

Supporting Information

Enantioselective Meerwein-Ponndorf-Verley Reduction of β,γ - Unsaturated α -Keto Esters by Asymmetric Binary-Acid Catalysis in Green Solvent *i*PrOH

Huixin Qiu,^a Jiayi Ren,^a Long Zhang,^{*b} Ran Song,^a Wen Si,^a Daoshan Yang,^a Lirong Wen,^{*a} and Jian Lv^{*a}

^a Key Laboratory of Optic-electric Sensing and Analytic Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao 266042 (China), E-mail: lvjian@iccas.ac.cn (J. Lv); wenlirong@qust.edu.cn (L. Wen).

^b Center of Basic Molecular Science, Department of Chemistry, Tsinghua University, Beijing 100084 (China), E-mail: zhanglong@tsinghua.edu.cn (L. Zhang).

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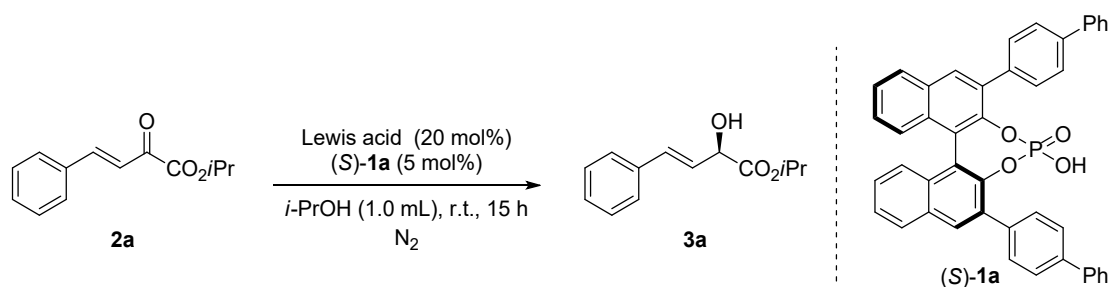
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I. General Experiment Information and Materials

All commercial reagents were used without further purification unless otherwise noted. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a Bruker Avance 400 and 500MHz spectrometer. Tetramethylsilane (TMS) served as the internal standard for ^1H NMR, and CDCl_3 served as the internal standard for ^{13}C NMR. ^1H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet is10. The X-ray single-crystal diffraction was performed on Saturn 724+ instrument. High resolution mass spectra were obtained on an Ultima Global spectrometer with an ESI source.

II. Optimization

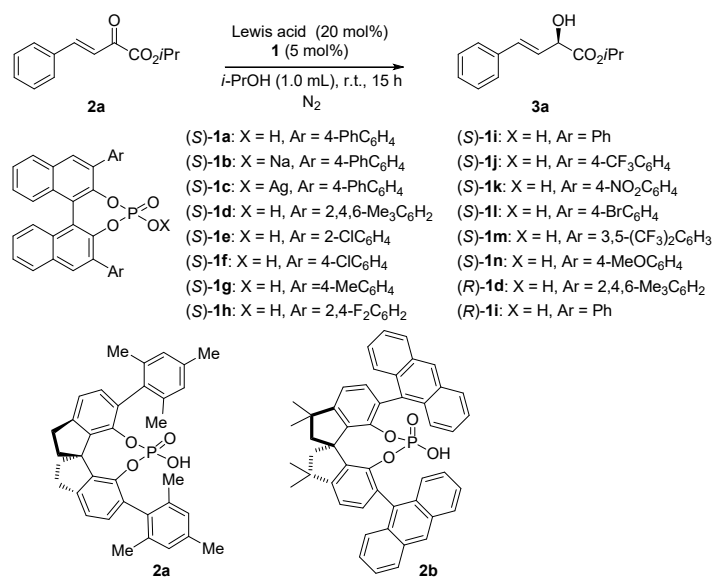
Table S1. Screening of different Lewis acids in MPV reaction of **2a**^a



Entry	Lewis acid	Yield (%) ^b	ee (%) ^c
1	HfCl ₄	95	24
2	ScBr ₃	75	59
3	Ni(OTf) ₂	NR	—
4	FeCl ₃	NR	—
5	Cu(OTf) ₂	NR	—
6	InBr ₃	NR	—
7	FeBr ₃	NR	—
8	Bi(OAc) ₃	NR	—
9	Zn(OTf) ₂	trace	—
10	Hf(OTf) ₄	NR	—
11	InCl	trace	—
12	In(OAc) ₃	NR	—
13	InI ₃	trace	—
14	CuBr ₂	NR	—
15	CuBr	NR	—
16	Zn(OAc) ₂	NR	—
17	In(OTf) ₃	trace	—
18	Sc(OTf) ₃	97	91
19	Mg(OTf) ₂	NR	—
20	InCl ₃	NR	—
21	Bi(OTf) ₃	NR	—
22 ^d	Sc(OTf) ₃	98	90

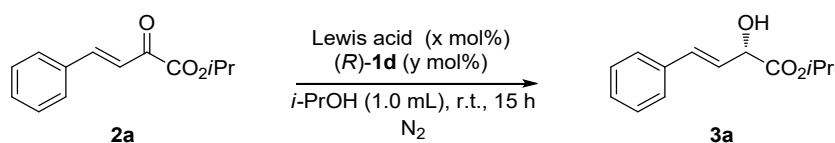
^a Reaction conditions: **2a** (0.1 mmol) and Lewis acid (20 mol %), (*S*)-**1a** (5 mol%) in *i*-PrOH (1.0 mL) under N₂ at room temperature for 15 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase. ^d At 50 °C for 8 h. NR = No Reaction.

Table S2. Screening of different chiral ligands in MPV reaction of **2a** ^a



Entry	Lewis acid	Ligands	Yield (%) ^b	ee (%) ^c
1	Sc(OTf) ₃	(S)- 1a	97	91
2	Sc(OTf) ₃	(S)- 1b	83	82
3	Sc(OTf) ₃	(S)- 1c	97	84
4	Sc(OTf) ₃	(S)- 1d	96	93
5	Sc(OTf) ₃	(S)- 1e	97	92
6	Sc(OTf) ₃	(S)- 1f	84	56
7	Sc(OTf) ₃	(S)- 1g	95	58
8	Sc(OTf) ₃	(S)- 1h	96	78
9	Sc(OTf) ₃	(S)- 1i	96	88
10	Sc(OTf) ₃	(S)- 1j	98	84
11	Sc(OTf) ₃	(S)- 1k	88	64
12	Sc(OTf) ₃	(S)- 1l	97	88
13	Sc(OTf) ₃	(S)- 1m	90	Racemic
14	Sc(OTf) ₃	(S)- 1o	88	84
15	Sc(OTf) ₃	(R)- 1d	98	96 (S)
16	Sc(OTf) ₃	(R)- 1i	95	88 (S)
17	Sc(OTf) ₃	2a	99	94
18	Sc(OTf) ₃ =	2b	98	90

^a Reaction conditions: **2a** (0.1 mmol) and Lewis acid (20 mol %), **1** (5 mol%) in *i*-PrOH (1.0 mL) under N₂ at room temperature for 15 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase.

Table S3. Screening of different ratio of binary acid in MPV reaction of **2a** ^a

Entry	x	y	Yield (%) ^b	ee (%) ^c
1	20	5	98	96
2	15	5	98	94
3	10	5	97	96
4	5	5	97	98
5	20	1	98	94
6	15	1	99	94
7	10	1	98	96
8 ^d	5	1	98	98
9 ^d	5	0.5	85	96
10 ^d	3	1	98	98
11 ^d	1	1	89	98
12 ^d	3	0.5	99	98
13 ^d	1	0.5	88	98
14 ^e	0.5	0.5	90	98
15 ^e	0.5	0.2	88	98
16 ^e	0.5	0.1	86	96

^a Reaction conditions: **2a** (0.1 mmol) and Lewis acid (20 mol %), **1** (5 mol%) in *i*-PrOH (1.0 mL) under N₂ at room temperature for 15 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase. ^d **2a** (0.2 mmol) in *i*-PrOH (2.0 mL). ^e **2a** (0.5 mmol) in *i*-PrOH (5.0 mL).

Table S4. Screening of different chiral ligands in MPV reaction of **14a**^a

14a Lewis acid (20 mol%)
1 (5 mol%)
 $\xrightarrow{i\text{-PrOH (1.0 mL), r.t., 15 h}$
 N_2}

15a

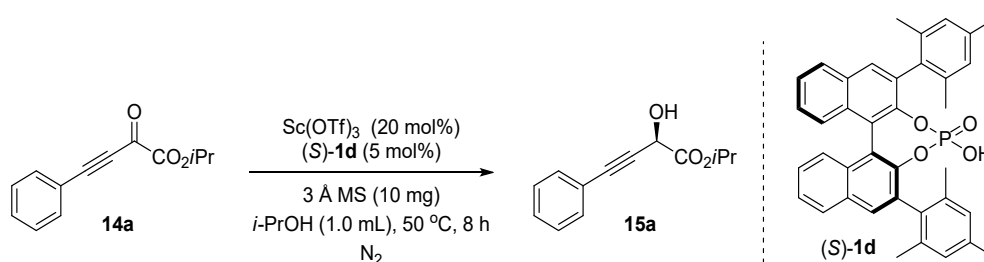
(S)-**1a**: X = H, Ar = 4-PhC₆H₄
 (S)-**1b**: X = Na, Ar = 4-PhC₆H₄
 (S)-**1c**: X = Ag, Ar = 4-PhC₆H₄
 (S)-**1d**: X = H, Ar = 2,4,6-Me₃C₆H₂
 (S)-**1e**: X = H, Ar = 2-ClC₆H₄
 (S)-**1f**: X = H, Ar = 4-ClC₆H₄
 (S)-**1g**: X = H, Ar = 4-MeC₆H₄

(S)-**1h**: X = H, Ar = 2,4-F₂C₆H₂
 (S)-**1i**: X = H, Ar = Ph
 (S)-**1j**: X = H, Ar = 4-CF₃C₆H₄
 (S)-**1k**: X = H, Ar = 4-NO₂C₆H₄
 (S)-**1l**: X = H, Ar = 4-BrC₆H₄
 (S)-**1m**: X = H, Ar = 3,5-(CF₃)₂C₆H₃
 (S)-**1n**: X = H, Ar = 4-MeOC₆H₄

entry	Lewis acid	Ligands	Yield (%) ^b	ee (%) ^c
1	Sc(OTf) ₃	(S)- 1a	36	Racemic
2	Sc(OTf) ₃	(S)- 1b	22	racemic
3	Sc(OTf) ₃	(S)- 1c	24	2
4	Sc(OTf) ₃	(S)- 1d	67	58
5	Sc(OTf) ₃	(S)- 1e	21	Racemic
6	Sc(OTf) ₃	(S)- 1f	21	Racemic
7	Sc(OTf) ₃	(S)- 1g	33	Racemic
8	Sc(OTf) ₃	(S)- 1h	47	2
9	Sc(OTf) ₃	(S)- 1i	36	Racemic
10	Sc(OTf) ₃	(S)- 1j	35	2
11	Sc(OTf) ₃	(S)- 1k	37	2
12	Sc(OTf) ₃	(S)- 1l	48	Racemic
13	Sc(OTf) ₃	(S)- 1m	36	6
14	Sc(OTf) ₃	(S)- 1n	33	racemic
15 ^d	Sc(OTf) ₃	(S)- 1d	89	88
16 ^e	Sc(OTf) ₃	(S)- 1d	34	12
17 ^f	Sc(OTf) ₃	(S)- 1d	76	78

^a Reaction conditions: **14a** (0.1 mmol) and Sc(OTf)₃ (20 mol %), **1** (5 mol%) in *i*-PrOH (1.0 mL) under N₂ at 50 °C for 8 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase. ^d 3 Å MS (10 mg). ^e 4 Å MS (10 mg). ^f 5 Å MS (10 mg).

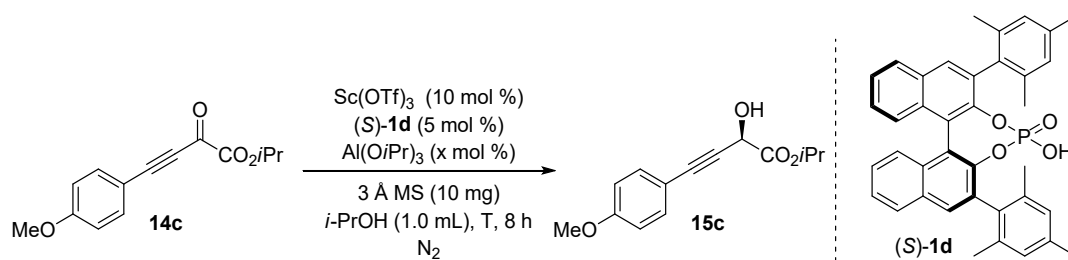
Table S5. Screening of different ratio of binary acid in MPV reaction of **14a**^a



Entry	x	y	Yield (%) ^b	ee (%) ^c
1	20	5	89	88
2	20	10	87	88
3	10	10	92	90
4	10	5	90	92
5	5	5	93	90

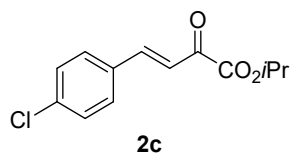
^a Reaction conditions: **14a** (0.1 mmol), $\text{Sc}(\text{OTf})_3$ (x mol %), **(S)-1d** (y mol%), and 3 Å MS (10 mg) in *i*-PrOH (1.0 mL) under N_2 at 50 °C for 8 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase. nr = no reaction.

Table S6. Screening of different amount of Al(O*i*Pr)₃ as additive in MPV reaction of **14f**^a

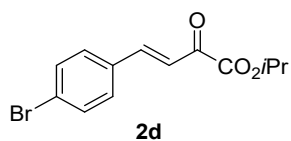


Entry	x	T (°C)	Yield (%) ^b	ee (%) ^c
1	20	50	95	90
2	10	50	94	86
3	5	50	90	86
4 ^d	20	rt	90	92
5 ^d	20	0	94	95
6 ^d	20	-20	90	92

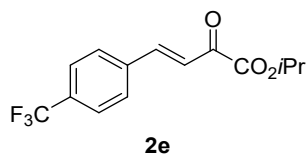
^a Reaction conditions: **14f** (0.1 mmol), Sc(OTf)₃ (10 mol %), (S)-**1d** (5 mol %), Al(O*i*Pr)₃ (x mol %), and 3 Å MS (10 mg) in *i*-PrOH (1.0 mL) under N₂ at 50 °C for 8 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase. ^d For 12 h.



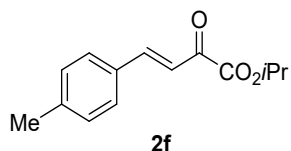
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 16.1$ Hz, 1H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 16.1$ Hz, 1H), 5.24 – 5.15 (m, 1H), 1.37 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 182.4, 161.2, 146.0, 137.0, 132.1, 129.6, 128.9, 120.5, 70.3, 21.1 ppm.



Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 16.1$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 16.1$ Hz, 1H), 5.24 – 5.15 (m, 1H), 1.37 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 182.4, 161.2, 146.1, 132.5, 131.9, 129.8, 125.5, 120.6, 70.3, 21.2 ppm.

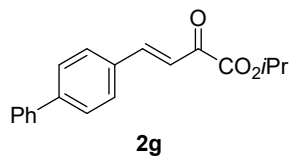


Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 16.2$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 16.2$ Hz, 1H), 5.26 – 5.17 (m, 1H), 1.38 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 182.8, 161.5, 145.8, 137.4, 132.7 (q, $J = 32.8$ Hz), 129.0, 126.0 (q, $J = 3.7$ Hz), 123.7 (q, $J = 272.4$ Hz), 122.8, 70.9, 21.6 ppm.

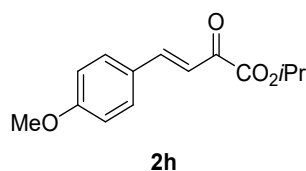


Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 16.1$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 16.1$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz,

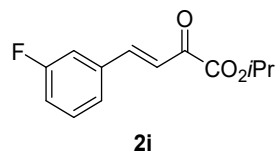
2H), 5.29 – 5.20 (m, 1H), 2.41 (s, 3H), 1.41 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 182.8, 161.6, 147.8, 141.9, 130.9, 129.3, 128.6, 119.2, 70.0, 21.2, 21.1 ppm.



Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 16.1$ Hz, 1H), 7.73 – 7.60 (m, 6H), 7.49 – 7.44 (m, 2H), 7.42 – 7.35 (m, 2H), 5.32 – 5.17 (m, 1H), 1.41 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 183.2, 162.0, 147.8, 144.3, 139.9, 133.0, 129.6, 129.0, 128.2, 127.7, 127.1, 120.5, 70.7, 21.7 ppm.

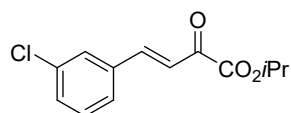


Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 16.0$ Hz, 1H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.19 (d, $J = 16.0$ Hz, 1H), 6.91 (d, $J = 8.6$ Hz, 2H), 5.24 – 5.15 (m, 1H), 3.83 (s, 3H), 1.37 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 183.1, 162.6, 162.2, 148.1, 131.0, 126.8, 118.4, 114.6, 70.5, 55.4, 21.7 ppm.



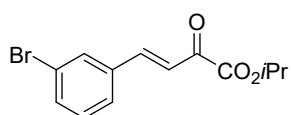
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 16.1$ Hz, 1H), 7.38 (s, 2H), 7.35 – 7.28 (m, 2H), 7.16 – 7.10 (m, 1H), 5.25 – 5.16 (m, 1H), 1.38 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 182.9, 163.0 (d, $^1J_{\text{C-F}} = 247.0$ Hz), 161.6, 146.5 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 136.3 (d, $^3J_{\text{C-F}} = 7.6$ Hz), 130.6 (d, $^3J_{\text{C-F}} = 8.8$ Hz), 125.0 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 121.8, 118.3 (d, $^2J_{\text{C-F}} = 21.4$ Hz), 115.0 (d, $J = 21.4$

Hz), 70.8, 21.6 ppm.



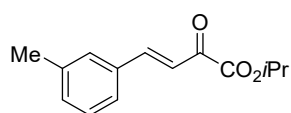
2j

Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 16.1 Hz, 1H), 7.59 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.30 (m, 2H), 5.25 – 5.17 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 182.9, 161.6, 146.3, 135.9, 135.1, 131.3, 130.3, 128.5, 127.1, 121.8, 70.9, 21.6 ppm.



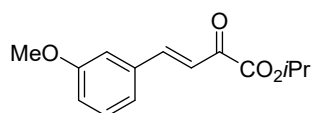
2k

Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.73 (m, 2H), 7.56 (t, *J* = 9.1 Hz, 2H), 7.38 – 7.29 (m, 2H), 5.29 – 5.20 (m, 1H), 1.41 (d, *J* = 6.3 Hz, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 182.8, 161.6, 146.1, 136.1, 134.2, 131.5, 130.6, 127.6, 123.2, 121.8, 70.9, 21.7 ppm.



2l

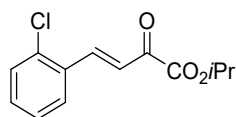
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 16.1 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 2H), 7.37 – 7.27 (m, 3H), 5.30 – 5.21 (m, 1H), 2.41 (s, 3H), 1.42 (d, *J* = 6.3 Hz, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 183.3, 162.0, 148.5, 138.8, 134.0, 132.5, 129.6, 129.0, 126.3, 120.5, 70.6, 21.7, 21.3 ppm.



2m

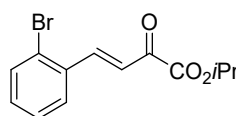
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* =

16.1 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.20 (d, $J = 7.5$ Hz, 1H), 7.11 (s, 1H), 6.98 (d, 1H), 5.25 – 5.16 (m, 1H), 3.82 (s, 3H), 1.37 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 183.2, 161.9, 160.0, 148.2, 135.4, 130.1, 121.8, 120.9, 117.6, 113.5, 70.7, 55.4, 21.6 ppm.



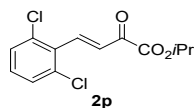
2n

Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.25 (d, $J = 16.2$ Hz, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.37 (t, $J = 7.1$ Hz, 1H), 7.34 – 7.28 (m, 2H), 5.29 – 5.20 (m, 1H), 1.40 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 183.4, 161.8, 143.8, 136.0, 132.2, 132.2, 130.4, 127.9, 127.2, 123.1, 70.8, 21.7 ppm.

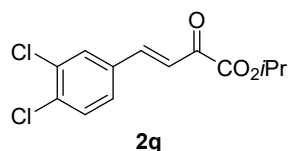


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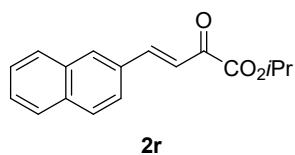
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 16.1$ Hz, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.20 (t, 1H), 7.14 (d, $J = 16.1$ Hz, 1H), 5.20 – 5.11 (m, 1H), 1.32 (d, $J = 6.2$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 178.1, 156.5, 141.2, 128.7, 128.4, 127.0, 122.8, 122.6, 121.2, 118.1, 65.5, 16.4 ppm.



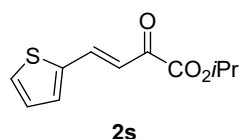
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 16.6$ Hz, 1H), 7.48 (d, $J = 16.6$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 8.1$ Hz, 1H), 5.26 – 5.18 (m, 1H), 1.38 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 183.5, 161.4, 141.3, 135.5, 131.5, 130.6, 129.0, 128.9, 70.9, 21.7 ppm.



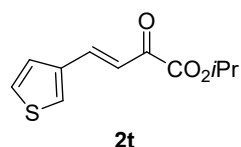
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.67 (m, 2H), 7.50 – 7.41 (m, 2H), 7.32 (d, $J = 16.2$ Hz, 1H), 5.26 – 5.15 (m, 1H), 1.38 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 182.6, 161.5, 145.0, 135.5, 134.1, 133.5, 131.1, 130.4, 127.8, 122.1, 71.0, 21.6 ppm.



Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 16.5$ Hz, 2H), 7.89 – 7.81 (m, 3H), 7.74 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.57 – 7.49 (m, 2H), 7.44 (d, $J = 16.0$ Hz, 1H), 5.30 – 5.19 (m, 1H), 1.41 (d, $J = 6.3$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 183.2, 162.0, 148.3, 134.8, 133.2, 131.9, 131.6, 128.9, 128.9, 128.0, 127.9, 127.0, 123.6, 120.8, 70.7, 21.7 ppm.

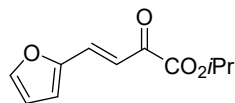


Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 15.7$ Hz, 1H), 7.49 (d, $J = 5.1$ Hz, 1H), 7.40 (d, $J = 3.6$ Hz, 1H), 7.14 – 7.07 (m, 2H), 5.25 – 5.14 (m, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 182.6, 161.8, 140.3, 139.8, 133.6, 130.8, 128.7, 119.4, 70.7, 21.7 ppm.



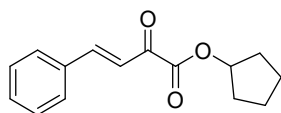
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 16.0$ Hz, 1H), 7.68 – 7.65 (m, 1H), 7.40 – 7.35 (m, 2H), 7.13 (d, $J = 16.0$ Hz, 1H), 5.25

– 5.15 (m, 1H), 1.38 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 183.4, 161.9, 141.3, 137.7, 131.2, 127.4, 125.3, 120.5, 70.6, 21.7 ppm.



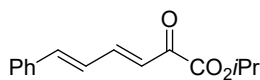
2u

Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 15.6 Hz, 2H), 7.18 (d, J = 15.8 Hz, 1H), 6.80 (d, J = 3.4 Hz, 1H), 6.52 (dd, J = 3.5, 1.8 Hz, 1H), 5.24 – 5.13 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 182.8, 161.7, 151.1, 146.2, 133.4, 118.4, 118.2, 113.1, 70.6, 21.6 ppm.



2v

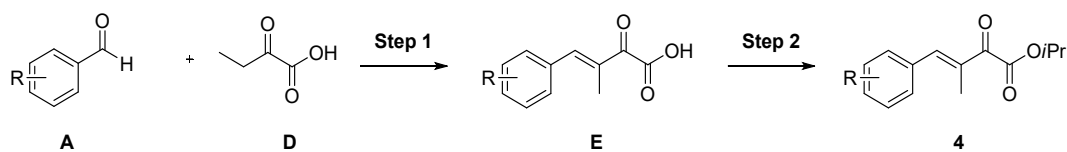
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 16.2 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.38 – 7.30 (m, 3H), 7.21 (d, J = 16.2 Hz, 1H), 5.32 – 5.25 (m, 1H), 1.95 – 1.83 (m, 2H), 1.81 – 1.67 (m, 4H), 1.61 – 1.51 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 183.4, 162.3, 148.2, 134.1, 131.6, 129.1, 129.0, 120.8, 79.7, 32.6, 23.8 ppm.



6

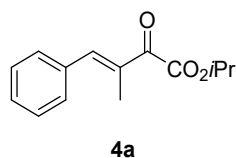
Prepared according to the general procedure I above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.67 – 7.58 (m, 1H), 7.50 (d, J = 6.9 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.08 (d, J = 15.5 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.87 (d, J = 15.3 Hz, 1H), 5.25 – 5.16 (m, 1H), 1.38 (d, J = 6.3 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 183.3, 161.9, 148.2, 144.4, 135.7, 129.9, 129.0, 127.6, 126.6, 124.2, 70.5, 21.7 ppm.

B) Synthesis of β,γ -unsaturated α -keto esters **4**

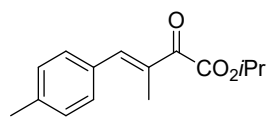


General procedure II: To a solution of aqueous 0.5 M NaOH (0.6 g, 15 mmol) in water (30 mL), under N_2 at room temperature, 2-oxobutyric acid **D** (0.936 mL, 11 mmol) was added in portions (5 mL of EtOH were used to wash the product container). The reaction was then left stirring for 5 min and a solution of benzaldehyde derivatives **A** (1.4 g, 10 mmol) in EtOH (5 mL) was then slowly added. The reaction was left to stir at 25 °C overnight. Water was added (5.6 mL) and the solution evaporated under reduced pressure to eliminate the excess of EtOH. The solution was then washed with toluene and evaporated (3 x 4 mL) to eliminate traces of this solvent. The aqueous solution was then cooled down in an ice bath and conc. HCl (2 mL) was slowly added under magnetically stirring. A white solid precipitated from the solution which was kept at 0 °C for another hour. The solid **E** was filtered and dried at 40 °C under vacuum.

To a stirred solution of **E** (8.5 mmol) and isopropyl alcohol (12.75 mmol) in CH_2Cl_2 (40 mL) in an ice bath was added a solution of 4-Dimethylaminopyridine (0.85 mmol, 10 mol%) and *N,N'*-diisopropylcarbodiimide (9.4 mmol) in CH_2Cl_2 (10 mL) via a dropping funnel. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **4**.

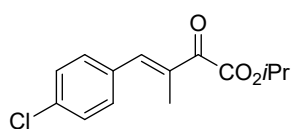


Prepared according to the general procedure II above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 6H), 5.35 – 5.25 (m, 1H), 2.14 (d, $J = 1.3$ Hz, 3H), 1.41 (s, 3H), 1.39 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 165.0, 146.6, 134.8, 133.3, 130.2, 129.7, 128.7, 70.4, 21.7, 12.1 ppm.



4b

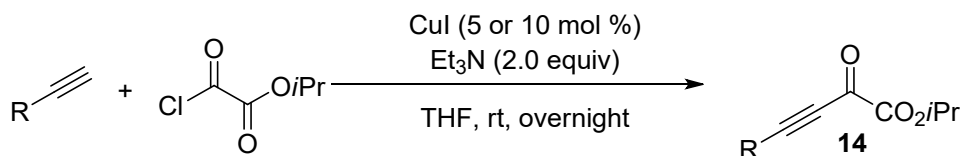
Prepared according to the general procedure II above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.42 (d, $J = 8.5$ Hz, 3H), 7.28 (d, $J = 7.8$ Hz, 2H), 5.37 – 5.29 (m, 1H), 2.42 (s, 3H), 2.17 (s, 3H), 1.43 (d, $J = 6.2$ Hz, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 190.3, 165.1, 146.8, 140.3, 132.4, 132.1, 130.4, 129.4, 70.2, 21.7, 21.5, 12.1 ppm.



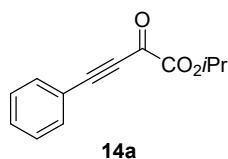
4c

Prepared according to the general procedure II above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (20:1 to 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.36 (m, 5H), 5.33 – 5.23 (m, 1H), 2.10 (d, $J = 1.3$ Hz, 3H), 1.39 (s, 3H), 1.38 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 189.8, 164.7, 144.9, 135.8, 133.8, 133.3, 131.4, 129.0, 70.5, 21.7, 12.1 ppm.

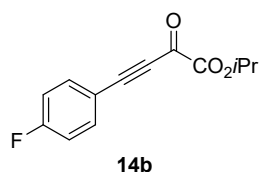
C) Synthesis of α,β -alkynyl keto esters **14**



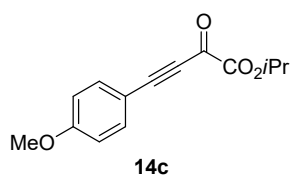
General procedure III: In a two-necked round-bottomed flask equipped with a magnetic stirred bar, a rubber septum, and a nitrogen balloon was placed CuI (5 or 10 mol %), and to it was added THF (0.4 M), triethylamine (2.0 equiv), alkyne and isopropyl 2-chloro-2-oxoacetate (1.2 equiv). After the mixture was stirred overnight at room temperature, the reaction was quenched with sat. NaHCO_3 aq, and the whole mixture was filtered with a celite pad and extracted with ethyl acetate (10 mL \times 3). The combined extracts were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 20/1) to give the α,β -alkynyl ketoester **14**.



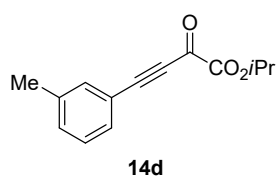
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 8.3$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 5.25 – 5.13 (m, 1H), 1.39 (s, 3H), 1.38 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 158.8, 133.8, 131.8, 128.8, 119.2, 97.8, 87.2, 71.7, 21.6 ppm.



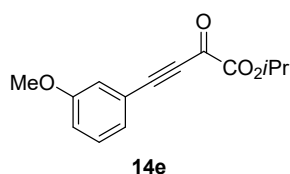
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.65 (dd, $J = 8.6, 5.5$ Hz, 2H), 7.10 (t, $J = 8.6$ Hz, 2H), 5.24 – 5.11 (m, 1H), 1.39 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.9, 164.6 (d, $^1J_{\text{C-F}} = 256.2$ Hz), 158.8, 136.2 (d, $^3J_{\text{C-F}} = 9.3$ Hz), 116.4 (d, $^2J_{\text{C-F}} = 22.6$ Hz), 115.3 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 96.6, 87.2, 71.7, 21.5 ppm.



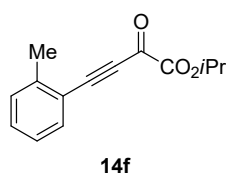
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.60 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 5.23 – 5.09 (m, 1H), 3.84 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.8, 162.6, 159.1, 136.0, 114.6, 110.9, 99.5, 87.8, 71.5, 55.5, 21.6 ppm.



Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, $J = 8.2$ Hz, 2H), 7.30 (q, $J = 8.2, 7.6$ Hz, 2H), 5.25 – 5.11 (m, 1H), 2.36 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 158.9, 138.7, 134.2, 132.8, 130.9, 128.7, 119.0, 100.0, 98.3, 87.0, 71.6, 21.6, 21.1 ppm.

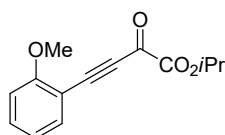


Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.31 (t, $J = 7.9$ Hz, 1H), 7.26 – 7.24 (m, 1H), 7.14 (s, 1H), 7.08 – 7.03 (m, 1H), 5.25 – 5.10 (m, 1H), 3.81 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 159.5, 158.8, 129.9, 126.3, 120.1, 118.7, 118.0, 97.7, 86.8, 71.7, 55.4, 21.6 ppm.



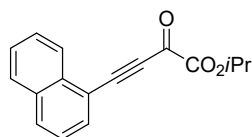
Prepared according to the general procedure III above and obtained as yellow oil,

eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.7$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 5.26 – 5.17 (m, 1H), 2.56 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.9, 158.7, 143.6, 134.4, 131.9, 130.0, 126.0, 119.0, 97.1, 91.1, 71.6, 21.6, 20.5.



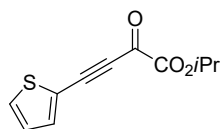
14g

Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.56 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.49 – 7.43 (m, 1H), 6.99 – 6.89 (m, 2H), 5.24 – 5.13 (m, 1H), 3.91 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 162.4, 158.9, 135.8, 133.8, 120.7, 111.1, 108.4, 95.5, 91.5, 71.5, 56.0, 21.6 ppm.



14h

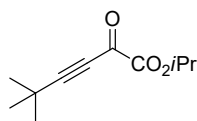
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.47 (d, $J = 8.3$ Hz, 1H), 8.02 (d, $J = 8.2$ Hz, 1H), 7.91 (dd, $J = 18.0, 7.6$ Hz, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 1H), 5.34 – 5.23 (m, 1H), 1.47 (s, 3H), 1.46 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.8, 158.7, 134.6, 134.2, 133.1, 132.9, 128.7, 128.1, 127.2, 125.8, 125.3, 116.7, 96.5, 92.2, 71.8, 21.7 ppm.



14i

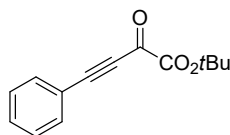
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.61 (s, 2H), 7.15 – 7.07 (m, 1H), 5.24 – 5.09 (m, 1H), 1.39 (d, $J = 3.8$ Hz, 3H), 1.38 – 1.34

(m, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.4, 158.8, 138.6, 133.7, 128.1, 119.0, 92.6, 92.1, 71.8, 21.6 ppm.



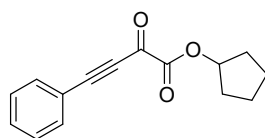
14j

Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 5.17 – 5.10 (m, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (s, 9H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 158.9, 109.2, 78.3, 71.4, 29.7, 28.2, 21.5 ppm.



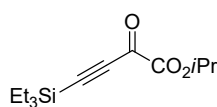
14k

Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 8.3$ Hz, 2H), 7.50 (t, $J = 8.1$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 1.59 (s, 9H) ppm. ^{13}C NMR (126 MHz, CDCl_3) 170.9, 158.2, 133.7, 131.7, 128.8, 119.3, 97.3, 87.3, 84.9, 27.8



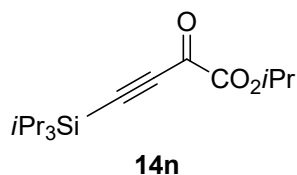
14l

Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.67 – 7.61 (m, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 2H), 5.41 – 5.30 (m, 1H), 2.01 – 1.93 (m, 2H), 1.90 – 1.79 (m, 4H), 1.70 – 1.62 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 159.1, 133.8, 131.8, 128.8, 119.2, 97.7, 87.2, 80.6, 32.6, 23.7.

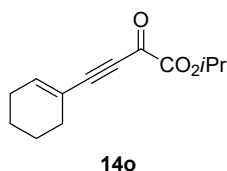


14m

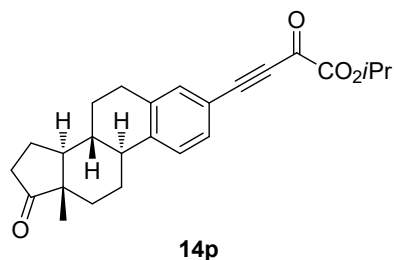
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 5.26 – 5.05 (m, 1H), 1.37 – 1.32 (m, 6H), 1.07 – 0.99 (m, 9H), 0.75 – 0.65 (m, 6H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.7, 158.4, 105.1, 101.6, 71.6, 21.5, 7.2, 3.7.



Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 5.21 – 5.12 (m, 1H), 1.35 (s, 3H), 1.34 (s, 3H), 1.12 (d, $J = 6.0$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.6, 158.3, 104.7, 102.5, 71.5, 21.5, 18.4, 11.0.



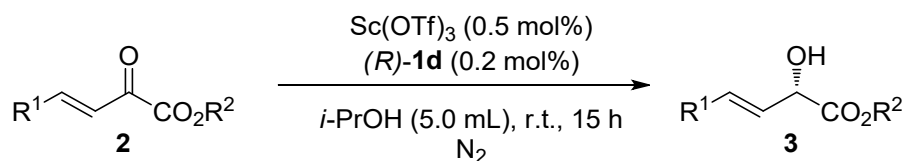
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 6.68 – 6.53 (m, 1H), 5.19 – 5.06 (m, 1H), 2.22 – 2.16 (m, 4H), 1.67 – 1.59 (m, 4H), 1.35 (s, 3H), 1.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 159.0, 146.0, 118.9, 100.6, 85.8, 71.4, 27.9, 26.4, 21.8, 21.5, 20.9 ppm



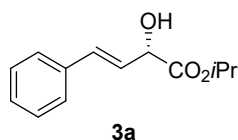
Prepared according to the general procedure III above and obtained as yellow oil, eluent: petroleum ether/ethyl acetate (30:1 to 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.49 – 7.38 (m, 2H), 7.34 (d, $J = 8.1$ Hz, 1H), 5.25 – 5.09 (m, 1H), 2.96 – 2.87 (m, 2H), 2.52 (dd, $J = 19.0, 8.8$ Hz, 1H), 2.42 (dd, $J = 12.7, 3.8$ Hz, 1H), 2.37 – 2.30 (m, 1H), 2.15 (dd, $J = 18.8, 9.0$ Hz, 1H), 2.10 – 1.96 (m, 3H), 1.66 – 1.60 (m, 2H), 1.57 – 1.43 (m,

4H), 1.40 (s, 3H), 1.39 (s, 3H), 0.92 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 159.0, 144.6, 137.4, 134.4, 131.2, 125.9, 116.4, 98.7, 87.2, 71.6, 50.5, 47.9, 44.7, 37.7, 35.8, 31.5, 29.0, 26.1, 25.5, 21.6, 13.8 ppm.

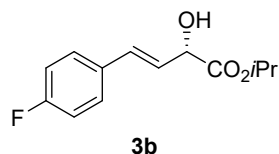
D) Synthesis of 2-hydroxy-3-enoic acid esters **3**



General procedure IV: To a 25 mL flask, β,γ -unsaturated α -keto ester **2** (0.5 mmol), $Sc(OTf)_3$ (0.0025 mmol, 1.23 mg), (R) -**1d** (0.001 mmol, 0.58 mg) were dissolved in solvent i -PrOH (5 mL) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 15 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **3**.

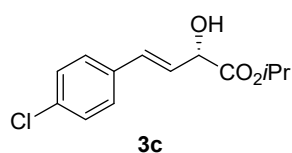


3a: Prepared according to the general procedure IV above and obtained as white solid (96 mg, 88% yield, 98% ee, M.P. = 94 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +39.7$ ($c = 0.68$, CH_2Cl_2). 1H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, $J = 7.5$ Hz, 2H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 6.73 (d, $J = 15.8$ Hz, 1H), 6.17 (dd, $J = 15.9, 5.4$ Hz, 1H), 5.10 – 4.99 (m, 1H), 4.70 (s, 1H), 3.10 (s, 1H), 1.24 (d, $J = 6.2$ Hz, 3H), 1.20 (d, $J = 6.2$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 136.3, 132.0, 128.6, 127.9, 126.7, 125.6, 71.3, 70.3, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3446, 2979, 2928, 1730, 1636, 1450, 1385, 1241, 1201, 1105, 1076, 966, 781, 744, 693, 561. HRMS (ESI) calcd for $C_{13}H_{16}O_3Na^+$ ($M+Na$) $^+$ 243.0997, found 243.0997. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 10.6 min (major) and 9.0 min (minor)

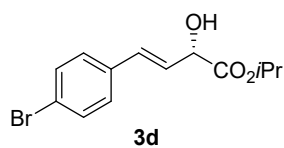


3b: Prepared according to the general procedure IV above and obtained as yellow oil (111 mg, 95% yield, 96% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +30.8$ ($c = 0.50$, CH_2Cl_2). 1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.00 (t,

$J = 8.6$ Hz, 2H), 6.77 (d, $J = 15.9$ Hz, 1H), 6.16 (dd, $J = 15.8, 5.4$ Hz, 1H), 5.18 – 5.07 (m, 1H), 4.77 (d, $J = 5.3$ Hz, 1H), 3.20 (s, 1H), 1.31 (d, $J = 6.3$ Hz, 3H), 1.27 (d, $J = 6.3$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 172.3, 162.0 (d, $^1J_{\text{C-F}} = 247.0$ Hz), 132.0 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 130.3, 127.7 (d, $^3J_{\text{C-F}} = 7.6$ Hz), 124.9 (d, $^5J_{\text{C-F}} = 1.26$ Hz), 115.0 (d, $^2J_{\text{C-F}} = 21.4$ Hz), 70.7, 69.8, 21.2, 21.2 ppm. IR (KBr, cm^{-1}): 3386, 2923, 1632, 1383, 1050. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 261.0903, found 261.0883. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 0.8$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 11.8 min (major) and 9.3 min (minor).

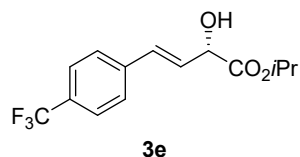


3c: Prepared according to the general procedure IV above and obtained as yellow oil (123 mg, 98% yield, 96% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +52.6$ ($c = 0.65$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.26 (m, 4H), 6.76 (dd, $J = 15.9, 1.4$ Hz, 1H), 6.22 (dd, $J = 15.9, 5.3$ Hz, 1H), 5.19 – 5.05 (m, 1H), 4.77 (s, 1H), 3.21 (s, 1H), 1.31 (d, $J = 6.3$ Hz, 3H), 1.27 (d, $J = 6.3$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 172.7, 134.8, 133.6, 130.6, 128.8, 127.9, 126.3, 71.1, 70.4, 21.8, 21.8 ppm. IR (KBr, cm^{-1}): 3385, 2922, 1646, 1384, 1049. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{ClO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 277.0606, found 277.0607. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 15.0 min (major) and 10.6 min (minor)

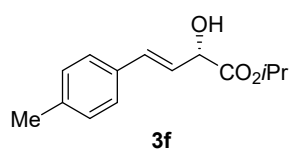


3d: Prepared according to the general procedure IV above and obtained as yellow solid (143 mg, 96% yield, 92% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +55.9$ ($c = 0.59$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.75 (d, $J = 15.9$ Hz, 1H), 6.24 (dd, $J = 15.9, 5.2$ Hz, 1H), 5.19 – 5.07 (m, 1H), 4.76 (s, 1H), 3.14 (s, 1H), 1.32 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.3$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 172.6, 135.2, 131.7, 130.7, 126.4, 121.8, 71.2,

70.4, 21.7. IR (KBr, cm^{-1}): 3386, 2923, 1383, 1050. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{BrO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 321.0102, found 321.0115. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL}\cdot\text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 15.2 min (major) and 10.7 min (minor)

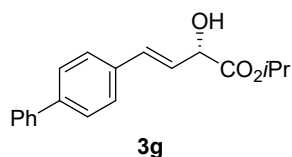


3e: Prepared according to the general procedure IV above and obtained as yellow oil (139 mg, 97% yield, 90% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +23.3$ ($c = 2.16$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, $J = 8.2 \text{ Hz}$, 2H), 7.47 (d, $J = 8.0 \text{ Hz}$, 2H), 6.86 (dd, $J = 15.8, 2.1 \text{ Hz}$, 1H), 6.35 (dd, $J = 15.9, 5.1 \text{ Hz}$, 1H), 5.21 – 5.03 (m, 1H), 4.90 – 4.71 (m, 1H), 3.28 (d, $J = 5.6 \text{ Hz}$, 1H), 1.32 (d, $J = 6.3 \text{ Hz}$, 3H), 1.28 (d, $J = 6.2 \text{ Hz}$, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 172.5, 139.8, 130.3, 129.7 (q, $J = 32.5 \text{ Hz}$), 128.3, 126.8, 125.6 (q, $J = 4.0 \text{ Hz}$), 124.1 (q, $J = 271.8 \text{ Hz}$), 100.0, 71.1, 70.5, 21.7 ppm. IR (KBr, cm^{-1}): 3442, 3051, 2989, 2936, 1732, 1670, 1626, 1577, 1458, 1418, 1378, 1366, 1326, 1169, 1129, 1102, 1069, 991, 843, 645. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 311.0871, found 311.0879. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8 \text{ mL}\cdot\text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 19.1 min (major) and 13.9 min (minor).

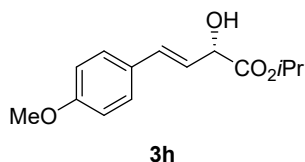


3f: Prepared according to the general procedure IV above and obtained as yellow oil (113 mg, 97% yield, 98% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +17.9$ ($c = 0.98$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, $J = 8.0 \text{ Hz}$, 2H), 7.13 (d, $J = 7.9 \text{ Hz}$, 2H), 6.82 – 6.73 (m, 1H), 6.19 (dd, $J = 15.8, 5.6 \text{ Hz}$, 1H), 5.17 – 5.08 (m, 1H), 4.77 (s, 1H), 3.12 (d, $J = 4.9 \text{ Hz}$, 1H), 2.34 (s, 3H), 1.31 (d, $J = 6.3 \text{ Hz}$, 3H), 1.27 (d, $J = 6.3 \text{ Hz}$, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.0, 137.9, 133.5, 131.9, 129.3, 126.6, 124.6, 71.4, 70.2, 21.8, 21.7, 21.2 ppm. IR (KBr, cm^{-1}): 3386, 2923, 2853, 1632, 1383, 1049. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 257.1154, found

257.1160. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 0.8 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 12.0 min (major) and 9.8 min (minor).

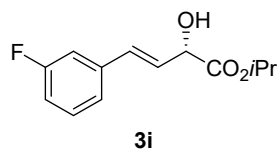


3g: Prepared according to the general procedure IV above and obtained as white solid (137 mg, 93% yield, 96% ee, M.P. = 92 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +91.5$ ($c = 0.32$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (dd, $J = 11.1, 7.9 \text{ Hz}$, 4H), 7.46 (dd, $J = 15.3, 8.0 \text{ Hz}$, 4H), 7.36 (t, $J = 7.3 \text{ Hz}$, 1H), 6.87 (d, $J = 16.9 \text{ Hz}$, 1H), 6.31 (dd, $J = 15.9, 5.4 \text{ Hz}$, 1H), 5.22 – 5.09 (m, 1H), 4.84 (dd, $J = 5.4, 1.4 \text{ Hz}$, 1H), 3.26 (d, $J = 11.1 \text{ Hz}$, 1H), 1.34 (d, $J = 6.3 \text{ Hz}$, 3H), 1.31 (d, $J = 6.3 \text{ Hz}$, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.8, 139.7, 139.5, 134.3, 130.5, 127.8, 126.3, 126.2, 126.1, 125.9, 124.7, 70.3, 69.2, 20.7, 20.7 ppm. IR (KBr, cm^{-1}): 3446, 3029, 2981, 2932, 1729, 1488, 1465, 1450, 1408, 1385, 1375, 1288, 1206, 1106, 1076, 1006, 968, 952, 829, 755, 692 ppm. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 319.1310, found 319.1306. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 16.3 min (major) and 12.9 min (minor).

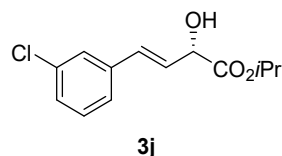


3h: Prepared according to the general procedure IV above and obtained as yellow oil (118 mg, 95% yield, 99% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +44.39$ ($c = 0.89$, in CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.32 (d, $J = 8.6 \text{ Hz}$, 2H), 6.86 (d, $J = 8.6 \text{ Hz}$, 2H), 6.74 (d, $J = 15.8 \text{ Hz}$, 1H), 6.09 (dd, $J = 15.8, 5.7 \text{ Hz}$, 1H), 5.12 (hept, $J = 6.3 \text{ Hz}$, 1H), 4.75 (t, $J = 5.2 \text{ Hz}$, 1H), 3.81 (s, 3H), 3.12 (d, $J = 5.8 \text{ Hz}$, 1H), 1.31 (d, $J = 6.3 \text{ Hz}$, 3H), 1.27 (d, $J = 6.3 \text{ Hz}$, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.1, 159.5, 131.6, 129.0, 127.9, 123.4, 114.0, 71.4, 70.1, 55.3, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3418, 2922, 1730, 1632, 1513, 1252, 1069. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 273.1103, found 273.1107. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 0.8 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 17.9 min

(major) and 14.1 min (minor).

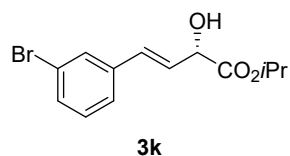


3i: Prepared according to the general procedure IV above and obtained as yellow solid (108 mg, 91% yield, 90% ee, M.P. = 70 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +31.1$ ($c = 1.19$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.23 – 7.17 (m, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 7.03 – 6.98 (m, 1H), 6.91 – 6.84 (m, 1H), 6.71 (dd, $J = 15.9, 1.3$ Hz, 1H), 6.18 (dd, $J = 15.8, 5.2$ Hz, 1H), 5.12 – 4.98 (m, 1H), 4.71 (s, 1H), 3.17 (d, $J = 4.3$ Hz, 1H), 1.24 (d, $J = 6.3$ Hz, 3H), 1.20 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.6, 163.1 (d, $^1J_{\text{C-F}} = 246.4$ Hz), 138.6 (d $^3J_{\text{C-F}} = 8.1$ Hz), 130.6 (d, $^4J_{\text{C-F}} = 3.0$ Hz), 130.1 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 127.0, 122.6 (d, $^4J_{\text{C-F}} = 3.0$ Hz), 114.7 (d, $^2J_{\text{C-F}} = 22.2$ Hz), 113.1 (d, $^2J_{\text{C-F}} = 22.2$ Hz), 71.1, 70.4, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3444, 3082, 2983, 2933, 1729, 1611, 1582, 1489, 1447, 1386, 1261, 1205, 1139, 1104, 1071, 965, 843, 683. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 261.0903, found 261.0898. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 9.1 min (major) and 7.9 min (minor)

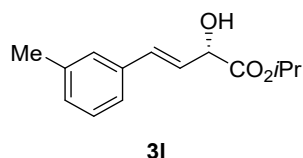


3j: Prepared according to the general procedure IV above and obtained as yellow oil (117 mg, 92% yield, 89% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +27.8$ ($c = 0.49$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 (s, 1H), 7.28 – 7.19 (m, 3H), 6.76 (d, $J = 15.9$ Hz, 1H), 6.26 (dd, $J = 15.8, 5.2$ Hz, 1H), 5.23 – 5.06 (m, 1H), 4.79 (s, 1H), 3.23 (s, 1H), 1.32 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.2$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.1, 137.7, 134.1, 129.9, 129.3, 127.4, 126.7, 126.0, 124.5, 70.6, 69.9, 21.2, 21.2 ppm. IR (KBr, cm^{-1}): 3443, 2983, 2923, 1729, 1695, 1607, 1567, 1555, 1470, 1454, 1431, 1375, 1255, 1201, 1100, 1078, 907, 784, 684. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{ClO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 277.0607, found 277.0614. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 9.1

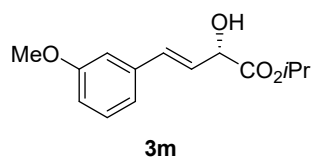
min (major) and 7.8 min (minor).



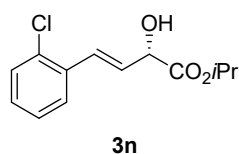
3k: Prepared according to the general procedure IV above and obtained as yellow oil (140 mg, 94% yield, 95% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +32.3$ ($c = 0.39$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.52 (s, 1H), 7.36 (d, $J = 7.9$ Hz, 1H), 7.28 (d, $J = 7.7$ Hz, 1H), 7.17 (t, $J = 7.8$ Hz, 1H), 6.74 (d, $J = 15.8$ Hz, 1H), 6.25 (dd, $J = 15.8, 5.2$ Hz, 1H), 5.16 – 5.07 (m, 1H), 4.79 (dd, $J = 5.1, 1.5$ Hz, 1H), 3.31 (s, 1H), 1.29 (dd, $J = 17.6, 6.3$ Hz, 6H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.1, 138.0, 130.3, 129.8, 129.6, 128.9, 126.7, 124.9, 122.3, 70.6, 69.9, 21.3 ppm. IR (KBr, cm^{-1}): 3442, 2979, 2926, 1730, 1591, 1561, 1469, 1376, 1261, 1203, 1103, 1071, 966, 905, 788, 761, 680. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{BrO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 321.0102, found 321.0081. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 9.6 min (major) and 8.1 min (minor).



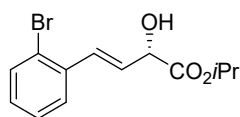
3l: Prepared according to the general procedure IV above and obtained as yellow oil (114 mg, yield 98%, ee 97%), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +55.1$ ($c = 0.37$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (d, $J = 6.1$ Hz, 3H), 7.13 – 7.06 (m, 1H), 6.78 (dd, $J = 15.9, 1.6$ Hz, 1H), 6.23 (dd, $J = 15.9, 5.5$ Hz, 1H), 5.20 – 5.07 (m, 1H), 4.79 (s, 1H), 3.23 (d, $J = 4.5$ Hz, 1H), 2.35 (s, 3H), 1.32 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.0, 138.2, 136.2, 132.1, 128.8, 128.5, 127.4, 125.4, 123.8, 71.4, 70.2, 21.8, 21.8, 21.4 ppm. IR (KBr, cm^{-1}): 3421, 2968, 2922, 1382, 1253, 1066, 895. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 257.1154, found 257.1165. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 8.5 min (major) and 7.4 min (minor).



3m: Prepared according to the general procedure IV above and obtained as yellow oil (121 mg, 97% yield, 94% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +31.1$ ($c = 0.30$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19 – 7.13 (m, 1H), 6.91 (d, $J = 7.7$ Hz, 1H), 6.87 – 6.83 (m, 1H), 6.76 – 6.67 (m, 2H), 6.16 (dd, $J = 15.8, 5.4$ Hz, 1H), 5.11 – 5.00 (m, 1H), 4.70 (t, $J = 4.2$ Hz, 1H), 3.74 (s, 3H), 3.10 (d, $J = 5.5$ Hz, 1H), 1.24 (d, $J = 6.3$ Hz, 3H), 1.20 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.9, 159.8, 137.8, 137.7, 131.8, 129.6, 126.0, 119.3, 113.5, 112.1, 71.3, 70.3, 55.2, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3444, 2981, 2934, 1729, 1603, 1581, 1489, 1455, 1433, 1375, 1266, 1157, 1102, 1045, 971, 777, 689. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 273.1103, found 273.1107. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL} \cdot \text{min}^{-1}$, $\lambda = 254$ nm, retention time: 12.6 min (major) and 10.9 min (minor).

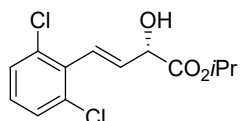


3n: Prepared according to the general procedure IV above and obtained as yellow solid (118 mg, 93% yield, 97% ee, M.P. = 98 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +41.6$ ($c = 0.38$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.49 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.34 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.23 – 7.13 (m, 3H), 6.24 (dd, $J = 15.9, 5.3$ Hz, 1H), 5.20 – 5.07 (m, 1H), 4.83 (t, $J = 4.6$ Hz, 1H), 3.37 (d, $J = 5.8$ Hz, 1H), 1.31 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.6, 134.5, 133.4, 129.7, 128.9, 128.7, 128.2, 127.1, 126.8, 71.4, 70.3, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3442, 2981, 2935, 1727, 1467, 1433, 1385, 1290, 1203, 1144, 1104, 1072, 965, 776, 755, 684. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{ClO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 277.0607, found 277.0606. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL} \cdot \text{min}^{-1}$, $\lambda = 254$ nm, retention time: 15.7 min (major) and 14.0 min (minor).



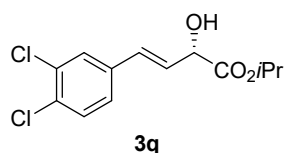
3o

3o: Prepared according to the general procedure IV above and obtained as yellow solid (139 mg, 93% yield, 97% ee, M.P. = 53 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +71.0$ ($c = 0.29$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.22 – 7.11 (m, 2H), 6.24 (dd, $J = 15.8, 5.3$ Hz, 1H), 5.23 – 5.11 (m, 1H), 4.87 (s, 1H), 3.43 – 3.29 (m, 1H), 1.36 (d, $J = 6.3$ Hz, 3H), 1.32 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.6, 136.3, 133.0, 130.9, 129.2, 128.9, 127.5, 127.3, 123.9, 71.3, 70.3, 21.8 ppm. IR (KBr, cm^{-1}): 3436, 2979, 2928, 1725, 1463, 1374, 1277, 1200, 1101, 1070, 962, 775, 748, 662, 562. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{BrO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 321.0102, found 321.0103. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 15.8 min (major) and 14.3 min (minor).

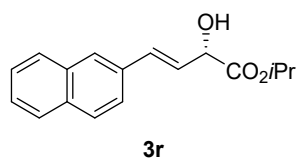


3p

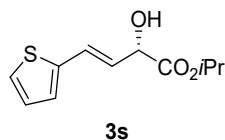
3o: Prepared according to the general procedure IV above and obtained as yellow oil (134 mg, 93% yield, 78% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +31.9$ ($c = 0.37$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 (d, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.82 (dd, $J = 16.2, 1.7$ Hz, 1H), 6.31 (dd, $J = 16.2, 5.0$ Hz, 1H), 5.20 – 5.10 (m, 1H), 4.84 (dd, $J = 4.9, 1.7$ Hz, 1H), 3.21 (s, 1H), 1.32 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.2$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.5, 134.5, 134.4, 133.9, 128.4, 128.4, 125.3, 71.2, 70.4, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3359, 2921, 2359, 2339, 1648, 1555, 1383, 1254, 1066, 669. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 311.0218, found 311.0210. HPLC analysis: Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 8.2 min (major) and 7.6 min (minor).



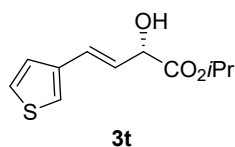
3q: Prepared according to the general procedure IV above and obtained as yellow oil (134 mg, 93% yield, 92% ee, M.P. = 58 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +53.0$ ($c = 0.23$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.46 (d, $J = 1.8$ Hz, 1H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.20 (dd, $J = 8.3, 1.9$ Hz, 1H), 6.73 (dd, $J = 15.8, 1.4$ Hz, 1H), 6.25 (dd, $J = 15.8, 5.1$ Hz, 1H), 5.20 – 5.09 (m, 1H), 4.78 (d, $J = 3.7$ Hz, 1H), 3.18 (s, 1H), 1.32 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.9, 135.9, 132.2, 131.1, 130.0, 128.9, 127.8, 127.1, 125.4, 70.4, 70.1, 21.3 ppm. IR (KBr, cm^{-1}): 3433, 2981, 2920, 2128, 1719, 1719, 1692, 1605, 1553, 1469, 1375, 1248, 1204, 1131, 1079, 968, 827, 786, 686. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 311.0218, found 311.0228. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 17.9 min (major) and 13.8 min (minor).



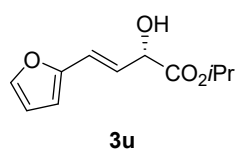
3r: Prepared according to the general procedure IV above and obtained as yellow oil (109 mg, 81% yield, 98% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +100.0$ ($c = 0.10$, in CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (dd, $J = 17.4, 9.0$ Hz, 4H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.50 – 7.41 (m, 2H), 6.99 (d, $J = 15.8$ Hz, 1H), 6.38 (dd, $J = 15.8, 5.4$ Hz, 1H), 5.20 – 5.11 (m, 1H), 4.85 (d, $J = 5.1$ Hz, 1H), 3.24 (s, 1H), 1.34 (d, $J = 6.2$ Hz, 3H), 1.30 (d, $J = 6.2$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.9, 133.7, 133.5, 133.2, 132.1, 128.3, 128.1, 127.7, 126.9, 126.4, 126.1, 126.0, 123.6, 71.4, 70.3, 21.8, 21.8 ppm. IR (KBr, cm^{-1}): 3466, 2977, 1745, 1722, 1687, 1602, 1590, 1366, 1302, 1243, 1114, 1085, 994, 862, 819, 787, 750, 700. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 293.1154, found 293.1153. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 14.2 min (major) and 12.0 min (minor).



3s: Prepared according to the general procedure IV above and obtained as yellow oil (104 mg, 92% yield, 94% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +48.1$ ($c = 0.89$, in CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.17 (d, $J = 4.9$ Hz, 1H), 7.00 – 6.89 (m, 3H), 6.08 (dd, $J = 15.6, 5.3$ Hz, 1H), 5.16 – 5.06 (m, 1H), 4.73 (s, 1H), 3.20 (s, 1H), 1.31 (d, $J = 6.2$ Hz, 3H), 1.27 (d, $J = 6.2$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.2, 140.8, 127.0, 125.9, 124.5, 124.5, 124.2, 70.5, 69.8, 21.2, 21.2 ppm. IR (KBr, cm^{-1}): 3421, 2922, 1633, 1393, 1066. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 249.0561, found 249.0560. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 11.5 min (major) and 9.1 min (minor).

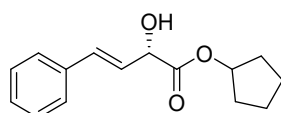


3t: Prepared according to the general procedure IV above and obtained as yellow solid (105 mg, 93% yield, 98% ee, M.P. = 60 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1); $[\alpha]_D^{30} = +96.3$ ($c = 0.11$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20 (dd, $J = 5.2, 3.1$ Hz, 1H), 7.14 – 7.10 (m, 2H), 6.73 (dd, $J = 15.8, 1.3$ Hz, 1H), 6.02 (dd, $J = 15.8, 5.5$ Hz, 1H), 5.10 – 4.99 (m, 1H), 4.67 (dd, $J = 5.5, 1.5$ Hz, 1H), 3.08 (s, 1H), 1.24 (d, $J = 6.3$ Hz, 3H), 1.20 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.9, 138.9, 126.2, 126.1, 125.4, 125.1, 123.0, 71.2, 70.2, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3440, 2976, 2918, 2849, 1730, 1464, 1376, 1198, 1102, 1069, 963, 866, 791, 627. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 249.0561, found 249.0561. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 15.4 min (major) and 12.2 min (minor).



3u: Prepared according to the general procedure IV above and obtained as yellow oil

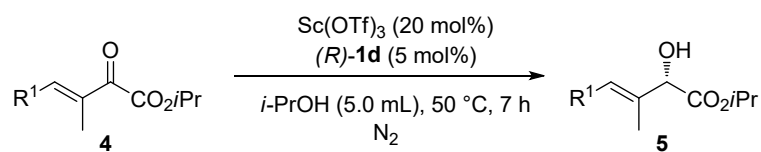
(84 mg, 82% yield, 93% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +78.0$ ($c = 0.1$, in CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35 (t, $J = 2.8$ Hz, 1H), 6.62 (dd, $J = 15.7, 1.9$ Hz, 1H), 6.37 (dd, $J = 3.4, 1.9$ Hz, 1H), 6.28 – 6.15 (m, 2H), 5.15 – 5.06 (m, 1H), 4.75 (d, $J = 3.3$ Hz, 1H), 3.14 (s, 1H), 1.31 (d, $J = 6.1$ Hz, 3H), 1.28 (d, $J = 6.3$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.8, 152.1, 142.2, 124.1, 119.8, 111.4, 108.9, 100.0, 70.8, 70.3, 21.7, 21.7 ppm. IR (KBr, cm^{-1}): 3398, 2918, 2849, 2297, 2100, 1725, 1463, 1375, 1260, 1102, 965, 820, 742. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 233.0790, found 233.0786. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 0.8$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 10.2 min (major) and 8.9 min (minor).



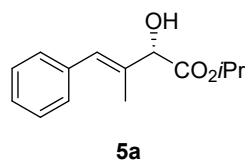
3v

3v: Prepared according to the general procedure IV above and obtained as yellow solid (119 mg, 97% yield, 97% ee, M.P. = 91 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1); $[\alpha]_D^{30} = +27.7$ ($c = 0.35$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 (d, $J = 7.7$ Hz, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 6.80 (d, $J = 15.9$ Hz, 1H), 6.22 (dd, $J = 15.9, 5.4$ Hz, 1H), 5.33 – 5.23 (m, 1H), 4.83 – 4.73 (m, 1H), 3.25 (d, $J = 5.8$ Hz, 1H), 1.94 – 1.82 (m, 2H), 1.80 – 1.67 (m, 4H), 1.65 – 1.55 (m, 2H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.2, 134.4, 130.0, 126.7, 126.0, 124.7, 123.8, 77.4, 69.4, 30.8, 30.7, 21.7, 21.7. IR (KBr, cm^{-1}): 3451, 2972, 1731, 1494, 1449, 1353, 1320, 1291, 1239, 1196, 1167, 1093, 1076, 1063, 965, 780, 747, 695, 573 ppm. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 269.1154, found 269.1146. HPLC analysis: Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 1.0$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 18.5 min (major) and 15.0 min (minor).

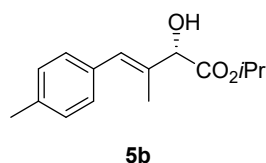
E) Synthesis of 2-hydroxy-3-enoic acid esters **5**



General procedure V: To a 25 mL flask, β,γ -unsaturated α -keto ester **4** (0.5 mmol), Sc(OTf)₃ (0.1 mmol, 49.2 mg), (*R*)-**1d** (0.025 mmol, 14.5 mg) were dissolved in solvent *i*-PrOH (5 mL) under nitrogen atmosphere at 50 °C. The reaction mixture was stirred for 7 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **5**.

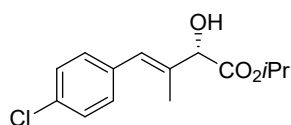


5a: Prepared according to the general procedure V above and obtained as yellow oil (111 mg, yield 95%, ee 84%), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +25.6$ ($c = 0.32$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.27 (t, $J = 7.5$ Hz, 2H), 7.21 (d, $J = 7.4$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 1H), 6.57 (s, 1H), 5.11 – 5.02 (m, 1H), 4.56 (d, $J = 5.0$ Hz, 1H), 3.28 (d, $J = 5.2$ Hz, 1H), 1.78 (s, 3H), 1.23 (d, $J = 6.3$ Hz, 3H), 1.19 (d, $J = 6.2$ Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.3, 137.1, 134.7, 129.6, 129.0, 128.2, 126.9, 70.1, 21.7, 21.6, 13.5 ppm. IR (KBr, cm⁻¹): 3501, 2981, 2932, 1727, 1492, 1450, 1375, 1259, 1208, 1176, 1104, 1076, 1015, 906, 820, 748, 699. HRMS (ESI) calcd for C₁₄H₁₈O₃Na⁺ (M+Na)⁺ 257.1154, found 257.1156. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 9.1 min (major) and 8.0 min (minor).



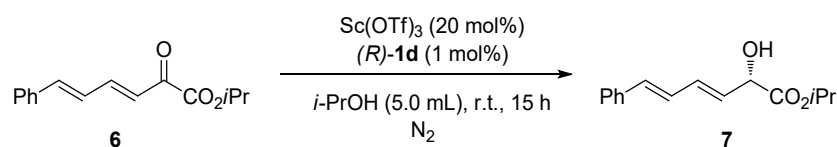
5b: Prepared according to the general procedure V above and obtained as yellow oil (110 mg, 89% yield, 86% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +30.0$ ($c = 0.20$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.18 (m, 4H), 6.64 (s,

1H), 5.22 – 5.13 (m, 1H), 4.66 (d, $J = 5.0$ Hz, 1H), 3.39 (d, $J = 5.2$ Hz, 1H), 2.40 (s, 3H), 1.89 (s, 3H), 1.35 (d, $J = 6.3$ Hz, 3H), 1.30 (d, $J = 6.2$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.4, 136.6, 134.2, 133.9, 129.6, 128.9, 128.9, 100.0, 70.0, 21.7, 21.6, 21.2, 13.5 ppm. IR (KBr, cm^{-1}): 3373, 2974, 2899, 1729, 1452, 1380, 1268, 1085, 1049, 880, 639. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 271.1310, found 271.1310. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 1.0$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 10.2 min (major) and 9.2 min (minor).

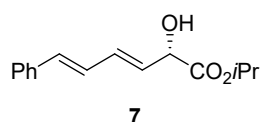


5c: Prepared according to the general procedure V above and obtained as yellow oil (119.5 mg, 89% yield, 82% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_{\text{D}}^{30} = +30.9$ ($c = 0.27$, in CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.34 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.62 (s, 1H), 5.24 – 5.08 (m, 1H), 4.65 (d, $J = 4.2$ Hz, 1H), 3.45 (d, $J = 4.9$ Hz, 1H), 1.86 (s, 3H), 1.34 (d, $J = 6.3$ Hz, 3H), 1.29 (d, $J = 6.2$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.1, 135.5, 135.4, 132.6, 130.3, 128.3, 128.3, 76.5, 70.2, 21.7, 21.6, 13.6 ppm. IR (KBr, cm^{-1}): 3499, 2980, 2927, 2359, 1727, 1490, 1466, 1375, 1259, 1103, 1012, 906, 821, 727, 571. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{17}\text{ClO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 291.0764, found 291.0760. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 1.0$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 11.0 min (major) and 9.2 min (minor).

F) Synthesis of 2-hydroxy-3-enoic acid esters **7**

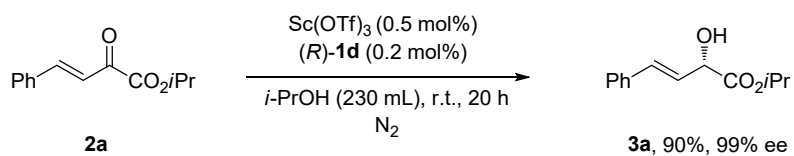


Reaction procedure I: To a 25 mL flask, β,γ -unsaturated α -keto ester **6** (0.5 mmol), $\text{Sc}(\text{OTf})_3$ (0.1 mmol, 49.2 mg), $(R)\text{-1d}$ (0.005 mmol, 2.9 mg) were dissolved in solvent $i\text{-PrOH}$ (5 mL) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 15 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **7**.



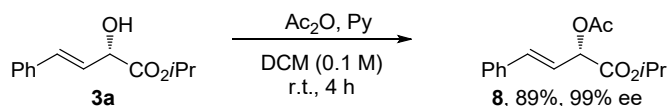
7: Prepared according to the reaction procedure I above and obtained as yellow oil (92 mg, 75% yield, 92% ee, M.P. = 53 °C), eluent: petroleum ether/ethyl acetate (10:1 to 8:1), $[\alpha]_D^{30} = +11.2$ ($c = 0.27$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 6.78 (dd, $J = 15.5, 10.7$ Hz, 1H), 6.60 (dd, $J = 15.3, 6.9$ Hz, 2H), 5.84 (dd, $J = 15.3, 5.5$ Hz, 1H), 5.16 – 5.07 (m, 1H), 4.71 (t, $J = 4.8$ Hz, 1H), 3.07 (d, $J = 5.6$ Hz, 1H), 1.31 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.2$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 172.8, 137.0, 133.7, 132.3, 129.3, 128.6, 127.8, 127.6, 126.5, 71.1, 70.2, 21.8, 21.7 ppm. IR (KBr, cm^{-1}): 3360, 2977, 2922, 2852, 1730, 1659, 1451, 1376, 1263, 1214, 1103, 1050, 991, 745, 692. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 269.1154, found 269.1153. Daicel Chiralpak AD-H, n-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 16.0 min (major) and 15.1 min (minor).

G) Gram-scale reaction

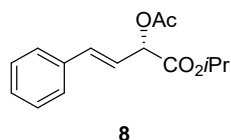


To a 250 mL flask, β,γ -unsaturated α -keto ester **2a** (22.9 mmol, 5.0 g), $\text{Sc}(\text{OTf})_3$ (11.5 mmol, 5.66 mg), $(R)\text{-1d}$ (4.6 mmol, 2.67 mg) were dissolved in solvent $i\text{-PrOH}$ (230 ml) under nitrogen atmosphere. The reaction mixture was stirred for 20 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **3a** (4.53 g, 90% yield, 99% ee).

H) Transformation of chiral allyl alcohol **3a**

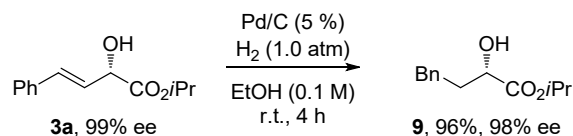


Reaction procedure II: Ac₂O (102 mg, 1 mmol) was added to a solution of **3a** (110 mg, 0.5 mmol) and pyridine (80 μL, 1 mmol) in DCM (5 mL). And the resulting mixture was stirred at room temperature for 4 hours. After the reaction completed, water (5 mL) was added and the resulting residue was extracted by DCM (100 mL x 2). The combined organic layer was dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1-10/1) to afford **8** (117 mg, 89% yield, 99% ee).

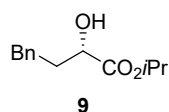


8: Prepared according to the reaction procedure II above and obtained as colorless oil (117 mg, 89% yield, 99% ee), eluent: petroleum ether/ethyl acetate (20:1 to 10:1), $[\alpha]_D^{30} = +41.2$ ($c = 0.26$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, $J = 7.3$ Hz, 2H), 7.35 (d, $J = 7.3$ Hz, 2H), 7.30 – 7.26 (m, 1H), 6.81 (d, $J = 15.9$ Hz, 1H), 6.31 – 6.17 (m, 1H), 5.56 (d, $J = 6.0$ Hz, 1H), 5.20 – 4.99 (m, 1H), 2.20 (d, $J = 2.5$ Hz, 3H), 1.30 (dd, $J = 6.2, 2.3$ Hz, 3H), 1.25 (dd, $J = 6.3, 2.3$ Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 168.9, 167.0, 134.5, 133.8, 127.4, 127.3, 125.6, 119.8, 72.2, 68.4, 20.5, 20.4, 19.5 ppm. IR (KBr, cm⁻¹): 3444, 2981, 2930, 1744, 1451, 1373, 1258, 1226, 1104, 1045, 967, 738, 692.

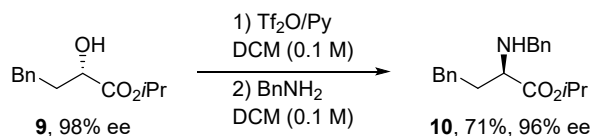
HRMS (ESI) calcd for C₁₅H₁₈O₄Na⁺ (M+Na)⁺ 285.1103, found 285.1103. Daicel Chiralpak AD-H, n-hexane/2-propanol = 98/2, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 5.6 min (major) and 5.2 min (minor).



Reaction procedure III: Take starting material **3a** (110 mg, 0.5 mmol), Pd/C (3 mg, 0.025 mmol) and ethanol (5 mL) in a round bottom flask, fit with a balloon fill with H₂. The reaction mixture was stirred at room temperature for 4 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired products **9** (107 mg, 96% yield, 98% ee).

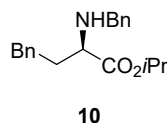


9: Prepared according to the reaction procedure III above and obtained as white solid (107 mg, 96% yield, 98% ee), eluent: petroleum ether/ethyl acetate (10:1 to 8:1); $[\alpha]_{\text{D}}^{30} = +9.0$ ($c = 0.29$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (t, $J = 7.5$ Hz, 2H), 7.24 (d, $J = 4.7$ Hz, 3H), 5.18 – 5.08 (m, 1H), 4.19 (dd, $J = 7.8, 4.0$ Hz, 1H), 3.05 (s, 1H), 2.87 – 2.72 (m, 2H), 2.19 – 2.09 (m, 1H), 2.01 – 1.92 (m, 1H), 1.31 (dd, $J = 6.4, 4.1$ Hz, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 141.3, 128.6, 128.4, 126.0, 69.8, 69.6, 36.2, 31.1, 21.8, 21.8 ppm. IR (KBr, cm⁻¹): 3444, 2979, 2925, 1727, 1495, 1454, 1376, 1252, 1179, 1103, 904, 746, 700. HRMS (ESI) calcd for C₁₃H₁₈O₃Na⁺ (M+Na)⁺ 245.1154, found 245.1156. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 8.5 min (major) and 7.1 min (minor).

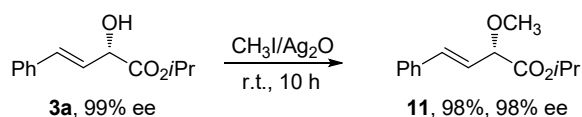


Reaction procedure IV: To a solution of **9** (111 mg, 0.5 mmol) and pyridine (60 μL , 0.75 mmol) in CH_2Cl_2 (5 mL) was added dropwise trifluoromethanesulfonic anhydride (126 μL , 0.75 mmol) slowly in an ice bath. The mixture was stirred for 0.5 h in an ice bath and concentrated in vacuo. Purification of mixture by column chromatography on silica gel (PE/EA = 30:1, v/v) gave the desired products.

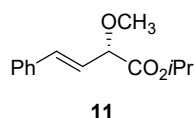
To a suspension of products in CH_2Cl_2 (5 mL) were added Et_3N (69 μL , 0.5 mmol) and then a solution of benzylamine (60 μL , 0.55 mmol) in CH_2Cl_2 (5 mL). After being stirred at room temperature for 5 h, the reaction mixture was concentrated in vacuo. The residue was dissolved in EtOAc, washed with H_2O , dried over MgSO_4 , and concentrated in vacuo. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1, v/v) gave the desired products **10** (110 mg, 71% yield, 96% ee).



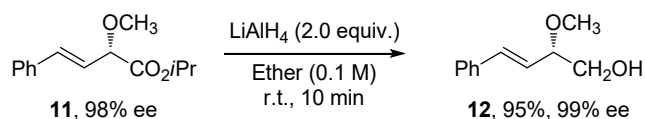
10: Prepared according to the reaction procedure IV above and obtained as colorless oil (110 mg, 71% yield, 96% ee), eluent: petroleum ether/ethyl acetate (20:1 to 10:1), $[\alpha]_{\text{D}}^{30} = +25.0$ ($c = 0.32$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 7.34 – 7.29 (m, 4H), 7.25 (t, $J = 7.6$ Hz, 3H), 7.16 (dd, $J = 10.4$, 7.5 Hz, 3H), 5.20 – 4.75 (m, 1H), 3.77 (d, $J = 13.4$ Hz, 1H), 3.55 (d, $J = 13.4$ Hz, 1H), 3.09 (t, $J = 6.8$ Hz, 1H), 2.75 – 2.56 (m, 2H), 2.45 (s, 1H), 1.90 – 1.74 (m, 2H), 1.21 (dd, $J = 6.4$, 4.3 Hz, 6H) ppm. $^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ 174.0, 141.5, 140.3, 128.3, 128.2, 128.1, 128.0, 126.6, 125.7, 67.4, 59.4, 50.9, 34.6, 31.4, 21.7, 21.5 ppm. IR (KBr, cm^{-1}): 3443, 2926, 2854, 1727, 1494, 1454, 1374, 1247, 1182, 1106, 1028, 735, 698. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_2^+$ ($\text{M}+\text{H}$) $^+$ 312.1964, found 312.1962. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ $\text{mL}\cdot\text{min}^{-1}$, $\lambda = 254$ nm, retention time: 5.5 min (major) and 4.9 min (minor).



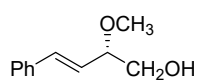
Reaction procedure V: Take starting material **3a** (110 mg, 0.5 mmol), Ag₂O (0.95 g, 3.5 mmol) and CH₃I (5 mL) in a round bottom flask. The reaction mixture was stirred until the reaction completed. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 10:1, v/v) gave the desired products **11** (114 mg, 98% yield, 98% ee).



11: Prepared according to the reaction procedure V above and obtained as yellow oil (114 mg, 98% yield, 98% ee), eluent: petroleum ether/ethyl acetate (20:1 to 10:1), $[\alpha]_{\text{D}}^{30} = +11.5$ ($c = 0.26$, in CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.42 (m, 2H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.33 – 7.30 (m, 1H), 6.81 (d, $J = 16.0$ Hz, 1H), 6.24 (dd, $J = 15.9$, 6.7 Hz, 1H), 5.23 – 5.10 (m, 1H), 4.42 (dd, $J = 6.8$, 1.4 Hz, 1H), 3.49 (s, 3H), 1.34 (d, $J = 6.3$ Hz, 3H), 1.31 (d, $J = 6.2$ Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 170.1, 136.1, 134.1, 128.6, 128.2, 126.7, 123.9, 81.4, 69.0, 57.3, 21.8, 21.7 ppm. IR (KBr, cm⁻¹): 3443, 2981, 2931, 1744, 1452, 1375, 1261, 1193, 1104, 1048, 968, 738, 693. HRMS (ESI) calcd for C₁₄H₁₈O₃Na⁺ (M+Na)⁺ 257.1154, found 257.1162. Daicel Chiralpak AD-H, n-hexane/2-propanol = 95/5, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 8.0 min (major) and 7.6 min (minor).

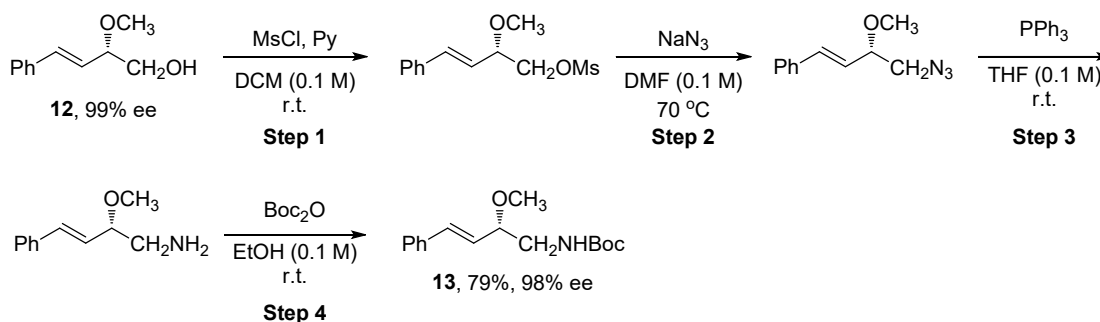


Reaction procedure VI: Take starting material **11** (117 mg, 0.5 mmol), LiAlH₄ (38 mg, 1 mmol) and ether (5 mL) in a round bottom flask. The reaction mixture was stirred until the reaction completed. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1, v/v) gave the desired products **12** (85 mg, 95% yield, 99% ee).



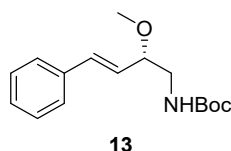
12

12: Prepared according to the reaction procedure VI above and obtained as colorless oil (85 mg, yield 95%, ee 99%), eluent: petroleum ether/ethyl acetate (5:1 to 3:1), $[\alpha]_{\text{D}}^{30} = +20.6$ ($c = 0.31$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, $J = 7.5$ Hz, 2H), 7.38 (t, $J = 7.5$ Hz, 2H), 7.34 – 7.29 (m, 1H), 6.70 (d, $J = 16.0$ Hz, 1H), 6.09 (dd, $J = 16.0$, 7.7 Hz, 1H), 3.98 – 3.89 (m, 1H), 3.75 – 3.62 (m, 2H), 3.44 (s, 3H), 2.27 (s, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 135.7, 133.8, 128.2, 127.6, 126.1, 125.4, 82.5, 65.0, 56.1 ppm. IR (KBr, cm⁻¹): 3360, 2922, 2852, 1730, 1659, 1632, 1452, 1384, 1260, 1063, 969, 748, 693. HRMS (ESI) calcd for C₁₁H₁₄O₂Na⁺ (M+Na)⁺ 201.0891, found 201.0900. Daicel Chiralpak AD-H, n-hexane/2-propanol = 95/5, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 14.7 min (major) and 14.0 min (minor).



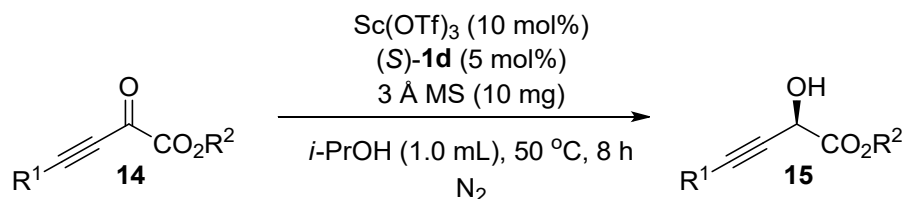
Reaction procedure VII: Step 1) Methanesulfonyl chloride (46 μL , 0.6 mmol) was added successively to a solution of **12** (89 mg, 0.5 mmol) and pyridine (80 μL , 1 mmol) in DCM (5 mL) at 0 $^\circ\text{C}$. The mixture was then heated to room temperature and stirred for 5 hours at this temperature. After the reaction completed, it was poured into ice water. The organic layer was washed successively by 1 M HCl solution (10 mL x 2) and saturated aqueous sodium bicarbonate solution (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 . After the solvent was removed under reduced pressure, the crude product was obtained, which could be used directly in the next step without further purification. Step 2) Sodium azide (65 mg, 1 mmol) was added to a solution of the crude from the previous step in DMF (5 mL) under nitrogen atmosphere. The resulting mixture was stirred at 70 $^\circ\text{C}$ for 12 hours. Then the reaction was allowed to cool to room temperature and diluted with water (20 mL). The aqueous layer was extracted by EtOAc (20 mL x 3) and the combined organic layers were dried over Na_2SO_4 . After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50/1-20/1) to afford (4-azido-3-methoxybut-1-en-1-yl)benzene (75 mg, 74% yield). Step 3) PPh_3 (97 mg, 0.74 mmol) was added to a solution of (4-azido-3-methoxybut-1-en-1-yl)benzene (75 mg, 0.37 mmol) in THF (4 mL) under nitrogen atmosphere and the resulting mixture was stirred at room temperature for 4 hours. Then water (4 mL) was added and the mixture was allowed to stir for 8 hours. After the reaction completed, the mixture was concentrated and the residue was extracted by DCM (5 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel and eluted with dichloromethane/methanol (5/1)

to afford 2-methoxy-4-phenylbut-3-en-1-amine (58 mg, 89% yield). Step 4) Boc₂O (131 mg, 0.6 mmol) was added to a solution of 2-methoxy-4-phenylbut-3-en-1-amine (58 mg, 0.3 mmol) and Et₃N (83 μL, 0.6 mmol) in DCM (3 mL). And the resulting mixture was stirred at room temperature for 3 h. After the reaction completed, water (5 mL) was added and the resulting residue was extracted by DCM (50 mL x 2). The combined organic layer was dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20/1-10/1) to afford (2-methoxy-4-phenylbut-3-en-1-yl)carbamate **13** (66 mg, 79% yield, 98% ee).

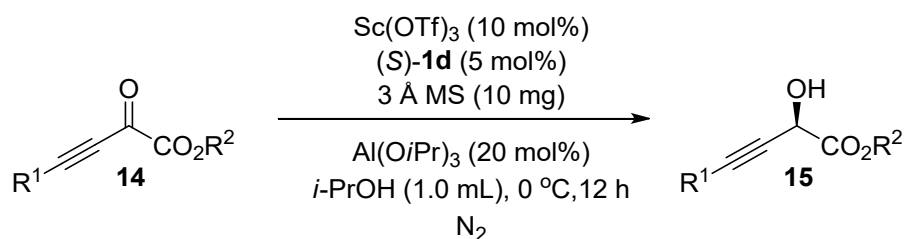


13: Prepared according to the reaction procedure VII above and obtained as colorless oil (66 mg, 79% yield, 98% ee), eluent: petroleum ether/ethyl acetate (20:1 to 10:1), $[\alpha]_D^{30} = +3.1$ ($c = 0.26$, CH₂Cl₂). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.45 (d, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.25 (t, $J = 7.3$ Hz, 1H), 6.84 (t, $J = 5.7$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.08 (dd, $J = 16.0, 7.7$ Hz, 1H), 3.78 (q, $J = 6.5$ Hz, 1H), 3.22 (s, 3H), 3.08 (t, $J = 5.9$ Hz, 2H), 1.33 (s, 9H) ppm. ¹³C NMR (126 MHz, DMSO-*d*₆) δ 156.1, 136.8, 133.0, 129.0, 128.7, 128.2, 126.9, 81.1, 78.1, 56.3, 44.5, 28.7 ppm. IR (KBr, cm⁻¹): 3355, 2922, 2851, 2388, 1715, 1504, 1464, 1365, 1250, 1166, 1105, 968, 749, 693, 511. HRMS (ESI) calcd for C₁₆H₂₃NO₃Na⁺ (M+Na)⁺ 284.1263, found 284.1259. Daicel Chiralpak AD-H, n-hexane/2-propanol = 98/2, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 22.0 min (major) and 20.8 min (minor).

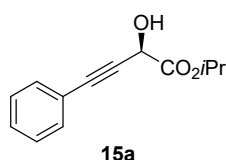
I) Synthesis of 2-hydroxy-3-ynoic acid esters **15**



General procedure VI: To a 25 mL flask, 2-oxo-3-ynoates **14** (0.1 mmol), Sc(OTf)₃ (0.01 mmol, 4.92 mg), (S)-**1d** (0.005 mmol, 2.90 mg) and 3 Å MS (10 mg) were dissolved in solvent *i*-PrOH (1 mL) under nitrogen atmosphere at 50 °C. The reaction mixture was stirred for 8 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 30:1 to 10:1, v/v) gave the desired products **15**.

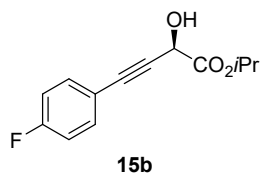


General procedure VII: To a 25 mL flask, 2-oxo-3-ynoates **14** (0.1 mmol), Sc(OTf)₃ (0.01 mmol, 4.92 mg), (S)-**1d** (0.005 mmol, 2.90 mg), Al(O*i*Pr)₃ (0.02 mmol, 4.08 mg), and 3 Å MS (10 mg) were dissolved in solvent *i*-PrOH (1 mL) under nitrogen atmosphere at 0 °C. The reaction mixture was stirred for 12 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 30:1 to 10:1, v/v) gave the desired products **15**.

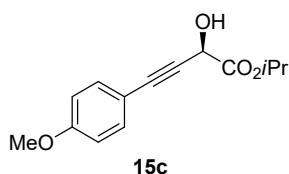


15a: Prepared according to the general procedure VI above and obtained as yellow oil (20.5 mg, 94% yield, 92% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -18.8$ ($c = 0.33$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, $J = 6.0$ Hz, 2H), 7.33 (t, $J = 7.9$ Hz, 3H), 5.24 – 5.14 (m, 1H), 5.13 (s, 1H), 5.01 (d, $J = 7.3$ Hz,

1H), 3.20 (d, $J = 7.4$ Hz, 1H), 1.34 (s, 3H), 1.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.9, 131.9, 128.7, 128.3, 121.9, 85.2, 84.4, 71.0, 62.1, 21.7, 21.5 ppm. IR (KBr, cm^{-1}): 3458, 2982, 2931, 2226, 1740, 1599, 1491, 1376, 1270, 1146, 1103, 990, 758, 691, 528. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 241.0841, found 241.0843. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 9.3 min (major) and 8.2 min (minor).

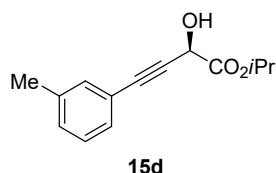


15b: Prepared according to the general procedure VI above and obtained as yellow oil (21.7 mg, 92% yield, 90% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_{\text{D}}^{30} = -62.2$ ($c = 0.27$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.41 (dd, $J = 8.3, 5.6$ Hz, 2H), 6.99 (t, $J = 8.6$ Hz, 2H), 5.22 – 5.11 (m, 1H), 5.00 (d, $J = 7.0$ Hz, 1H), 3.35 (d, $J = 7.2$ Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.9, 162.8 (d, $^1J_{\text{C-F}} = 250.7$ Hz), 133.8 (d, $^3J_{\text{C-F}} = 8.3$ Hz), 118.0 (d, $^4J_{\text{C-F}} = 3.7$ Hz), 115.6 (d, $^2J_{\text{C-F}} = 22.3$ Hz), 84.2, 84.1, 71.0, 62.0, 21.6, 21.5 ppm. IR (KBr, cm^{-1}): 3471, 2984, 2937, 2229, 1741, 1601, 1507, 1468, 1377, 1271, 1231, 1104, 838, 798, 531. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{FO}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 259.0746, found 259.0759. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 9.7 min (major) and 8.0 min (minor).

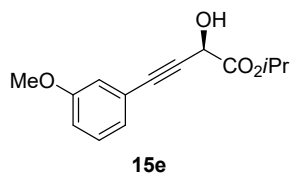


15c: Prepared according to the general procedure VII above and obtained as yellow oil (23.3 mg, 94% yield, 95% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_{\text{D}}^{30} = -20.8$ ($c = 0.34$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 5.22 – 5.12 (m, 1H), 5.00 (d, $J = 6.9$ Hz, 1H), 3.80 (s, 3H), 3.23 (d, $J = 7.1$ Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 160.0, 133.4, 114.0, 113.9, 85.3, 83.2, 70.8, 62.1, 55.3, 21.7, 21.5 ppm.

IR (KBr, cm^{-1}): 3467, 2982, 2936, 2840, 2225, 1740, 1606, 1510, 1465, 1291, 1250, 1175, 1105, 1091, 834, 790, 537. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 271.0946, found 271.0957. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL}\cdot\text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 16.8 min (major) and 13.7 min (minor).

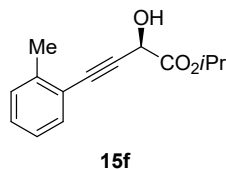


15d: Prepared according to the general procedure VII above and obtained as yellow oil (19.2 mg, 83% yield, 90% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_{\text{D}}^{30} = -32.3$ ($c = 1.43$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, $J = 12.8 \text{ Hz}$, 2H), 7.22 (t, $J = 7.5 \text{ Hz}$, 1H), 7.17 (d, $J = 7.5 \text{ Hz}$, 1H), 5.23 – 5.16 (m, 1H), 5.02 (d, $J = 7.4 \text{ Hz}$, 1H), 3.20 (d, $J = 7.5 \text{ Hz}$, 1H), 2.34 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 138.0, 132.4, 129.7, 129.0, 128.2, 121.8, 85.4, 84.1, 70.9, 62.1, 21.7, 21.5, 21.2 ppm. IR (KBr, cm^{-1}): 3457, 2983, 2933, 2231, 1740, 1602, 1485, 1275, 1208, 1103, 1022, 786, 691, 589, 442. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 255.0997, found 255.1001. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL}\cdot\text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 10.5 min (major) and 8.8 min (minor).

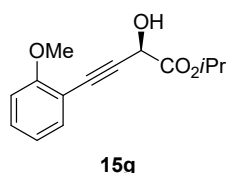


15e: Prepared according to the general procedure VII above and obtained as yellow oil (22.8 mg, 92% yield, 90% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_{\text{D}}^{30} = -41.5$ ($c = 0.93$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 7.22 (t, $J = 8.0 \text{ Hz}$, 1H), 7.04 (d, $J = 7.6 \text{ Hz}$, 1H), 6.97 (s, 1H), 6.89 (dd, $J = 8.3, 2.1 \text{ Hz}$, 1H), 5.22 – 5.14 (m, 1H), 5.01 (s, 1H), 3.79 (s, 3H), 3.20 (s, 1H), 1.34 (s, 3H), 1.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 169.9, 159.3, 129.4, 124.4, 122.9, 116.7, 115.4, 85.1, 84.2, 71.0, 62.0, 55.3, 21.7, 21.5 ppm. IR (KBr, cm^{-1}): 3457, 2982, 2937, 2232, 1740, 1601, 1483, 1287, 1205, 1103, 1045, 786, 687, 584. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}^+$

(M+Na)⁺ 271.0946, found 271.0961. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 10.6 min (major) and 9.8 min (minor).

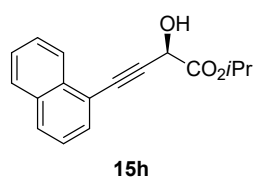


15f: Prepared according to the general procedure VI above and obtained as yellow oil (22.7 mg, 98% yield, 92% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -25.6$ ($c = 0.50$, CH_2Cl_2). ¹H NMR (500 MHz, CDCl_3) δ 7.39 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.33 – 7.27 (m, 1H), 6.91 – 6.83 (m, 2H), 5.23 – 5.13 (m, 1H), 5.06 (d, $J = 7.6$ Hz, 1H), 3.85 (s, 3H), 3.19 (d, $J = 7.6$ Hz, 1H), 1.34 (d, $J = 2.8$ Hz, 3H), 1.33 (d, $J = 2.8$ Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl_3) δ 170.0, 160.4, 133.9, 130.3, 120.4, 111.3, 110.8, 88.4, 81.7, 70.7, 62.3, 55.7, 21.7, 21.4 ppm. IR (KBr, cm^{-1}): 3472, 2982, 2937, 2839, 2230, 1740, 1596, 1493, 1464, 1263, 1146, 1106, 1023, 755, 595. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Na}^+$ (M+Na)⁺ 255.0997, found 255.1004. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 8.8 min (major) and 7.9 min (minor).

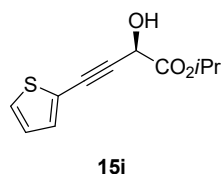


15g: Prepared according to the general procedure VI above and obtained as yellow oil (23.5 mg, 95% yield, 92% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -34.0$ ($c = 0.43$, CH_2Cl_2). ¹H NMR (500 MHz, CDCl_3) δ 7.39 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.32 – 7.27 (m, 1H), 6.91 – 6.84 (m, 2H), 5.21 – 5.14 (m, 1H), 5.06 (d, $J = 7.4$ Hz, 1H), 3.85 (s, 3H), 3.26 (d, $J = 7.6$ Hz, 1H), 1.34 (d, $J = 2.8$ Hz, 3H), 1.32 (d, $J = 2.8$ Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl_3) δ 170.0, 160.37, 133.8, 130.3, 120.4, 111.2, 110.7, 88.5, 81.7, 70.7, 62.3, 55.7, 21.7, 21.5 ppm. IR (KBr, cm^{-1}): 3457, 2982, 2937, 2839, 2230, 1739, 1493, 1262, 1104, 1081, 754, 554. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}^+$ (M+Na)⁺ 271.0946, found 271.0954. Daicel Chiralpak AD-H, n-

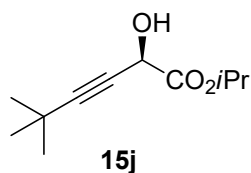
hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 13.6 min (major) and 12.7 min (minor).



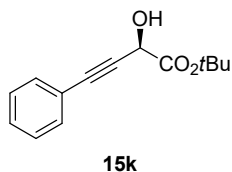
15h: Prepared according to the general procedure VI above and obtained as yellow oil (25.4 mg, 95% yield, 93% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -17.0$ ($c = 0.43$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.30 (d, $J = 8.2 \text{ Hz}$, 1H), 7.85 (d, $J = 8.1 \text{ Hz}$, 2H), 7.69 (d, $J = 7.1 \text{ Hz}$, 1H), 7.57 – 7.50 (m, 2H), 7.42 (t, $J = 7.7 \text{ Hz}$, 1H), 5.24 (p, $J = 6.3 \text{ Hz}$, 1H), 5.18 (d, $J = 6.6 \text{ Hz}$, 1H), 3.33 (d, $J = 7.0 \text{ Hz}$, 1H), 1.40 (s, 3H), 1.37 (s, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.0, 133.4, 133.1, 130.8, 129.4, 128.3, 126.9, 126.5, 126.0, 125.1, 119.5, 89.3, 83.4, 71.1, 62.3, 21.7, 21.6 ppm. IR (KBr, cm^{-1}): 3454, 2981, 2931, 2227, 1740, 1394, 1276, 1211, 1105, 1077, 801, 774, 566, 438. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 291.0997, found 291.1005. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 10.0 min (major) and 9.0 min (minor).



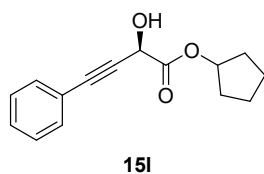
15q: Prepared according to the general procedure VII above and obtained as yellow oil (18.4 mg, 82% yield, 84% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -10.8$ ($c = 0.67$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.27 (d, $J = 5.2 \text{ Hz}$, 1H), 7.23 (d, $J = 3.6 \text{ Hz}$, 1H), 6.97 (dd, $J = 5.1, 3.8 \text{ Hz}$, 1H), 5.17 (p, $J = 6.3 \text{ Hz}$, 1H), 5.02 (d, $J = 7.2 \text{ Hz}$, 1H), 3.24 (d, $J = 7.3 \text{ Hz}$, 1H), 1.34 (s, 3H), 1.32 (s, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.6, 133.0, 127.9, 127.0, 121.8, 100.0, 88.3, 78.7, 71.1, 62.2, 21.7, 21.5 ppm. IR (KBr, cm^{-1}): 3421, 2922, 1740, 1694, 1476, 1393, 1066. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 247.0405, found 247.0408. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 10.4 min (major) and 9.3 min (minor).



15j: Prepared according to the general procedure VI above and obtained as yellow oil (19.1 mg, 96% yield, 94% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -13.7$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.18 – 5.10 (m, 1H), 4.75 (d, $J = 7.4$ Hz, 1H), 2.95 (d, $J = 7.5$ Hz, 1H), 1.30 (t, $J = 6.1$ Hz, 6H), 1.21 (s, 9H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.5, 94.3, 74.4, 70.3, 61.7, 30.6, 27.4, 21.6, 21.4 ppm. IR (KBr, cm^{-1}): 3455, 2934, 1740, 1504, 1461, 1356, 1150, 1102, 972, 755, 593, 411. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 221.1154, found 221.1158. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 20.5 min (major) and 19.0 min (minor).

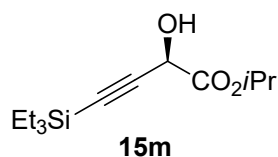


15k: Prepared according to the general procedure VI above and obtained as yellow oil (21.3 mg, 92% yield, 86% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -19.1$ ($c = 1.05$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.44 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.36 – 7.29 (m, 3H), 4.92 (d, $J = 7.3$ Hz, 1H), 3.18 (d, $J = 7.3$ Hz, 1H), 1.55 (s, 9H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.5, 131.9, 128.8, 128.3, 122.1, 84.9, 84.8, 84.0, 62.3, 27.9 ppm. IR (KBr, cm^{-1}): 3445, 2956, 2851, 2488, 1741, 1604, 1464, 1305, 1101, 993, 549, 451. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 242.0919, found 242.0922. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 9.2 min (major) and 8.0 min (minor).

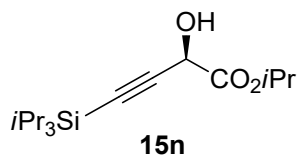


15l: Prepared according to the general procedure VI above and obtained as yellow oil (23.1 mg, 95% yield, 90% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1),

$[\alpha]_D^{30} = -22.6$ ($c = 1.21$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 (d, $J = 7.1$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 3H), 5.37 – 5.32 (m, 1H), 5.01 (d, $J = 6.1$ Hz, 1H), 3.25 (d, $J = 6.9$ Hz, 1H), 1.95 – 1.86 (m, 2H), 1.78 (dd, $J = 22.1, 10.6$ Hz, 4H), 1.63 (s, 2H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.2, 131.9, 128.9, 128.3, 121.9, 85.2, 84.5, 80.1, 62.0, 32.6, 32.5, 23.6, 23.6 ppm. IR (KBr, cm^{-1}): 3466, 2964, 2873, 2227, 1739, 1599, 1491, 1269, 1208, 1084, 1031, 758, 692, 528. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 267.0997, found 267.0999. Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, $v = 1.0$ mL \cdot min $^{-1}$, $\lambda = 254$ nm, retention time: 10.9 min (major) and 9.6 min (minor).

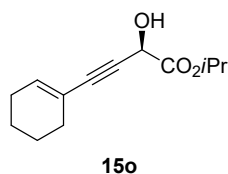


15m: Prepared according to the general procedure VI above and obtained as yellow oil (24.5 mg, 96% yield, 84% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -15.6$ ($c = 1.01$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.20 – 5.08 (m, 1H), 4.79 (s, 1H), 3.07 (s, 1H), 1.30 (t, $J = 6.1$ Hz, 6H), 0.98 (t, $J = 7.9$ Hz, 9H), 0.60 (q, $J = 7.9$ Hz, 6H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.9, 101.5, 88.1, 70.8, 62.0, 21.6, 21.4, 7.3, 4.1 ppm. IR (KBr, cm^{-1}): 3453, 2911, 2877, 2838, 1740, 1727, 1672, 1504, 1461, 1249, 1165, 1110, 1021, 839. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{24}\text{O}_3\text{SiNa}^+$ ($\text{M}+\text{Na}$) $^+$ 279.1392, found 279.1395. Daicel Chiralpak AS-H, n-hexane/2-propanol = 95/5, $v = 0.5$ mL \cdot min $^{-1}$, $\lambda = 210$ nm, retention time: 9.8 min (major) and 8.9 min (minor).

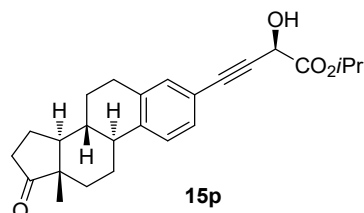


15n: Prepared according to the general procedure VI above and obtained as yellow oil (29.2 mg, 98% yield, 82% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -15.6$ ($c = 1.01$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.14 (d, $J = 6.2$ Hz, 1H), 4.80 (s, 1H), 3.05 (s, 1H), 1.30 (t, $J = 6.9$ Hz, 6H), 1.06 (s, 21H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.9, 102.3, 87.0, 70.8, 62.1, 21.7, 21.4, 18.5, 11.1, 1.0 ppm. IR (KBr, cm^{-1}): 3355, 2943, 2865, 1740, 1605, 1512, 1465, 1248, 1175, 1105, 1029, 884. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{30}\text{O}_3\text{SiNa}^+$ ($\text{M}+\text{Na}$) $^+$ 321.1862, found 321.1864. Daicel

Chiralpak AS-H, n-hexane/2-propanol = 95/5, $v = 0.5 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 210 \text{ nm}$, retention time: 9.1 min (major) and 7.9 min (minor).



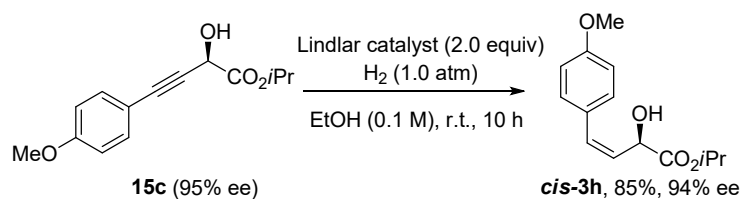
15o: Prepared according to the general procedure VI above and obtained as yellow oil (21.3 mg, 96% yield, 87% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -29.4$ ($c = 0.93$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.17 – 6.12 (m, 1H), 5.19 – 5.09 (m, 1H), 4.88 (s, 1H), 3.03 (s, 1H), 2.09 (d, $J = 5.0 \text{ Hz}$, 4H), 1.60 (dd, $J = 10.1, 5.3 \text{ Hz}$, 4H), 1.31 (d, $J = 6.3 \text{ Hz}$, 6H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.2, 136.5, 119.7, 87.1, 81.8, 70.7, 62.0, 29.7, 28.8, 25.6, 22.2, 21.7, 21.5, 21.4 ppm. IR (KBr, cm^{-1}): 3455, 2942, 2908, 2862, 2840, 2179, 1740, 1601, 1499, 1249, 1164, 1025, 835, 531. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 245.1154, found 245.1155. Daicel Chiralpak AD-H, n-hexane/2-propanol = 75/25, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, retention time: 6.7 min (major) and 6.4 min (minor).



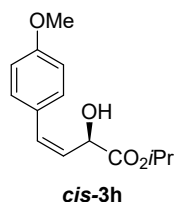
15p: Prepared according to the general procedure VI above and obtained as yellow oil (38.6 mg, 98% yield, 89% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -22.9$ ($c = 0.63$, CH_2Cl_2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.47 – 7.39 (m, 2H), 7.34 (d, $J = 8.1 \text{ Hz}$, 1H), 5.24 – 5.15 (m, 1H), 2.96 – 2.89 (m, 2H), 2.52 (dd, $J = 19.0, 8.8 \text{ Hz}$, 1H), 2.42 (dd, $J = 12.7, 3.8 \text{ Hz}$, 1H), 2.36 – 2.30 (m, 1H), 2.20 – 2.12 (m, 1H), 2.09 – 1.96 (m, 3H), 1.70 – 1.56 (m, 4H), 1.56 – 1.43 (m, 4H), 1.40 (d, $J = 6.2 \text{ Hz}$, 6H), 0.92 (s, 3H) ppm. $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.0, 140.9, 136.6, 132.3, 129.2, 125.3, 119.3, 85.3, 83.8, 70.9, 62.1, 50.5, 47.9, 44.5, 37.9, 35.8, 31.6, 29.1, 26.3, 25.6, 21.7, 21.6, 21.5, 13.8 ppm. IR (KBr, cm^{-1}): 3453, 2931, 2225, 1739, 1459, 1261, 1104, 1008, 822. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 417.2042, found 417.2044.

Daicel Chiralpak AD-H, n-hexane/2-propanol = 75/25, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$,
retention time: 9.5 min (major) and 8.1 min (minor).

J) Synthesis of *cis*-allyl alcohol **3h**



Reaction procedure VII: Take starting material (*R*)-**15c** (49 mg, 0.2 mmol), Lindlar catalyst (42.5 mg, 0.4 mmol) and ethanol (2 mL) in a round bottom flask, fit with a balloon fill with H₂. Stirring the reaction mixture at room temperature for 10 h. Then, the reaction solution was filtrated, and the corresponding solution was concentrated under reduced pressure. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1, v/v) gave the desired products *cis*-**3h**.



***cis*-3h:** Prepared according to the reaction procedure VII above and obtained as yellow oil (45.0 mg, 85% yield, 94% ee), eluent: petroleum ether/ethyl acetate (30:1 to 10:1), $[\alpha]_D^{30} = -19.3$ ($c = 0.72$, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.73 (d, $J = 11.3$ Hz, 1H), 5.52 (dd, $J = 11.1, 9.7$ Hz, 1H), 5.15 – 5.09 (m, 1H), 4.99 (dd, $J = 9.3, 5.0$ Hz, 1H), 3.82 (s, 3H), 3.09 (d, $J = 5.3$ Hz, 1H), 1.31 (d, $J = 6.3$ Hz, 3H), 1.28 (d, $J = 6.3$ Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 172.6, 158.3, 133.1, 129.3, 127.5, 125.0, 112.7, 69.1, 66.5, 54.3, 20.7 ppm. Daicel Chiralpak AD-H, n-hexane/2-propanol = 75/25, $v = 1.0$ mL·min⁻¹, $\lambda = 254$ nm, retention time: 8.7 min (major) and 6.8 min (minor).

IV. X-ray Structure

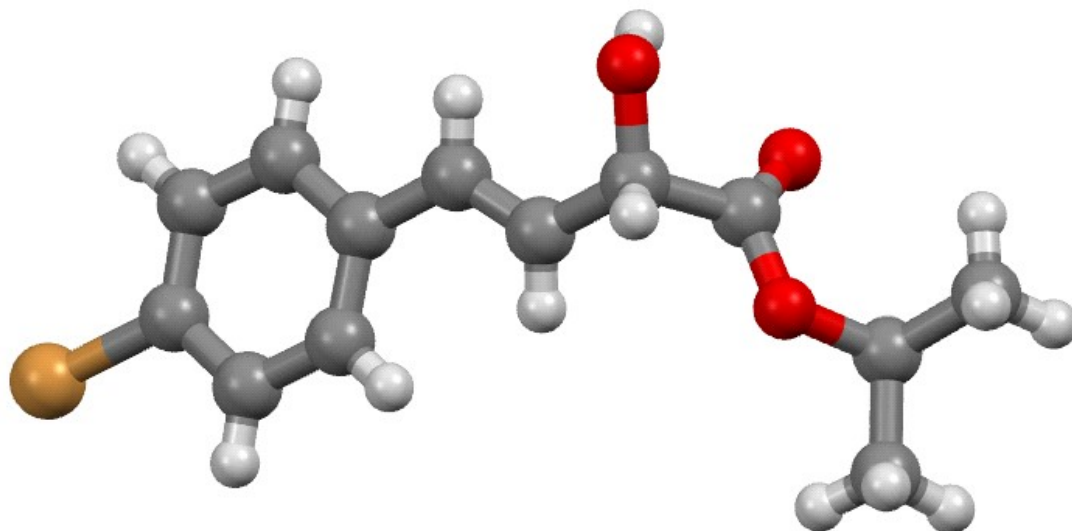


Figure S1. X-ray Structure of Compound 3d (CCDC 2131745)

V. Computational Data

All of the DFT calculations conducted in this study were carried out using the Gaussian09 programs. DFT method B3LYP/D3^{1,2} with a standard 6-31+G(d) basis set (LANL08-f³ basis set for Sc atoms) was used for the geometry optimizations in solution phase (solvent = 2-isopropanol) with SMD solvent model. The M06 functional, proposed by Truhlar et al.,⁴ was used with a 6-311+G(d,p) basis set (LANL08-f basis set for Sc atoms) to calculate the single point energies. The solvent effects were taken into consideration using single point calculations based on the gas-phase stationary points with a SMD continuum solvation model.⁵ The energies presented in this paper are the M06 calculated Gibbs free energies in 2-isopropanol solvent with B3LYP-D3 calculated thermodynamic corrections. Molecular structures were visualized in CYLview.

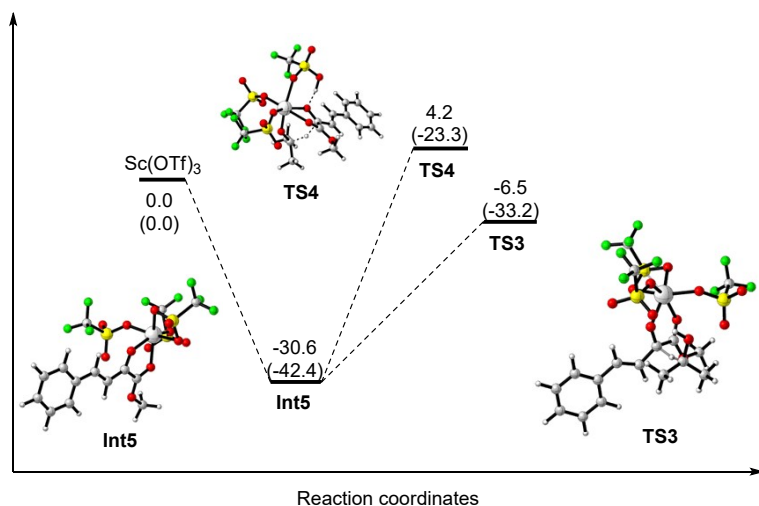


Figure S2. DFT-Computed free-energy profiles on the Sc(OTf)₃ catalyzed-Meerwein-Ponndorf-Verley reduction of β,γ -unsaturated α -keto ester

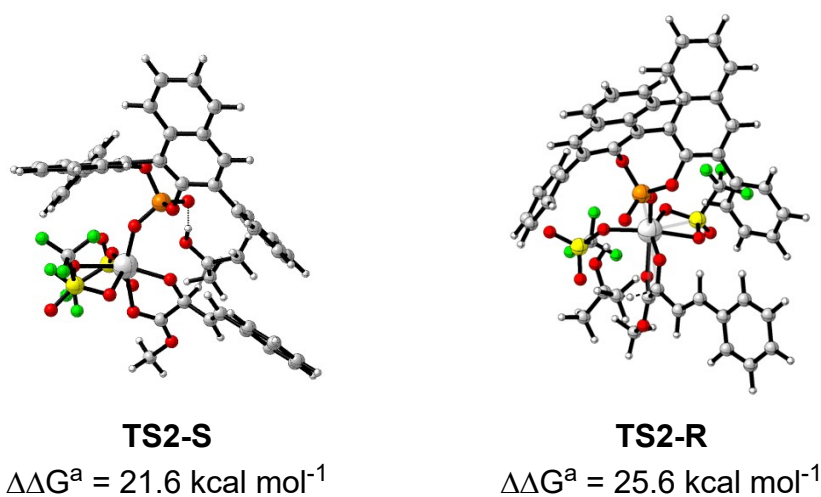


Figure S3. Analysis of the enantioinduction model, with optimized structures of transition states (TS2-S and TS2-R) in the outer-sphere transfer hydrogenation step.

Table S7. The computed energies of the intermediates and transition states

Entry	E	ZPE	Ecorr	Hcorr	Gcorr
Sc(OTf) ₃	-2930.862039	0.087273	0.112705	0.113650	0.029191
Sub: 2a	-650.587860	0.187697	0.200494	0.201438	0.146367
PA: (<i>R</i>)- 1i	-1873.711834	0.445651	0.473863	0.474807	0.386344
<i>i</i> PrOH	-194.2761094	0.108546	0.11384	0.114784	0.081311
<i>i</i> PrO ⁻	-193.7718293	0.093724	0.098676	0.099621	0.06674
TfOH	-961.9724966	0.038418	0.046139	0.047083	0.005431
TfO ⁻	-961.563247	0.026969	0.034202	0.035146	-0.00585
Int1	-3843.036608	0.507149	0.552774	0.553718	0.428103
Int2	-4493.672731	0.697297	0.757284	0.758228	0.599149
Int3	-4687.550851	0.794628	0.861388	0.862332	0.688333
TS1-S	-4687.526669	0.790656	0.855851	0.856795	0.68887
TS1-R	-4687.518512	0.78933	0.855169	0.856113	0.684478
Int4	-4687.578581	0.794412	0.860932	0.861876	0.689896
TS2-S	-4687.522291	0.790755	0.856499	0.857444	0.686337
TS2-R	-4687.517585	0.790588	0.855387	0.856331	0.688067
Prod: 3a	-651.790105	0.210344	0.223873	0.224817	0.168443
CH ₃ COCH ₃	-193.081002	0.084253	0.089404	0.090349	0.056779
Int5	-3581.519549	0.27591	0.316245	0.31719	0.196507
TS3	-3775.778127	0.382323	0.428112	0.429056	0.2986
TS4	-3775.760322	0.380476	0.426143	0.427087	0.297893

Coordinates of the intermediates and transition states:

1) Sc(OTf)₃

S	-2.398184	-1.825304	0.08212
O	-1.68326	-1.485218	-1.211916
O	-1.502963	-1.180087	1.130119
C	3.118507	-2.517834	0.261698
S	2.69077	-0.790738	-0.314907
F	3.920538	-2.436142	1.316816
F	1.989638	-3.146566	0.591889
F	3.722517	-3.159423	-0.732061
O	1.852738	-0.210952	0.819831
O	3.927418	-0.113562	-0.661984
O	1.656516	-1.012997	-1.40178
Sc	-0.060137	-0.239109	-0.226156
C	0.928436	3.523267	0.543096
S	-0.331298	2.571193	-0.461523
F	0.284487	4.261542	1.440562
F	1.744277	2.669035	1.152912
F	1.616256	4.299937	-0.287149
O	-1.011165	1.619454	0.512447
O	-1.159575	3.550781	-1.143083
O	0.490383	1.612421	-1.309385
C	-3.951547	-0.779847	0.097941
F	-3.644715	0.466838	-0.251134
F	-4.454439	-0.798614	1.328192
F	-4.822209	-1.293387	-0.763993
O	-2.807248	-3.202793	0.300439

2) Sub: 2a

C	3.111497	-1.13199	0.00145
C	4.41099	-0.63008	0.002062
C	4.623894	0.750563	0.000552
C	3.530515	1.626203	-0.00167
C	2.232318	1.128122	-0.00222
H	2.944196	-2.20623	0.002566
H	5.255329	-1.31386	0.00366
H	5.63616	1.145736	0.001013
H	3.695525	2.700163	-0.00301
H	1.396497	1.821212	-0.00418
C	-1.76893	-0.96908	-0.00037
C	-3.10934	-0.19365	-3.4E-05
O	-1.84989	-2.19425	-0.00115
O	-4.18465	-0.7576	-0.00077

O	-2.94266	1.131445	0.001079
C	-4.1517	1.926546	0.001512
H	-3.8174	2.963879	0.002422
H	-4.74217	1.713141	-0.89359
H	-4.74253	1.711644	0.89602
C	2.000073	-0.26442	-0.0005
C	0.668446	-0.8527	-0.00064
H	0.638945	-1.94198	-0.00124
C	-0.52333	-0.20694	0.000156
H	-0.5935	0.874023	0.001192

3) PA: (R)-1i

C	-2.589761	4.247086	2.359739
C	-1.18413	4.25331	2.189652
C	-0.558164	3.259342	1.469072
C	-1.305942	2.204154	0.877343
C	-2.724204	2.17625	1.087881
C	-3.340527	3.225774	1.823961
C	-0.700924	1.147462	0.114931
C	-1.505035	0.104215	-0.308885
C	-2.90745	0.037073	-0.087584
C	-3.488678	1.091576	0.589826
C	0.762929	1.10746	-0.17023
C	1.431121	2.152608	-0.894206
C	2.849311	2.061988	-1.08322
C	3.553113	0.935247	-0.590872
C	2.912101	-0.108693	0.048902
C	1.50692	0.010255	0.230883
C	0.744143	3.258122	-1.467693
C	1.428599	4.238287	-2.152937
C	2.83494	4.16798	-2.302741
C	3.527376	3.098704	-1.782381
O	-0.902082	-0.973866	-0.978673
O	0.840956	-1.059148	0.857299
P	-0.048278	-2.026512	-0.087514
O	0.644449	-3.000628	-0.958503
O	-1.006604	-2.599444	1.05598
C	-3.706732	-1.140055	-0.515243
C	3.665472	-1.307356	0.499829
C	-3.609119	-1.668416	-1.81395
C	-4.377909	-2.769638	-2.190288
C	-5.25296	-3.364529	-1.276725
C	-5.357311	-2.847593	0.016687

C	-4.590046	-1.744652	0.394679
C	4.591333	-1.913155	-0.365712
C	5.330951	-3.022617	0.045847
C	5.157003	-3.544976	1.329436
C	4.238817	-2.949378	2.199004
C	3.497513	-1.841588	1.789007
H	-3.069541	5.041909	2.924301
H	-0.592005	5.047498	2.636359
H	0.520038	3.275954	1.359549
H	-4.418159	3.196984	1.965184
H	-4.561511	1.087094	0.762592
H	4.629617	0.891683	-0.731477
H	-0.33369	3.32385	-1.372872
H	0.882827	5.07143	-2.587446
H	3.360988	4.952779	-2.839407
H	4.604756	3.021968	-1.906691
H	-1.51941	-3.374743	0.754765
H	-4.294665	-3.161998	-3.200508
H	-6.030835	-3.306337	0.735995
H	6.0376	-3.482449	-0.640216
H	4.101187	-3.345665	3.201775
H	5.730445	-4.410954	1.649663
H	4.717114	-1.52131	-1.371366
H	2.793892	-1.37979	2.474121
H	-4.660302	-1.356915	1.407312
H	-5.847285	-4.225734	-1.570654
H	-2.937133	-1.208366	-2.531174

4) *i*PrOH

O	0.000003	1.418275	0.022465
C	0	0.03624	-0.37599
H	0.000003	0.071608	-1.472908
C	1.270206	-0.666977	0.100357
H	2.160329	-0.132788	-0.250907
H	1.30075	-0.701377	1.197854
H	1.315103	-1.697372	-0.27223
C	-1.270205	-0.666979	0.100354
H	-1.300739	-0.701405	1.197851
H	-2.160329	-0.132779	-0.250891
H	-1.315107	-1.697366	-0.272255
H	-0.000038	1.431573	0.995448

5) *i*PrO⁻

O	0	1.432117	0.149343
C	0	0.170358	-0.333913
H	0	0.10543	-1.474319
C	1.26273	-0.636936	0.087209
H	2.166459	-0.096776	-0.228274
H	1.298654	-0.721131	1.18416
H	1.306336	-1.652734	-0.337616
C	-1.26273	-0.636936	0.087209
H	-1.298655	-0.721131	1.18416
H	-2.166459	-0.096775	-0.228273
H	-1.306336	-1.652733	-0.337617

6) TfOH

H	-1.33736	1.967997	0.061736
C	1.011558	0.008433	0.0043
S	-0.852835	-0.140144	-0.055936
F	1.374541	1.132066	-0.610944
F	1.413764	0.03136	1.270348
F	1.534108	-1.042535	-0.621793
O	-1.275207	1.220075	0.697468
O	-1.24036	-0.093527	-1.460554
O	-1.232977	-1.234586	0.821704

7) TfO⁻

C	0.953031	-0.000154	0.000441
S	-0.906445	0.000102	-0.000048
F	1.431066	-1.137452	0.535008
F	1.430789	0.105395	-1.251954
F	1.432079	1.031458	0.717627
O	-1.243478	-1.19233	-0.81562
O	-1.246035	-0.10967	1.439733
O	-1.243046	1.302586	-0.625113

8) Int1

C	7.608333	0.090586	-1.19651
C	6.799583	1.10903	-1.7572
C	5.484214	1.255107	-1.3728
C	4.907781	0.387438	-0.40472
C	5.716361	-0.66908	0.132156
C	7.07455	-0.78166	-0.27549
C	3.542696	0.499777	0.028704

C	3.057622	-0.47716	0.878488
C	3.82548	-1.53905	1.421717
C	5.153621	-1.59697	1.044145
C	2.644619	1.601312	-0.4287
C	2.951175	2.983649	-0.1806
C	2.048274	3.987165	-0.66519
C	0.855611	3.603218	-1.32679
C	0.515726	2.276743	-1.51536
C	1.445343	1.307885	-1.05277
C	4.091087	3.40312	0.559547
C	4.345386	4.741895	0.76596
C	3.476297	5.73265	0.247777
C	2.348552	5.360471	-0.44739
O	1.676986	-0.44568	1.218027
O	1.097984	-0.05847	-1.22455
P	0.656272	-0.87141	0.075354
O	-0.74407	-0.54393	0.566109
O	0.85927	-2.37307	-0.30827
C	3.226885	-2.55588	2.324146
C	-0.78517	1.898846	-2.12668
C	2.442038	-2.18478	3.429868
C	1.901396	-3.15646	4.272016
C	2.132838	-4.51286	4.022762
C	2.913169	-4.8913	2.927409
C	3.456042	-3.92051	2.083744
C	-1.96566	2.521774	-1.68062
C	-3.20604	2.18089	-2.22923
C	-3.2801	1.234223	-3.25704
C	-2.10966	0.628137	-3.72293
C	-0.87332	0.951879	-3.16086
H	8.645781	-0.00579	-1.50434
H	7.219583	1.780148	-2.50132
H	4.878496	2.035066	-1.81969
H	7.679378	-1.57831	0.150046
H	5.785503	-2.38287	1.44819
H	0.184138	4.379108	-1.68369
H	4.763917	2.66122	0.973328
H	5.220601	5.039901	1.336662
H	3.696249	6.783694	0.41278
H	1.661254	6.108959	-0.83333
H	1.303481	-2.85347	5.127739
H	3.095239	-5.94325	2.72379
H	-4.10683	2.662519	-1.85936
H	-2.15793	-0.10599	-4.52084

H	-4.24153	0.970182	-3.6888
H	-1.91517	3.254093	-0.88033
H	0.027392	0.471635	-3.52899
H	4.047577	-4.2189	1.222564
H	1.708513	-5.26842	4.678709
H	2.267618	-1.13344	3.636873
C	-2.13487	-3.01586	-3.00919
S	-2.71104	-3.1702	-1.24275
F	-1.87319	-4.23149	-3.48232
F	-1.02566	-2.27197	-3.04321
F	-3.08705	-2.44	-3.74032
O	-1.52844	-3.62721	-0.47871
O	-3.89216	-4.02556	-1.2337
O	-3.04857	-1.70109	-0.93994
C	-5.00006	1.634788	3.096923
S	-4.35443	1.951447	1.373618
F	-4.50431	0.476272	3.5309
F	-6.32598	1.575487	3.052392
F	-4.6066	2.623823	3.890822
O	-4.73564	0.708296	0.582854
O	-2.84849	1.807759	1.478618
O	-4.89469	3.226384	0.931154
Sc	-2.71249	-0.14506	0.338542
H	0.011443	-2.90137	-0.38264

9) Int2

C	-7.628275	-1.567975	-2.08449
C	-6.825917	-2.732396	-2.165165
C	-5.597327	-2.785281	-1.543019
C	-5.105765	-1.67175	-0.807679
C	-5.901669	-0.479993	-0.759236
C	-7.172586	-0.465223	-1.398618
C	-3.830087	-1.674958	-0.148652
C	-3.391904	-0.491113	0.41889
C	-4.153832	0.705396	0.486236
C	-5.410016	0.669721	-0.092586
C	-2.96703	-2.8909	-0.088494
C	-3.409113	-4.11019	0.530856
C	-2.520807	-5.236473	0.540644
C	-1.214542	-5.109999	0.006622
C	-0.751824	-3.922685	-0.529275
C	-1.672722	-2.84426	-0.571587

C	-4.673654	-4.243482	1.168371
C	-5.054425	-5.438628	1.739678
C	-4.194333	-6.563214	1.707407
C	-2.951786	-6.459803	1.125224
O	-2.077404	-0.450037	0.95243
O	-1.212115	-1.622022	-1.125253
P	-0.879402	-0.445197	-0.106494
O	0.411771	-0.591198	0.670686
O	-0.951443	0.817901	-1.047335
C	-3.644451	1.939983	1.138296
C	0.661328	-3.770958	-0.961188
C	-2.983344	1.90169	2.380311
C	-2.578544	3.081286	3.006072
C	-2.83113	4.319834	2.408311
C	-3.478272	4.369486	1.171458
C	-3.873805	3.190539	0.538173
C	1.68553	-4.209798	-0.1042
C	3.024544	-4.087402	-0.475931
C	3.360788	-3.525098	-1.709714
C	2.350261	-3.084733	-2.568307
C	1.010282	-3.201118	-2.197136
H	-8.597006	-1.545302	-2.575752
H	-7.180656	-3.59152	-2.727885
H	-4.992746	-3.681514	-1.623757
H	-7.770568	0.440944	-1.344192
H	-6.042969	1.551128	-0.044447
H	-0.551258	-5.969727	0.040621
H	-5.34345	-3.392745	1.213952
H	-6.023727	-5.517487	2.22424
H	-4.5133	-7.500209	2.155341
H	-2.271574	-7.307649	1.113811
H	-0.294142	1.516281	-0.800238
H	-2.075498	3.031291	3.968049
H	-3.666331	5.325408	0.691608
H	3.802967	-4.416147	0.205414
H	2.604205	-2.63454	-3.522358
H	4.40283	-3.41704	-1.993186
H	1.42879	-4.629447	0.864697
H	0.232583	-2.854716	-2.870208
H	-4.361079	3.238399	-0.43168
H	-2.521238	5.237573	2.90051
H	-2.809396	0.949561	2.870544

C	1.152073	2.519684	2.484922
C	0.796625	3.001976	1.089827
O	1.749972	1.434352	2.585306
O	1.133225	2.160018	0.188836
C	4.542007	0.376731	-2.833529
S	2.72652	0.764015	-2.690328
F	5.019009	0.918133	-3.956106
F	4.736581	-0.943602	-2.859373
F	5.189086	0.895283	-1.782454
O	2.057366	0.0424	-3.77494
O	2.633531	2.228791	-2.657803
O	2.43104	0.12993	-1.326033
C	5.528134	-1.79613	1.171552
S	4.368366	-0.762455	2.208321
F	6.769049	-1.354078	1.355936
F	5.191896	-1.673709	-0.112701
F	5.439094	-3.069935	1.548251
O	4.327392	0.564369	1.473343
O	4.890604	-0.772415	3.566635
O	2.986262	-1.331934	1.975879
Sc	2.252398	0.390368	0.697078
C	-0.890778	5.769113	-0.823869
C	-1.244307	6.802002	0.084238
C	-1.248765	5.899002	-2.190233
C	-1.935686	7.91456	-0.366401
H	-0.971024	6.724364	1.130941
C	-1.946794	7.014452	-2.631789
H	-0.97539	5.110253	-2.885489
C	-2.290905	8.020722	-1.72113
H	-2.204816	8.704925	0.327402
H	-2.223515	7.106318	-3.677466
H	-2.836567	8.894826	-2.065515
O	0.783804	3.265735	3.475916
C	1.054814	2.785143	4.831525
H	2.134869	2.71589	4.974728
H	0.615093	3.536526	5.484083
H	0.57921	1.811691	4.965783
C	0.151486	4.222858	0.865164
H	-0.072282	4.840876	1.724147
C	-0.207727	4.58244	-0.422723
H	0.041552	3.882775	-1.21908

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C	8.101006	-0.51706	2.058861
C	7.468321	-1.78048	2.157305
C	6.25173	-2.00697	1.550608
C	5.602832	-0.97884	0.812997
C	6.225336	0.311035	0.747278
C	7.488651	0.506432	1.371919
C	4.336998	-1.16656	0.161743
C	3.73225	-0.06125	-0.41267
C	4.322492	1.229	-0.49578
C	5.574425	1.374944	0.074572
C	3.65573	-2.49365	0.103156
C	4.268706	-3.63715	-0.51629
C	3.547001	-4.87661	-0.53721
C	2.233145	-4.93756	-0.00958
C	1.605208	-3.82881	0.525907
C	2.362964	-2.62866	0.576576
C	5.54162	-3.58848	-1.14968
C	6.087915	-4.714	-1.72798
C	5.393329	-5.94792	-1.70701
C	4.14691	-6.02332	-1.12853
O	2.434033	-0.21014	-0.94583
O	1.732473	-1.48803	1.124287
P	1.221465	-0.37237	0.096346
O	-0.01751	-0.67987	-0.69161
O	1.138794	0.885901	1.050329
C	3.645669	2.373041	-1.16175
C	0.179415	-3.87583	0.941195
C	2.992902	2.226975	-2.40019
C	2.426142	3.330037	-3.03952
C	2.504083	4.599084	-2.45796
C	3.141095	4.755241	-1.2248
C	3.700742	3.651701	-0.57957
C	-0.76242	-4.45618	0.074682
C	-2.11375	-4.50047	0.417712
C	-2.54575	-3.96531	1.633465
C	-1.61542	-3.39528	2.507304
C	-0.26447	-3.34516	2.164306
H	9.063246	-0.35683	2.537483
H	7.945022	-2.57814	2.720483
H	5.776621	-2.97694	1.643927
H	7.955473	1.485859	1.303999
H	6.0796	2.334641	0.012405
H	1.698452	-5.88249	-0.0514

H	6.084877	-2.65168	-1.18734
H	7.059605	-4.65207	-2.21038
H	5.840804	-6.82774	-2.16117
H	3.59168	-6.95802	-1.12601
H	0.390549	1.485362	0.796626
H	1.929477	3.19792	-3.99712
H	3.191413	5.734016	-0.7568
H	-2.82813	-4.92723	-0.2784
H	-1.94328	-2.9646	3.447712
H	-3.60085	-3.97545	1.889028
H	-0.43668	-4.84544	-0.886
H	0.447	-2.89045	2.845731
H	4.178713	3.779339	0.387675
H	2.063372	5.457729	-2.95735
H	2.948619	1.252672	-2.8747
C	-1.14962	2.167204	-2.48432
C	-0.87482	2.754327	-1.10379
O	-1.57052	1.011087	-2.56243
O	-1.06021	1.92639	-0.17181
C	-3.98619	-0.20533	3.134911
S	-2.2375	0.377632	2.854572
F	-4.35701	0.103908	4.382776
F	-4.07394	-1.53028	2.969817
F	-4.82223	0.390787	2.275408
O	-1.45452	-0.23605	3.936402
O	-2.32599	1.845974	2.820223
O	-1.90943	-0.238	1.509011
C	-5.15785	-2.65815	-0.77356
S	-3.97587	-2.37644	-2.2169
F	-6.40608	-2.40344	-1.18082
F	-4.87209	-1.86094	0.262266
F	-5.0909	-3.93064	-0.36225
O	-4.63943	-1.36735	-3.05756
O	-3.76302	-3.71224	-2.7922
O	-2.72106	-1.85264	-1.53609
Sc	-2.13654	-0.03227	-0.58147
C	-4.74479	1.8436	-0.91229
H	-4.61103	2.214605	-1.9425
C	-4.57329	3.015269	0.057497
H	-5.32393	3.792707	-0.13135
H	-4.67995	2.667192	1.090837
H	-3.57835	3.461982	-0.05183
C	-6.12257	1.188022	-0.80319
H	-6.1969	0.343609	-1.49611

H	-6.28337	0.813913	0.21443
H	-6.91661	1.9065	-1.04086
O	-3.74867	0.876356	-0.66812
C	0.260326	5.902901	0.656738
C	0.5261	6.90378	-0.31026
C	0.493008	6.190971	2.022196
C	1.011945	8.142142	0.083603
H	0.353388	6.705382	-1.36262
C	0.98226	7.43319	2.409736
H	0.290881	5.425028	2.766126
C	1.243145	8.408611	1.441662
H	1.214648	8.906222	-0.66094
H	1.16151	7.644177	3.459742
H	1.625581	9.380069	1.742585
O	-0.88412	2.944606	-3.49766
C	-1.07806	2.389665	-4.83165
H	-2.12963	2.125863	-4.96395
H	-0.78498	3.186353	-5.51283
H	-0.44239	1.510081	-4.95318
C	-0.447	4.094003	-0.9446
H	-0.30498	4.685117	-1.83905
C	-0.21175	4.589057	0.315122
H	-0.39032	3.915259	1.152215

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C	8.153966	-0.351173	1.846945
C	7.56808	-1.637217	1.944444
C	6.338252	-1.894296	1.378111
C	5.629147	-0.875918	0.683539
C	6.204287	0.435737	0.6207
C	7.482607	0.663006	1.202713
C	4.349168	-1.095878	0.072706
C	3.687347	-0.003103	-0.462724
C	4.225334	1.310388	-0.532801
C	5.491581	1.488991	-0.004163
C	3.708591	-2.442902	0.013184
C	4.328493	-3.555375	-0.653783
C	3.631607	-4.808744	-0.693243
C	2.330098	-4.910035	-0.141406
C	1.697263	-3.831424	0.446062
C	2.435693	-2.621057	0.524533
C	5.582378	-3.461421	-1.319388
C	6.136103	-4.558186	-1.943939

C	5.467929	-5.806795	-1.940779
C	4.238875	-5.925038	-1.333108
O	2.380836	-0.193544	-0.965254
O	1.797866	-1.505542	1.121105
P	1.205162	-0.418377	0.106146
O	-0.028322	-0.833222	-0.64909
O	1.031911	0.845534	1.028236
C	3.479588	2.447943	-1.133148
C	0.273546	-3.908255	0.866413
C	2.783929	2.321012	-2.349728
C	2.146212	3.423067	-2.920609
C	2.191951	4.670286	-2.290224
C	2.874575	4.807322	-1.079465
C	3.505912	3.704858	-0.503003
C	-0.677399	-4.384517	-0.052255
C	-2.030522	-4.434274	0.285758
C	-2.451853	-4.015755	1.550759
C	-1.51096	-3.554743	2.475467
C	-0.159394	-3.492436	2.135493
H	9.127585	-0.166645	2.292643
H	8.091747	-2.427989	2.474638
H	5.899696	-2.881557	1.469179
H	7.913131	1.659065	1.136568
H	5.958218	2.468431	-0.059232
H	1.805527	-5.85907	-0.21076
H	6.105052	-2.512631	-1.344079
H	7.093141	-4.461928	-2.44948
H	5.921293	-6.663581	-2.431643
H	3.70275	-6.870776	-1.34386
H	0.231567	1.377958	0.72559
H	1.620514	3.30815	-3.864508
H	2.899913	5.767336	-0.572592
H	-2.754003	-4.778793	-0.446434
H	-1.832571	-3.210513	3.452758
H	-3.507086	-4.02766	1.805547
H	-0.355739	-4.688356	-1.044728
H	0.561344	-3.113392	2.85321
H	4.0142	3.81492	0.450829
H	1.693531	5.527031	-2.735481
H	2.761472	1.364903	-2.861546
C	-1.312243	2.024084	-2.39113
C	-1.339636	2.612294	-0.981364
O	-1.516752	0.810489	-2.511083
O	-1.202593	1.666687	-0.087418

C	-3.903798	-0.367234	3.295013
S	-2.152111	0.116205	2.890544
F	-4.204519	0.045078	4.530897
F	-4.048054	-1.696069	3.228982
F	-4.747221	0.204505	2.426172
O	-1.311482	-0.549932	3.893233
O	-2.149982	1.585924	2.86818
O	-2.004388	-0.520743	1.517533
C	-5.33022	-2.557909	-0.63381
S	-4.422099	-2.092402	-2.20754
F	-6.644636	-2.439495	-0.841552
F	-4.979204	-1.755374	0.382036
F	-5.056882	-3.823157	-0.293683
O	-5.138385	-0.918147	-2.724371
O	-4.42055	-3.315406	-3.02017
O	-3.026064	-1.765283	-1.690297
Sc	-2.102572	-0.226776	-0.540263
C	-3.912516	2.277453	-0.810516
H	-2.710654	2.793444	-1.036775
C	-4.295318	3.102666	0.401964
H	-4.302433	4.17227	0.173458
H	-5.303994	2.802457	0.715582
H	-3.605567	2.899761	1.226541
C	-4.595379	2.590948	-2.129871
H	-4.143747	2.016239	-2.943627
H	-5.647859	2.289693	-2.046375
H	-4.553713	3.659846	-2.357796
O	-3.685797	1.000495	-0.574138
C	0.21907	5.614906	0.825064
C	0.131657	6.752715	-0.00317
C	0.958274	5.7064	2.020357
C	0.783176	7.931748	0.345936
H	-0.451751	6.716001	-0.918164
C	1.615406	6.886556	2.365325
H	1.029223	4.835684	2.667636
C	1.533311	8.001764	1.527022
H	0.707064	8.801241	-0.30145
H	2.190497	6.936183	3.28594
H	2.044162	8.923274	1.793092
O	-1.123555	2.856455	-3.376612
C	-1.1282	2.303952	-4.726997
H	-2.107736	1.869313	-4.937117
H	-0.927755	3.153083	-5.377823
H	-0.345464	1.547856	-4.813118

C	-0.83499	3.965055	-0.740429
H	-0.841976	4.637373	-1.590701
C	-0.371951	4.328037	0.474551
H	-0.387083	3.583947	1.268822

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C	2.33405	0.765122	-2.52036
C	2.106533	1.904282	-1.53088
O	2.134177	-0.38762	-2.1216
O	1.427411	1.486447	-0.49209
C	3.167076	-1.12467	3.815485
S	1.864276	0.171905	3.491014
F	3.615511	-1.00492	5.069143
F	2.646552	-2.34628	3.648543
F	4.190539	-0.96922	2.969188
O	0.886626	0.028608	4.578233
O	2.590293	1.445144	3.385636
O	1.291517	-0.3092	2.163709
C	5.047165	-3.1711	0.617392
S	3.714995	-3.29176	-0.68238
F	6.037414	-4.01531	0.304018
F	5.53896	-1.9304	0.675234
F	4.548491	-3.50446	1.812465
O	4.276836	-2.65904	-1.88395
O	3.383379	-4.72176	-0.74873
O	2.590171	-2.48992	-0.03875
Sc	1.815381	-0.55456	0.136508
C	4.285698	1.281239	-0.25396
H	3.442219	1.817031	-1.09773
C	4.508965	2.476665	0.653347
H	4.942027	3.318859	0.106276
H	5.199849	2.176712	1.451803
H	3.565302	2.77909	1.116969
C	5.415974	0.884573	-1.18937
H	5.10148	0.067402	-1.84483
H	6.25273	0.523614	-0.57731
H	5.759616	1.734173	-1.78634
O	3.623676	0.276286	0.288143
C	1.275416	5.647677	-1.52737
C	1.557842	6.19495	-2.79664
C	0.817151	6.507706	-0.5093
C	1.391431	7.556645	-3.02989
H	1.893597	5.55189	-3.605

C	0.655712	7.871898	-0.74444
H	0.596454	6.094223	0.470676
C	0.941957	8.400403	-2.00598
H	1.60799	7.964768	-4.01344
H	0.305209	8.520583	0.053806
H	0.81236	9.46269	-2.19491
O	2.788098	1.087261	-3.69933
C	3.095827	-0.00693	-4.61771
H	3.738684	-0.73477	-4.12005
H	3.606017	0.466023	-5.4551
H	2.162135	-0.4717	-4.93694
C	2.016304	3.288958	-1.98904
H	2.475069	3.512714	-2.946
C	1.433463	4.231638	-1.21486
H	1.038935	3.917842	-0.24949
C	-8.49863	1.546776	-0.11868
C	-8.23819	0.297772	-0.73373
C	-6.99447	-0.28805	-0.6373
C	-5.94376	0.344832	0.082757
C	-6.19593	1.631077	0.666756
C	-7.49596	2.19976	0.5614
C	-4.63386	-0.22745	0.217472
C	-3.65673	0.533711	0.837142
C	-3.86037	1.830972	1.377799
C	-5.14471	2.337783	1.303439
C	-4.27377	-1.569	-0.33206
C	-4.93018	-2.77928	0.079778
C	-4.49319	-4.02608	-0.48095
C	-3.39322	-4.05343	-1.37492
C	-2.71687	-2.90423	-1.73493
C	-3.20798	-1.68113	-1.20798
C	-5.96297	-2.8061	1.057647
C	-6.56347	-3.99241	1.420524
C	-6.1636	-5.21596	0.830113
C	-5.1457	-5.23018	-0.09596
O	-2.34751	0.010245	0.907376
O	-2.5021	-0.5023	-1.55761
P	-1.48229	0.025247	-0.44249
O	-0.265	-0.83145	-0.22506
O	-1.18672	1.49606	-0.91151
C	-2.73027	2.641477	1.905193
C	-1.47322	-2.95169	-2.54827
C	-1.76829	2.116022	2.787275
C	-0.70925	2.907693	3.233314

C	-0.589	4.234143	2.8066
C	-1.54353	4.768461	1.937227
C	-2.60208	3.977446	1.487884
C	-0.43153	-3.80897	-2.15658
C	0.762321	-3.85503	-2.87908
C	0.931248	-3.04486	-4.00437
C	-0.10251	-2.19274	-4.40557
C	-1.29412	-2.14114	-3.6813
H	-9.48666	1.991809	-0.19759
H	-9.02605	-0.2018	-1.29089
H	-6.81062	-1.23989	-1.12253
H	-7.67671	3.168686	1.020154
H	-5.35547	3.317842	1.722216
H	-3.05823	-5.01083	-1.7644
H	-6.27538	-1.88216	1.530035
H	-7.34827	-3.98926	2.172141
H	-6.65213	-6.14169	1.121503
H	-4.81187	-6.16488	-0.5393
H	-0.2215	1.721113	-0.73277
H	0.017586	2.488834	3.921797
H	-1.46338	5.798246	1.600336
H	1.561923	-4.51233	-2.55201
H	0.017474	-1.56667	-5.28595
H	1.864652	-3.07243	-4.55968
H	-0.54981	-4.42068	-1.26631
H	-2.09261	-1.47686	-3.99748
H	-3.32539	4.390219	0.790107
H	0.239557	4.845665	3.154273
H	-1.8485	1.090115	3.130746

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C	7.946639	-1.977709	1.795475
C	7.082837	-3.097246	1.882437
C	5.817271	-3.05237	1.338349
C	5.348064	-1.882698	0.678621
C	6.209271	-0.738537	0.624268
C	7.51513	-0.822848	1.183078
C	4.041433	-1.788845	0.093411
C	3.627297	-0.564306	-0.407667
C	4.467627	0.581517	-0.488479
C	5.749325	0.456432	0.017788
C	3.118506	-2.957013	0.007378
C	3.477138	-4.147403	-0.714344

C	2.532711	-5.223928	-0.775204
C	1.254129	-5.067181	-0.18736
C	0.870435	-3.898562	0.444308
C	1.84382	-2.8652	0.542417
C	4.709247	-4.297254	-1.411275
C	5.004833	-5.461861	-2.087038
C	4.087237	-6.540553	-2.107133
C	2.874521	-6.41861	-1.468285
O	2.309055	-0.447704	-0.86972
O	1.482333	-1.674244	1.192949
P	1.132727	-0.386432	0.262591
O	-0.149341	-0.667248	-0.543576
O	1.141896	0.859161	1.100609
C	4.022509	1.857442	-1.10618
C	-0.529567	-3.726422	0.910212
C	3.306126	1.882447	-2.317526
C	2.98129	3.095901	-2.92419
C	3.362666	4.30543	-2.335178
C	4.069449	4.292437	-1.131075
C	4.389389	3.080586	-0.519516
C	-1.577445	-4.088141	0.044664
C	-2.908544	-3.952078	0.437902
C	-3.215313	-3.45298	1.705868
C	-2.181543	-3.09798	2.576347
C	-0.849214	-3.223498	2.181761
H	8.944408	-2.030982	2.222442
H	7.420322	-3.998796	2.386646
H	5.164611	-3.914386	1.421479
H	8.162631	0.048605	1.124104
H	6.433049	1.297911	-0.050033
H	0.545333	-5.88732	-0.261082
H	5.421868	-3.480943	-1.421535
H	5.950161	-5.550829	-2.615691
H	4.337362	-7.453913	-2.640011
H	2.149044	-7.228085	-1.494504
H	-0.128747	1.866766	0.461155
H	2.442164	3.09594	-3.867029
H	4.354879	5.2248	-0.654046
H	-3.701268	-4.214979	-0.255316
H	-2.411145	-2.697092	3.557721
H	-4.25053	-3.323877	2.005921
H	-1.34526	-4.451674	-0.952582
H	-0.055678	-2.931729	2.861555
H	4.917572	3.082539	0.429557

H	3.106241	5.249639	-2.80845
H	3.024834	0.950964	-2.79711
C	-0.774713	2.434636	-2.267509
C	-0.882331	3.142738	-0.919039
O	-1.173137	1.265621	-2.383226
O	-1.015259	2.122144	0.067251
C	-4.055149	0.385272	3.263625
S	-2.257861	0.625888	2.842532
F	-4.268964	0.780287	4.523093
F	-4.406432	-0.89836	3.142244
F	-4.813595	1.123296	2.441311
O	-1.504222	-0.170798	3.81715
O	-2.061229	2.080975	2.847808
O	-2.227587	0.004881	1.45123
C	-5.723308	-1.532719	-0.572118
S	-4.605816	-1.426512	-2.076795
F	-6.958793	-1.170769	-0.933256
F	-5.296081	-0.713718	0.394153
F	-5.755274	-2.782424	-0.102194
O	-5.075431	-0.242431	-2.812316
O	-4.702022	-2.735253	-2.730414
O	-3.232139	-1.211855	-1.445644
Sc	-1.989148	0.213538	-0.595859
C	-4.525356	2.171898	-1.309665
H	-1.861752	3.643453	-0.964951
C	-5.871646	2.326251	-0.684916
H	-6.286901	3.317917	-0.890843
H	-6.532932	1.589655	-1.162461
H	-5.832552	2.12816	0.38696
C	-4.267275	2.787041	-2.644976
H	-3.428665	2.307264	-3.150004
H	-5.165623	2.753302	-3.267898
H	-4.029393	3.847507	-2.475994
O	-3.63688	1.551243	-0.702013
C	1.735388	5.322892	0.957211
C	1.885429	6.533071	0.256385
C	2.603157	5.055335	2.030633
C	2.89339	7.432441	0.60078
H	1.205754	6.772617	-0.556701
C	3.616869	5.951458	2.370268
H	2.493113	4.124742	2.58256
C	3.768599	7.142255	1.653592
H	2.995116	8.364099	0.050001
H	4.286888	5.721094	3.194574

H	4.554902	7.843924	1.91934
O	-0.340506	3.155769	-3.259933
C	-0.309487	2.534289	-4.580185
H	-1.324624	2.259715	-4.874437
H	0.094358	3.299152	-5.240869
H	0.335929	1.654497	-4.553863
C	0.179665	4.161492	-0.61739
H	0.450772	4.799055	-1.453374
C	0.727517	4.315421	0.59567
H	0.443637	3.640105	1.400501

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C	-0.586541	5.751861	2.135387
C	-1.005655	7.01086	2.561945
C	-0.259029	8.144893	2.23041
C	0.910943	8.011552	1.472487
C	1.336591	6.753457	1.054423
H	-1.176294	4.871688	2.376691
H	-1.918901	7.108434	3.142636
H	-0.5888	9.128863	2.553127
H	1.487266	8.892661	1.203165
H	2.234658	6.664688	0.449994
C	2.474786	2.479228	0.153813
C	3.803673	1.855299	0.59935
O	1.507454	1.595391	0.192847
O	3.799437	0.660654	0.921361
O	4.856472	2.618039	0.586299
C	6.127671	1.997769	0.964626
H	6.863611	2.794633	0.873186
H	6.061373	1.639957	1.994008
H	6.338181	1.176057	0.278687
O	2.183845	1.155788	-2.547873
C	2.610079	2.417308	-2.450638
H	2.78641	2.609836	-1.121382
C	4.025674	2.60529	-2.930248
H	4.659658	1.782087	-2.592546
H	4.012401	2.609487	-4.028868
H	4.429789	3.559825	-2.583929
C	1.591842	3.498409	-2.692946
H	1.284781	3.454904	-3.745809
H	0.710383	3.331049	-2.068652
H	2.007174	4.486181	-2.481844
H	1.184521	1.067422	-2.492327

Sc	1.926644	-0.419627	0.358065
C	5.433961	-2.472591	0.00065
S	4.632436	-1.574721	-1.421651
F	6.701183	-2.755817	-0.317483
F	5.42081	-1.711165	1.100527
F	4.77927	-3.611761	0.254736
O	5.333848	-0.285172	-1.510526
O	4.730549	-2.487028	-2.565859
O	3.199798	-1.452128	-0.919165
C	-0.361782	-2.237223	3.039171
S	1.409466	-1.63937	2.909148
F	-0.838771	-1.918995	4.241492
F	-1.106901	-1.667575	2.096944
F	-0.372841	-3.563295	2.886725
O	1.322063	-0.172465	2.5638
O	2.047844	-2.005428	4.168539
O	1.939024	-2.280987	1.647581
C	0.595604	5.601126	1.385375
C	0.989425	4.258484	0.963442
H	0.215233	3.495118	1.018395
C	2.216046	3.875899	0.553261
H	3.061196	4.555526	0.503845
C	-8.237705	-0.504811	-1.756578
C	-7.589224	-1.747344	-1.550725
C	-6.257267	-1.797078	-1.19995
C	-5.498865	-0.603517	-1.038501
C	-6.14877	0.648832	-1.280846
C	-7.528152	0.667607	-1.628048
C	-4.109127	-0.605843	-0.673669
C	-3.409439	0.593405	-0.707954
C	-4.039391	1.849638	-0.940153
C	-5.398925	1.84638	-1.19247
C	-3.426966	-1.870985	-0.278368
C	-3.868028	-2.6616	0.838022
C	-3.172588	-3.879722	1.132577
C	-2.060033	-4.264091	0.343188
C	-1.586086	-3.477651	-0.688332
C	-2.299303	-2.278368	-0.964871
C	-4.926412	-2.264511	1.701003
C	-5.291614	-3.043511	2.778484
C	-4.620976	-4.260414	3.05128
C	-3.580809	-4.665254	2.245302
O	-2.042395	0.603505	-0.404374
O	-1.789049	-1.41545	-1.950102

P	-0.947094	-0.157534	-1.351864
O	0.078066	-0.721379	-0.353739
O	-0.443062	0.68122	-2.488483
C	-3.322948	3.153995	-0.883867
C	-0.345309	-3.83738	-1.418857
C	-3.820835	4.164608	-0.042343
C	-3.248706	5.437107	-0.03719
C	-2.17363	5.723512	-0.881356
C	-1.669328	4.725245	-1.718245
C	-2.229488	3.444755	-1.715232
C	0.783669	-4.256909	-0.694277
C	1.965072	-4.598013	-1.35352
C	2.035685	-4.531582	-2.747252
C	0.917745	-4.117456	-3.477052
C	-0.262847	-3.769377	-2.819883
H	-9.289749	-0.482567	-2.027604
H	-8.146264	-2.671832	-1.677461
H	-5.776183	-2.758248	-1.05824
H	-8.007145	1.628425	-1.800241
H	-5.905105	2.791423	-1.369691
H	-1.549961	-5.193224	0.580966
H	-5.442518	-1.328933	1.517913
H	-6.098152	-2.716394	3.429252
H	-4.921117	-4.864107	3.903484
H	-3.043683	-5.587089	2.454446
H	-3.640021	6.202326	0.627677
H	-0.843671	4.950092	-2.387093
H	2.838338	-4.887719	-0.777041
H	0.963631	-4.06566	-4.561929
H	2.959482	-4.785163	-3.259158
H	0.744432	-4.273393	0.390204
H	-1.127239	-3.451318	-3.394148
H	-1.836733	2.679959	-2.376698
H	-1.725999	6.713467	-0.879996
H	-4.660597	3.94544	0.611792

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C	-0.79928	4.817505	-3.32125
C	-0.69781	5.99804	-4.05551
C	-1.77529	6.431309	-4.83236
C	-2.95443	5.675878	-4.87166
C	-3.05882	4.497235	-4.13934
H	0.037062	4.483283	-2.7136

H	0.220146	6.578475	-4.01999
H	-1.70007	7.351875	-5.40497
H	-3.79327	6.010149	-5.47632
H	-3.98062	3.924243	-4.17984
C	-2.931	0.780291	-1.56338
C	-4.17299	0.312971	-0.79954
O	-1.85006	0.603484	-0.8471
O	-4.01983	-0.07261	0.365503
O	-5.30618	0.335815	-1.4373
C	-6.48278	-0.15684	-0.71937
H	-7.28234	-0.147	-1.45805
H	-6.70324	0.519605	0.109022
H	-6.28409	-1.16673	-0.35825
O	-1.74776	-1.94084	-2.18123
C	-2.39011	-1.24119	-3.1218
H	-2.92402	-0.21031	-2.46744
C	-3.63691	-1.93037	-3.61818
H	-4.19978	-2.35306	-2.78301
H	-3.3307	-2.7488	-4.28383
H	-4.26544	-1.23826	-4.18413
C	-1.5384	-0.4854	-4.11273
H	-0.98506	-1.22176	-4.70985
H	-0.81315	0.153616	-3.60045
H	-2.15626	0.121831	-4.77814
H	-0.83023	-1.57174	-1.99828
Sc	-1.88114	-0.29705	0.988088
C	-4.36274	-3.16205	2.253693
S	-3.44984	-3.33013	0.63635
F	-5.32436	-4.08865	2.315133
F	-4.91856	-1.94991	2.358899
F	-3.5121	-3.34051	3.270688
O	-4.40541	-2.91498	-0.40017
O	-2.96916	-4.71649	0.609802
O	-2.30283	-2.34315	0.845519
C	-1.00539	2.071835	4.082173
S	-2.52653	1.411316	3.225702
F	-0.90326	3.377733	3.838869
F	0.075452	1.444058	3.612754
F	-1.11078	1.86122	5.392996
O	-2.32347	1.791651	1.778118
O	-3.67633	1.974944	3.922839
O	-2.35343	-0.08984	3.240705
C	-1.98023	4.04844	-3.34881
C	-2.0246	2.826997	-2.55132

H	-1.12052	2.60231	-1.98918
C	-3.06007	1.969839	-2.42086
H	-4.00816	2.093966	-2.93407
C	7.784327	-1.84106	-2.7379
C	7.720805	-0.66715	-1.94952
C	6.620553	-0.40794	-1.16016
C	5.522252	-1.31056	-1.11346
C	5.566953	-2.47459	-1.95341
C	6.724976	-2.7202	-2.74241
C	4.353048	-1.09045	-0.30369
C	3.303753	-1.98019	-0.42967
C	3.298357	-3.10821	-1.29656
C	4.447255	-3.34439	-2.02367
C	4.203879	0.099599	0.587818
C	5.157196	0.386852	1.624748
C	5.067671	1.633472	2.32573
C	4.033466	2.544845	1.997326
C	3.051999	2.237233	1.074851
C	3.137336	0.975259	0.418384
C	6.174996	-0.53015	2.009132
C	7.069306	-0.21722	3.010367
C	6.998447	1.029304	3.679213
C	6.014462	1.931934	3.34439
O	2.14465	-1.71841	0.309047
O	2.138993	0.684763	-0.51641
P	1.155086	-0.60817	-0.34674
O	0.136453	-0.39336	0.78715
O	0.659738	-0.94442	-1.72007
C	2.05598	-3.90355	-1.47691
C	2.011955	3.244937	0.726187
C	1.326486	-4.39033	-0.37931
C	0.101771	-5.02924	-0.56837
C	-0.41534	-5.19269	-1.85723
C	0.314445	-4.73634	-2.95793
C	1.542184	-4.0982	-2.76942
C	0.638331	2.960537	0.784491
C	-0.30381	3.944373	0.479632
C	0.109619	5.225601	0.103017
C	1.474028	5.519715	0.040725
C	2.417052	4.537863	0.352136
H	8.661984	-2.0366	-3.34798
H	8.545258	0.040649	-1.96978
H	6.588579	0.502743	-0.5739
H	6.749693	-3.61354	-3.36167

H	4.491573	-4.20138	-2.69059
H	3.997405	3.502008	2.510622
H	6.238022	-1.4928	1.513917
H	7.833277	-0.93647	3.293133
H	7.713604	1.263916	4.462955
H	5.937548	2.885547	3.861077
H	-0.45997	-5.38321	0.290097
H	-0.07959	-4.85844	-3.9637
H	-1.36033	3.705296	0.540356
H	1.806697	6.511405	-0.25523
H	-0.62612	5.985987	-0.14474
H	0.307543	1.975413	1.083683
H	3.47765	4.767377	0.292395
H	2.087555	-3.70646	-3.62389
H	-1.38255	-5.66751	-1.9984
H	1.713674	-4.25352	0.625303

16) Prod: 3a

H	1.845716	-2.2847	0.575921
C	2.861906	-0.10887	0.133565
C	1.870169	-0.87508	-0.75068
O	3.275213	-0.53079	1.197575
O	1.864847	-2.24198	-0.39779
H	2.229876	-0.81218	-1.78569
C	-1.93229	-0.23637	-0.07741
C	-2.23414	1.111739	-0.35513
C	-2.97716	-1.07086	0.361225
C	-3.52986	1.5989	-0.2009
H	-1.45187	1.785493	-0.69335
C	-4.27515	-0.58291	0.516023
H	-2.7642	-2.11451	0.581879
C	-4.55803	0.75524	0.235103
H	-3.74019	2.642563	-0.42112
H	-5.06445	-1.2487	0.856015
H	-5.56772	1.139517	0.354123
O	3.172717	1.08016	-0.38912
C	4.045798	1.920149	0.404236
H	5.015552	1.433995	0.540488
H	4.157673	2.841833	-0.16708
H	3.591893	2.125223	1.377431
C	0.520699	-0.19155	-0.64689
H	0.519983	0.855997	-0.93984
C	-0.58673	-0.81325	-0.22049

H	-0.50581	-1.86656	0.043907
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17) CH₃COCH₃

C	0.000019	0.180458	-0.00017
C	-1.28584	-0.61413	-0.00218
H	-2.14577	0.048089	-0.13041
H	-1.27158	-1.36977	-0.79716
H	-1.38145	-1.15489	0.948773
C	1.285902	-0.61404	0.002169
H	1.271915	-1.36842	0.798386
H	1.381014	-1.15641	-0.9479
H	2.145906	0.048326	0.12918
O	-6.4E-05	1.404914	0.00003

18) Int5

C	6.004447	1.039199	0.888319
C	7.382441	0.956471	1.049469
C	8.160099	0.33661	0.065242
C	7.558732	-0.201084	-1.082658
C	6.18331	-0.129566	-1.246409
H	5.392003	1.518295	1.647449
H	7.852883	1.372535	1.935248
H	9.23772	0.272941	0.188632
H	8.170962	-0.674537	-1.844456
H	5.726831	-0.543115	-2.139755
C	1.748037	0.127242	-1.245703
C	0.842331	-0.634234	-2.20217
O	1.091293	0.81559	-0.414732
O	-0.383464	-0.504264	-2.046101
O	1.399452	-1.363416	-3.112717
C	0.51413	-2.135091	-3.987713
H	1.184797	-2.71726	-4.616367
H	-0.118523	-2.777175	-3.372178
H	-0.089586	-1.44508	-4.58059
C	-4.22522	-2.075964	0.616491
S	-3.370672	-1.744112	-1.003701
F	-4.748365	-3.304926	0.592127
F	-3.352357	-1.988193	1.623915
F	-5.201225	-1.181937	0.802593
O	-2.300953	-2.743023	-1.107308
O	-4.426428	-1.73962	-2.02141
O	-2.847584	-0.323485	-0.742287

C	-2.632565	4.237901	0.368621
S	-0.969453	3.450422	0.072117
F	-2.851261	5.1688	-0.556845
F	-3.578022	3.297586	0.296046
F	-2.640966	4.790201	1.580036
O	-1.126572	2.70426	-1.231295
O	0.02492	4.51326	0.137155
O	-0.901437	2.359901	1.12368
C	1.477268	-1.679838	2.364548
S	0.245866	-2.22422	1.079474
F	2.320305	-2.682931	2.62091
F	2.170304	-0.627437	1.913375
F	0.839849	-1.33581	3.485712
O	1.033103	-2.442376	-0.145947
O	-0.470687	-3.358326	1.662642
O	-0.624356	-0.965775	0.998568
C	5.379998	0.491206	-0.257795
C	3.949384	0.57915	-0.356336
H	3.450208	1.142375	0.429825
C	3.152224	0.002069	-1.316014
H	3.556305	-0.612161	-2.111682
Sc	-1.056467	0.591683	-0.279644

19) TS-3

C	-5.76095	0.706533	-1.12599
C	-7.08711	0.772283	-1.55024
C	-7.77895	-0.4012	-1.86118
C	-7.13768	-1.64099	-1.74326
C	-5.81336	-1.70935	-1.32296
H	-5.2219	1.619385	-0.88409
H	-7.58001	1.73666	-1.63767
H	-8.81339	-0.35391	-2.19078
H	-7.67599	-2.55523	-1.97852
H	-5.33342	-2.67906	-1.22979
C	-1.48521	-1.44748	-0.07593
C	-0.42194	-2.27536	-0.8037
O	-1.01184	-0.26459	0.239029
O	0.620235	-1.69377	-1.13799
O	-0.67805	-3.52845	-1.01707
C	0.358655	-4.3149	-1.69095
H	-0.01083	-5.33823	-1.66615
H	0.463587	-3.95638	-2.71675
H	1.295333	-4.21317	-1.14228

O	-0.41642	-1.47163	2.747961
C	-1.44278	-2.2578	2.38851
H	-1.50653	-2.13132	1.067096
C	-1.11984	-3.72526	2.506596
H	-0.12115	-3.93151	2.115659
H	-1.14356	-3.99421	3.571432
H	-1.86324	-4.32801	1.979121
C	-2.82699	-1.78476	2.753328
H	-2.91927	-1.82159	3.846329
H	-2.9881	-0.75133	2.428787
H	-3.59102	-2.42785	2.311167
H	-0.68538	-0.5233	2.846843
Sc	0.902599	0.293015	-0.20302
C	4.113547	-2.20674	-0.16779
S	2.921989	-2.06209	1.25837
F	4.879565	-3.28625	0.017371
F	3.447632	-2.33568	-1.3196
F	4.886311	-1.11803	-0.22687
O	1.983156	-3.1806	1.095841
O	3.751911	-2.0217	2.466072
O	2.286011	-0.69763	0.981347
C	0.046864	3.666696	2.945442
S	-0.67786	2.216517	2.034239
F	-0.84936	4.124325	3.822711
F	1.149738	3.286186	3.592814
F	0.351831	4.631678	2.075203
O	-0.96566	1.212899	3.083264
O	-1.81107	2.732631	1.260336
O	0.525334	1.831966	1.176571
C	1.978992	3.071449	-2.78851
S	1.576662	1.250569	-2.80793
F	1.137155	3.717029	-3.59172
F	1.848725	3.526754	-1.53912
F	3.231117	3.248104	-3.2036
O	0.202847	1.16985	-2.17849
O	1.726732	0.789103	-4.1812
O	2.495554	0.662399	-1.75866
C	-5.09967	-0.53268	-1.01085
C	-3.70665	-0.53621	-0.57637
H	-3.30239	0.428725	-0.27433
C	-2.87264	-1.59821	-0.53757
H	-3.17015	-2.60023	-0.82991

20) TS-4

C	7.608333	0.090586	-1.19651
C	6.799583	1.10903	-1.7572
C	5.484214	1.255107	-1.3728
C	4.907781	0.387438	-0.40472
C	5.716361	-0.66908	0.132156
C	7.07455	-0.78166	-0.27549
C	3.542696	0.499777	0.028704
C	3.057622	-0.47716	0.878488
C	3.82548	-1.53905	1.421717
C	5.153621	-1.59697	1.044145
C	2.644619	1.601312	-0.4287
C	2.951175	2.983649	-0.1806
C	2.048274	3.987165	-0.66519
C	0.855611	3.603218	-1.32679
C	0.515726	2.276743	-1.51536
C	1.445343	1.307885	-1.05277
C	4.091087	3.40312	0.559547
C	4.345386	4.741895	0.76596
C	3.476297	5.73265	0.247777
C	2.348552	5.360471	-0.44739
O	1.676986	-0.44568	1.218027
O	1.097984	-0.05847	-1.22455
P	0.656272	-0.87141	0.075354
O	-0.74407	-0.54393	0.566109
O	0.85927	-2.37307	-0.30827
C	3.226885	-2.55588	2.324146
C	-0.78517	1.898846	-2.12668
C	2.442038	-2.18478	3.429868
C	1.901396	-3.15646	4.272016
C	2.132838	-4.51286	4.022762
C	2.913169	-4.8913	2.927409
C	3.456042	-3.92051	2.083744
C	-1.96566	2.521774	-1.68062
C	-3.20604	2.18089	-2.22923
C	-3.2801	1.234223	-3.25704
C	-2.10966	0.628137	-3.72293
C	-0.87332	0.951879	-3.16086
H	8.645781	-0.00579	-1.50434
H	7.219583	1.780148	-2.50132
H	4.878496	2.035066	-1.81969
H	7.679378	-1.57831	0.150046
H	5.785503	-2.38287	1.44819
H	0.184138	4.379108	-1.68369
H	4.763917	2.66122	0.973328

H	5.220601	5.039901	1.336662
H	3.696249	6.783694	0.41278
H	1.661254	6.108959	-0.83333
H	1.303481	-2.85347	5.127739
H	3.095239	-5.94325	2.72379
H	-4.10683	2.662519	-1.85936
H	-2.15793	-0.10599	-4.52084
H	-4.24153	0.970182	-3.6888
H	-1.91517	3.254093	-0.88033
H	0.027392	0.471635	-3.52899
H	4.047577	-4.2189	1.222564
H	1.708513	-5.26842	4.678709
H	2.267618	-1.13344	3.636873
C	-2.13487	-3.01586	-3.00919
S	-2.71104	-3.1702	-1.24275
F	-1.87319	-4.23149	-3.48232
F	-1.02566	-2.27197	-3.04321
F	-3.08705	-2.44	-3.74032
O	-1.52844	-3.62721	-0.47871
O	-3.89216	-4.02556	-1.2337
O	-3.04857	-1.70109	-0.93994
C	-5.00006	1.634788	3.096923
S	-4.35443	1.951447	1.373618
F	-4.50431	0.476272	3.5309
F	-6.32598	1.575487	3.052392
F	-4.6066	2.623823	3.890822
O	-4.73564	0.708296	0.582854
O	-2.84849	1.807759	1.478618
O	-4.89469	3.226384	0.931154
Sc	-2.71249	-0.14506	0.338542
H	0.011443	-2.90137	-0.38264

VI. Non-linear Effect

ee Value of the product **3a** was found to correlate linearly with *ee* value of the chiral phosphoric acid **1d**, suggesting that a higher ligand/metal complex is unlikely to be the catalytically active species (Figure S4).

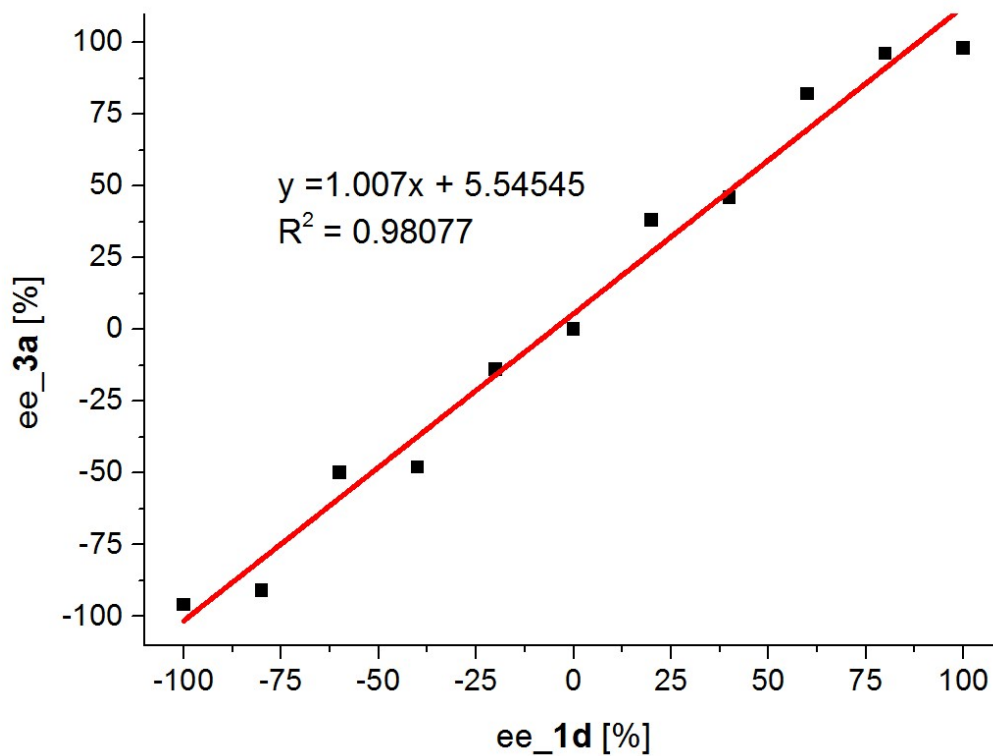


Figure S4. Nonlinear effect in enantioselective Meerwein-Ponndorf-Verley Reduction of β,γ -unsaturated α -ketoester **3a** with *i*PrOH

VII. Control Experiments

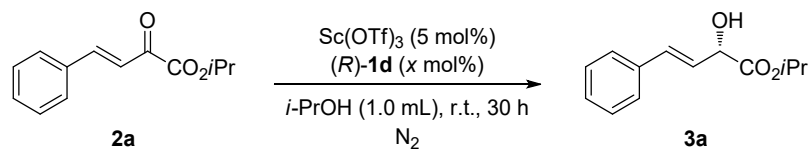
A) Lewis acid catalysis with chiral basic ligands

Scheme 5, entries 1-2 and 4-5: To a 25 mL flask, β,γ -unsaturated α -keto ester **2a** (0.1 mmol), Sc(OTf)₃ (0.01 mmol, 4.92 mg), Ligands (0.005-0.01 mmol) were dissolved in solvent *i*-PrOH (1 mL) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 20 h. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **3a**.

Scheme 5, entry 3: To a 25 mL flask, β,γ -unsaturated α -keto ester **2a** (0.1 mmol), Sc(OTf)₃ (0.01 mmol, 4.92 mg), NO-1 (0.01 mmol, 6.52 mg), Al(*O**i*Pr)₃ (0.01 mmol, 2.04 mg), and 3 Å MS (25 mg) were dissolved in solvent *i*-PrOH (1 mL) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 20 h. Purification of mixture by column chromatography on silica gel (PE/EA = 20:1 to 10:1, v/v) gave the desired products **3a**.

B) Lewis acid catalysis with chiral acid ligand

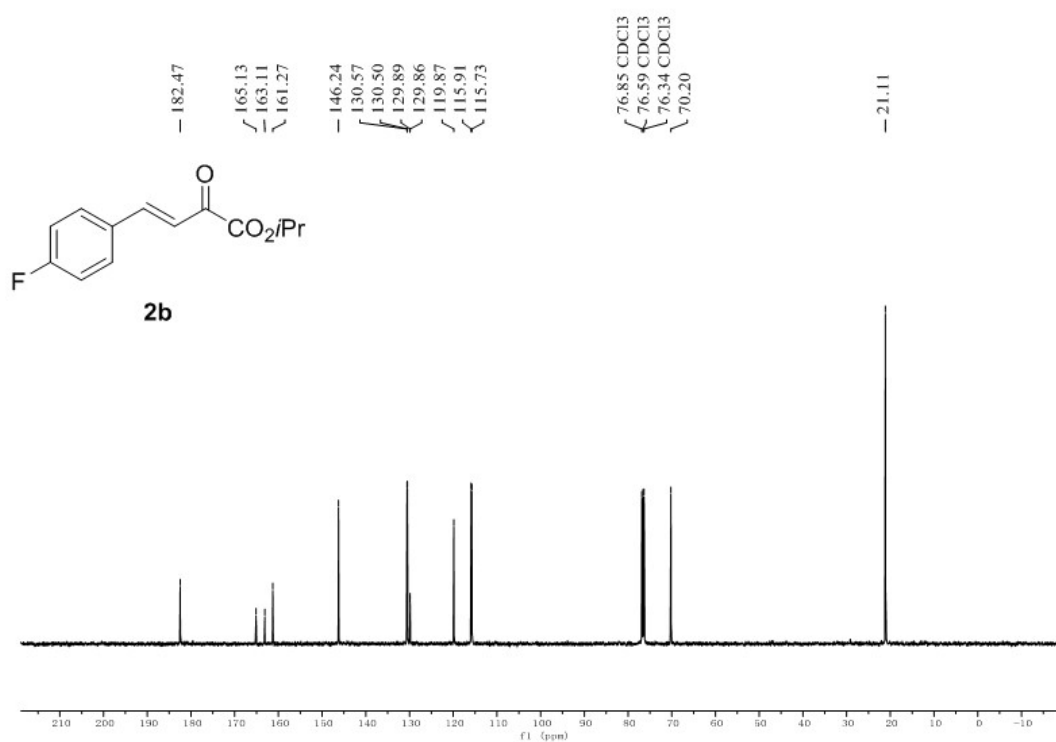
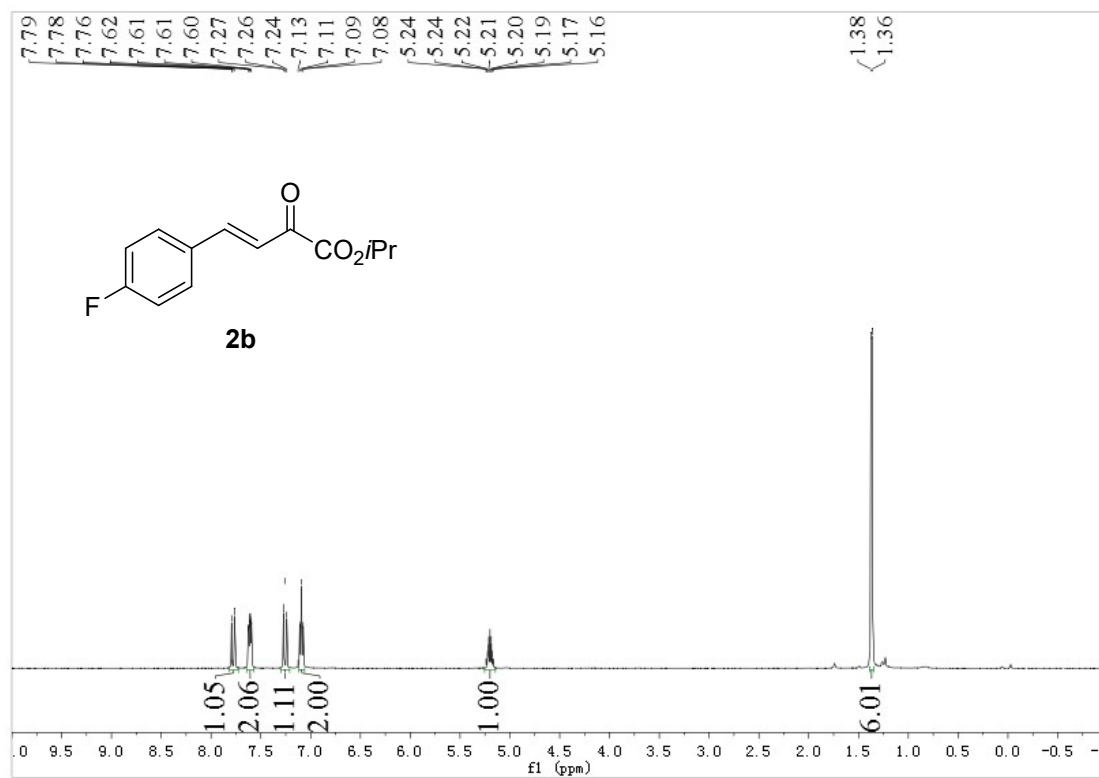
Table S9. Binary acid ratio effect in reaction activity and enantioselectivity ^a

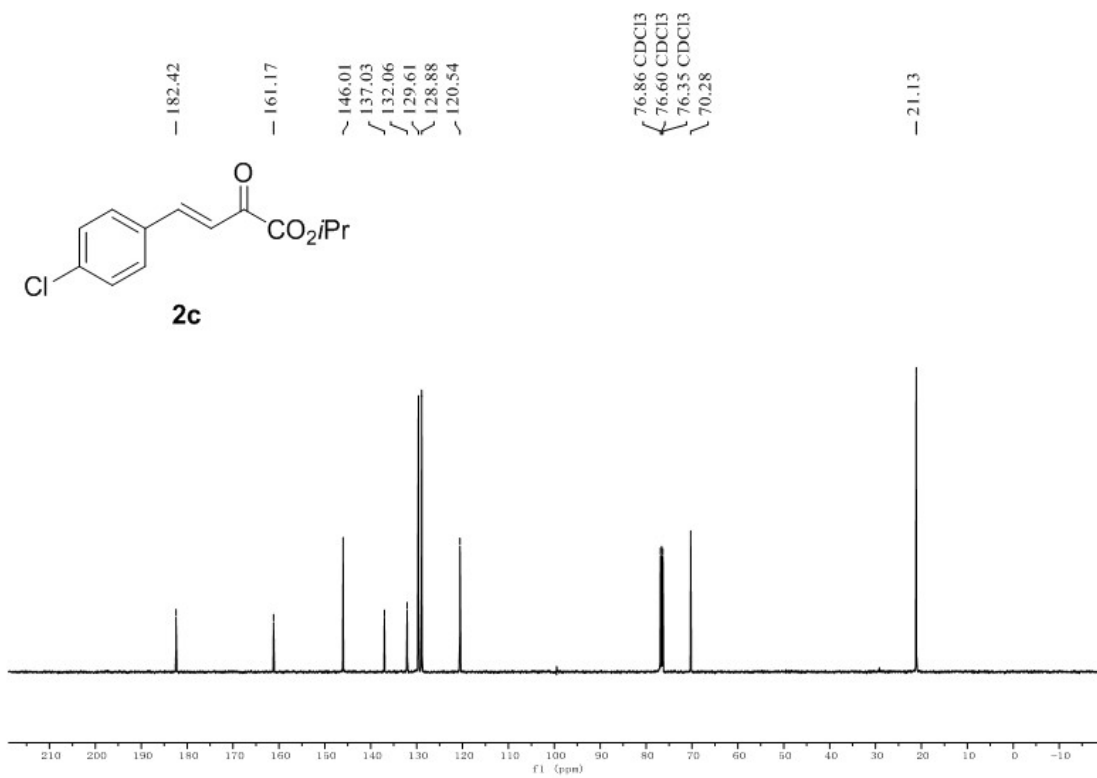
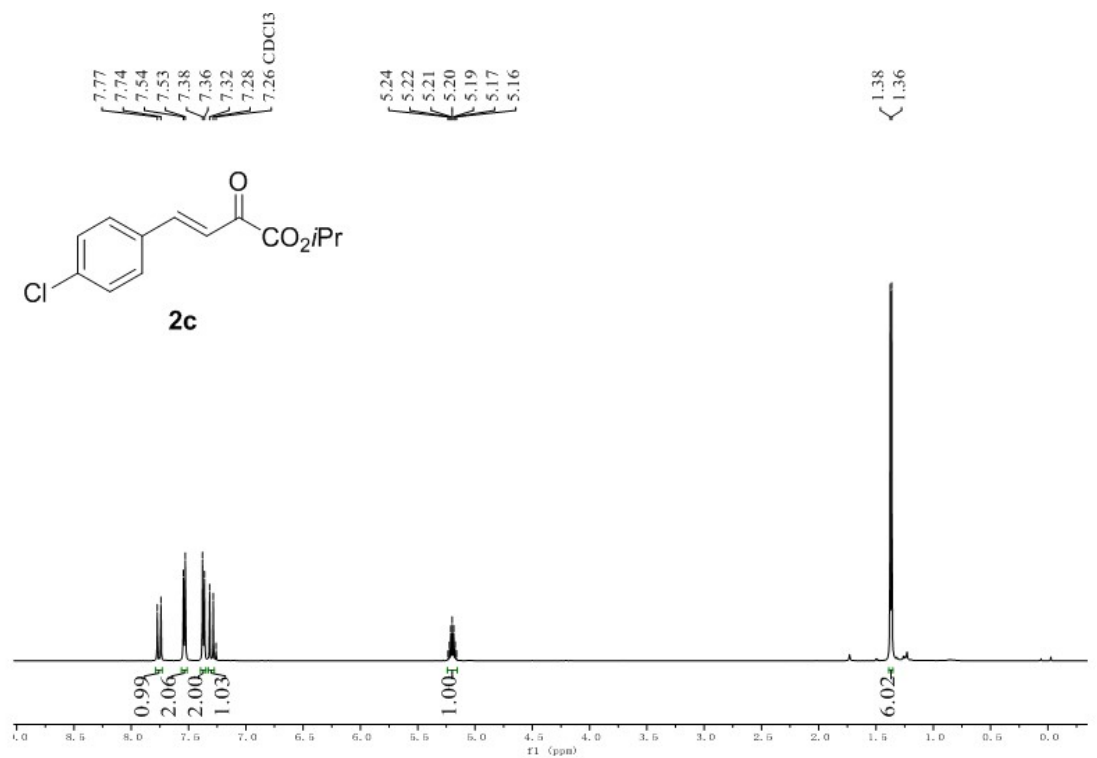


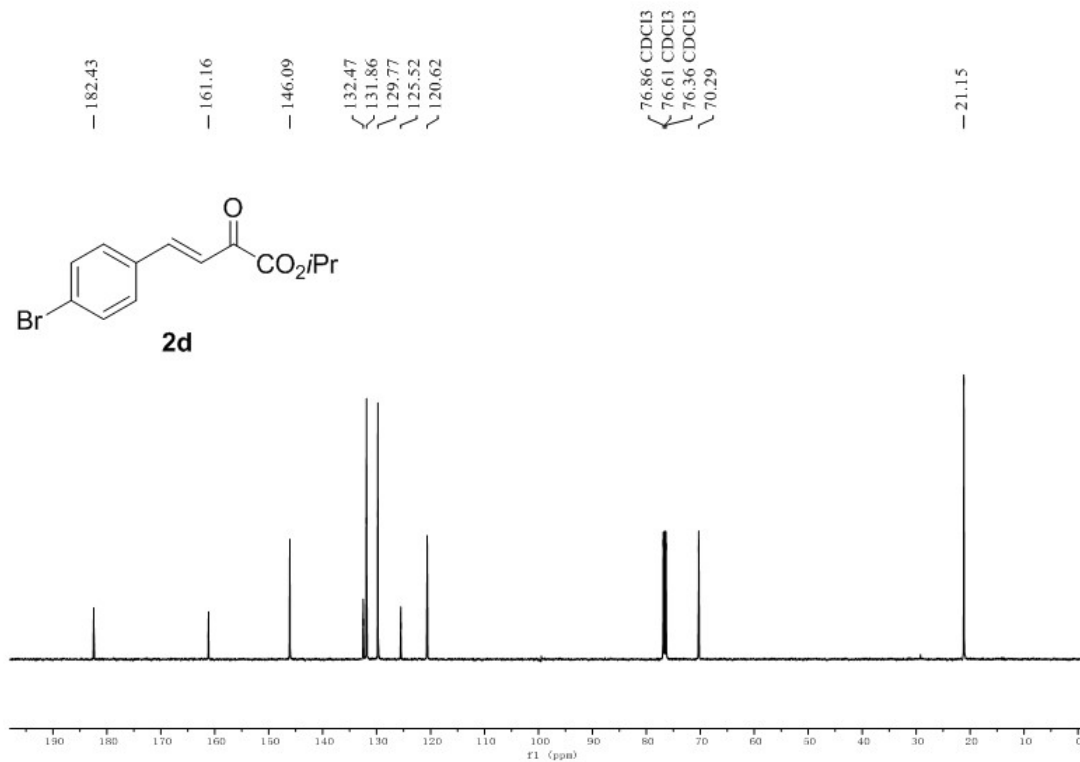
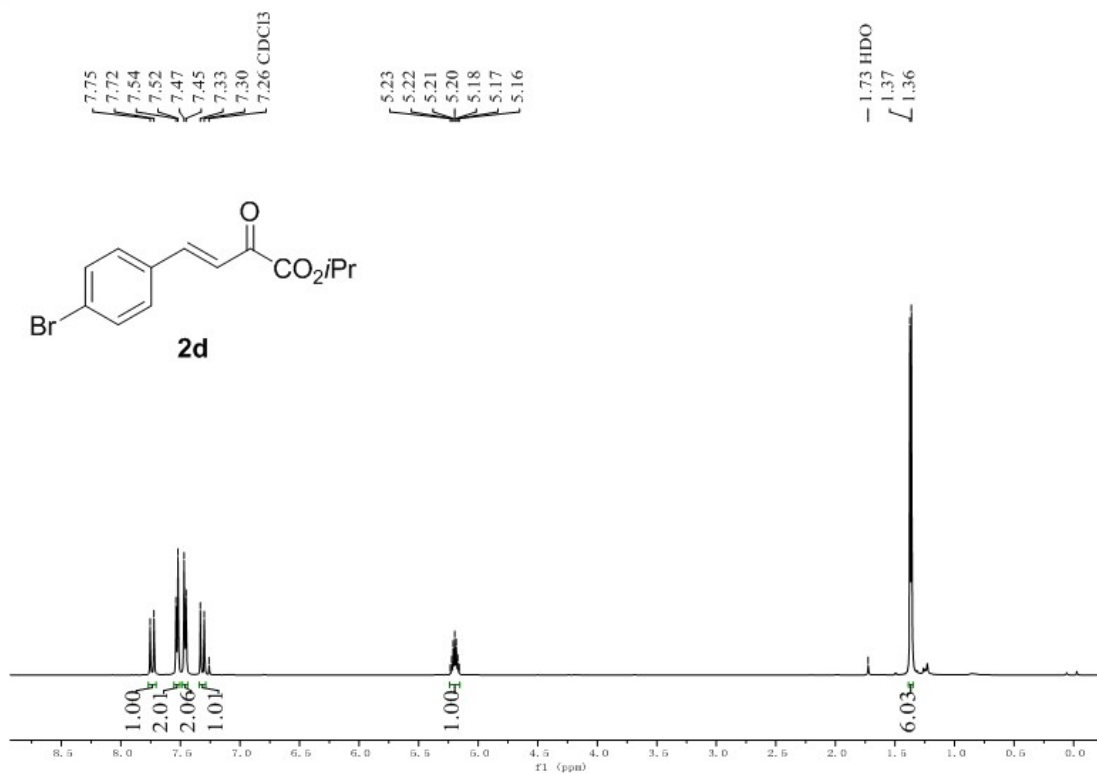
Entry	X (5/x)	Yield (%) ^b	ee (%) ^c
1	1	97	98
2	2	97	96
3	4	98	96
4	5	98	98
5 ^d	10	98	96
6 ^d	20	94	94
7 ^d	30	72	62
8 ^e	40	53	54
9 ^e	50	30	46
10 ^e	60	31	24
11 ^e	80	trace	22
12 ^e	100	NR	-

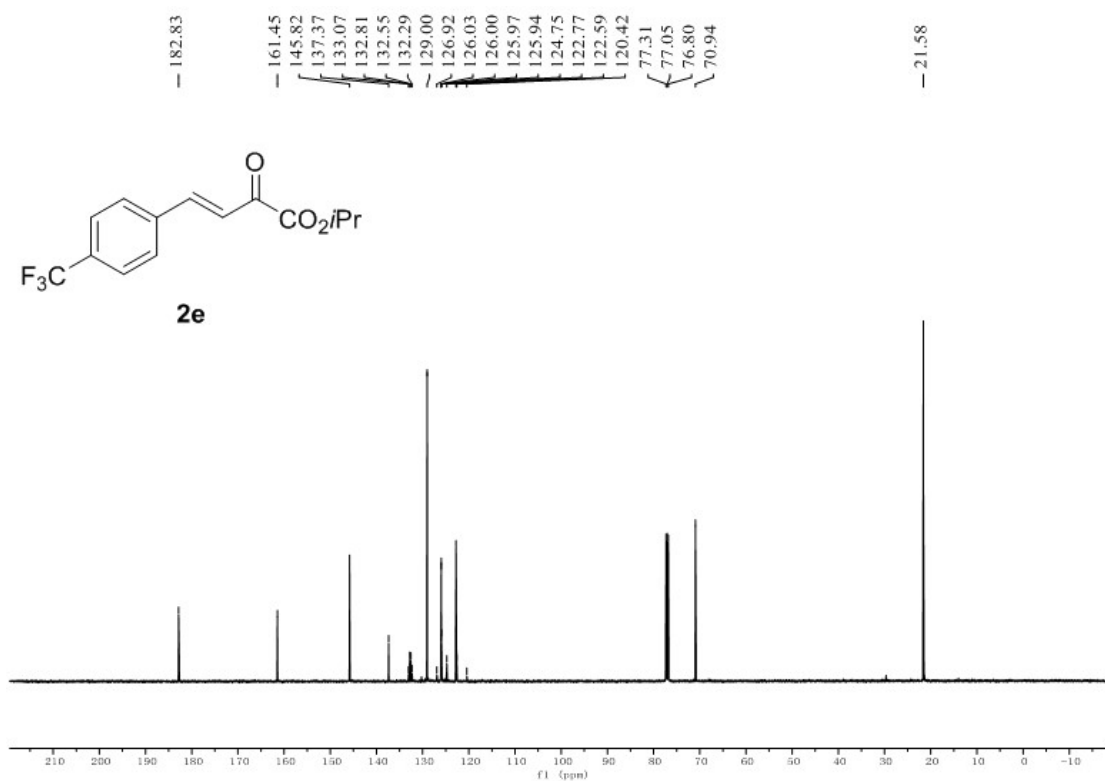
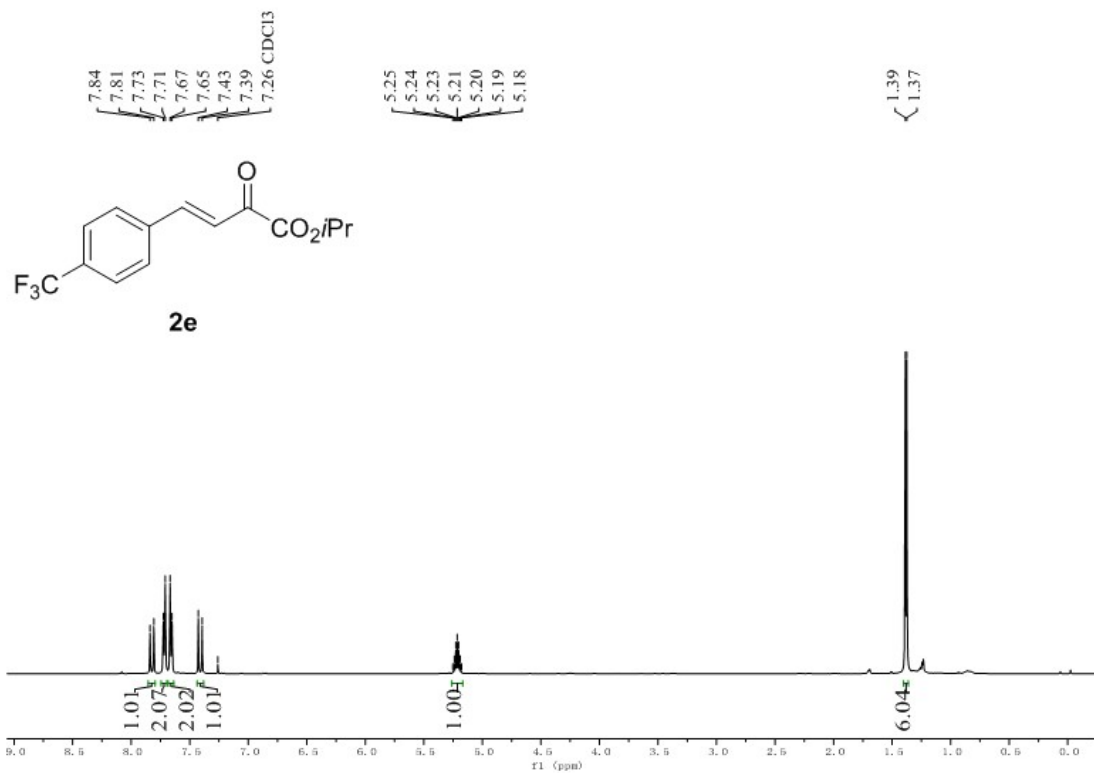
^a Reaction conditions: **2a** (0.1 mmol) and Sc(OTf)₃ (5 mol %), (*R*)-**1d** (*x* mol%) in *i*-PrOH (1.0 mL) under N₂ at room temperature for 30 h. ^b Isolated yield. ^c Determined by HPLC analysis on a chiral stationary phase. ^d **2a** (0.5 mmol) in *i*-PrOH (5.0 mL). ^e **2a** (1.0 mmol) in *i*-PrOH (10.0 mL). NR = No Reaction.

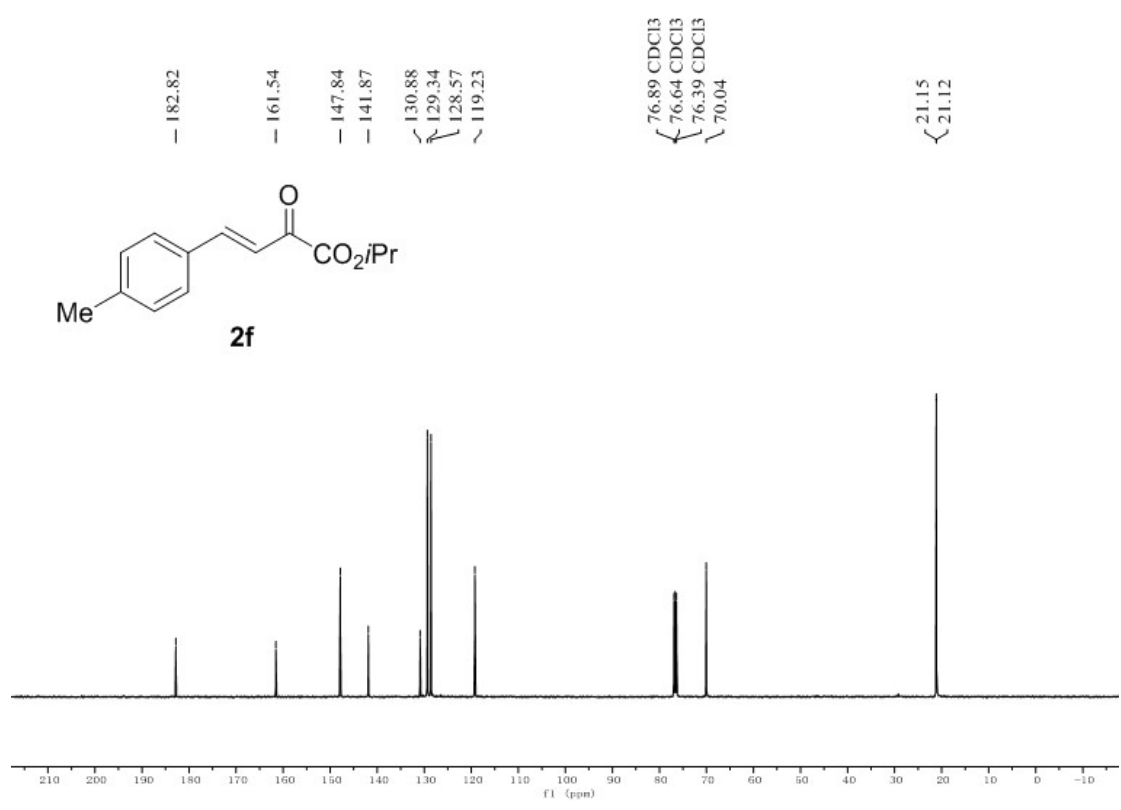
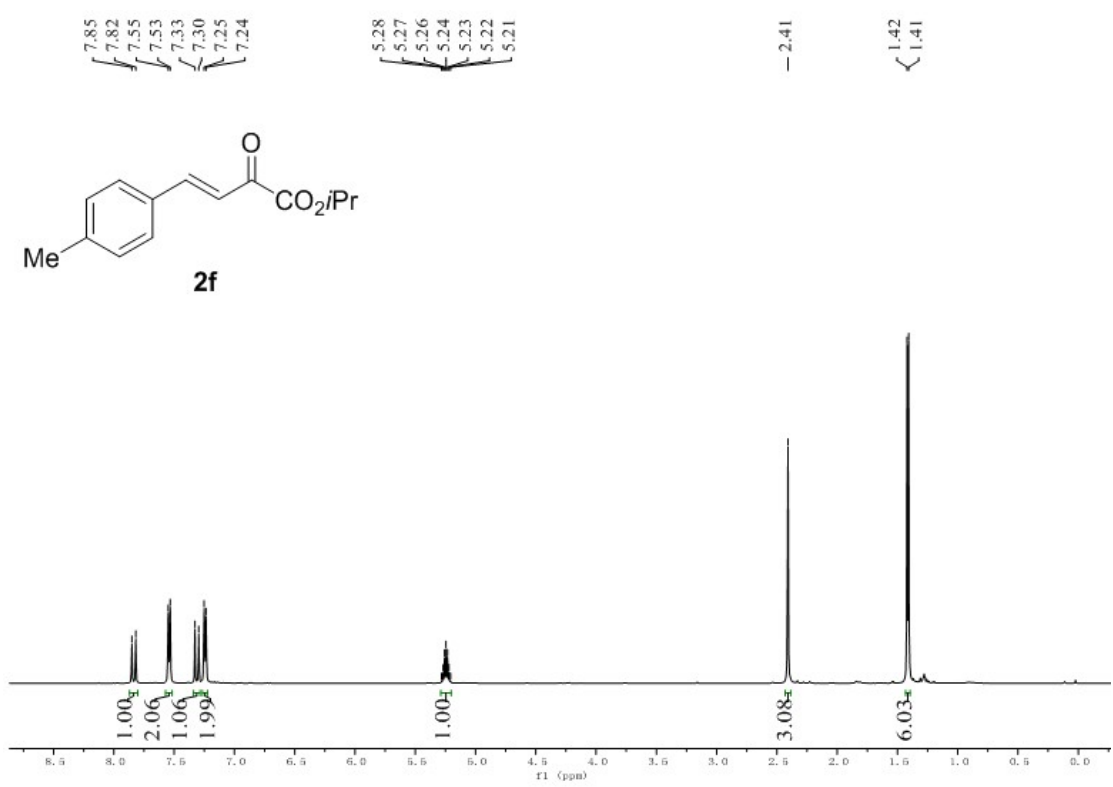
VIII. NMR Spectrum

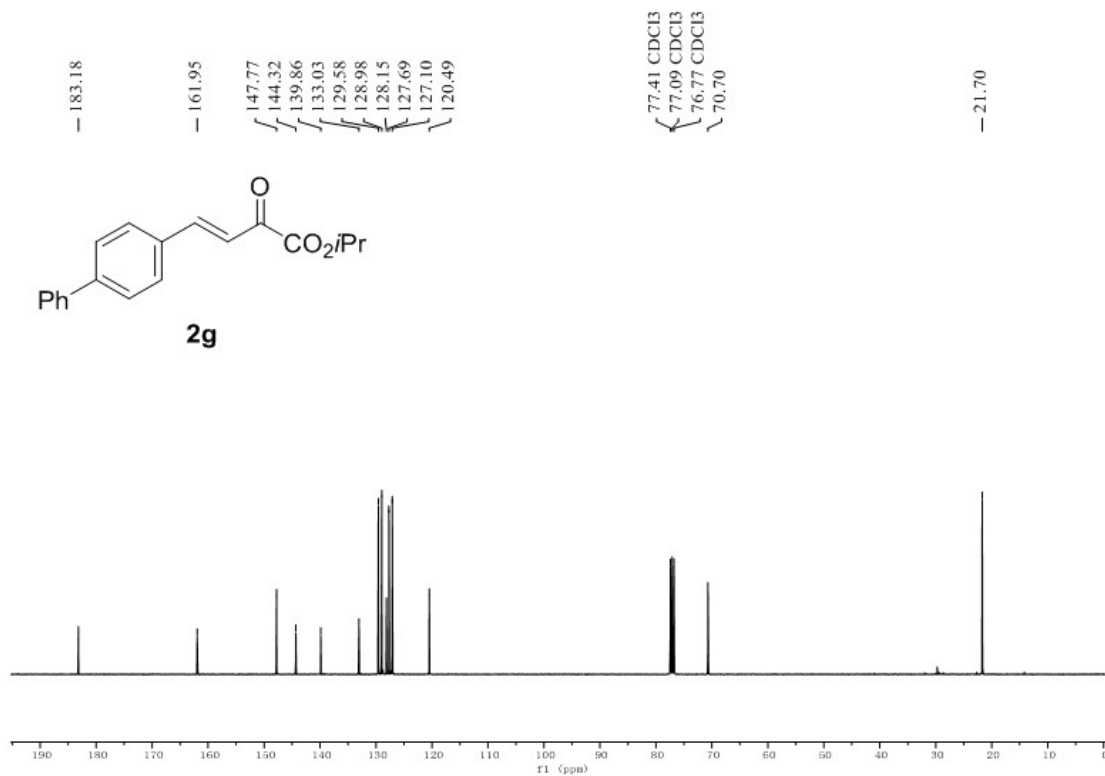
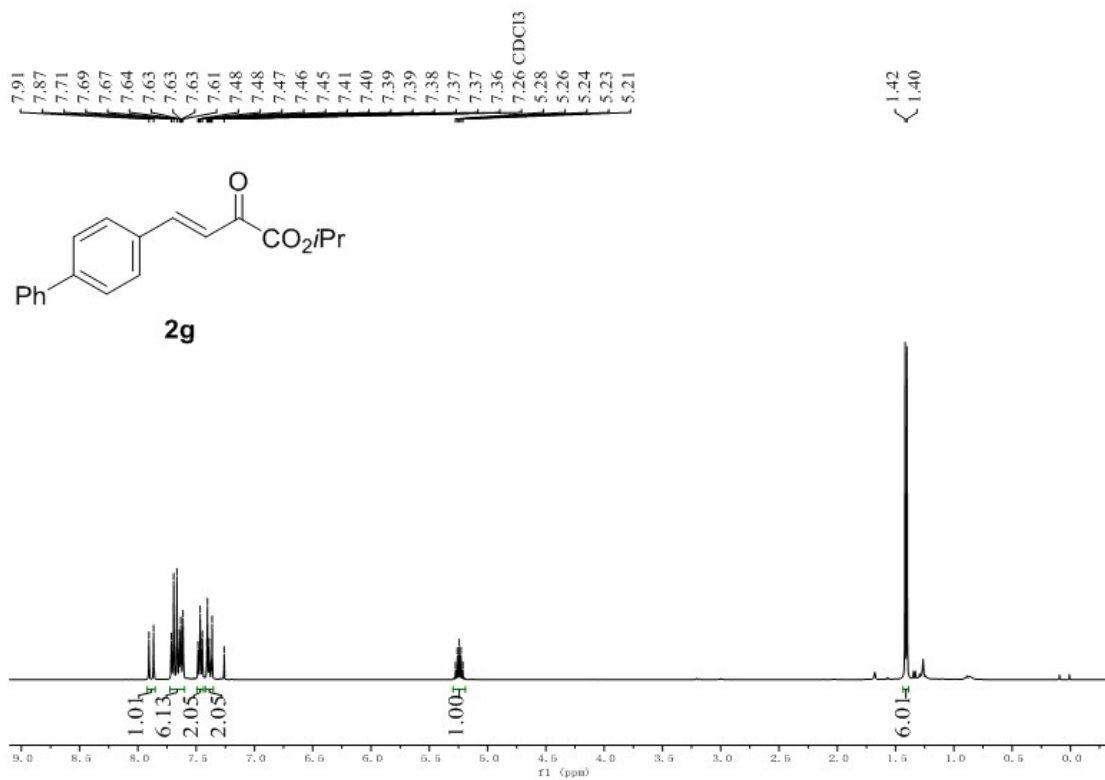


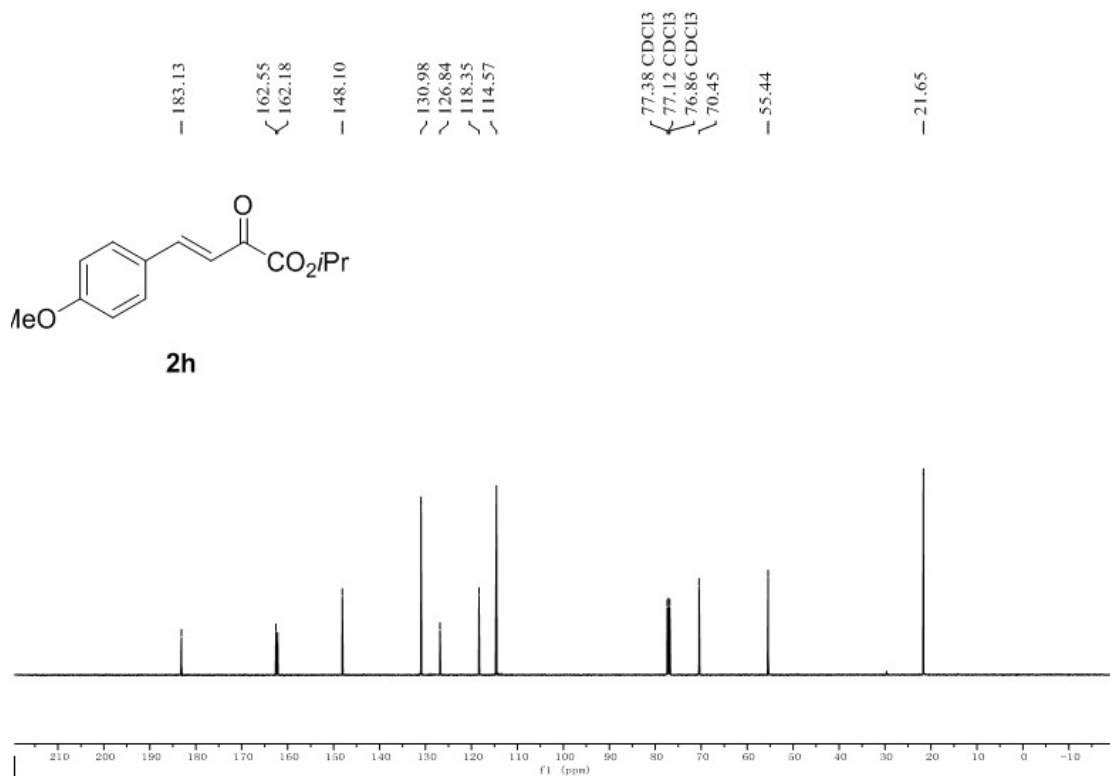
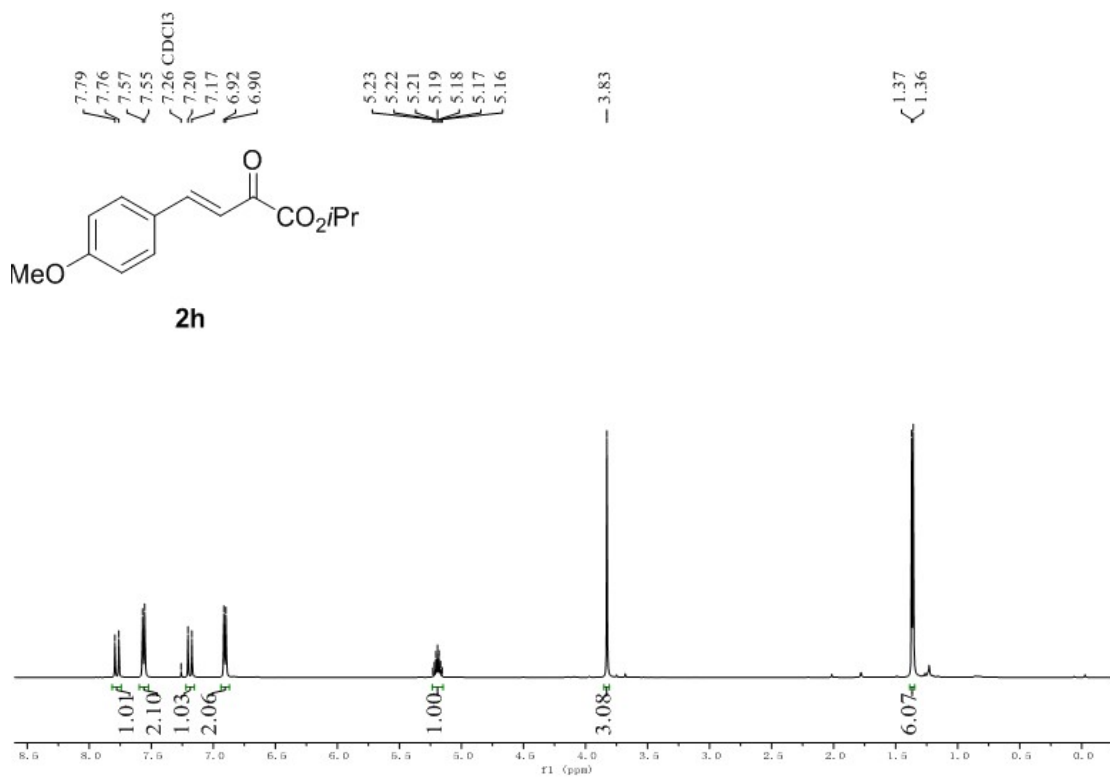


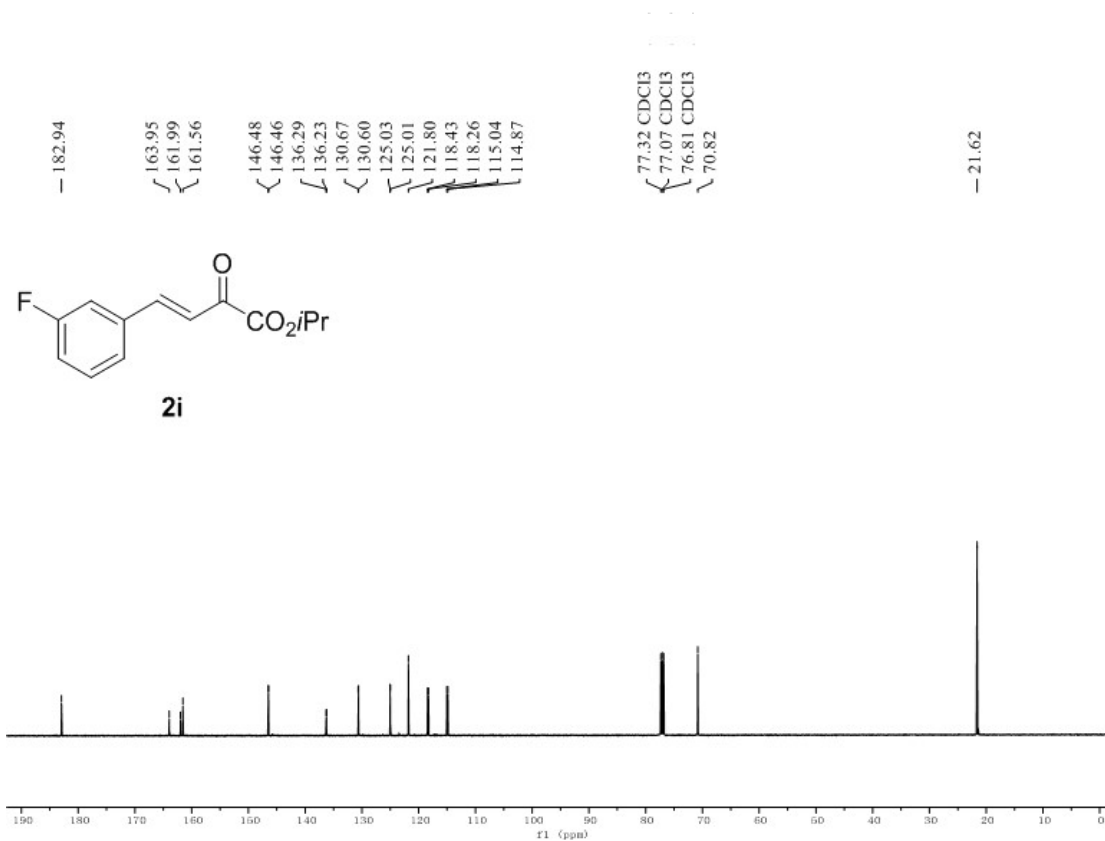
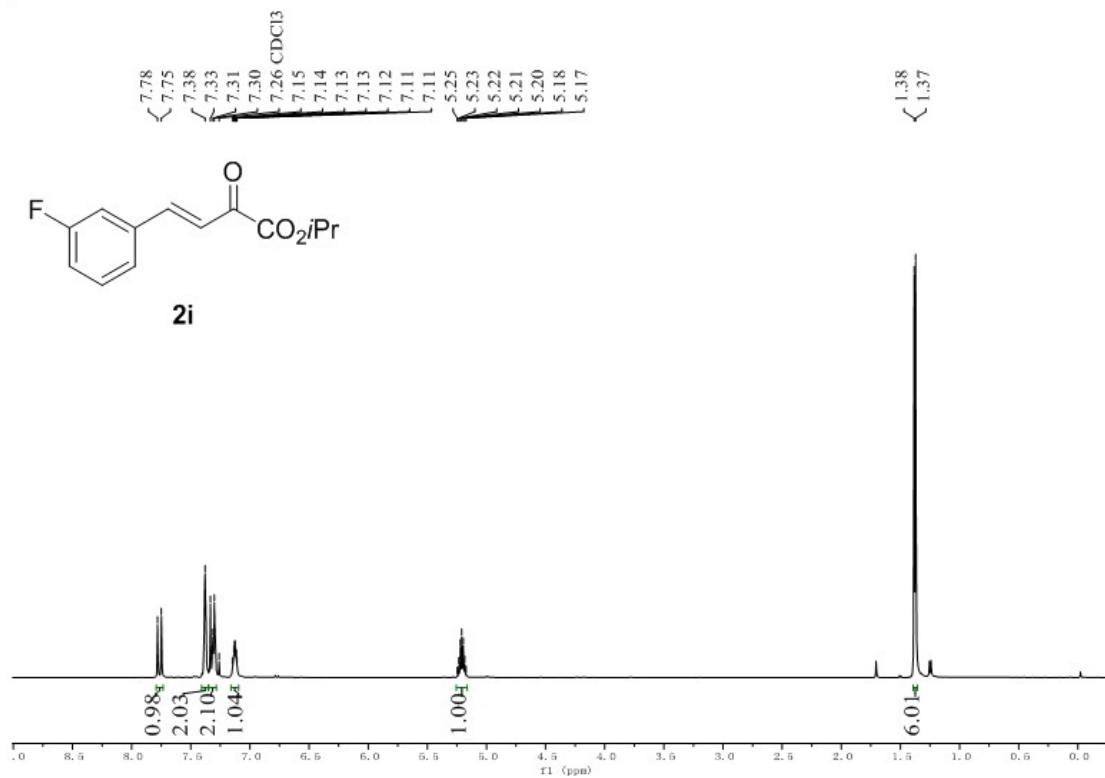


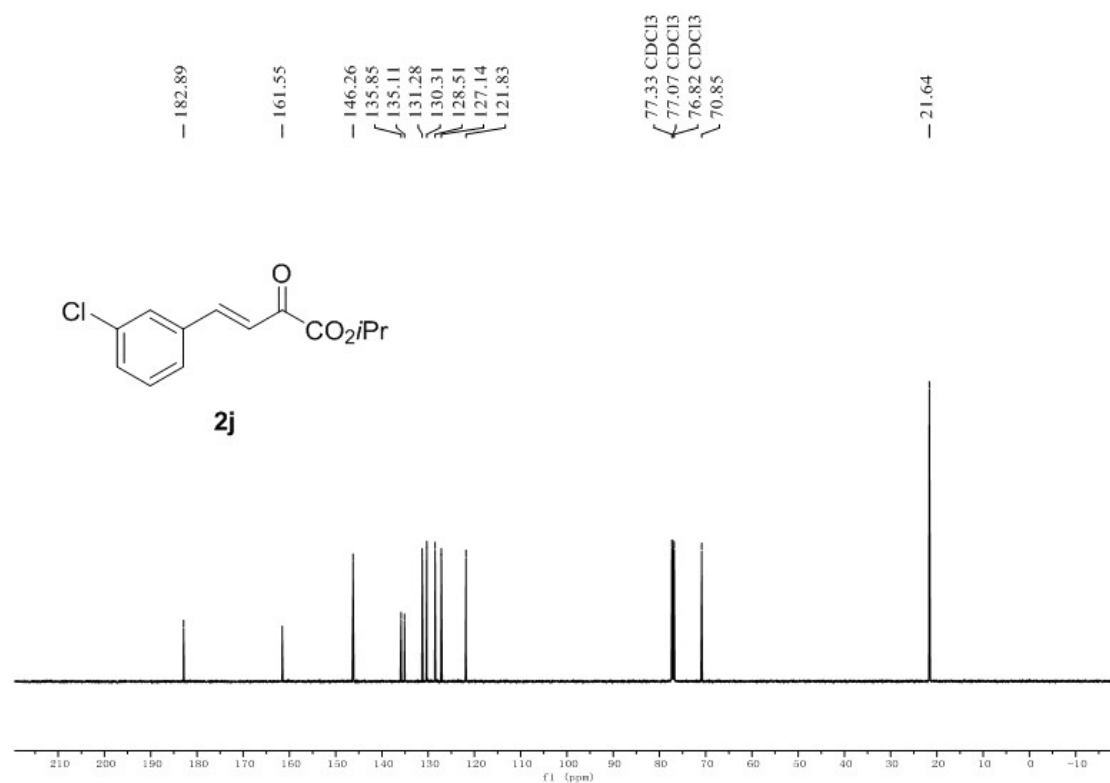
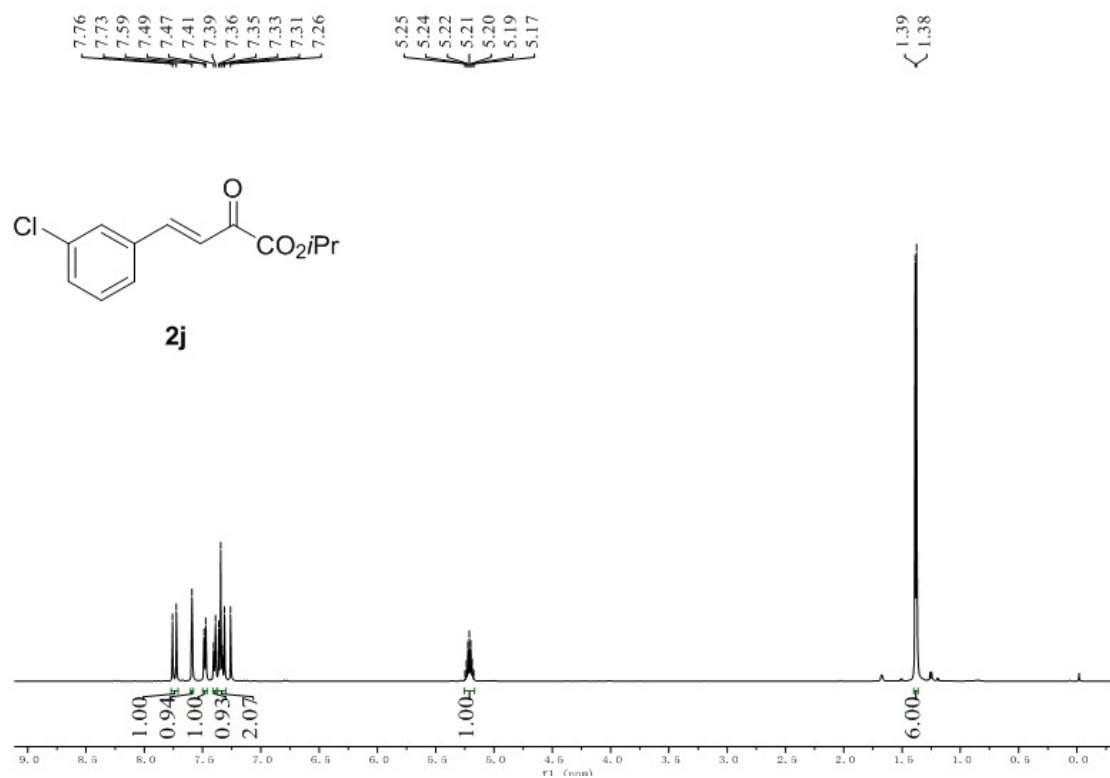


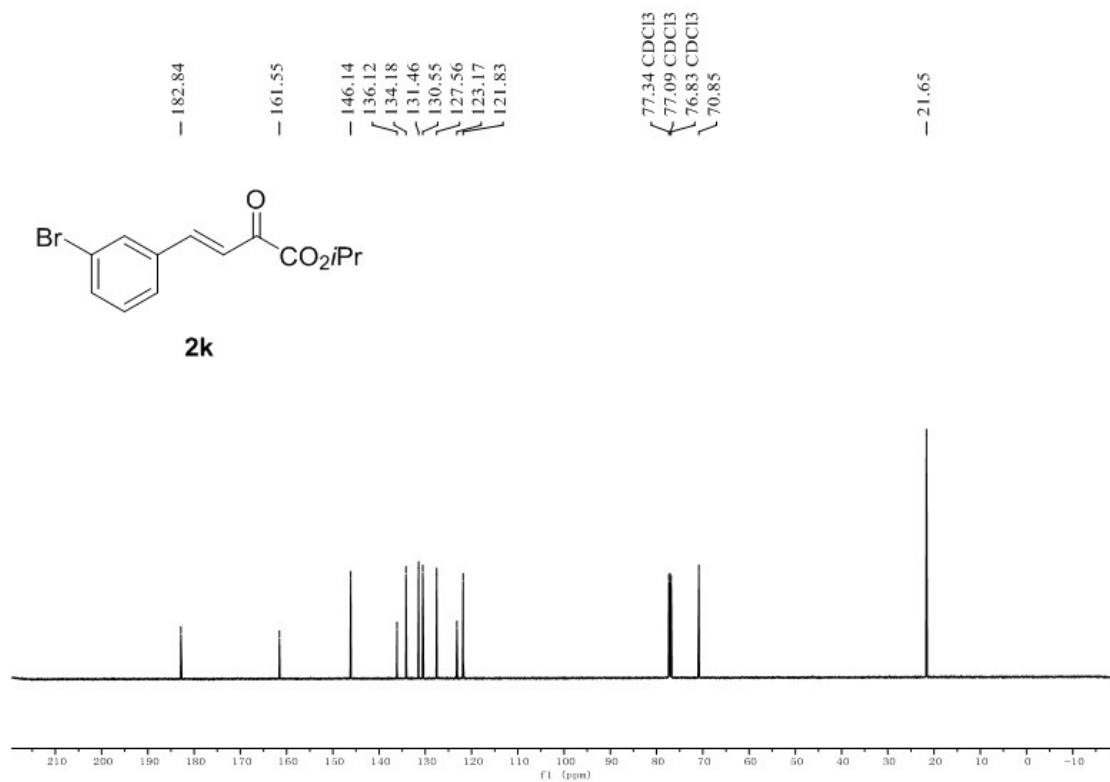
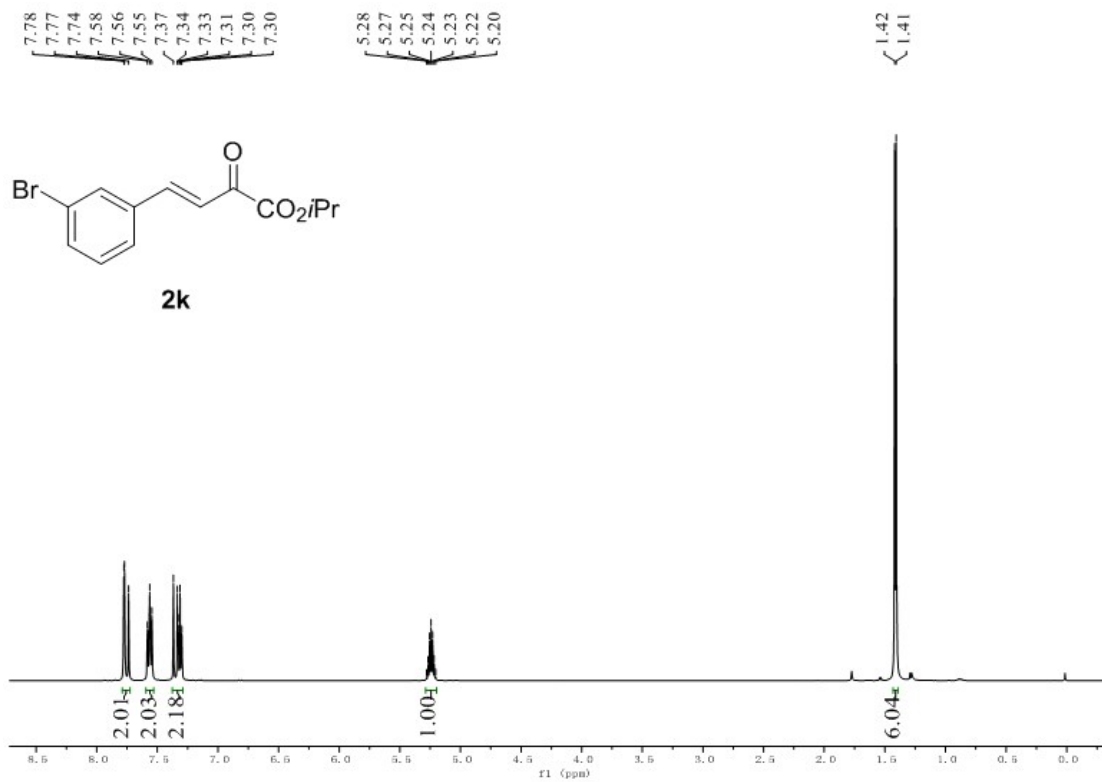


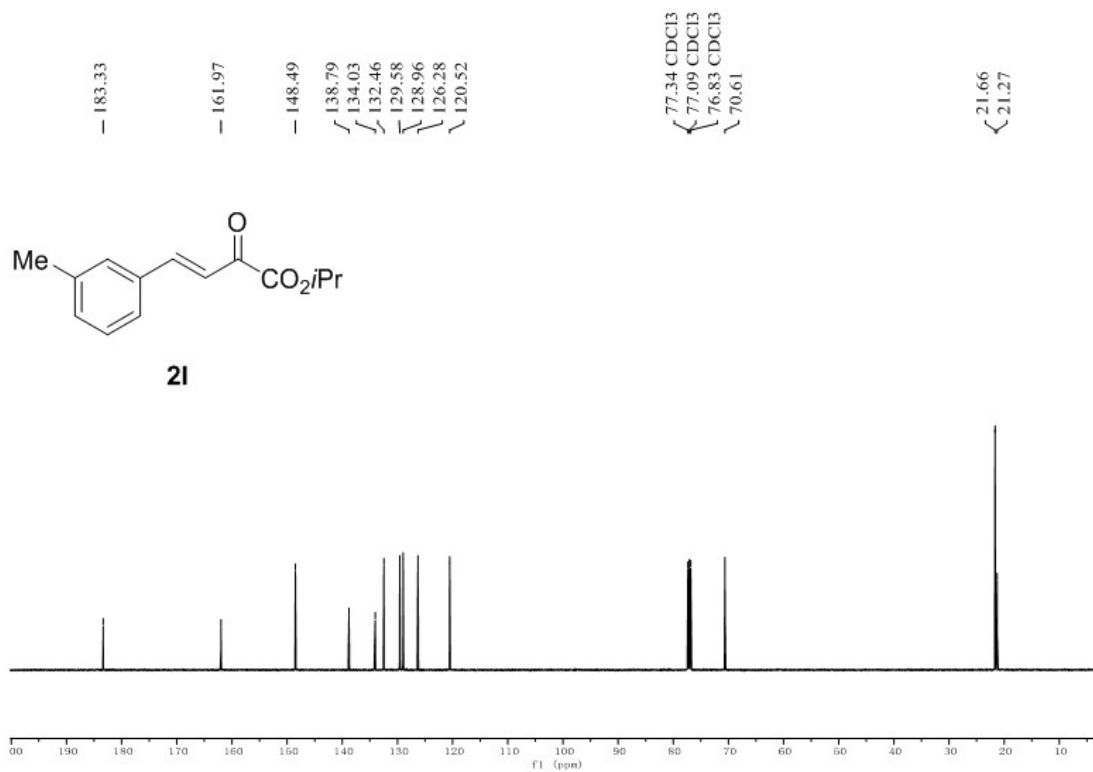
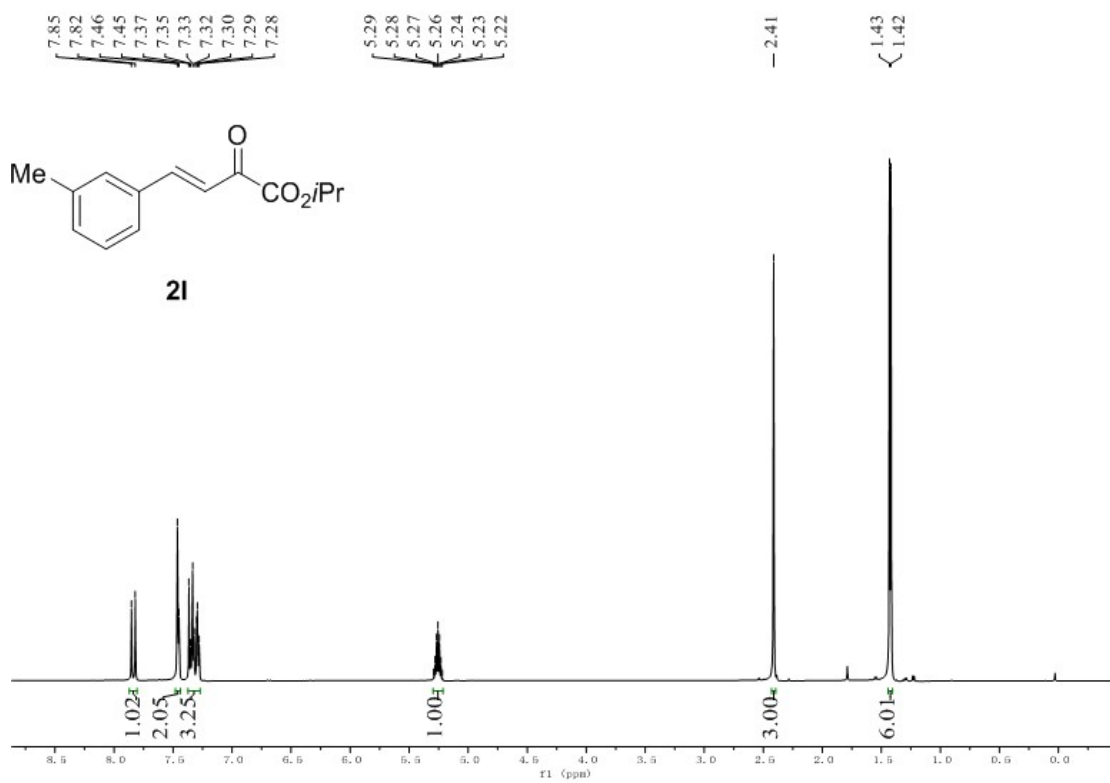


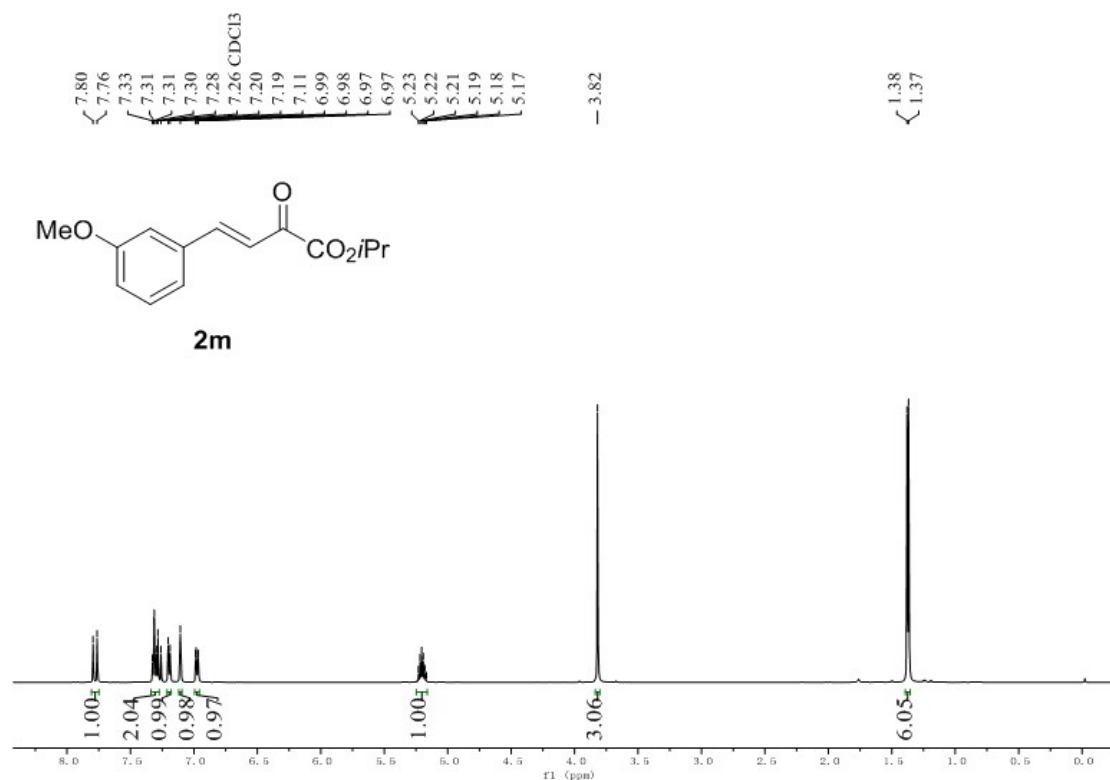




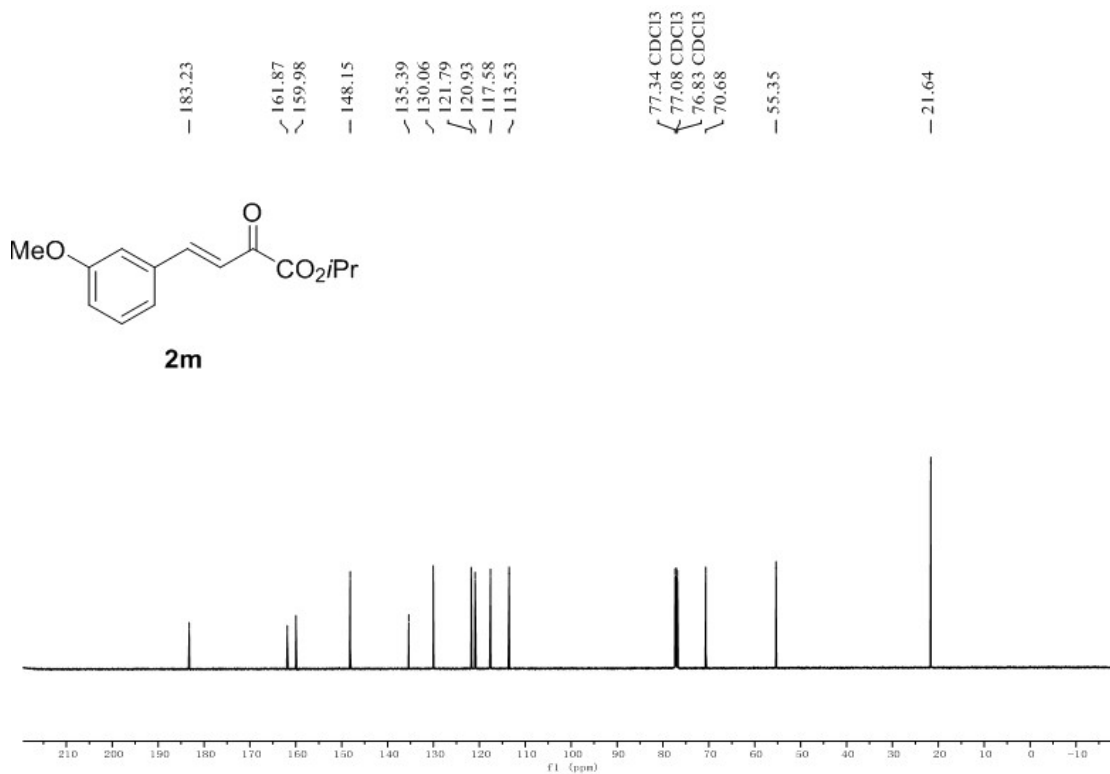


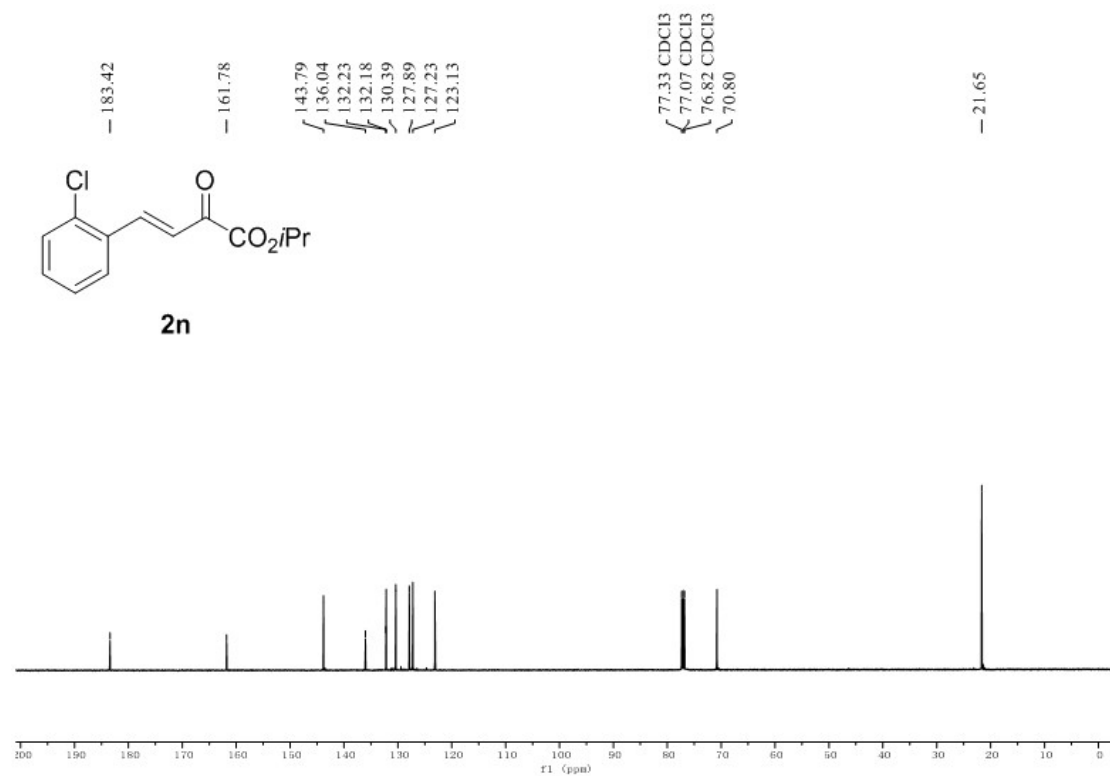
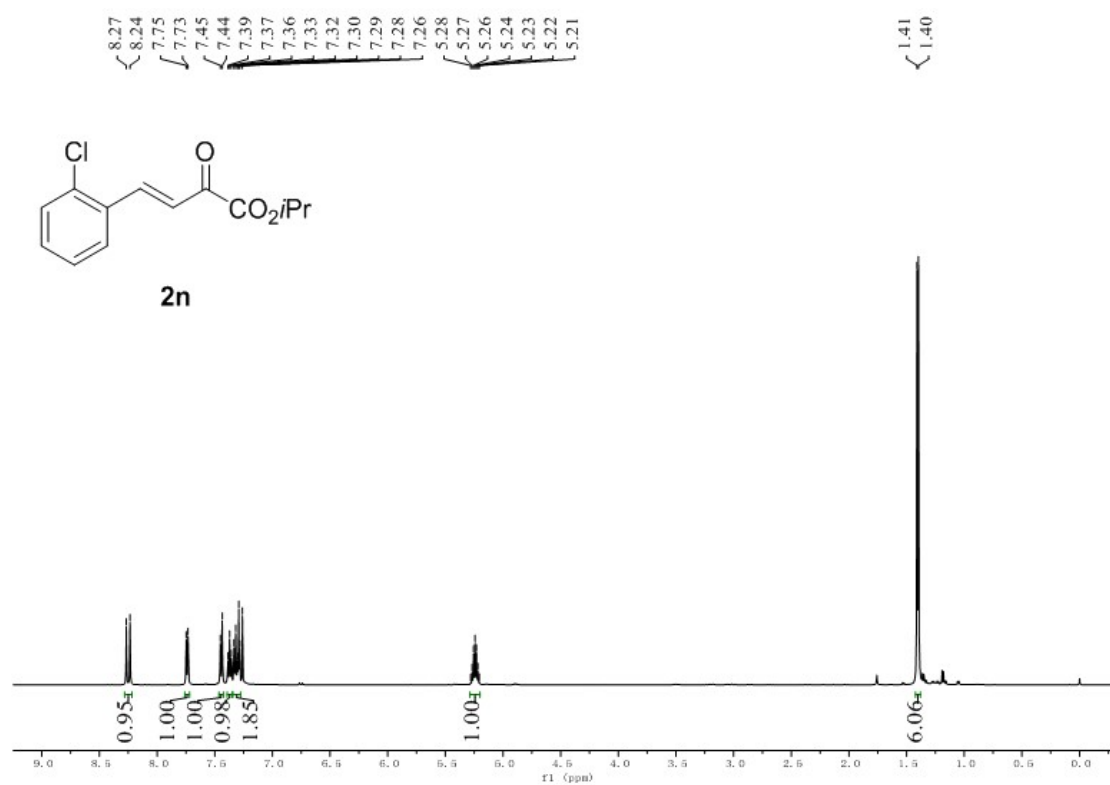


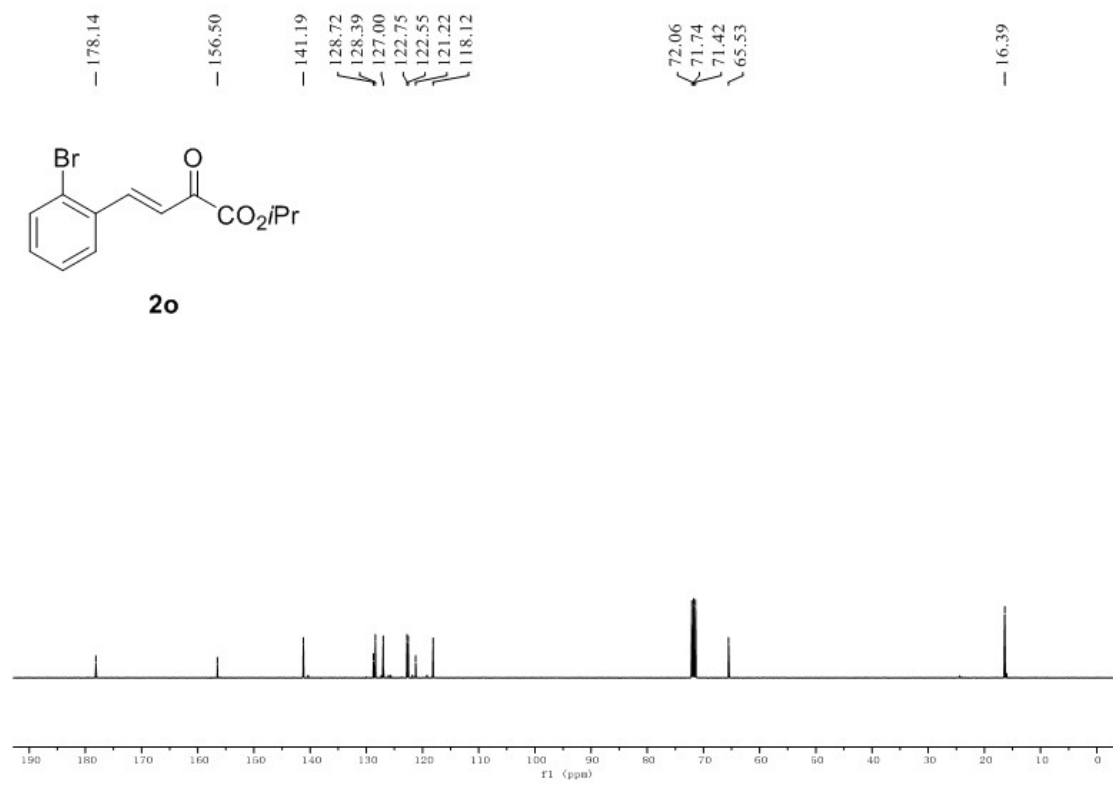
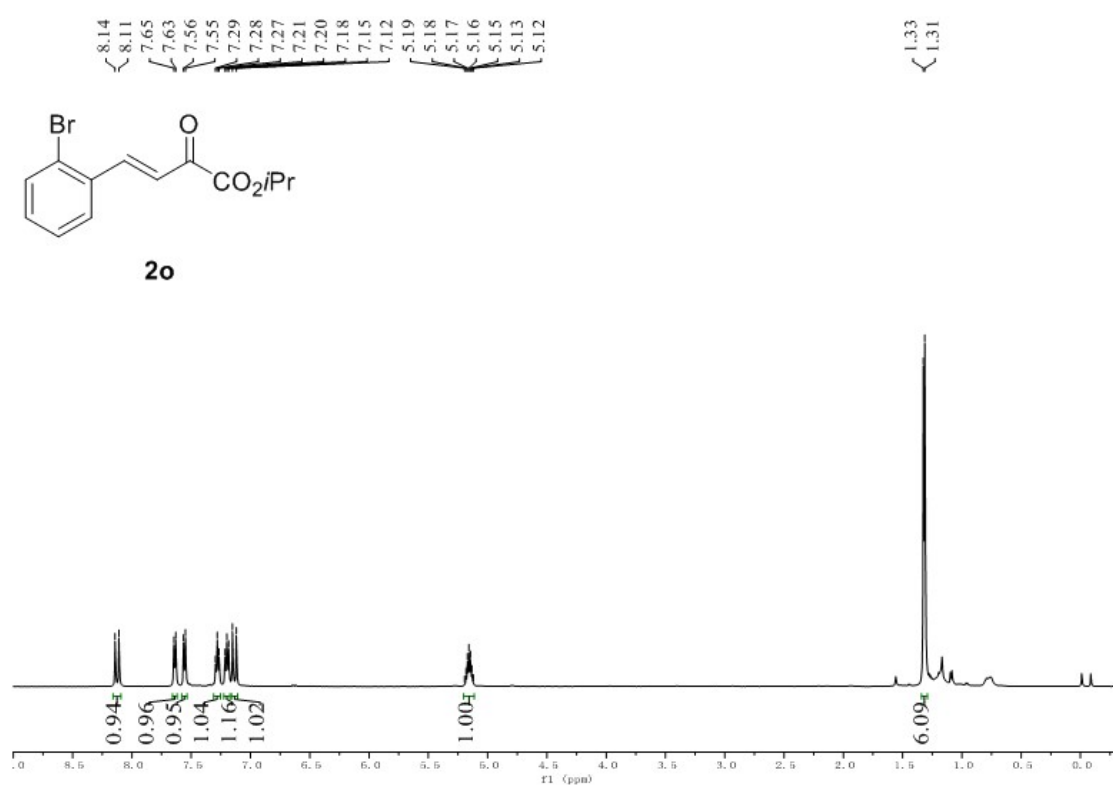


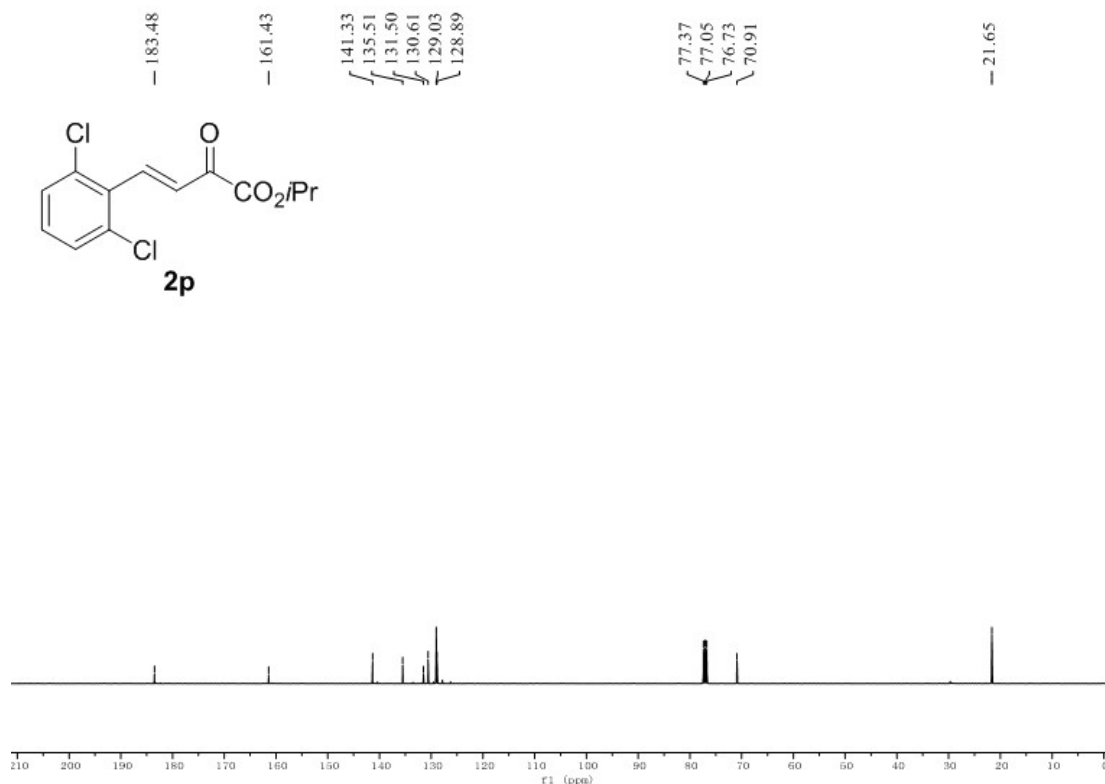
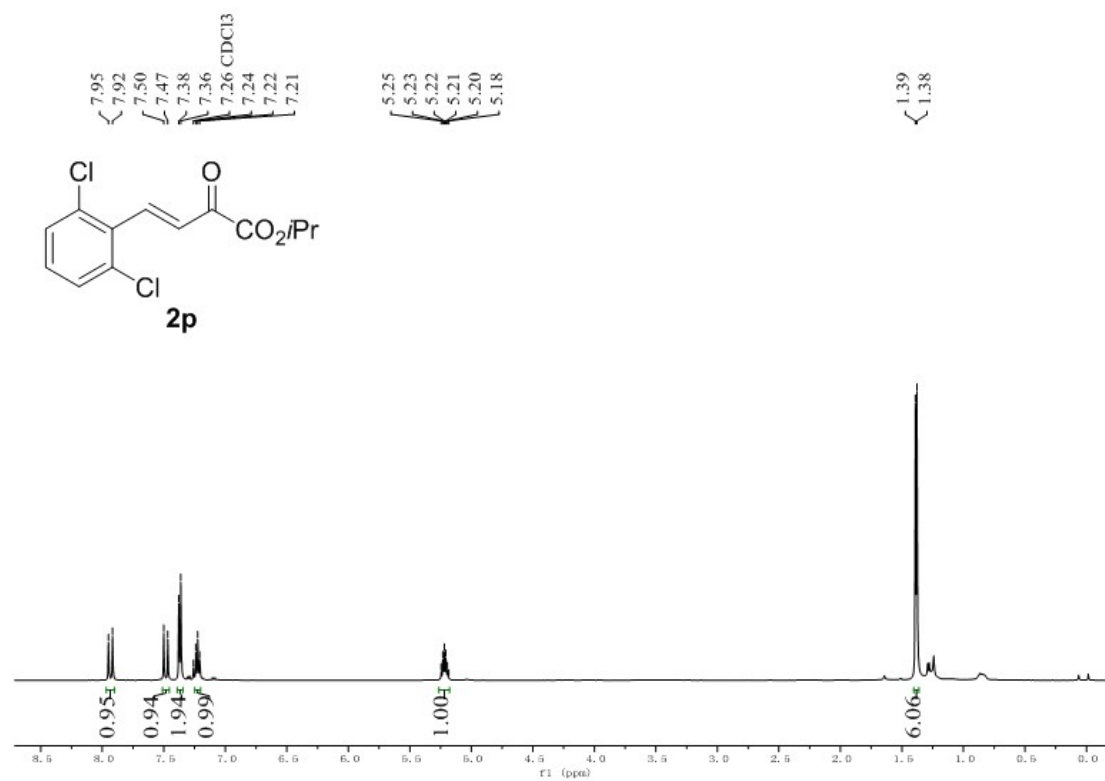


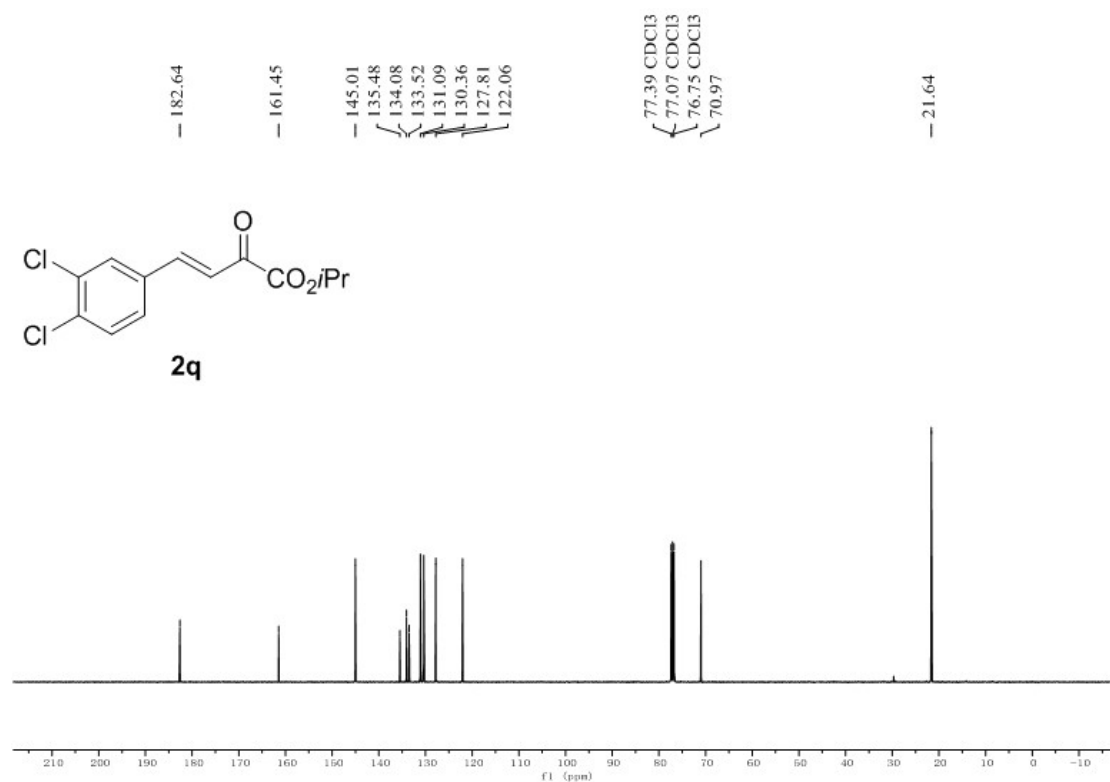
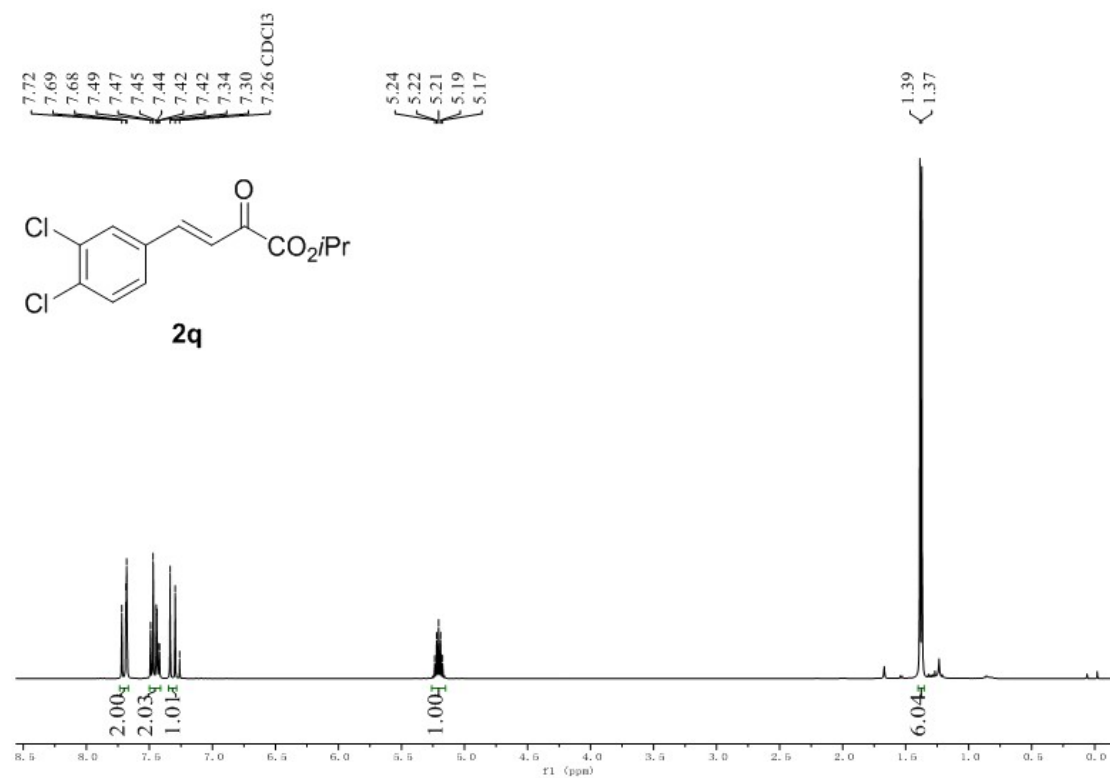
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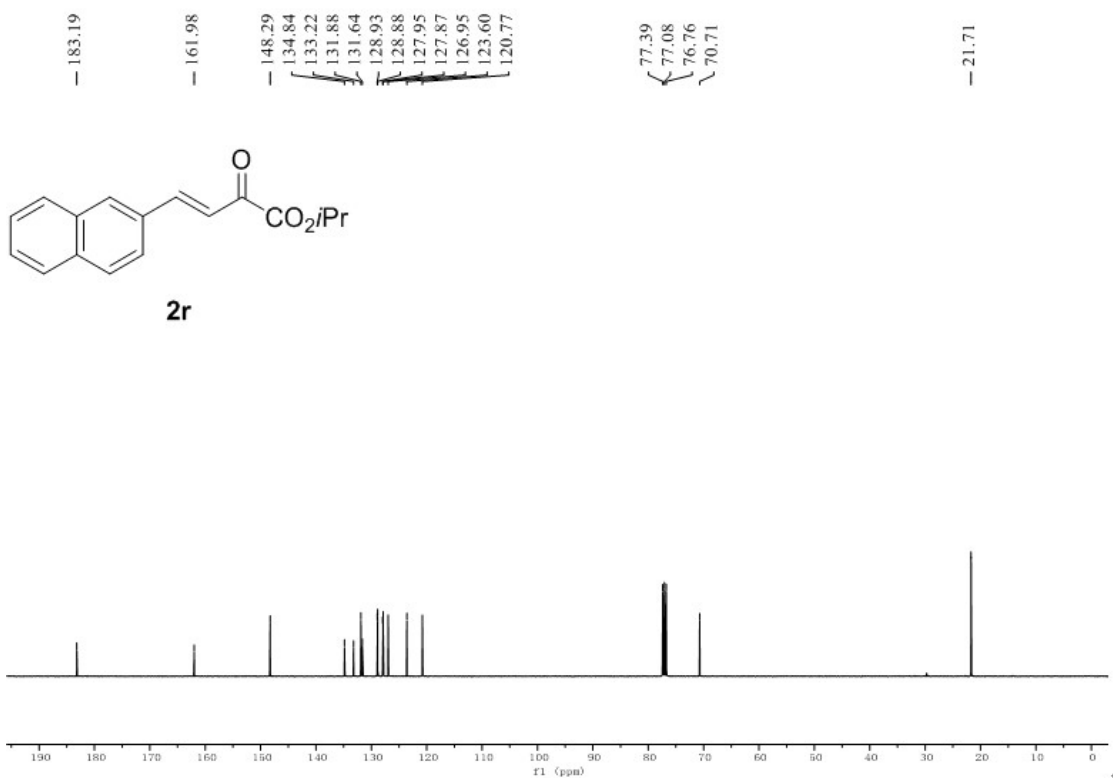
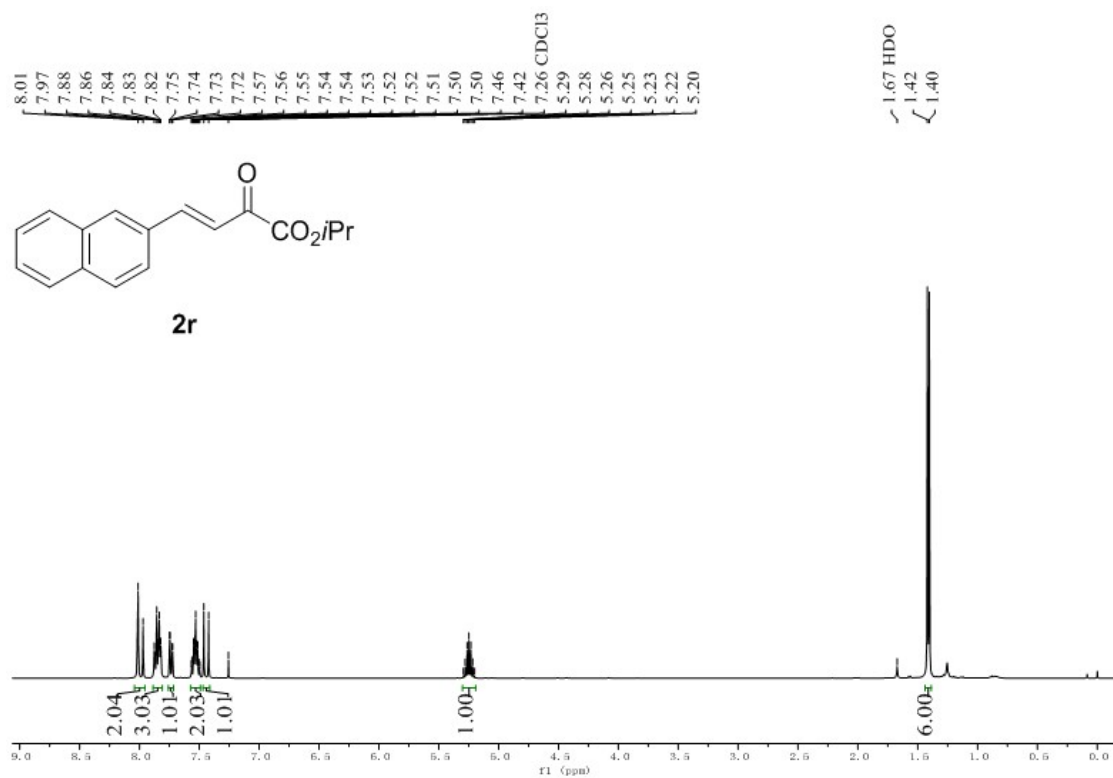


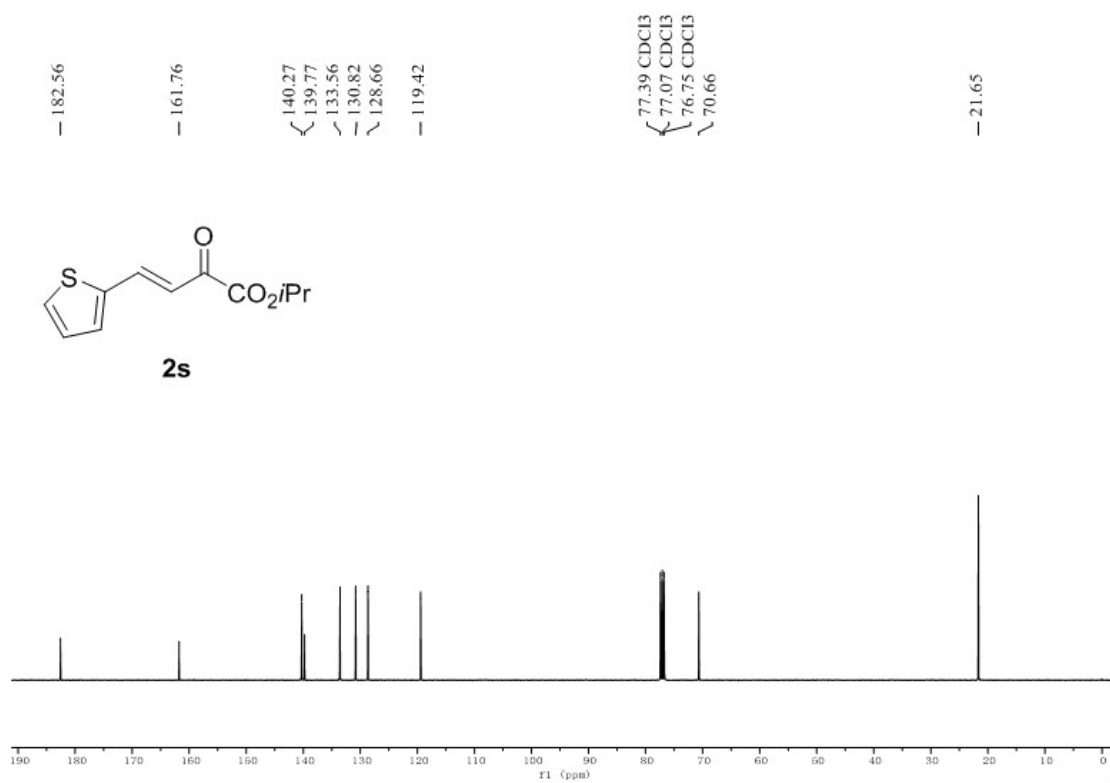
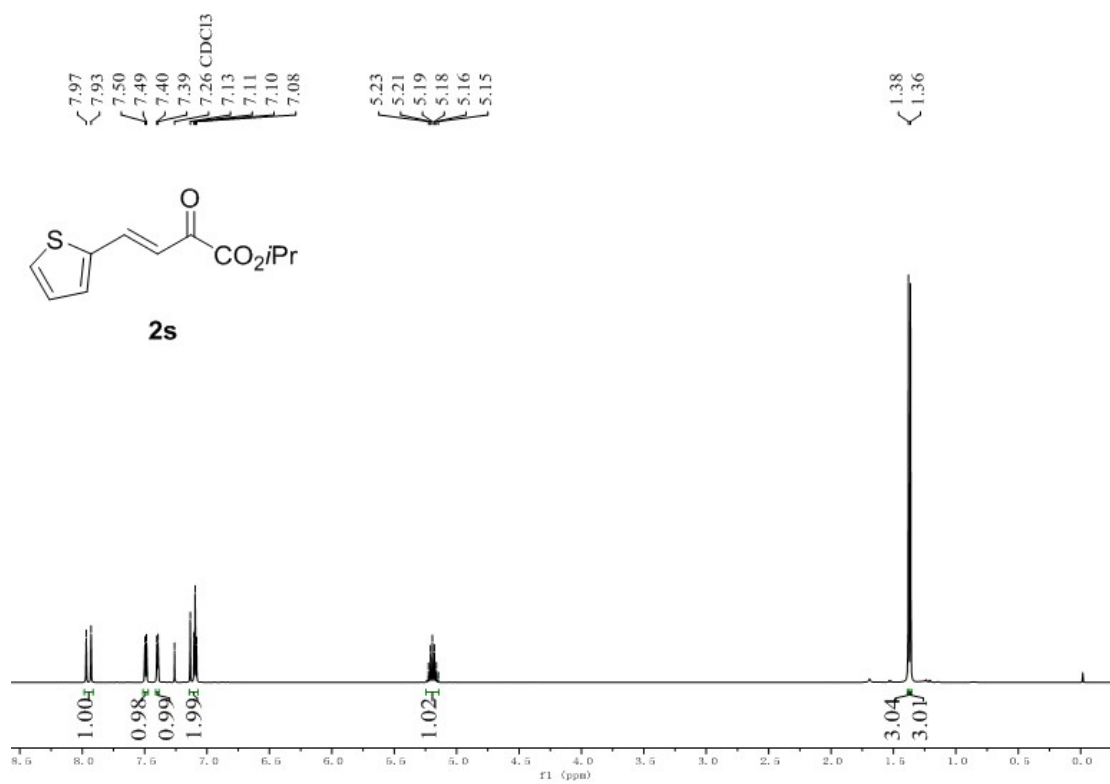


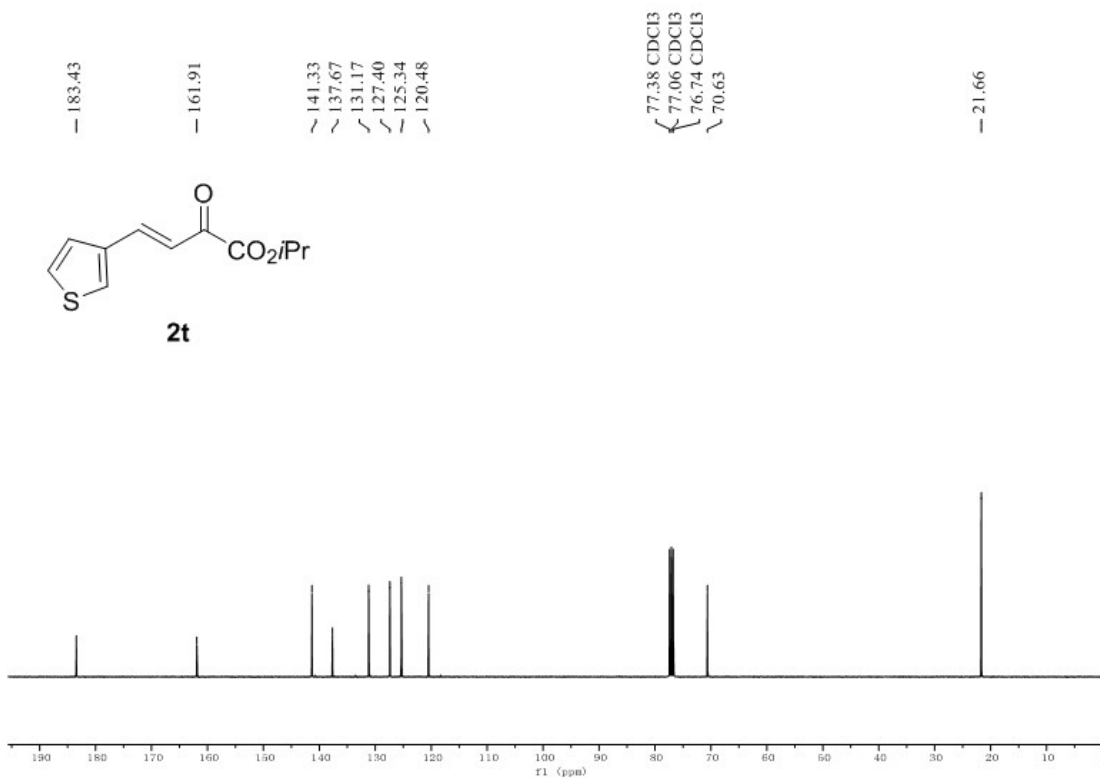
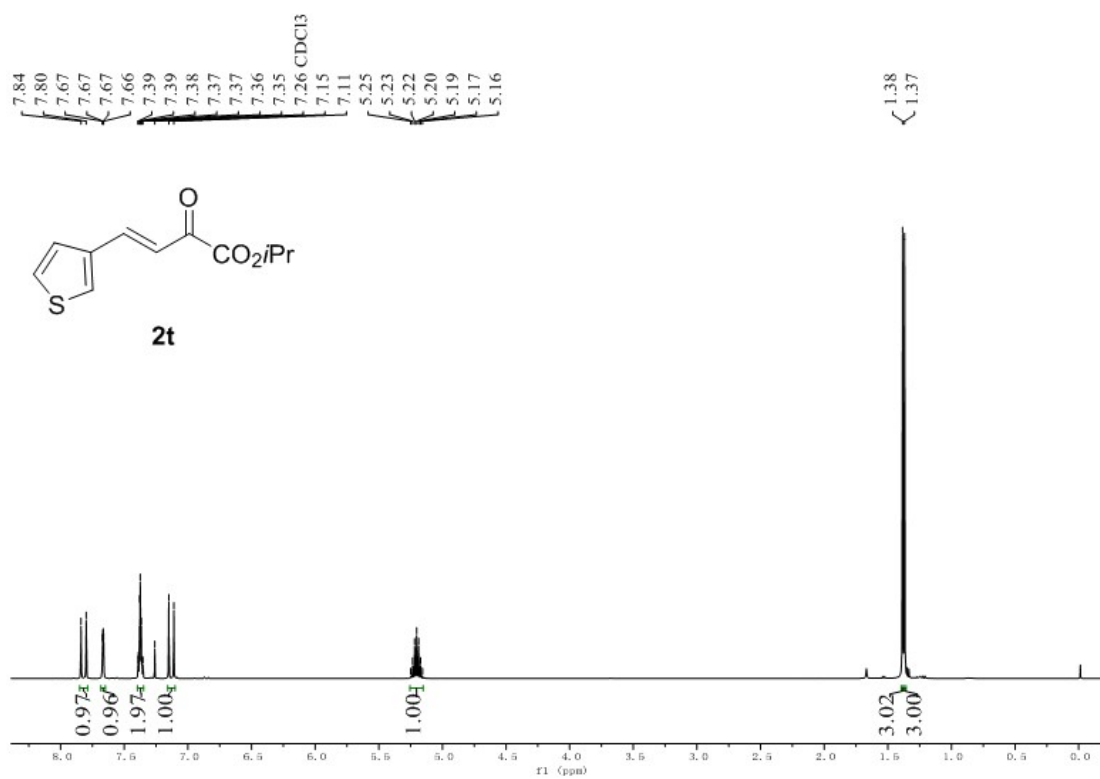


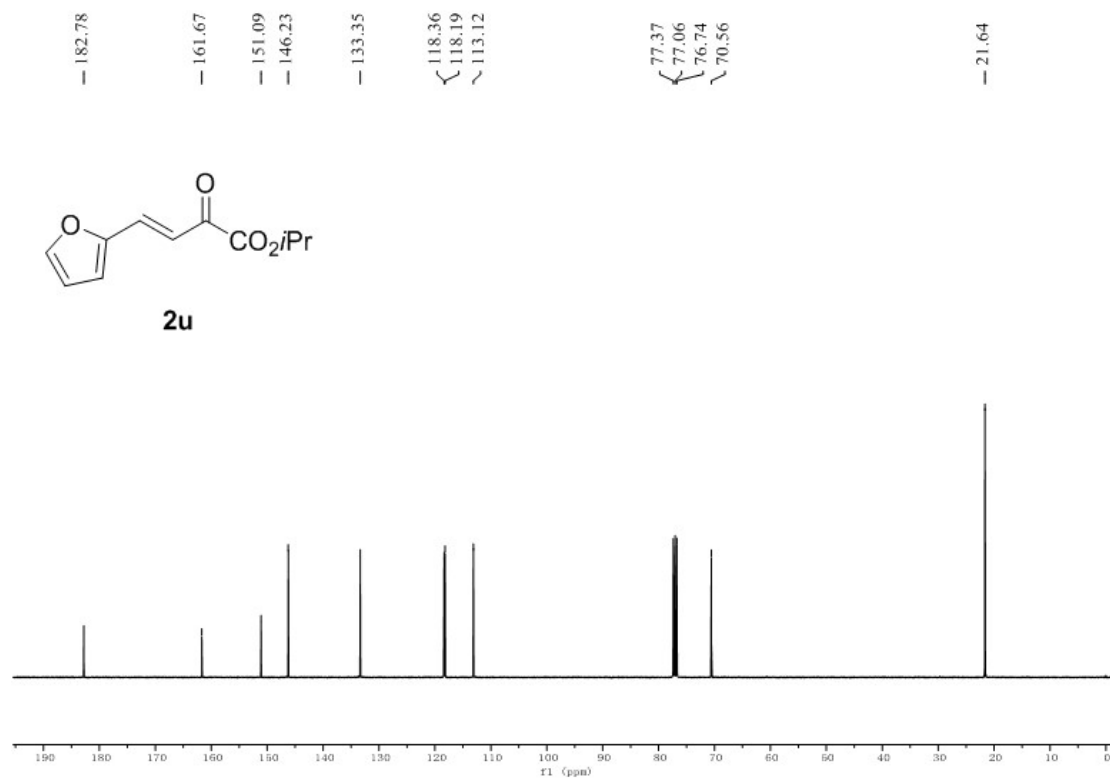
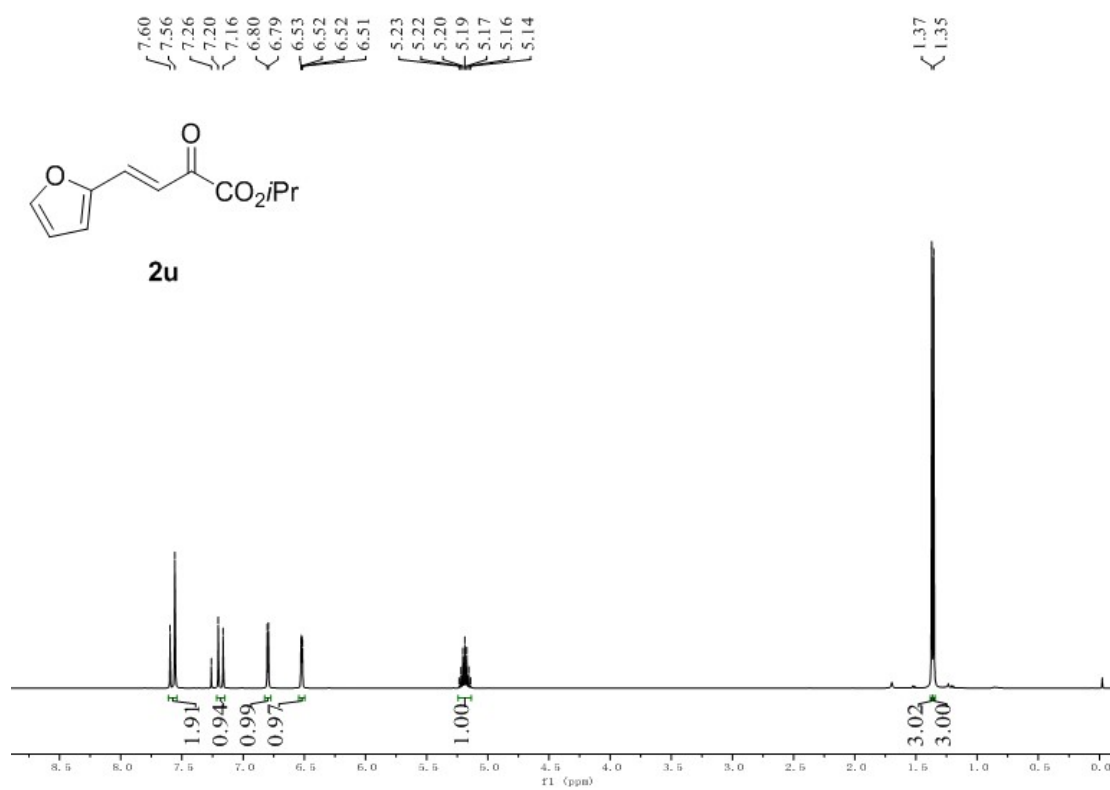


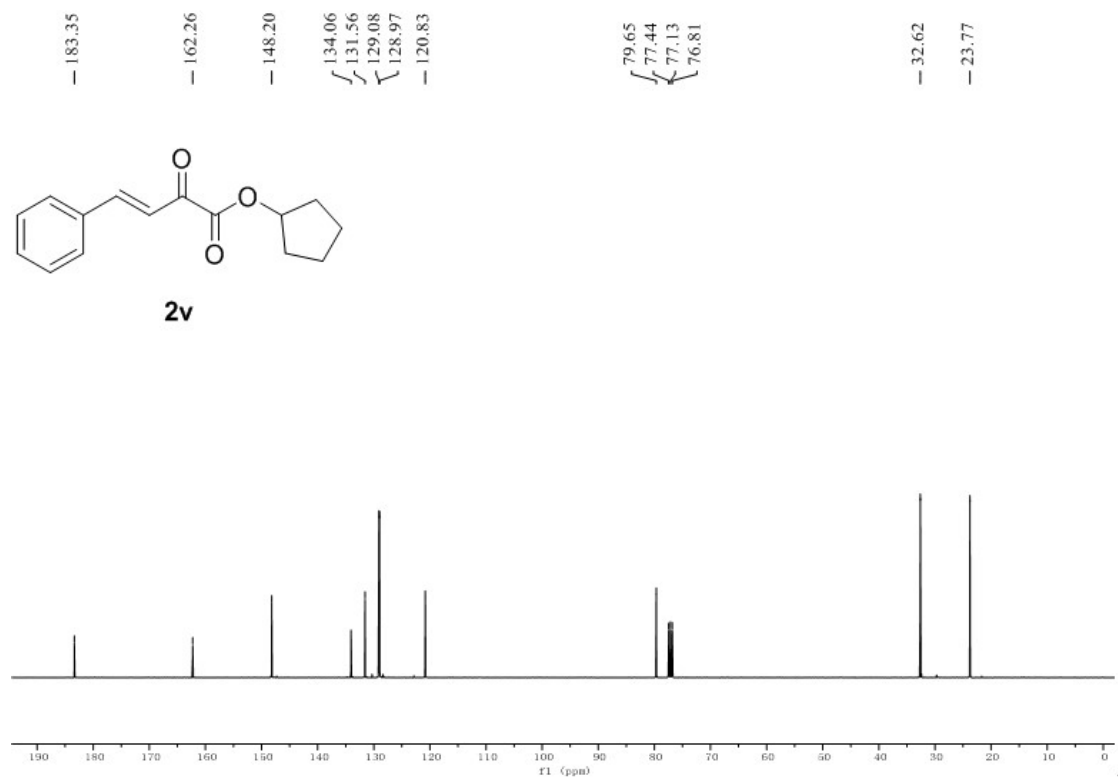
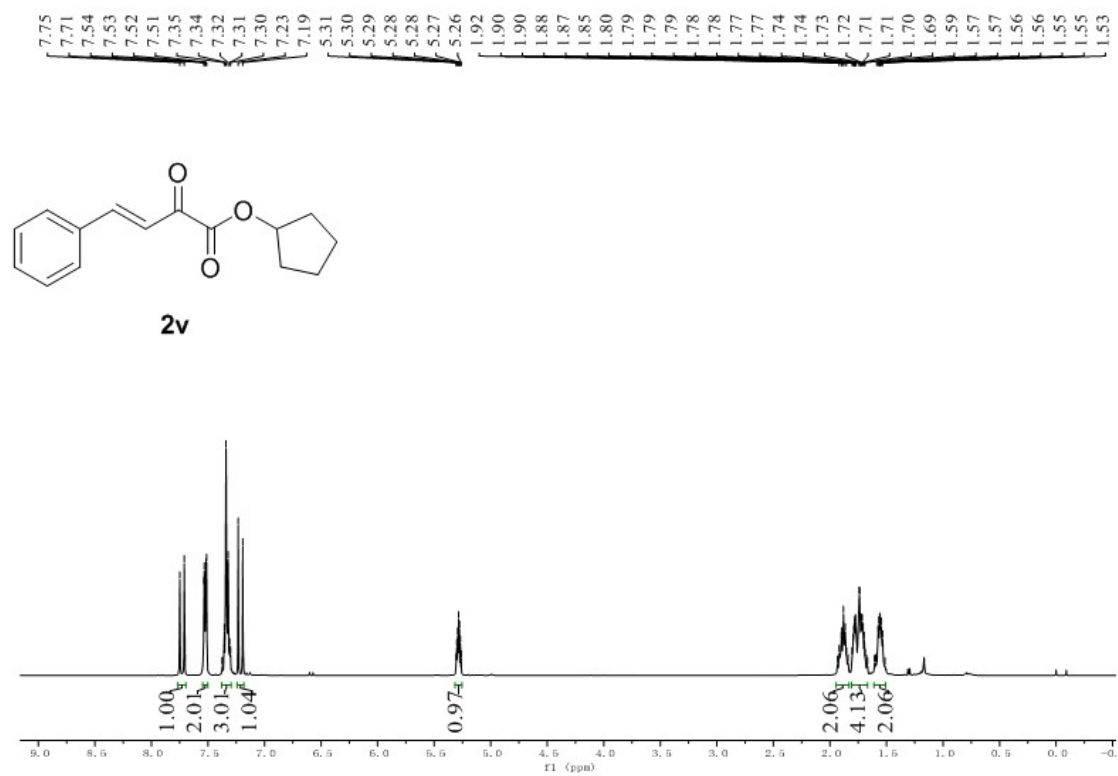


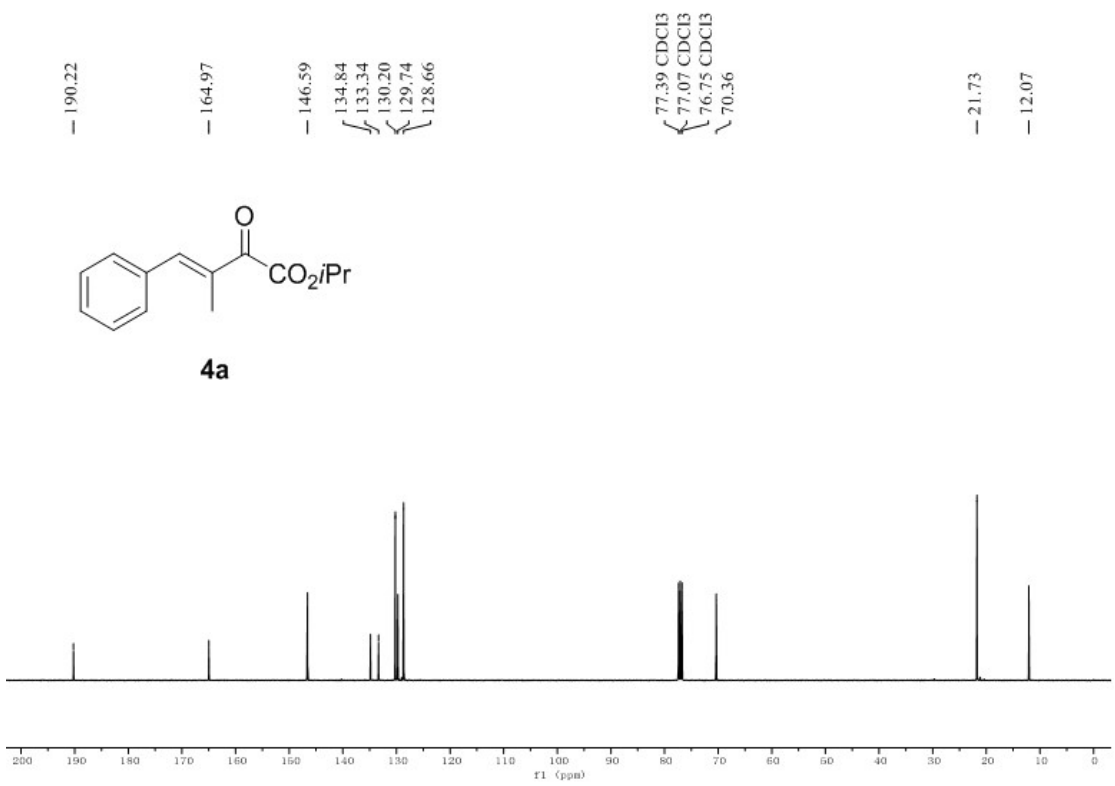
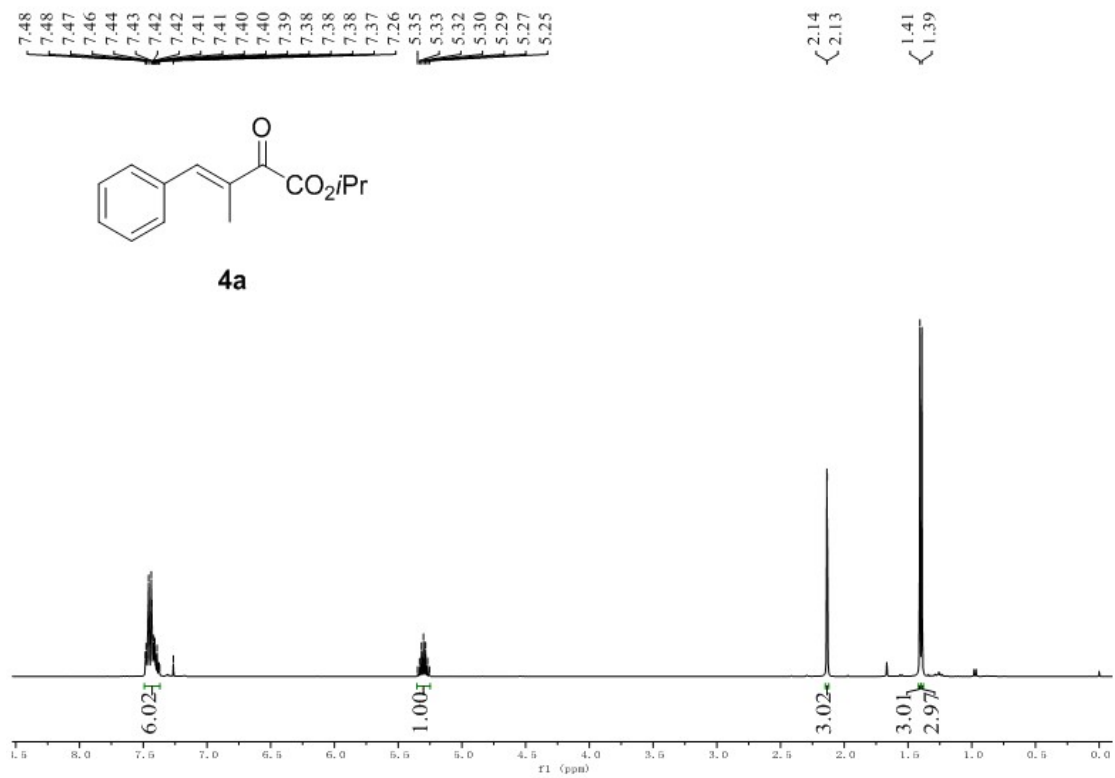


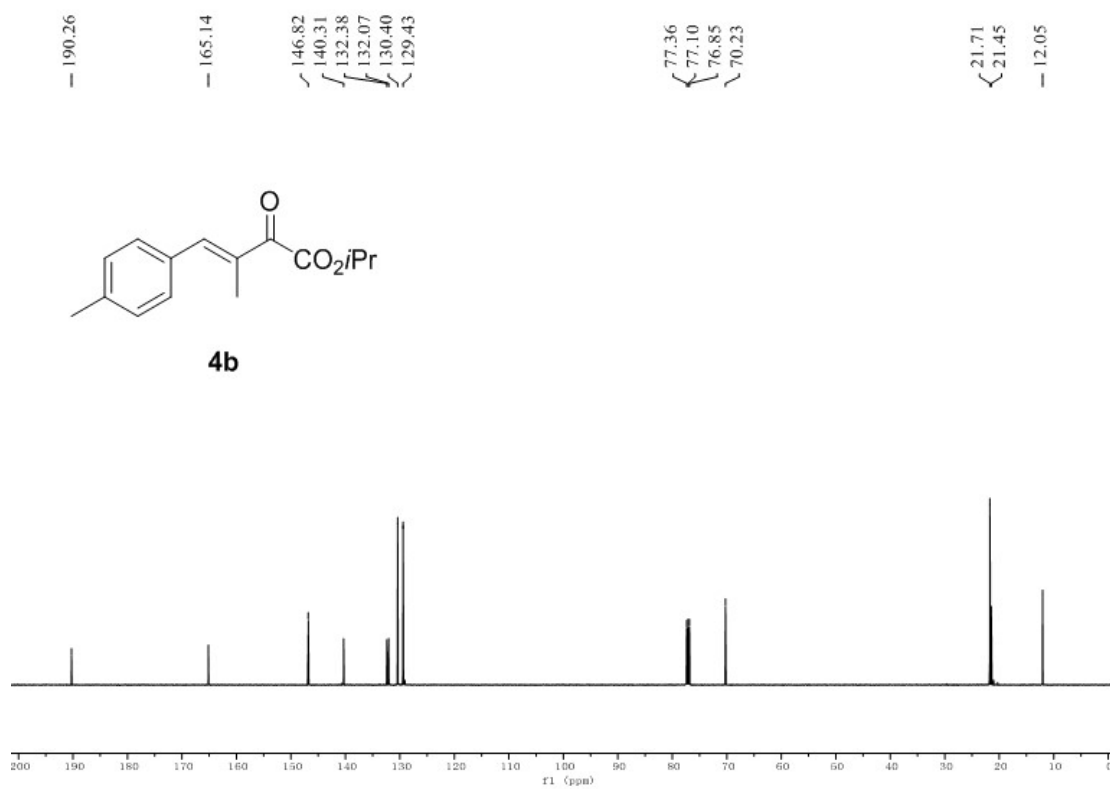
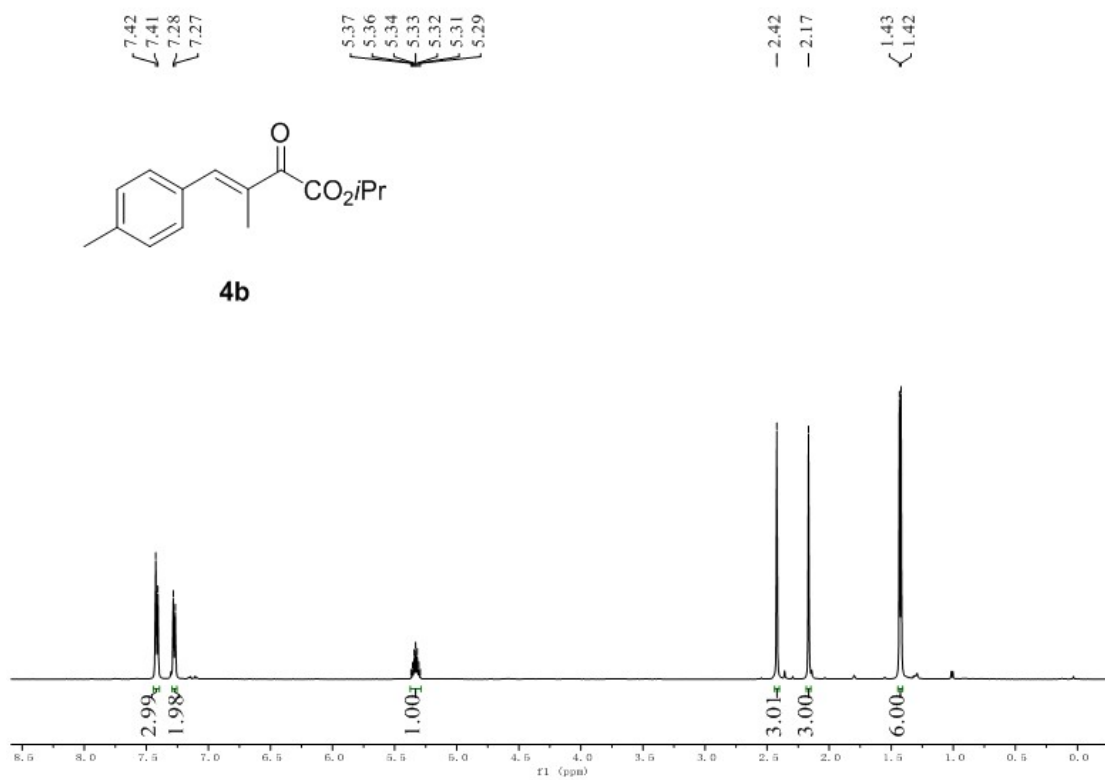


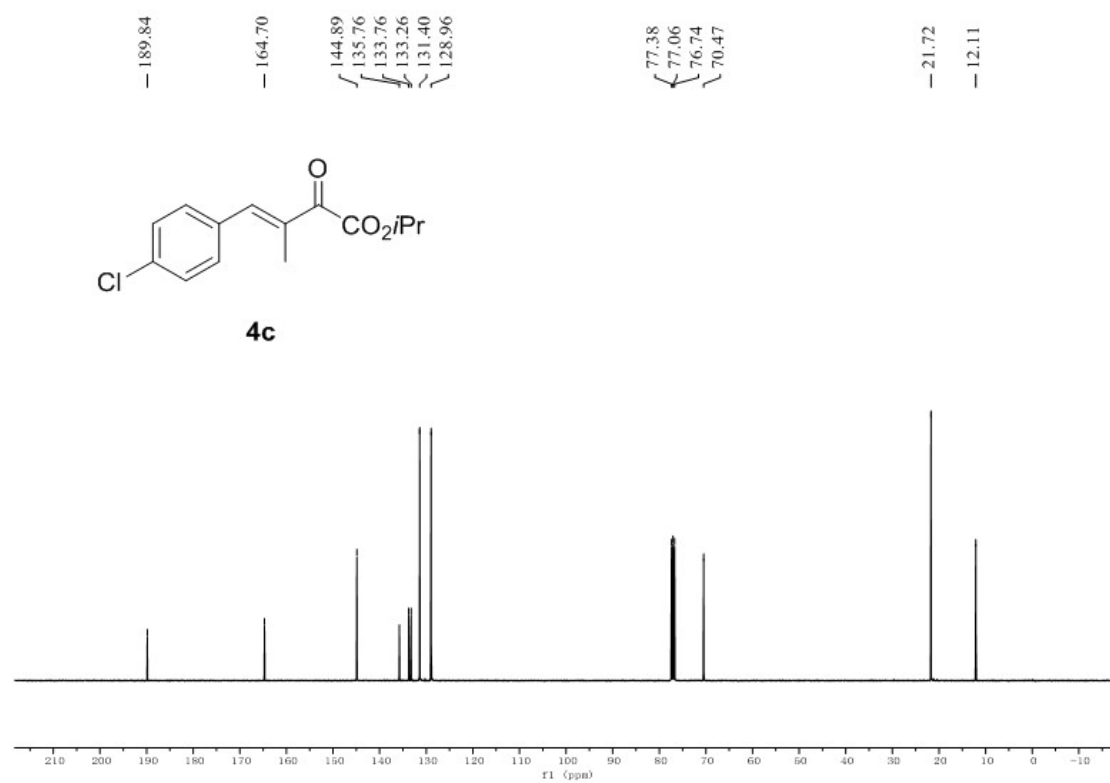
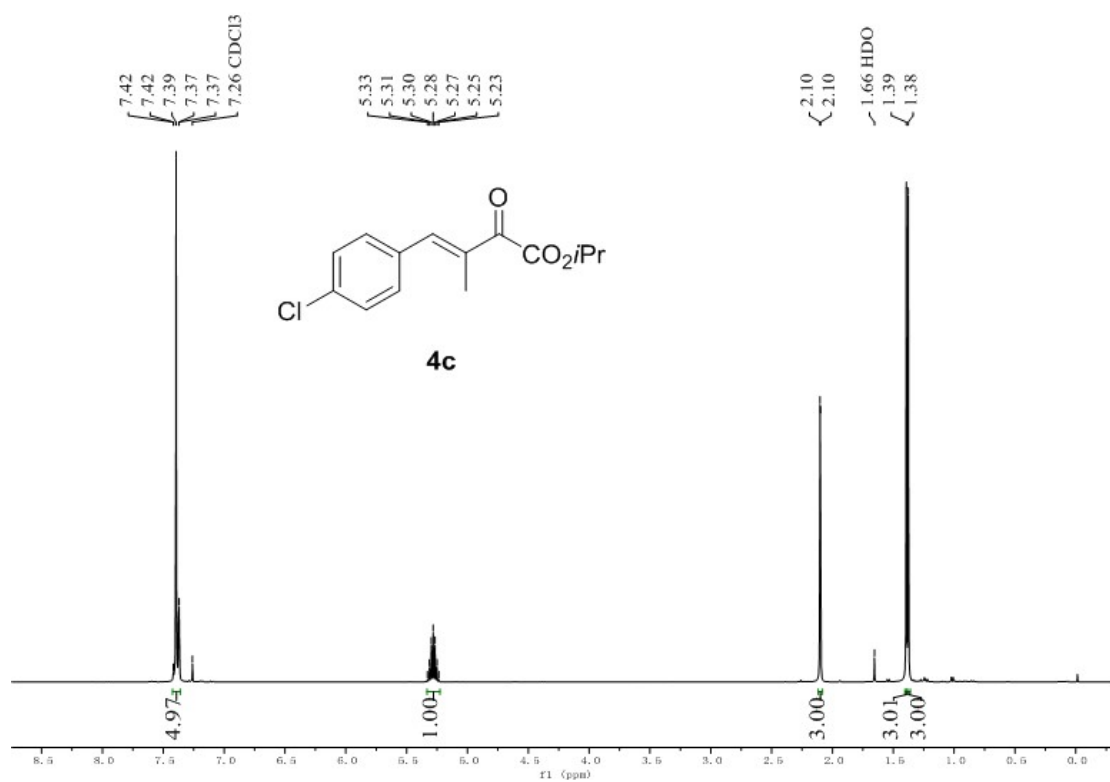


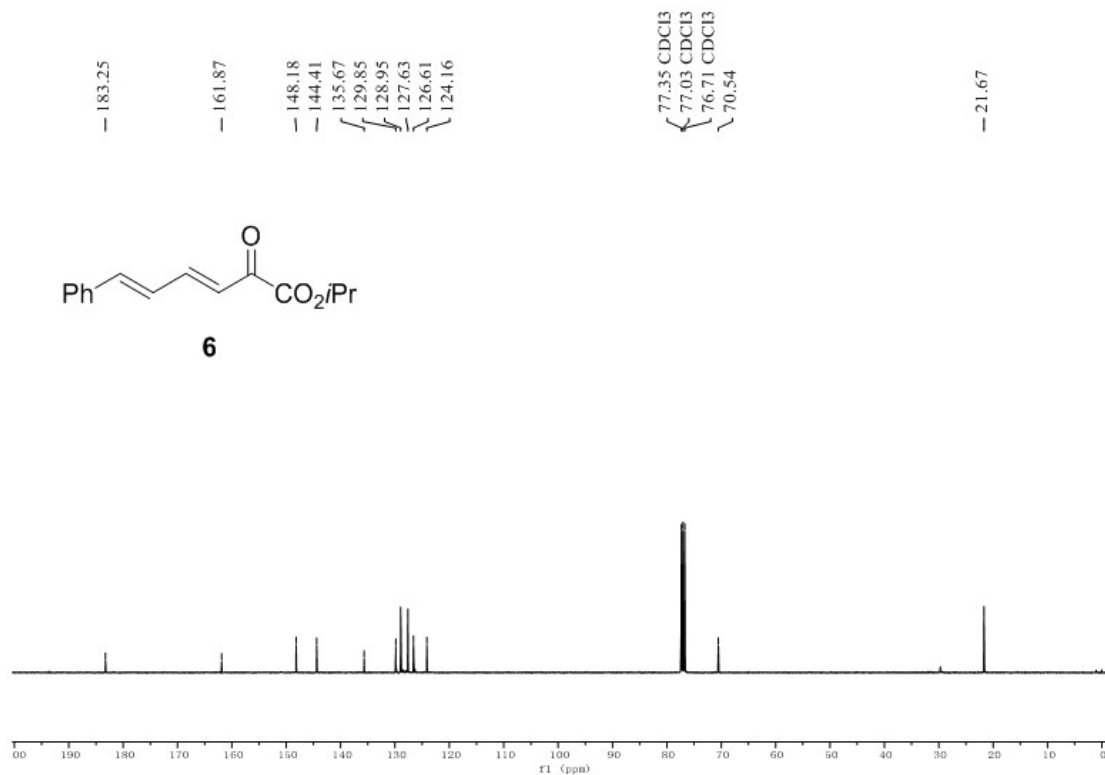
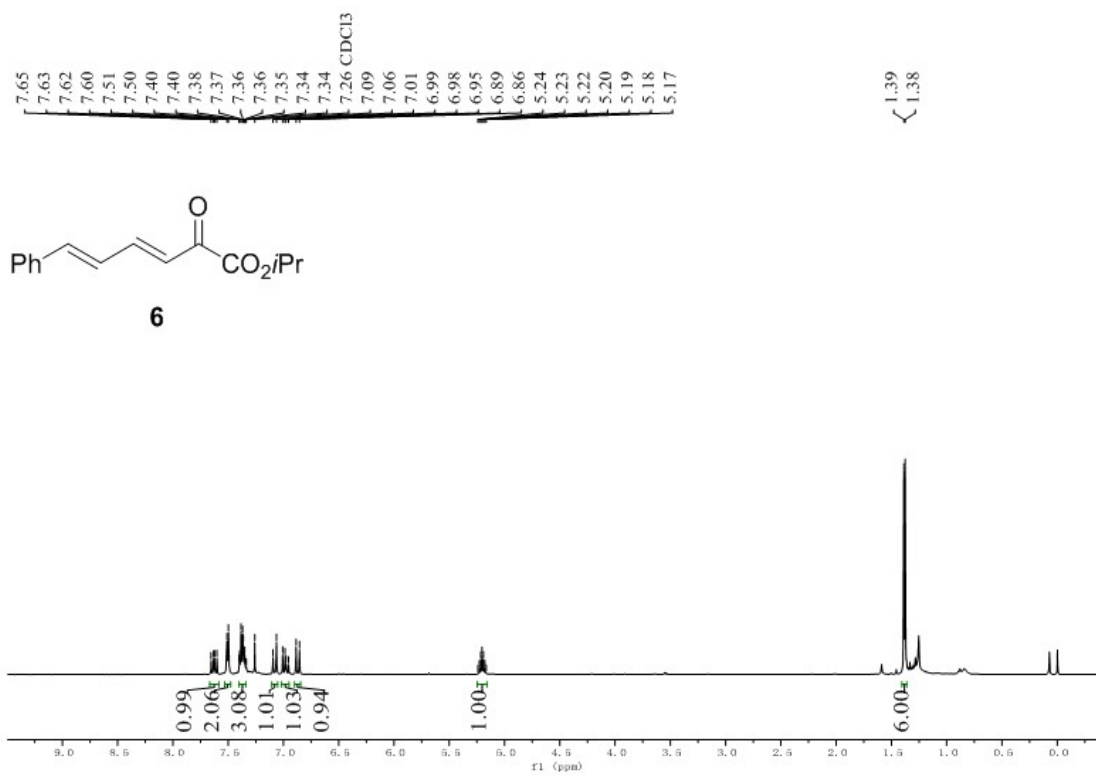


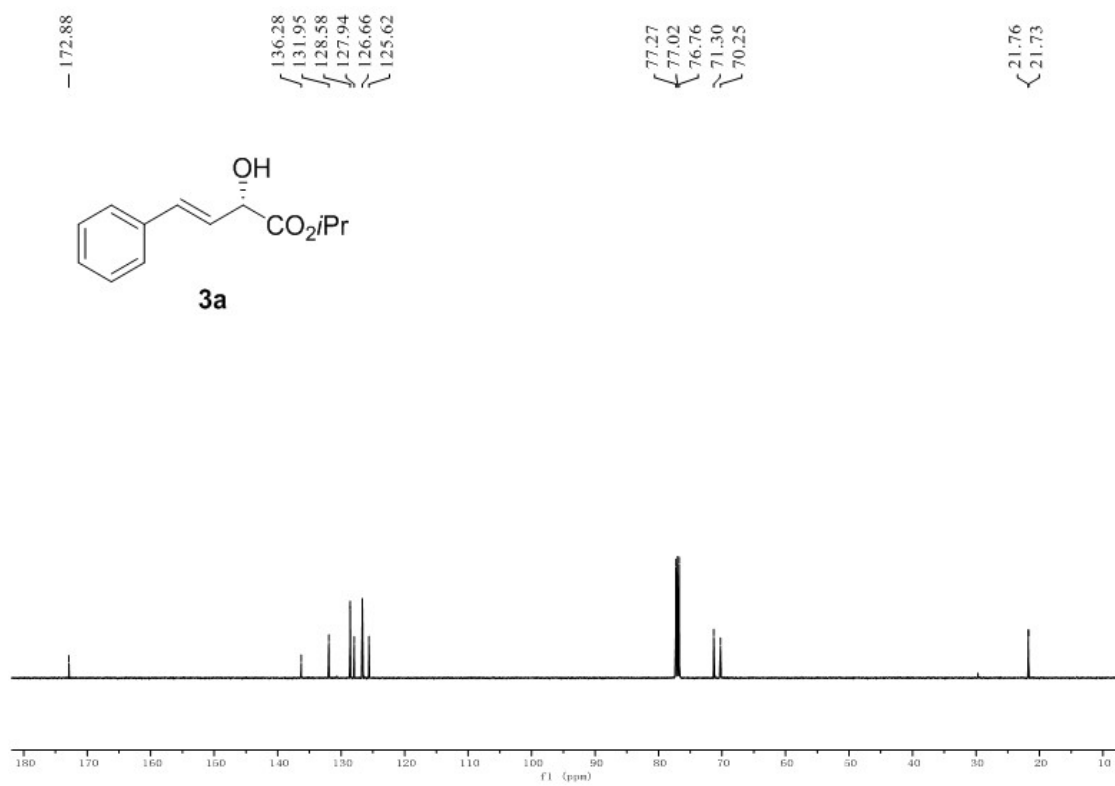
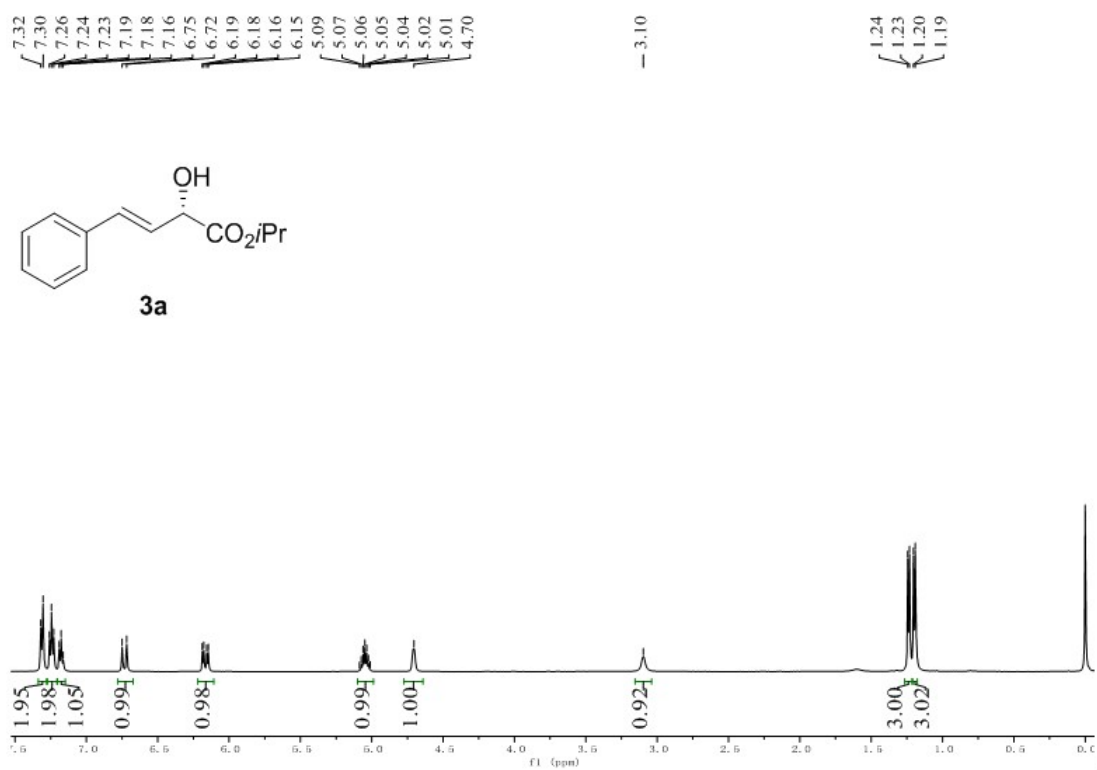


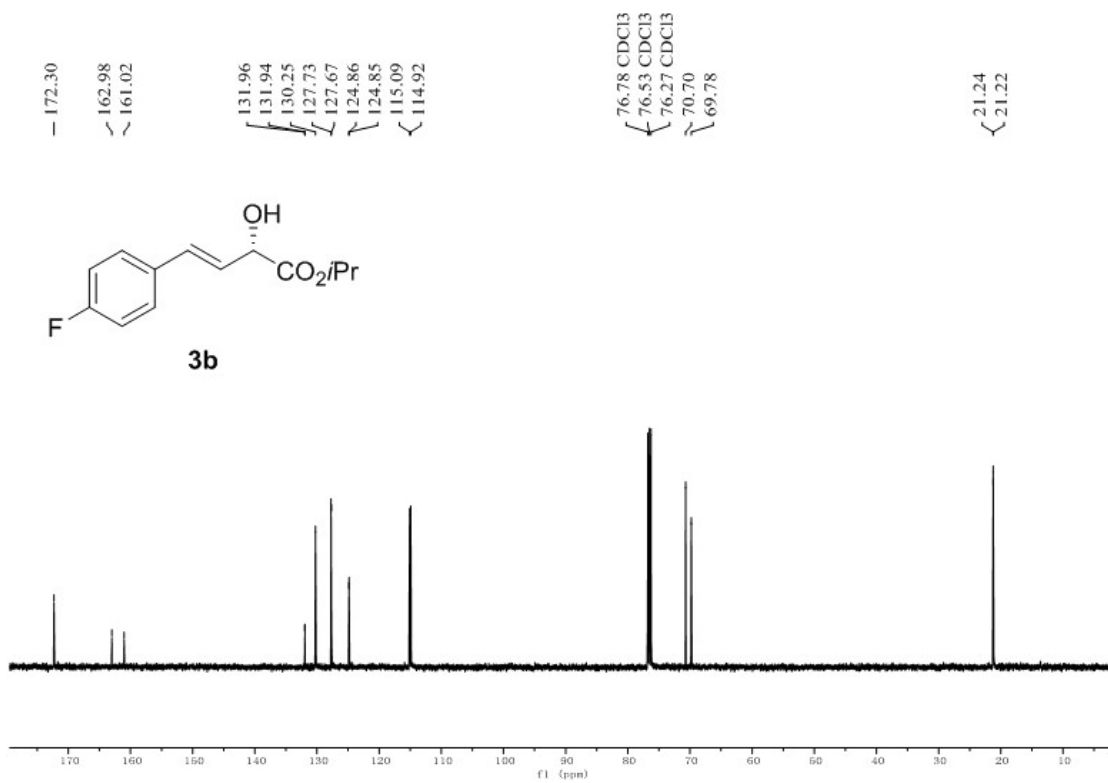
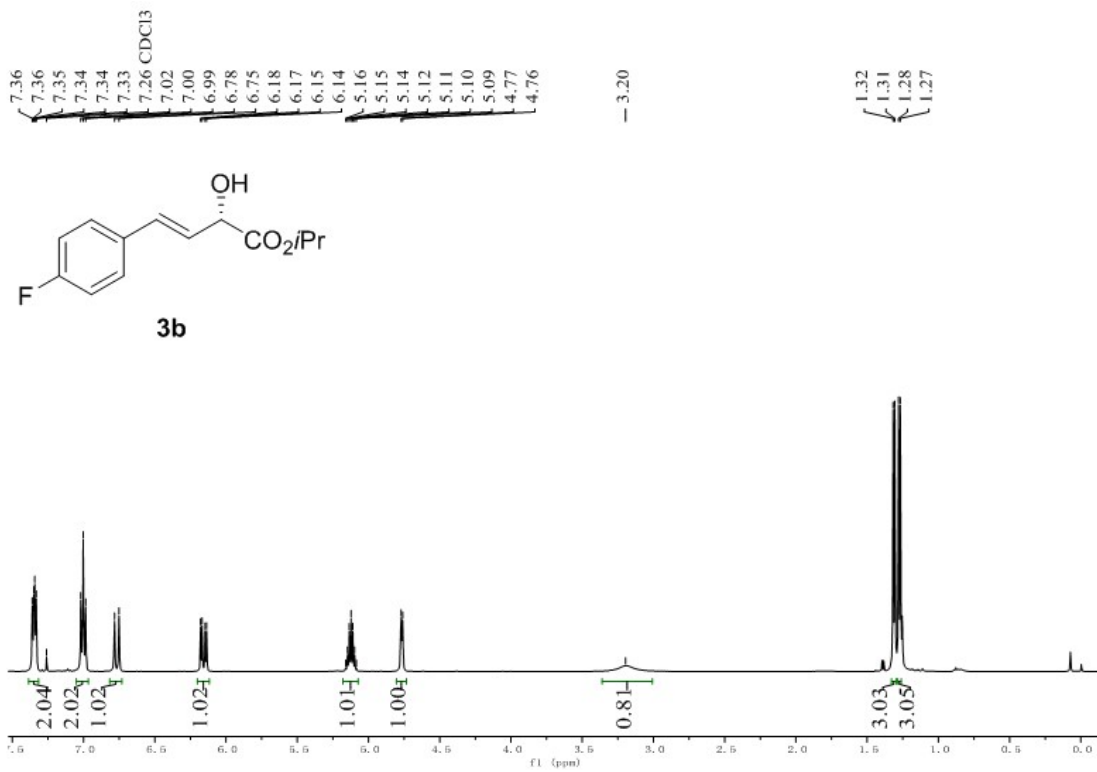


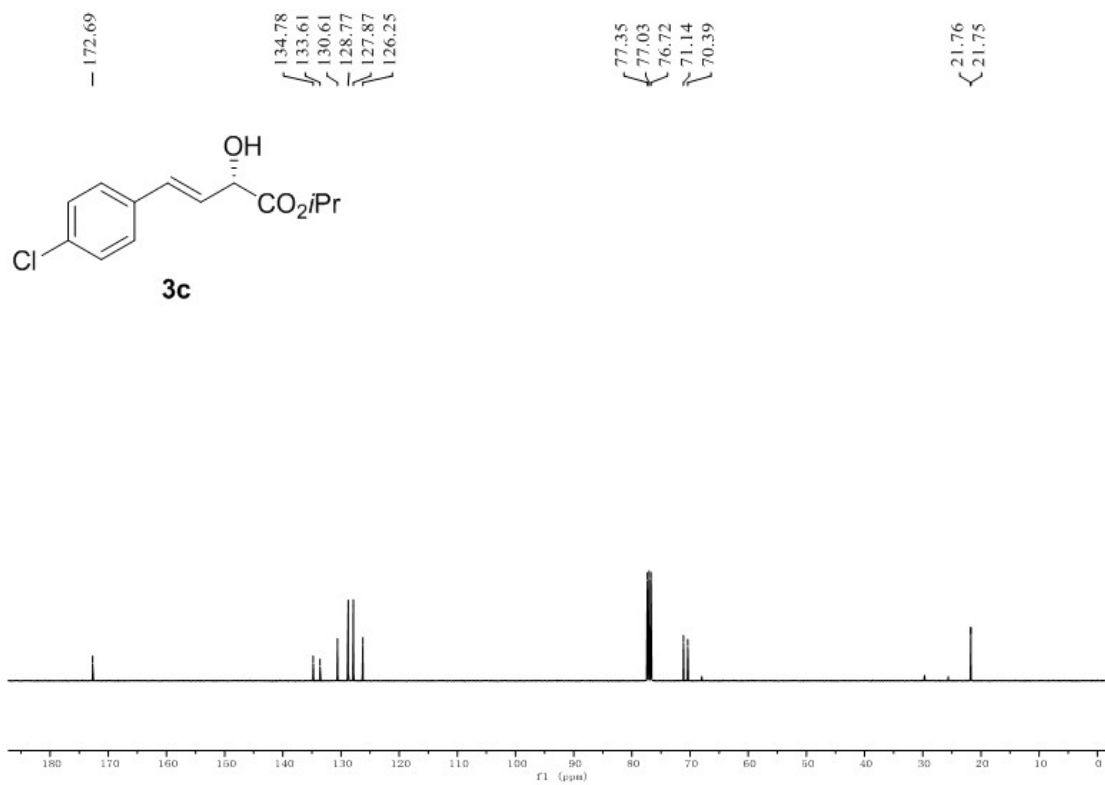
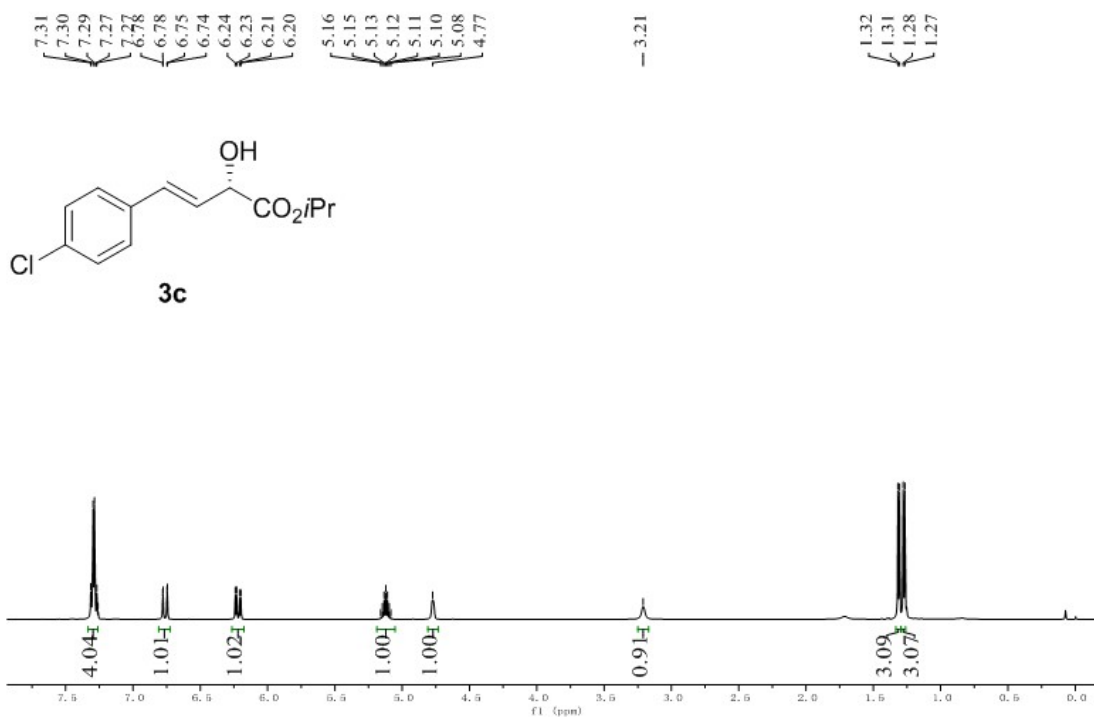


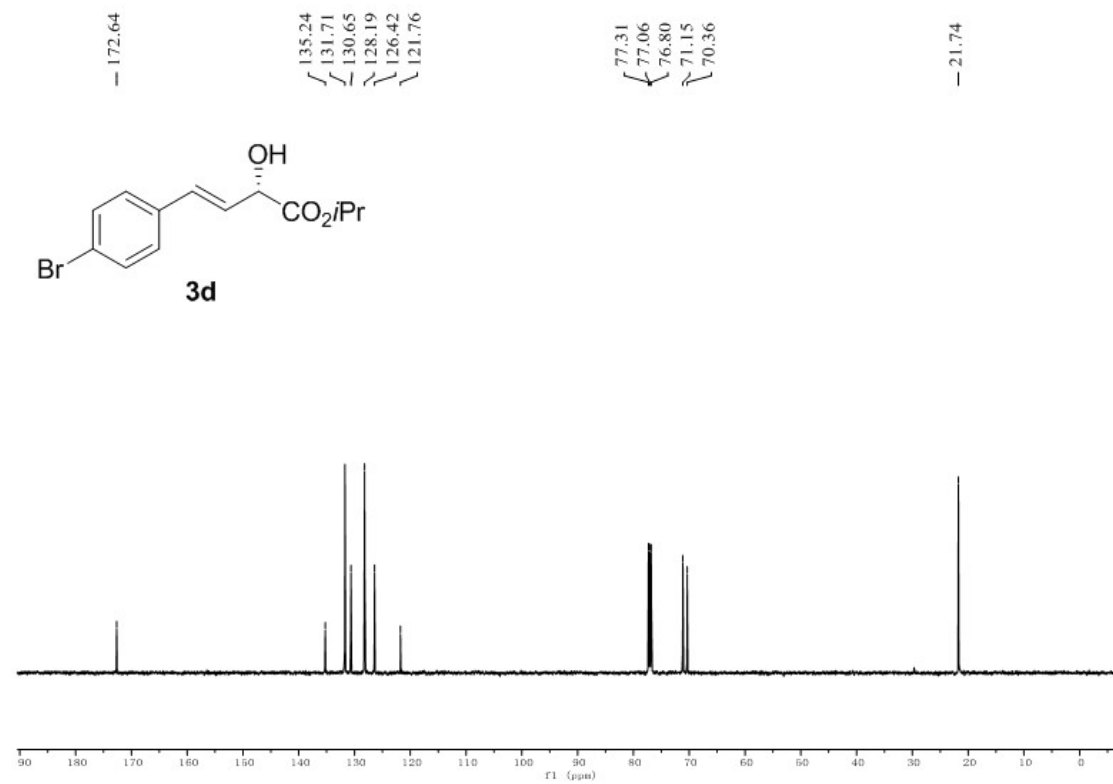
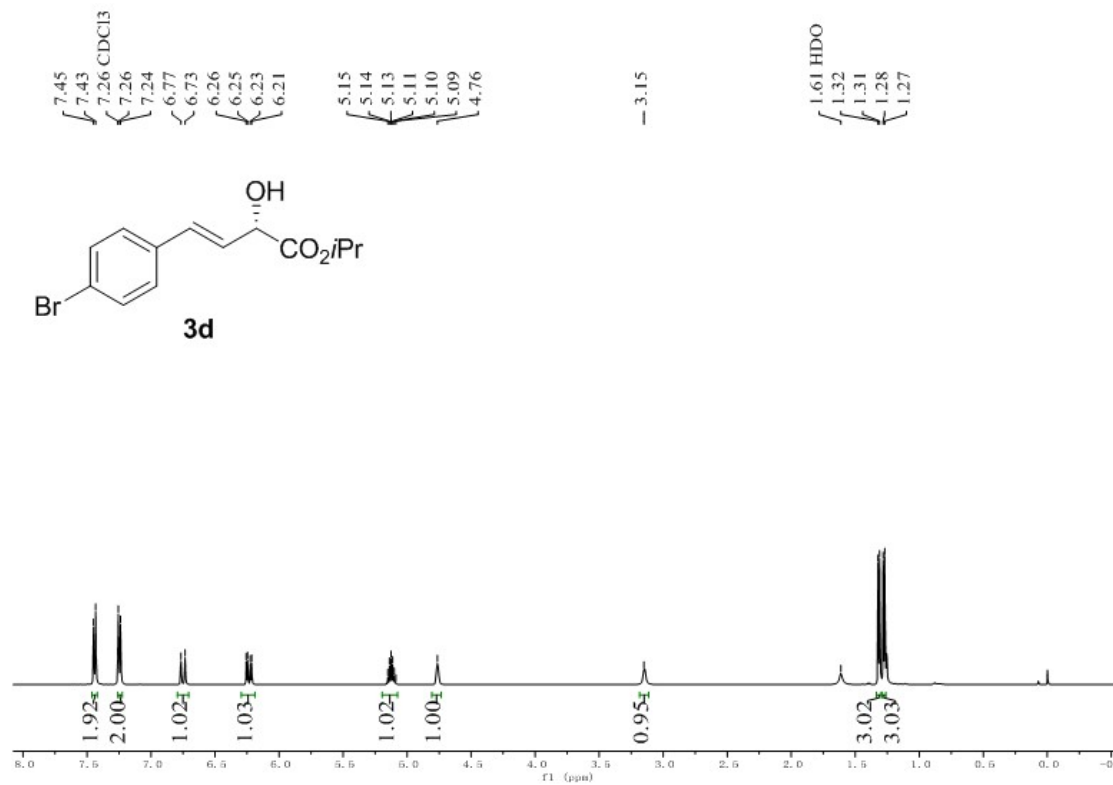


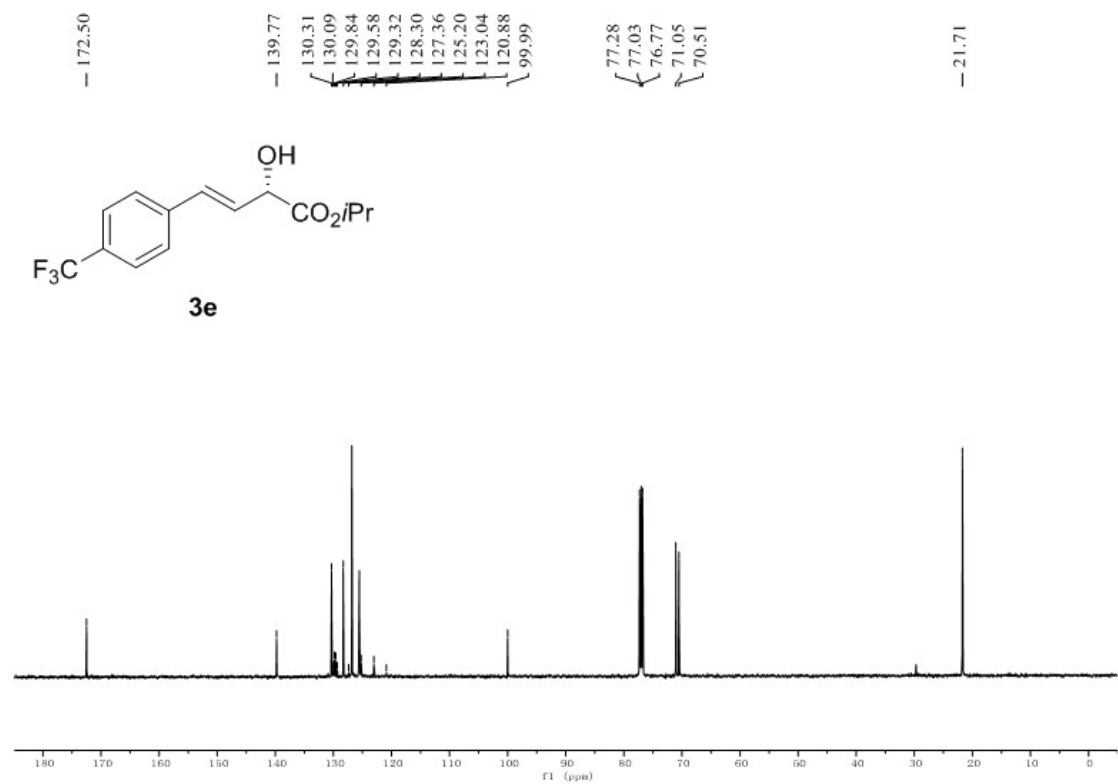
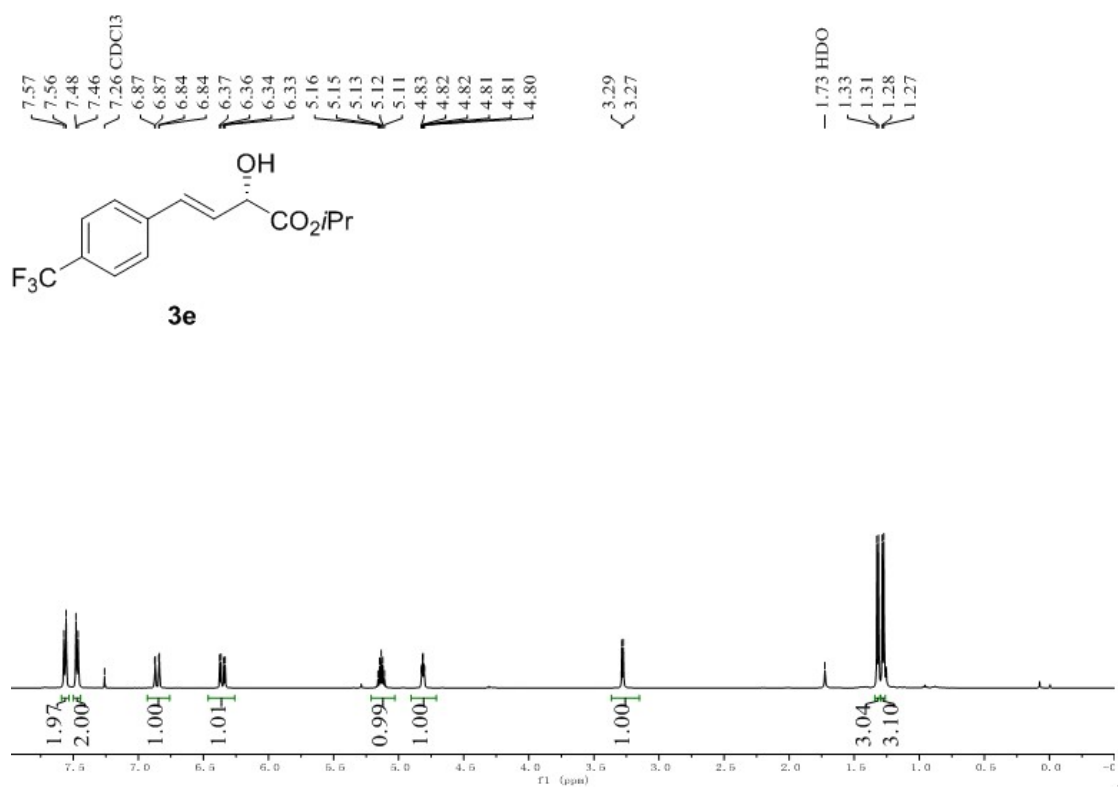


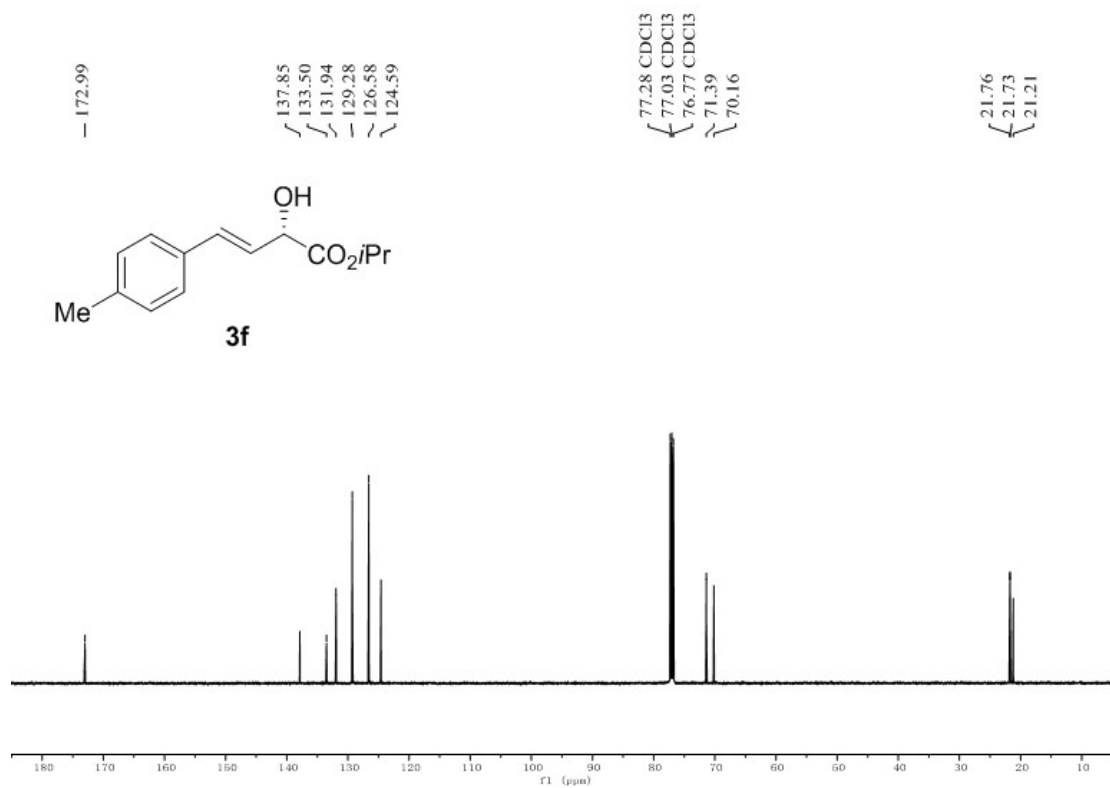
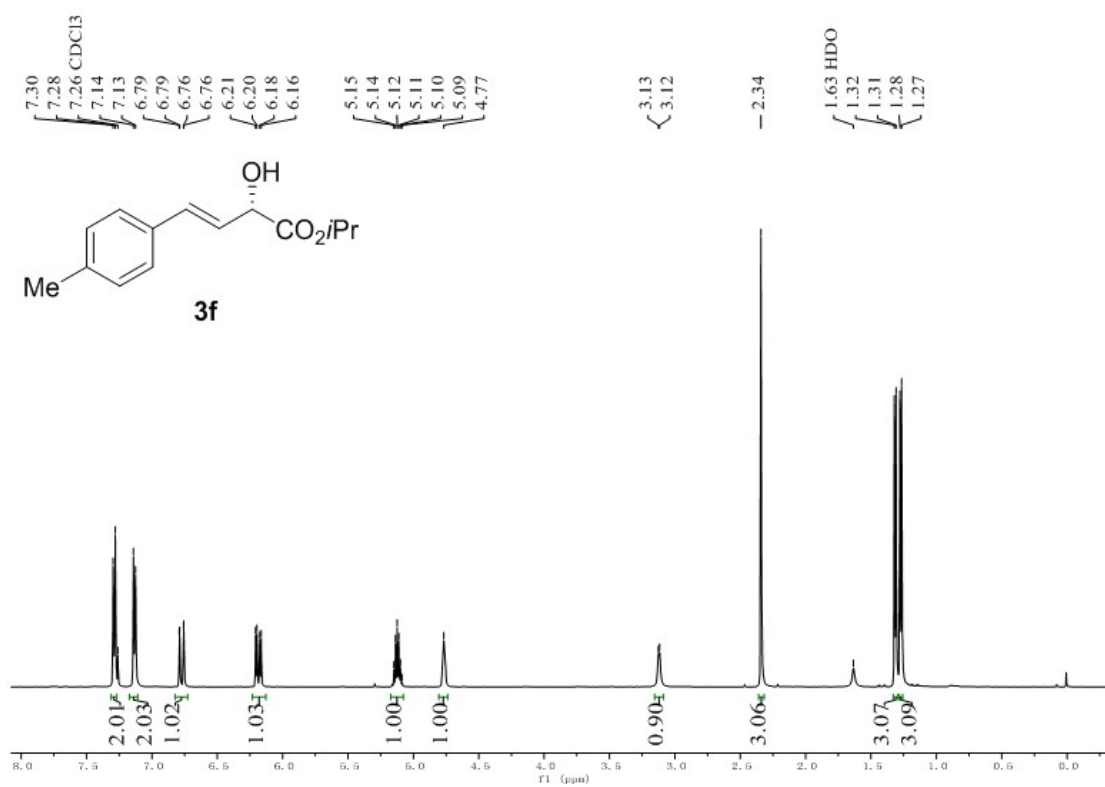


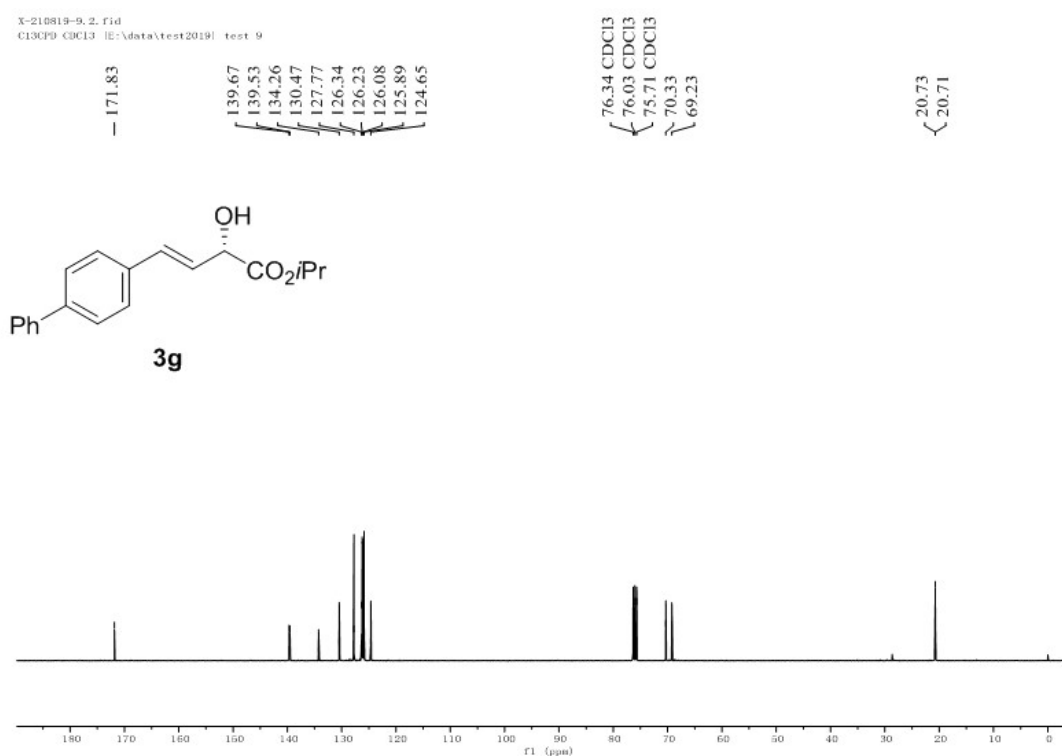
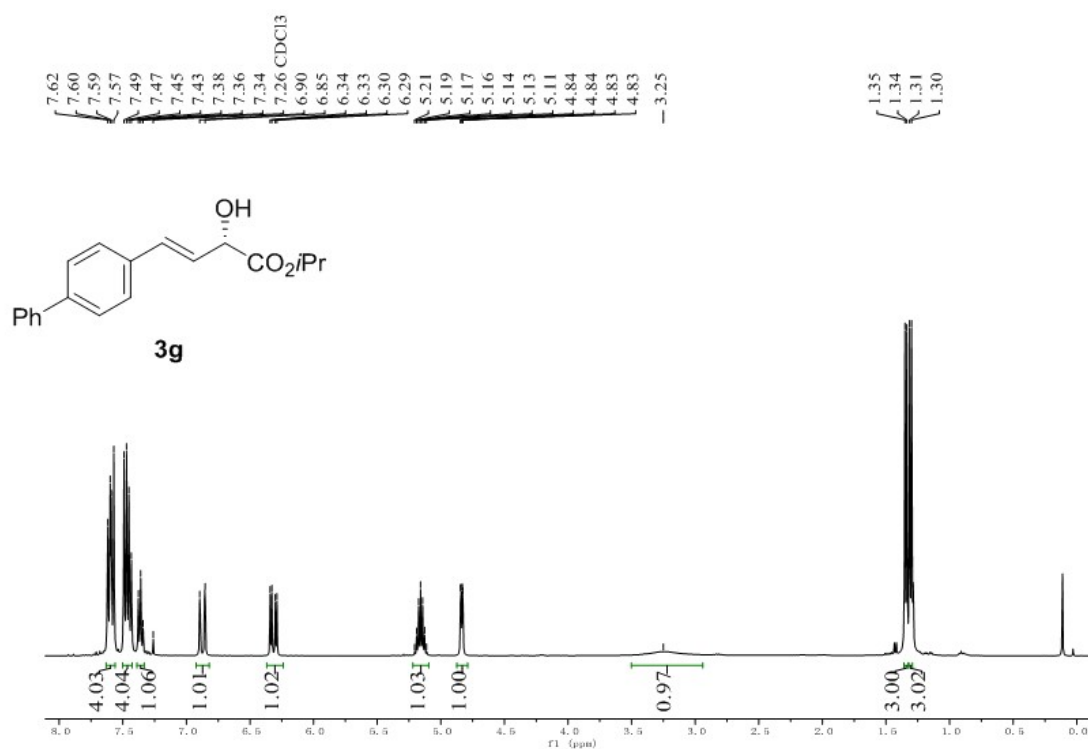


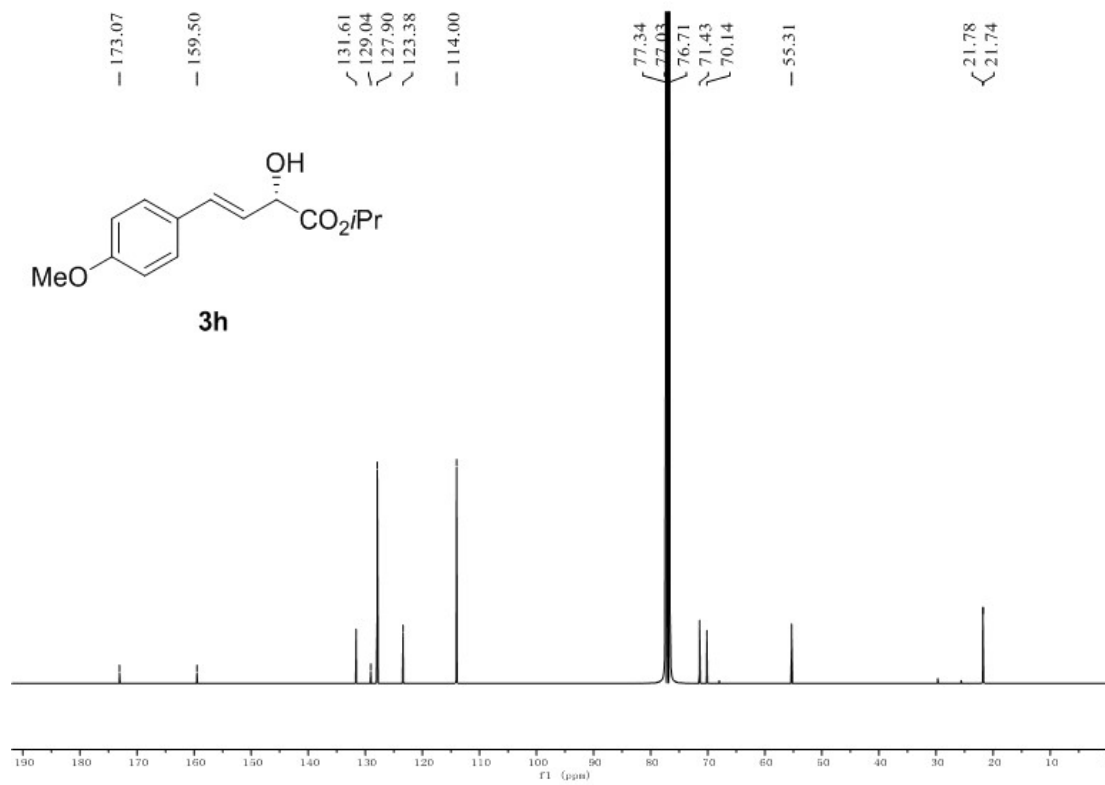
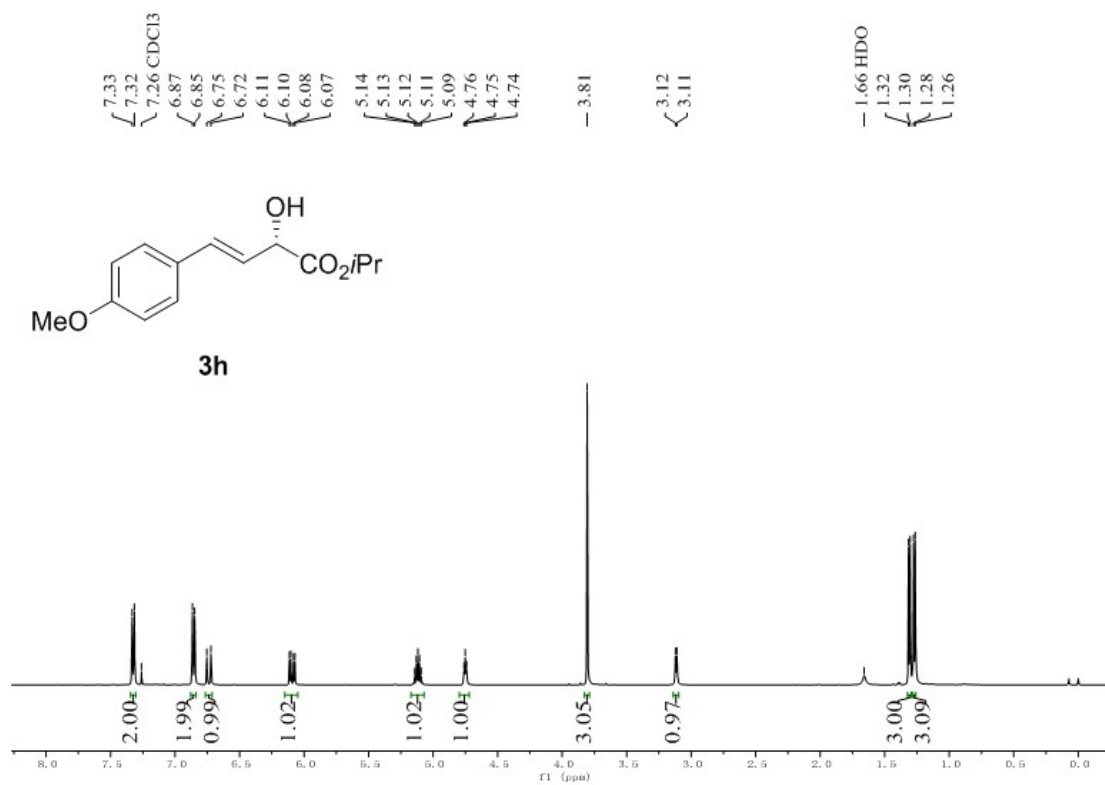




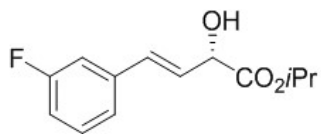




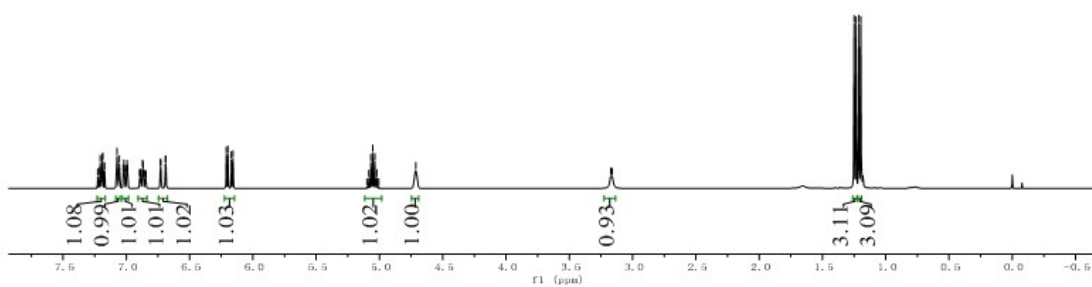




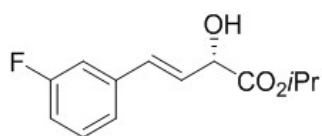
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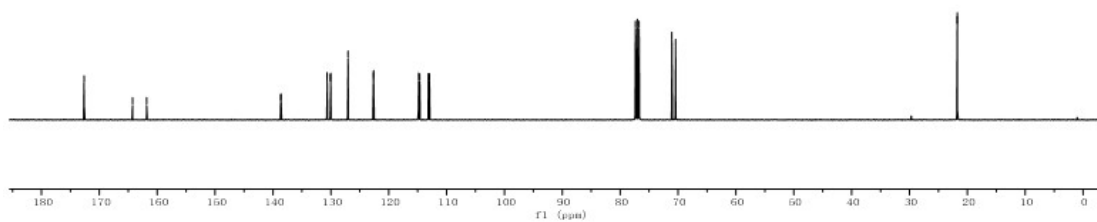
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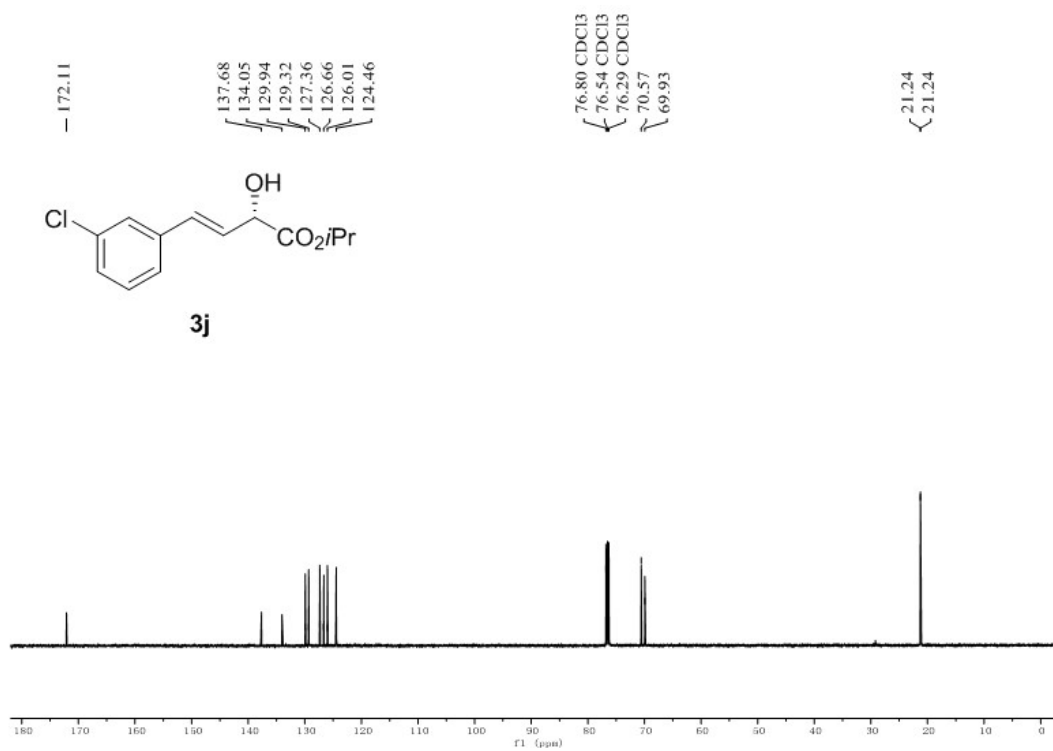
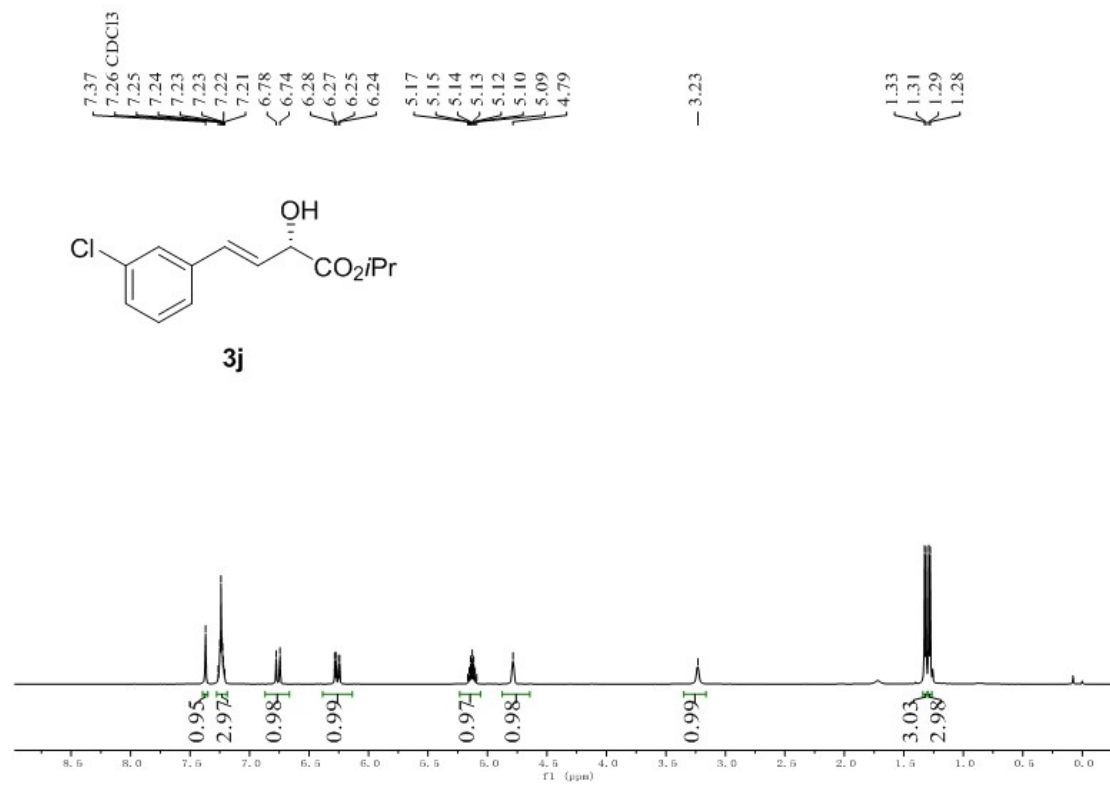


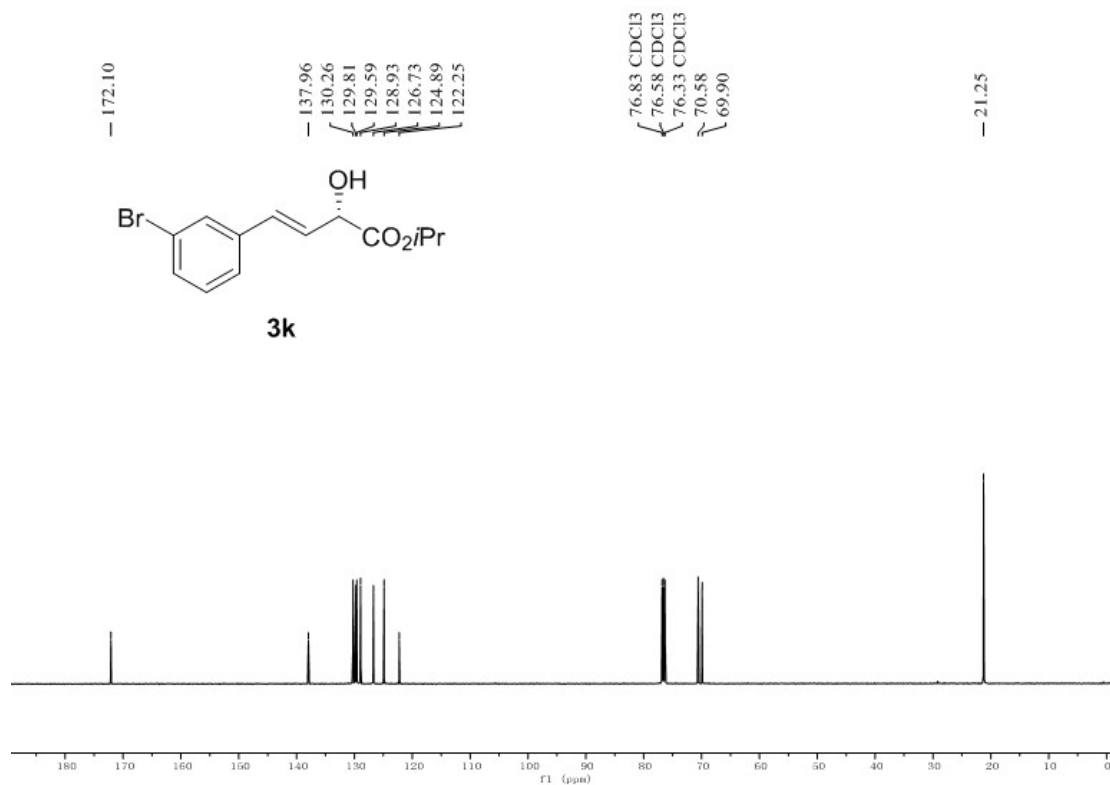
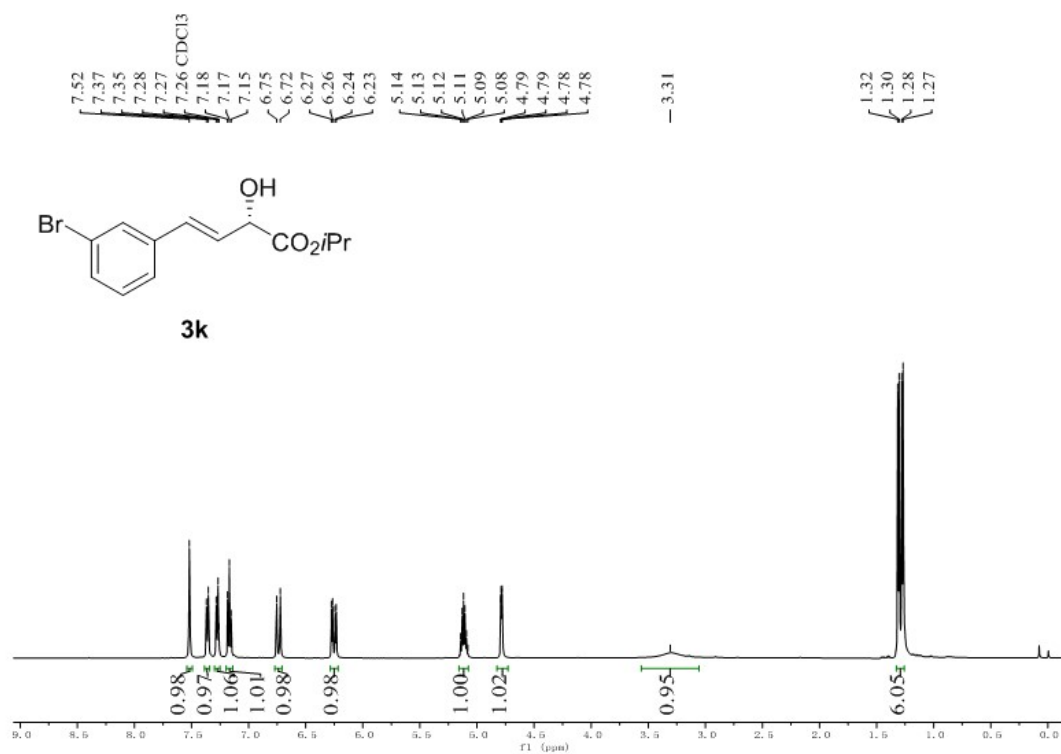
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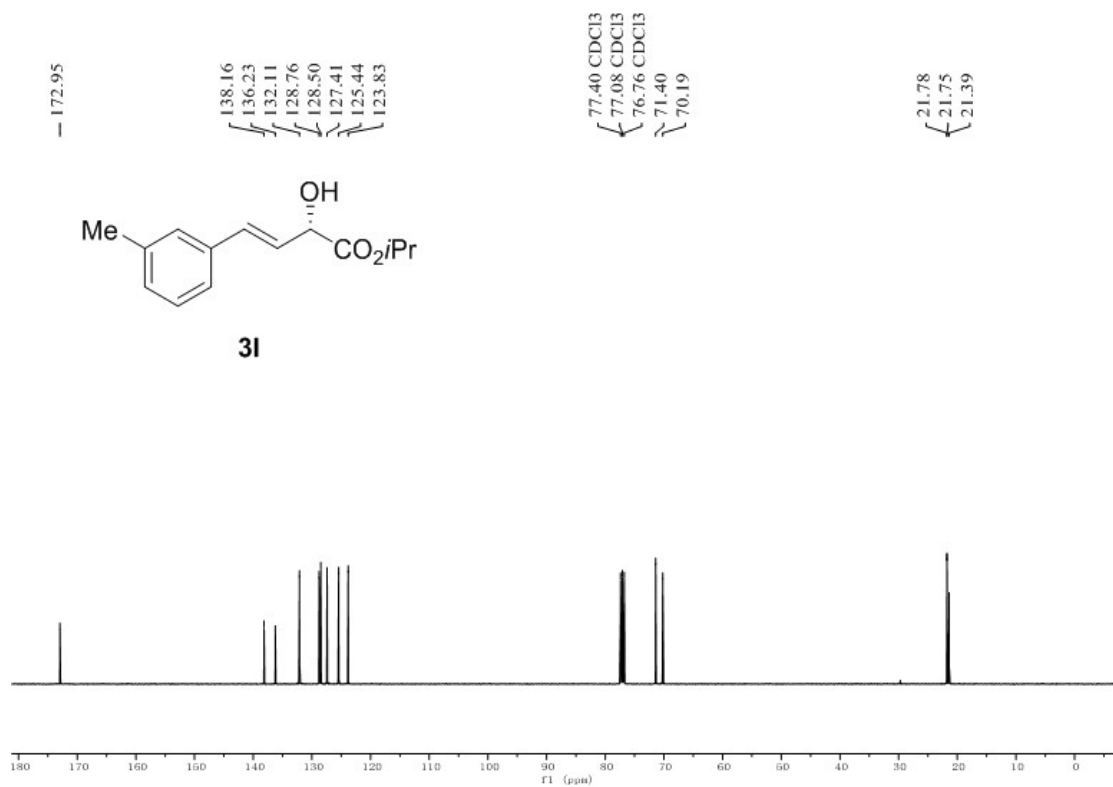
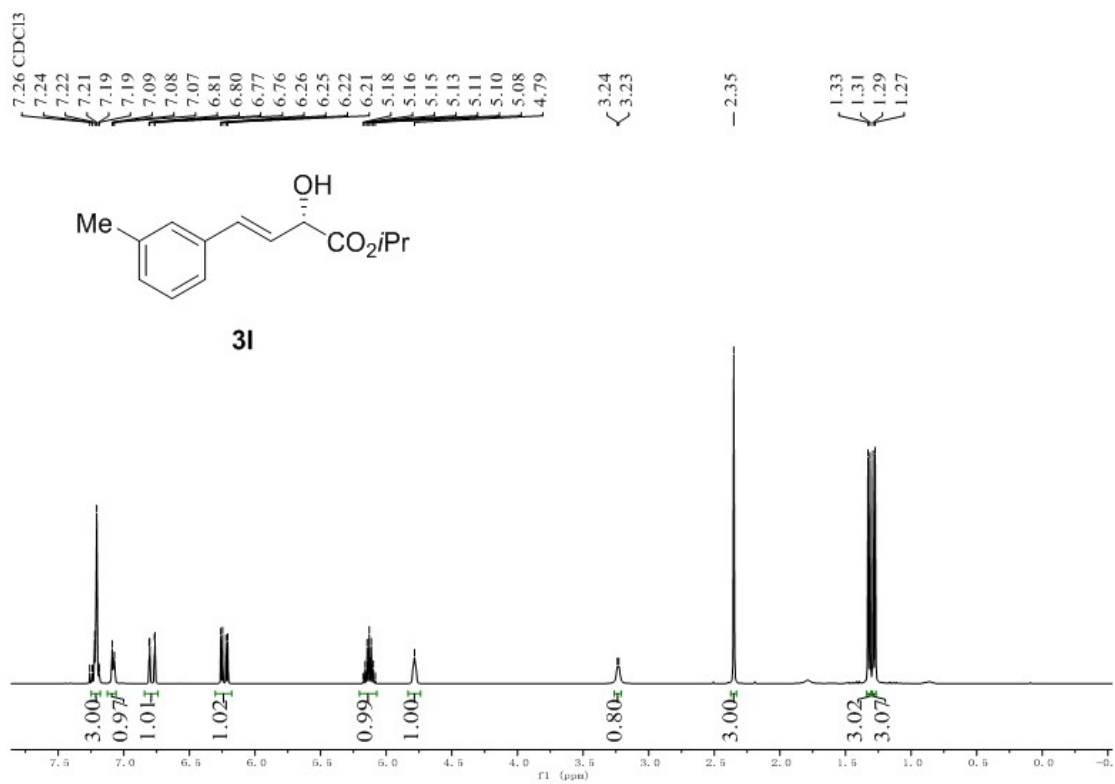


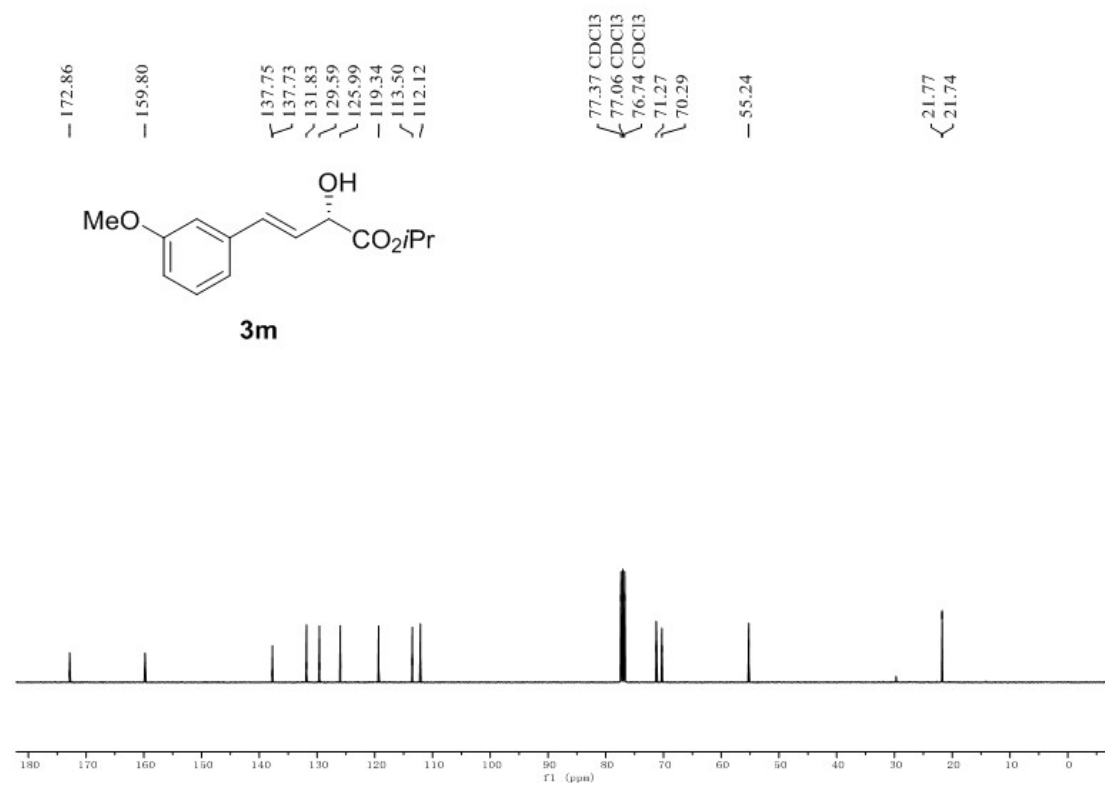
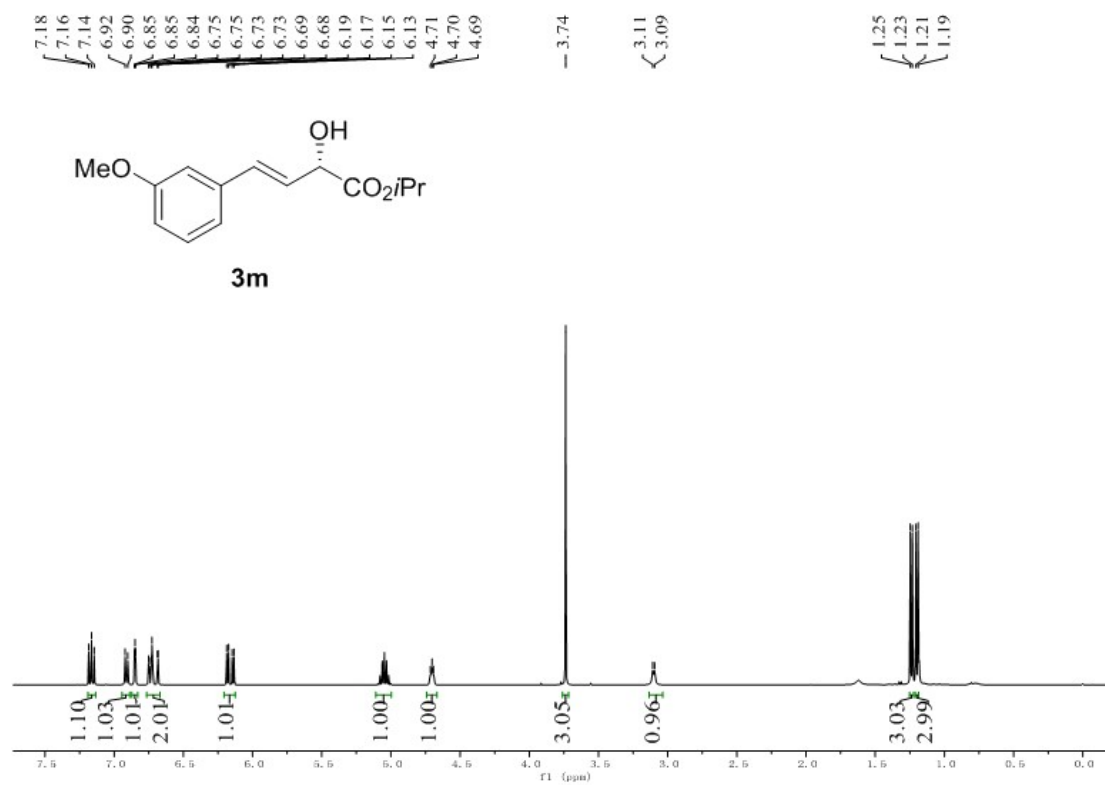
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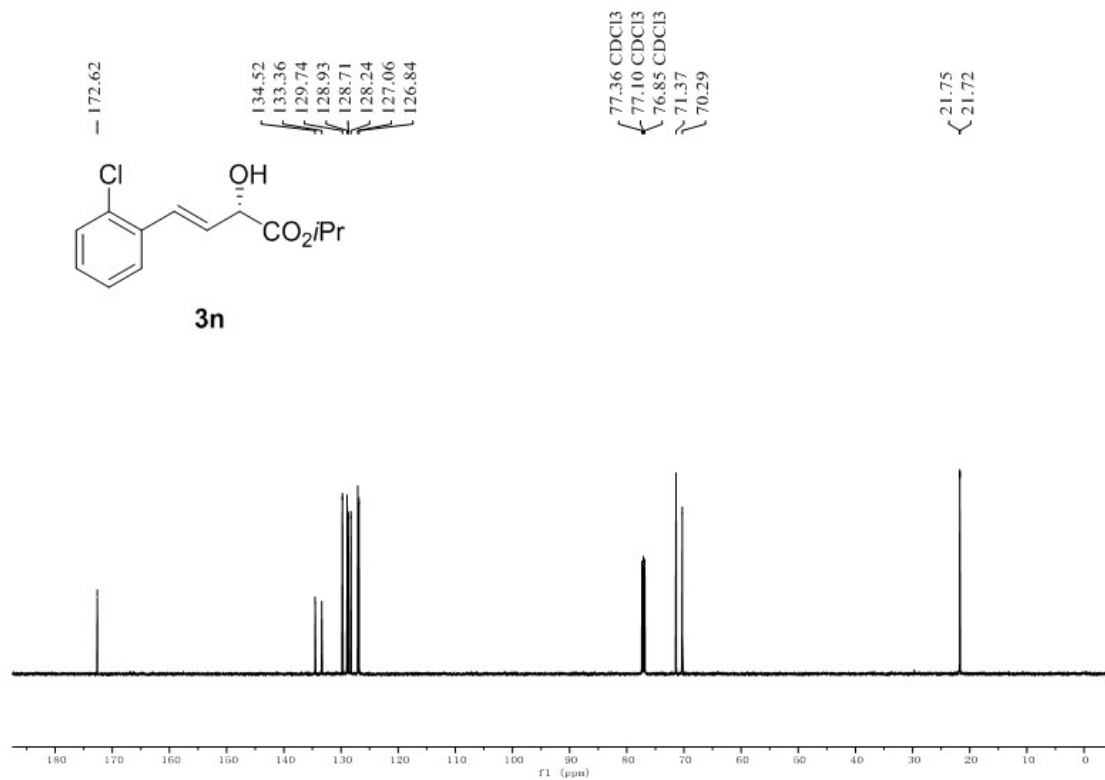
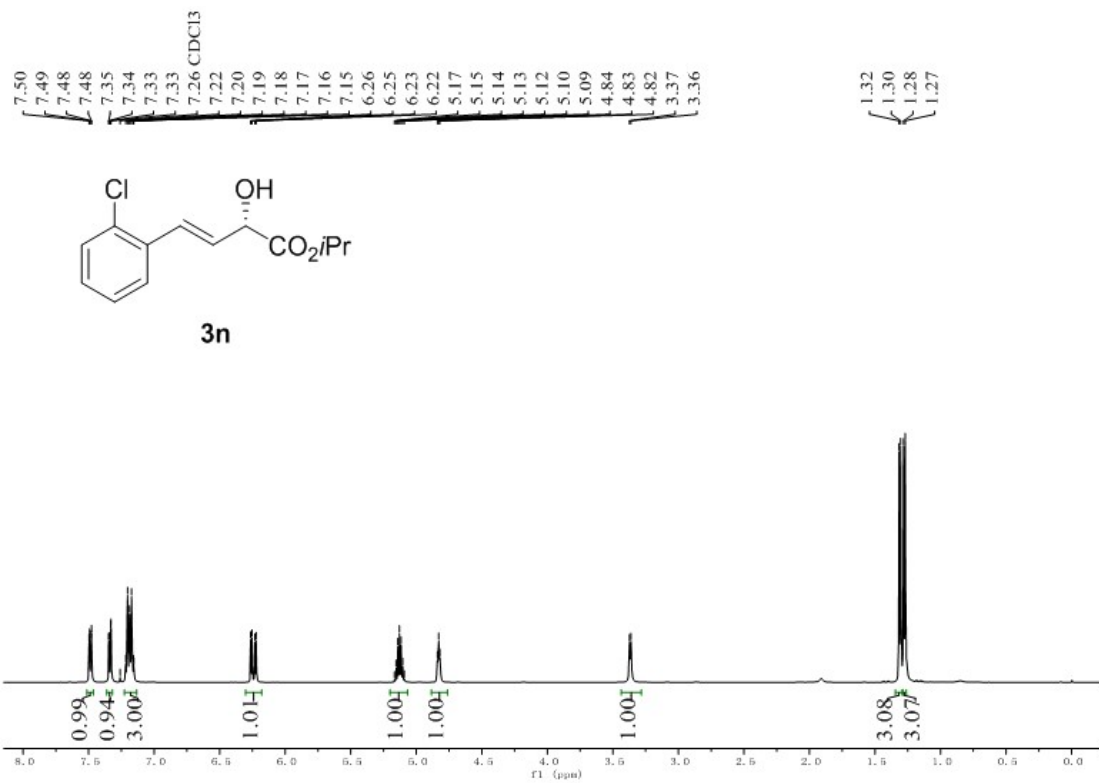


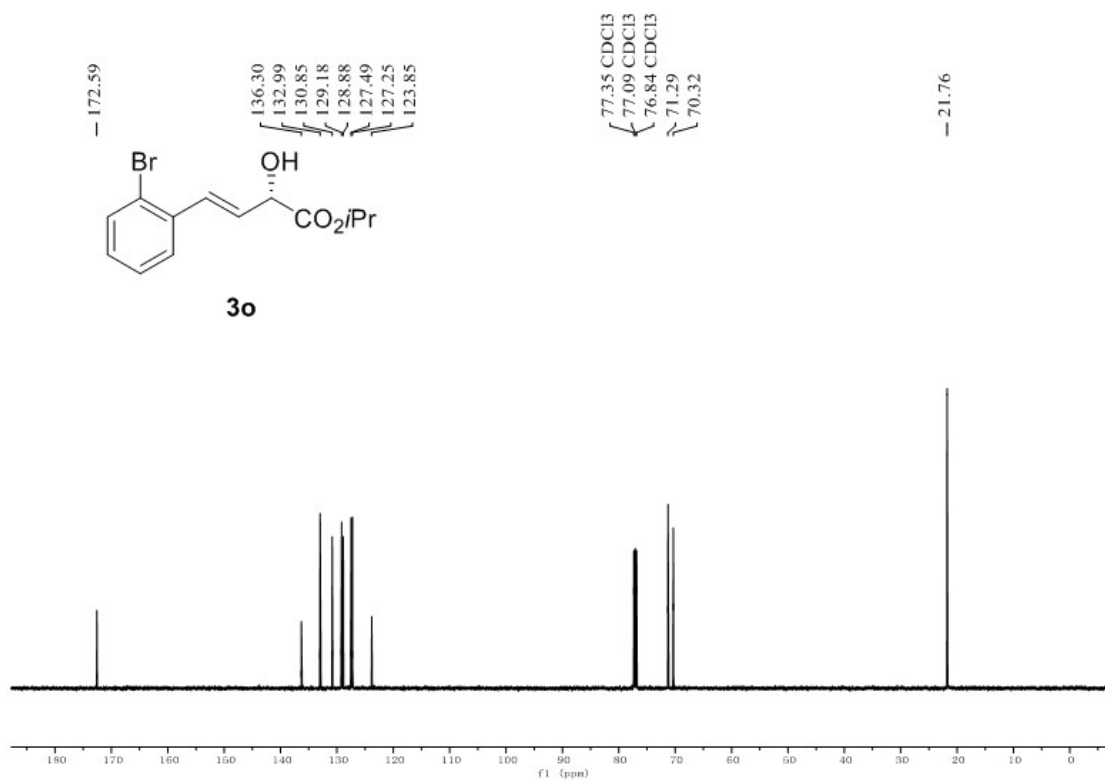
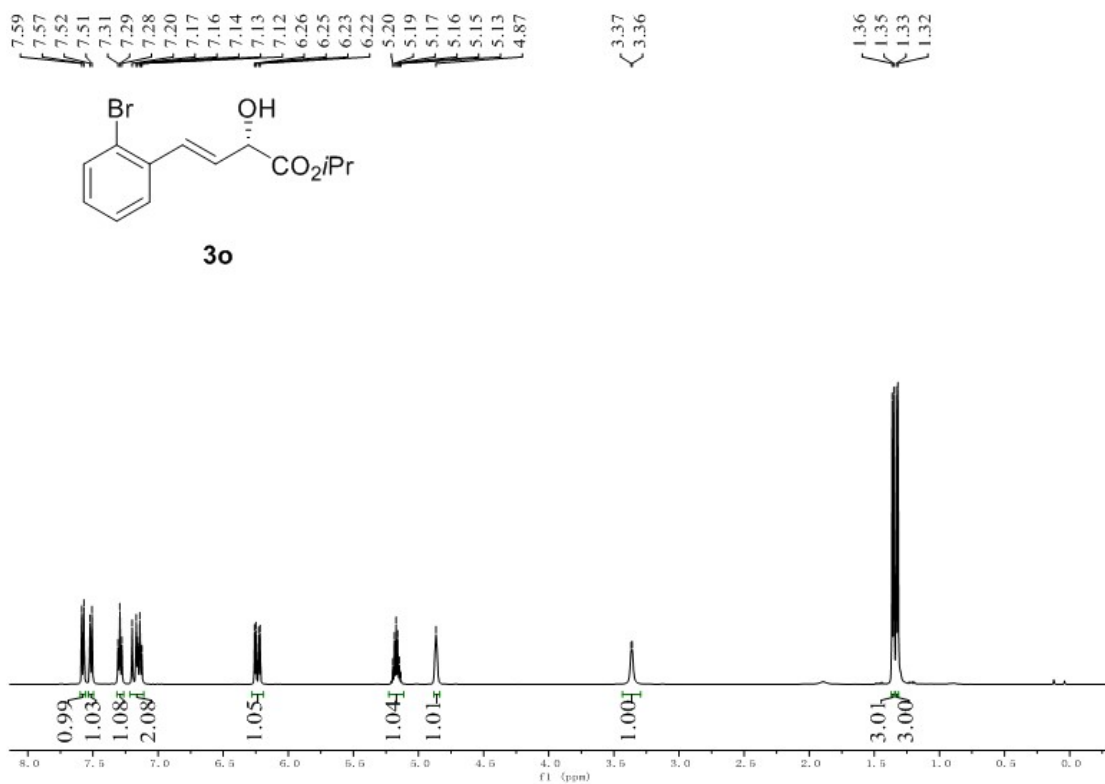


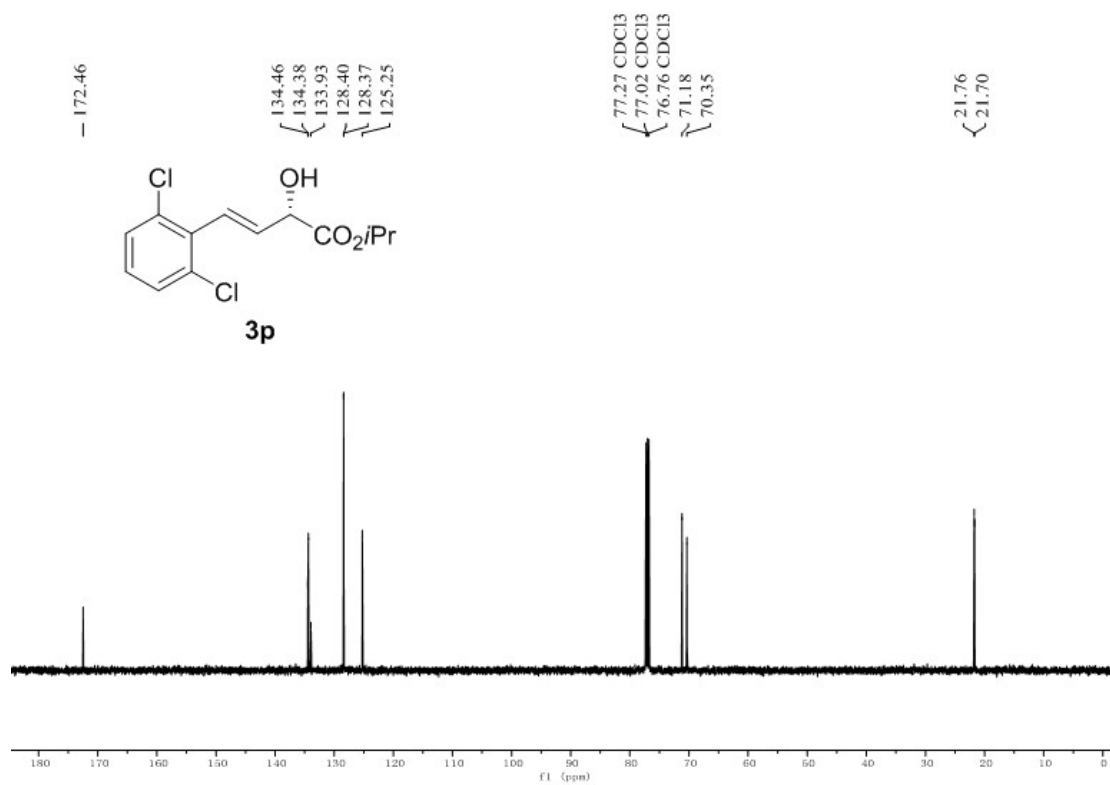
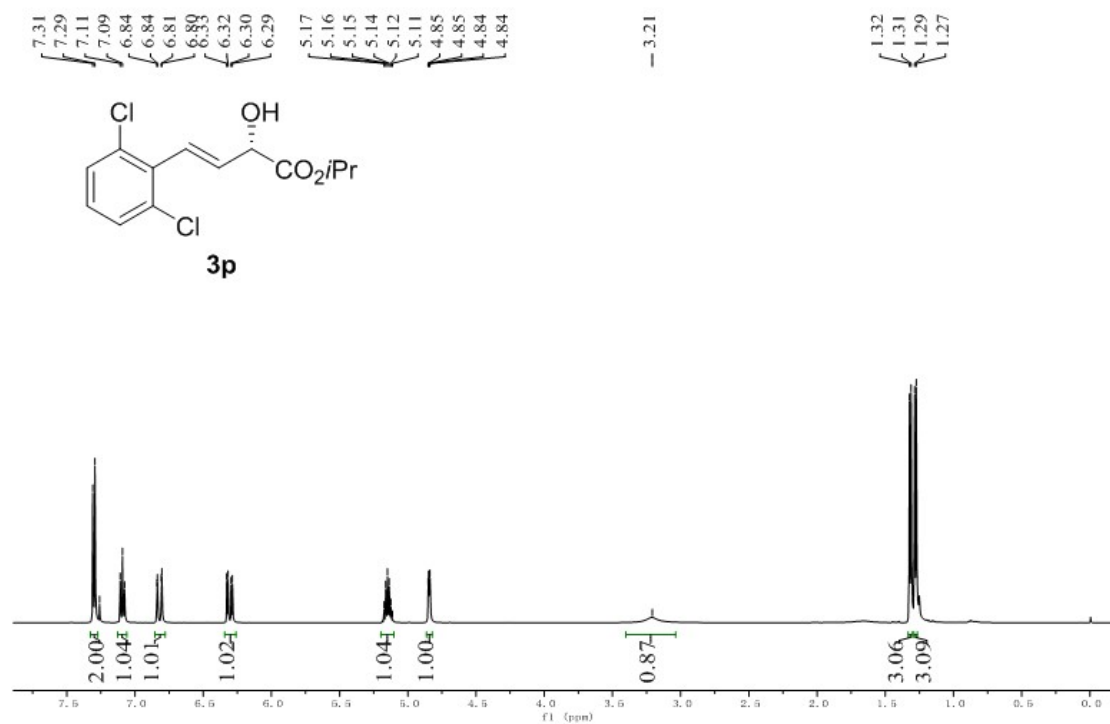


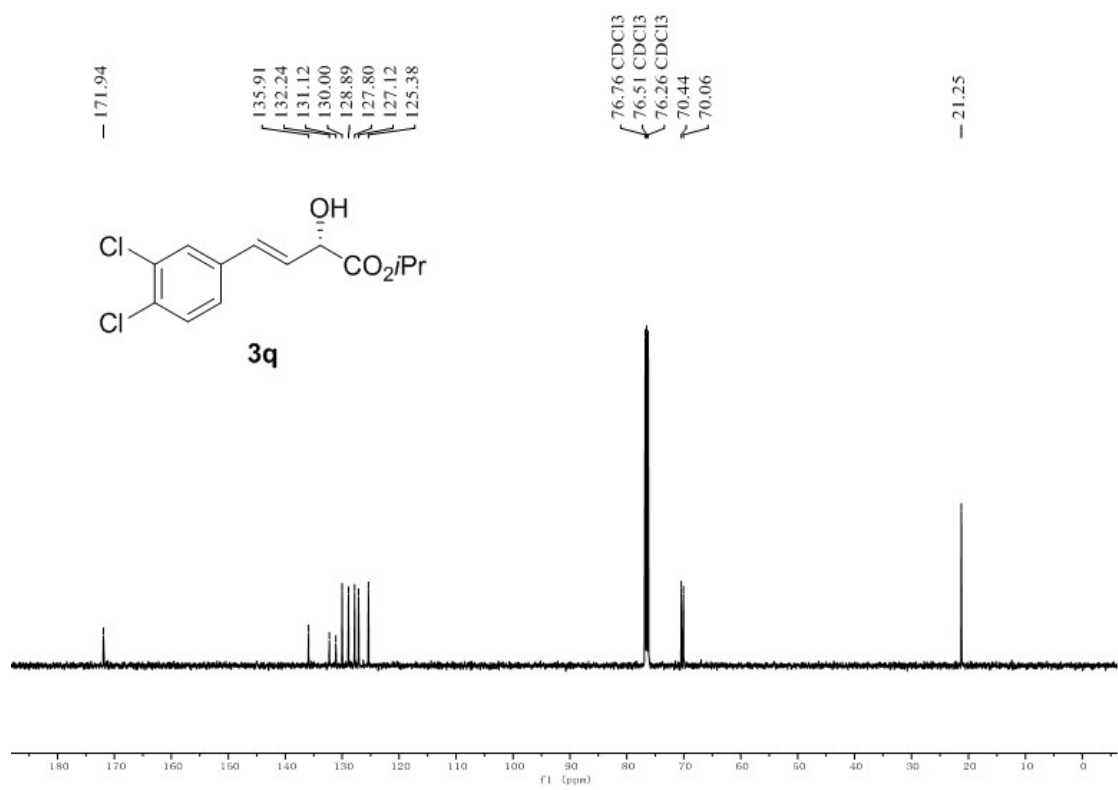
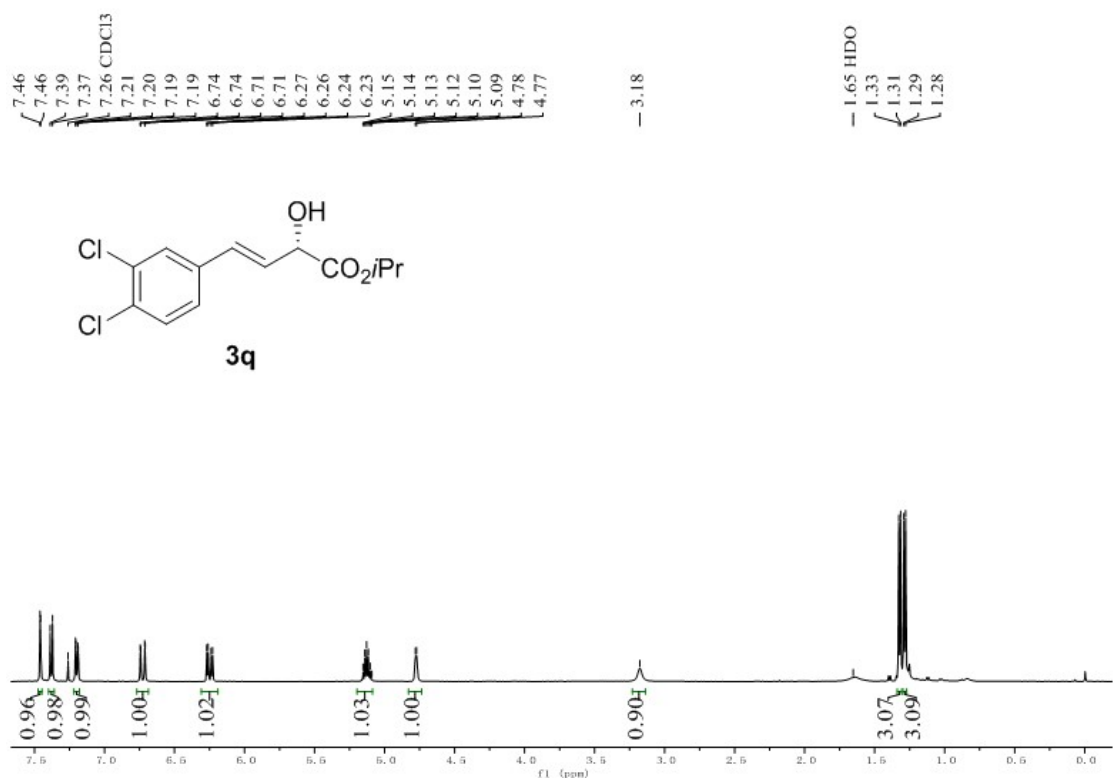


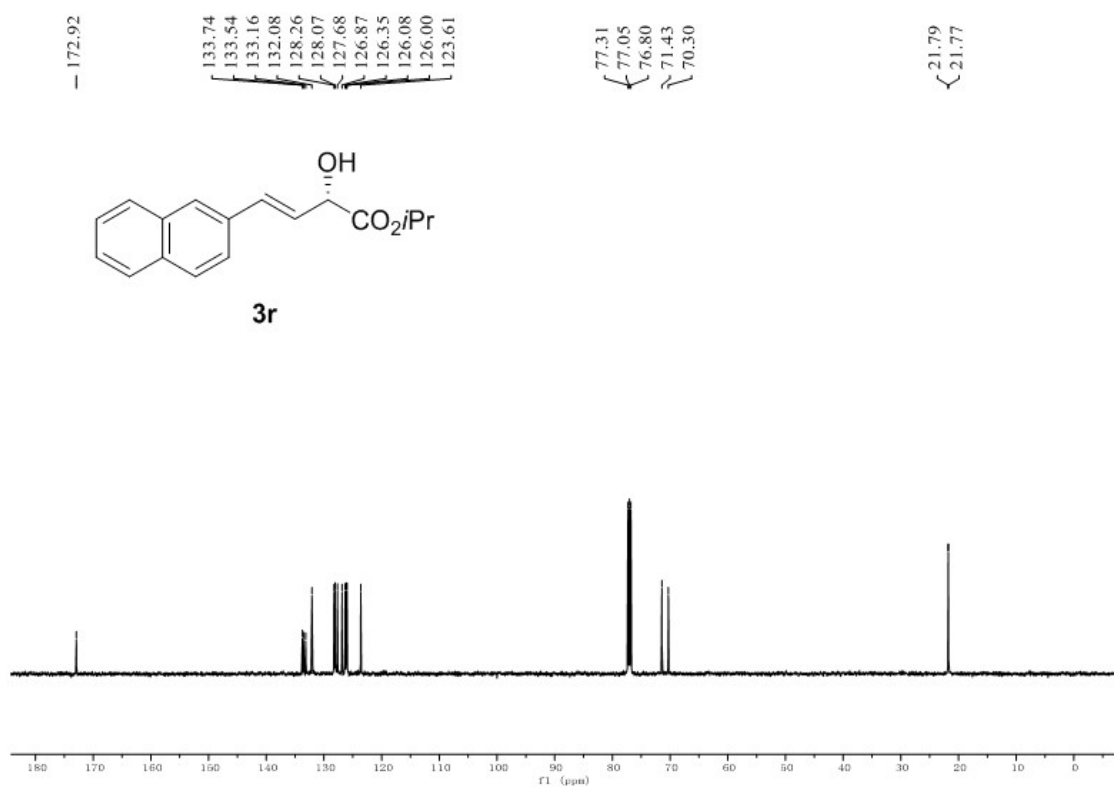
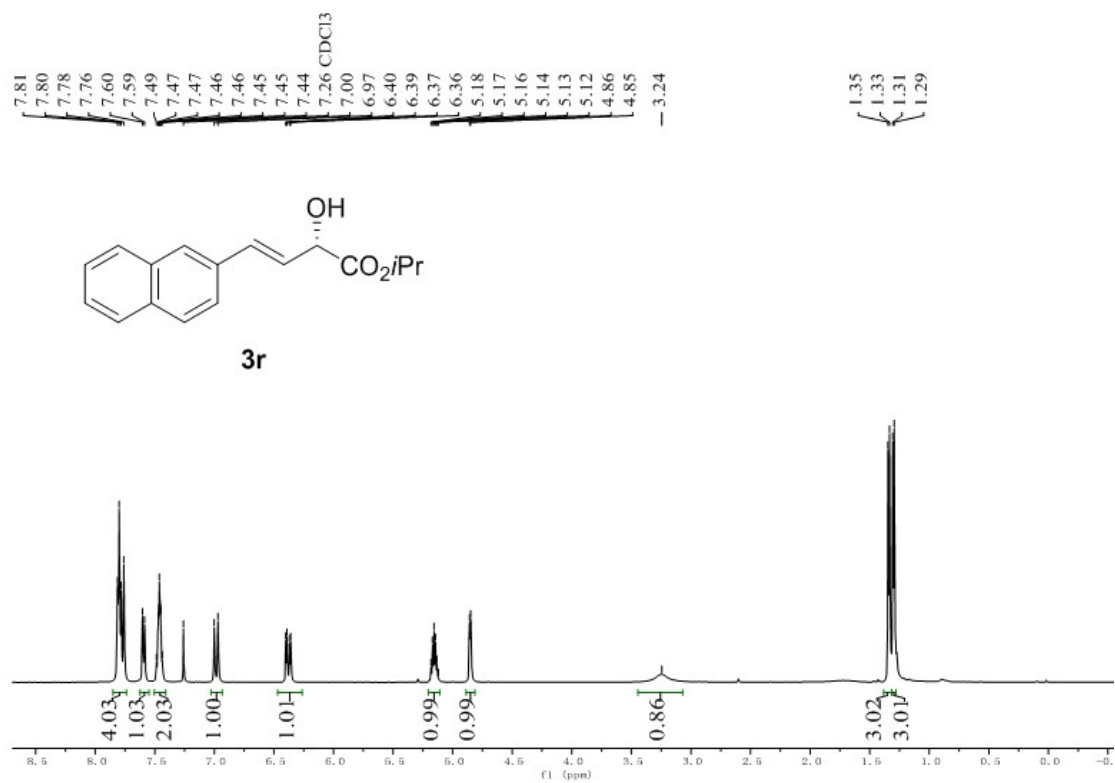


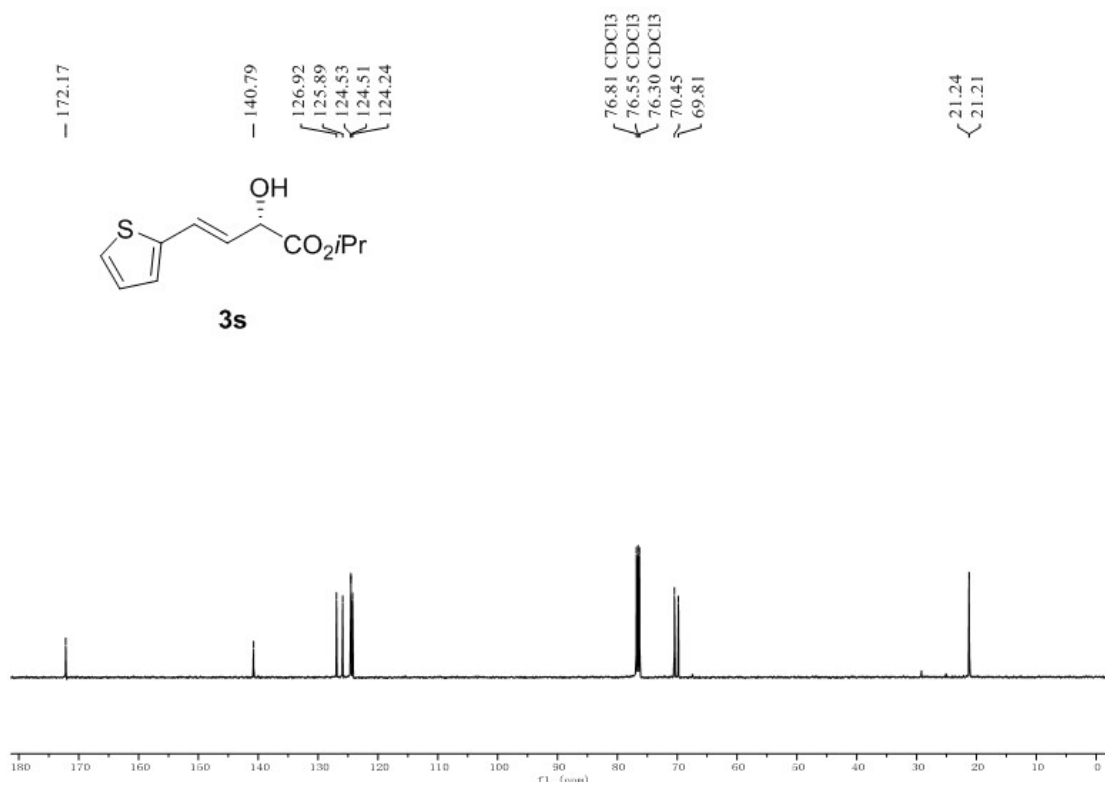
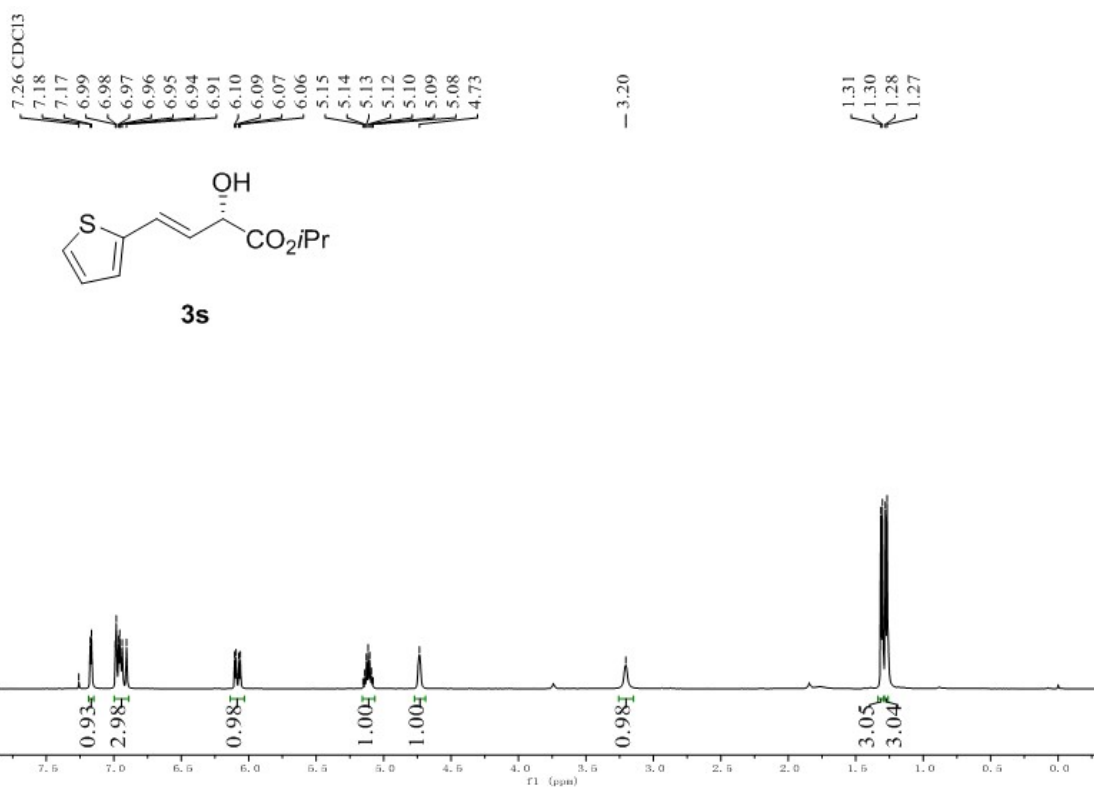


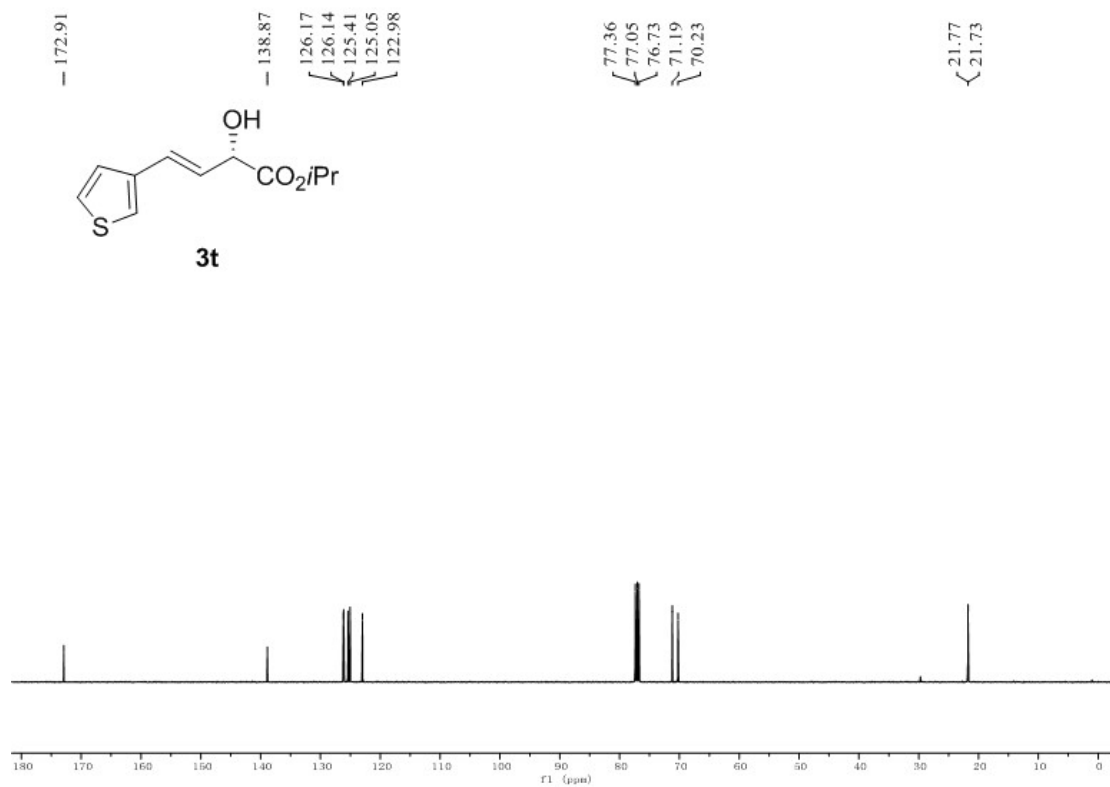
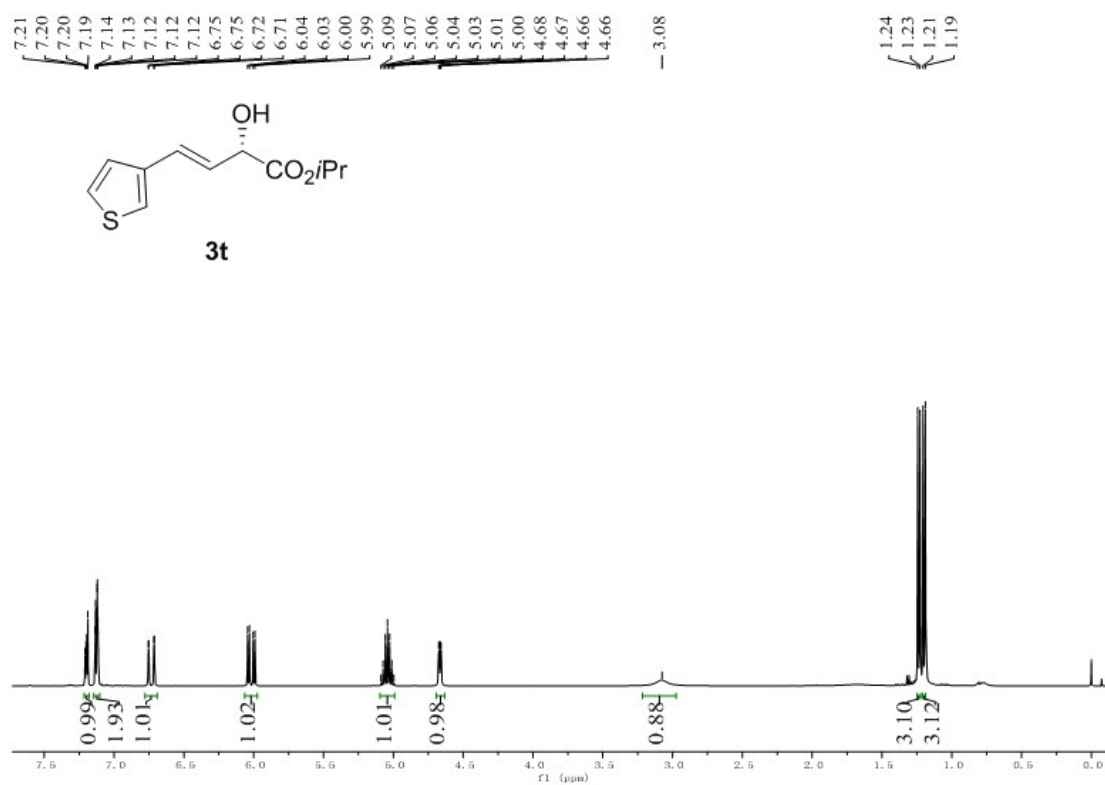


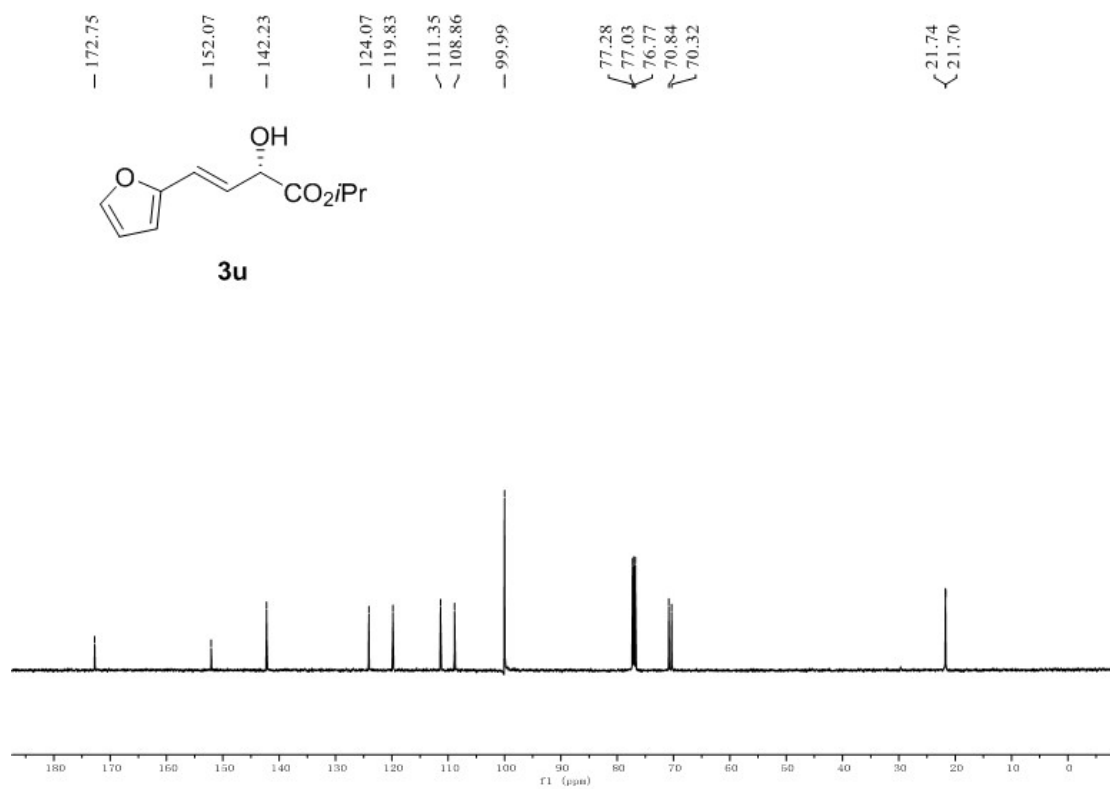
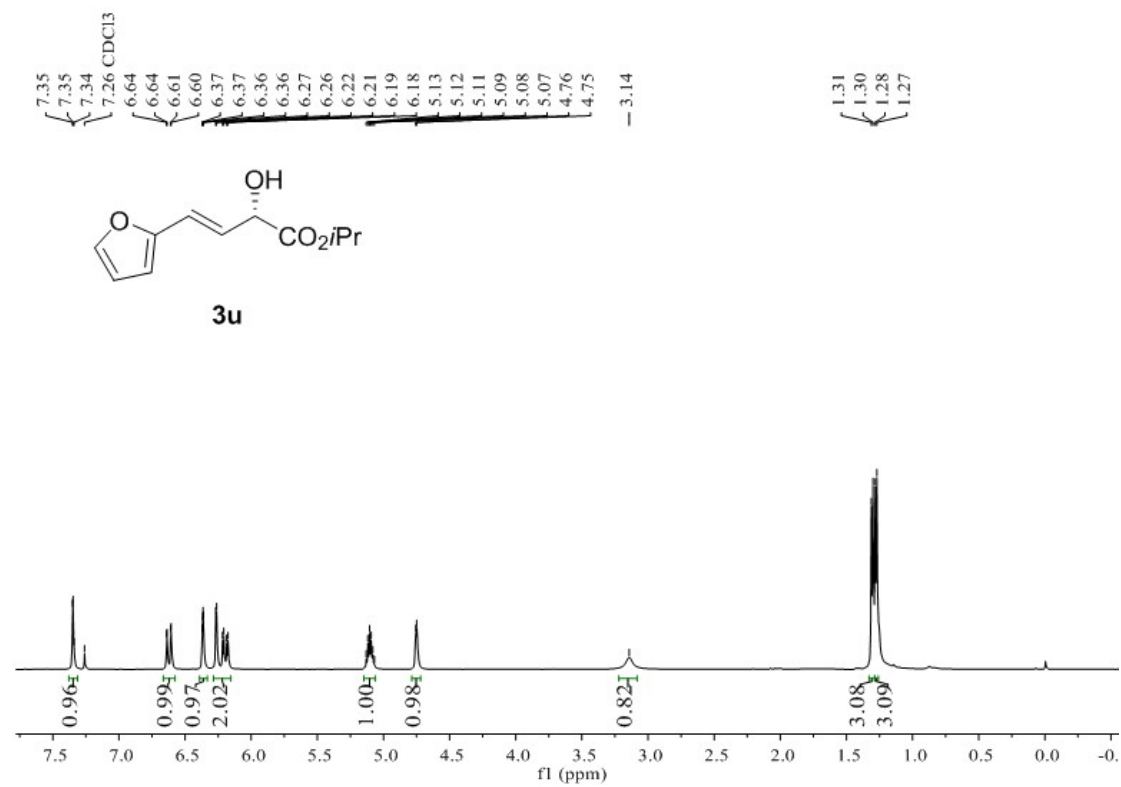


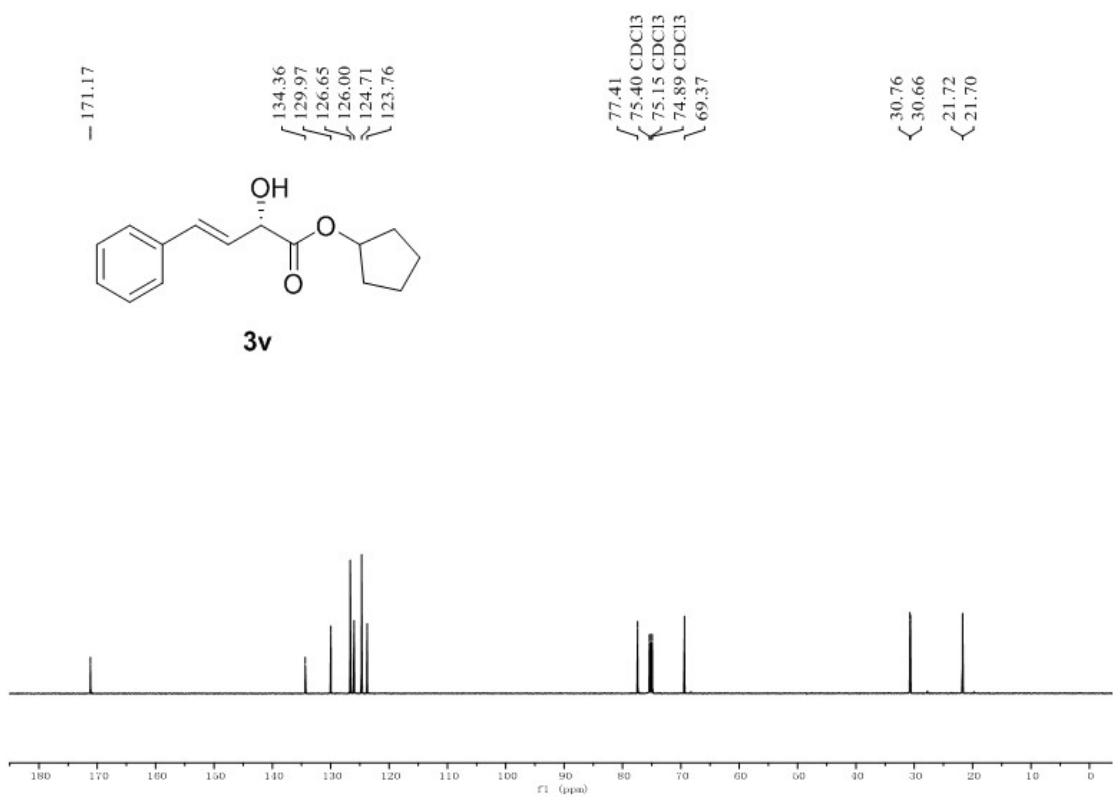
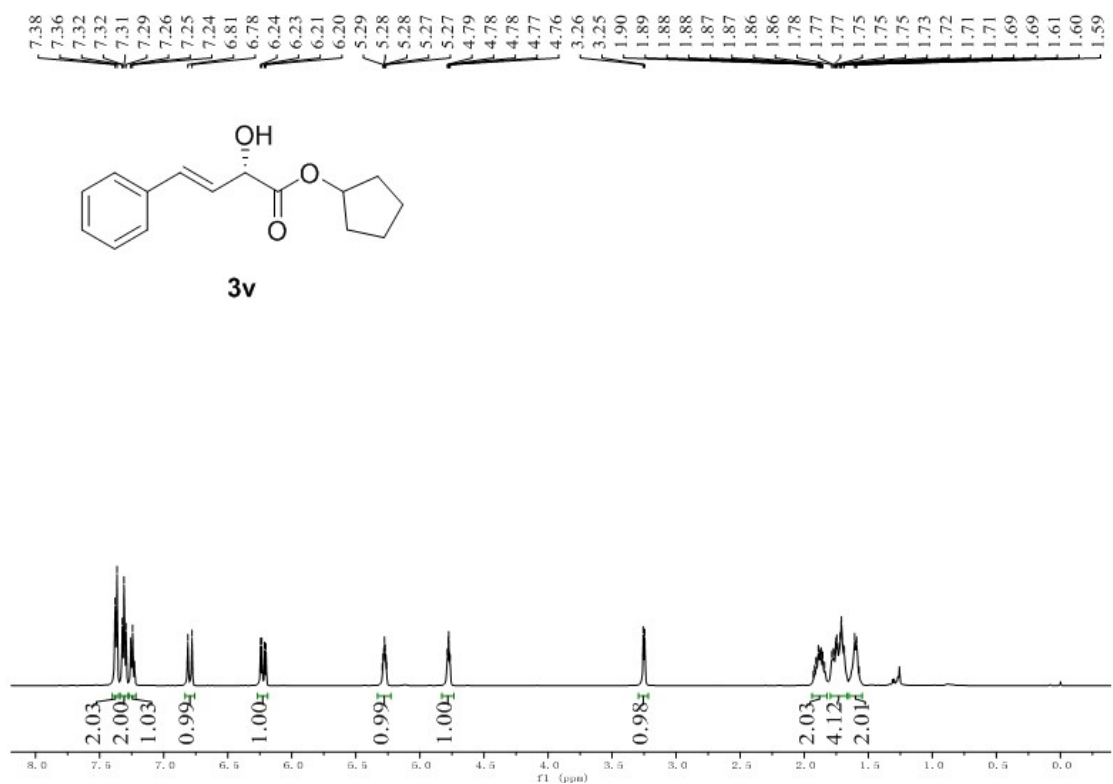


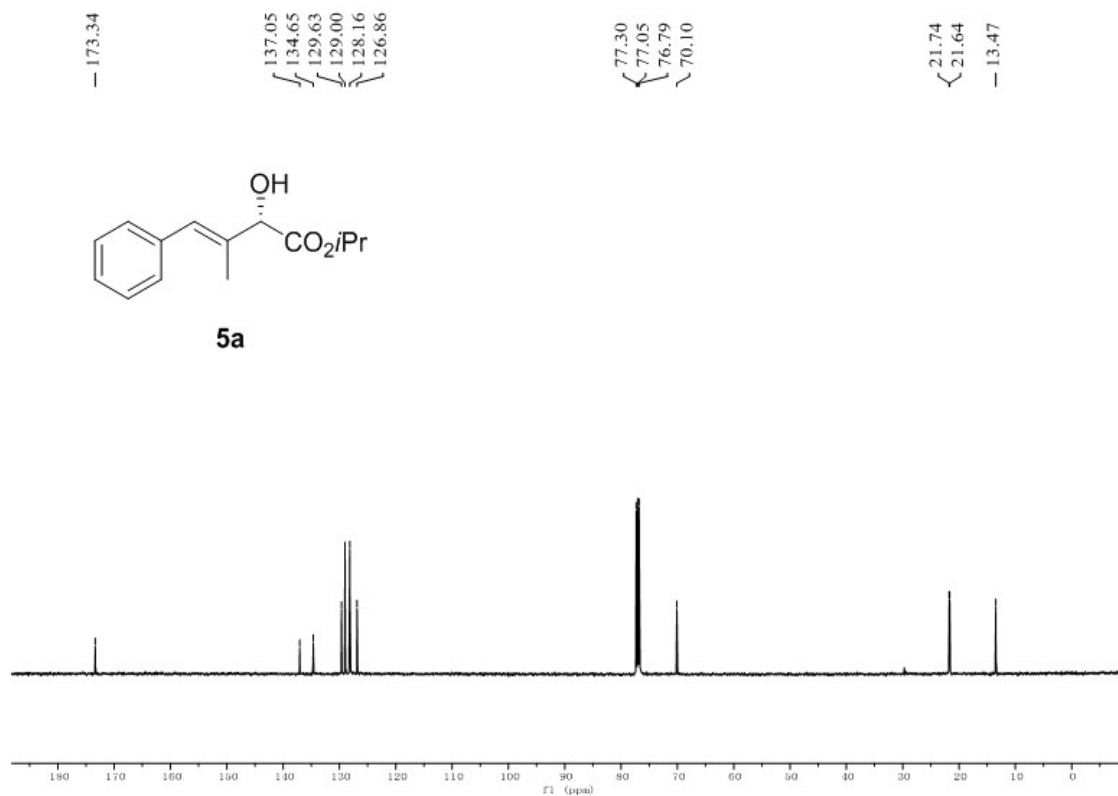
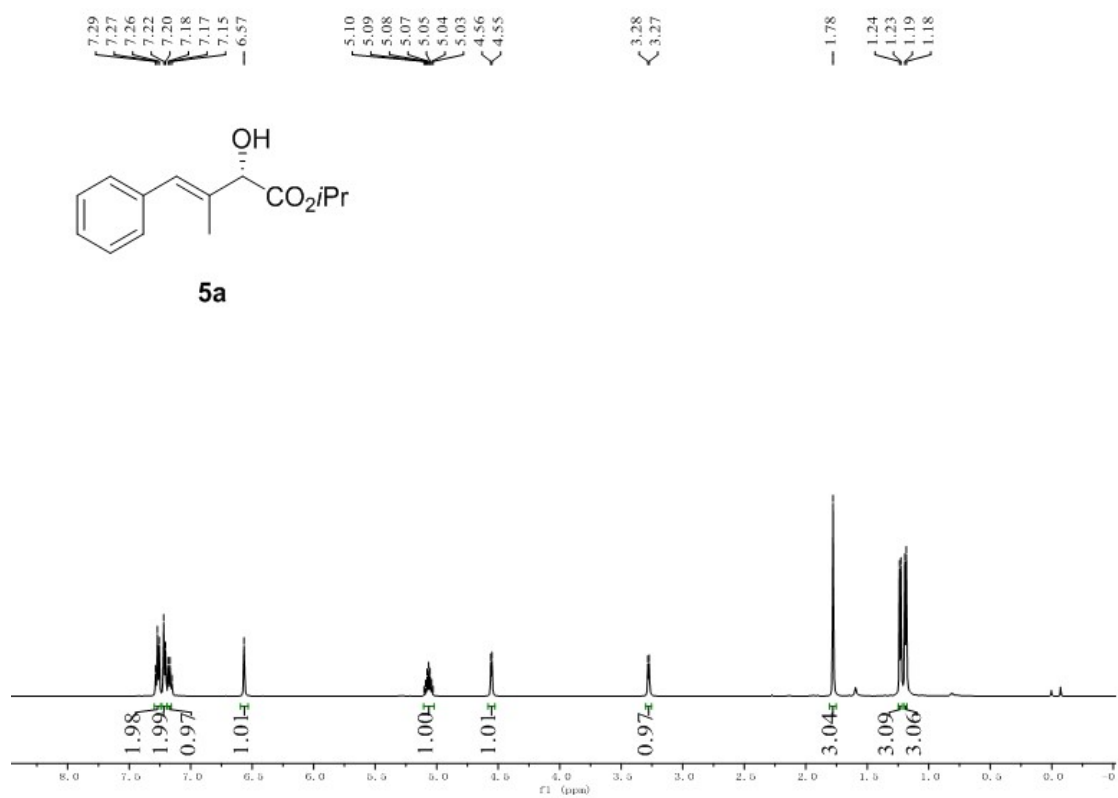


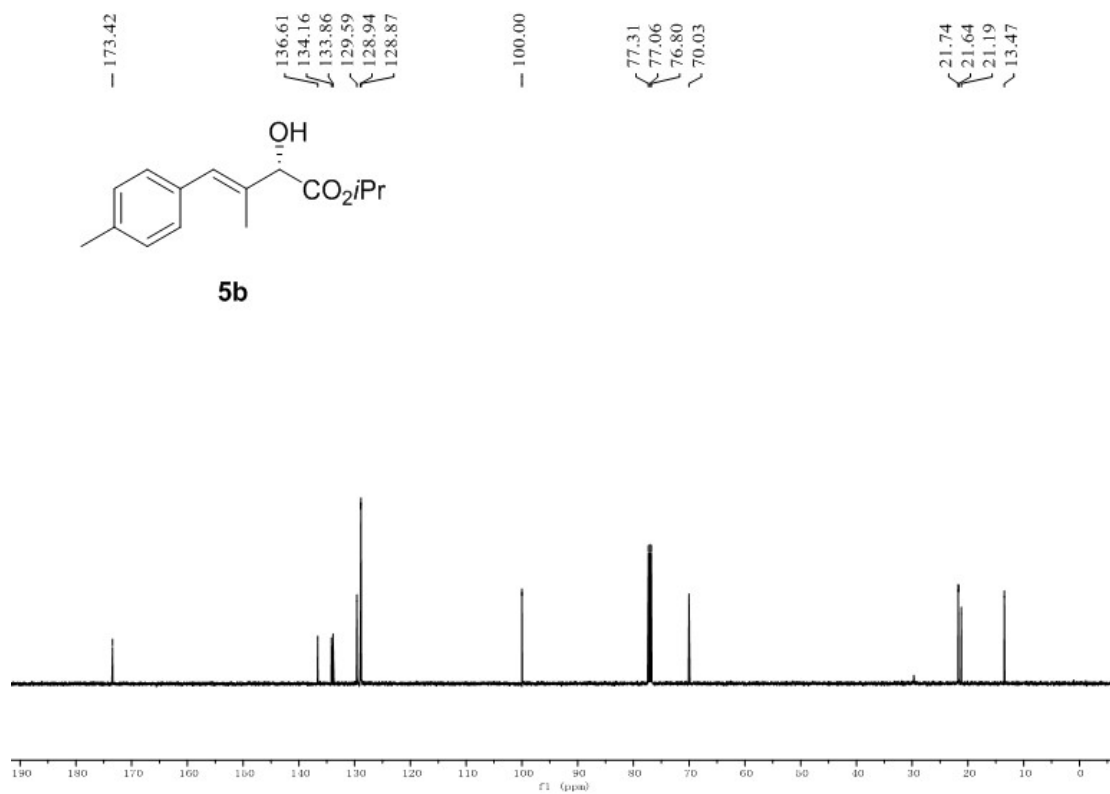
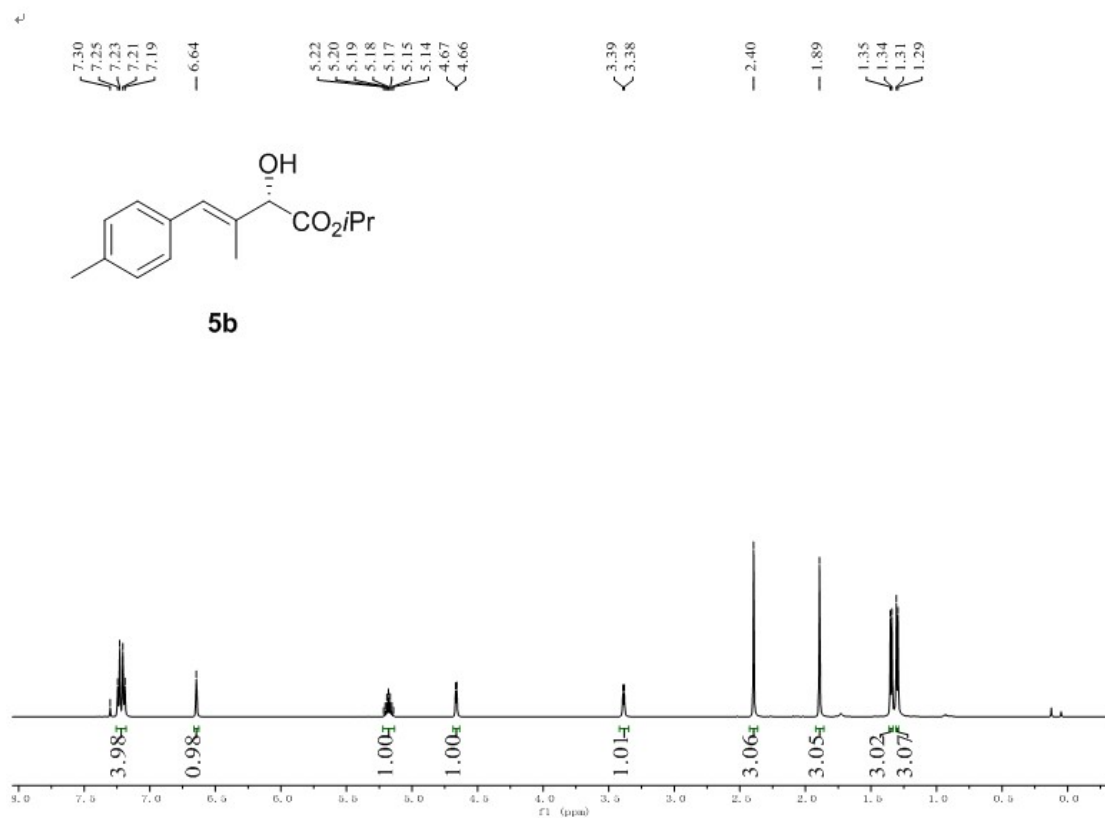


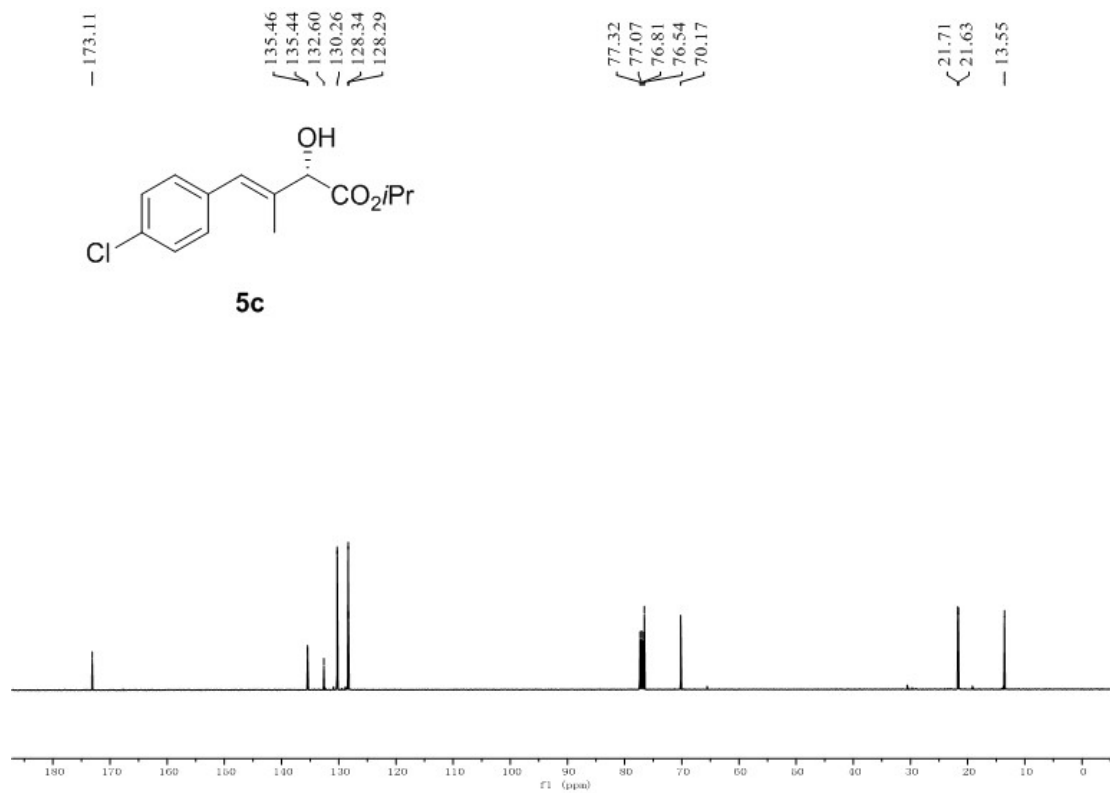
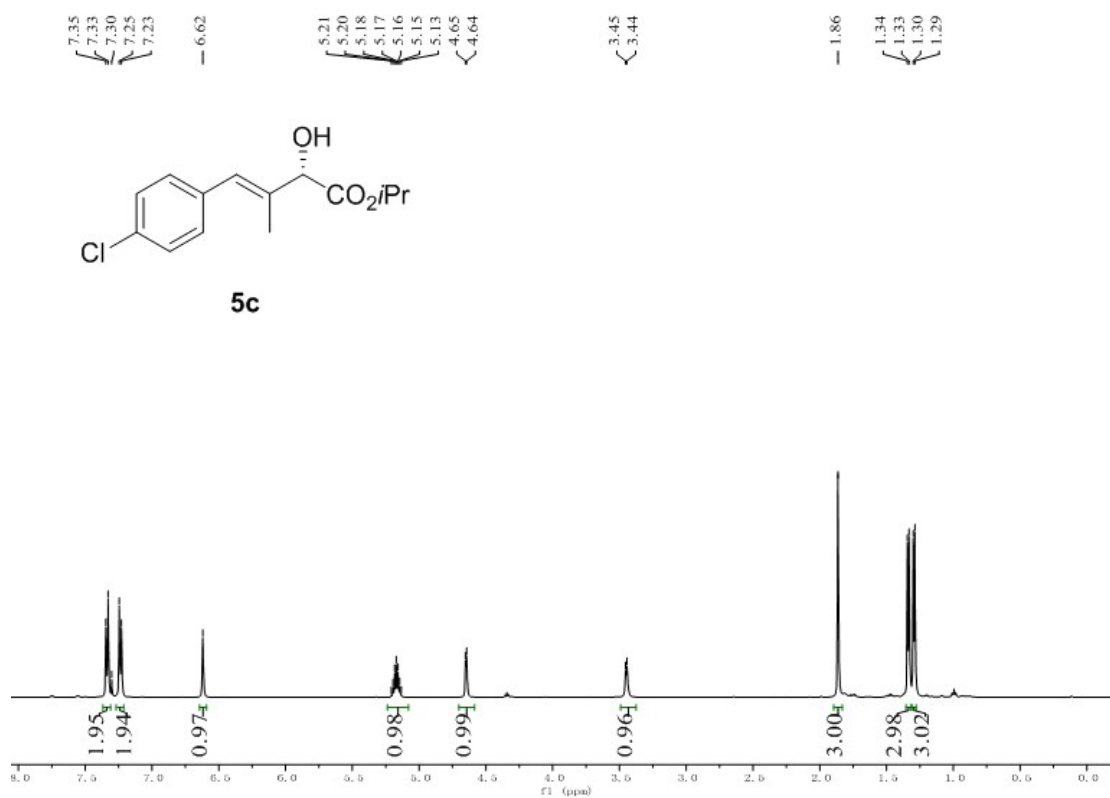


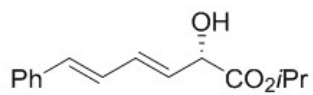
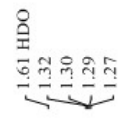




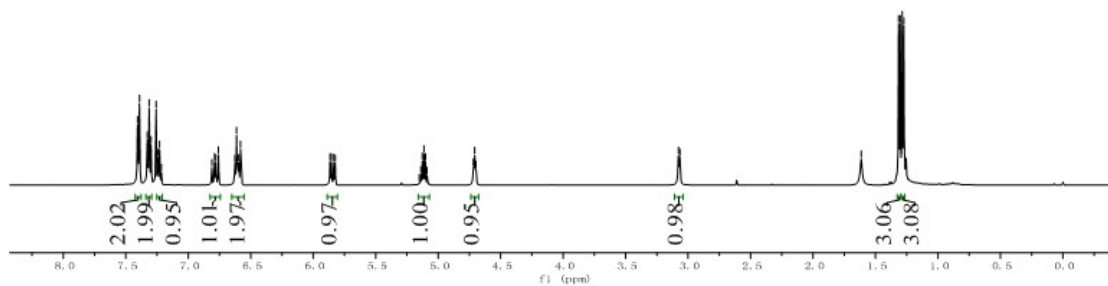








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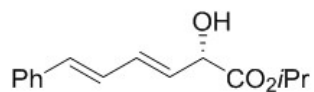


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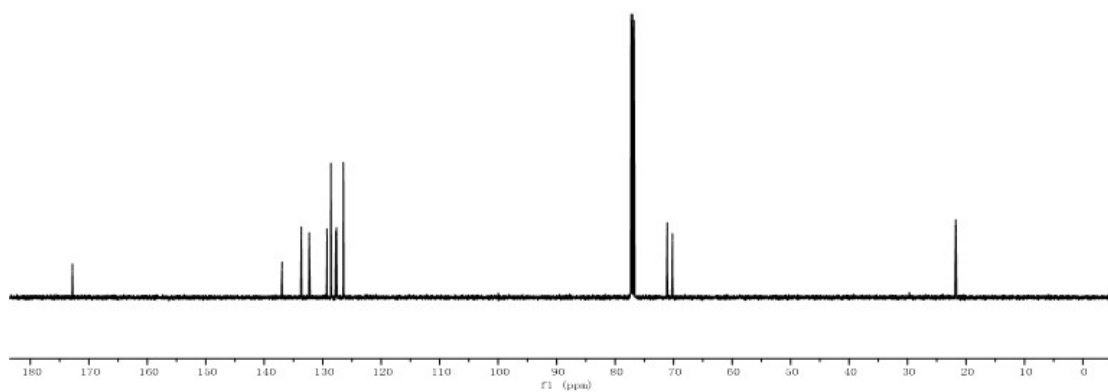
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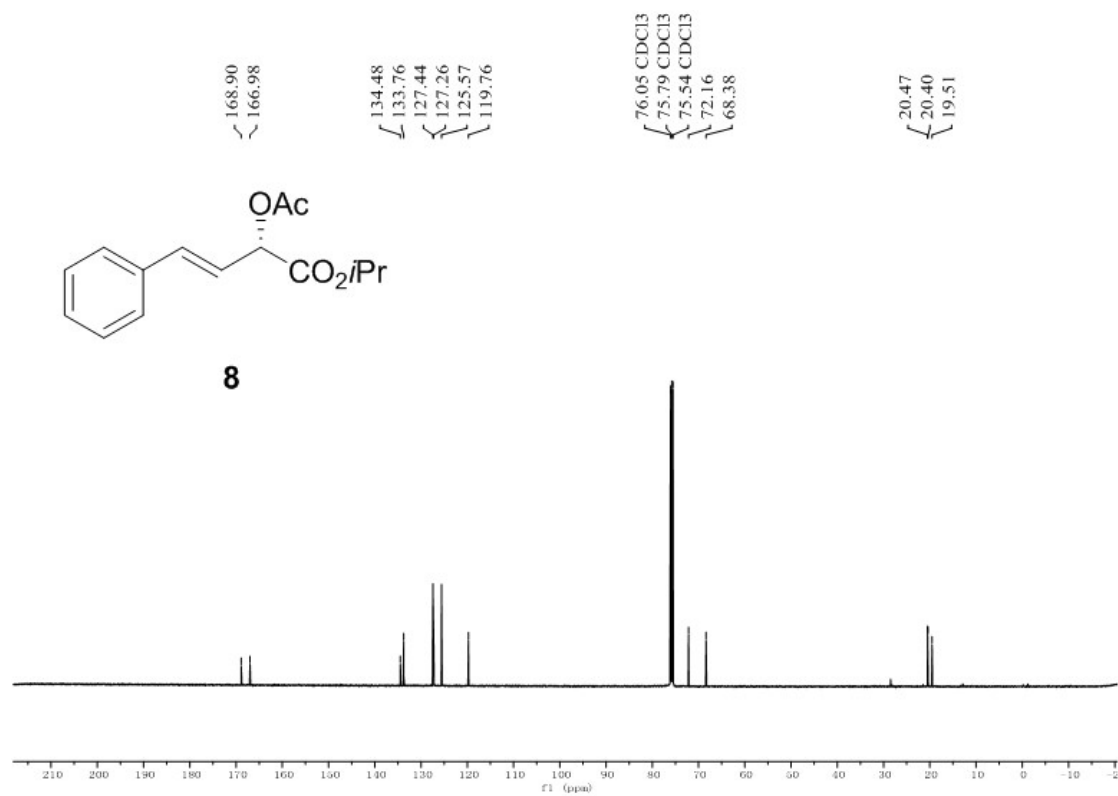
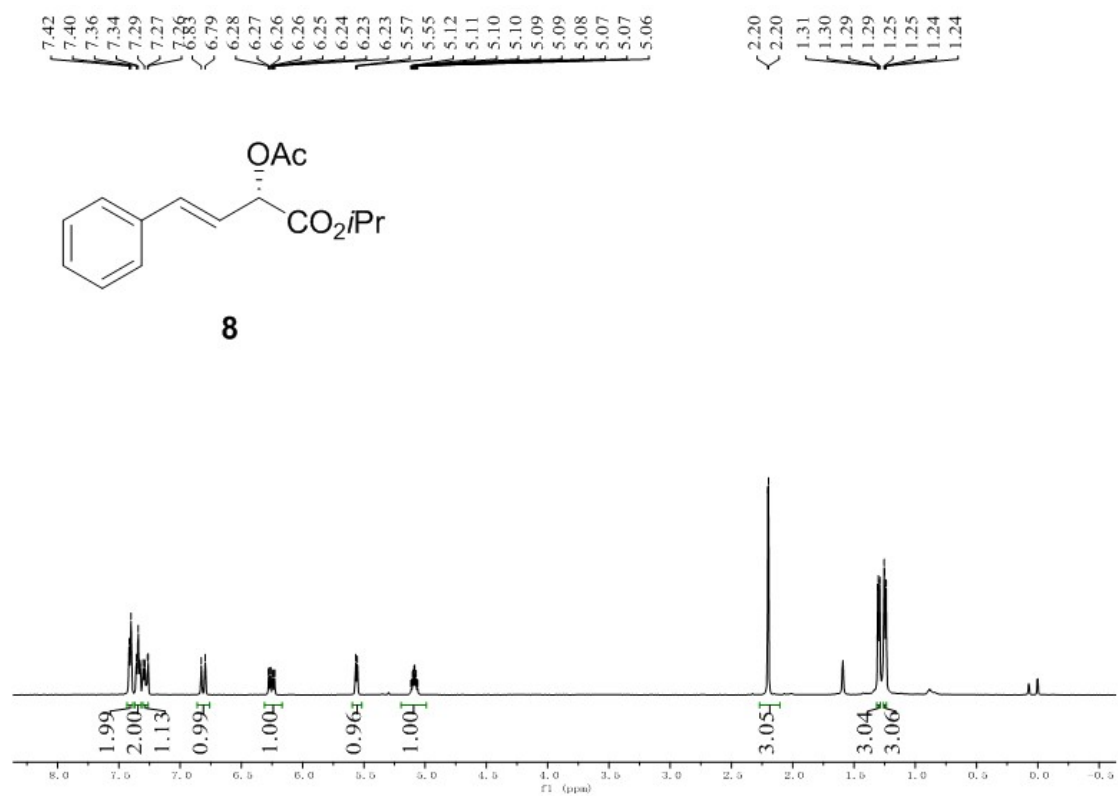
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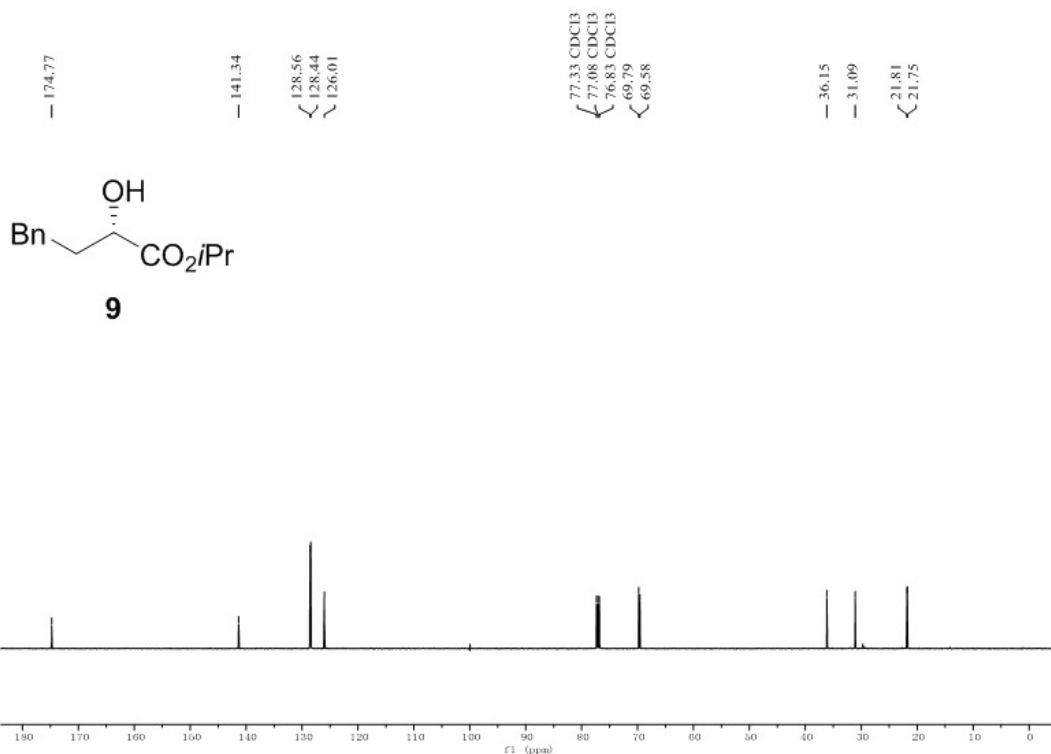
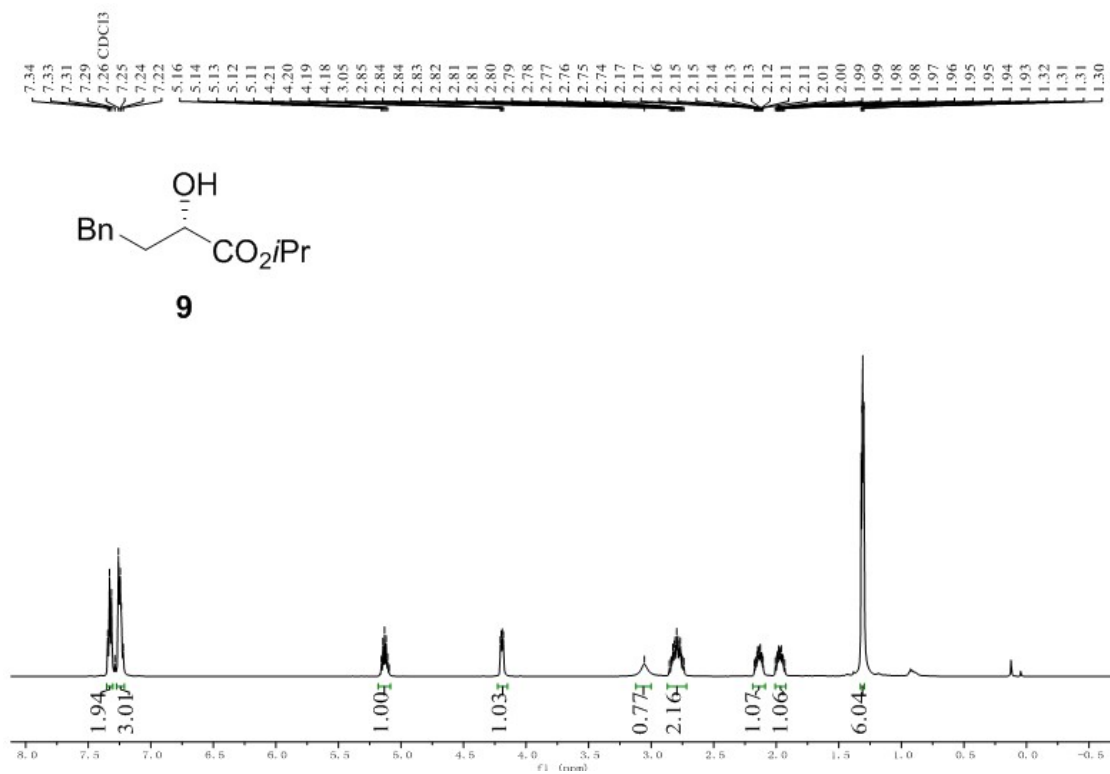
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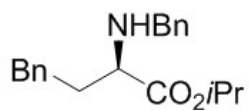
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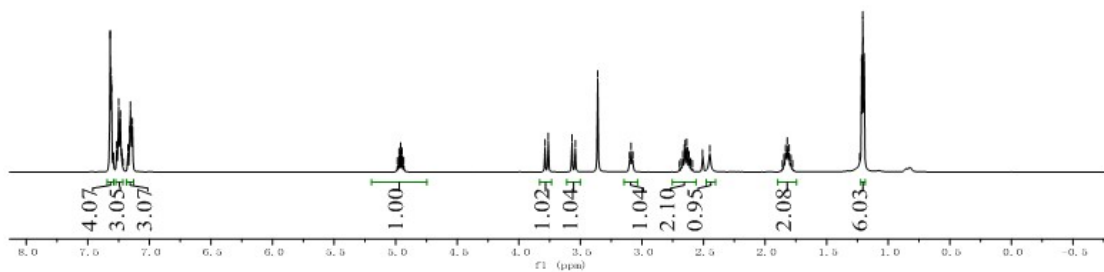




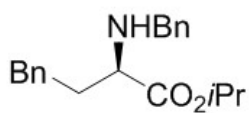
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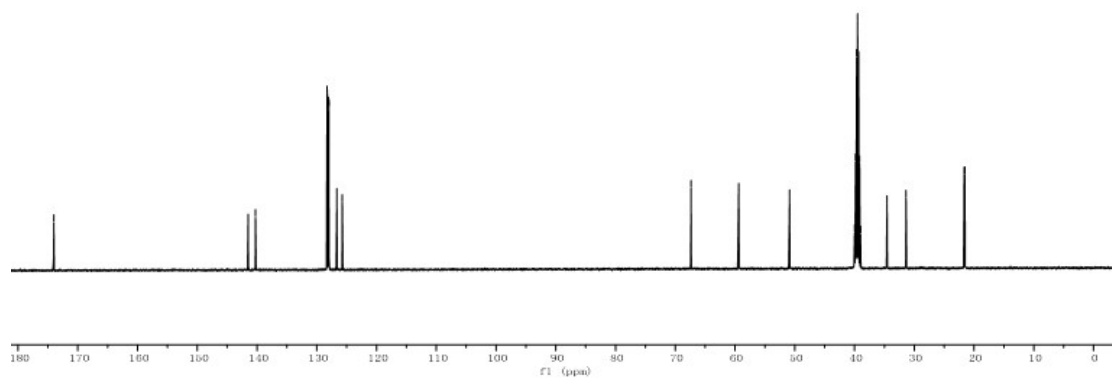
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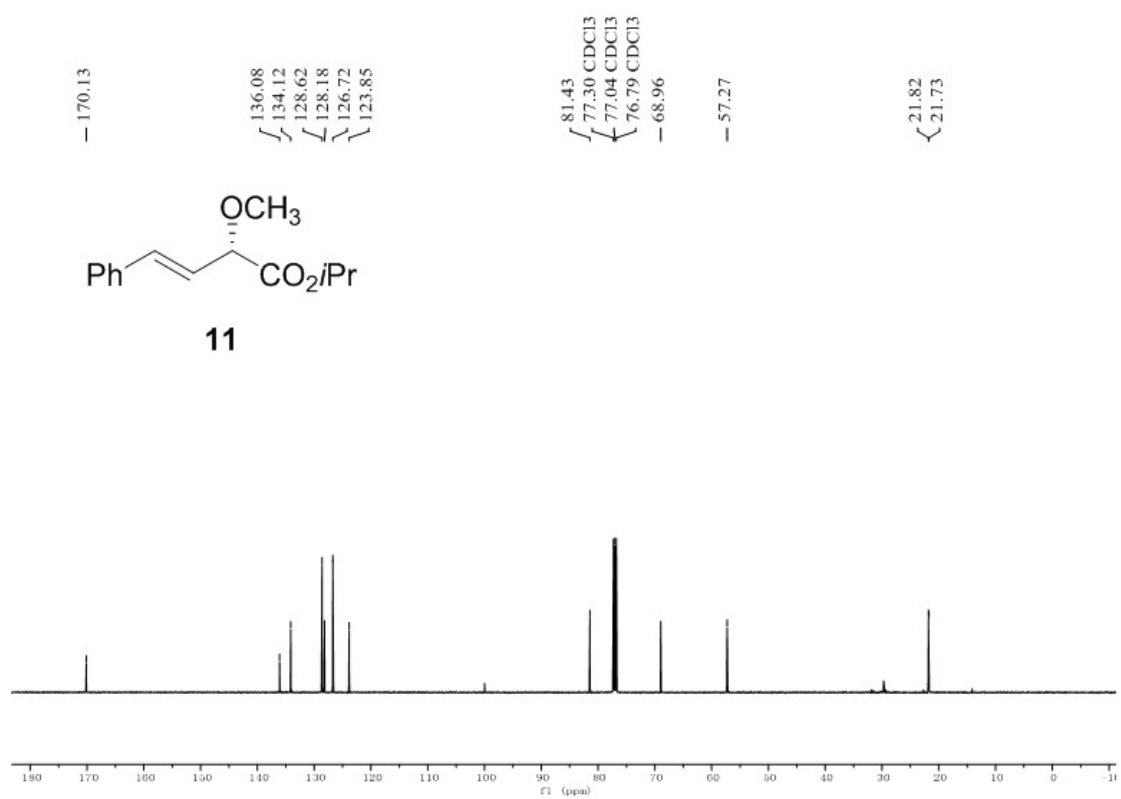
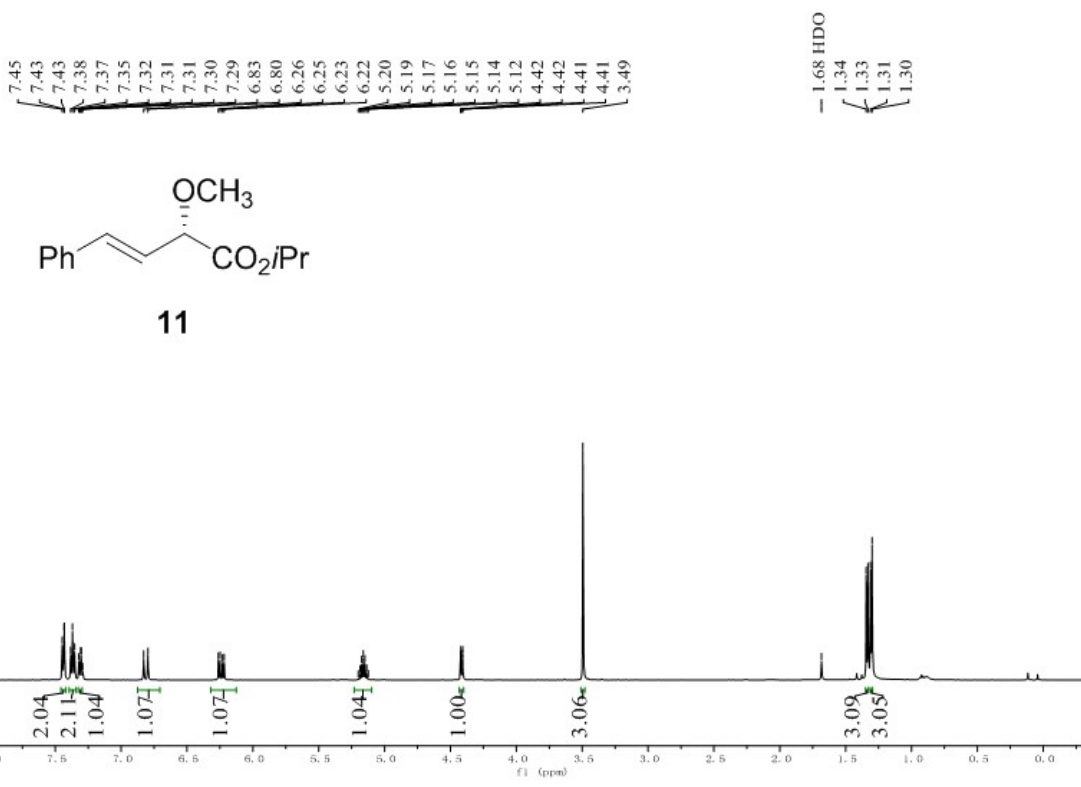


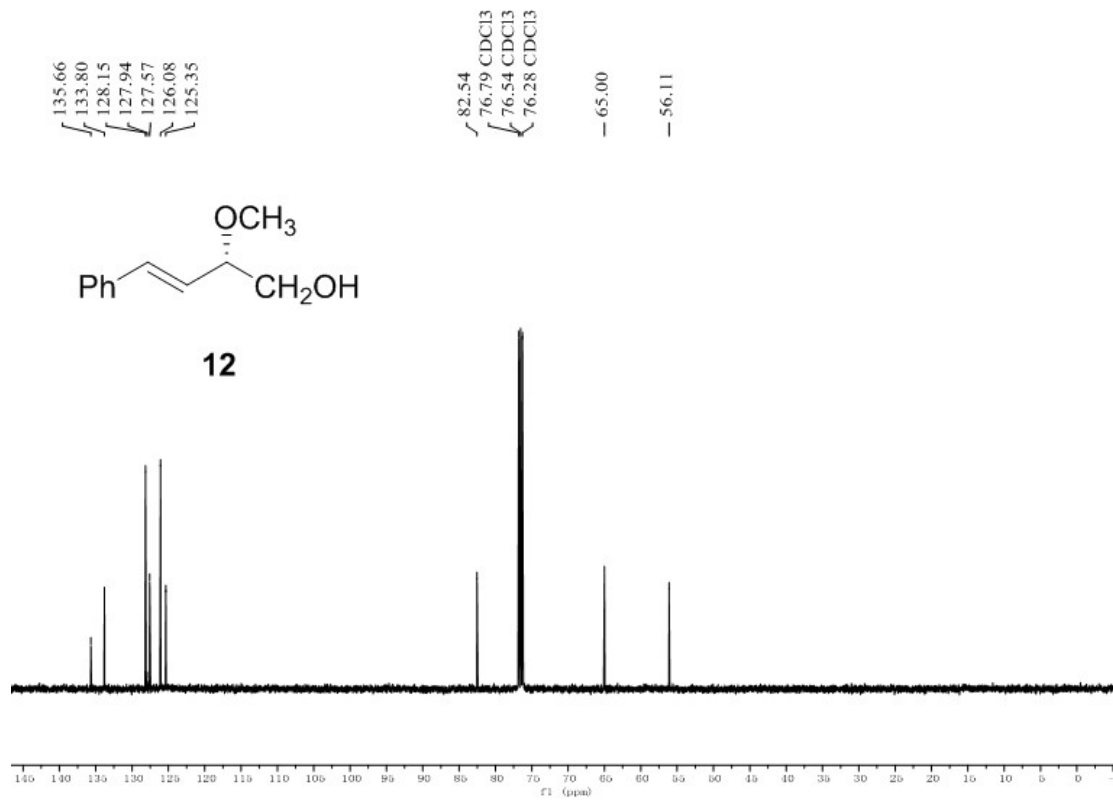
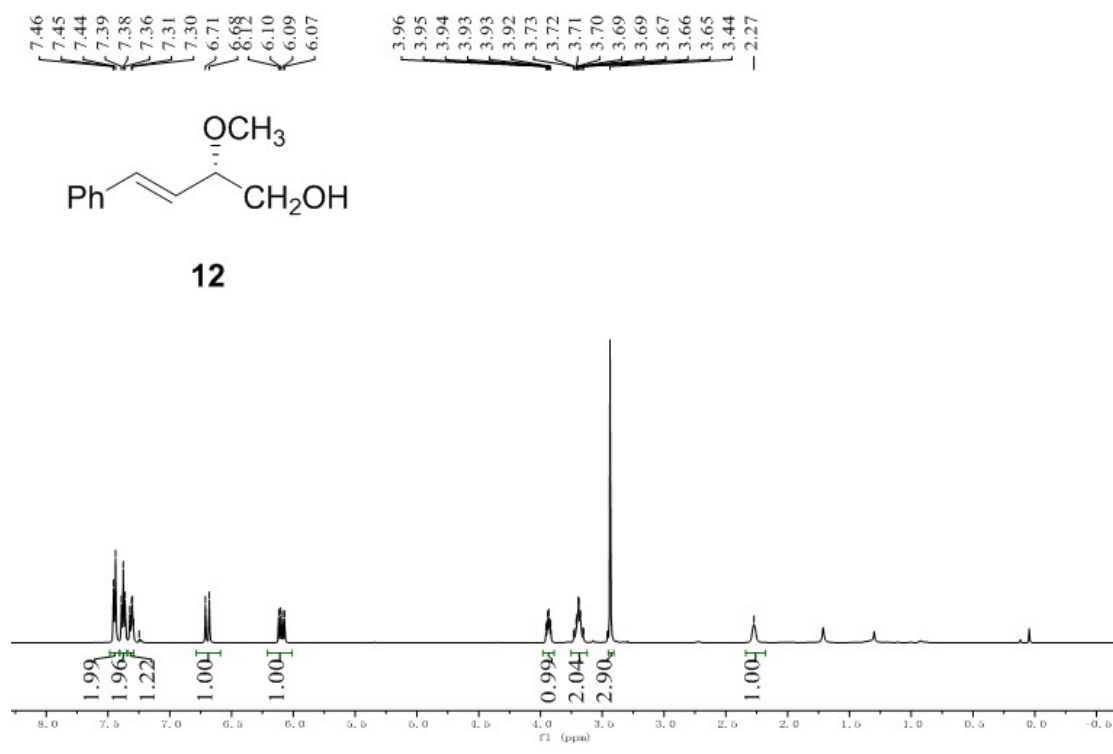
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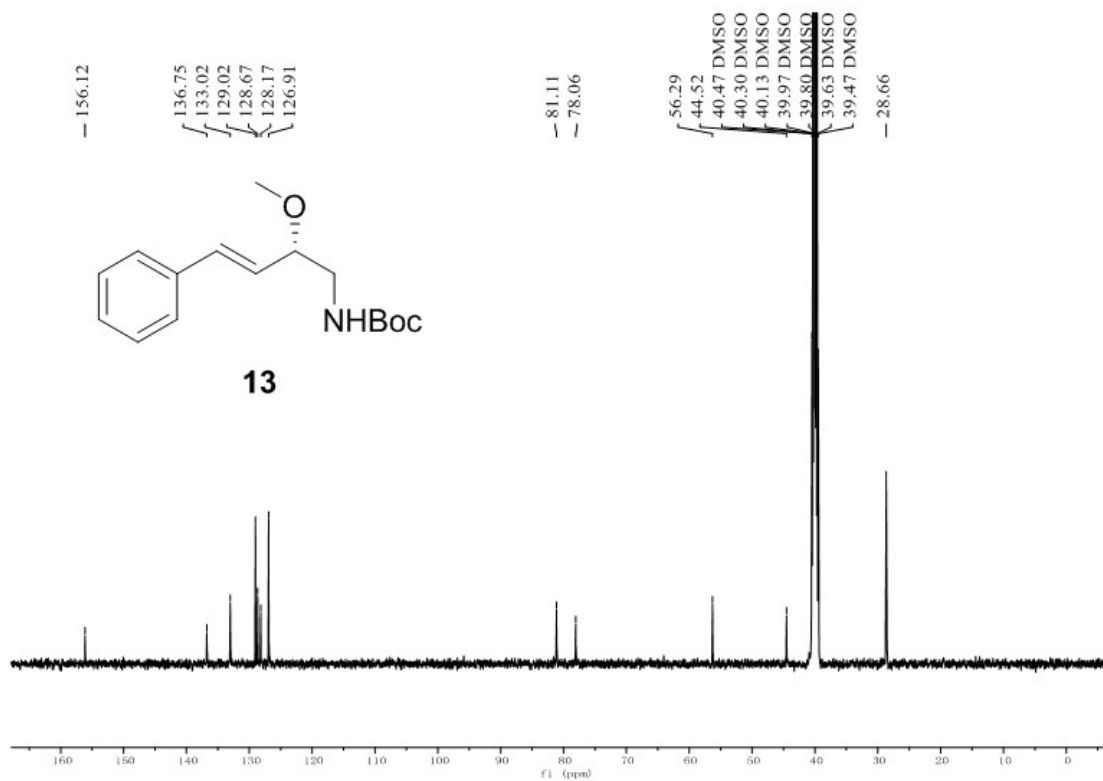
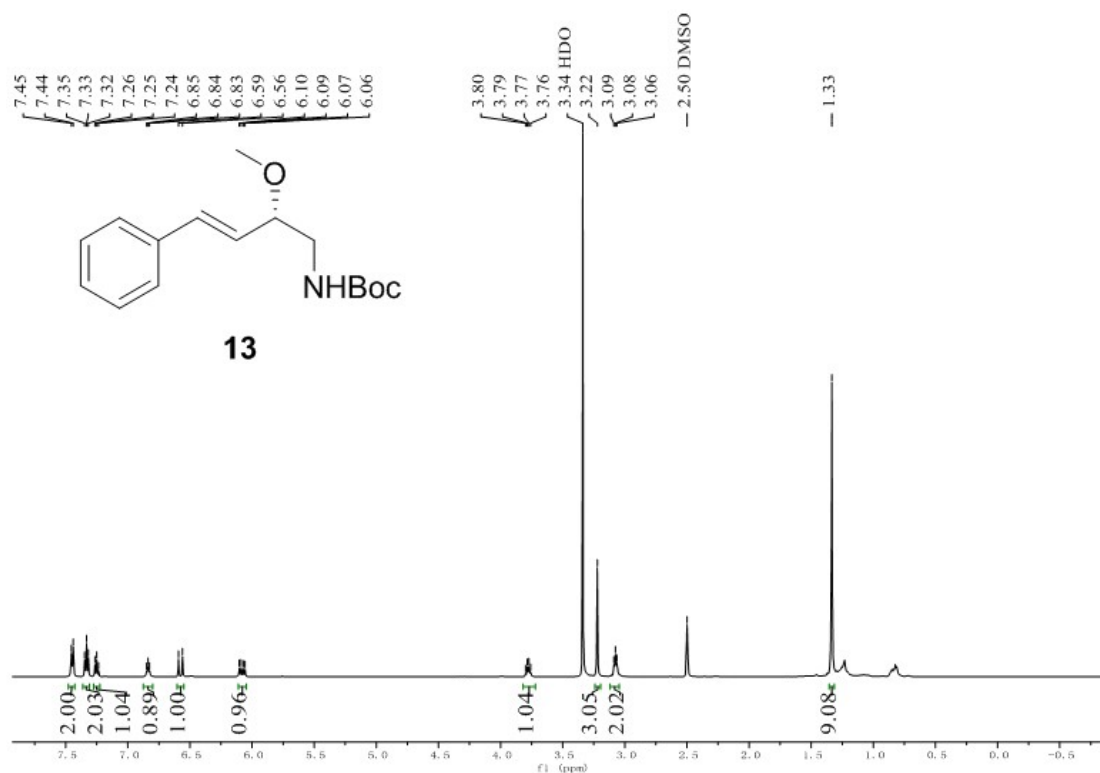


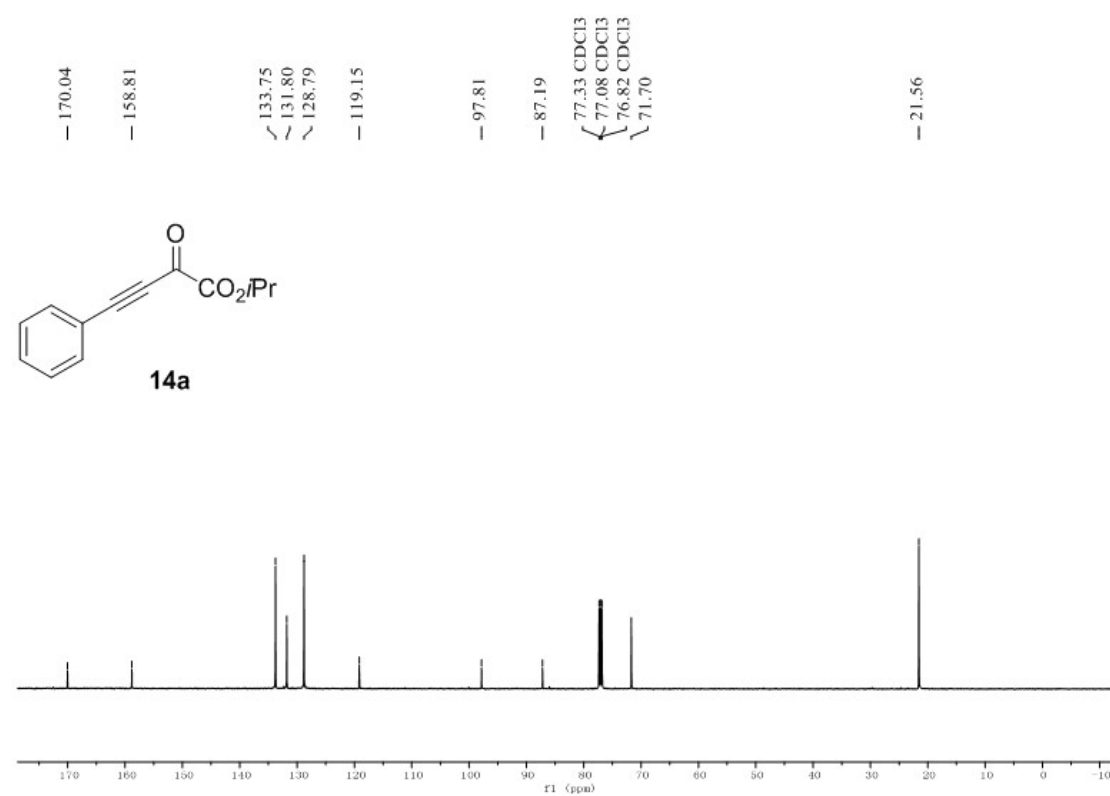
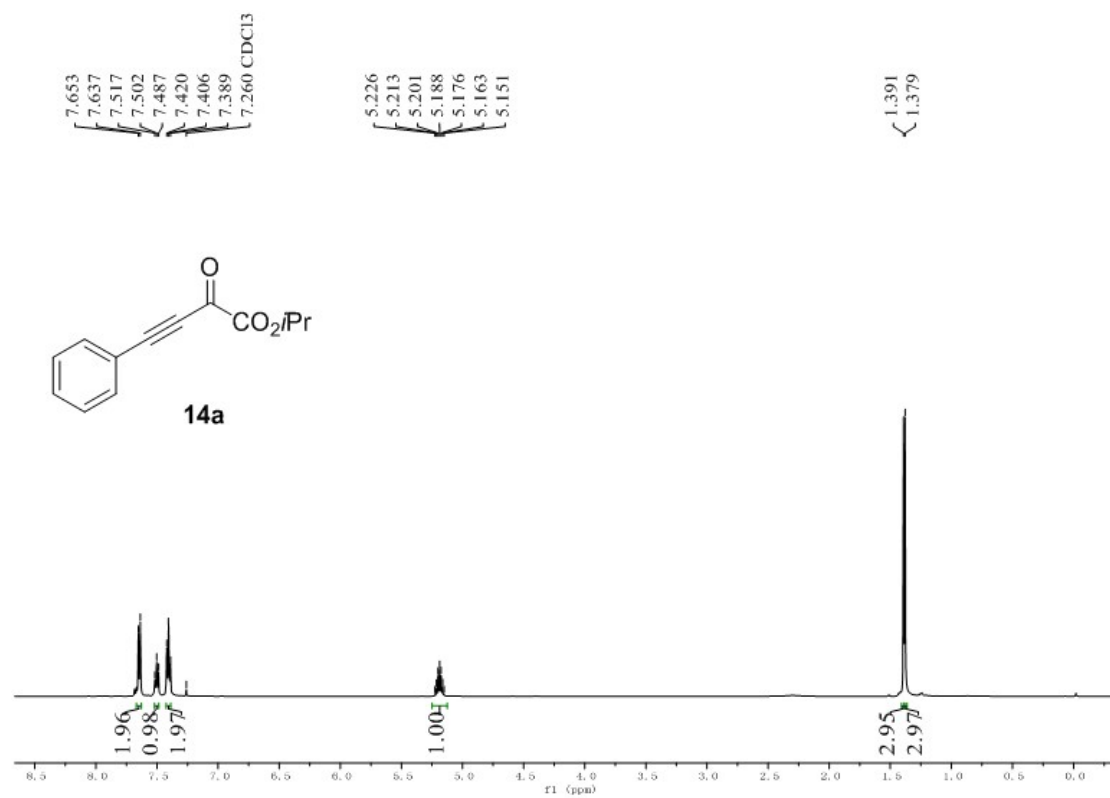
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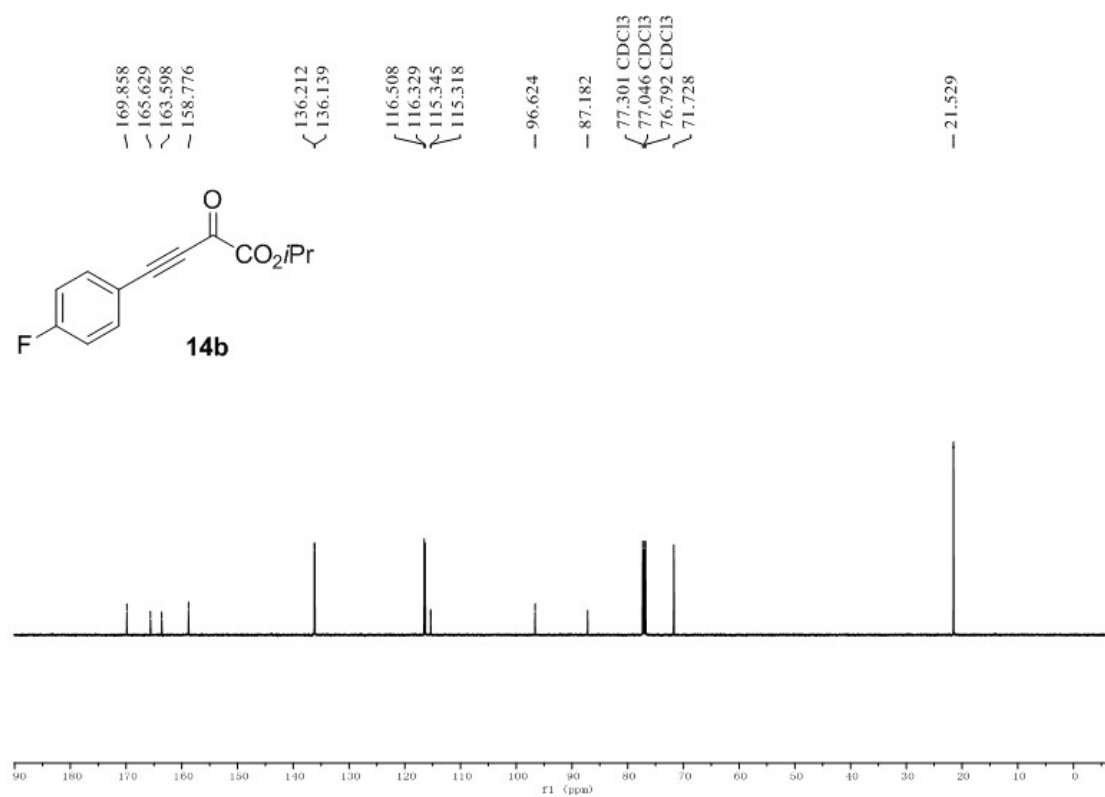
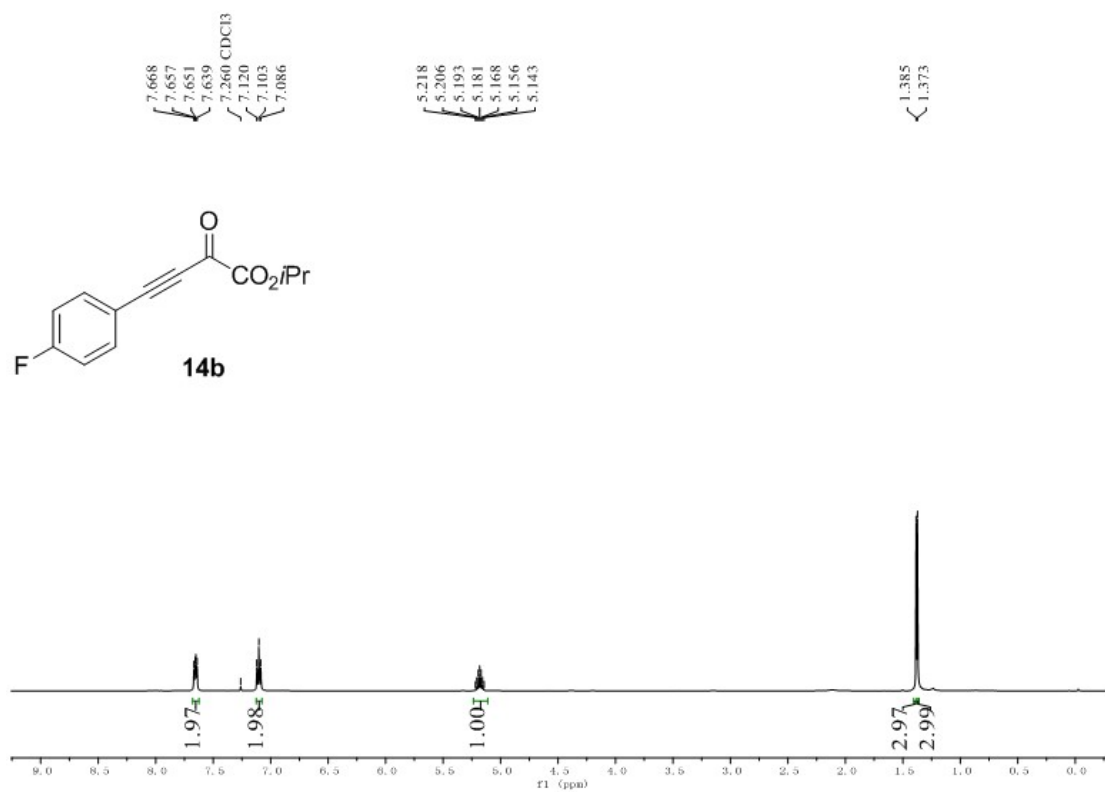


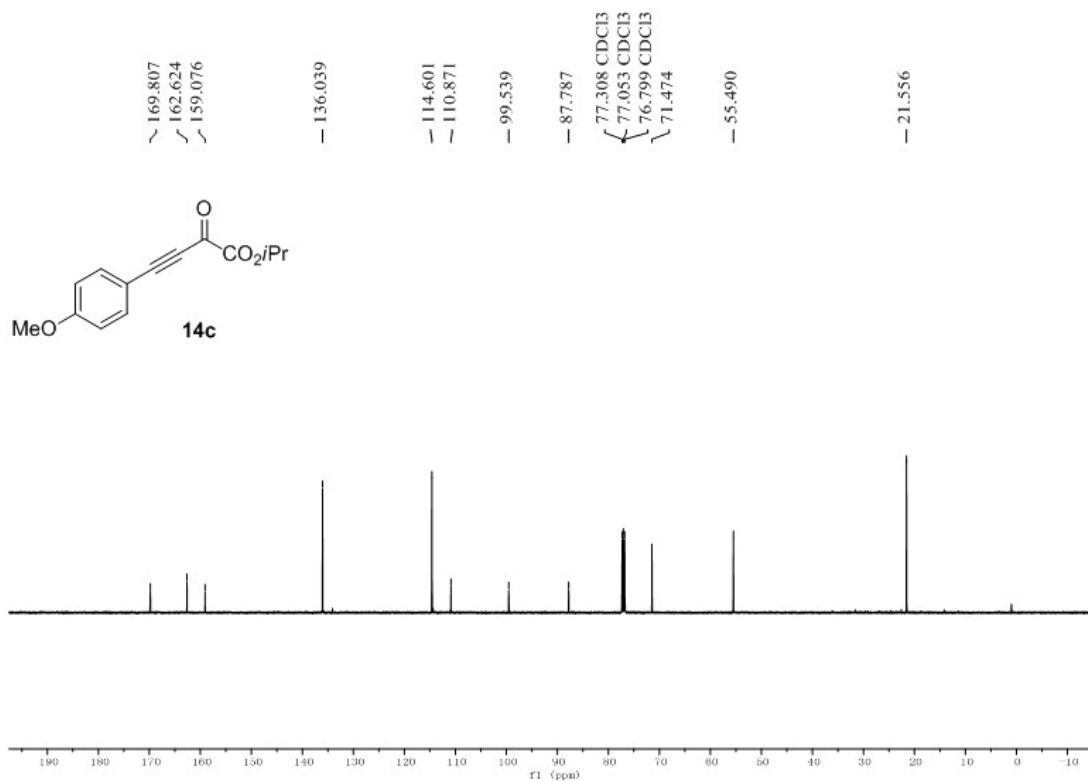
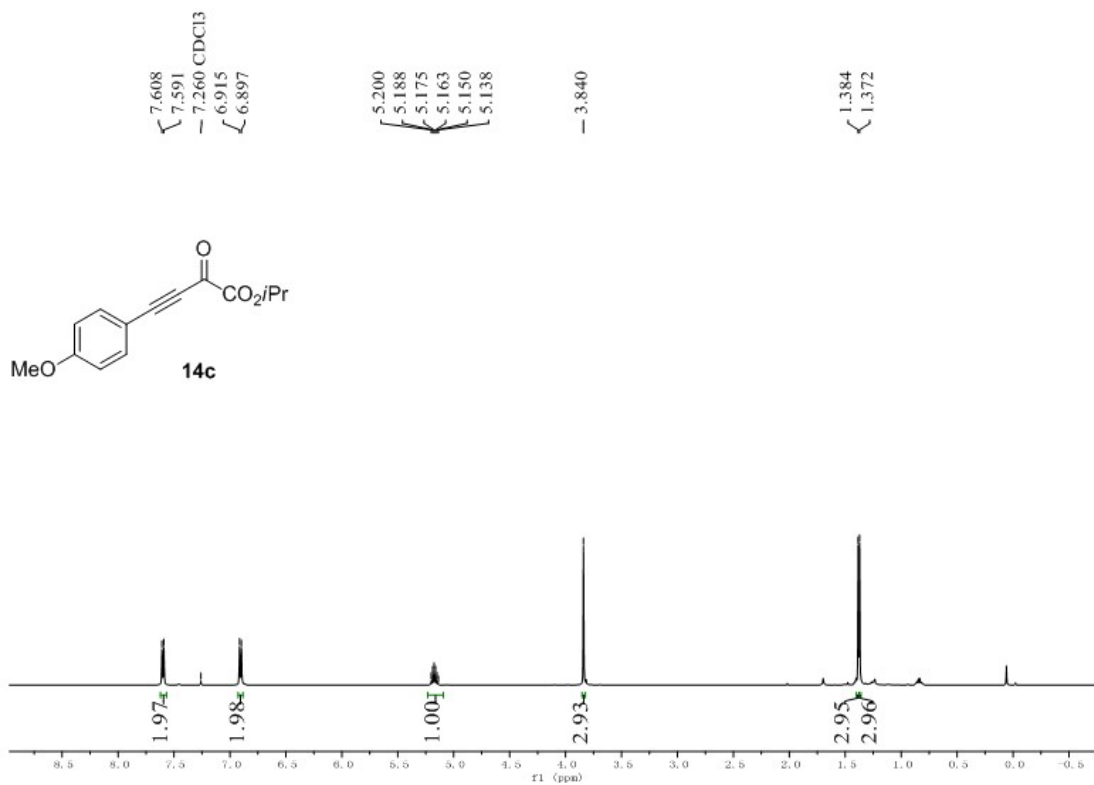


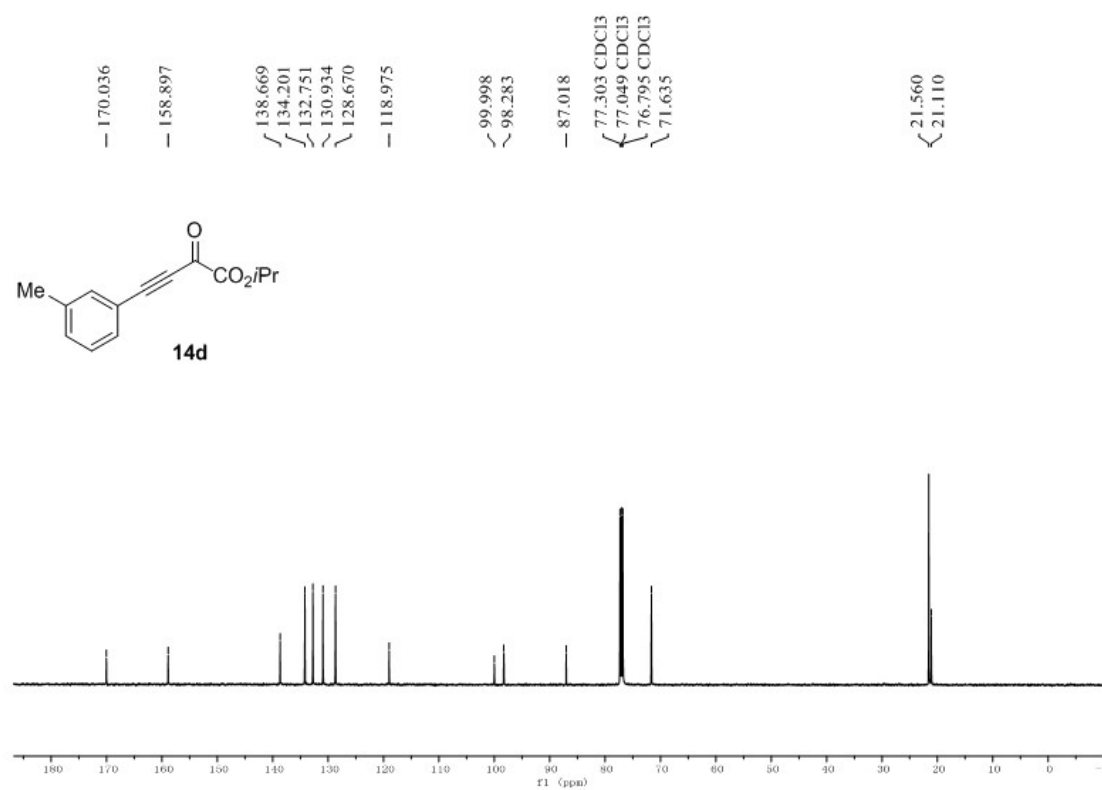
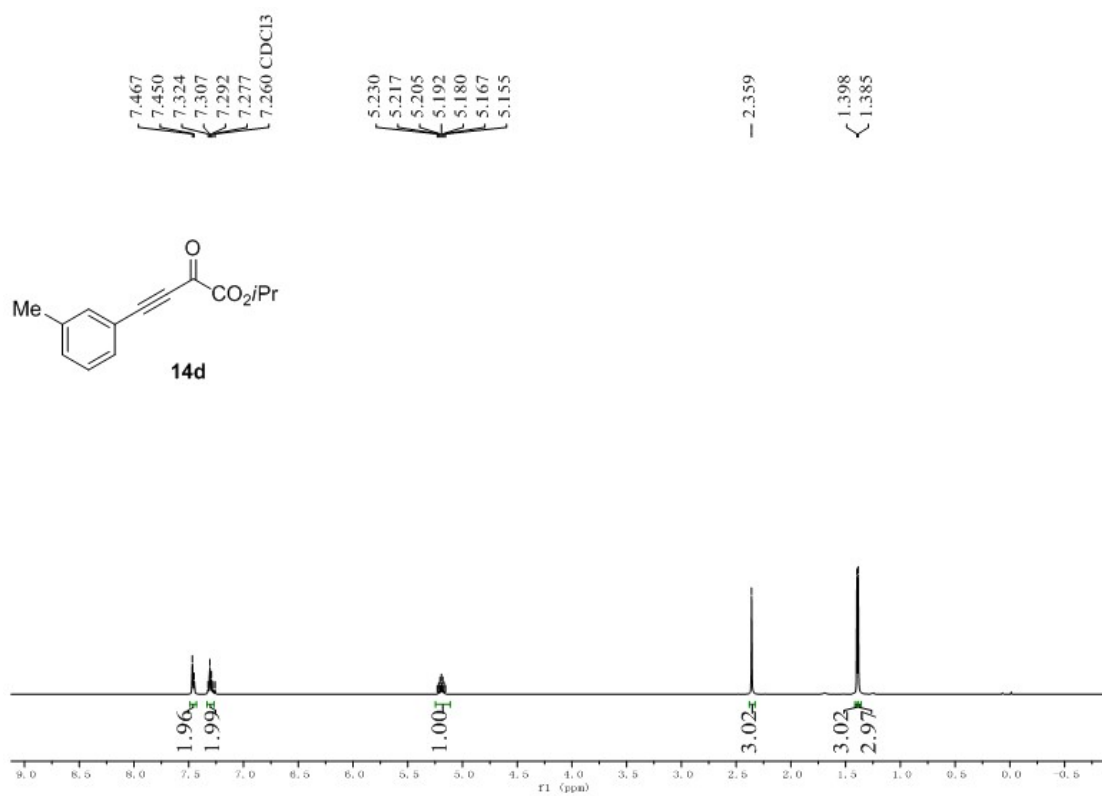


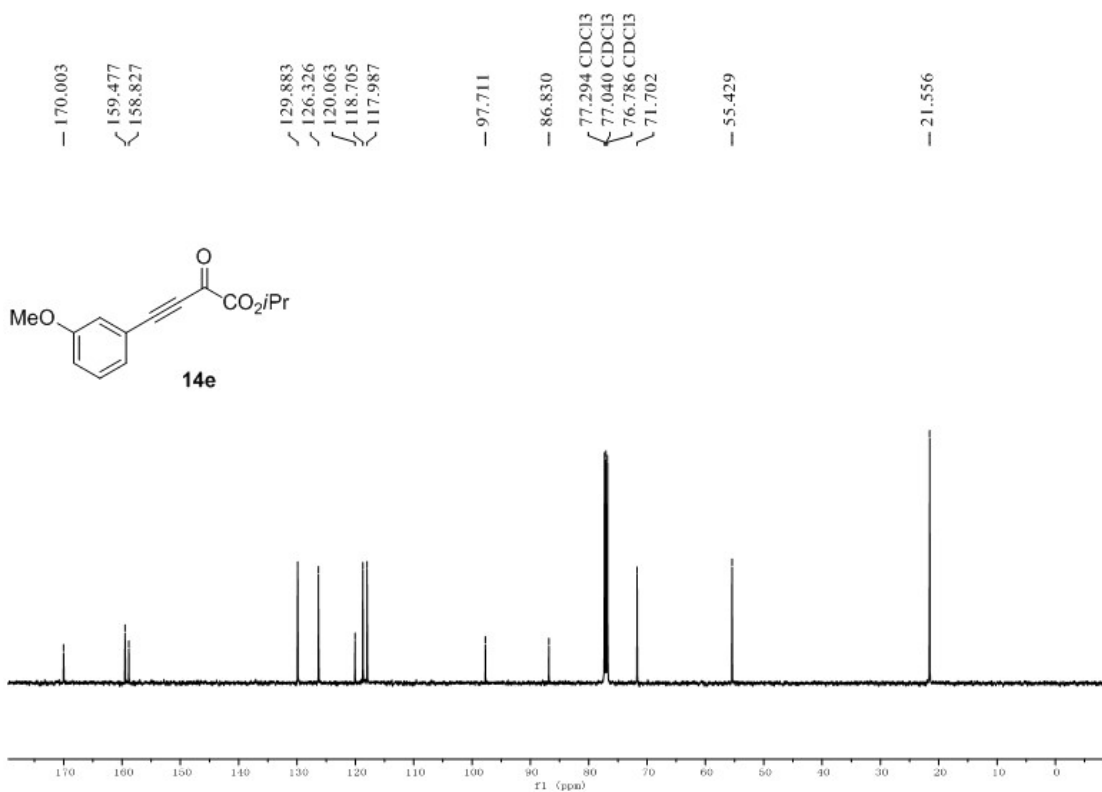
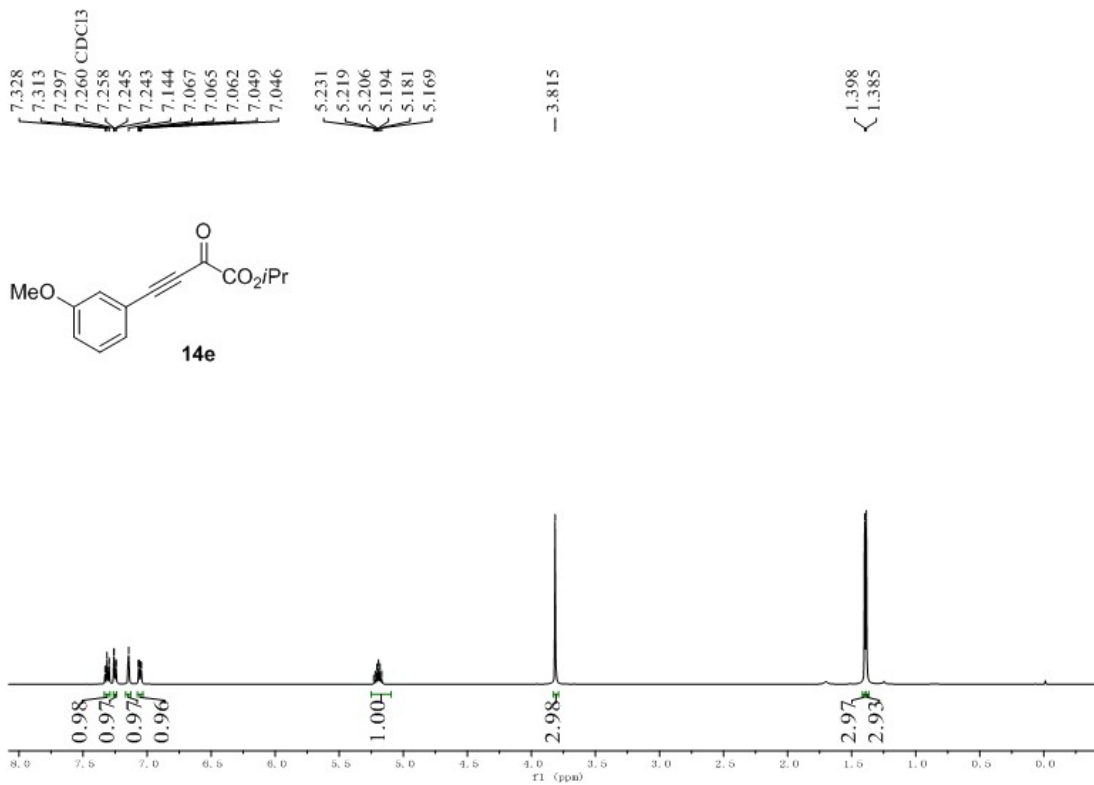


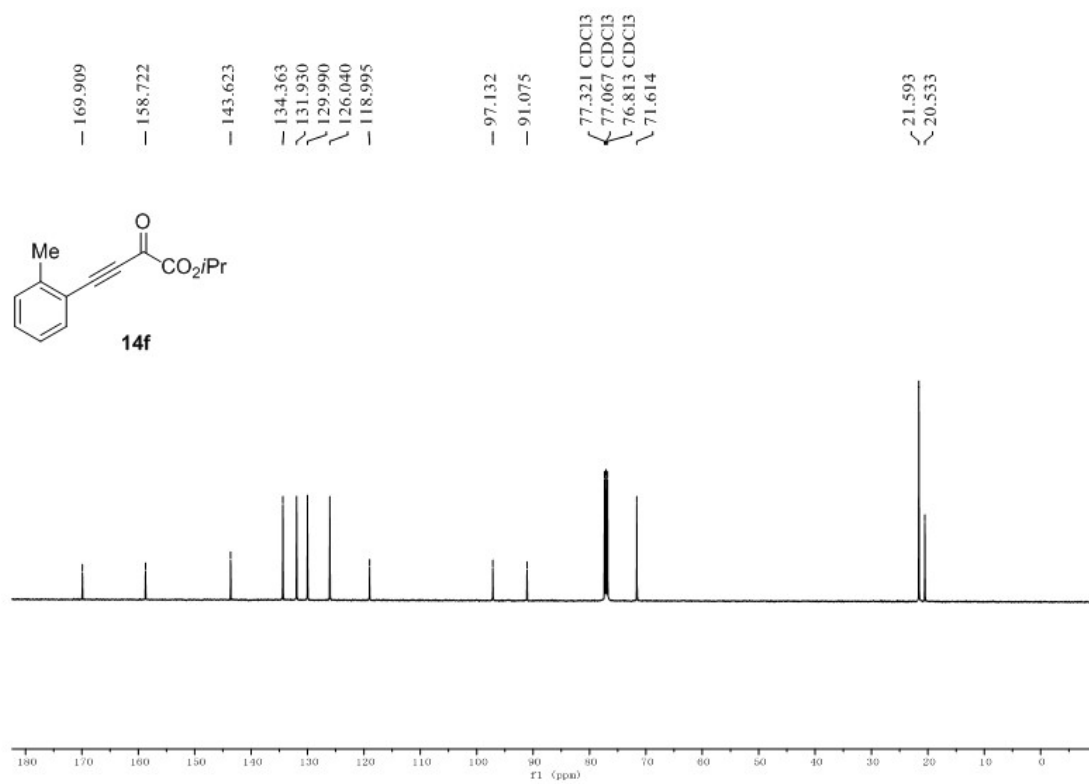
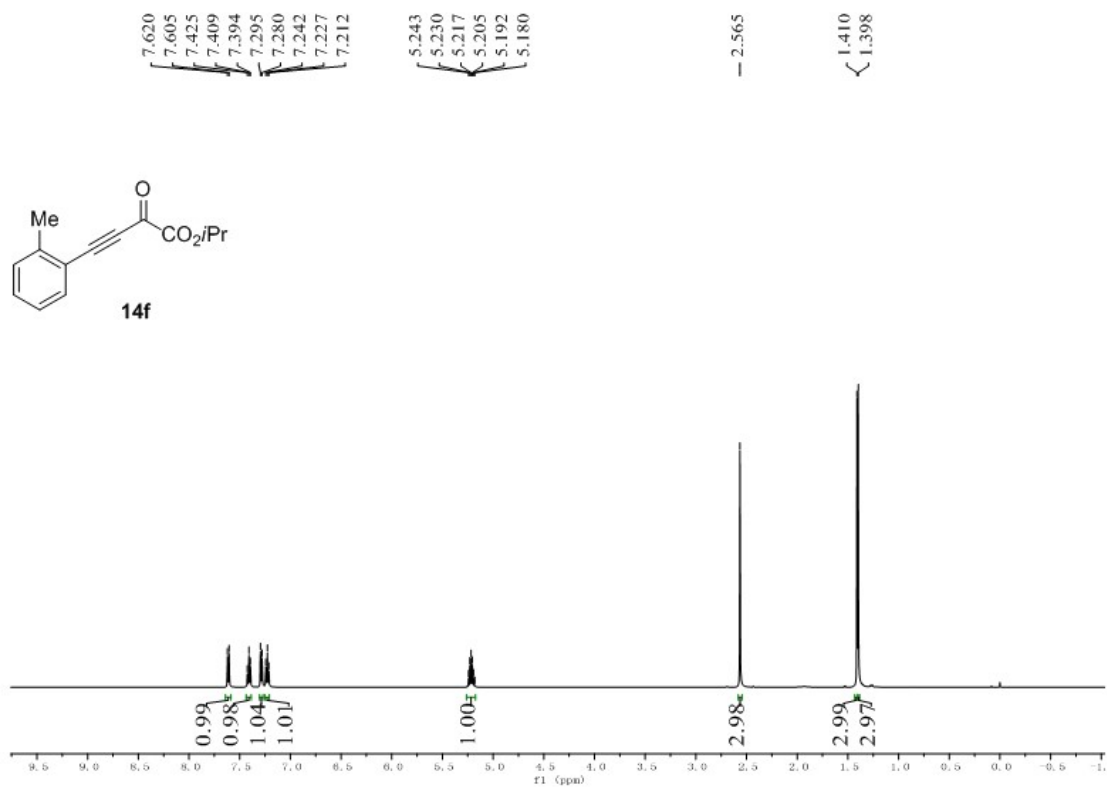


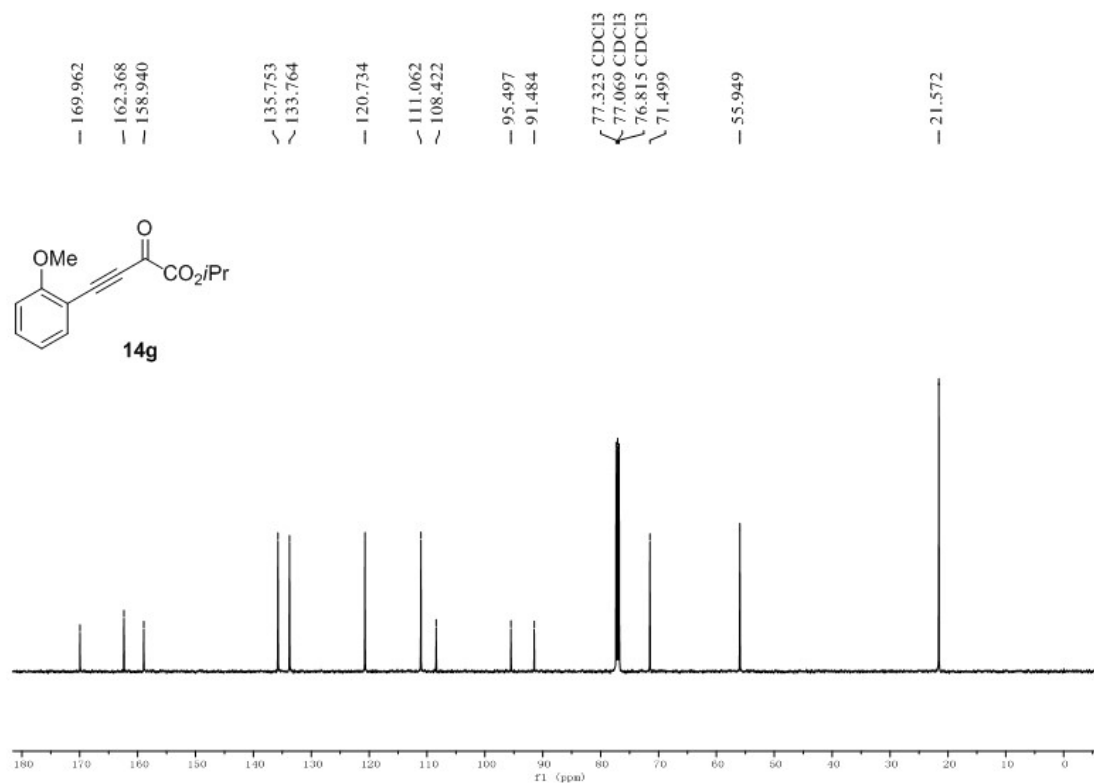
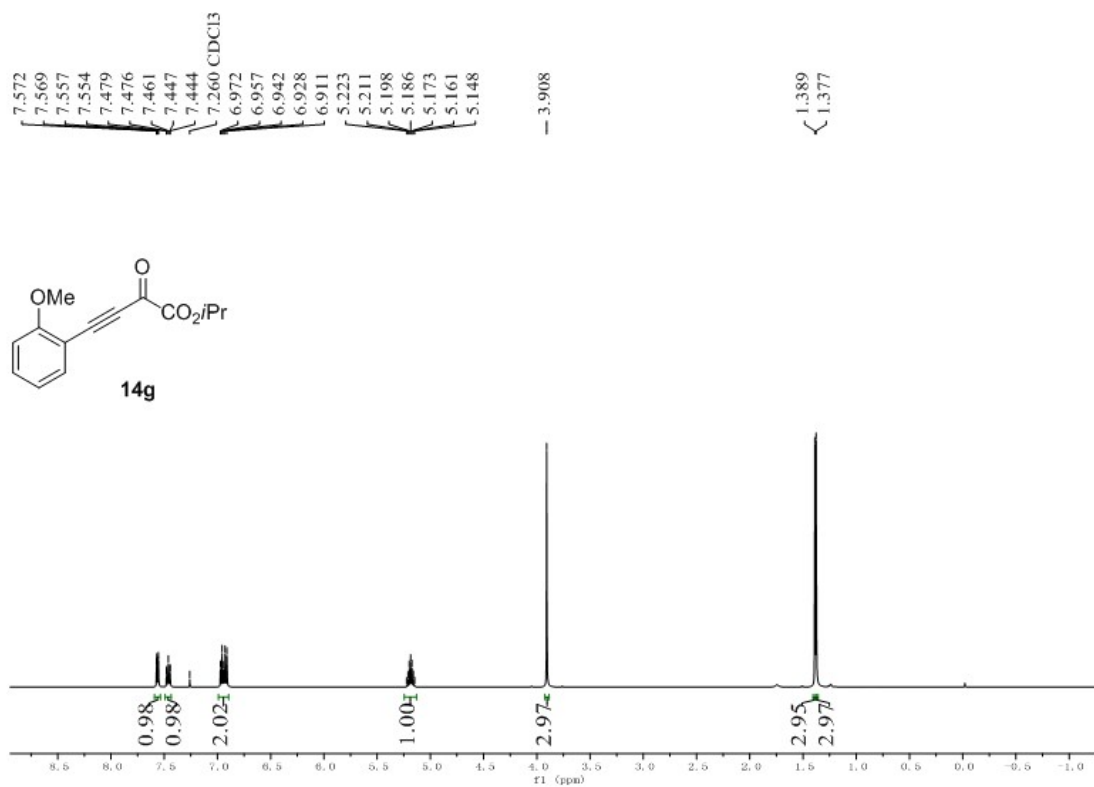


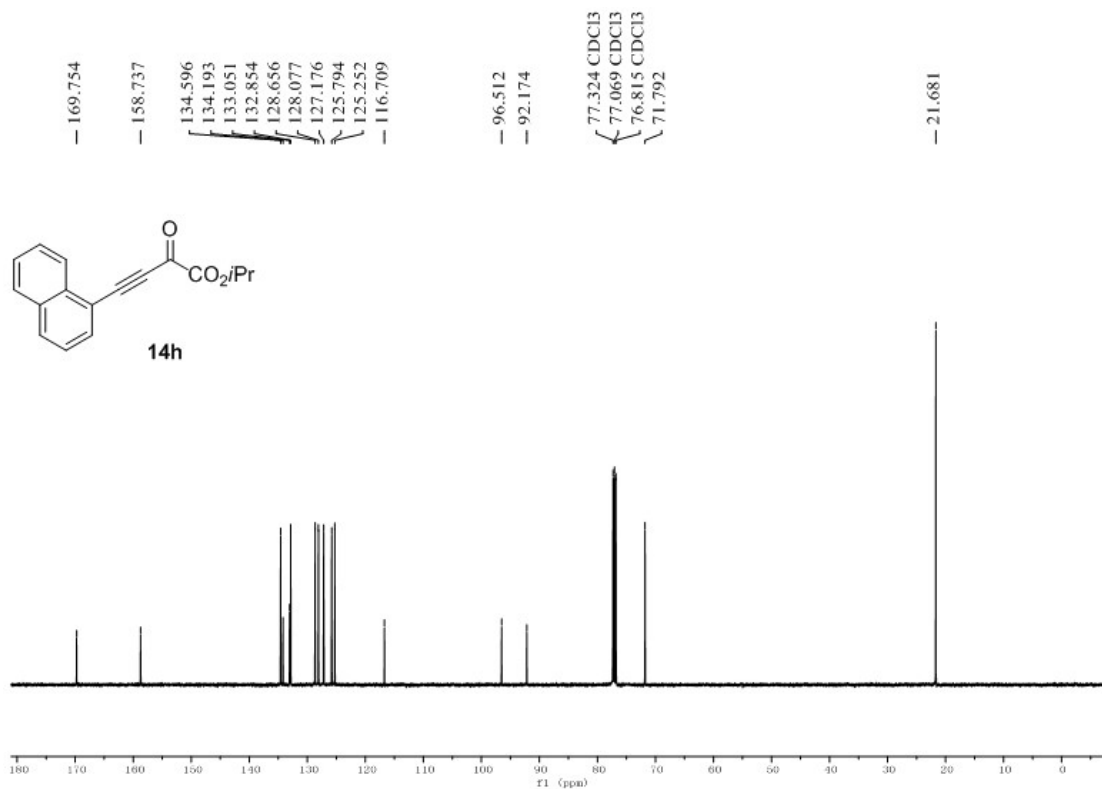
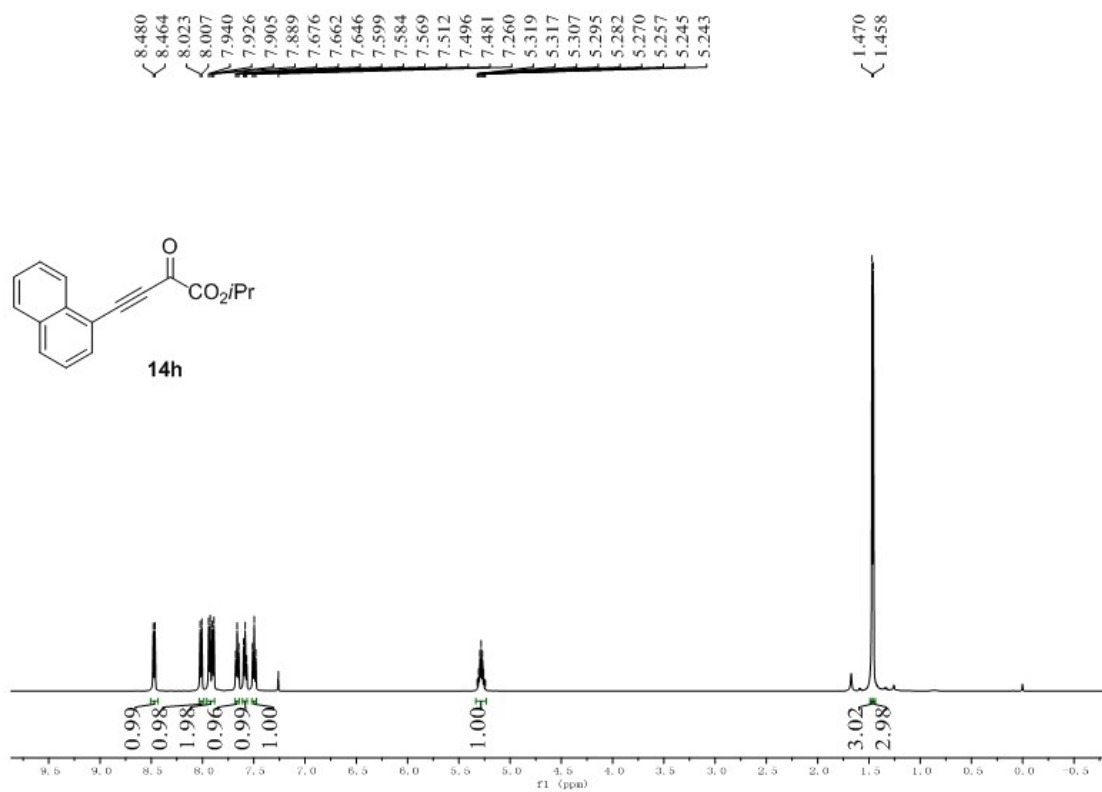


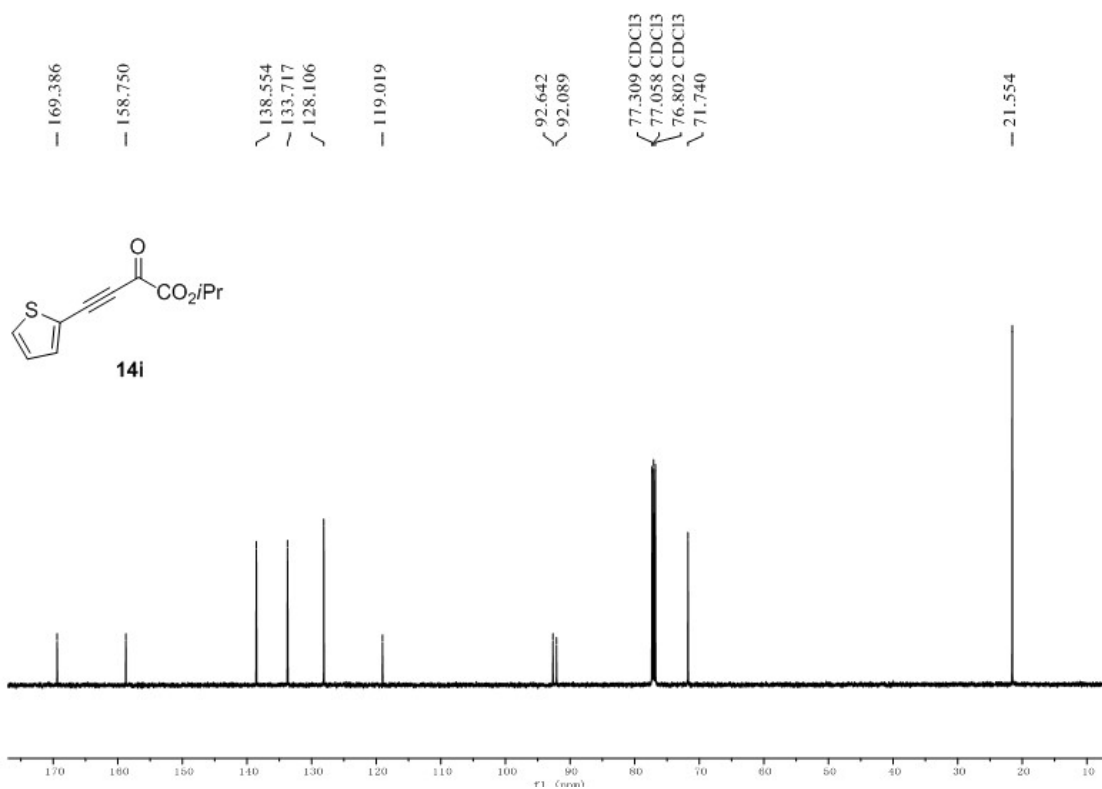
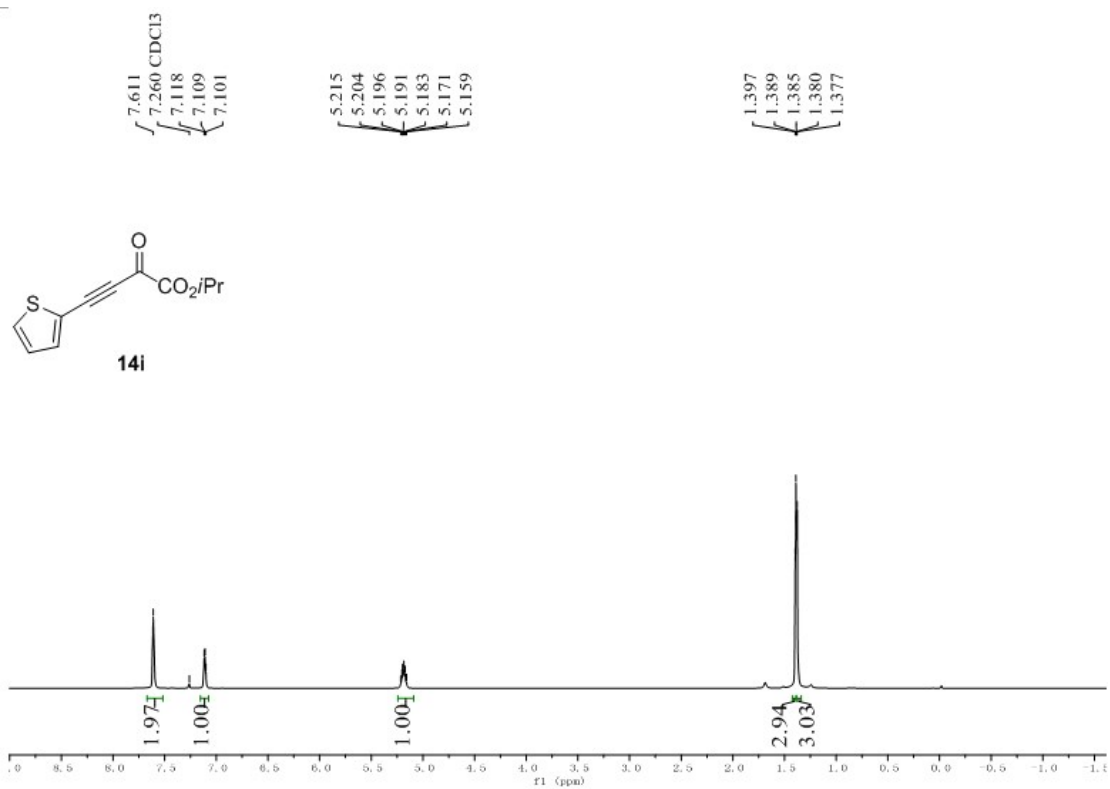


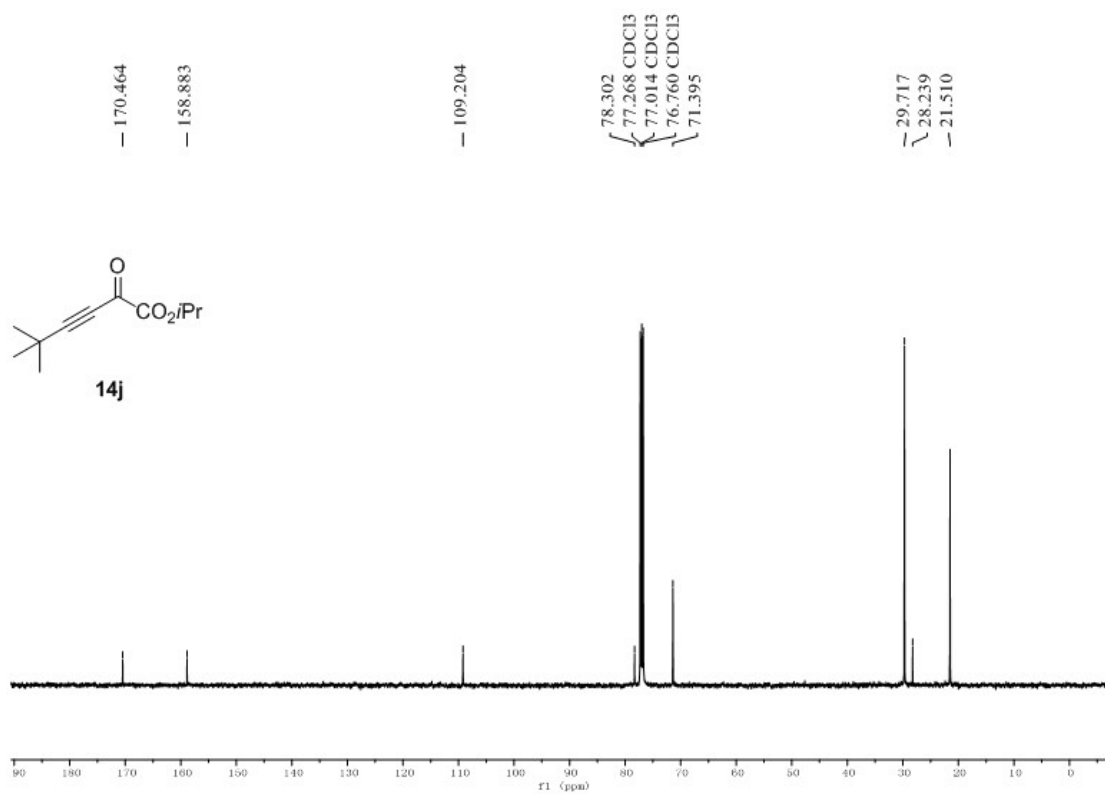
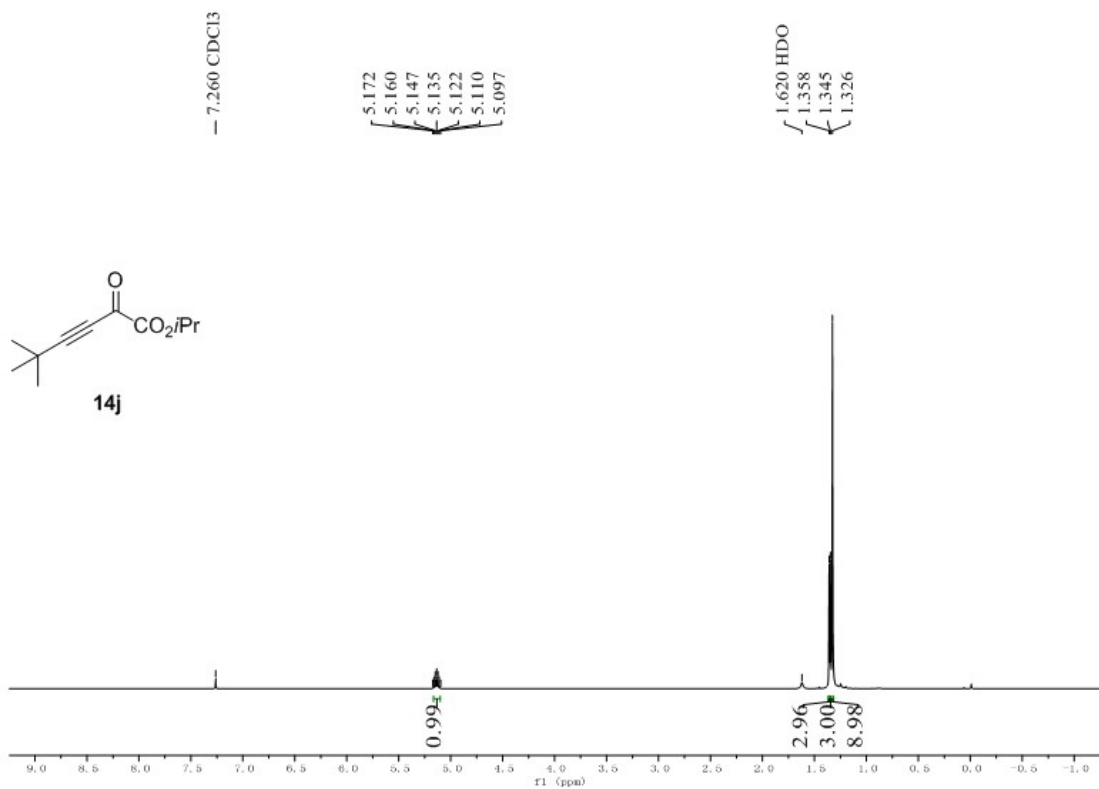


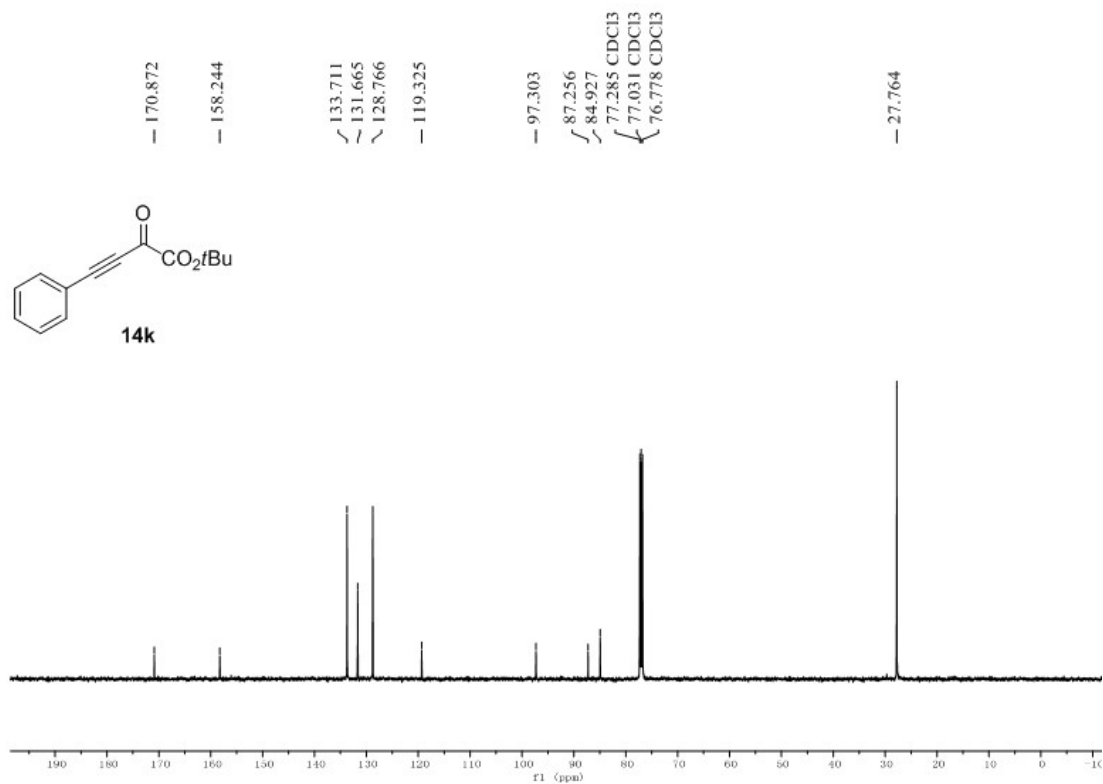
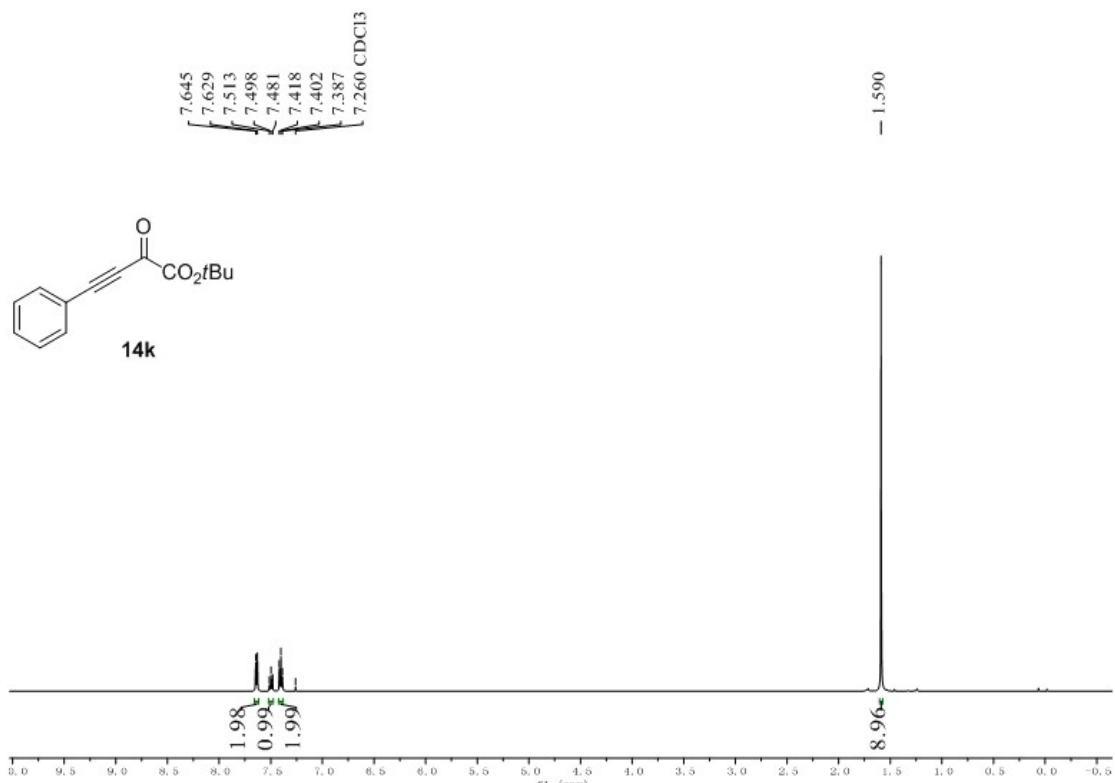


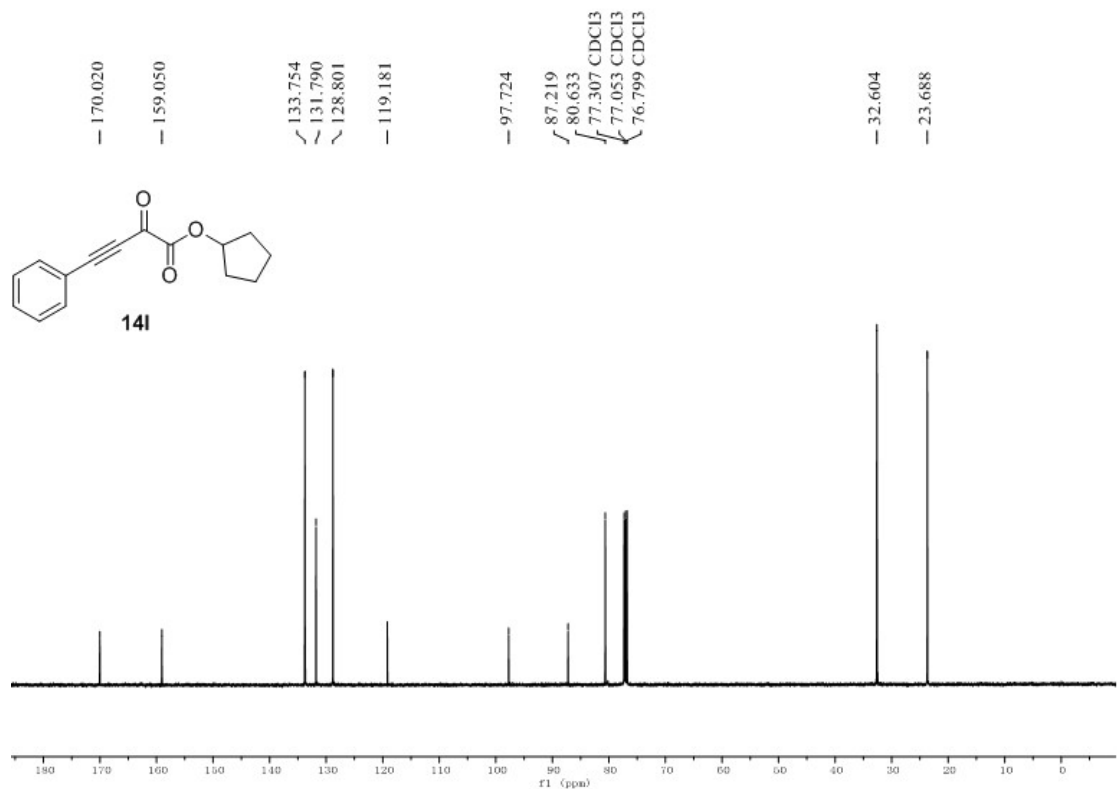
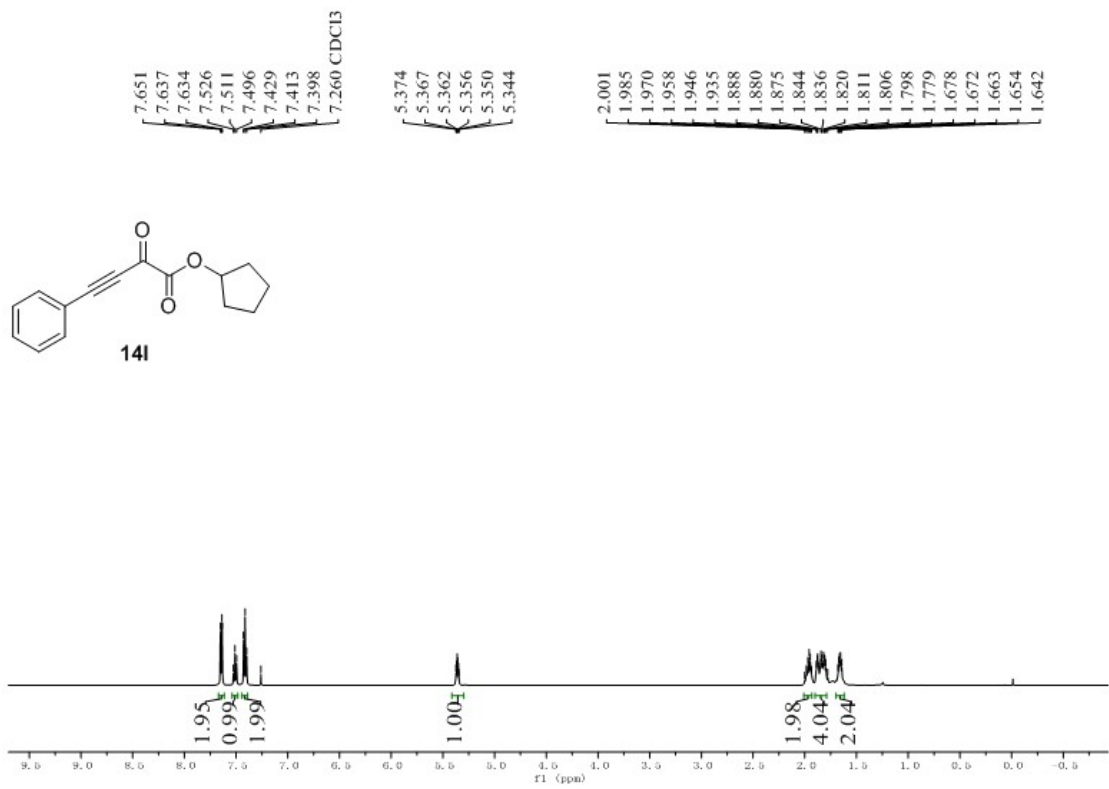


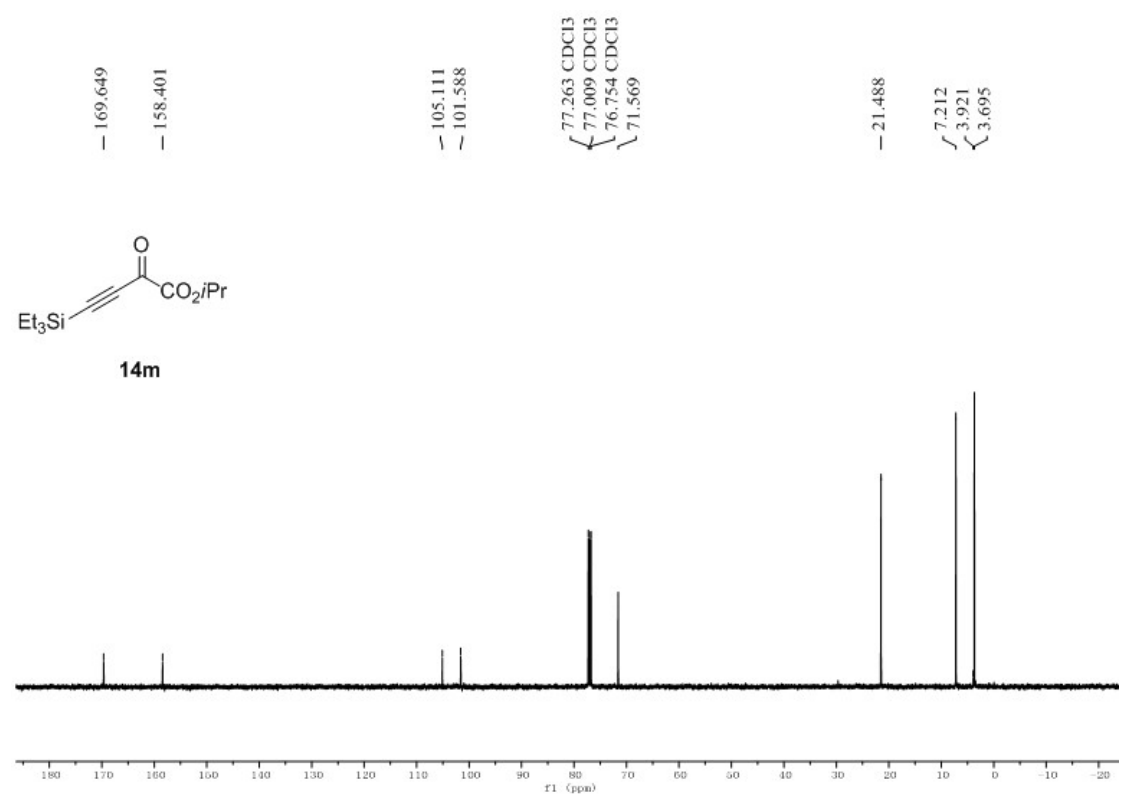
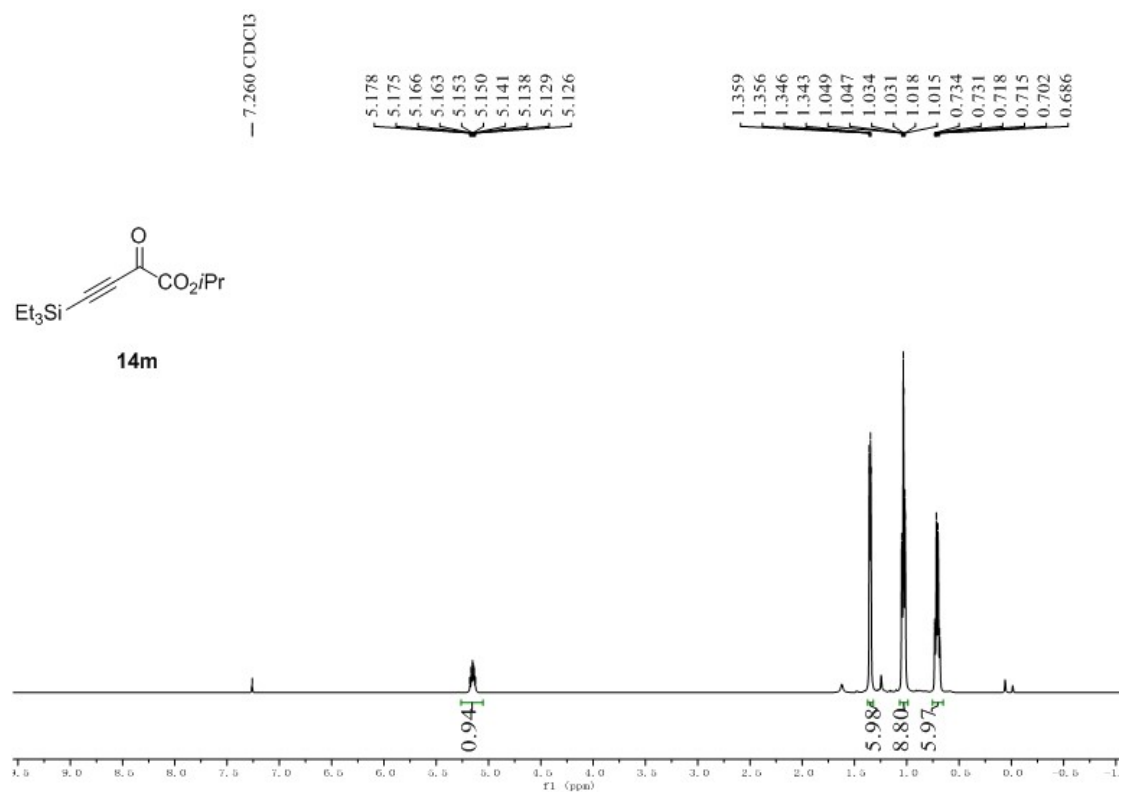


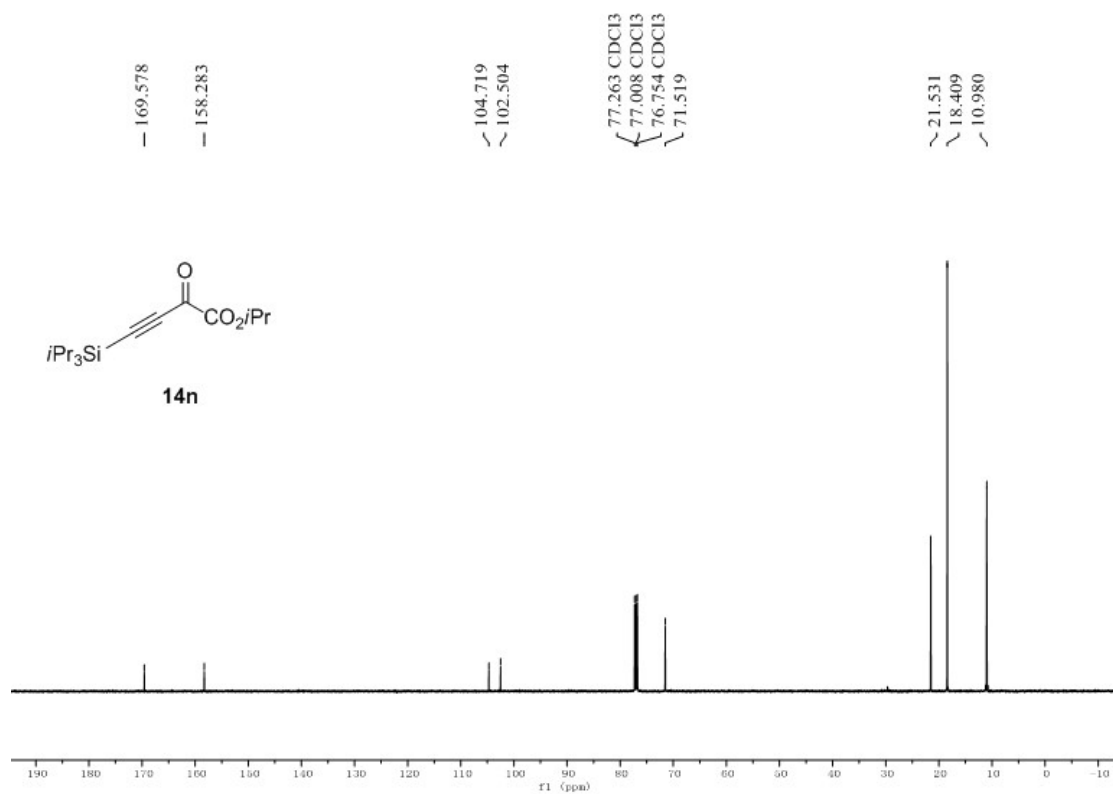
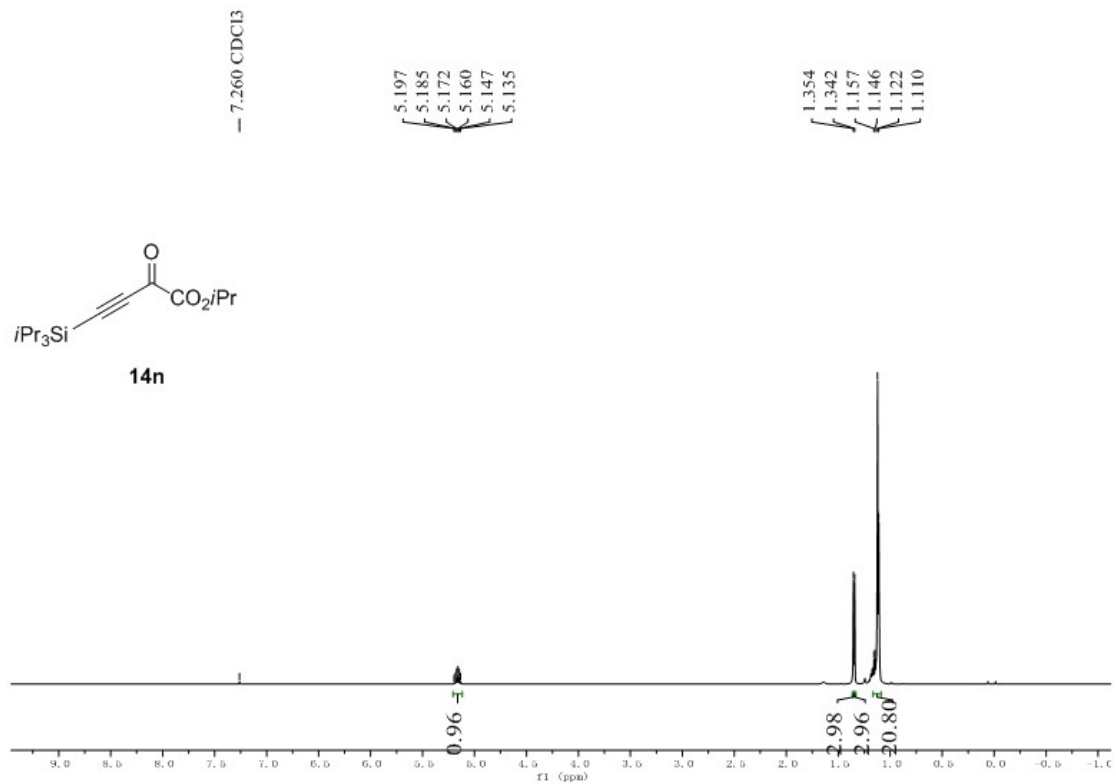


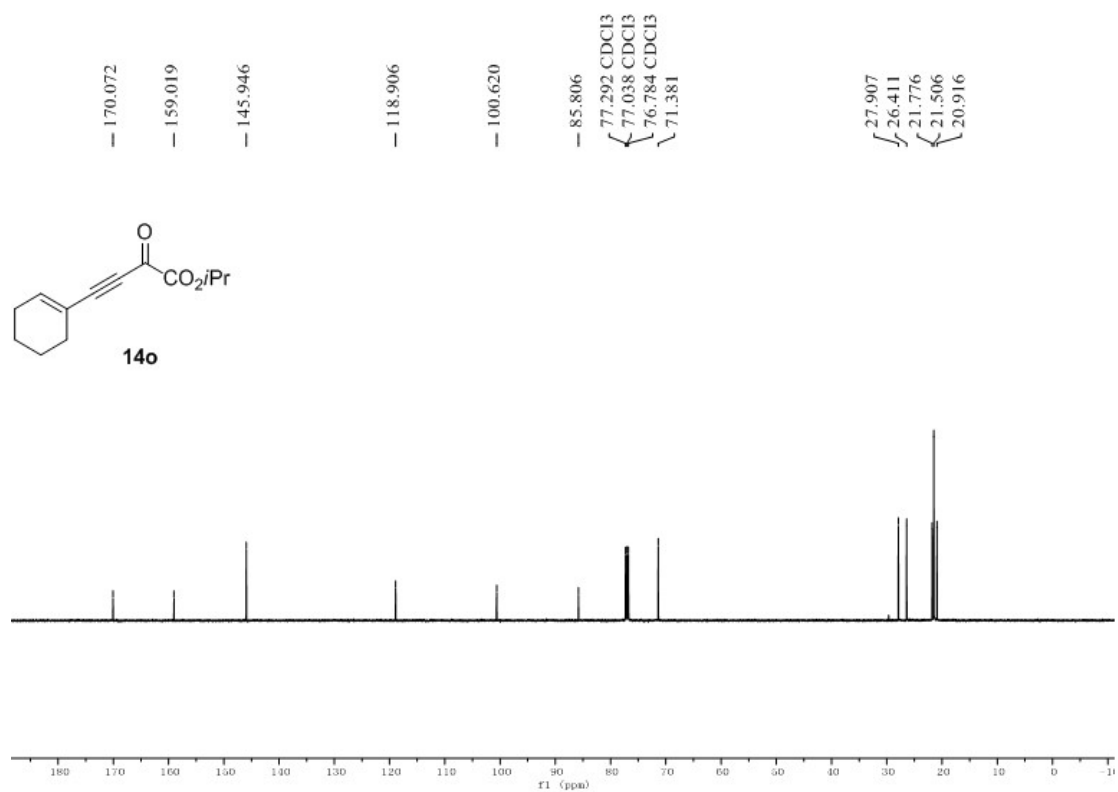
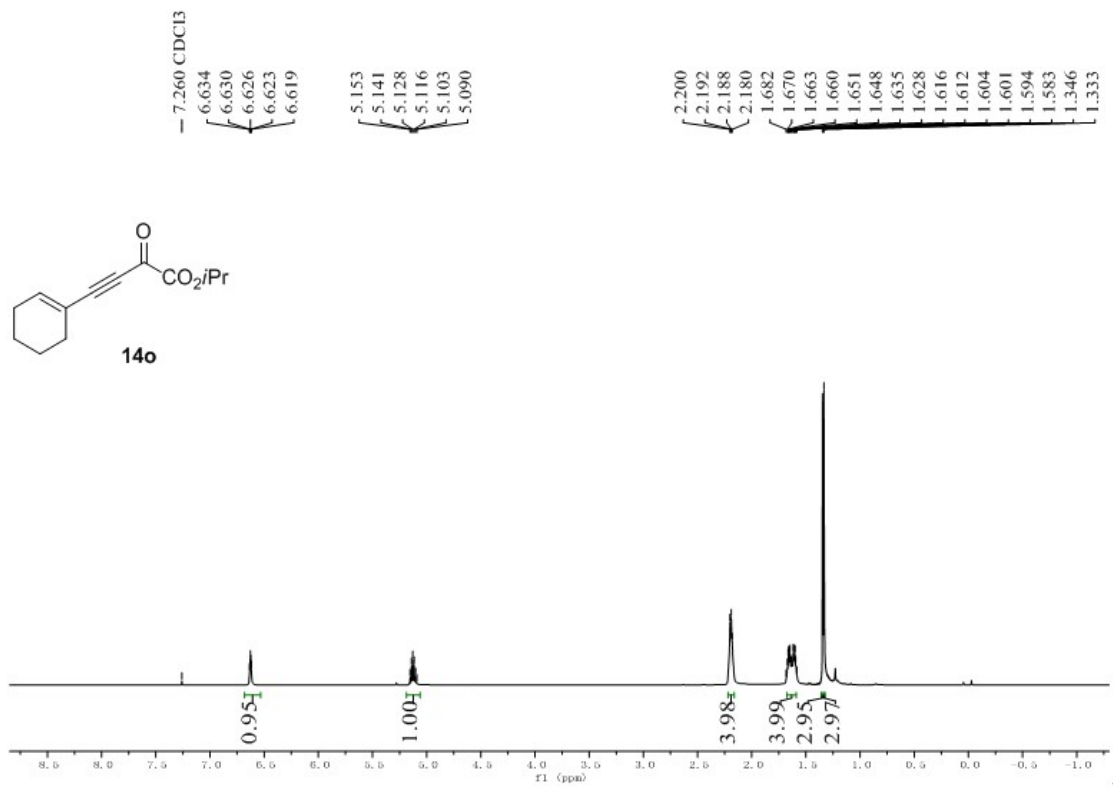


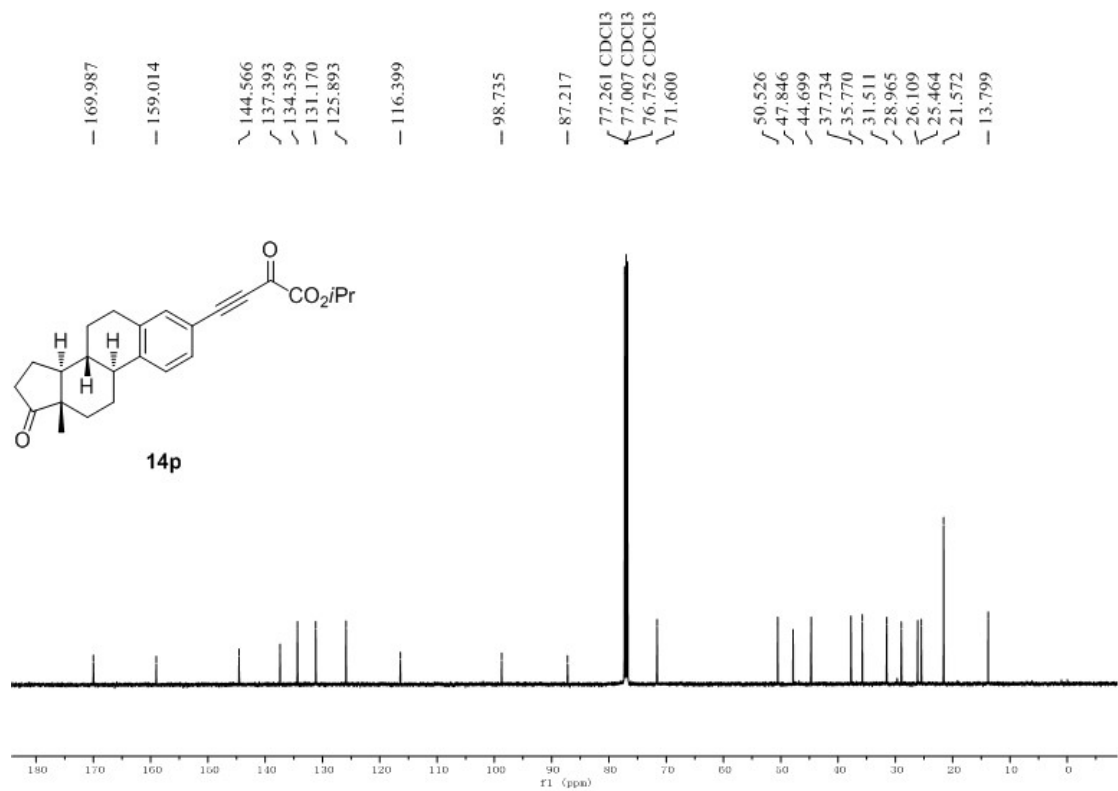
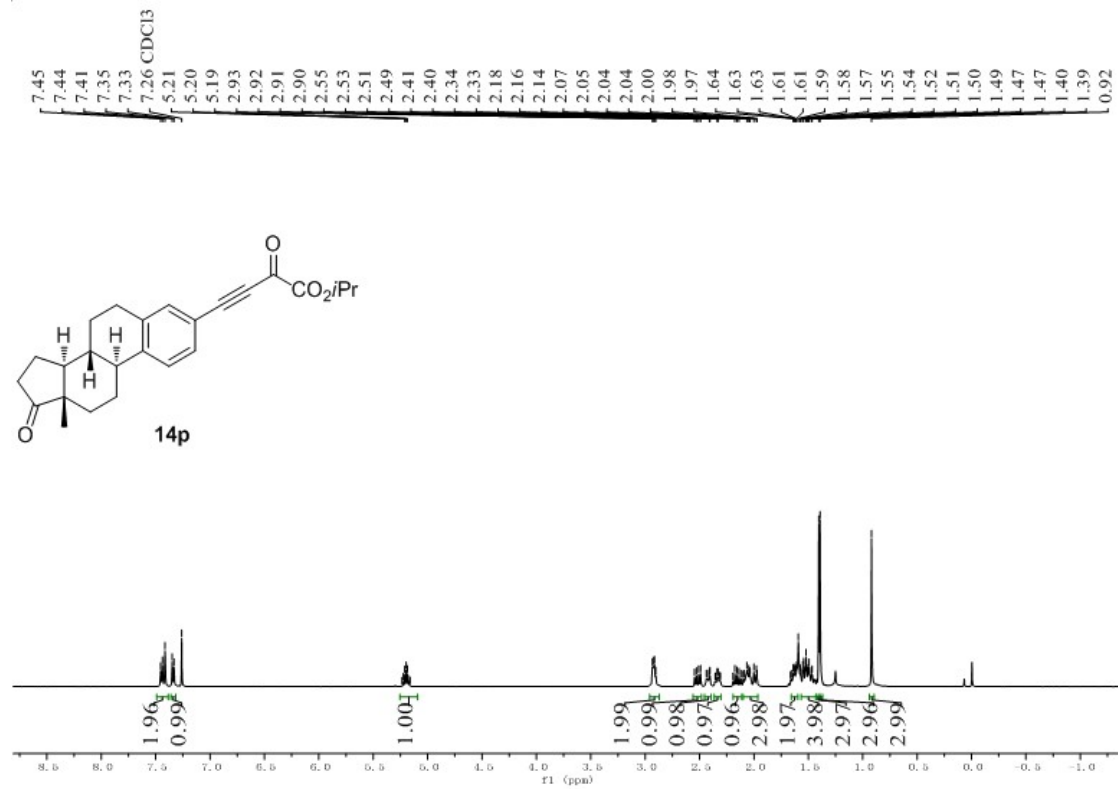


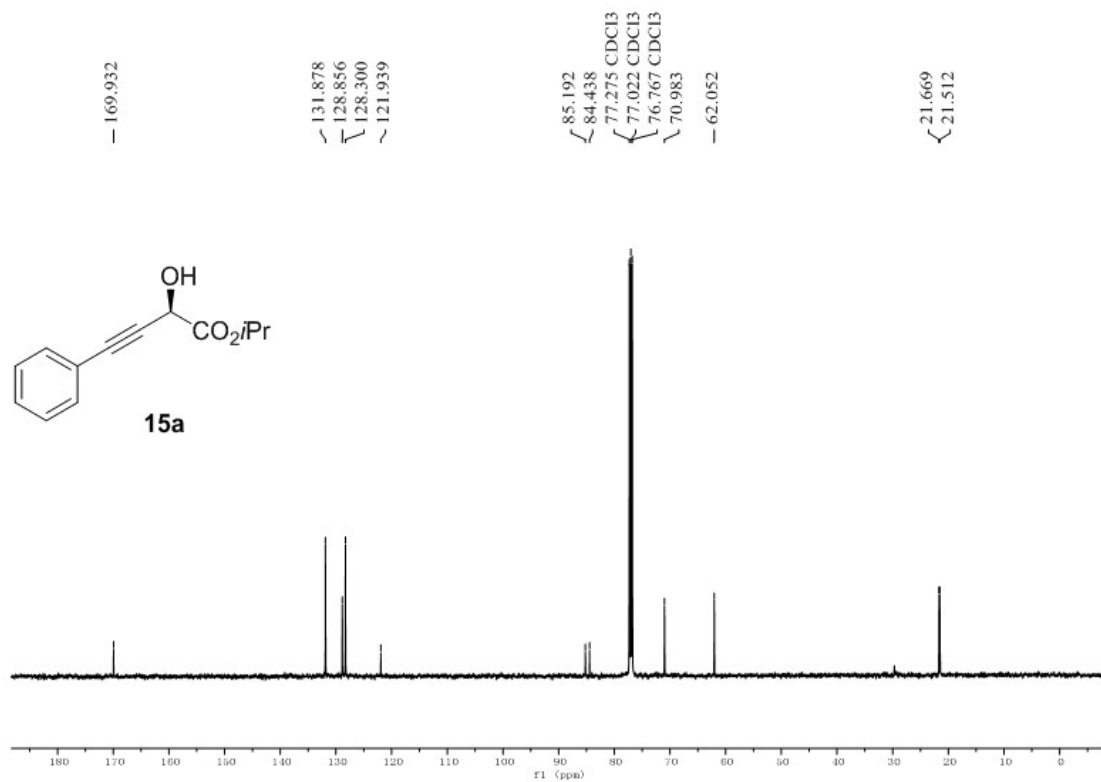
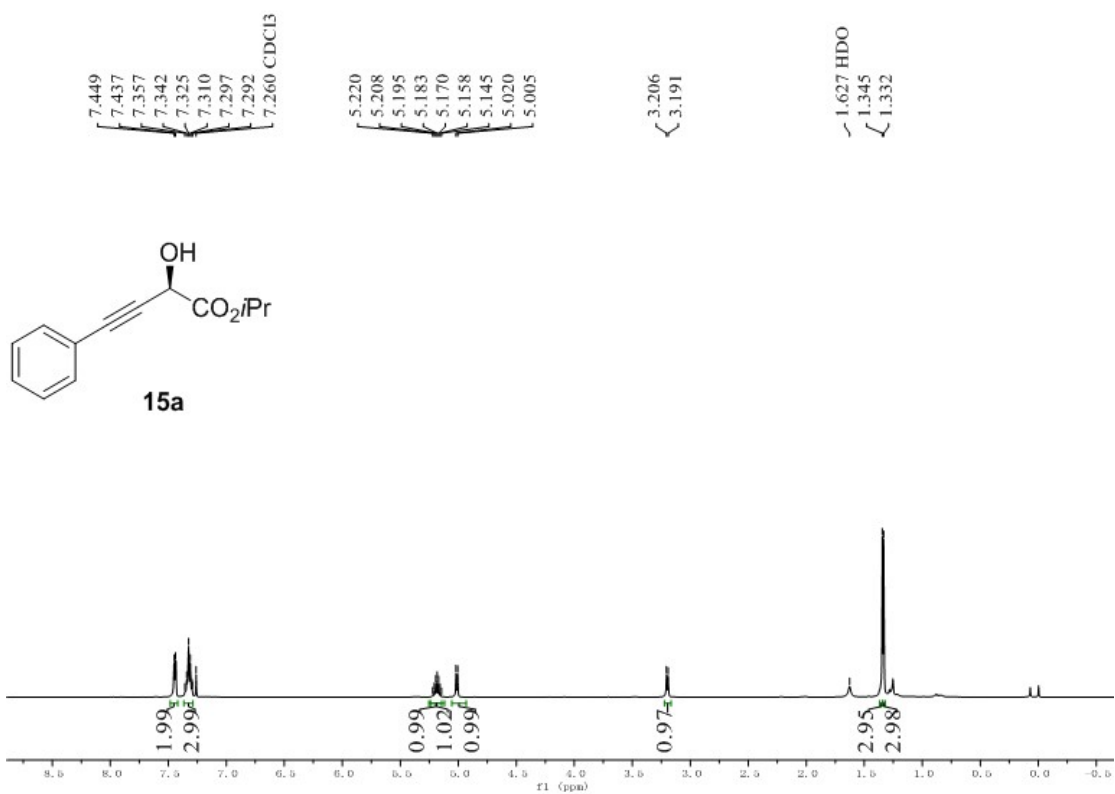


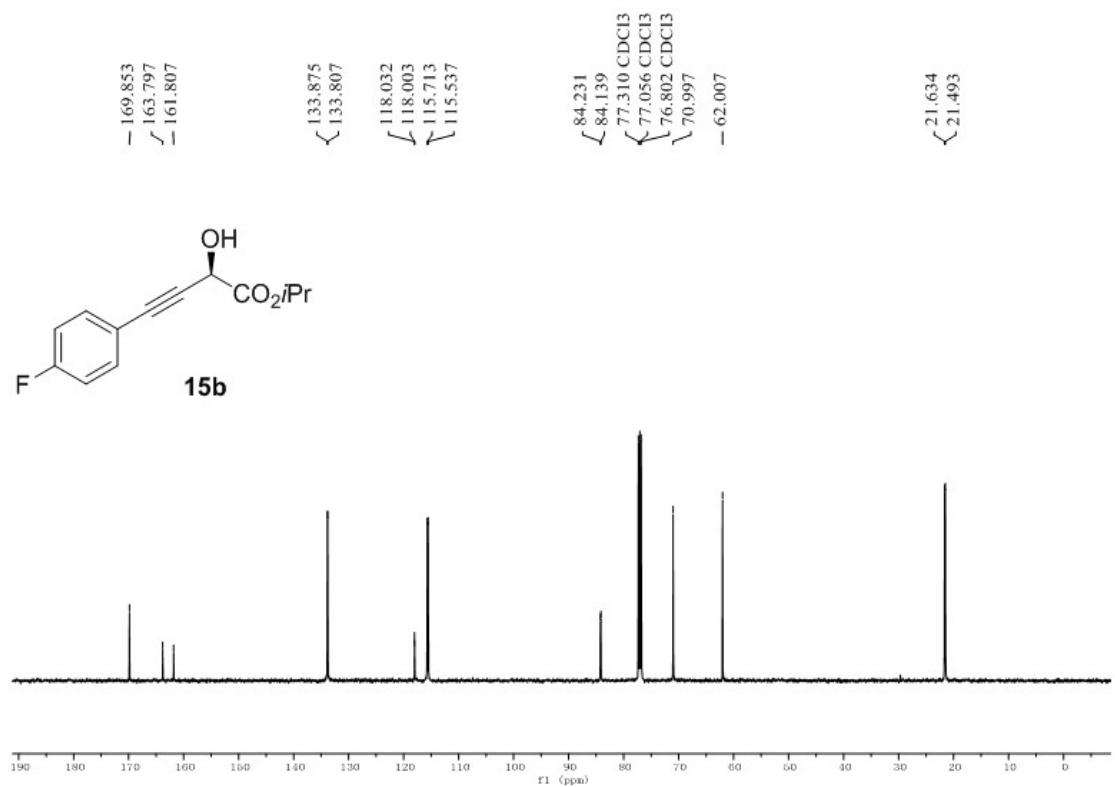
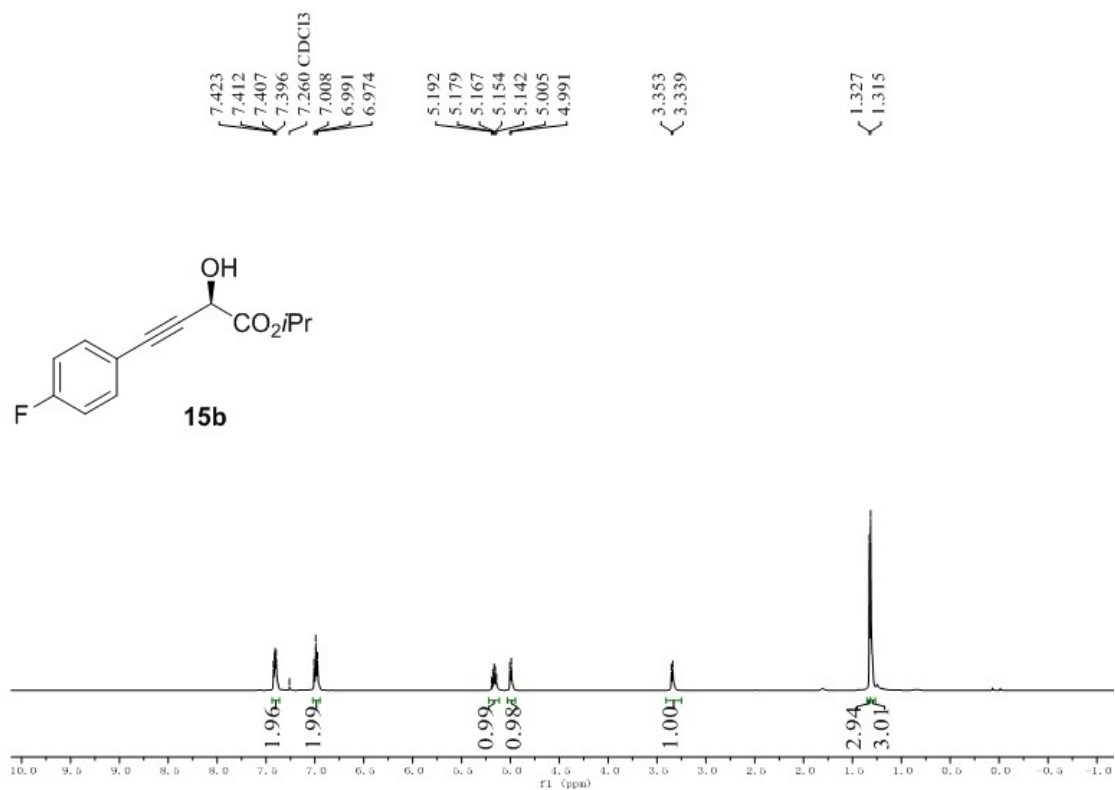


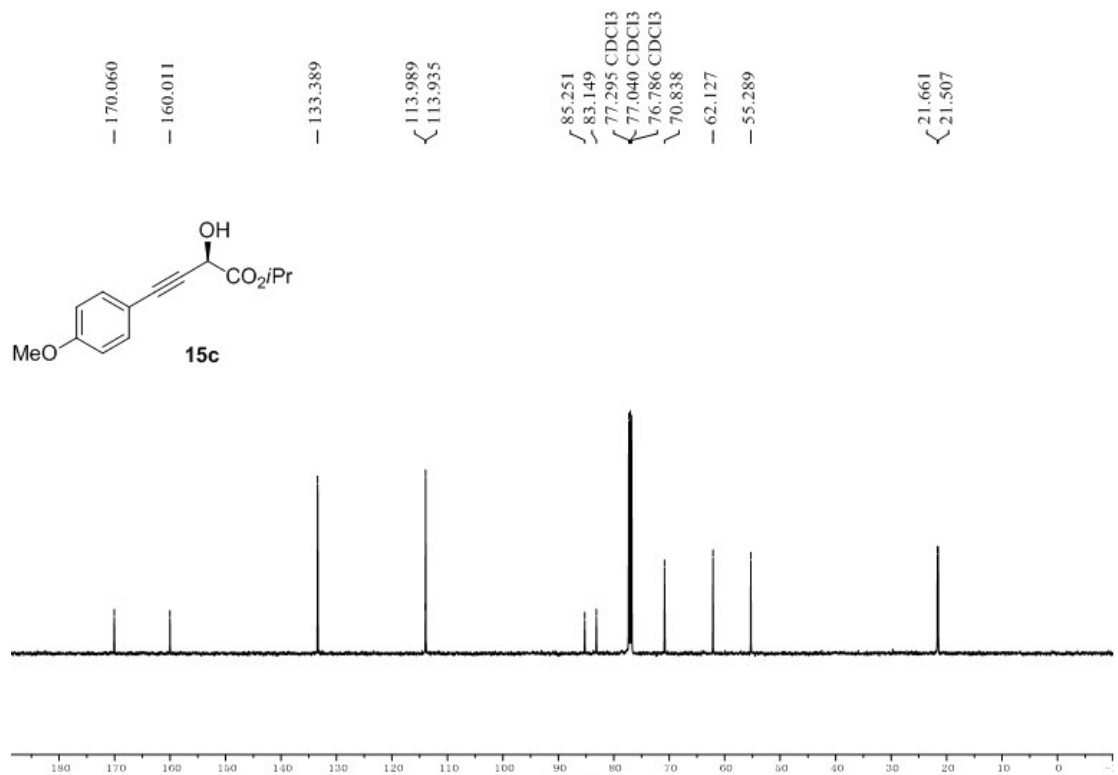
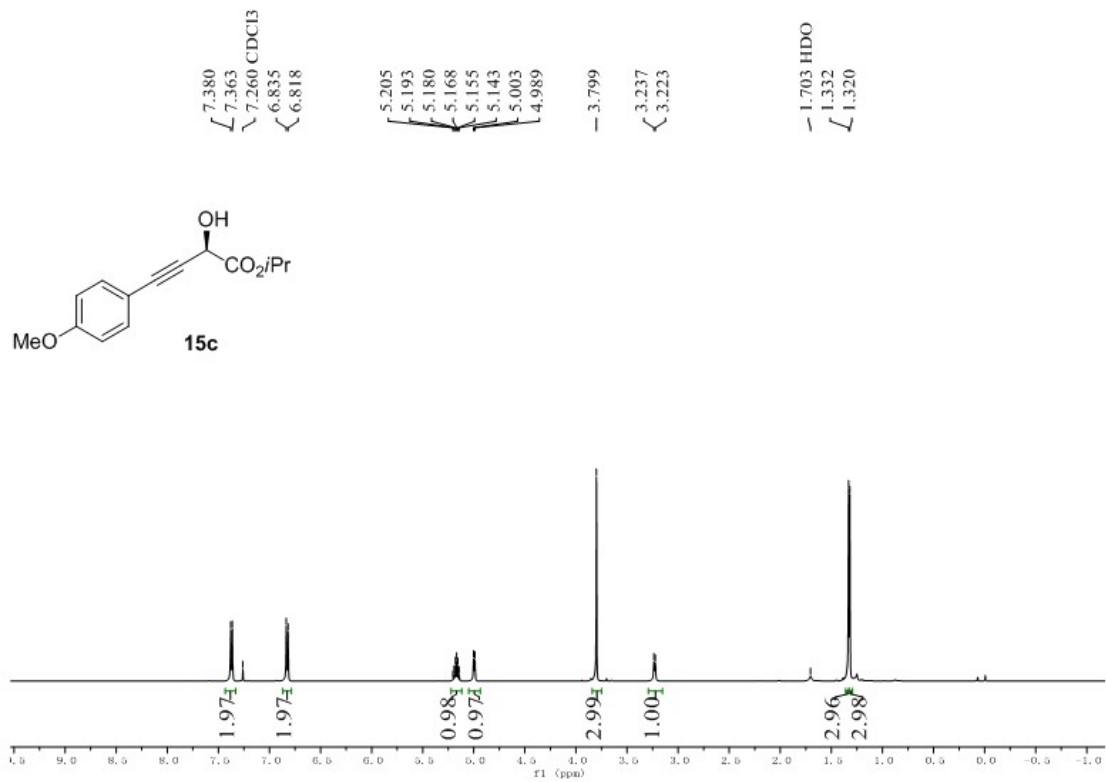


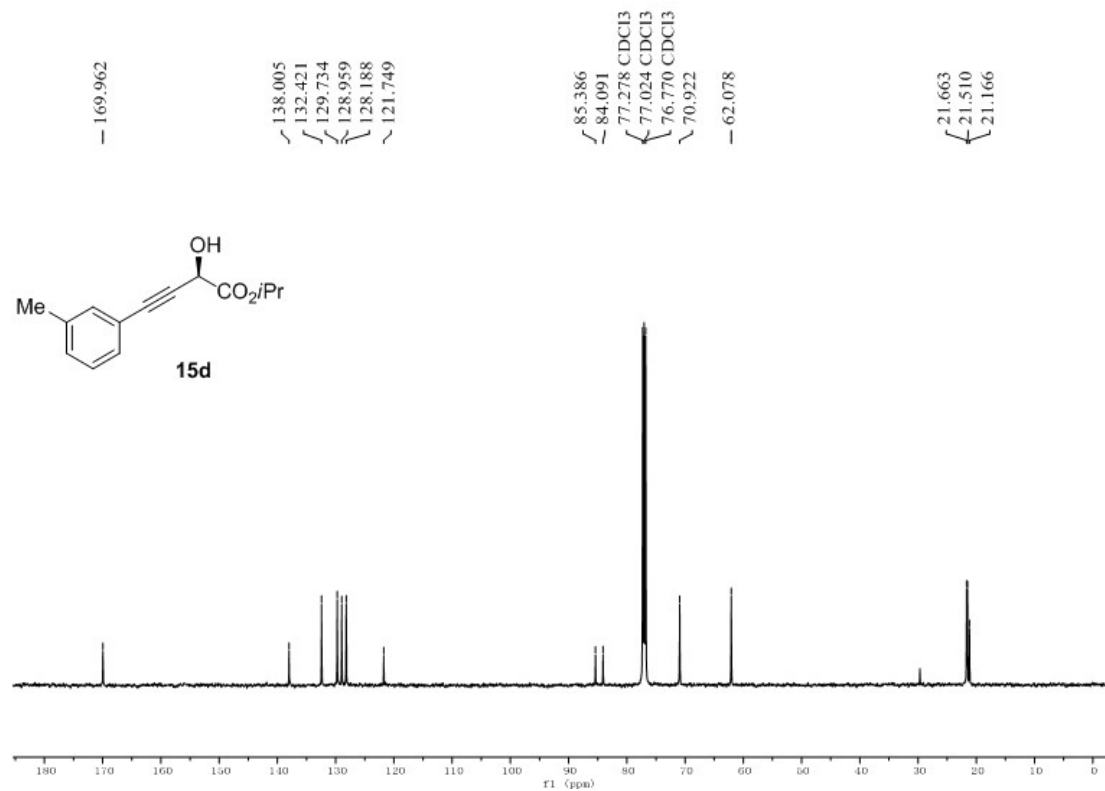
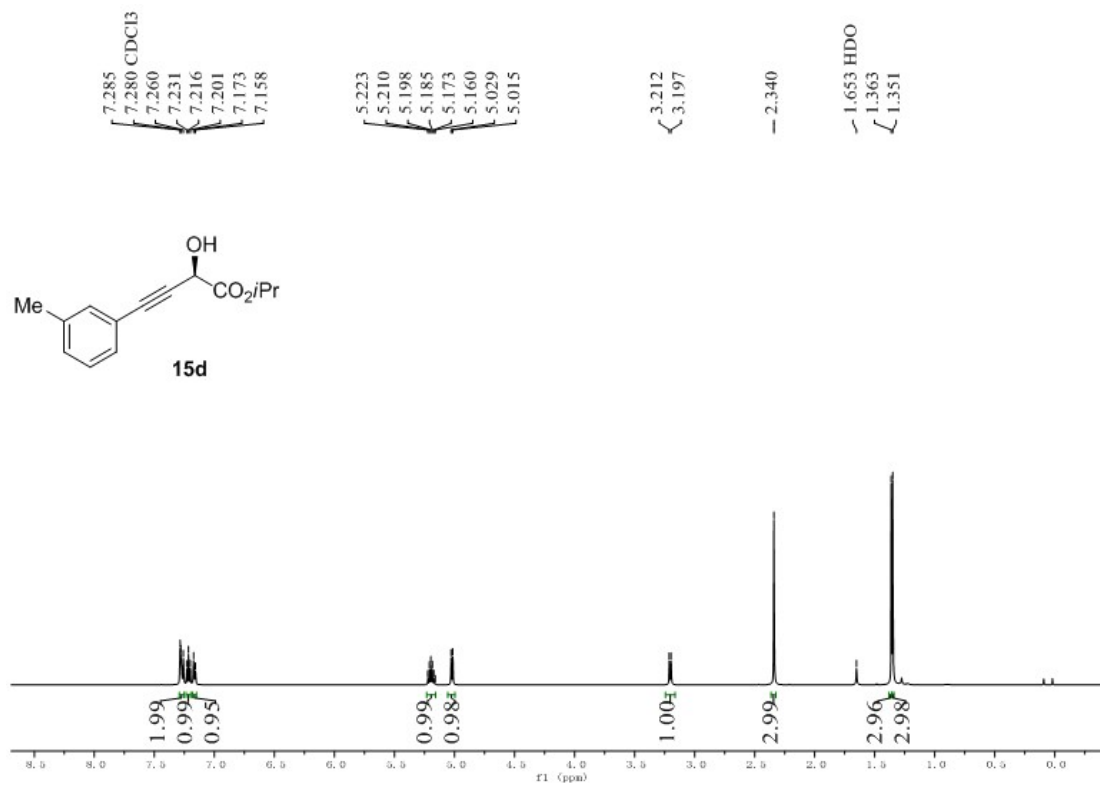


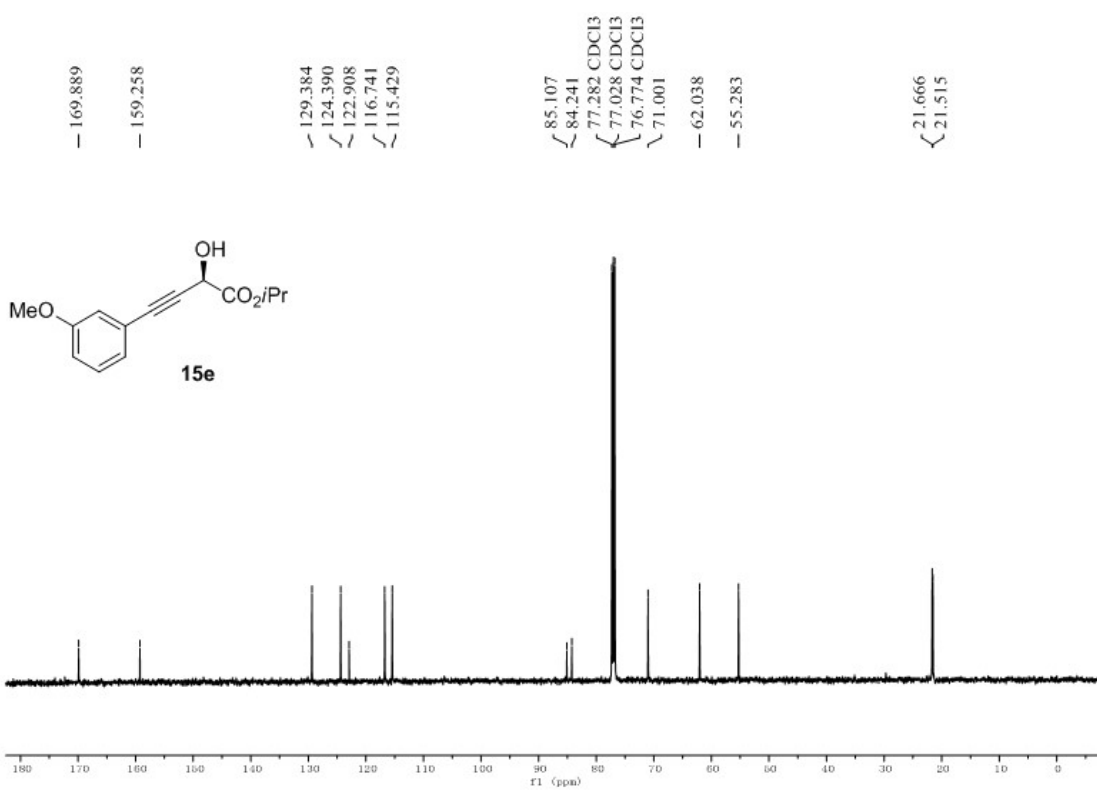
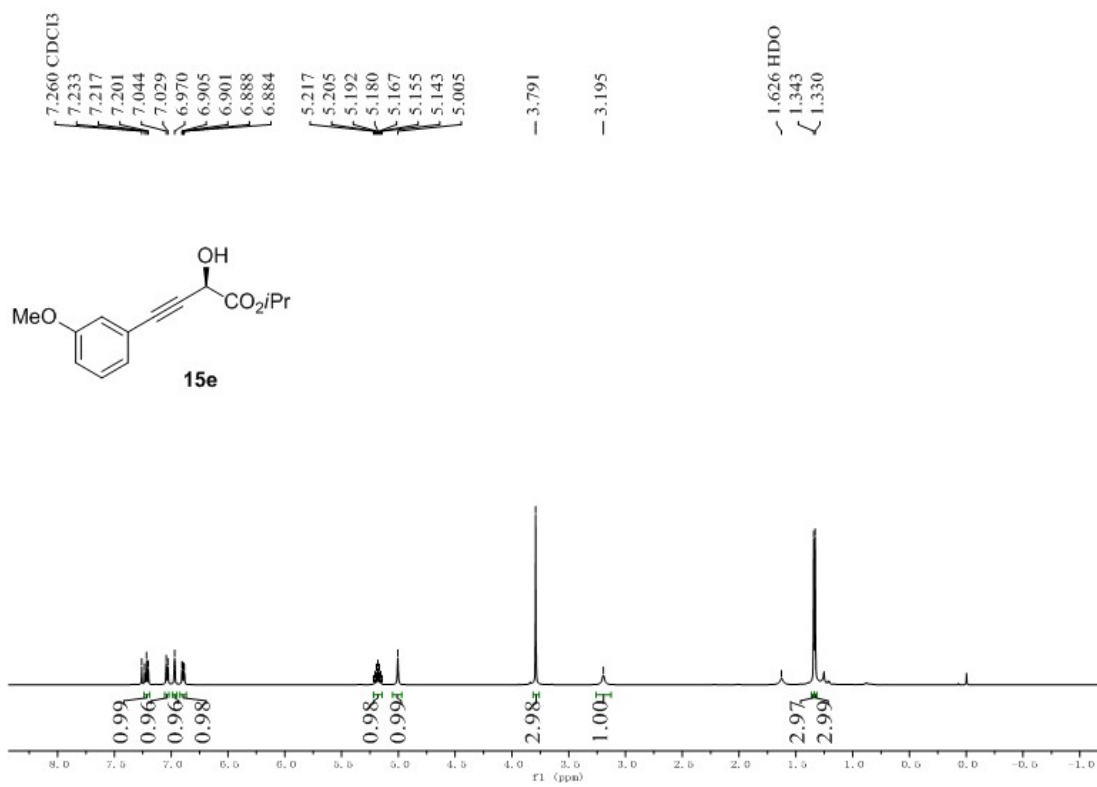


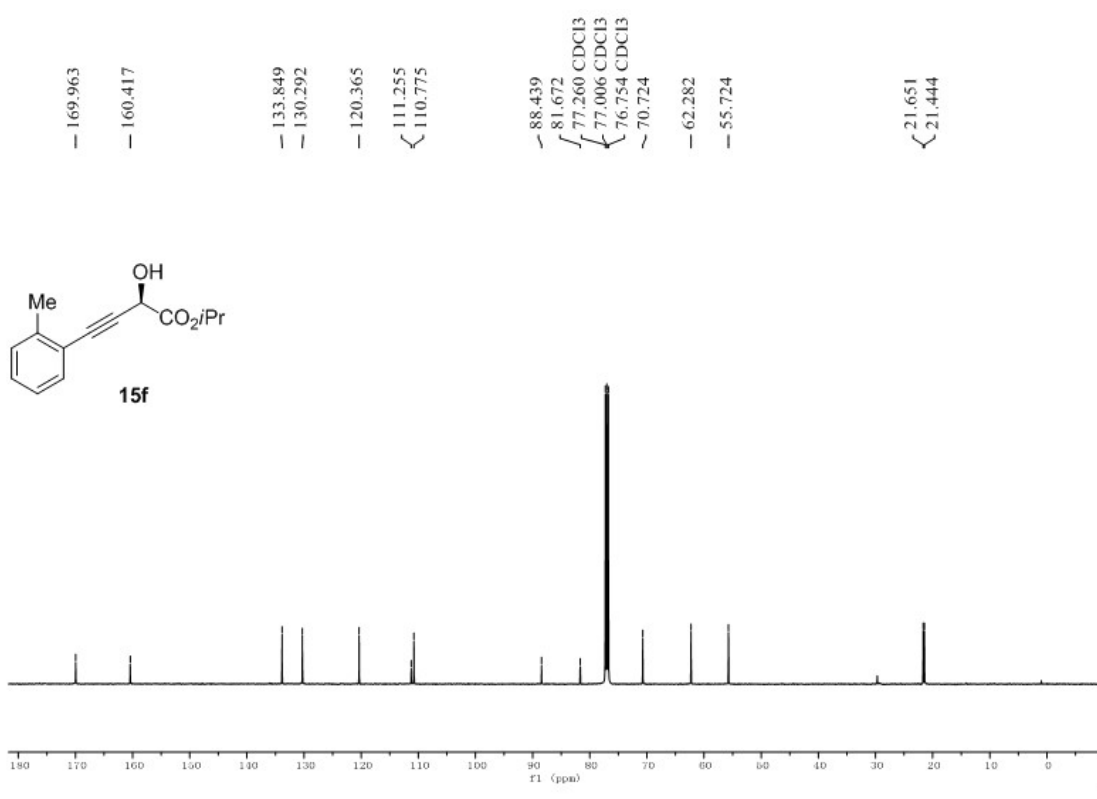
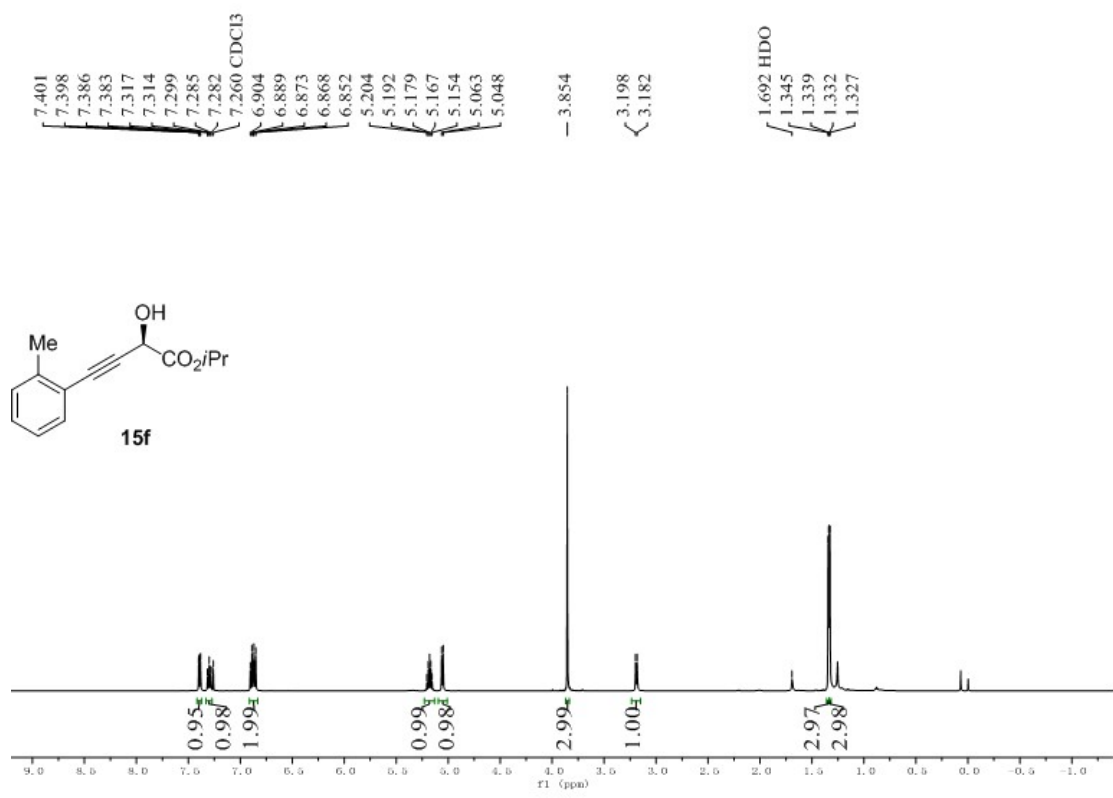


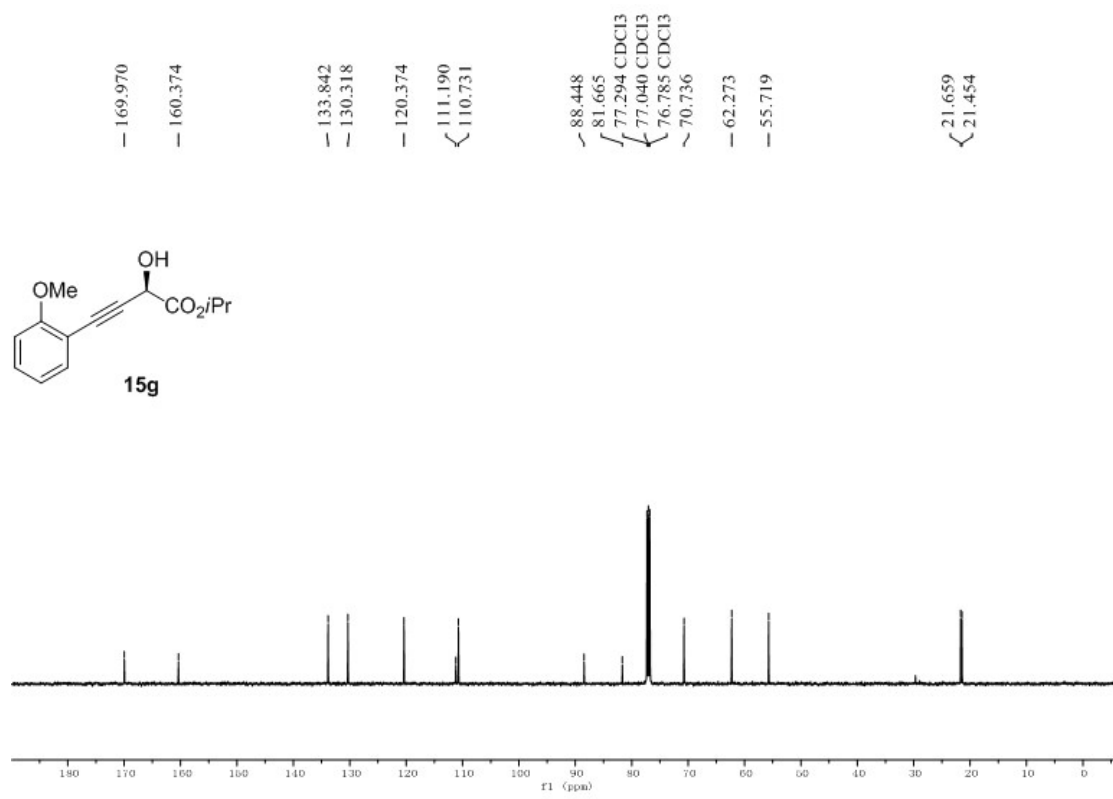
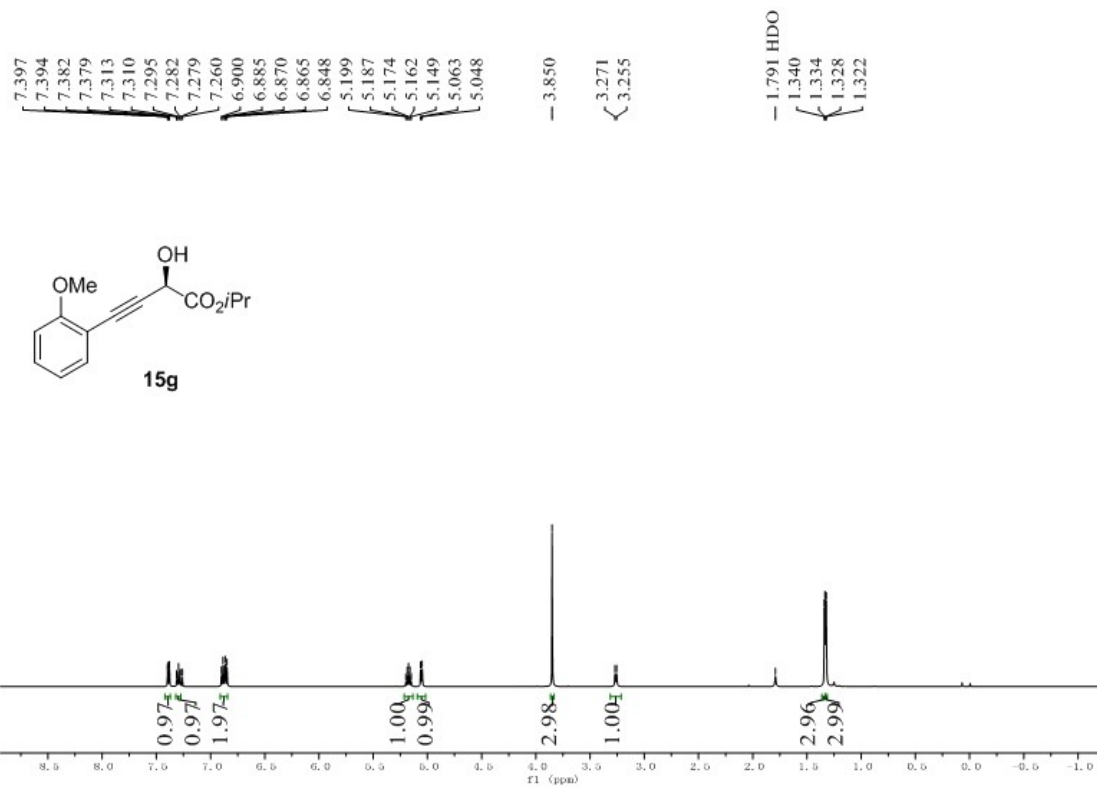


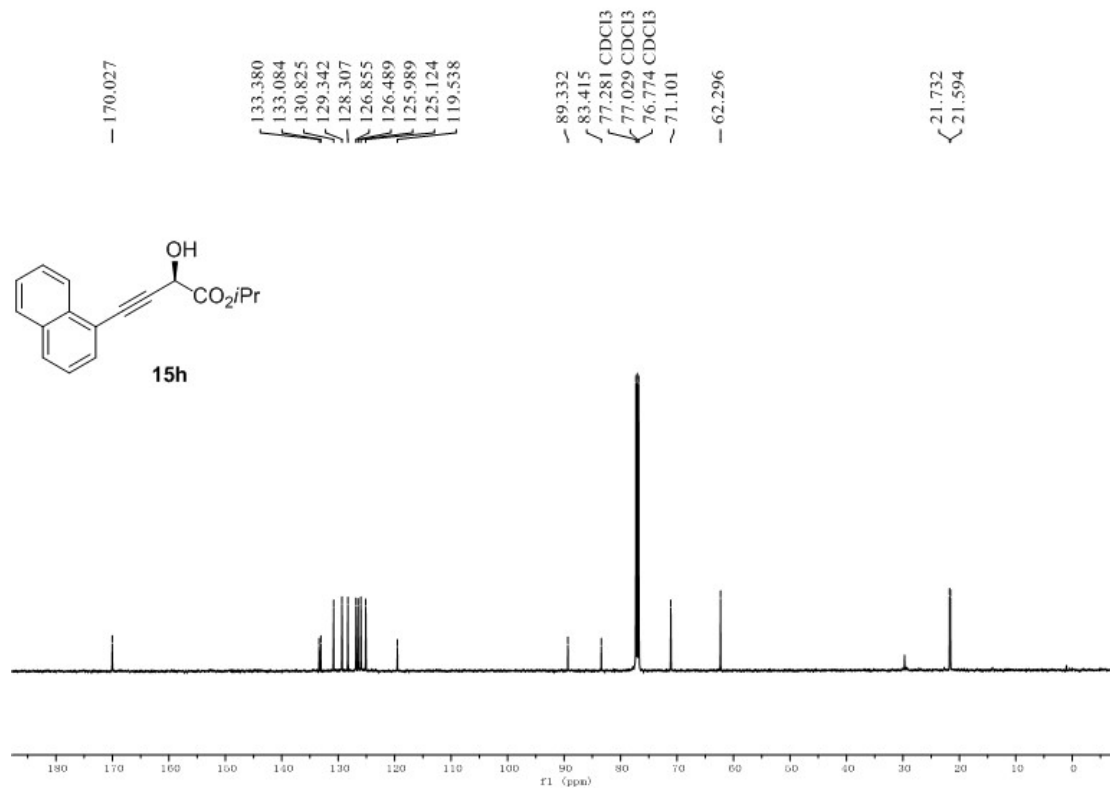
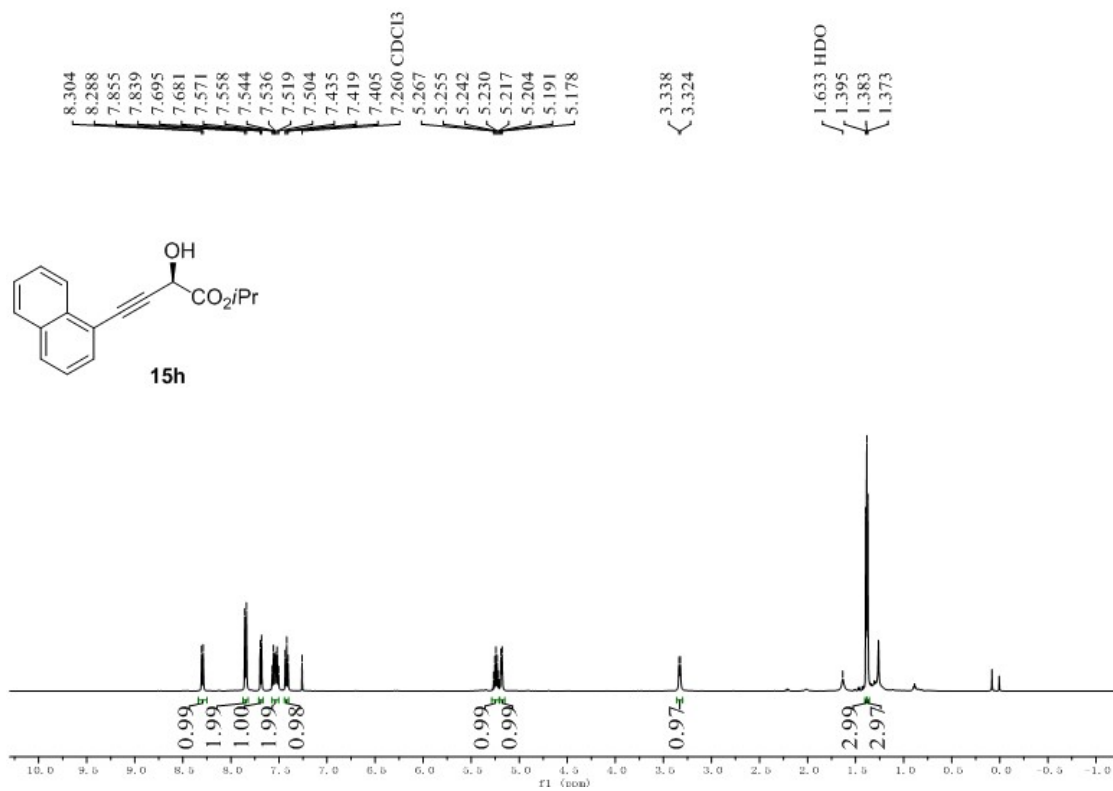


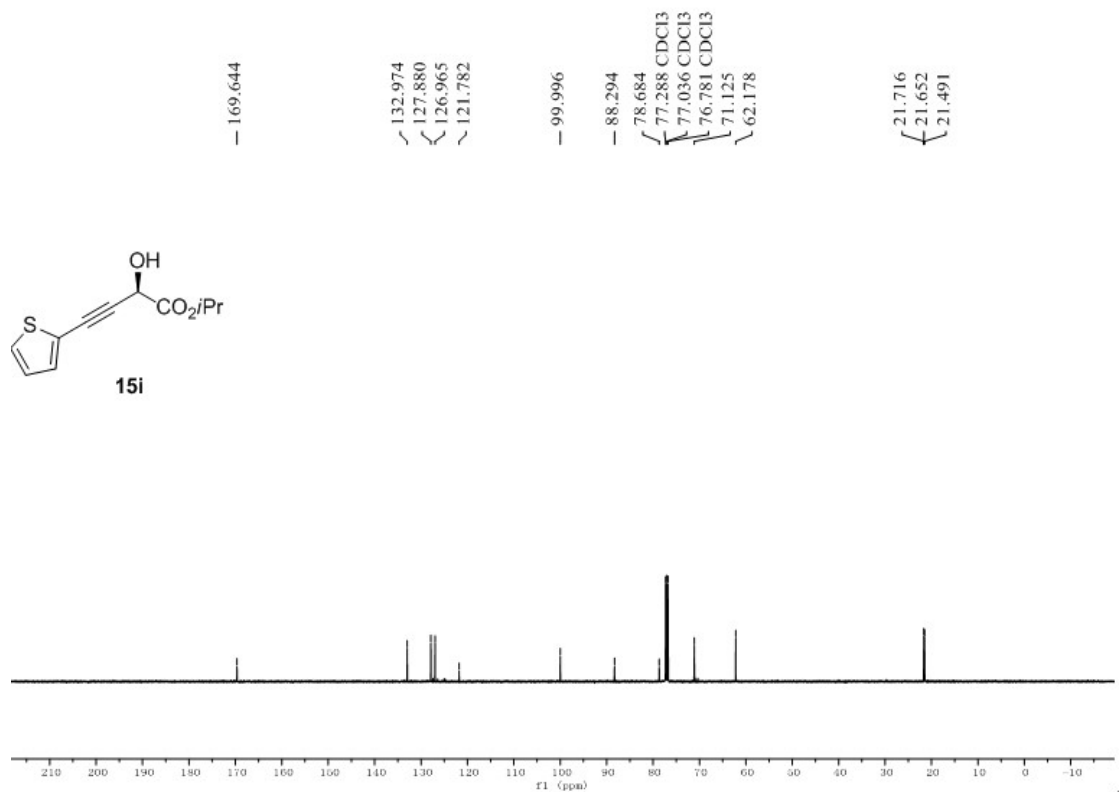
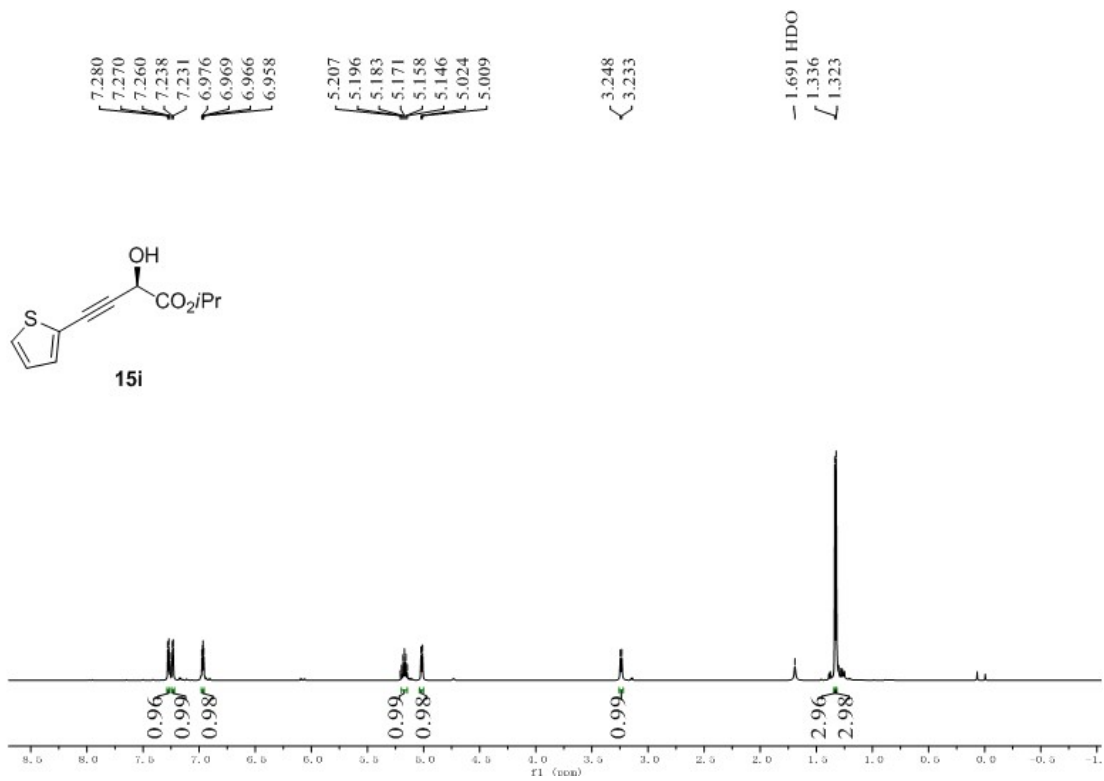


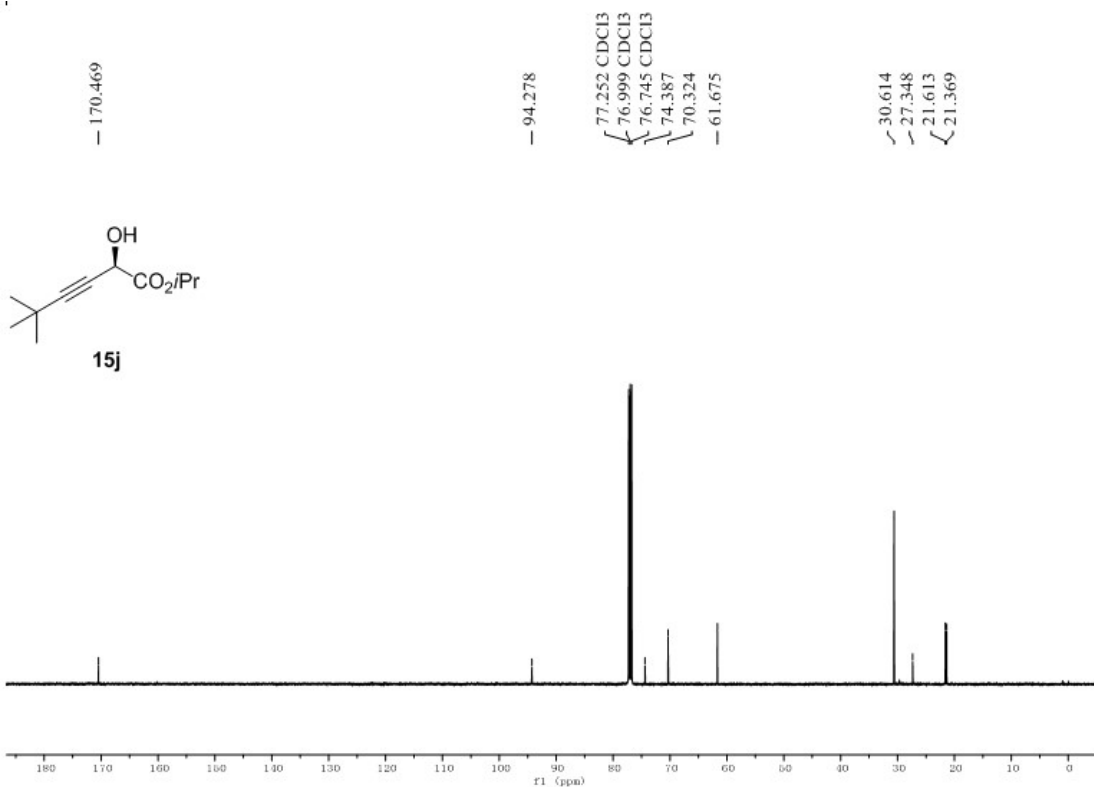
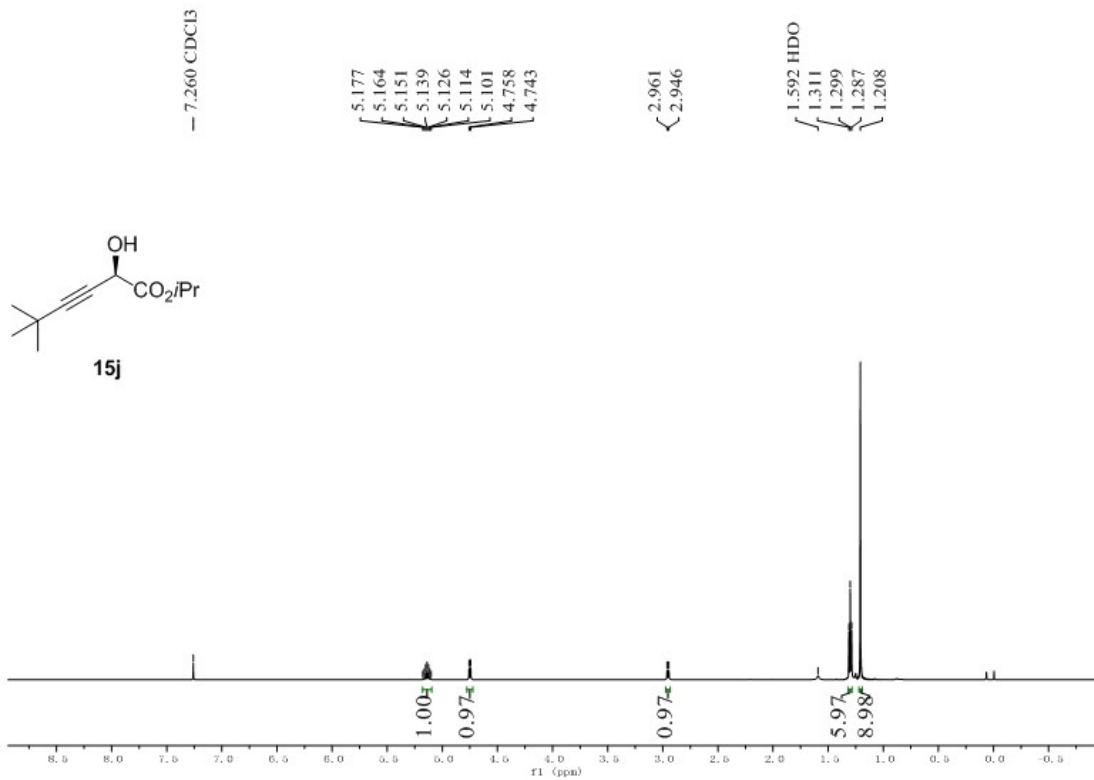


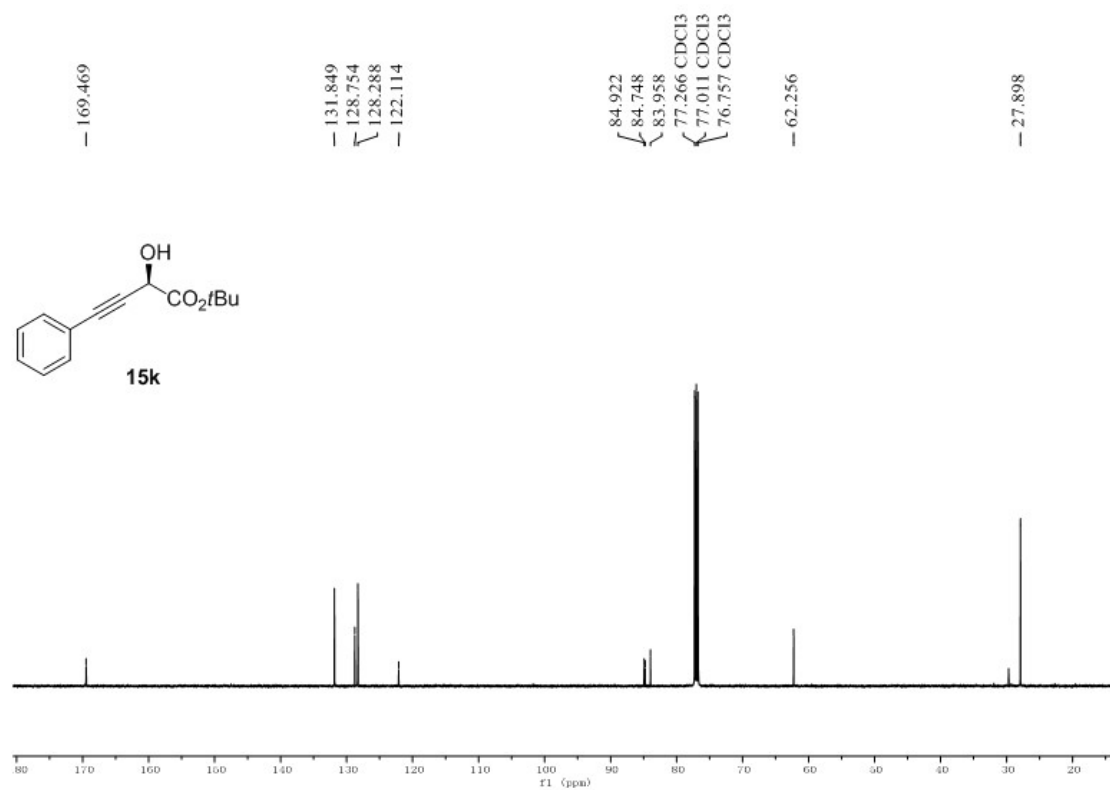
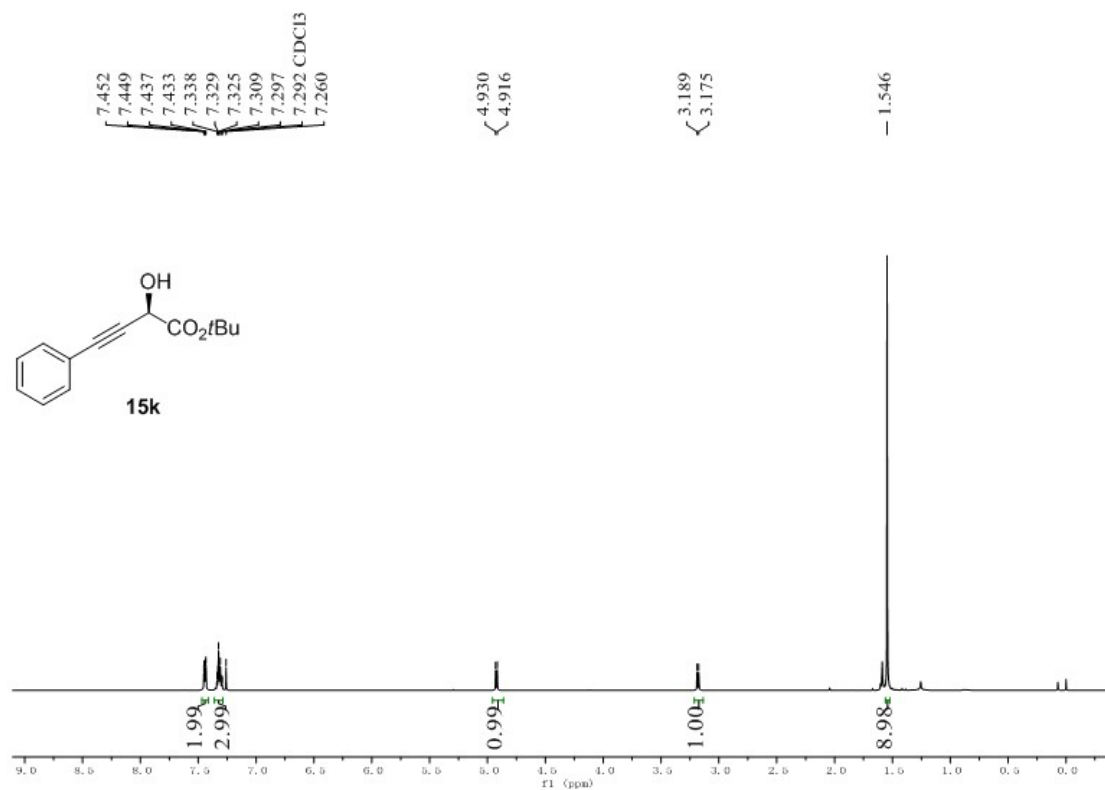


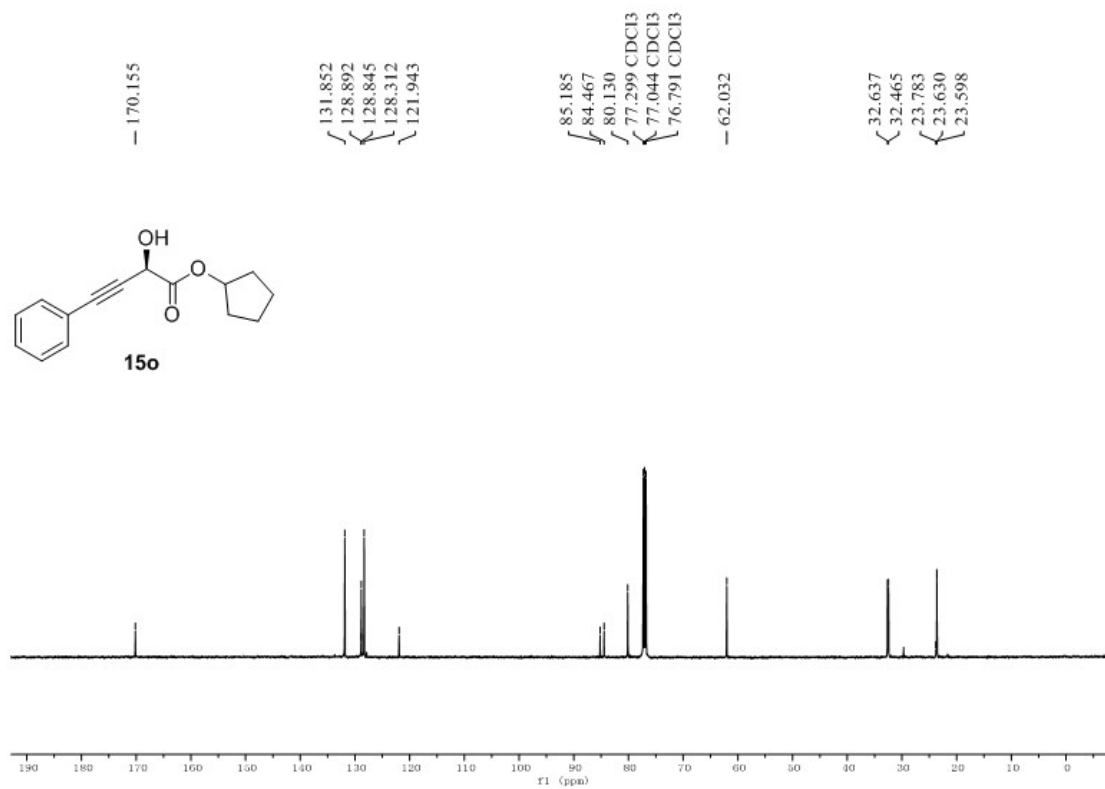
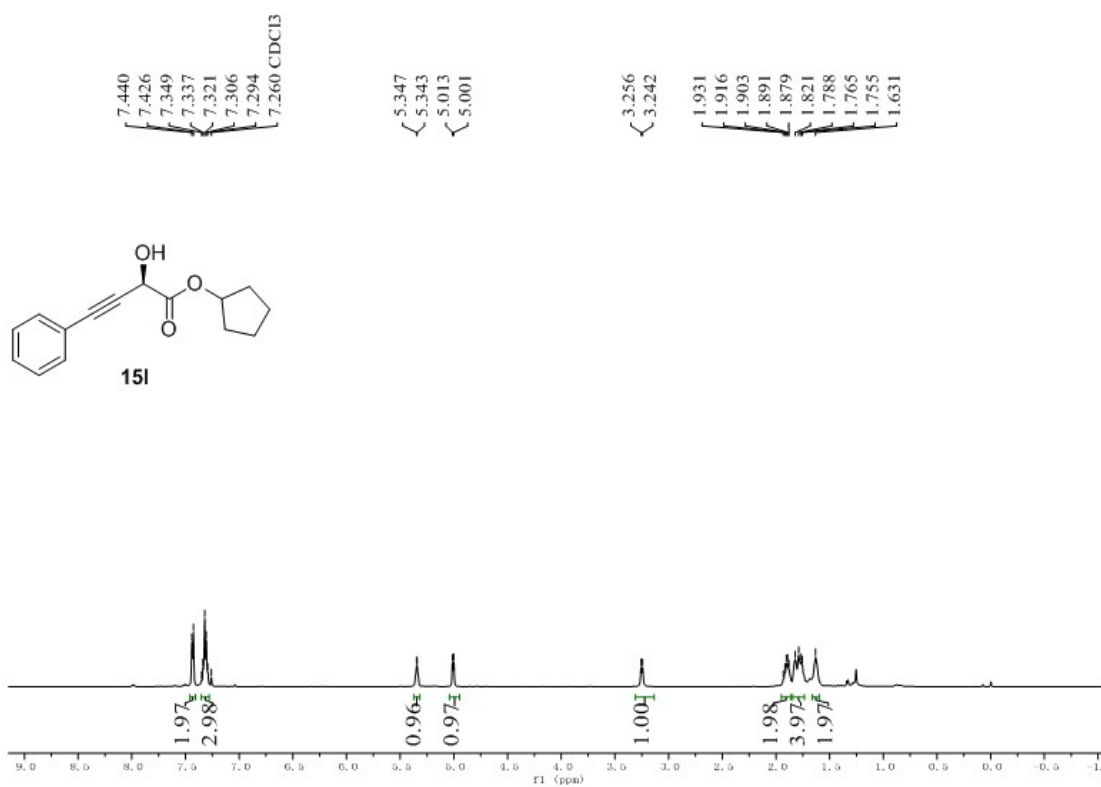


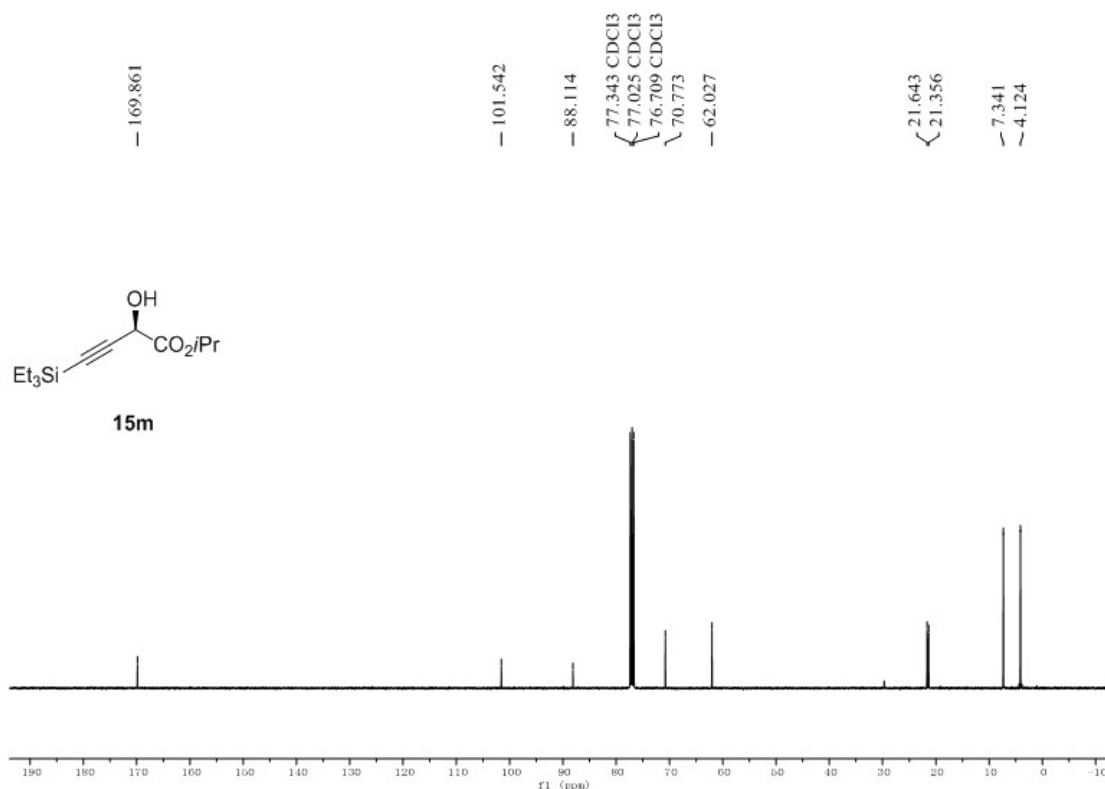
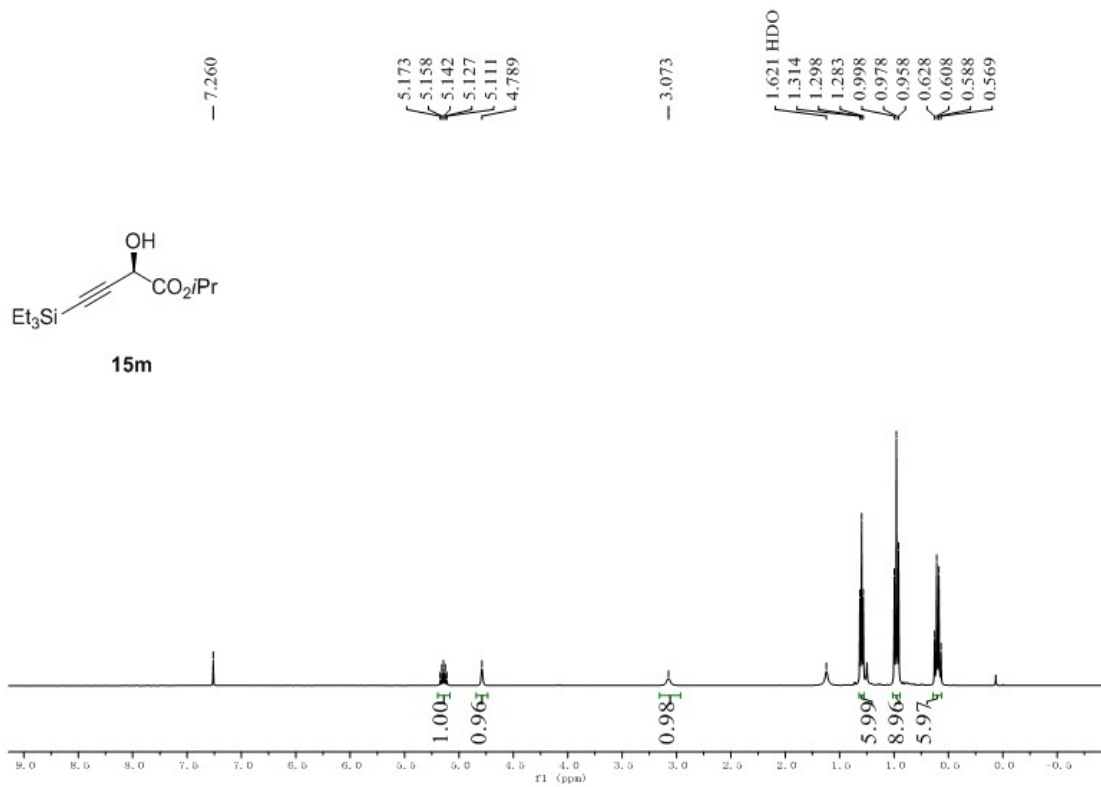


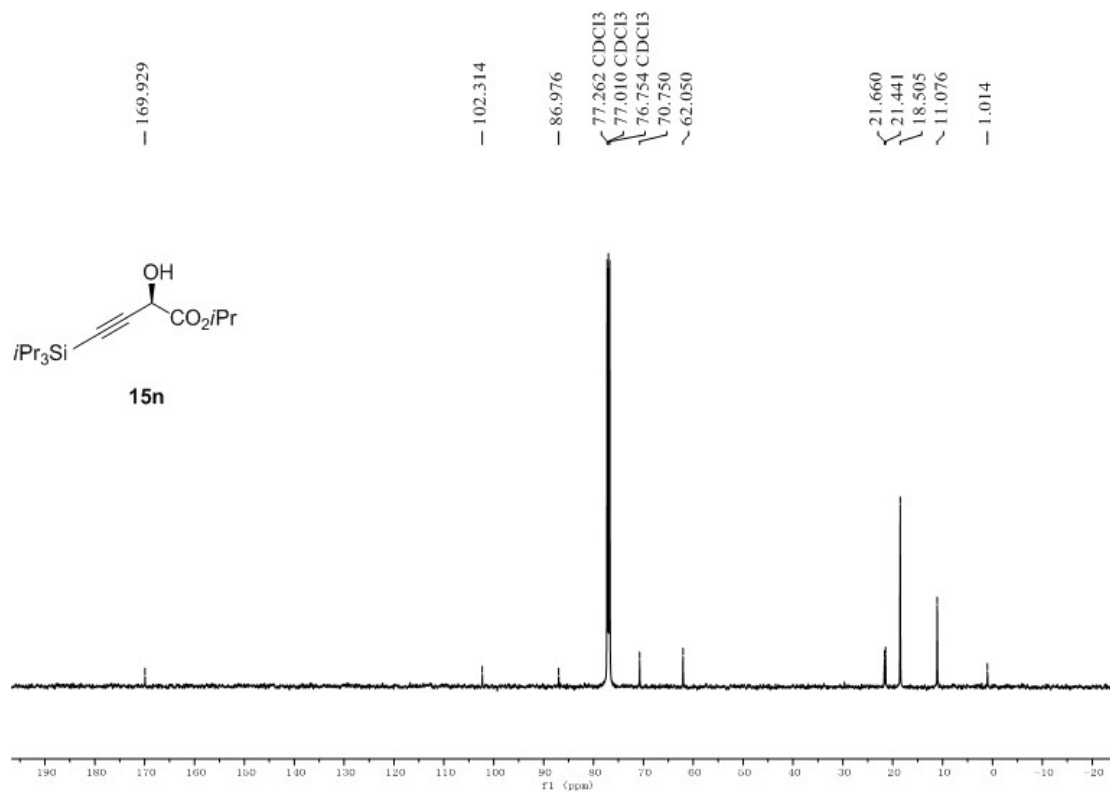
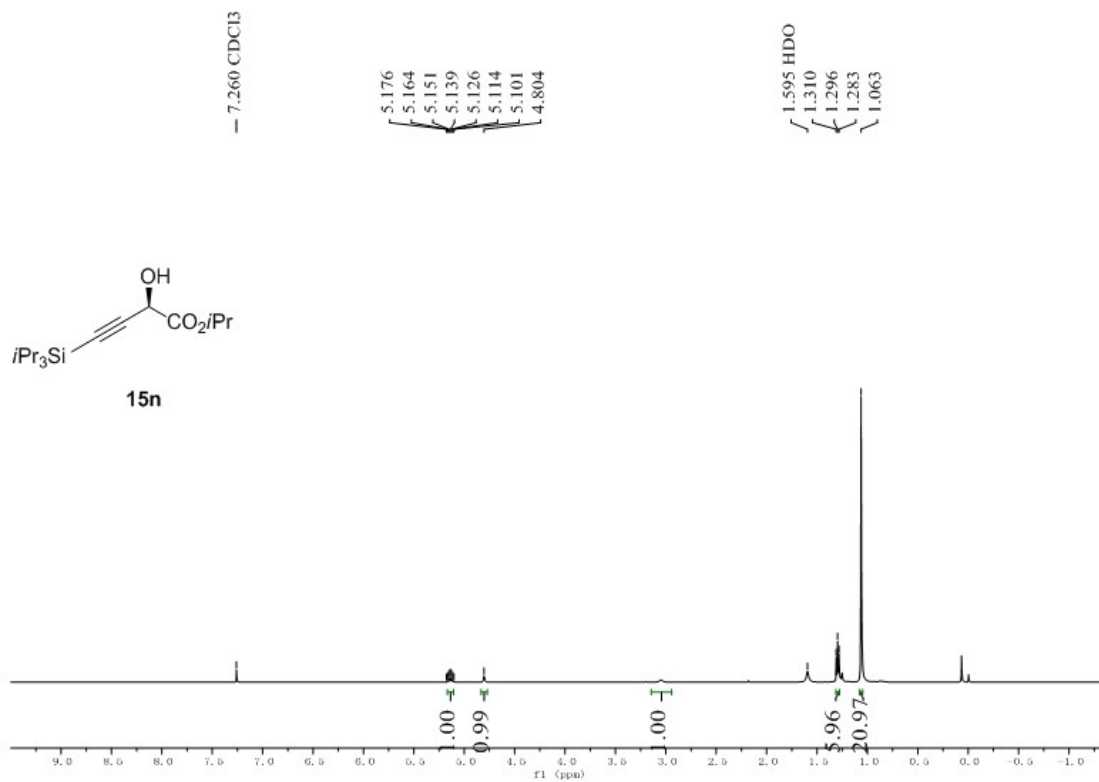


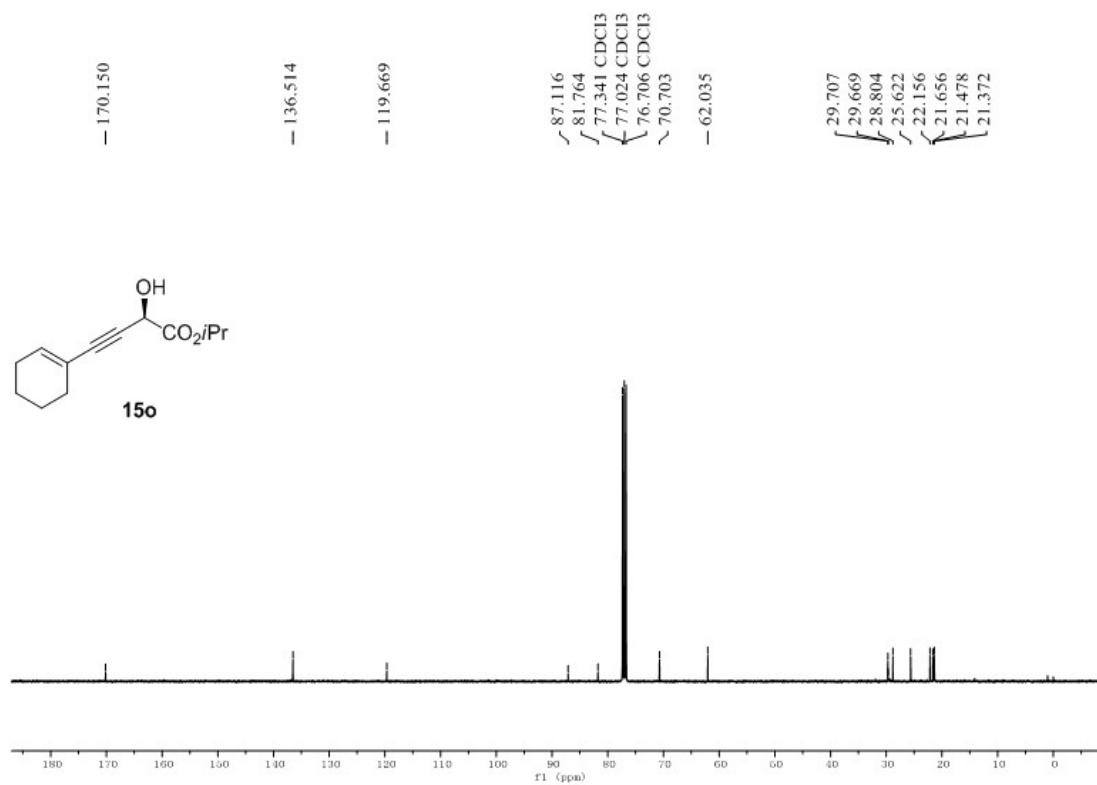
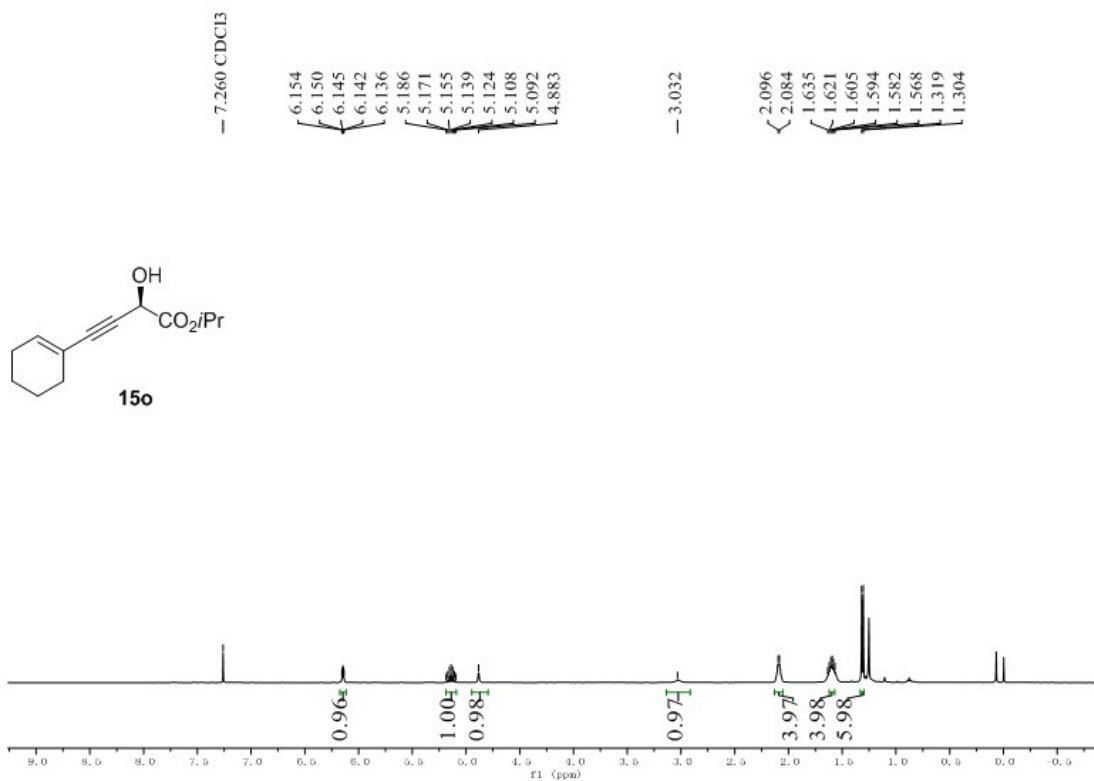


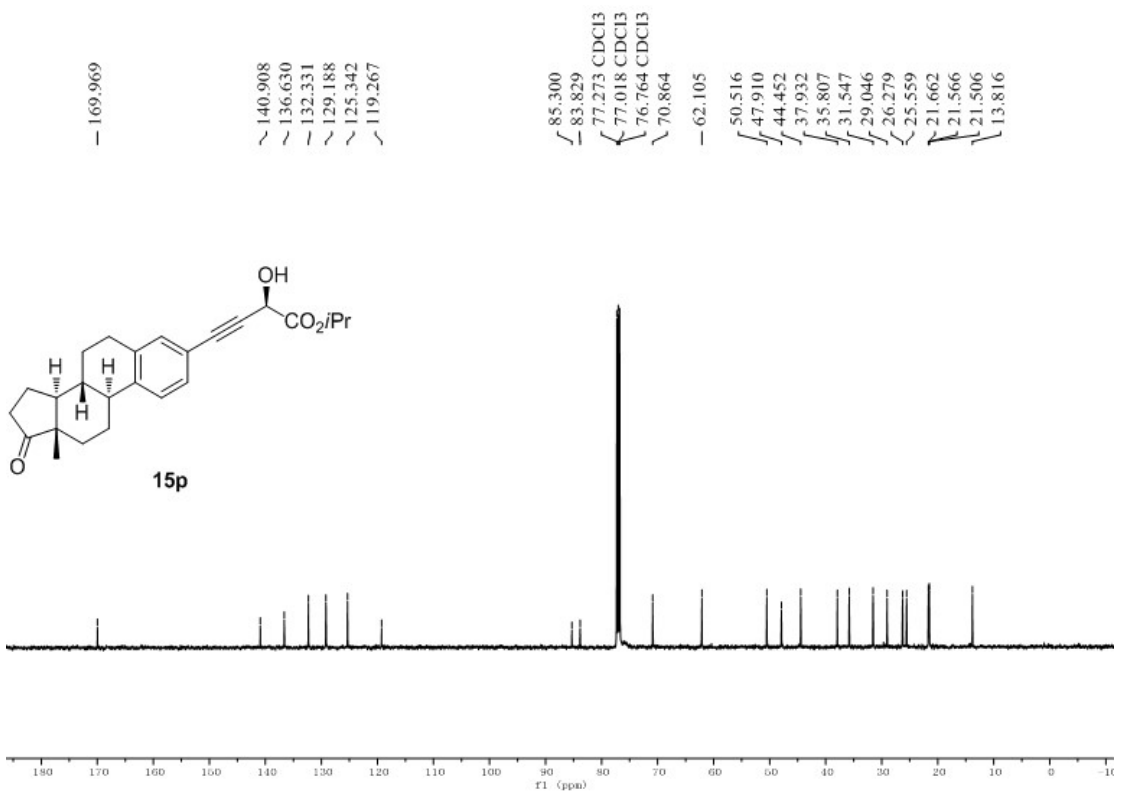
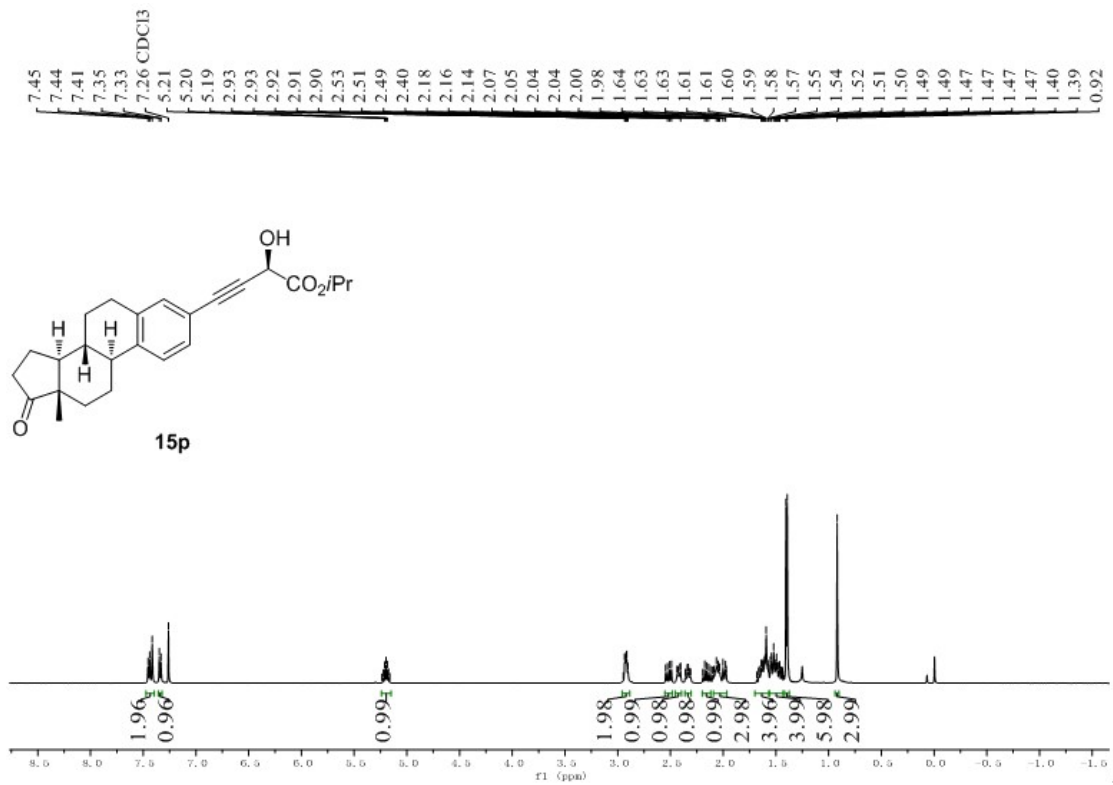


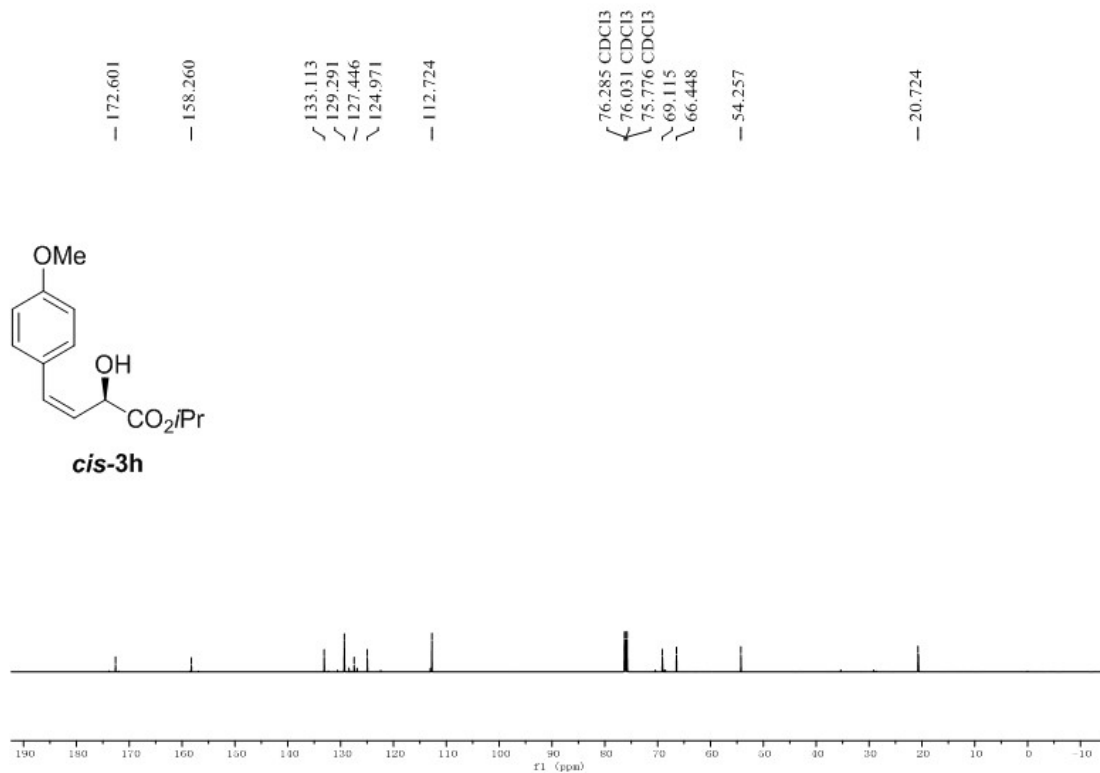
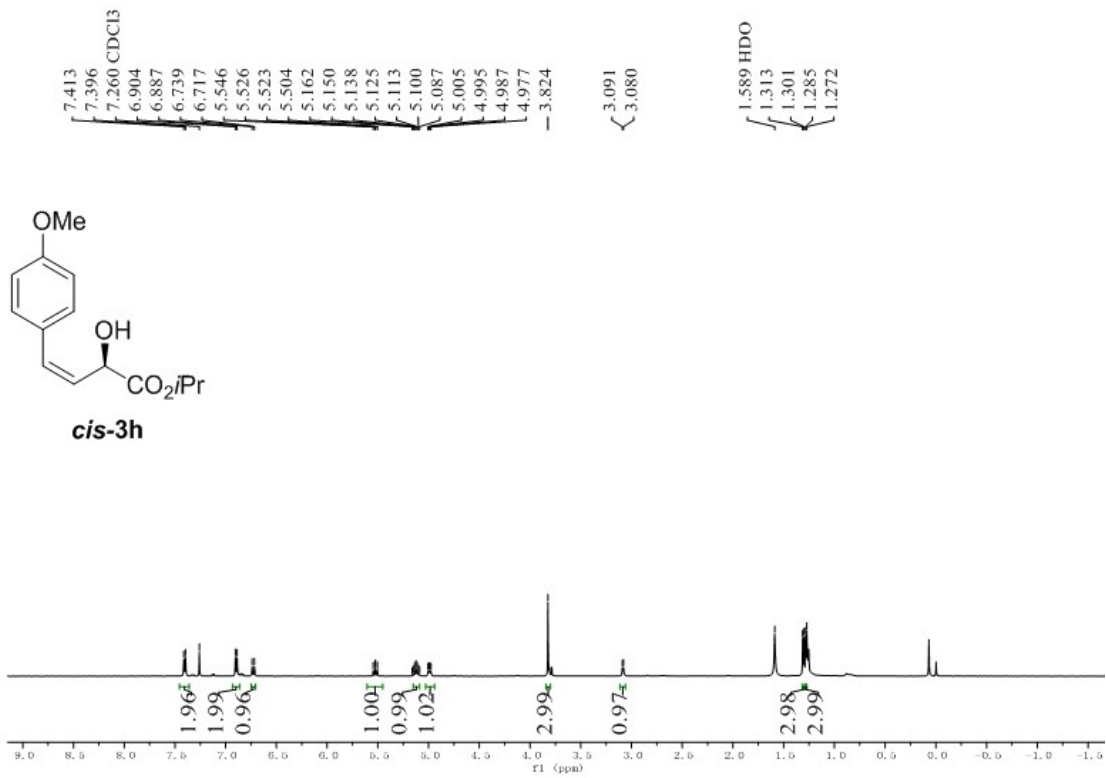




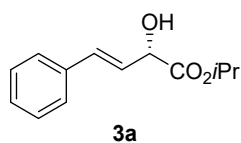




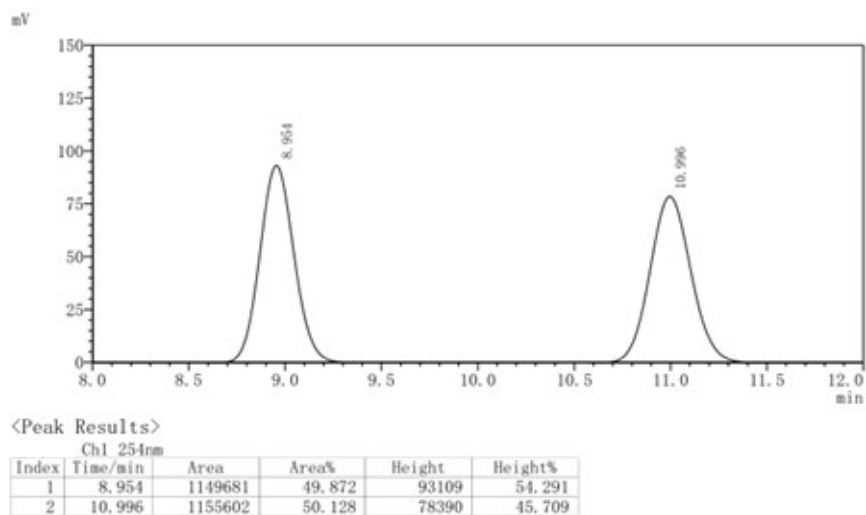




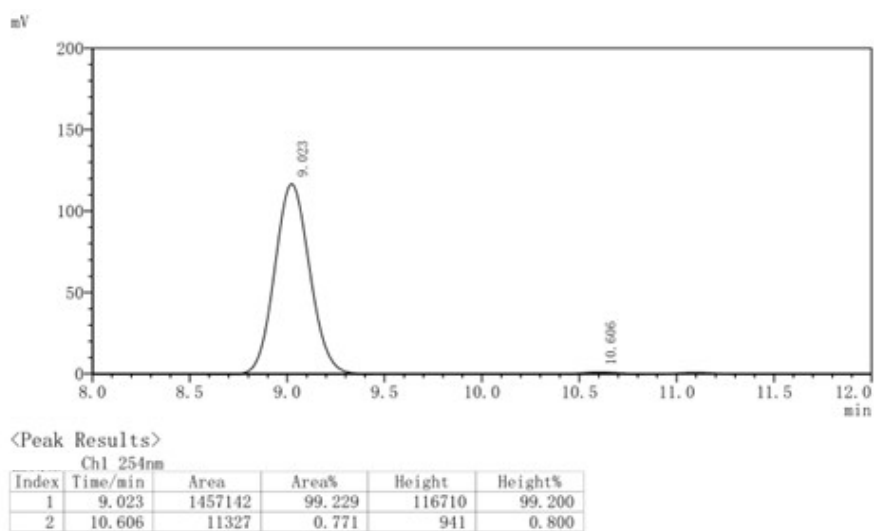
IX. HPLC Data

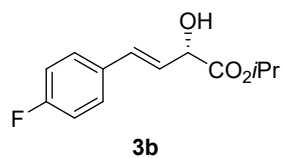


Chiral HPLC spectrum of racemic 3a

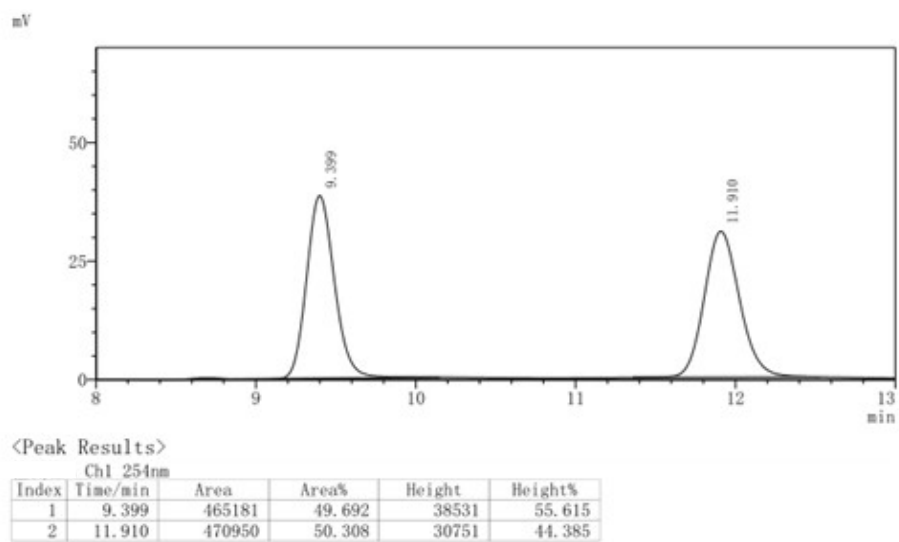


Chiral HPLC spectrum of (S)-3a

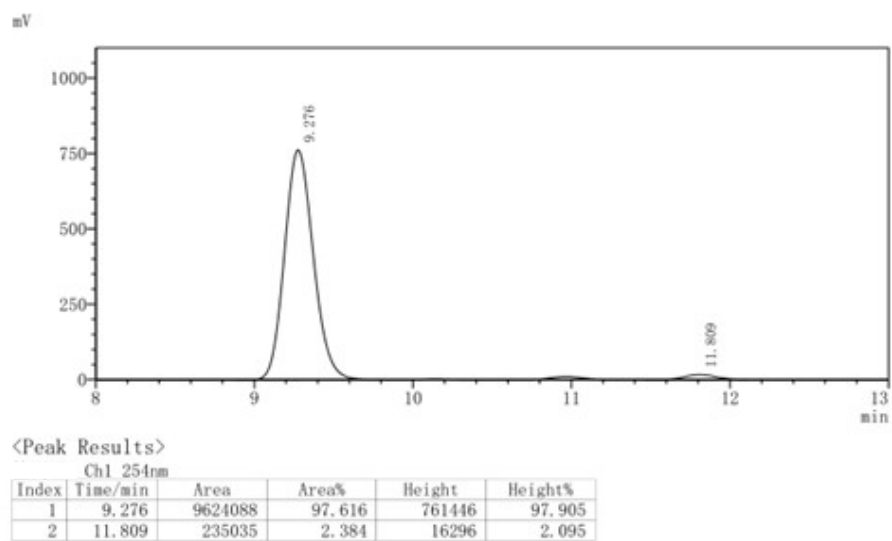


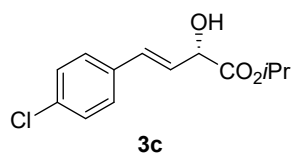


Chiral HPLC spectrum of racemic 3b

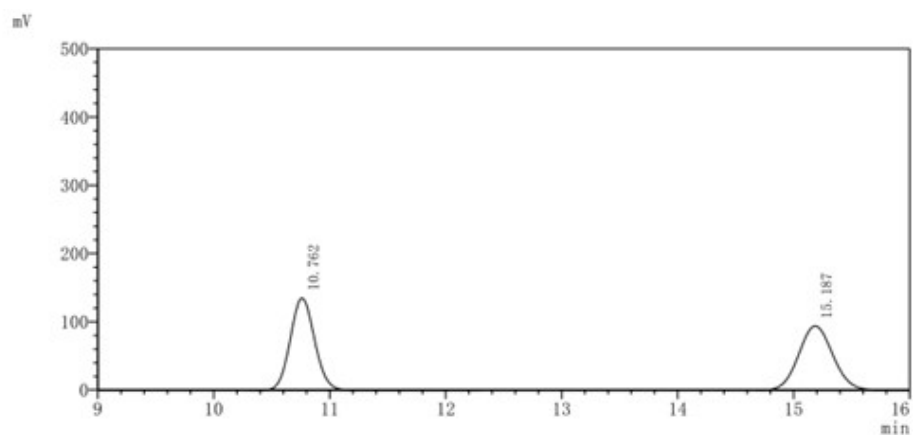


Chiral HPLC spectrum of chiral (S)-3b





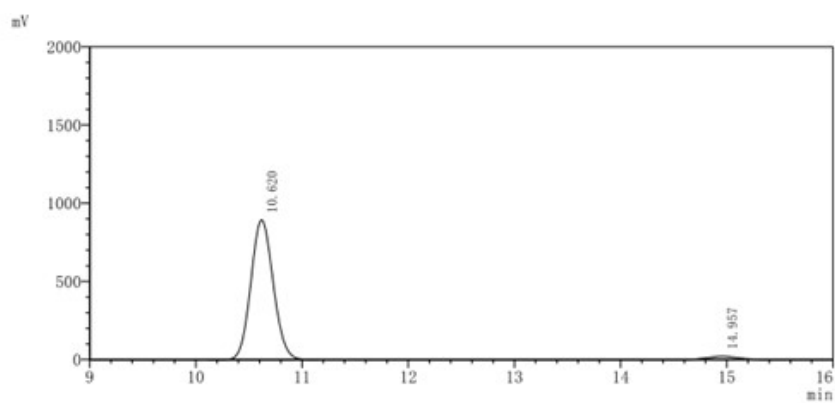
Chiral HPLC spectrum of racemic 3c



<Peak Results>

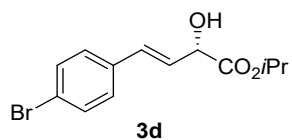
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	10.762	1979703	50.472	134867	58.892
2	15.187	1942652	49.528	94142	41.108

Chiral HPLC spectrum of chiral (S)-3c

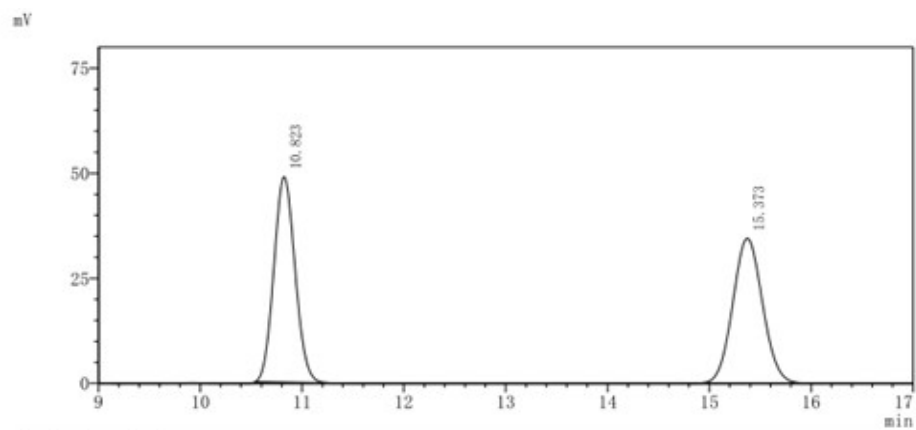


<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	10.620	13084016	97.732	892906	98.020
2	14.957	303603	2.268	18039	1.980



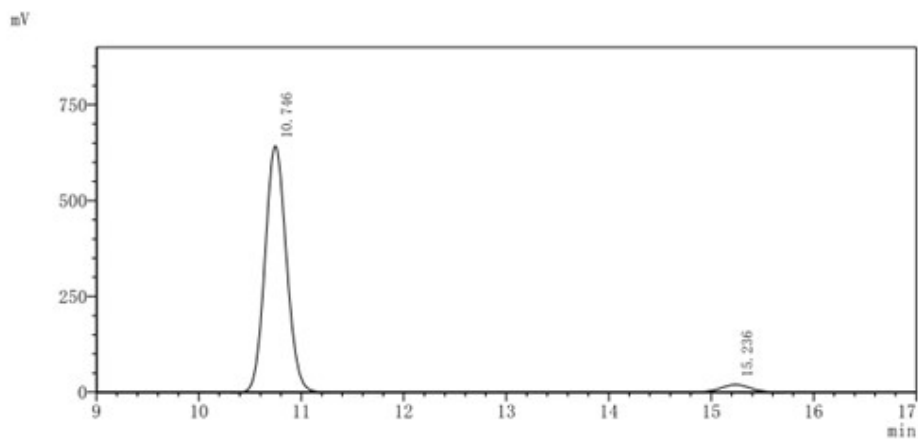
Chiral HPLC spectrum of racemic 3d



<Peak Results>

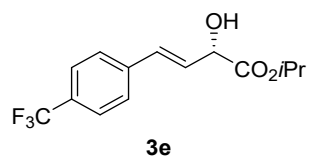
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	10.823	707918	50.230	48850	58.623
2	15.373	701446	49.770	34479	41.377

Chiral HPLC spectrum of chiral (S)-3d

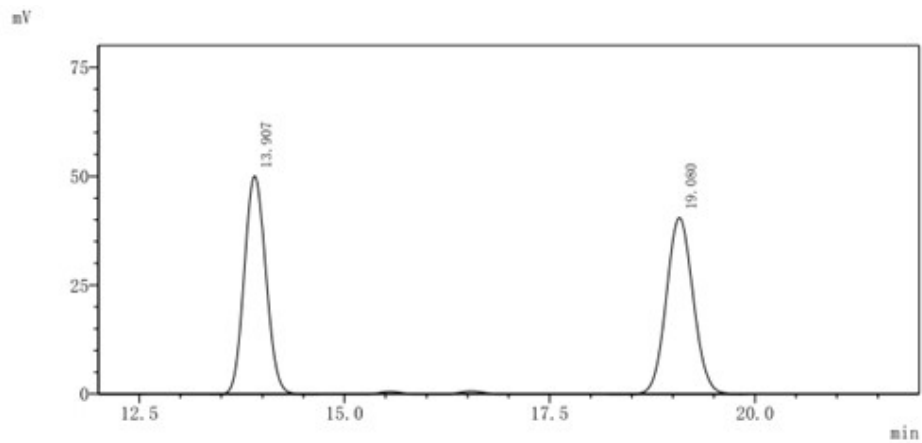


<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	10.746	9322537	96.136	641806	97.121
2	15.236	374720	3.864	19027	2.879



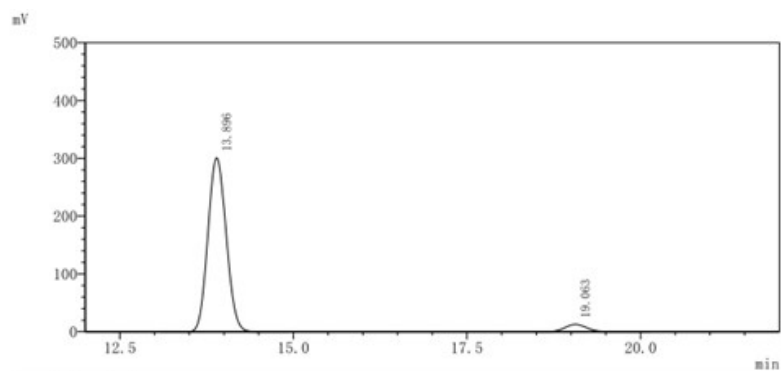
Chiral HPLC spectrum of racemic **3e**



<Peak Results>
Chl 254nm

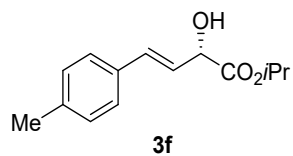
Index	Time/min	Area	Area%	Height	Height%
1	13.907	910622	49.744	50062	55.307
2	19.080	920000	50.256	40455	44.693

Chiral HPLC spectrum of chiral (*S*)-**3e**

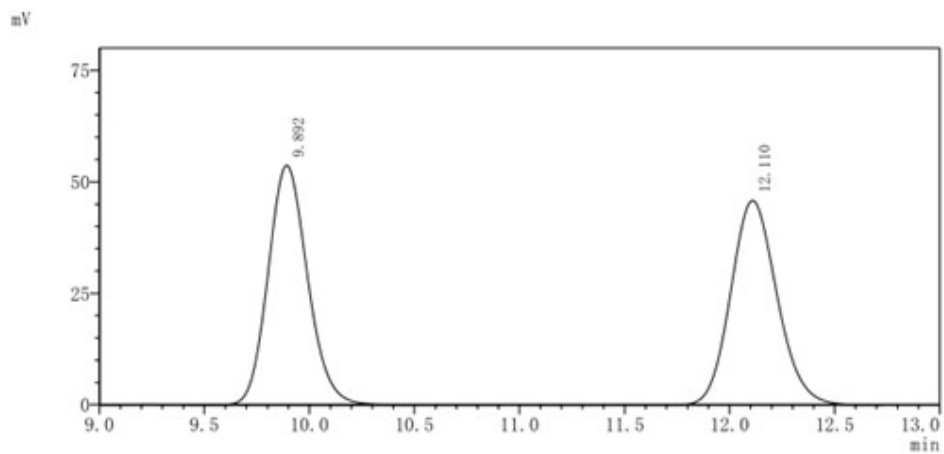


<Peak Results>
Chl 254nm

Index	Time/min	Area	Area%	Height	Height%
1	13.896	5496963	95.017	300833	95.912
2	19.063	288257	4.983	12824	4.088



Chiral HPLC spectrum of racemic **3f**

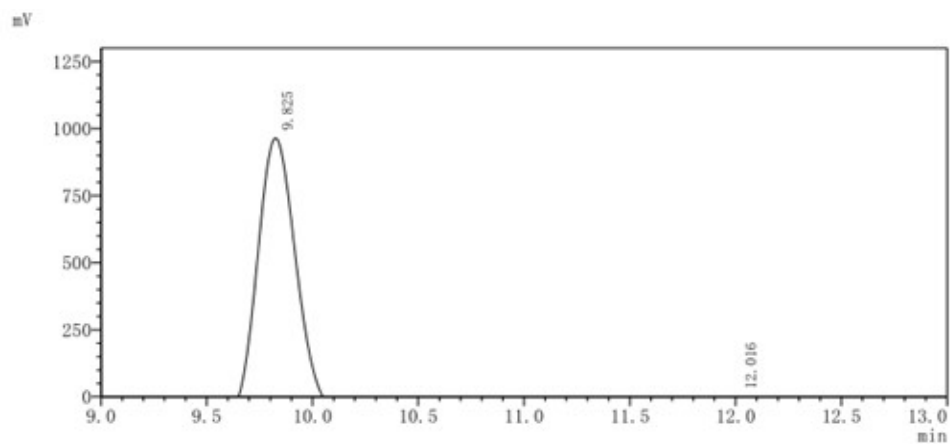


<Peak Results>

Ch1 254nm

Index	Time/min	Area	Area%	Height	Height%
1	9.892	698919	49.853	53672	53.916
2	12.110	703042	50.147	45875	46.084

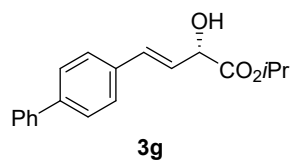
Chiral HPLC spectrum of chiral (*S*)-**3f**



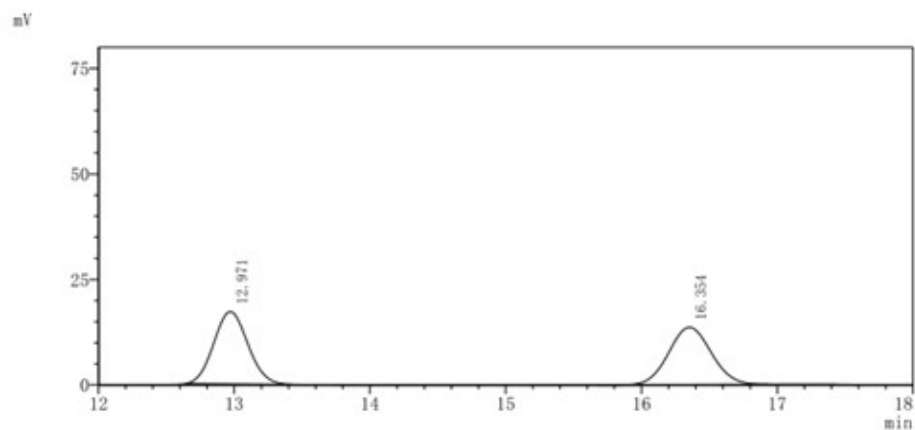
<Peak Results>

Ch1 254nm

Index	Time/min	Area	Area%	Height	Height%
1	9.825	13565170	99.120	1045216	99.241
2	12.016	120431	0.880	7995	0.759



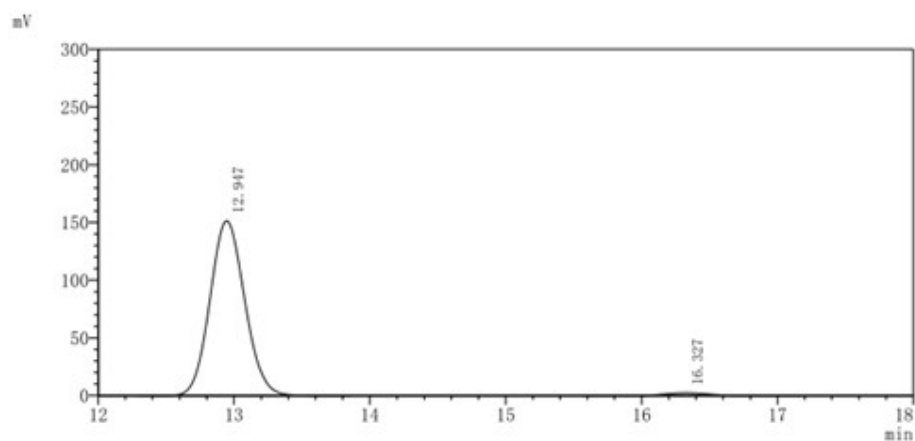
Chiral HPLC spectrum of racemic **3g**



<Peak Results>

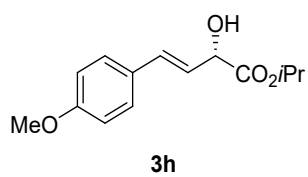
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	12.971	300491	50.254	17150	55.808
2	16.354	297456	49.746	13580	44.192

Chiral HPLC spectrum of chiral (*S*)-**3g**

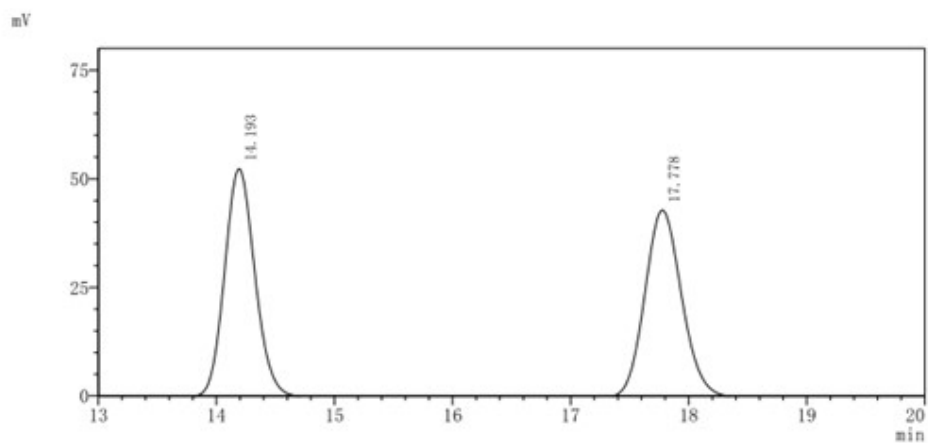


<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	12.947	2695250	98.086	151367	98.433
2	16.327	52603	1.914	2410	1.567



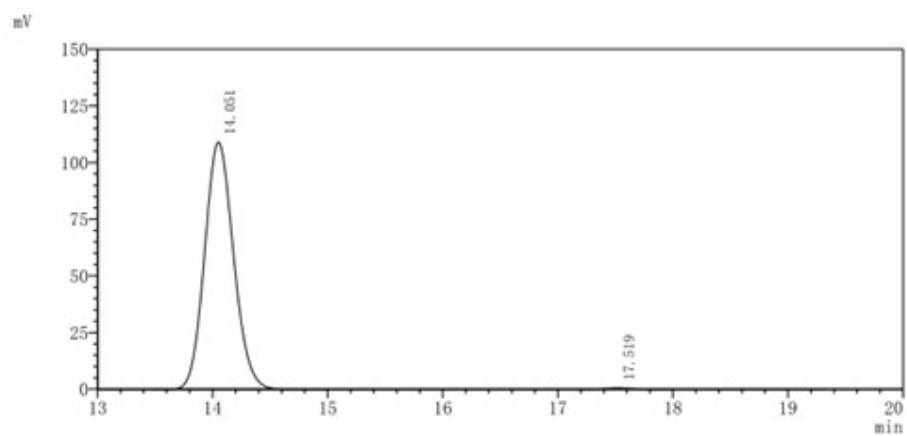
Chiral HPLC spectrum of racemic **3h**



<Peak Results>

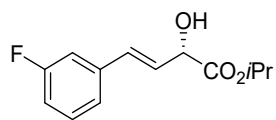
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.193	938481	50.135	52492	54.955
2	17.778	933438	49.865	43025	45.045

Chiral HPLC spectrum of chiral (*S*)-**3h**



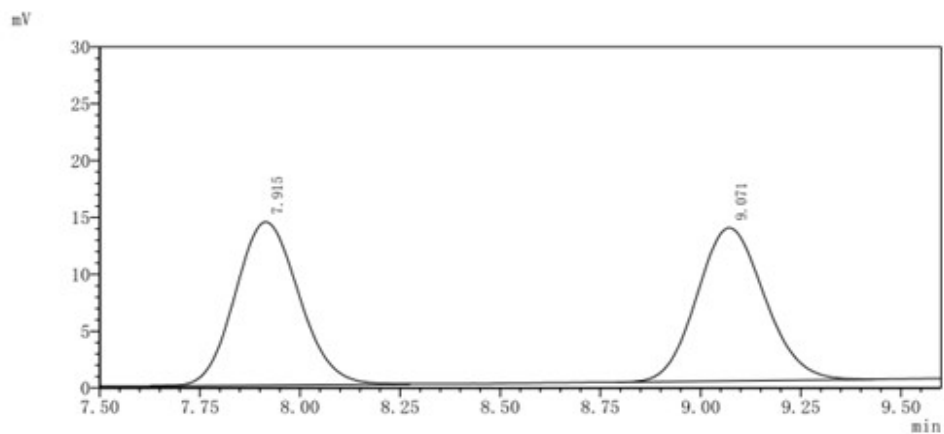
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.051	1907943	99.452	109022	99.524
2	17.519	10516	0.548	522	0.476



3i

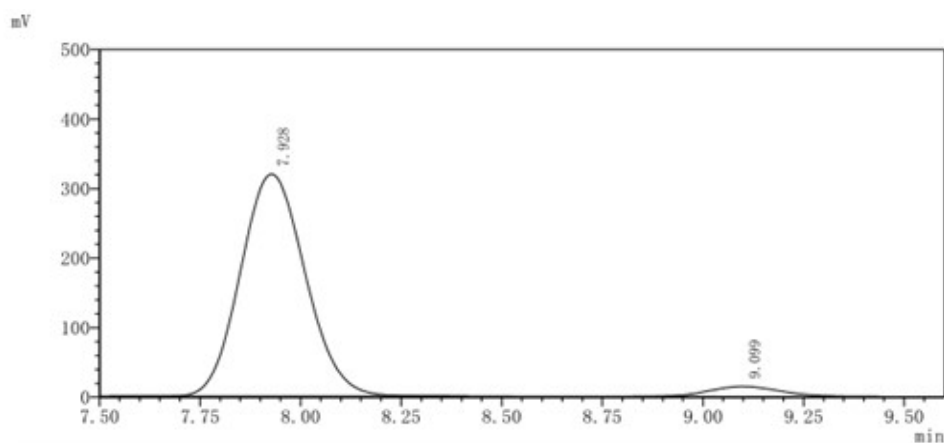
Chiral HPLC spectrum of racemic 3i



<Peak Results>

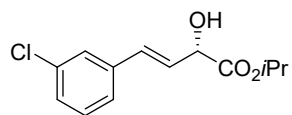
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.915	159387	50.044	14350	51.603
2	9.071	159107	49.956	13459	48.397

Chiral HPLC spectrum of chiral (S)-3i



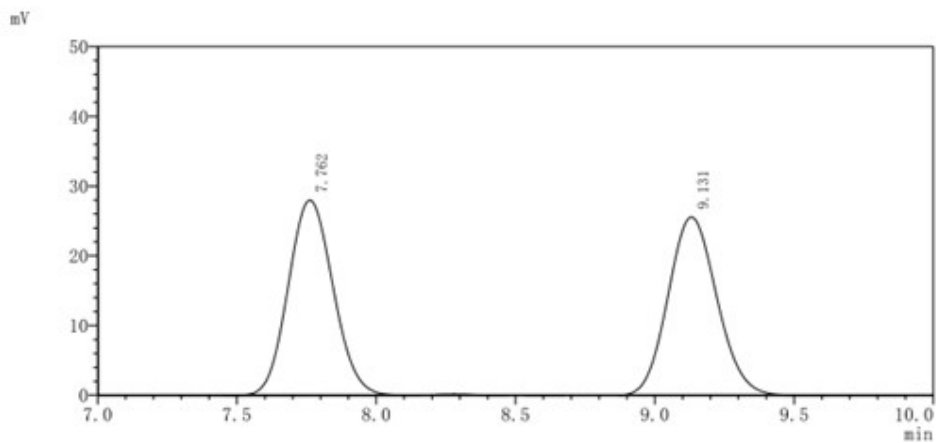
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.928	3588009	95.227	319724	95.666
2	9.099	179858	4.773	14485	4.334



3j

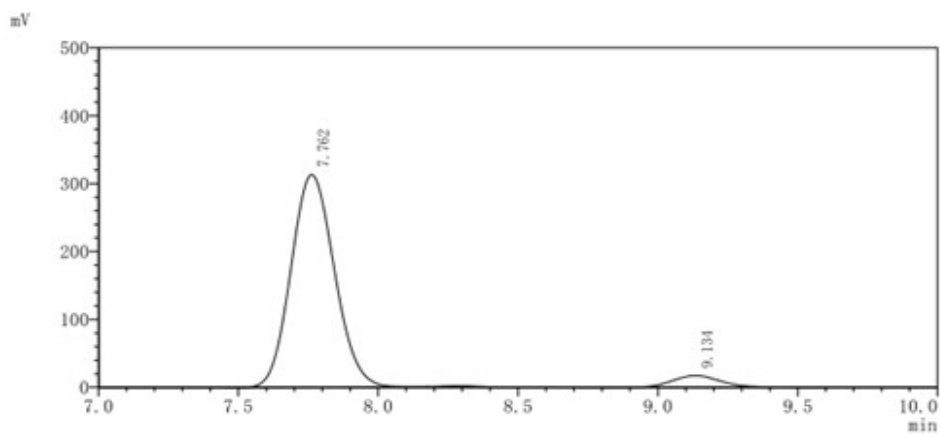
Chiral HPLC spectrum of racemic 3j



<Peak Results>

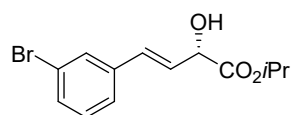
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.762	312928	49.984	27946	52.180
2	9.131	313122	50.016	25611	47.820

Chiral HPLC spectrum of chiral (S)-3j



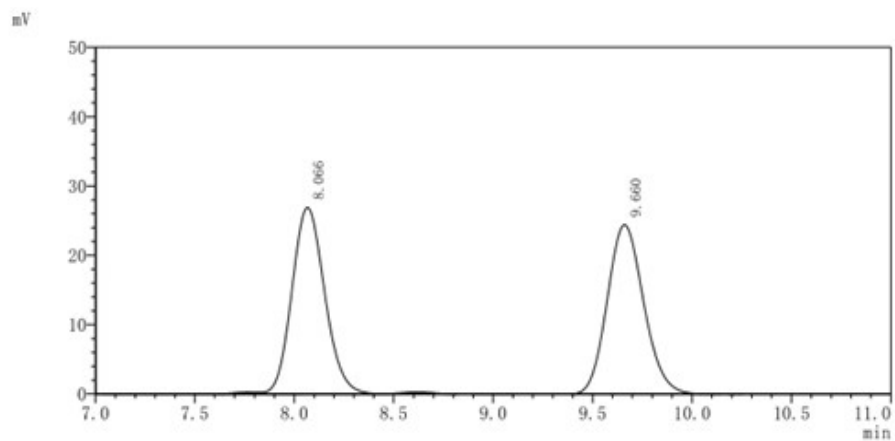
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.762	3380033	94.420	312579	94.849
2	9.134	199755	5.580	16974	5.151



3k

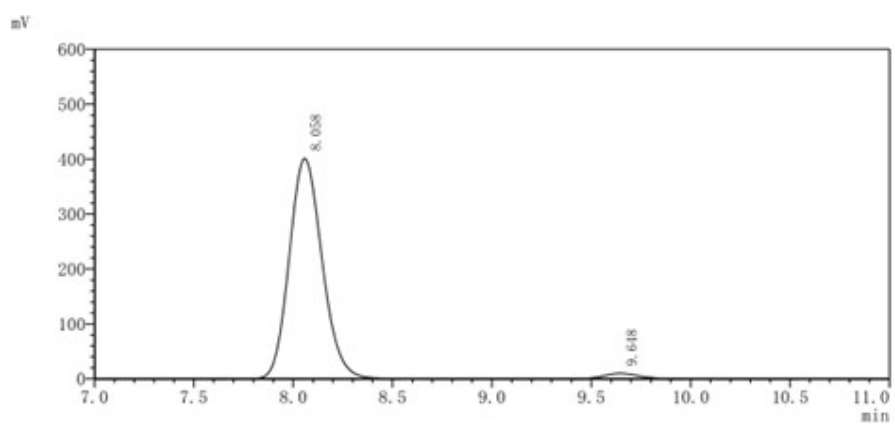
Chiral HPLC spectrum of racemic 3k



<Peak Results>

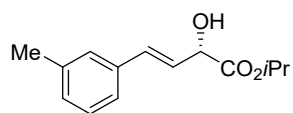
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	8.066	309966	49.789	26880	52.372
2	9.660	312595	50.211	24445	47.628

Chiral HPLC spectrum of chiral (S)-3k



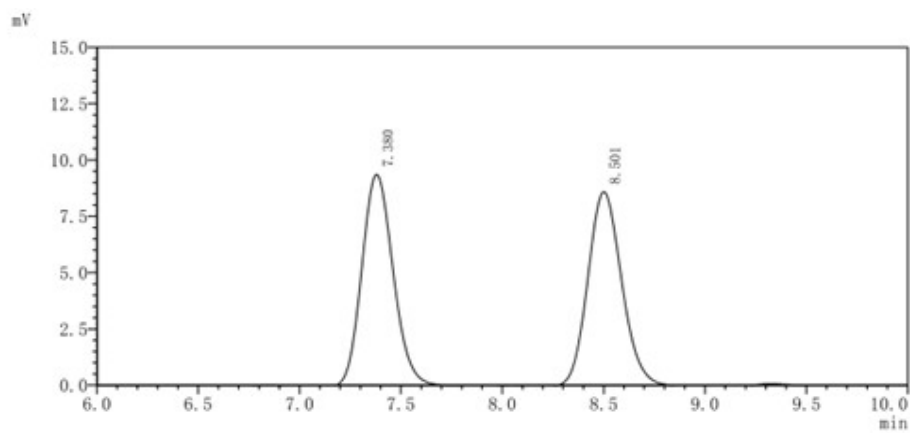
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	8.058	4617426	97.393	401298	97.607
2	9.648	123597	2.607	9837	2.393



3I

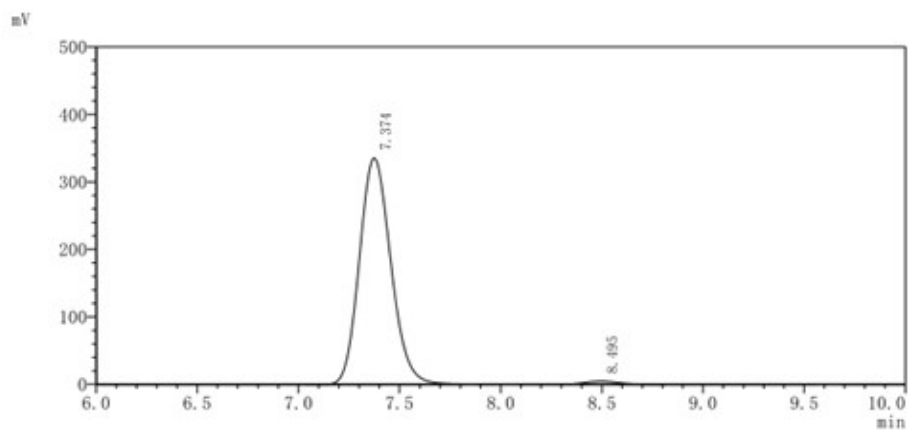
Chiral HPLC spectrum of racemic 3I



<Peak Results>

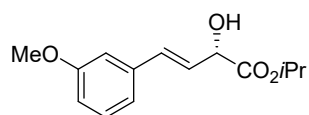
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.380	101102	50.193	9380	52.111
2	8.501	100327	49.807	8620	47.889

Chiral HPLC spectrum of chiral (S)-3I



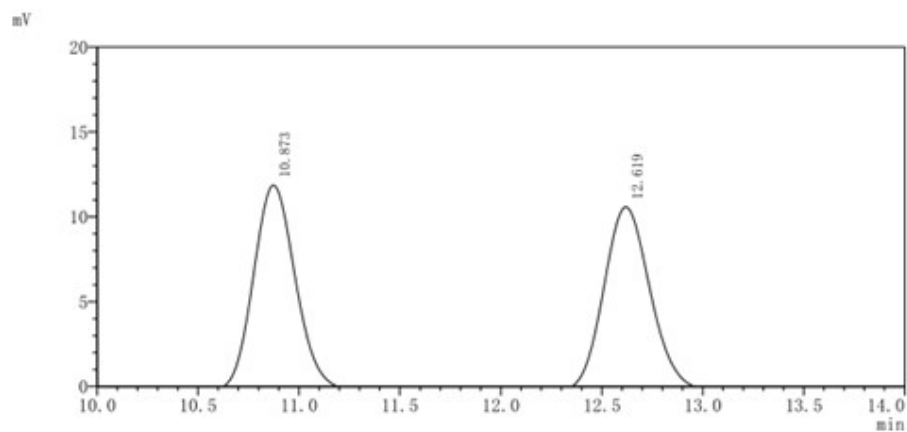
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.374	3618468	98.625	335505	98.671
2	8.495	50458	1.375	4520	1.329



3m

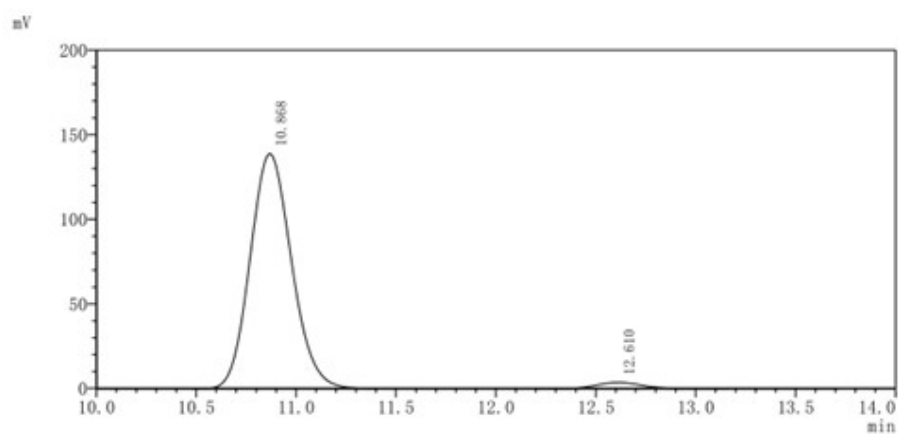
Chiral HPLC spectrum of racemic 3m



<Peak Results>

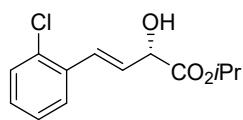
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	10.873	175334	50.198	12097	52.777
2	12.619	173951	49.802	10824	47.223

Chiral HPLC spectrum of chiral (S)-3m



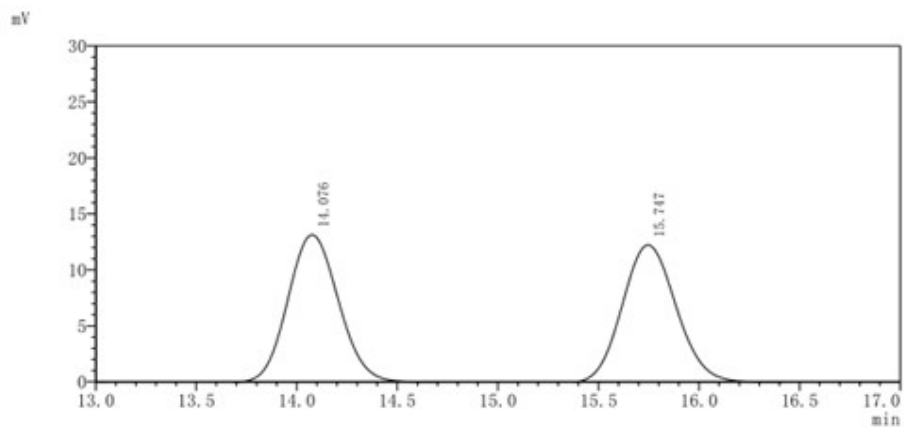
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	10.868	2002339	97.150	138824	97.414
2	12.610	58748	2.850	3685	2.586



3n

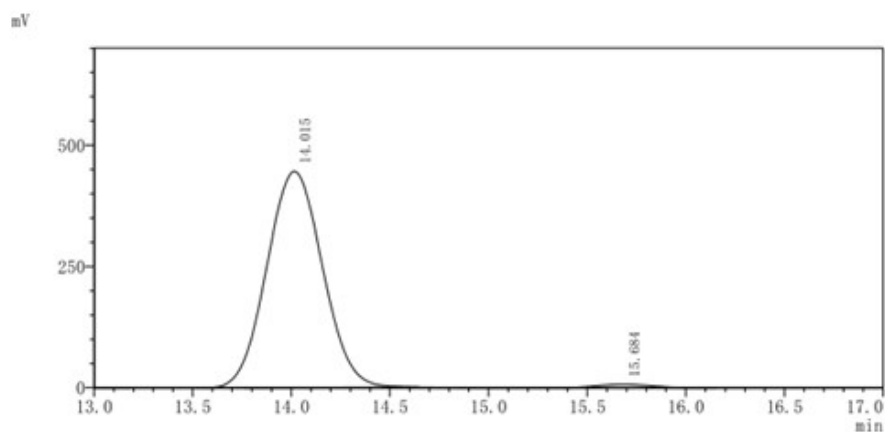
Chiral HPLC spectrum of racemic 3n



<Peak Results>

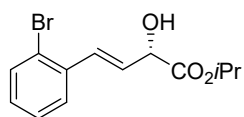
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.076	235219	50.407	13206	51.789
2	15.747	231416	49.593	12293	48.211

Chiral HPLC spectrum of chiral (S)-3n



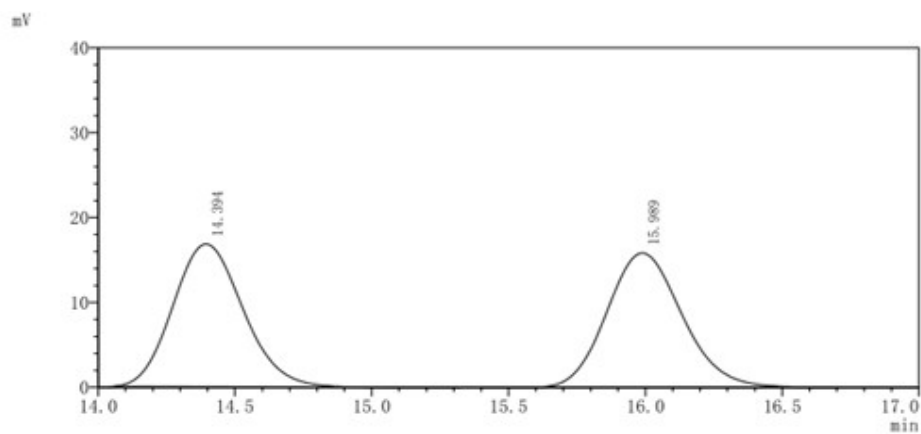
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.015	8778561	98.337	445672	98.336
2	15.684	148485	1.663	7544	1.664



3o

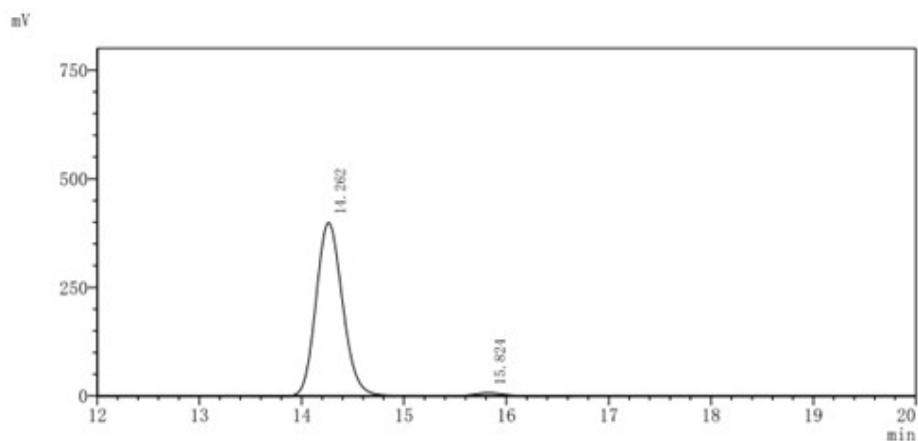
Chiral HPLC spectrum of racemic 3o



<Peak Results>

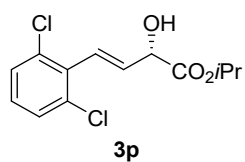
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.394	300689	49.641	16799	51.464
2	15.989	305034	50.359	15843	48.536

Chiral HPLC spectrum of chiral (S)-3o

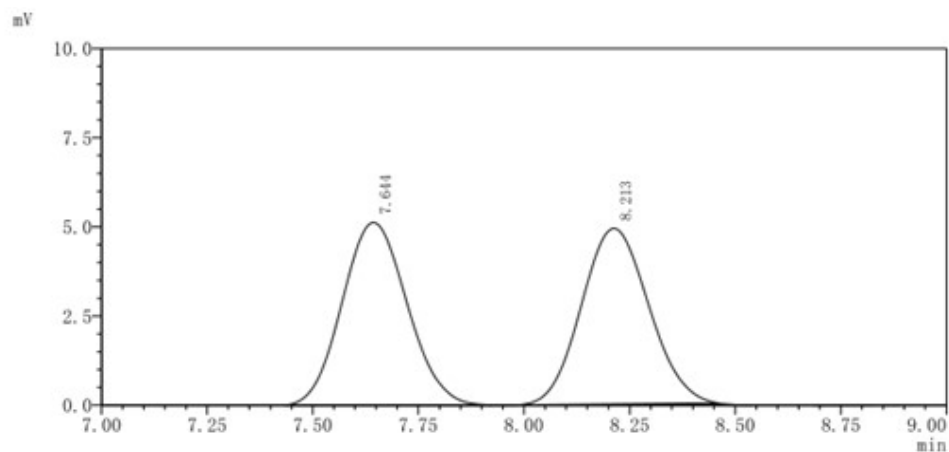


<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.262	7152880	98.265	398367	98.302
2	15.821	126278	1.735	6882	1.698



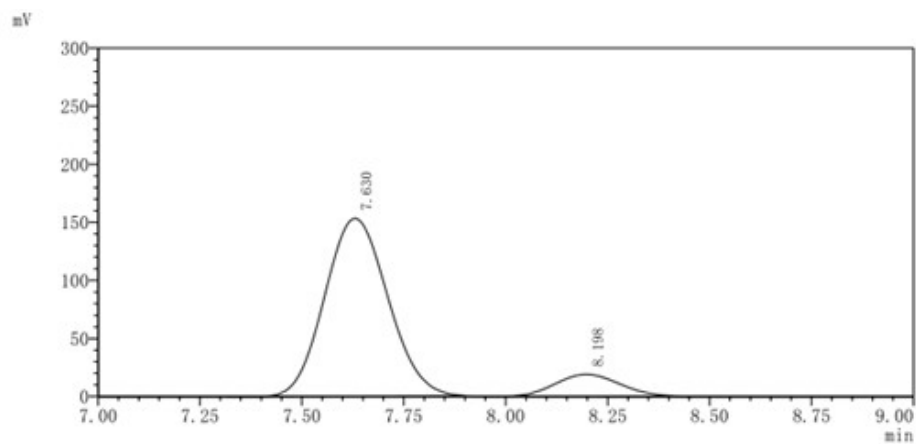
Chiral HPLC spectrum of racemic 3p



<Peak Results>

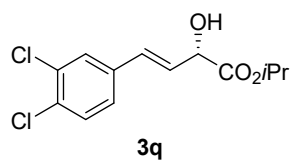
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.644	54897	50.123	5125	51.017
2	8.213	54628	49.877	4920	48.983

Chiral HPLC spectrum of chiral (S)-3p

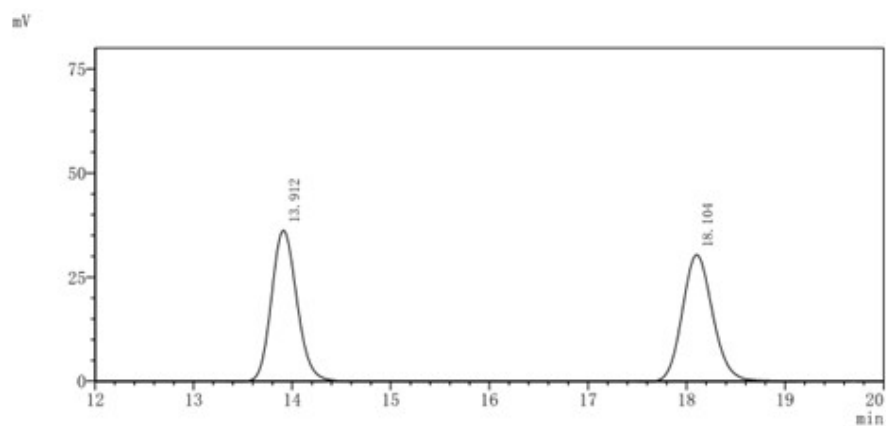


<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.630	1652133	88.756	153016	88.987
2	8.198	209289	11.244	18938	11.013



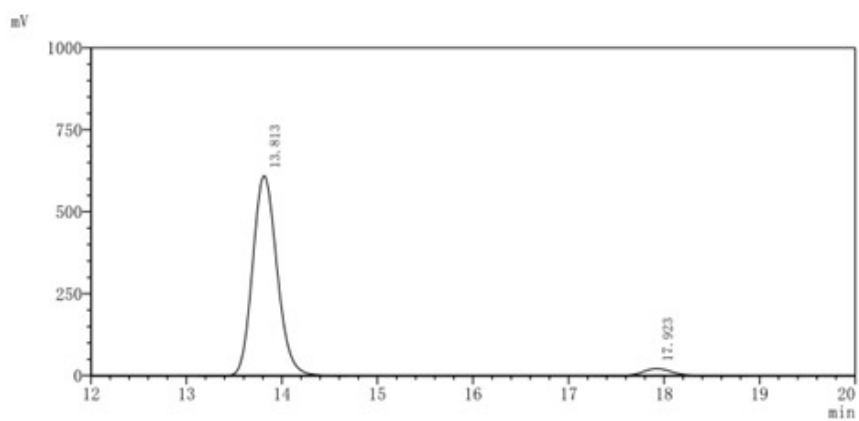
Chiral HPLC spectrum of racemic 3q



<Peak Results>

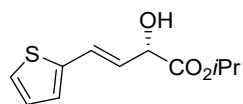
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	13.912	644977	49.646	36183	54.351
2	18.104	654176	50.354	30390	45.649

Chiral HPLC spectrum of chiral (S)-3q



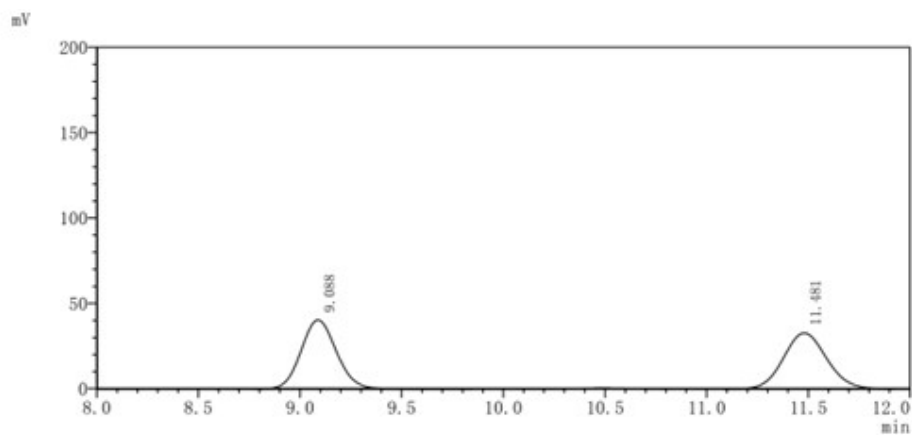
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	13.813	10831604	95.902	609344	96.552
2	17.923	462902	4.098	21759	3.448



3s

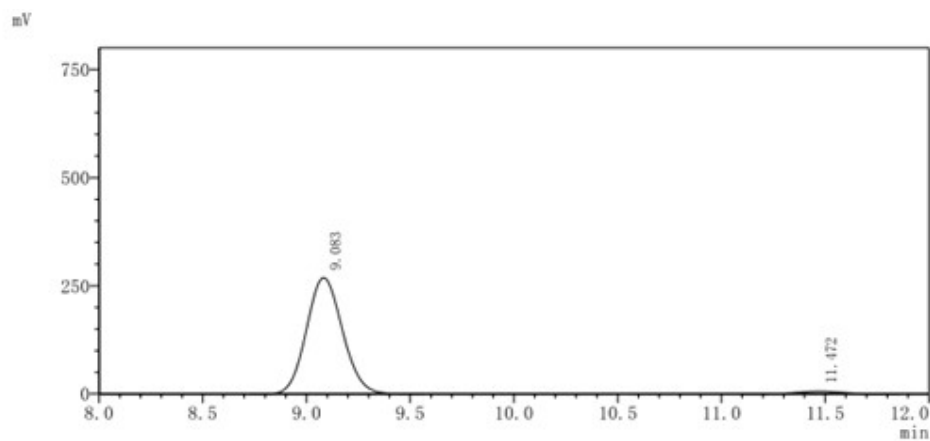
Chiral HPLC spectrum of racemic 3s



<Peak Results>

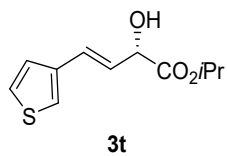
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	9.088	487785	50.380	40267	55.228
2	11.481	480428	49.620	32643	44.772

Chiral HPLC spectrum of chiral (S)-3s

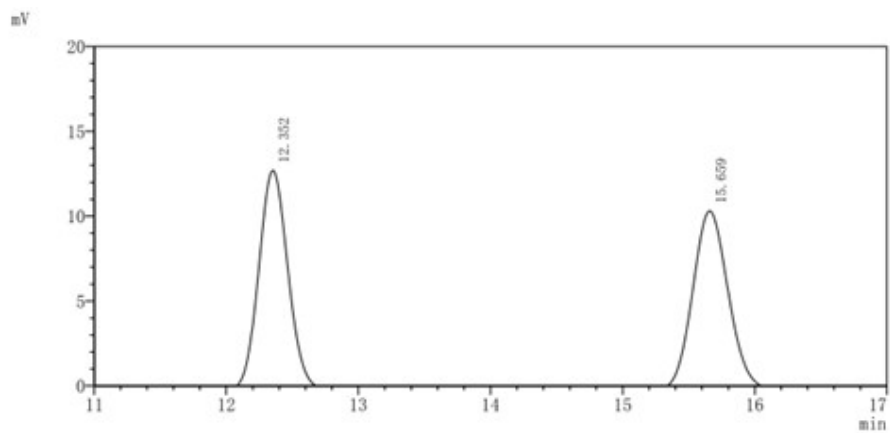


<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	9.083	3243801	97.346	268946	97.845
2	11.472	88431	2.654	5924	2.155



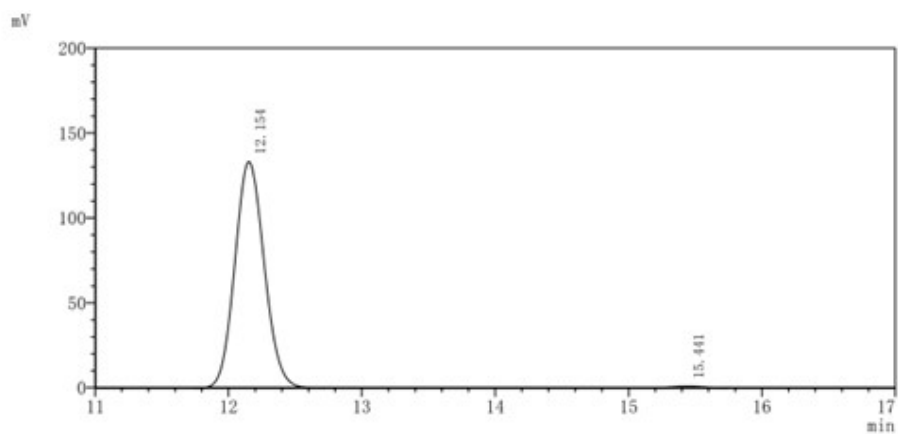
Chiral HPLC spectrum of racemic **3t**



<Peak Results>

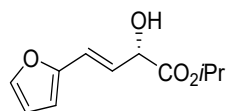
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	12.352	196577	50.114	12880	55.080
2	15.659	195683	49.886	10504	44.920

Chiral HPLC spectrum of chiral (*S*)-**3t**



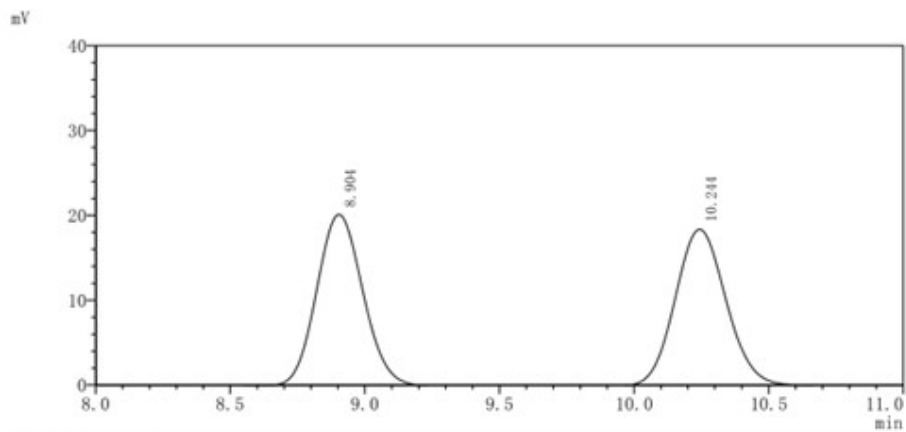
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	12.154	2026368	99.352	133029	99.375
2	15.441	13220	0.648	836	0.625



3u

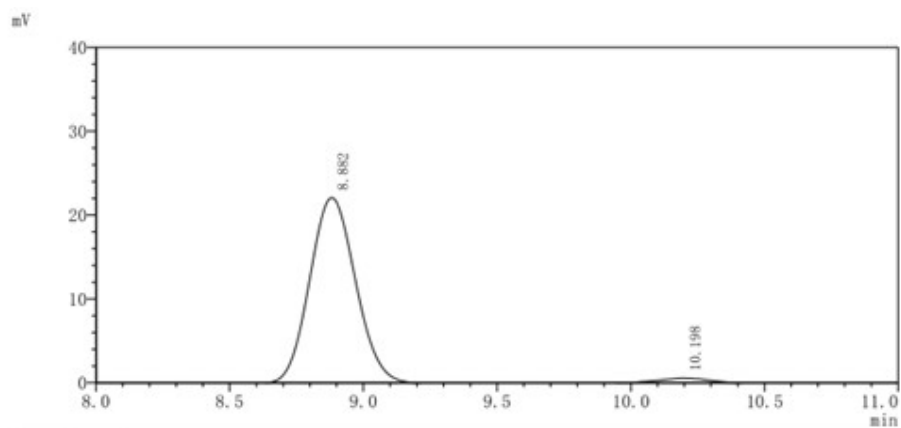
Chiral HPLC spectrum of racemic 3u



<Peak Results>

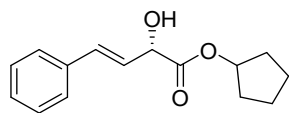
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	8.904	242264	49.791	20184	52.235
2	10.244	244297	50.209	18457	47.765

Chiral HPLC spectrum of chiral (S)-3u



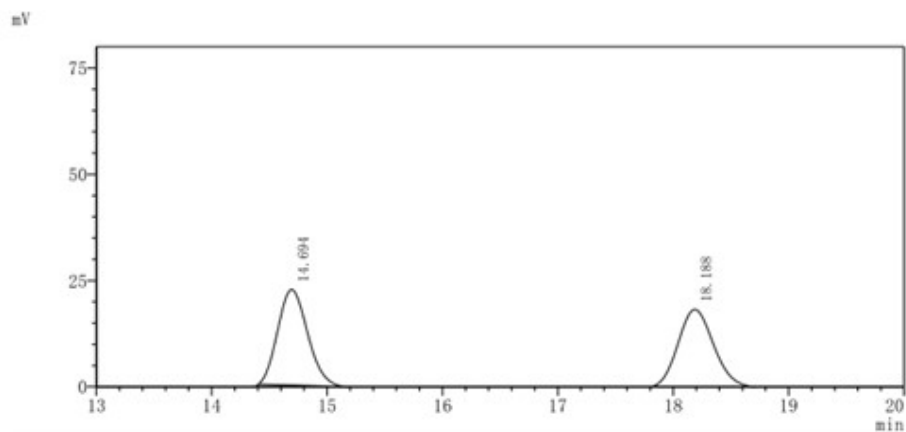
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	8.882	265058	96.574	22173	97.257
2	10.198	9403	3.426	625	2.743



3v

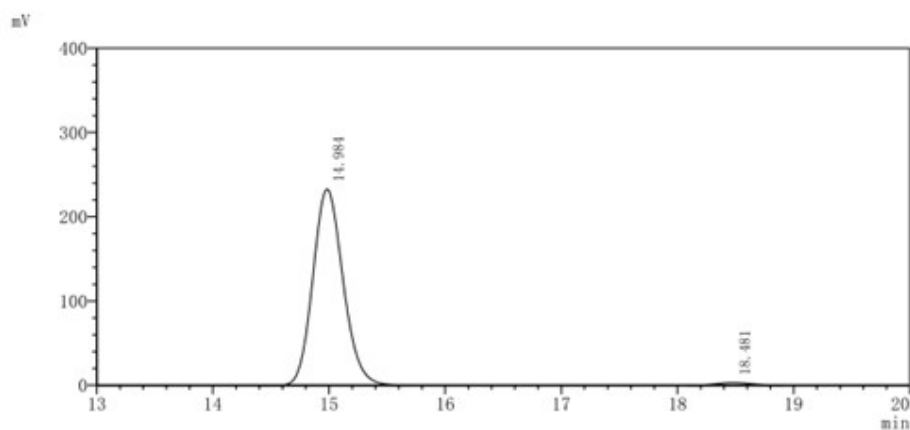
Chiral HPLC spectrum of racemic 3v



<Peak Results>

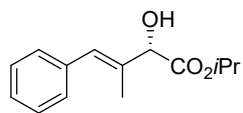
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.694	406075	50.290	22509	54.974
2	18.188	401395	49.710	18436	45.026

Chiral HPLC spectrum of chiral (S)-3v



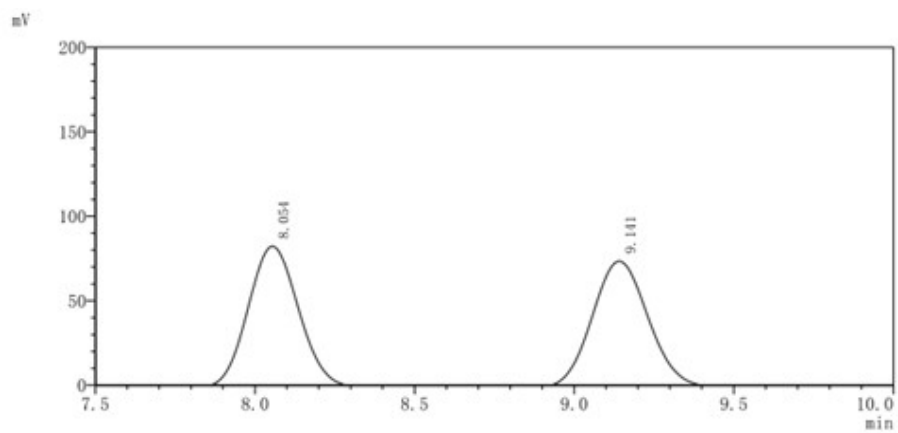
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	14.984	4207399	98.426	232690	98.622
2	18.481	67273	1.574	3252	1.378



5a

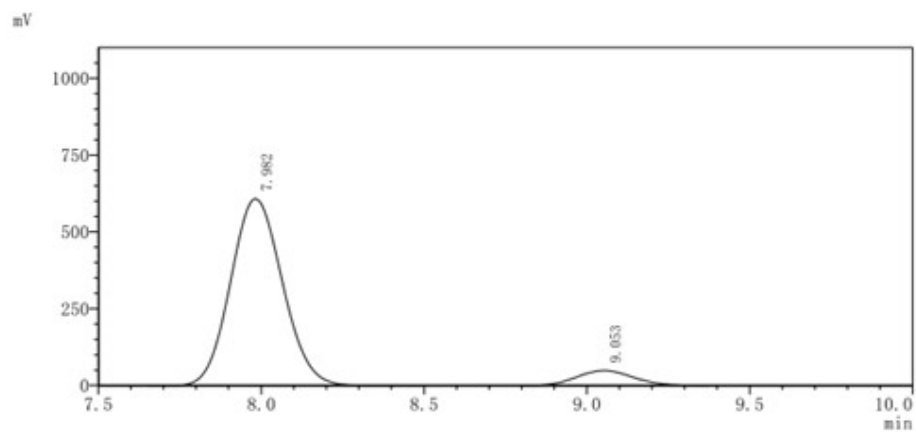
Chiral HPLC spectrum of racemic 5a



<Peak Results>

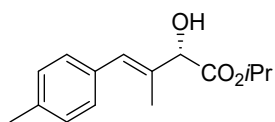
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	8.054	932578	49.992	83814	52.719
2	9.141	932875	50.008	75169	47.281

Chiral HPLC spectrum of chiral (S)-5a



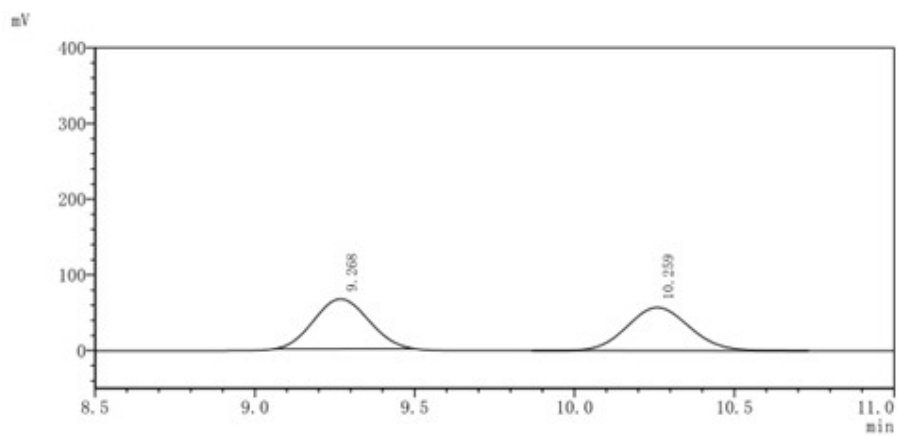
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	7.982	6735226	91.846	608648	92.573
2	9.053	597952	8.154	48831	7.427



5b

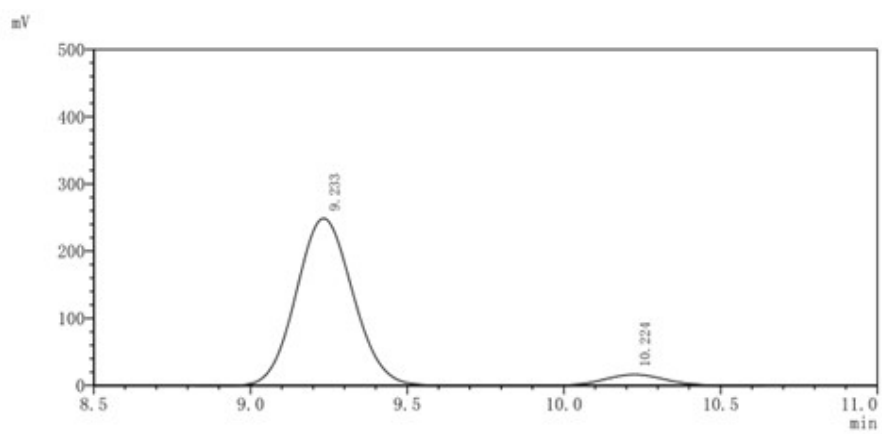
Chiral HPLC spectrum of racemic 5b



<Peak Results>

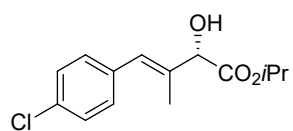
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	9.268	789848	50.333	65973	53.648
2	10.259	779391	49.667	57001	46.352

Chiral HPLC spectrum of chiral (S)-5b



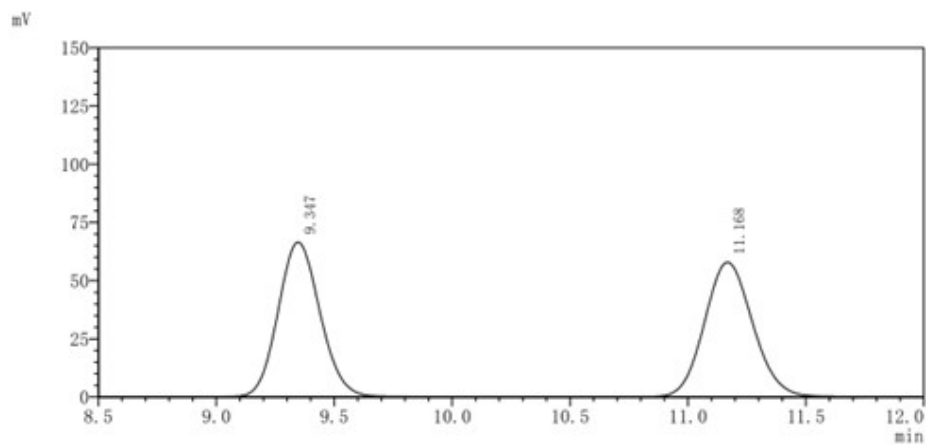
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	9.233	3144689	93.306	249009	93.784
2	10.224	225592	6.694	16503	6.216



5c

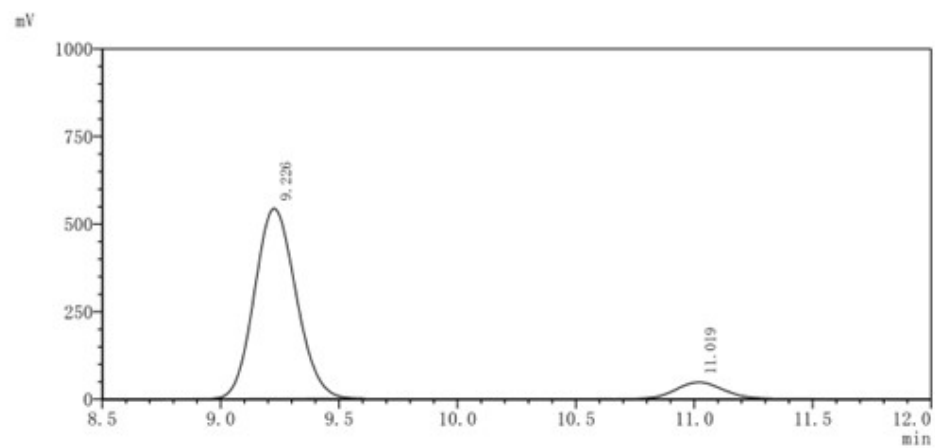
Chiral HPLC spectrum of racemic 5c



<Peak Results>

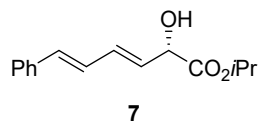
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	9.347	818813	49.918	66295	53.451
2	11.168	821499	50.082	57735	46.549

Chiral HPLC spectrum of chiral (S)-5c

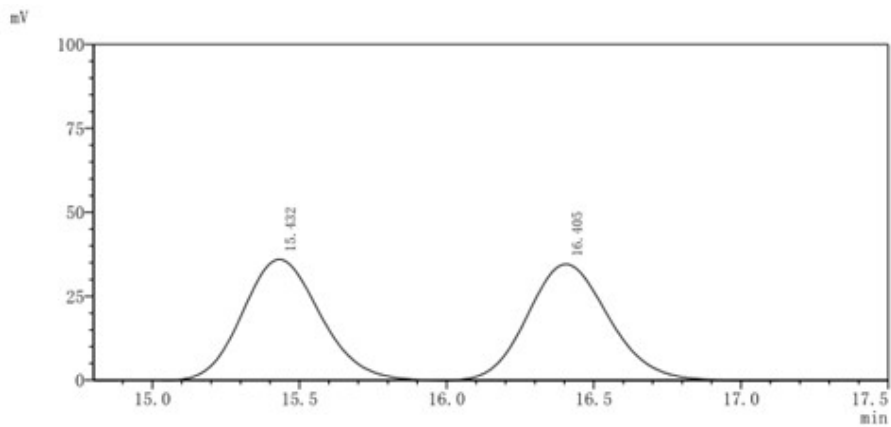


<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	9.226	6661893	90.831	543499	91.949
2	11.019	672513	9.169	47589	8.051



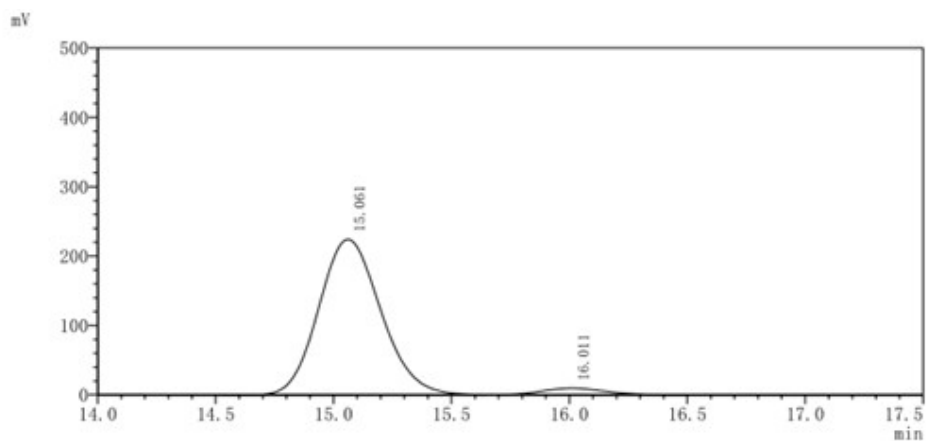
Chiral HPLC spectrum of racemic 7



<Peak Results>

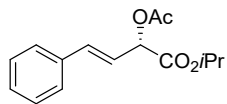
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	15.432	663624	49.992	36035	51.059
2	16.405	663836	50.008	34541	48.941

Chiral HPLC spectrum of chiral (S)-7



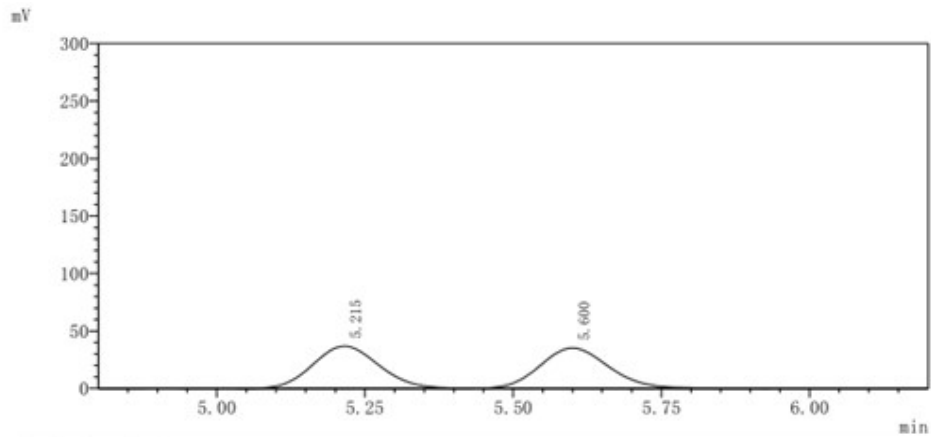
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	15.061	4104927	96.047	224051	96.019
2	16.011	168927	3.953	9290	3.981



8

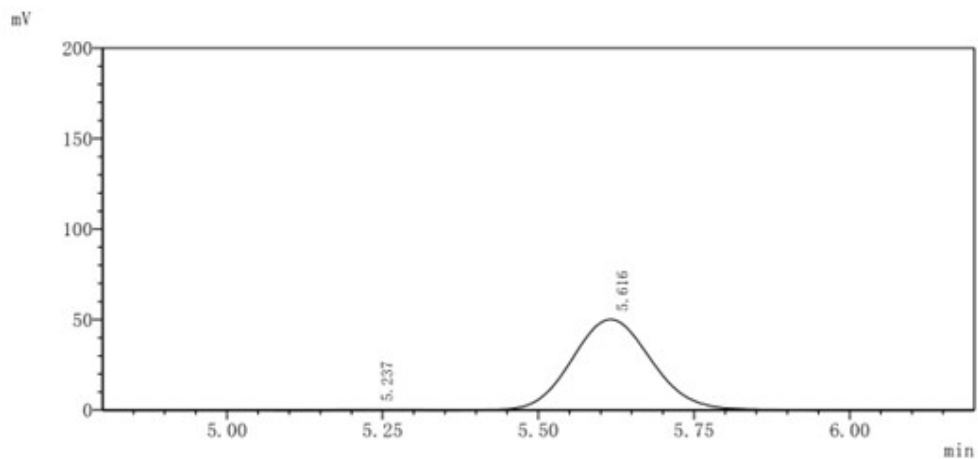
Chiral HPLC spectrum of racemic **8**



<Peak Results>

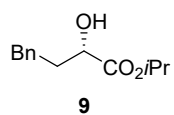
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	5.215	285579	50.458	36792	51.274
2	5.600	280399	49.542	34964	48.726

Chiral HPLC spectrum of chiral (*S*)-**8**

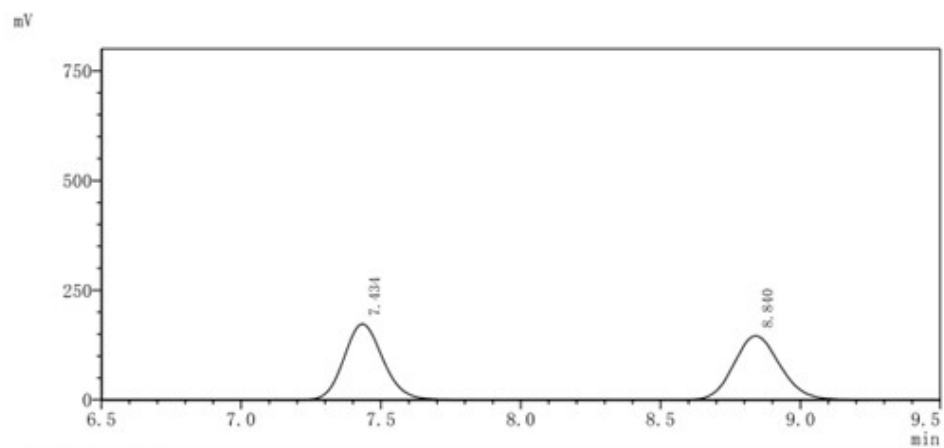


<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	5.237	2095	0.473	243	0.484
2	5.616	440590	99.527	49976	99.516



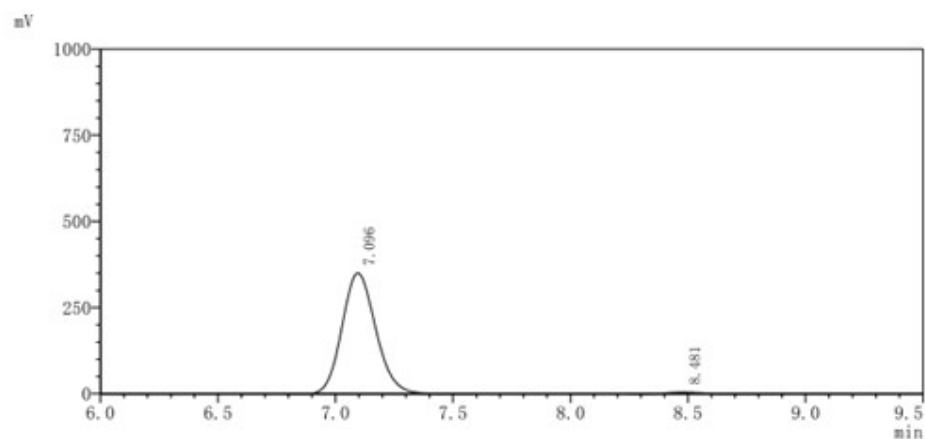
Chiral HPLC spectrum of racemic 9



<Peak Results>
Chl 254nm

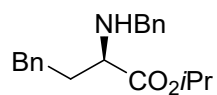
Index	Time/min	Area	Area%	Height	Height%
1	7.434	1664380	49.961	172527	54.243
2	8.840	1666984	50.039	145538	45.757

Chiral HPLC spectrum of chiral (S)-9



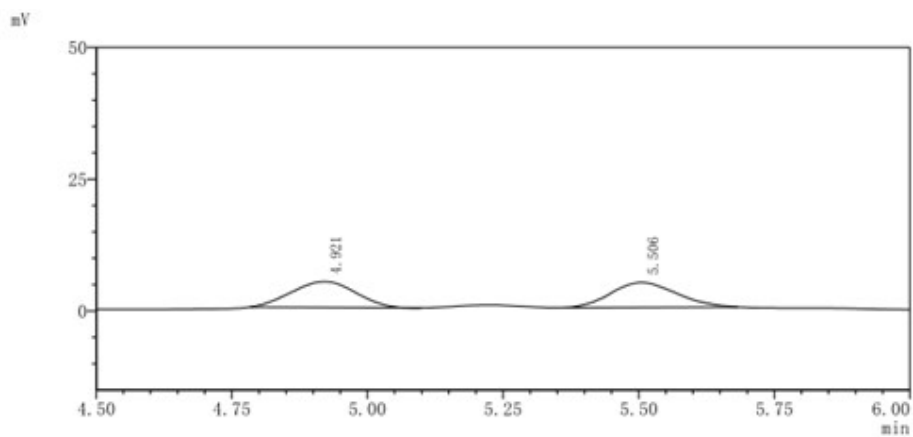
<Peak Results>
Chl 254nm

Index	Time/min	Area	Area%	Height	Height%
1	7.096	3514277	98.592	350251	98.761
2	8.481	50195	1.408	4395	1.239



10

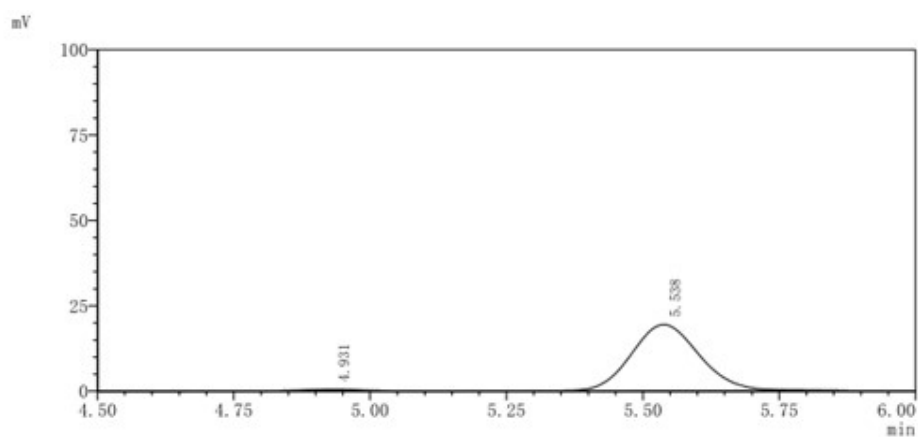
Chiral HPLC spectrum of racemic 10



<Peak Results>
Ch1 254nm

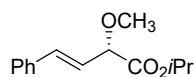
Index	Time/min	Area	Area%	Height	Height%
1	4.921	40350	50.261	4900	50.998
2	5.506	39932	49.739	4708	49.002

Chiral HPLC spectrum of chiral (R)-10



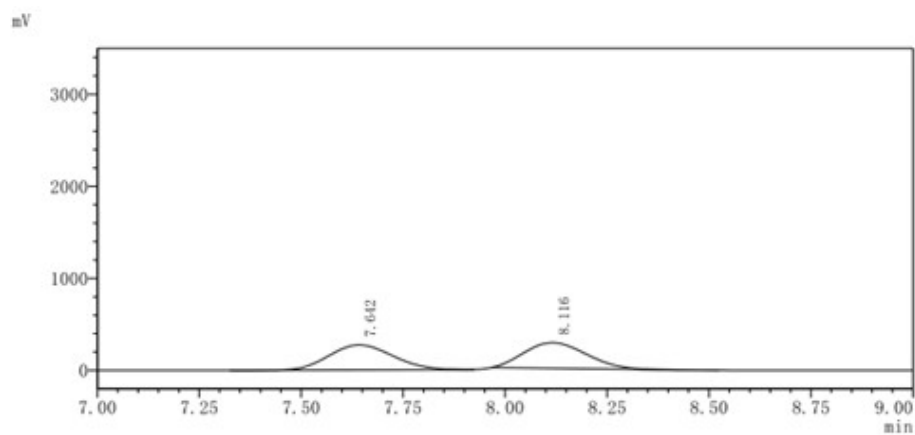
<Peak Results>
Ch1 254nm

Index	Time/min	Area	Area%	Height	Height%
1	4.931	2596	1.530	395	2.004
2	5.538	167057	98.470	19327	97.996



11

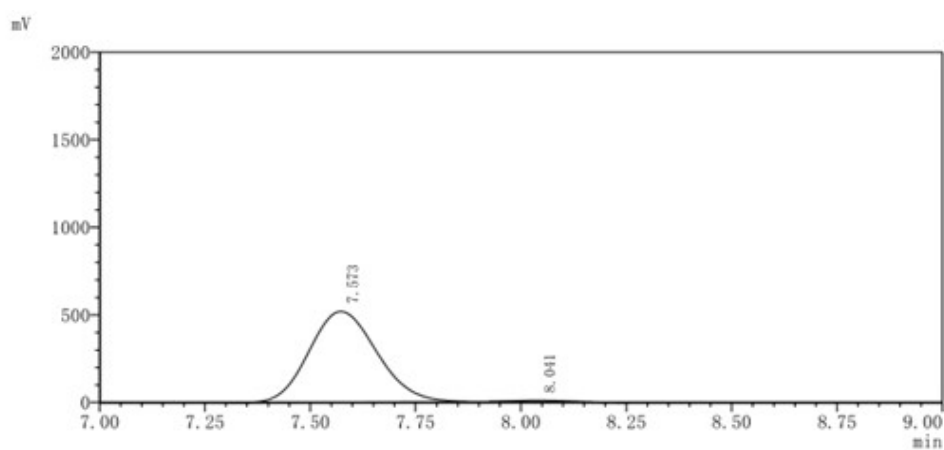
Chiral HPLC spectrum of racemic 11



<Peak Results>
Chl 254nm

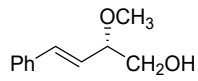
Index	Time/min	Area	Area%	Height	Height%
1	7.642	2963930	50.316	272553	49.424
2	8.116	2926698	49.684	278902	50.576

Chiral HPLC spectrum of chiral (S)-11



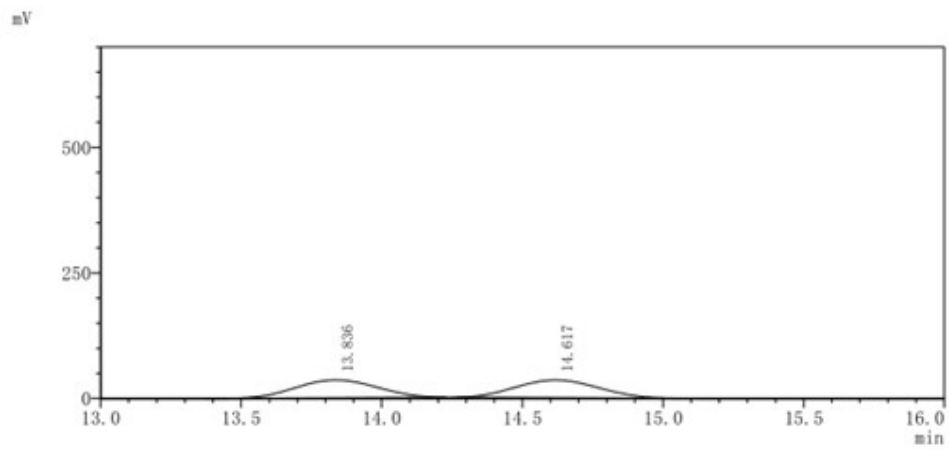
<Peak Results>
Chl 254nm

Index	Time/min	Area	Area%	Height	Height%
1	7.573	5799534	98.608	517617	98.342
2	8.041	81863	1.392	8729	1.658



12

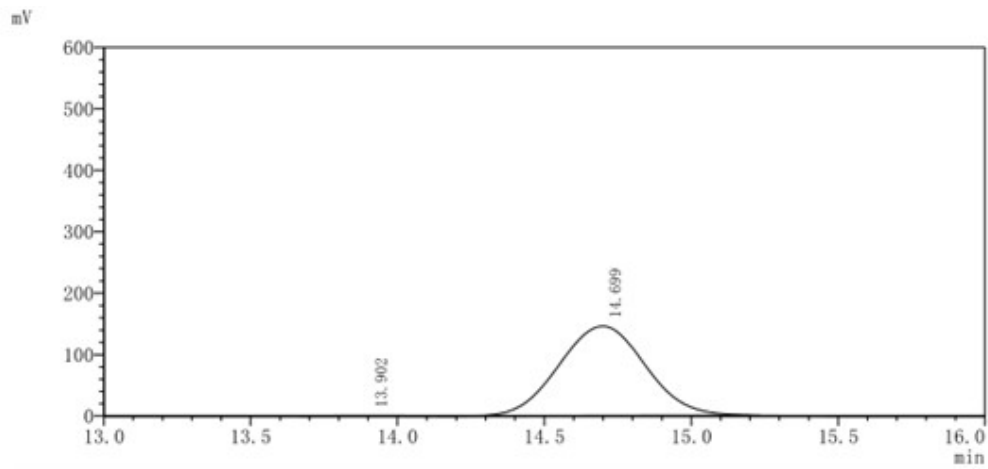
Chiral HPLC spectrum of racemic 12



<Peak Results>

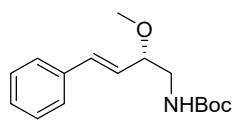
Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	13.836	725834	49.937	35600	50.216
2	14.617	727651	50.063	35294	49.784

Chiral HPLC spectrum of chiral (S)-12



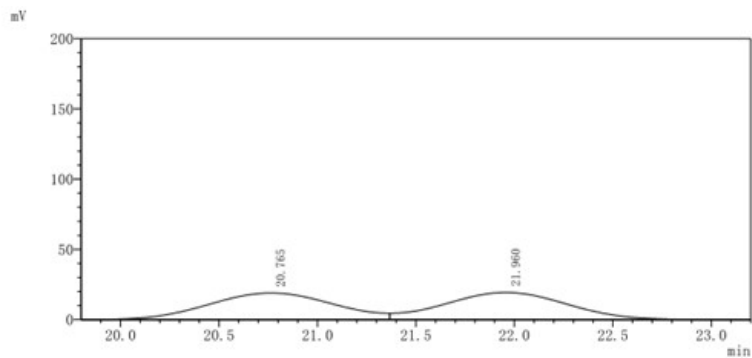
<Peak Results>

Chl 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	13.902	13706	0.458	799	0.546
2	14.699	2978318	99.542	145431	99.454



13

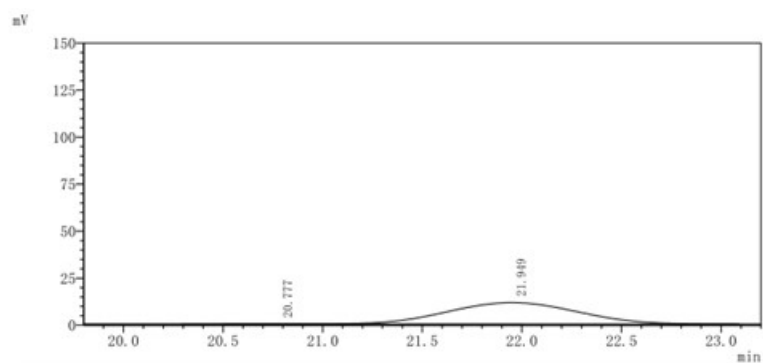
Chiral HPLC spectrum of racemic 13



<Peak Results>

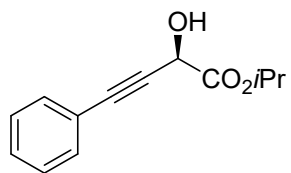
Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	20.765	845900	49.993	19024	49.514
2	21.960	846128	50.007	19398	50.486

Chiral HPLC spectrum of chiral (S)-13



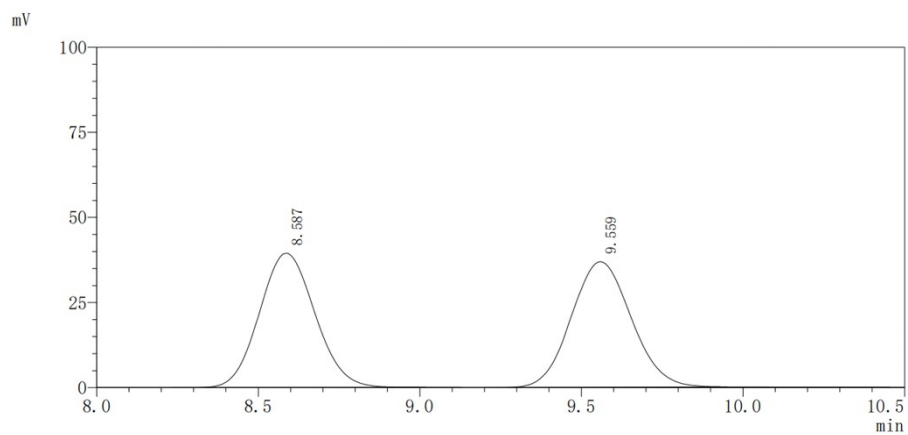
<Peak Results>

Ch1 254nm					
Index	Time/min	Area	Area%	Height	Height%
1	20.777	3096	0.586	142	1.234
2	21.949	525089	99.414	11393	98.766



15a

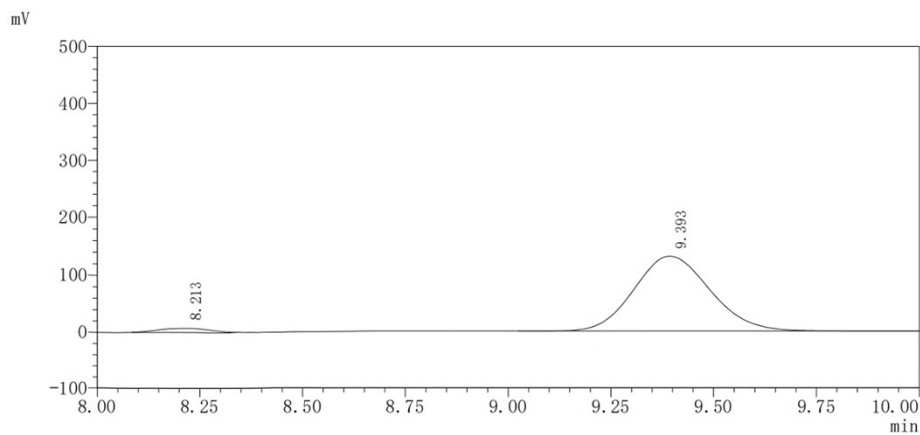
Chiral HPLC spectrum of racemic 15a



<Peak Results>

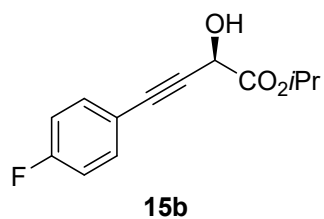
Index	Time/min	Area	Area%	Height	Height%
1	8.587	471469	49.778	39430	51.663
2	9.559	475674	50.222	36892	48.337

Chiral HPLC spectrum of chiral (R)-15a

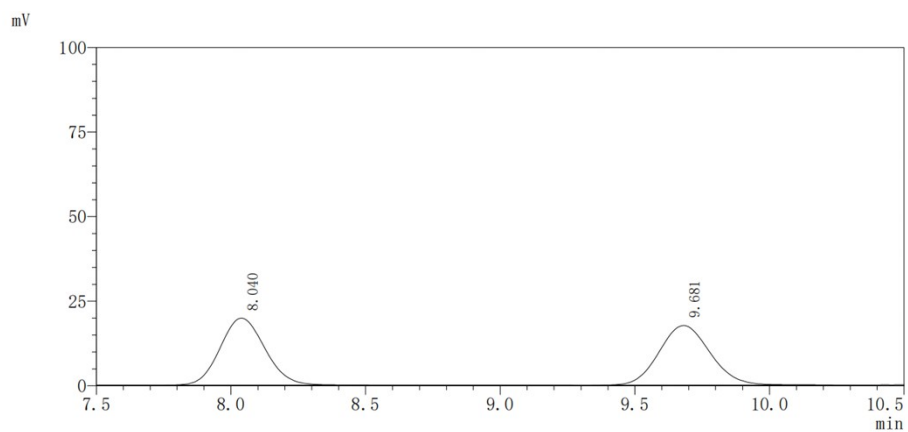


<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	8.213	65751	3.718	7391	5.324
2	9.393	1702875	96.282	131420	94.676



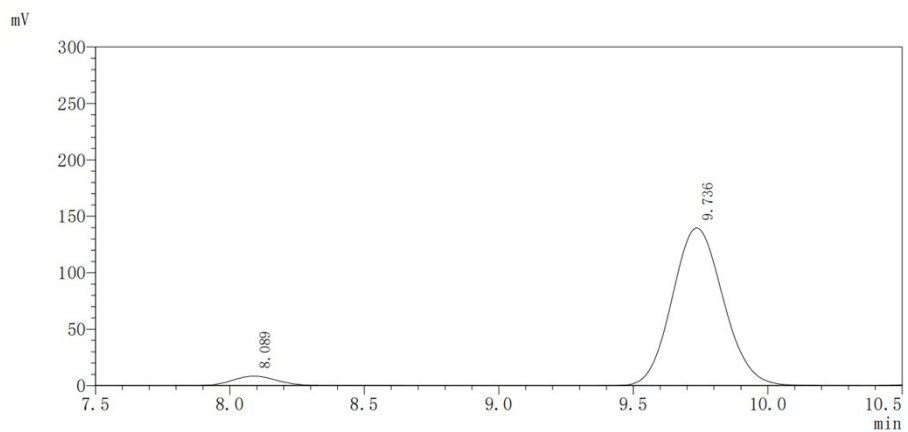
Chiral HPLC spectrum of racemic 15b



<Peak Results>

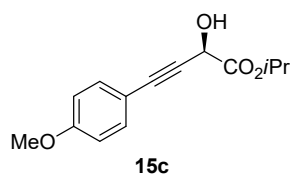
Index	Time/min	Area	Area%	Height	Height%
1	8.040	228563	49.568	19822	52.926
2	9.681	232544	50.432	17631	47.074

Chiral HPLC spectrum of chiral (R)-15b

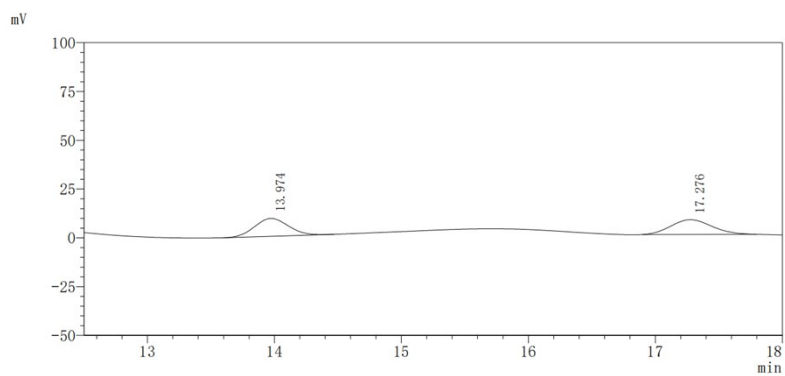


<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	8.089	98516	5.054	8477	5.719
2	9.736	1850916	94.946	139743	94.281



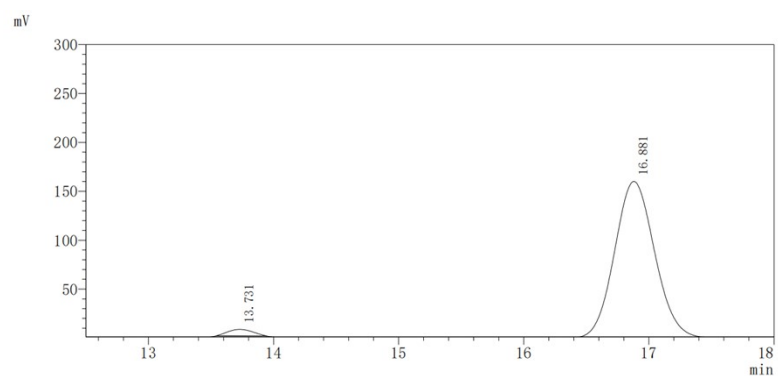
Chiral HPLC spectrum of racemic 15c



<Peak Results>

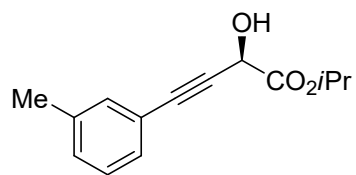
Index	Time/min	Area	Area%	Height	Height%
1	13.974	169587	50.125	9141	54.821
2	17.276	168744	49.875	7533	45.179

Chiral HPLC spectrum of chiral (R)-15c



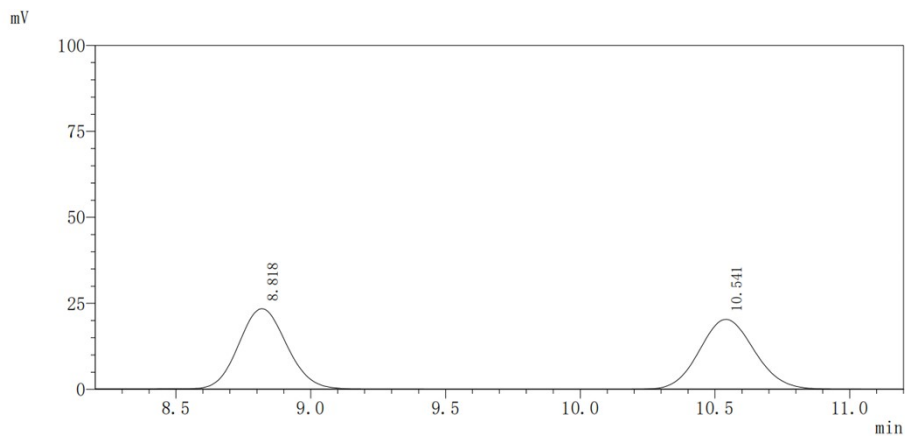
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	13.731	90495	2.468	6583	3.947
2	16.881	3576019	97.532	160184	96.053



15d

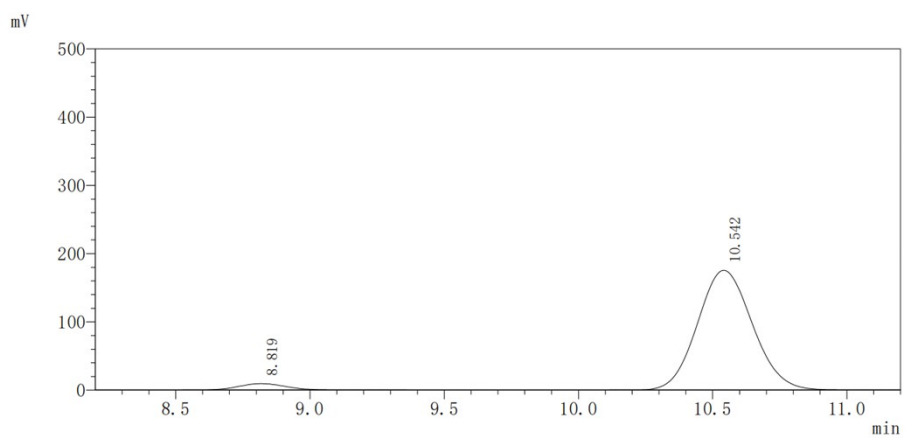
Chiral HPLC spectrum of racemic 15d



<Peak Results>

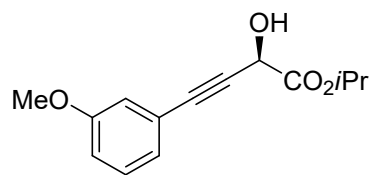
Index	Time/min	Area	Area%	Height	Height%
1	8.818	296540	50.426	23497	53.519
2	10.541	291533	49.574	20407	46.481

Chiral HPLC spectrum of chiral (R)-15d



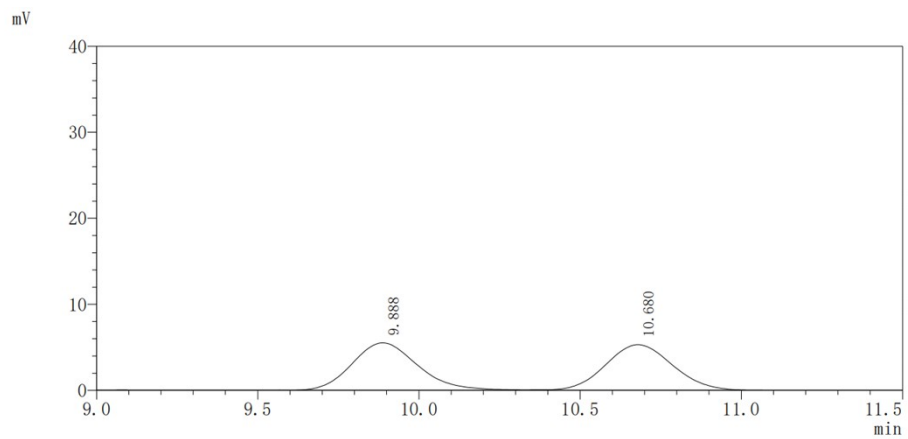
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	8.819	119742	4.556	9590	5.172
2	10.542	2508500	95.444	175823	94.828



15e

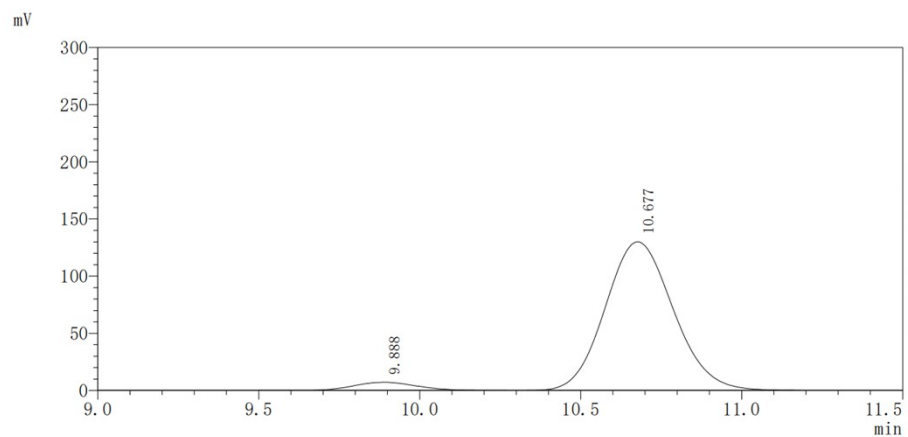
Chiral HPLC spectrum of racemic 15e



<Peak Results>

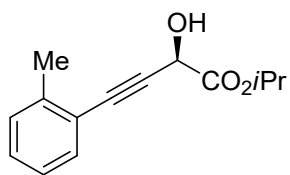
Index	Time/min	Area	Area%	Height	Height%
1	9.888	79834	50.201	5540	50.860
2	10.680	79196	49.799	5352	49.140

Chiral HPLC spectrum of chiral (R)-15e



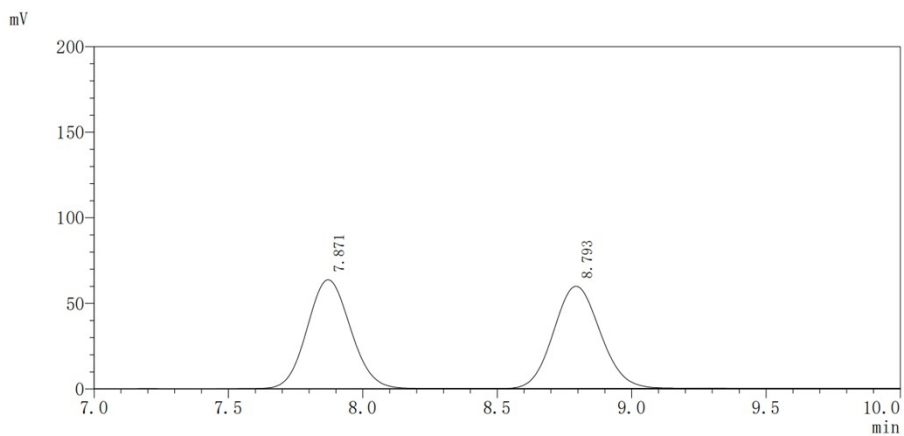
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	9.888	100059	4.964	7211	5.256
2	10.677	1915740	95.036	129968	94.744



15f

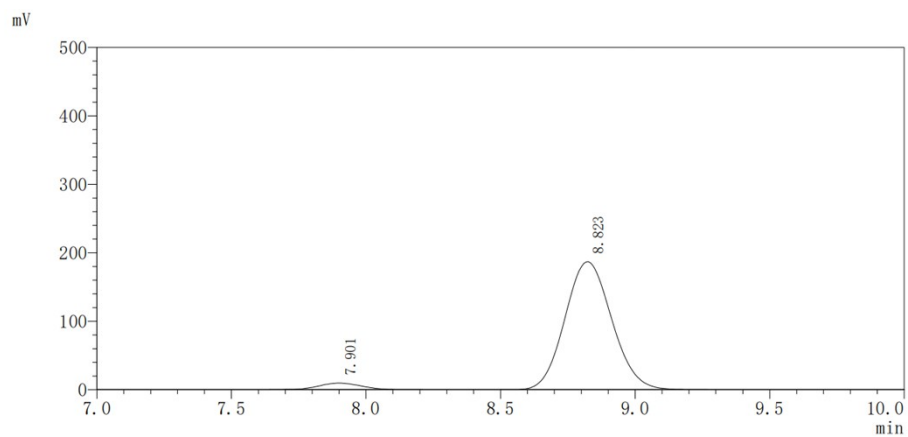
Chiral HPLC spectrum of racemic 15f



<Peak Results>

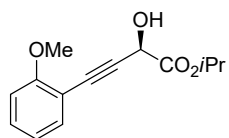
Index	Time/min	Area	Area%	Height	Height%
1	7.871	719590	49.961	63681	51.594
2	8.793	720725	50.039	59747	48.406

Chiral HPLC spectrum of chiral (R)-15f



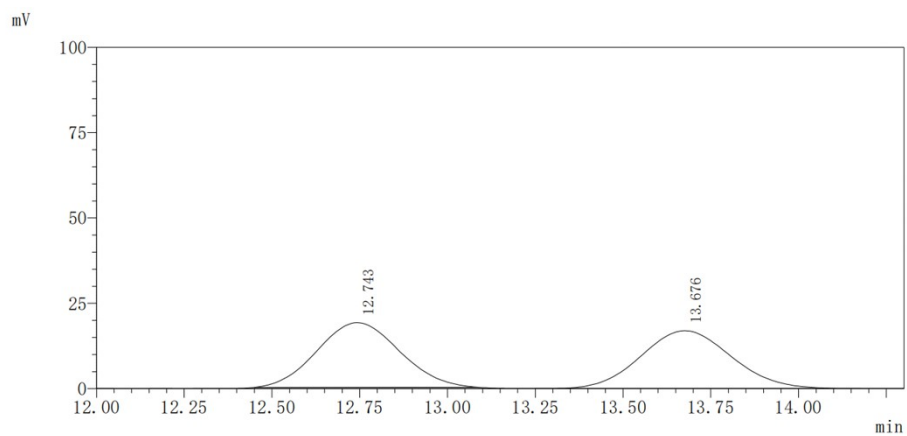
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	7.901	105248	4.447	9576	4.868
2	8.823	2261330	95.553	187135	95.132



15g

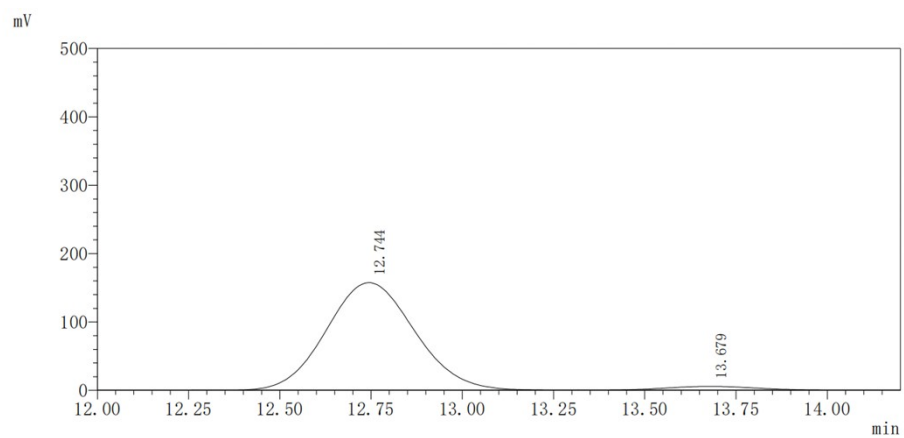
Chiral HPLC spectrum of racemic 15g



<Peak Results>

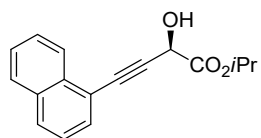
Index	Time/min	Area	Area%	Height	Height%
1	12.743	308749	50.178	18947	52.715
2	13.676	306559	49.822	16996	47.285

Chiral HPLC spectrum of chiral (R)-15g



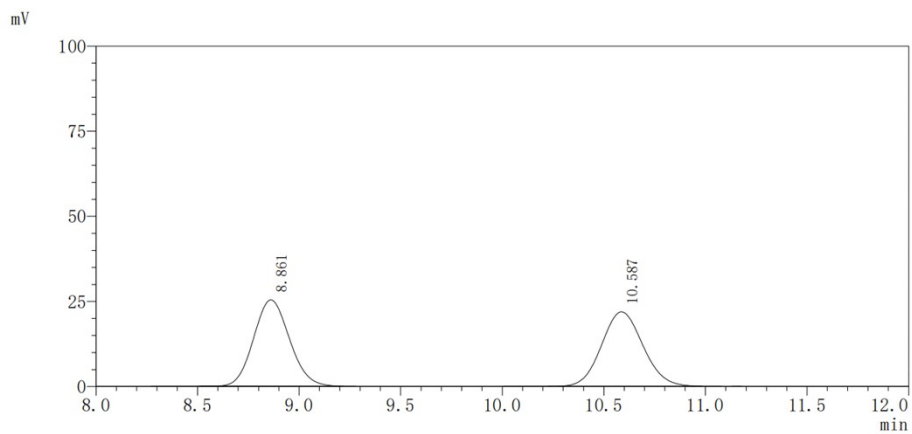
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	12.744	2674330	96.101	157671	96.386
2	13.679	108504	3.899	5912	3.614



15h

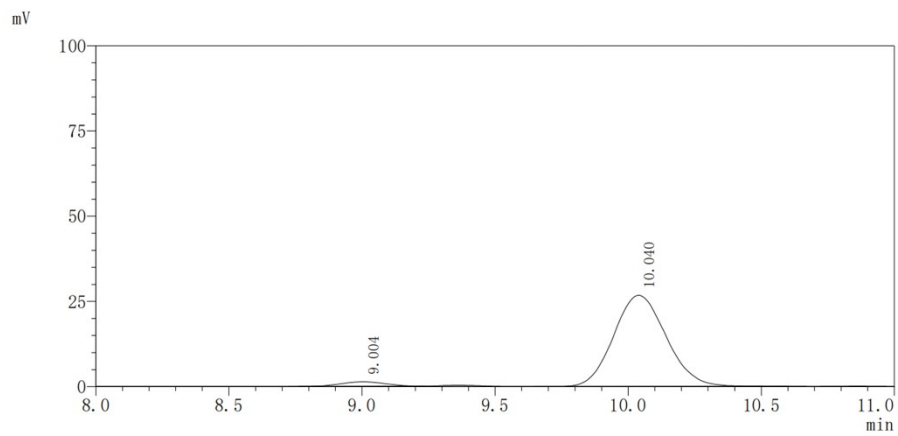
Chiral HPLC spectrum of racemic 15h



<Peak Results>

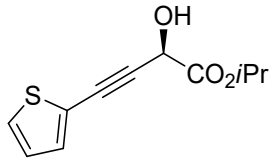
Index	Time/min	Area	Area%	Height	Height%
1	8.861	311138	50.101	25348	53.676
2	10.587	309879	49.899	21876	46.324

Chiral HPLC spectrum of chiral (R)-15h



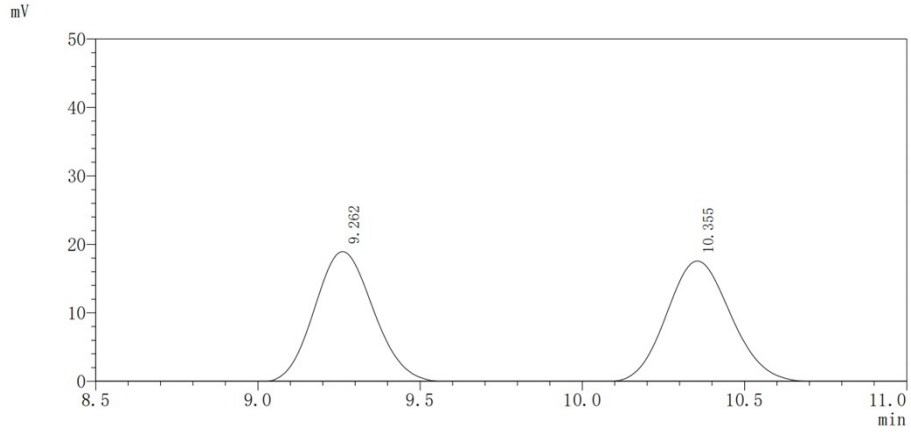
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	9.004	15477	4.016	1311	4.661
2	10.040	369871	95.984	26815	95.339



15i

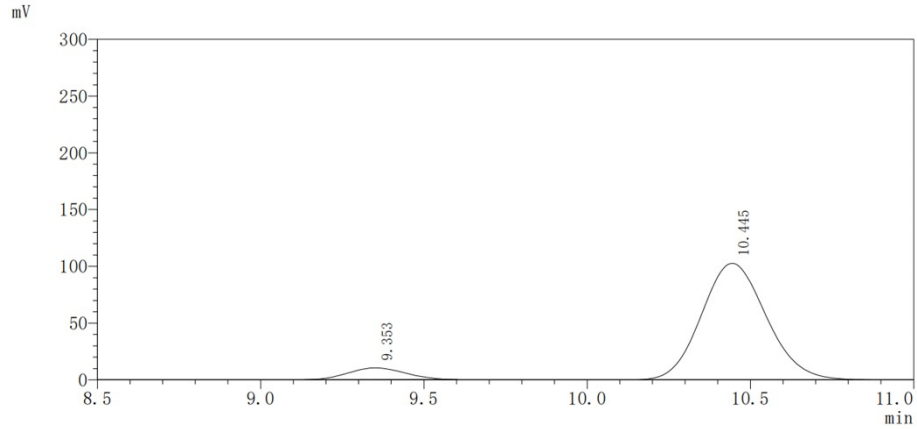
Chiral HPLC spectrum of racemic 15i



<Peak Results>

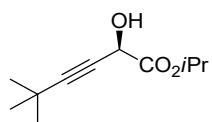
Index	Time/min	Area	Area%	Height	Height%
1	9.262	248118	49.681	19234	51.908
2	10.355	251307	50.319	17820	48.092

Chiral HPLC spectrum of chiral (R)-15i



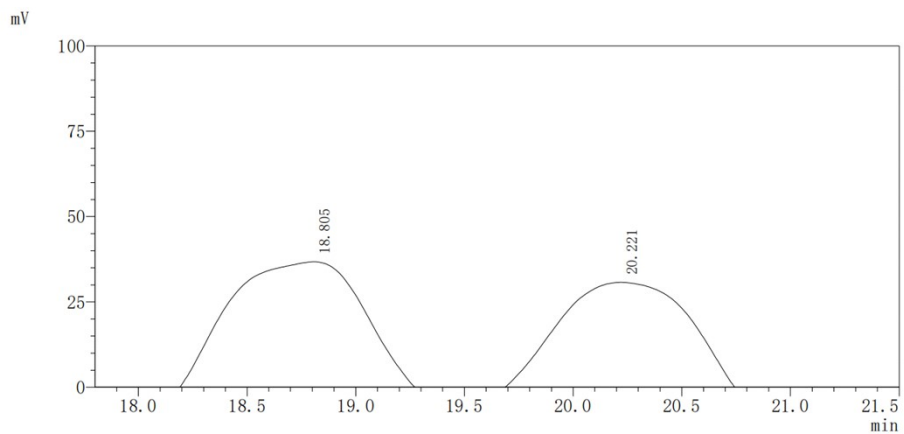
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	9.353	125912	8.183	10389	9.199
2	10.445	1412872	91.817	102547	90.801



15j

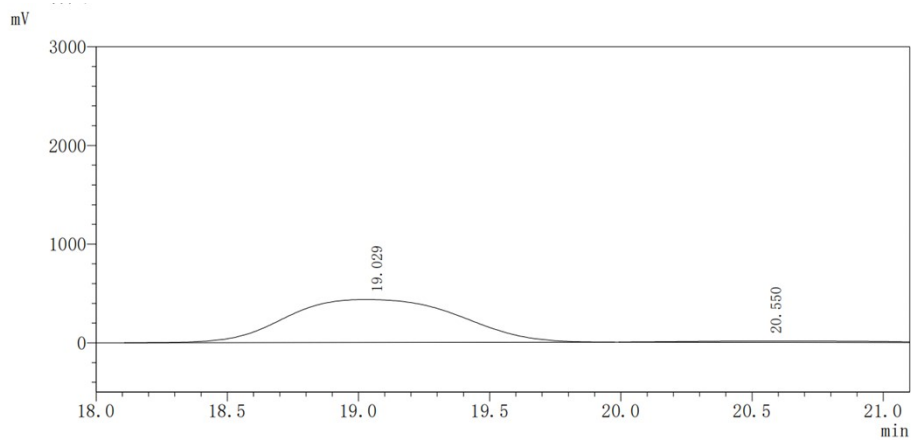
Chiral HPLC spectrum of racemic 15j



<Peak Results>

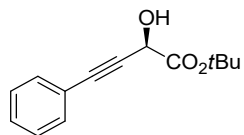
Index	Time/min	Area	Area%	Height	Height%
1	18.805	1917649	49.649	42164	51.205
2	20.221	1944768	50.351	40178	48.795

Chiral HPLC spectrum of chiral (R)-15j



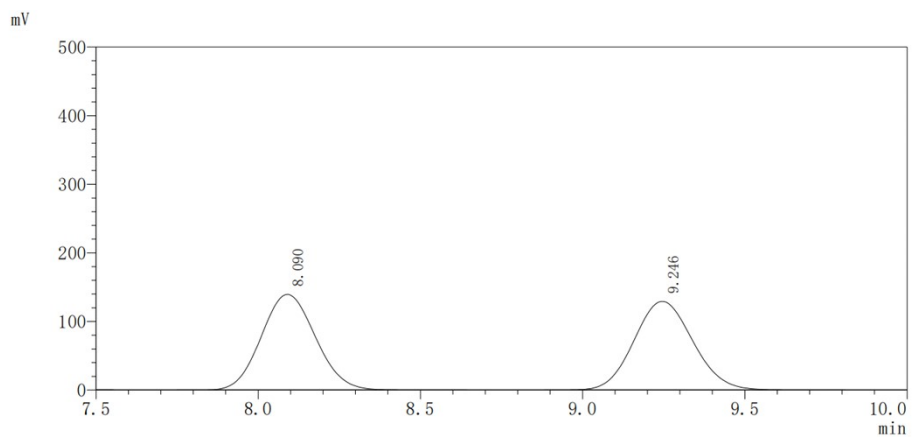
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	19.029	19623474	96.791	435368	97.038
2	20.550	650582	3.209	13291	2.962



15k

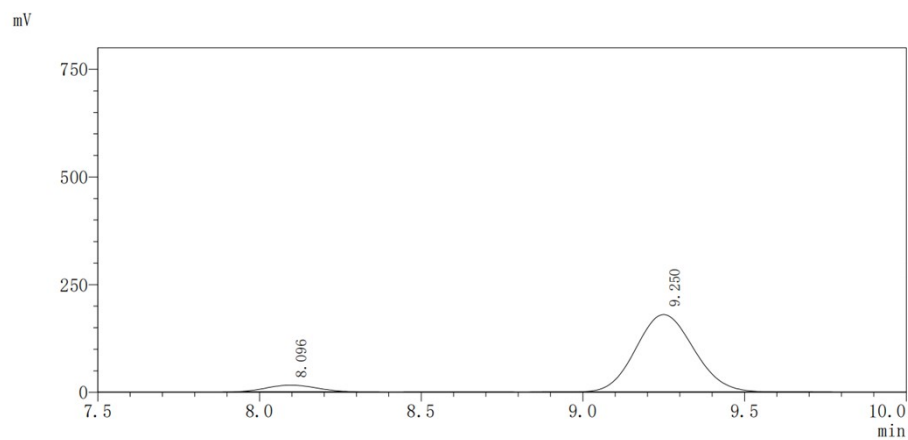
Chiral HPLC spectrum of racemic 15k



<Peak Results>

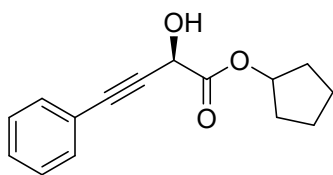
Index	Time/min	Area	Area%	Height	Height%
1	8.090	1618813	49.753	139377	51.905
2	9.246	1634909	50.247	129146	48.095

Chiral HPLC spectrum of chiral (R)-15k



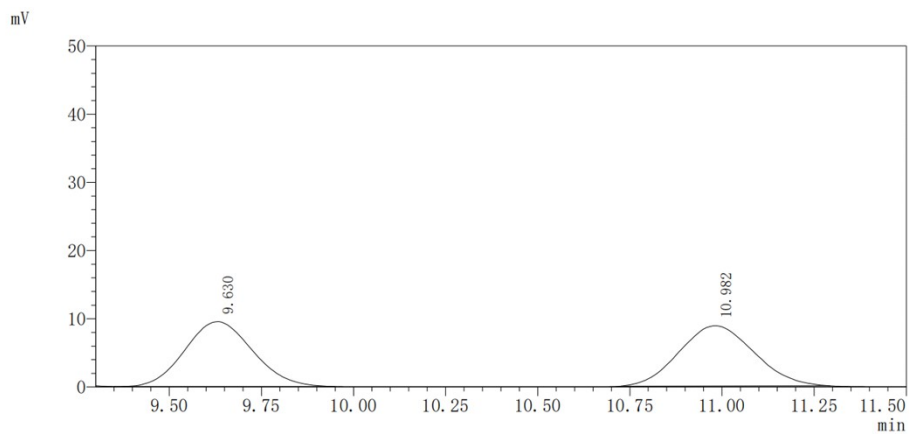
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	8.096	160848	6.642	15269	7.813
2	9.250	2260752	93.358	180164	92.187



15I

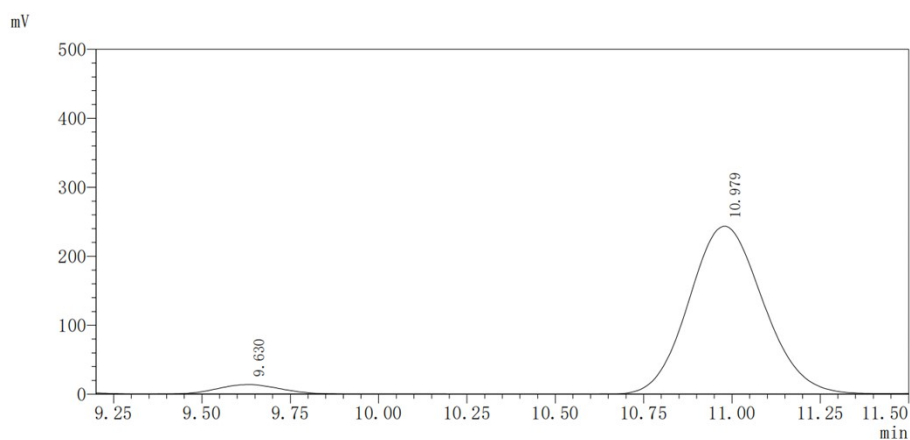
Chiral HPLC spectrum of racemic 15I



<Peak Results>

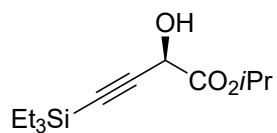
Index	Time/min	Area	Area%	Height	Height%
1	9.630	121995	49.515	9518	51.893
2	10.982	124386	50.485	8823	48.107

Chiral HPLC spectrum of chiral (R)-15I



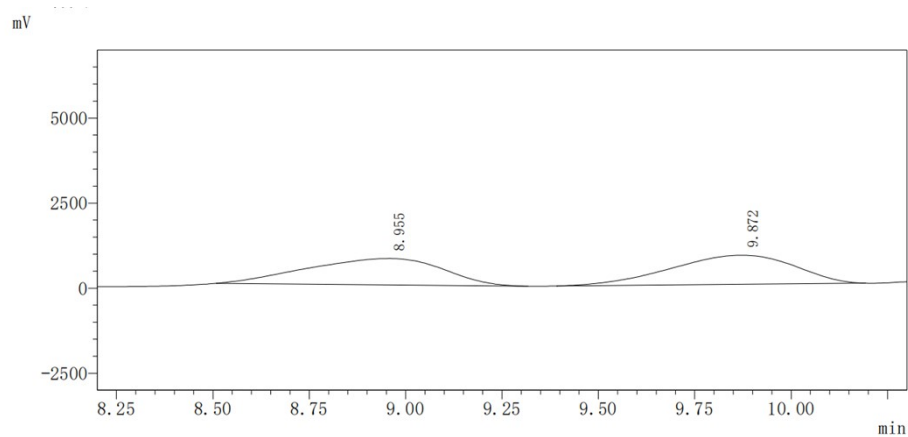
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	9.630	174866	4.640	13942	5.408
2	10.979	3593516	95.360	243866	94.592



15m

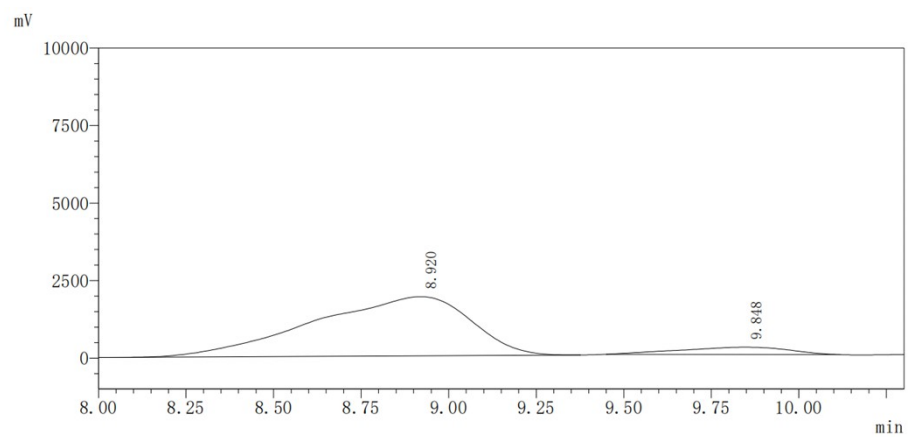
Chiral HPLC spectrum of racemic 15m



<Peak Results>

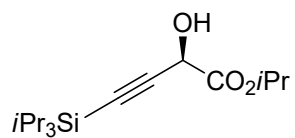
Index	Time/min	Area	Area%	Height	Height%
1	8.955	18957347	49.844	776118	47.561
2	9.872	19075766	50.156	855733	52.439

Chiral HPLC spectrum of chiral (R)-15m



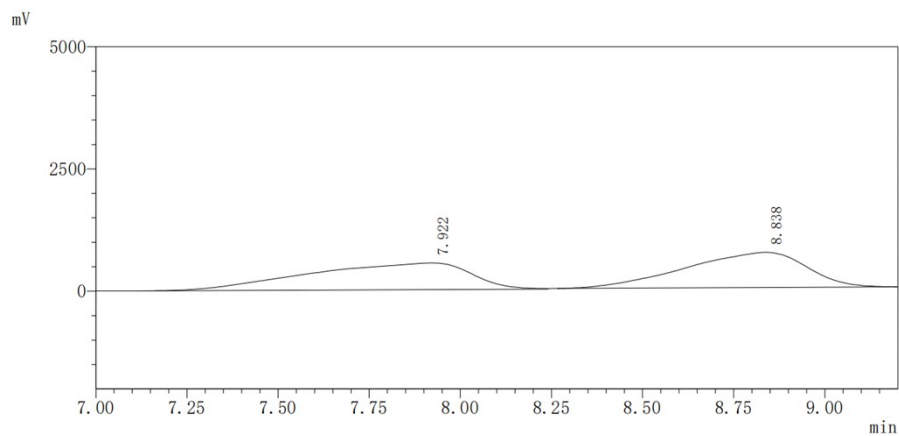
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	8.920	59746685	92.188	1909460	89.041
2	9.848	5062808	7.812	235023	10.959



15n

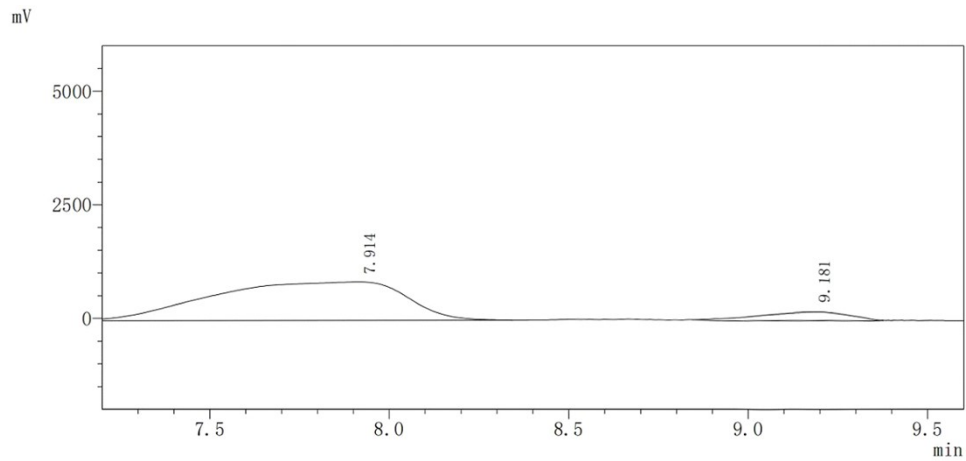
Chiral HPLC spectrum of racemic 15n



<Peak Results>

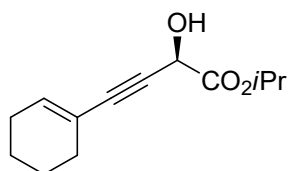
Index	Time/min	Area	Area%	Height	Height%
1	7.922	16901803	50.421	545086	43.162
2	8.838	16619743	49.579	717790	56.838

Chiral HPLC spectrum of chiral (R)-15n



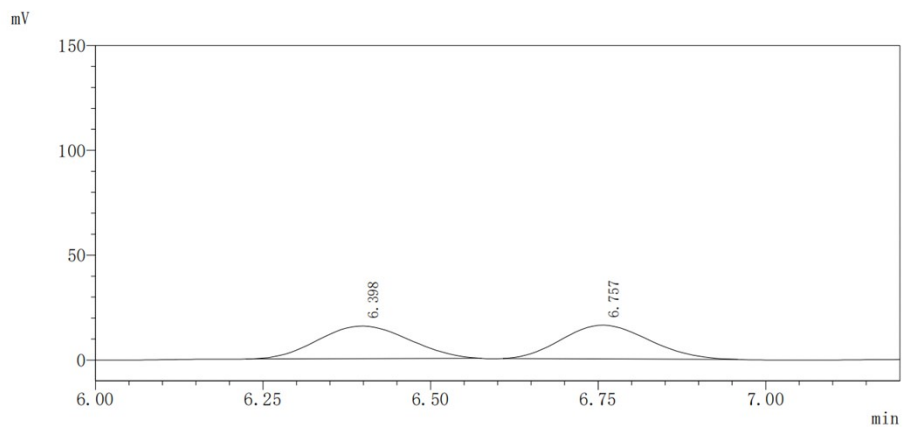
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	7.914	31488987	91.397	844779	84.098
2	9.181	2963952	8.603	159736	15.902



15o

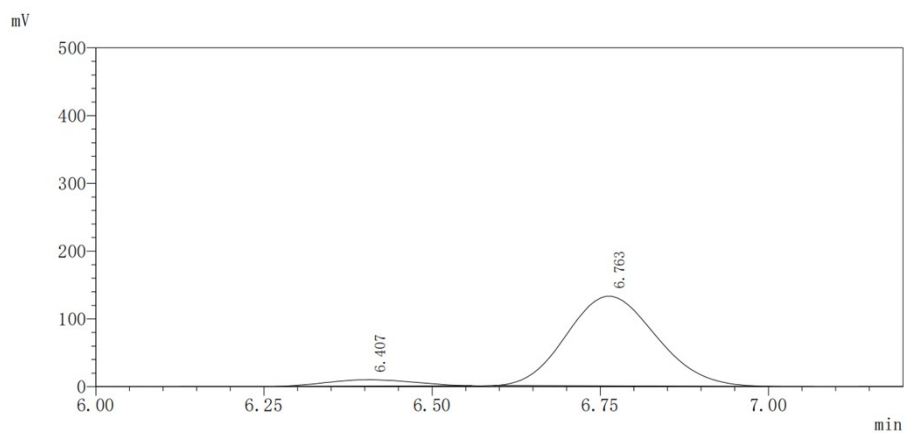
Chiral HPLC spectrum of racemic 15o



<Peak Results>

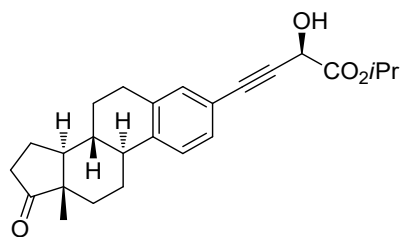
Index	Time/min	Area	Area%	Height	Height%
1	6.398	147565	50.311	15602	49.219
2	6.757	145739	49.689	16098	50.781

Chiral HPLC spectrum of chiral (R)-15o



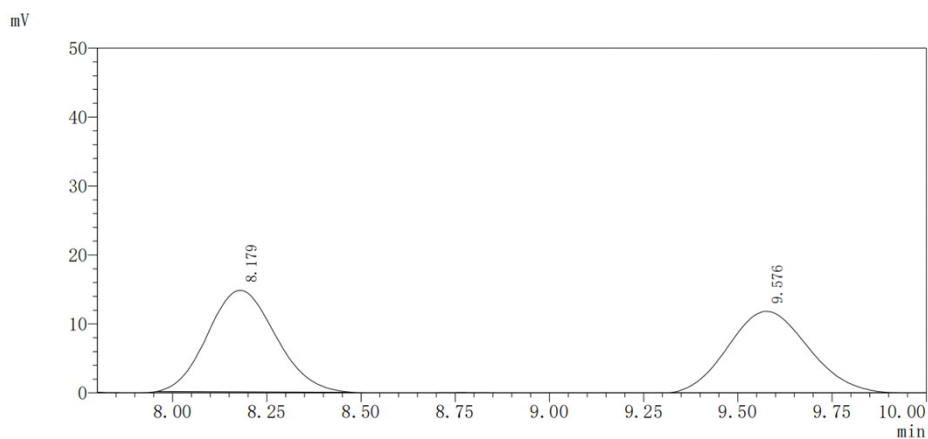
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	6.407	84579	6.416	9418	6.644
2	6.763	1233584	93.584	132333	93.356



15p

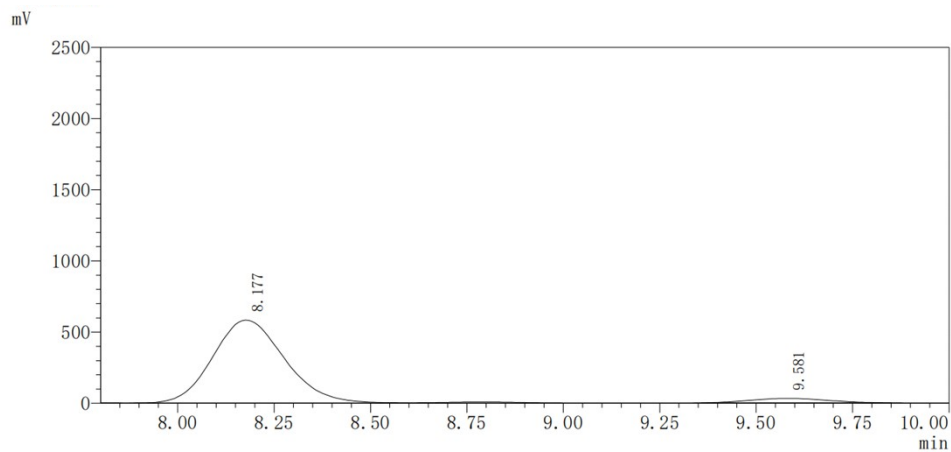
Chiral HPLC spectrum of racemic 15p



<Peak Results>

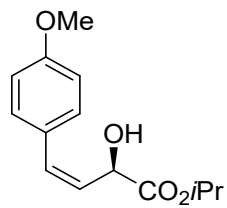
Index	Time/min	Area	Area%	Height	Height%
1	8.179	184520	50.363	14702	55.040
2	9.576	181862	49.637	12010	44.960

Chiral HPLC spectrum of chiral (R)-15p



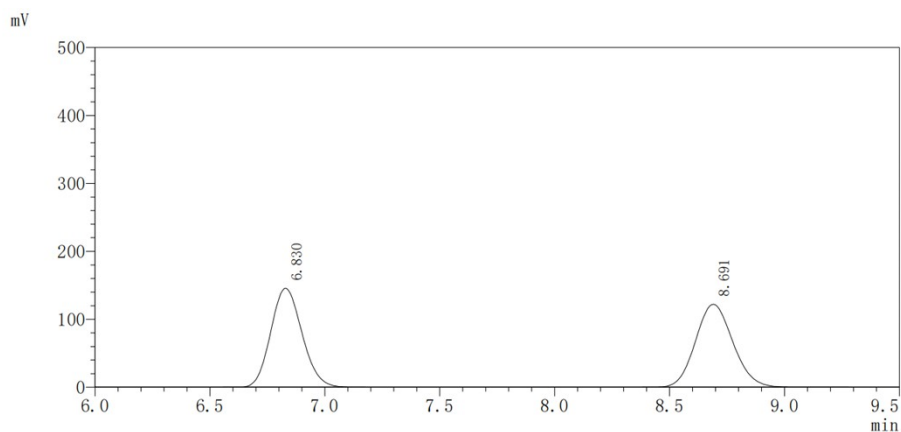
<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	8.177	7590954	94.426	583730	94.826
2	9.581	448101	5.574	31853	5.174



cis-3h

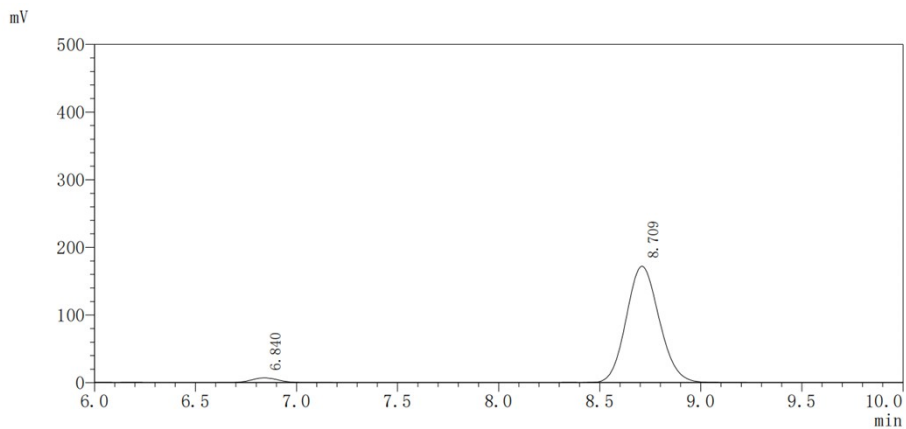
Chiral HPLC spectrum of racemic cis-3h



<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	6.830	1384645	50.043	145749	54.415
2	8.691	1382243	49.957	122100	45.585

Chiral HPLC spectrum of chiral cis-(R)-3h



<Peak Results>

Index	Time/min	Area	Area%	Height	Height%
1	6.840	68895	3.412	7154	3.995
2	8.709	1950040	96.588	171909	96.005

X. Reference

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2. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
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4. R. Peverati, D. G. Truhlar, *J. Phys. Chem. Lett.* 2011, **2**, 2810-2817.
5. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.