Supporting Information

Highly Regio- and Enantio-Selective Dienylation of p-Quinone Methides Enabled by Organocatalyzed Isomerization/Addition Cascade of Allenoates

De Wang,* Ze-Feng Song, Wei-Jia Wang and Tao Xu*

School of Medicine and Pharmacy, Ocean University of China

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1. General Informations

Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Chiral HPLC was performed on Agilent 1290 Infinity II LC System with chiral columns [Chiralpak IB-H, IC-H and AD-H columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd.)]. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica-gel-coated plates. Flash column chromatography was carried out by using silica gel at increased pressure.

Catalysts **CP3-CP10** were purchased from J&K Chemical Ltd., STREM or Alfa Aesar companies and used directly without further purification. **S1** and different aldehydes **S2** were purchased from Energy Chemical Company and used directly.

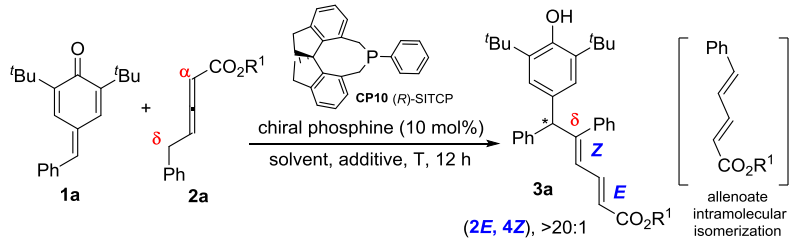
CP1[1] and **CP2**[2] were prepared according to the previously reported procedures.

Compounds *p*-quinone methides **1**[3] and δ-allenoates **2**[4] were prepared according to the previously reported procedures. Compounds **1a-1t,**[3] **2a**[4] and **4**[5] are known products, The known **S3(a-g)** and **S4(a-d)** were prepared according to the previously reported procedures [6]

All the racemic products were carried out with triphenylphosphine PPh_3 (20 mol%) or diphenylmethylphosphine Ph_2MeP (20 mol%) as catalyst in toluene at room temperature.

2. The condition optimizations

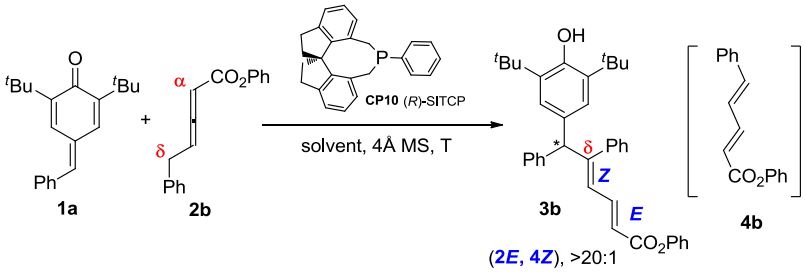
Table S1



entry[a]	cat.*	**2**: R^1	solvent	T (^oC)	additive	yield[b] (%)	ee[c] (%)
1	**CP10**	**2a**: Bn	DCM	20	-	64	57
2	**CP10**	**2a**: Bn	THF	20	-	24	67
3	**CP10**	**2a**: Bn	Et_2O	20	-	42	62
4	**CP10**	**2a**: Bn	benzene	20	-	47	71
5	**CP10**	**2a**: Bn	chlorobenzene	20	-	62	70
6	**CP10**	**2a**: Bn	*p*-xylene	20	-	69	71
7	**CP10**	**2a**: Bn	*o*-xylene	20	-	82	67
8[f]	**CP10**	**2a**: Bn	toluene	20	H_2O	16	80
9[f]	**CP10**	**2a**: Bn	toluene	20	(*R*)-BINOL	16	70
10[f]	**CP10**	**2a**: Bn	toluene	20	benzoic acid	-[e]	-
11	**CP10**	**2a**: Bn	toluene	20	4Å MS	73	77
12[g]	**CP10**	**2a**: Bn	toluene	0	4Å MS	65	82
13[g]	**CP10**	**2a**: Bn	*o*-xylene	0	4Å MS	68	65
14[g]	**CP10**	**2a**: Bn	toluene	-20	4Å MS	8	75
15[g]	**CP10**	**2a-1**: Et	toluene	0	4Å MS	65	81
16[g]	**CP10**	**2a-2**: ^{t}Bu	toluene	0	4Å MS	72	77
17[g]	**CP10**	**2a-3**: $CH(Ph)_2$	toluene	0	4Å MS	85	79

[a] All reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (10 mol%) in corresponding solvent (1.0 mL); [b] Isolated yield; [c] Determined by chiral HPLC; [d] Obtained an allenotae isomerized product; [e] Trace product, starting materials recover; [f] Adding 20 mol% additives to the reaction system. [g] The reaction run 48 hours.

Table S2

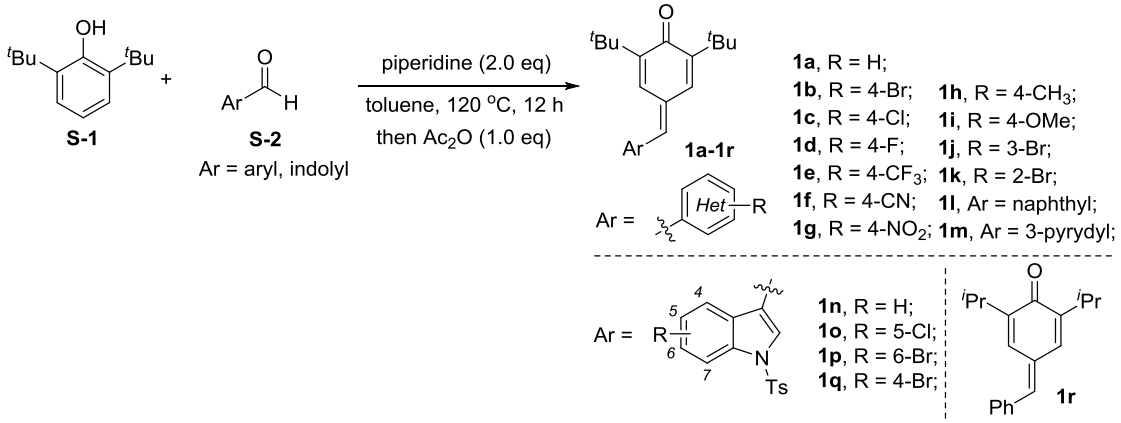


entry[a]	cat. (x mol%)	solvent	T (^oC)	mol (1a/2)	yield[b] (%)	ee[c] (%)
1[d]	10	toluene	0	1/1	30 (38)	93 (90)
2	10	toluene	10	1/1	47	85
3	10	toluene	20	1/1	58	82
4	10	toluene	0	1/2	48	92
5	10	toluene	0	2/1	15	93
6	20	toluene	0	1/2	65	93
7	20	toluene	0	1/3	63	92
8	20	chlorobenzene	0	1/2	17	93
9	10	*o*-xylene	0	1/2	35	90
10	20	toluene/DCM	0	1/2	30	90
11	25	toluene	0	1/2	69	91
12[e]	10	*p*-xylene	15	1/2	73	85
13[f]	10	toluene	0	1/2	69	93
14[g]	10	toluene	0	1/2	64	93

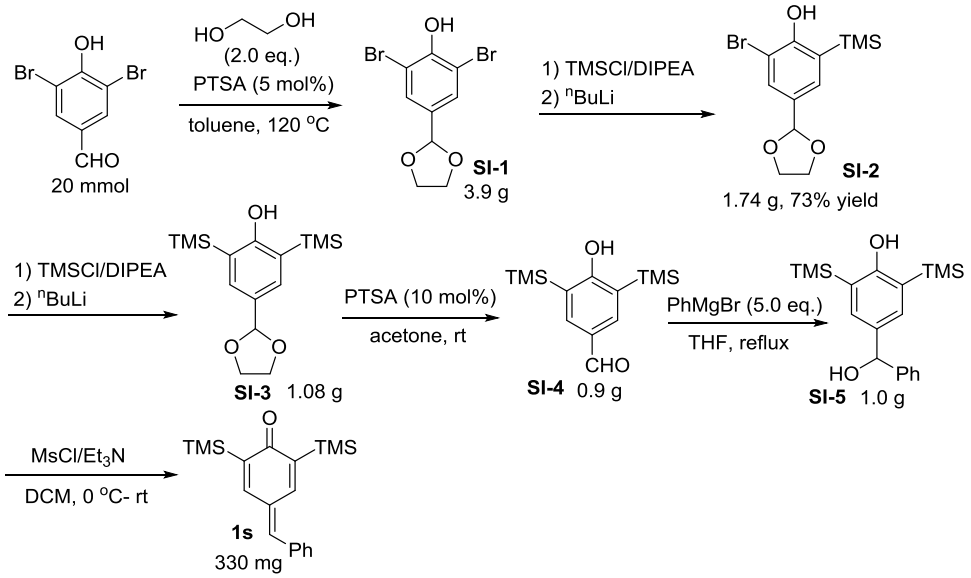
[a] All reactions were carried out with **1a** (0.1 mmol), **2b** (0.2 mmol), (R)-SITCP (10 mol%) in corresponding solvent (1.0 mL) at indicated solvent; [b] Isolated yield; [c] Determined by chiral HPLC; [d] Repeat result in parentheses. [e] Diluted in 2 mL *p*-Xylene, without 4A MS as additive. [f] Diluted in 4 mL toluene, without 4A MS as additive. [g] Diluted in 6 mL toluene, without 4A MS as additive.

3. Experimental procedure and characterization datas

General procedure (I) for the synthesis of *p*-QM (1a-1r) [3]



To a solution of 2,6-di-*tert*-butylphenol **S-1** (10 mmol) in toluene (30 mL) was added different aldehyde **S-2** (10 mmol). The reaction mixture was heated in a dry Schlenk tube to reflux. Piperidine (20 mmol) was added drop wise slowly (approx. 0.5 h), and the reaction mixture continued to reflux for 12 h. After the mixture had cooled just below the boiling point of toluene, acetic anhydride (20 mmol) was added, and then the solution was stirred for one hour. The residue was extracted three times with dichloromethane. The combined organic layers were washed with water and brine sequentially, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (pure PE to PE/EA = 200:1, R_f = 0.9-0.6) to afford the corresponding product yellow to red solid **1a-1r** (Known products).



In a Dean-Stark apparatus, 3,5-dibromo-4-hydroxybenzaldehyde (20 mmol, 5.56 g) and PTSA (1 mmol, 190 mg) were dissolved in toluene (60 mL) under N_2 atmosphere and heated to reflux. To the stirred solution was added glycol (40 mmol, 2.23 mL). After stirred overnight, K_2CO_3 (4.0 mmol, 552 mg) was added and stirring was continued for 1 h. Then, the mixture was filtered and the solvents were removed under reduce pressure. The residue was purified by chromatography (PE/EA = 10/1) to obtain the pure product **SI-1** (white solid, 3.9 g, 61% yield).

A mixture of **SI-1** (2.44 g, 7.5 mmol), TMSCl (11.25 mmol, 1.43 mL), DIPEA (11.25 mmol, 1.85 mL) in THF (15 mL) was stirred for 1 hour at room temperature and then the solids were removed by filtration and the solution was concentrated by rotary evaporation. The crude TMS protecting product was cooled to -78 ℃. 2.5M ^{n}BuLi (7.5 mmol, 3.0 mL) was slowly added and the mixture was allowed warm to room temperature for 3 hours. After quenching with saturated NH_4Cl, the mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography (PE/EA = 12/1) to afford product **SI-2** (white solid, 1.74 g, 73% yield).

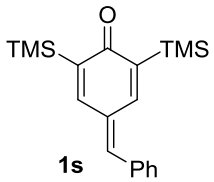
A mixture of **SI-2** (5.5 mmol, 1.74 g), TMSCl (8.26 mmol, 1.05 mL), DIPEA (8.26 mmol, 1.36 mL) in THF (15 mL) was stirred for 1 hour at room temperature and then the solids were removed by filtration and the solution was concentrated by rotary evaporation. The crude product was then cooled to -78 ℃. 2.5M ^{n}BuLi (4.92 mmol, 3.1 mL) was slowly added and the mixture was allowed warm to room temperature for 3 hours. After quenching with saturated NH_4Cl, the mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The solids were removed by filtration and the solution was concentrated by rotary evaporation to obtain a slight pink solid. The solid was washed with a small amount of n-hexane (5 mL) and filtered to afford white solid product **SI-3** (1.08 g, 63% yield).

SI-3 (3.5 mmol, 1.08 g) was dissolved in acetone, and PTSA (0.35 mmol, 66 mg) was added. The mixture was stirred for 1 h and diluted with EtOAc and H_2O. The mixture was extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The

solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue **SI-4** (white solid, 901 mg, 97% yield) was pure enough for next step.

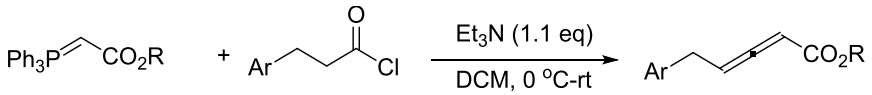
SI-4 (3.38 mmol, 0.9 g) was dissolved in anhydrous THF (15 mL) at 0 ℃ under N_2 atmosphere. Then PhMgBr (3 M in Et_2O, 13.54 mmol, 4.5 mL) was slowly added. Then the reaction mixture was refluxed for 1 hour and quenched with saturated NH_4Cl. After extraction with EtOAc, the mixture was washed with brine, and dried over anhydrous Na_2SO_4. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography (PE/EA = 20/1) to afford product **SI-5** (yellowish oil, 1.0 g, 86% yield).

A mixture of **SI-5** (1.0 mmol, 344 mg), Et_3N (2.2 mmol, 0.3 mL) in dry DCM (15 mL) was slowly added MsCl (1.1 mmol, 90 L) at 0 °C. The mixture was allowed warm to room temperature and stirred for 30 mins. The mixture was then diluted with DCM and H_2O, then the mixture was extracted with DCM, and dried over anhydrous Na_2SO_4. The mixture was filtrated and concentrated by rotary evaporation. The crude product **1s** (yellow solid, 330 mg) was used directly without any purification.



Compound **1s**: This is a known compound, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J_1 = 0.8 Hz, J_2 = 2.8 Hz, 1H), 7.50-7.41 (m, 5H), 7.35 (dd, J_1 = 0.4 Hz, J_2 = 2.8 Hz, 1H), 7.27 (s, 1H), 0.25 (s, 9H), 0.22 (s, 9H). The data was in accordance with reported ref[3b]

General procedure (II) for the synthesis of δ-substituted allenoates (2a-2i) [4]



S3-a, R = Bn
S3-b, R = Ph
S3-c, R = 4-MeC_6H_4
S3-d, R = 4-$MeOC_6H_4$
S3-e, R = 3,5-$(MeO)_2C_6H_3$
S3-f, R = 4-ClC_6H_4
S3-g, R = Et

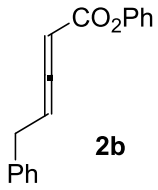
S4-a, Ar = Ph
S4-b, Ar = 4-MeC_6H_4
S4-c, Ar = 4-BrC_6H_4
S4-d, Ar = 4-FC_6H_4

2a, R = Bn, Ar = Ph
2b, R = Ph, Ar = Ph
2c, R = Ph, Ar = 4-MeC_6H_4
2d, R = Ph, Ar = 4-BrC_6H_4
2e, R = Ph, Ar = 4-FC_6H_4
2f, R = 4-MeC_6H_4, Ar = Ph
2g, R = 4-$MeOC_6H_4$, Ar = Ph
2h, R = 3,5-$(MeO)_2C_6H_3$, Ar = Ph
2i, R = 4-ClC_6H_4, R = Ph

To a solution of phosphine ylide **S3** (5 or 10 mmol) in DCM (40 mL) was added 3-arylpropanoyl chloride **S4** (1.1 eq.) and triethylamine (1.1 eq.) sequentially under nitrogen protection at 0 °C, then the reaction mixture was allowed warm to room temperature. After two to three hours later (TLC monitor), Et_2O was added to the

reaction mixture and filter to remove the white salt ($Et_3N{\cdot}HCl$). The organic phase was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/Et_2O：20/1 to 10/1, R_f = 0.5-0.6) to afford the corresponding allenoate product **2**. (all the allenoates contain an alkynyl isomer as minor products, inseparable).

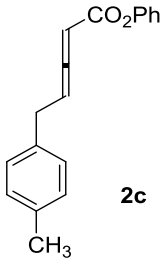
Phenyl 5-phenylpenta-2,3-dienoate (2b)



2b

Compound **2b** (2.12 g, 85% yield, allenoate: isomer = >19:1) was obtained as a yellowish oil following the *general procedure II* from **S3-b** (10 mmol, 3.96 g) and **S4-a** (11 mmol, 1.65 mL) stirred for 3 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.32-7.31 (m, 4H), 7.26-7.22 (m, 2H), 7.14-7.12 (m, 2H), 5.89 (dt, J_1 = 6.0 Hz, J_2 = 7.6 Hz, 1H), 5.80 (dt, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 1H), 3.60-3.48 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.8, 164.4, 150.8, 138.3, 129.4, 128.6, 128.5, 126.7, 125.8, 121.5, 95.4, 88.3, 34.0; **IR** (neat) ν 3028, 2917, 1957, 1739, 1724, 1590, 1488, 1451, 1409, 1195, 1128, 748, 700 cm^{-1}; **HRMS** Calcd. for $C_{17}H_{15}O_2^+$ $[M+H]^+$: 251.1072, found: 251.1067.

Metyl-4-(5-phenoxy-5-penta-2,3-dien-1-yl)benzene (2c)

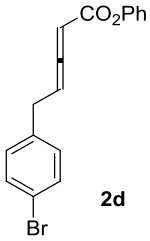


2c

Compound **2c** (2.01 g, 76% yield, allenoate:isomer = 5.6:1) was obtained as a yellowish oil following the *general procedure II* from **S3-b** (10 mmol, 3.96 g) and **S4-b** (11 mmol, 1.82 g) stirred for 3 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.28-7.25 (m, 2H), 7.20-7.18 (m, 1H), 7.14-7.11 (m, 4H), 5.87 (dt, J_1 = 6.0

Hz, J_2 = 7.2 Hz, 1H), 5.79 (dt, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 1H), 3.56-3.44 (m, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.8, 164.4, 150.8, 136.3, 135.3, 129.5, 129.4, 129.2, 128.4, 127.8, 126.1, 125.8, 121.5, 121.3, 95.6, 88.2, 33.6, 21.0; **IR** (neat) ν 3028, 2917, 1957, 1723, 1491, 1231, 1194, 1160, 1127, 802, 686 cm^{-1}; **HRMS** Calcd. for $C_{18}H_{17}O_2^+$ $[M+H]^+$: 265.1229, found: 265.1221.

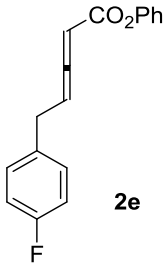
1-Bromo-4-(5-phenoxy-5-penta-2,3-dien-1-yl)benzene (2d)



2d

Compound **2d** (2.69 g, 82% yield, allenoate: isomer = 4.7:1) was obtained as a yellowish oil following the *general procedure II* from **S3-b** (10 mmol, 3.96 g) and **S4-c** (11 mmol, 2.46 g) stirred for 3 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 4H), 7.29-7.24 (m, 1H), 7.21-7.17 (m, 2H), 7.16-7.13 (m, 2H), 5.90-5.81 (m, 2H), 3.54-3.43 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.8, 164.1, 150.6, 137.2, 131.5, 130.3, 129.4, 125.8, 121.4, 94.9, 88.5, 33.3; **IR** (neat) ν 3032, 2918, 1960, 1723, 1488, 1409, 1194, 1129, 1011, 802, 686 cm^{-1}; **HRMS** Calcd. for $C_{17}H_{14}O_2Br^+$ $[M+H]^+$: 329.0177, found: 329.0170.

Fluoro-4-(5-phenoxy-5-penta-2,3-dien-1-yl)benzene (2e)

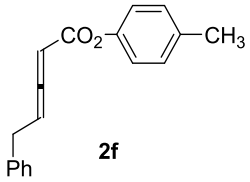


2e

Compound **2e** (2.44 g, 91% yield, allenoate: isomer = 5.0:1) was obtained as a yellowish oil following the *general procedure II* from **S3-b** (10 mmol, 3.96 g) and **S4-d** (11 mmol, 1.86 g) stirred for 2 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.28-7.22 (m, 3H), 7.13-7.11 (m, 2H), 7.02-6.97 (m, 2H), 5.87 (dt, J_1 = 6.0

Hz, J_2 = 7.6 Hz, 1H), 5.79 (dt, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 1H), 3.56-3.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.8, 164.3, 161.7 (d, J = 243.4 Hz), 150.8, 133.9 (d, J = 3.0 Hz), 130.1 (d, J = 8.0 Hz), 129.4, 125.9, 121.5, 115.3 (d, J = 21.2 Hz), 95.4, 88.5, 33.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.07 to -116.13 (m) ppm; **IR** (neat) ν 3042, 2917, 1960, 1725, 1593, 1508, 1491, 1412, 1223, 1194, 1160, 1129, 821, 686 cm^{-1}; **HRMS** Calcd. for $C_{17}H_{14}O_2F^+$ $[M+H]^+$: 269.0978, found: 269.0972.

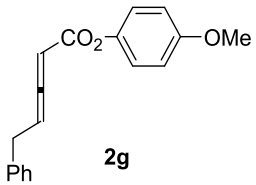
_p_-Tolyl 5-phenylpenta-2,3-dienoate (2f)



2f

Compound **2f** (830 mg, 63% yield, allenoate: isomer = 5.8:1) was obtained as a yellowish oil following the *general procedure II* from **S3-c** (5 mmol, 2.05 g) and **S4-a** (5.5 mmol, 0.82 mL) stirred for 2 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.30 (m, 4H), 7.24-7.22 (m, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.91-5.85 (m, 1H), 5.80-5.77 (m, 1H), 3.57-3.48 (m, 2H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.7, 164.6, 148.6, 138.4, 135.4, 129.9, 128.6, 128.5, 126.7, 121.2, 95.3, 88.3, 34.0, 20.9; **IR** (neat) ν 3028, 2917, 1957, 1723, 1599, 1505, 1451, 1193, 1127, 1030, 698 cm^{-1}; **HRMS** Calcd. for $C_{18}H_{17}O_2^+$ $[M+H]^+$: 265.1229, found: 265.1220.

4-Methoxyphenyl 5-phenylpenta-2,3-dienoate (2g)

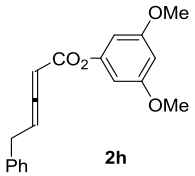


2g

Compound **2g** (1.74 g, 62% yield, allenoate: isomer = 16.7:1) was obtained as a yellow oil following the *general procedure II* from **S3-d** (10 mmol, 4.26 g) and **S4-a** (11 mmol, 1.65 mL) stirred for 2 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.26-7.22 (m, 1H), 7.07-7.03 (m, 2H), 6.93-6.89 (m, 2H), 5.88 (dt, J_1 = 6.4 Hz, J_2 = 7.2 Hz, 1H), 5.78 (dt, J_1 = 2.8 Hz, J_2 = 6.4 Hz, 1H), 3.81 (s, 3H), 3.59-3.48 (m,

2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.7, 164.8, 157.2, 144.3, 138.4, 128.6, 128.5, 126.7, 122.3, 114.4, 95.3, 88.3, 55.6, 34.0; **IR** (neat) ν 3028, 2917, 1957, 1728, 1598, 1505, 1451, 1234, 1192, 1127, 1031, 697 cm^{-1}; **HRMS** Calcd. for $C_{18}H_{17}O_3^+$ $[M+H]^+$: 281.1178, found: 281.1169.

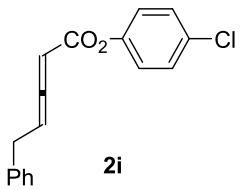
3,5-Dimethoxyphenyl 5-phenylpenta-2,3-dienoate (2h)



2h

Compound **2h** (1.79 g, 58% yield, allenoate: isomer = 2.4:1) was obtained as a yellow oil following the general procedure from **S3-e** (10 mmol, 4.56 g) and **S4-a** (11 mmol, 1.65 mL) stirred for 3 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.28 (m, 4H), 7.25-7.22 (m, 1H), 6.36 (t, J = 2.4 Hz, 1H), 6.31-6.30 (m, 2H), 5.89 (dt, J_1 = 6.0 Hz, J_2 = 7.6 Hz, 1H), 5.78 (dt, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 1H), 3.78 (s, 6H), 3.57-3.52 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.8, 171.2, 164.2, 161.0, 152.3, 140.0, 138.3, 128.6, 128.5, 128.4, 127.9, 126.7, 126.4, 100.1, 98.3, 98.2, 95.4, 88.2, 55.5, 55.4, 36.0, 34.0, 30.9; **IR** (neat) ν 3028, 2937, 1957, 1737, 1612, 1474, 1426, 1208, 1155, 1132, 1059, 830, 697 cm^{-1}; **HRMS** Calcd. for $C_{19}H_{19}O_4^+$ $[M+H]^+$: 311.1283, found: 311.1274.

4-Chlorophenyl 5-phenylpenta-2,3-dienoate (2i)

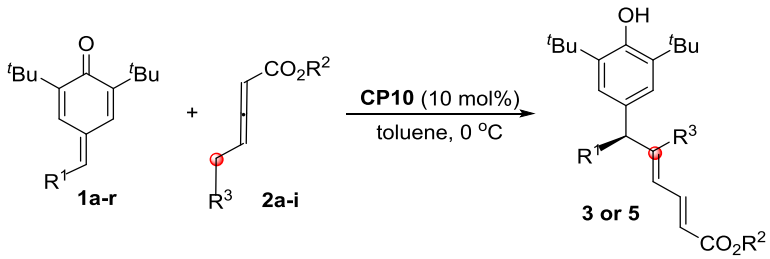


2i

Compound **2i** (1.46 g, 52% yield, allenoate: isomer = 8.3:1) was obtained as a yellowish oil following the *general procedure II* from **S3-f** (10 mmol, 4.3 g) and **S4-a** (11 mmol, 1.65 mL) stirred for 3 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.23 (m, 1H), 7.08-7.06 (m, 2H), 5.93-5.87 (m, 1H), 5.79-5.76 (m, 1H), 3.57-3.48 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.0, 164.1,

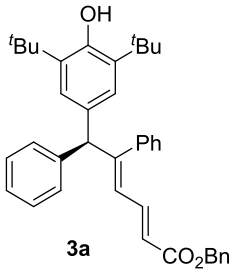
149.3, 138.3, 131.1, 129.5, 128.6, 128.5, 127.9, 126.8, 122.9, 95.6, 88.1, 34.0; **IR** (neat) ν 3025, 2920, 1960, 1734, 1486, 1201, 1127, 1087, 1014, 737, 700 cm^{-1}; **HRMS** Calcd. for $C_{17}H_{12}O_3Cl^-$ [M-H]$^-$: 283.0526, found: 283.0527.

General procedure (III) for enantioselective dienylation to prepare 3 and 5.



Compounds *p*-quinone methides **1** (0.1 mmol), (*R*)-SITCP (0.01 mmol) and anhydrous toluene (4.0 mL) were added into a pre-heated Schlenk tube and cooled to 0 ^oC, then allenoate **2** (0.2 mmol) was added to the above mixture under nitrogen protection. The reaction mixture was stirred at this temperature for the indicated time (TLC monitored). The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA：100/1-20/1) to afford the corresponding product **3** or **5**.

(S)-Benzyl (2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-diphenylhexa-2,4-dienoate (**3a**)

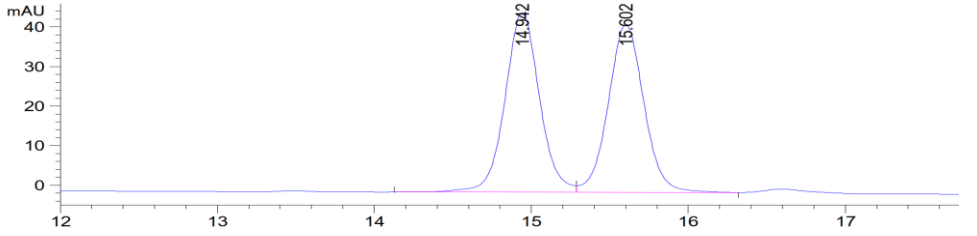


Compound **3a** (37.7 mg, 65% yield) was obtained as a yellowish solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2a** (0.12 mmol, 32 mg, 30 μL) stirred for 12 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.33-7.25 (m, 9H), 7.23-7.18 (m, 3H), 7.15-7.13 (m, 2H), 6.93 (s, 2H), 5.99 (d, *J* = 11.6 Hz, 1H), 5.85 (d, *J* = 15.4 Hz, 1H), 5.19 (s, 1H), 5.13 (s, 2H), 5.09 (s, 1H), 1.37 (s, 18H); **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 167.1, 156.1, 152.5, 142.9, 142.2, 140.3, 136.4, 135.7, 131.6, 129.6, 129.0, 128.8, 128.6, 128.4, 128.24, 128.16, 128.1, 127.8, 126.6, 126.2, 121.1, 66.0, 59.9, 34.5, 30.5; **IR** (neat) ν 3624, 2957, 1697, 1621, 1494, 1434, 1375, 1262, 1234, 1149, 1121, 991, 771, 694 cm^{-1}; **Mp**: 122-124 ℃. **HRMS** Calcd. for $C_{39}H_{42}O_3Na^+$ $[M+Na]^+$: 581.3032, found: 581.3026.

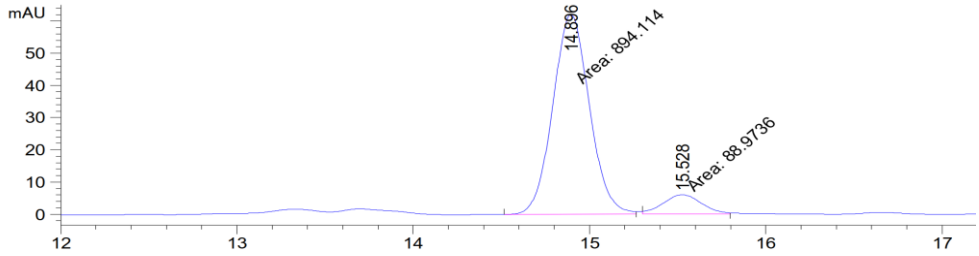
$[\alpha]^{20}_D$ = +1.2 (c 0.27, CH_2Cl_2) for 82% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 15.528 min, t_{major} = 14.896 min.

Racemic Sample 3a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.942	BV	0.2324	694.20300	45.39057	50.8804
2	15.602	VB	0.2424	670.17993	42.40434	49.1196

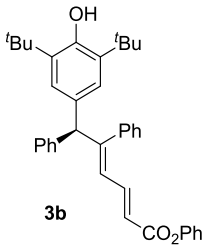
Enantiomeric Sample 3a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.896	MM	0.2406	894.11377	61.94126	90.9496
2	15.528	MM	0.2509	88.97361	5.91143	9.0504

(S)-Phenyl

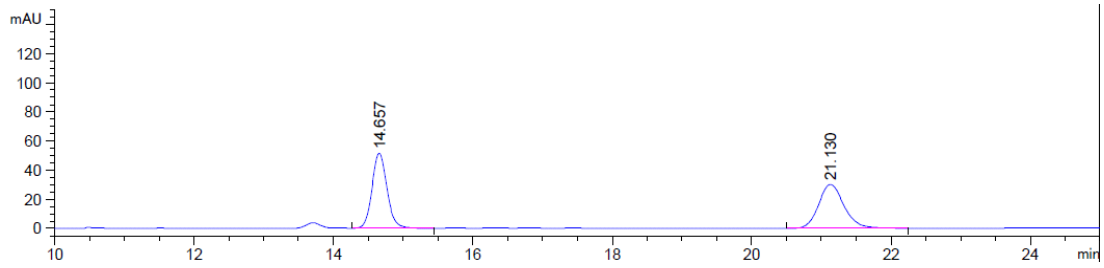
(2E,4Z)-6-(3,5-ditert-butyl-4-hydroxyphenyl)-5,6-diphenylhexa-2,4-dienoate (**3b**)



Compound **3b** (39.1 mg, 69% yield) was obtained as a yellowish solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dd, J_1 = 11.6, J_2 = 15.2 Hz, 1H), 7.37-7.28 (m, 7H), 7.23-7.21 (m, 3H), 7.20-7.17 (m, 3H), 7.07 (d, J = 7.6 Hz, 2H), 6.97 (s, 2H), 6.09 (d, J = 11.6 Hz, 1H), 6.01 (d, J = 15.2 Hz, 1H), 5.24 (s, 1H), 5.13 (s, 1H), 1.40 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 156.9, 152.4, 150.8, 144.0, 141.9, 140.0, 135.6, 131.4, 129.4, 129.2, 128.8, 128.3, 128.1, 128.0, 127.8, 126.5, 126.1, 125.5, 121.6, 120.4, 59.8, 34.3, 30.3; **IR** (neat) ν 3630, 2957, 1726, 1621, 1590, 1491, 1434, 1231, 1194, 1160, 1115, 751, 700 cm^{-1}; **MP**: 77-79 ℃. **HRMS** Calcd. for $C_{38}H_{40}O_3Na^+$ $[M+Na]^+$: 567.2875, found: 567.2871.

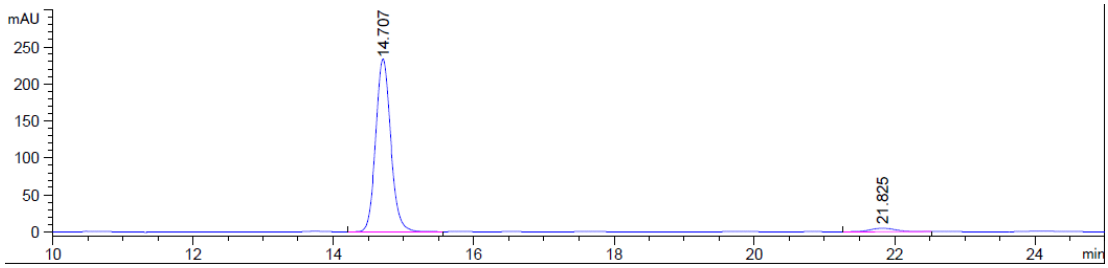
$[\alpha]^{20}_D$ = +10.5 (c 0.2, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 270 nm, t_{minor} = 21.825 min, t_{major} = 14.707 min.

Racemic Sample of 3b



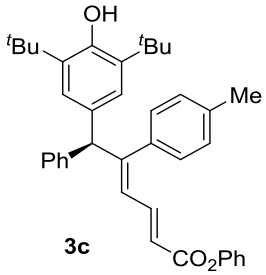
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.657	BB	0.2288	761.67566	51.42732	50.1279
2	21.130	BB	0.3860	757.78992	30.07109	49.8721

Enantiomeric Sample of 3b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.707	BB	0.2275	3473.40381	233.61415	96.5428
2	21.825	BB	0.3968	124.38183	4.82471	3.4572

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-phenyl-5-(p-tolyl)hex a-2,4-dienoate (**3c**)

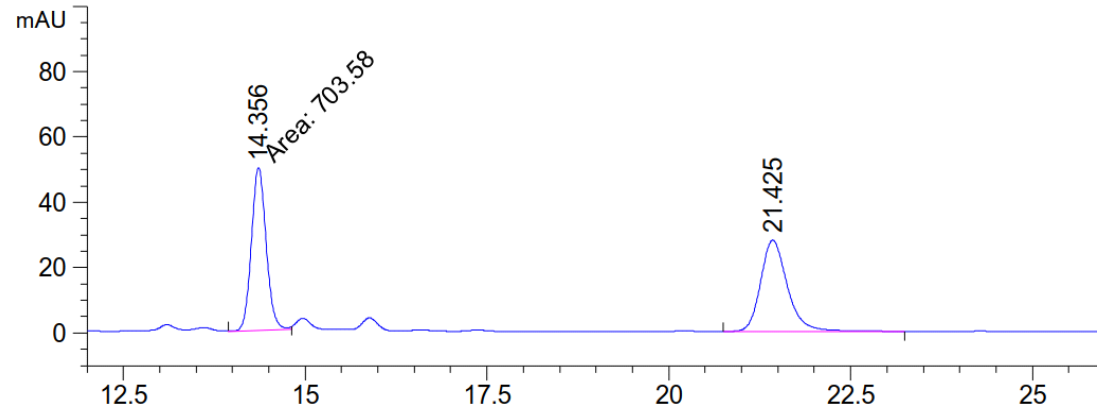


3c

Compound **3b** (34.5 mg, 62% yield) was obtained as a white solid following the *general procedure III* from **1b** (0.1 mmol, 29.4 mg) and **2c** (0.2 mmol, 53 mg, 50 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, J_1 = 11.6, J_2 = 15.2 Hz, 1H), 7.36-7.28 (m, 4H), 7.23-7.18 (m, 4H), 7.10-7.04 (m, 6H), 6.93 (s, 2H), 6.03 (d, *J* = 11.6 Hz, 1H), 5.97 (d, *J* = 15.2 Hz, 1H), 5.22 (s, 1H), 5.10 (s, 1H), 2.30 (s, 3H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 157.0, 152.4, 150.8, 144.3, 142.1, 137.7, 137.1, 135.5, 131.5, 129.4, 129.3, 128.9, 128.7, 128.3, 127.8, 126.5, 126.1, 125.5, 121.6, 120.0, 59.7, 34.3, 30.3, 21.2; **IR** (neat) ν 3629, 2957, 2920, 1728, 1621, 1491, 1434, 1234, 1195, 1160, 1116, 1128, 701 cm^{-1}; **MP**: 46-47 ℃. **HRMS** Calcd. for $C_{39}H_{41}O_3^-$ [M-H]$^-$: 557.3056, found: 557.3061.

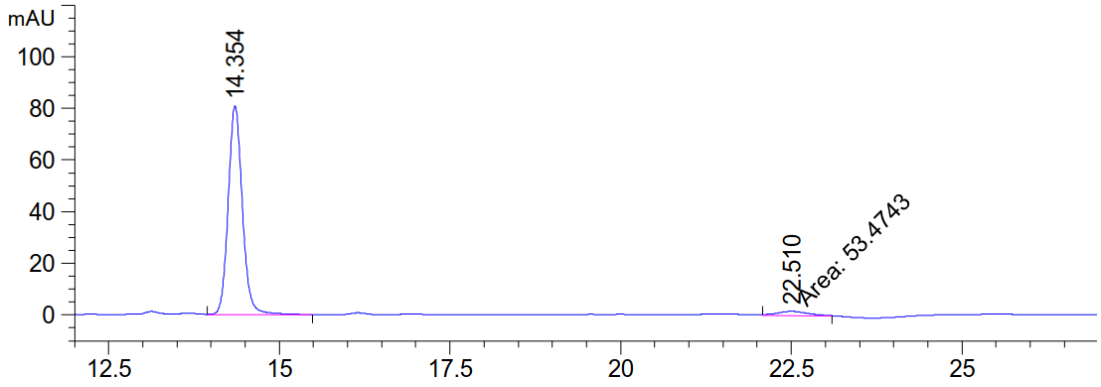
$[\alpha]^{20}_D$ = +5.9 (c 0.46, CH_2Cl_2) for 91% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 22.510 min, t_{major} = 14.354 min.

Racemic Sample of 3c



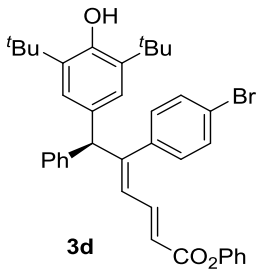
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.356	MM	0.2353	703.58002	49.84529	49.7040
2	21.425	BB	0.3874	711.95978	27.92680	50.2960

Enantiomeric Sample of 3c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.354	BB	0.2199	1161.74377	80.71028	95.5996
2	22.510	MM	0.5369	53.47429	1.66005	4.4004

(S)-Phenyl(2E,4Z)-5-(4-bromophenyl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-phenylhexa-2,4-dienoate (**3d**)



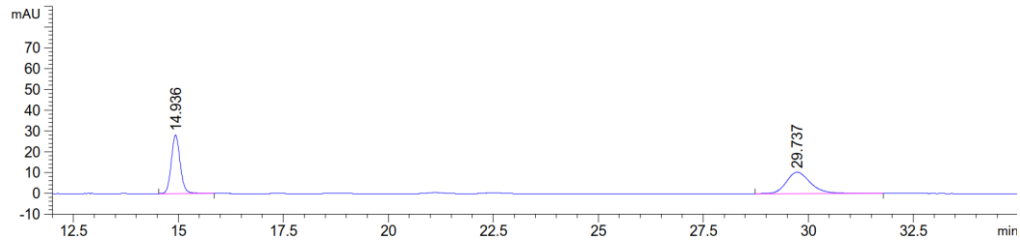
3d

Compound **3d** (49.7 mg, 81% yield) was obtained as a corlorless solid following the

general procedure III from **1a** (0.1 mmol, 29.4 mg) and **2d** (0.2 mmol, 66 mg, 65 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 3H), 7.37-7.29 (m, 5H), 7.25-7.21 (m, 1H), 7.20-7.16 (m, 3H), 7.06-7.01 (m, 4H), 6.91 (s, 2H), 6.06 (d, *J* = 11.6 Hz, 1H), 6.00 (d, *J* = 15.2 Hz, 1H), 5.15 (s, 1H), 5.13 (s, 1H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 155.4, 152.5, 150.7, 143.3, 141.5, 138.9, 135.7, 131.4, 130.9, 130.5, 129.4, 129.3, 128.4, 128.3, 126.7, 126.0, 125.6, 122.0, 121.6, 121.1, 59.8, 34.3, 30.3; **IR** (neat) ν 3629, 2957, 1728, 1621, 1489, 1434, 1234, 1195, 1160, 1119, 1008, 737, 700 cm^{-1}; **MP**: 49-51 ℃. **HRMS** Calcd. for $C_{38}H_{38}O_3Br^{-1}$ $(M-H)^-$: 621.2004, found: 621.2008.

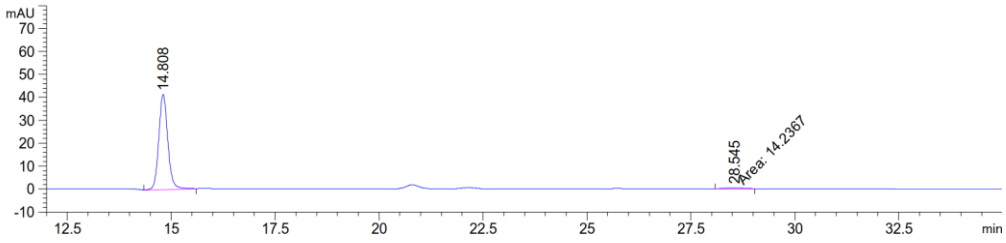
$[\alpha]^{20}_D$ = +3.3 (c 0.21, CH_2Cl_2) for 96% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 28.545 min, t_{major} = 14.808 min.

Racemic Sample of 3d



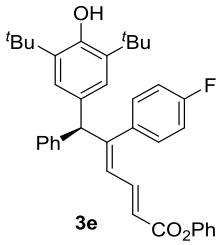
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.936	BB	0.2286	415.84842	28.10236	50.3111
2	29.737	BB	0.6049	410.70514	10.26165	49.6889

Enantiomeric Sample of 3d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.808	BB	0.2299	625.92816	41.52230	97.7761
2	28.545	MM	0.5443	14.23669	4.35904e-1	2.2239

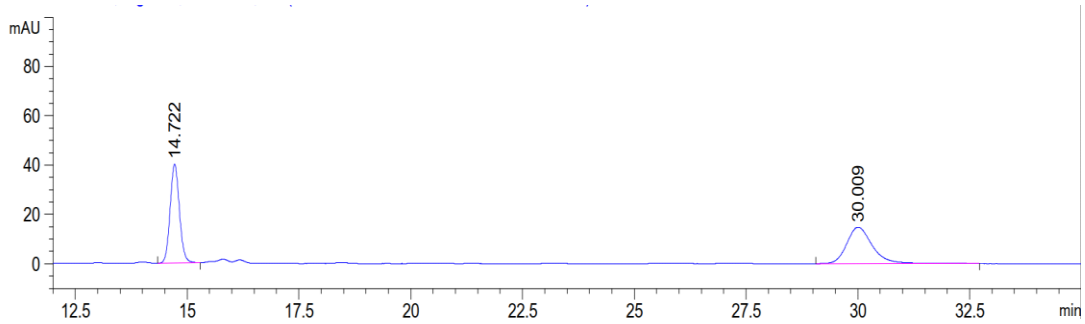
(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-(4-fluorophenyl)-6-phenylhexa-2,4-dienoate (**3e**)



Compound **3e** (39.2 mg, 70% yield) was obtained as a white solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2e** (0.2 mmol, 54 mg, 50 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, J_1 = 11.2, J_2 = 15.2 Hz, 1H), 7.36-7.29 (m, 4H), 7.25-7.17 (m, 4H), 7.13-7.09 (m, 2H), 7.06-7.04 (m, 2H), 6.99-6.95 (m, 2H), 6.92 (s, 2H), 6.07 (d, J = 11.2 Hz, 1H), 6.00 (d, J = 15.2 Hz, 1H), 5.15 (s, 1H), 5.12 (s, 1H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 162.3 (d, J = 246.2 Hz), 155.7, 152.5, 150.7, 143.6, 141.6, 135.9, 135.7, 131.1, 130.5 (d, J = 8 Hz), 129.4, 129.3, 128.4, 128.1, 126.6, 126.0, 125.6, 121.5, 120.7, 115.2 (d, J = 21.5 Hz), 60.0, 34.3, 30.3; **^{19}F NMR** (376 MHz, $CFCl_3$) δ -110.96 to -110.90 (m); **IR** (neat) ν 3630, 2957, 1725, 1621, 1595, 1505, 1491, 1432, 1231, 1195, 1158, 1116, 844, 734, 700 cm^{-1}; **MP**: 65-66 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3F^-$ $[M-H]^-$: 561.2809, found: 561.2811.

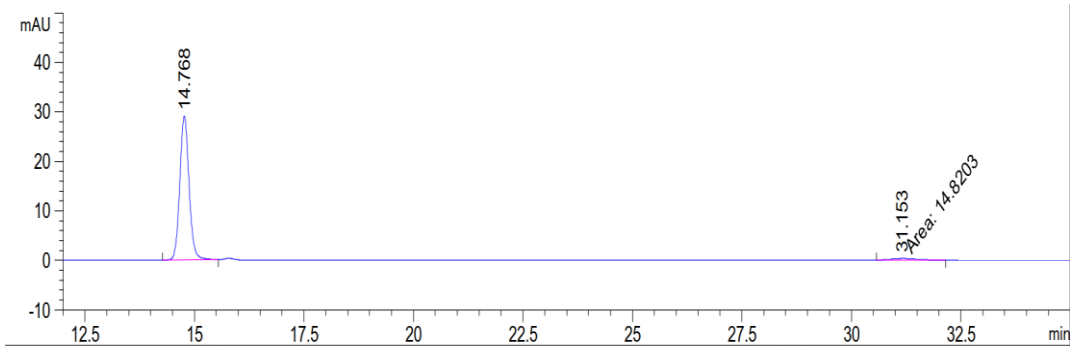
$[\alpha]^{20}_D$ = +6.7 (c 0.15, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 31.153 min, t_{major} = 14.768 min.

Racemic Sample of 3e



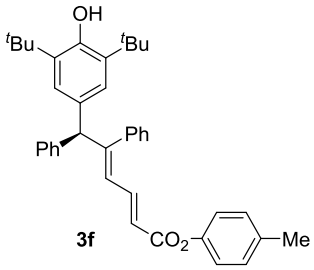
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.722	BB	0.2231	580.75952	40.06743	49.8065
2	30.009	BB	0.6068	585.27295	14.75284	50.1935

Enantiomeric Sample of 3e



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.768	BB	0.2259	427.41980	29.01622	96.6488
2	31.153	MM	0.7142	14.82030	3.45828e-1	3.3512

(S)-*p*-Tolyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-diphenylhexa-2,4-di enoate (**3f**)

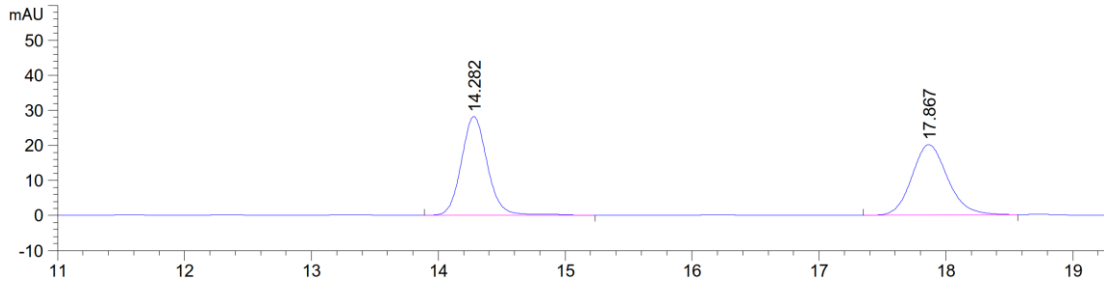


3f

Compound **3f** (31.7 mg, 57% yield) was obtained as a white solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2f** (0.2 mmol, 53 mg, 50 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, J_1 = 11.6, J_2 = 15.2 Hz, 1H), 7.32-7.28 (m, 4H), 7.24-7.19 (m, 4H), 7.16-7.12 (m, 4H), 6.94-6.92 (m, 4H), 6.05 (d, J = 11.6, 1H), 5.98 (d, J = 15.2 Hz, 1H), 5.21 (s, 1H), 5.11 (s, 1H), 2.32 (s, 3H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 156.7, 152.4, 148.5, 143.8, 142.0, 140.0, 135.6, 135.1, 131.4, 129.8, 129.4, 128.8, 128.3, 128.1, 128.0, 127.8, 126.5, 126.1, 121.2, 120.5, 59.8, 34.3, 30.3, 20.8; **IR** (neat) ν 3629, 2954, 1728, 1621, 1505, 1434, 1197, 1115, 768, 701 cm^{-1}; **MP**: 56-57 ℃; **HRMS** Calcd. for $C_{39}H_{41}O_3^-$ $[M-H]^-$: 557.3062, found: 557.3061.

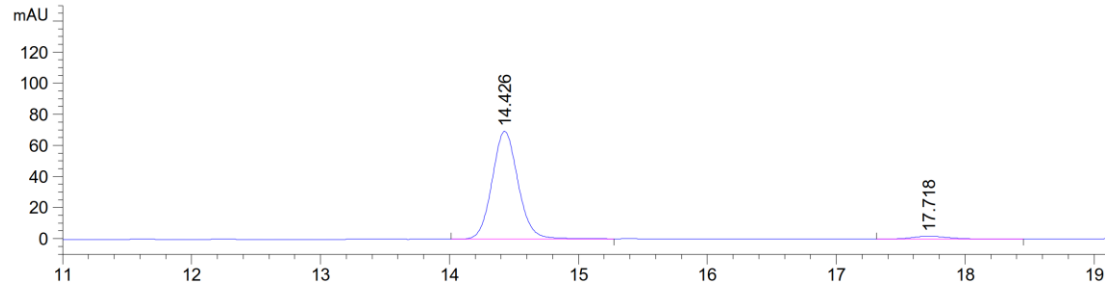
$[\alpha]^{20}_D$ = +12.8 (c 0.25, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 17.718 min, t_{major} = 14.282 min.

Racemic Sample of 3f



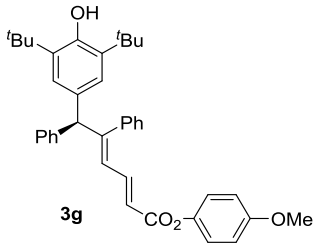
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.282	BB	0.2198	400.11951	28.16045	50.4397
2	17.867	BB	0.3005	393.14371	20.07274	49.5603

Enantiomeric Sample of 3f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.426	BB	0.2150	968.38171	69.31493	96.3793
2	17.718	BB	0.2982	36.37924	1.82784	3.6207

(S)-4-Methoxyphenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-diphenyl hexa-2,4-dienoate (**3g**)



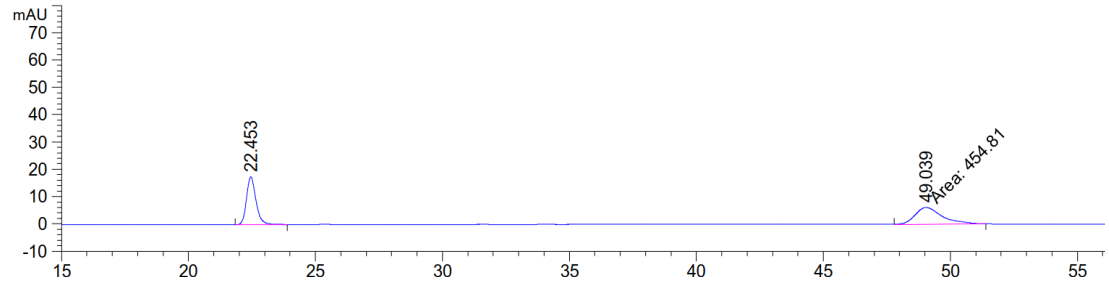
3g

Compound **3g** (30.3 mg, 53% yield) was obtained as a yellow solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2g** (0.2 mmol, 56 mg, 55 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.33-7.27 (m, 4H), 7.24-7.15 (m, 6H), 6.97 (d, J = 8.8 Hz, 2H), 6.95 (s, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.07 (d, J = 11.6 Hz, 1H), 5.98 (d, J = 15.2 Hz, 1H), 5.22 (s,

1H), 5.11 (s, 1H), 3.78 (s, 3H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 157.0, 156.7, 152.4, 144.3, 143.8, 141.9, 140.0, 135.6, 131.4, 129.4, 128.8, 128.3, 128.1, 128.0, 127.8, 126.5, 126.1, 122.3, 120.5, 114.3, 59.8, 55.5, 34.3, 30.3; **IR** (neat) ν 3627, 2957, 1725, 1624, 1502, 1434, 1234, 1194, 1118, 1033, 836, 703 cm^{-1}; **MP**: 68-70 ℃; **HRMS** Calcd. for $C_{39}H_{41}O_4^-$ [M-H]$^-$: 573.3005, found: 573.3012.

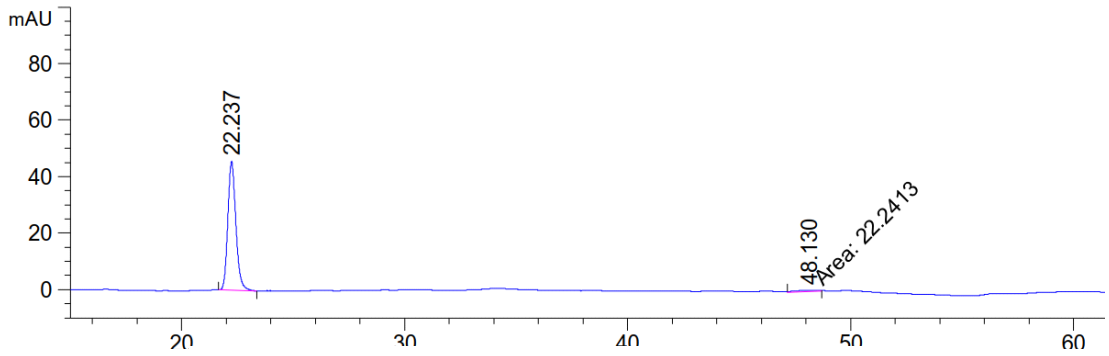
$[\alpha]^{20}_D$ = +6.7 (c 0.37, CH_2Cl_2) for 96% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 48.130 min, t_{major} = 22.237 min.

Racemic Sample of 3g



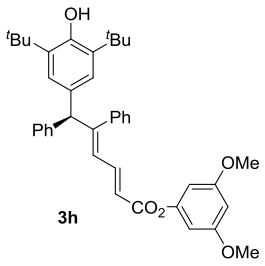
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.453	BB	0.3933	452.29367	17.51589	49.8613
2	49.039	MM	1.2361	454.81006	6.13218	50.1387

Enantiomeric Sample of 3g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.237	BB	0.3854	1145.32532	45.54688	98.0951
2	48.130	MM	1.2891	22.24134	2.87566e-1	1.9049

(S)-4-Chlorophenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-diphenylhexa-2,4-dienoate (**3h**)

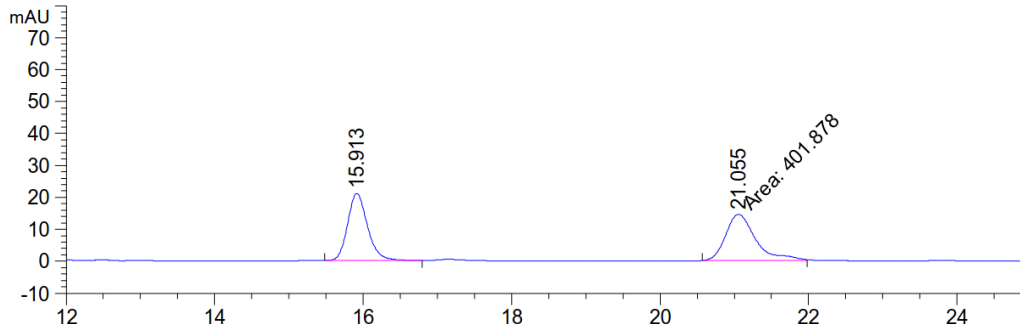


3h

Compound **3h** (28.2 mg, 47% yield) was obtained as a yellow solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2g** (0.2 mmol, 62 mg, 60 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.32-7.26 (m, 4H), 7.24-7.18 (m, 4H), 7.16-7.13 (m, 2H), 6.97 (s, 2H), 6.30 (t, J = 2.4 Hz, 1H), 6.23 (d, J = 2.0 Hz, 2H), 6.05 (d, J = 11.6 Hz, 1H), 5.96 (d, J = 15.2 Hz, 1H), 5.21 (s, 1H), 5.10 (s, 1H), 3.74 (s, 6H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 161.0, 157.0, 152.4, 152.3, 144.1, 141.9, 140.0, 135.6, 131.3, 129.4, 128.8, 128.3, 128.1, 128.0, 127.9, 126.5, 126.1, 120.3, 100.2, 98.1, 59.8, 55.4, 53.4, 34.3, 30.3; **IR** (neat) ν 3028, 2917, 1957, 1739, 1724, 1590, 1488, 1451, 1409, 1195, 1128, 748, 700 cm^{-1}; **MP**: 66-68 ℃; **HRMS** Calcd. for $C_{40}H_{43}O_5^-$ $[M-H]^-$: 603.3110, found: 603.3118.

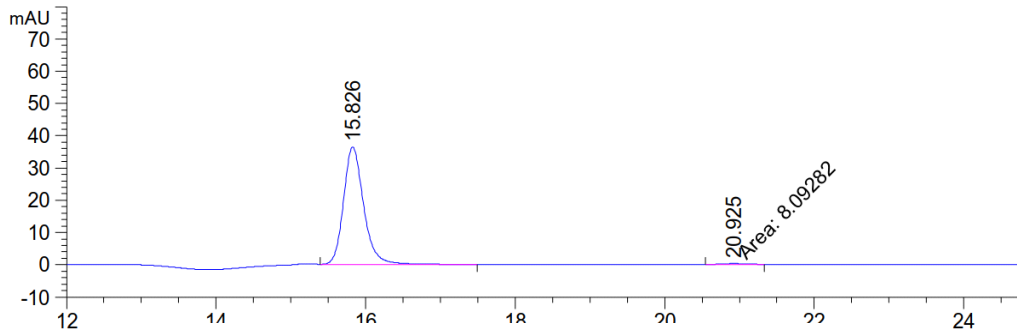
$[\alpha]^{20}_D$ = +6.9 (c 1.3, CH_2Cl_2) for 98% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 15.057 min, t_{major} = 13.902 min.

Racemic Sample of 3h



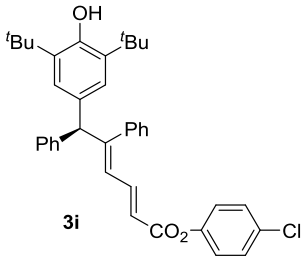
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.913	BB	0.2836	391.80411	21.00743	49.3654
2	21.055	MM	0.4648	401.87796	14.41138	50.6346

Enantiomeric Sample of 3h



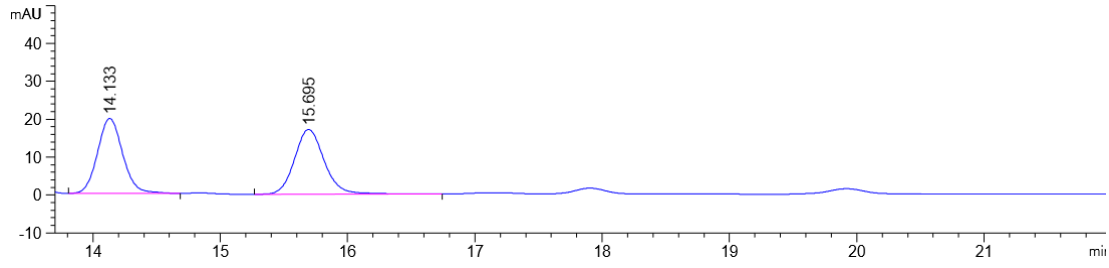
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.826	BB	0.2839	679.57343	36.38337	98.8231
2	20.925	MM	0.4394	8.09282	3.06954e-1	1.1769

(S)-4-Chlorophenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-diphenylhexa-2,4-dienoate (**3i**)



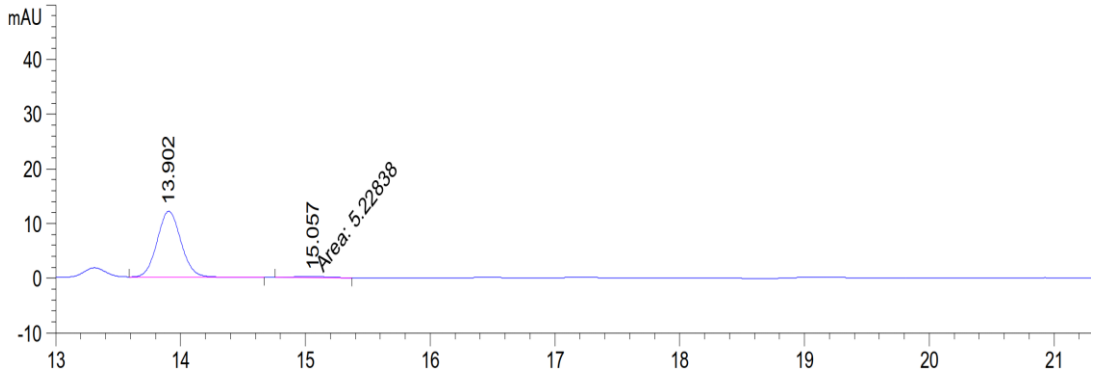
Compound **3i** (15.6 mg, 27% yield) was obtained as a yellow solid following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2i** (0.2 mmol, 57 mg, 55 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.31-7.30 (m, 2H), 7.29-7.26 (m, 4H), 7.22-7.19 (m, 3H), 7.16-7.14 (m, 3H), 7.00 (d, J = 8.8 Hz, 2H), 6.94 (s, 2H), 6.06 (d, J = 11.6 Hz, 1H), 5.97 (d, J = 15.2 Hz, 1H), 5.21 (s, 1H), 5.10 (s, 1H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 157.4, 152.4, 149.3, 144.5, 141.9, 140.0, 135.6, 131.3, 130.8, 129.4, 129.3, 128.8, 128.5, 128.3, 128.2, 127.9, 126.6, 126.1, 122.9, 119.9, 59.9, 34.3, 30.3; **IR** (neat) ν 3028, 2917, 1957, 1739, 1724, 1590, 1488, 1451, 1409, 1195, 1128, 748, 700 cm^{-1}; **MP**: 54-55 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3Cl^-$ [M-H]$^-$: 577.2509, found: 577.2516. $[\alpha]^{20}_D$ = +3.7 (c 0.4, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 15.057 min, t_{major} = 13.902 min.

Racemic Sample of 3i



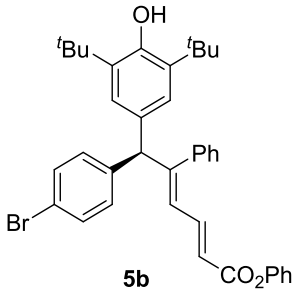
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.133	BB	0.2125	272.34174	19.79357	49.5038
2	15.695	BB	0.2493	277.80081	17.12155	50.4962

Enantiomeric Sample of 3i



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.902	BB	0.2050	160.07901	12.04660	96.8372
2	15.057	MM	0.3330	5.22838	2.61674e-1	3.1628

(S)-Phenyl(2E,4Z)-6-(4-bromophenyl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (**5b**)



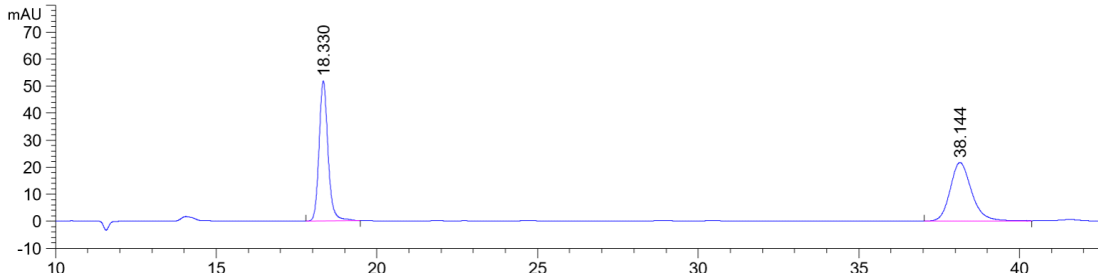
5b

Compound **5b** (42.8 mg, 69% yield) was obtained as a yellowish solid following the *general procedure III* from **1b** (0.1 mmol, 37.2 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 3H), 7.36-7.28 (m,

5H), 7.21-7.19 (m, 1H), 7.17-7.13 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 4H), 6.91 (s, 2H), 6.04 (d, *J* = 10.4 Hz, 1H), 6.01 (d, *J* = 14.4 Hz, 1H), 5.17 (s, 1H), 5.14 (s, 1H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 156.1, 152.6, 150.7, 143.7, 141.1, 139.7, 135.8, 131.4, 131.2, 130.8, 129.3, 128.8, 128.2, 128.1, 128.0, 125.9, 125.6, 121.6, 120.8, 120.4, 59.2, 34.4, 30.3; **IR** (neat) ν 3626, 2957, 1728, 1621, 1488, 1432, 1234, 1198, 1161, 1119, 765, 700 cm^{-1}; **MP**: 67-69 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3Br^-$ $[M-H]^-$: 621.2004, found: 621.2010.

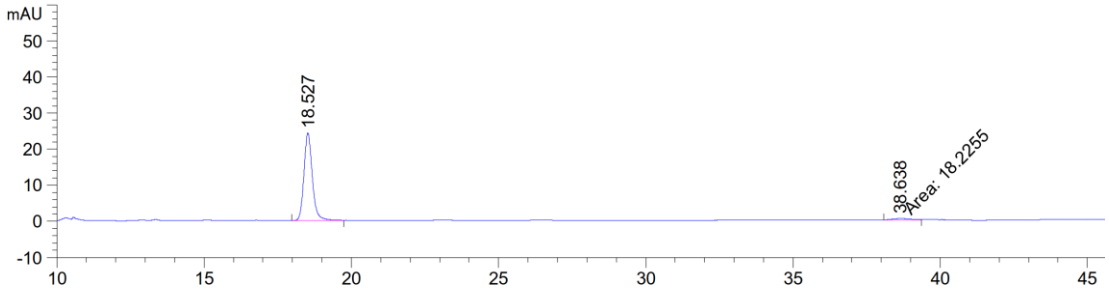
$[\alpha]^{20}_D$ = +19.3 (c 0.15, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 38.638 min, t_{major} = 18.527 min.

Racemic Sample of 5b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.330	BB	0.2956	1000.43799	51.74294	50.1437
2	38.144	BB	0.7003	994.70502	21.64046	49.8563

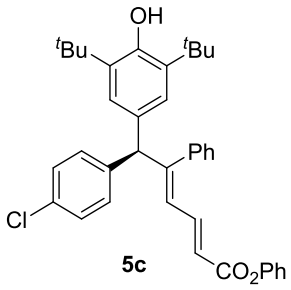
Enantiomeric Sample of 5b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.527	BB	0.3017	476.79578	24.21634	96.3182
2	38.638	MM	0.7217	18.22553	4.20878e-1	3.6818

(S)-Phenyl(2E,4Z)-6-(4-chlorophenyl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-p

henylhexa-2,4-dienoate (**5c**)

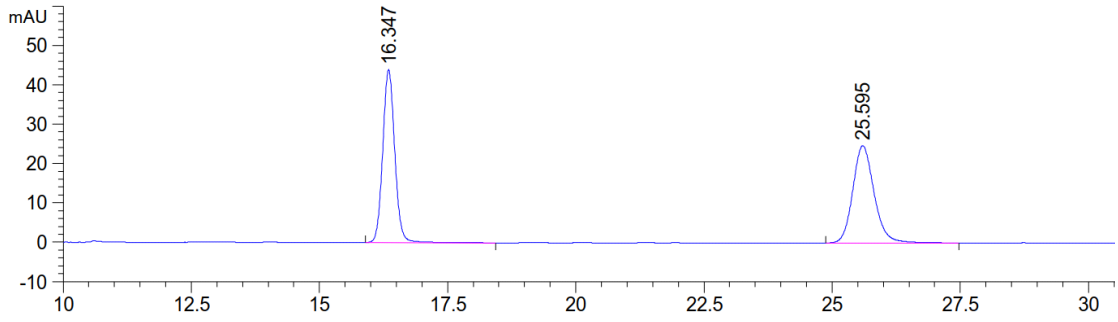


5c

Compound **5c** (42.1 mg, 73% yield) was obtained as a yellowish solid following the *general procedure III* from **1c** (0.1 mmol, 32.8 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J_1 = 11.6 Hz, J_2 = 15.6 Hz, 1H), 7.37-7.28 (m, 7H), 7.22-7.13 (m, 5H), 7.06 (d, J = 8.0 Hz, 2H), 6.93 (s, 2H), 6.06 (d, J = 11.6 Hz, 1H), 6.02 (d, J = 15.6 Hz, 1H), 5.20 (s, 1H), 5.15 (s, 1H), 1.40 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 156.2, 152.6, 150.7, 143.7, 140.6, 139.7, 135.8, 132.3, 130.9, 130.8, 129.3, 128.8, 128.5, 128.2, 128.1, 125.94, 125.88, 125.6, 121.6, 120.8, 59.1, 34.3, 30.3; **IR** (neat) ν 3629, 2957, 1725, 1624, 1593, 1488, 1434, 1231, 1194, 1160, 1118, 751, 703 cm^{-1}; **MP**: 61-63 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3Cl^-$ $[M-H]^-$: 577.2509, found: 577.2515.

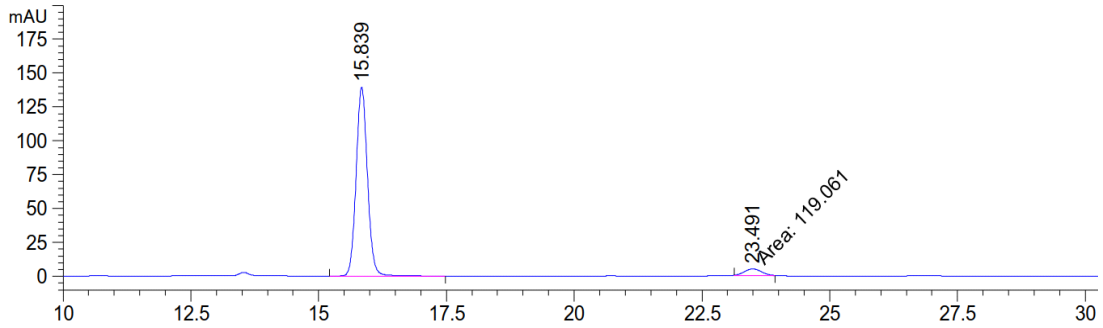
$[\alpha]^{20}_D$ = +22.7 (c 0.15, CH_2Cl_2) for 90% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 23.491 min, t_{major} = 15.839 min.

Racemic Sample of 5c



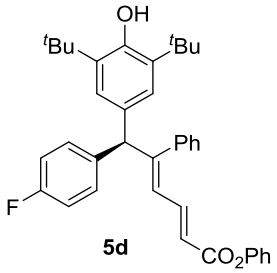
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.347	BB	0.2539	722.45801	43.92097	50.2901
2	25.595	BB	0.4456	714.12323	24.67511	49.7099

Enantiomeric Sample of 5c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.839	BB	0.2382	1463.90247	94.78428	95.0189
2	23.491	MM	0.3891	76.74154	3.28674	4.9811

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-(4-fluorophenyl)-5-phenylhexa-2,4-dienoate (**5d**)

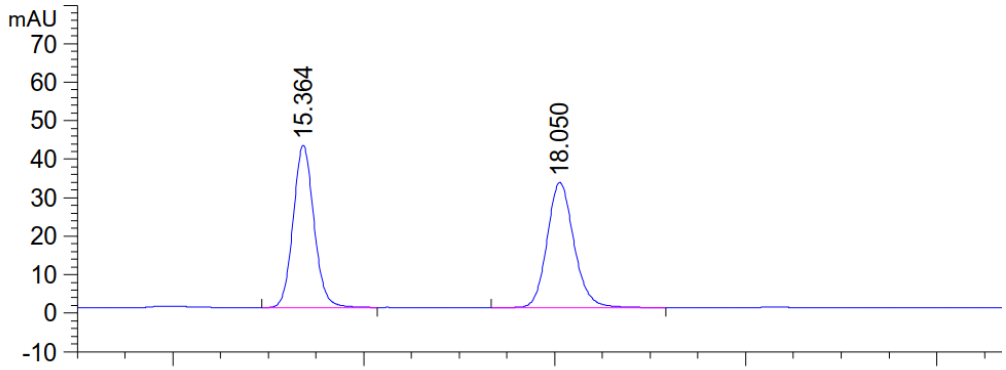


Compound **5d** (42.6 mg, 76% yield) was obtained as a white solid following the *general procedure III* from **1d** (0.1 mmol, 31.2 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, J_1 = 11.6 Hz, J_2 = 15.6 Hz, 1H), 7.36-7.32 (m, 2H), 7.29-7.25 (m, 2H), 7.21-7.14 (m, 6H), 7.05 (d, J = 7.6 Hz, 2H), 6.99 (t, J = 8.8 Hz, 2H), 6.92 (s, 2H), 6.04 (d, J = 11.6 Hz, 1H), 6.00 (d, J = 15.6 Hz, 1H), 5.20 (s, 1H), 5.13 (s, 1H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 161.5 (d, J = 243.8 Hz), 156.6, 152.5, 150.8, 143.8, 139.8, 137.6, 135.7, 131.2, 130.9 (d, J = 7.9 Hz), 129.3, 128.8, 128.2, 128.0 (d, J = 3.8 Hz), 125.9, 125.6, 121.6, 120.6, 115.2 (d, J = 21.1 Hz), 59.0, 34.3, 30.3; **^{19}F NMR** (376 MHz, $CFCl_3$) δ -116.24 to -116.31 (m); **IR** (neat) ν 3629, 2957, 1728, 1621, 1505, 1491, 1432, 1231, 1194, 1158, 1115, 700 cm^{-1}; **MP**: 50-52 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3F^-$ $[M-H]^-$: 561.2805, found: 561.2810.

$[\alpha]^{20}_D$ = +29.7 (c 0.31, $CHCl_3$) for 94% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm,

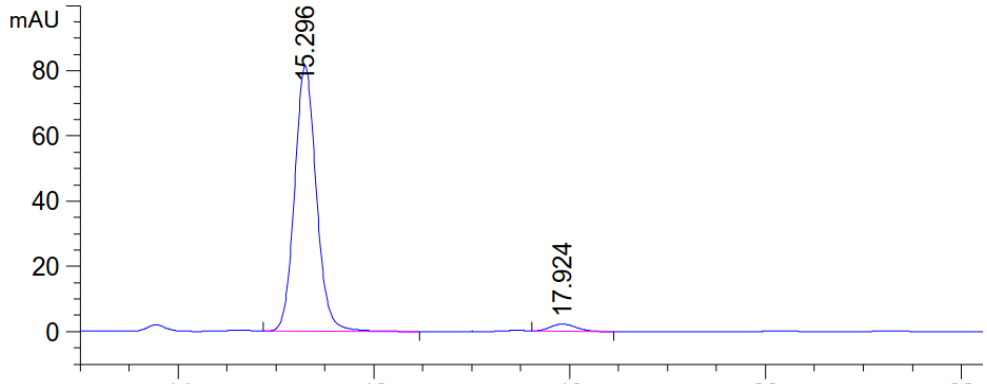
t_{minor} = 17.924 min, t_{major} = 15.296 min.

Racemic Sample 5d



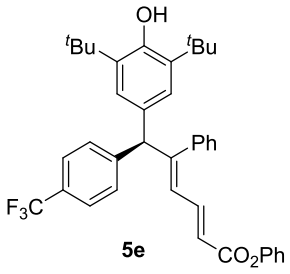
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.364	BB	0.2344	636.55414	42.09072	49.9212
2	18.050	BB	0.2985	638.56488	32.60904	50.0788

Enantiomeric Sample 5d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.296	BB	0.2373	1251.87915	81.45790	96.8283
2	17.924	BB	0.2836	41.00590	2.21863	3.1717

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenyl-6-(4-(trifluoromethyl)phenyl)hexa-2,4-dienoate (5e)

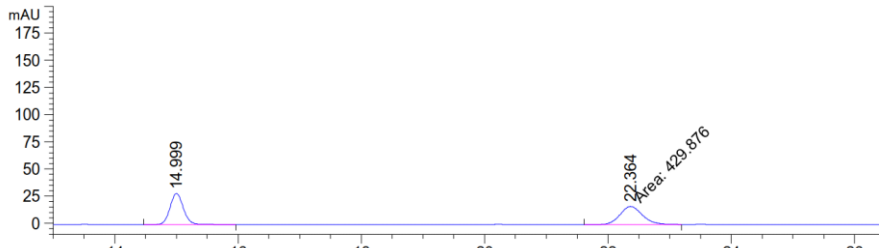


5e

Compound **5e** (38.4 mg, 63% yield) was obtained as a yellowish solid following the *general procedure III* from **1e** (0.1 mmol, 36.2 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.36-7.28 (m, 7H), 7.21-7.15 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.92 (s, 2H), 6.03 (d, *J* = 11.6 Hz, 1H), 6.01 (d, *J* = 15.2 Hz, 1H), 5.27 (s, 1H), 5.15 (s, 1H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 155.7, 152.7, 150.7, 146.3, 143.6, 139.5, 135.9. 130.4, 129.7, 129.3, 128.79 (q, *J* = 32.2 Hz), 128.77, 128.4, 128.3, 128.1, 127.5 (q, *J* = 270.5 Hz), 126.0, 125.6, 125.3 (q, *J* = 3.8 Hz), 121.5, 121.0, 59.5, 34.4, 30.3; **^{19}F NMR** (376 MHz, $CFCl_3$) δ -62.2; **IR** (neat) ν 3632, 2957, 1731, 1621, 1491, 1434, 1324, 1197, 1160, 1121, 1067, 700 cm^{-1}; **MP**: 82-83 ℃; **HRMS** Calcd. for $C_{39}H_{38}O_3F_3^-$ $[M-H]^-$: 611.2773, found: 611.2769.

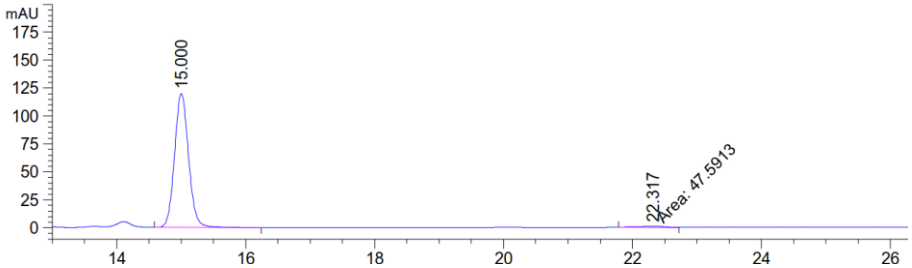
$[\alpha]^{20}_D$ = +19.1 (c 1.1, CH_2Cl_2) for 95% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 22.317 min, t_{major} = 15.000 min.

Racemic Sample 5e



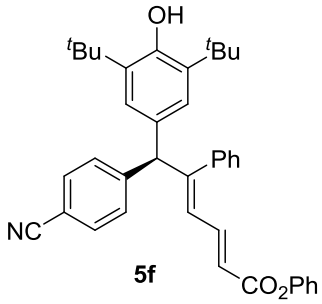
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.999	BB	0.2327	433.89789	28.64876	50.2328
2	22.364	MM	0.4272	429.87582	16.77128	49.7672

Enantiomeric Sample 5e



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.000	BB	0.2325	1816.81799	120.12213	97.4474
2	22.317	MM	0.5318	47.59127	1.49161	2.5526

(S)-Phenyl (2E,4Z)-6-(4-cyanophenyl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (**5f**)

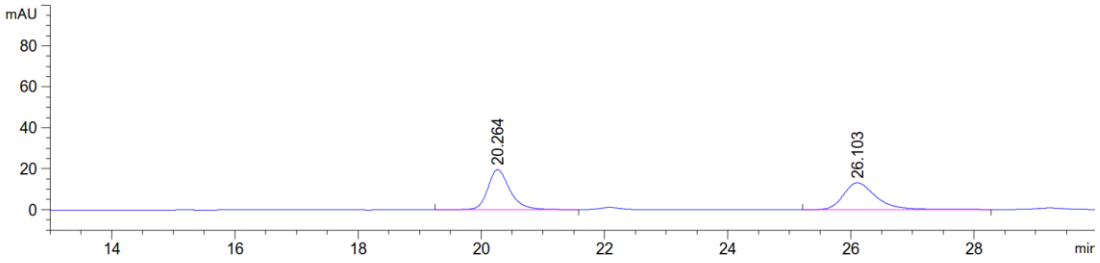


5f

Compound **5f** (46.5 mg, 82% yield) was obtained as a yellowish solid following the *general procedure III* from **1f** (0.1 mmol, 31.9 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.37-7.28 (m, 7H), 7.22-7.14 (m, 3H), 7.07-7.04 (m, 2H), 6.90 (s, 2H), 6.03 (d, *J* = 15.2 Hz, 1H), 6.02 (d, *J* = 11.6 Hz, 1H), 5.28 (s, 1H), 5.19 (s, 1H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 155.0, 152.8, 150.7, 147.7, 143.3, 139.3, 136.0, 132.2, 130.2, 130.0, 129.3, 128.7, 128.5, 128.4, 128.2, 125.9, 125.6, 121.5, 121.3, 118.9, 110.4, 59.7, 34.4, 30.2; **IR** (neat) ν 3629, 2957, 2225, 1728, 1624, 1488, 1434, 1197, 1160, 1118, 737, 700 cm^{-1}; **MP**: 75-77 ℃; **HRMS** Calcd. for $C_{39}H_{38}NO_3^-$ $[M-H]^-$: 568.2852, found: 568.2848.

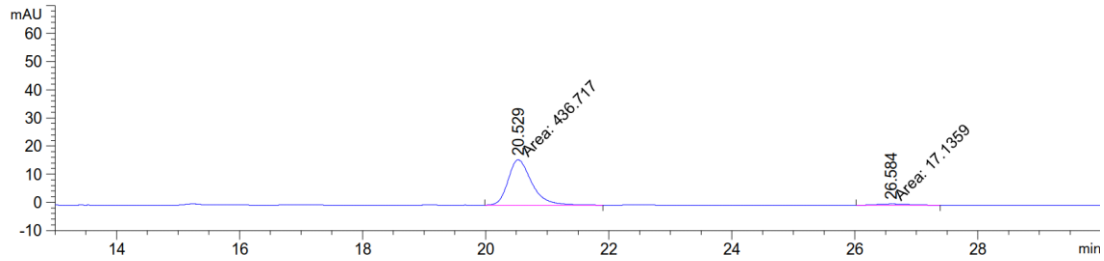
$[\alpha]^{20}_D$ = +1.7 (c 0.3, CH_2Cl_2) for 92% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 26.584 min, t_{major} = 20.529 min.

<u>Racemic Sample of 5f</u>



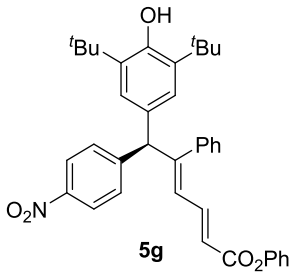
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.264	BB	0.3777	494.01389	19.62379	50.6014
2	26.103	BB	0.5528	482.27063	13.12228	49.3986

Enantiomeric Sample of 5f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.529	MM	0.4505	436.71713	16.15591	96.2243
2	26.584	MM	0.6492	17.13591	4.39940e-1	3.7757

(S)-Phenyl (2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-(4-nitrophenyl)-5-phenylhexa-2,4-dienoate (**5g**)

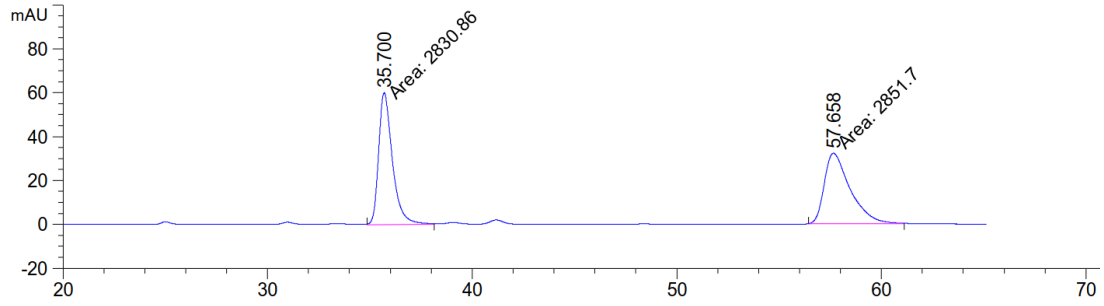


5g

Compound **5g** (41.2 mg, 70% yield) was obtained as a yellow solid following the *general procedure III* from **1g** (0.1 mmol, 33.9 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, J_1 = 12.0 Hz, J_2 = 15.6 Hz, 1H), 7.39-7.27 (m, 7H), 7.22-7.17 (m, 3H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.93 (s, 2H), 6.05 (d, *J* = 12.0 Hz, 1H), 6.04 (d, *J* = 15.6 Hz, 1H), 5.34 (s, 1H), 5.20 (s, 1H), 1.40 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 154.9, 152.9, 150.7, 149.9, 146.6, 143.3, 139.2, 136.1, 130.2, 129.9, 129.3, 128.7, 128.6, 128.4, 128.3, 125.9, 125.6, 123.6, 121.5, 121.4, 57.5, 34.4, 30.2; **IR** (neat) ν 3626, 2957, 1725, 1624, 1519, 1488, 1434, 1344, 1194, 1160, 1118, 700 cm^{-1}; **MP**: 74-76 ℃; **HRMS** Calcd. for $C_{38}H_{38}NO_5^-$ $[M-H]^-$: 588.2750, found: 588.2756.

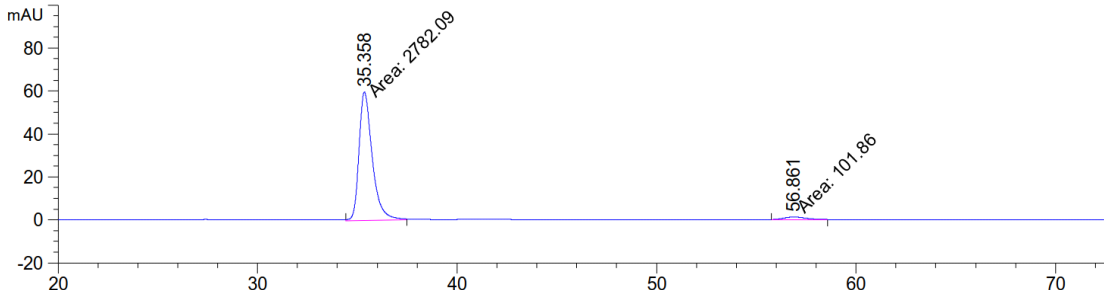
$[\alpha]^{20}_D$ = -1.33 (c 0.2, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.3 mL/min, 254 nm, t_{minor} = 56.861 min, t_{major} = 35.358 min.

Racemic Sample of 5g



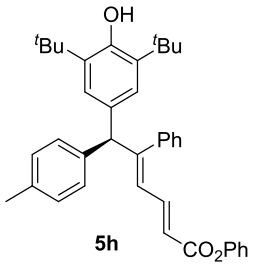
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.700	MM	0.7846	2830.85889	60.13656	49.8166
2	57.658	MM	1.4762	2851.69751	32.19553	50.1834

Enantiomeric Sample of 5g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.358	MM	0.7745	2782.09033	59.87202	96.4681
2	56.861	MM	1.3528	101.85952	1.25489	3.5319

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenyl-6-(p-tolyl)hexa-2,4-dienoate (**5h**)

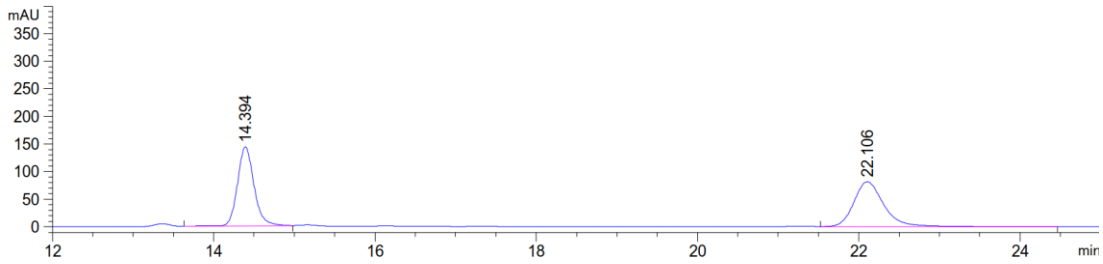


Compound **5h** (35.6 mg, 64% yield) was obtained as a yellowish solid following the *general procedure III* from **1h** (0.1 mmol, 30.8 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.41-7.32 (m, 2H), 7.31-7.24 (m, 2H), 7.21-7.15 (m, 4H), 7.13-7.05 (m, 6H),

6.95 (s, 2H), 6.08 (d, J = 11.6 Hz, 1H), 6.00 (d, J = 15.2 Hz, 1H), 5.18 (s, 1H), 5.10 (s, 1H), 2.34 (s, 3H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 157.2, 152.3, 150.8, 144.1, 140.1, 138.9, 136.0, 135.5, 131.5, 129.3, 129.0, 128.8, 128.1, 127.8, 126.0, 125.5, 121.6, 120.3, 59.5, 34.3, 30.3, 21.0; **IR** (neat) ν 3629, 2957, 1729, 1621, 1488, 1435, 1231, 1198, 1161, 1156, 700 cm^{-1}; **MP**: 49-51 ℃; **HRMS** Calcd. for $C_{39}H_{41}O_3^-$ [M-H]$^-$: 557.3060, found: 557.3061.

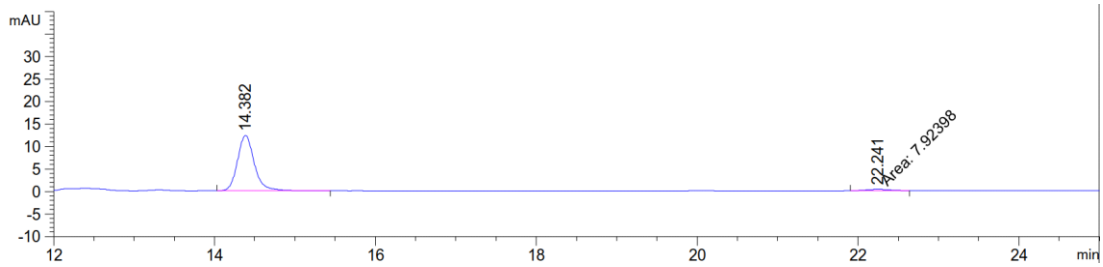
$[\alpha]^{20}_D$ = +6.2 (c 0.26, CH_2Cl_2) for 91% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 22.241 min, t_{major} = 14.382 min.

Racemic Sample 5h



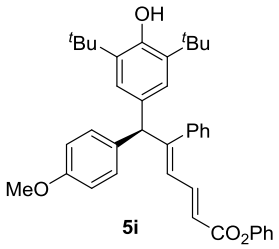
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.394	BB	0.2180	2033.20422	142.89140	49.3666
2	22.106	BB	0.3914	2085.37769	81.25133	50.6334

Enantiomeric Sample 5h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.382	BB	0.2213	178.02982	12.26985	95.7387
2	22.241	MM	0.4028	7.92398	3.27903e-1	4.2613

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-(4-methoxyphenyl)-5-phenylhexa-2,4-dienoate (**5i**)

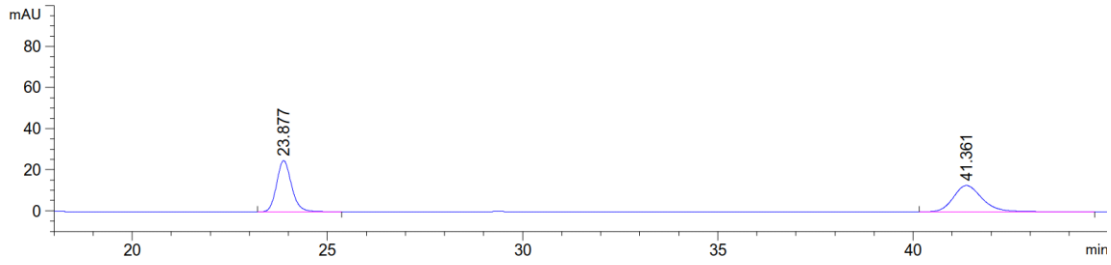


5i

Compound **5i** (24.6 mg, 43% yield) was obtained as a yellowish solid following the *general procedure III* from **1i** (0.1 mmol, 32.4 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.36-7.30 (m, 2H), 7.29-7.24 (m, 3H), 7.21-7.10 (m, 5H), 7.06 (dd, J_1 = 1.2 Hz, J_2 = 8.8 Hz, 2H), 6.94 (s, 2H), 6.85 (dd, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 2H), 6.06 (d, J = 11.6 Hz, 1H), 6.00 (d, J = 15.2 Hz, 1H), 5.16 (s, 1H), 5.11 (s, 1H), 3.81 (s, 3H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 158.1, 157.3, 152.3, 150.8, 144.1, 140.1, 135.6, 134.0, 131.7, 130.4, 129.2, 128.8, 128.1, 127.8, 126.0, 125.5, 121.6, 120.3, 113.7, 59.0, 55.2, 34.3, 30.3; **IR** (neat) ν 3629, 2954, 1728, 1621, 1508, 1488, 1434, 1248, 1197, 1160, 1119, 1033, 734, 703 cm^{-1}; **MP**: 62-63 ℃; **HRMS** Calcd. for $C_{39}H_{41}O_4^-$ [M-H]$^-$: 573.3005, found: 573.3010.

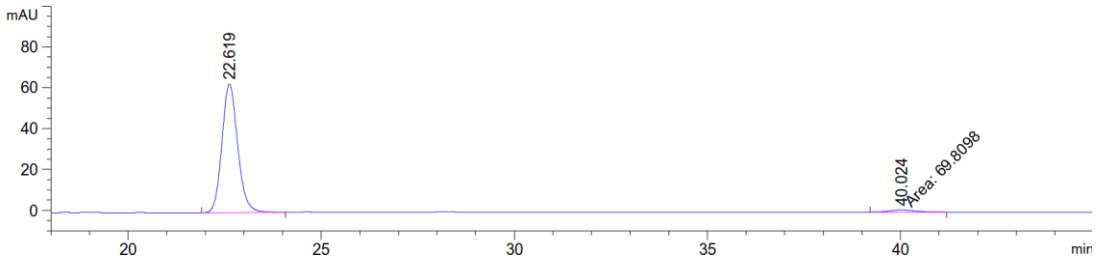
$[\alpha]^{20}_D$ = -2.0 (c 0.3, CH_2Cl_2) for 92% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 40.024 min, t_{major} = 22.619 min.

Racemic Sample 5i



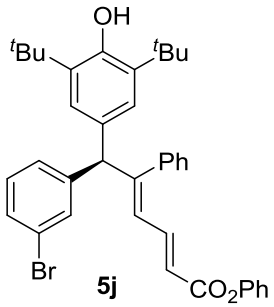
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.877	BB	0.4104	664.51697	24.97576	50.0577
2	41.361	BB	0.7801	662.98492	12.84585	49.9423

Enantiomeric Sample 5i



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.619	BB	0.4362	1780.77258	62.92469	96.2277
2	40.024	MM	0.9959	69.80977	1.16824	3.7723

(S)-Phenyl(2E,4Z)-6-(3-bromophenyl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (**5j**)

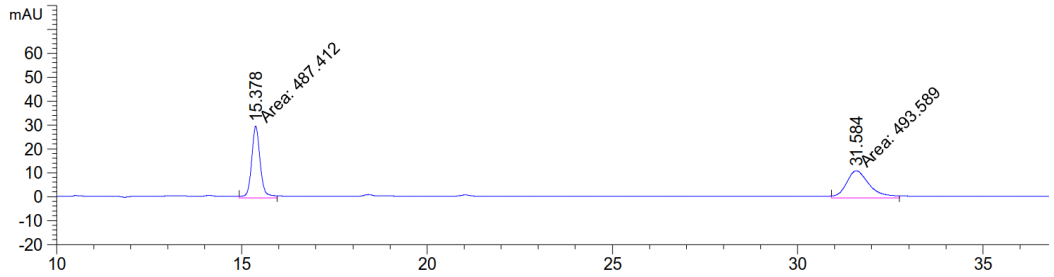


5j

Compound **5j** (40.3 mg, 65% yield) was obtained as a yellowish solid following the *general procedure III* from **1j** (0.1 mmol, 37.2 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.39-7.27 (m, 7H), 7.27-7.14 (m, 5H), 7.08 (d, J = 8.0 Hz, 2H), 6.94 (s, 2H), 6.07 (d, J = 11.6 Hz, 1H), 6.04 (d, J = 15.2 Hz, 1H), 5.20 (s, 1H), 5.17 (s, 1H), 1.41 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 155.9, 152.6, 150.7, 144.4, 143.7, 139.6, 135.8, 132.5, 130.6, 129.8, 129.7, 129.3, 128.8, 128.2, 128.0, 126.0, 125.5, 122.5, 121.5, 120.9, 59.4, 34.3, 30.3; **IR** (neat) ν 3629, 2957, 1731, 1621, 1590, 1488, 1434, 1234, 1197, 1160, 1118, 756, 701 cm^{-1}; **MP**: 67-69 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3Br^-$ [M-H]$^-$: 621.2004, found: 621.1999.

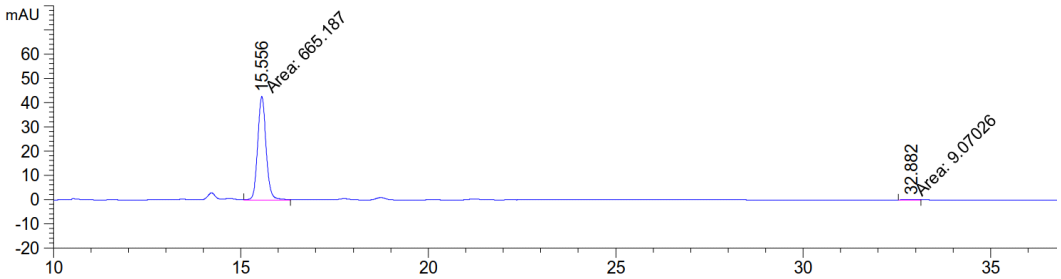
$[\alpha]^{20}_D$ = +2.8 (c 0.32, CH_2Cl_2) for 97% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 32.882 min, t_{major} = 15.556 min.

Racemic Sample of 5j



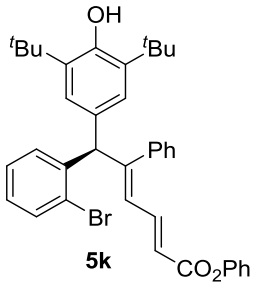
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.378	MM	0.2713	487.41220	29.94630	49.6852
2	31.584	MM	0.7289	493.58936	11.28644	50.3148

Enantiomeric Sample of 5j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.556	MM	0.2600	665.18732	42.63344	98.6548
2	32.882	MM	0.5332	9.07026	2.83518e-1	1.3452

(S)-Phenyl(2E,4Z)-6-(2-bromophenyl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (**5k**)



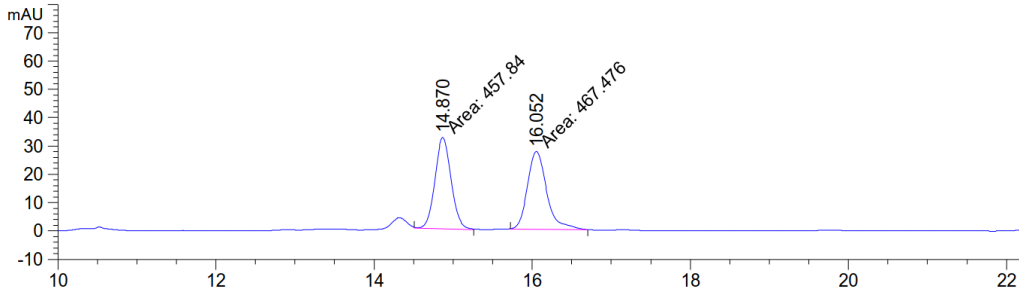
5k

Compound **5k** (25.4 mg, 41% yield) was obtained as a yellowish solid following the *general procedure III* from **1k** (0.1 mmol, 37.2 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.36-7.28 (m, 6H), 7.25-7.17 (m, 3H), 7.12-7.04 (m, 3H), 7.00-6.99 (m, 3H), 5.96 (d, *J* = 15.2 Hz, 1H), 5.88 (d, *J* = 11.6 Hz, 1H), 5.58 (s, 1H), 5.13 (s, 1H), 1.40 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 155.1, 152.6, 150.8, 143.9, 142.0, 139.7, 135.8, 133.1, 131.3, 129.8, 129.3, 129.0, 128.1, 127.4,

127.2, 126.44, 126.39, 125.6, 125.5, 121.6, 120.6, 58.9, 34.4, 30.3; **IR** (neat) ν 3629, 2957, 1732, 1621, 1488, 1434, 1194, 1160, 1118, 748, 700 cm^{-1}; **MP**: 65-67 ℃; **HRMS** Calcd. for $C_{38}H_{38}O_3Br^-$ [M-H]$^-$: 621.2004, found: 621.2012.

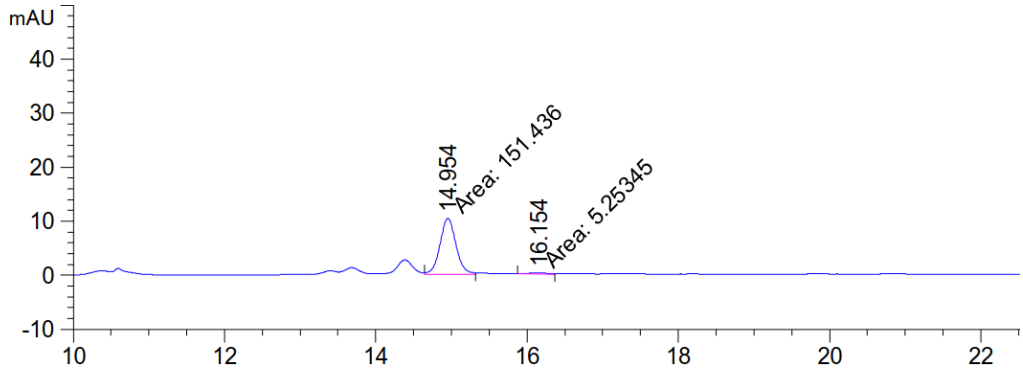
$[\alpha]^{20}_D$ = +18.9 (c 0.44, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 16.154 min, t_{major} = 14.954 min.

Racemic Sample 5k



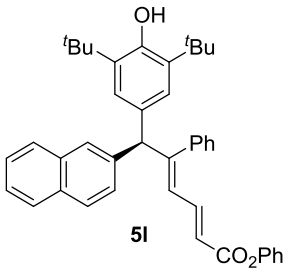
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.870	MM	0.2366	457.84033	32.24985	49.4793
2	16.052	MM	0.2836	467.47623	27.47148	50.5207

Enantiomeric Sample 5k



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.954	MM	0.2444	151.43576	10.32679	96.6472
2	16.154	MM	0.3213	5.25345	2.72482e-1	3.3528

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-(naphthalen-2-yl)-5-phenylhexa-2,4-dienoate (**5l**)

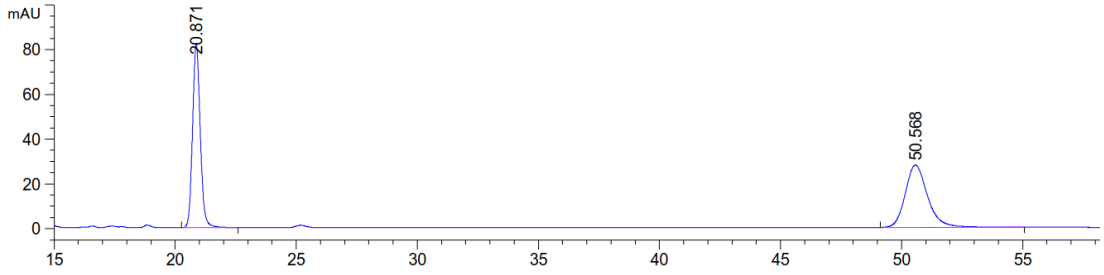


5l

Compound **5l** (36.5 mg, 62% yield) was obtained as a yellowish solid following the *general procedure III* from **1l** (0.1 mmol, 34.4 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.75 (m, 3H), 7.58 (s, 1H), 7.53-7.39 (m, 5H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.28-7.26 (m, 1H), 7.21-7.15 (m, 4H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.01 (s, 2H), 6.12 (d, *J* = 11.6 Hz, 1H), 5.99 (d, *J* = 15.2 Hz, 1H), 5.38 (s, 1H), 5.13 (s, 1H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 156.6, 152.5, 150.8, 144.0, 140.0, 139.6, 135.7, 133.4, 132.3, 131.2, 129.3, 128.8, 128.2, 127.9, 127.6, 126.2, 125.9, 125.6, 125.5, 121.6, 120.5, 59.9, 34.3, 30.3; **IR** (neat) ν 3629, 2960, 1728, 1621, 1488, 1434, 1234, 1194, 1160, 1115, 748, 700 cm^{-1}; **MP**: 62-64 ℃; **HRMS** Calcd. for $C_{42}H_{41}O_3^-$ [M-H]$^-$: 593.3056, found: 593.3063.

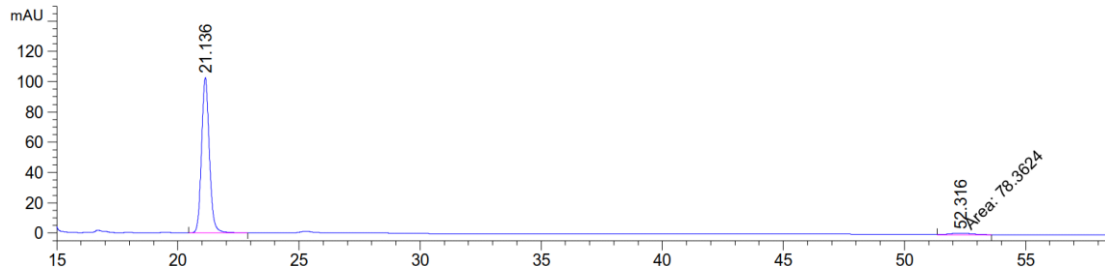
$[\alpha]^{20}_D$ = +18.5 (c 0.2, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 52.316 min, t_{major} = 21.136 min.

Racemic Sample of 5l



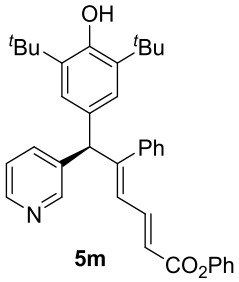
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.871	BB	0.3378	1817.16931	82.23213	50.4208
2	50.568	BB	0.9622	1786.83728	27.86278	49.5792

Enantiomeric Sample of 5l



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.136	BB	0.3441	2302.51611	102.50829	96.7087
2	52.316	MM	1.1576	78.36243	1.12821	3.2913

(S)-Phenyl (2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenyl-6-(pyridin-3-yl)hexa-2,4-dienoate (**5m**)

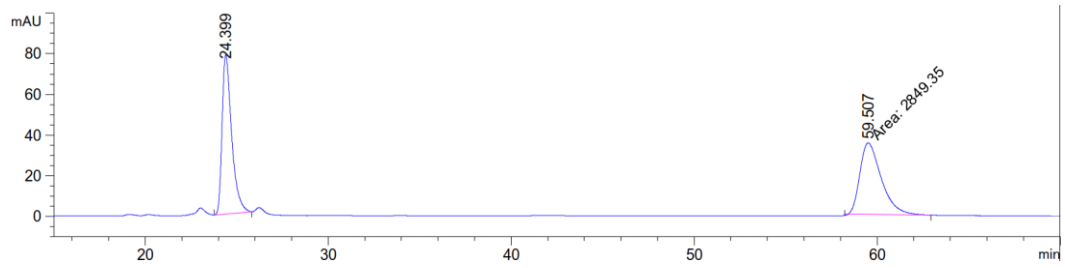


5m

Compound **5m** (40.8 mg, 75% yield) was obtained as a brown solid following the *general procedure III* from **1m** (0.1 mmol, 29.5 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48-8.47 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.45 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.36-7.28 (m, 6H), 7.21-7.15 (m, 3H), 7.06-7.04 (m, 2H), 6.93 (s, 2H), 6.04 (d, J = 11.6 Hz, 1H), 6.01 (d, J = 15.2 Hz, 1H), 5.25 (s, 1H), 5.19 (s, 1H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 155.4, 152.7, 150.9, 150.7, 147.9, 143.5, 139.3, 137.6, 136.7, 136.0, 130.1, 129.3, 128.8, 128.3, 128.1, 125.9, 125.6, 123.2, 121.5, 121.1, 57.3, 34.4, 30.3; **IR** (neat) ν 3629, 2957, 1728, 1624, 1491, 1434, 1262, 1197, 1160, 1118, 703 cm^{-1}; **MP**: 69-71 ℃; **HRMS** Calcd. for $C_{37}H_{38}NO_3^-$ [M-H]$^-$: 544.2852, found: 544.2857.

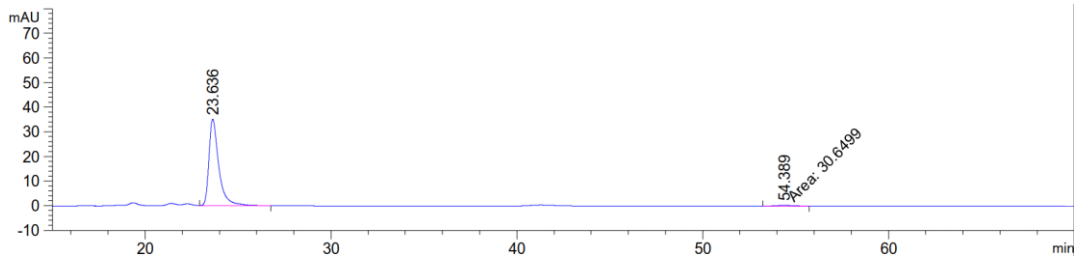
$[\alpha]^{20}_D$ = +5.3 (c 0.3, CH_2Cl_2) for 95% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 99/1, 0.3 mL/min, 254 nm, t_{minor} = 54.389 min, t_{major} = 23.636 min.

Racemic Sample of 5m



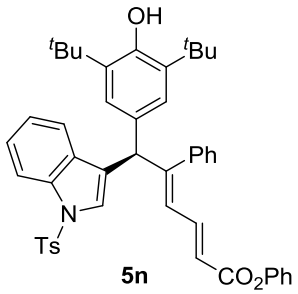
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.399	BB	0.5447	2841.53149	78.42898	49.9313
2	59.507	MM	1.3497	2849.34888	35.18368	50.0687

Enantiomeric Sample of 5m



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.636	BB	0.5458	1287.24341	35.10599	97.6743
2	54.389	MM	1.2903	30.64991	3.95906e-1	2.3257

(S)-Phenyl(2E,4Z)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenyl-6-(1-tosyl-1H-indol-3-yl)hexa-2,4-dienoate (**5n**)



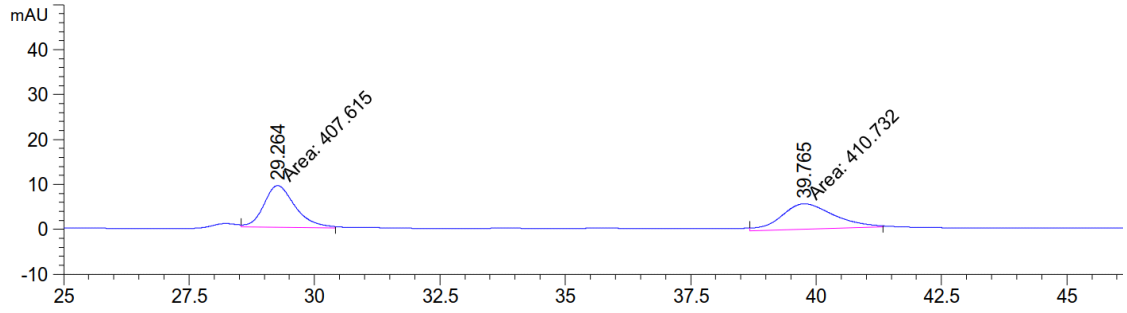
5n

Compound **5n** (43.4 mg, 59% yield) was obtained as a yellow solid following the *general procedure III* from **1n** (0.1 mmol, 48.7 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.45 (dd, J_1 = 11.6 Hz, J_2 = 15.6 Hz, 1H), 7.40-7.38 (m, 1H), 7.36-7.29 (m, 6H), 7.24-7.21 (m, 2H), 7.20-7.16 (m, 4H), 7.06-7.02 (m, 2H),

6.99-6.94 (m, 3H), 5.97 (d, *J* = 11.6 Hz, 1H), 5.80 (d, *J* = 15.6 Hz, 1H), 5.19 (s, 1H), 5.18 (s, 1H), 2.37 (s, 3H), 1.40 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 153.6, 152.8, 150.7, 144.9, 143.6, 139.6, 135.9, 135.0, 130.4, 129.8, 129.5, 129.3, 128.7, 128.3, 128.1, 127.3, 126.7, 126.13, 126.07, 125.6, 125.4, 124.9, 123.4, 121.5, 120.9, 120.1, 114.1, 50.9, 34.4, 30.3, 21.6; **IR** (neat) ν 3629, 2954, 1728, 1624, 1488, 1434, 1369, 1192, 1172, 1118, 980, 745 cm^{-1}; **MP**: 85-87 ℃.; **HRMS** Calcd. for $C_{47}H_{46}NO_5S^-$ [M-H]$^-$: 736.3097, found: 736.3101.

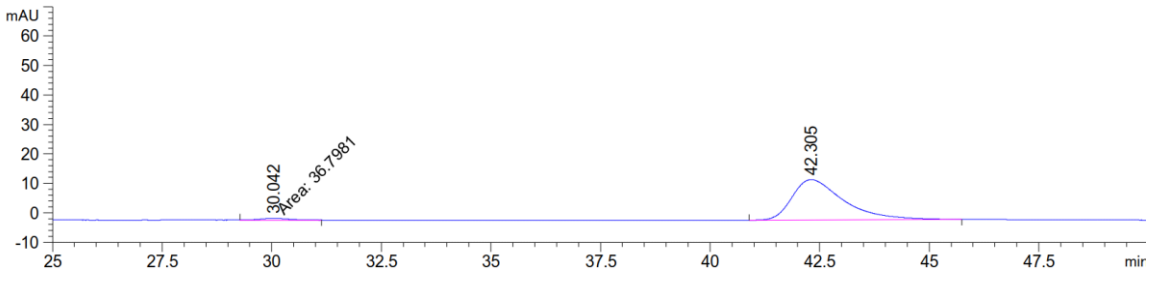
$[\alpha]^{20}_D$ = +66.2 (c 0.5, CH_2Cl_2) for 94% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 254 nm, t_{minor} = 30.042 min, t_{major} = 42.305 min.

Racemic Sample of 5n



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.264	MM	0.7297	407.61496	9.30970	49.8096
2	39.765	MM	1.2146	410.73193	5.63614	50.1904

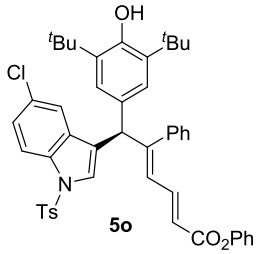
Enantiomeric Sample of 5n



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.042	MM	0.8707	36.79813	7.04384e-1	3.1937
2	42.305	BB	1.1603	1115.42908	13.69350	96.8063

(S)-Phenyl(2E,4Z)-6-(5-chloro-1-tosyl-1H-indol-3-yl)-6-(3,5-di-tert-butyl-4-hydro

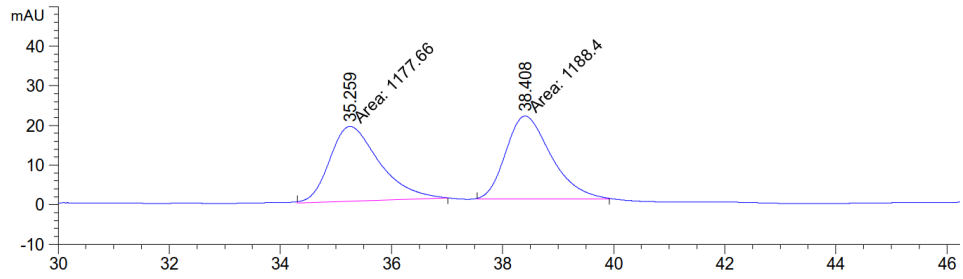
xyphenyl)-5-phenylhexa-2,4-dienoate (5o)



Compound **5o** (40.0 mg, 52% yield) was obtained as a yellow solid following the *general procedure III* from **1o** (0.1 mmol, 52.1 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, J_1 = 11.6 Hz, J_2 = 15.6 Hz, 1H), 7.37-7.29 (m, 7H), 7.23-7.20 (m, 3H), 7.18-7.16 (m, 2H), 7.07-7.03 (m, 3H), 6.96 (s, 2H), 5.95 (d, *J* = 11.6 Hz, 1H), 5.83 (d, *J* = 15.6 Hz, 1H), 5.20 (s, 1H), 5.14 (s, 1H), 2.39 (s, 3H), 1.40 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 153.3, 152.9, 150.7, 145.2, 143.4, 139.3, 136.0, 134.7, 134.2, 131.6, 129.9, 129.34, 129.29, 129.2, 128.7, 128.4, 128.2, 127.4, 127.3, 126.6, 125.6, 125.4, 125.2, 121.5, 121.2, 119.8, 115.2, 50.7, 34.4, 30.3, 21.6; **IR** (neat) ν 3626, 2957, 1725, 1624, 1491, 1440, 1372, 1197, 1118, 810, 669 cm^{-1}; **MP**: 89-91 ℃; **HRMS** Calcd. for $C_{47}H_{45}NO_5SCl^-$ $[M-H]^-$: 770.2707, found: 770.2713.

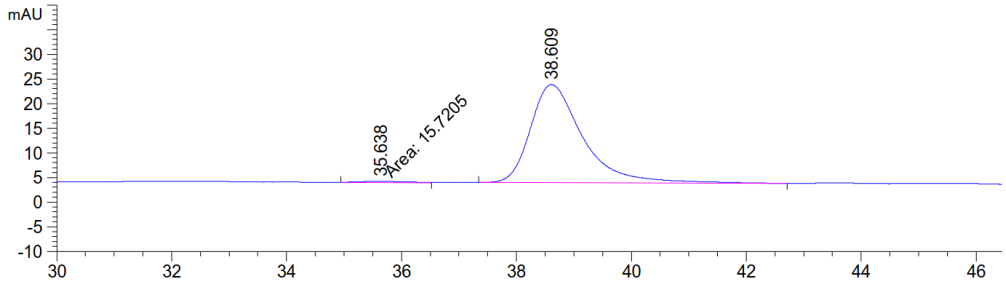
$[\alpha]^{20}_D$ = +62.3 (c 0.35, CH_2Cl_2) for 98% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 254 nm, t_{minor} = 35.638 min, t_{major} = 38.609 min.

Racemic Sample of 5o



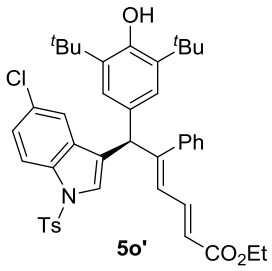
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.259	MM	1.0376	1177.65723	18.91718	49.7729
2	38.408	MM	0.9468	1188.40234	20.92020	50.2271

Enantiomeric Sample of 5o



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.638	MM	1.0252	15.72054	2.55559e-1	1.2325
2	38.609	BB	0.9162	1259.75977	19.91010	98.7675

(S)-Ethyl(2E,4Z)-6-(5-chloro-1-tosyl-1H-indol-3-yl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (5o')

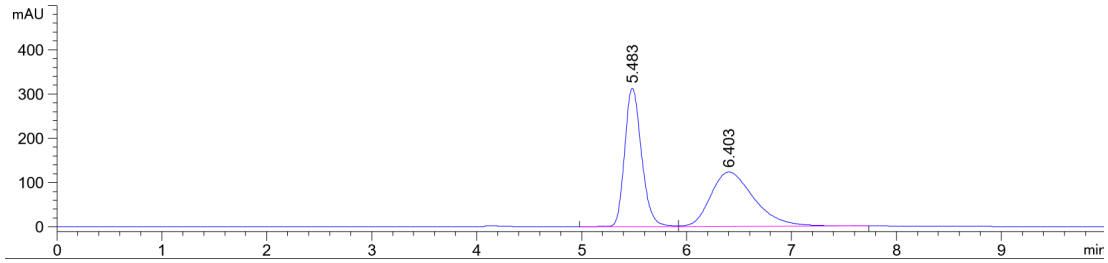


5o'

Compound **5o'** (41.8 mg, 58% yield) was obtained as a yellow solid following the *general procedure III* from **1o** (0.1 mmol, 52.1 mg) and **2k** (0.2 mmol, 40 mg, 40 μL) stirred for 48 hours. **^{1}H NMR** (400 M, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.31-7.27 (m, 5H), 7.25-7.24 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14-7.12 (m, 2H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.94 (s, 2H), 5.85 (d, *J* = 11.6 Hz, 1H), 5.63 (d, *J* = 15.2 Hz, 1H), 5.17 (s, 1H), 5.09 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.38 (s, 18H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (400 M, $CDCl_3$) δ 167.0, 152.9, 152.0, 145.1, 141.4, 139.5, 136.0, 134.7, 134.2, 131.7, 129.9, 129.4, 129.3, 128.7, 128.3, 128.0, 127.5, 127.4, 126.6, 125.5, 125.4, 125.2, 122.2, 119.9, 115.1, 60.2, 50.7, 34.4, 30.3, 21.5, 14.2. **IR** (neat) υ 3626, 2957, 1711, 1621, 1432, 1265, 1172, 1118, 980, 807, 669 cm^{-1}; **MP**: 190-192 ^{o}C; **HRMS** Calcd. for $C_{43}H_{45}O_5NSCl^-$ [M-H]$^-$: 722.2713, found: 722.2711;

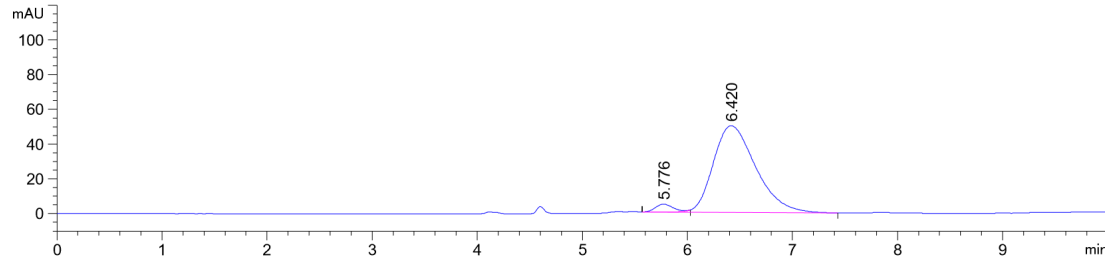
$[\alpha]^{20}_D$ = +48.7 (c 0.15, CH_2Cl_2) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.5 mL/min, 254 nm, t_{minor} = 5.776 min, t_{major} = 6.420 min.

Racemic Sample of 5o'



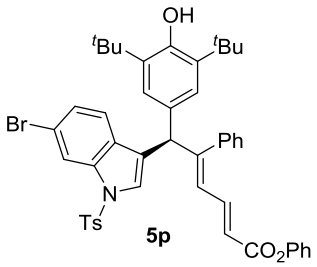
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.483	BV	0.1723	3496.87231	313.06070	49.7926
2	6.403	VB	0.4415	3526.00098	122.60867	50.2074

Enantiomeric Sample of 5o'



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.776	BV E	0.1802	50.91850	4.42570	3.5081
2	6.420	VB R	0.4338	1400.53296	49.84637	96.4919

(S)-Phenyl(2E,4Z)-6-(6-bromo-1-tosyl-1H-indol-3-yl)-6-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (**5p**)

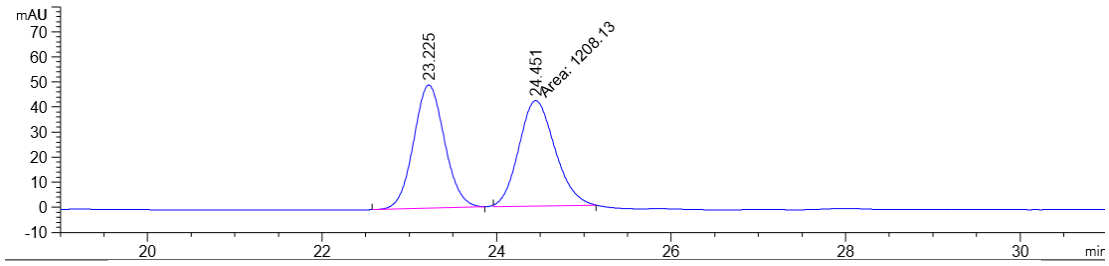


Compound **5p** (51.2 mg, 63% yield) was obtained as a yellowish solid following the *general procedure III* from **1p** (0.1 mmol, 56.5 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.2 Hz, 1H), 7.65-7.63 (m, 2H), 7.44 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 7.36-7.29 (m, 6H), 7.25-7.19 (m, 4H), 7.15-7.13 (m, 2H), 7.06-7.03 (m, 2H), 6.96 (d, *J* = 1.2 Hz, 1H),

6.95 (s, 2H), 5.94 (d, J = 11.6 Hz, 1H), 5.82 (d, J = 15.2 Hz, 1H), 5.19 (s, 1H), 5.15 (s, 1H), 2.40 (s, 3H), 1.39 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 153.4, 152.9, 150.7, 145.3, 143.4, 139.3, 136.5, 136.0, 134.8, 130.0, 129.30, 129.27, 129.2, 128.7, 128.4, 128.2, 127.4, 126.8, 126.7, 126.5, 125.7, 125.6, 125.4, 121.5, 121.3, 121.1, 118.7, 117.1, 50.8, 34.4, 30.3, 21.6; **IR** (neat) ν 3629, 2957, 2920, 1731, 1621, 1595, 1491, 1434, 1372, 1259, 1194, 1118, 807, 667 cm^{-1}; **MP**: 80-82 ℃; **HRMS** Calcd. for $C_{47}H_{45}NO_5BrS^-$ [M-H]$^-$: 814.2207, found: 814.2207.

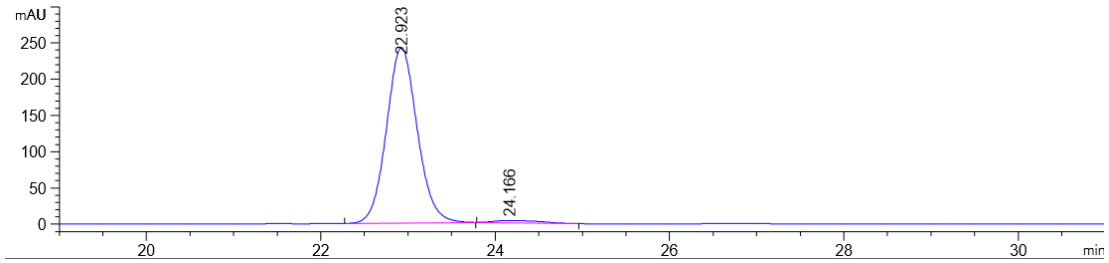
$[\alpha]^{20}_D$ = +70.2 (c 0.25, CH_2Cl_2) for 96% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 230 nm, t_{minor} = 24.166 min, t_{major} = 22.923 min.

Racemic Sample of 5p



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.225	BB	0.3810	1209.81140	49.17106	50.0348
2	24.451	MM	0.4789	1208.13037	42.04684	49.9652

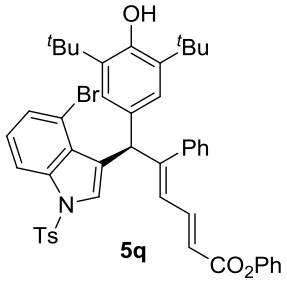
Enantiomeric Sample of 5p



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.923	BB	0.3782	5942.64111	242.20766	98.0683
2	24.166	BB	0.5276	117.05723	3.10683	1.9317

(S)-Phenyl(2E,4Z)-6-(6-bromo-1-tosyl-1H-indol-3-yl)-6-(3,5-di-tert-butyl-4-hydro

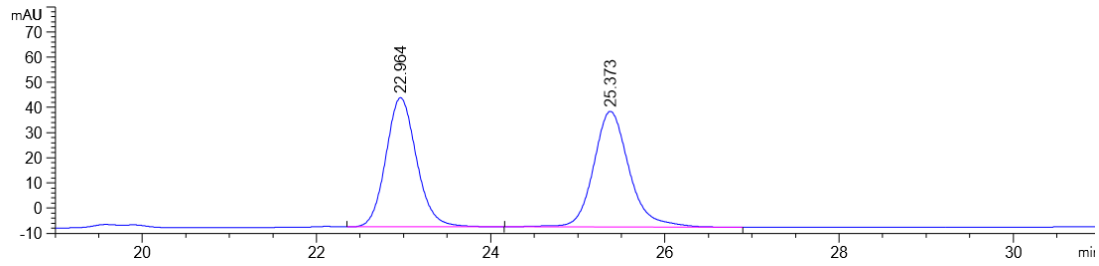
xyphenyl)-5-phenylhexa-2,4-dienoate (5q)



Compound **5q** (39.0 mg, 48% yield) was obtained as a yellow solid following the *general procedure III* from **1q** (0.1 mmol, 56.5 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (dd, J_1 = 12.0 Hz, J_2 = 15.2 Hz, 1H), 7.41-7.35 (m, 4H), 7.28-7.14 (m, 8H), 7.07-7.05 (m, 2H), 7.01 (s, 3H), 5.89 (s, 1H), 5.76 (d, *J* = 12.0 Hz, 1H), 5.72 (d, *J* = 15.2 Hz, 1H), 5.17 (s, 1H), 2.40 (s, 3H), 1.42 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 154.8, 152.7, 150.7, 145.4, 143.9, 139.2, 137.1, 135.9, 134.5, 130.3, 129.9, 129.31, 129.29, 128.6, 128.4, 128.3, 128.1, 128.0, 127.1, 126.7, 126.1, 125.9, 125.7, 125.6, 121.6, 120.7, 114.7, 113.3, 50.3, 34.4, 30.4, 21.6; IR (neat) ν 3629, 2957, 2920, 1728, 1621, 1593, 1491, 1434, 1372, 1237, 1192, 1172, 1160, 1118, 985, 700 cm^{-1}; **MP**: 78-81 ℃; **HRMS** Calcd. for $C_{47}H_{45}NO_5BrS^-$ [M-H]$^-$: 814.2207, found: 814.2206.

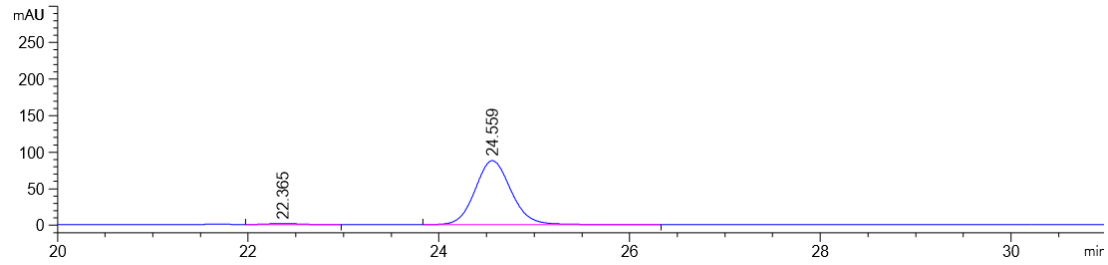
$[\alpha]^{20}_D$ = +234.4 (c 0.4, CH_2Cl_2) for 97% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 254 nm, t_{minor} = 22.365 min, t_{major} = 24.559 min.

Racemic Sample of 5q



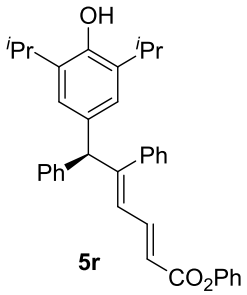
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.964	BB	0.3754	533.30829	21.80332	49.8166
2	25.373	BB	0.4255	537.23523	19.37229	50.1834

Enantiomeric Sample of 5q



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.365	BB	0.3347	33.50868	1.52278	1.4411
2	24.559	BB	0.4033	2291.67798	87.56066	98.5589

(S)-Phenyl(2E,4Z)-6-(4-hydroxy-3,5-diisopropylphenyl)-5,6-diphenylhexa-2,4-die noate (**5r**)

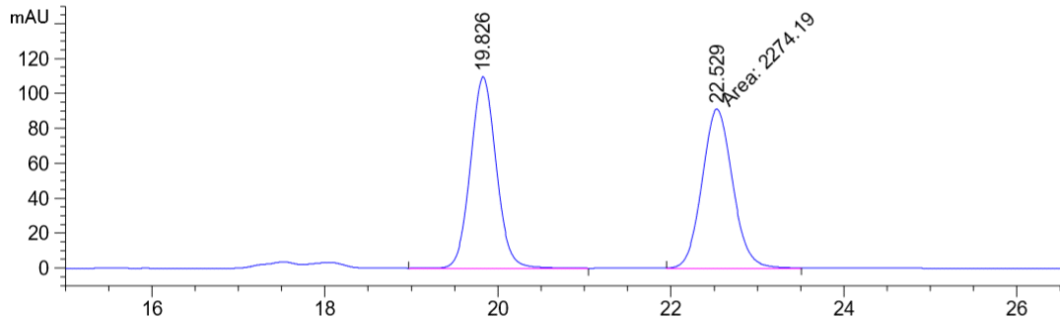


Compound **5r** (29.0 mg, 57% yield) was obtained as a yellowish solid following the *general procedure III* from **1r** (0.1 mmol, 26.6 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, J_1 = 11.6 Hz, J_2 = 15.6 Hz, 1H), 7.36-7.27 (m, 6H), 7.24-7.23 (m, 1H), 7.21-7.17 (m, 6H), 7.07-7.04 (m, 2H), 6.84 (s, 2H), 6.05 (d, *J* = 11.6 Hz, 1H), 5.99 (d, *J* = 15.6 Hz, 1H), 5.25 (s, 1H), 4.72 (s, 1H), 3.16-3.06 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 156.8, 150.8, 148.6, 144.0, 142.0, 140.0, 133.5, 132.6, 129.4, 129.3, 128.8, 128.4, 128.2, 128.0, 127.9, 126.6, 125.5, 124.7, 121.6, 120.5, 59.7, 27.2, 22.74, 22.67; **IR** (neat) ν 3499, 2960, 2923, 1731, 1652, 1618, 1593, 1491, 1457, 1265, 1197, 1160, 1118, 703 cm^{-1}; **MP**: 65-66 ℃; **HRMS** Calcd. for $C_{36}H_{35}O_3^-$ [M-H]$^-$: 515.2592, found: 515.2595.

$[\alpha]^{20}_D$ = +1.0 (c 0.4, CH_2Cl_2) for 95% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.3 mL/min, 254 nm,

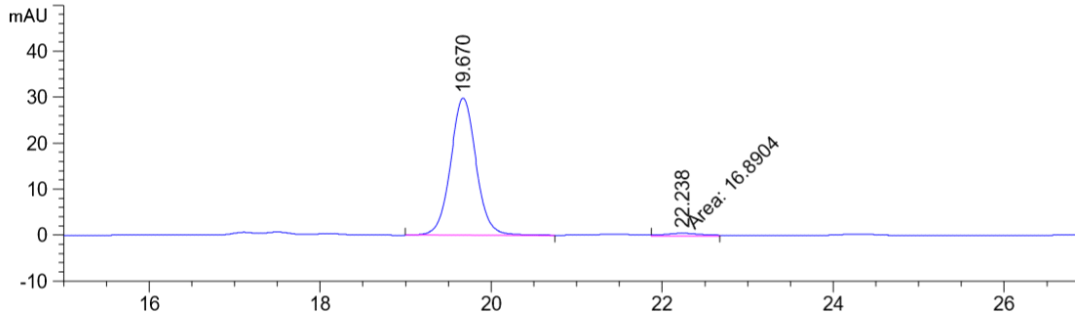
t_{minor} = 22.238 min, t_{major} = 19.670 min.

Racemic Sample of 5r



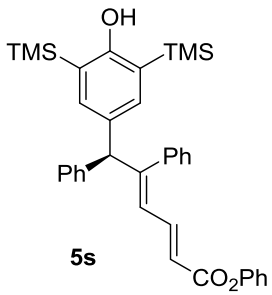
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.826	BB	0.3198	2275.56665	109.78253	50.0152
2	22.529	MM	0.4139	2274.18701	91.57488	49.9848

Enantiomeric Sample of 5r



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.670	BB	0.3176	617.86621	29.83572	97.3391
2	22.238	MM	0.4760	16.89036	5.91358e-1	2.6609

(S)-Phenyl(2E,4Z)-6-(4-hydroxy-3,5-diTMS)-5,6-diphenylhexa-2,4-dienoate (**5s**)



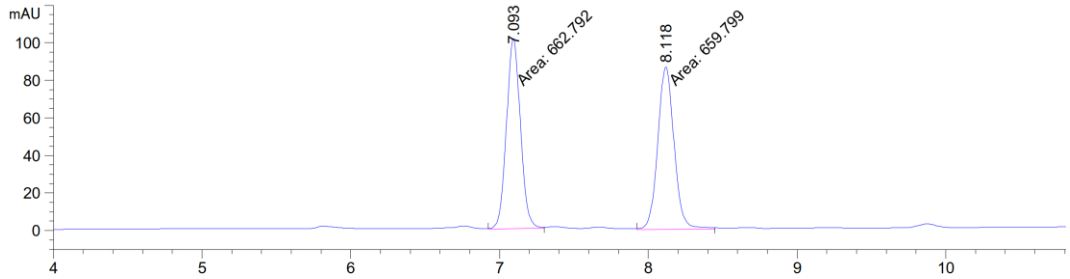
5s

Compound **5s** (38.2 mg, 66% yield) was obtained as a colorless oil following the *general procedure III* from **1s** (0.1 mmol, 32.6 mg) and **2b** (0.2 mmol, 50 mg, 45 μL) stirred for 48 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, J_1 = 11.6 Hz, J_2 = 15.2

Hz, 1H), 7.36-7.24 (m, 7H), 7.21-7.17 (m, 6H), 7.12 (s, 2H), 7.07-7.05 (m, 2H), 6.06 (d, *J* = 11.6 Hz, 1H), 6.01 (d, *J* = 15.2 Hz, 1H), 5.25 (s, 1H), 4.96 (s, 1H), 0.30 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 164.0, 156.5, 150.8, 143.9, 141.7, 139.9, 137.7, 132.3, 129.4, 129.3, 128.8, 128.4, 128.2, 128.1, 127.9, 126.6, 125.5, 123.9, 121.6, 120.6, 59.2, -0.6; **IR** (neat) ν 3604, 2954, 2920, 1728, 1621, 1590, 1491, 1401, 1242, 1197, 1160, 1112, 855, 836, 697 cm^{-1}; **HRMS** Calcd. for $C_{36}H_{39}O_3Si_2^-$ $[M-H]^-$: 575.2443, found: 575.2450.

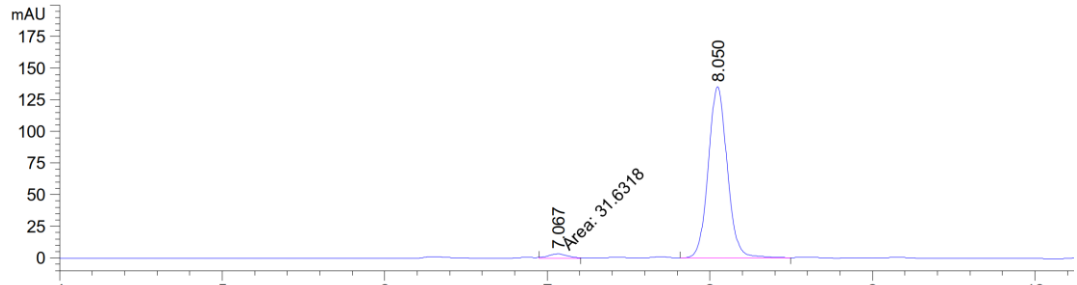
$[\alpha]^{20}_D$ = +16.3 (c 0.4, CH_2Cl_2) for 94% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 270 nm, t_{minor} = 7.067 min, t_{major} = 8.050 min.

Racemic Sample of 5S



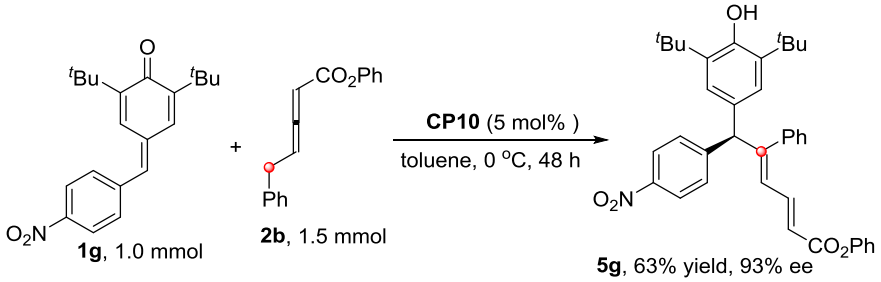
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.093	MM	0.1091	662.79199	101.27503	50.1132
2	8.118	MM	0.1270	659.79889	86.59129	49.8868

Enantiomeric Sample of 5S



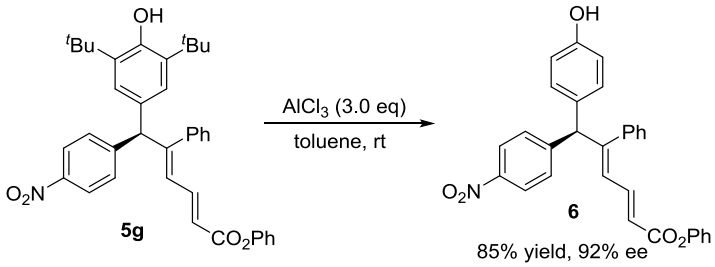
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.067	MM	0.1446	31.63176	3.64496	2.8030
2	8.050	BB	0.1246	1096.86060	135.32040	97.1970

General procedure for the subgram-scale reaction



Enlarging the reaction scale up to 1.0 mmol afforded compound **5g** in 63% yield and 93% ee value under reducing the catalyst loading to 5 mol% following the *general procedure III* from **1g** (1.0 mmol, 339 mg) and **2b** (1.5 mmol, 380 mg).

Transformation experiments to afford compounds 6 and 7



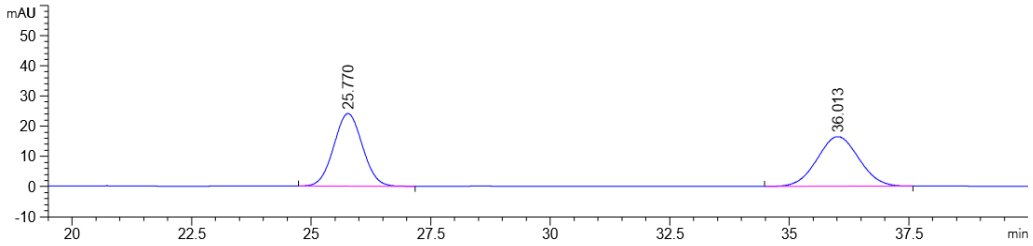
To a solution of **5g** (0.1 mmol, 59 mg) in toluene (3.0 mL) was added $AlCl_3$ (0.3 mmol, 40 mg) at room temperature. The reaction mixture was vigorously stirred for 12 hours, then quenched by saturated NH_4Cl aqueous. The resulting mixture was extracted with EA twice (5 mLx2). The combined organic phases were collected and dried with Na_2SO_4. The organic phase was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA： 4/1, R_f = 0.3) to afford the corresponding product **6** as a brown solid.

Compound **6** (85% yield, 40.5 mg): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 2H), 7.47 (dd, J_1 = 11.2 Hz, J_2 = 15.6 Hz, 1H), 7.37-7.27 (m, 7H), 7.21-7.17 (m, 3H), 7.06-7.02 (m, 4H), 6.82-6.78 (m, 2H), 6.03 (d, J = 15.6 Hz, 1H), 6.00 (d, J = 11.6 Hz, 1H), 5.36 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 155.0, 154.5, 150.6, 149.3, 146.7, 143.1, 139.0, 131.5, 130.6, 130.2, 129.3, 128.7, 128.6, 128.5, 128.4, 125.7, 123.7, 121.6, 121.5, 115.8, 58.6; **IR** (neat) ν 3420, 2957, 2923, 1723, 1618, 1593, 1514, 1344, 1262, 1194, 1118, 853, 700 cm^{-1}; **MP**: 106-109 ℃; **HRMS** Calcd. for

$C_{30}H_{22}NO_5^-$ [M-H]$^-$: 476.1504, found: 476.1495.

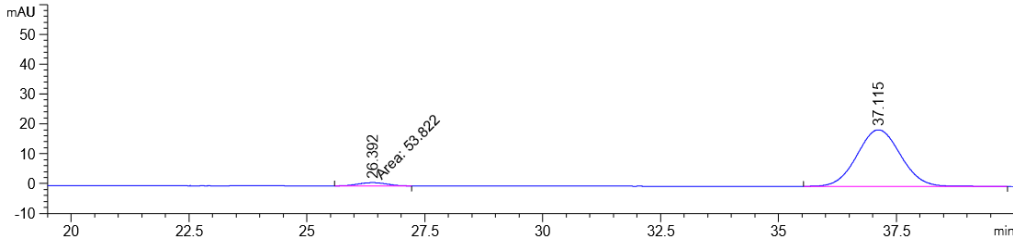
$[\alpha]^{20}_D$ = -1.6 (c 0.25, CH_2Cl_2) for 92% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.5 mL/min, 230 nm, t_{minor} = 26.392 min, t_{major} = 37.115 min.

Racemic sample of 6

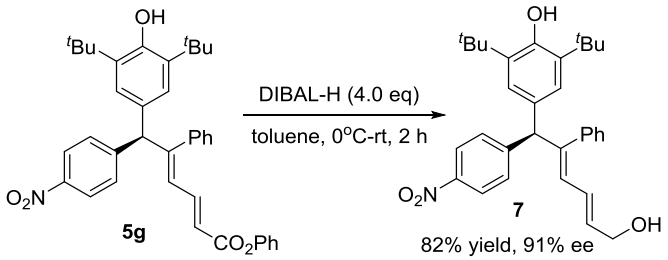


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.770	BB	0.6481	999.60461	23.98972	50.0344
2	36.013	BB	0.9131	998.23016	16.42344	49.9656

Eantiomeric sample of 6



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.392	MM	0.7653	53.82195	1.17215	4.2243
2	37.115	BB	0.9569	1220.28479	18.95998	95.7757



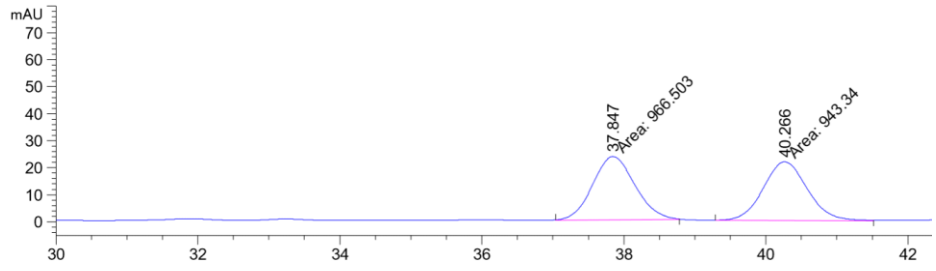
To a solution of **5g** (0.1 mmol, 59 mg) in toluene (3.0 mL) was added DIBAL-H (1.0 M in toluene, 0.4 mmol, 40 μL) at 0 ^{o}C. After addition of DIBAL-H, the reaction mixture was allowed to warm to room temperature for 2 hours, then quenched by

saturated NH_4Cl aq. The resulting mixture was extracted with EA twice (5 mLx2). The combined organic phases were collected and dried with Na_2SO_4. The organic phase was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/EA：6/1, R_f = 0.4) to afford the corresponding product **7** as a yellowish solid.

Compound **7** (82% yield, 40.8 mg): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15-8.11 (m, 2H), 7.38-7.35 (m, 2H), 7.29-7.21 (m, 3H), 7.13-7.11 (m, 2H), 6.91 (s, 2H), 6.28-6.22 (m, 1H), 5.83 (d, *J* = 10.8 Hz, 1H), 5.77 (dt, J_1 = 6.0 Hz, J_2 = 15.2 Hz, 1H), 5.20 (s, 1H), 5.14 (s, 1H), 4.09 (d, *J* = 6.0 Hz, 2H), 1.37 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 150.9, 146.4, 145.2, 140.4, 135.9, 133.2, 130.6, 130.3, 128.9, 128.5, 128.2, 127.2, 126.0, 123.4, 63.4, 59.2, 34.4, 30.3; **IR** (neat) ν 3389, 2957, 2920, 1519, 1434, 1344, 1234, 1152, 974, 703 cm^{-1}; **MP**: 61-63 ℃; **HRMS** Calcd. for $C_{32}H_{36}NO_4^-$ $[M-H]^-$: 498.2649, found: 498.2654.

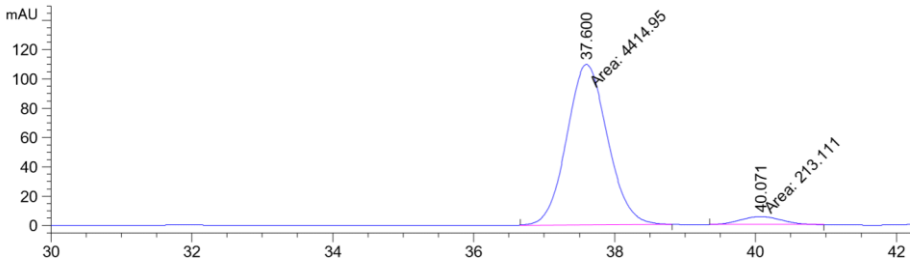
$[\alpha]^{20}_D$ = -1.2 (c 0.25, CH_2Cl_2) for 91% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IB-H column, Hexane/^{i}PrOH = 90/10, 0.5 mL/min, 230 nm, t_{minor} = 40.071 min, t_{major} = 37.600 min.

Racemic sample of 7



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.847	MM	0.6890	966.50342	23.38048	50.6064
2	40.266	MM	0.7229	943.34027	21.74756	49.3936

Enantiomeric sample of 7



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.600	MM	0.6717	4414.95068	109.54562	95.3952
2	40.071	MM	0.6579	213.11075	5.39861	4.6048

4. References

[1] (a) H. Xiao, Z. Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang, G. Zhao, *Angew. Chem., Int. Ed.* **2010**, *49*, 4467; (b) X. Han, Y. Wang, F. Zhong, Y. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 1726.

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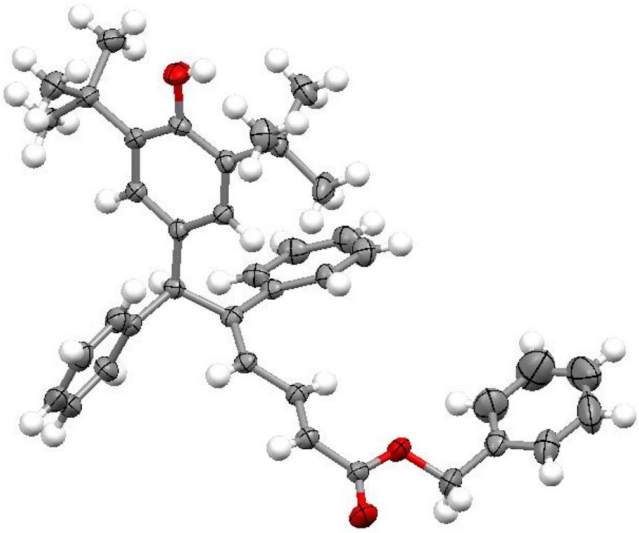
[4] (a) R. W. Lange, H.-J. Hansen, *Org. Synth.* **1984**, *62*, 202; (b) B. T. B. Hue, J. Dijkink, S. Kuiper, S. Schaik, J. H. Maarseveen, H. Hiemstra, *Eur. J. Org. Chem.* **2006**, 127.

[5] L. Schwarz, U. Girreser, B. Clement, *Eur. J. Org. Chem.* **2014**, 1961.

[6] (a) Y. Fukata, K. Asano, S. Matsubara*J. Am. Chem. Soc.* **2013**, *135*, 12160; (b) D. Wang, Y. Lei, Y. Wei, M. Shi, *Chem. Eur. J.* **2014**, *20*, 15325.

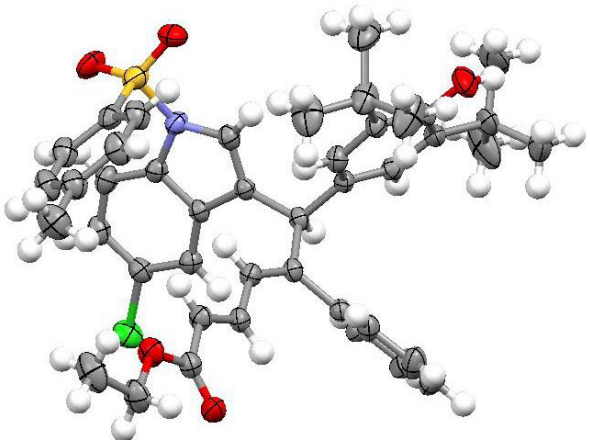
5. X-ray data



Crystal data and structure refinement for compound 3a.

Identification code	exp_8822
Empirical formula	$C_{39}H_{42}NO_3$
Formula weight	558.73
Temperature/K	293(2)
Crystal system	N/A
Space group	P21
a/Å	9.6333(6)
b/Å	16.6755(10)
c/Å	10.1957(6)
α/°	90.00
β/°	97.399(6)
γ/°	90.00
Volume/Å^3	1624.20(17)
Z	2
ρ_{calc}g/cm^3	1.142
μ/mm^{-1}	0.547
F(000)	600.0
Crystal size/mm^3	0.30 × 0.20 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	8.74 to 132.98
Index ranges	$-11 \leq h \leq 10$, $-19 \leq k \leq 19$, $-12 \leq l \leq 8$
Reflections collected	6333
Independent reflections	4596 [R_{int} = 0.0286, R_{sigma} = N/A]
Data/restraints/parameters	4596/1/387

Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0815, wR_2 = 0.1330
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.12
Flack parameter	-0.0(4)

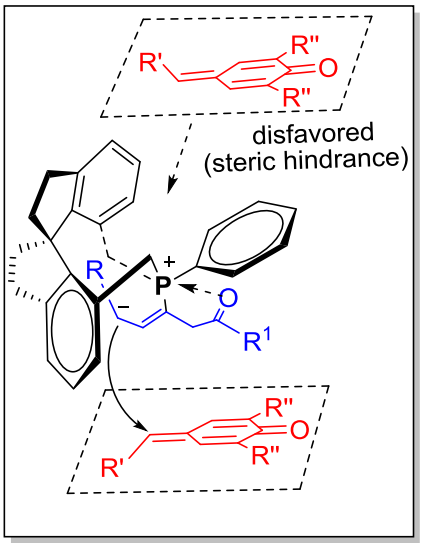


Crystal data and structure refinement for compound 5o'.

Identification code	181205a
Empirical formula	$C_{43}H_{46}ClNO_5S$
Formula weight	724.32
Temperature/K	298(2)
Crystal system	N/A
Space group	P-1
a/Å	10.4270(9)
b/Å	13.9139(11)
c/Å	14.0151(12)
α/°	76.993(10)
β/°	85.818(2)
γ/°	82.698(2)
Volume/$Å^3$	1963.0(3)
Z	2
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.195
F(000)	768.0
Crystal size/mm^3	0.20 × 0.17 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.84 to 50.04
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -16 ≤ l ≤ 10

Reflections collected	9917
Independent reflections	6839 [R_{int} = 0.0307, R_{sigma} = N/A]
Data/restraints/parameters	6839/0/460
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.0592
Final R indexes [all data]	R_1 = 0.1246 wR_2 = 0.0666
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.15

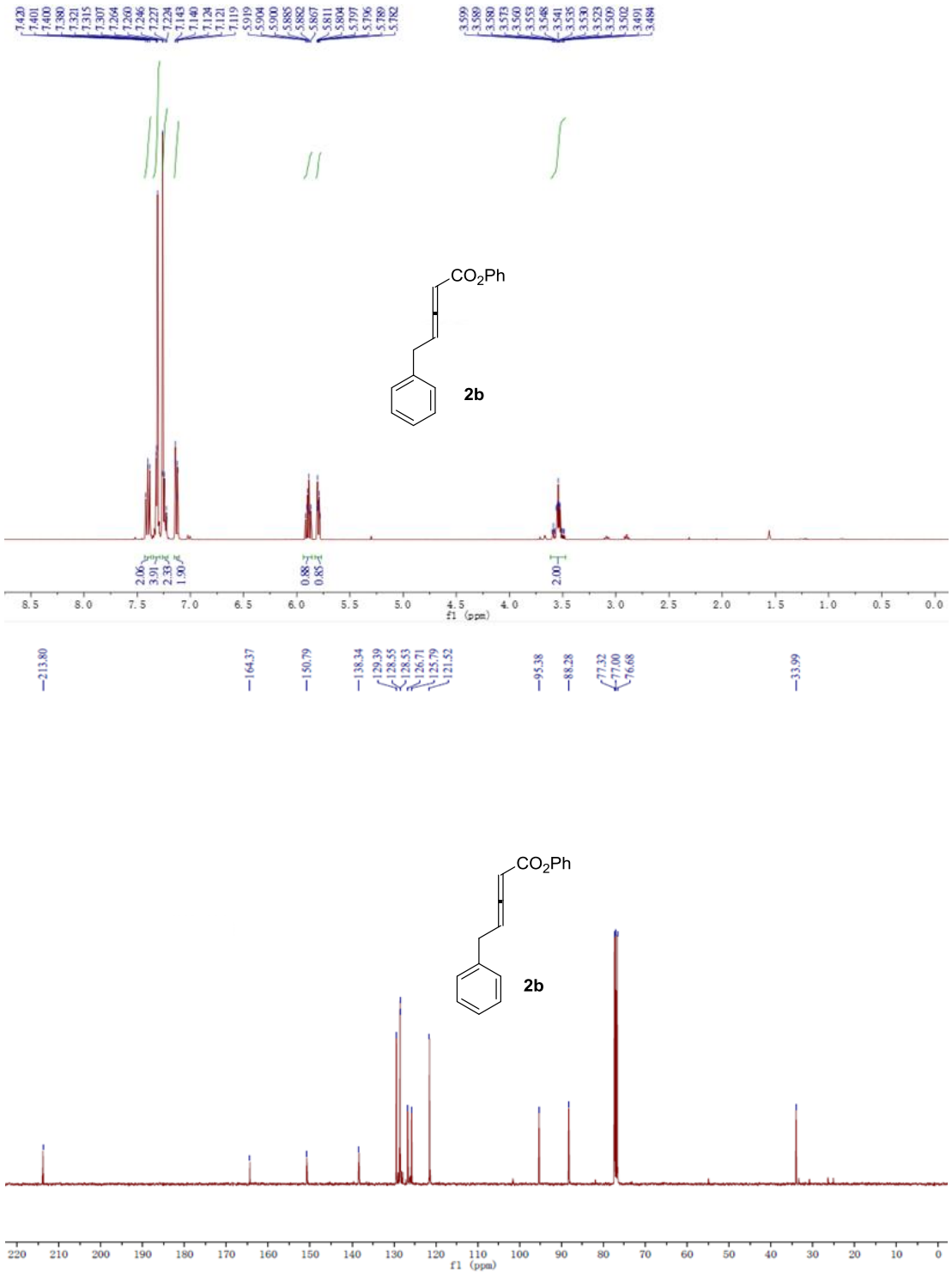
A plausible transition state



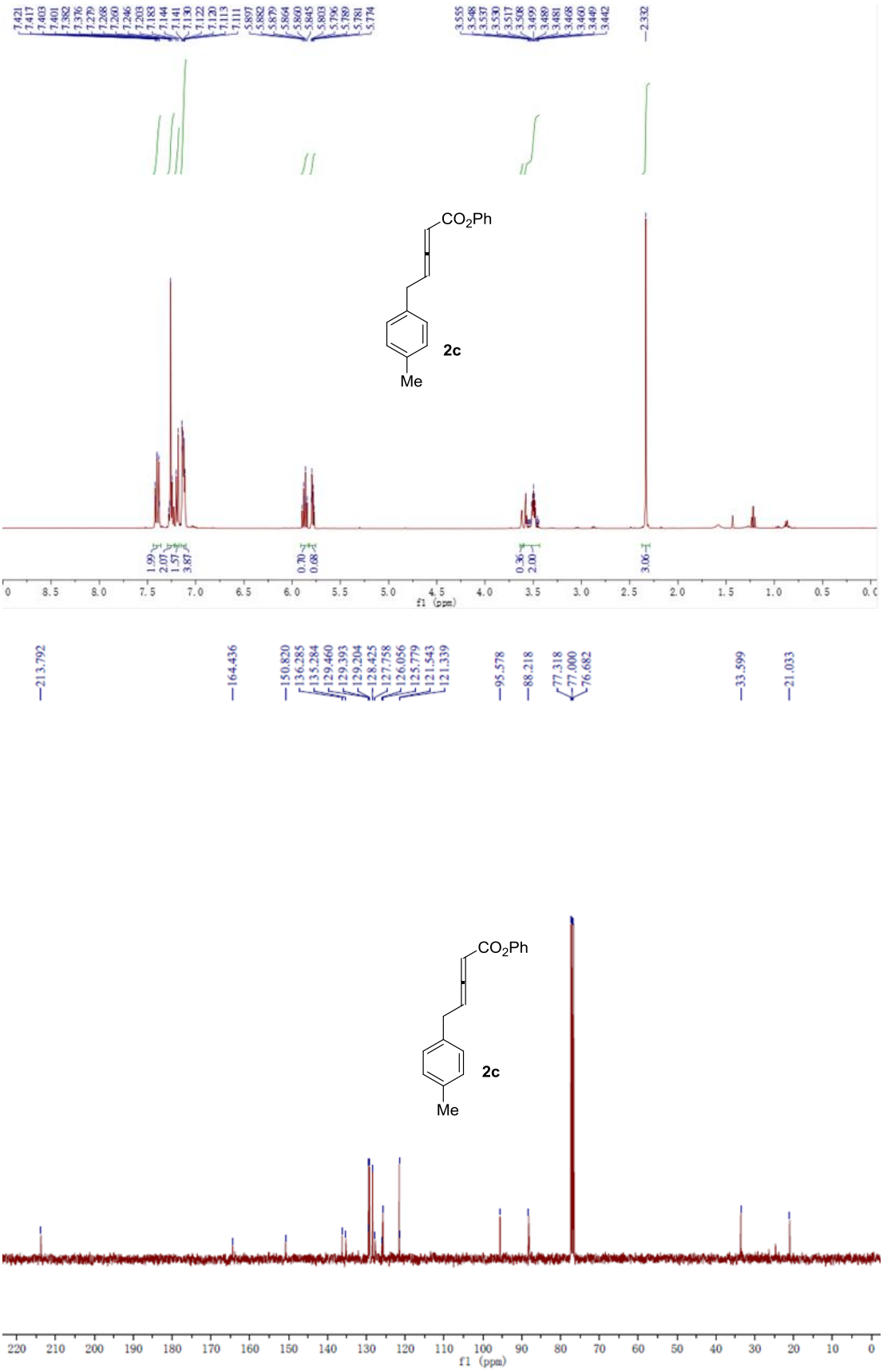
Scheme S1 A plausible transition state

The plausible transition state of this reaction is illustrated in Scheme S1 which may account for the stereoselectivity. The *p*-QMs approach the zwitterionic intermediate from (*R*)-SITCP and allenoate to form the corresponding products through less steric hindrance face due to the zwitterionic species stereochemistry, which is accordance with our experimental results.

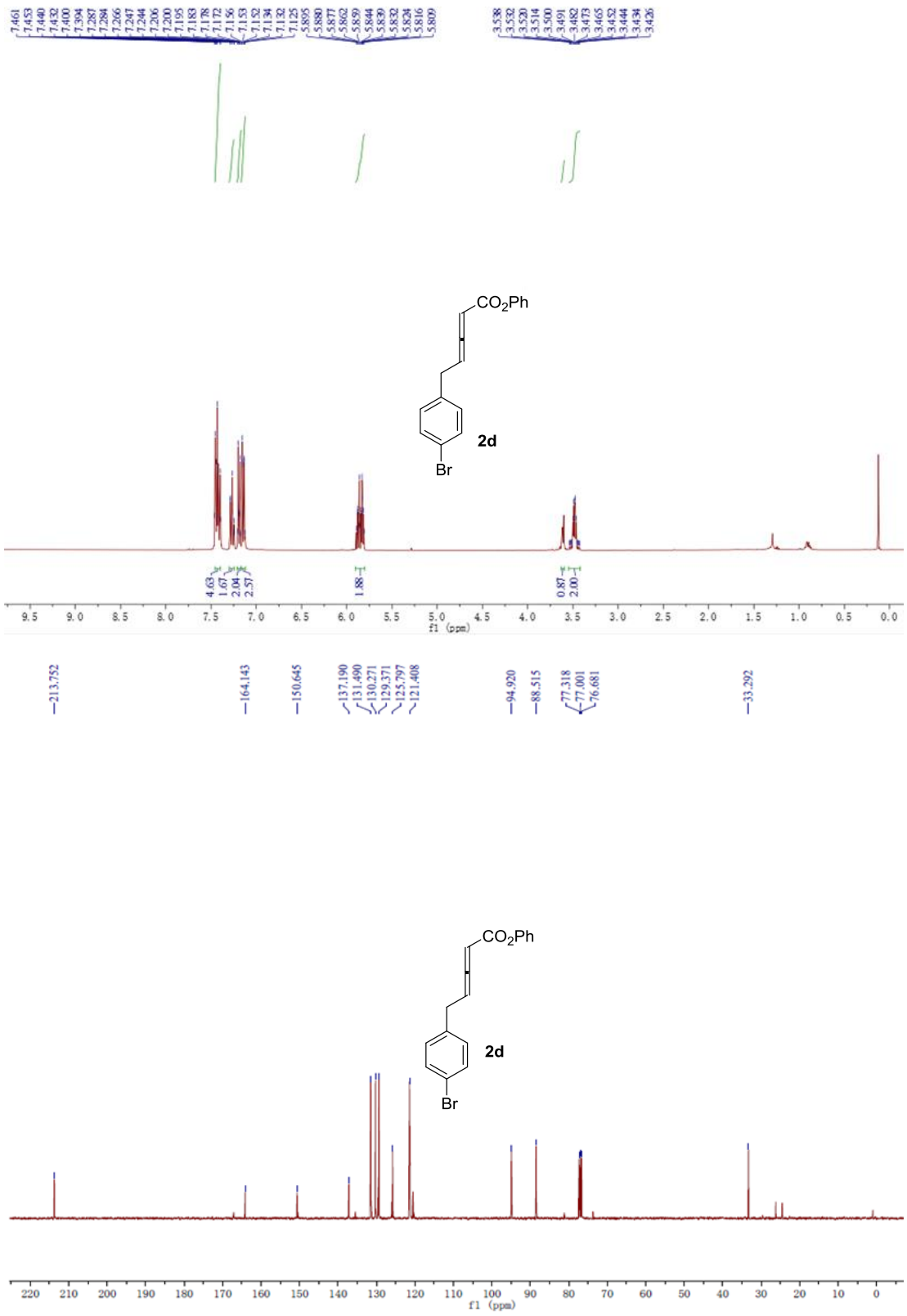
6. NMR Spectra



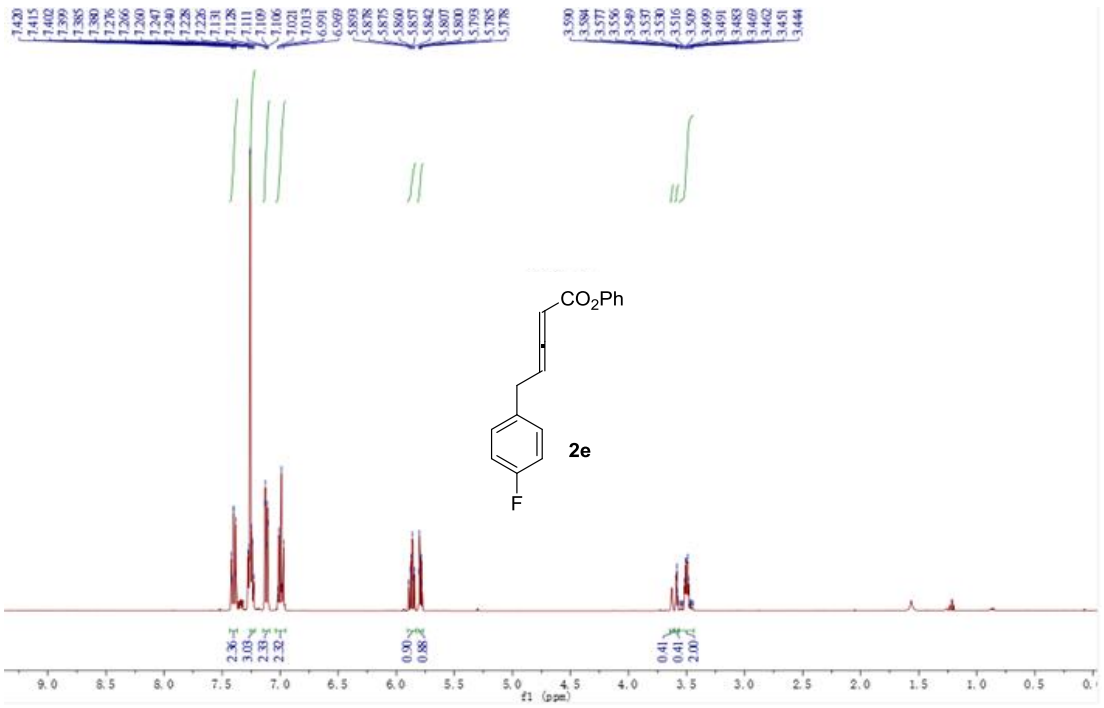
^{1}H and ^{13}C NMR spectra of compound **2b**

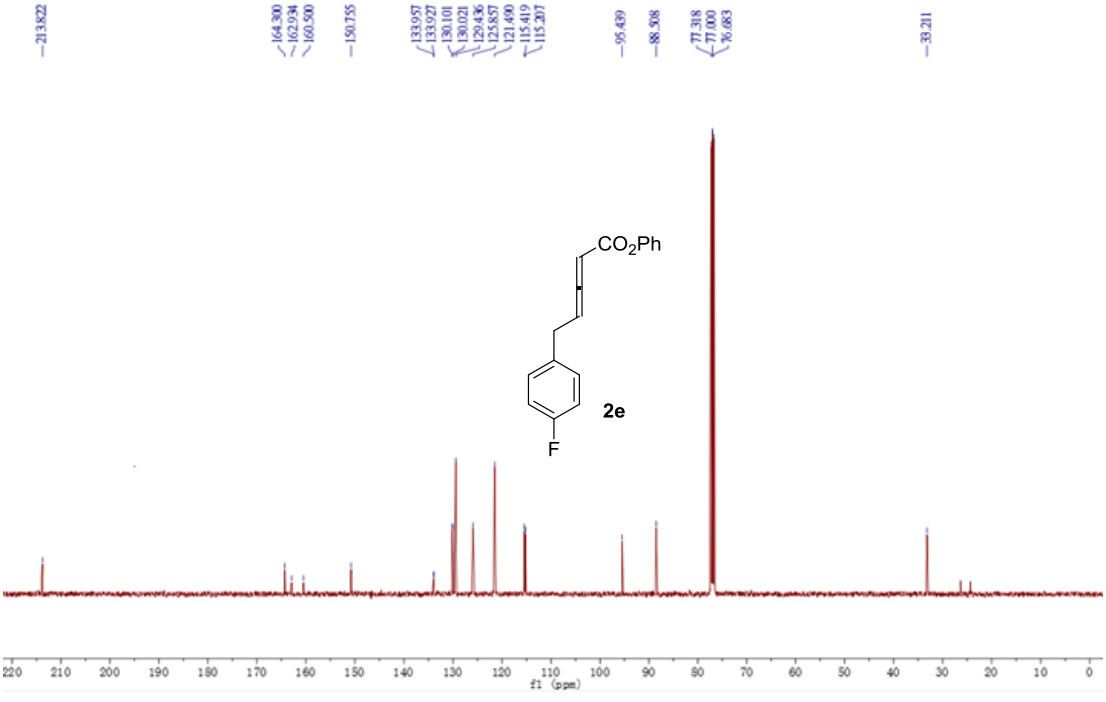


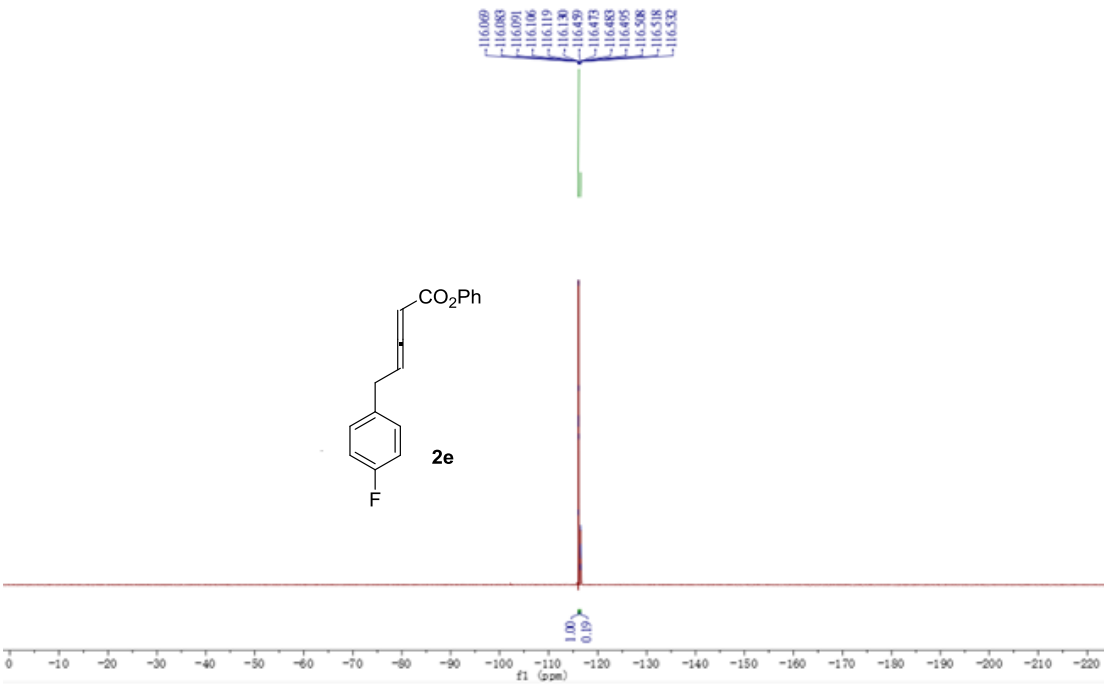
^{1}H and ^{13}C NMR spectra of compound **2c**



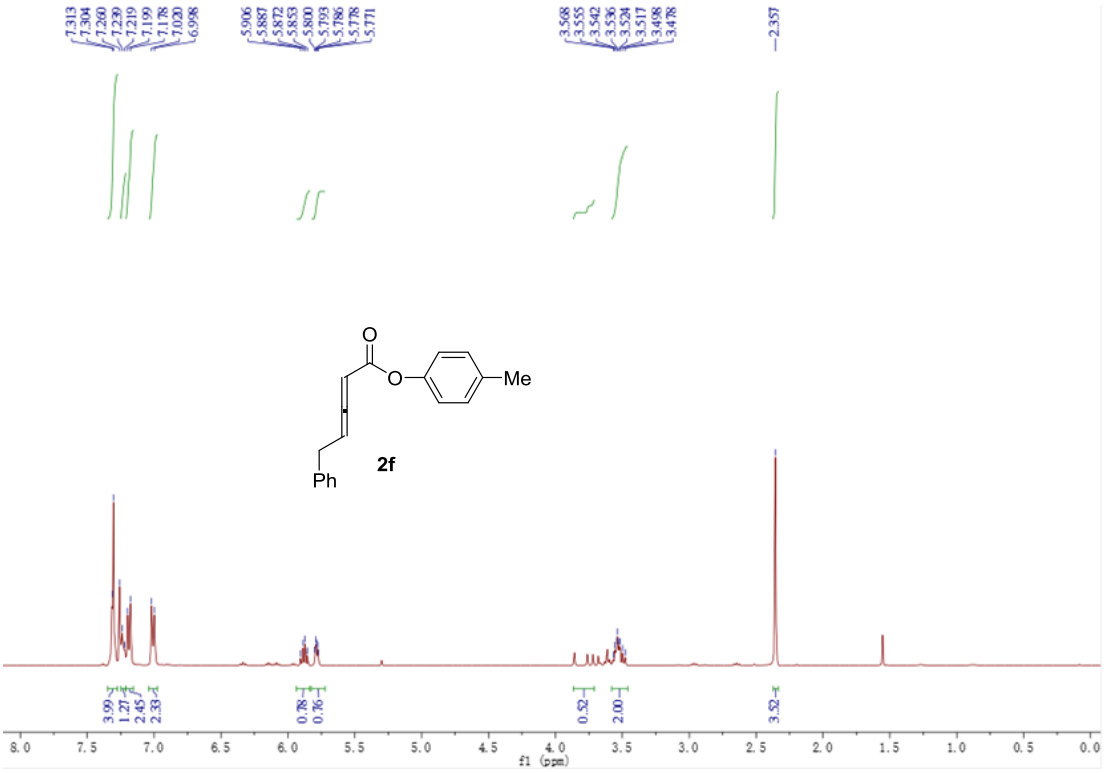
^{1}H and ^{13}C NMR spectra of compound **2d**

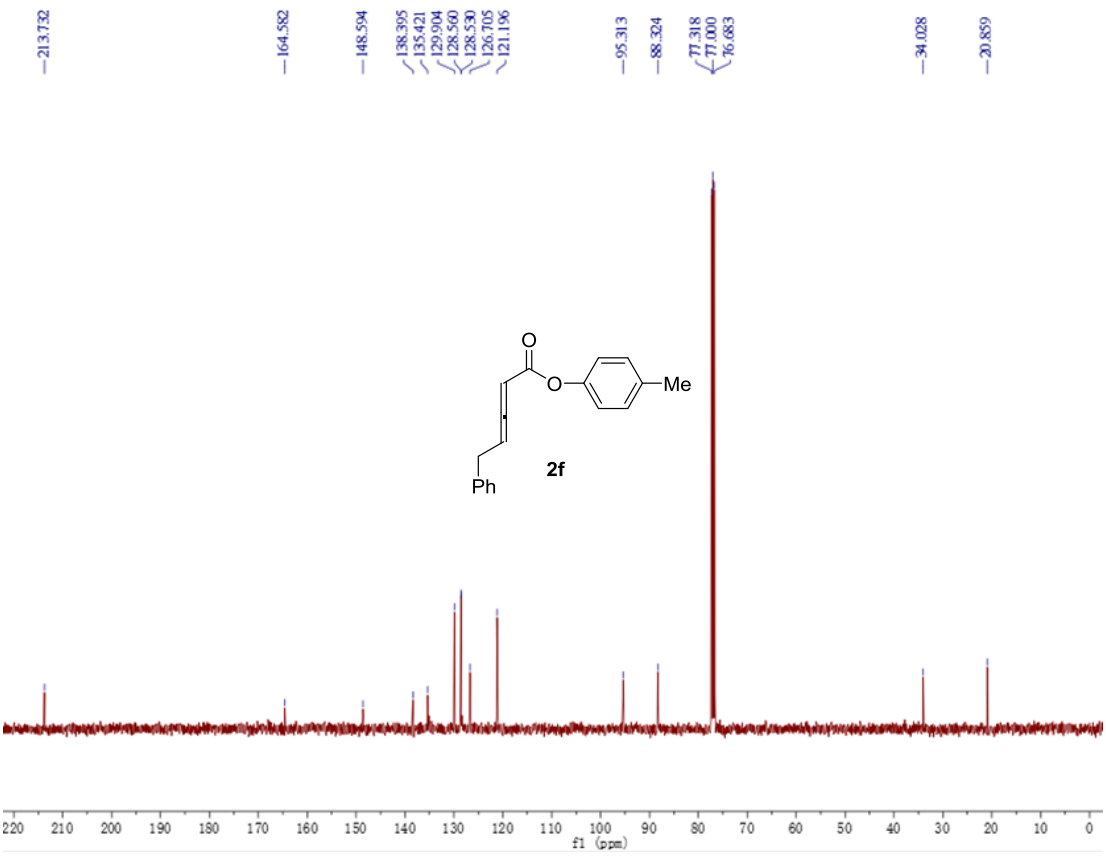

7.420
7.415
7.402
7.399
7.385
7.380
7.276
7.266
7.260
7.247
7.240
7.228
7.226
7.131
7.128
7.111
7.109
7.106
7.021
7.013
6.991
6.969
5.893
5.878
5.875
5.860
5.857
5.842
5.807
5.800
5.793
5.785
5.778
3.590
3.584
3.577
3.556
3.549
3.537
3.530
3.516
3.509
3.499
3.491
3.483
3.469
3.462
3.451
3.444
CO2Ph
2e
F
2.36
3.03
2.33
2.32
0.90
0.88
0.41
0.41
2.00
f1 (ppm)


213.822
164.300
162.994
160.500
150.755
133.957
133.927
130.101
130.021
129.436
125.857
121.490
115.419
115.207
95.439
88.508
77.318
77.000
76.683
39.211
CO2Ph
2e
F
f1 (ppm)

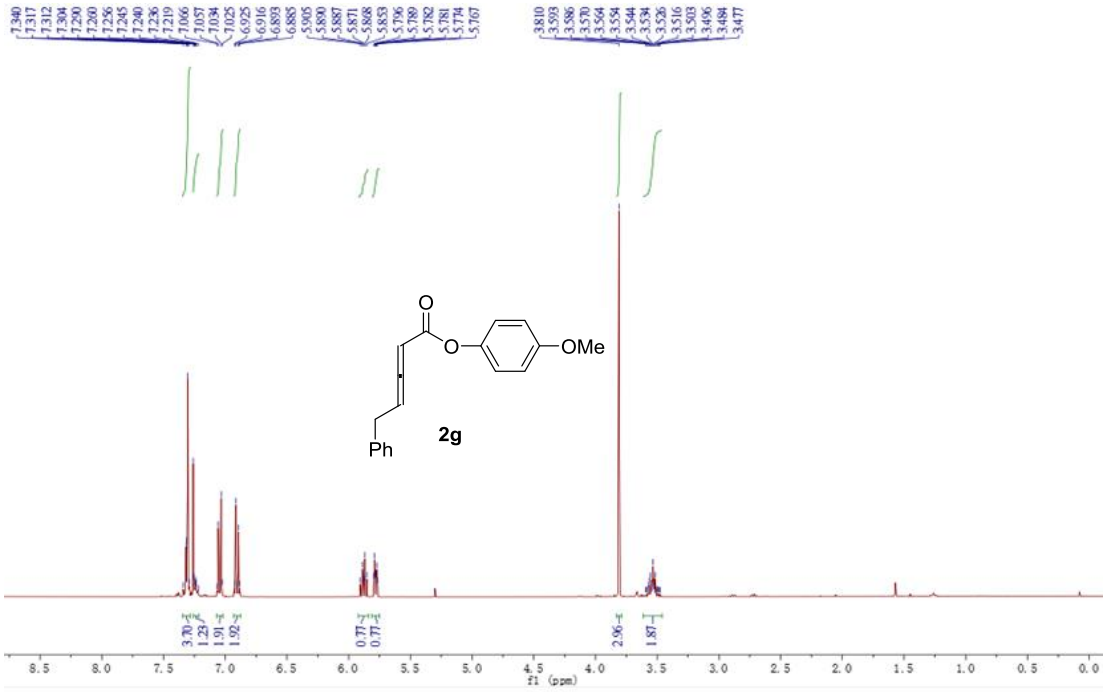


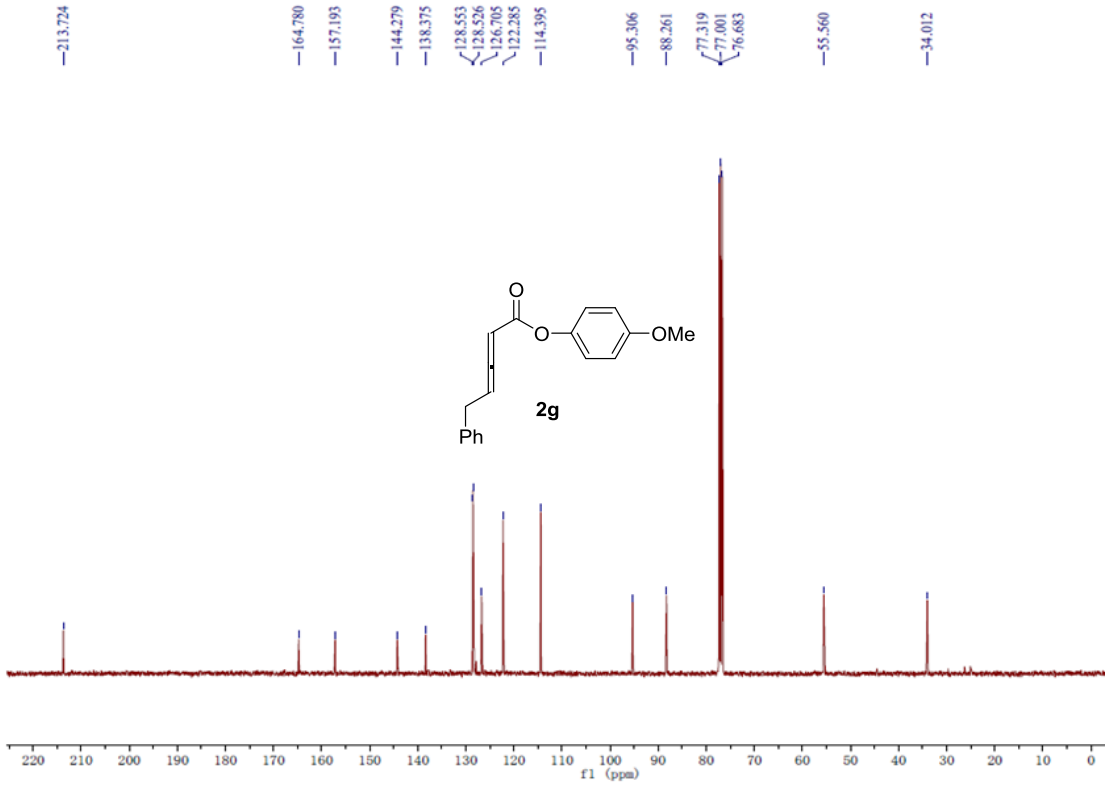
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **2e**



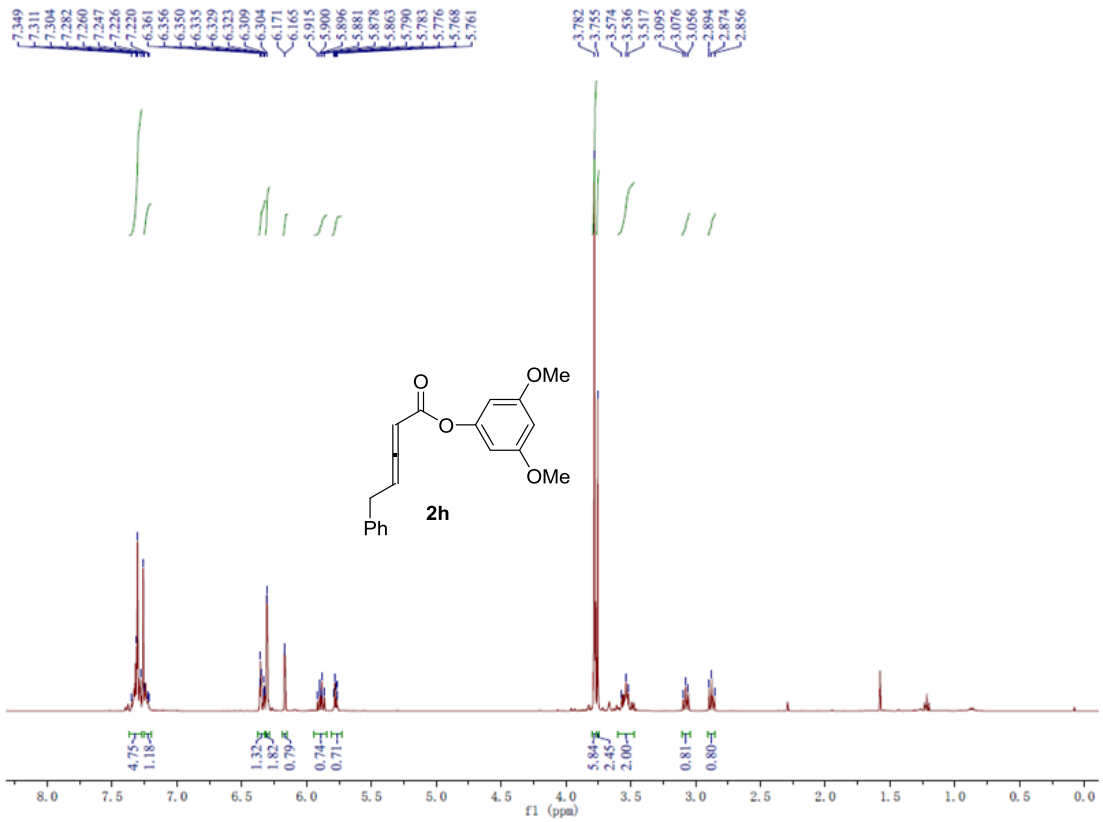


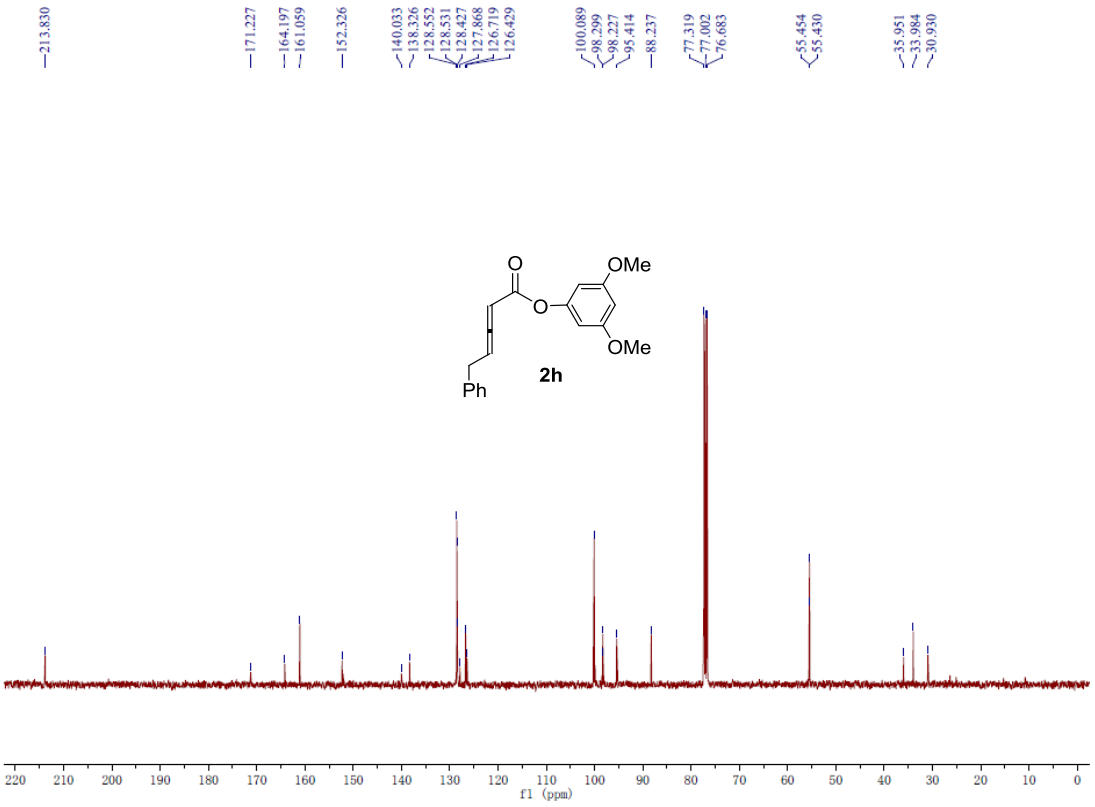
^{1}H and ^{13}C NMR spectra of compound **2f**



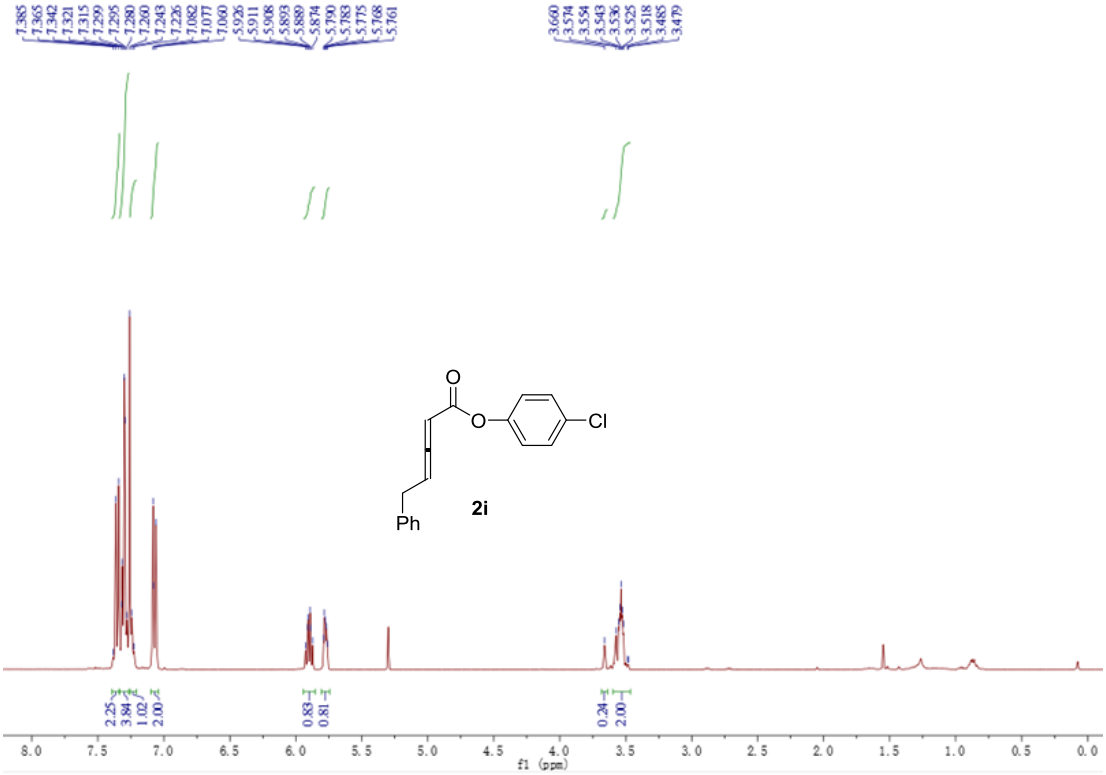


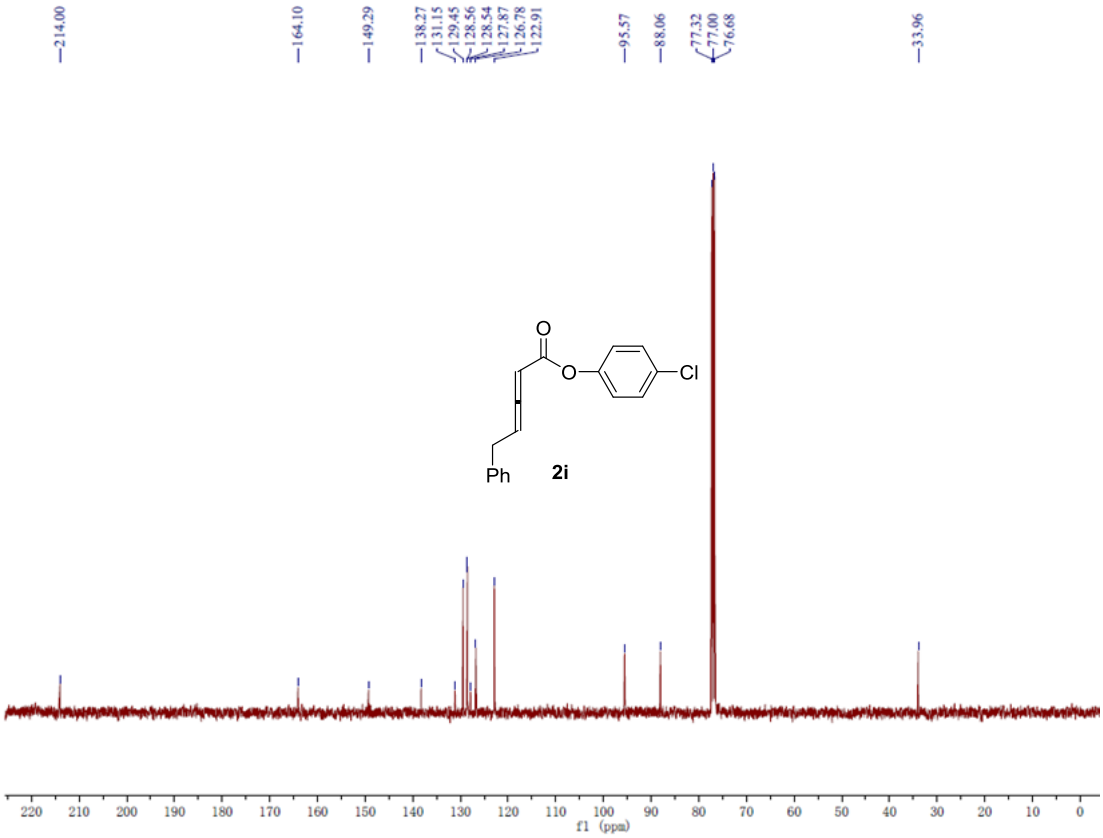
^{1}H and ^{13}C NMR spectra of compound **2g**



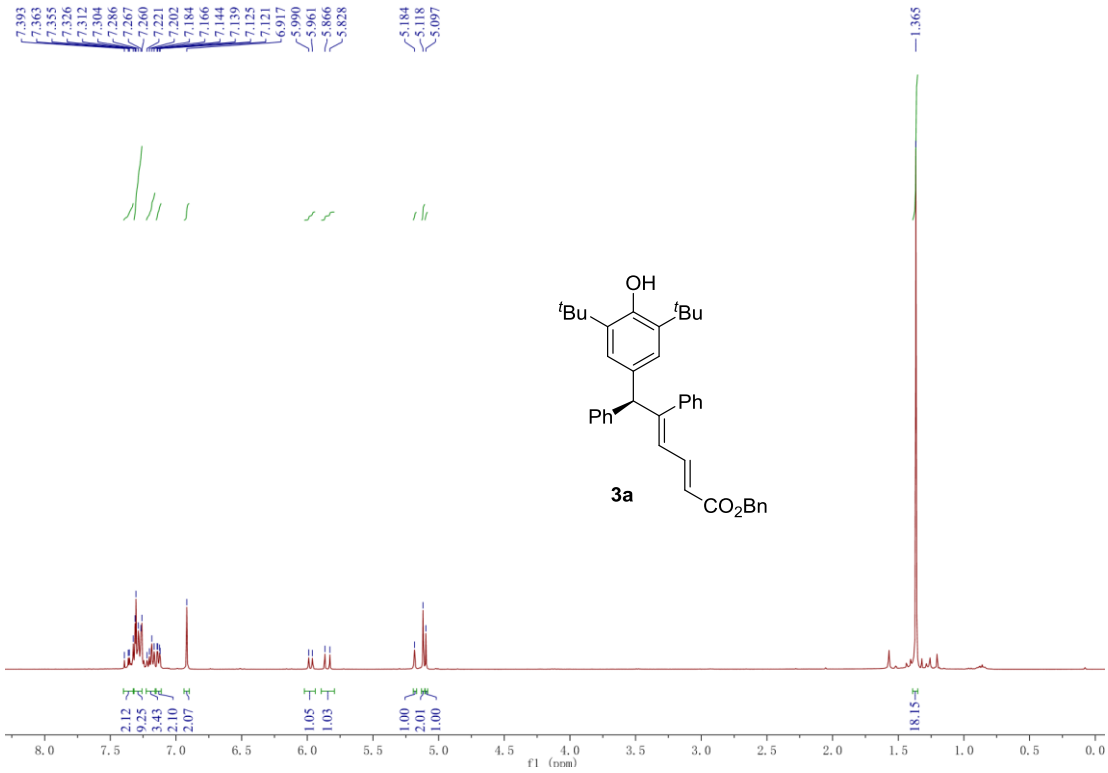


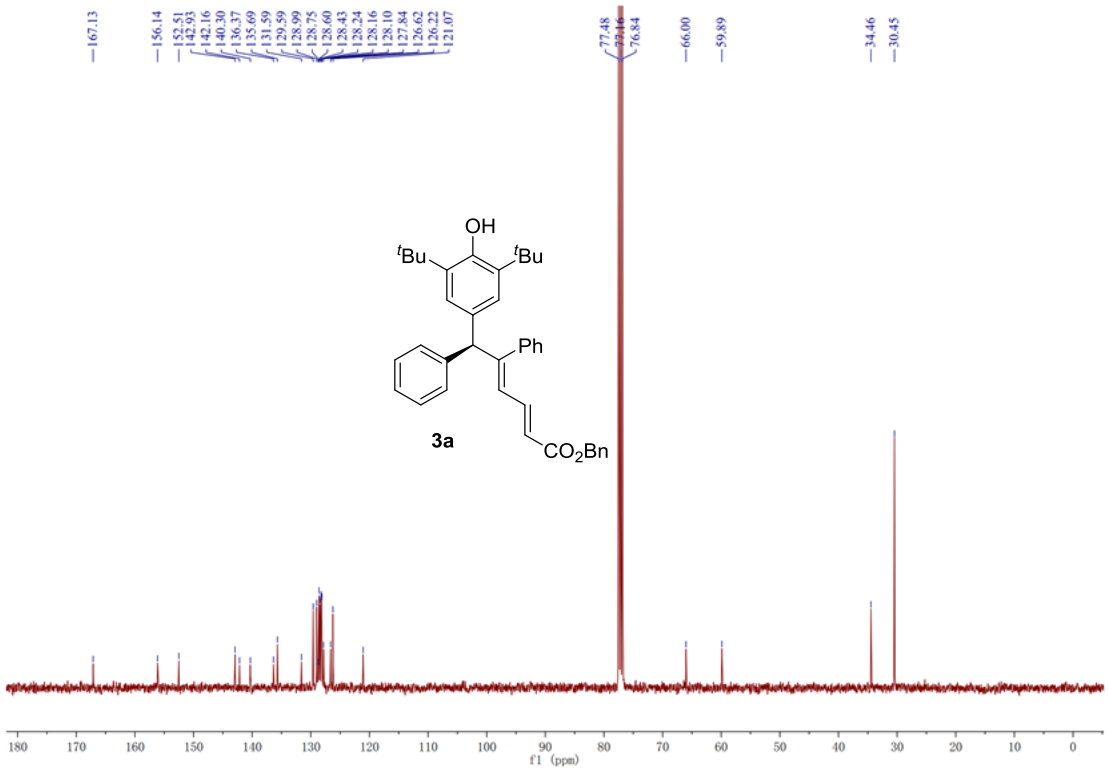
^{1}H and ^{13}C NMR spectra of compound **2h**



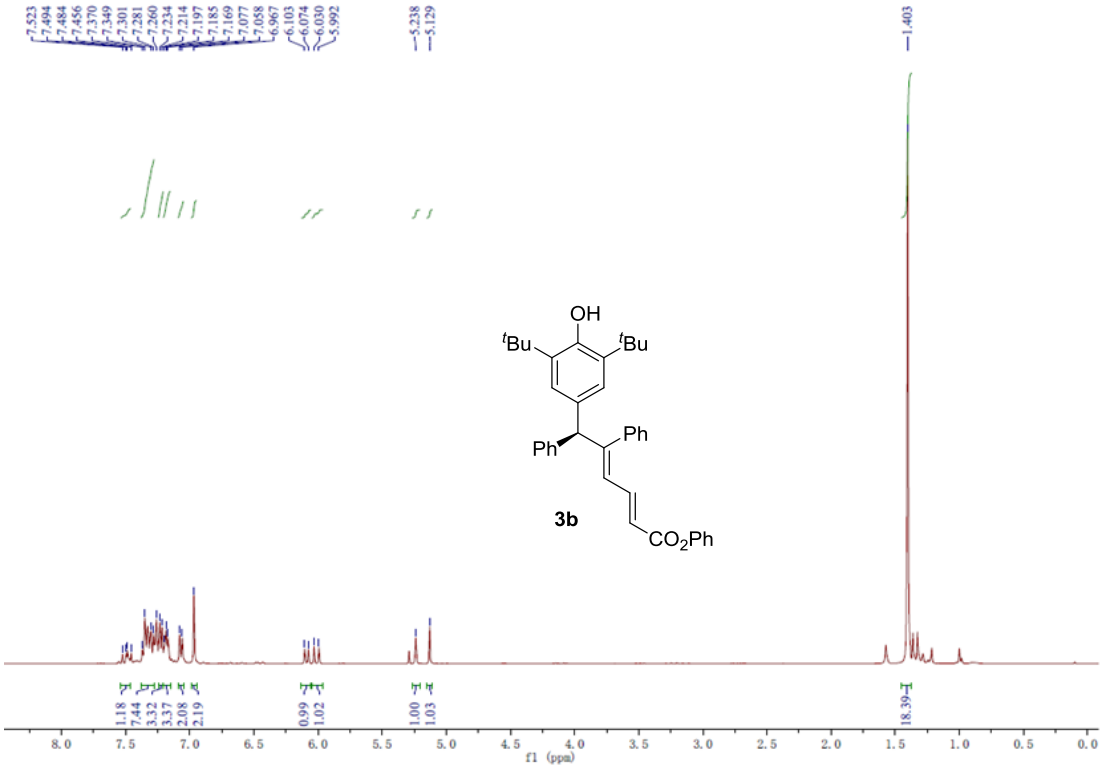


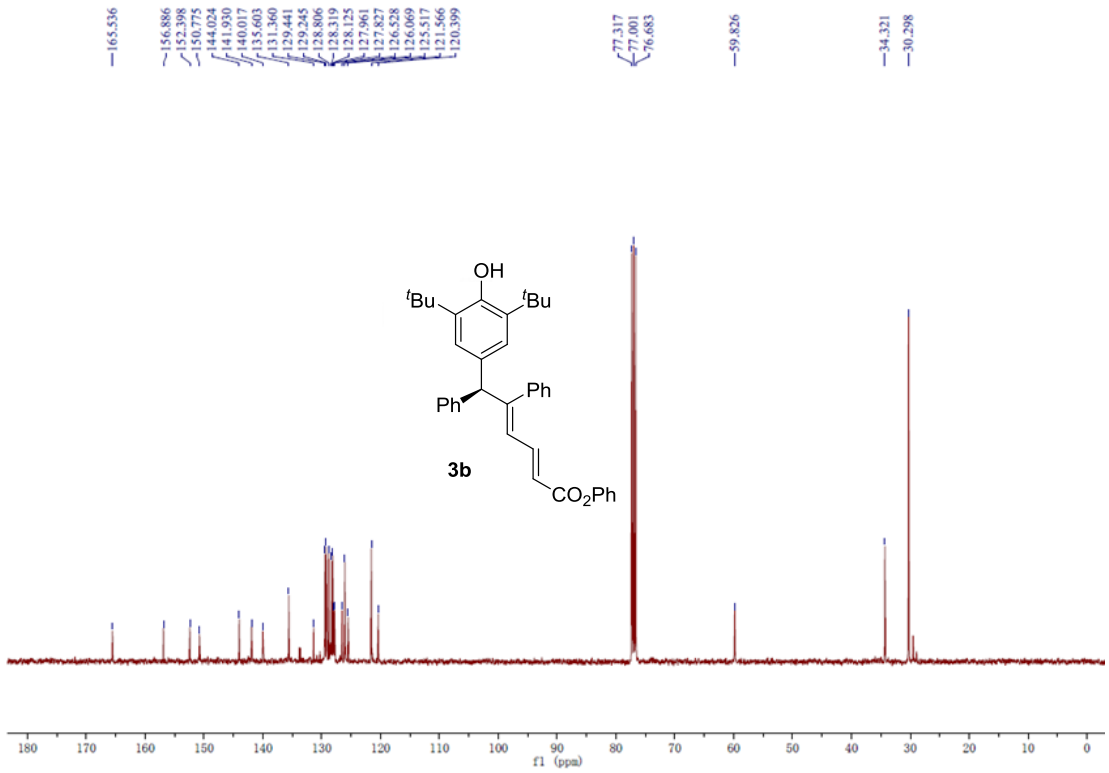
^{1}H and ^{13}C NMR spectra of compound **2i**



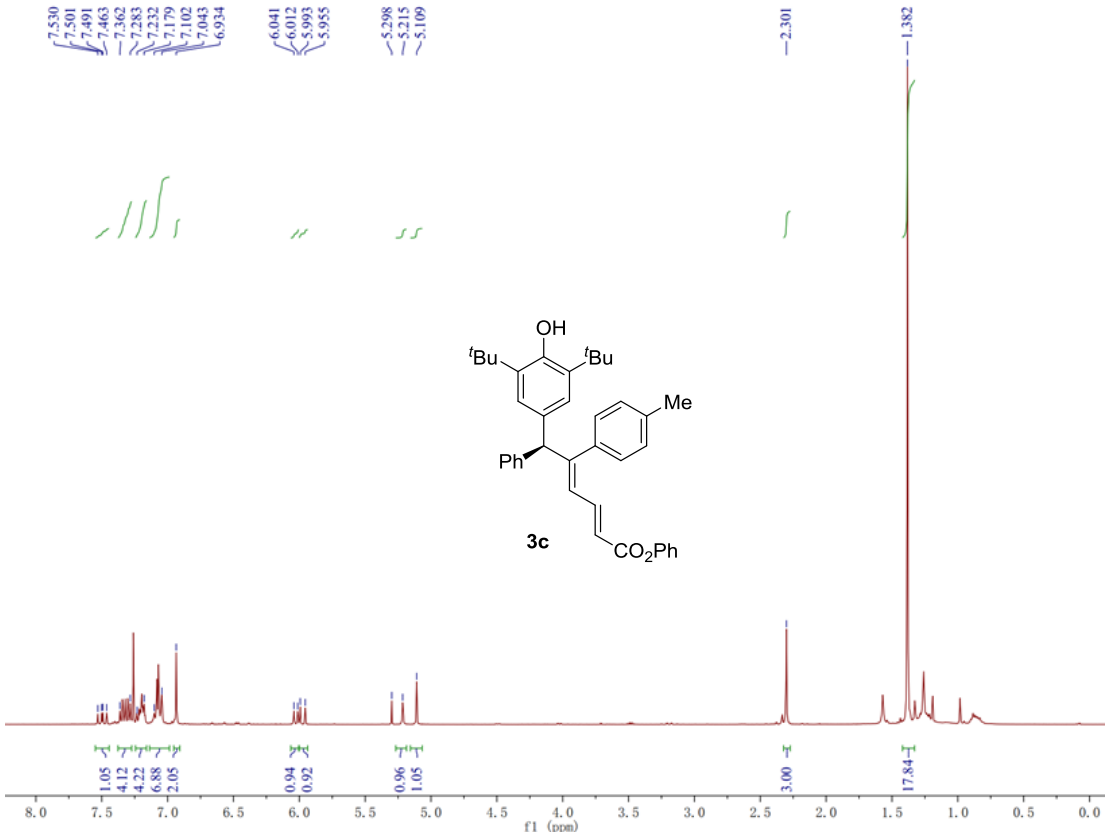


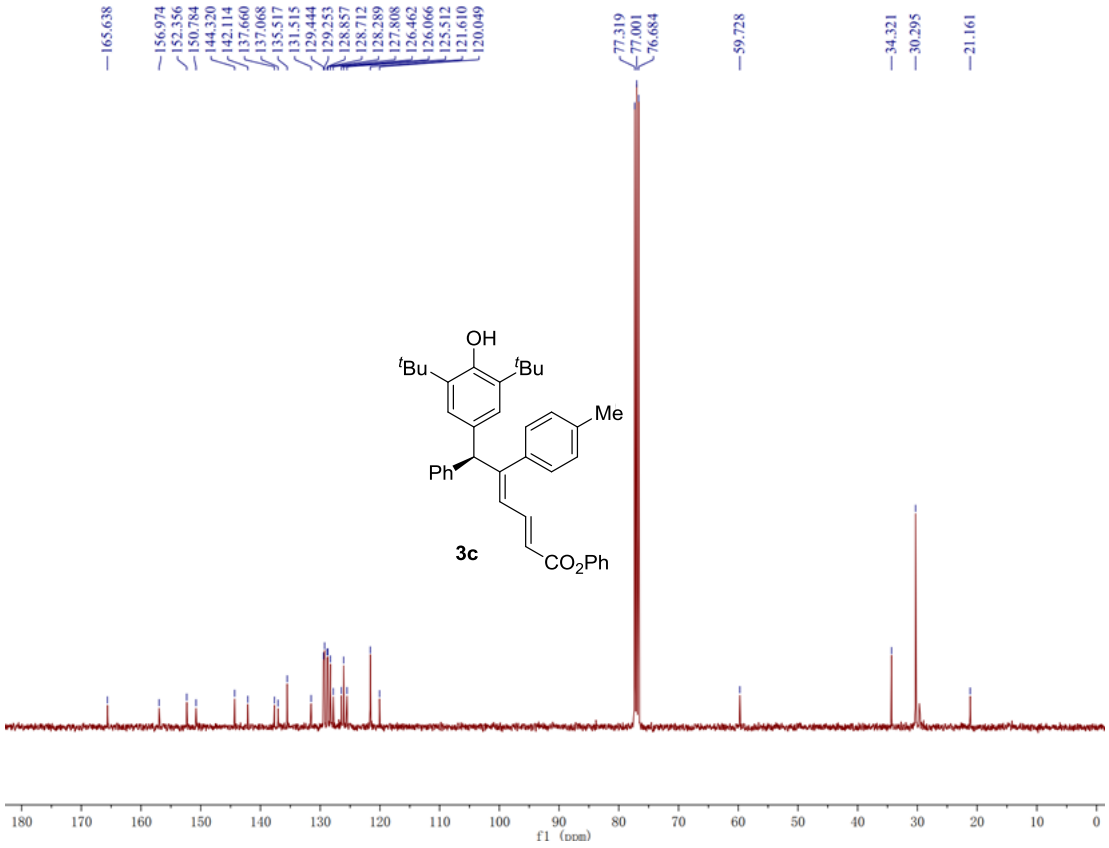
^{1}H and ^{13}C NMR spectra of compound **3a**



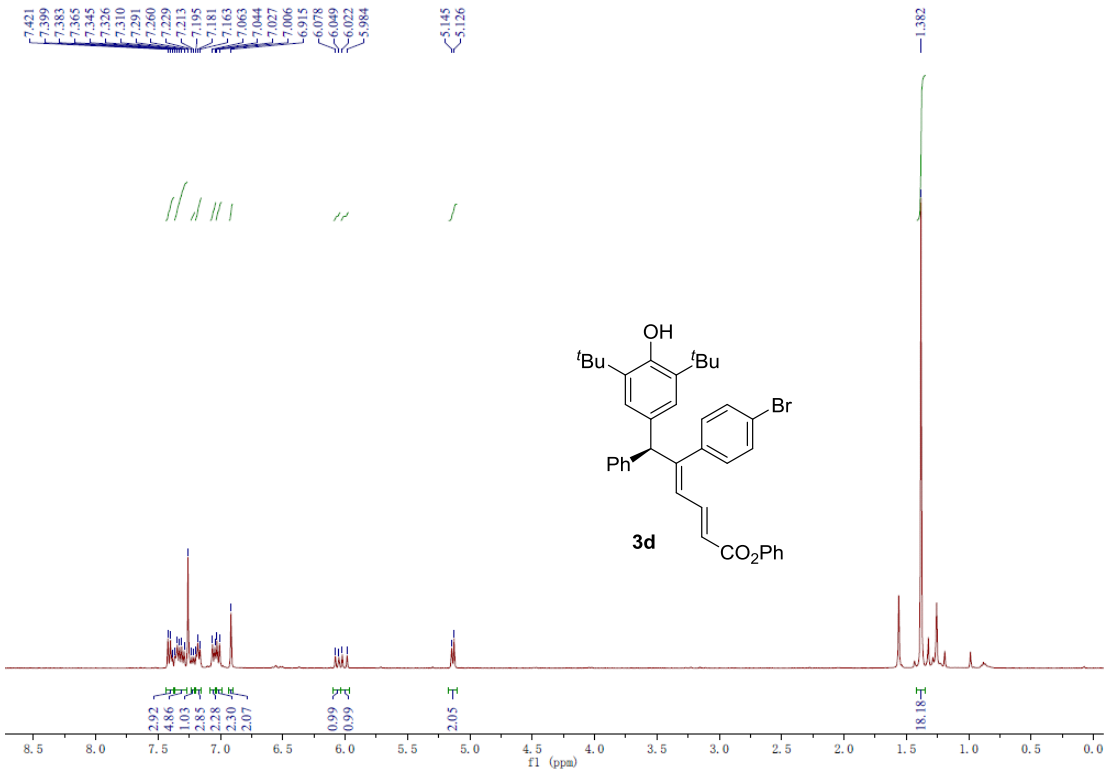


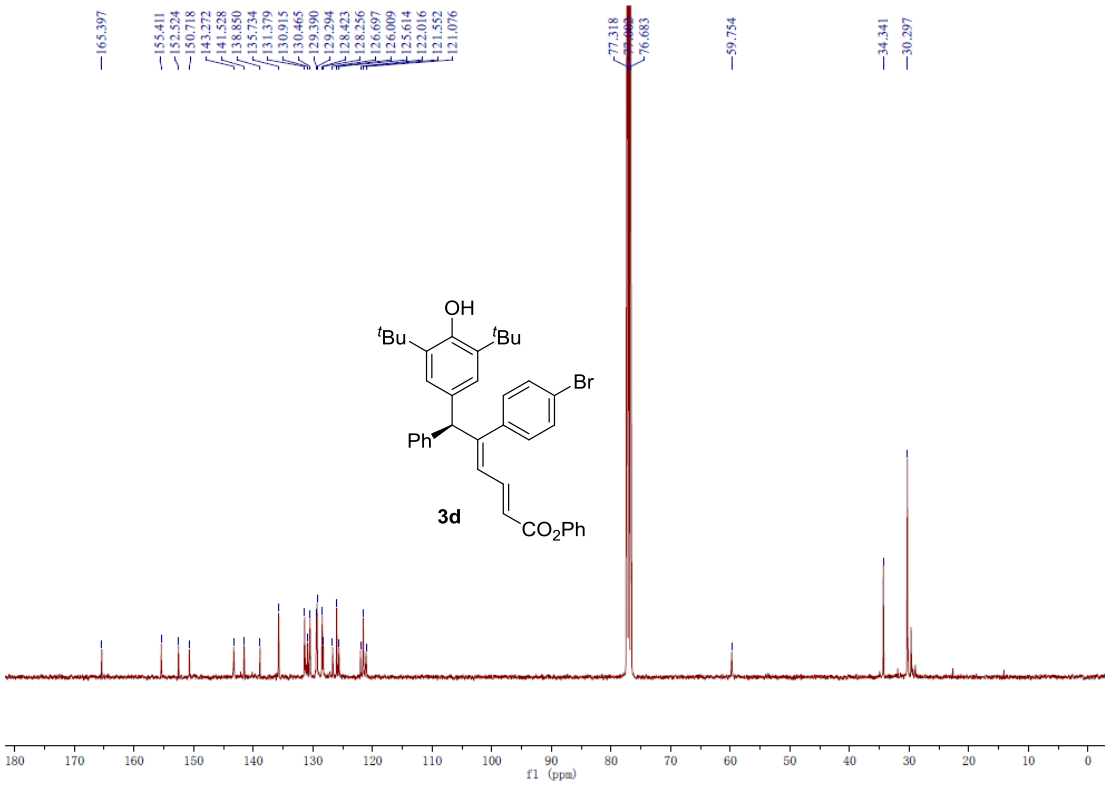
^{1}H and ^{13}C NMR spectra of compound **3b**



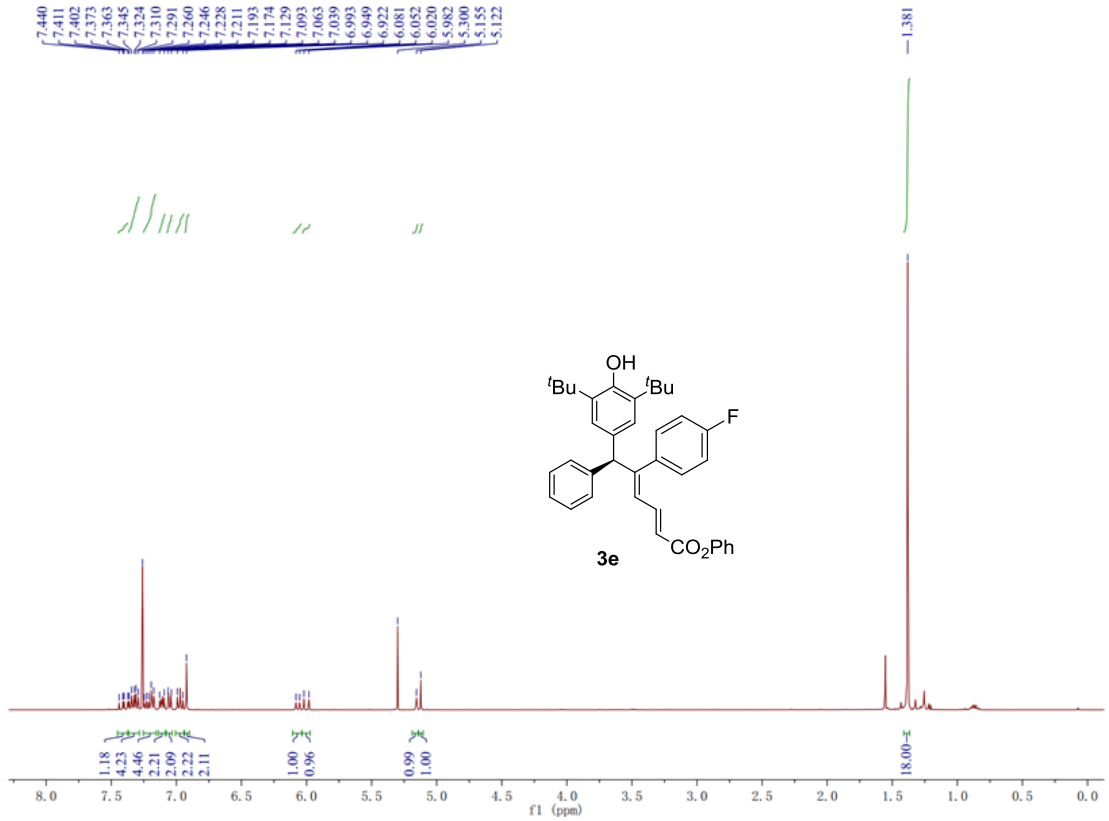


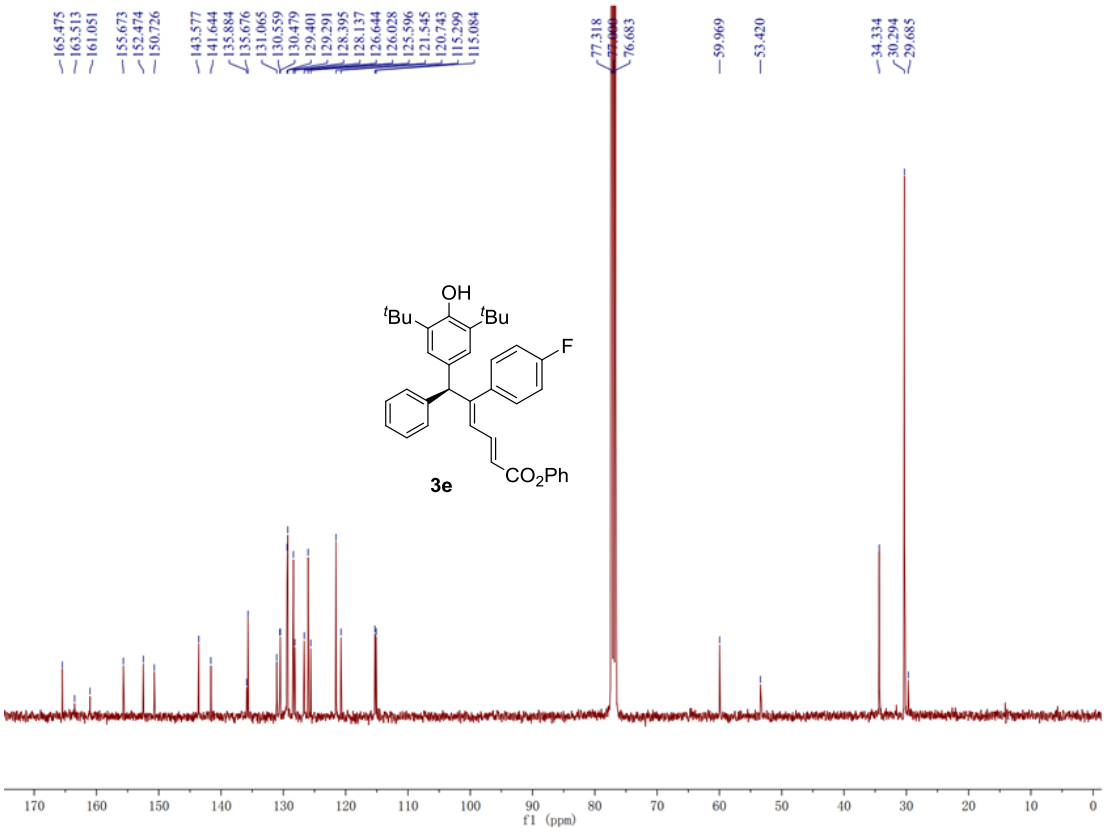
^{1}H and ^{13}C NMR spectra of compound **3c**

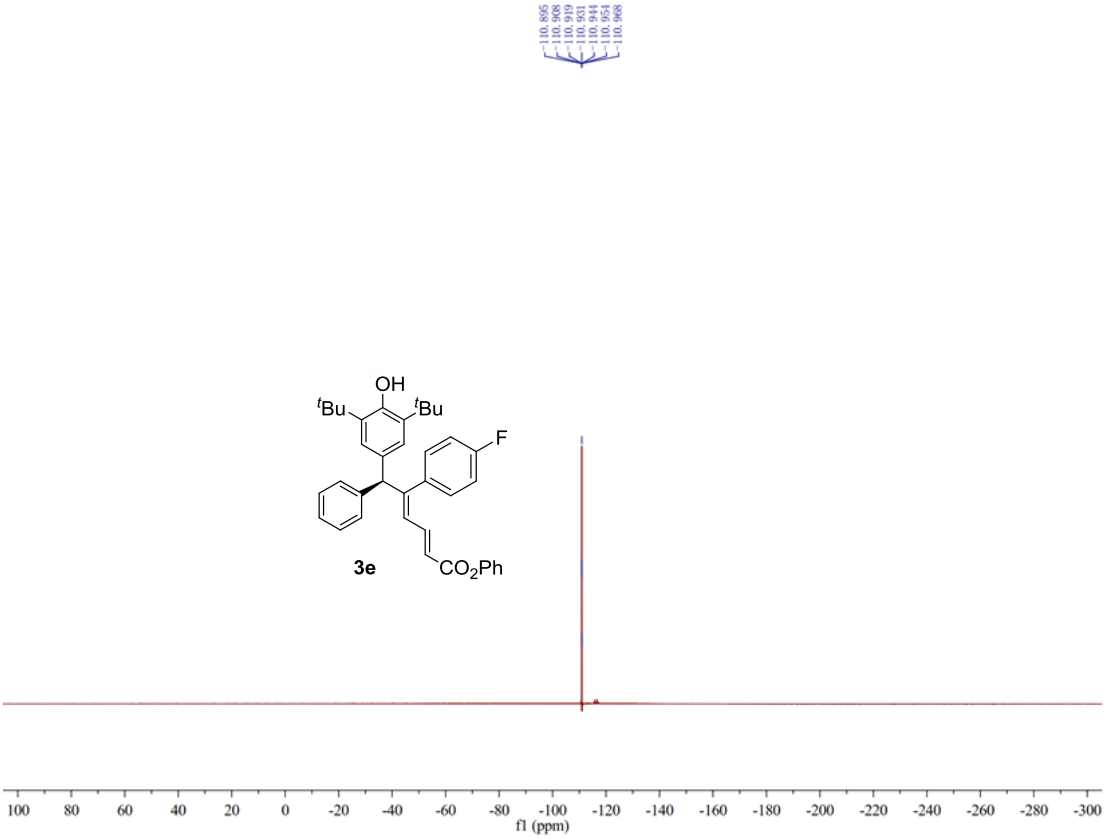




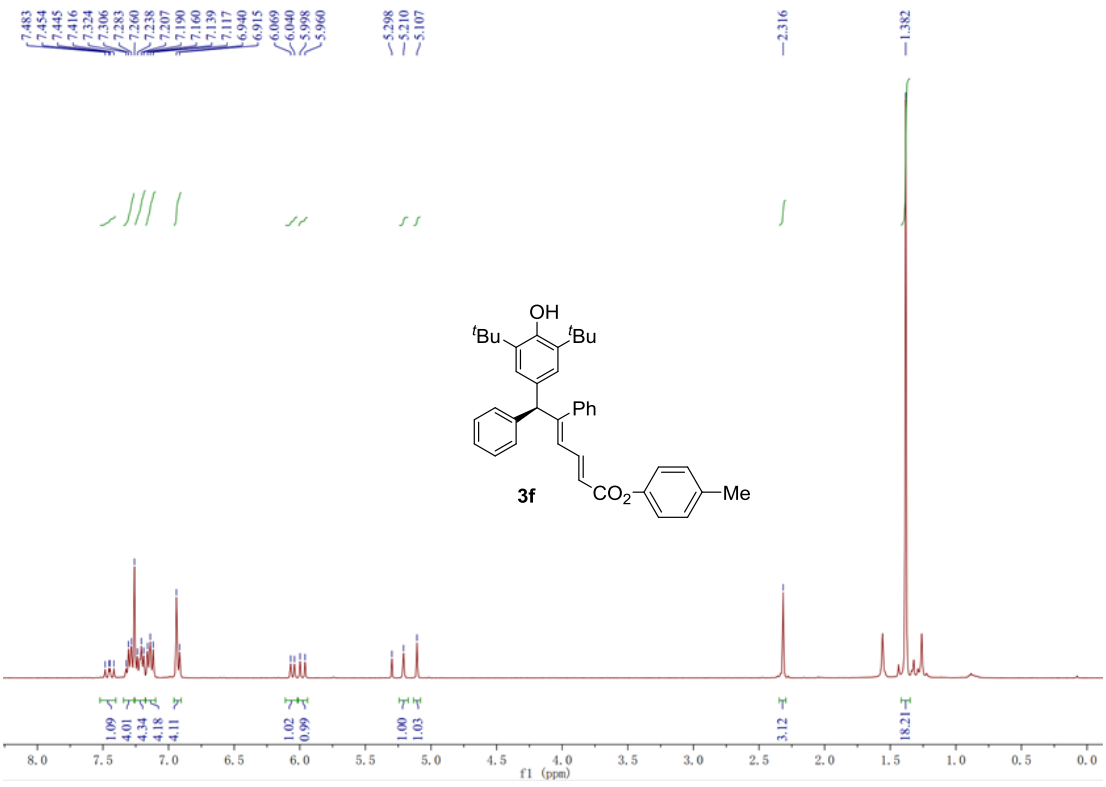
^{1}H and ^{13}C NMR spectra of compound **3d**

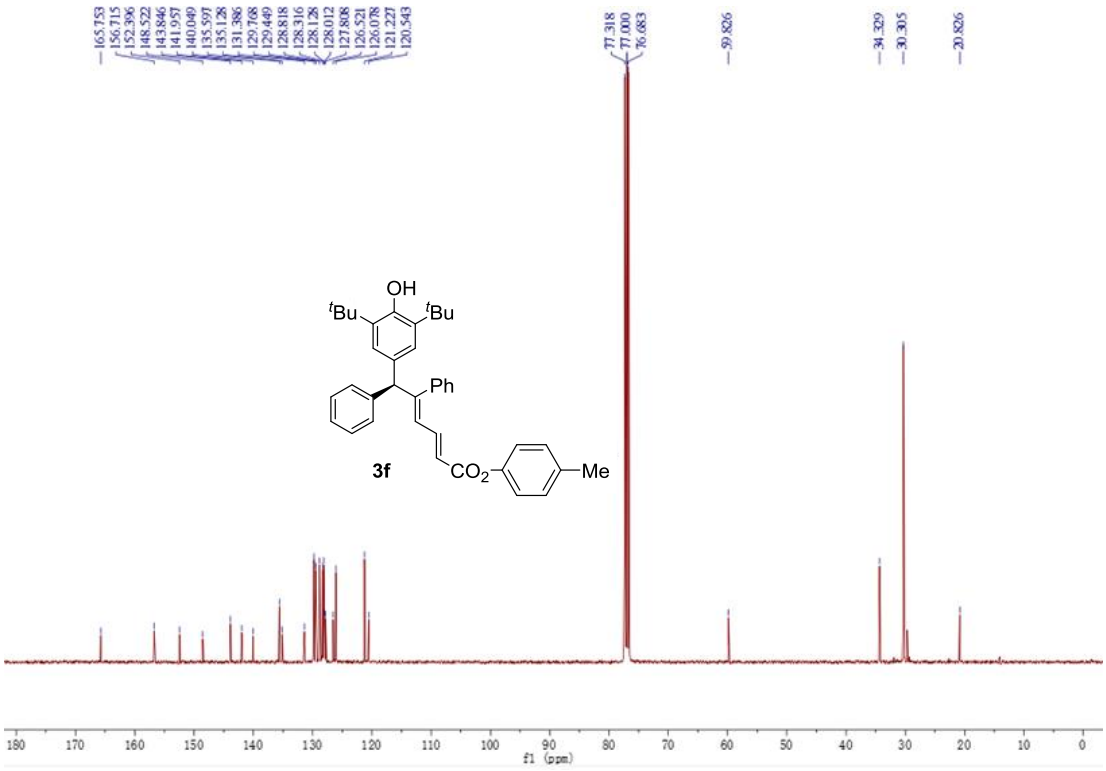




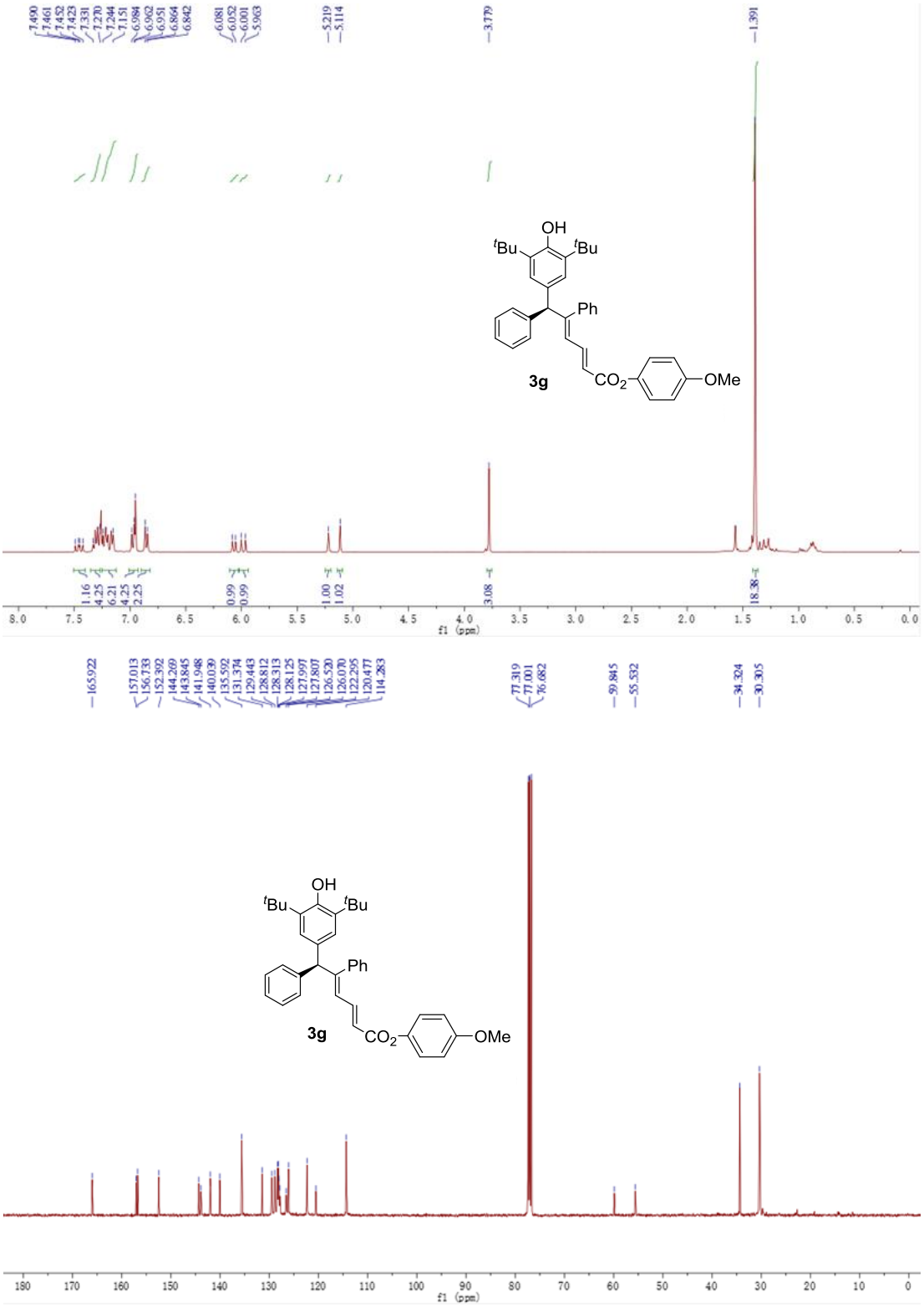


^{1}H, ^{13}C and ^{19}F NMR spectra of compound **3e**

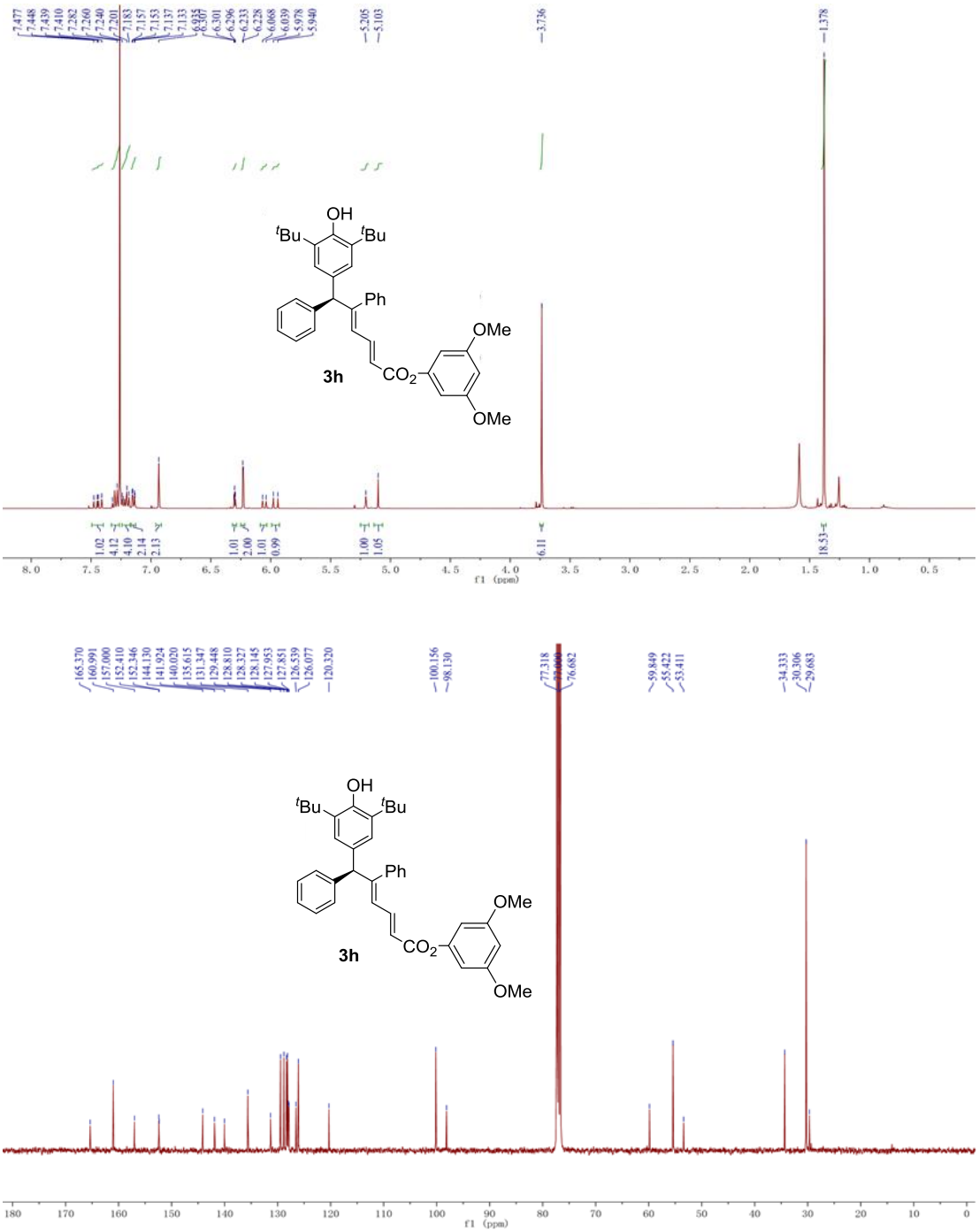




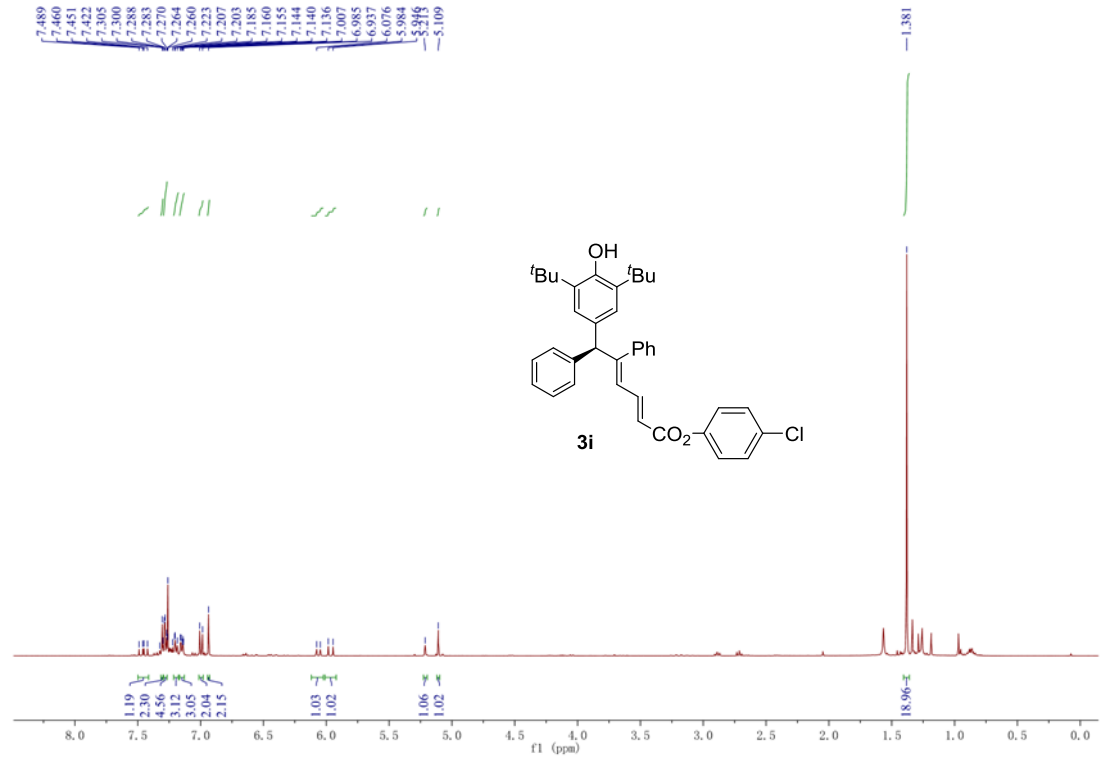
^{1}H and ^{13}C NMR spectra of compound **3f**

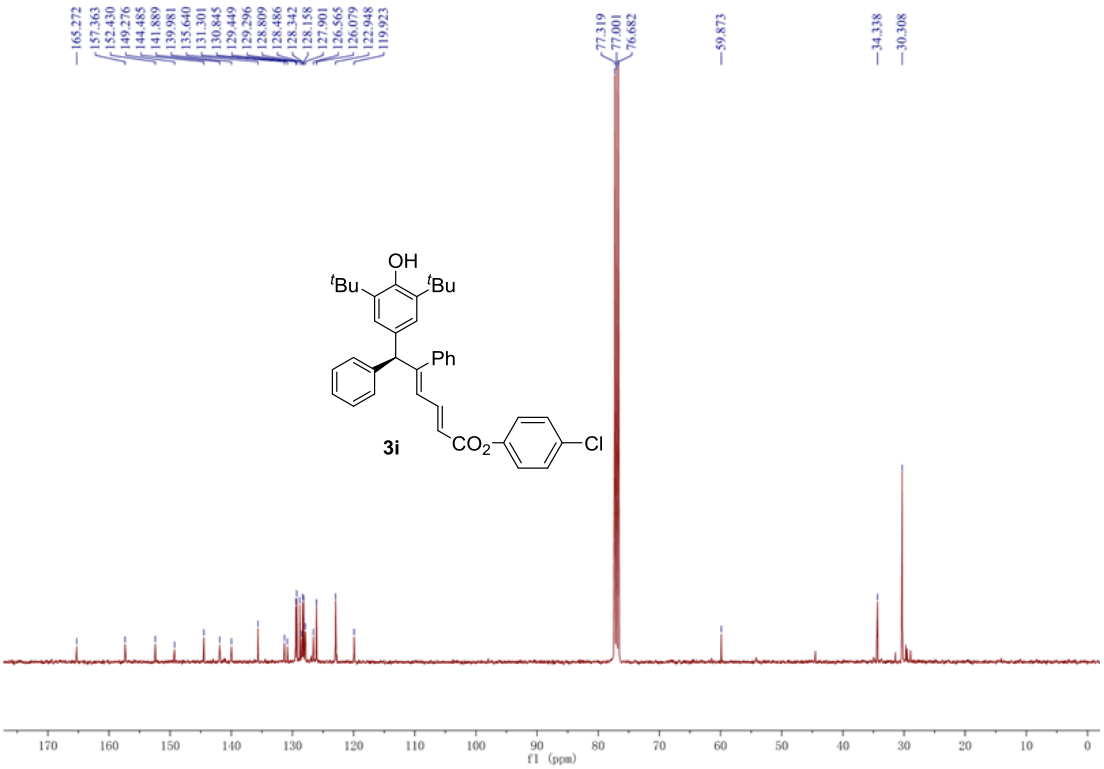


^{1}H and ^{13}C NMR spectra of compound **3g**

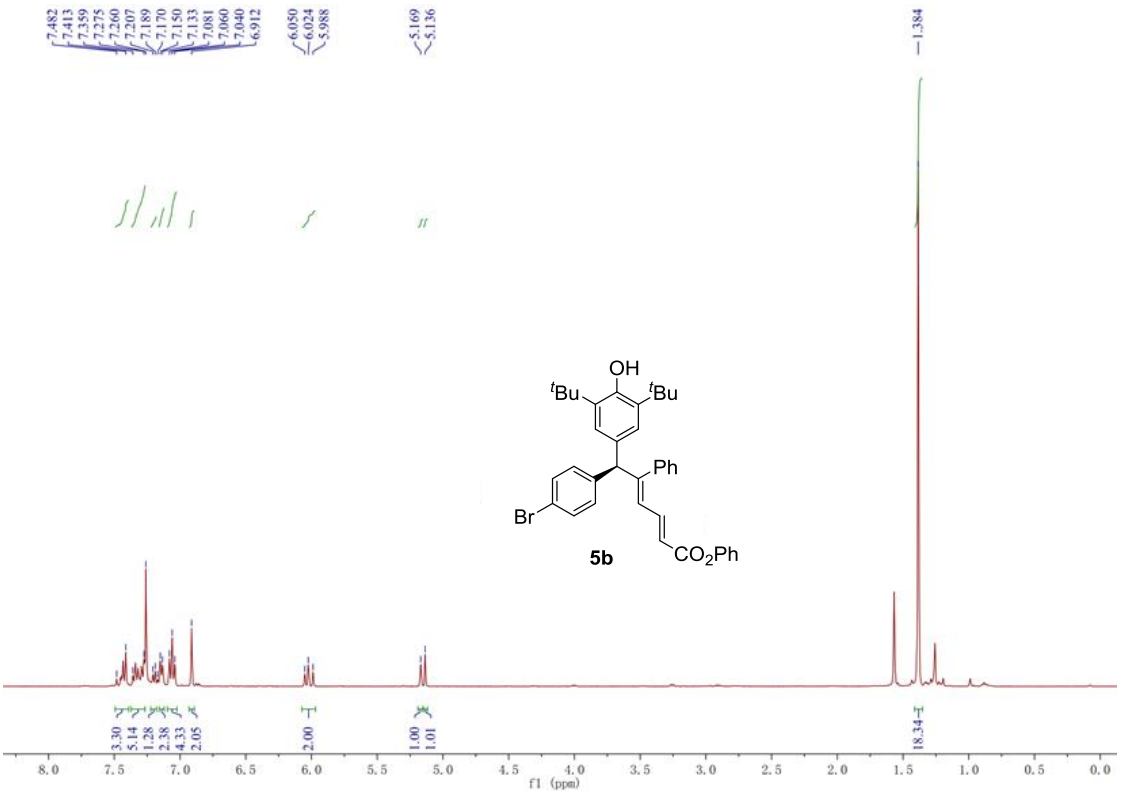


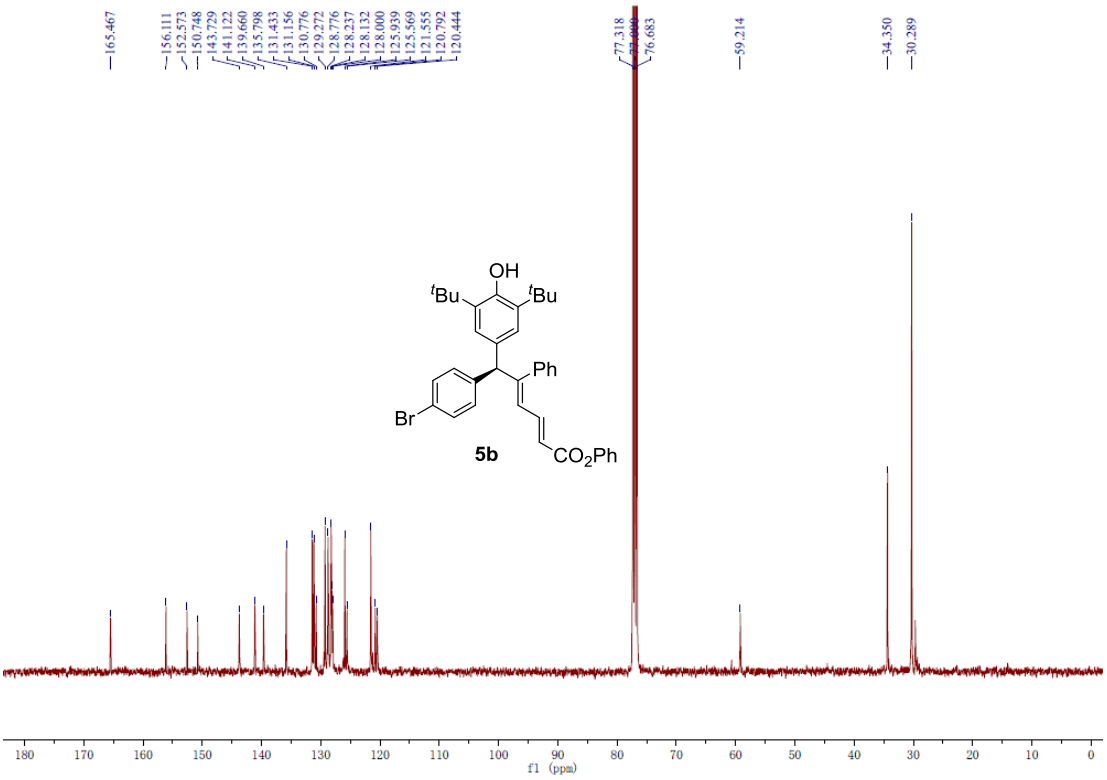
^{1}H and ^{13}C NMR spectra of compound **3h**



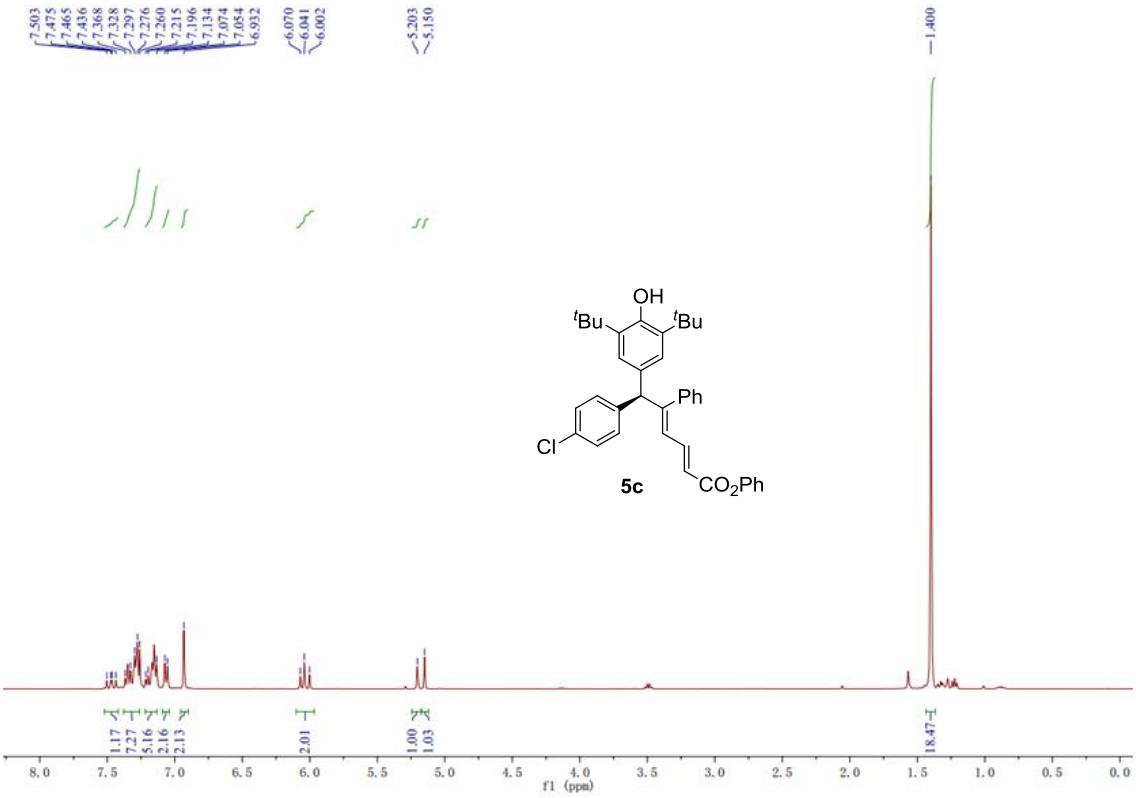


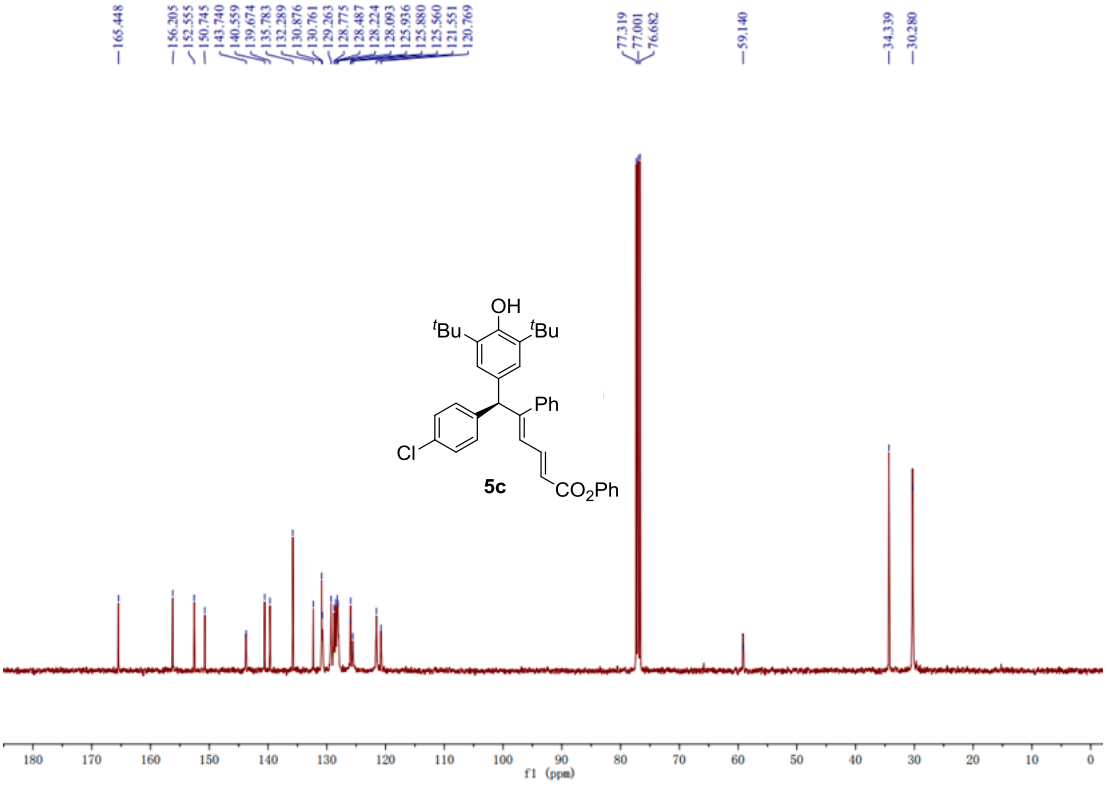
^{1}H and ^{13}C NMR spectra of compound **3i**



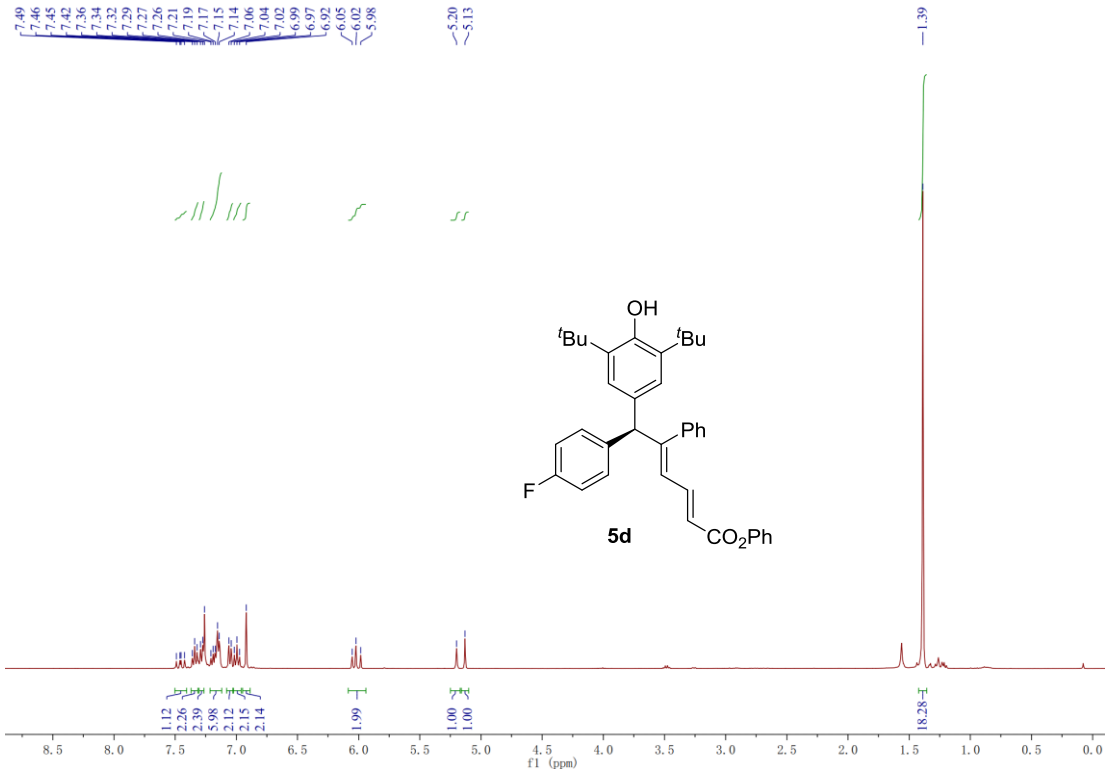


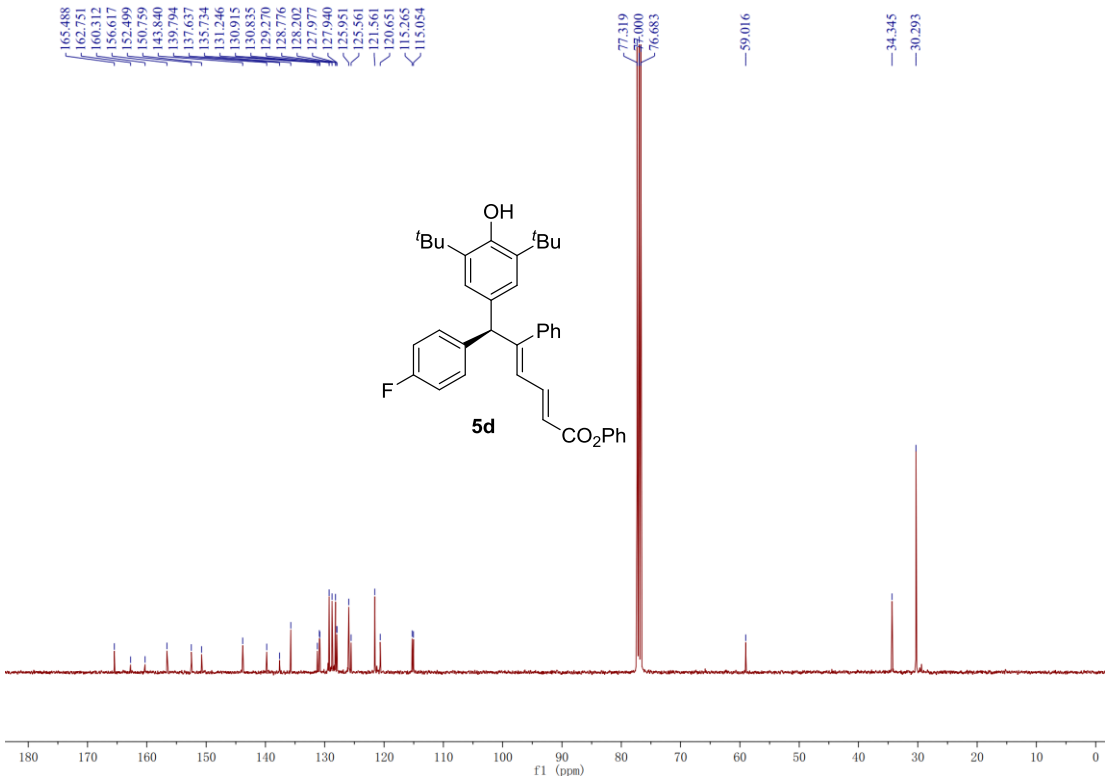
^{1}H and ^{13}C NMR spectra of compound **5b**





^{1}H and ^{13}C NMR spectra of compound **5c**


7.49
7.46
7.45
7.42
7.36
7.34
7.32
7.29
7.27
7.26
7.21
7.19
7.17
7.15
7.14
7.06
7.04
7.02
6.99
6.97
6.92
6.05
6.02
5.98
5.20
5.13
1.39
OH
tBu
tBu
Ph
F
5d
CO2Ph
1.12
2.26
2.39
5.98
2.12
2.15
2.14
1.99
1.00
1.00
18.28
f1 (ppm)


165.488
162.751
160.312
156.617
152.499
150.759
143.840
139.794
137.637
135.734
131.246
130.915
130.835
129.270
128.776
128.202
127.977
127.940
125.951
125.561
121.561
120.651
115.265
115.054
77.319
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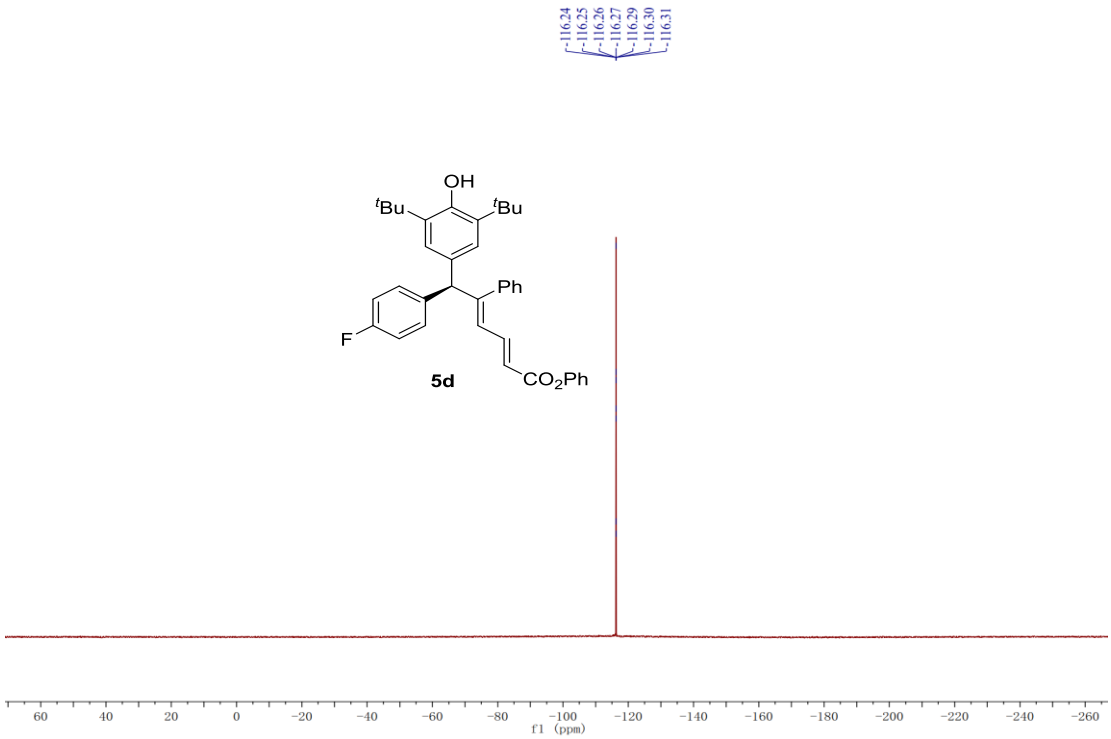
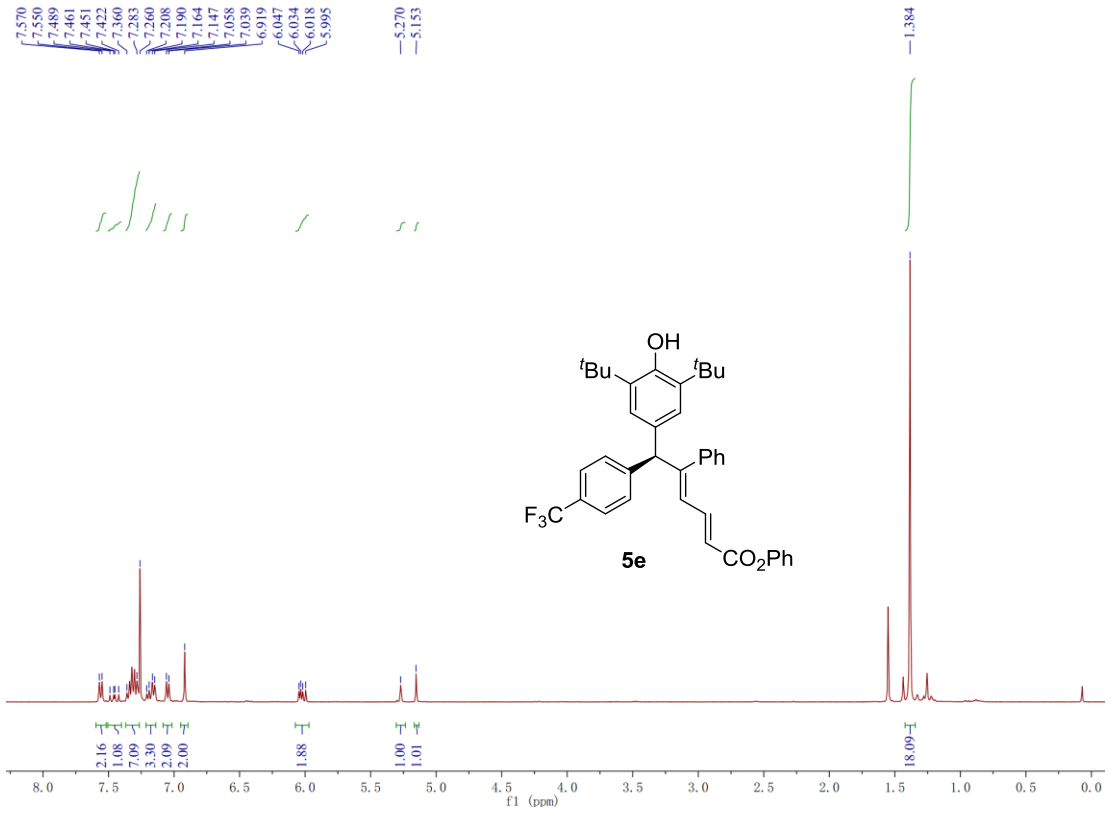
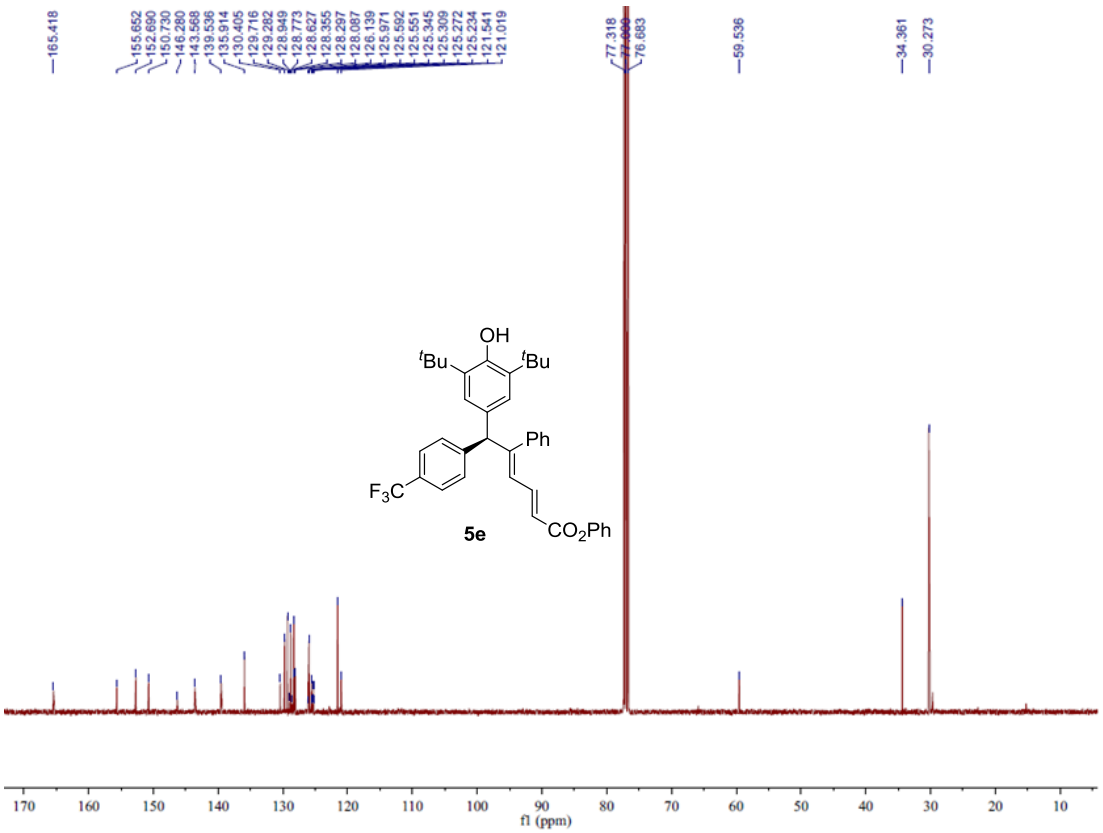
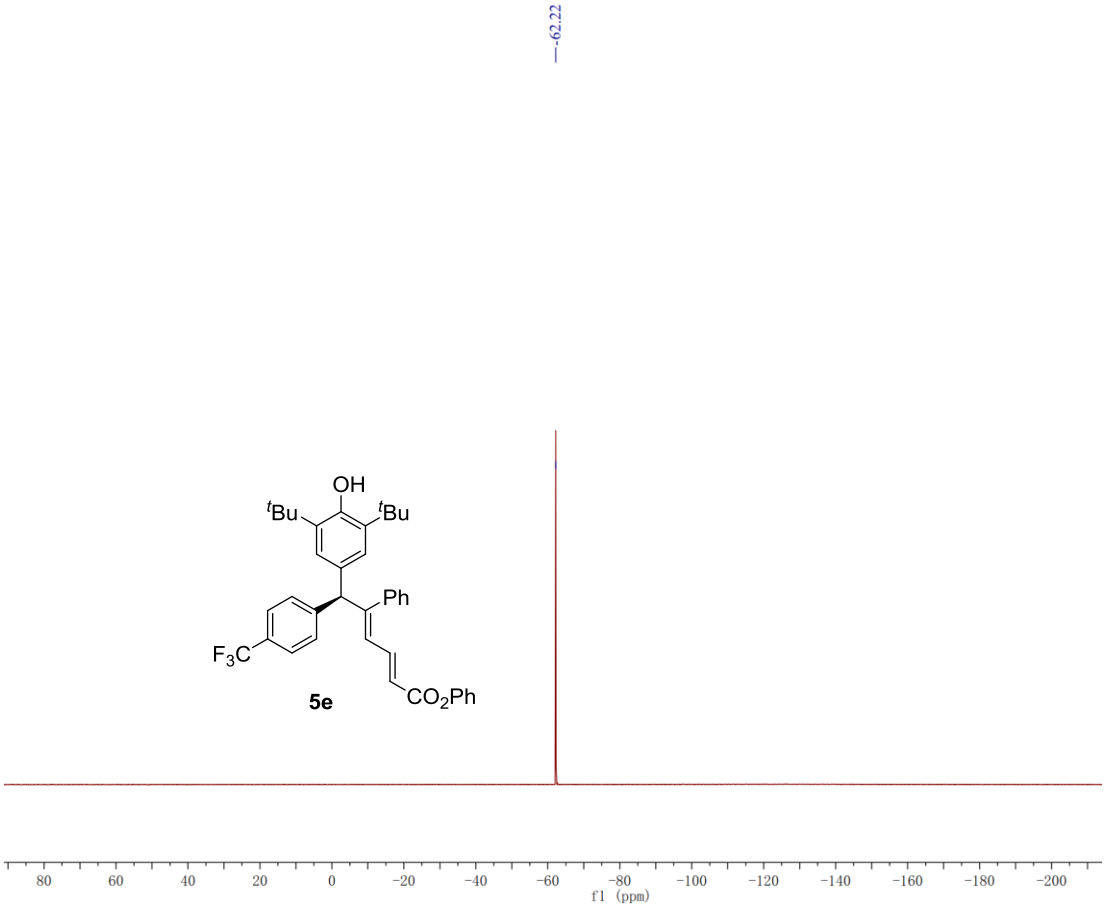
tBu
tBu
Ph
F
5d
CO2Ph
f1 (ppm)



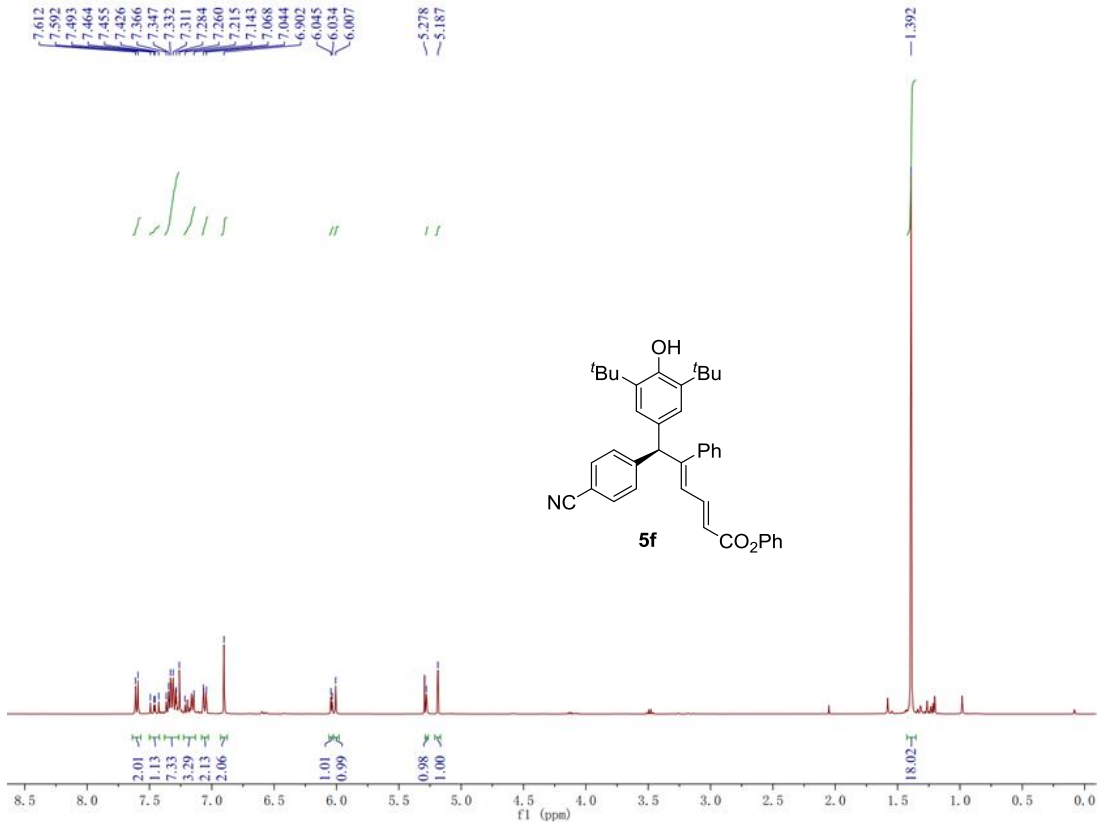
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **5d**

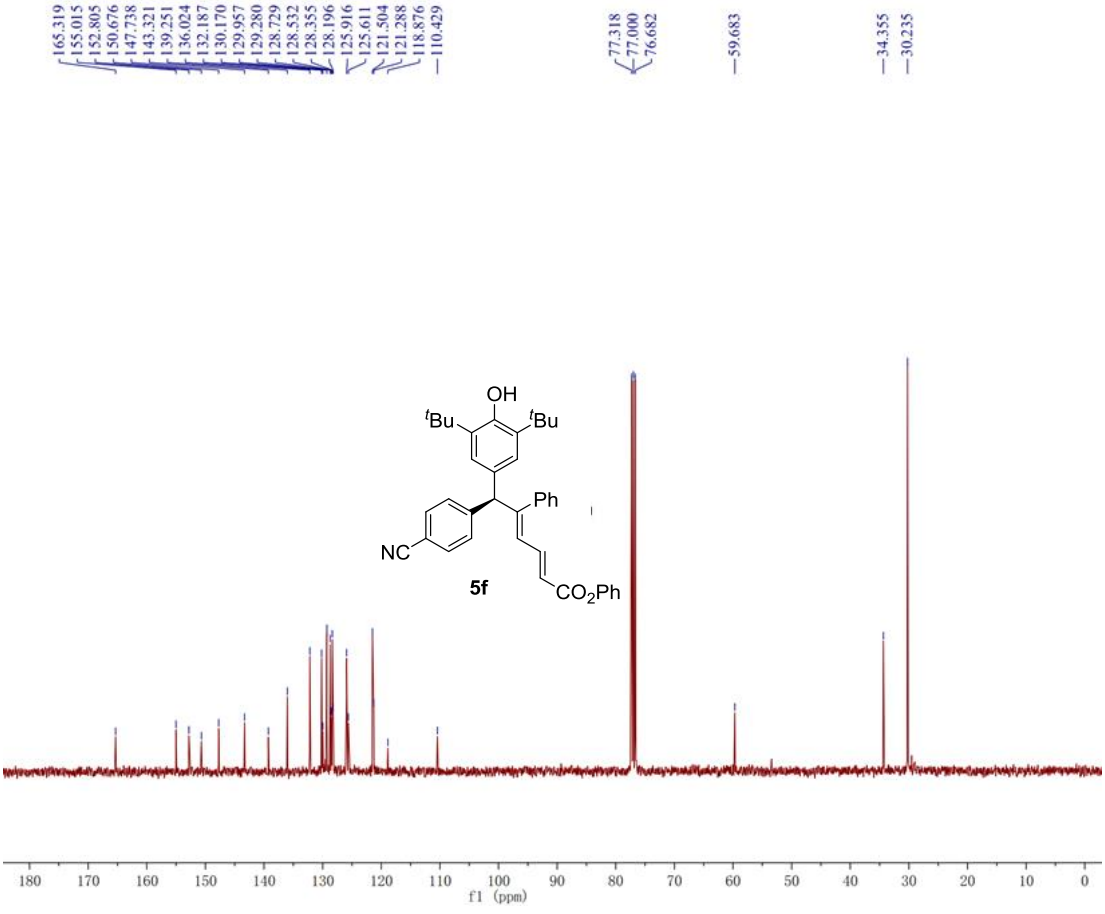




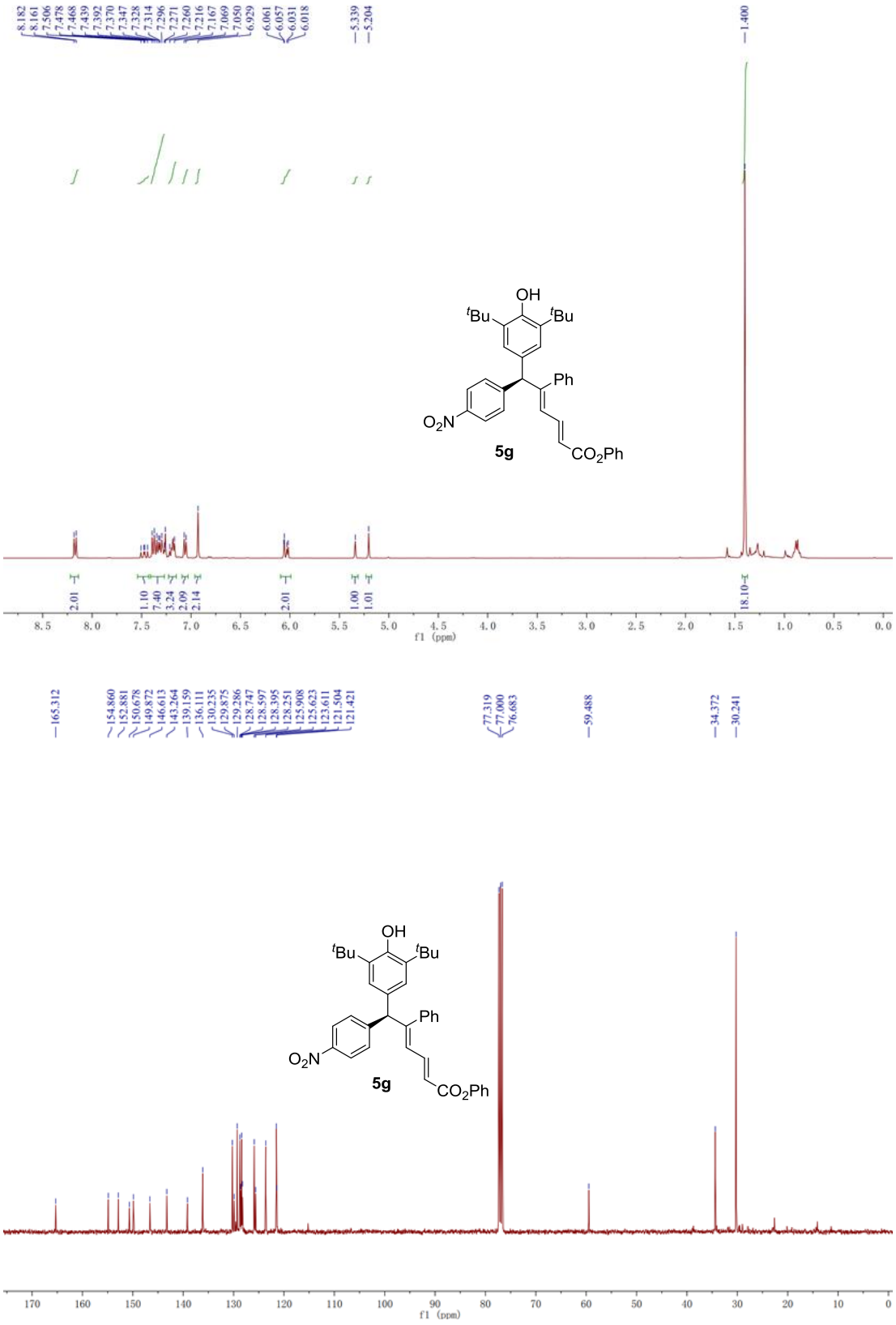


^{1}H, ^{13}C and ^{19}F NMR spectra of compound **5e**

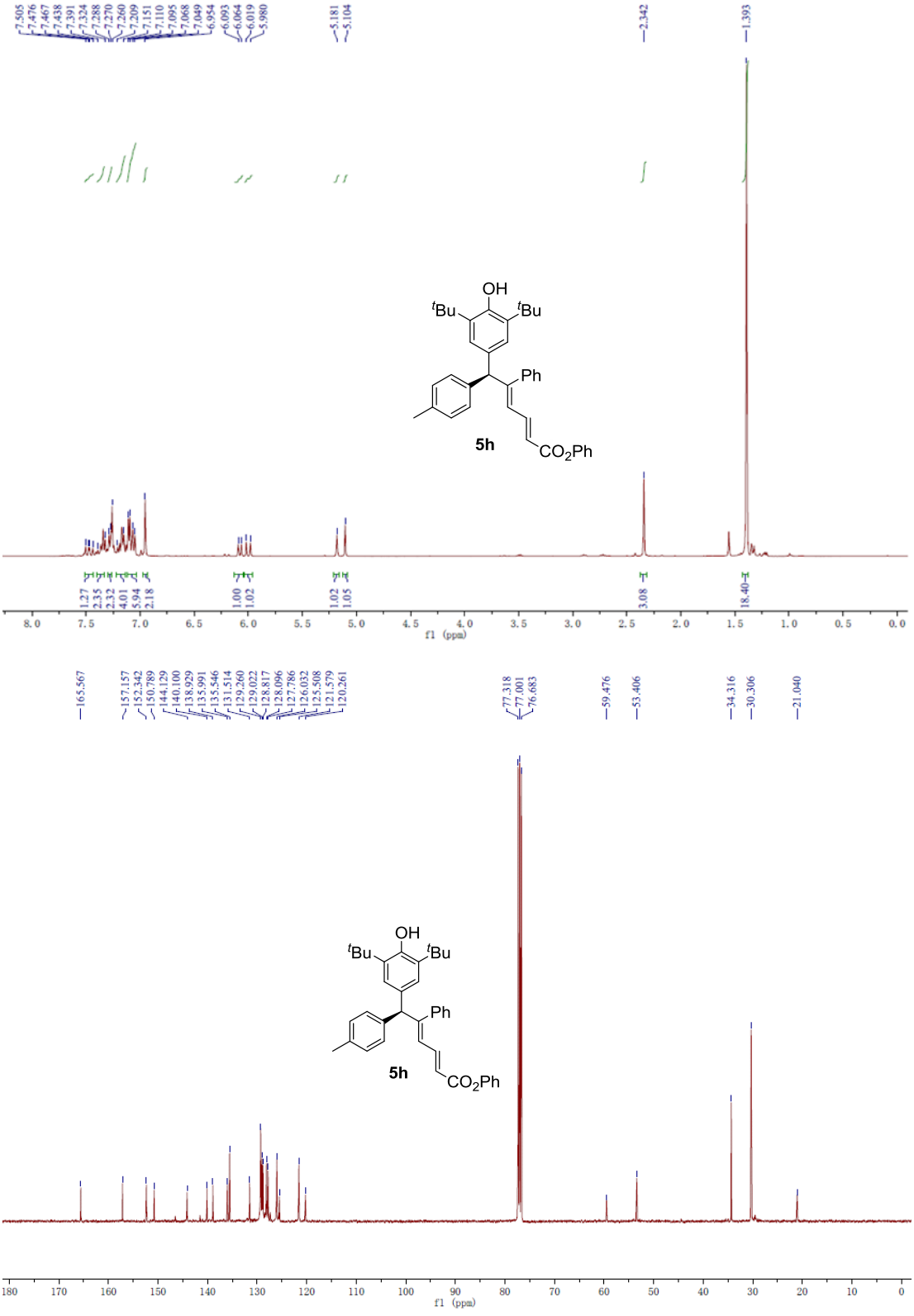




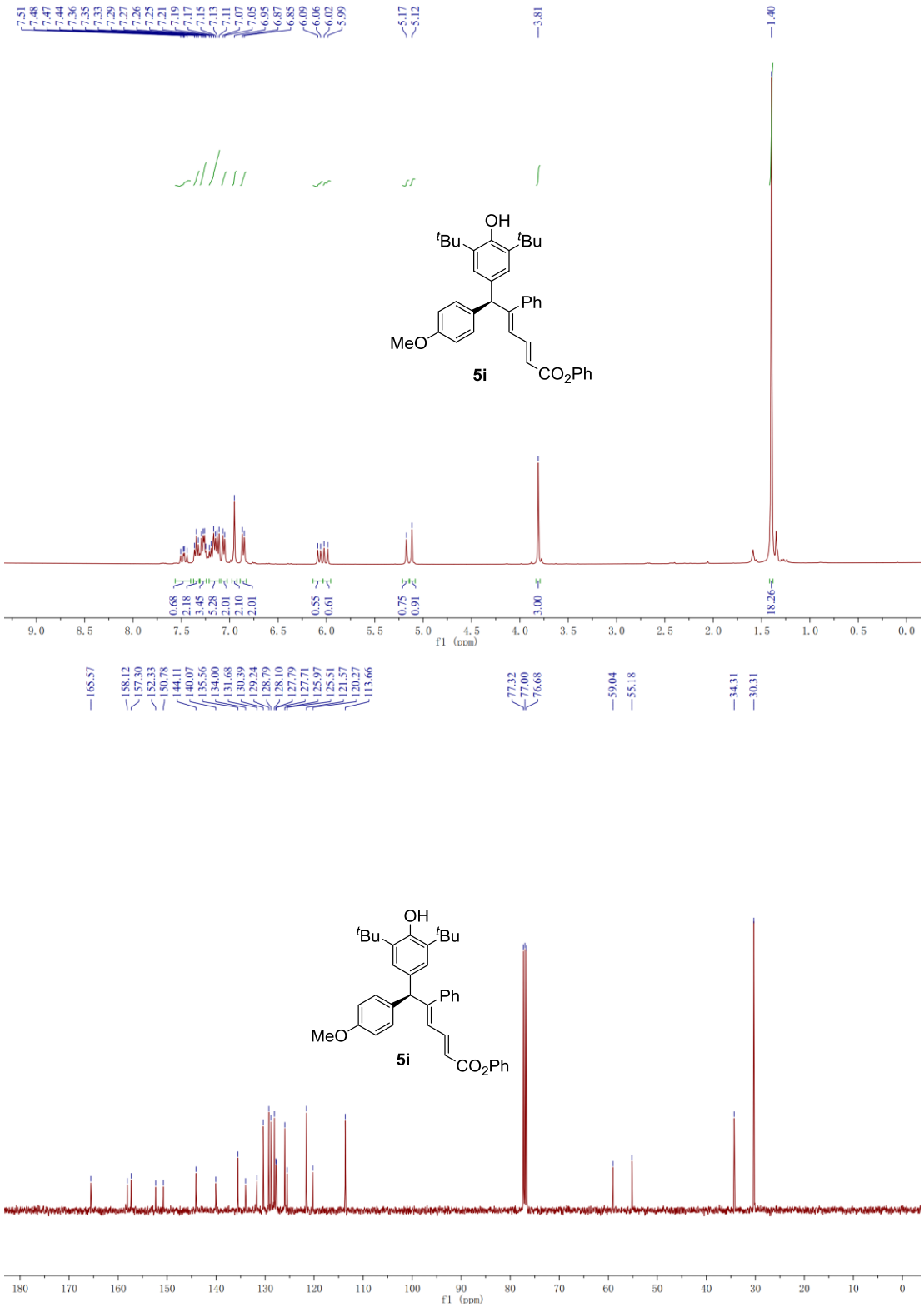
^{1}H and ^{13}C NMR spectra of compound **5f**



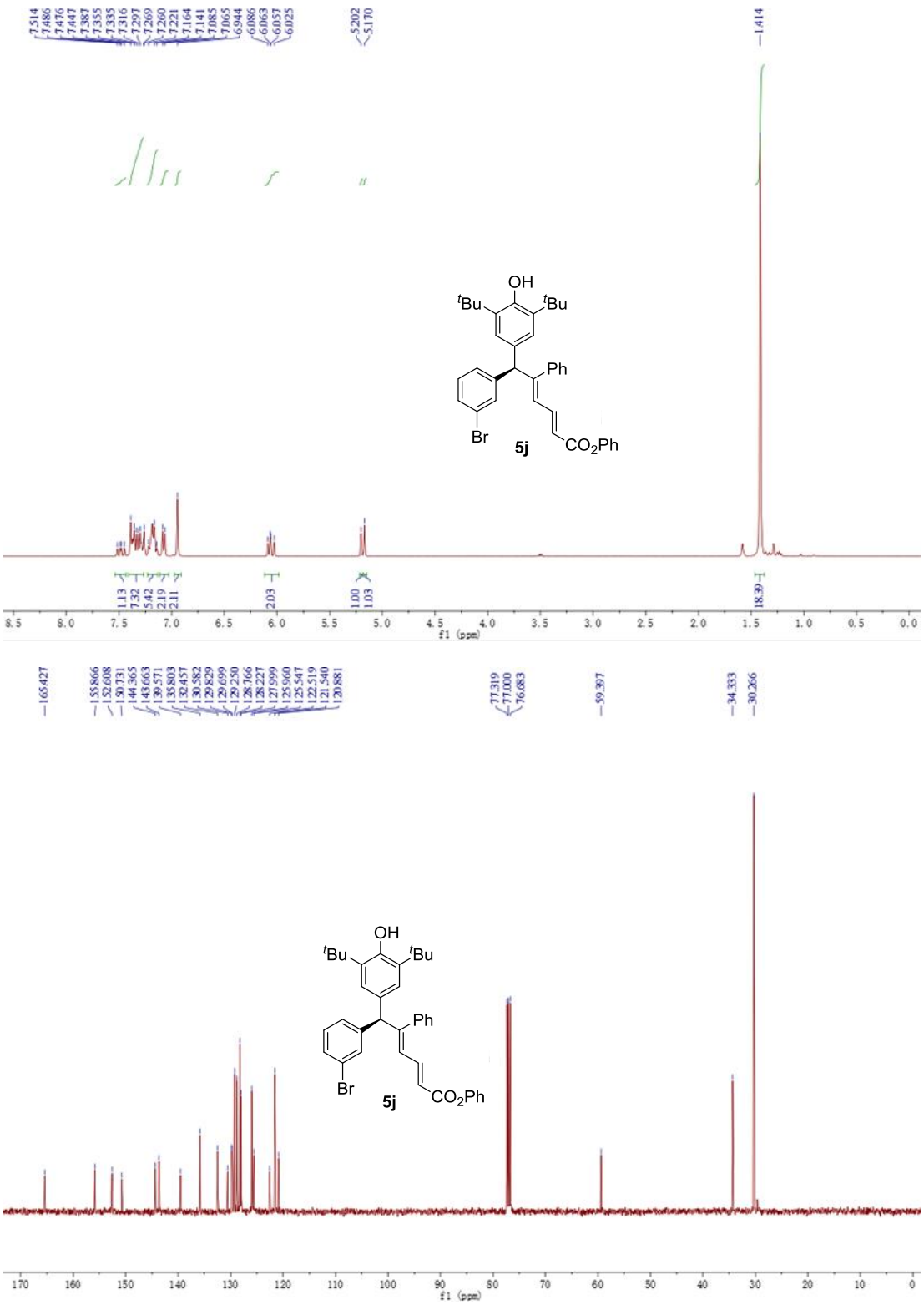
^{1}H and ^{13}C NMR spectra of compound **5g**



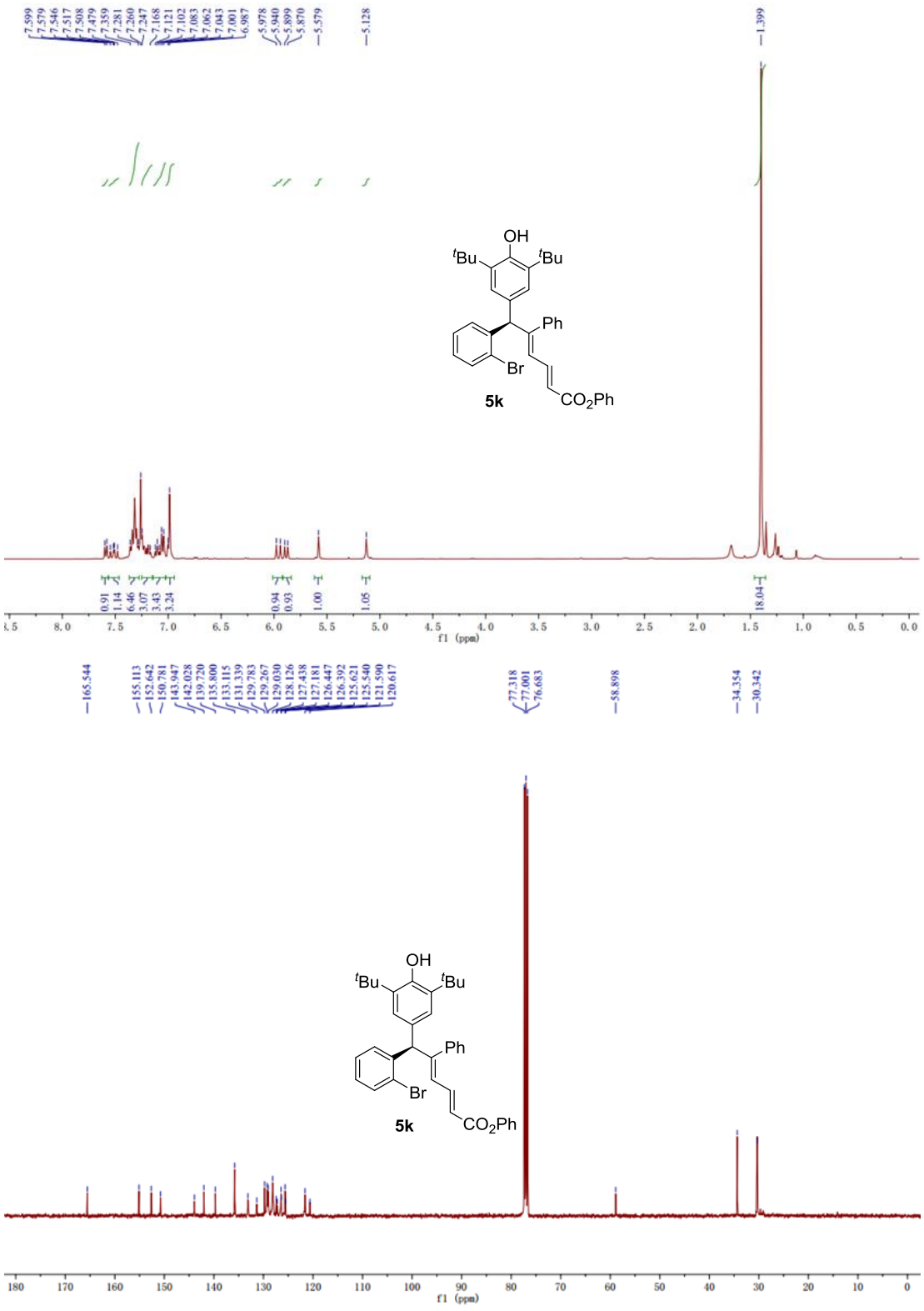
^{1}H and ^{13}C NMR spectra of compound **5h**



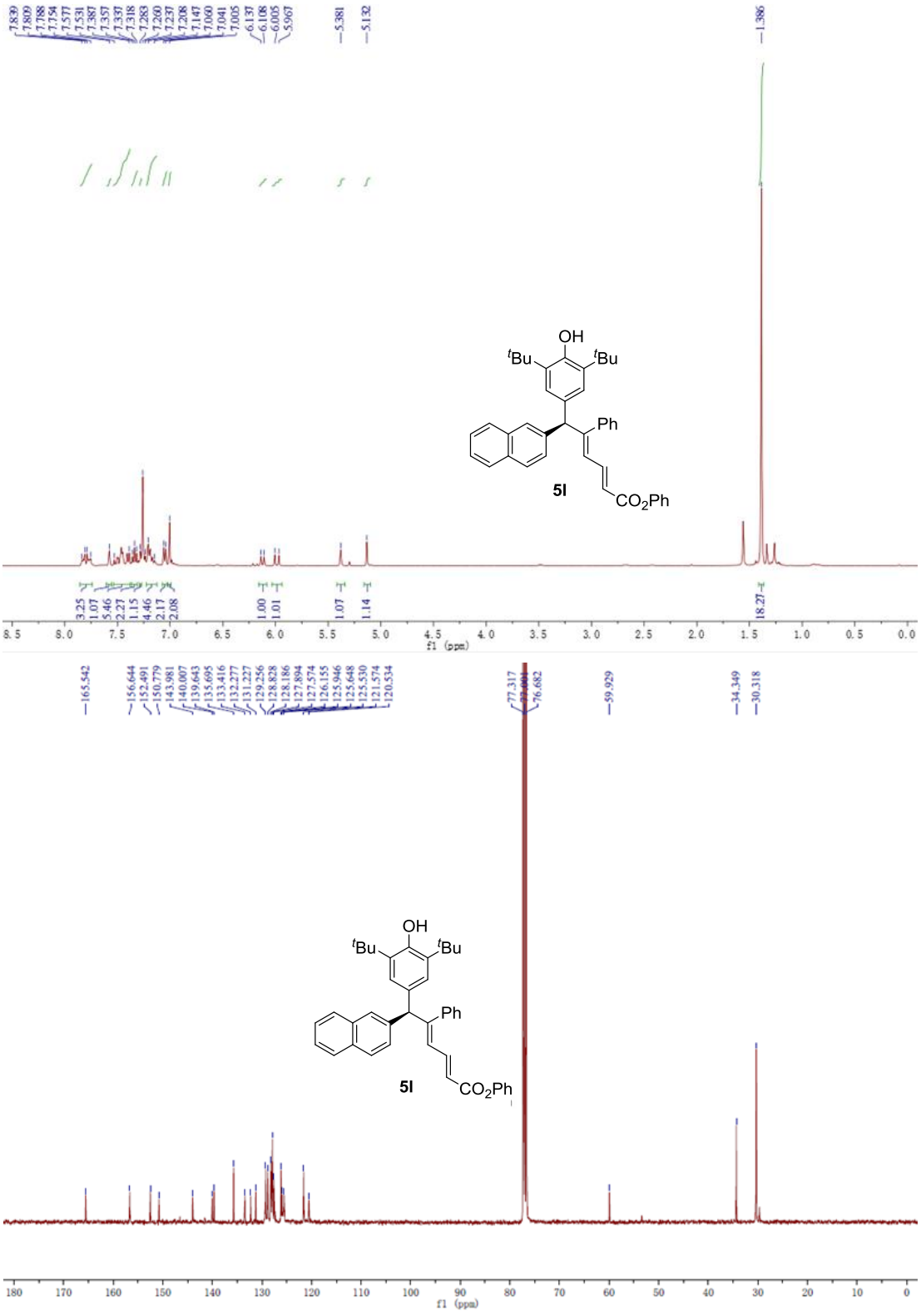
^{1}H and ^{13}C NMR spectra of compound **5i**



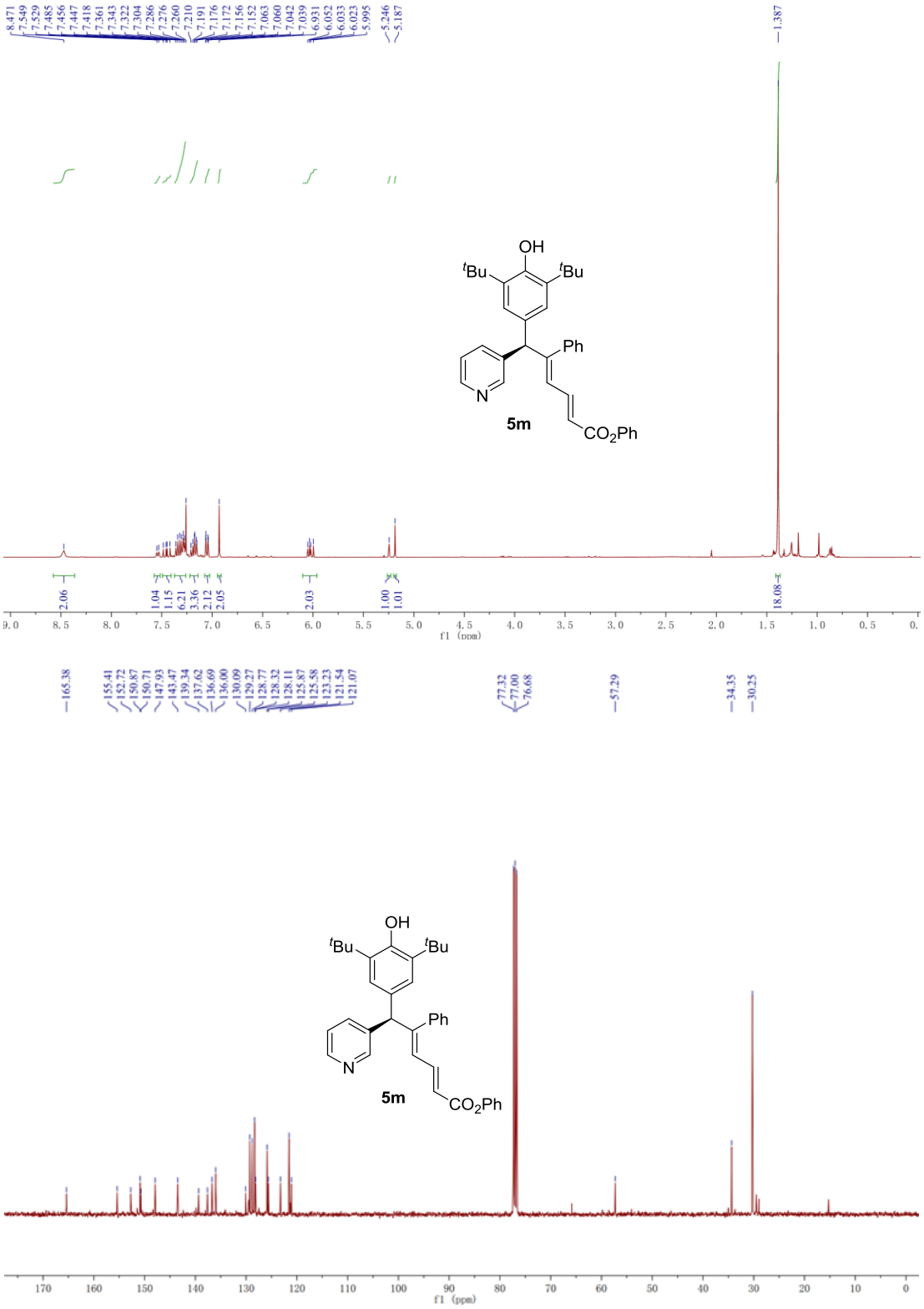
^{1}H and ^{13}C NMR spectra of compound **5j**



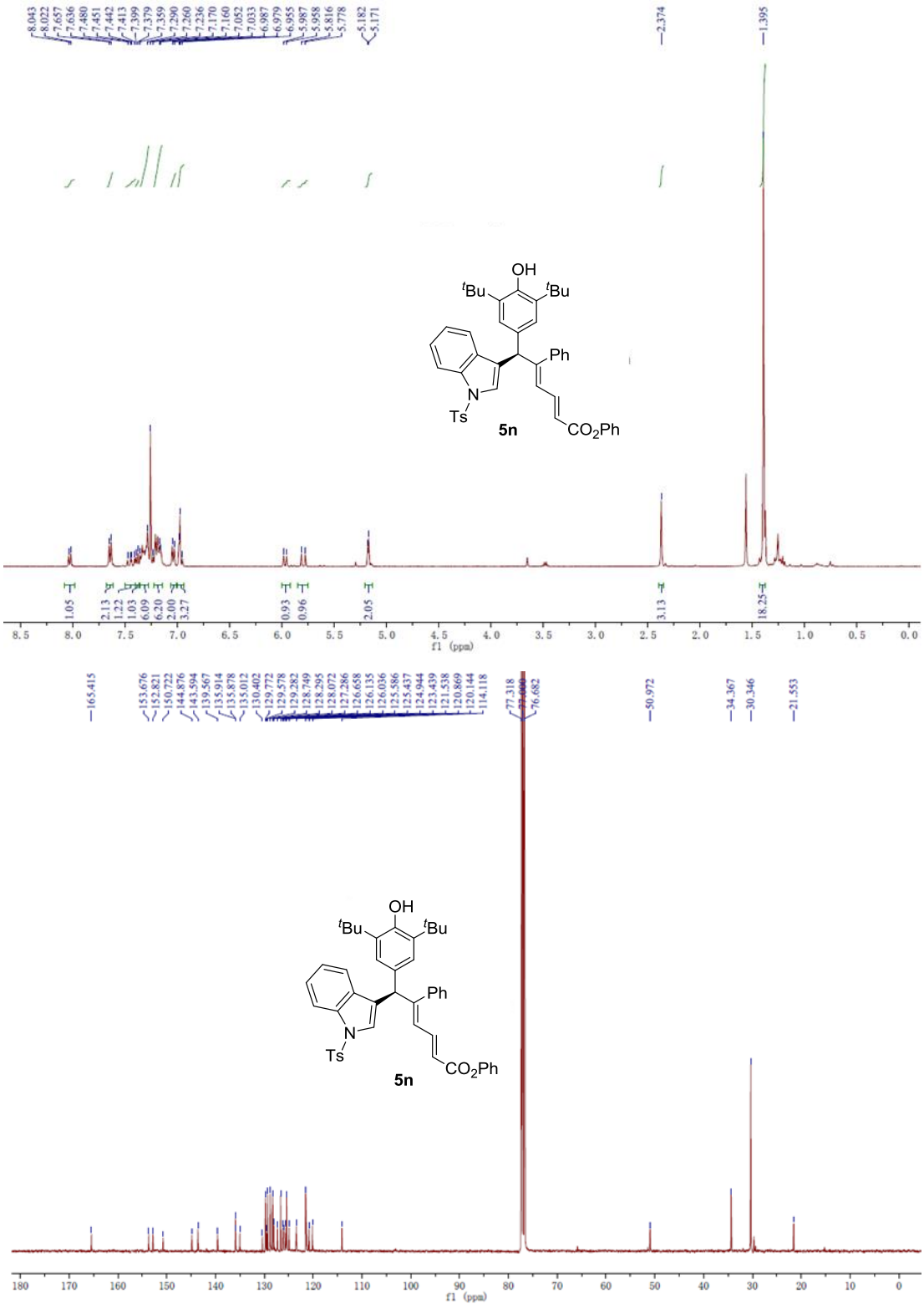
^{1}H and ^{13}C NMR spectra of compound **5k**



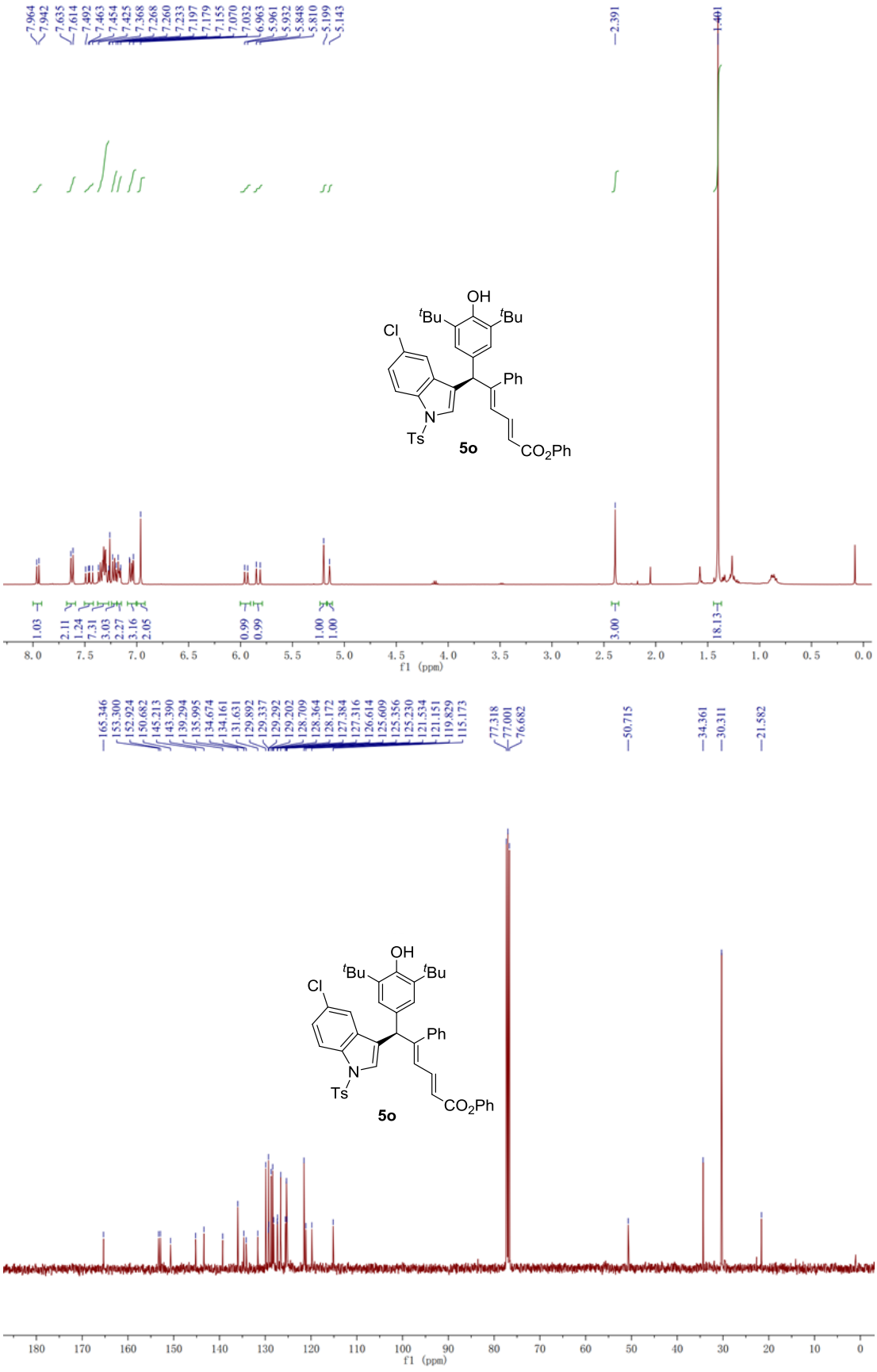
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **5l**



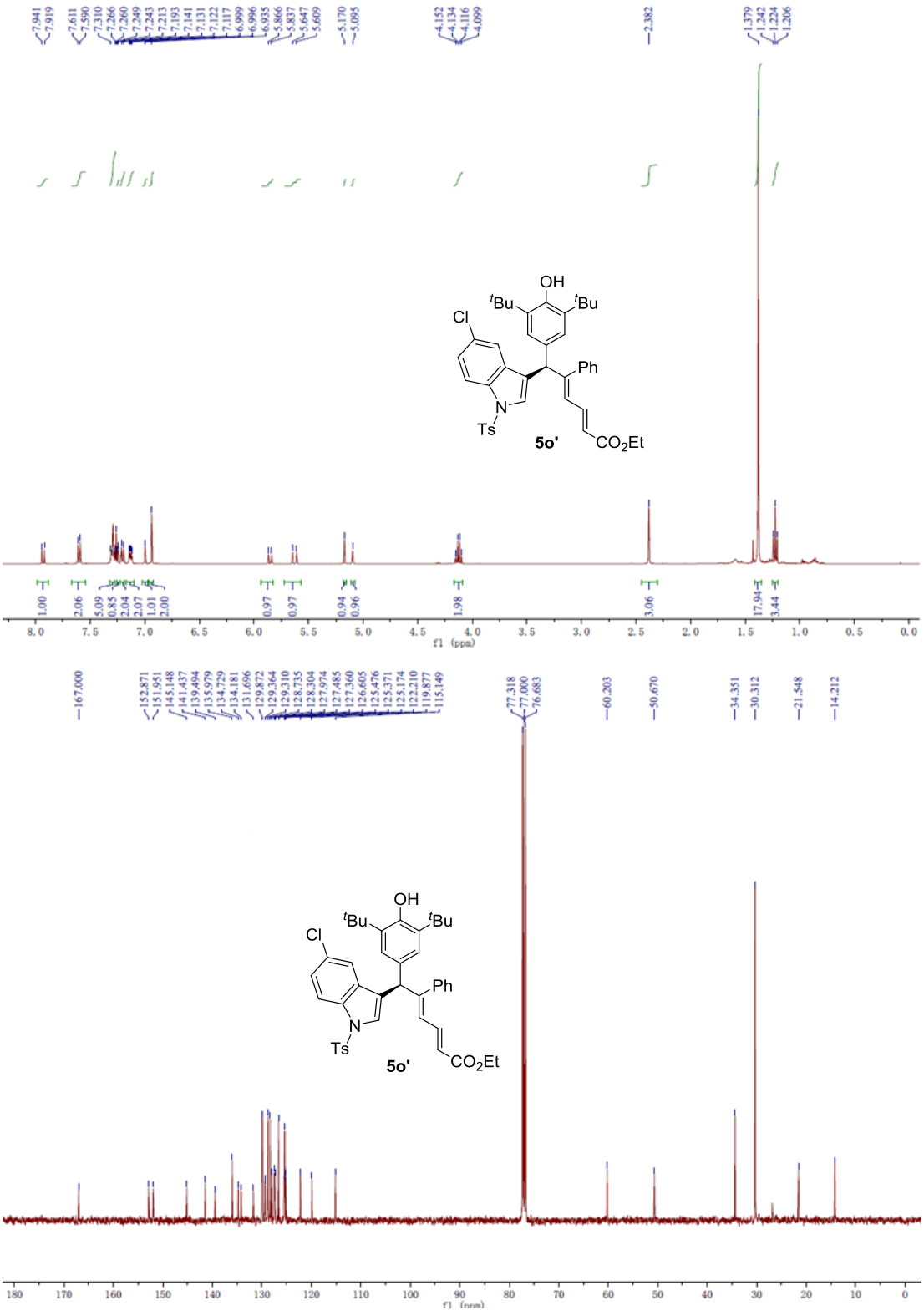
^{1}H and ^{13}C NMR spectra of compound **5m**



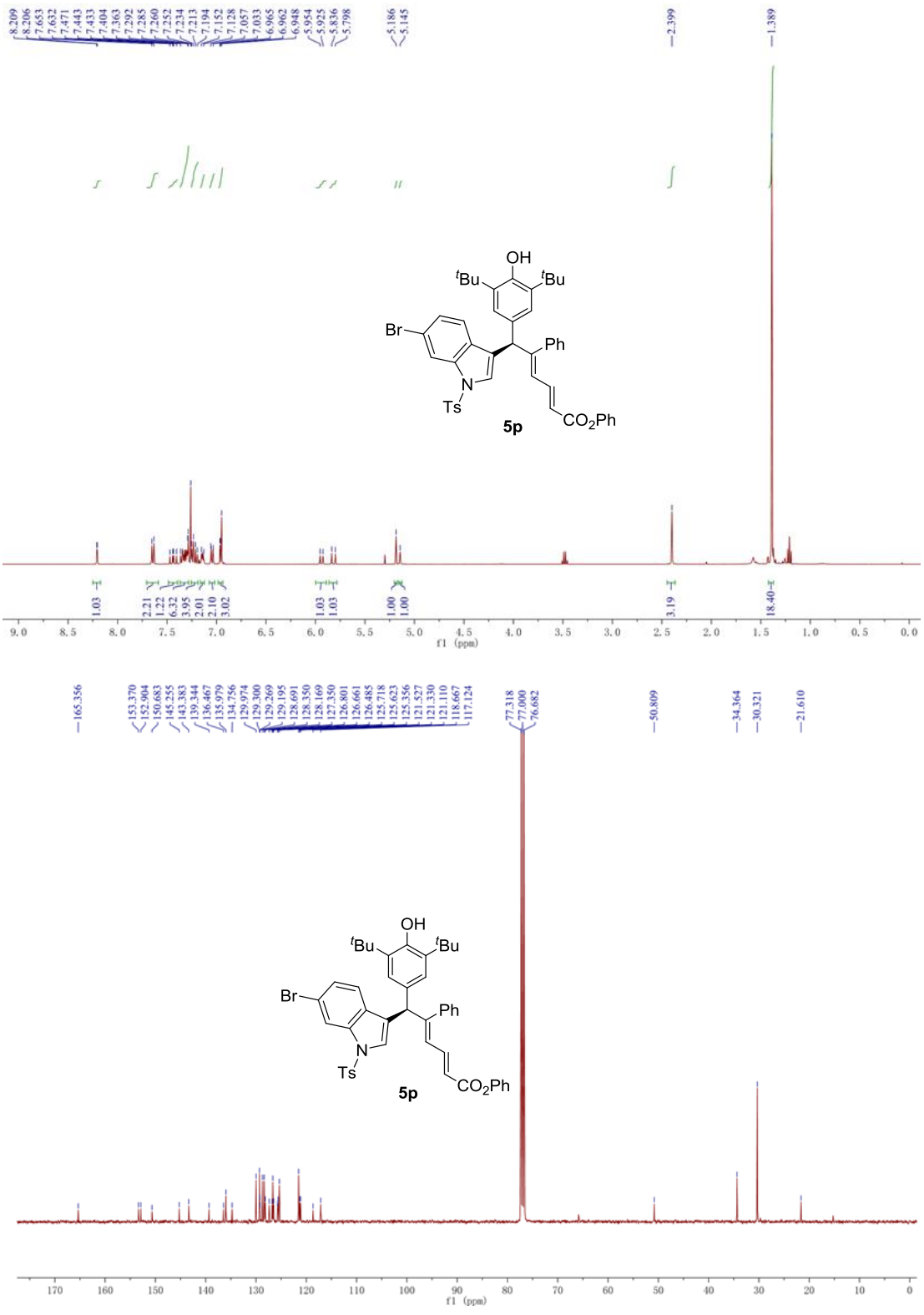
^{1}H and ^{13}C NMR spectra of compound **5n**



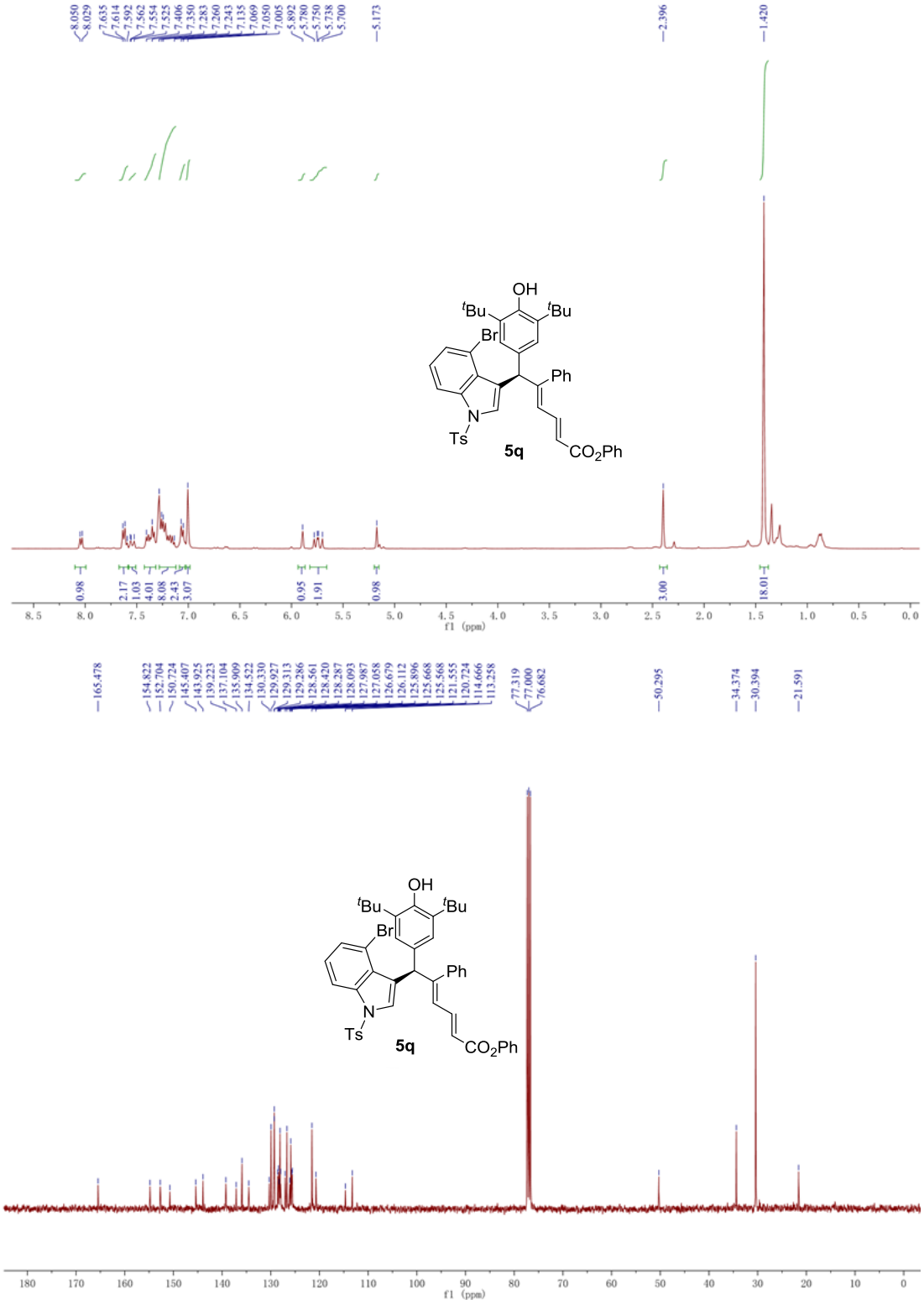
^{1}H and ^{13}C NMR spectra of compound **5o**



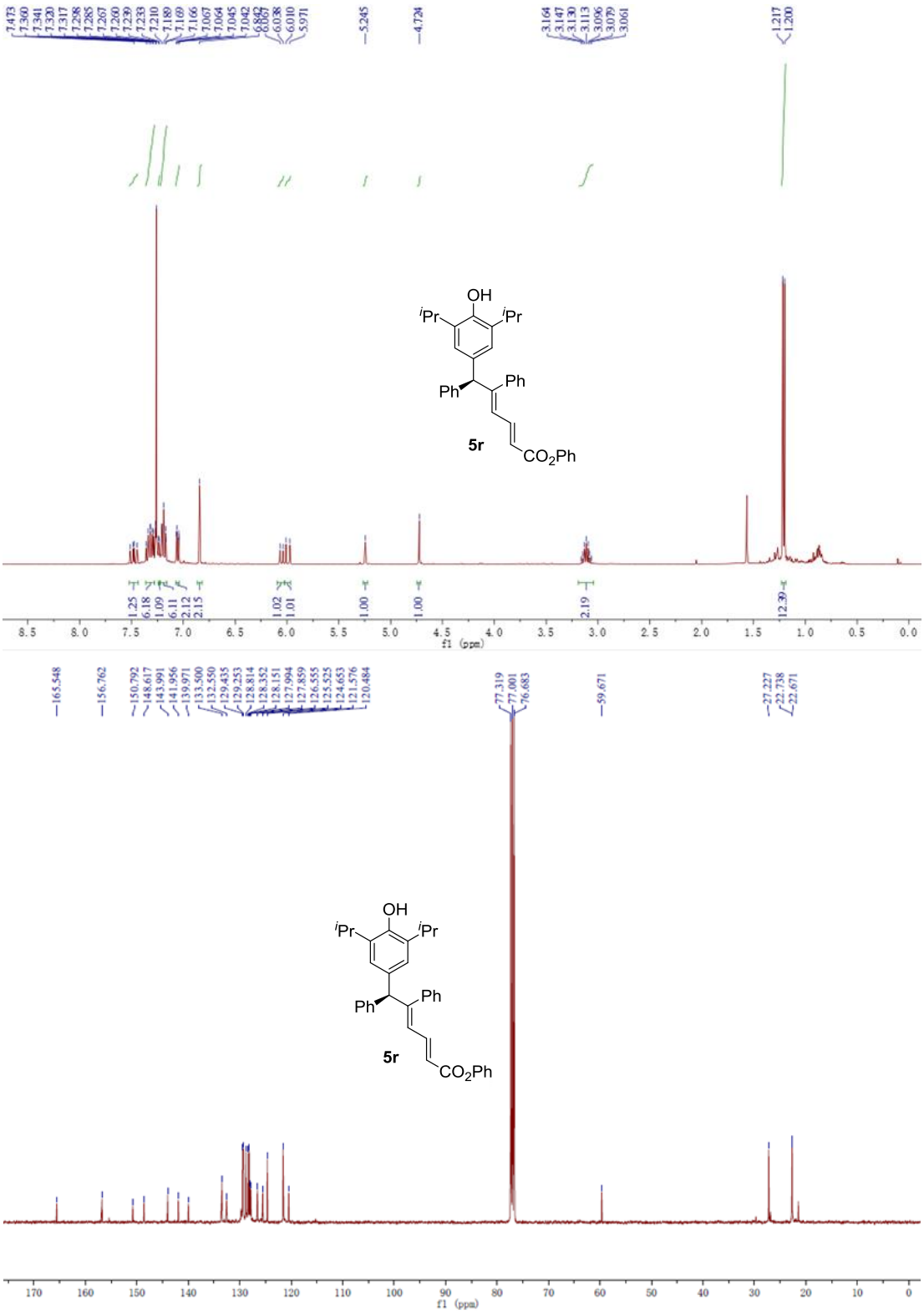
^{1}H and ^{13}C NMR spectra of compound **5o'**



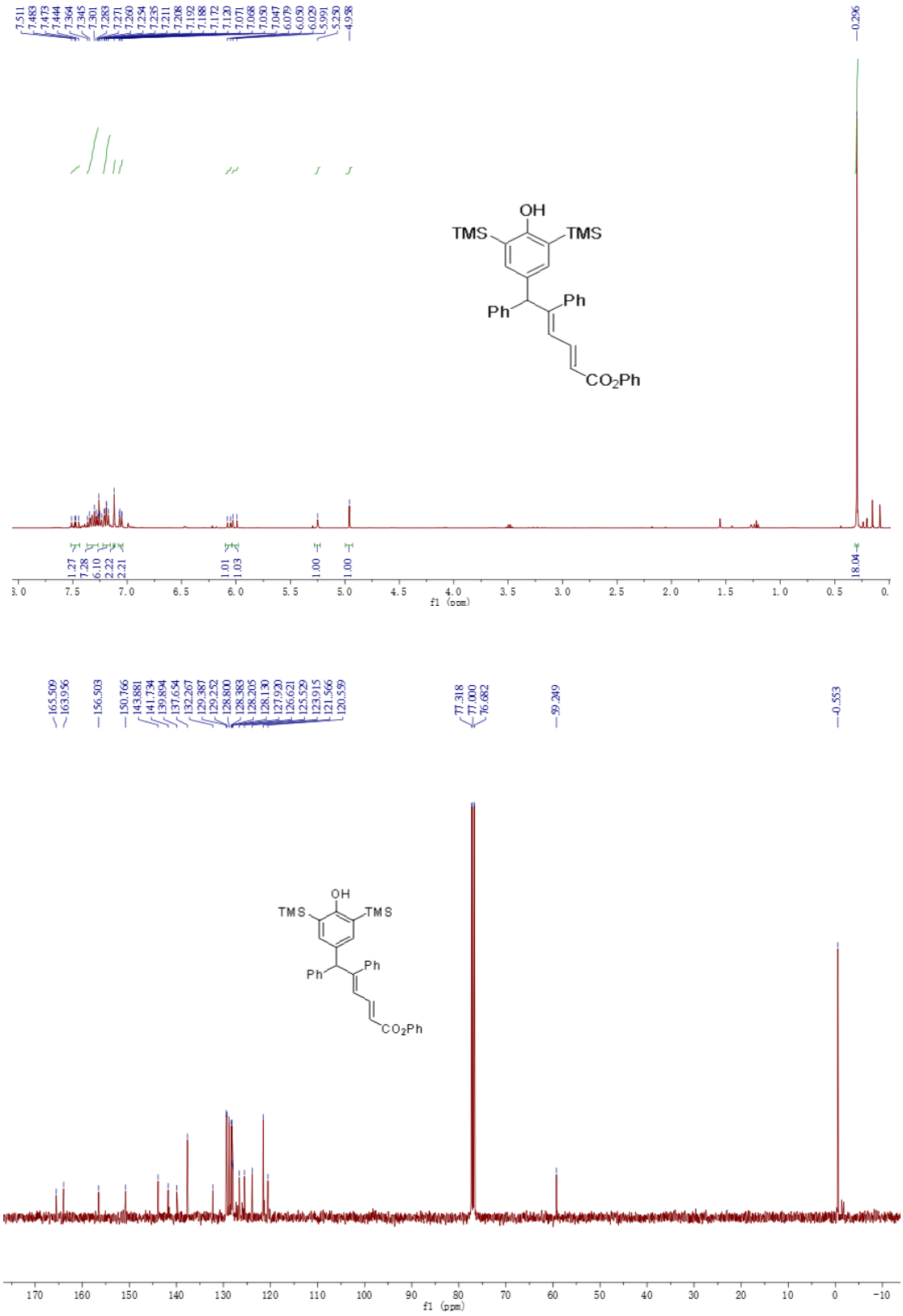
^{1}H and ^{13}C NMR spectra of compound **5p**



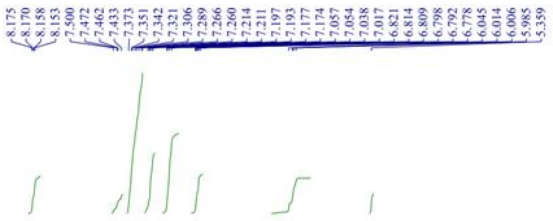
^{1}H and ^{13}C NMR spectra of compound **5q**

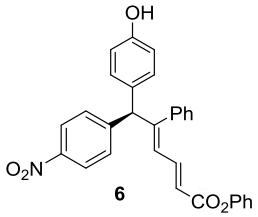


^{1}H and ^{13}C NMR spectra of compound **5r**

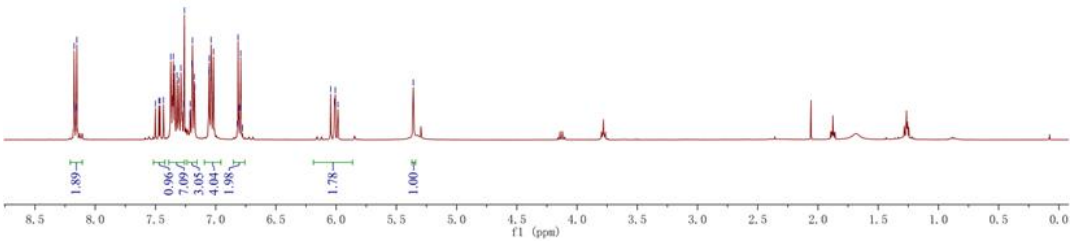


^{1}H and ^{13}C NMR spectra of compound **5s**

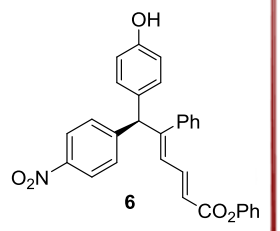

8.175
8.170
8.158
8.153
7.500
7.472
7.462
7.433
7.373
7.351
7.342
7.321
7.306
7.289
7.266
7.260
7.214
7.211
7.197
7.193
7.177
7.174
7.057
7.054
7.038
7.017
6.821
6.814
6.809
6.798
6.792
6.778
6.045
6.014
6.006
5.985
5.359


OH
Ph
O_2N
CO_2Ph

6

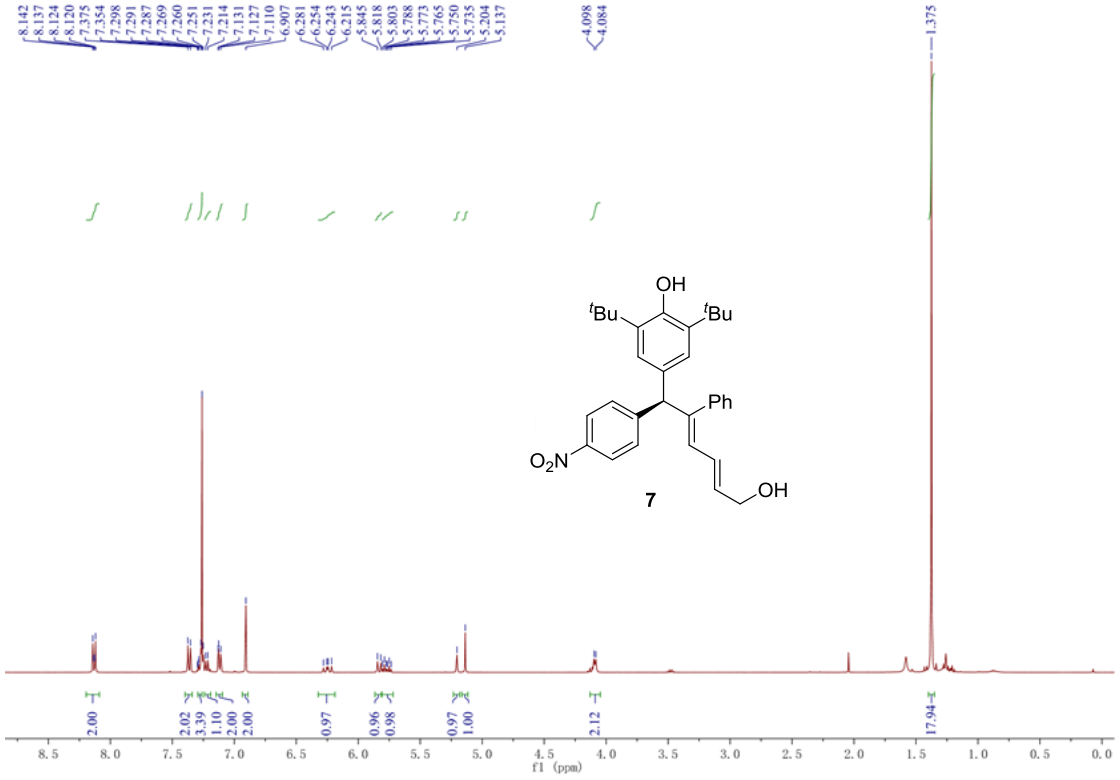

1.89
0.96
7.09
3.05
4.04
1.98
1.78
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

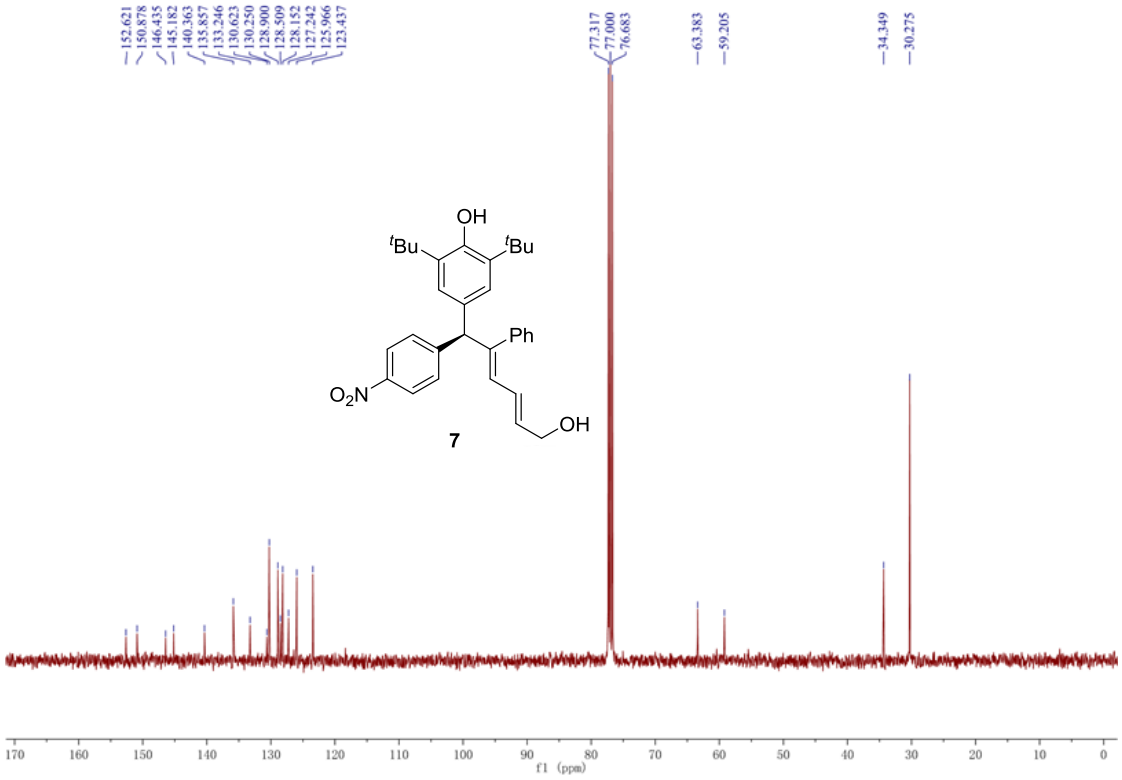

165.400
154.972
154.513
150.611
149.274
146.724
143.136
139.040
131.513
130.558
130.236
129.308
128.669
128.612
128.509
128.392
125.682
123.728
121.638
121.487
115.751
77.318
77.001
76.683
58.643


OH
Ph
O_2N
CO_2Ph

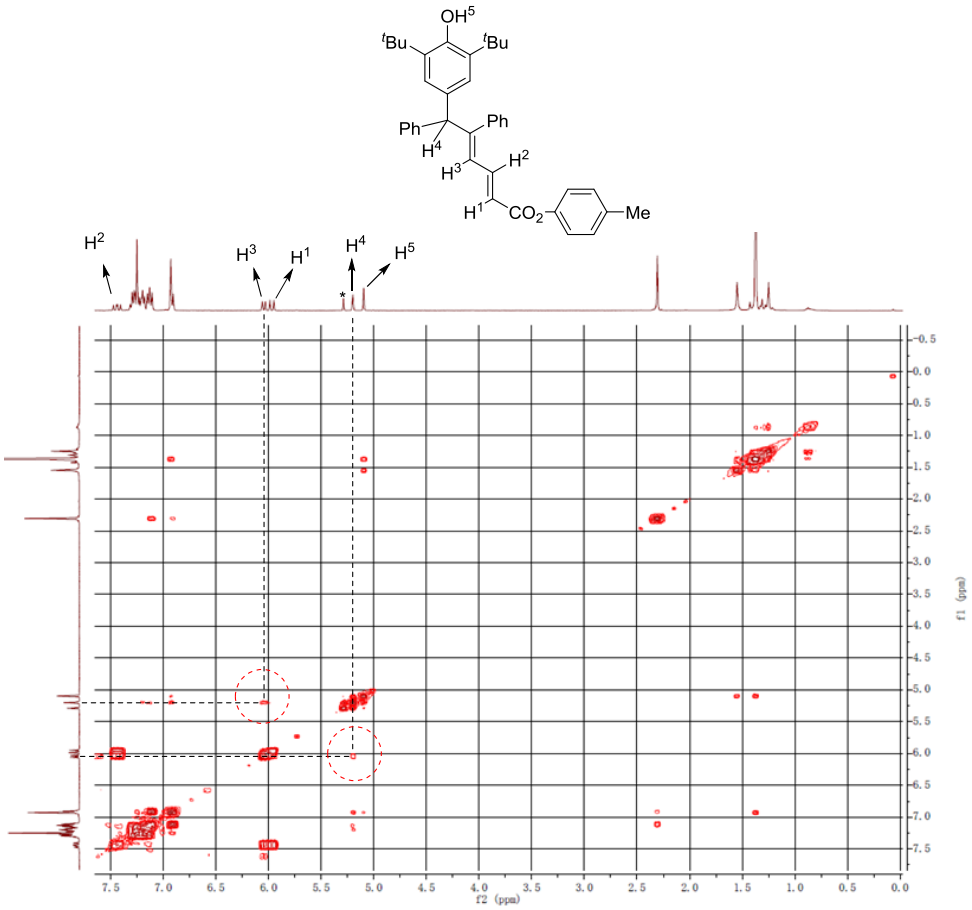
6

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.142
8.137
8.124
8.120
7.375
7.354
7.298
7.291
7.287
7.269
7.260
7.251
7.231
7.214
7.131
7.127
7.110
6.907
6.281
6.254
6.243
6.215
5.845
5.818
5.803
5.788
5.773
5.765
5.750
5.735
5.204
5.137
4.098
4.084
1.375
OH
tBu
tBu
Ph
O2N
OH
7
2.00
2.02
3.39
1.10
2.00
2.00
0.97
0.96
0.98
0.97
1.00
2.12
17.94
f1 (ppm)


152.621
150.878
146.435
145.182
140.363
135.857
133.246
130.623
130.250
128.900
128.509
128.152
127.242
125.966
123.437
77.317
77.000
76.683
63.383
59.205
34.349
30.275
OH
tBu
tBu
Ph
O2N
OH
7
f1 (ppm)

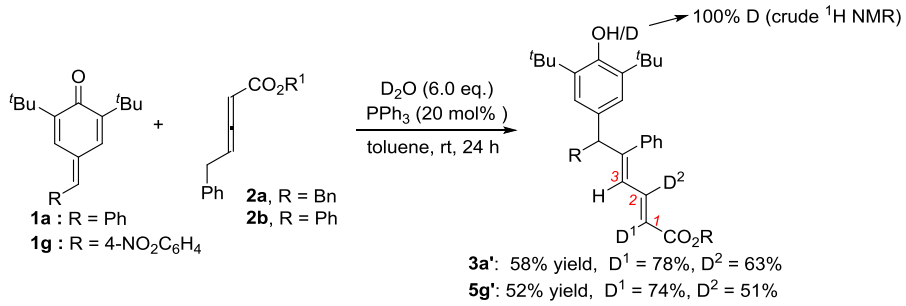
7. Deuterium-labeling experiments (^{1}H-^{1}H COSY NMR of 3f)



* is the peak of DCM

To identify the different protons, we run a ^{1}H-^{1}H COSY NMR (400M, $CDCl_3$). It clearly shows a signal of allylic proton "H^3" interact with diaryl substituted proton "H^4" labelled as red cycle; The asterisk is the residue DCM peak.

Deuterium-labeling of product 3a' and 5g'

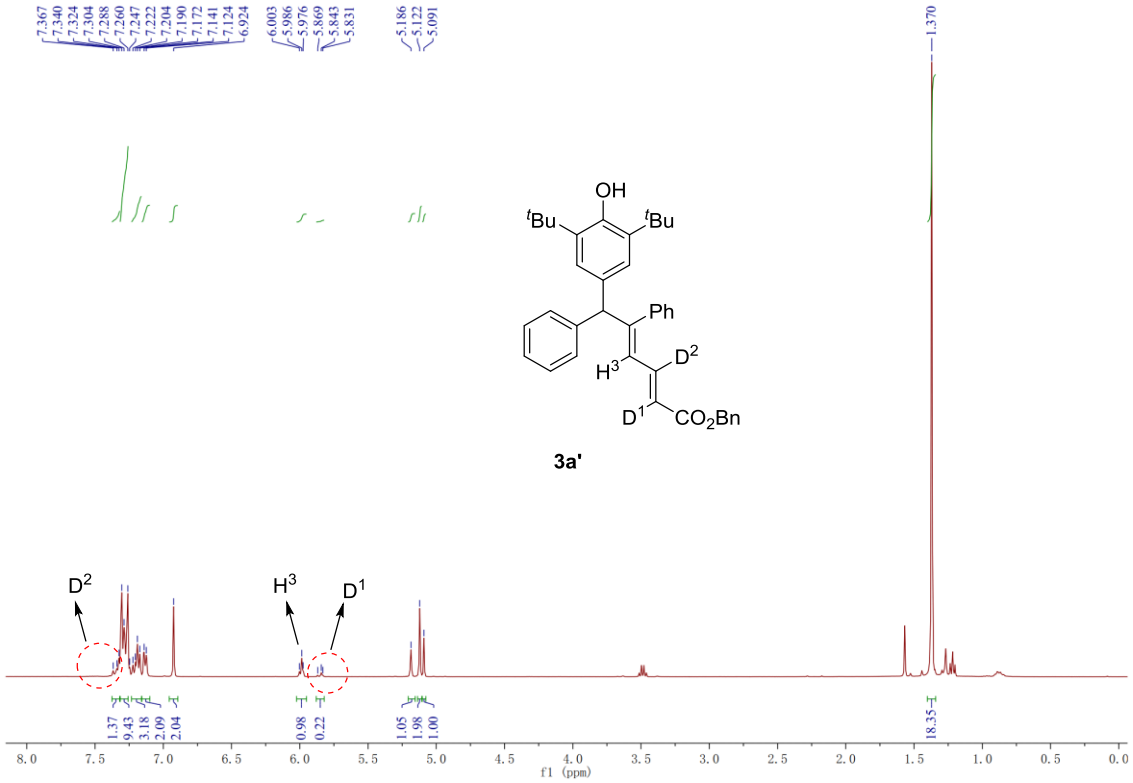


Compound **1a** or **1g** (0.1 mmol), PPh_3 (0.02 mmol) and anhydrous toluene (1.0 mL) were added into a dry Schlenk tube, then δ-substituted allenic ester **2a** or **2b** (0.2 mmol) and D_2O (0.6 mmol, 6 equiv.) were added subsequently under nitrogen

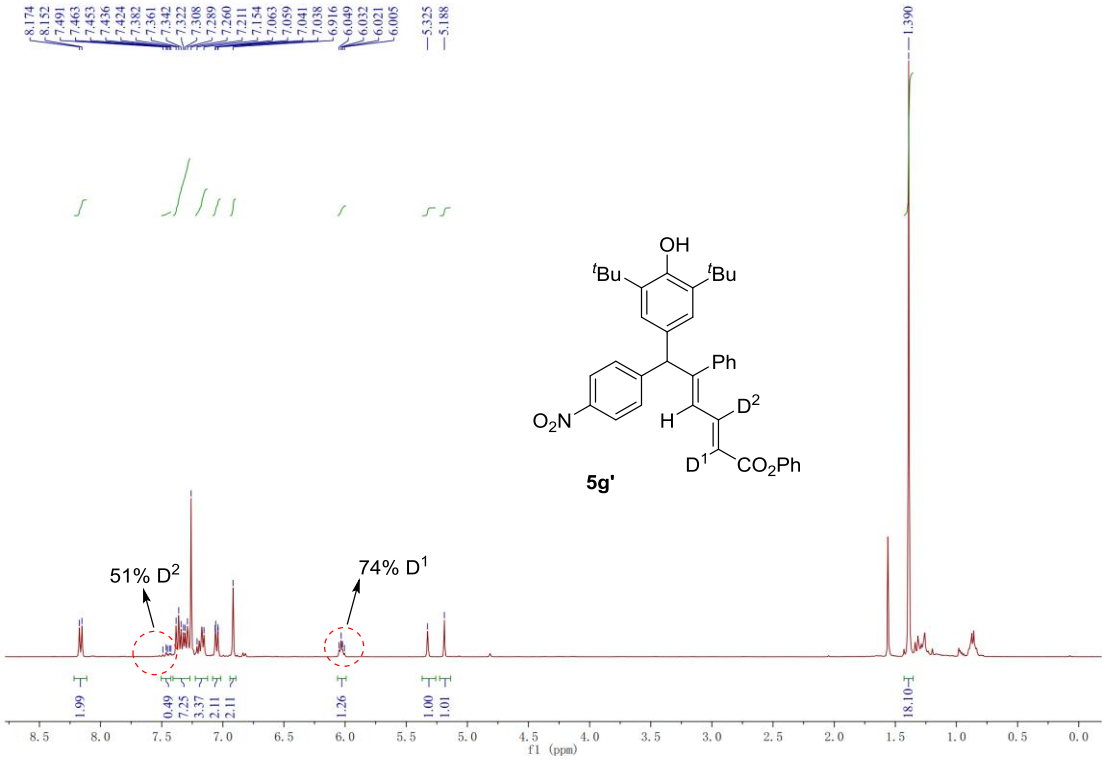
atmosphere. The reaction mixture was stirred at room temperature for 48 h under nitrogen atmosphere. The reaction mixture was then concentrated on a rotary evaporator under reduced pressure and the residue was subjected to purification by column chromatography (PE/EA = 100/1~50/1) to afford the corresponding product **3a'** or **5g'**.

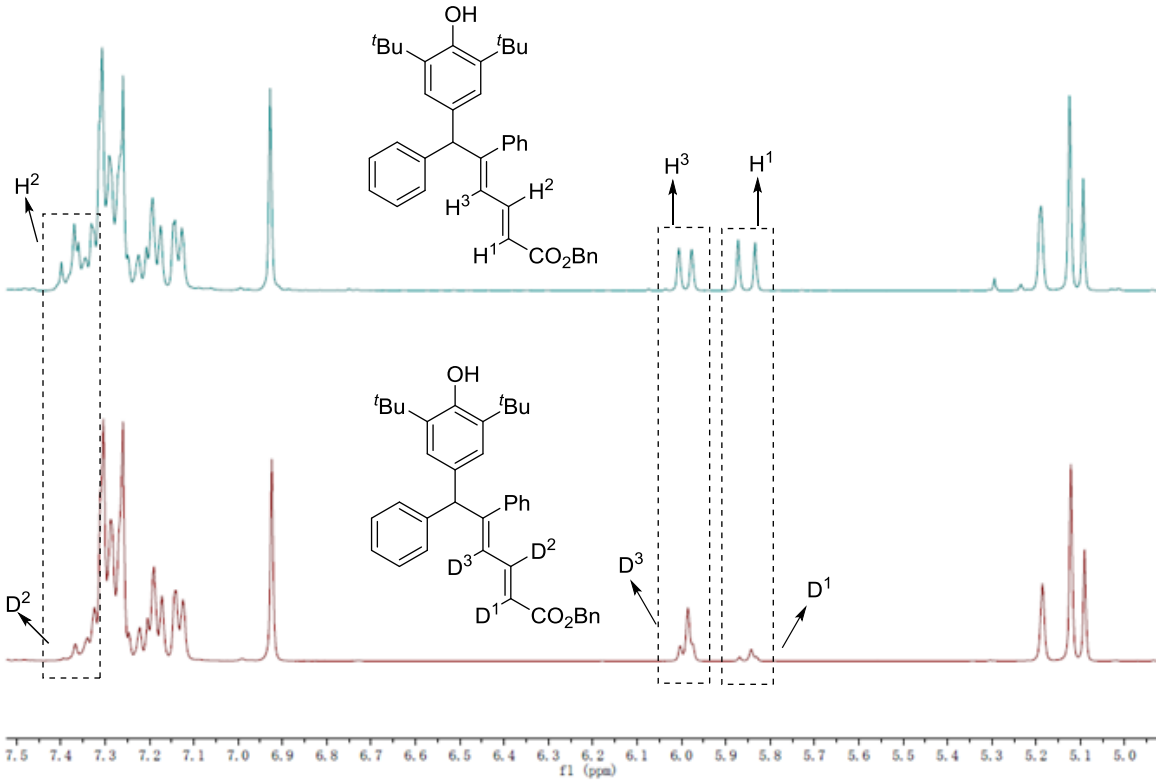
The crude ^{1}H NMR ($CDCl_3$, 400M) spectra showed that the phenol -OH group was completely deuterated (100% -OD group), during column chromatography on silica gel the –OD group exchanged to –OH again.

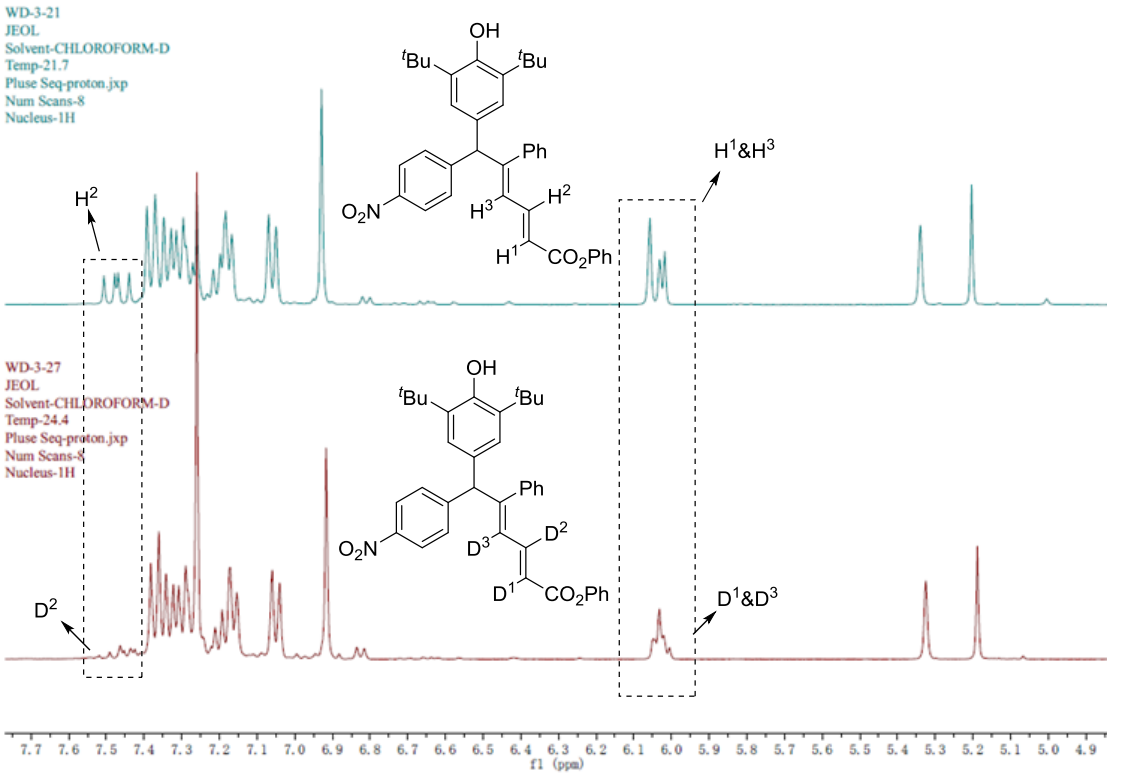
Comound **3a'**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 1.37H, 63%D), 7.33-7.25 (m, 9H), 7.23-7.18 (m, 3H), 7.15-7.13 (m, 2H), 6.93 (s, 2H), 6.00-5.98 (m, 1H), 5.87-5.83 (m, 0.22H, 78%D), 5.19 (s, 1H), 5.12 (s, 2H), 5.09 (s, 1H), 1.37 (s, 18H).

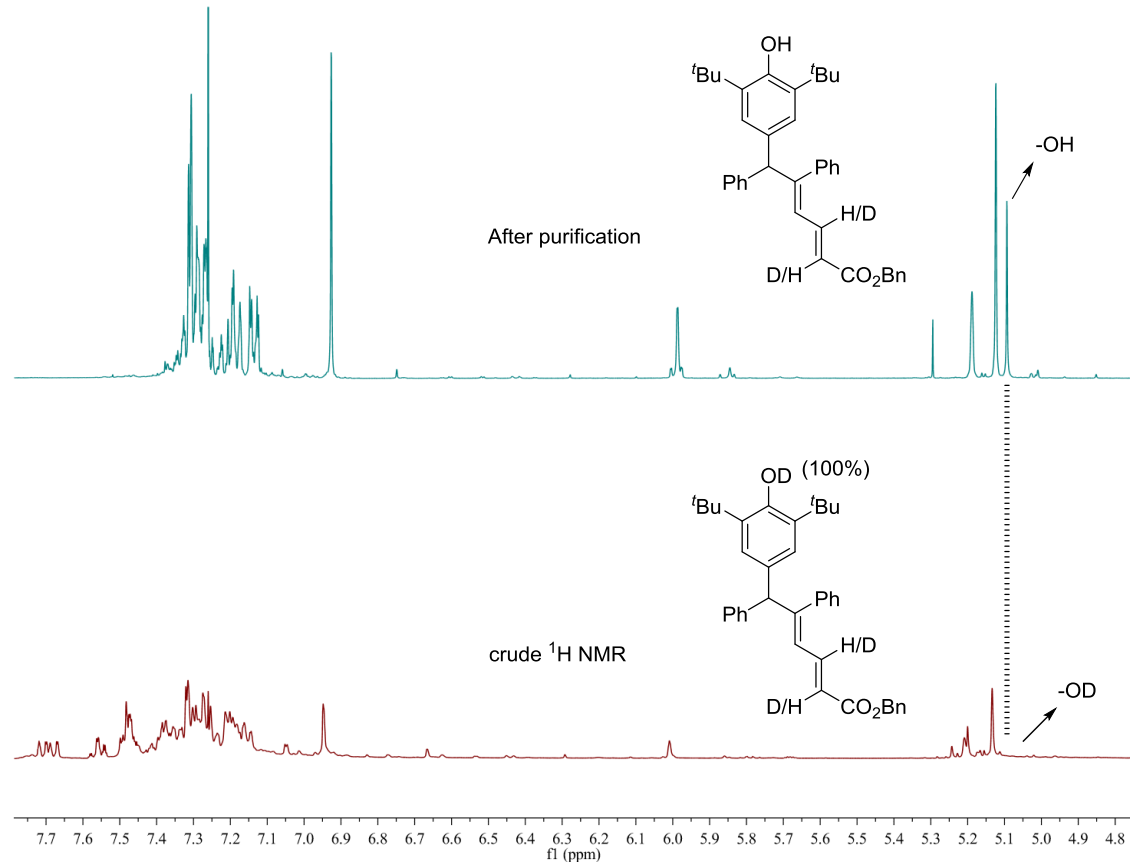


Comound **5g'**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.49-7.42 (m, 0.49H, 51%D), 7.38-7.27 (m, 7H), 7.22-7.17 (m, 3H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.93 (s, 2H), 6.05-6.01 (m, 1.26H, 74%D), 5.33 (s, 1H), 5.19 (s, 1H), 1.39 (s, 18H).

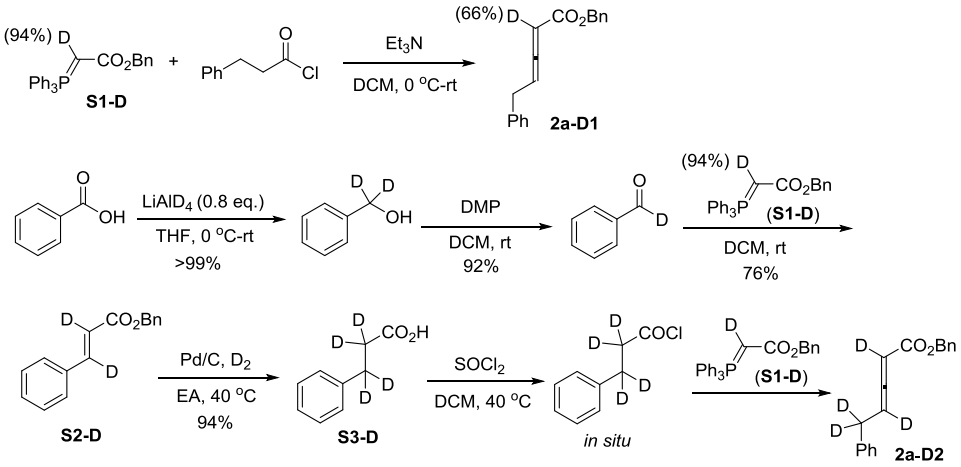

8.174
8.152
7.491
7.463
7.453
7.436
7.424
7.382
7.361
7.342
7.322
7.308
7.289
7.260
7.211
7.154
7.063
7.059
7.041
7.038
6.916
6.049
6.032
6.021
6.005
5.325
5.188
1.390
OH
tBu
tBu
Ph
O2N
H
D2
D1
CO2Ph
5g'
51% D2
74% D1
1.99
0.49
7.25
3.37
2.11
2.11
1.26
1.00
1.01
18.10
f1 (ppm)


OH
tBu
tBu
Ph
H3
H2
H1
CO2Bn
H2
H3
H1
D2
D3
D1
D3
D2
D1
CO2Bn
D2
D3
D1
f1 (ppm)


WD-3-21
JEOL
Solvent-CHLOROFORM-D
Temp-21.7
Pluse Seq-proton.jxp
Num Scans-8
Nucleus-1H
OH
tBu
tBu
Ph
O2N
H3
H2
H1
CO2Ph
H2
H1&H3
WD-3-27
JEOL
Solvent-CHLOROFORM-D
Temp-24.4
Pluse Seq-proton.jxp
Num Scans-8
Nucleus-1H
OH
tBu
tBu
Ph
O2N
D3
D2
D1
CO2Ph
D2
D1&D3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9
f1 (ppm)

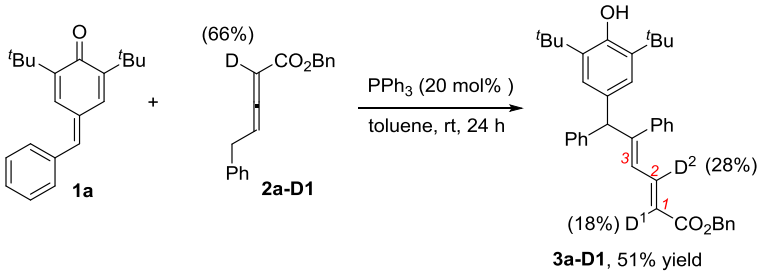

After purification
OH
tBu
tBu
Ph
Ph
H/D
D/H
CO2Bn
-OH
crude 1H NMR
OD (100%)
tBu
tBu
Ph
Ph
H/D
D/H
CO2Bn
-OD
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8
f1 (ppm)

Synthesis of deuterated allenoate **2a-D1** and **2a-D2**



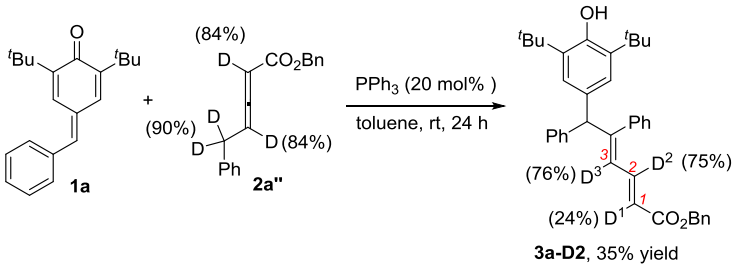
Compounds **S1-D**, **S2-D** and **S3-D** were known compound and prepared according to the previous literatures (For **S1-D** see: *Chem. Sci.* **2014**, *5*, 2416; *Tetrahedron Lett.* **1983**, *24*, 743; For **S2-D** see: *Adv. Synth. Catal.* **2018**, 360, 2303; For **S3-D** see: *J. Am. Chem. Soc.* **2017**, 139, 13969).

The deuterated ratio of allenoate **2a-D1** and **2a-D2** decrease was due to H/D exchange during purification process on silica gel. And the deuterated allenoates containing small amount of isomers.



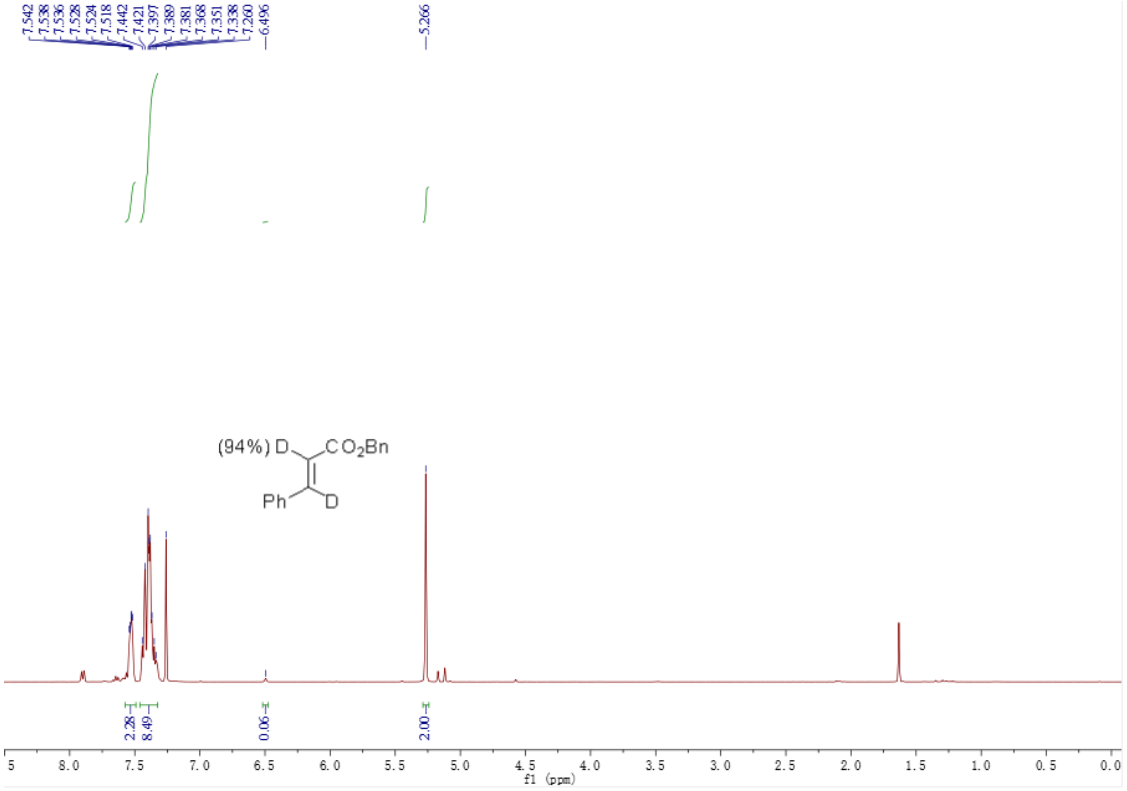
3a-D1, 51% yield

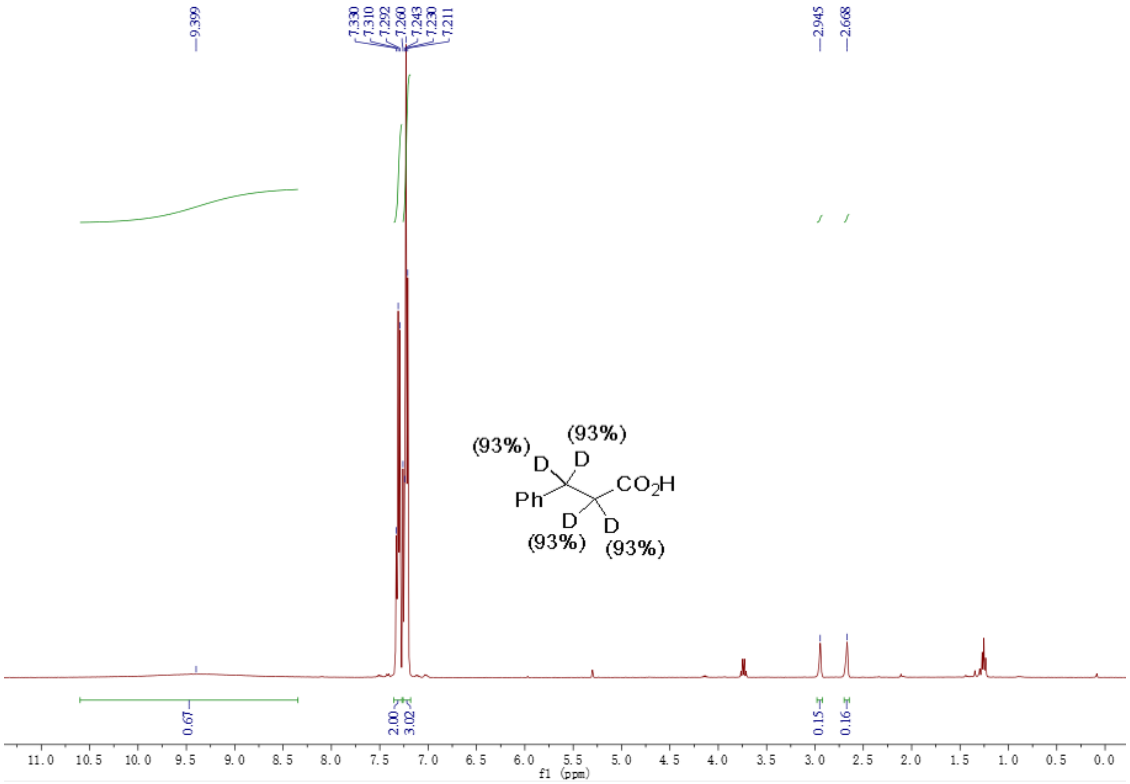
Comound **3a-D1** (51% yield, 29 mg) was obtained as a slurry oil following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2a-D1** (0.2 mmol, 52 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 1.72H, 28%D), 7.33-7.25 (m, 9H), 7.23-7.18 (m, 3H), 7.15-7.13 (m, 2H), 6.93 (s, 2H), 6.00-5.98 (m, 1H), 5.88-5.84 (m, 0.22H, 78%D), 5.20 (s, 1H), 5.13 (s, 2H), 5.10 (s, 1H), 1.38 (s, 18H).

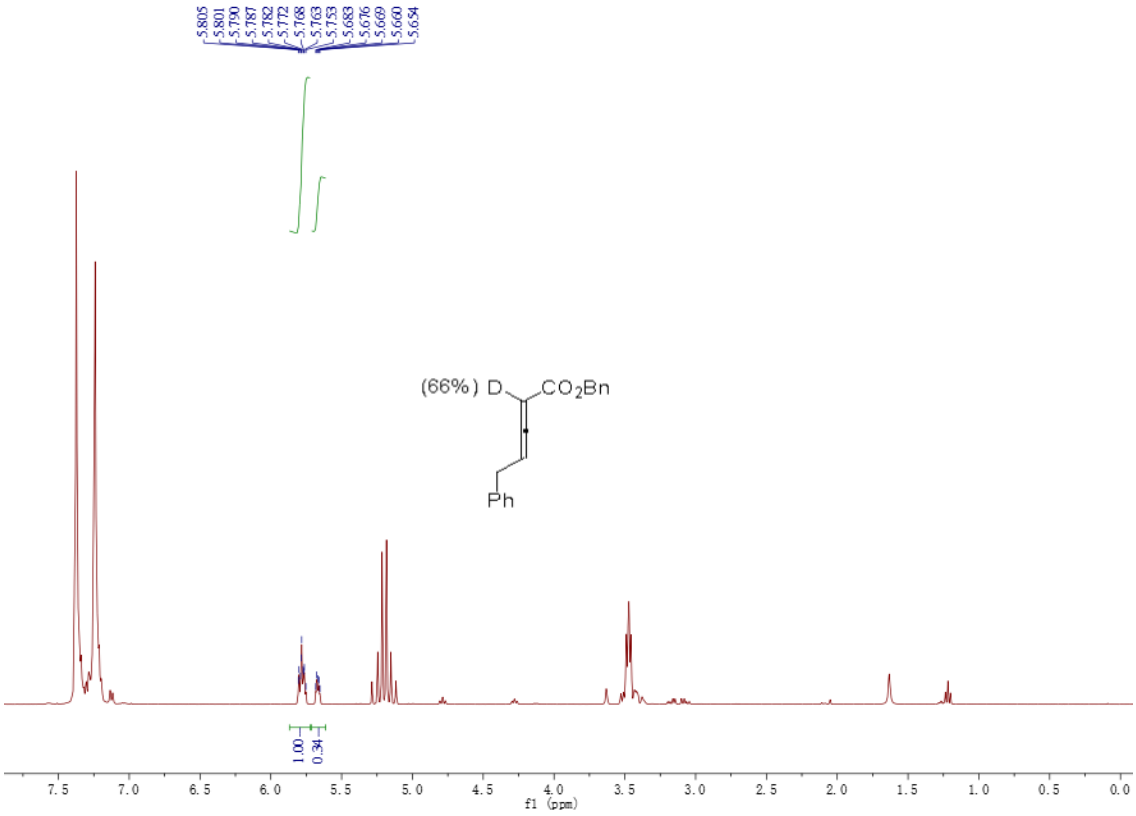


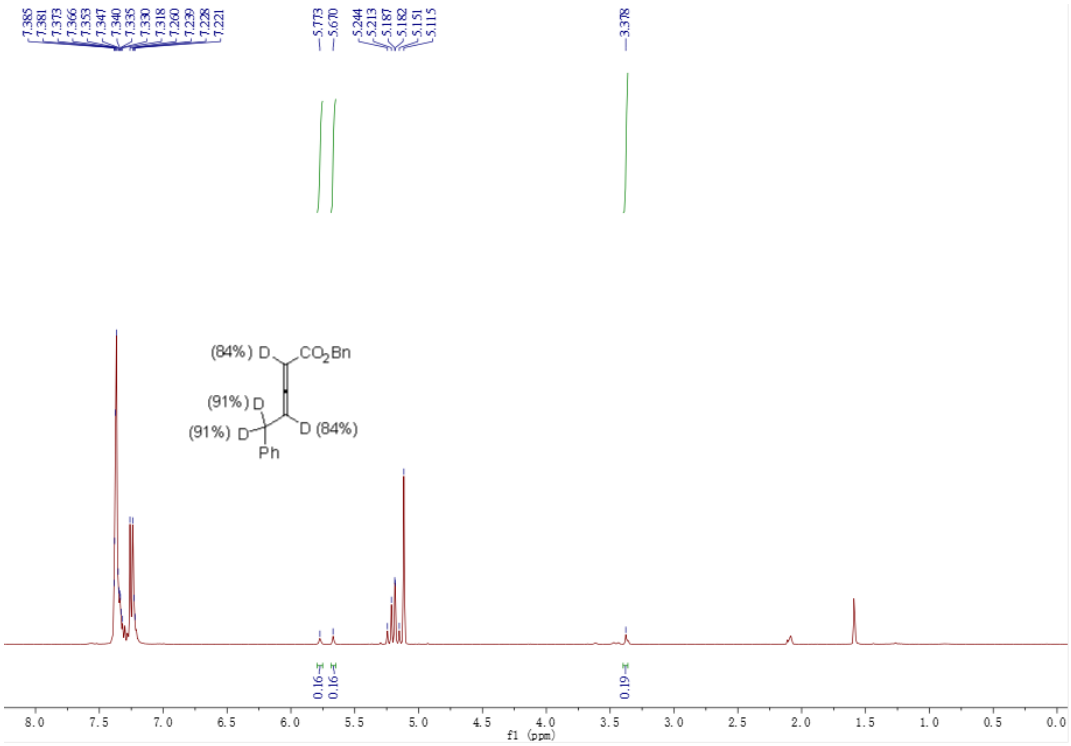
3a-D2, 35% yield

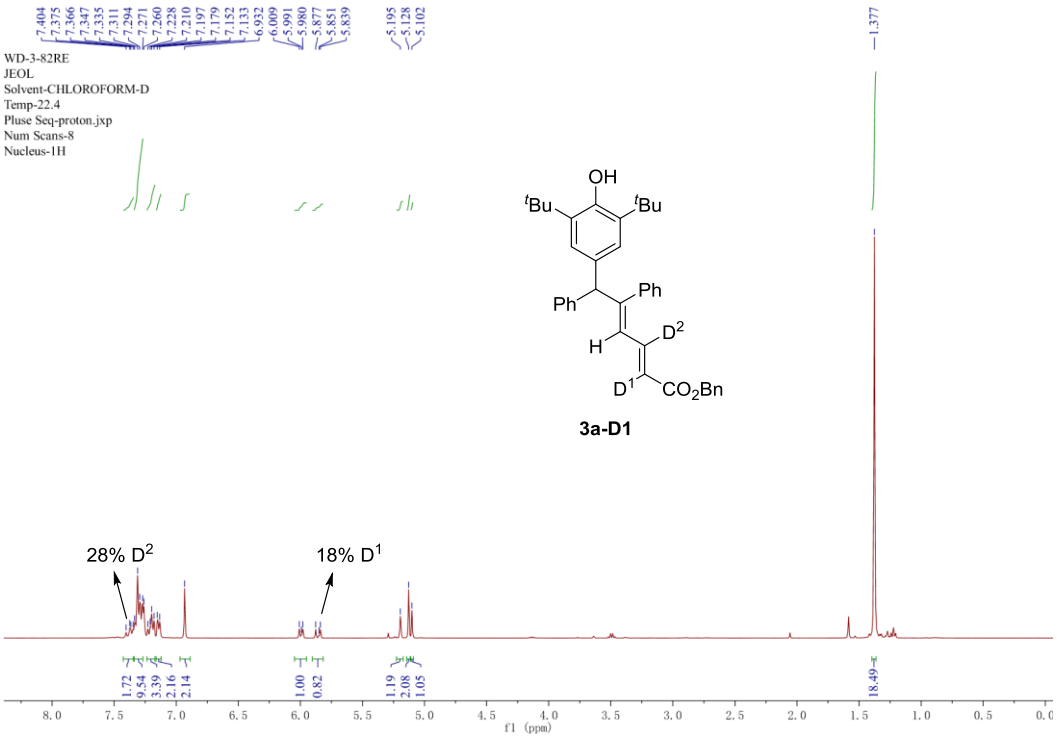
Comound **3a-D2** (35% yield, 20 mg) was obtained as a slurry oil following the *general procedure III* from **1a** (0.1 mmol, 29.4 mg) and **2a-D2** (0.2 mmol, 52 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 1.25H, 75%D), 7.32-7.26 (m, 9H), 7.20-7.16 (m, 3H), 7.14-7.12 (m, 2H), 6.93 (s, 2H), 5.99-5.96 (m, 0.24H, 76%D), 5.86-5.82 (m, 0.76H, 24%D), 5.18 (s, 1H), 5.12 (s, 2H), 5.09 (s, 1H), 1.36 (s, 18H).

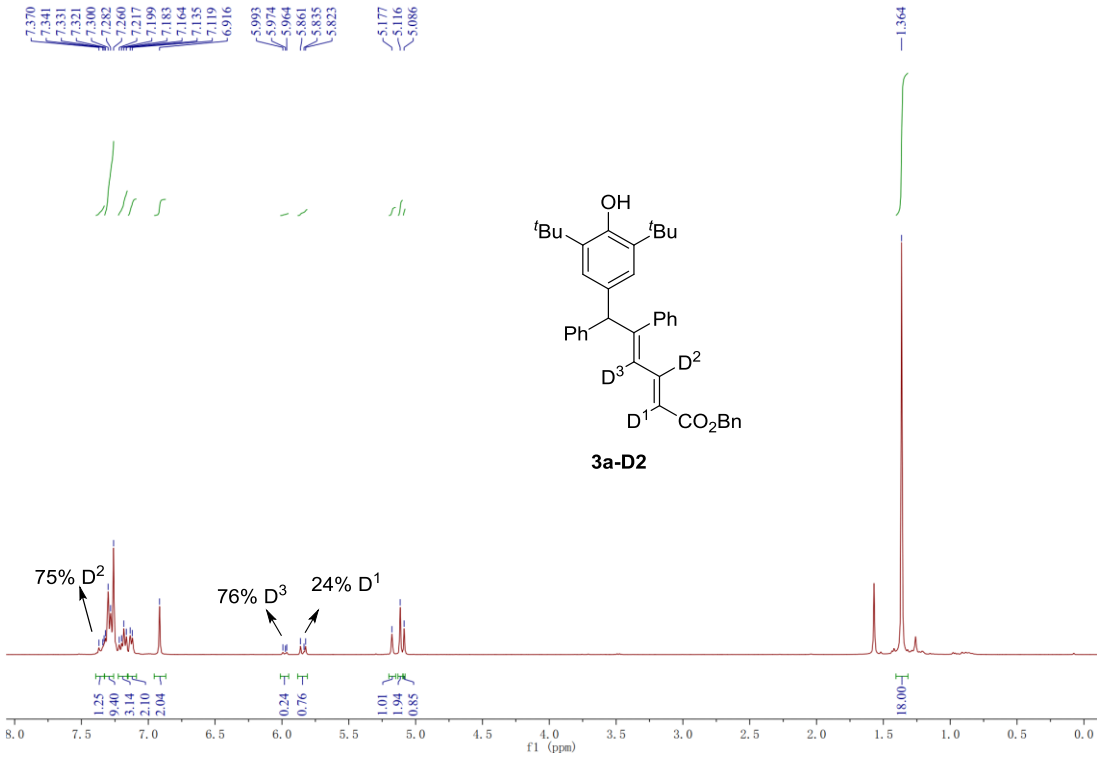



9.399
7.330
7.310
7.292
7.260
7.243
7.230
7.211
2.945
2.668
(93%)
(93%)
D
D
Ph
CO2H
D
D
(93%)
(93%)
0.67
2.00
3.02
0.15
0.16
f1 (ppm)


5.805
5.801
5.790
5.787
5.782
5.772
5.768
5.763
5.753
5.683
5.676
5.669
5.660
5.654
(66%) D
CO2Bn
Ph
1.00
0.34
f1 (ppm)


(84%) D
CO2Bn
(91%) D
(91%) D
D (84%)
Ph
f1 (ppm)


WD-3-82RE
JEOL
Solvent-CHLOROFORM-D
Temp-22.4
Pluse Seq-proton.jxp
Num Scans-8
Nucleus-1H
OH
tBu
tBu
Ph
Ph
H
D2
D1
CO2Bn
3a-D1
28% D2
18% D1
f1 (ppm)


7.370
7.341
7.331
7.321
7.300
7.282
7.260
7.217
7.199
7.183
7.164
7.135
7.119
6.916
5.993
5.974
5.964
5.861
5.835
5.823
5.177
5.116
5.086
1.364
OH
tBu
tBu
Ph
Ph
D3
D2
D1
CO2Bn
3a-D2
75% D2
76% D3
24% D1
1.25
9.40
3.14
2.10
2.04
0.24
0.76
1.01
1.94
0.85
18.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)