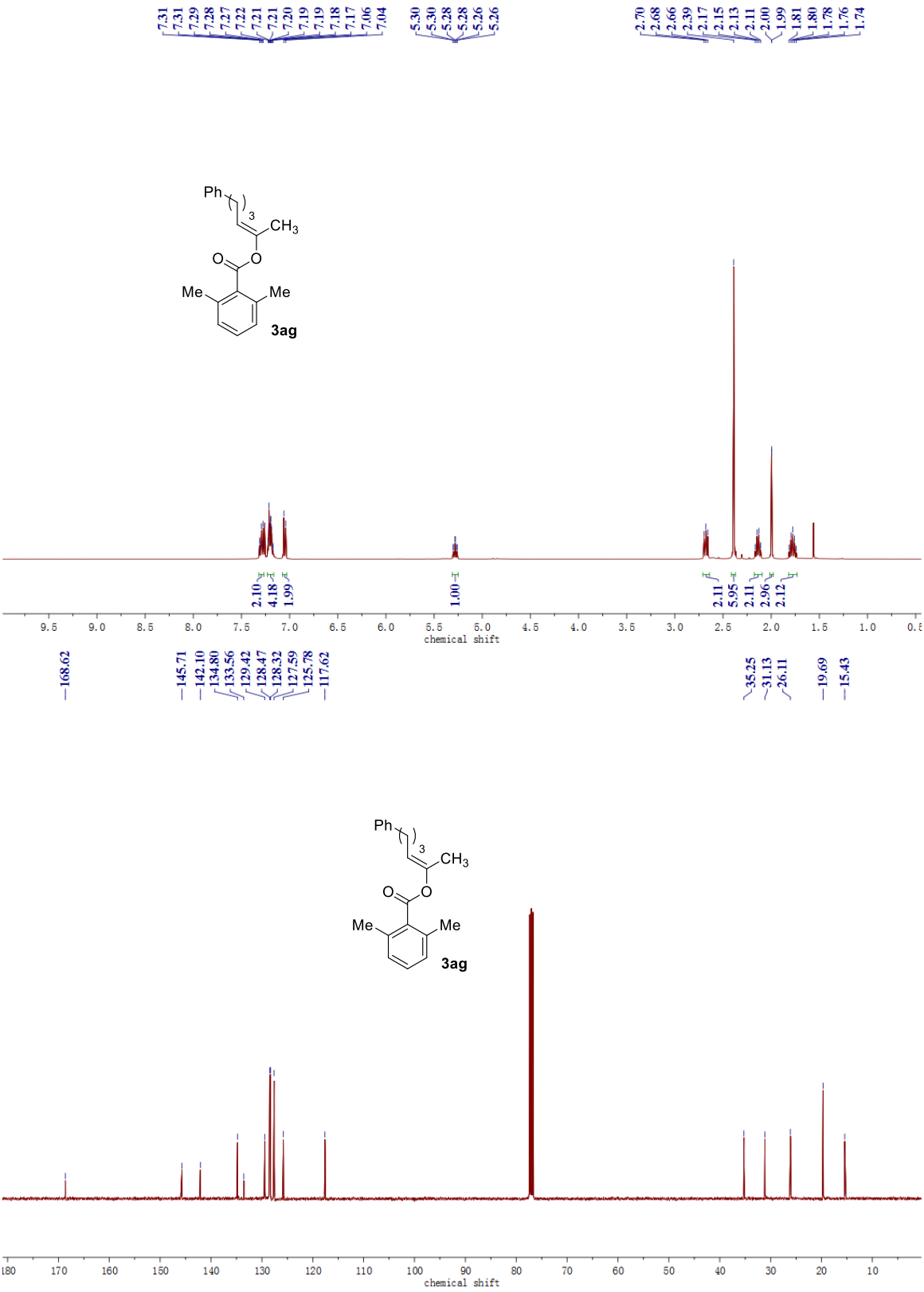




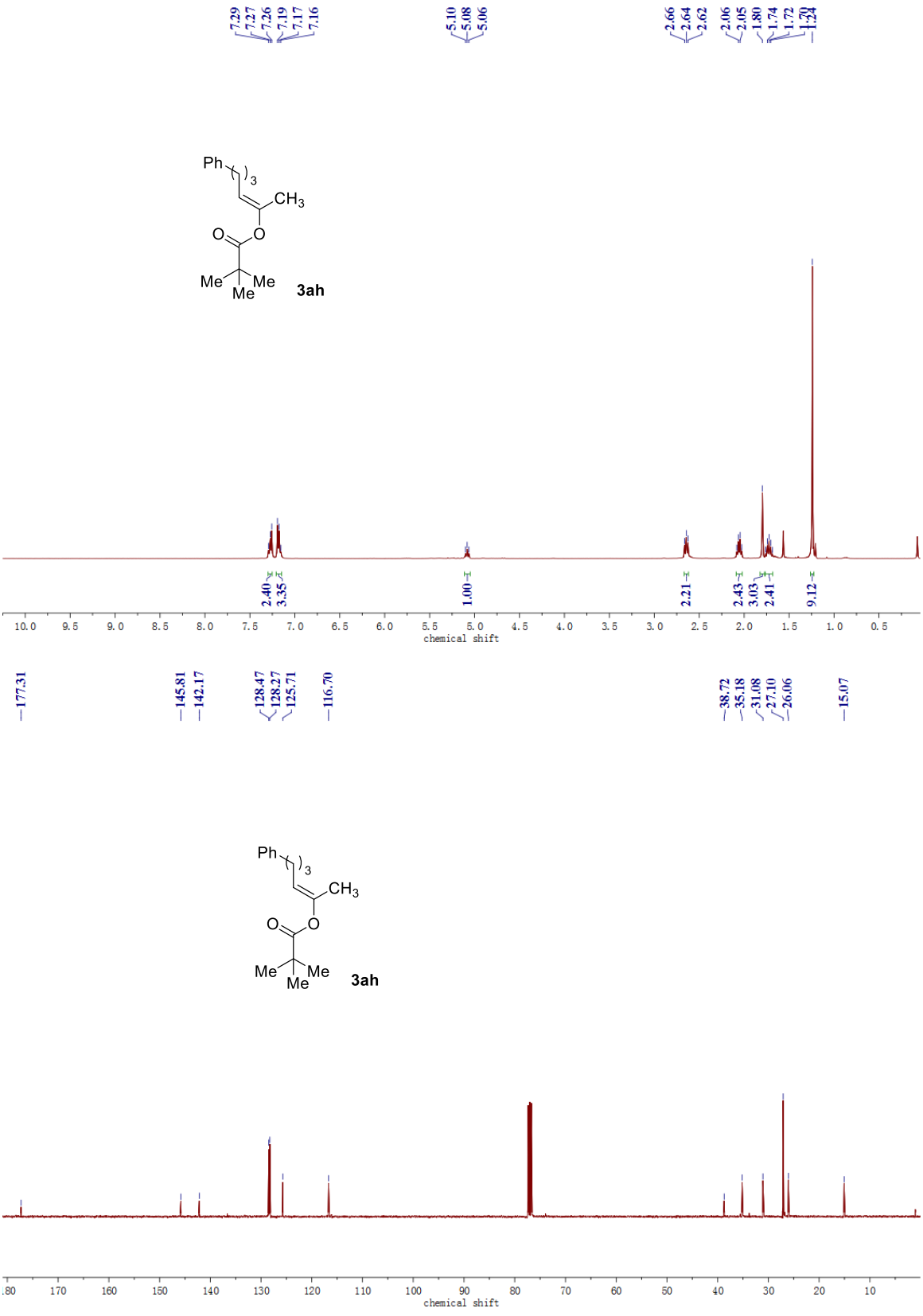
(E)-6-phenylhex-2-en-2-yl 2-hydroxybenzoate(**3af**).



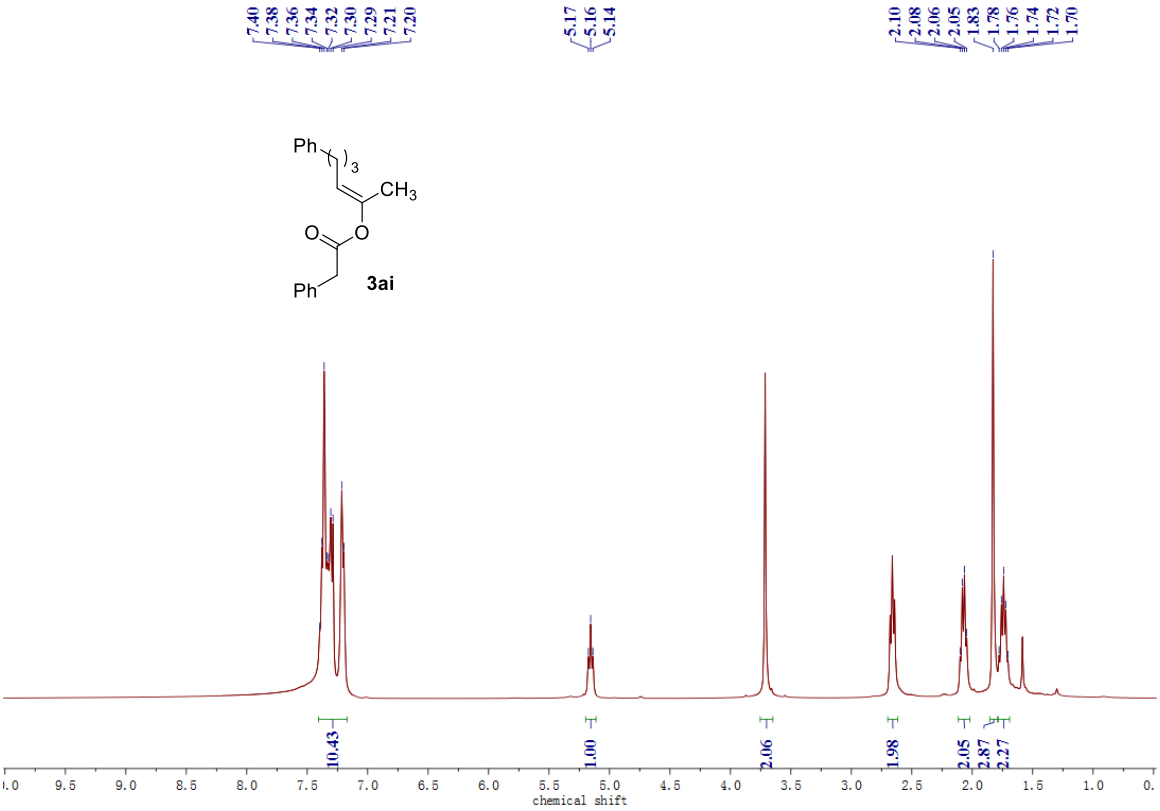
(E)-6-phenylhex-2-en-2-yl 2,6-dimethylbenzoate (**3ag**).

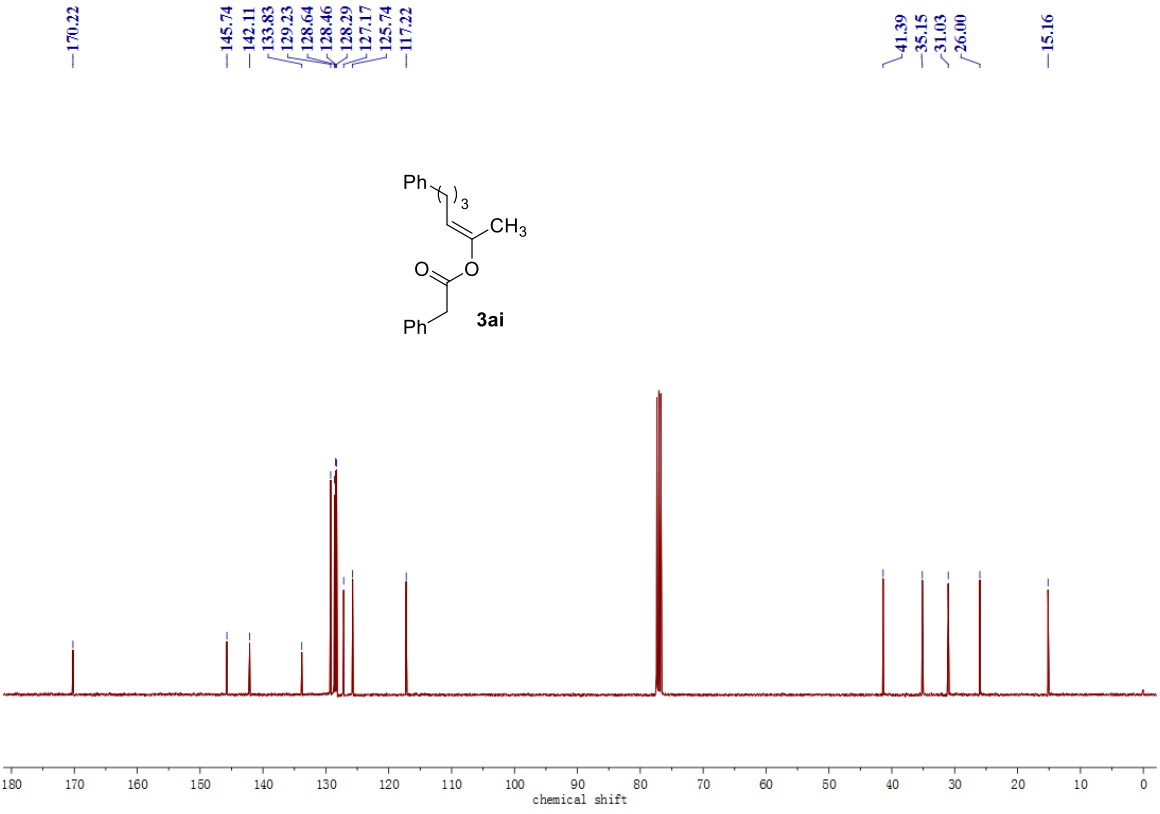


(E)-6-phenylhex-2-en-2-yl pivalate (**3ah**).

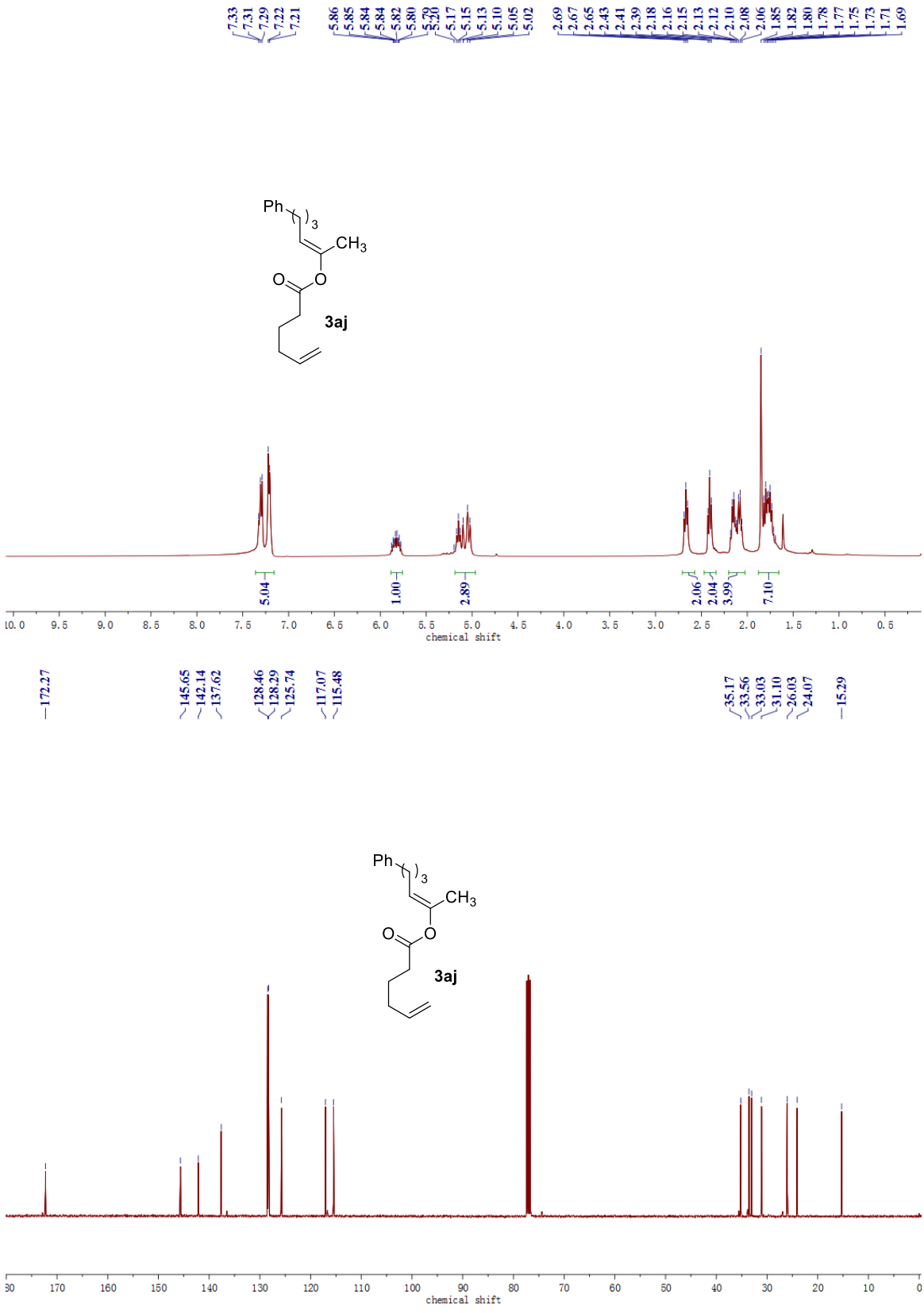


(E)-6-phenylhex-2-en-2-yl 2-phenylacetate (**3ai**).

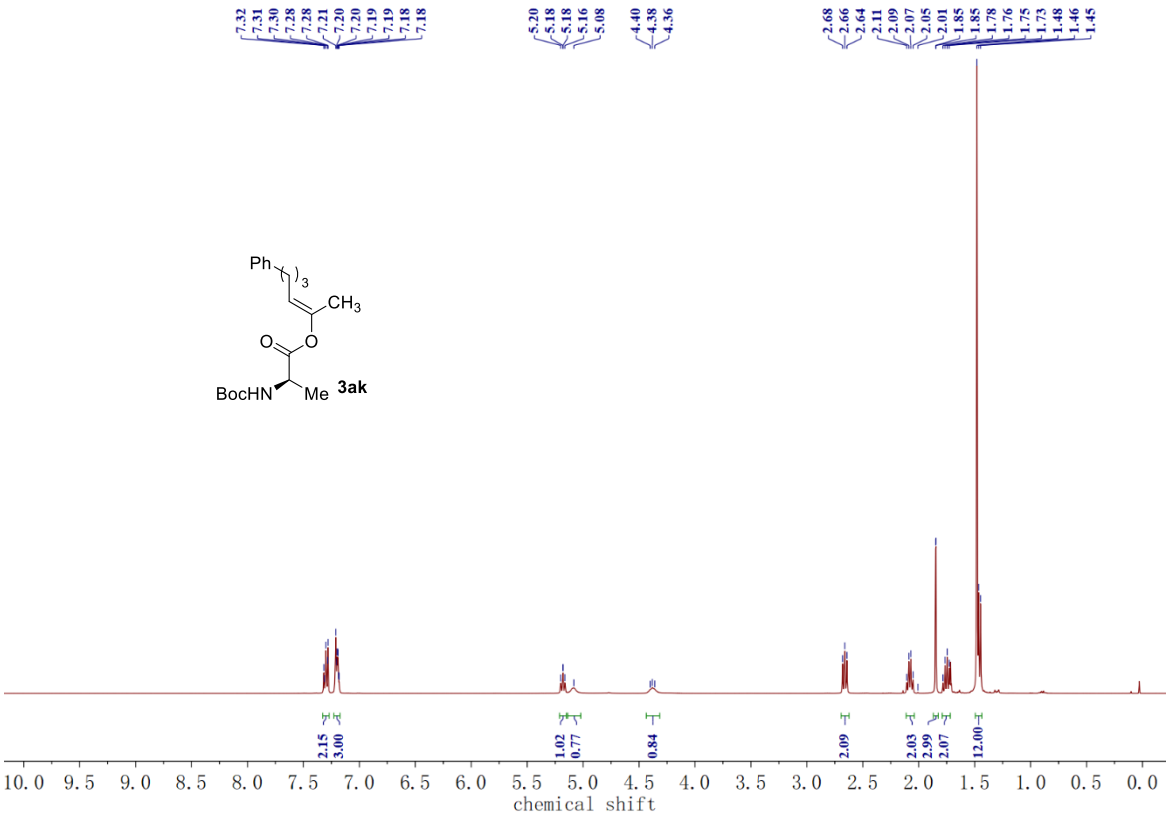


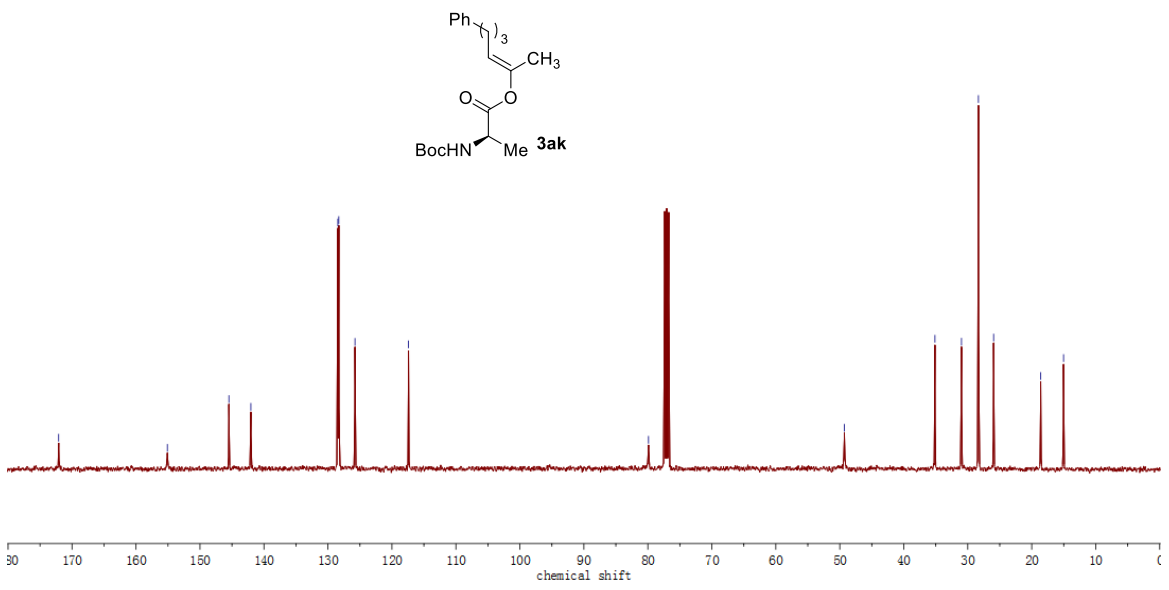


(E)-6-phenylhex-2-en-2-yl hex-5-enoate (**3aj**).

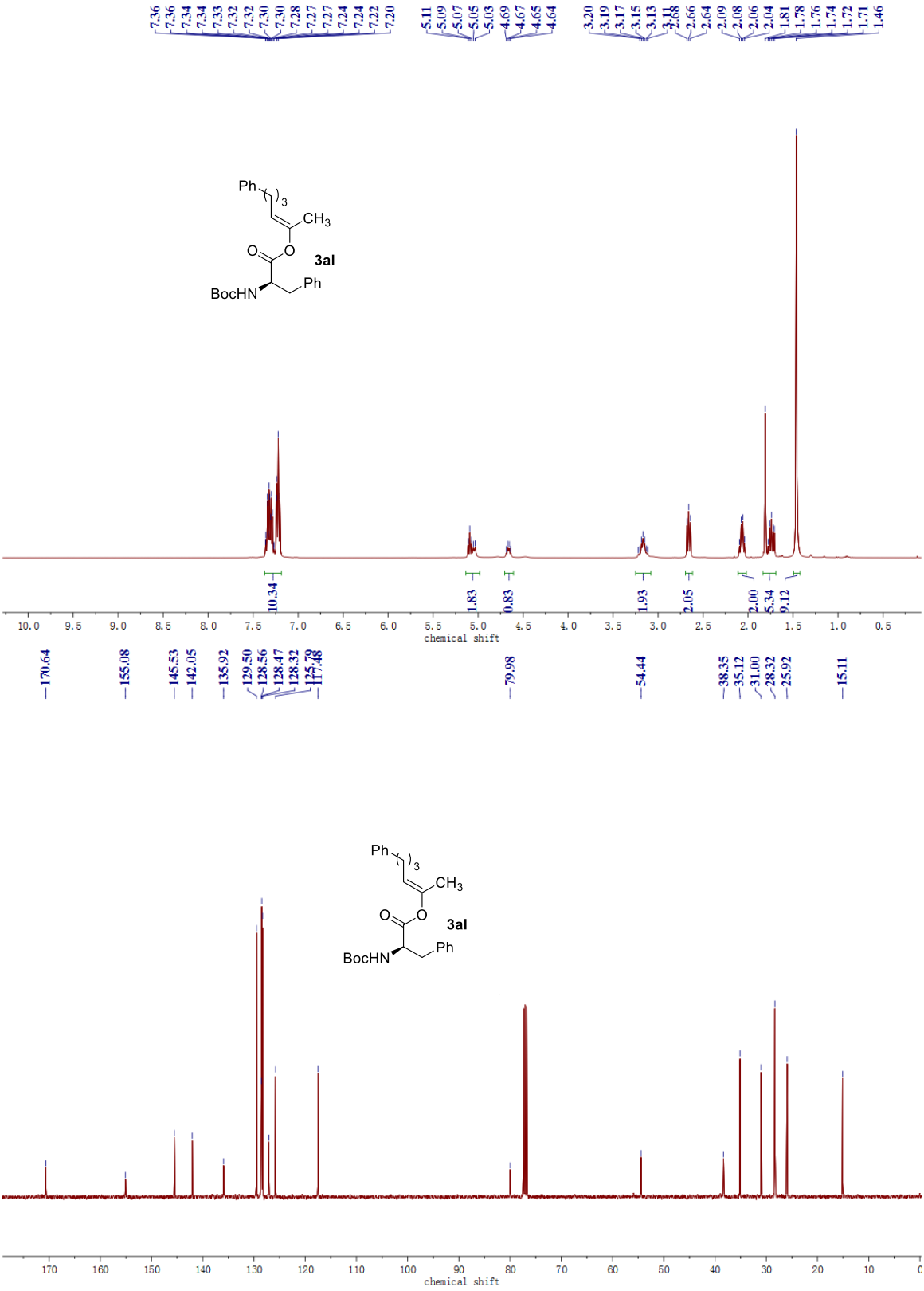


(R,E)-6-phenylhex-2-en-2-yl 2-((tert-butoxycarbonyl)amino)propanoate (**3ak**).

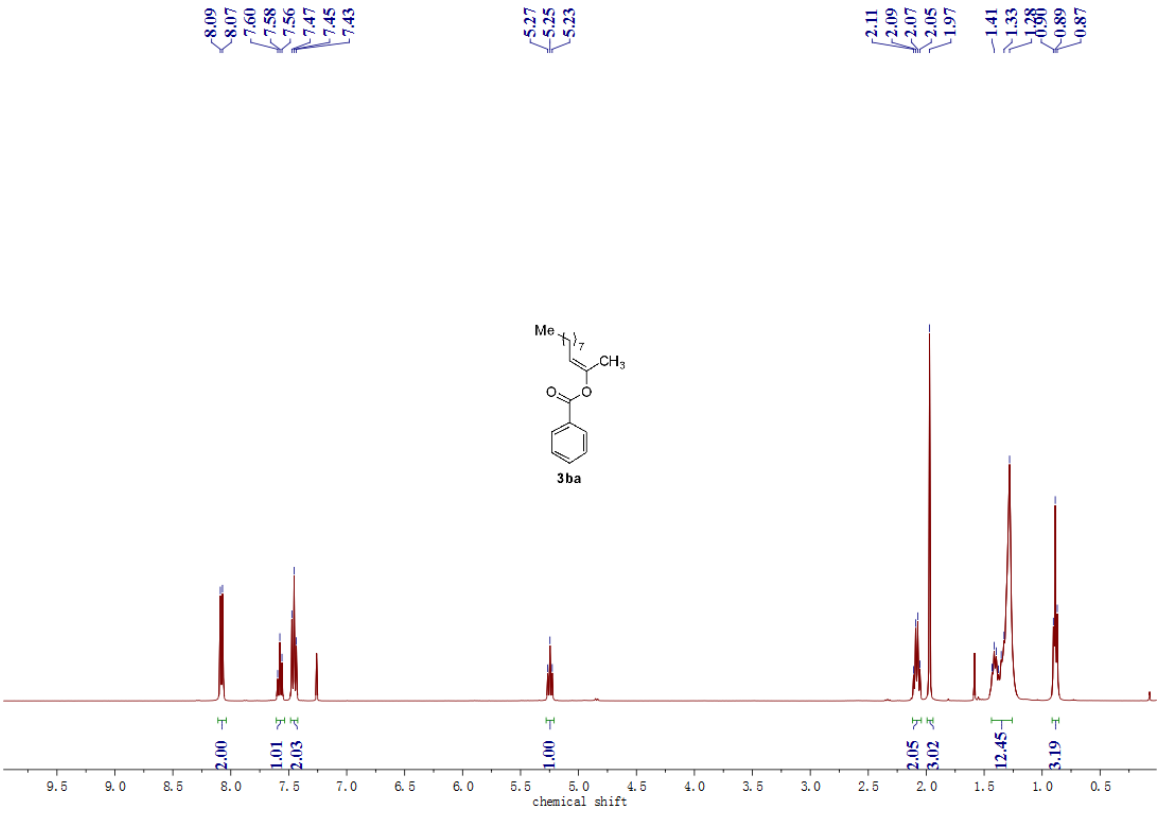


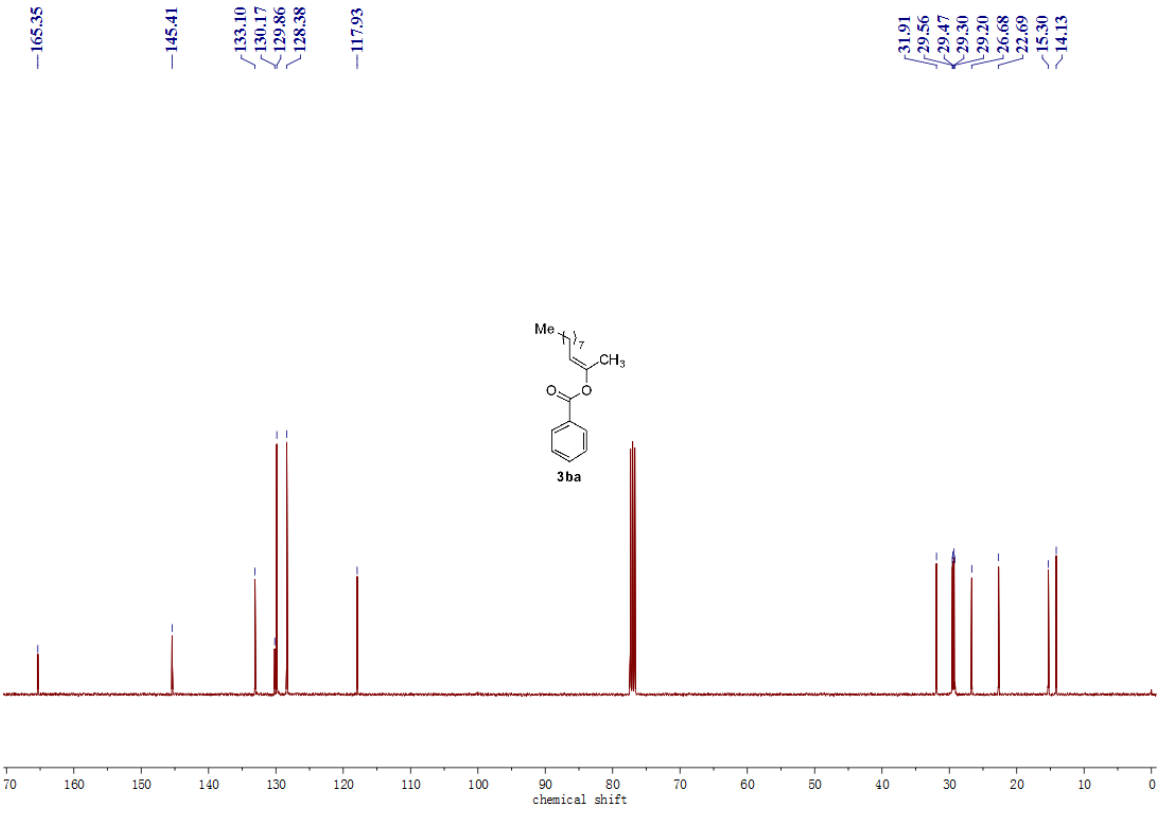


(R,E)-6-phenylhex-2-en-2-yl 2-((tert-butoxycarbonyl)amino)-3-phenylpropanoate (**3al**).

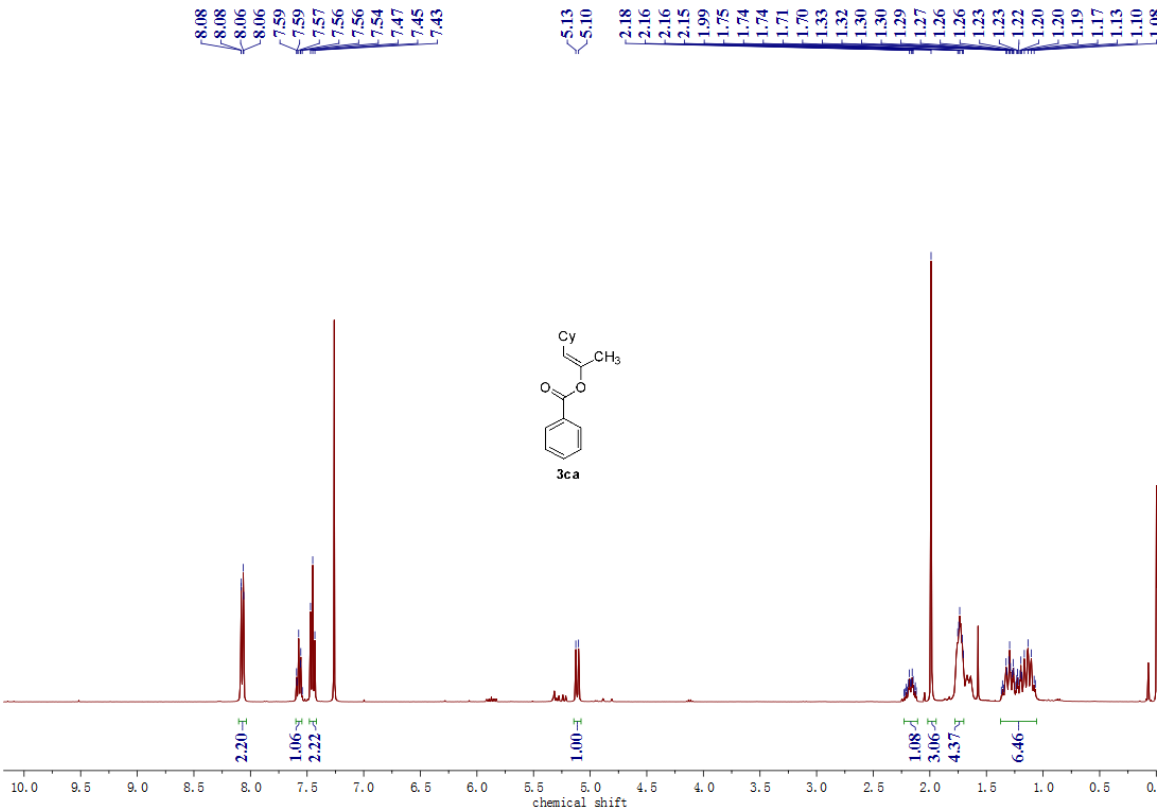


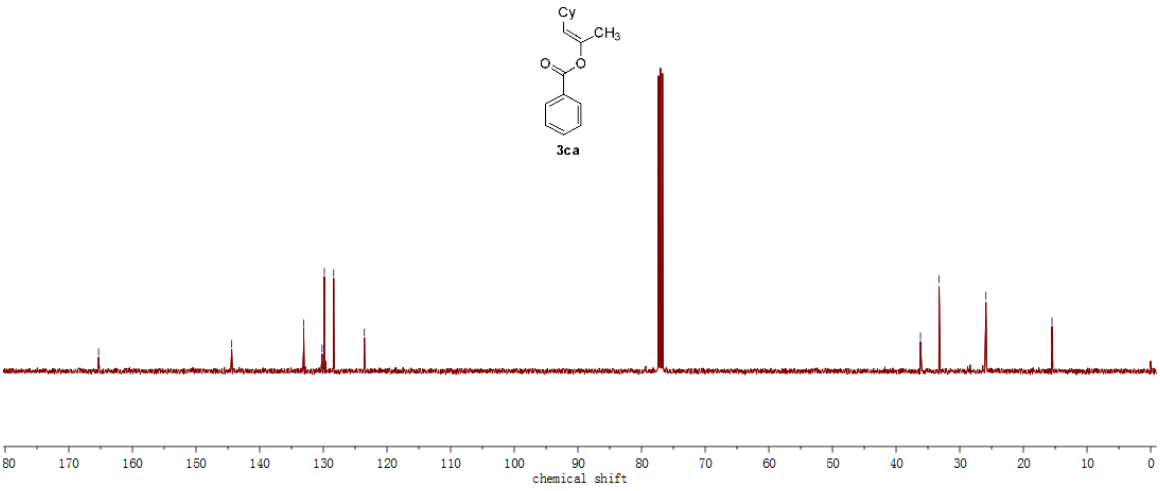
(E)-undec-2-en-2-yl benzoate (**3ba**).



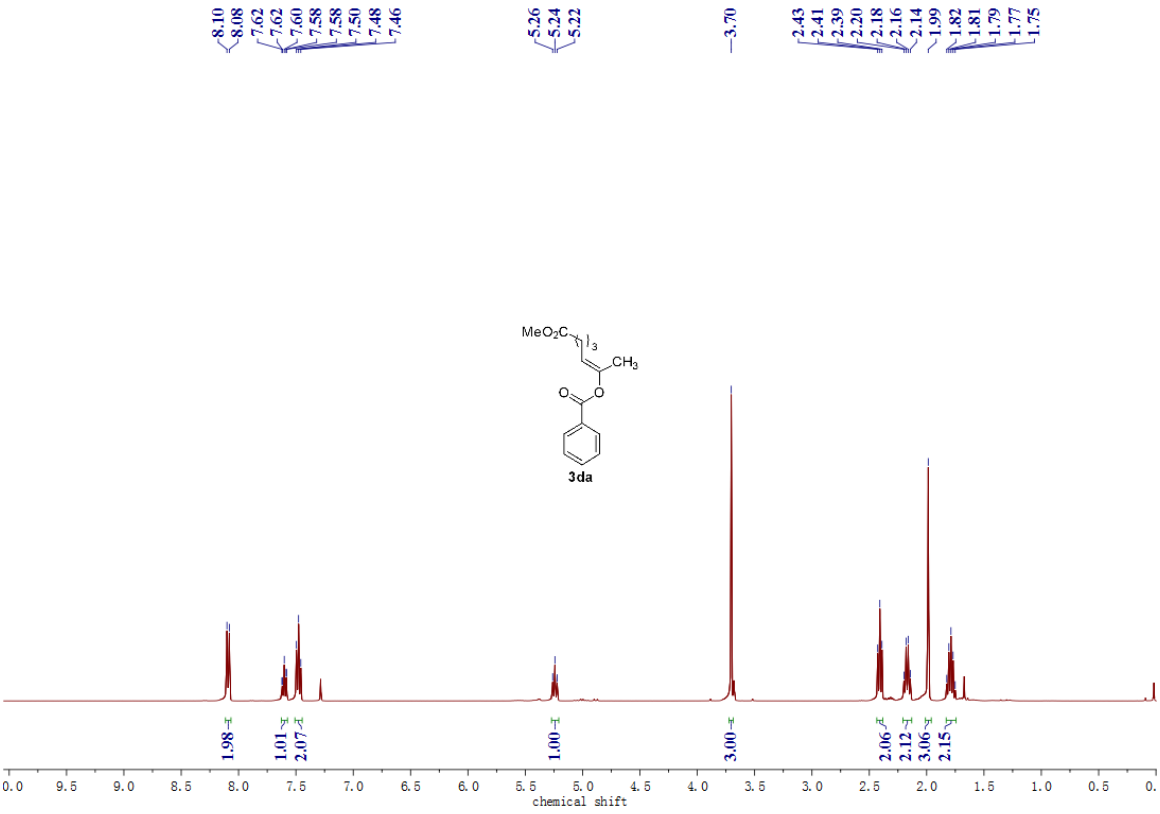


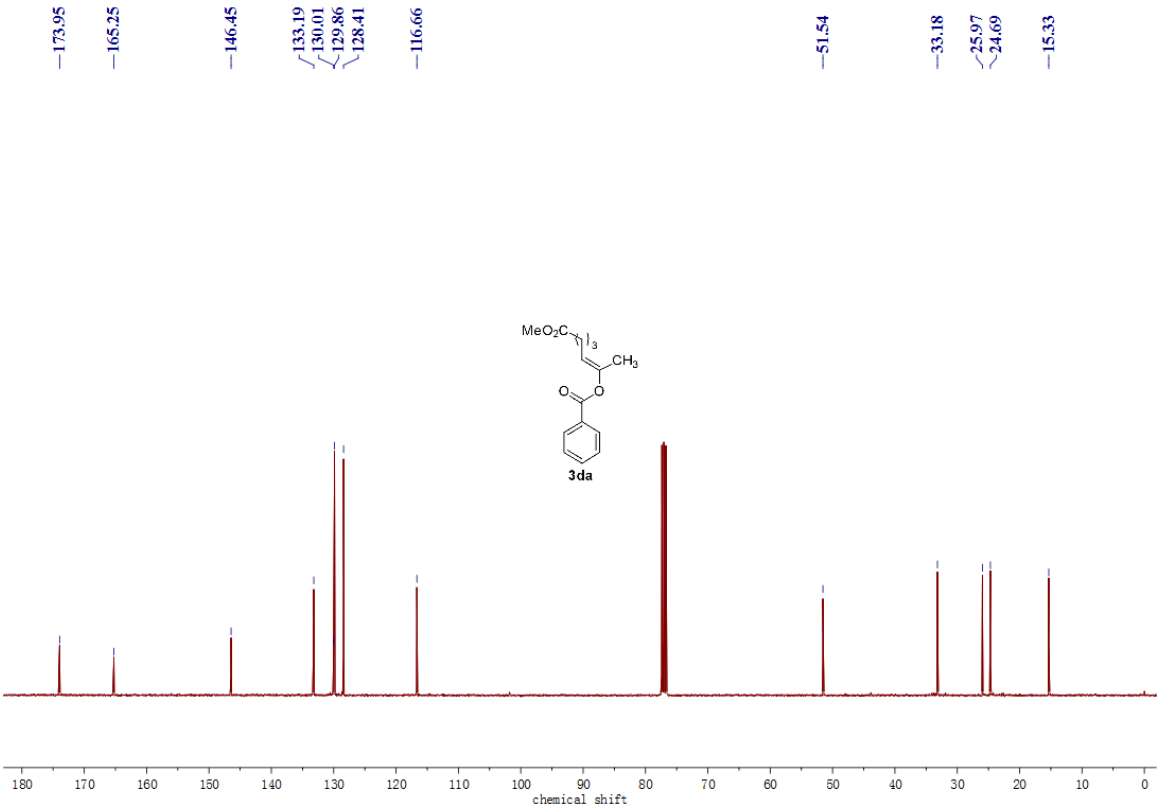
(E)-1-cyclohexylprop-1-en-2-yl benzoate (**3ca**).



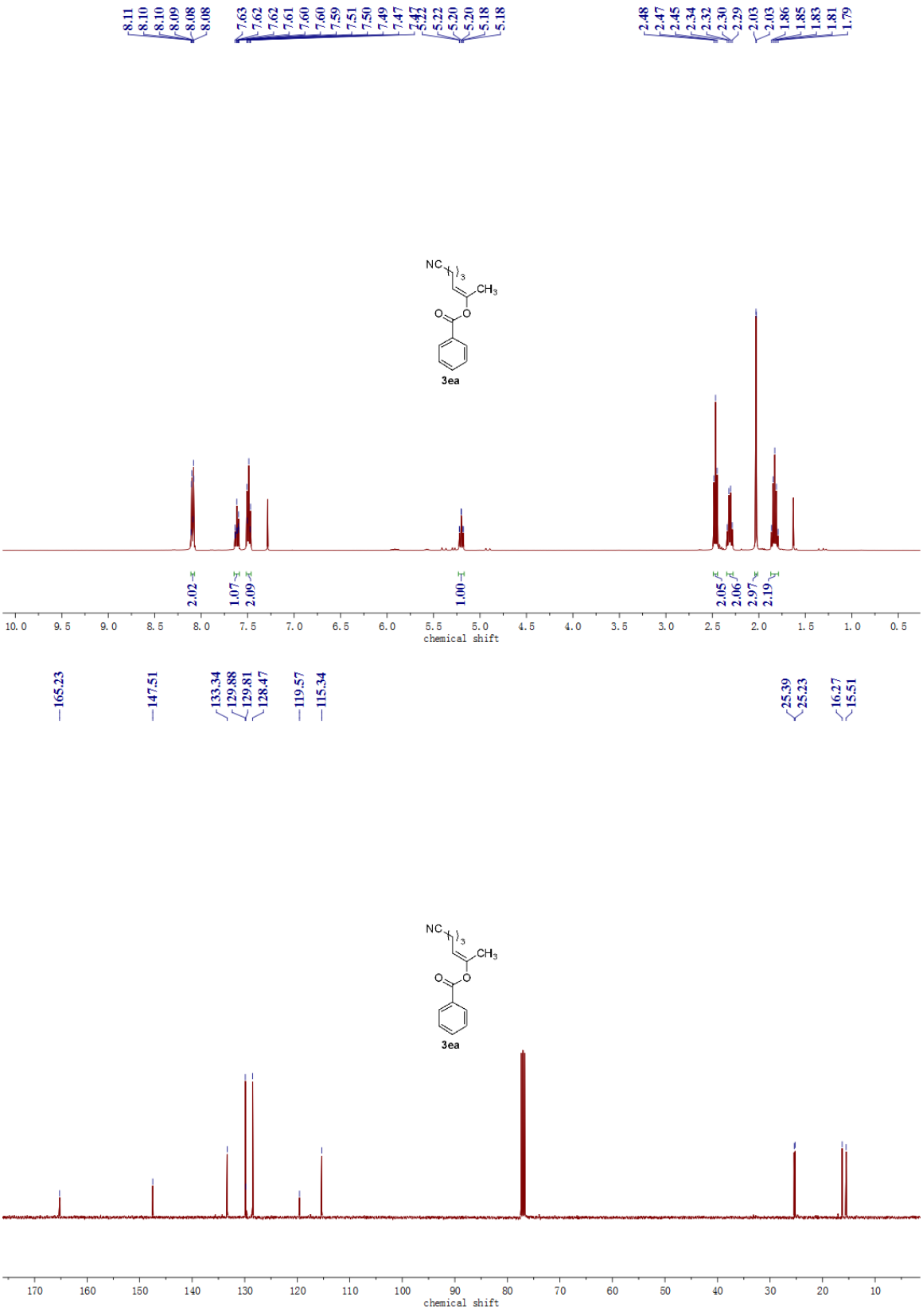


(E)-7-methoxy-7-oxohept-2-en-2-yl benzoate (**3da**).

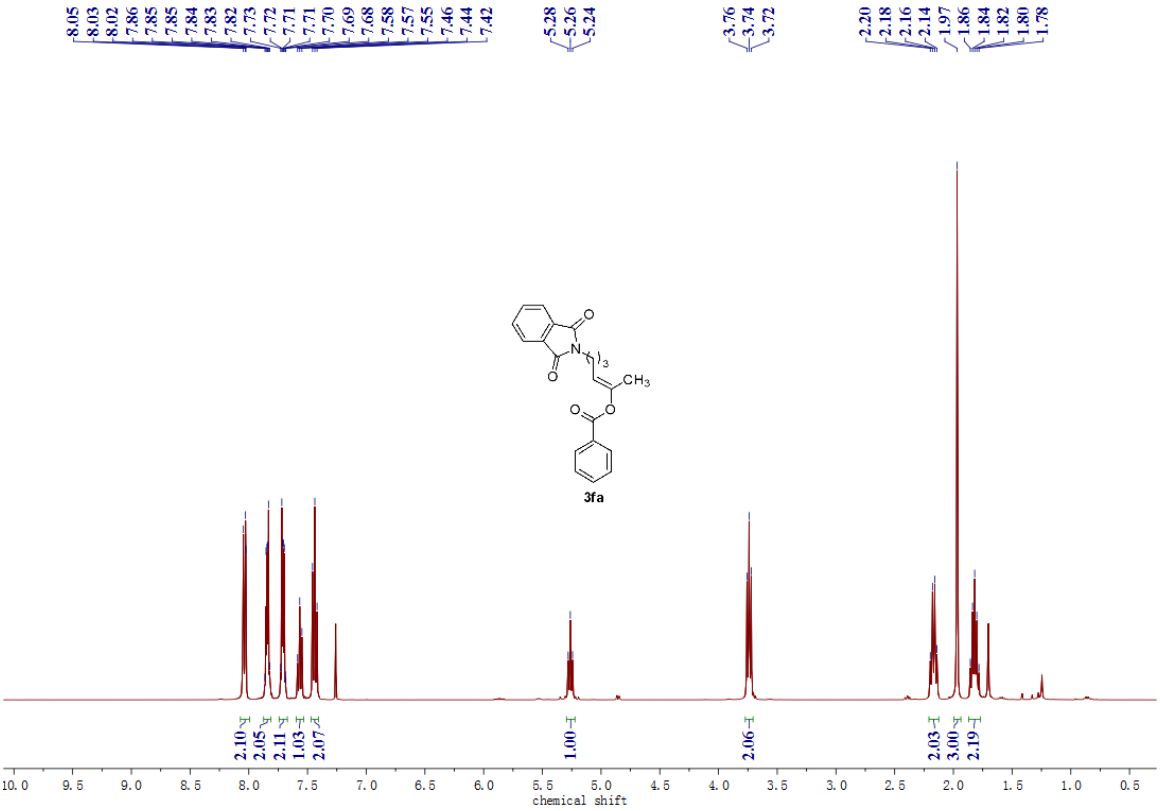


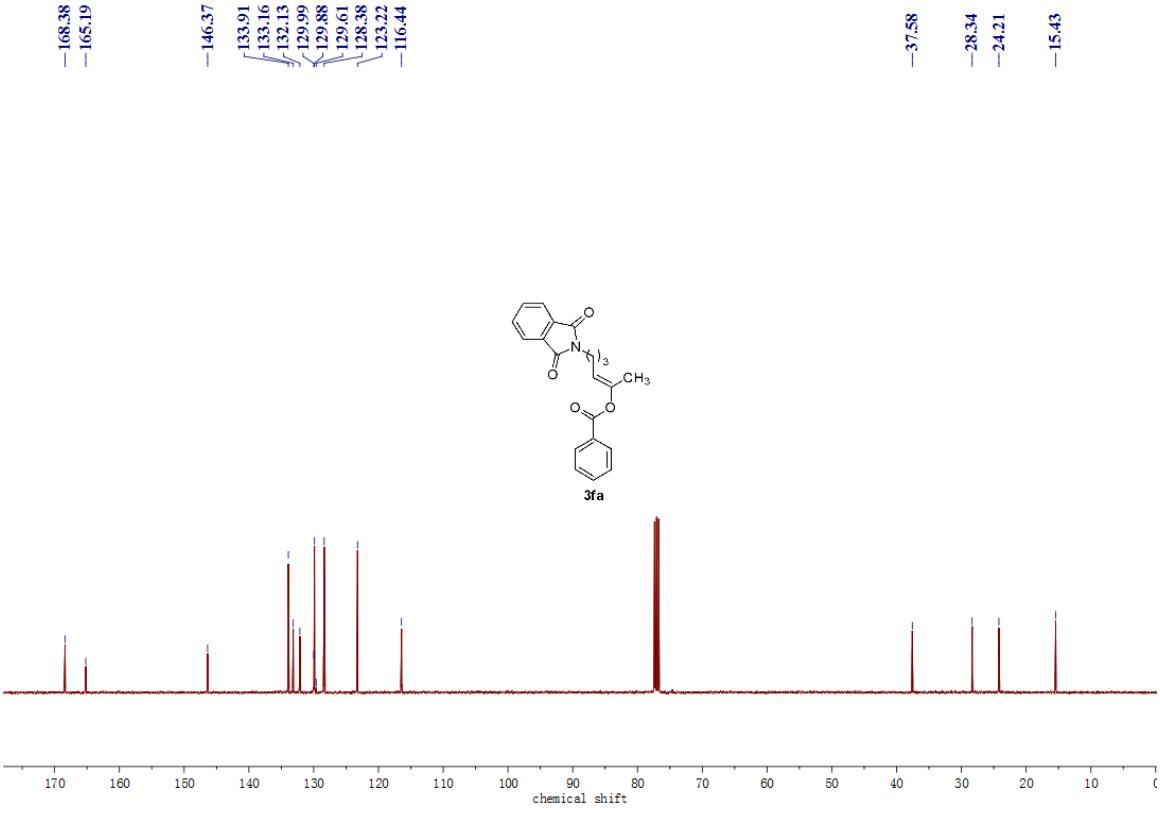


(E)-6-cyanohex-2-en-2-yl benzoate (**3ea**).

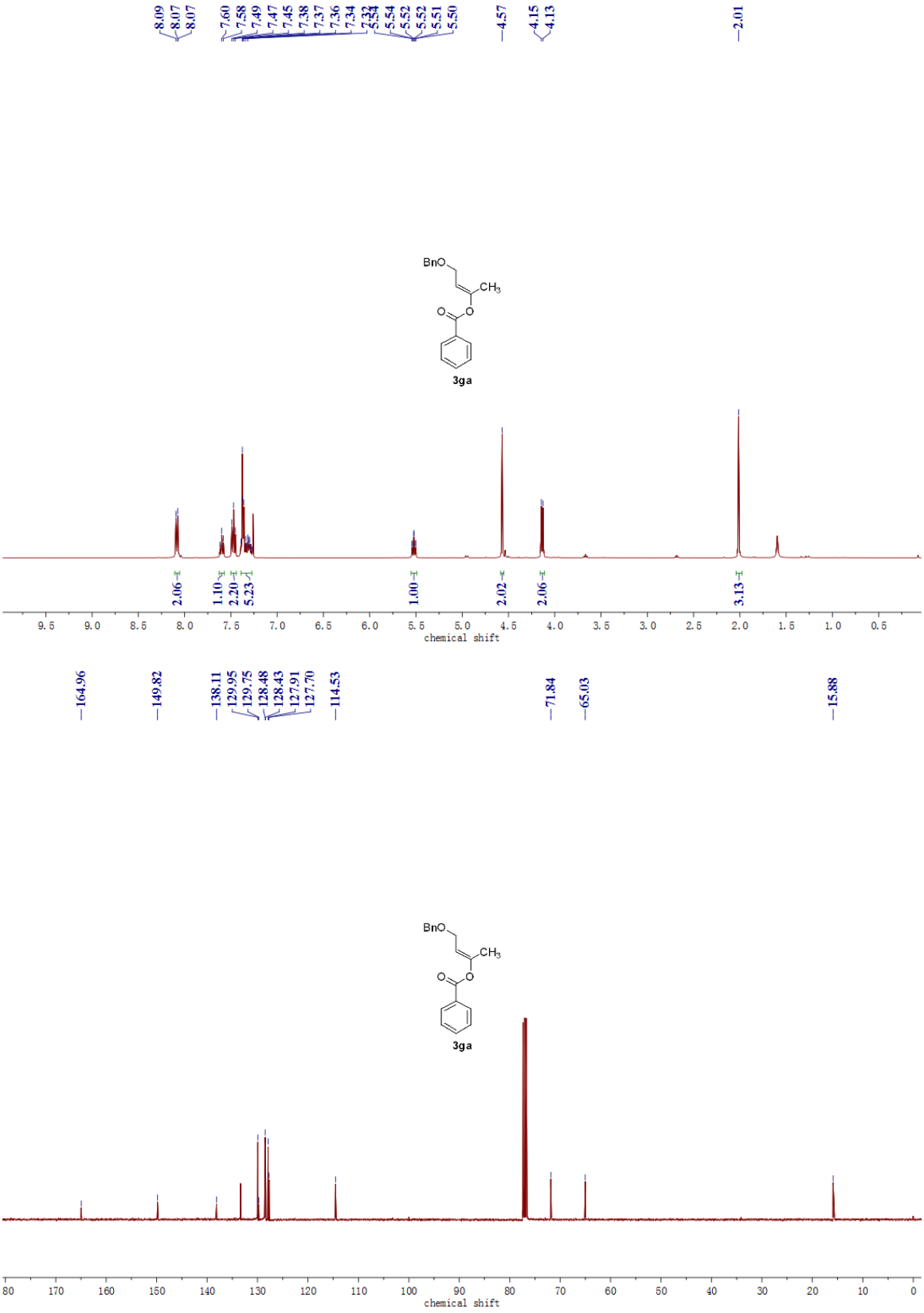


(E)-6-(1,3-dioxoisoindolin-2-yl)hex-2-en-2-yl benzoate (**3fa**).

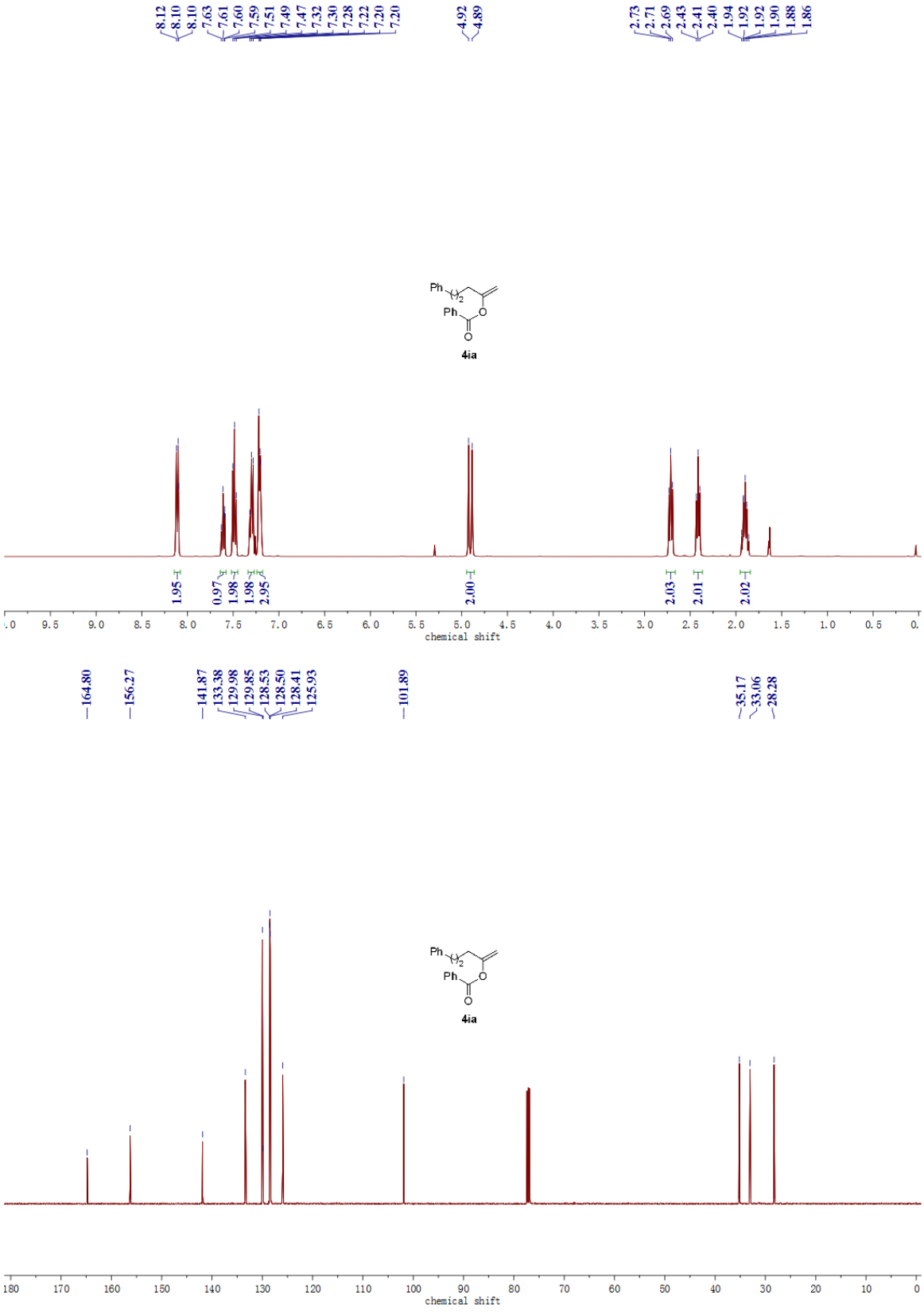




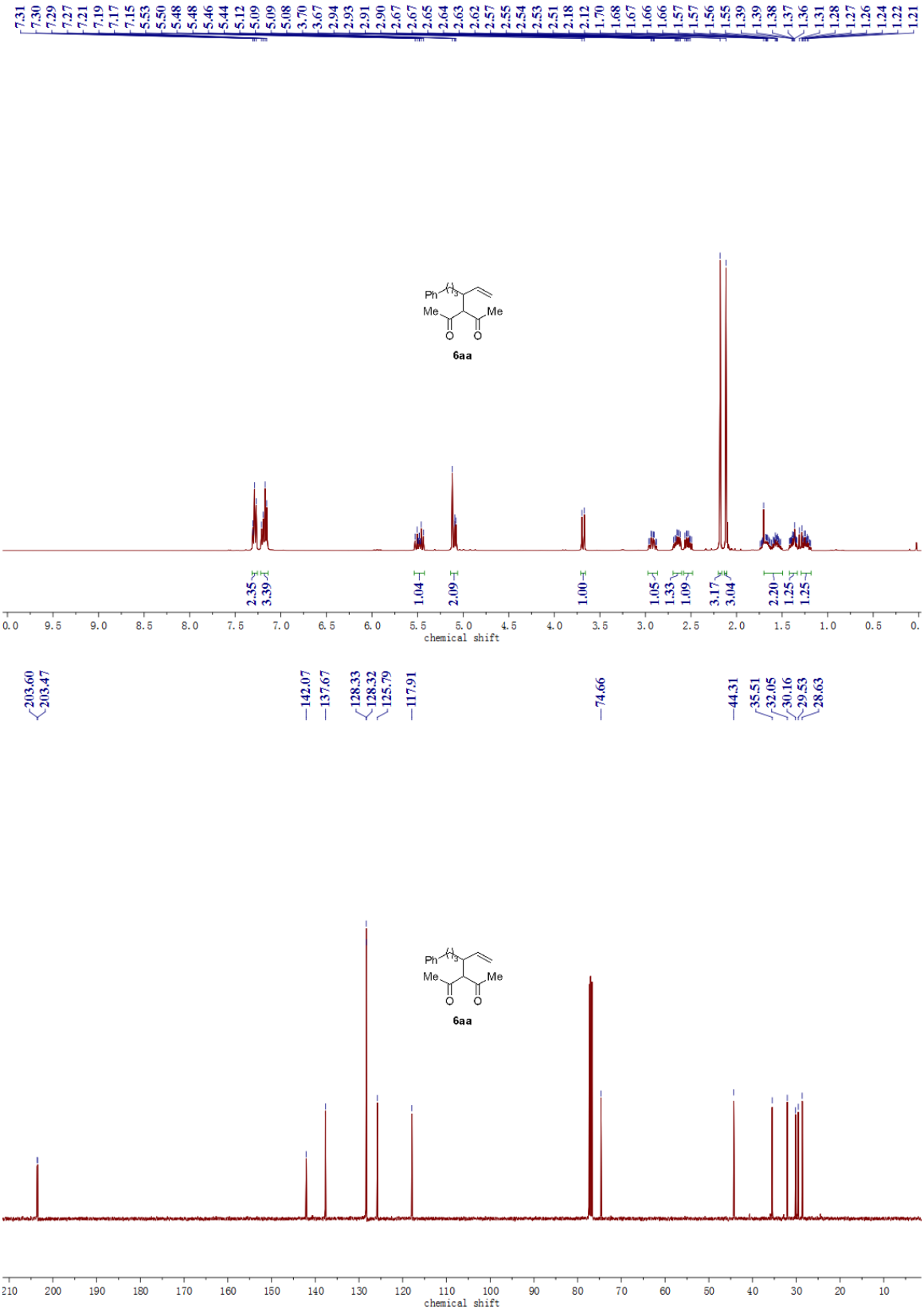
(E)-4-(benzyloxy)but-2-en-2-yl benzoate (**3ga**).



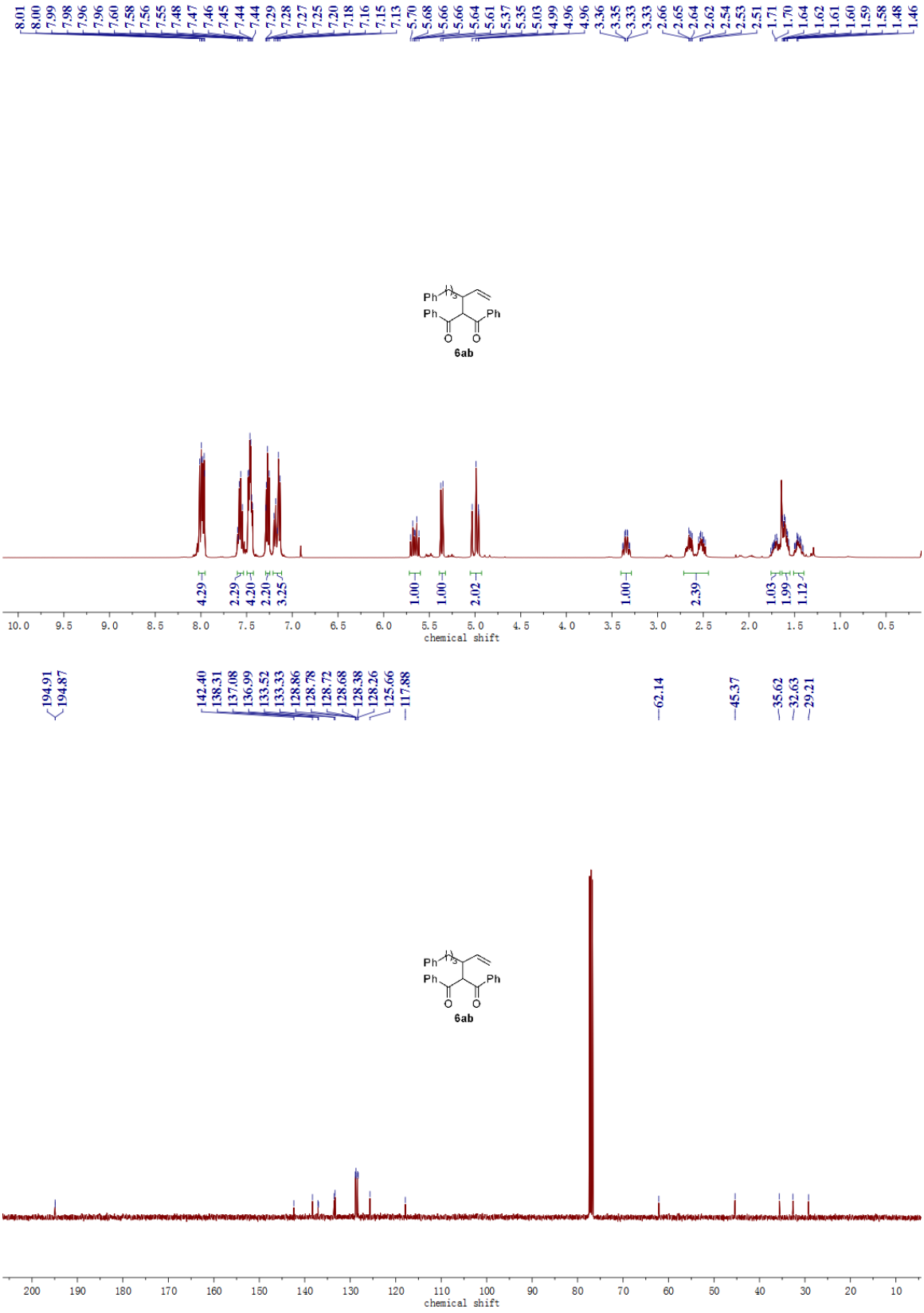
5-phenylpent-1-en-2-yl benzoate (**4ia**).



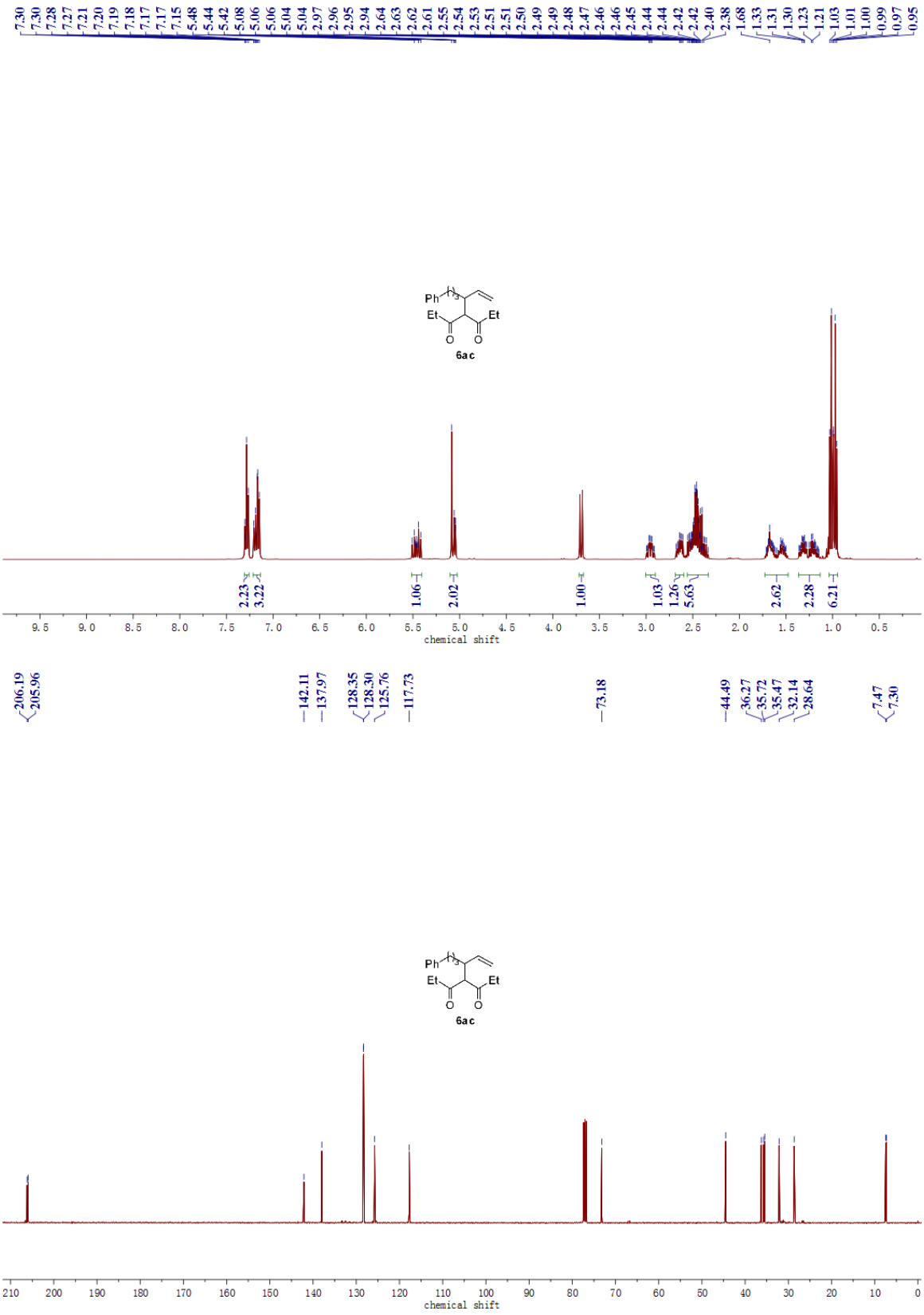
3-(6-phenylhex-1-en-3-yl)pentane-2,4-dione (**6aa**).



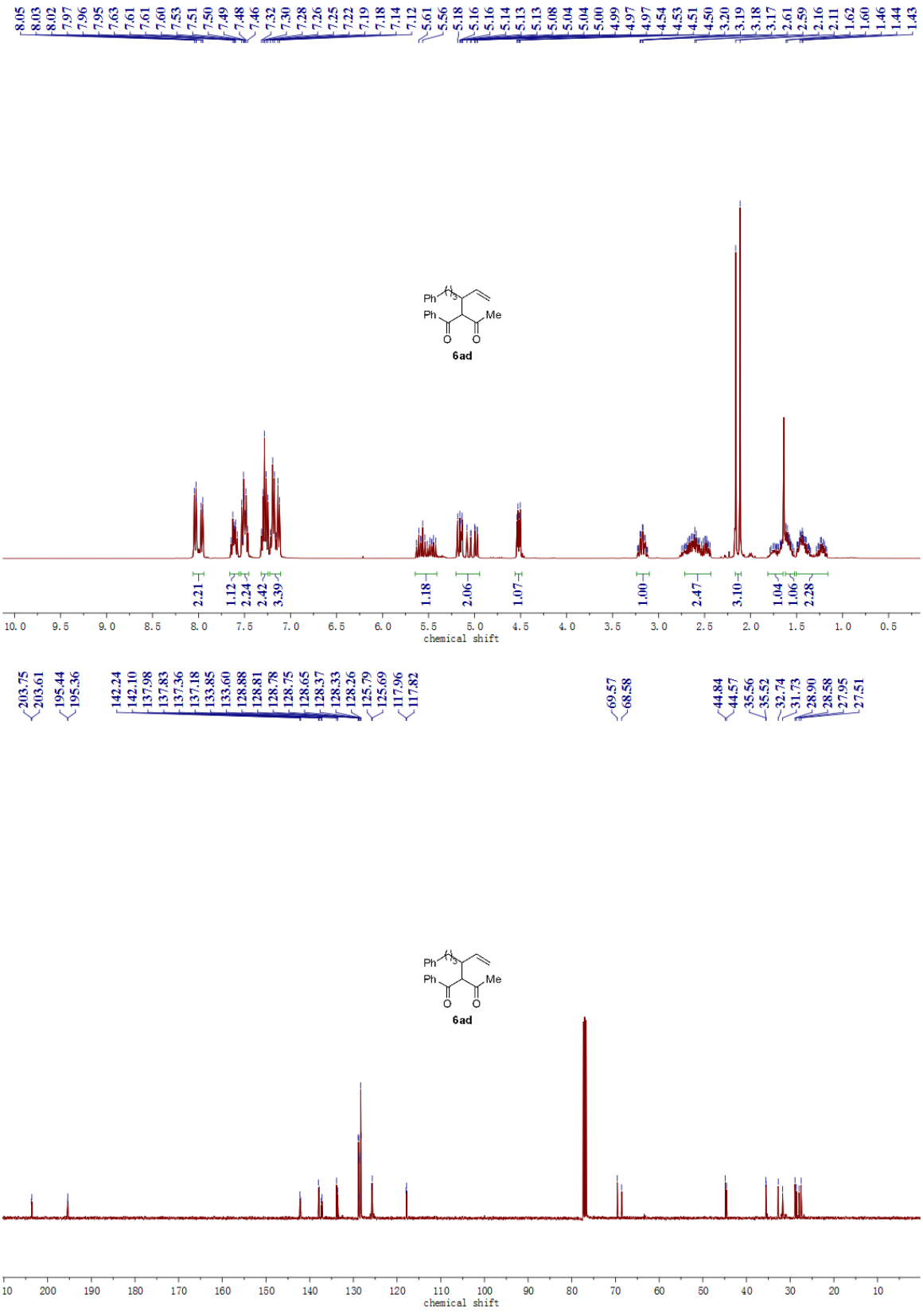
1,3-diphenyl-2-(6-phenylhex-1-en-3-yl)propane-1,3-dione (**6ab**)



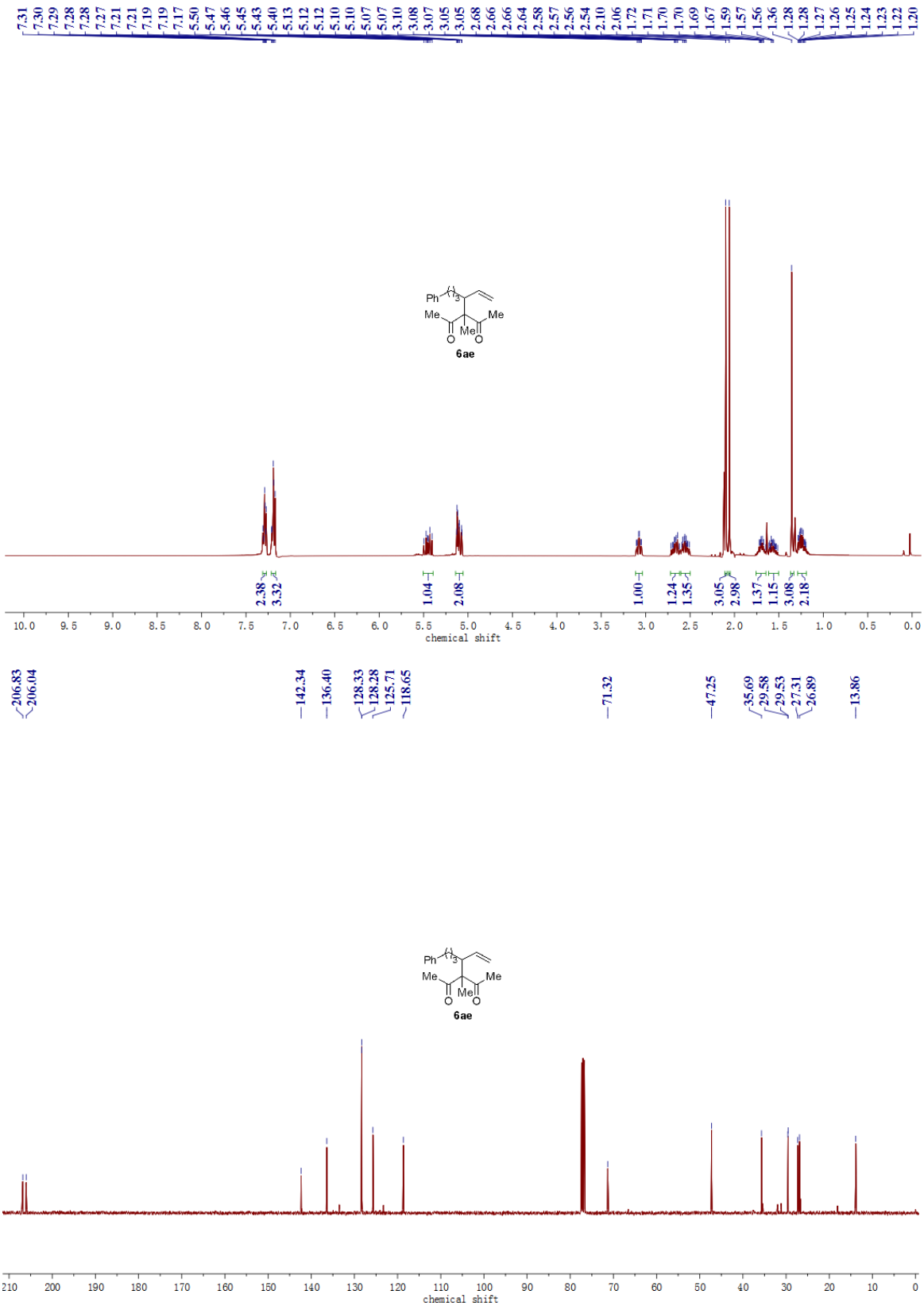
4-(6-phenylhex-1-en-3-yl)heptane-3,5-dione (**6ac**)



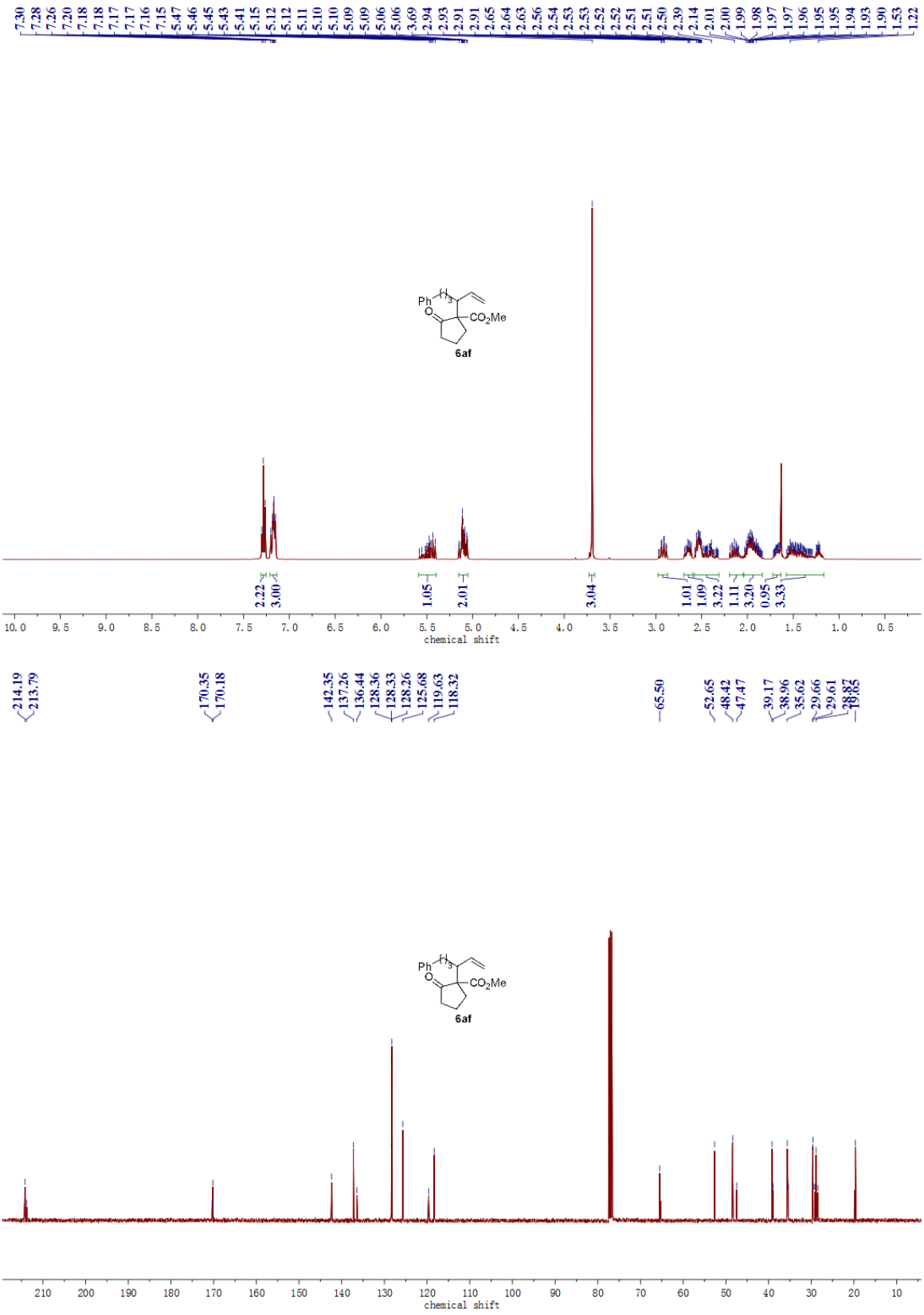
1-phenyl-2-(6-phenylhex-1-en-3-yl)butane-1,3-dione (**6ad**)



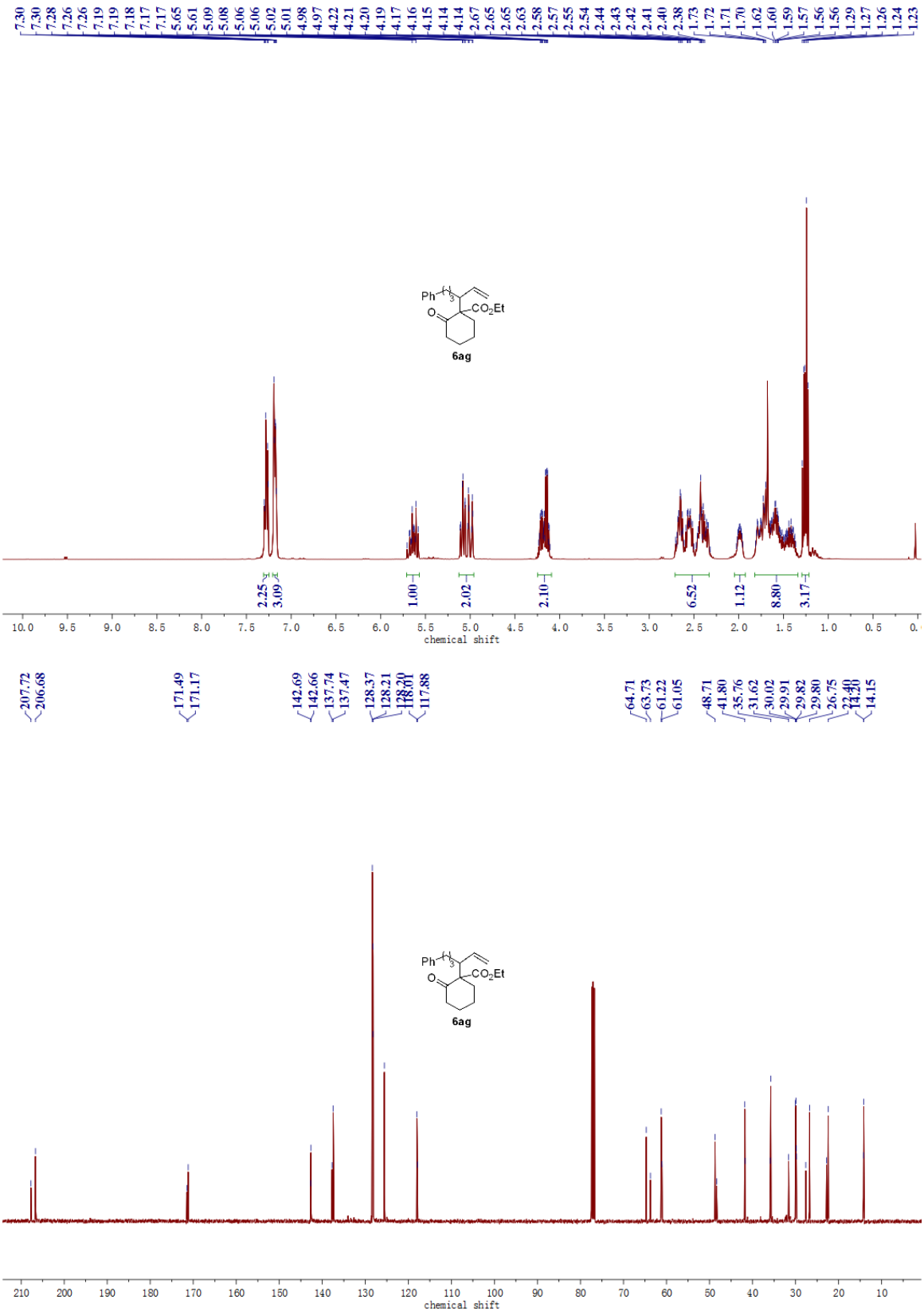
3-methyl-3-(6-phenylhex-1-en-3-yl)pentane-2,4-dione (**6ae**)



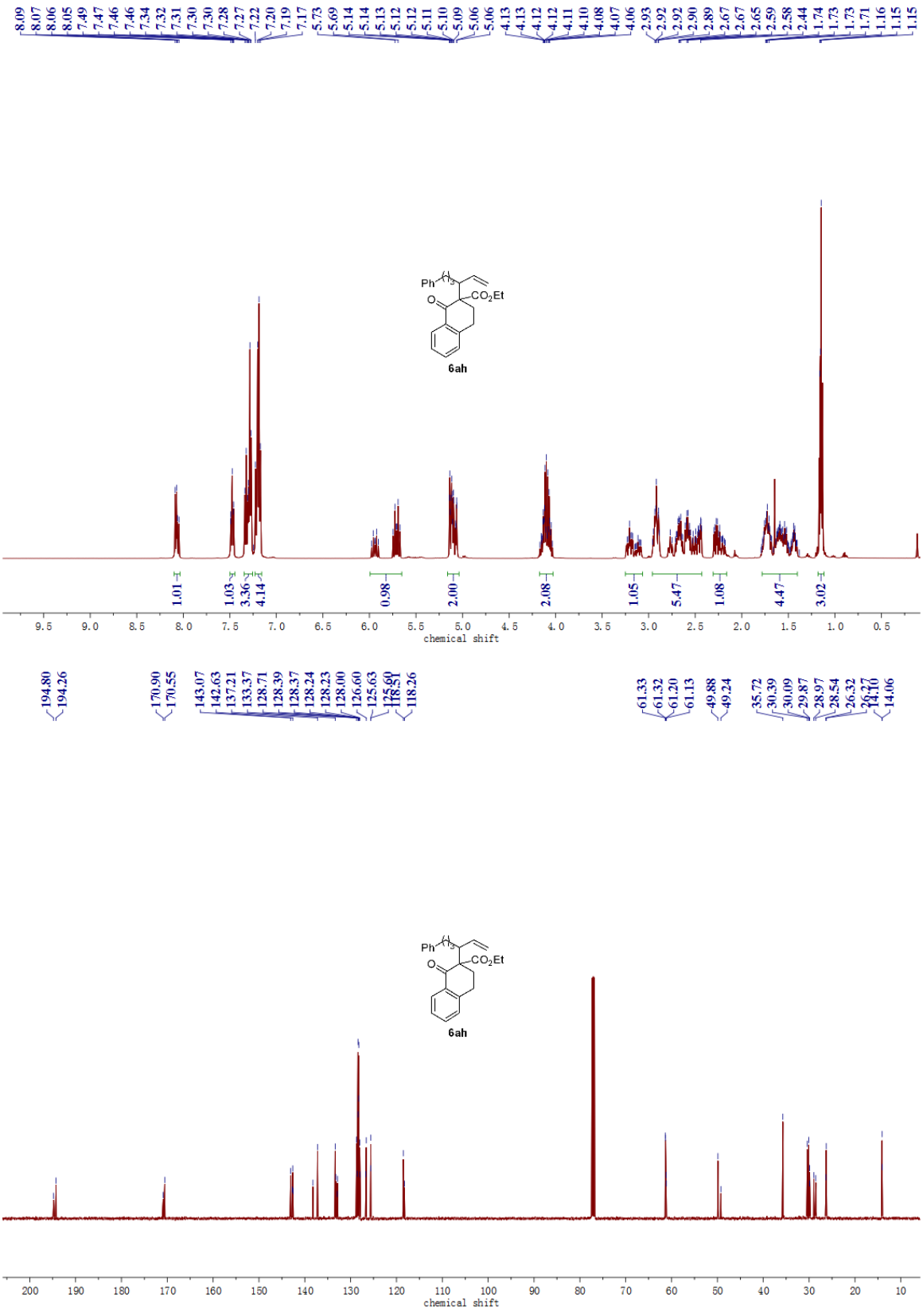
methyl 2-oxo-1-(6-phenylhex-1-en-3-yl)cyclopentanecarboxylate (**6af**).



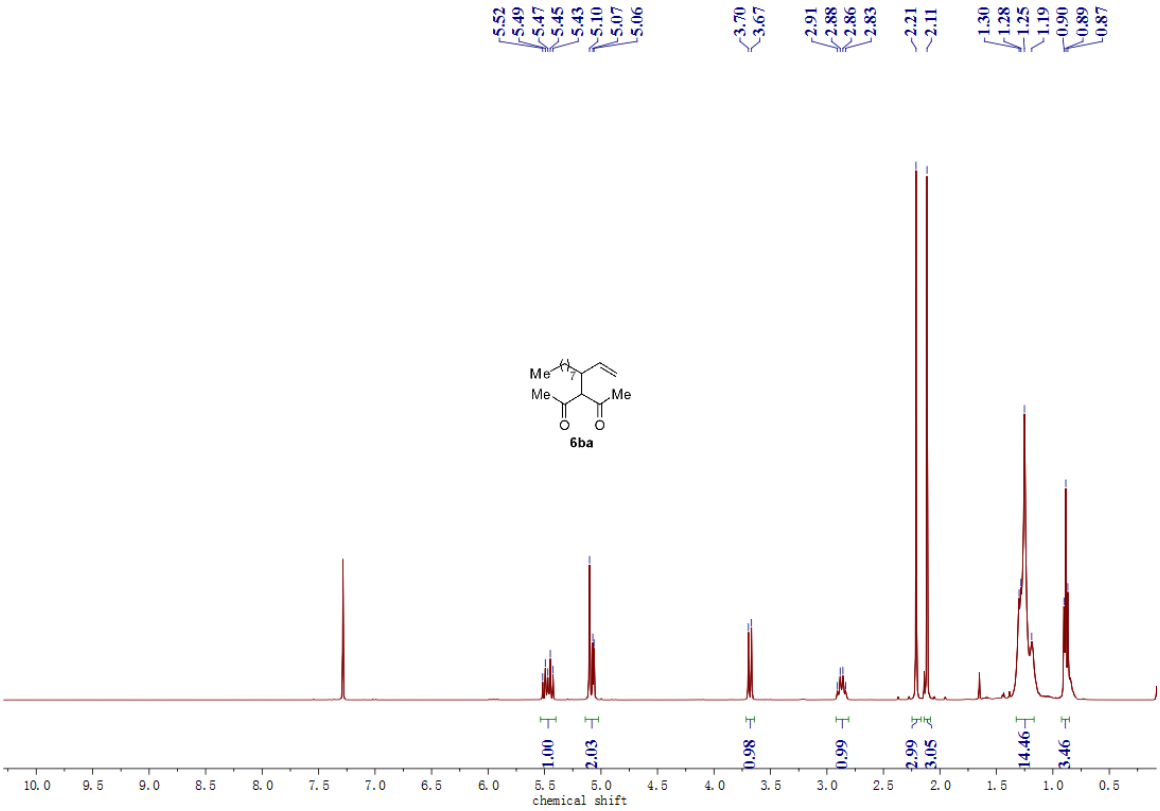
ethyl 2-oxo-1-(6-phenylhex-1-en-3-yl)cyclohexanecarboxylate (**6ag**).

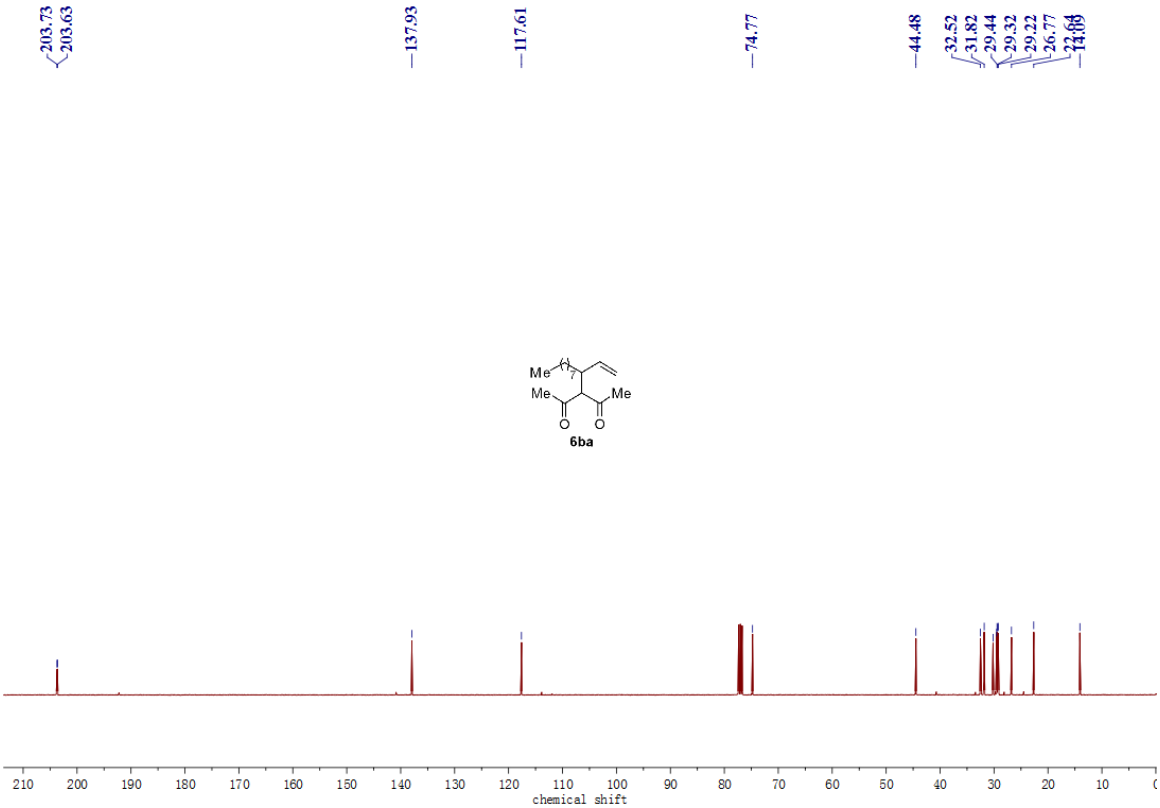


ethyl 2-oxo-1-(6-phenylhex-1-en-3-yl)cyclohexanecarboxylate (**6ah**).

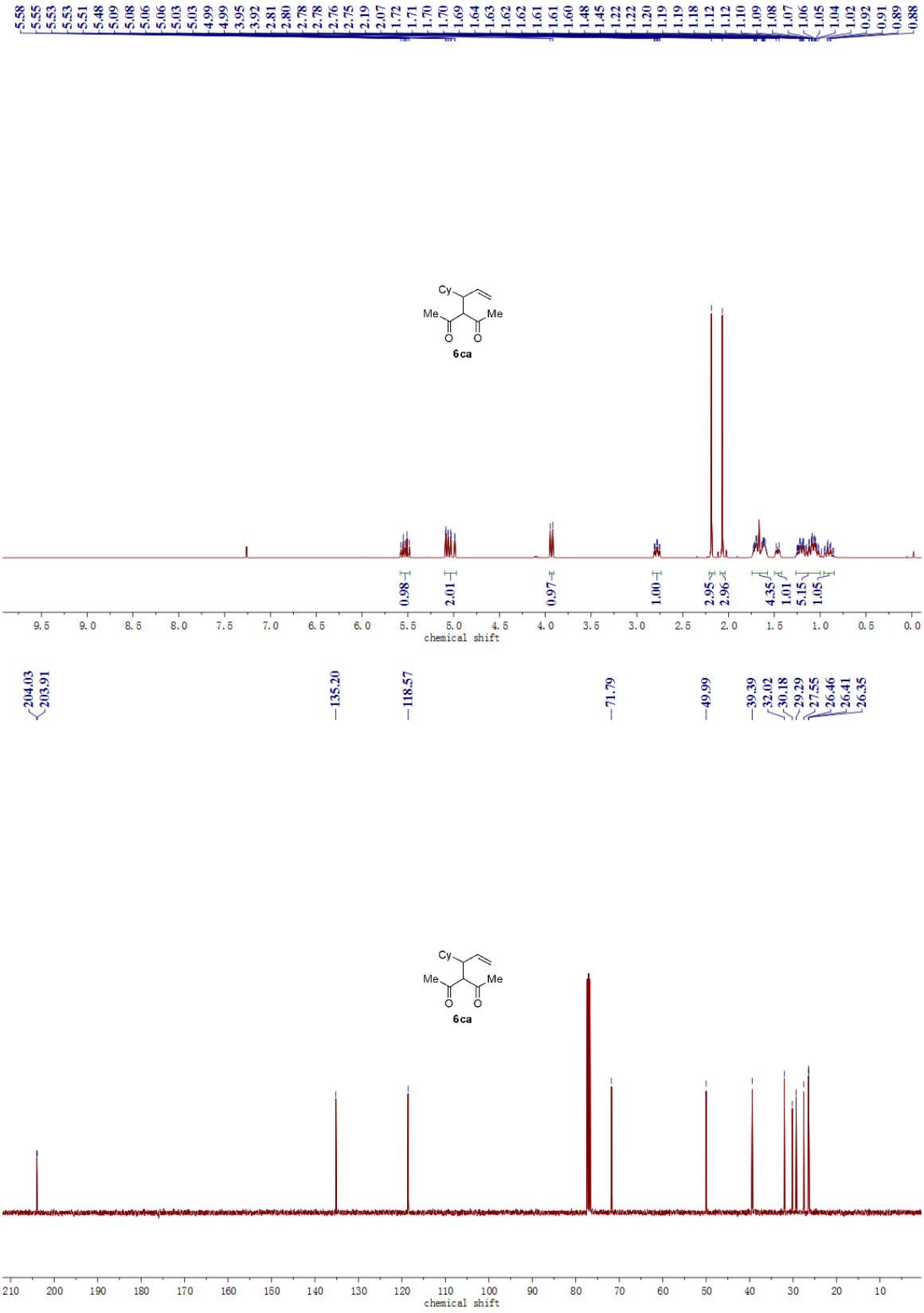


3-(undec-1-en-3-yl)pentane-2,4-dione (**6ba**).

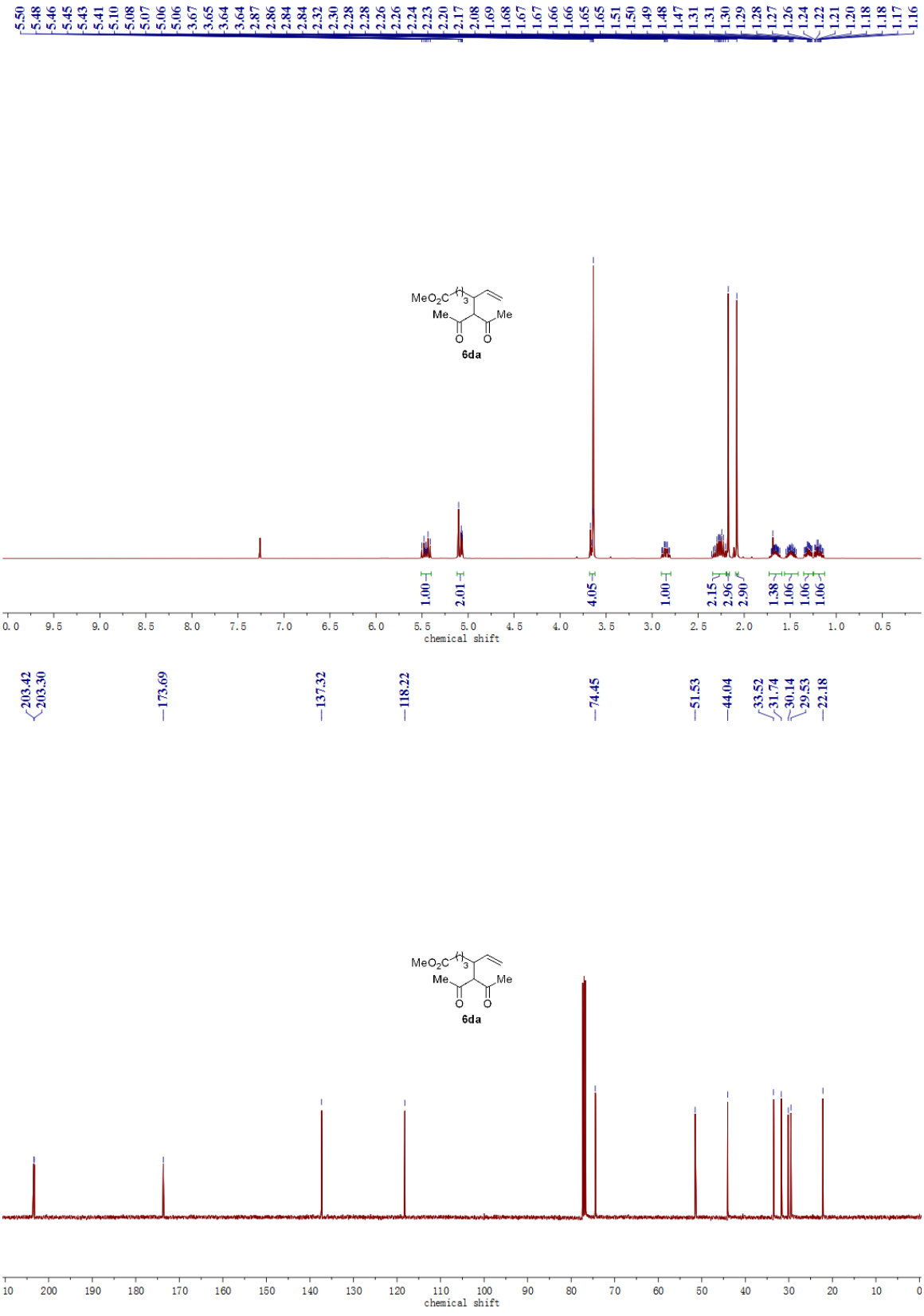




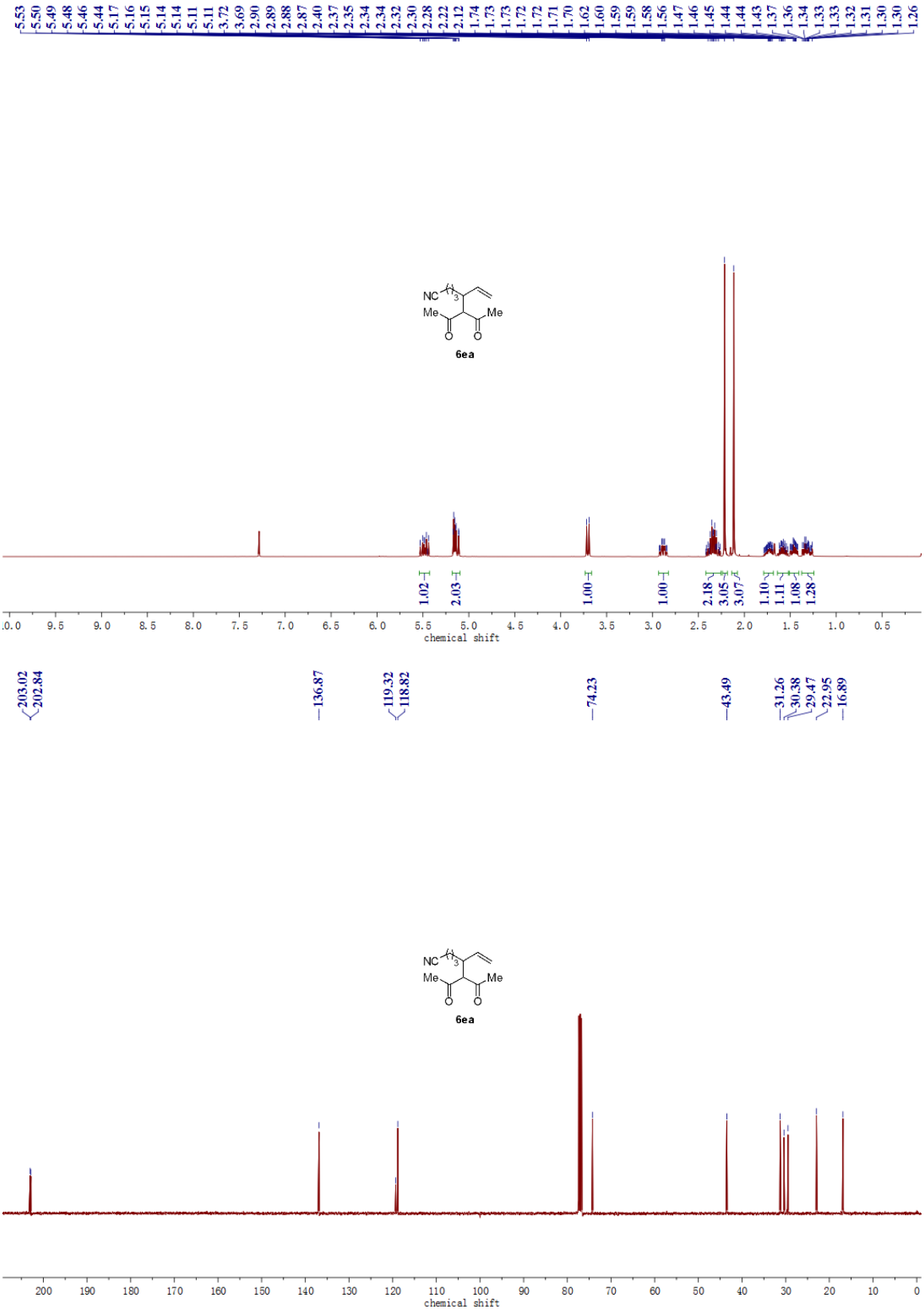
3-(1-cyclohexylallyl)pentane-2,4-dione (**6ca**).



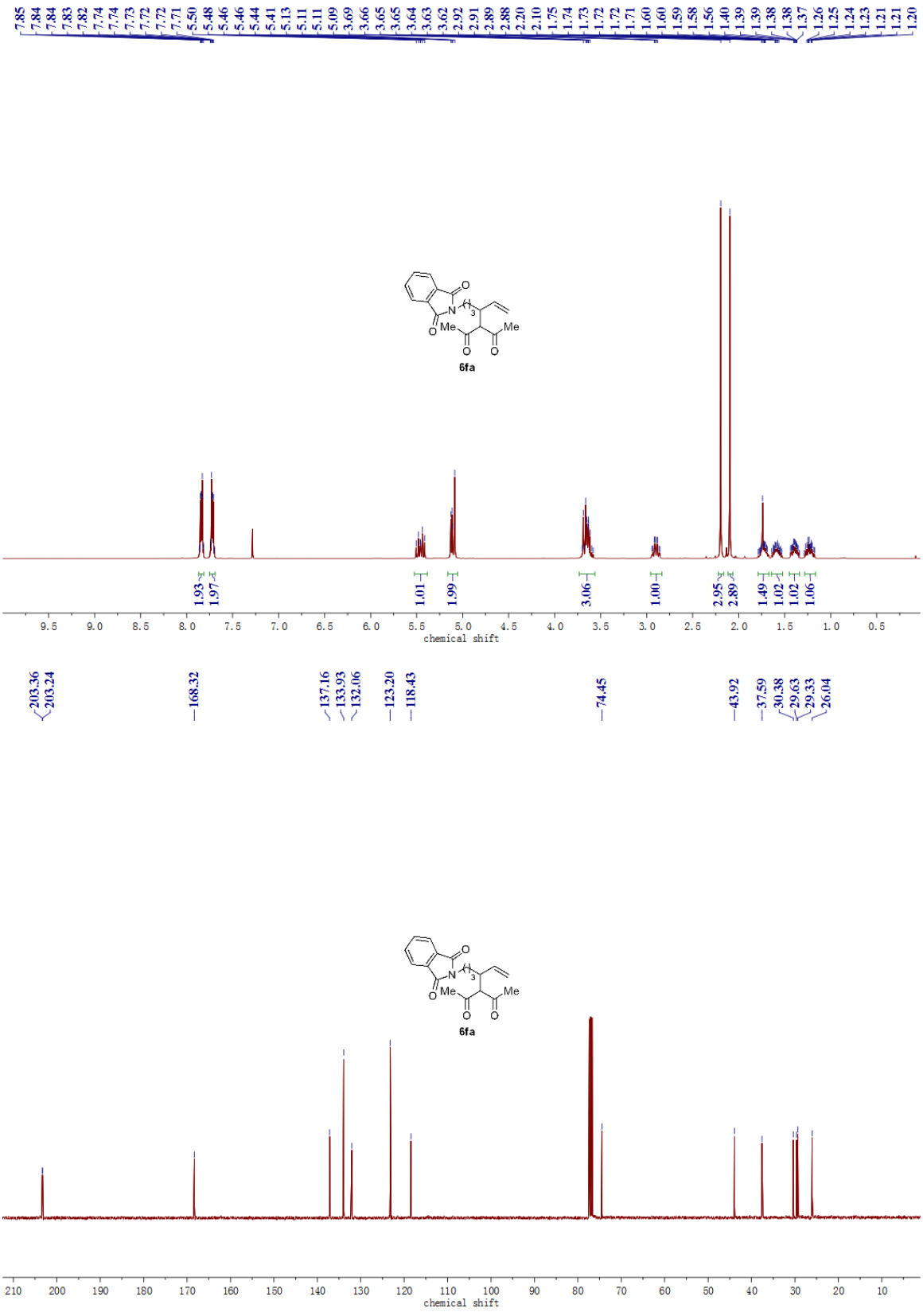
methyl 6-acetyl-7-oxo-5-vinyloctanoate (**6da**).



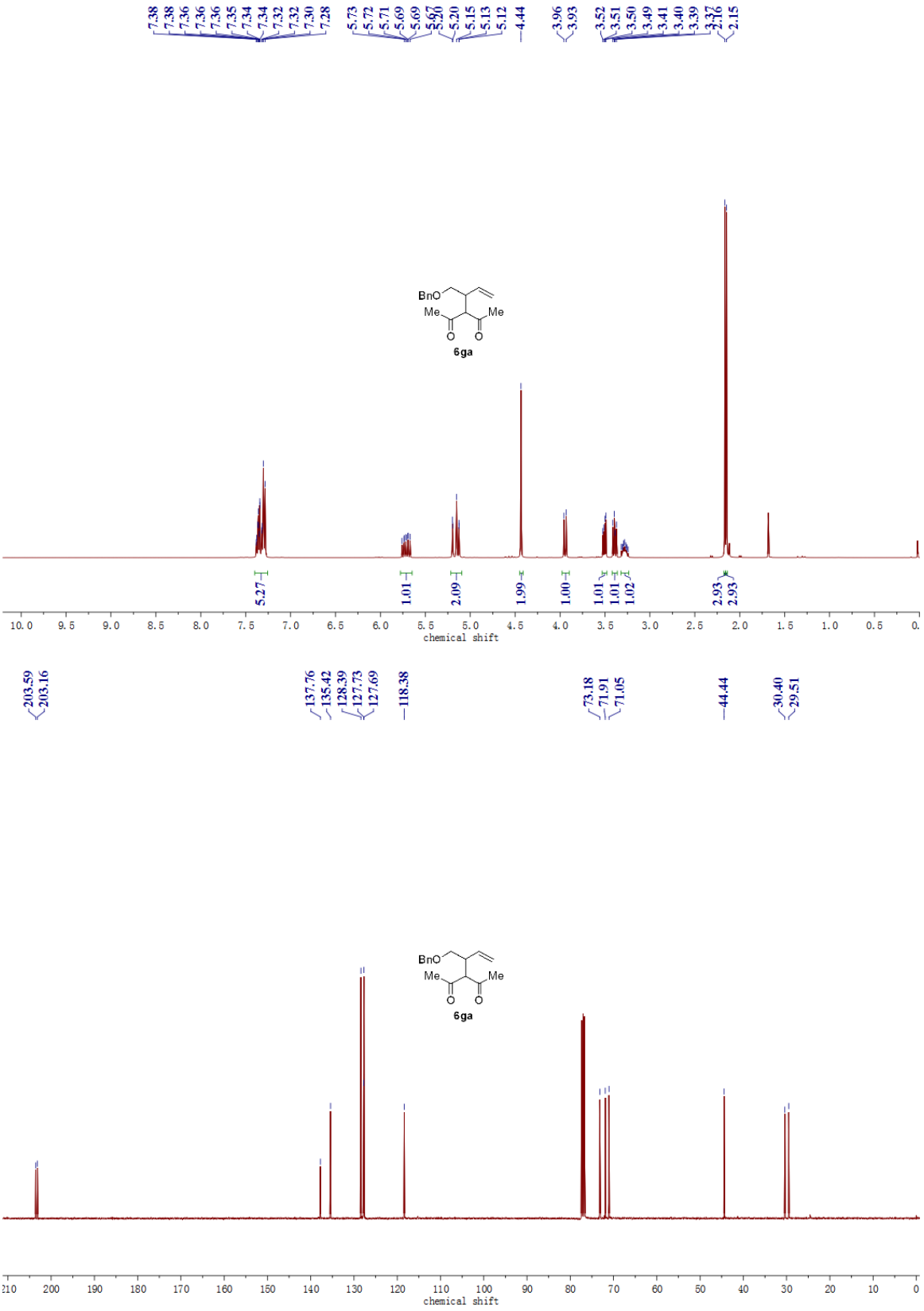
6-acetyl-7-oxo-5-vinyloctanenitrile (**6ea**).



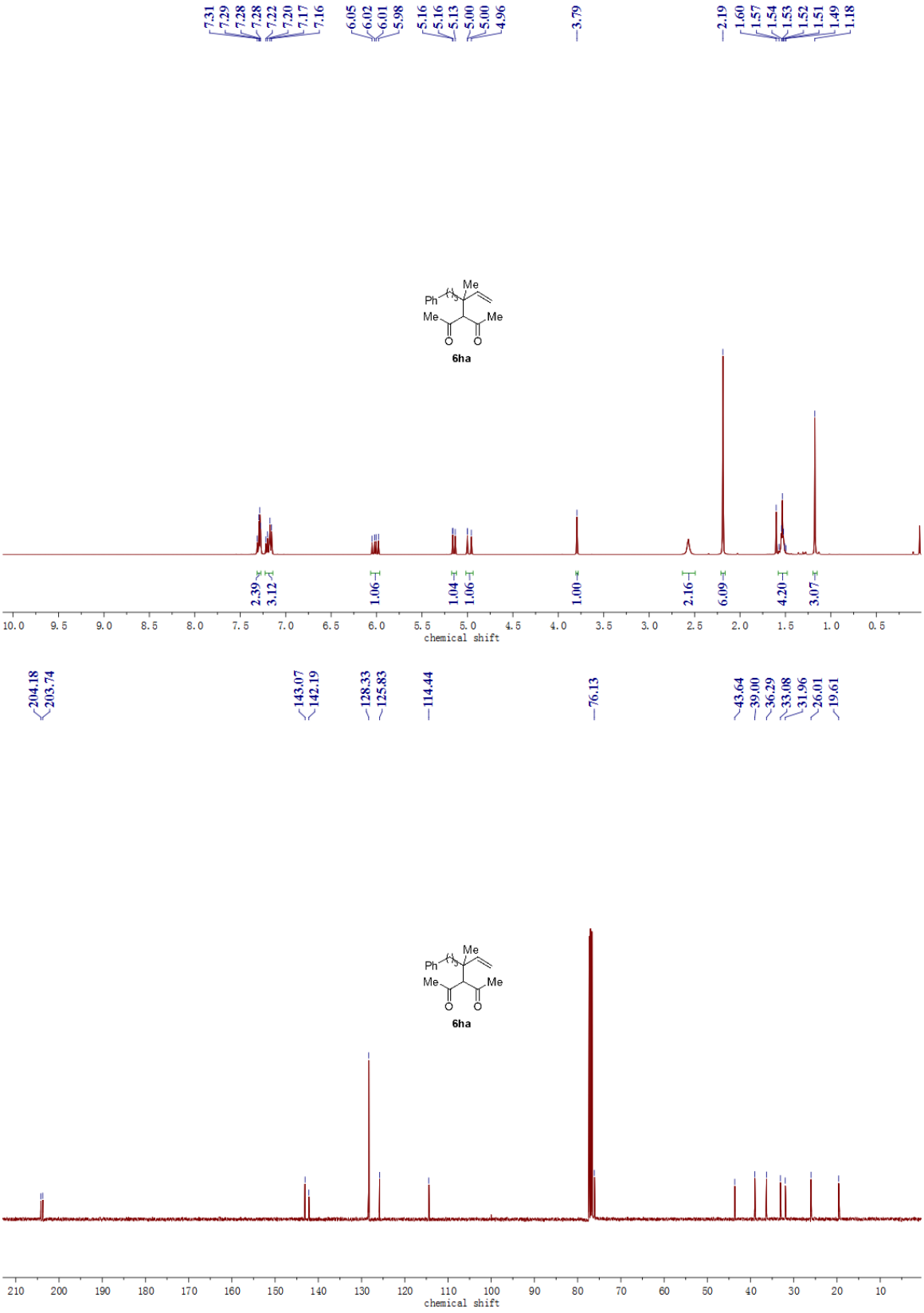
2-(5-acetyl-6-oxo-4-vinylheptyl)isoindoline-1,3-dione (**6fa**).



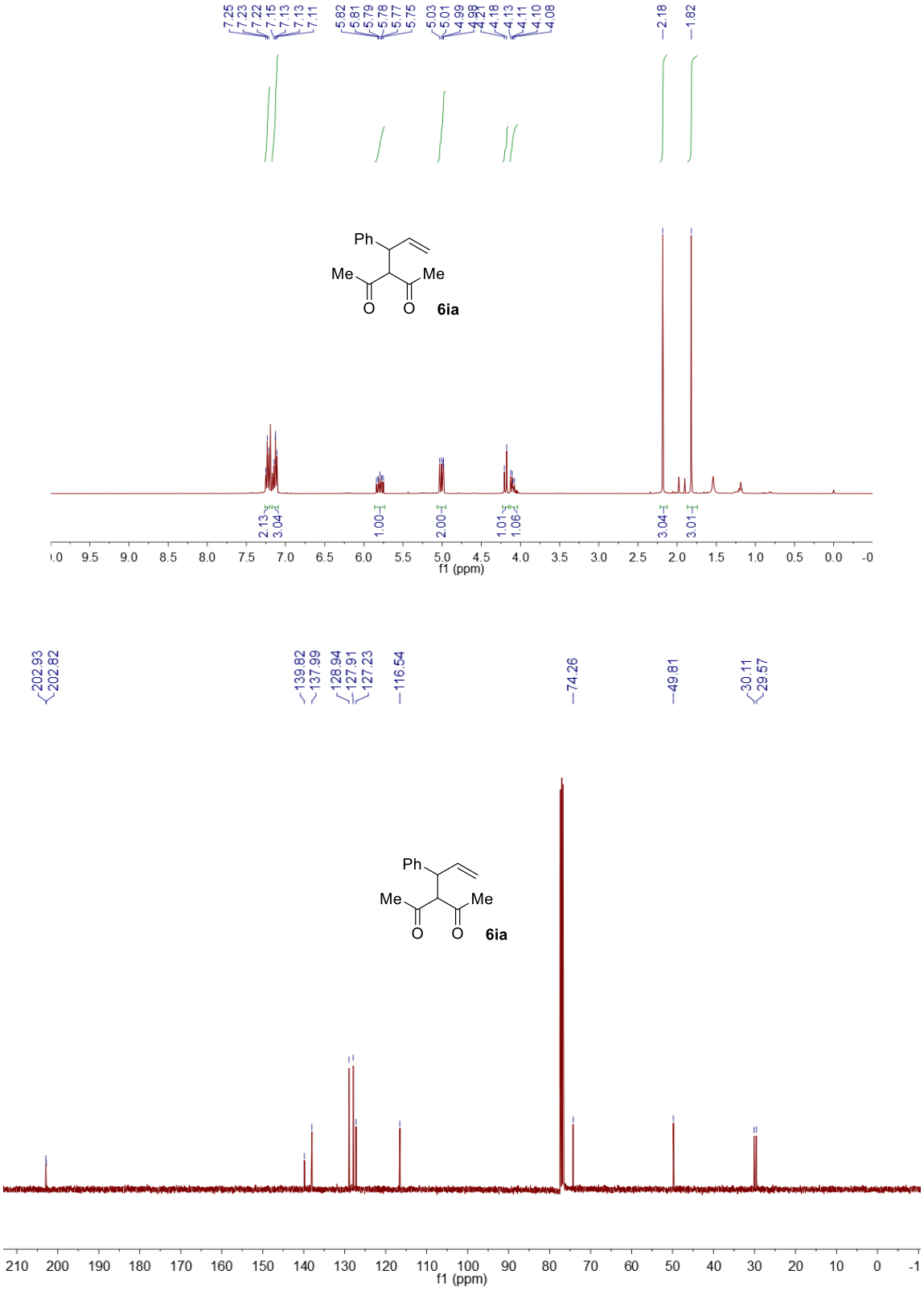
3-(1-(benzyloxy)but-3-en-2-yl)pentane-2,4-dione (**6ga**)



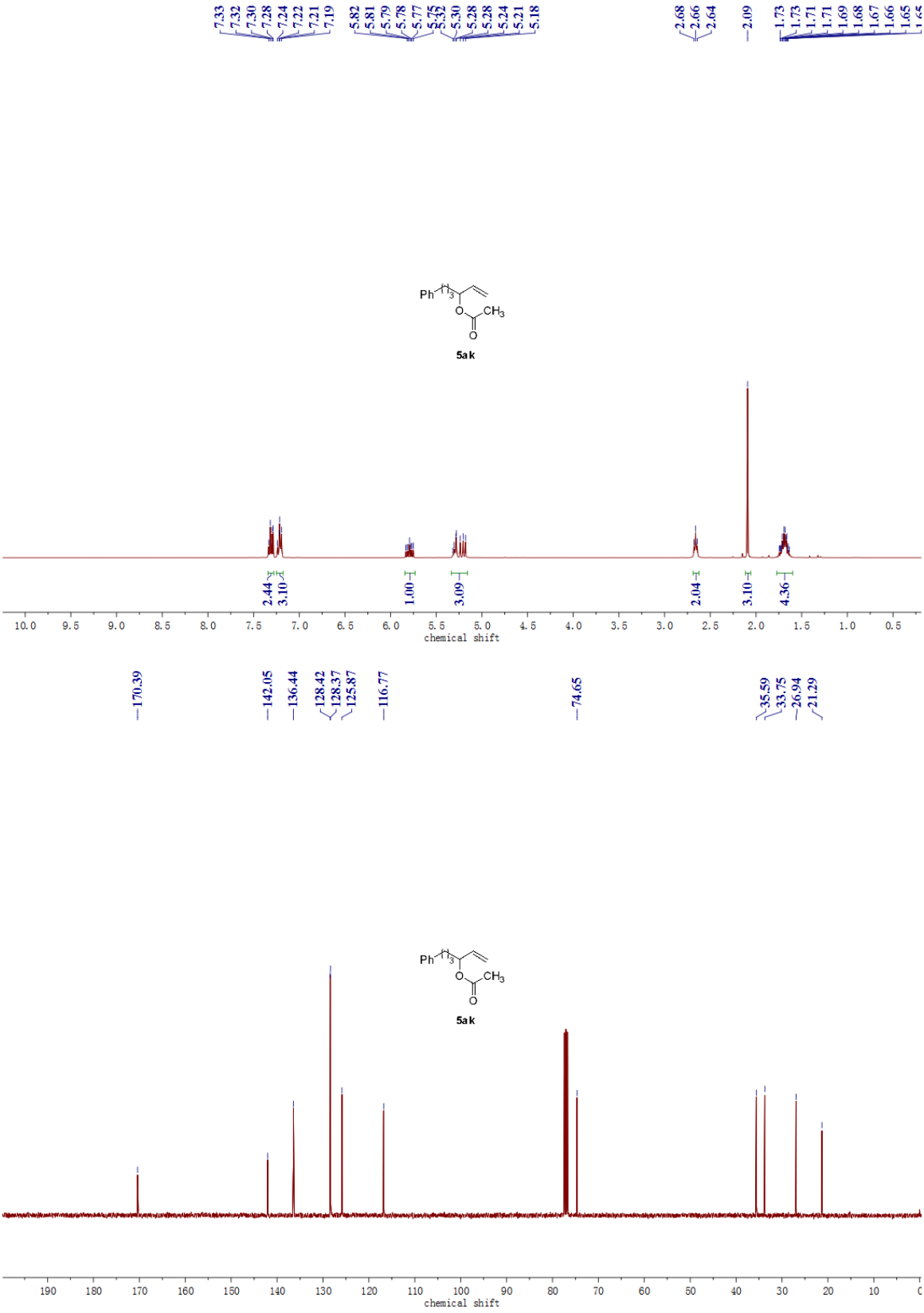
3-(3-methyl-6-phenylhex-1-en-3-yl)pentane-2,4-dione (**6ha**).



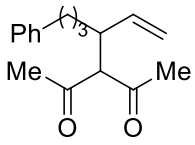
3-(1-Phenylallyl)pentane-2,4-dione (**6ia**)



6-phenylhex-1-en-3-yl acetate (**5ak**).



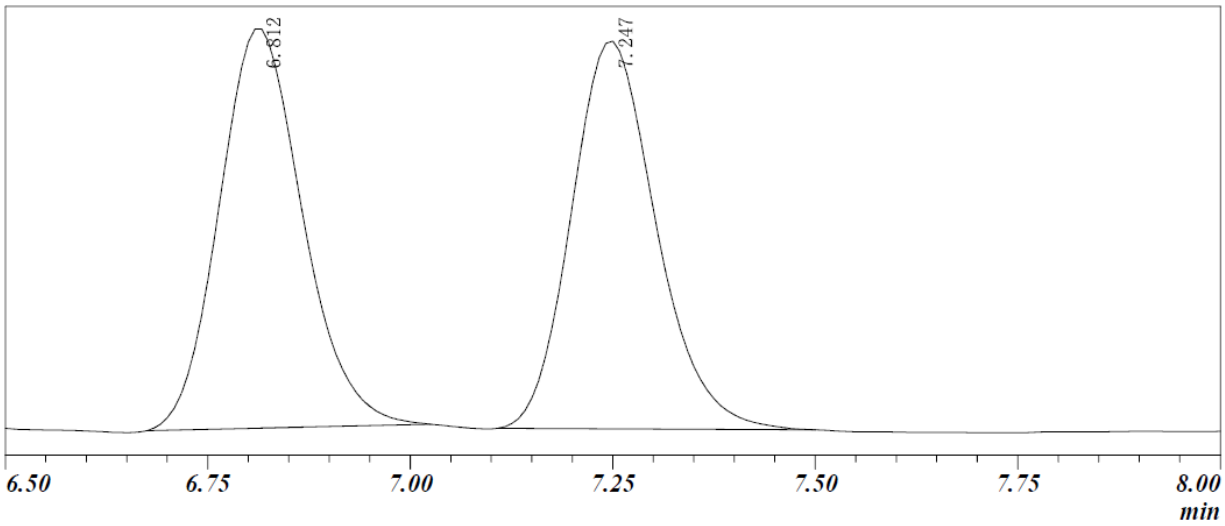
11. HPLC Results



racemic

6aa

Analysis condition: Chiralpak AD-H column (99 : 1 n-hexane : i-PrOH, 1 mL/min, 254 nm, 40 °C); t_r (1) = 6.8 min, t_r (2) = 7.2 min.

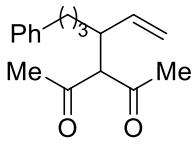


PEAK TABLE

<峰表>

检测器A Ch1 254nm

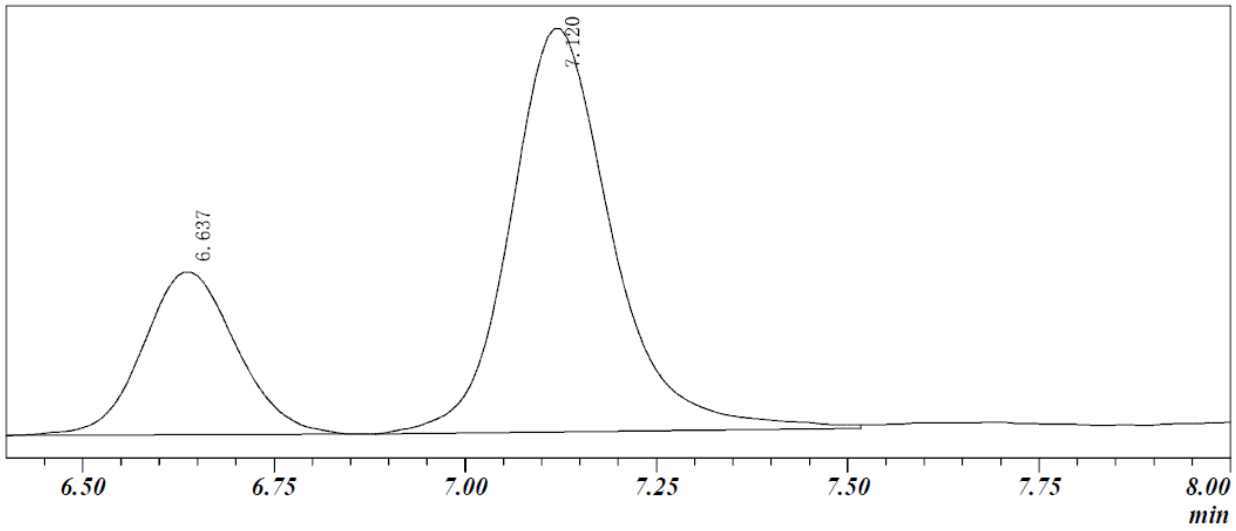
Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*6.812*	*81397*	*50.348*	*11346*	*50.734*
2	*7.247*	*80273*	*49.652*	*11017*	*49.266*



with **L7**

6aa

Analysis condition: Chiralpak AD-H column (99 : 1 n-hexane : i-PrOH, 1 mL/min, 254 nm, 40 °C); t_r (minor) = 6.6 min, t_r (major) = 7.1 min, 46 % *ee*.

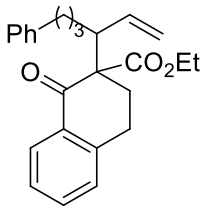


PEAK TABLE

<峰表>

检测器A Ch1 254nm

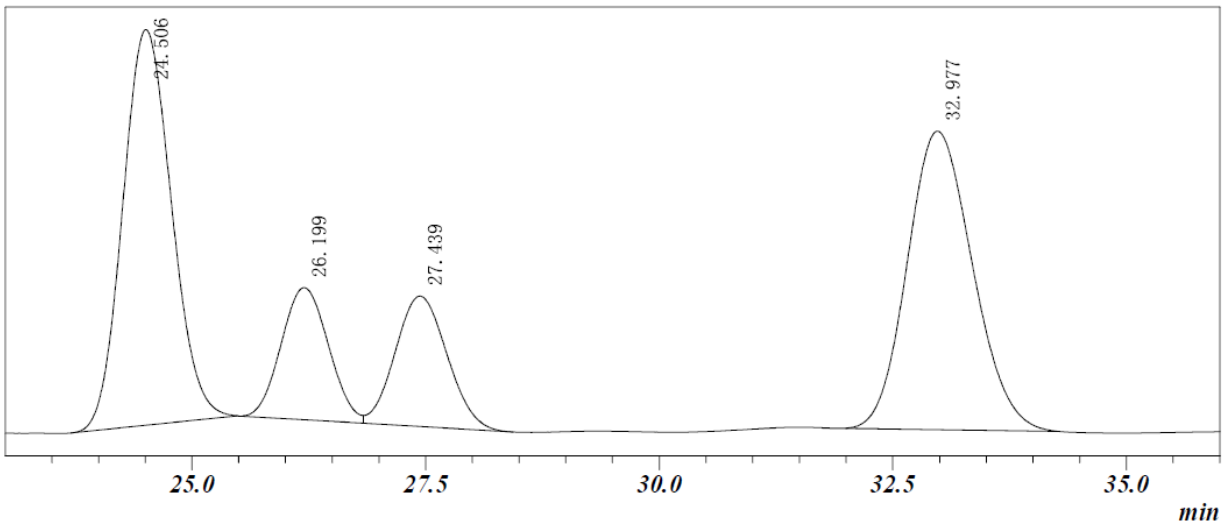
Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*6.637*	*11916*	*27.119*	*1398*	*28.758*
2	*7.120*	*32024*	*72.881*	*3464*	*71.242*



racemic

6ah

Analysis condition: Chiralpak IC column (99.5 : 0.5 n-hexane : i-PrOH, 0.5 mL/min, 254 nm, 40 °C); t_r (1) = 24.5 min, t_r (2) = 26.2 min, t_r (2') = 27.4 min, t_r (1') = 33.0 min.

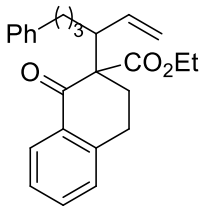


PEAK TABLE

<峰表>

检测器A Ch1 254nm

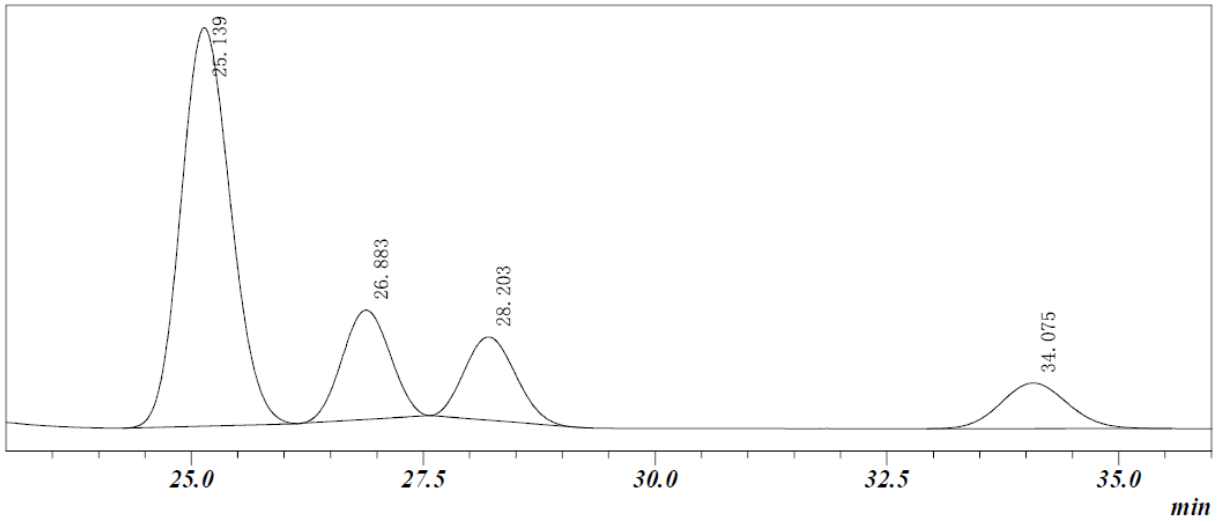
Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*24.506*	*3018194*	*37.270*	*83150*	*41.357*
2	*26.199*	*977912*	*12.076*	*27769*	*13.812*
3	*27.439*	*1057033*	*13.053*	*27413*	*13.634*
4	*32.977*	*3044993*	*37.601*	*62724*	*31.197*



with **L8**

6ah

Analysis condition: Chiralpak IC column (99.5 : 0.5 n-hexane : i-PrOH, 0.5 mL/min, 254 nm, 40 °C); t_r (1 major) = 25.1 min, t_r (2 major) = 26.8 min, t_r (2' minor) = 28.2 min, t_r (1' minor) = 34.1 min, major: 73 % *ee*, minor: 11 % *ee*.



PEAK TABLE

<峰表>

检测器A Ch1 254nm

Peak NO.	*Retention time*	*Area*	*Area%*	*Height*	*Height%*
1	*25.139*	*3043110*	*61.093*	*81468*	*62.559*
2	*26.883*	*808842*	*16.238*	*22382*	*17.187*
3	*28.203*	*653658*	*13.123*	*17030*	*13.078*
4	*34.075*	*475508*	*9.546*	*9345*	*7.176*