Supplementary Information for

Harnessing P^V-Oxirene for the Modular Synthesis of α-Oxy Carbonyls

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1. General Information

Unless otherwise noted, all reactions were conducted in oven-dried Test tube with a magnetic stirrer under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Flash column chromatography was performed using EM Science (200-300 mesh) silica gel. ^{1}H, ^{13}C, ^{31}P, ^{19}Fand ^{11}B NMR spectra were recorded on Bruker 400 MHz at 20 °C with $CDCl_3$, DMSO-d_6 or MeCN-d_3 as solvent. Chemical shifts (δ values) were reported in ppm with $CDCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively). Chemical shifts (δ values) were reported in ppm with MeCN-d_3 (1.94 and 1.32 ppm for ^{1}H and ^{13}C respectively). Chemical shifts (δ values) were reported in ppm with DMSO-d_6 (2.50 and 39.52 ppm for ^{1}H and ^{13}C respectively). The datas are reported as follows: chemical shift (ppm), mμLtiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = mμLtiplet, br = broad, hept =heptet), coupling constant J (Hz), and integration. High resolution mass spectra were recorded on a Thermo Scientific Orbitrap Exploris 120. Chiral HPLC (High Pressure Liquid Chromatography) was performed on an Agilent HPLC apparatus with columns. Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. Anhydrous 1,2-dichloroethane purchased from Energy Chemical. All other reagents were purchased and used without further purification unless specified otherwise.

2. Synthesis and Characterization of Substrates

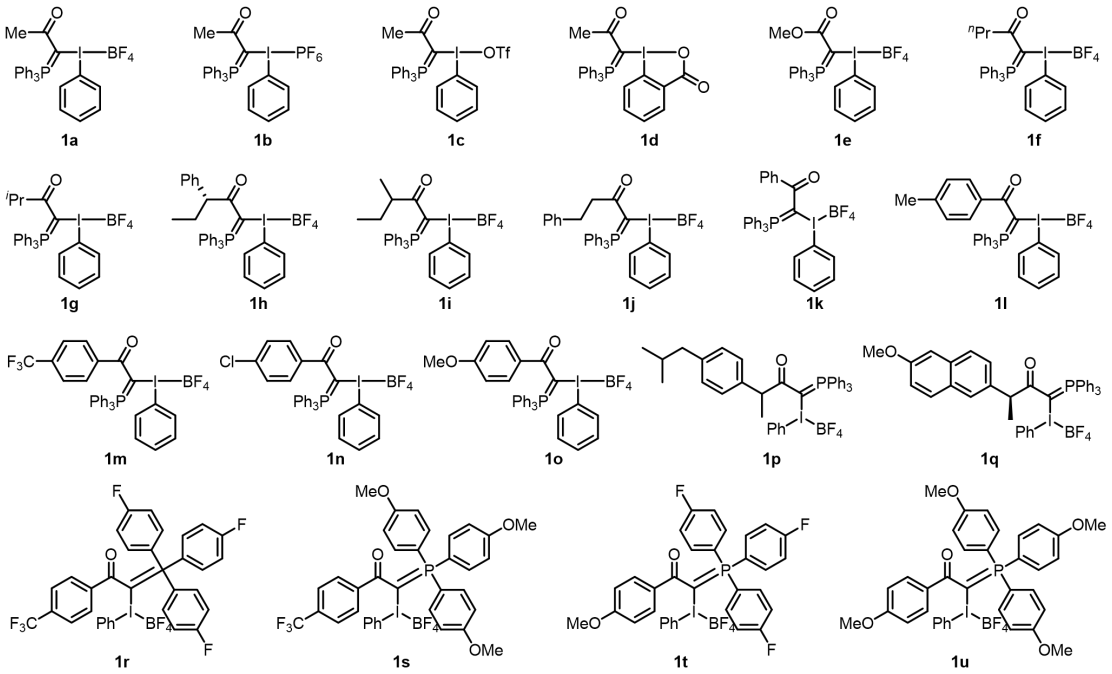
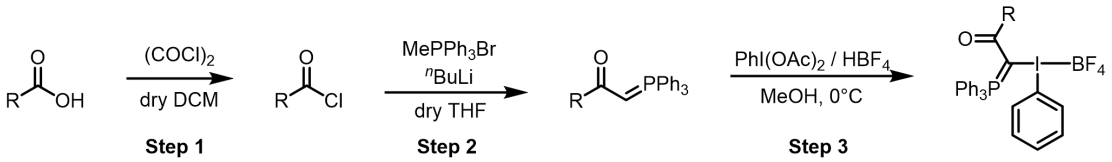


Figure S1. Hypervalent iodine reagents **1a-1w**

Hypervalent iodine reagents **1a-1i**, **1k-1m** are known compounds and synthesized according to our previous reported procedures[1]. Reagents **1n-1o, 1r-1u** were synthesized from substituted 2-bromoethanone according to our previous reported procedures[1]. Reagents **1j, 1p-1q** were synthesized from aicd.

General procedure for synthesized reagents 1j, 1p-1q:



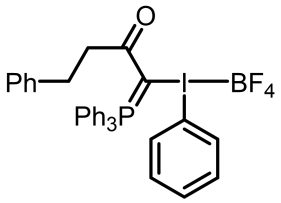
Step 1: According to the literature procedures[2]. The acid (5 mmol, 1.0 equiv) was dissolved in anhydrous DCM (10 mL) and DMF (a few drops) added. Oxalyl chloride (10 mmol, 2.0 equiv) was added dropwise to the solution after cooling with ice water. The resulting mixture was allowed to stir at room temperature for an additional six hours and the solvent was evaporated to afford the crude acyl chloride, which was used directly in the next step.

Step 2: According to the literature procedures[3]. The $MePPh_3Br$ (11.0 mmol, 2.1 equiv) in dry THF (50 mL) was treated with n-BuLi (12 mmol, 1.6 M solution in hexane, 2.2 equiv) and the resulting mixture was stirred for 30 min at 0 °C. To the above reaction mixture was added a solution of the corresponding acyl chloride (5.0 mmol, 1.0 equiv)

in THF (6 mL), the reaction was allowed to warm to room temperature and stirred overnight. Water was added then the mixture was extracted with EA. The organic layer was washed with brine and dried with anhydrous Na_2SO_4. Evaporation of the solvent afforded the crude phosphorus ylide which was used without further purification.

Step 3: While stirring, the solution of $PhI(OAc)_2$ (4 mmol) and HBF_4 (48% w/w) (4 mmol) in MeOH (4 mL) was added dropwise to the ice bath-cooled solution of ylide (5 mmol) in MeOH (4 mL) for 20 min. During the addition process, a large amount of precipitate was formed. After complete addition, the reaction mixture was stirred at 0 °C for 1.0 h. After filtration, the precipitate was washed with Et_2O (5 mL × 3), recrystallized from DCM/Et_2O, and dried under vacuum to give corresponding substrates.

4-phenyl-1-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-1-(triphenyl-λ^5-phosphanylidene)butan-2-one (1j)



1j

Prepared as a white solid in 46% yield (three-steps).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (t, J = 7.6 Hz, 3H), 7.62 – 7.51 (m, 8H), 7.50 – 7.40 (m, 6H), 7.39 – 7.29 (m, 6H), 7.24 (d, J = 7.2 Hz, 2H), 3.33 – 3.10 (m, 2H), 2.87 (t, J = 7.0 Hz, 2H).

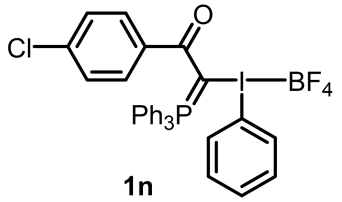
^{13}C NMR (101 MHz, DMSO-d_6) δ 192.7 (d, J = 5.0 Hz), 141.5, 133.5 (d, J = 10.3 Hz), 133.4, 131.9, 131.2, 131.0, 129.9 (d, J = 11.6 Hz), 129.3 (d, J = 12.6 Hz), 128.8, 128.4, 125.1 (d, J = 199.2 Hz), 123.2, 119.2 (d, J = 2.9 Hz), 44.1 (d, J = 102.6 Hz), 31.0.

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.20.

^{31}P NMR (162 MHz, DMSO-d_6) δ 26.02.

^{11}B NMR (128 MHz, DMSO-d_6) δ -1.19.

1-(4-chlorophenyl)-2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-2-(triphenyl-λ^5-phosphanylidene)ethan-1-one (1n)



1n

Prepared as a white solid in 65% yield (two-steps)[1].

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 – 7.72 (m, 5H), 7.69 – 7.55 (m, 15H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H).

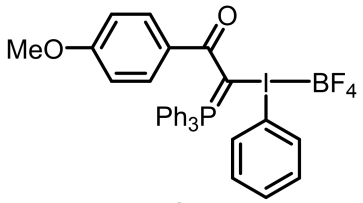
^{13}C NMR (101 MHz, DMSO-d_6) δ 189.9, 138.8 (d, J = 8.7 Hz), 134.8, 133.71, 133.67, 133.6, 132.1, 131.5, 131.4, 129.6, 129.5 (d, J = 12.7 Hz), 128.4, 123.10 (d, J = 92.7 Hz), 119.4 (d, J = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -148.24.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.12.

^{11}B NMR (128 MHz, $CDCl_3$) δ -1.22.

1-(4-methoxyphenyl)-2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-2-(triphenyl-λ^5-phosphanylidene)ethan-1-one (1o)



1o

Prepared as a white solid in 72% yield (two-steps)[1].

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 – 7.71 (m, 5H), 7.68 – 7.54 (m, 13H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7 .6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H).

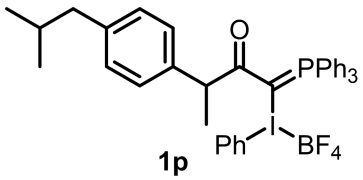
^{13}C NMR (101 MHz, DMSO-d_6) δ 190.4 (d, J = 5.6 Hz), 160.9, 133.7 (d, J = 10.3 Hz), 133.6 (d, J = 3.1 Hz), 132.1, 131.9 (d, J = 8.6 Hz), 131.43, 131.36, 129.9, 129.4 (d, J = 12.7 Hz), 123.6 (d, J = 92.9 Hz), 119.7 (d, J = 2.8 Hz), 113.5, 55.4

^{19}F NMR (376 MHz, $CDCl_3$) δ -148.20.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.26.

^{11}B NMR (128 MHz, $CDCl_3$) δ -1.18.

3-(4-isobutylphenyl)-1-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-1-(triphenyl-λ^5-phosphanylidene)butan-2-one (1p)



Prepared as a white solid in 40% yield (three-steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, J = 7.6 Hz, 4H), 7.50 – 7.28 (m, 14H), 7.19 (d, J = 7.6 Hz, 2H), 7.11 – 6.88 (m, 4H), 2.50 – 2.34 (m, 2H), 1.88 – 1.77 (m, 1H), 1.33 (d, J = 7.2 Hz, 3H), 1.26 – 1.22 (m, 1H), 0.90 (t, J = 6.8 Hz, 6H).

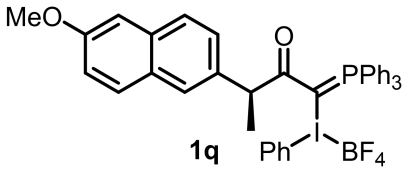
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 140.9, 137.5, 133.67, 133.6, 131.4, 130.9, 130.0, 129.5 (d, J = 12.9 Hz), 127.8, 123.2 (d, J = 94.0 Hz), 65.9, 46.8 (d, J = 5.5 Hz), 45.0, 30.3, 22.5.

^{19}F NMR (376 MHz, DMSO-d_6) δ -149.38.

^{31}P NMR (162 MHz, DMSO-d_6) δ 29.01.

^{11}B NMR (128 MHz, DMSO-d_6) δ -0.86.

(*S*)-3-(6-methoxynaphthalen-2-yl)-1-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-1-(triphenyl-λ^5-phosphanylidene)butan-2-one (1q)



Prepared as a white solid in 43% yield (three-steps).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.0 Hz, 1H), 7.81 – 7.65 (m, 6H), 7.62 – 7.51 (m, 7H), 7.51 – 7.39 (m, 7H), 7.38 – 7.30 (m, 1H), 7.23 – 7.09 (m, 2H), 6.68 (t, J = 7.6 Hz, 1H), 6.35 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H), 3.36 (q, J = 6.8 Hz, 1H), 1.35 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 194.2 (d, J = 4.7 Hz), 157.3, 137.3, 137.2, 133.6, 133.5, 133.4, 131.3, 130.7, 129.9, 129.4, 129.25, 129.17, 129.0, 128.9, 128.8, 127.8, 126.3 (d, J = 21.5 Hz), 123.7 (d, J = 93.0 Hz), 105.8, 65.0, 55.3, 46.2, 42.7 (d, J = 102.4 Hz).

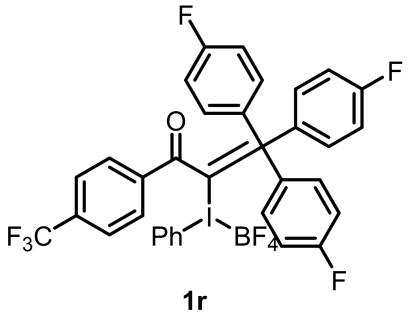
^{19}F NMR (376 MHz, DMSO-d_6) δ -148.19.

^{31}P NMR (162 MHz, DMSO-d_6) δ 25.73.

^{11}B NMR (128 MHz, DMSO-d_6) δ -1.23.

3,3,3-tris(4-fluorophenyl)-2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-1-(4-(trifl

uoromethyl)phenyl)-3λ^5-prop-2-en-1-one (1s)



1r

Prepared as a white solid in 58% yield (two-steps)[1].

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 – 7.89 (m, 4H), 7.84 – 7.69 (m, 6H), 7.63 – 7.50 (m, 7H), 7.50 – 7.37 (m, 4H).

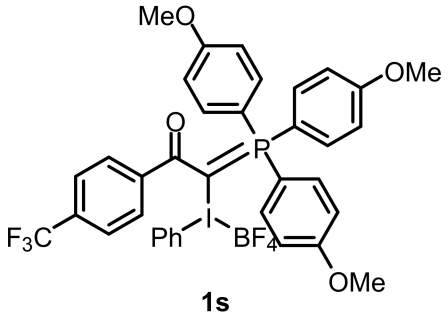
^{13}C NMR (101 MHz, DMSO-d_6) δ 190.1 (d, J = 4.7 Hz), 166.7 (d, J = 3.5 Hz), 164.2 (d, J = 3.3 Hz), 144.1 (d, J = 9.1 Hz), 136.9 (dd, J = 11.0, 11.0 Hz), 132.1, 131.6, 130.4 (q, J = 32.1 Hz), 128.5, 125.5, 124.0 (q, J = 272.6 Hz), 119.2, 119.0 (dd, J = 97.7, 3.2 Hz), 117.2 (dd, J = 22.1, 14.2 Hz), 46.9 (d, J = 102.2 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.25, -104.11, -148.22.

^{31}P NMR (162 MHz, DMSO-d_6) δ 24.76.

^{11}B NMR (128 MHz, DMSO-d_6) δ -1.11.

2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-1-(4-(trifluoromethyl)phenyl)-2-(tris(4-methoxyphenyl)- λ^5-phosphanylidene)ethan-1-one (1s)



1s

Prepared as a white solid in 63% yield (two-steps)[1].

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 – 7.82 (m, 4H), 7.64 – 7.49 (m, 7H), 7.48 – 7.41 (m, 2H), 7.40 – 7.30 (m, 2H), 7.27 – 7.09 (m, 6H), 3.86 (s, 9H).

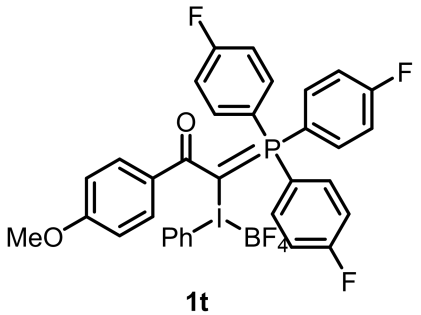
^{13}C NMR (101 MHz, DMSO-d_6) δ 189.6 (d, J = 6.1 Hz), 163.1 (d, J = 2.9 Hz), 144.9 (q, J = 10.2 Hz), 135.6 (d, J = 11.9 Hz), 131.8 (d, J = 2.8 Hz), 131.4, 129.9 (d, J = 34.0 Hz), 128.3, 125.4, 120.9 (q, J = 359.9 Hz), 115.1 (d, J = 13.8 Hz), 114.1 (d, J = 100.8 Hz), 55.7, 48.6 (d, J = 111.0 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.10, -148.23.

^{31}P NMR (162 MHz, DMSO-d_6) δ 24.87.

^{11}B NMR (128 MHz, DMSO-d_6) δ -1.22.

1-(4-methoxyphenyl)-2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-2-(tris(4-fluorophenyl)- λ^5-phosphanylidene)ethan-1-one (1t)



1t

Prepared as a white solid in 67% yield (two-steps)[1].

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 – 7.65 (m, 8H), 7.62 – 7.49 (m, 7H), 7.46 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 3.84 (s, 3H).

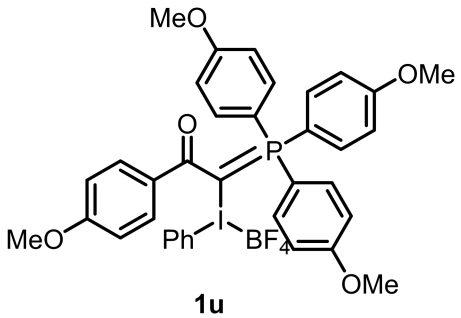
^{13}C NMR (101 MHz, DMSO-d_6) δ 190.5 (d, J = 4.9 Hz), 166.6 (d, J = 3.2 Hz), 164.0 (d, J = 3.3 Hz), 161.1, 136.8 (dd, J = 11.1, 10.4 Hz), 132.1, 131.7 (d, J = 8.7 Hz), 131.5, 130.0, 119.71 (dd, J = 97.5, 3.3 Hz), 119.67 (d, J = 2.7 Hz), 117.1 (dd, J = 21.9, 14.2 Hz),113.6, 55.5, 45.2 (d, J = 105.1 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -104.42, -148.17.

^{31}P NMR (162 MHz, DMSO-d_6) δ 24.82.

^{11}B NMR (128 MHz, DMSO-d_6) δ -1.11.

1-(4-methoxyphenyl)-2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-2-(tris(4-methoxyphenyl)- λ^5-phosphanylidene)ethan-1-one (1u)



1u

Prepared as a white solid in 61% yield (two-steps)[1].

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, J = 8.8 Hz, 2H), 7.75 (dd, J = 12.8, 8.8 Hz, 6H), 7.30 (dd, J = 8.8, 2.8 Hz, 6H), 7.13 (d, J = 8.8 Hz, 2H), 5.92 (d, J = 13.2 Hz, 2H), 3.89 (s, 12H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 190.7 (d, J = 6.2 Hz), 164.5, 163.9 (d, J = 2.9 Hz), 135.7 (d, J = 12.2 Hz), 131.7, 128.4 (d, J = 6.1 Hz), 115.7 (d, J = 14.0 Hz), 114.2,

110.7, 109. 8, 55.9, 35.2 (d, J = 63.0 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.19.

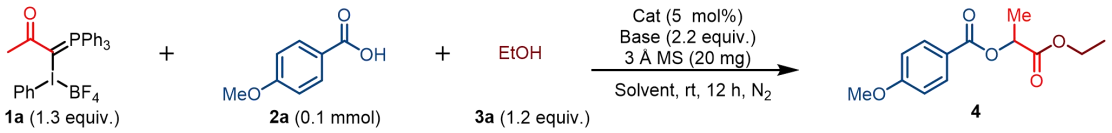
^{31}P NMR (162 MHz, DMSO-d_6) δ 19.04.

^{11}B NMR (128 MHz, DMSO-d_6) δ -1.19.

3. Reaction Optimization

3.1 Reaction Optimization for the formation of 4

Table S1. Optimization of Phosphonium-iodonium ylides, bases, catalysts and solvents.

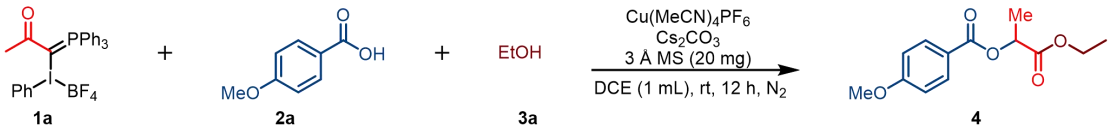


Entry[a]	1	Base	Catalyst	Solvent	Yield[b]
1	1a	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	75%
2	1a	Cs_2CO_3	-	DCE	< 10%
3	1a	Cs_2CO_3	*hv*	DCE	trace
4	1b	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	28%
5	1c	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	42%
6	1d	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	NR
7	1e	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	NR
8[c]	1a	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	53%
9[d]	1a	Cs_2CO_3	$Cu(MeCN)_4PF_6$	DCE	41%
10	1a	Cs_2CO_3	$Cu(MeCN)_4BF_4$	DCE	66%
11	1a	Cs_2CO_3	CuCl	DCE	75%
12	1a	Cs_2CO_3	CuBr	DCE	73%
13	1a	Cs_2CO_3	CuI	DCE	66%
14	1a	Cs_2CO_3	CuOTf	DCE	64%
15	1a	Cs_2CO_3	CuCN	DCE	84% (79%)[e]
16	1a	Cs_2CO_3	CuOAc	DCE	71%
17	1a	Cs_2CO_3	Cu_2O	DCE	< 10%
18	1a	Cs_2CO_3	$Cu(phen)Cl_2$	DCE	53%
19	1a	Cs_2CO_3	$CuCl_2$	DCE	39%
20	1a	Cs_2CO_3	$CuBr_2$	DCE	71%
21	1a	Cs_2CO_3	$Cu(OTf)_2$	DCE	53%
22	1a	Cs_2CO_3	$Cu(hfacac)_2$	DCE	60%
23	1a	Cs_2CO_3	$Cu(acac)_2$	DCE	trace
24	1a	Cs_2CO_3	$Rh_2(OAc)_4$	DCE	10%
25	1a	Cs_2CO_3	$Rh_2(cap)_4$	DCE	14%
26	1a	Cs_2CO_3	Rh_2(*S*-TFTPA)$_4$	DCE	42%
27	1a	Cs_2CO_3	Rh_2(*S*-DOSP)$_4$	DCE	46%
28	1a	Cs_2CO_3	$FeCl_2$	DCE	< 10%
29	1a	Cs_2CO_3	$Fe(OTf)_3$	DCE	20%
30	1a	Cs_2CO_3	AgOTf	DCE	< 10%
31	1a	Cs_2CO_3	$(Ph_3P)AuCl$	DCE	< 10%

Entry[a]	1	Base	Catalyst	Solvent	Yield[b]
32	**1a**	Cs_2CO_3	$Zn(OTf)_2$	DCE	< 10%
33	**1a**	Cs_2CO_3	$Ni(OTf)_2$	DCE	NR
34	**1a**	Cs_2CO_3	$CoBr_2$	DCE	13%
35	**1a**	Na_2CO_3	CuCN	DCE	61%
36	**1a**	K_2CO_3	CuCN	DCE	49%
37	**1a**	Li_2CO_3	CuCN	DCE	< 10%
38	**1a**	$NaHCO_3$	CuCN	DCE	< 10%
39	**1a**	K_3PO_4	CuCN	DCE	29%
40	**1a**	KH_2PO_4	CuCN	DCE	NR
41	**1a**	$KOBu^t$	CuCN	DCE	26%
42	**1a**	NaOAc	CuCN	DCE	16%
43	**1a**	Et_3N	CuCN	DCE	32%
44	**1a**	Cs_2CO_3	CuCN	DCM	48%
45	**1a**	Cs_2CO_3	CuCN	$CHCl_3$	42%
46	**1a**	Cs_2CO_3	CuCN	Et_2O	22%
47	**1a**	Cs_2CO_3	CuCN	$MeOBu^t$	50%
48	**1a**	Cs_2CO_3	CuCN	Dioxane	37%
49	**1a**	Cs_2CO_3	CuCN	THF	57%
50	**1a**	Cs_2CO_3	CuCN	EA	30%
51	**1a**	Cs_2CO_3	CuCN	PhCl	34%
52	**1a**	Cs_2CO_3	CuCN	PhF	44%
53	**1a**	Cs_2CO_3	CuCN	PhMe	44%
54	**1a**	Cs_2CO_3	CuCN	1,2-Dichlorobenzene	54%

[a] The reactions were carried out in a 0.1 mmol scale, using **1** (1.3 equiv.), **2a** (1.0 equiv.) and **3a** (1.2 equiv.), base (2.2 equiv.), catalyst (5 mol%), solvent (1 mL), at 26 ℃ under N_2 atmosphere for 12 hours. [b] Yields are determined by GC analysis, used *n*-dodecane as the internal standard. [c] NO 3Å MS. [d] At air state, without nitrogen protection. [e] The yield data in parentheses refers to the isolated yield.

Table S2. Optimization of material ratio.



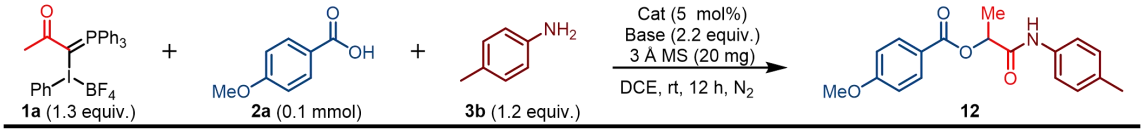
Entry[a]	1a (eq.)	2a (eq.)	3a (eq.)	Cat (mol%)	Cs_2CO_3 (eq.)	Yield[b]
1	1.0	1.0	1.2	5	2.2	47%
2	1.1	1.0	1.2	5	2.2	56%
3	1.2	1.0	1.2	5	2.2	77%
4	1.4	1.0	1.2	5	2.2	73%
5	1.3	1.1	1.0	5	2.2	56%
6	1.3	1.2	1.0	5	2.2	57%
7	1.3	1.0	1.0	5	2.2	46%

Entry[a]	1a (eq.)	2a (eq.)	3a (eq.)	Cat (mol%)	Cs_2CO_3 (eq.)	Yield[b]
8	1.3	1.0	1.5	5	2.2	75%
9	1.3	1.0	1.2	5	1.5	70%
10	1.3	1.0	1.2	5	2.2	76%
11	1.3	1.0	1.2	5	2.5	74%
12	1.3	1.0	1.2	2	2.2	71%
13	1.3	1.0	1.2	10	2.2	78%

[a]The reactions were carried out in a 0.1 mmol scale, using **1** (1.3 equiv.), **2a** (1.0 equiv.) and **3a** (1.2 equiv.), base (2.2 equiv.), catalyst (5 mol%), solvent (1 mL), at 26 ℃ under N_2 atmosphere for 12 hours. [b] Yields are determined by GC analysis, used *n*-dodecane as the internal standard.

3.2 Reaction Optimization for the formation of 12

Table S3. Optimization of bases and catalysts.

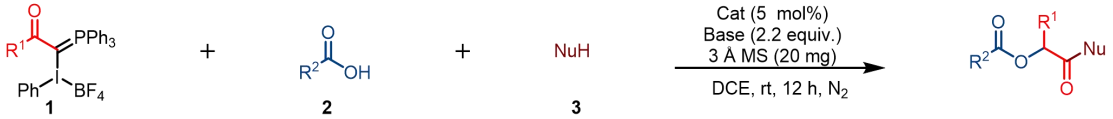


Entry[a]	catalyst	Base	Yield[b]
1	$Cu(MeCN)_4BF_4$	Cs_2CO_3	25%
2	CuCN	Cs_2CO_3	78%
3	CuCl	Cs_2CO_3	48%
4	CuBr	Cs_2CO_3	63%
5	CuOAc	Cs_2CO_3	74%
6	$CuBr_2$	Cs_2CO_3	59%
7	CuCN	Na_2CO_3	90% (86%)[c]
8	CuCN	K_2CO_3	79%
9	CuCN	Li_2CO_3	11%
10	CuCN	K_3PO_4	18%

[a] The reactions were carried out in a 0.1 mmol scale, using **1** (1.3 equiv.), **2a** (1.0 equiv.) and **3b** (1.2 equiv.), base (2.2 equiv.), catalyst (5 mol%), solvent (1 mL), at 26 ℃ under N_2 atmosphere for 12 hours. [b] Yields are determined by GC analysis, used *n*-dodecane as the internal standard. [c] The yield data in parentheses refers to the isolated yield.

3. General Procedure and Characterization of Products

3.1 General procedure for the synthesis of peoducts



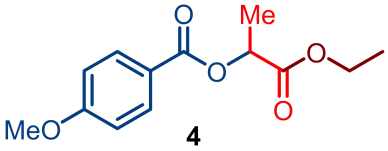
General procedure A (amines as nucleophile): Phosphonium-iodonium ylides **1** (0.13 mmol, 1.3 equiv.), acid **2** (0.1 mmol, 1.0 equiv.), Amine nucleophile (0.12 mmol, 1.2 equiv. If amine is a solid), CuCN (0.5 mg, 0.005 mmol, 5 mol%), Na_2CO_3 (23.3 mg, 0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then Amine nucleophile (0.12 mmol, 1.2 equiv. If amine is a liquid) and Dry DCE (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

General procedure B (hydroxyls as nucleophile): Phosphonium-iodonium ylides **1** (0.13 mmol, 1.3 equiv.), acid **2** (0.1 mmol, 1.0 equiv.), Oxygen nucleophile (0.12 mmol, 1.2 equiv. If oxygen nucleophile is a solid), CuCN (0.5 mg, 0.005 mmol, 5 mol%), Cs_2CO_3 (71.2 mg, 0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then Oxygen nucleophile (0.12 mmol, 1.2 equiv. If oxygen nucleophile is a liquid) and Dry DCE (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

General procedure C (thiohydroxyls as nucleophile): Phosphonium-iodonium ylides **1** (0.13 mmol, 1.3 equiv.), acid **2** (0.1 mmol, 1.0 equiv.), Sulfur nucleophile (0.12 mmol, 1.2 equiv. If Sulfur nucleophile is a solid), $Cu(MeCN)_4BF_4$ (1.9 mg, 0.005 mmol, 5 mol%), Na_2CO_3 (23.3 mg, 0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then Sulfur nucleophile (0.12 mmol, 1.2 equiv. If Sulfur nucleophile is a liquid) and Dry DCE (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

3.2 Characterization of Product

1-ethoxy-1-oxopropan-2-yl 4-methoxybenzoate (**4**)



4

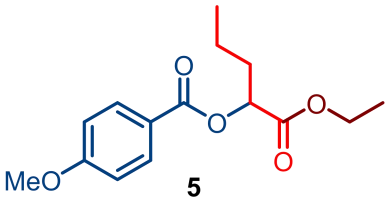
Prepared according to the **general procedure B**, White solid (19.9 mg, 79% yield), R_f = 0.28 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.27 (q, J = 7.2 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.60 (d, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 165.8, 163.8, 132.1, 122.0, 113.8, 69.0, 61.4, 55.6, 17.2, 14.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{13}H_{17}O_5]^+$ m/z: 253.1071, found, 253.1070.

1-ethoxy-1-oxopentan-2-yl 4-methoxybenzoate **(5)**



5

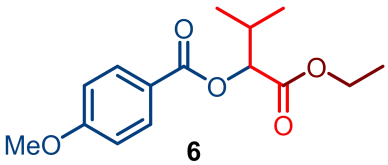
Prepared according to the **general procedure B**, White solid (22.5 mg, 81% yield), R_f = 0.29 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dt, J = 8.8, 2.4 Hz, 2H), 6.92 (dt, J = 8.8, 2.4 Hz, 2H), 5.18 (dd, J = 7.6, 5.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.00 – 1.89 (m, 2H), 1.59 – 1.48 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 166.0, 163.8, 132.0, 122.1, 113.8, 72.6, 61.4, 55.6, 33.4, 18.7, 14.3, 13.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{21}O_5]^+$ m/z: 281.1384, found, 281.1383.

1-ethoxy-3-methyl-1-oxobutan-2-yl 4-methoxybenzoate (**6**)



6

Prepared according to the **general procedure B**, White solid (15.2 mg, 54% yield), R_f

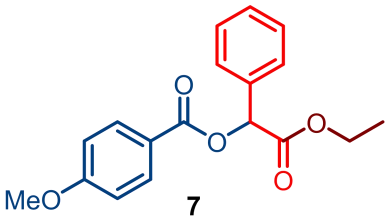
= 0.29 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 4.4 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 2.42 – 2.29 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.13 – 1.04 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 166.1, 163.8, 132.0, 122.2, 113.8, 61.2, 55.6, 30.5, 19.1, 17.6, 14.3.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{21}O_5]^+$ m/z: 281.1384, found, 281.1381.

2-ethoxy-2-oxo-1-phenylethyl 4-methoxybenzoate (**7**)



7

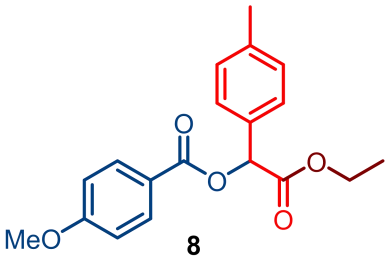
Prepared according to the **general procedure B**, White solid (22.5 mg, 72% yield), R_f = 0.16 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 6.0 Hz, 2H), 7.47 – 7.37 (m, 3H), 6.93 (d, J = 8.4 Hz, 2H), 6.12 (s, 1H), 4.30 – 4.13 (m, 2H), 3.86 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 165.7, 163.9, 134.4, 132.2, 129.2, 128.9, 127.7, 121.8, 113.8, 74.9, 61.8, 55.6, 14.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{18}H_{18}O_5Na]^+$ m/z: 337.1046, found, 337.1044.

2-ethoxy-2-oxo-1-(*p*-tolyl)ethyl 4-methoxybenzoate (**8**)



8

Prepared according to the **general procedure B**, Colorless oil (22.8 mg, 70% yield), R_f = 0.18 (PE/EA = 10/1).

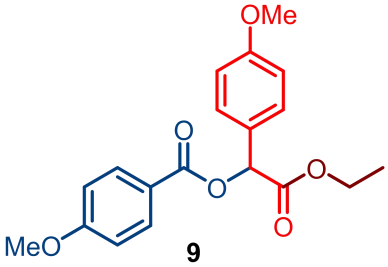
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.08 (s, 1H), 4.29 – 4.12 (m, 2H), 3.86 (s, 3H), 2.38 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 165.8, 163.9, 139.2, 132.2, 131.5, 129.6, 127.7,

121.9, 113.8, 74.8, 61.7, 55.6, 21.4, 14.2.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{19}H_{20}O_5Na]^+$ m/z: 351.1203, found, 351.1200.

2-ethoxy-1-(4-methoxyphenyl)-2-oxoethyl 4-methoxybenzoate (**9**)



9

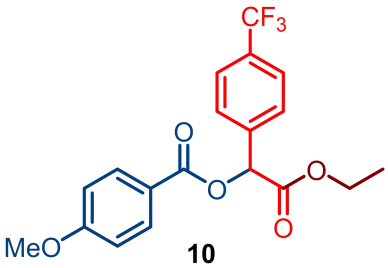
Prepared according to the **general procedure B**, White solid (21.9 mg, 65% yield), R_f = 0.16 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, J = 8.8, 2.4 Hz, 2H), 7.49 (dt, J = 8.8, 2.4 Hz, 2H), 6.97 – 6.89 (m, 4H), 6.06 (s, 1H), 4.29 – 4.11 (m, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 165.8, 163.9, 160.4, 132.2, 129.2, 126.5, 121.9, 114.3, 113.8, 74.6, 61.7, 55.6, 55.4, 14.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{21}O_6]^+$ m/z: 345.1333, found, 345.1332.

2-ethoxy-2-oxo-1-(4-(trifluoromethyl)phenyl)ethyl 4-methoxybenzoate **(10)**



10

Prepared according to the **general procedure B**, Colorless oil (20.3 mg, 53% yield), R_f = 0.18 (PE/EA = 10/1).

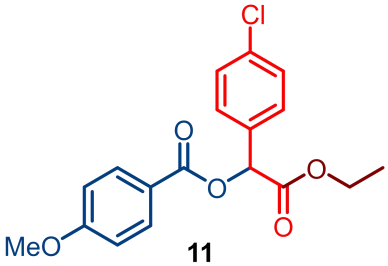
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.73 (q, J = 8.4 Hz, 4H), 7.00 – 6.94 (m, 2H), 6.20 (s, 1H), 4.33 – 4.16 (m, 2H), 3.89 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.5, 164.1, 138.3, 132.2, 131.4 (q, J = 32.6 Hz), 128.0, 125.9 (q, J = 3.8 Hz), 124.0 (q, J = 272.2 Hz), 121.4, 113.9, 74.1, 62.2, 55.6, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{19}H_{17}F_3O_5Na]^+$ m/z: 405.0920, found, 405.0917.

1-(4-chlorophenyl)-2-ethoxy-2-oxoethyl 4-methoxybenzoate (**11**)



11

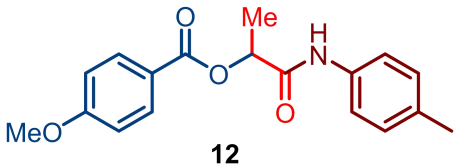
Prepared according to the **general procedure B**, Colorless oil (23.7 mg, 68% yield), R_f = 0.18 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dt, J = 8.8, 2.4 Hz, 2H), 7.52 (dt, J = 8.8, 2.4 Hz, 2H), 7.40 (dt, J = 8.8, 2.4 Hz, 2H), 6.94 (dt, J = 8.8, 2.4 Hz, 2H), 6.08 (s, 1H), 4.29 – 4.13 (m, 2H), 3.86 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 165.6, 164.0, 135.3, 133.0, 132.2, 129.2, 129.1, 121.6, 113.9, 74.1, 62.0, 55.6, 14.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C18H17ClO5Na]^+$ m/z: 371.0657, found, 371.0655.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-methoxybenzoate (**12**)



12

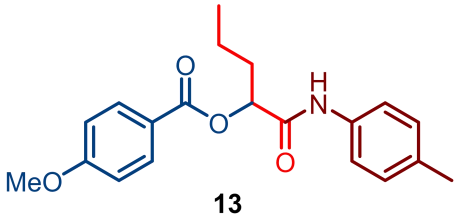
Prepared according to the **general procedure A**, White solid (23.7 mg, 86% yield), R_f = 0.31 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 5.54 (q, J = 6.8 Hz, 1H), 3.86 (s, 3H), 2.30 (s, 3H), 1.65 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.2, 164.0, 134.6, 134.4, 131.9, 129.6, 121.6, 120.3, 114.0, 71.0, 55.6, 20.9, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{18}H_{20}NO_4]^+$ m/z: 314.1387, found, 314.1384.

1-oxo-1-(*p*-tolylamino)pentan-2-yl 4-methoxybenzoate (**13**)



13

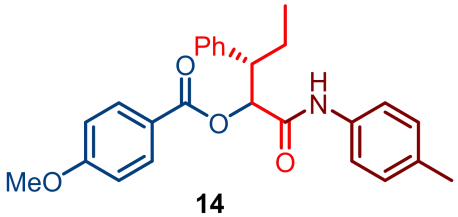
Prepared according to the **general procedure A**, White solid (24.0 mg, 71% yield), R_f = 0.34 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dt, J = 8.8, 2.4 Hz, 2H), 7.82 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.98 (dt, J = 8.8, 2.4 Hz, 2H), 5.53 (t, J = 6.0 Hz, 1H), 3.89 (s, 3H), 2.30 (s, 3H), 2.09 – 2.01 (m, 2H), 1.57 – 1.47 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 165.3, 164.2, 134.6, 132.0, 129.6, 121.6, 120.3, 114.1, 74.4, 55.7, 34.1, 21.0, 18.5, 13.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{20}H_{24}NO_4]^+$ m/z: 342.1700, found, 342.1697.

(3*S*)-1-oxo-3-phenyl-1-(*p*-tolylamino)pentan-2-yl 4-methoxybenzoate (**14**)



14

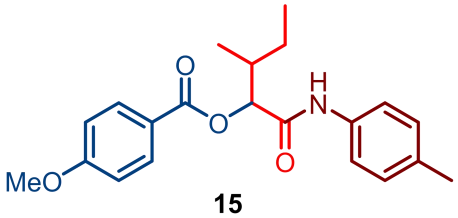
Prepared according to the **general procedure A**, Colorless oil (24.9 mg, 60% yield, d.r. 1:1), R_f = 0.29 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.97 (d, J = 8.8 Hz, 2H*), 7.92 (d, J = 8.8 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 7.10 – 7.06 (m, 1H), 7.00 – 6.94 (m, 3H), 6.92 – 6.87 (m, 2H), 5.70 (d, J = 4.4 Hz, 1H*), 5.50 (d, J = 5.6 Hz, 1H), 3.82 (s, 3H*), 3.81 (s, 3H), 3.38 – 3.31 (m, 1H*), 3.30 – 3.23 (m, 1H), 2.20 (s, 3H*), 2.19 (s, 3H), 2.06 – 1.80 (m, 3H), 0.84 (t, J = 7.3 Hz, 3H*), 0.79 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 166.9, 165.09, 165.06, 164.2, 164.1, 139.7, 139.2, 134.7, 134.6, 134.2, 133.9, 132.1, 132.0, 129.49, 129.45, 129.0, 128.8, 128.7, 128.5, 127.4, 127.3, 121.6, 121.4, 121.0, 120.6, 114.2, 114.1, 77.9, 55.69, 55.67, 49.7, 49.4, 24.6, 23.2, 21.0, 12.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{26}H_{28}NO_4]^+$ m/z: 418.2013, found, 418.2010.

3-methyl-1-oxo-1-(*p*-tolylamino)pentan-2-yl 4-methoxybenzoate (**15**)



15

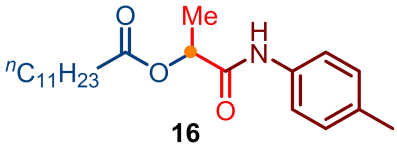
Prepared according to the **general procedure A**, Colorless oil (26.8 mg, 76% yield, d.r. 1.7:1), R_f = 0.31 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 8.11 – 8.04 (m, 2H), 7.76 (s, 1H), 7.75 (s, 1H*), 7.41 – 7.35 (m, 2H), 7.13 – 7.08 (m, 2H), 7.01 – 6.97 (m, 2H), 5.58 (d, J = 3.6 Hz, 1H*), 5.45 (d, J = 3.6 Hz, 1H), 3.89 (s, 3H*), 3.88 (s, 3H), 2.30 (s, 3H), 1.76 – 1.63 (m, 1H), 1.54 – 1.27 (m, 2H), 1.09 (d, J = 6.8 Hz, 1H*), 1.05 (d, J = 6.8 Hz, 1H), 1.00 – 0.95 (m, 2H),

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 167.3, 165.3, 165.1, 164.2, 164.1, 134.60, 134.56, 134.44, 134.39, 132.0, 129.6, 121.60, 121.56, 120.42, 120.36, 114.20, 114.16, 78.2, 76.7, 55.69, 55.68, 37.7, 37.5, 26.3, 24.5, 21.0, 15.5, 14.4, 11.9, 11.7.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{26}NO_4]^+$ m/z: 356.1856, found,356.1855.

1-oxo-1-(*p*-tolylamino)propan-2-yl dodecanoate (**16**)



16

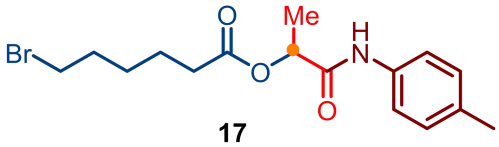
Prepared according to the **general procedure A**, Yellow solid (33.8 mg, 94% yield), R_f = 0.35 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.34 (q, J = 6.8 Hz, 1H), 2.44 (t, J = 7.6 Hz, 2H), 2.32 (s, 3H), 1.73 – 1.63 (m, 3H), 1.54 (d, J = 6.8 Hz, 3H), 1.33 – 1.21 (m, 14H), 0.88 (t, J = 6.8 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 168.5, 134.5, 129.6, 120.2, 70.7, 34.5, 32.0, 29.7, 29.6, 29.5, 29.43, 29.37, 29.2, 25.0, 22.8, 21.0, 17.9, 14.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{22}H_{36}NO_3]^+$ m/z: 362.2690, found, 362.2687.

1-oxo-1-(*p*-tolylamino)propan-2-yl 6-bromohexanoate (**17**)



17

Prepared according to the **general procedure A**, Light yellow oil (29.7 mg, 84%

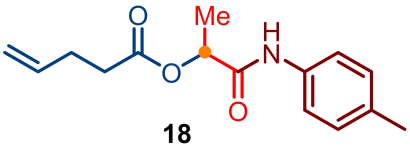
yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 5.32 (q, J = 6.8 Hz, 1H), 3.40 (t, J = 6.4 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.88 (p, J = 6.8 Hz, 2H), 1.71 (p, J = 7.2 Hz, 2H), 1.57 – 1.48 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 168.4, 134.6, 134.5, 129.6, 120.2, 70.9, 34.2, 33.5, 32.4, 27.6, 24.1, 21.0, 17.9.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{16}H_{22}BrNO_3Na]^+$ m/z: 378.0675, found, 378.0671.

1-oxo-1-(*p*-tolylamino)propan-2-yl pent-4-enoate (**18**)



18

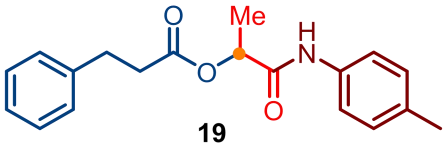
Prepared according to the **general procedure A**, Colorless oil (24.8 mg, 96% yield), R_f = 0.42 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.92 – 5.81 (m, 1H), 5.34 (q, J = 6.8 Hz, 1H), 5.16 – 5.01 (m, 2H), 2.56 (t, J = 7.2 Hz, 2H), 2.48 – 2.41 (m, 2H), 2.31 (s, 3H), 1.54 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 168.4, 136.4, 134.6, 134.5, 129.6, 120.3, 116.2, 70.9, 33.6, 28.8, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{20}NO_3]^+$ m/z: 262.1438, found, 262.1435.

1-oxo-1-(*p*-tolylamino)propan-2-yl 3-phenylpropanoate (**19**)



19

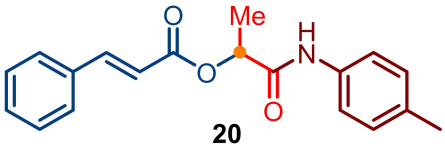
Prepared according to the **general procedure A**, Colorless oil (29.3 mg, 94% yield), R_f = 0.40 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.33 – 7.26 (m, 4H), 7.24 – 7.18 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 5.31 (q, J = 6.8 Hz, 1H), 3.02 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 2.32 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 168.3, 140.0, 134.6, 134.4, 129.6, 128.8, 128.3, 126.7, 120.4, 71.0, 36.0, 30.9, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_3]^+$ m/z: 312.1594, found, 312.1591.

1-oxo-1-(*p*-tolylamino)propan-2-yl cinnamate (**20**)



20

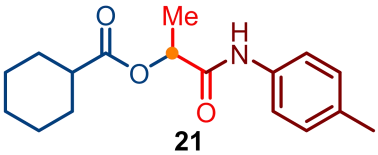
Prepared according to the **general procedure A**, White solid (20.5 mg, 66% yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.80 (d, J = 16.0 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.45 – 7.39 (m, 5H), 7.13 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 5.48 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.8, 146.9, 134.6, 134.0, 131.1, 129.7, 129.2, 128.4, 120.4, 117.0, 116.9, 71.0, 21.0, 18.0.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{20}NO_3]^+$ m/z: 310.1438, found, 310.1434.

1-oxo-1-(*p*-tolylamino)propan-2-yl cyclohexanecarboxylate (**21**)



21

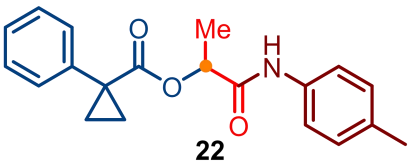
Prepared according to the **general procedure A**, Light yellow oil (23.3 mg, 81% yield), R_f = 0.32 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.44 – 7.36 (m, 2H), 7.17 – 7.09 (m, 2H), 5.33 (q, J = 6.0 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.32 (s, 3H), 2.02 – 1.94 (m, 2H), 1.86 – 1.75 (m, 2H), 1.57 – 1.47 (m, 5H), 1.38 – 1.23 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 168.4, 134.4, 129.6, 120.0, 70.4, 43.1, 29.0, 28.9, 25.6, 25.3, 25.3, 20.9, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{24}NO_3]^+$ m/z: 290.1751, found, 290.1747.

1-oxo-1-(*p*-tolylamino)propan-2-yl 1-phenylcyclopropane-1-carboxylate (**22**)



22

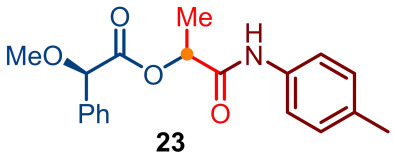
Prepared according to the **general procedure A**, Colorless oil (25.9 mg, 80% yield), R_f = 0.35 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 5H), 7.23 (s, 1H), 7.12 – 7.05 (m, 4H), 5.22 (q, J = 6.8 Hz, 1H), 2.30 (s, 3H), 1.78 – 1.72 (m, 1H), 1.66 – 1.60 (m, 1H), 1.50 (d, J = 6.8 Hz, 3H), 1.37 – 1.32 (m, 1H), 1.31 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 168.3, 139.4, 134.5, 134.2, 130.7, 129.5, 128.9, 127.9, 119.7, 71.5, 29.4, 21.0, 18.2, 17.8, 17.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{20}H_{22}NO_3]^+$ m/z: 324.1594, found, 324.1590.

1-oxo-1-(*p*-tolylamino)propan-2-yl (2*R*)-2-methoxy-2-phenylacetate (**23**)



23

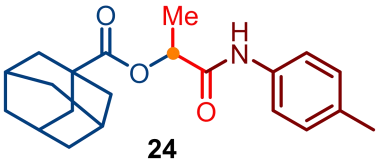
Prepared according to the **general procedure A**, Brown solid (13.8 mg, 42% yield, d.r. 1.3:1), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.57 – 7.36 (m, 5H), 7.23 (d, J = 8.4 Hz, 1H), 7.13 – 6.99 (m, 3H), 5.43 (q, J = 6.8 Hz, 1H), 5.34 (q, J = 6.8 Hz, 1H*), 4.92 (s, 1H*), 4.88 (s, 1H), 3.48 (s, 3H*), 3.45 (s, 3H), 2.31 (s, 3H*), 2.28 (s, 3H), 1.55 (d, J = 6.8 Hz, 3H), 1.50 (d, J = 6.8 Hz, 3H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 168.7, 167.9, 167.8, 136.0, 135.8, 134.6, 134.5, 134.4, 134.2, 129.6, 129.5, 129.4, 129.3, 129.2, 127.5 126.9, 120.1, 120.0, 82.9, 82.5, 71.4, 70.9, 57.8, 57.6, 21.01, 21.98, 17.9, 17.7.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_4]^+$ m/z: 328.1543, found, 328.1541.

1-oxo-1-(*p*-tolylamino)propan-2-yl adamantane-1-carboxylate (**24**)



24

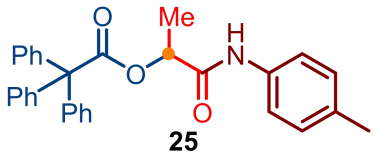
Prepared according to the **general procedure A**, Yellow solid (25.7 mg, 75% yield), R_f = 0.40 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.33 (q, J = 6.8 Hz, 1H), 2.32 (s, 3H), 2.011 – 2.05 (m, 6H), 1.99 – 1.90 (m, 6H), 1.82 – 1.69 (m, 7H), 1.53 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 168.6, 134.6, 134.5, 129.7, 120.0, 70.3, 40.9, 38.9, 36.5, 27.9, 21.0, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{28}NO_3]^+$ m/z: 342.2064, found, 342.2060.

1-oxo-1-(*p*-tolylamino)propan-2-yl 2,2,2-triphenylacetate (**25**)



25

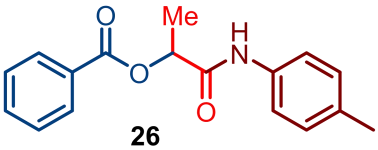
Prepared according to the **general procedure A**, Light yellow solid (36.6 mg, 82% yield), R_f = 0.41 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 15H), 7.01 – 6.94 (m, 5H), 5.41 (q, J = 6.8 Hz, 1H), 2.21 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 168.1, 142.4, 134.4, 134.2, 130.2, 129.4, 128.3, 127.5, 120.3, 71.9, 67.5, 21.0, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{30}H_{28}NO_3]^+$ m/z: 450.2064, found, 450.2061.

1-oxo-1-(*p*-tolylamino)propan-2-yl benzoate (**26**)



26

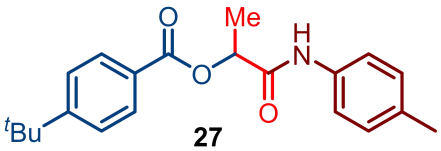
Prepared according to the **general procedure A**, White solid (24.7 mg, 88% yield), R_f = 0.50 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.06 (m, 2H), 7.95 (s, 1H), 7.76 – 7.31 (m, 5H), 7.19 – 7.04 (m, 2H), 5.60 (q, J = 7.2 Hz, 1H), 2.31 (s, 3H), 1.75 – 1.60 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.5, 134.6, 134.5, 133.9, 129.9, 129.7, 129.4, 128.9, 120.4, 71.5, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{18}NO_3]^+$ m/z: 284.1281, found, 284.1276.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-(*tert*-butyl)benzoate (**27**)



27

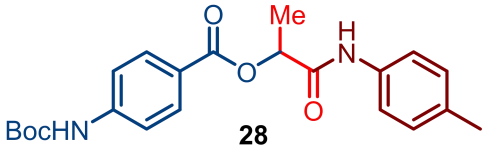
Prepared according to the **general procedure A**, Light yellow solid (31.2 mg, 93% yield), R_f = 0.58 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.98 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.60 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.67 (d, J = 6.8 Hz, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.4, 157.7, 134.5, 134.5, 129.8, 129.6, 126.5, 125.8, 120.3, 71.2, 35.3, 31.2, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{26}NO_3]^+$ m/z: 340.1907, found, 340.1902.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-((*tert*-butoxycarbonyl)amino)benzoate (**28**)



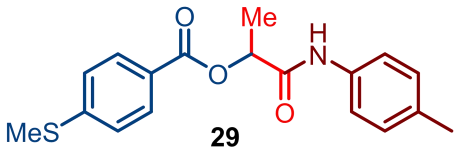
Prepared according to the **general procedure A**, White solid (37.5 mg, 95% yield), R_f = 0.35 (PE/EA = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.94 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 5.57 (q, J = 6.8 Hz, 1H), 2.30 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H), 1.53 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.0, 152.3, 143.7, 134.6, 134.5, 131.2, 129.6, 123.2, 120.3, 117.7, 81.5, 71.2, 28.4, 21.0, 17.9.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{22}H_{26}N_2O_5Na]^+$ m/z: 421.1734, found, 421.1730.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-(methylthio)benzoate (**29**)



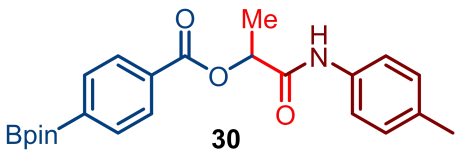
Prepared according to the **general procedure A**, Light yellow solid (12.6 mg, 38% yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.87 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.58 (q, J = 6.8 Hz, 1H), 2.54 (s, 3H), 2.31 (s, 3H), 1.67 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.2, 147.0, 134.6, 134.5, 130.1, 129.7, 125.2, 125.2, 120.3, 71.3, 21.0, 17.9, 14.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{18}H_{20}NO_3S]^+$ m/z: 330.1158, found, 330.1155.

1-oxo-1-(*p*-tolylamino)propan-2-yl
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**30**)



Prepared according to the **general procedure A**, White solid (33.8 mg, 83% yield), R_f = 0.37 (PE/EA = 5/1).

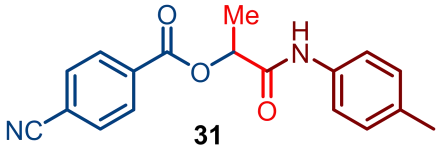
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 2H), 7.95 – 7.89 (m, 3H), 7.39 (d,

J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 5.59 (q, J = 6.8 Hz, 1H), 2.30 (s, 3H), 1.68 (d, J = 6.8 Hz, 3H), 1.36 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 165.5, 135.1, 134.6, 134.5, 131.4, 129.6, 128.8, 120.3, 84.4, 71.5, 25.0, 21.0, 17.9.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{23}H_{28}BNO_5Na]^+$ m/z: 432.1953, found, 432.1948.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-cyanobenzoate (**31**)



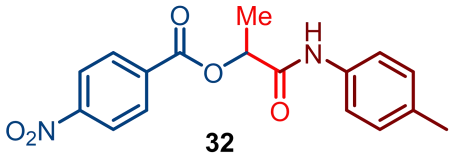
Prepared according to the **general procedure A**, Yellow solid (9.0 mg, 29% yield), R_f = 0.36 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 7.83 – 7.73 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.56 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.70 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 164.1, 134.9, 134.3, 133.2, 132.6, 130.4, 129.7, 120.3, 117.9, 117.3, 72.3, 21.0, 17.8.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{18}H_{16}N_2O_3Na]^+$ m/z: 331.1053, found, 331.1049.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-nitrobenzoate (**32**)



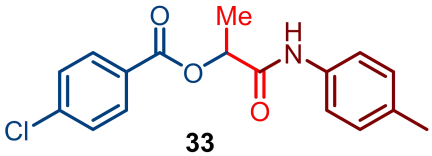
Prepared according to the **general procedure A**, White solid (19.8 mg, 60% yield), R_f = 0.40 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.24 (m, 4H), 7.74 (s, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.58 (q, J = 6.8 Hz, 1H), 2.32 (s, 3H), 1.74 – 1.70 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 163.9, 134.9, 134.7, 134.3, 131.1, 130.9, 129.8, 124.0, 120.3, 72.4, 21.0, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}N_2O_5]^+$ m/z: 329.1132, found, 329.1129.

1-oxo-1-(*p*-tolylamino)propan-2-yl 4-chlorobenzoate (**33**)



33

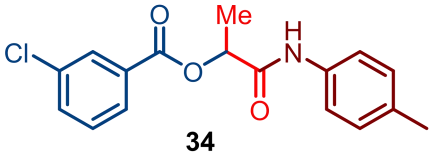
Prepared according to the **general procedure A**, Yellow solid (26.4 mg, 84% yield), R_f = 0.44 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.81 (s, 1H), 7.51 – 7.37 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 5.57 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.68 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 164.7, 140.5, 134.7, 134.5, 131.3, 129.7, 129.2, 127.8, 120.3, 71.7, 21.0, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}ClNO_3]^+$ m/z: 318.0892, found, 318.0888.

1-oxo-1-(*p*-tolylamino)propan-2-yl 3-chlorobenzoate (**34**)



34

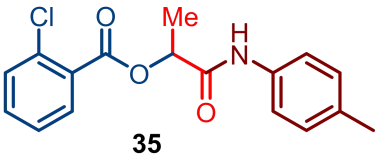
Prepared according to the **general procedure A**, Light brown solid (25.5 mg, 81% yield), R_f = 0.40 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.85 (s, 1H), 7.60 (d, J = 6.0 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.12 (d, J = 8.0 Hz, 2H), 5.57 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.69 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 164.4, 135.0, 134.7, 134.4, 133.9, 131.1, 130.2, 129.9, 129.7, 128.0, 120.4, 71.9, 21.0, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}ClNO_3]^+$ m/z: 318.0892, found, 318.0889.

1-oxo-1-(*p*-tolylamino)propan-2-yl 2-chlorobenzoate (**35**)



35

Prepared according to the **general procedure A**, Light yellow oil (23.9 mg, 76% yield), R_f = 0.22 (PE/EA = 10/1).

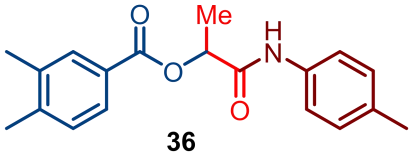
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.63 (q, J = 6.8 Hz, 1H), 2.34 (s, 3H), 1.72 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 164.6, 134.64, 134.59, 133.5, 133.1, 132.4,

131.3, 129.7, 129.6, 127.3, 120.1, 72.5, 21.0, 18.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}ClNO_3]^+$ m/z: 318.0892, found, 318.0888.

1-oxo-1-(*p*-tolylamino)propan-2-yl 3,4-dimethylbenzoate (**36**)



36

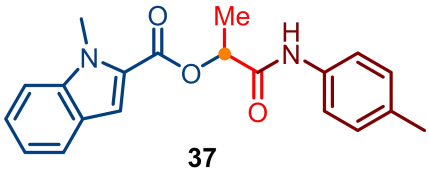
Prepared according to the **general procedure A**, White solid (27.5 mg, 89% yield), R_f = 0.25 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.79 – 7.72 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 5.49 (q, J = 6.8 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 1.58 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.7, 143.4, 137.3, 134.6, 134.5, 130.9, 130.0, 129.6, 127.4, 126.8, 120.3, 71.1, 21.0, 20.2, 19.8, 17.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_3]^+$ m/z: 312.1594, found, 312.1591.

1-oxo-1-(*p*-tolylamino)propan-2-yl 1-methyl-1*H*-indole-2-carboxylate (**37**)



37

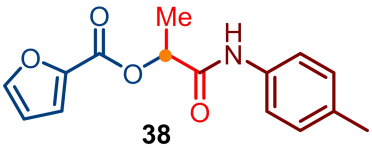
Prepared according to the **general procedure A**, White solid (14.3 mg, 42% yield), R_f = 0.45 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.46 – 7.39 (m, 5H), 7.22 – 7.18 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 5.61 (q, J = 6.8 Hz, 1H), 4.11 (s, 3H), 2.32 (s, 3H), 1.70 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 160.6, 140.2, 134.7, 134.5, 129.7, 126.6, 125.9, 125.8, 122.9, 121.2, 120.3, 110.9, 110.6, 70.8, 31.9, 21.0, 18.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{20}H_{20}N_2O_3Na]^+$ m/z: 359.1366, found, 359.1362.

1-oxo-1-(*p*-tolylamino)propan-2-yl furan-2-carboxylate (**38**)



38

Prepared according to the **general procedure A**, Yellow oil (15.0 mg, 55% yield), R_f

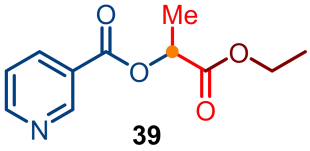
= 0.28 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.65 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 3.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.62 – 6.56 (m, 1H), 5.56 (q, J = 6.8 Hz, 1H), 2.32 (s, 3H), 1.67 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 157.1, 147.1, 143.9, 134.7, 134.5, 129.7, 120.3, 119.5, 112.5, 71.3, 21.0, 18.0.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{16}NO_4]^+$ m/z: 274.1074, found, 274.1072.

1-ethoxy-1-oxopropan-2-yl nicotinate (**39**)



39

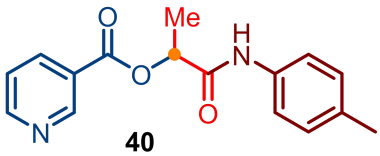
Prepared according to the **general procedure B**, White solid (11.6 mg, 52% yield), R_f = 0.24 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 – 8.51 (m, 2H), 8.34 (d, J = 7.6 Hz, 1H), 7.46 (s, 1H), 5.33 (q, J = 6.8 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.64 (d, J = 7.2 Hz, 3H), 1.28 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 164.9, 158.0, 156.1, 153.6, 151.1, 137.4, 69.7, 61.7, 17.1, 14.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{11}H_{14}NO_4]^+$ m/z: 224.0917, found, 224.0914.

1-oxo-1-(p-tolylamino)propan-2-yl nicotinate (**40**)



40

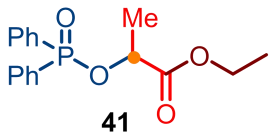
Prepared according to the **general procedure B**, Yellow oil (10.6 mg, 38% yield), R_f = 0.18 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 7.6 Hz, 1H), 7.87 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.59 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.92 (s, 1H), 1.71 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 134.8, 134.4, 129.7, 120.4, 72.0, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{16}H_{17}N_2O_3]^+$ m/z: 285.1234, found, 285.1234.

Ethyl 2-((diphenylphosphoryl)oxy)propanoate (**41**)



41

Prepared according to the **general procedure B**, White solid (15.4 mg, 48% yield), R_f = 0.18 (PE/EA = 2/1).

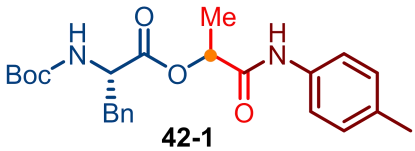
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 4H), 7.57 – 7.40 (m, 6H), 4.99 – 4.89 (m, 1H), 4.20 – 4.06 (m, 2H), 1.58 (d, J = 6.8 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 (d, J = 5.1 Hz), 132.0 (d, J = 10.4 Hz), 131.8 (d, J = 10.2 Hz), 128.7 (d, J = 8.0 Hz), 128.5 (d, J = 7.9 Hz), 69.5 (d, J = 5.4 Hz), 61.5, 20.1 (d, J = 3.2 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.03.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{20}O_4P]^+$ m/z: 319.1094, found, 319.1092.

1-oxo-1-(*p*-tolylamino)propan-2-yl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (**42-1**)



42-1

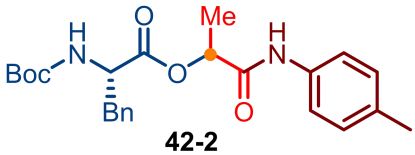
Prepared according to the **general procedure A**, Yellow oil (10.9 mg, 24% yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 5.32 (q, J = 6.8 Hz, 1H), 4.90 (d, J = 6.4 Hz, 1H), 4.54 (q, J = 6.4 Hz, 1H), 3.17 (d, J = 6.4 Hz, 2H), 2.31 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 168.4, 155.4, 135.9, 135.6, 134.1, 129.4, 129.19, 129.17, 127.7, 120.4, 81.0, 71.8, 55.1, 37.2, 28.4, 21.0, 18.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{24}H_{30}N_2O_5Na]^+$ m/z: 449.2047, found, 449.2043.

1-oxo-1-(*p*-tolylamino)propan-2-yl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (**42-2**)



42-2

Prepared according to the **general procedure A**, Yellow oil (9.0 mg, 20% yield), R_f = 0.33 (PE/EA = 5/1).

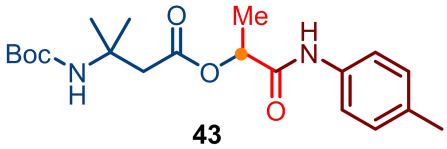
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.26 – 7.21 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.34 (q, J = 6.8 Hz, 1H), 5.07 (d, J

= 4.8 Hz, 1H), 4.39 (q, J = 7.2 Hz, 1H), 3.10 (d, J = 7.2 Hz, 2H), 2.32 (s, 3H), 1.41 (s, 9H), 1.31 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 168.4, 156.0, 135.5, 135.3, 134.0, 129.3, 129.0, 127.6, 120.5, 81.1, 70.8, 56.2, 37.4, 28.3, 21.0, 17.4.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{24}H_{30}N_2O_5Na]^+$ m/z: 449.2047, found, 449.2045.

1-oxo-1-(*p*-tolylamino)propan-2-yl
3-((*tert*-butoxycarbonyl)amino)-3-methylbutanoate (**43**)



43

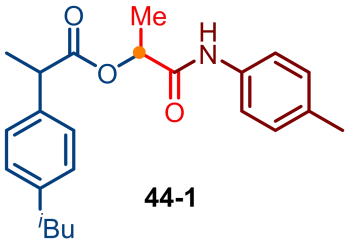
Prepared according to the **general procedure A**, Brown oil (34.1 mg, 91% yield), R_f = 0.30 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.44 (d, J = 8.4, 2H), 7.10 (d, J = 8.4, 2H), 5.31 (d, J = 6.8 Hz, 1H), 4.76 (s, 1H), 2.90 (d, J = 13.6 Hz, 1H), 2.83 (d, J = 13.6 Hz, H), 2.29 (s, 3H), 1.52 (d, J = 6.8 Hz, 3H), 1.42 – 1.35 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.5, 154.9, 134.7, 134.4, 129.5, 120.3, 79.6, 70.7, 51.4, 44.3, 28.5, 28.3, 28.1, 21.0, 17.9.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{20}H_{30}N_2O_5Na]^+$ m/z: 401.2047, found, 401.2042.

1-oxo-1-(*p*-tolylamino)propan-2-yl 2-(4-isobutylphenyl)propanoate (**44-1**)



44-1

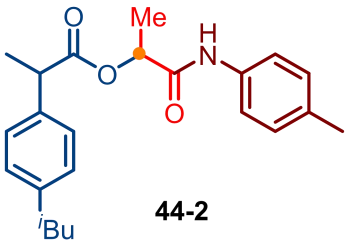
Prepared according to the **general procedure A**, Colorless oil (16.3 mg, 44% yield), R_f = 0.35 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.99 – 6.91 (m, 3H), 6.88 (d, J = 8.4 Hz, 2H), 5.30 (q, J = 6.8 Hz, 1H), 3.73 (q, J = 7.2 Hz, 1H), 2.39 (d, J = 7.2 Hz, 2H), 2.20 (s, 3H), 1.81 – 1.73 (m, 1H), 1.47 – 1.44 (m, 6H), 0.83 – 0.80 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 168.4, 141.5, 137.8, 134.31, 134.25, 130.2, 129.3, 127.3, 120.0, 70.4, 45.3, 45.1, 30.2, 22.5, 21.0, 18.02, 17.99.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{23}H_{29}NO_3Na]^+$ m/z: 390.2040, found, 390.2037.

1-oxo-1-(*p*-tolylamino)propan-2-yl 2-(4-isobutylphenyl)propanoate (**44-2**)



44-2

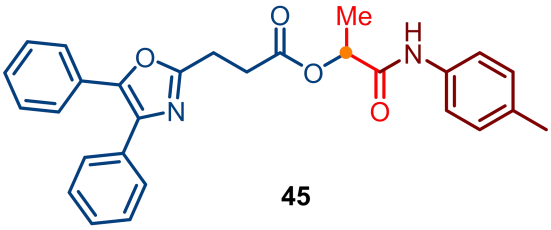
Prepared according to the **general procedure A**, Colorless oil (16.0 mg, 44% yield), R_f = 0.34 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.13 – 7.07 (m, 4H), 7.00 (d, J = 8.4 Hz, 2H), 5.23 (q, J = 6.8 Hz, 1H), 3.78 (q, J = 7.2 Hz, 1H), 2.40 (d, J = 7.2 Hz, 2H), 2.23 (s, 3H), 1.83 – 1.74 (m, 1H), 1.53 (d, J = 7.2 Hz, 3H), 1.40 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 168.3, 141.3, 136.8, 134.4, 129.9, 129.5, 127.3, 120.1, 70.9, 45.6, 45.1, 30.3, 22.52, 22.51, 21.0, 17.8, 17.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{23}H_{29}NO_3Na]^+$ m/z: 390.2040, found, 390.2036.

1-oxo-1-(*p*-tolylamino)propan-2-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (**45**)



45

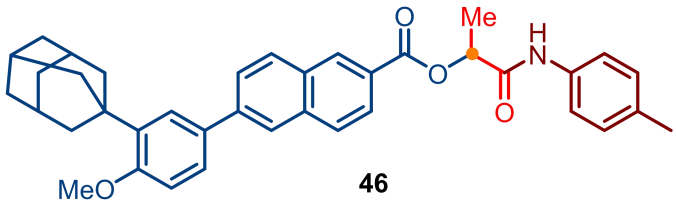
Prepared according to the **general procedure A**, Colorless oil (37.6 mg, 83% yield), R_f = 0.40 (PE/EA = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.49 – 7.42 (m, 4H), 7.27 – 7.17 (m, 8H), 6.93 (d, J = 8.4 Hz, 2H), 5.31 (q, J = 6.8 Hz, 1H), 3.18 (t, J = 6.4 Hz, 2H), 3.05 – 2.87 (m, 2H), 2.19 (s, 3H), 1.47 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 168.4, 161.8, 145.8, 135.1, 134.5, 134.4, 131.9, 129.4, 128.80, 128.77, 128.68, 128.65, 128.3, 128.0, 126.5, 120.7, 71.4, 31.5, 23.5, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{28}H_{27}N_2O_4]^+$ m/z: 455.1965, found, 455.1964.

1-oxo-1-(*p*-tolylamino)propan-2-yl
6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (**46**)



46

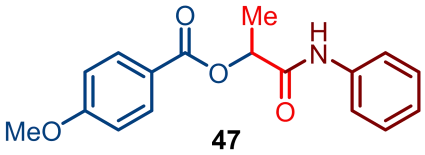
Prepared according to the **general procedure A**, Colorless oil (38.7 mg, 68% yield), R_f = 0.45 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.02 (dd, J = 8.4, 1.6 Hz, 1H), 7.98 – 7.87 (m, 4H), 7.76 (dd, J = 8.4, 1.6 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.48 (dd, J = 8.4, 2.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 1H), 5.60 (q, J = 6.8 Hz, 1H), 3.83 (s, 3H), 2.24 (s, 3H), 2.13 – 2.10 (m, 6H), 1.75 – 1.71 (m, 6H), 1.67 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.7, 159.2, 142.1, 139.2, 136.4, 134.64, 134.58, 132.5, 131.4, 131.3, 129.9, 129.7, 128.8, 127.0, 126.1, 126.0, 125.9, 125.4, 124.9, 120.3, 112.3, 71.5, 55.3, 40.8, 37.4, 37.3, 29.2, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{38}H_{40}NO_4]^+$ m/z: 574.2952, found, 574.2950.

1-oxo-1-(phenylamino)propan-2-yl 4-methoxybenzoate (**47**)



47

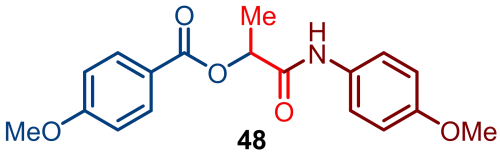
Prepared according to the **general procedure A**, White solid (26.5 mg, 89% yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 3H), 7.53 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 5.56 (q, J = 6.8 Hz, 1H), 3.87 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.2, 164.1, 137.2, 132.0, 129.1, 124.8, 121.5, 120.2, 114.1, 71.1, 55.6, 17.8.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{17}H_{17}NO_4Na]^+$ m/z: 322.1050, found, 322.1050.

1-((4-methoxyphenyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**48**)



48

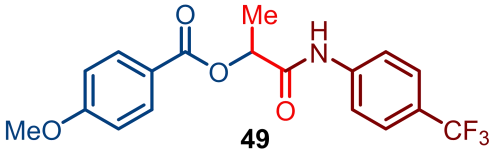
Prepared according to the **general procedure A**, Yellow solid (14.0 mg, 42% yield), R_f = 0.20 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, J = 8.8, 2.4 Hz, 2H), 7.86 (s, 1H), 7.43 (dt, J = 8.8, 2.4 Hz, 2H), 6.98 (dt, J = 8.8, 2.4 Hz, 2H), 6.86 (dt, J = 8.8 2.4 Hz, 2H), 5.58 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 1.67 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 165.2, 164.1, 156.9, 132.0, 130.2, 122.1, 121.7, 114.3, 114.1, 71.1, 55.7, 55.6, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{18}H_{20}NO_5]^+$ m/z: 330.1336, found, 330.1332.

1-oxo-1-((4-(trifluoromethyl)phenyl)amino)propan-2-yl 4-methoxybenzoate (**49**)



49

Prepared according to the **general procedure A**, White solid (29.5 mg, 81% yield), R_f = 0.35 (PE/EA = 5/1).

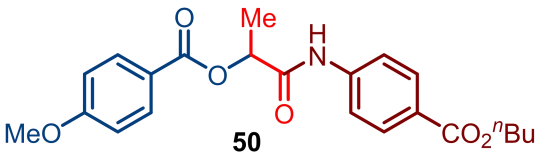
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.00 – 7.96 (m, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.90 (dd, J = 8.8, 1.2 Hz, 2H), 5.49 (q, J = 6.8 Hz, 1H), 3.820 (s, 3H), 1.60 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.5, 164.3, 140.3, 132.1, 126.4 (q, J = 3.7 Hz), 124.1 (q, J = 269.8 Hz), 121.3, 119.8, 114.2, 71.1, 55.7, 17.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.18.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{18}H_{17}F_3NO_4]^+$ m/z: 368.1104, found, 368.1099.

1-((4-(butoxycarbonyl)phenyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**50**)



50

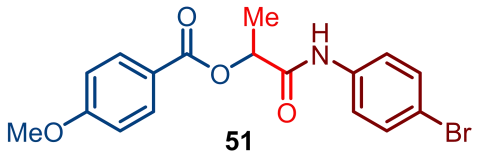
Prepared according to the **general procedure A**, White solid (20.1 mg, 50% yield), R_f = 0.25 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.09 – 7.97 (m, 4H), 7.62 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 7.6 Hz, 2H), 5.58 (q, J = 6.8 Hz, 1H), 4.29 (t, J = 6.0 Hz, 2H), 3.89 (s, 3H), 1.79 – 1.65 (m, 4H), 1.46 (q, J = 7.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 166.2, 165.3, 164.2, 141.3, 132.1, 130.9, 126.6, 121.4, 119.3, 114.2, 71.1, 65.0, 55.7, 30.9, 19.4, 17.7, 13.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{22}H_{26}NO_6]^+$ m/z: 400.1755, found, 400.1752.

1-((4-bromophenyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**51**)



51

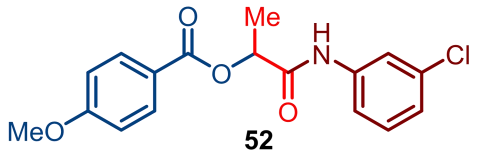
Prepared according to the **general procedure A**, Light orange solid (31.1 mg, 82% yield), R_f = 0.39 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, J = 8.8, 2.4 Hz, 2H), 8.01 (s, 1H), 7.46 – 7.37 (m, 4H), 6.97 (dt, J = 8.8, 2.4 Hz, 2H), 5.56 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.3, 164.2, 136.3, 132.1, 132.0, 121.7, 121.4, 117.5, 114.1, 71.1, 55.7, 17.7.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}BrNO_4]^+$ m/z: 378.0336, found, 378.0332.

1-((3-chlorophenyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**52**)



52

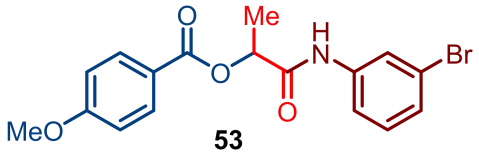
Prepared according to the **general procedure A**, Light orange solid (25.1 mg, 76% yield), R_f = 0.40 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.99 (s, 1H), 7.67 – 7.62 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 5.57 (q, J = 6.8, 1H), 3.89 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 165.3, 164.2, 138.3, 134.8, 132.1, 130.2, 124.9, 121.4, 120.2, 118.1, 114.2, 71.1, 55.7, 17.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{17}H_{16}ClNO_4Na]^+$ m/z: 356.0660, found, 356.0657.

1-((3-bromophenyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**53**)



53

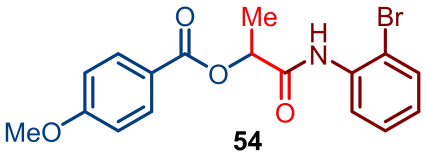
Prepared according to the **general procedure A**, Light yellow solid (35.2 mg, 94% yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.03 (dd, J = 8.8, 1.2 Hz, 2H), 7.78 (t, J = 2.0 Hz, 1H), 7.43 (dd, J = 8.4, 2.0 Hz, 1H), 7.22 (d, J = 6.4 Hz, 1H), 7.14 (td, J = 8.0, 2.4 Hz, 1H), 6.95 (dd, J = 8.8, 2.0 Hz, 2H), 5.52 (q, J = 6.8, 1H), 3.86 (s, 3H), 1.65 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 165.4, 164.1, 138.5, 132.0, 130.4, 127.7, 123.0, 122.6, 121.3, 118.6, 114.1, 71.0, 55.6, 17.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{17}H_{16}BrNO_4Na]^+$ m/z: 400.0155, found, 400.0153.

1-((2-bromophenyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**54**)



54

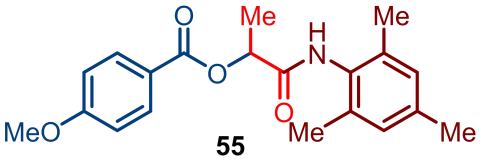
Prepared according to the **general procedure A**, Light yellow solid (25.6 mg, 68% yield), R_f = 0.42 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.44 (dd, J = 8.4, 1.6 Hz, 1H), 8.16 – 8.11 (m, 2H), 7.52 (dd, J = 8.0, 1.6 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.02 – 6.95 (m, 3H), 5.65 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 1.70 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 164.7, 164.2, 135.1, 132.4, 132.1, 128.7, 125.6, 121.7, 121.4, 114.0, 113.5, 71.1, 55.7, 18.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}BrNO_4]^+$ m/z: 378.0336, found, 378.0333.

1-(mesitylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**55**)



55

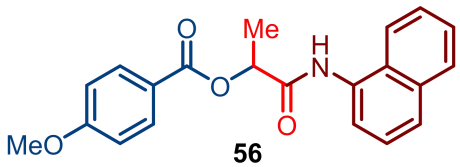
Prepared according to the **general procedure A**, Yellow solid (8.9 mg, 26% yield), R_f = 0.30 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, J = 8.8, 2.4 Hz, 2H), 7.35 (s, 1H), 6.96 (dt, J = 8.8, 2.4 Hz, 2H), 6.88 (s, 2H), 5.61 (q, J = 6.8 Hz, 1H), 3.88 (s, 3H), 2.26 (s, 3H), 2.16 (s, 6H), 1.72 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 165.2, 164.1, 137.4, 135.3, 132.0, 130.2, 129.1, 121.7, 114.1, 71.3, 55.7, 21.1, 18.3, 18.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{20}H_{24}NO_4]^+$ m/z: 342.1700, found, 342.1697.

1-(naphthalen-1-ylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**56**)



56

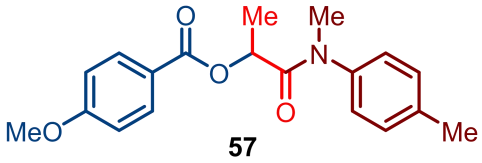
Prepared according to the **general procedure A**, White solid (27.4 mg, 78% yield), R_f = 0.26 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.17 – 8.11 (m, 2H), 8.04 (d, J = 7.6 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.82 – 7.76 (m, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.51 – 7.46 (m, 3H), 6.99 (d, J = 8.8 Hz, 2H), 5.75 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 1.77 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 165.4, 164.2, 134.2, 132.1, 131.6, 129.0, 127.0, 126.6, 126.2, 126.1, 125.9, 121.6, 120.6, 120.3, 114.2, 71.5, 55.7, 18.0.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{21}H_{19}NO_4Na]^+$ m/z: 372.1206, found, 372.1202.

1-(methyl(*p*-tolyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**57**)



57

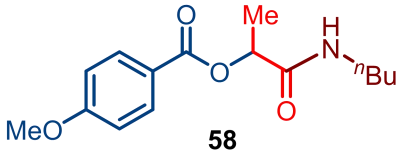
Prepared according to the **general procedure A**, White solid (23.0 mg, 70% yield), R_f = 0.19 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.16 (q, J = 6.8 Hz, 1H), 3.84 (s, 3H), 3.27 (s, 3H), 2.36 (s, 3H), 1.39 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 166.0, 163.6, 140.3, 138.3, 132.0, 130.6, 127.4, 122.2, 113.6, 68.0, 55.5, 37.9, 21.2, 17.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_4]^+$ m/z: 328.1543, found, 328.1541.

1-(butylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**58**)



58

Prepared according to the **general procedure A**, White solid (15.7 mg, 56% yield), R_f = 0.16 (PE/EA = 5/1).

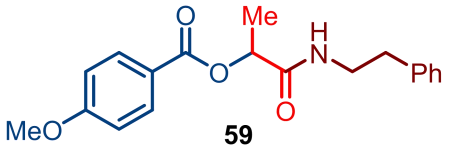
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dt, J = 8.8, 2.4 Hz, 2H), 6.94 (dt, J = 8.8, 2.4 Hz, 2H), 6.18 (s, 1H), 5.43 (q, J = 6.8 Hz, 1H), 3.87 (s, 3H), 3.27 (q, J = 6.8 Hz, 2H), 1.57

(d, J = 6.8 Hz, 3H), 1.52 – 1.44 (m, 2H), 1.37 – 1.26 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 165.1, 164.0, 131.9, 121.8, 114.0, 70.9, 55.6, 39.1, 31.7, 20.1, 18.04, 13.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{22}NO_4]^+$ m/z: 280.1543, found, 280.1539.

1-oxo-1-(phenethylamino)propan-2-yl 4-methoxybenzoate (**59**)



59

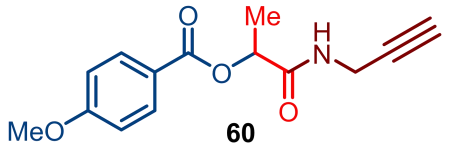
Prepared according to the **general procedure A**, White solid (24.6 mg, 75% yield), R_f = 0.16 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.25 – 7.12 (m, 5H), 6.92 (d, J = 8.4 Hz, 2H), 6.18 (s, 1H), 5.42 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 3.61 – 3.52 (m, 2H), 2.88 – 2.75 (m, 2H), 1.55 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 164.9, 163.9, 138.7, 131.9, 128.9, 128.8, 126.7, 121.7, 113.9, 70.8, 55.7, 40.2, 35.6, 18.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_4]^+$ m/z: 328.1543, found, 328.1540.

1-oxo-1-(prop-2-yn-1-ylamino)propan-2-yl 4-methoxybenzoate (**60**)



60

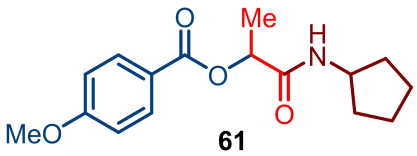
Prepared according to the **general procedure A**, White solid (21.2 mg, 82% yield), R_f = 0.16 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, J = 8.8, 2.4 Hz, 2H), 6.95 (dt, J = 8.8, 2.4 Hz, 2H), 6.42 (s, 1H), 5.47 (q, J = 6.8 Hz, 1H), 4.16 – 4.01 (m, 2H), 3.87 (s, 3H), 2.24 (t, J = 2.8 Hz, 1H), 1.58 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 165.0, 164.1, 132.0, 121.6, 114.0, 72.0, 70.6, 55.7, 29.2, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{14}H_{16}NO_4]^+$ m/z: 262.1074, found, 262.1070.

1-(cyclopentylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**61**)



61

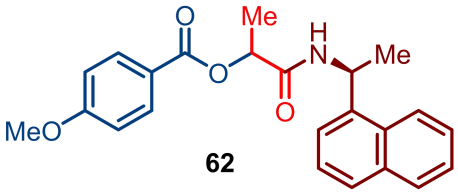
Prepared according to the **general procedure A**, White solid (26.0 mg, 90% yield), R_f = 0.20 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.8, 2.4 Hz 2H), 6.93 (dt, J = 8.8, 2.4 Hz 2H), 6.13 (s, 1H), 5.38 (q, J = 6.8 Hz, 1H), 4.26 – 4.14 (m, 1H), 3.86 (s, 3H), 2.06 – 1.90 (m, 2H), 1.69 – 1.56 (m, 4H), 1.55 (d, J = 6.8 Hz, 3H), 1.43 – 1.29 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 165.0, 163.8, 131.7, 121.7, 113.9, 70.8, 55.5, 51.0, 33.10, 33.05, 23.7, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{16}H_{22}NO_4]^+$ m/z: 292.1543, found, 292.1541.

1-(((S)-1-(naphthalen-1-yl)ethyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**62**)



62

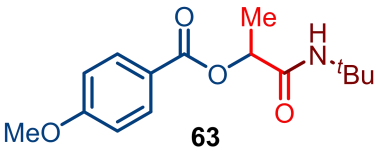
Prepared according to the **general procedure A**, Yellow solid (33.4 mg, 89% yield, d.r. 1.7:1), R_f = 0.21 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 8.12 – 8.04 (m, 1H), 7.94 – 7.75 (m, 4H), 7.56 – 7.39 (m, 4H), 6.96 – 6.80 (m, 2H), 6.57 – 6.38 (m, 1H), 6.09 – 5.78 (m, 1H), 5.48 (q, J = 6.8 Hz, 1H), 5.37 (q, J = 6.8 Hz, 1H*), 1.70 (d, J = 6.7 Hz, 3H*), 1.66 (d, J = 6.8 Hz, 3H), 1.59 (d, J = 6.8 Hz, 3H*), 1.55 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 165.2, 165.0, 163.9, 163.8, 138.0, 134.1, 134.0, 131.9, 131.8, 131.1, 131.0, 128.94, 128.91, 128.6, 128.5, 126.68, 126.65, 126.0, 125.9, 125.32, 125.29, 123.45, 123.35, 122.7, 122.6, 121.8, 121.7, 113.91, 113.87, 71.0, 70.9, 55.58, 55.57, 45.0, 44.9, 21.1, 20.9, 17.94, 17.88.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{23}H_{24}NO_4]^+$ m/z: 378.1700, found, 378.1698.

1-(*tert*-butylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**63**)



63

Prepared according to the **general procedure A**, White solid (26.0 mg, 93% yield), R_f = 0.35 (PE/EA = 5/1).

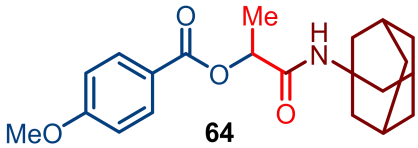
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.8, 2.4 Hz 2H), 6.94 (dt, J = 8.8, 2.4 Hz, 2H), 6.00 (s, 1H), 5.31 (q, J = 6.8 Hz, 1H), 3.86 (s, 3H), 1.53 (d, J = 6.8 Hz, 3H), 1.34

(s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 165.0, 163.9, 131.8, 121.9, 114.0, 71.1, 55.6, 51.2, 28.8, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{22}NO_4]^+$ m/z: 280.1543, found, 280.1539.

1-(adamantan-1-ylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**64**)



64

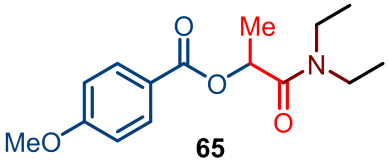
Prepared according to the **general procedure A**, White solid (31.2 mg, 87% yield), R_f = 0.34 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dt, J = 8.8, 2.4 Hz, 2H), 6.95 (dt, J = 8.8, 2.4 Hz, 2H), 5.86 (s, 1H), 5.31 (q, J = 6.8 Hz, 1H), 3.87 (s, 3H), 2.07 (s, 3H), 1.99 (d, J = 2.8 Hz, 6H), 1.66 (t, J = 3.2 Hz, 6H), 1.54 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 165.0, 163.9, 131.8, 122.0, 114.0, 71.1, 55.6, 51.9, 41.6, 36.4, 29.5, 18.0.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{28}NO_4]^+$ m/z: 358.2013, found, 358.2011.

1-(diethylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**65**)



65

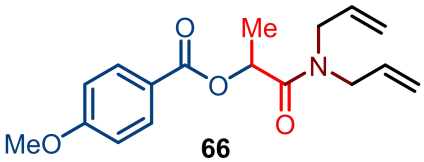
Prepared according to the **general procedure A**, White solid (26.3 mg, 95% yield), R_f = 0.16 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.54 (q, J = 6.8 Hz, 1H), 3.83 (s, 3H), 3.55 – 3.22 (m, 4H), 1.53 (d, J = 6.8 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 166.0, 163.7, 132.0, 122.2, 113.7, 67.3, 55.5, 41.7, 40.7, 17.5, 14.4, 12.9.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{15}H_{21}NO_4Na]^+$ m/z: 302.1363, found, 302.1360.

1-(diallylamino)-1-oxopropan-2-yl 4-methoxybenzoate (**66**)



66

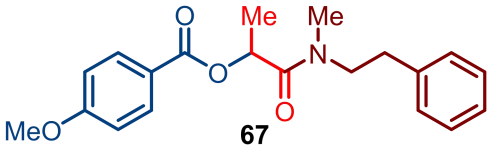
Prepared according to the **general procedure A**, Light yellow oil (28.8 mg, 96% yield), R_f = 0.35 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.89 – 5.69 (m, 2H), 5.53 (q, J = 6.8 Hz, 1H), 5.27 – 5.09 (m, 4H), 4.10 (dd, J = 17.6, 4.8 Hz, 1H), 4.00 (t, J = 4.8 Hz, 2H), 3.90 (dd, J = 17.6, 4.8 Hz, 1H), 3.84 (s, 3H), 1.55 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 165.9, 163.68, 132.9, 132.7, 132.1, 122.0, 117.6, 117.5, 113.7, 67.3, 55.5, 49.1, 48.2, 17.5.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{22}NO_4]^+$ m/z: 304.1543, found, 304.1540.

1-(methyl(phenethyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**67**)



67

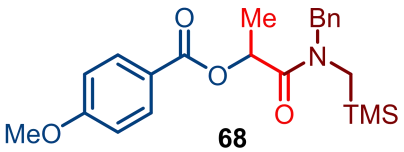
Prepared according to the **general procedure A**, Colorless oil (31.9 mg, 94% yield, *cis*:*trans* = 1.5:1), R_f = 0.20 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor isomer indicated by *) δ 7.96 (d, J = 8.8 Hz, 2H), 7.26 – 7.08 (m, 5H), 6.86 – 6.80 (m, 2H), 5.50 – 5.41 (m, 1H), 3.80 – 3.74 (m, 3H), 3.69 – 3.55 (m, 1H), 3.54 – 3.42 (m, 1H), 2.94 – 2.86 (m, 4H), 2.80 (t, J = 7.6 Hz, 1H), 1.41 (d, J = 6.8 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 170.3, 166.0, 165.9, 163.72, 163.70, 139.1, 138.1, 132.10, 132.07, 129.0, 128.94, 128.90, 128.6, 126.9, 126.5, 122.0, 113.7, 67.4, 66.9, 55.5, 51.5, 50.5, 35.8, 34.9, 34.3, 33.6, 17.3, 16.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{20}H_{23}NO_4Na]^+$ m/z: 364.1519, found, 364.1516.

1-(benzyl((trimethylsilyl)methyl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**68**)



68

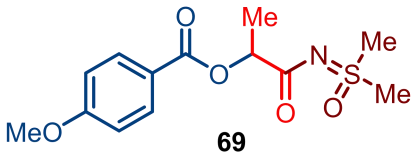
Prepared according to the **general procedure A**, White solid (36.1 mg, 91% yield, *cis*:*trans* = 4.7:1), R_f = 0.43 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor isomer indicated by *) δ 8.12 – 8.07 (m, 2H*), 8.06 – 8.00 (m, 2H), 7.43 – 7.20 (m, 5H), 6.97 – 6.88 (m, 2H), 5.74 – 5.65 (m, 1H), 4.82 (d, J = 14.8 Hz, 1H*), 4.70 (d, J = 16.6 Hz, 1H), 4.61 (d, J = 16.6 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H*), 3.88 (s, 3H*), 3.87 (s, 3H), 2.92 (s, 2H), 1.62 (d, J = 6.8 Hz, 3H*), 1.54 (d, J = 6.8 Hz, 3H), 0.18 (s, 9H*), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.6, 165.83, 165.76, 163.7, 163.6, 137.0, 136.5, 132.11, 132.06, 129.0, 128.7, 127.9, 127.8, 127.2, 127.0, 122.2, 122.1, 113.7, 113.6, 67.2, 67.1, 55.5, 53.1, 50.4, 38.9, 37.8, 17.6, 17.1, -1.1, -1.3.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{22}H_{30}NO_4Si]^+$ m/z: 400.1939, found, 400.1935.

1-((dimethyl(oxo)-λ^6-sulfanylidene)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**69**)



69

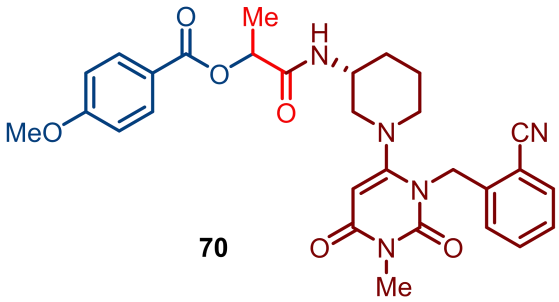
Prepared according to the **general procedure A**, White solid (22.7 mg, 76% yield), R_f = 0.13 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 6.94 – 6.86 (m, 2H), 5.19 (q, J = 7.2 Hz, 1H), 3.84 (s, 3H), 3.27 (s, 3H), 3.26 (s, 3H), 1.60 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 166.0, 163.6, 132.0, 122.5, 113.7, 72.5, 55.5, 41.7, 41.6, 17.6.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{13}H_{18}NO_5S]^+$ m/z: 300.0900, found, 300.0898.

1-(((*R*)-1-(3-(2-cyanobenzyl)-1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)piperidin-3-yl)amino)-1-oxopropan-2-yl 4-methoxybenzoate (**70**)



70

Prepared according to the **general procedure A**, Colorless oil (33.1 mg, 61% yield, d.r. 1:1), R_f = 0.42 (PE/DCM = 1/1).

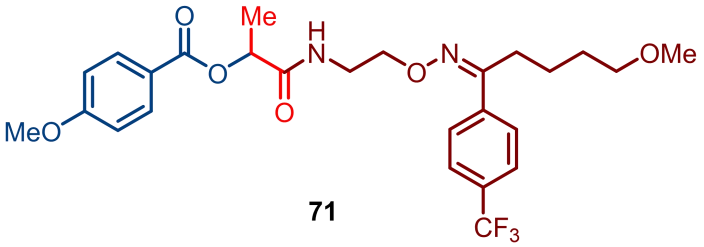
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.65 – 7.50 (m, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.89 (t, J = 8.8 Hz, 2H), 6.31 (s, 1H), 5.43 – 5.08

(m, 4H), 4.14 – 3.99 (m, 1H), 3.86 (s, 3H), 3.28 – 3.13 (m, 4H), 3.05 – 2.60 (m, 3H), 1.92 – 1.58 (m, 4H), 1.53 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 170.1, 165.2, 165.1, 163.91, 163.88, 163.1, 163.0, 159.5, 152.4, 152.3, 140.3, 133.2, 133.10, 133.05, 132.2, 132.1, 132.0, 131.8, 128.6, 128.5, 128.11, 128.06, 128.0, 121.5, 121.4, 117.4, 113.9, 111.0, 90.4, 90.3, 70.7, 55.5, 55.2, 46.45, 46.36, 27.91, 27.88, 17.7, 17.5.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{29}H_{32}N_5O_6]^+$ m/z: 546.2347, found, 546.2344.

(*Z*)-13-oxo-7-(4-(trifluoromethyl)phenyl)-2,9-dioxa-8,12-diazapentadec-7-en-14-yl 4-methoxybenzoate (**71**)



71

Prepared according to the **general procedure B**, Colorless oil (42.5 mg, 81% yield), R_f = 0.42 (PE/EA = 2/1).

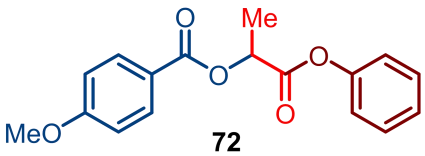
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.65 (s, 1H), 5.44 (q, J = 6.8 Hz, 1H), 4.29 (t, J = 4.4 Hz, 2H), 3.83 (s, 3H), 3.66 (q, J = 5.6 Hz, 2H), 3.33 – 3.29 (m, 2H), 3.28 (s, 3H), 2.68 (t, J = 6.8 Hz, 2H), 1.60 – 1.50 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 165.0, 163.9, 158.1, 138.8, 131.8, 131.0 (q, J = 32.6 Hz), 126.6, 125.5 (q, J = 3.8 Hz), 124.1 (q, J = 270.5 Hz), 121.7, 113.9, 72.7, 72.2, 70.8, 58.7, 55.5, 39.4, 29.5, 26.1, 23.1, 18.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{26}H_{32}F_3N_2O_6]^+$ m/z: 525.2207, found, 525.2202.

1-oxo-1-phenoxypropan-2-yl 4-methoxybenzoate (**72**)



72

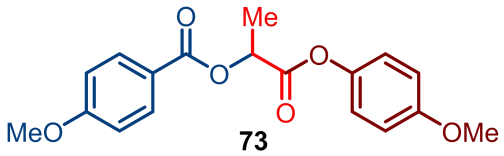
Prepared according to the **general procedure B**, White solid (26.6 mg, 88% yield), R_f = 0.34 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.42 – 7.34 (m, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.16 – 7.11 (m, 2H), 6.97 – 6.91 (m, 2H), 5.48 (q, J = 7.2 Hz, 1H), 3.86 (s, 3H), 1.78 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 165.9, 163.9, 150.5, 132.1, 129.6, 126.2, 121.7, 121.5, 113.8, 69.1, 55.6, 17.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{17}H_{17}O_5]^+$ m/z: 301.1071, found, 301.1068.

1-(4-methoxyphenoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**73**)



73

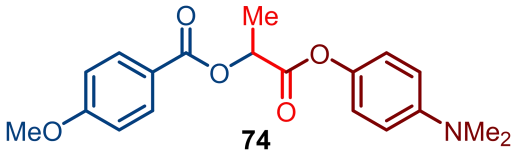
Prepared according to the **general procedure B**, White solid (27.8 mg, 84% yield), R_f = 0.25 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.08 – 7.02 (m, 2H), 6.96 – 6.91 (m, 2H), 6.90 – 6.85 (m, 2H), 5.46 (q, J = 7.2 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 1.77 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 165.9, 163.9, 157.5, 143.9, 132.1, 122.2, 121.7, 114.6, 113.8, 69.1, 55.7, 55.6, 17.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C18H19O6]^+$ m/z: 330.1098, found, 330.1094.

1-(4-(dimethylamino)phenoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**74**)



74

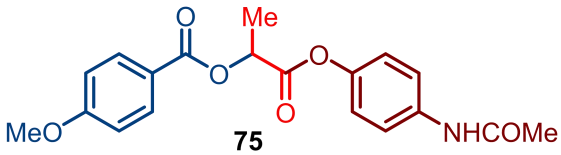
Prepared according to the **general procedure B**, White solid (31.3 mg, 92% yield), R_f = 0.32 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dt, J = 8.8, 2.8 Hz, 2H), 7.00 (dt, J = 8.8, 2.8 Hz, 2H), 6.93 (dt, J = 8.8, 2.4 Hz, 2H), 6.71 (dt, J = 8.8, 2.4 Hz, 2H), 5.47 (q, J = 7.2 Hz, 1H), 3.86 (s, 3H), 2.92 (s, 6H), 1.76 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 165.8, 163.8, 148.8, 141.5, 132.1, 121.9, 121.7, 113.8, 113.3, 69.1, 55.6, 41.1, 17.3.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_5]^+$ m/z: 344.1493, found, 344.1492.

1-(4-acetamidophenoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**75**)



75

Prepared according to the **general procedure B**, Colorless oil (33.2 mg, 93% yield),

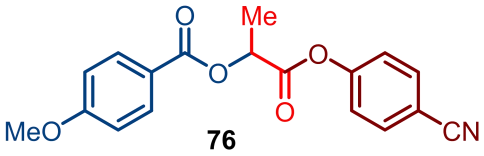
R_f = 0.20 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 9.2 Hz, 2H), 7.76 (s, 1H), 7.44 (d, J = 9.2 Hz, 2H), 7.01 (d, J = 9.2 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 5.44 (q, J = 7.2 Hz, 1H), 3.85 (s, 3H), 2.07 (s, 3H), 1.77 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.7, 165.9, 163.9, 146.4, 136.1, 132.1, 121.7, 121.6, 121.0, 113.9, 69.1, 55.6, 24.4, 17.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{20}NO_6]^+$ m/z: 358.1285, found, 358.1283.

1-(4-cyanophenoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**76**)



76

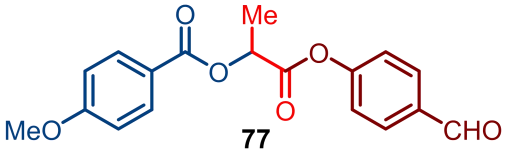
Prepared according to the **general procedure B**, Colorless oil (26.8 mg, 83% yield), R_f = 0.30 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.36 (q, J = 7.2 Hz, 1H), 3.80 (s, 3H), 1.71 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 166.0, 164.1, 153.7, 133.9, 132.2, 122.7, 121.3, 116.5, 113.9, 110.2, 69.0, 55.6, 17.0.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{18}H_{15}NO_5Na]^+$ m/z: 348.0842, found, 348.0840.

1-(4-formylphenoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**77**)



77

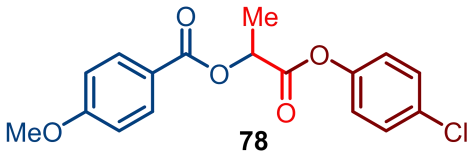
Prepared according to the **general procedure B**, Yellow solid (25.9 mg, 79% yield), R_f = 0.42 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.46 (q, J = 7.2 Hz, 1H), 3.87 (s, 3H), 1.79 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 169.3, 165.9, 164.0, 155.1, 134.4, 132.2, 131.4, 122.3, 121.5, 113.9, 69.0, 55.6, 17.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{18}H_{16}O_6Na]^+$ m/z: 351.0839, found, 351.0836.

1-(4-chlorophenoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**78**)



78

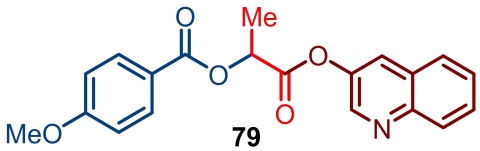
Prepared according to the **general procedure B**, White solid (21.2 mg, 63% yield), R_f = 0.39 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dt, J = 8.8, 2.4 Hz, 2H), 7.33 (dt, J = 8.8, 2.8 Hz, 2H), 7.08 (dt, J = 8.8, 2.8 Hz, 2H), 6.94 (dt, J = 8.8, 2.4 Hz, 2H), 5.44 (q, J = 6.8 Hz, 1H), 3.87 (s, 3H), 1.77 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 165.9, 164.0, 148.9, 132.2, 131.6, 129.7, 122.9, 121.6, 113.9, 69.0, 55.6, 17.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{17}H_{15}ClO_5Na]^+$ m/z: 357.0500, found, 357.0504.

1-oxo-1-(quinolin-3-yloxy)propan-2-yl 4-methoxybenzoate (**79**)



79

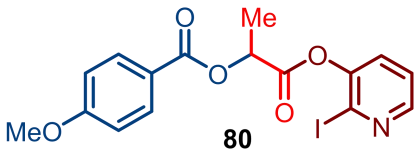
Prepared according to the **general procedure B**, Light yellow solid (28.8 mg, 82% yield), R_f = 0.35 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.46 – 8.37 (m, 3H), 8.32 (d, J = 2.8 Hz, 1H), 8.13 – 8.09 (m, 1H), 8.04 – 7.99 (m, 1H), 7.90 – 7.85 (m, 1H), 7.25 (dt, J = 9.2, 2.4 Hz, 2H), 5.84 (q, J = 7.2 Hz, 1H), 4.16 (s, 3H), 2.14 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 165.6, 163.7, 145.8, 144.8, 143.6, 131.9, 129.2, 129.0, 127.9, 127.5, 127.3, 126.2, 121.1, 113.6, 68.7, 55.3, 16.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{20}H_{18}NO_5]^+$ m/z: 352.1180, found, 352.1177.

1-((2-iodopyridin-3-yl)oxy)-1-oxopropan-2-yl 4-methoxybenzoate (**80**)



80

Prepared according to the **general procedure B**, White solid (20.3 mg, 48% yield), R_f = 0.34 (PE/EA = 10/1).

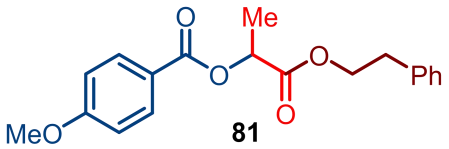
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.25 (m, 1H), 8.10 – 8.05 (m, 2H), 7.48 – 7.45 (m, 1H), 7.32 – 7.27 (m, 1H), 6.96 – 6.92 (m, 2H), 5.52 (q, J = 6.8 Hz, 1H), 3.87 (s, 3H), 1.88 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.9, 164.0, 148.3, 132.2, 132.1, 130.2, 123.8,

121.4, 114.4, 113.9, 69.1, 55.6, 17.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{16}H_{15}INO_5]^+$ m/z: 427.9989, found, 427.9991.

1-oxo-1-phenethoxypropan-2-yl 4-methoxybenzoate (**81**)



81

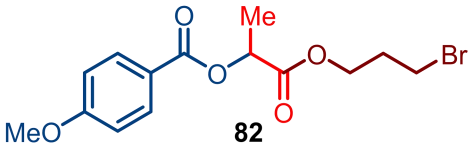
Prepared according to the **general procedure B**, White solid (26.4 mg, 81% yield), R_f = 0.38 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.28 – 7.15 (m, 5H), 6.92 (d, J = 8.0 Hz, 2H), 5.28 (q, J = 6.4 Hz, 1H), 4.46 – 4.29 (m, 2H), 3.86 (s, 3H), 2.95 (t, J = 7.2 Hz, 2H), 1.54 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 165.7, 163.8, 137.6, 132.1, 129.1, 128.6, 126.7, 122.0, 113.8, 69.0, 65.8, 55.6, 35.1, 17.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{21}O_5]^+$ m/z: 329.1384, found, 329.1383.

1-(3-bromopropoxy)-1-oxopropan-2-yl 4-methoxybenzoate (**82**)



82

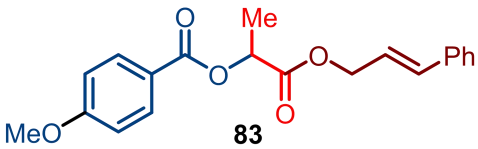
Prepared according to the **general procedure B**, Colorless oil (27.4 mg, 80% yield), R_f = 0.42 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.8 Hz, 2H), 7.27 – 7.23 (m, 2H), 5.59 (q, J = 7.2 Hz, 1H), 4.64 (t, J = 6.0 Hz, 2H), 4.19 (s, 3H), 3.75 (t, J = 6.4 Hz, 2H), 2.55 – 2.47 (m, 2H), 1.94 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.8, 163.8, 132.1, 121.8, 113.8, 69.0, 63.1, 55.6, 31.6, 29.3, 17.2.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{14}H_{17}BrO_5Na]^+$ m/z: 367.0152, found, 367.0150.

1-(cinnamyloxy)-1-oxopropan-2-yl 4-methoxybenzoate (**83**)



83

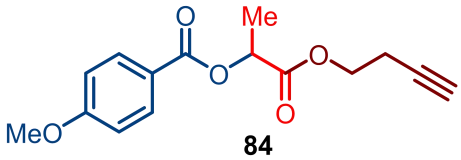
Prepared according to the **general procedure B**, Colorless oil (26.6 mg, 78% yield), R_f = 0.41 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, J = 8.8, 2.4 Hz, 2H), 7.40 – 7.26 (m, 5H), 6.93 (dt, J = 8.8, 2.4 Hz, 2H), 6.66 (d, J = 15.6 Hz, 1H), 6.27 (dt, J = 15.6, 6.4 Hz, 1H), 5.35 (q, J = 7.2 Hz, 1H), 4.83 (d, J = 6.4 Hz, 2H), 3.86 (s, 3H), 1.65 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 165.6, 163.6, 136.0, 134.4, 131.9, 128.5, 128.0, 126.6, 122.4, 121.7, 113.6, 68.8, 65.7, 55.4, 17.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{20}H_{20}O_5Na]^+$ m/z: 363.1203, found, 363.1200.

1-(but-3-yn-1-yloxy)-1-oxopropan-2-yl 4-methoxybenzoate (**84**)



84

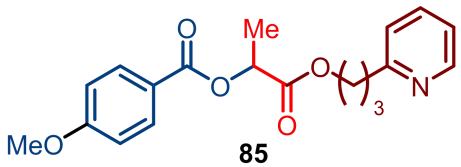
Prepared according to the **general procedure B**, Colorless oil (16.2 mg, 58% yield), R_f = 0.32 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dt, J = 8.8, 2.4 Hz, 2H), 6.93 (dt, J = 8.8, 2.4 Hz, 2H), 5.30 (q, J = 7.2 Hz, 1H), 4.34 – 4.21 (m, 2H), 3.86 (s, 3H), 2.55 (td, J = 6.8, 2.8 Hz, 2H), 1.96 (t, J = 2.8 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 165.8, 163.8, 132.1, 121.9, 113.8, 79.7, 70.2, 68.9, 62.9, 55.6, 19.0, 17.3.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{17}O_5]^+$ m/z: 277.1071, found, 277.1068.

1-oxo-1-(3-(pyridin-2-yl)propoxy)propan-2-yl 4-methoxybenzoate (**85**)



85

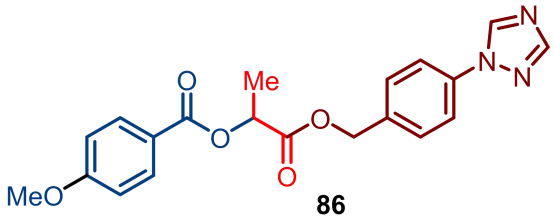
Prepared according to the **general procedure B**, Light yellow oil (30.5 mg, 90% yield), R_f = 0.25 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 4.8 Hz, 1H), 8.04 (dt, J = 8.8, 2.4 Hz, 2H), 7.59 (td, J = 7.8, 1.6 Hz, 1H), 7.17 – 7.08 (m, 2H), 6.92 (dt, J = 8.8, 2.4 Hz, 2H), 5.28 (q, J = 7.2 Hz, 1H), 4.20 (t, J = 6.4 Hz, 2H), 3.85 (s, 3H), 2.85 (t, J = 7.6 Hz, 2H), 2.16 – 2.07 (m, 2H), 1.61 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 165.8, 163.8, 160.7, 149.1, 136.9, 132.0, 123.3, 122.0, 121.5, 113.8, 69.1, 64.7, 55.6, 34.2, 28.5, 17.3.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{22}NO_5]^+$ m/z: 344.1493, found, 344.1490.

1-((4-(1*H*-1,2,4-triazol-1-yl)benzyl)oxy)-1-oxopropan-2-yl 4-methoxybenzoate (**86**)



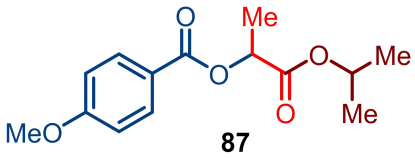
Prepared according to the **general procedure B**, White solid (24.1 mg, 63% yield), R_f = 0.20 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.12 (s, 1H), 8.03 (dt, J = 8.8, 2.4 Hz, 2H), 7.66 (dt, J = 8.8, 2.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.92 (dt, J = 8.8, 2.4 Hz, 2H), 5.34 (q, J = 7.2 Hz, 1H), 5.25 (s, 2H), 3.86 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.8, 163.9, 152.6, 136.9, 135.9, 132.1, 129.6, 128.7, 121.7, 120.3, 113.8, 69.0, 66.1, 55.6, 17.2.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{20}H_{19}N_3O_5Na]^+$ m/z: 404.1217, found, 404.1213.

1-isopropoxy-1-oxopropan-2-yl 4-methoxybenzoate (**87**)



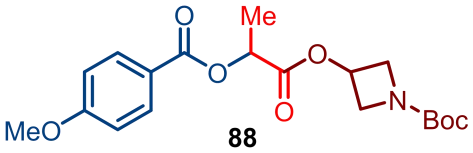
Prepared according to the **general procedure B**, White solid (19.3 mg, 72% yield), R_f = 0.40 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.23 (q, J = 7.2 Hz, 1H), 5.14 – 5.02 (m, 1H), 3.86 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H), 1.27 (d, J = 6.4 Hz, 3H), 1.23 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 165.8, 163.7, 132.0, 122.1, 113.8, 69.2, 69.1, 55.6, 21.8, 21.8, 17.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{14}H_{19}O_5]^+$ m/z: 267.1227, found, 267.1224.

tert-butyl 3-((2-((4-methoxybenzoyl)oxy)propanoyl)oxy)azetidine-1-carboxylate (**88**)



Prepared according to the **general procedure B**, White solid (29.4 mg, 77% yield), R_f

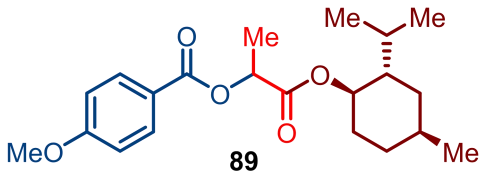
= 0.22 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.26 (q, J = 7.2 Hz, 1H), 5.23 – 5.16 (m, 1H), 4.28 – 4.20 (m, 2H), 3.97 – 3.88 (m, 2H), 3.86 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 165.8, 163.9, 156.1, 132.1, 121.6, 113.8, 80.1, 68.8, 64.3, 56.3, 55.6, 28.4, 17.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{19}H_{26}NO_7]^+$ m/z: 380.1704, found, 380.1702.

1-(((1*R*,2*S*,4*S*)-2-isopropyl-4-methylcyclohexyl)oxy)-1-oxopropan-2-yl 4-methoxybenzoate (**89**)



89

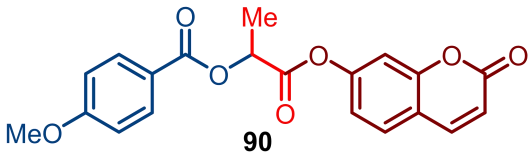
Prepared according to the **general procedure B**, White solid (17.6 mg, 48% yield, d.r. 1:1), R_f = 0.35 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.33 – 5.17 (m, 1H), 4.80 – 4.65 (m, 1H), 3.86 (s, 3H), 2.11 – 1.78 (m, 2H), 1.72 – 1.56 (m, 6H), 1.51 – 1.44 (m, 1H), 1.48 (s, 1H), 1.38 (t, J = 11.6 Hz, 1H), 1.04 (t, J = 11.6 Hz, 1H), 0.92 – 0.86 (m, 5H), 0.83 (d, J = 6.8 Hz, 2H), 0.76 (dd, J = 20.4, 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.7, 165.8, 165.7, 163.71, 163.69, 132.0, 122.2, 122.1, 113.7, 75.6, 75.4, 69.4, 69.1, 55.6, 47.1, 47.0, 40.73, 40.68, 34.3, 31.53, 31.48, 26.4, 26.1, 23.7, 23.2, 22.12, 22.10, 20.9, 20.8, 17.3, 16.6, 16.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{31}O_5]^+$ m/z: 363.2166, found, 363.2163.

1-oxo-1-((2-oxo-2H-chromen-7-yl)oxy)propan-2-yl 4-methoxybenzoate (**90**)



90

Prepared according to the **general procedure B**, White solid (26.7 mg, 72% yield), R_f = 0.25 (PE/EA = 5/1).

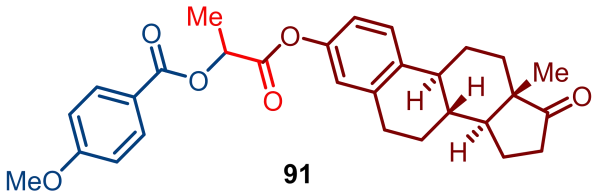
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.68 (d, J = 9.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.96 – 6.92 (m, 2H), 6.40 (dd, J = 9.6, 1.2 Hz, 1H), 5.45 (q, J = 7.2 Hz, 1H), 3.87 (s, 3H), 1.79 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 165.9, 164.0, 160.4, 154.8, 152.9, 143.0, 132.2,

128.8, 121.4, 118.3, 117.0, 116.4, 113.9, 110.4, 69.0, 55.6, 17.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{20}H_{17}O_7]^+$ m/z: 369.0969, found, 369.0966.

1-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)-1-oxopropan-2-yl 4-methoxybenzoate (**91**)



91

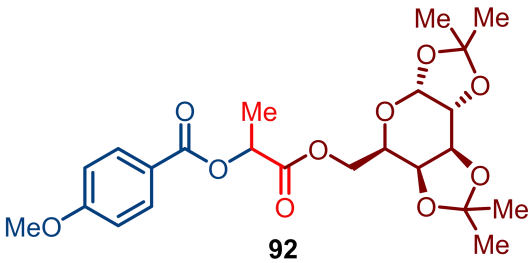
Prepared according to the **general procedure B**, White solid (26.8 mg, 56% yield, d.r. >20:1), R_f = 0.25 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 9.6 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.91 – 6.85 (m, 2H), 5.46 (q, J = 7.2 Hz, 1H), 3.86 (s, 3H), 2.90 (dd, J = 9.2, 4.0 Hz, 2H), 2.50 (dd, J = 18.8, 8.8 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.33 – 2.24 (m, 1H), 2.19 – 1.93 (m, 4H), 1.76 (d, J = 7.2 Hz, 3H), 1.67 – 1.41 (m, 6H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 165.9, 163.9, 148.4, 138.2, 137.8, 132.1, 126.5, 121.8, 121.4, 118.6, 113.8, 69.1, 55.6, 50.5, 48.1, 44.3, 38.1, 31.0, 31.7, 29.5, 26.4, 25.9, 21.7, 17.2, 13.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{29}H_{33}O_6]^+$ m/z: 477.2272, found, 477.2273.

1-oxo-1-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-yl)methoxy)propan-2-yl 4-methoxybenzoate (**92**)



92

Prepared according to the **general procedure B**, Colorless oil (36.4 mg, 78% yield, d.r. 1:1), R_f = 0.40 (PE/EA = 5/1).

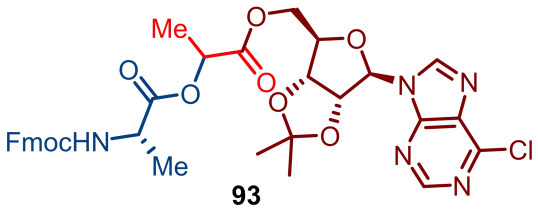
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 5.52 (d, J = 5.2 Hz, 1H), 5.31 (qd, J = 7.2, 2.0 Hz, 1H), 4.62 – 4.56 (m, 1H), 4.48 – 4.17 (m, 4H), 4.05 – 3.98 (m, 1H), 3.85 (s, 3H), 1.62 (d, J = 7.2Hz, 3H), 1.51 – 1.41 (m, 6H), 1.31 (dd, J = 7.2, 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 171.0, 165.75, 165.71, 163.8, 132.1, 122.02,

121.98, 113.7, 109.81, 109.76, 108.94, 108.91, 96.40, 96.37, 71.08, 71.05, 70.8, 70.58, 70.56, 69.04, 68.96, 66.2, 65.9, 64.2, 64.1, 55.6, 26.12, 26.06, 26.0, 25.1, 24.6, 24.5, 17.34, 17.30.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{23}H_{31}O_{10}]^+$ m/z: 467.1912, found, 467.1907.

1-(((3*aR*,4*R*,6*R*,6*aR*)-6-(6-chloro-9*H*-purin-9-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methoxy)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-alaninate (**93**)



93

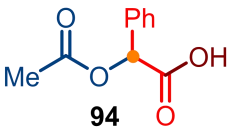
Prepared according to the **general procedure B**, Colorless oil (51.5 mg, 75% yield, d.r. 1.7:1), R_f = 0.50 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.73 (m, 1H), 8.27 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 6.22 – 6.04 (m, 1H), 5.54 – 5.35 (m, 2H), 5.12 – 4.93 (m, 2H), 4.52 – 4.16 (m, 8H), 2.21 – 2.10 (m, 1H), 1.63 – 1.57 (m, 3H), 1.51 – 1.42 (m, 4H), 1.39 – 1.36 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 172.5, 169.9, 155.8, 152.3, 144.0, 143.8, 143.7, 141.4, 127.8, 127.2, 127.1, 125.1, 120.10, 120.08, 115.34, 115.31, 115.2, 91.1, 91.0, 84.8, 84.6, 84.4, 84.3, 84.1, 83.9, 81.3, 69.5, 69.2, 67.2, 64.3, 64.2, 49.6, 47.2, 27.3, 27.23, 27.17, 25.42, 25.35, 18.5, 18.4, 16.9, 16.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{34}H_{35}ClN_5O_9]^+$ m/z: 692.2118, found, 692.2112.

2-acetoxy-2-phenylacetic acid (**94**)



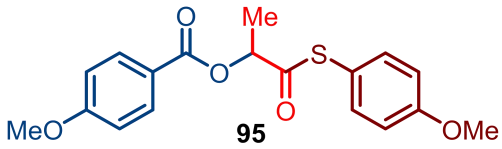
94

Prepared according to the **general procedure B**, White solid (10.1 mg, 53% yield), R_f = 0.24 (DCM/MeOH = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 3H), 6.68 (s, 1H), 5.93 (s, 1H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 170.6, 133.2, 129.6, 129.0, 127.8, 20.8.

1-((4-methoxyphenyl)thio)-1-oxopropan-2-yl 4-methoxybenzoate (**95**)



95

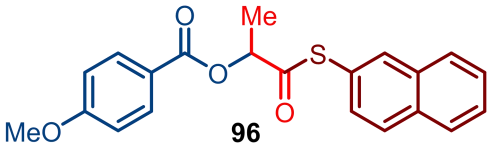
Prepared according to the **general procedure C**, Colorless oil (12.9 mg, 37% yield), R_f = 0.35 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dt, J = 9.2, 2.4 Hz, 2H), 7.32 (dt, J = 8.8, 2.4 Hz, 2H), 7.00 – 6.92 (m, 4H), 5.64 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 1.64 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 165.1, 163.9, 160.8, 136.4, 132.2, 121.6, 117.0, 115.0, 113.9, 75.1, 55.5, 55.4, 18.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{18}H_{19}O_5S]^+$ m/z: 347.0948, found, 347.0945.

1-(naphthalen-2-ylthio)-1-oxopropan-2-yl 4-methoxybenzoate (**96**)



96

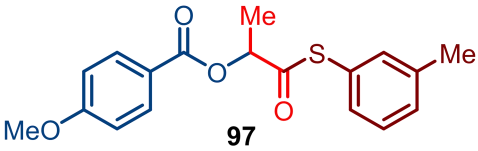
Prepared according to the **general procedure C**, White solid (15.2 mg, 42% yield), R_f = 0.45 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.14 (m, 2H), 7.97 (s, 1H), 7.92 – 7.81 (m, 3H), 7.57 – 7.43 (m, 3H), 7.05 – 6.97 (m, 2H), 5.69 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 1.69 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 164.1, 135.0, 133.7, 133.6, 132.3, 131.2, 129.0, 128.1, 127.9, 127.4, 126.7, 123.9, 121.7, 114.0, 103.8, 75.3, 55.7, 18.3.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{21}H_{18}O_4SNa]^+$ m/z: 389.0818, found, 389.0814.

1-oxo-1-(*m*-tolylthio)propan-2-yl 4-methoxybenzoate (**97**)



97

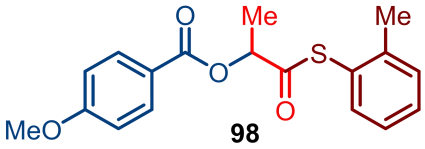
Prepared according to the **general procedure C**, White solid (17.6 mg, 53% yield), R_f = 0.42 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 – 7.20 (m, 3H), 7.01 – 6.95 (m, 2H), 5.64 (q, J = 6.8 Hz, 1H), 3.88 (s, 3H), 2.36 (s, 3H), 1.65 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 165.2, 164.0, 139.3, 135.5, 132.3, 132.0, 130.6, 129.2, 126.2, 121.7, 114.0, 55.6, 21.4, 18.3.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C18H18O4SNa]^+$ m/z: 353.0818, found, 353.0814.

1-oxo-1-(*o*-tolylthio)propan-2-yl 4-methoxybenzoate (**98**)



98

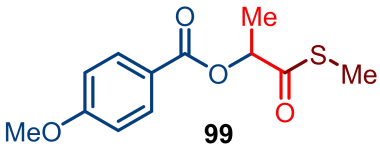
Prepared according to the **general procedure C**, Colorless oil (9.4 mg, 28% yield), R_f = 0.44 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.41 – 7.29 (m, 3H), 7.25 – 7.18 (m, 1H), 6.98 (d, J = 8.8 Hz, 2H), 5.62 (q, J = 6.8 Hz, 1H), 3.89 (s, 3H), 2.33 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 165.2, 163.9, 142.5, 136.2, 132.2, 130.9, 130.3, 126.7, 125.9, 121.6, 113.9, 55.5, 20.6, 18.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{18}H_{18}O_4SNa]^+$ m/z: 353.0818, found, 353.0813.

1-(methylthio)-1-oxopropan-2-yl 4-methoxybenzoate (**99**)



99

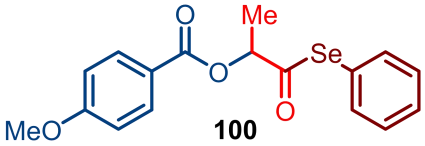
Prepared according to the **general procedure C**, White solid (11.7 mg, 46% yield), R_f = 0.45 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 5.54 (q, J = 7.2 Hz, 1H), 3.88 (s, 4H), 2.30 (s, 3H), 1.59 (d, J = 7.2 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 165.2, 164.0, 132.2, 121.8, 113.9, 75.2, 55.6, 18.3, 11.1.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{12}H_{14}O_4SNa]^+$ m/z: 277.0505, found, 277.0502.

1-oxo-1-(phenylselanyl)propan-2-yl 4-methoxybenzoate (**100**)



100

Prepared according to the **general procedure C**, Colorless oil (9.7 mg, 27% yield), R_f = 0.43 (PE/EA = 10/1).

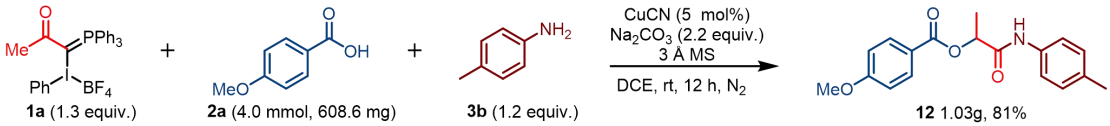
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.42 – 7.35 (m, 3H), 7.00 (d, J = 8.4 Hz, 2H), 5.59 (q, J = 6.8 Hz, 1H), 3.90 (s, 3H), 1.60 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 165.0, 164.1, 136.2, 132.4, 129.5, 129.2, 125.2, 121.5, 114.1, 77.3, 55.7, 18.0.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{17}H_{16}O_4SeNa]^+$ m/z: 387.0106, found, 387.0107.

4. Gram-sale Reaction and Synthetic Transformations

4.1 Gram-sale Reaction



Phosphonium-iodonium ylides **1a** (3.17g, 5.2 mmol, 1.3 equiv.), 4-Methoxybenzoic acid **2a** (608.6 mg, 4.0 mmol, 1.0 equiv.), *p*-Toluidine **3b** (514.3 mg, 4.8 mmol, 1.2 equiv.), CuCN (18.0 mg, 0.2 mmol, 5 mol%), Na_2CO_3 (932.7 mg, 8.8 mmol, 2.2 equiv.) and 3Å MS (800 mg) were added to a dry 100 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then Dry DCE (40 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography (R_f = 0.2 (PE/EA = 5/1)) to afford **12** as a white solid in 81% yield (1.03 g).

4.2 α-Hydroxyl acid in the synthesis of polypeptides

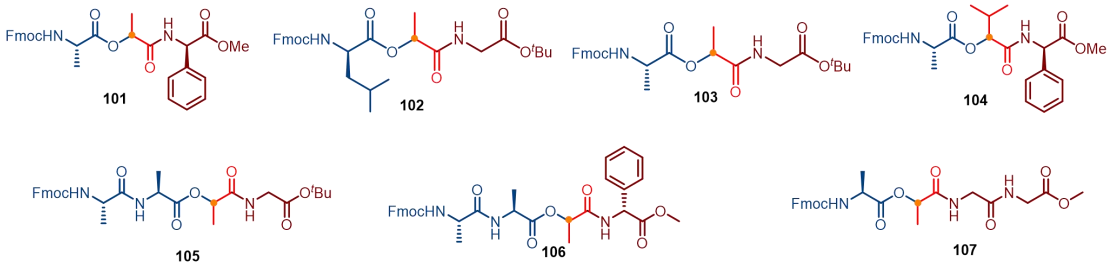
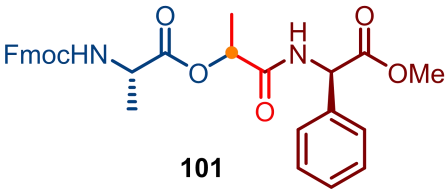


Figure S2. Synthetic peptides

1-(((*R*)-2-methoxy-2-oxo-1-phenylethyl)amino)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-L-alaninate (**101**)



Prepared according to the **general procedure A**, White solid (27.2 mg, 52% yield, dr 3:1), R_f = 0.32 (PE/EA = 2/1).

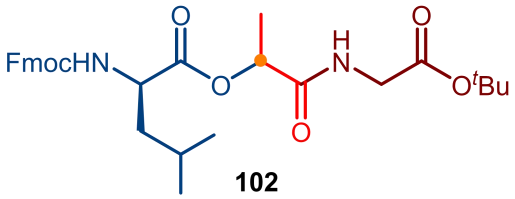
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.77 (d, J = 7.6 Hz, 2H), 7.61 – 7.53 (m, 2H), 7.44 – 7.27 (m, 11H), 5.58 (d, J = 7.2 Hz, 1H), 5.53 (d, J =

7.2 Hz, 1H*), 5.47 – 5.25 (m, 2H), 4.48 – 4.29 (m, 3H), 4.27 – 4.18 (m, 1H), 3.71 (s, 3H*), 3.66 (s, 3H), 1.54 (s, 3H*), 1.52 (s, 3H*), 1.48 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 171.0, 169.6, 156.0, 144.0, 143.8, 141.4, 136.1, 129.1, 128.7, 127.9, 127.5, 127.2, 125.2, 125.1, 120.1, 71.3, 67.4, 56.3, 52.9, 50.0, 47.2, 17.9, 17.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{30}H_{30}N_2O_7Na]^+$ m/z: 553.1945, found, 553.1938.

1-((2-(*tert*-butoxy)-2-oxoethyl)amino)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*D*-leucinate (**102**)



102

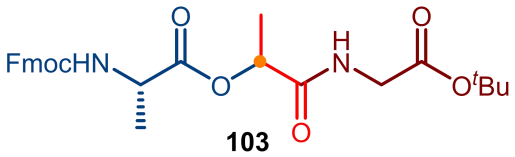
Prepared according to the **general procedure A**, Colorless oil (25.1 mg, 47% yield, d.r. 1.3:1), R_f = 0.30 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.76 (d, J = 7.6 Hz, 2H), 7.63 – 7.55 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.03 (s, 1H), 6.84 (s, 1H*), 5.37 – 5.14 (m, 2H), 4.48 – 4.31 (m, 3H), 4.26 – 4.17 (m, 1H), 4.03 – 3.70 (m, 2H), 1.79 – 1.58 (m, 3H), 1.53 – 1.48 (m, 3H), 1.43 (s, 9H*), 1.42 (s, 9H), 0.98 (t, J = 5.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 171.8, 170.2, 168.6, 156.5, 143.8, 141.45, 141.41, 127.91, 127.88, 127.3, 127.2, 125.1, 120.2, 120.1, 82.2, 71.4, 71.2, 67.4, 53.1, 52.8, 47.3, 47.2, 41.8, 41.0, 40.8, 28.1, 25.0, 23.0, 22.7, 22.1, 21.6, 17.9, 17.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{30}H_{38}N_2O_7Na]^+$ m/z: 561.2571, found, 561.2567.

1-((2-(*tert*-butoxy)-2-oxoethyl)amino)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-alaninate (**103**)



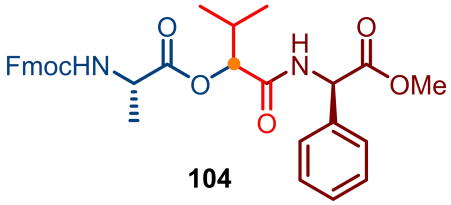
103

Prepared according to the **general procedure A**, Colorless oil (21.9 mg, 44% yield, d.r. 2.5:1), R_f = 0.29 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.03 – 6.80 (m, 1H), 5.47 – 5.24 (m, 2H), 4.49 – 4.35 (m, 3H), 4.26 – 4.18 (m, 1H), 4.04 – 3.74 (m, 2H), 1.53 – 1.41 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 172.2, 170.21, 170.15, 168.8, 168.7, 156.1, 143.9, 143.8, 141.4, 127.9, 127.8, 127.24, 127.21, 125.1, 120.14, 120.12, 82.6, 82.5, 71.44, 71.35, 67.3, 50.0, 47.25, 47.17, 41.8, 28.15, 28.11, 18.1, 17.9, 17.85, 17.77.
HRMS (ESI) $[M+K]^+$ calcd. for $[C_{27}H_{32}N_2O_7K]^+$ m/z: 535.1841, found, 535.1842.

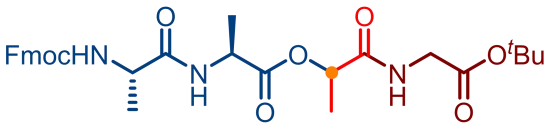
1-(((*R*)-2-methoxy-2-oxo-1-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-alaninate (**104**)



104

Prepared according to the **general procedure A**, White solid (17.9 mg, 32% yield, d.r. 1.5:1), R_f = 0.28 (PE/EA = 2/1).
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.77 (d, J = 7.6 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.44 – 7.23 (m, 11H), 5.59 (d, J = 7.2 Hz, 1H), 5.43 (d, J = 7.2 Hz, 1H), 5.25 (d, J = 7.2 Hz, 1H*), 5.20 – 5.14 (m, 1H), 4.56 – 4.44 (m, 1H), 4.36 (d, J = 7.2 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.71 (s, 3H), 3.69 (s, 3H*), 2.32 (s, 1H), 1.57 (d, J = 7.2 Hz, 3H), 1.52 (d, J = 7.2 Hz, 3H*), 0.96 – 0.90 (m, 3H), 0.85 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H*).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 171.7, 170.97, 170.95, 168.4, 155.9, 143.8, 143.7, 141.3, 136.2, 128.90, 128.87, 128.5, 127.8, 127.41, 127.38, 127.1, 125.10, 125.06, 125.02, 124.99, 120.0, 78.5, 67.3, 67.2, 56.1, 56.0, 52.9, 50.0, 49.8, 47.1, 47.0, 30.8, 30.6, 18.8, 18.1, 18.0, 16.58, 16.56.
HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{32}H_{34}N_2O_7Na]^+$ m/z: 581.2258, found, 581.2250.

1-((2-(*tert*-butoxy)-2-oxoethyl)amino)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-alanyl-*L*-alaninate (**105**)



105

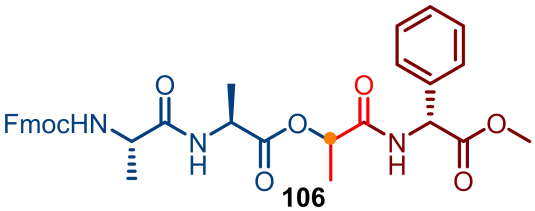
Prepared according to the **general procedure A**, White solid (19.7 mg, 35% yield, d.r. 1:1), R_f = 0.25 (PE/EA = 2/1).
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.76 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 6.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (s, 1H), 6.97 (s, 1H*), 6.86 (s, 1H), 6.67 (s, 1H*), 5.72 (d, J = 7.2 Hz, 1H), 5.56 (d, J =

7.2 Hz, 1H*), 5.34 – 5.22 (m, 1H), 4.48 – 4.17 (m, 5H), 4.18 – 4.00 (m, 1H), 3.82 (td, J = 17.6, 4.8 Hz, 1H), 1.52 – 1.39 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 171.4, 170.3, 168.9, 143.8, 143.7, 141.4, 127.9, 127.3, 127.2, 125.2, 125.1, 120.2, 82.5, 71.4, 71.3, 67.3, 50.5, 50.2, 49.0, 48.8, 47.2, 41.8, 41.7, 28.2, 17.9, 17.7, 17.3.

HRMS (ESI) $[M+K]^+$ calcd. for $[C_{30}H_{37}N_3O_8K]^+$ m/z: 606.2212, found, 606.2211.

1-(((*R*)-2-methoxy-2-oxo-1-phenylethyl)amino)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-alanyl-*L*-alaninate (**106**)



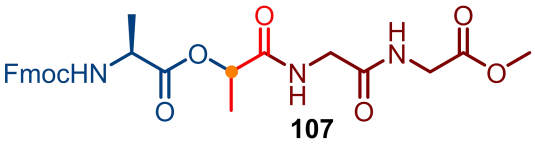
Prepared according to the **general procedure A**, White solid (28.5 mg, 48% yield, d.r. 1.3:1), R_f = 0.33 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.81 – 7.76 (m, 2H), 7.59 (t, J = 6.8 Hz, 2H), 7.46 – 7.29 (m, 10H), 6.81 (s, 1H), 5.67 – 5.56 (m, 1H), 5.35 – 5.27 (m, 1H), 4.53 – 4.36 (m, 3H), 4.24 (d, J = 6.4 Hz, 1H), 3.74 (d, J = 4.0 Hz, 3H*), 3.72 (d, J = 4.0 Hz, 3H), 1.55 – 1.37 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 171.10, 171.06, 169.7, 156.1, 143.8, 141.43, 141.40, 136.1, 136.0, 129.2, 129.1, 129.0, 128.9, 128.82, 128.75, 128.7, 127.90, 127.88, 127.7, 127.6, 127.2, 125.12, 125.09, 125.05, 120.2, 120.1, 71.2, 67.1, 56.6, 56.4, 56.2, 52.9, 50.2, 48.8, 48.5, 47.2, 19.0, 18.7, 17.9, 17.7.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{33}H_{35}N_3O_8Na]^+$ m/z: 624.2316, found, 624.2310.

1-((2-((2-methoxy-2-oxoethyl)amino)-2-oxoethyl)amino)-1-oxopropan-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-alaninate (**107**)



Prepared according to the **general procedure A**, White solid (27.9 mg, 55% yield, d.r. 1.4:1), R_f = 0.37 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.76 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 6.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 6.8 Hz, 2H), 6.67 (s,

1H), 5.48 (d, J = 6.0 Hz, 1H*), 5.41 (d, J = 6.0 Hz, 1H), 5.28 – 5.19 (m, 1H), 4.51 – 4.28 (m, 3H), 4.21 (t, J = 7.2 Hz, 1H), 4.07 – 3.86 (m, 4H), 3.69 (s, 3H), 3.66 (s, 3H*), 2.06 (s, 1H), 1.57 – 1.43 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 171.0, 170.13, 170.10, 169.2, 168.9, 156.64, 156.57, 143.8, 143.7, 141.42, 141.39, 127.9, 127.3, 127.2, 125.1, 125.06, 120.2, 120.1, 71.75, 71.65, 67.5, 67.3, 52.5, 52.4, 50.22, 50.17, 47.2, 47.1, 43.0, 42.8, 41.23, 41.22, 17.7, 17.6, 17.2.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{26}H_{30}N_3O_8]^+$ m/z: 512.2027, found, 512.2024.

4.3 Synthesis of Lactofen and its analogues

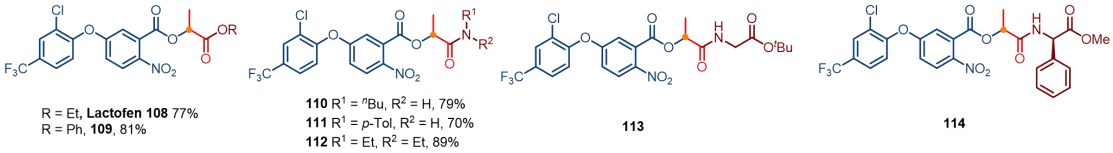
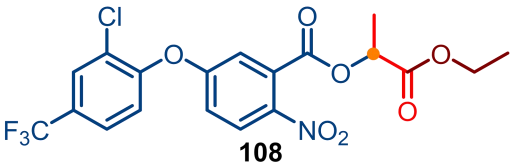


Figure S3. Synthetic Lactofen and its analogues

1-ethoxy-1-oxopropan-2-yl 5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**108**)



Prepared according to the **general procedure B**, Colorless oil (27.9 mg, 77% yield), R_f = 0.40 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 9.2 Hz, 1H), 7.81 (d, J = 1.6 Hz, 1H), 7.61 (dd, J = 8.4, 1.6 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.05 (dd, J = 9.2, 2.8 Hz, 1H), 5.35 (q, J = 7.2 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.58 (d, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H).

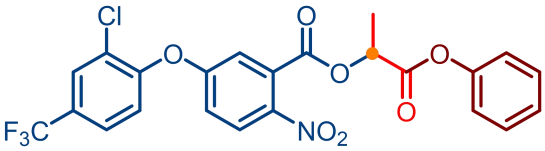
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 164.5, 160.3, 152.9, 142.3, 130.9, 129.4 (q, J = 33.8 Hz), 128.9 (q, J = 3.6 Hz), 127.7, 126.0 (q, J = 3.6 Hz), 123.1 (q, J = 270.9 Hz), 122.6, 118.7, 117.9, 70.7, 61.8, 16.7, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.42.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{19}H_{15}ClF_3NO_7Na]^+$ m/z: 484.0381, found, 484.0376.

1-oxo-1-phenoxypropan-2-yl

5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**109**)



109

Prepared according to the **general procedure B**, Colorless oil (41.0 mg, 81% yield), R_f = 0.39 (PE/EA = 10/1).

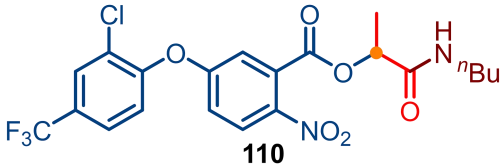
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 9.2 Hz, 1H), 7.70 (d, J = 2.0 Hz, 1H), 7.49 (dd, J = 8.4, 2.4 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.21 – 7.11 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 6.97 (dd, J = 9.2, 2.8 Hz, 1H), 5.50 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 164.7, 160.3, 152.8, 150.3, 142.2, 130.7, 129.7, 129.4 (q, J = 33.8 Hz), 128.9 (q, J = 4.0 Hz), 127.6, 127.0, 126.5, 125.9 (q, J = 3.7 Hz), 123.0 (q, J = 270.8 Hz), 122.6, 121.3, 118.8, 118.0, 70.6, 16.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{23}H_{15}ClF_3NO_7Na]^+$ m/z: 532.0381, found, 532.0378.

1-(butylamino)-1-oxopropan-2-yl
5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**110**)



110

Prepared according to the **general procedure A**, Colorless oil (38.4 mg, 79% yield), R_f = 0.35 (PE/EA = 3/1).

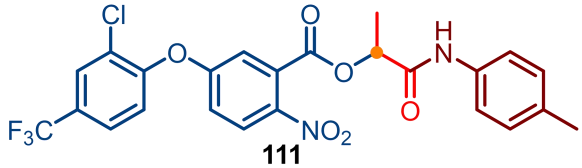
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.2 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.63 (dd, J = 8.4, 2.4 Hz, 1H), 7.29 – 7.20 (m, 2H), 7.08 (dd, J = 9.2, 2.8 Hz, 1H), 6.19 (s, 1H), 5.42 (q, J = 6.8 Hz, 1H), 3.35 – 3.23 (m, 2H), 1.58 – 1.48 (m, 5H), 1.39 – 1.30 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 163.9, 160.3, 152.5, 142.2, 130.4, 129.5 (q, J = 33.8 Hz), 128.9 (q, J = 3.8 Hz), 127.6, 127.0, 125.9 (q, J = 3.7 Hz), 122.9 (q, J = 270.9 Hz), 122.7, 118.8, 117.9, 73.1, 39.2, 31.3, 20.0, 17.6, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{21}ClF_3N_2O_6]^+$ m/z: 489.1035, found, 489.1031.

1-oxo-1-(*p*-tolylamino)propan-2-yl
5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**111**)



111

Prepared according to the **general procedure A**, Colorless oil (38.4 mg, 70% yield), R_f = 0.36 (PE/EA = 3/1).

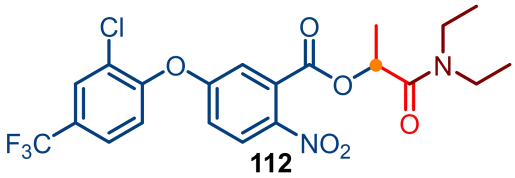
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 9.2 Hz, 1H), 7.89 (s, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.63 (dd, J = 8.4, 2.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.16 – 7.09 (m, 3H), 5.57 (q, J = 6.8 Hz, 1H), 2.32 (s, 3H), 1.65 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 164.0, 160.6, 152.6, 142.3, 134.7, 134.6, 130.3, 129.7 (q, J = 33.5 Hz), 129.6, 129.0 (q, J = 3.8 Hz), 127.8, 127.2, 126.1 (q, J = 3.8 Hz), 123.0 (q, J = 271.2 Hz), 122.9, 120.3, 119.1, 118.1, 73.3, 21.0, 17.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{24}H_{19}ClF_3N_2O_6]^+$ m/z: 523.0878, found, 523.0873.

1-(diethylamino)-1-oxopropan-2-yl
5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**112**)



112

Prepared according to the **general procedure A**, Colorless oil (43.1 mg, 89% yield), R_f = 0.34 (PE/EA = 3/1).

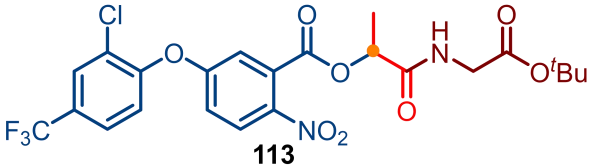
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.59 (dd, J = 8.4, 2.4 Hz, 1H), 7.34 (d, J = 2.8 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.00 (dd, J = 8.8, 2.8 Hz, 1H), 5.56 (q, J = 6.8 Hz, 1H), 3.55 – 3.22 (m, 4H), 1.52 (d, J = 6.8 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 164.8, 160.2, 153.0, 142.3, 131.2, 129.2 (q, J = 33.8 Hz), 128.9 (q, J = 3.8 Hz), 127.5, 126.9, 125.9 (q, J = 3.7 Hz), 123.1 (q, J = 270.8 Hz), 122.4, 118.5, 69.4, 41.8, 40.7, 17.1, 14.4, 12.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.40.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{21}H_{21}ClF_3N_2O_6]^+$ m/z: 489.1035, found, 489.1031.

1-((2-(*tert*-butoxy)-2-oxoethyl)amino)-1-oxopropan-2-yl
5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**113**)



113

Prepared according to the **general procedure A**, Colorless oil (22.7 mg, 42% yield), R_f = 0.25 (PE/EA = 2/1).

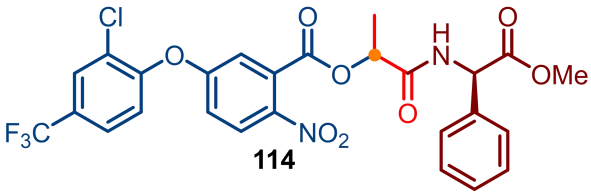
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 9.2 Hz, 1H), 7.83 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.10 (dd, J = 9.2, 2.4 Hz, 1H), 6.62 (t, J = 4.4 Hz, 1H), 5.50 (q, J = 7.2 Hz, 1H), 3.99 – 3.95 (m, 2H), 1.62 (d, J = 6.6.8 Hz, 3H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 168.6, 164.1, 160.5, 152.7, 142.0, 130.7, 129.5 (q, J = 33.7 Hz), 129.0 (q, J = 3.7 Hz), 127.6, 127.2, 126.0 (q, J = 3.7 Hz), 123.0 (q, J = 270.9 Hz), 122.6, 118.9, 117.8, 82.6, 72.8, 41.9, 28.1, 17.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.41.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{23}H_{23}ClF_3N_2O_8]^+$ m/z: 547.1089, found, 547.1089.

1-(((*R*)-2-methoxy-2-oxo-1-phenylethyl)amino)-1-oxopropan-2-yl
5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrobenzoate (**114**)



114

Prepared according to the **general procedure A**, Colorless oil (37.3 mg, 64% yield, d.r. 1:1), R_f = 0.27 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 8.12 (d, J = 2.0 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H*), 7.86 – 7.81 (m, 1H), 7.67 – 7.62 (m, 21H), 7.41 – 7.34 (m, 5H), 7.32 – 7.28 (m, 1H), 7.26 (d, J = 2.8 Hz, 1H), 7.21 (d, J = 2.8 Hz, 1H*), 7.14 – 7.09 (m, 1H), 5.60 (d, J = 3.6 Hz, 1H), 5.59 (d, J = 3.6 Hz, 1H*), 5.55 – 5.47 (m, 1H), 3.74 (s, 3H), 3.74 (s, 3H*), 1.61 (d, J = 6.8 Hz, 3H), 1.57 (d, J = 6.8 Hz, 3H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 169.0, 168.9, 164.2, 164.1, 160.5, 152.72, 152.67, 142.1, 142.0, 136.04, 135.98, 135.5 (q, J = 65.9 Hz), 130.7, 130.6, 129.13, 129.11, 128.9 (q, J = 3.7 Hz), 127.65, 127.64, 127.4, 127.3, 127.21, 127.15, 126.0 (q, J = 3.8 Hz), 123.04 (q, J = 270.8 Hz), 123.03 (q, J = 271.2 Hz), 122.73, 122.71, 119.0,

118.9, 117.67, 117.66, 72.72, 72.66, 56.4, 56.3, 53.02, 53.01, 17.4, 17.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39, -62.40.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{26}H_{21}ClF_3N_2O_8]^+$ m/z: 581.0933, found, 581.0931.

4.4 Synthesis of α-Hydroxyl acid

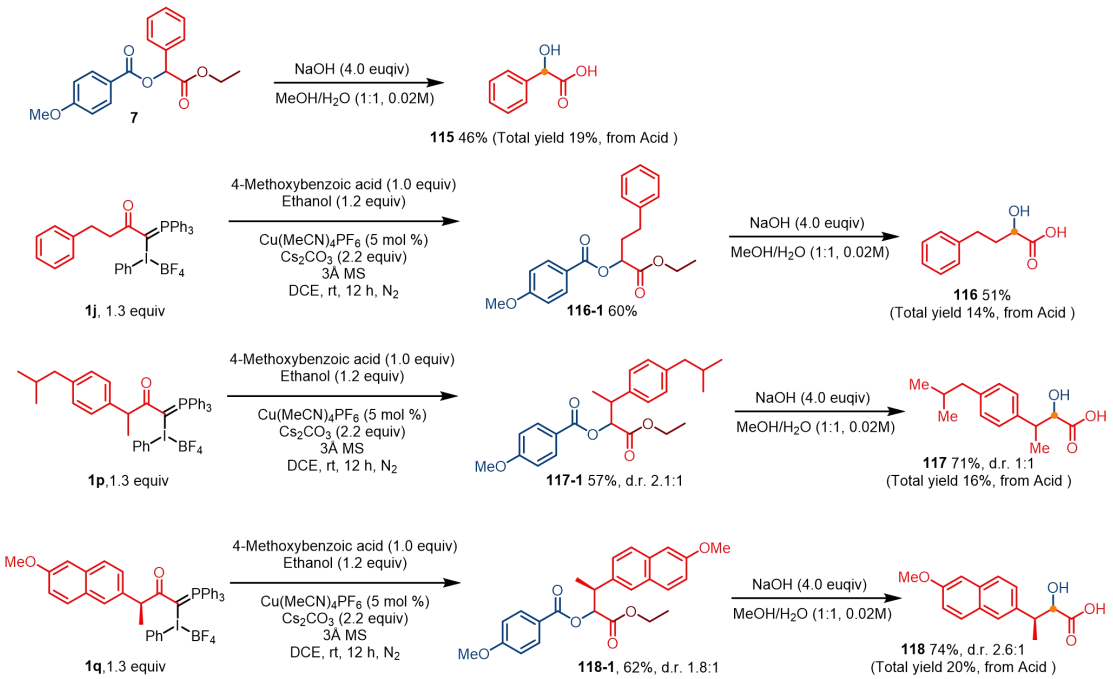
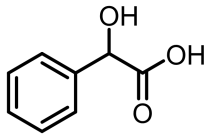


Figure S4. Synthesis of α-Hydroxyl acid

Hydrolysis steps

Following the literature procedure[4]. Sodium hydroxide solution (2 M, 2 mL) was added to standard product (0.2 mmol) in 2 mL methanol. The mixture was stirred at room temperature for 8 hours. Then hydrochloric acid (1 M) was added to adjust the pH to 1-2, the mixture was extracted with EA (15 × 5 mL). And the organic layer was dried over anhydrous sodium sulfate. After removing the solvents in vacuo, by flash column chromatography to get α-Hydroxyl acid.

2-hydroxy-2-phenylacetic acid (**115**)

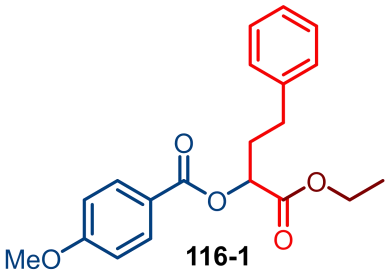


White solid (18 mg, 46% yield), R_f = 0.17 (DCM/MeOH = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.31 (m, 3H), 5.23 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 137.7, 128.9, 128.9, 126.7, 72.8.

1-ethoxy-1-oxo-4-phenylbutan-2-yl 4-methoxybenzoate (**116-1**)



116-1

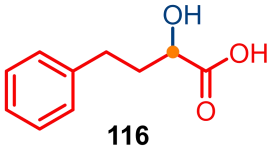
Prepared according to the **general procedure B**, Colorless oil (20.7 mg, 60% yield), R_f = 0.29 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 5.21 (t, J = 6.0 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 2.90 – 2.78 (m, 2H), 2.38 – 2.27 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 70.4, 165.8, 163.8, 140.6, 132.0, 128.6, 128.5, 126.3, 121.9, 113.8, 72.1, 61.4, 55.5, 33.0, 31.6, 14.2.

HRMS (ESI) $[M+Na]^+$ calcd. for $[C_{20}H_{23}O_5]^+$ m/z: 343.1540, found, 343.1543.

2-hydroxy-4-phenylbutanoic acid (**116**)



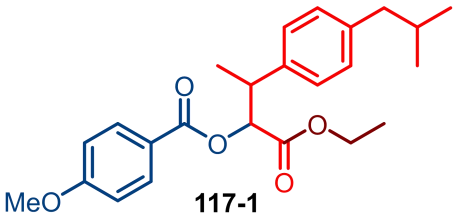
116

White solid (18.1 mg, 51% yield), R_f = 0.18 (DCM/MeOH = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.29 – 7.20 (m, 3H), 4.30 (dd, J = 8.0, 4.0 Hz, 1H), 2.83 (t, J = 8.0 Hz, 2H), 2.27 – 2.16 (m, 1H), 2.11 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 140.8, 128.7, 128.6, 126.3, 69.6, 35.8, 31.1.

1-ethoxy-3-(4-isobutylphenyl)-1-oxobutan-2-yl 4-methoxybenzoate (**117-1**)



117-1

Prepared according to the **general procedure B**, Colorless oil (22.8 mg, 57% yield, d.r. 2.1:1), R_f = 0.26 (PE/EA = 10/1).

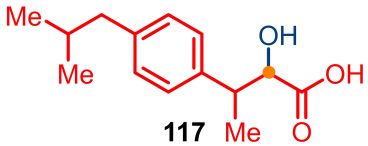
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 8.06 (d, J = 8.8 Hz,

2H*), 7.97 (d, J = 8.8 Hz, 2H), 7.26 (t, J = 8.4 Hz, 2H), 7.14 – 7.08 (m, 2H), 6.98 – 6.90 (m, 2H), 5.31 (d, J = 6.0 Hz, 1H), 5.26 (d, J = 5.6 Hz, 1H*), 4.19 – 4.09 (m, 2H), 3.89 – 3.86 (m, 3H), 3.55 – 3.43 (m, 1H), 2.50 – 2.44 (m, 2H), 1.91 – 1.81 (m, 1H), 1.51 (d, J = 7.2 Hz, 3H*), 1.46 (d, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H*), 0.92 – 0.88 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.6, 165.9, 165.8, 163.74, 163.71, 140.6, 140.5, 138.8, 138.6, 132.1, 131.99, 131.97, 129.3, 129.1, 127.8, 127.6, 122.05, 122.01, 113.80, 113.76, 77.2, 77.0, 61.2, 55.54, 55.53, 45.14, 45.10, 41.2, 30.3, 22.49, 22.45, 22.42, 17.8, 17.4, 14.2, 14.1.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{24}H_{31}O_5]^+$ m/z: 399.2166, found, 399.2162.

2-hydroxy-3-(4-isobutylphenyl)butanoic acid (**117**)



117

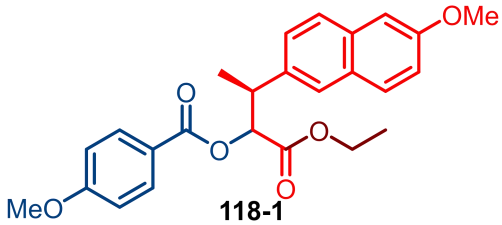
White solid (33.2 mg, 71% yield, d.r. 1:1), R_f = 0.21 (DCM/MeOH = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.6 Hz, 1H), 7.16 – 7.08 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.07 (s, 2H), 4.38 – 4.25 (m, 1H), 3.34 – 3.18 (m, 1H), 2.48 – 2.40 (m, 2H), 1.92 – 1.76 (m, 1H), 1.46 – 1.39 (m, 1H), 1.28 – 1.22 (m, 2H), 0.89 (t, J = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 178.1, 140.7, 140.5, 139.6, 137.5, 129.3, 129.2, 128.0, 127.6, 75.2, 45.2, 42.9, 42.3, 30.32, 30.30, 22.52, 22.49, 17.9, 13.8.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{14}H_{21}O_3]^+$ m/z: 237.1485, found, 237.1487.

(3*S*)-1-ethoxy-3-(6-methoxynaphthalen-2-yl)-1-oxobutan-2-yl 4-methoxybenzoate (**118-1**)



118-1

Prepared according to the **general procedure B**, Colorless oil (26.4 mg, 62% yield, d.r. 1.8:1), R_f = 0.23 (PE/EA = 10/1).

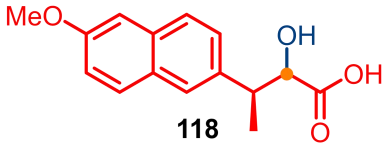
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 8.06 (d, J = 8.4 Hz, 2H*), 7.98 (d, J = 8.4 Hz, 2H), 7.77 – 7.65 (m, 3H), 7.52 – 7.43 (m, 1H), 7.19 – 7.09

(m, 2H), 6.94 (d, J = 8.0 Hz, 2H*), 6.90 (d, J = 8.0 Hz, 2H), 5.42 (d, J = 6.0 Hz, 1H), 5.36 (d, J = 5.6 Hz, 1H*), 4.18 – 4.06 (m, 2H), 3.91 (s, 3H), 3.90 (s, 3H*), 3.85 (s, 3H*), 3.83 (s, 3H), 3.72 – 3.60 (m, 1H), 1.60 (d, J = 7.2 Hz, 3H*), 1.54 (d, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.5, 165.9, 165.8, 163.74, 163.71, 157.64, 157.61, 136.7, 136.6, 133.79, 133.77, 131.98, 131.95, 129.3, 128.9, 127.0, 126.9, 126.8, 126.7, 126.6, 126.4, 122.0, 121.9, 118.99, 118.97, 113.79, 113.77, 105.63, 105.58, 77.1, 76.9, 61.3, 55.5, 55.35, 55.33, 41.5, 17.9, 16.2, 14.2, 14.0.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{25}H_{27}O_6]^+$ m/z: 423.1802, found, 423.1798.

(3*S*)-2-hydroxy-3-(6-methoxynaphthalen-2-yl)butanoic acid (**118**)



118

White solid (38.2 mg, 74% yield, d.r. 2.6:1), R_f = 0.19 (DCM/MeOH = 5/1).

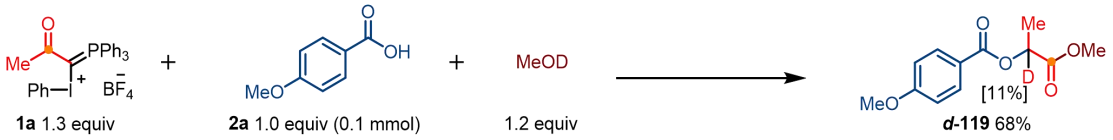
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer indicated by *) δ 7.72 – 7.56 (m, 3H), 7.38 (d, J = 8.4 Hz, 1H*), 7.30 (d, J = 8.4 Hz, 1H), 7.16 – 7.06 (m, 2H), 4.40 – 4.33 (m, 1H), 3.95 – 3.83 (m, 3H), 3.44 – 3.33 (m, 1H), 1.49 (d, J = 7.2 Hz, 3H), 1.34 (d, J = 7.2 Hz, 3H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 178.0, 157.7, 137.3, 135.4, 133.9, 133.7, 129.4, 129.0, 128.9, 127.12, 127.08, 127.0, 126.9, 126.8, 126.3, 119.0, 105.69, 105.66, 74.9, 74.8, 55.4, 43.1, 42.7, 18.0.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{15}H_{17}O_4]^+$ m/z: 261.1121, found, 261.1121.

5. Mechanistic Studies

5.1 Deuterium experiments



Phosphonium-iodonium ylides **1a** (0.13 mmol, 1.3 equiv.), 4-Methoxybenzoic acid **2a** (0.1 mmol, 1.0 equiv.), $Cu(MeCN)_4PF_6$ (0.005 mmol, 5 mol%), Cs_2CO_3 (0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then MeOD (0.12 mmol, 1.2 equiv.) and Dry DCE (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

White solid (16.3 mg, 68% yield, 11% D), R_f = 0.27 (PE/EA = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 5.31 (q, J = 7.2 Hz, 0.89H, 0.11D), 3.86 (s, 3H), 3.77 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 165.8, 163.8, 132.1, 121.9, 113.8, 68.9, 55.6, 52.5, 17.3.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{12}H_{15}O_5]^+$ m/z: 239.0914, found, 239.0912.

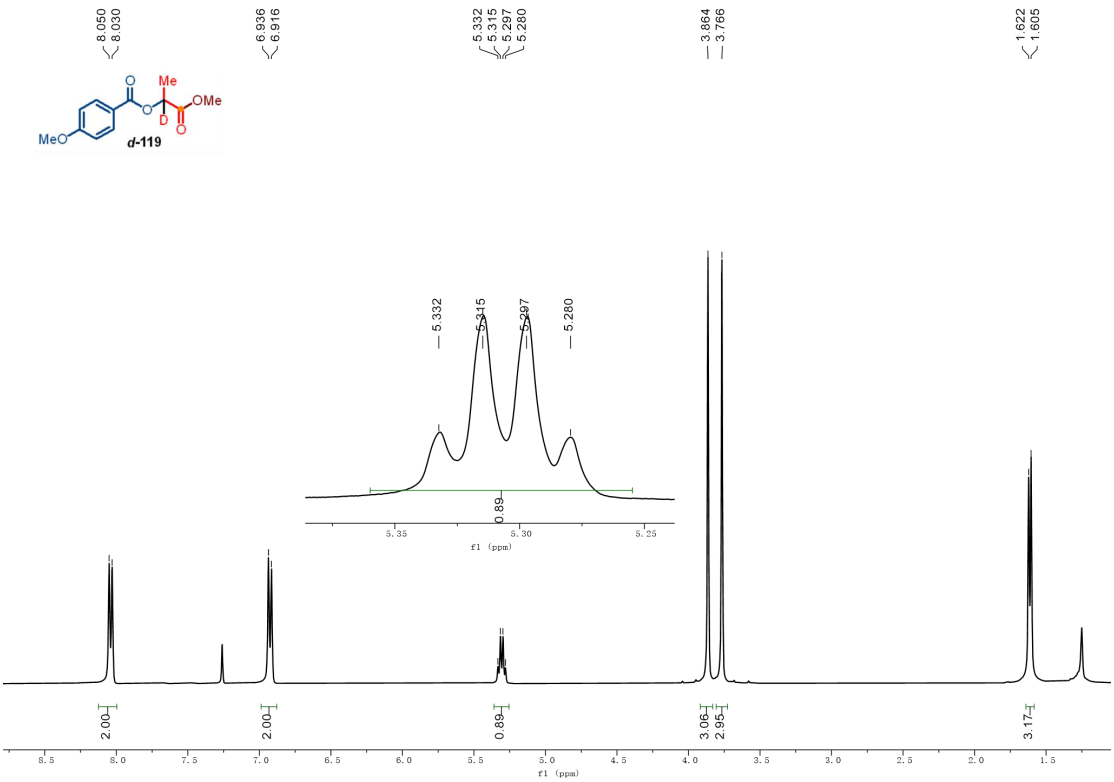
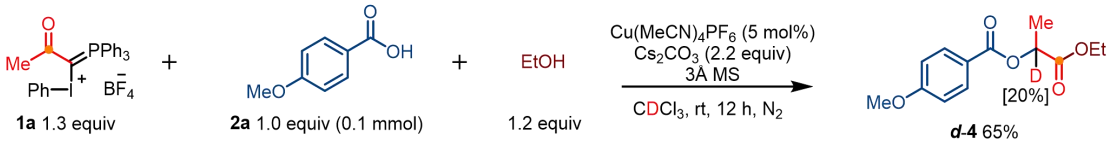


Figure S5. The ^{1}**H NMR** (101 MHz, $CDCl_3$) of ***d*-199**



Phosphonium-iodonium ylides **1a** (0.13 mmol, 1.3 equiv.), 4-Methoxybenzoic acid **2a** (0.1 mmol, 1.0 equiv.), $Cu(MeCN)_4PF_6$ (0.005 mmol, 5 mol%), Cs_2CO_3 (0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then EtOH **3a** (0.12 mmol, 1.2 equiv.) and $CDCl_3$ (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

White solid (15.9 mg, 68% yield, 20% D), R_f = 0.28 (PE/EA = 10:1)

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 5.27 (q, J = 7.2 Hz, 0.80H, 0.20D), 4.22 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H).

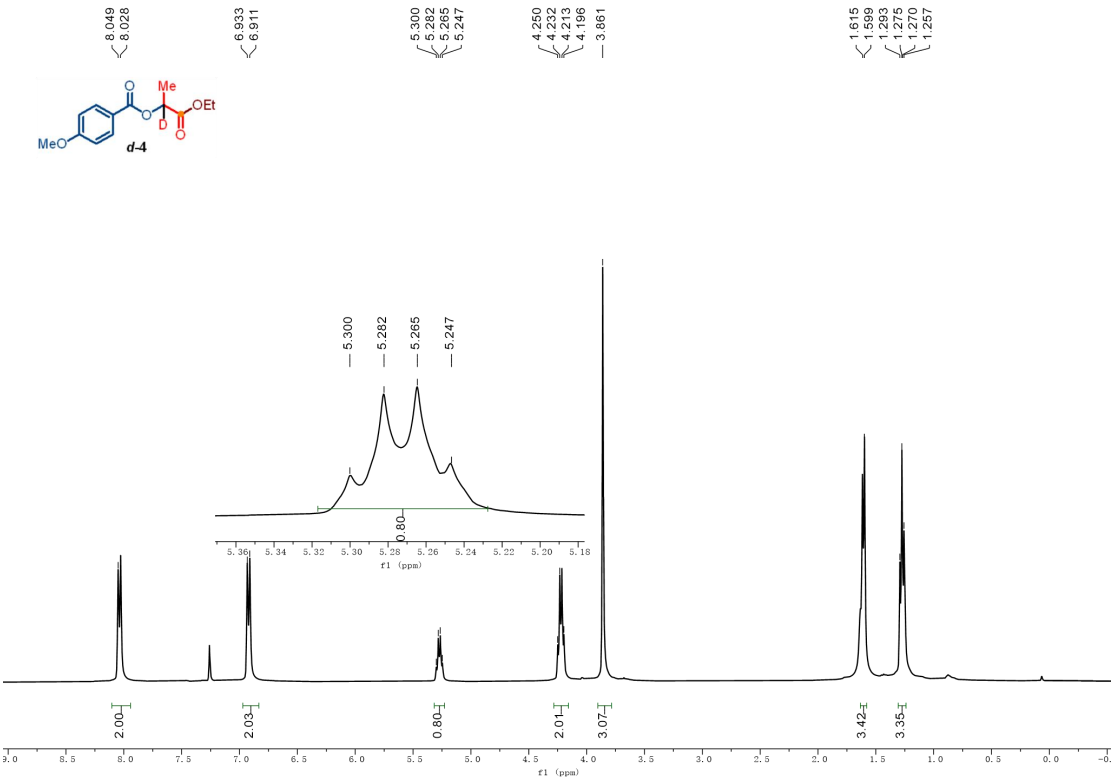
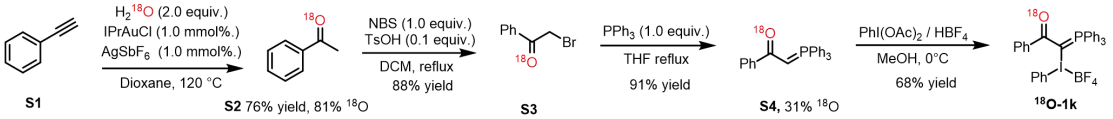


Figure S6. The ^{1}**H NMR** (101 MHz, $CDCl_3$) of ***d*-4**

5.2 ^{18}O-and ^{13}C-Labeling experiment.



Following the literature procedure. In an oven-dried 50 mL two necked flask equipped with a stir bar was added phenylacetylene (1.02 g, 10.0 mmol, 1.0 eq.), IPrAuCl (62 mg, 0.1 mmol, 1.0 mol%), $AgSbF_6$ (34 mg, 0.1 mmol, 1.0 mol%), 1,4-dioxane (10 mL) and $H_2{}^{18}O$ (99% ^{18}O, 400 mg, 20 mmol, 2.0 eq.) under dry argon atmosphere. The resulting mixture was stirred at 120 °C for 4.0 h. After removing the solvents in vacuo, the crude product obtained was filtered by a short column of silica gel (eluent: PE/EA = 20/1) to give acetophenone-^{18}O **S2** (0.93 g, 76% yield, 81% ^{18}O)[5a].

In a round-bottom flask, acetophenone (0.92 g, 7.5 mmol, 1.0 eq.), *N*-bromosuccinimide (1.34 g, 7.5 mmol, 1.0 eq.), and *p*-toluenesulfonic acid (1.43 g, 7.5 mmol, 1.0 eq.) were dissolved in acetonitrile (13.5 mL). The reaction mixture was stirred at 80°C for 8 hours. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was extracted with DCM and water, and the organic layer was dried over anhydrous sodium sulfate. After removing the solvents in vacuo, the crude product obtained was filtered by a short column of silica gel (eluent: PE/EA = 10/1) to give 2-bromo-1-phenylethan-1-one-^{18}O **S3** (1.30 g, 88% yield)[5b].

S3 (6 mmol, 1.0 eq.) was added to a stirred solution of triphenylphosphine (6.0 mmol, 1.0 eq.) in THF (10 mL). The reaction mixture was refluxed for 4 h, then cooled to room temperature. Filter the solids and wash them with THF (20 mL × 3), then dry them on the funnel. After transferring to a separatory funnel, add DCM to dissolve solids and aqueous NaOH (20 w%, 20 mL) were added and the mixture was shaken vigorously for 10 min. The phases were separated and the aqueous phase was extracted with DCM (10 mL × 3). Combined organic layers and dried over Na_2SO_4, filtered and evaporated to dryness. The crude product **S4** (2.08 g, 91% yield, 31% ^{18}O) was carried forward to the next step without purification[1].

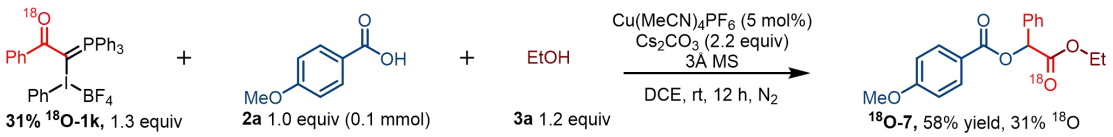
While stirring, the solution of $PhI(OAc)_2$ (5 mmol, 1.0 eq.) and HBF_4 (48% w/w) (5 mmol, 1.0 eq.) in MeOH (5 mL) was added dropwise to the ice bath-cooled solution of **S4** (5 mmol, 1.0 eq.) in MeOH (5 mL) for 20 min. During the addition process, a large amount of precipitate was formed. After complete addition, the reaction mixture was stirred at 0 °C for 1.5 h. After filtration, the precipitate was washed with Et_2O (5 mL × 3), recrystallized from DCM/Et_2O, and dried under vacuum to give corresponding substrates **^{18}O-1k** (2.29 g, 68% yield, 31% ^{18}O)[1].

Table S4. GC-MS date of acetophenone-^{18}O **S2**

m/z	Absolute Intensity	Relative Intensity
117.15	840	0.01
118.15	3924	0.05
119.15	24066	0.29
120.10	919823	10.96
121.15	199244	2.37
122.10	4307740	51.31
123.10	369446	4.40
124.10	14996	0.18
125.10	404	0.00
126.10	119	0.00

Table S5. GC-MS date of ^{18}O-S4

m/z	Absolute Intensity	Relative Intensity
300.15	5604	0.09
301.10	115156	1.85
302.15	116987	1.88
303.10	5614628	90.03
304.10	1348028	21.61
305.10	2491561	39.95
306.10	551980	8.85
307.05	58072	0.93
308.05	4723	0.08
309.00	1263	0.02



Phosphonium-iodonium ylides **^{18}O-1k** (0.13 mmol, 1.3 equiv.), 4-Methoxybenzoic acid **2a** (0.1 mmol, 1.0 equiv.), $Cu(MeCN)_4PF_6$ (0.005 mmol, 5 mol%), Cs_2CO_3 (0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then EtOH **3a** (0.12 mmol, 1.2 equiv.) and dry DCE (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

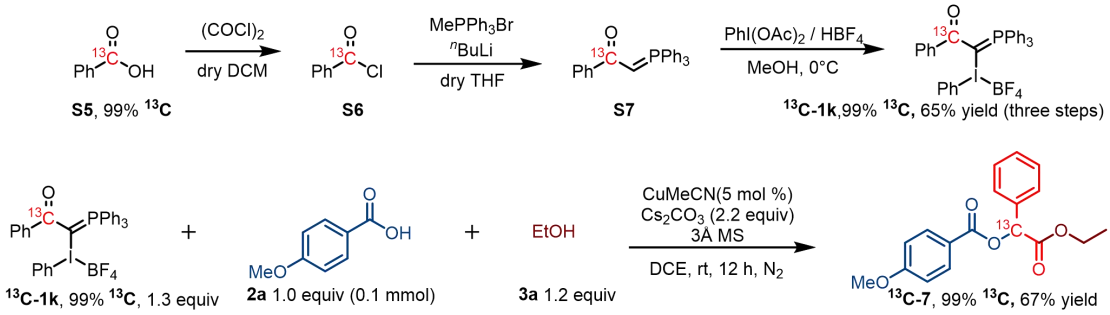
White solid (18.6 mg, 58% yield, 31% ^{18}O), R_f = 0.28 (PE/EA = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, J = 6.8, 2.0 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.46 – 7.37 (m, 3H), 6.93 (dt, J = 6.8, 2.0 Hz, 2H), 6.11 (s, 1H), 4.30 – 4.12 (m, 2H),

3.86 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

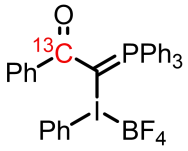
Table S6. GC-MS date of ^{18}O-7

m/z	Absolute Intensity	Relative Intensity
310.10	54	0.00
311.15	1072	0.01
312.15	1896	0.02
313.15	45659	0.54
314.15	970357	11.57
315.10	240754	2.87
316.15	422837	5.04
317.10	91980	1.10
318.10	14980	0.18
319.10	1618	0.02



^{13}C-1k was synthesized according General procedure for synthesized hypervalent iodine reagents:

1-phenyl-2-(phenyl(tetrafluoro-λ^5-boranyl)-λ^3-iodanyl)-2-(triphenyl-λ^5-phosphanylidene)ethan-1-one-1-^{13}C (**^{13}C-1k**)



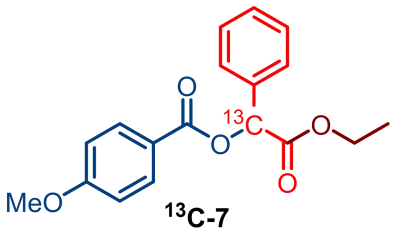
^{13}C-1k

Prepared as a white solid in 65% yield (three-steps).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 – 7.70 (m, 5H), 7.68 – 7.56 (m, 13H), 7.55 – 7.48 (m, 3H), 7.43 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 191.2, 140.0 (dd, J = 57.6, 8.4 Hz), 133.7, 133.6, 132.1, 131.4, 131.3, 130.2, 129.4 (d, J = 12.7 Hz), 128.3 (d, J = 3.9 Hz), 127.6 (d, J = 2.3 Hz), 123.8, 122.9, 119.4.

2-ethoxy-2-oxo-1-phenylethyl 4-methoxybenzoate (**^{13}C-7**)

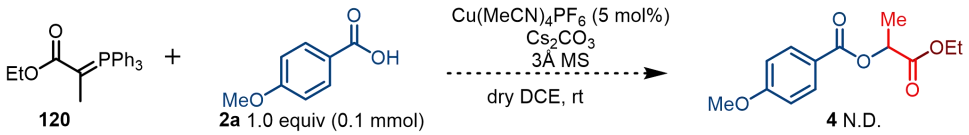


Prepared according to the **general procedure B**, White solid (21.3 mg, 67% yield), R_f = 0.16 (PE/EA = 10/1).

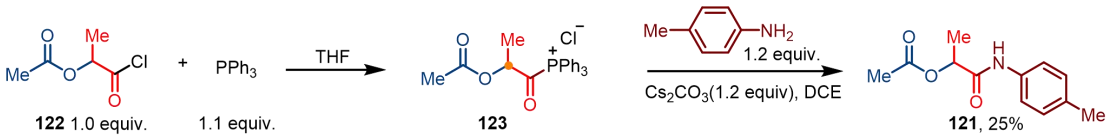
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, J = 8.8, 2.4 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.46 – 7.37 (m, 3H), 6.93 (dt, J = 8.8, 2.4 Hz, 2H), 6.11 (d, J = 152.9 Hz, 1H), 4.30 – 4.13 (m, 2H), 3.86 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, J = 64.3 Hz), 165.7 (d, J = 2.1 Hz), 163. 9, 134.4 (d, J = 48.6 Hz), 132.2 129.2, 128.9 (d, J = 3.9 Hz), 127.7 (d, J = 3.1 Hz), 121.8, 113.8, 74.9, 61.8, 55.6, 14.1.

5.3 Control experiment



Ethyl 2-(triphenyl-λ^5-phosphanylidene)propanoate **120** (0.13 mmol, 1.3 equiv.), 4-Methoxybenzoic acid **2a** (0.1 mmol, 1.0 equiv.), $Cu(MeCN)_4PF_6$ (0.005 mmol, 5 mol%), Cs_2CO_3 (0.10 mmol, 1.1 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then Dry DCE (1 mL) were added to the reaction tube and stirred at 26 °C for 12 h. Through detection and analysis, no expected product **4** generation was observed

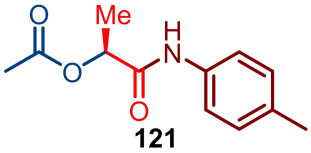


According to the literature procedures[6]. To a dry THF (2 mL, 0.5 M) solution of (*S*)-1-chloro-1-oxopropan-2-yl acetate **122** (1.0 mmol, 1.0 equiv.) cooled to -20 °C, PPh_3 (1.1 mmol, 1.1 equiv.) was added under an argon atmosphere and the resulting mixture was stirred for 20 min. After the reaction was completed, the solvent was removed under reduced pressure to afford a colorless oil. Hexane (10 mL) was then added, and the mixture was sonicated for 2 minutes. The solvent was decanted (this process was repeated three times), yielding a white, low-melting-point solid **123**.

(***Caution:*** *This intermediate is highly unstable and moisture-sensitive. Do not dry under vacuum.* ***After washing, use the product immediately in the next step. The acyl chloride showed high solubility in hexane. Therefore, after washing the reaction mixture with hexane, no or only trace residual acyl chloride*** *should remain.*)

Weigh **123** (0.1 mmol, 1.0 equiv.) into a reaction vial, then add *p*-toluidine (0.12 mmol, 1.2 equiv.), Na_2CO_3 (0.12 mmol, 1.2 equiv.), and finally Dry DCE (1 mL). Stir the mixture at room temperature for 1 h. Then stirred at 26 °C for 12 h. Solvent was removed in vacuo and the crude mixture was purified by flash column chromatography.

(*S*)-1-oxo-1-(*p*-tolylamino)propan-2-yl acetate (**121**)



White solid (5.6 mg, 25% yield), R_f = 0.27 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.31 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 2.19 (s, 3H), 1.55 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 168.3, 134.6, 134.5, 129.7, 120.3, 71.0, 21.3, 21.0, 17.9.

HRMS (ESI) $[M+H]^+$ calcd. for $[C_{12}H_{16}NO_3]^+$ m/z: 222.1225, found, 222.1223.

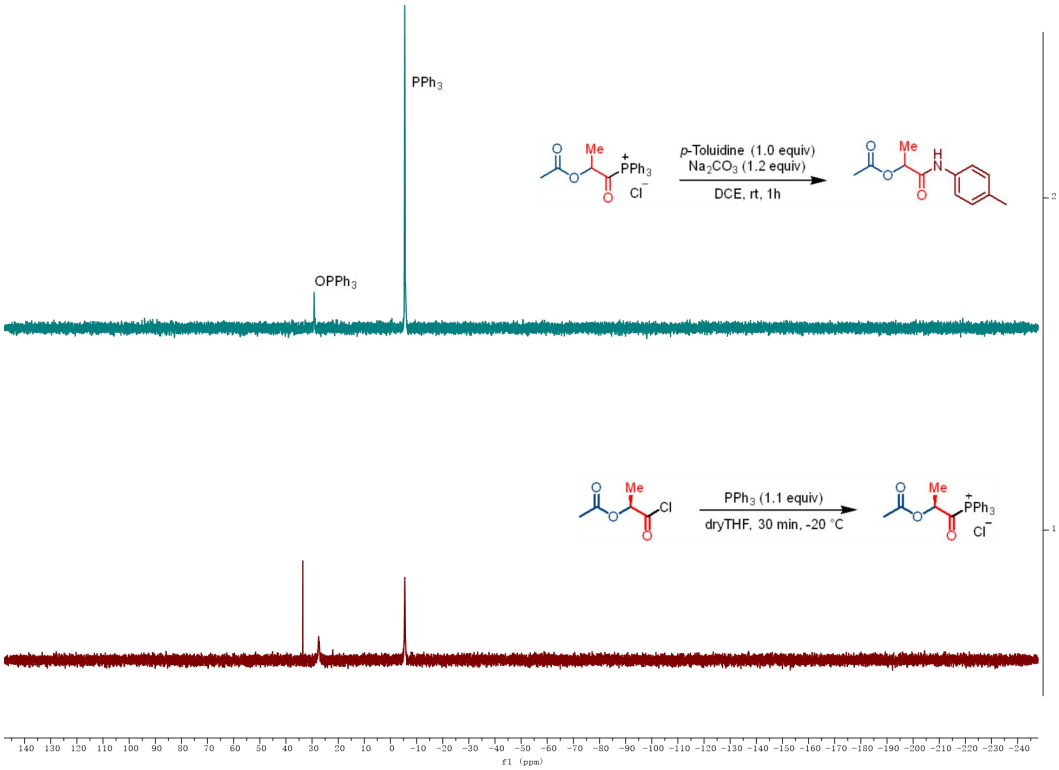


Figure S7. The **^{1}P NMR** (101 MHz, $CDCl_3$) of **Reaction Intermediate** and **121**

5.4 Hammett plot analysis

1k (0.065 mmol, 0.65 equiv.), the corresponding p-substituted ethylbenzene (0.065 mmol, 0.65 equiv.), 4-methoxybenzoic acid **2a** (0.1 mmol, 1.0 equiv.), CuCN (0.005 mmol, 5 mol%), Cs_2CO_3 (0.22 mmol, 2.2 equiv.) and 3Å MS (20 mg) were added to a dry 10 mL reaction tube, successively. The vial was sealed, degassed, and filled with nitrogen. Then EtOH **3a** (0.12 mmol, 1.2 equiv.) and dry DCE (1 mL) were added to the reaction tube successively. Then stirred at 26 °C for 12 h. The composition of mixture was analyzed by GC with *n*-dodecane as the internal standard.

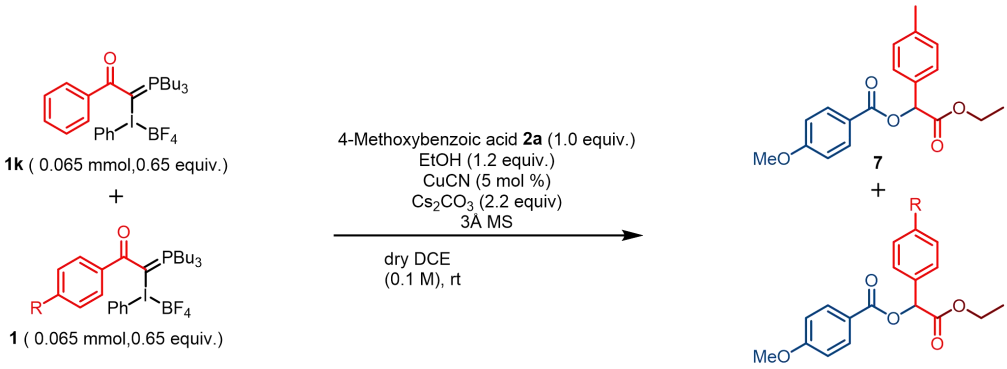


Table S7 Data for Hammett plot.

Para group	σ_p	k_X/k_H	$\log(k_X/k_H)$
OMe	-0.27	-2.4894	-0.3961
Me	-0.17	-1.4030	-0.1471
H	0	1.0000	0
Cl	0.24	1.4900	0.1732

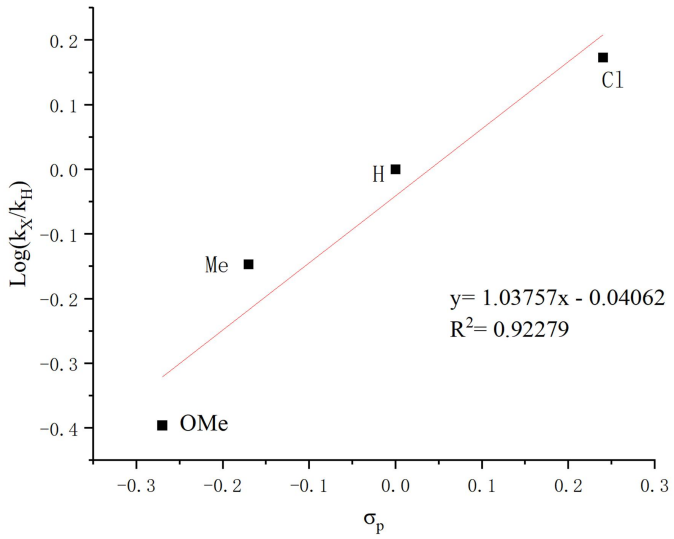
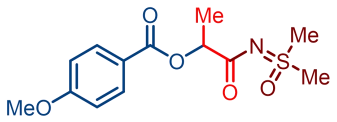


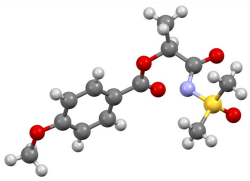
Figure S8. Hammett plot

6. Single Crystal X-ray Structure of Compound 69



69

≡



CCDC 2454723

Table S8 Crystal data and structure refinement for 69

Identification code	exps-3-169-4-20250527_auto
Empirical formula	$C_{13}H_{17}NO_5S$
Formula weight	299.33
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.6727(2)
b/Å	9.9079(2)
c/Å	21.3568(5)
α/°	90
β/°	96.547(2)
γ/°	90
Volume/Å^3	1402.74(6)
Z	4
ρ_{calc}g/cm^3	1.417
μ/mm^{-1}	2.236
F(000)	632.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.334 to 152.47
Index ranges	$-8 \leq h \leq 7$, $-12 \leq k \leq 11$, $-26 \leq l \leq 26$
Reflections collected	8164
Independent reflections	2810 [R_{int} = 0.0257, R_{sigma} = 0.0224]
Data/restraints/parameters	2810/0/185
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1025
Final R indexes [all data]	R_1 = 0.0384, wR_2 = 0.1032
Largest diff. peak/hole / e Å^{-3}	0.66/-0.54

Thermal ellipsoid plot (50% probability) of X-ray structure of compound **69**. Hydrogen, white; Carbon, gray; oxygen, red; sulfur, yellow; bromine, brown. CCDC of compound **69**: 2454723

7. Reference

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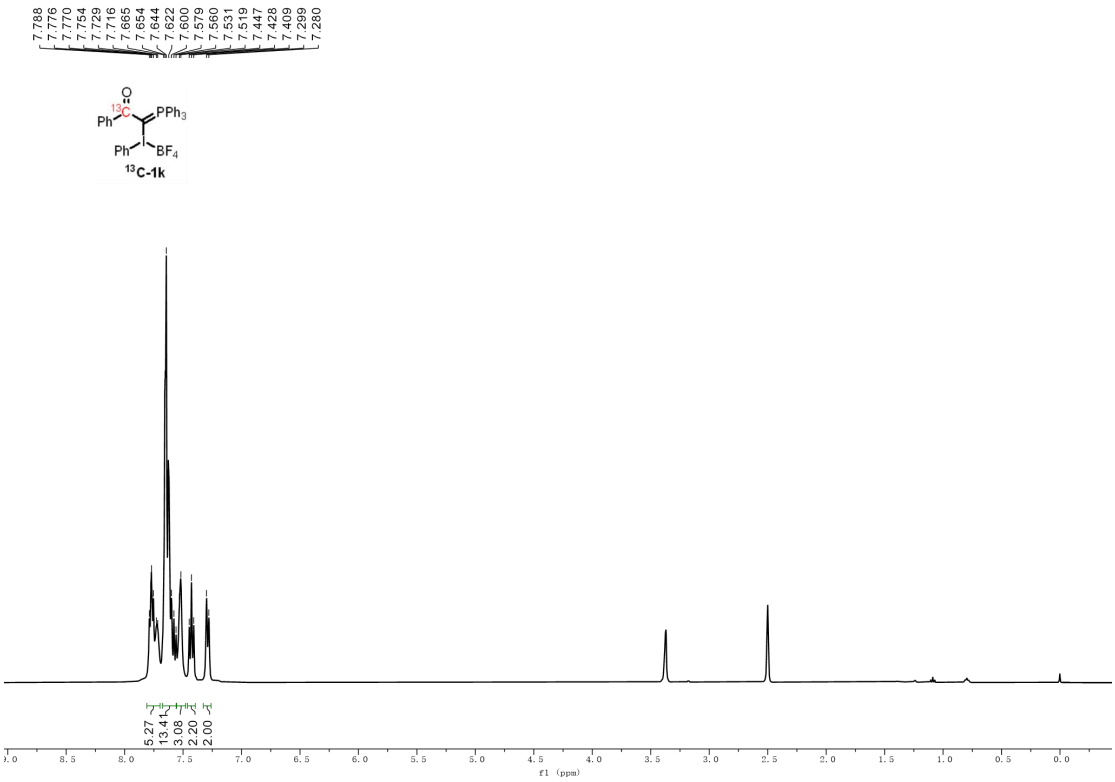
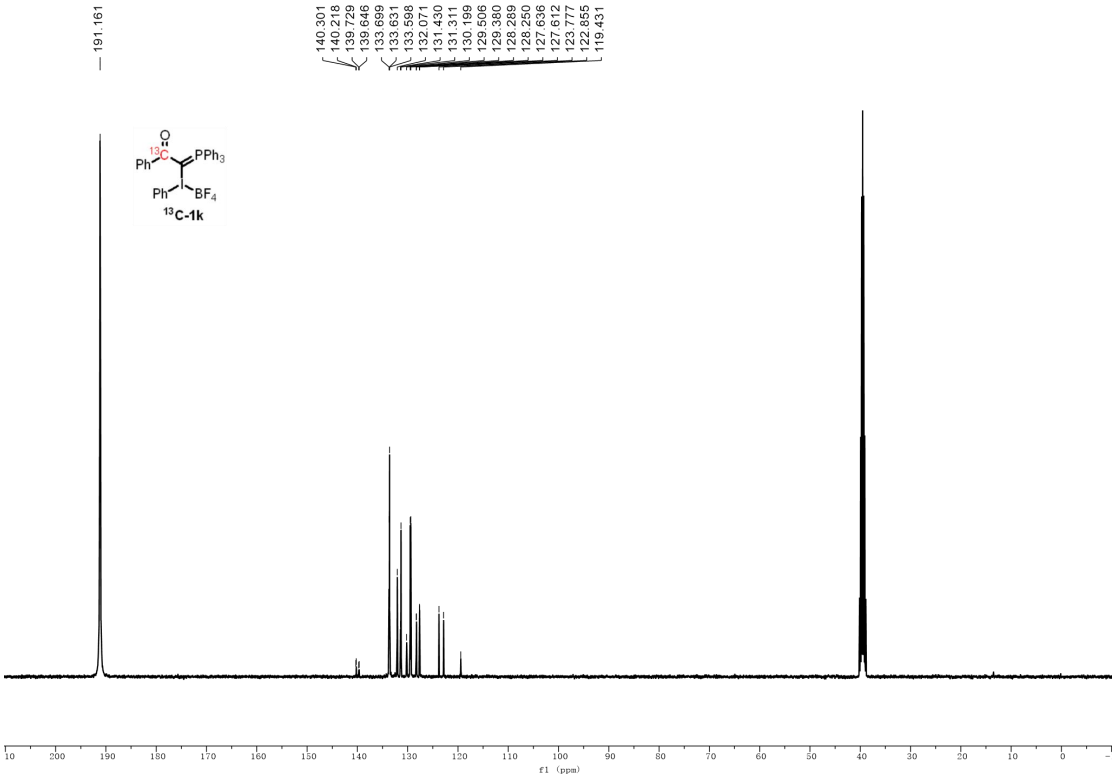
[7]. White, A. R.; Kozlowski, R. A.; Tsai, S. C.; Vanderwal, C. D. A Direct Synthesis of Highly Substituted π-Rich Aromatic Heterocycles from Oxetanes. *Angew. Chem., Int. Ed.* **2017**, *56*, 10525−10529.

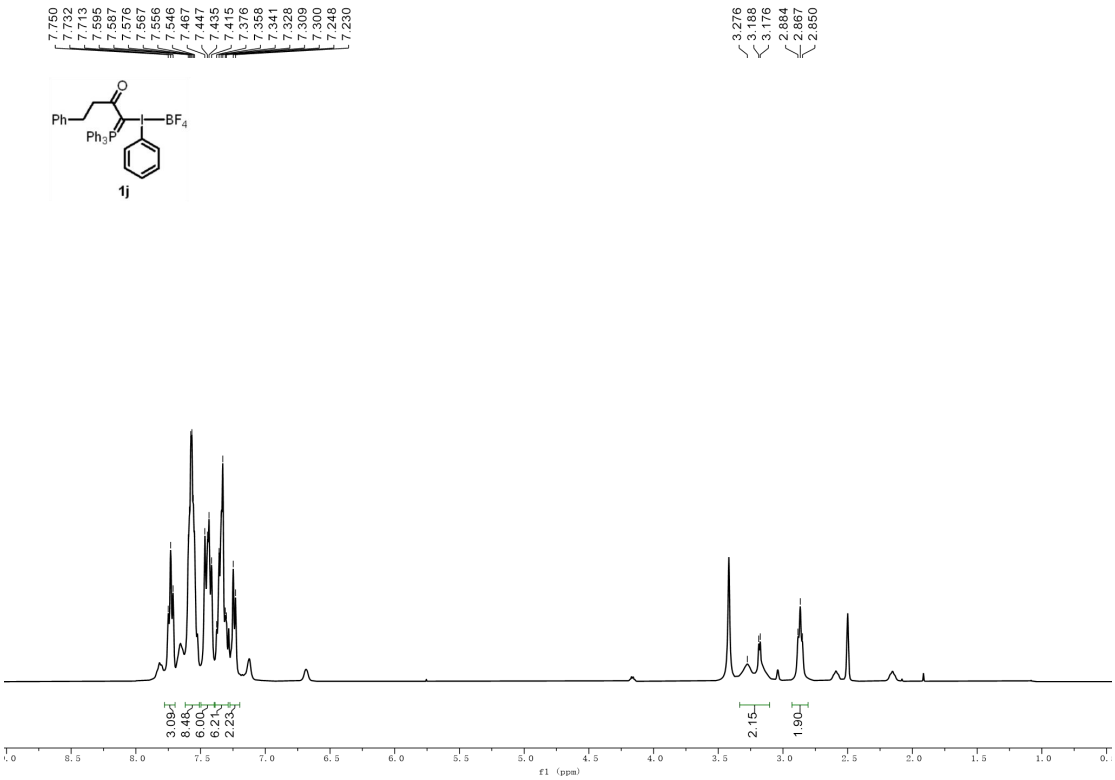
8. ^{1}H, ^{13}C, ^{31}P, ^{19}F and ^{11}B NMR Spectrum of Starting Materials, Catalysts and Products



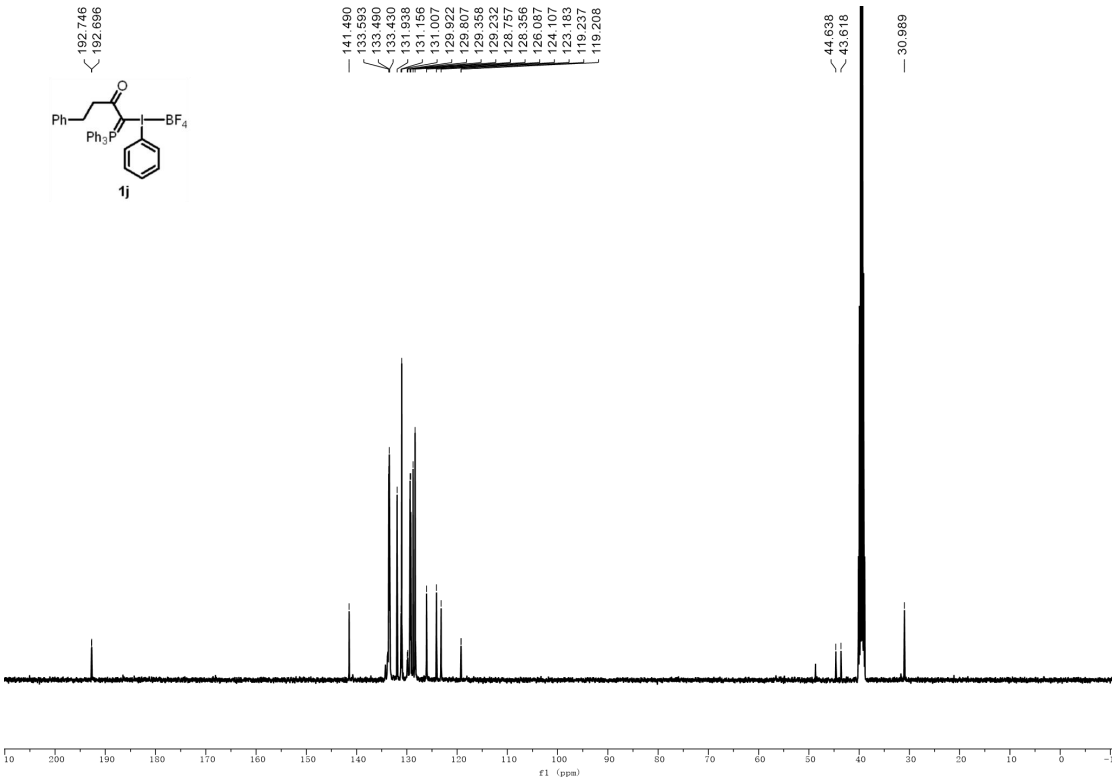
^{1}H NMR (400 MHz, DMSO-d_6) of ^{13}C-1k



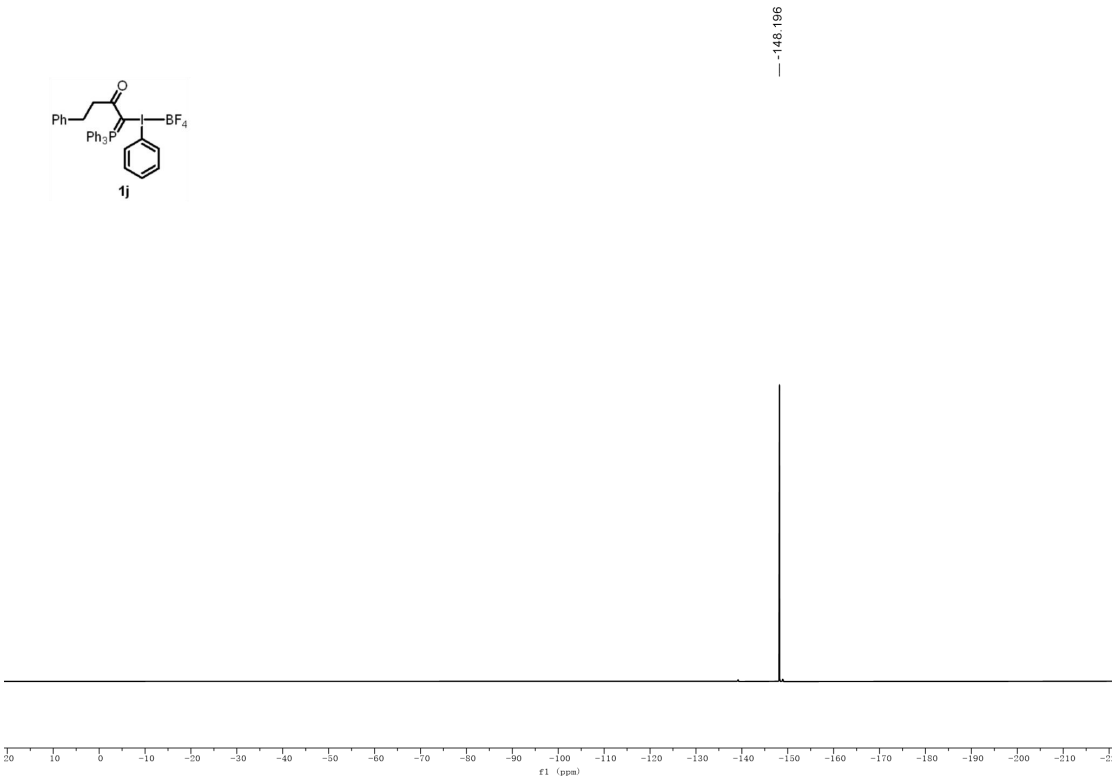
^{13}C NMR (101 MHz, DMSO-d_6) of ^{13}C-1k



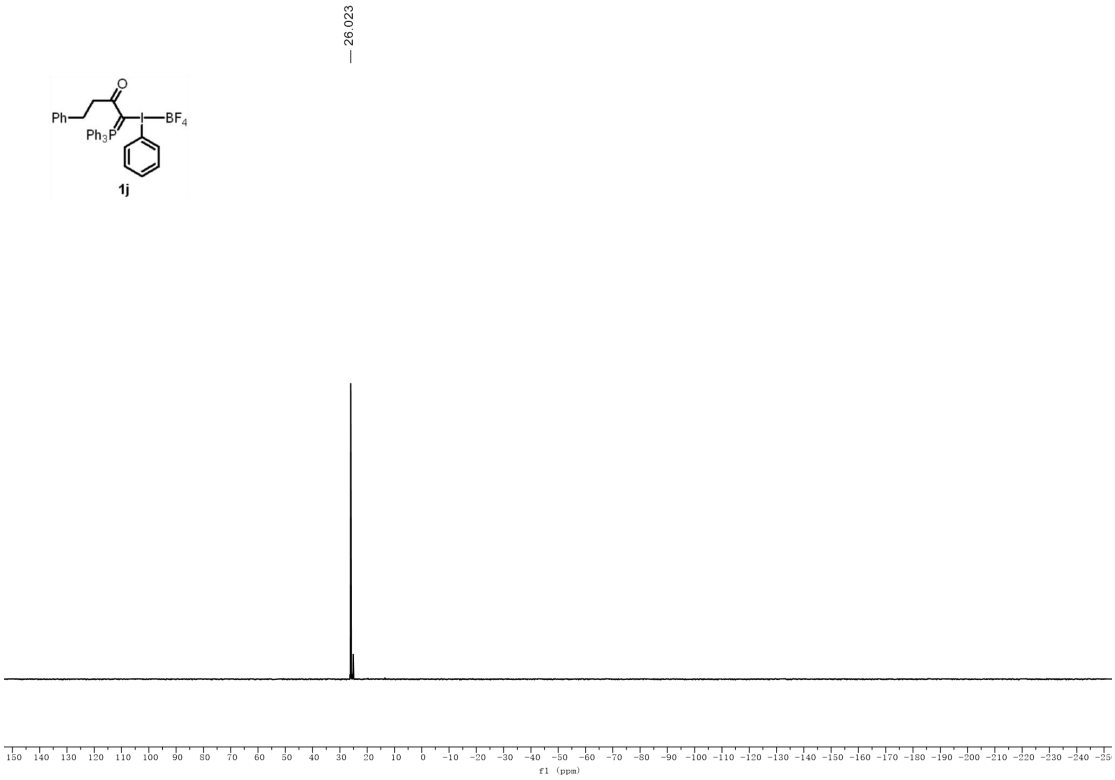
^{1}H NMR (400 MHz, DMSO-*d*$_6$) of 1j



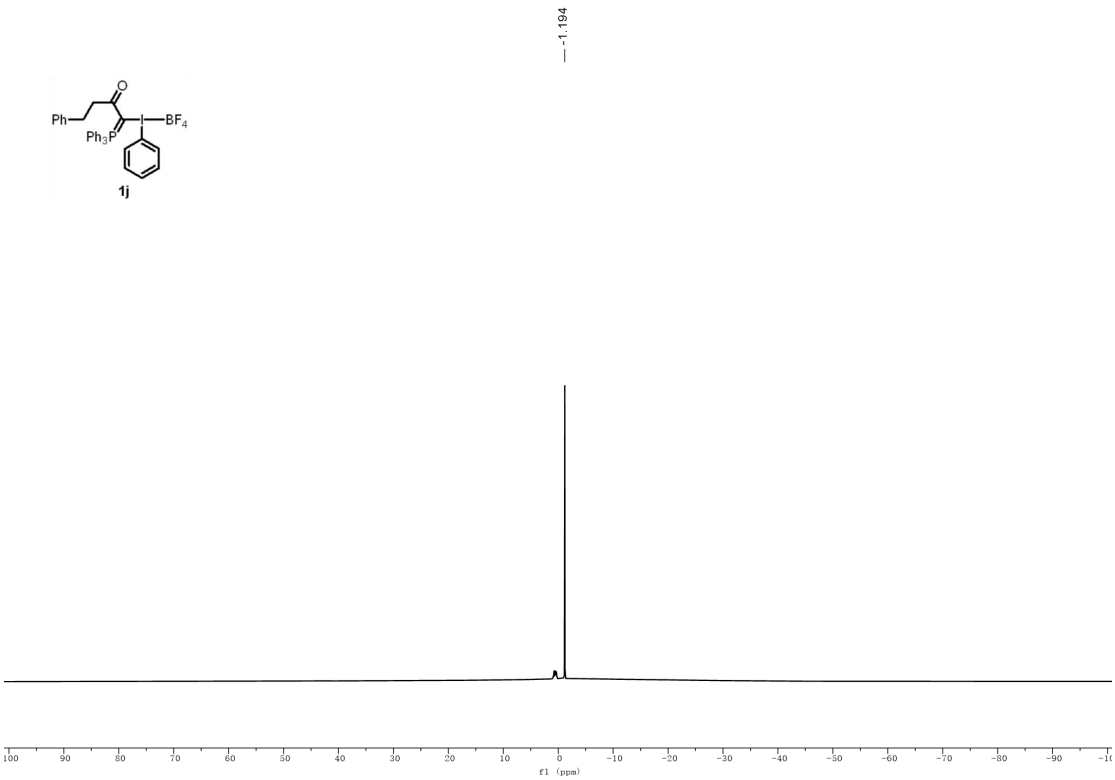
^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 1j



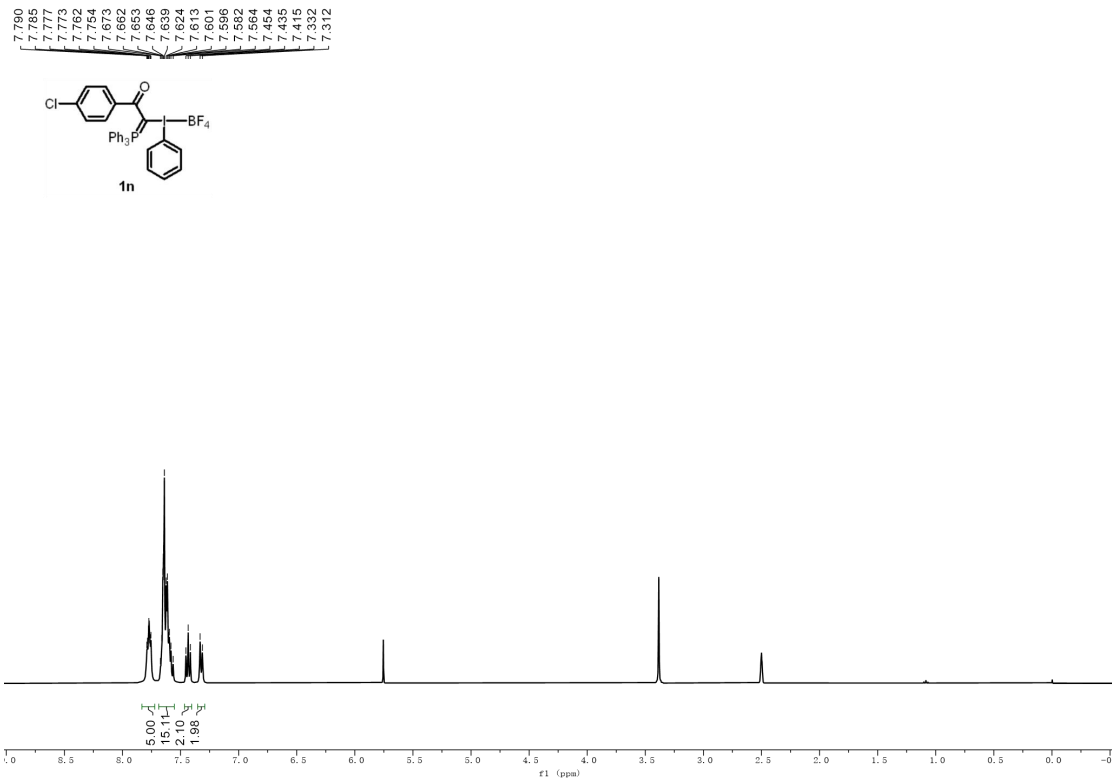
^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 1j



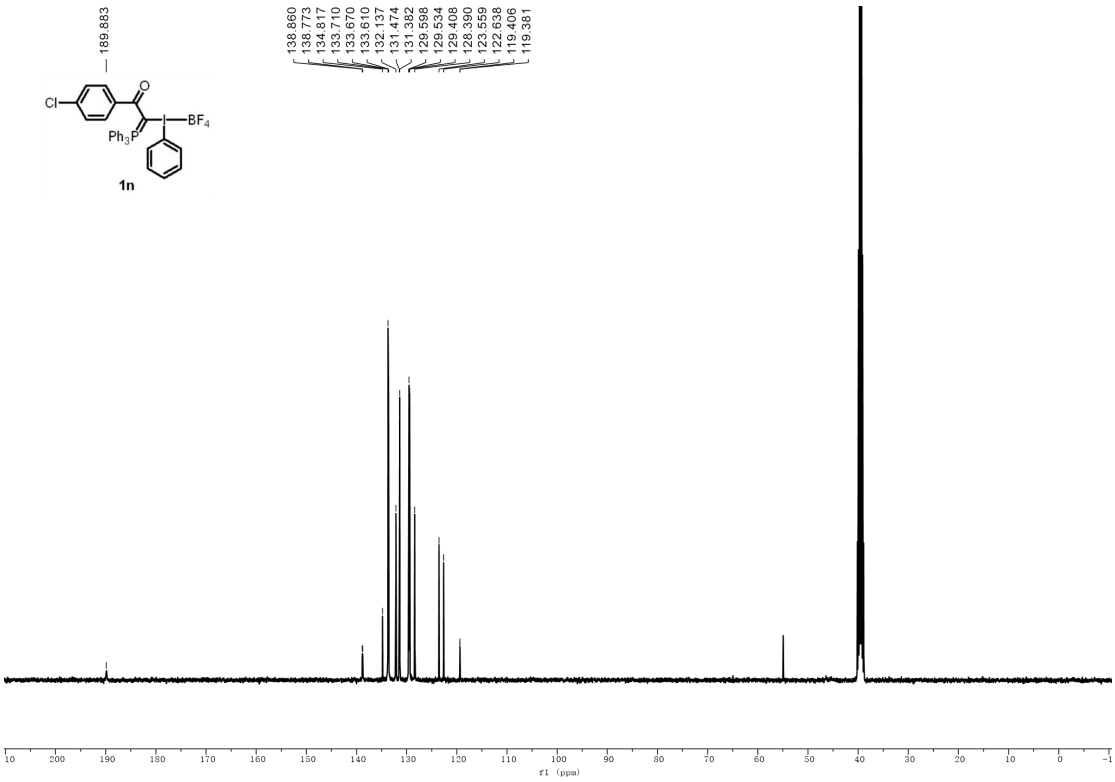
^{31}P NMR (162 MHz, DMSO-*d*$_6$) of 1j



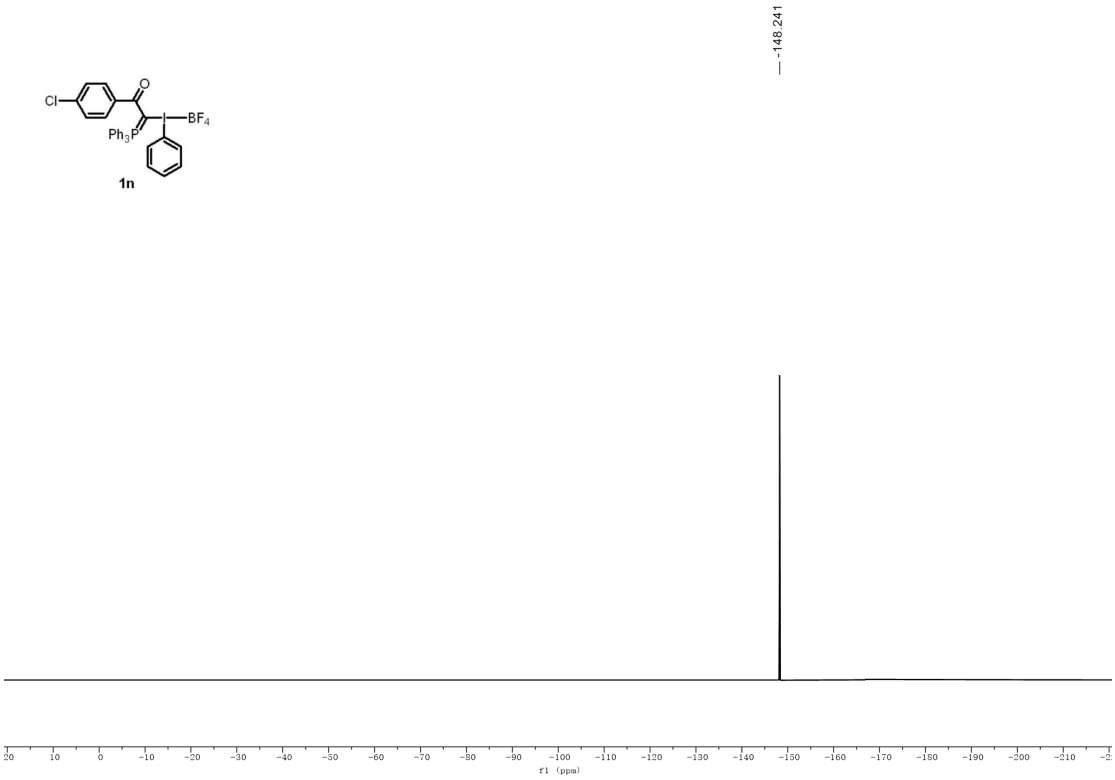
^{11}B NMR (128 MHz, DMSO-d_6) of 1j



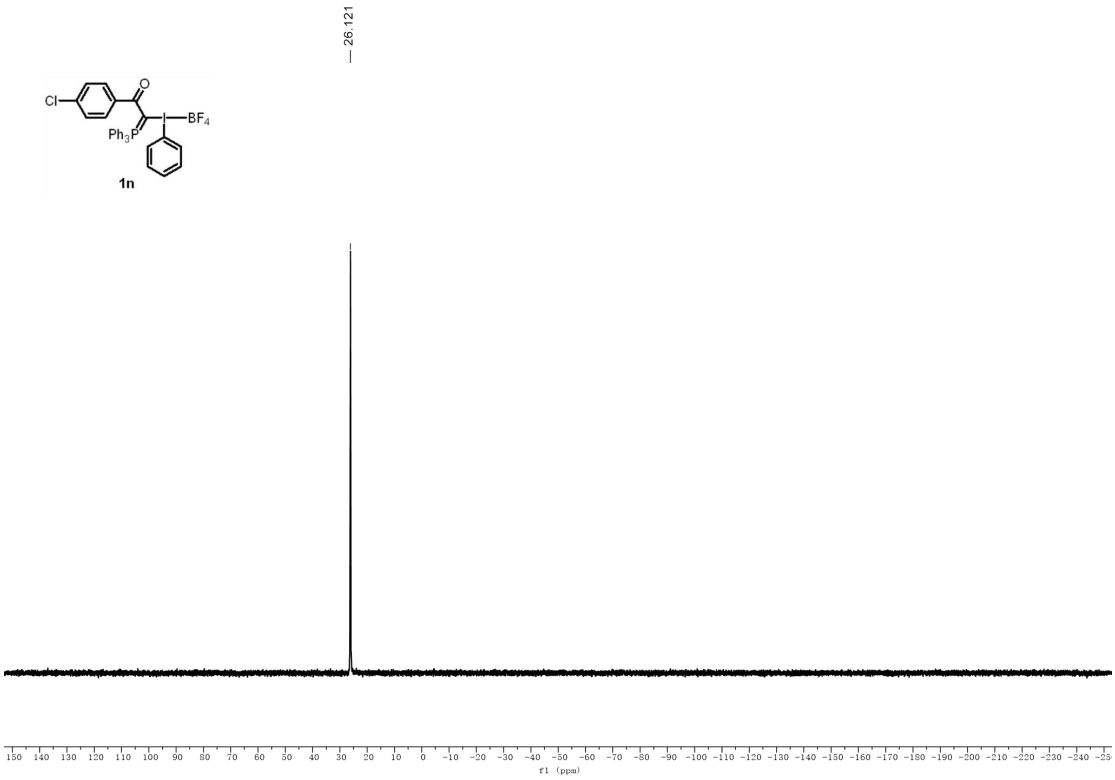
^{1}H NMR (400 MHz, DMSO-d_6) of 1n



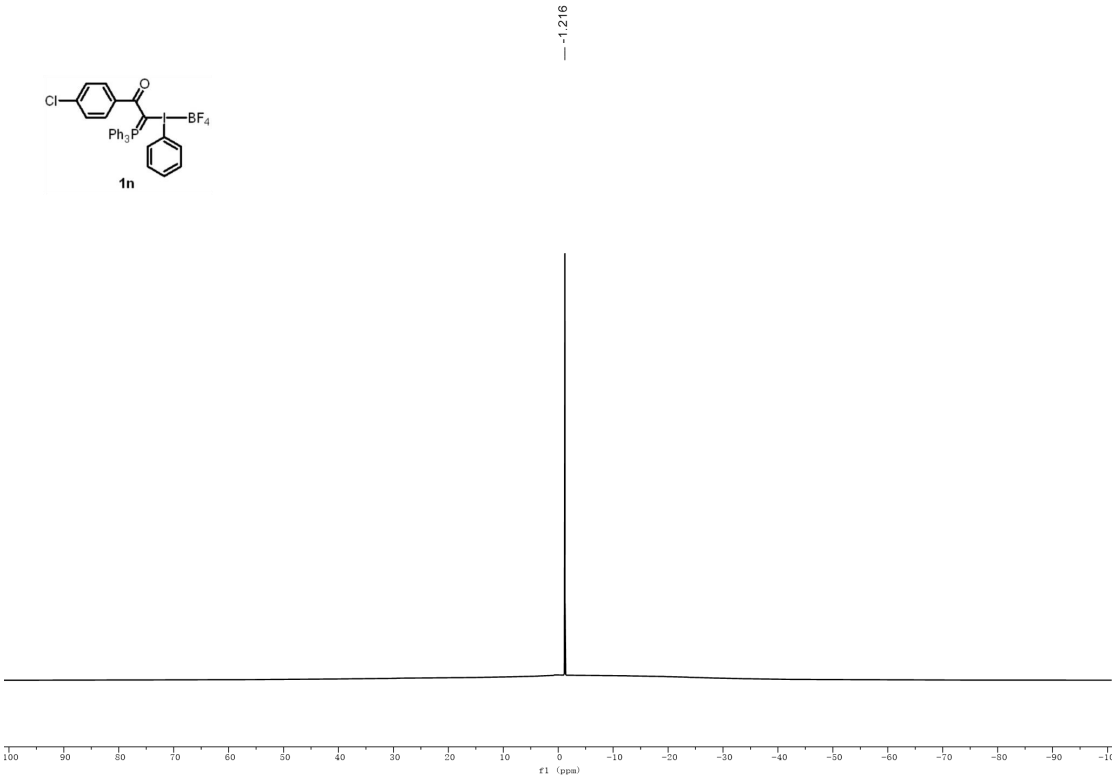
^{13}C NMR (101 MHz, DMSO-d_6) of 1n



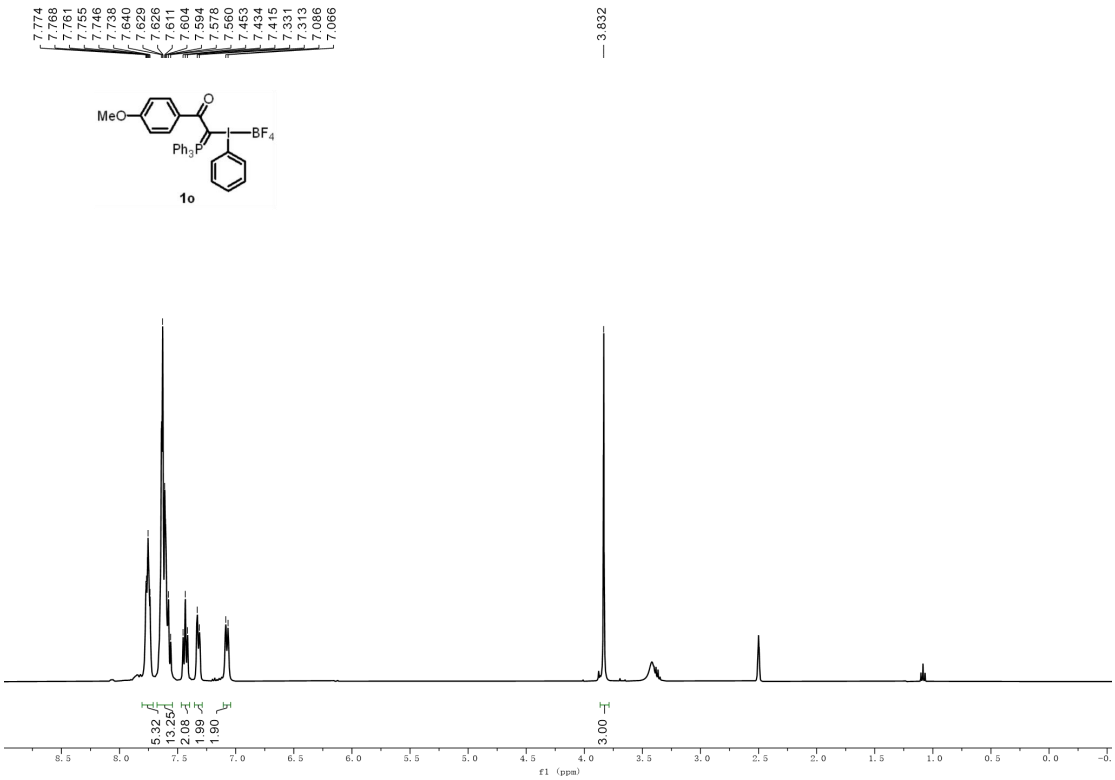
^{19}F NMR (376 MHz, DMSO-d_6) of 1n



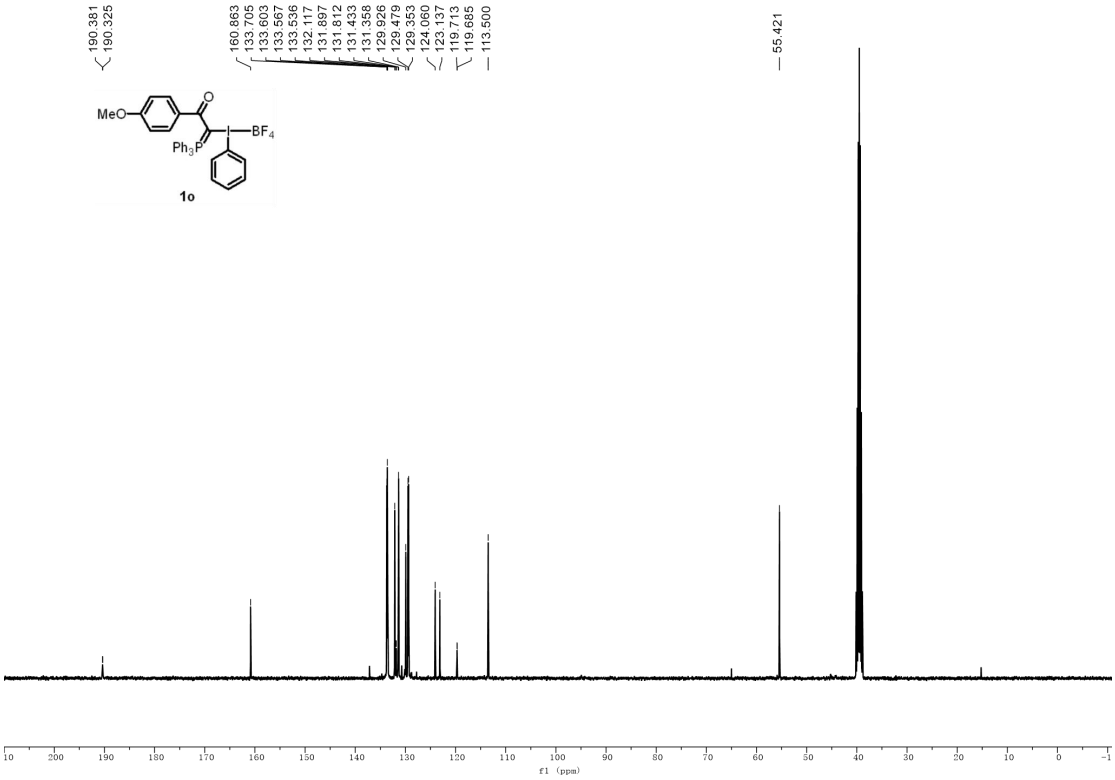
^{31}P NMR (162 MHz, DMSO-*d*$_6$) of 1n



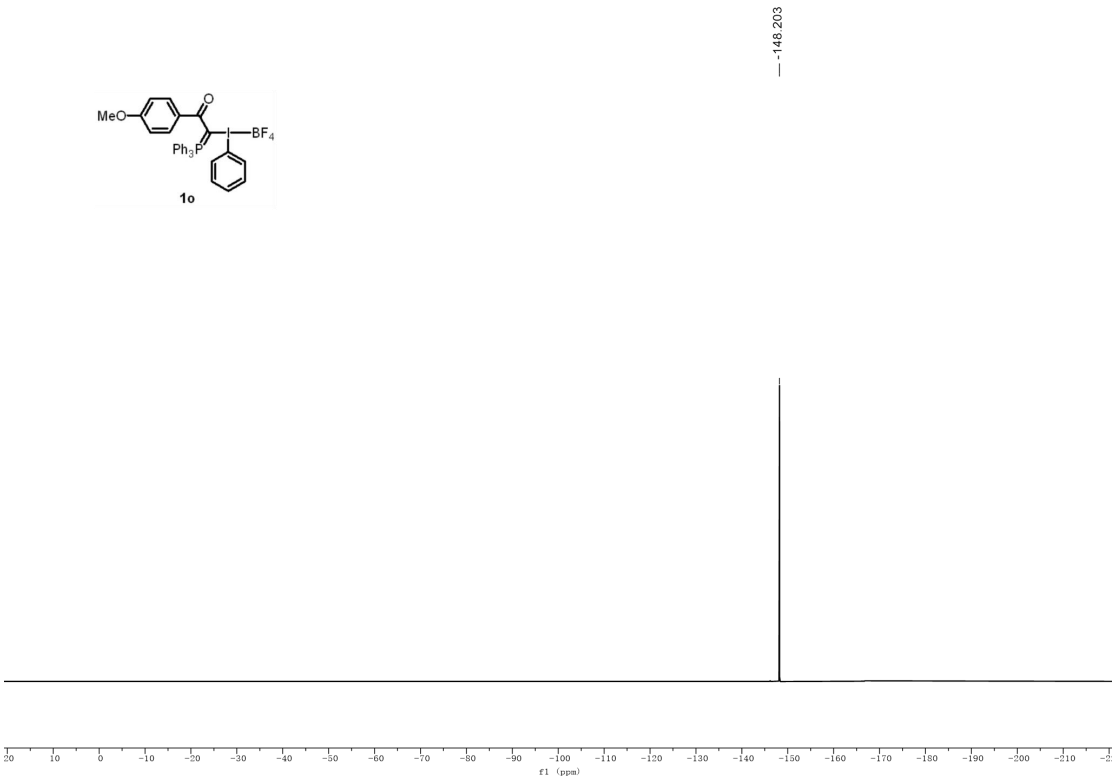
^{11}B NMR (128 MHz, DMSO-*d*$_6$) of 1n



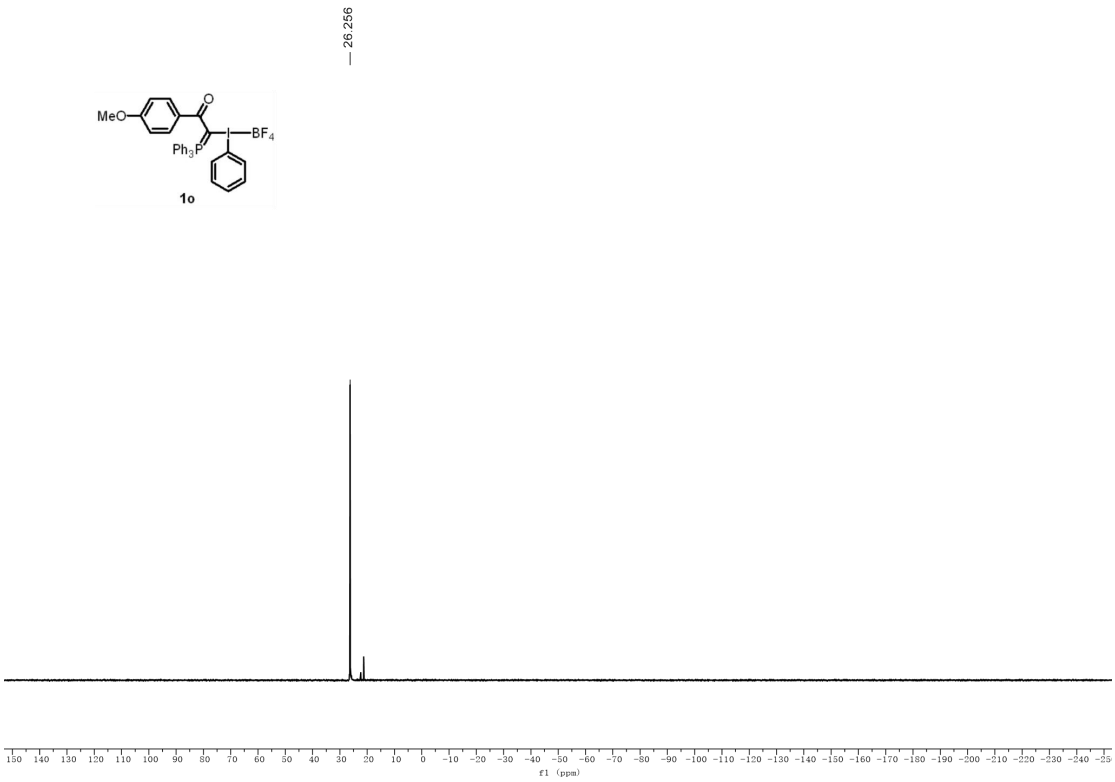
^{1}H NMR (400 MHz, DMSO-d_6) of 1o



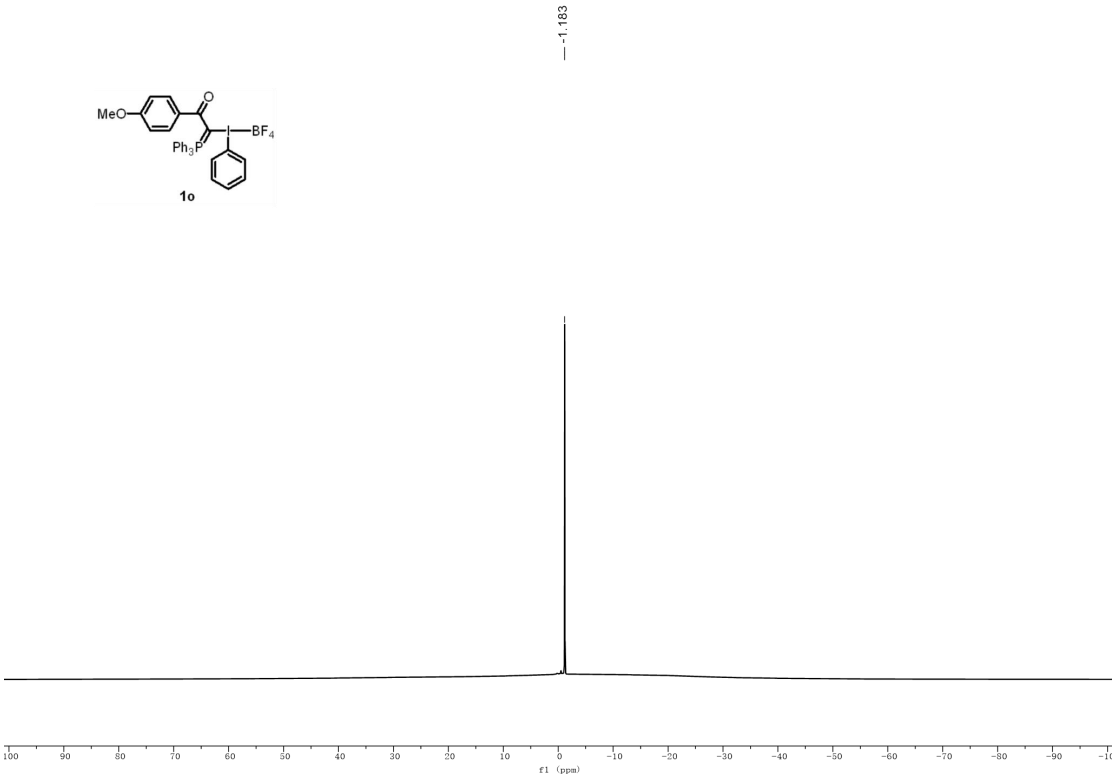
^{13}C NMR (101 MHz, DMSO-d_6) of 1o



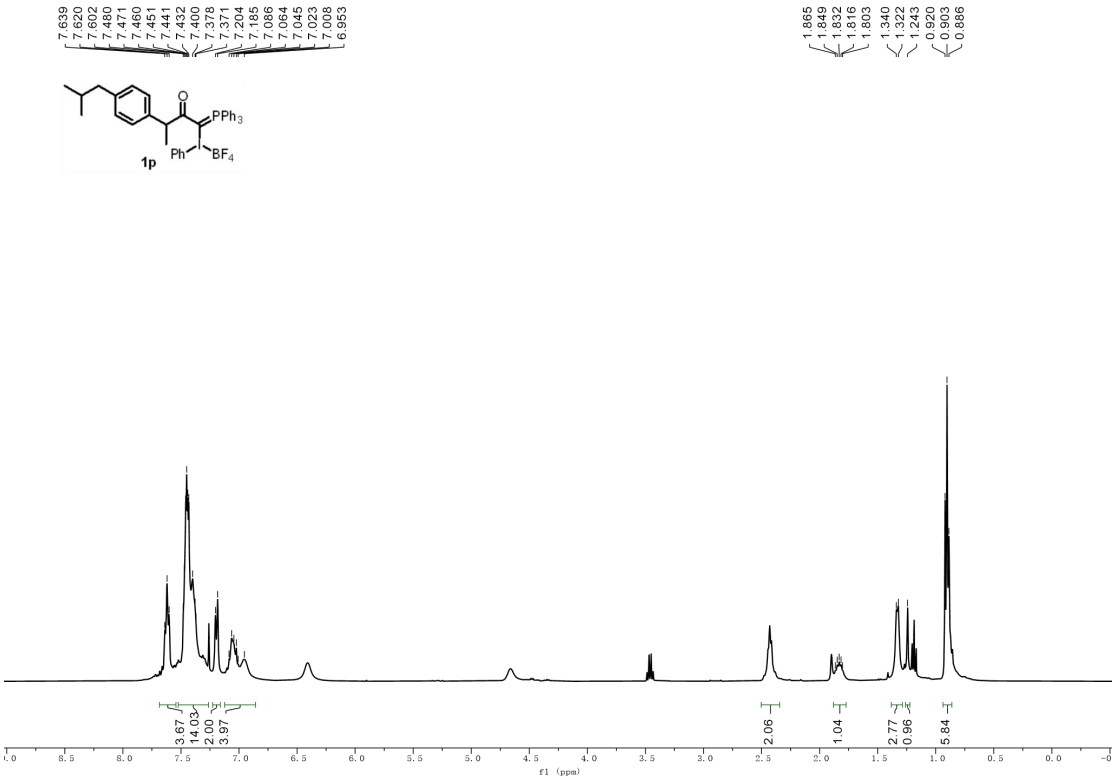
^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 1o



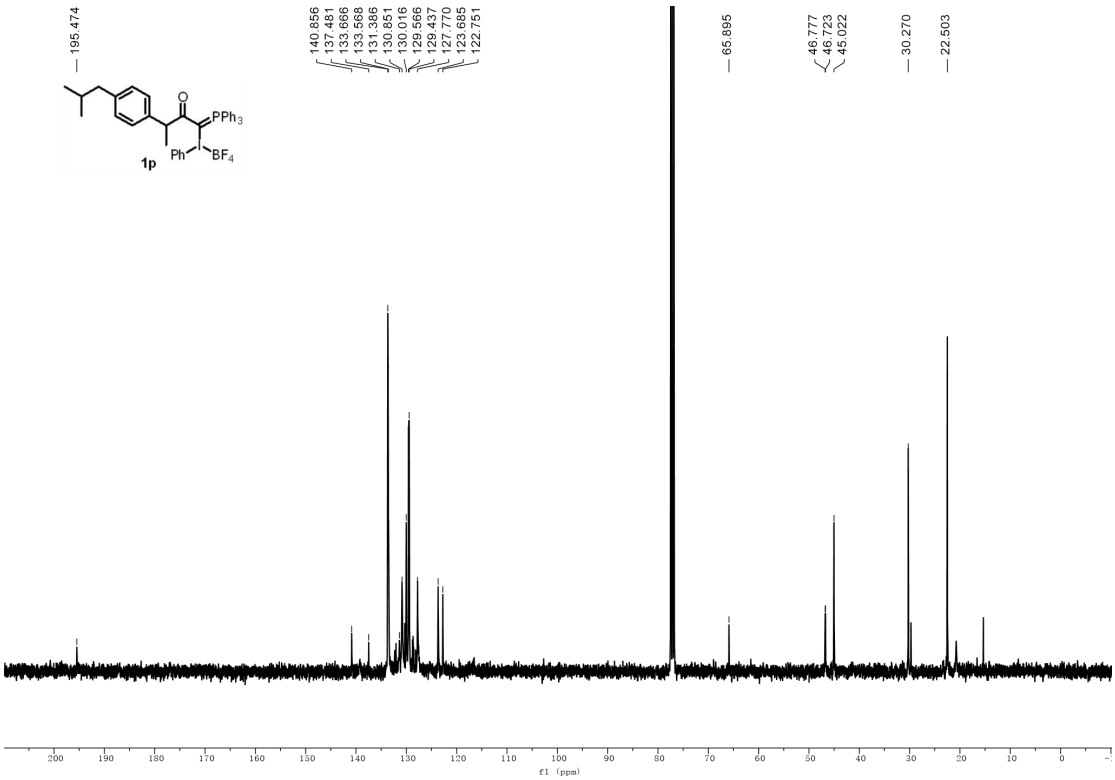
^{31}P NMR (162 MHz, DMSO-*d*$_6$) of 1o



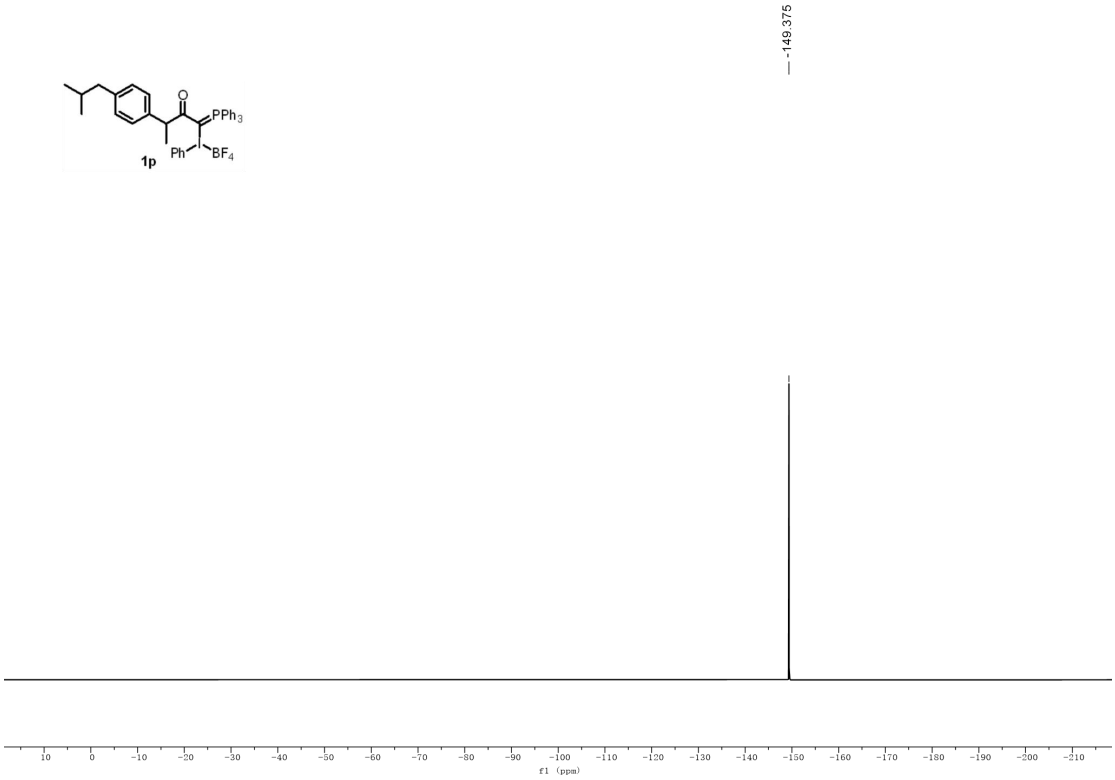
^{11}B NMR (128 MHz, DMSO-d_6) of 1o



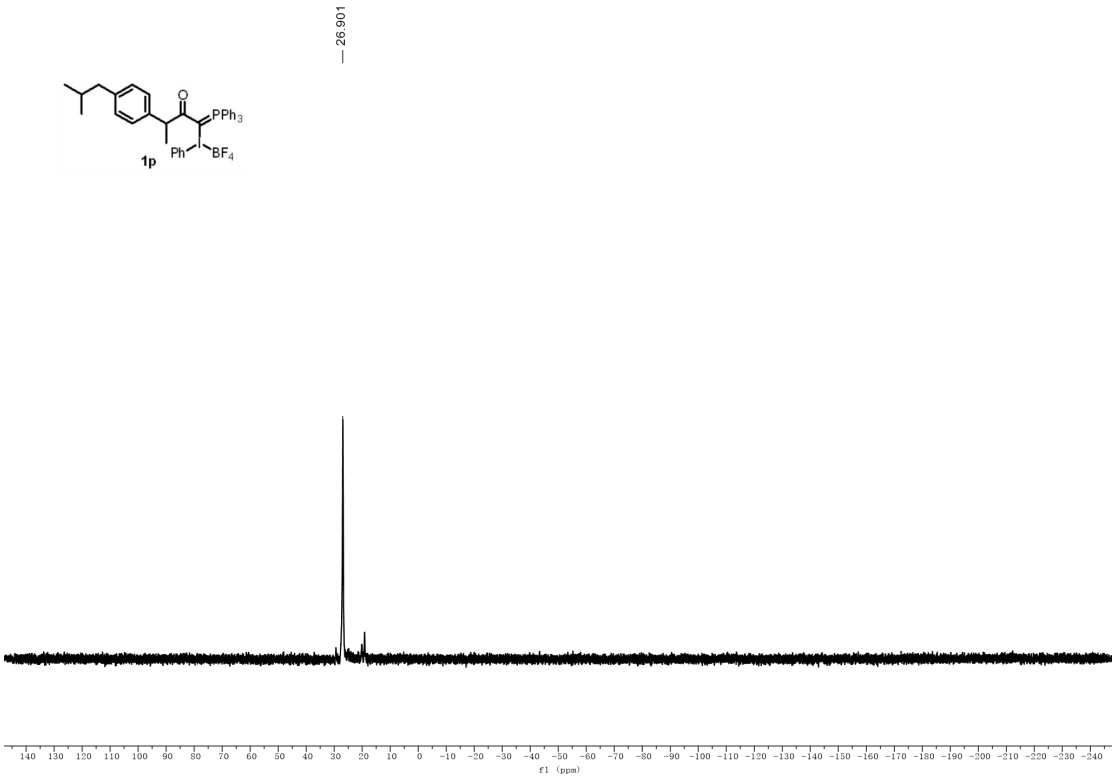
^{1}H NMR (400 MHz, DMSO-d_6) of 1p



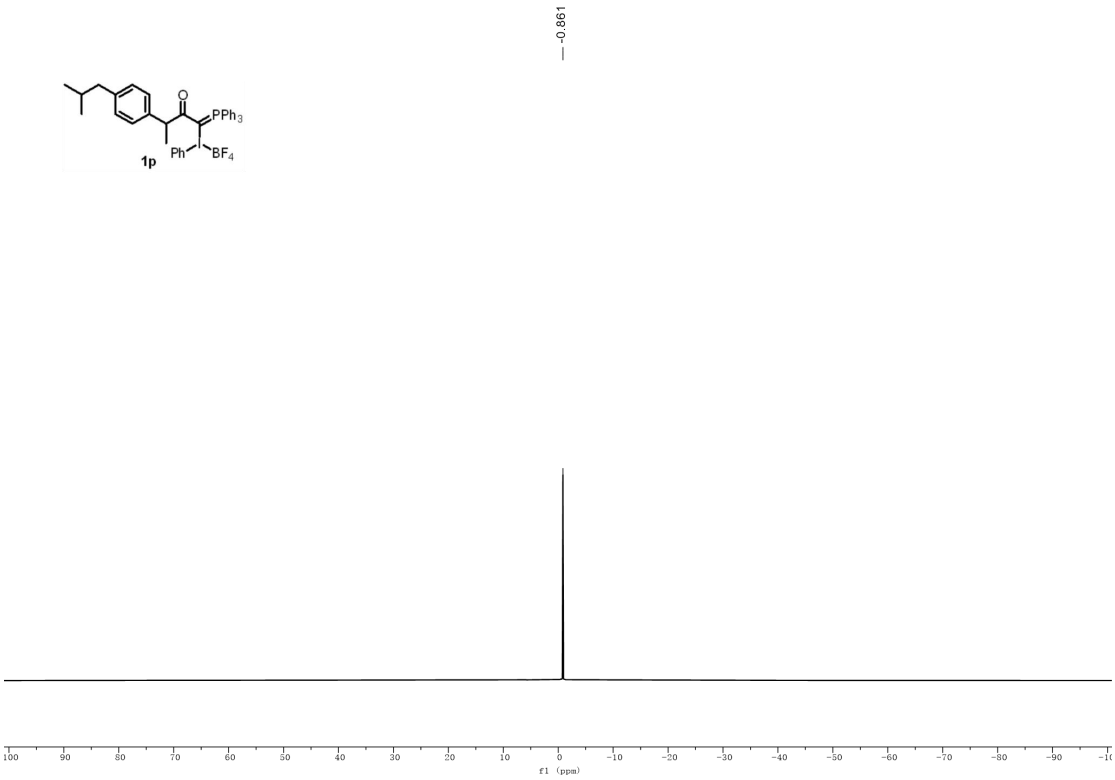
^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 1p



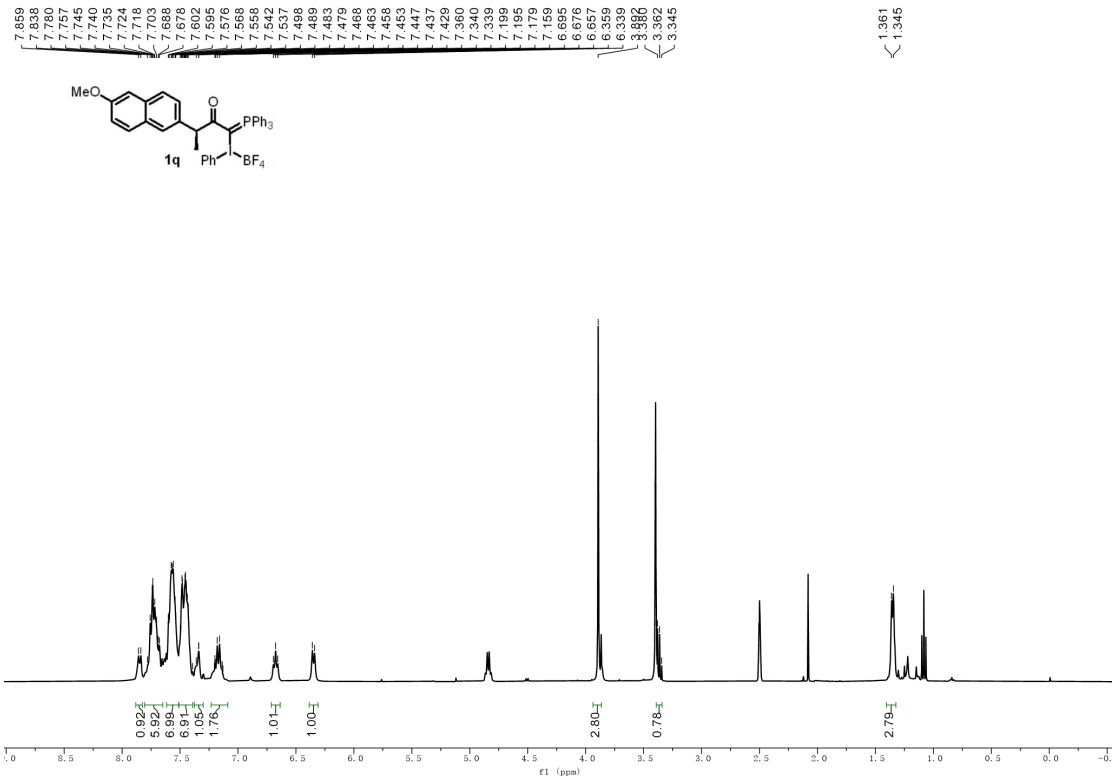
^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 1p



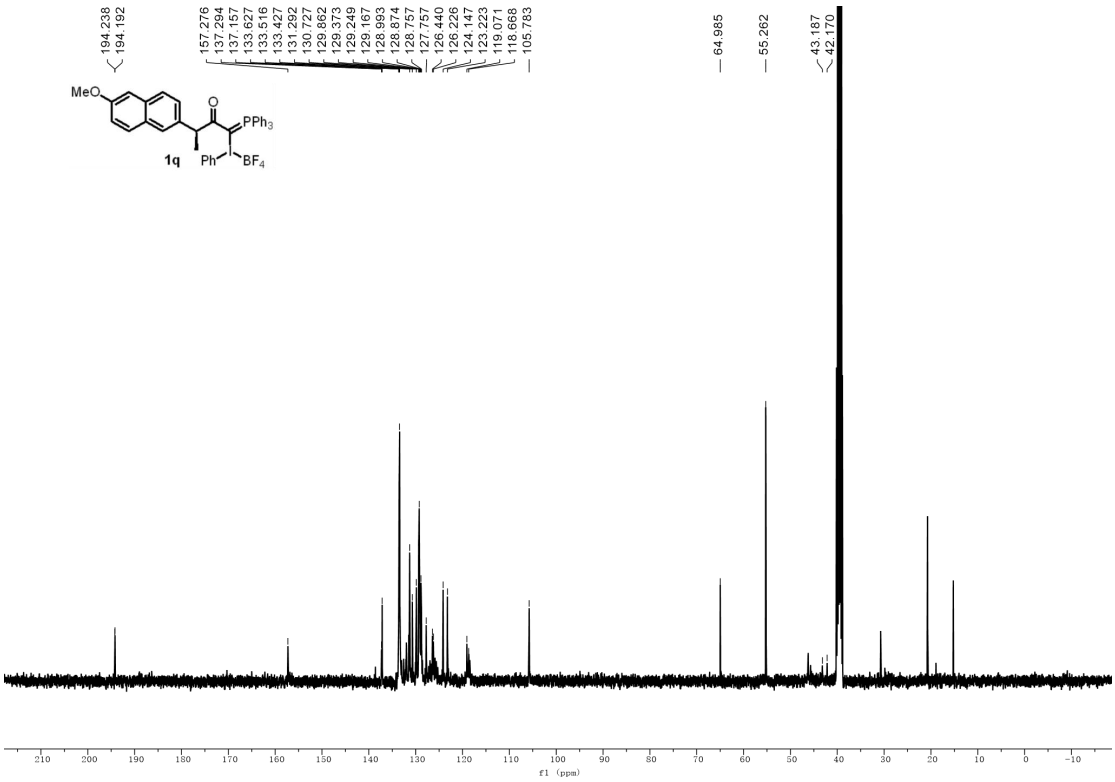
^{31}P NMR (162 MHz, DMSO-d_6) of 1p



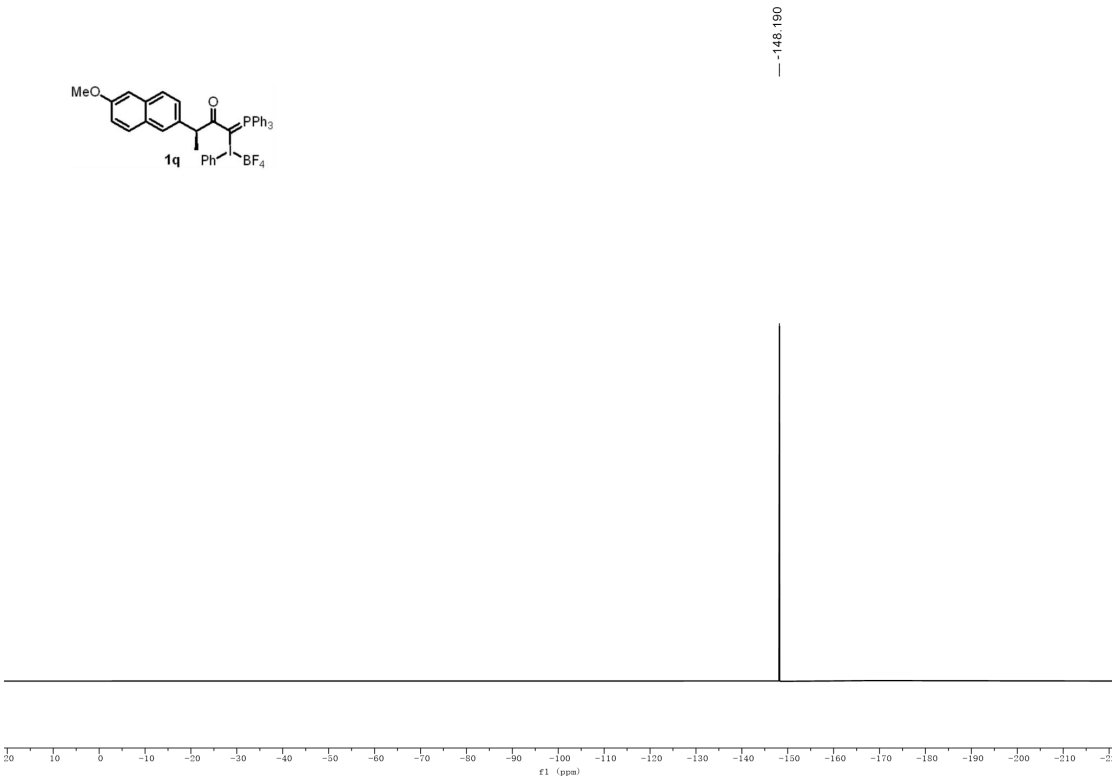
^{11}B NMR (128 MHz, DMSO-d_6) of 1p



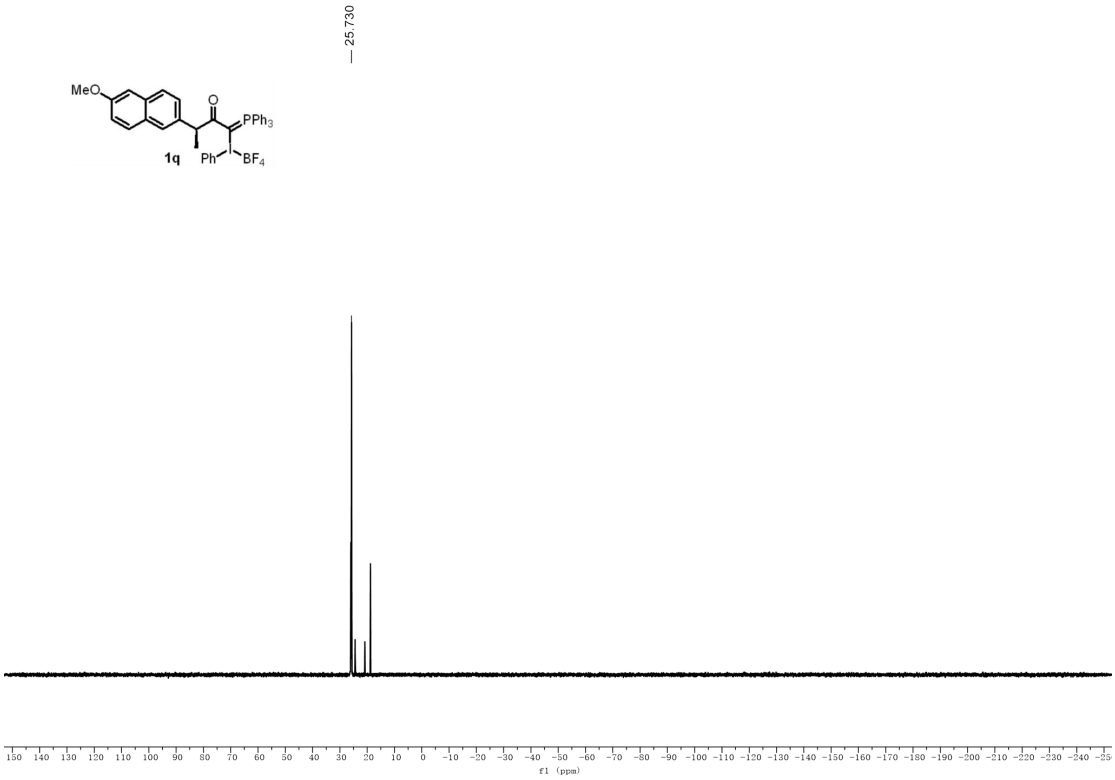
^{1}H NMR (400 MHz, DMSO-*d*$_6$) of 1q



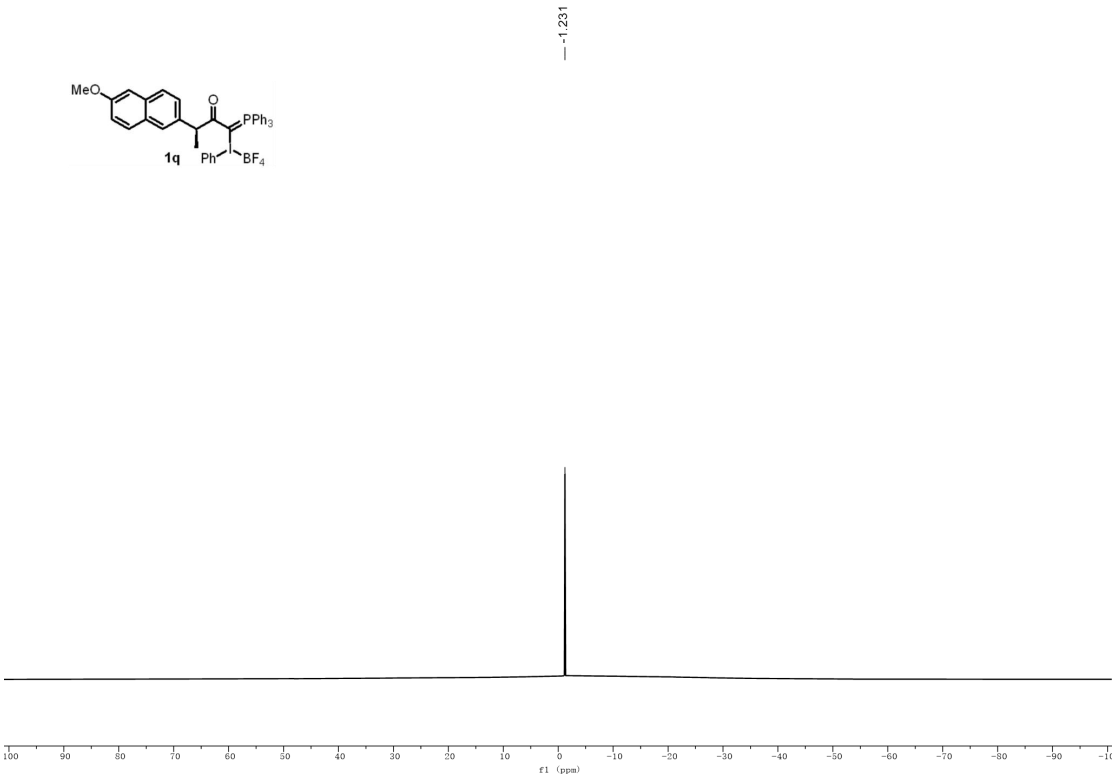
^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 1q



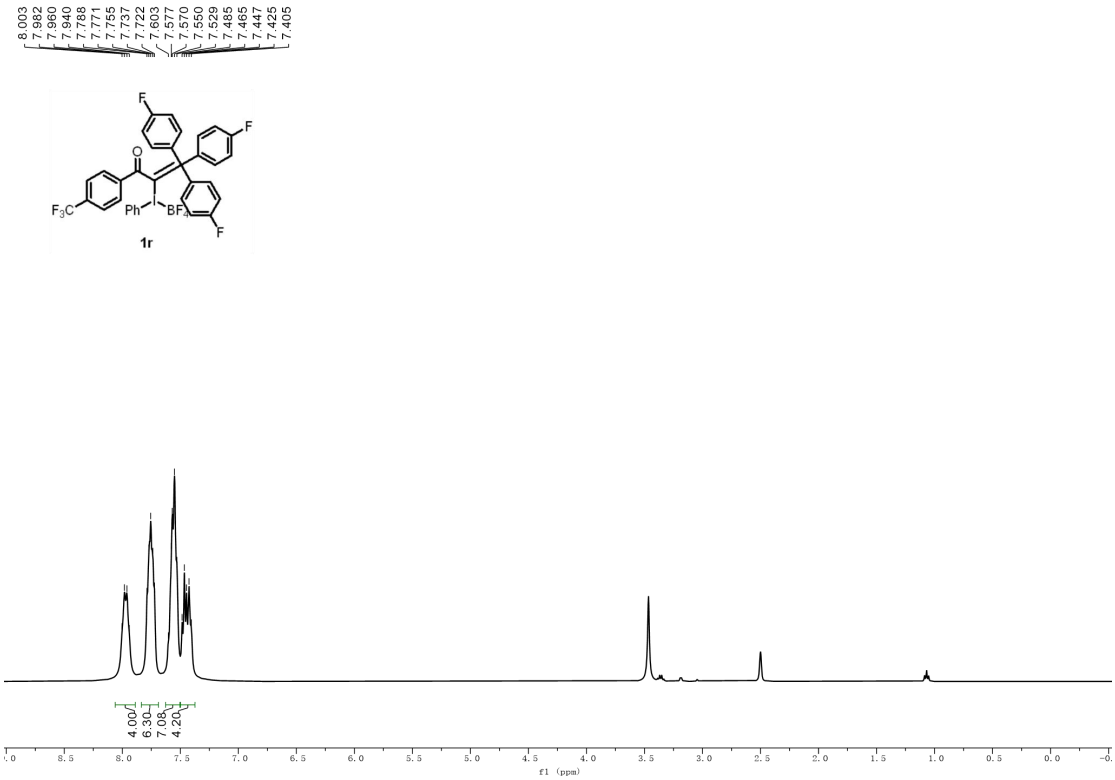
^{19}F NMR (376 MHz, DMSO-d_6) of 1q



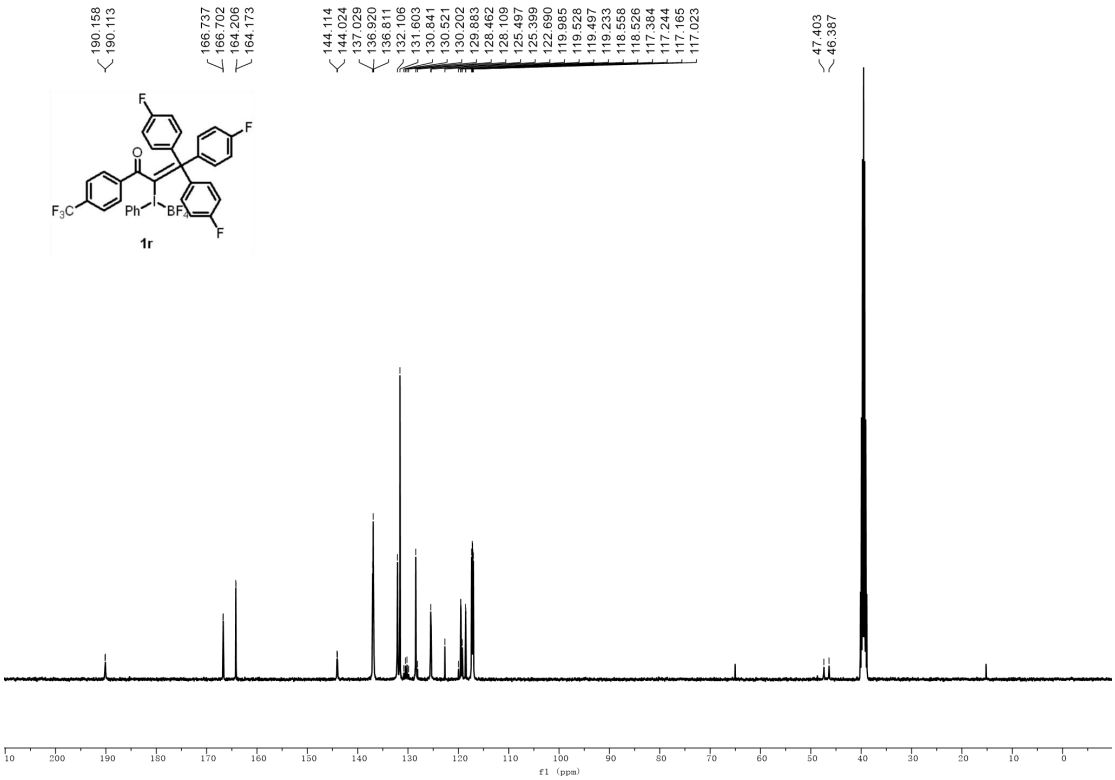
^{31}P NMR (162 MHz, DMSO-d_6) of 1q



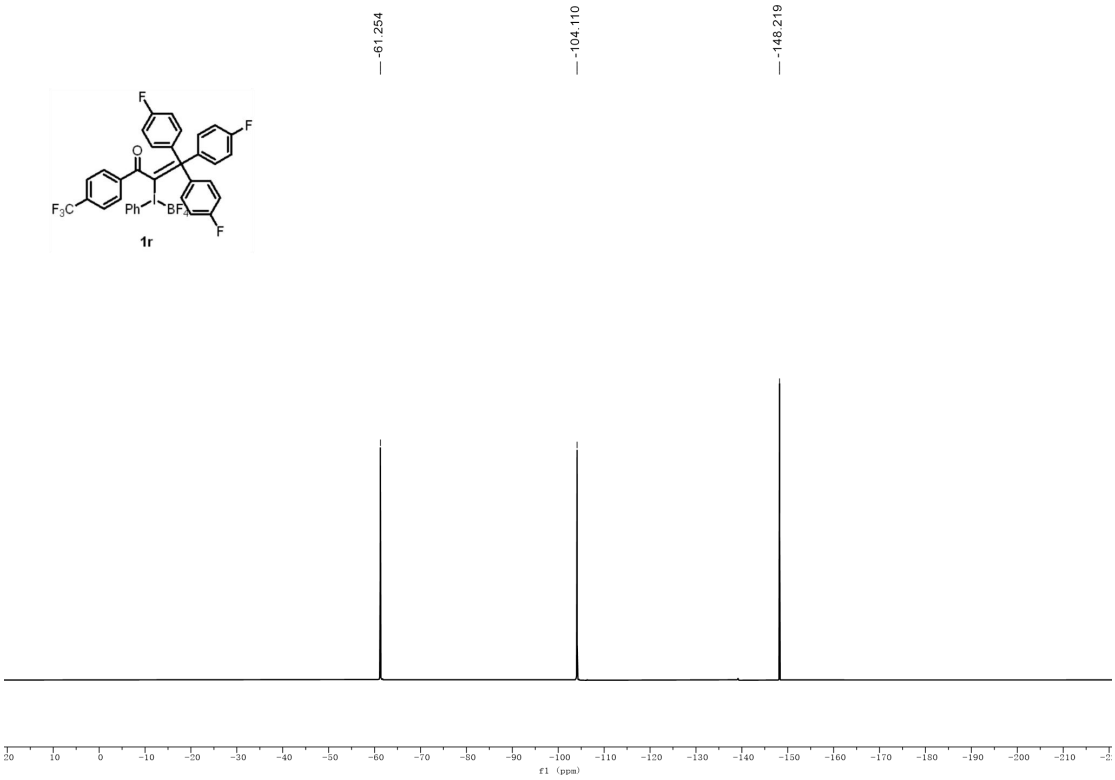
^{11}B NMR (128 MHz, DMSO-d_6) of 1q



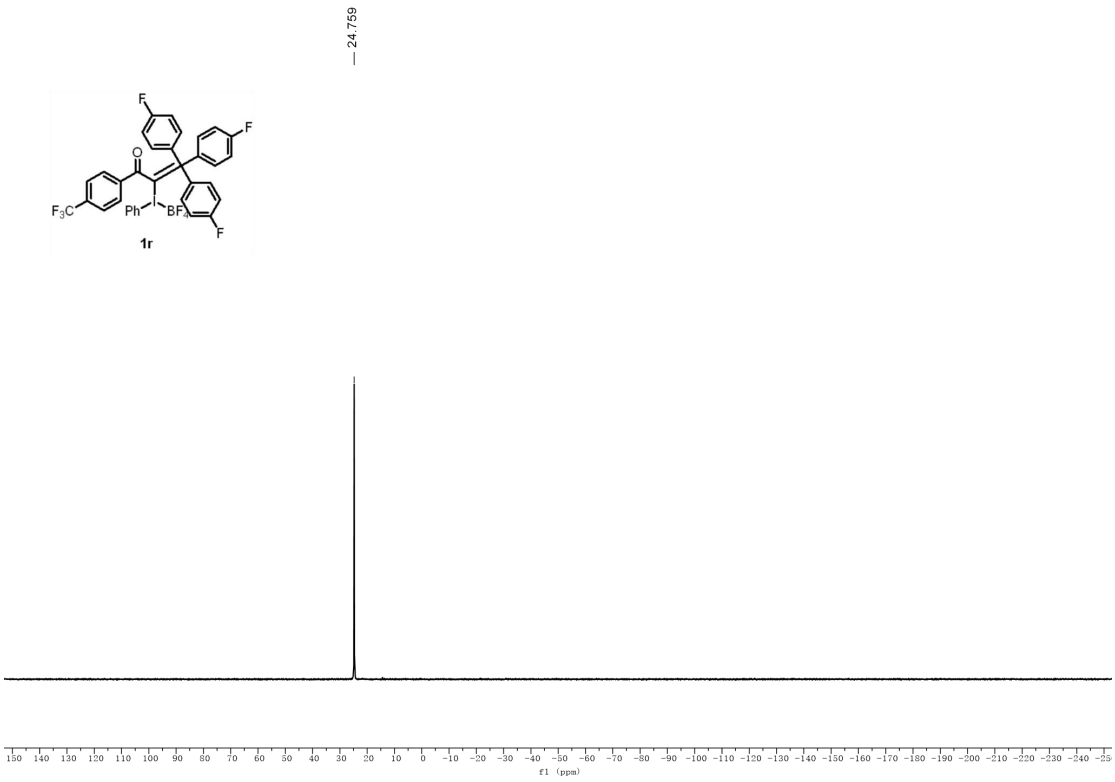
^{1}H NMR (400 MHz, DMSO-d_6) of 1r



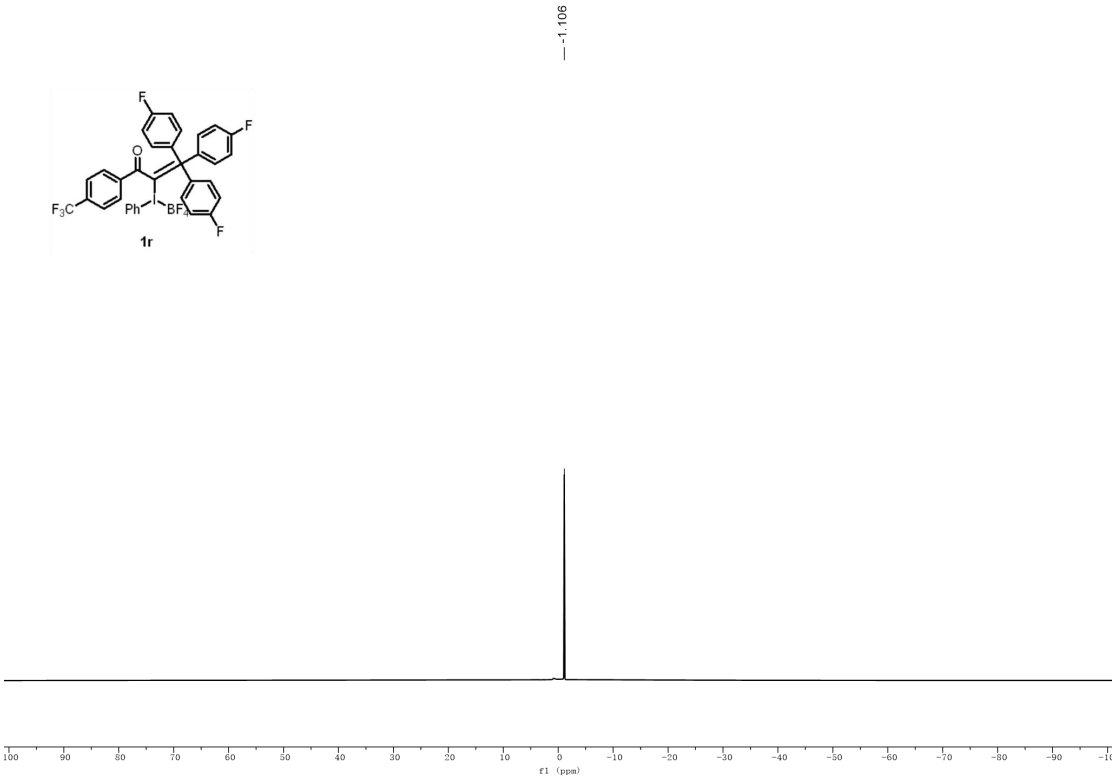
^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 1r



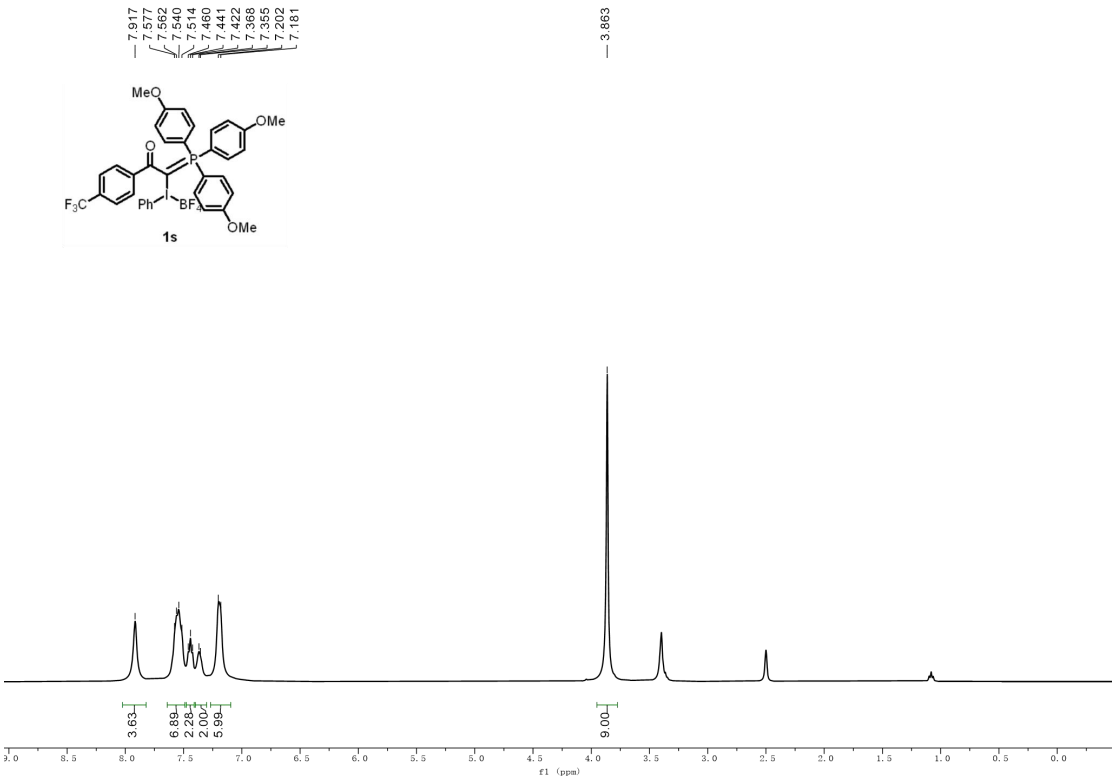
^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 1r



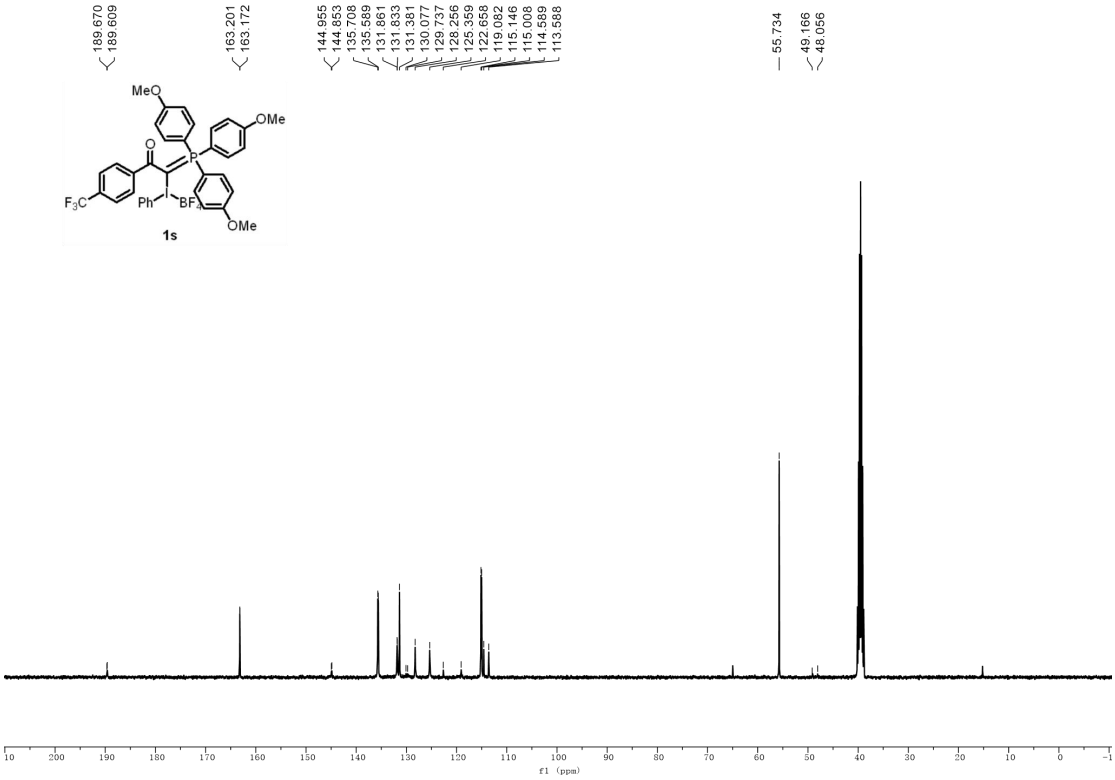
^{31}P NMR (162 MHz, DMSO-*d*$_6$) of 1r



^{11}B NMR (128 MHz, DMSO-*d*$_6$) of 1r



^{1}H NMR (400 MHz, DMSO-*d*$_6$) of 1s



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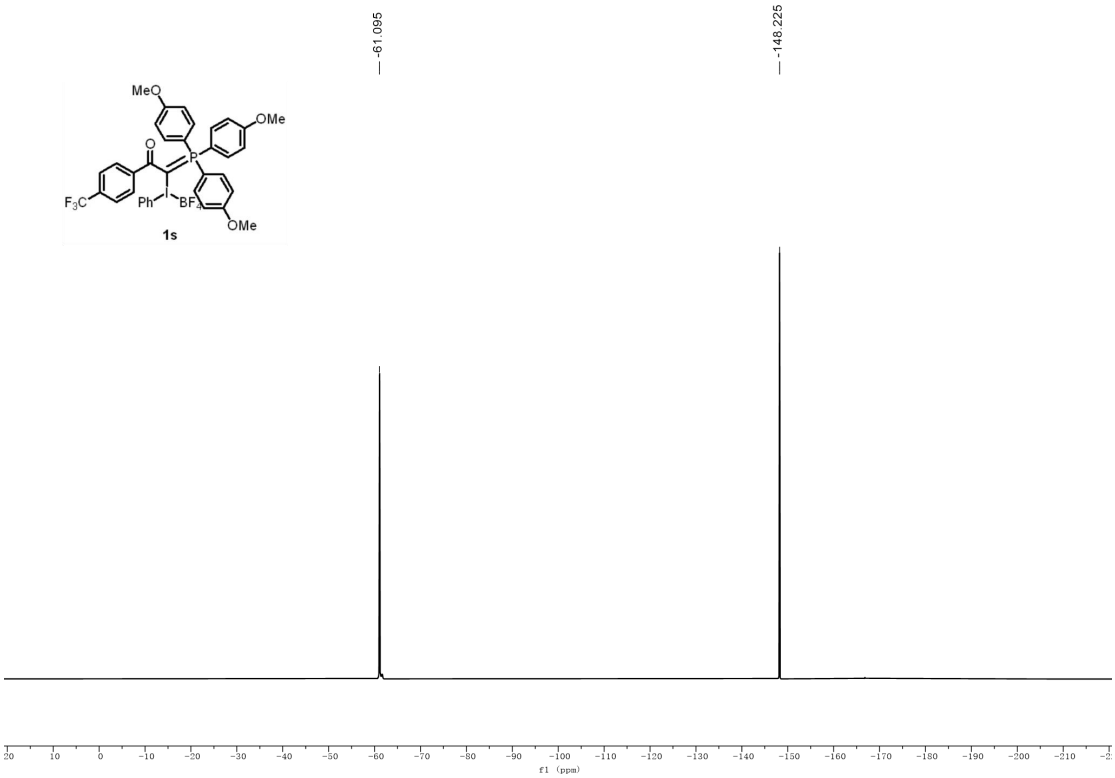
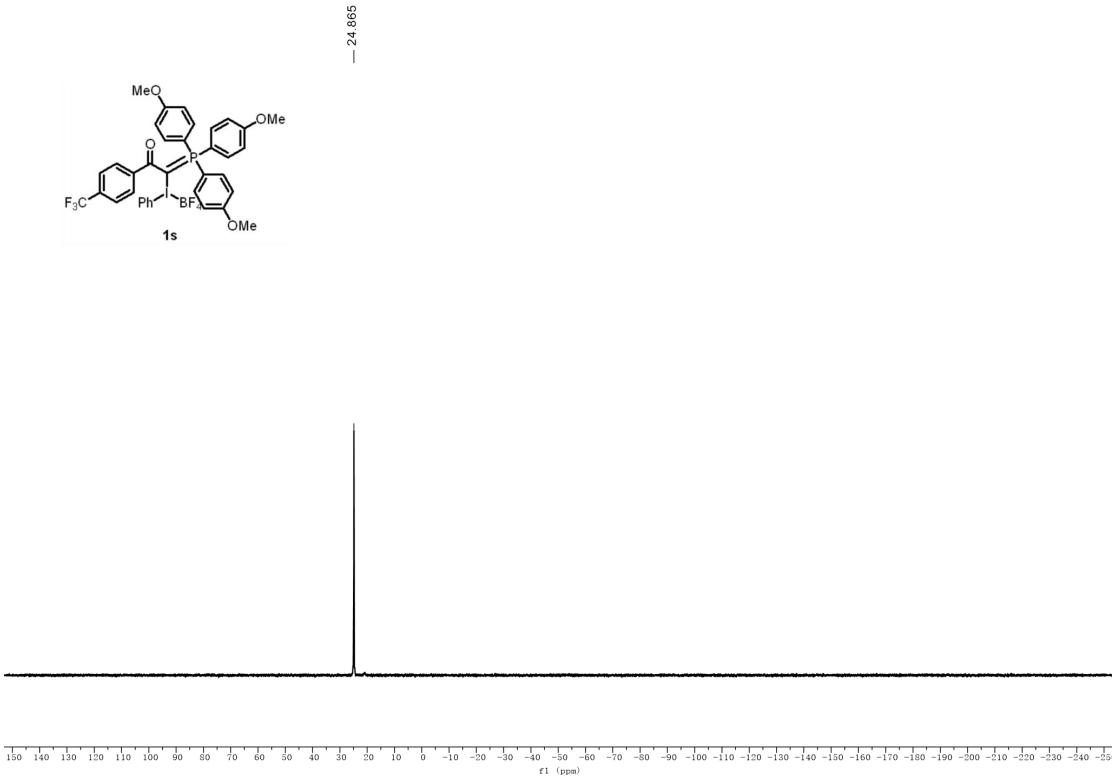
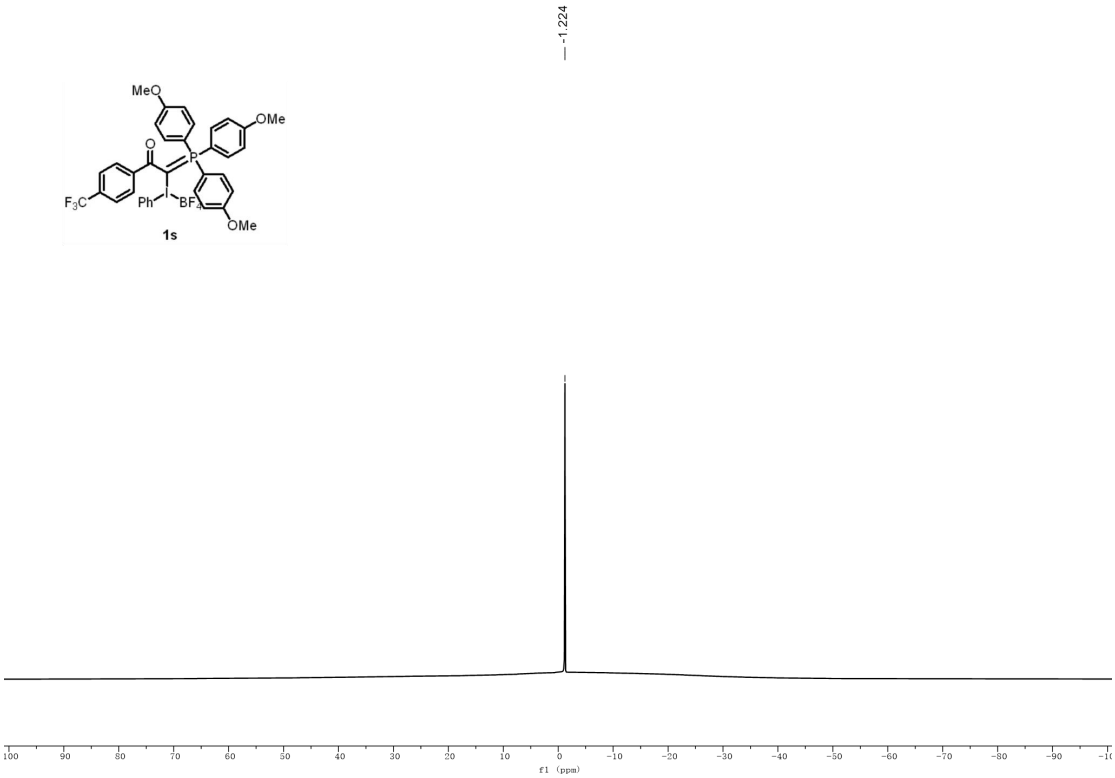


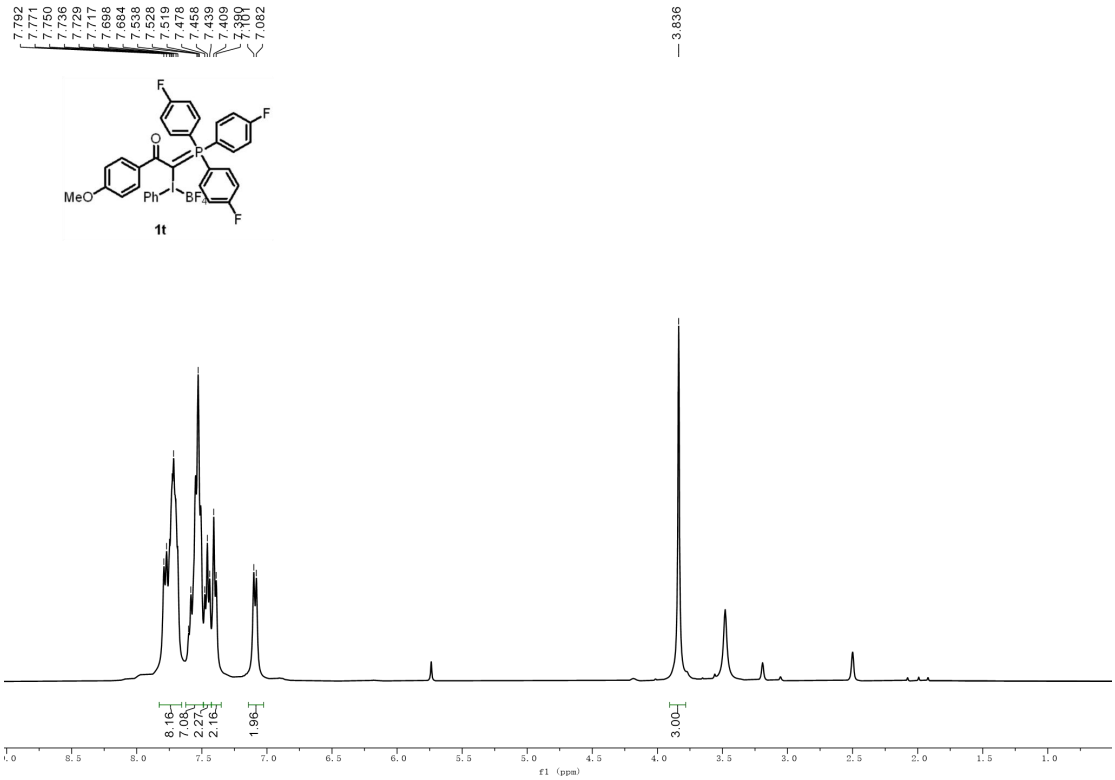
^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 1s



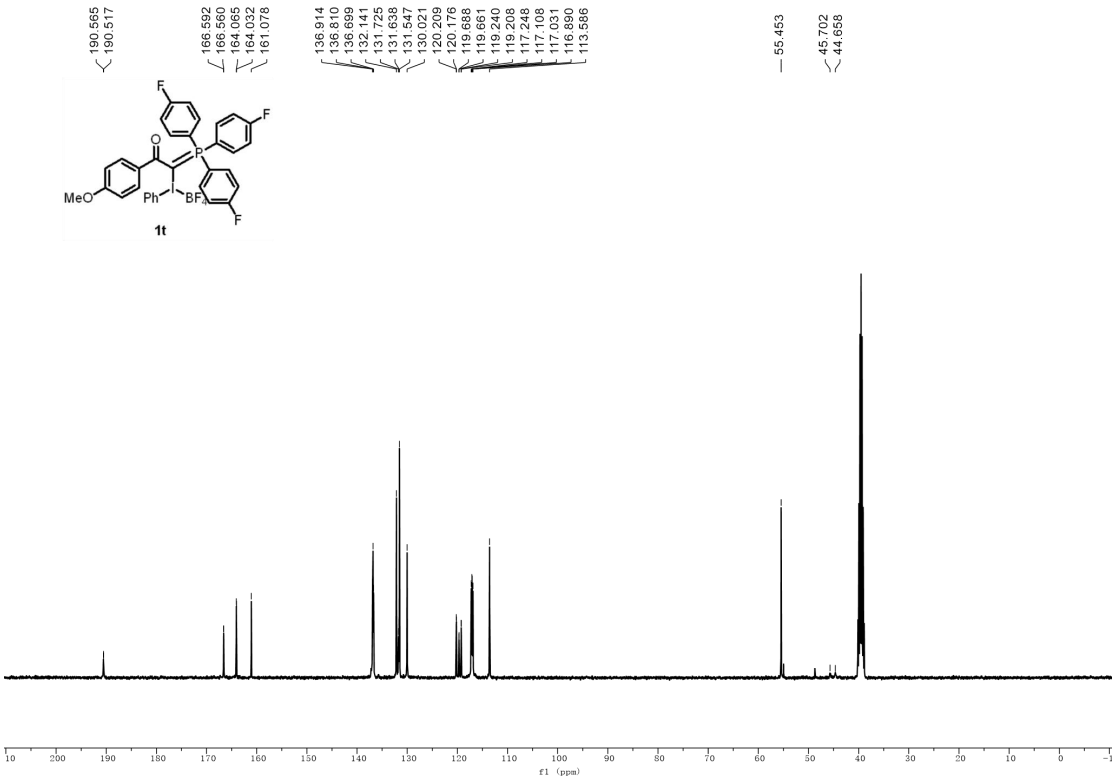
^{31}P NMR (162 MHz, DMSO-*d*$_6$) of 1s



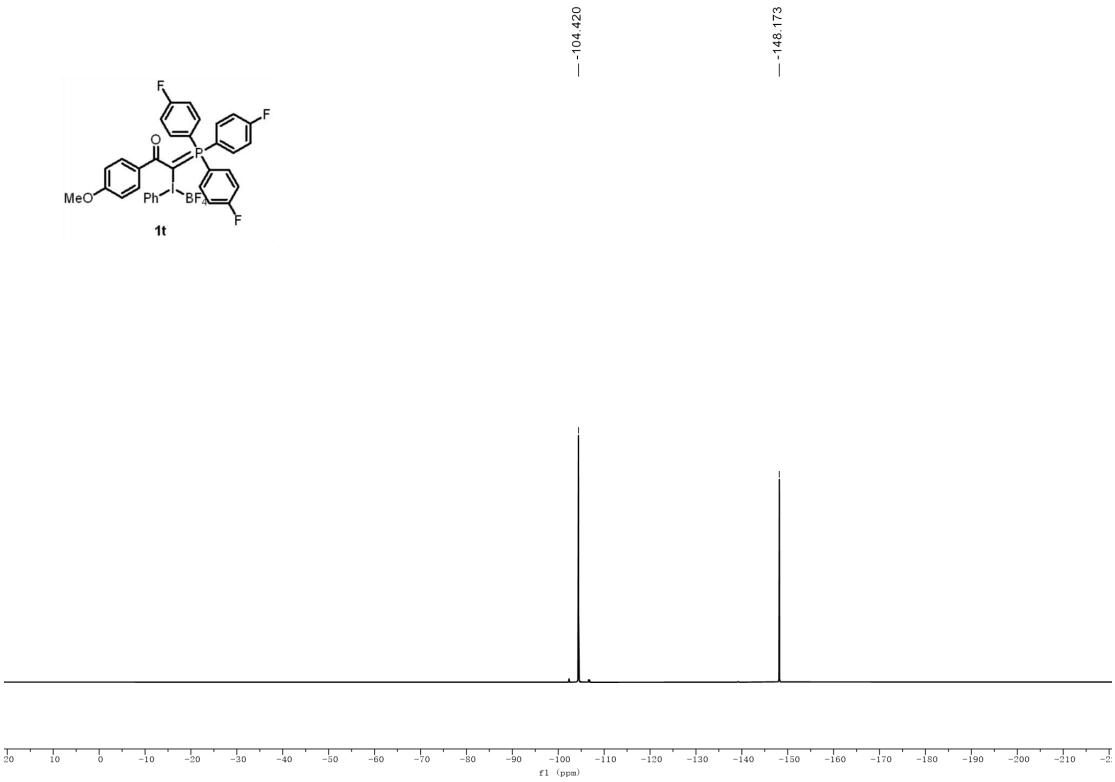
^{11}B NMR (128 MHz, DMSO-d_6) of 1s



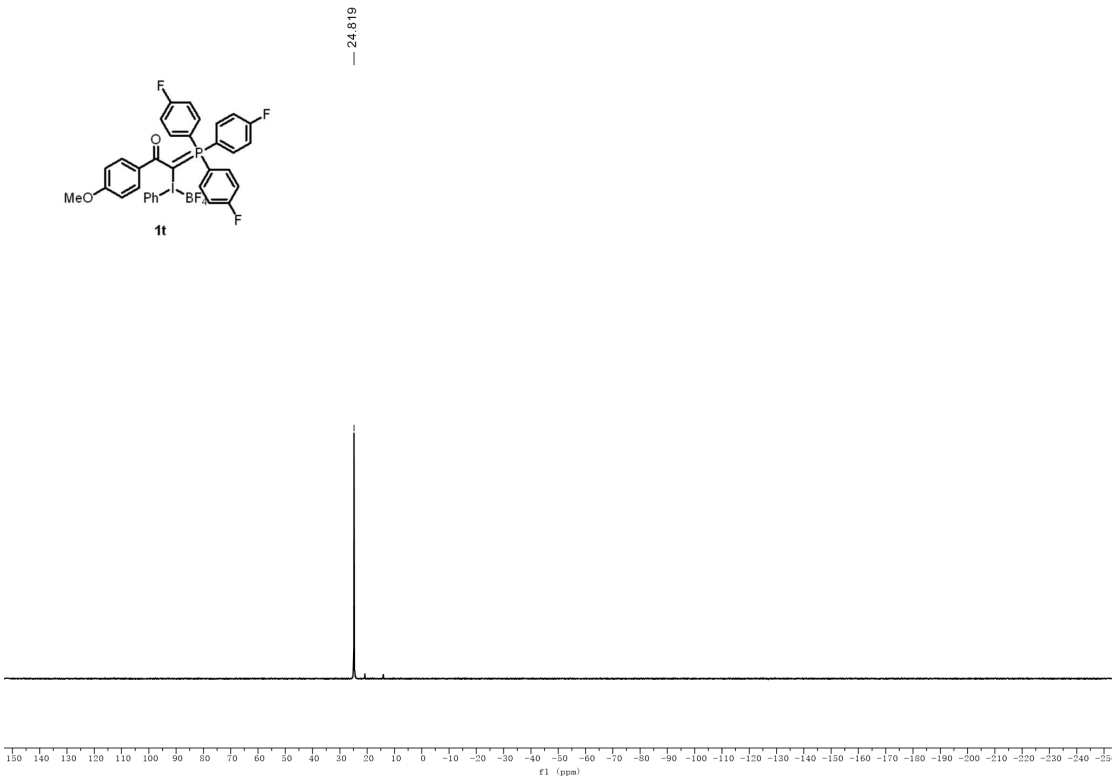
^{1}H NMR (400 MHz, DMSO-d_6) of 1t



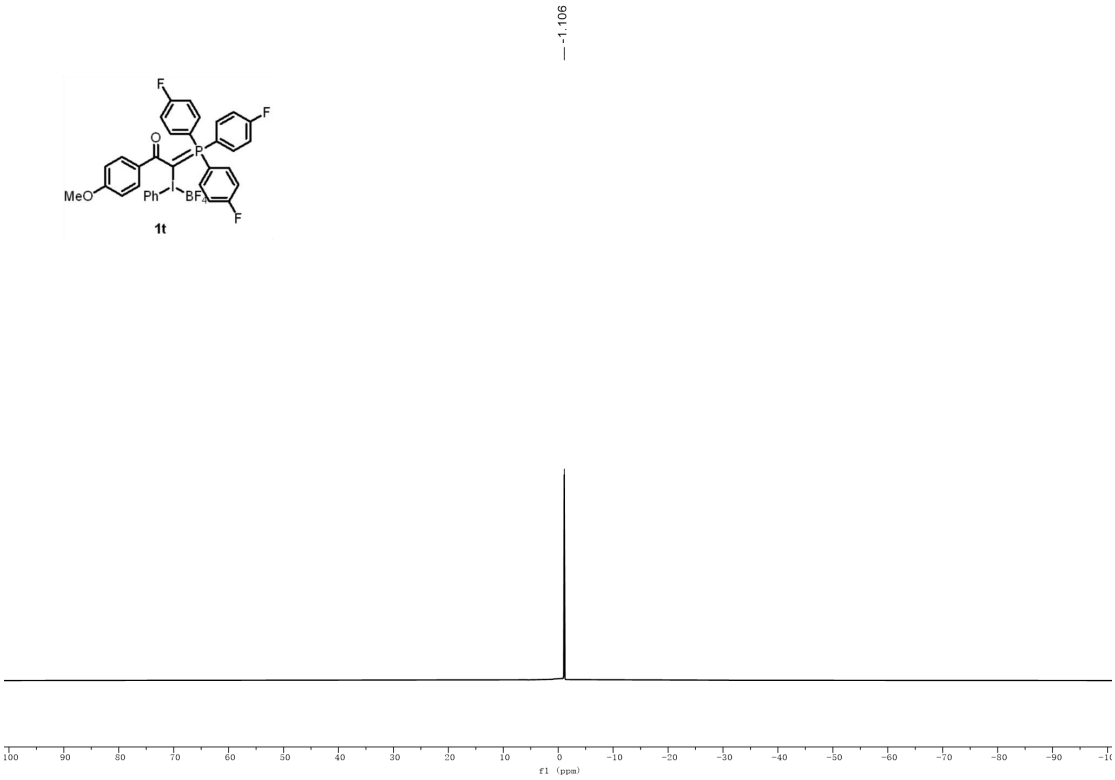
^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 1t



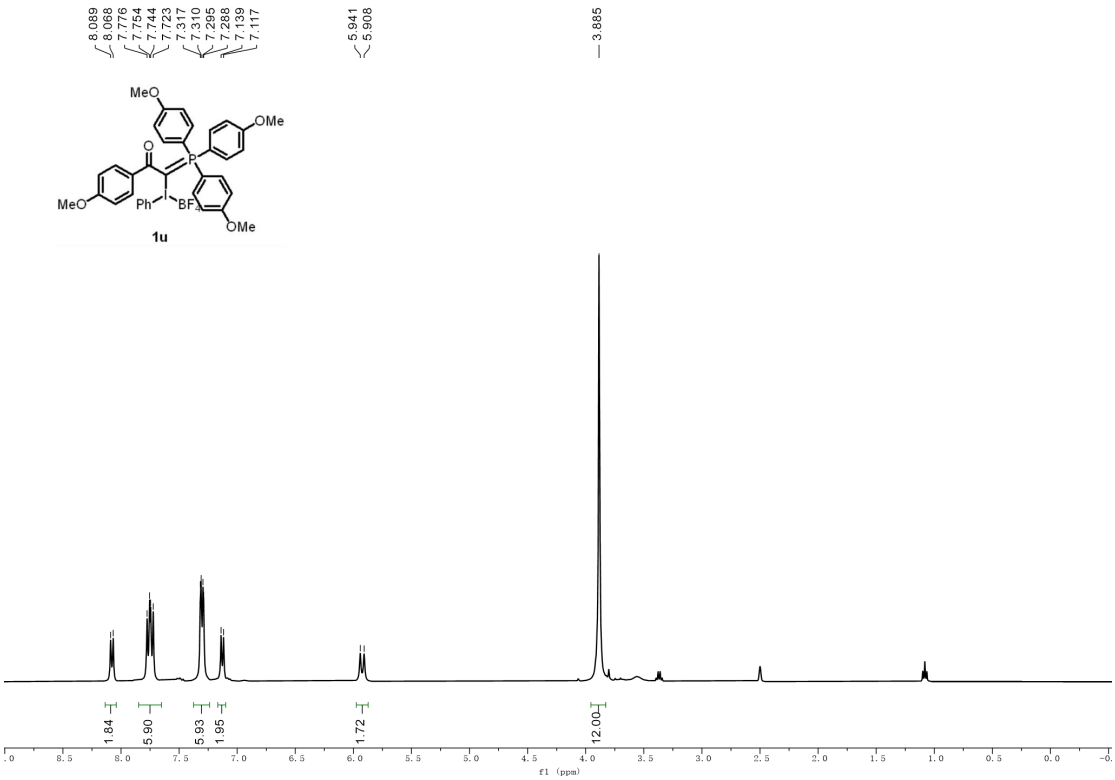
^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 1t



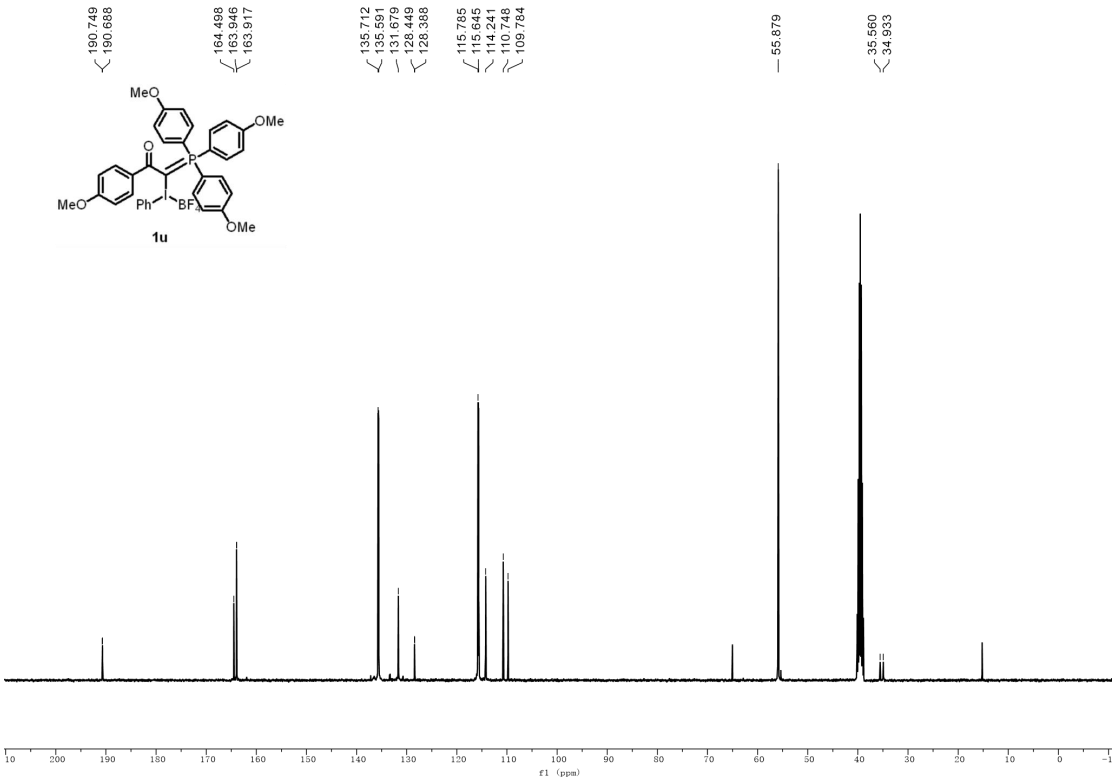
^{31}P NMR (162 MHz, DMSO-d_6) of 1t



^{11}B NMR (128 MHz, DMSO-d_6) of 1t



^{1}H NMR (400 MHz, DMSO-d_6) of 1u



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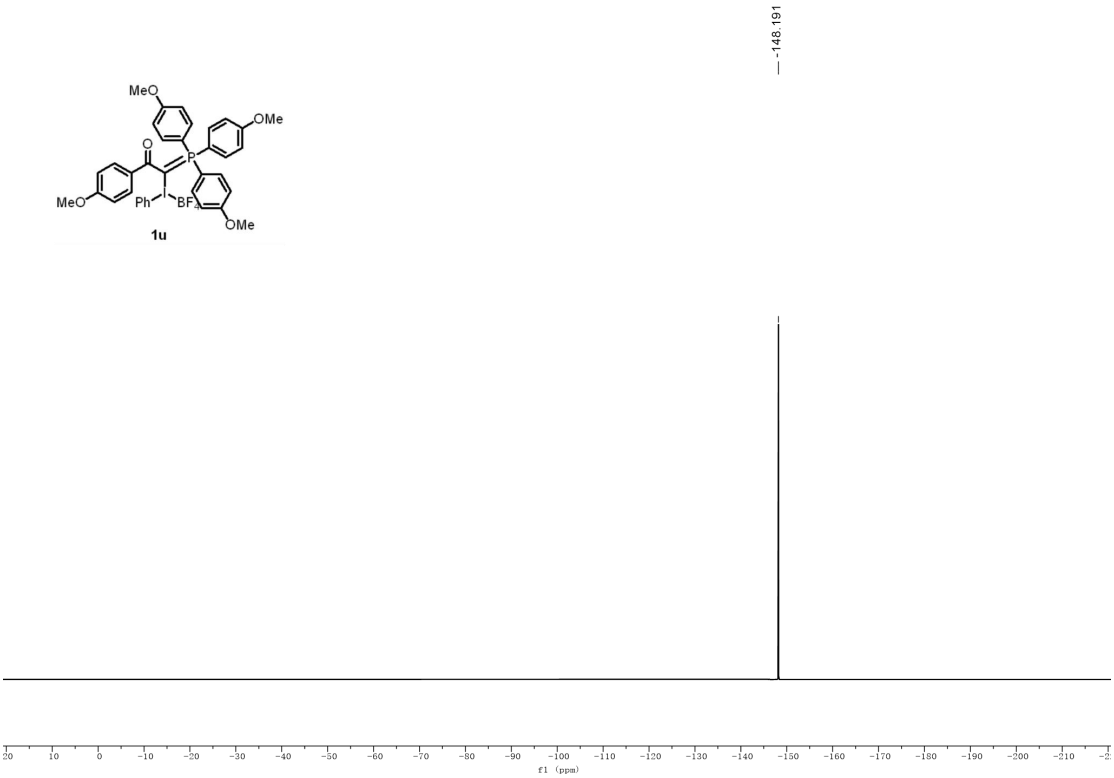
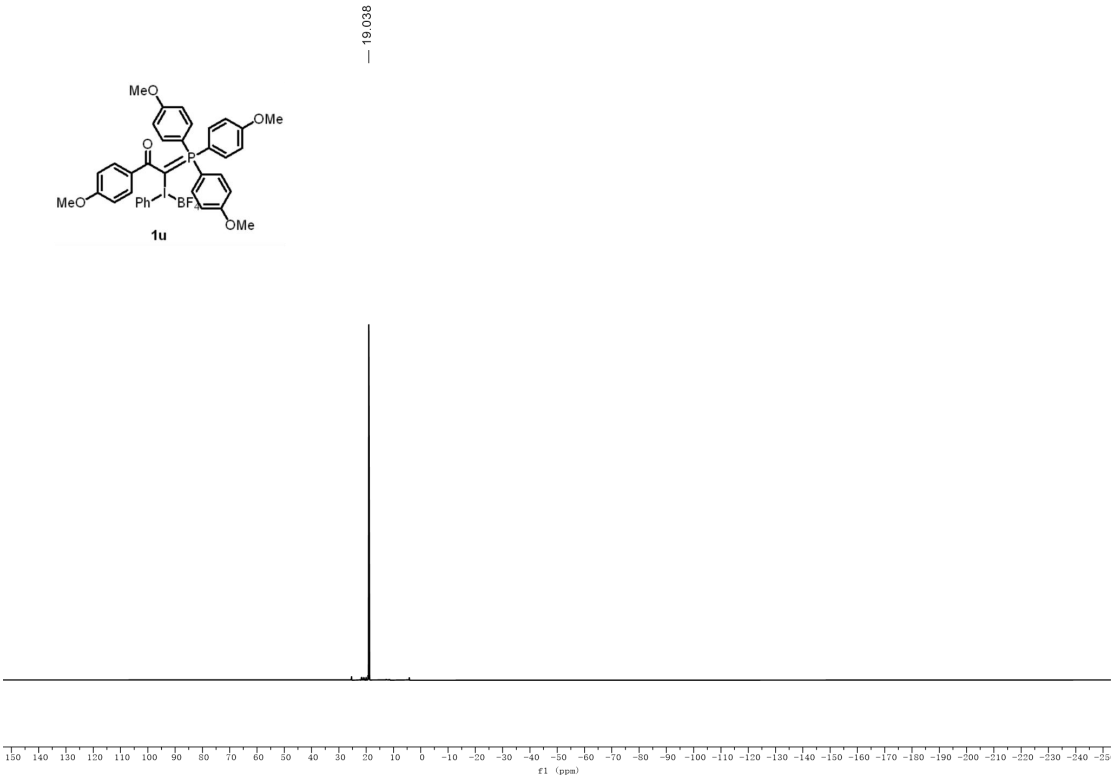
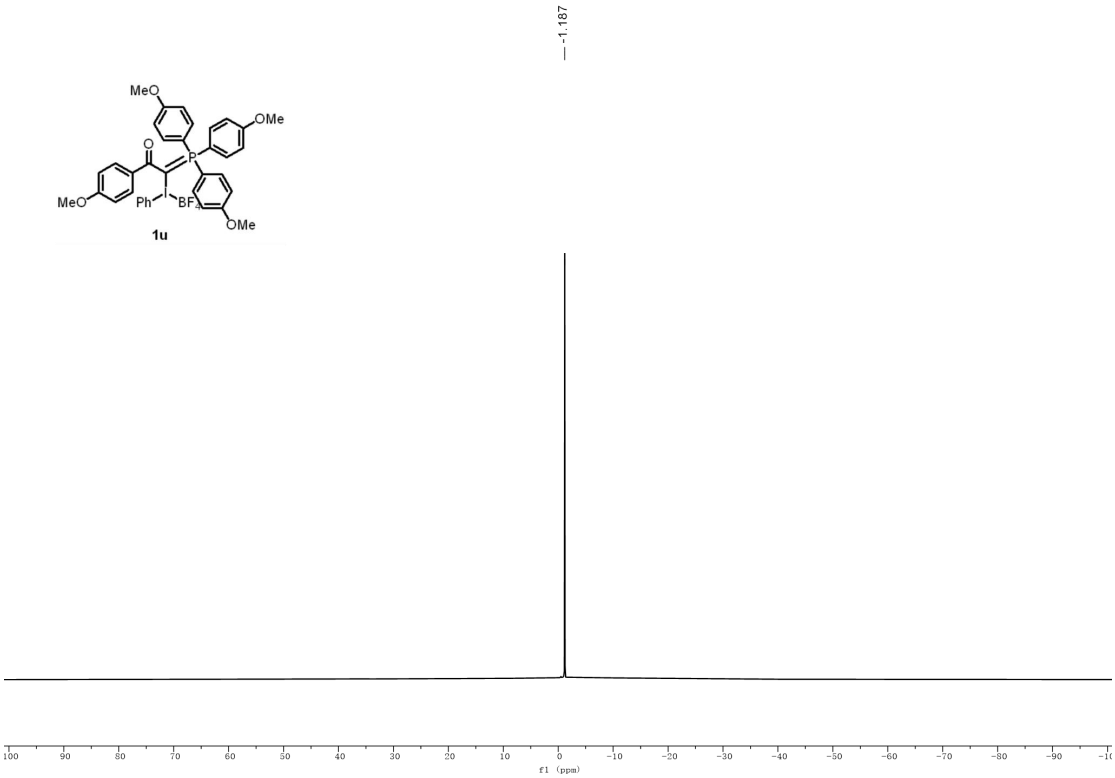


^{19}F NMR (376 MHz, DMSO-d_6) of 1u



^{31}P NMR (162 MHz, DMSO-d_6) of 1u



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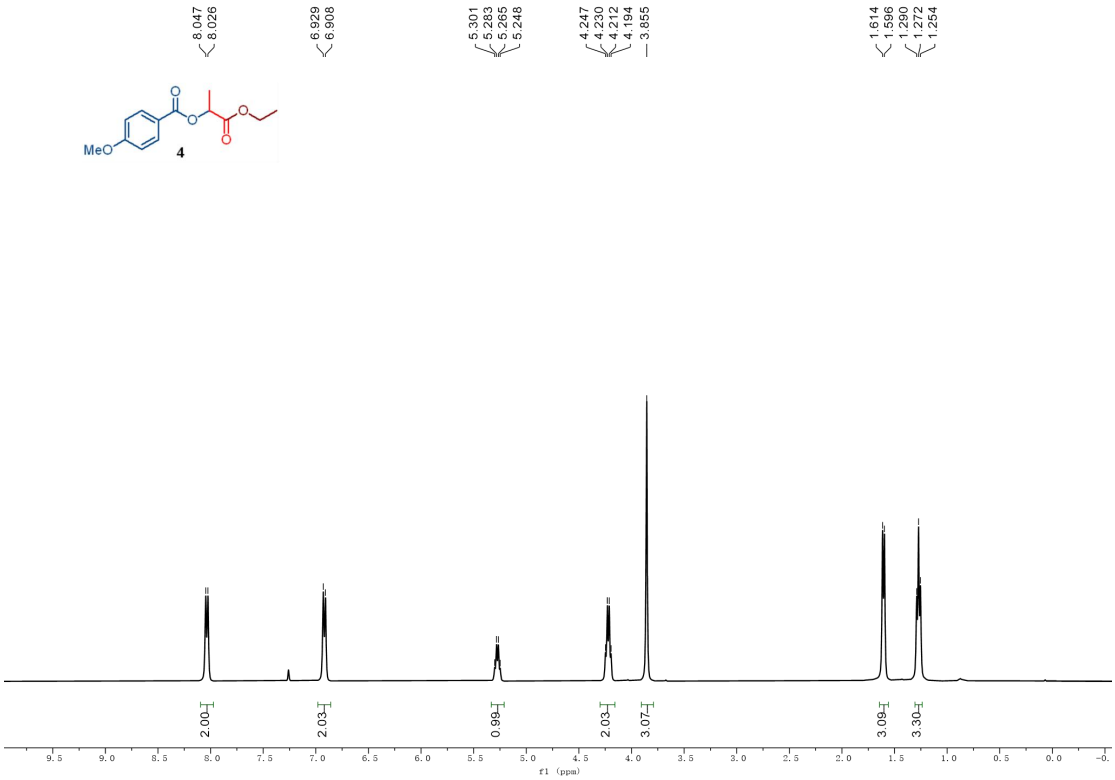
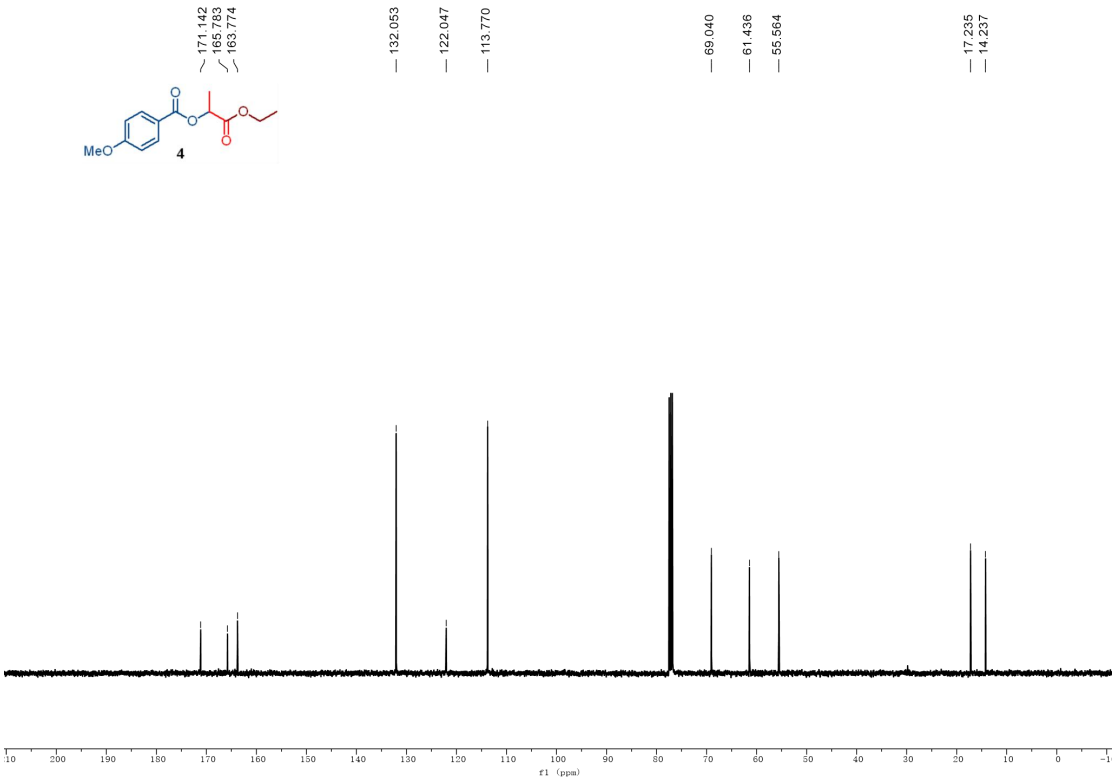
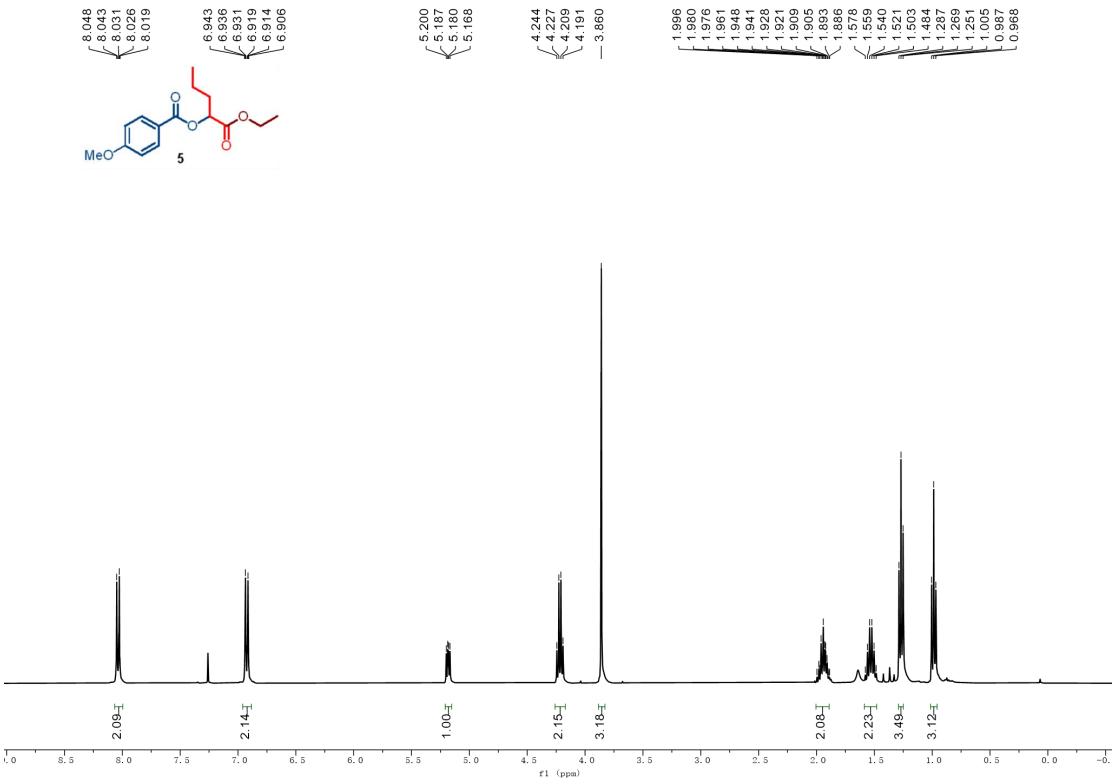


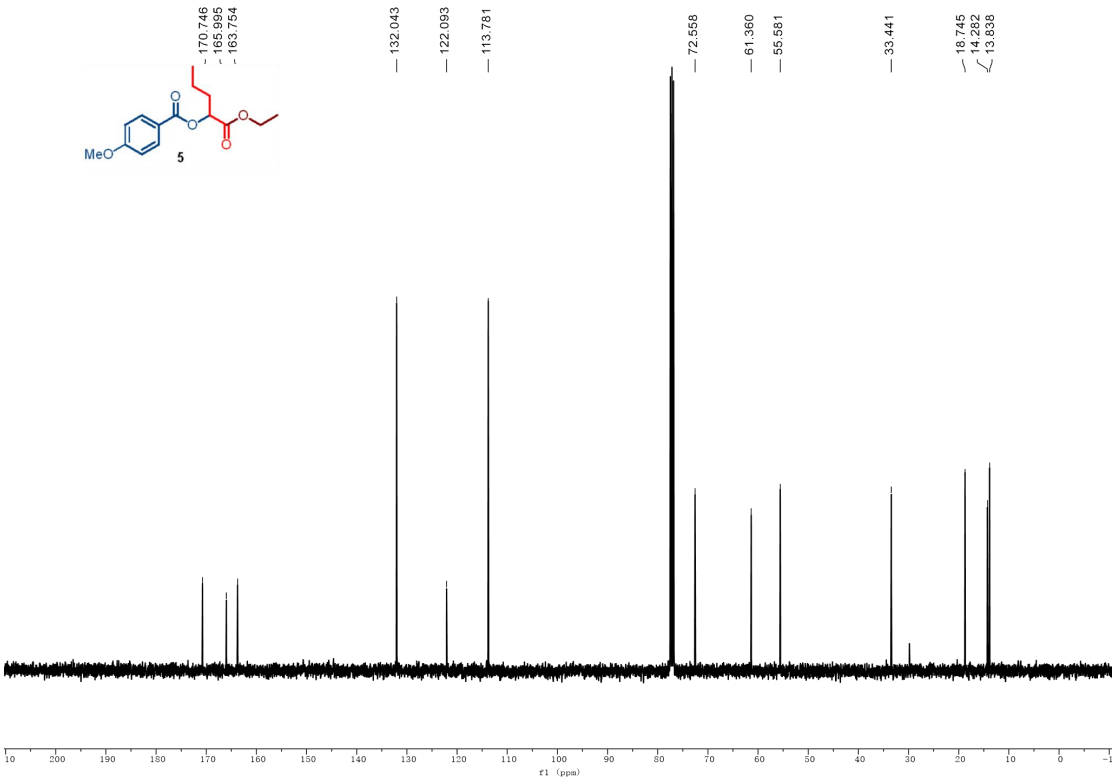
^{1}H NMR (400 MHz, $CDCl_3$) of 4



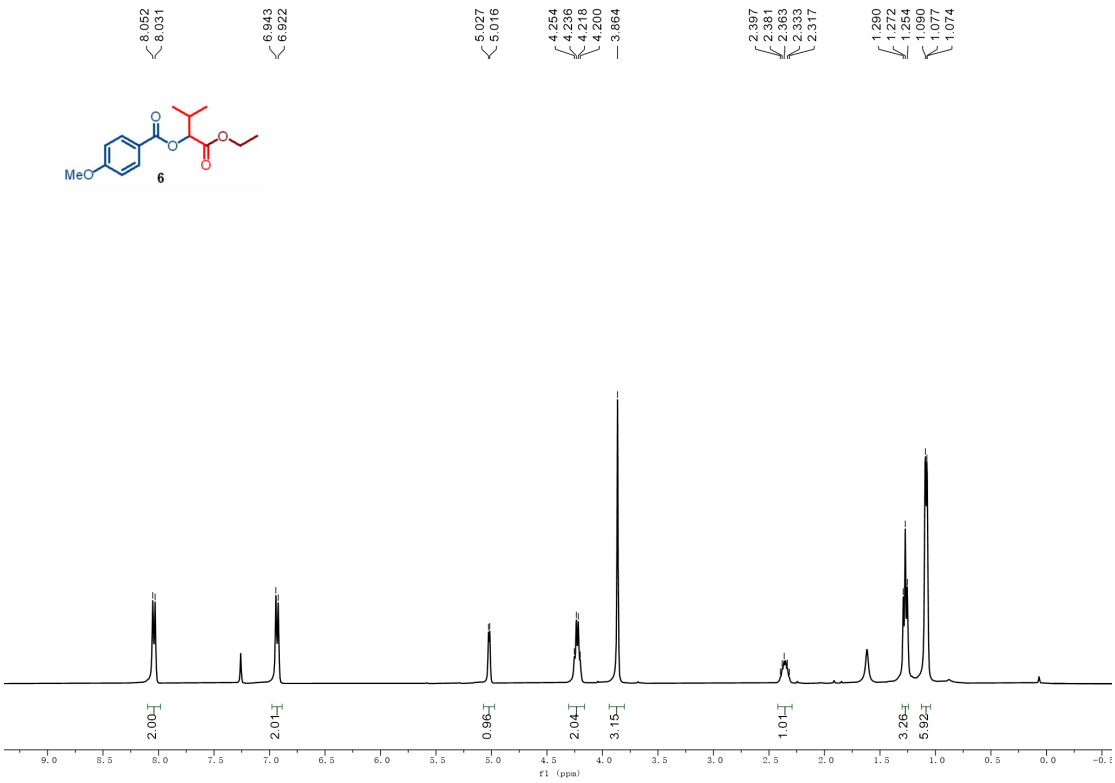
^{13}C NMR (101 MHz, $CDCl_3$) of 4



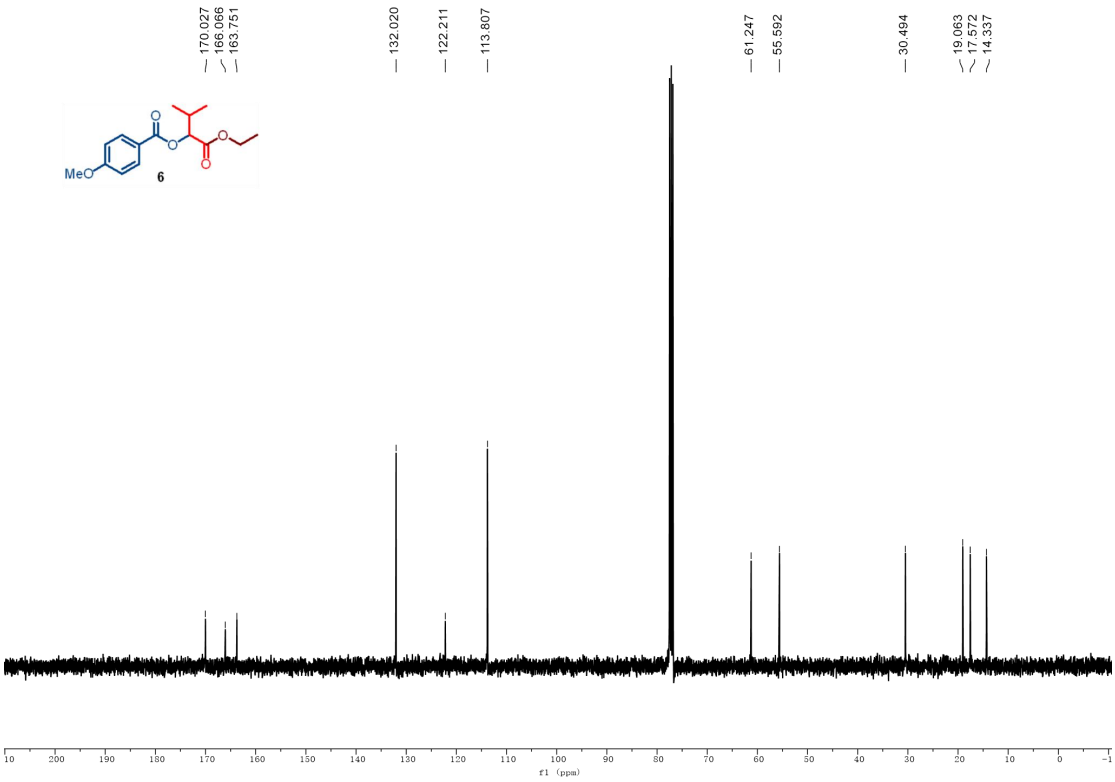
^{1}H NMR (400 MHz, $CDCl_3$) of 5



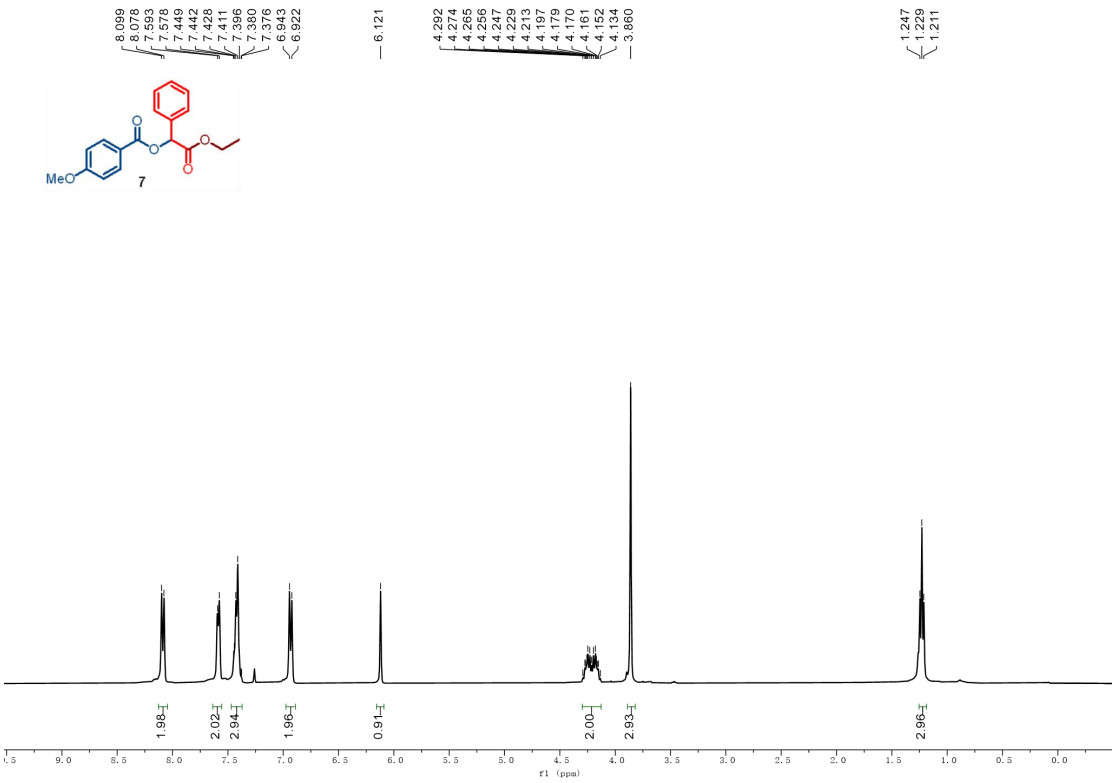
^{13}C NMR (101 MHz, $CDCl_3$) of 5



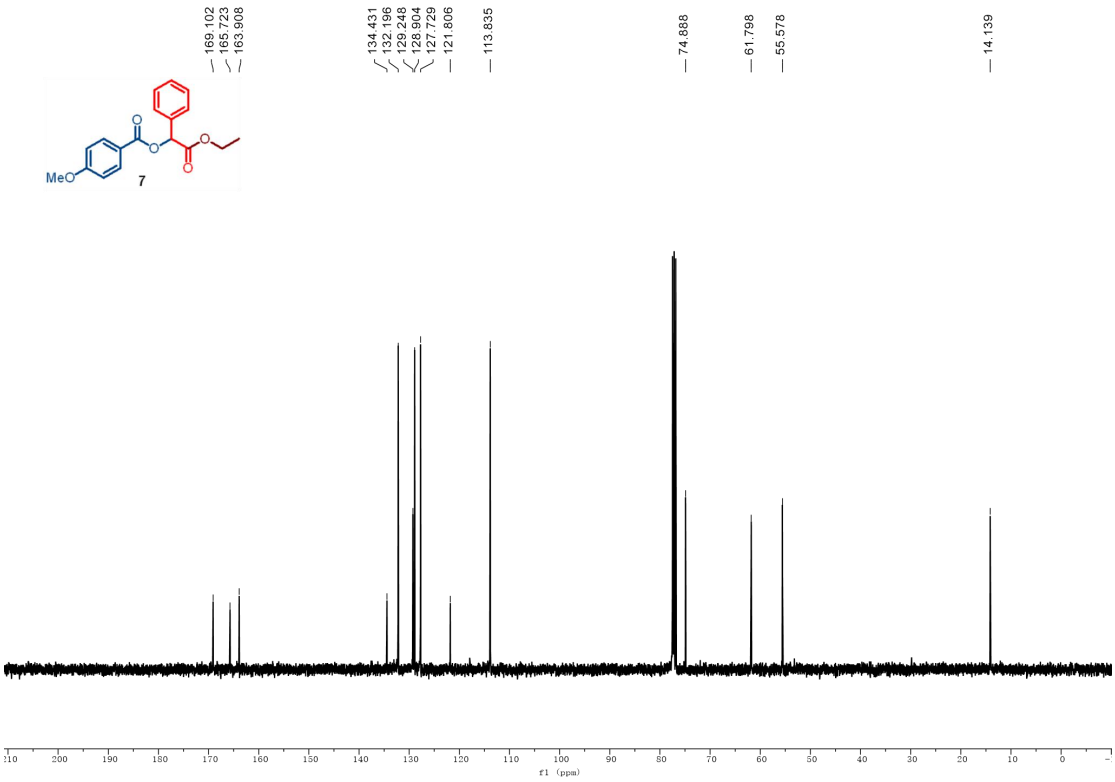
^{1}H NMR (400 MHz, $CDCl_3$) of 6



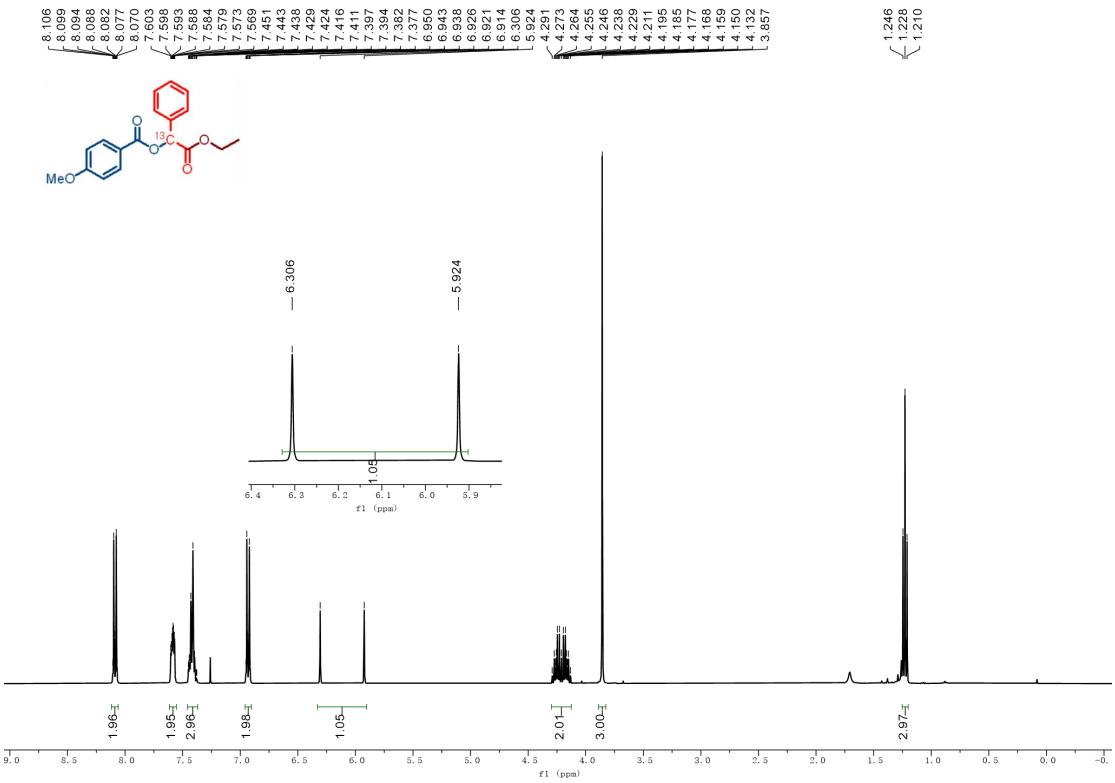
^{13}C NMR (101 MHz, $CDCl_3$) of 6



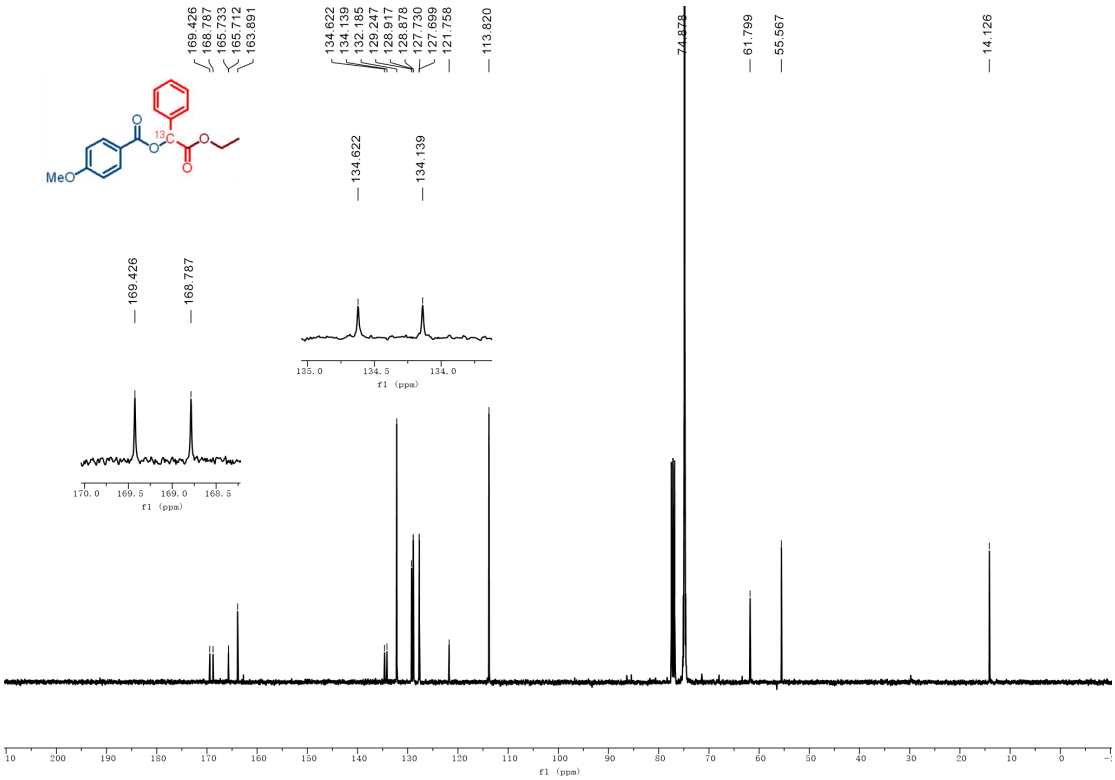
^{1}H NMR (400 MHz, $CDCl_3$) of 7



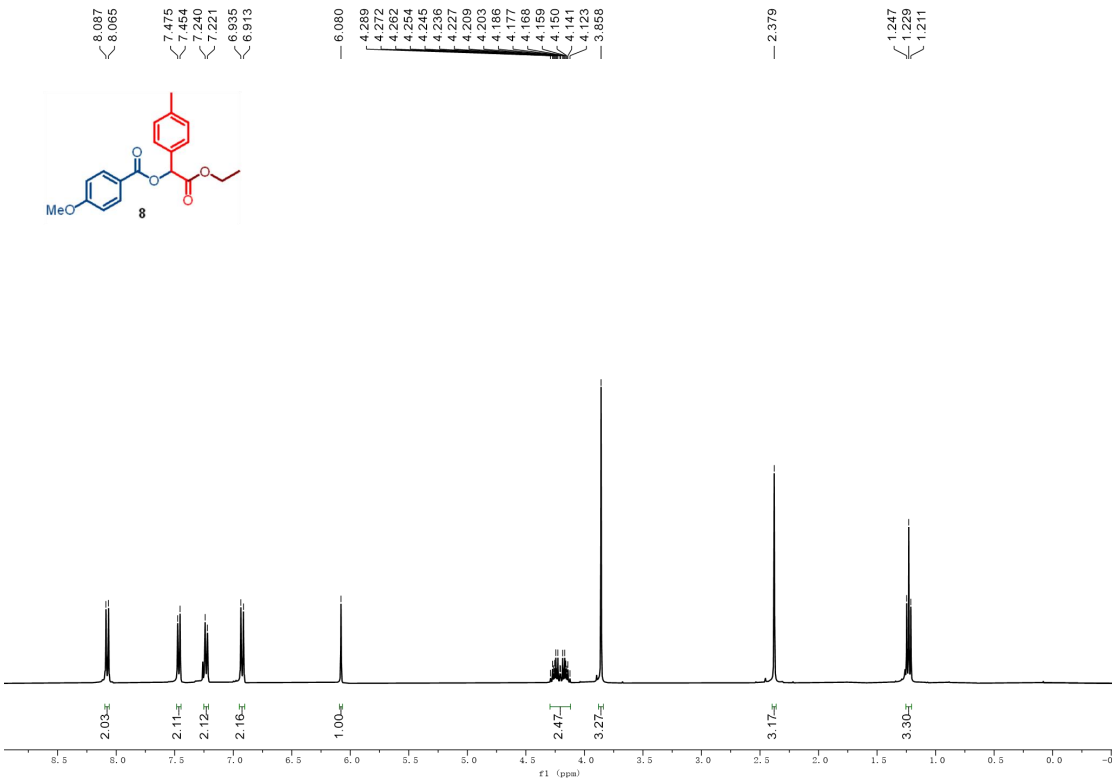
^{13}C NMR (101 MHz, $CDCl_3$) of 7



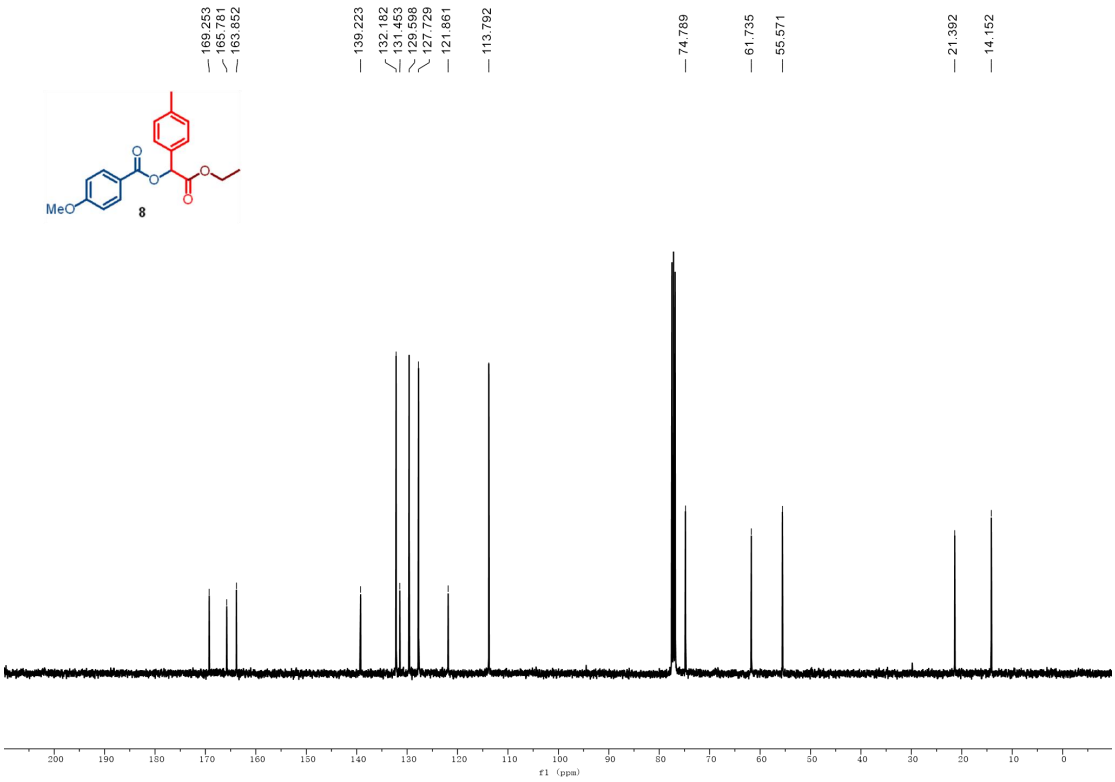
^{1}H NMR (400 MHz, $CDCl_3$) of ^{13}C-7



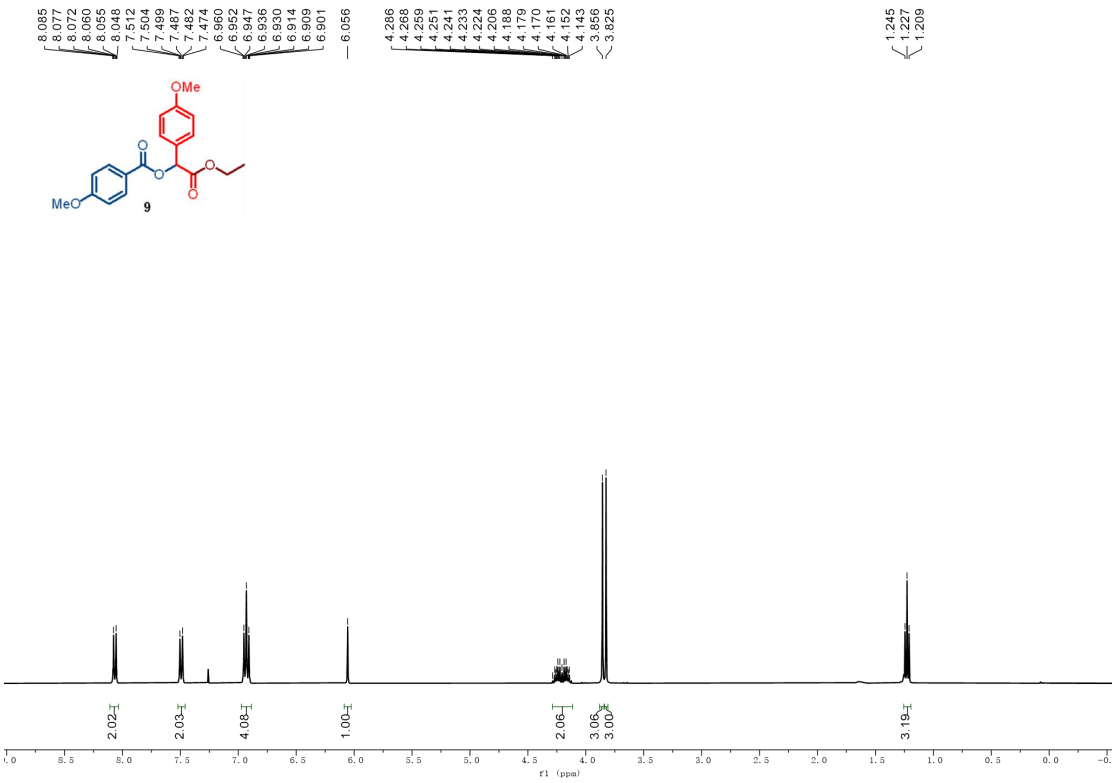
^{13}C NMR (101 MHz, $CDCl_3$) of ^{13}C-7



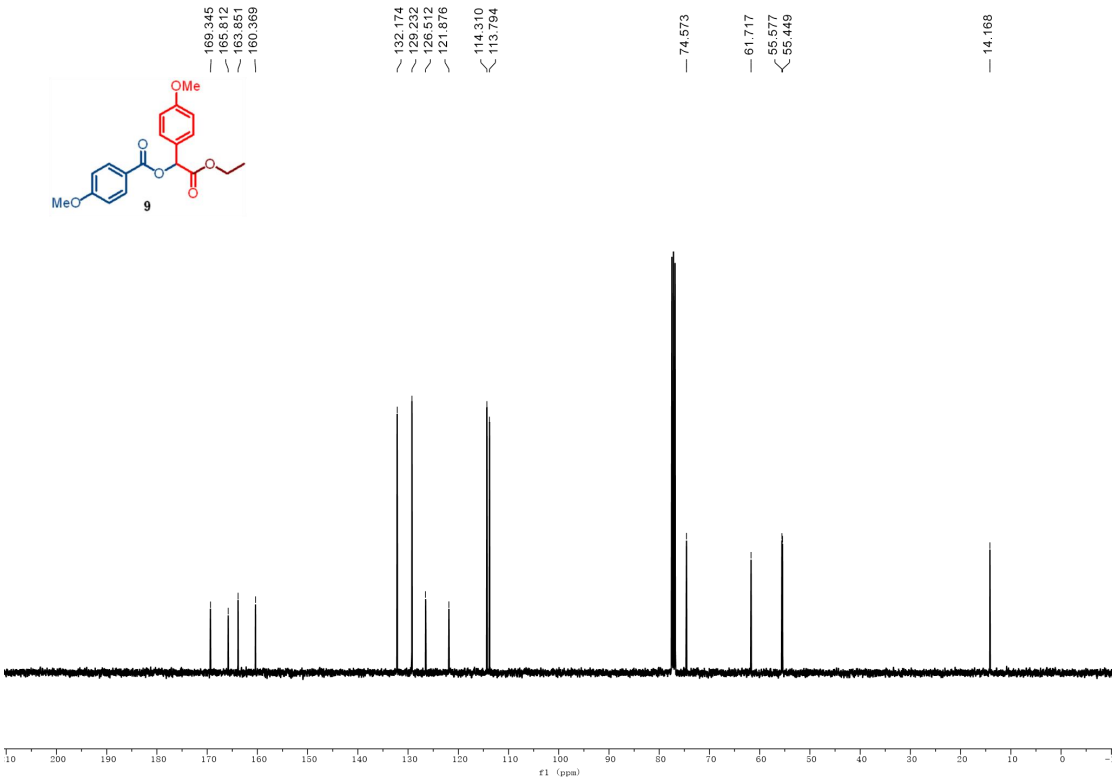
^{1}H NMR (400 MHz, $CDCl_3$) of 8



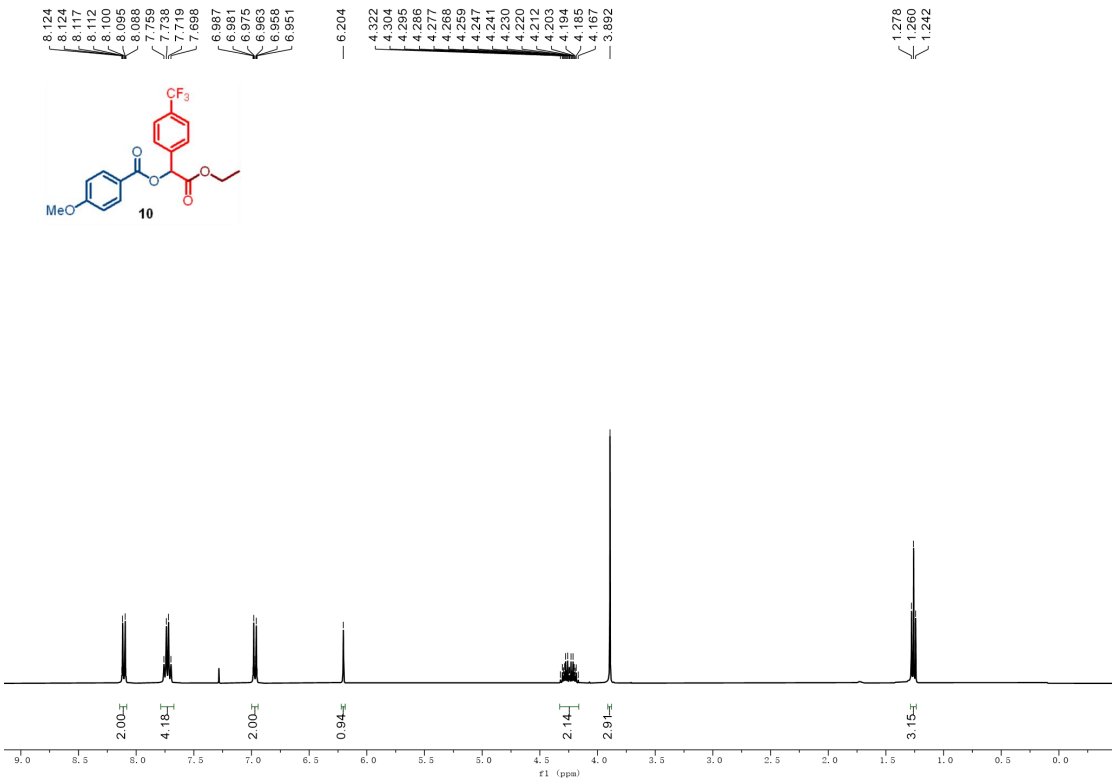
^{13}C NMR (101 MHz, $CDCl_3$) of 8



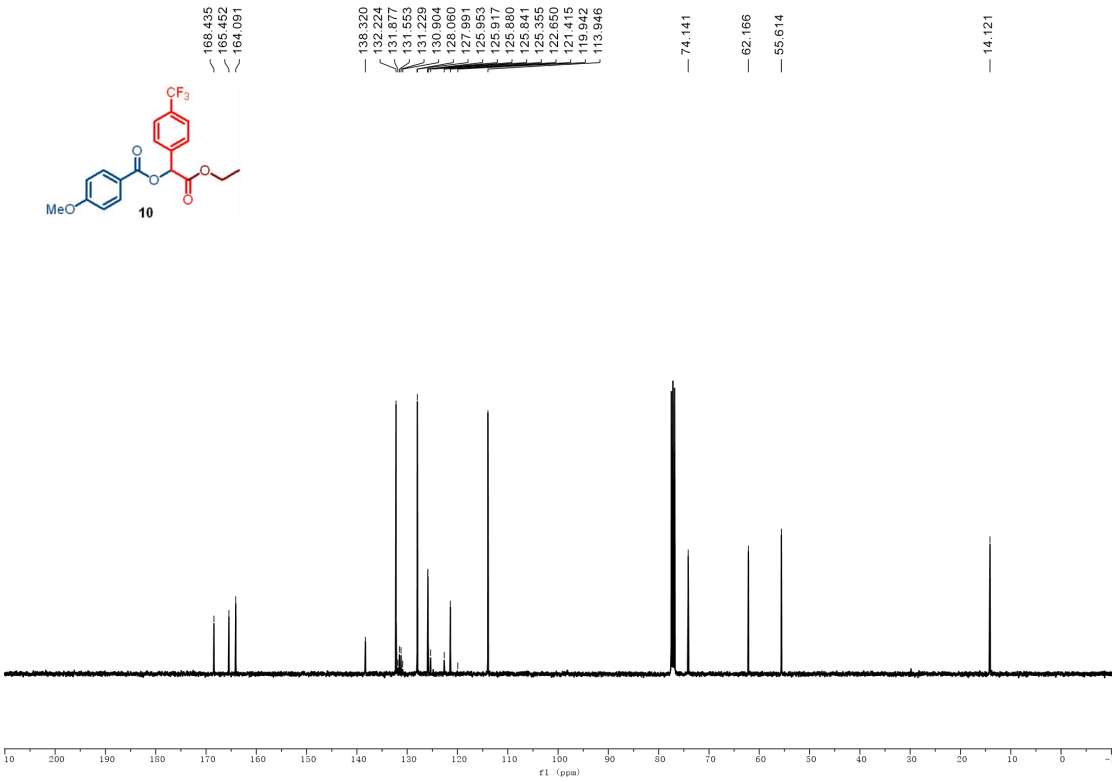
^{1}H NMR (400 MHz, $CDCl_3$) of 9



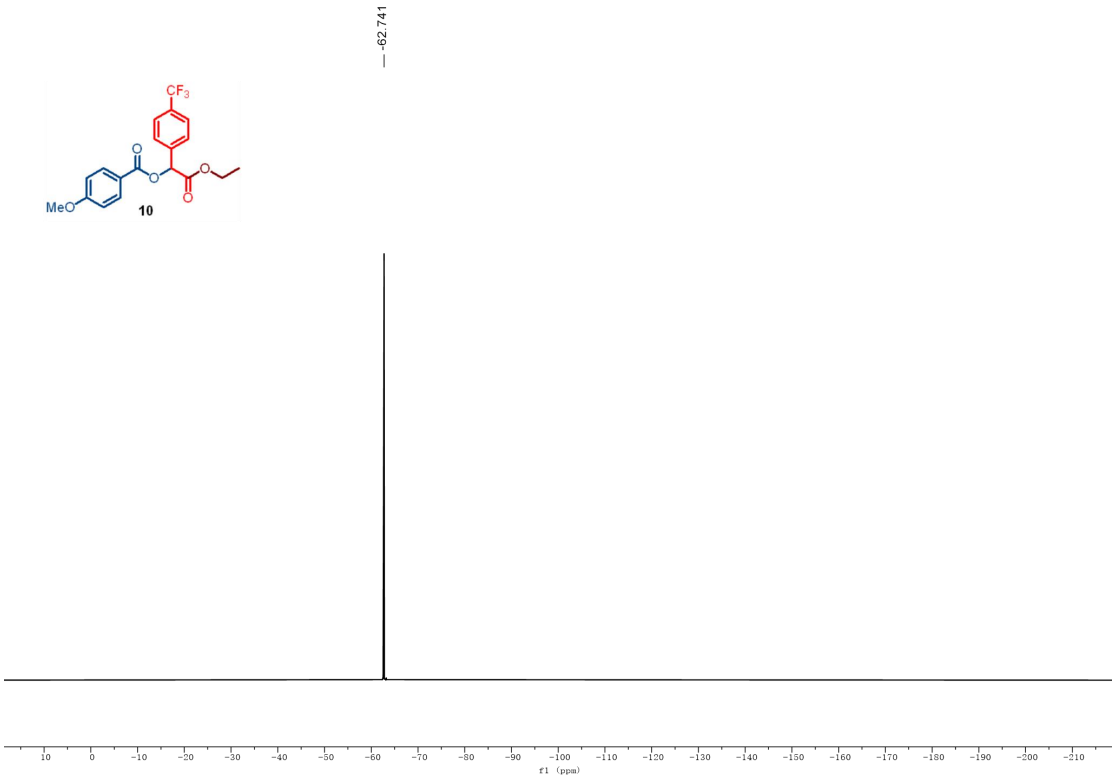
^{13}C NMR (101 MHz, $CDCl_3$) of 9



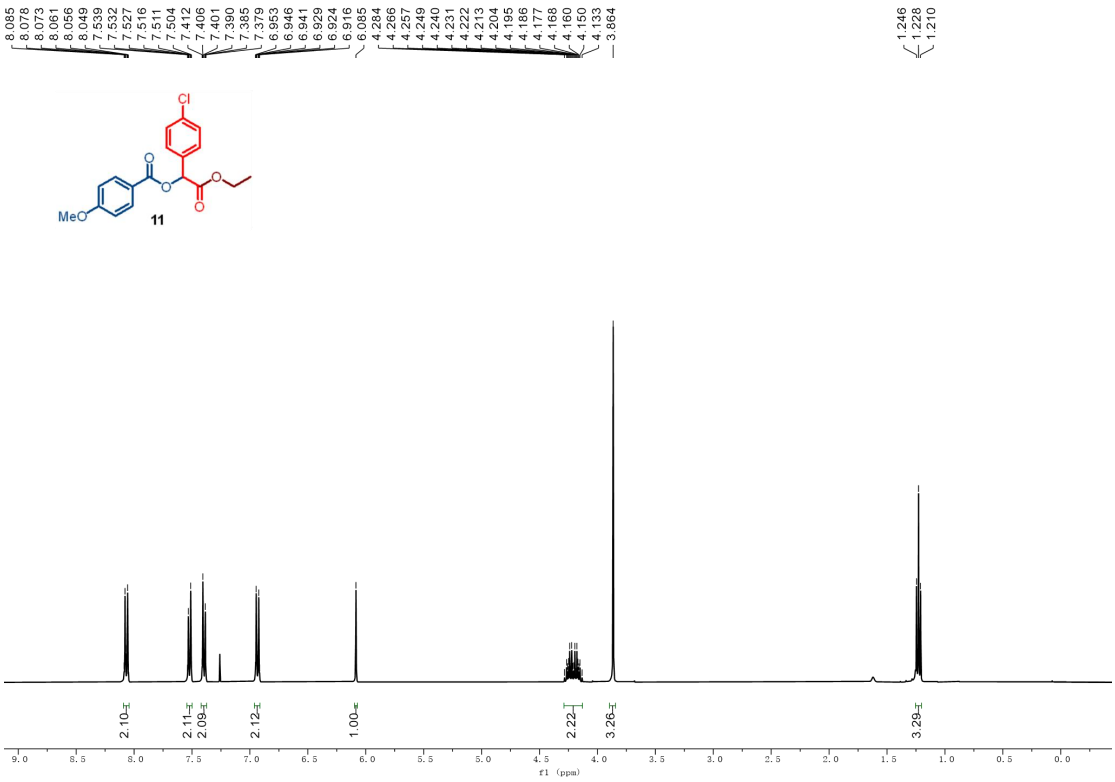
^{1}H NMR (400 MHz, $CDCl_3$) of 10



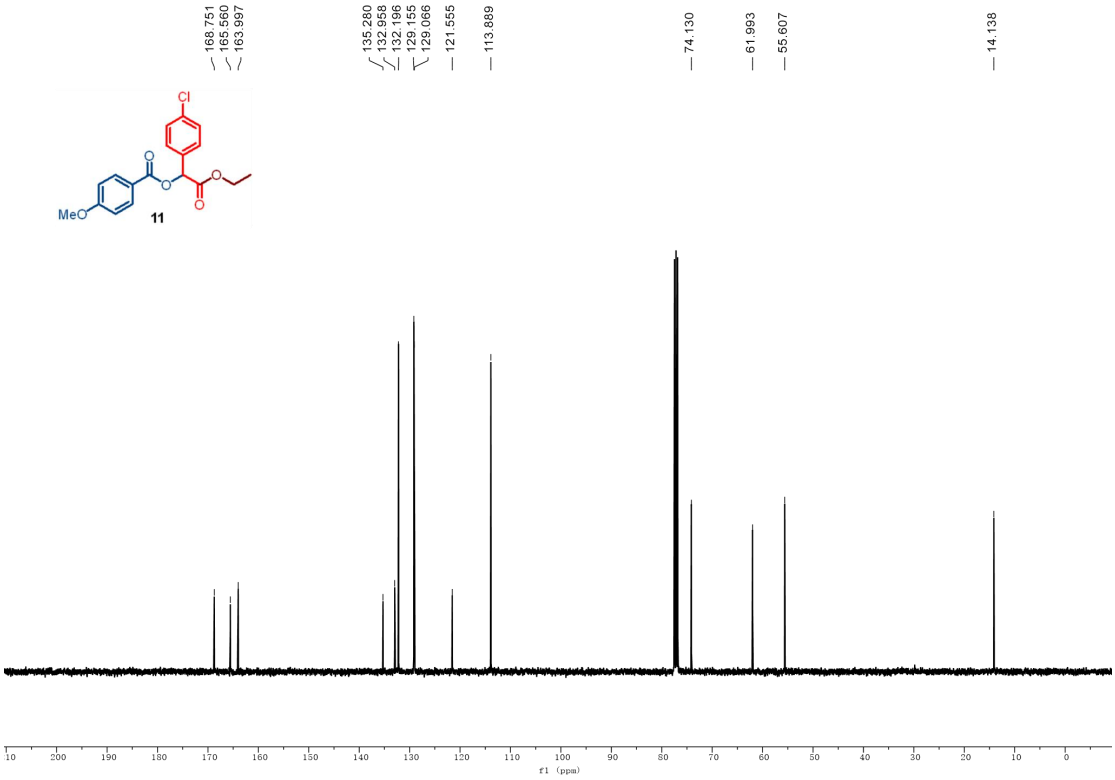
^{13}C NMR (101 MHz, $CDCl_3$) of 10



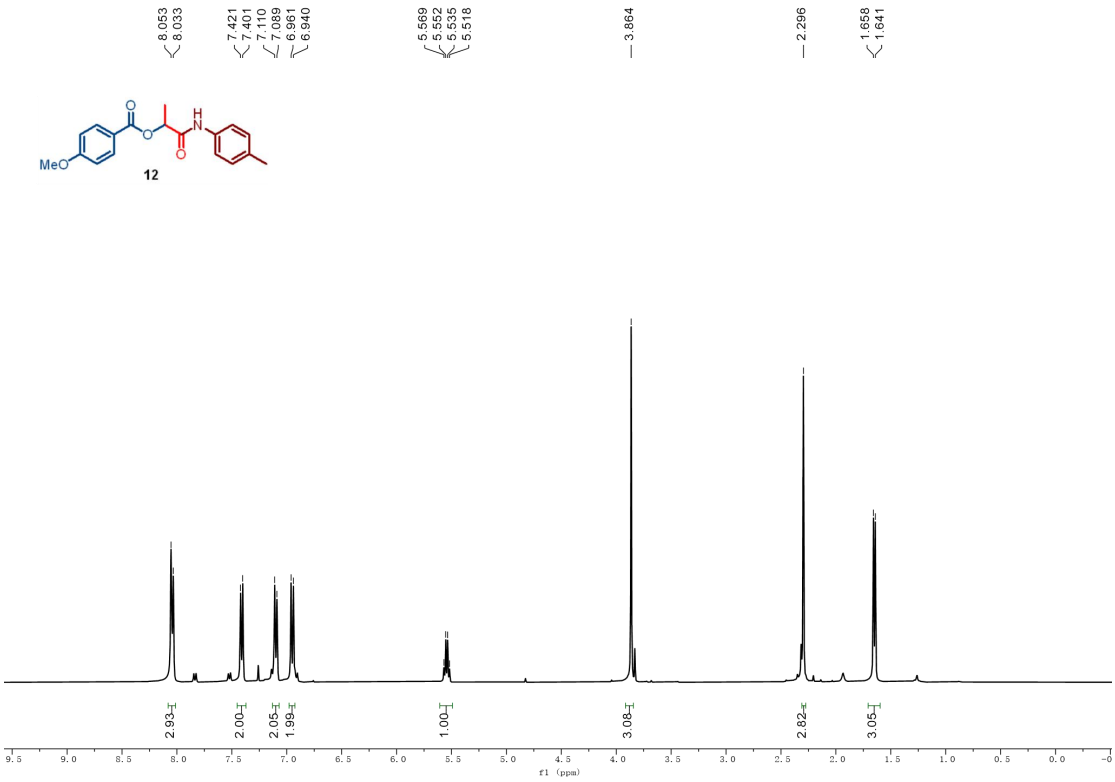
^{19}F NMR (376 MHz, $CDCl_3$) of 10



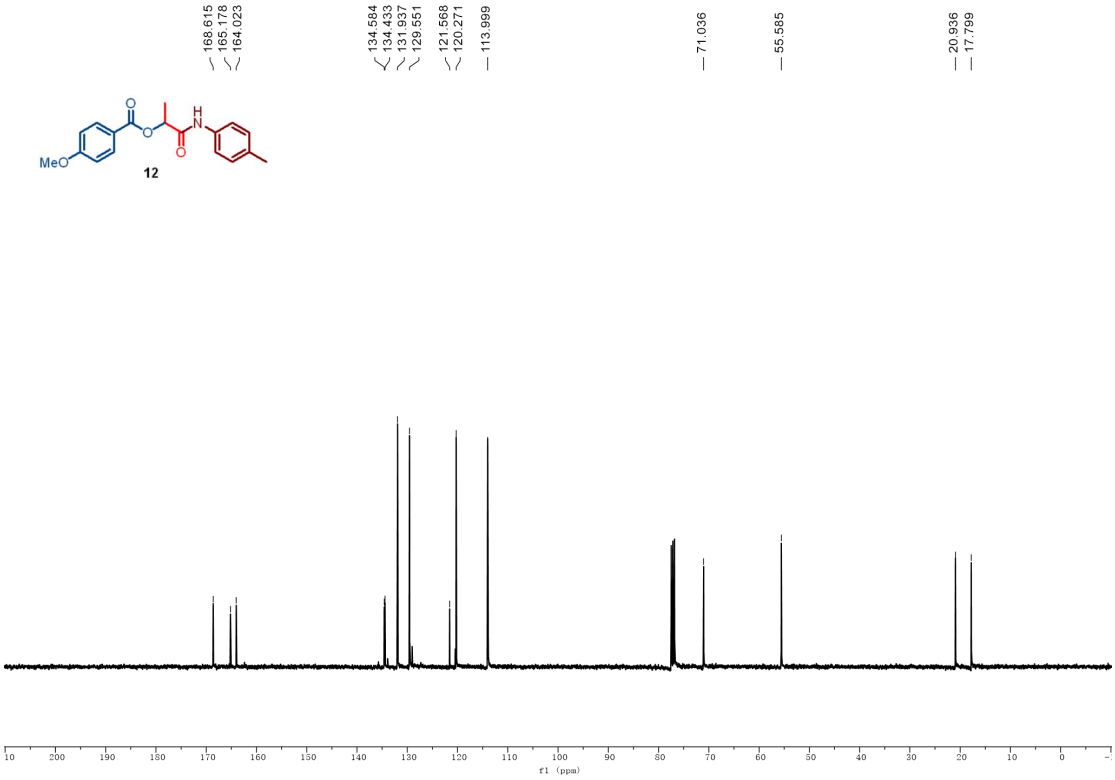
^{1}H NMR (400 MHz, $CDCl_3$) of 11



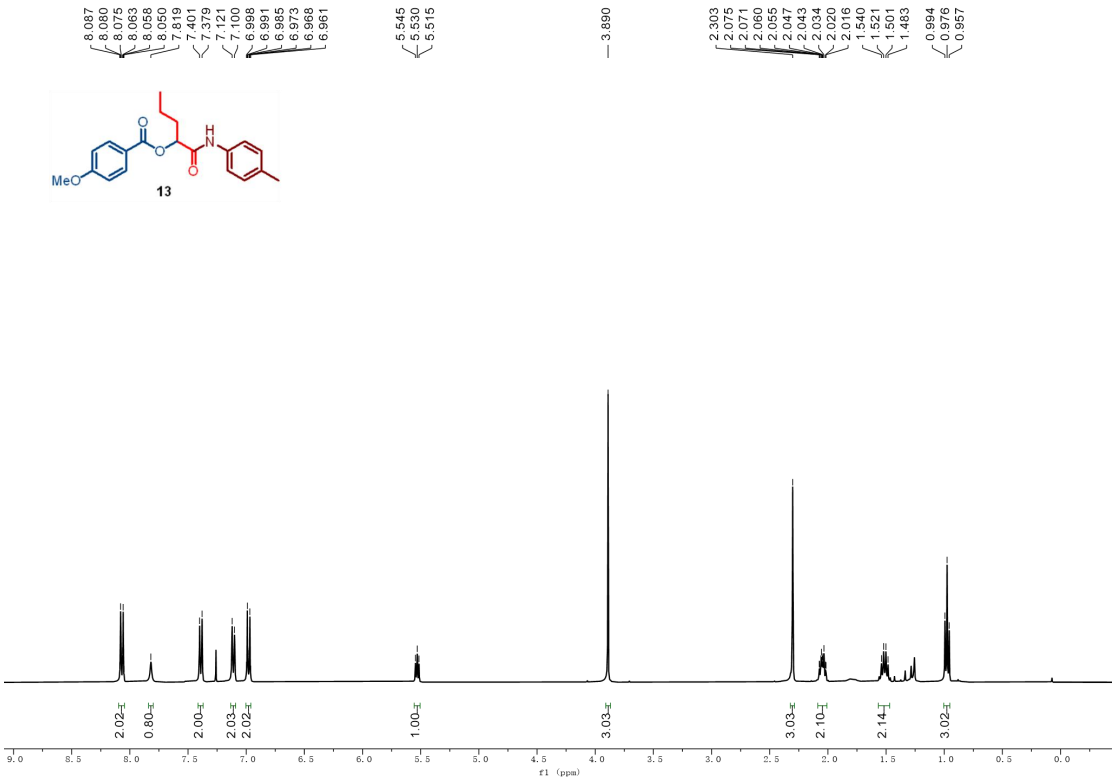
^{13}C NMR (101 MHz, $CDCl_3$) of 11



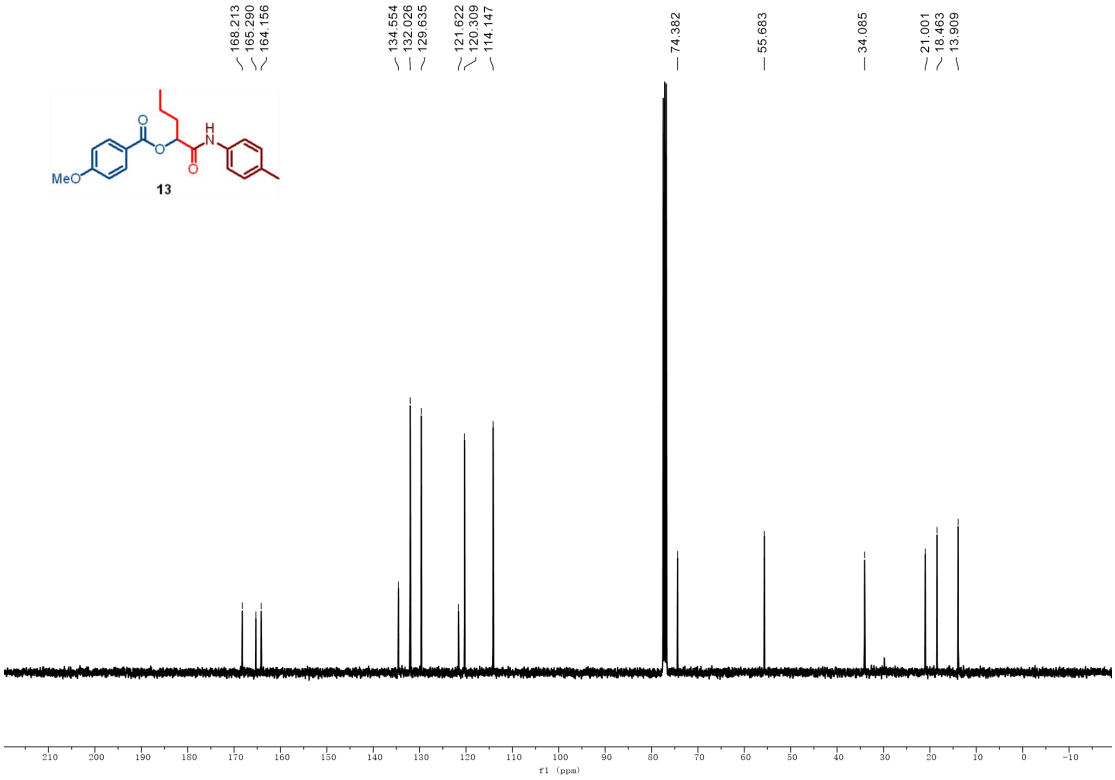
^{1}H NMR (400 MHz, $CDCl_3$) of 12



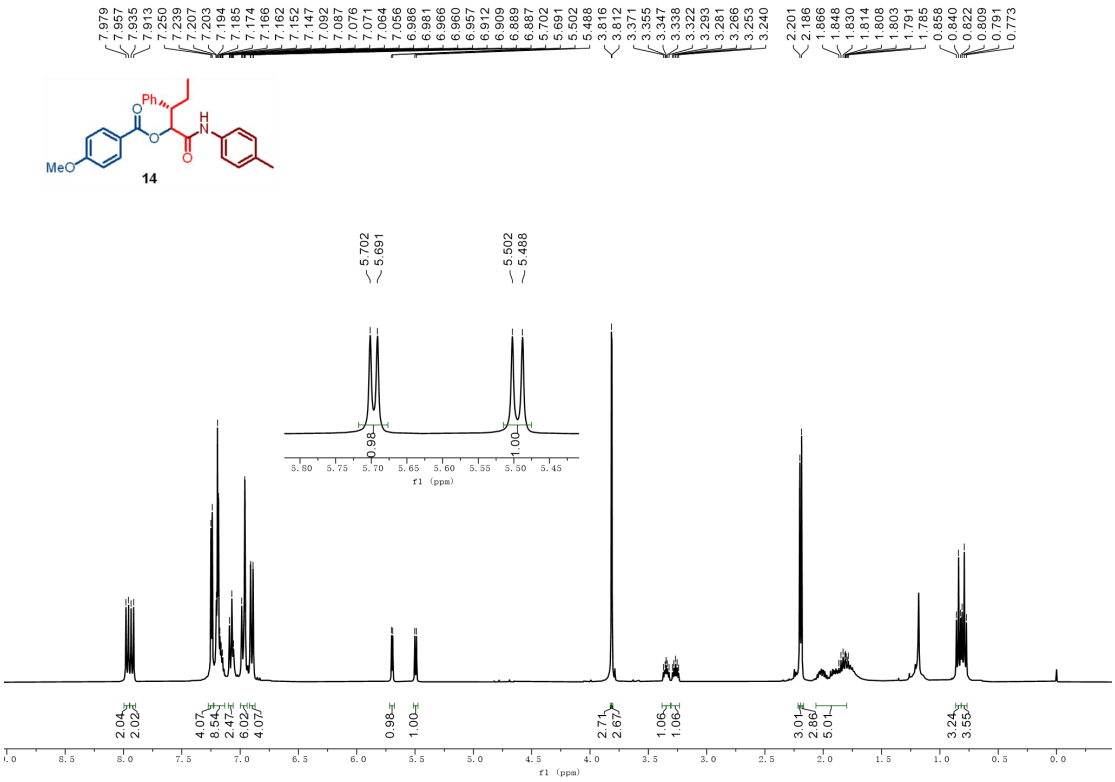
^{13}C NMR (101 MHz, $CDCl_3$) of 12



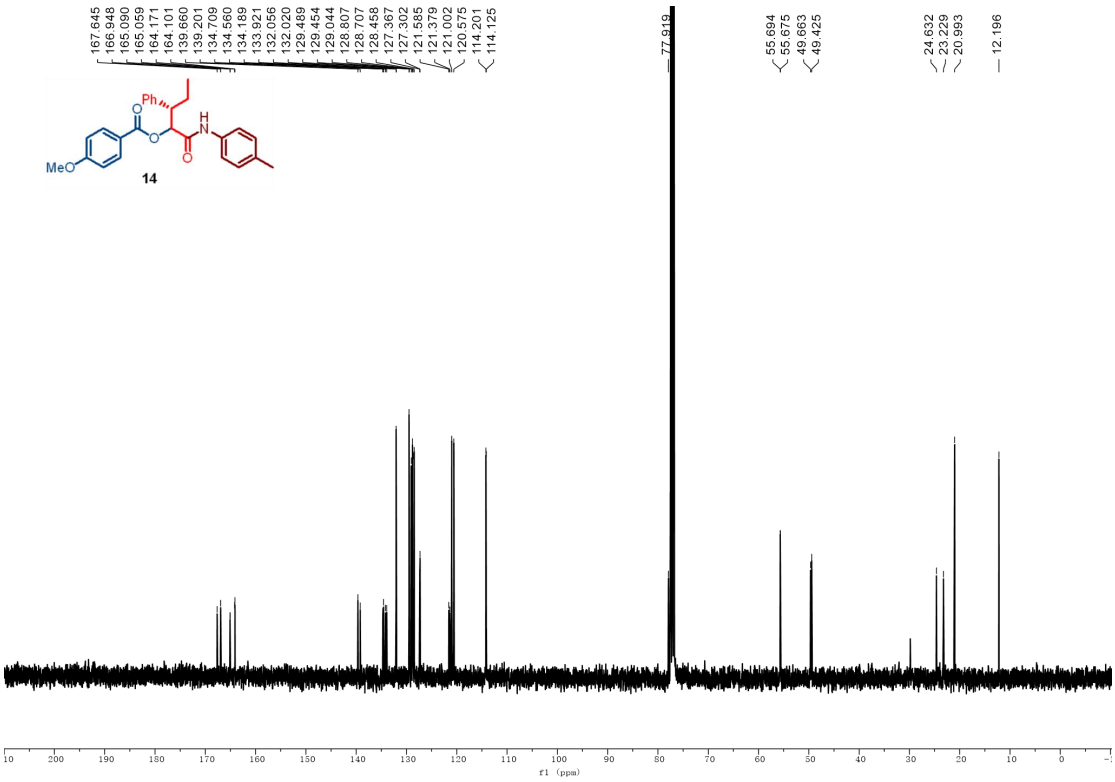
^{1}H NMR (400 MHz, $CDCl_3$) of 13



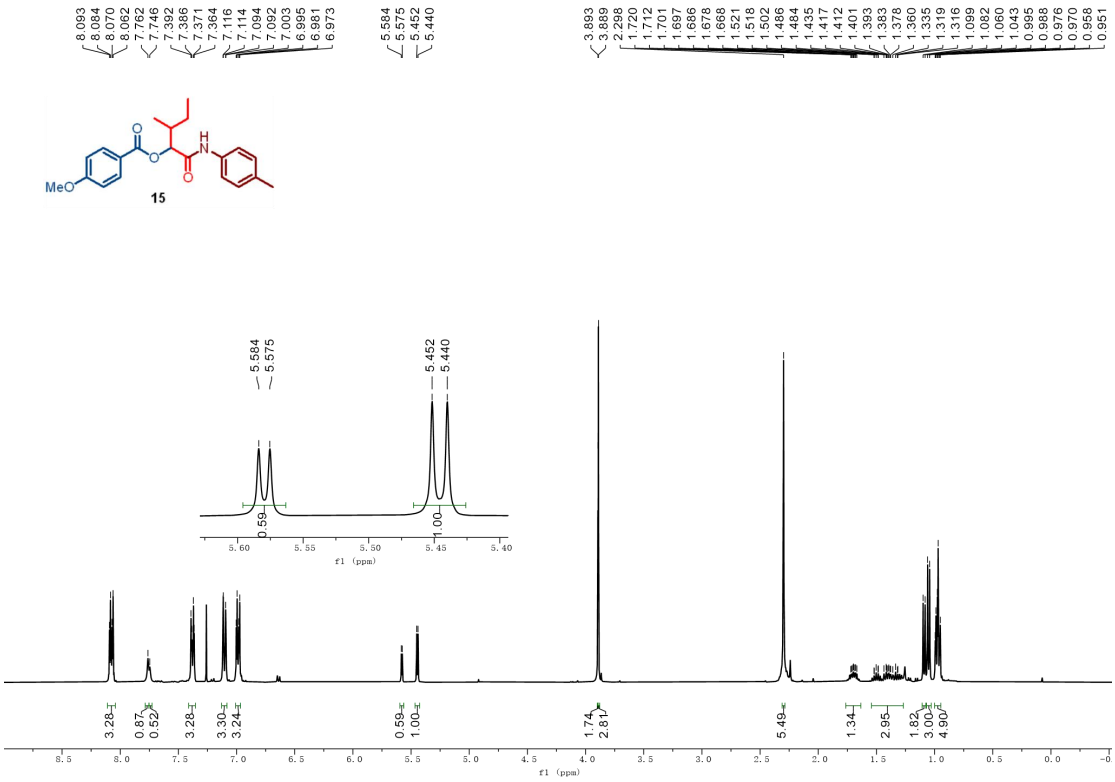
^{13}C NMR (101 MHz, $CDCl_3$) of 13



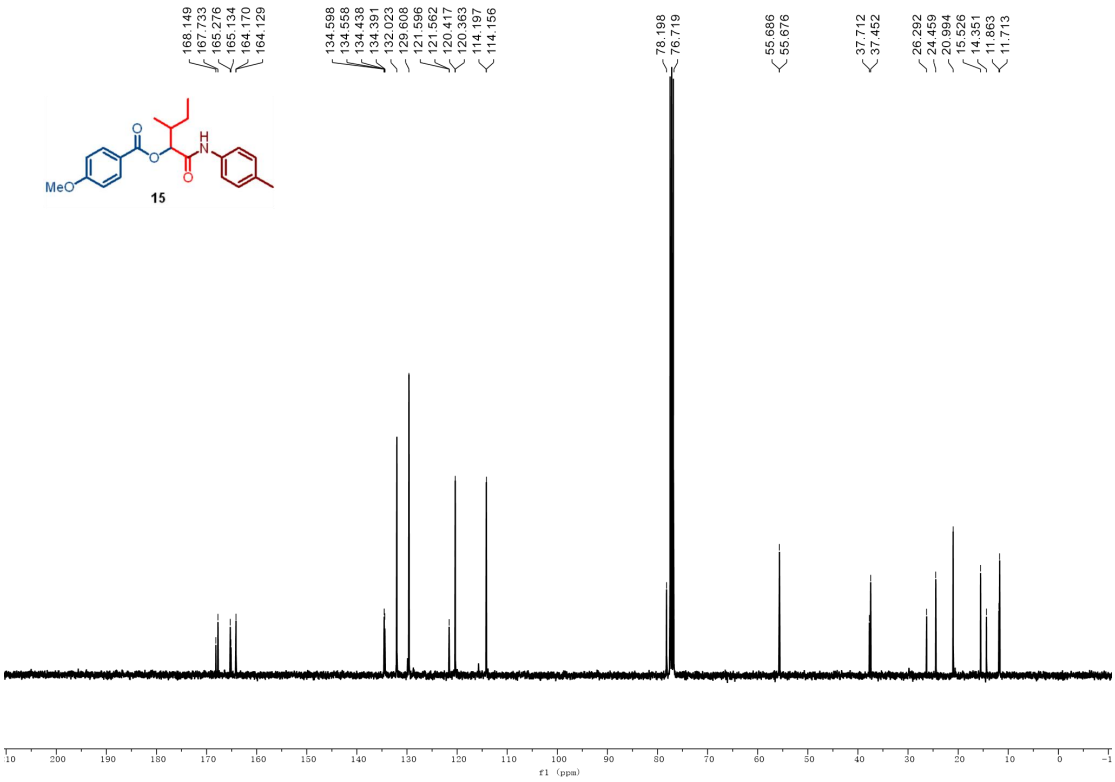
^{1}H NMR (400 MHz, $CDCl_3$) of 14



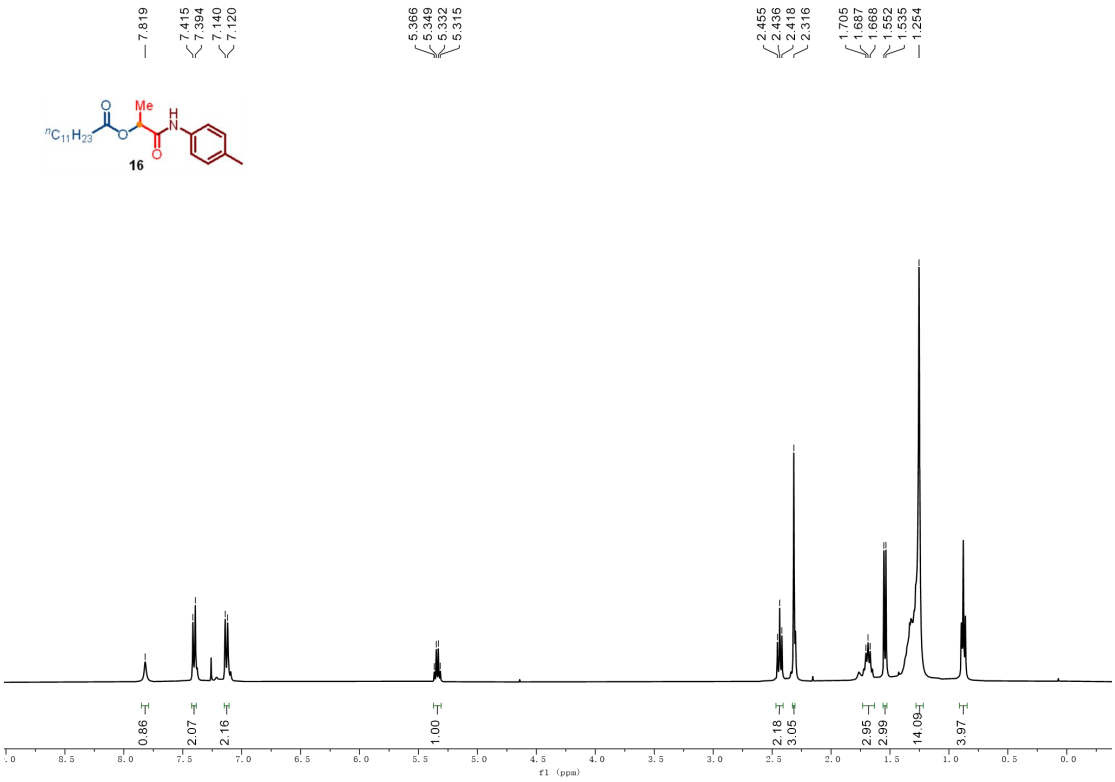
^{13}C NMR (101 MHz, $CDCl_3$) of 14



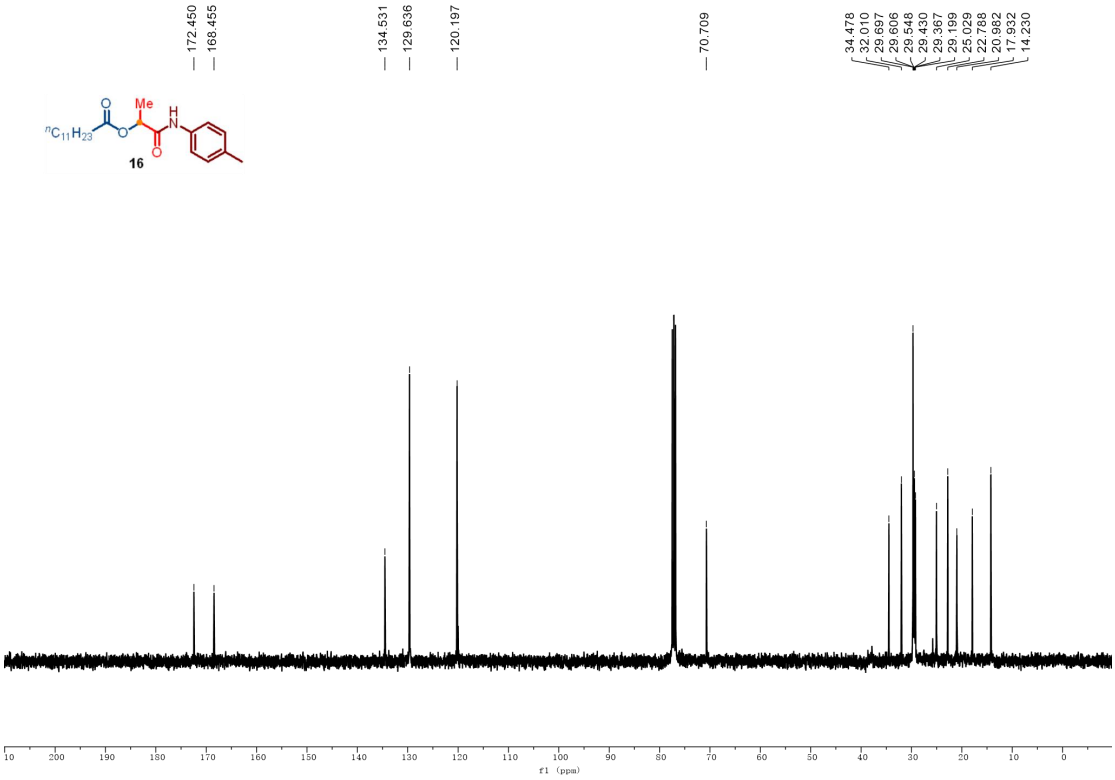
^{1}H NMR (400 MHz, $CDCl_3$) of 15



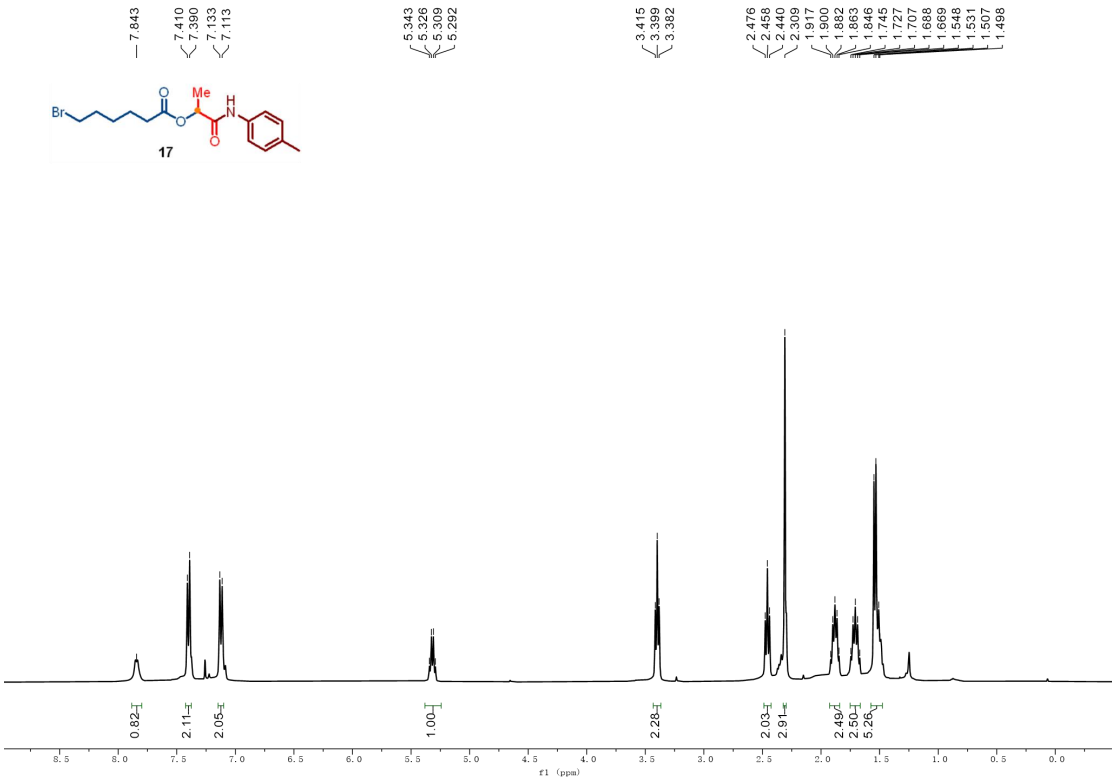
^{13}C NMR (101 MHz, $CDCl_3$) of 15



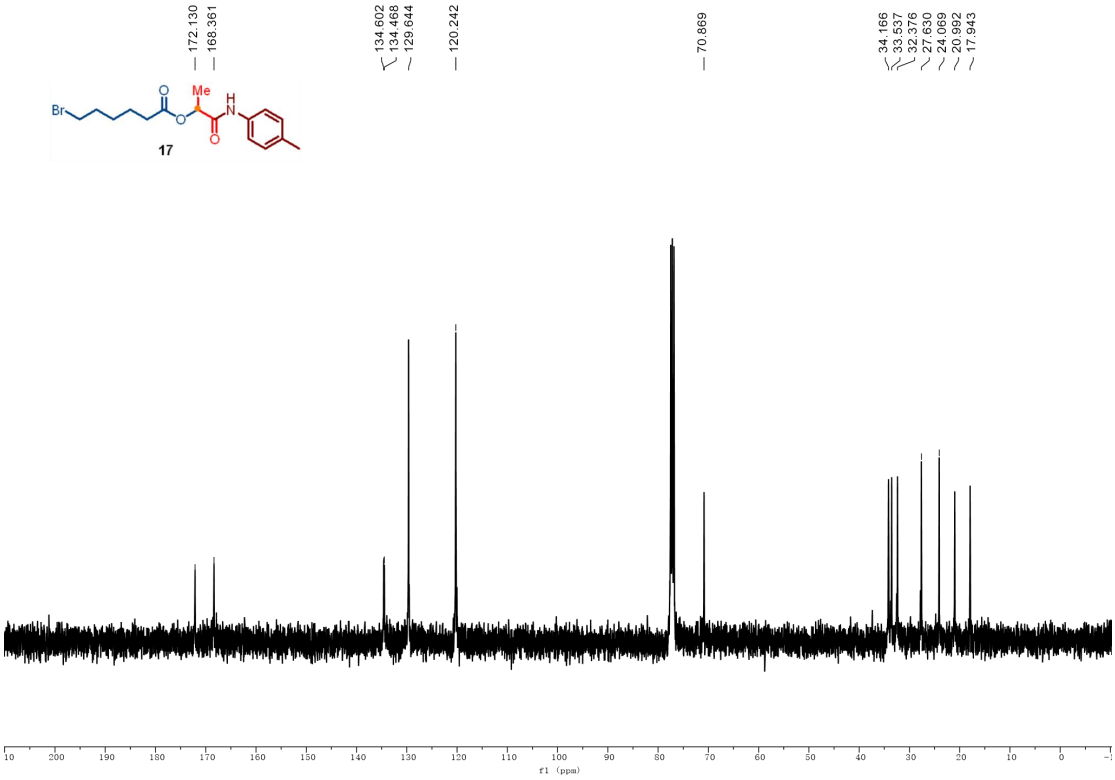
^{1}H NMR (400 MHz, $CDCl_3$) of 16



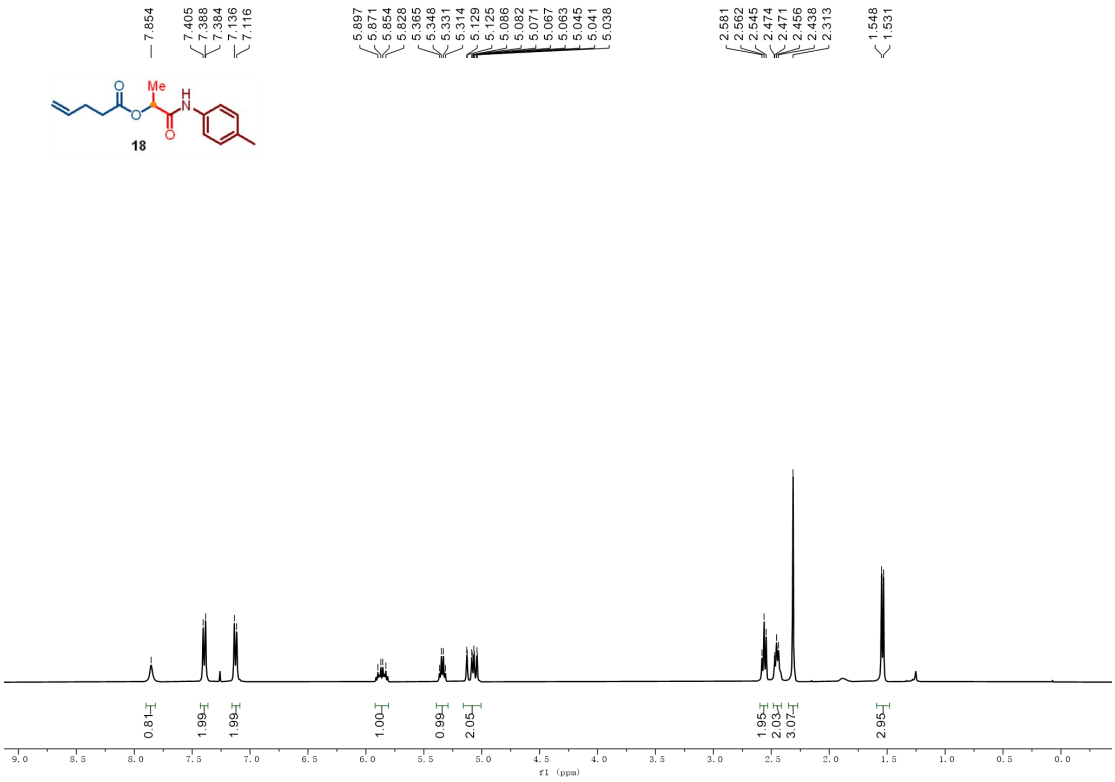
^{13}C NMR (101 MHz, $CDCl_3$) of 16



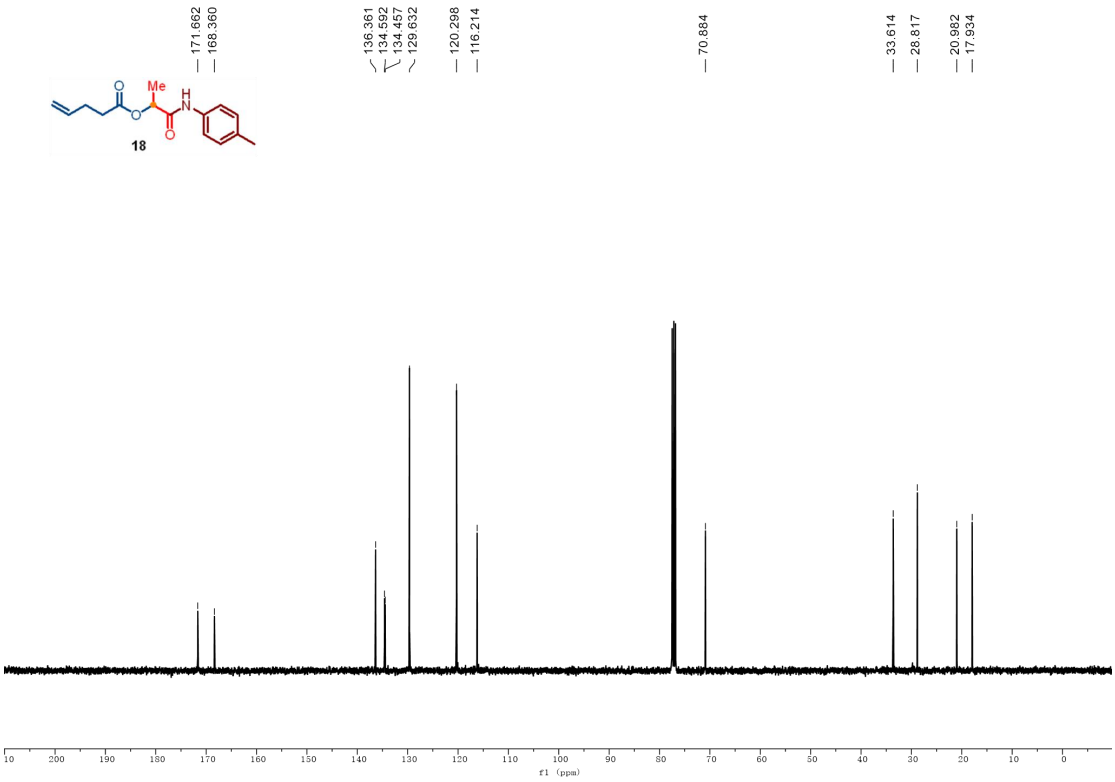
^{1}H NMR (400 MHz, $CDCl_3$) of 17



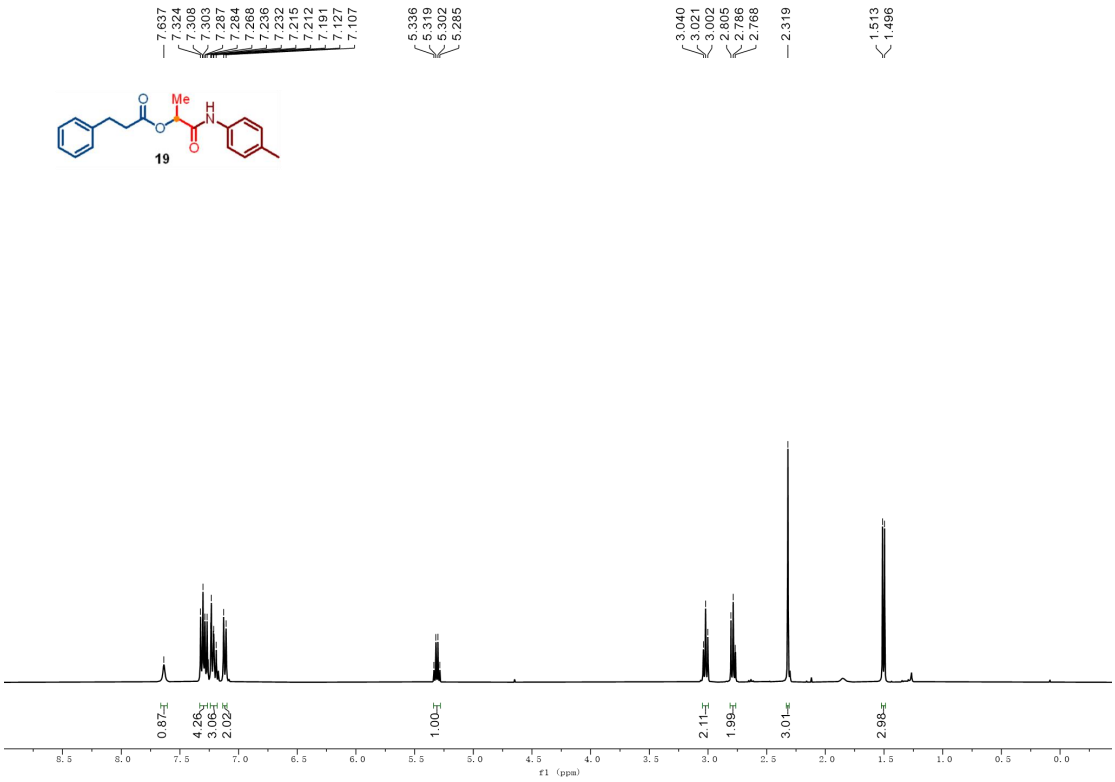
^{13}C NMR (101 MHz, $CDCl_3$) of 17



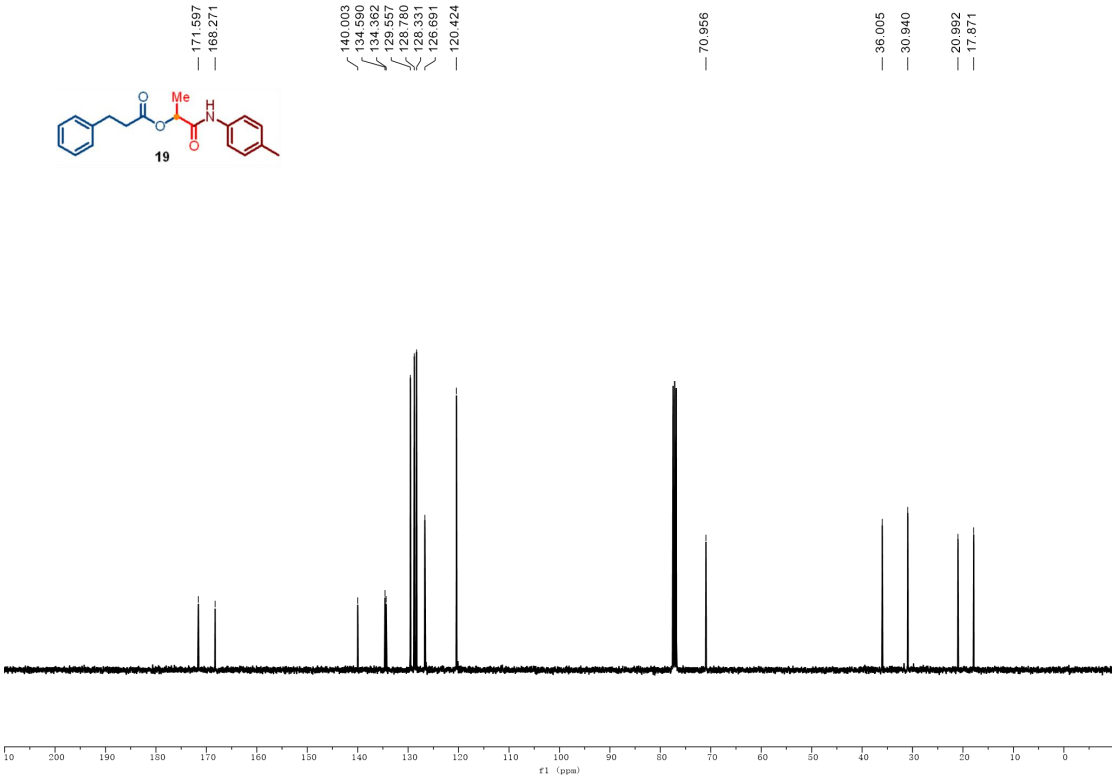
^{1}H NMR (400 MHz, $CDCl_3$) of 18



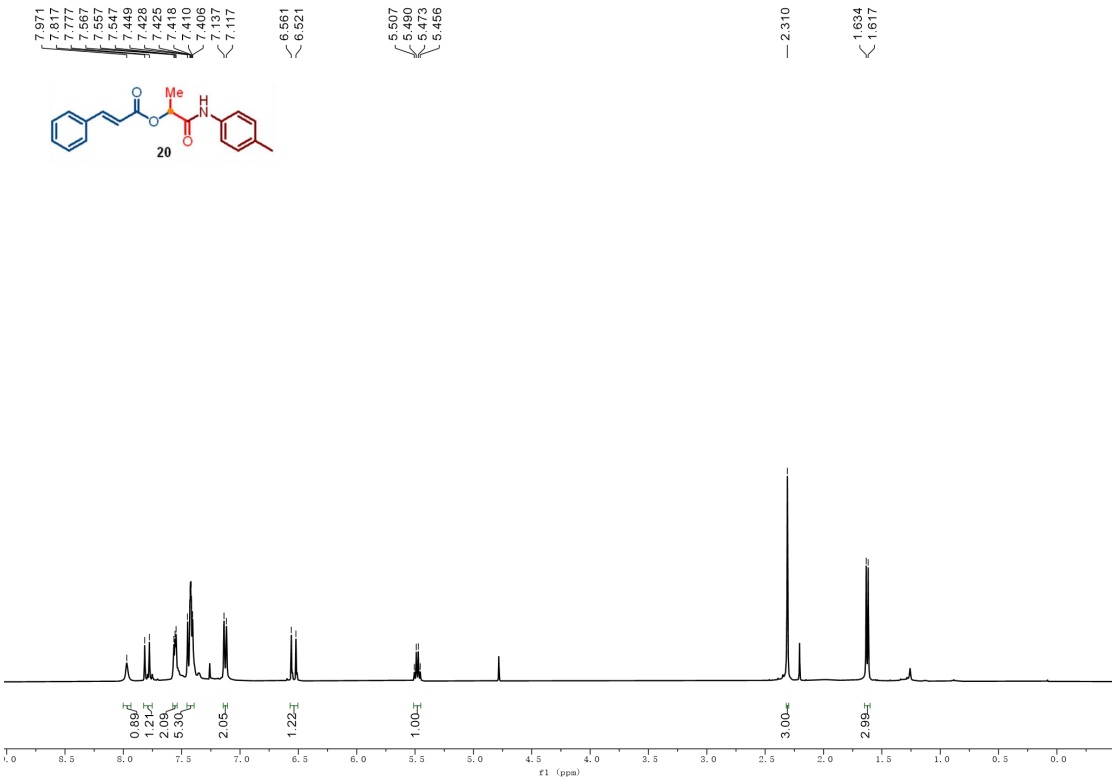
^{13}C NMR (101 MHz, $CDCl_3$) of 18



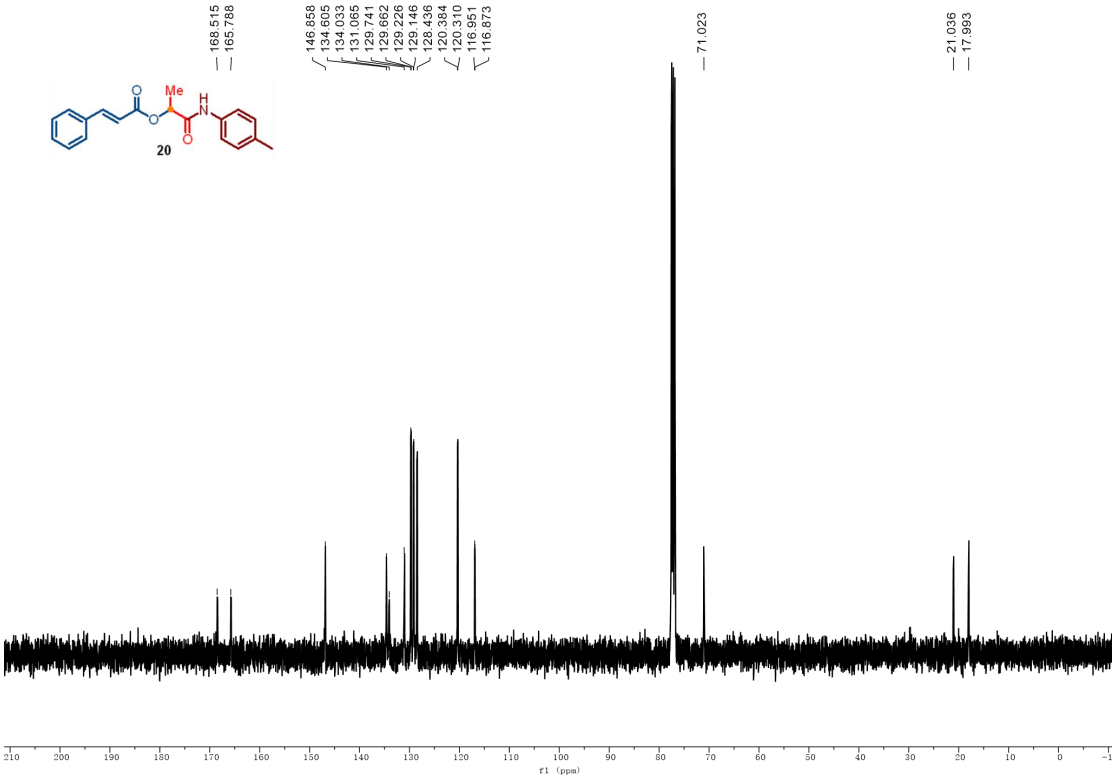
^{1}H NMR (400 MHz, $CDCl_3$) of 19



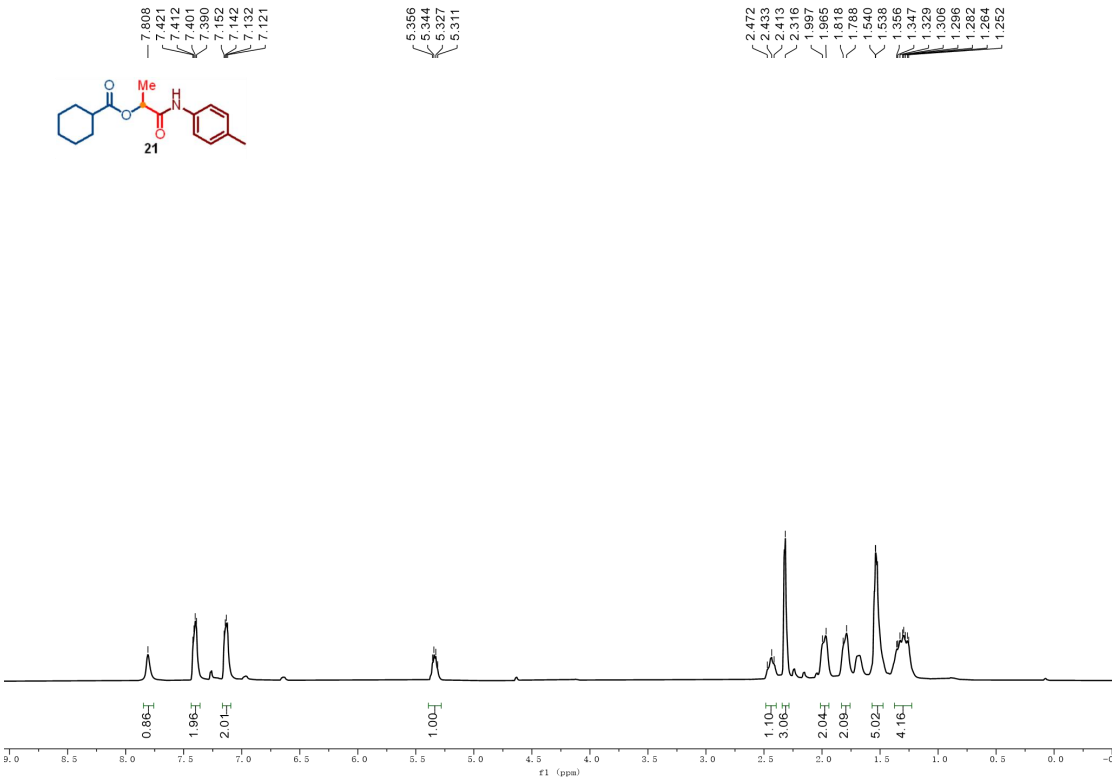
^{13}C NMR (101 MHz, $CDCl_3$) of 19



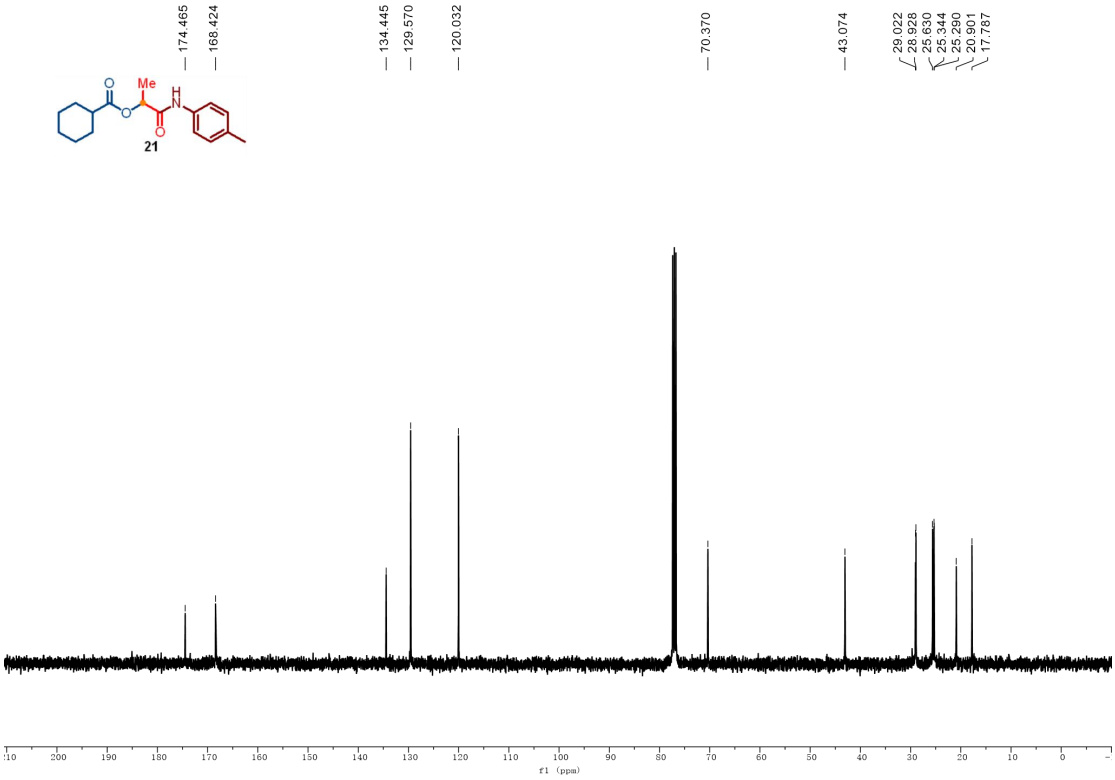
^{1}H NMR (400 MHz, $CDCl_3$) of 20



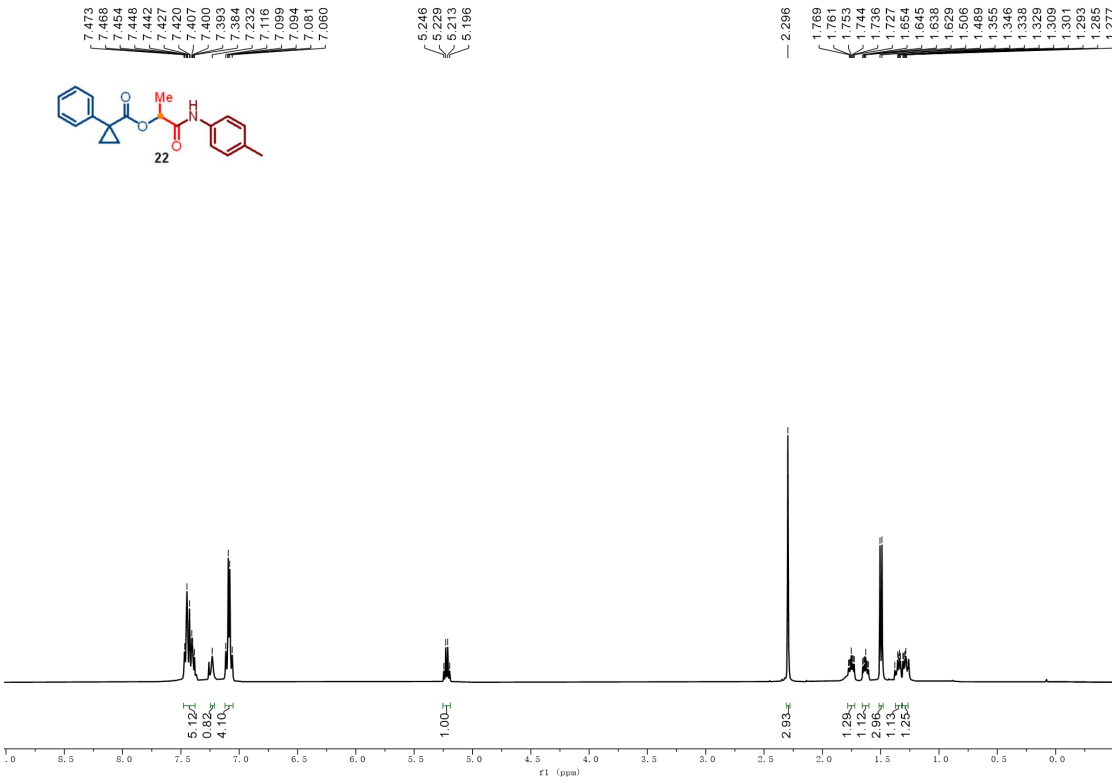
^{13}C NMR (101 MHz, $CDCl_3$) of 20



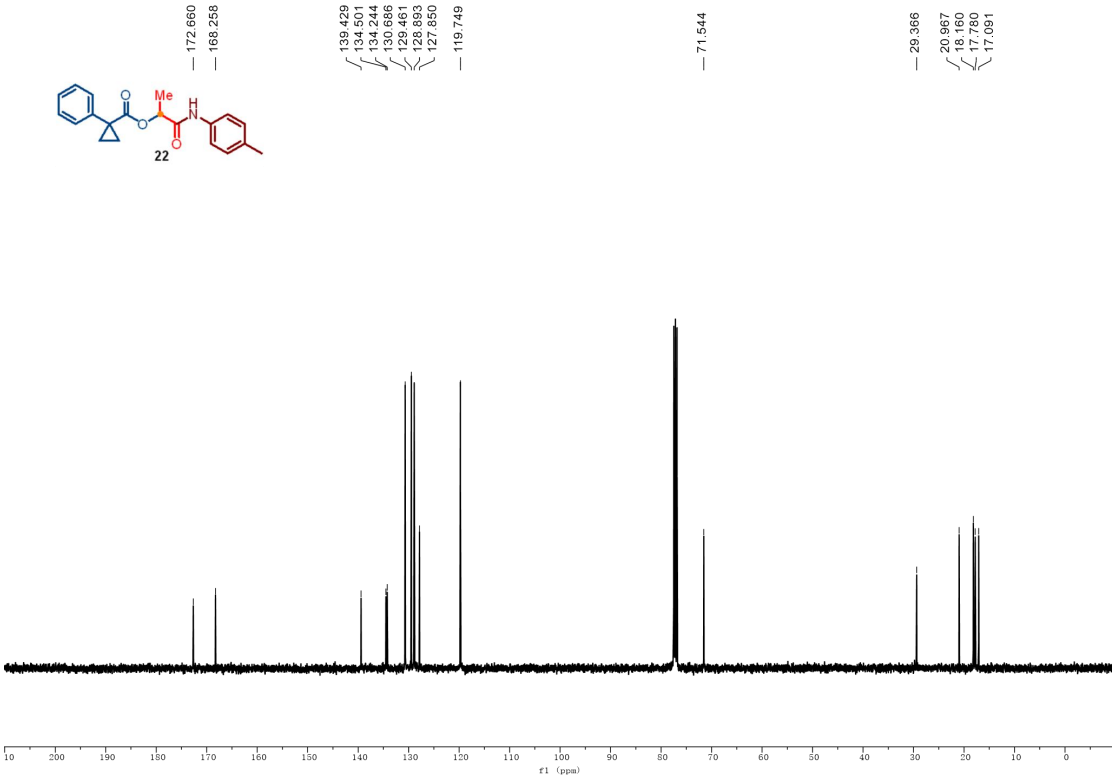
^{1}H NMR (400 MHz, $CDCl_3$) of 21



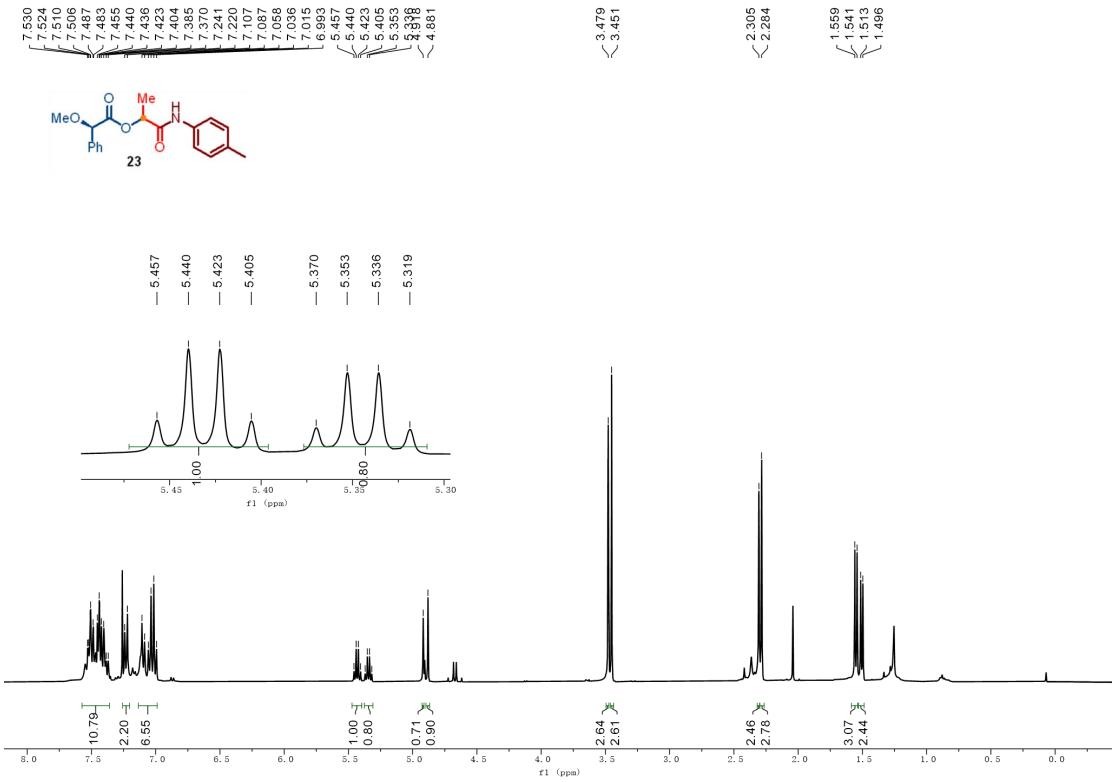
^{13}C NMR (101 MHz, $CDCl_3$) of 21



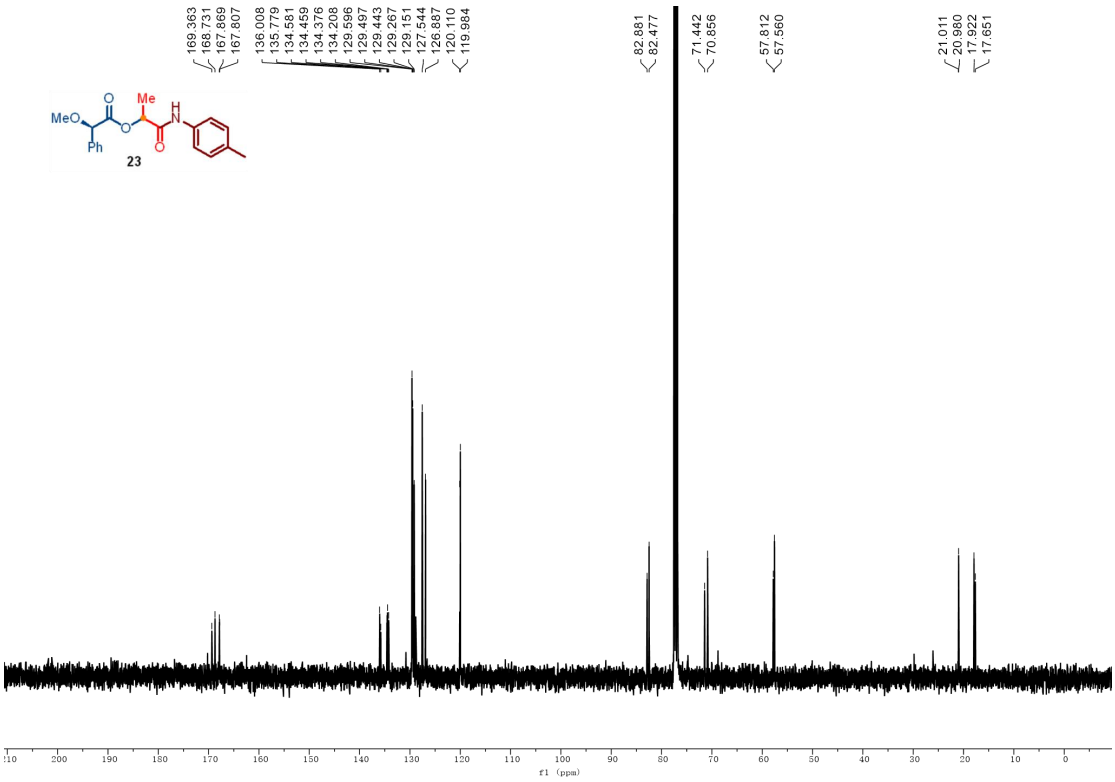
^{1}H NMR (400 MHz, $CDCl_3$) of 22



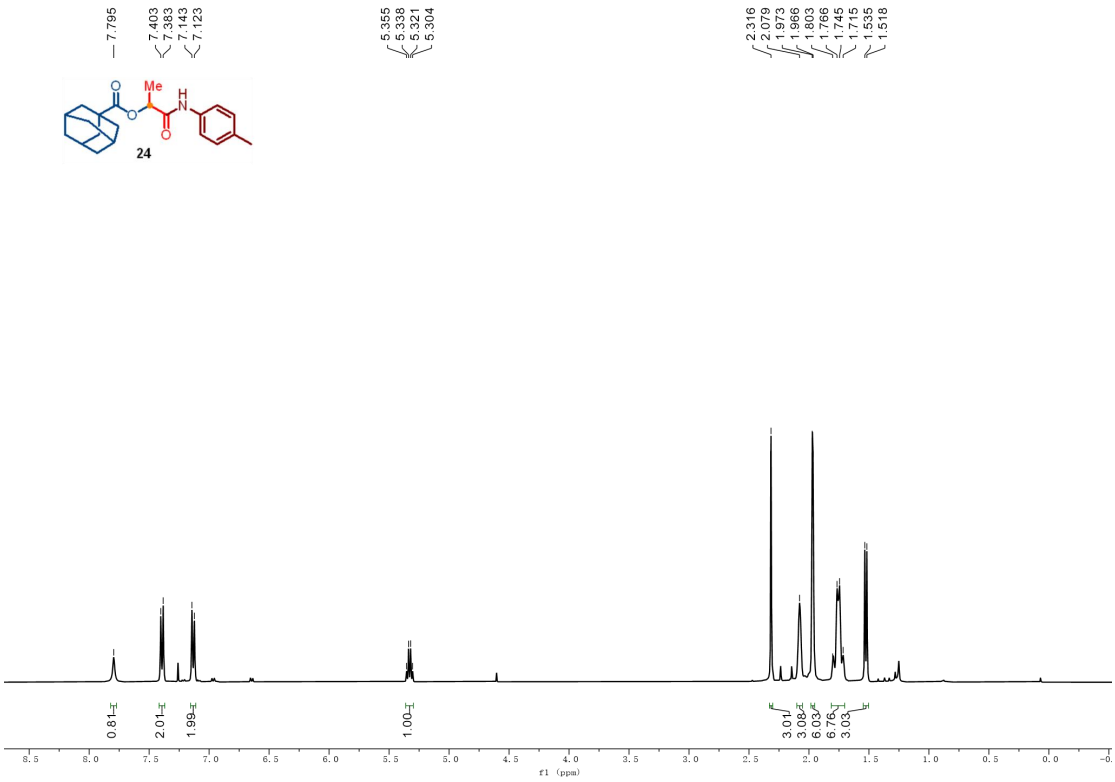
^{13}C NMR (101 MHz, $CDCl_3$) of 22



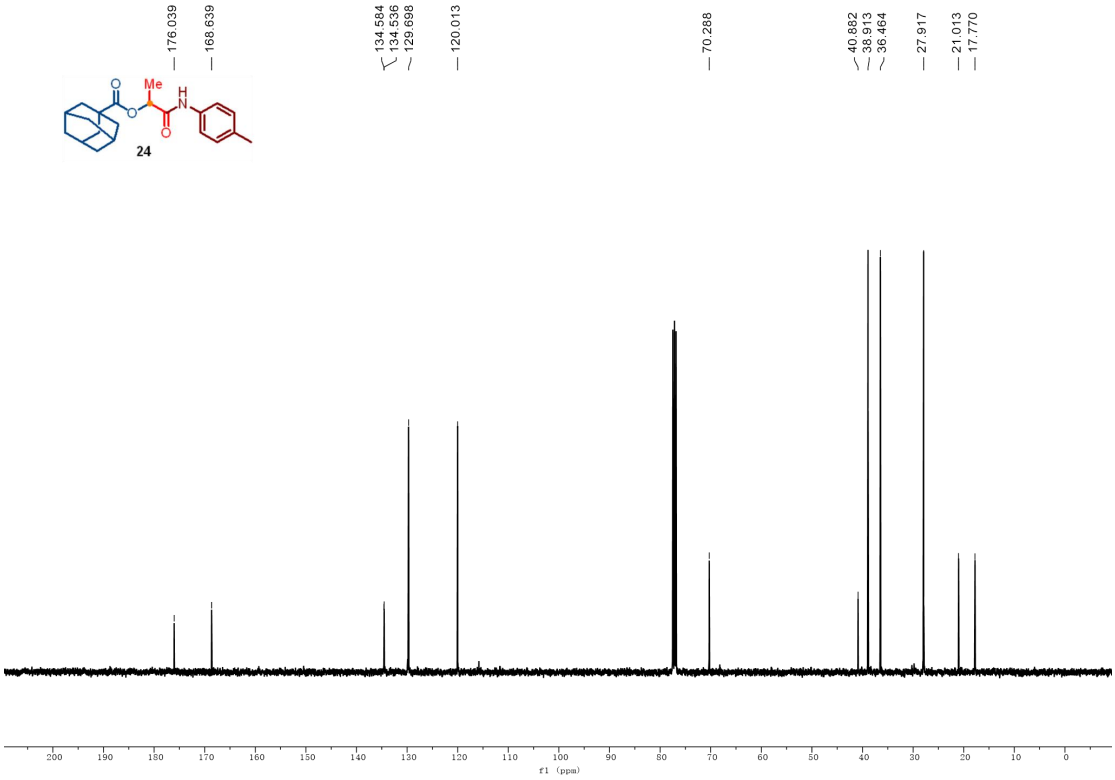
^{1}H NMR (400 MHz, $CDCl_3$) of 23



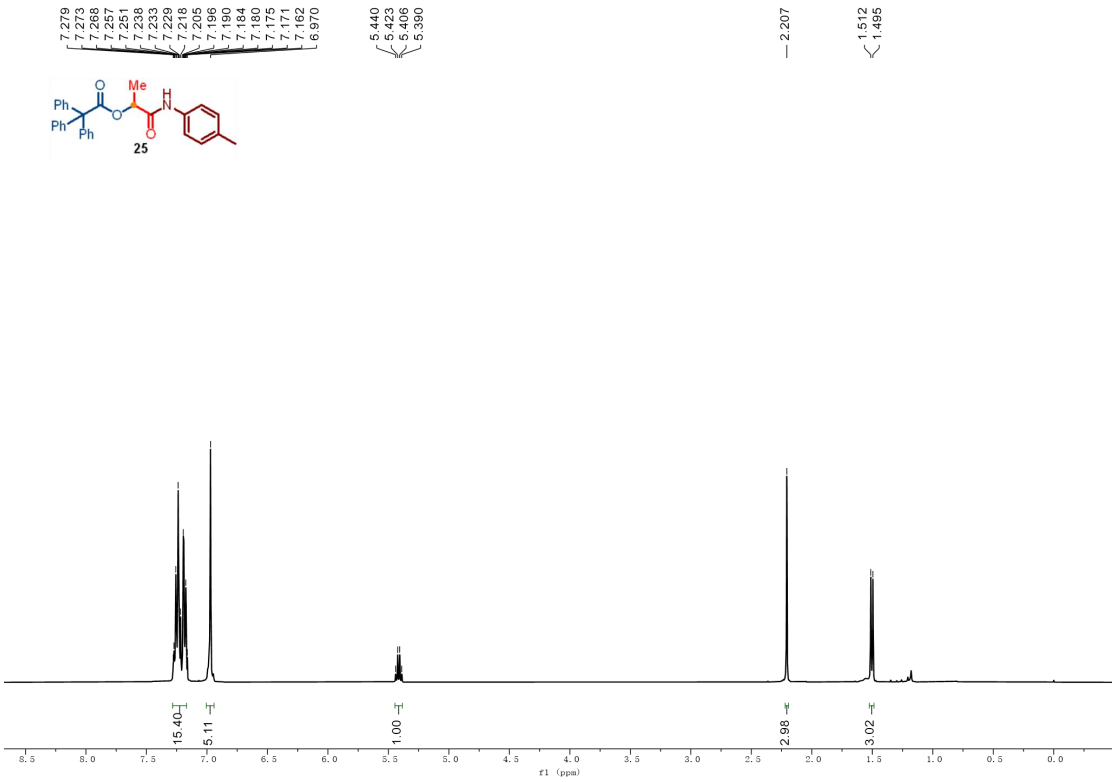
^{13}C NMR (101 MHz, $CDCl_3$) of 23



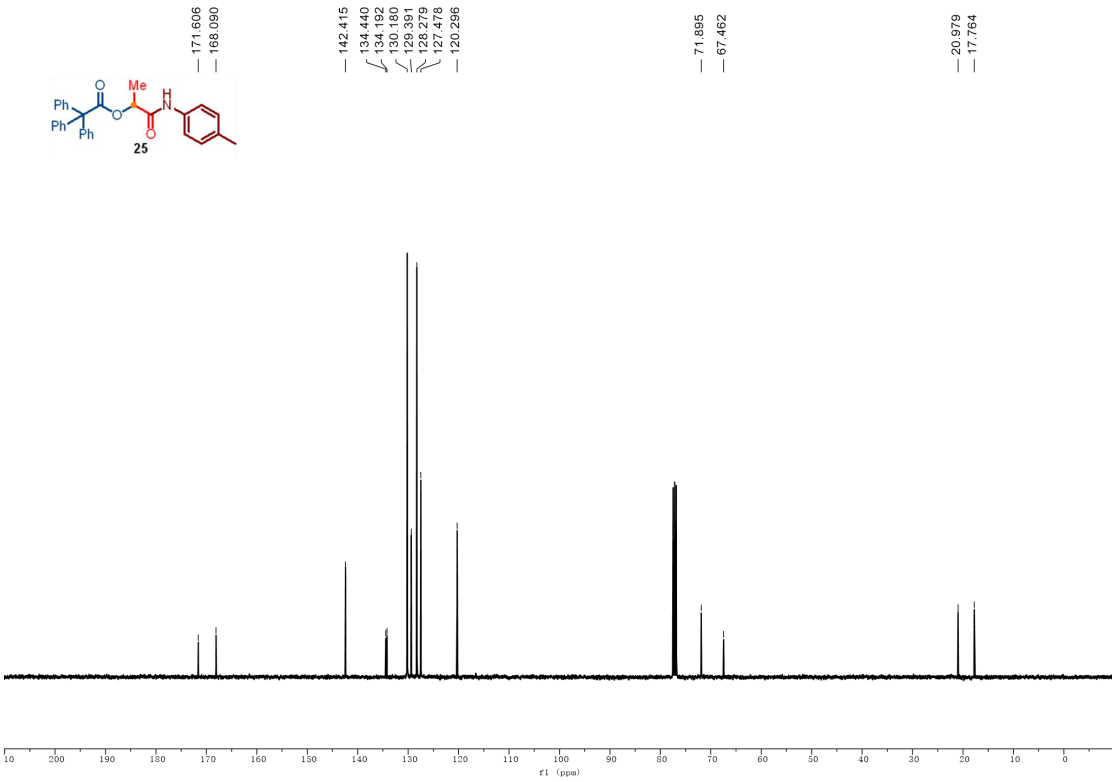
^{1}H NMR (400 MHz, $CDCl_3$) of 24



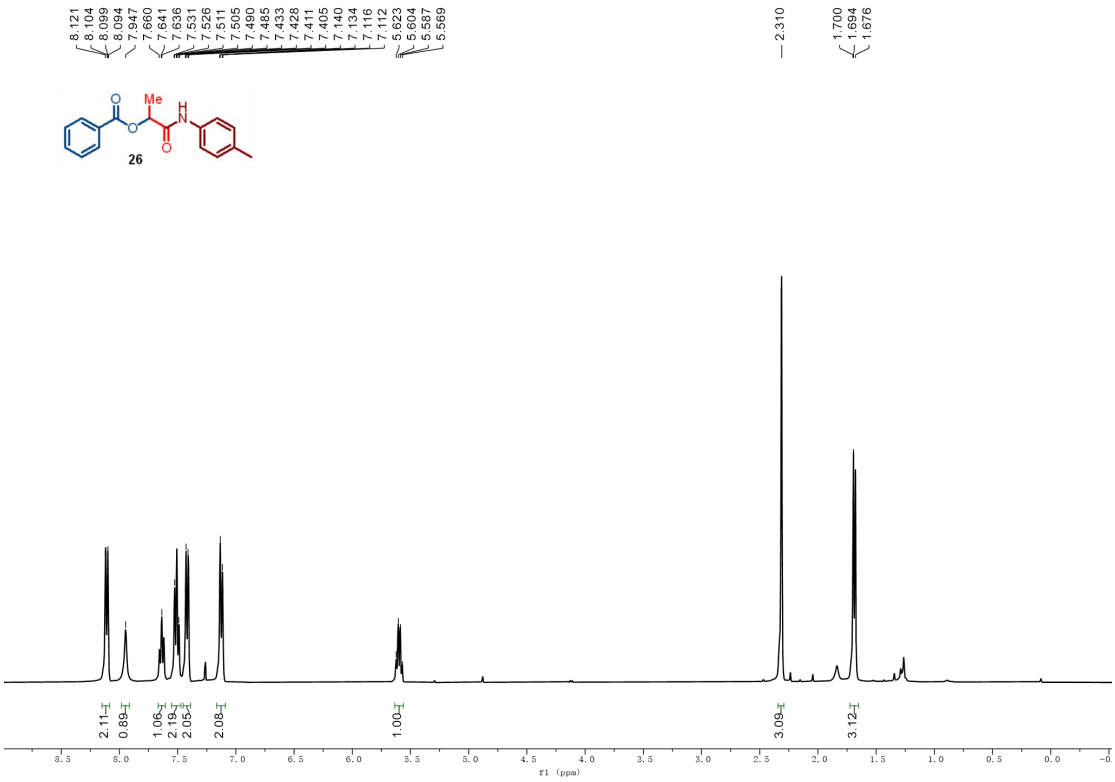
^{13}C NMR (101 MHz, $CDCl_3$) of 24



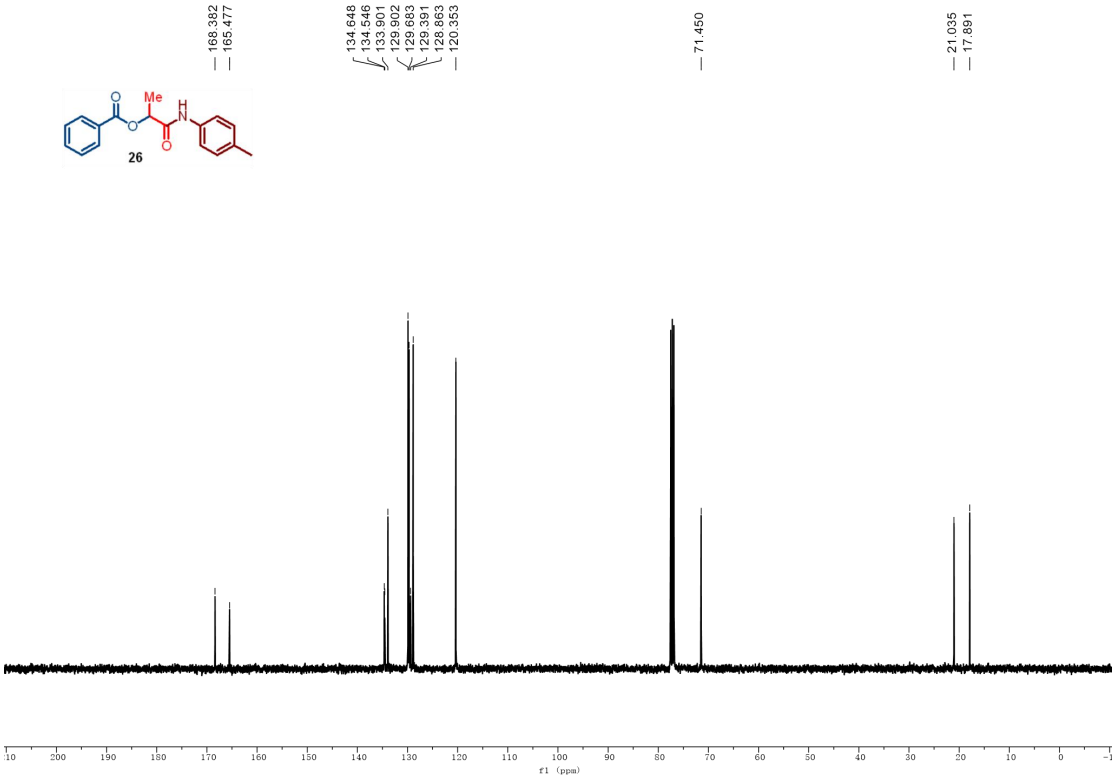
^{1}H NMR (400 MHz, $CDCl_3$) of 25



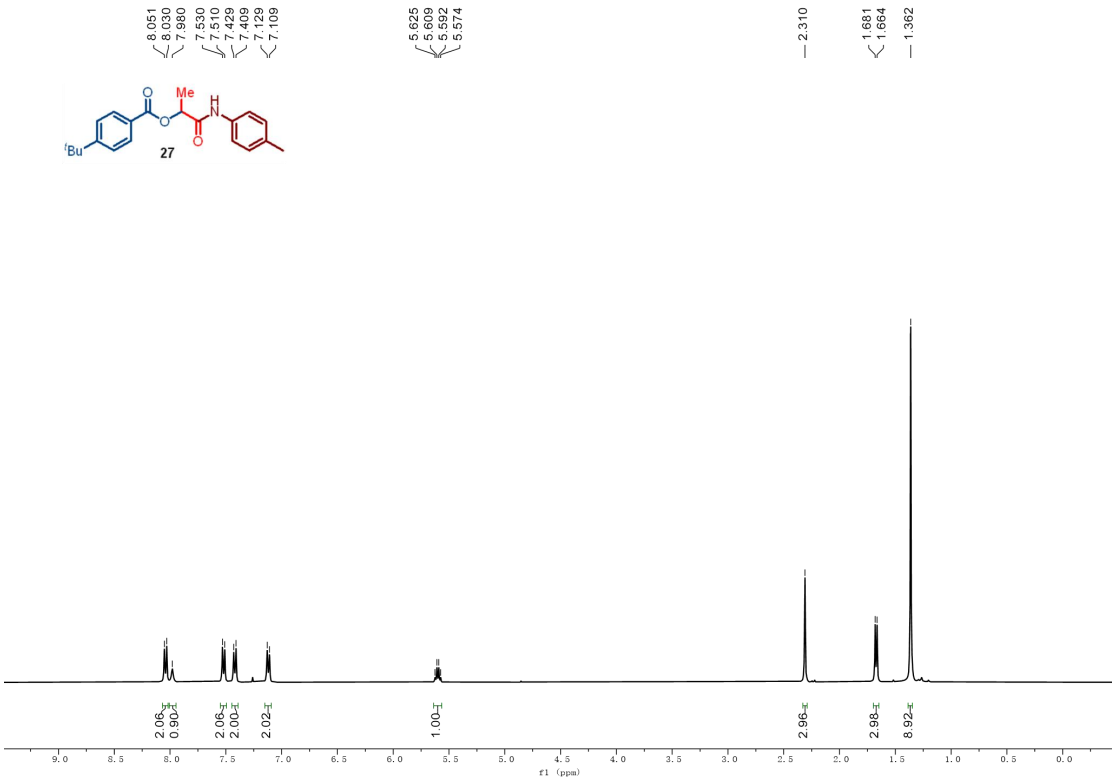
^{13}C NMR (101 MHz, $CDCl_3$) of 25



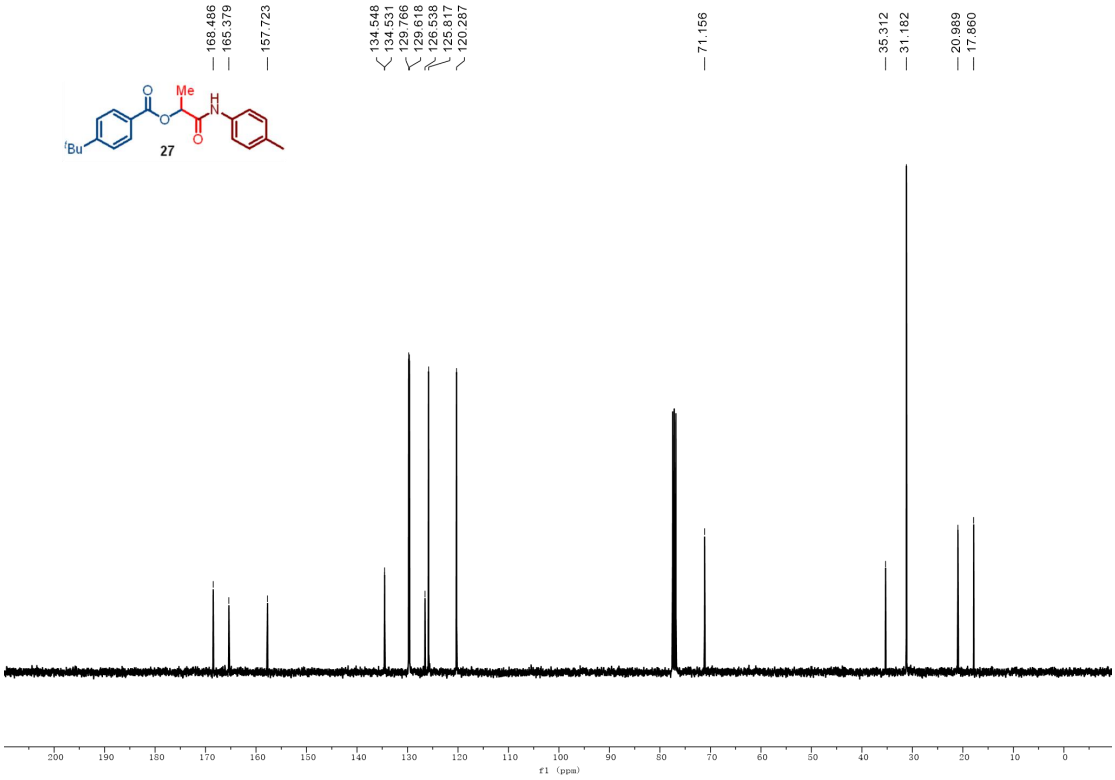
^{1}H NMR (400 MHz, $CDCl_3$) of 26



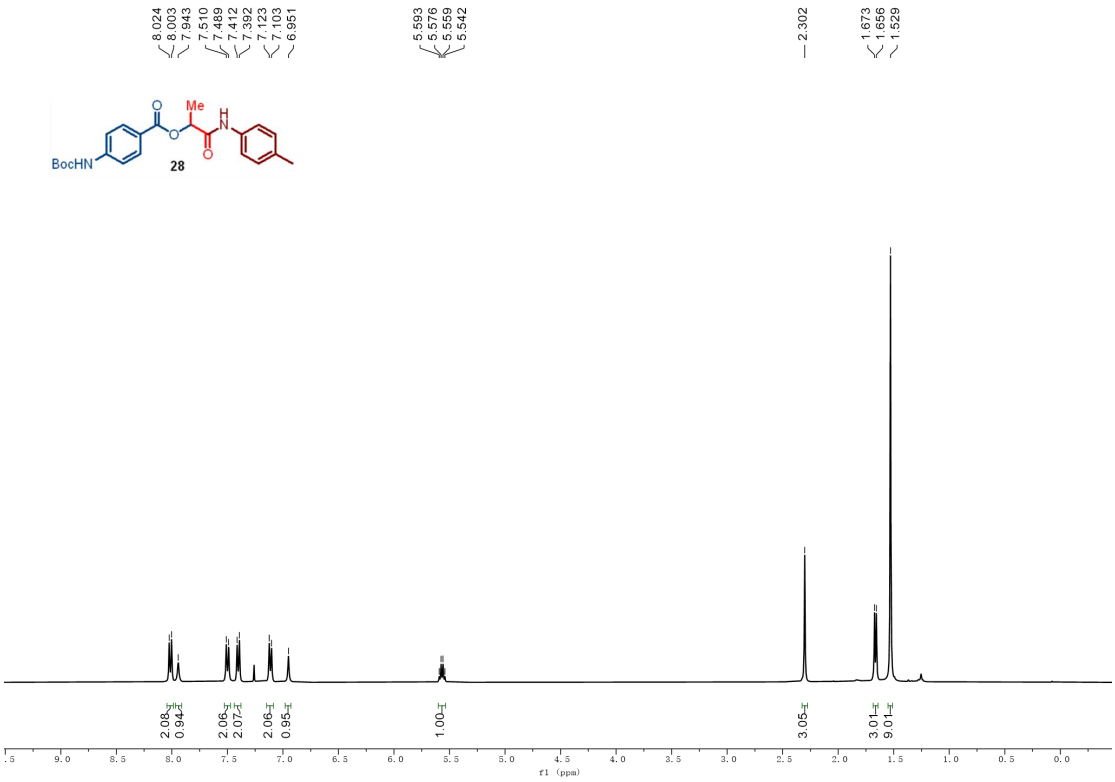
^{13}C NMR (101 MHz, $CDCl_3$) of 26



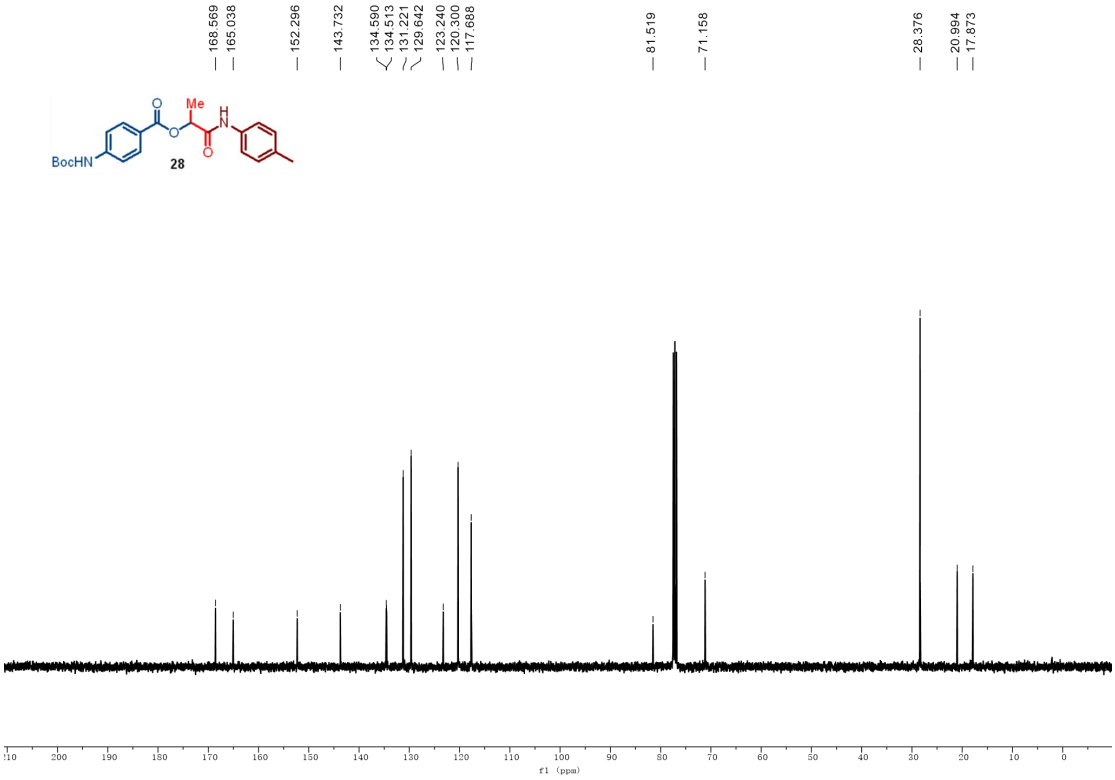
^{1}H NMR (400 MHz, $CDCl_3$) of 27



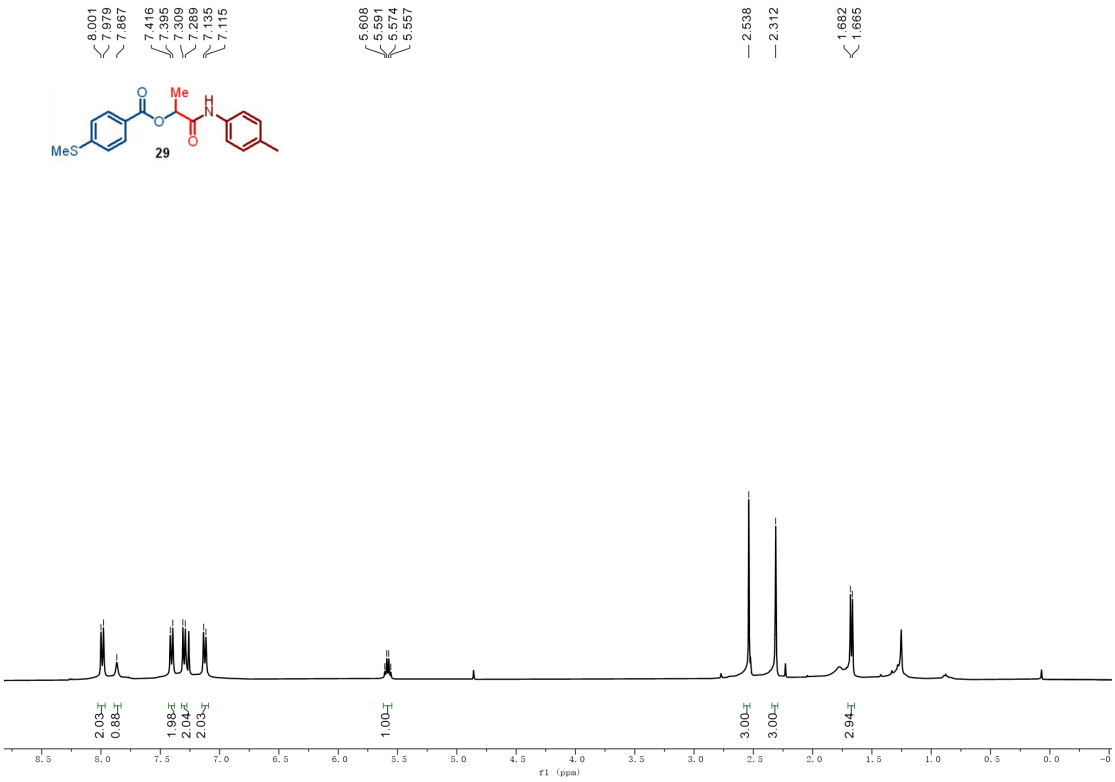
^{13}C NMR (101 MHz, $CDCl_3$) of 27



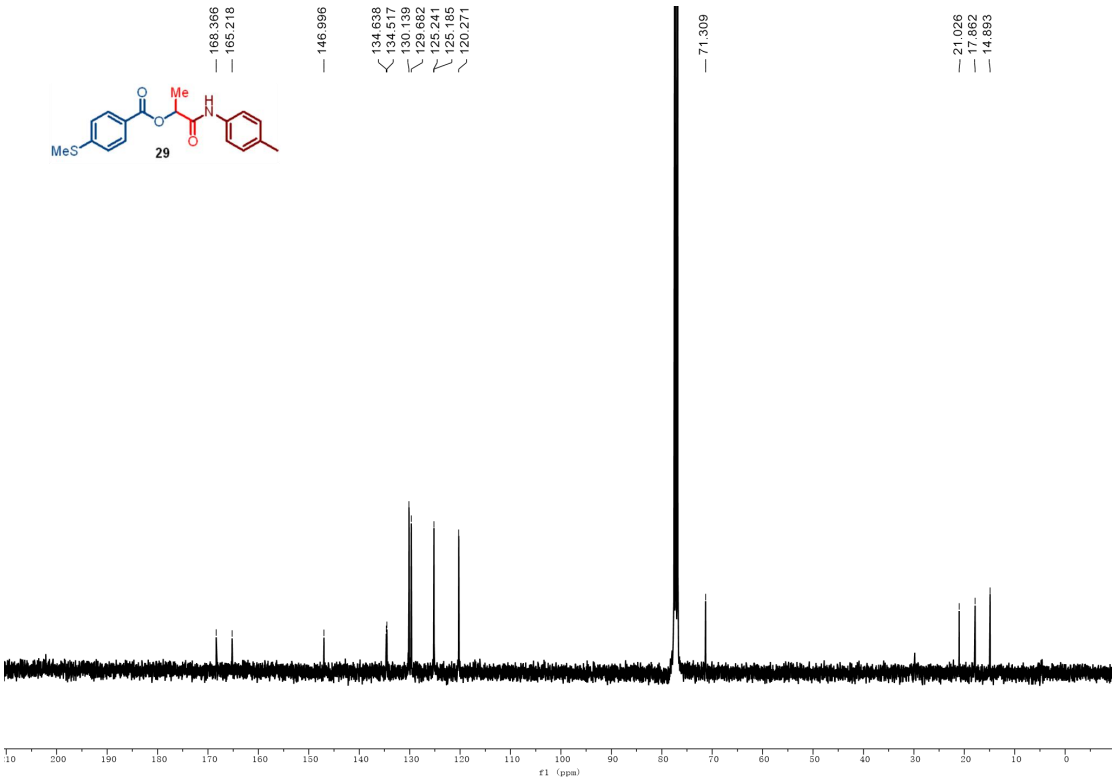
^{1}H NMR (400 MHz, $CDCl_3$) of 28



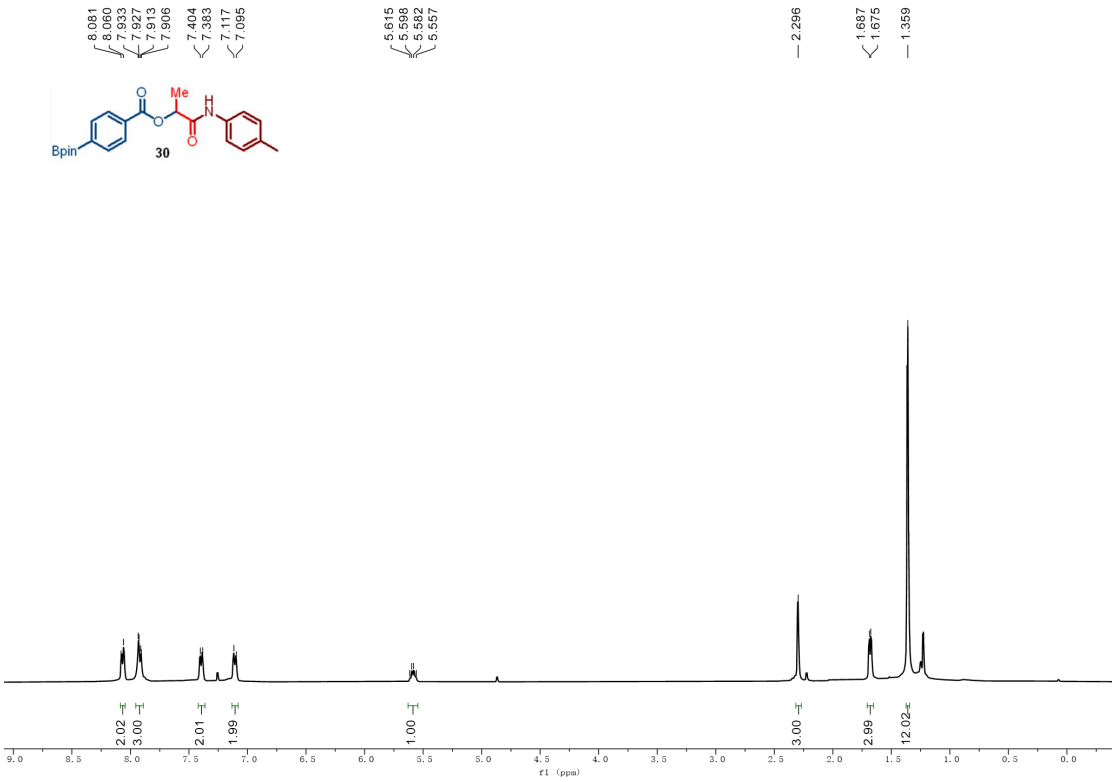
^{13}C NMR (101 MHz, $CDCl_3$) of 28



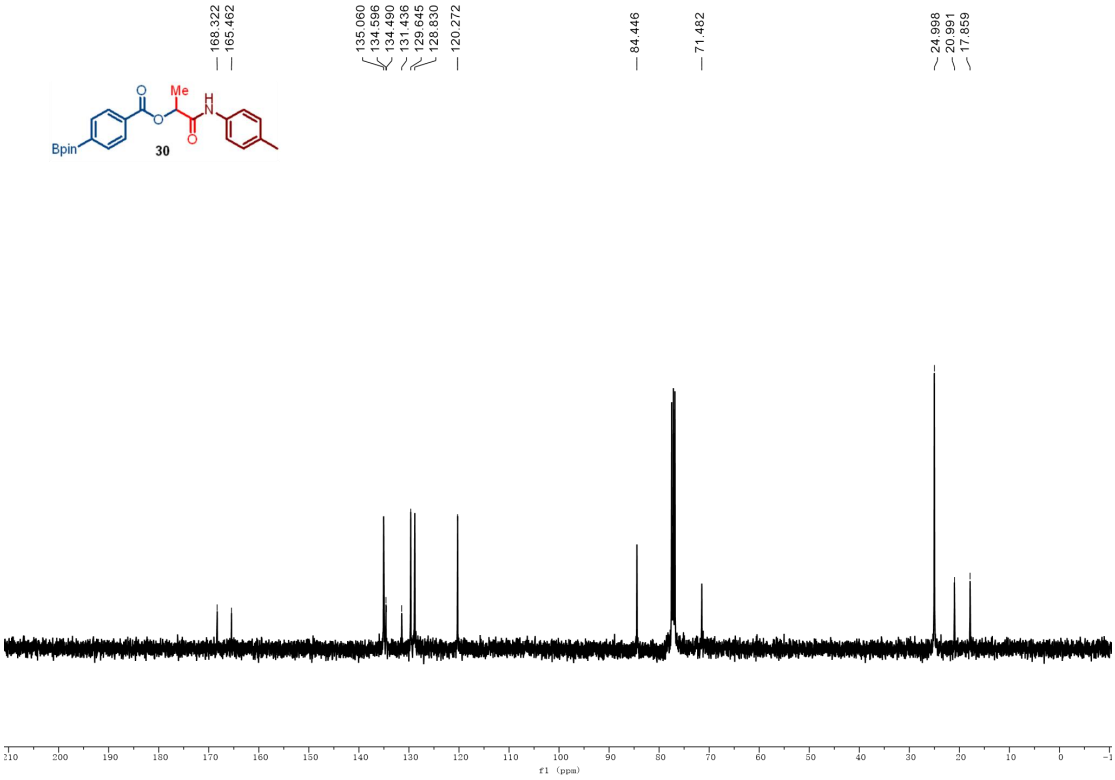
^{1}H NMR (400 MHz, $CDCl_3$) of 29



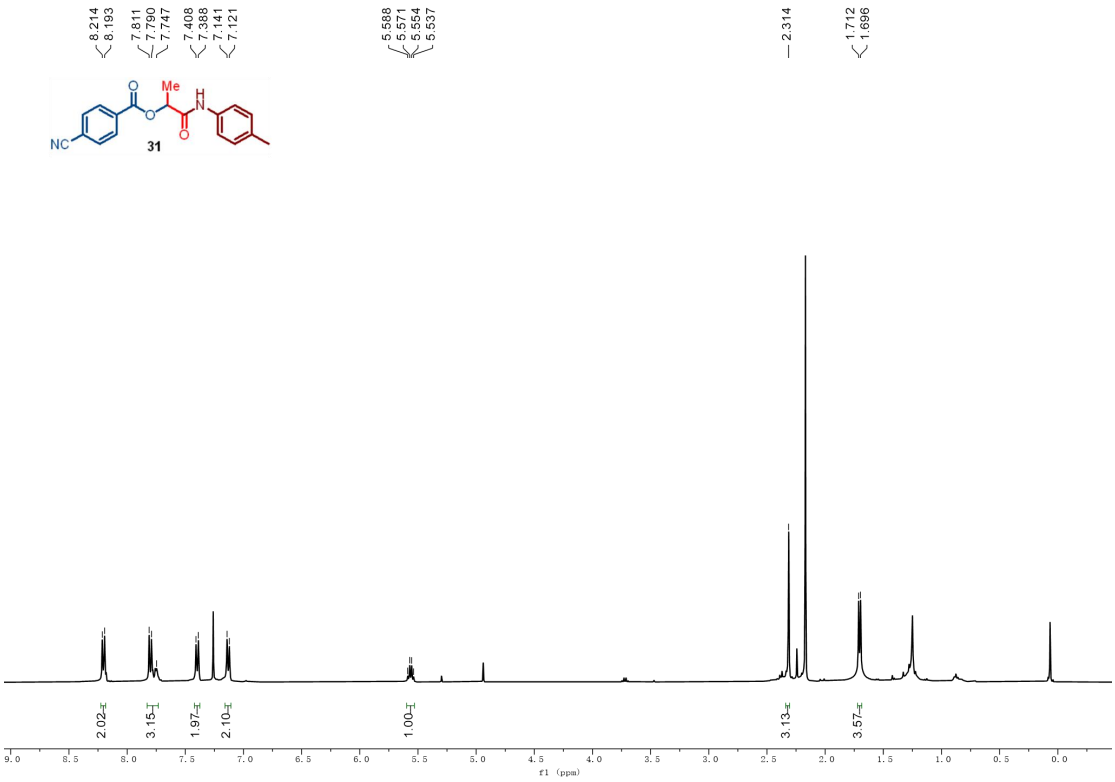
^{13}C NMR (101 MHz, $CDCl_3$) of 29



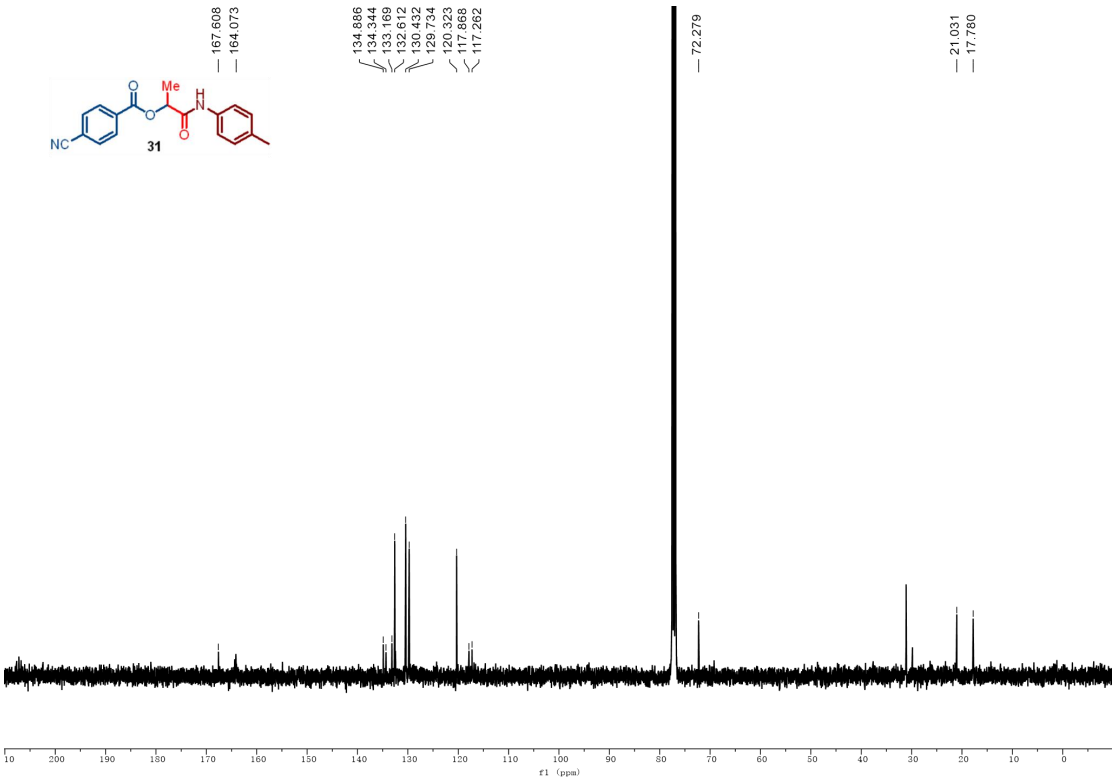
^{1}H NMR (400 MHz, $CDCl_3$) of 30



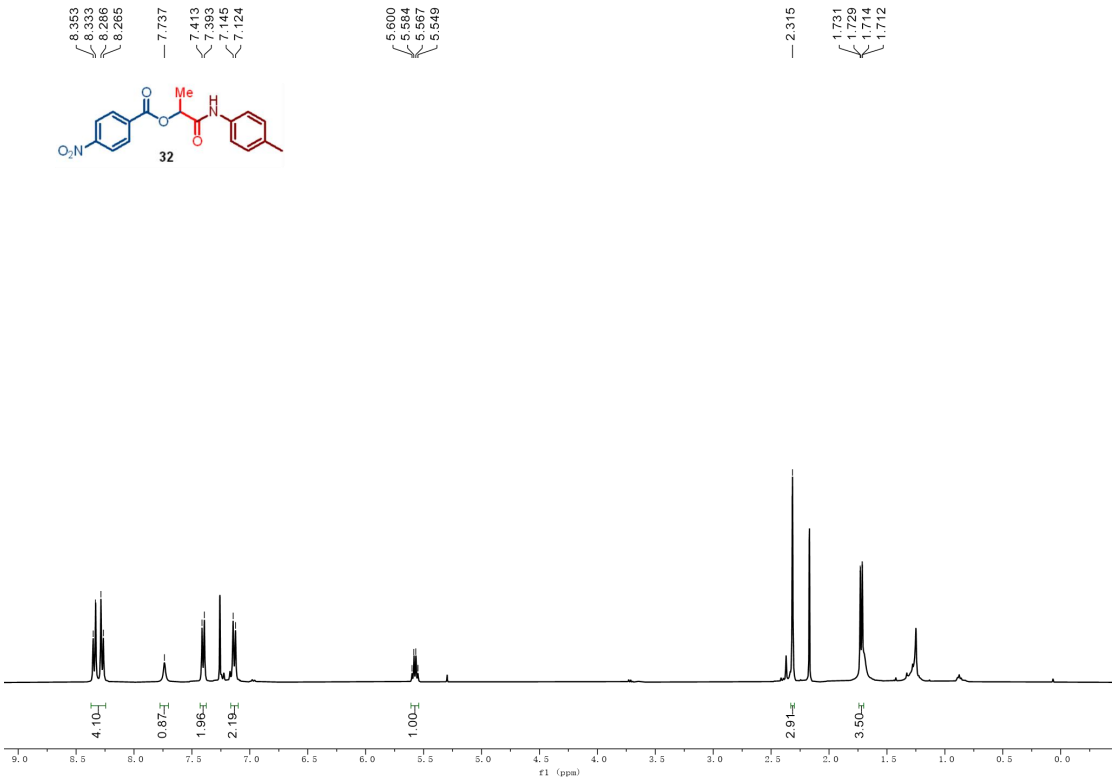
^{13}C NMR (101 MHz, $CDCl_3$) of 30



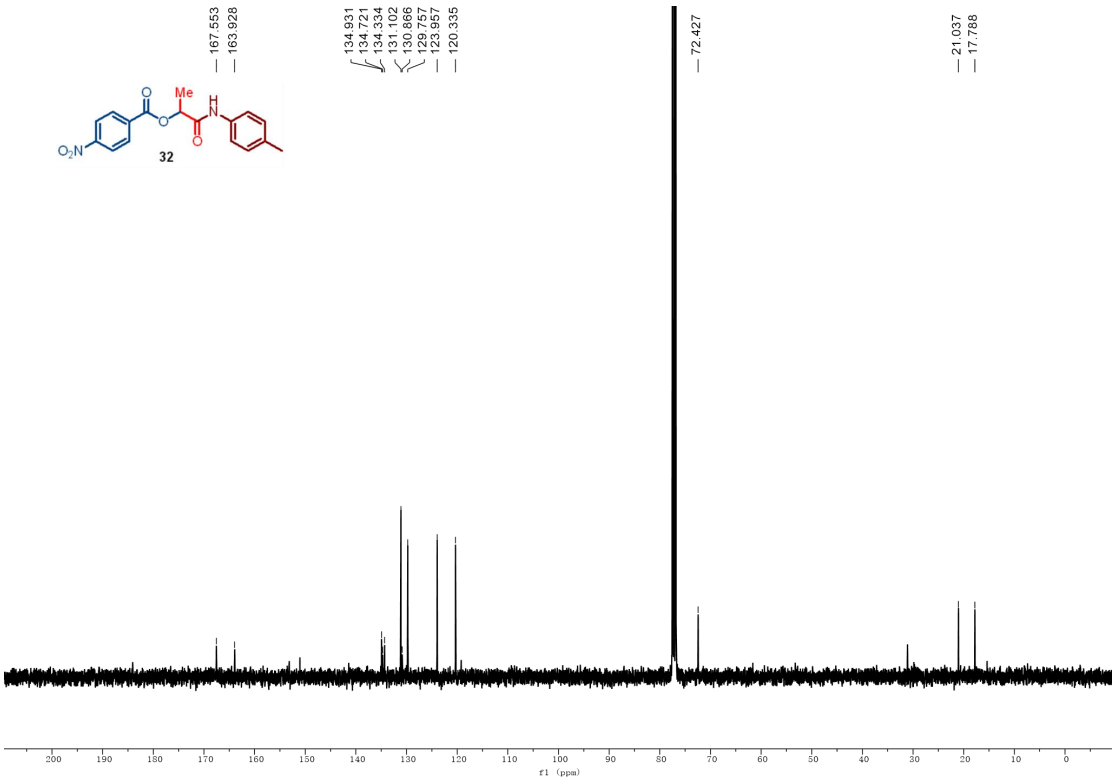
^{1}H NMR (400 MHz, $CDCl_3$) of 31



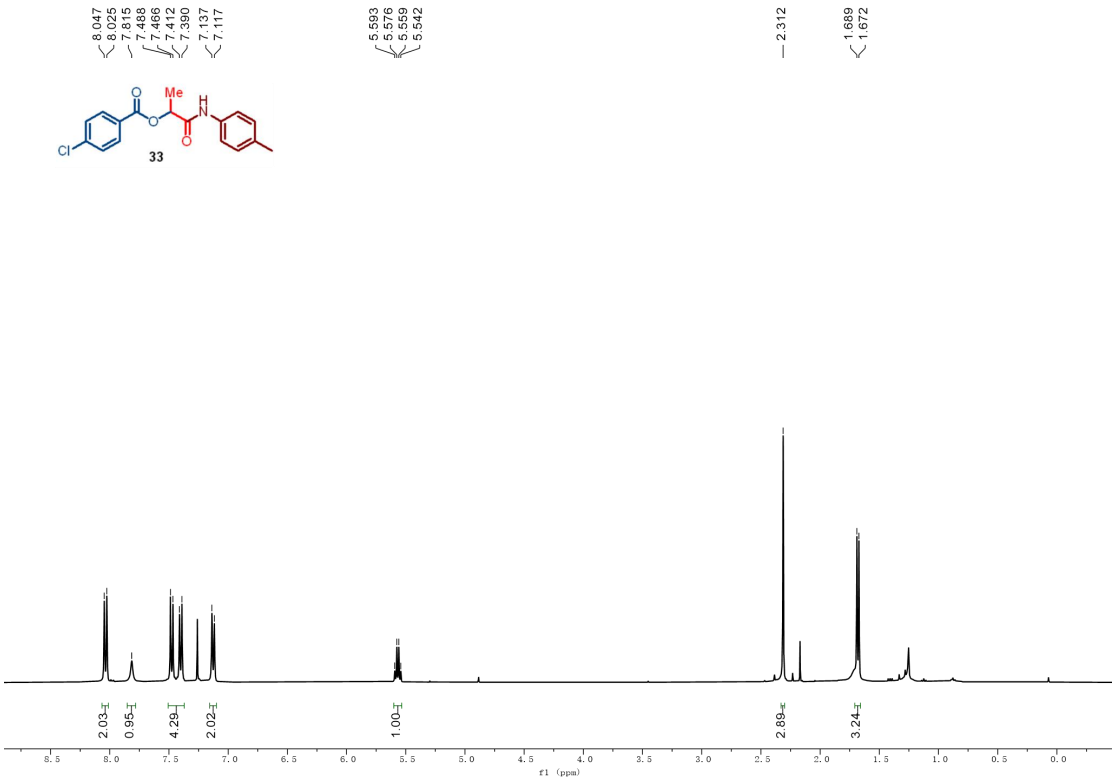
^{13}C NMR (101 MHz, $CDCl_3$) of 31



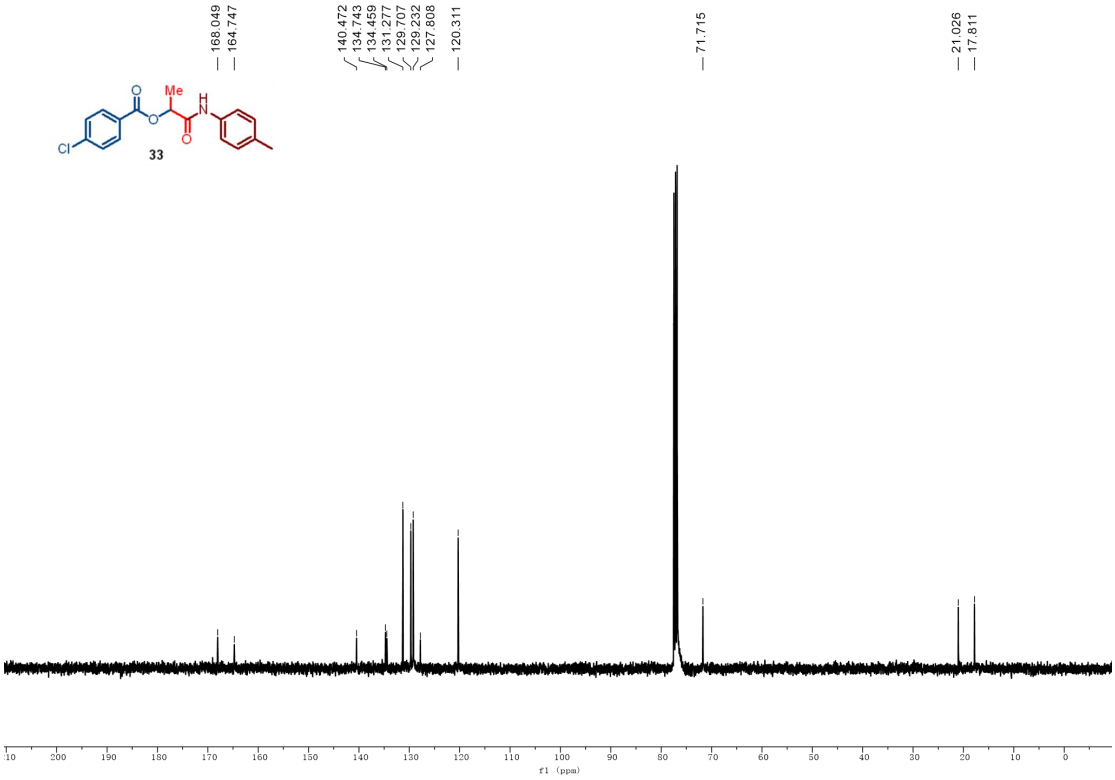
^{1}H NMR (400 MHz, $CDCl_3$) of 32



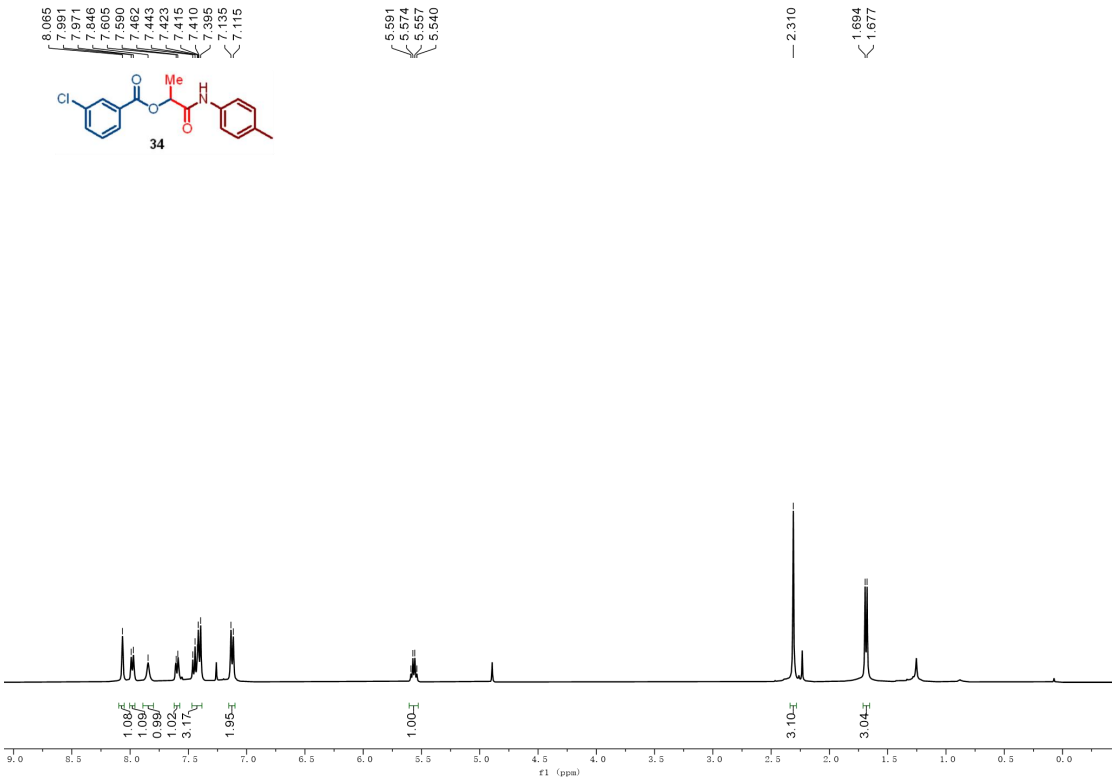
^{13}C NMR (101 MHz, $CDCl_3$) of 32



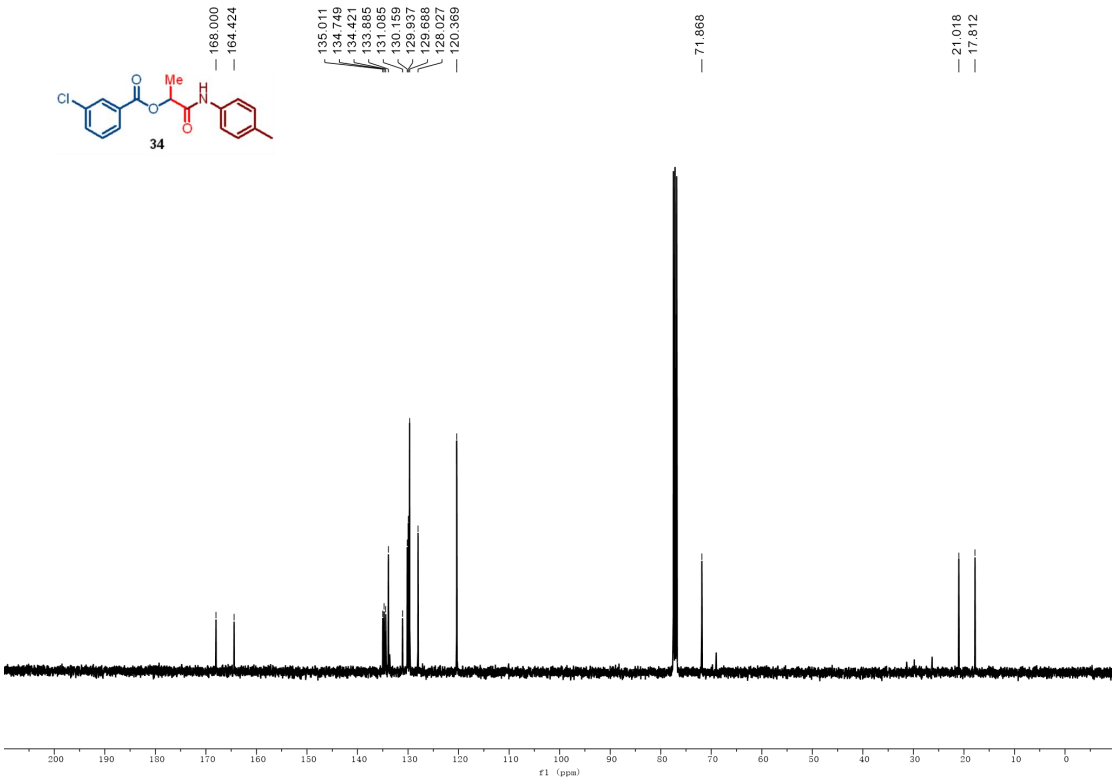
^{1}H NMR (400 MHz, $CDCl_3$) of 33



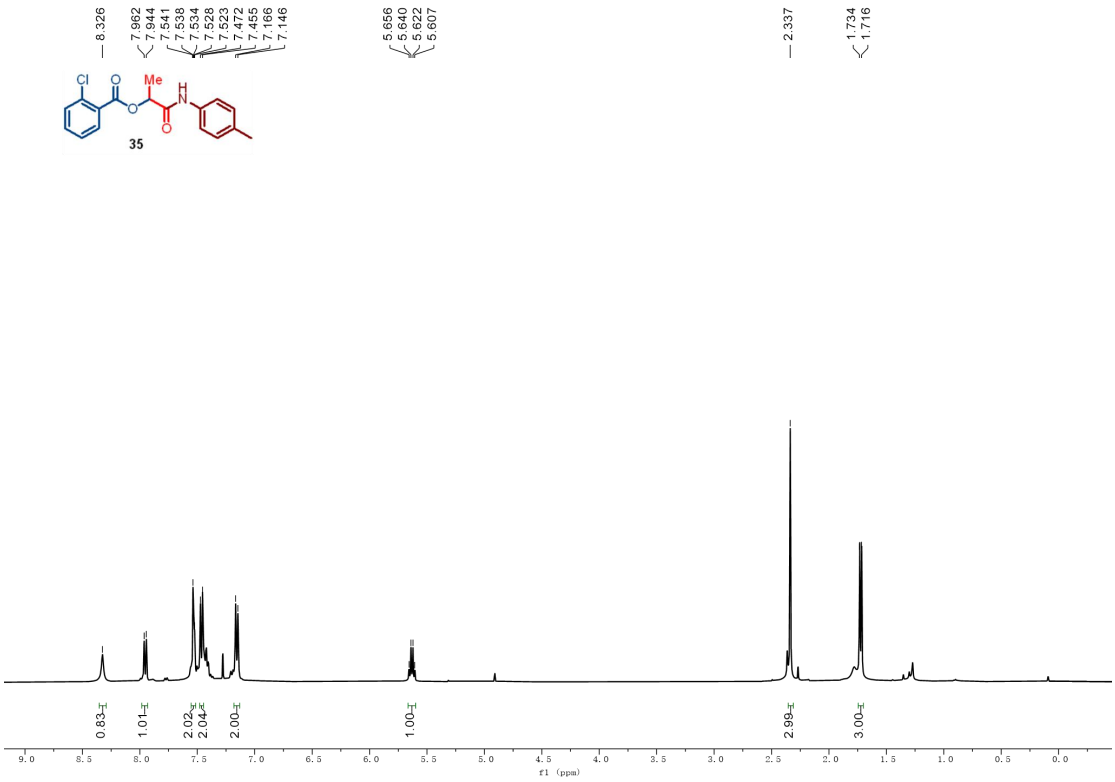
^{13}C NMR (101 MHz, $CDCl_3$) of 33



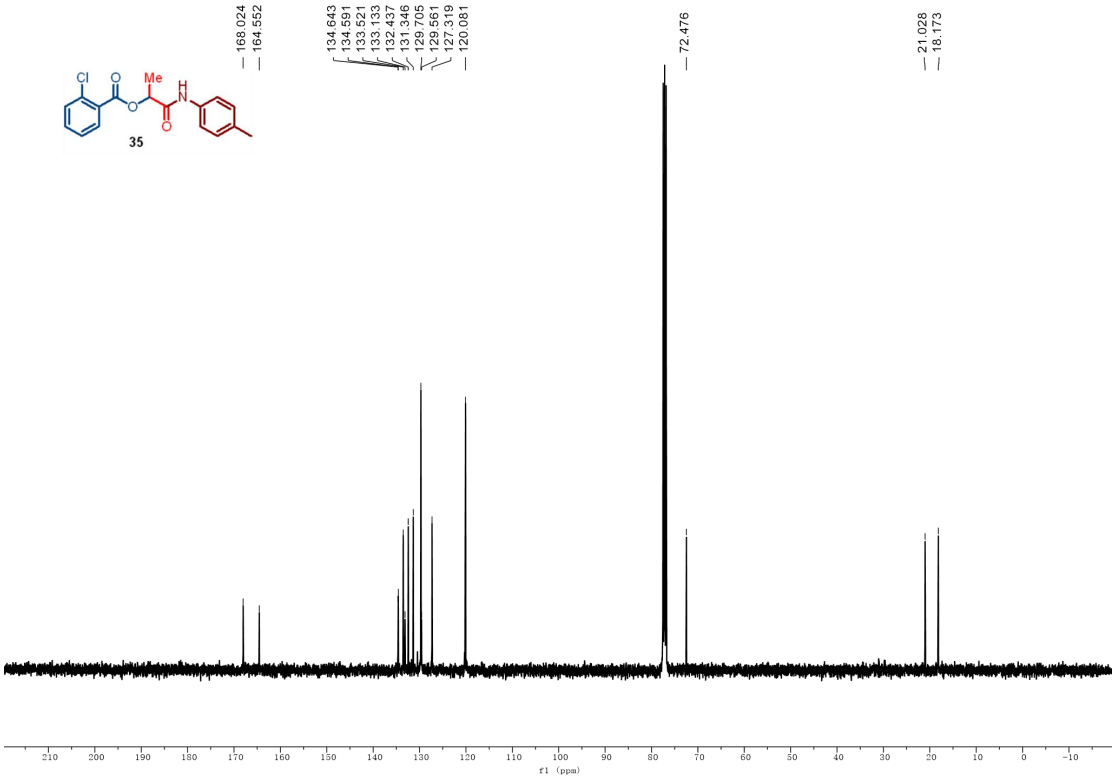
^{1}H NMR (400 MHz, $CDCl_3$) of 34



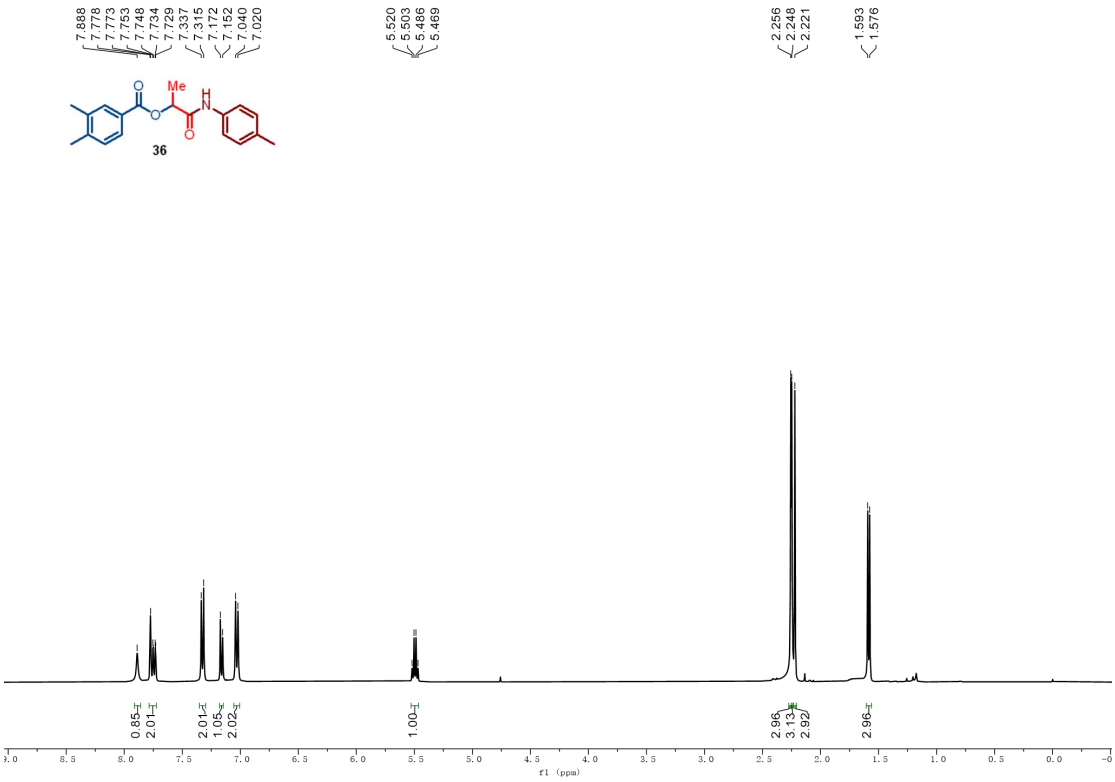
^{13}C NMR (101 MHz, $CDCl_3$) of 34



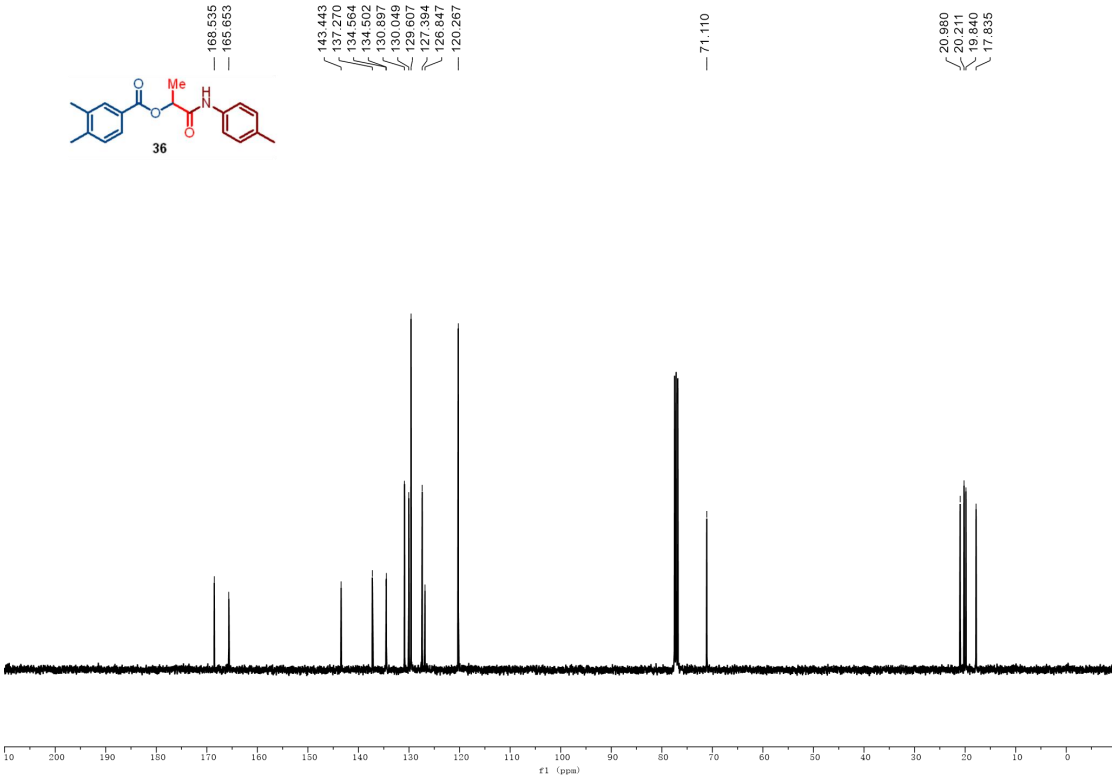
^{1}H NMR (400 MHz, $CDCl_3$) of 35



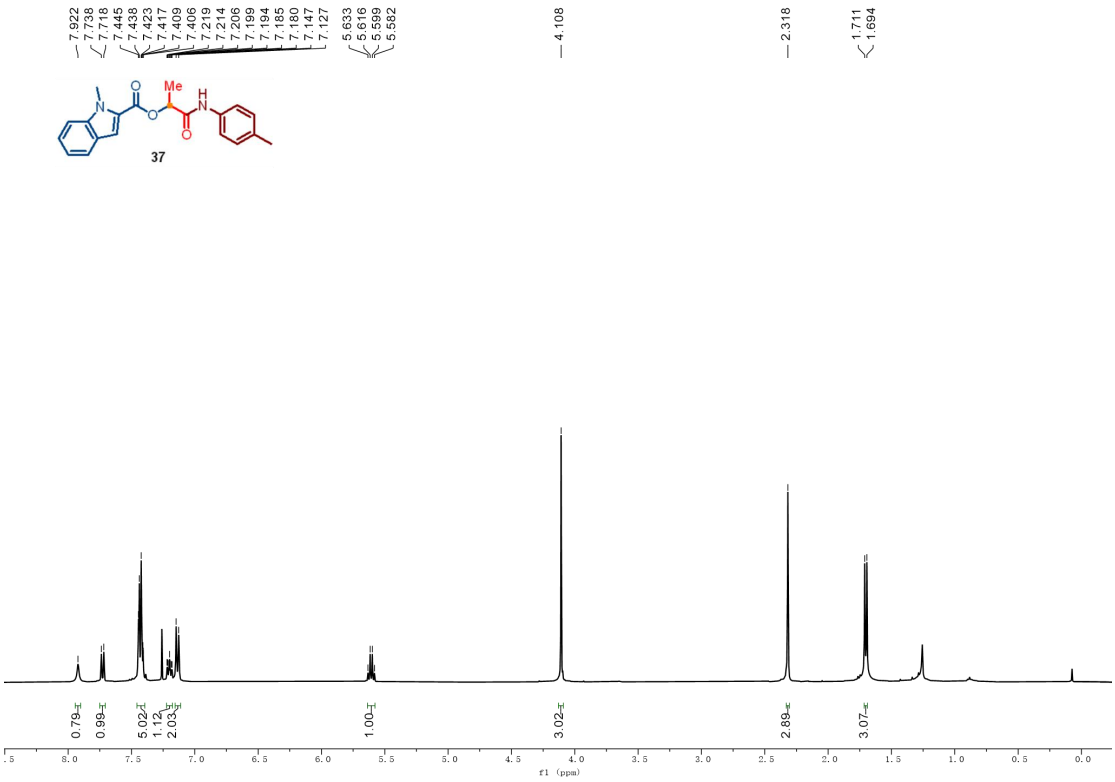
^{13}C NMR (101 MHz, $CDCl_3$) of 35



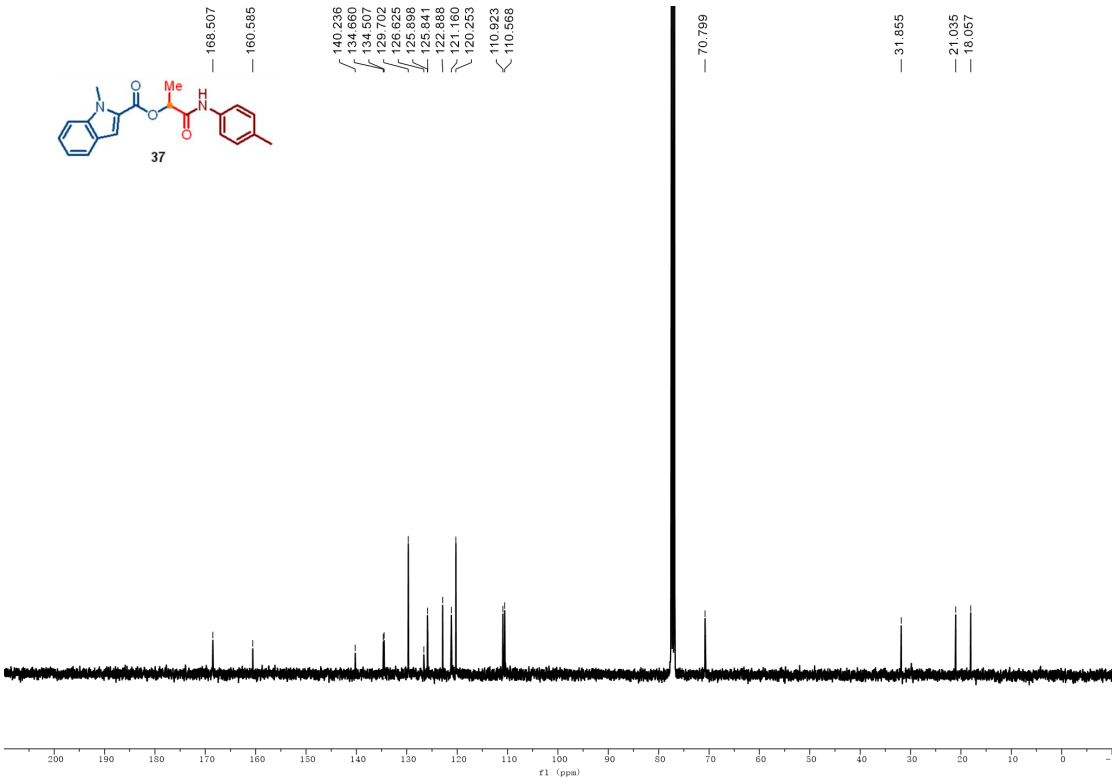
^{1}H NMR (400 MHz, $CDCl_3$) of 36



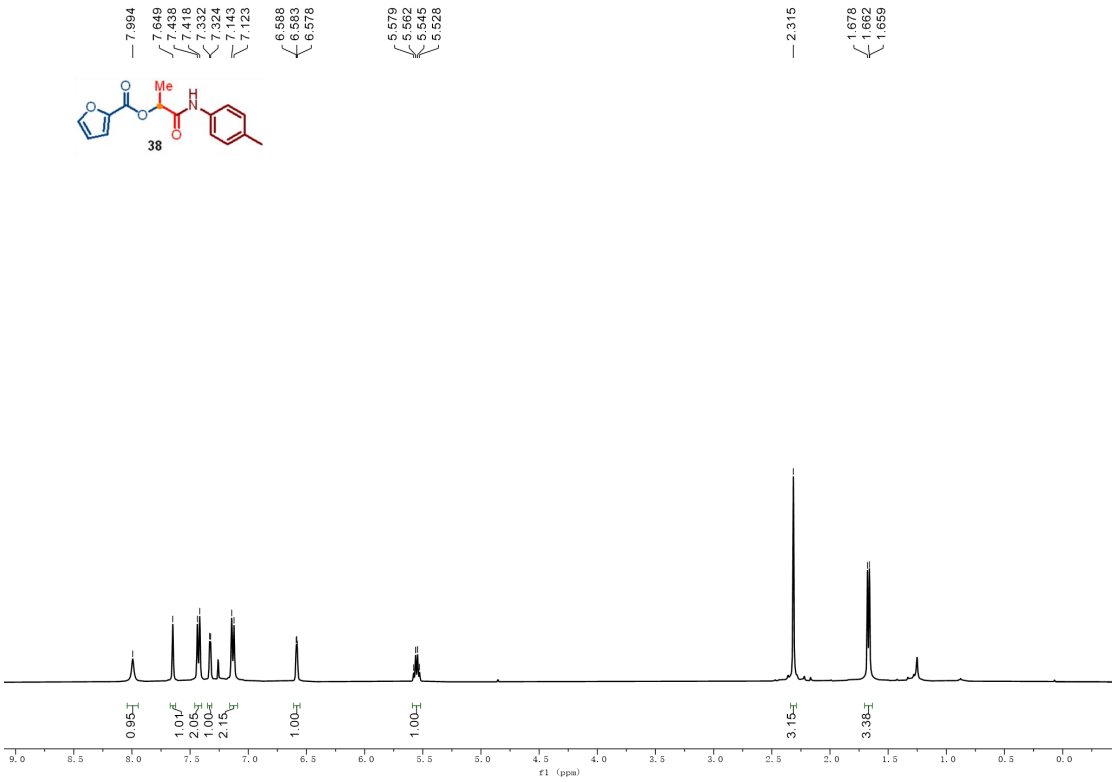
^{13}C NMR (101 MHz, $CDCl_3$) of 36



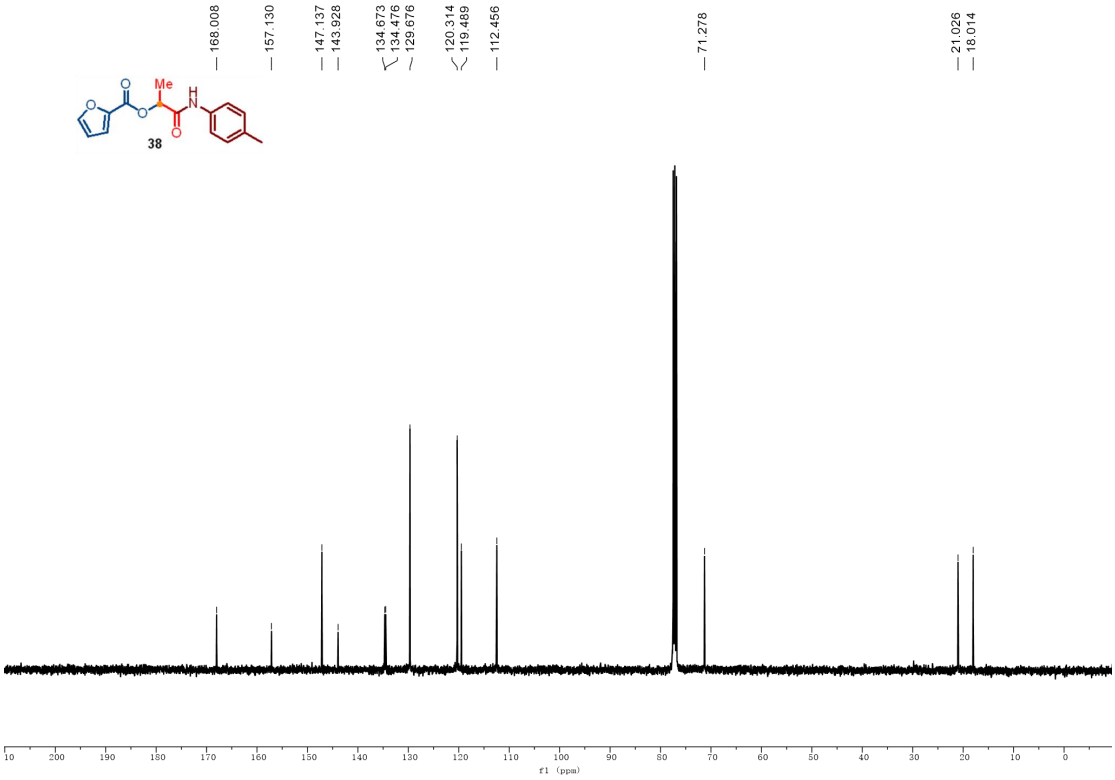
^{1}H NMR (400 MHz, $CDCl_3$) of 37



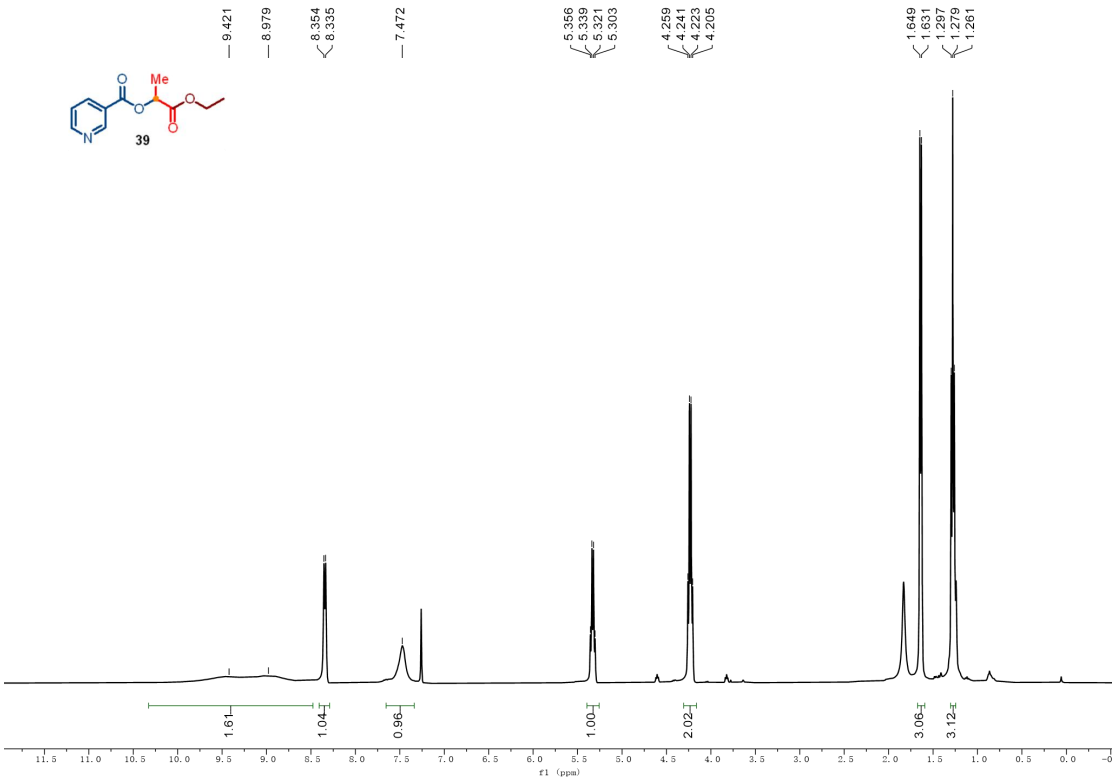
^{13}C NMR (101 MHz, $CDCl_3$) of 37



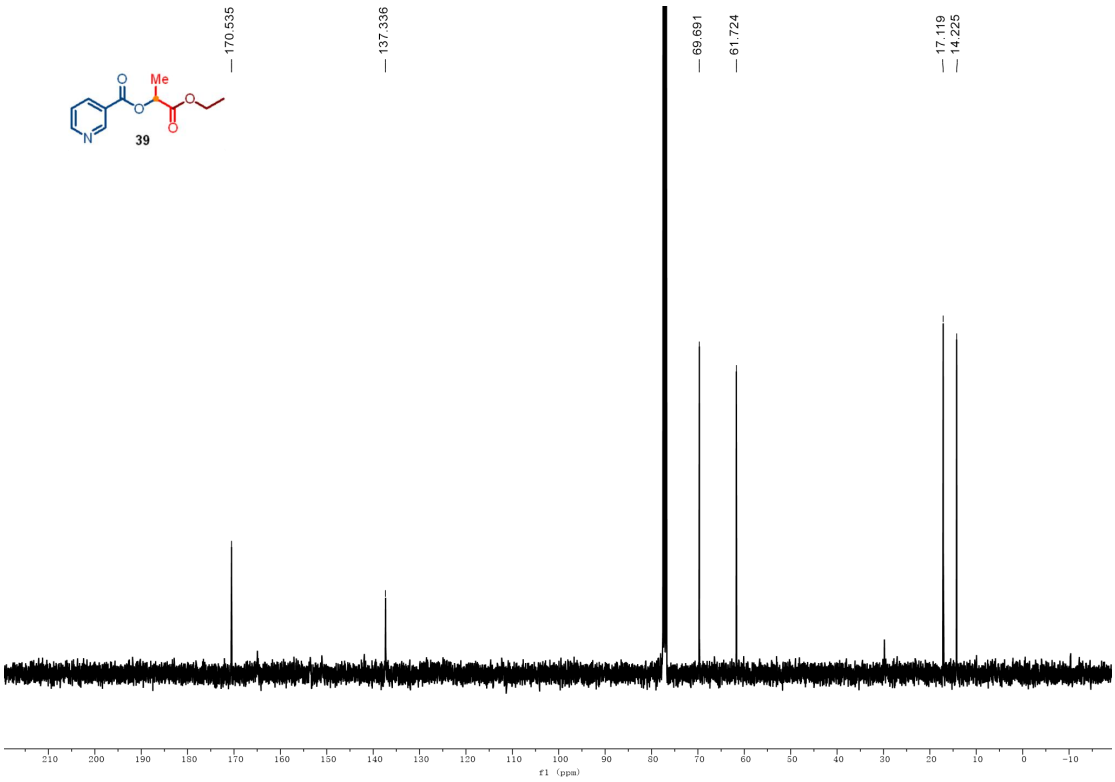
^{1}H NMR (400 MHz, $CDCl_3$) of 38



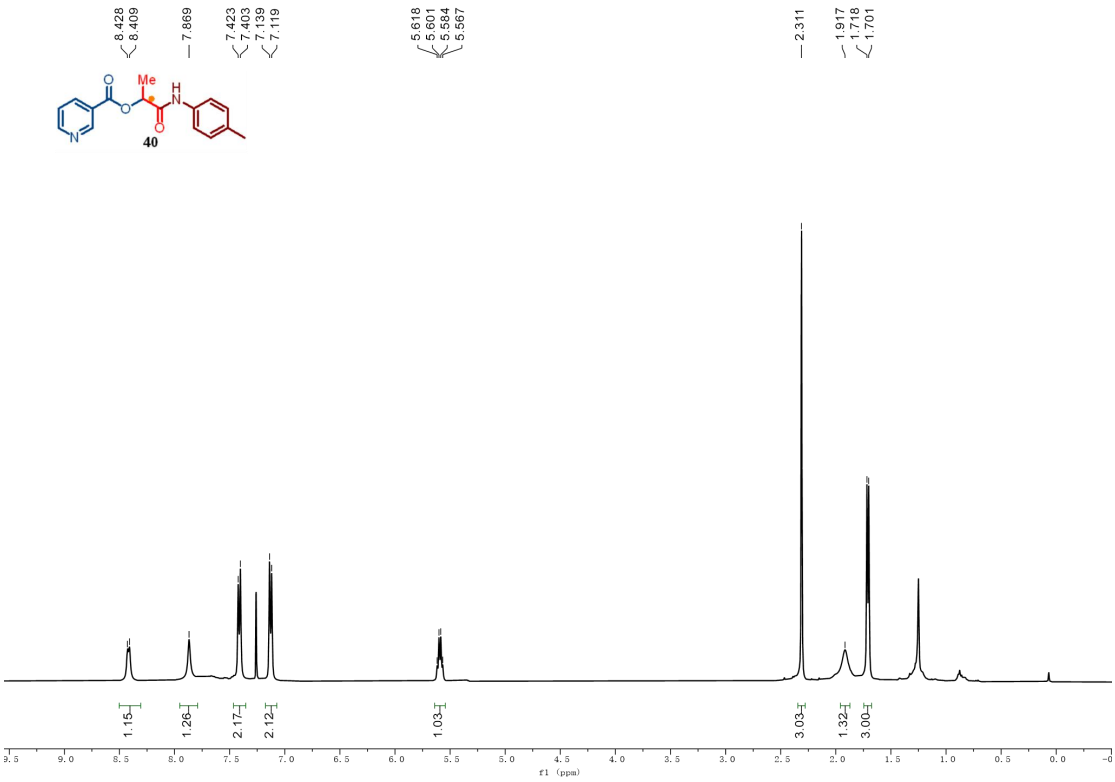
^{13}C NMR (101 MHz, $CDCl_3$) of 38



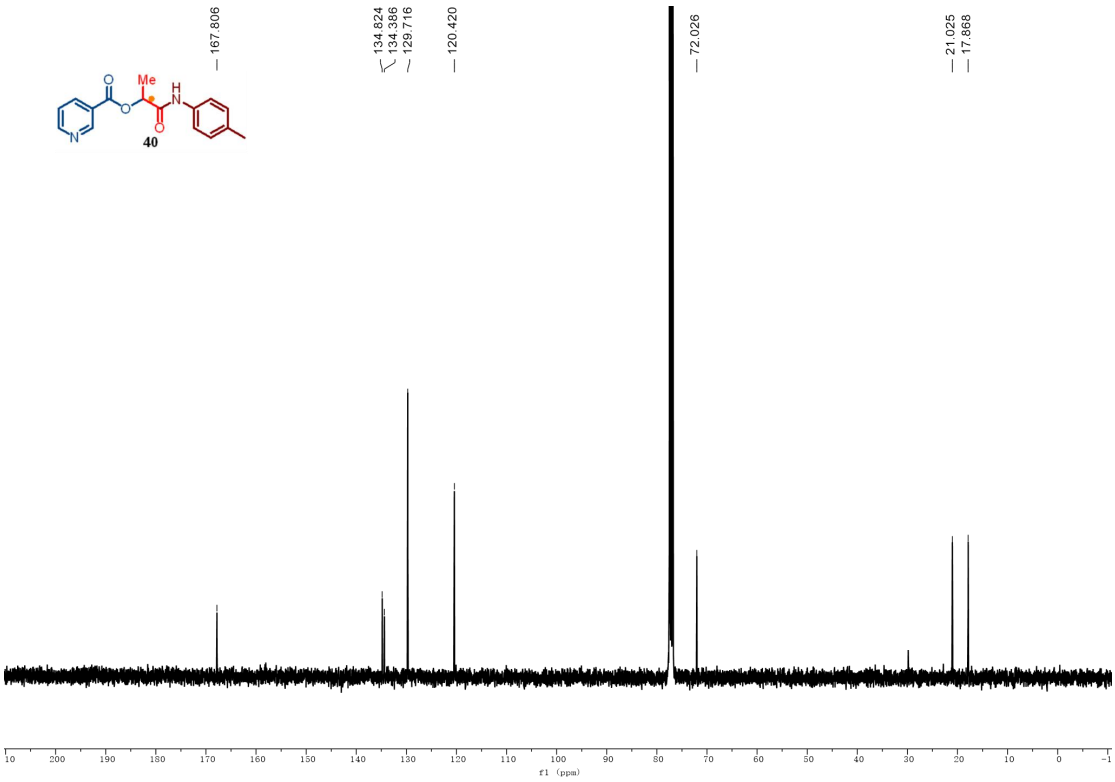
^{1}H NMR (400 MHz, $CDCl_3$) of 39



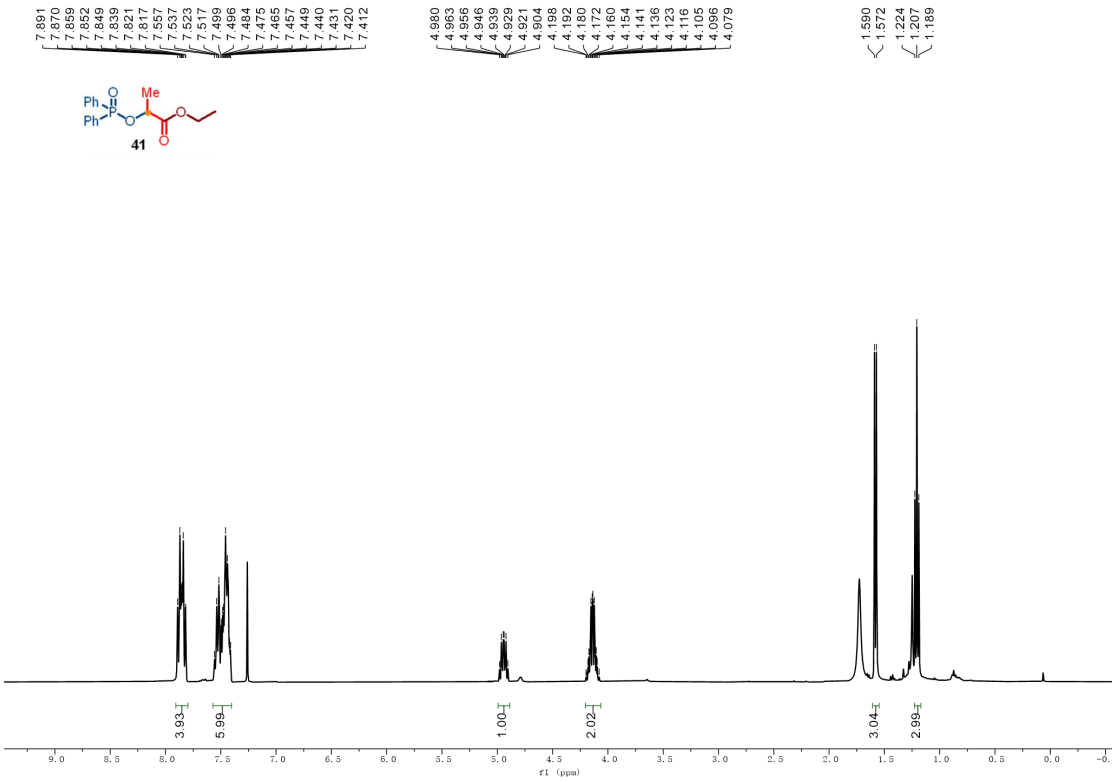
^{13}C NMR (101 MHz, $CDCl_3$) of 39



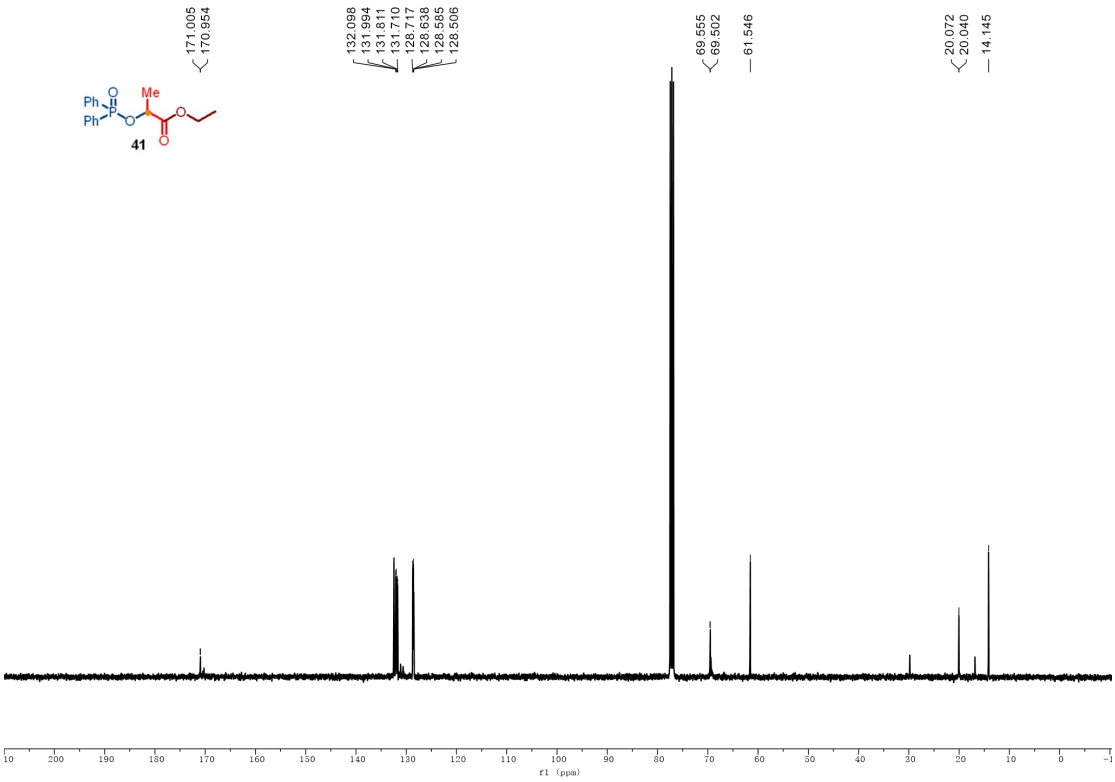
^{1}H NMR (400 MHz, $CDCl_3$) of 40



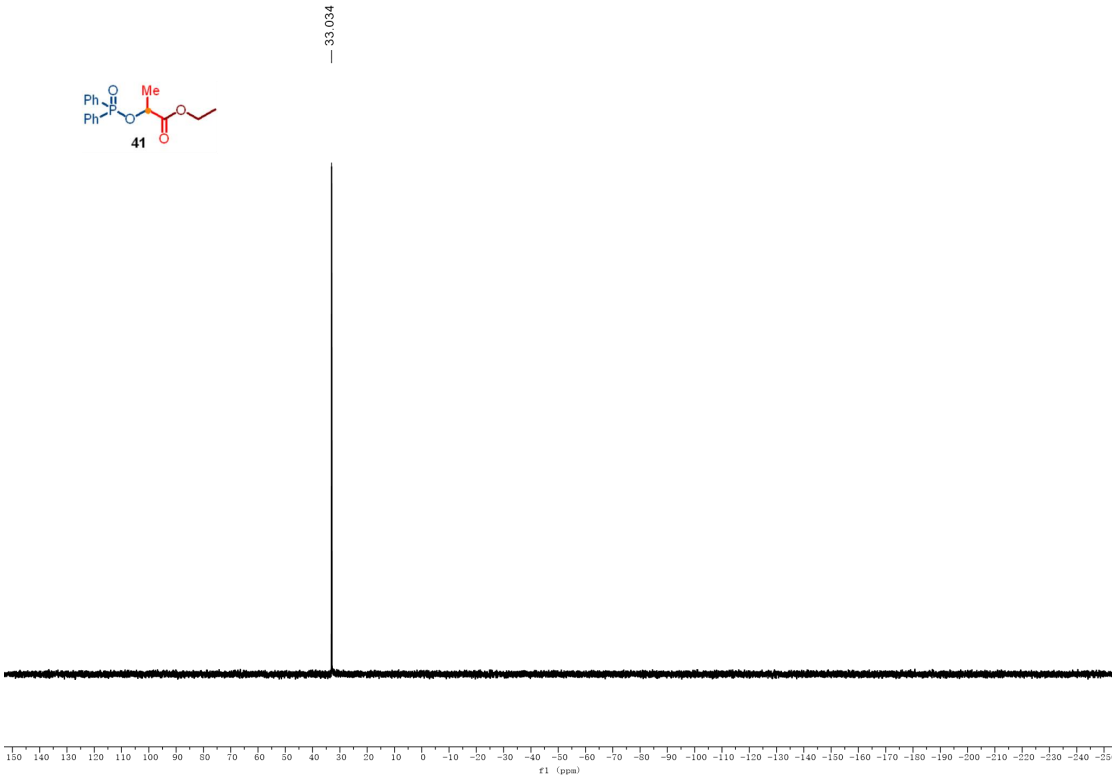
^{13}C NMR (101 MHz, $CDCl_3$) of 40



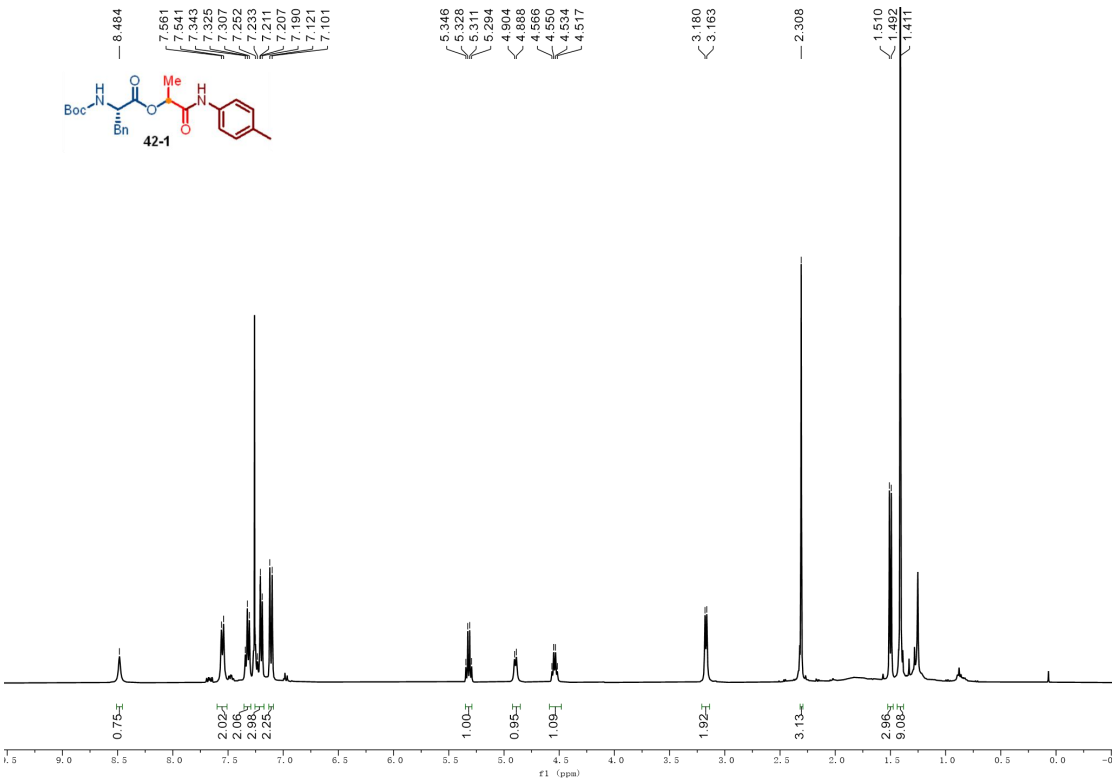
^{1}H NMR (400 MHz, $CDCl_3$) of 41



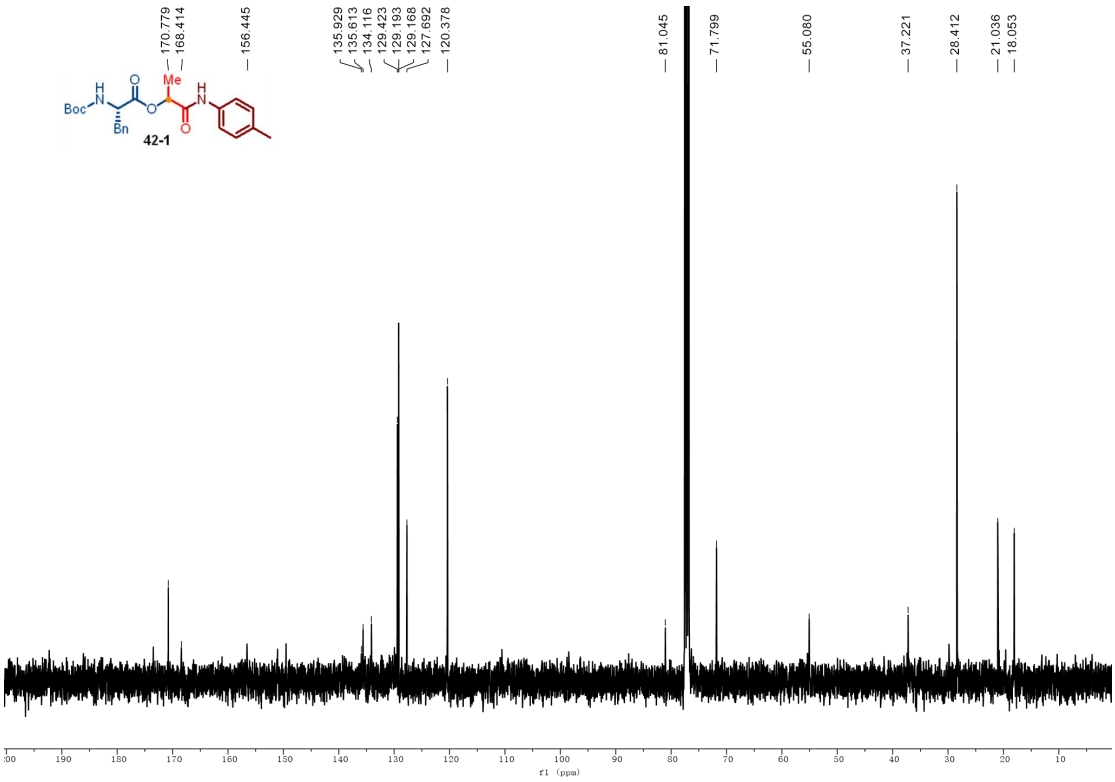
^{13}C NMR (101 MHz, $CDCl_3$) of 41



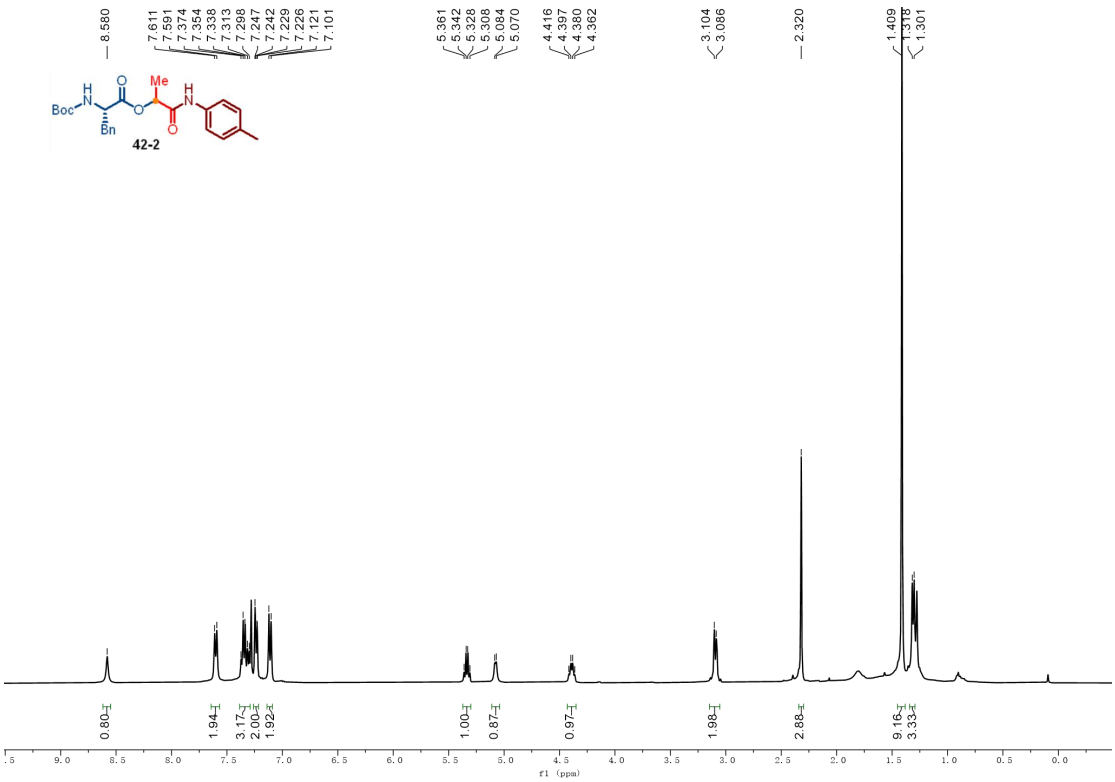
^{31}P NMR (162 MHz, $CDCl_3$) of 41



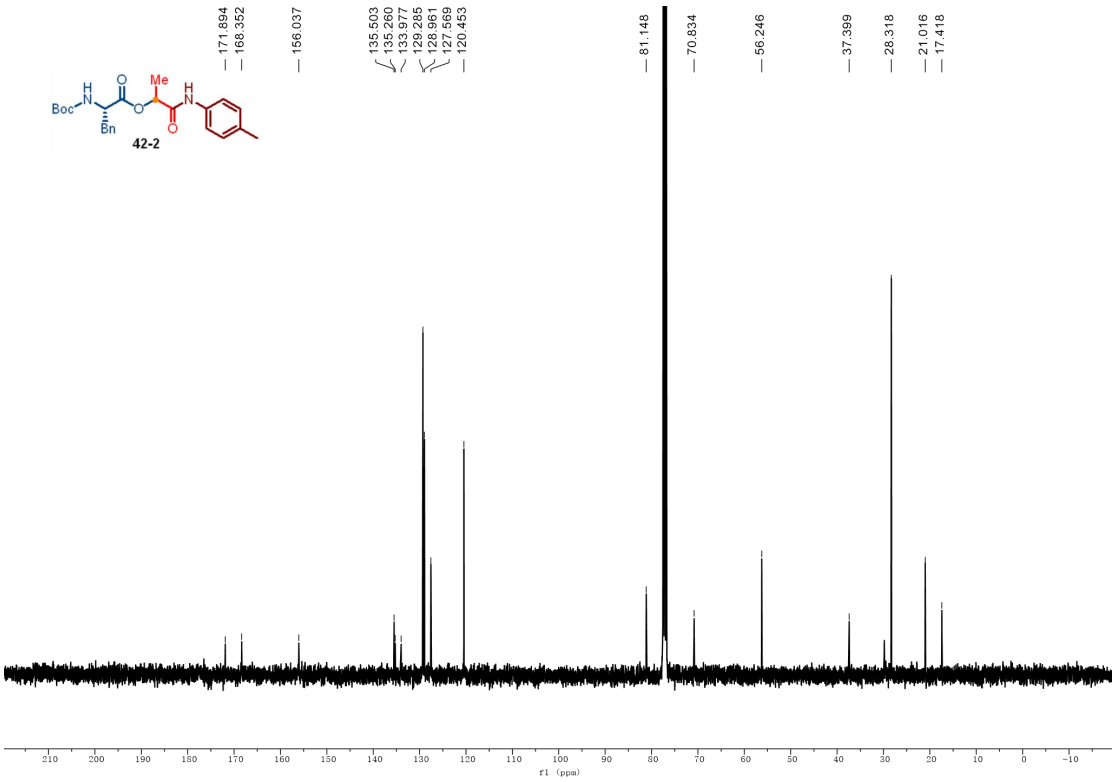
^{1}H NMR (400 MHz, $CDCl_3$) of 42-1



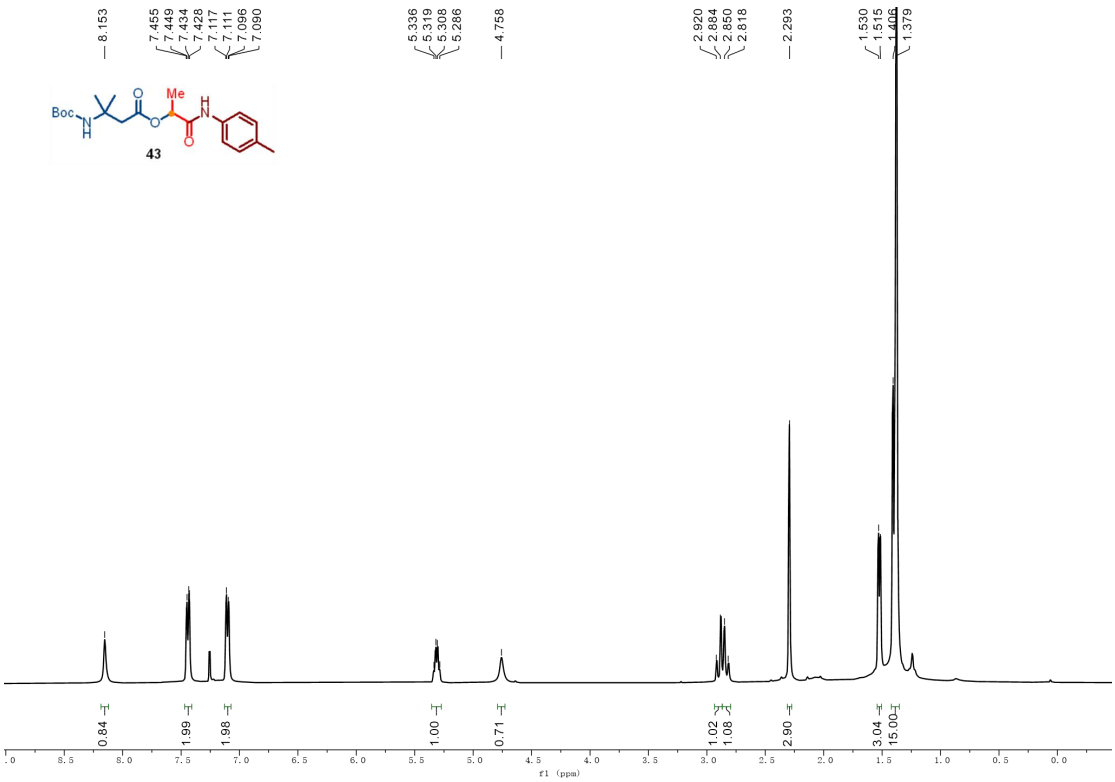
^{13}C NMR (101 MHz, $CDCl_3$) of 42-1



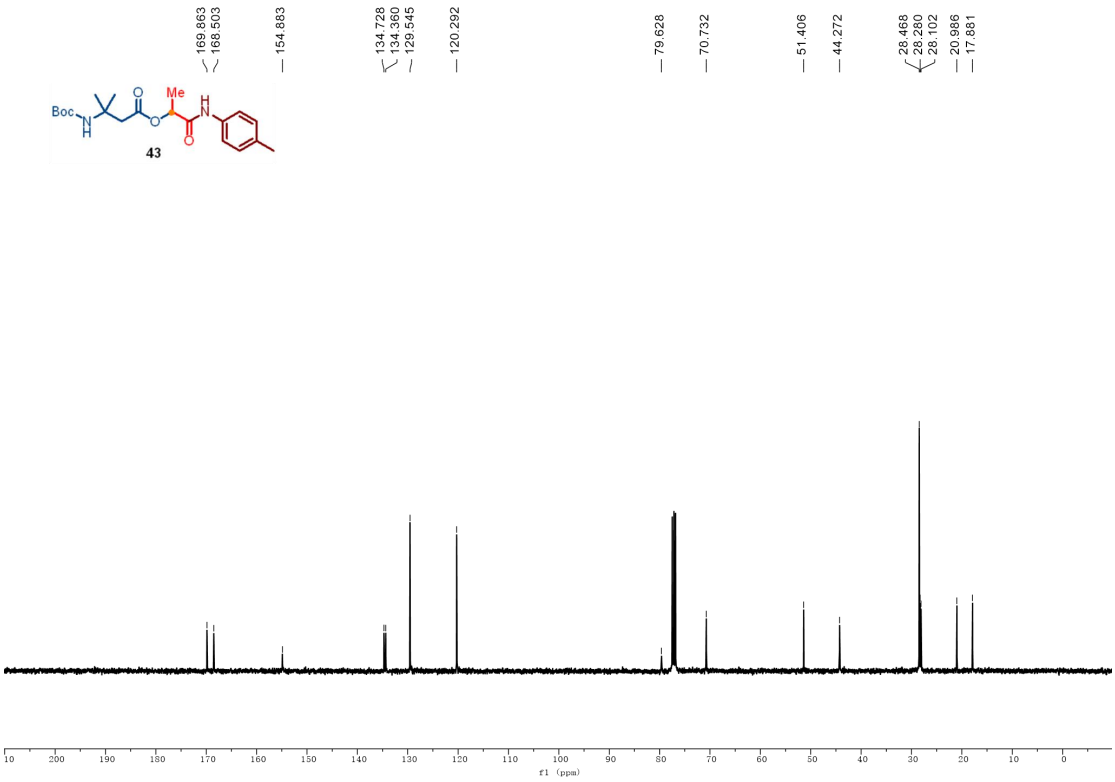
^{1}H NMR (400 MHz, $CDCl_3$) of 42-2



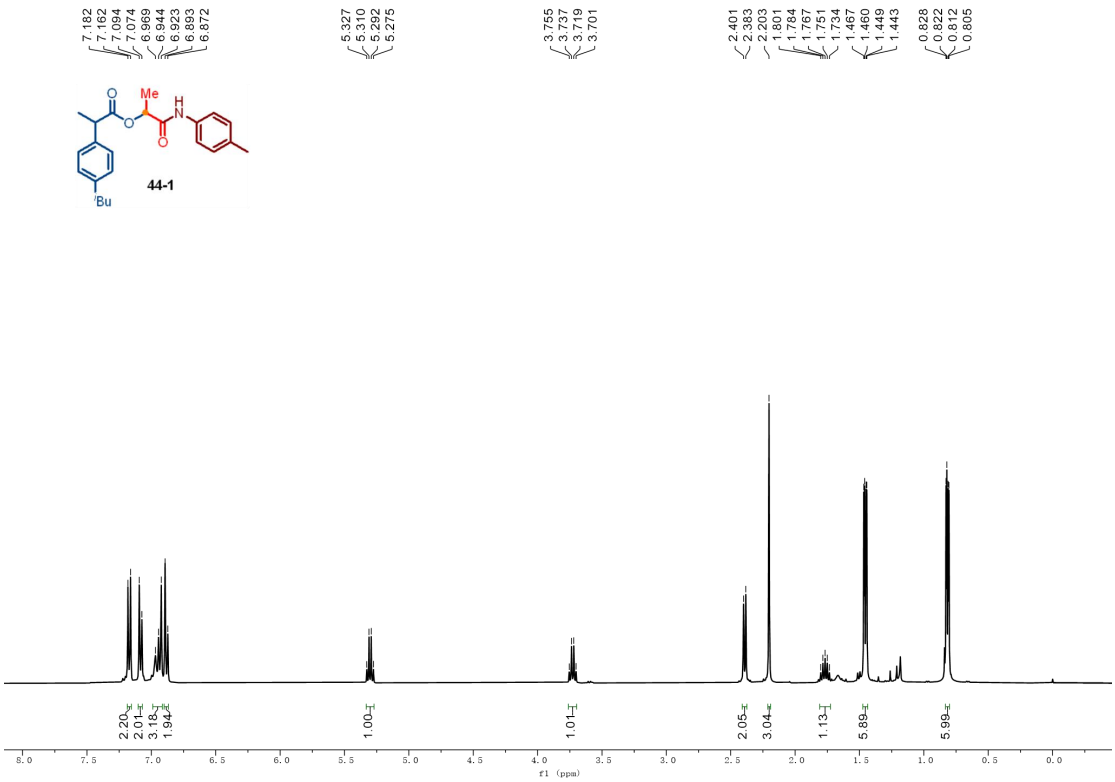
^{13}C NMR (101 MHz, $CDCl_3$) of 42-2



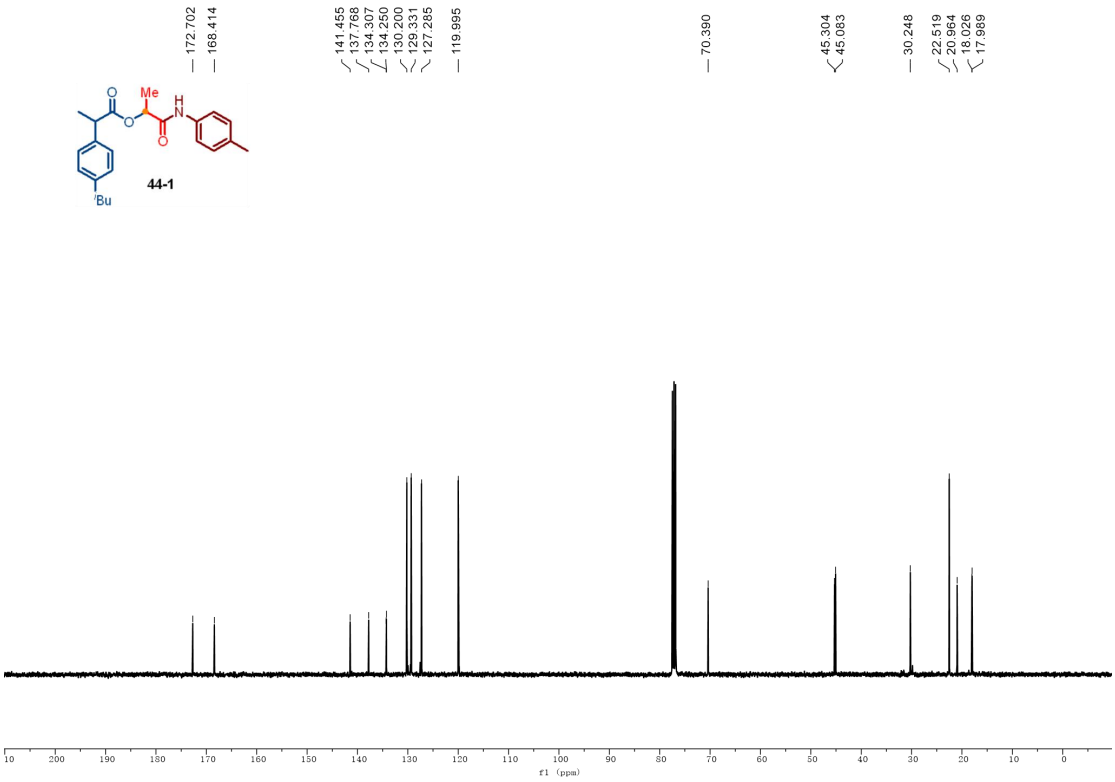
^{1}H NMR (400 MHz, $CDCl_3$) of 43



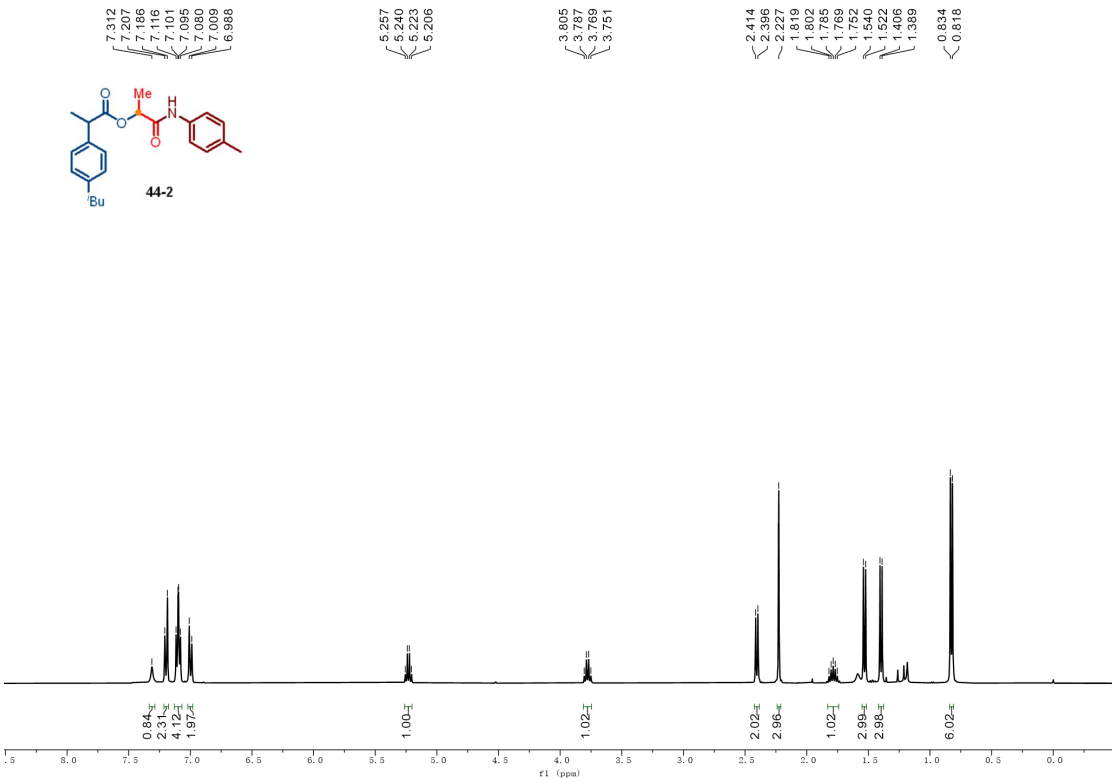
^{13}C NMR (101 MHz, $CDCl_3$) of 43



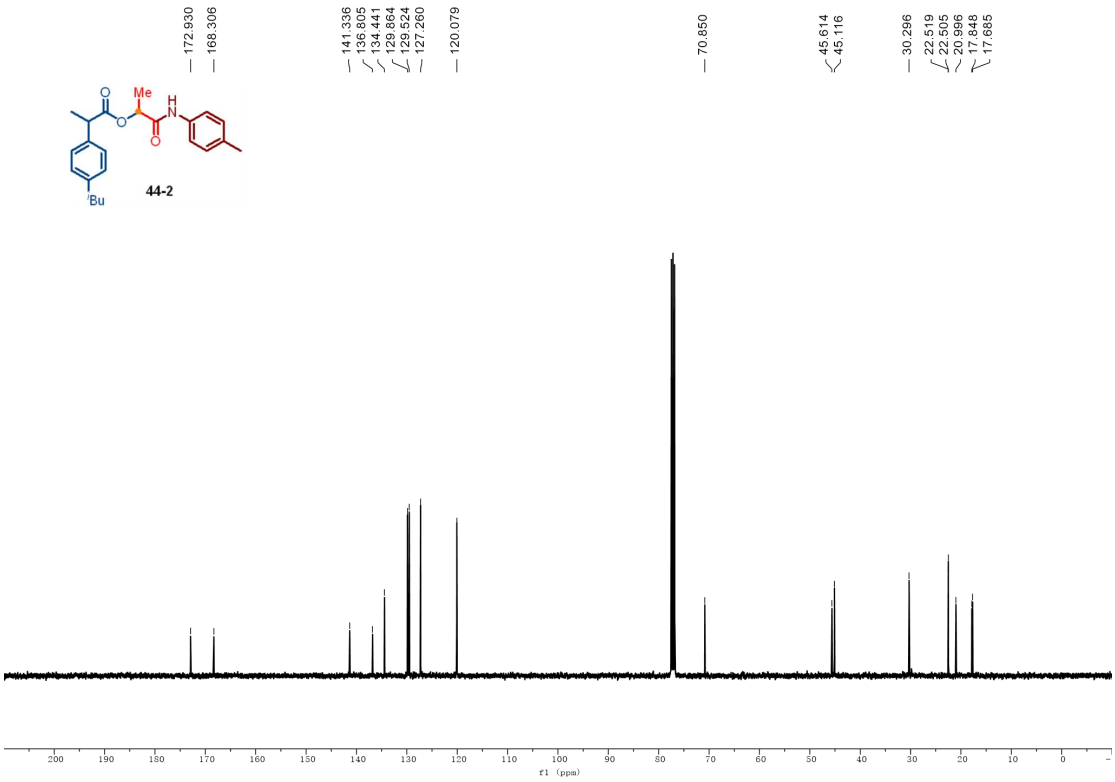
^{1}H NMR (400 MHz, $CDCl_3$) of 44-1



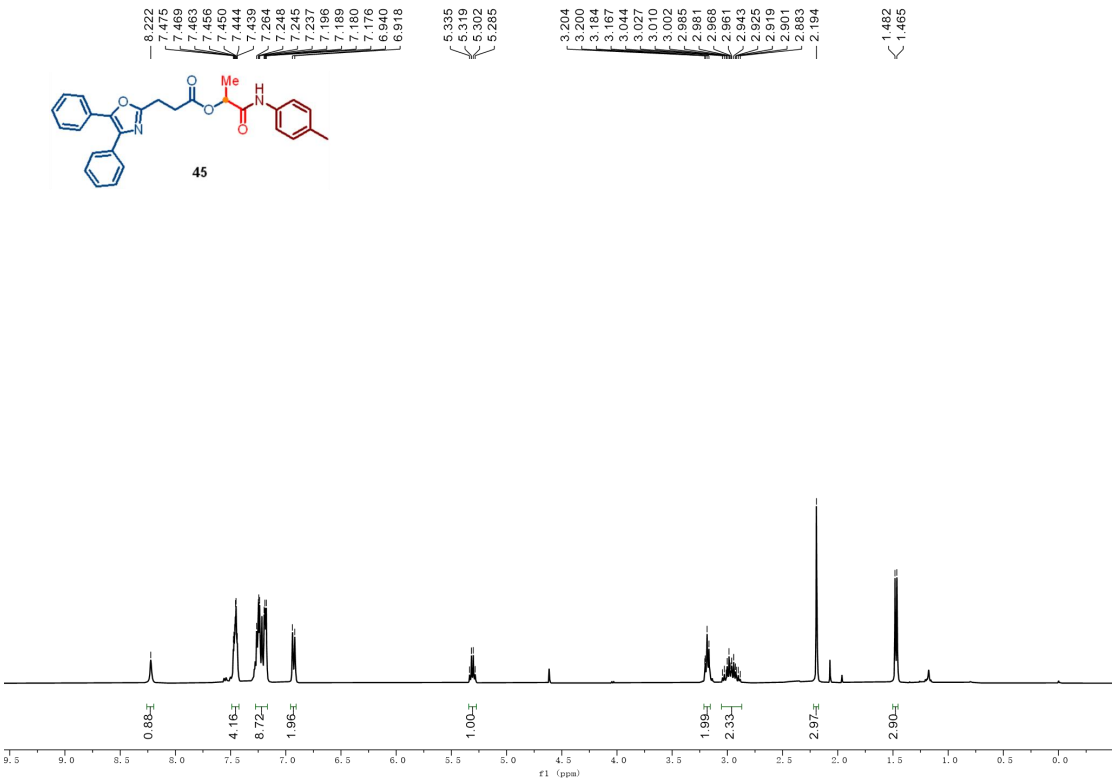
^{13}C NMR (101 MHz, $CDCl_3$) of 44-1



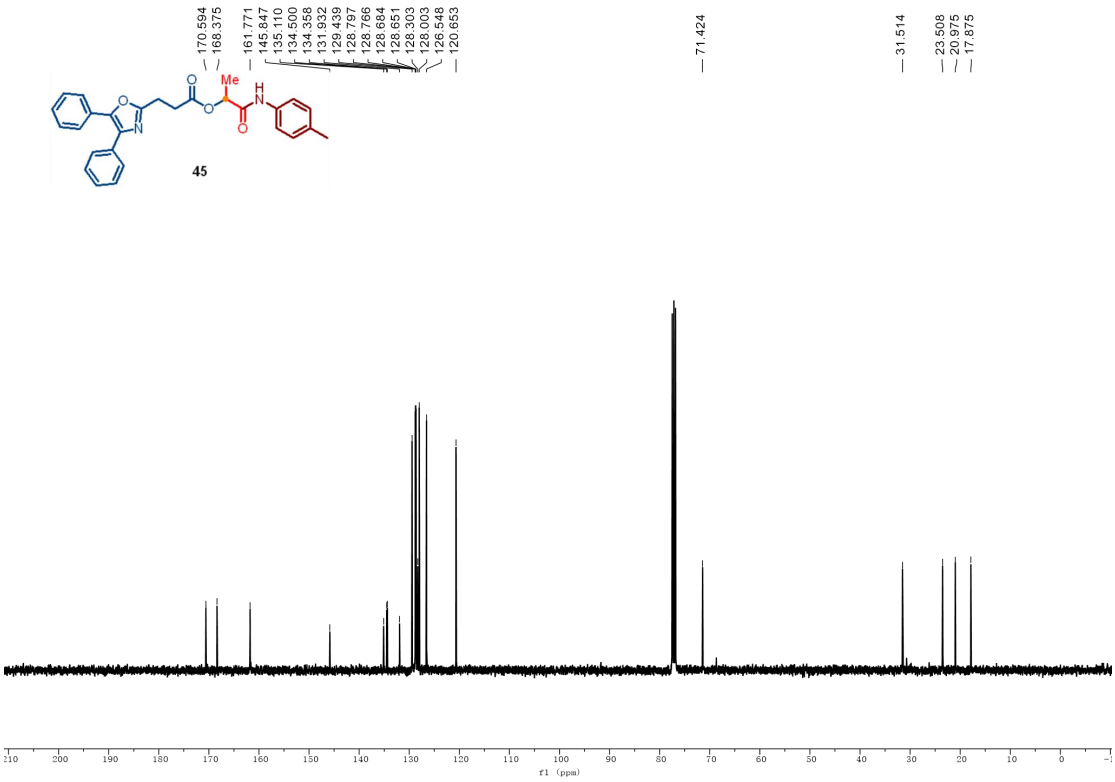
^{1}H NMR (400 MHz, $CDCl_3$) of 44-2



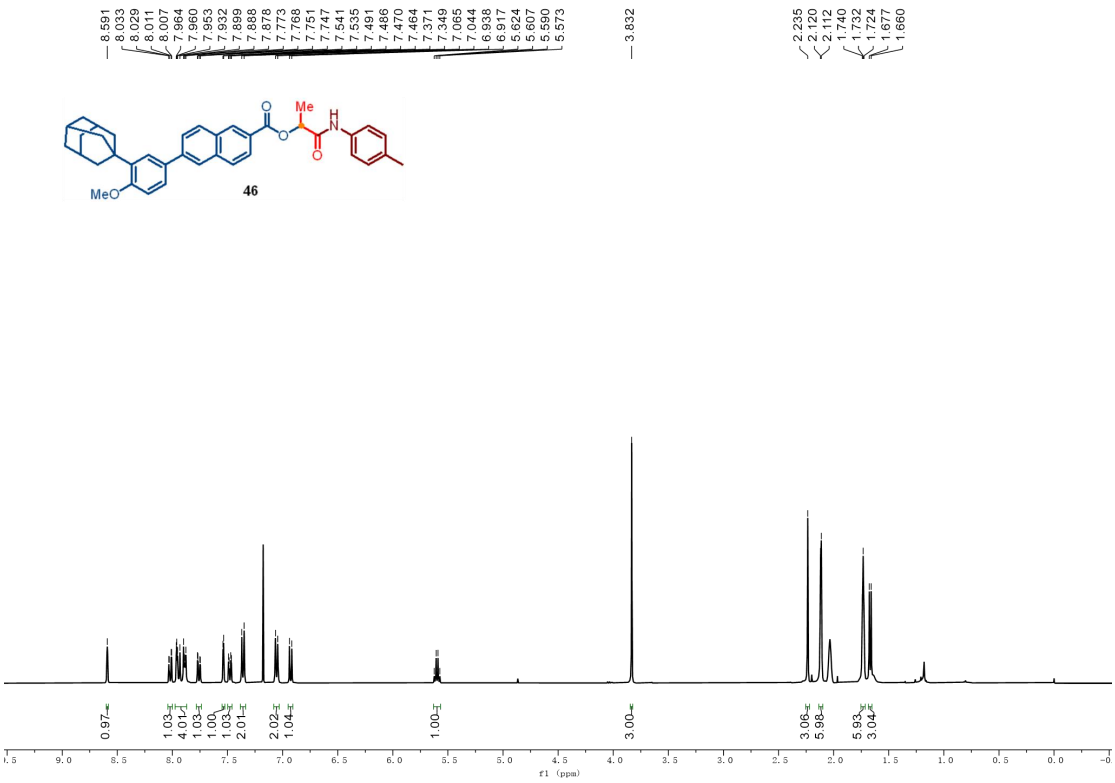
^{13}C NMR (101 MHz, $CDCl_3$) of 44-2



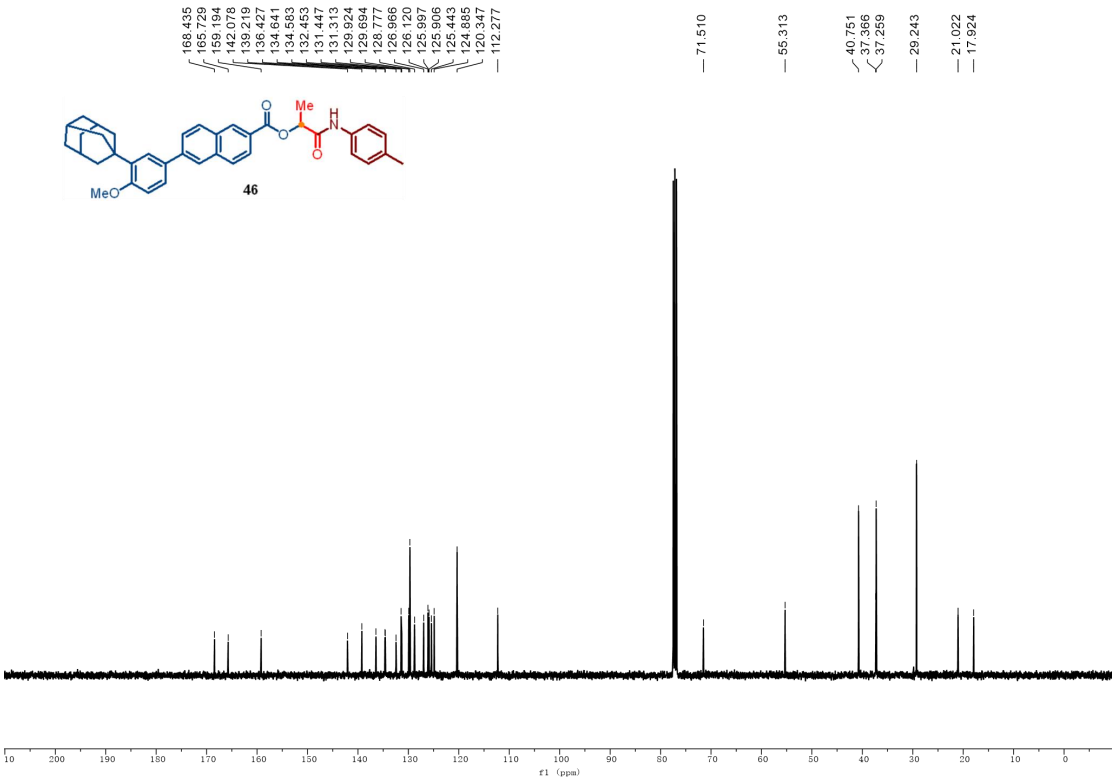
^{1}H NMR (400 MHz, $CDCl_3$) of 45



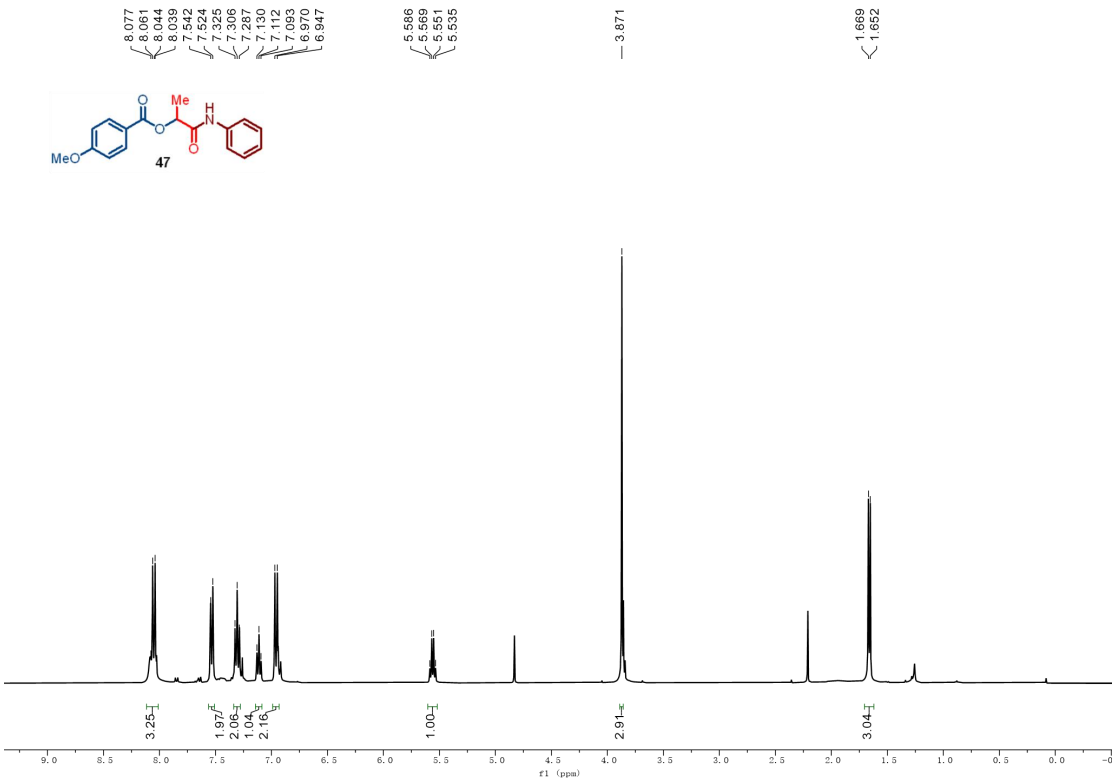
^{13}C NMR (101 MHz, $CDCl_3$) of 45



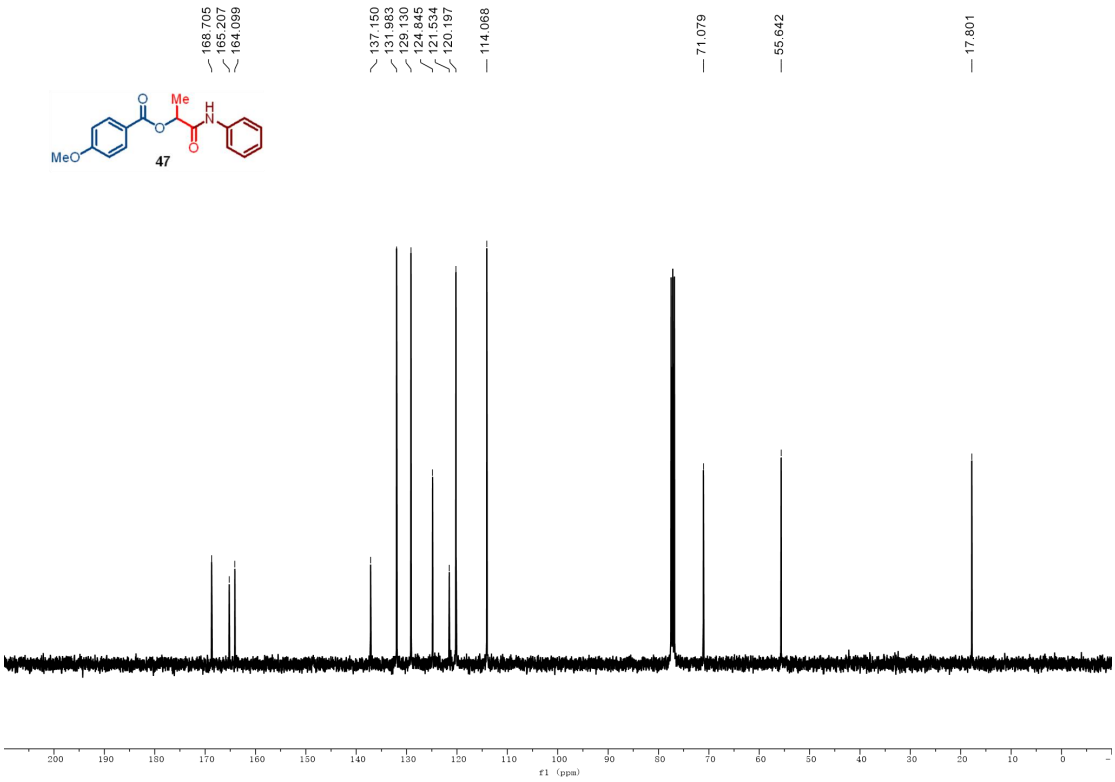
^{1}H NMR (400 MHz, $CDCl_3$) of 46



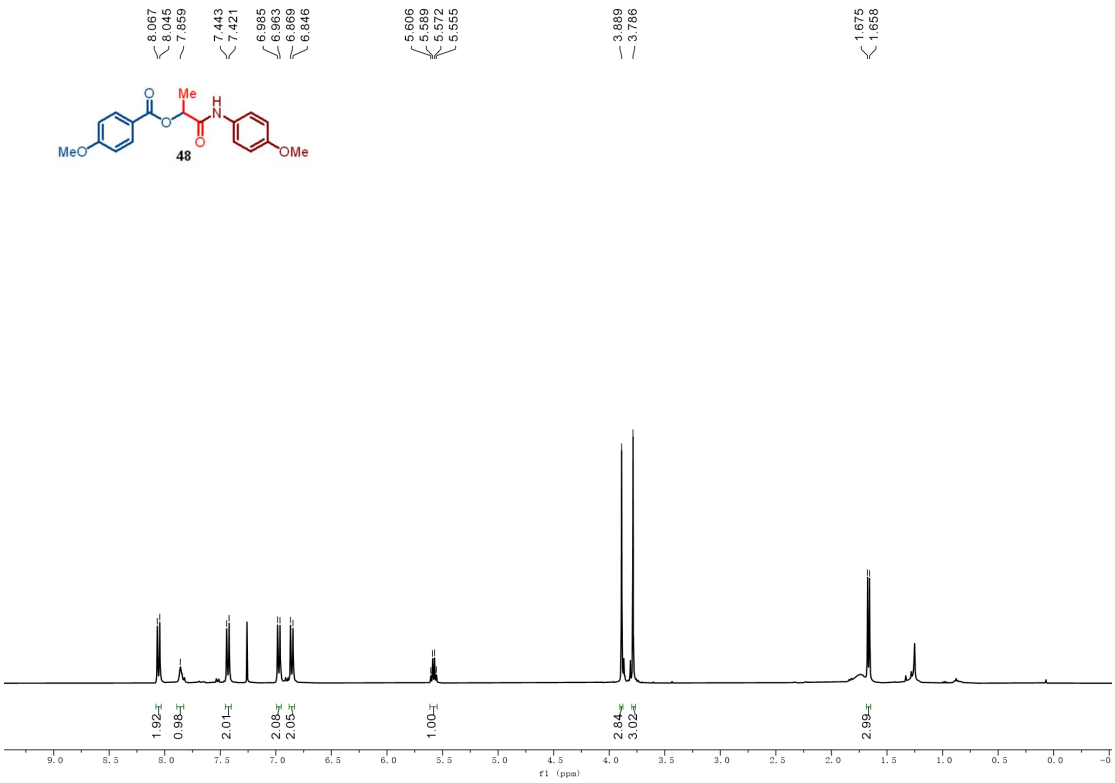
^{13}C NMR (101 MHz, $CDCl_3$) of 46



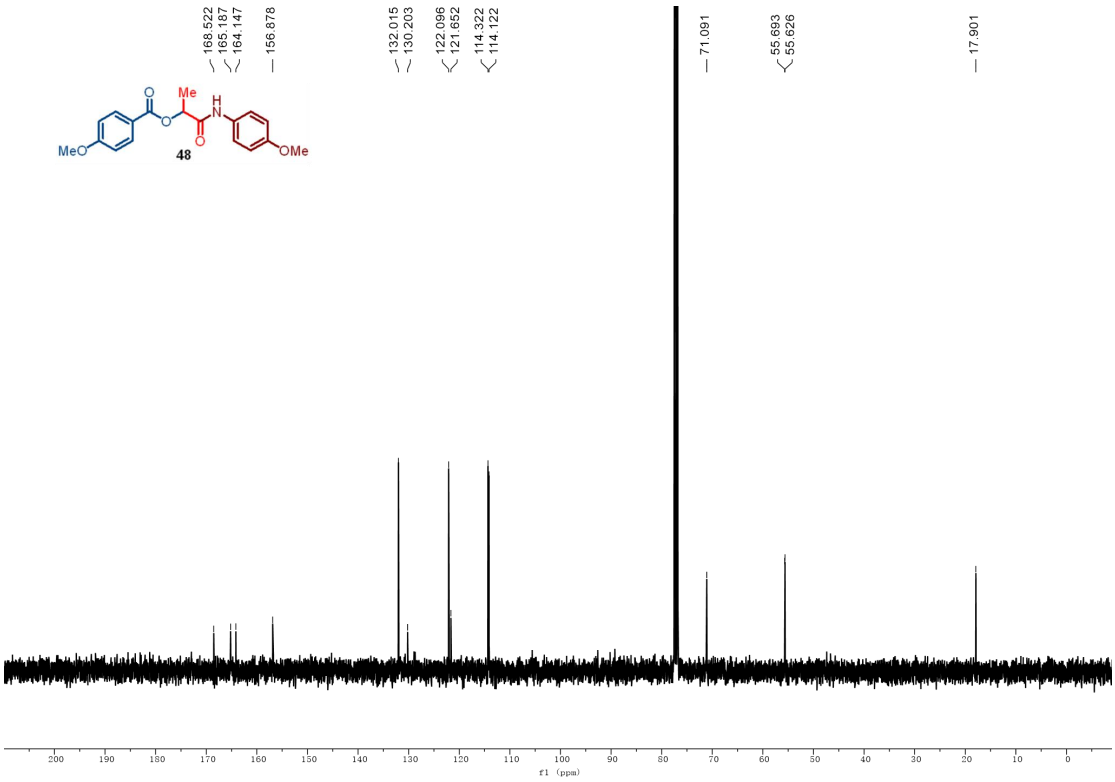
^{1}H NMR (400 MHz, $CDCl_3$) of 47



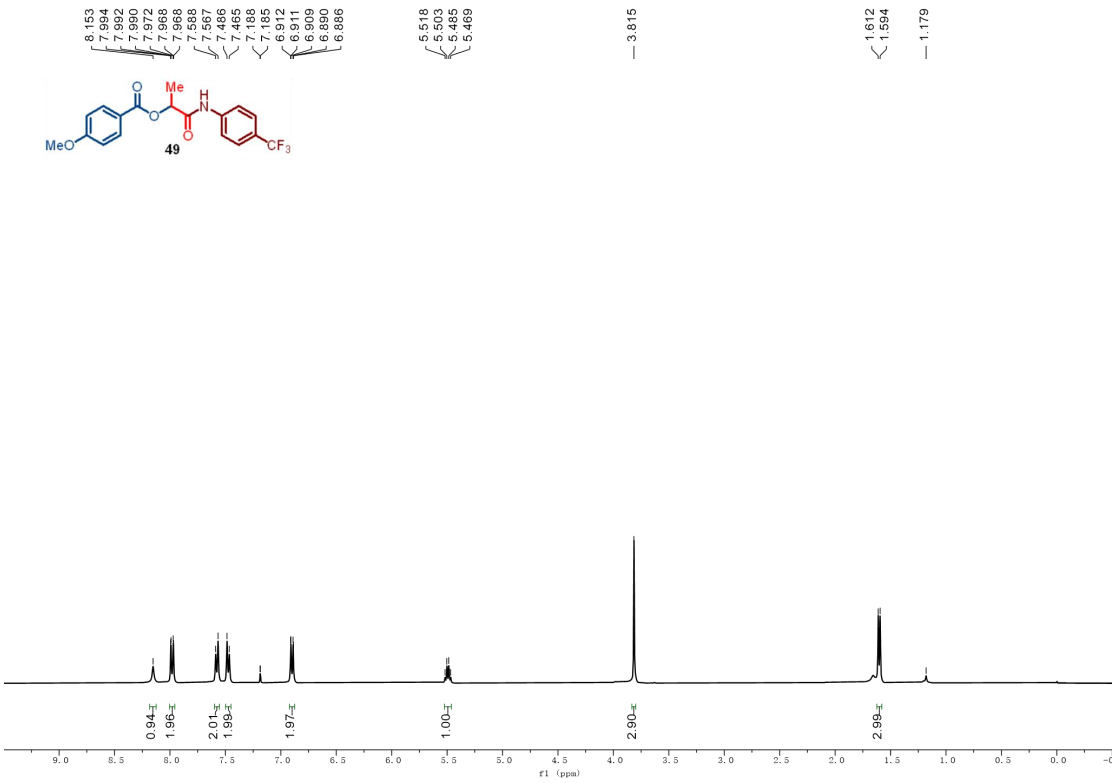
^{13}C NMR (101 MHz, $CDCl_3$) of 47



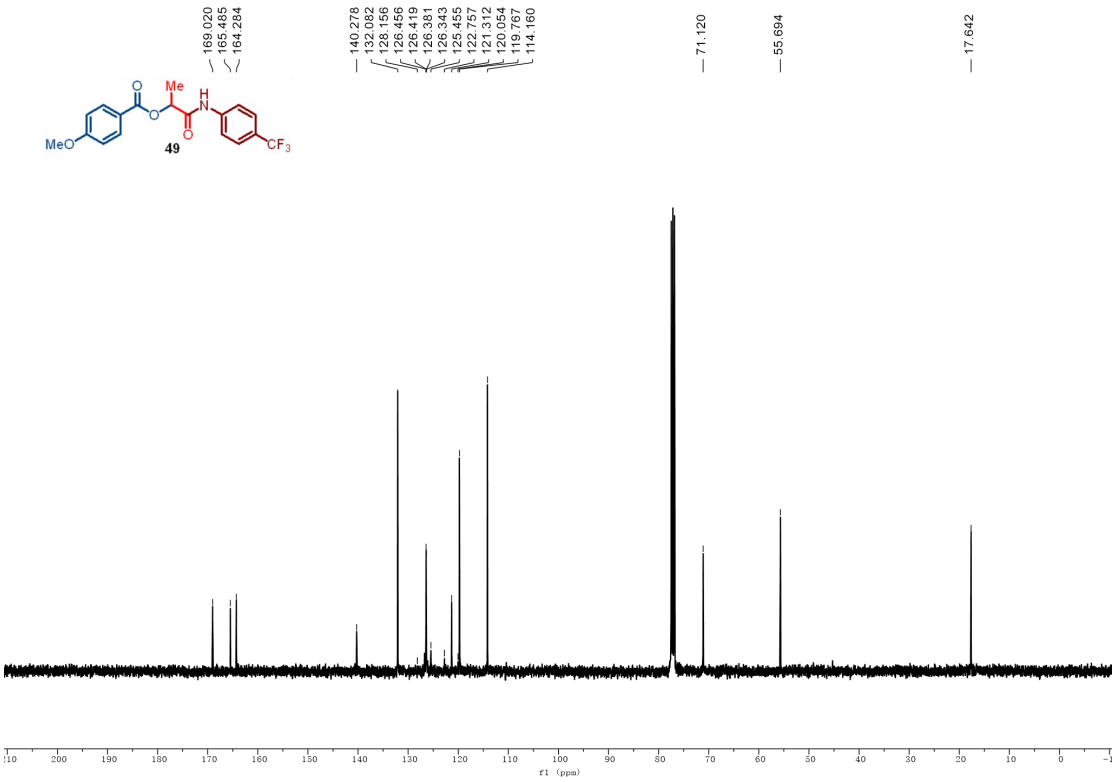
^{1}H NMR (400 MHz, $CDCl_3$) of 48



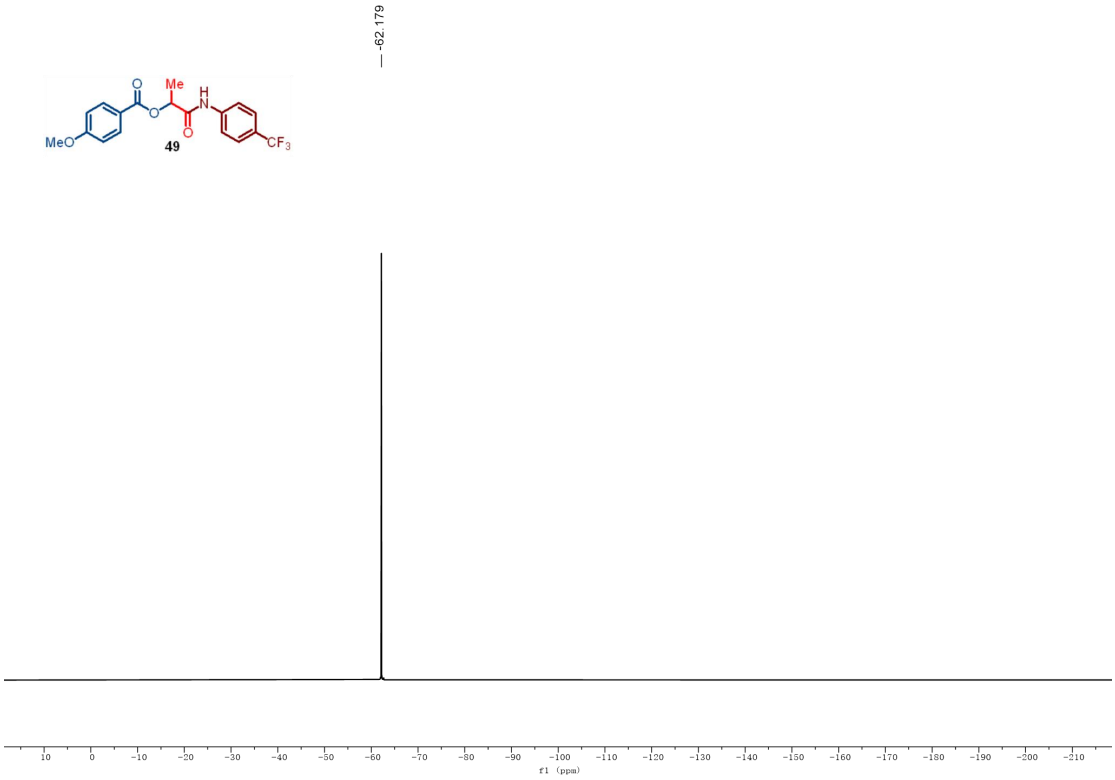
^{13}C NMR (101 MHz, $CDCl_3$) of 48



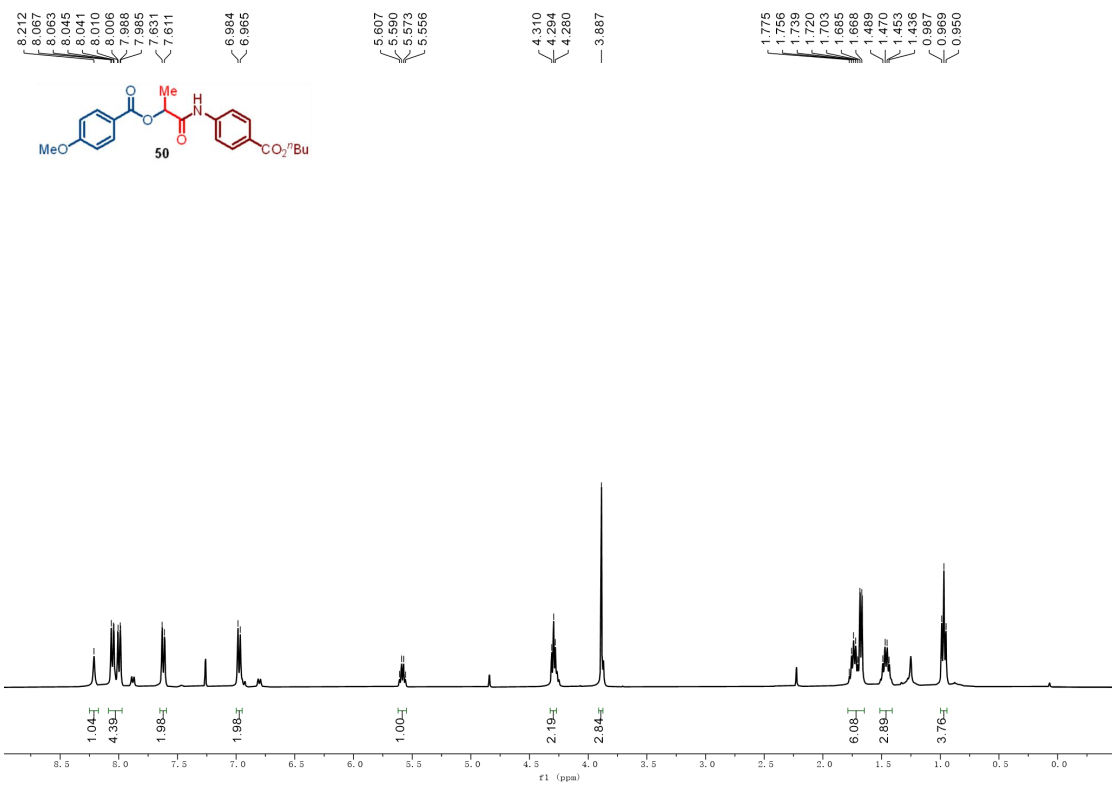
^{1}H NMR (400 MHz, $CDCl_3$) of 49



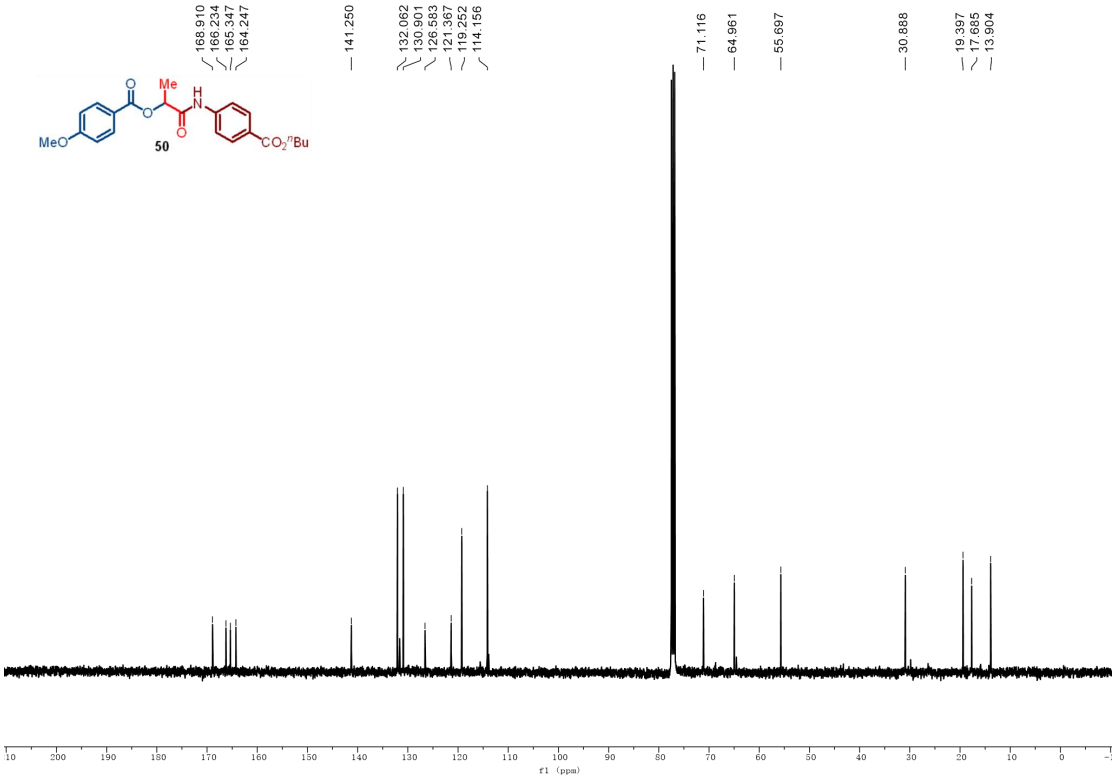
^{13}C NMR (101 MHz, $CDCl_3$) of 49



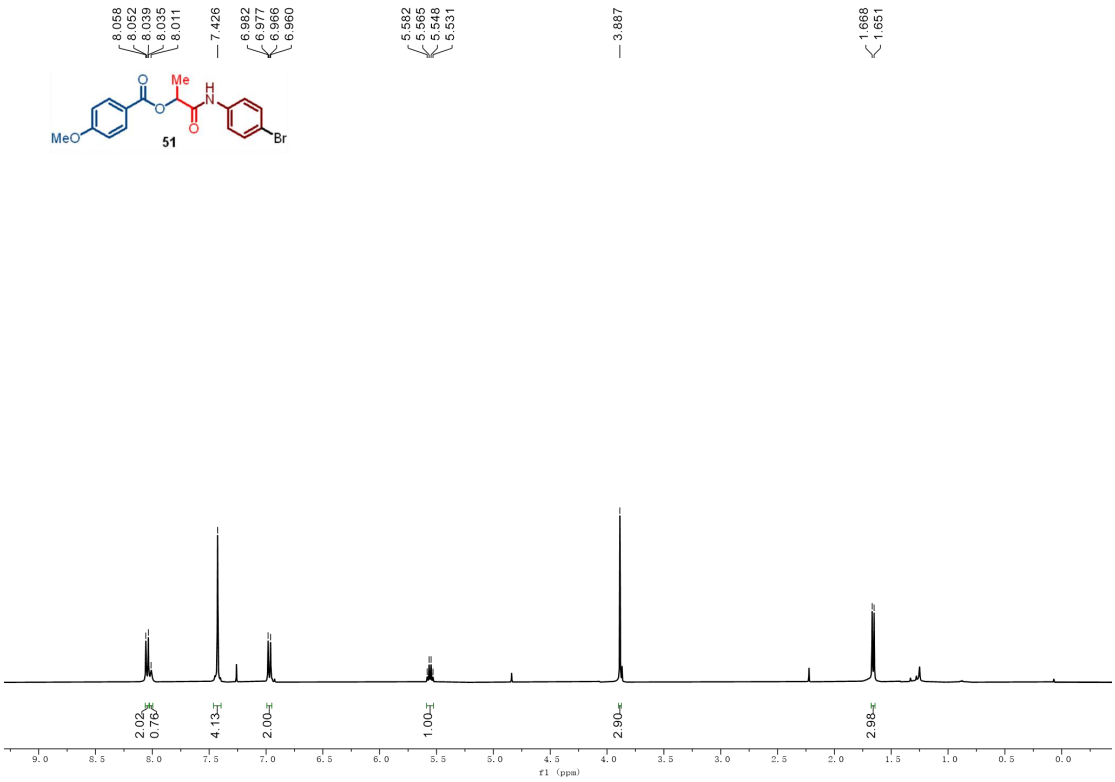
^{19}F NMR (376 MHz, $CDCl_3$) of 49



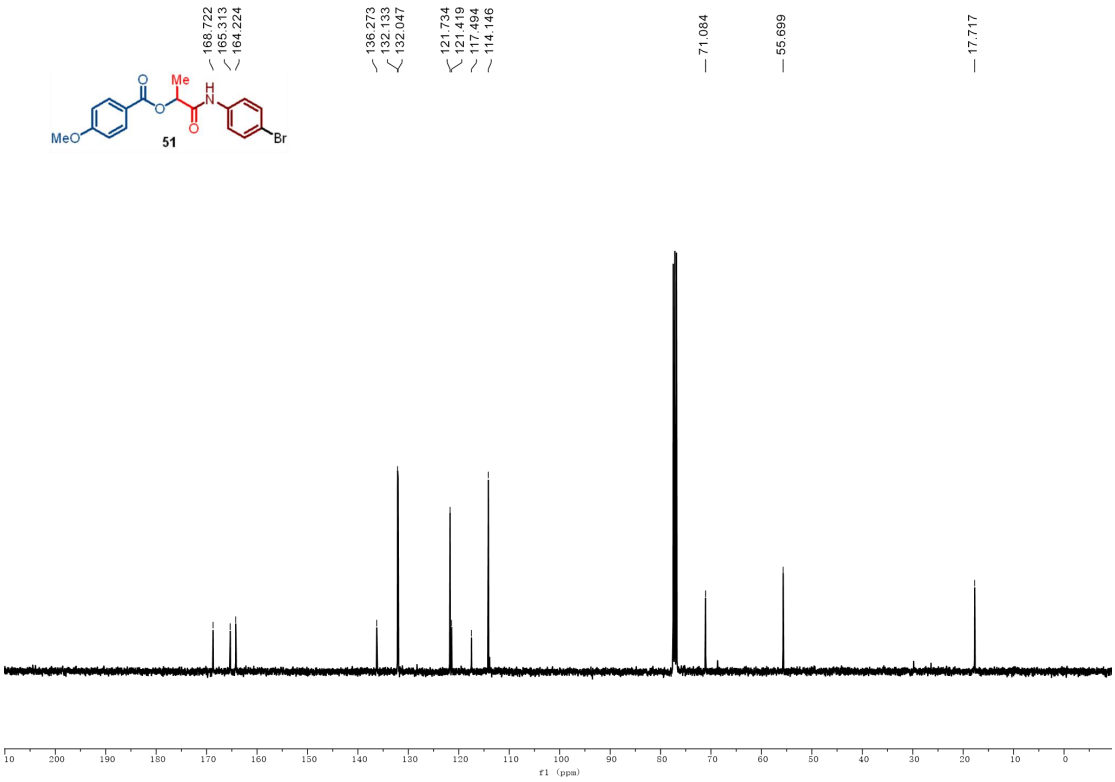
^{1}H NMR (400 MHz, $CDCl_3$) of 50



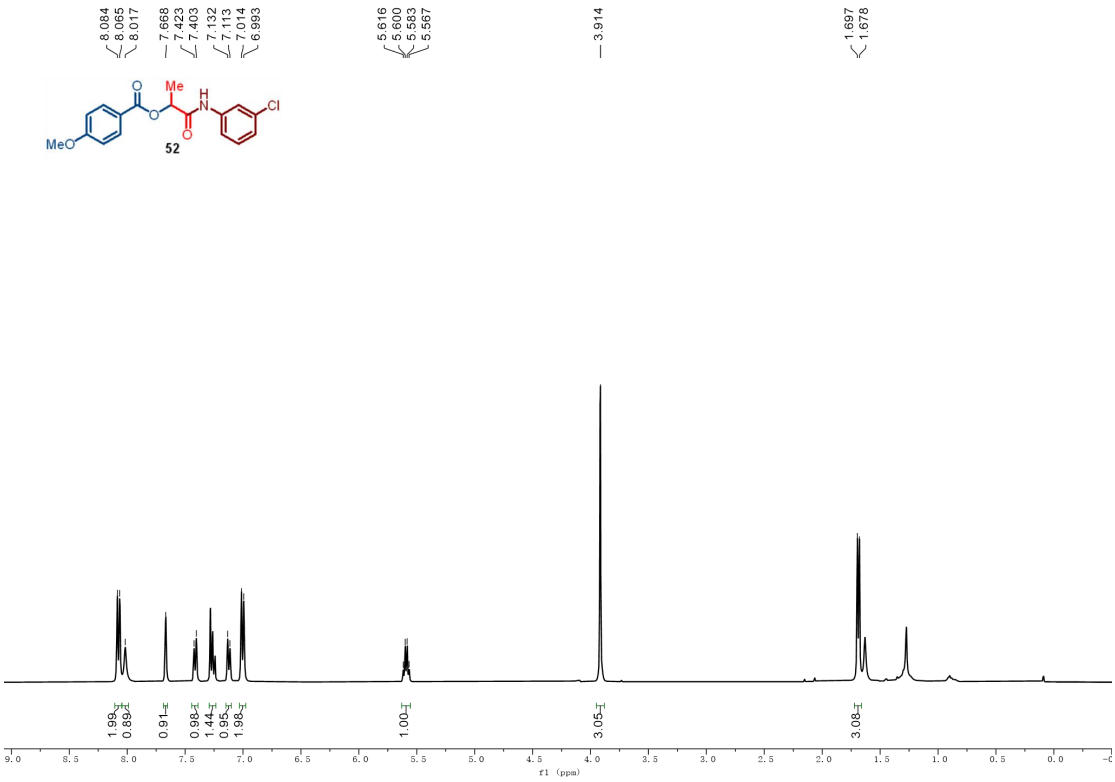
^{13}C NMR (101 MHz, $CDCl_3$) of 50



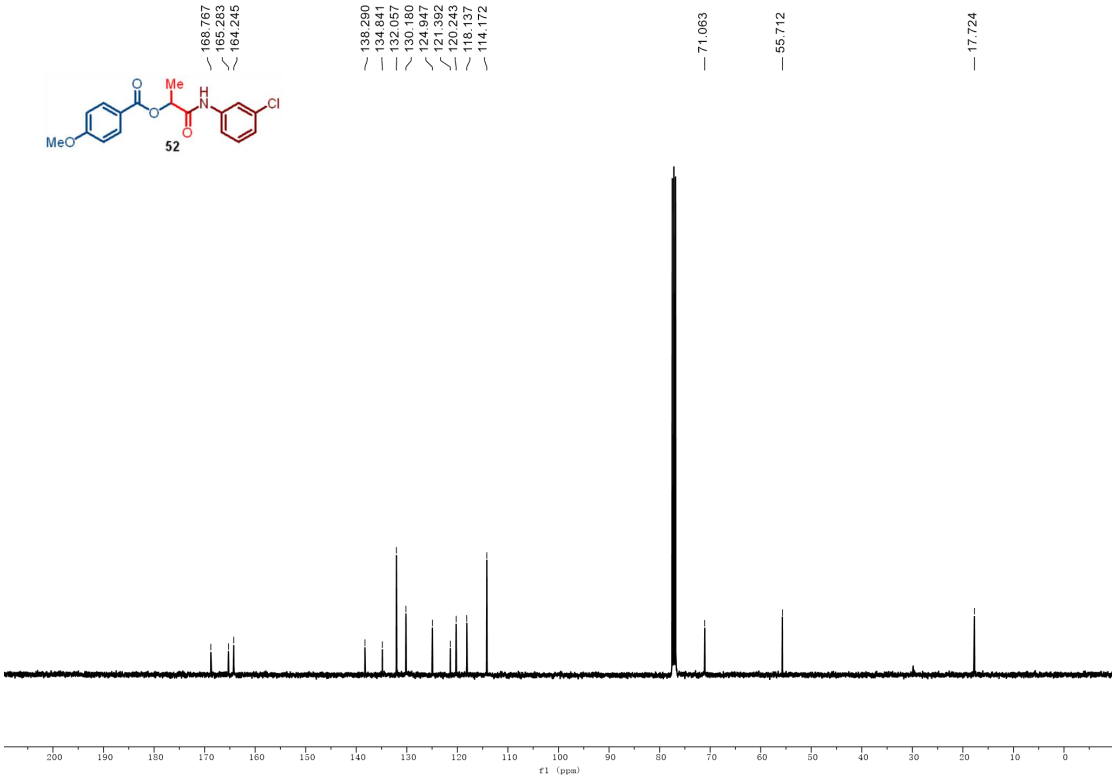
^{1}H NMR (400 MHz, $CDCl_3$) of 51



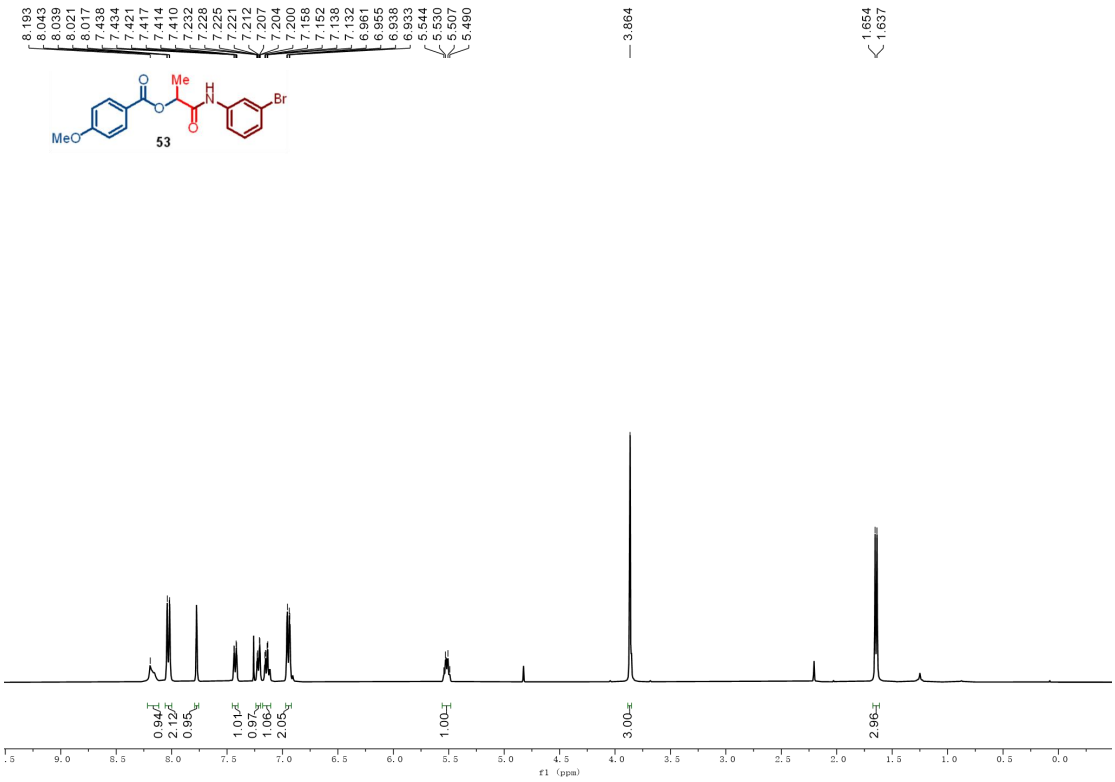
^{13}C NMR (101 MHz, $CDCl_3$) of 51



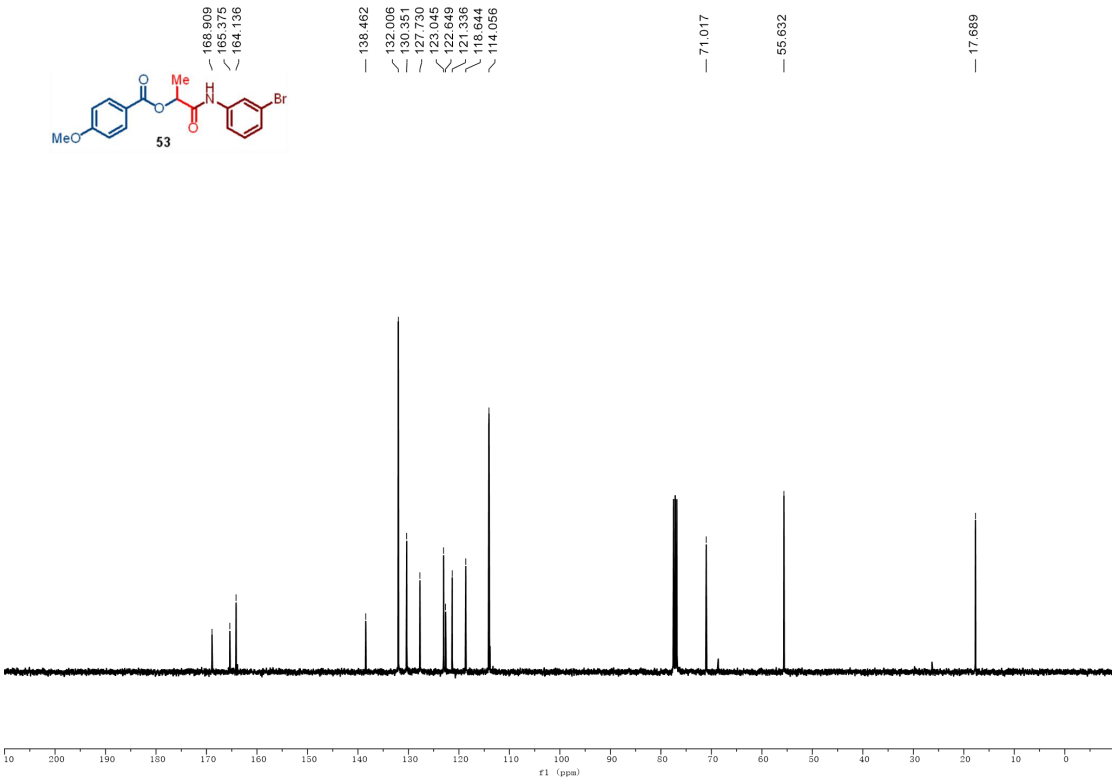
^{1}H NMR (400 MHz, $CDCl_3$) of 52



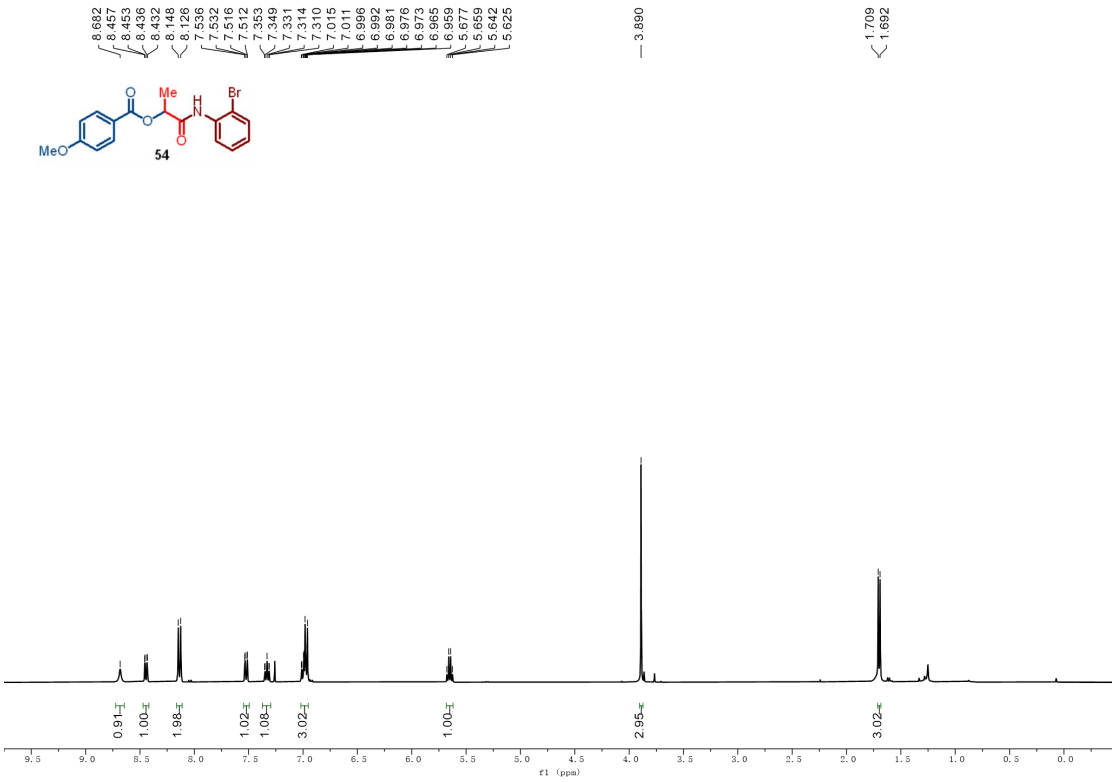
^{13}C NMR (101 MHz, $CDCl_3$) of 52



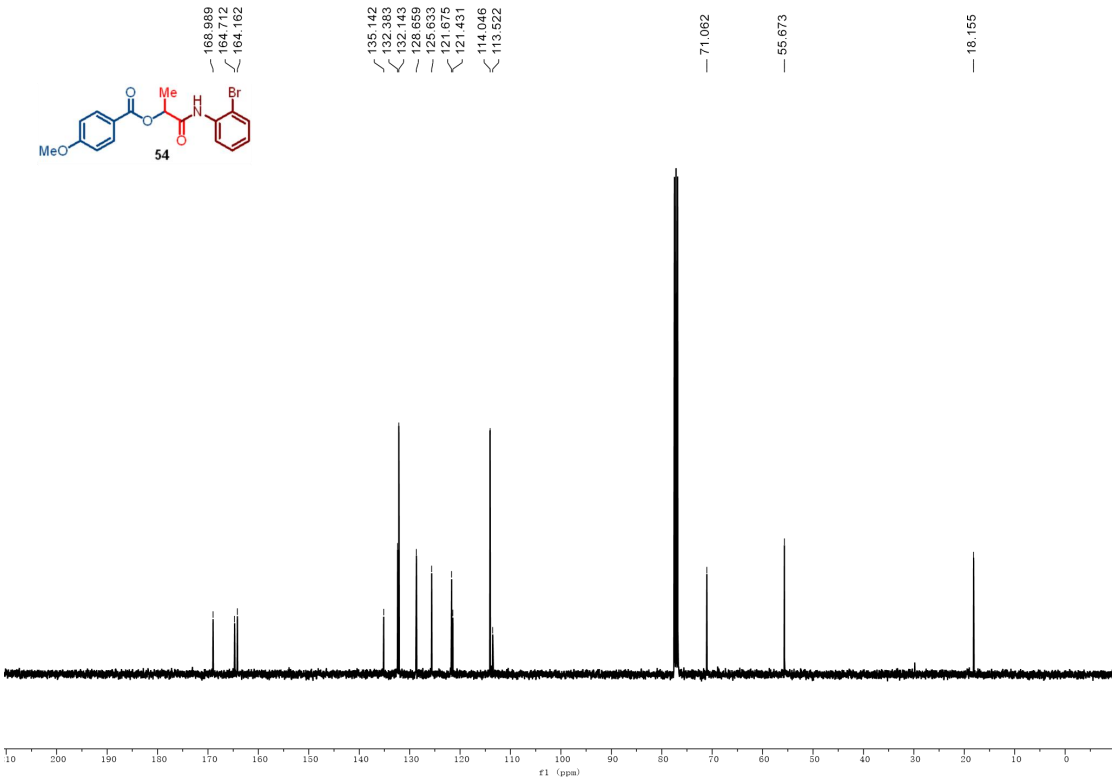
^{1}H NMR (400 MHz, $CDCl_3$) of 53



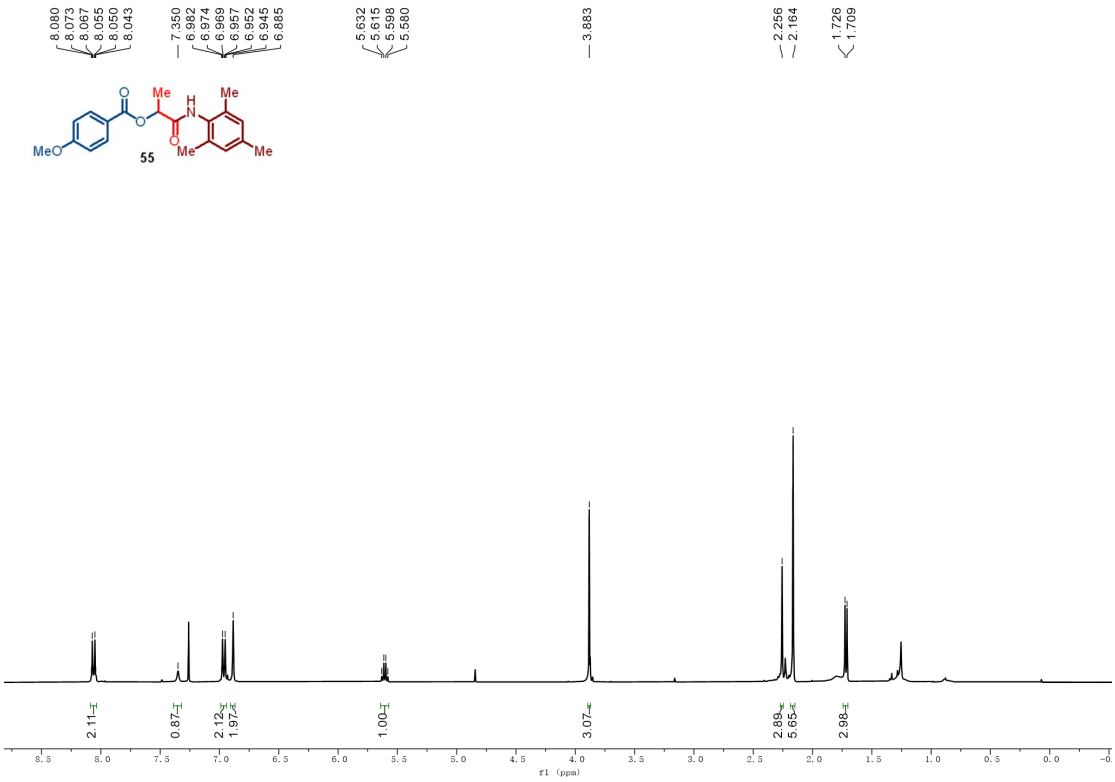
^{13}C NMR (101 MHz, $CDCl_3$) of 53



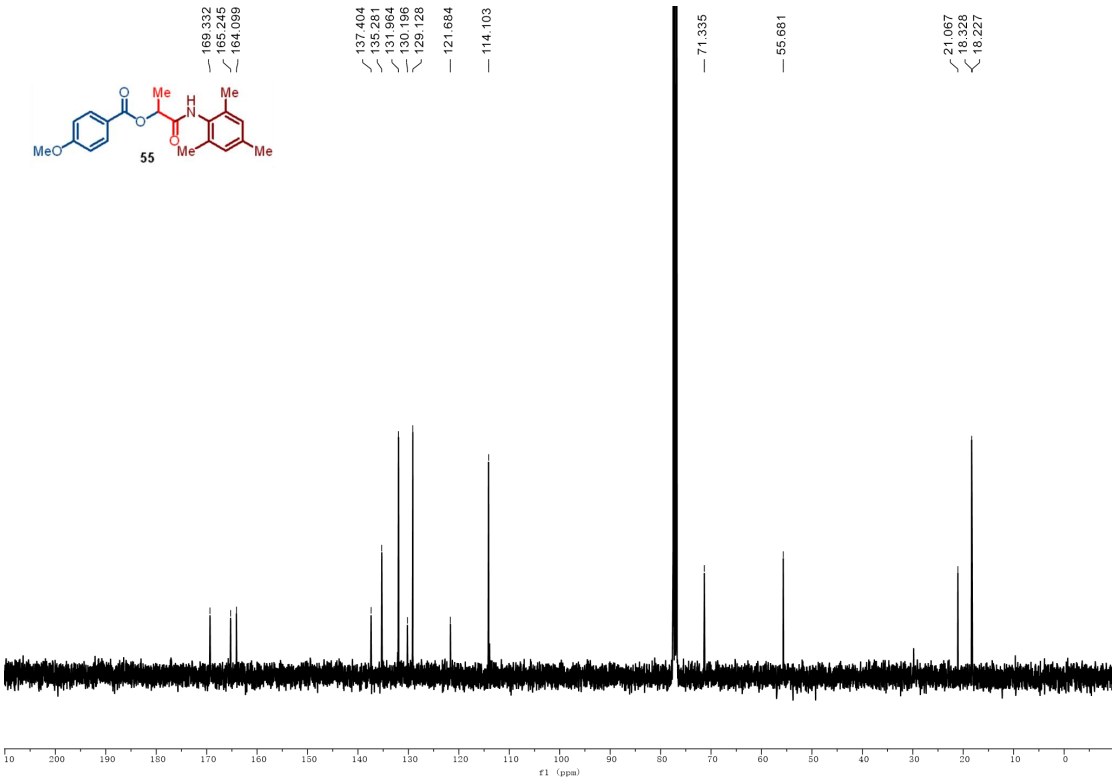
^{1}H NMR (400 MHz, $CDCl_3$) of 54



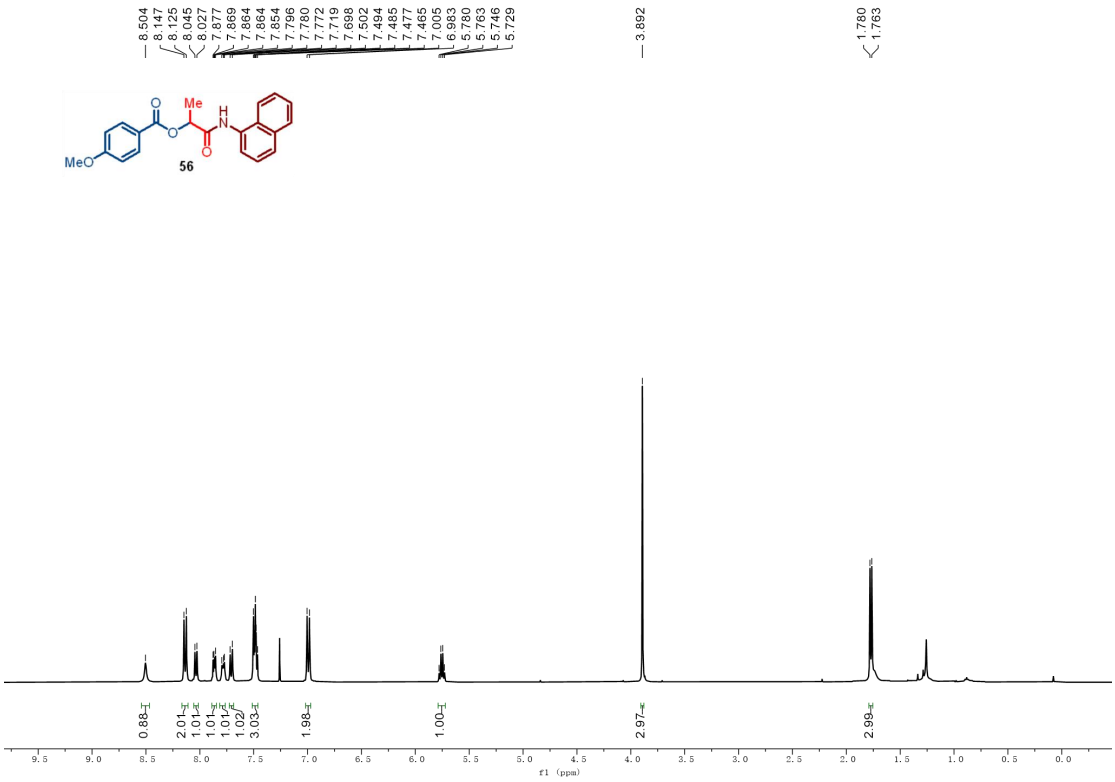
^{13}C NMR (101 MHz, $CDCl_3$) of 54



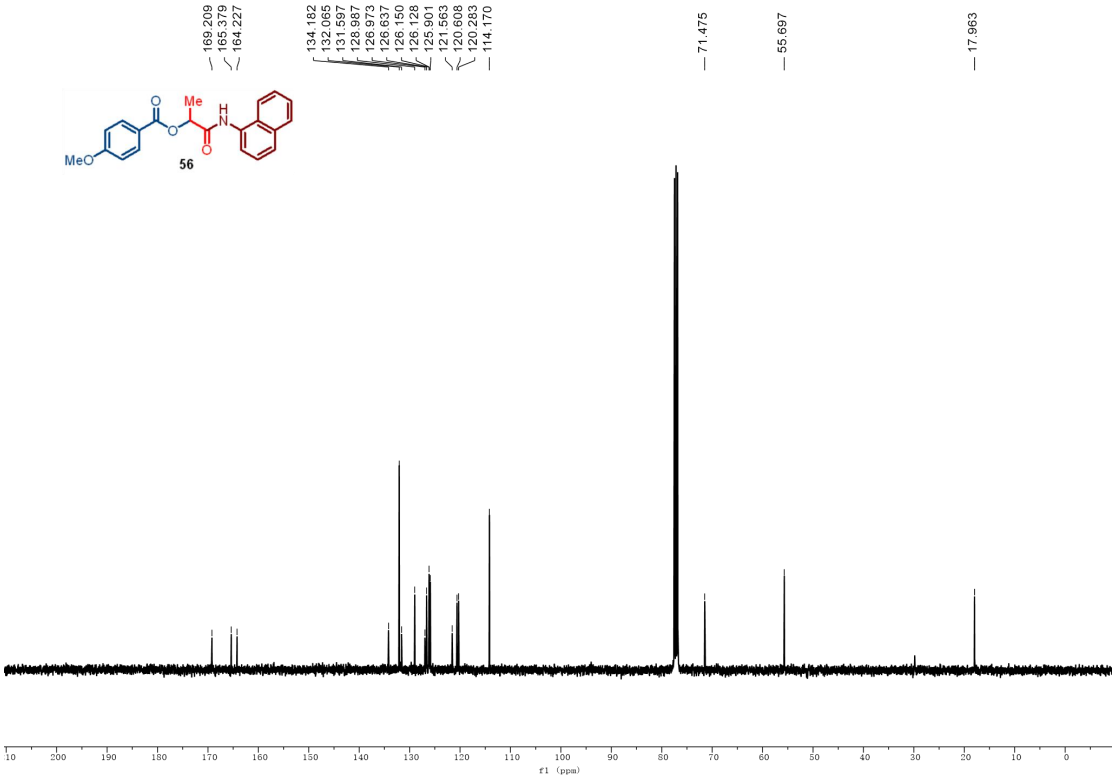
^{1}H NMR (400 MHz, $CDCl_3$) of 55



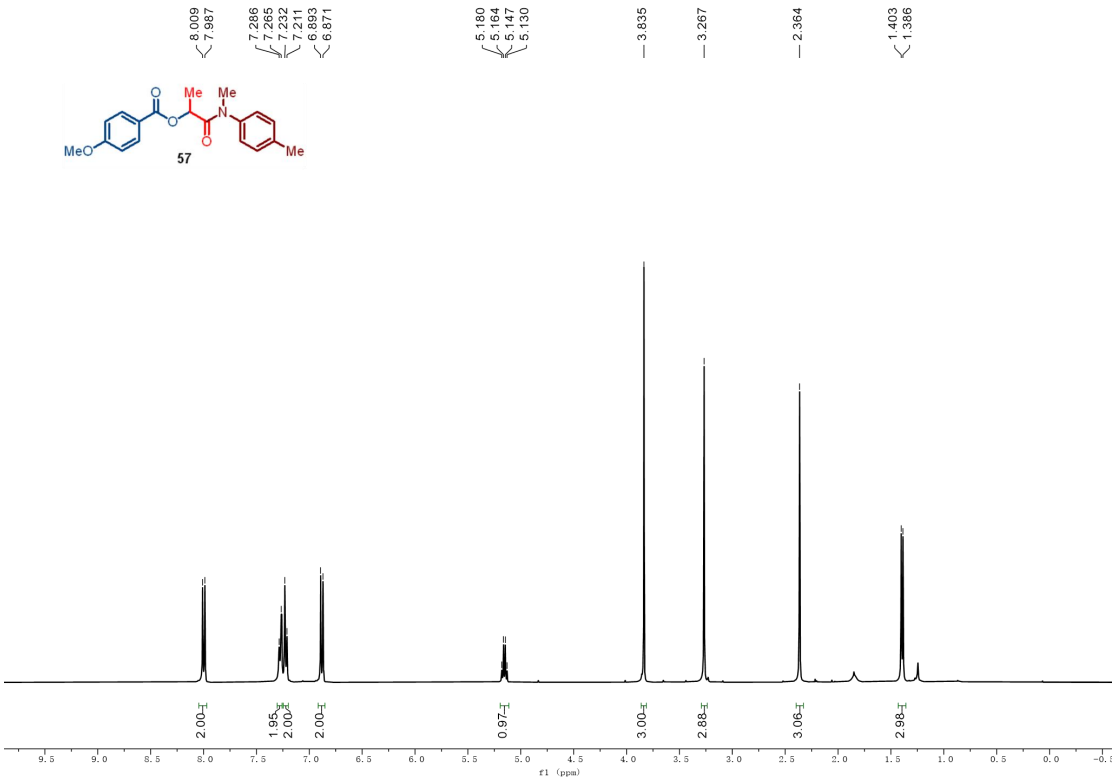
^{13}C NMR (101 MHz, $CDCl_3$) of 55



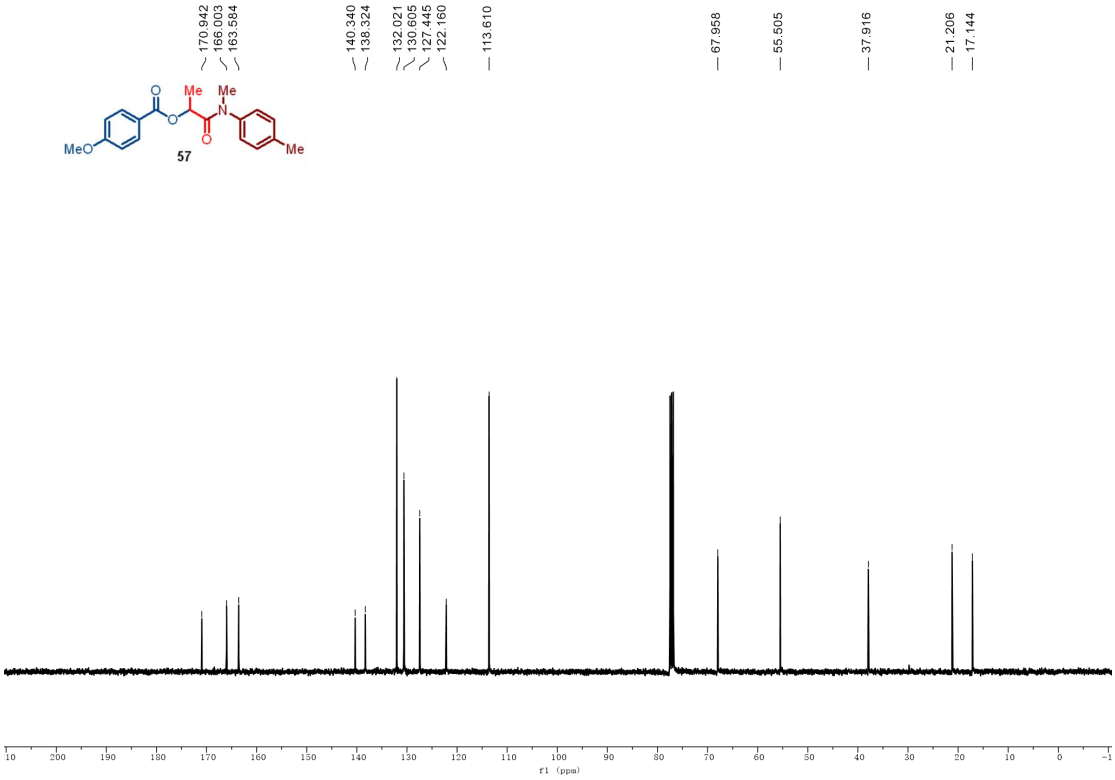
^{1}H NMR (400 MHz, $CDCl_3$) of 56



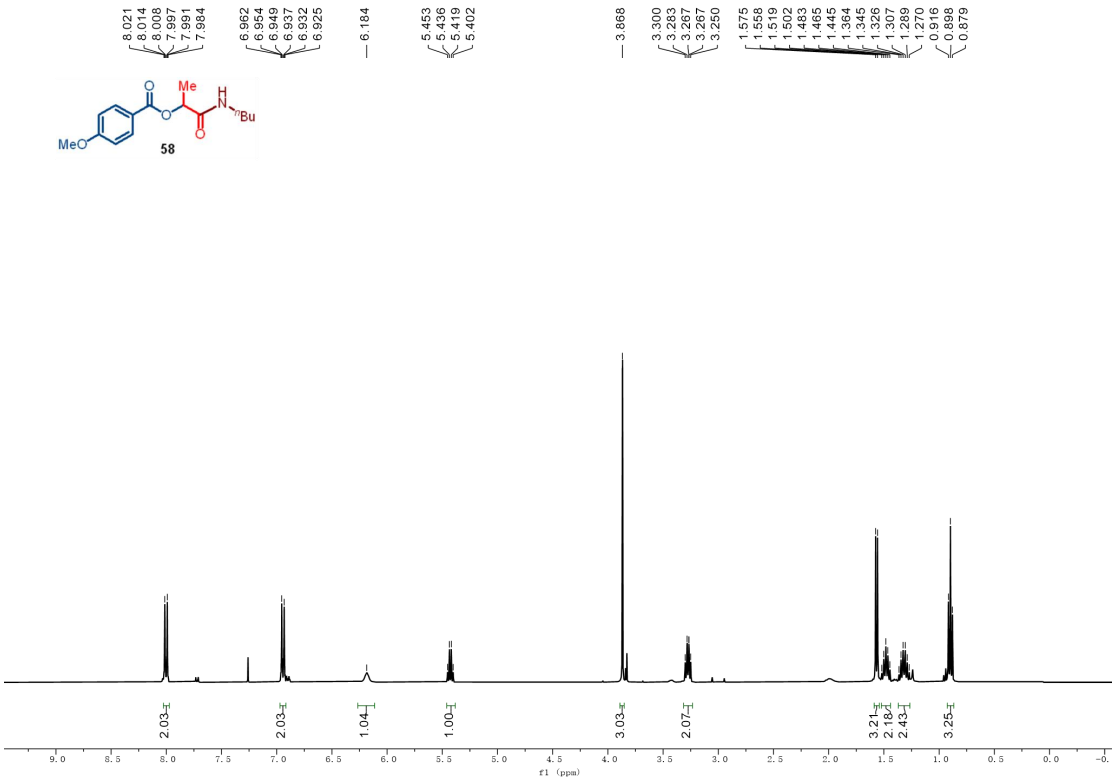
^{13}C NMR (101 MHz, $CDCl_3$) of 56



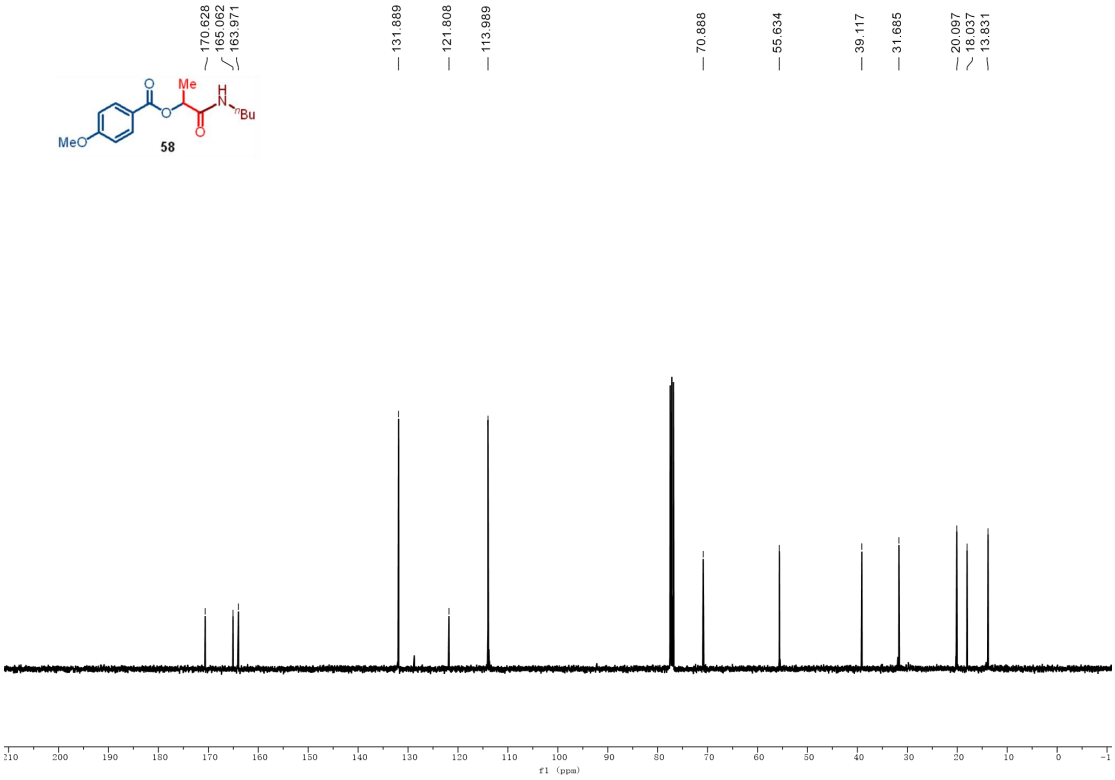
^{1}H NMR (400 MHz, $CDCl_3$) of 57



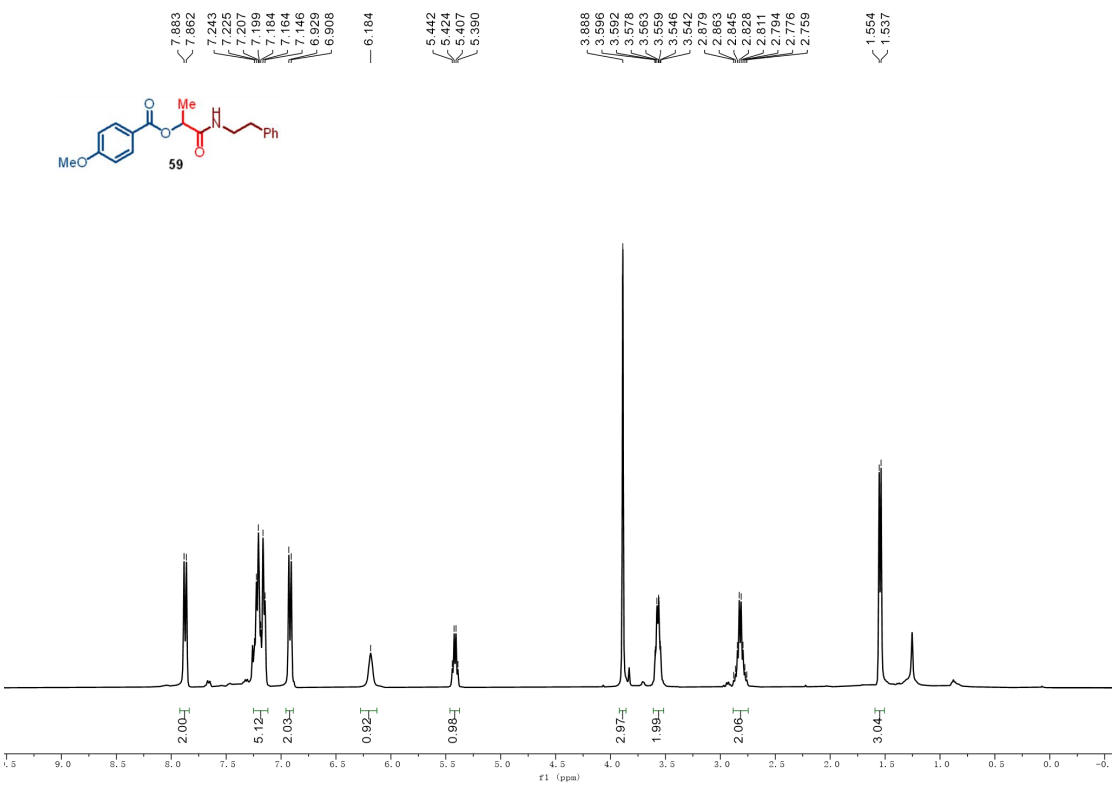
^{13}C NMR (101 MHz, $CDCl_3$) of 57



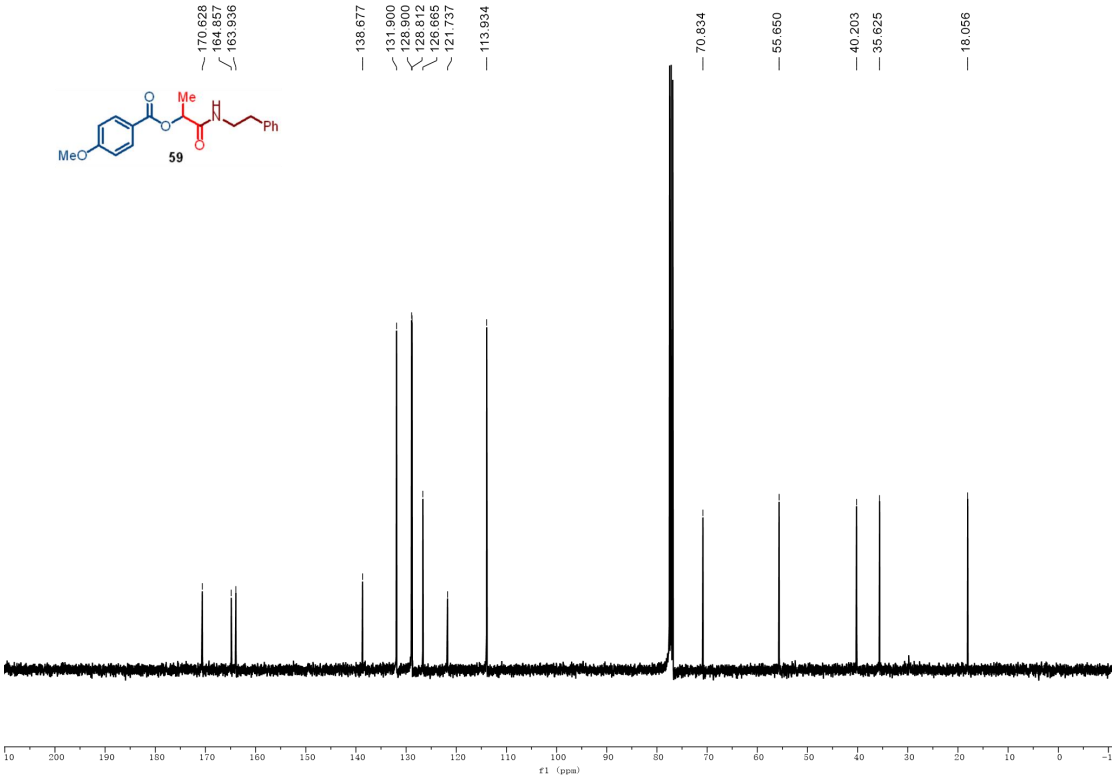
^{1}H NMR (400 MHz, $CDCl_3$) of 58



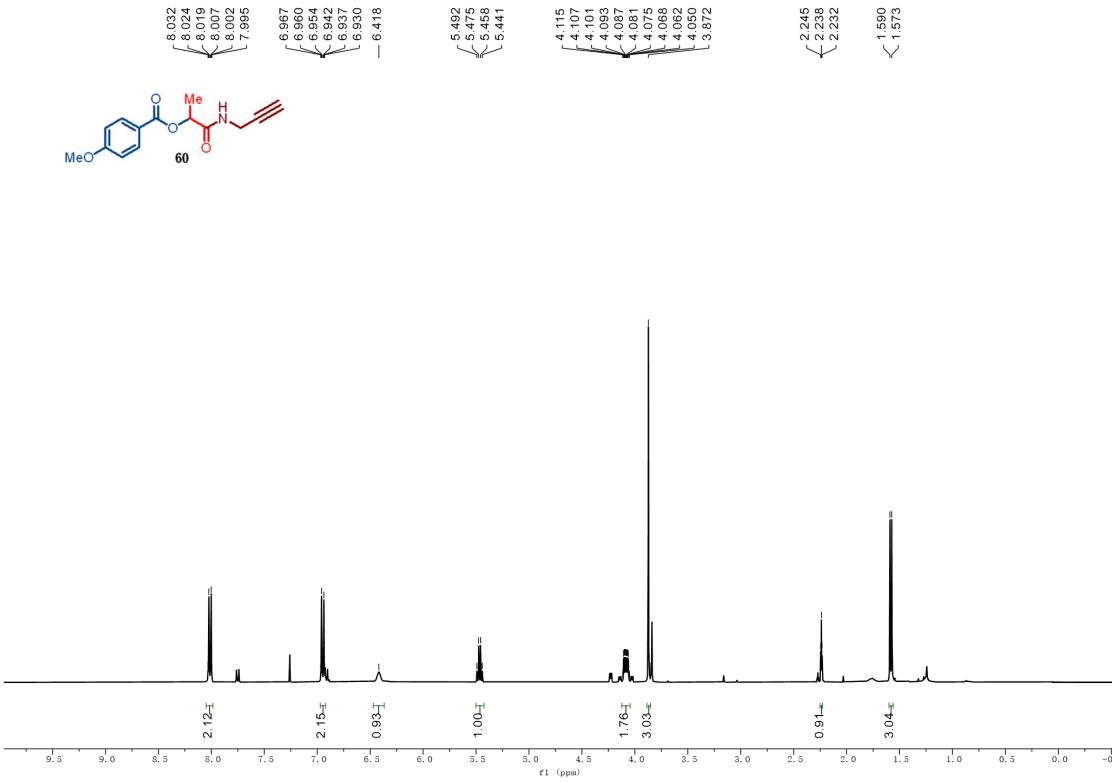
^{13}C NMR (101 MHz, $CDCl_3$) of 58



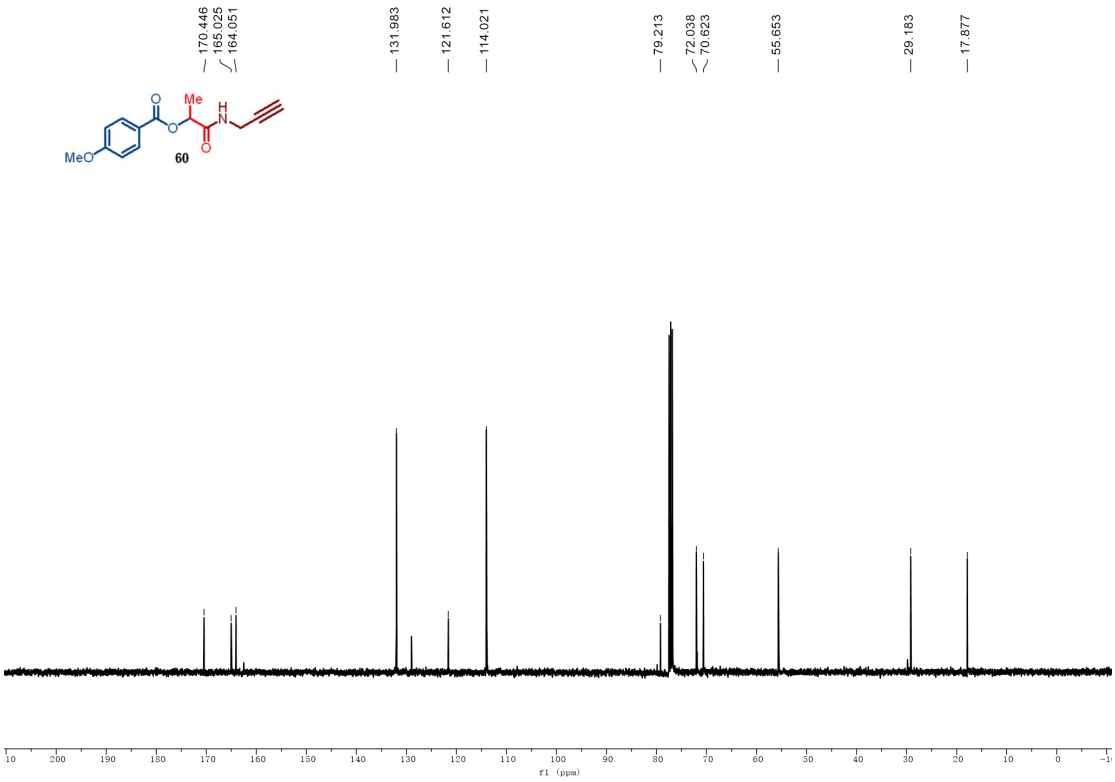
^{1}H NMR (400 MHz, $CDCl_3$) of 59



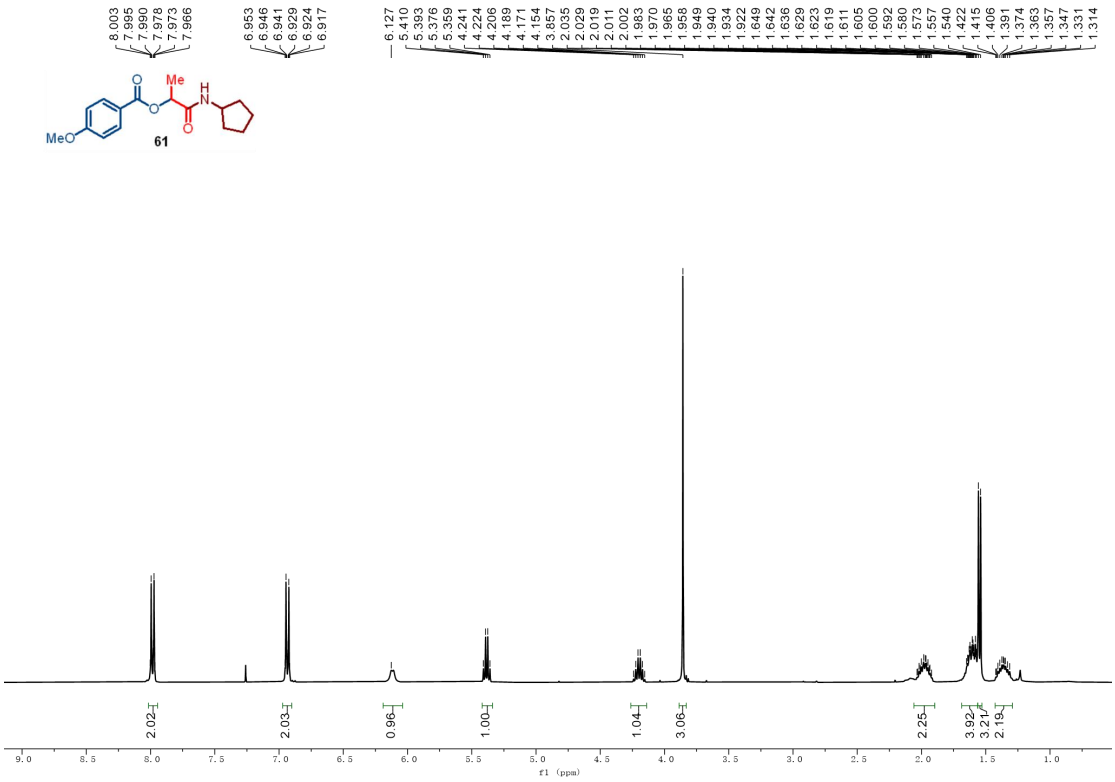
^{13}C NMR (101 MHz, $CDCl_3$) of 59



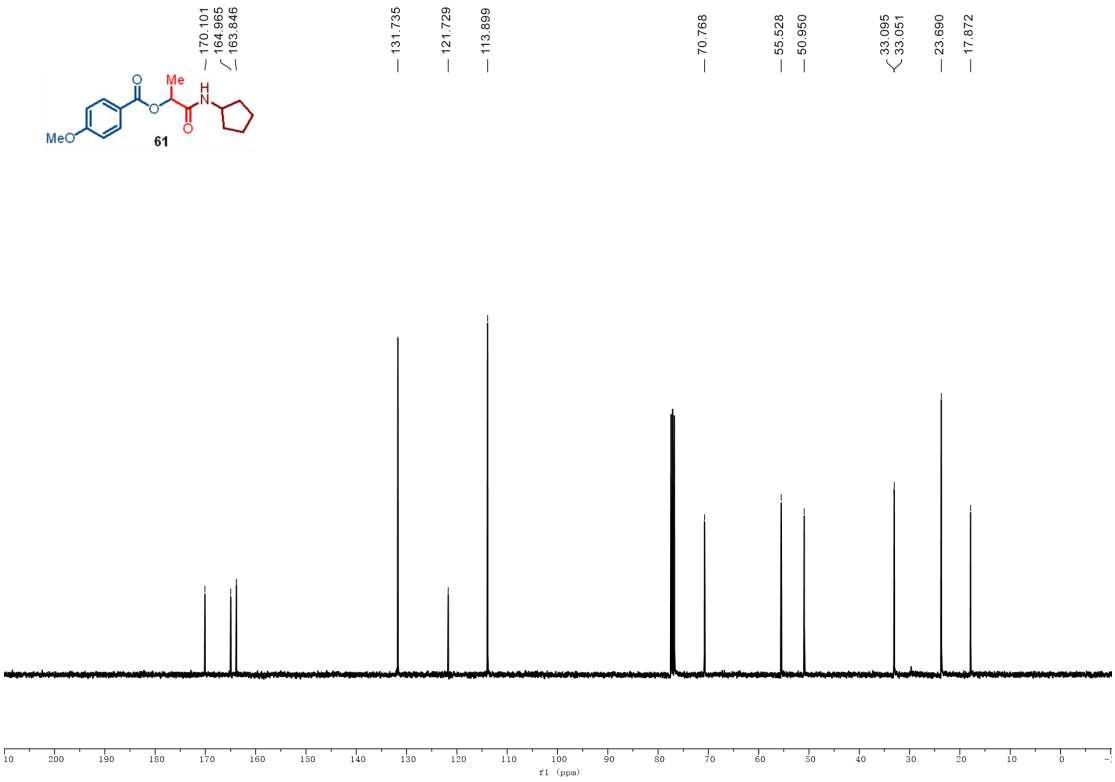
^{1}H NMR (400 MHz, $CDCl_3$) of 60



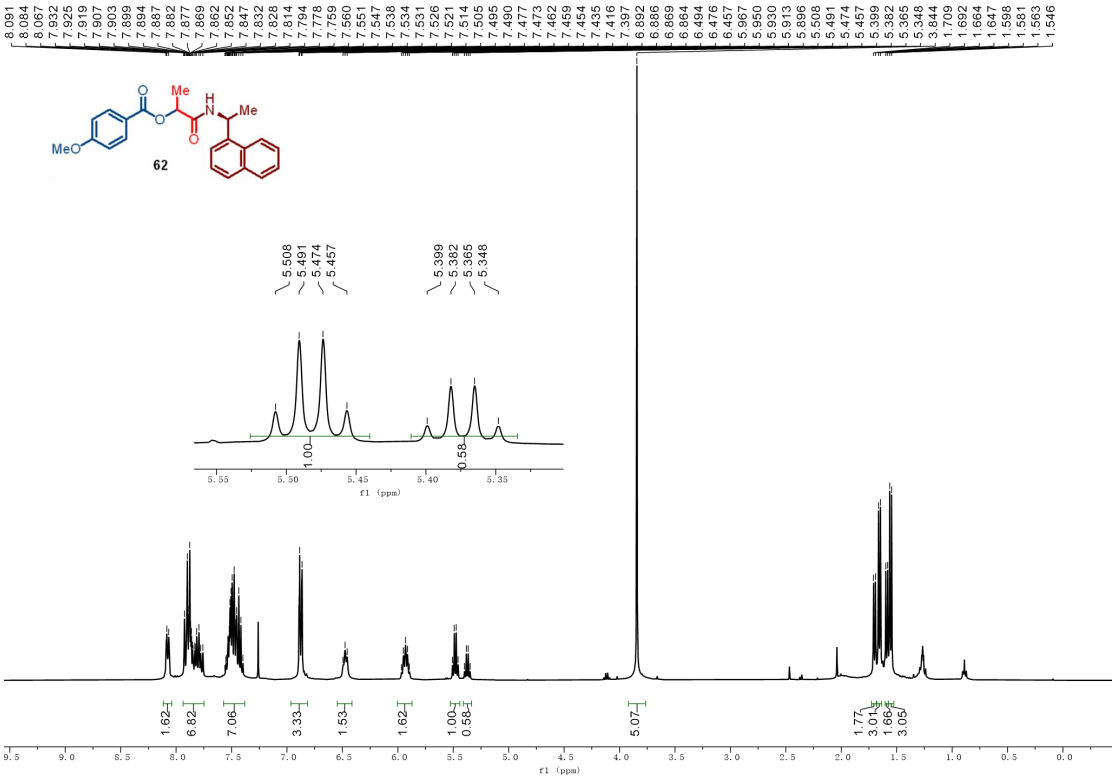
^{13}C NMR (101 MHz, $CDCl_3$) of 60



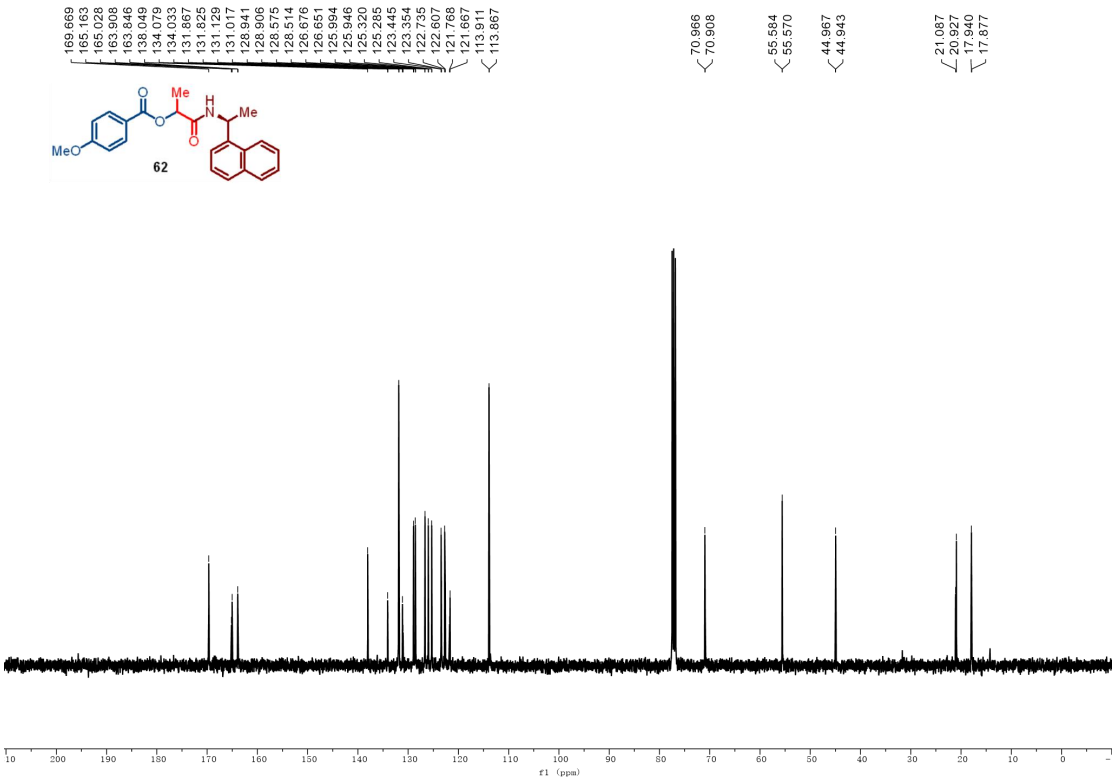
^{1}H NMR (400 MHz, $CDCl_3$) of 61



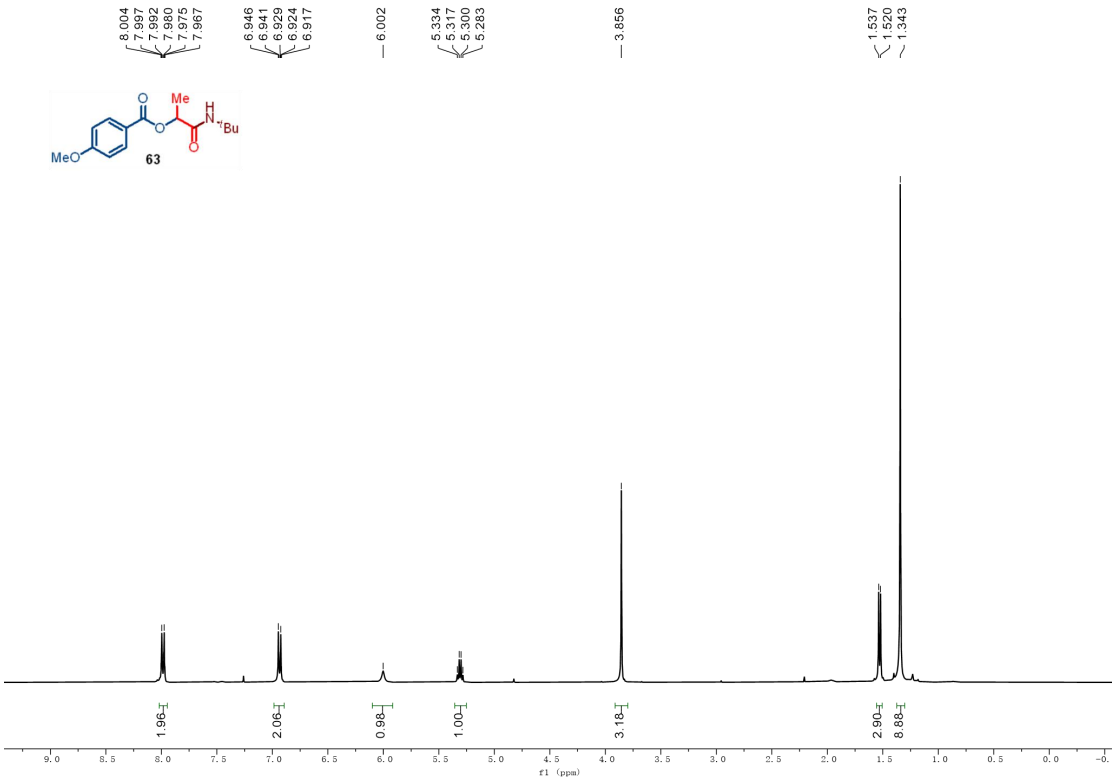
^{13}C NMR (101 MHz, $CDCl_3$) of 61



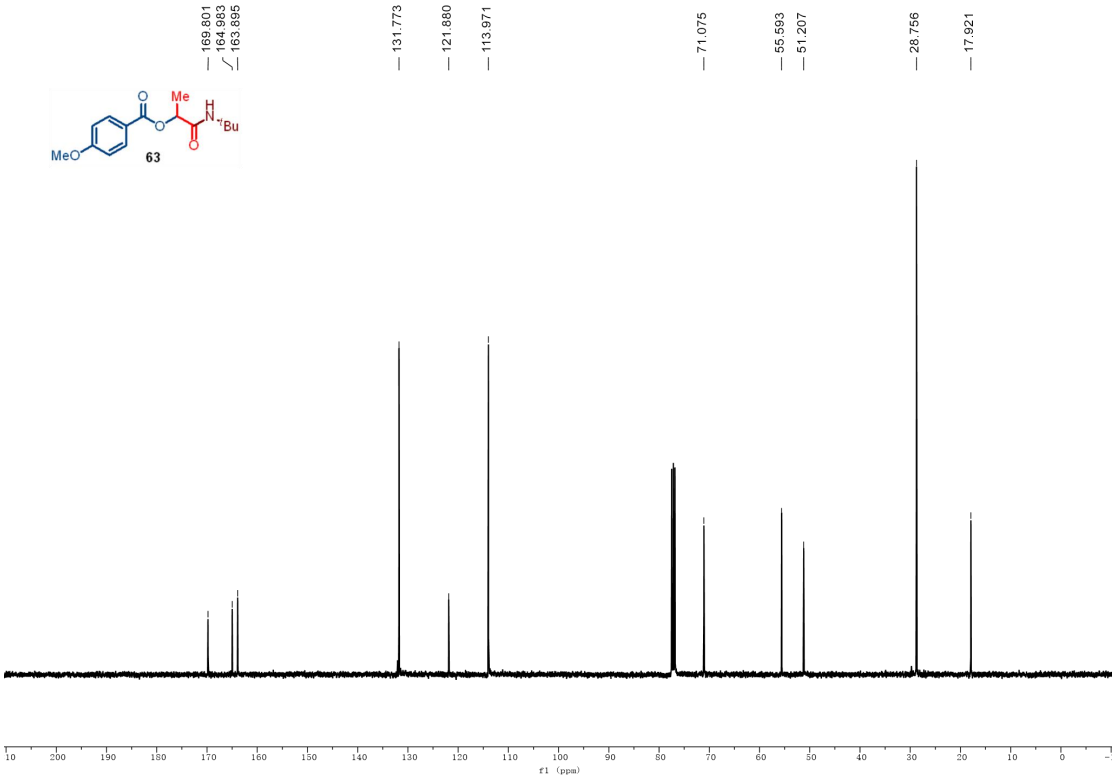
^{1}H NMR (400 MHz, $CDCl_3$) of 62



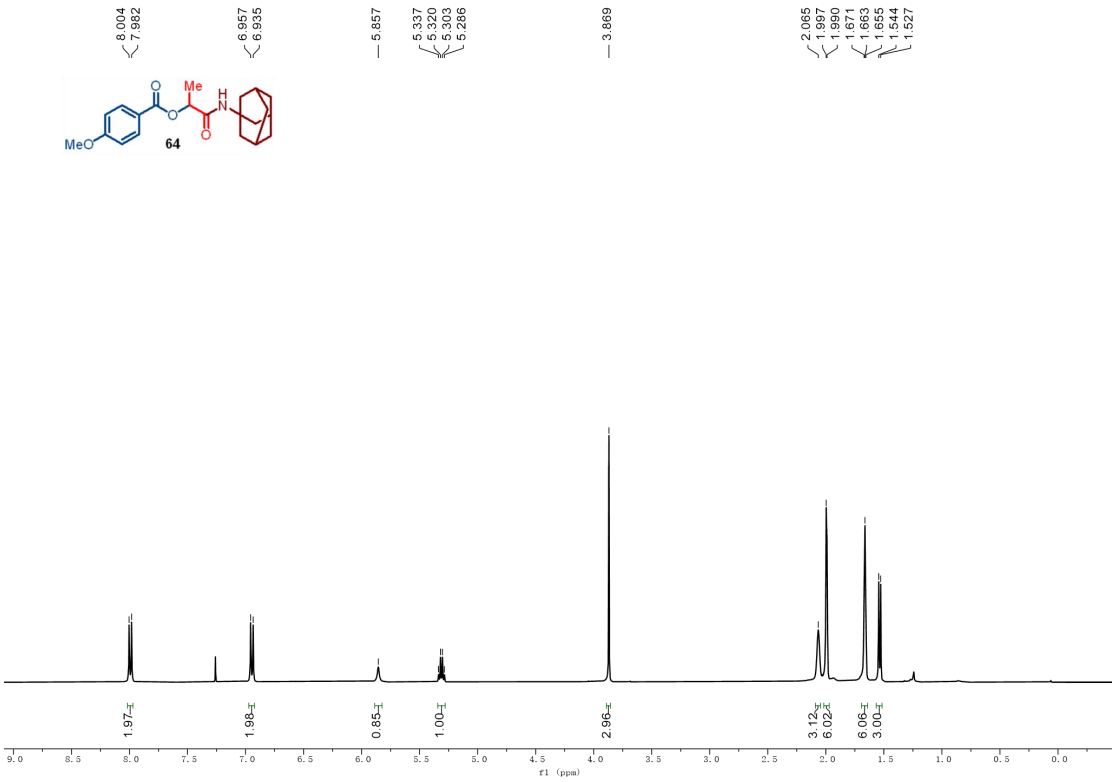
^{13}C NMR (101 MHz, $CDCl_3$) of 62



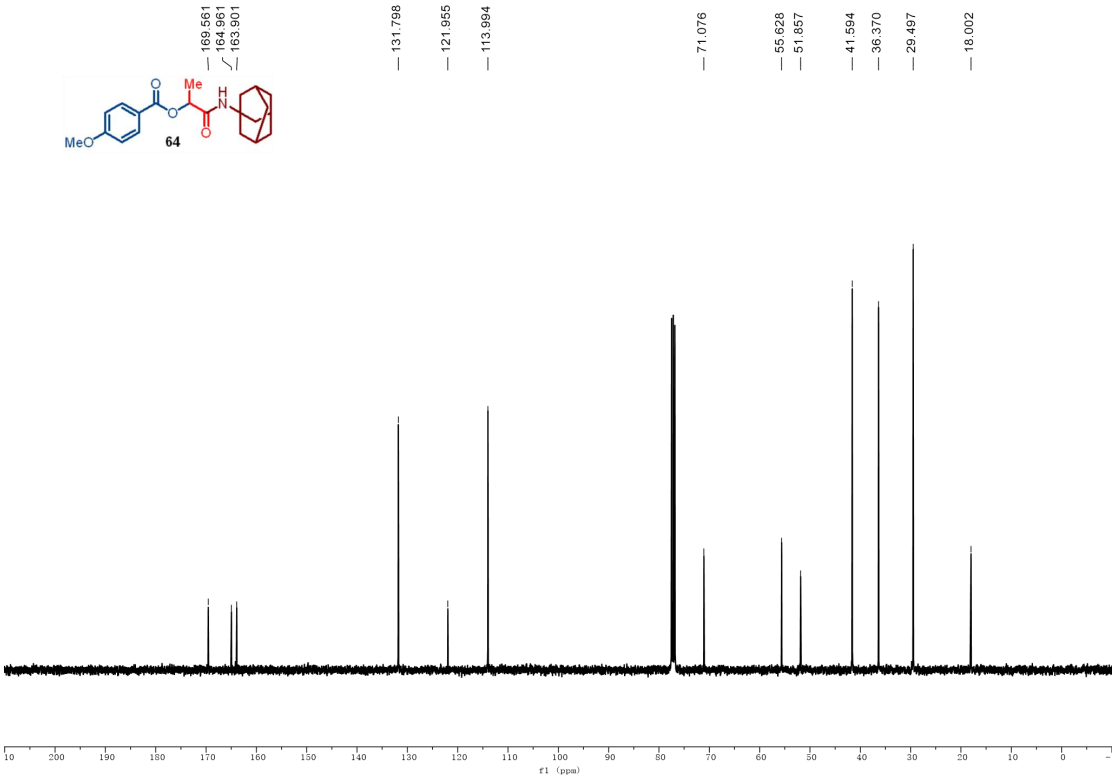
^{1}H NMR (400 MHz, $CDCl_3$) of 63



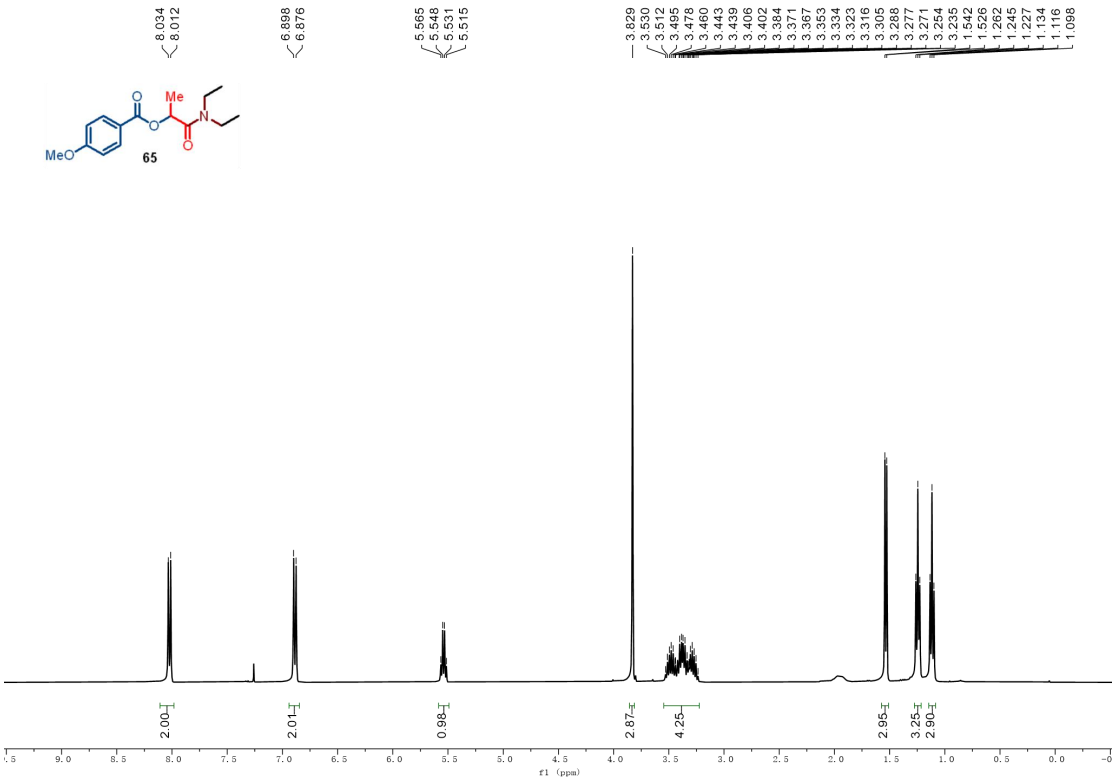
^{13}C NMR (101 MHz, $CDCl_3$) of 63



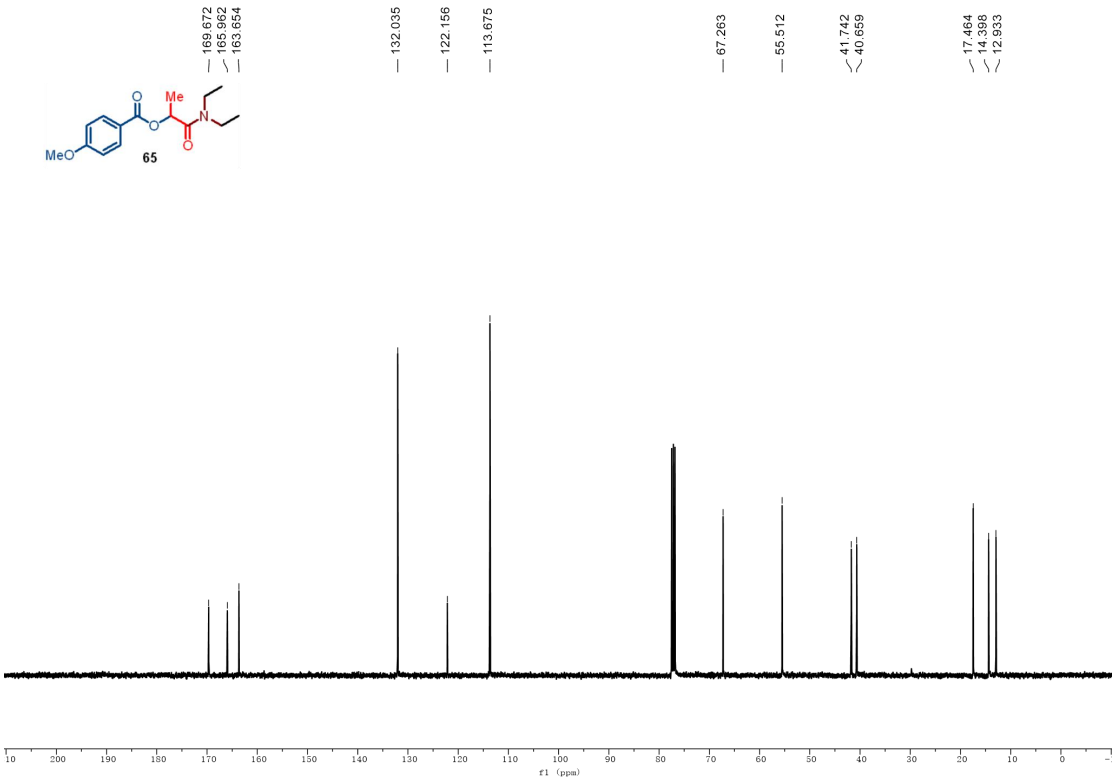
^{1}H NMR (400 MHz, $CDCl_3$) of 64



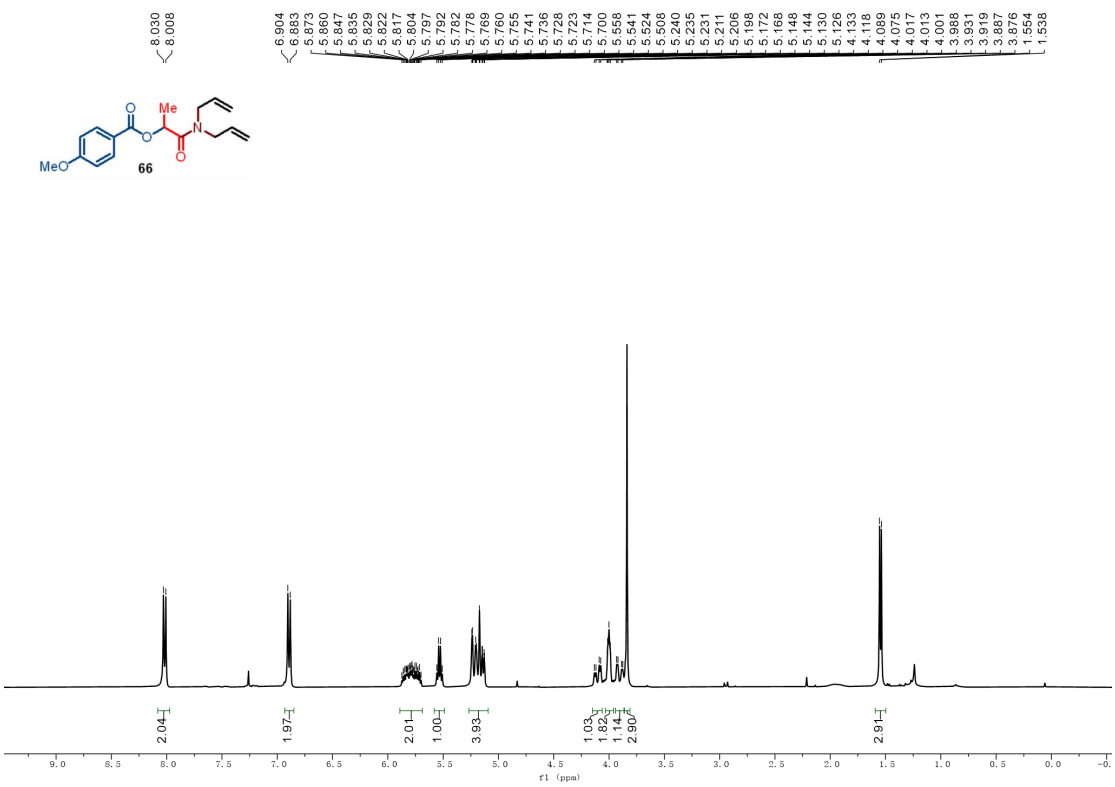
^{13}C NMR (101 MHz, $CDCl_3$) of 64



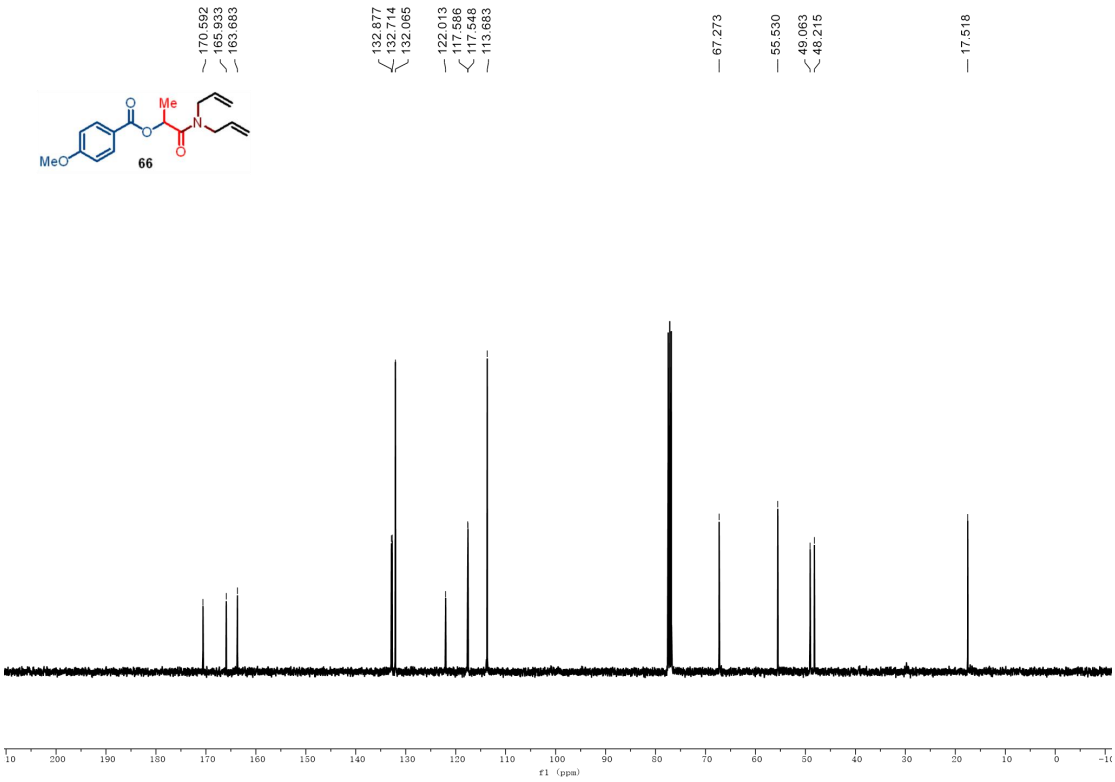
^{1}H NMR (400 MHz, $CDCl_3$) of 65



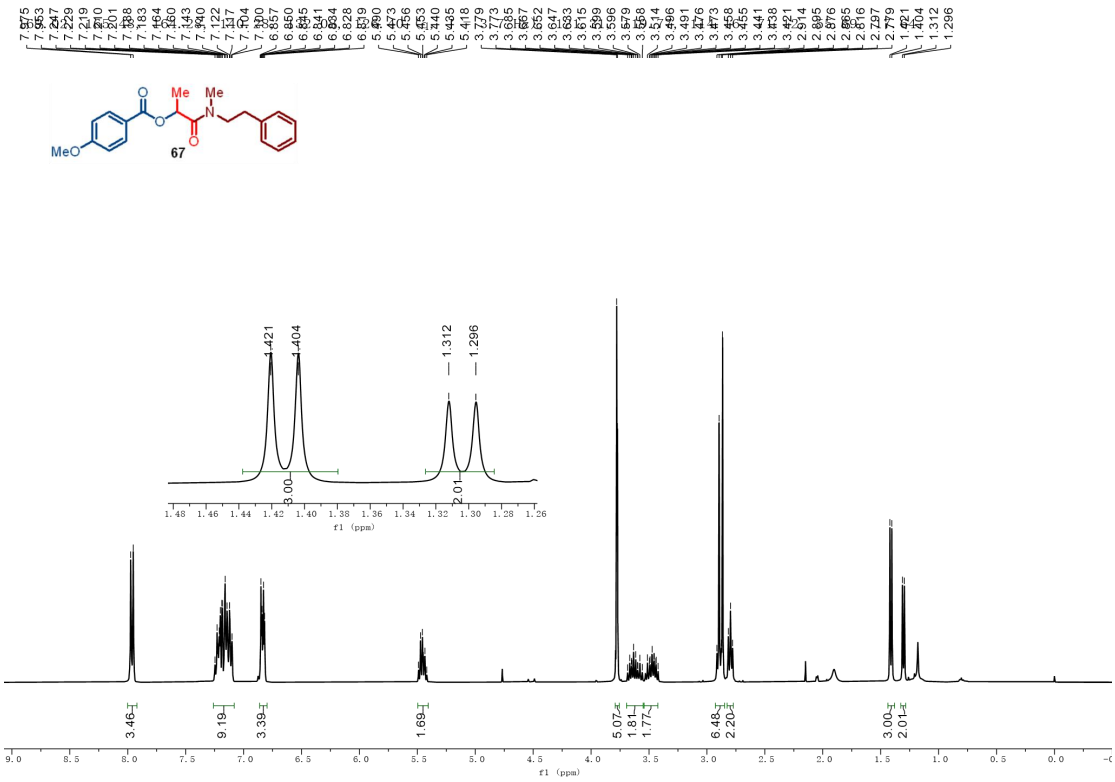
^{13}C NMR (101 MHz, $CDCl_3$) of 65



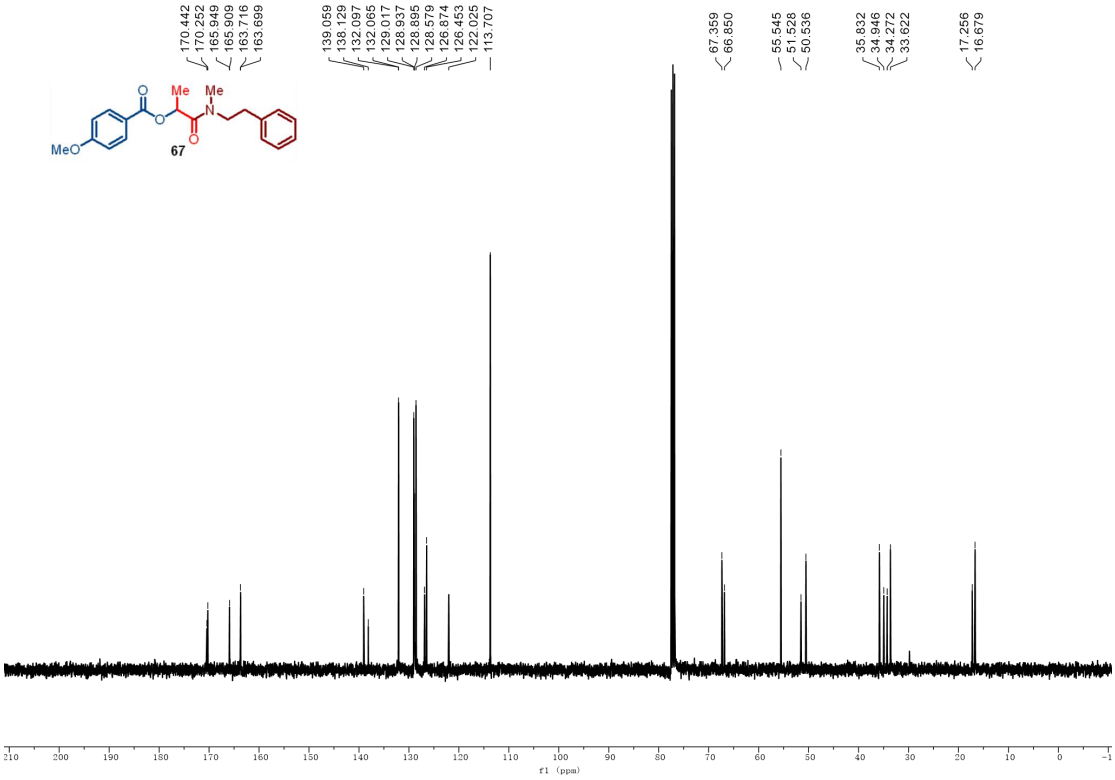
^{1}H NMR (400 MHz, $CDCl_3$) of 66



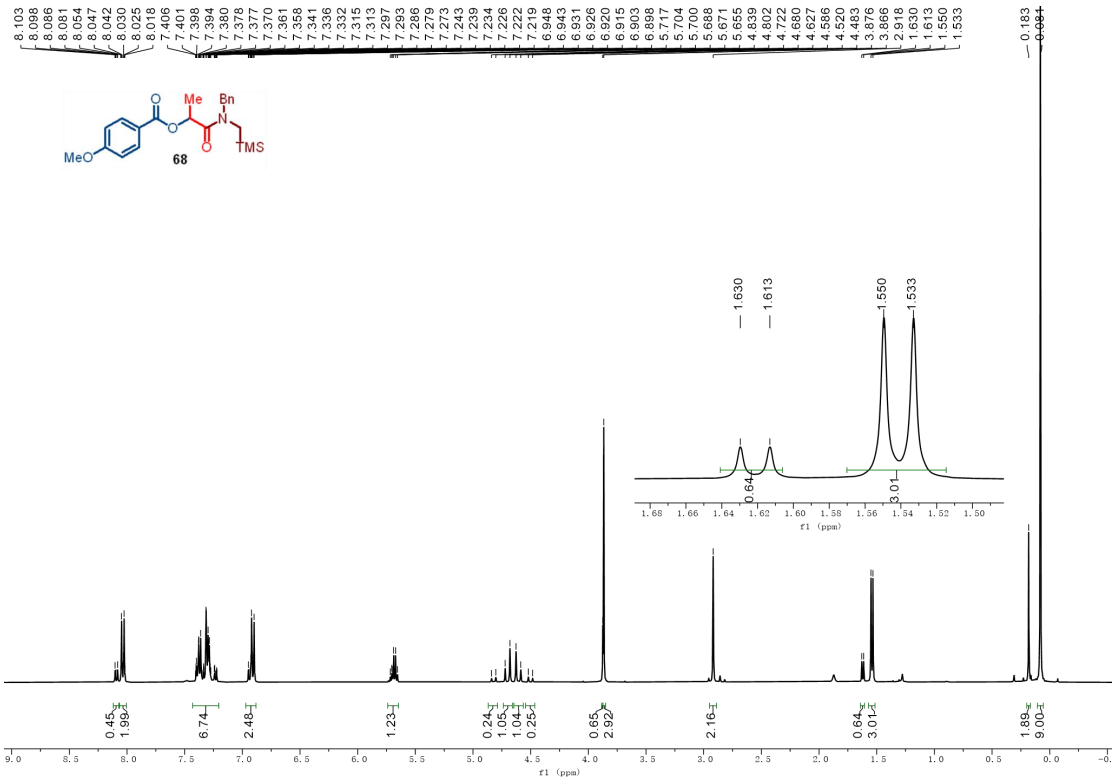
^{13}C NMR (101 MHz, $CDCl_3$) of 66



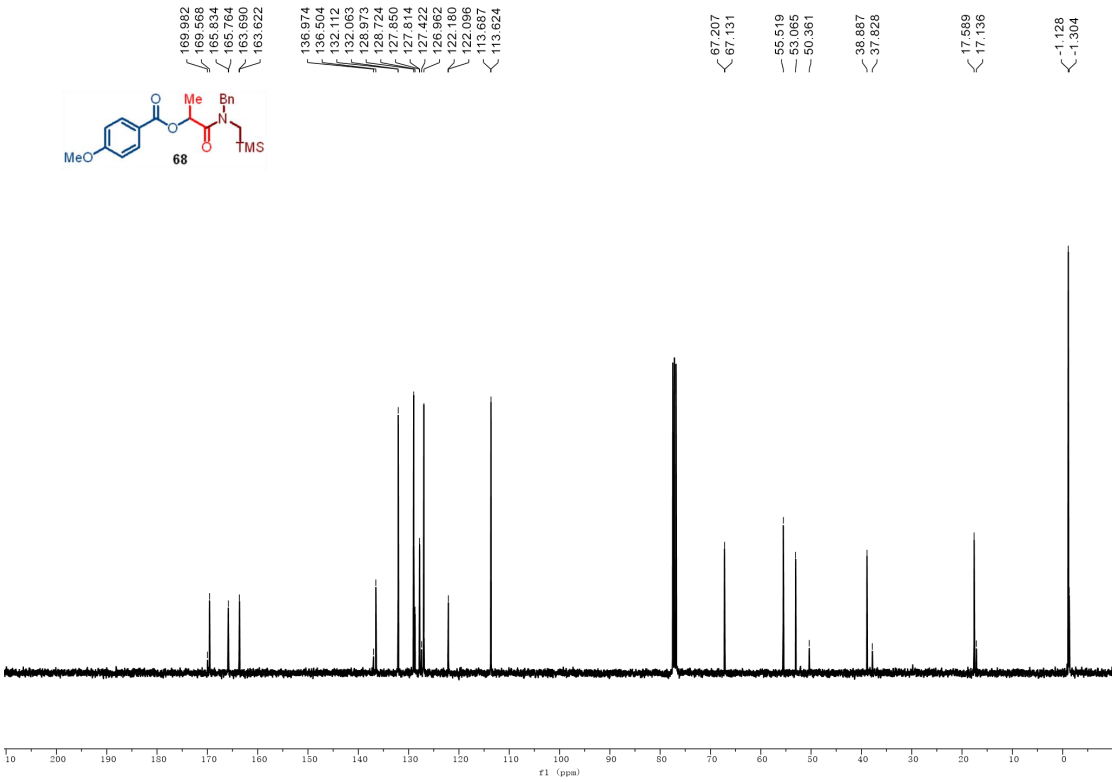
^{1}H NMR (400 MHz, $CDCl_3$) of 67



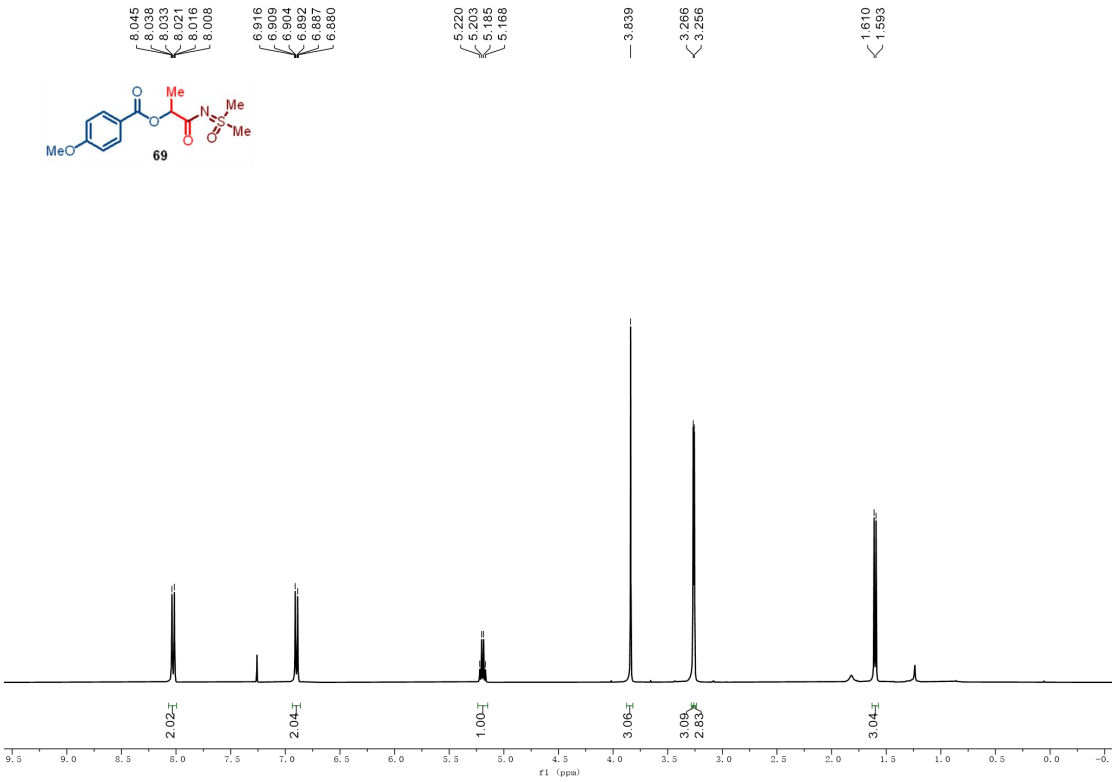
^{13}C NMR (101 MHz, $CDCl_3$) of 67



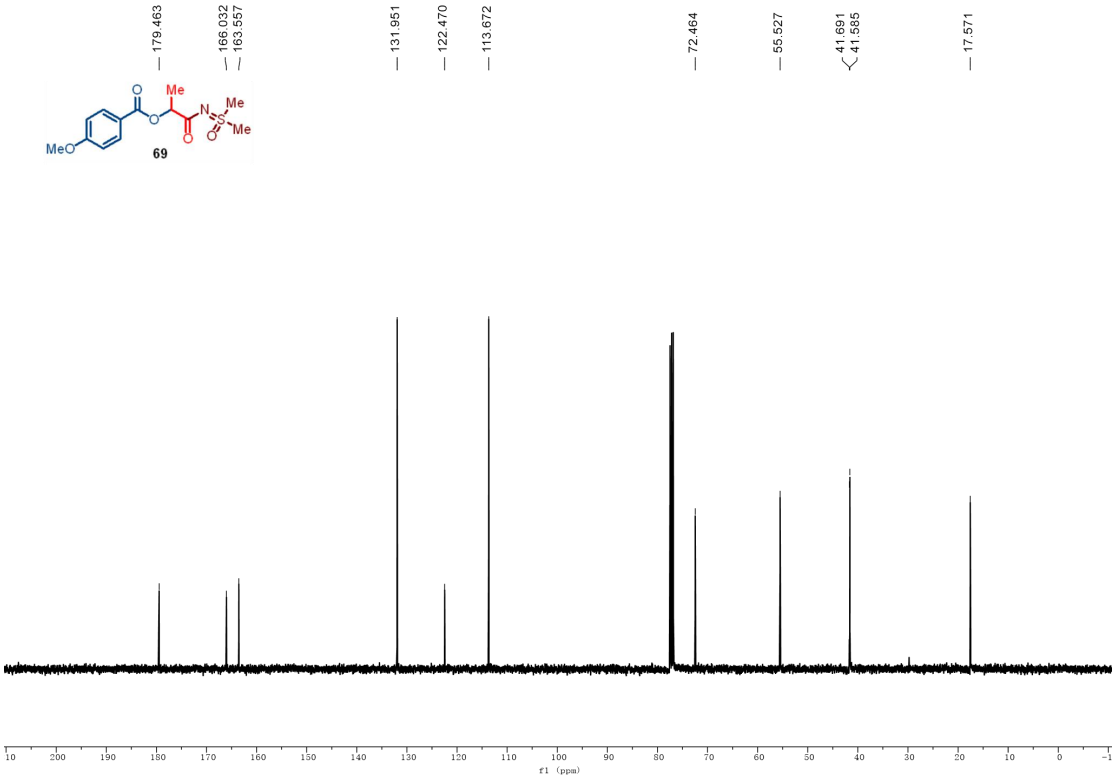
^{1}H NMR (400 MHz, $CDCl_3$) of 68



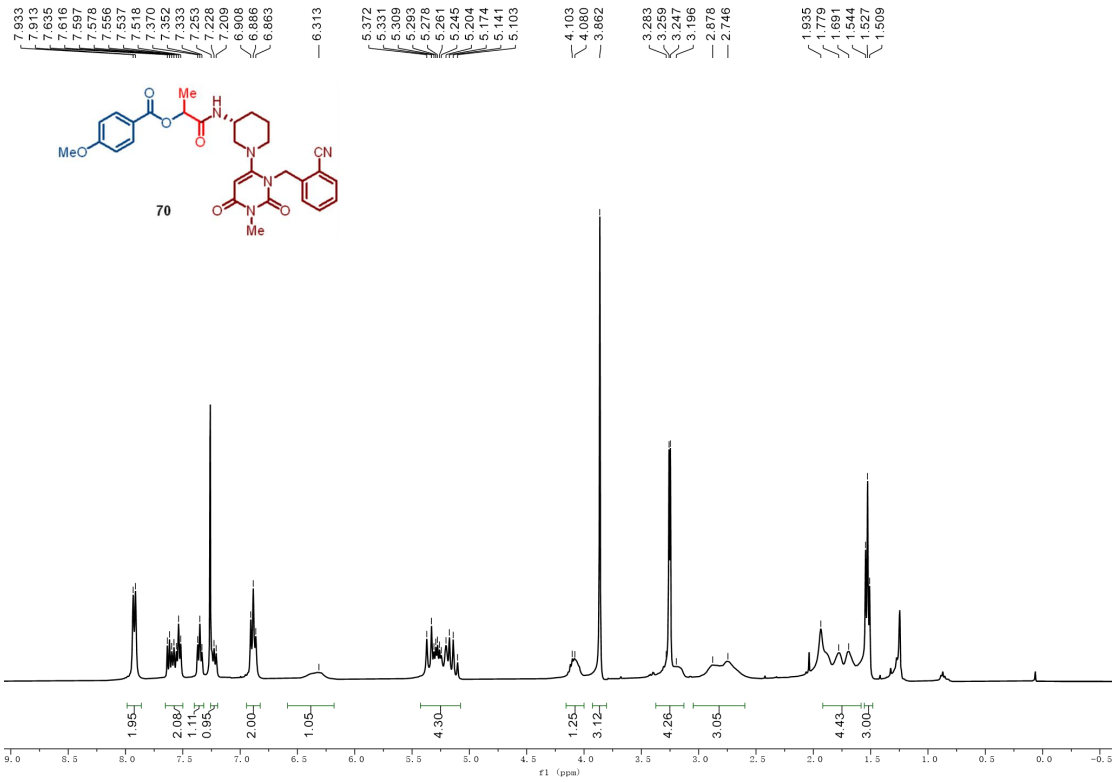
^{13}C NMR (101 MHz, $CDCl_3$) of 68



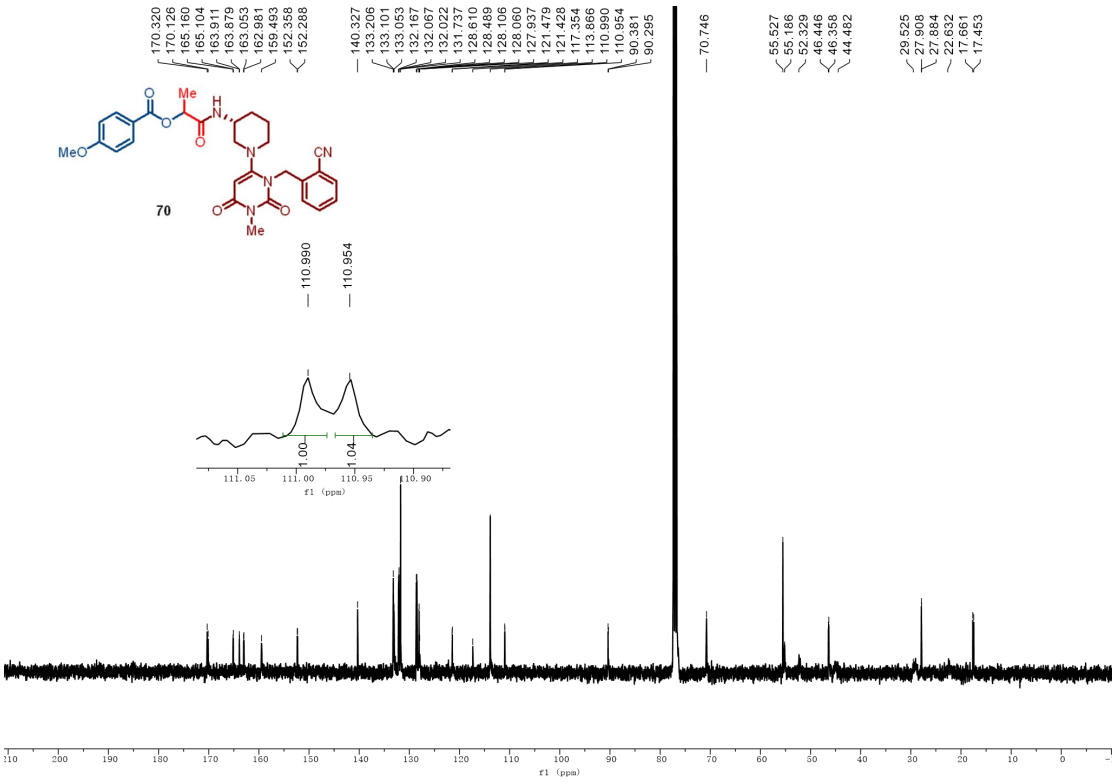
^{1}H NMR (400 MHz, $CDCl_3$) of 69



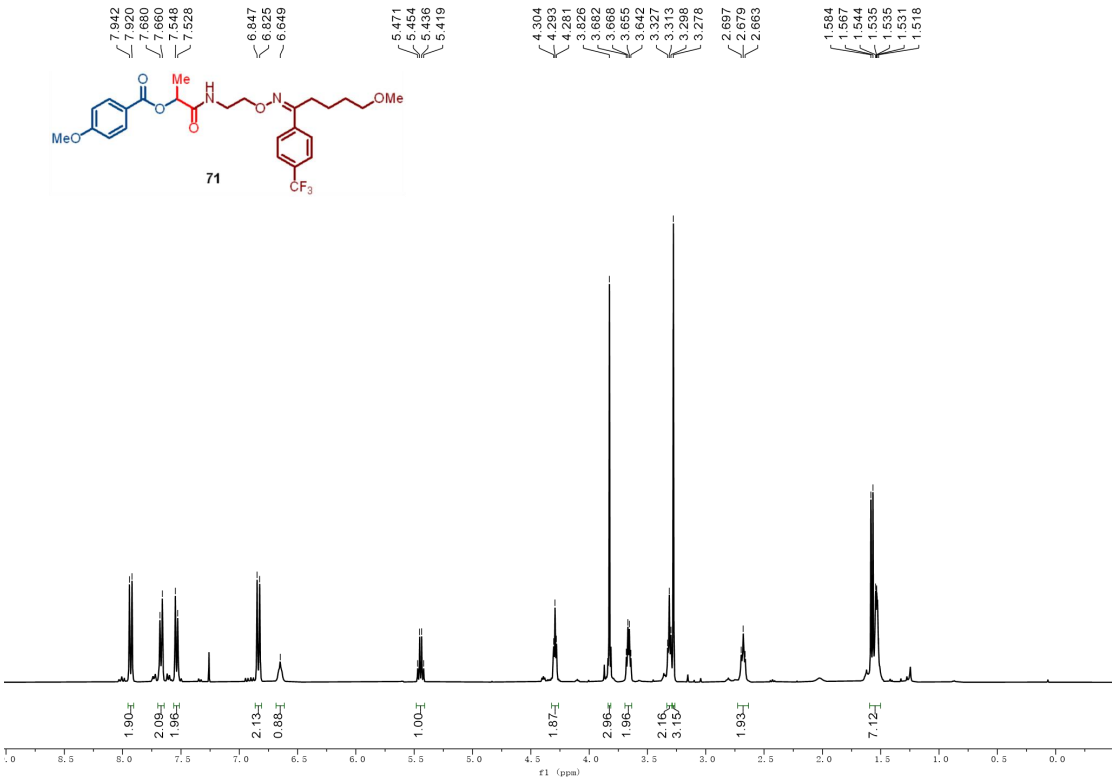
^{13}C NMR (101 MHz, $CDCl_3$) of 69



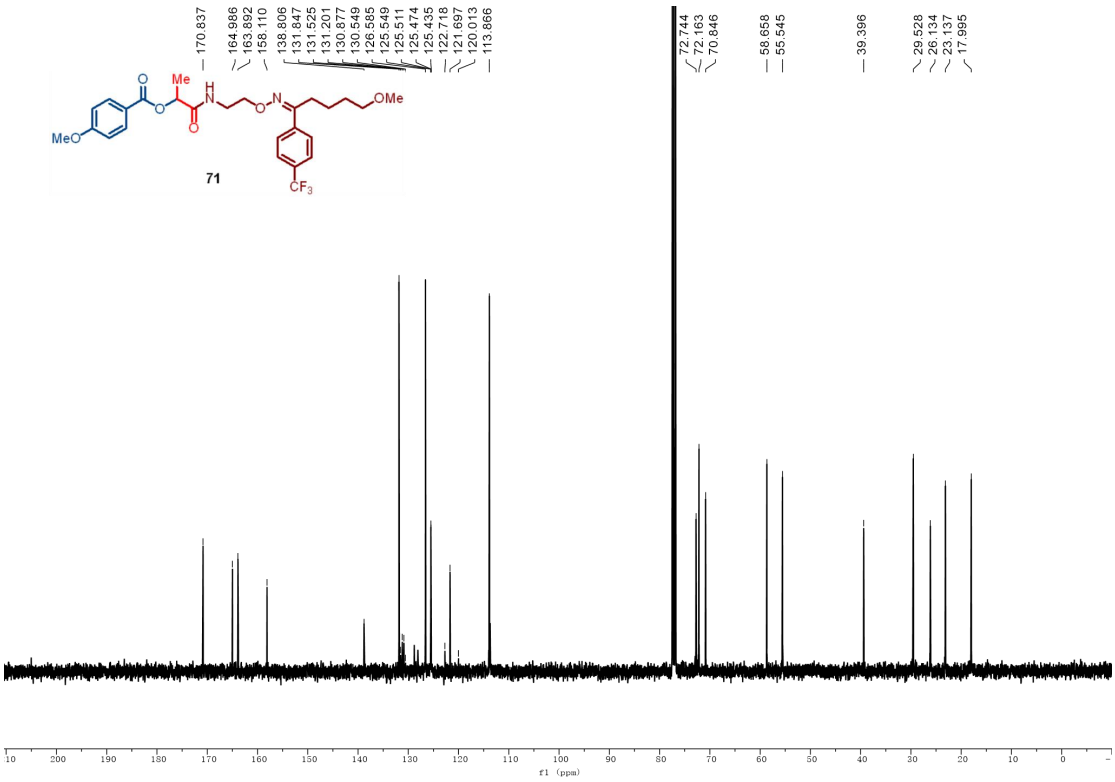
^{1}H NMR (400 MHz, $CDCl_3$) of 70



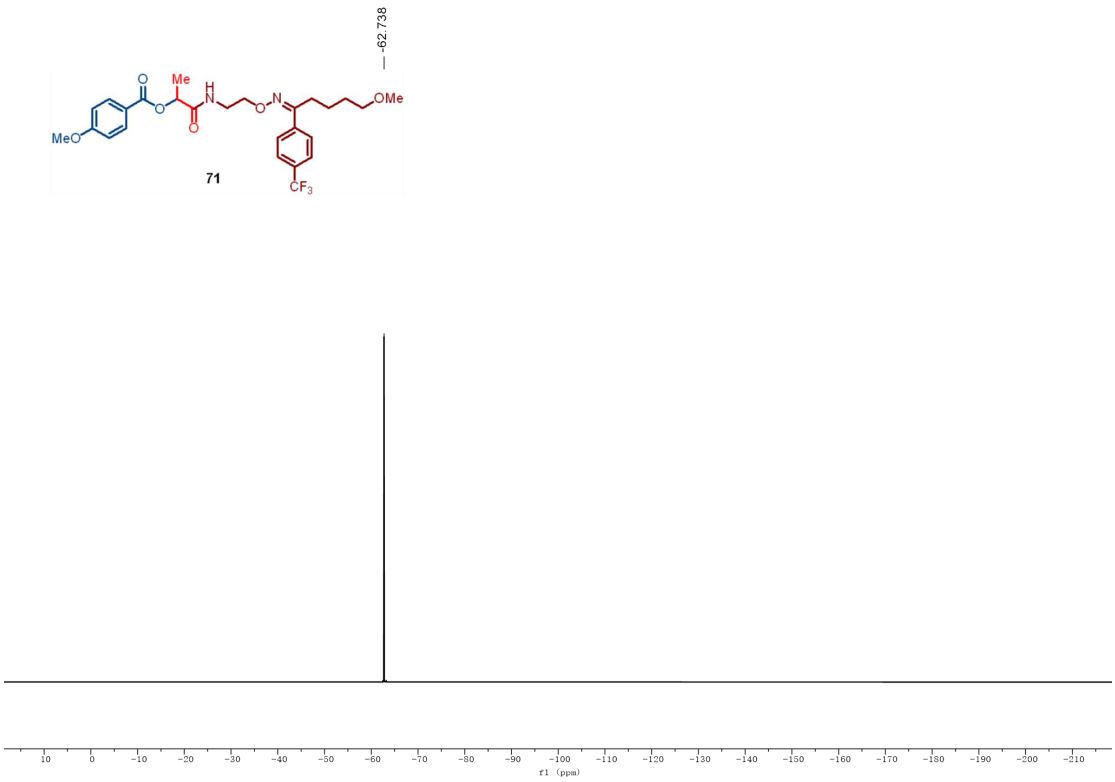
^{13}C NMR (101 MHz, $CDCl_3$) of 70



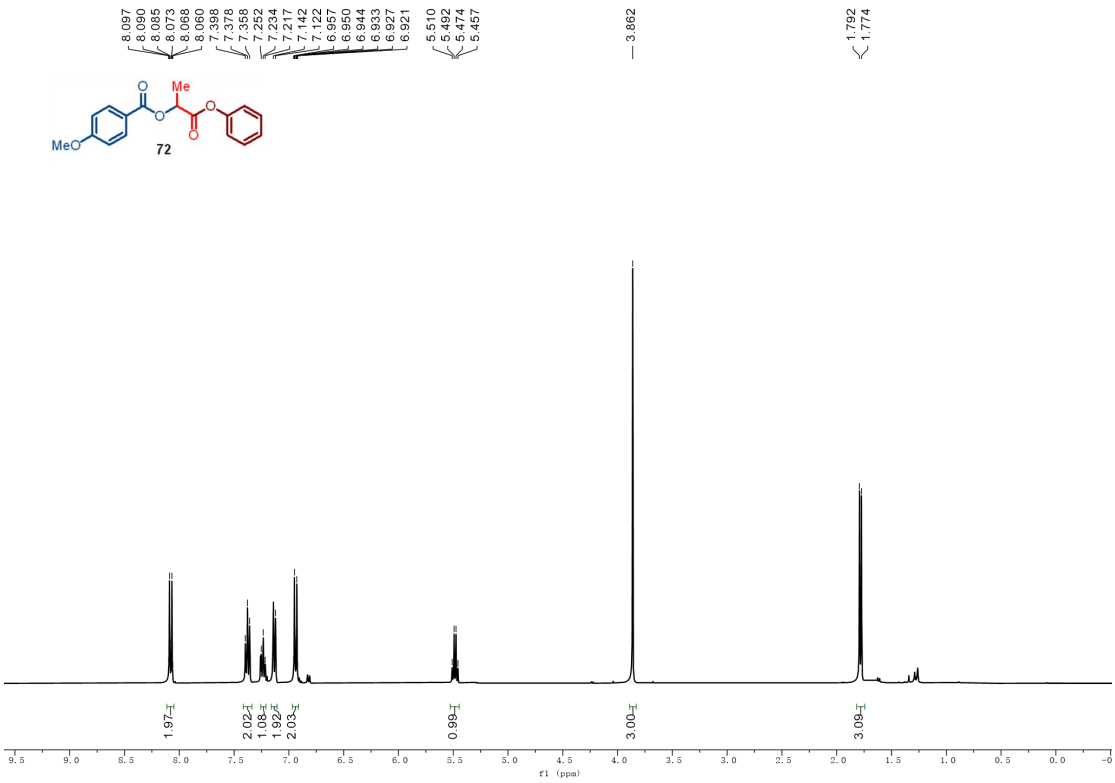
^{1}H NMR (400 MHz, $CDCl_3$) of 71



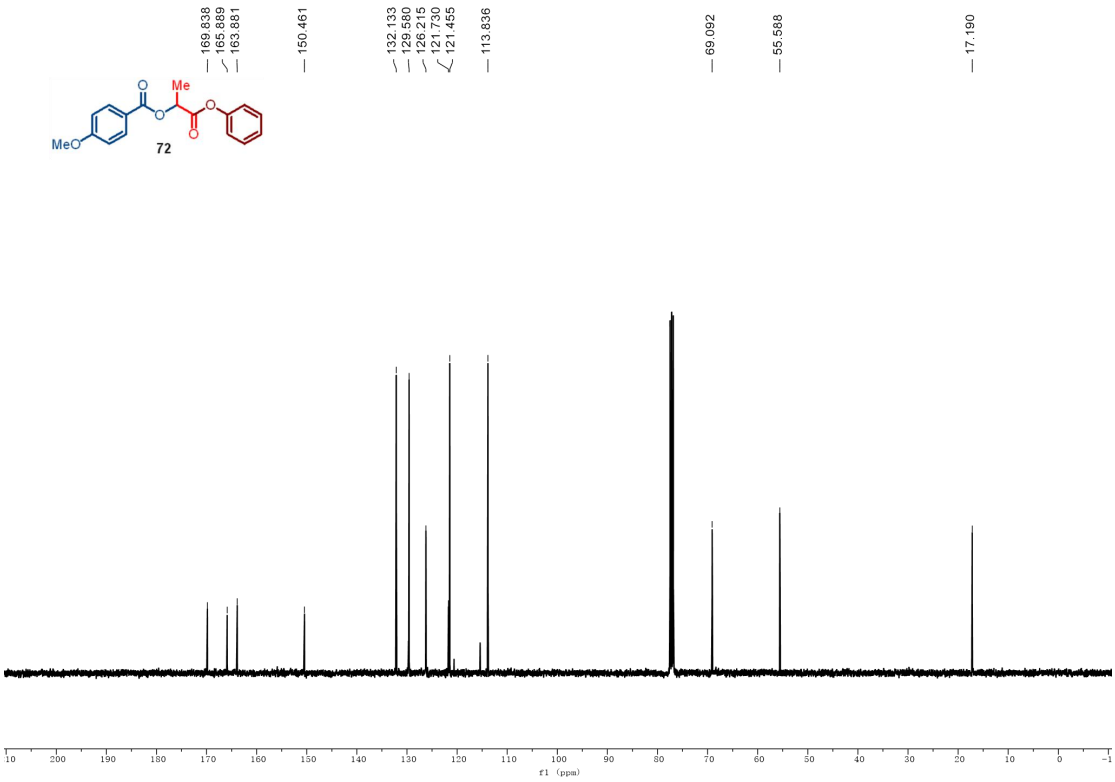
^{13}C NMR (101 MHz, $CDCl_3$) of 71



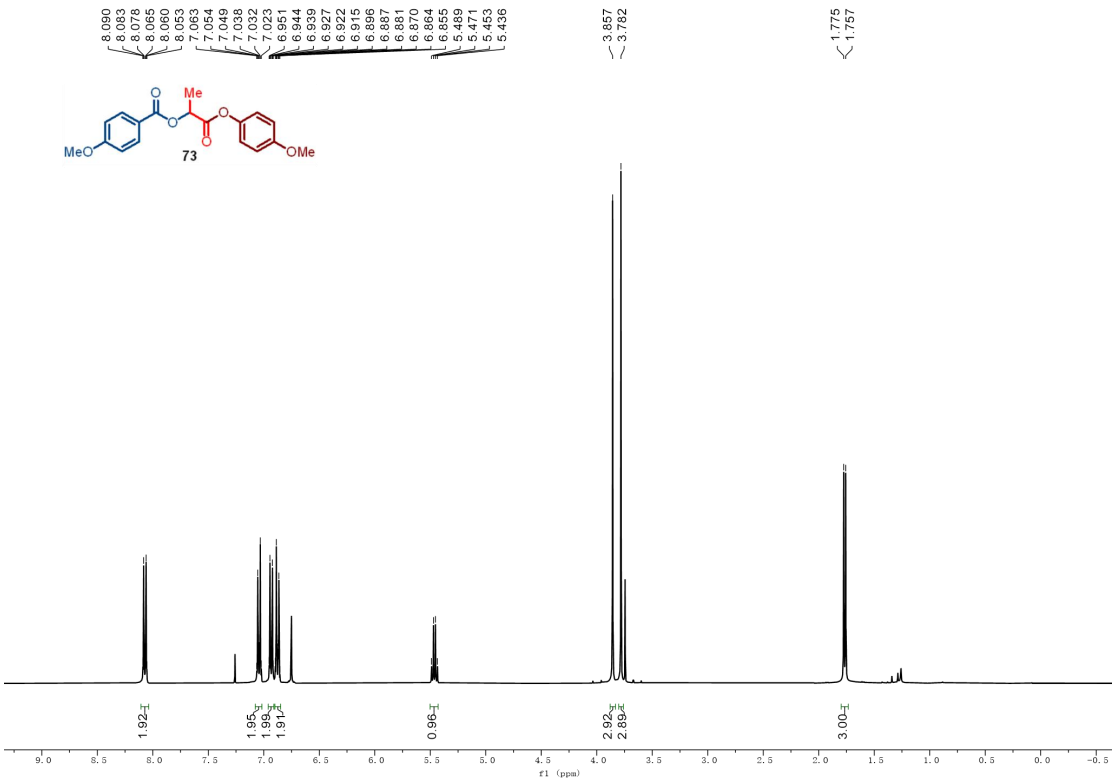
^{19}F NMR (376 MHz, $CDCl_3$) of 71



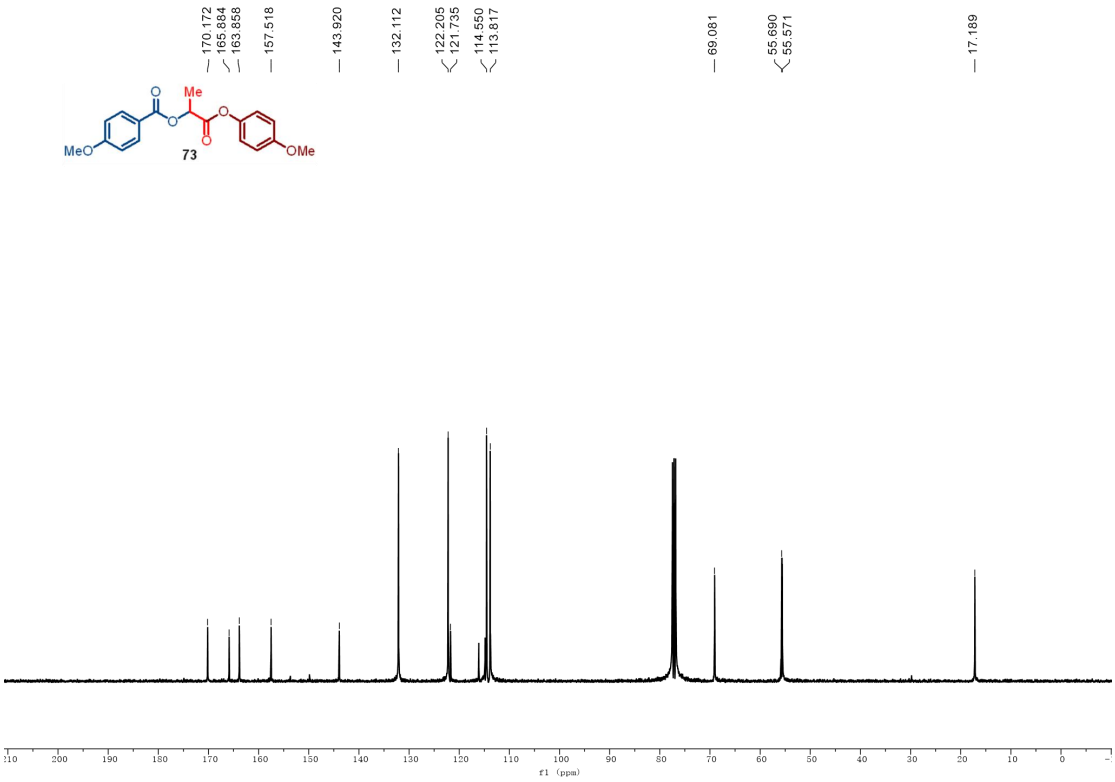
^{1}H NMR (400 MHz, $CDCl_3$) of 72



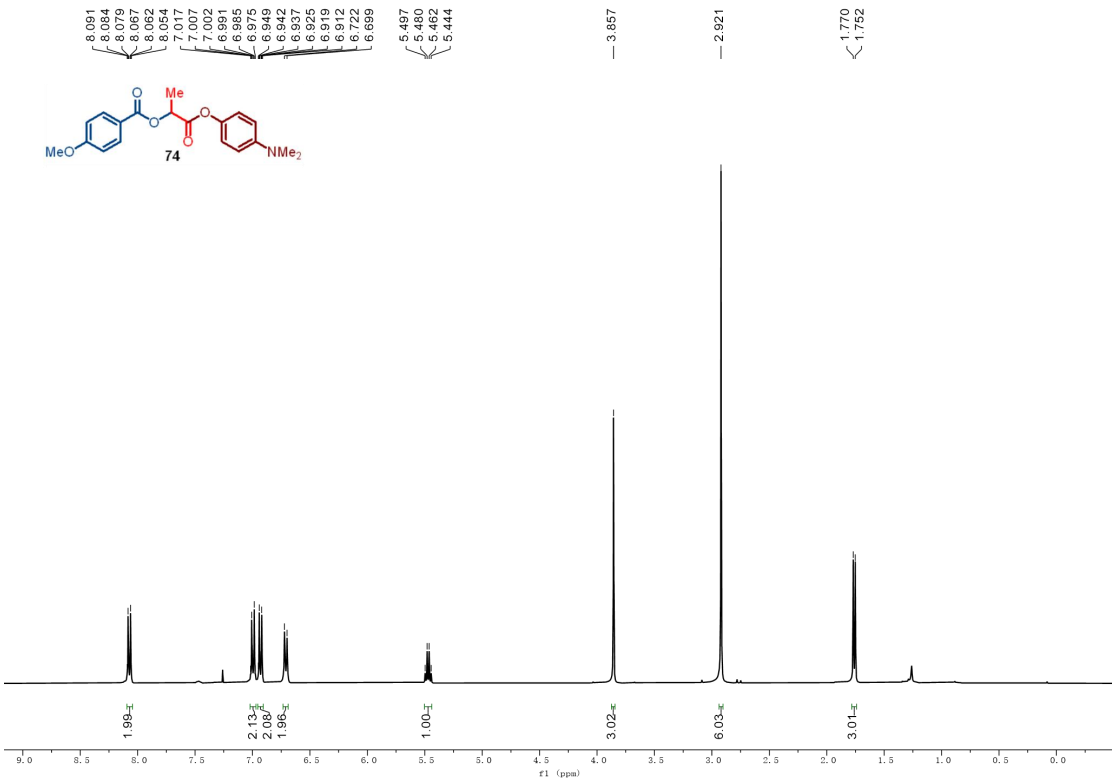
^{13}C NMR (101 MHz, $CDCl_3$) of 72



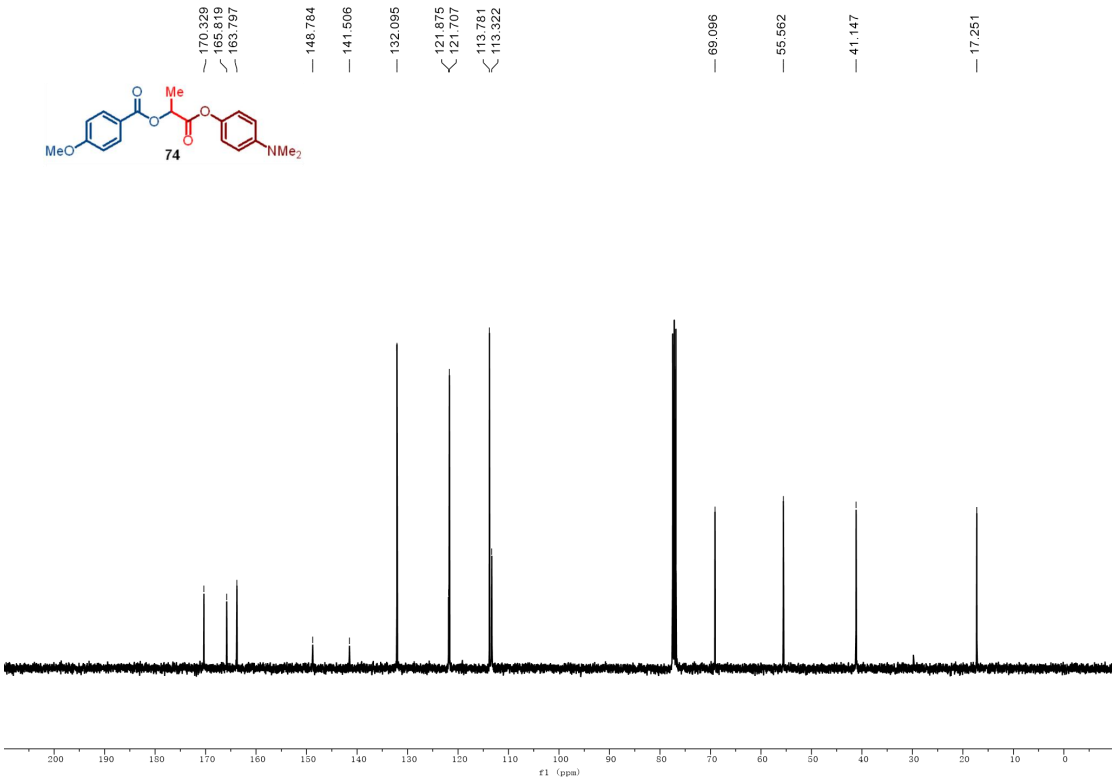
^{1}H NMR (400 MHz, $CDCl_3$) of 73



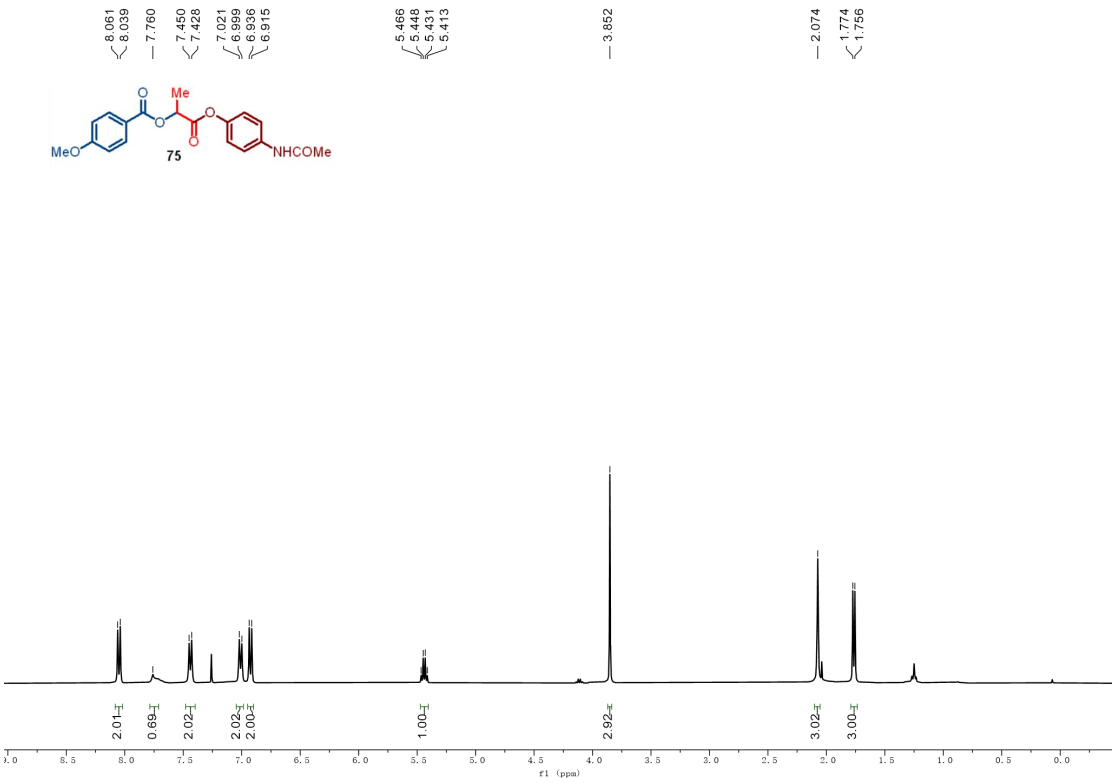
^{13}C NMR (101 MHz, $CDCl_3$) of 73



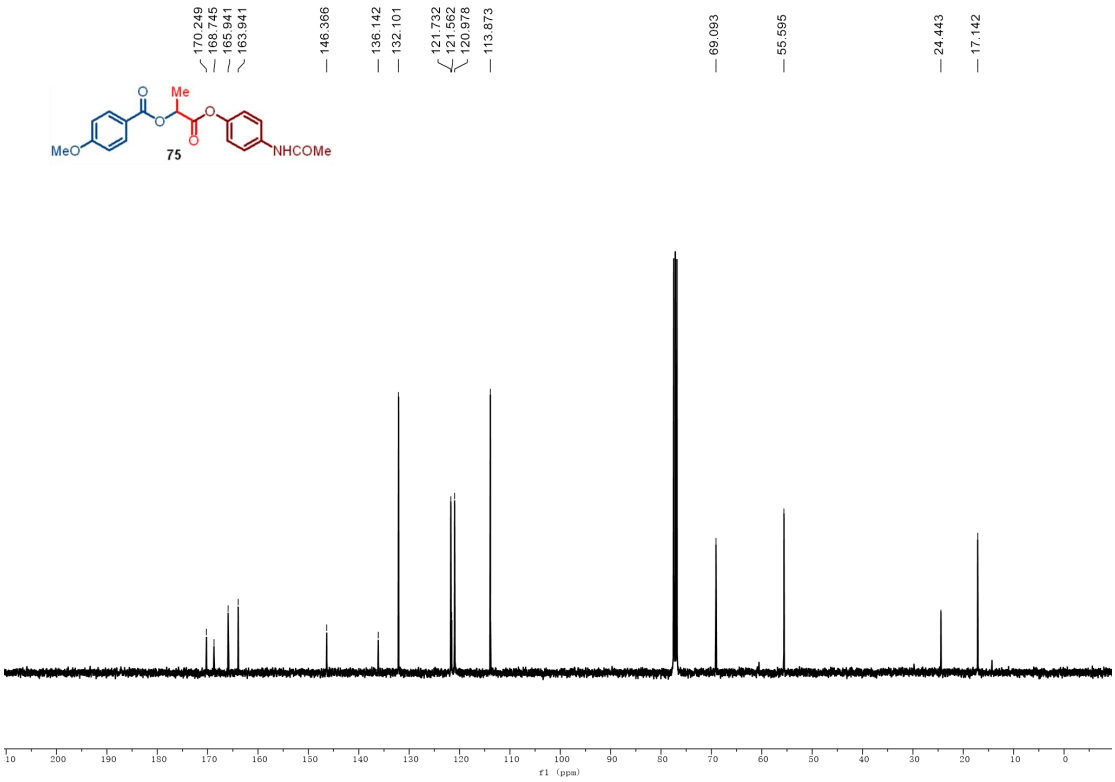
^{1}H NMR (400 MHz, $CDCl_3$) of 74



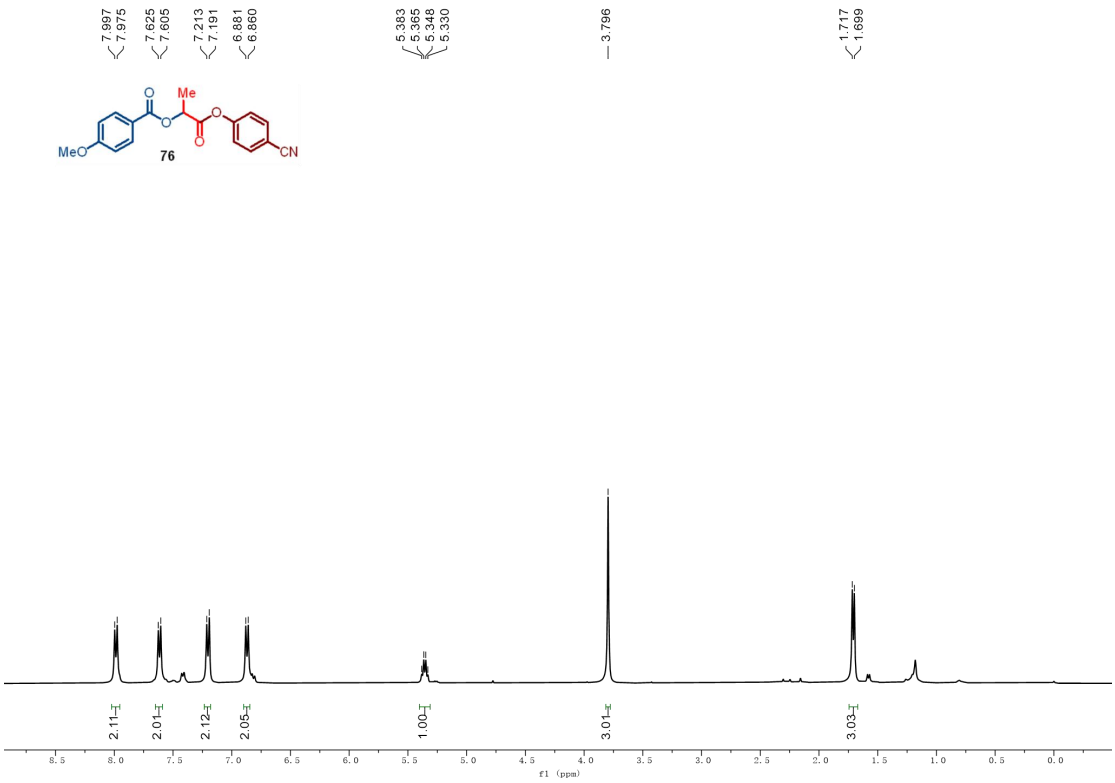
^{13}C NMR (101 MHz, $CDCl_3$) of 74



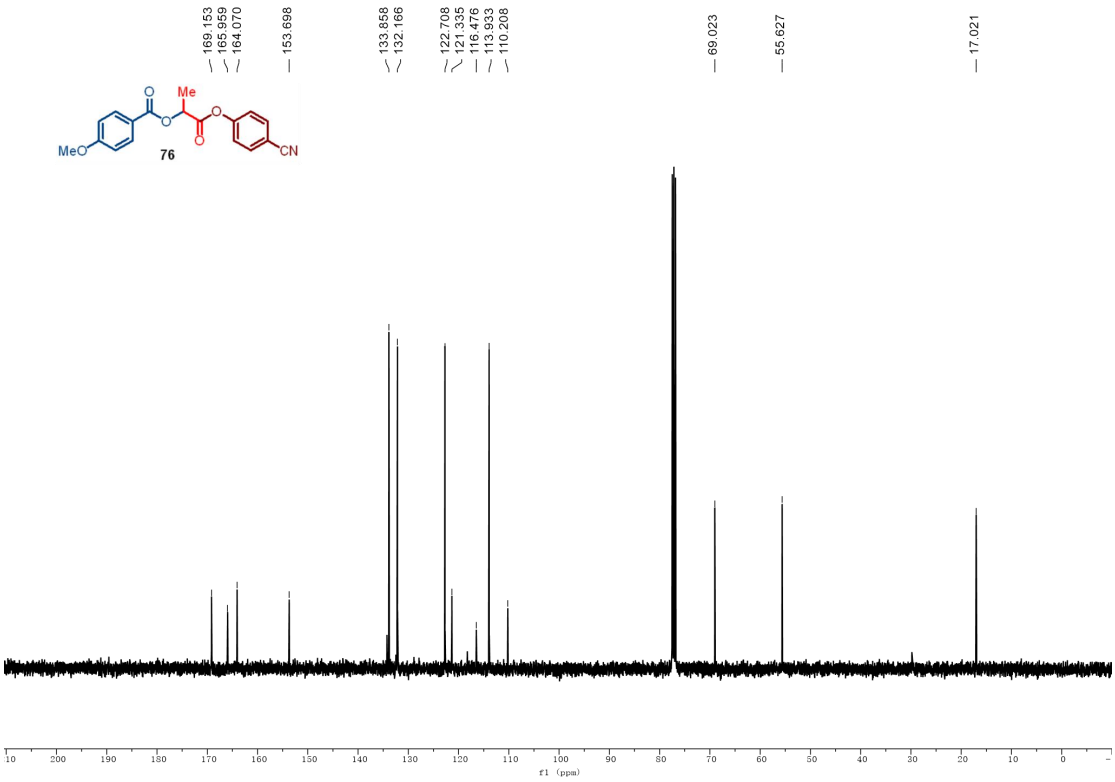
^{1}H NMR (400 MHz, $CDCl_3$) of 75



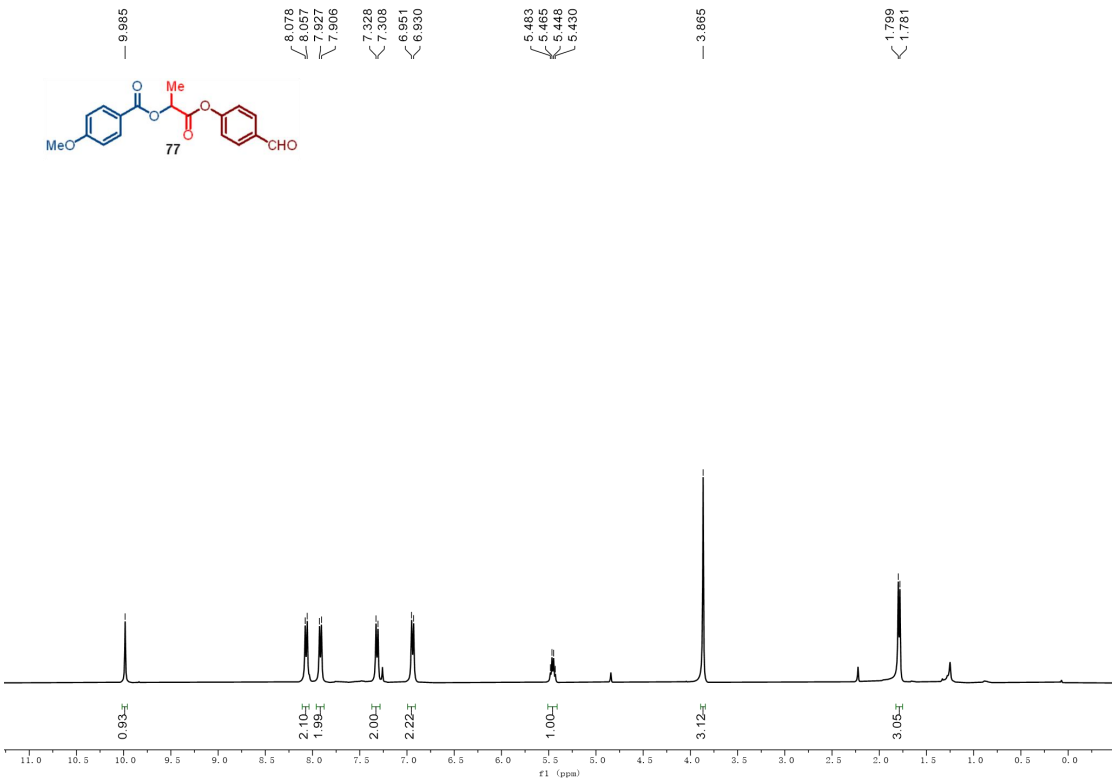
^{13}C NMR (101 MHz, $CDCl_3$) of 75



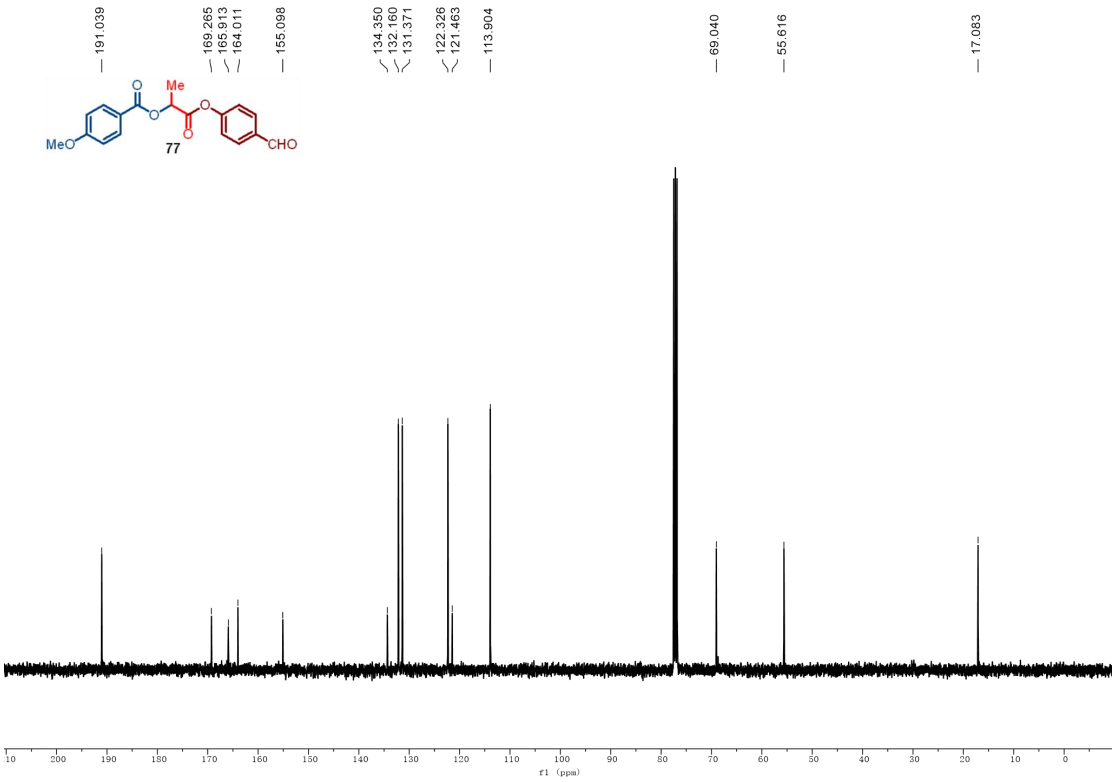
^{1}H NMR (400 MHz, $CDCl_3$) of 76



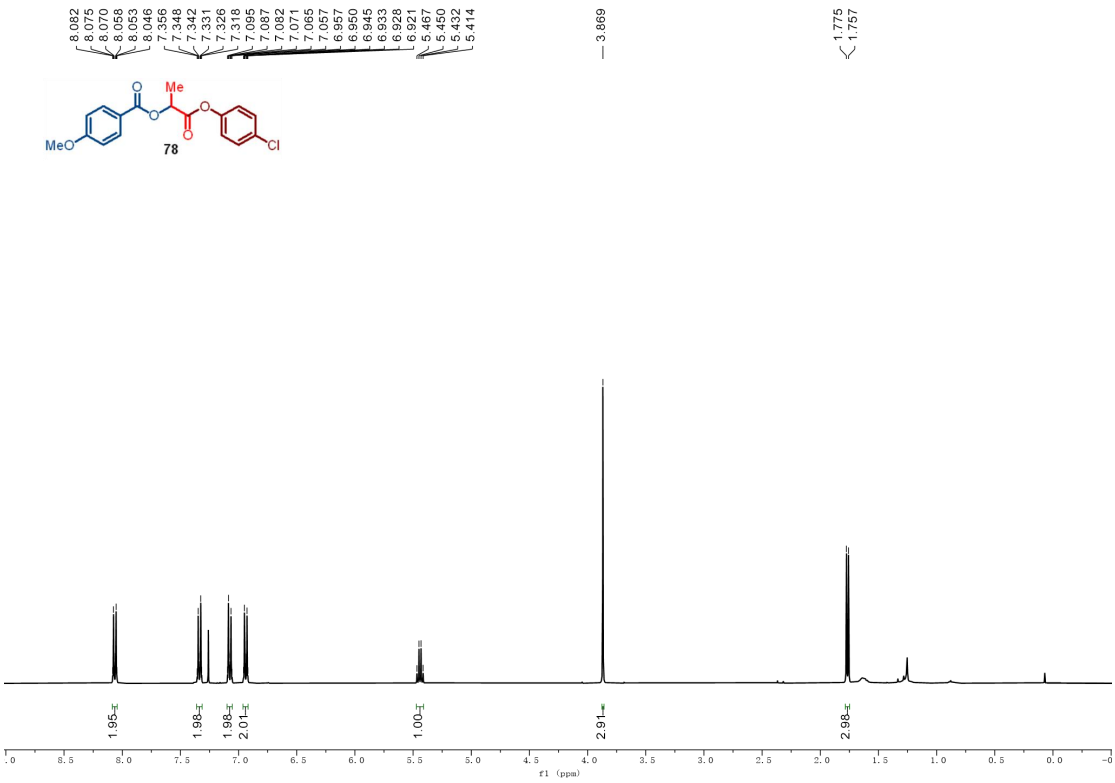
^{13}C NMR (101 MHz, $CDCl_3$) of 76



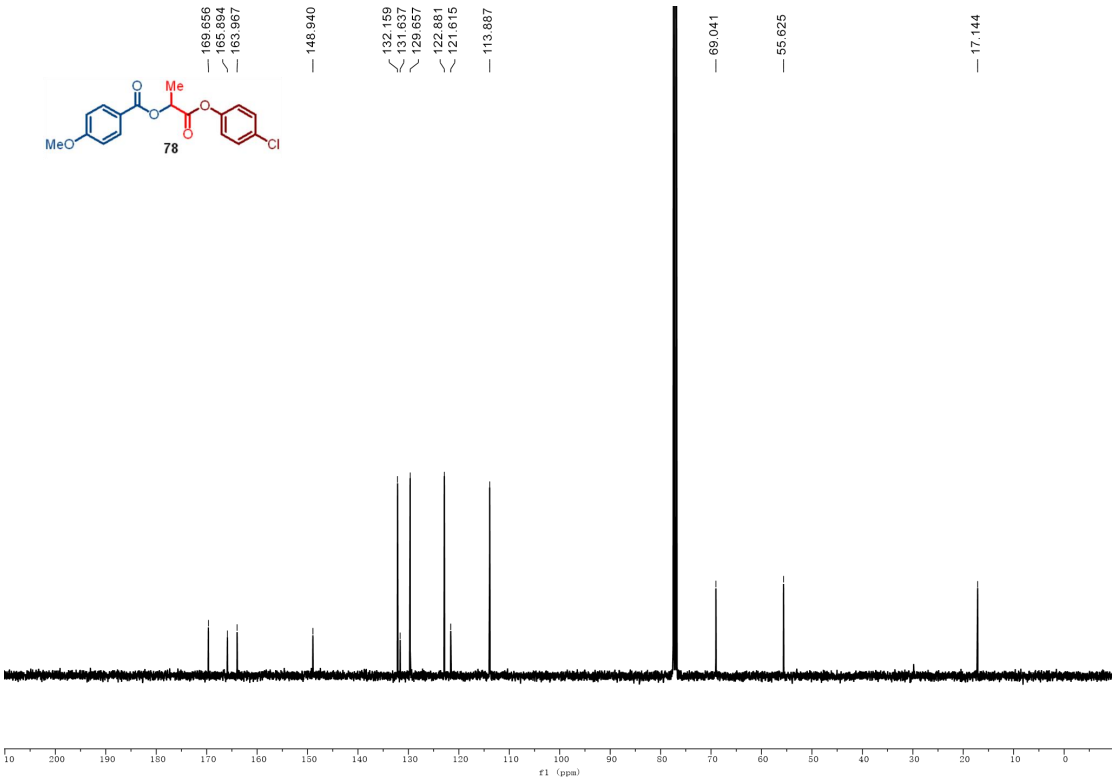
^{1}H NMR (400 MHz, $CDCl_3$) of 77



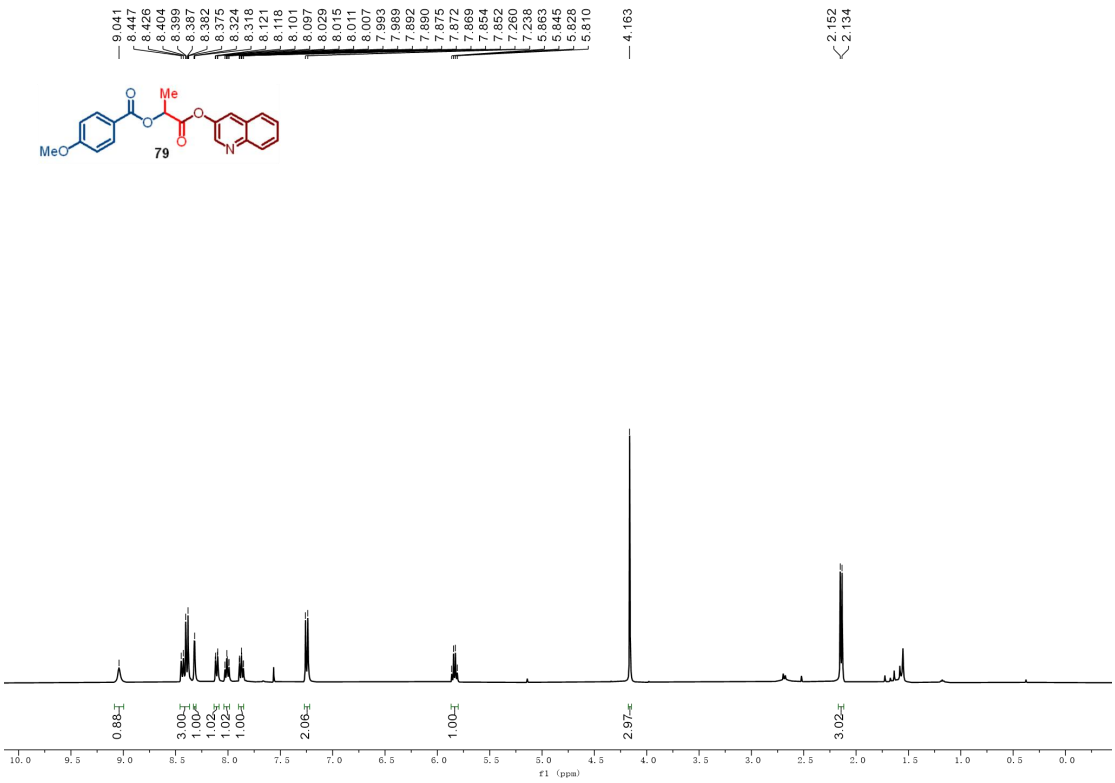
^{13}C NMR (101 MHz, $CDCl_3$) of 77



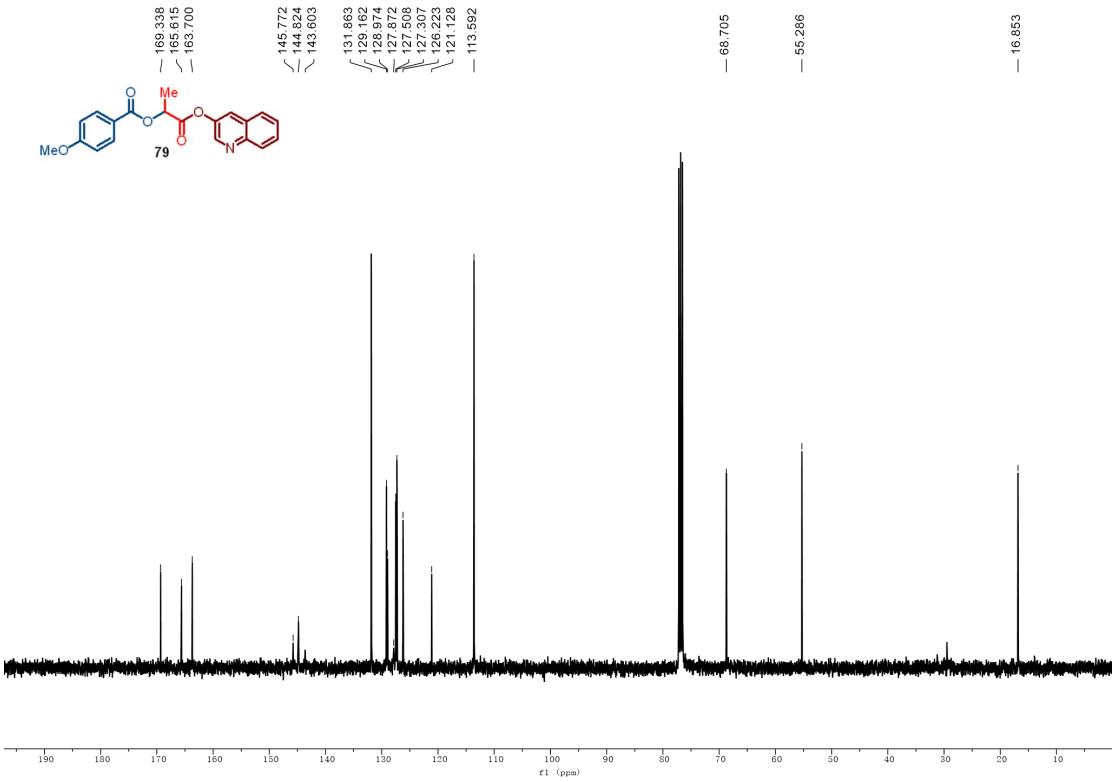
^{1}H NMR (400 MHz, $CDCl_3$) of 78



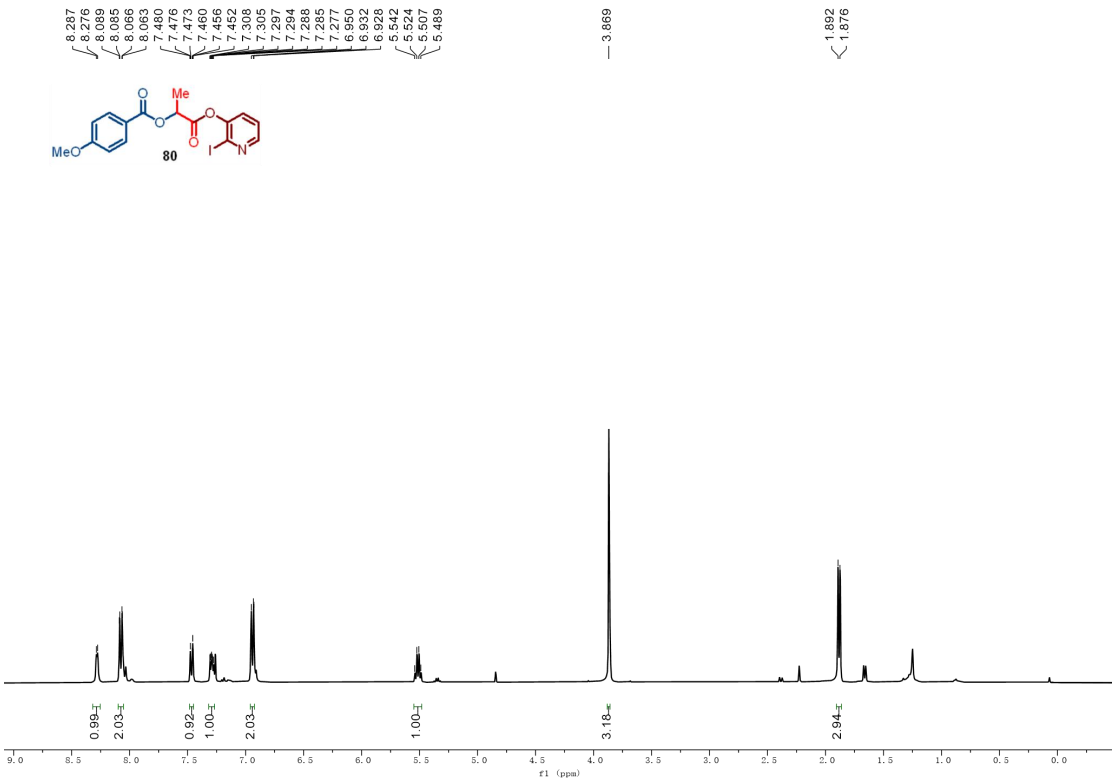
^{13}C NMR (101 MHz, $CDCl_3$) of 78



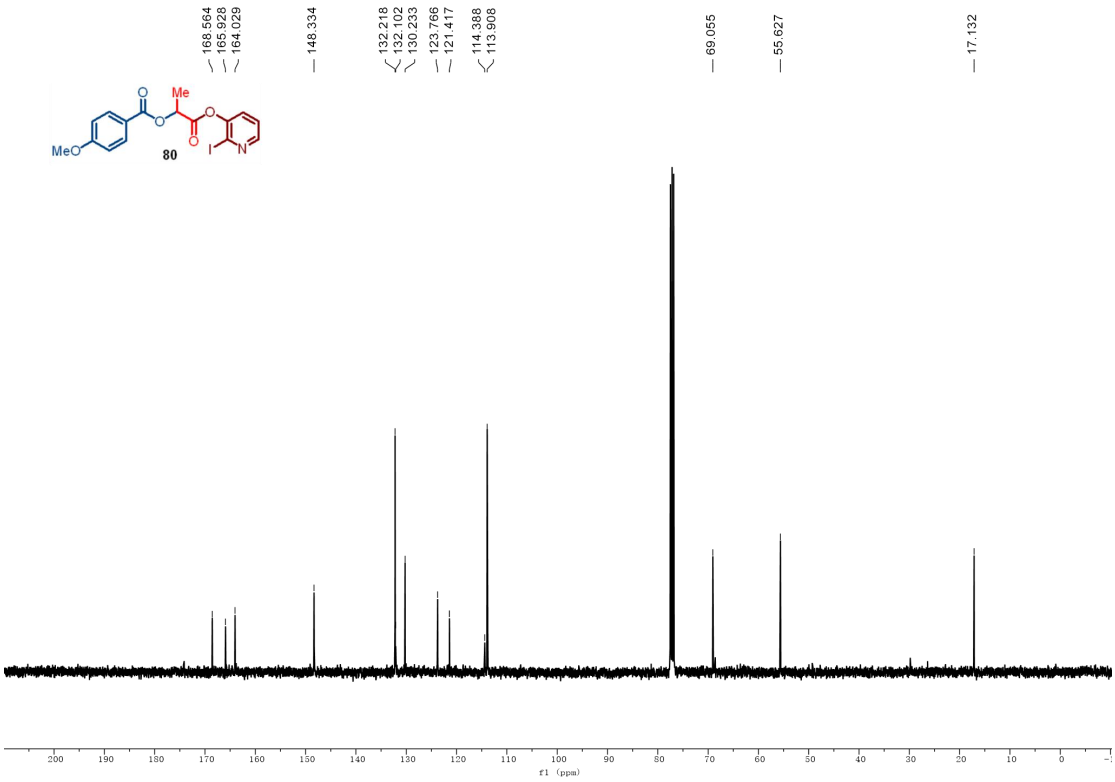
^{1}H NMR (400 MHz, $CDCl_3$) of 79



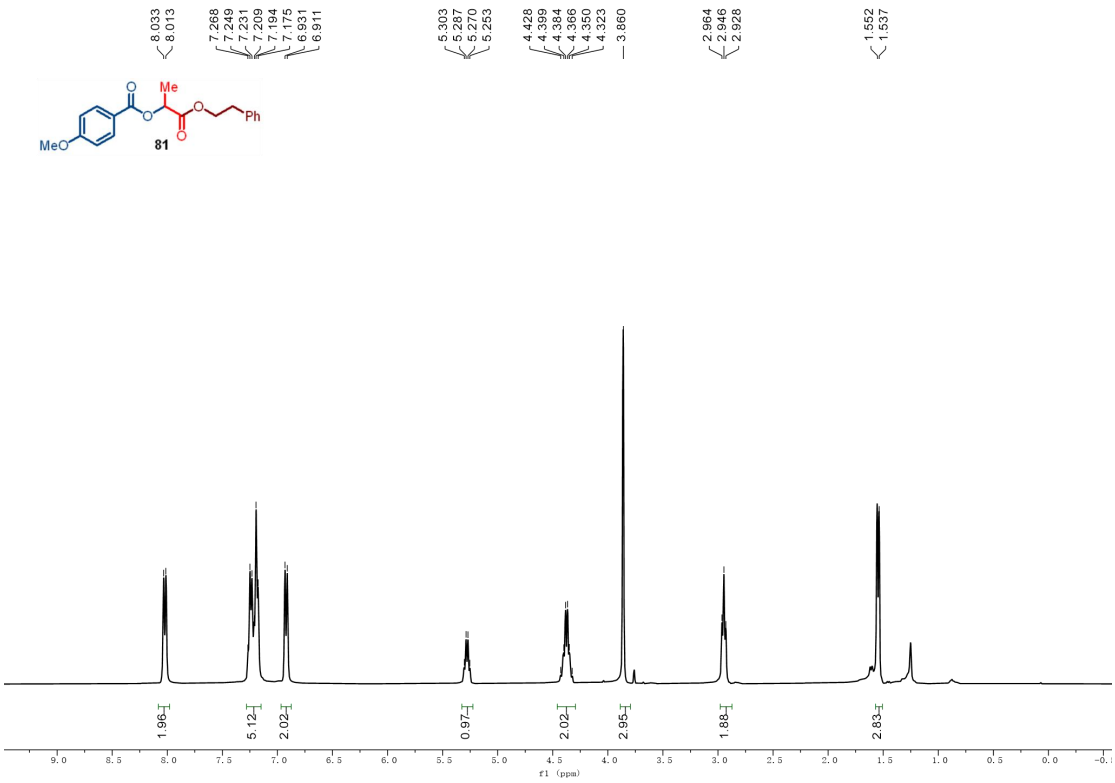
^{13}C NMR (101 MHz, $CDCl_3$) of 79



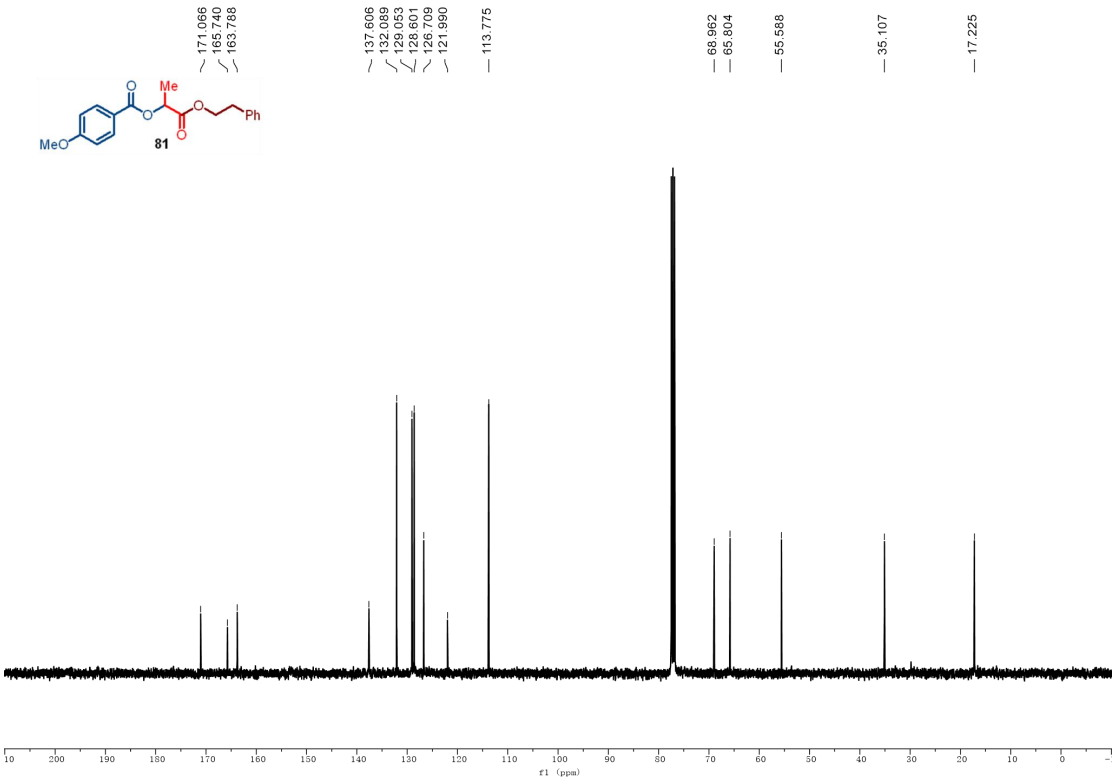
^{1}H NMR (400 MHz, $CDCl_3$) of 80



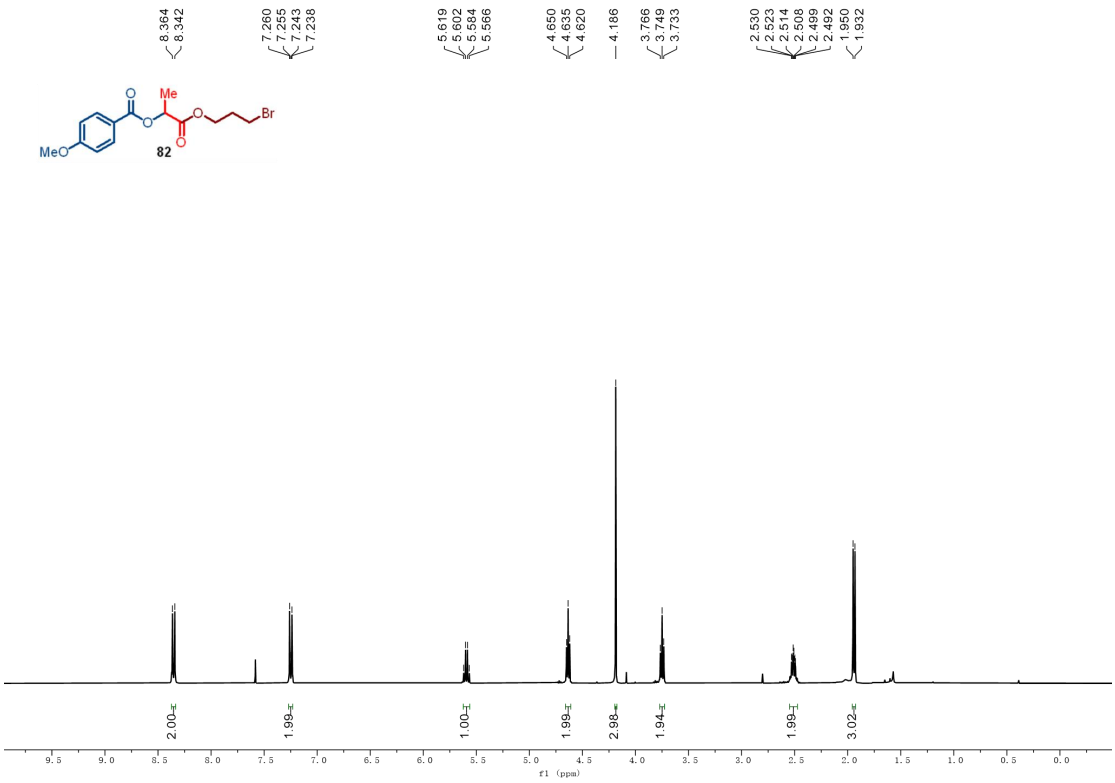
^{13}C NMR (101 MHz, $CDCl_3$) of 80



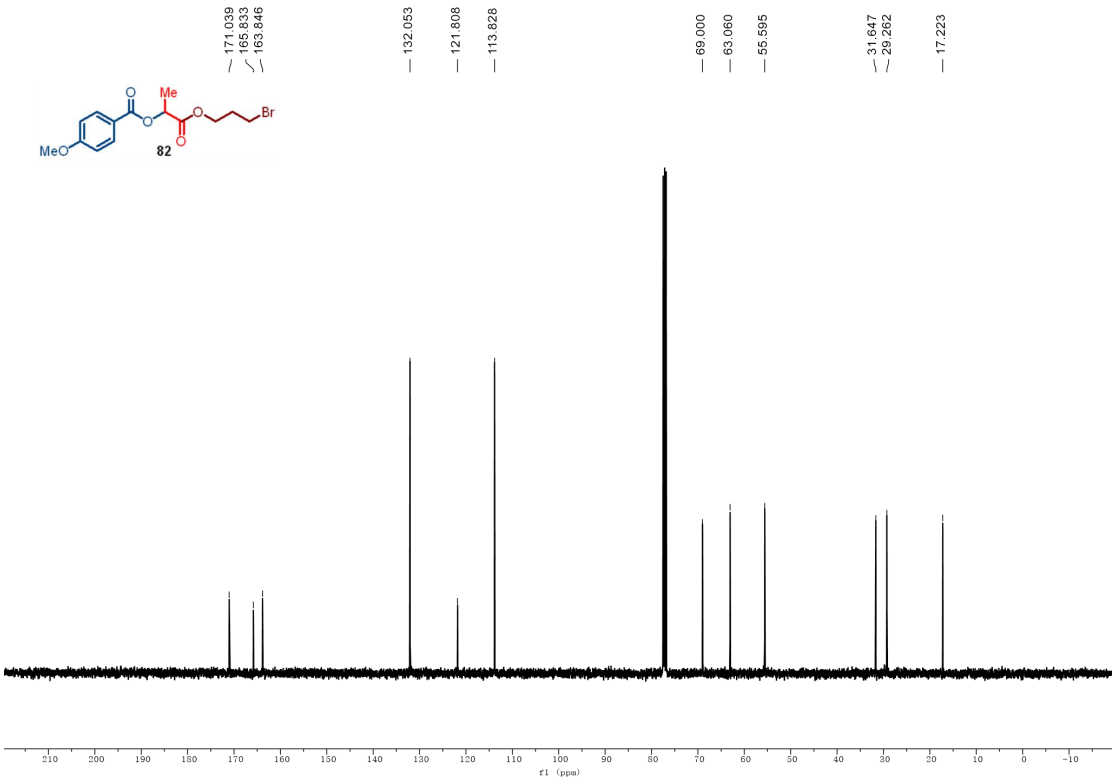
^{1}H NMR (400 MHz, $CDCl_3$) of 81



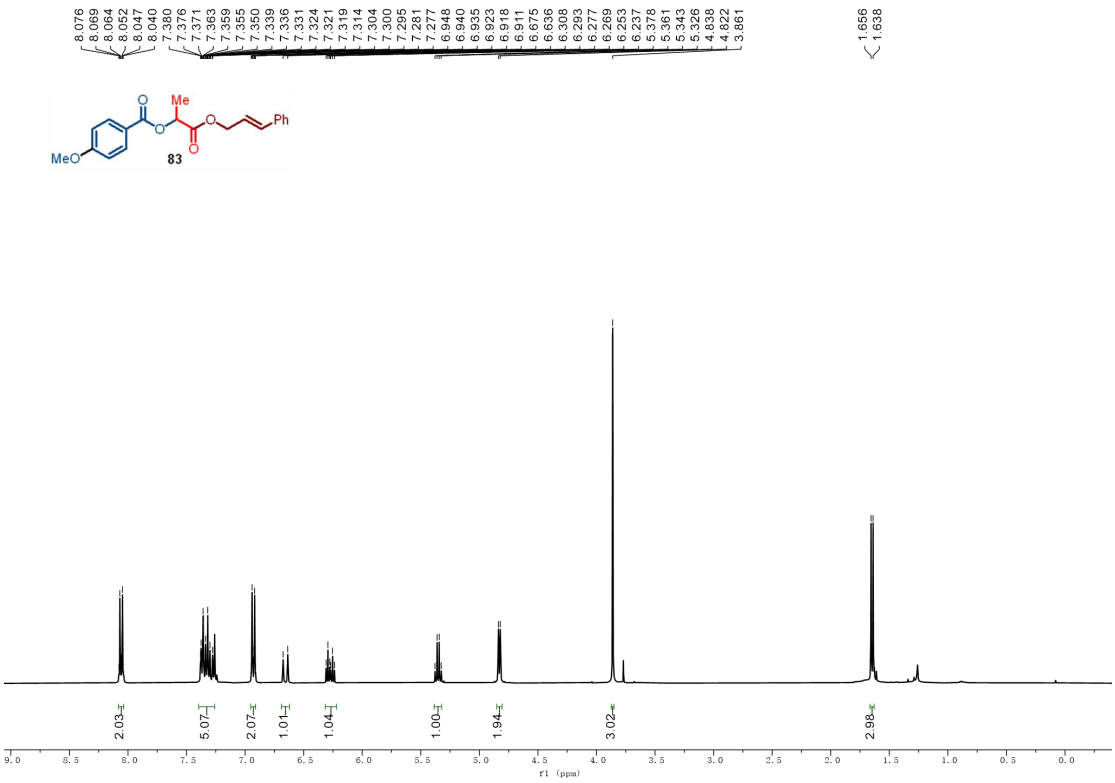
^{13}C NMR (101 MHz, $CDCl_3$) of 81



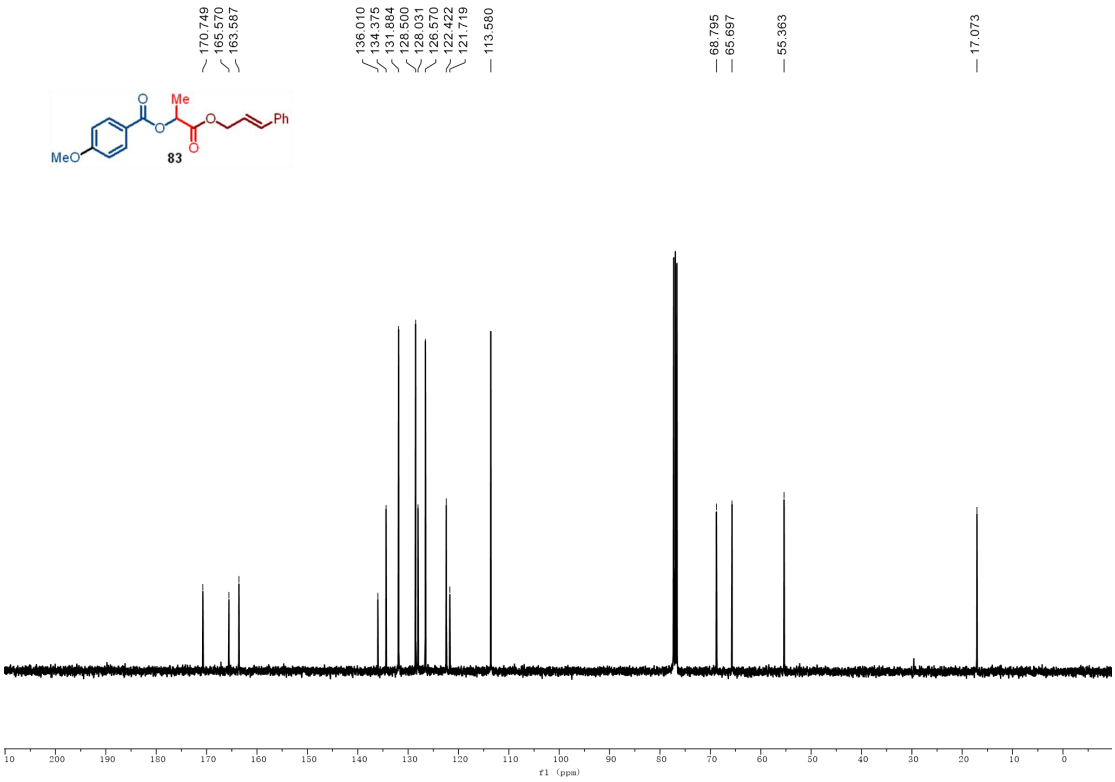
^{1}H NMR (400 MHz, $CDCl_3$) of 82



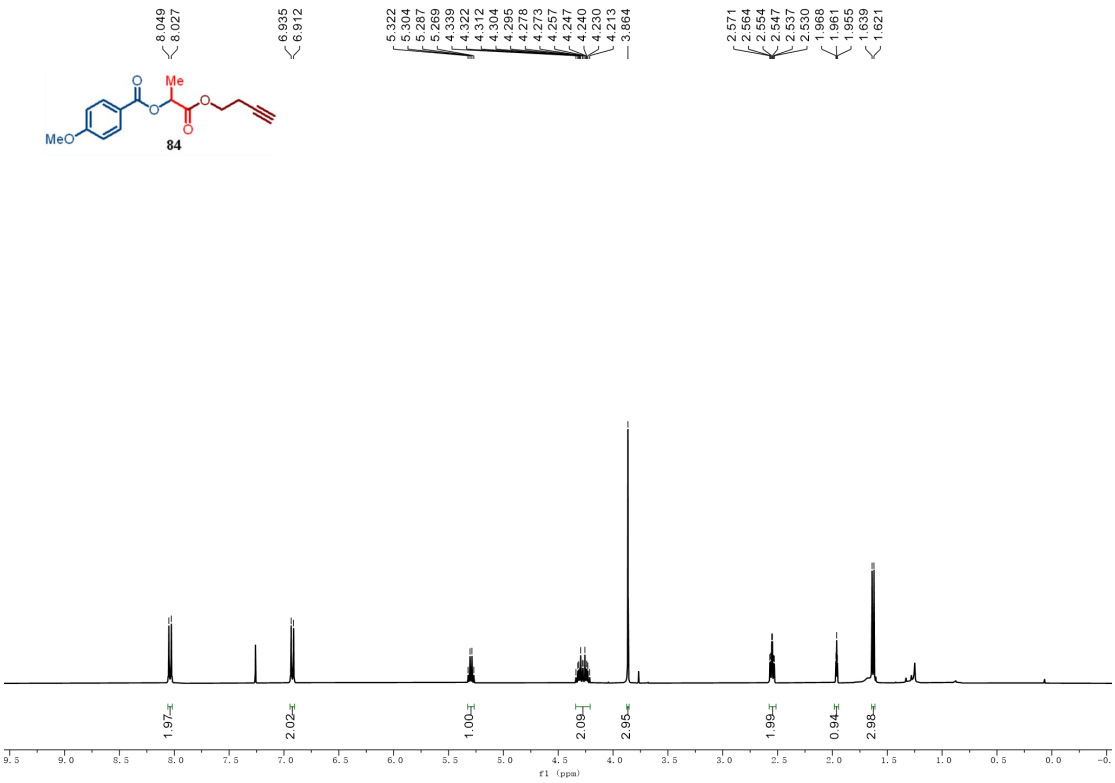
^{13}C NMR (101 MHz, $CDCl_3$) of 82



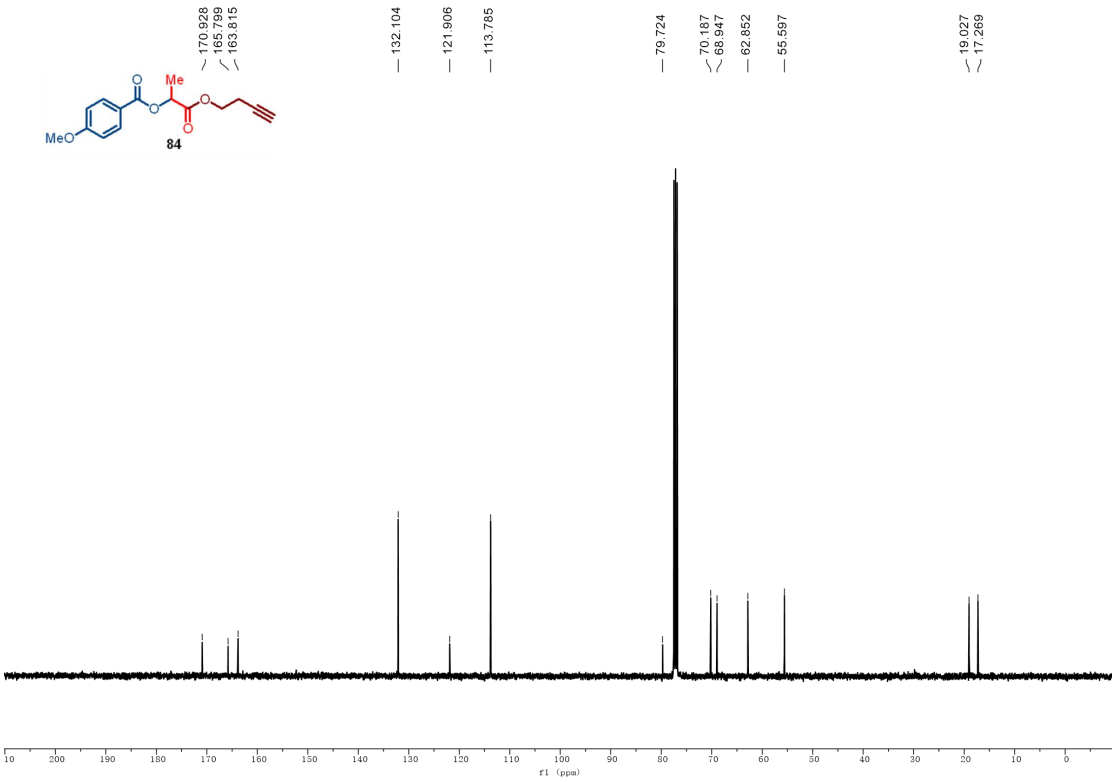
^{1}H NMR (400 MHz, $CDCl_3$) of 83



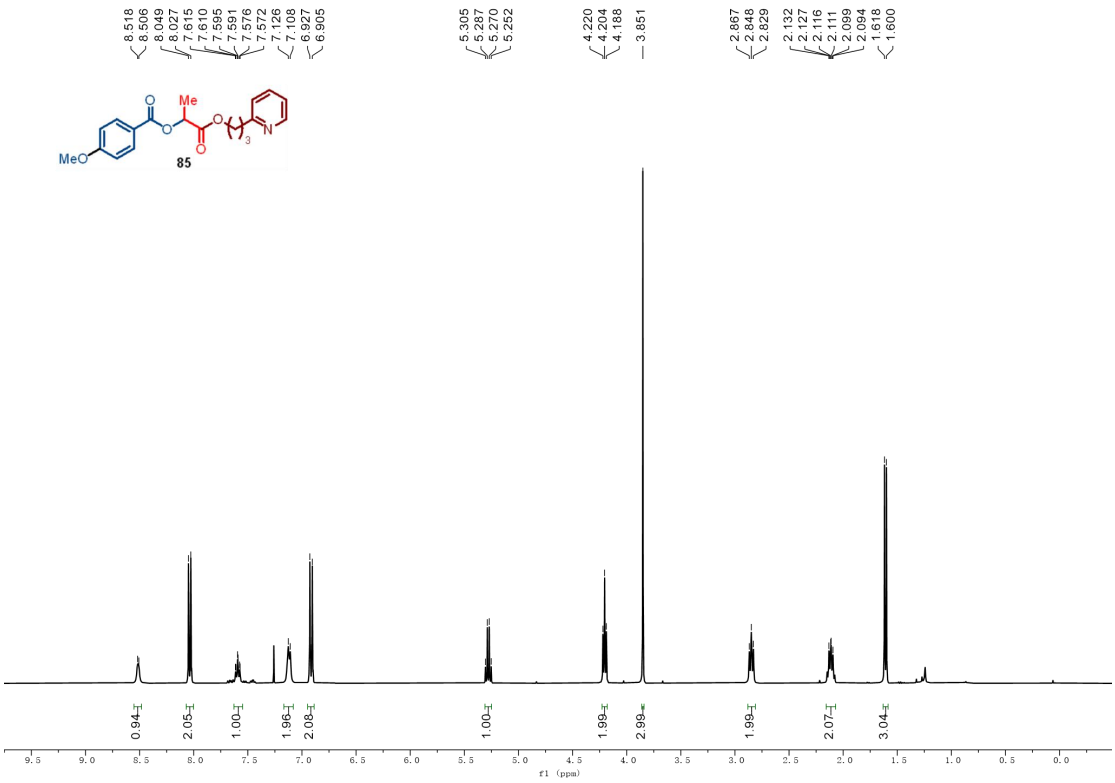
^{13}C NMR (101 MHz, $CDCl_3$) of 83



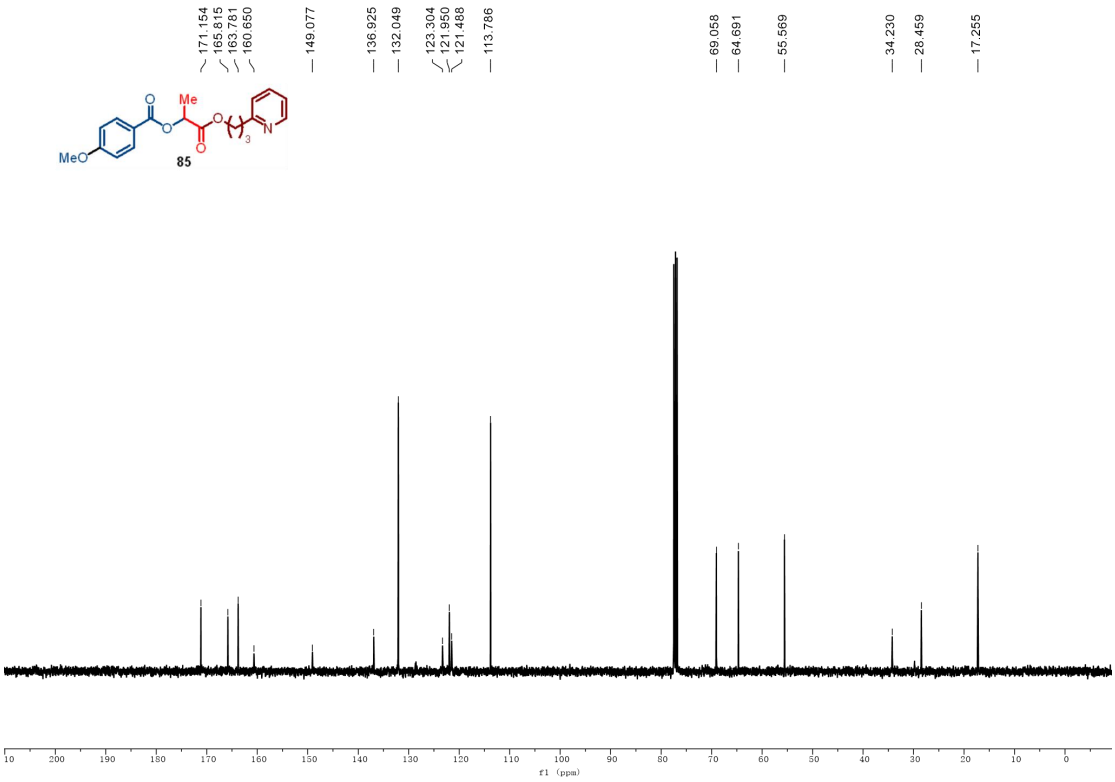
^{1}H NMR (400 MHz, $CDCl_3$) of 84



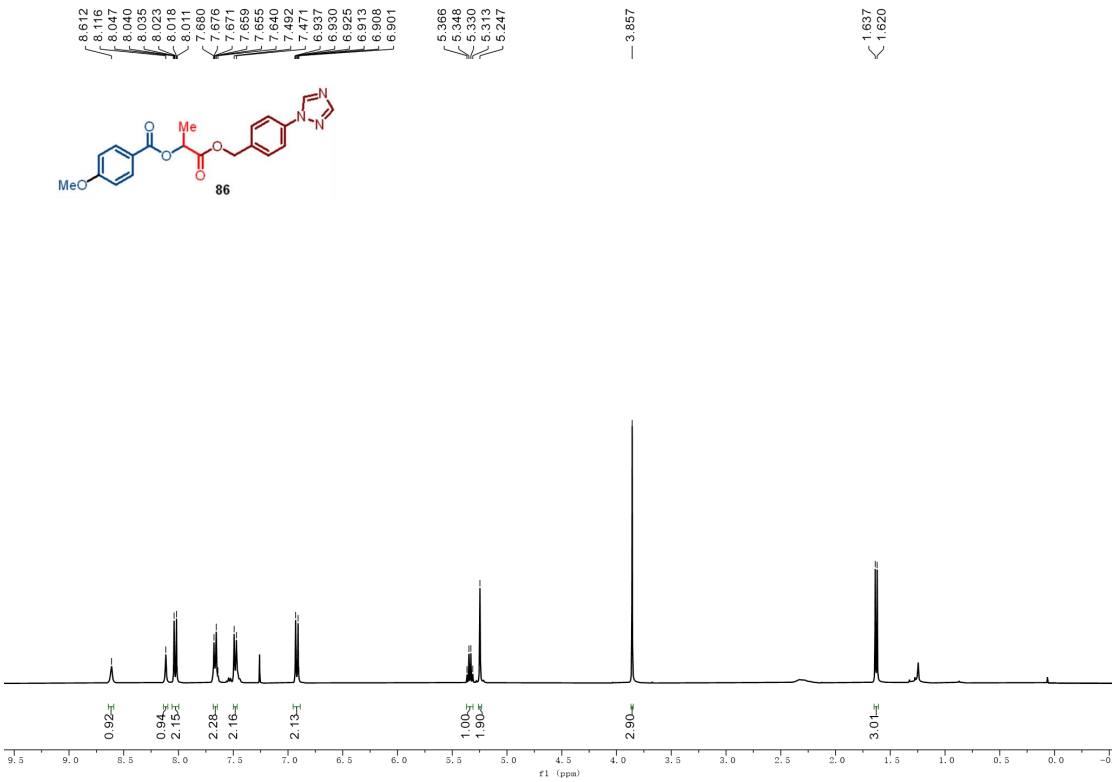
^{13}C NMR (101 MHz, $CDCl_3$) of 84



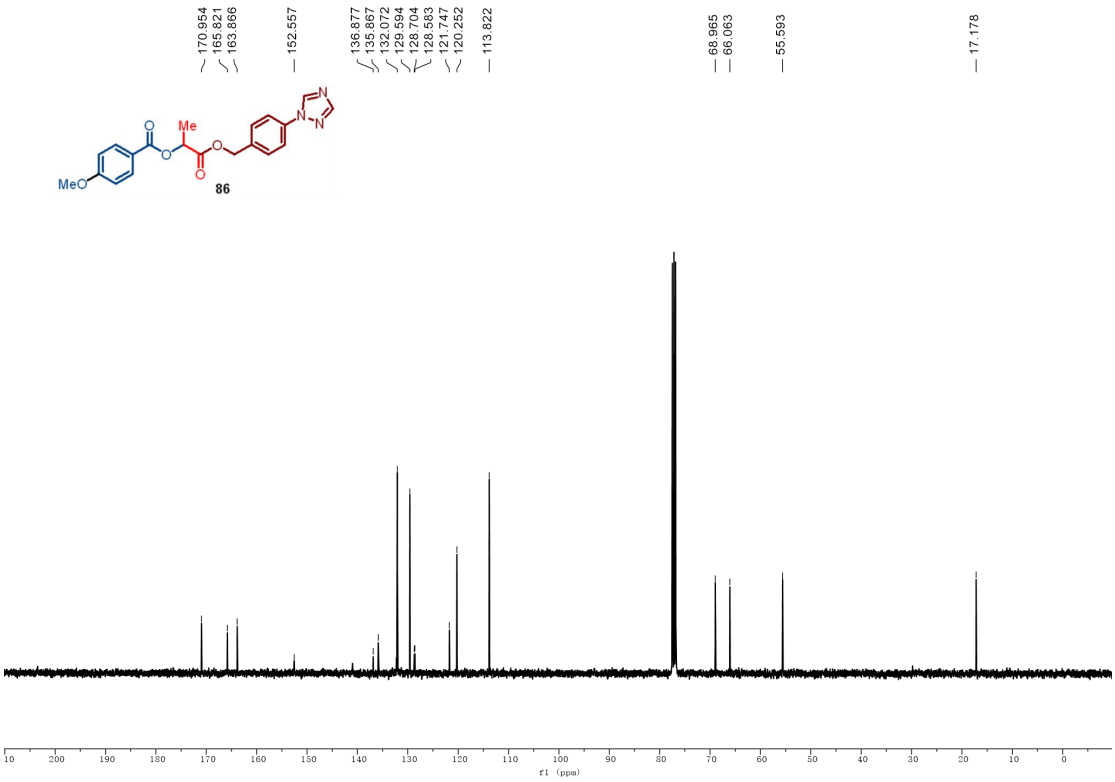
^{1}H NMR (400 MHz, $CDCl_3$) of 85



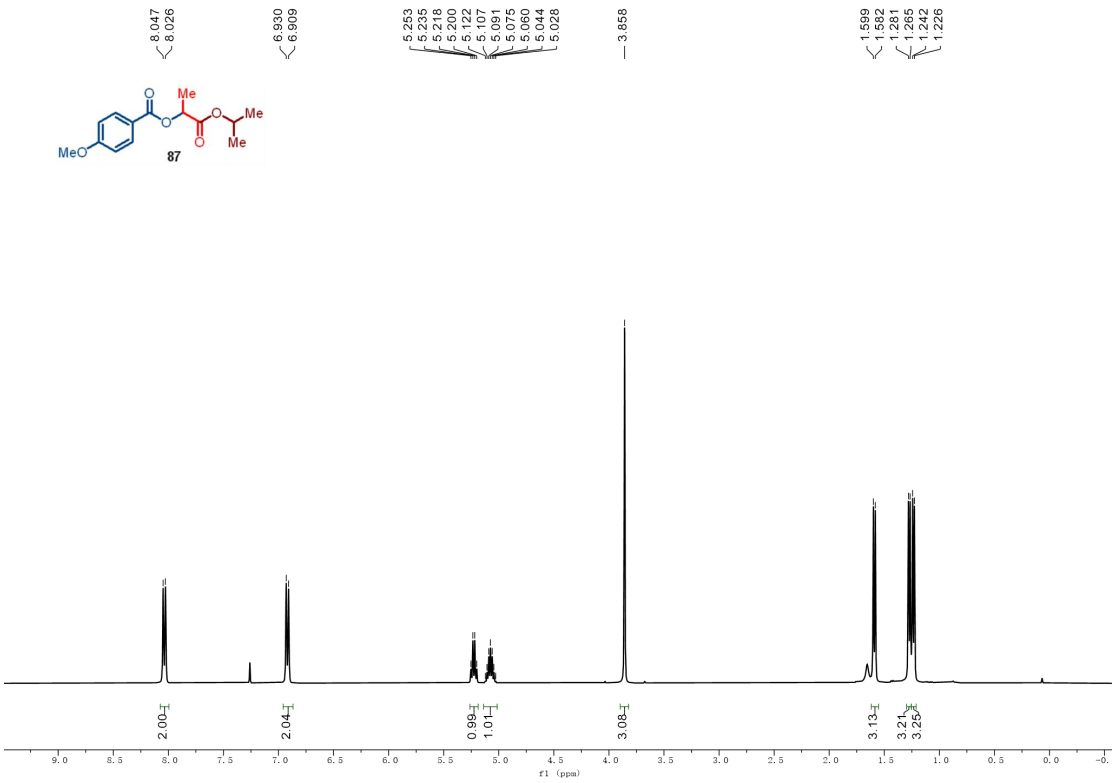
^{13}C NMR (101 MHz, $CDCl_3$) of 85



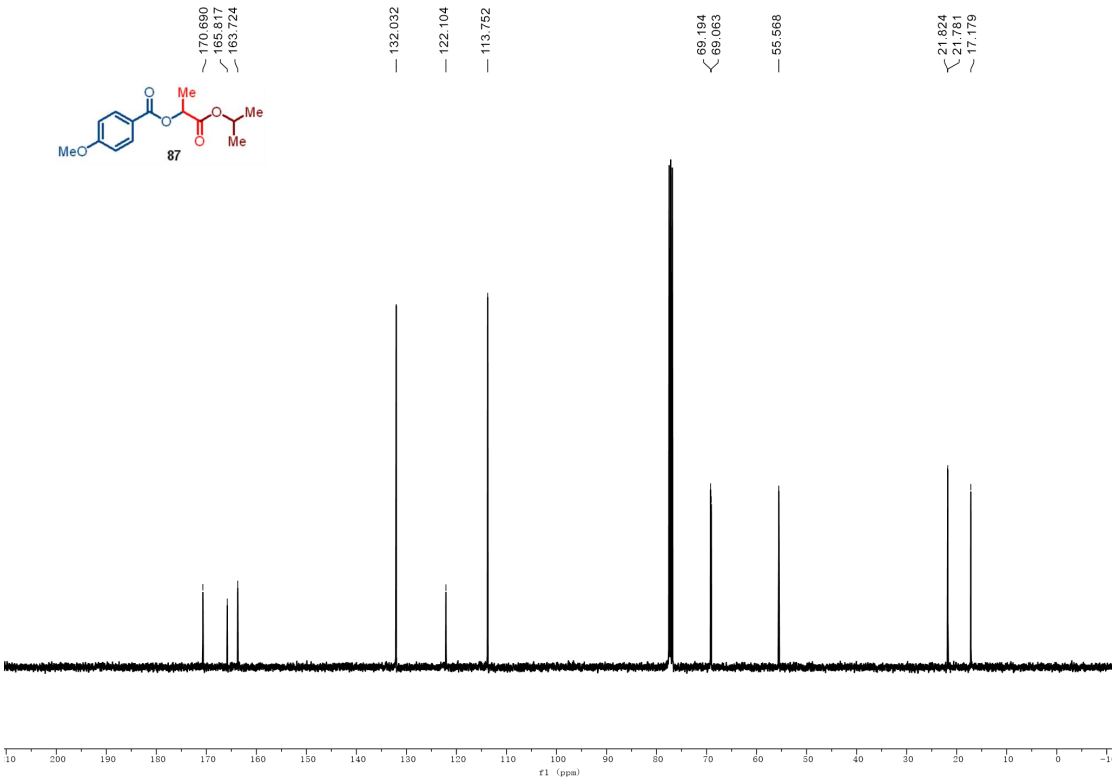
^{1}H NMR (400 MHz, $CDCl_3$) of 86



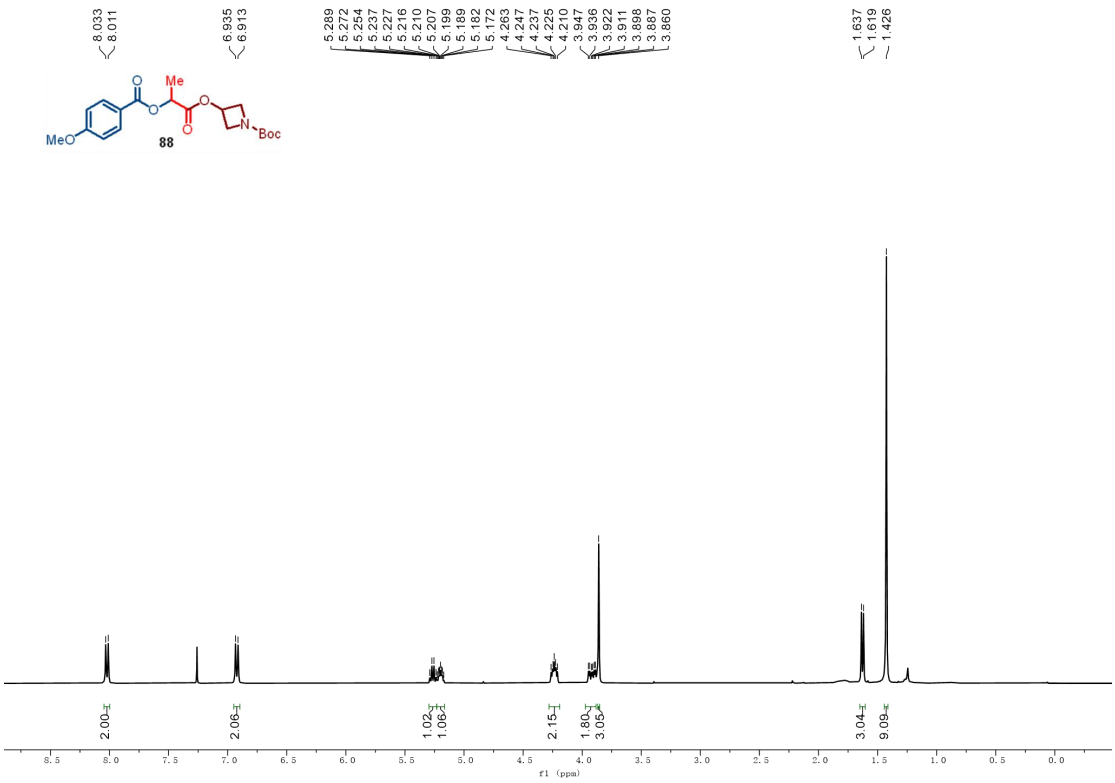
^{13}C NMR (101 MHz, $CDCl_3$) of 86



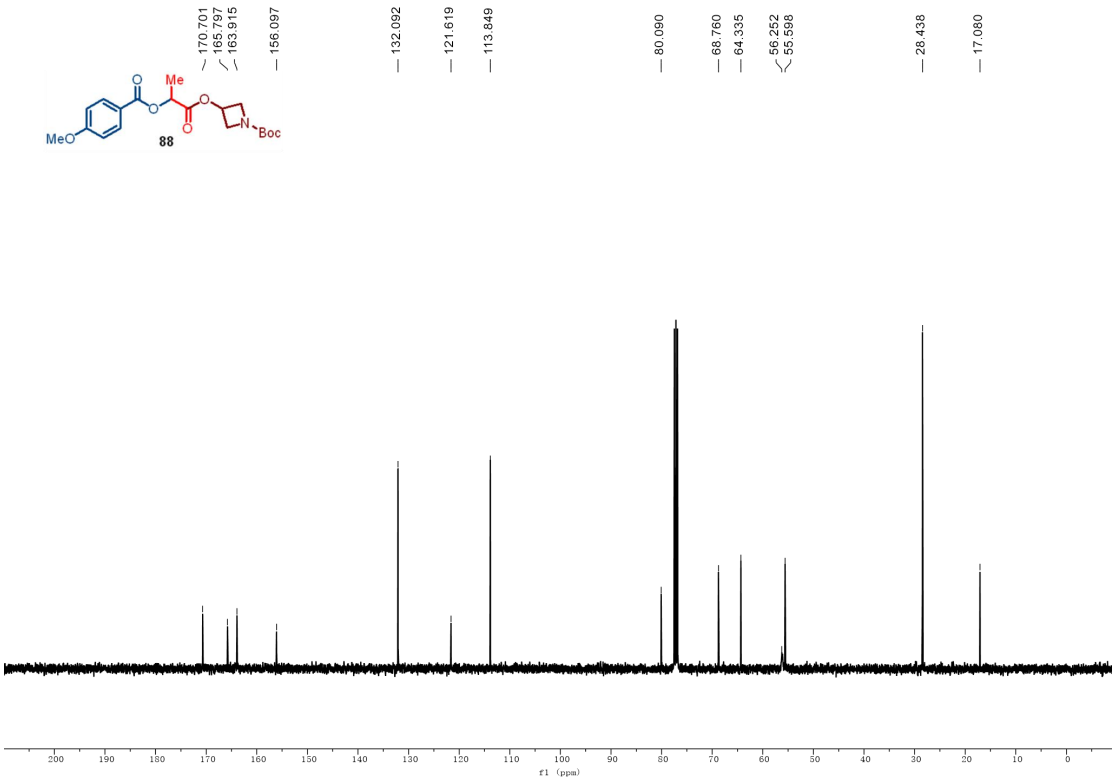
^{1}H NMR (400 MHz, $CDCl_3$) of 87



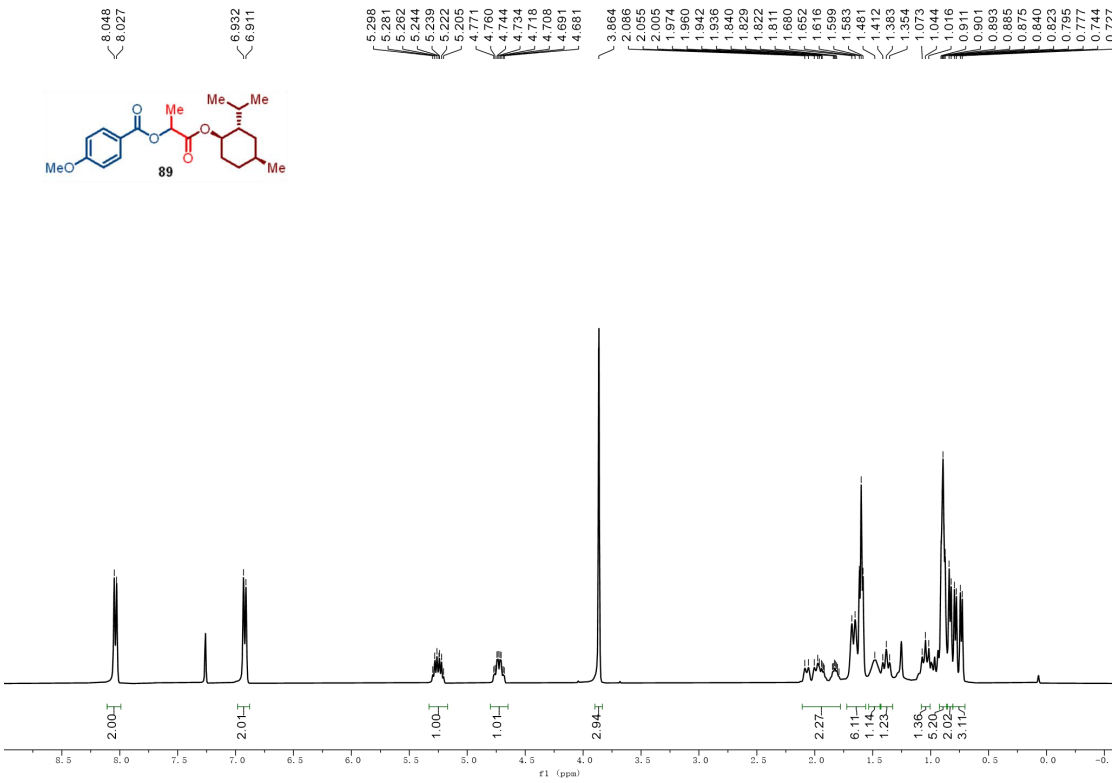
^{13}C NMR (101 MHz, $CDCl_3$) of 87



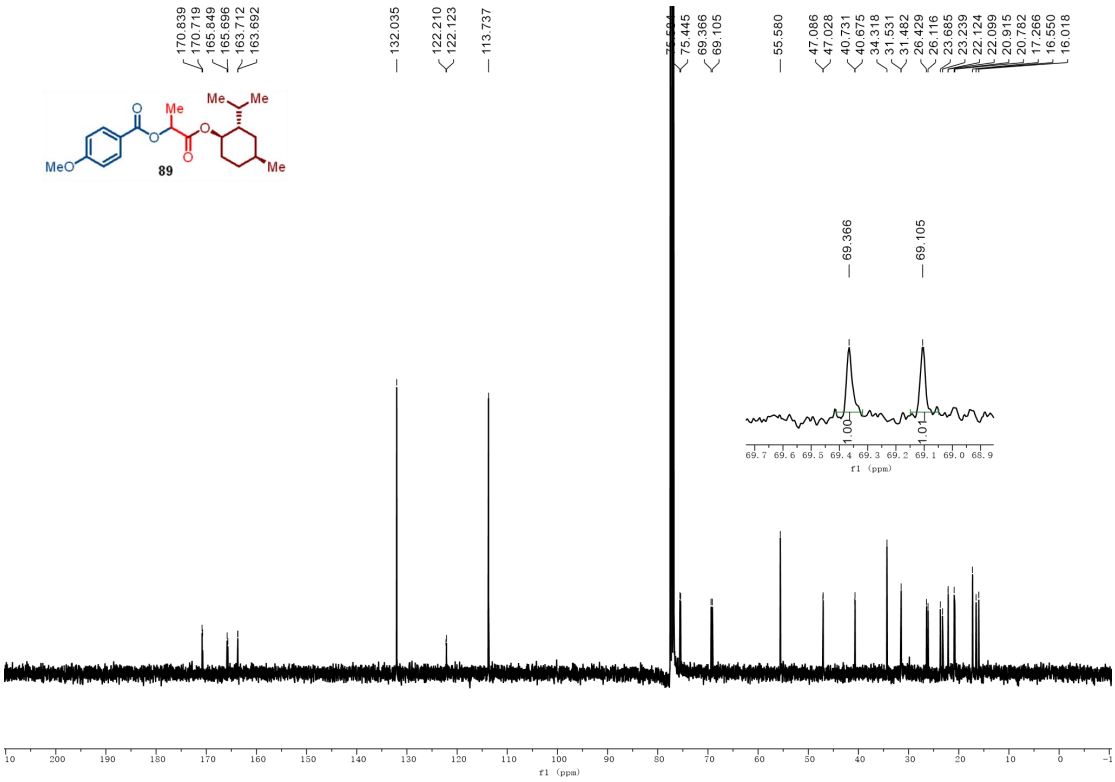
^{1}H NMR (400 MHz, $CDCl_3$) of 88



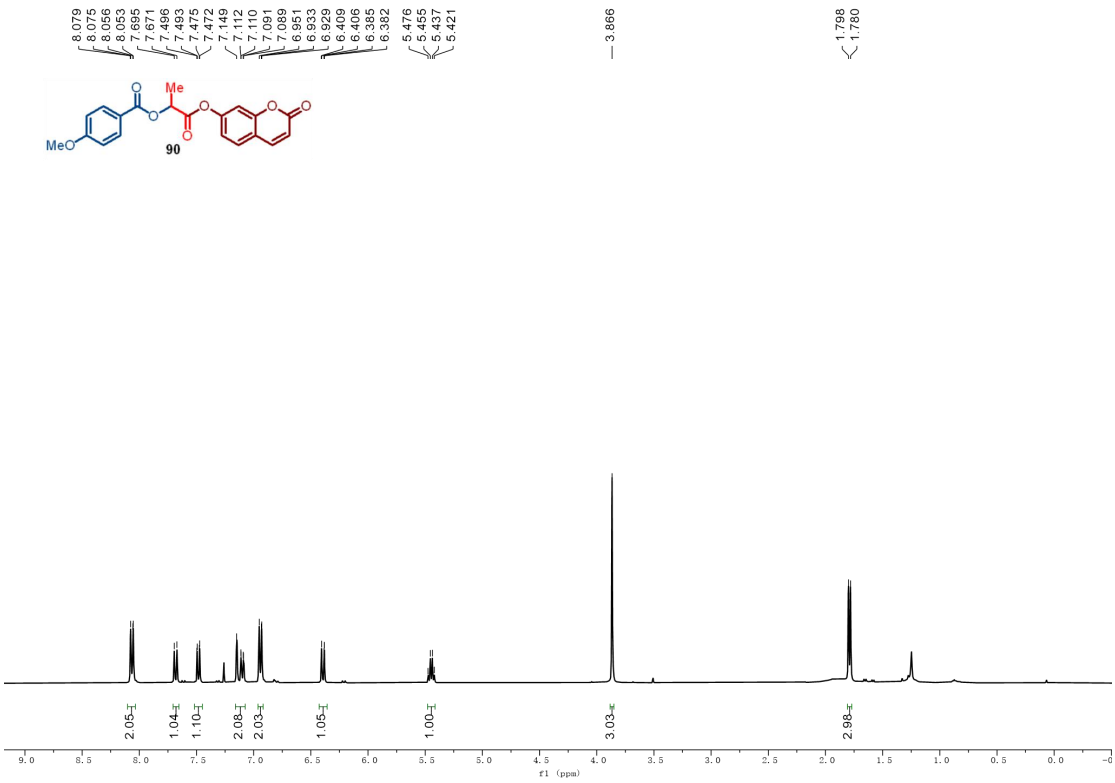
^{13}C NMR (101 MHz, $CDCl_3$) of 88



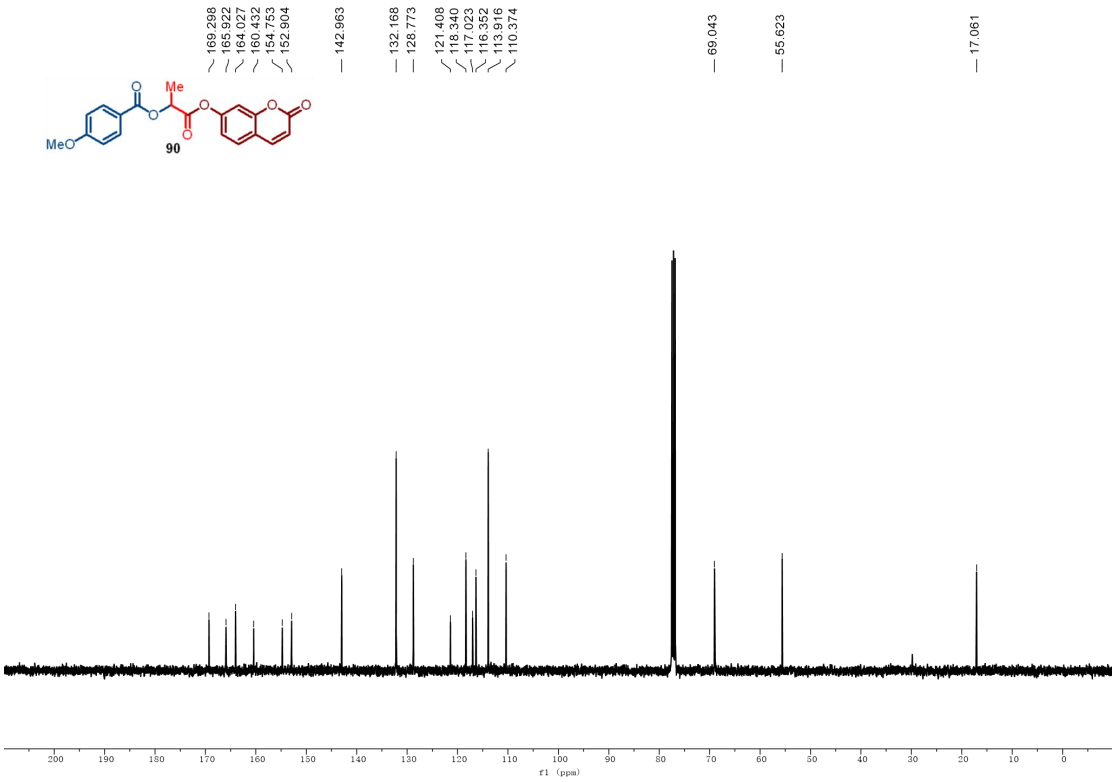
^{1}H NMR (400 MHz, $CDCl_3$) of 89



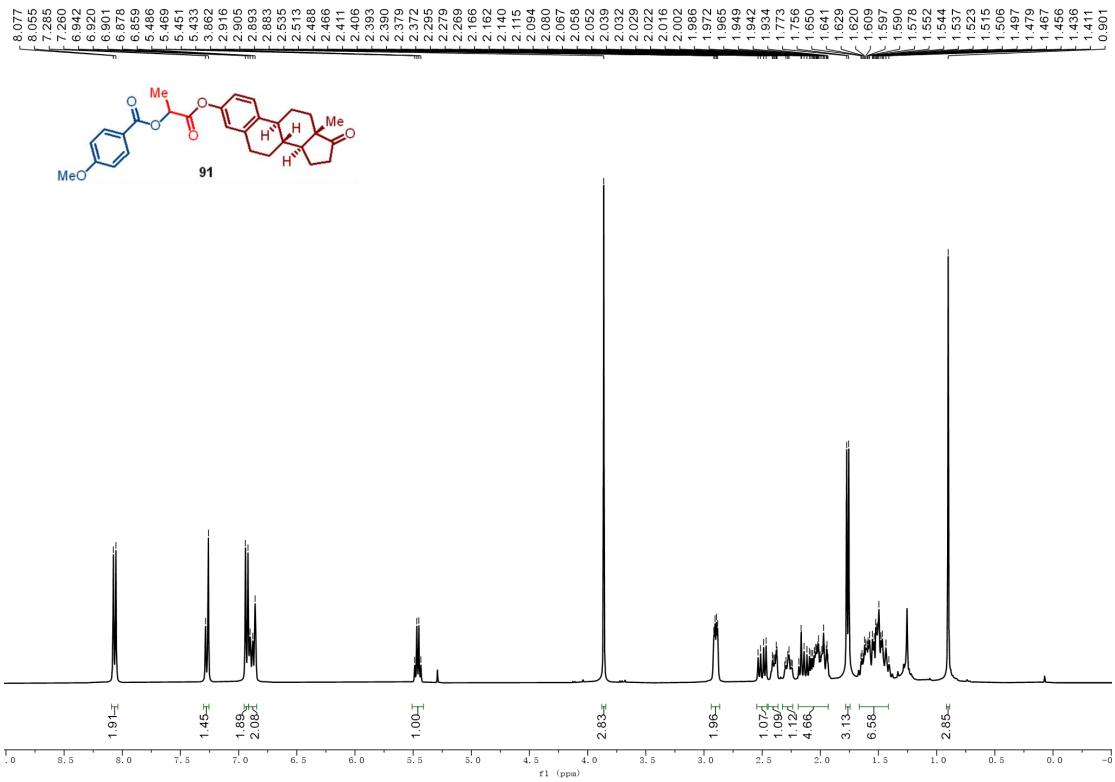
^{13}C NMR (101 MHz, $CDCl_3$) of 89



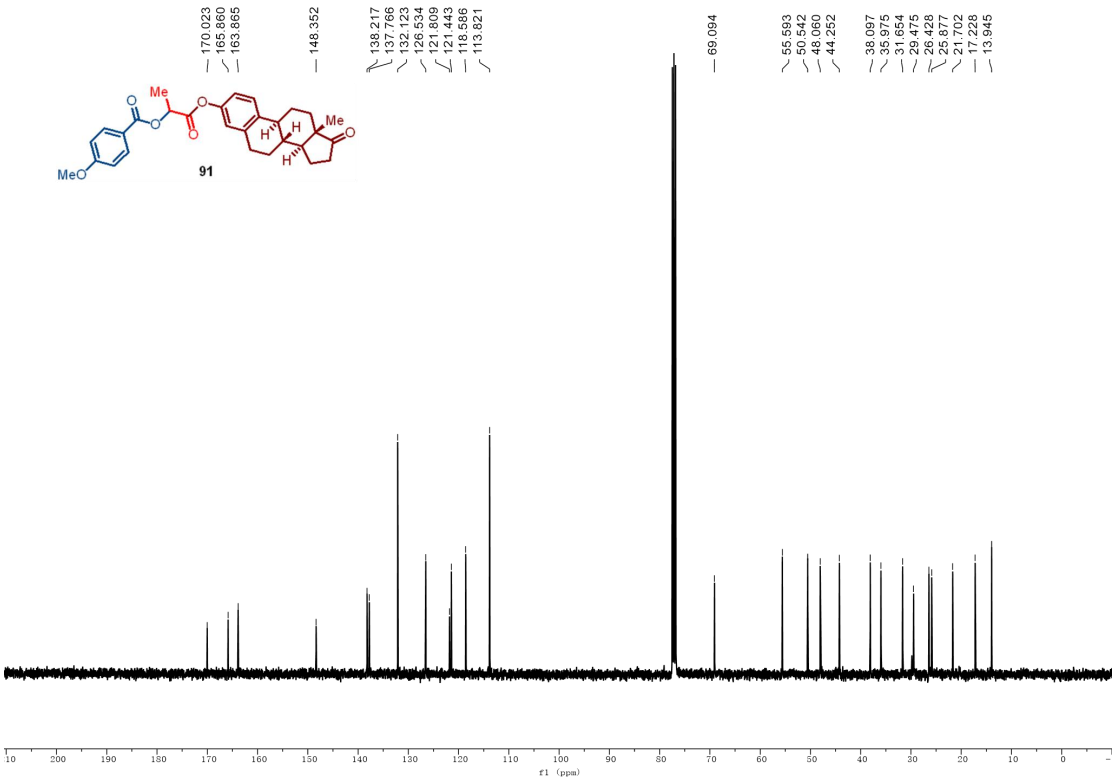
^{1}H NMR (400 MHz, $CDCl_3$) of 90



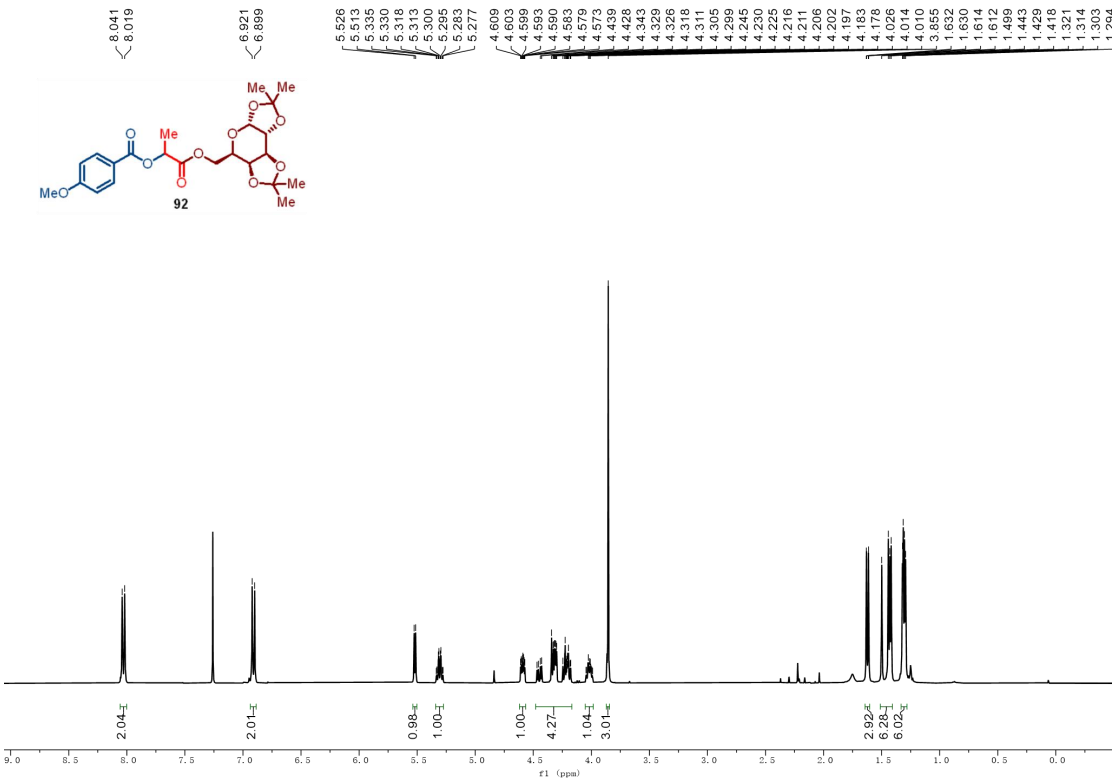
^{13}C NMR (101 MHz, $CDCl_3$) of 90



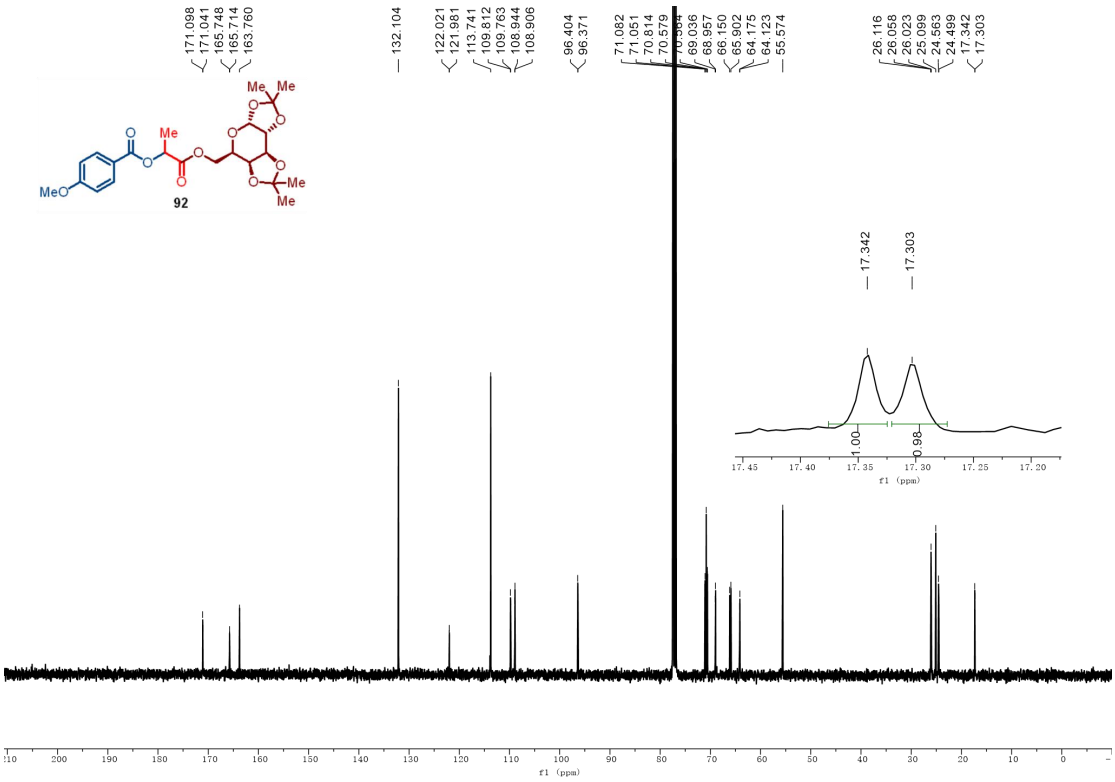
^{1}H NMR (400 MHz, $CDCl_3$) of 91



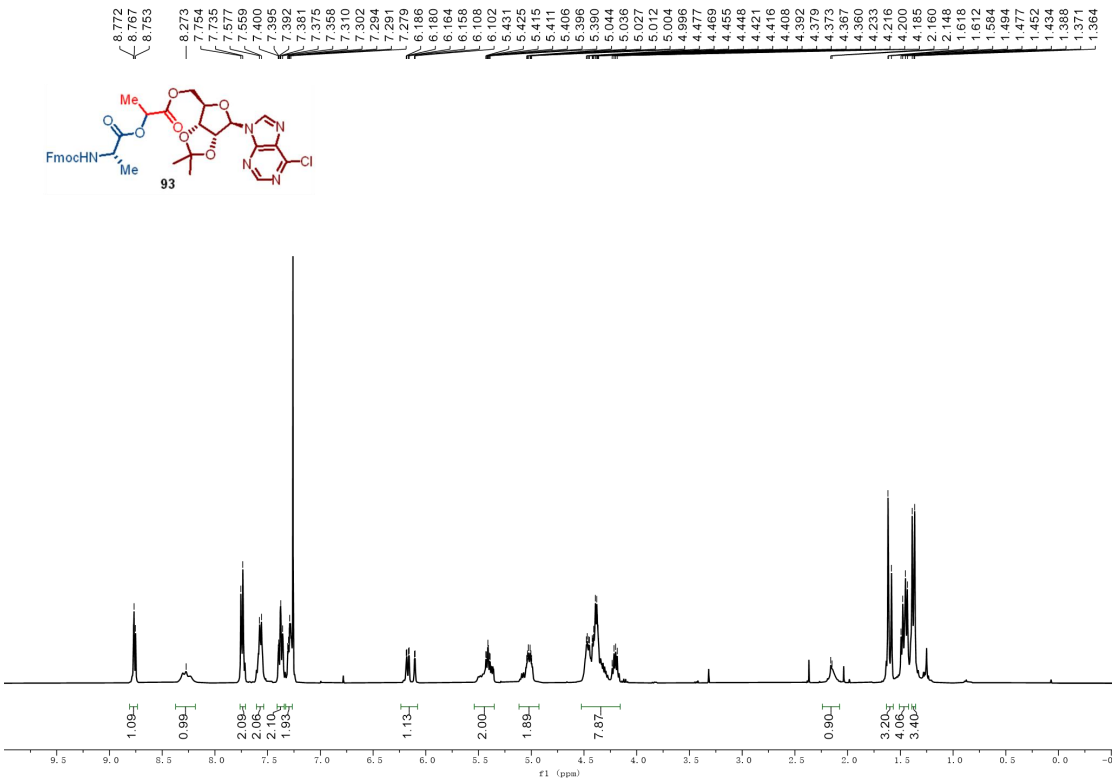
^{13}C NMR (101 MHz, $CDCl_3$) of 91



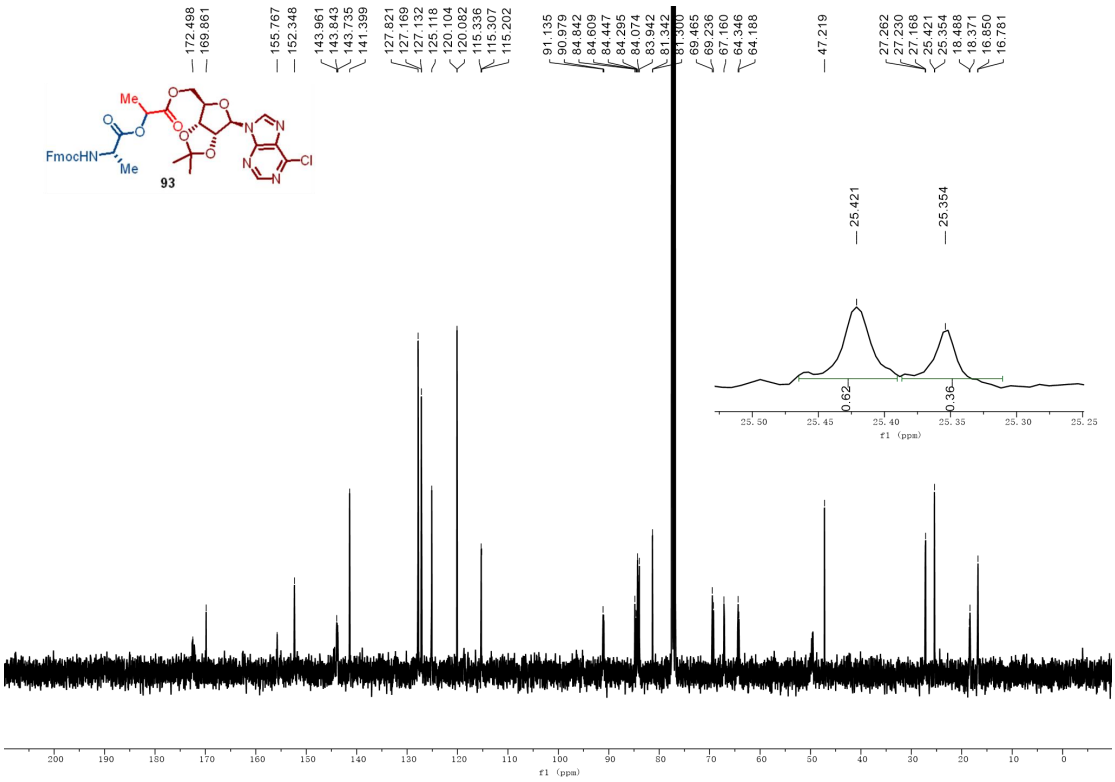
^{1}H NMR (400 MHz, $CDCl_3$) of 92



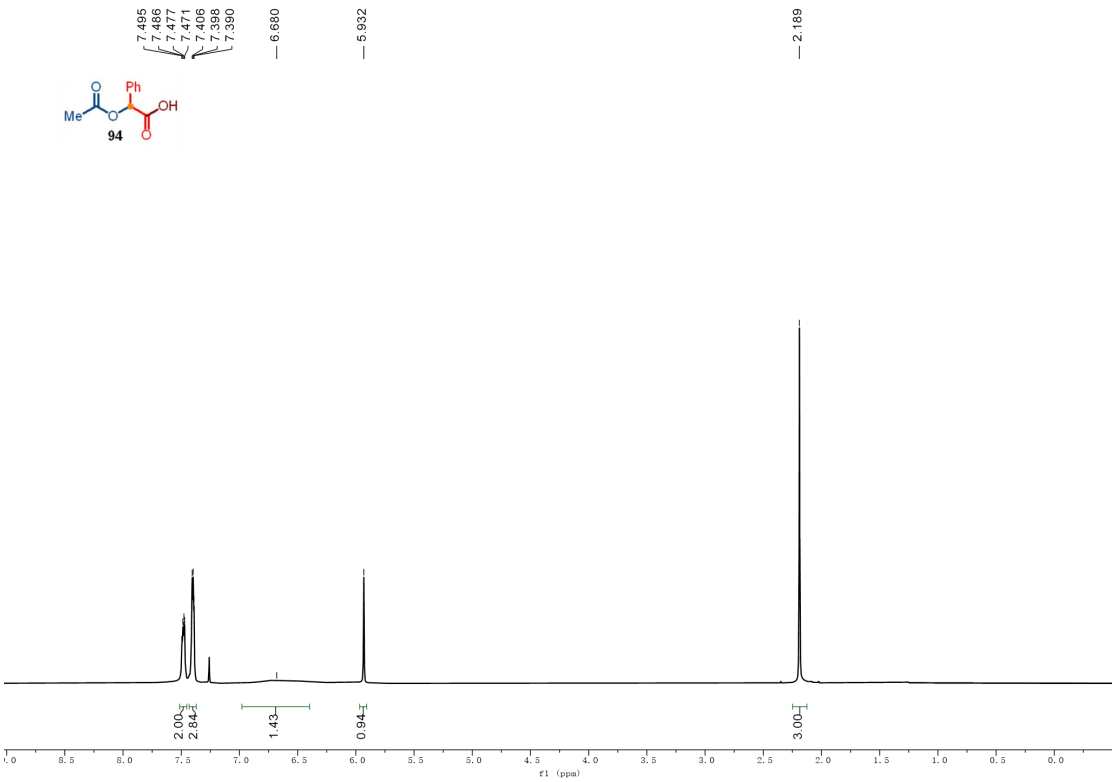
^{13}C NMR (101 MHz, $CDCl_3$) of 92



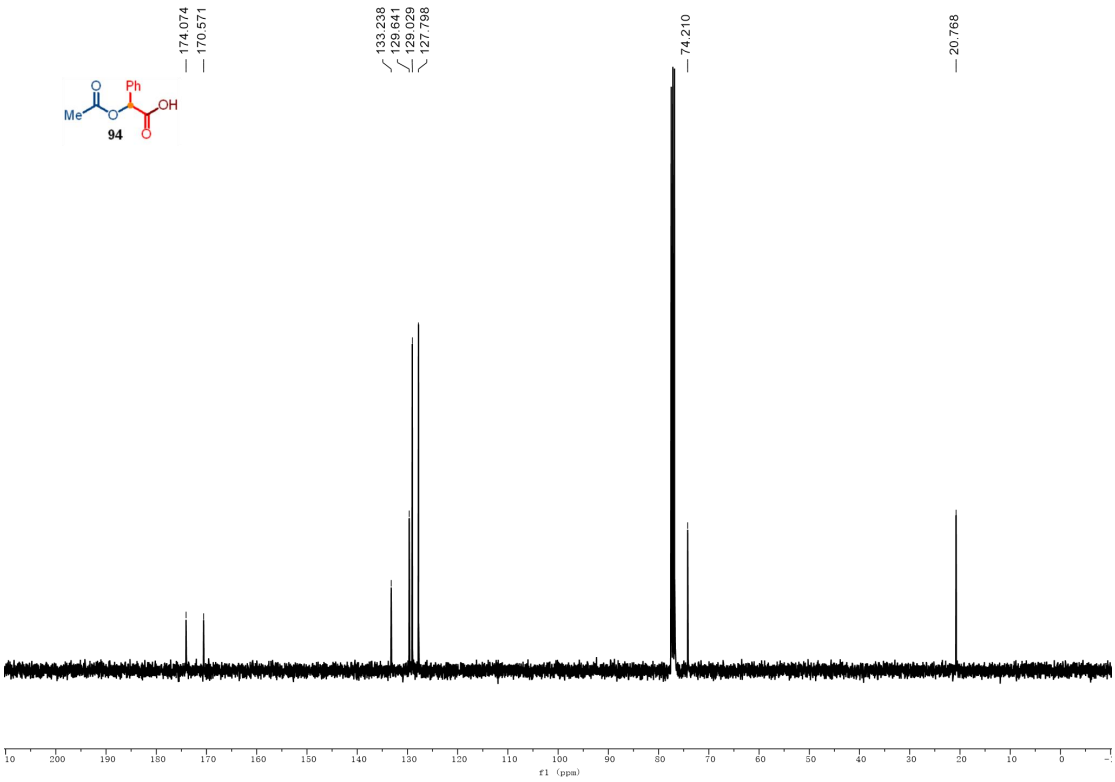
^{1}H NMR (400 MHz, $CDCl_3$) of 93



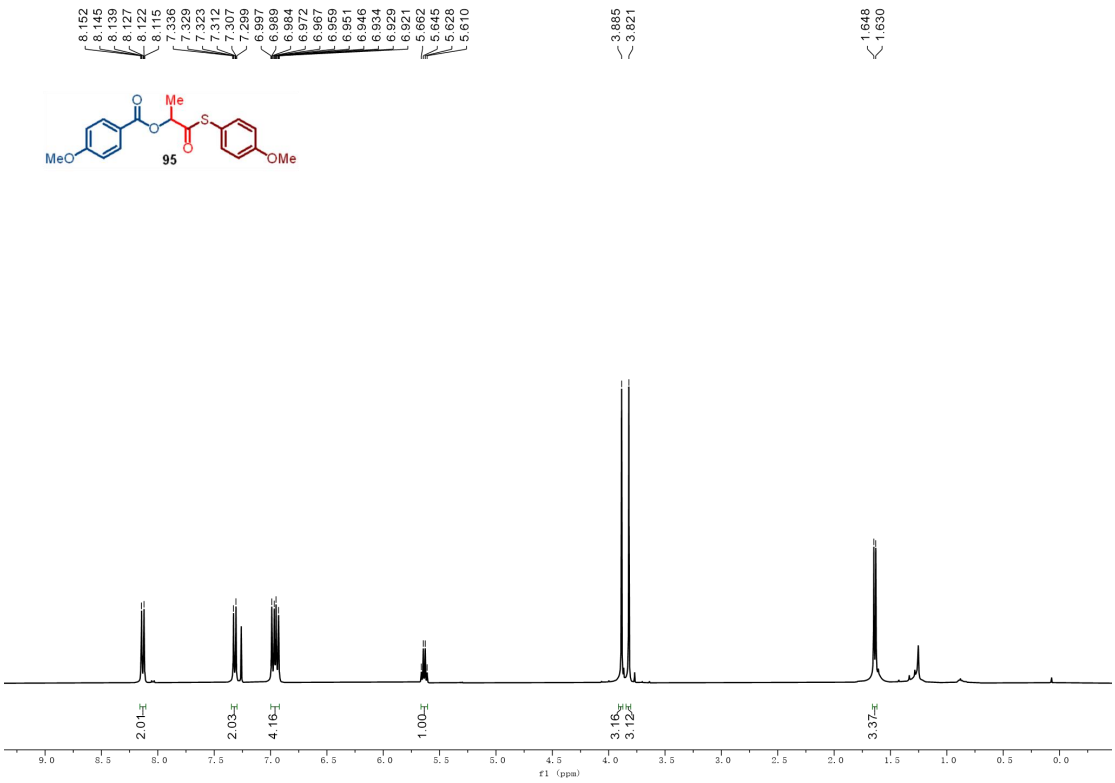
^{13}C NMR (101 MHz, $CDCl_3$) of 93



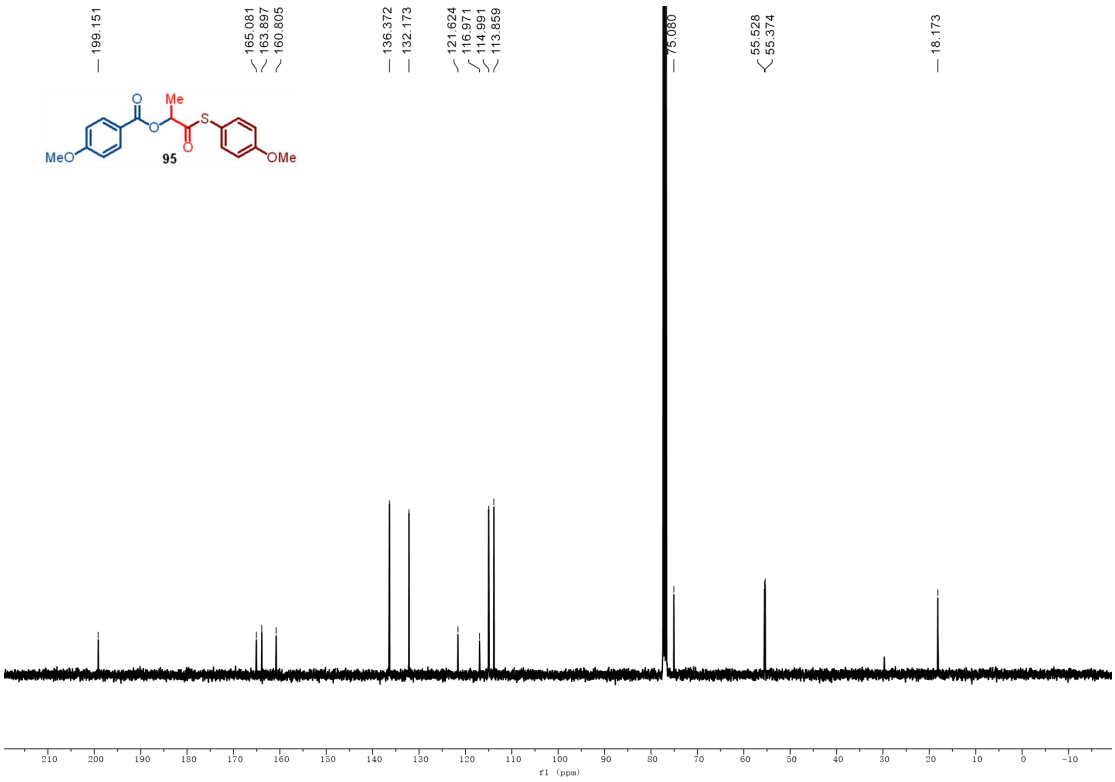
^{1}H NMR (400 MHz, $CDCl_3$) of 94



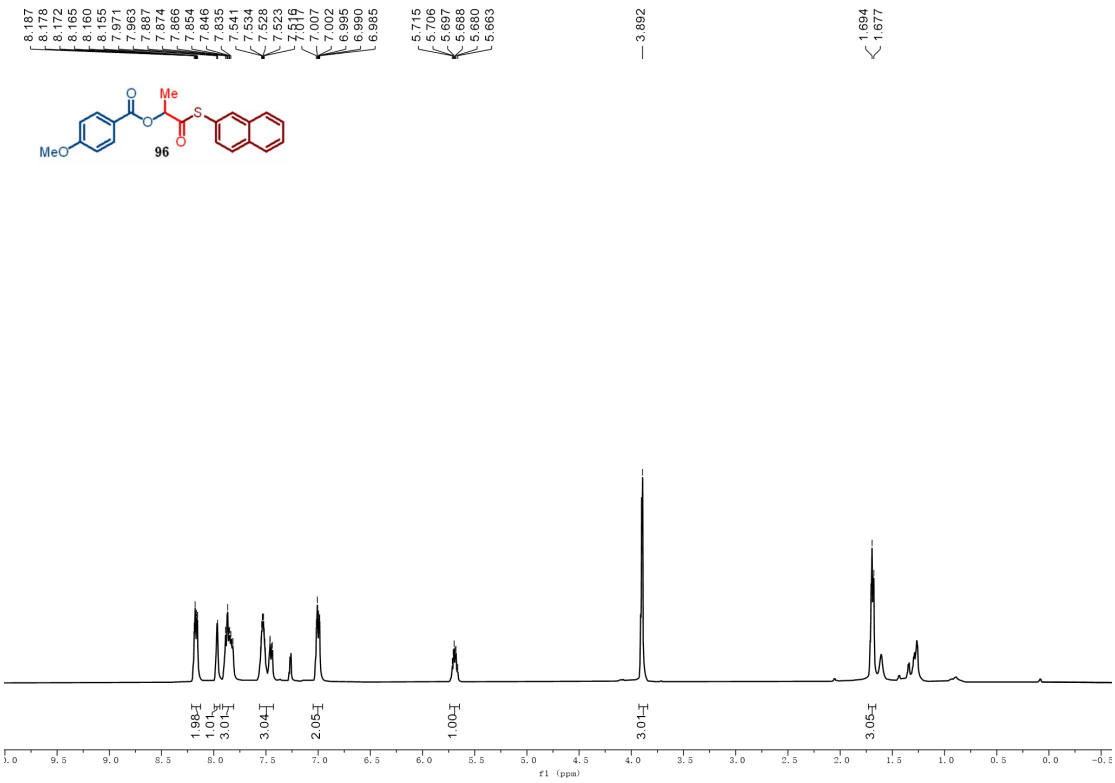
^{13}C NMR (101 MHz, $CDCl_3$) of 94



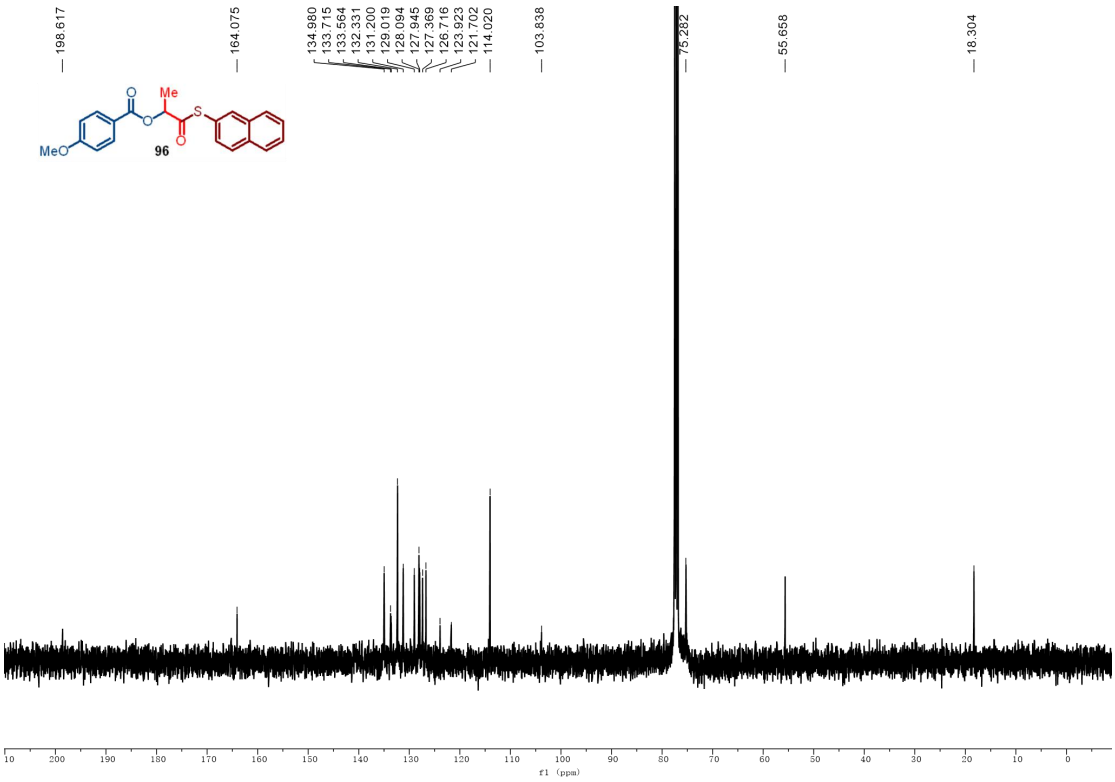
^{1}H NMR (400 MHz, $CDCl_3$) of 95



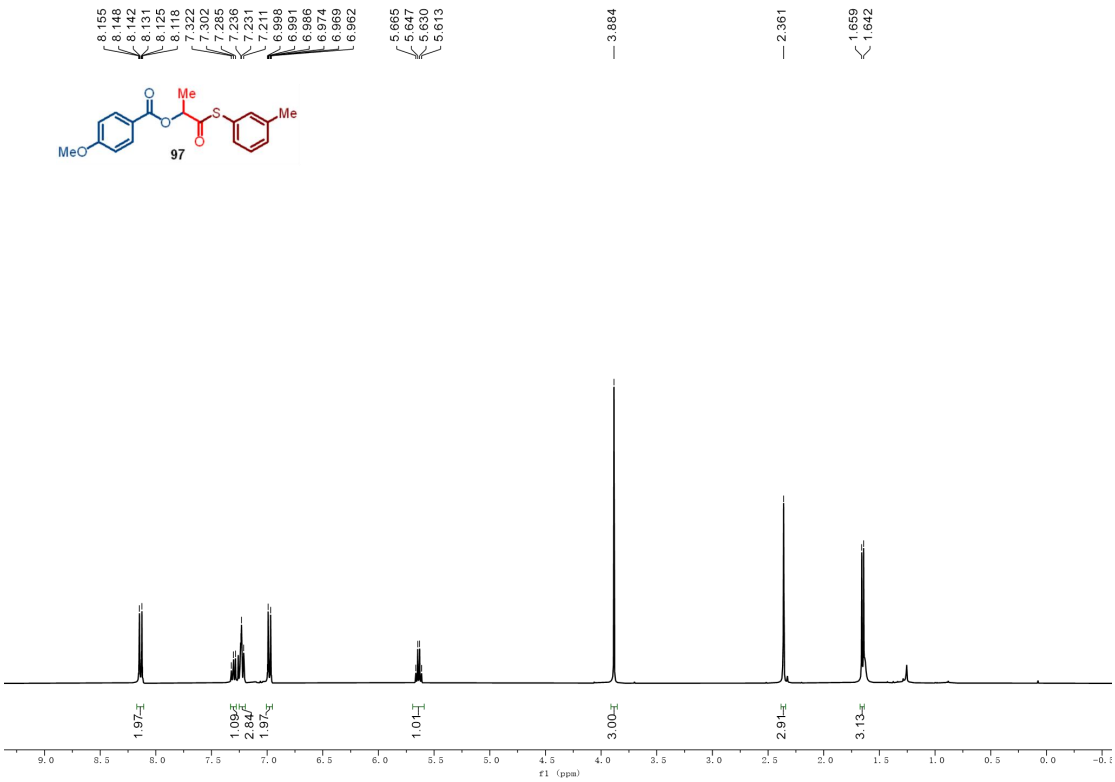
^{13}C NMR (101 MHz, $CDCl_3$) of 95



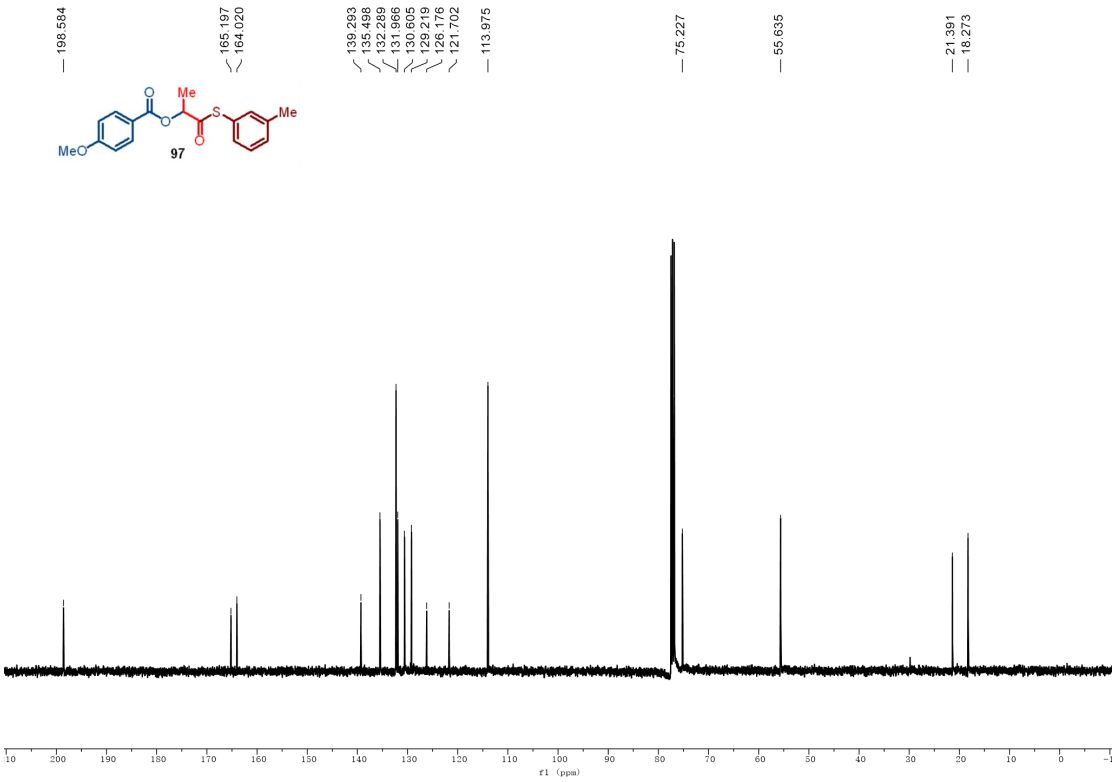
^{1}H NMR (400 MHz, $CDCl_3$) of 96



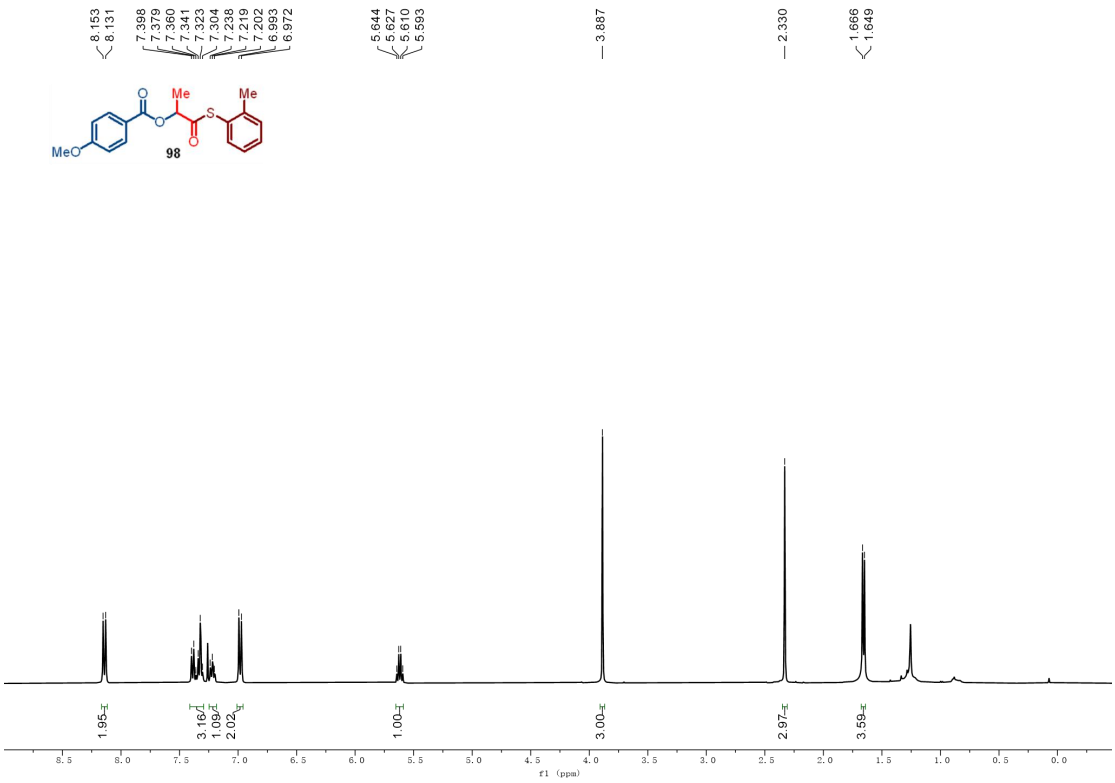
^{13}C NMR (101 MHz, $CDCl_3$) of 96



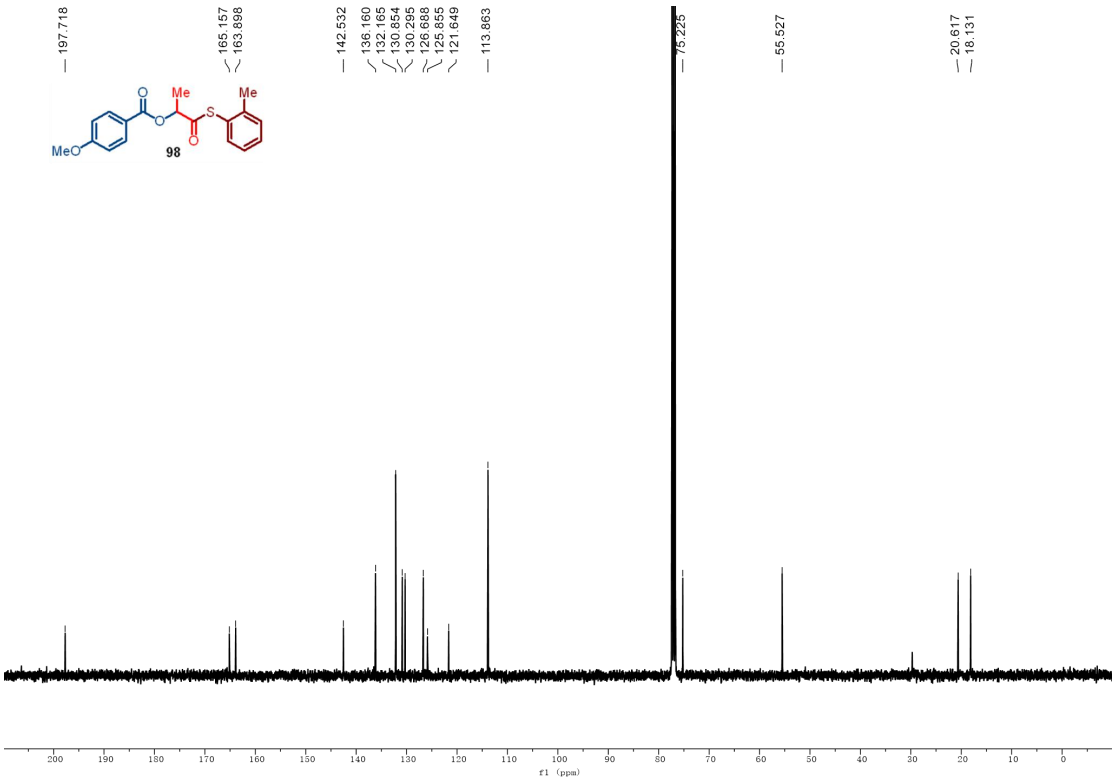
^{1}H NMR (400 MHz, $CDCl_3$) of 97



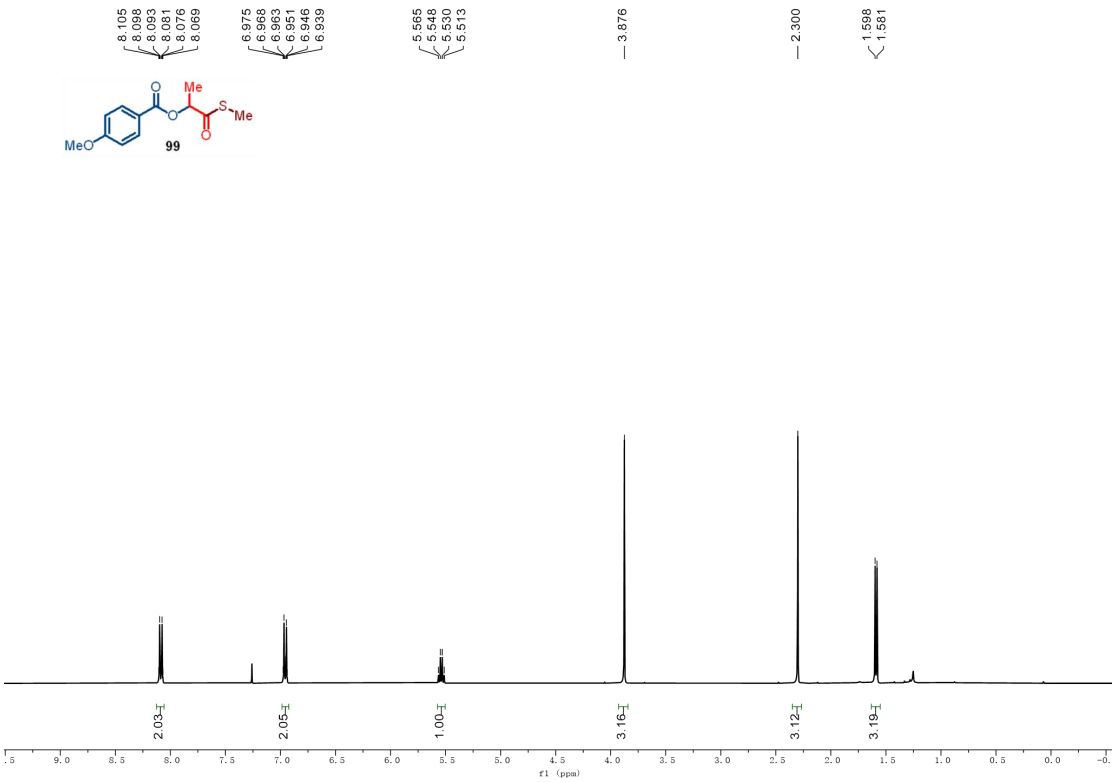
^{13}C NMR (101 MHz, $CDCl_3$) of 97



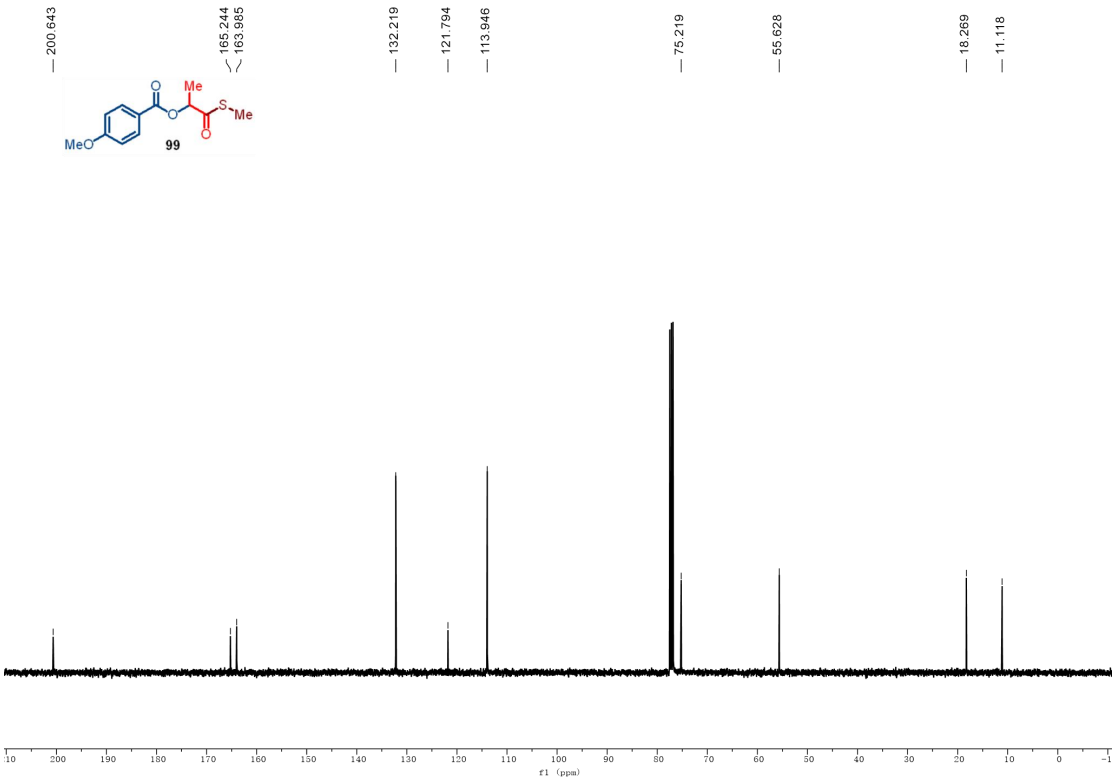
^{1}H NMR (400 MHz, $CDCl_3$) of 98



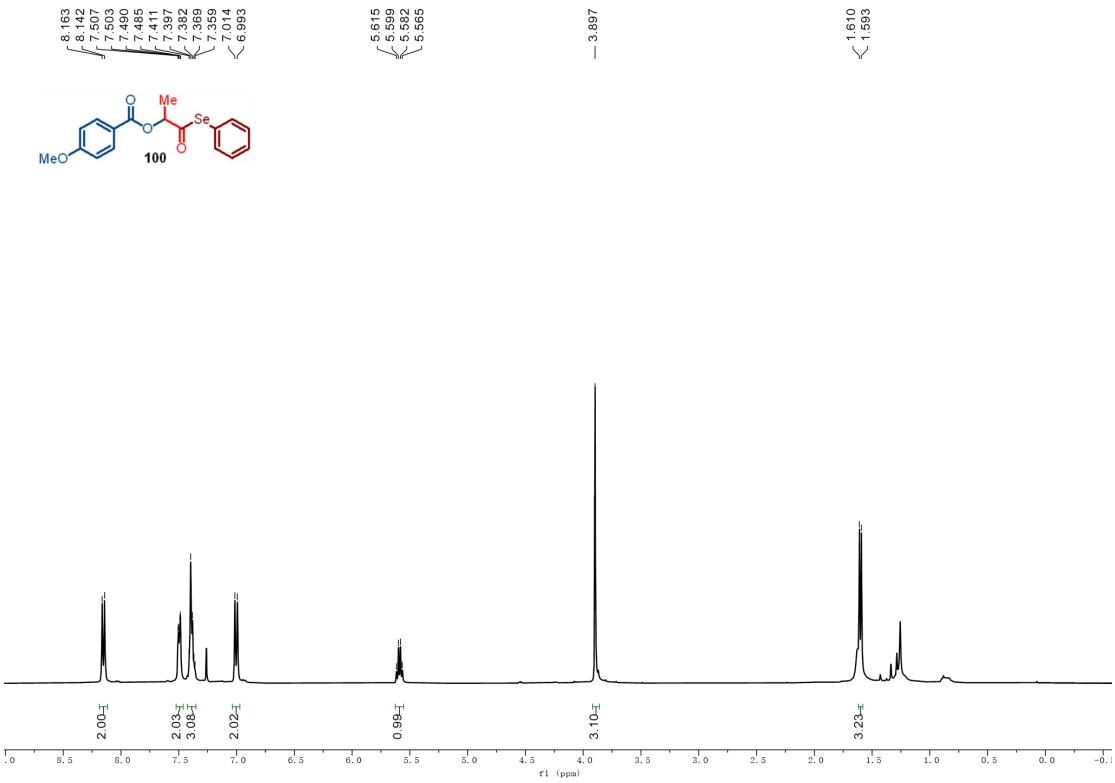
^{13}C NMR (101 MHz, $CDCl_3$) of 98



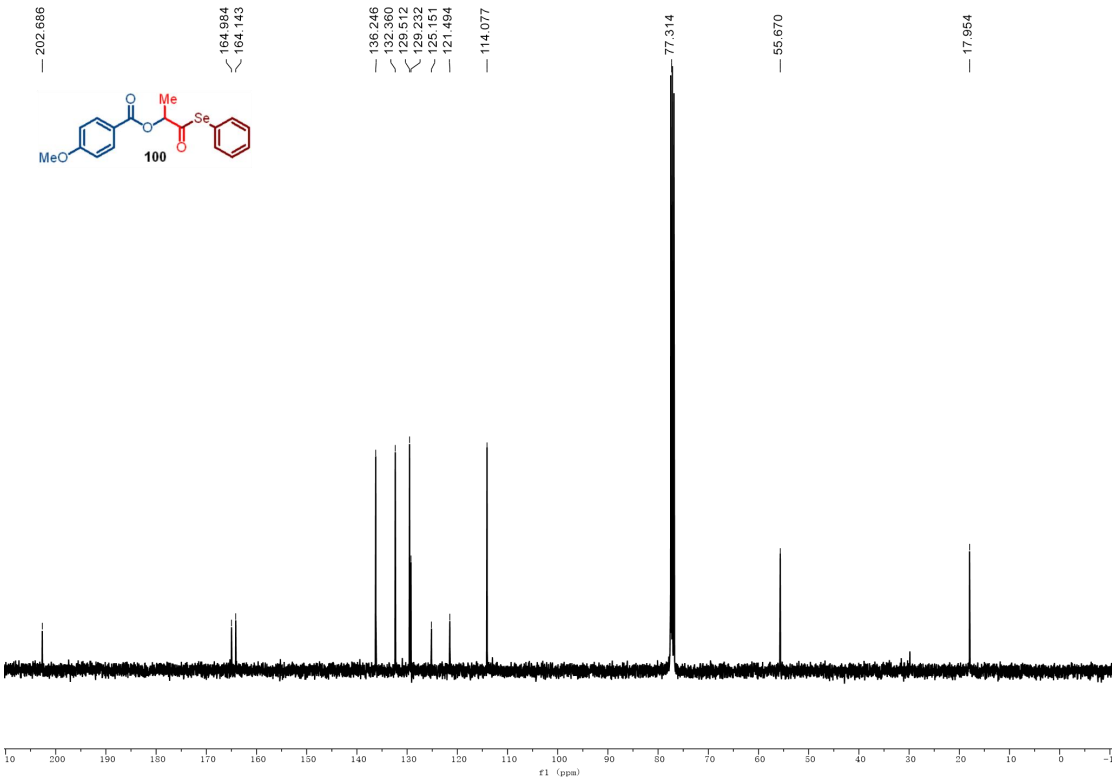
^{1}H NMR (400 MHz, $CDCl_3$) of 99



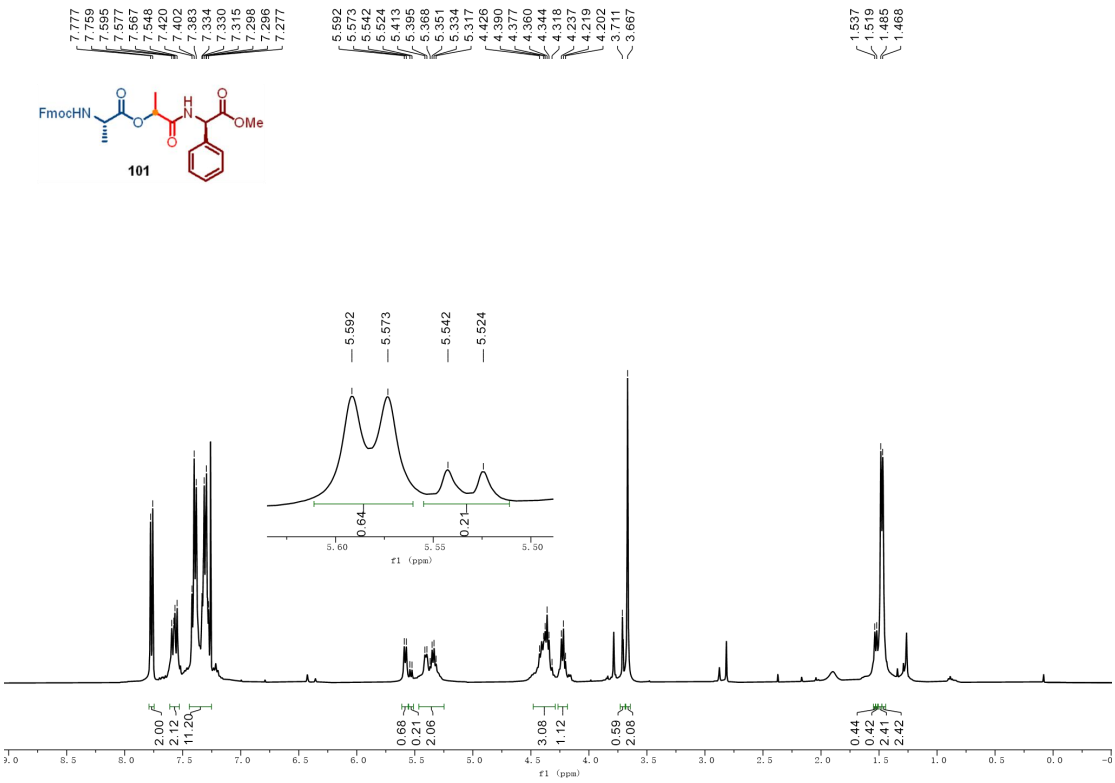
^{13}C NMR (101 MHz, $CDCl_3$) of 99



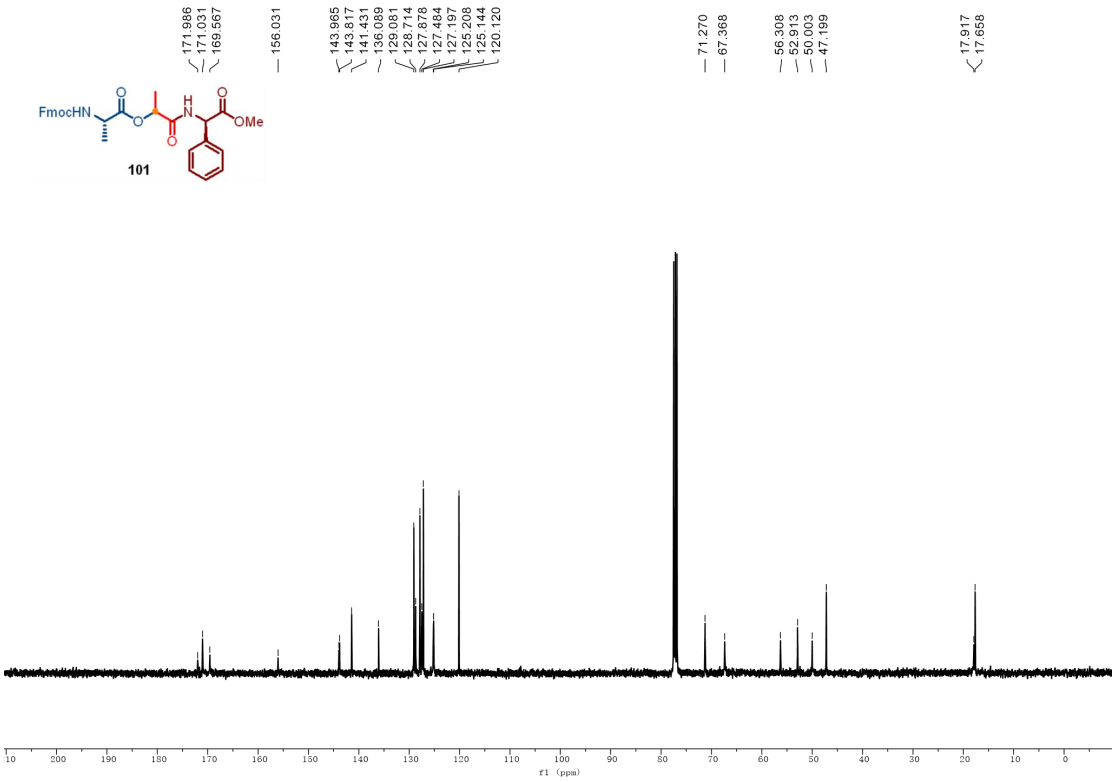
^{1}H NMR (400 MHz, $CDCl_3$) of 100



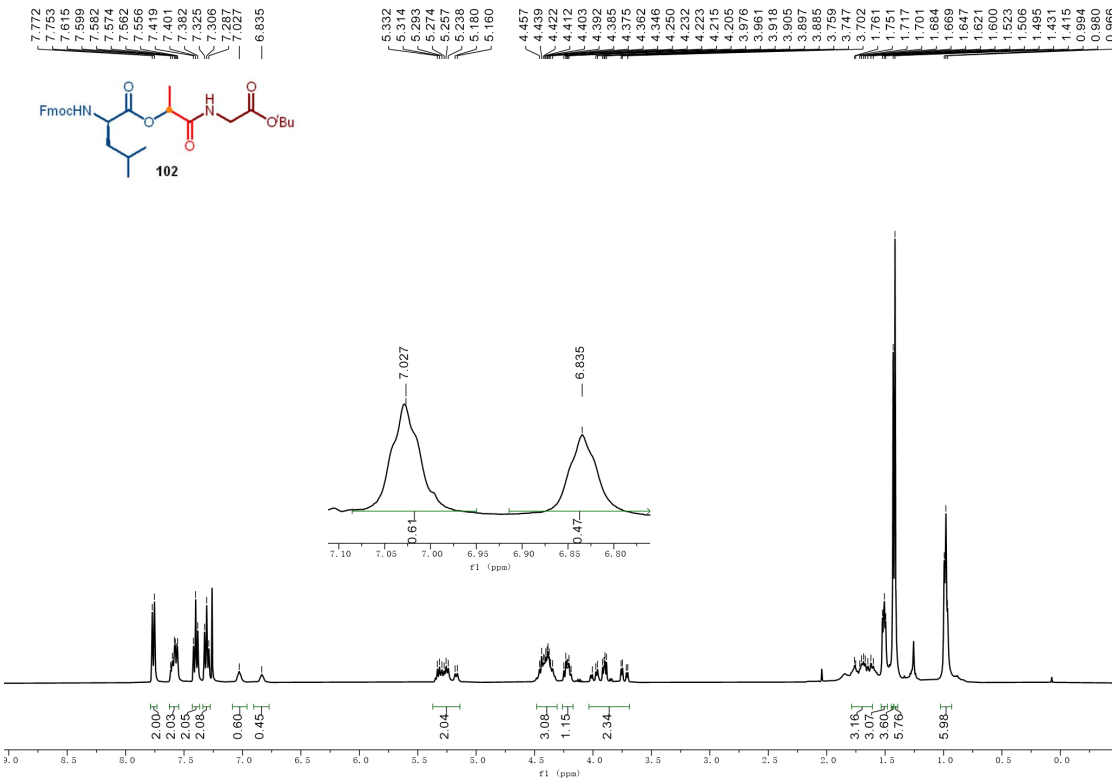
^{13}C NMR (101 MHz, $CDCl_3$) of 100



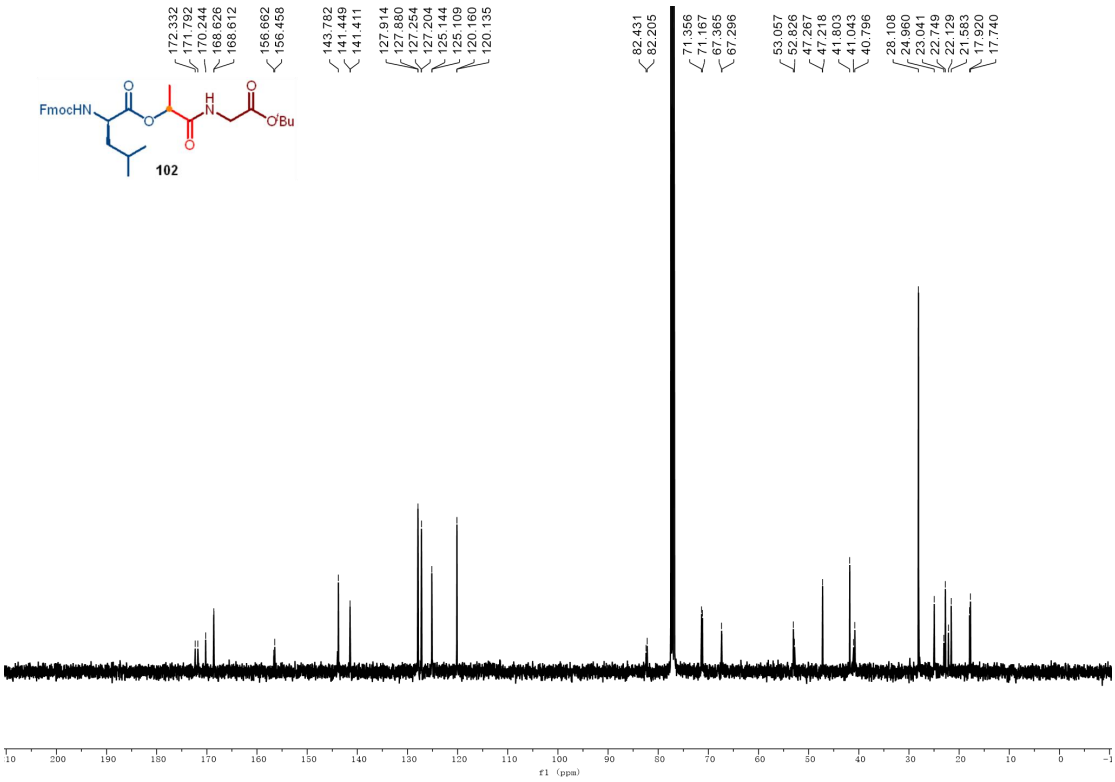
^{1}H NMR (400 MHz, $CDCl_3$) of 101



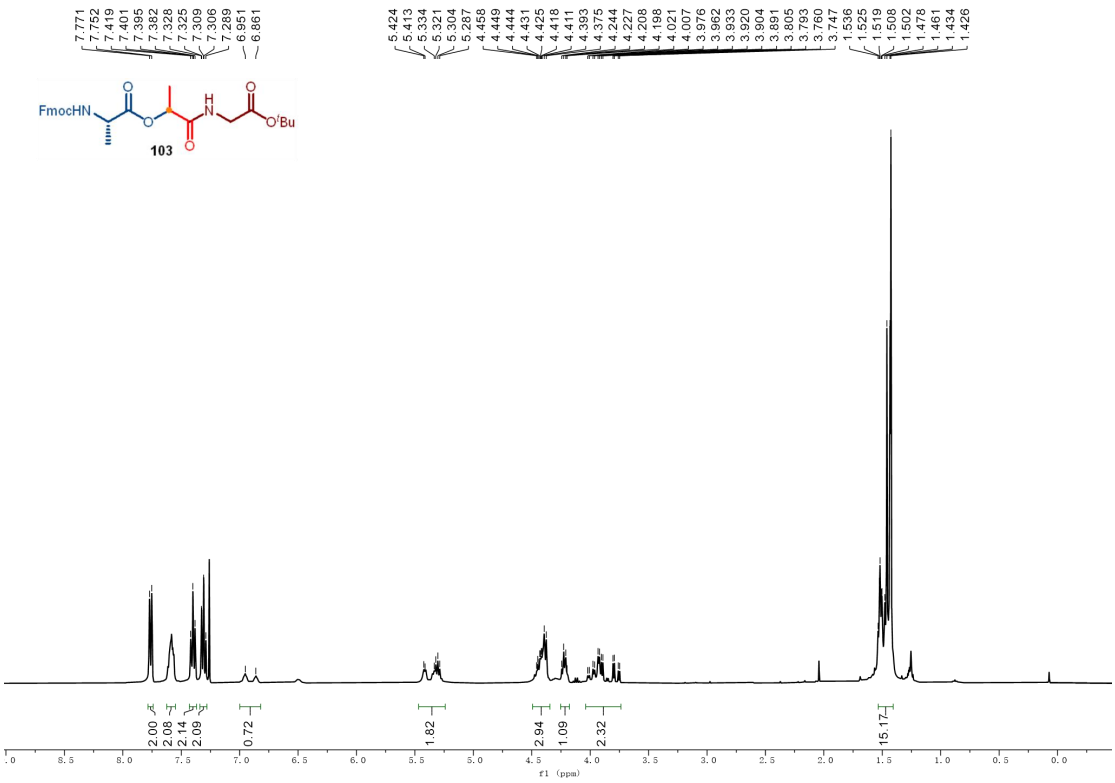
^{13}C NMR (101 MHz, $CDCl_3$) of 101



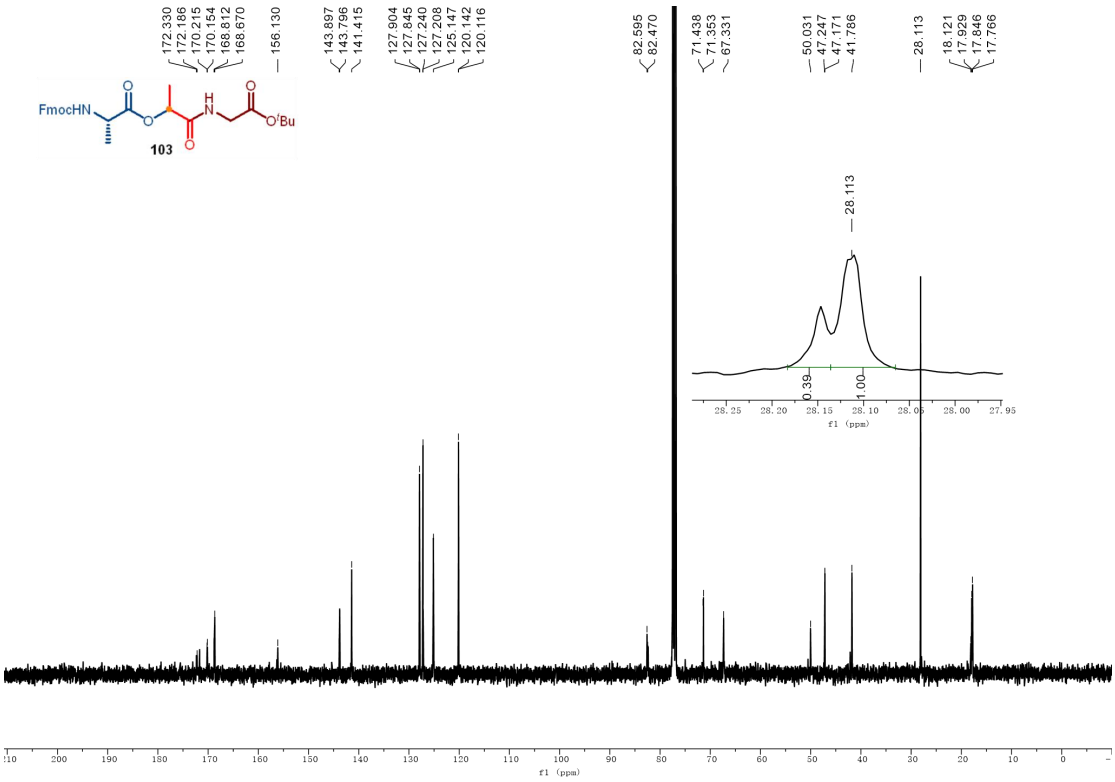
^{1}H NMR (400 MHz, $CDCl_3$) of 102



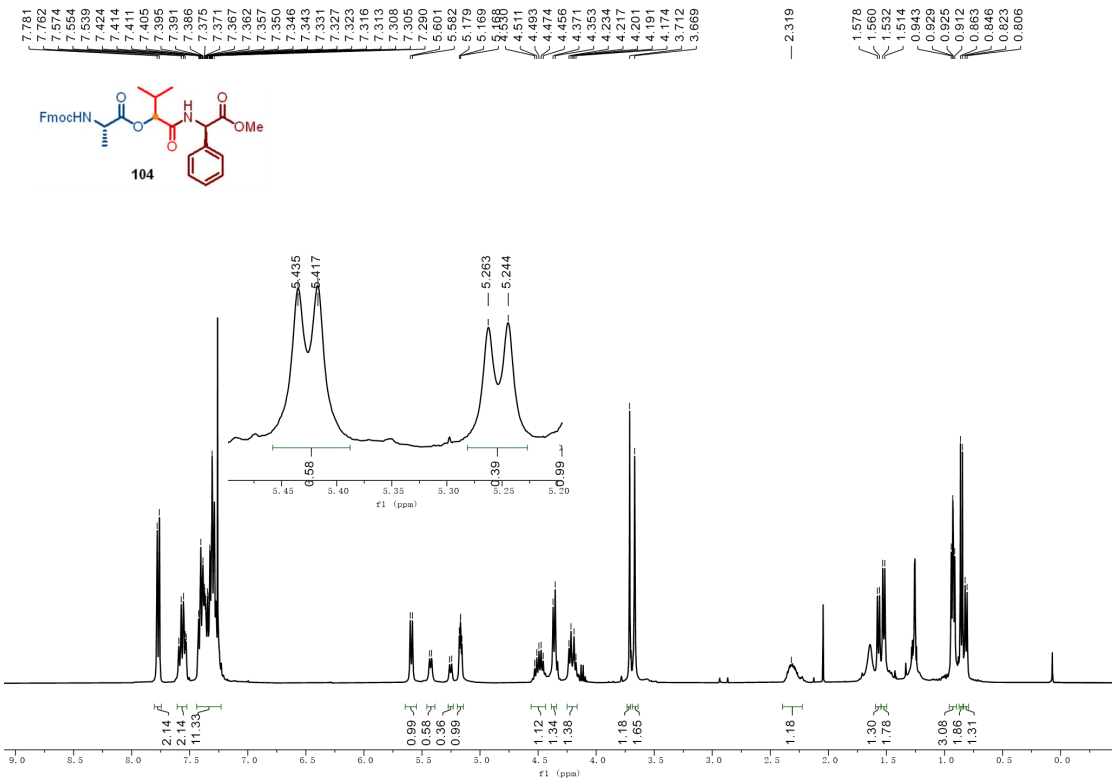
^{13}C NMR (101 MHz, $CDCl_3$) of 102



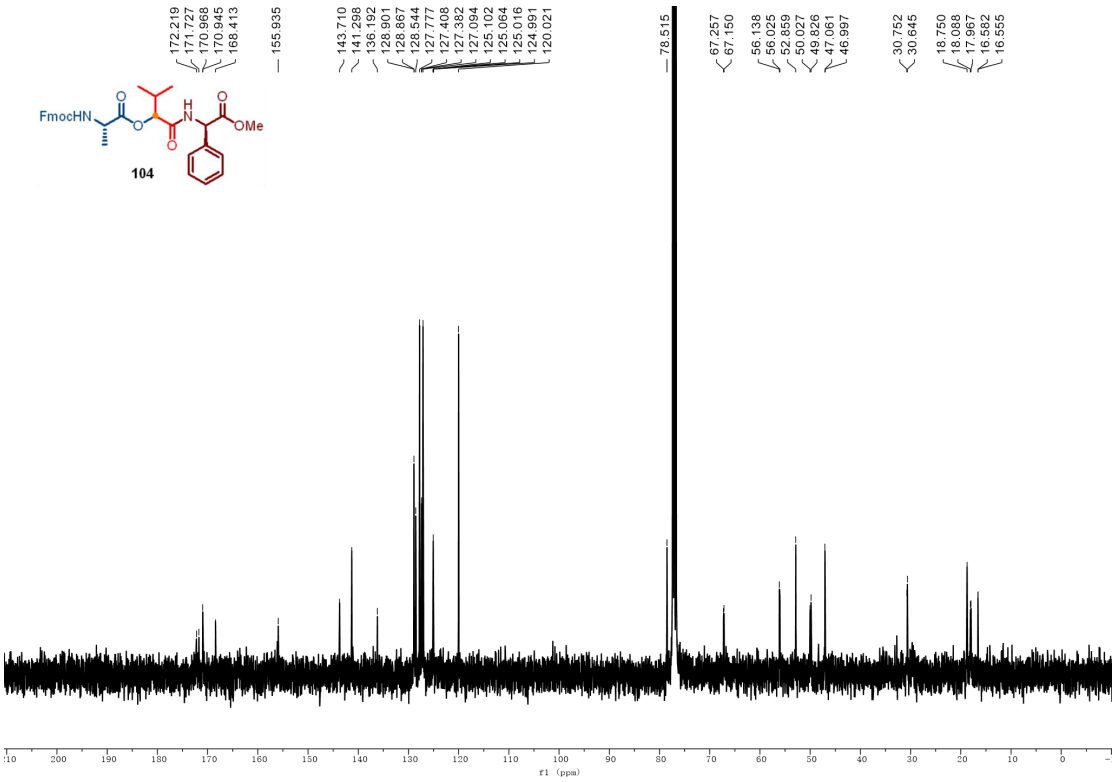
^{1}H NMR (400 MHz, $CDCl_3$) of 103



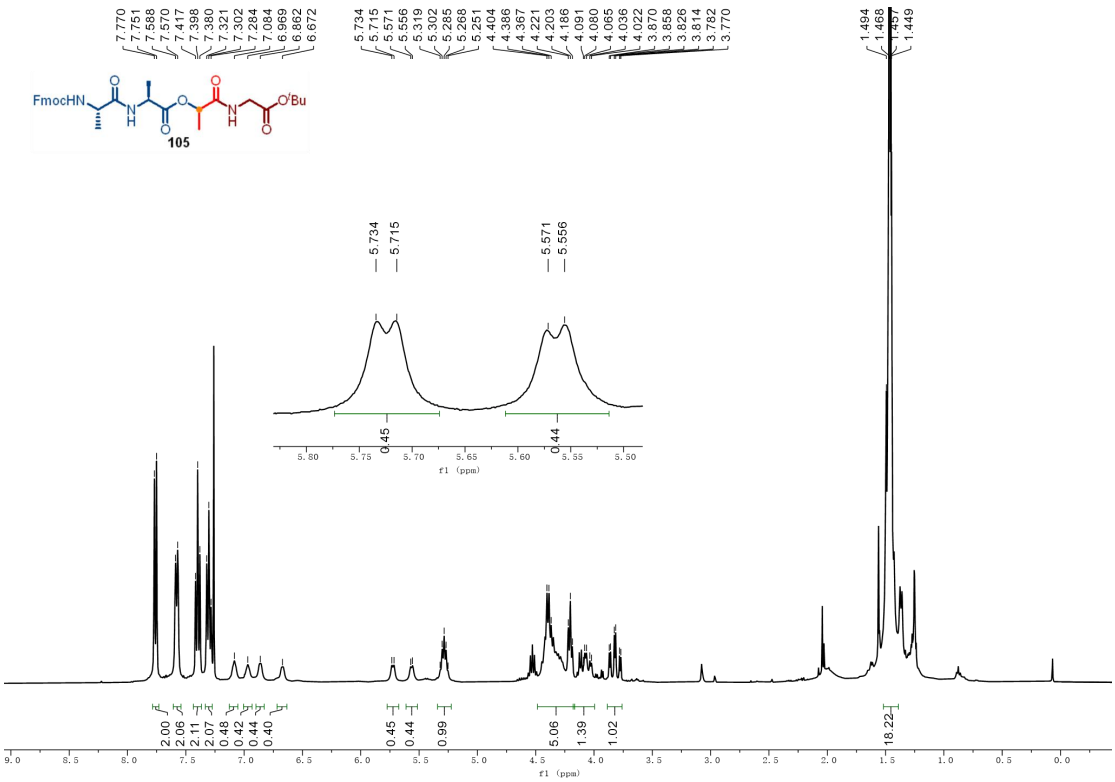
^{13}C NMR (101 MHz, $CDCl_3$) of 103



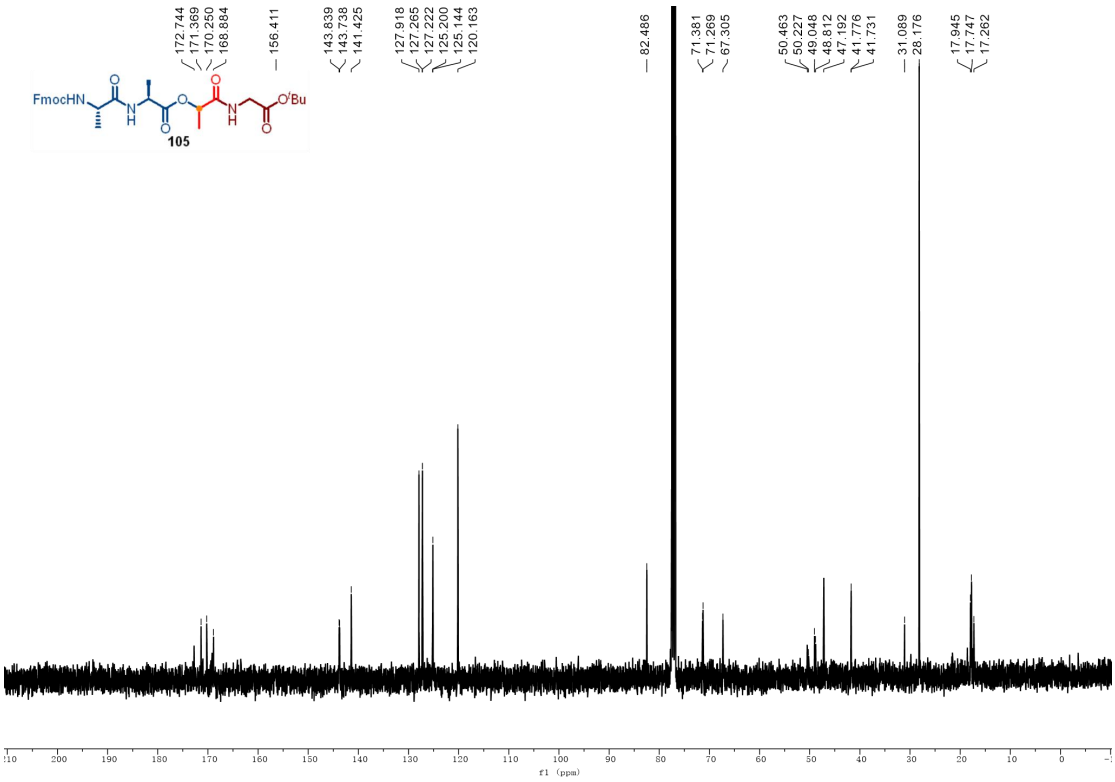
^{1}H NMR (400 MHz, $CDCl_3$) of 104



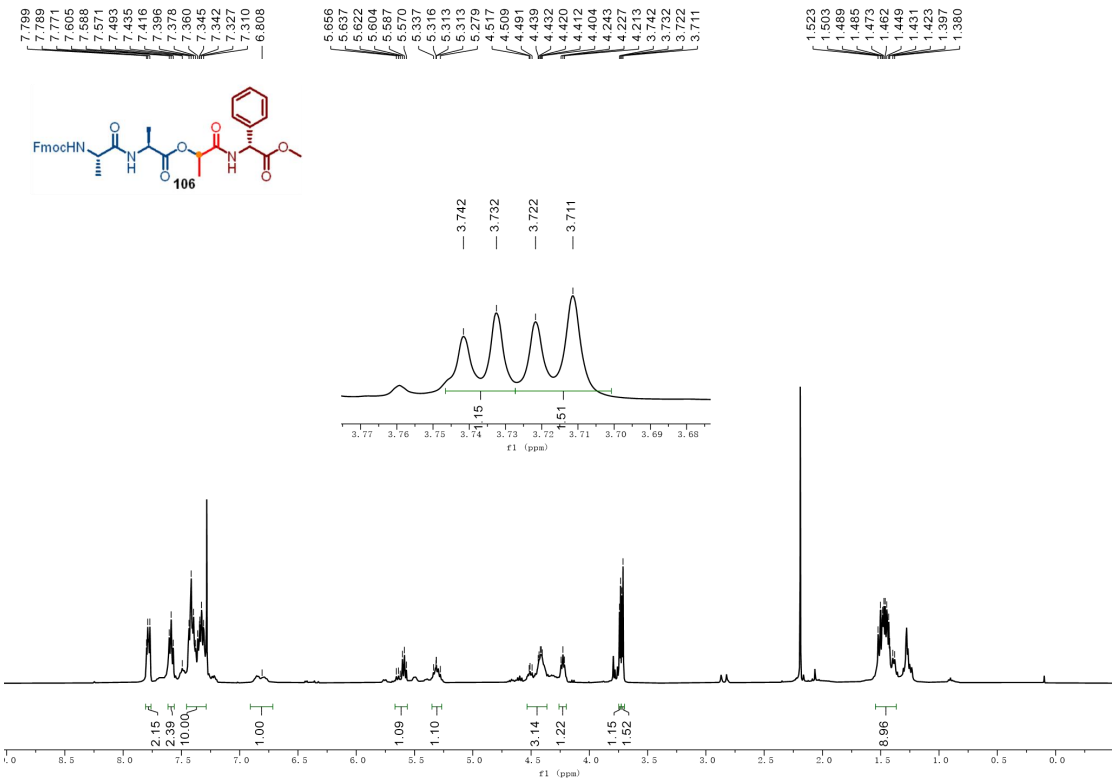
^{13}C NMR (101 MHz, $CDCl_3$) of 104



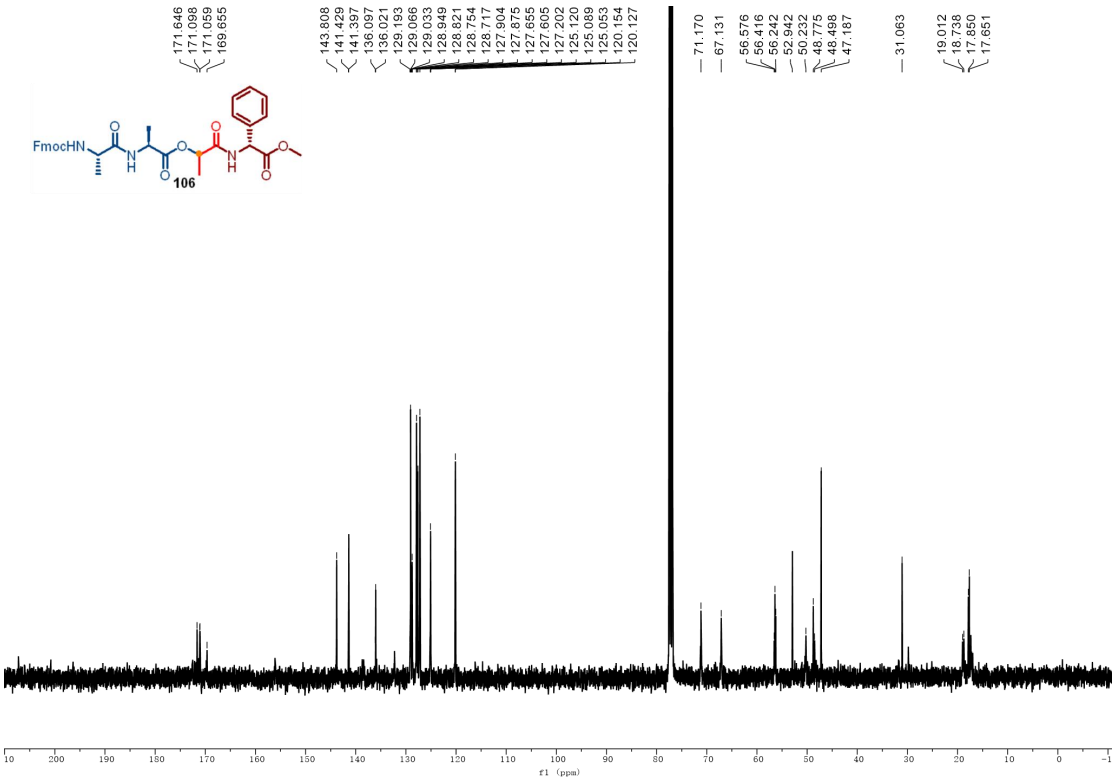
^{1}H NMR (400 MHz, $CDCl_3$) of 105



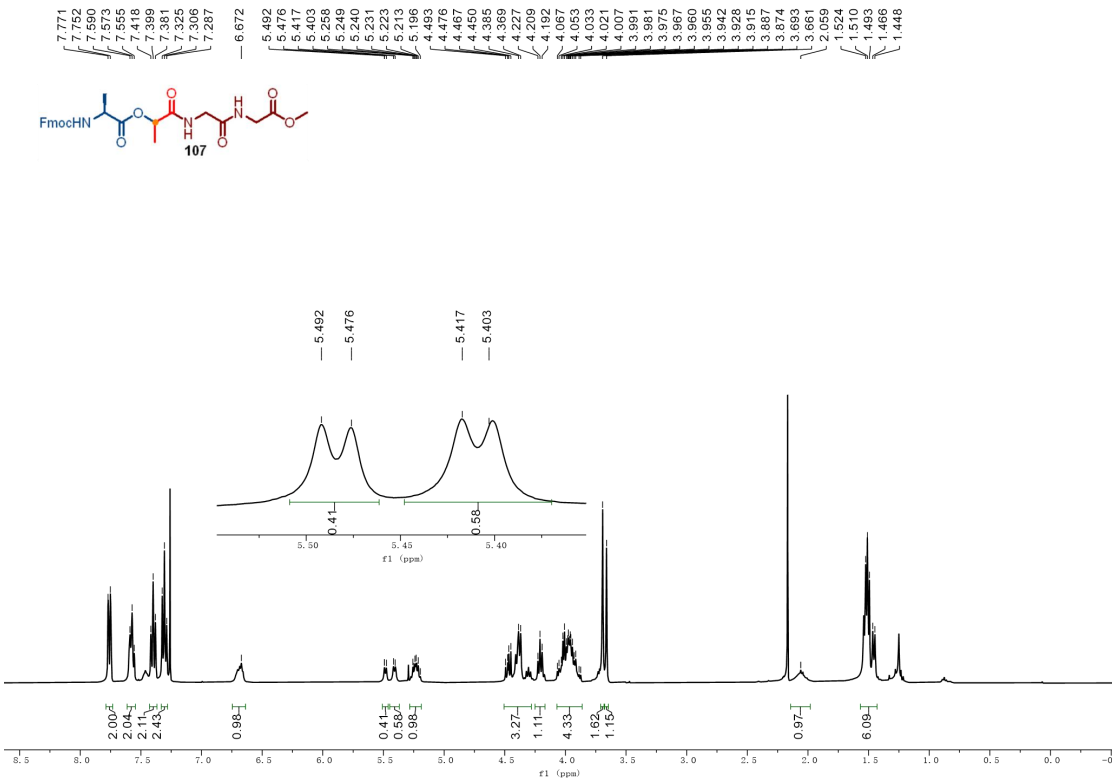
^{13}C NMR (101 MHz, $CDCl_3$) of 105



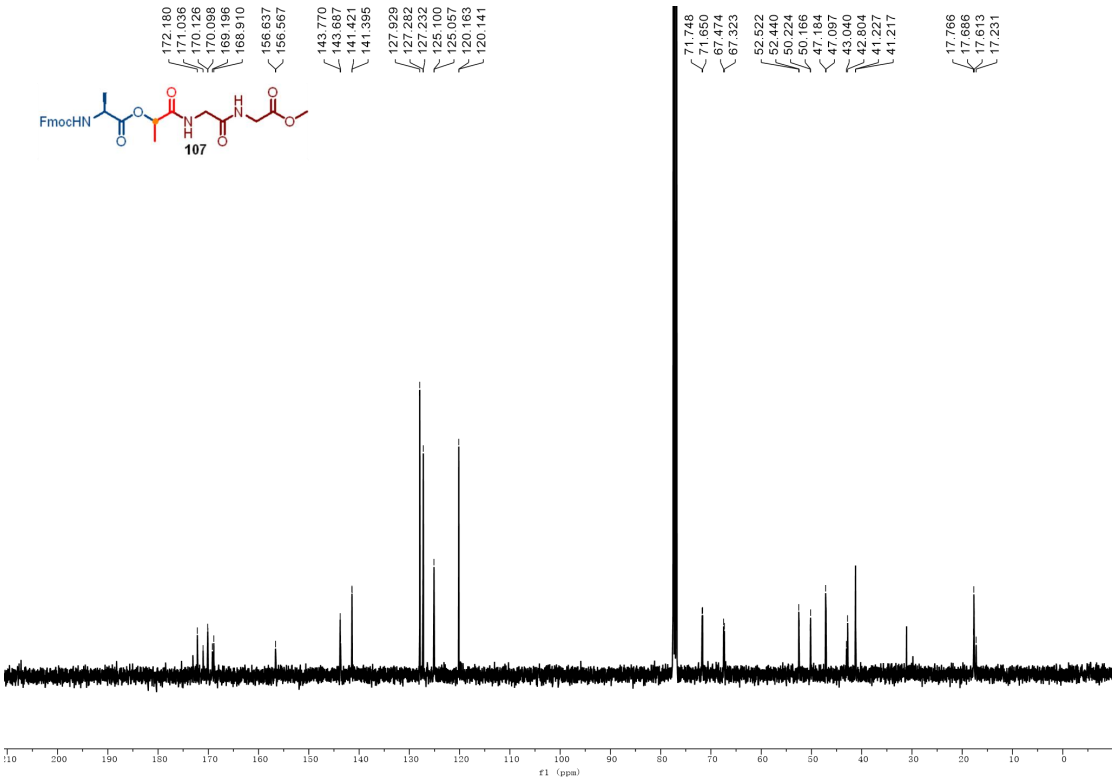
^{1}H NMR (400 MHz, $CDCl_3$) of 106



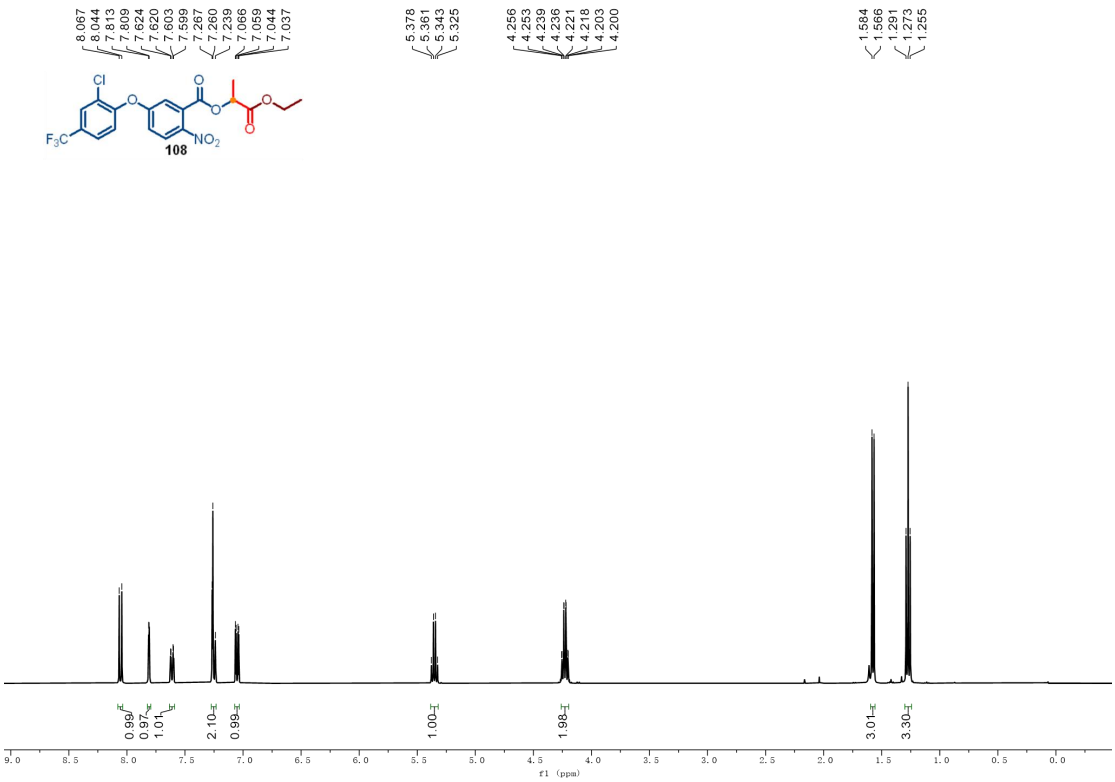
^{13}C NMR (101 MHz, $CDCl_3$) of 106



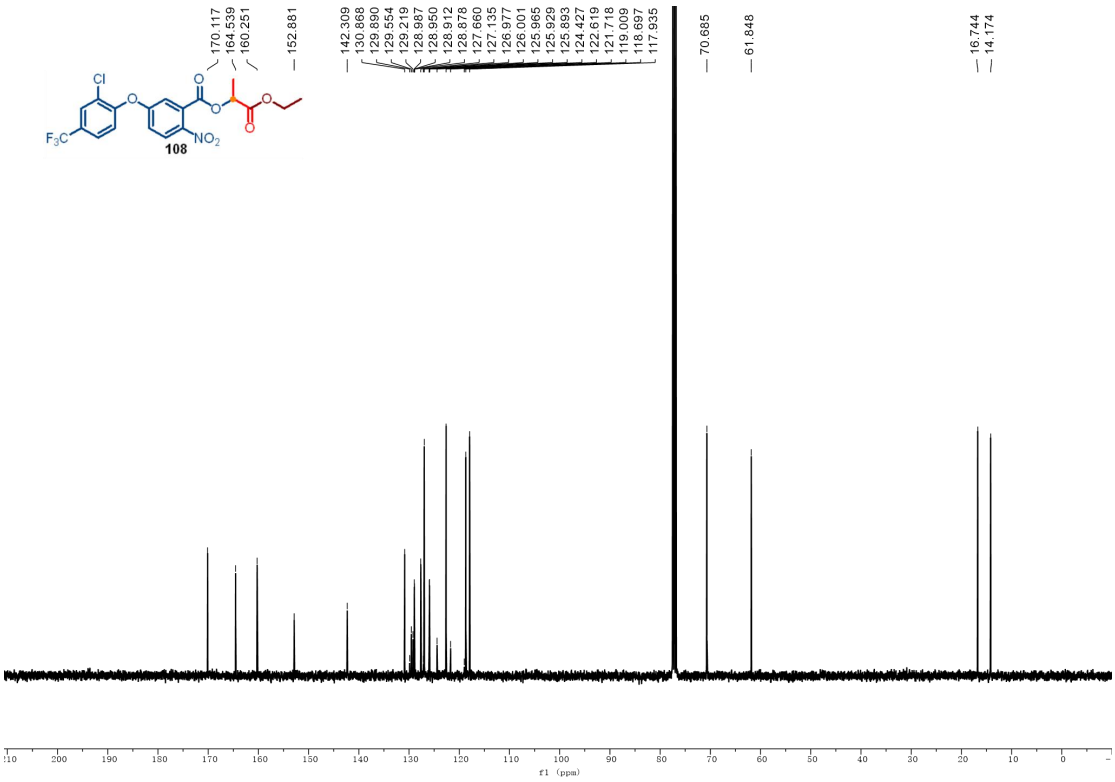
^{1}H NMR (400 MHz, $CDCl_3$) of 107



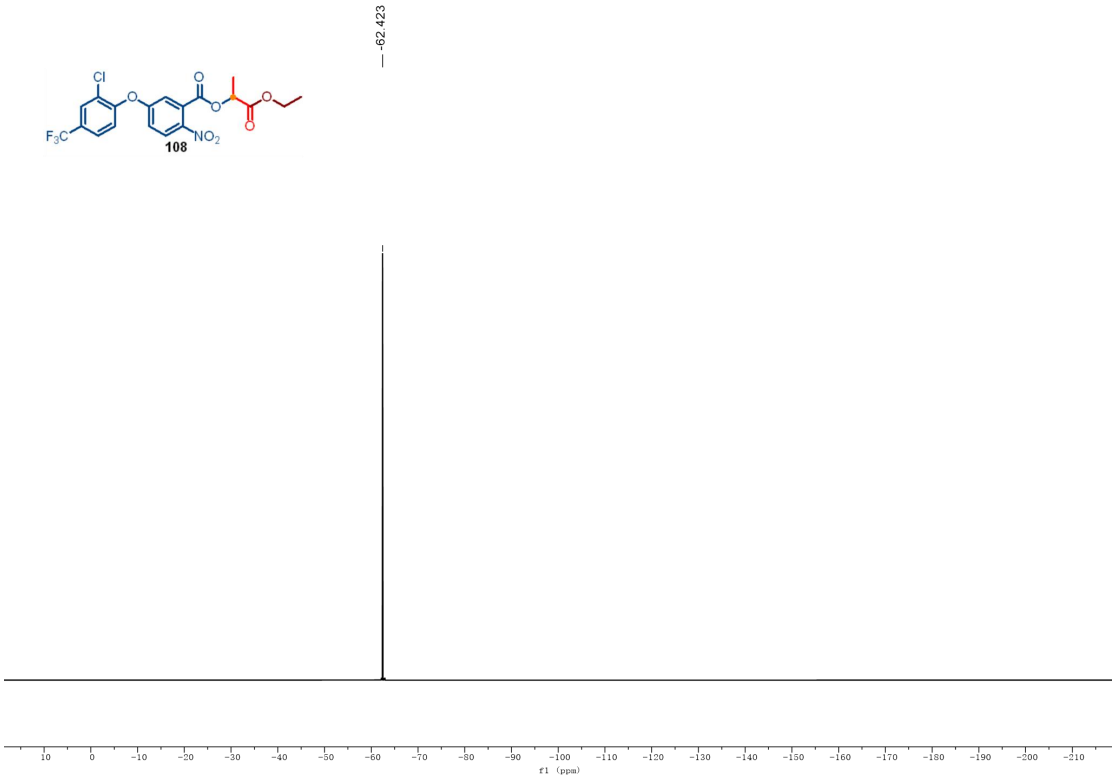
^{13}C NMR (101 MHz, $CDCl_3$) of 107



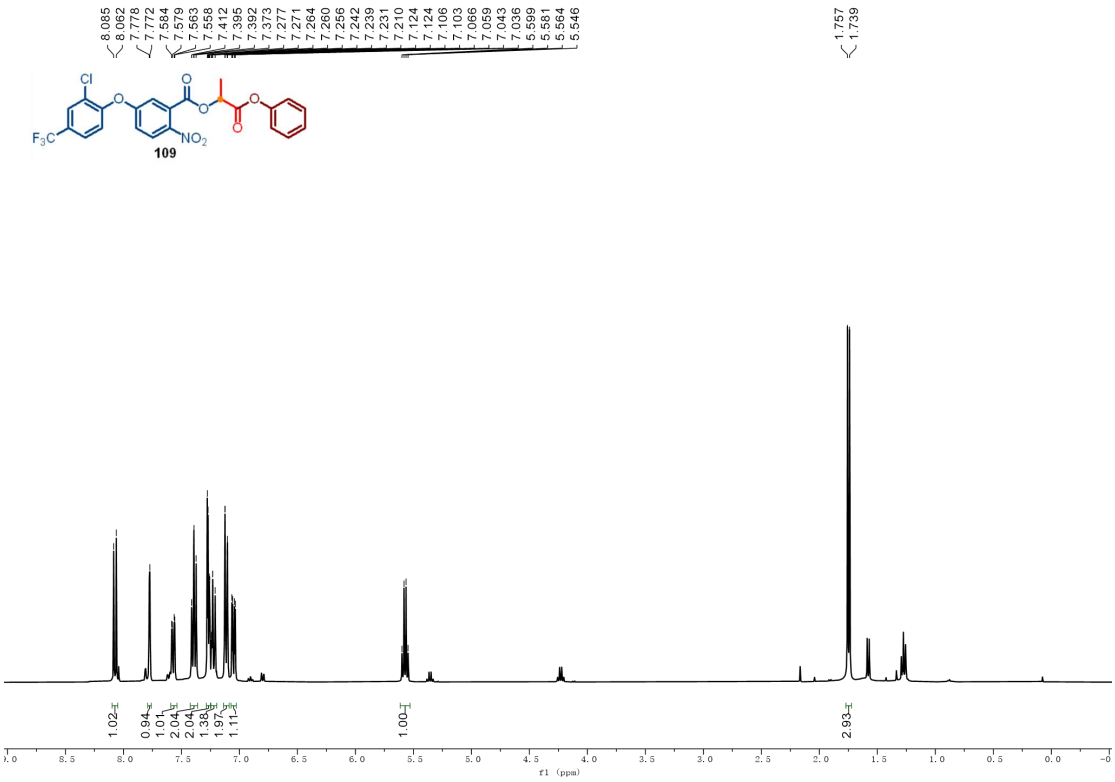
^{1}H NMR (400 MHz, $CDCl_3$) of 108



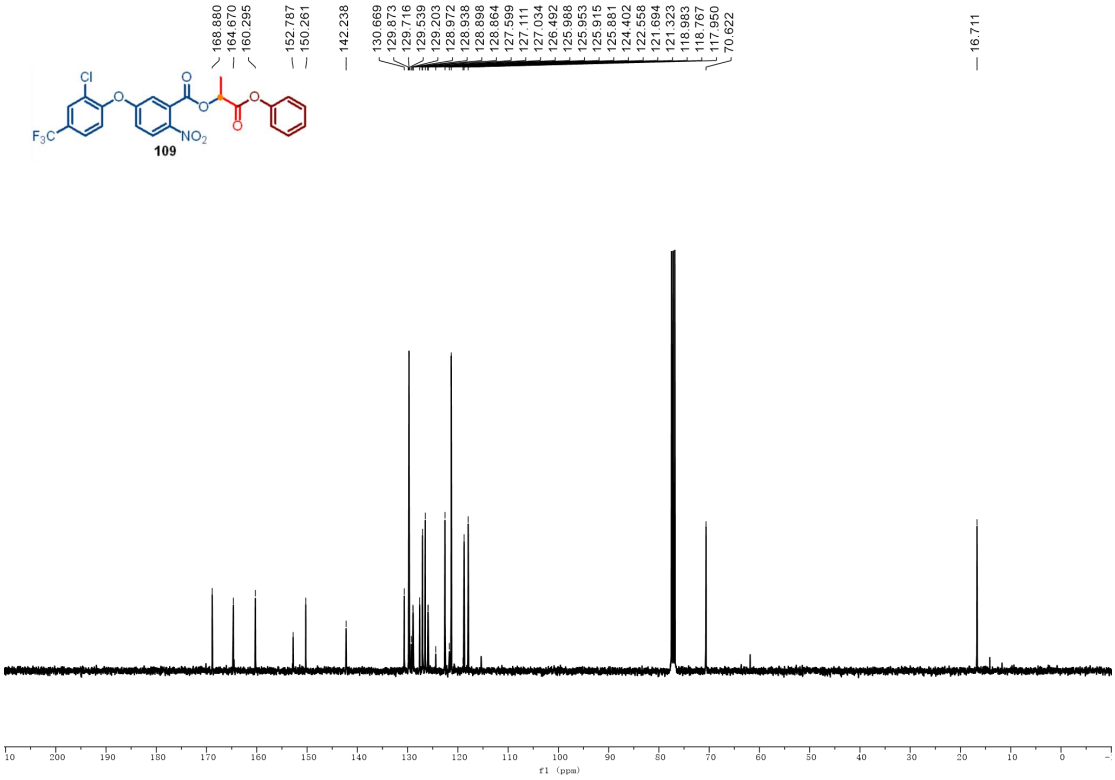
^{13}C NMR (101 MHz, $CDCl_3$) of 108



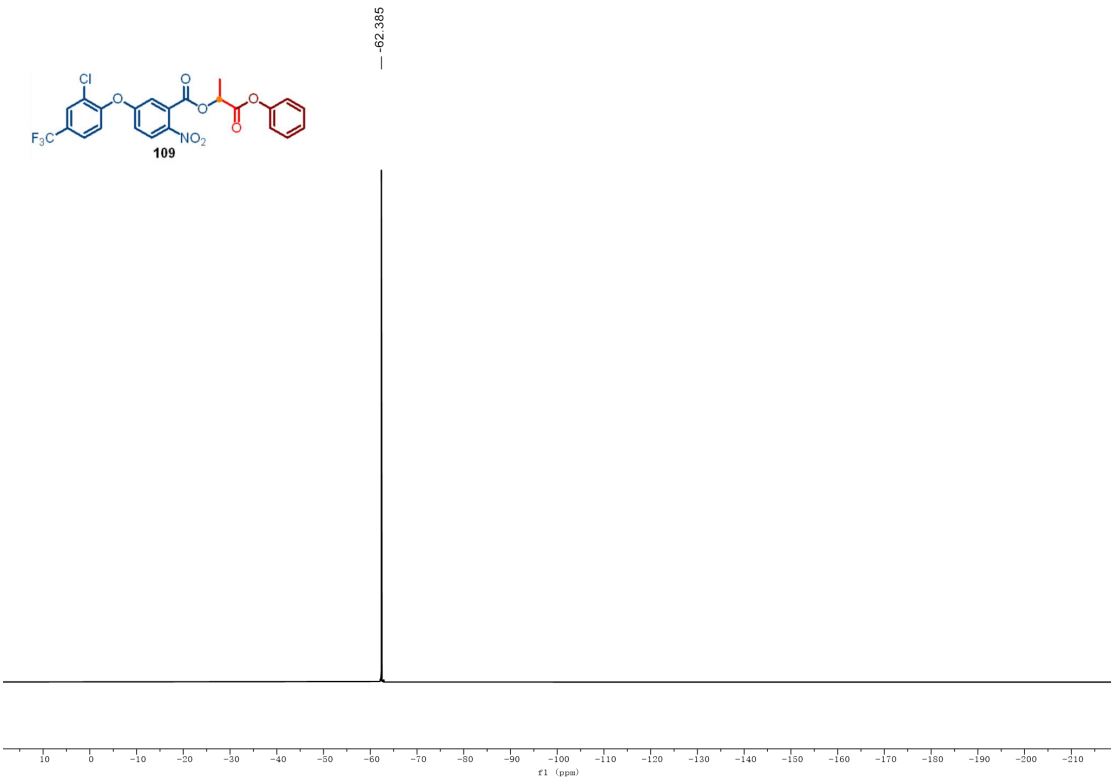
^{19}F NMR (376 MHz, $CDCl_3$) of 108



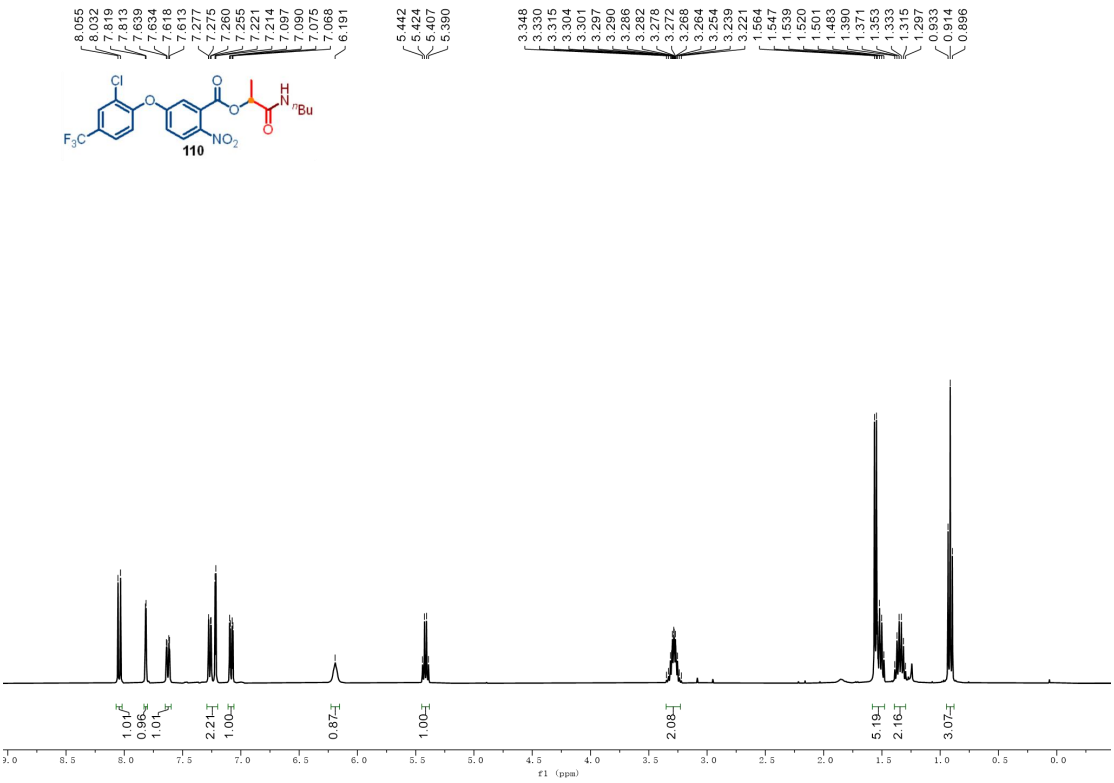
^{1}H NMR (400 MHz, $CDCl_3$) of 109



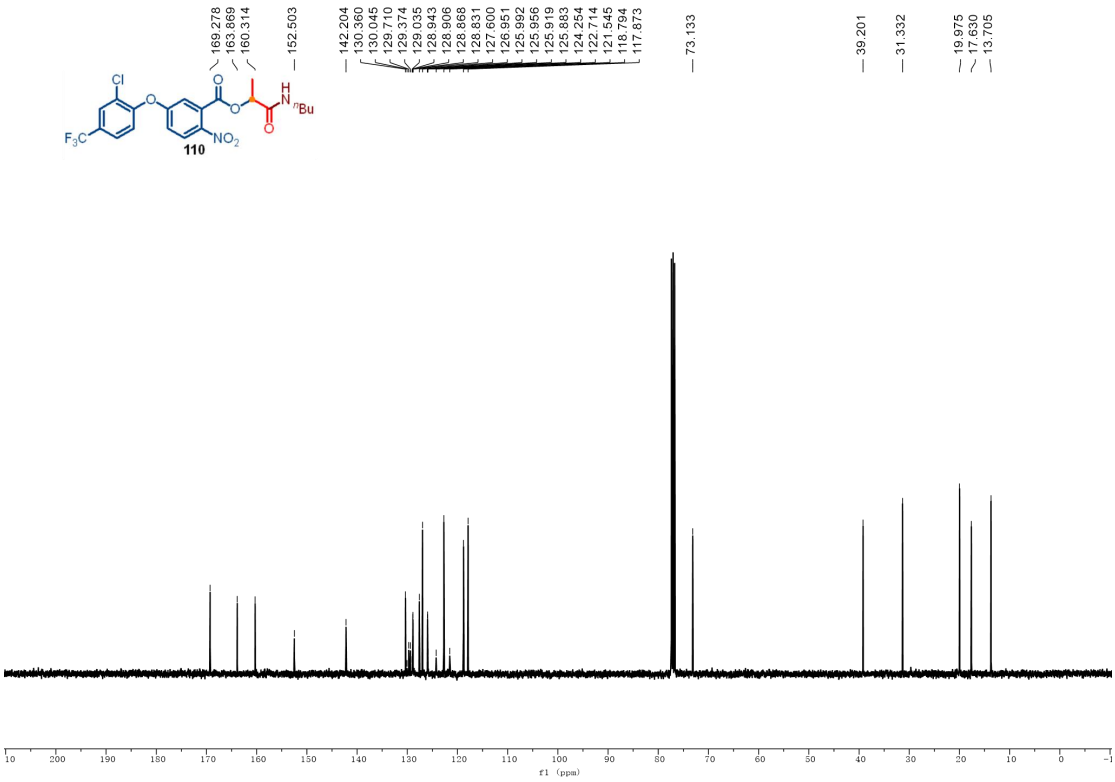
^{13}C NMR (101 MHz, $CDCl_3$) of 109



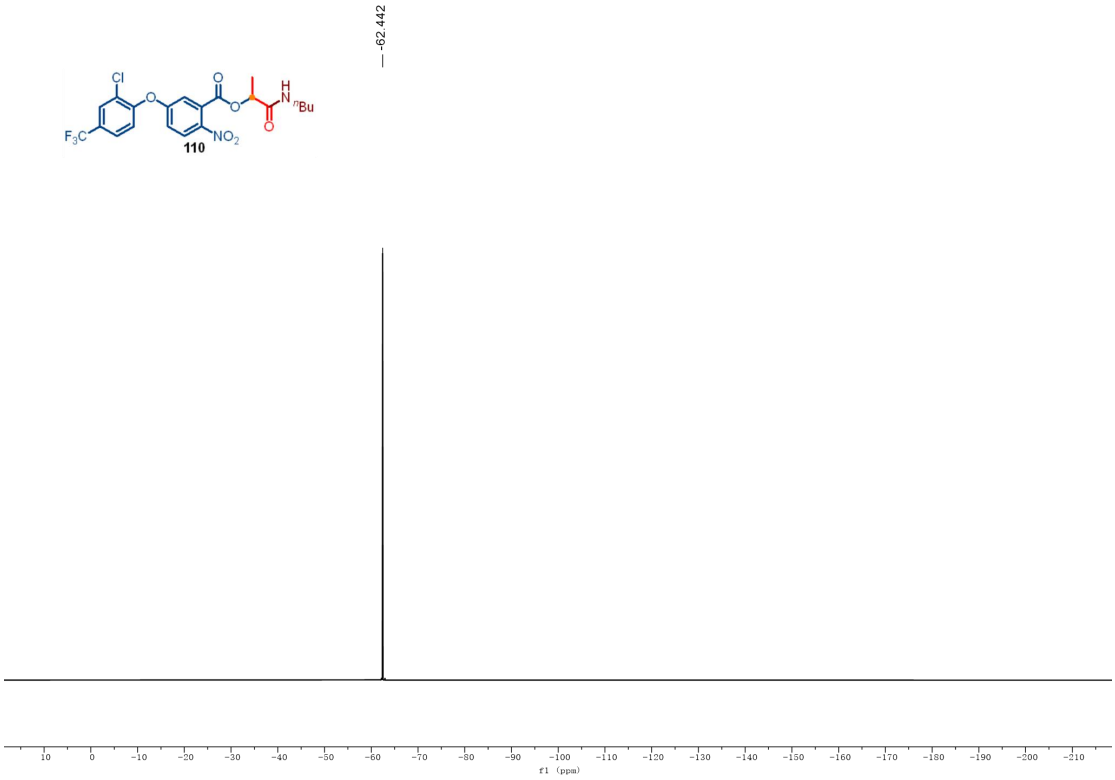
^{19}F NMR (376 MHz, $CDCl_3$) of 109



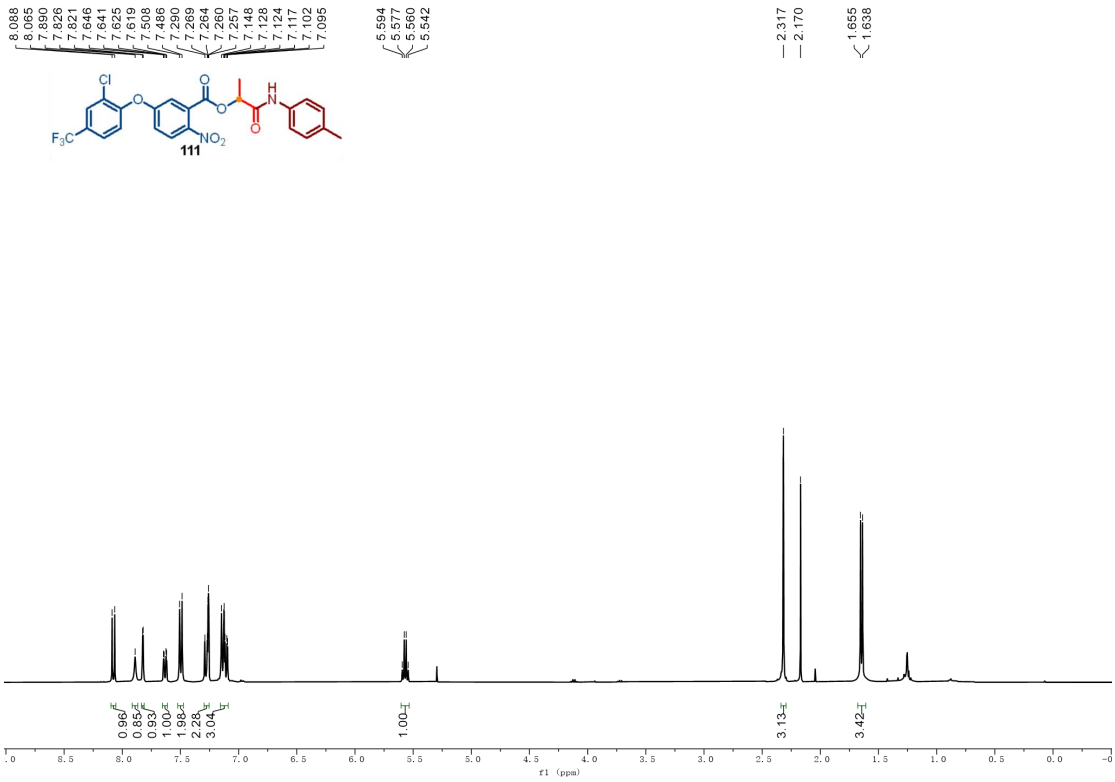
^{1}H NMR (400 MHz, $CDCl_3$) of 110



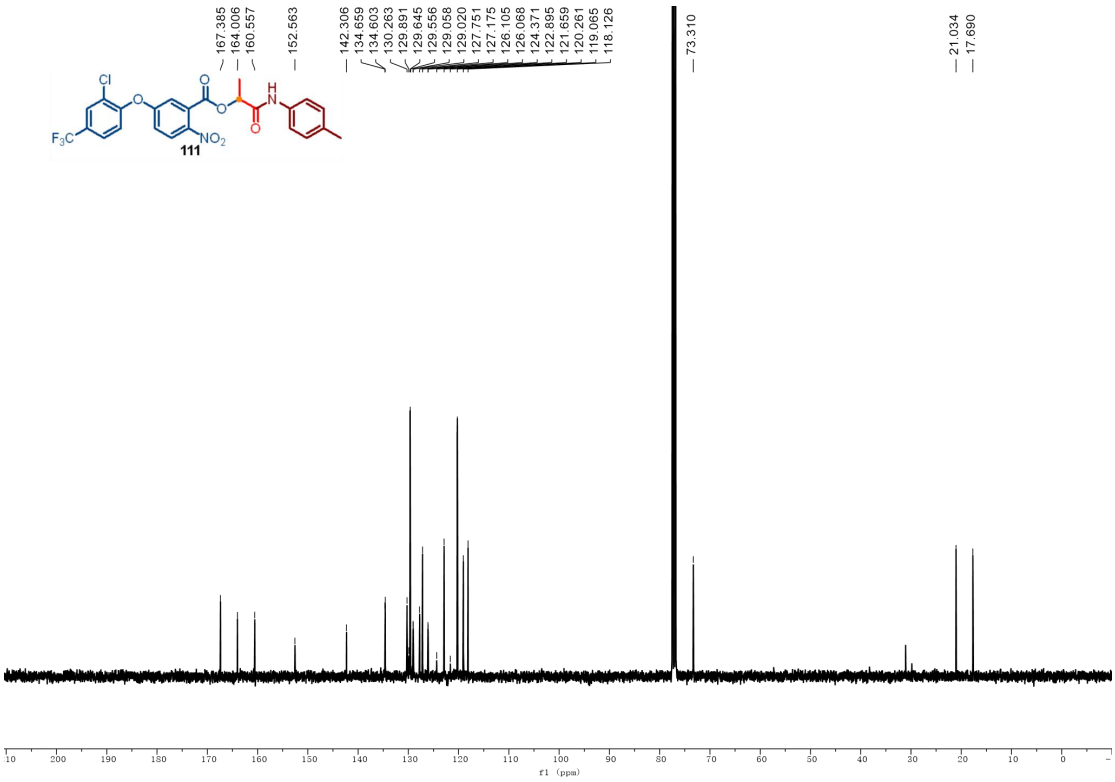
^{13}C NMR (101 MHz, $CDCl_3$) of 110



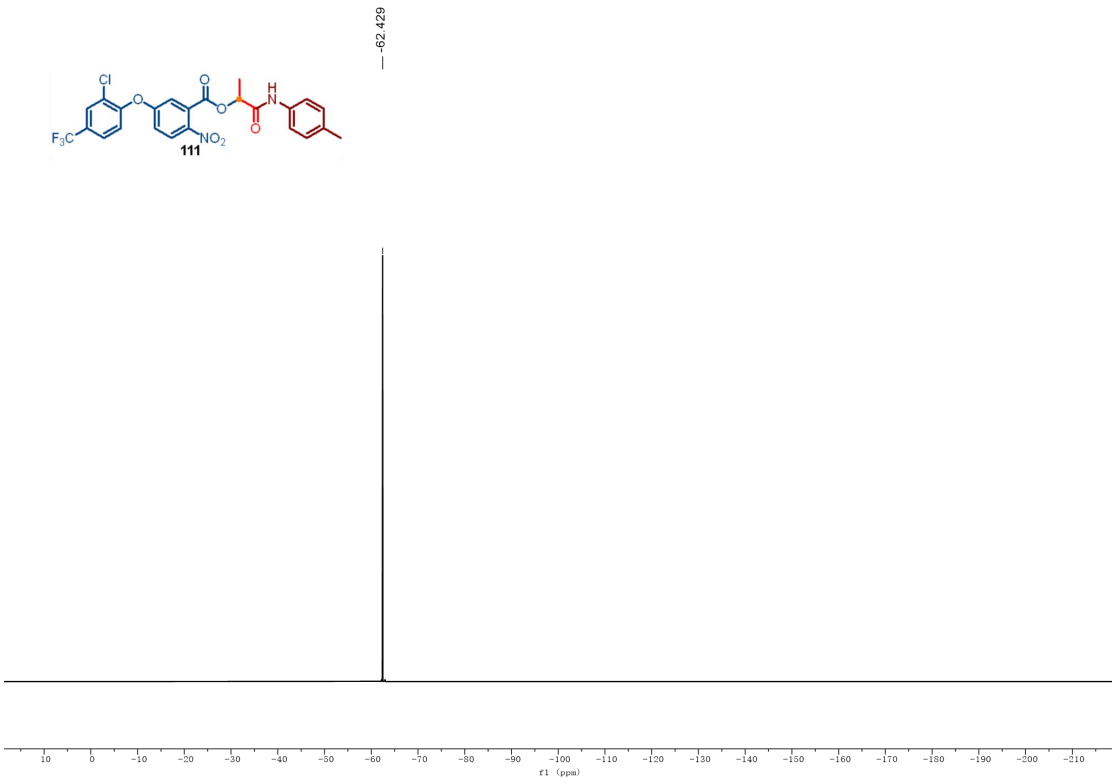
^{19}F NMR (376 MHz, $CDCl_3$) of 110



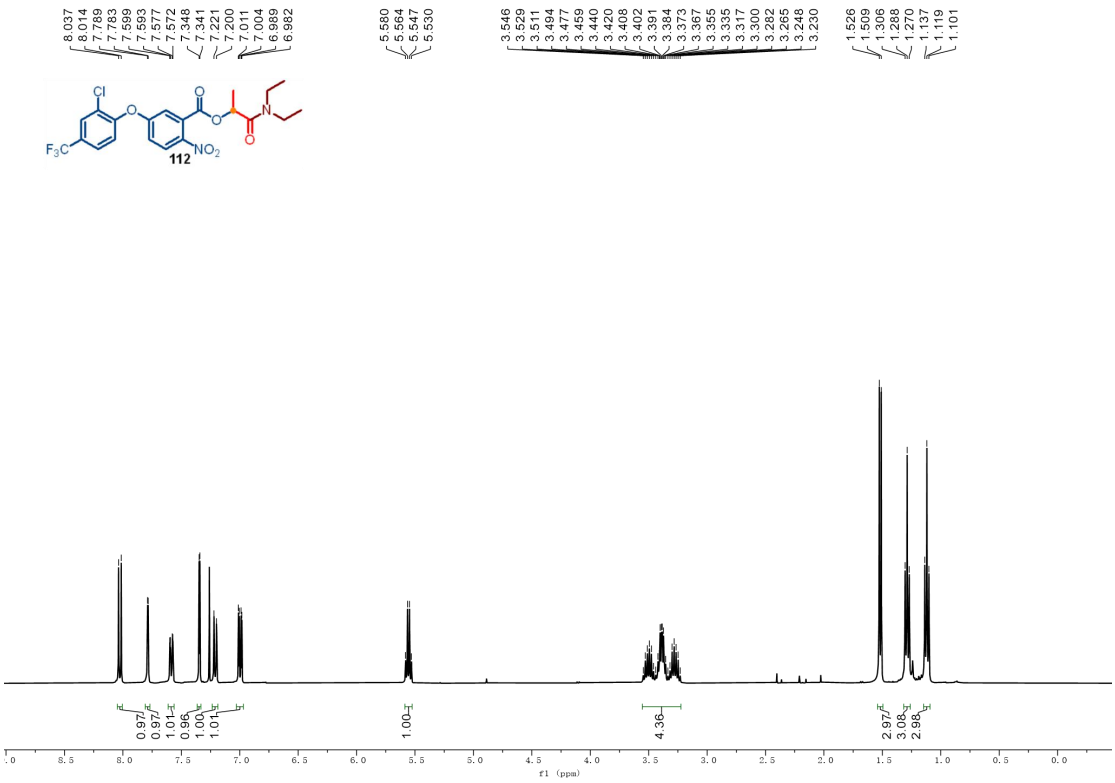
^{1}H NMR (400 MHz, $CDCl_3$) of 111



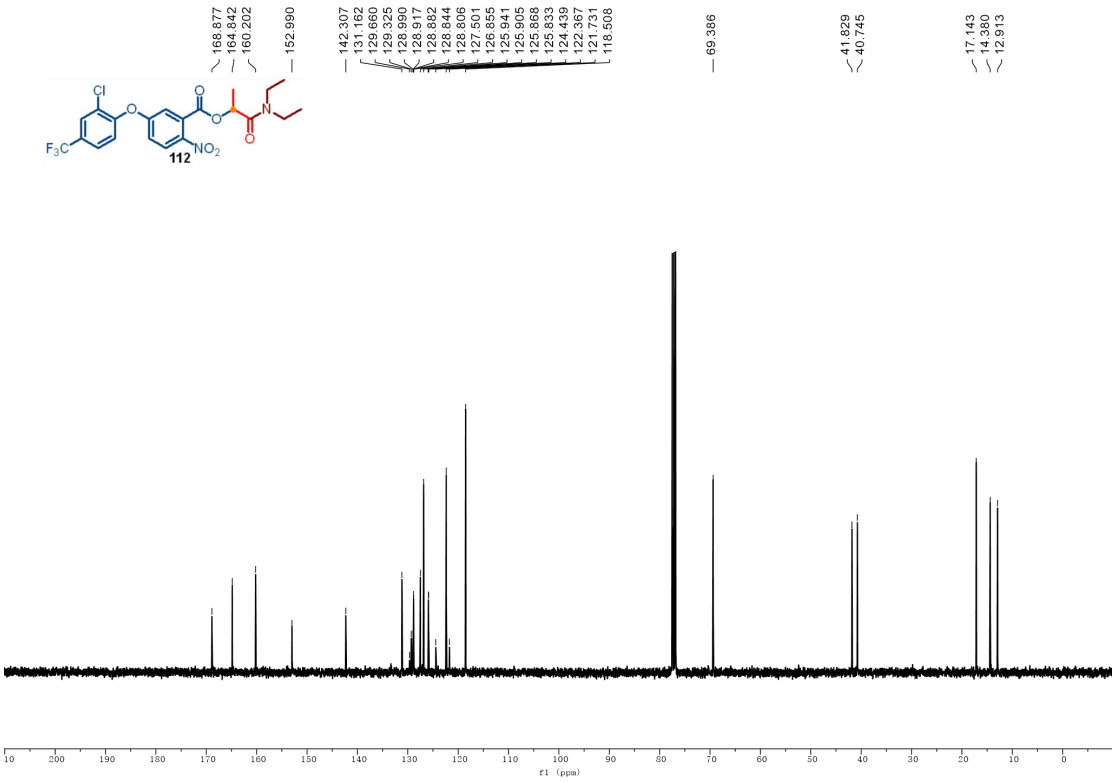
^{13}C NMR (101 MHz, $CDCl_3$) of 111



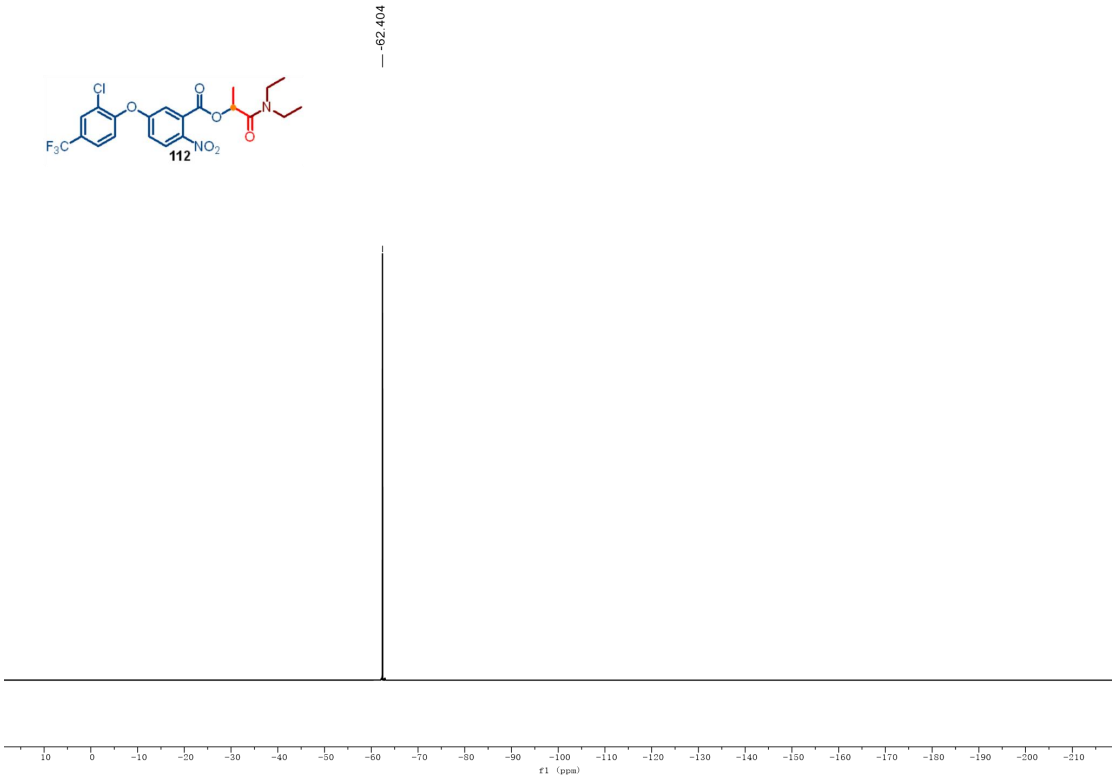
^{19}F NMR (376 MHz, $CDCl_3$) of 111



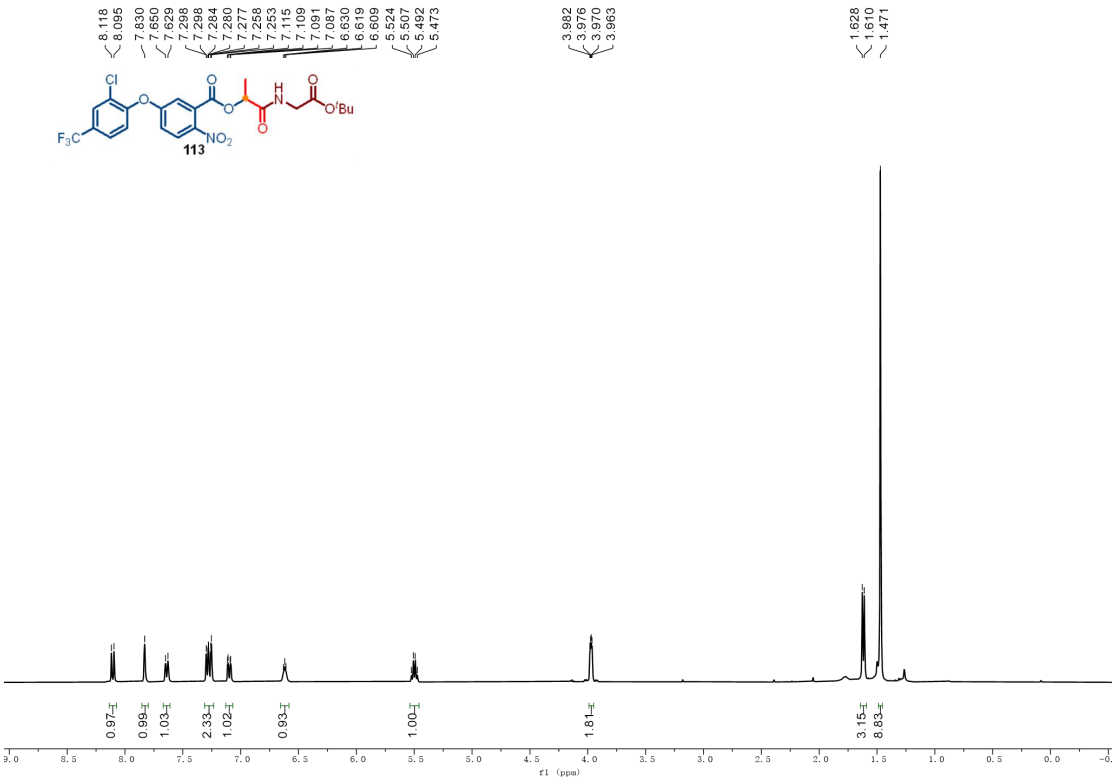
^{1}H NMR (400 MHz, $CDCl_3$) of 112



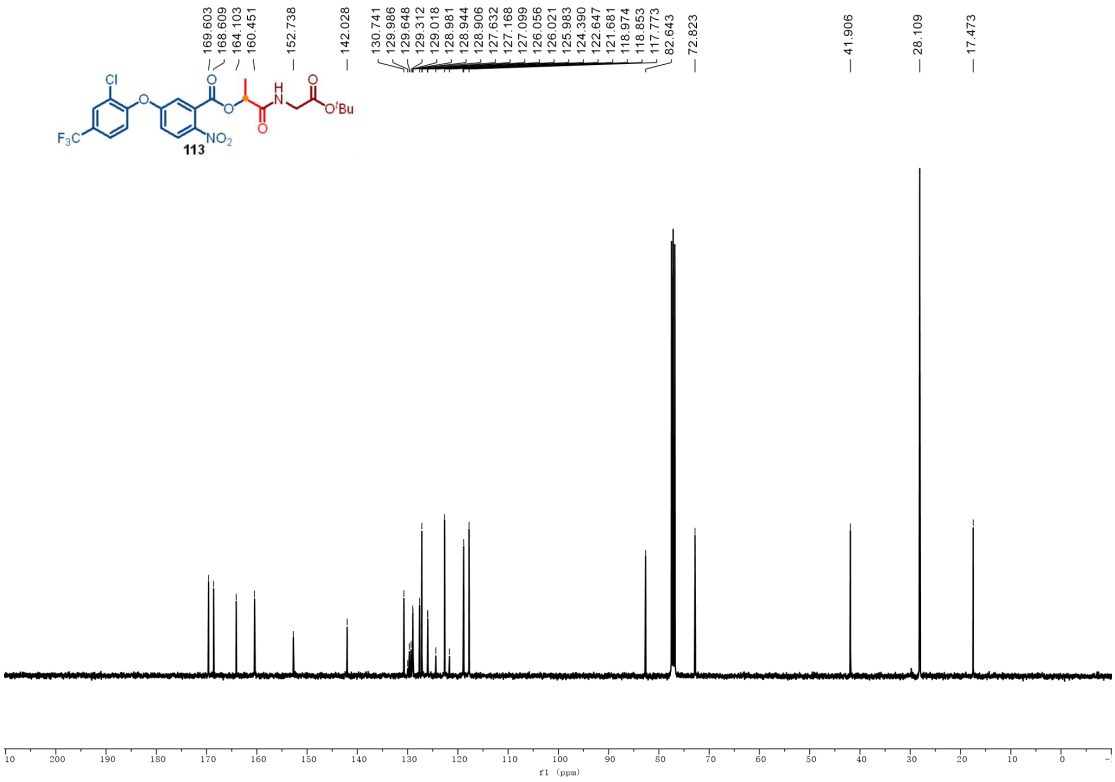
^{13}C NMR (101 MHz, $CDCl_3$) of 112



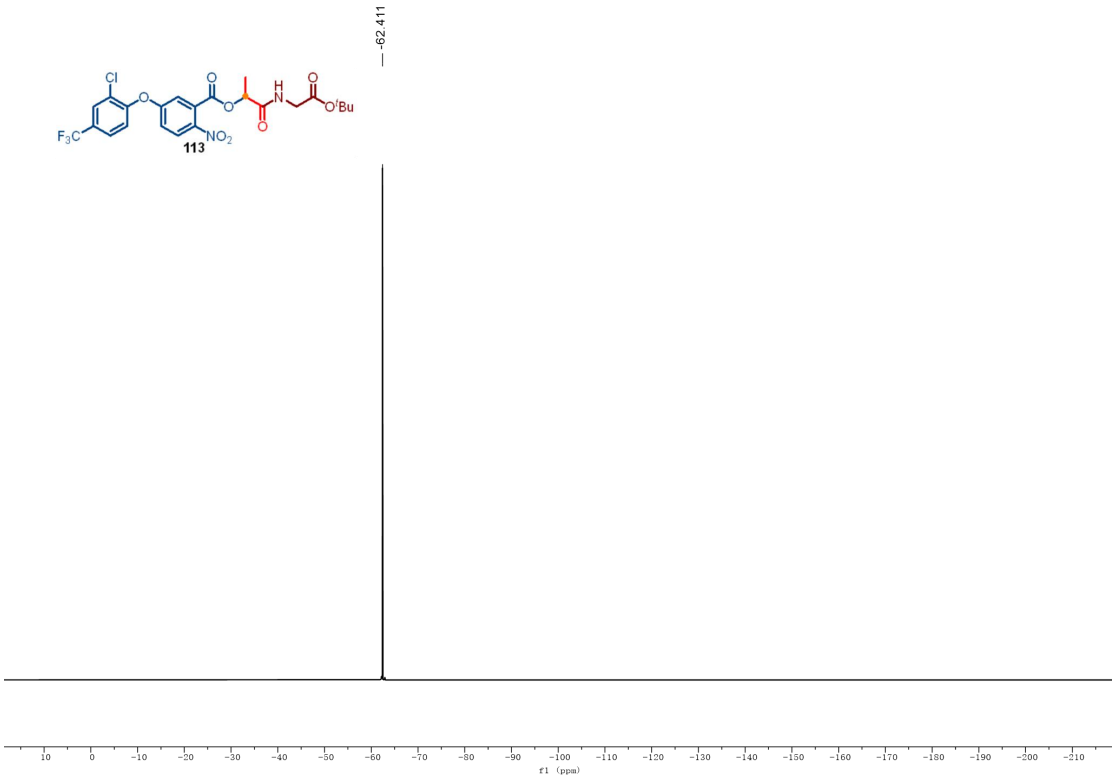
^{19}F NMR (376 MHz, $CDCl_3$) of 112



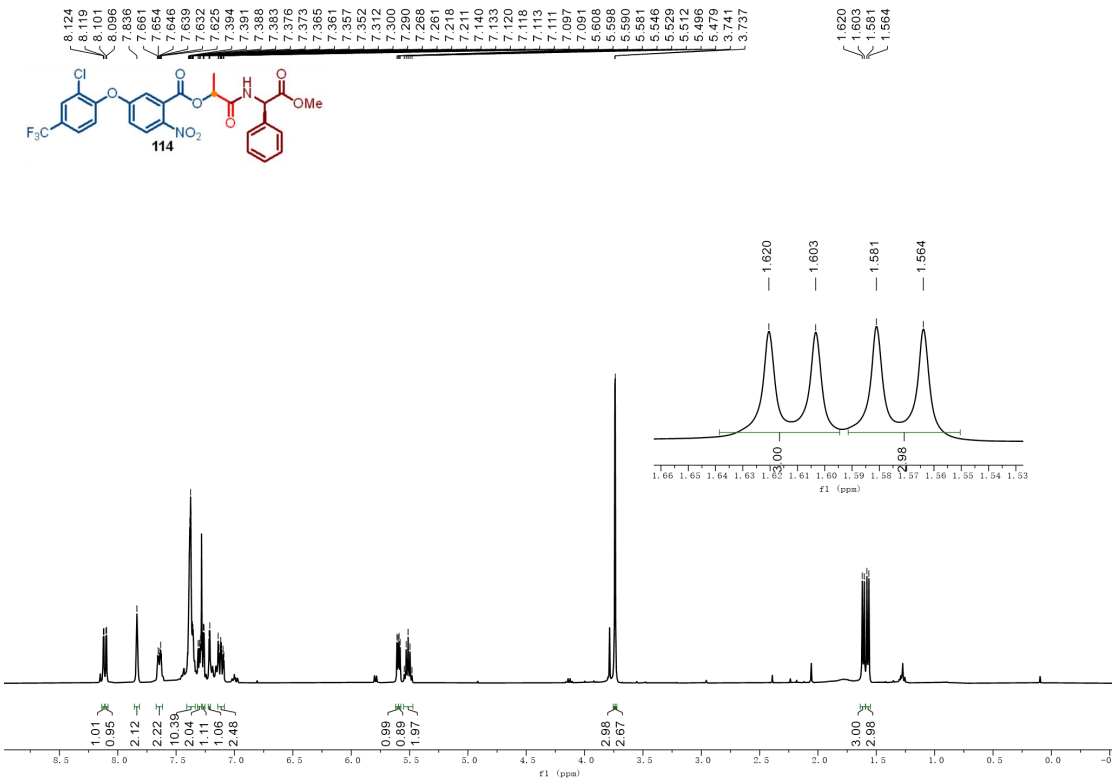
^{1}H NMR (400 MHz, $CDCl_3$) of 113



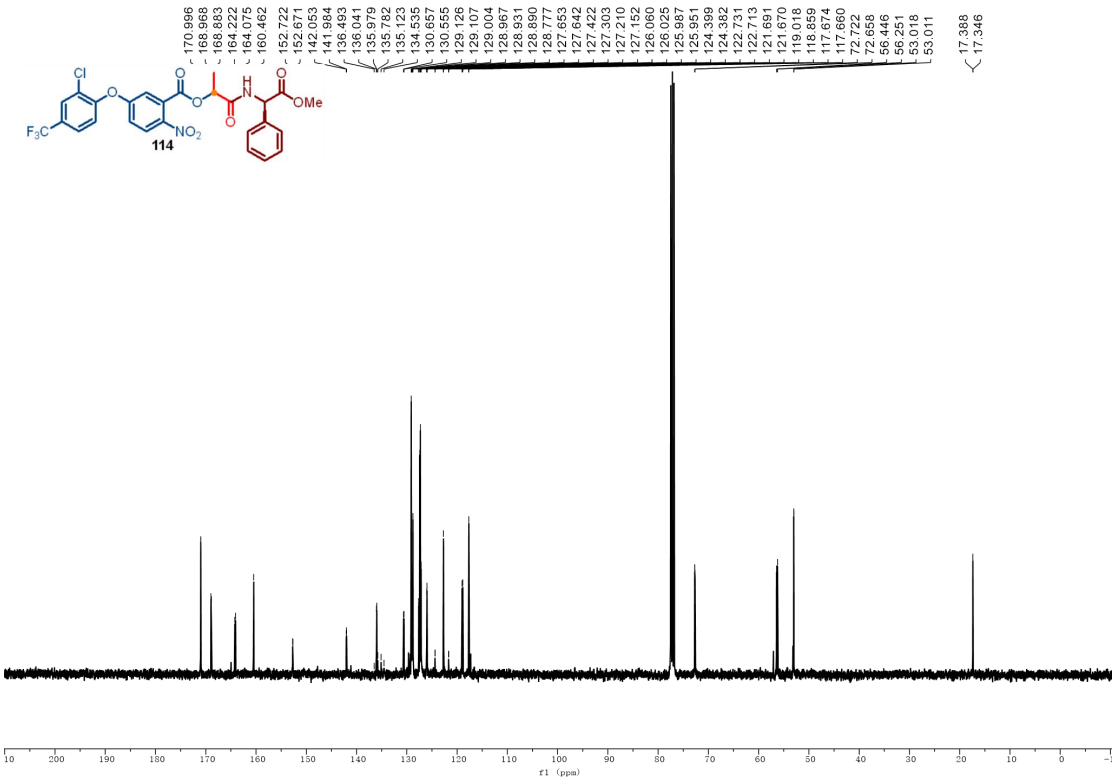
^{13}C NMR (101 MHz, $CDCl_3$) of 113



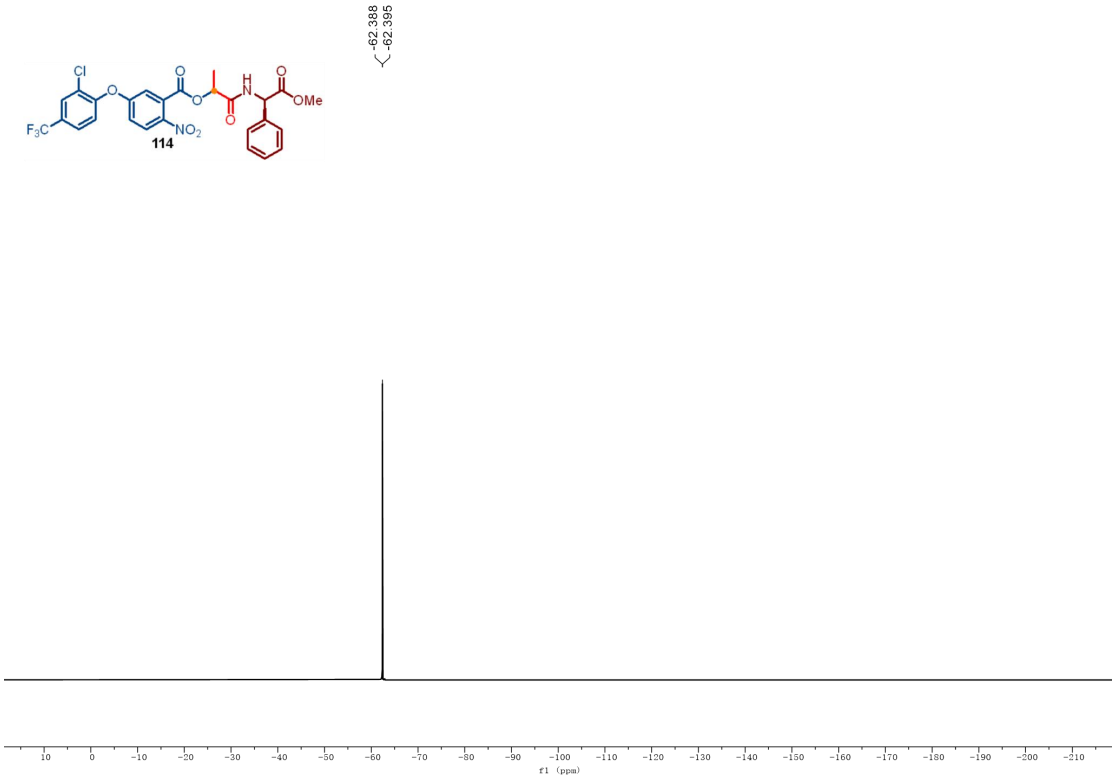
^{19}F NMR (376 MHz, $CDCl_3$) of 113



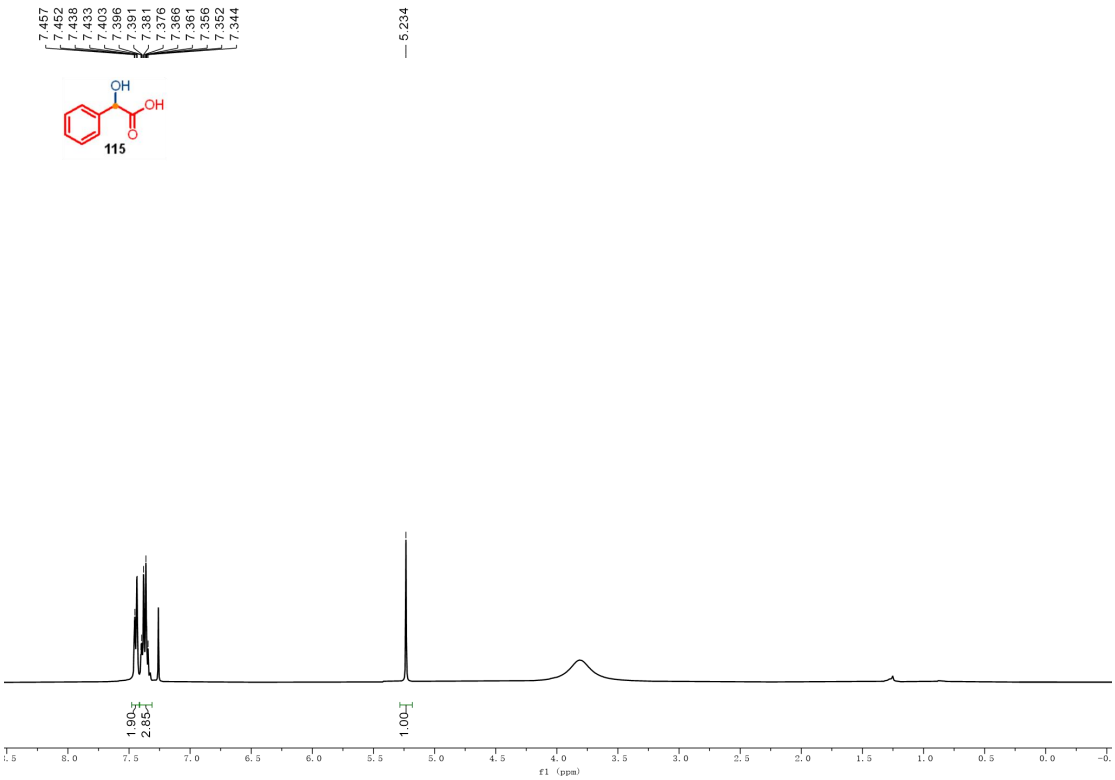
^{1}H NMR (400 MHz, $CDCl_3$) of 114



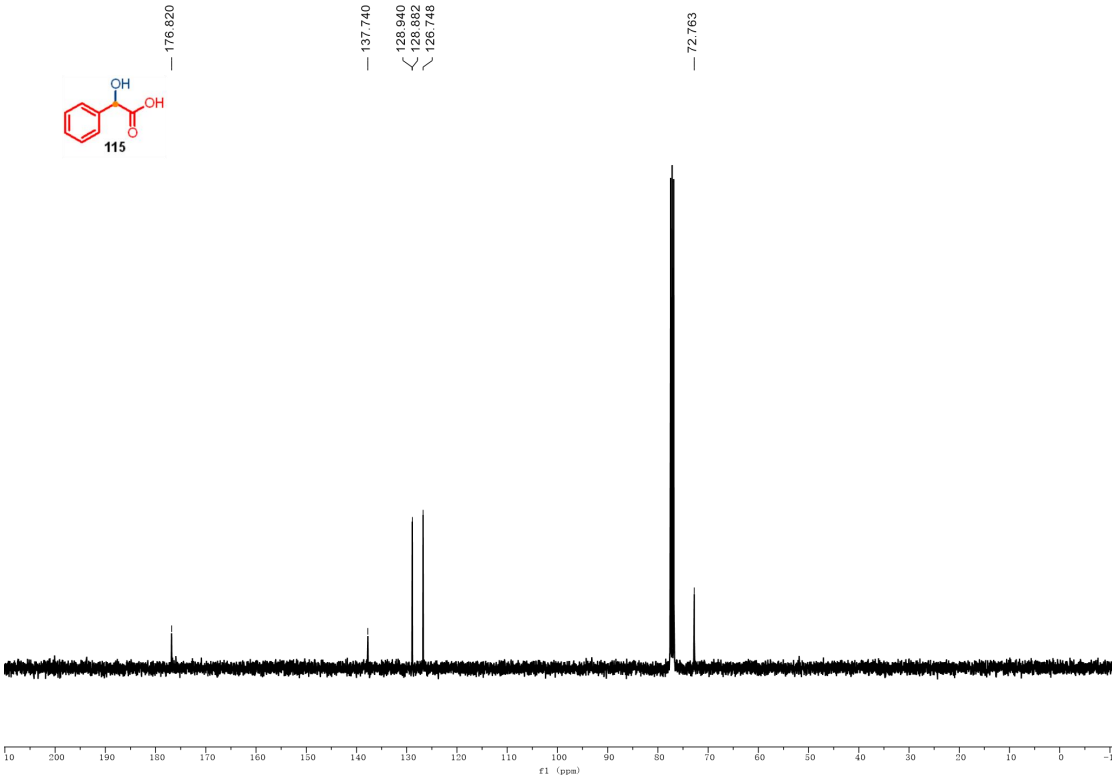
^{13}C NMR (101 MHz, $CDCl_3$) of 114



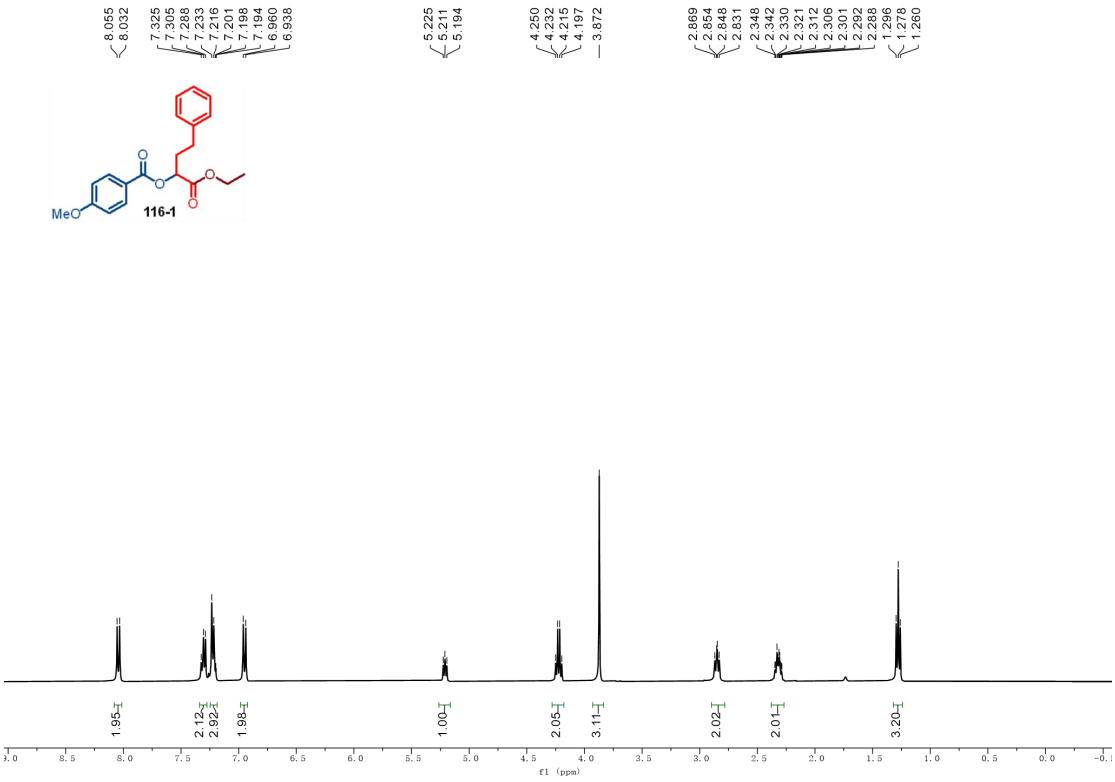
^{19}F NMR (376 MHz, $CDCl_3$) of 114



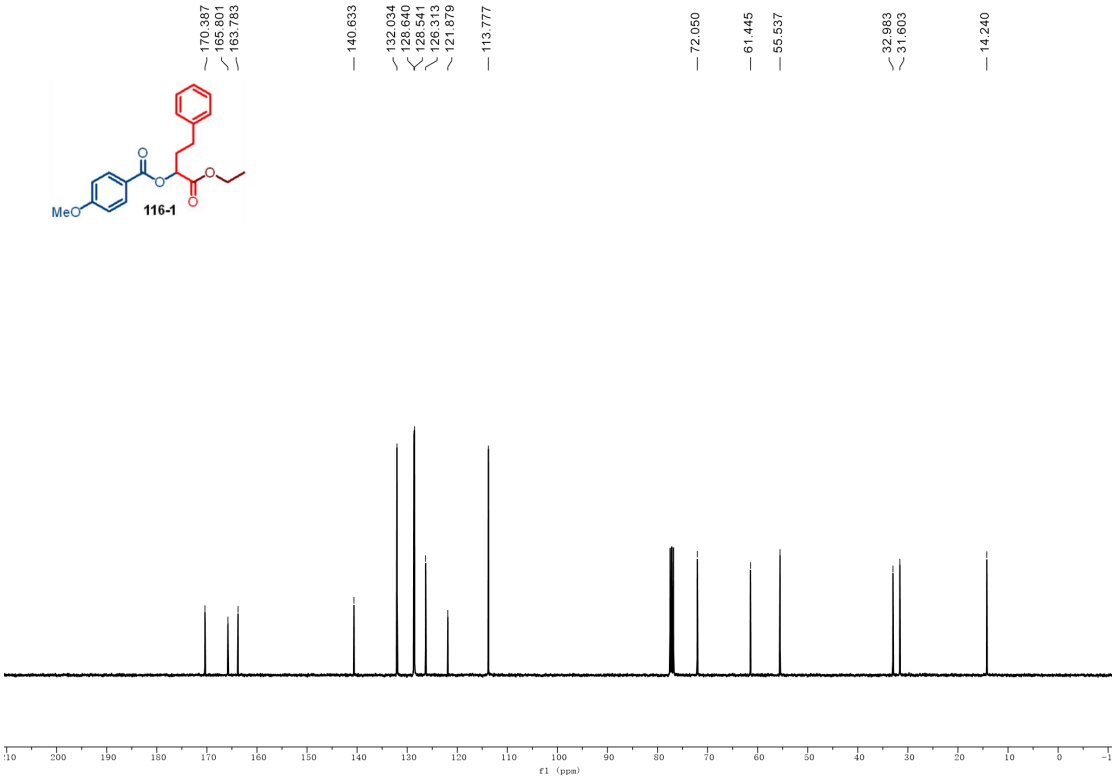
^{1}H NMR (400 MHz, $CDCl_3$) of 115



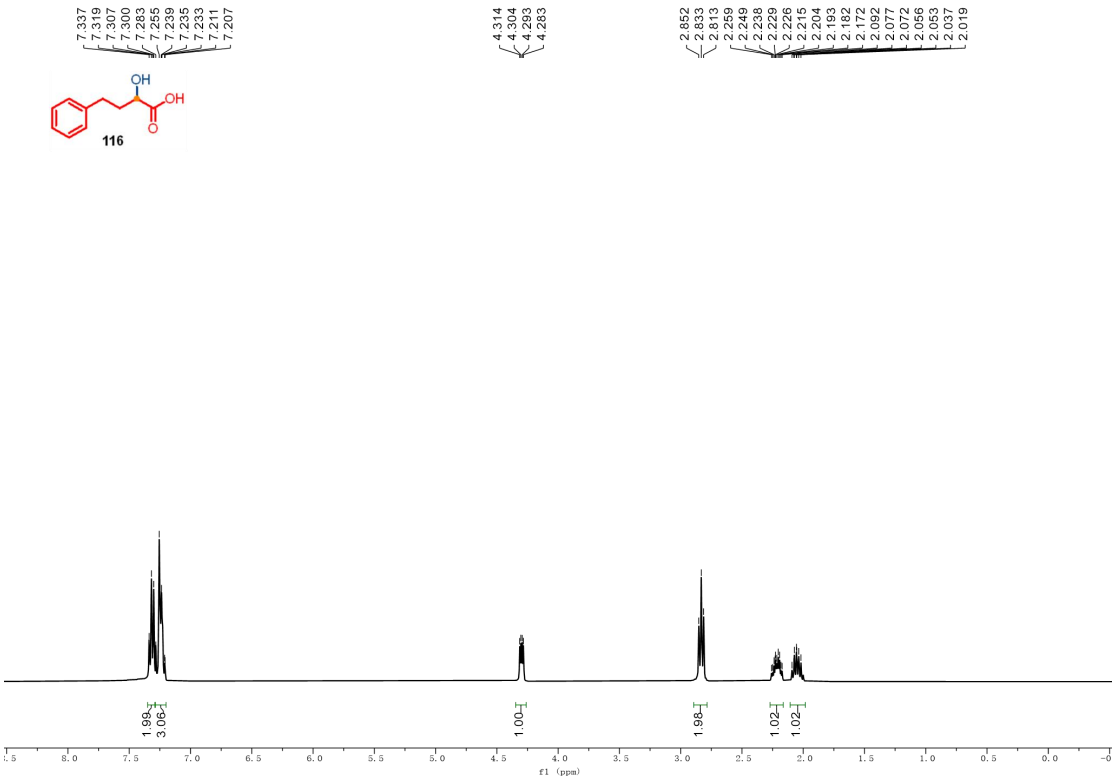
^{13}C NMR (101 MHz, $CDCl_3$) of 115



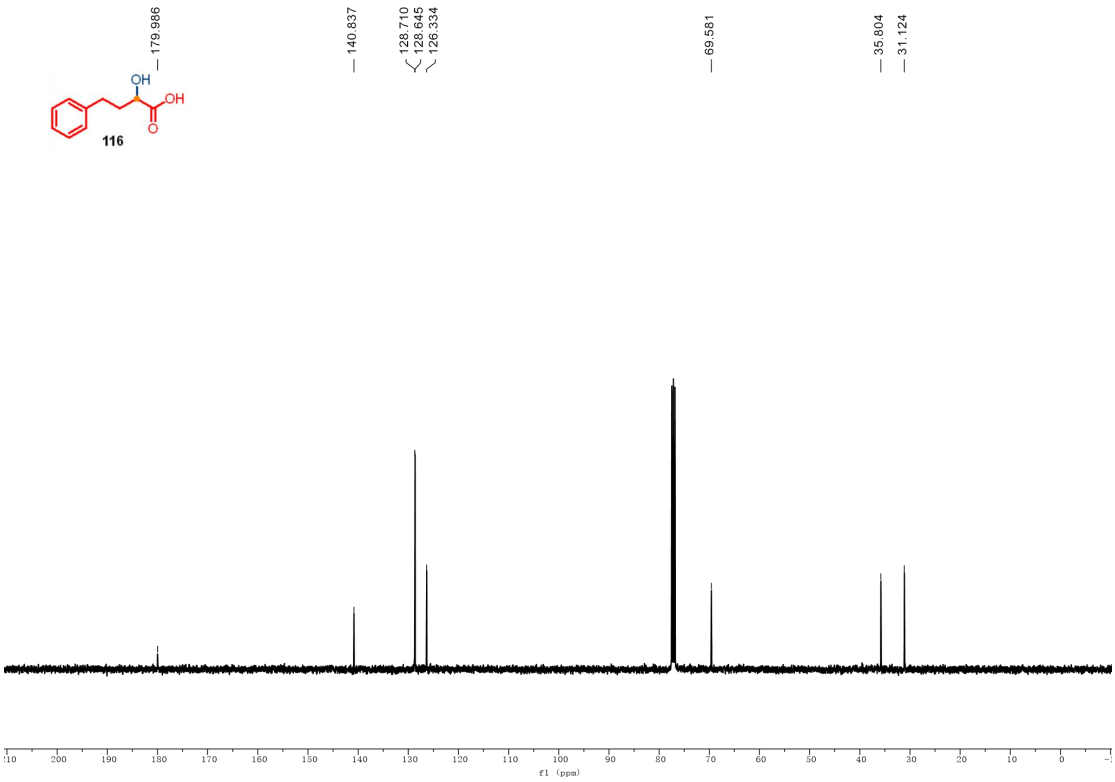
^{1}H NMR (400 MHz, $CDCl_3$) of 116-1



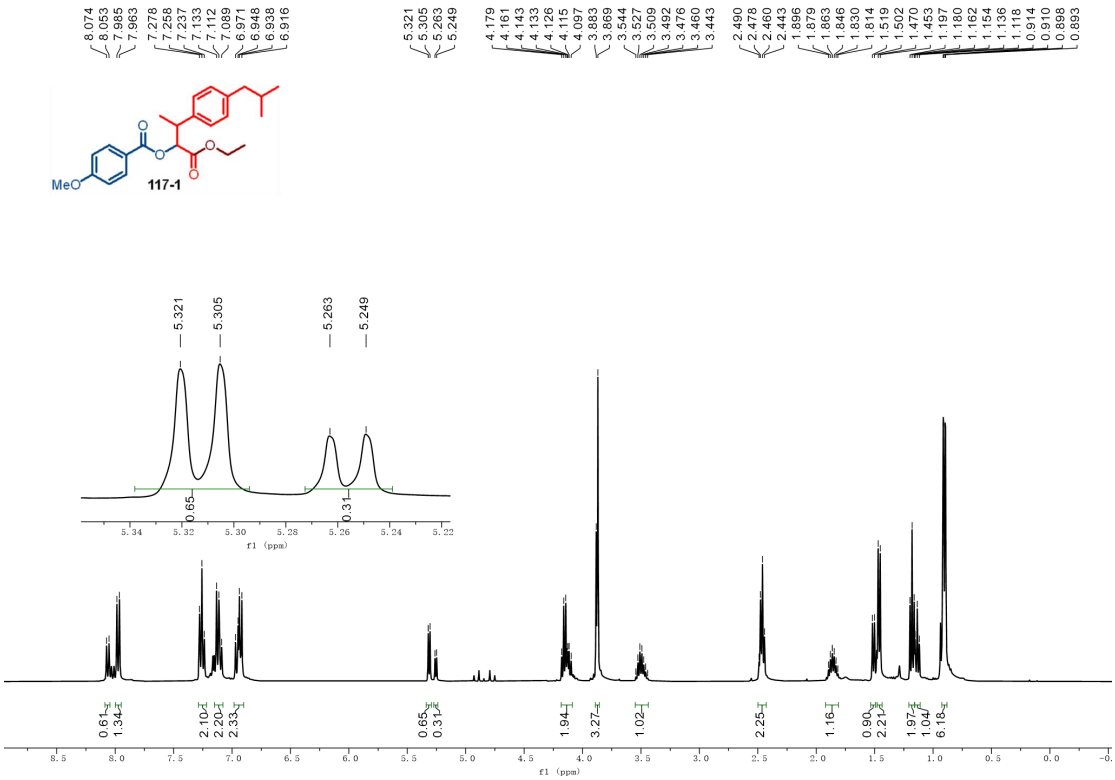
^{13}C NMR (101 MHz, $CDCl_3$) of 116-1



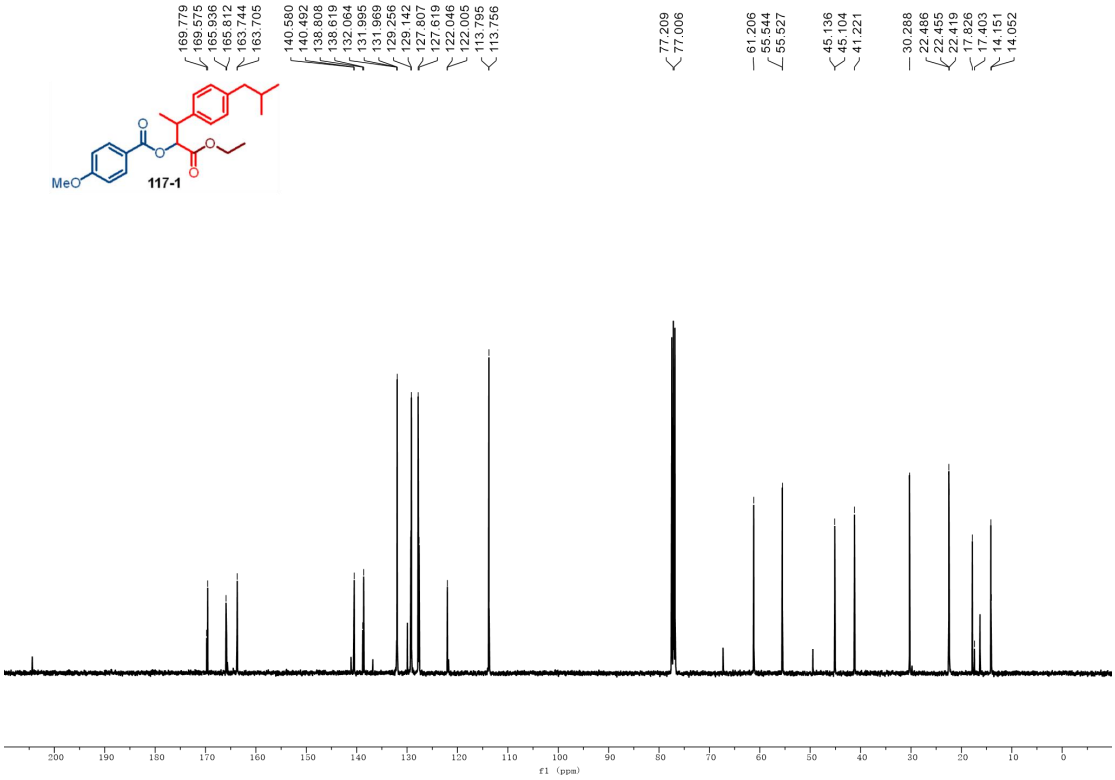
^{1}H NMR (400 MHz, $CDCl_3$) of 116



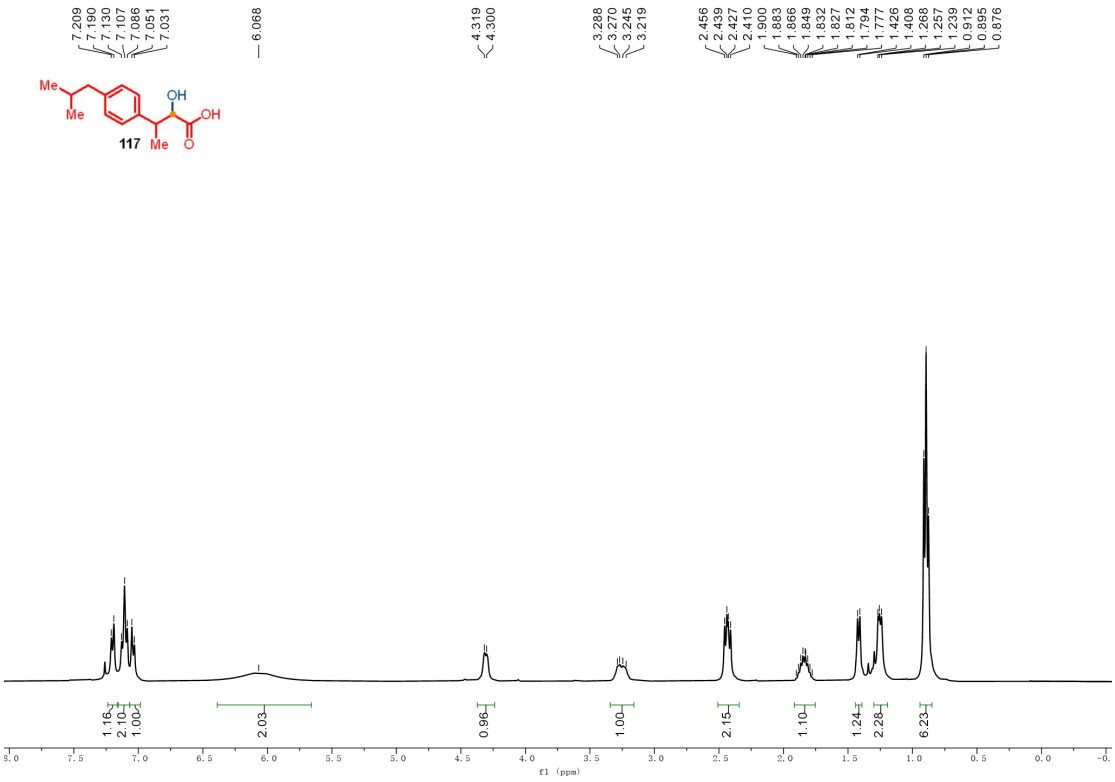
^{13}C NMR (101 MHz, $CDCl_3$) of 116



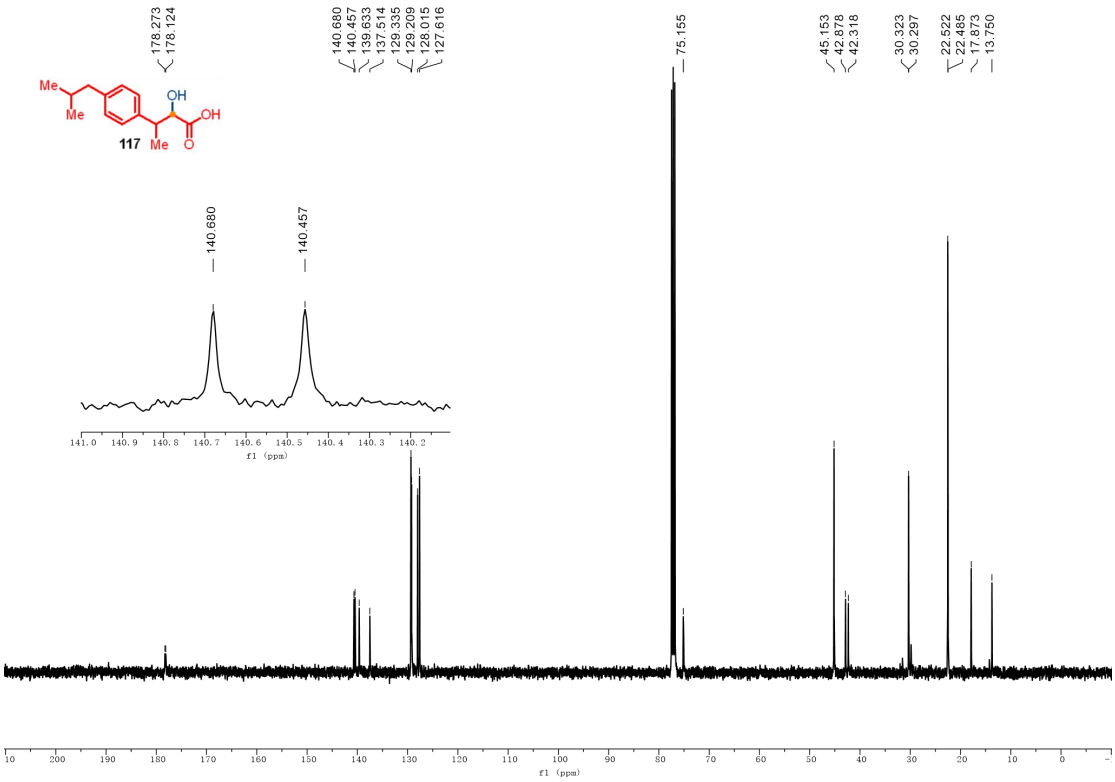
^{1}H NMR (400 MHz, $CDCl_3$) of 117-1



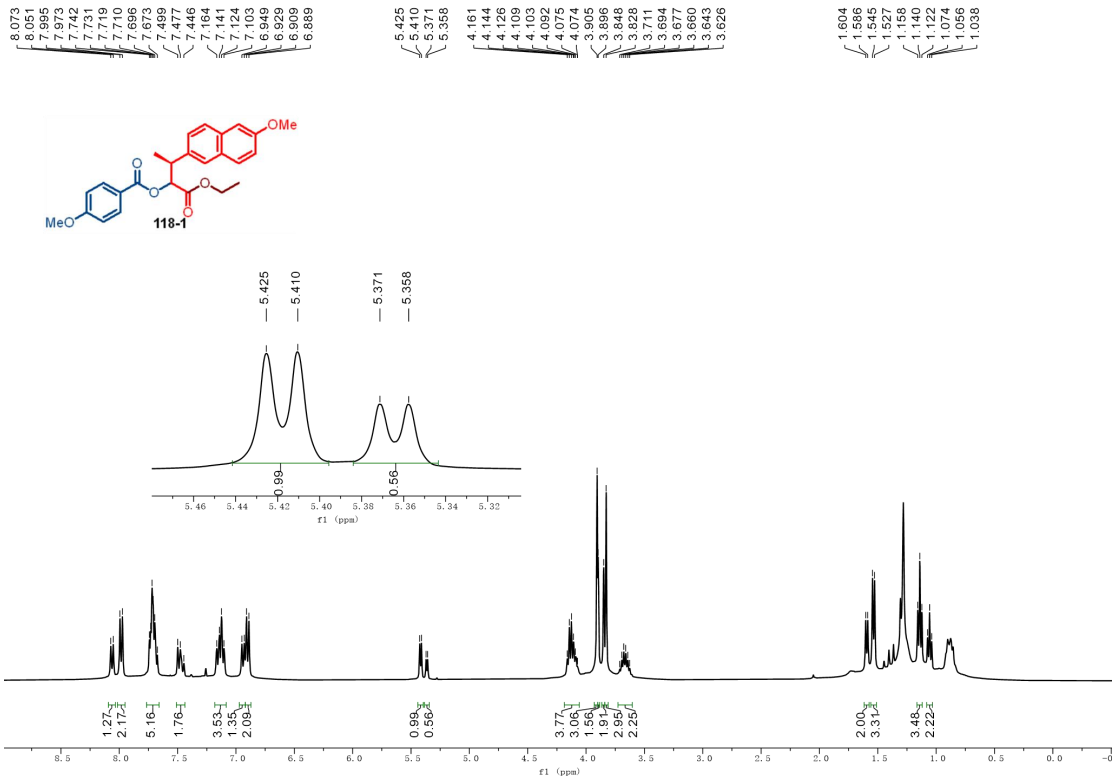
^{13}C NMR (101 MHz, $CDCl_3$) of 117-1



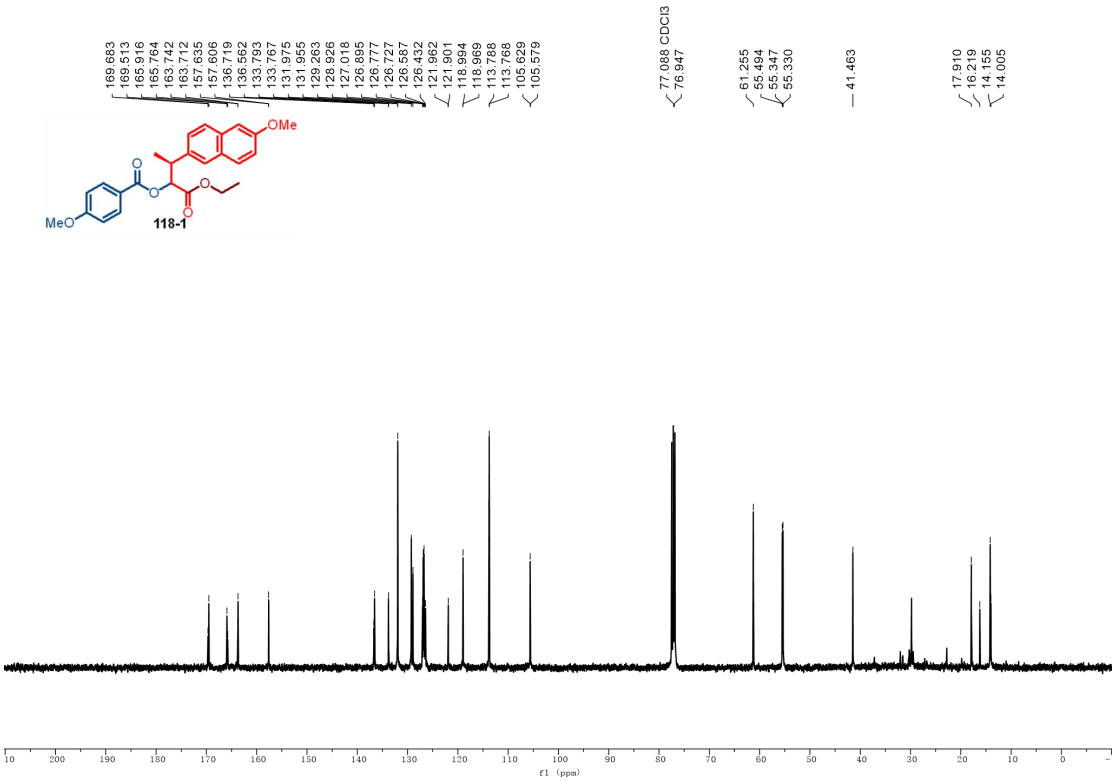
^{1}H NMR (400 MHz, $CDCl_3$) of 117



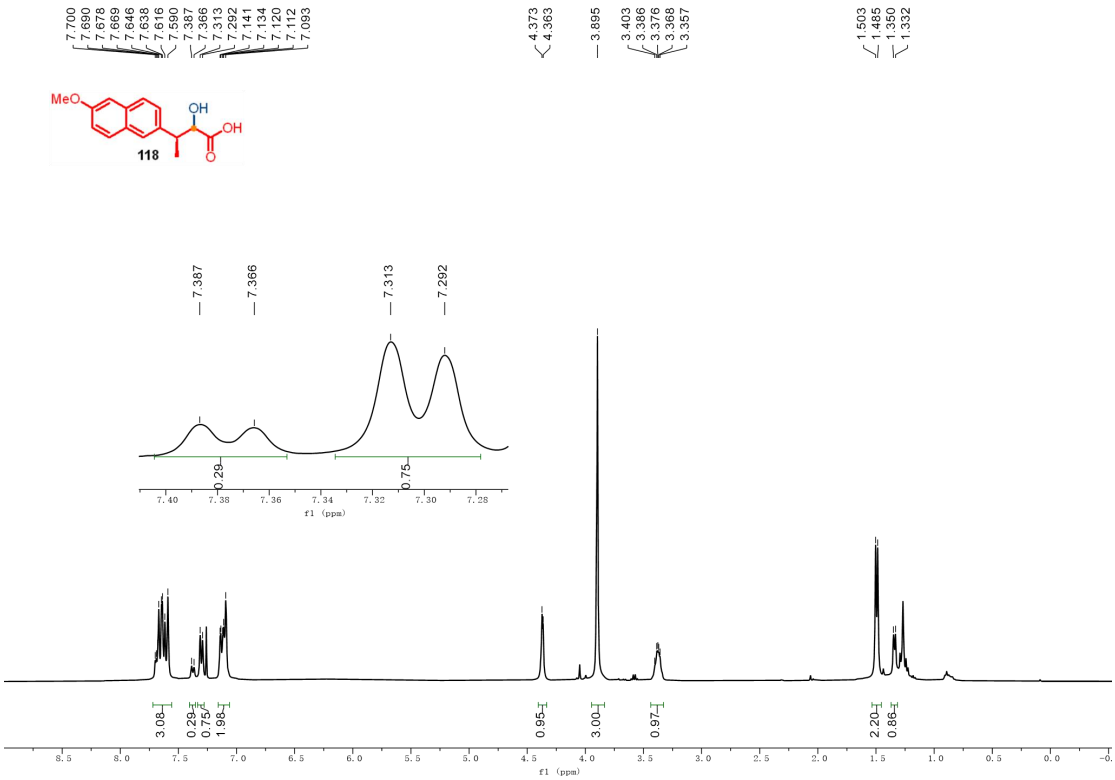
^{13}C NMR (101 MHz, $CDCl_3$) of 117



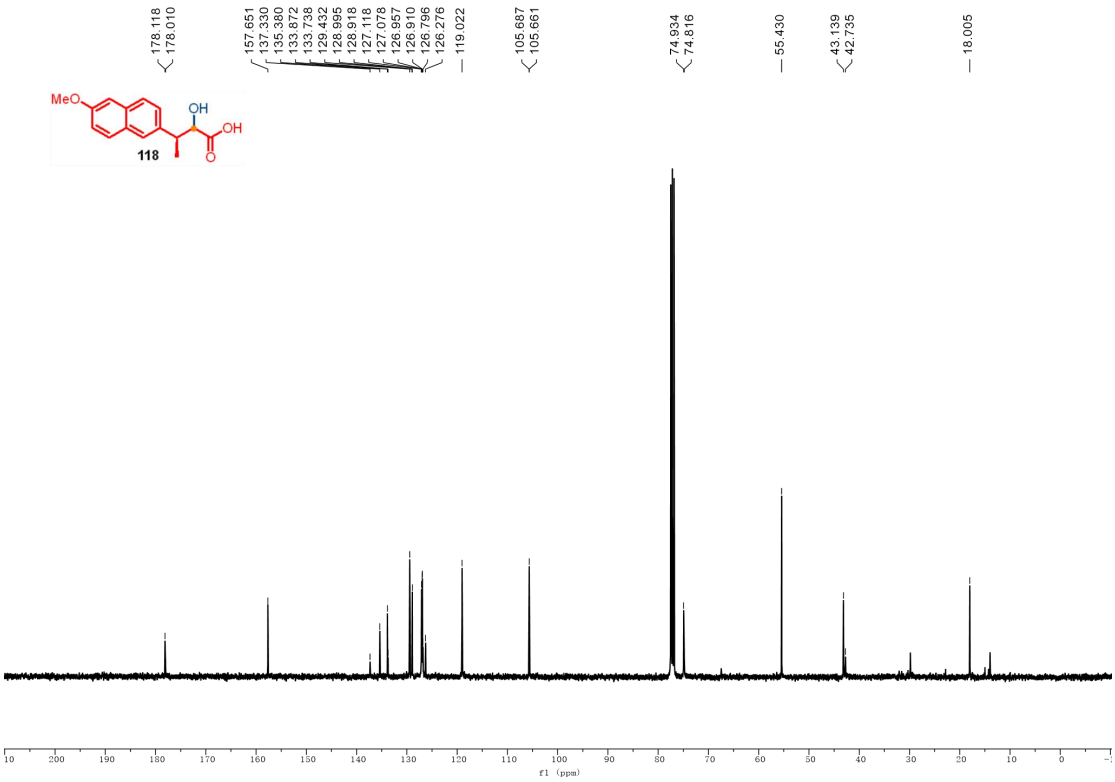
^{1}H NMR (400 MHz, $CDCl_3$) of 118-1



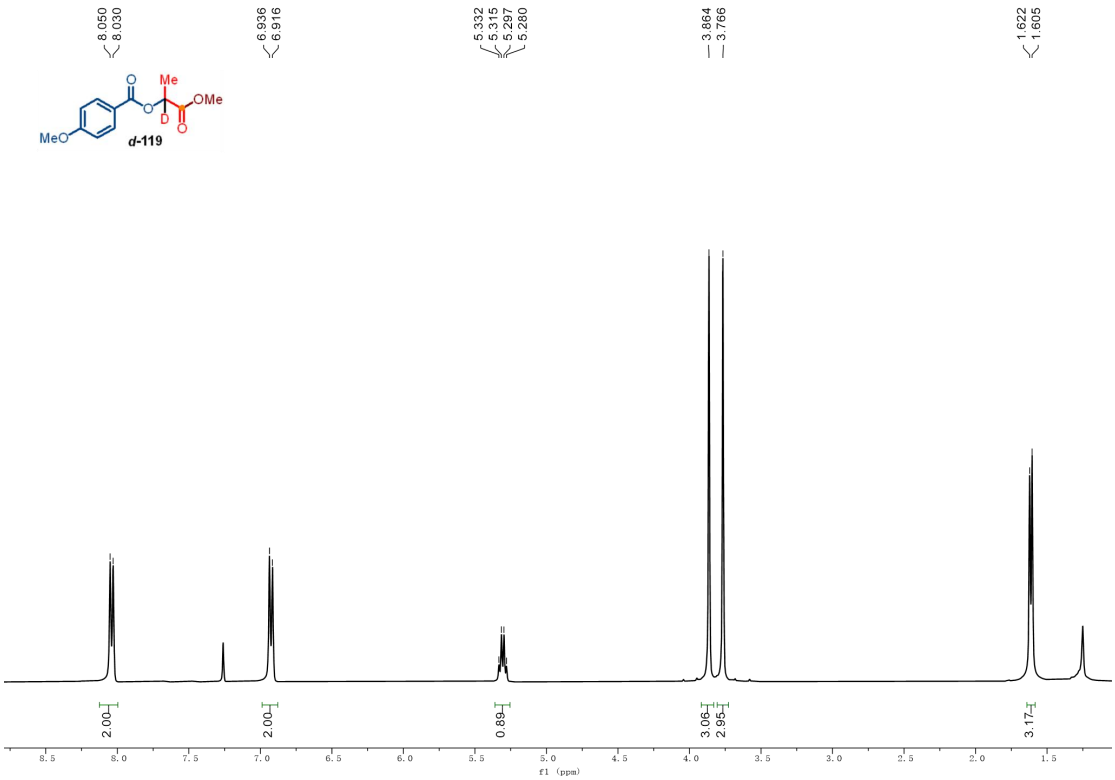
^{13}C NMR (101 MHz, $CDCl_3$) of 118-1



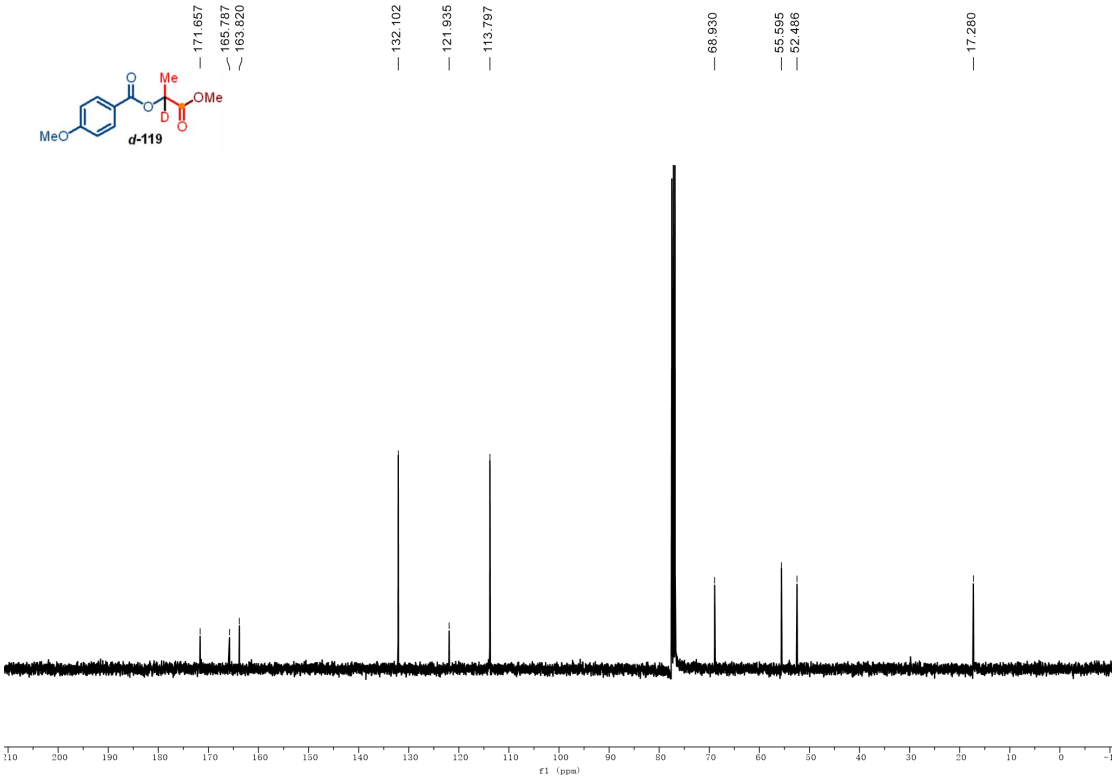
^{1}H NMR (400 MHz, $CDCl_3$) of 118



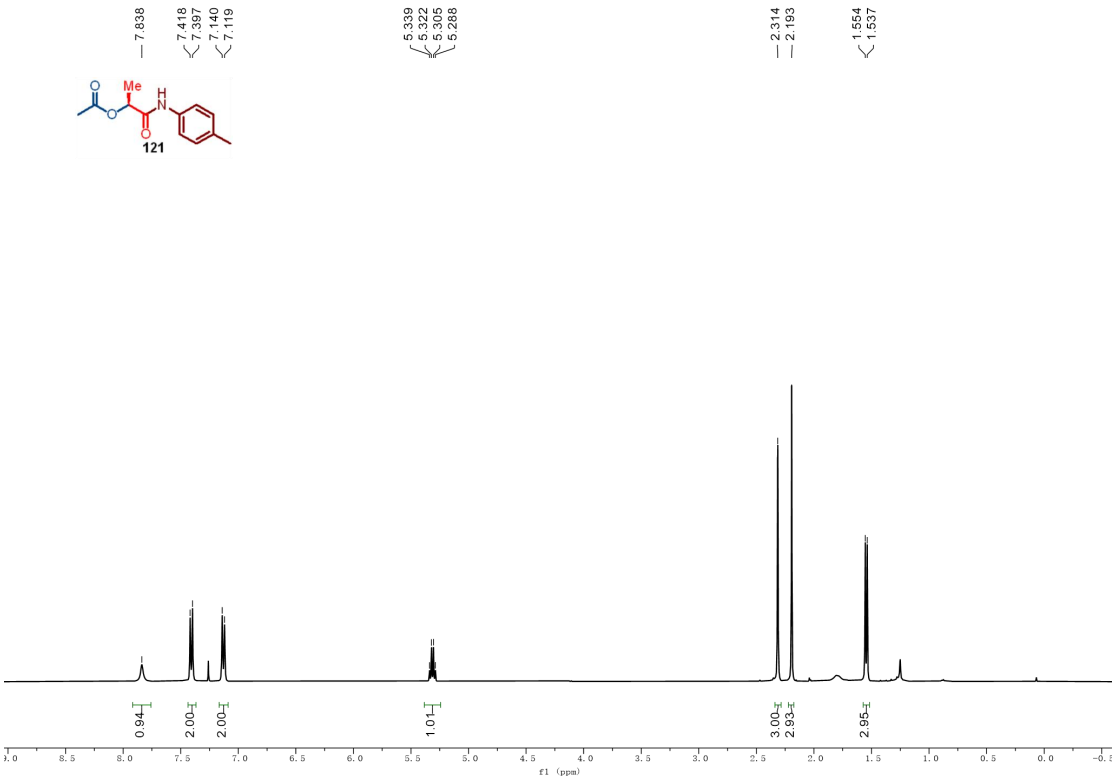
^{13}C NMR (101 MHz, $CDCl_3$) of 118



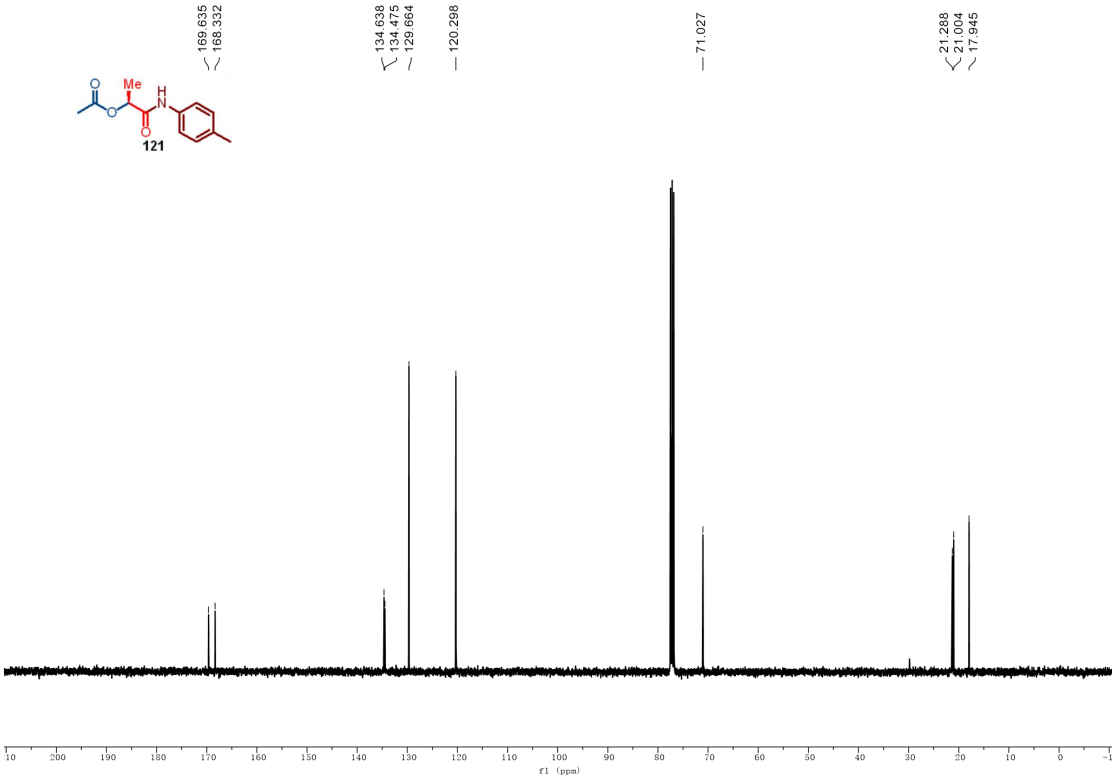
^{1}H NMR (400 MHz, $CDCl_3$) of 119



^{13}C NMR (101 MHz, $CDCl_3$) of 119



^{1}H NMR (400 MHz, $CDCl_3$) of 121



^{13}C NMR (101 MHz, $CDCl_3$) of 121