Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Catalyst-controlled and visible-light-induced acylmethylation and bromoacylmethylation of Morita-Baylis-Hillman acetates with *a*-bromo ketones: access to highly functionalized 1,5-dicarbonyl compounds

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1. Experimental section

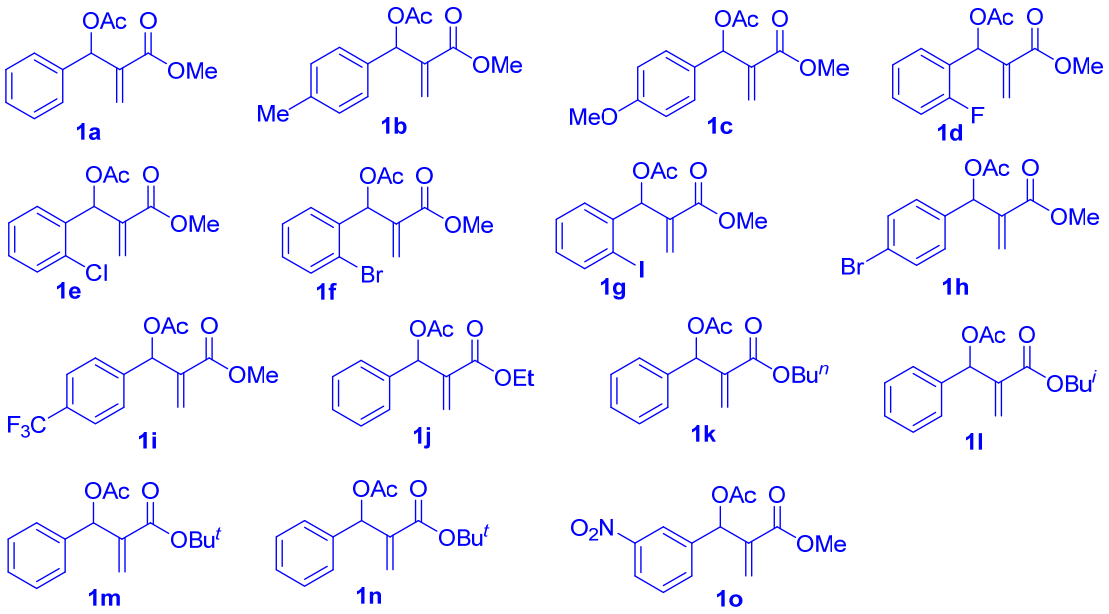
All reagents were used directly as obtained commercially unless otherwise noted and were used directly without any purification. Solvents were freshly distilled prior to use. All reactions were carried out under argon atmosphere unless noted. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance III 500 MHz spectrometer in $CDCl_3$ solution. High resolution mass (HRMS) spectra were measured with a VG Auto Spec-3000 spectrometer. Melting points (Mp) were determined with a digital electro thermal apparatus without further correction. TLC analyses were performed on commercial glass plates bearing a 0.25mm layer of Merck silica gel 60 F254. Silica gel (200-300 mesh) was used for column chromatography. Morita-Baylis-Hillman acetates **1** were prepared according to the previous reported protocols.[1] The *a*-bromo ketones **2** were purchased from the Wencai New Material Technology and Merck in high purity.

2. Experimental procedures

A. General procedure for preparation of Morita-Baylis-Hillman acetates (1a-m)[1]

The Morita-Baylis-Hillman (MBH) adducts was synthesized by the literature[2]. To a stirred solution of MBH products (1.0 equiv.) in dichloromethane was added acetic anhydride (1.5 equiv.) and *N,N*-dimethylaminopyridine (0.2 equiv.) at room temperature. After stirring at the same temperature for 1 hour, the reaction mixture was treated with water and extracted with dichlorormethane. The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure and purified by silica gel column chromatography.

Morita-Baylis-Hillman acetates (1a-1o) were synthesized using the above method:



B. General experimental procedure for photocatalytic acylmethylation of Morita-Baylis-Hillman acetates with *a*-bromo ketones

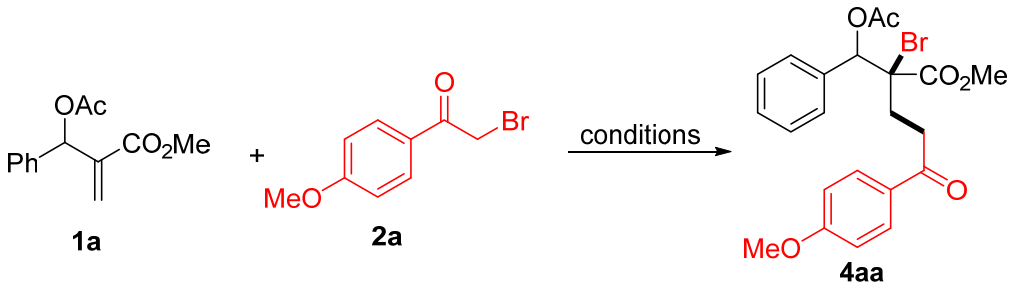
An 10 mL oven-dried Schlenk tube was equipped with a stirring bar, Morita-Baylis-Hillman acetates **1** (0.2 mmol), *a*-bromo ketones **2** (0.3 mmol, 1.5 equiv.), and Rose bengal (0.004 mmol, 2 mol%). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then TIPA (0.4 mmol, 2.0 equiv.) and MeOH (2 mL) were injected into the reaction tube. The solution was placed in a distance of 3 cm from 15 W blue LED at room temperature for 12 h under argon atmosphere. Upon completion, quench the reaction with saturated NaCl (10 mL), and the mixture was extracted with dichloromethane (3×15 mL). The combined organic layer was washed three times with H_2O (3×10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by SiO_2 column chromatography to afford the desired products.

C. General experimental procedure for photocatalytic bromoacylmethylation of Morita-Baylis-Hillman acetates with *a*-bromo ketones

An 10 mL oven-dried Schlenk tube was equipped with a stirring bar, Morita-Baylis-Hillman acetates **1** (0.2 mmol), *a*-bromo ketones **2** (0.3 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.01 mmol, 5 mol%), and K_2HPO_4 (0.1 mmol, 0.5 equiv.). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then CH_2Cl_2 (2 mL) were injected into the reaction tube. The solution was placed in a distance of 3 cm from 15 W blue LED at room temperature for 24 h under argon atmosphere. Upon completion, quench the reaction with saturated NaCl (10 mL), and the mixture was extracted with dichloromethane (3×15 mL). The combined organic layer was washed three times with H_2O (3×10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by SiO_2 column chromatography to afford the desired products.

3. Optimization of the reaction conditions

3.1 Table S1 Optimization of the reaction conditions for photocatalytic bromoacylmethylation of Morita-Baylis-Hillman acetates with *a*-bromo ketones[a]



Entry	Photocatalyst	Base	Solvent	Yield (%)[b]
1	Ir(ppy)$_3$	K_2HPO_4	DMF	73(60)[c]
2	Ru(bpy)$_3$Cl$_2$•6H$_2$O	K_2HPO_4	DMF	N.R.[d]
3	[Ir(dtbbpy)(bpy)$_2$]PF$_6$	K_2HPO_4	DMF	N.R.[d]
4	Ru(bpy)$_3$PF$_6$	K_2HPO_4	DMF	trace
5	Na$_2$-eosin Y	K_2HPO_4	DMF	trace
6	4-CzIPN	K_2HPO_4	DMF	trace
7	Rose Bengal	K_2HPO_4	DMF	trace
8	Ir(ppy)$_3$	DIPEA	DMF	N.R.[d]
9	Ir(ppy)$_3$	Et_3N	DMF	trace
10	Ir(ppy)$_3$	DMAP	DMF	16
11	Ir(ppy)$_3$	DABCO	DMF	24
12	Ir(ppy)$_3$	DBU	DMF	trace
13	Ir(ppy)$_3$	K_3PO_4	DMF	35
14	Ir(ppy)$_3$	Cs_2CO_3	DMF	trace
15	Ir(ppy)$_3$	K_2CO_3	DMF	trace
16	Ir(ppy)$_3$	$NaHCO_3$	DMF	50
17	Ir(ppy)$_3$	K_2HPO_4	THF	58
18	Ir(ppy)$_3$	K_2HPO_4	DCE	74

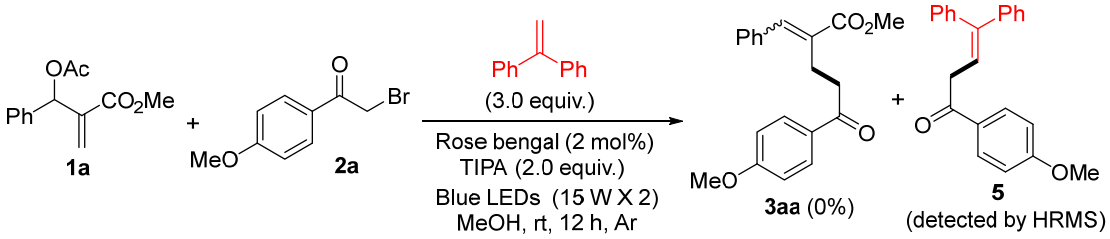
19	*$Ir(ppy)_3$*	*K_2HPO_4*	*CH_2Cl_2*	*92*
20	$Ir(ppy)_3$	K_2HPO_4	CH_3CN	91
21	$Ir(ppy)_3$	K_2HPO_4	DMA	77
22	$Ir(ppy)_3$	K_2HPO_4	DMSO	49
23	$Ir(ppy)_3$	K_2HPO_4	DCE/H_2O	86
24	$Ir(ppy)_3$	K_2HPO_4	CH_3CN/H_2O	48
25	$Ir(ppy)_3$	K_2HPO_4	CH_2Cl_2/H_2O	67

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), photocatalyst (5.0 mol%, 0.01mmol), Base (0.1 mmol, 0.5 equiv.) solvent (2 mL) at room temperature under visible light irradiation (blue LEDs 15 W) in argon for 24 h. [b] NMR yield based on **1a** using 1,3,5-trimethoxybenzene as the internal standard. [c] Using 2.0 mol% $Ir(ppy)_3$. [d] N.R. = no reaction.

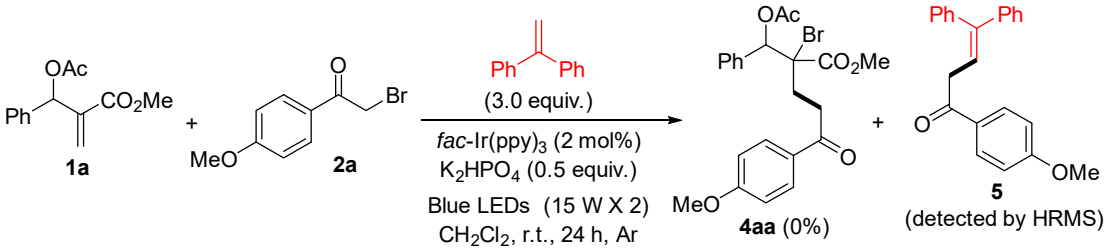
4. Evidence for a radical pathway

Catalytic reaction interfered with a radical quencher:

A. acylmethylation: An 10 mL oven-dried Schlenk tube was equipped with a stirring bar, Morita-Baylis-Hillman acetate **1a** (0.2 mmol), *a*-bromo ketone **2a** (0.3 mmol, 1.5 equiv.), rose bengal (0.004 mmol, 2 mol%) and 1,1-diphenylethylene (0.6 mmol, 3.0 equiv.). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then TIPA (0.4 mmol, 2.0 equiv.) and MeOH (2 mL) were in jected into the reaction tube. The solution was placed in a distance of 3 cm from 15 W blue LED at room temperature. After being stirred at room temperature for 12 h under argon atmosphere, the solution was used directly for HRMS analysis.



B. bromoacylmethylation: An 10 mL oven-dried Schlenk tube was equipped with a stirring bar, Morita-Baylis-Hillman acetate **1a** (0.2 mmol), *a*-bromo ketone **2a** (0.3 mmol, 1.5 equiv.), *fac*-$Ir(ppy)_3$ (0.01 mmol, 5 mol%), K_2HPO_4 (0.1 mmol, 0.5 equiv.) and 1,1-diphenylethylene (0.6 mmol, 3.0 equiv.). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then CH_2Cl_2 (2 mL) were in jected into the reaction tube. The solution was placed in a distance of 3 cm from 15 W blue LED at room temperature. After being stirred at room temperature for 24 h under argon atmosphere, the solution was used directly for HRMS analysis.



定性化合物报告

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IRM 校正状态	成功	数据方法	ZNZ-2022.m
注释			
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Info.		Stream Name	LC 1
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)		

化合物列表

化合物标签	RT	质量数	丰度	分子式	目标质量	误差 (ppm)
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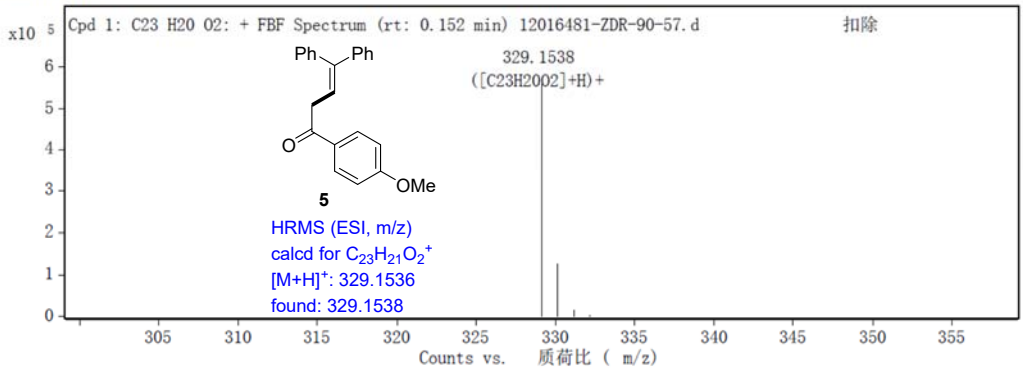
MS 缩放的质谱图



MS 质谱图峰列表

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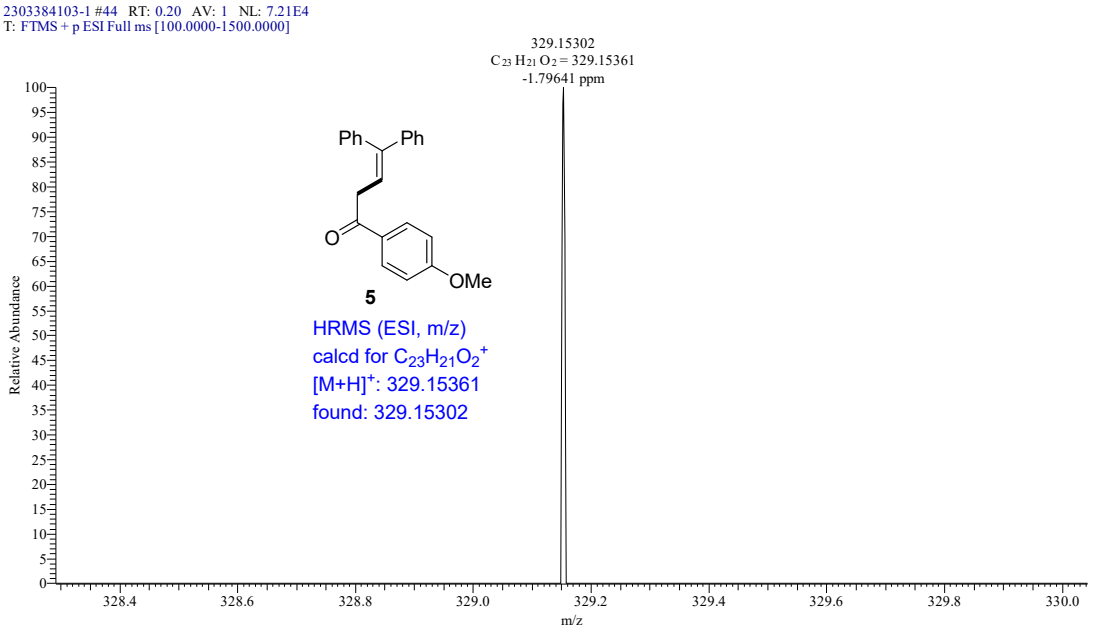
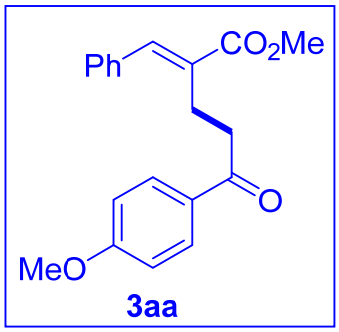
330.1577	1	129032.55	C23H20O2	(M+H)+
331.1625	1	18435.92	C23H20O2	(M+H)+
332.1666	1	2135.94	C23H20O2	(M+H)+

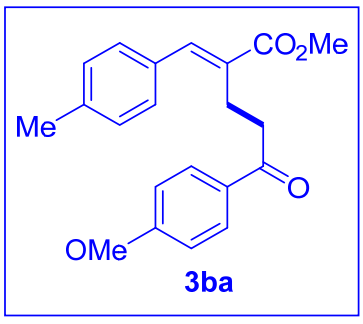
--- 报告结束 ---



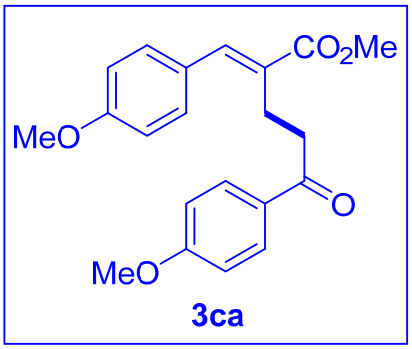
5. NMR data of acylmethylated products (3aa-3ma and 3ab-3ap)



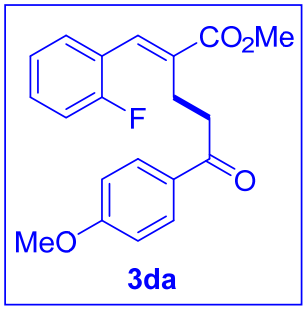
methyl (*E*)-2-benzylidene-5-(4-methoxyphenyl)-5-oxopentanoate (3aa): Yellow liquid, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.9 Hz, 2H), 7.76 (s, 1H), 7.34 (m, 5H), 6.92 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.21-3.12 (m, 2H), 3.00-2.92 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.7, 168.6, 163.5, 140.2, 135.3, 131.8, 130.4, 129.7, 129.2, 128.7, 128.6, 113.7, 55.4, 52.1, 37.7, 22.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{21}O_4$: 325.1434, Found: 325.1440.



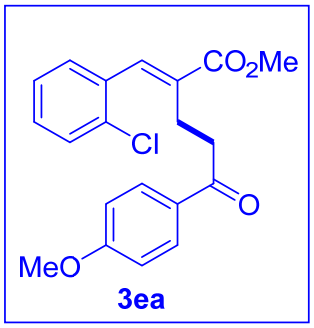
methyl (*E*)-5-(4-methoxyphenyl)-2-(4-methylbenzylidene)-5-oxopentanoate (3ba): Colourless liquid, yield: 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.19-3.15 (m, 2H), 3.00-2.95 (m, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.8, 168.7, 163.5, 140.2, 138.9, 132.4, 130.9, 130.4, 129.8, 129.4, 129.3, 113.7, 55.4, 52.0, 37.7, 22.9, 21.3 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{23}O_4$: 339.1591, Found: 339.1595.



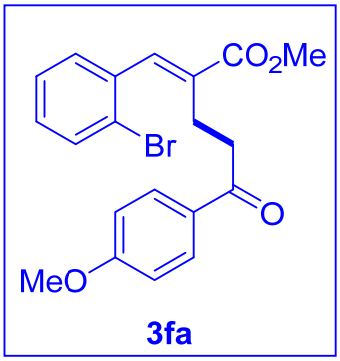
methyl (*E*)-2-(4-methoxybenzylidene)-5-(4-methoxyphenyl)-5-oxopentanoate (3ca): Colourless liquid, yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.9 Hz, 2H), 7.70 (s, 1H), 7.37 (d, J = 8.7 Hz, 2H), 6.91 (dd, J = 10.6, 8.7 Hz, 4H), 3.86 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.20-3.16 (m, 2H), 3.01-2.96 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.1, 169.0, 163.6, 160.1, 139.9, 131.3, 130.6, 129.6, 127.8, 114.3, 113.8, 55.6, 55.4, 52.1, 37.7, 23.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{23}O_5$: 355.1540, Found: 355.1548.



methyl (*E*)-2-(2-fluorobenzylidene)-5-(4-methoxyphenyl)-5-oxopentanoate (3da): Colourless liquid, yield: 60%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.8 Hz, 2H), 7.76 (s, 1H), 7.31 (m, 2H), 7.16-7.05 (m, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.18-3.14 (m, 2H), 2.88-2.83 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.7, 168.1, 163.6, 160.3 (d, J_{CF} = 249.5 Hz), 134.3, 133.1 (d, J_{CF} = 3.8 Hz), 130.5, 130.1 (d, J_{CF} = 2.5 Hz), 129.8, 124.3 (d, J_{CF} = 3.8 Hz), 123.4 (d, J_{CF} = 13.9 Hz), 115.8 (d, J_{CF} = 22.7 Hz), 113.8, 55.6, 52.3, 37.6, 23.4 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -113.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{20}FO_4$: 343.1340, Found: 343.1348.

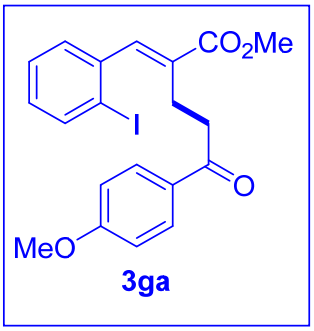


methyl (*E*)-2-(2-chlorobenzylidene)-5-(4-methoxyphenyl)-5-oxopentanoate (3ea): Colourless liquid, yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.9 Hz, 2H), 7.80 (s, 1H), 7.43-7.39 (m, 1H), 7.28 (dd, J = 7.6, 3.8 Hz, 2H), 7.21 (d, J = 32.2 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 3.85 (s, 6H), 3.14-3.09 (m, 2H), 2.83-2.77 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.6, 168.1, 163.6, 137.7, 134.2, 133.9, 133.9, 130.5, 123.0, 129.8, 129.8, 126.9, 113.8, 55.6, 52.3, 37.8, 23.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{20}ClO_4$: 359.1045, Found: 359.1040.



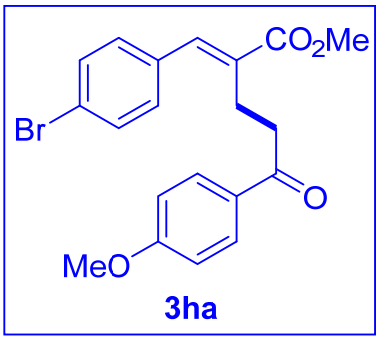
3fa

methyl (*E*)-2-(2-bromobenzylidene)-5-(4-methoxyphenyl)-5-oxopentanoate (3fa): Colourless liquid, yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.32-7.26 (m, 2H), 7.18-7.15 (m, 1H), 6.89 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.12-3.08 (m, 2H), 2.81-2.76 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.6, 168.0, 163.5, 139.8, 136.1, 133.6, 132.9, 130.5, 123.0, 129.8, 129.7, 127.5, 123.8, 113.8, 55.5, 52.3, 37.7, 23.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{20}BrO_4$: 403.0539, Found: 403.0544.



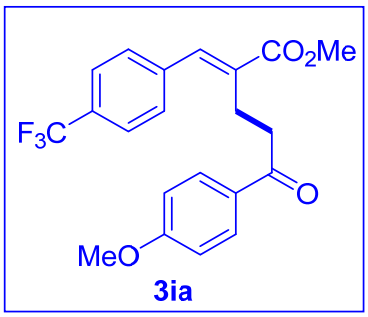
3ga

methyl (*E*)-2-(2-iodobenzylidene)-5-(4-methoxyphenyl)-5-oxopentanoate (3ga): Colourless liquid, yield: 61%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.8 Hz, 3H), 7.62 (s, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 9.4 Hz, 1H), 6.99 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 9.1 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.12-3.06 (m, 2H), 2.78-2.72 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.5, 167.9, 163.5, 143.8, 139.8, 139.2, 133.2, 130.4, 129.8, 129.7, 129.3, 128.3, 113.8, 99.1, 55.6, 52.3, 37.6, 22.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{20}IO_4$: 451.0401, Found: 451.0405.



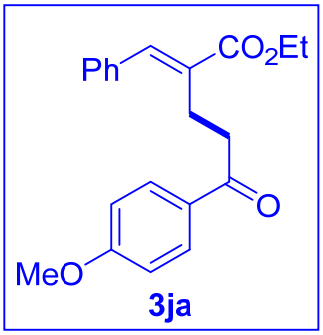
3ha

methyl (*E*)-2-(4-bromobenzylidene)-5-(4-methoxyphenyl)-5-oxopentanoate (3ha): Colourless liquid, yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94-7.91 (m, 2H), 7.65 (s, 1H), 7.51-7.47 (m, 2H), 7.25-7.21 (m, 2H), 6.93-6.89 (m, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.17-3.12 (m, 2H), 2.94-2.89 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.6, 168.4, 163.6, 138.9, 134.3, 132.6, 131.9, 130.8, 130.5, 129.7, 122.9, 113.8, 55.5, 52.2, 37.5, 22.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{20}BrO_4$: 403.0539, Found: 403.0542.



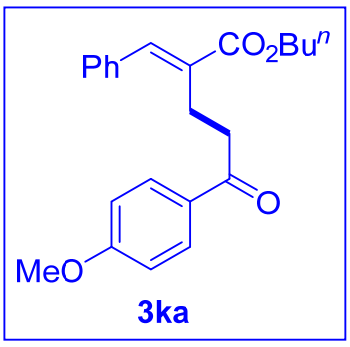
3ia

methyl (*E*)-5-(4-methoxyphenyl)-5-oxo-2-(4-(trifluoromethyl)benzylidene)pentanoate (3ia): Colourless liquid, yield: 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, J = 8.9 Hz, 2H), 7.74 (s, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.18-3.13 (m, 2H), 2.95-2.89 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.5, 168.2, 163.7, 139.0, 138.6, 134.1, 130.5, 129.7, 129.4, 125.7 (q, J_{CF} = 3.8 Hz), 113.9, 55.6, 52.4, 38.1, 23.0 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -62.7. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{20}F_3O_4$: 393.1308, Found: 393.1310.



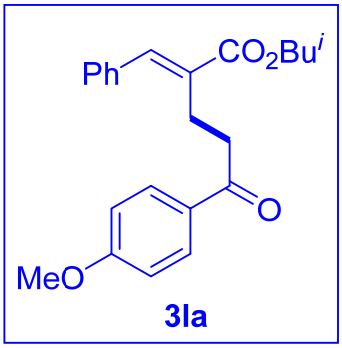
3ja

ethyl (*E*)-2-benzylidene-5-(4-methoxyphenyl)-5-oxopentanoate (3ja): Colourless liquid, yield: 64%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.9 Hz, 2H), 7.76 (s, 1H), 7.38 (d, J = 4.8 Hz, 4H), 7.34-7.30 (m, 1H), 6.92 (d, J = 8.9 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.20-3.14 (m, 2H), 2.99-2.93 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.9, 168.2, 163.6, 140.6, 135.5, 132.2, 130.5, 129.8, 129.3, 128.7, 128.7, 113.8, 61.0, 55.5, 37.8, 23.0, 14.4 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{23}O_4$: 339.1591, Found: 339.1595.

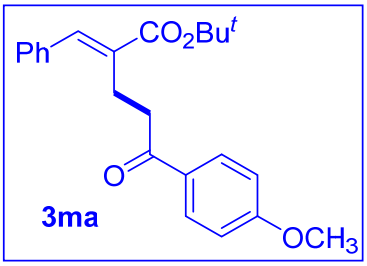


3ka

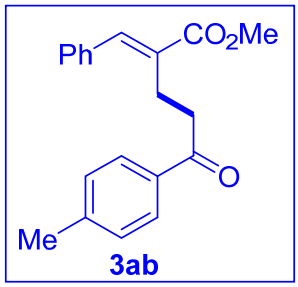
butyl (*E*)-2-benzylidene-5-(4-methoxyphenyl)-5-oxopentanoate (3ka): Colourless liquid, yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.8 Hz, 2H), 7.75 (s, 1H), 7.38 (d, J = 4.8 Hz, 4H), 7.31 (m, 1H), 6.92 (d, J = 8.9 Hz, 2H), 4.24 (t, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.21-3.15 (m, 2H), 2.95 (d, J = 7.9 Hz, 2H), 1.70 (dd, J = 15.3, 6.4 Hz, 2H), 1.48-1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.8, 168.3, 163.6, 140.0, 135.5, 132.2, 130.5, 129.9, 129.3, 128.7, 113.8, 65.4, 55.5, 39.2, 32.4, 23.0, 19.4, 13.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{27}O_4$: 367.1904, Found: 367.1906.



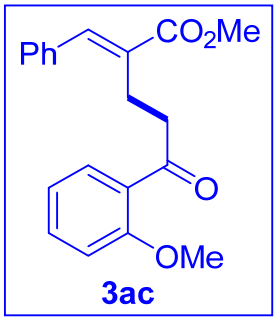
***iso*-butyl (*E*)-2-benzylidene-5-(3-methoxyphenyl)-5-oxopentanoate (3la)**: Colourless liquid, yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.8 Hz, 2H), 7.77 (s, 1H), 7.39-7.34 (m, 4H), 7.33-7.29 (m, 1H), 6.91 (d, J = 8.9 Hz, 2H), 4.02 (d, J = 6.6 Hz, 2H), 3.85 (s, 3H), 3.21-3.16 (m, 2H), 3.00-2.93 (m, 2H), 2.08-1.99 (m, 1H), 0.99 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.8, 168.2, 163.5, 140.0, 135.4, 132.2, 130.5, 129.8, 129.3, 128.7, 113.8, 71.2, 55.5, 37.8, 27.9, 23.0, 19.3 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{27}O_4$: 367.1904, Found: 367.1909.



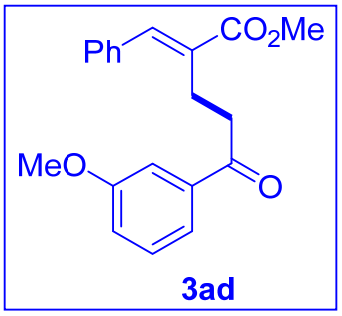
***tert*-butyl (*E*)-2-benzylidene-5-(4-methoxyphenyl)-5-oxopentanoate (3ma)**: White solid, yield: 78%, Mp: 89-91 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.9 Hz, 2H), 7.66 (s, 1H), 7.38-7.29 (m, 5H), 6.92 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.18-3.13 (m, 2H), 2.94-2.89 (m, 2H), 1.55 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.0, 167.4, 163.6, 139.2, 135.8, 133.8, 130.5, 130.0, 129.2, 128.7, 113.8, 81.0, 55.6, 37.9, 28.3, 23.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{27}O_4$: 367.1904, Found: 367.1905.



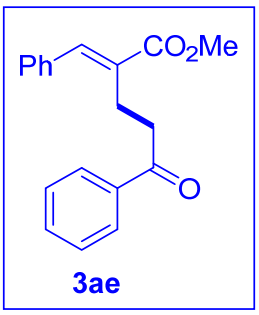
methyl *(E)*-2-benzylidene-5-oxo-5-(*p*-tolyl)pentanoate (3ab): White solid, yield: 77%, Mp: 74-76 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.3 Hz, 2H), 7.77 (s, 1H), 7.38 (d, J = 4.4 Hz, 4H), 7.35-7.29 (m, 1H), 7.25 (d, J = 7.9 Hz, 2H), 3.84 (s, 3H), 3.23-3.18 (m, 2H), 3.01-2.94 (m, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.9, 168.7, 143.9, 140.4, 135.4, 134.3, 131.9, 129.4, 129.3, 128.8, 128.7, 128.4, 52.2, 38.0, 22.8, 21.7 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{21}O_3$: 309.1485, Found: 309.1489.



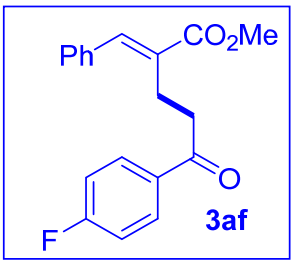
methyl (*E*)-2-benzylidene-5-(2-methoxyphenyl)-5-oxopentanoate (3ac): Colourless liquid, yield: 56%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.70 (dd, J = 7.7, 1.9 Hz, 1H), 7.47-7.42 (m, 1H), 7.38 (d, J = 6.6 Hz, 4H), 7.32 (d, J = 6.6 Hz, 1H), 6.99 (m, 1H), 6.94 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.26-3.21 (m, 2H), 2.98-2.94 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 201.5, 168.8, 158.7, 140.0, 135.6, 133.5, 132.3, 130.4, 129.4, 128.7, 128.6, 128.3, 120.7, 111.6, 55.6, 52.1, 42.9, 22.7 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{21}O_4$: 325.1434, Found: 325.1439.



methyl (*E*)-2-benzylidene-5-(3-methoxyphenyl)-5-oxopentanoate (3ad): Colourless liquid, yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (s, 1H), 7.58-7.49 (m, 2H), 7.39-7.31 (m, 6H), 7.10 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.24-3.20 (m, 2H), 3.00-2.95 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.0, 168.6, 160.0, 140.4, 138.1, 135.4, 131.7, 129.7, 129.3, 128.8, 120.9, 119.7, 112.4, 55.5, 52.2, 38.8, 16.5 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{21}O_4$: 325.1434, Found: 325.1438.

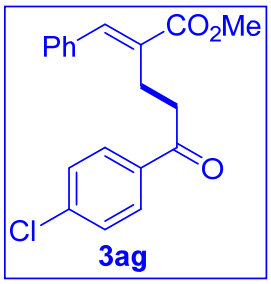


methyl (*E*)-2-benzylidene-5-oxo-5-phenylpentanoate (3ae): Colourless liquid, yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00 (d, J = 7.1 Hz, 2H), 7.80 (s, 1H), 7.58 (m, 1H), 7.48 (m, 2H), 7.40 (d, J = 2.8 Hz, 4H), 7.37-7.34 (m, 1H), 3.86 (s, 3H), 3.28-3.24 (m, 2H), 3.04-2.97 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.1, 168.6, 140.4, 136.6, 135.3, 133.1, 131.7, 129.2, 128.7, 128.6, 128.1, 52.1, 38.0, 22.6 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{19}H_{19}O_3$: 295.1329, Found: 295.1335.

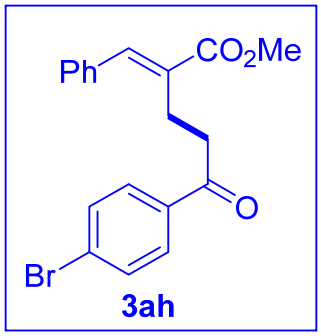


methyl (*E*)-2-benzylidene-5-(4-fluorophenyl)-5-oxopentanoate (3af): Colourless liquid, yield: 60%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00 (dd, J = 8.7, 5.5 Hz, 2H), 7.77 (s, 1H), 7.40-7.31 (m, 5H), 7.11 (m, 2H), 3.84 (s, 3H), 3.24-3.12 (m, 2H), 3.02-2.90 (m, 2H)) ppm. ^{13}C NMR (126

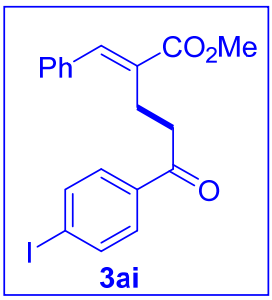
MHz, $CDCl_3$) δ = 197.7, 168.6, 165.9 (d, J_{CF} = 254.6 Hz), 140.6, 135.3, 133.1 (d, J_{CF} = 2.9 Hz), 131.6, 130.90 (d, J_{CF} = 9.3 Hz), 129.3, 128.8, 115.8 (d, J_{CF} = 21.8 Hz), 52.2, 38.0, 22.8 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -105.3 ppm. HRMS (ESI) [M+H^+] Calcd For $C_{19}H_{18}FO_3$: 313.1234, Found: 313.1236.



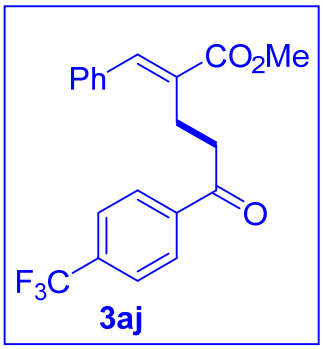
methyl (*E*)-2-benzylidene-5-(4-chlorophenyl)-5-oxopentanoate (3ag): White solid, yield: 78%, Mp: 81-83 °C. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.5 Hz, 2H), 7.77 (s, 1H), 7.43-7.33 (m, 7H), 3.83 (s, 3H), 3.22-3.16 (m, 2H), 2.99-2.94 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.0, 168.9, 140.6, 139.6, 135.3, 135.0, 131.5, 129.7, 129.2, 129.0, 128.8, 128.3, 128.2, 55.0, 40.5, 22.7 ppm. HRMS (ESI) [M+H^+] Calcd For $C_{19}H_{18}ClO_3$: 329.0939, Found: 329.0938.



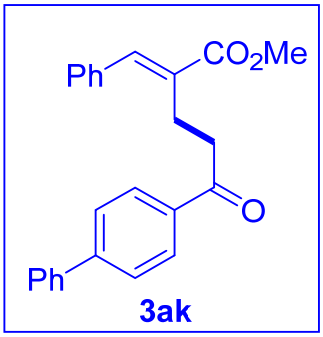
methyl (*E*)-2-benzylidene-5-(4-bromophenyl)-5-oxopentanoate (3ah): White solid, yield: 68%, Mp: 75-77 °C. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.6 Hz, 2H), 7.77 (s, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.39-7.30 (m, 5H), 3.83 (s, 3H), 3.21-3.16 (m, 2H), 2.98-2.94 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.2, 168.5, 140.6, 135.4, 135.3, 132.0, 131.5, 129.8, 129.2, 128.8, 128.3, 52.2, 38.1, 22.7 ppm. HRMS (ESI) [M+H^+] Calcd For $C_{19}H_{18}BrO_3$: 373.0434, Found: 373.0437.



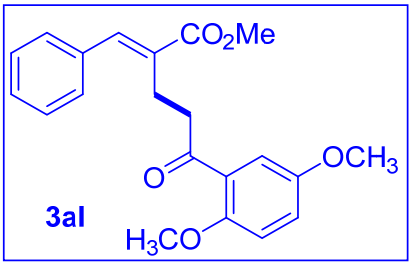
methyl (*E*)-2-benzylidene-5-(4-iodophenyl)-5-oxopentanoate (3ai): Yellow solid, yield: 70%, Mp: 81-83 °C. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, J = 8.5 Hz, 2H), 7.77 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.39-7.32 (m, 5H), 3.83 (s, 3H), 3.20-3.15 (m, 2H), 2.98-2.93 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.5, 168.5, 140.6, 138.0, 135.9, 135.3, 131.5, 129.7, 129.2, 128.8, 128.8, 101.2, 52.2, 38.0, 22.7 ppm. HRMS (ESI) [M+H^+] Calcd For $C_{19}H_{18}IO_3$: 421.0295, Found: 421.0299.



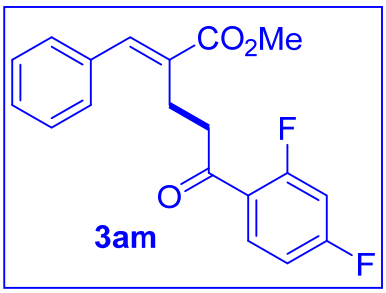
methyl (*E*)-2-benzylidene-5-oxo-5-(4-(trifluoromethyl)phenyl)pentanoate (3aj): Colourless liquid, yield: 64%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.1 Hz, 2H), 7.79 (s, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.41-7.30 (m, 5H), 3.83 (s, 3H), 3.27-3.22 (m, 2H), 3.01-2.96 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.3, 168.5, 140.8, 139.3, 135.3, 134.5 (q, J_{CF} = 37.8 Hz), 131.4, 129.2, 128.9, 128.8, 128.6, 125.8 (q, J_{CF} = 3.8 Hz), 124.8 (q, J_{CF} = 273.4 Hz), 52.3, 38.4, 22.7 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -63.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{18}F_3O_3$: 363.1203, Found: 363.1209.



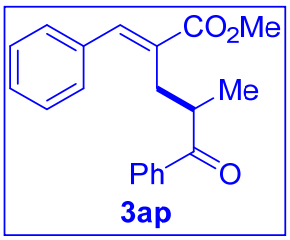
methyl (*E*)-5-([1,1'-biphenyl]-4-yl)-2-benzylidene-5-oxopentanoate (3ak): White solid, yield: 72%, Mp: 65-67 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.2 Hz, 2H), 7.79 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.48 (m, 2H), 7.39 m, 5H), 7.33 (dd, J = 9.0, 4.3 Hz, 1H), 3.85 (s, 3H), 3.29-3.24 (m, 2H), 3.03-2.99 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.9, 168.7, 145.9, 140.5, 140.0, 135.5, 135.4, 131.8, 129.3, 129.1, 128.9, 128.8, 128.8, 128.4, 127.4, 127.4, 52.3, 38.2, 22.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{25}H_{23}O_3$: 371.1642, Found: 371.1648.



methyl (*E*)-2-benzylidene-5-(3,4-dimethoxyphenyl)-5-oxopentanoate (3al): White solid, yield: 54%, Mp: 65-67 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (s, 1H), 7.61 (dd, J = 8.4, 2.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.34 (dd, J = 30.0, 4.3 Hz, 5H), 6.86 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 3.92 (s, 3H), 3.82 (s, 3H), 3.21-3.15 (m, 2H), 2.99-2.93 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.8, 168.5, 153.3, 149.0, 140.2, 135.3, 131.7, 129.9, 129.2, 128.6, 122.8, 110.3, 110.1, 56.0, 56.0, 52.1, 37.6, 23.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{23}O_5$: 355.1540, Found: 355.1549.

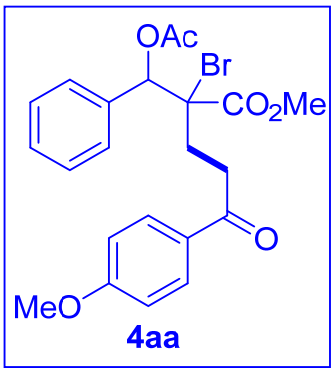


methyl (*E*)-2-benzylidene-5-(2,4-difluorophenyl)-5-oxopentanoate (3am): White solid, yield: 63%, Mp: 65-67 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97-7.90 (m, 1H), 7.76 (s, 1H), 7.39-7.30 (m, 5H), 6.98-6.92 (m, 1H), 6.84 (m, 1H), 3.82 (s, 3H), 3.24-3.17 (m, 2H), 3.01-2.94 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.7, 168.4, 164.3 (dd, J_{CF} = 376.0, 257.3 Hz), 140.4, 135.3, 132.6 (dd, J_{CF} = 10.5, 4.3 Hz), 131.5, 129.1, 128.6, 128.1 (d, J_{CF} = 5.5 Hz), 122.0 (d, J_{CF} = 13.2 Hz), 112.1 (dd, J_{CF} = 21.4, 3.4 Hz), 104.7 (dd, J_{CF} = 27.8, 25.4 Hz), 52.1, 42.5, 22.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{19}H_{17}F_2O_3$: 331.1140, Found: 331.1148.

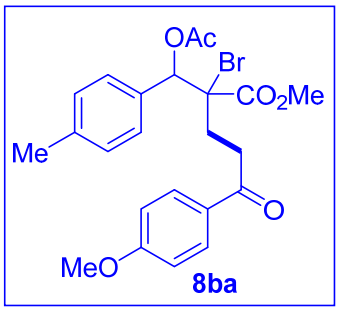


methyl (*E*)-2-benzylidene-4-methyl-5-oxo-5-phenylpentanoate (3ap): Colourless liquid, yield: 18%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.3 Hz, 2H), 7.79 (s, 1H), 7.54 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.41-7.32 (m, 5H), 3.89-3.82 (m, 1H), 3.82 (s, 3H), 2.97-2.78 (m, 2H), 1.08 (d, J = 6.9 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 168.7, 141.7, 136.5, 135.6, 133.1, 130.9, 129.2, 128.7, 128.6, 128.2, 52.1, 39.7, 31.0, 16.4. HRMS (ESI) [M+H$^+$] Calcd For $C_{20}H_{21}O_3$: 309.1485, Found: 309.1489.

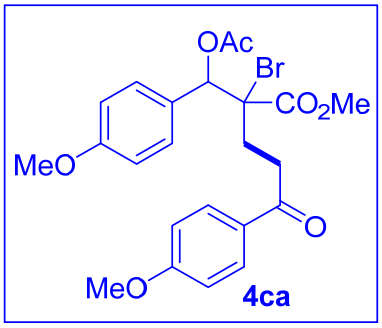
6. NMR data of bromoacylmethylated products (4aa-4oa and 4ab-4ao)



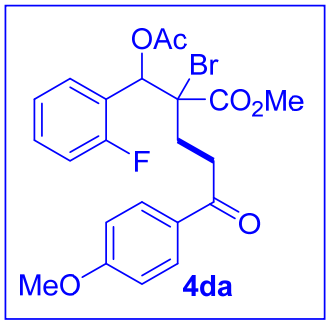
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4aa): White solid, yield: 92%, Mp: 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, J = 8.9 Hz, 2H), 7.48-7.40 (m, 2H), 7.34 (dd, J = 5.1, 1.9 Hz, 3H), 6.91 (d, J = 8.9 Hz, 2H), 6.38 (s, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.28-3.05 (m, 2H), 2.72-2.23 (m, 2H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.0, 169.3, 169.1, 163.7, 135.0, 130.4, 129.9, 129.2, 128.4, 128.3, 113.9, 78.7, 70.7, 55.6, 53.6, 35.4, 30.7, 21.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{24}BrO_6$: 463.0751, Found: 463.0757.



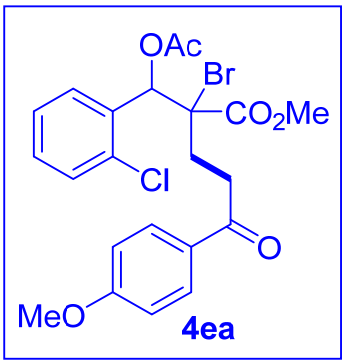
methyl 2-(acetoxy(p-tolyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ba): Yellow liquid, yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.35 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.29-3.02 (m, 2H), 2.75-2.33 (m, 2H), 2.32 (s, 3H), 2.14 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 169.1, 169.0, 163.6, 139.0, 131.9, 130.3, 129.8, 129.0, 128.1, 113.7, 78.5, 70.6, 55.5, 53.4, 35.3, 30.5, 21.2, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{26}BrO_6$: 477.0907, Found: 477.0909.



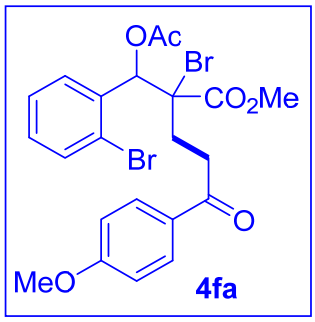
methyl 2-(acetoxy(4-methoxyphenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ca): Yellow liquid, yield: 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.33 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.28-3.04 (m, 2H), 2.57-2.24 (m, 2H), 2.13 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.0, 169.2, 169.1, 163.7, 160.2, 130.4, 129.8, 129.6, 127.0, 113.9, 113.8, 78.4, 70.9, 55.6, 55.3, 53.5, 35.4, 30.7, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{26}BrO_7$: 493.0856, Found: 493.0859.



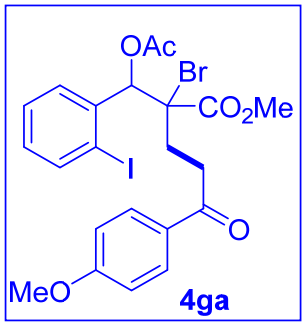
methyl 2-(acetoxy(2-fluorophenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4da): Yellow solid, yield: 85%, Mp: 100-102 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.9 Hz, 2H), 7.77-7.56 (m, 1H), 7.40-7.35 (m, 1H), 7.32-7.26 (m, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.82 (s, 1H), 3.84 (d, J = 6.0 Hz, 3H), 3.78 (d, J = 20.1 Hz, 3H), 3.28-3.15 (m, 1H), 2.98-2.57 (m, 2H), 2.11 (m, 1H), 2.08 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.4, 168.8 (d, J_{CF} = 7.6 Hz), 163.7, 134.5, 133.3, 130.6, 130.3, 130.2, 129.7, 129.6, 126.6, 113.9, 74.2, 73.5, 55.5, 54.0, 34.9, 31.9, 20.8 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -63.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{23}BrFO_6$: 481.0657, Found: 481.0659.



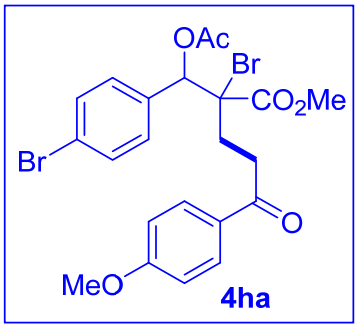
methyl 2-(acetoxy(2-chlorophenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ea): White solid, yield: 94%, Mp: 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.8 Hz, 2H), 7.61 (m, 1H), 7.33 (m, 1H), 7.16 (m, 1H), 7.05 (m, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.64 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.27-3.14 (m, 1H), 3.06-2.94 (m, 1H), 2.66 (m, 1H), 2.21 (m, 1H), 2.11 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.4, 168.8, 168.7, 163.6, 130.7, 130.3, 129.9, 129.7, 124.0, 122.7, 122.6, 115.3, 113.8, 77.3, 71.8, 55.5, 53.8, 34.7, 31.4, 20.7 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{23}BrClO_6$: 497.0361, Found: 497.0369.



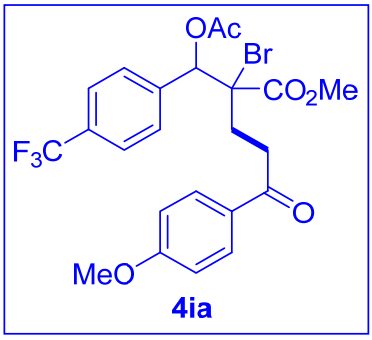
methyl 2-(acetoxy(2-bromophenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4fa): Yellow liquid, yield: 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.33 (m, 1H), 7.19 (m, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.80 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.21 (dd, J = 21.5, 9.8 Hz, 1H), 3.03-2.58 (m, 2H), 2.07 (s, 3H), 2.02 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.3, 168.8, 168.7, 163.6, 134.9, 132.9, 130.9, 130.5, 130.2, 129.6, 127.1, 125.0, 113.8, 76.3, 73.6, 55.5, 54.0, 34.9, 32.1, 20.7 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{23}Br_2O_6$: 540.9856, Found: 540.9858.



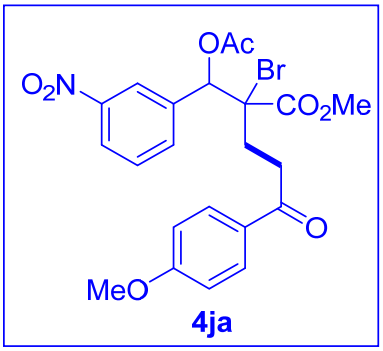
methyl 2-(acetoxy(2-iodophenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ga): Brown solid, yield: 90%, Mp: 131-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (m, 3H), 7.74 (dd, J = 7.9, 1.6 Hz, 1H), 7.36 (m, 1H), 7.04 (m, 1H), 6.90 (d, J = 8.9 Hz, 2H), 6.65 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.29-3.02 (m, 2H), 2.95-2.62 (m, 1H), 2.07 (s, 3H), 2.04-2.01 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.3, 168.8, 168.7, 163.6, 139.9, 138.0, 130.7, 130.5, 130.3, 129.6, 127.9, 113.8, 101.2, 80.7, 73.8, 55.5, 54.0, 35.0, 32.6, 20.7 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{23}BrIO_6$: 588.9717, Found: 588.9723.



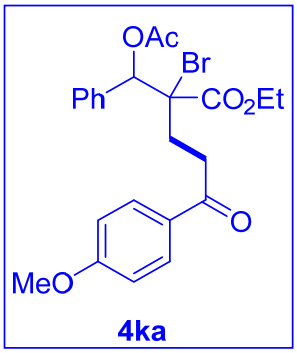
methyl 2-(acetoxy(4-bromophenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ha): Yellow solid, yield: 95%, Mp: 83-85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 6.95-6.86 (m, 2H), 6.29 (s, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.27-3.01 (m, 2H), 2.73-2.45 (m, 1H), 2.27 (m, 1H), 2.12 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.7, 169.0, 168.8, 163.7, 134.1, 131.5, 130.3, 130.0, 129.7, 123.4, 113.8, 78.0, 70.3, 55.5, 53.6, 35.1, 30.9, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{23}Br_2O_6$: 540.9856, Found: 540.9859.



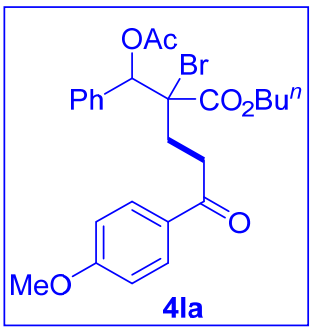
methyl 2-(acetoxy(4-(trifluoromethyl)phenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ia): Yellow solid, yield: 92%, Mp: 123-125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.9 Hz, 2H), 7.64-7.50 (m, 4H), 6.91 (d, J = 8.7 Hz, 2H), 6.38 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.29-3.00 (m, 2H), 2.76-2.49 (m, 1H), 2.47-2.22 (m, 1H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.6, 168.9 (d, J_{CF} = 41.6 Hz), 163.8, 139.1, 131.3 (d, J_{CF} = 32.8 Hz), 130.4, 129.4 (d, J_{CF} = 71.8 Hz), 128.9, 125.3 (q, J_{CF} = 3.8 Hz), 122.8, 113.9, 78.1, 70.1, 55.6, 53.7, 35.1, 31.1, 20.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -62.8 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{23}BrF_3O_6$: 531.0625, Found: 531.0626.



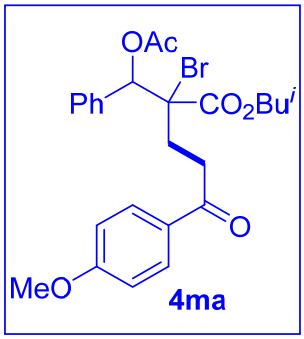
methyl 2-(acetoxy(4-nitrophenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ja): Yellow liquid, yield: 33%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.32-8.16 (m, 2H), 7.98-7.75 (m, 3H), 7.56 (m, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.40 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.31-3.02 (m, 2H), 2.55 (m, 1H), 2.46-2.19 (m, 1H), 2.20 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.5, 169.1, 168.6, 163.9, 148.2, 137.4, 134.5, 130.4, 129.7, 129.4, 124.2, 123.5, 114.0, 77.7, 69.9, 55.6, 53.9, 35.0, 31.3, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{23}BrNO_8$: 508.0602, Found: 508.0609.



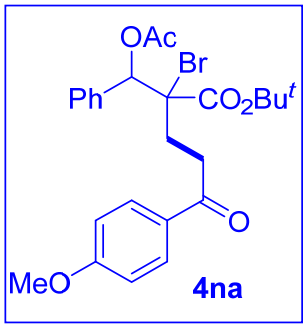
ethyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ka): Yellow solid, yield: 86%, Mp: 107-109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 5.5 Hz, 2H), 7.37-7.29 (m, 3H), 6.91 (d, J = 8.9 Hz, 2H), 6.37 (s, 1H), 4.31-4.14 (m, 2H), 3.84 (s, 3H), 3.30-3.02 (m, 2H), 2.61-2.21 (m, 2H), 2.14 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.8, 169.0, 168.3, 163.6, 135.0, 130.3, 129.7, 129.0, 128.3, 128.2, 113.8, 78.6, 71.2, 62.9, 55.5, 35.2, 30.9, 20.9, 14.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{26}BrO_6$: 477.0907, Found: 477.0912.



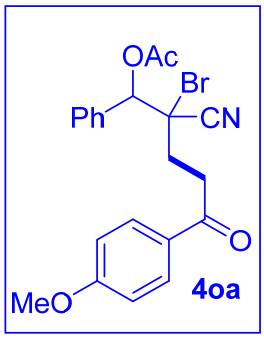
butyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4la): Yellow liquid, yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.9 Hz, 2H), 7.49-7.40 (m, 2H), 7.36-7.29 (m, 3H), 6.91 (d, J = 8.9 Hz, 2H), 6.36 (s, 1H), 4.24-4.07 (m, 2H), 3.84 (s, 3H), 3.28-2.97 (m, 2H), 2.75-2.22 (m, 2H), 2.13 (s, 3H), 1.71-1.52 (m, 2H), 1.37 (q, J = 7.5 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 169.1, 168.5, 163.7, 135.1, 130.3, 129.8, 129.1, 128.4, 128.3, 113.8, 78.8, 71.2, 66.8, 55.5, 35.3, 30.9, 30.5, 21.0, 19.1, 13.7 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{25}H_{30}BrO_6$: 505.1220, Found: 505.1225.



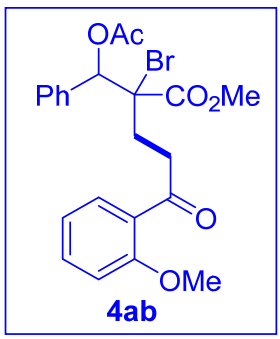
***iso*-butyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4ma)**: Yellow solid, yield: 88%, Mp: 97-99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.8 Hz, 2H), 7.44 (dd, J = 7.5, 2.0 Hz, 2H), 7.37-7.29 (m, 3H), 6.90 (d, J = 8.9 Hz, 2H), 6.36 (s, 1H), 4.01-3.86 (m, 2H), 3.84 (s, 3H), 3.31-2.99 (m, 2H), 2.74-2.26 (m, 2H), 2.13 (s, 3H), 2.03-1.89 (m, 1H), 0.94 (s, 3H), 0.93 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 169.1, 168.5, 163.7, 135.1, 130.3, 129.8, 129.1, 128.3, 128.3, 113.8, 78.8, 72.9, 71.2, 55.5, 35.3, 30.9, 27.7, 21.0, 19.1 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{25}H_{30}BrO_6$: 505.1220, Found: 505.1226.



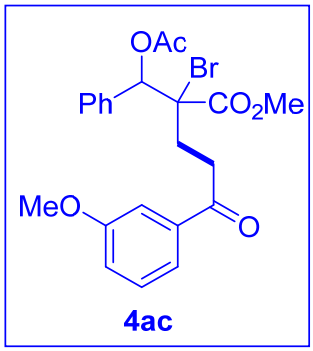
***tert*-butyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-methoxyphenyl)-5-oxopentanoate (4na)**: Yellow liquid, yield: 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.9 Hz, 2H), 7.54-7.44 (m, 2H), 7.34 (d, J = 9.3 Hz, 3H), 6.91 (d, J = 8.9 Hz, 2H), 6.30 (s, 1H), 3.84 (s, 3H), 3.34-2.92 (m, 2H), 2.70-2.17 (m, 2H), 2.13 (s, 3H), 1.47 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 169.1, 166.9, 163.7, 135.3, 130.3, 129.8, 129.0, 128.7, 128.1, 113.9, 84.0, 79.0, 73.3, 55.5, 35.0, 31.7, 27.8, 21.0 ppm. HRMS (ESI) [M+H+] Calcd For $C_{25}H_{30}BrO_6$ [M+H$^+$]: 505.1220, Found: 505.1221.



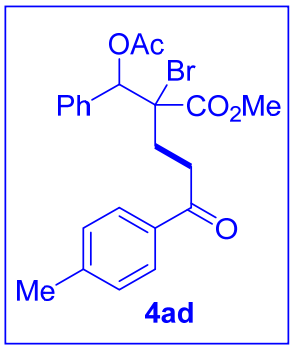
2-bromo-2-cyano-5-(4-methoxyphenyl)-5-oxo-1-phenylpentyl acetate (4oa): Colourless liquid, yield: 68%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, J = 8.9 Hz, 2H), 7.60-7.50 (m, 2H), 7.42 (m, 3H), 6.99-6.89 (m, 2H), 6.09 (s, 1H), 3.87 (s, 3H), 3.48-3.21 (m, 2H), 2.66-2.23 (m, 2H), 2.22 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.4, 169.0, 164.0, 133.8, 130.4, 129.4, 129.0, 128.6, 128.3, 117.0, 114.0, 78.9, 55.6, 53.2, 35.4, 33.4, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{21}BrNO_4$: 430.0648, Found: 430.0653.



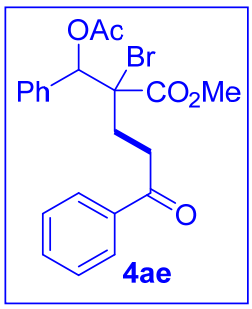
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(2-methoxyphenyl)-5-oxopentanoate (4ab): Yellow solid, yield: 78%, Mp: 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (d, J = 9.2 Hz, 1H), 7.47-7.40 (m, 3H), 7.34 (d, J = 5.1 Hz, 3H), 7.01-6.89 (m, 2H), 6.35 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.39-3.07 (m, 2H), 2.72-2.24 (m, 2H), 2.14 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 200.5, 169.1, 169.0, 158.7, 135.1, 133.6, 130.3, 129.1 128.4, 128.2, 128.0, 120.7, 111.7, 78.7, 70.9, 55.6, 53.5, 40.7, 31.1, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For$C_{22}H_{24}BrO_6$: 463.0751, Found: 463.0756



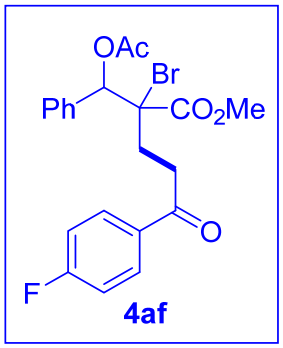
2-(acetoxy(phenyl)methyl)-2-bromo-5-(3-methoxyphenyl)-5-oxopentanoate (4ac): Yellow solid, yield: 60%, Mp: 122-124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 (d, J = 7.5 Hz, 1H), 7.48-7.39 (m, 3H), 7.38-7.31 (m, 4H), 7.09 (dd, J = 8.1, 2.3 Hz, 1H), 6.39 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.33-3.10 (m, 2H), 2.60-2.25 (m, 2H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.3, 169.2, 169.0, 160.0, 138.1, 135.0, 129.7, 129.2, 128.4, 128.3, 120.7, 119.6, 112.5, 78.6, 70.3, 55.5, 53.6, 36.0, 30.5, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For$C_{22}H_{24}BrO_6$: 463.0751, Found: 463.0755



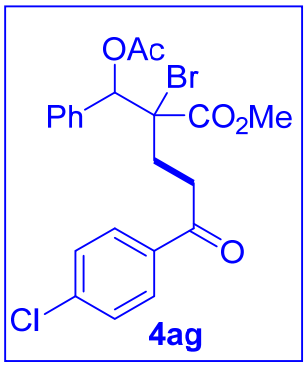
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-oxo-5-(p-tolyl)pentanoate (4ad): White solid, yield: 80%, Mp: 114-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (dd, J = 8.2, 6.4 Hz, 2H), 7.50-7.39 (m, 2H), 7.39-7.29 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 6.39 (s, 1H), 3.77 (s, 3H), 3.31-3.05 (m, 2H), 2.77-2.49 (m, 1H), 2.39 (s, 3H), 2.38-2.26 (m, 1H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.0, 169.2, 169.0, 144.1, 135.0, 134.3, 129.4, 129.2, 128.4, 128.3, 128.2, 78.6, 70.6, 53.5, 35.6, 30.5, 21.7, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{24}BrO_5$: 447.0802, Found: 447.0803.



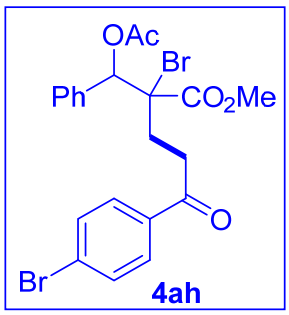
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-oxo-5-phenylpentanoate (4ae): Yellow liquid, yield: 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.3 Hz, 2H), 7.55 (m, 1H), 7.49-7.39 (m, 4H), 7.39-7.30 (m, 3H), 6.39 (d, J = 11.5 Hz, 1H), 3.78 (s, 3H), 3.35-3.12 (m, 2H), 2.47 (m 2H), 2.16 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.4, 169.2, 169.0, 136.7, 135.0, 133.3, 129.2, 128.7, 128.4, 128.3, 128.1, 78.6, 70.4, 53.5, 35.8, 30.4, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{22}BrO_5$: 433.0645, Found: 433.0649.



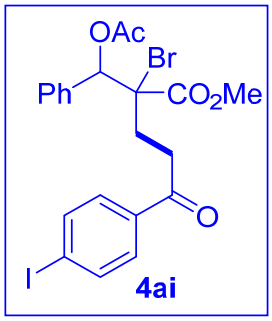
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-fluorophenyl)-5-oxopentanoate (4af): White solid, yield: 90%, Mp: 106-108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.8 Hz, 2H), 7.50-7.39 (m, 2H), 7.38-7.30 (m, 3H), 7.12 (d, J = 8.6 Hz, 2H), 6.39 (s, 1H), 3.78 (s, 3H), 3.31-3.07 (m, 2H), 2.59-2.26 (m, 2H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 169.1 (d, J_{CF} = 25.2 Hz), 165.9 (d, J_{CF} = 255.8 Hz), 134.9, 133.2 (d, J_{CF} = 2.5 Hz), 130.7 (d, J_{CF} = 8.8 Hz), 129.2, 128.4, 128.2, 115.8 (d, J_{CF} = 22.7 Hz), 78.6, 70.2, 53.5, 35.8, 30.3, 21.0 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -105.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For$C_{21}H_{21}BrFO_5$: 451.0551, Found: 451.0556



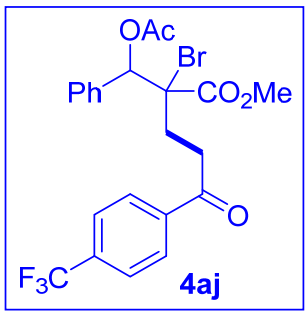
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-chlorophenyl)-5-oxopentanoate (4ag): White solid, yield: 93%, Mp: 164-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.4 Hz, 4H), 7.38-7.30 (m, 3H), 6.40 (s, 1H), 3.78 (s, 3H), 3.32-3.03 (m, 2H), 2.45 (m, 2H), 2.16 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.3, 169.2, 169.0, 139.8, 135.1, 134.9, 129.5, 129.3, 129.1, 128.5, 128.2, 78.6, 70.2, 53.6, 35.9, 30.2, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{21}BrClO_5$: 467.0255, Found: 467.0259.



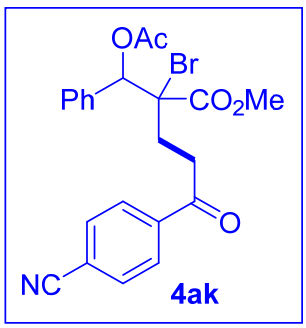
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-bromophenyl)-5-oxopentanoate (4ah): White solid, yield: 80%, Mp: 107-109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.41 (dd, J = 6.6, 2.9 Hz, 2H), 7.38-7.31 (m, 3H), 6.39 (s, 1H), 3.78 (s, 3H), 3.29-3.05 (m, 2H), 2.59-2.30 (m, 2H), 2.16 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.4, 169.1, 168.8, 135.3, 134.8, 131.9, 129.5, 129.1, 128.4, 128.3, 128.1, 78.5, 70.0, 53.5, 35.8, 30.0, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{21}Br_2O_5$: 510.9750, Found: 510.9751.



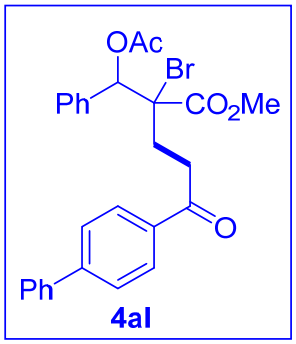
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-iodophenyl)-5-oxopentanoate (4ai): White solid, yield: 85%, Mp: 137-139 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.41 (dd, J = 6.5, 2.8 Hz, 2H), 7.34 (d, J = 4.9 Hz, 3H), 6.38 (d, J = 12.3 Hz, 1H), 3.78 (s, 3H), 3.28-3.08 (m, 2H), 2.57-2.27 (m, 2H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.8, 169.2, 168.9, 138.1, 136.0, 134.9, 129.5, 129.3, 128.4, 128.2, 101.3, 78.6, 70.1, 53.6, 35.8, 30.1, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{21}BrIO_5$: 558.9612, Found: 558.9615.



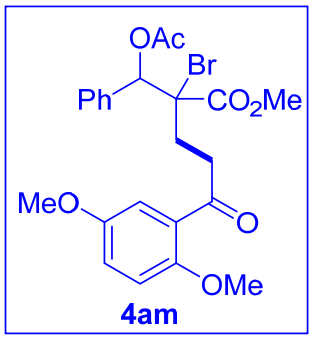
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-oxo-5-(4-(trifluoromethyl)phenyl)pentanoate (4aj): Yellow solid, yield: 80%, Mp: 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 9.4 Hz, 2H), 7.38-7.30 (m, 3H), 6.42 (s, 1H), 3.79 (s, 3H), 3.36-3.16 (m, 2H), 2.60-2.28 (m, 2H), 2.16 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.4, 168.9 (d, J_{CF} = 29.0 Hz), 139.3, 134.8, 129.2, 128.6, 128.4, 128.3, 128.1, 125.7 (q, J_{CF} = 3.6 Hz), 78.4, 69.8, 53.5, 36.2, 29.8, 20.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -61.3 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{21}BrF_3O_5$: 501.0519, Found: 501.0521.



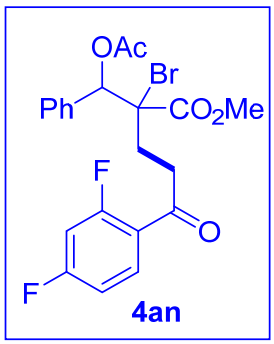
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(4-cyanophenyl)-5-oxopentanoate (4ak): White solid, yield: 91%, Mp: 133-135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.48-7.30 (m, 5H), 6.39 (s, 1H), 3.78 (s, 3H), 3.36-3.12 (m, 2H), 2.65-2.27 (m, 2H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.1, 169.1, 168.8, 139.5, 134.7, 132.5, 129.2, 128.4, 128.4, 128.0, 117.9, 116.5, 78.4, 69.6, 53.5, 36.3, 29.6, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{22}H_{21}BrNO_5$ [M+H$^+$]: 458.0598, Found: 458.0596.



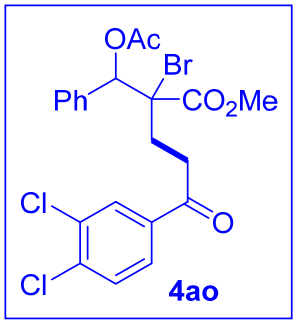
methyl 5-([1,1'-biphenyl]-4-yl)-2-(acetoxy(phenyl)methyl)-2-bromo-5-oxopentanoate (4al): Yellow solid, yield: 94%, Mp: 106-108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.02 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.51-7.43 (m, 4H), 7.35 (s, 4H), 6.41 (d, J = 11.4 Hz, 1H), 3.80 (s, 3H), 3.42-3.09 (m, 2H), 2.83-2.34 (m, 2H), 2.17 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.0, 169.2, 169.0, 146.0, 139.9, 135.4, 135.0, 129.1, 128.7, 128.4, 128.3, 127.3, 78.6, 70.5, 53.6, 35.9, 30.4, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{27}H_{26}BrO_5$: 509.0958, Found: 509.0962.



methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(2,5-dimethoxyphenyl)-5-oxopentanoate (4am): Yellow liquid, yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.53 (m, 1H), 7.47 (d, J = 1.8 Hz, 1H), 7.45-7.37 (m, 2H), 7.32 (dd, J = 5.0, 2.2 Hz, 3H), 6.85 (d, J = 8.4 Hz, 1H), 6.37 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.76 (s, 3H), 3.28-3.03 (m, 2H), 2.59-2.29 (m, 2H), 2.13 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.0, 169.1, 168.9, 153.5, 149.1, 134.9, 129.9, 129.1, 128.3, 128.2, 122.8, 110.2, 110.1, 78.6, 70.5, 56.1, 56.0, 53.5, 35.2, 30.8, 20.9 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{23}H_{26}BrO_7$: 493.0856, Found: 493.0858.



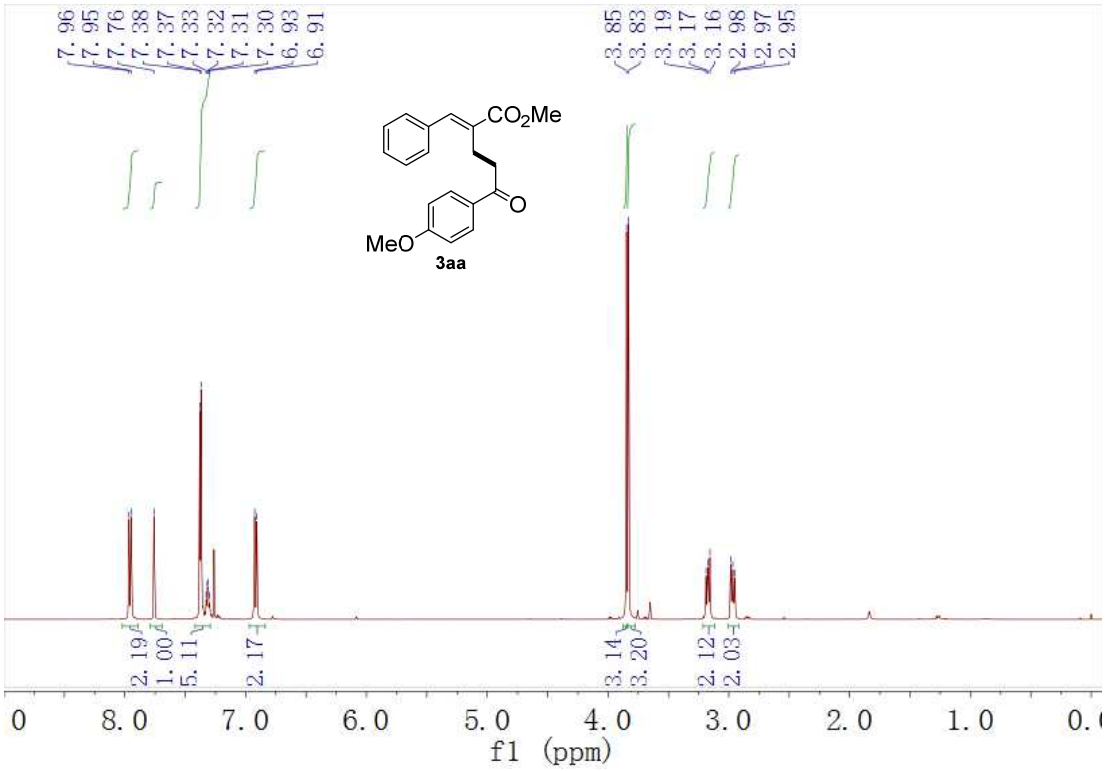
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(2,4-difluorophenyl)-5-oxopentanoate (4an): Yellow liquid, yield: 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.95-7.85 (m, 1H), 7.46-7.32 (m, 5H), 6.99-6.81 (m, 2H), 6.39 (s, 1H), 3.77 (s, 3H), 3.37-3.08 (m, 2H), 2.45 (m, 2H), 2.15 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.0, 168.9 (d, J_{CF} = 25.2 Hz), 165.8 (dd, J_{CF} = 257.1, 12.3 Hz), 162.8 (dd, J_{CF} = 257.8, 12.5 Hz), 134.9, 132.5 (dd, J_{CF} = 10.6, 4.1 Hz), 129.1, 128.3, 128.1, 112.2 (dd, J_{CF} = 3.8 Hz), 105.0, 104.8 (dd, J_{CF} = 27.8, 25.3 Hz), 78.5, 69.7, 53.4, 40.4, 29.9, 20.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ = -101.6, -104.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{20}BrF_2O_5$: 469.0457, Found: 469.0465.



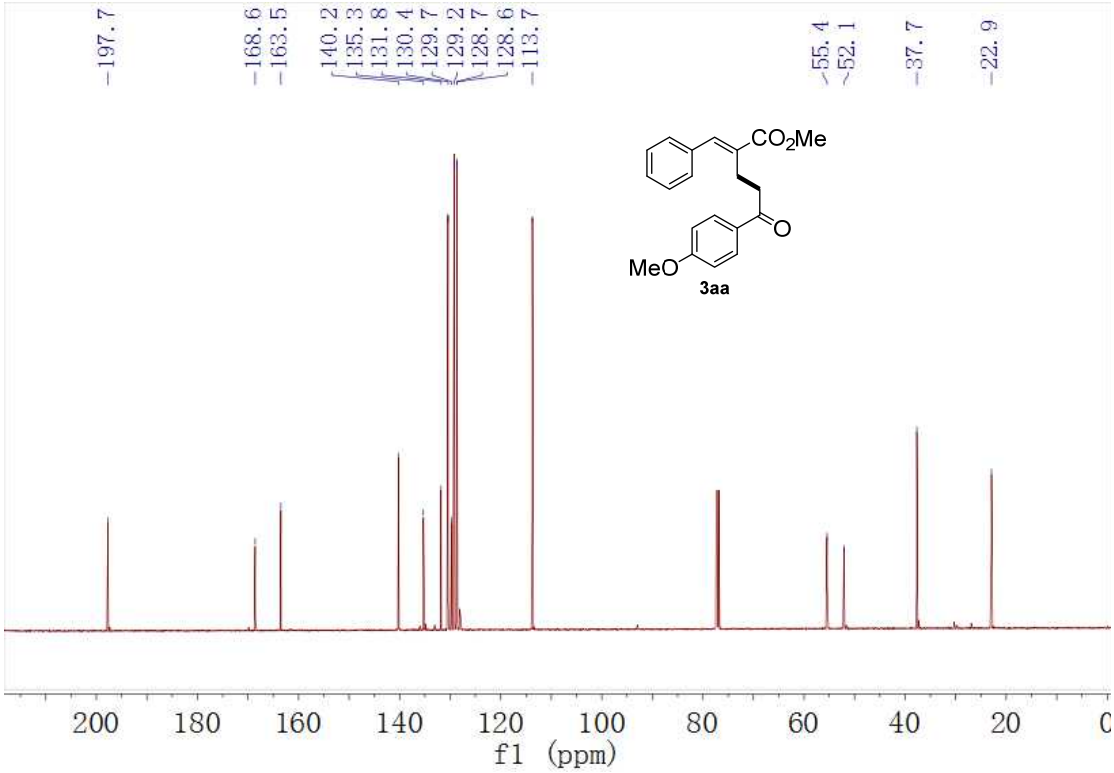
methyl 2-(acetoxy(phenyl)methyl)-2-bromo-5-(3,4-dichlorophenyl)-5-oxopentanoate (4ao): Colourless liquid, yield: 61%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (d, J = 2.0 Hz, 1H), 7.75 (dd, J = 8.4, 2.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 6.6, 3.0 Hz, 2H), 7.37-7.31 (m, 3H), 6.40 (s, 1H), 3.79 (s, 3H), 3.28-3.09 (m, 2H), 2.45 (m, 2H), 2.16 (s, 3H).ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.3, 169.2, 168.9, 137.9, 136.2, 134.8, 133.5, 130.9, 130.19, 129.3, 128.5, 128.2, 127.1, 78.5, 69.8, 53.6, 36.0, 29.9, 21.0 ppm. HRMS (ESI) [M+H$^+$] Calcd For $C_{21}H_{20}BrCl_2O_5$: 500.9866, Found: 500.9867.

7. NMR spectra of acylmethylated products (3aa-3ma and 3ab-3ap)

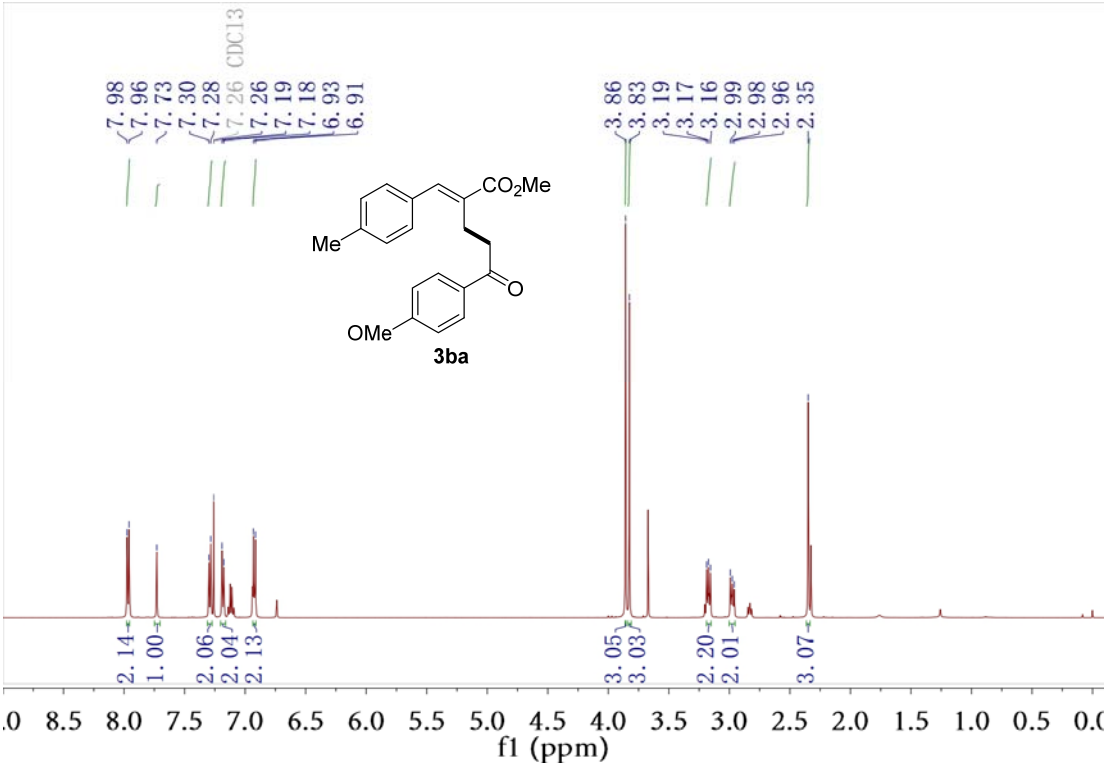
^{1}H NMR of **3aa** in $CDCl_3$



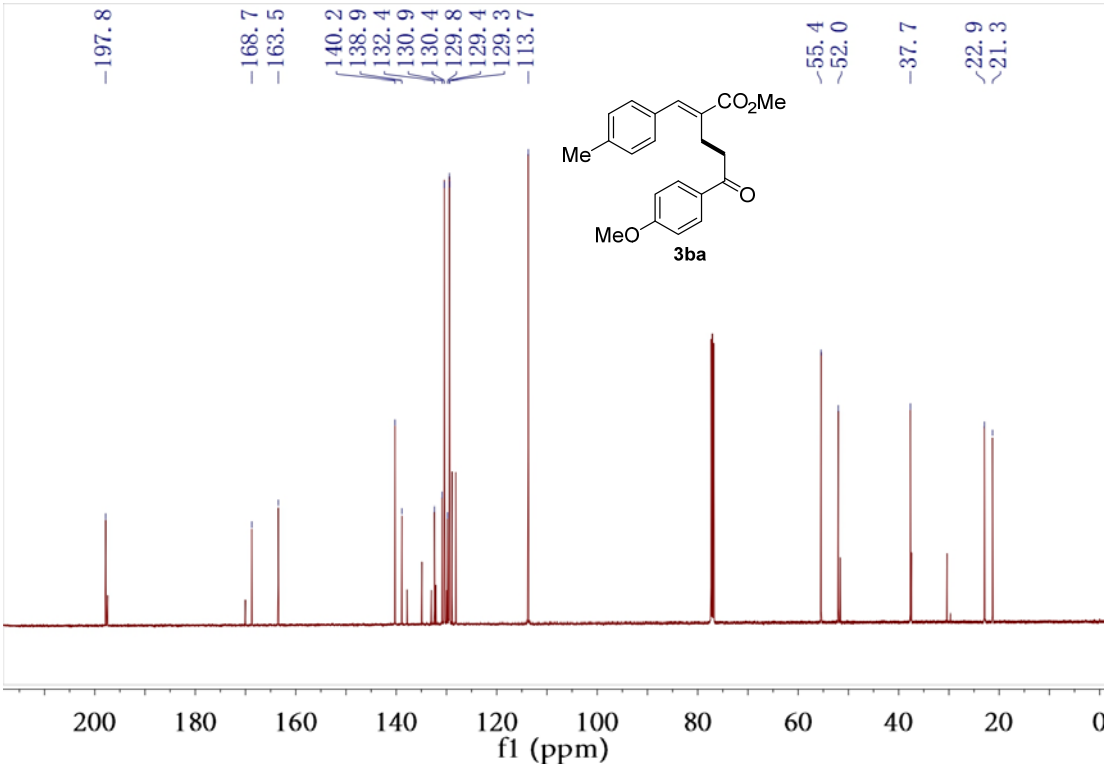
^{13}C NMR of **3aa** in $CDCl_3$



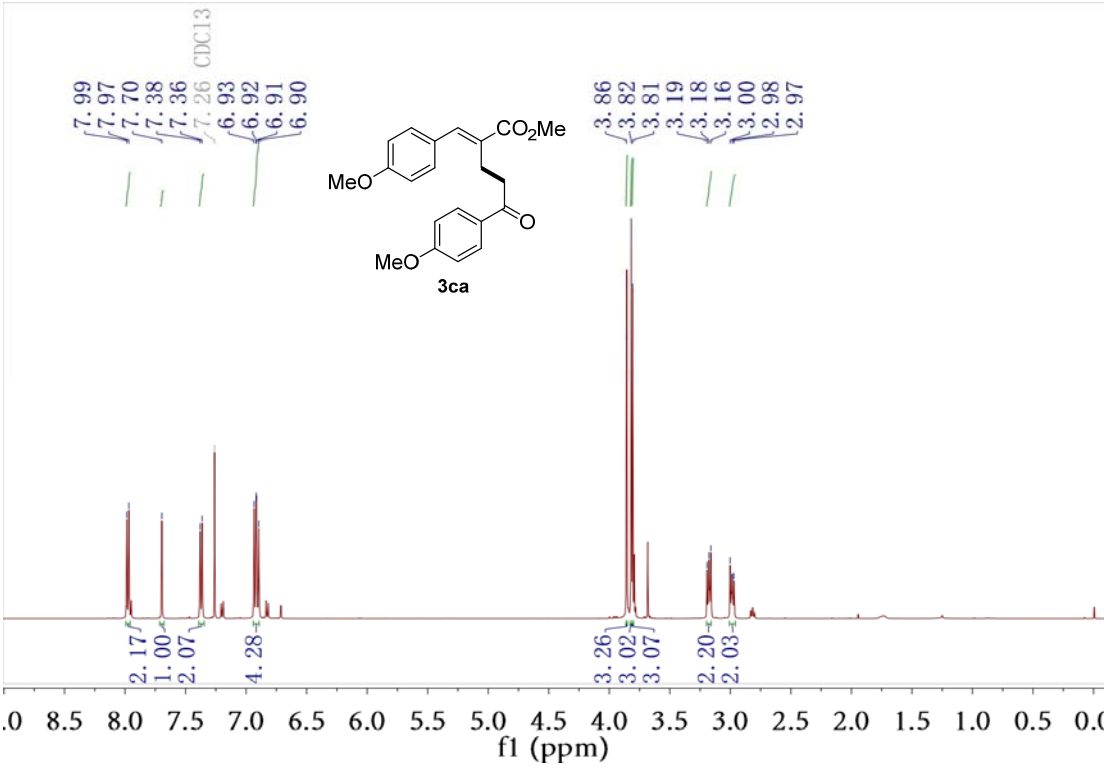
^{1}H NMR of **3ba** in $CDCl_3$



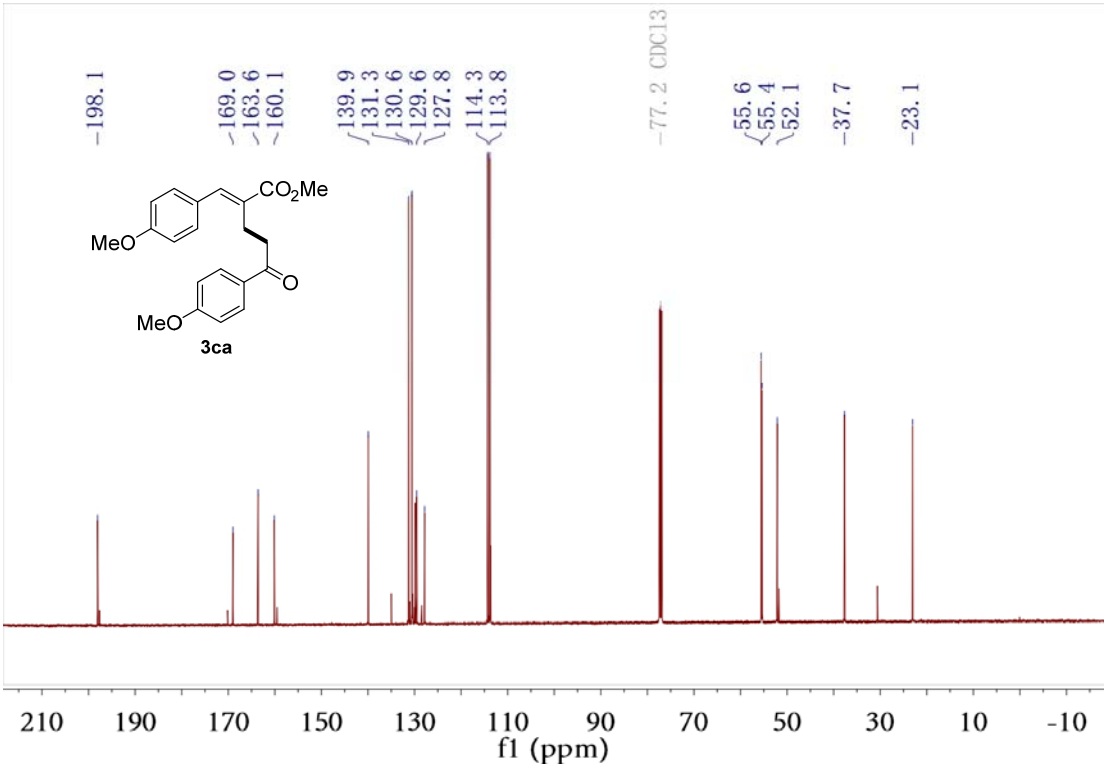
^{13}C NMR of **3ba** in $CDCl_3$



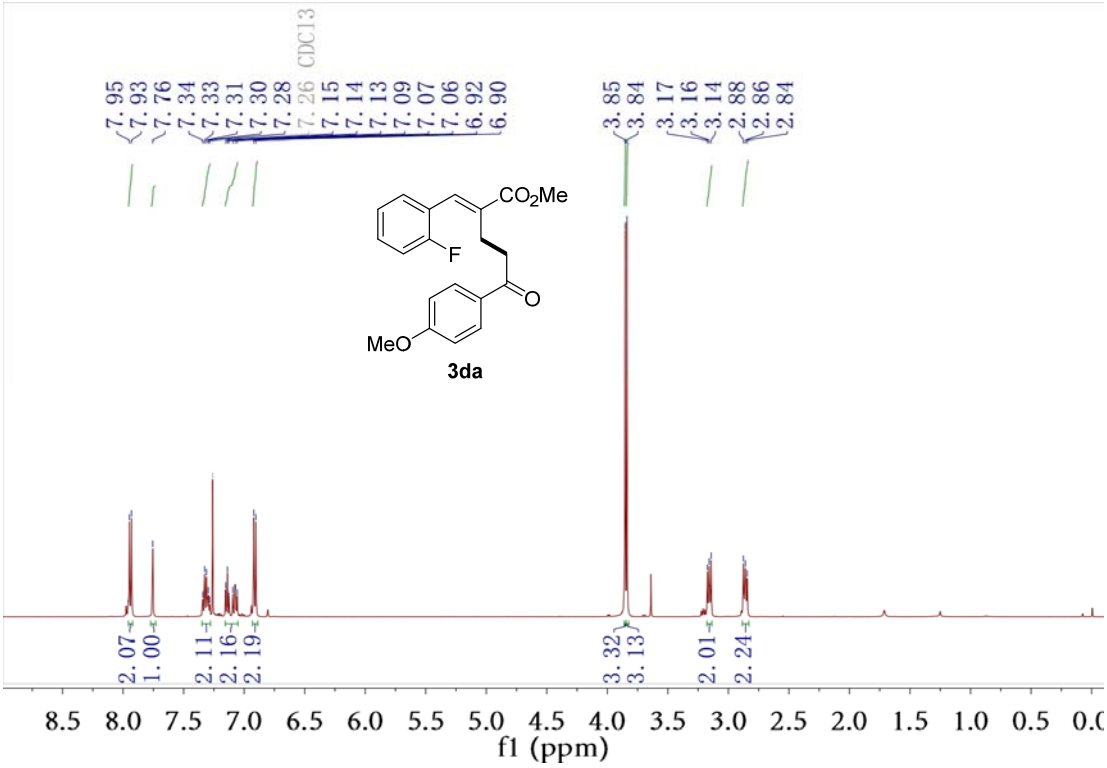
^{1}H NMR of **3ca** in $CDCl_3$



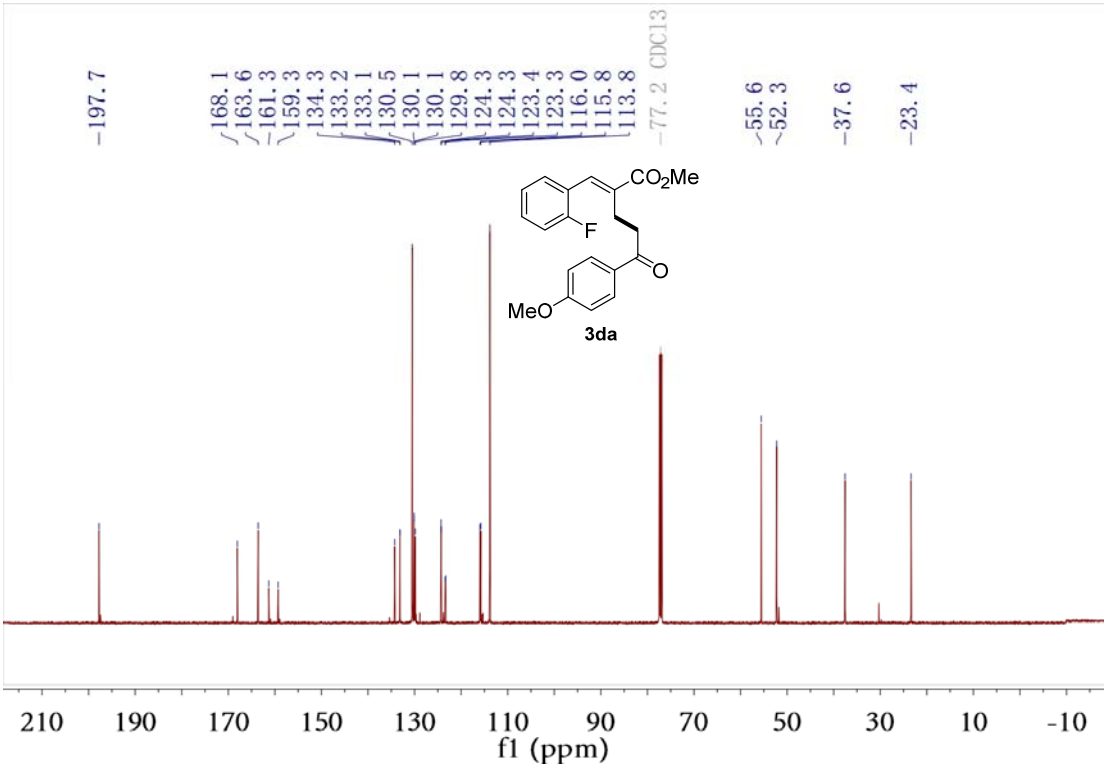
^{13}C NMR of **3ca** in $CDCl_3$



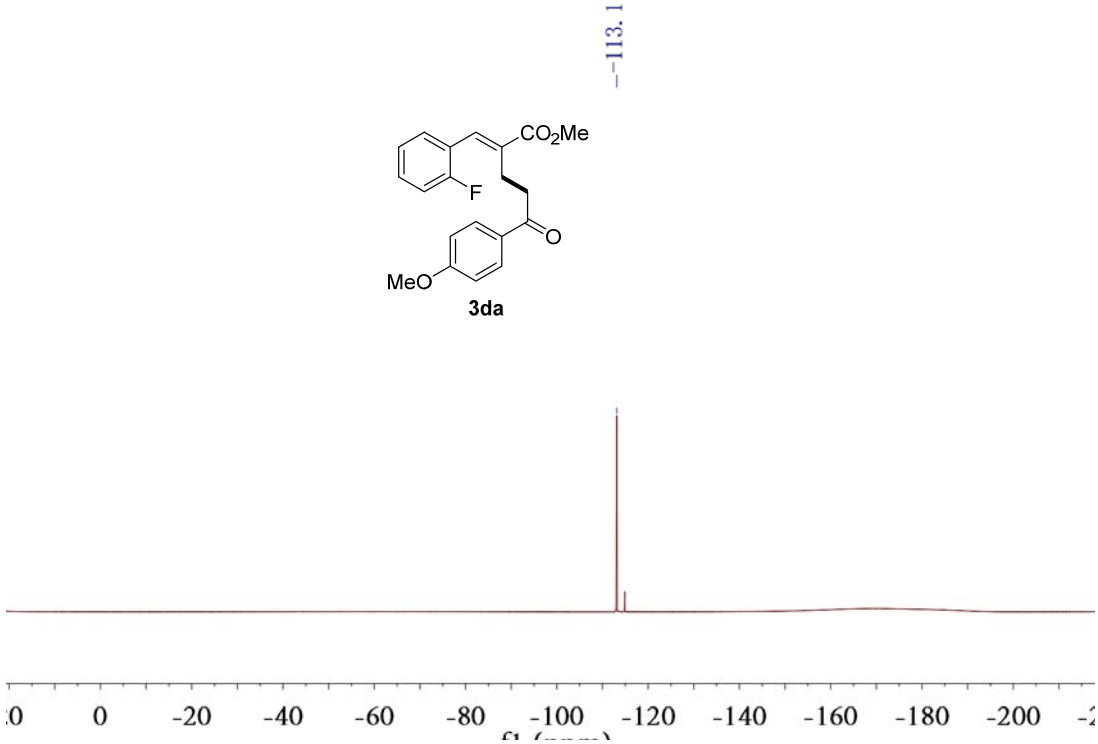
^{1}H NMR of **3da** in $CDCl_3$



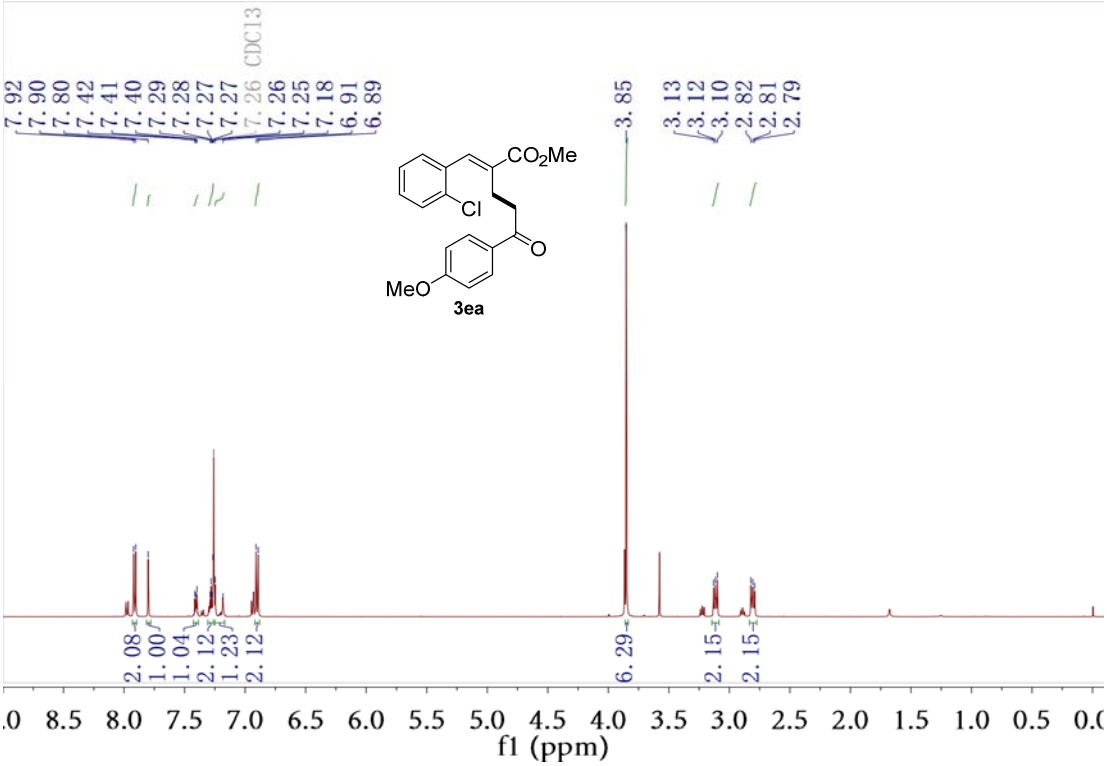
^{13}C NMR of **3da** in $CDCl_3$



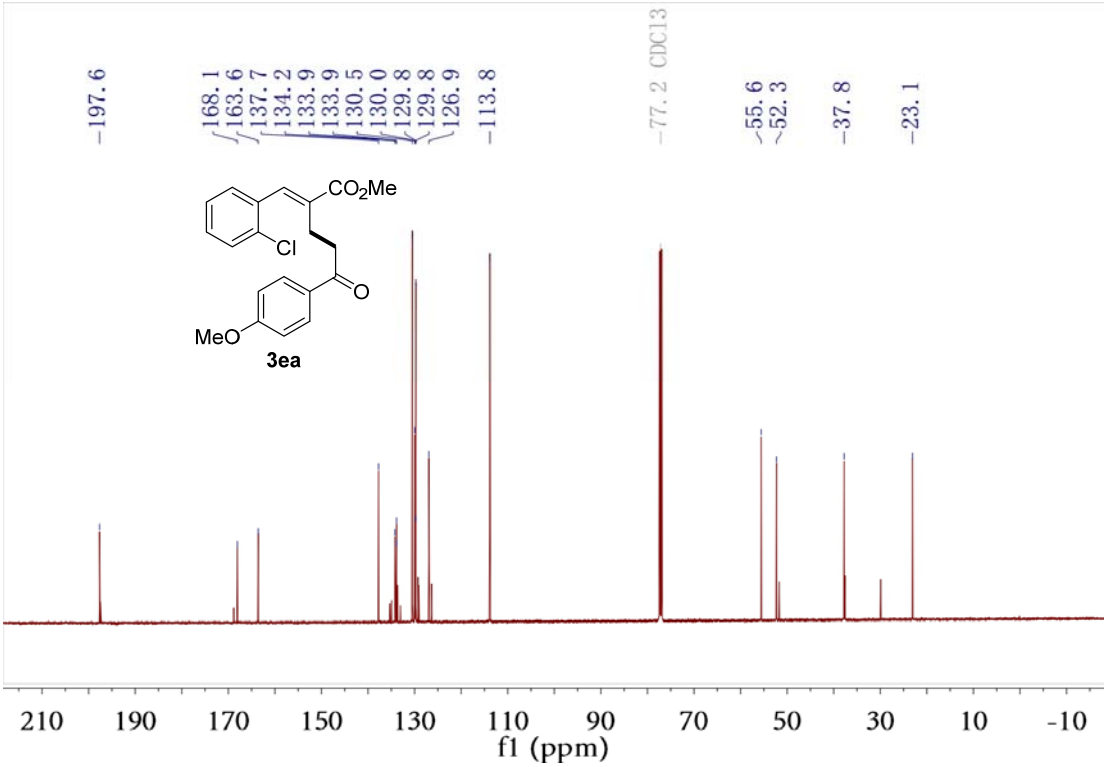
^{19}F NMR of **7da** in $CDCl_3$



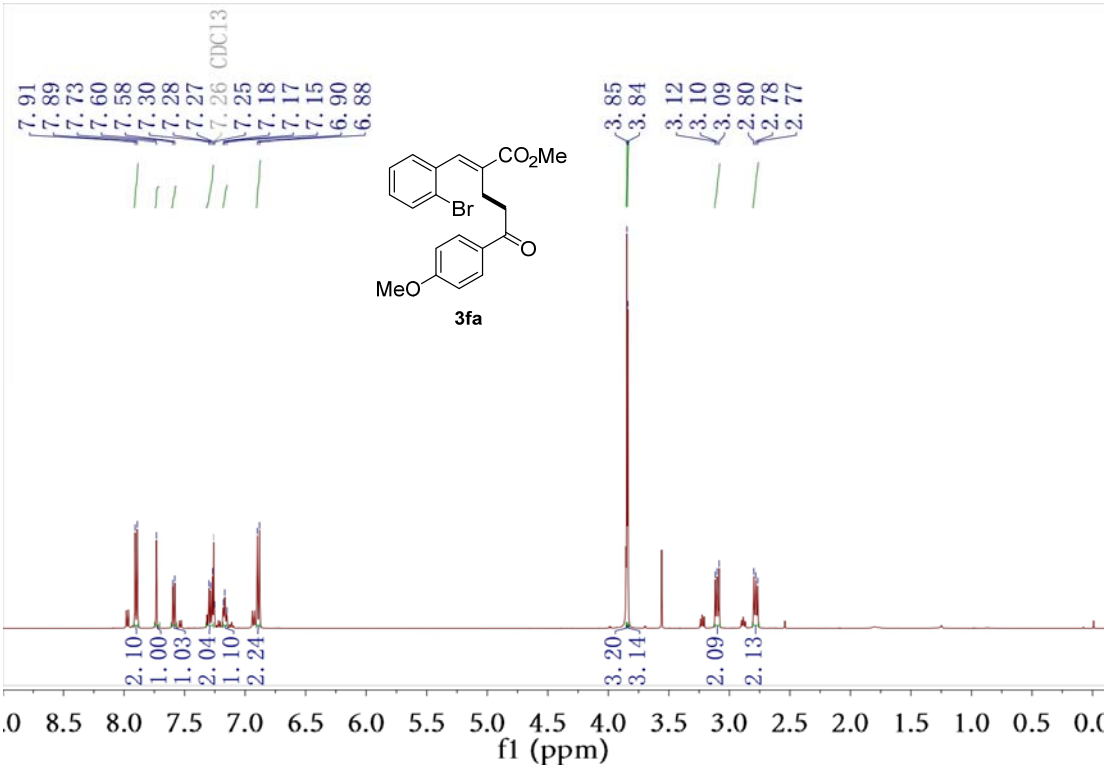
^{1}H NMR of **3ea** in $CDCl_3$



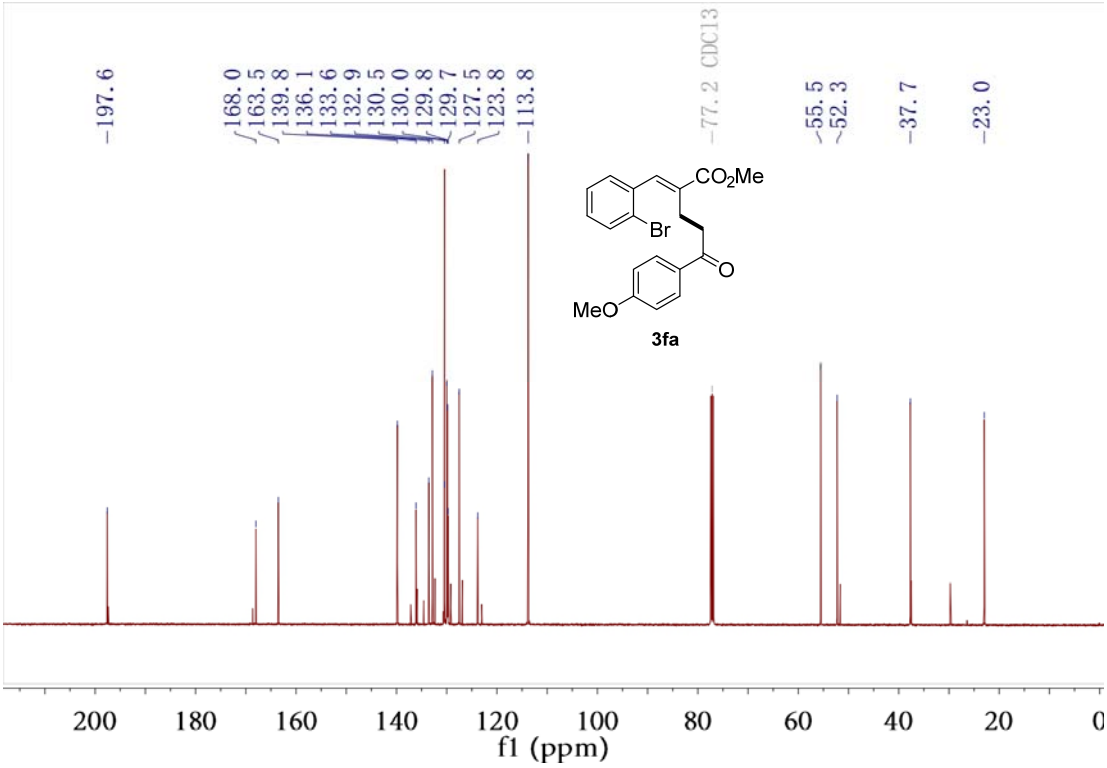
^{13}C NMR of **3ea** in $CDCl_3$



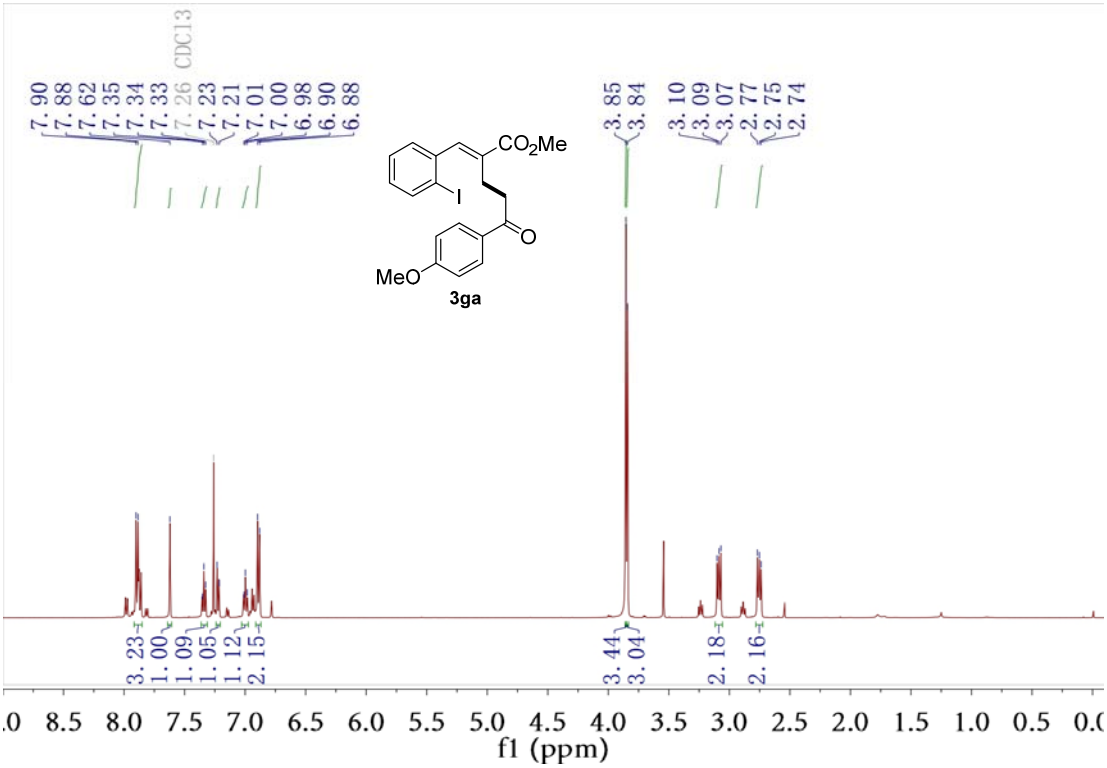
^{1}H NMR of **3fa** in $CDCl_3$



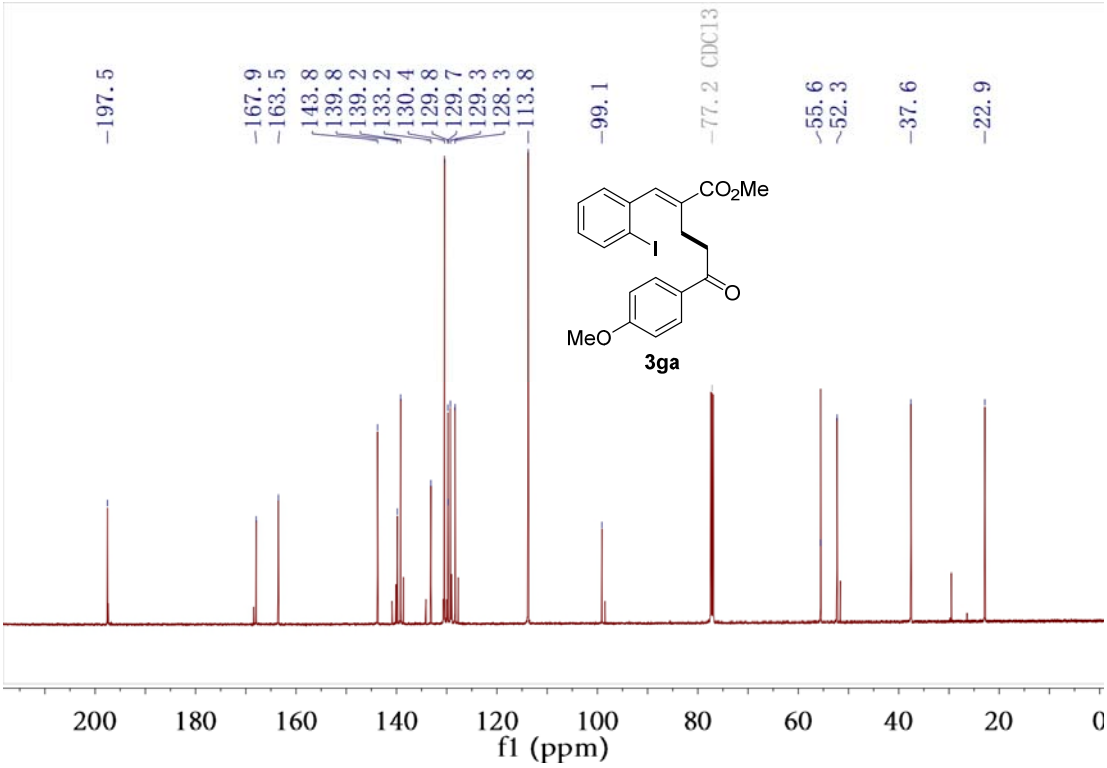
^{13}C NMR of **3fa** in $CDCl_3$



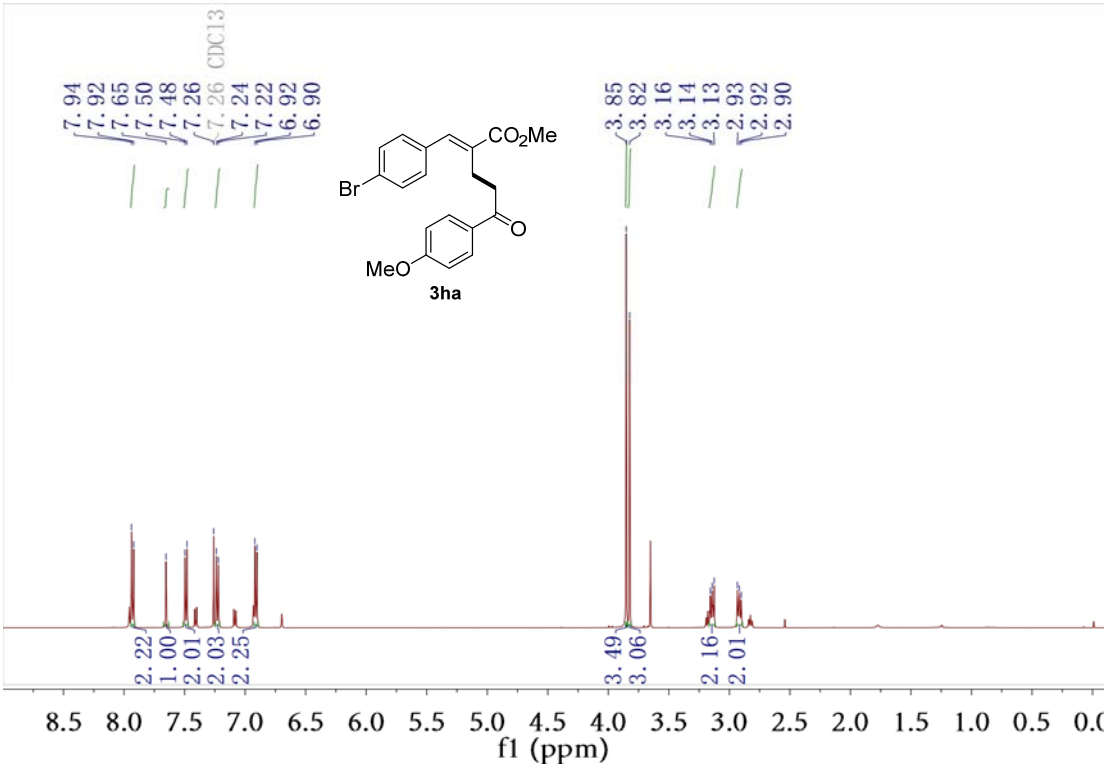
^{1}H NMR of **3ga** in $CDCl_3$



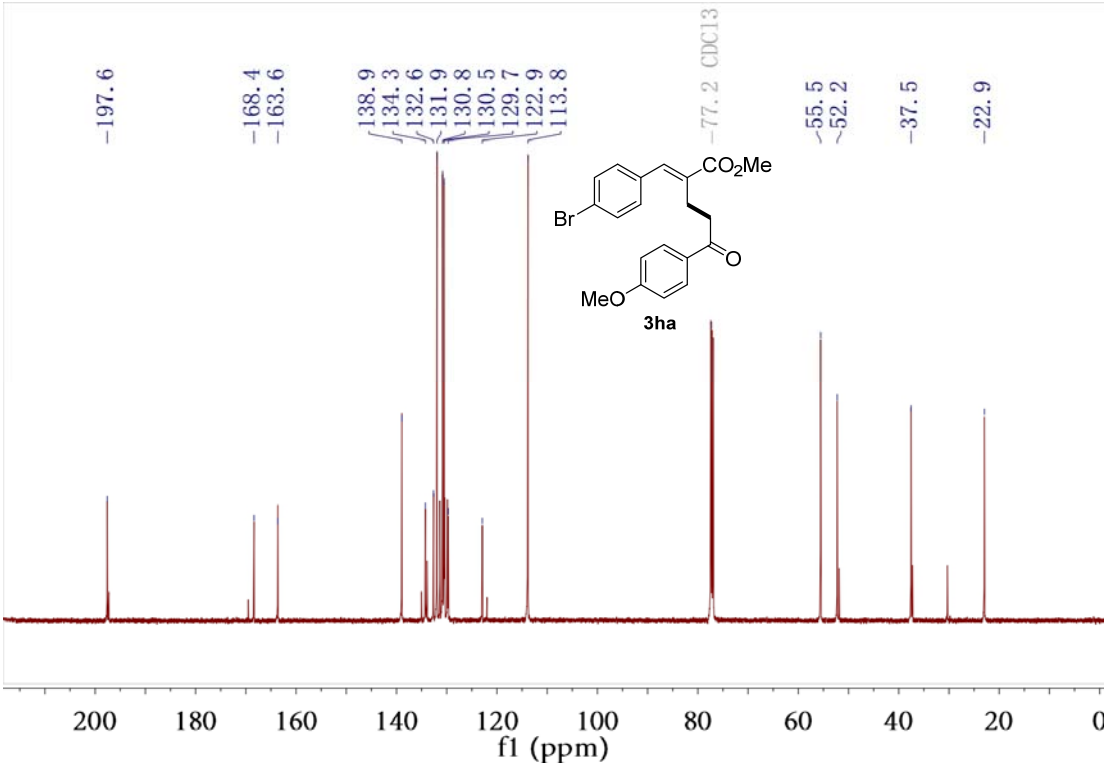
^{13}C NMR of **3ga** in $CDCl_3$



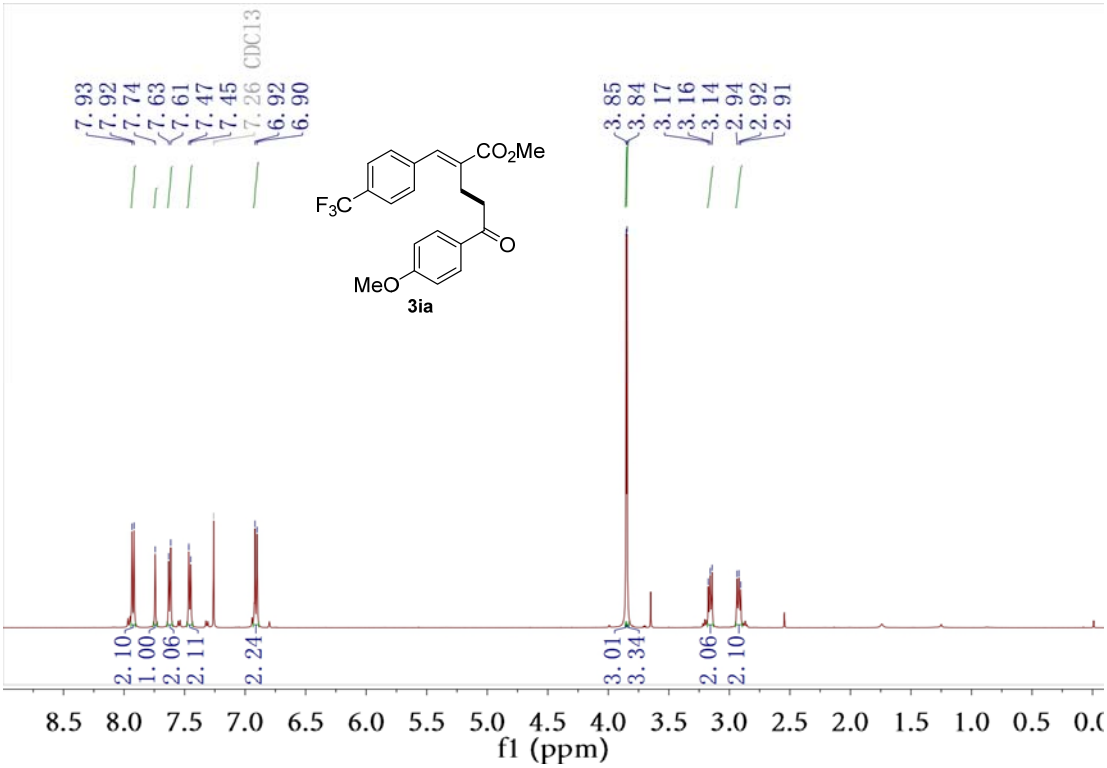
^{1}H NMR of **3ha** in $CDCl_3$



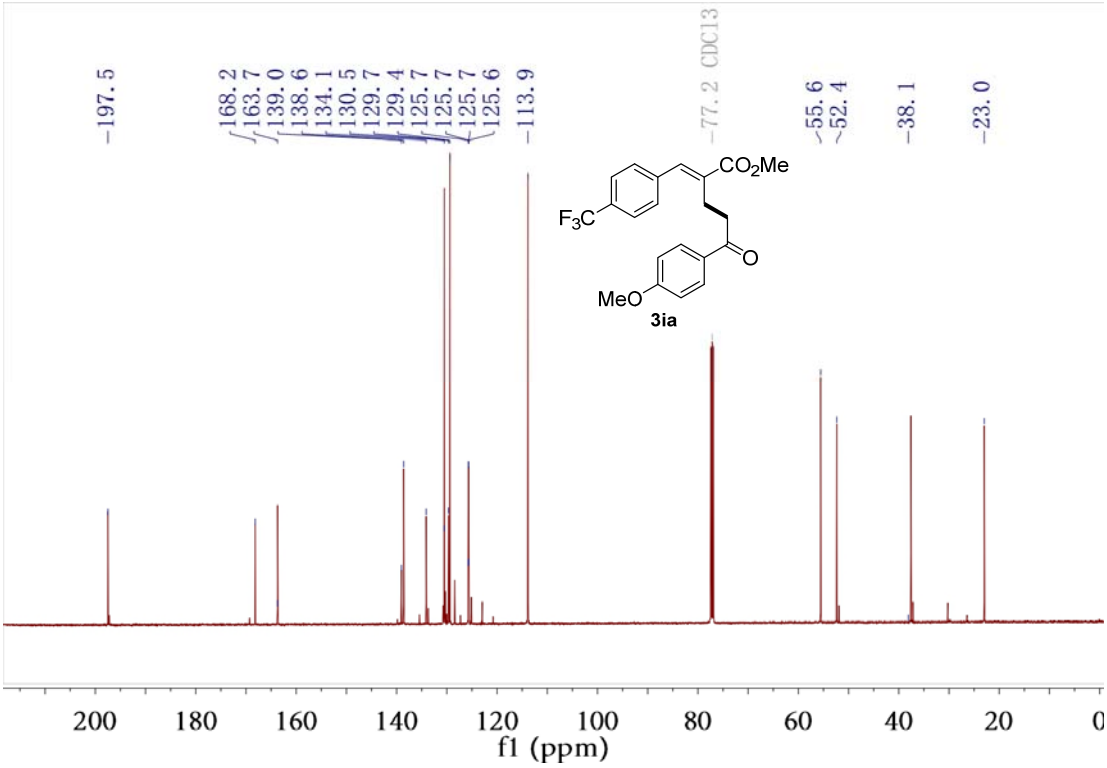
^{13}C NMR of **3ha** in $CDCl_3$



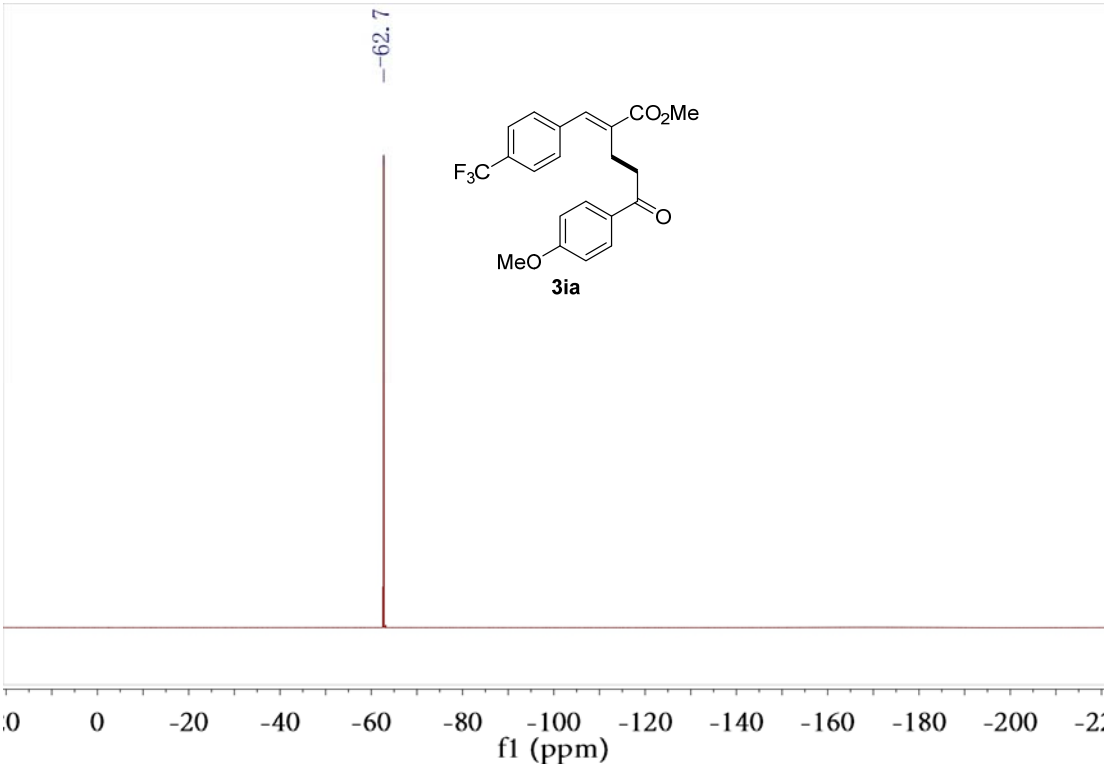
^{1}H NMR of **3ia** in $CDCl_3$



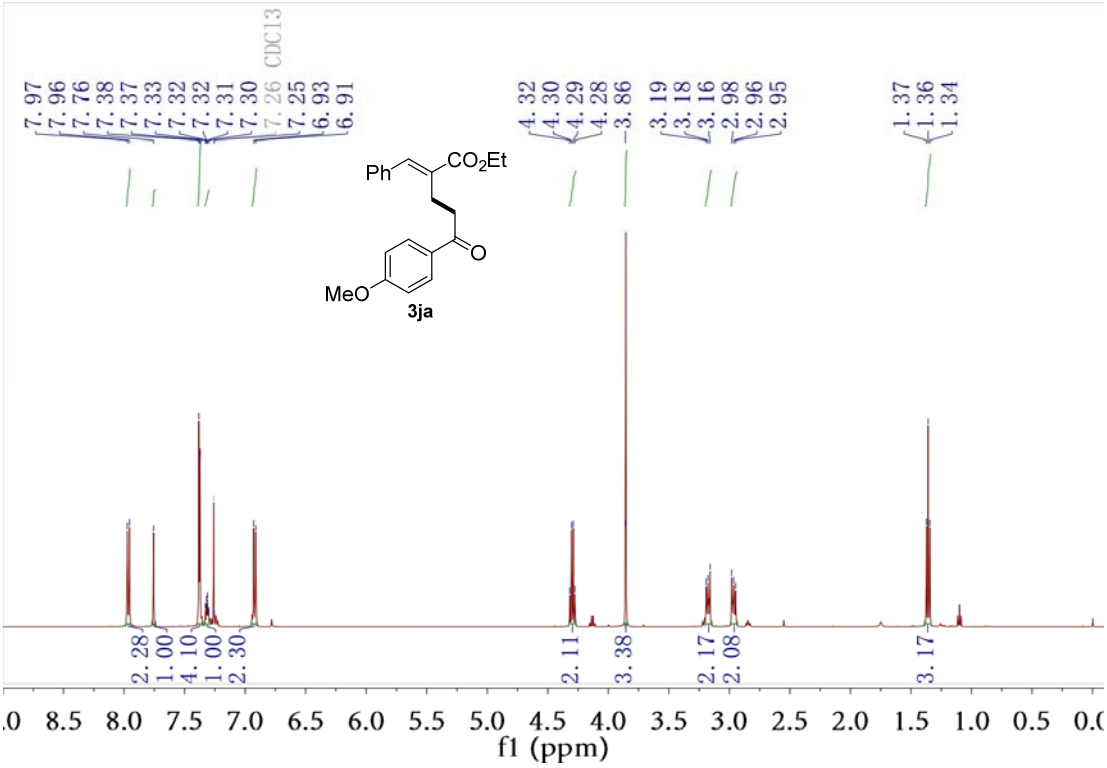
^{13}C NMR of **3ia** in $CDCl_3$



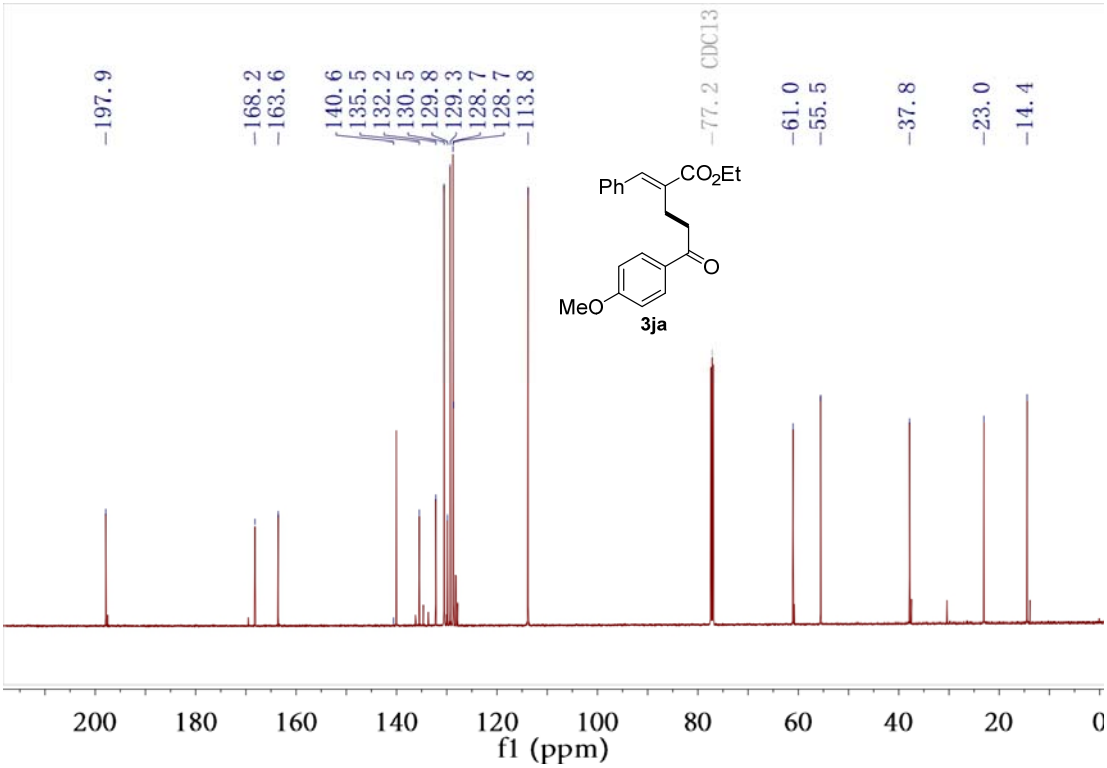
^{19}F NMR of **3ia** in $CDCl_3$



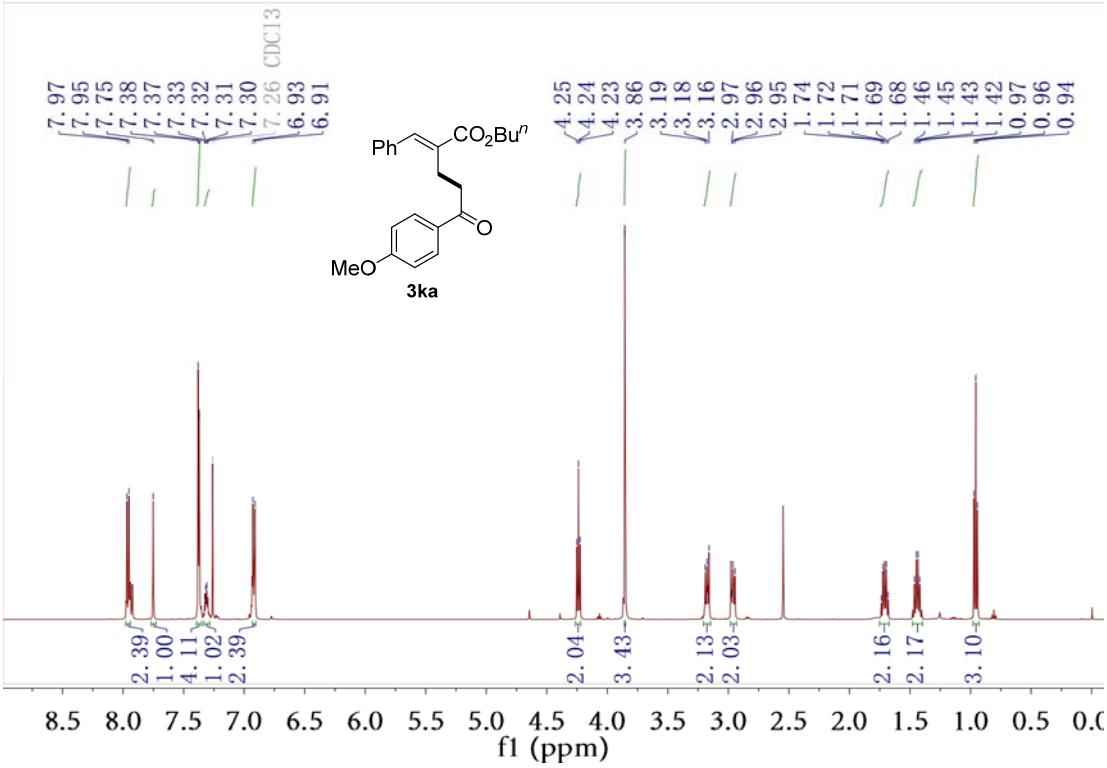
^{1}H NMR of **3ja** in $CDCl_3$



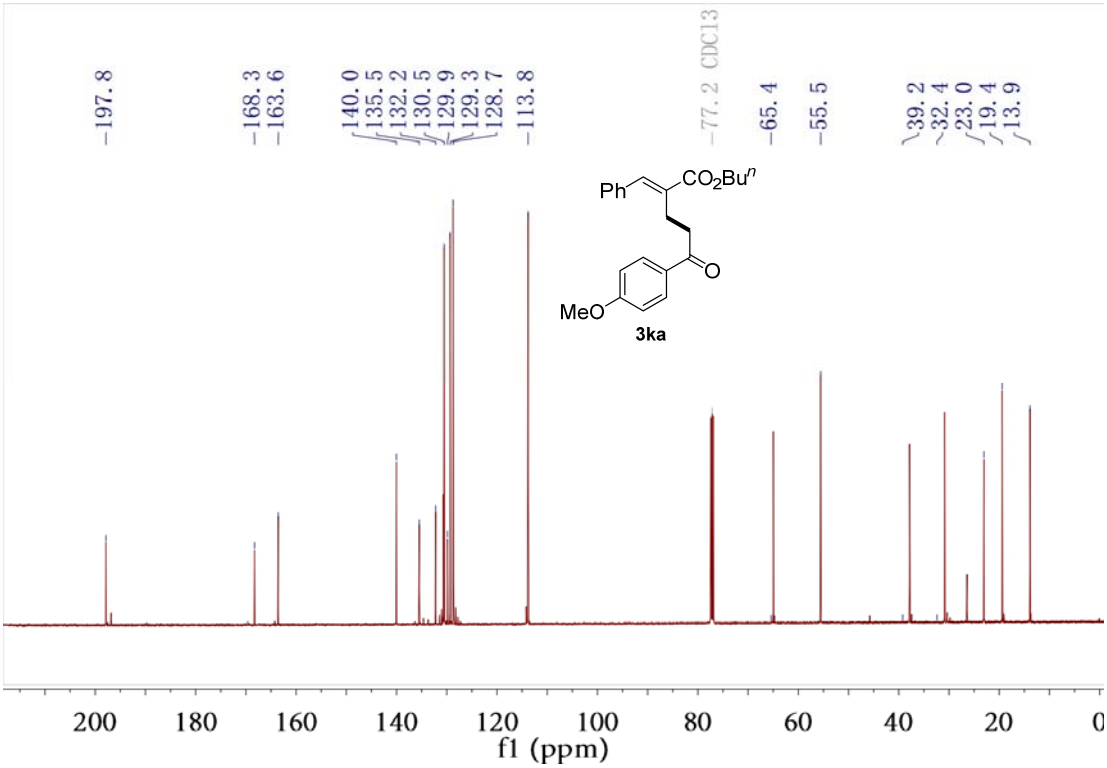
^{13}C NMR of **3ja** in $CDCl_3$



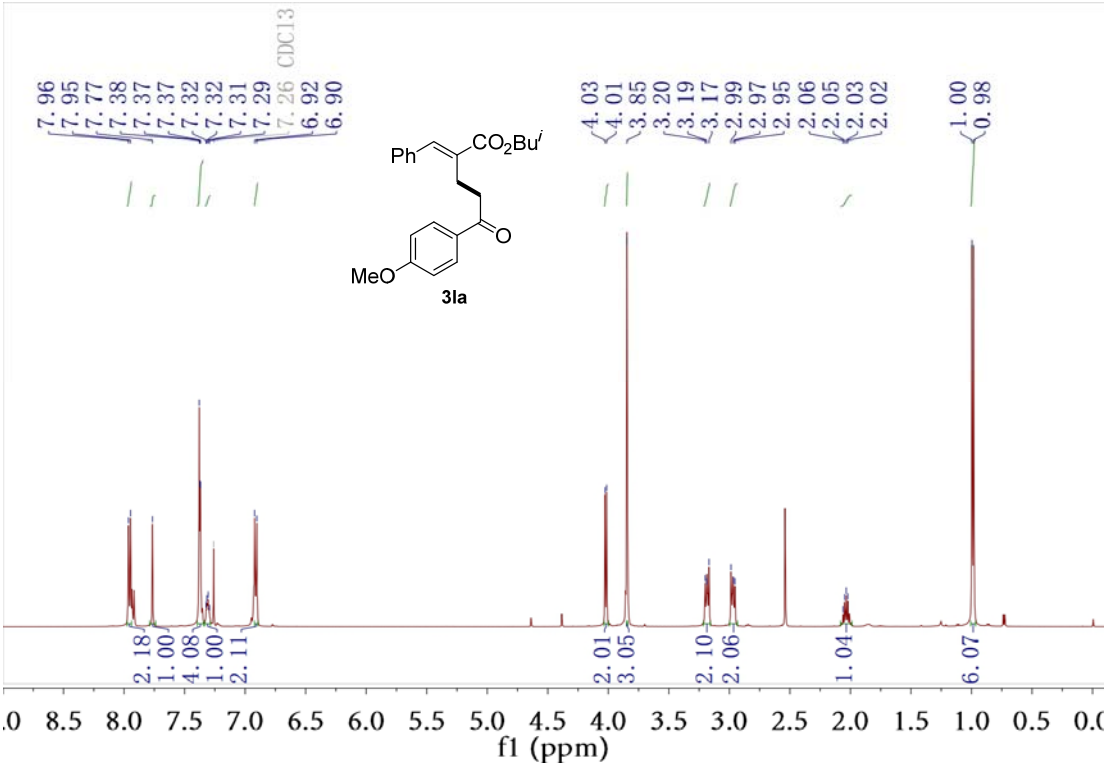
^{1}H NMR of **3ka** in $CDCl_3$



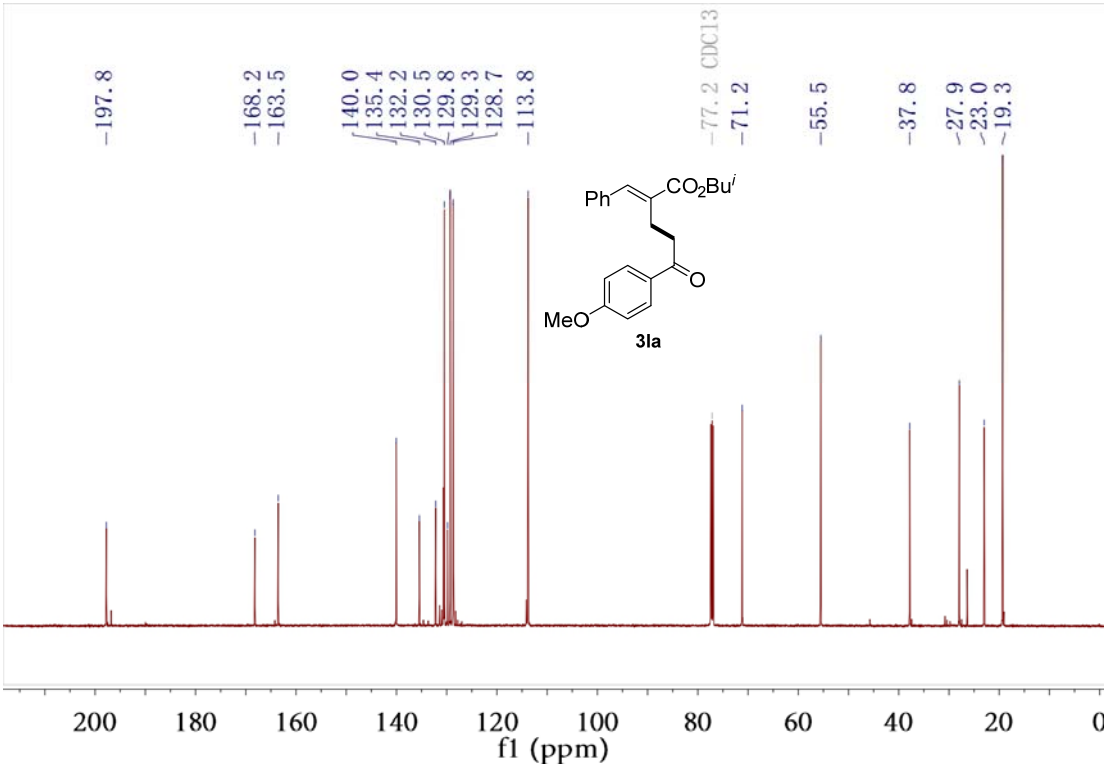
^{13}C NMR of **3ka** in $CDCl_3$



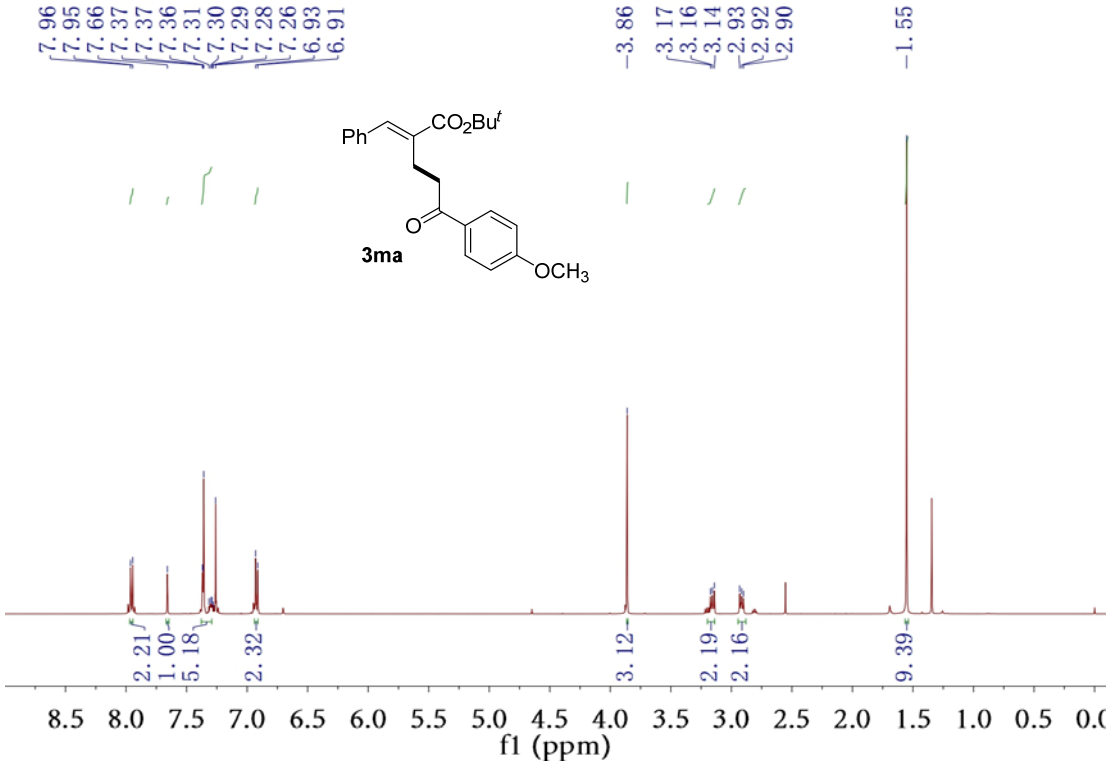
^{1}H NMR of **3la** in $CDCl_3$



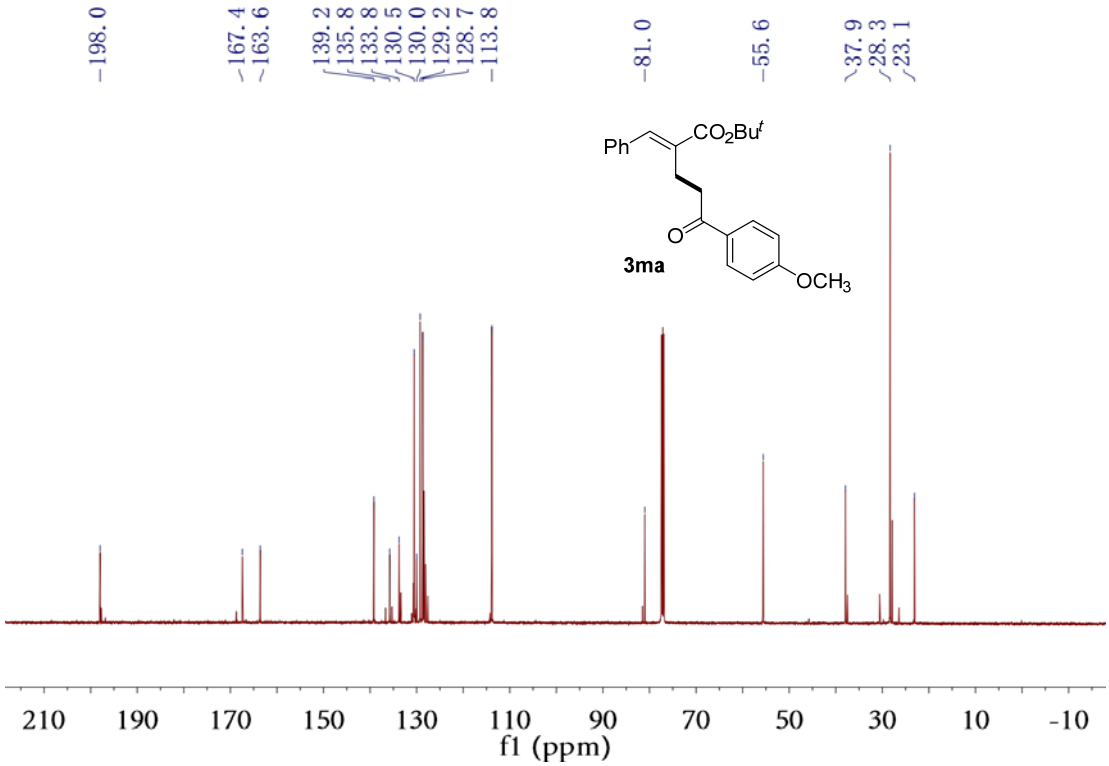
^{13}C NMR of **3la** in $CDCl_3$



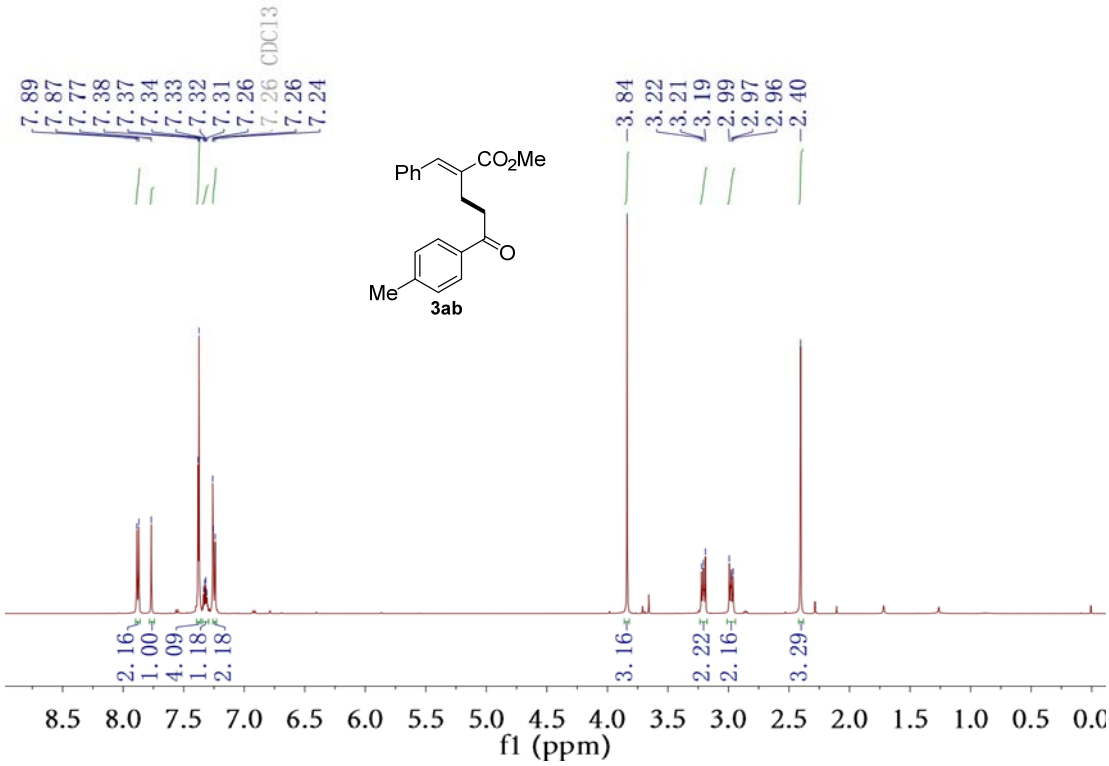
^{1}H NMR of **3ma** in $CDCl_3$



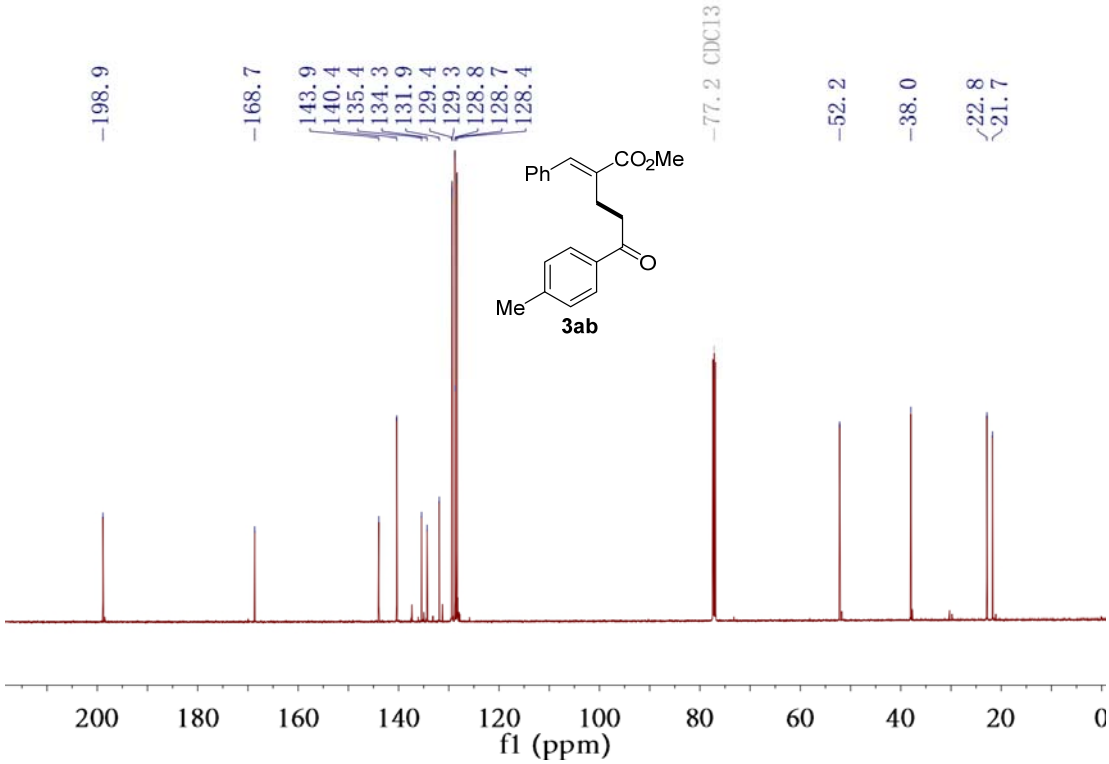
^{13}C NMR of **3ma** in $CDCl_3$



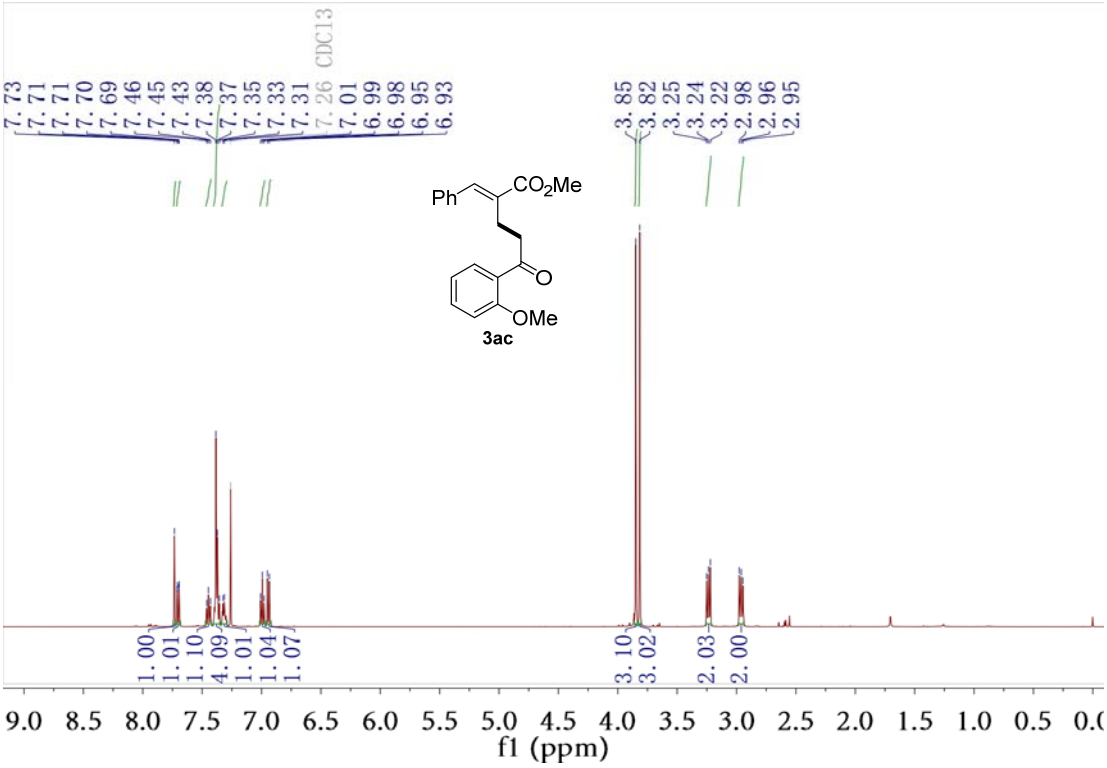
^{1}H NMR of **3ab** in $CDCl_3$



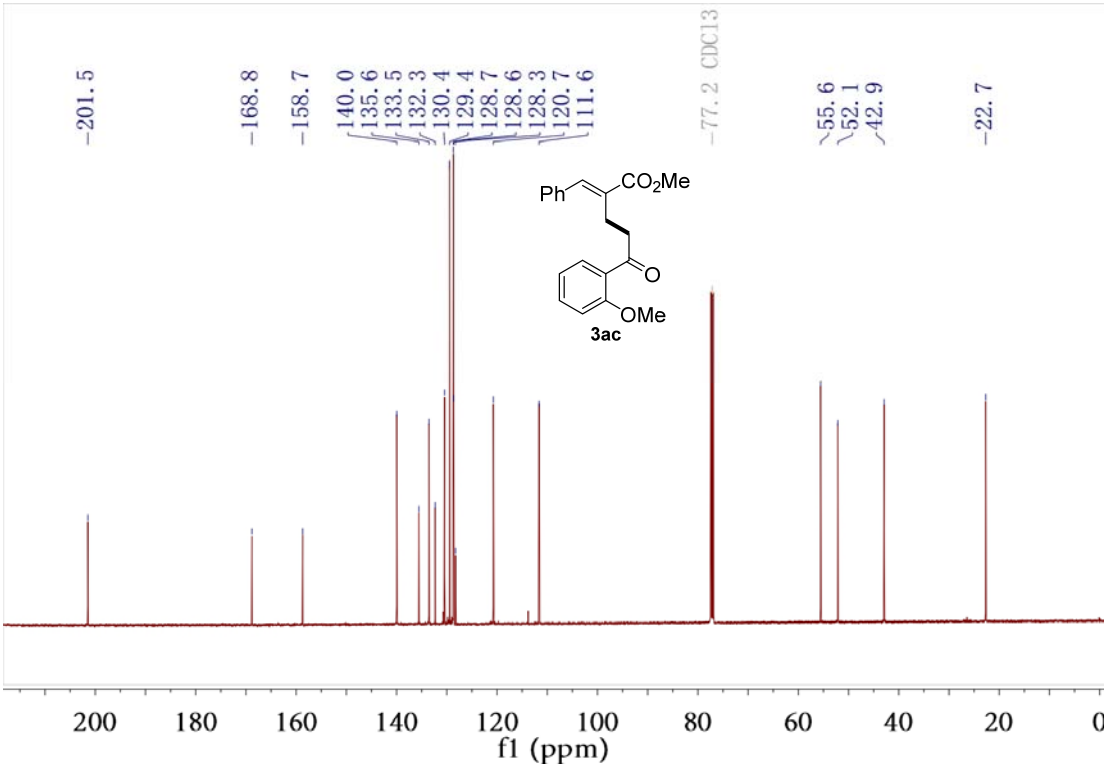
^{13}C NMR of **3ab** in $CDCl_3$



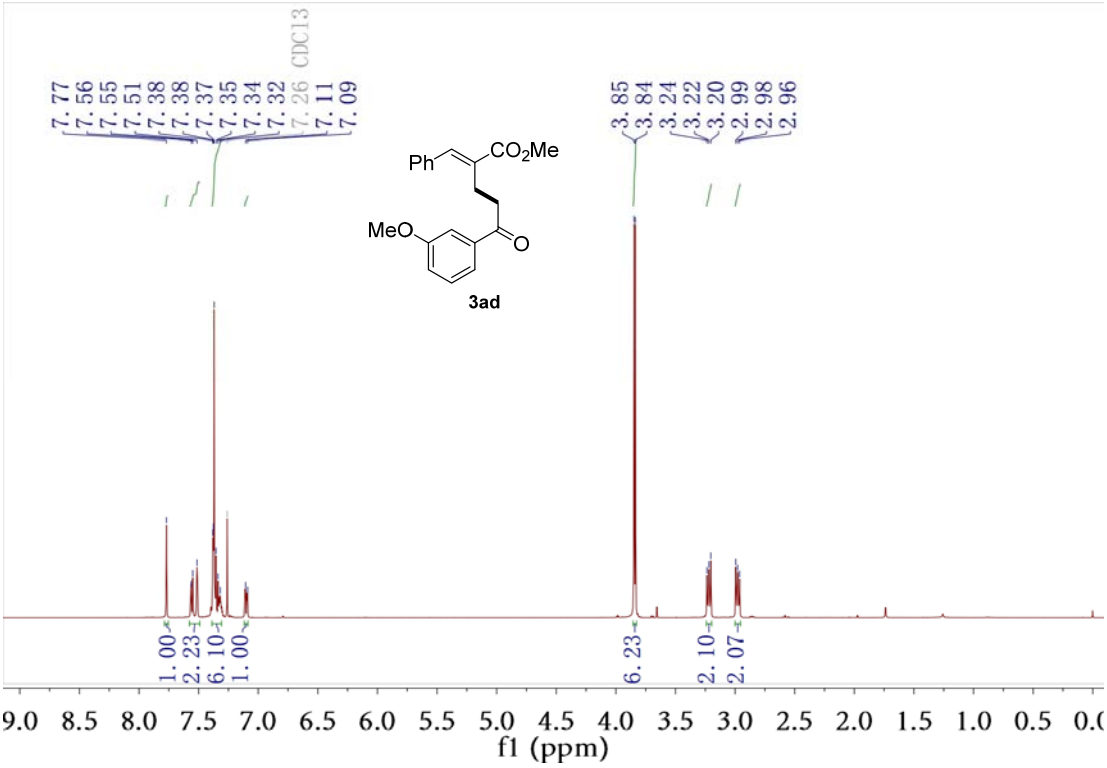
^{1}H NMR of **3ac** in $CDCl_3$



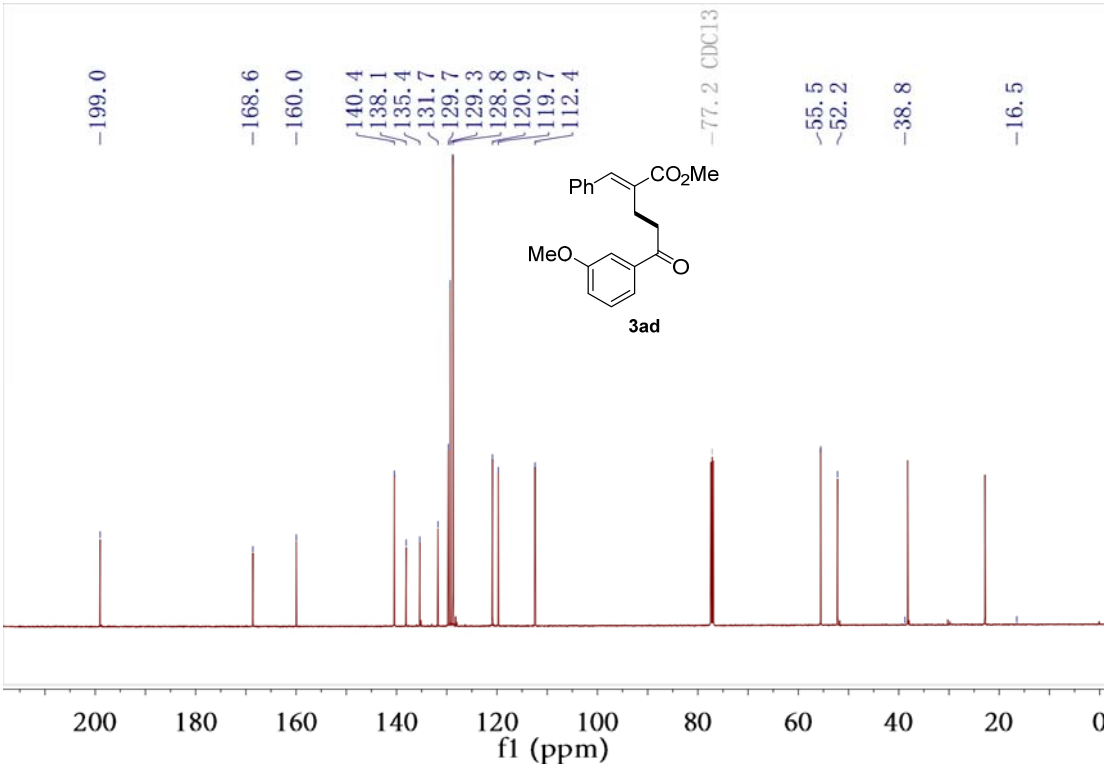
^{13}C NMR of **3ac** in $CDCl_3$



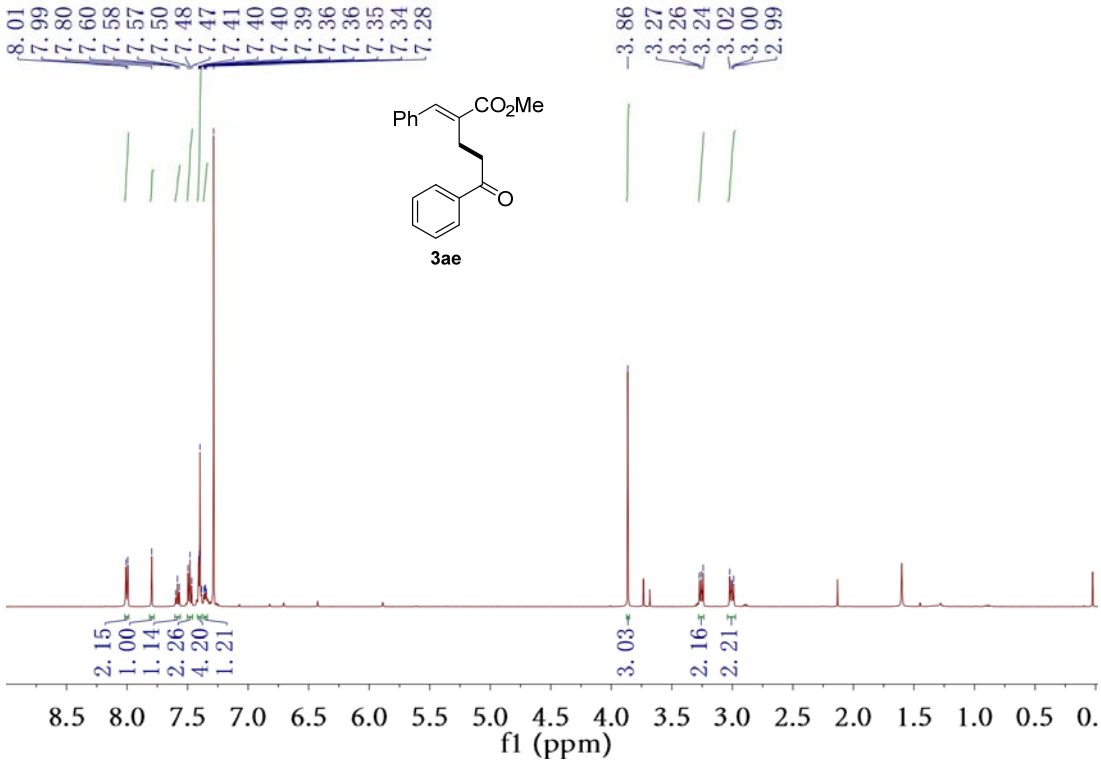
^{1}H NMR of **3ad** in $CDCl_3$



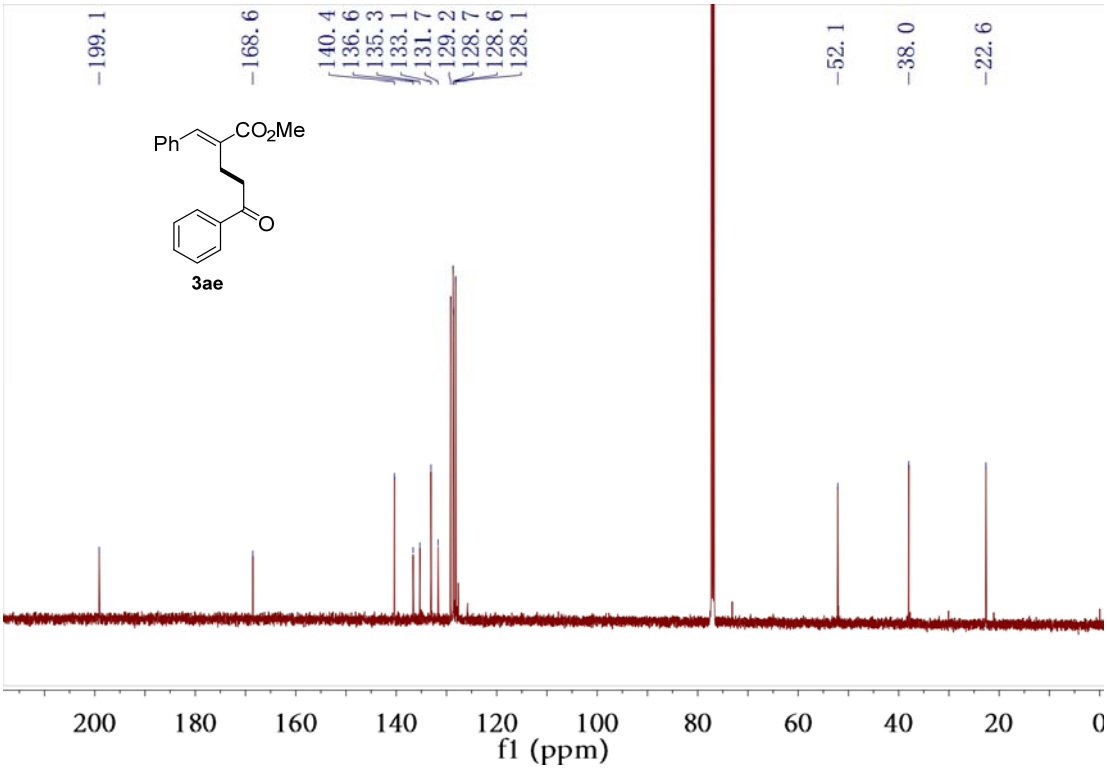
^{13}C NMR of **3ad** in $CDCl_3$



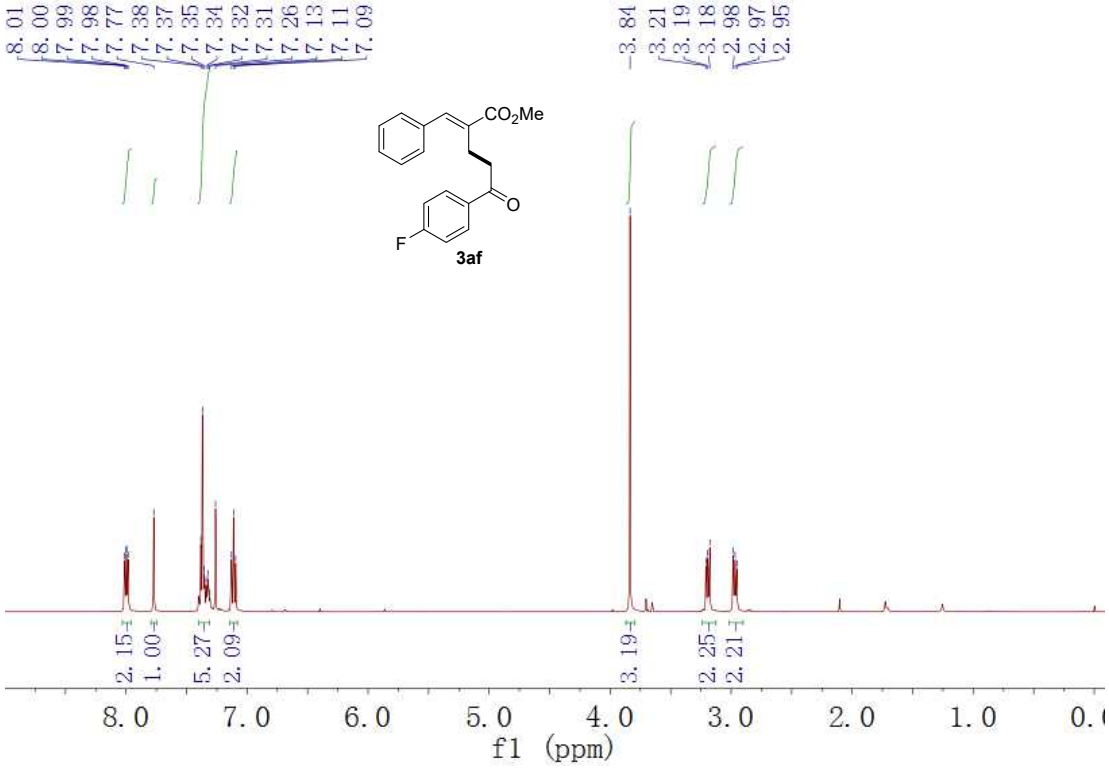
^{1}H NMR of **3ae** in $CDCl_3$



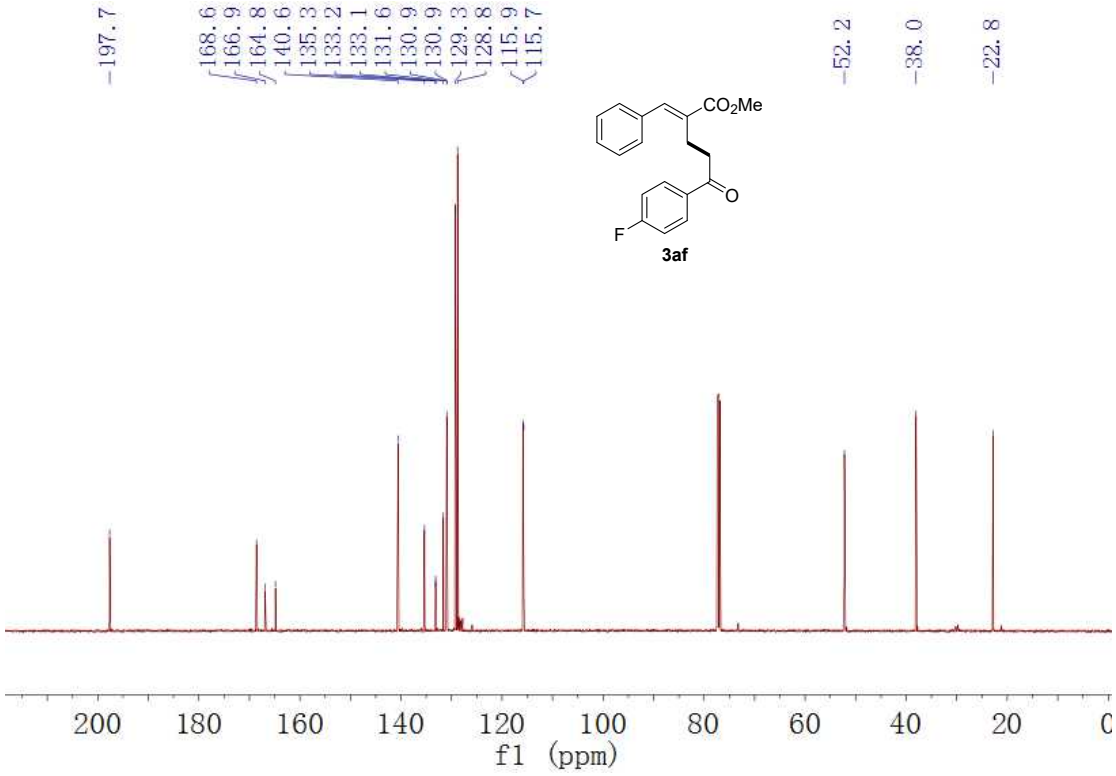
^{13}C NMR of **3ae** in $CDCl_3$



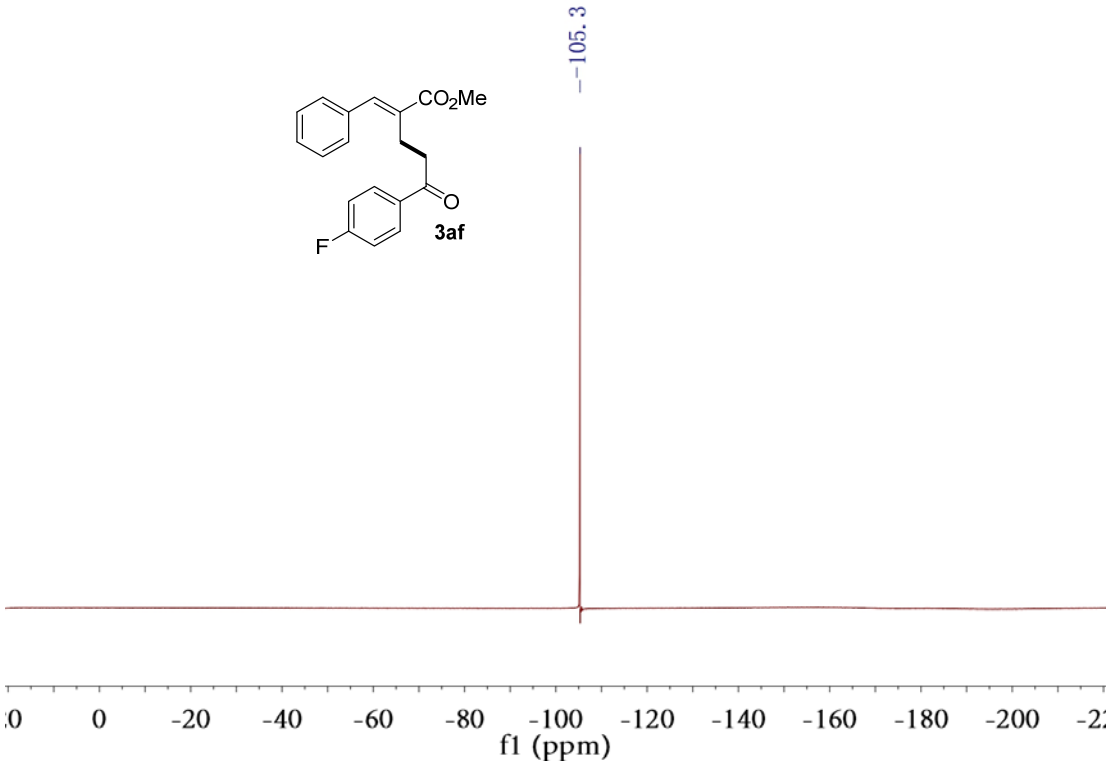
^{1}H NMR of **3af** in $CDCl_3$



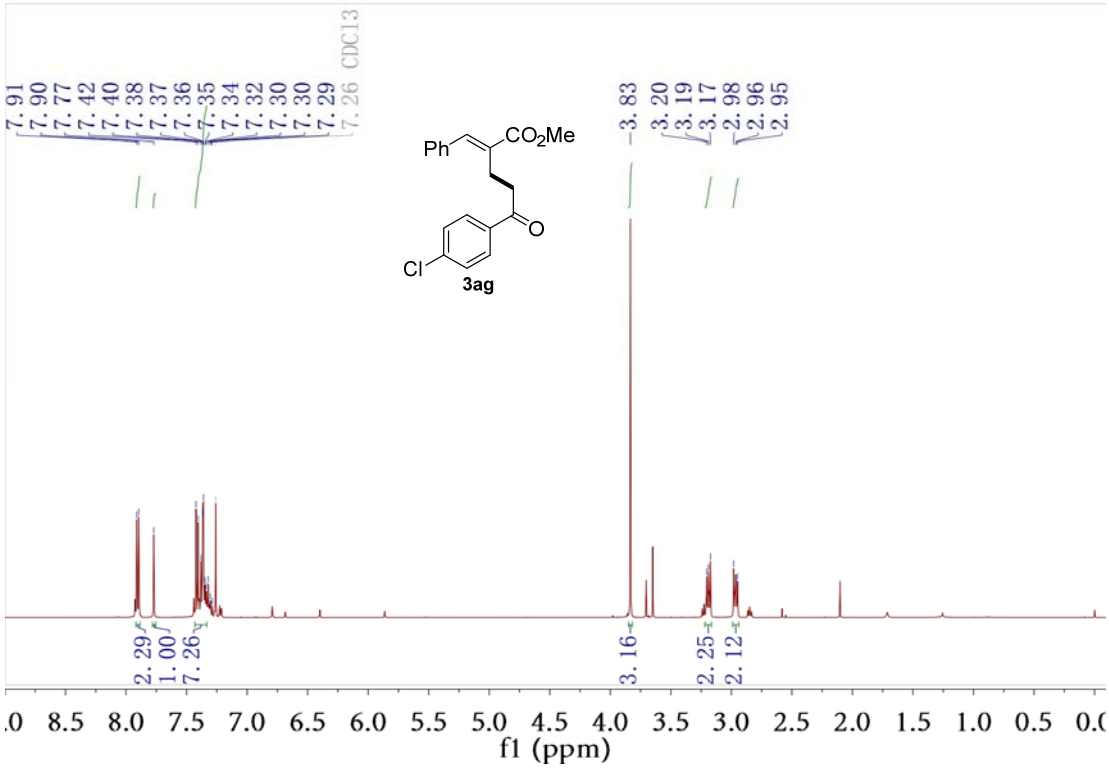
^{13}C NMR of **3ae** in $CDCl_3$



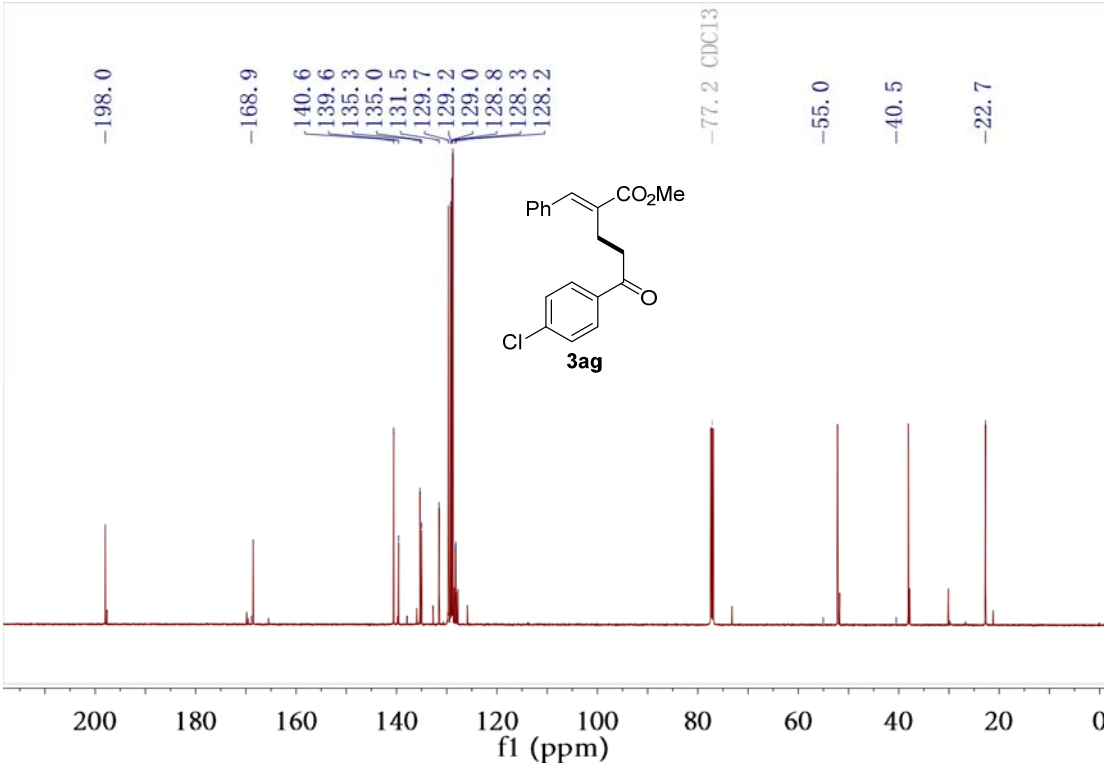
^{19}F NMR of **3af** in $CDCl_3$



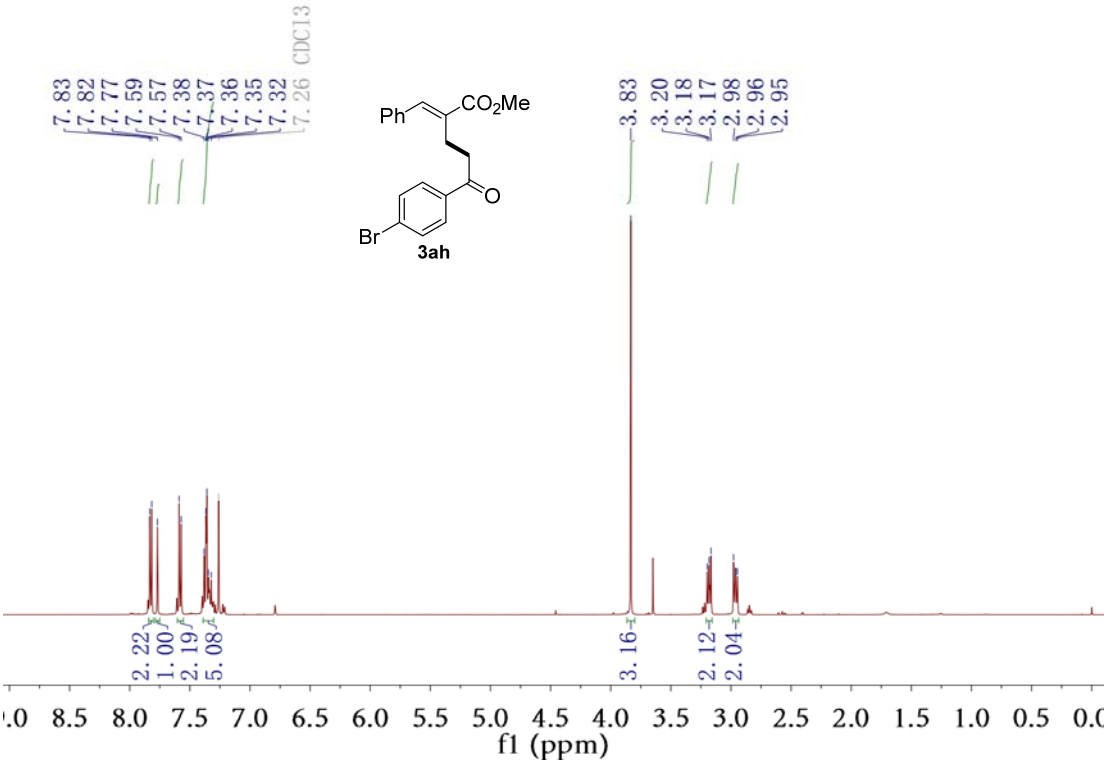
^{1}H NMR of **3ag** in $CDCl_3$



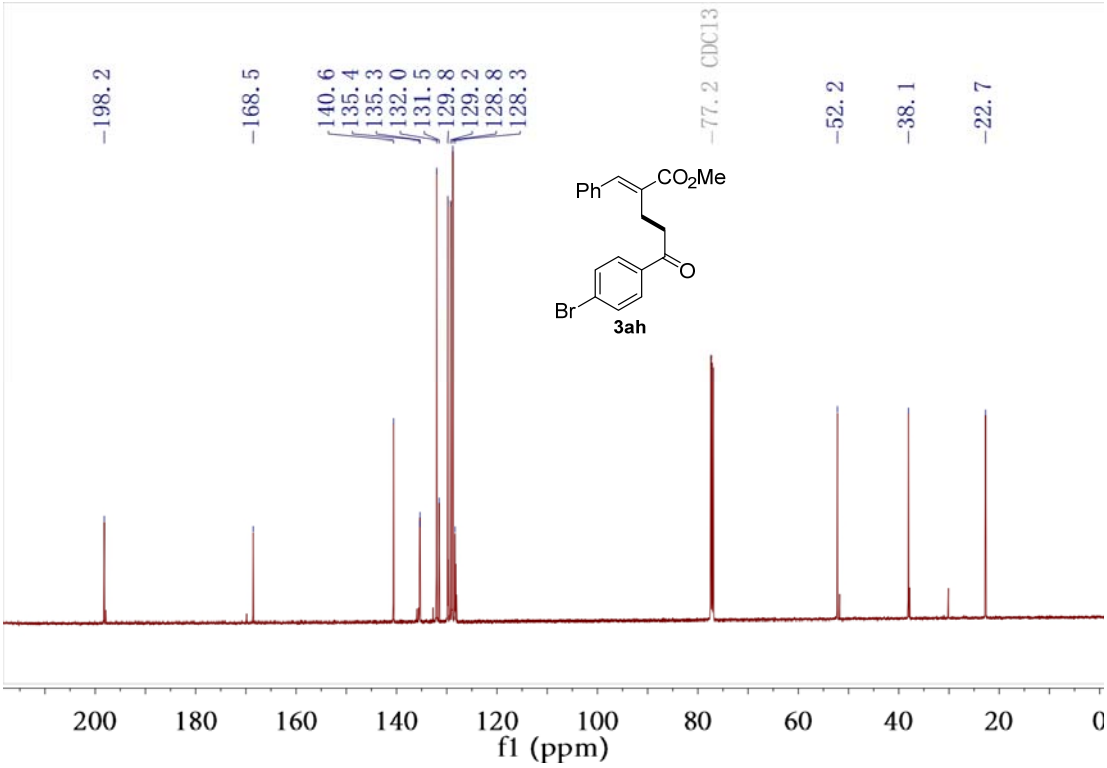
^{13}C NMR of **3ag** in $CDCl_3$



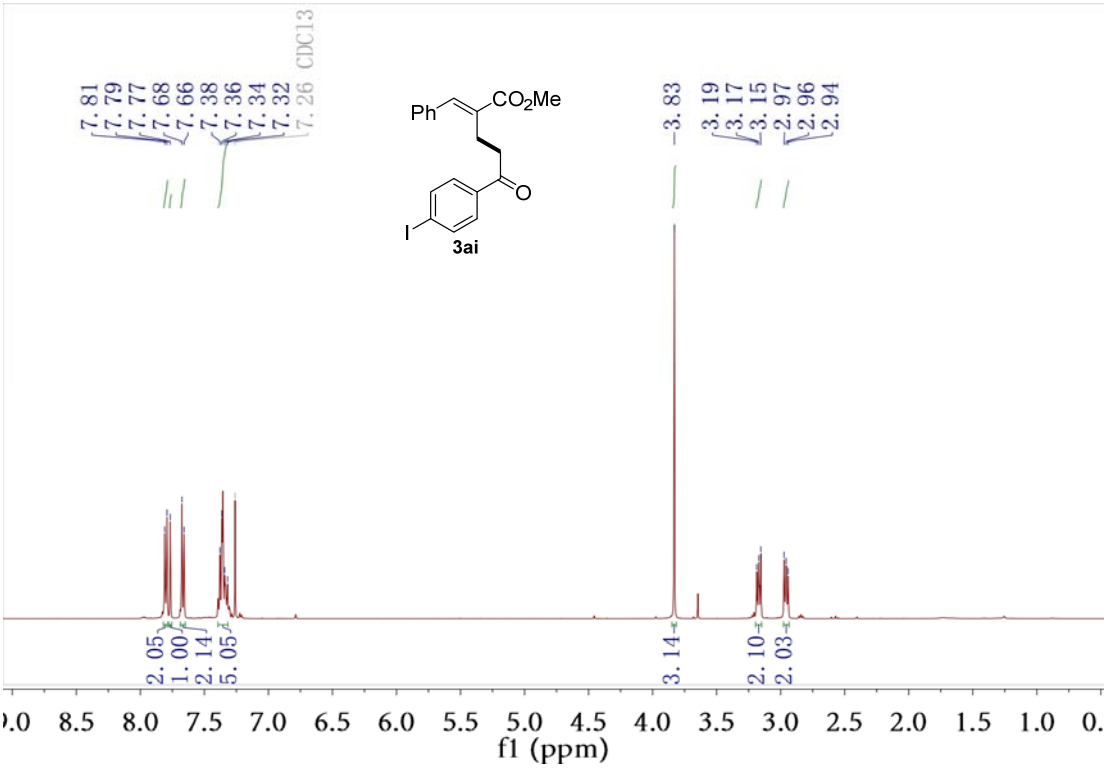
^{1}H NMR of **3ah** in $CDCl_3$



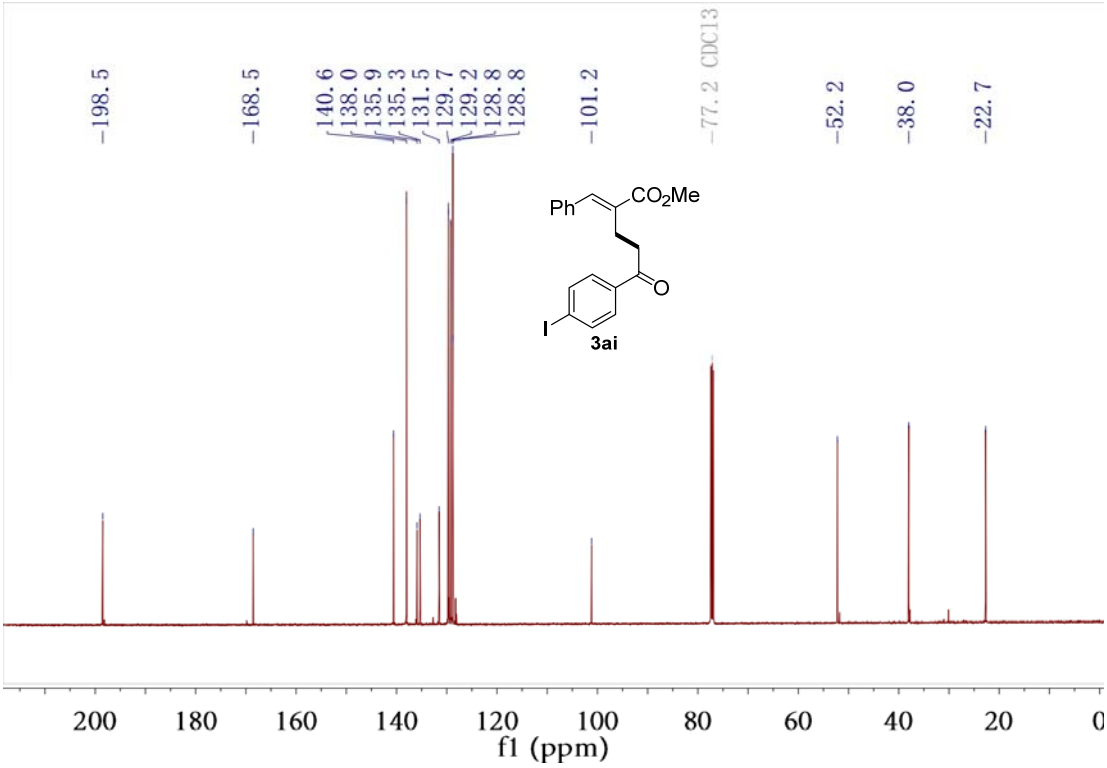
^{13}C NMR of **3ah** in $CDCl_3$



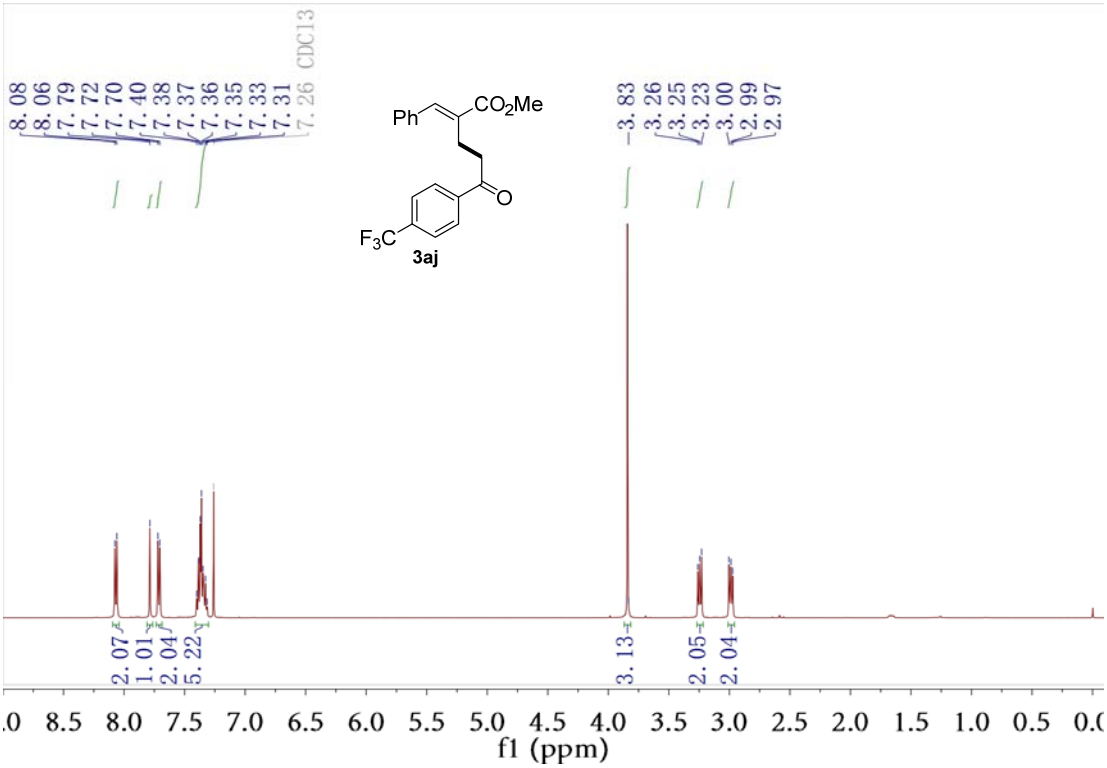
^{1}H NMR of **3ai** in $CDCl_3$



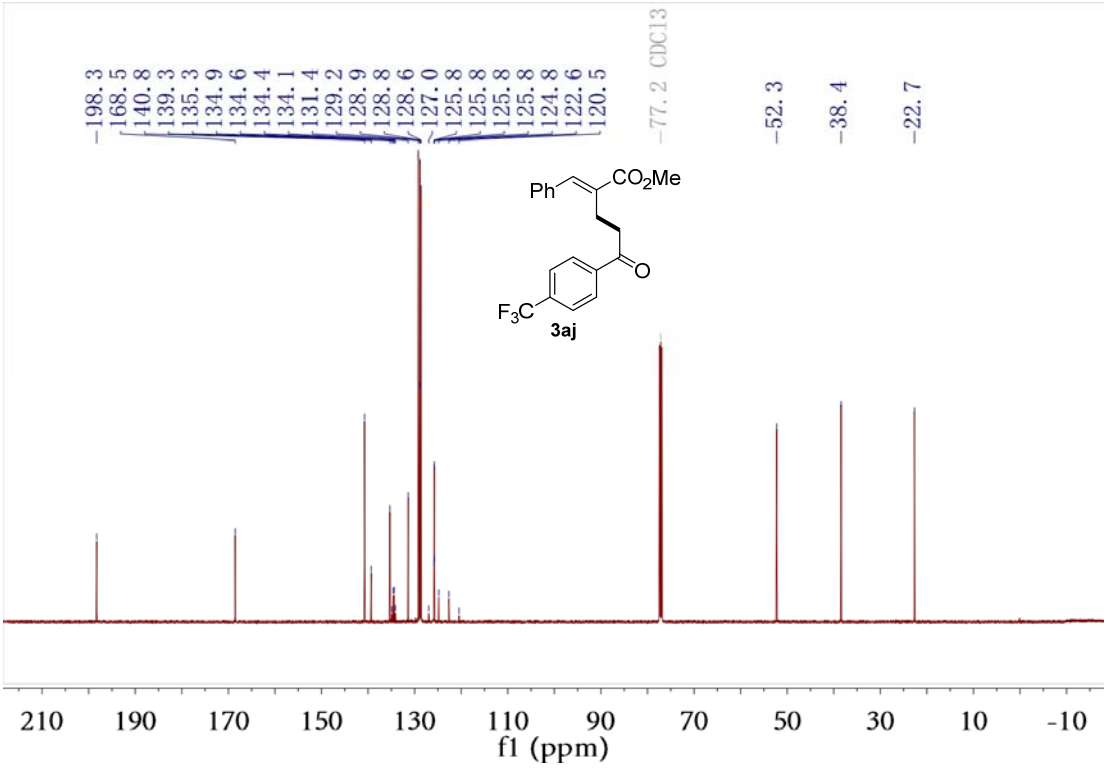
^{13}C NMR of **3ai** in $CDCl_3$



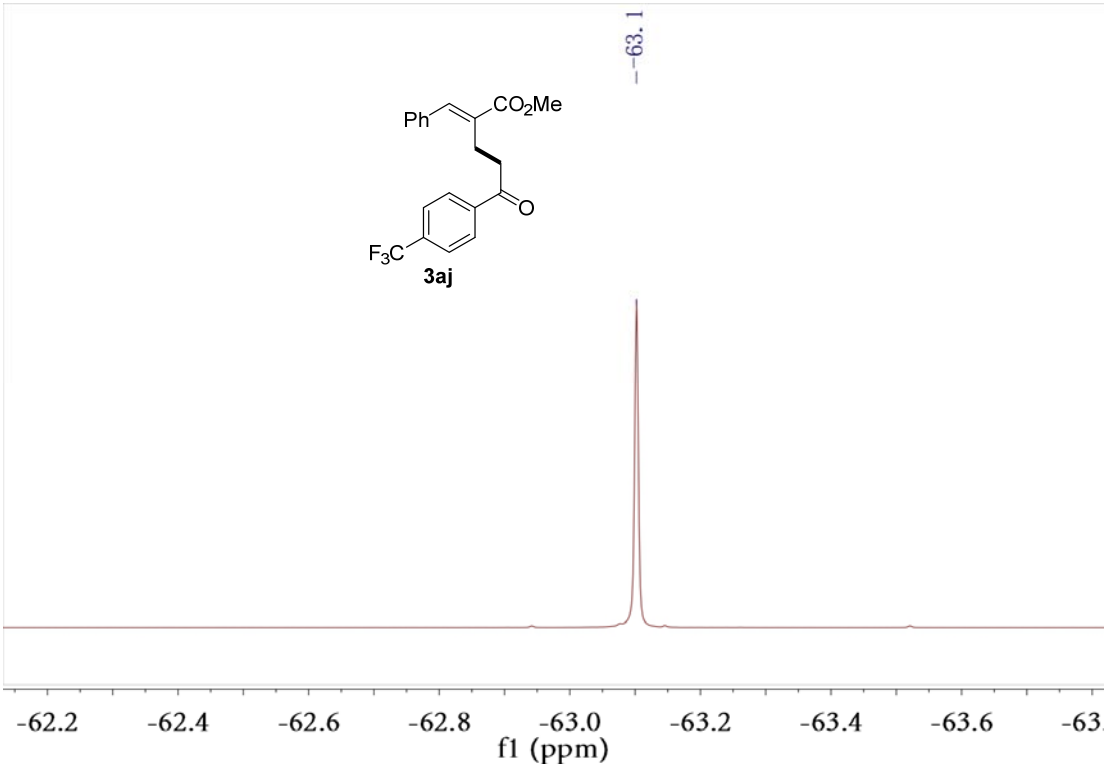
^{1}H NMR of **3aj** in $CDCl_3$



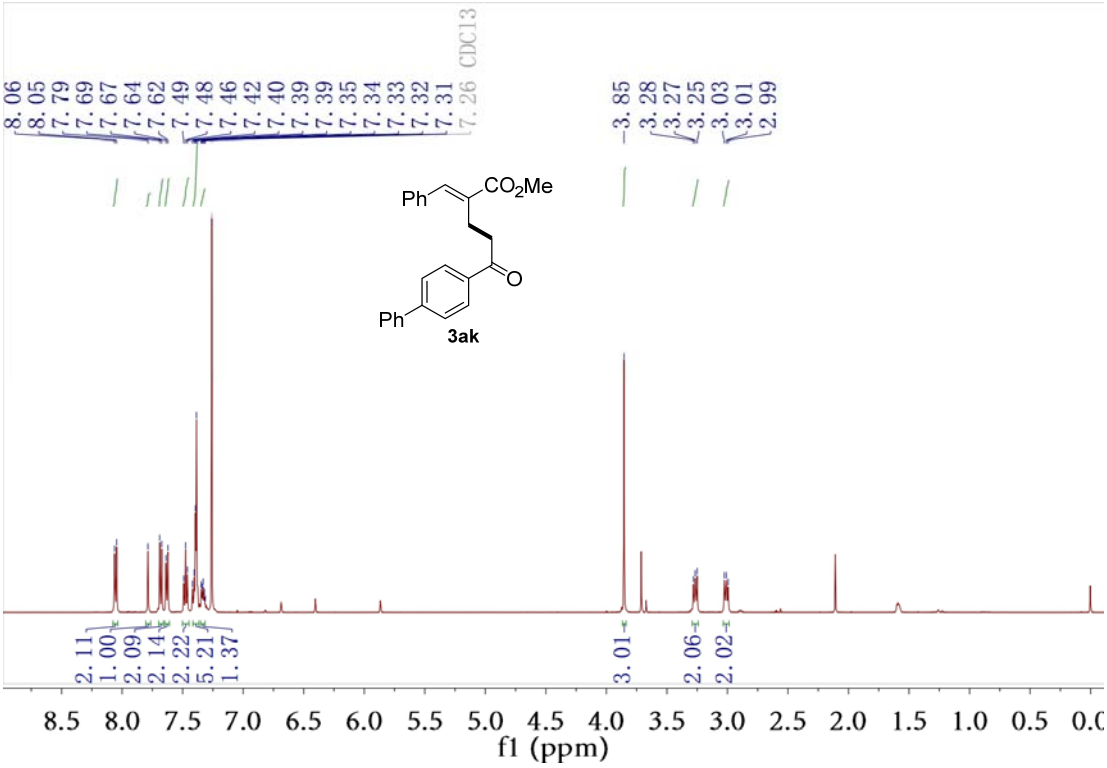
^{13}C NMR of **3aj** in $CDCl_3$



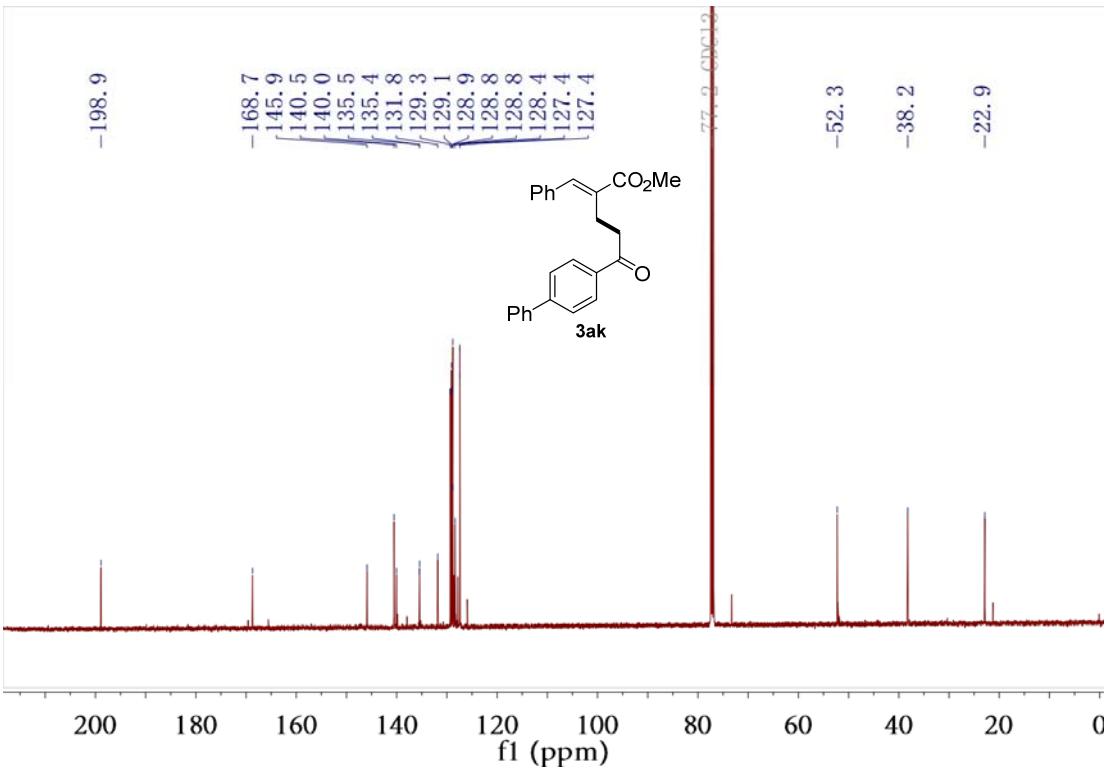
^{19}F NMR of **3aj** in $CDCl_3$



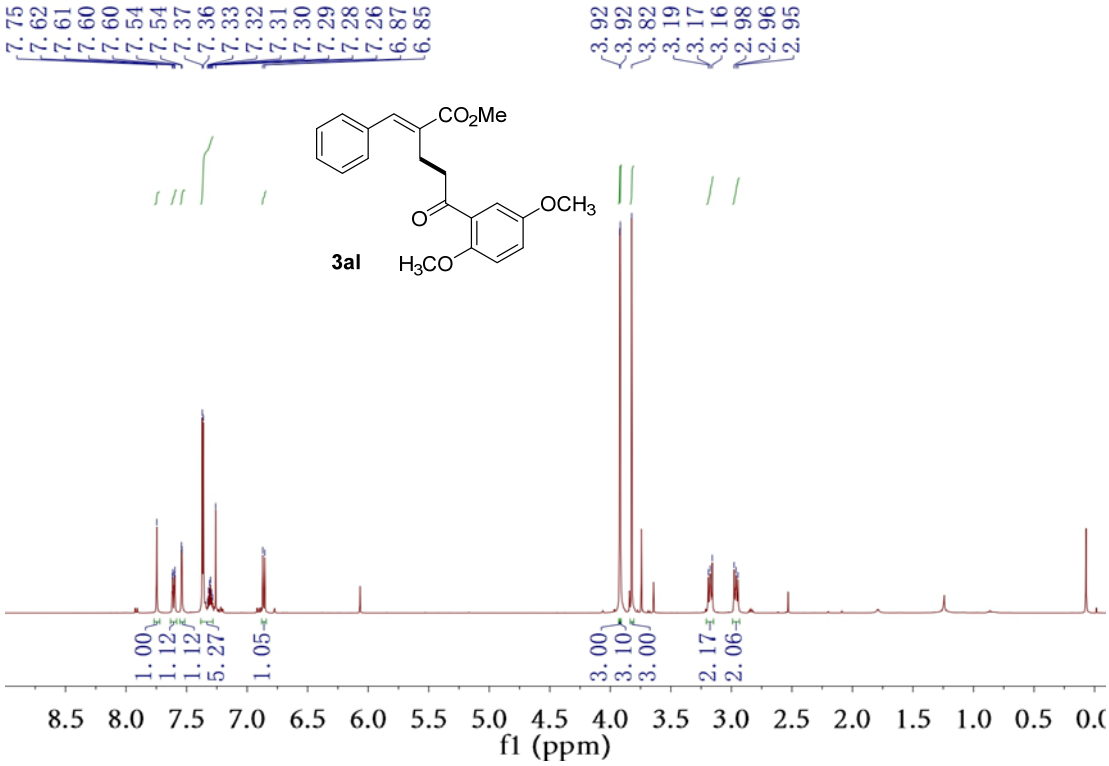
^{1}H NMR of **3ak** in $CDCl_3$



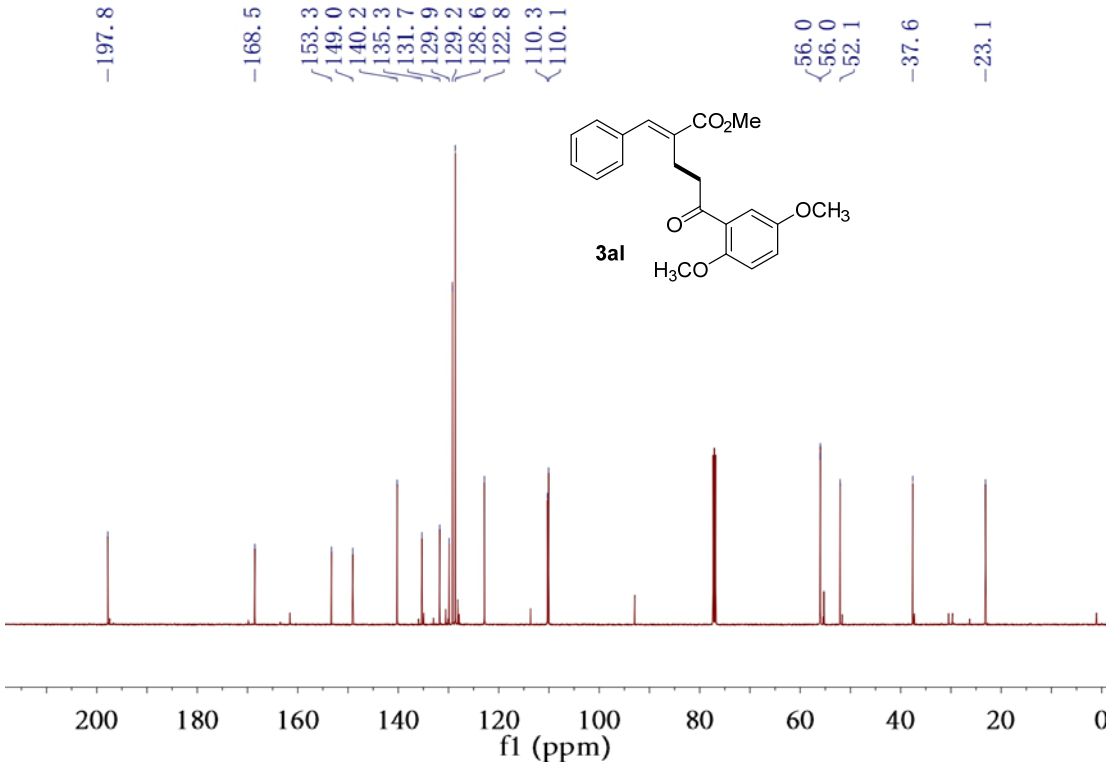
^{13}C NMR of **3ak** in $CDCl_3$



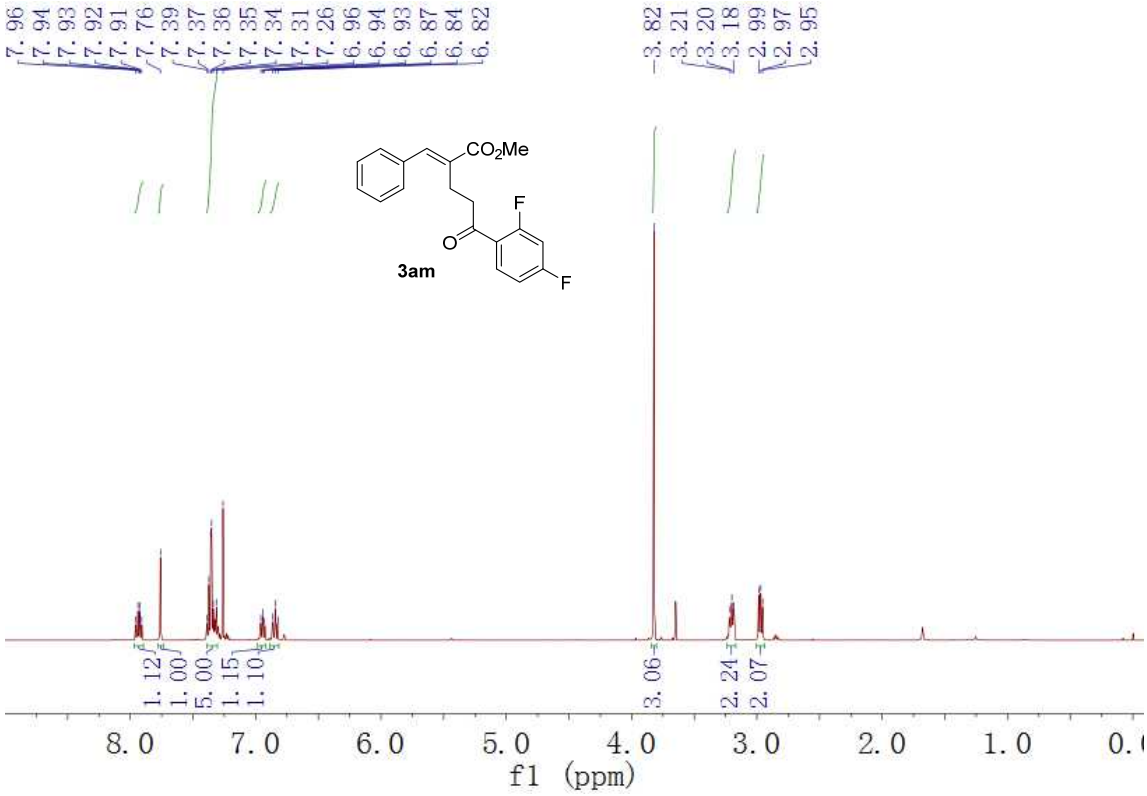
^{1}H NMR of **3al** in $CDCl_3$



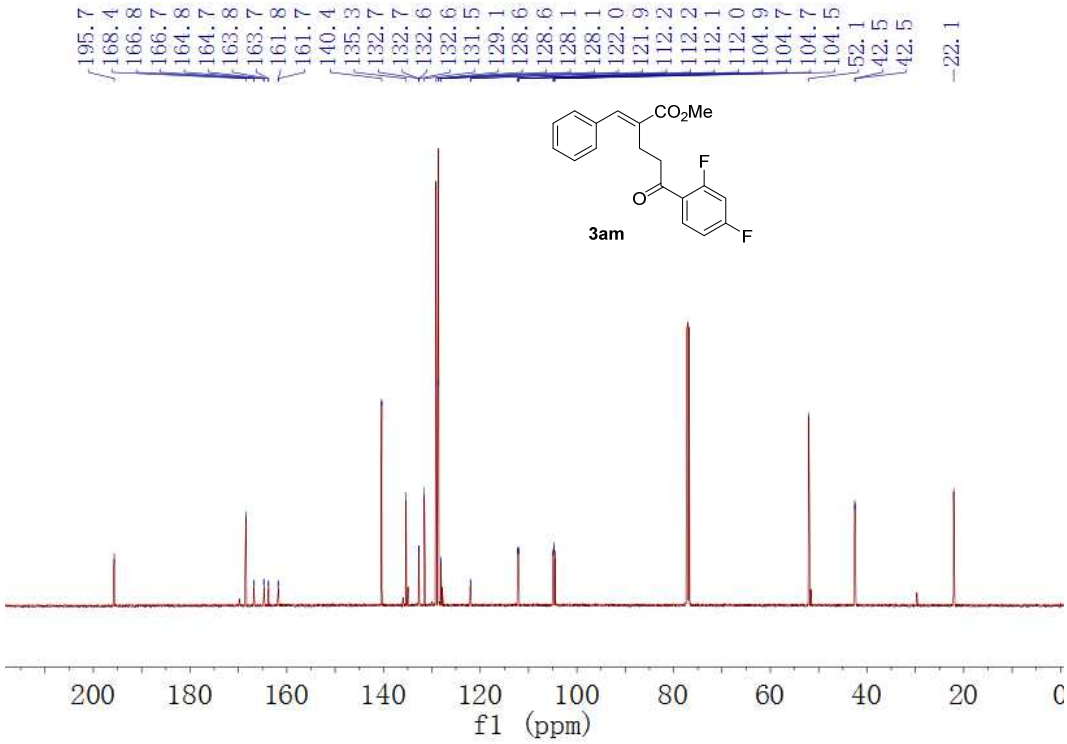
^{13}C NMR of **3al** in $CDCl_3$



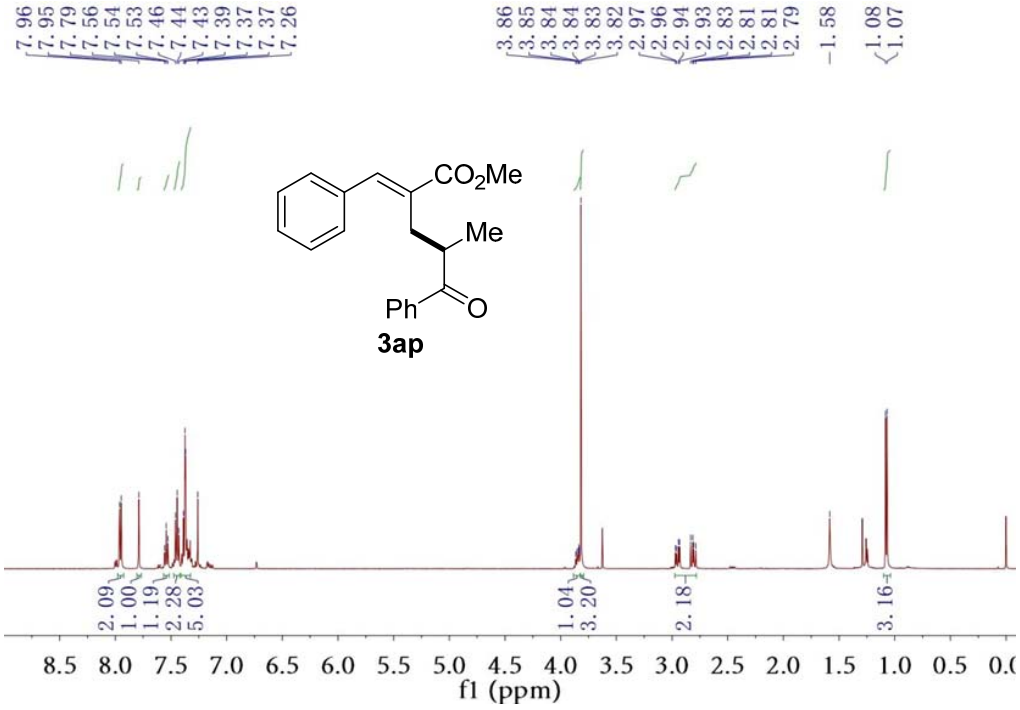
^{1}H NMR of **3am** in $CDCl_3$



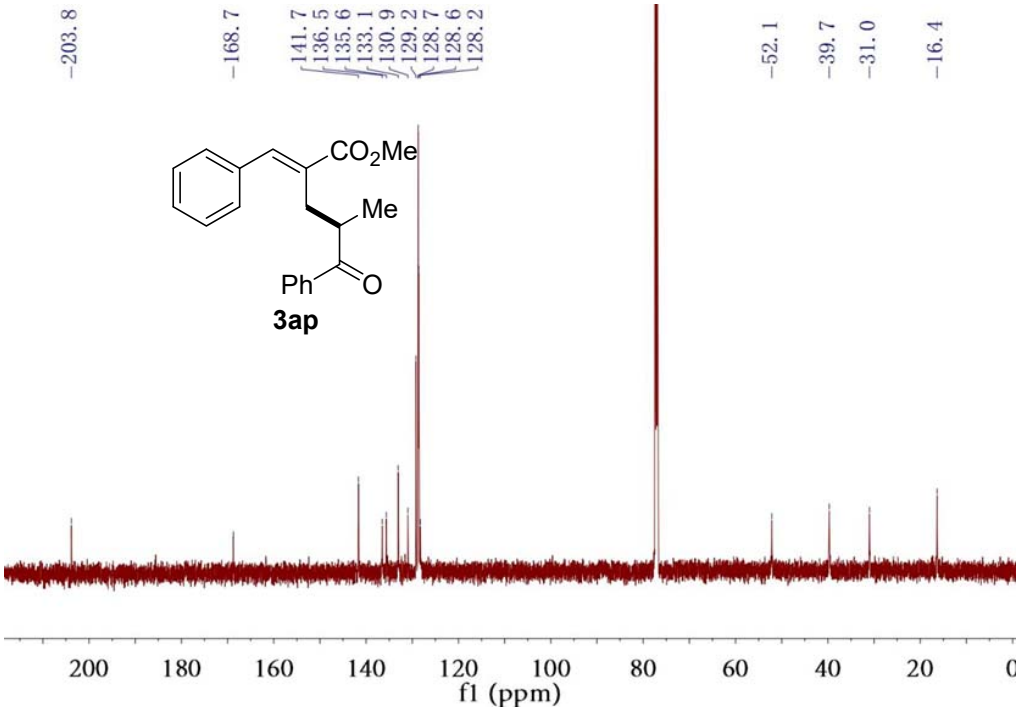
^{13}C NMR of **3am** in $CDCl_3$



^{1}H NMR of **3ap** in $CDCl_3$

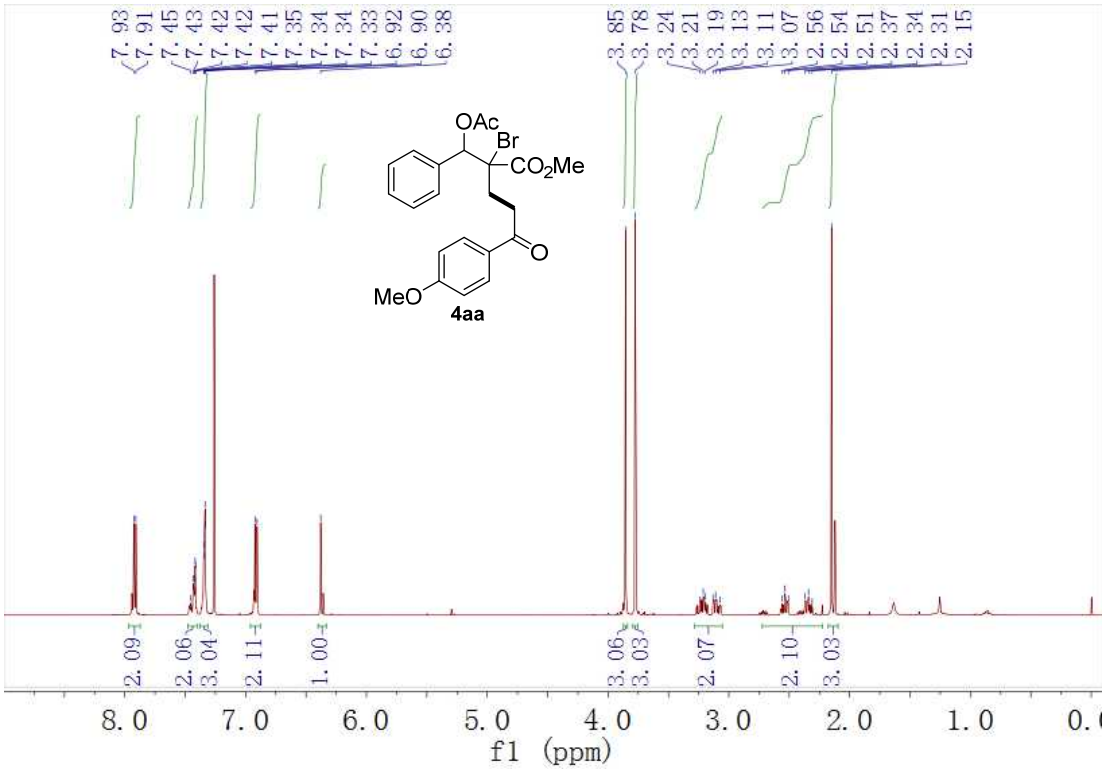


^{13}C NMR of **3ap** in $CDCl_3$

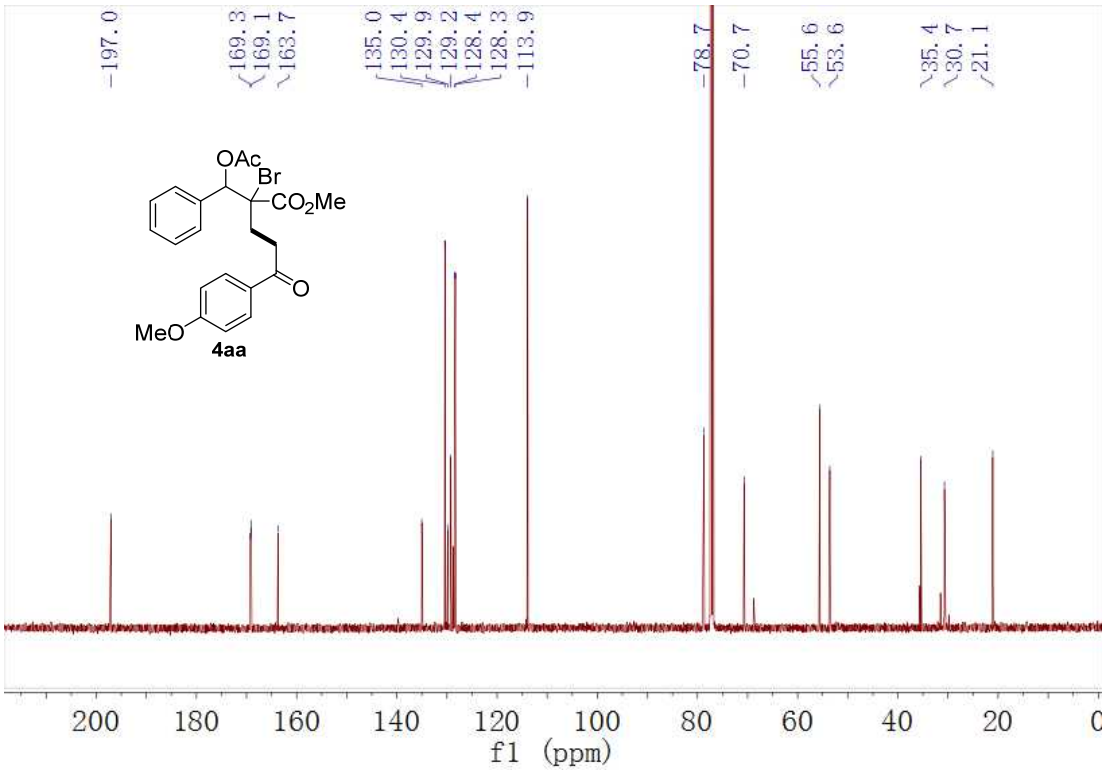


8. NMR spectra of bromoacylmethylated products (4aa-4oa and 4ab-4ao)

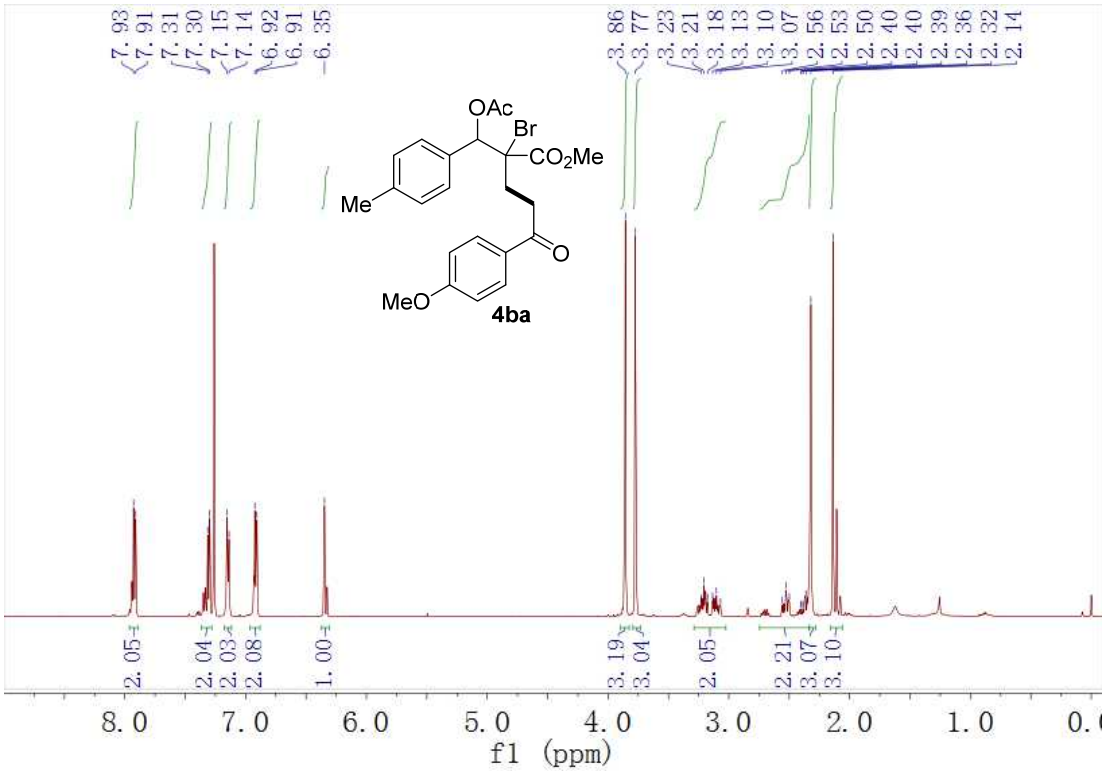
^{1}H NMR of **4aa** in $CDCl_3$



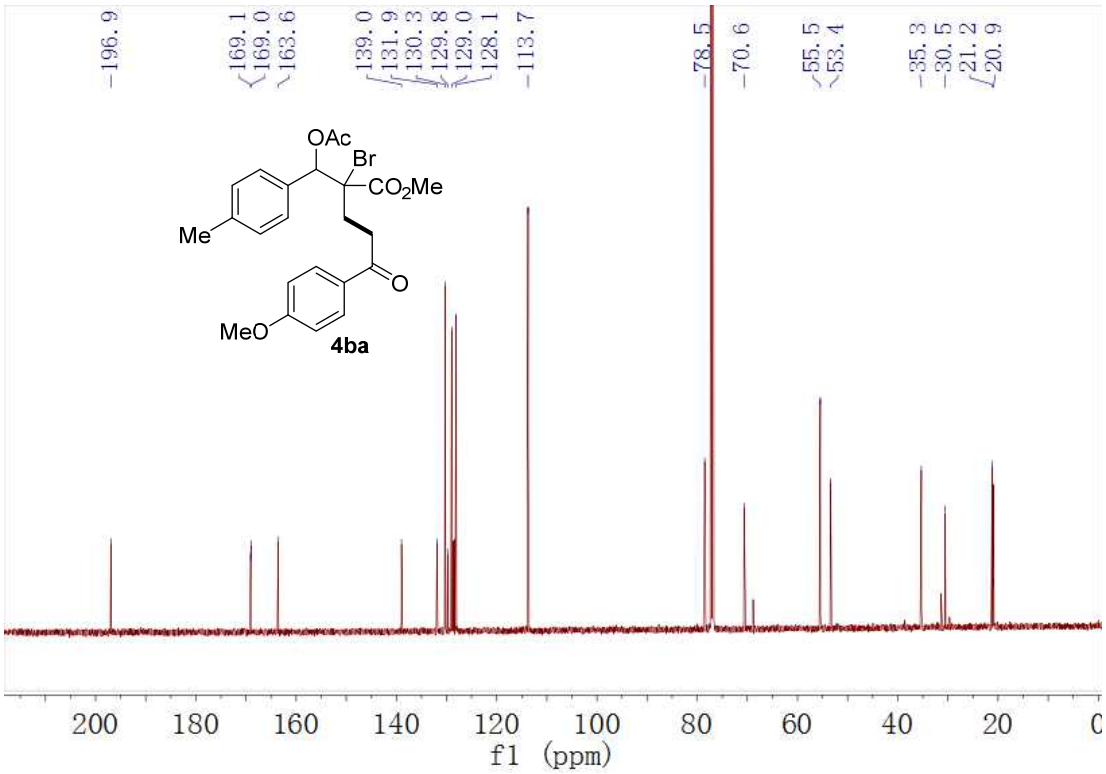
^{13}C NMR of **4aa** in $CDCl_3$



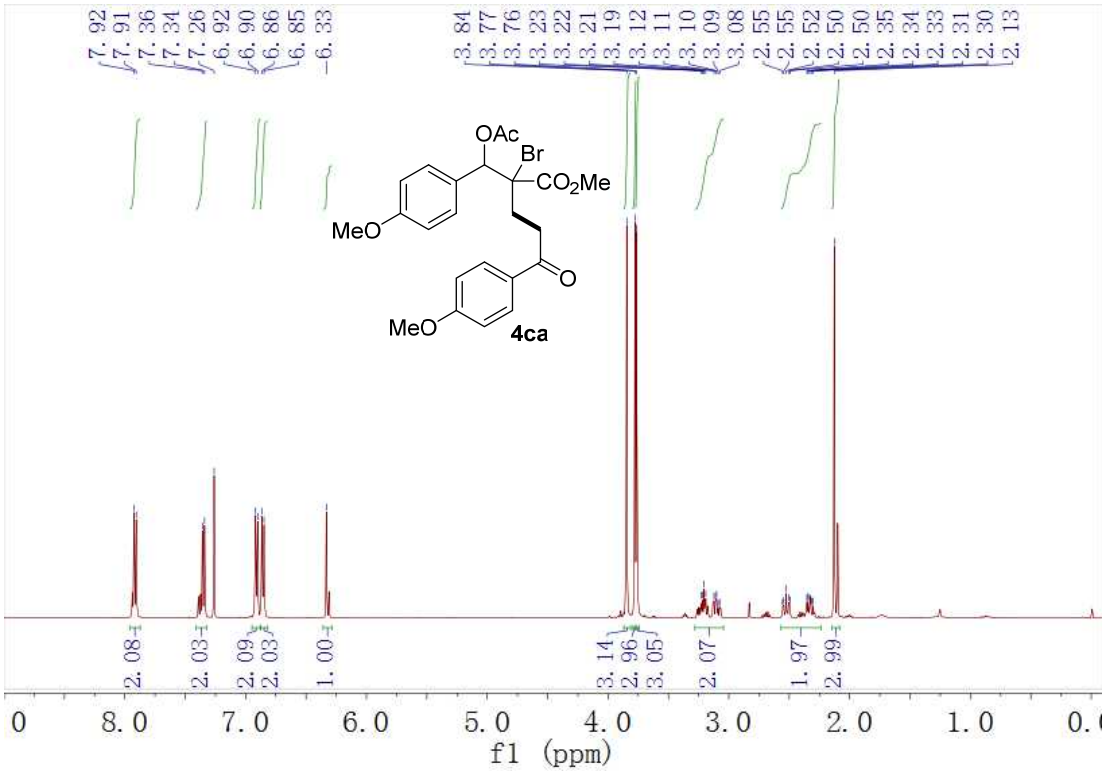
^{1}H NMR of **4ba** in $CDCl_3$



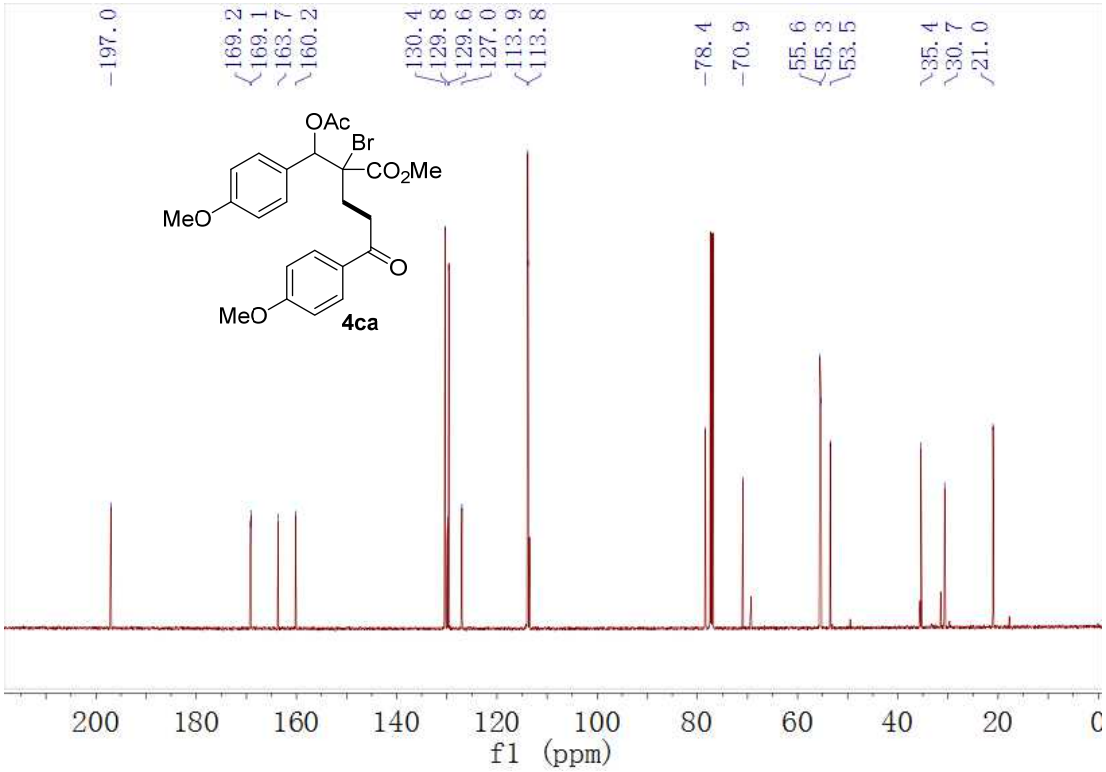
^{13}C NMR of **4ba** in $CDCl_3$



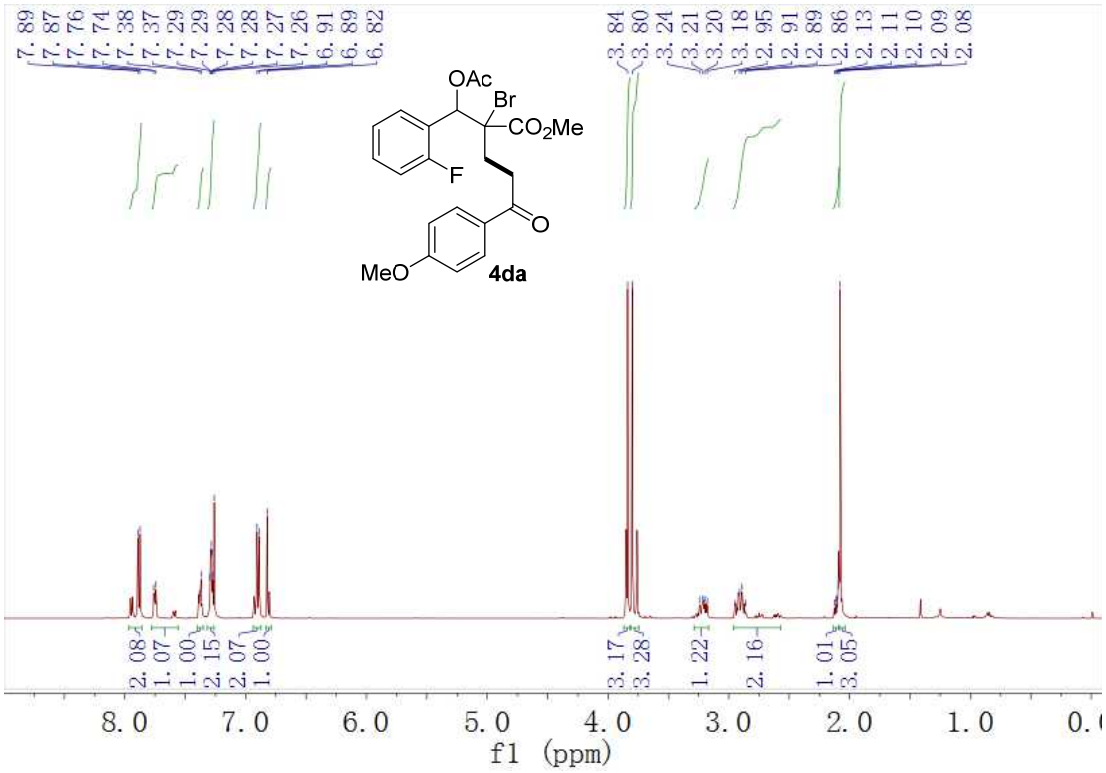
^{1}H NMR of **4ca** in $CDCl_3$



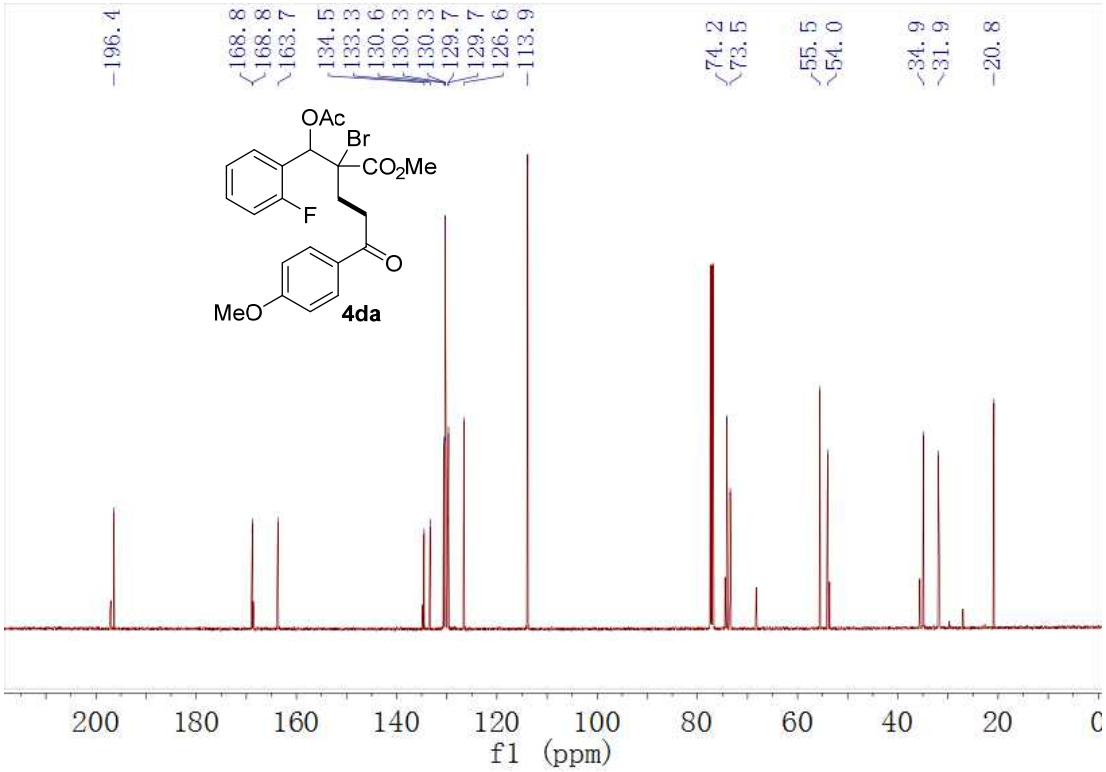
^{13}C NMR of **4ca** in $CDCl_3$



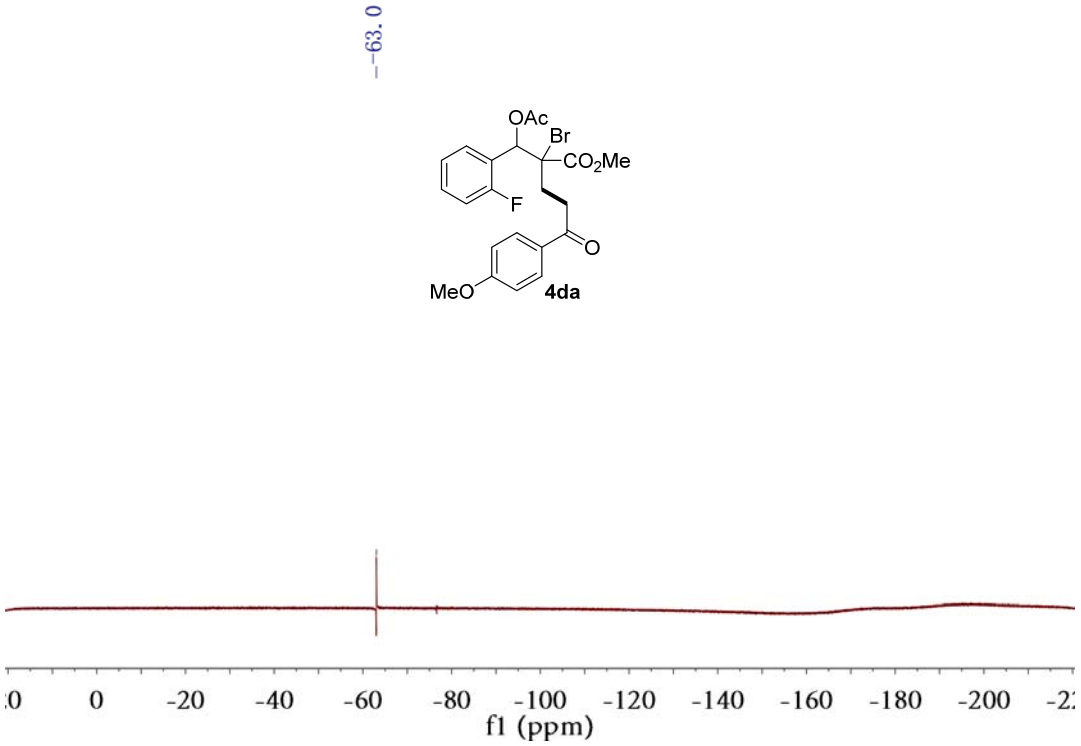
^{1}H NMR of **4da** in $CDCl_3$



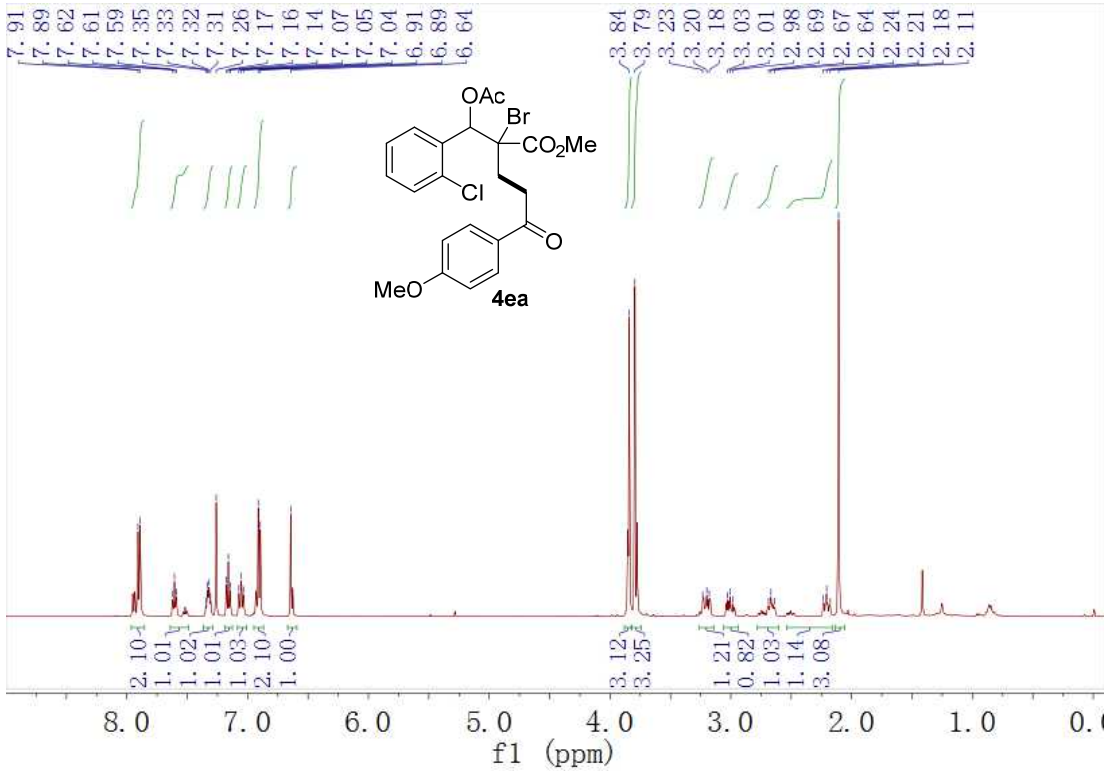
^{13}C NMR of **4da** in $CDCl_3$



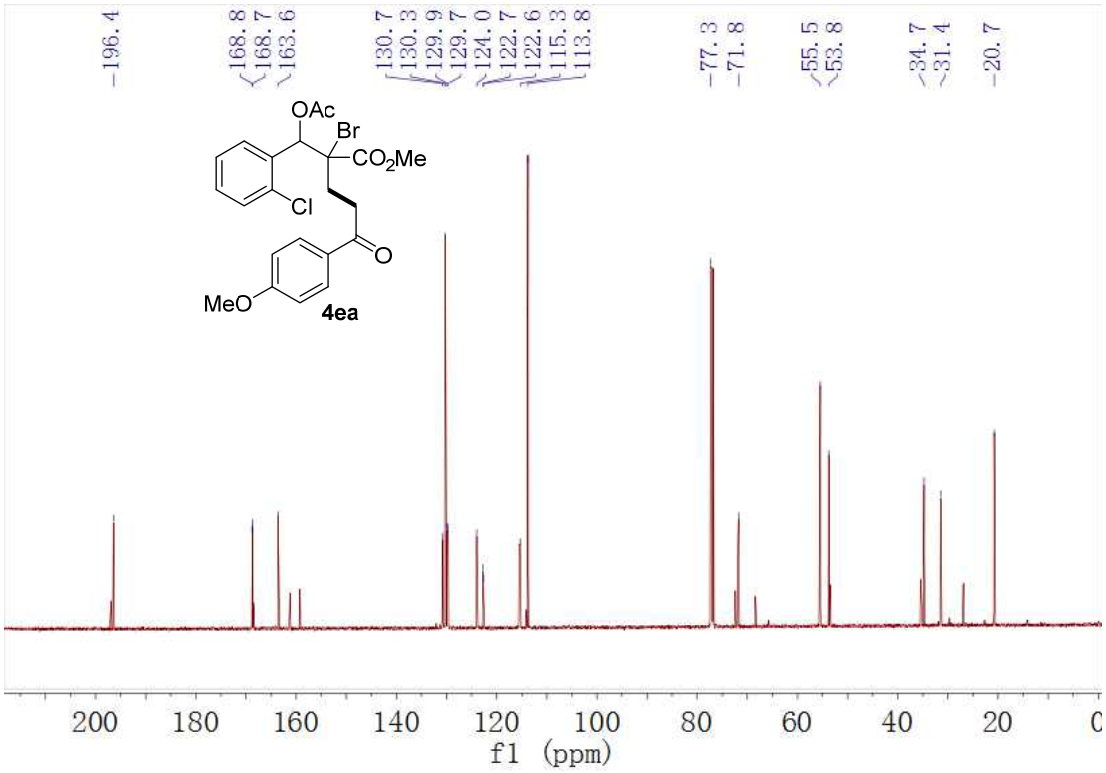
^{19}F NMR of **4da** in $CDCl_3$



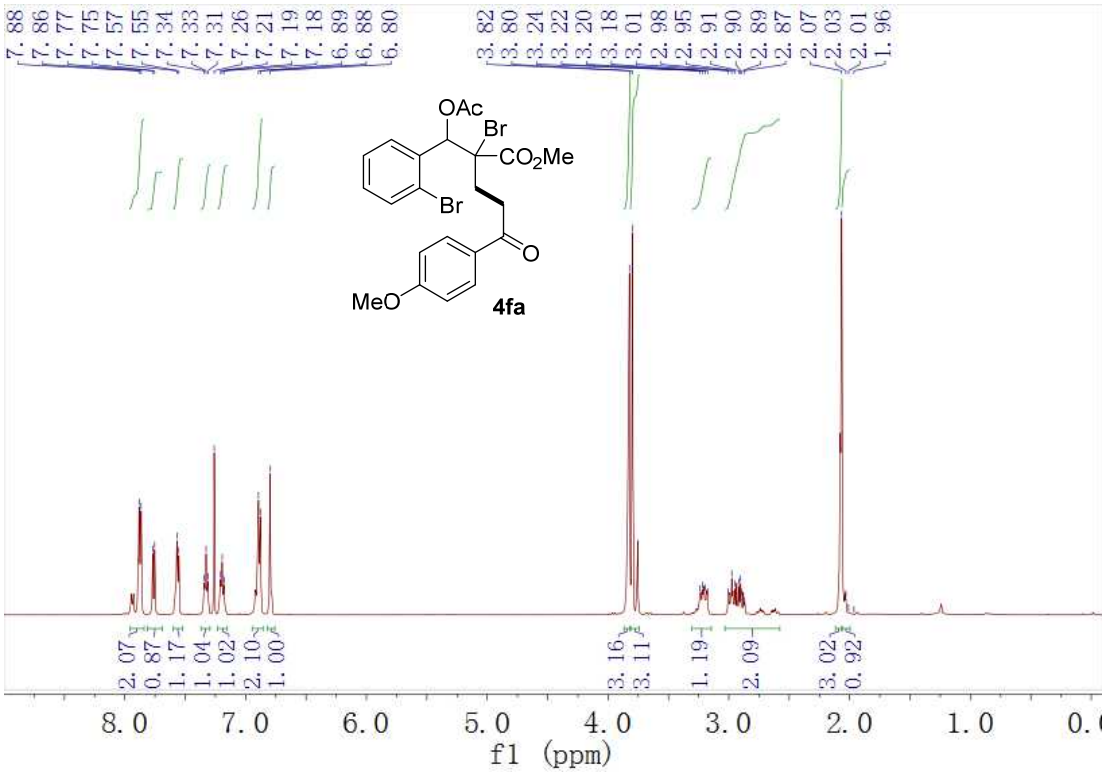
^{1}H NMR of **4ea** in $CDCl_3$



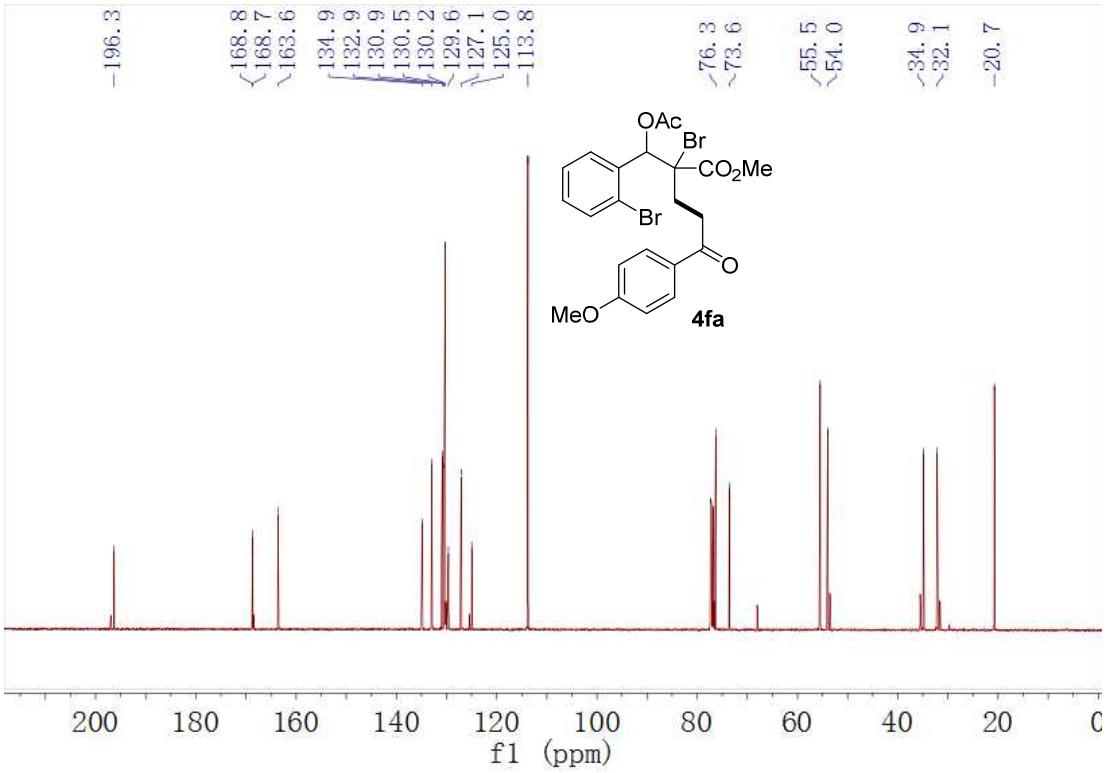
^{13}C NMR of **4ea** in $CDCl_3$



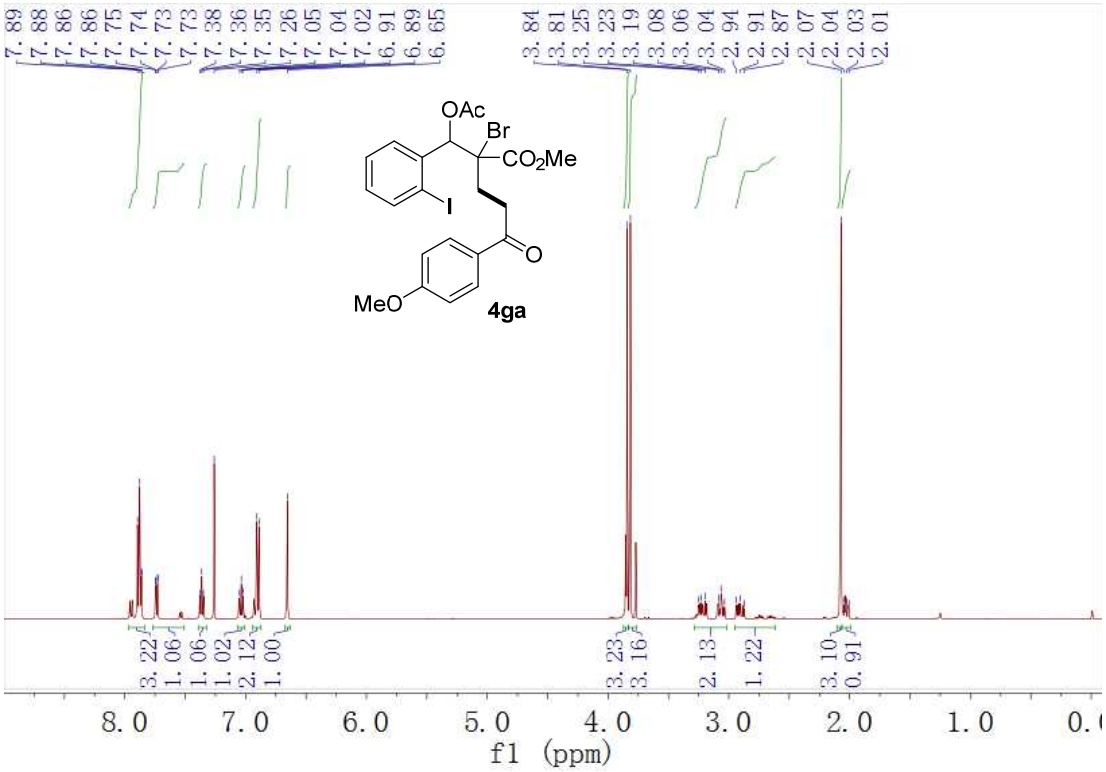
^{1}H NMR of **4fa** in $CDCl_3$



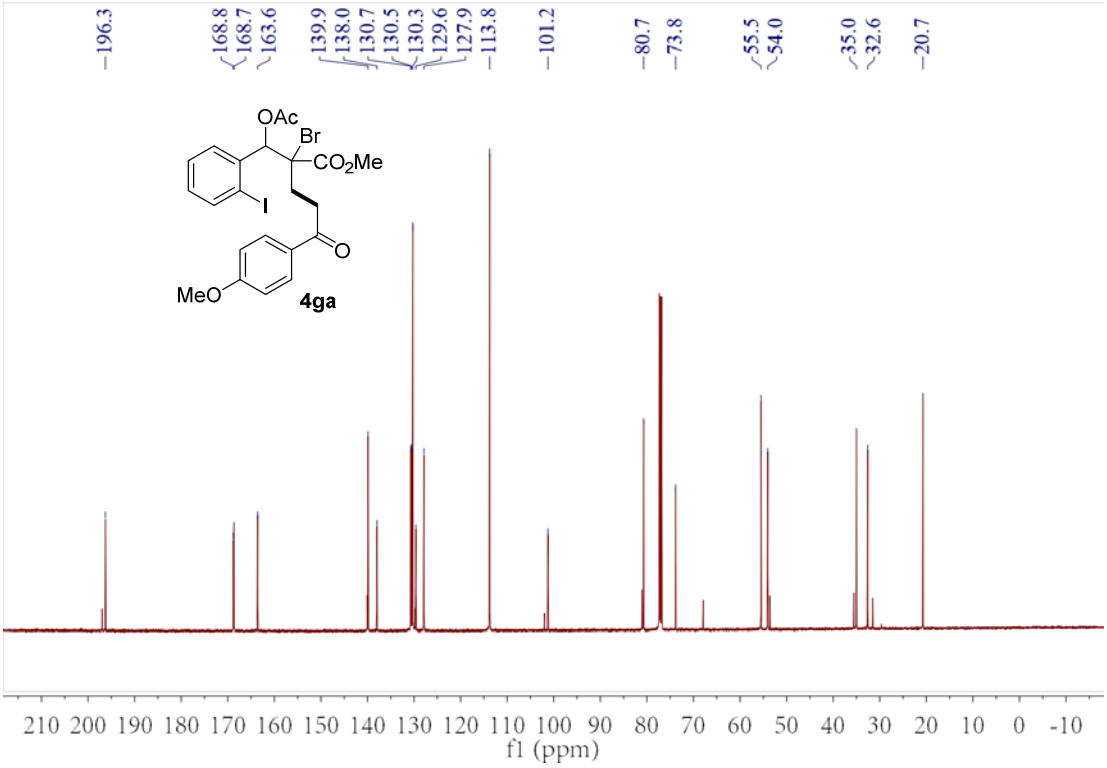
^{13}C NMR of **4fa** in $CDCl_3$



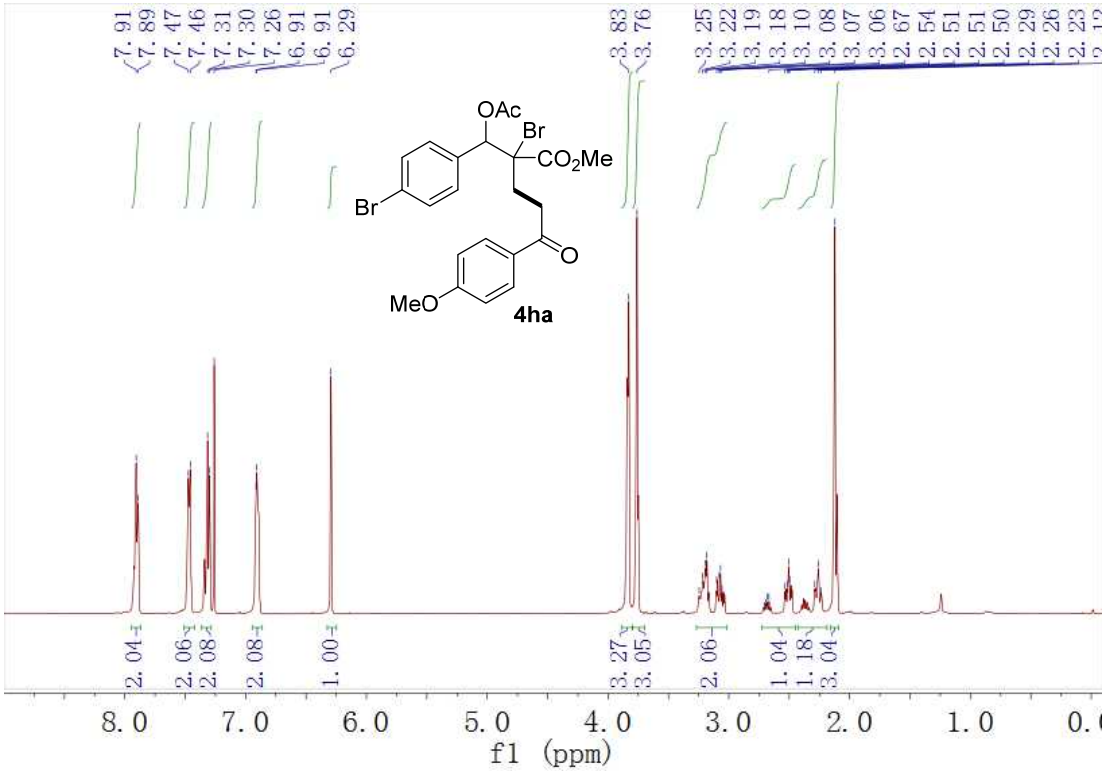
^{1}H NMR of **4ga** in $CDCl_3$



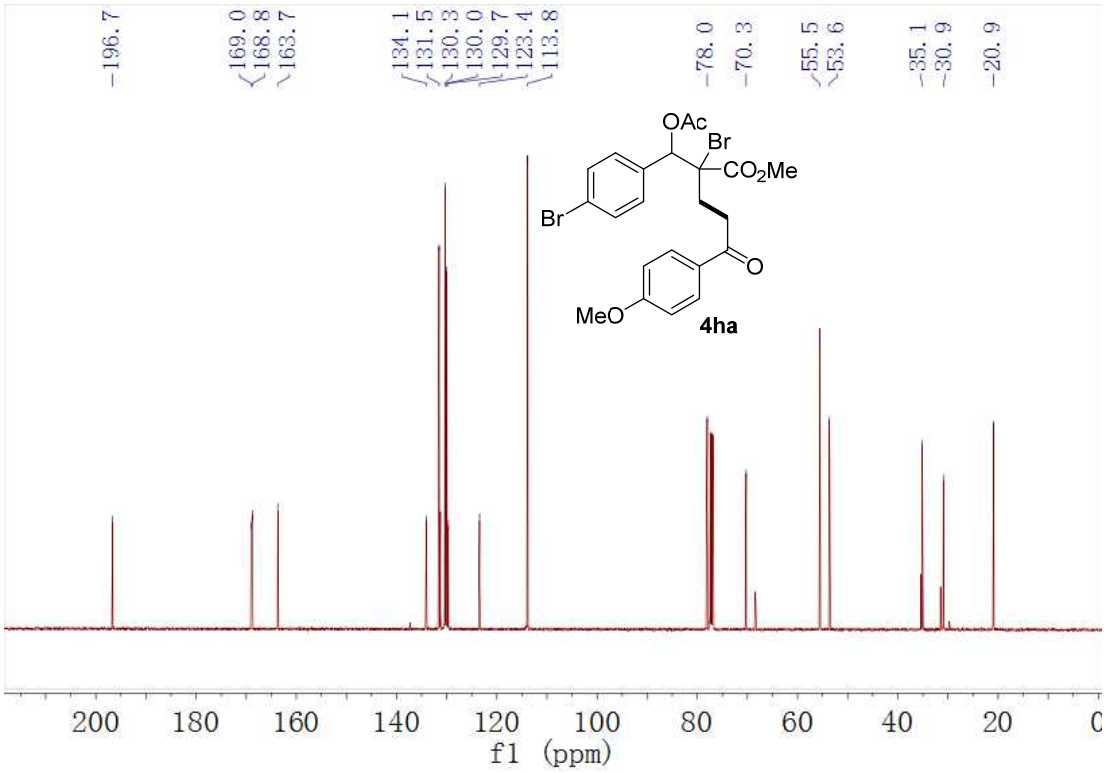
^{13}C NMR of **4ga** in $CDCl_3$



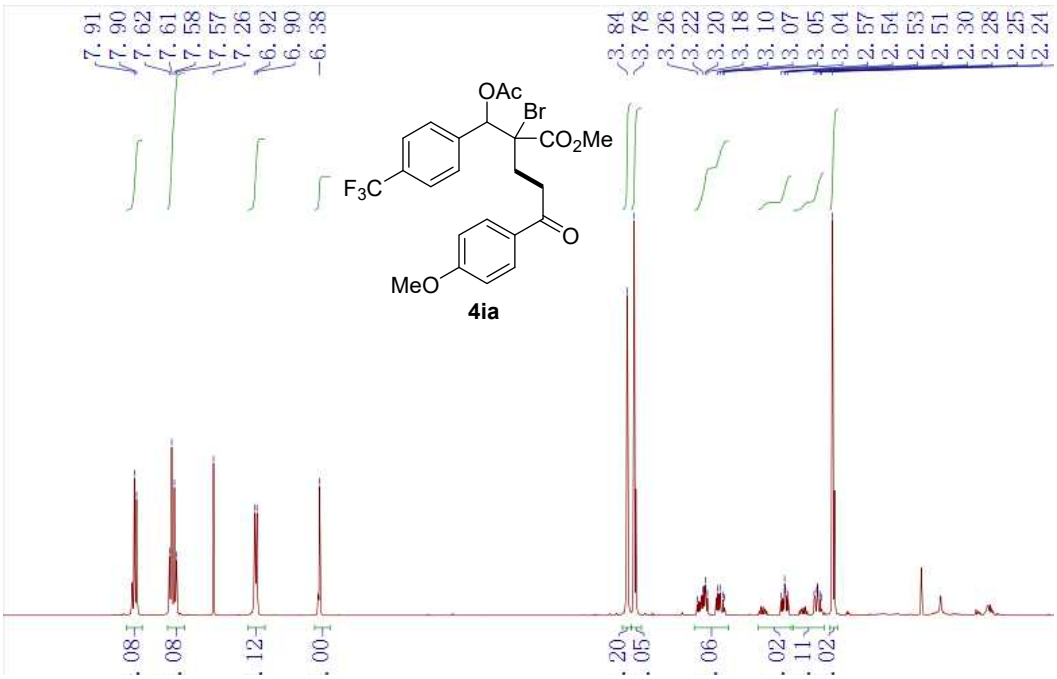
^{1}H NMR of **4ha** in $CDCl_3$



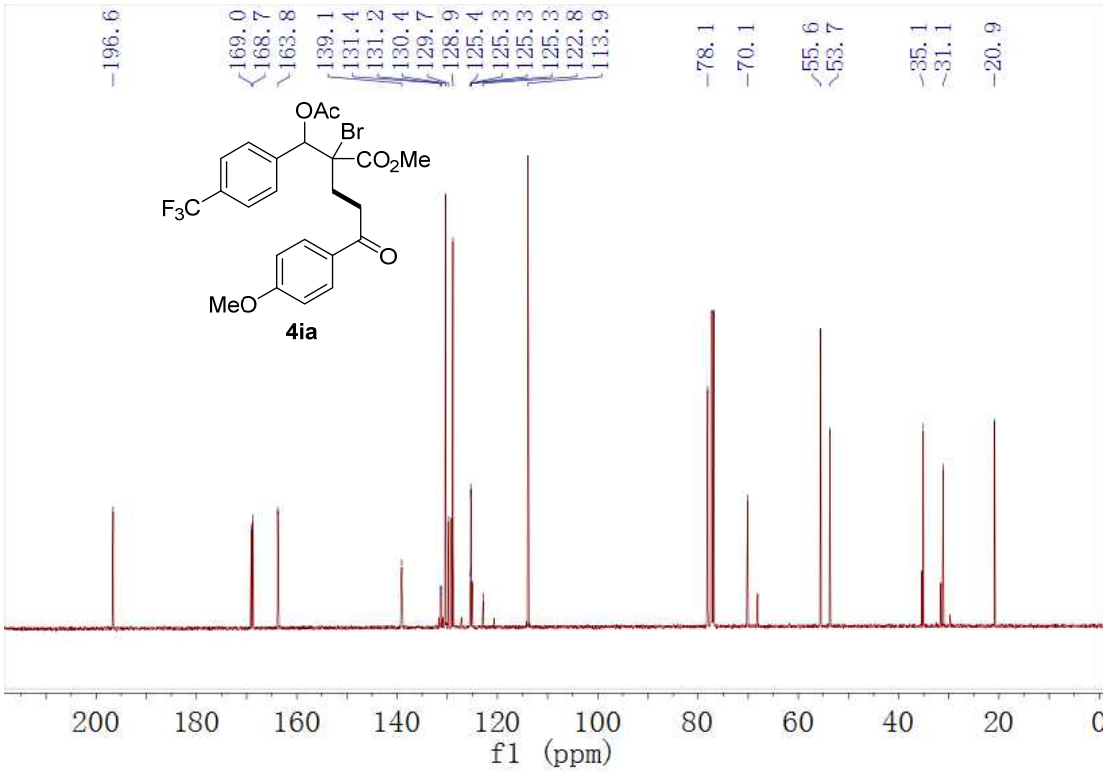
^{13}C NMR of **4ha** in $CDCl_3$



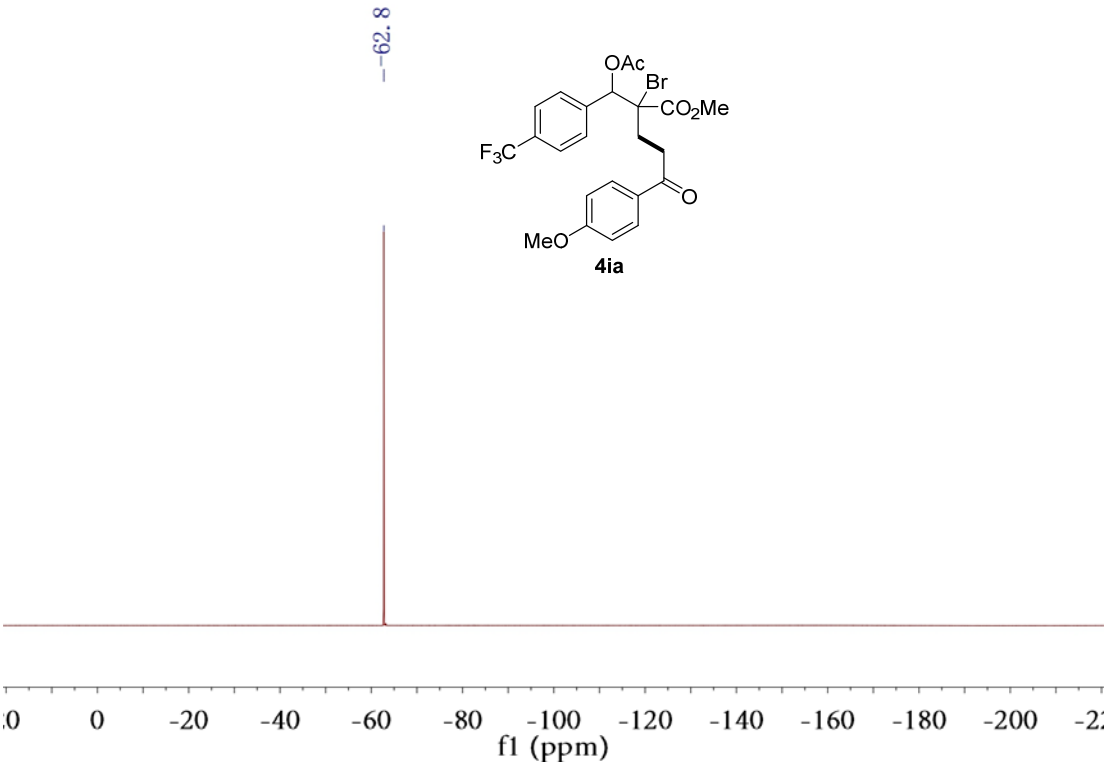
^{1}H NMR of **4ia** in $CDCl_3$



^{13}C NMR of **4ia** in $CDCl_3$



^{19}F NMR of **4ia** in $CDCl_3$



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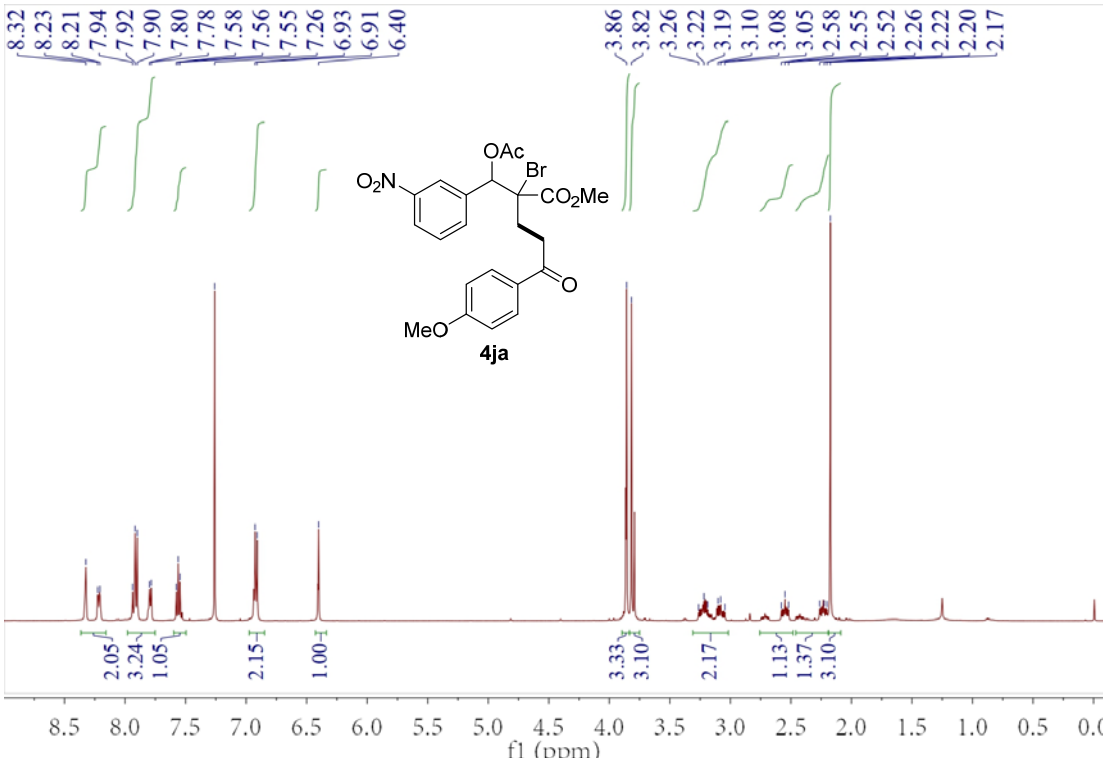

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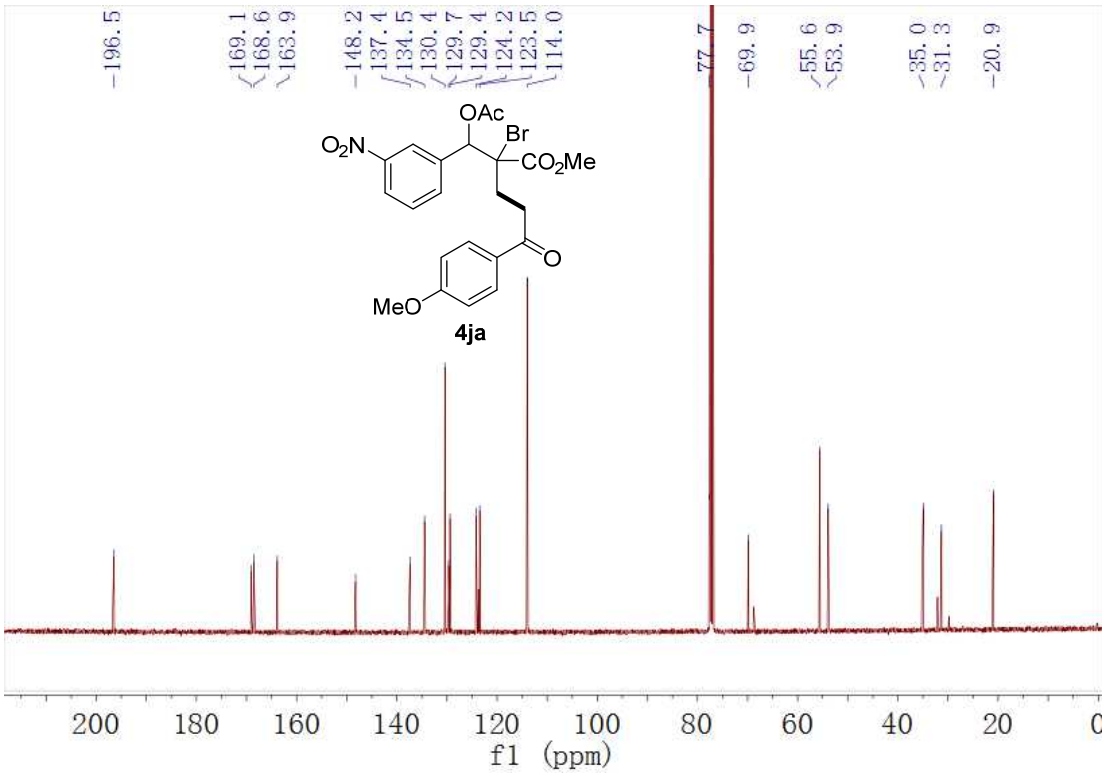
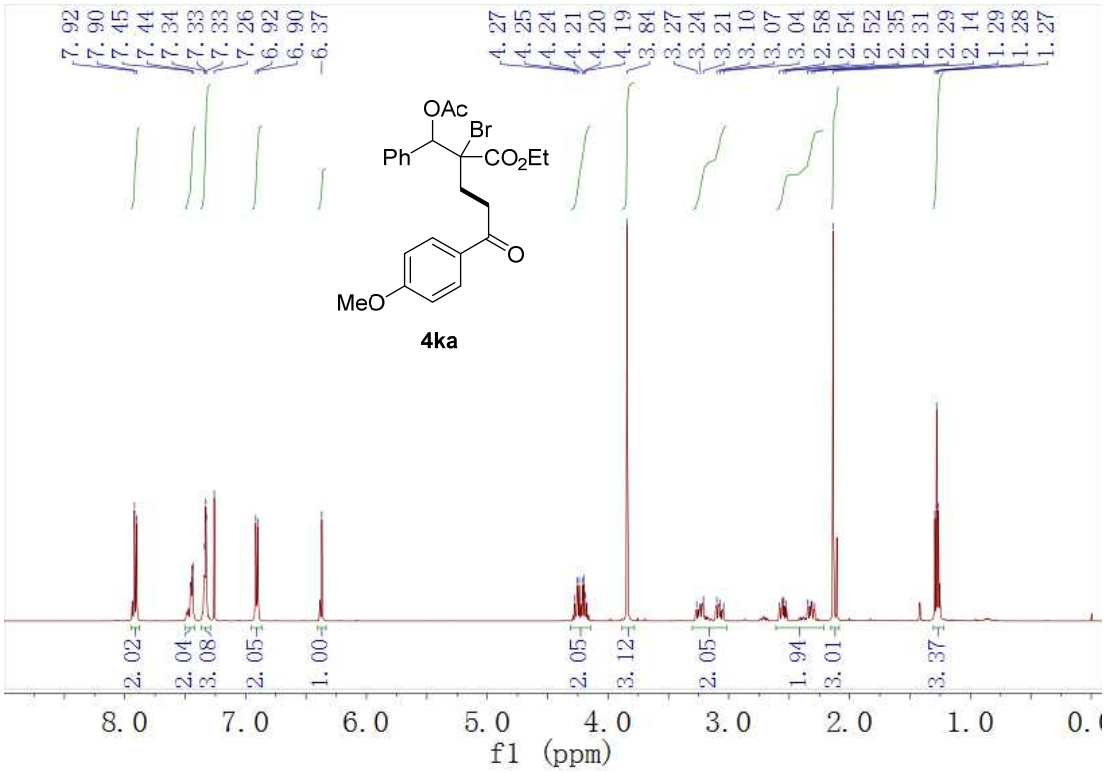


^{1}H NMR of **4ka** in $CDCl_3$



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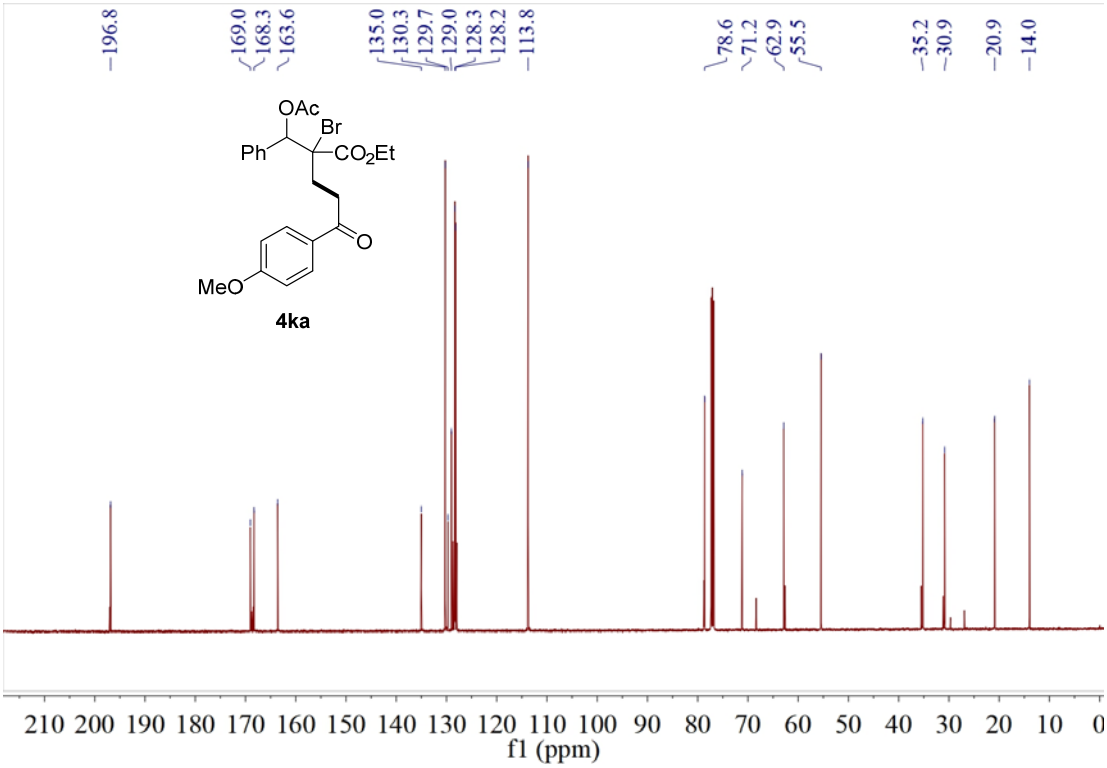

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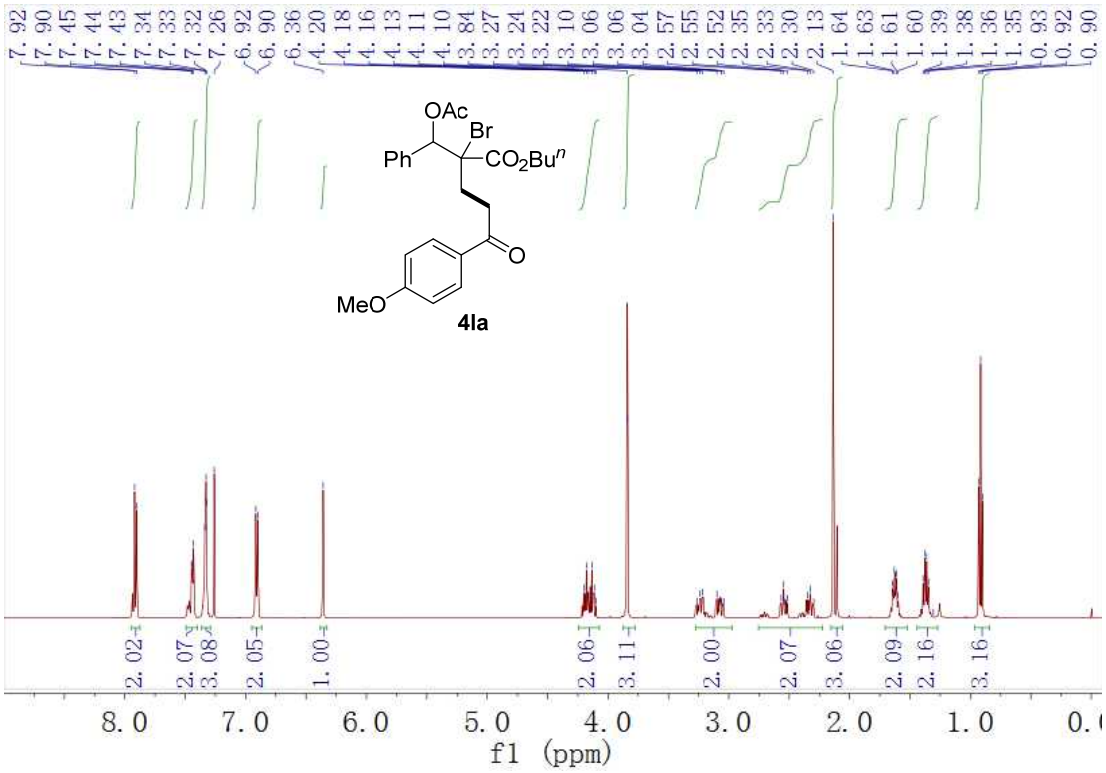

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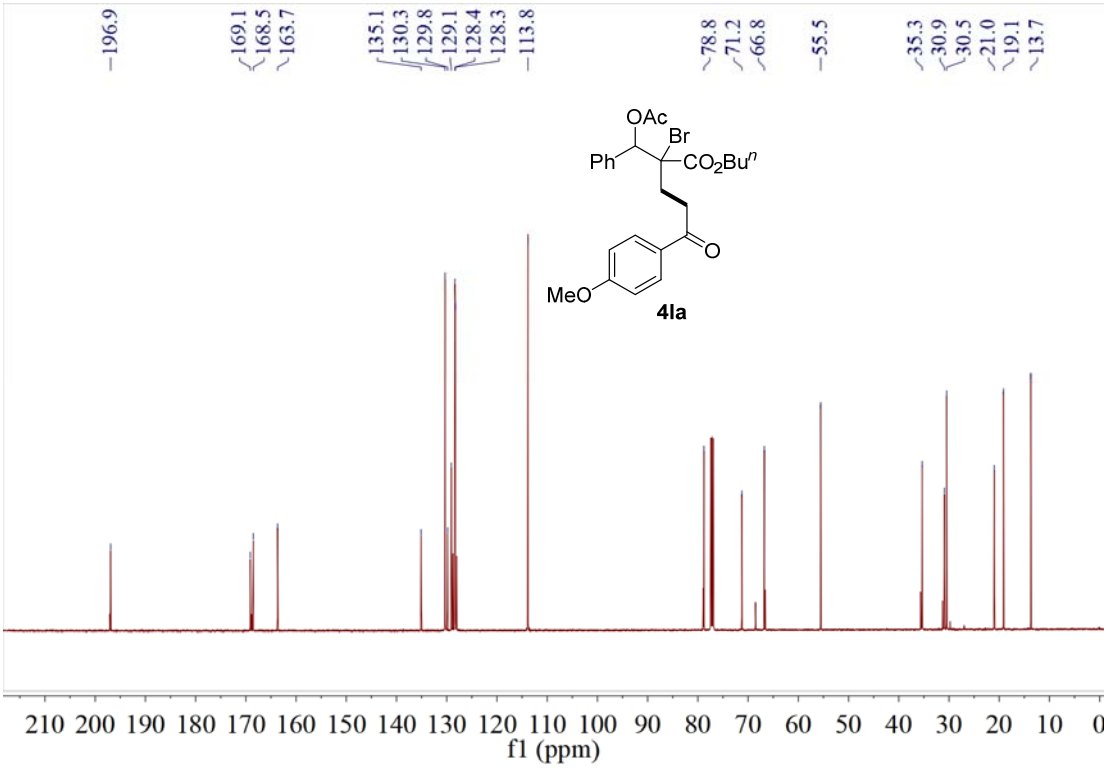
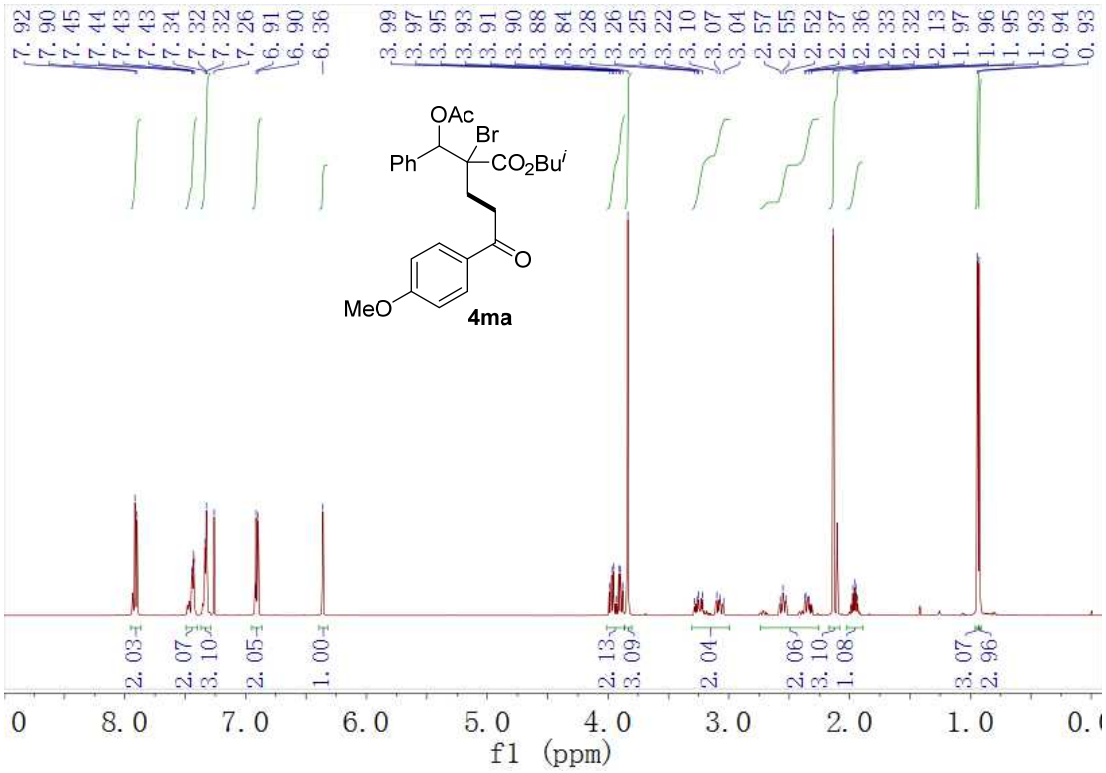
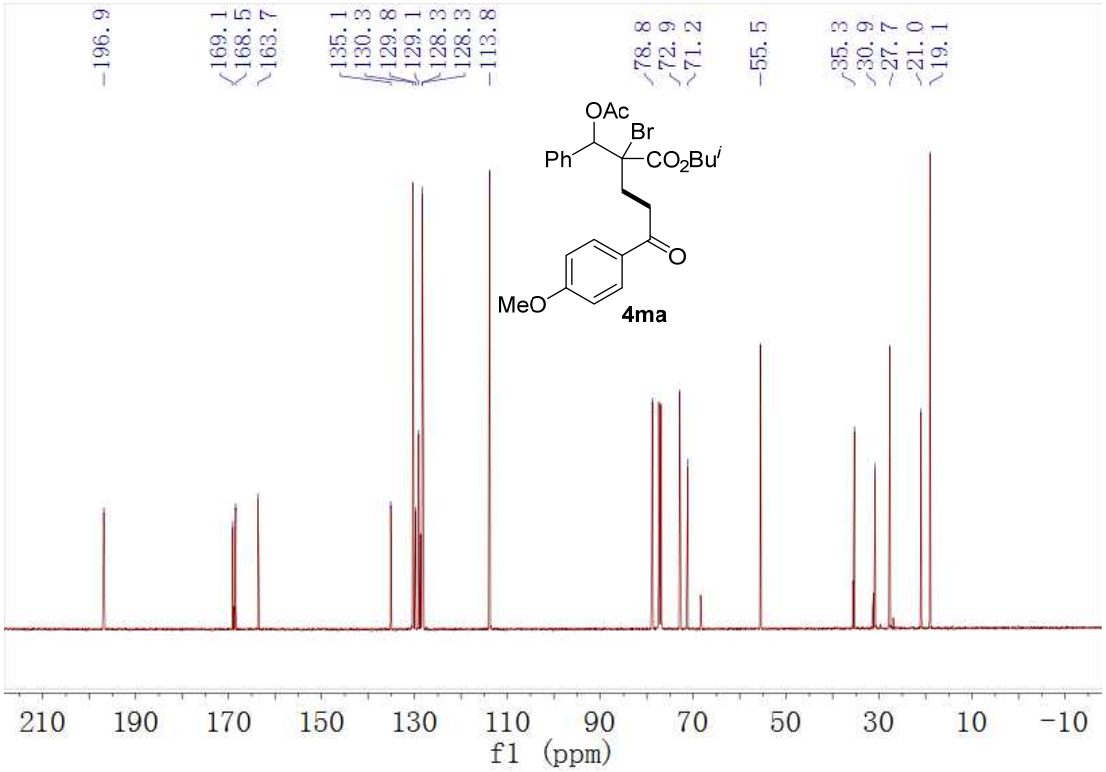


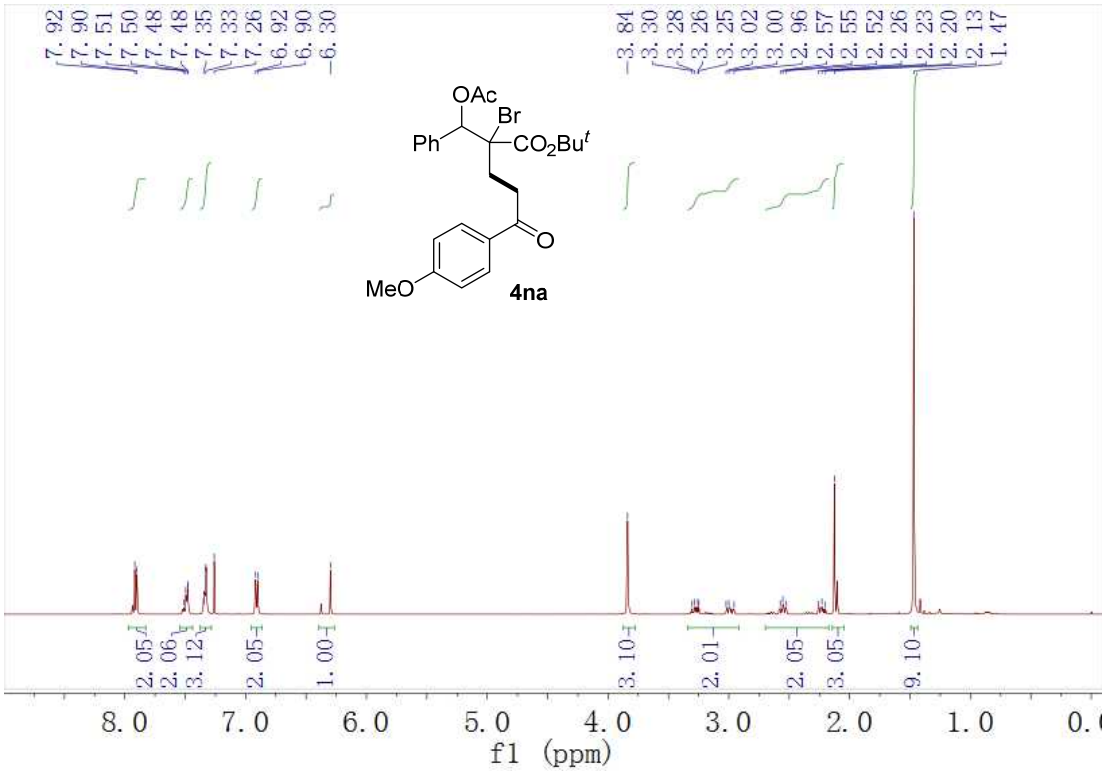
^{1}H NMR of **4ma** in $CDCl_3$



^{13}C NMR of **4ma** in $CDCl_3$



^{1}H NMR of **4na** in $CDCl_3$



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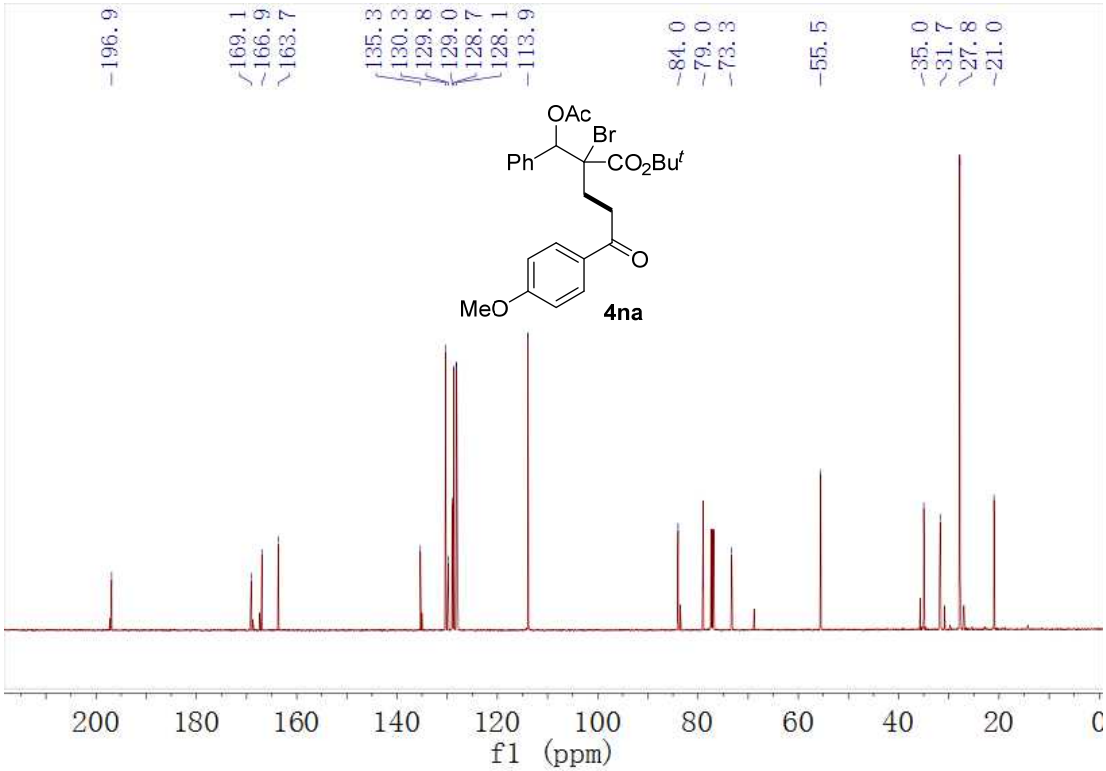
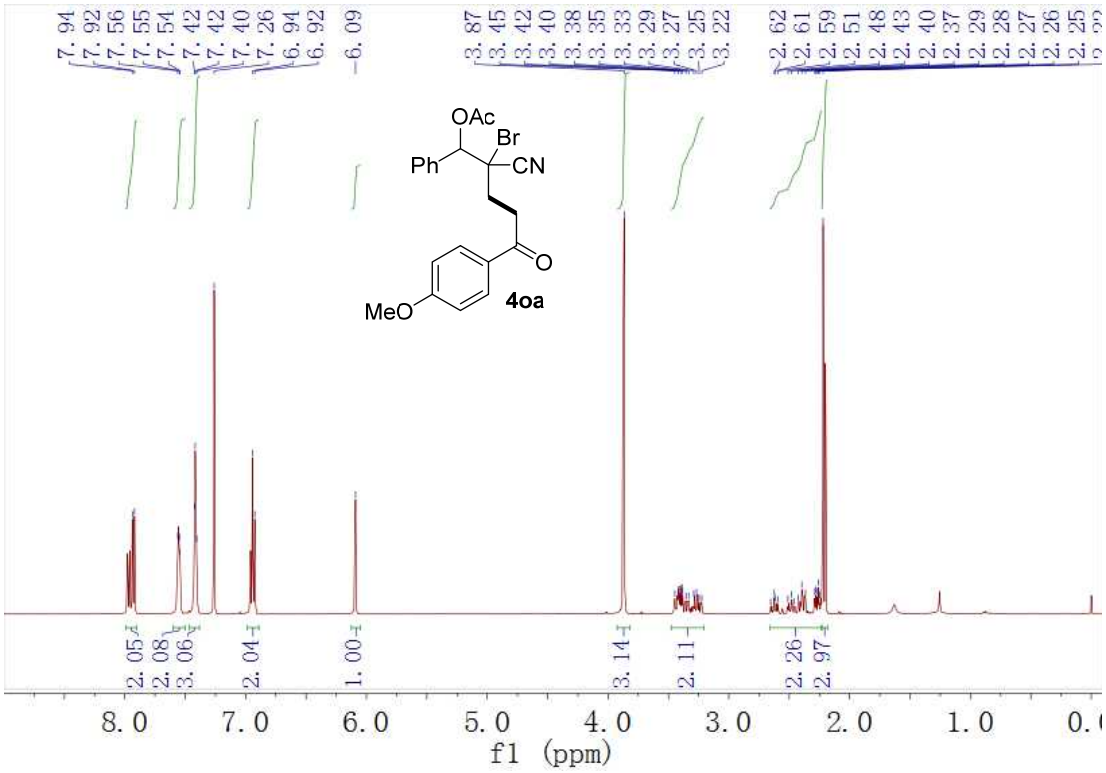


^{1}H NMR of **4oa** in $CDCl_3$



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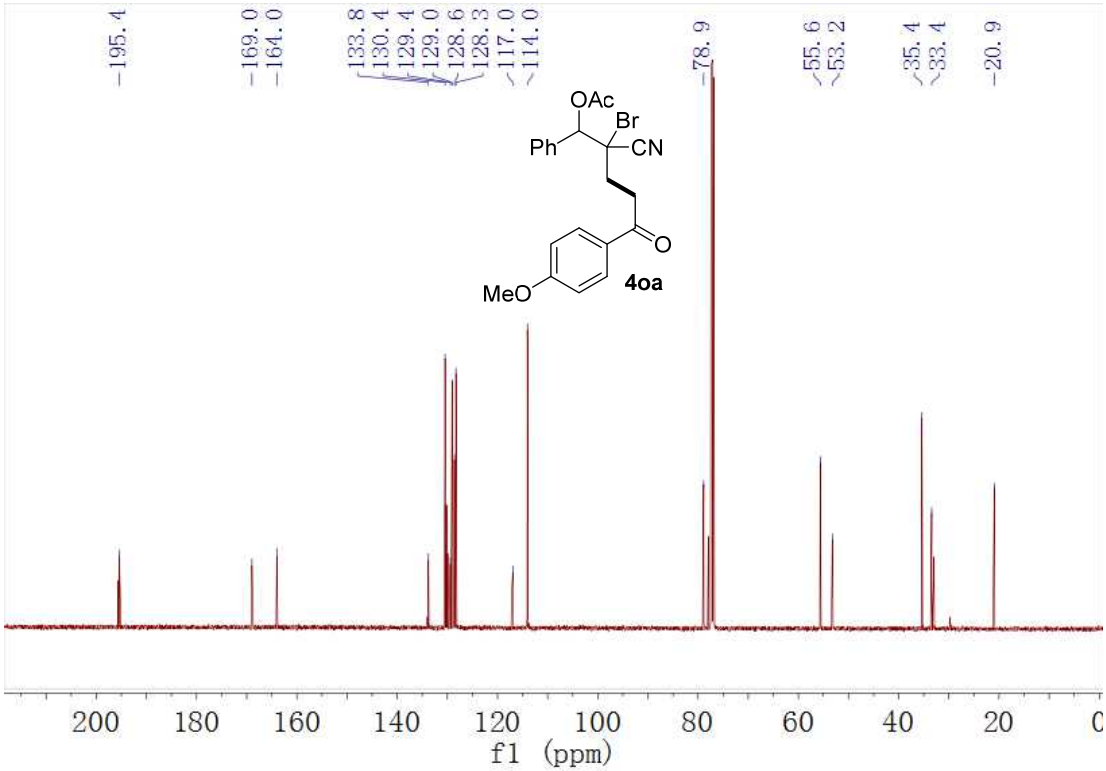
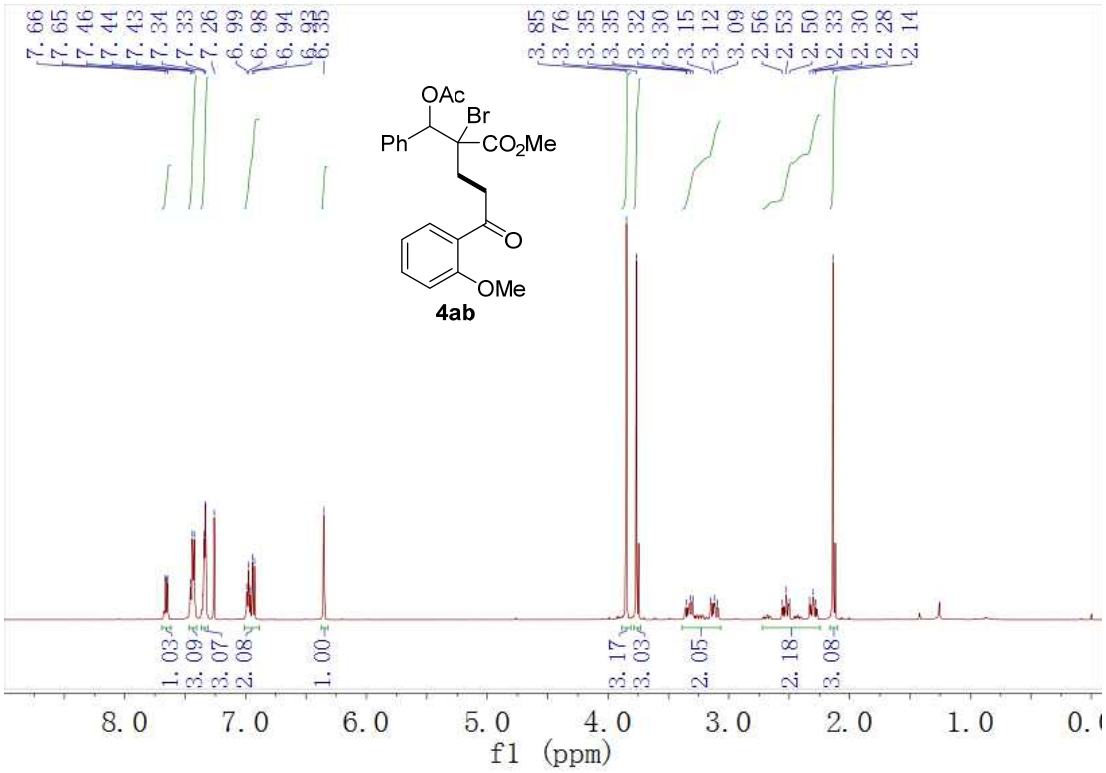
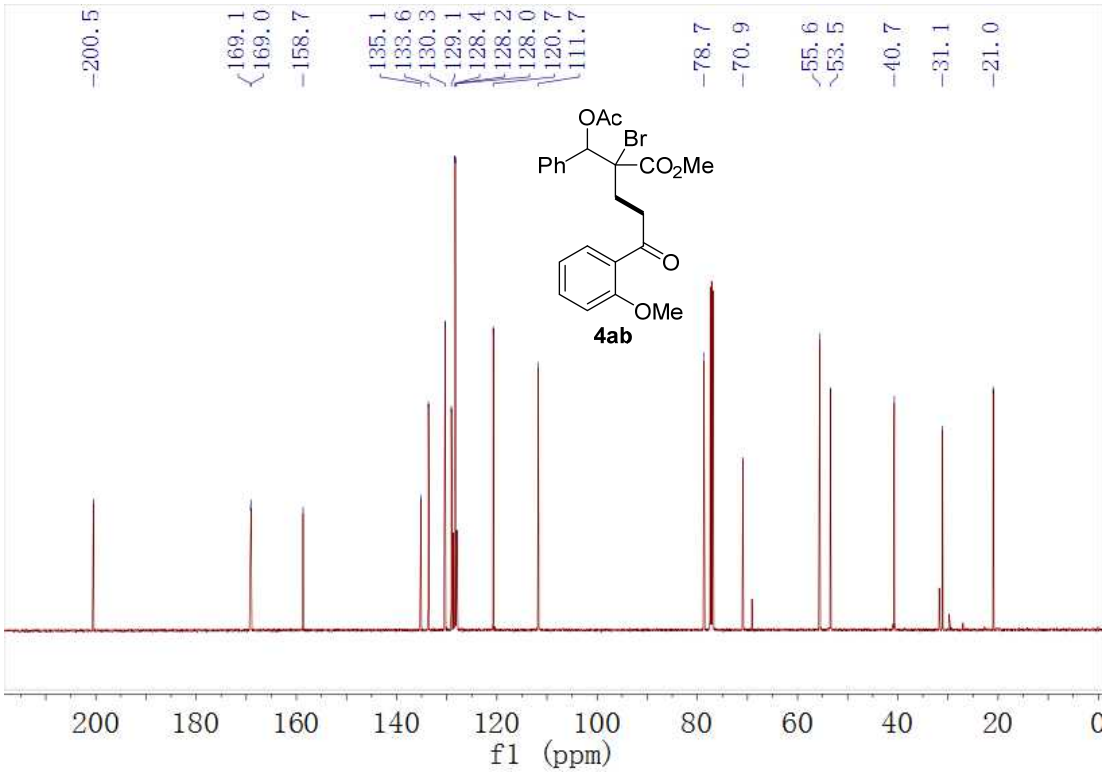


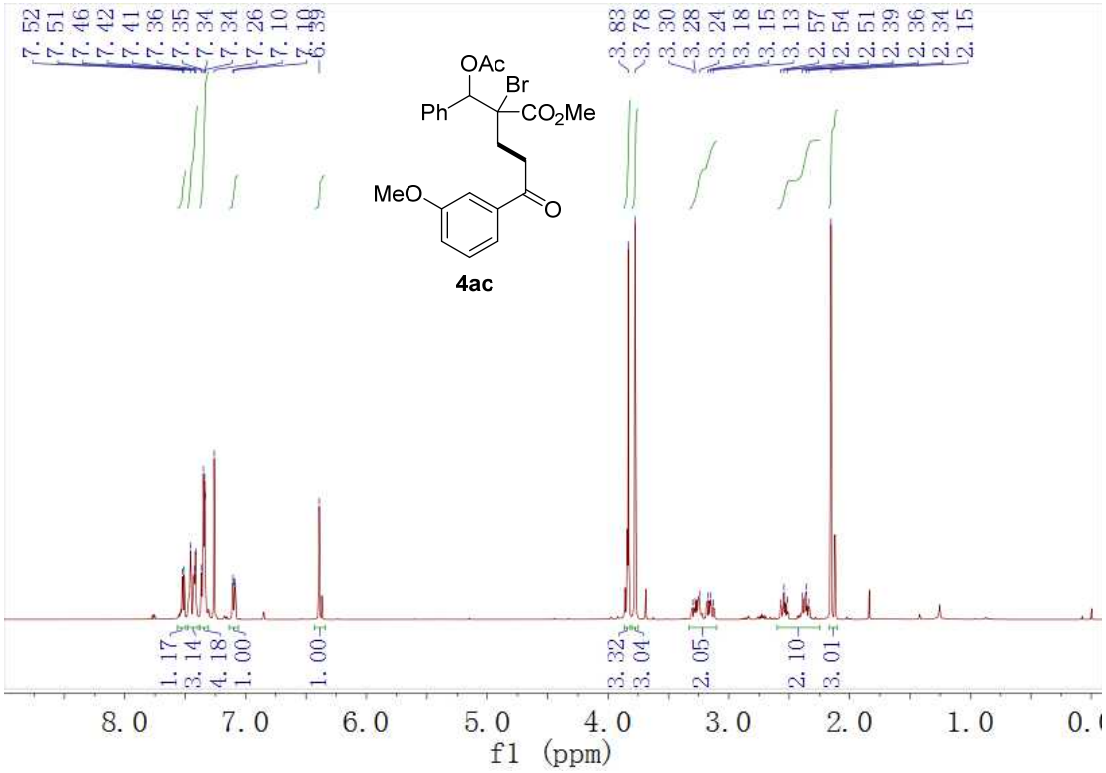
^{1}H NMR of **4ab** in $CDCl_3$



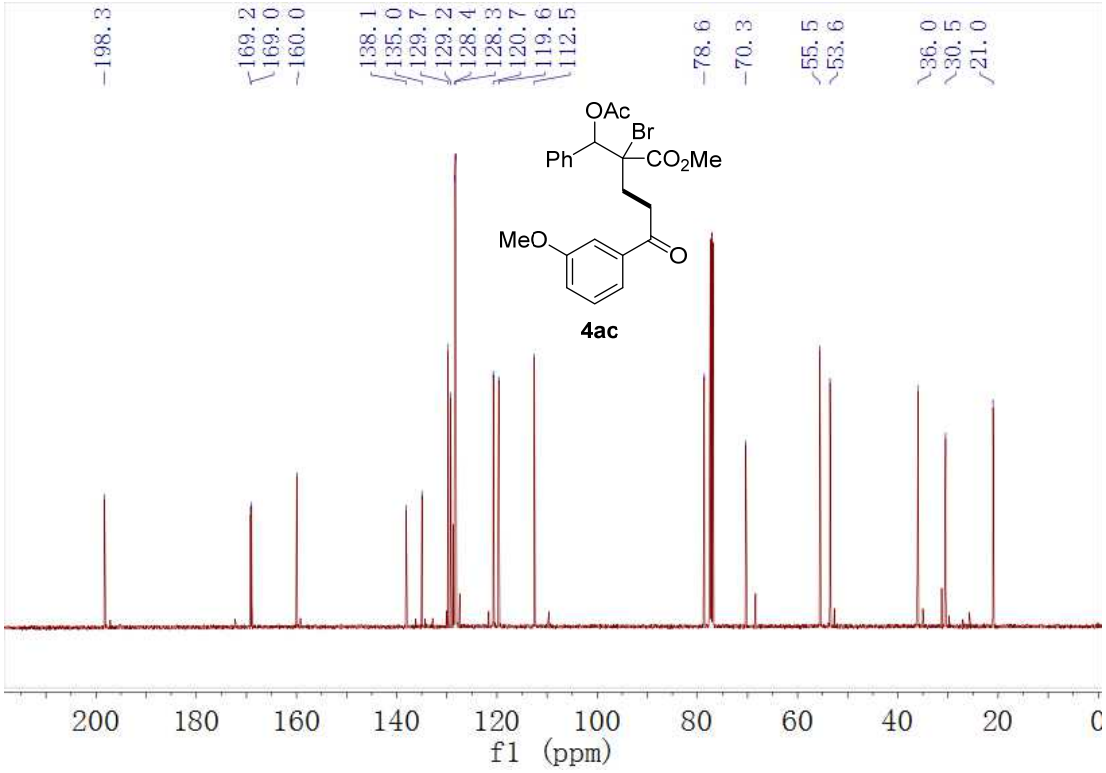
^{13}C NMR of **4ab** in $CDCl_3$



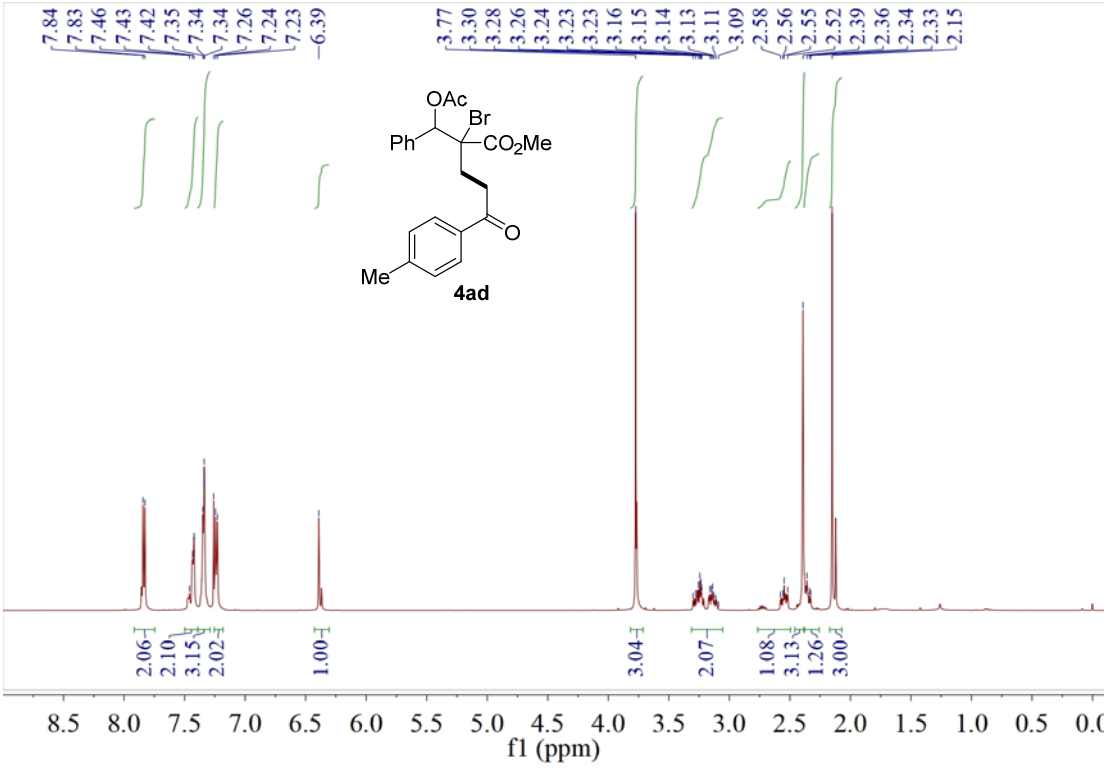
^{1}H NMR of **4ac** in $CDCl_3$



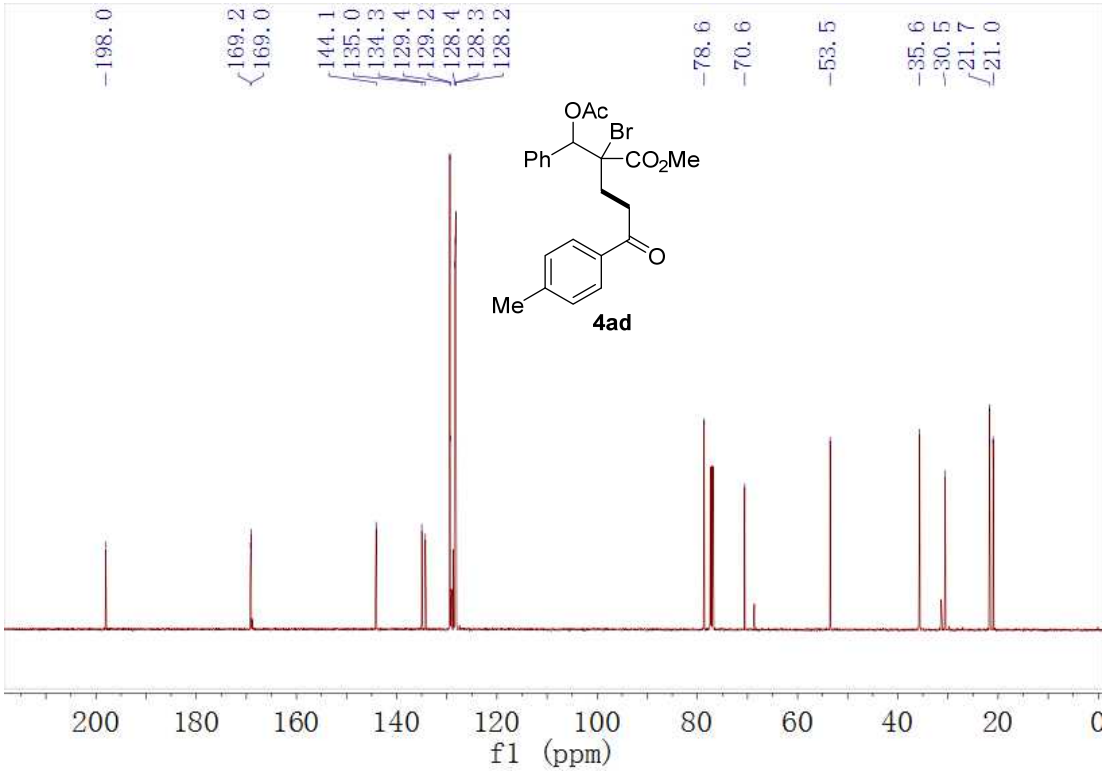
^{13}C NMR of **4ac** in $CDCl_3$



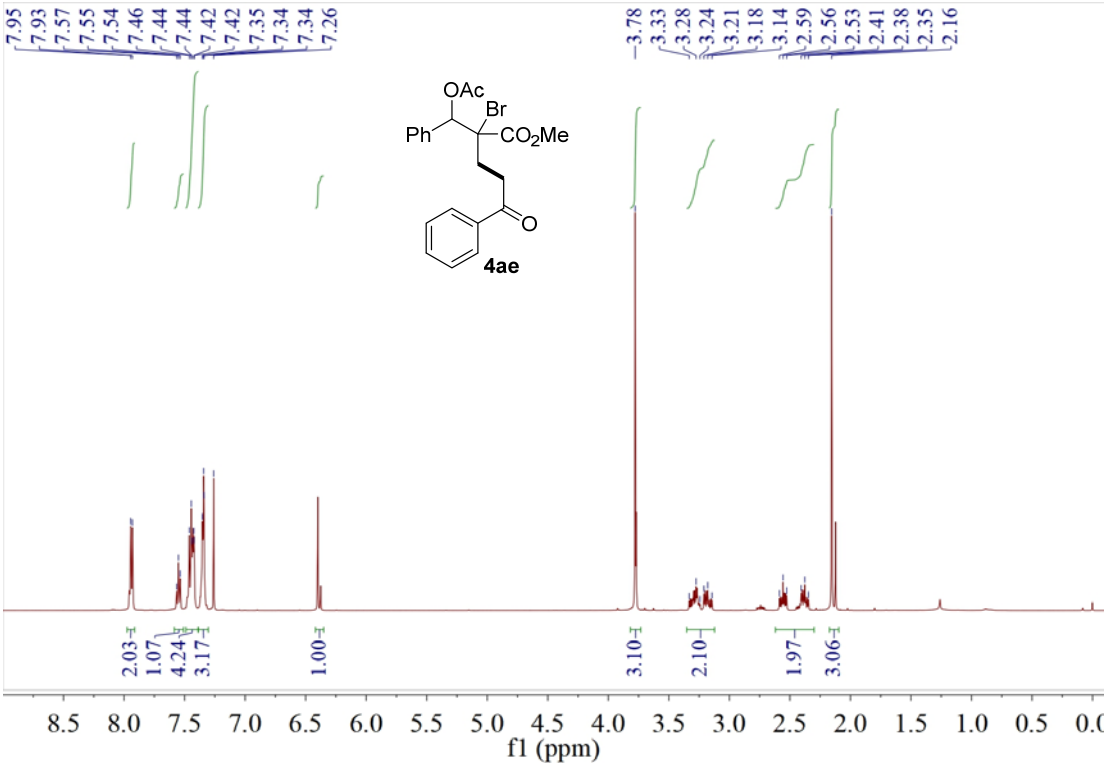
^{1}H NMR of **4ad** in $CDCl_3$



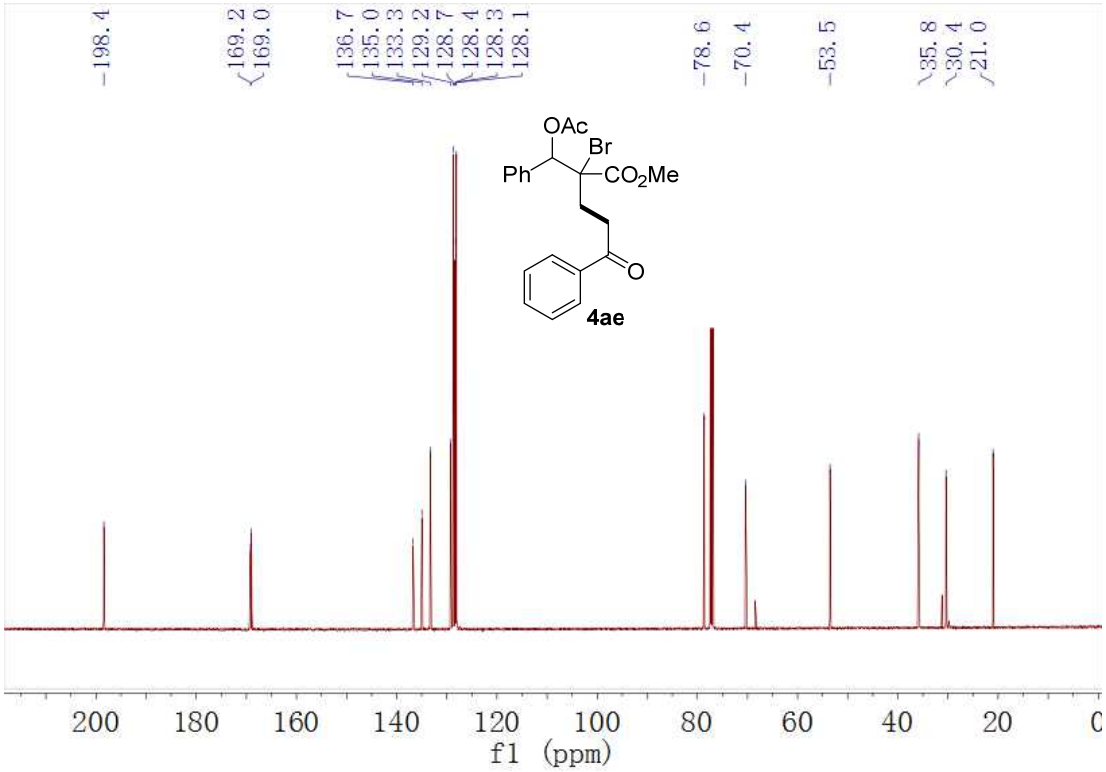
^{13}C NMR of **4ad** in $CDCl_3$



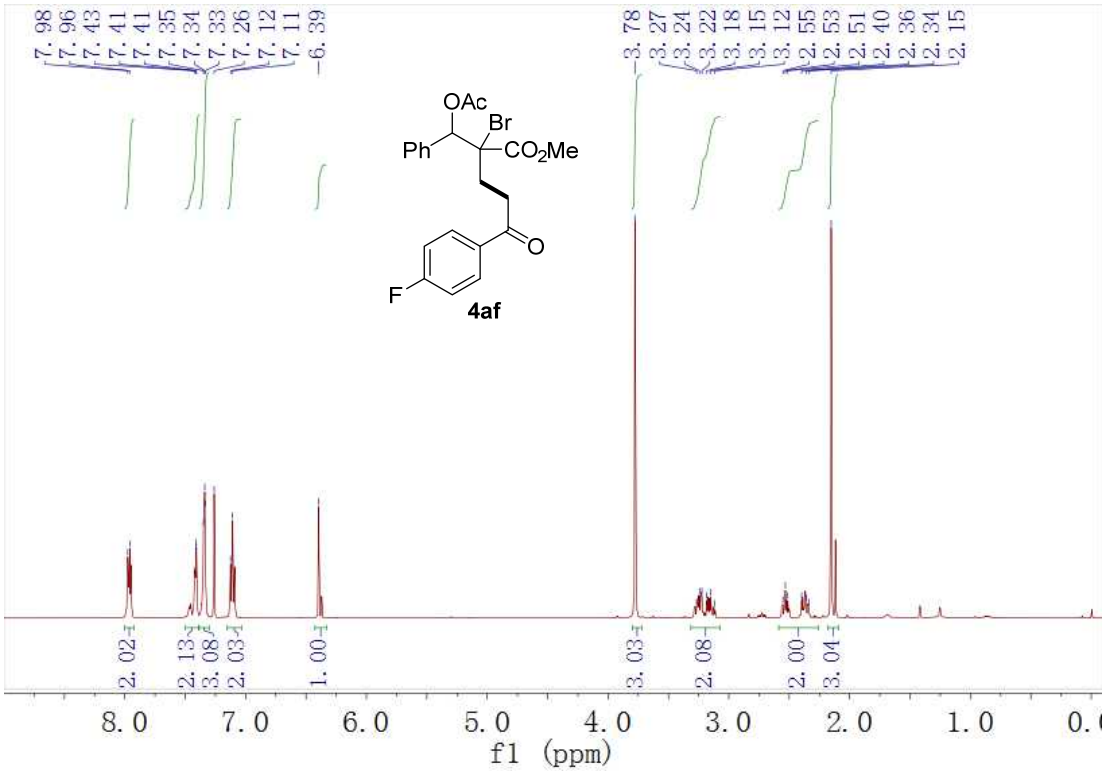
^{1}H NMR of **4ae** in $CDCl_3$



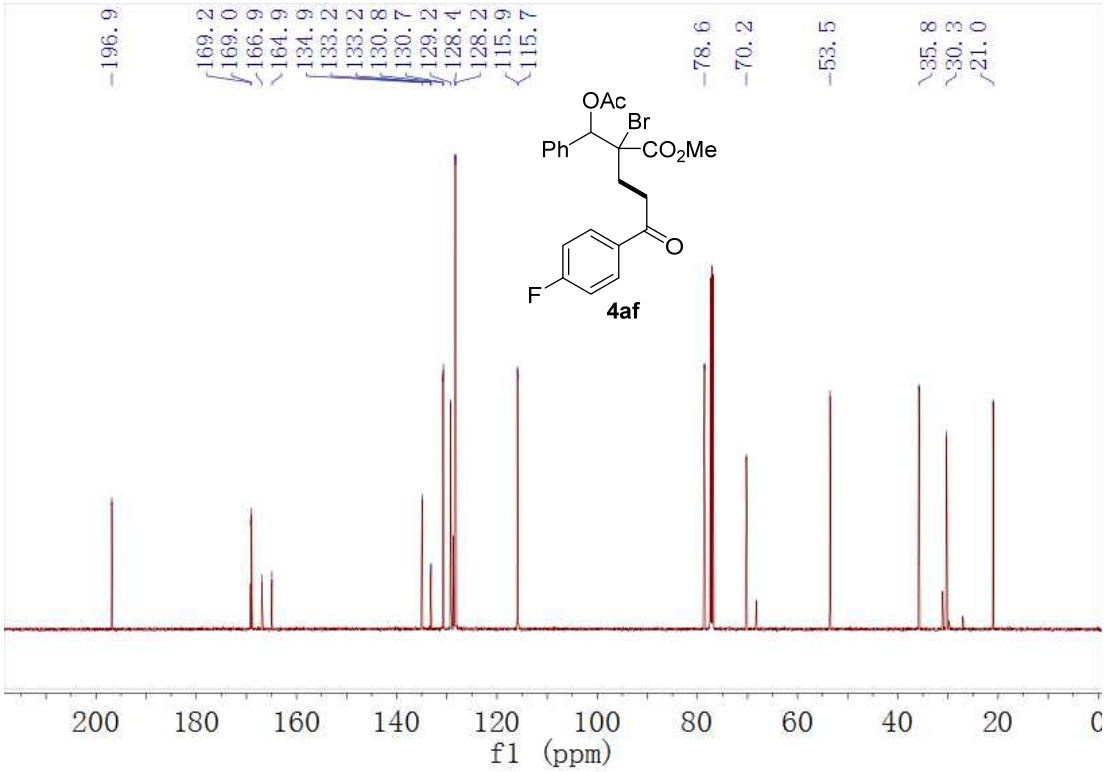
^{13}C NMR of **4ae** in $CDCl_3$



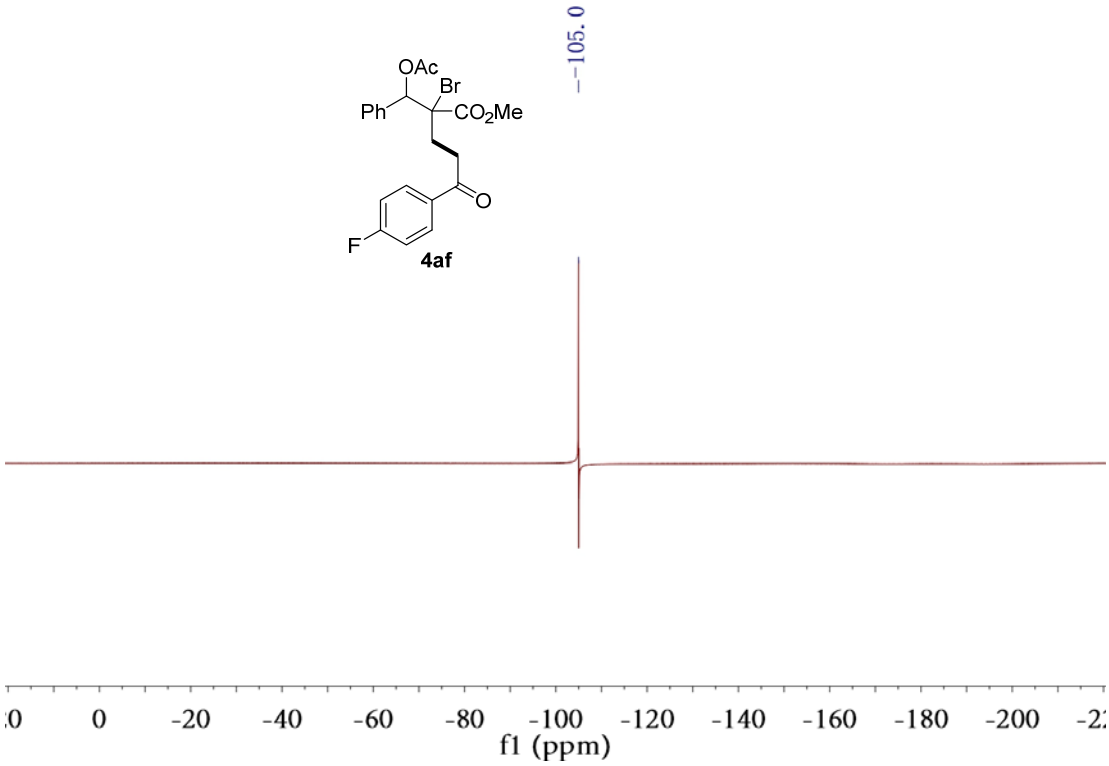
^{1}H NMR of **4af** in $CDCl_3$



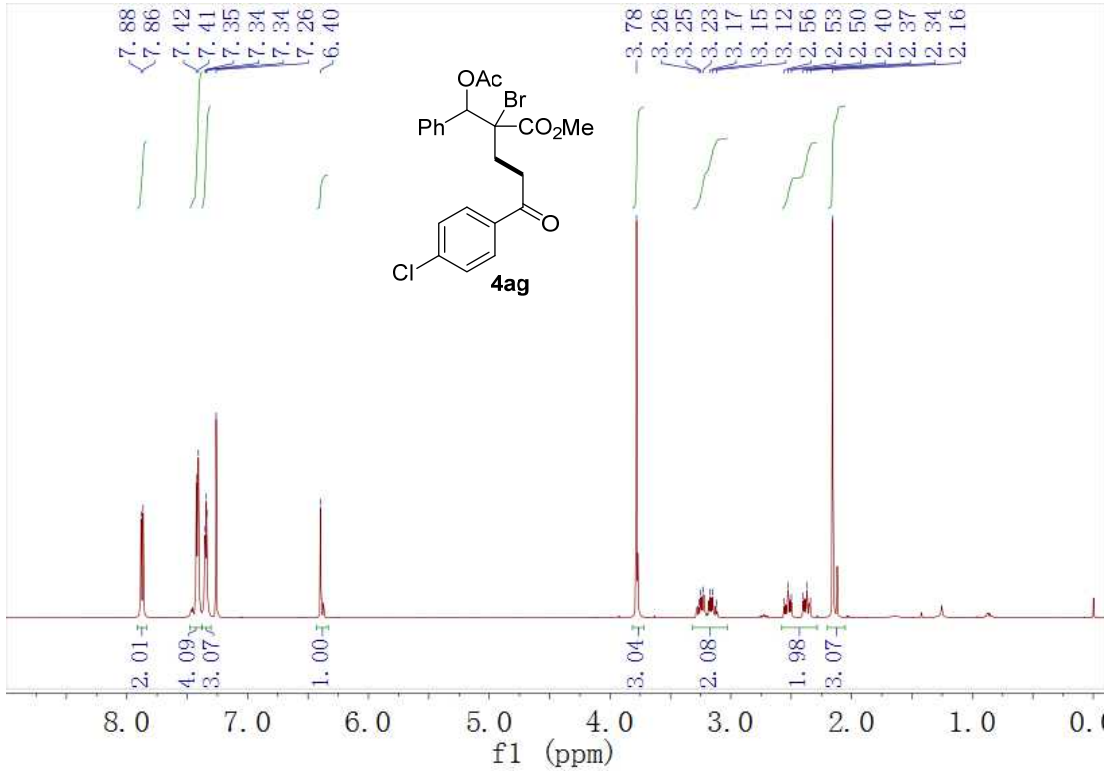
^{13}C NMR of **4af** in $CDCl_3$



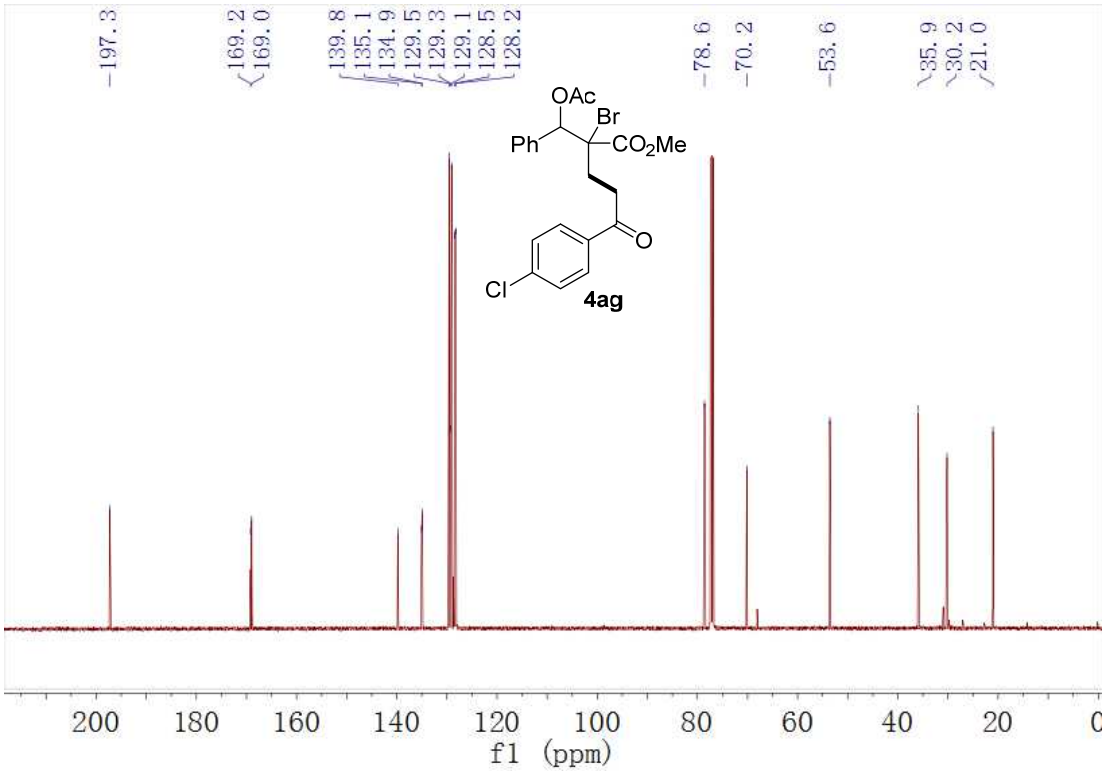
^{19}F NMR of **4af** in $CDCl_3$



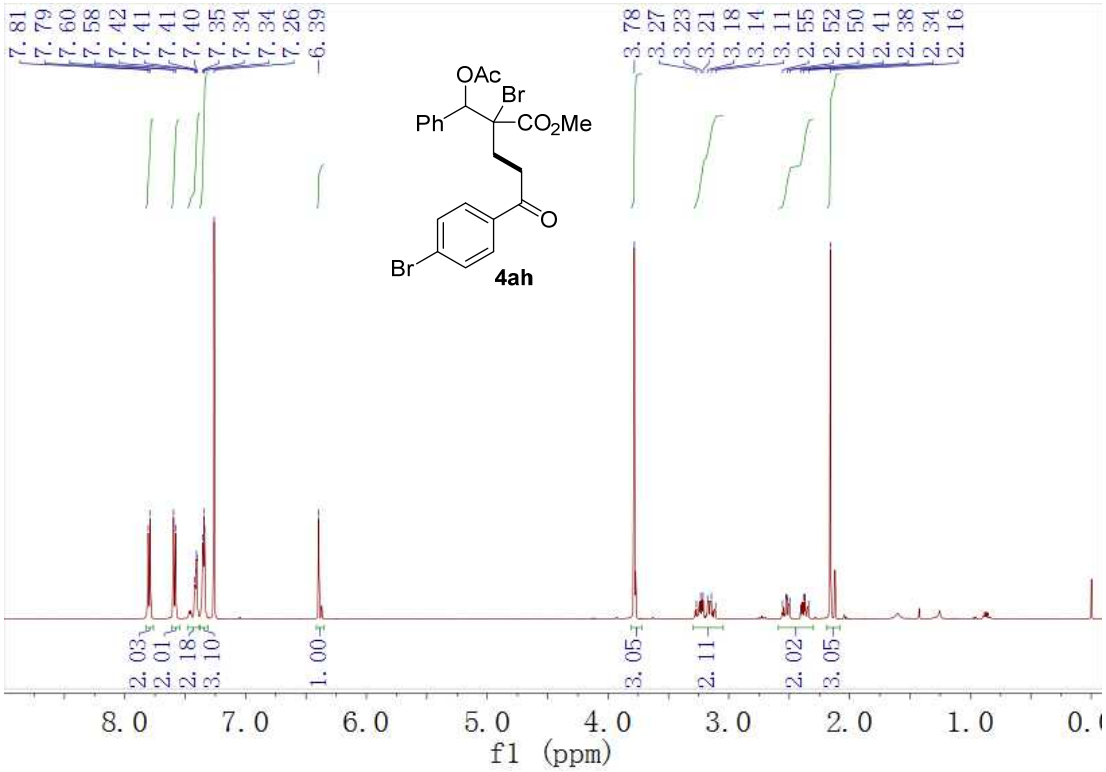
^{1}H NMR of **4ag** in $CDCl_3$



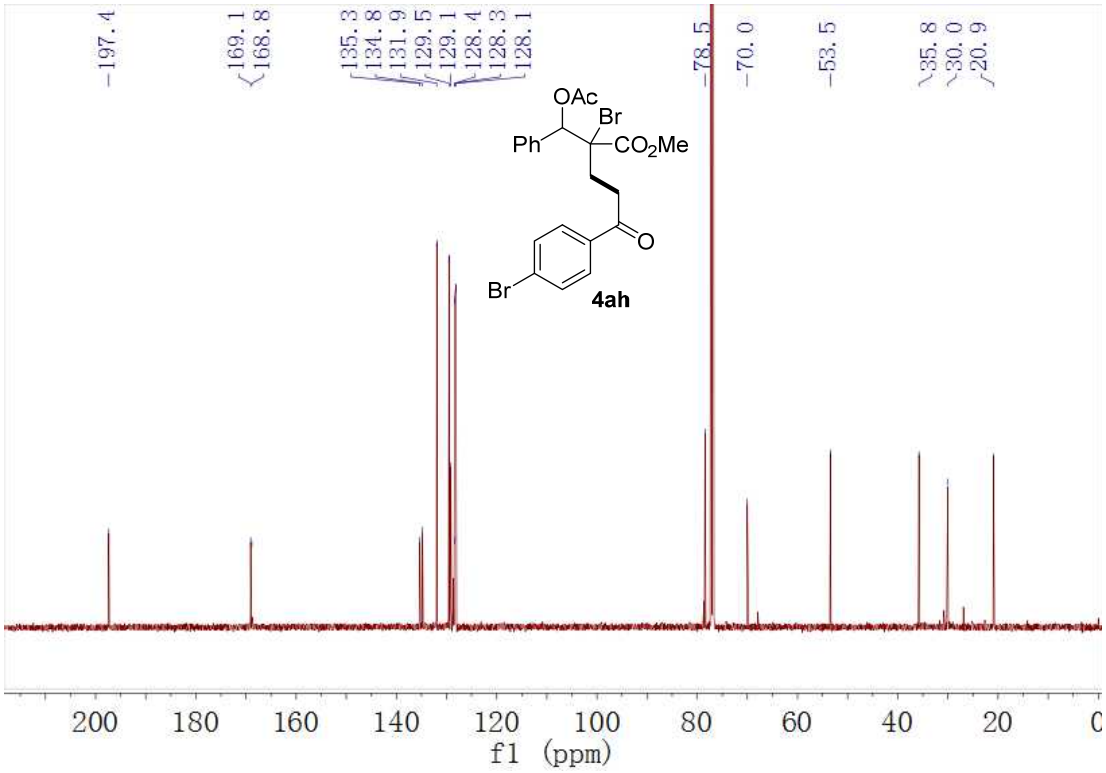
^{13}C NMR of **4ag** in $CDCl_3$



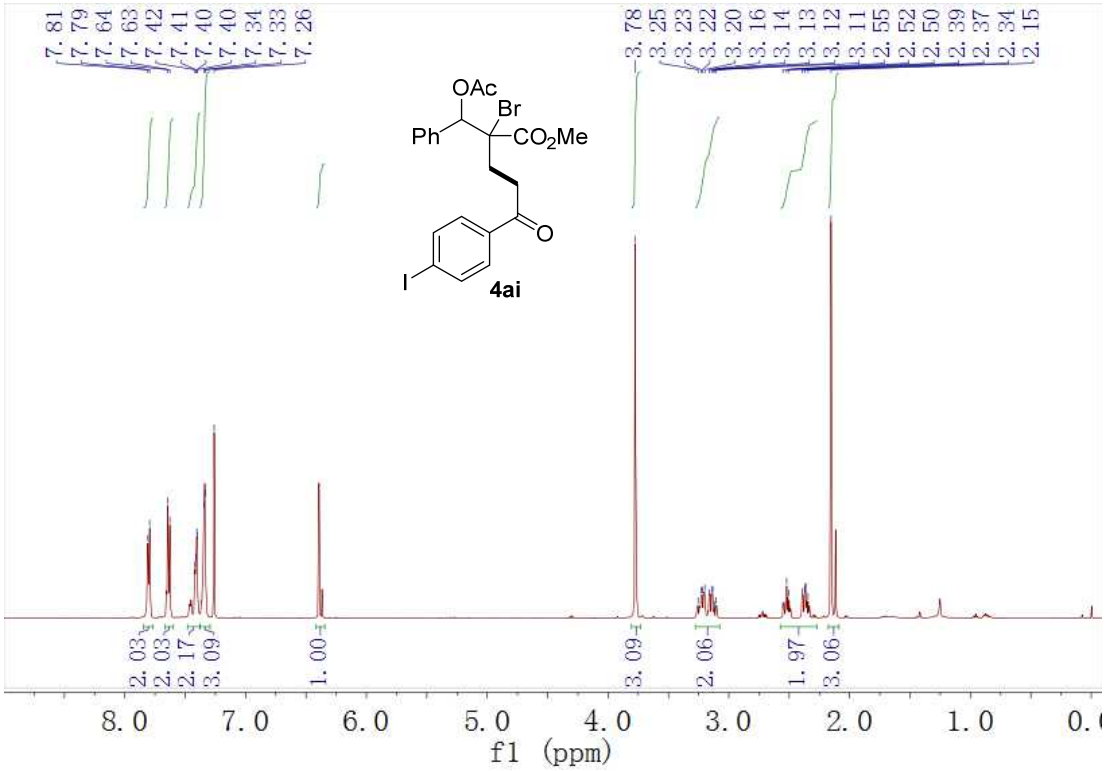
^{1}H NMR of **4ah** in $CDCl_3$



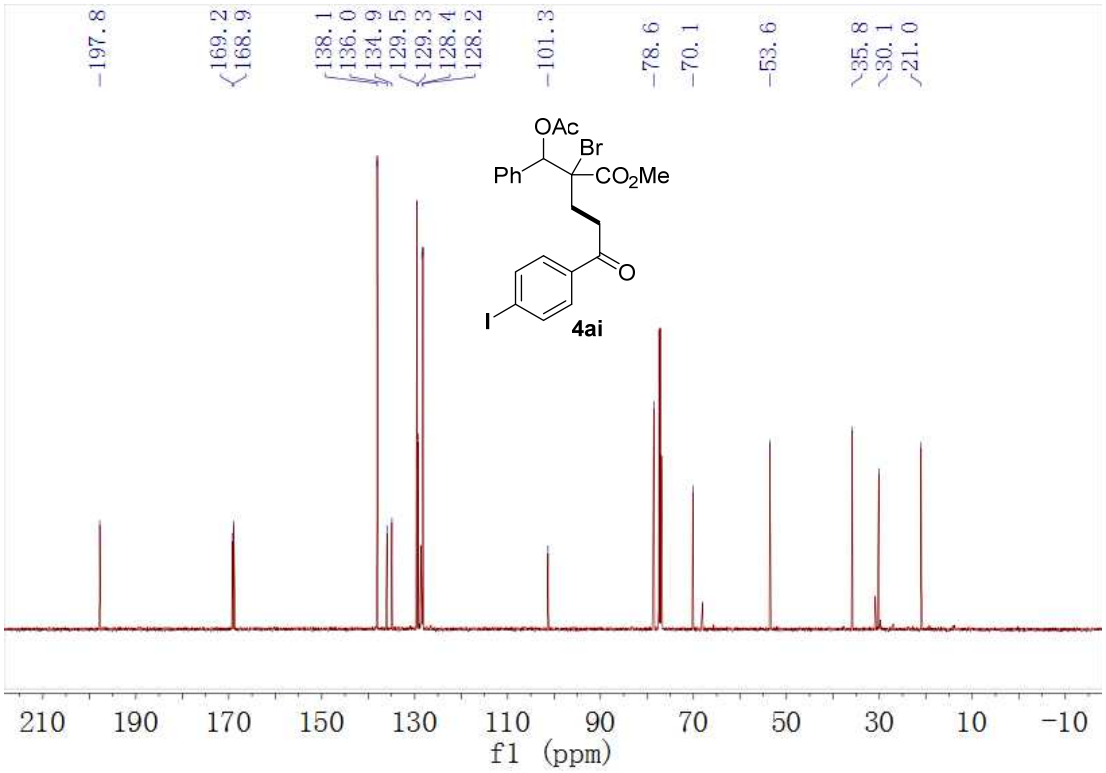
^{13}C NMR of **4ah** in $CDCl_3$



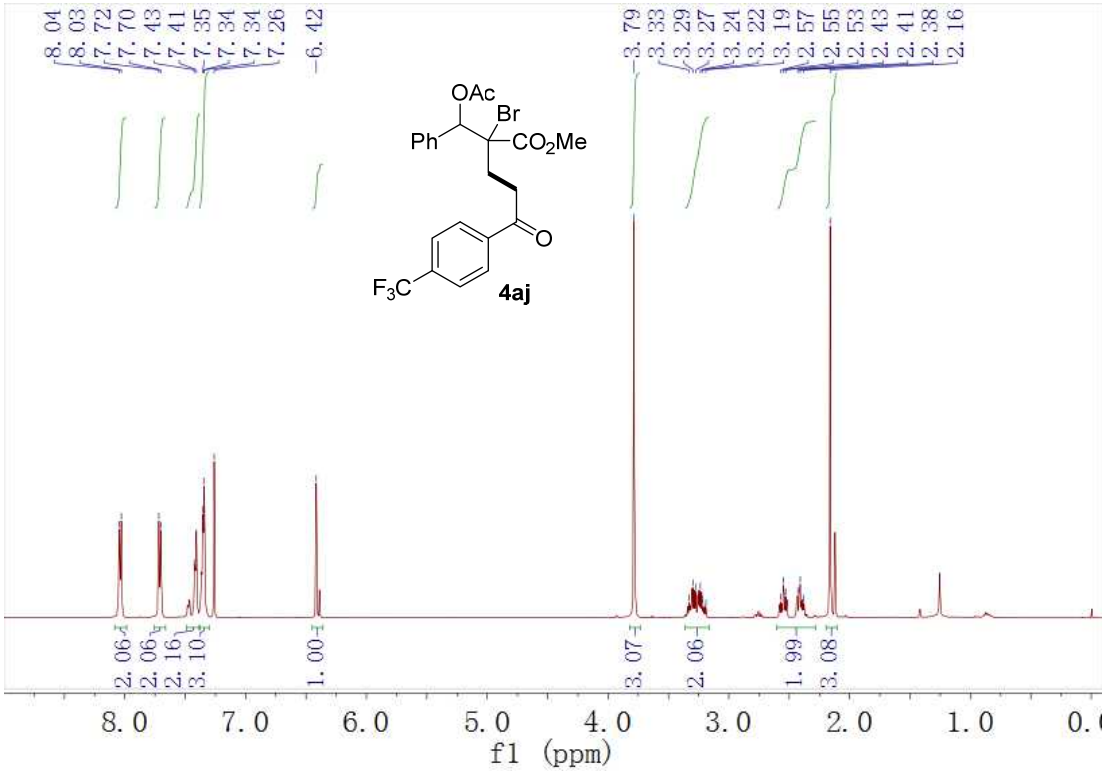
^{1}H NMR of **4ai** in $CDCl_3$



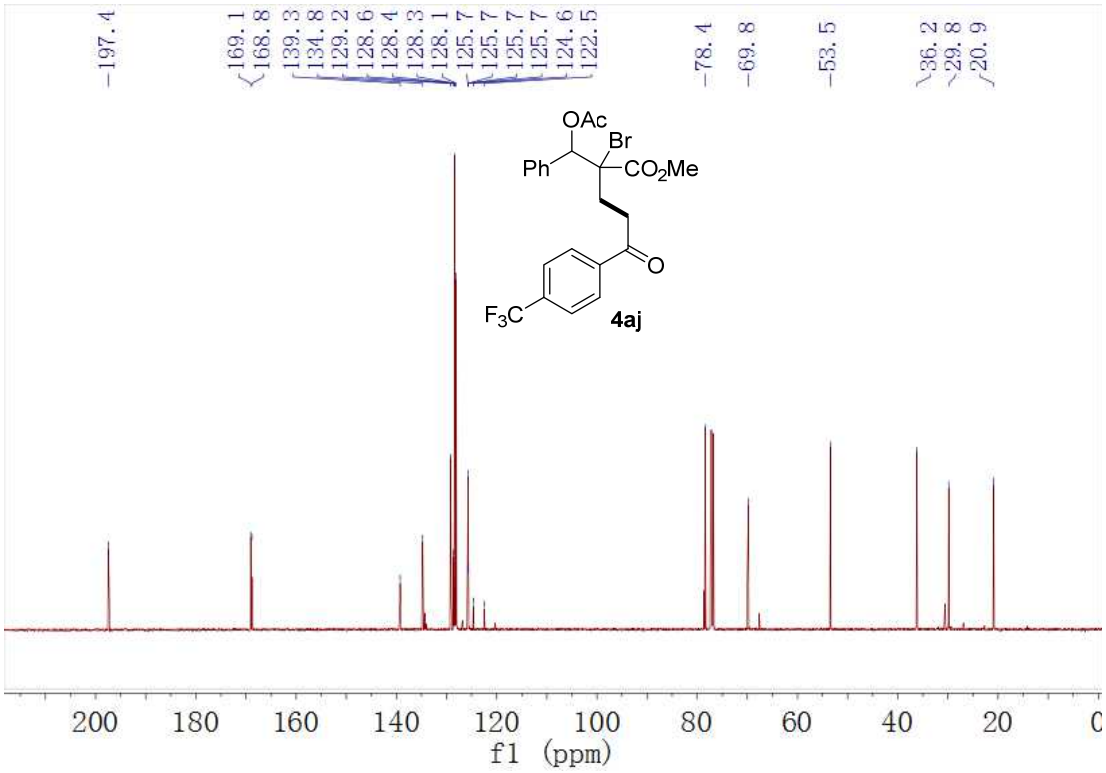
^{13}C NMR of **4ai** in $CDCl_3$



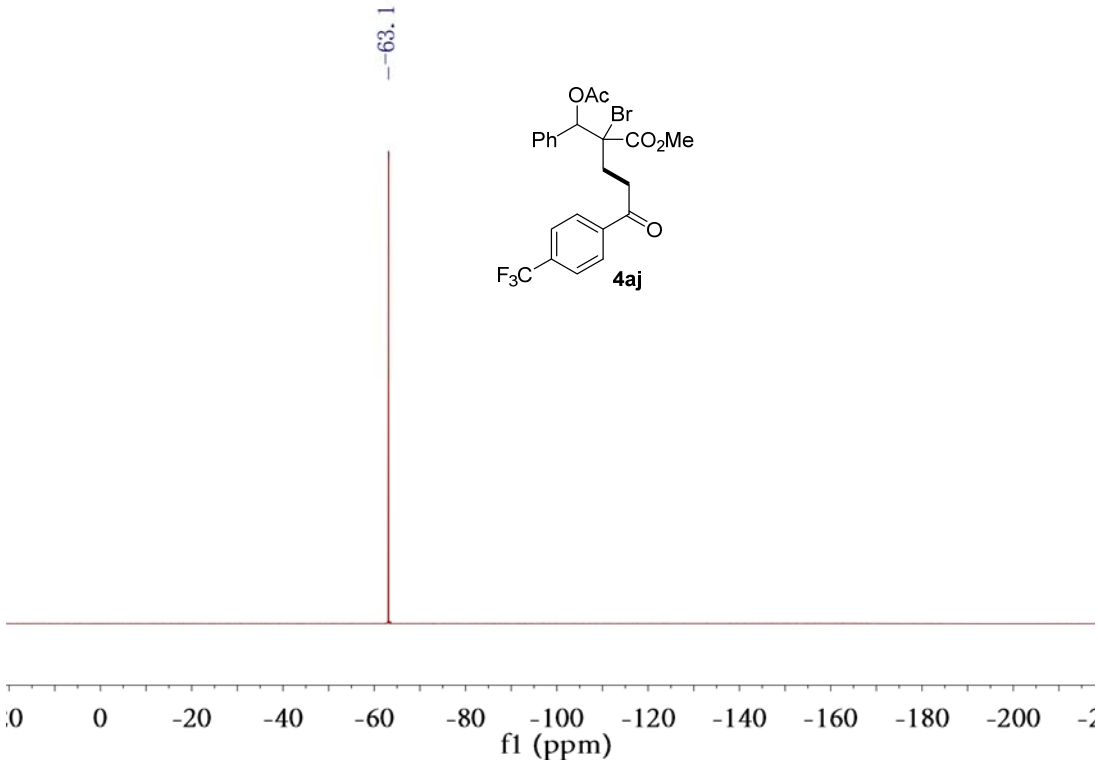
^{1}H NMR of **4aj** in $CDCl_3$



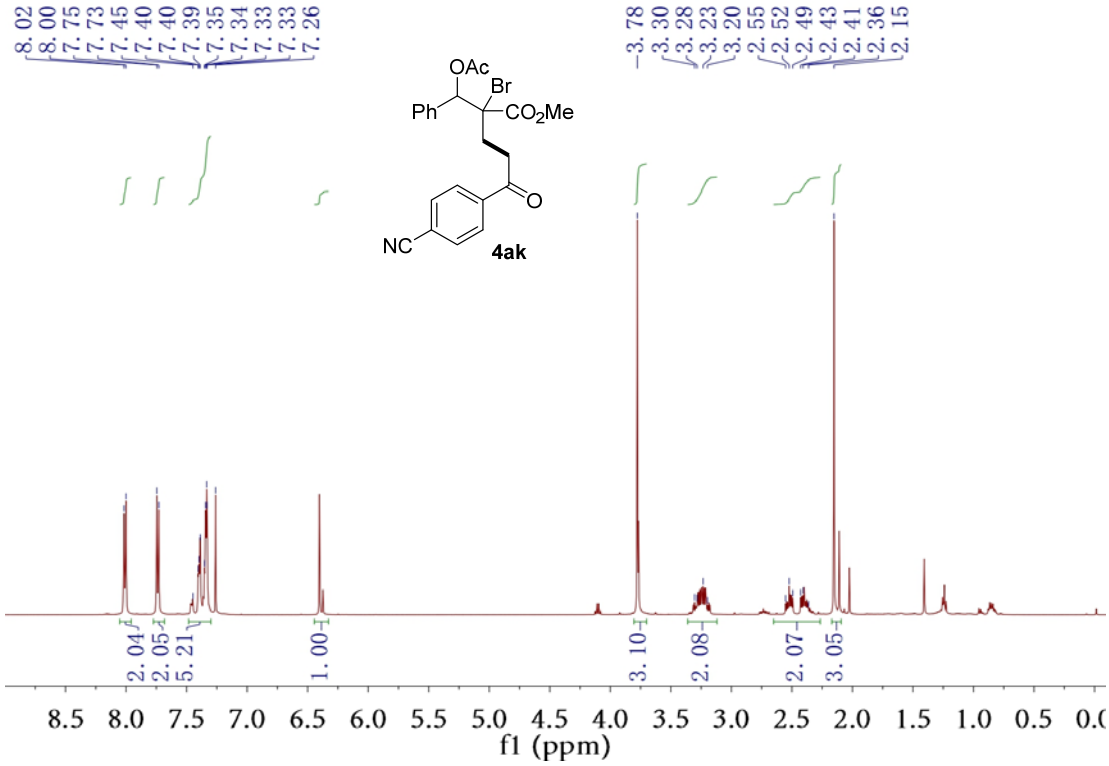
^{13}C NMR of **4aj** in $CDCl_3$



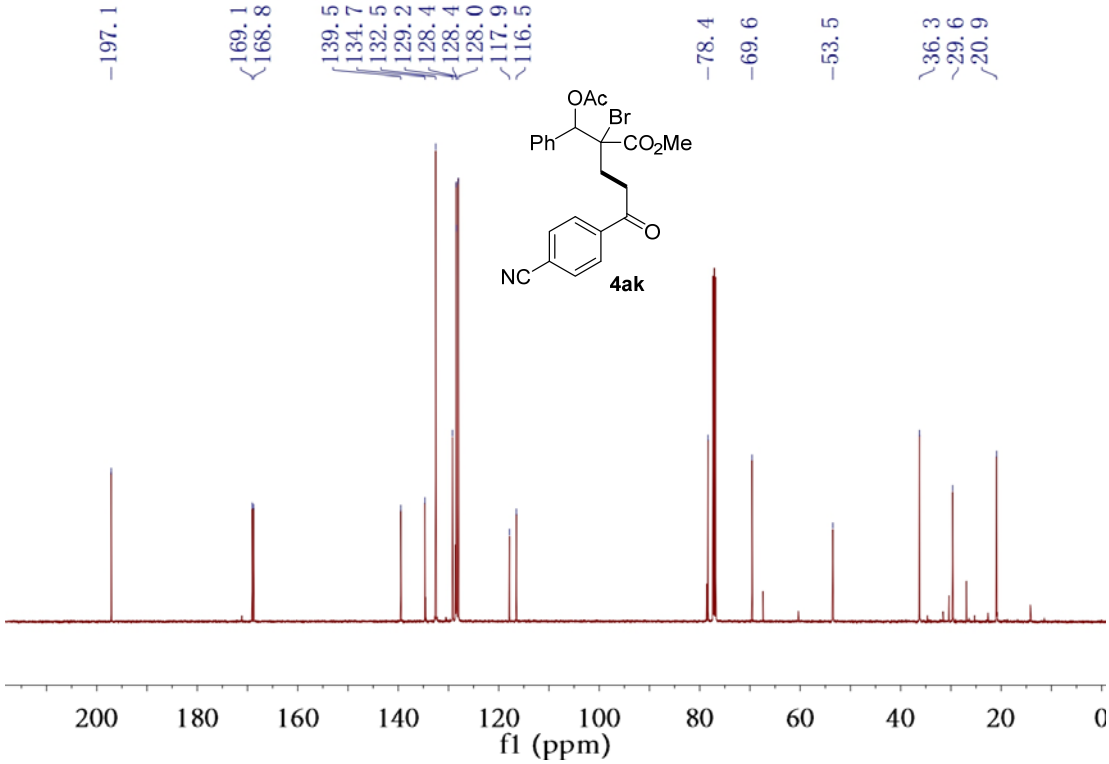
^{19}F NMR of **4aj** in $CDCl_3$



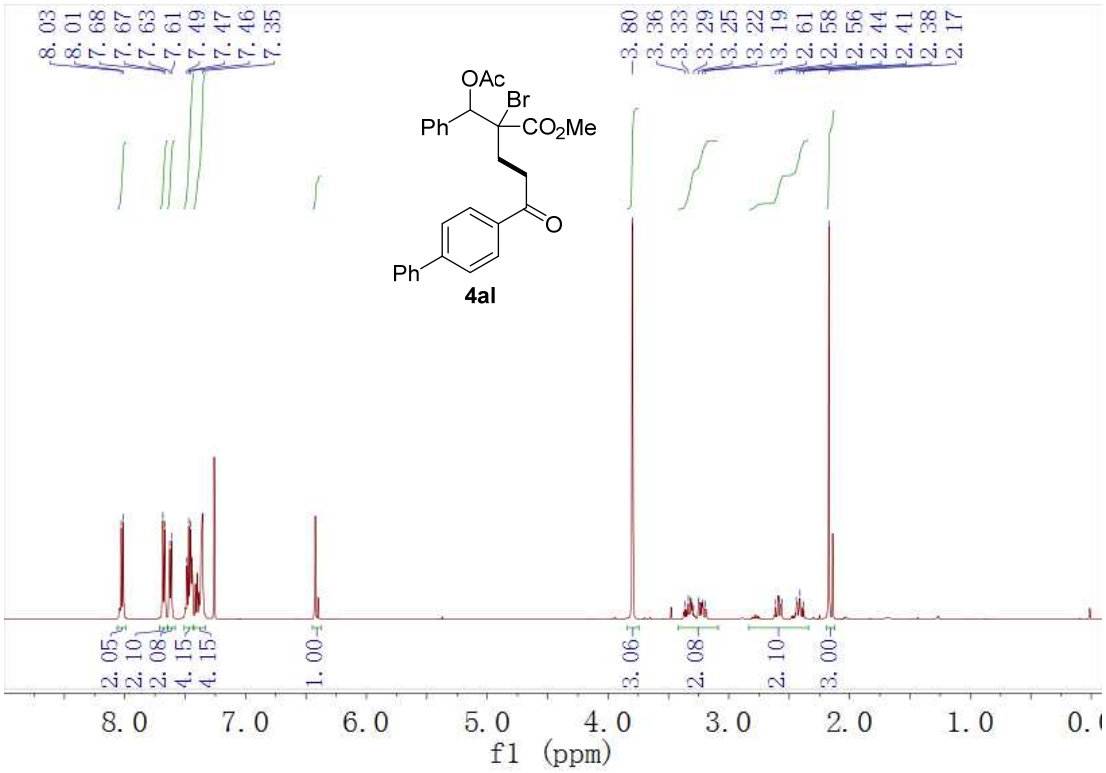
^{1}H NMR of **4ak** in $CDCl_3$



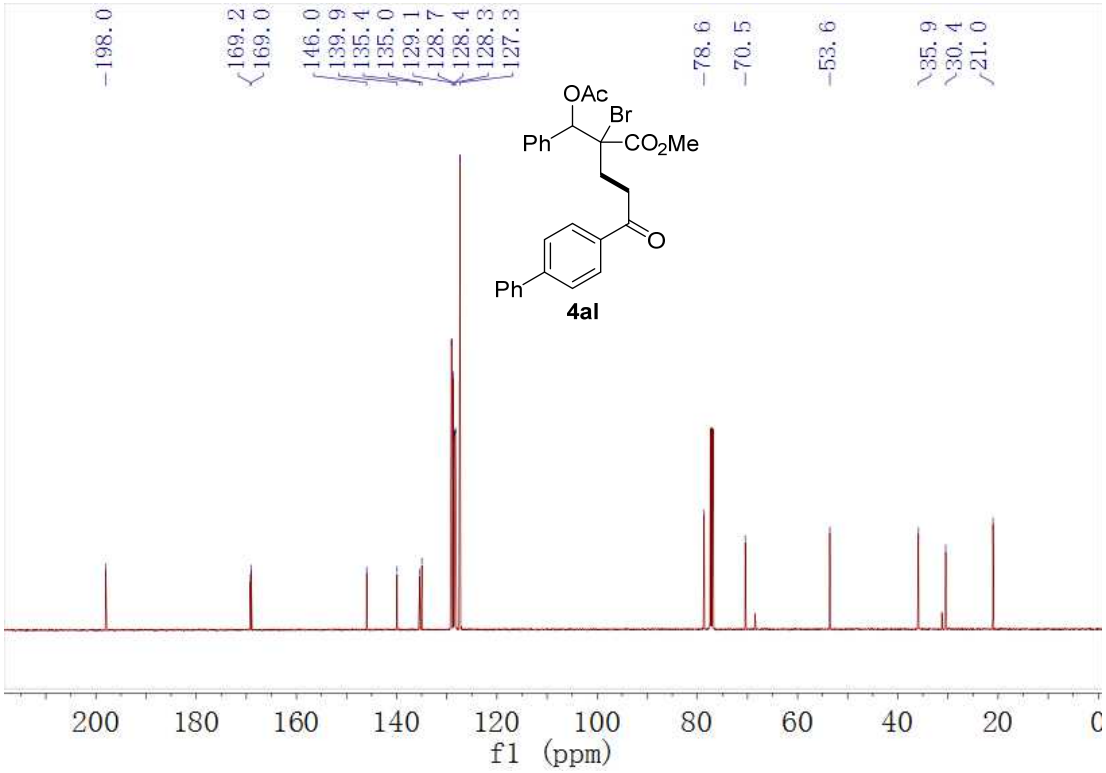
^{13}C NMR of **4ak** in $CDCl_3$



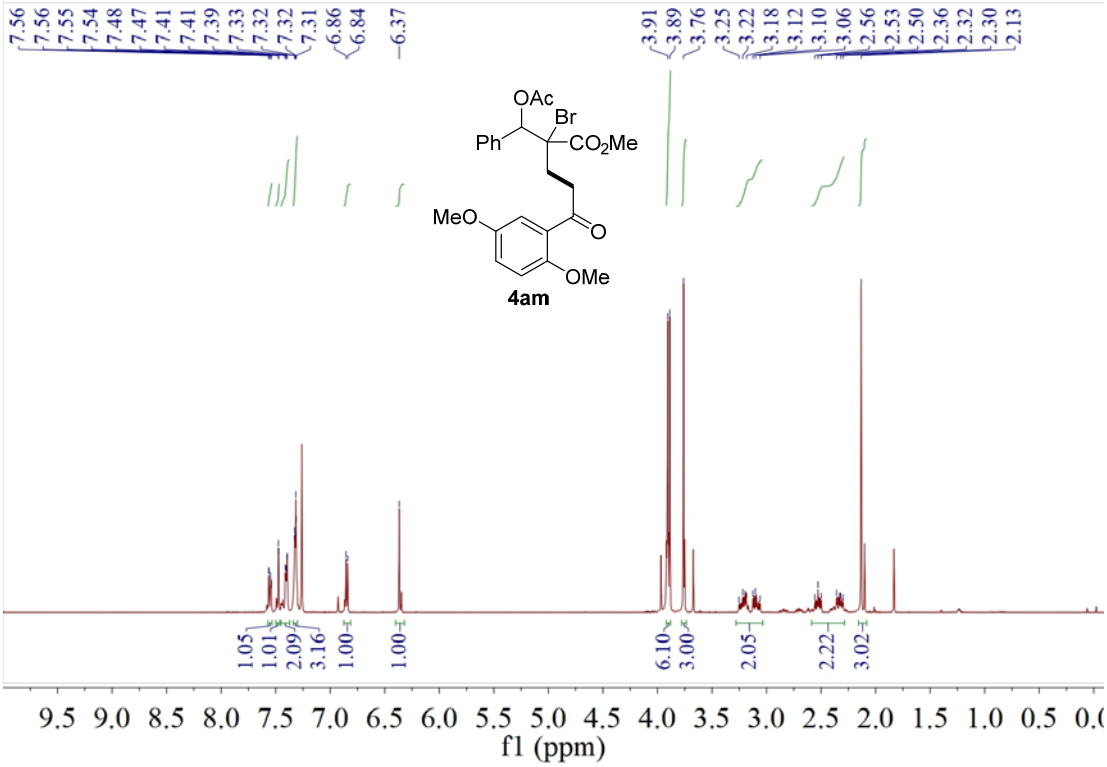
^{1}H NMR of **4al** in $CDCl_3$



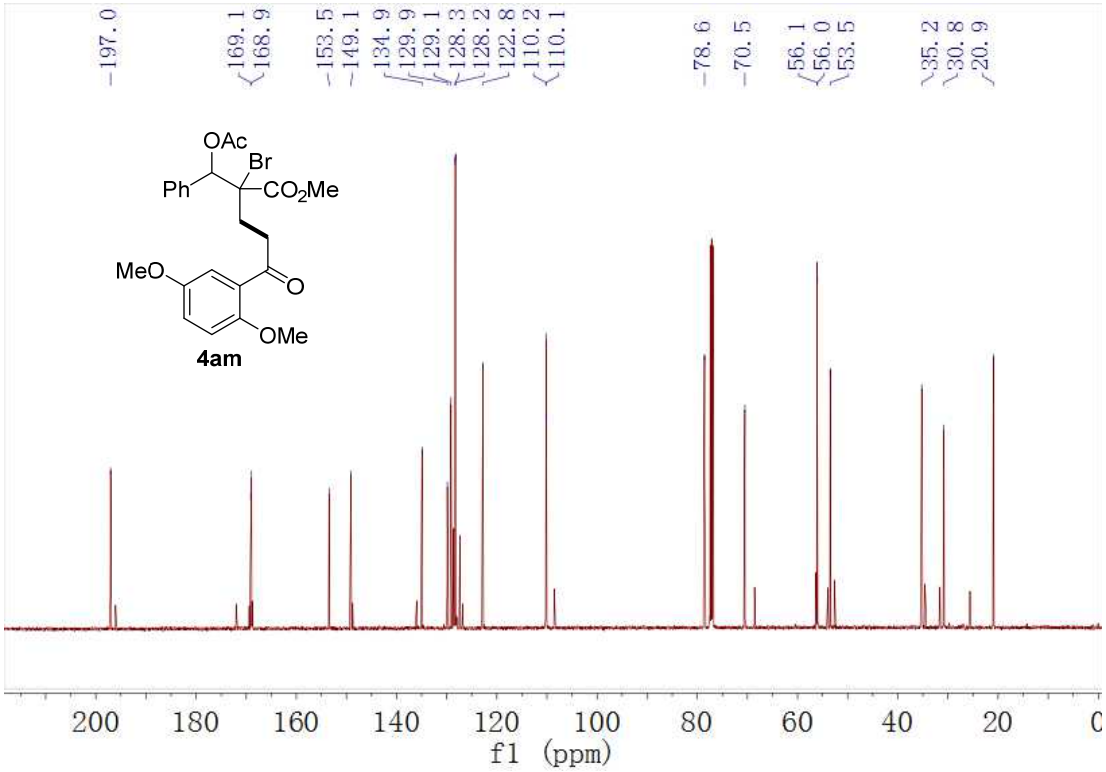
^{13}C NMR of **4al** in $CDCl_3$



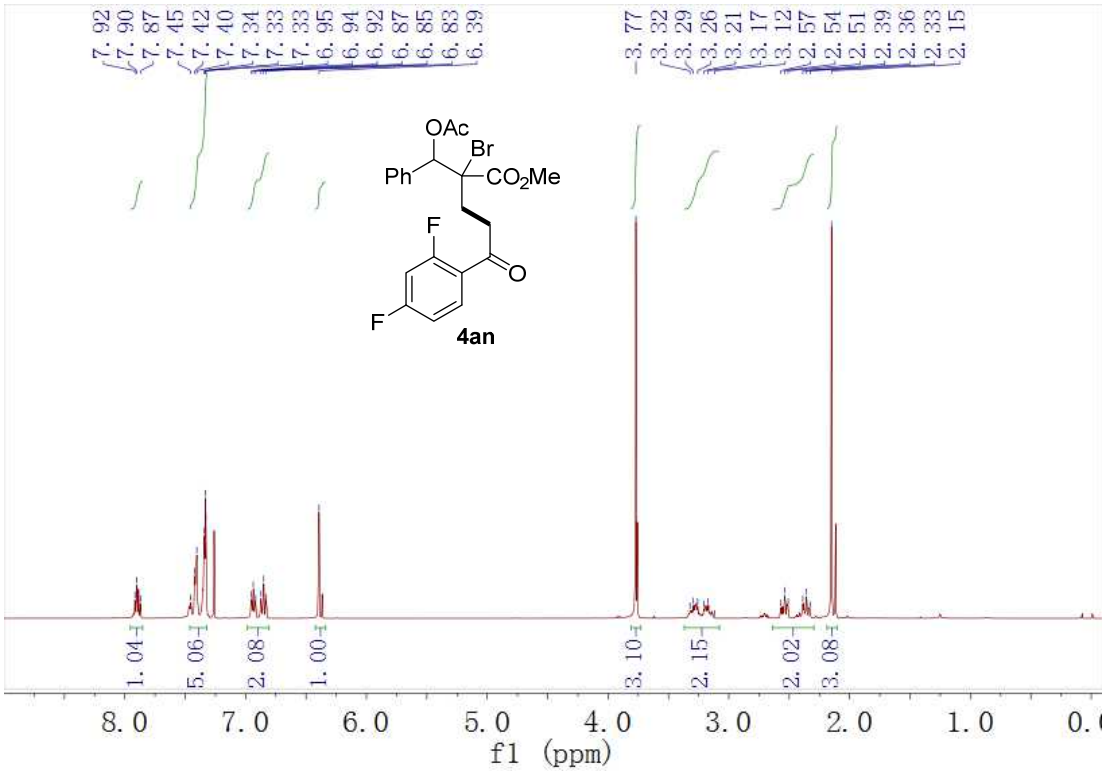
^{1}H NMR of **4am** in $CDCl_3$



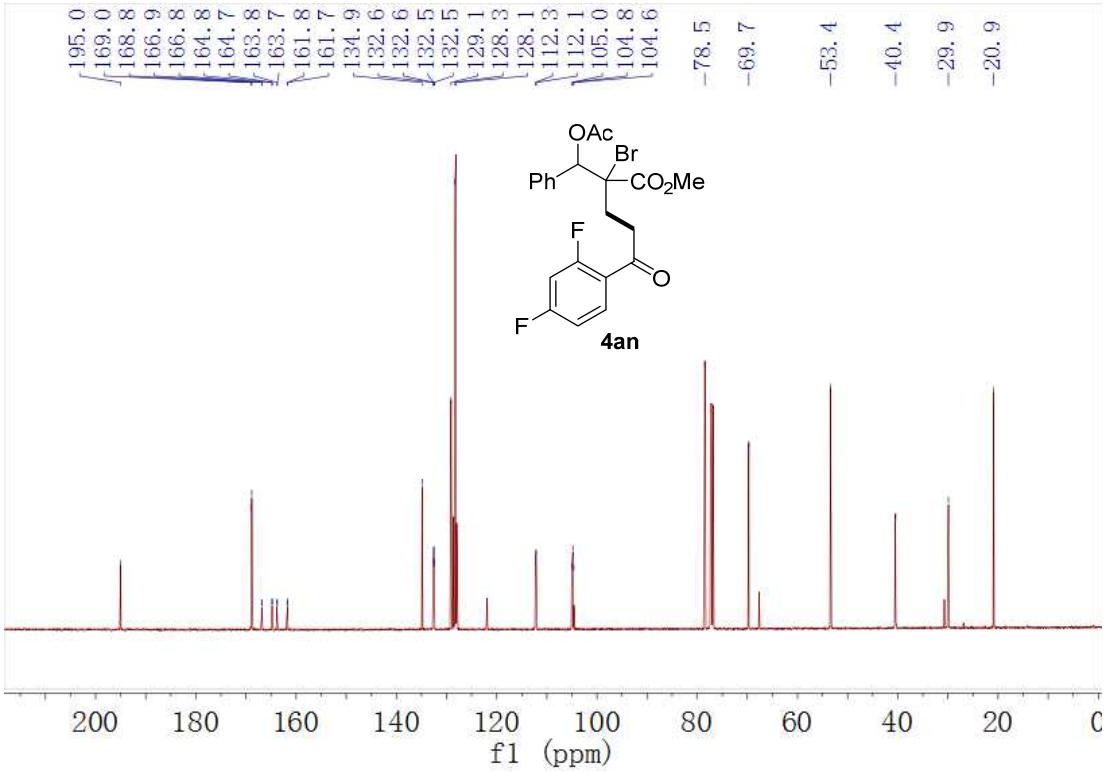
^{13}C NMR of **4am** in $CDCl_3$



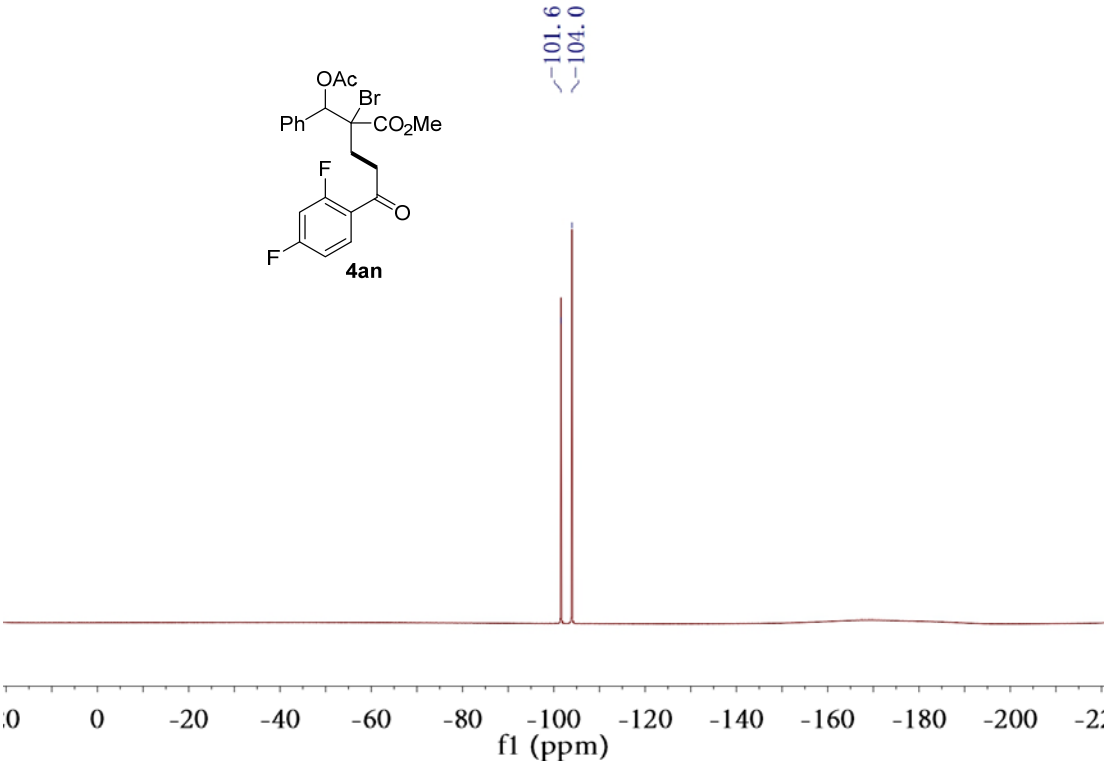
^{1}H NMR of **4an** in $CDCl_3$



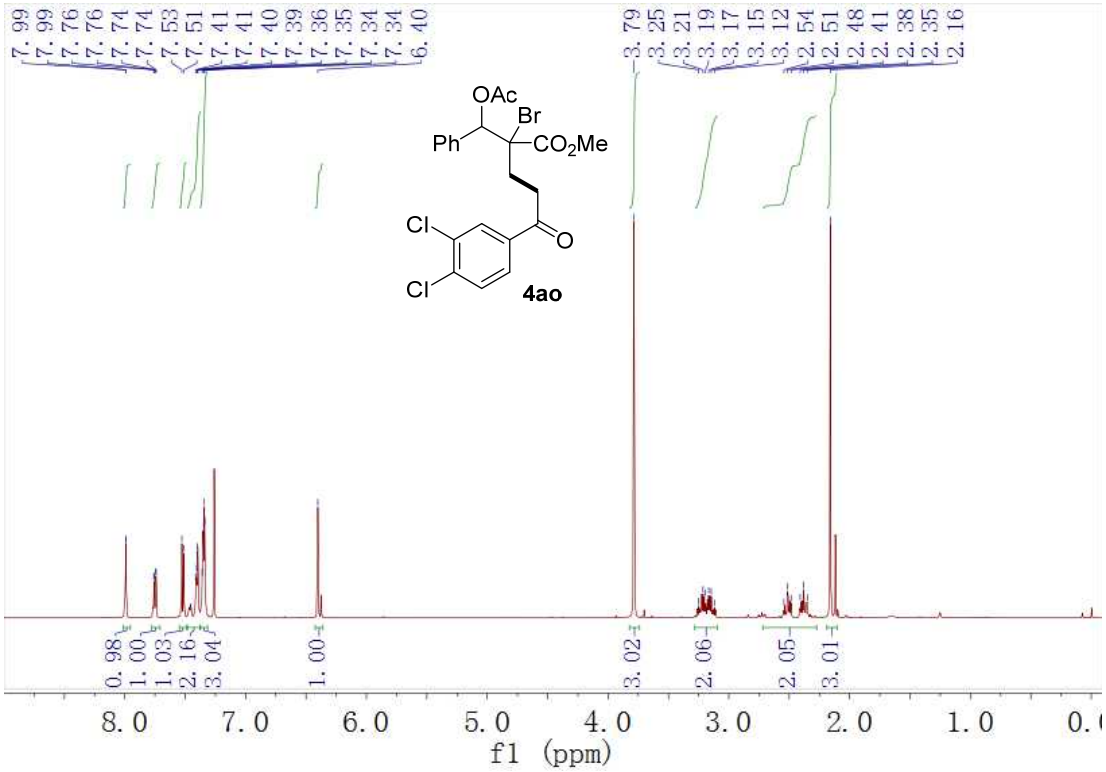
^{13}C NMR of **4an** in $CDCl_3$



^{19}FNMR of **4an** in $CDCl_3$



^{1}H NMR of **4ao** in $CDCl_3$



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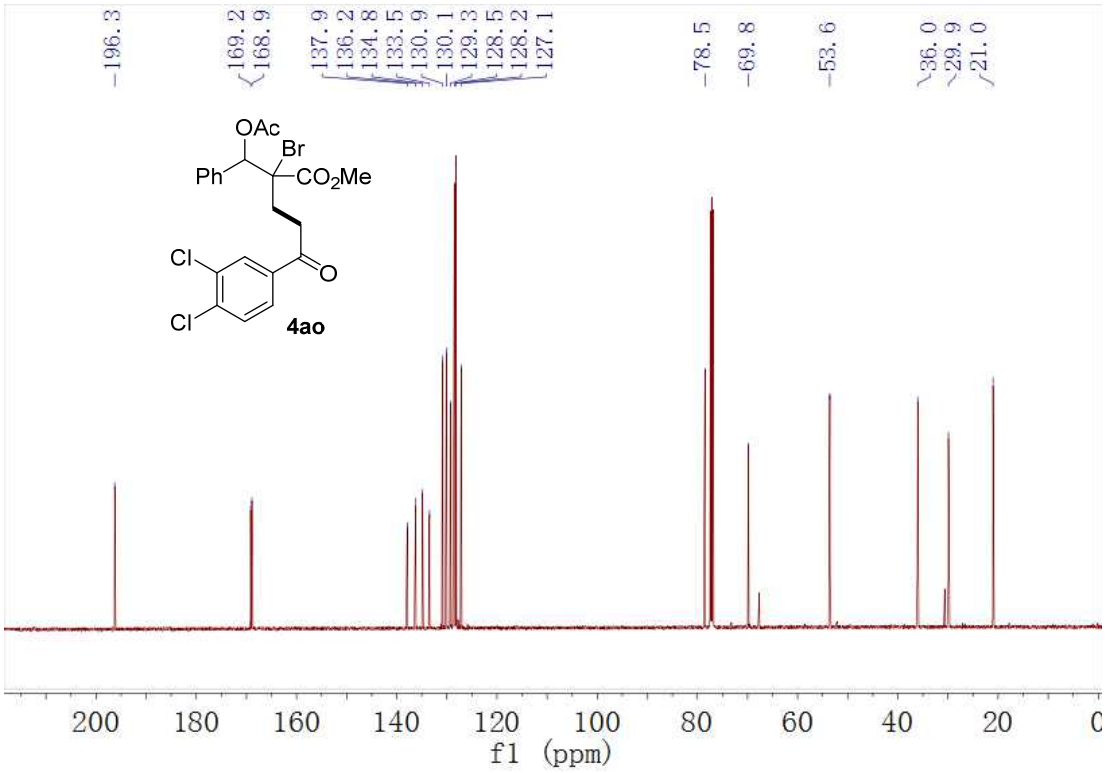

9. References

[1] W.-X. Wang, Q.-Z. Zhang, T.-Q. Zhang, Z.-S. Li, W. Zhang, W. Yu, *Adv. Synth. Catal.* 2015, **357**, 221.

[2] Z. He, B. Wibbeling, A. Studer, *Adv. Synth. Catal.* 2013, **355**, 3639.