Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Photocatalytic selective 1,2-hydroxyacylmethylation of 1,3-dienes with sulfur ylides as source of alkyl radicals

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. 1,3-dienes **1** and sulfur ylides **2** were prepared according to the known procedure.[1,2] All the solvents were treated according to standard methods.[3,4]

^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet), coupling constants (Hz) and integration **^{13}C NMR** spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm, t). **^{19}F NMR** spectra were recorded on 376 MHz with complete proton decoupling spectrophotometers. **IR** were measured on Bruker TENSOR 27. The high resolution mass spectra (**HRMS**) were measured on Bruker micrOTOF-II mass spectrometer by ESI. Blue LED lamps (20 W; Kessil PR160, λmax = 456 nm) were used to irradiate the reaction mixtures, which were bought from Anhui Kemi Machinery Technology Co., Ltd. (http://www.ahkemi.com/). **Electron Paramagnetic Resonance (EPR)**: Electron paramagnetic resonance studies was performed on JES X320, JEOL Inc.

Figure S1. Light source and photoreactor used in this research

References:

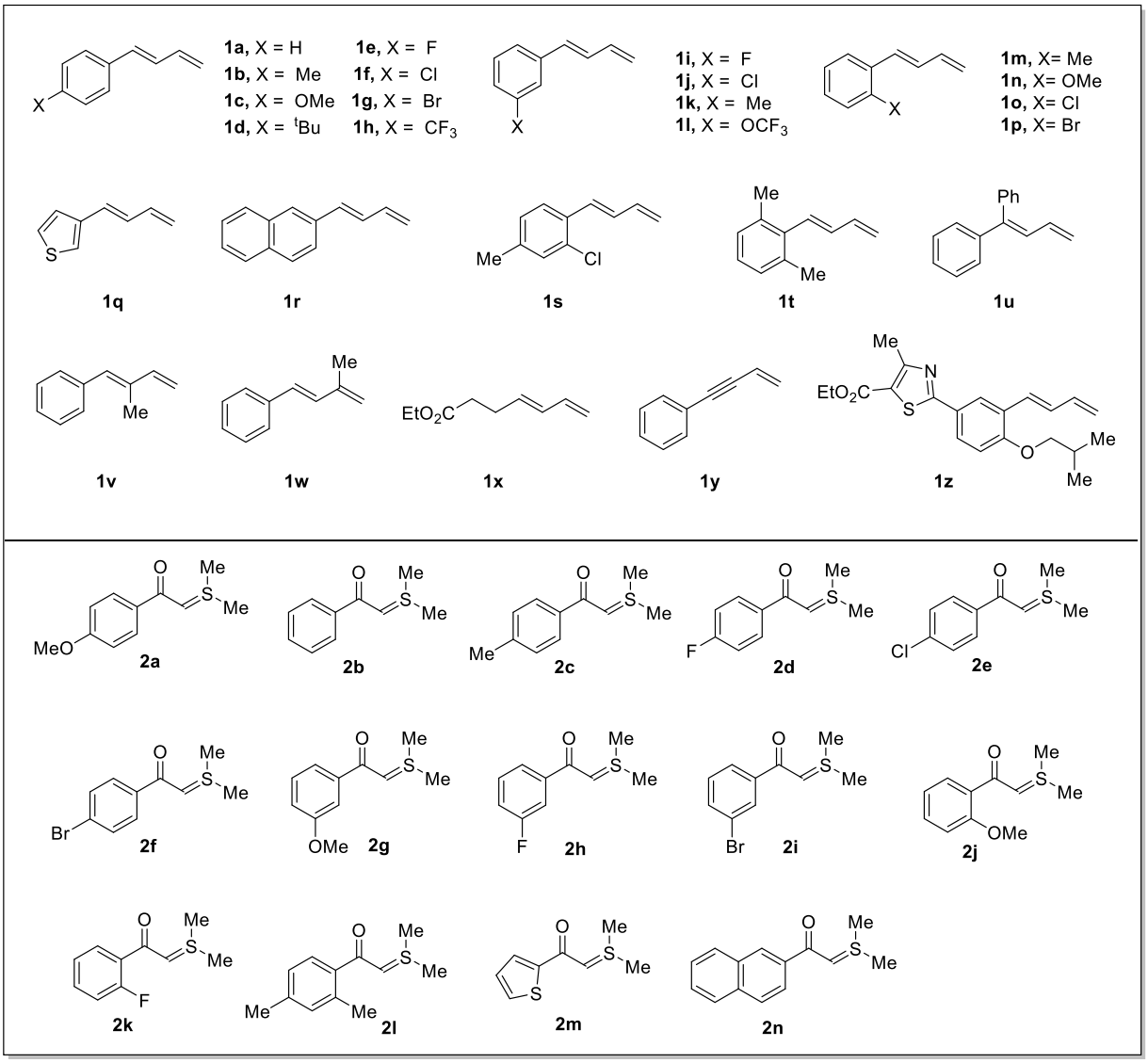
1. (a) Sun, X.; Li, X.; Song, S.; Zhu, Y.; Liang, Y.-F.; Jiao, N. *J. Am. Chem. Soc*. **2015**, 137, 6059. (b) Hemric, B. N., Chen, A. W.; Wang, Q. *ACS Catal*. **2019**, *9*, 10070. (c) Sardini, S. R.; Brown, M. K. *J. Am. Chem. Soc*. **2017**, *139*, 9823.

2. (a) Ratts, K. W.; Yao, A. N. *J. Org. Chem*. **1966**, *31*, 1185. (b) Anderson, W. K.; Jones, A. N. *J. Med.Chem*. **1984**, *27*, 1559. (c) Quintana, J.; Torres, M.; Serratosa, F. *Tetrahedron*, **1973**, *29*, 2065. (d) Payne, G. *J. Org. Chem.* **1967**, *32*, 3351.

3. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 4th ed.*; Pergamon Press: Oxford, **1997**.

4. CF_3CH_2OH is bubbled with argon for 20 mins before each experiment.

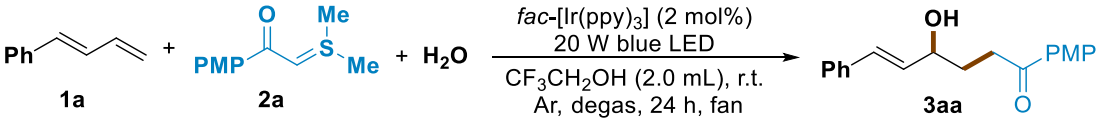
2. Scope of the Substrates



3. Detailed Optimization of Reaction Conditions and Control Experiments

3.1 Optimization of Reaction Conditions

Table S1. **Screening of the ratio of H_2O[a]**

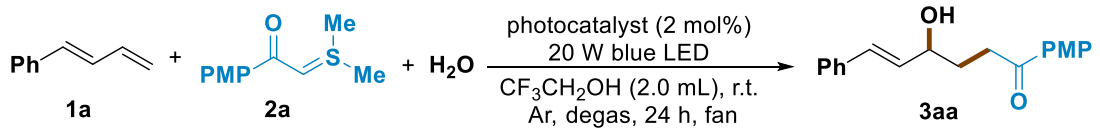


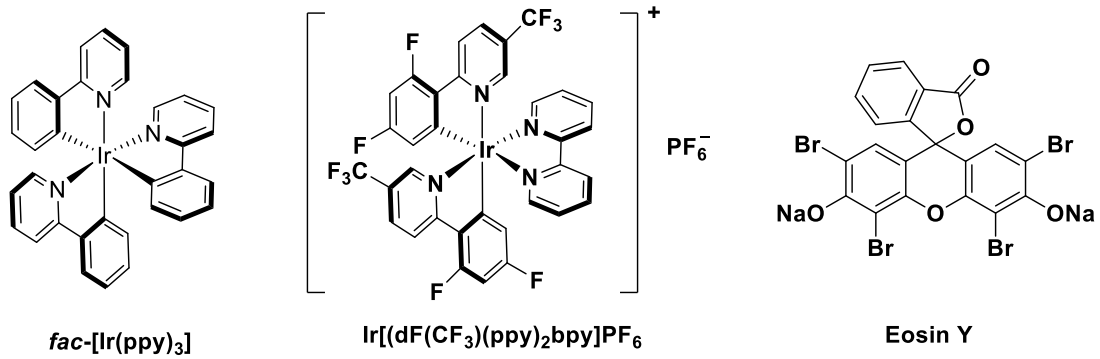
Entry	H_2O (x eq.)	Conversion (%)[b]	Yield (%)[b]
1	1.0	100	19
2	1.75	100	30
3	2.75	100	37
4	3	100	33
5	5	100	43
6	10	100	44
7	**15**	**100**	**59**
8	20	100	57
9	0.5 mL	30	<10

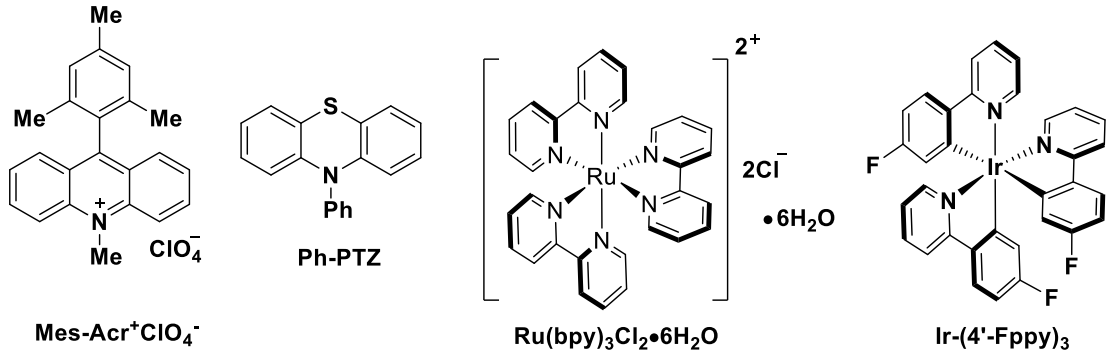
[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), **H_2O** (x eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), CF_3CH_2OH (2.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S1***, among the different ratios of H_2O tested, 15.0 eq. gave the best results in terms of yield (59% yield), and was thus selected for further optimization studies.

Table S2. **Optimization of the photocatalysts[a]**





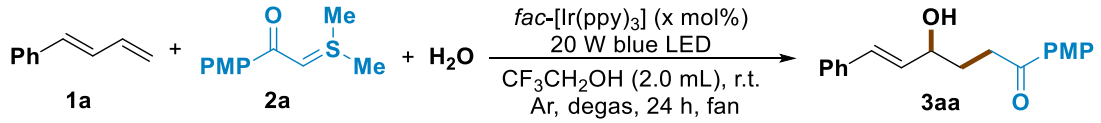


Entry	Photocatalysts (2 mol%)	Conversion (%)[b]	Yield (%)[b]
1	***fac*-[Ir(ppy)$_3$]**	**100**	**59**
2	Ir[(dF(CF$_3$)(ppy)$_2$bpy]PF$_6$	100	0
3	Eosin Y	48	0
4	Eosin Y (green LEDs, 20 W)	14	0
5	Mes-Acr$^+$ClO4$^-$	80	0
6	Ph-PTZ (UV light, 20 W)	36	10
7	Ru(bpy)$_3$Cl$_2$·6H$_2$O	4	0
8	Ir-(4'-Fppy)$_3$	93	15

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), **H$_2$O** (15.0 eq.), Photocatalyst (2 mol%), CF$_3$CH$_2$OH (2.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S2***, among all the photocatalysts tested, *fac*-[Ir(ppy)$_3$] gave the best results in terms of yield (59% yield), and was thus selected for further optimization studies.

Table S3. **Screening of the ratio of photocatalyst[a]**

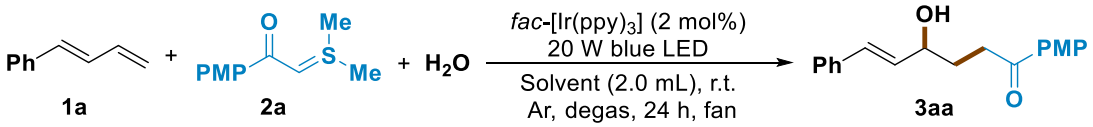


Entry	*fac*-[Ir(ppy)$_3$] (x mol%)	Conversion (%)[b]	Yield (%)[b]
1	1	100	40
2	**2**	**100**	**59**
3	3	100	63
4	4	100	61
5	**5**	**100**	**64**

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), **H$_2$O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (x mol%), CF_3CH_2OH (2.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S3***, among the ratio of *fac*-[Ir(ppy)$_3$] tested, 5 mol% gave slightly better results in terms of yield (64% yield) than 2 mol% (59%), and 2 mol% was thus selected for further optimization studies.

Table S4. **Optimization of solvent[a]**



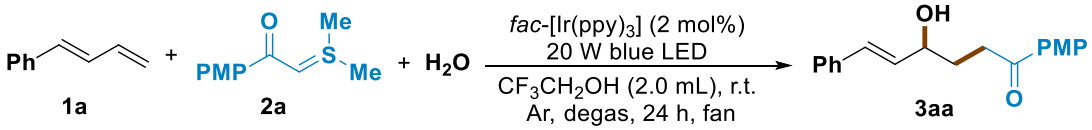
Entry	Solvent	Conversion (%)[b]	Yield (%)[b]
1	**CF_3CH_2OH**	**100**	**59**
2	MeOH	17	0
3	EtOH	0	0
4	^{i}PrOH	51	0

5	HFIP	10	8
6	DMF	85	0
7	DMSO	100	0
8	THF	100	0
9	DCM	0	0
10	MeCN	100	0

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), **H_2O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), Solvent (2.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S4***, among the solvent tested, CF_3CH_2OH gave the best result (59% yield), and was thus selected for further studies.

Table S5. **Optimization of substrate ratio[a]**

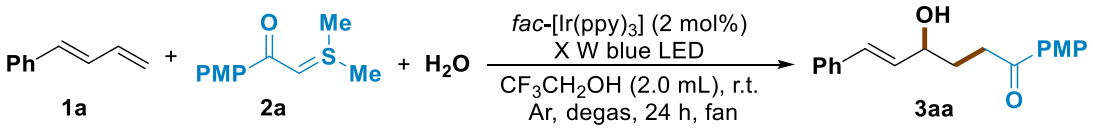


Entry	1a: 2a: H_2O	Yield (%)[b]
1	3/1/15	59
2	1/1/15	27
3	1/2/15	46
4	**1/3/15**	**63**
5	1/4/15	59

[a]At 0.2 mmol scale. Reaction conditions: The ratio of **1a**: **2a**: **H_2O** as shown in Table *S5*, *fac*-[Ir(ppy)$_3$] (2 mol%), CF_3CH_2OH (2.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S5***, among the ratios tested, a **1:3:15** ratio of **1a**:**2a**:**H_2O** gave the best result in terms of yield (63% yield), and was thus selected for further studies.

Table S6. **Optimization of light intensity[a]**

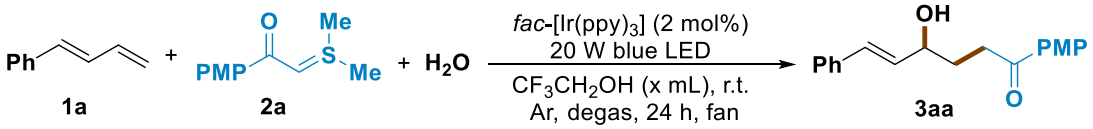


Entry	Light source	Light intensity	Yield (%)[b]
1	4 × 6 W blue LEDs	10 mW/cm^2	49
2	7 W blue LEDs	5 mW/cm^2	22
3	10 W kessil blue LED	15 mW/cm^2	40
4	**20 W kessil blue LED**	**32 mW/cm^2**	**63**
5	30 W kessil blue LED	48 mW/cm^2	56
6	40 W kessil blue LED	65 mW/cm^2	55

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **H$_2$O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), CF_3CH_2OH (2.0 mL), RT, 24 h, irradiation with X W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S6***, among the tested, 20 W Kessil blue LED gave the best result in terms of yield (63% yield), and was thus selected for further studies.

Table S7. **Optimization of concentration[a]**

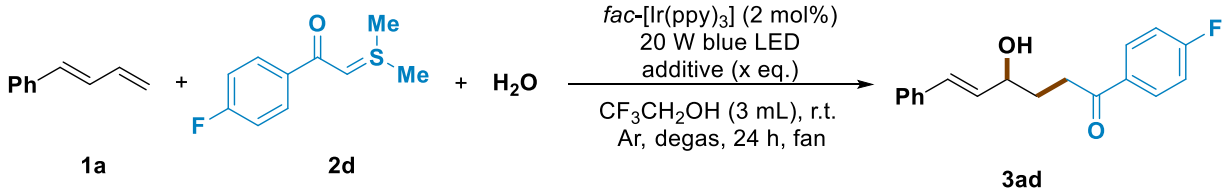


Entry	CF_3CH_2OH (x mL)	Yield (%)[b]
1	1	41
2	1.5	42
3	2	63
4	**3**	**74**
5	4	49

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **H_2O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), CF_3CH_2OH (x mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S7***, among the tested, 3.0 mL CF_3CH_2OH gave the best result in terms of yield (74% yield), and was thus selected for further studies.

Table S8. **Optimization of additive[a]**



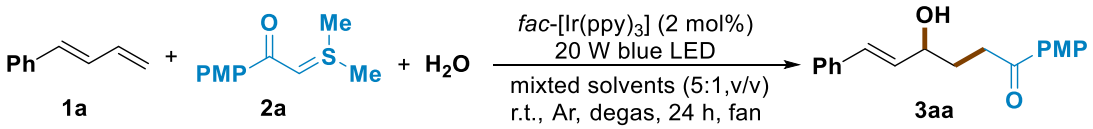
1a 2d 3ad

Entry	Additive (x eq.)	Yield (%)[b]
1	---	<10
2	**$Et_3N{\cdot}3HF$ (1.0)**	**90**
3	$Et_3N{\cdot}HCl$ (1.0)	14
4	NH_4Cl (1.0)	16
5	Py·HF (1.0)	34
6	CsF (1.0)	Trace
7	KF (1.0)	Trace
8	$Et_3N{\cdot}3HF$ (0.33)	12
9	$Et_3N{\cdot}3HF$ (0.5)	17
10	$Et_3N{\cdot}3HF$ (2.0)	28
11	$Et_3N{\cdot}3HF$ (3.0)	21
12	$Et_3N{\cdot}3HF$ (4.0)	48

[a]Reaction conditions: **1a** (0.2 mmol), **2d** (0.6 mmol), **H_2O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), additive (x eq.), CF_3CH_2OH (3.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

As shown in ***Table S8***, among all the additives tested, **$Et_3N{\cdot}3HF$ (1.0 eq.)** gave the best result in terms of yield (90% yield), and was thus selected for further studies.

Table S9. **Optimization of mixture solvents**



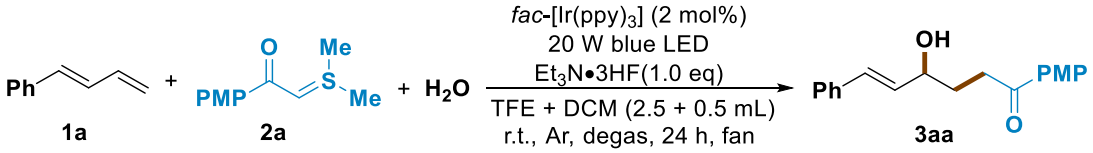
Entry	Solvent (5:1, v/v)	Yield (%)[b]
1	TFE + DCM	74
2	**TFE + DCM (with 1.0 eq. $Et_3N{\cdot}3HF$)**	**94 (90)[c]**
3	TFE + HFIP	62
4	TFE + EtOAc	14
5	TFE + THF	20
6	TFE + DMF	Trace
7	TFE + CH_3CN	19
8	TFE + Acetone	8

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **H_2O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), mixture solvent (3.0 mL), RT, 24 h, irradiation with 20 W blue LED under argon atmosphere. [b] Determined using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield.

As shown in ***Table S9***, among the tested, TFE: DCM (5:1, v/v) as the solvent, $Et_3N{\cdot}3HF$ (1.0 eq.) as the additive gave the best result in terms of yield (94% yield), and was thus selected for further studies.

3.2. Control Experiments

Table S10. **Control experiments[a]**



Entry	Variation	Yield (%)[b]	1a remained (%)[b]
1	**None**	**94**	**0**
2	No light	0	>95
3	No *fac*-[Ir(ppy)$_3$]	0	>95
4	No degas	0, messy	0
5	No Et$_3$N·3HF	74	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **H$_2$O** (15.0 eq.), *fac*-[Ir(ppy)$_3$] (2 mol%), Et$_3$N·3HF (1.0 eq.), CF_3CH_2OH (2.5 mL), DCM (0.5 mL), RT, 24 h, irradiation with 20 W blue LED.
[b]Determined using 1,3,5-trimethoxybenzene as an internal standard.

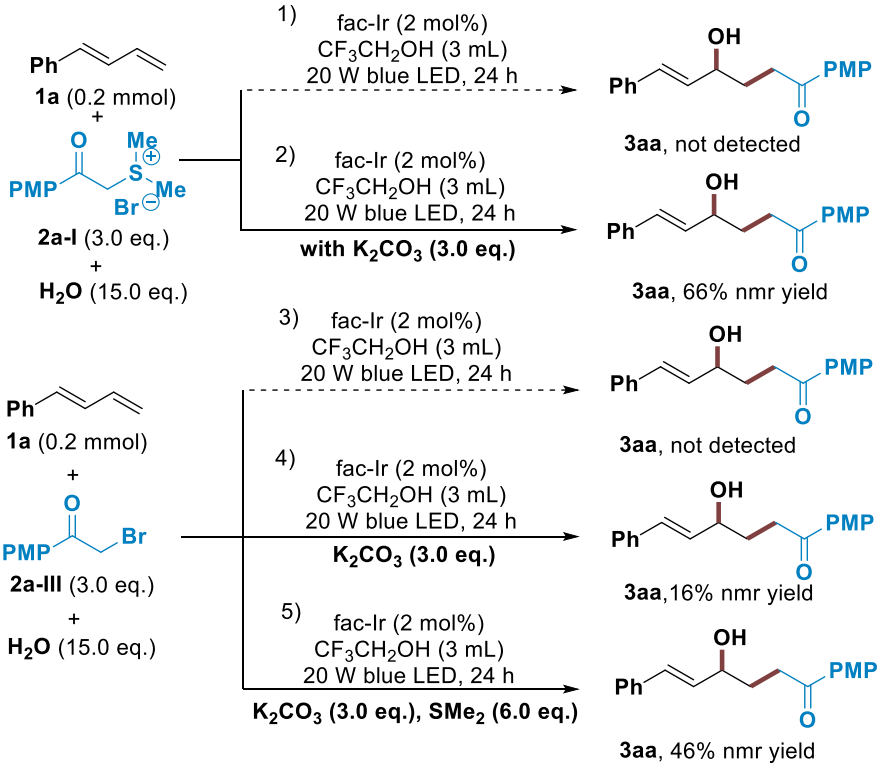
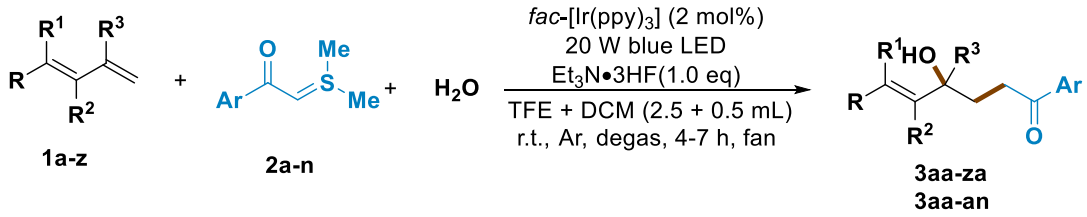


Figure S2. Control experiments with other radical precursors

These control experiments show that sulfonium salts **2a-I** and 2-bromo-4'-methoxyacetophen one **2a-III** cannot give better results in the current established catalytic system.

4. General Procedure and Spectral Data of Products

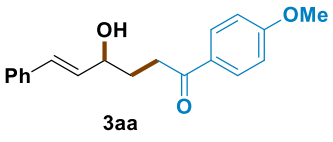
4.1 General Procedure for the Synthesis of Products



In a flame-dried 10.0 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with sulfur ylides **2a-n** (0.60 mmol, 3.0 eq.), *fac*-[Ir(ppy)$_3$] (2.6 mg, 0.004 mmol, 2 mol%) and **H$_2$O** (54 μL, 3 mmol, 15.0 eq.), followed by the addition of TFE (2.5 mL) and DCM (0.5 mL). The resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, diene **1a-z** (0.2 mmol, 1.0 eq.) and Et$_3$N·3HF (32 mg, 0.2 mmol, 1.0 eq.) were added. Then, the solution was stirred under irradiation of 20 W blue LEDs at room temperature about 4-7 h and monitored through TLC analysis. The crude product was purified by flash chromatography on silica gel directly to give the desired product.

4.2 Spectral Data of Products

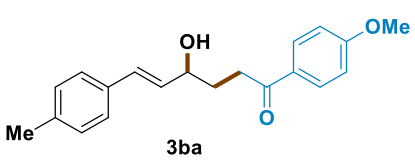
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-phenylhex-5-en-1-one



3aa

53.3 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.25), yellow solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 1H), 6.25 (dd, *J* = 16.0, 1H), 4.42 (q, *J* = 6.4 Hz, *J* = 12.8 Hz 1H), 3.86 (s, 3H), 3.12 (t, *J* = 6.8 Hz, 2H), 2.15-2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.5, 136.6, 132.0, 130.4, 130.3, 129.8, 128.5, 127.6, 126.4, 113.7, 72.1, 55.4, 34.0, 31.4. IR (in KBr): 2977, 2360, 1670, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{20}NaO_3$: 319.1305, found: 319.1303.

(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(p-tolyl)hex-5-en-1-one

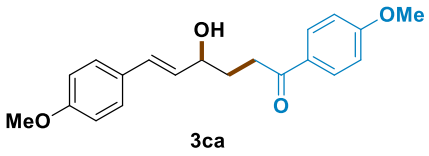


3ba

48.9 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.19 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.39 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.61 (s, 1H), 2.32 (s, 3H), 2.16 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.42, 137.4, 133.8, 130.9, 130.3, 130.2, 129.8, 129.2, 126.3, 113.6, 72.1, 55.4, 34.0, 31.4,

21.1. IR (in KBr): 2975, 2360, 1669, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1459, found: 333.1461.

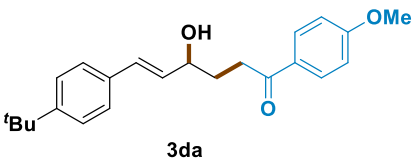
(*E*)-4-hydroxy-1,6-bis(4-methoxyphenyl)hex-5-en-1-one



3ca

45.2 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.37 (q, *J* = 6.4 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.65 (s, 1H), 2.08 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.4, 159.1, 130.3, 129.8, 129.8, 129.3, 127.6, 113.8, 113.6, 72.2, 55.3, 55.2, 34.0, 31.5. IR (in KBr): 2988, 2361, 1667, 1599, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{22}NaO_4$: 349.1419, found: 349.1410.

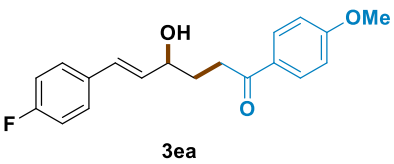
(*E*)-6-(4-(tert-butyl)phenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3da

55.0 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.29 (m, 4H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 15.6, 6.0 Hz, 1H), 4.40 (q, *J* = 6.0 Hz, 1H), 3.83 (s, 3H), 3.09 (t, *J* = 6.8 Hz, 2H), 2.60 (s, 1H), 2.14 – 1.98 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.4, 150.7, 133.8, 131.2, 130.4, 130.1, 129.9, 126.1, 125.40, 113.6, 72.1, 55.4, 34.5, 34.0, 31.4, 31.2. IR (in KBr): 2974, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{23}H_{28}NaO_3$: 375.1929, found: 375.1931.

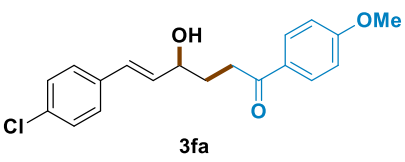
(*E*)-6-(4-fluorophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3ea

40.4 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.2), yellow solid, yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 9.2 Hz, 2H), 7.31 (dd, *J* = 8.4, 5.2 Hz, 2H), 6.98 (t, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.40 (q, *J* = 5.6 Hz, 1H), 3.85 (s, 3H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.75 (s, 1H), 2.16 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.21, 163.48, 160.99, 132.8 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 2.2 Hz), 130.36, 129.76, 129.00, 128.0 (d, *J* = 7.9 Hz), 115.4 (d, *J* = 21.4 Hz), 113.64, 72.0, 55.4, 34.0, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -114.4. IR (in KBr): 2973, 2360, 1669, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{19}FNaO_2$: 337.1202, found: 337.1210.

(*E*)-6-(4-chlorophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one

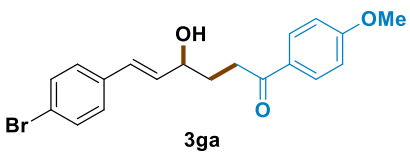


3fa

48.8 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.25), yellow solid, yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 9.2 Hz, 2H), 7.25 (s, 4H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.40 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.20 – 1.97 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.5, 135.1, 133.1, 132.7, 130.3, 129.7, 128.8, 128.6,

127.6, 113.6, 71.8, 71.8, 55.4, 34.0, 31.3. IR (in KBr): 2978, 2360, 1670, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{19}ClNaO_3$: 353.0913, found: 353.0915.

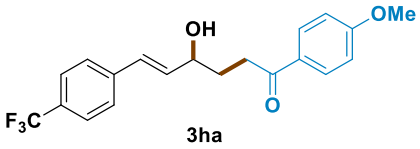
(*E*)-6-(4-bromophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3ga

74.8 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.25), yellow solid, yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 15.6, 5.6 Hz, 1H), 4.41 (q, *J* = 6.4 Hz, 1H), 3.86 (s, 4H), 3.12 (t, *J* = 6.8 Hz, 2H), 2.57 (s, 1H), 2.16 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.5, 135.6, 132.8, 131.6, 130.4, 129.8, 129.0, 128.0, 121.1, 113.7, 71.9, 55.4, 34.0, 31.3. IR (in KBr): 2970, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{19}BrNaO_3$: 399.0386, found: 399.0389.

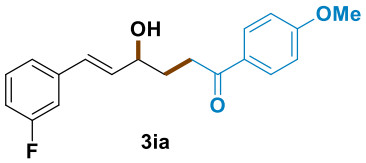
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(4-(trifluoromethyl)phenyl)hex-5-en-1-one



3ha

36.9 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.2), yellow solid, yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.28 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.39 (s, 1H), 3.80 (s, 3H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 1H), 2.11–1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.6, 140.2, 134.8, 130.4, 129.8, 128.7, 126.6, 125.5, 125.4, 113.7, 71.7, 55.4, 34.0, 31.2, 29.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.5. IR (in KBr): 2969, 2360, 1683, 1599, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{19}F_3NaO_3$: 387.1183, found: 387.1179.

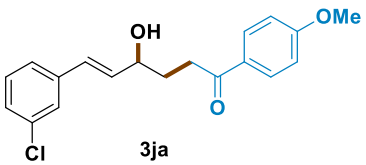
(*E*)-6-(3-fluorophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3ia

62.8 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.25), yellow solid, yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 10.0 Hz, 1H), 6.93 – 6.88 (m, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 15.6, 6.0 Hz, 1H), 4.41 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.11 (t, *J* = 6.8 Hz, 2H), 2.15 – 1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.48, 163.0 (d, *J* = 243.6 Hz), 139.0 (d, *J* = 7.6 Hz), 133.48, 130.35, 129.9 (d, *J* = 8.3H, 129.72, 128.9 (d, *J* = 2.6 Hz), 122.3, 114.2 (d, *J* = 21.6Hz), 113.63, 112.8, 71.6, 55.4, 33.9, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -113.52. IR (in KBr): 2983, 2360, 1680, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{19}FNaO_3$: 337.1208, found: 337.1210.

(*E*)-6-(3-chlorophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one

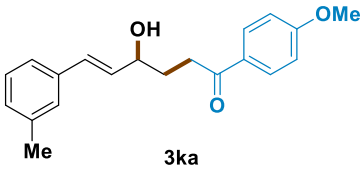


3ja

66.0 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.25), white solid, yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.32 (s, 1H), 7.23 – 7.16 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.41 (q, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 3.11 (t, *J* = 6.8 Hz, 2H), 2.87 (s, 1H), 2.14 –

1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.5, 138.5, 134.4, 133.6, 130.4, 129.7, 129.7, 128.7, 127.4, 126.3, 124.6, 113.7, 71.7, 55.4, 33.9, 31.2. IR (in KBr): 2988, 2360, 1669, 1597, 1049 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{19}ClNaO_3$: 353.0906, found: 353.0915.

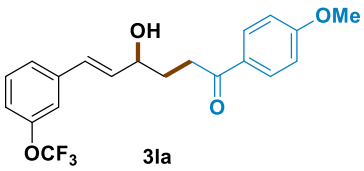
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(m-tolyl)hex-5-en-1-one



3ka

51.1 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.2), yellow solid, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.20 – 7.14 (m, 3H), 7.04 (d, *J* = 6.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.22 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.39 (q, *J* = 6.0 Hz, 1H), 3.83 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.11 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.4, 138.0, 136.5, 131.8, 130.3, 130.3, 129.8, 128.4, 128.3, 127.1, 123.6, 113.6, 72.0, 55.4, 34.0, 31.4, 21.3. IR (in KBr): 2987, 2360, 1683, 1599, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1455, found: 333.1461.

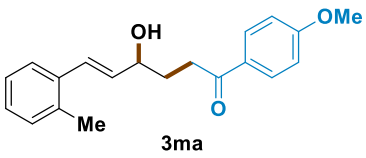
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(3-(trifluoromethoxy)phenyl)hex-5-en-1-one



3la

66.5 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.2), white solid, yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.18 (s, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.27 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.43 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.95 (s, 1H), 2.17 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.3, 163.5, 149.5, 149.5, 138.9, 133.9, 130.4, 129.8, 129.7, 128.6, 124.8, 118.6, 113.7,71.6, 55.4, 34.0, 31.2, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -57.70. IR (in KBr): 2973, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{19}F_3NaO_3$: 403.1129, found: 403.1128.

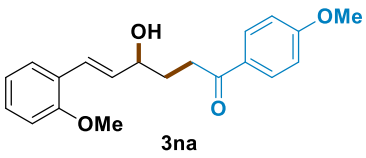
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(o-tolyl)hex-5-en-1-one



3ma

45.6 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.41 (m, 1H), 7.18 – 7.10 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.43 (q, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 3.12 (t, *J* = 6.8 Hz, 2H), 2.31 (s, 3H), 2.15 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.4, 135.7, 135.4, 133.4, 130.3, 130.2, 129.8, 128.0, 127.4, 126.0, 125.6, 113.7, 72.2, 55.4, 34.0, 31.4, 19.7. IR (in KBr): 2989, 2360, 1680, 1599, 1056 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1457, found: 333.1461.

(*E*)-4-hydroxy-6-(2-methoxyphenyl)-1-(4-methoxyphenyl)hex-5-en-1-one

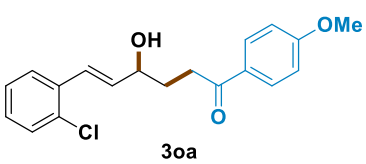


3na

50.8 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.98 – 6.93 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.31 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.45 (q, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.15 (t, *J* = 7.2 Hz, 2H),

2.61 (s, 1H), 2.19 – 2.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.5, 136.6, 135.2, 132.8, 130.4, 129.8, 129.0, 128.8, 127.4, 127.1, 123.6, 113.7, 72.3, 55.4, 34.0, 31.1. IR (in KBr): 2978, 2360, 1678, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_4$: 349.1410, found: 349.1411.

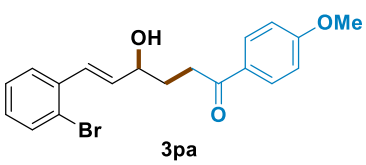
(*E*)-6-(2-chlorophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3oa

46.2 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.99 (d, *J* = 15.6 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.24 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.47 (q, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 1H), 2.19 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.5, 135.0, 134.8, 133.1, 130.4, 129.9, 129.7, 128.6, 126.9, 126.8, 126.5, 113.7, 72.1, 55.5, 34.0, 31.2. IR (in KBr): 2978, 2360, 1680, 1600, 1053 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{19}ClNaO_3$: 353.0915, found:353.0904.

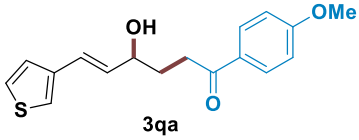
(*E*)-6-(2-bromophenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3pa

50.8 mg (petroleum ether:ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 12.4, 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.95 – 6.90 (m, 3H), 6.19 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.46 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.13 (t, *J* = 6.8 Hz, 2H), 2.73 (s, 1H), 2.17 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.5, 136.6, 135.2, 132.8, 130.4, 129.8, 129.0, 128.8, 127.4, 127.1, 123.6, 113.7, 71.9, 55.4, 34.0, 31.2. IR (in KBr): 2988, 2360, 1678, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{19}BrNaO_3$: 397.0410, found: 397.0399.

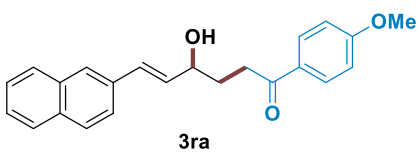
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(thiophen-3-yl)hex-5-en-1-one



3qa

44.7 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.25), yellow solid, yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.25 (dd, *J* = 5.6, 3.6 Hz, 1H), 7.19 (d, *J* = 5.2 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.37 (q, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.12 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.4, 139.2, 131.9, 130.4, 129.8, 126.0, 125.0, 124.5, 122.2, 113.6, 71.9, 55.4, 34.0, 31.4. IR (in KBr): 2987, 2360, 1667, 1599, 1054 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{18}NaO_3S$: 325.0858, found: 325.0869.

(*E*)-4-hydroxy-1-(4-methoxyphenyl)-6-(naphthalen-2-yl)hex-5-en-1-one

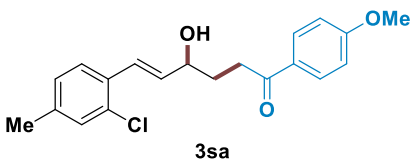


3ra

45.2 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), white solid, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J* = 8.8 Hz, 2H), 7.78 – 7.74 (m, 3H), 7.68 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.47 – 7.40 (m, 3H), , 6.88 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.36 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.46 (q, *J* = 6.0

Hz, 1H), 3.81 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.69 (s, 1H), 2.18 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 163.4, 134.0, 133.5, 132.9, 132.4, 130.4, 130.3, 129.8, 128.1, 127.9, 127.6, 126.4, 126.2, 125.8, 123.5, 113.6, 55.4, 34.0, 31.4. IR (in KBr): 2987, 2360, 1683, 1600, 1078 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{23}H_{22}NaO_3$: 369.1461, found: 369.1461.

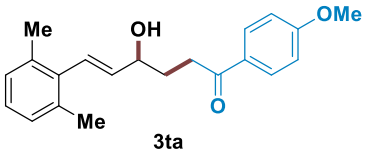
(*E*)-6-(2-chloro-4-methylphenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3sa

59.1 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.2), yellow solid, yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 3H), 6.23 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.48 (q, *J* = 6.0 Hz, 1H), 3.89 (s, 4H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.76 (s, 1H), 2.34 (s, 4H), 2.20 – 2.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.4, 138.8, 133.9, 132.7, 131.8, 130.3, 129.9, 129.8, 127.7, 126.6, 126.3, 113.6, 113.6, 72.1, 55.4, 34.0, 31.3, 20.8. IR (in KBr): 2974, 2360, 1670, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{21}ClNaO_3$: 367.1061, found: 367.1071.

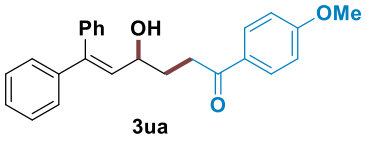
(*E*)-6-(2,6-dimethylphenyl)-4-hydroxy-1-(4-methoxyphenyl)hex-5-en-1-one



3ta

42.8 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 8.8 Hz, 2H), 7.06 – 7.00 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 16.4 Hz, 1H), 5.77 (q, dd, *J* = 16.4, 6.4 Hz, 1H), 4.45 (q, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.48 (s, 1H), 2.28 (s, 6H), 2.16 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 163.5, 137.3, 136.4, 135.8, 130.3, 129.8, 127.9, 127.7, 126.6, 113.7, 72.3, 55.4, 34.1, 31.4, 21.0. IR (in KBr): 2988, 2360, 1674, 1699, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{21}H_{24}NaO_3$: 347.1612, found: 347.1618.

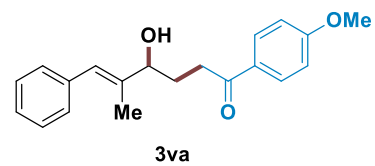
4-hydroxy-1-(4-methoxyphenyl)-6,6-diphenylhex-5-en-1-one



3ua

40.1mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.2), yellow solid, yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.27 – 7.22 (m, 5H), 7.19 – 7.17 (m, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 6.10 (d, *J* = 9.2 Hz, 1H), 4.30 – 4.24 (m, 1H), 3.84 (s, 3H), 3.10 – 2.94 (m, 2H), 2.34 (s, 1H), 2.10 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9, 163.4, 143.5, 141.6, 139.2, 130.8, 130.3, 129.8, 129.6,128.2, 128.1, 127.6, 127.4, 127.4, 113.61, 69.1, 55.4, 34.3, 31.8. IR (in KBr): 2988, 2360, 1670, 1599, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{25}H_{24}NaO_3$: 395.1615, found: 395.1619.

(*E*)-4-hydroxy-1-(4-methoxyphenyl)-5-methyl-6-phenylhex-5-en-1-one

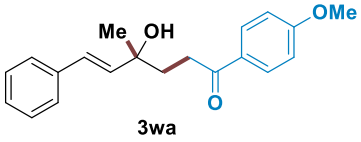


3va

38.9 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.54 (s, 1H), 4.28 (t, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 3.13 – 3.09 (m, 2H), 2.38 (s, 1H), 2.14 – 2.06 (m, 2H), 1.90 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$) δ (ppm) 199.2, 163.5, 140.1, 130.4, 128.9, 128.1, 126.4, 125.4, 113.7, 55.4, 34.4, 29.4, 13.8. IR (in KBr):2360, 1683, 1600, 1060 cm^{-1}. HRMS(ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1461, found: 333.1460.

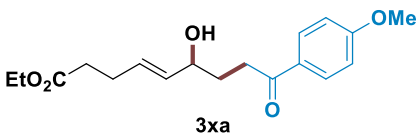
(*E*)-4-hydroxy-1-(4-methoxyphenyl)-4-methyl-6-phenylhex-5-en-1-one



3wa

56.4 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.23), yellow solid, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.4 Hz, 1H), 3.82 (s, 3H), 3.07 (t, *J* = 7.6 Hz, 2H), 2,73 (s, 1H), 2.16 – 2.01 (m, 2H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.7, 163.4, 136.8, 135.9, 130.4, 129.8, 128.4, 127.6, 127.3, 126.3, 113.6, 72.6, 55.3, 36.2, 33.1, 29.2. IR (in KBr): 2989, 2360, 1680, 1600, 1044 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{22}NaO_3$: 333.1454, found: 333.1461.

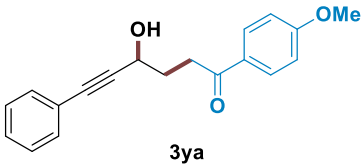
Ethyl (*E*)-6-hydroxy-9-(4-methoxyphenyl)-9-oxonon-4-enoate



3xa

40.2 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.4), colorless oil, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.72 – 5.65 (m, 1H), 5.55 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.17 (q, *J* = 6.0 Hz, 1H), 4.11 (q, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 4H), 2.01 – 1.89 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 173.0, 163.4, 133.7, 130.3, 129.8, 129.5, 113.6, 71.8, 60.3, 55.4, 34.0, 33.7, 31.3, 27.3, 14.1. IR (in KBr):1733,1669, 1600, 1170 cm^{-1}. HRMS(ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{24}NaO_5$: 343.1509, found: 343.1516.

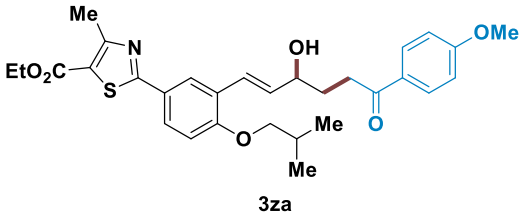
4-hydroxy-1-(4-methoxyphenyl)-6-phenylhex-5-yn-1-one



3ya

29.1 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.33), white solid, yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.31 – 7.26 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.78 (q, *J* = 5.6 Hz, 1H), 3.85 (s, 3H), 3.27 – 3.22 (m, 2H), 2.28 – 72.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.8, 163.5, 131.6, 130.4, 129.7, 128.4, 128.2, 122.5, 113.7, 89.6, 85.1, 62.1, 55.4, 33.9, 31.9. IR (in KBr): 2360, 1683, 1060 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{18}NaO_3$: 317.1146, found: 317.1148.

Ethyl(*E*)-2-(3-(3-hydroxy-6-(4-methoxyphenyl)-6-oxohex-1-en-1-yl)-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate

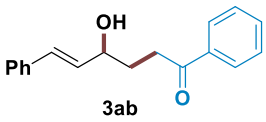


3za

76.4 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.35), yellow solid, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 – 7.95 (m, 3H), 7.78 (d, *J* = 10.0 Hz, 1H), 6.93 – 6.84 (m, 4H), 6.41 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.45 (q, *J* = 6.4 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.78 (d, *J* = 6.4 Hz, 2H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.76 (s, 3H), 2.18 – 2.03 (m, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 169.8, 163.4, 162.3, 160.9, 158.5, 134.0, 130.3, 129.9, 127.2, 126.3, 125.5, 125.3, 124.4, 120.7, 113.6, 111.8, 74.8, 72.4, 61.1, 55.4, 34.1, 31.4, 28.2, 19.3, 17.5, 14.3. IR (in KBr):

2988, 2360, 1678, 1599, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{30}H_{35}NNaO_6S$: 560.2074, found: 560.2077.

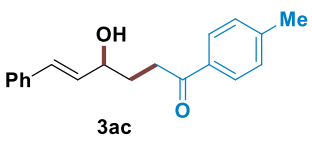
(*E*)-4-hydroxy-1,6-diphenylhex-5-en-1-one



3ab

34.0 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.4), yellow solid, yield: 68%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 – 7.95 (m, 2H), 7.56 – 7.52 (m, 1H), 7.45 – 7.41 (m, 2H), 7.37 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.42 (q, *J* = 5.6 Hz, 1H), 3.15 (t, *J* = 7.2Hz, 2H), 2.51 (s, 1H), 2.17 – 1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.6, 136.7, 136.5, 133.1, 131.9, 130.4, 128.5, 128.0, 127.6, 126.4, 72.0, 34.4, 31.2. IR (in KBr): 2974, 2360, 1680, 1605, 1054 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{18}NaO_2$: 289.1199, found: 289.1193.

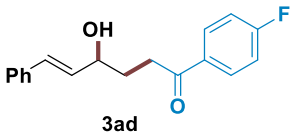
(*E*)-4-hydroxy-6-phenyl-1-(p-tolyl)hex-5-en-1-one



3ac

46.4 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.4), white solid, yield: 83%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 8.4 Hz, 2H), 7.36(d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.21 (m, 3H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.3 Hz, 1H), 4.41 (q, *J* = 6.2 Hz, 1H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.50 (s, 1H), 2.39 (s, 3H), 2.14 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.2, 143.9, 136.6, 134.3, 132.0, 130.3, 129.2, 128.5, 128.2, 127.6, 126.4, 72.0, 34.2, 31.3, 21.6. IR (in KBr): 2974, 2360, 1683, 1607, 1048 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{20}NaO_2$: 303.1356, found: 3030.1349.

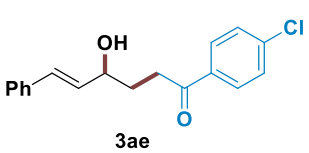
(*E*)-1-(4-fluorophenyl)-4-hydroxy-6-phenylhex-5-en-1-one



3ad

52.3 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.33), yellow solid, yield: 92%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 – 8.02 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.15 (t, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.47 (q, *J* = 6.0 Hz, 1H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 1H), 2.32 – 2.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9, 165.7 (d, *J* = 253.1 Hz), 136.5, 133.2, 133.2, 131.8, 130.7 (d, *J* = 9.2 Hz), 130.4, 128.5, 127.7, 126.4, 115.7 (d, *J* = 21.7 Hz), 71.9, 34.2, 31.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -105.22. IR (in KBr): 2974, 2360, 1667, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{17}FNaO_2$: 307.1105, found: 307.1106.

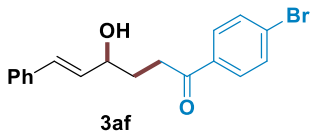
(*E*)-1-(4-chlorophenyl)-4-hydroxy-6-phenylhex-5-en-1-one



3ae

45.0 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.33), yellow solid, yield: 75%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.21 (m, 7H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.23 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 1H), 2.14 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 139.46, 136.4, 135.0, 131.7, 130.4, 129.5, 128.8, 128.5, 127.7, 126.4, 71.9, 34.3, 31.1. IR (in KBr): 2975, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{17}ClNaO_2$:323.0809, found: 323.0789.

(*E*)-1-(4-bromophenyl)-4-hydroxy-6-phenylhex-5-en-1-one

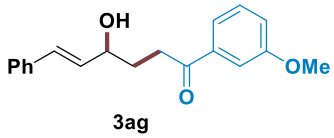


3af

43.8 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.5), yellow solid, yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.23 (dd, *J* = 16.0 Hz, 6.4 Hz, 1H), 4.40 (q, *J* = 6.0 Hz, 1H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 1H), 2.15 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.4, 136.4, 135.5, 131.8, 131.7, 130.5, 129.6, 128.5, 128.2, 127.7, 126.4, 71.9, 34.2, 31.1. IR (in KBr): 2973, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}BrNaO_2$: 369.0284, found: 369.0288.

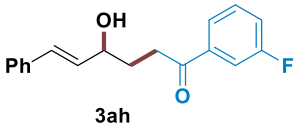
(*E*)-4-hydroxy-1-(3-methoxyphenyl)-6-phenylhex-5-en-1-one

46.4 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.48 (m, 1H), 7.36 – 7.33 (m, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.09 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.40 (q, *J* = 5.6 Hz, 1H), 3.82 (s, 3H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.53 (s, 1H), 2.13 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.3, 159.7, 138.1, 136.5, 131.8, 130.3, 129.5, 128.5, 127.6, 126.4, 120.7, 119.5, 112.2, 71.9, 55.3, 34.5, 31.2. IR (in KBr): 2971, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M +Na]$^+$ calcd for $C_{19}H_{20}NaO_3$: 319.1305, found: 319.1296.



3ag

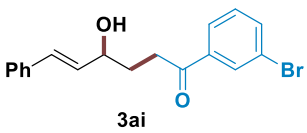
(*E*)-1-(3-fluorophenyl)-4-hydroxy-6-phenylhex-5-en-1-one



3ah

48.0 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.22 (m, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.43 (q, *J* = 6.0 Hz, 1H), 3.14 (t, *J* = 6.8 Hz, 2H), 2.18 – 2.01 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.11, 162.8 (d, *J* = 246.2 Hz), 138.9 (d, *J* = 6.3 Hz), 136.42, 131.71, 130.56, 130.2 (d, *J* = 7.8 Hz), 128.57, 127.74, 126.45, 123.8 (d, *J* = 3.1 Hz), 120.1 (d, *J* = 21.3 Hz), 114.8 (d, *J* = 22.0 Hz), 72.0, 34.5, 31.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -111.84. IR (in KBr): 2974, 2360, 1677, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}FNaO_2$: 307.1105, found: 307.1104.

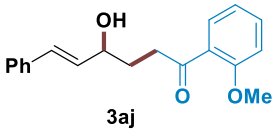
(*E*)-1-(3-bromophenyl)-4-hydroxy-6-phenylhex-5-en-1-one



3ai

34.5 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.3), yellow solid, yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.30 (m, 5H), 7.26 – 7.22 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.42 (q, *J* = 5.2 Hz, 1H), 3.13 (t, *J* = 6.8 Hz, 2H), 2.18 – 2.00 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 138.5, 136.4, 135.9, 131.7, 131.1, 130.6, 130.1, 128.6, 127.7, 126.6, 126.4, 122.9, 71.9, 34.4, 31.0. IR (in KBr): 2973, 2360, 1683, 1597, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}BrNaO_2$: 369.0284, found:369.0285.

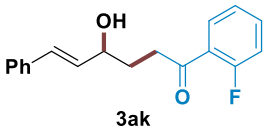
(*E*)-4-hydroxy-1-(2-methoxyphenyl)-6-phenylhex-5-en-1-one



3aj

43.2 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.33), yellow solid, yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 – 7.67 (m, 1H), 7.47 – 7.42 (m, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.00 – 6.93 (m, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 1H), 2.10 – 1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.0, 158.4, 136.7, 133.4, 132.2, 130.2, 130.0, 128.5, 128.2, 127.5, 126.4, 120.6, 111.5, 72.2, 55.4, 39.7, 31.6. IR (in KBr): 2971, 2360, 1688, 1600, 1055 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{20}NaO_3$: 319.1305, found:319.1307.

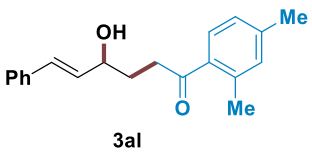
(*E*)-1-(2-fluorophenyl)-4-hydroxy-6-phenylhex-5-en-1-one



3ak

47.2 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.5), yellow solid, yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 –7.81 (m, 1H), 7.51 –7.46 (m, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.11 (dd, *J* = 11.2, 8.4 Hz, 1H),6.59 (d, *J* = 15.6 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.4 Hz, 1H),4.40 (q, *J* = 6.4 Hz, 1H), 3.17 –3,13 (m, 2H), 2.36 (s, 1H), 2.13 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9 (d, *J* = 4.0 Hz), 161.8 (d, *J* = 253.1 Hz), 136.5, 134.5 (d, *J* = 9.0 Hz), 131.87, 130.5 (d, *J* = 2.6 Hz), 130.3, 128.48, 127.58, 126.41, 125.6 (d, *J* = 12.9 Hz), 124.3 (d, *J* = 3.4 Hz), 116.6 (d, *J* = 23.7 Hz), 72.0, 39.4 (d, *J* = 7.4 Hz), 31.0 (d, *J* = 1.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -109.02. IR (in KBr): 2970, 2360, 1678, 1599, 1053 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}FNaO_2$: 307.1105, found: 307.1106.

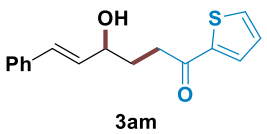
(*E*)-1-(2,4-dimethylphenyl)-4-hydroxy-6-phenylhex-5-en-1-one



3al

46.7 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.6), yellow solid, yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.39 (q, *J* = 6.0 Hz, 1H), 3.06 (t, *J* = 6.8 Hz, 2H), 2.47 (s, 3H), 2.33 (s, 3H), 2.07 – 1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.9, 141.9, 138.6, 136.6, 134.7, 132.8, 131.9, 130.2, 129.1, 128.5, 127.6, 126.40, 126.2, 72.0, 37.0, 31.4, 21.5, 21.5. IR (in KBr): 2976, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_2$: 317.1512, found: 317.1508.

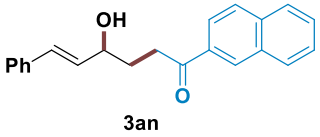
(*E*)-4-hydroxy-6-phenyl-1-(thiophen-2-yl)hex-5-en-1-one



3am

44.3 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.33), yellow solid, yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.54 (d, *J* = 4.8 Hz, 1H), 7.36 – 7.21 (m, 6H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 3.06 (t, *J* = 6.8 Hz, 2H), 2.53 (s, 1H), 2.15 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.9, 142.0, 136.5, 132.2, 131.8, 130.3, 128.5, 127.6, 126.9, 126.4, 126.3, 71.9, 35.6, 31.1. 2974, 2360, 1683, 1600, 1050 cm^{-1}. IR (in KBr): 2987, 2359, 1668, 1600, 1051 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{16}NaO_2S$: 295.0763, found: 295.0763.

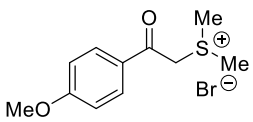
(*E*)-4-hydroxy-1-(naphthalen-2-yl)-6-phenylhex-5-en-1-one



3an

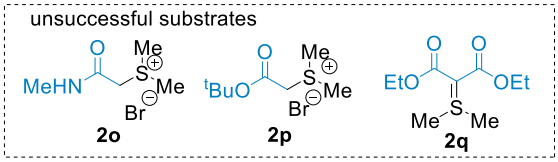
54.6 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.4), white solid, yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.46 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.59 – 7.49 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.27 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.45 (q, *J* = 5.6 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.54 (s, 1H), 2.21 – 2.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.4, 136.5, 135.5, 134.0, 132.4, 131.9, 130.4, 129.8, 129.5, 128.5, 128.4, 128.3, 127.7, 127.6, 126.7, 126.4, 123.8, 72.0, 34.4, 31.3. IR (in KBr): 2974, 2360, 1683, 1600, 1050 cm^{-1}. HRMS (ESI): m/z [M +Na]$^+$ calcd for $C_{22}H_{20}NaO_2$: 339.1356, found: 339.1347.

Sulfonium salts 2a-I



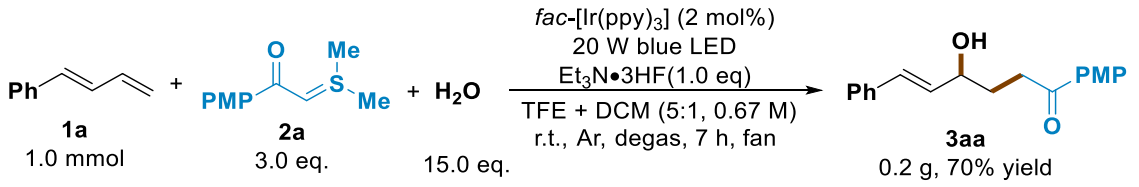
2a-I

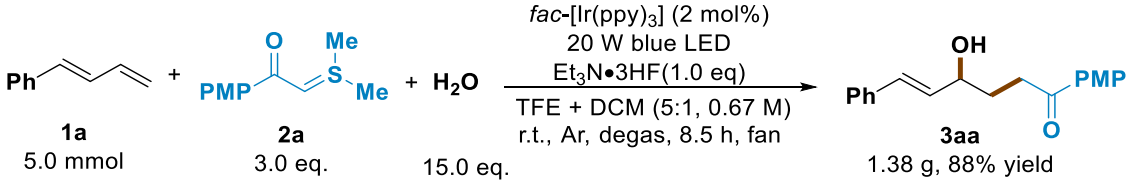
^{1}H NMR (400 MHz, D_2O) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.99 (s, 6H). ^{13}C NMR (101 MHz, D_2O) δ 190.2, 165.0, 131.4, 126.4, 114.5, 55.7, 24.8.



5. Gram Scale Reaction and Synthetic Utility

5.1 Gram Scale Reaction





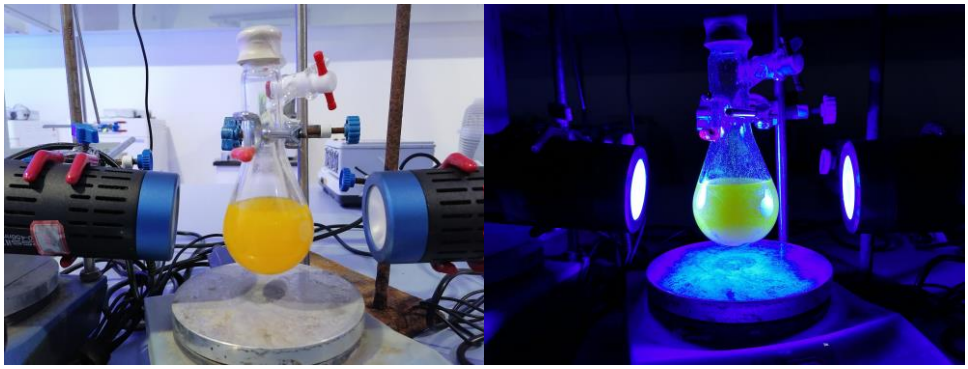
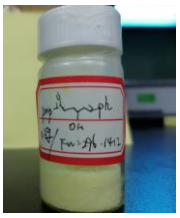


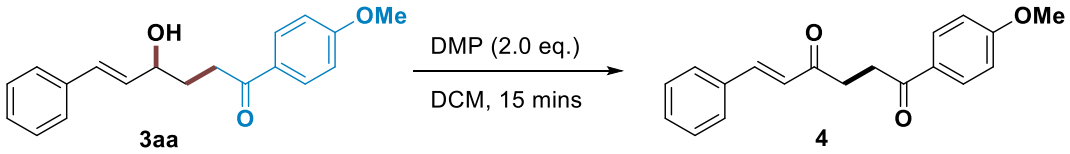
Figure S3. Set-up of the reaction (5 mmol scale)



5 mmol scale: In a flame-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with sulfur ylide **2a** (3.15 g, 15 mmol, 3.0 eq.), *fac*-[Ir(ppy)$_3$] (65 mg, 0.004 mmol, 2 mol%) and **H$_2$O** (1.35 mL, 75 mmol, 15.0 eq.) followed by the addition of TFE (62.5 mL) and DCM (12.5 mL). The resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, diene **1a** (0.65g, 5 mmol, 1.0 eq.) and Et$_3$N·3HF (0.8 g, 5 mmol, 1.0 eq.) were added. Then, the solution was stirred under irradiation of 20 W blue LEDs at room temperature about 8.5 h and monitored through TLC analysis. The crude product was purified by flash chromatography on silica gel directly to give the desired product.

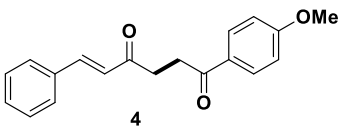
5.2 Synthetic Utility

Procedure for the Synthesis of 4



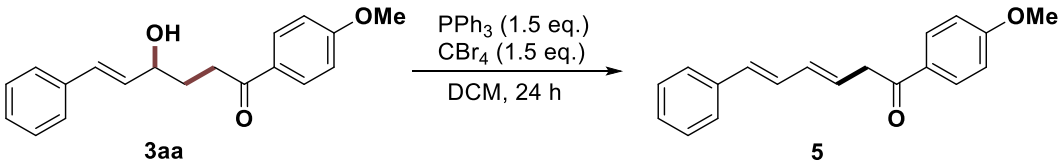
DMP (0.2 mmol, 82.8 mg, 2.0 eq.) was added to a solution of compound **3aa** (0.1 mmol, 29.6 mg) in DCM (2.0 mL) under argon atmosphere. The reaction flask was sealed and the mixture were stirred at room temperature for 15 minutes followed by the TLC monitoring. After the reaction was complete, the volatiles were removed under reduced pressure. The pure product was purified by flash column chromatography on silica with an eluent (petroleum ether/ ethyl acetate 7:1 v/v) to afford the pure product **4** as a white solid (23.5 mg, 80%).

(*E*)-1-(4-methoxyphenyl)-6-phenylhex-5-ene-1,4-dione



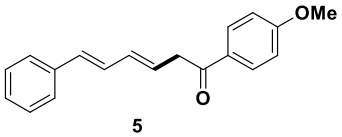
23.5 mg (petroleum ether: ethyl acetate = 3:1 R_f = 0.5), white solid, yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 16.4 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.40 – 7.39 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 16.4 Hz, 1H), 3.87 (s, 3H), 3.35 (t, *J* = 6.4 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.8, 197.1, 163.4, 142.7, 134.4, 130.4, 130.3, 129.7, 128.9, 128.25, 126.1, 113.6, 55.4, 34.4, 32.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{19}O_3$: 295.1329, found: 219.1327.

Procedure for the Synthesis of 5



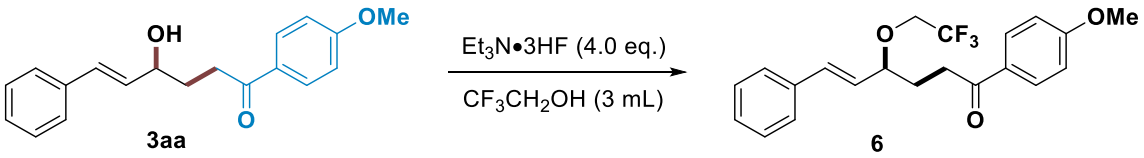
PPh_3 (0.3 mmol, 78.7 mg, 1.5 eq.), CBr_4 (0.3 mmol, 99.5 mg, 1.5 eq.) were added to a solution compound **3aa** (0.1 mmol, 29.6 mg) in DCM (2.0 mL) under argon atmosphere. The suspension was stirred at room temperature for 24 h. After the reaction was complete, the volatiles were removed under reduced pressure. The pure product was purified by flash column chromatography on silica with an eluent (petroleum ether/ ethyl acetate 8:1 v/v) to afford the pure product **5** as a colorless oil (40.0 mg, 72%).

(3*E*,5*E*)-1-(4-methoxyphenyl)-6-phenylhexa-3,5-dien-1-one



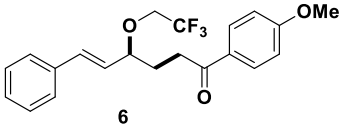
40.0 mg, colorless oil, yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.8, 2H), 6.86 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.55 (d, *J* = 15.6, 1H), 6.43 – 6.37 (m, 1H), 6.15 – 6.08 (m, 1H), 3.91 (s, 3H), 3.85 (d, *J* = 6.8Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.3, 163.5, 137.2, 133.9, 131.7, 130.6, 129.5, 128.6, 128.5, 127.4, 126.9, 126.2, 113.7, 55.4, 42.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{19}O_2$: 279.1380, found: 279.1372.

Procedure for the Synthesis of 6



$Et_3N{\cdot}3HF$ (0.4 mmol, 64.5 mg, 4.0 eq.) was added to a solution compound **3aa** (0.1 mmol, 29.6 mg) in CF_3CH_2OH (3.0 mL) under argon atmosphere. The suspension was stirred at room temperature for 18 h. After the reaction was complete, the volatiles were removed under reduced pressure. The pure product was purified by flash column chromatography on silica with an eluent (petroleum ether/ ethyl acetate 5:1 v/v) to afford the pure product **6** as a white solid (34.0 mg, 90%).

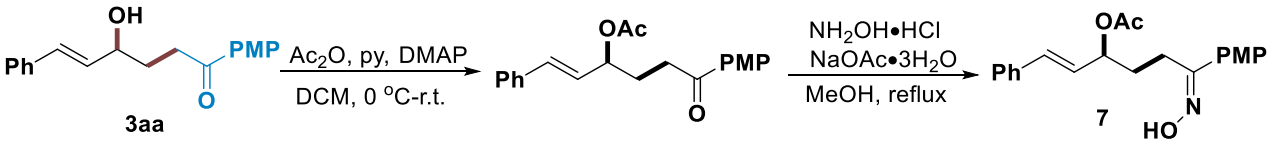
(*E*)-1-(4-methoxyphenyl)-6-phenyl-4-(2,2,2-trifluoroethoxy) hex-5-en-1-one



34.0 mg, white solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 9.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.07 (dd, *J* = 16.0, 8.0 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 3.91 – 3.85 (m, 4H), 3.78 – 3.69 (m, 1H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.11 (q, *J* = 6.98 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.1, 163.4, 135.8, 133.8, 130.2, 129.9, 128.6, 128.2, 128.0, 126.6, 125.5,

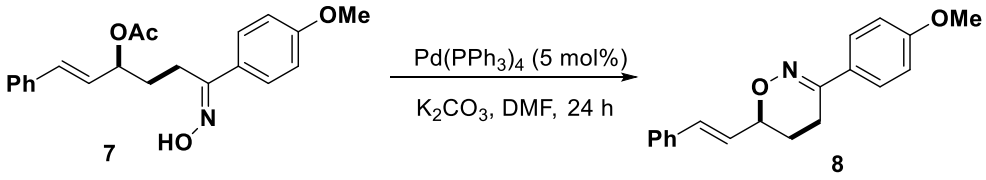
122.8, 117.2, 113.6, 81.7, 65.5 (q, J = 33.7), 55.4, 33.4, 29.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -74.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{21}H_{21}F_3NaO_3$: 401.1335, found: 401.1330.

Procedure for the Synthesis of 7



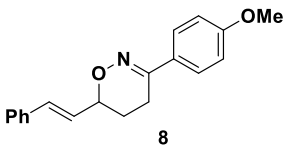
Pyridine (0.9 mmol, 71.2 mg, 1.5 eq.), acetic anhydride (1.2 mmol, 122.5 mg, 2.0 eq.) and DMAP (7.3 mg, 0.06 mmol, 0.1 eq.) were added to a solution compound **3aa** (0.6 mmol, 177 mg) in DCM (4 mL) under argon atmosphere at 0 °C and then stirred for 2 h at room temperature. After completion of the reaction, it was quenched 2 N HCl (5 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 15 mL). The combined organic layers were thoroughly washed with brine (10 mL), dried (Na_2SO_4) and concentrated. The residue was used for next reaction without further purification.

$NaOAc{\cdot}3H_2O$ (3.0 mmol, 408 mg, 5.0 eq.) and $NH_2OH{\cdot}HCl$ (1.8 mmol, 125.1 mg, 3.0 eq.) were added to the above compound in MeOH (4 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C for 12 h. Then, the solvent was evaporated and the residue dissolved in EtOAc (10 mL) and water (5 mL). The organic layer was separated and washed with brine, dried (Na_2SO_4) and concentrated. The pure product was purified by flash column chromatography on silica with an eluent (petroleum ether/ ethyl acetate 3:1 v/v) to afford the desired product **7** as a colorless oil (114.3 mg, 20%).



To the substrate **7** (0.2 mmol) was added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%), K_2CO_3 (110.6 mg, 0.8 mmol, 4.0 eq.) and anhydrous DMF (1.5 mL) under argon atmosphere. The reaction mixture was stirred for 24 h and then concentrated. The residue was purified by silica gel column chromatography with an eluent (petroleum ether/ ethyl acetate 4:1 v/v) to give the corresponding product **8** as a yellow solid (39.8 mg, 68%).

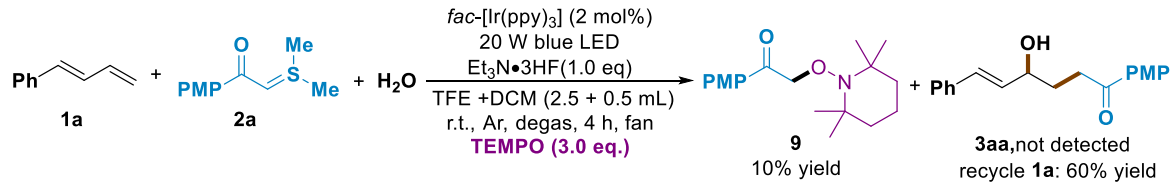
(*E*)-3-(4-methoxyphenyl)-6-styryl-5,6-dihydro-4H-1,2-oxazine



39.8 mg, yellow solid, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.24 – 7.27 (m, 1H), 6.91 (d, J = 8.8Hz, 2H), 6.74 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 6.0 Hz, 1H), 4.45 – 4.50 (m, 1H), 3.82 (s, 3H), 2.64 – 2.70 (m, 2H), 2.15 – 2.25 (m, 1H), 2.07 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.6, 153.9, 132.8, 128.6, 128.3, 127.9, 127.0, 126.7, 126.6, 113.7, 75.2, 55.3, 24.7, 21.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{20}NO_2$: 294.1489, found: 294.1490.

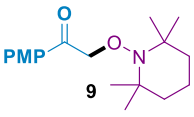
6. The Mechanism Studies

6.1 TEMPO Trapping Experiment



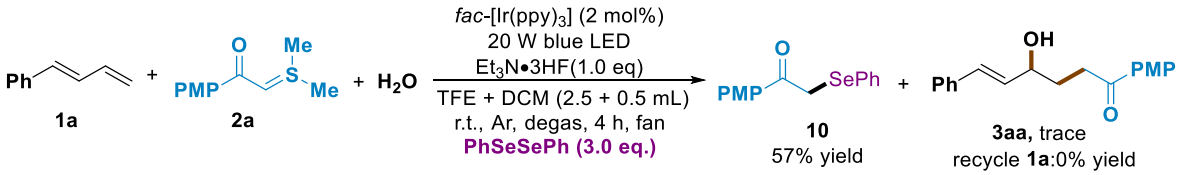
In a flame-dried 10.0 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with sulfur ylide **2a** (126 mg, 0.60 mmol, 3.0 eq.), *fac*-[Ir(ppy)$_3$] (2.6 mg, 0.004 mmol, 2 mol%), TEMPO (93.8 mg, 0.6 mmol, 3.0 eq.) and **H$_2$O** (54 μL, 3 mmol, 15.0 eq.) followed by the addition of TFE (2.5 mL) and DCM (0.5 mL). The resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, diene **1a** (26 mg, 0.2 mmol, 1.0 eq.) and Et$_3$N·3HF (32 mg, 0.2 mmol, 1.0 eq.) were added. Then, the solution was stirred under irradiation of 20 W blue LEDs at room temperature about 4 h and monitored through TLC analysis. The crude product was purified by flash chromatography on silica gel directly to give the desired product in 10% yield as a white solid.

1-(4-methoxyphenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one



18.8 mg (petroleum ether: ethyl acetate = 5:1 R_f = 0.5), white solid, yield: 10%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.94 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 2H), 3.87 (s, 3H), 1.50 – 1.44 (m, 4H), 1.38 – 1.30 (m, 1H), 1.22 (d, *J* = 1.6 Hz, 1H), 1.17 (s, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.4, 163.5, 130.3, 128.4, 113.7, 81.2, 60.1, 55.4, 39.7, 32.8, 20.2, 17.0. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{18}H_{28}NO_3$: 306.2064, found: 306.2057.

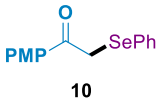
6.2 PhSeSePh Trapping Experiment



In a flame-dried 10.0 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with sulfur ylide **2a** (126 mg, 0.60 mmol, 3.0 eq.), *fac*-[Ir(ppy)$_3$] (2.6 mg, 0.004 mmol, 2 mol%), PhSeSePh (187.3 mg, 0.6 mmol, 3.0 eq.) and **H$_2$O** (54 μL, 3 mmol, 15.0 eq.) followed by the addition of TFE (2.5 mL) and DCM (0.5 mL). The resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, diene **1a** (26 mg, 0.2 mmol, 1.0 eq.) and Et$_3$N·3HF (32 mg, 0.2 mmol, 1.0 eq.) were added. Then, the solution was stirred under irradiation of 20 W blue LEDs at room temperature about 4 h and monitored through TLC

analysis. The crude product was purified by flash chromatography on silica gel directly to give the desired product in 57% yield as a colorless oil.

1-(4-methoxyphenyl)-2-(phenylselanyl)ethan-1-one



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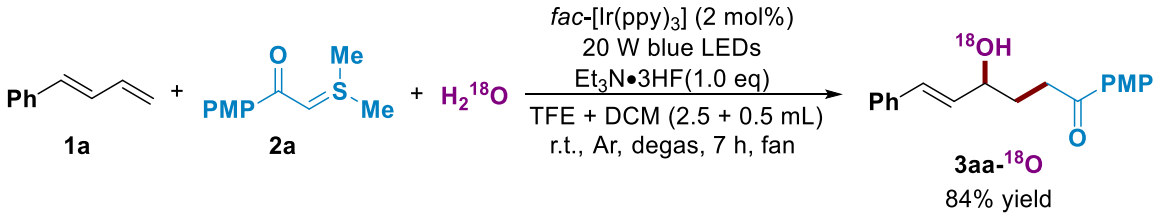
64.9 mg (petroleum ether: ethyl acetate = 5:1 R_f = 0.4), colorless oil, yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.25 (d, *J* = 6.0 Hz, 3H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.13 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 163.5, 133.7, 130.9, 129.2, 129.1, 128.3, 127.8, 113.7, 55.4, 32.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{15}O_2Se$: 307.0232, found: 307.0235.

6.3 $H_2{}^{18}O$ Labelling Experiment



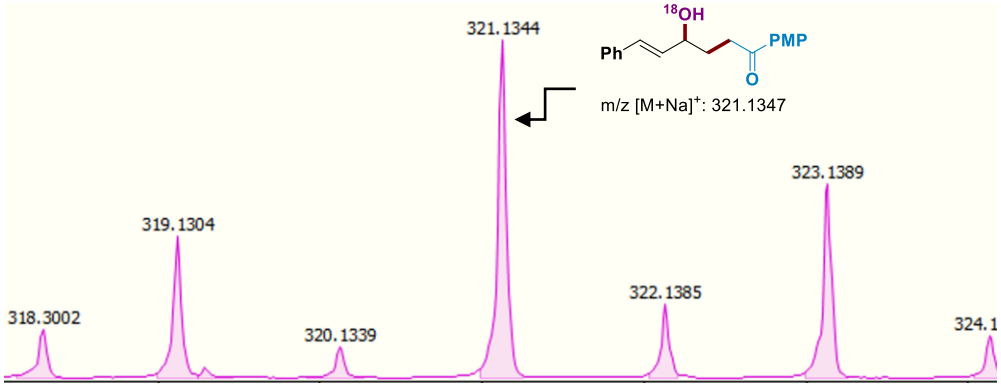
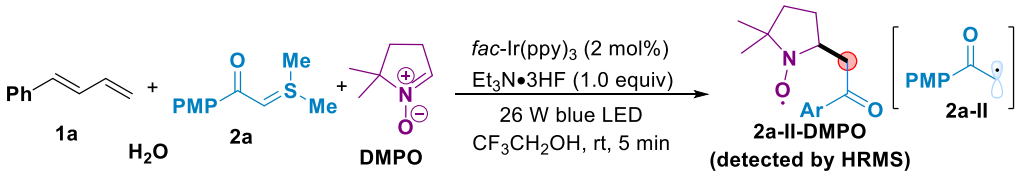


Figure S4. High resolution mass spectrometry of 3aa-^{18}O

6.4 EPR Experiment



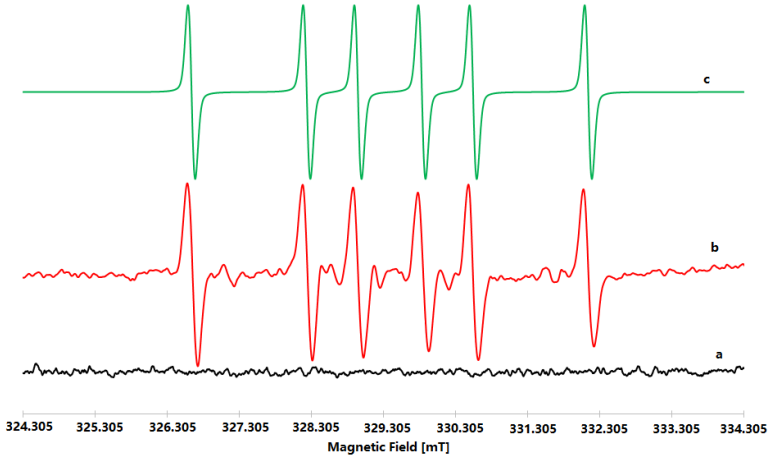


Fig. S5 Electron paramagnetic resonance studies

In a flame-dried 10.0 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with sulfur ylide **2a** (126 mg, 0.60 mmol, 3.0 eq.), *fac*-[Ir(ppy)$_3$] (2.6 mg, 0.004 mmol, 2 mol%), **H_2O** (54 μL, 3 mmol, 15.0 eq.) and DMPO (50 mg), followed by the addition of TFE (2.5 mL) and DCM (0.5 mL). The resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. Then, the mixed solution (40 uL) was transferred to a flat cell, and the flat cell was measured *in-vivo*. No signal occoured in dark for over 10 min (**Fig. S5a**), while a sharped sextet signal was obtained after the mixture was irradiated with a blue led (26 W) for 5 min (**Fig. S5b**), with a *g* value = 2.003, and A_N = 1.597 mT, A_H = 2.307 mT, which could be confirmed to be a carbon-centered radical adduct. The simulation EPR spectrum (**Fig. S5c**) was in perfectly agreement with the experimental one.

6.5. Luminescence Quenching Experiments

Fluorescence spectra were collected on Agilent Fluorescence Spectrophotometer G9800AS24 for all experiments. All *fac*-[Ir(ppy)$_3$] solutions were excited at 400 nm and the emission intensity was collected at 520 nm. In a typical experiment, the emission spectrum of a 1.0×10^{-4} M solution of in TFE+DCM (5:1, v/v) or DCM was collected. The significant decrease of *fac*-[Ir(ppy)$_3$] luminescence could be observed in the presence of substrate **2a** and additive **$Et_3N{\cdot}3HF$** in mixture solvent **(**TFE+DCM (5:1, v/v)). The results suggest the possible interaction between sulfur ylides and the photoexcited photocatalyst.

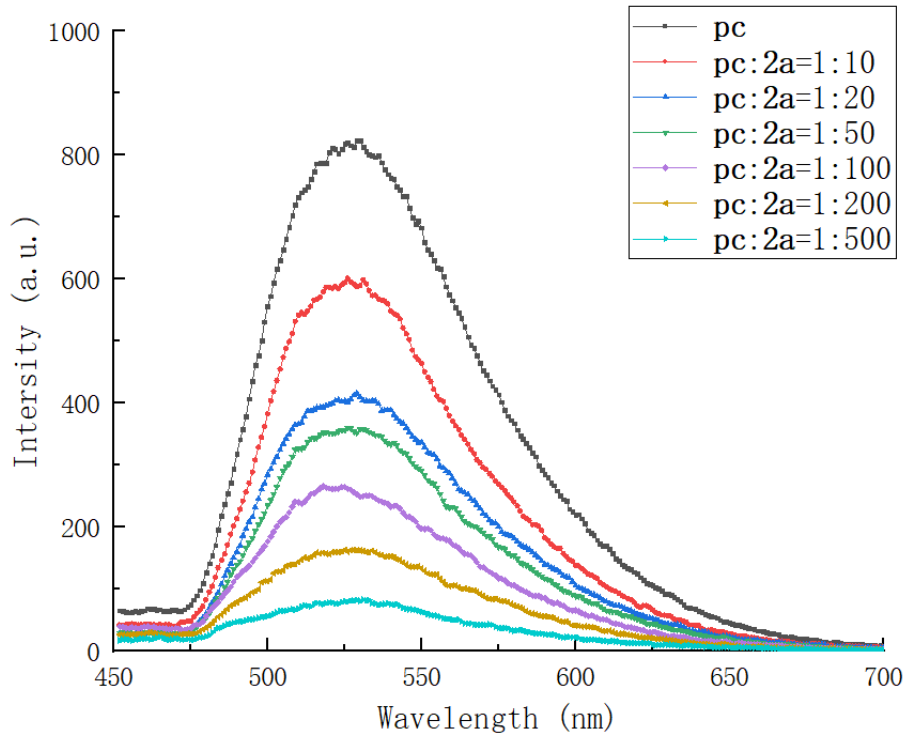


Fig. S6. Quenching of *fac*-[Ir(ppy)$_3$] by 2a in TFE+DCM (5:1, v/v)

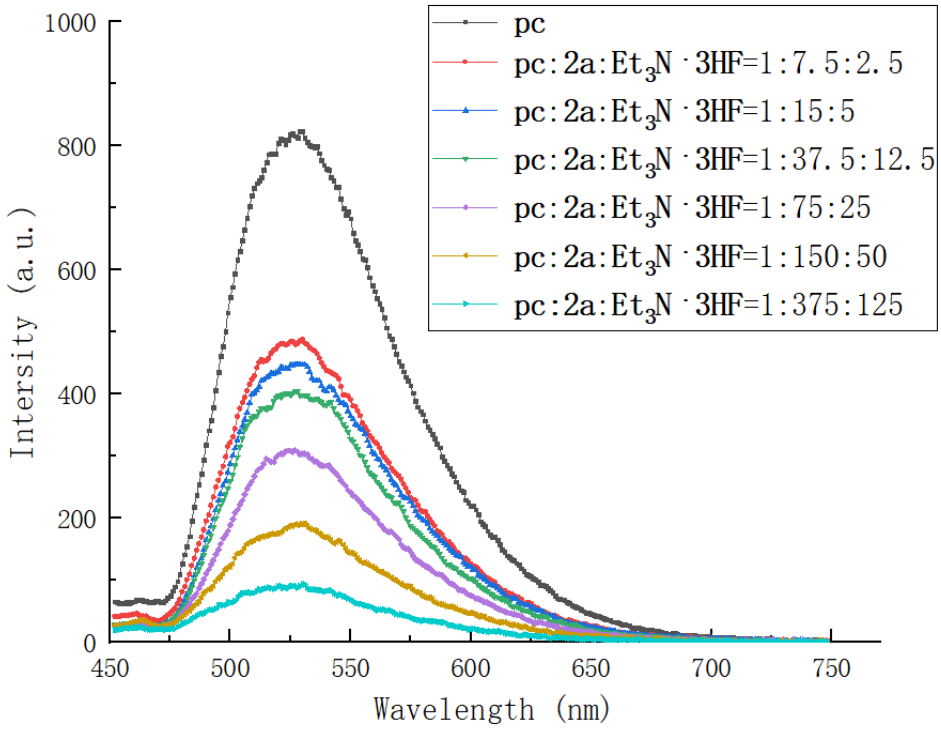


Fig. S7. Quenching of *fac*-[Ir(ppy)$_3$] by 2a+Et$_3$N·3HF in TFE+DCM (5:1, v/v)

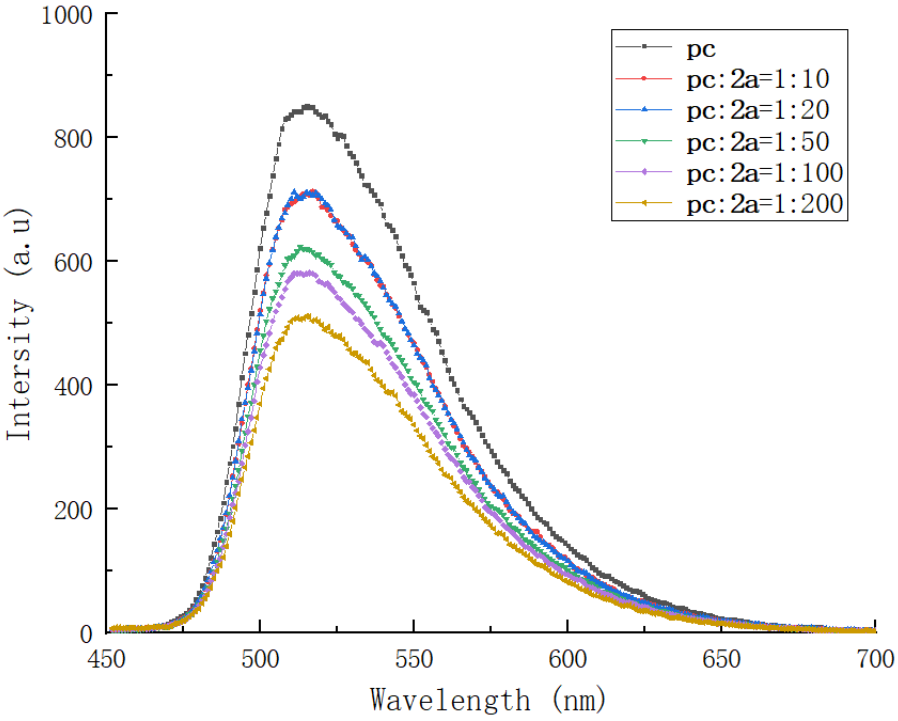


Fig. S8. Quenching of *fac*-[Ir(ppy)$_3$] by 2a in DCM

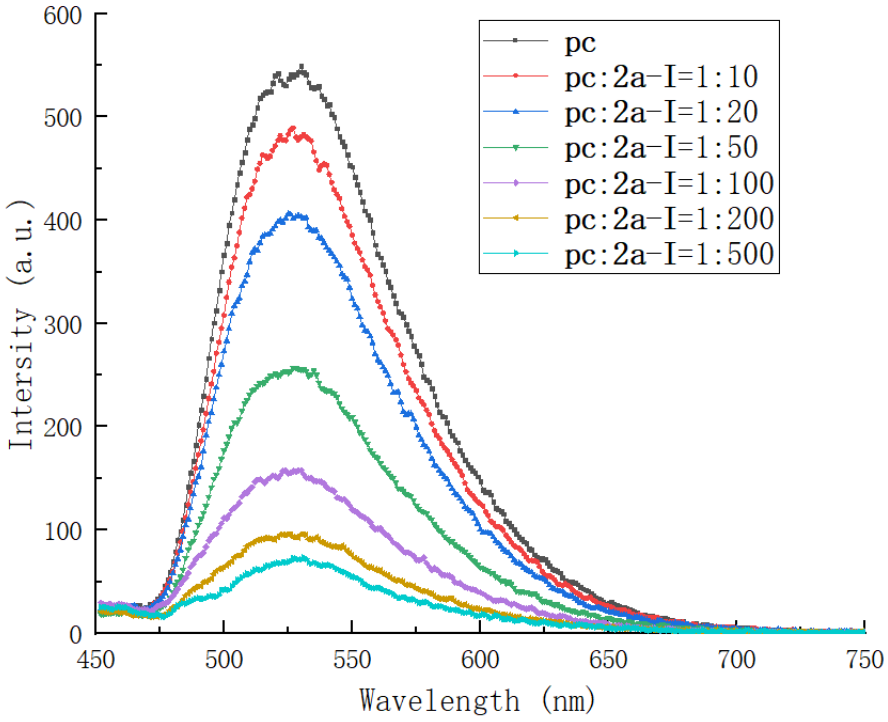


Fig. S8 Quenching of *fac*-[Ir(ppy)$_3$] by 2a-I in TFE+DCM (5:1, v/v)

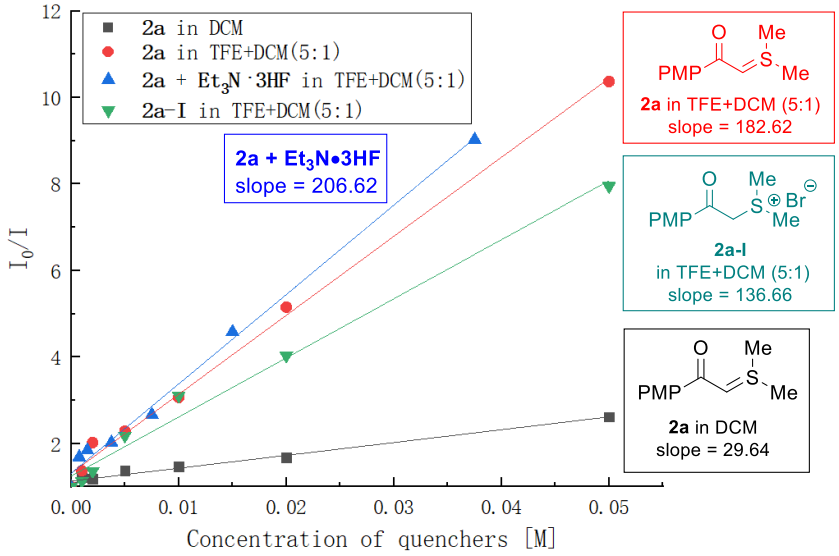


Fig. S9 The Stern-Volmer plot for the quenching of *fac*-[Ir(ppy)$_3$]

6.6 Cyclic Voltammogram of Sulfur Ylide 2a and sulfonium salt 2a-I

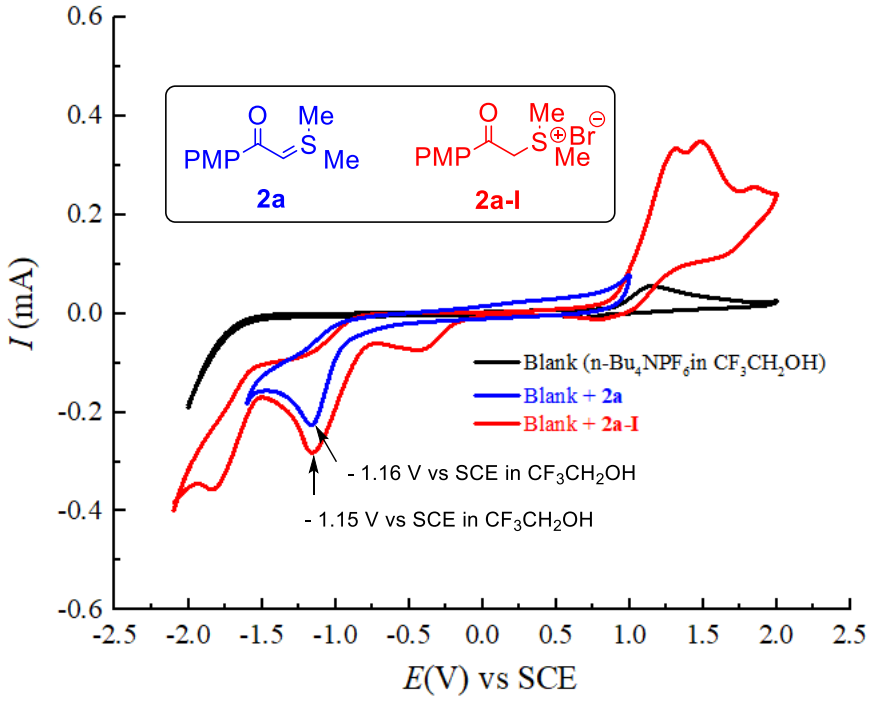


Fig. S10 Cyclic voltammogram of sulfur ylide 2a and sulfonium salt 2a-I

Cyclic voltammetry (CV) was taken using a CHI660D potentiostat. CV measurement of **2a** was carried out in 0.1 M of ^{n}Bu$_4$NPF$_6$/CF$_3$CH$_2$OH at a scan rate of 100 mV/s with the protection of argon atmosphere. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is Hg/Hg$_2$Cl$_2$. The results are as follow: **2a** (E_p = -1.16 V vs SCE in CF$_3$CH$_2$OH),

2a-I (E_p = -1.15 V vs SCE in CF_3CH_2OH), the excited *fac*-[Ir(ppy)$_3$]*: ($E_{1/2}$ = -1.73 V vs SCE in CH_3CN).

6.7 Interaction of sulfur ylide 2a with CF_3CH_2OH

In order to understand the interaction of sulfur ylide **2a** with CF_3CH_2OH, we explore it through ^1H NMR. In a mixture of **2a**: CF_3CH_2OH with a molar ration of 1:1, the signal assigned to the OH group of CF_3CH_2OH disappeared. When the amount of CF_3CH_2OH was increased (**2a**: CF_3CH_2OH), the new signal that can be assigned to the two α-hydrogens peak appears (δ = 4.62 (s, 2H)). These results suggest that CF_3CH_2OH might serve as a proton source to participate in the activation of sulfur ylide **2a** into the corresponding sulfonium salt **2a-I**.

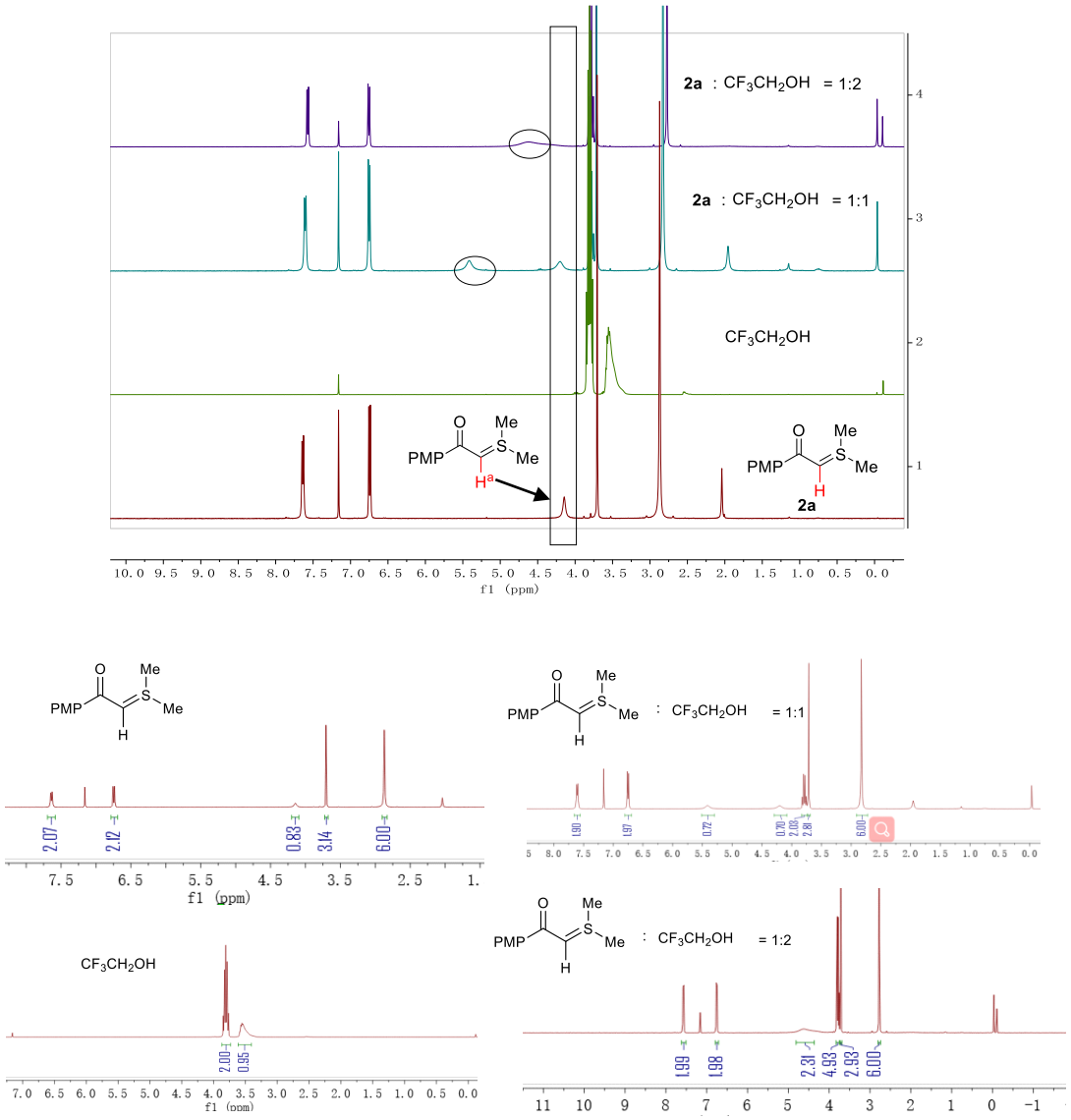
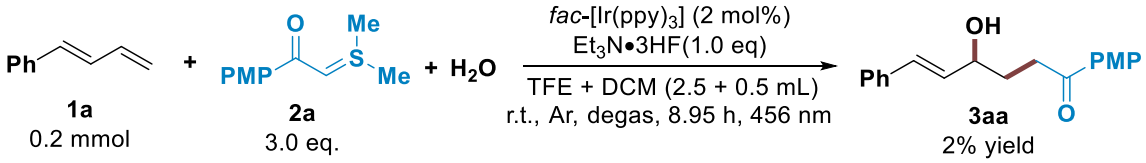


Fig. S11 Interaction of sulfur ylide 2a with CF_3CH_2OH

6.8 Determination of Quantum Yield



A cuvette was charged with **1a** (0.2 mmol), **2a** (0.6 mmol), **H_2O** (3.0 mmol), *fac*-[Ir(ppy)$_3$] (2 mol%) and $Et_3N{\cdot}3HF$ (0.2 mmol) in 2.4 mL mixture solvents (CF_3CH_2OH: DCM = 5:1, v/v). The sample was irradiated (λ = 450 nm, slit width = 3.0 mm, slit height 5.0 mm with intensity of 2.7100 $mW{\cdot}cm^{-2}$) for 32208s (8.9 h). The quantum yield was determined as follows.

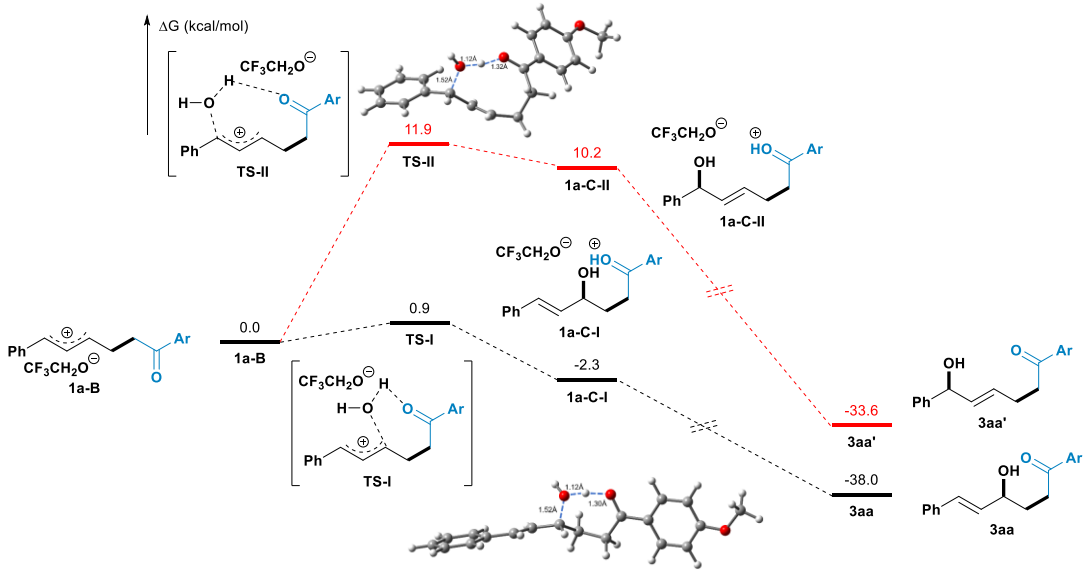
ϕ = Mole number for product/Mole number for absorption of photons = 0.03

$$\Phi = \frac{nN_A/t}{fP\lambda/hc}$$

n: the mole number of the product **3aa**; t: reaction time (32208 s); NA:6.02×10^{23} /mol; f: $1\text{-}10^{-A}$ (450 nm, A= 4.82); P: P=E*S (E: illumination intensity, E= 2.710 mW/cm^2 ; S: the area that irradiated S= 0.15 cm^2); λ: wavelength ($\lambda = 4.50\times10^{-7}$ m); h: planck constant (h = 6.626×10^{-34} J*s); c: velocity of light (c = 3×10^8 m/s).

6.9 Density Functional Theory Calculations

The energetics of the species were obtained at ωB97xD/6-311+G(d,p)//6-31+G(d) level of theory. Solvation effect of 2,2,2-trifluoroethanol was considered employing SMD method. Frequency analysis was performed to verify the nature of stationary points, and provide Gibbs free energy correction.



Coordinates of **1a-B**

C	7.64158500	-1.11056700	-0.58559700
C	6.32766000	-0.96563700	-0.99164600
C	5.39911900	-0.25897600	-0.18542100
C	5.83674300	0.30115700	1.04282000
C	7.15060100	0.15289800	1.43978800
C	8.04983400	-0.55206400	0.62823300
H	8.34901500	-1.65316200	-1.20314900
H	5.99886100	-1.39594600	-1.93382700
H	5.14751600	0.85091600	1.67494700
H	7.48886000	0.58141400	2.37703400
H	9.08120800	-0.66517500	0.94873900
C	4.06734100	-0.14703200	-0.65335700
C	2.98056100	0.48347700	-0.03393900
H	3.86544200	-0.61278300	-1.61883000
H	3.08686500	0.96698400	0.93270700
C	1.76151900	0.49605300	-0.66345300
C	0.54472000	1.14856700	-0.16343000
H	1.68118100	-0.00044100	-1.63304800
H	0.32982800	2.01005700	-0.82239800
C	-0.69095700	0.23852300	-0.22134300
H	-0.68586100	-0.46891700	0.61388200
H	-0.70129500	-0.35991200	-1.14282400
C	-1.96900800	1.09199300	-0.20526500
O	-1.86742900	2.29998100	-0.33873700

C	-3.27164500	0.41528200	-0.06000000
C	-3.40310100	-0.98029600	0.05441300
C	-4.43243000	1.19795700	-0.05543400
C	-4.64741400	-1.56721200	0.16920900
H	-2.53033900	-1.62701500	0.04979600
C	-5.68950500	0.62322700	0.06130500
H	-4.33523800	2.27502000	-0.14812200
C	-5.80333700	-0.76943800	0.17430000
H	-4.76021400	-2.64250300	0.25734500
H	-6.56643100	1.25999300	0.06140500
H	0.68735800	1.56201100	0.83894800
O	-6.96487100	-1.43223700	0.29096500
C	-8.18152200	-0.70058500	0.29079900
H	-8.31175800	-0.15820900	-0.65240300
H	-8.96998200	-1.44490400	0.39493400
H	-8.22120200	-0.00334300	1.13514700

Coordinates of **1a-C-II**

C	6.02154300	-1.27950200	-0.70065100
C	5.28191600	-0.13002800	-0.42810000
C	3.94936400	-0.22797700	-0.02686000
C	3.36439800	-1.49159400	0.10874000
C	4.10457800	-2.63951600	-0.15541200
C	5.43433200	-2.53427000	-0.56359600
H	7.05757300	-1.19252400	-1.01324000
H	5.74682400	0.84756300	-0.53222900

H	2.32841200	-1.57862000	0.42986500
H	3.64548800	-3.61718300	-0.04364600
H	6.01070600	-3.43063400	-0.77119500
C	3.14759900	1.02105500	0.24156000
C	1.99435000	1.25029700	-0.69953400
H	1.55372500	0.37488500	-1.17622000
C	1.38546400	2.43421300	-0.72458000
C	-0.03508600	2.64629000	-1.14383400
H	1.85776400	3.27854900	-0.21925600
H	-0.37016200	1.88484900	-1.85623900
C	-0.91097800	2.60199800	0.15088900
H	-1.87375400	3.07978600	-0.02777400
H	-0.41224800	3.18052800	0.93701300
C	-1.12328000	1.20816500	0.66171700
O	-0.19909300	0.60299600	1.33292100
C	-2.31567500	0.46319500	0.44455000
C	-3.37374400	0.96082700	-0.35291300
C	-2.45654900	-0.83498700	1.01348500
C	-4.51037200	0.21715900	-0.58332300
H	-3.30729400	1.93758700	-0.81850100
C	-3.58713200	-1.57601000	0.80160000
H	-1.65990000	-1.23479200	1.63044200
C	-4.63199900	-1.06096400	-0.00040500
H	-5.29785400	0.62347900	-1.20617400
H	-3.71083700	-2.56070400	1.23871800

H	-0.18478800	3.62679300	-1.60478000
O	-5.68228000	-1.85105800	-0.14350600
C	-6.80459900	-1.42587900	-0.91914900
H	-6.51237900	-1.26046300	-1.96053600
H	-7.51937000	-2.24449200	-0.86302400
H	-7.24487300	-0.52033700	-0.49103100
H	3.81013700	1.89476200	0.24920800
O	2.47169800	0.96589600	1.53085200
H	3.04355700	0.54530600	2.18925200
H	0.71189700	1.00814600	1.40210900

Coordinates of 1a-C-I

C	7.72022900	0.37348700	-0.35228300
C	6.45888400	0.89185100	-0.07378600
C	5.31909400	0.07914900	-0.12775000
C	5.47335800	-1.27089200	-0.47551600
C	6.73150100	-1.78949300	-0.75277300
C	7.85942100	-0.96935600	-0.69123300
H	8.59216500	1.01864000	-0.30477100
H	6.35648200	1.94204300	0.18979700
H	4.60893500	-1.92624300	-0.53396700
H	6.83630800	-2.83690600	-1.01903800
H	8.84129500	-1.37888600	-0.90785300
C	4.01544500	0.68064300	0.18650900
C	2.82310600	0.07144100	0.24159800
H	4.04831600	1.75165900	0.39541500

H	2.71438300	-0.99561800	0.05064900
C	1.56274200	0.80145800	0.57657400
C	0.48157000	0.63691700	-0.49074300
H	0.35078900	-0.42773700	-0.71936100
C	-0.88072600	1.28723400	-0.13501100
H	-1.32210700	1.72263900	-1.02914800
H	-0.72735500	2.11934100	0.56777500
C	-1.86314400	0.35643600	0.51798700
O	-1.45698800	-0.35333000	1.51557400
C	-3.22336700	0.20880500	0.13349300
C	-3.79475200	0.91125400	-0.96243600
C	-4.05806100	-0.66622600	0.87484600
C	-5.11573300	0.74897800	-1.28819900
H	-3.20064200	1.58758600	-1.56576200
C	-5.38483900	-0.83737600	0.55460400
H	-3.64123500	-1.20930600	1.71565700
C	-5.93048700	-0.12581400	-0.53506300
H	-5.56237200	1.27824800	-2.12249500
H	-5.99478600	-1.51156300	1.14331400
H	0.85613800	1.10650800	-1.40415700
O	-7.18991100	-0.21069800	-0.92891700
C	-8.10226400	-1.07453400	-0.24769100
H	-8.20576000	-0.77633800	0.79985900
H	-9.05332800	-0.94917800	-0.76143600
H	-7.77351700	-2.11529900	-0.32444200

H	1.77036200	1.87001400	0.72054200
O	0.99227300	0.29766000	1.80947500
H	1.67960100	0.15689200	2.47445000
H	-0.48851900	-0.17934700	1.74716300

Coordinates of TS-II

C	6.19965100	-0.99135100	-0.41207700
C	5.29872200	0.03021300	-0.11794500
C	3.93554400	-0.24747600	-0.00826400
C	3.47664700	-1.55760400	-0.18385100
C	4.37811600	-2.57671200	-0.46637700
C	5.73962100	-2.29351200	-0.58515500
H	7.25816600	-0.76945200	-0.50269300
H	5.66258100	1.04632900	0.01707800
H	2.41795500	-1.78381000	-0.08342200
H	4.02029800	-3.59323300	-0.59702600
H	6.44131500	-3.09052400	-0.81059500
C	2.97799800	0.87199800	0.26031600
C	1.89750000	1.13861500	-0.73631100
H	1.46157500	0.28143500	-1.24611000
C	1.32283800	2.34077700	-0.76272200
C	-0.07204200	2.61214700	-1.22100200
H	1.80001700	3.16057100	-0.22134100
H	-0.43041900	1.84475400	-1.91507900
C	-0.95568600	2.64597700	0.06364200
H	-1.91898300	3.10111000	-0.16692300

H	-0.47583800	3.28594400	0.81206400
C	-1.14141000	1.27847100	0.68729600
O	-0.24449500	0.78394700	1.41452600
C	-2.34849900	0.50681500	0.45991500
C	-3.37281700	0.93404500	-0.40497000
C	-2.49882900	-0.74497900	1.10453700
C	-4.49872500	0.16065100	-0.62872000
H	-3.30238100	1.88014600	-0.93029400
C	-3.61493200	-1.51789700	0.89920300
H	-1.72004700	-1.08703900	1.77719800
C	-4.63101700	-1.07378600	0.02839200
H	-5.26431800	0.51946800	-1.30589200
H	-3.74251400	-2.47354800	1.39608400
H	-0.15828700	3.58448500	-1.71456600
O	-5.67356700	-1.89166400	-0.10376100
C	-6.76200700	-1.51791000	-0.94281300
H	-6.43256700	-1.40814900	-1.98131800
H	-7.47882900	-2.33404800	-0.87035500
H	-7.22314500	-0.59051100	-0.58753800
H	3.50501900	1.79488300	0.51697500
O	2.15508900	0.51610100	1.48963700
H	2.63007900	0.56153700	2.33435000
H	1.07006000	0.81170600	1.47762600

Coordinates of TS-I

C	7.31223000	-0.92221800	1.33999900

C	5.92397600	-0.99580200	1.27708200
C	5.20401300	-0.22198700	0.35668100
C	5.91063700	0.62750400	-0.50945400
C	7.29513900	0.70186000	-0.44637400
C	7.99922000	-0.07129800	0.47909500
H	7.85315800	-1.52845400	2.05947500
H	5.39313200	-1.66121200	1.95392600
H	5.38618000	1.23695100	-1.23945500
H	7.82873400	1.36364100	-1.12155400
H	9.08223600	-0.00939000	0.52469500
C	3.74419600	-0.33948400	0.34827600
C	2.86103900	0.34130200	-0.40167100
H	3.34451000	-1.07048000	1.05322400
H	3.17689600	1.10778000	-1.10755900
C	1.39942900	0.10186200	-0.29671200
C	0.52665400	1.30114600	-0.66388400
H	0.48022000	1.38262900	-1.75795500
C	-0.89313100	1.30680500	-0.08740500
H	-1.36046800	2.26098600	-0.35864500
H	-0.86687800	1.28631600	1.00940400
C	-1.81186900	0.19862100	-0.57201400
O	-1.36670000	-0.70544200	-1.32351400
C	-3.20517100	0.18115700	-0.18709700
C	-3.77608300	1.17499500	0.64149100
C	-4.03262800	-0.85698900	-0.65640900

C	-5.10586900	1.12529400	0.98631000
H	-3.17963300	1.99666000	1.02504000
C	-5.37178500	-0.91615100	-0.32044200
H	-3.60596600	-1.62633800	-1.29099100
C	-5.91985700	0.07852700	0.50833700
H	-5.55516600	1.88337200	1.61832800
H	-5.98199000	-1.72670600	-0.70071600
H	1.03684800	2.20550800	-0.31793300
O	-7.19141800	0.11744100	0.89982400
C	-8.09639500	-0.89430200	0.46624900
H	-7.75660200	-1.88454300	0.78678300
H	-9.04380800	-0.65961900	0.94875100
H	-8.21711700	-0.86310700	-0.62143000
H	1.11794800	-0.33568900	0.66433300
O	1.01940200	-1.03792100	-1.23246500
H	1.48150300	-0.93648400	-2.08265700
H	-0.08648600	-0.93950800	-1.36818700

Coordinates of 3aa'

C	-6.53934600	1.35615100	-1.11935800
C	-6.01692400	0.16882100	-0.60507700
C	-4.81963400	0.17055100	0.10926200
C	-4.14804700	1.38070100	0.30938900
C	-4.67020200	2.56698300	-0.19467000
C	-5.86732800	2.55724700	-0.91350200
H	-7.47278000	1.34068400	-1.67511200

H	-6.54685600	-0.76831900	-0.76380800
H	-3.21216200	1.38039500	0.86244200
H	-4.14264100	3.50299700	-0.03302900
H	-6.27275100	3.48365000	-1.31050000
C	-4.24152400	-1.12409900	0.66204100
C	-2.96031100	-1.48706100	-0.04058700
H	-3.04449600	-1.55377300	-1.12563400
C	-1.79510700	-1.71995500	0.56072500
C	-0.52609300	-2.07730900	-0.15859500
H	-1.74613900	-1.64900900	1.64704200
H	-0.68876800	-2.10211400	-1.24108500
C	0.59888300	-1.09665500	0.17371400
H	0.76786500	-1.06959400	1.25917400
H	0.30680500	-0.07530400	-0.10847200
C	1.91215100	-1.43012000	-0.51535100
O	1.99096000	-2.36925900	-1.28929700
C	3.10566500	-0.57910300	-0.22544500
C	3.07627000	0.50500400	0.66531700
C	4.30861000	-0.87488900	-0.86956900
C	4.21074600	1.26125300	0.90394900
H	2.15916700	0.76850000	1.18354900
C	5.45715100	-0.12527300	-0.64254800
H	4.33284500	-1.71156900	-1.56103900
C	5.41036400	0.95036100	0.25100900
H	4.19519100	2.09891100	1.59374700

H	6.37242500	-0.38613700	-1.16158400
H	-0.20633400	-3.08712600	0.12818100
O	6.46469700	1.74463300	0.54876000
C	7.70058100	1.49516300	-0.09117500
H	7.61091000	1.60129100	-1.17924000
H	8.39060000	2.24786400	0.29072000
H	8.08084600	0.49568300	0.15290100
H	-4.97315000	-1.92708000	0.47147200
O	-3.99248000	-1.03470100	2.05679500
H	-4.79141200	-0.70196800	2.48303400

Coordinates of 3aa

C	7.61854600	-0.24617600	1.21512000
C	6.28495500	-0.64474000	1.24685200
C	5.35218900	-0.12509000	0.34015800
C	5.79232300	0.82448900	-0.59282600
C	7.12367200	1.22355600	-0.62704800
C	8.04388300	0.68891900	0.27508500
H	8.32459700	-0.66450000	1.92702300
H	5.96000000	-1.37529500	1.98436500
H	5.08642700	1.26711900	-1.28983400
H	7.44404900	1.96248200	-1.35608800
H	9.08269600	1.00518300	0.24804700
C	3.95611600	-0.59394800	0.40777300
C	2.99948400	-0.41960500	-0.51056000
H	3.70188900	-1.15037100	1.31198900

H	3.19831400	0.10104000	-1.44759200
C	1.59856600	-0.93874800	-0.35410400
C	0.56499700	0.18198100	-0.40384900
H	0.66777200	0.72529000	-1.35005300
C	-0.85743000	-0.34646500	-0.26345000
H	-0.94702900	-0.96489500	0.64178700
H	-1.09420900	-1.01055300	-1.10320100
C	-1.89928300	0.75554700	-0.18666700
O	-1.57508900	1.93095100	-0.22588600
C	-3.33561600	0.36605600	-0.05056100
C	-3.76818700	-0.96914800	-0.04359800
C	-4.29315000	1.37363400	0.08027800
C	-5.11020300	-1.28116900	0.08814600
H	-3.05442700	-1.78100000	-0.14503200
C	-5.64488700	1.07779400	0.21657600
H	-3.95986700	2.40703300	0.07471100
C	-6.05842800	-0.25893800	0.21999800
H	-5.45187800	-2.31129500	0.09141300
H	-6.35839600	1.88763900	0.31769500
H	0.78232000	0.89701900	0.39627200
O	-7.34460200	-0.66199400	0.34372200
C	-8.34919300	0.32199500	0.48952700
H	-8.38396900	0.98723900	-0.38195000
H	-9.29043200	-0.22254800	0.56715200
H	-8.19447700	0.91350900	1.40025600

H	1.51385900	-1.45838000	0.61496700
O	1.28022700	-1.84902200	-1.40874400
H	1.97834500	-2.51387200	-1.45577300

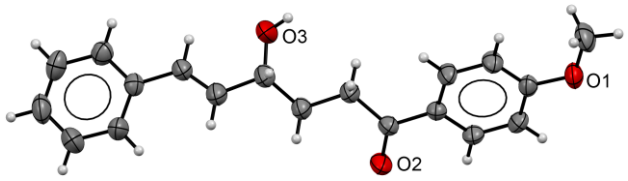
7. X-Ray Structures of Compounds

Single crystals of $C_{19}H_{20}O_3$[**3aa**]. A suitable crystal was selected and [**3aa**] on a Bruker APEX-II CCD using Mo-Kα radiation (λ = 0.71073 Å). The crystal was kept at 296 (1) K during data collection.

Crystal structure determination of [3aa]

Crystal Data for $C_{19}H_{20}O_3$ (*M* =296.35 g/mol): triclinic, space group P-1, *a* = 5.7272(12) Å, *b* = 7.6083(16) Å, *c* = 18.734(4) Å, V = 794.1(3) $Å^3$, Z = 2, T = 269(1) K, μ(Mo-Kα) = 0.083 mm^{-1}, *Dcalc* = 1.239 g/cm^3, 5749 reflections measured (2.728° ≤ 2Θ ≤ 25.947°), 2900 unique (R_{int} = 0.0257) which were used in all calculations. The final R_1 was 0.0546 (I > 2σ(I)) and wR_2 was 0.0.1660(all data).

CCDC 2151471 contains the supplementary data for this structure.



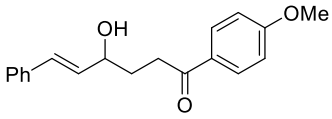


Table 1. Crystal data and structure refinement for mo_210909A_0m.

Identification code	mo_210909a_0m	
Empirical formula	$C_{19}H_{20}O_3$	
Formula weight	296.35	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.7272(12) Å	α= 79.036(3)°.
	b = 7.6083(16) Å	β= 82.382(3)°.
	c = 18.734(4) Å	γ = 87.161(4)°.
Volume	794.1(3) $Å^3$	

Z	2
Density (calculated)	1.239 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	316
Crystal size	0.12 x 0.1 x 0.1 mm^3
Theta range for data collection	2.728 to 25.497°.
Index ranges	-6<=h<=6, -8<=k<=9, -22<=l<=22
Reflections collected	5749
Independent reflections	2900 [R(int) = 0.0257]
Completeness to theta = 25.242°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7463 and 0.6609
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2900 / 0 / 201
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0546, wR2 = 0.1443
R indices (all data)	R1 = 0.0861, wR2 = 0.1660
Extinction coefficient	n/a
Largest diff. peak and hole	0.567 and -0.286 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_210909A_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

x	y	z	U(eq)	
O(1)	4201(3)	2859(2)	13866(1)	52(1)
O(2)	2816(3)	2253(3)	10647(1)	61(1)
O(3)	11082(4)	1908(4)	9327(1)	99(1)
C(1)	6070(5)	3586(4)	14138(1)	65(1)
C(2)	4435(4)	2839(3)	13133(1)	39(1)

C(3)	2621(4)	2051(3)	12890(1)	44(1)
C(4)	2701(4)	1959(3)	12166(1)	41(1)
C(5)	4621(4)	2616(3)	11656(1)	36(1)
C(6)	6419(4)	3381(3)	11913(1)	44(1)
C(7)	6327(4)	3519(3)	12640(1)	44(1)
C(8)	4638(4)	2504(3)	10874(1)	39(1)
C(9)	6945(4)	2706(4)	10380(1)	48(1)
C(10)	6878(4)	2490(3)	9596(1)	44(1)
C(11)	9176(4)	2944(4)	9118(1)	55(1)
C(12)	9050(4)	2933(4)	8325(1)	50(1)
C(13)	10631(4)	2177(3)	7898(1)	43(1)
C(14)	10674(4)	2163(3)	7113(1)	40(1)
C(15)	8931(4)	2976(4)	6703(1)	56(1)
C(16)	9086(5)	2946(5)	5968(1)	72(1)
C(17)	10948(5)	2095(4)	5620(1)	65(1)
C(18)	12665(5)	1287(4)	6011(1)	60(1)
C(19)	12542(4)	1324(3)	6754(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for mo-210909A_0m.

O(1)-C(1)	1.422(3)
O(1)-C(2)	1.366(2)
O(2)-C(8)	1.215(3)
O(3)-H(3)	0.8200
O(3)-C(11)	1.370(3)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-C(3)	1.391(3)
C(2)-C(7)	1.379(3)

C(3)-H(3A)	0.9300
C(3)-C(4)	1.368(3)
C(4)-H(4)	0.9300
C(4)-C(5)	1.401(3)
C(5)-C(6)	1.388(3)
C(5)-C(8)	1.482(3)
C(6)-H(6)	0.9300
C(6)-C(7)	1.380(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.506(3)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(9)-C(10)	1.515(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(10)-C(11)	1.506(3)
C(11)-H(11)	0.9800
C(11)-C(12)	1.498(3)
C(12)-H(12)	0.9300
C(12)-C(13)	1.313(3)
C(13)-H(13)	0.9300
C(13)-C(14)	1.470(3)
C(14)-C(15)	1.389(3)
C(14)-C(19)	1.382(3)
C(15)-H(15)	0.9300
C(15)-C(16)	1.373(3)
C(16)-H(16)	0.9300
C(16)-C(17)	1.374(4)
C(17)-H(17)	0.9300
C(17)-C(18)	1.357(4)

C(18)-H(18)	0.9300
C(18)-C(19)	1.388(3)
C(19)-H(19)	0.9300
C(2)-O(1)-C(1)	117.45(18)
C(11)-O(3)-H(3)	109.5
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(3)	115.90(19)
O(1)-C(2)-C(7)	124.3(2)
C(7)-C(2)-C(3)	119.76(19)
C(2)-C(3)-H(3A)	119.9
C(4)-C(3)-C(2)	120.24(19)
C(4)-C(3)-H(3A)	119.9
C(3)-C(4)-H(4)	119.5
C(3)-C(4)-C(5)	121.04(19)
C(5)-C(4)-H(4)	119.5
C(4)-C(5)-C(8)	119.50(18)
C(6)-C(5)-C(4)	117.63(19)
C(6)-C(5)-C(8)	122.86(19)
C(5)-C(6)-H(6)	119.1
C(7)-C(6)-C(5)	121.73(19)
C(7)-C(6)-H(6)	119.1
C(2)-C(7)-H(7)	120.2
C(6)-C(7)-C(2)	119.6(2)
C(6)-C(7)-H(7)	120.2
O(2)-C(8)-C(5)	119.87(19)

O(2)-C(8)-C(9)	121.66(19)
C(5)-C(8)-C(9)	118.47(18)
C(8)-C(9)-H(9A)	108.3
C(8)-C(9)-H(9B)	108.3
C(8)-C(9)-C(10)	116.15(18)
H(9A)-C(9)-H(9B)	107.4
C(10)-C(9)-H(9A)	108.3
C(10)-C(9)-H(9B)	108.3
C(9)-C(10)-H(10A)	109.1
C(9)-C(10)-H(10B)	109.1
H(10A)-C(10)-H(10B)	107.8
C(11)-C(10)-C(9)	112.61(18)
C(11)-C(10)-H(10A)	109.1
C(11)-C(10)-H(10B)	109.1
O(3)-C(11)-C(10)	115.2(2)
O(3)-C(11)-H(11)	106.5
O(3)-C(11)-C(12)	108.4(2)
C(10)-C(11)-H(11)	106.5
C(12)-C(11)-C(10)	113.1(2)
C(12)-C(11)-H(11)	106.5
C(11)-C(12)-H(12)	117.6
C(13)-C(12)-C(11)	124.8(2)
C(13)-C(12)-H(12)	117.6
C(12)-C(13)-H(13)	116.0
C(12)-C(13)-C(14)	128.0(2)
C(14)-C(13)-H(13)	116.0
C(15)-C(14)-C(13)	123.3(2)
C(19)-C(14)-C(13)	119.2(2)
C(19)-C(14)-C(15)	117.5(2)
C(14)-C(15)-H(15)	119.7

C(16)-C(15)-C(14)	120.6(2)
C(16)-C(15)-H(15)	119.7
C(15)-C(16)-H(16)	119.5
C(15)-C(16)-C(17)	121.0(3)
C(17)-C(16)-H(16)	119.5
C(16)-C(17)-H(17)	120.4
C(18)-C(17)-C(16)	119.2(2)
C(18)-C(17)-H(17)	120.4
C(17)-C(18)-H(18)	119.8
C(17)-C(18)-C(19)	120.3(2)
C(19)-C(18)-H(18)	119.8
C(14)-C(19)-C(18)	121.2(2)
C(14)-C(19)-H(19)	119.4
C(18)-C(19)-H(19)	119.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_210909A_0m.

The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
O(1)	58(1)	70(1)	31(1)	-13(1)	-1(1)	-7(1)
O(2)	42(1)	106(2)	42(1)	-21(1)	-9(1)	-15(1)
O(3)	53(1)	206(3)	46(1)	-43(1)	-17(1)	25(2)
C(1)	78(2)	85(2)	37(1)	-21(1)	-10(1)	-15(2)
C(2)	42(1)	43(1)	32(1)	-9(1)	-2(1)	3(1)
C(3)	35(1)	53(2)	39(1)	-7(1)	4(1)	-6(1)
C(4)	31(1)	50(1)	42(1)	-9(1)	-4(1)	-8(1)

C(5)	33(1)	40(1)	36(1)	-8(1)	-5(1)	-2(1)
C(6)	38(1)	59(2)	34(1)	-7(1)	1(1)	-15(1)
C(7)	42(1)	55(2)	39(1)	-12(1)	-6(1)	-14(1)
C(8)	37(1)	46(1)	35(1)	-9(1)	-7(1)	-4(1)
C(9)	38(1)	72(2)	36(1)	-16(1)	-4(1)	-6(1)
C(10)	43(1)	54(2)	36(1)	-12(1)	-5(1)	-5(1)
C(11)	45(1)	85(2)	40(1)	-21(1)	-6(1)	-8(1)
C(12)	44(1)	69(2)	39(1)	-14(1)	-4(1)	-5(1)
C(13)	43(1)	51(2)	35(1)	-8(1)	-7(1)	-2(1)
C(14)	43(1)	40(1)	35(1)	-6(1)	-1(1)	-6(1)
C(15)	47(1)	83(2)	40(1)	-18(1)	-5(1)	11(1)
C(16)	66(2)	109(3)	41(1)	-14(2)	-16(1)	10(2)
C(17)	78(2)	86(2)	34(1)	-18(1)	-1(1)	-9(2)
C(18)	69(2)	60(2)	48(1)	-18(1)	12(1)	-1(1)
C(19)	53(2)	49(2)	44(1)	-8(1)	-2(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for mo_210909A_0m.

x	y	z	U(eq)
H(3)	11506	2213	9685	149
H(1A)	6267	4815	13903	97
H(1B)	7502	2916	14038	97
H(1C)	5702	3519	14658	97
H(3A)	1349	1586	13222	52
H(4)	1462	1452	12008	49
H(6)	7720	3812	11586	53

H(7)	7531	4067	12796	53
H(9A)	8067	1830	10594	58
H(9B)	7537	3883	10373	58
H(10A)	6506	1263	9592	52
H(10B)	5632	3261	9394	52
H(11)	9512	4176	9150	66
H(12)	7756	3505	8120	60
H(13)	11878	1575	8119	51
H(15)	7647	3547	6929	68
H(16)	7912	3509	5701	86
H(17)	11031	2074	5123	78
H(18)	13930	706	5781	71
H(19)	13739	774	7014	59

Table 6. Torsion angles [°] for mo_210909A_0m.

O(1)-C(2)-C(3)-C(4)	-179.7(2)
O(1)-C(2)-C(7)-C(6)	178.1(2)
O(2)-C(8)-C(9)-C(10)	-2.8(4)
O(3)-C(11)-C(12)-C(13)	-5.3(4)
C(1)-O(1)-C(2)-C(3)	177.4(2)
C(1)-O(1)-C(2)-C(7)	-1.9(3)
C(2)-C(3)-C(4)-C(5)	1.3(3)
C(3)-C(2)-C(7)-C(6)	-1.2(4)
C(3)-C(4)-C(5)-C(6)	-0.8(3)
C(3)-C(4)-C(5)-C(8)	-179.6(2)
C(4)-C(5)-C(6)-C(7)	-0.8(3)
C(4)-C(5)-C(8)-O(2)	17.4(3)
C(4)-C(5)-C(8)-C(9)	-162.6(2)
C(5)-C(6)-C(7)-C(2)	1.8(4)

C(5)-C(8)-C(9)-C(10)	177.1(2)
C(6)-C(5)-C(8)-O(2)	-161.4(2)
C(6)-C(5)-C(8)-C(9)	18.7(3)
C(7)-C(2)-C(3)-C(4)	-0.3(3)
C(8)-C(5)-C(6)-C(7)	177.9(2)
C(8)-C(9)-C(10)-C(11)	172.7(2)
C(9)-C(10)-C(11)-O(3)	60.9(3)
C(9)-C(10)-C(11)-C(12)	-173.6(2)
C(10)-C(11)-C(12)-C(13)	-134.3(3)
C(11)-C(12)-C(13)-C(14)	-177.7(2)
C(12)-C(13)-C(14)-C(15)	-0.9(4)
C(12)-C(13)-C(14)-C(19)	178.3(2)
C(13)-C(14)-C(15)-C(16)	178.9(3)
C(13)-C(14)-C(19)-C(18)	-179.6(2)
C(14)-C(15)-C(16)-C(17)	0.7(5)
C(15)-C(14)-C(19)-C(18)	-0.4(4)
C(15)-C(16)-C(17)-C(18)	-0.5(5)
C(16)-C(17)-C(18)-C(19)	-0.2(4)
C(17)-C(18)-C(19)-C(14)	0.6(4)
C(19)-C(14)-C(15)-C(16)	-0.3(4)

Symmetry transformations used to generate equivalent atoms:

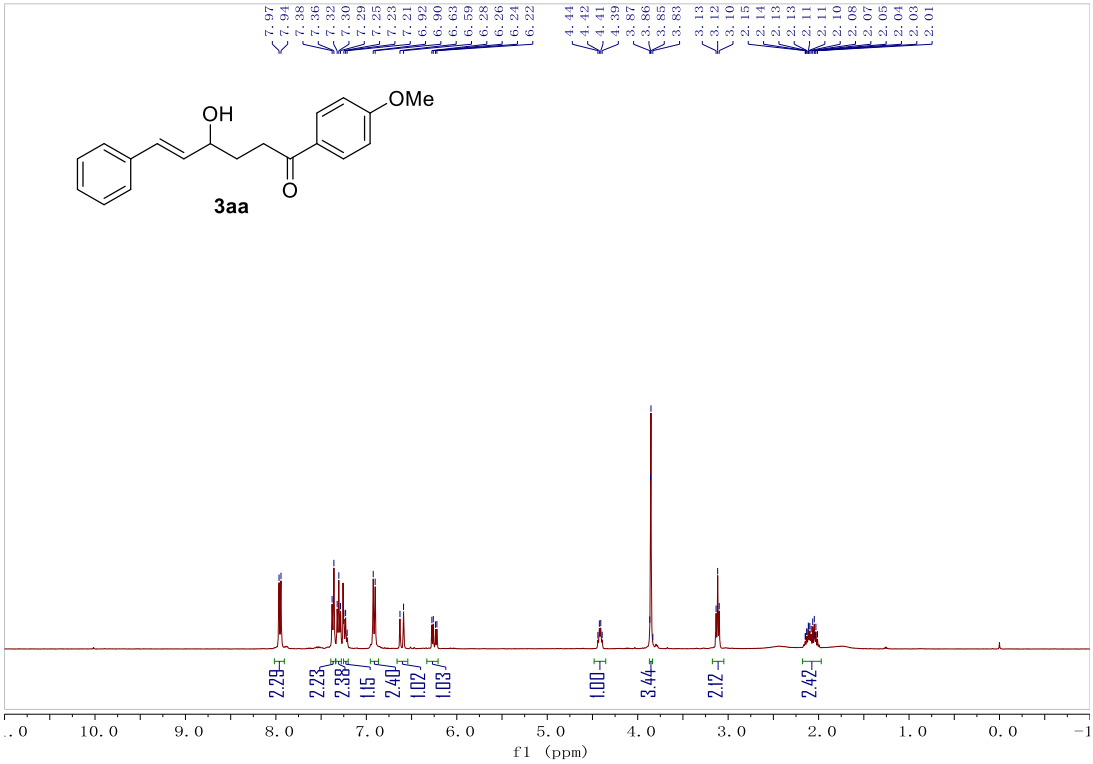
Table 7. Hydrogen bonds for mo_210909A_0m [Å and °].

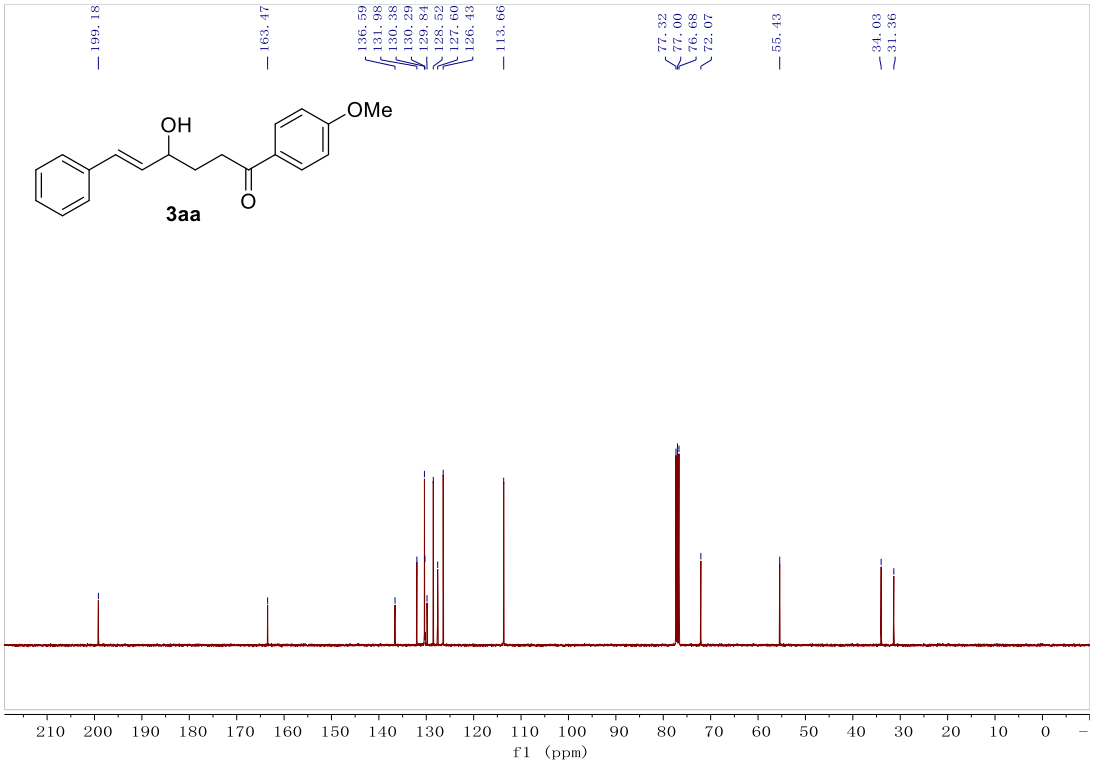
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(2)#1	0.82	2.05	2.845(2)	164.4

Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z

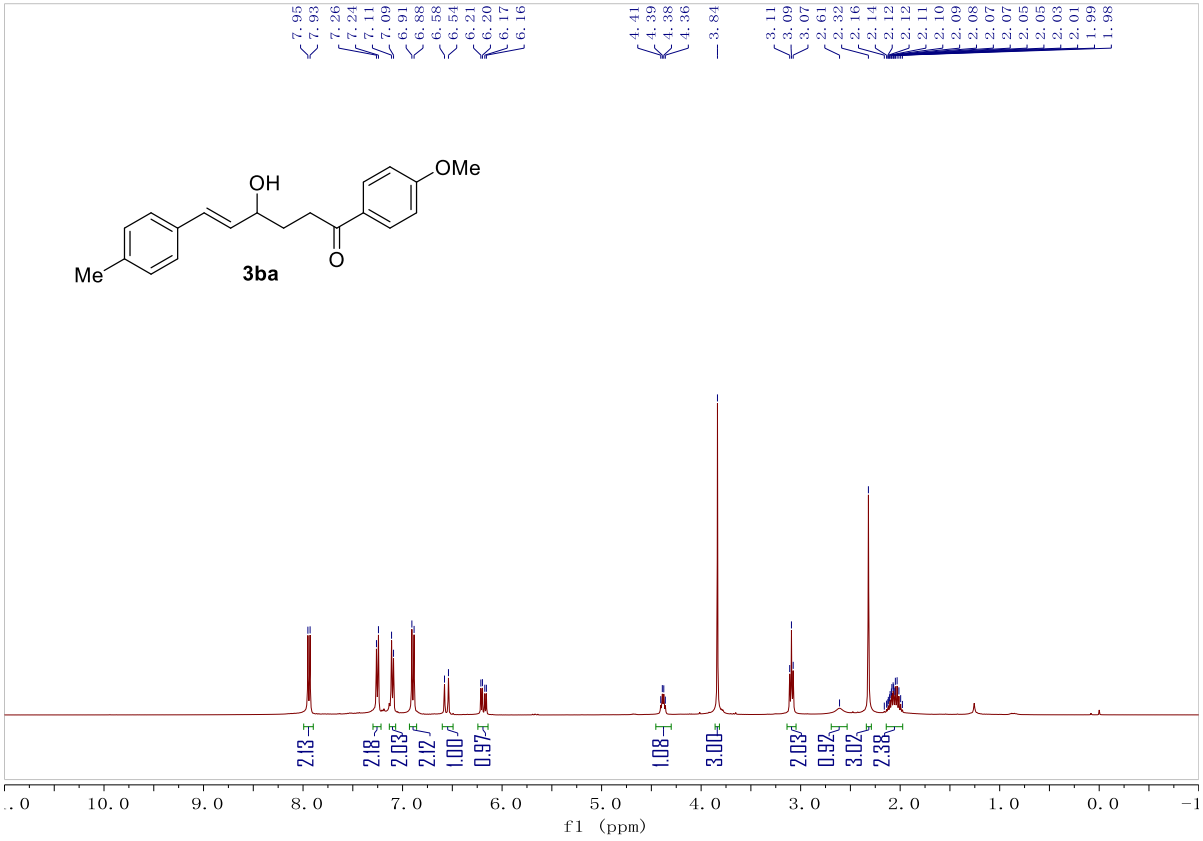
8. Spectra of Products

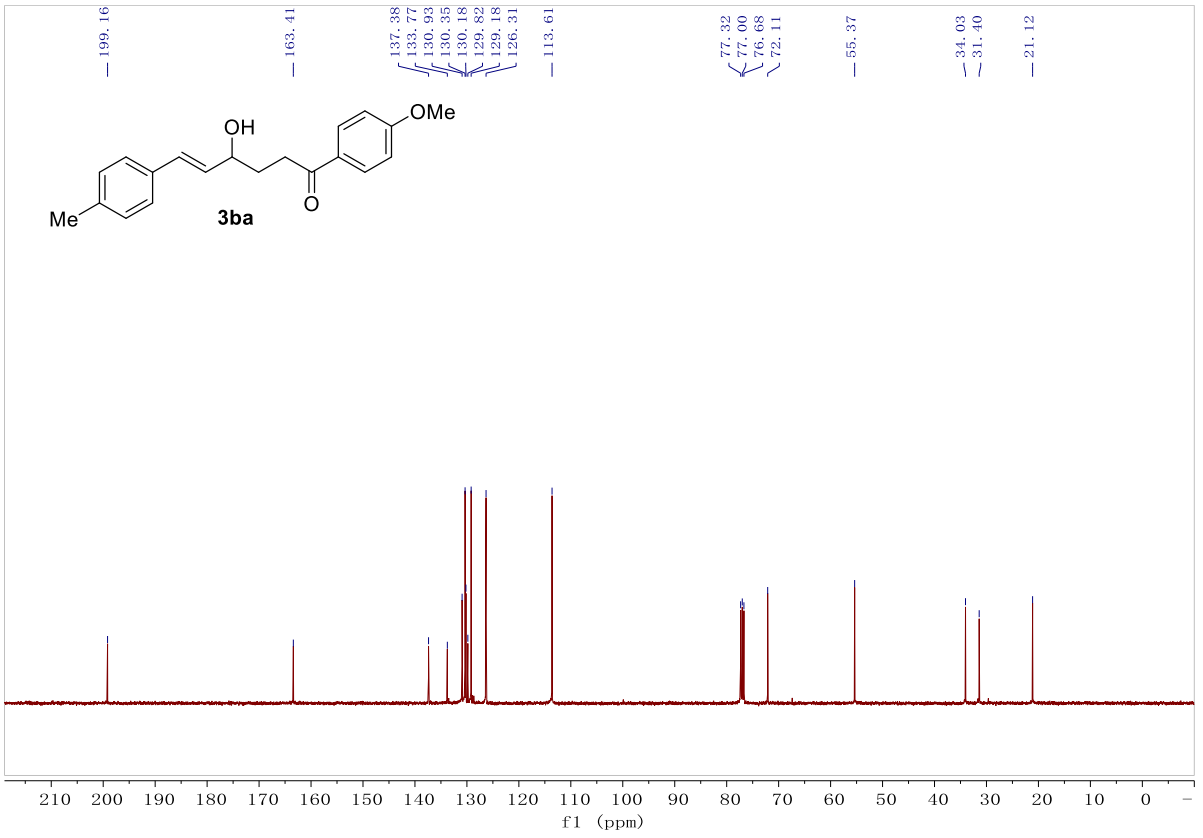
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3aa



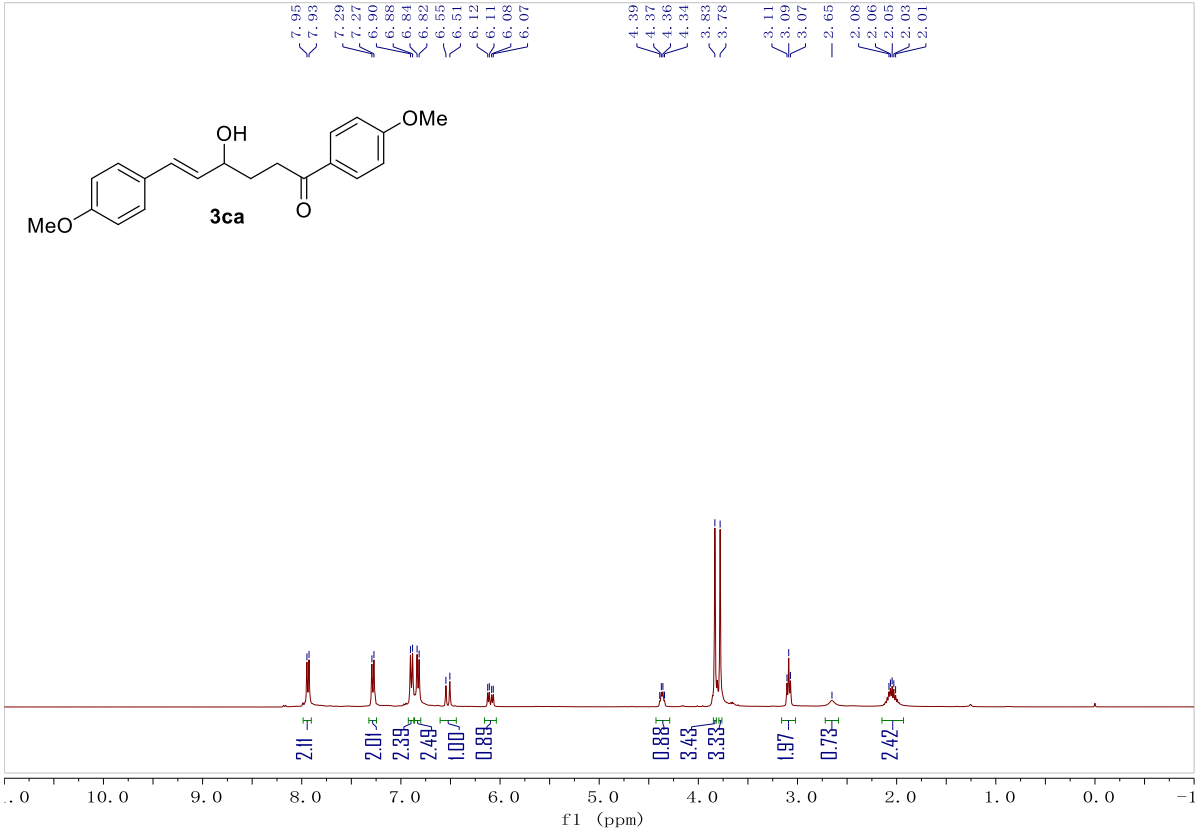


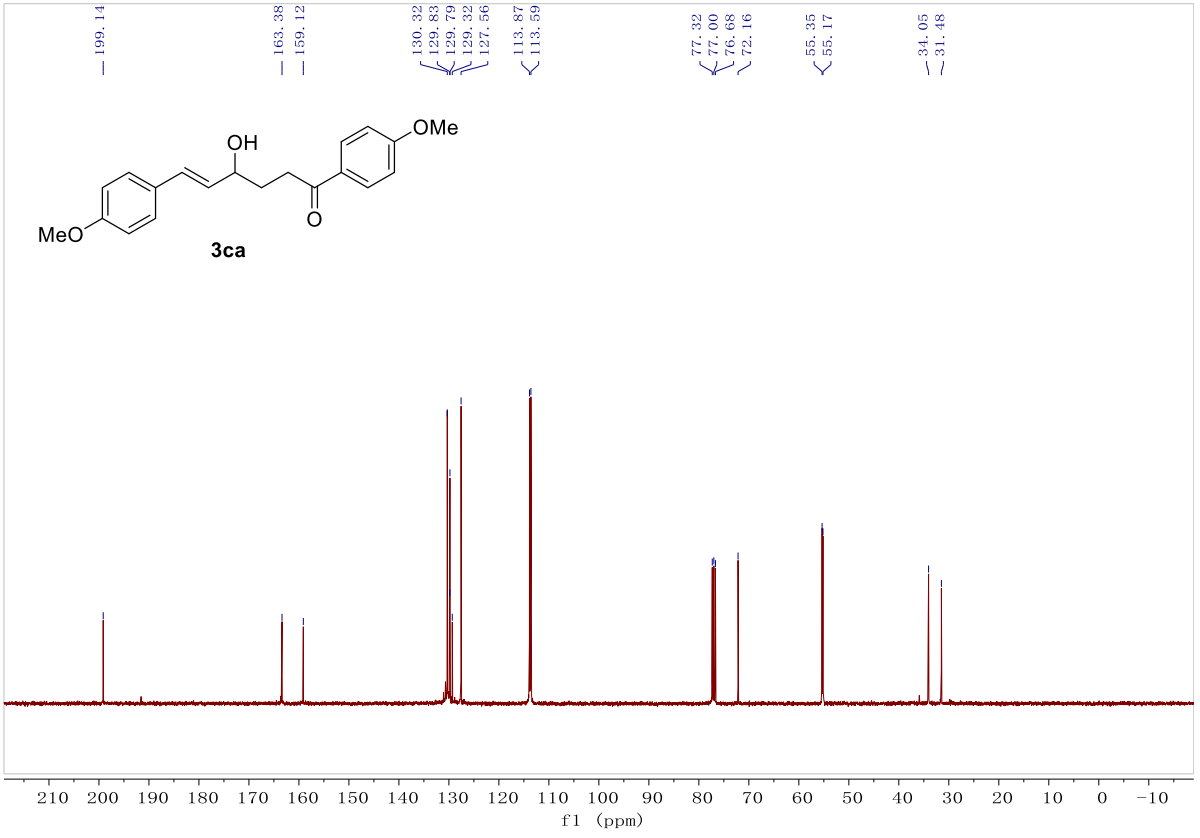
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ba



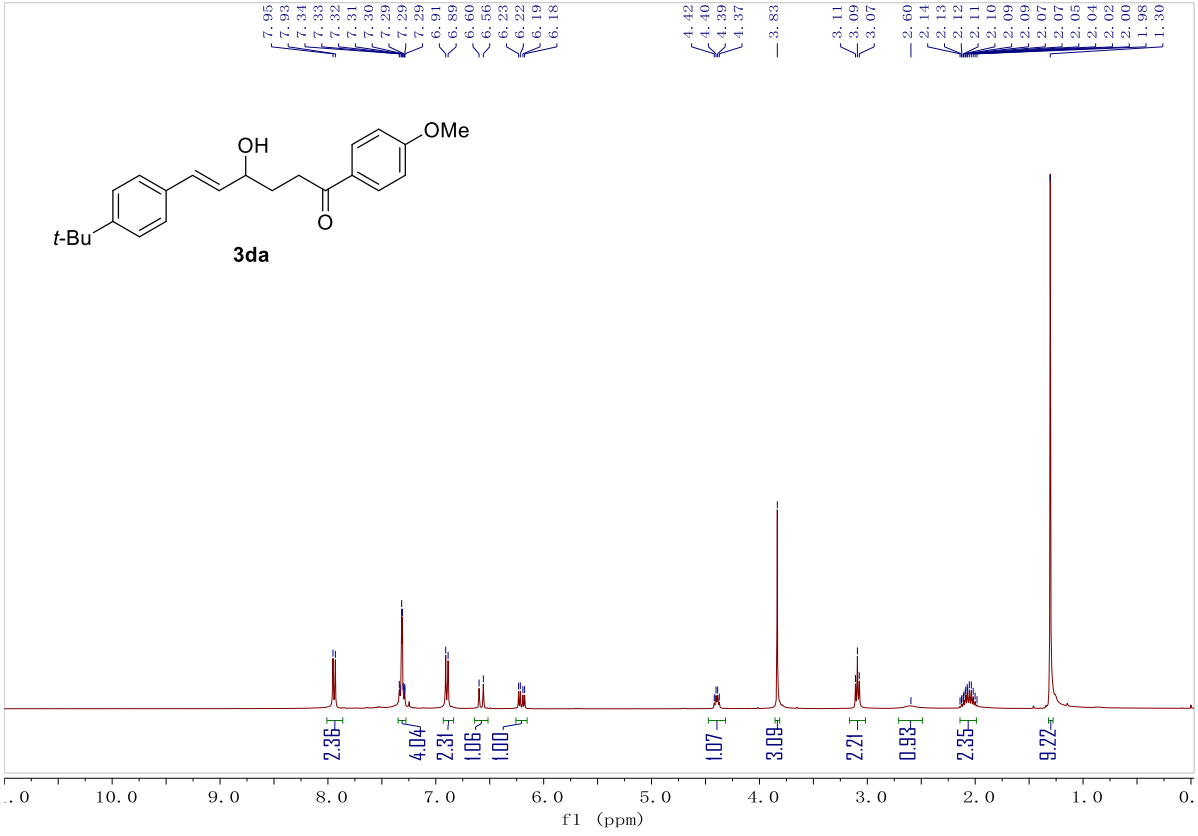


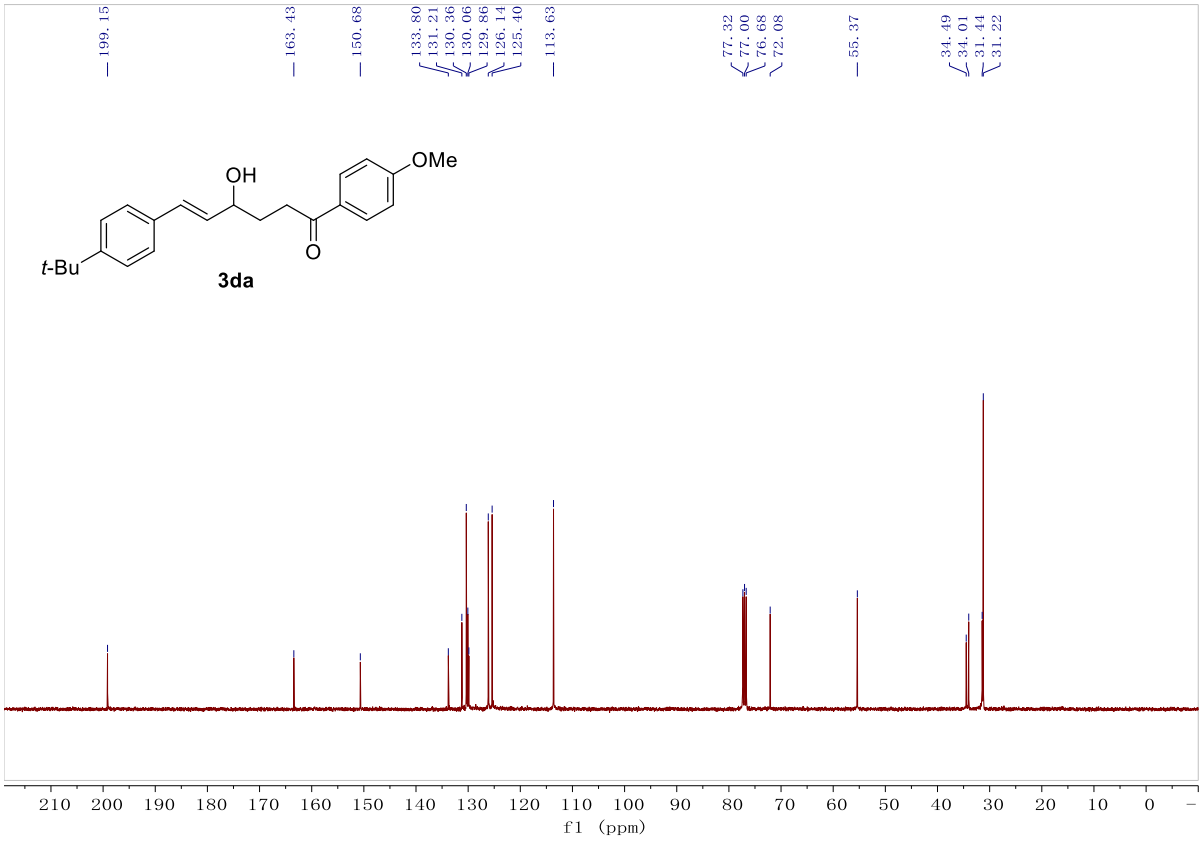
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ca



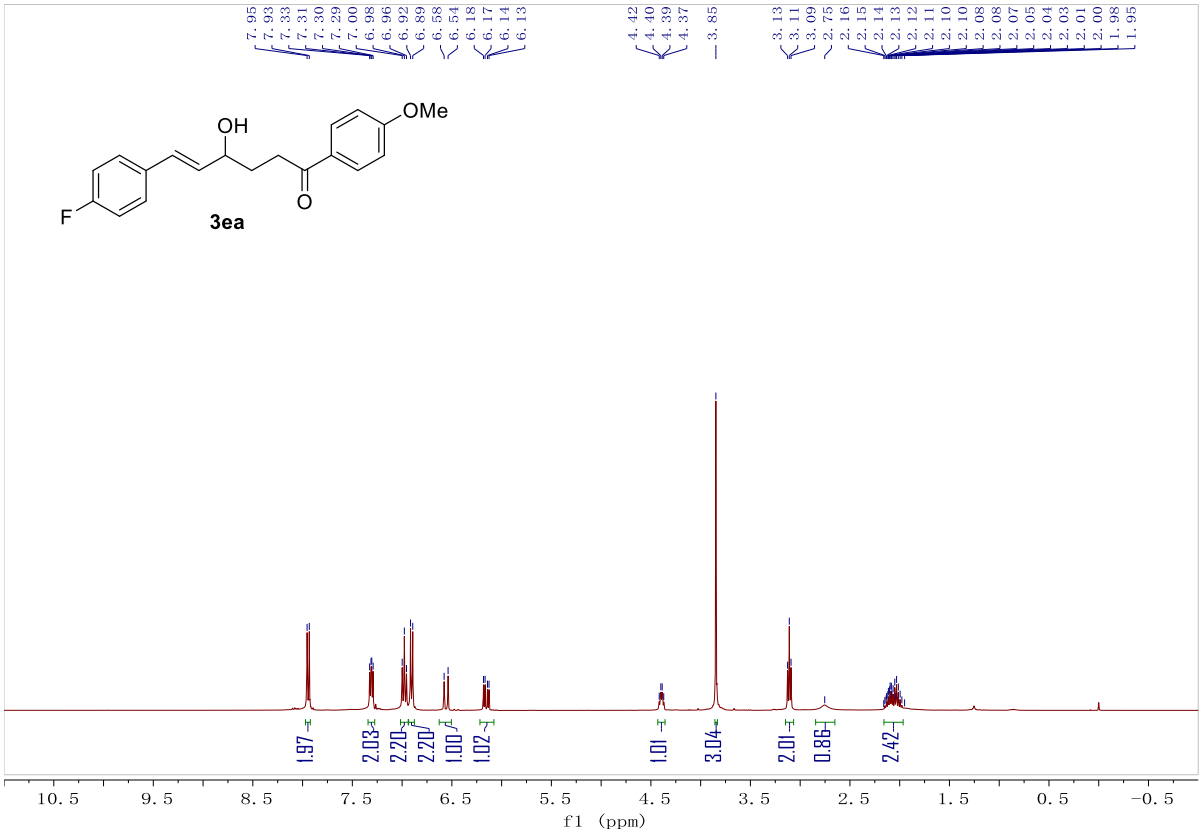


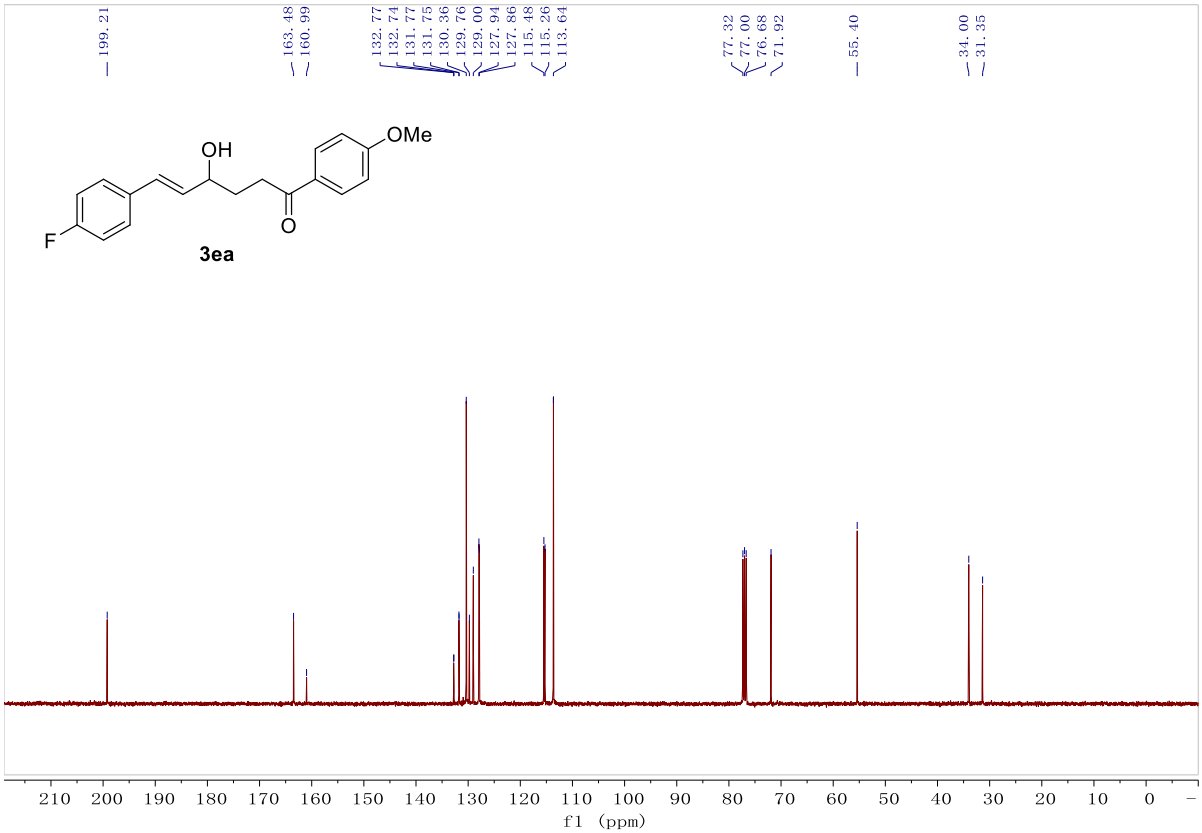
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3da

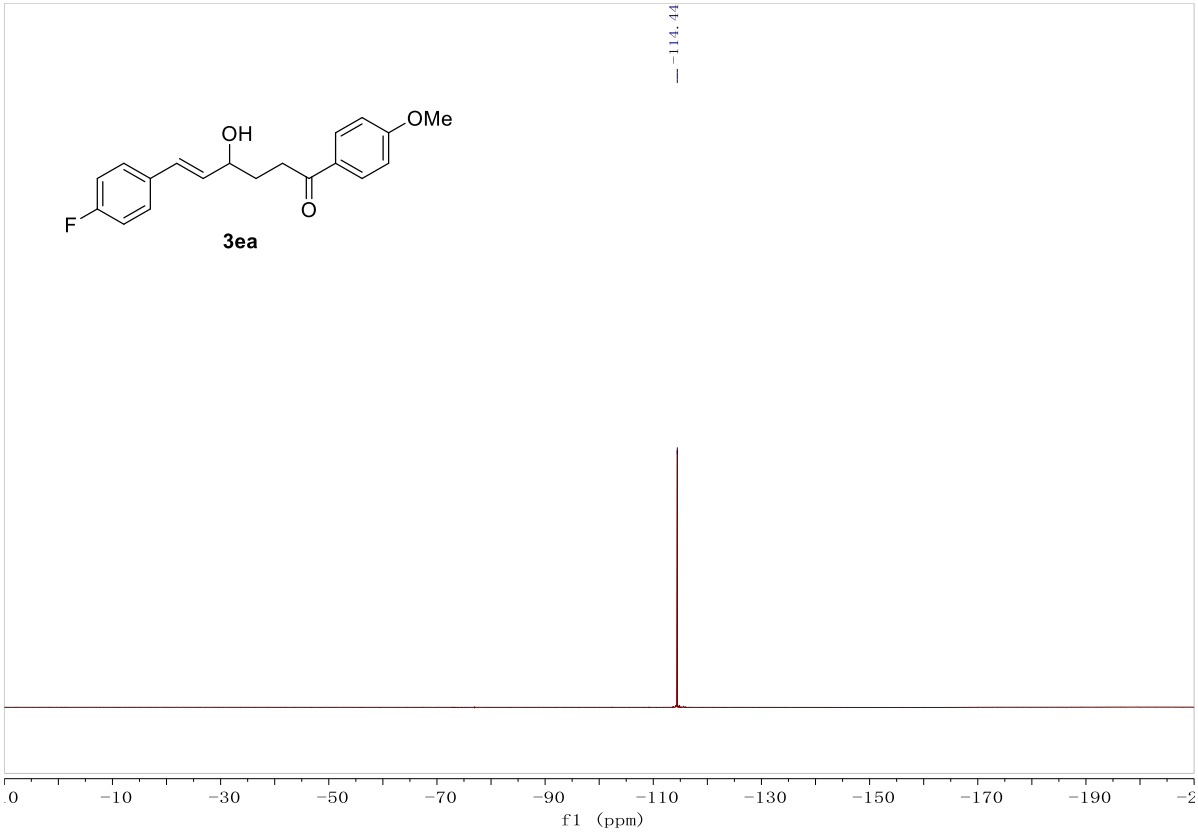




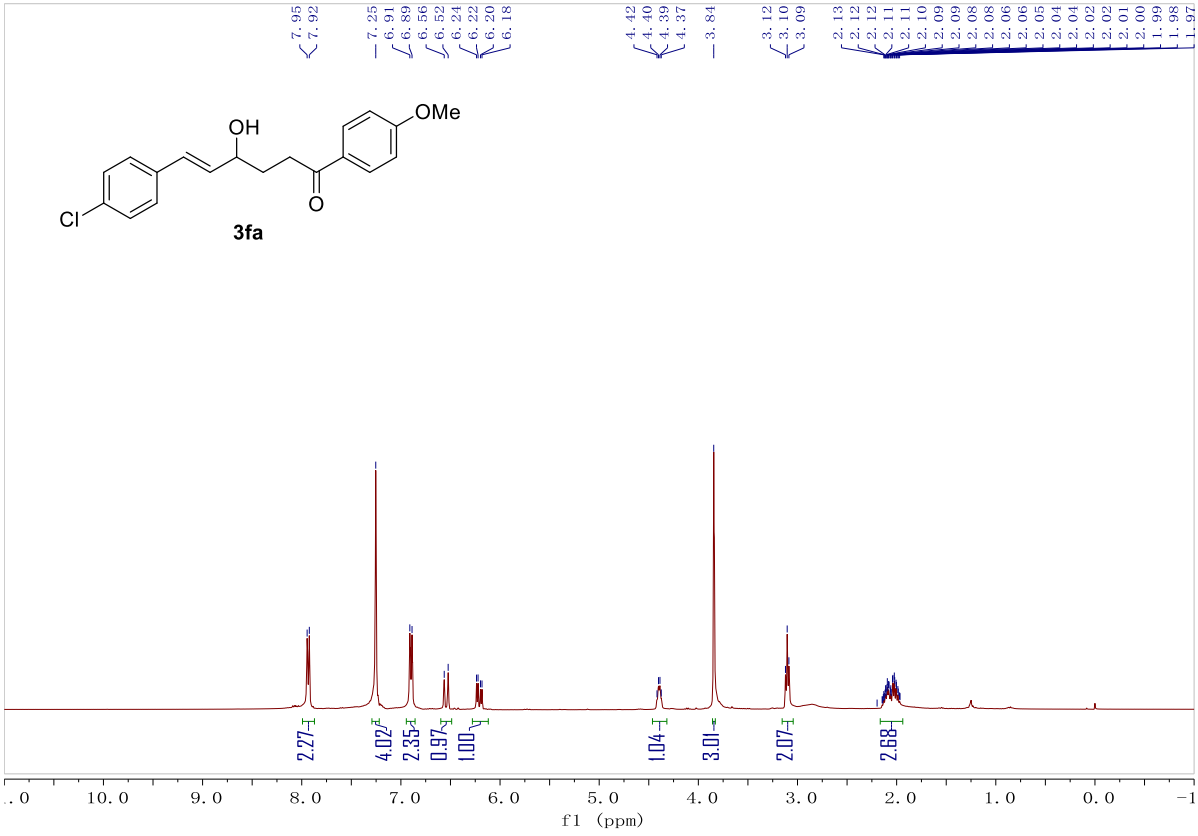
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ea

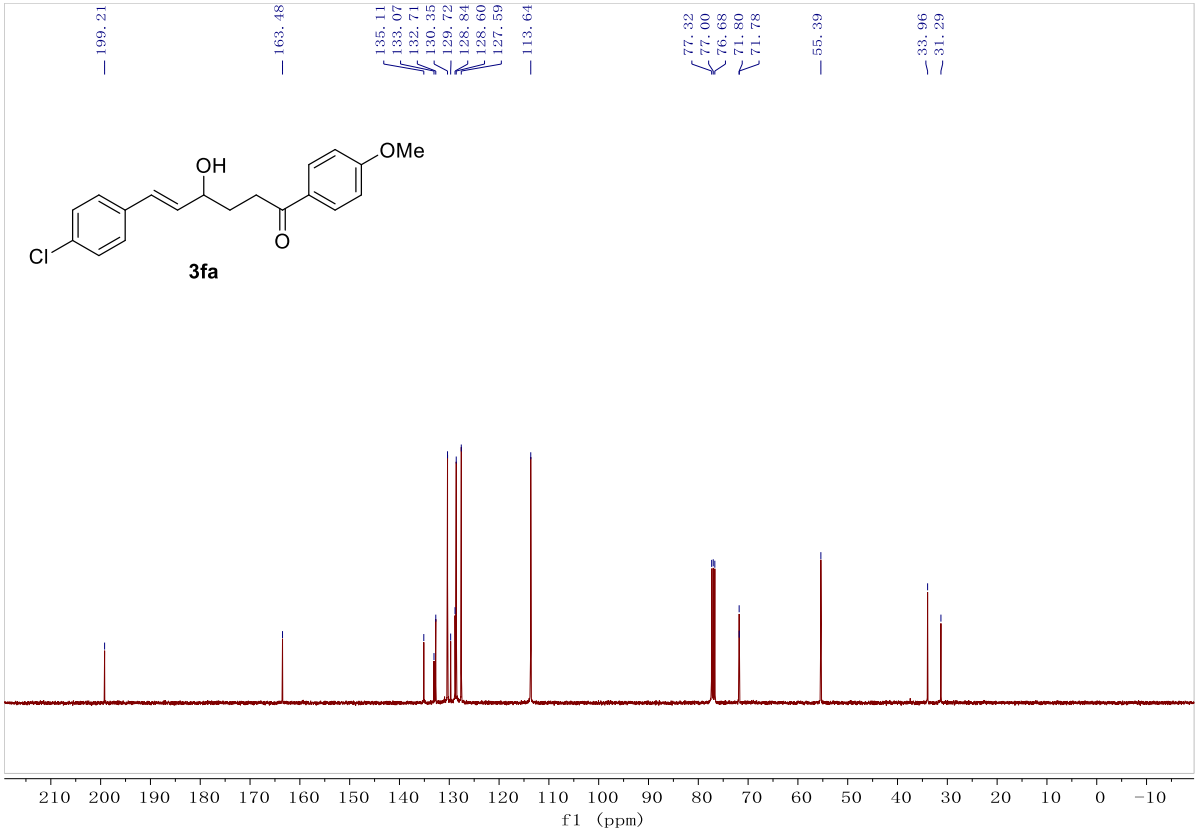




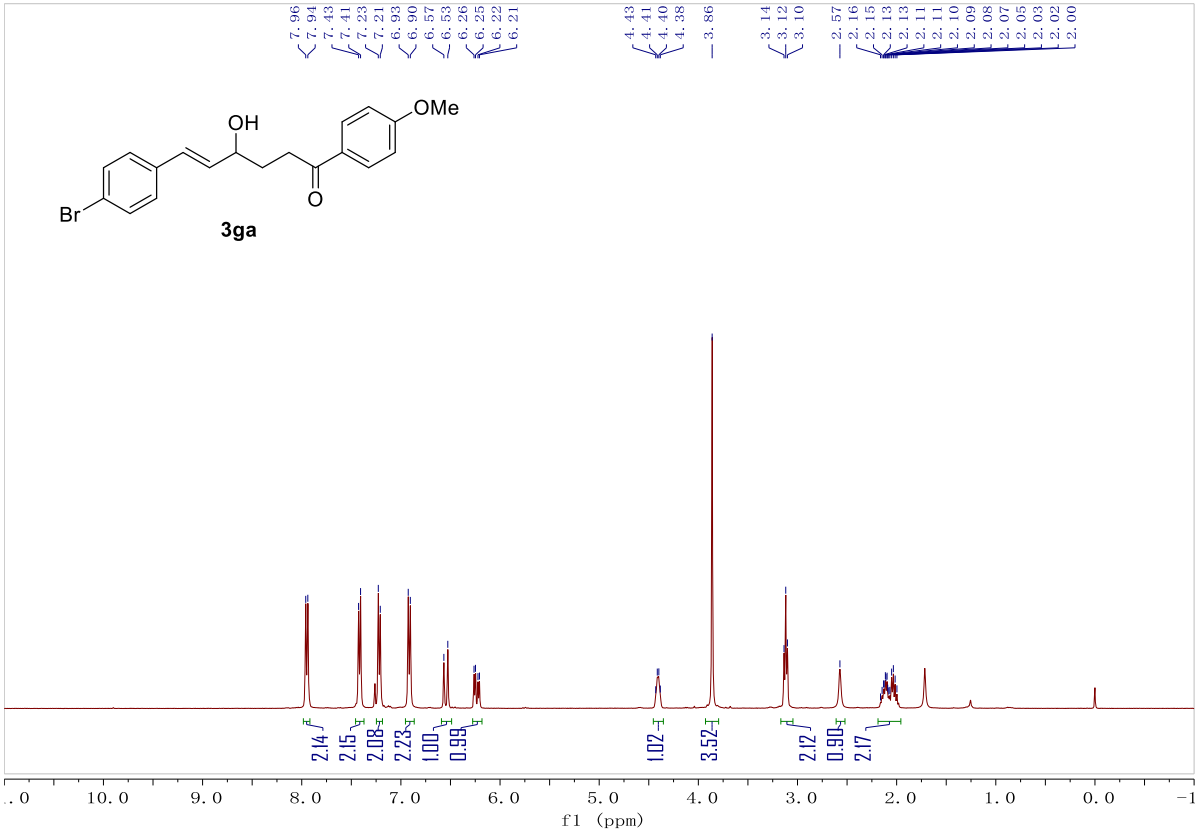


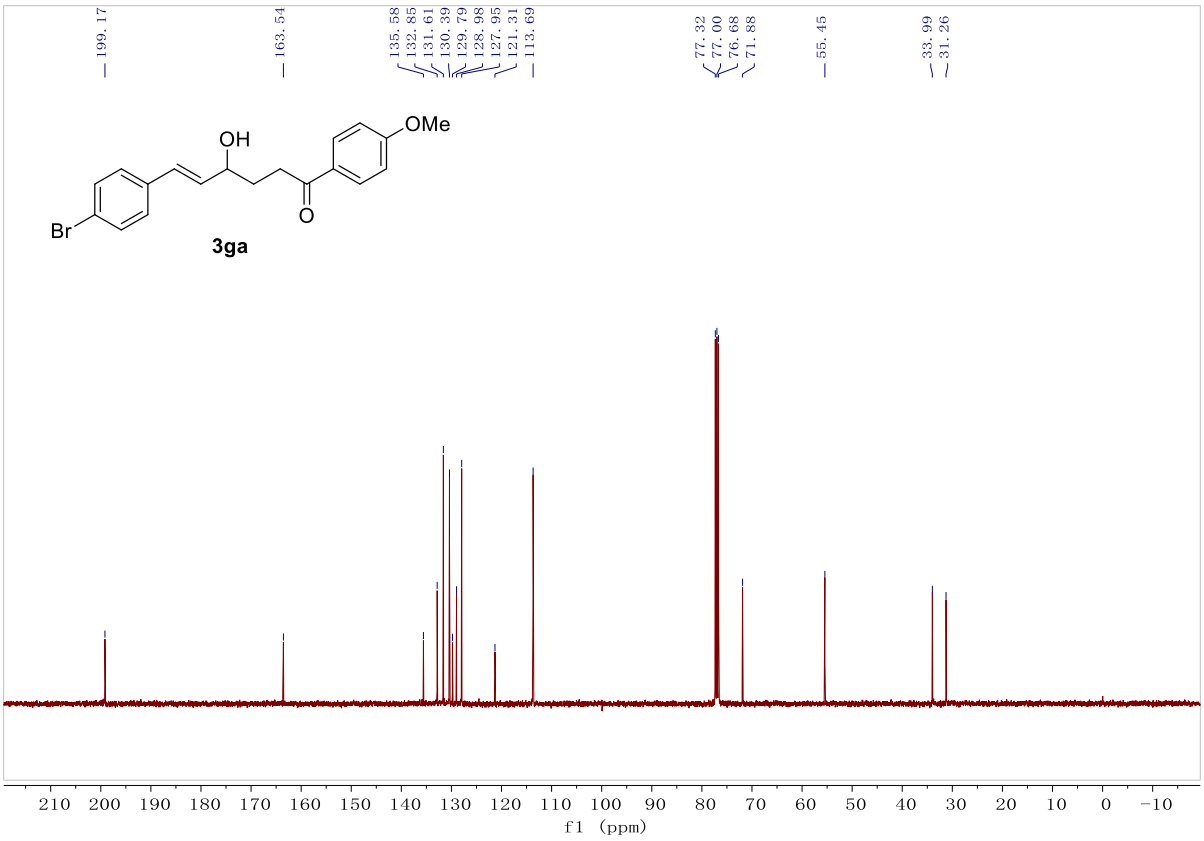
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3fa



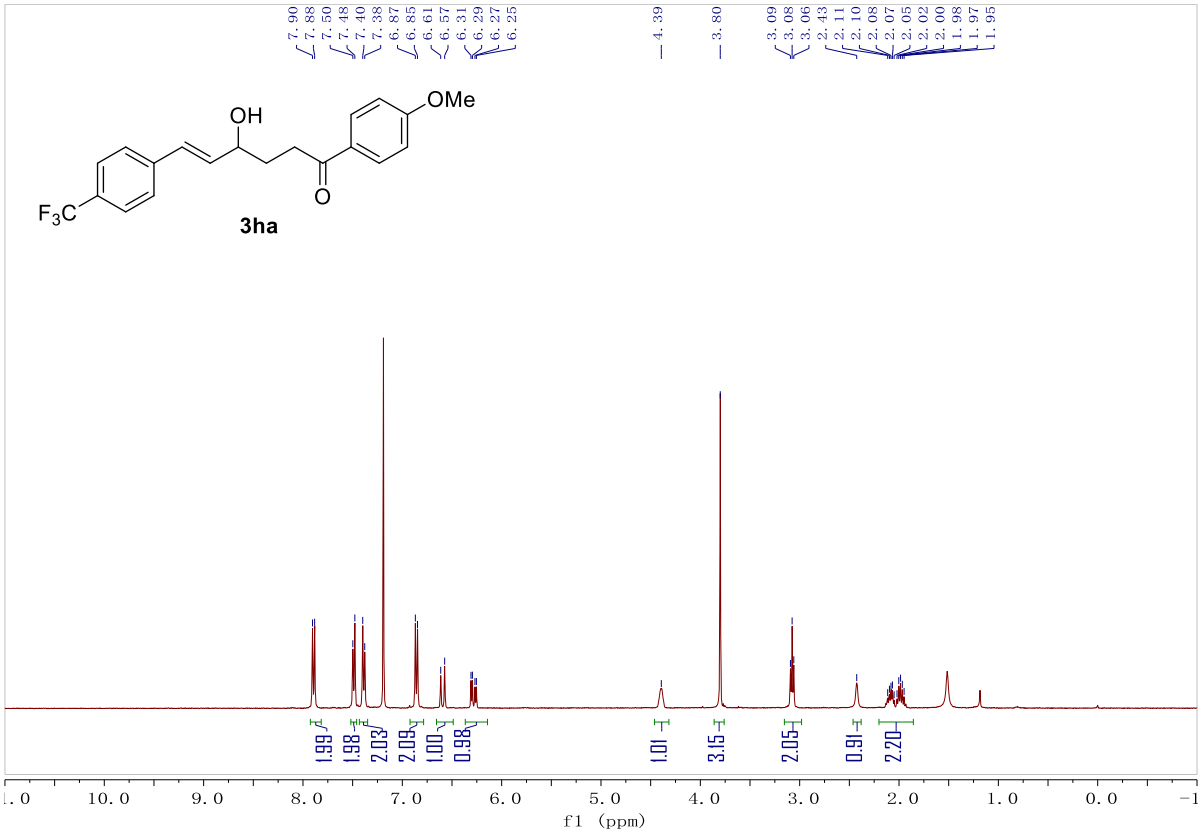


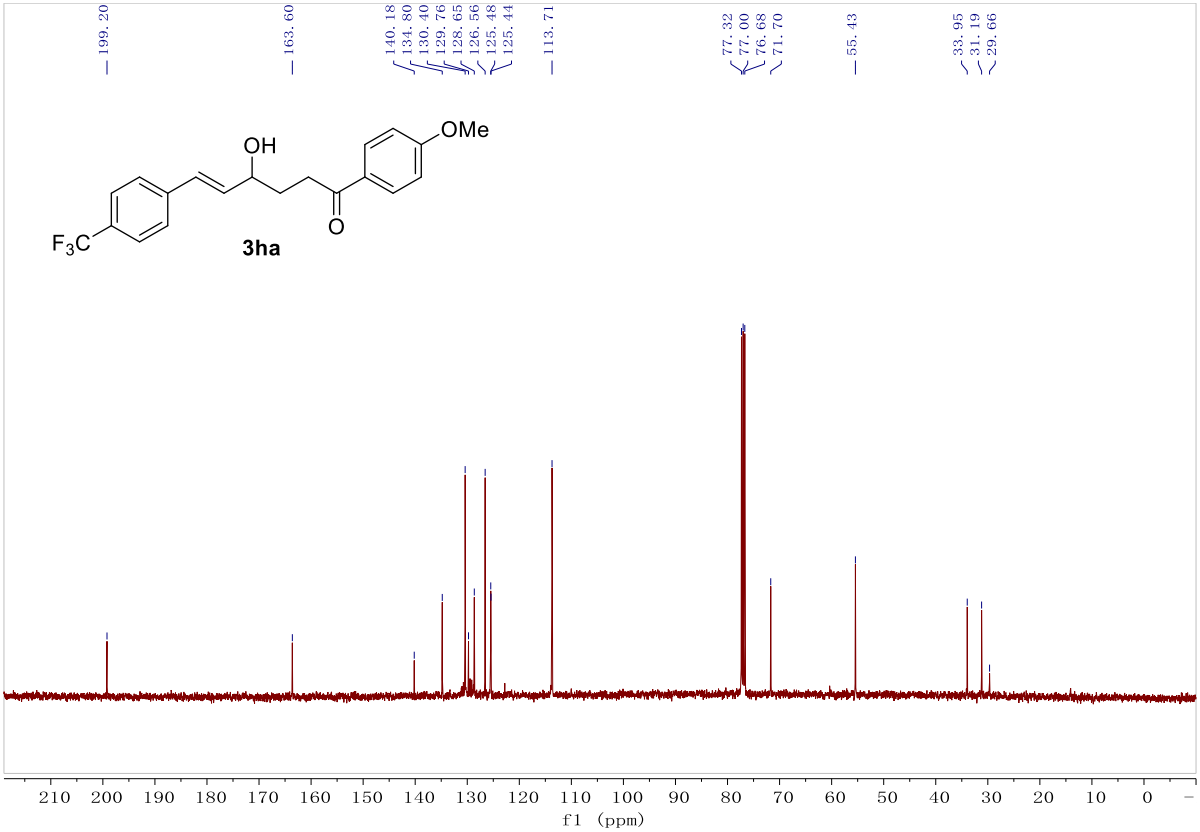
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ga





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product spectra of product 3ha

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140.18
134.80
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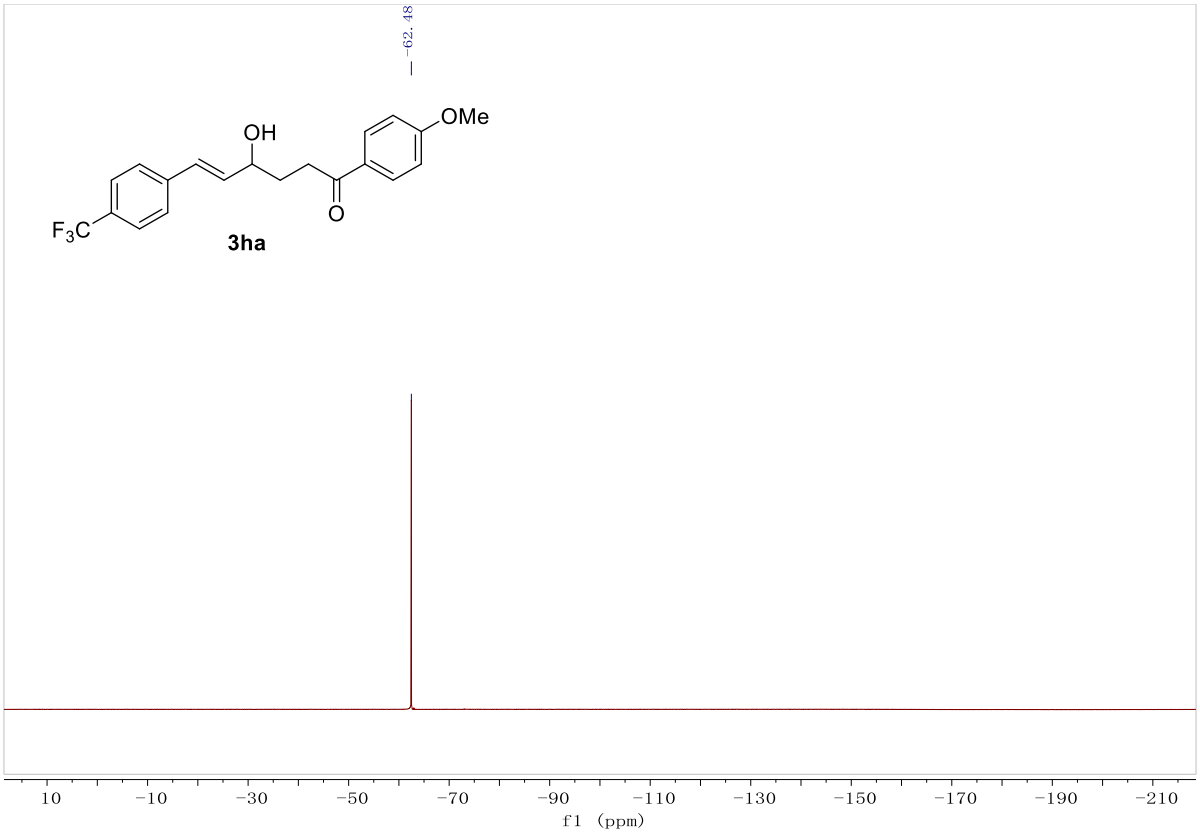
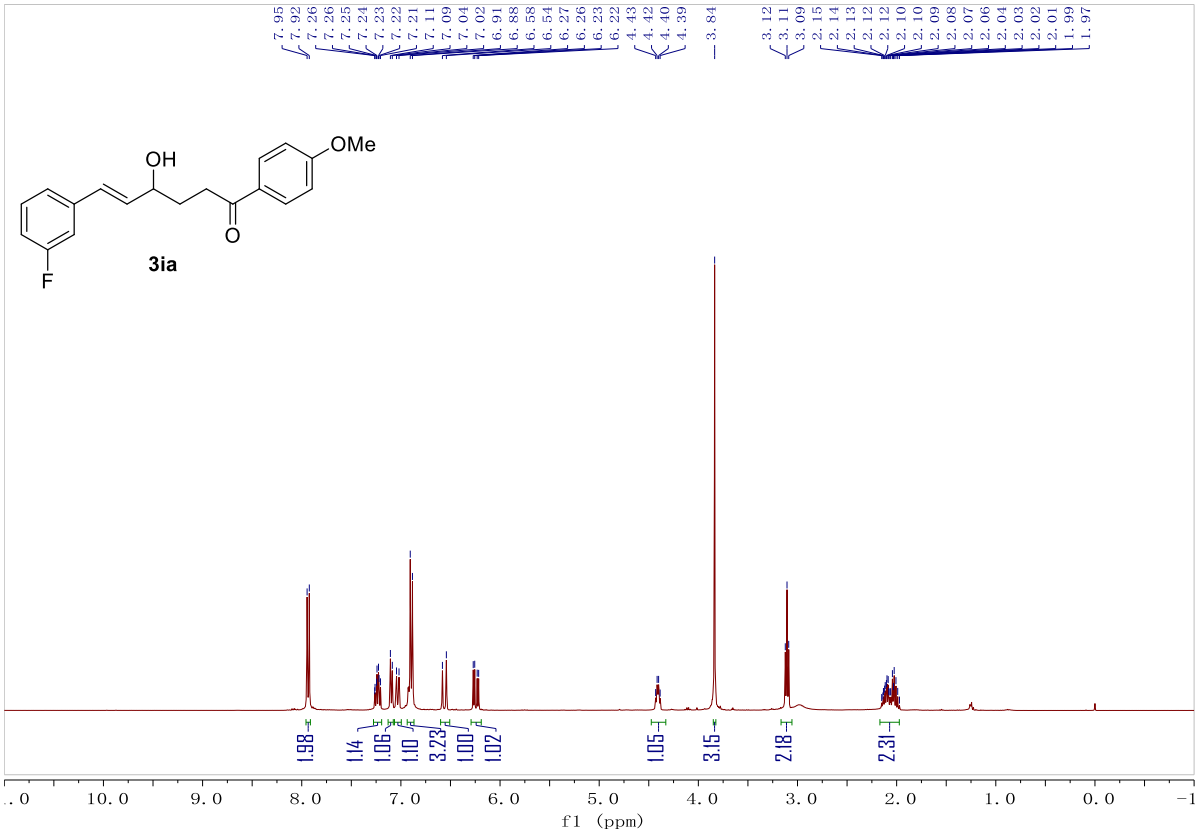
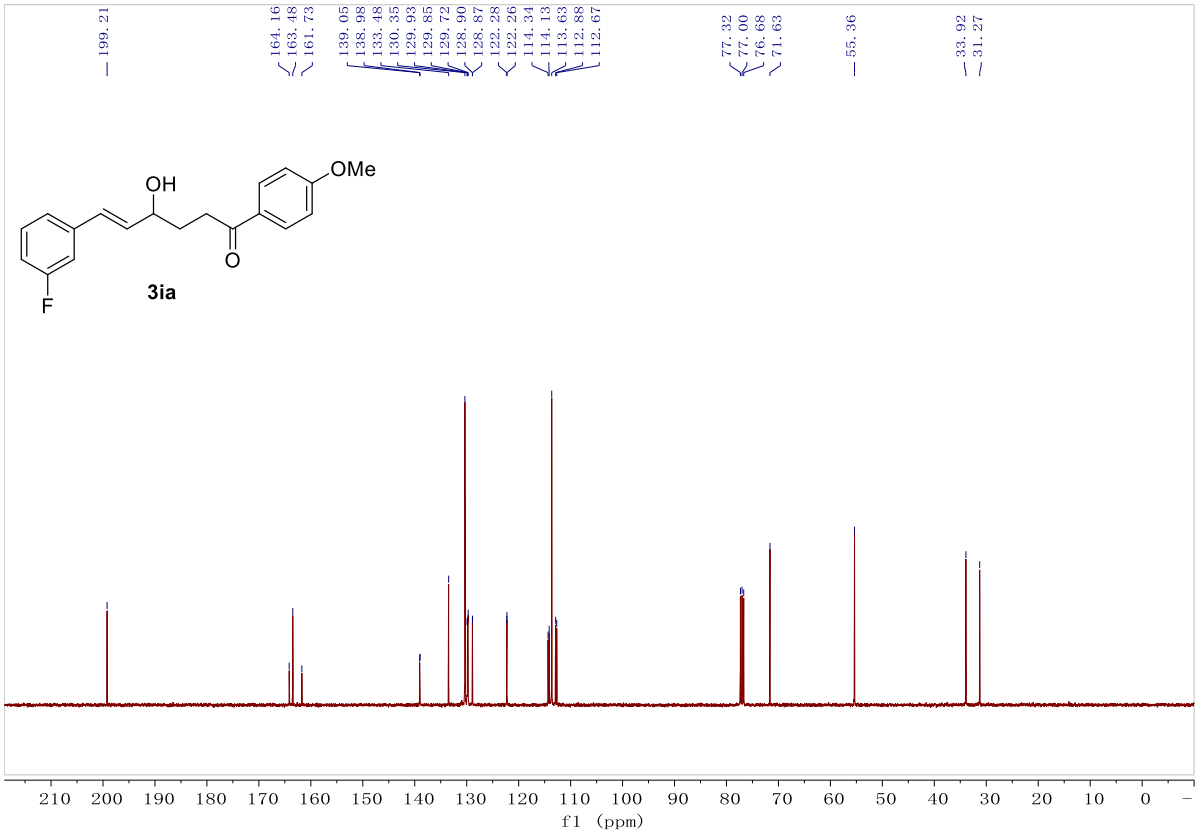
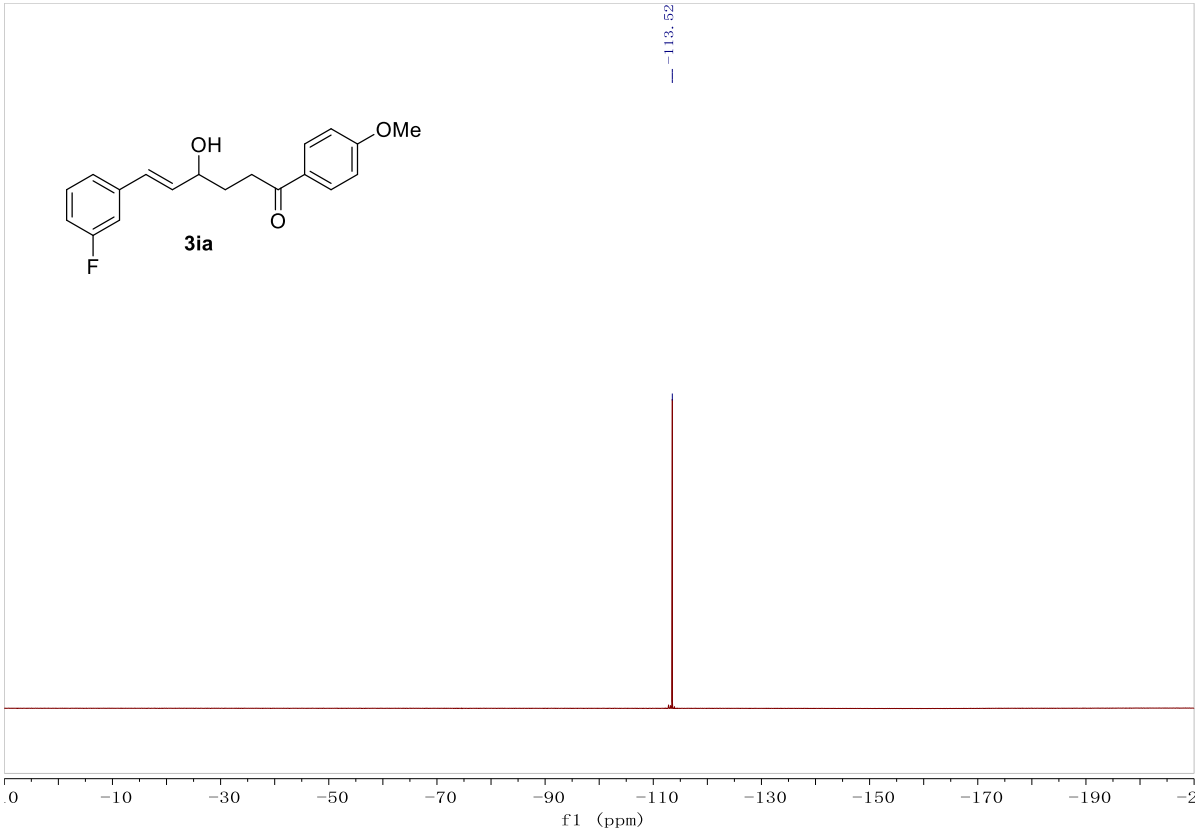
128.65
126.56
125.48
125.44
113.71
77.32
77.00
76.68
71.70
55.43
33.95
31.19
29.66
OH
OMe
F3C
O
3ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.48
OH
OMe
F3C
O
3ha
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

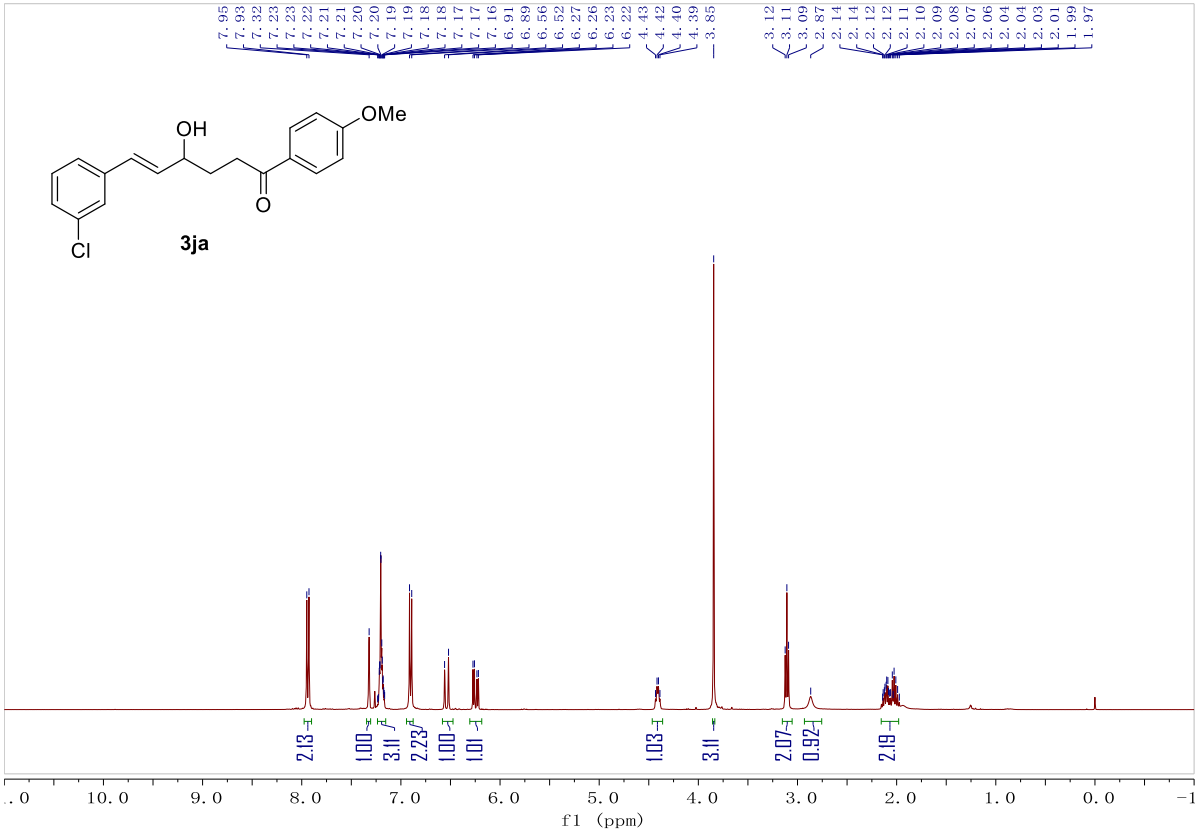
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product spectra of product 3ia

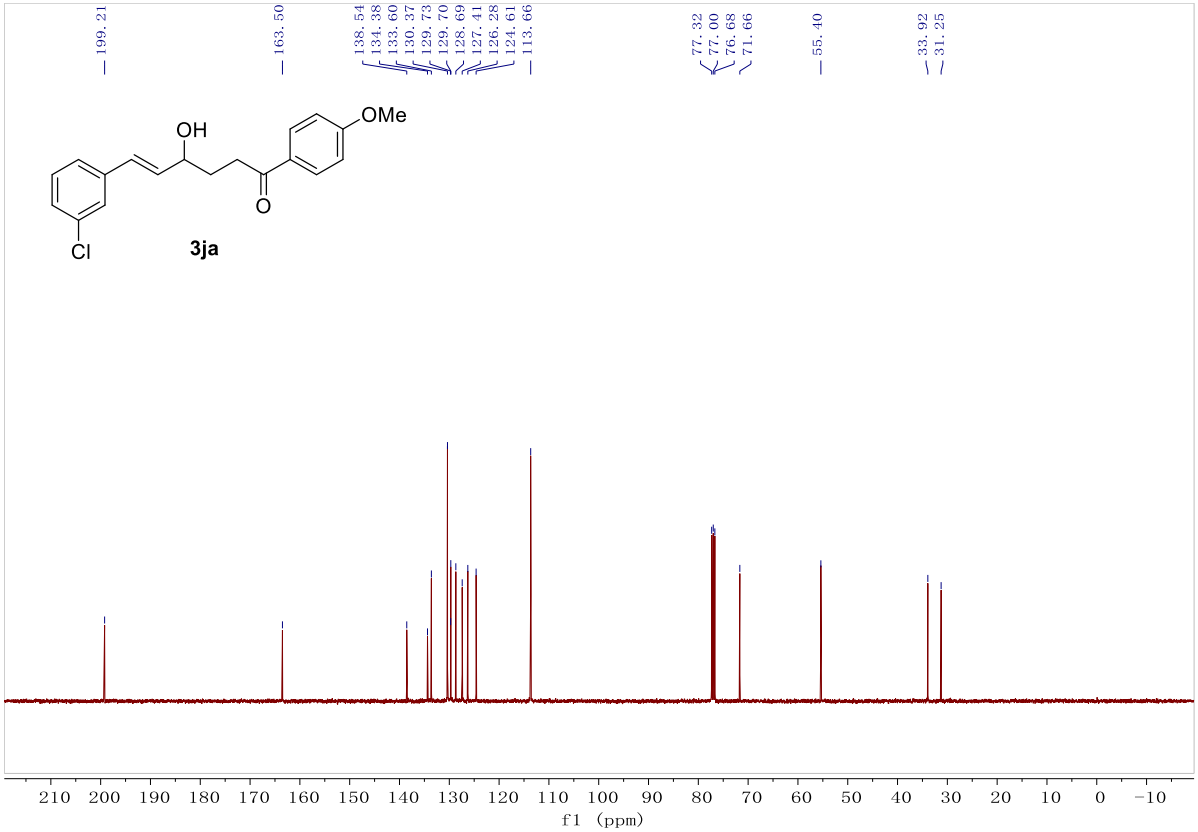




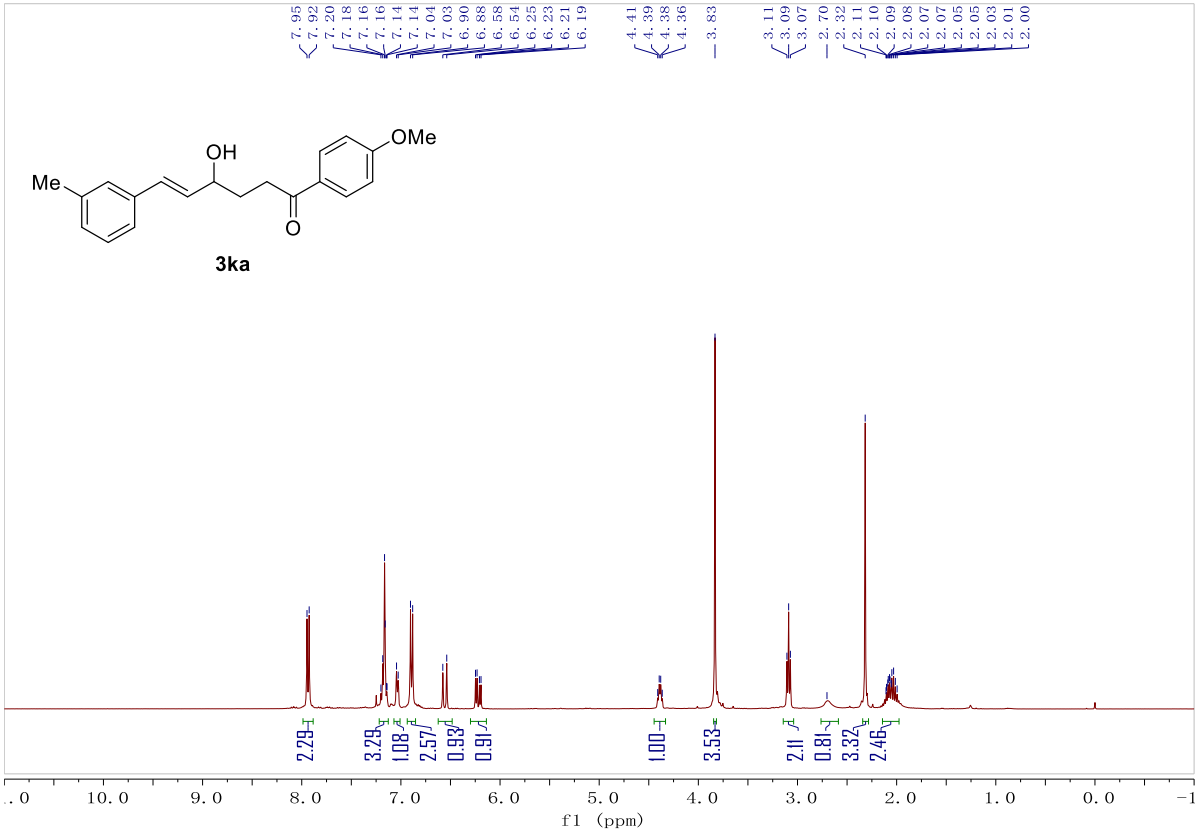


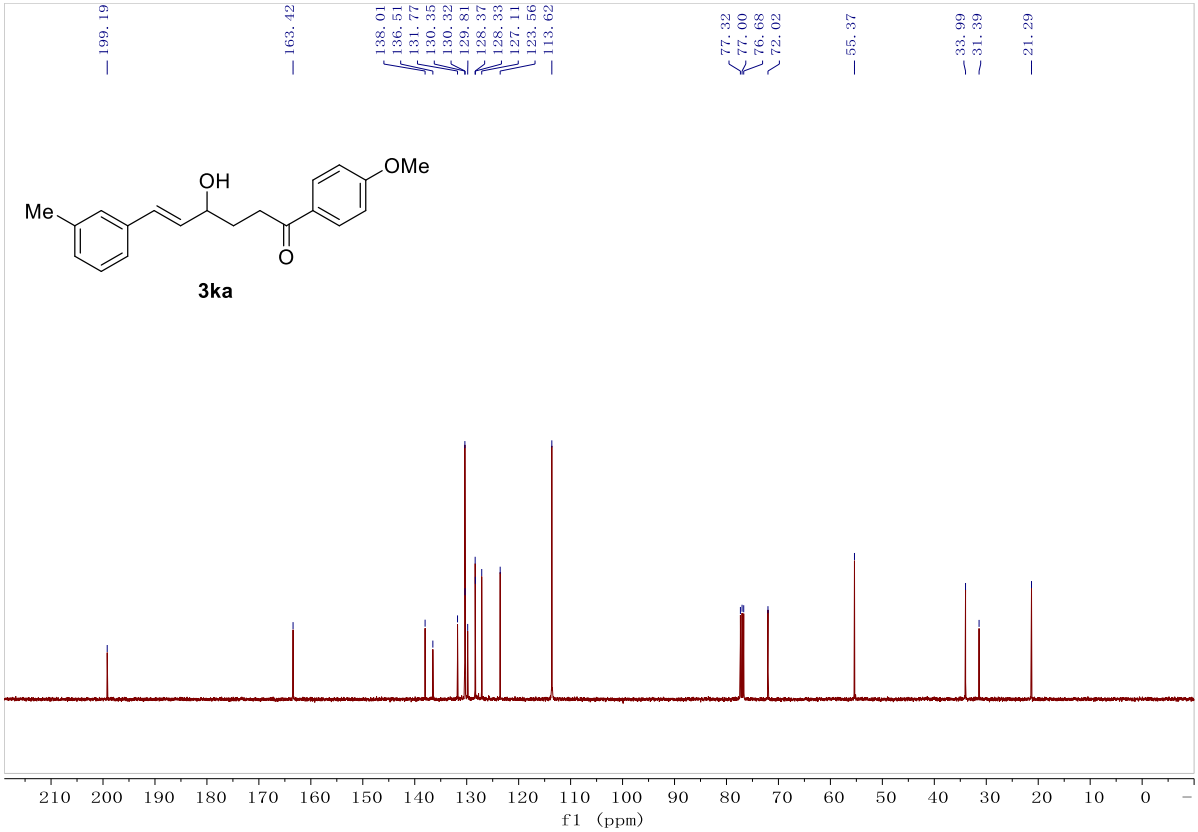
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ja



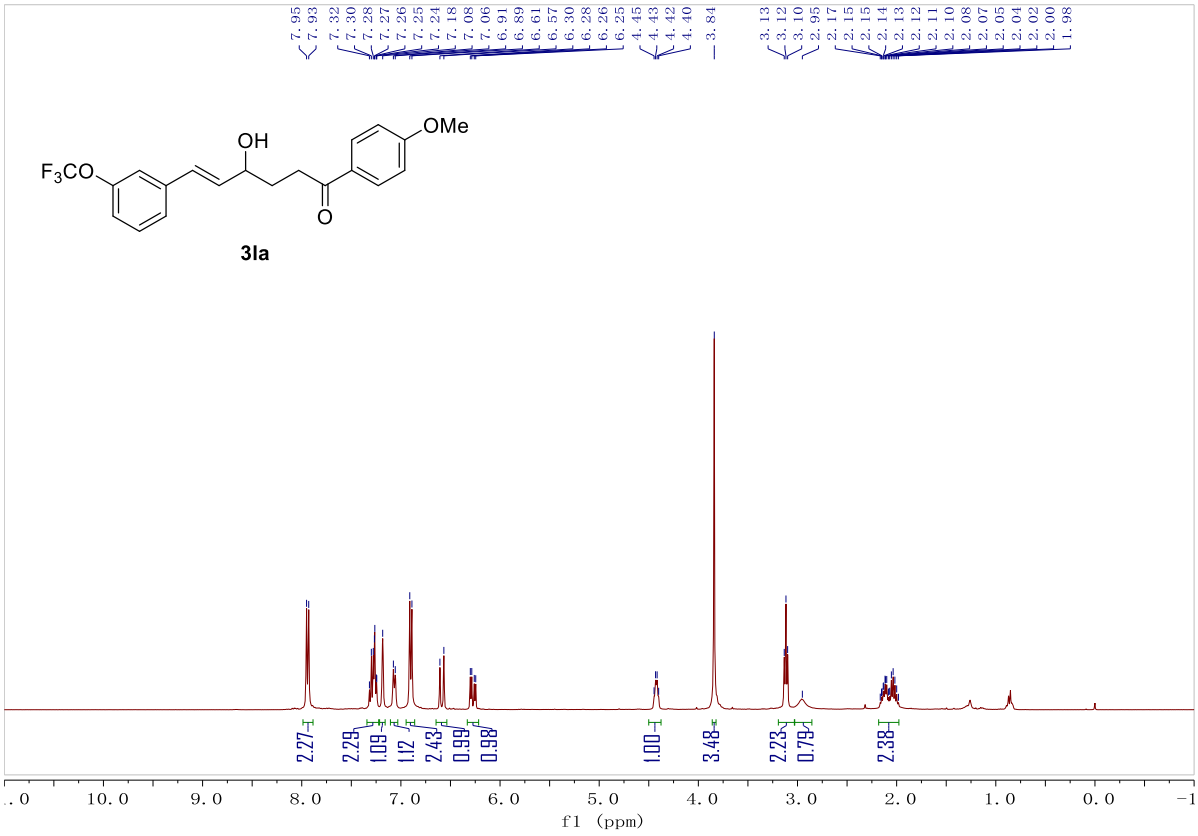


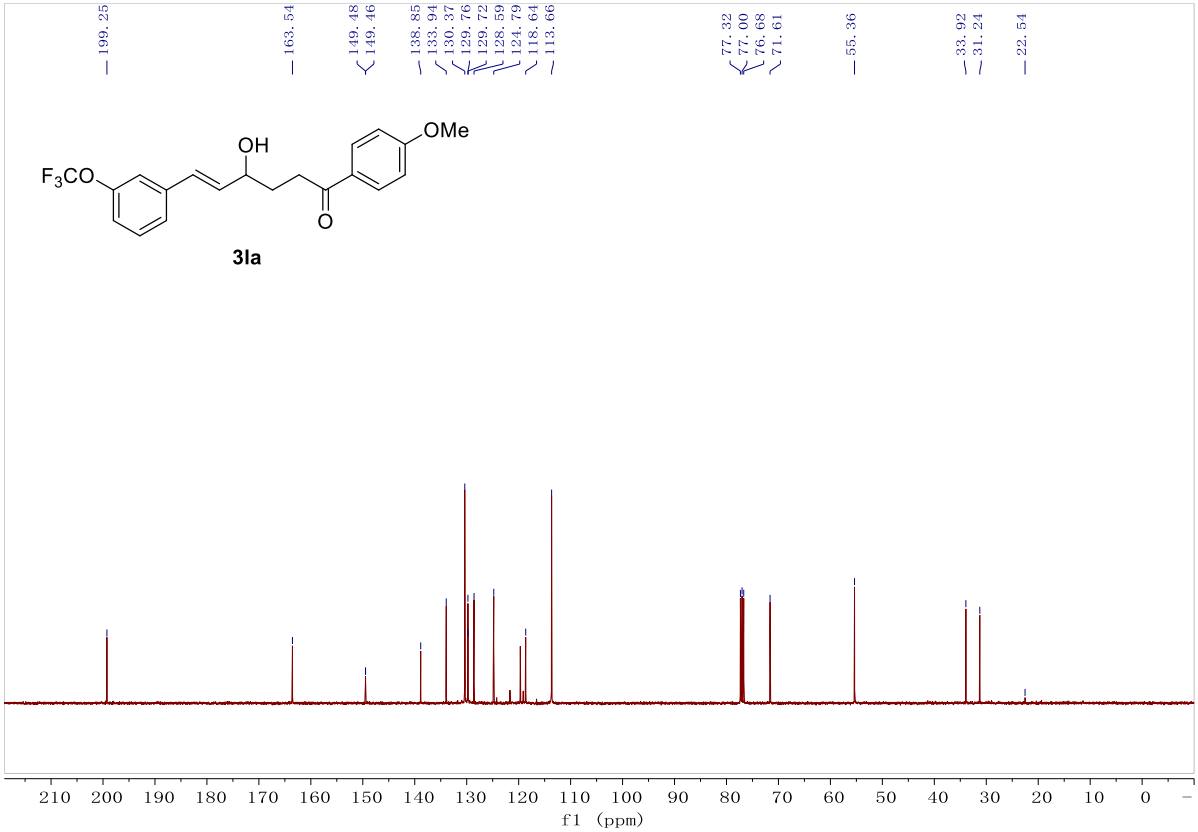
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ka





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}C NMR (376 MHz, $CDCl_3$) spectra of product 3la

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149.46
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118.64
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77.32
77.00
76.68
71.61
55.36
33.92
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3la
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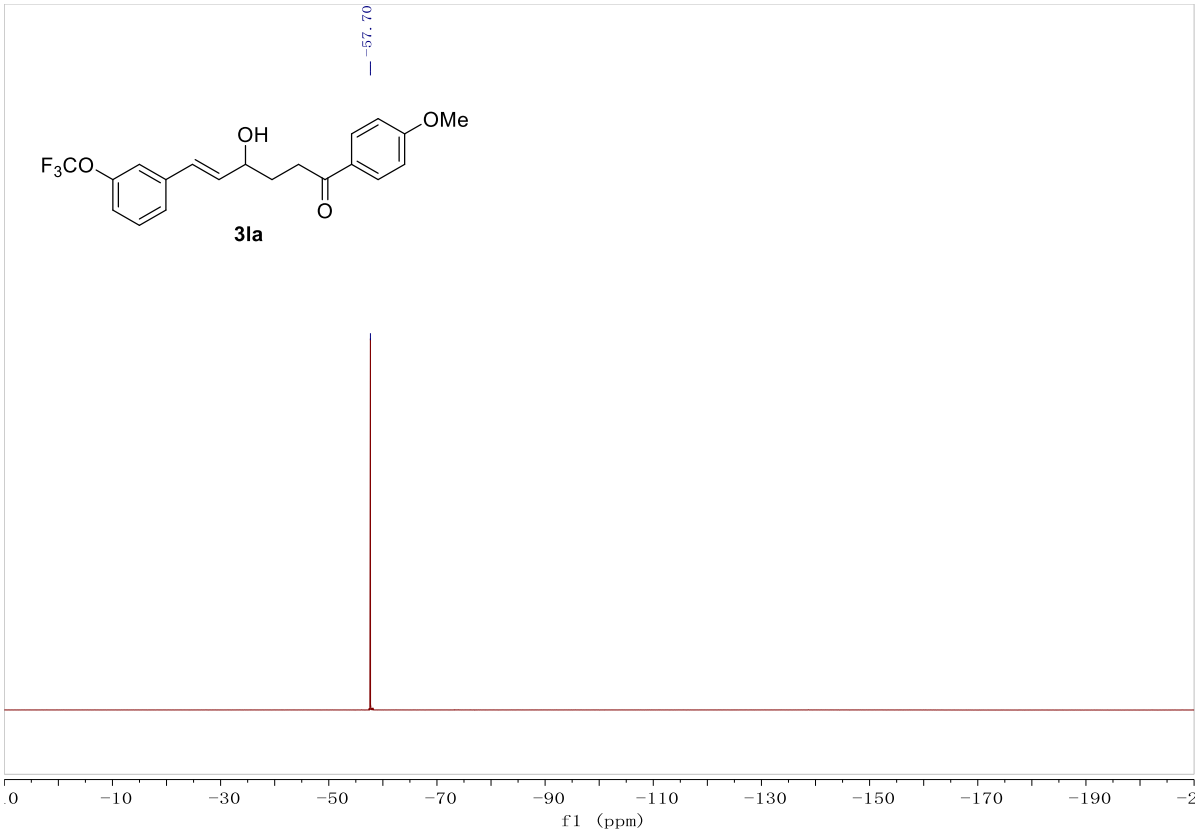
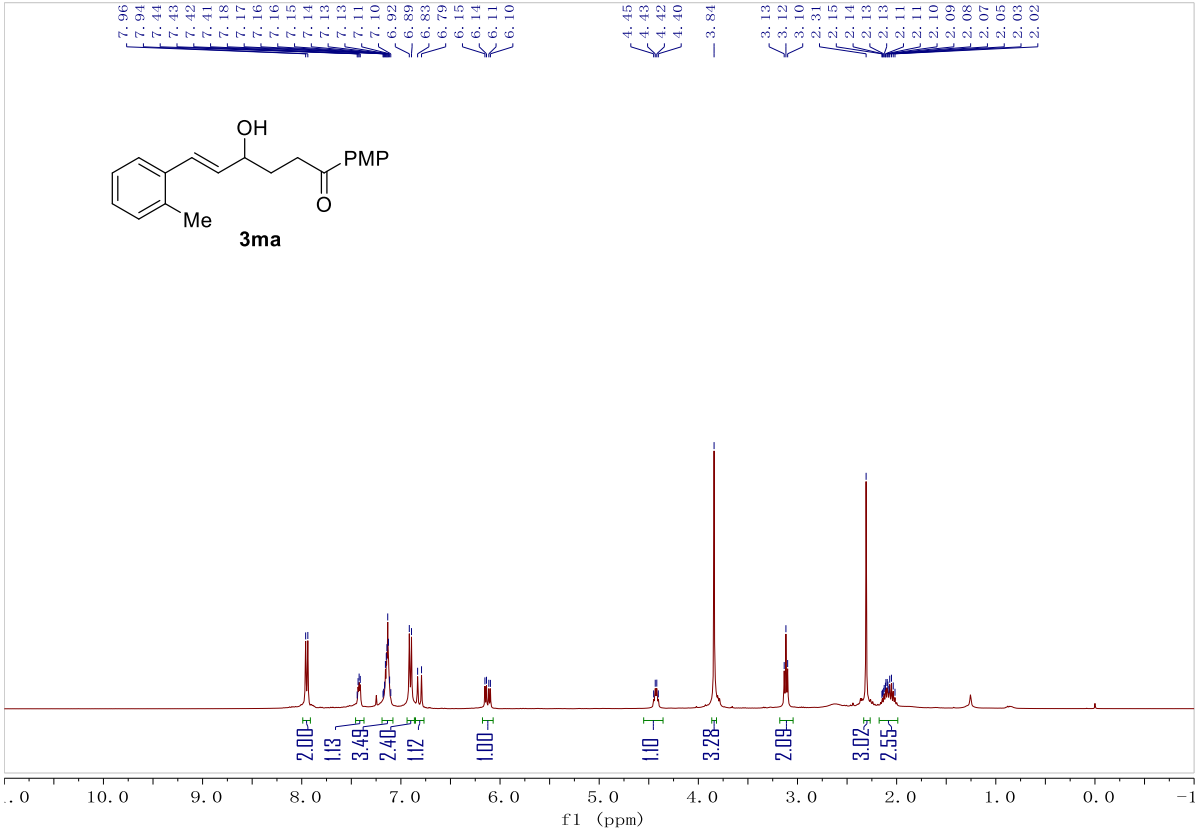
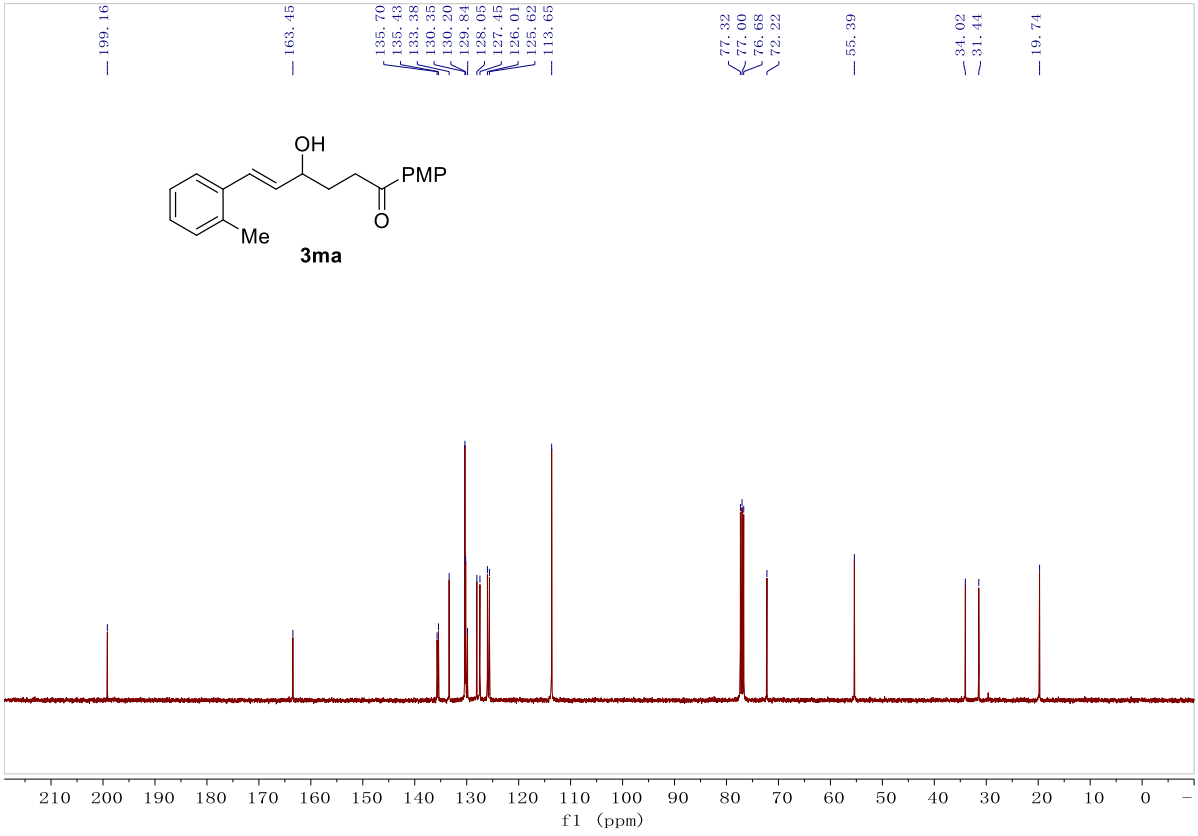
f1 (ppm)

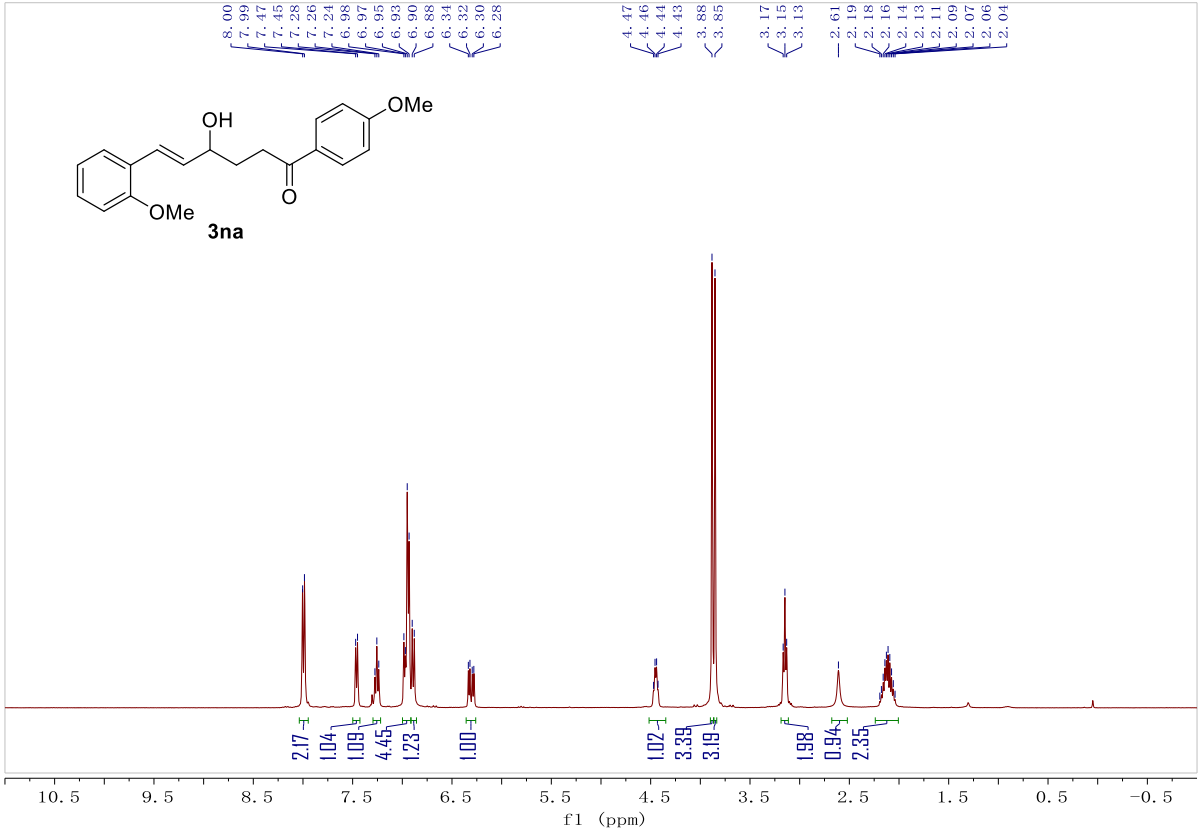

-57.70
OH
OMe
F3CO
O
3la
0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)

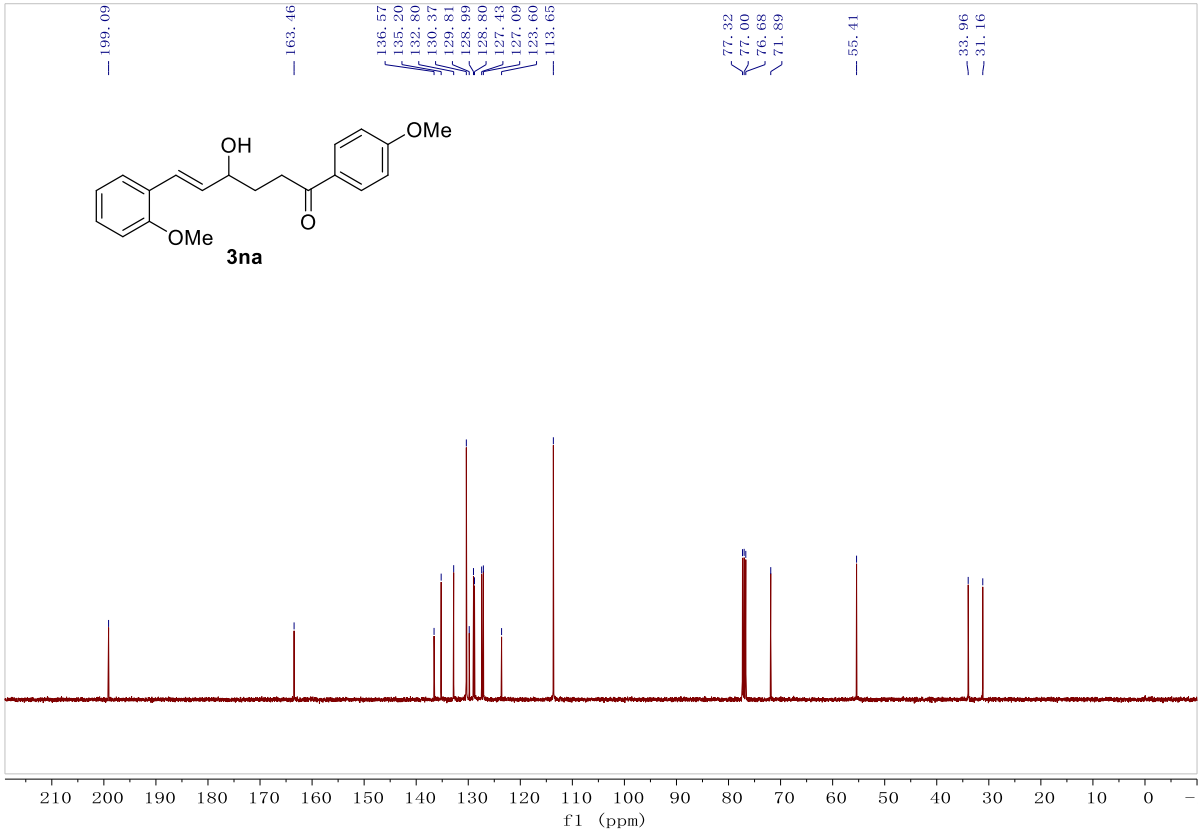
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ma



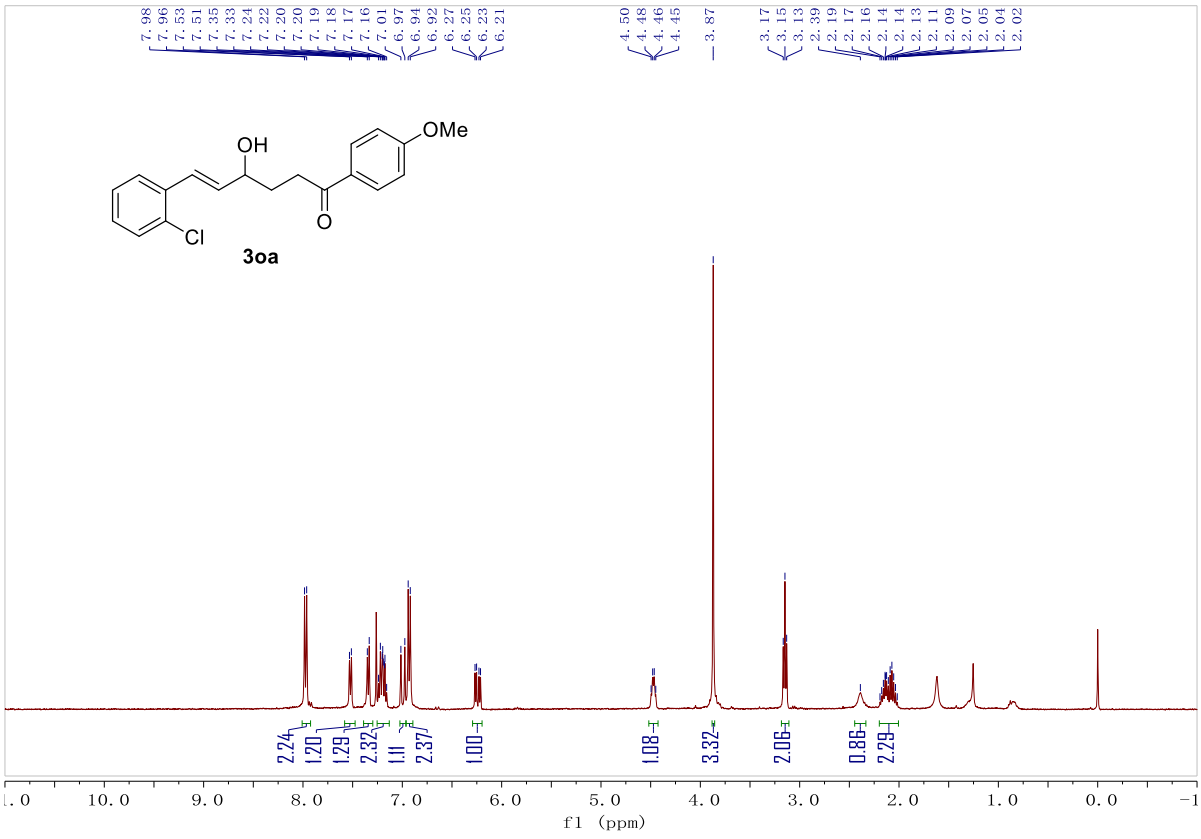


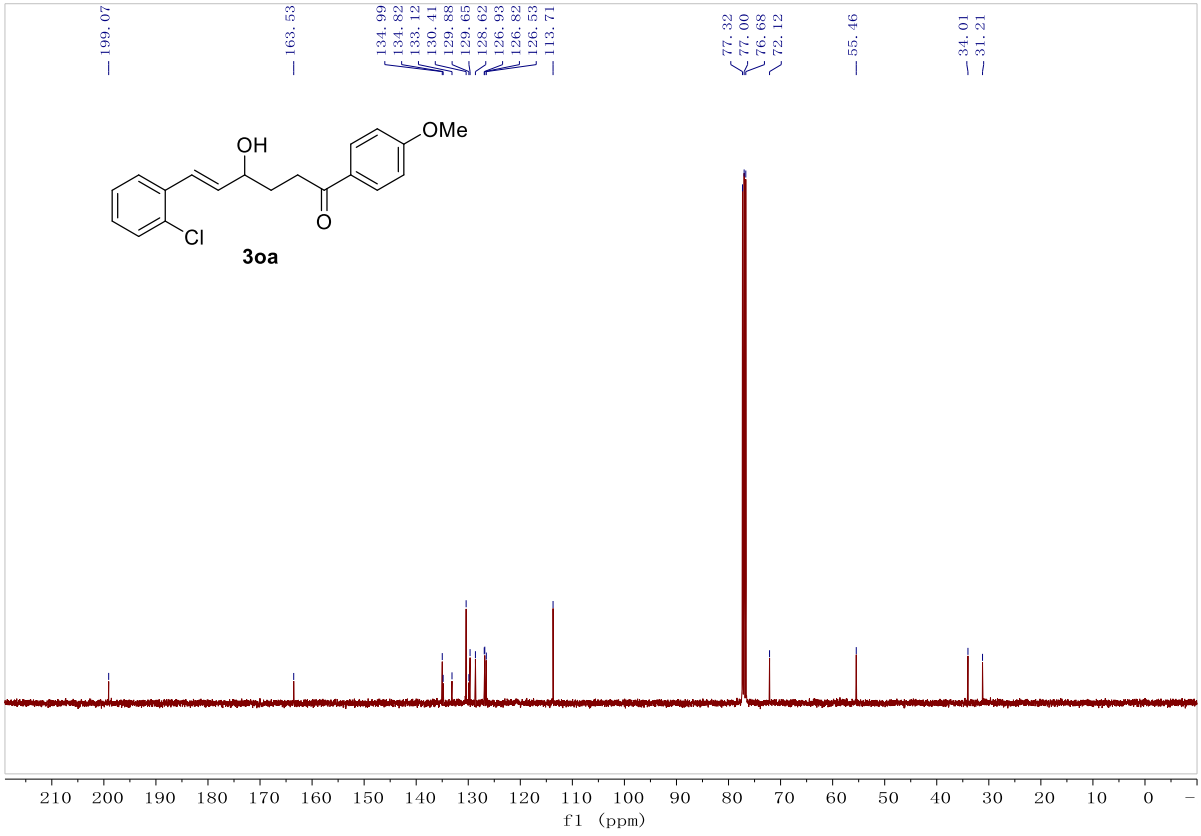
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3na



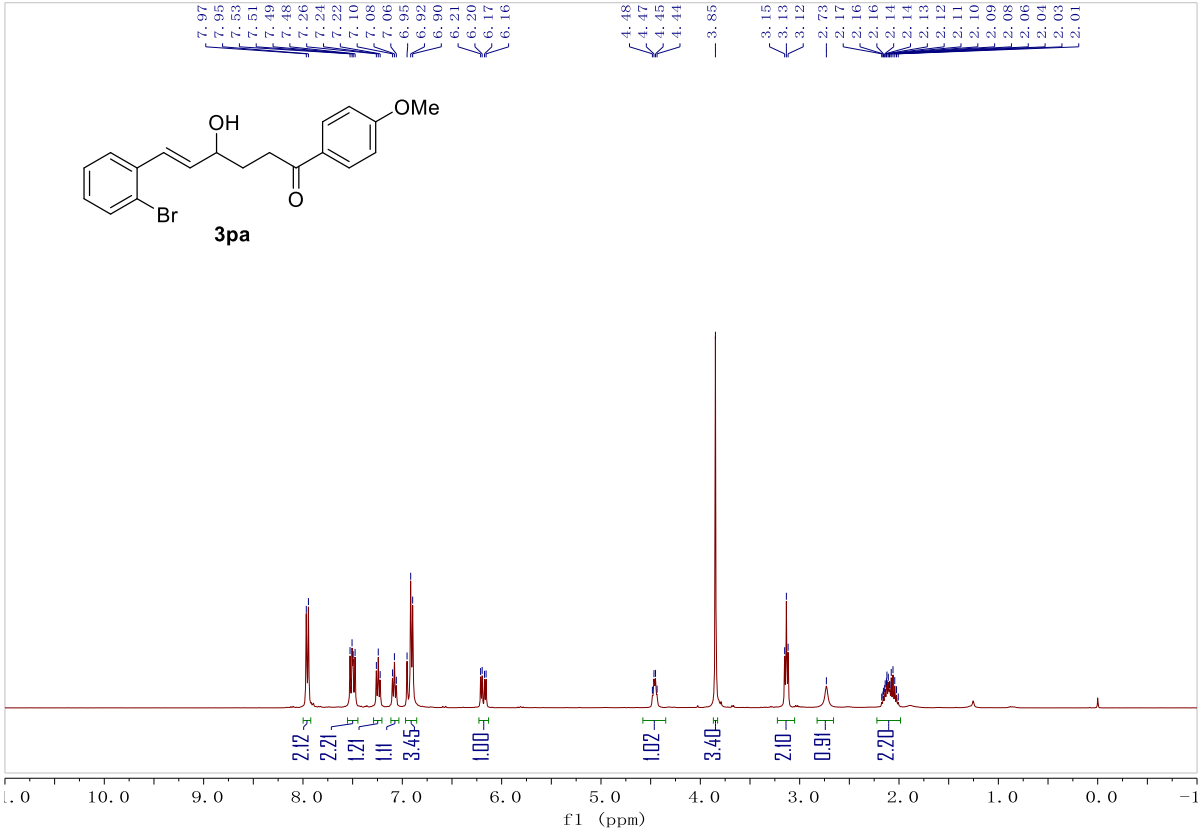


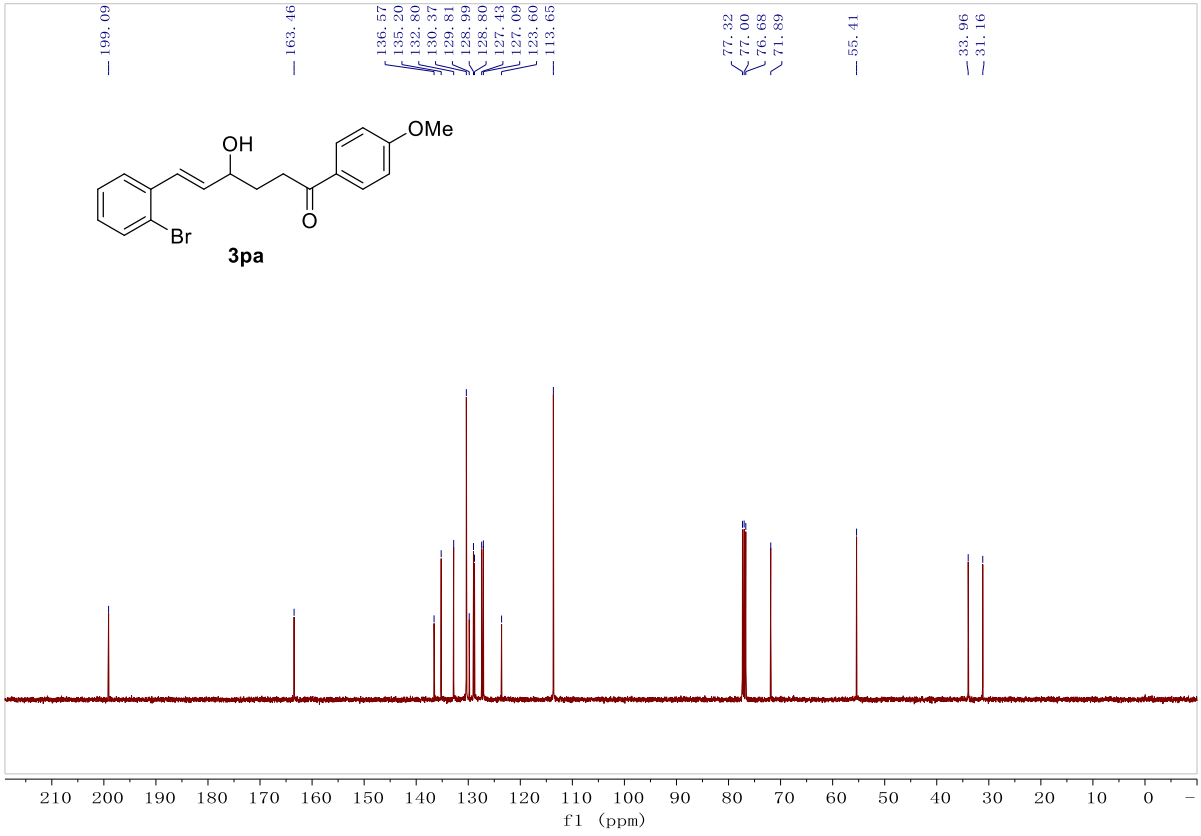
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3oa



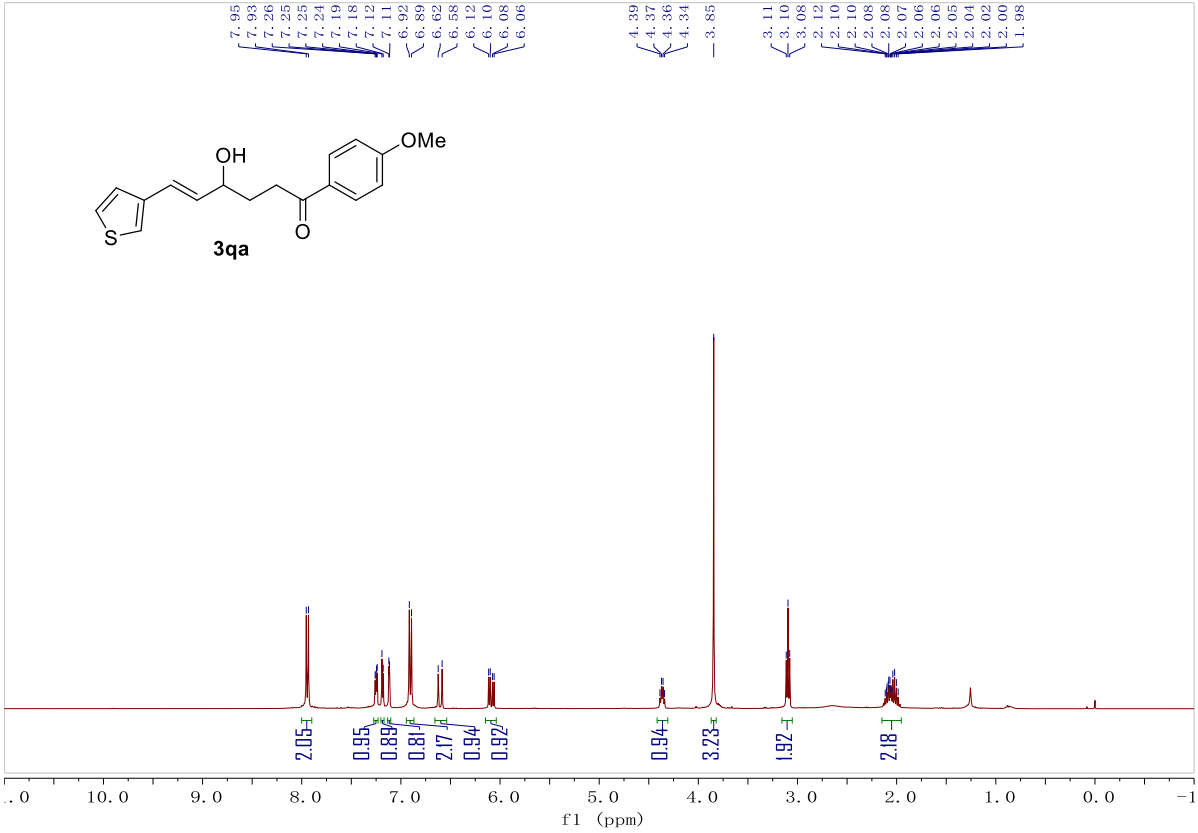


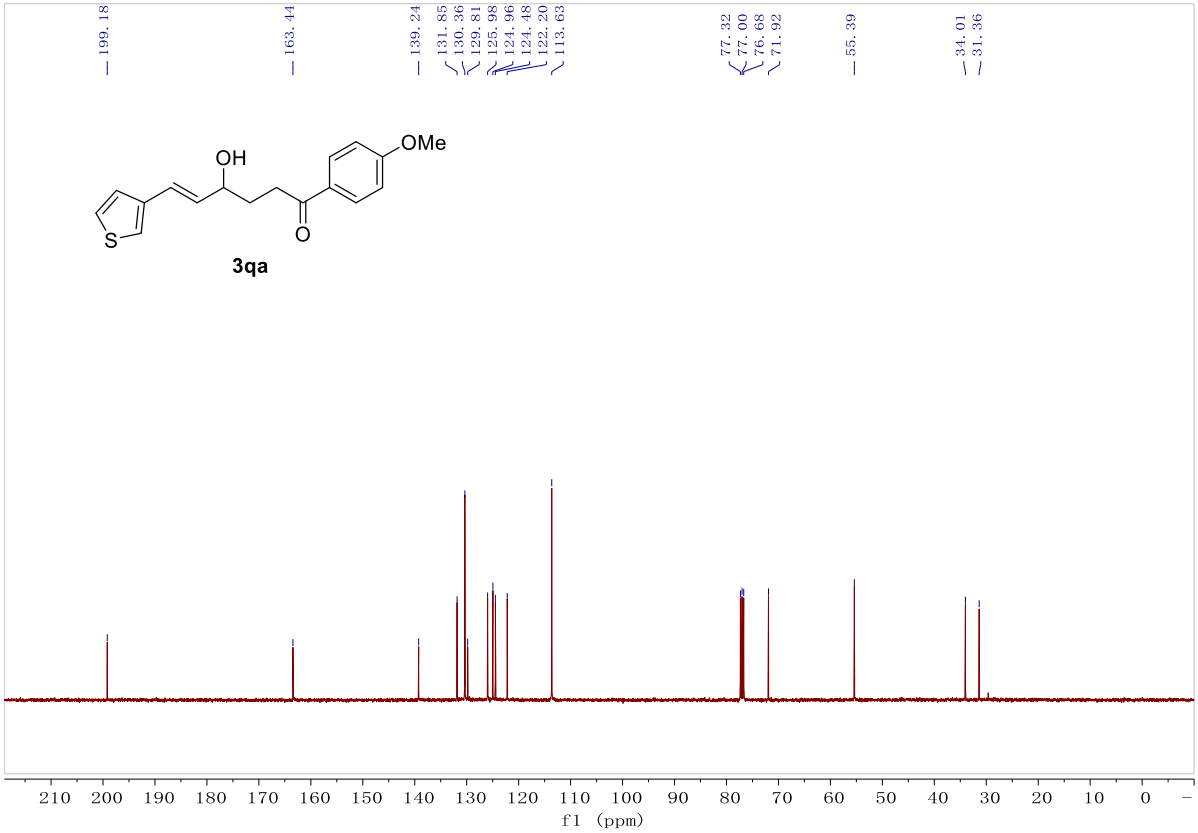
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3pa



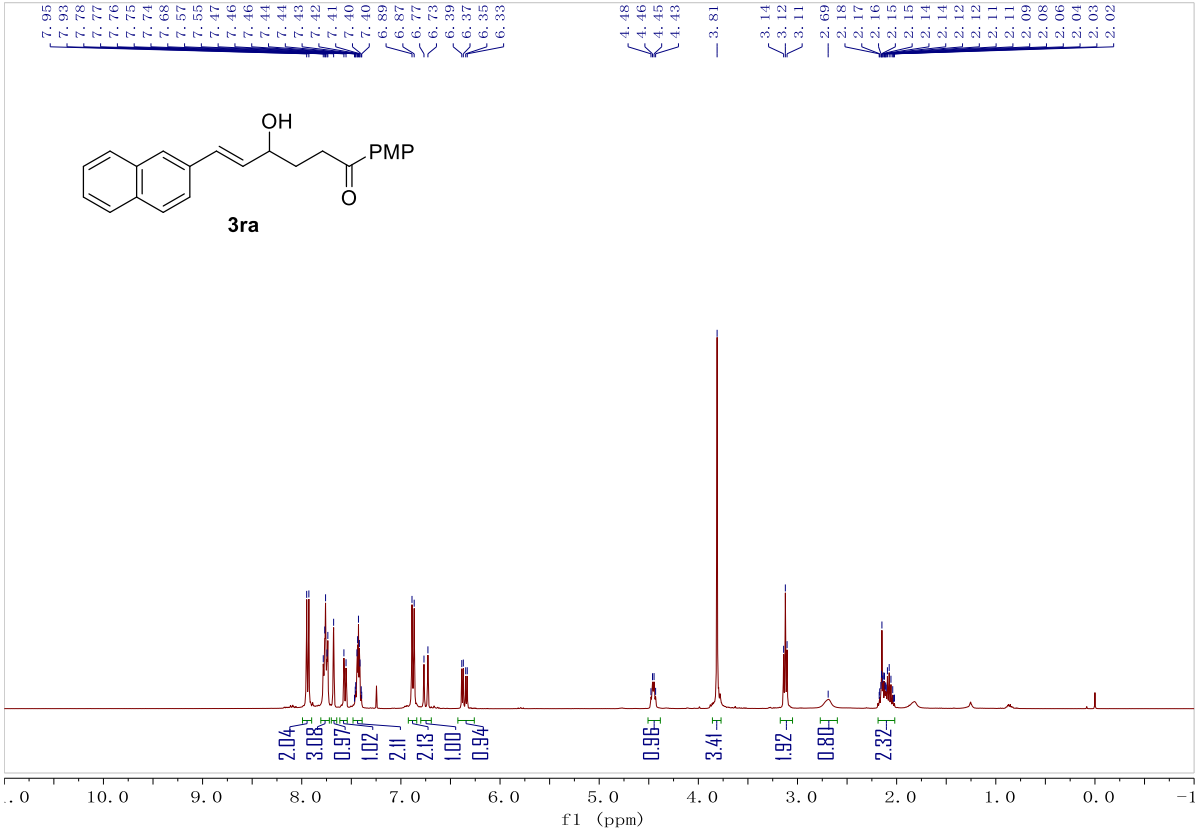


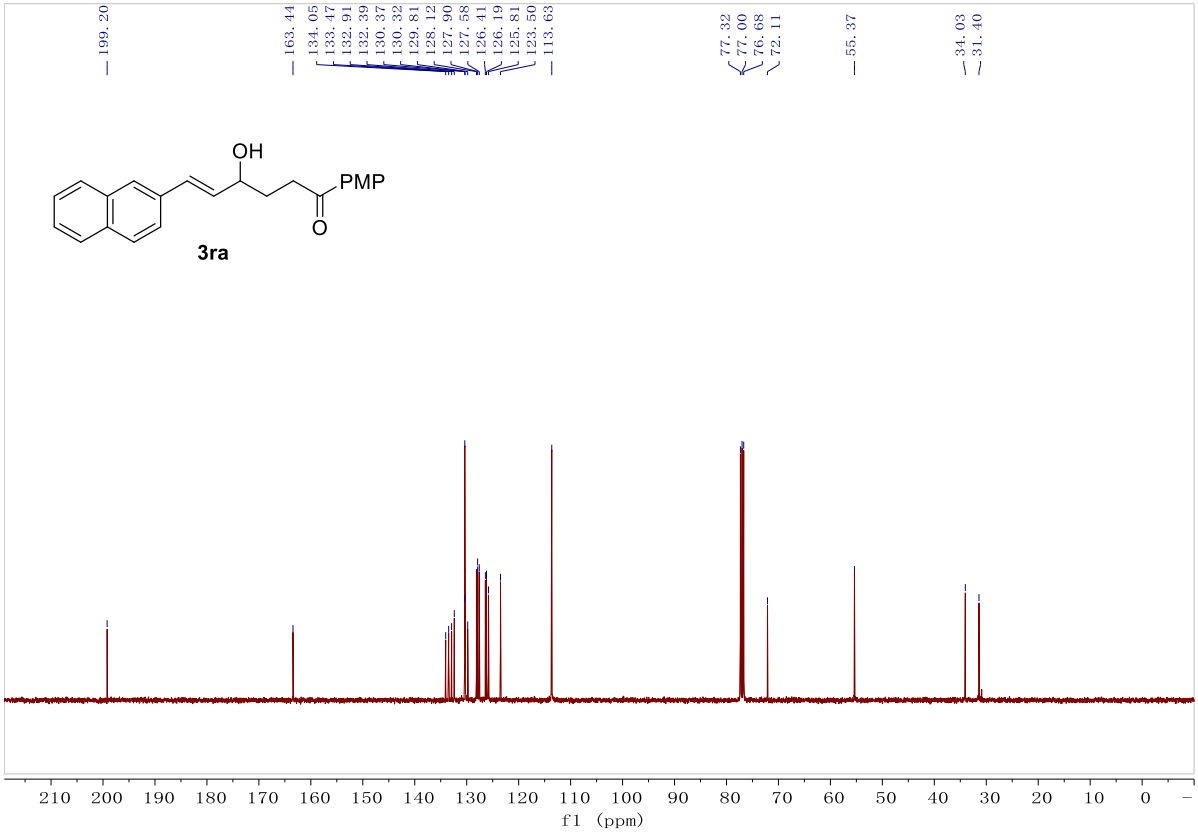
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3qa



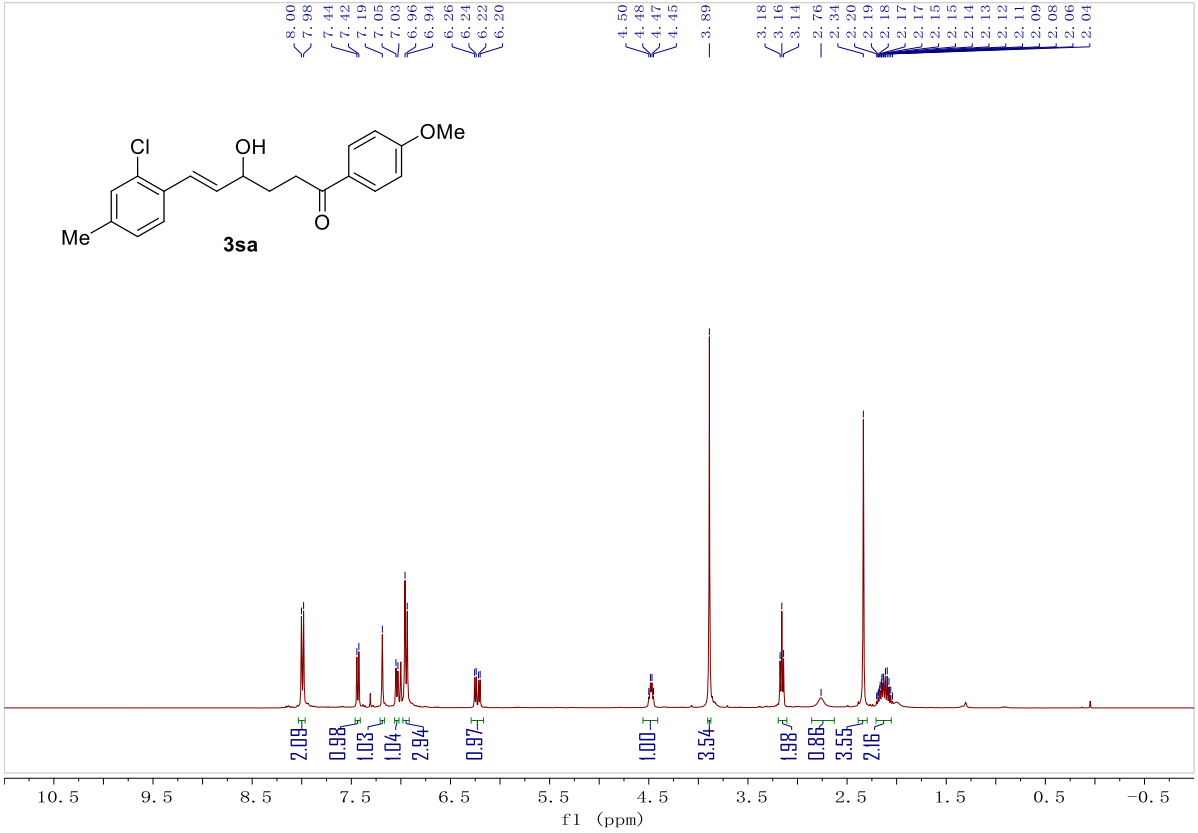


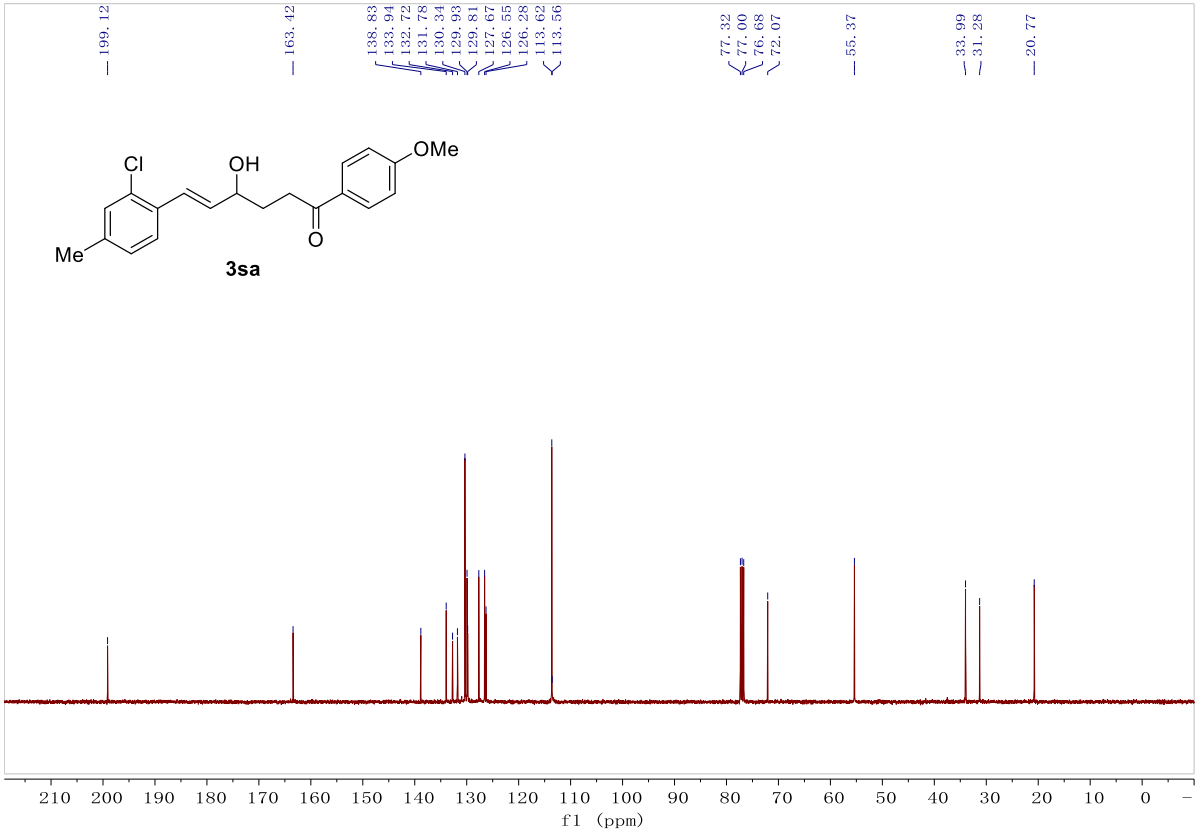
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ra



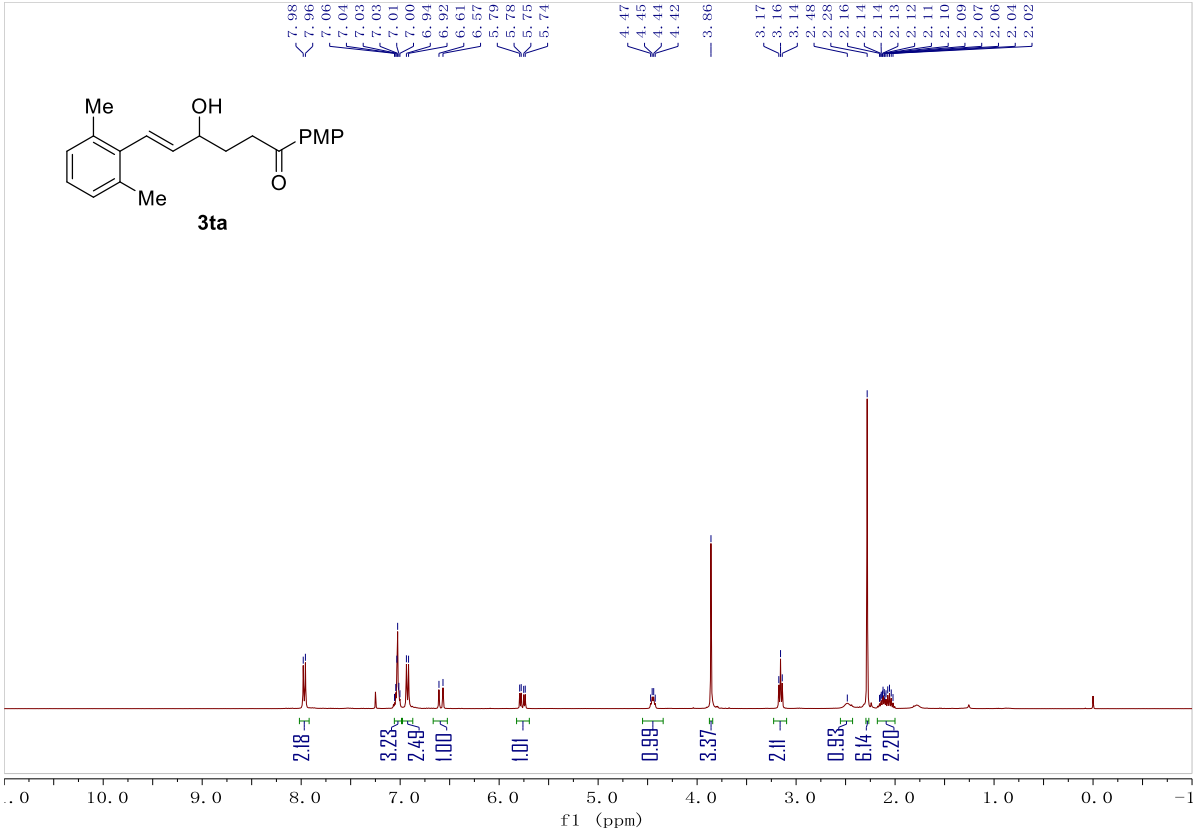


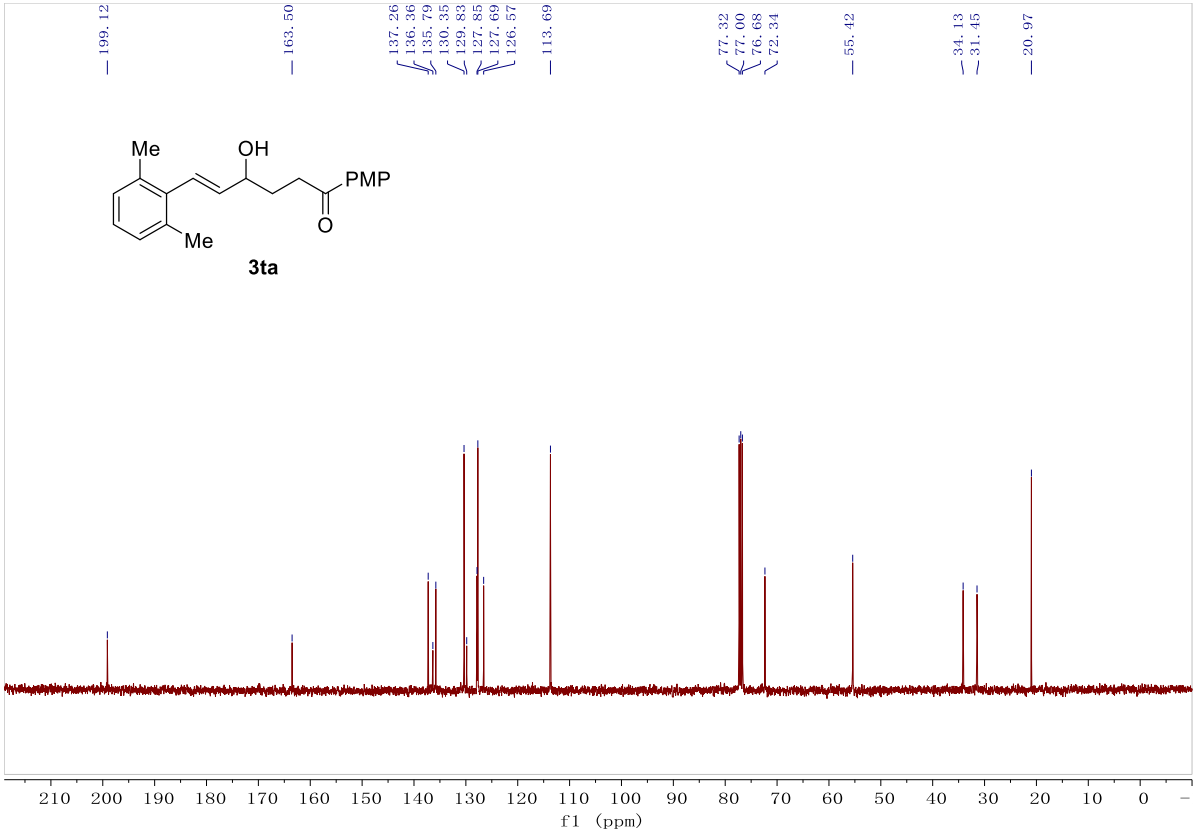
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3sa



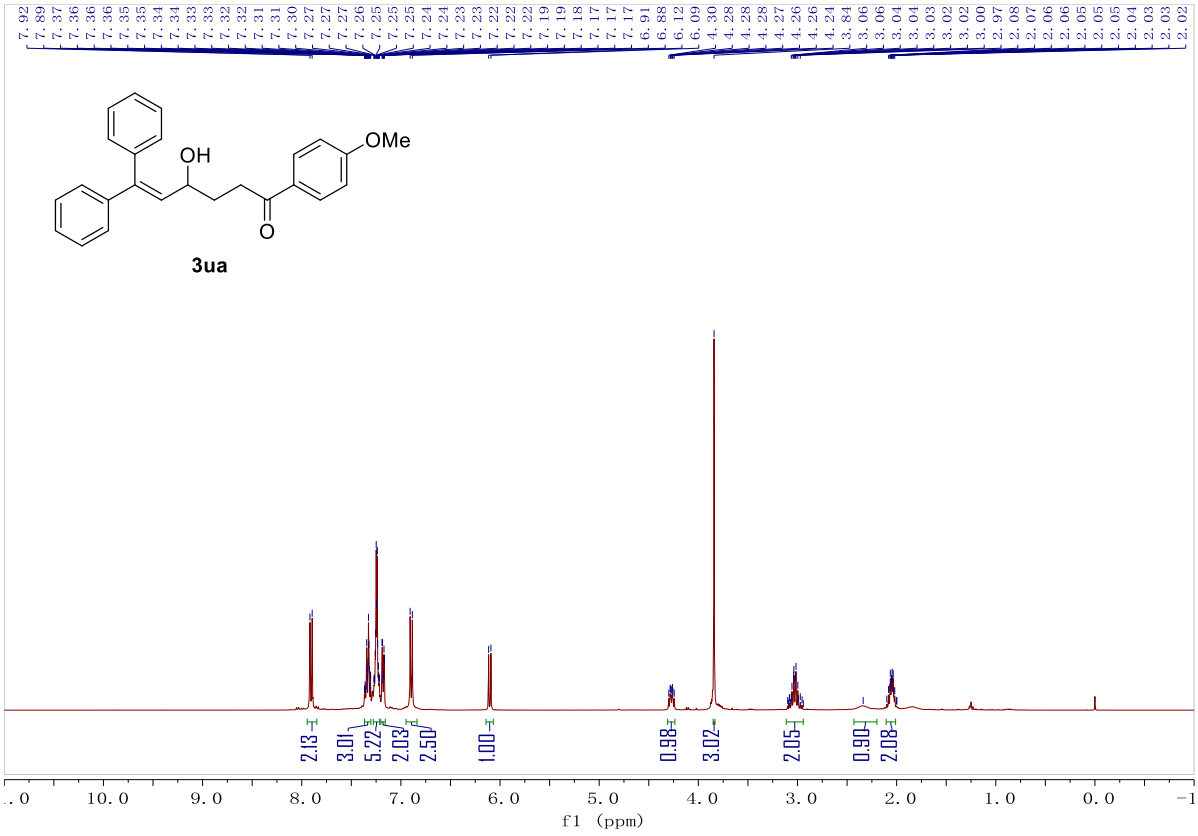


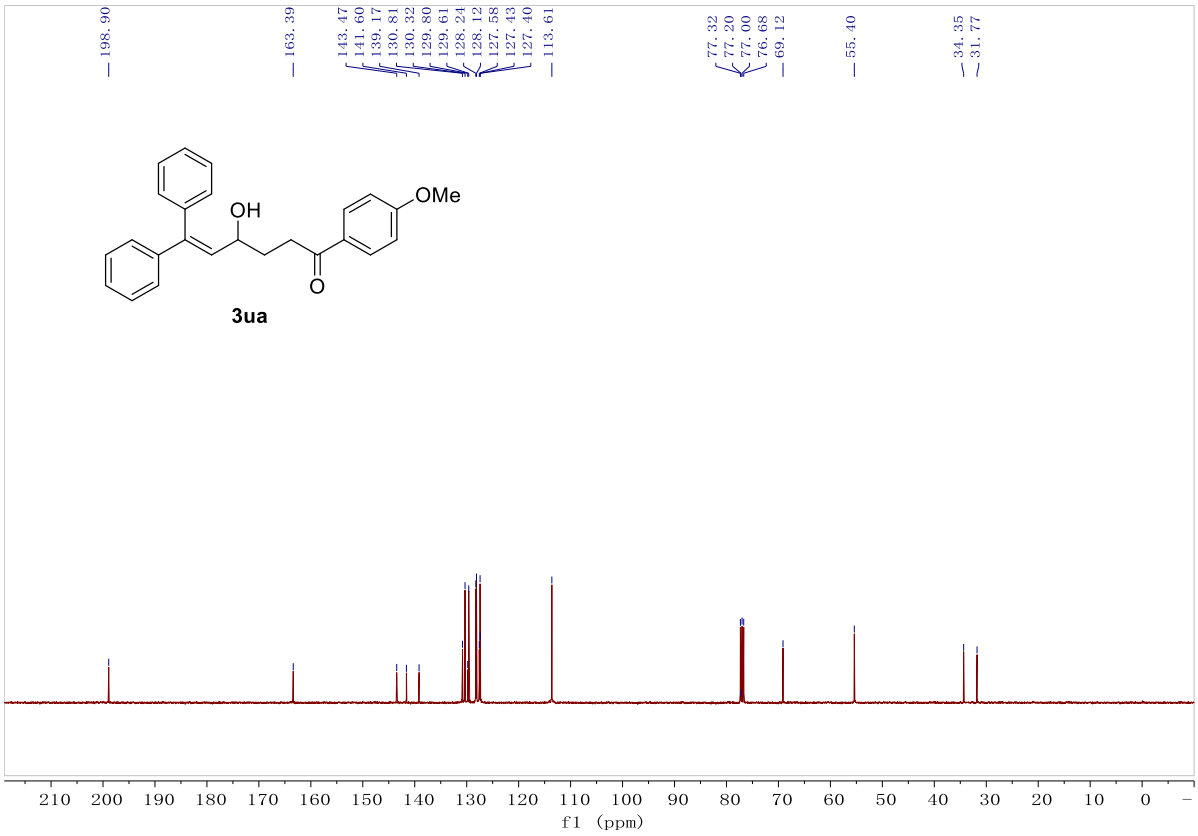
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ta



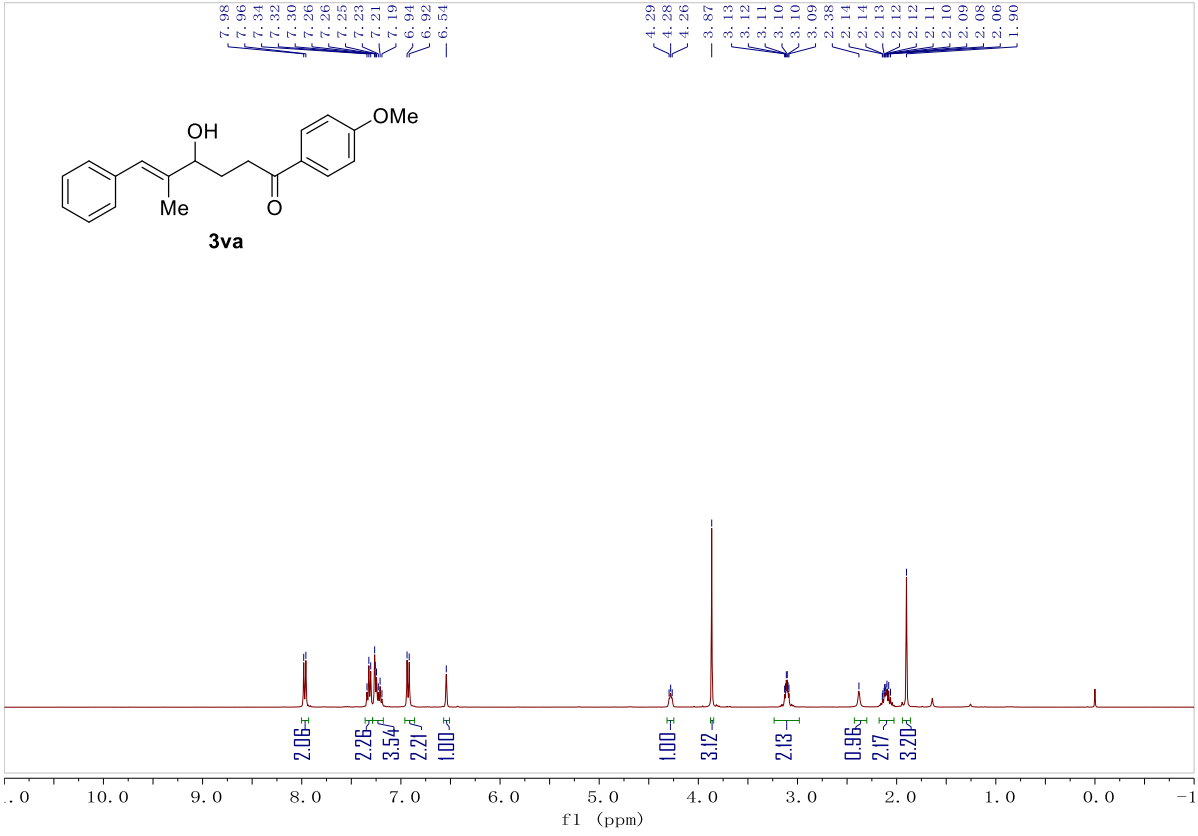


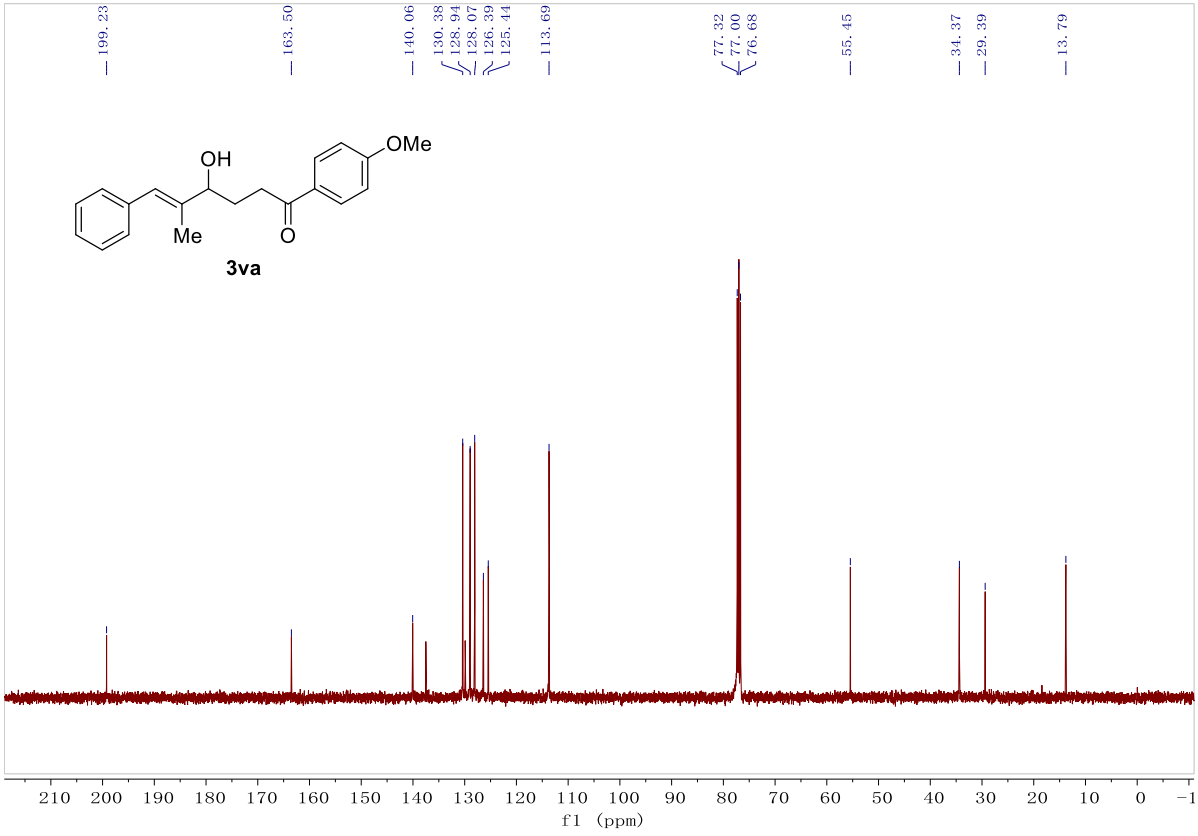
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ua



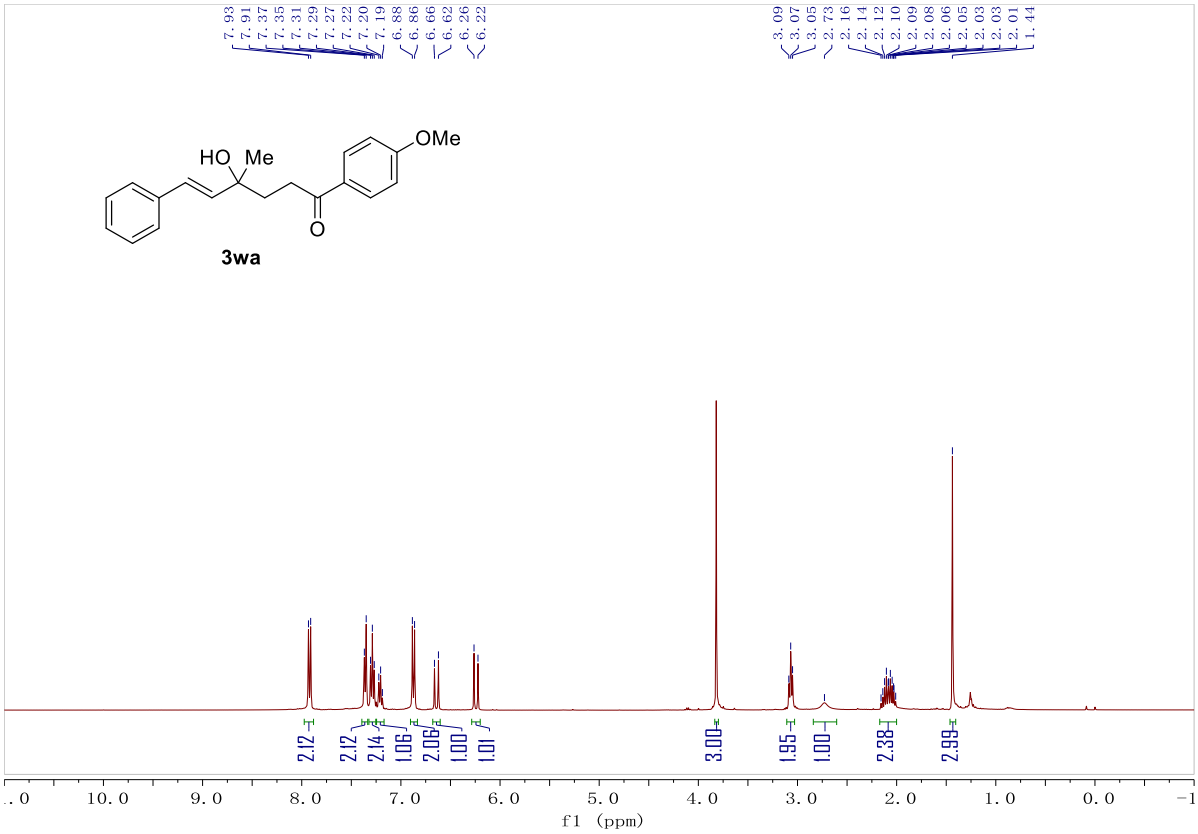


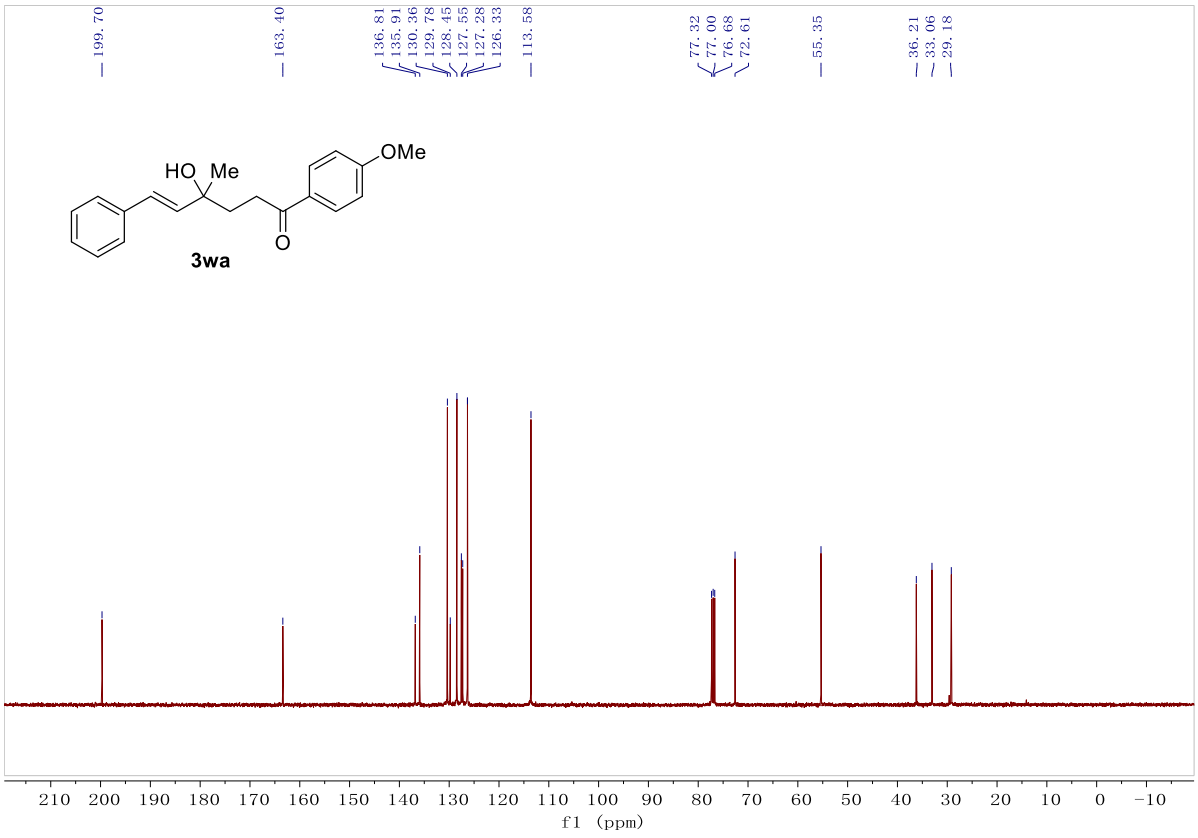
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3va



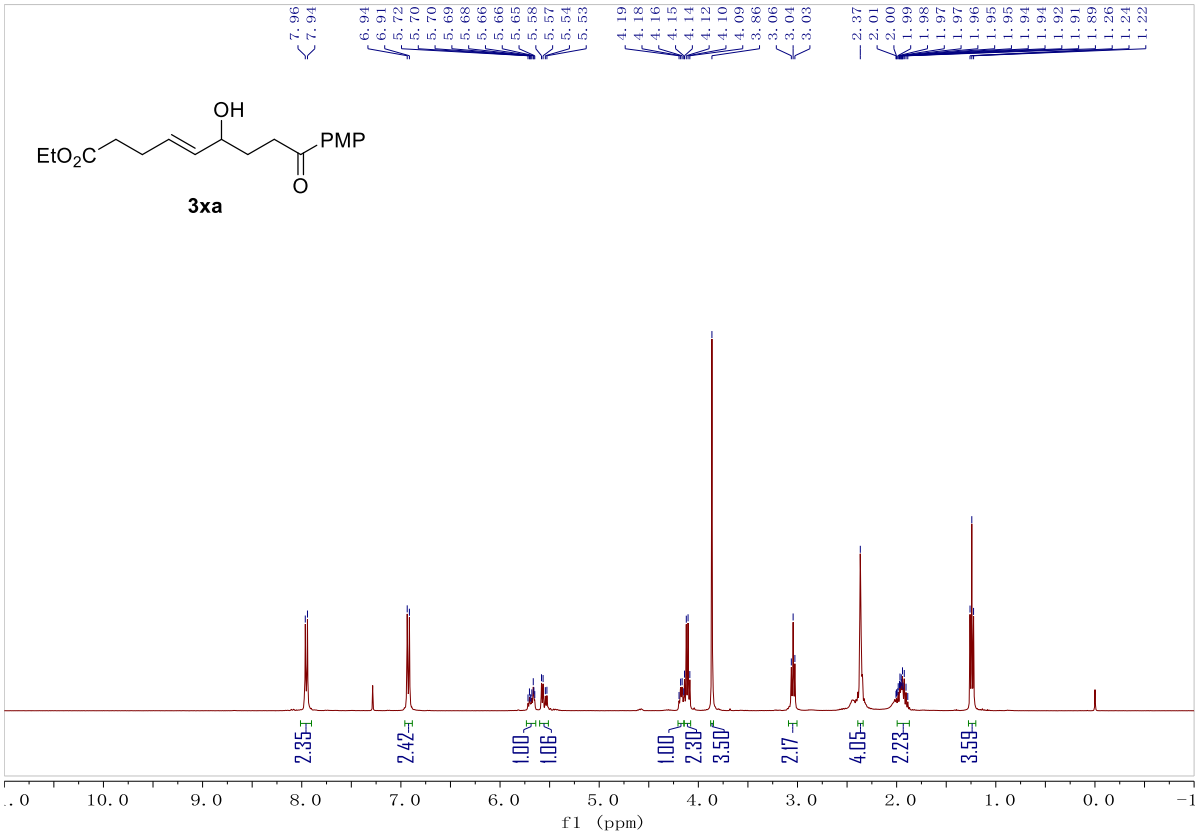


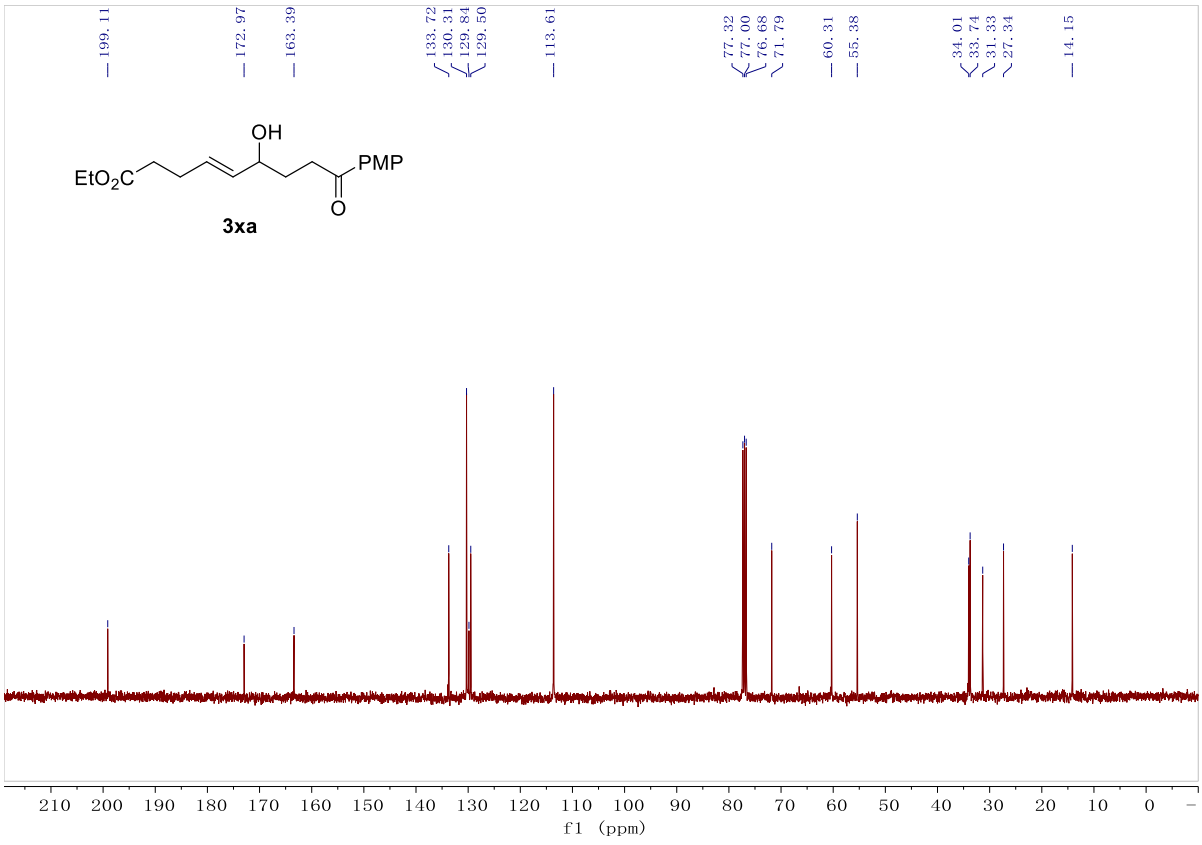
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3wa



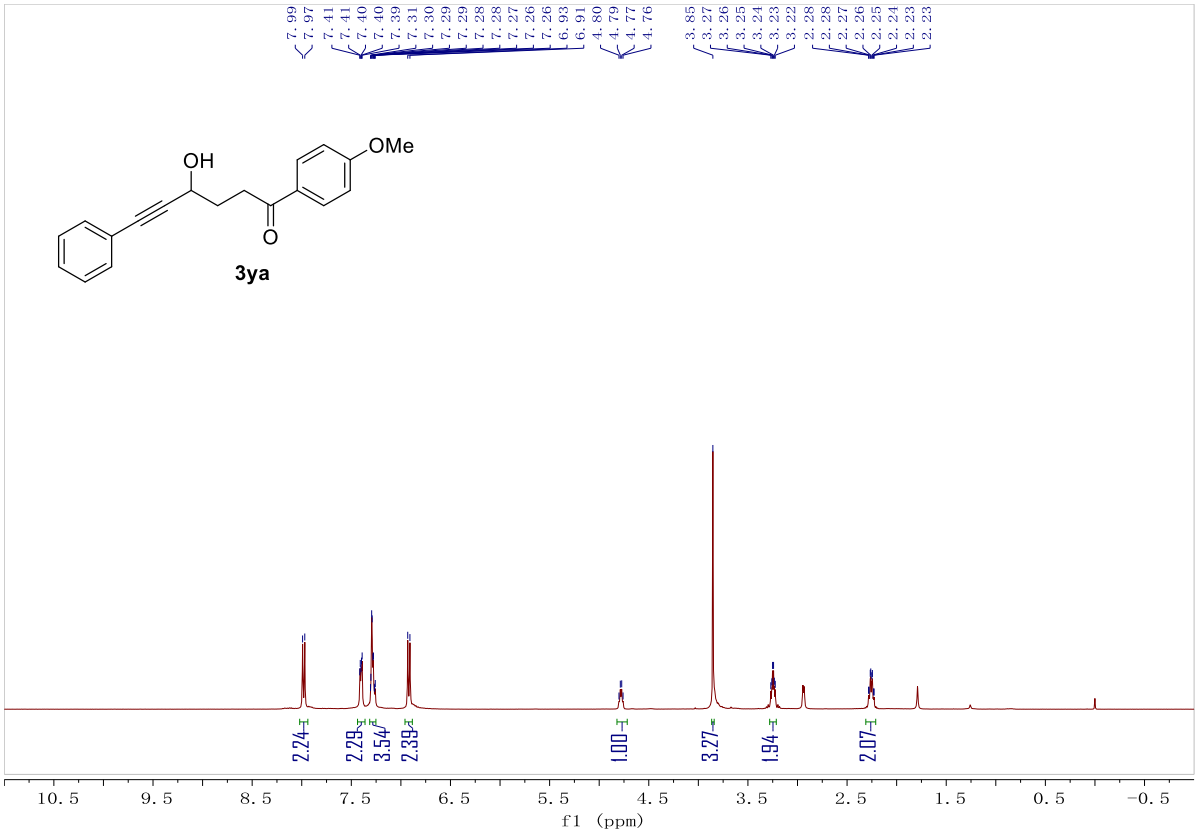


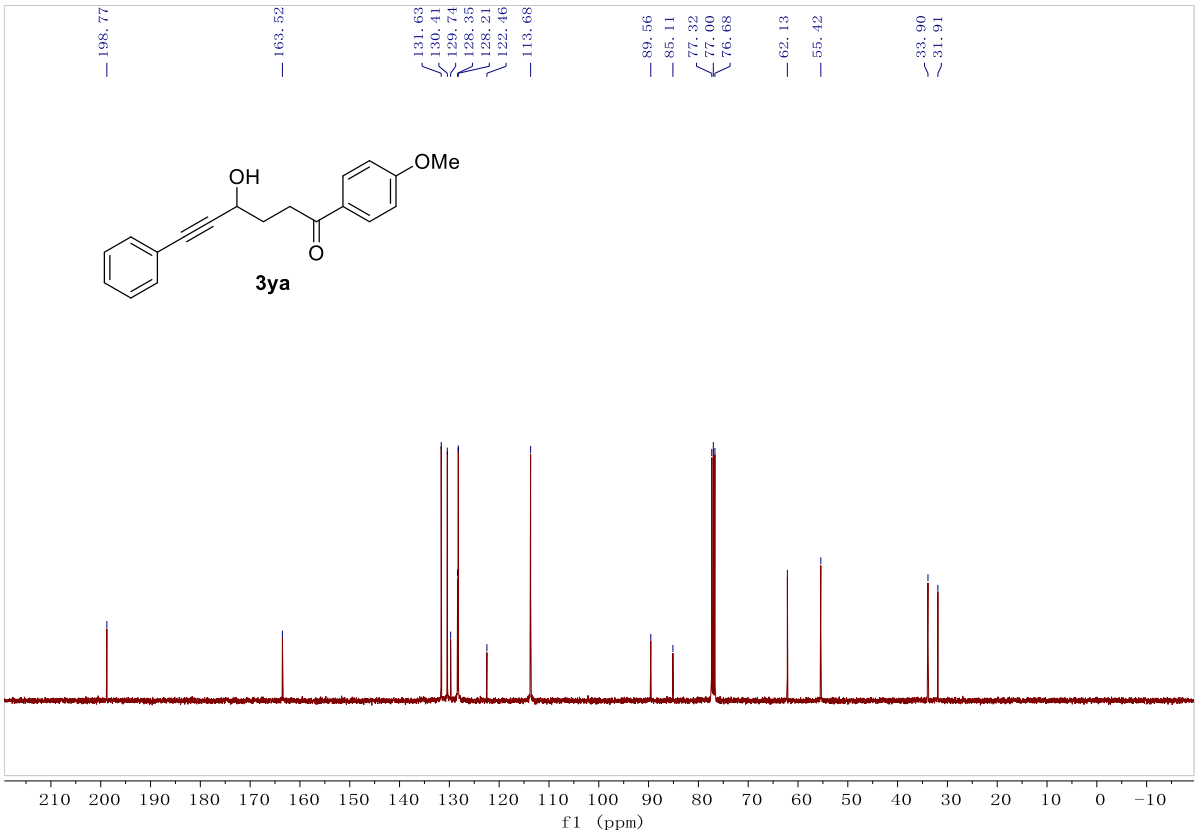
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3xa



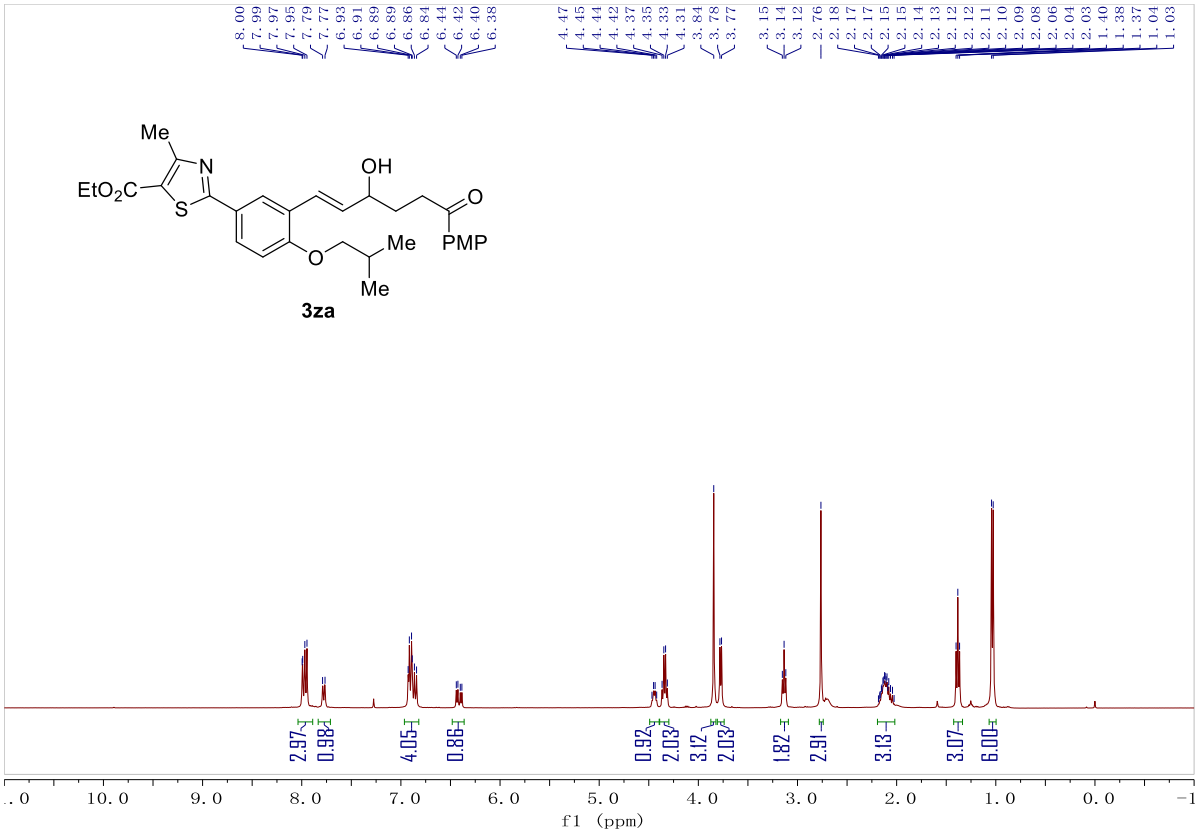


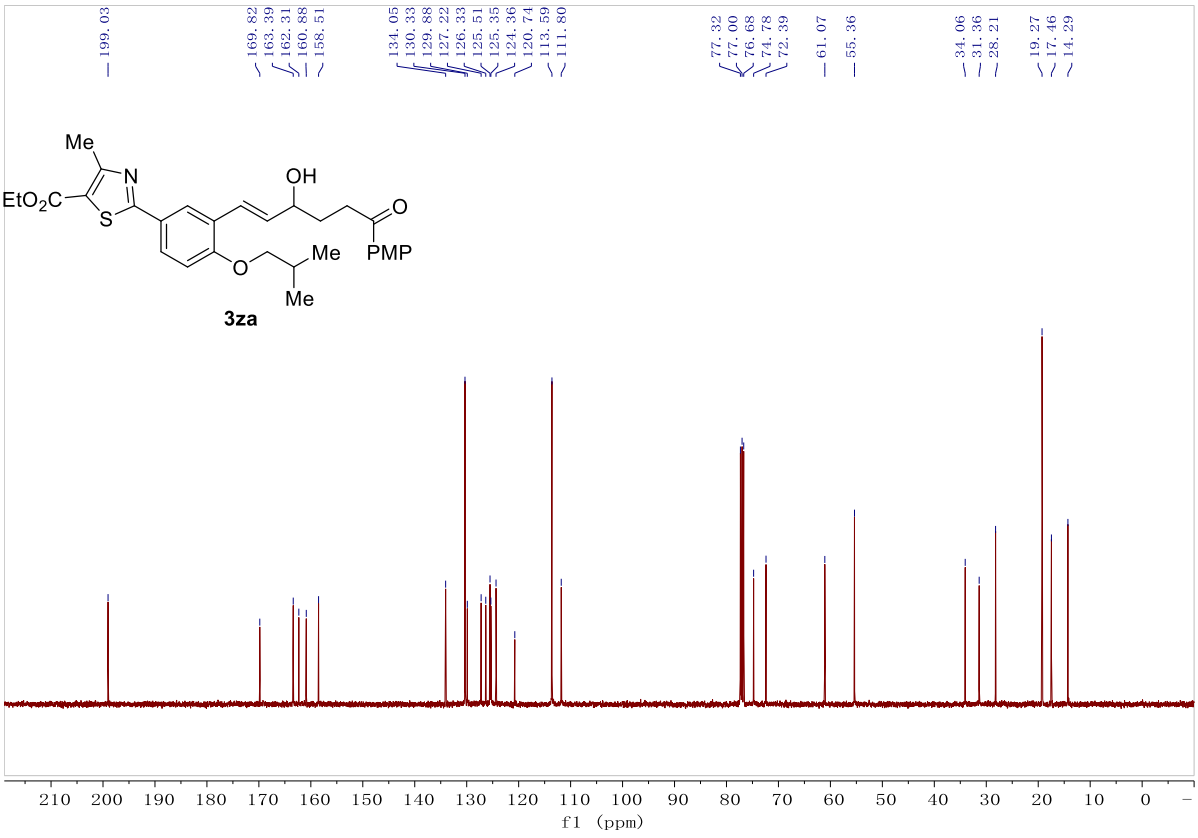
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ya



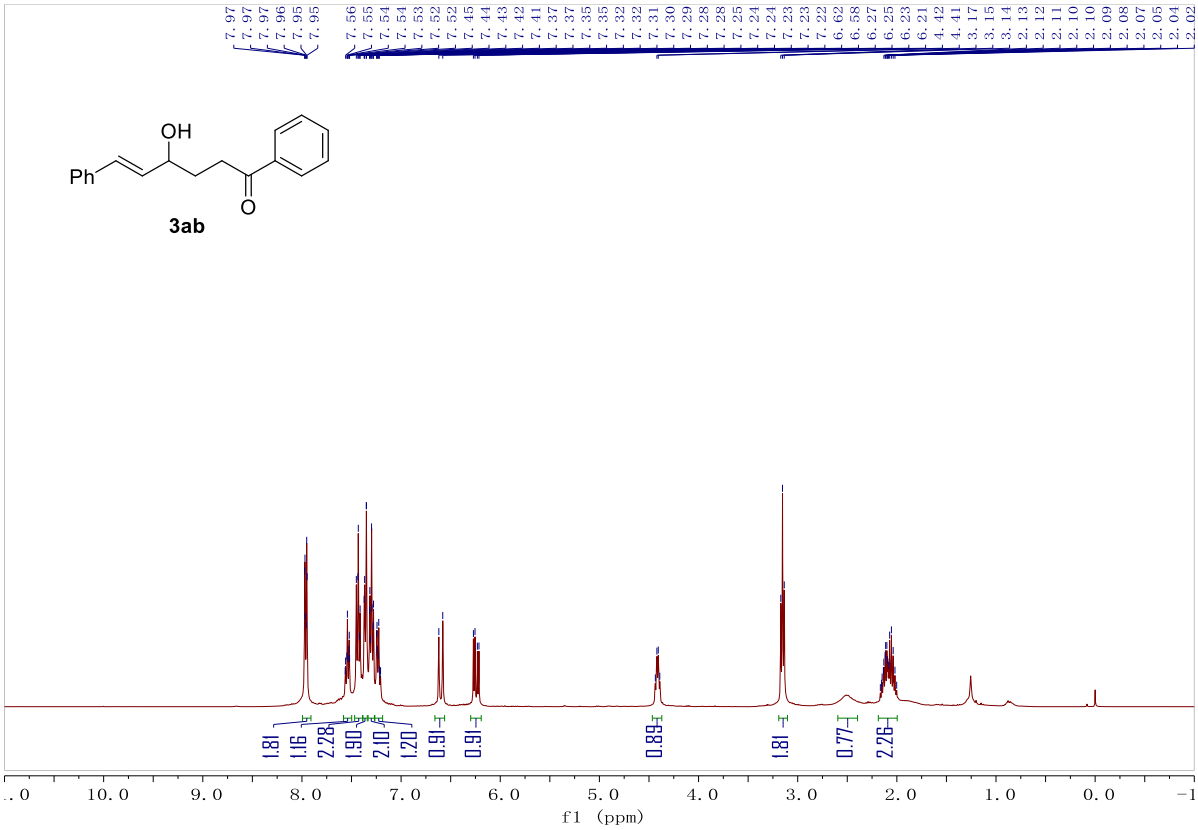


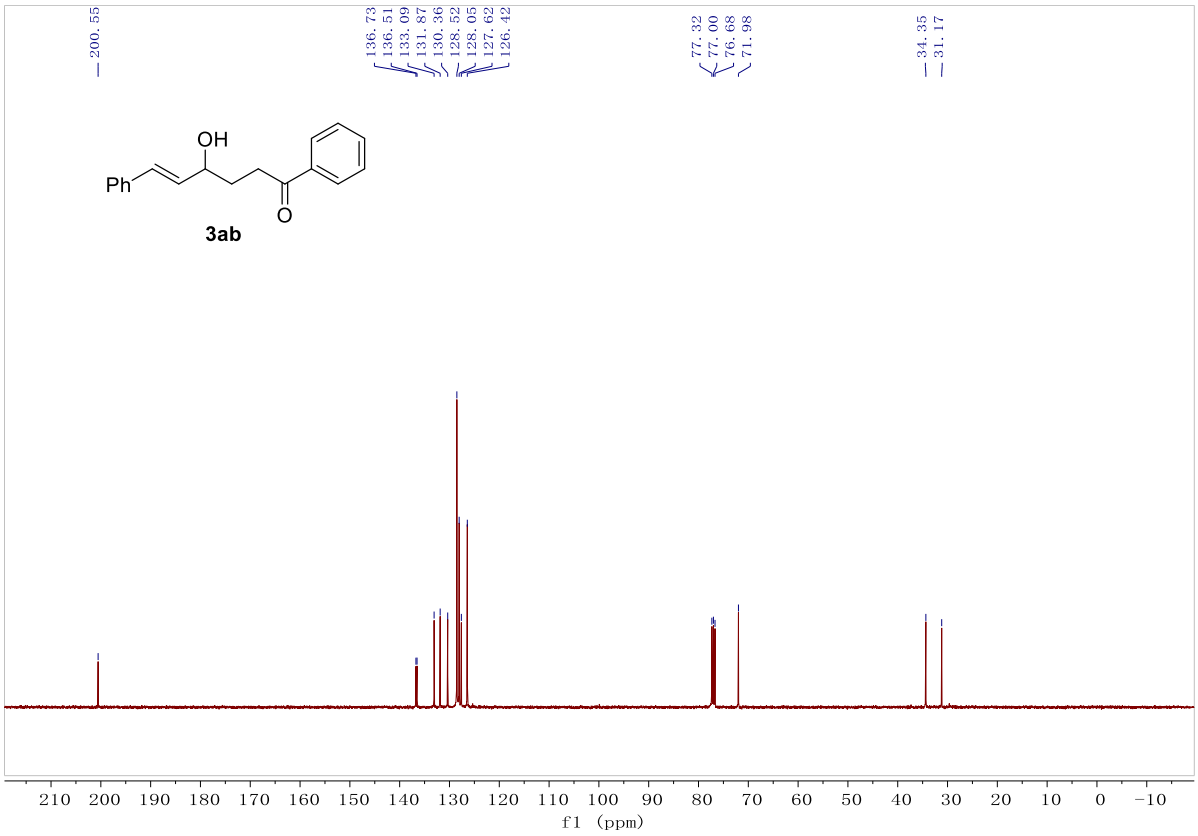
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3za



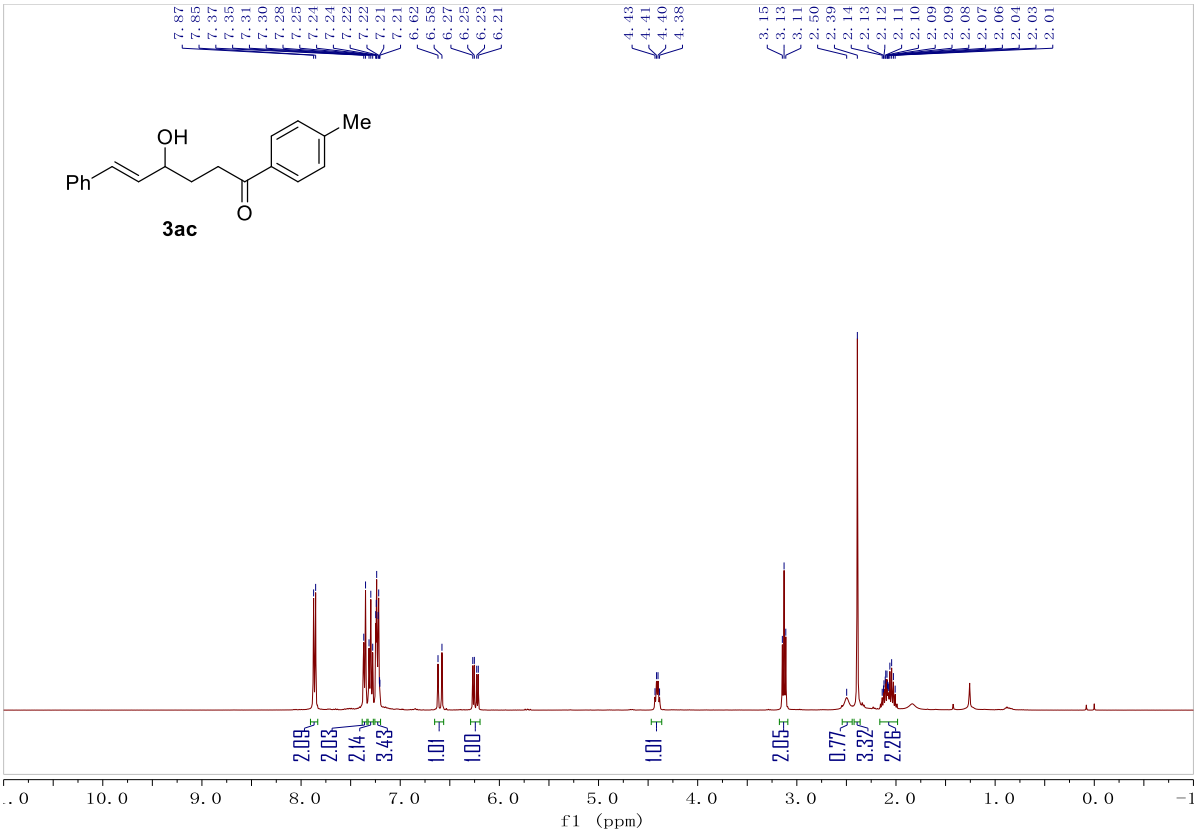


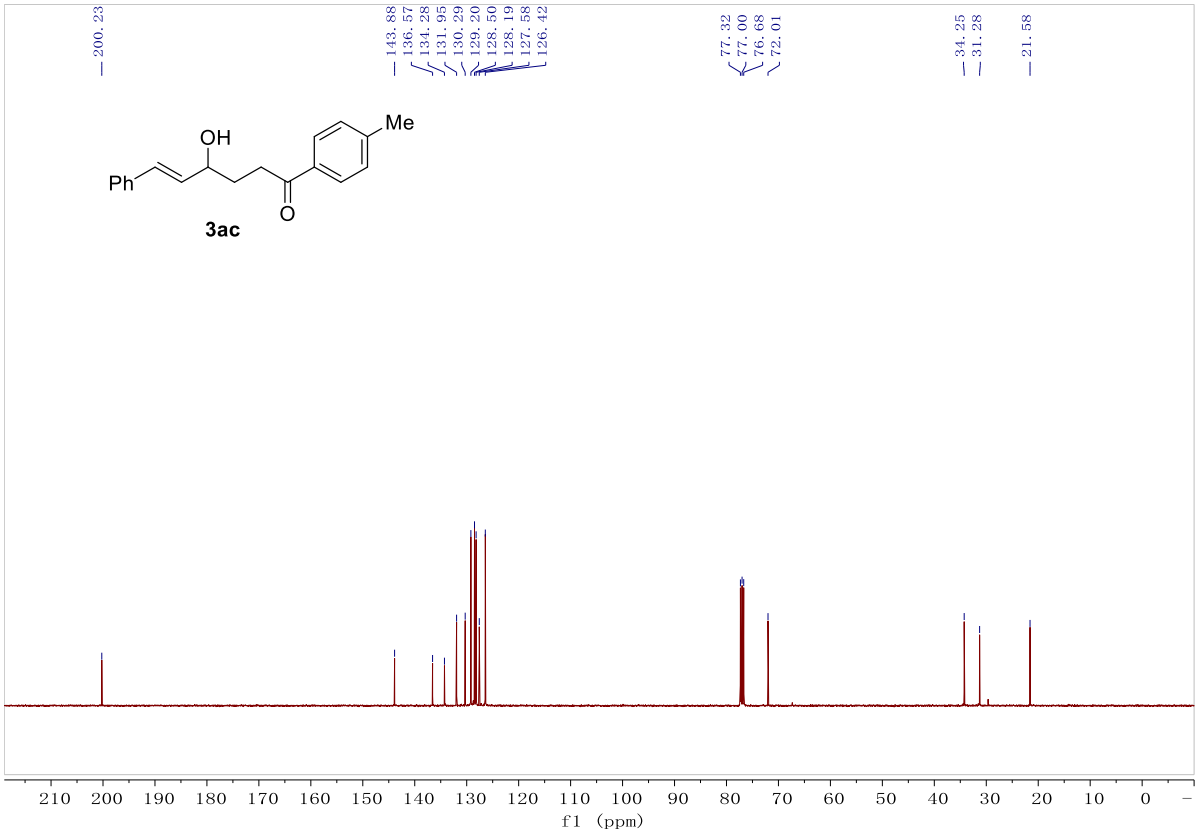
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ab



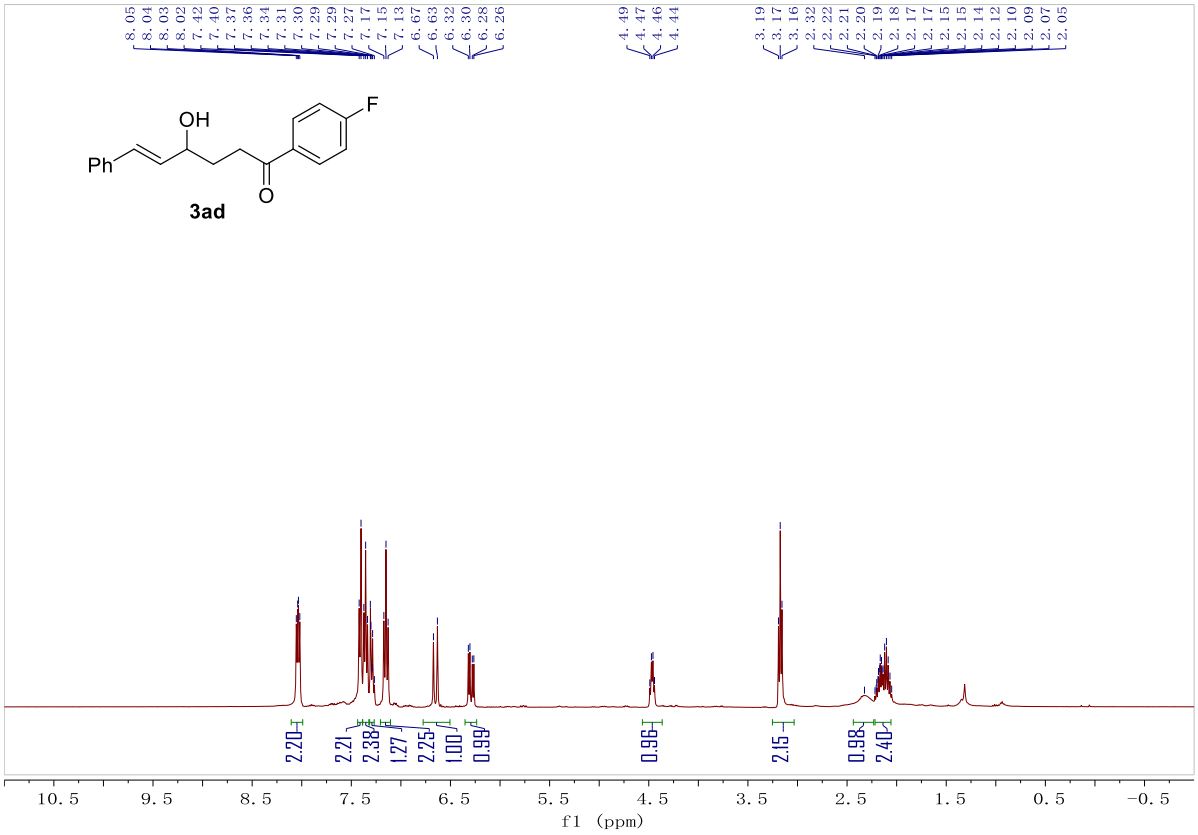


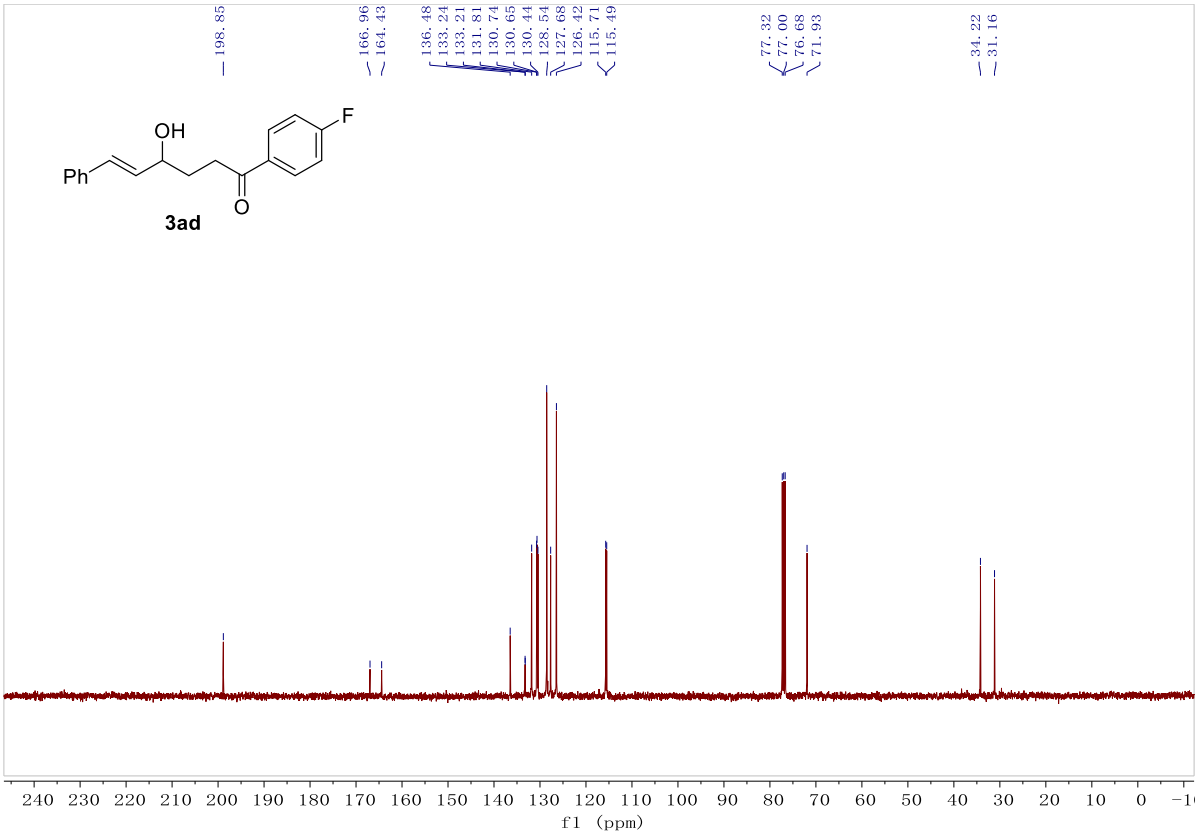
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ac

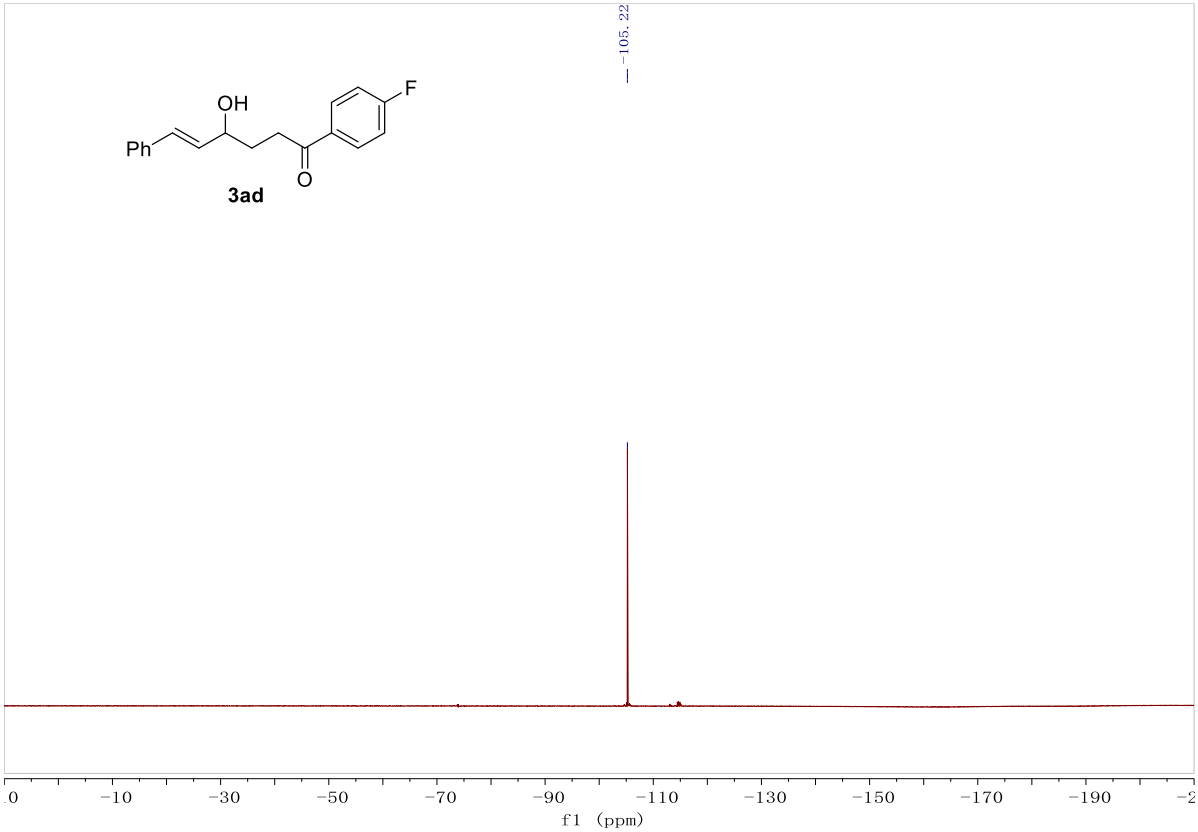




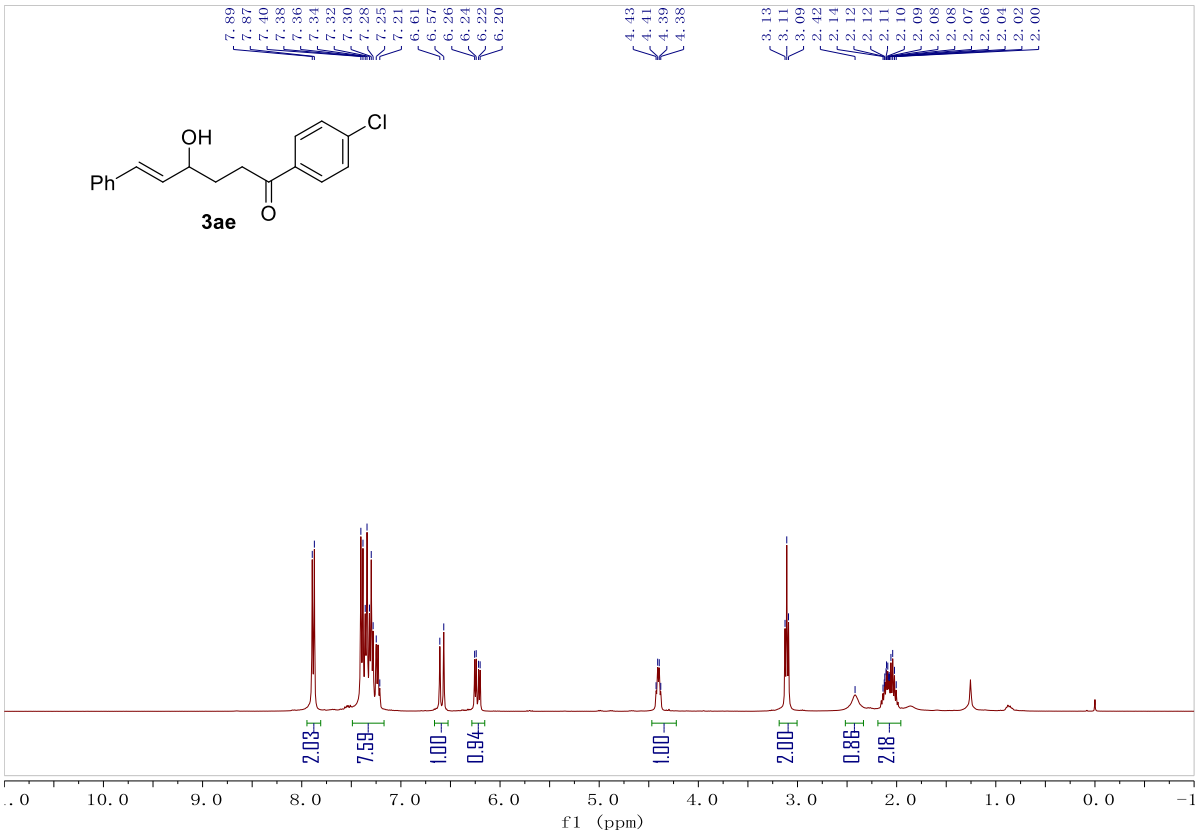
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ad

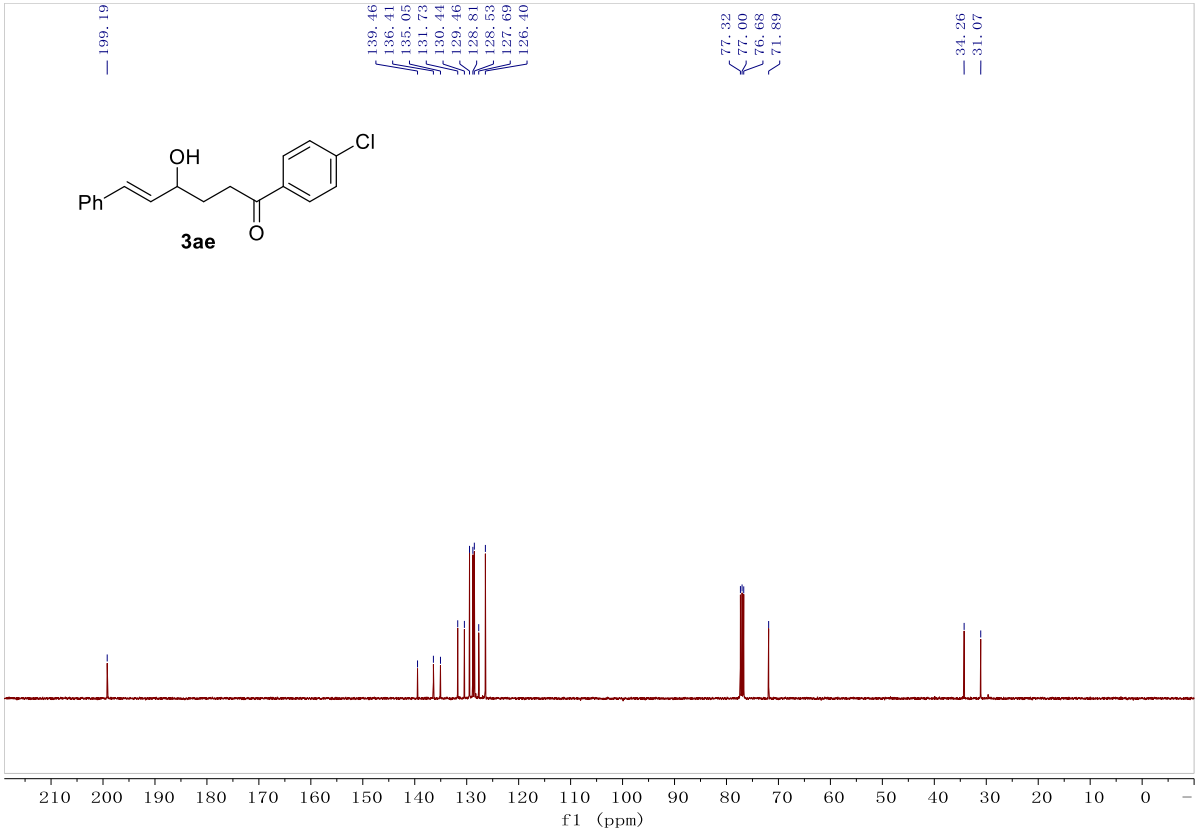




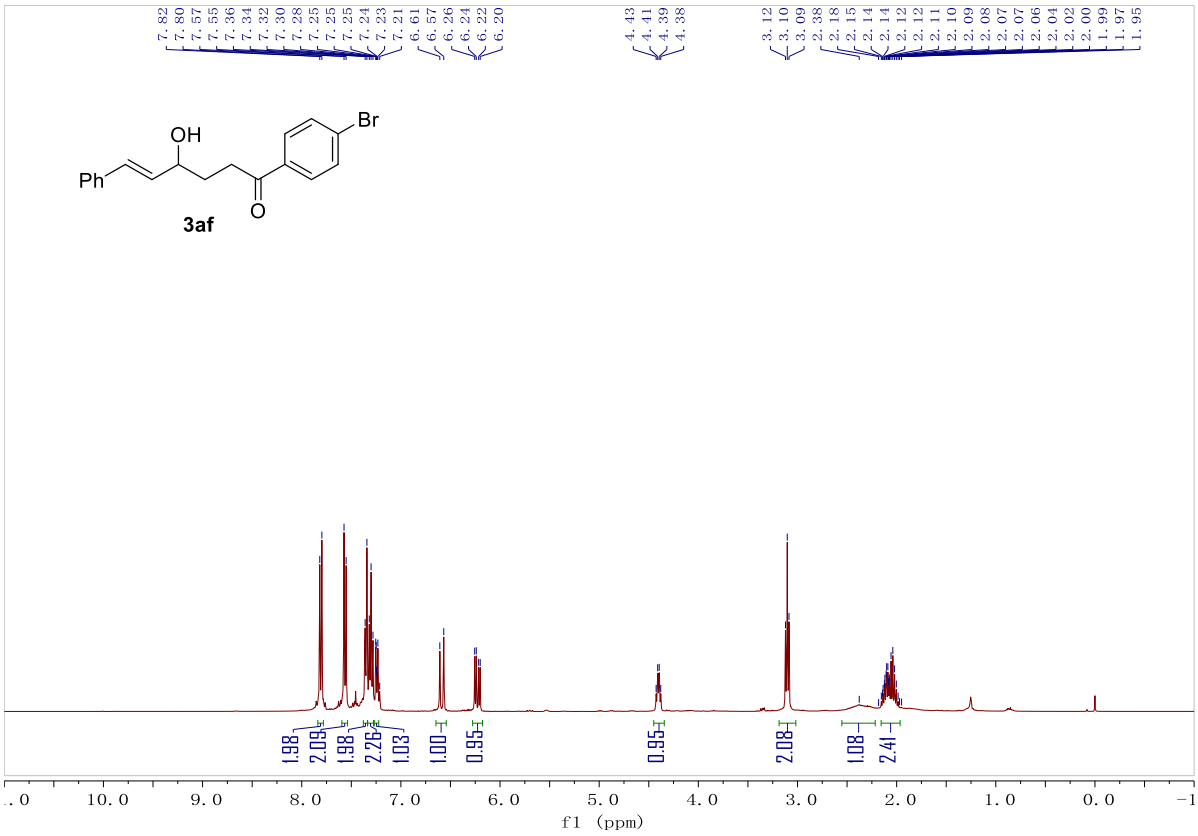


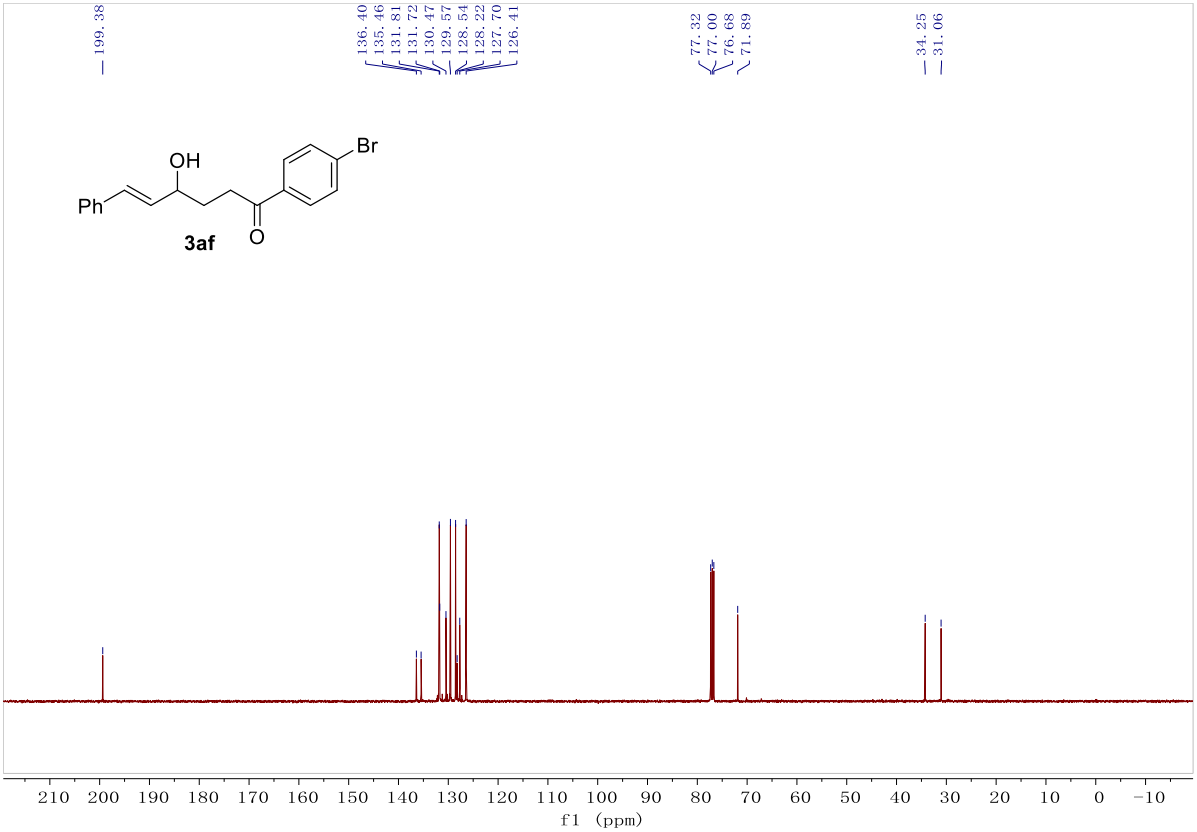
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ae



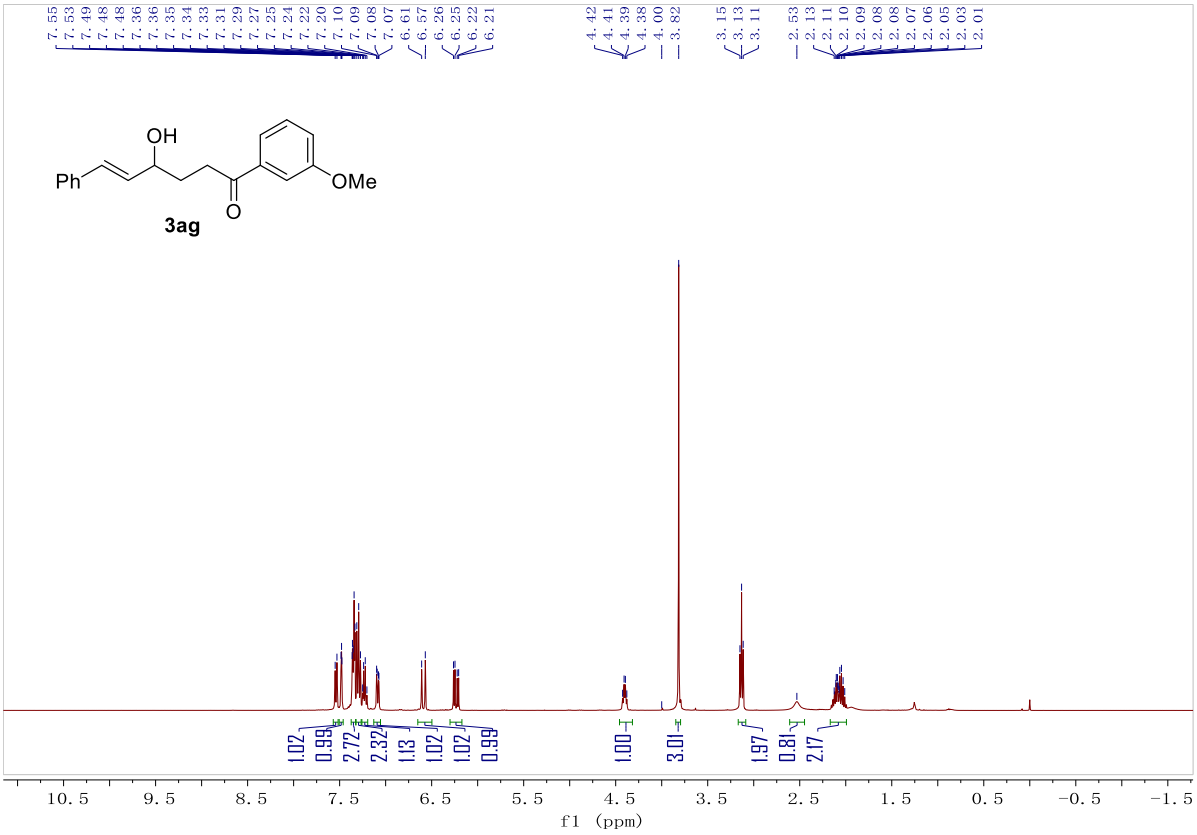


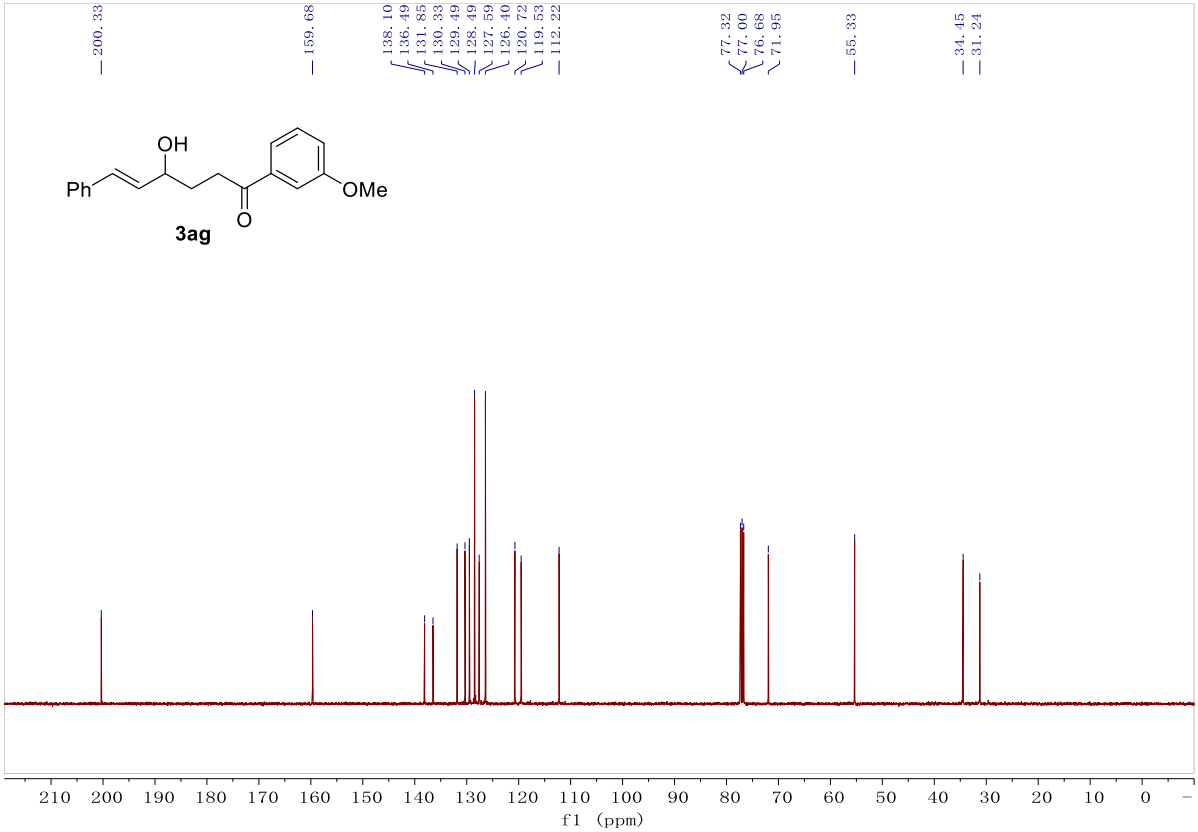
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3af



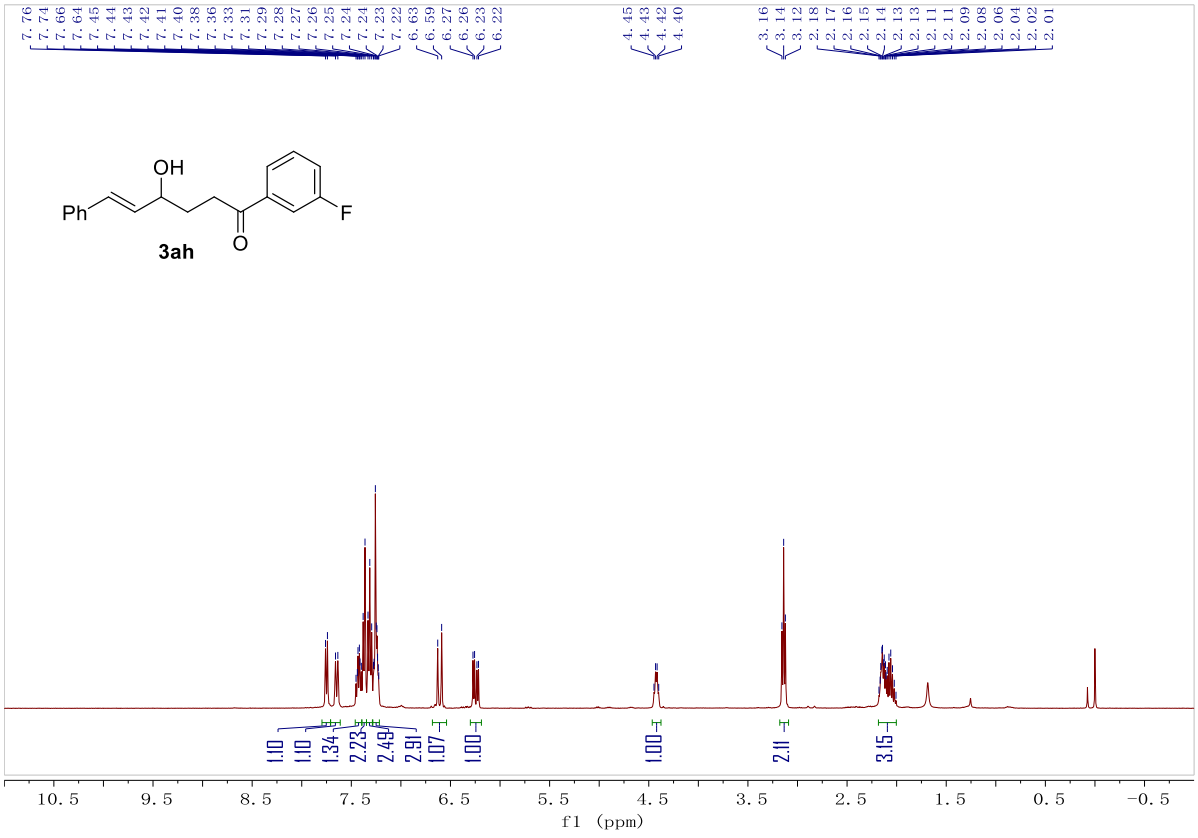


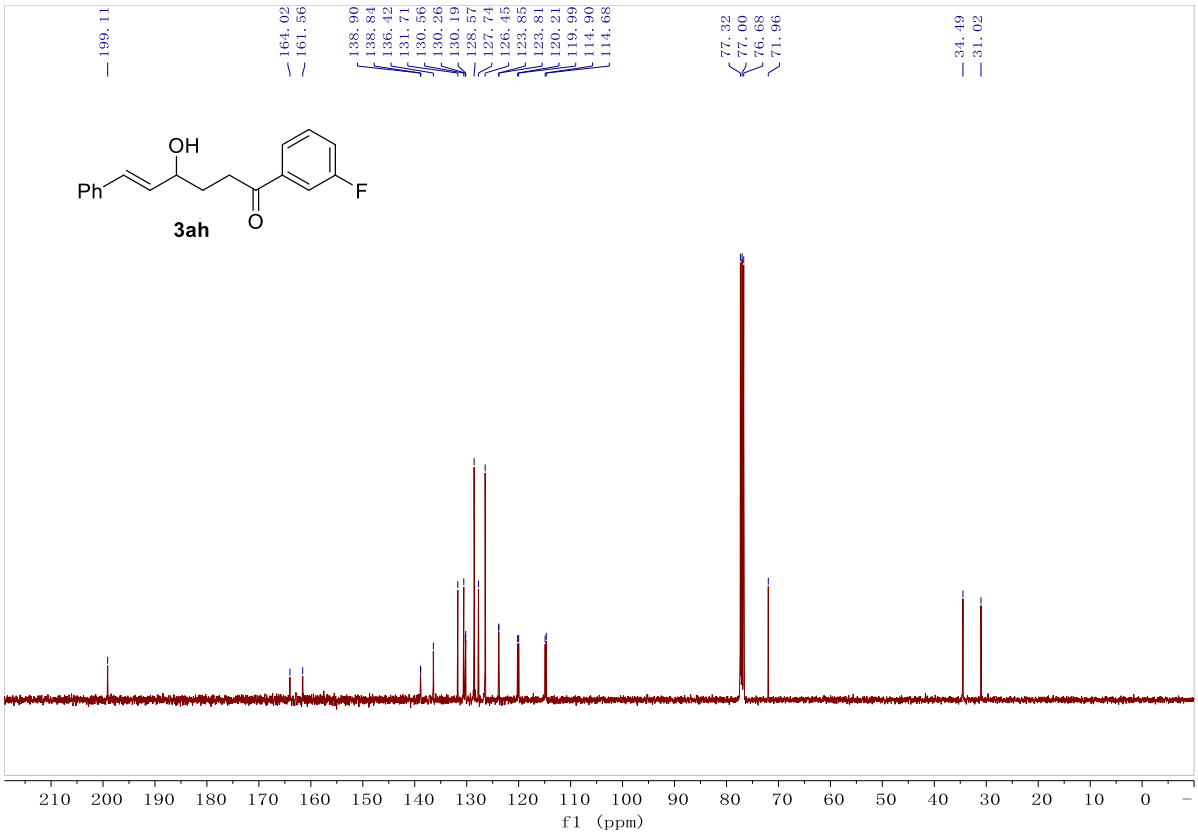
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ag





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ah

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77.32
77.00
76.68
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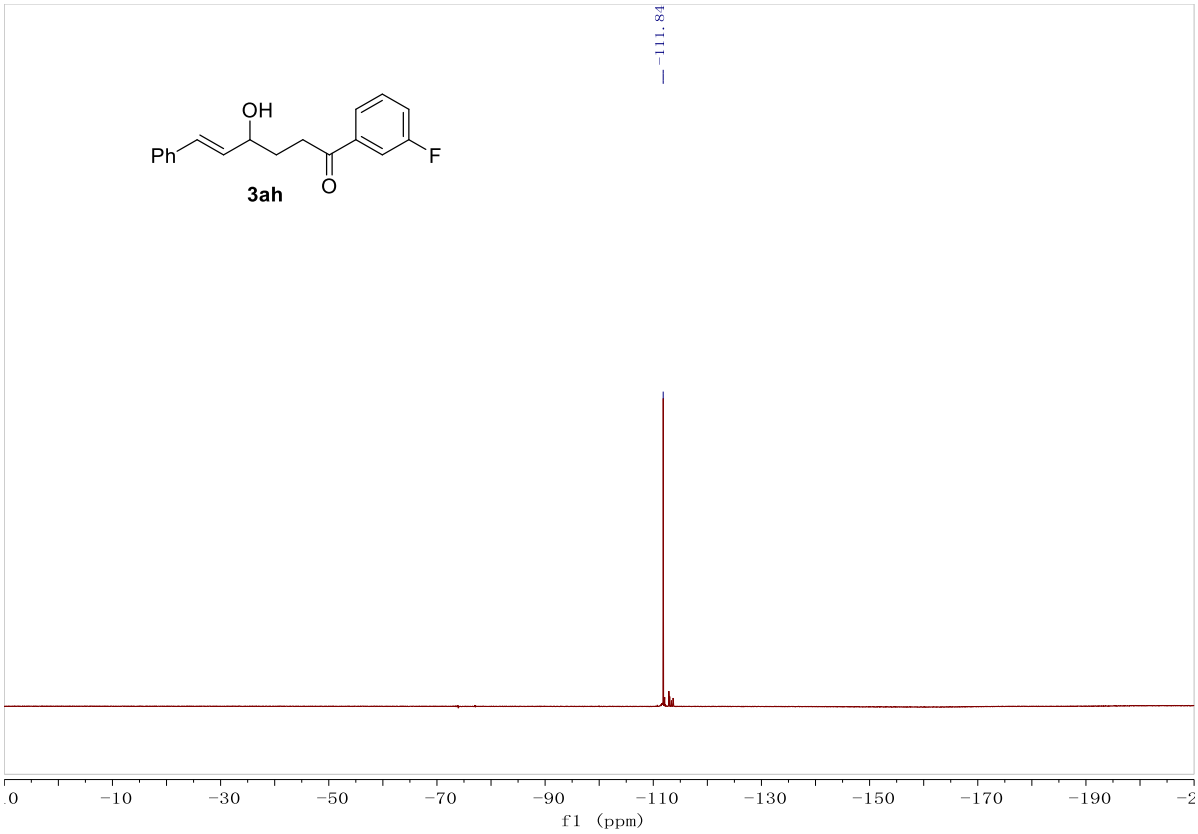
OH
Ph
F
O
3ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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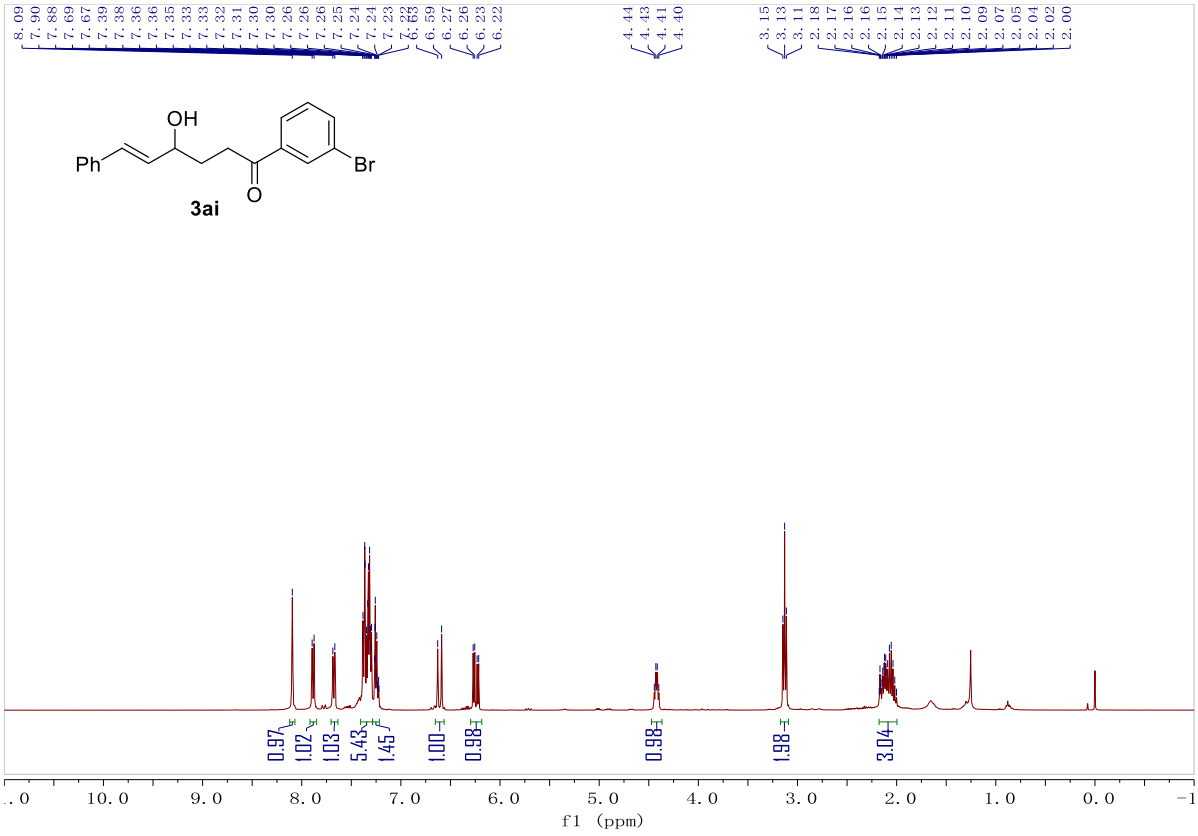
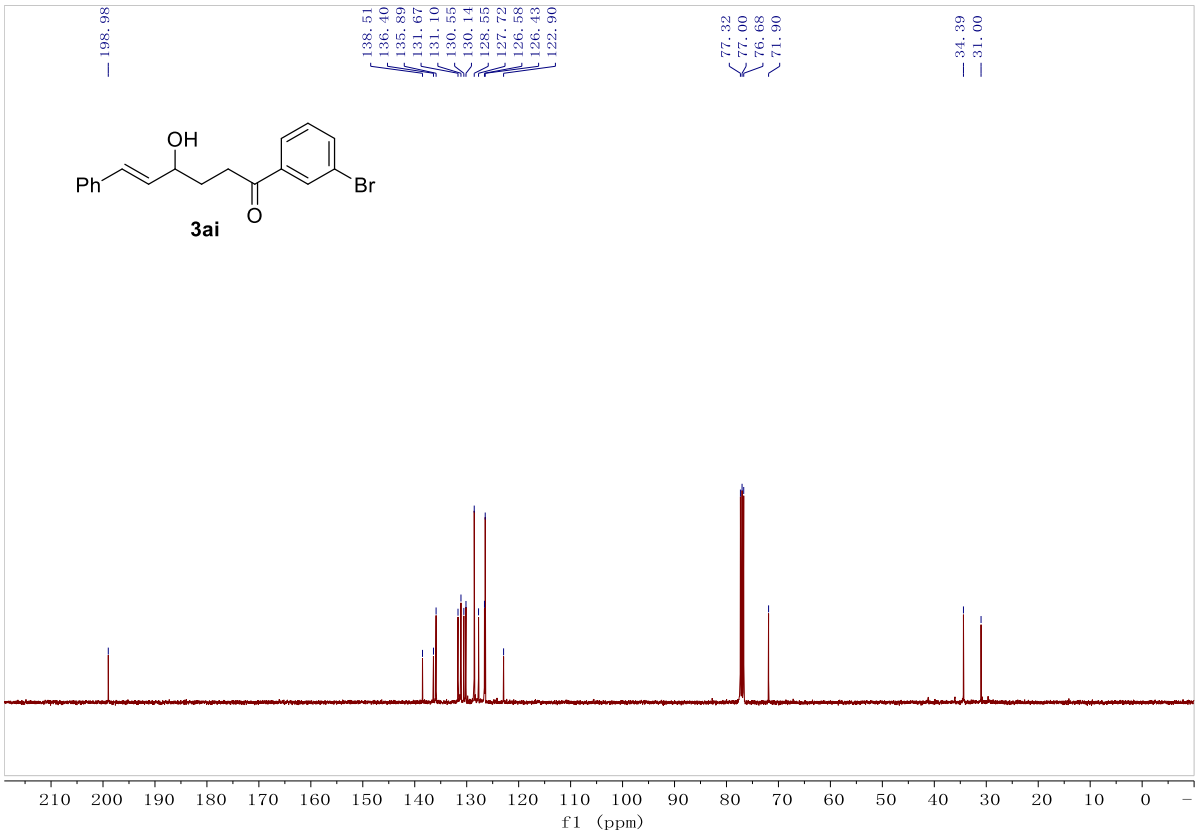
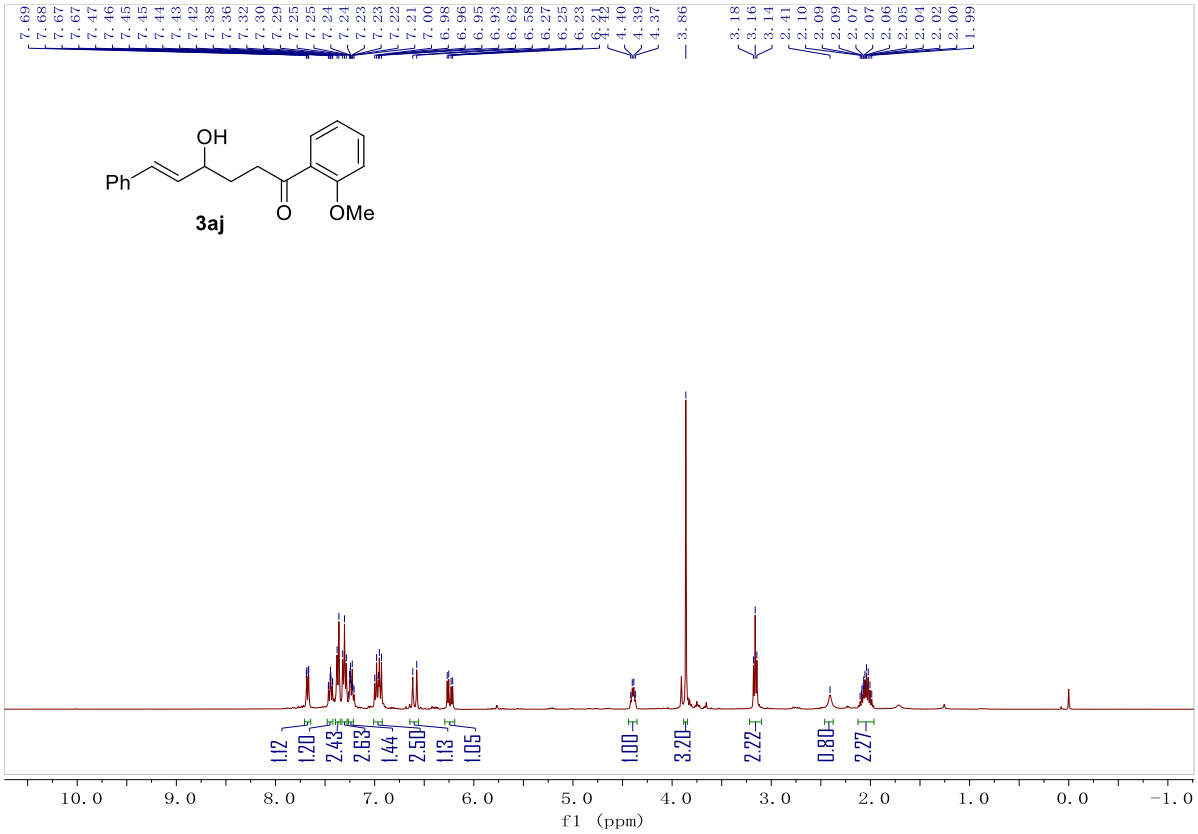
Ph
F
O
3ah
0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -2
f1 (ppm)

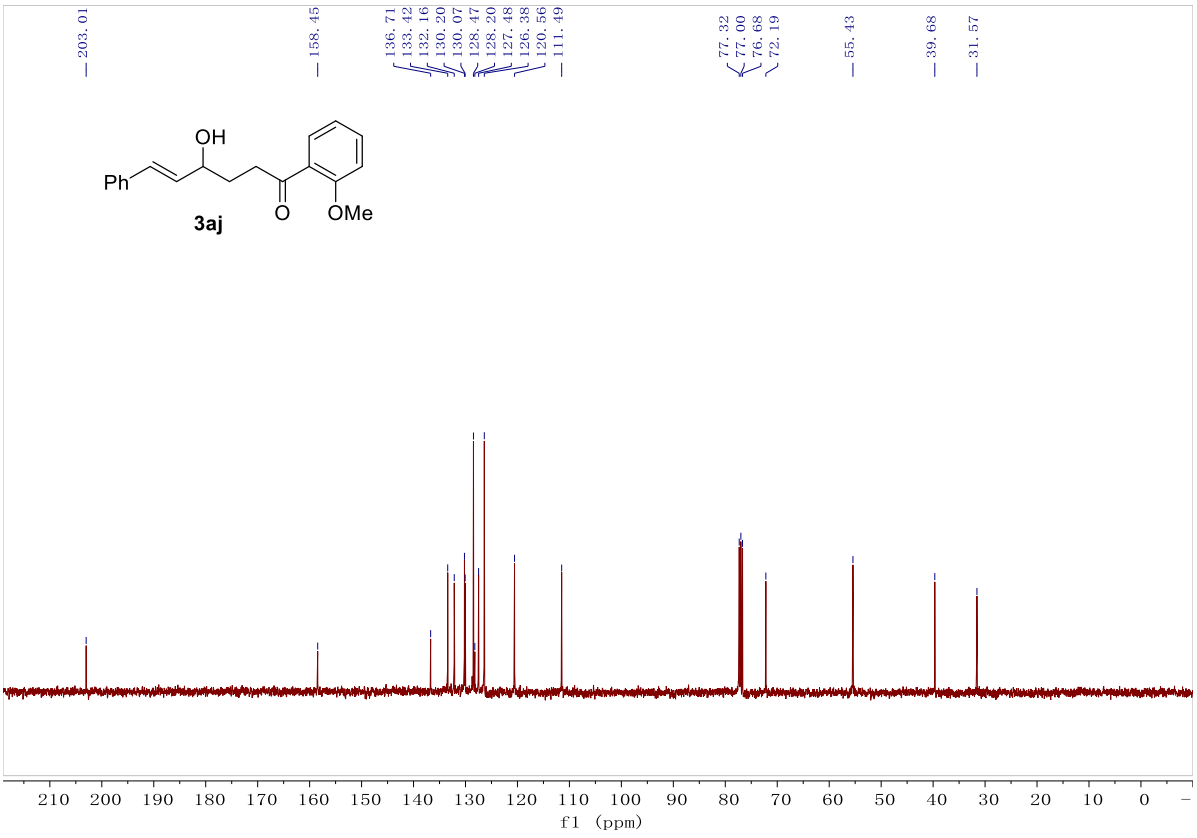
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ai



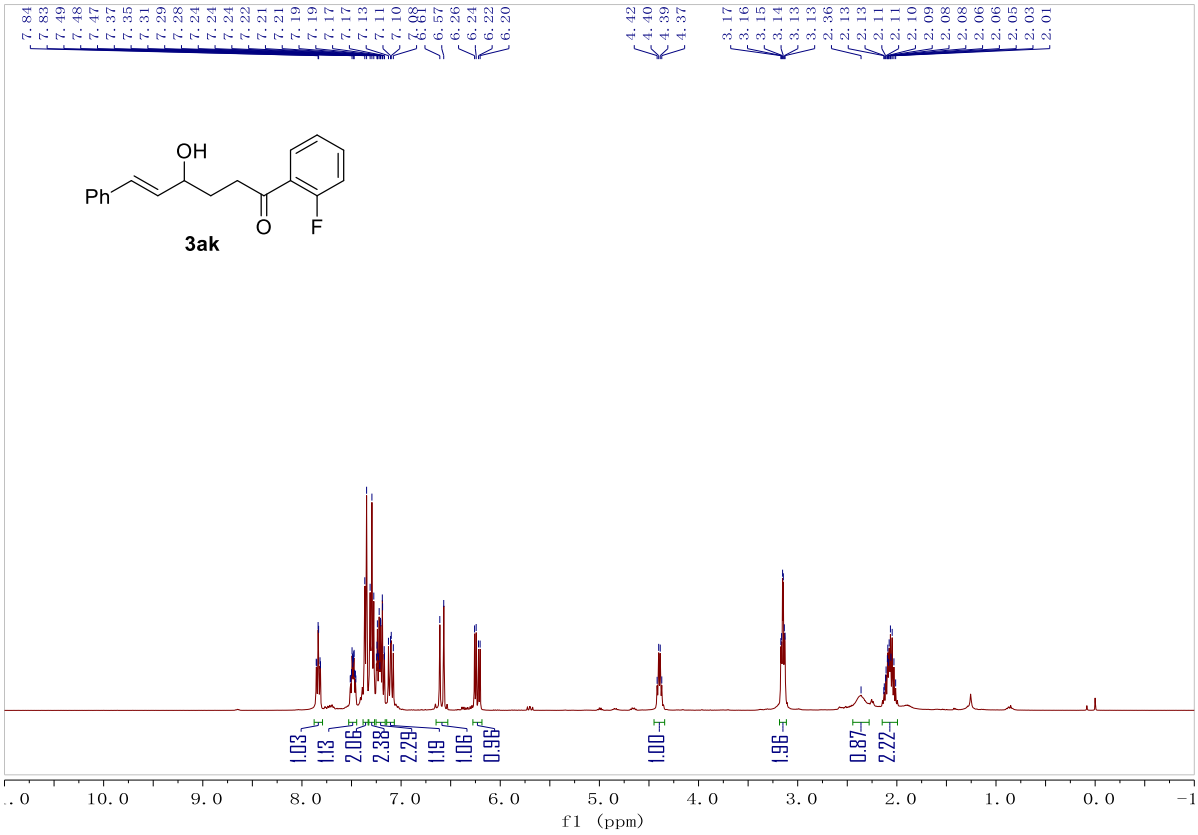


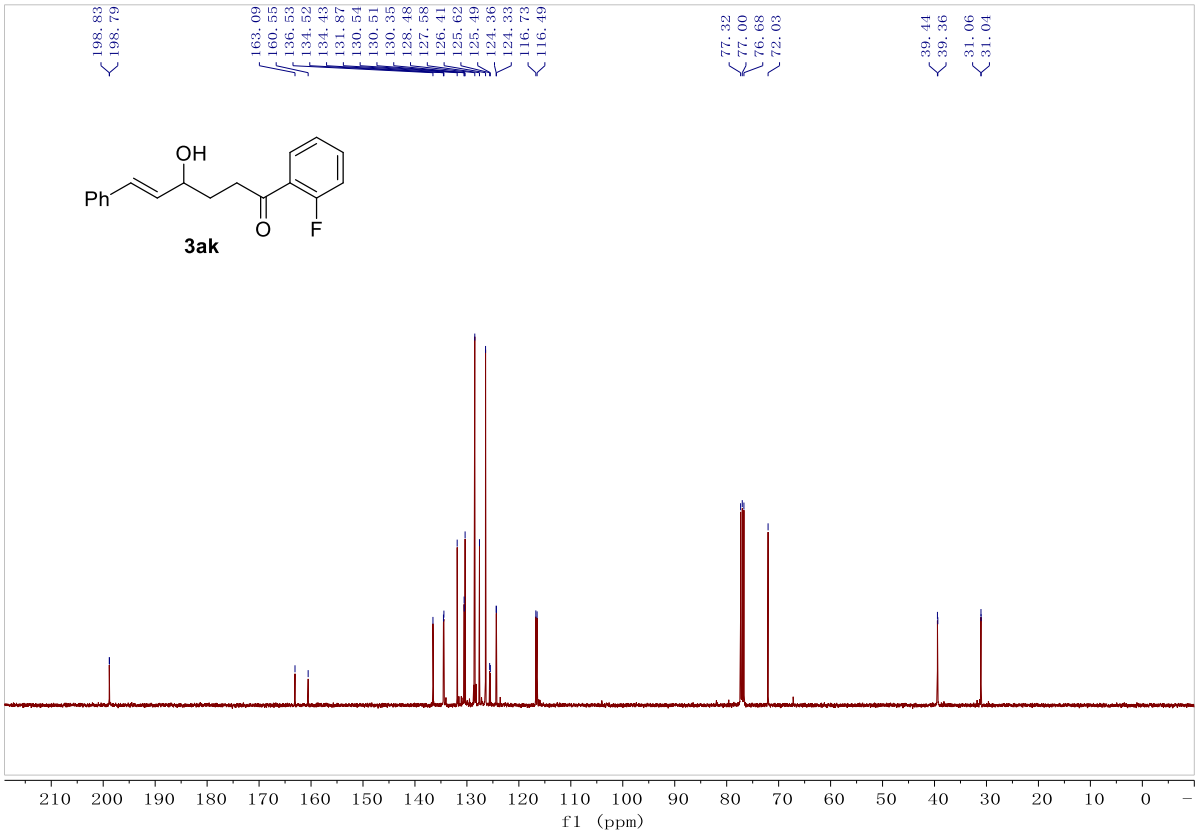
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3aj

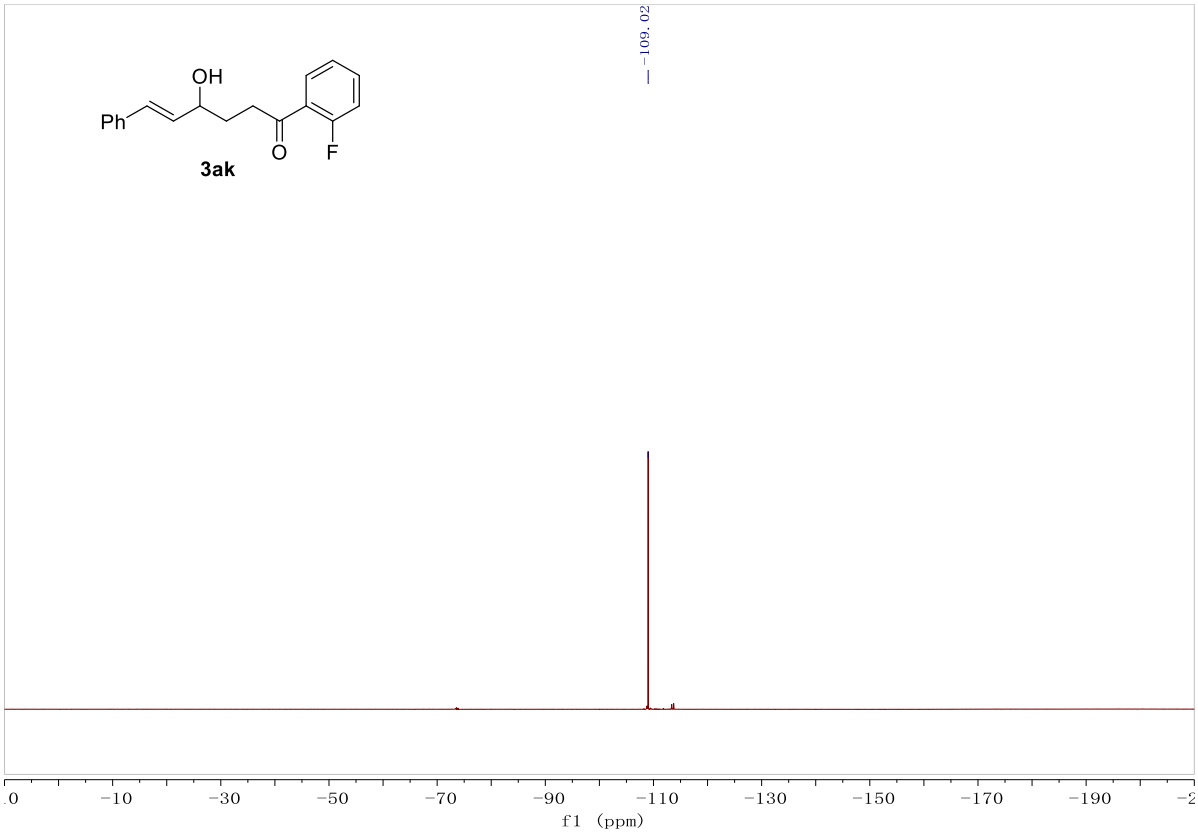




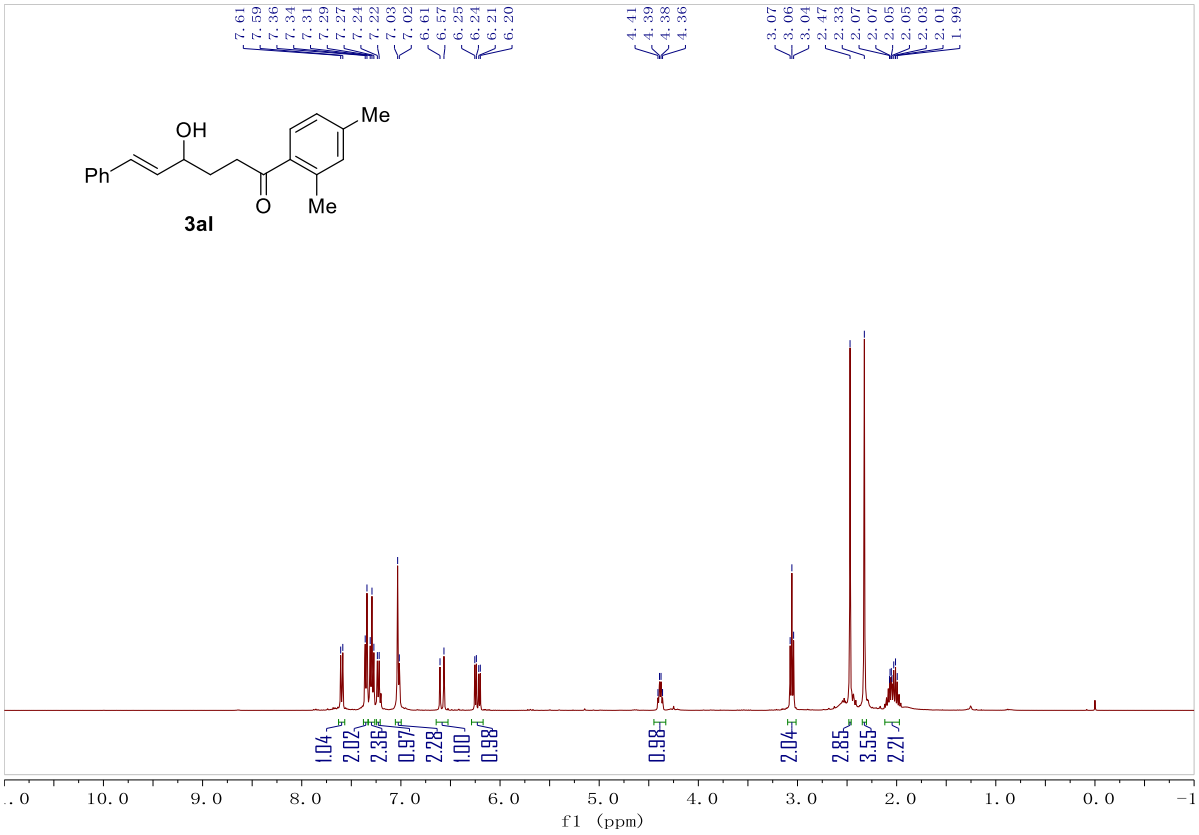
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ak

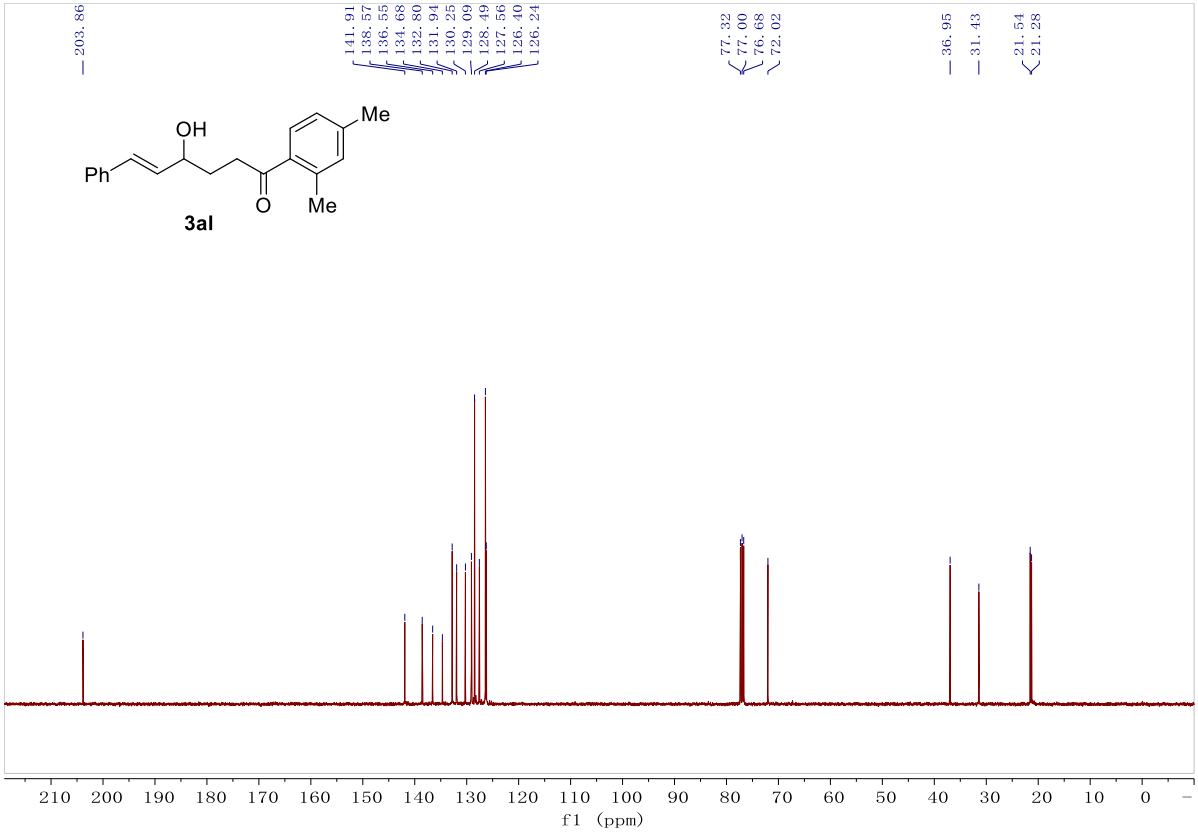




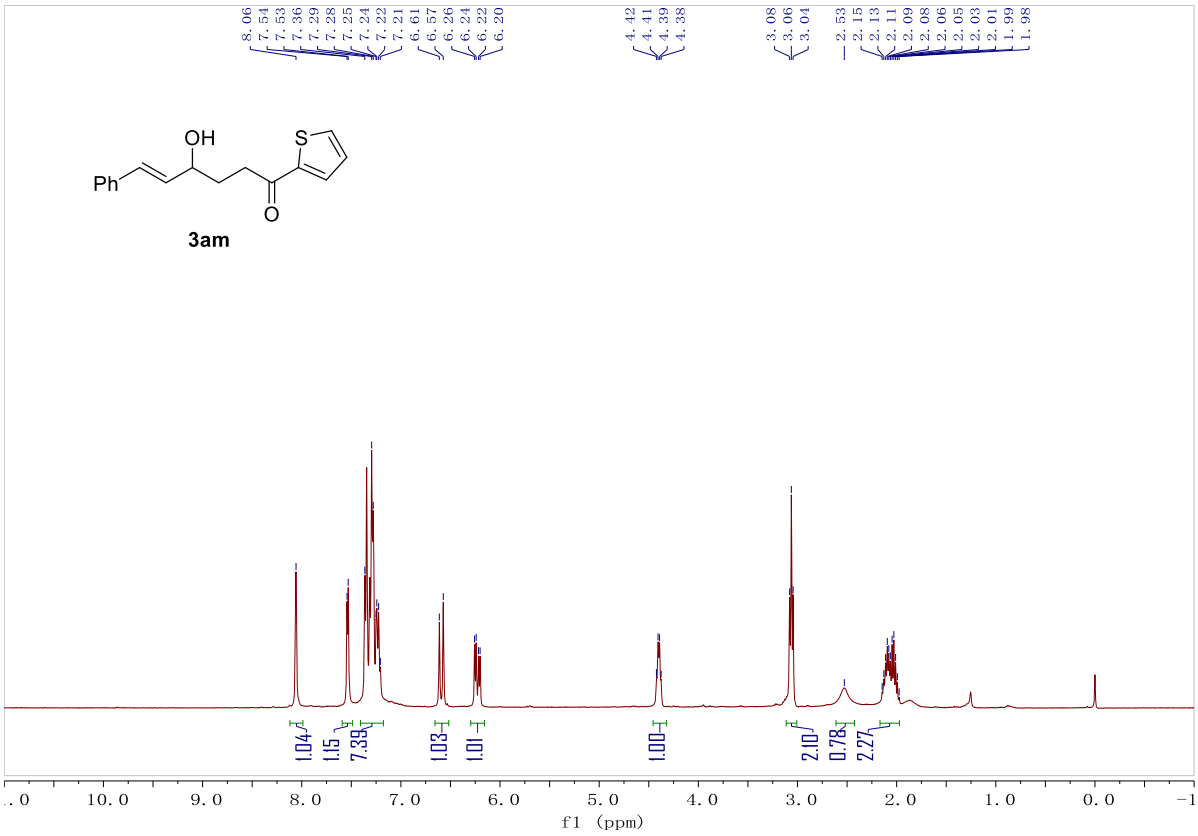


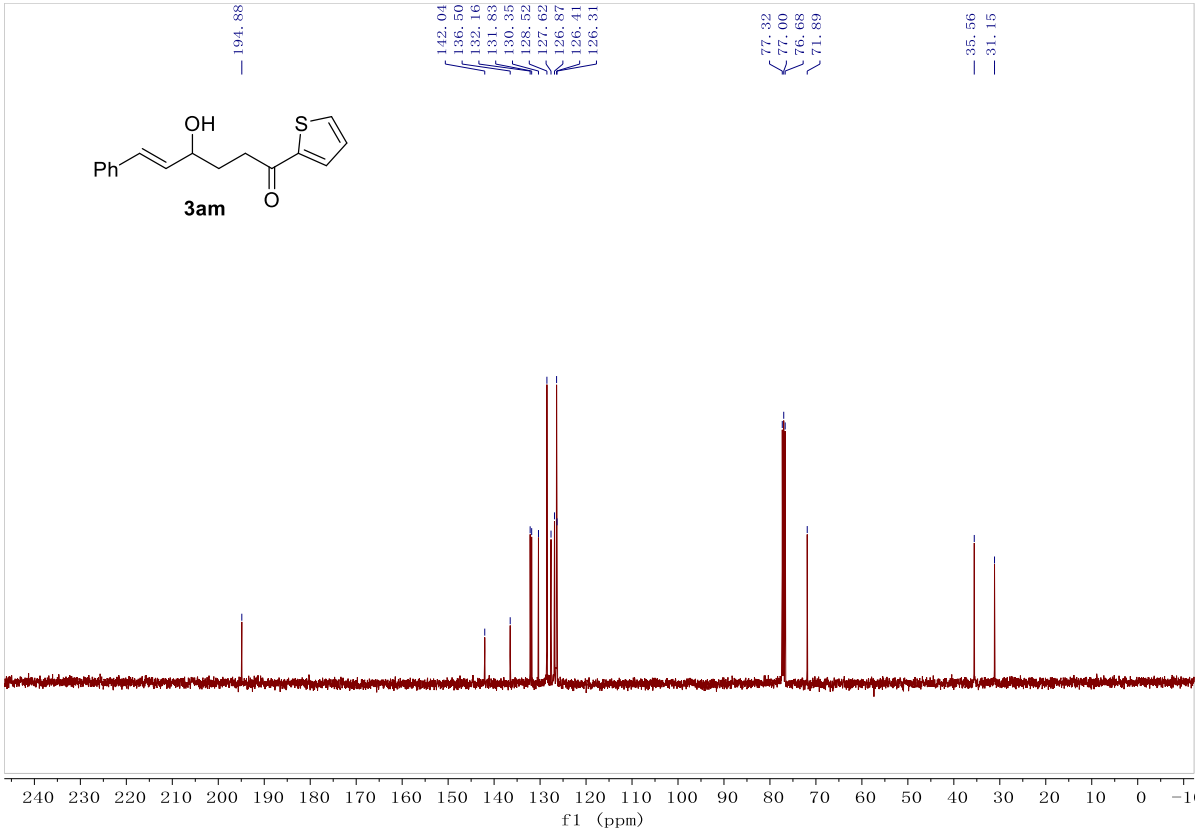
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3al



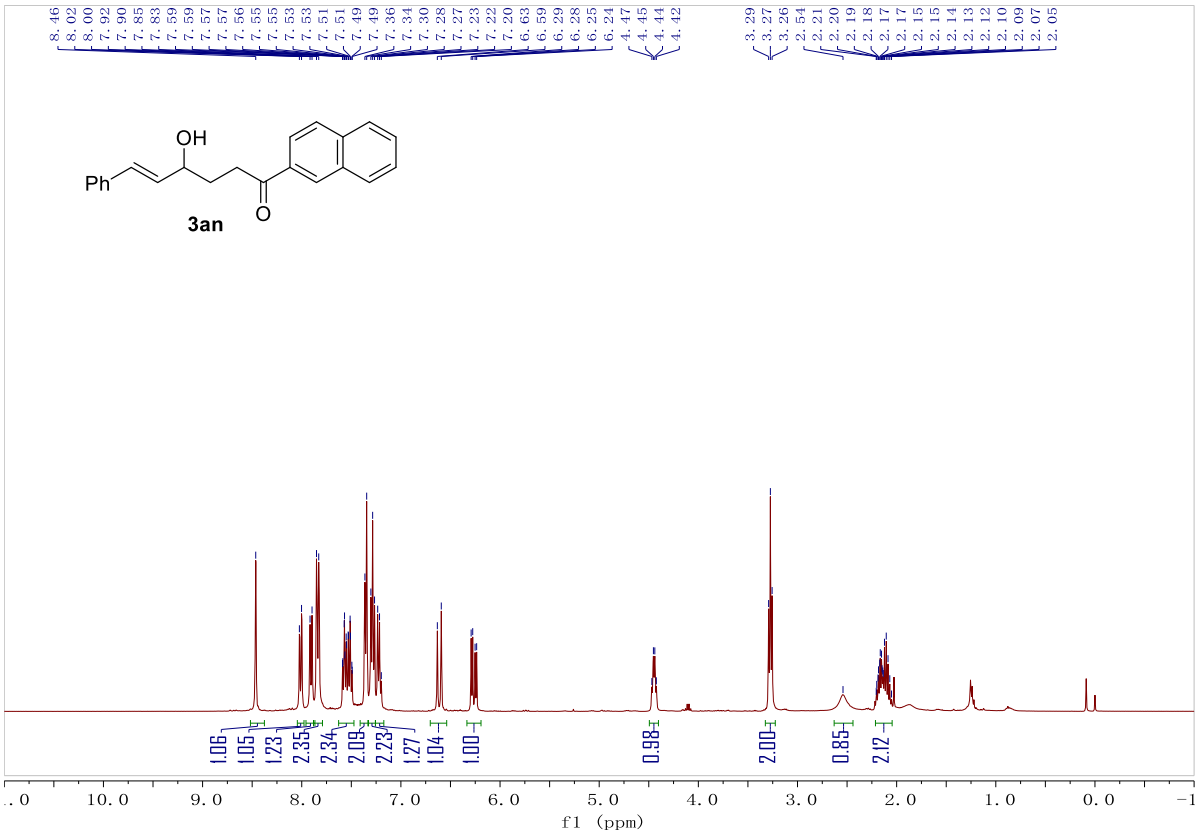


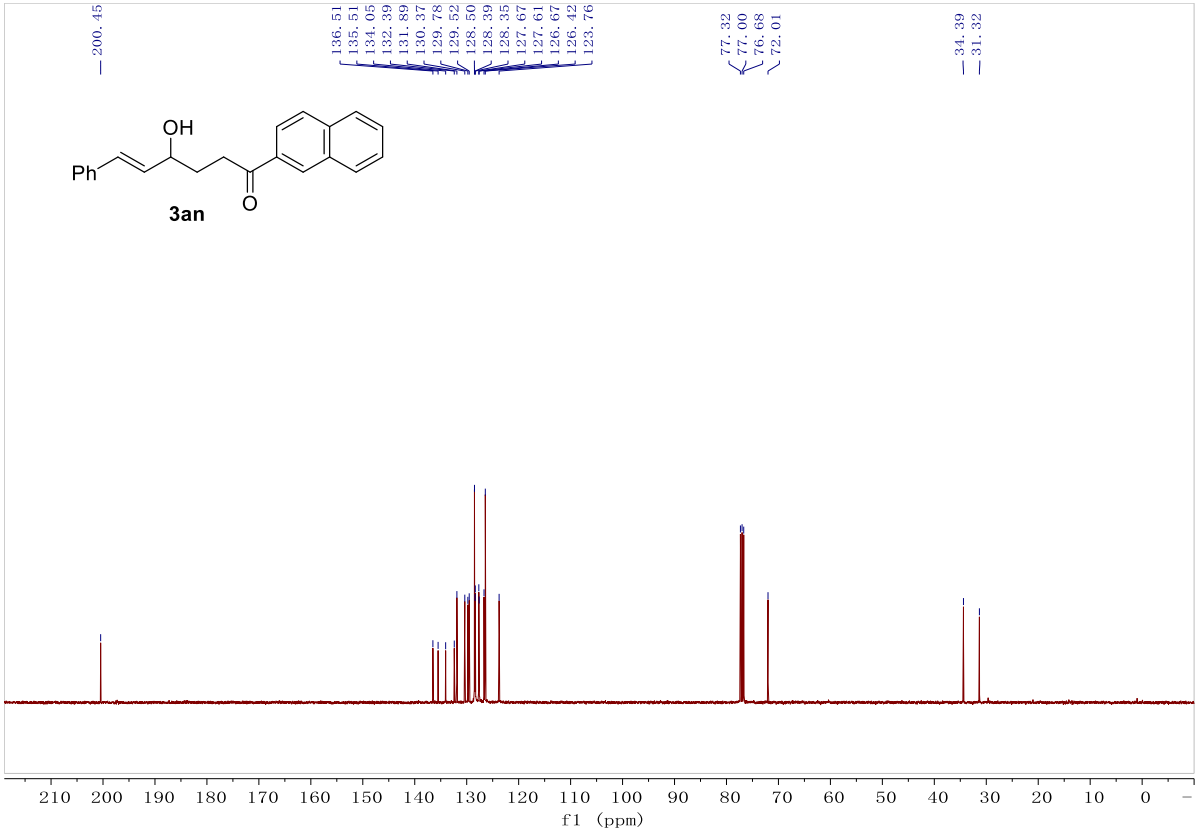
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3am



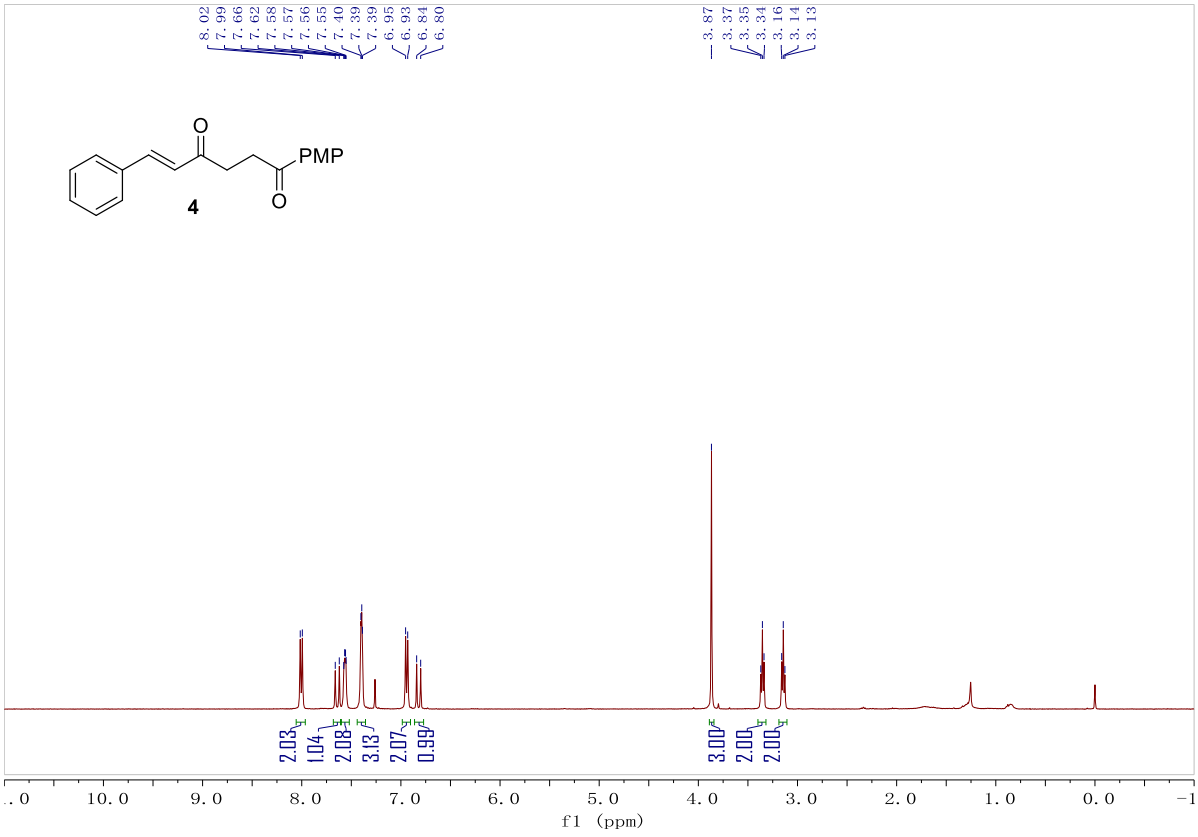


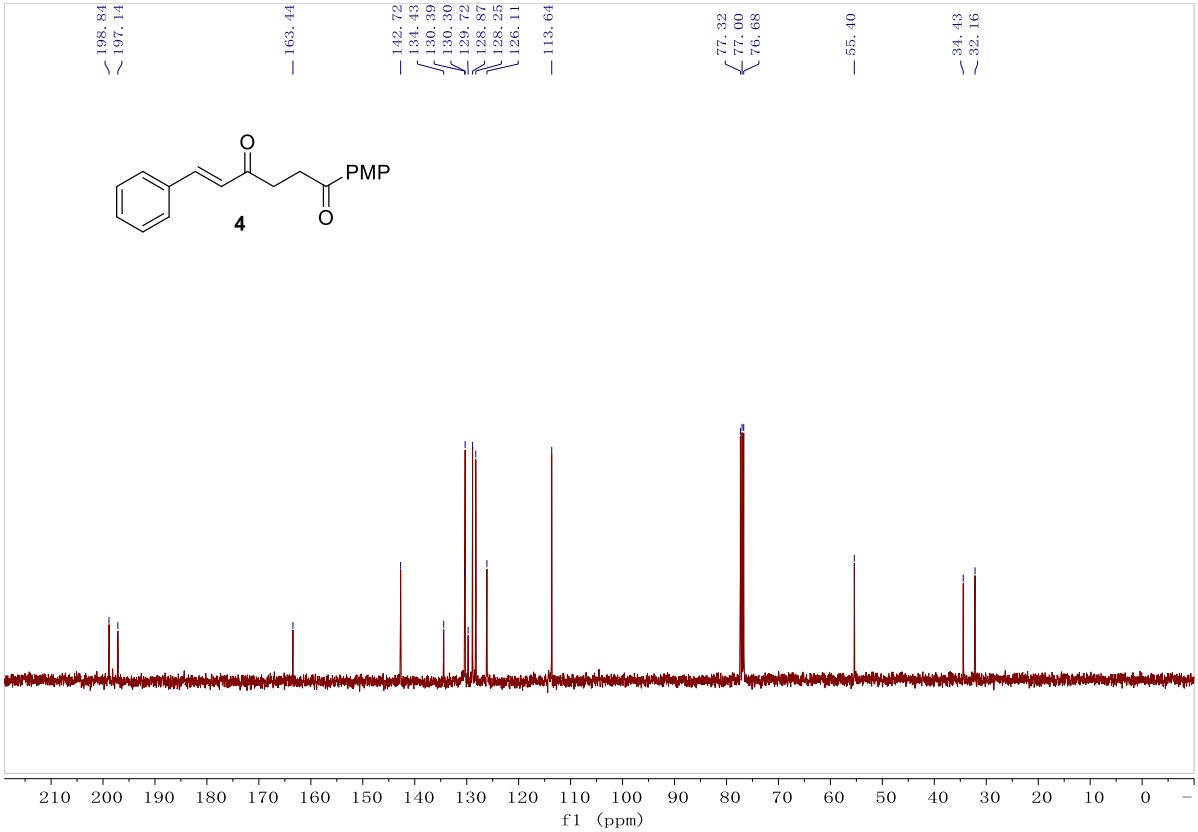
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3an



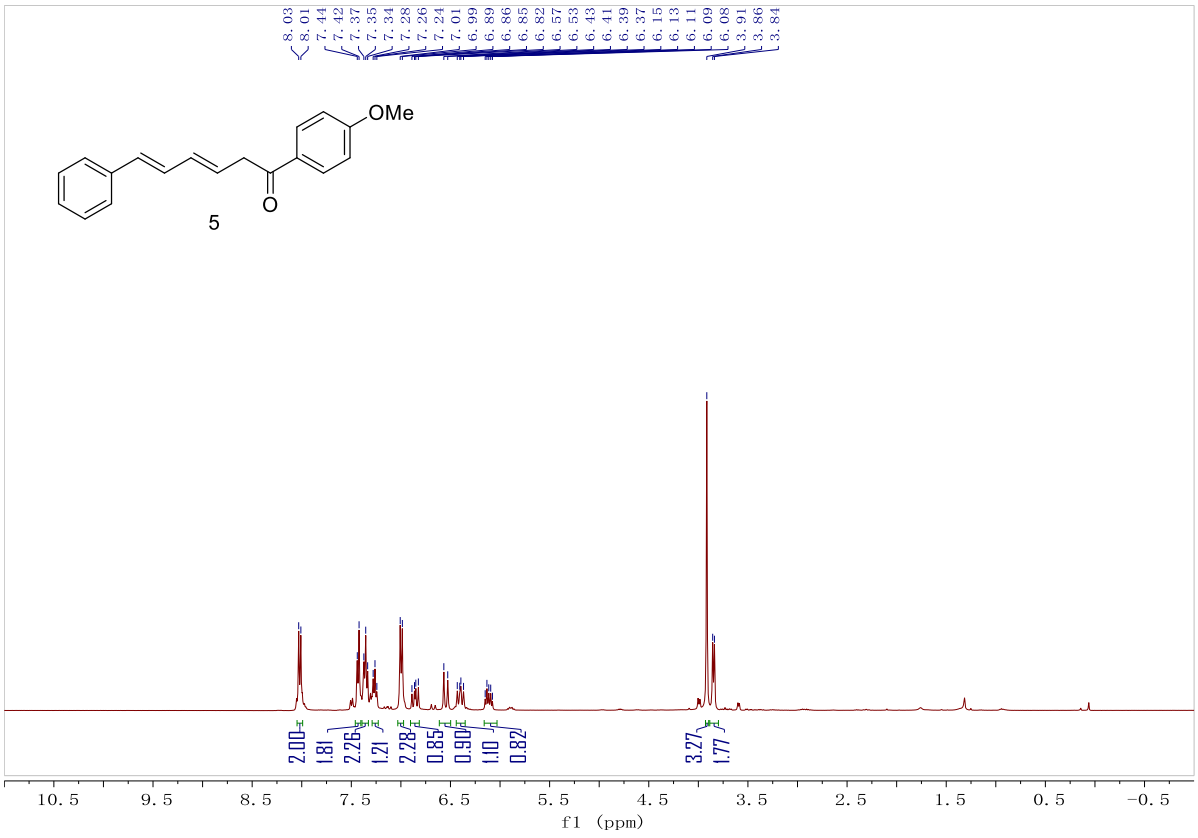


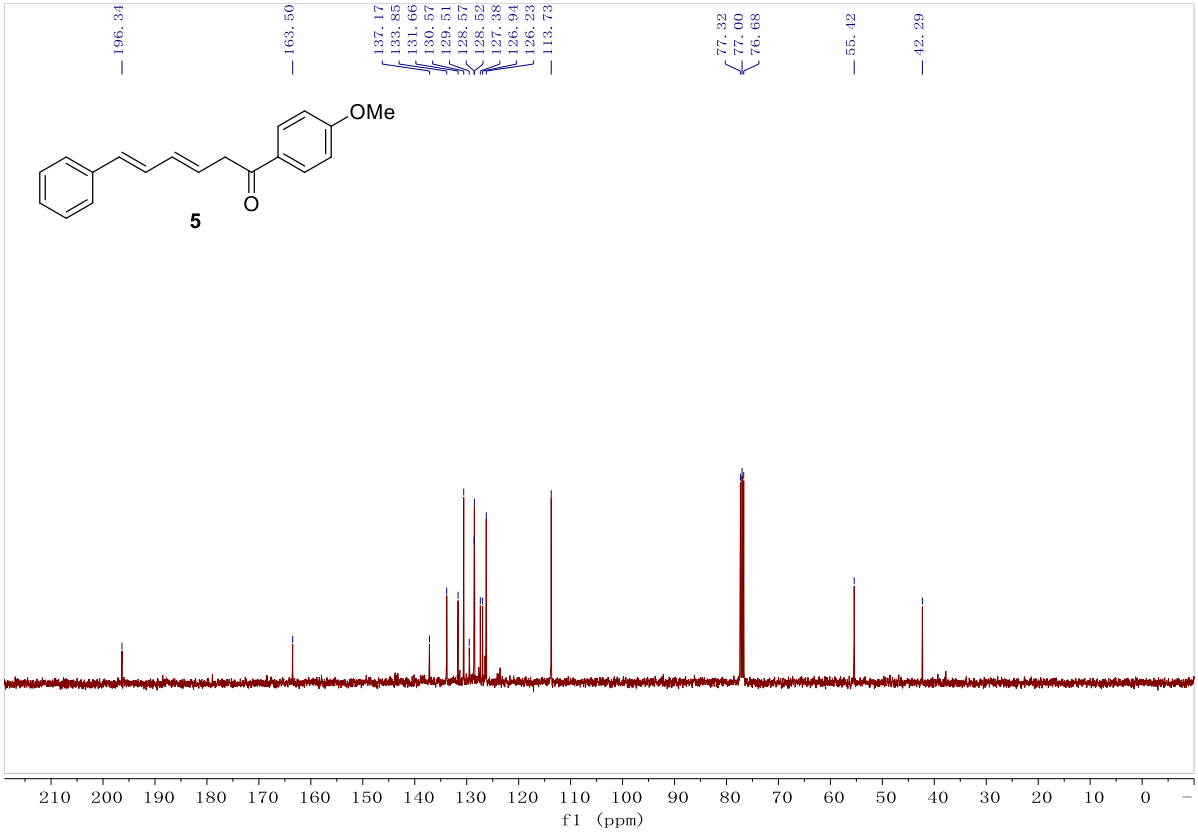
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4



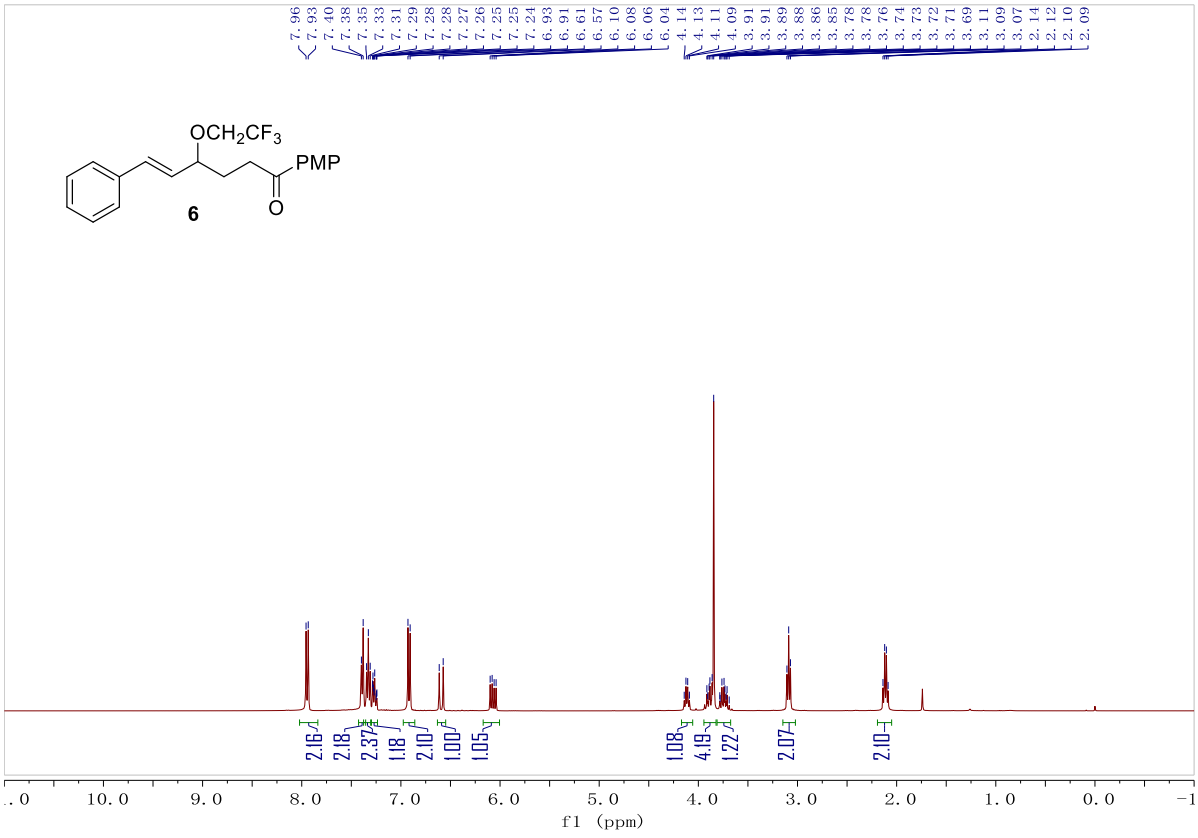


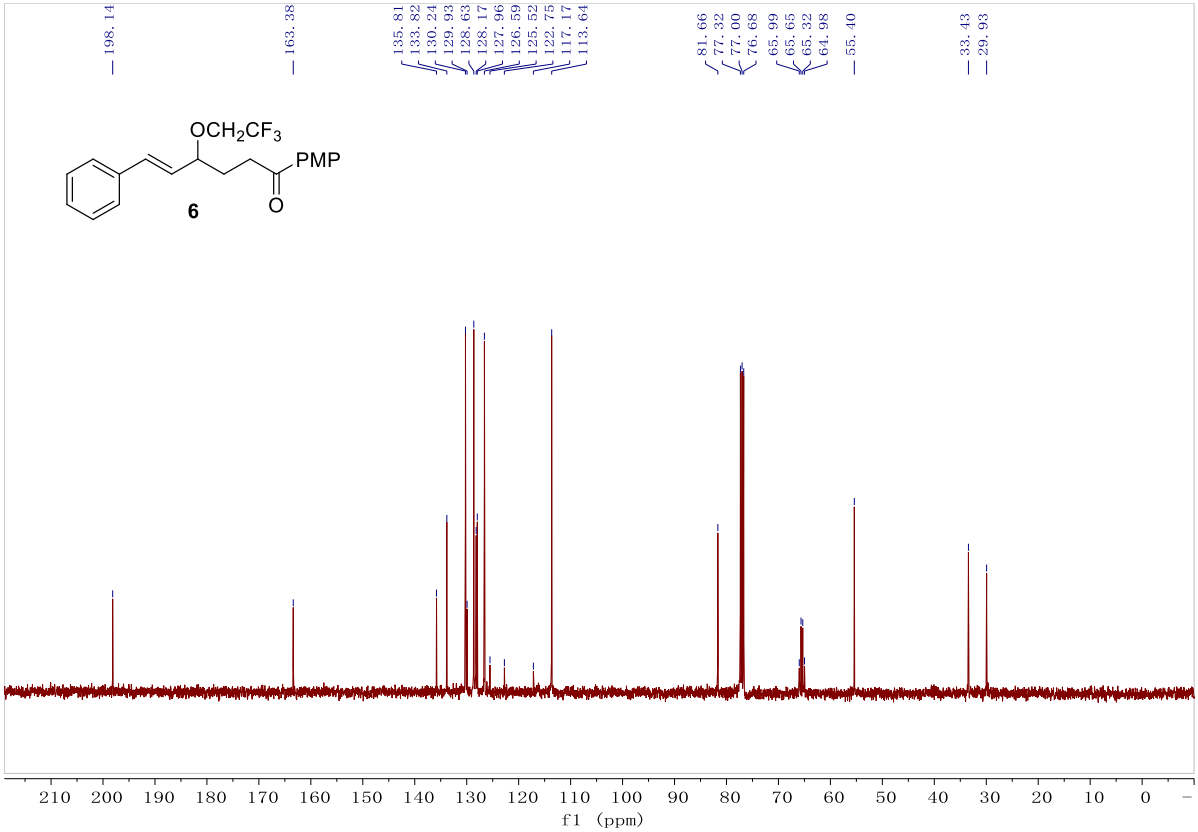
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$)spectra of product 6

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135.81
133.82
130.24
129.93
128.63
128.17
127.96
126.59
125.52
122.75
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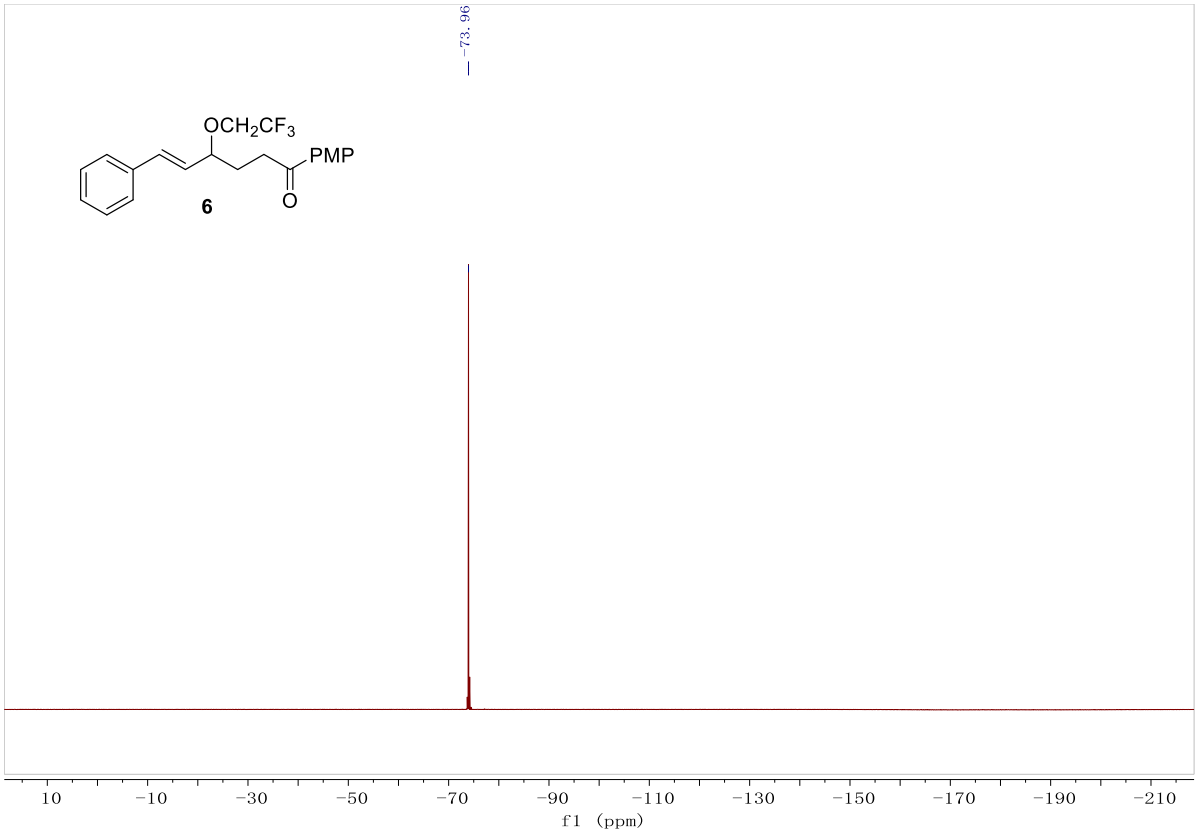
113.64
81.66
77.32
77.00
76.68
65.99
65.65
65.32
64.98
55.40
33.43
29.93
OCH2CF3
PMP
O
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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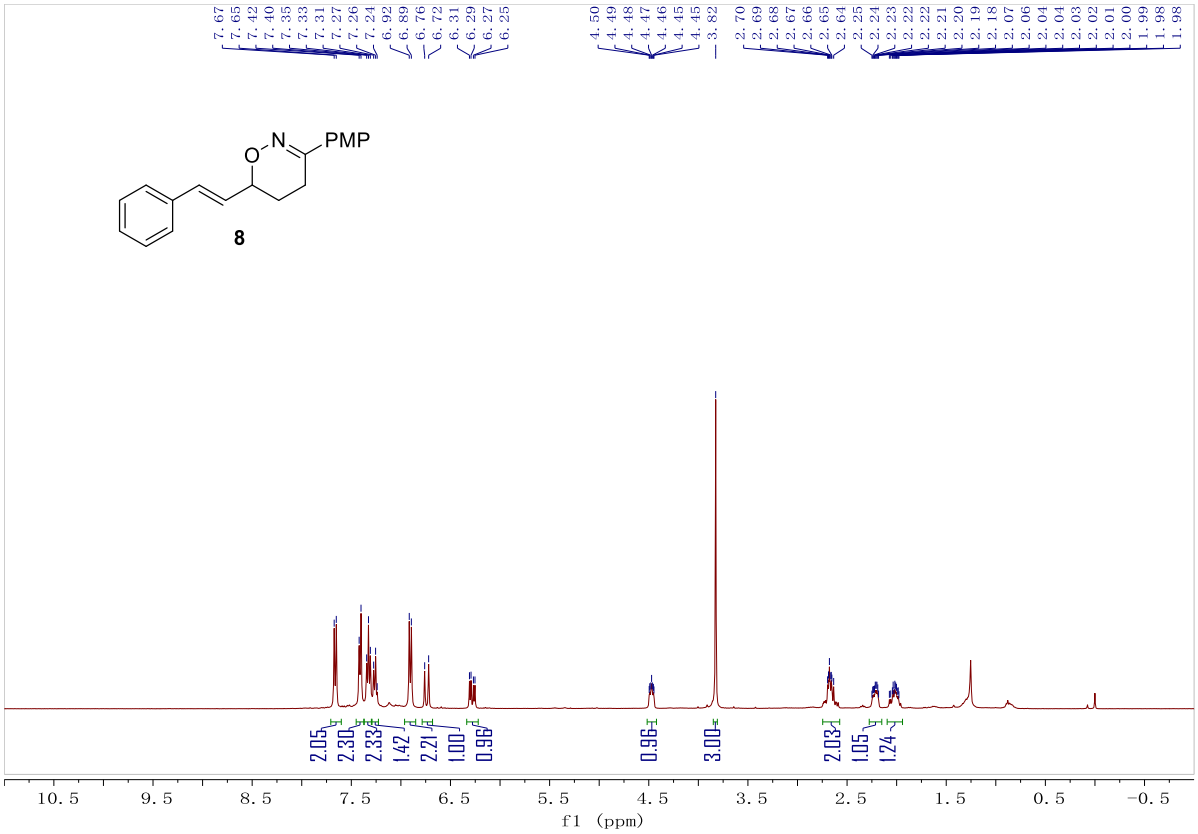
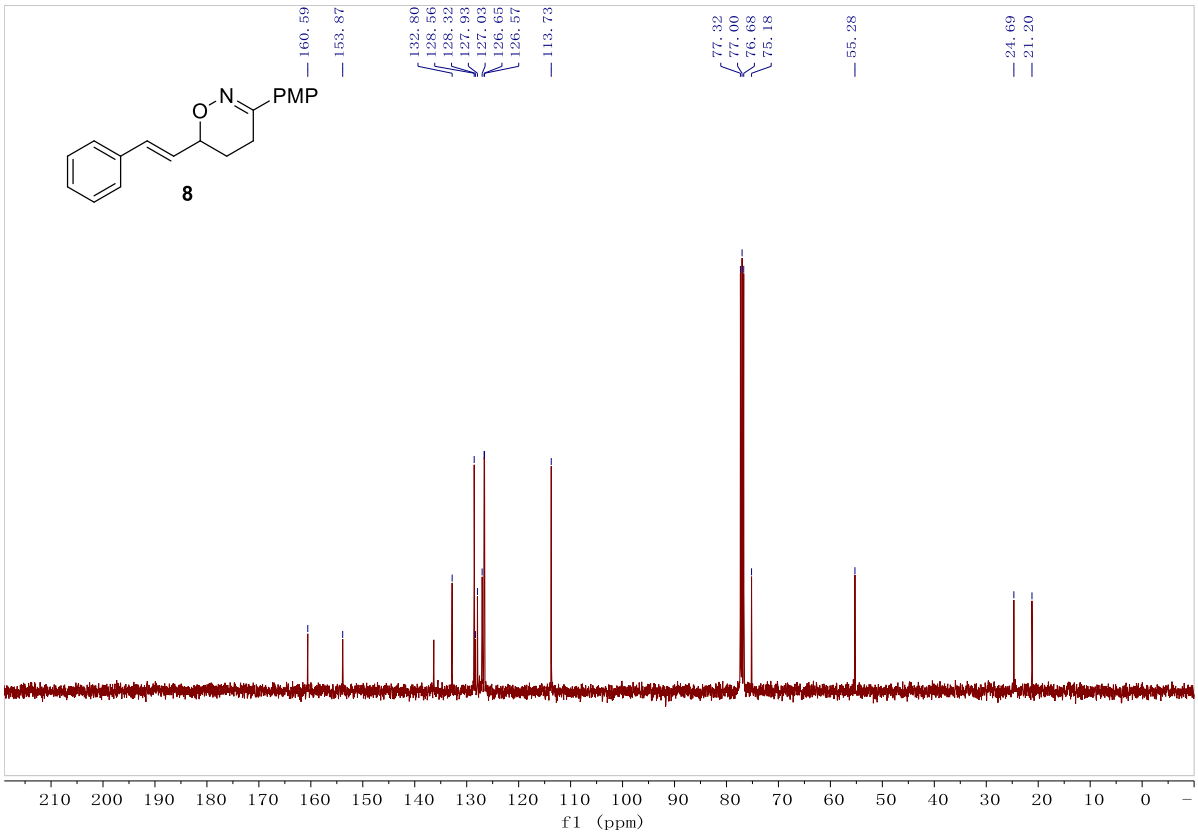
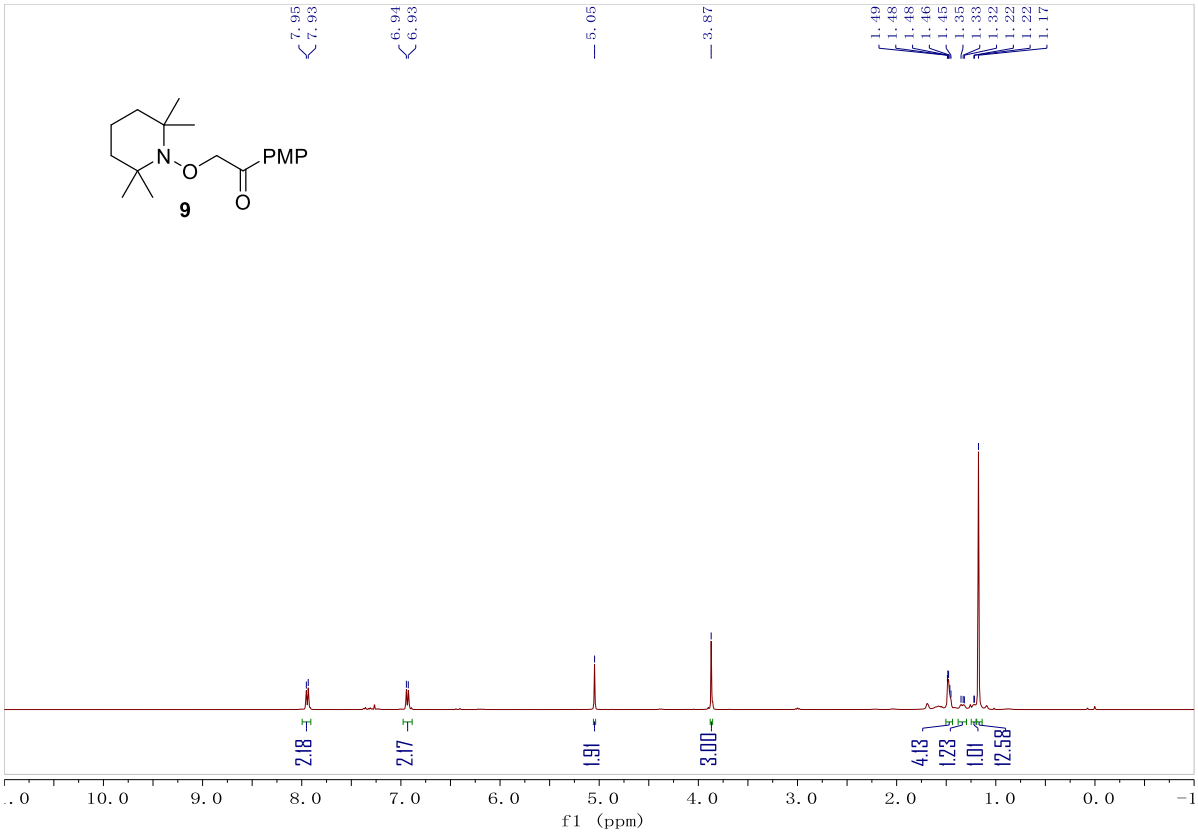
PMP
O
6
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

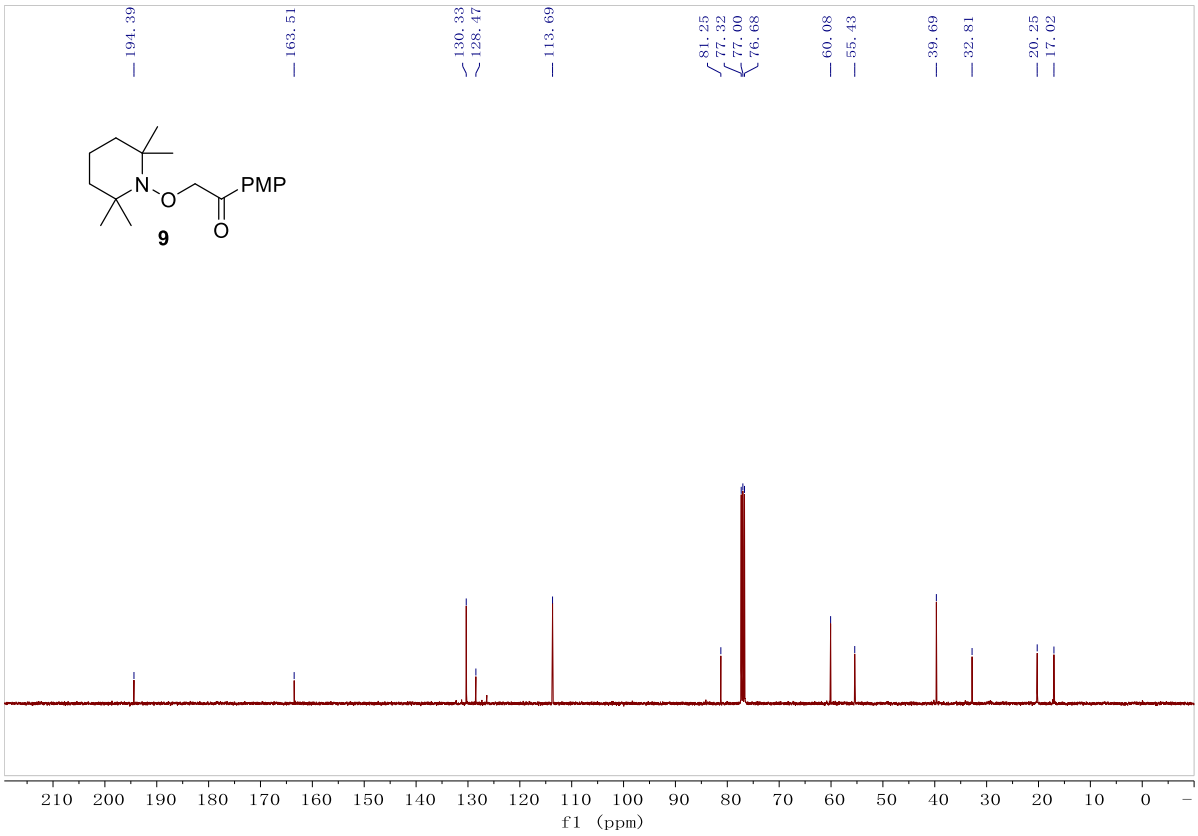
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 8



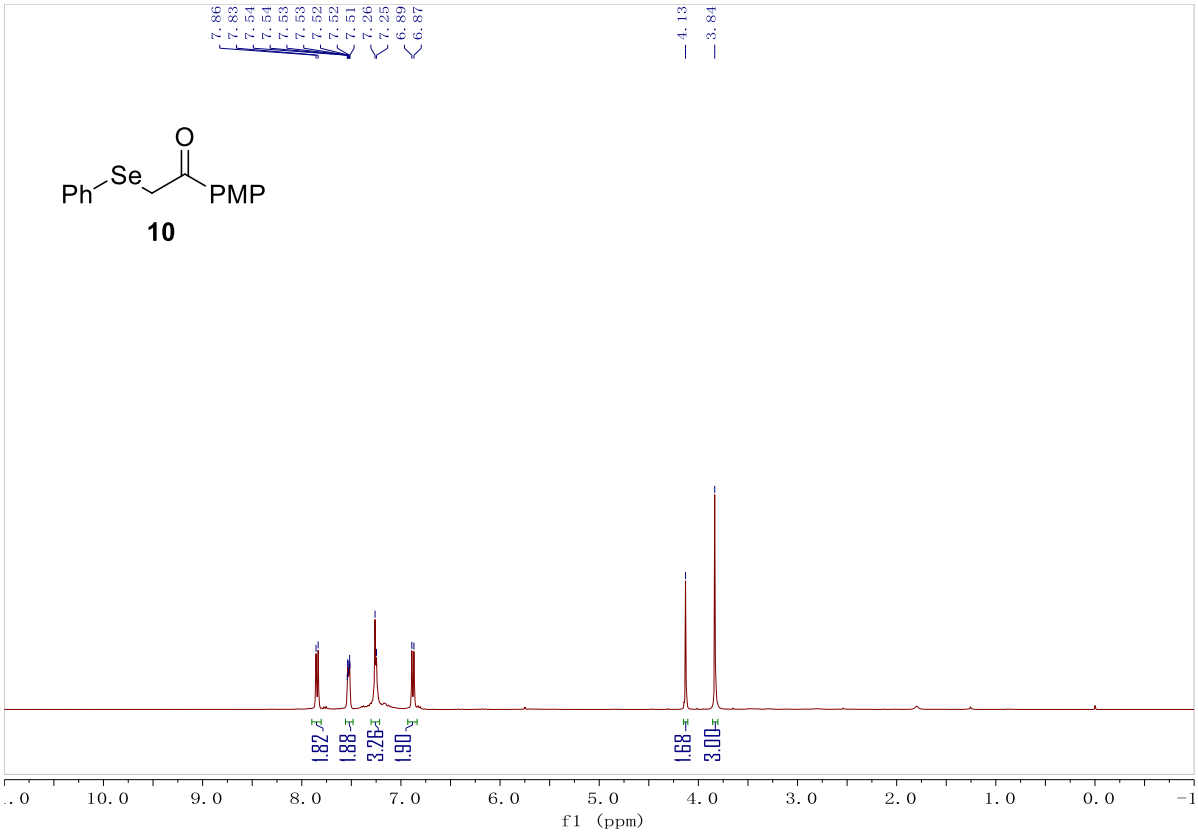


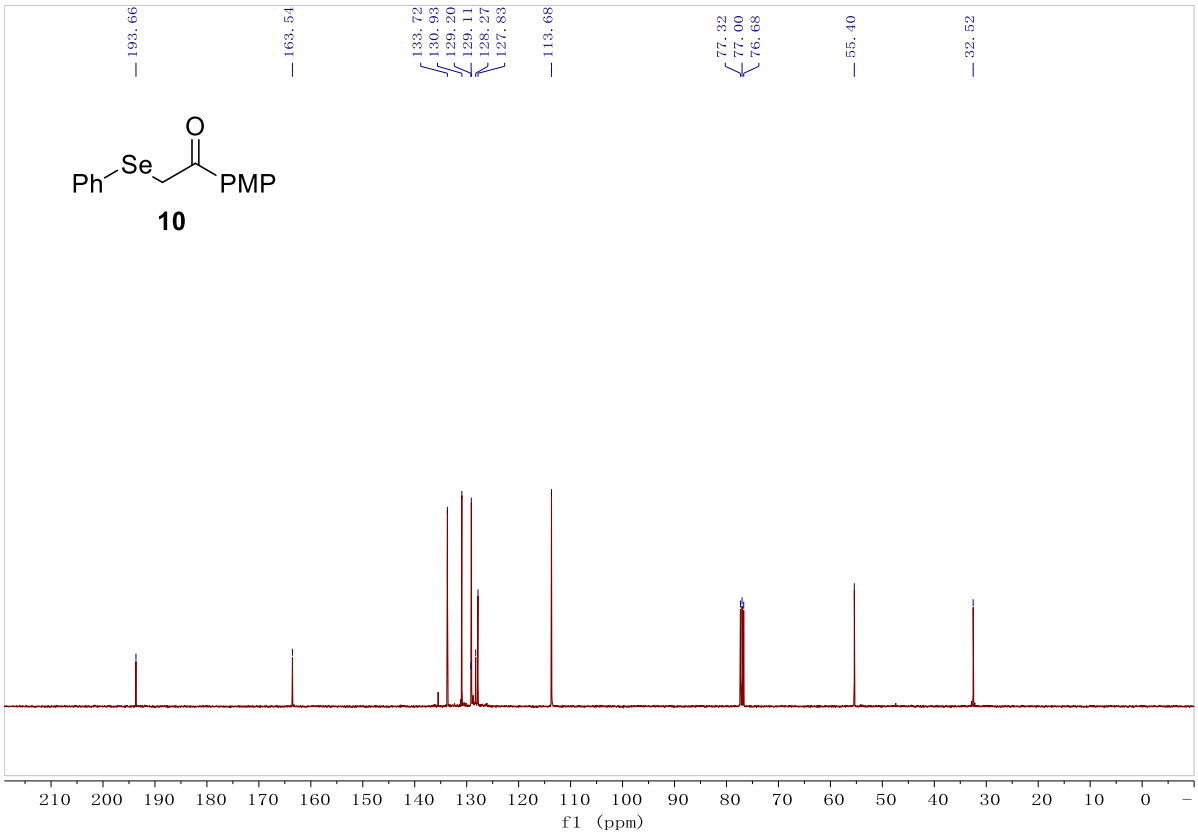
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 9





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 10





^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) spectra of 2a-I