Supplementary Information

Rh(I)-catalyzed regioselective arylcarboxylation of acrylamides with arylboronic acids and CO_2

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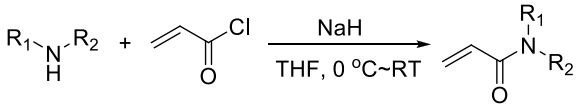
1. General Information

Unless otherwise noted, commercially available reagents were purchased from commercial suppliers (such as Adamas, Strem, J&K Chemical Co., Energy Chemical, etc.), and used as received. Rhodium catalysts were purchased from Sinocompound. Sensitive reagents, such as Cs_2CO_3 (Energy Chemical) and AgOTf (Energy Chemical), were stored and weighed in glove box. CO_2 was provided by Linde Gas (Xiamen) and its purity was ≥ 99.995%. Solvents were generally dried over 4 Å molecular sieves and degassed. The reaction vessels used were 50 mL Schlenk sealed tube (Synthware). Purification of products was performed by flash chromatography (FC) using silica gel or preparative thin layer chromatography (PTLC). ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz, 101 MHz and 376 MHz respectively) and JEOL ECZ600S (600 MHz and 151 MHz, respectively). Chemical shifts are reported parts per million (ppm) referenced to $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm) for ^1H NMR; $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptaplet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Impact II UHR-TOF mass spectrometry equipped with an ESI source from Bruker at Fujian Institute of Research on the Structure of Matter.

2. Experimental Section

2.1 Preparation of substrates

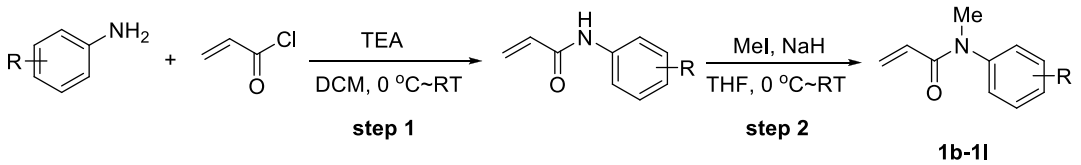
General Procedure for Preparation of Substrates 1a, 1m and 1n



1a, 1m, 1n

Secondary amine (5 mmol) was dissolved in anhydrous THF (20 mL) in a round-bottomed flask equipped with a magnetic stirring bar, NaH (10 mmol, 2 equiv.) was added slowly at 0 ºC under an argon atmosphere. Acryloyl chloride (6 mmol, 1.2 equiv.) was added dropwise via syringe with vigorous stirring. and the resulting mixture was stirred for 15 minutes and warmed to room temperature. The reaction was monitored by TLC analysis and once the reaction was completed, the suspension was brought to 0 °C and diluted with H_2O. The mixture was extracted with EA (10 mL, × 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The resulting was purified by flash silica gel chromatography using PE/EA (5/1-3/1) as the eluent.

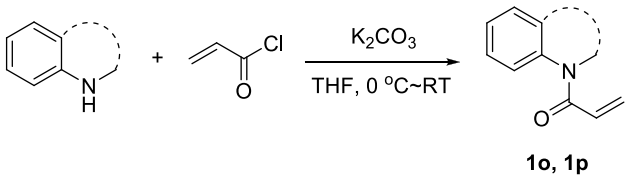
General Procedure for Preparation of Substrates 1b-1l



Step 1: to a solution of DCM (15 mL), aniline (5 mol, 1 equiv) and TEA (2.0 equiv.) were added in a round-bottomed flask equipped with a magnetic stirring bar. The reaction mixture was cooled to 0°C and stirred for 5 minutes under an argon atmosphere. Acryloyl chloride (1.2 equiv) was added dropwise and the resulting mixture was stirred for 15 minutes and warmed to room temperature. The reaction was monitored by TLC analysis and once the reaction was completed, the suspension was brought to 0 °C and diluted with H_2O. The mixture was extracted with DCM (10 mL, × 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The resulting was purified by flash silica gel chromatography using PE/EA (5/1-3/1) as the eluent.

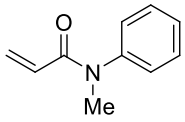
Step 2: The amide was dissolved in anhydrous THF (20 mL) in a round-bottomed flask equipped with a magnetic stirring bar, NaH (2 equiv) was added slowly at 0 ºC under an argon atmosphere. The reaction mixture was warmed to room temperature. 15 minutes afterwards, the solution was re-cooled to 0 °C and MeI (3 equiv) was added dropwise. At this time, the resulting solution was warmed to room temperature and once TLC analysis indicated full conversion of starting material, the reaction was slowly quenched at 0 °C by the addition of a saturated aqueous solution of ammonium chloride. The layers of the resulting biphasic mixture were separated and aqueous layer was extracted with EA (10 mL, × 3). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The pure alkylated acrylamides were obtained by silica gel flash column chromatography using PE/EA (5/1-3/1) as the eluent.

General Procedure for Preparation of Substrates 1o and 1p



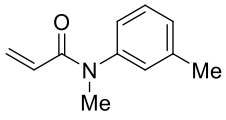
Indoline or tetrahydroquinoline (5 mmol) was dissolved in anhydrous THF (20 mL) in a round-bottomed flask equipped with a magnetic stirring bar, K_2CO_3 (10 mmol, 2 equiv.) was added and the mixture was cooled to 0 ºC under an argon atmosphere. Acryloyl chloride (6 mmol, 1.2 equiv.) was added dropwise via syringe with vigorous stirring. and the resulting mixture was stirred for 15 minutes and warmed to room temperature. The reaction was monitored by TLC analysis and once the reaction was completed, the suspension was brought to 0 °C and diluted with H_2O. The mixture was extracted with EA (10 mL, × 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The resulting was purified by flash silica gel chromatography using PE/EA (5/1-3/1) as the eluent.

2.2 Characterization of substrates



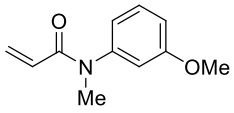
1a

***N*-methyl-*N*-phenylacrylamide:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.34 (m, 1H), 7.19 (m, 2H), 6.37 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.08 (dd, *J* = 16.7, 10.3 Hz, 1H), 5.52 (dd, *J* = 10.3, 1.3 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 143.5, 129.7, 128.6, 127.7, 127.5, 127.4, 37.5.



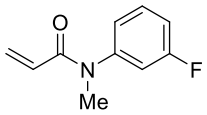
1b

***N*-methyl-*N*-(*m*-tolyl)acrylamide:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.01-6.94 (m, 2H), 6.36 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.09 (dd, *J* = 16.7, 10.3 Hz, 1H), 5.51 (dd, *J* = 10.3, 1.7 Hz, 1H), 3.34 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 143.4, 139.8, 129.4, 128.6, 128.5, 127.9, 127.3, 124.4, 37.5, 21.4.



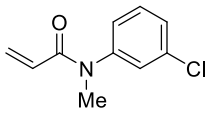
1c

***N*-(3-methoxyphenyl)-*N*-methylacrylamide:** colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.77 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.72 (t, *J* = 2.1 Hz, 1H), 6.37 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.12 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.53 (dd, *J* = 10.3, 1.9 Hz, 1H), 3.82 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 160.5, 144.7, 130.4, 128.7, 127.5, 119.7, 113.3, 55.6, 37.5.



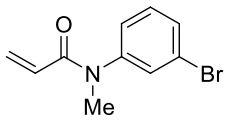
1d

***N*-(3-fluorophenyl)-*N*-methylacrylamide:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.09 – 7.02 (m, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 9.4 Hz, 1H), 6.39 (d, *J* = 16.8 Hz, 1H), 6.10 (dd, *J* = 16.7, 10.3 Hz, 1H), 5.57 (d, *J* = 10.3 Hz, 1H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 163.0 (d, J_{C-F} = 249.0 Hz), 145.0 (d, J_{C-F} = 9.4 Hz), 130.8 (d, J_{C-F} = 9.2 Hz), 128.3, 128.2, 123.2 (d, J_{C-F} = 3.1 Hz), 114.9 (d, J_{C-F} = 4.4 Hz), 114.7 (d, J_{C-F} = 5.6 Hz), 37.4.



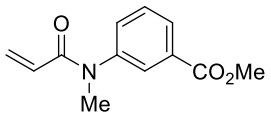
1e

***N*-(3-chlorophenyl)-*N*-methylacrylamide:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 2H), 7.21 (s, 1H), 7.09 (dt, *J* = 7.2, 1.8 Hz, 1H), 6.40 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.08 (dd, *J* = 16.7, 10.4 Hz, 1H), 5.58 (dd, *J* = 10.3, 1.7 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 144.7, 135.2, 130.7, 128.3, 128.2, 128.0, 127.7, 125.7, 37.5.



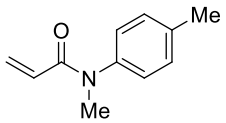
1f

***N*-(3-bromophenyl)-*N*-methylacrylamide:** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.39 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.08 (dd, *J* = 16.6, 10.3 Hz, 1H), 5.58 (dd, *J* = 10.3, 1.6 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 144.9, 130.9, 130.9, 130.6, 128.3, 128.3, 126.2, 123.0, 37.5.



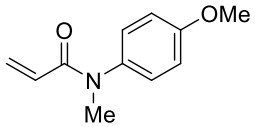
1g

methyl 3-(*N*-methylacrylamido)benzoate: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.88 (s, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 6.40 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.04 (dd, *J* = 16.4, 10.4 Hz, 1H), 5.56 (d, *J* = 10.0 Hz,1H), 3.95 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.7, 143.7, 131.9, 129.8, 128.8, 128.3, 128.2, 128.2, 52.6, 37.5.



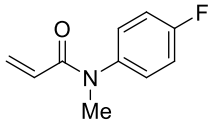
1h

***N*-methyl-*N*-(*p*-tolyl)acrylamide:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.35 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.08 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.50 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.34 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 140.9, 137.6, 130.2, 128.6, 127.2, 127.1, 37.5, 21.1.



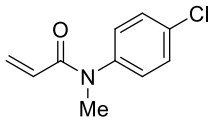
1i

***N*-(4-methoxyphenyl)-*N*-methylacrylamide：** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz 2H), 6.34 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.07 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.50 (dd, *J* = 10.3, 1.7 Hz, 1H), 3.84 (s, 3H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 158.9, 136.3, 128.6, 128.5, 127.3, 114.8, 55.6, 37.7.



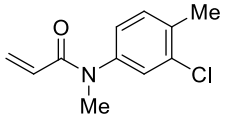
1j

***N*-(4-fluorophenyl)-*N*-methylacrylamide:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.13 (m, 2H), 7.13-7.07 (m, 2H), 6.37 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.04 (dd, *J* = 16.6, 10.4 Hz, 1H), 5.54 (d, *J* = 9.9 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 161.7 (d, $J_{C\text{-}F}$ = 248.0 Hz), 139.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.3, 127.9, 116.6 (d, $J_{C\text{-}F}$ = 22.7 Hz), 37.7.



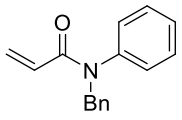
1k

***N*-(4-chlorophenyl)-*N*-methylacrylamide：** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.38 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.06 (dd, *J* = 16.3, 10.5 Hz, 1H), 5.56 (d, *J* = 10.4 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 142.0, 133.5, 129.9, 128.7, 128.3, 128.0, 37.5.



1l

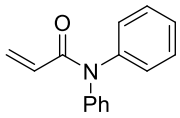
***N*-(3-chloro-4-methylphenyl)-*N*-methylacrylamide：** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.37 (dd, *J* = 16.8, 1.7 Hz, 1H), 5.55 (dd, *J* = 10.4, 1.2 Hz 1H), 3.33 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 142.3, 135.9, 135.1, 131.8, 128.4, 128.0, 127.9, 125.7, 37.5, 19.9.



1m

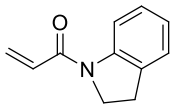
***N*-benzyl-*N*-phenylacrylamide：** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 3H), 7.28-7.19 (m, 5H), 7.00 (d, *J* = 6.5 Hz, 2H), 6.43 (dd, *J* = 16.8, 1.9 Hz, 1H), 6.04 (dd, *J* = 16.7, 10.3 Hz, 1H), 5.55 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.98 (s, 2H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 165.7, 141.9, 137.4, 129.6, 128.8, 128.7, 128.5, 128.5, 128.1, 128.0, 127.5, 53.3.



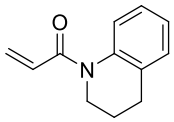
1n

***N, N*-diphenylacrylamide:** white solid; ^{1}H NMR (400 MHz, CDCl3) δ 7.37 (t, *J* = 7.4 Hz, 4H), 7.30-7.20 (m, 6H), 6.47 (dd, *J* = 16.8, 1.9 Hz, 1H), 6.20 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.63 (dd, *J* = 10.3, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 142.6, 129.7, 129.4, 128.6, 127.1.



1o

1-(indolin-1-yl)prop-2-en-1-one: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.8 Hz, 1H), 7.25-7.15 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.67-6.46 (m, 2H), 5.80 (dd, *J* = 9.6, 2.3 Hz, 1H), 4.18 (t, *J* = 8.5 Hz, 2H), 3.22 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 142.9, 131.6, 129.1, 129.0, 127.6, 124.6, 124.1, 117.6, 48.1, 28.1.



1p

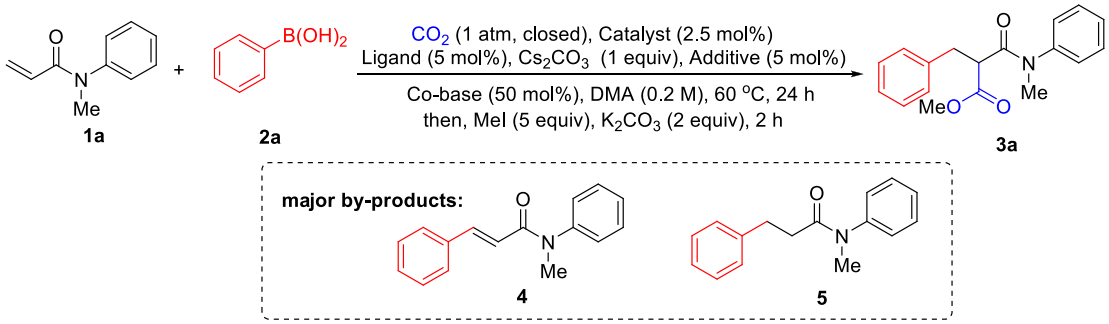
1-(3,4-dihydroquinolin-1(2*H*)-yl)prop-2-en-1-one: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.01 (m, 4H), 6.54 (dd, *J* = 16.8, 10.0 Hz, 1H), 6.44 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.66 (dd, *J* = 10.0, 1.3 Hz, 1H), 3.87 (t, *J* = 6.7 Hz, 2H), 2.72 (t, *J* = 6.5 Hz, 2H), 2.03-1.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 138.4, 130.1, 128.5, 127.6, 126.2, 125.4, 125.1, 43.3, 27.1, 24.1.

2.3 Optimization of reaction conditions

General procedure: In a glove box, acrylamide **1a** (0.2 mmol, 1.0 equiv.), arylboronic acid **2a** (0.3 mmol, 1.5 equiv.), catalyst, ligand, base and additive were added sequentially to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar. The tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3) after taken out of the glove box. Then anhydrous solvent (1.0 mL) was added along the inside wall of the tube under a flow of CO_2. Again, the reaction tube was evacuated briefly under vacuum and charged with CO_2 (1 atm, × 4). The tube was capped and then placed into a preheated hotplate. The reaction was stirred vigorously (1000 r/min) for 24 h, the additional K_2CO_3 (55 mg, 0.4mmol) and MeI (62 μL, 1.0

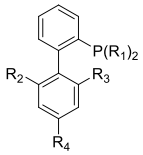
mmol) was added and stirred for another 2 h at the same temperature. Upon completion, cooled to room temperature, removed the volatile matter under reduced pressure, the residue was diluted with EA (5 mL), and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 20 mL of EA. The filtrate was concentrated under vacuum, and crude ^{1}H NMR spectrum was taken using CH_2Br_2 as the internal standard.

Table S1 Reaction conditions screening[a]

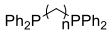


Entry	Catalyst	Ligand	Co-base	Additive	Yield (%)[b] (**3a**/**4**/**5**/**1a**)
1	$[Rh(cod)Cl]_2$	--	--	--	40/25/7/--
2	$[Rh(cod)Cl]_2$	**L1**	--	--	42/25/10/--
3	$[Rh(cod)Cl]_2$	**L2**	--	--	28/23/29/--
4	$[Rh(cod)Cl]_2$	**L3**	--	--	24/21/28/--
5	$[Rh(cod)Cl]_2$	**L4**	--	--	32/23/15/--
6	$[Rh(cod)Cl]_2$	**L5**	--	--	25/28/20/--
7	$[Rh(cod)Cl]_2$	**L6**	--	--	20/27/--/13
8	$[Rh(cod)Cl]_2$	**L7**	--	--	3/--/5/40
9	$[Rh(cod)Cl]_2$	**L8**	--	--	30/31/1/11
10	$[Rh(cod)Cl]_2$	**L9**	--	--	10/43/14/--
11	$[Rh(cod)Cl]_2$	**L10**	--	--	43/18/16/--
12	$[Rh(cod)Cl]_2$	**L11**	--	--	11/33/4/12
13	$[Rh(cod)Cl]_2$	**L12**	--	--	36/23/5/--
14	$[Rh(cod)Cl]_2$	**L13**	--	--	8/10/2/39
15	$[Rh(cod)Cl]_2$	**L14**	--	--	14/23/1/22
16	$[Rh(cod)Cl]_2$	--	TMEDA	--	47/27/6/--
17	$[Rh(cod)Cl]_2$	--	PMDETA	--	49/27/3/--
18	$[Rh(cod)Cl]_2$	--	Et_3N	--	42/30/5/--
19	$[Rh(cod)Cl]_2$	--	$^iPr_2NEt$	--	43/28/5/--
20	$[Rh(cod)Cl]_2$	--	DABCO	--	45/28/3/--
21	$[Rh(cod)Cl]_2$	--	DBU	--	4/1/5/24
22	$[Rh(cod)Cl]_2$	--	PMDETA	AgF	73/5/14/--
23	$[Rh(cod)Cl]_2$	--	PMDETA	AgTFA	69/9/14/--
24	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTs	71/11/11/--
25	$[Rh(cod)Cl]_2$	--	PMDETA	$AgNTf_2$	71/8/16/--
26	$[Rh(cod)Cl]_2$	--	PMDETA	Ag_2WO_4	68/16/6/--

27	$[Rh(cod)Cl]_2$	--	PMDETA	Ag_2O	75/6/13/--
28	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	83/6/5/--
29	$[Rh(cod)Cl]_2$	--	PMDETA	AgOAc	62/9/6/5
30	$[Rh(cod)Cl]_2$	--	PMDETA	AgOBz	69/12/6/5
31	$[Rh(cod)Cl]_2$	--	PMDETA	AgCl	77/6/13/--
32	$[Rh(cod)Cl]_2$	--	PMDETA	$AgBF_4$	67/10/9/4
33	$[Rh(cod)Cl]_2$	--	PMDETA	$AgSbF_6$	52/10/2/22
34	$[Rh(cod)Cl]_2$	--	PMDETA	AgOPiv	69/5/15/1
35	$[Rh(cod)Cl]_2$	--	PMDETA	CuCl	58/18/7/--
36	$[Rh(cod)Cl]_2$	--	PMDETA	CuI	60/19/6/--
37	$[Rh(cod)Cl]_2$	--	PMDETA	CuBr	62/19/4/2
38	$[Rh(cod)Cl]_2$	--	PMDETA	$Cu(MeCN)_4PF_6$	73/13/8/--
39	$[Rh(cod)Cl]_2$	--	PMDETA	Cu_2O	48/25/4/--
40[c]	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	13/14/57/2
41[d]	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	43/14/12/--
42[e]	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	19/9/52/--
43[f]	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	15/9/73/--
44	$Rh(cod)_2OTf$	--	PMDETA	AgOTf	59/16/8/--
45	$Rh(cod)_2BF_4$	--	PMDETA	AgOTf	57/18/9/6
46	$[Rh(CO)_2Cl]_2$	--	PMDETA	AgOTf	--/10/--/81
47	$[Rh(cod)OH]_2$	--	PMDETA	AgOTf	80/9/11/--
48	$[Rh(coe)_2Cl]_2$	--	PMDETA	AgOTf	--/--/--/84
49	--	--	PMDETA	AgOTf	--/--/--/53
50[g]	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	46/14/3/18
51	$[Rh(cod)Cl]_2$	--	--	AgOTf	46/17/13/--
52[h]	$[Rh(cod)Cl]_2$	--	PMDETA	AgOTf	--/8/70/--

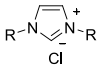


L1: R_1 = Cy, R_2 = R_3 = OMe, R_4 = H
L2: R_1 = Cy, R_2 = R_3 = O^{i}Pr, R_4 = H
L3: R_1 = ^{t}Bu, R_2 = R_3=R_4 = H
L4: R_1 = ^{t}Bu, R_2 = R_3 = R_4 = ^{i}Pr
L5: R_1 = Ph, R_2 = N(Me)$_2$, R_3 = R_4 = H



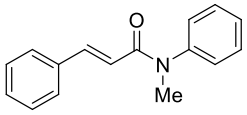
L6: R = 4-Me-Ph
L7: R = 4-CF_3-Ph
L8: R = Cy

L9: n = 1
L10: n = 2
L11: n = 3



L12: R = 2,6-diisopropylphenyl
L13: R = 2,4,6-trimethylphenyl
L14: R = Cy

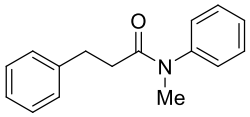
[a] Reaction conditions: **1a** (0.2 mmol), **2b** (0.3 mmol), CO_2 (1 atm, closed), Catalyst (2.5 mol%), Ligand (5 mol%), Cs_2CO_3 (0.2 mmol), Additive (5 mol%), Co-base (50 mol%), DMA (1 mL), 60 °C, 24 h. [b] Yield was determined by ^{1}H NMR with CH_2Br_2 as the internal standard. [c] CsF (0.2 mmol) as base. [d] KO^{t}Bu (0.2 mmol) as base, [e] DMF as solvent, [f] NMP as solvent, [g] $[Rh(cod)Cl]_2$ (1 mol%) as catalyst, [h] Ar (1 atm, closed) was used instead of CO_2. TMEDA: *N*, *N*, *N'*, *N'*-Tetramethylethylenediamine; PMDETA: *N*, *N*, *N'*, *N'*, *N''*-pentamethyldiethylenetriamine; DABCO: 1,4-diaza[2.2.2]bicyclooctane; DBU: 1,8-Diazabicyclo[5.4.0]undecane-7-ene.



4

***N*-methyl-*N*-phenylcinnamamide:** colorless sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.27 (m, 6H), 7.24 (d, *J* = 8.1

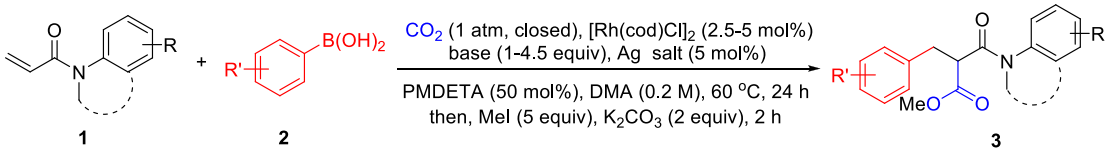
Hz, 2H), 6.37 (d, J = 15.6 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 143.8, 141.9, 135.3, 129.8, 129.6, 128.8, 128.0, 127.7, 127.5, 118.9, 37.7.



5

***N*-methyl-*N*,3-diphenylpropanamide:** colorless sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 3H), 7.23 (t, J = 7.3 Hz, 2H), 7.20-7.13 (m, 1H), 7.04 (dd, J = 14.4, 6.8 Hz, 4H), 3.25 (s, 3H), 2.91 (t, J = 7.9 Hz, 2H), 2.37 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 144.1, 141.3, 129.9, 128.5, 128.5, 127.9, 127.4, 126.1, 37.5, 36.1, 31.9.

2.4 General procedure for preparation of arylcarboxylation products



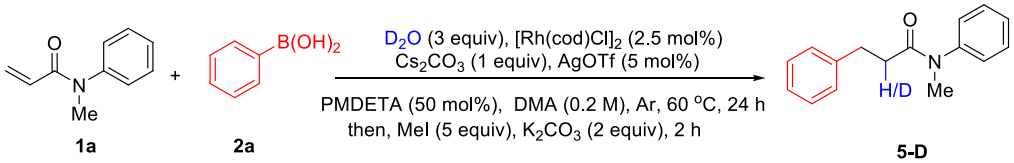
1 **2** **3**

In a glove box, acrylamide **1** (0.2 mmol, 1.0 equiv), arylboronic acid **2** (0.3 mmol, 1.5 equiv), $[Rh(cod)Cl]_2$ (2.5-5 mol%), Ag salt (0.01 mmol, 5 mol%) and Cs_2CO_3 (1.0-3.0 equiv) were added sequentially to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar. The tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3) after taken out of the glove box. Then PMDETA (21 μL, 0.1 mmol, 0.5 equiv) and anhydrous DMA (1.0 mL) were added along the inside wall of the tube under a flow of CO_2. Again, the reaction tube was evacuated briefly under vacuum and charged with CO_2 (1 atm, × 4). The tube was capped and then placed into a preheated hotplate (60 °C). The reaction was stirred vigorously (1000 r/min) for 24 h and MeI (62 μL, 1.0 mmol, 5.0 equiv) and K_2CO_3 (55 mg, 0.4 mmol, 2.0 equiv) were added and stirred for another 2 h at the same temperature. Upon completion, cooled to room temperature, removed the volatile solvent under reduced pressure, the residue was diluted with EA (5 mL), and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 20 mL of EA. The filtrate was concentrated under vacuum, and the resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using PE/EA (5/1-3/1) as the eluent. (Note: the quality of Cs_2CO_3 and AgOTf is of vital importance for reproducibility and they should be kept dry; the solvent should also be dry and the stirring should be fast and even for good results.)

Scale-up synthesis of product ***3a***

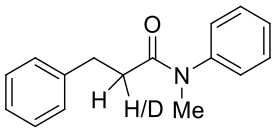
In a glove box, acrylamide **1a** (161 mg, 1.0 mmol, 1.0 equiv), phenylboronic acid **2a** (183 mg, 1.5 mmol, 1.5 equiv), $[Rh(cod)Cl]_2$ (12.5 mg, 0.025 mmol, 2.5 mol%), AgOTf (13 mg, 0.05 mmol, 5 mol%) and Cs_2CO_3 (325.8 mg, 1.0 mmol, 1.0 equiv) were added sequentially to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar. The tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3) after taken out of the glove box. Then PMDETA (105 µL, 0.5 mmol, 0.5 equiv) and anhydrous DMA (5.0 mL) was added along the inside wall of the tube under a flow of CO_2. Again, the reaction tube was evacuated briefly under vacuum and charged with CO_2 (1 atm, × 4). The tube was capped and then placed into a preheated hotplate (60 °C). The reaction was stirred vigorously (1000 r/min) for 24 h and MeI (310 µL, 5.0 mmol, 5.0 equiv) K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv) were added and stirred for another 2 h at the same temperature. Upon completion, cooled to room temperature, removed the volatile solvent under reduced pressure, the residue was diluted with EA (5 mL), and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 20 mL of EA. The filtrate was concentrated under vacuum, and the resulting residue was purified by flash silica gel chromatography using PE/EA (5/1-3/1) as the eluent to give product **3a** (202mg, 68%; The side product from Heck type coupling is 11%, and that from 1,4-addition is 12% from crude ^1H NMR.).

2.5 Control experiment



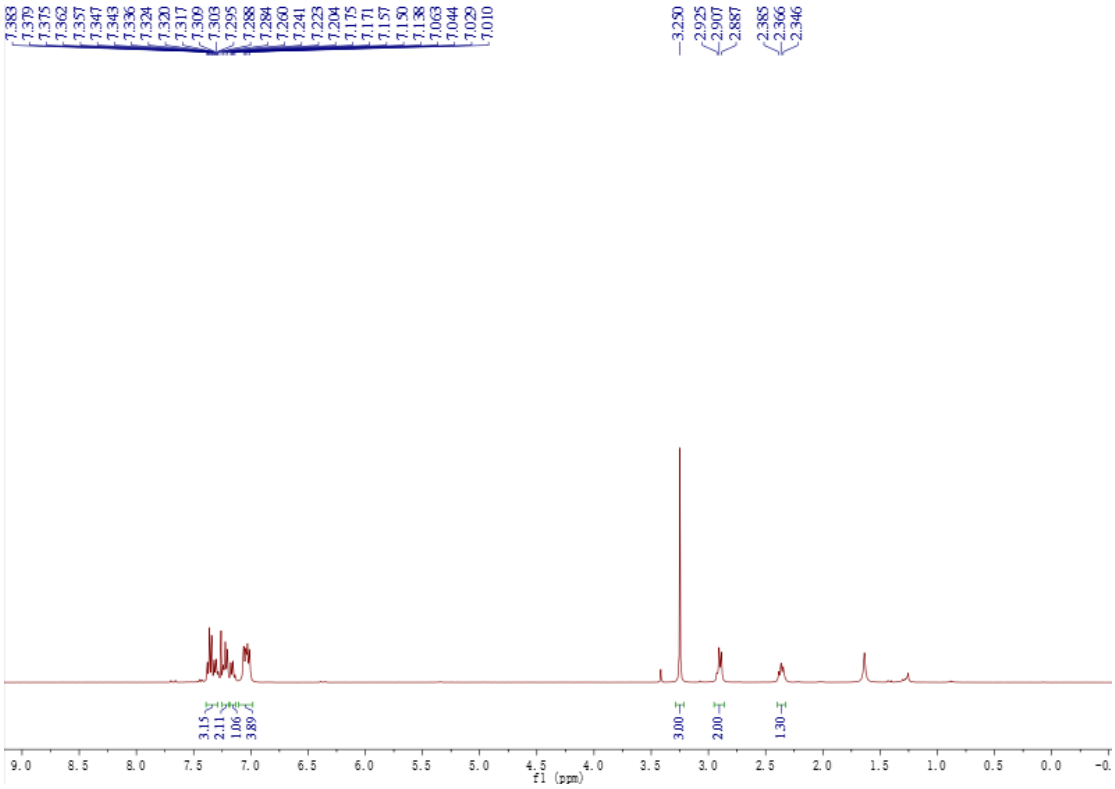
In a glove box, acrylamide **1a** (32.2 mg, 0.2 mmol, 1.0 equiv), phenylboronic acid **2a** (36.6 mg, 0.3 mmol, 1.5 equiv), $[Rh(cod)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), AgOTf (2.6 mg, 0.01 mmol, 5 mol%), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) and D_2O (10.8 µL, 0.6 mmol, 3.0 equiv) were added sequentially to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar. The tube was evacuated under vacuum and charged with argon (1 atm, × 3) after taken out of the glove box. Then PMDETA (21 µL, 0.1 mmol, 0.5 equiv) and anhydrous DMA (1.0 mL) was added along the inside wall of the tube under a flow of argon. Again, the reaction tube was evacuated briefly under vacuum and charged with argon (1 atm, × 4). The tube was capped and then placed into a preheated hotplate (60 °C). The reaction was stirred vigorously (1000 r/min) for 24 h and MeI (62 µL, 1.0 mmol) and K_2CO_3 (55 mg, 0.4 mmol) were added and stirred for another 2 h at the same temperature. Upon completion, cooled to room temperature, removed the volatile solvent under reduced pressure, the residue was diluted with EA (5 mL), and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 20 mL of EA. The filtrate

was concentrated under vacuum, and the resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using PE/EA (5/1-3/1) as the eluent.



5-D

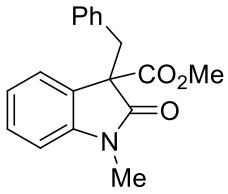
colorless sticky oil; 34.9 mg; yield: 73%; 70% deuterated: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.19-7.13 (m, 1H), 7.04 (dd, *J* = 13.4, 7.5 Hz, 4H), 3.25 (s, 3H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.37 (t, *J* = 7.9 Hz, 1.3H).



2.6 Product elaboration[S1]

To a 38 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with product **3a** (29.7 mg, 0.10 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (20 mg, 0.10 mmol, 1.0 equiv) and KO^{t}Bu (12.3mg, 0.11 mmol, 1.1 equiv) sequentially. DMF (1.0 mL) was added to the mixture along the inside wall of the tube. The reaction tube was capped, then submerged into a preheated oil bath (110 ºC). The reaction was stirred for 24 h and cooled to room temperature. The reaction was diluted with ethyl acetate (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 15 mL of EA. The filtrate was concentrated *in vacuo*, and

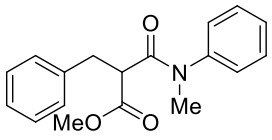
the resulting residue was purified by preparative thin layer chromatography using PE/EA (5/1-3/1) as the eluent.



6

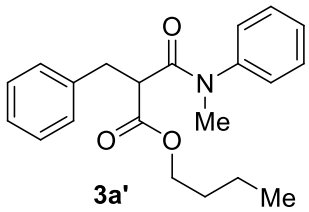
methyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate: white solid; 23.6 mg; yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.11-6.96 (m, 4H), 6.84 (dd, *J* = 7.7, 1.8 Hz 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.55 (s, 2H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 169.9, 144.1, 134.4, 130.1, 129.2, 127.7, 127.4, 126.9, 124.1, 122.7, 108.3, 60.9, 53.2, 40.2, 26.3.

2.7 Characterization of products



3a

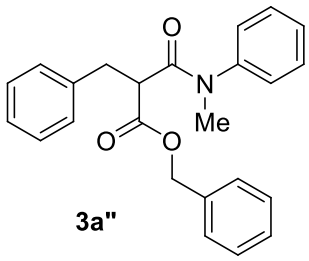
methyl 2-benzyl-3-(methyl(phenyl)amino)-3-oxopropanoate： pale yellow oil; 47.6 mg; yield: 80% (known compound)[S2]. (The side product from Heck type coupling is 6%, and that from 1,4-addition is 5% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 6H), 7.06-7.00 (m, 2H), 6.62 (br, 2H), 3.71 (s, 3H), 3.56 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.26-3.15 (m, 4H), 3.09 (dd, *J* = 13.3, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.6, 143.2, 138.4, 129.7, 129.3, 128.5, 128.1, 127.6, 126.7, 52.6, 51.0, 37.6, 35.5.



3a'

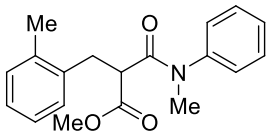
butyl 2-benzyl-3-(methyl(phenyl)amino)-3-oxopropanoate: colorless sticky oil; 51.5 mg; yield: 76%. (The side product from Heck type coupling is 9%, and that from 1,4-addition is 10% from crude ^{1}H NMR; BuBr (1.0 mmol) was used for esterification).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 6H), 7.05 – 7.02 (m, 2H), 6.60 (br, 2H), 4.14 – 4.05 (m, 2H), 3.53 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.22 (dd, *J* = 13.4, 10.4 Hz, 1H), 3.16 (s, 3H), 3.06 (dd, *J* = 13.4, 4.9 Hz, 1H), 1.63 – 1.57 (m, 2H), 1.40 – 1.32 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 168.7, 143.3, 138.6, 129.6, 129.4, 128.5, 128.1, 127.7, 126.7, 65.3, 51.1, 37.5, 35.4, 30.6, 19.2,

13.8. HRMS (m/z, ESI-TOF): Calcd for $C_{21}H_{25}NO_3Na^+$ [M+Na^+] 362.1727, found 362.1727.



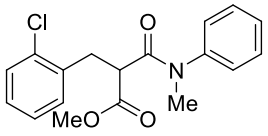
3a"

benzyl 2-benzyl-3-(methyl(phenyl)amino)-3-oxopropanoate: colorless sticky oil; 54.5 mg; yield: 73%. (The side product from Heck type coupling is 10%, and that from 1,4-addition is 14% from crude ^{1}H NMR; BnBr (1.0 mmol) was used for esterification).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3H), 7.33 – 7.30 (m, 2H), 7.26 – 7.21 (m, 4H), 7.16 (td, *J* = 7.4, 1.4 Hz, 2H), 7.06 – 7.03 (m, 2H), 6.52 (br, 2H), 5.18 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 3.58 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.27 (dd, *J* = 13.4, 10.4 Hz, 1H), 3.15 (s, 3H), 3.10 (dd, *J* = 13.4, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 168.4, 143.2, 138.5, 135.7, 129.6, 129.4, 128.7, 128.5, 128.4, 128.3, 128.1, 127.7, 126.7, 67.1, 51.1, 37.5, 35.4. HRMS (m/z, ESI-TOF): Calcd for $C_{24}H_{23}NO_3Na^+$ [M+Na^+] 396.1570, found 396.1571.



3b

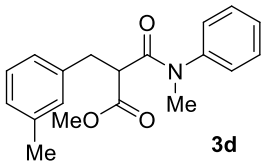
methyl 3-(methyl(phenyl)amino)-2-(2-methylbenzyl)-3-oxopropanoate : pale yellow oil; 42.3 mg; yield: 68%. (The side product from Heck type coupling is 6%, and that from 1,4-addition is 23% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.14 (m, 4H), 7.14 -7.05 (m, 3H), 6.49 (br, 2H), 3.73 (s, 3H), 3.60 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.23-3.11 (m, 5H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.7, 143.2, 136.7, 136.2, 130.4, 130.4, 129.6, 128.0, 127.5, 127.0, 126.0, 52.6, 48.4, 37.4, 32.9, 18.9. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{21}NO_3Na^+$ [M+Na^+] 334.1414, found 334.1414.



3c

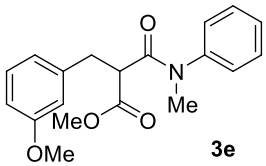
methyl 2-(2-chlorobenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate: pale yellow oil; 33.8 mg; yield: 51%. (The side product from Heck type coupling is 12%, and that from 1,4-addition is 20% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.15 (m, 7H), 6.62 (br, 2H), 3.82 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.72 (s, 3H), 3.33 (dd, *J* = 13.3, 4.9 Hz, 1H), 3.25-3.10 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.5,

143.0, 135.8, 134.6, 132.2, 129.7, 129.4, 128.4, 128.2, 127.4, 126.9, 52.6, 47.7, 37.5, 33.5. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}ClNO_3Na^+$ [M+Na^+] 354.0867, found 354.0867.



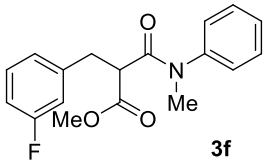
3d

methyl 3-(methyl(phenyl)amino)-2-(3-methylbenzyl)-3-oxopropanoate: pale yellow oil; 35.5 mg; yield: 57%. (The side product from Heck type coupling is 14%, and that from 1,4-addition is 12% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.60 (br, 2H), 3.71 (s, 3H), 3.56 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.22 -3.12 (m, 4H), 3.05 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.7, 143.3, 138.3, 138.0, 130.0, 129.6, 128.4, 128.1, 127.7, 127.4, 126.4, 52.6, 51.0, 37.5, 35.4, 21.4. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{21}NO_3Na^+$ [M+Na^+] 334.1414, found 334.1412.



3e

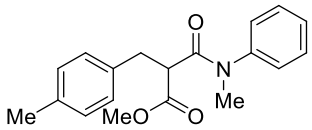
methyl 2-(3-methoxybenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate: pale yellow oil; 45.2 mg; yield: 69%. (The side product from Heck type coupling is 17%, and that from 1,4-addition is 13% from crude ^{1}H NMR.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 3H), 7.09 (t, *J* = 8.1 Hz, 1H), 6.90 – 6.10 (m, 5H), 3.67 (s, 3H), 3.64 (s, 3H), 3.50 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.16 – 3.08 (m, 4H), 3.00 (dd, *J* = 13.4, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.6, 159.8, 143.3, 140.0, 129.7, 129.5, 128.1, 127.7, 121.7, 114.3, 112.8, 55.3, 52.6, 50.9, 37.6, 35.6. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{21}NO_4Na^+$ [M+Na^+] 350.1363, found 350.1363.



3f

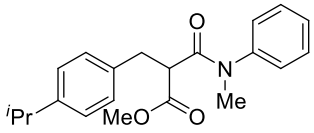
methyl 2-(3-fluorobenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate: pale yellow oil; 41.6 mg; yield: 66%. (The side product from Heck type coupling is 7%, and that from 1,4-addition is 27% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 3H), 7.25-7.18 (m, 1H), 7.10-6.40 (m, 5H), 3.72 (s, 3H), 3.57 (dd, *J* = 10.1, 5.1 Hz, 1H), 3.26-3.16 (m, 4H), 3.08 (dd, *J* = 13.4, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.3, 162.9 (d, J_{C-F} = 245.8 Hz), 143.1, 140.9 (d, J_{C-F} = 7.4 Hz), 129.9 (d, J_{C-F} = 8.2 Hz), 129.8, 128.3, 127.5, 125.1 (d, J_{C-F} = 2.7 Hz), 116.1 (d, J_{C-F} = 21.1 Hz), 113.6 (d, J_{C-F} = 20.9 Hz), 52.7, 50.7, 37.6, 35.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -

113.54. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}FNO_3Na^+$ [M+Na^+] 338.1163, found 338.1163.



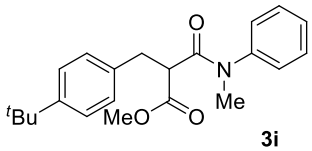
3g

methyl 3-(methyl(phenyl)amino)-2-(4-methylbenzyl)-3-oxopropanoate: pale yellow oil; 41.7 mg; yield: 67% (known compound)[S3]. (The side product from Heck type coupling is 11%, and that from 1,4-addition is 22% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.67 (br, 2H), 3.70 (s, 3H), 3.55 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.21-3.12 (m, 4H), 3.07 (dd, *J* = 13.6, 5.3 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.7, 143.3, 136.2, 135.3, 129.7, 129.2, 129.1, 128.1, 127.7, 52.6, 51.1, 37.6, 35.0, 21.2.



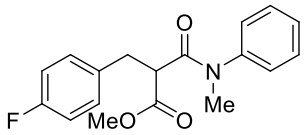
3h

methyl 2-(4-isopropylbenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate: pale yellow oil; 37.3 mg; yield: 55%. (The side product from Heck type coupling is 17%, and that from 1,4-addition is 20% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.56 (br, 2H), 3.71 (s, 3H), 3.53 (dd, *J* = 10.1, 4.9 Hz, 1H), 3.24-3.13 (m, 4H), 3.05 (dd, *J* = 13.4, 4.9 Hz, 1H), 2.96-2.84 (m, 1H), 1.29-1.24 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.8, 147.5, 143.3, 135.8, 129.6, 129.3, 128.1, 127.6, 126.5, 52.6, 51.1, 37.6, 35.1, 34.0, 24.4, 24.2. HRMS (m/z, ESI-TOF): Calcd for $C_{21}H_{25}NO_3Na^+$ [M+Na^+] 362.1727, found 362.1727.



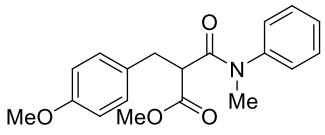
3i

methyl 2-(4-(tert-butyl)benzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate: pale yellow oil; 38.9 mg; yield: 55%. (The side product from Heck type coupling is 17%, and that from 1,4-addition is 8% from crude ^{1}H NMR.).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.16 (m, 5H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.55 (br, 2H), 3.71 (s, 3H), 3.53 (dd, *J* = 10.1, 5.0 Hz, 1H), 3.22-3.12 (m, 4H), 3.06 (dd, *J* = 13.4, 4.9 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.8, 149.7, 143.3, 135.4, 129.6, 129.0, 128.1, 127.6, 125.4, 52.6, 51.1, 37.6, 35.0, 34.6, 31.6. HRMS (m/z, ESI-TOF): Calcd for $C_{22}H_{27}NO_3Na^+$ [M+Na^+] 376.1883, found 376.1884.



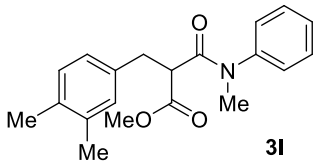
3j

methyl 2-(4-fluorobenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate: pale yellow oil; 42.9 mg; yield: 68%. (The side product from Heck type coupling is 14%, and that from 1,4-addition is 7% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 3H), 7.02-6.89 (m, 4H), 6.71 (br, 2H), 3.71 (s, 3H), 3.54 (dd, J = 10.1, 5.2 Hz, 1H), 3.23-3.15 (m, 4H), 3.06 (dd, J = 13.5, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.4, 161.9 (d, $J_{C\text{-}F}$ = 244.7 Hz), 143.2, 134.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.8, 128.3, 127.6, 115.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 52.7, 51.0, 37.6, 34.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.37. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}FNO_3Na^+$ [M+Na^+] 338.1163, found 338.1163.



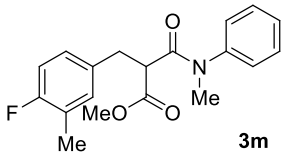
3k

methyl 2-(4-methoxybenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate： pale yellow oil; 32.7 mg; yield: 50% (known compound)[S3]. (The side product from Heck type coupling is 18%, and that from 1,4-addition is 13% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 6.94 (d, J = 8.5 Hz, 2H), 6.60-6.45 (m, 4H), 3.81 (s, 3H), 3.70 (s, 3H), 3.54 (dd, J = 10.0, 5.2 Hz, 1H), 3.20-3.11 (m, 4H), 3.03 (dd, J = 13.5, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.7, 158.5, 143.3, 130.5, 130.3, 129.7, 128.2, 127.7, 113.8, 55.5, 52.6, 51.2, 37.6, 34.6.



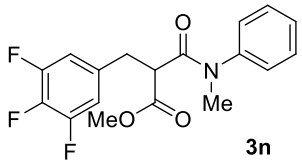
3l

methyl 2-(3,4-dimethylbenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate： pale yellow oil; 44.3 mg; yield: 68%. (The side product from Heck type coupling is 10%, and that from 1,4-addition is 13% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 3H), 7.00 (d, J = 7.5 Hz, 1H), 6.96 – 6.40 (m, 4H), 3.70 (s, 3H), 3.56 (dd, J = 9.7, 5.4 Hz, 1H), 3.18 (s, 3H), 3.12 (dd, J = 13.4, 9.8 Hz, 1H), 3.03 (dd, J = 13.4, 5.4 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.8, 143.3, 136.5, 135.7, 134.8, 130.5, 129.7, 129.6, 128.1, 127.7, 126.7, 52.5, 51.0, 37.6, 35.0, 19.8, 19.5. HRMS (m/z, ESI-TOF): Calcd for $C_{20}H_{23}NO_3Na^+$ [M+Na^+] 348.1570, found 348.1570.



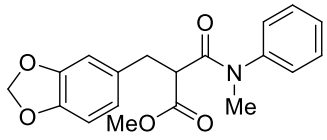
3m

methyl 2-(4-fluoro-3-methylbenzyl)-3-(methyl(phenyl)amino)-3-oxopropanoate： pale yellow oil; 34.9 mg; yield: 53%. (The side product from Heck type coupling is 12%, and that from 1,4-addition is 17% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.26 (m, 3H), 7.02-6.30 (m, 5H), 3.71 (s, 3H), 3.55 (dd, J = 10.1, 5.1 Hz, 1H), 3.18 (s, 3H), 3.13 (dd, J = 13.5, 10.2 Hz, 1H), 3.02 (dd, J = 13.5, 5.1 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.5, 160.4 (d, J_{C-F} = 243.4 Hz), 143.2, 133.8 (d, J_{C-F} = 3.6 Hz), 132.2 (d, J_{C-F} = 5.1 Hz), 129.7, 128.2, 128.0 (d, J_{C-F} = 7.9 Hz), 127.6, 124.7 (d, J_{C-F} = 17.3 Hz), 114.8 (d, J_{C-F} = 22.1 Hz), 52.6, 51.0, 37.5, 34.6, 14.5 (d, J_{C-F} = 3.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.95. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{20}FNO_3Na^+$ [M+Na^+] 352.1319, found 352.1320.



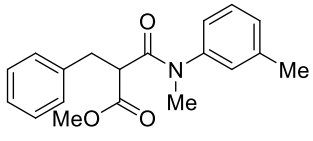
3n

methyl 3-(methyl(phenyl)amino)-3-oxo-2-(3,4,5-trifluorobenzyl)propanoate： pale yellow oil; 49.9 mg; yield: 71%. (The side product from 1,4-addition is 22% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 3H), 6.86 (br, 2H), 6.68-6.60 (m, 2H), 3.71 (s, 3H), 3.56 (dd, J = 9.4, 5.6 Hz, 1H), 3.23 (s, 3H), 3.13 (dd, J = 13.6, 9.6 Hz, 1H), 3.03 (dd, J = 13.7, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 167.9, 151.0 (ddd, J_{C-F} = 250.0, 9.8, 4.0 Hz), 143.0, 138.7 (dt, J_{C-F} = 250.5, 15.3 Hz), 134.8-134.6 (m), 130.0, 128.6, 127.5, 113.4-113.1 (m), 52.8, 50.5, 37.7, 34.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.66 (d, J = 20.5 Hz), -163.15 (t, J = 20.5 Hz). HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{16}F_3NO_3Na^+$ [M+Na^+] 374.0974, found 374.0974.



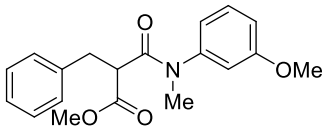
3o

methyl 2-(benzo[d][1,3]dioxol-5-ylmethyl)-3-(methyl(phenyl)amino)-3-oxopropanoate： pale yellow oil; 36.9mg; yield: 54%. (The side product from Heck type coupling is 12%, and that from 1,4-addition is 15% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 3H), 7.01-6.61 (m, 3H), 6.54-6.41 (m, 2H), 5.94 (s, 2H), 3.70 (s, 3H), 3.54 (dd, J = 9.7, 5.4 Hz, 1H), 3.21 (s, 3H), 3.12 (dd, J = 13.5, 9.8 Hz, 1H), 3.01 (dd, J = 13.6, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.6, 147.6, 146.3, 143.3, 132.1, 129.7, 128.3, 127.7, 122.3, 109.8, 108.3, 101.0, 52.6, 51.1, 37.6, 35.2. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{19}NO_5Na^+$ [M+Na^+] 364.1155, found 364.1155.



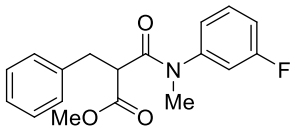
3ab

methyl 2-benzyl-3-(methyl(m-tolyl)amino)-3-oxopropanoate： pale yellow oil; 38.6 mg; yield: 62%. (The side product from Heck type coupling is 8%, and that from 1,4-addition is 17% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 -7.22 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (s, 1H), 7.07-7.02 (m, 2H), 6.55 (br, 2H), 3.71 (s, 3H), 3.57 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.23 (dd, *J* = 13.2, 10.5 Hz, 1H), 3.16 (s, 3H), 3.08 (dd, *J* = 13.3, 4.7 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.6, 143.2, 139.7, 138.5, 129.4, 128.9, 128.5, 128.1, 126.7, 124.5, 52.6, 50.9, 37.5, 35.5, 21.3. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{21}NO_3Na^+$ [M+Na^+] 334.1414, found 334.1414.



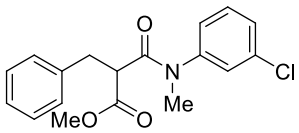
3ac

methyl 2-benzyl-3-((3-methoxyphenyl)(methyl) amino)-3-oxopropanoate： pale yellow oil; 41.2 mg; yield: 63%. (The side product from 1,4-addition is 22% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.09-6.99 (m, 2H), 6.82 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.24 (br, 2H), 3.72 (s, 6H), 3.63 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.23 (dd, *J* = 13.3, 10.3 Hz, 1H), 3.17 (s, 3H), 3.10 (dd, *J* = 13.4, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.5, 160.4, 144.3, 138.5, 130.3, 129.3, 128.5, 126.7, 119.7, 114.0, 113.0, 55.5, 52.6, 51.0, 37.5, 35.5. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{21}NO_4Na^+$ [M+Na^+] 350.1363, found 350.1363.



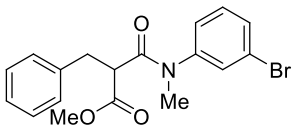
3ad

methyl 2-benzyl-3-((3-fluorophenyl)(methyl)amino)-3-oxopropanoate： pale yellow oil; 44.1 mg; yield: 70%. (The side product from Heck type coupling is 1%, and that from 1,4-addition is 21% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.16 (m, 4H), 7.00-6.95 (m, 3H), 6.31 (br d, *J* = 106.8 Hz, 2H), 3.73 (s, 3H), 3.54 (dd, *J* = 10.7, 4.5 Hz, 1H), 3.27-3.19 (m, 1H), 3.15 (s, 3H), 3.09 (dd, *J* = 13.3, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.5, 162.8 (d, J_{C-F} = 249.3 Hz), 144.6 (d, J_{C-F} = 9.5 Hz), 138.2, 130.8 (d, J_{C-F} = 9.1 Hz), 129.3, 128.6, 126.9, 123.4 (d, J_{C-F} = 3.2 Hz), 115.3 (d, J_{C-F} = 20.9 Hz), 115.1 (d, J_{C-F} = 22.1 Hz), 52.7, 51.1, 37.4, 35.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.45. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}FNO_3Na^+$ [M+Na^+] 338.1163, found 338.1163.



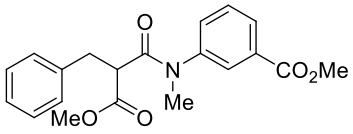
3ae

methyl 2-benzyl-3-((3-chlorophenyl)(methyl)amino)-3-oxopropanoate: pale yellow oil; 51.7 mg; yield: 78%. (The side product from Heck type coupling is 6%, and that from 1,4-addition is 15% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 4H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.07-7.00 (m, 2H), 6.58 (br, 2H), 3.74 (s, 3H), 3.52 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.24 (dd, *J* = 13.2, 10.8 Hz,1H), 3.14 (s, 3H), 3.08 (dd, *J* = 13.3, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.4, 144.3, 138.2, 135.0, 130.6, 129.3, 128.7, 128.5, 128.0, 127.0, 125.9, 52.7, 51.1, 37.5, 35.5. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}ClNO_3Na^+$ [M+Na^+] 354.0867, found 354.0867.



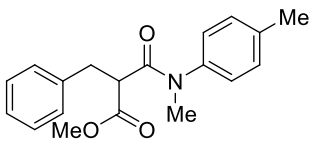
3af

methyl 2-benzyl-3-((3-bromophenyl)(methyl)amino)-3-oxopropanoate : pale yellow oil; 40.3 mg; yield: 54%. (The side product from Heck type coupling is 5%, and that from 1,4-addition is 19% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.32-7.27 (m, 3H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.07-7.01 (m, 2H), 6.64 (br, 2H), 3.74 (s, 3H), 3.52 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.24 (dd, 13.3, 10.9 Hz 1H), 3.13 (s, 3H), 3.08 (dd, *J* = 13.3, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.4, 144.5, 138.2, 131.4, 130.9, 130.8, 129.3, 128.7, 127.0, 126.4, 122.9, 52.7, 51.1, 37.5, 35.6. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}BrNO_3Na^+$ [M+Na^+] 398.0362, found 398.0362.



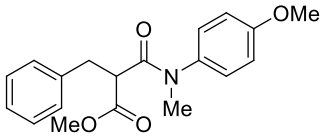
3ag

methyl 3-(2-benzyl-3-methoxy-N-methyl-3-oxopropanamido)benzoate : pale yellow oil; 55.8 mg; yield: 79%. (The side product from 1,4-addition is 17% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.55-7.29 (m, 2H), 7.26-7.22 (m, 3H), 7.10-6.50 (m, 3H), 3.93 (s, 3H), 3.73 (s, 3H), 3.51 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.23 (dd, *J* = 13.2, 10.6 Hz, 1H), 3.18 (s, 3H), 3.08 (dd, *J* = 13.4, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.5, 166.0, 143.4, 138.2, 132.2, 131.8, 129.8, 129.2, 129.2, 128.8, 128.6, 126.8, 52.7, 52.5, 51.1, 37.5, 35.5. HRMS (m/z, ESI-TOF): Calcd for $C_{20}H_{21}NO_5Na^+$ [M+Na^+] 378.1312, found 378.1311.



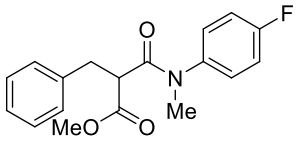
3ah

methyl 2-benzyl-3-(methyl(p-tolyl)amino)-3-oxopropanoate： pale yellow oil; 33 mg; yield: 53%. (The side product from Heck type coupling is 18% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 3H), 7.11-6.98 (m, 4H), 6.49 (br, 2H), 3.70 (s, 3H), 3.58 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.22 (dd, *J* = 13.3, 10.3 Hz, 1H), 3.15 (s, 3H), 3.08 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.7, 140.7, 138.5, 138.1, 130.3, 129.4, 128.5, 127.4, 126.7, 52.6, 50.9, 37.6, 35.5, 21.2. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{21}NO_3Na^+$ [M+Na^+] 334.1414, found 334.1414.



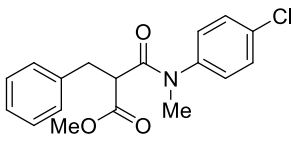
3ai

methyl 2-benzyl-3-((4-methoxyphenyl)(methyl)amino)-3-oxopropanoate： pale yellow oil; 35.4 mg; yield: 54% (known compound) [S4]. (The side product from Heck type coupling is 27%, and that from 1,4-addition is 6% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 3H), 7.07-7.01 (m, 2H), 6.90-5.90 (m, 4H), 3.79 (s, 3H), 3.70 (s, 3H), 3.58 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.22 (dd, *J* = 13.3, 10.4 Hz, 1H), 3.14 (s, 3H), 3.08 (dd, *J* = 13.3, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.9, 159.1, 138.6, 136.1, 129.4, 128.7, 128.5, 126.7, 114.7, 55.6, 52.5, 50.9, 37.7, 35.5.



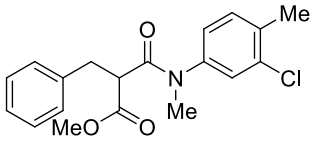
3aj

methyl 2-benzyl-3-((4-fluorophenyl)(methyl)amino)-3-oxopropanoate： pale yellow oil; 33.8 mg; yield: 54%. (The side product from Heck type coupling is 13%, and that from 1,4-addition is 17% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 3H), 7.01 – 6.93 (m, 2H), 6.85 (t, *J* = 6.8 Hz, 2H), 6.47 (br, 2H), 3.65 (s, 3H), 3.44 (dd, *J* = 10.7, 4.6 Hz, 1H), 3.17 (dd, *J* = 13.3, 10.7 Hz, 1H), 3.07 (s, 3H), 3.01 (dd, *J* = 13.3, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.7, 161.9 ((d, J_{C-F} = 249.5 Hz)), 139.3 (d, J_{C-F} = 3.0 Hz), 138.4, 129.5 (d, J_{C-F} = 8.4 Hz), 129.4, 128.6, 126.9, 116.6 (d, J_{C-F} = 22.6 Hz), 52.7, 51.0, 37.7, 35.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.98. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}FNO_3Na^+$ [M+Na^+] 338.1163, found 338.1160.



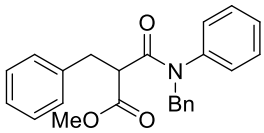
3ak

methyl 2-benzyl-3-((4-chlorophenyl)(methyl)amino)-3-oxopropanoate: pale yellow oil; 37.8 mg; yield: 57%. (The side product from Heck type coupling is 10%, and that from 1,4-addition is 15% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.4 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.09-7.02 (m, 2H), 6.47 (br, 2H), 3.72 (s, 3H), 3.51 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.24 (dd, *J* = 13.2, 10.8 Hz, 1H), 3.13 (s, 3H), 3.08 (dd, *J* = 13.3, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.5, 141.8, 138.4, 134.0, 129.9, 129.4, 129.1, 128.6, 126.9, 52.7, 51.0, 37.5, 35.5. HRMS (m/z, ESI-TOF): Calcd for $C_{18}H_{18}ClNO_3Na^+$ [M+Na$^+$] 354.0867, found 354.0867.



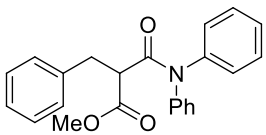
3al

methyl 2-benzyl-3-((3-chloro-4-methylphenyl) (methyl)amino)-3-oxopropanoate: pale yellow oil; 45.9 mg; yield: 67%. (The side product from Heck type coupling is 6%, and that from 1,4-addition is 23% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.07-7.03 (m, 2H), 6.47 (br, 2H), 3.72 (s, 3H), 3.54 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.24 (dd, *J* = 13.2, 11.2 Hz, 1H), 3.11 (s, 3H), 3.08 (dd, *J* = 13.3, 4.5 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.5, 141.9, 138.2, 136.4, 134.9, 131.7, 129.3, 128.6, 128.2, 126.9, 125.9, 52.6, 51.0, 37.5, 35.5, 19.9. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{20}ClNO_3Na^+$ [M+Na$^+$] 368.1024, found 368.1024.



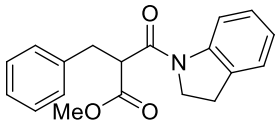
3am

methyl 2-benzyl-3-(benzyl(phenyl)amino)-3-oxopropanoate: pale yellow wax; 44.8 mg; yield: 60%. (The side product from Heck type coupling is 13%, and that from 1,4-addition is trace from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.10 (m, 9H), 7.09-6.99 (m, 4H), 6.05 (br, 2H), 4.91 (d, *J* = 14.3 Hz, 1H), 4.68 (d, *J* = 14.3 Hz, 1H), 3.71 (s, 3H), 3.52 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.33-3.23 (m, 1H), 3.11 (dd, *J* = 13.3, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.4, 141.5, 138.3, 136.9, 129.5, 129.4, 128.9, 128.8, 128.5, 128.3, 128.3, 127.4, 126.7, 53.3, 52.6, 51.1, 35.3. HRMS (m/z, ESI-TOF): Calcd for $C_{24}H_{23}NO_3Na^+$ [M+Na$^+$] 396.1570, found 396.1572.



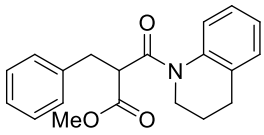
3an

methyl 2-benzyl-3-(diphenylamino)-3-oxopropanoate: white solid; 44.6 mg; yield: 62%. (The side product from Heck type coupling is 6%, and that from 1,4-addition is 18% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 8H), 7.19-7.06 (m, 5H), 6.73 (br, 2H), 3.80-3.72 (m, 4H), 3.34 (dd, *J* = 13.2, 10.8 Hz, 1H), 3.18 (dd, *J* = 13.3, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.8, 142.3, 142.2, 138.3, 129.7, 129.6, 129.0, 129.0, 128.6, 128.2, 126.9, 126.6, 126.5, 52.7, 51.7, 35.6. HRMS (m/z, ESI-TOF): Calcd for $C_{23}H_{21}NO_3Na^+$ [M+Na^+] 382.1414, found 382.1413.



3ao

methyl 2-benzyl-3-(indolin-1-yl)-3-oxopropanoate: pale yellow oil; 39.6 mg; yield: 64%. (The side product from 1,4-addition is 24% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.29-7.11 (m, 7H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.17-4.08 (m, 1H), 3.90-3.83 (m, 1H), 3.77-3.62 (m, 4H), 3.42-3.28 (m, 2H), 3.16-3.06 (m, 1H), 3.05-2.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 166.3, 142.6, 138.4, 131.6, 129.0, 128.7, 127.7, 126.9, 124.6, 124.3, 117.7, 54.0, 52.8, 48.5, 35.3, 27.9. HRMS (m/z, ESI-TOF): Calcd for $C_{19}H_{19}NO_3Na^+$ [M+Na^+] 332.1257, found 332.1258.



3ap

methyl 2-benzyl-3-(3,4-dihydroquinolin-1(2*H*)-yl)-3-oxopropanoate: pale yellow oil; 43.9 mg; yield: 68%. (The side product from Heck type coupling is 9%, and that from 1,4-addition is 13% from crude ^{1}H NMR.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-6.99 (m, 7H), 6.93 (s, 2H), 4.38 (t, *J* = 5.8 Hz, 1H), 4.05-3.90 (m, 1H), 3.79 (s, 3H), 3.36-3.24 (m, 1H), 3.23-3.13 (m, 2H), 2.47-2.29 (m, 1H), 1.89-1.73 (m, 1H), 1.64-1.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 168.8, 138.9, 137.9, 135.0, 129.0, 128.5, 128.4, 126.7, 126.3, 126.1, 124.5, 52.8, 50.2, 42.8, 36.0, 26.0, 23.8. HRMS (m/z, ESI-TOF): Calcd for $C_{20}H_{21}NO_3Na^+$ [M+Na^+] 346.1414, found 346.1411.

2.8 References

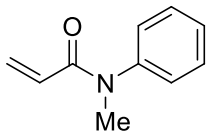
[S1] A. Perry, R. J. K. Taylor, *Chem. Commun.,* 2009, **45**, 3249.

[S2] Z. -J. Wu, S. -R. Li, H. Long, H.-C. Xu, *Chem. Commun.,* 2018, **54**, 4601.

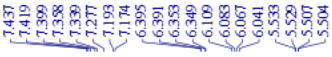
[S3] C. Hayashi, T. Hayashi, T. Yamada, *Bull. Chem. Soc. Jpn.,* 2015**, 88**, 862.

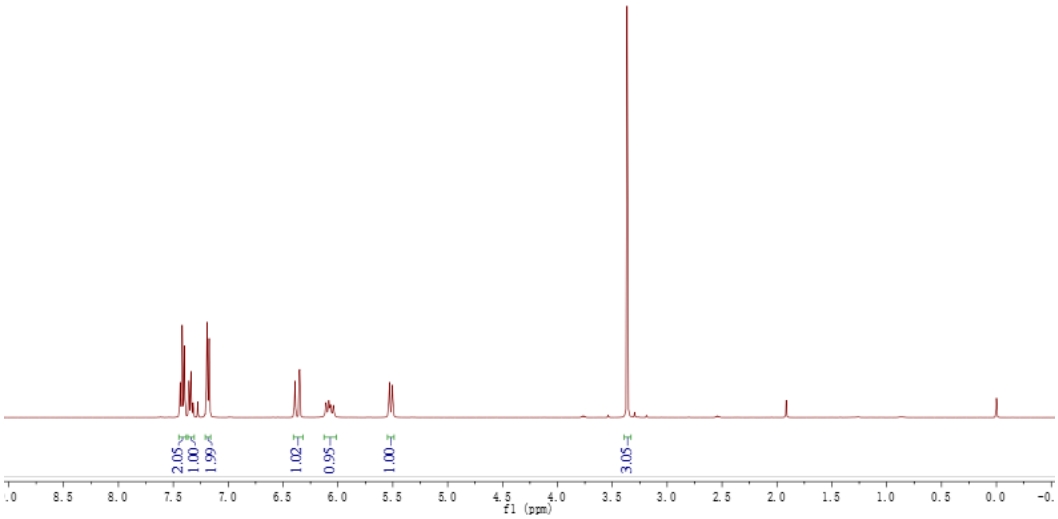
[S4] S. Ghosh, S. De, B. N. Kakde, S. Bhunia, A. Adhikary, A. Bisai, *Org. Lett.,* 2012**, 14**, 5864.

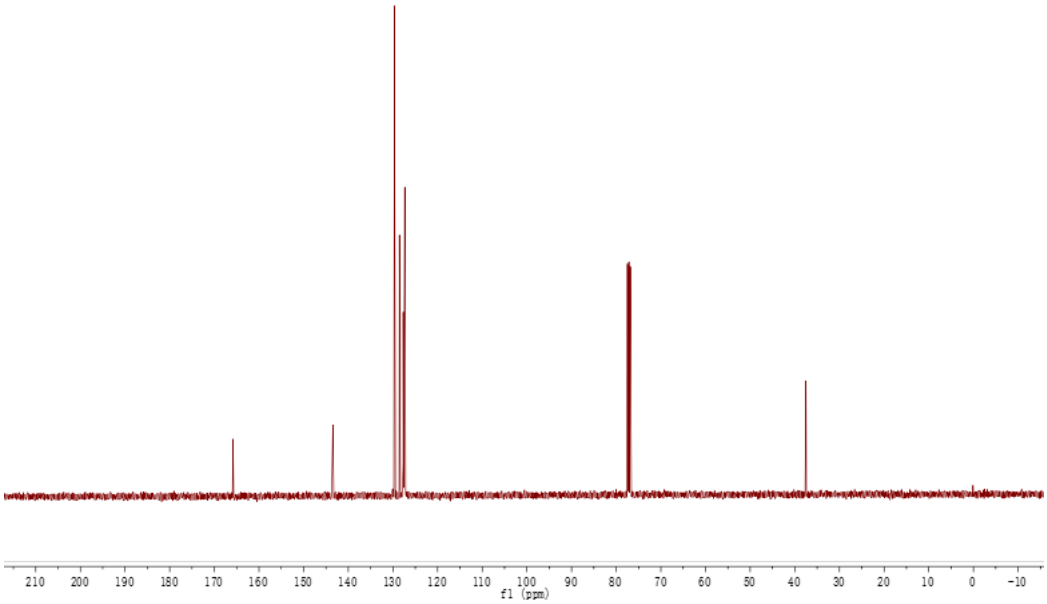
3. NMR Spectra of Substrates and Products

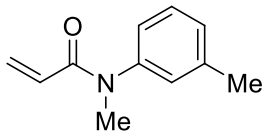


1a








O
N
Me
Me

1b


7.309
7.290
7.271
7.157
7.138
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6.989
6.965
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6.381
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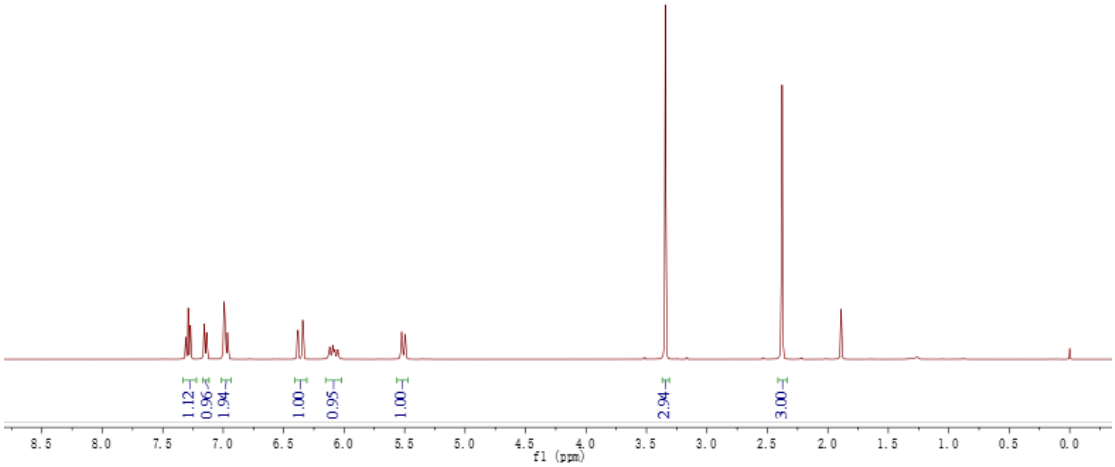
5.521
5.499
5.495
3.343
2.378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0.95
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3.00
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128.638
128.445
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124.387
77.476
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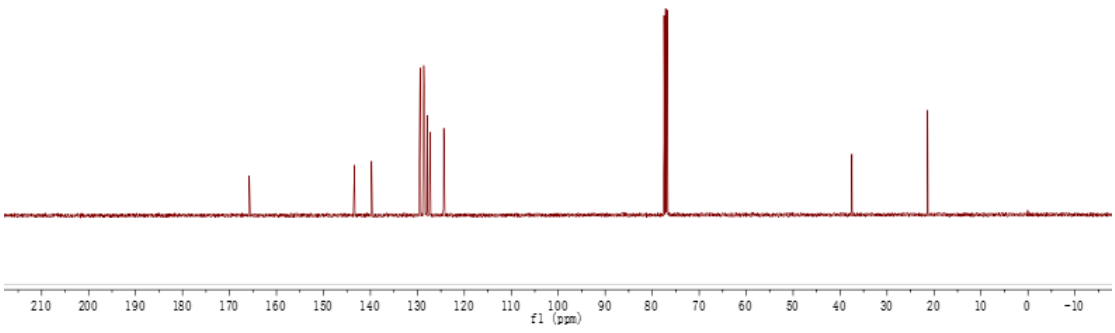
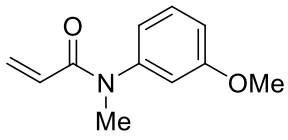
21.363


f1 (ppm)


O
N
Me
OMe

1c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6.870
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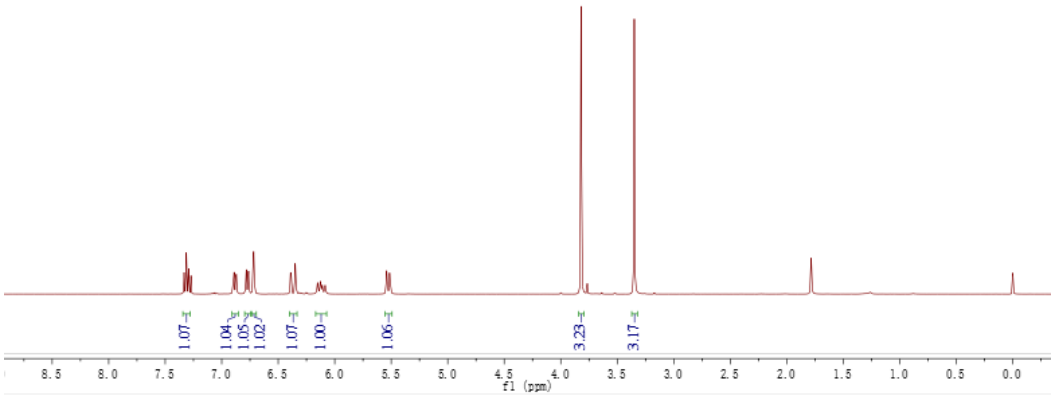
3.349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1.02
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1.00
1.06
3.23
3.17
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f1 (ppm)


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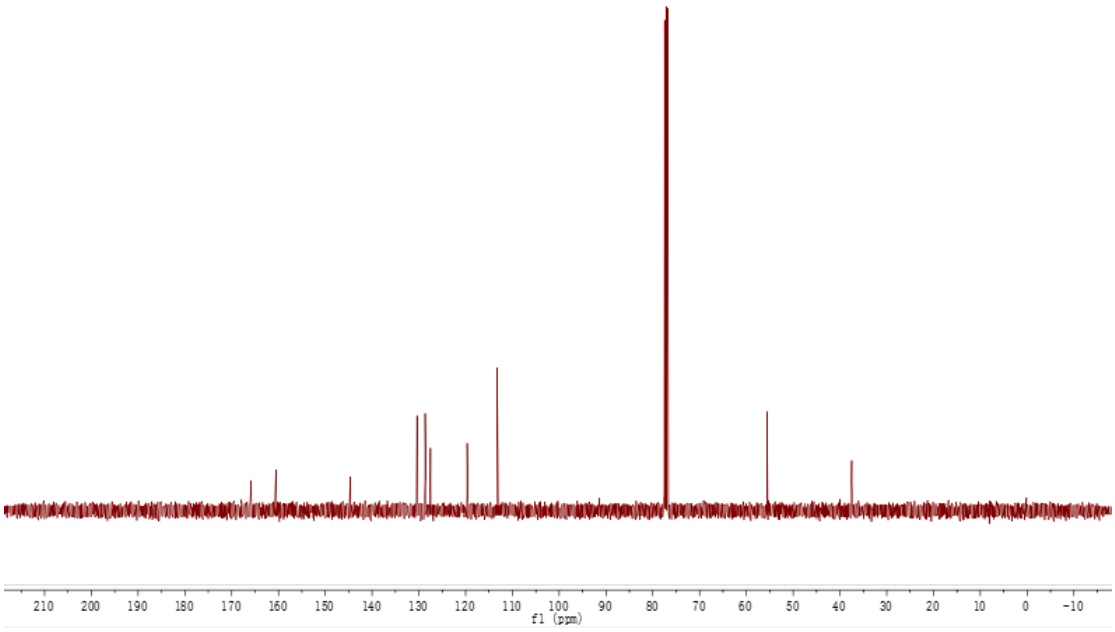
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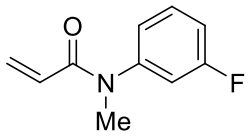
O
N
Me
F

1d


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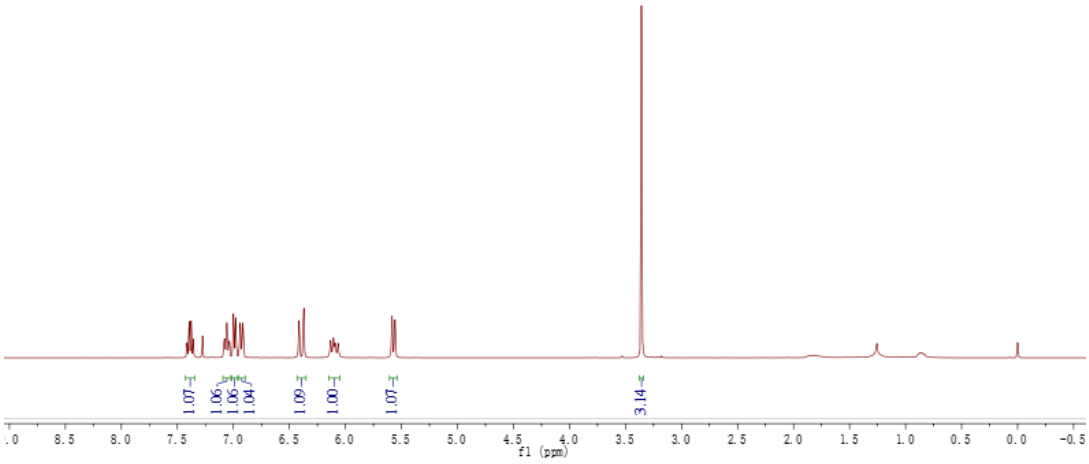
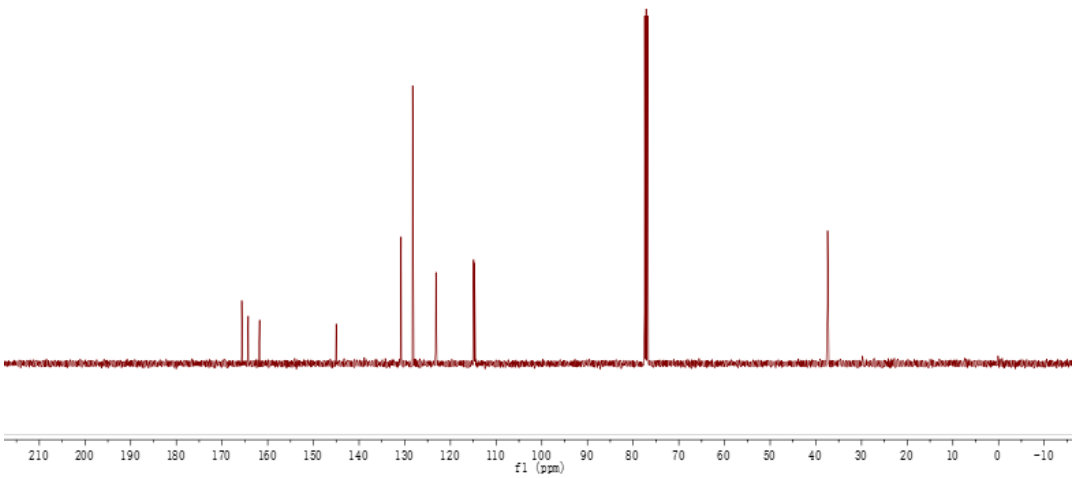
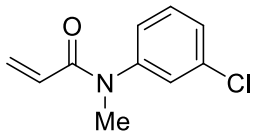
7.000
6.980
6.939
6.916
6.414
6.372
6.133
6.107
6.091
6.065
5.584
5.558
3.398

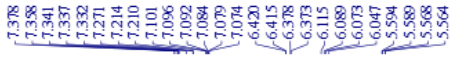

1.07
1.06
1.06
1.04
1.09
1.00
1.07
3.14
f1 (ppm)

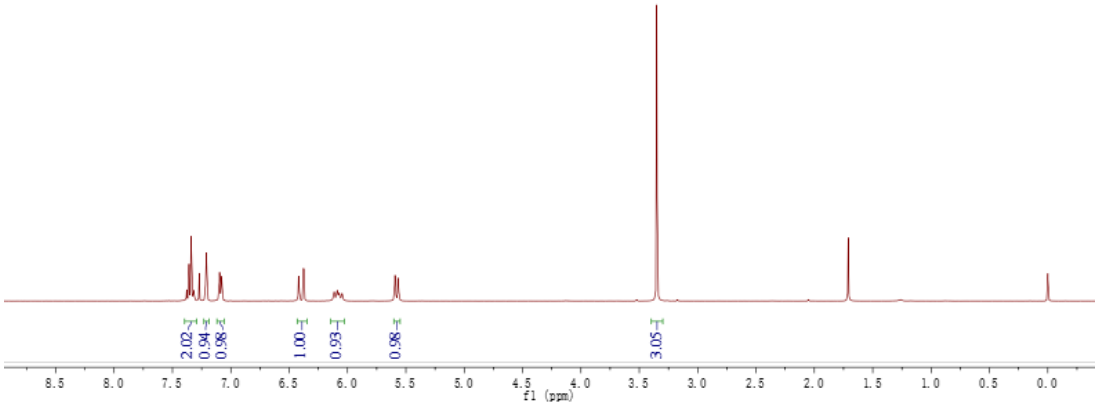

165.685
164.250
161.775
145.013
144.920
130.882
130.790
128.283
128.154
123.214
123.183
114.917
114.873
114.708
114.652
77.475
77.158
76.839
37.432

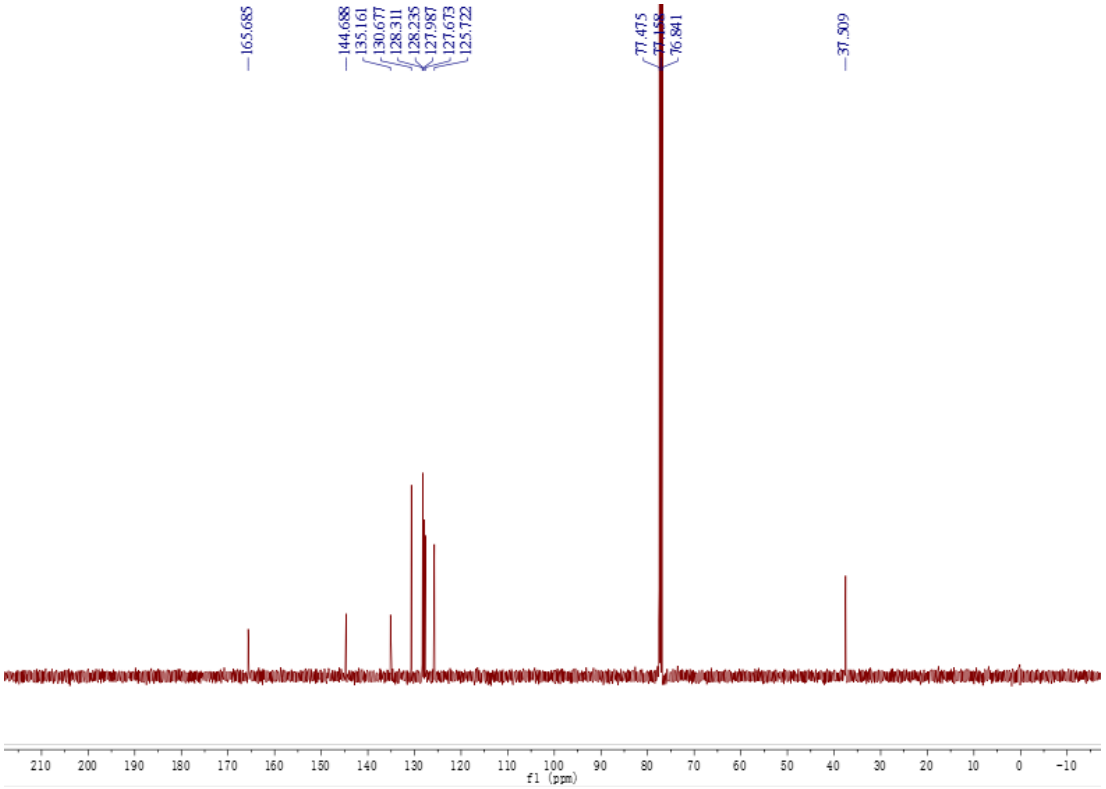

f1 (ppm)

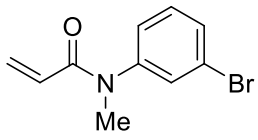

O
N
Me
Cl

1e


7.378
7.358
7.341
7.337
7.332
7.271
7.214
7.210
7.101
7.096
7.092
7.084
7.079
7.074
6.420
6.415
6.378
6.373
6.115
6.089
6.073
6.047
5.594
5.589
5.568
5.564
3.350

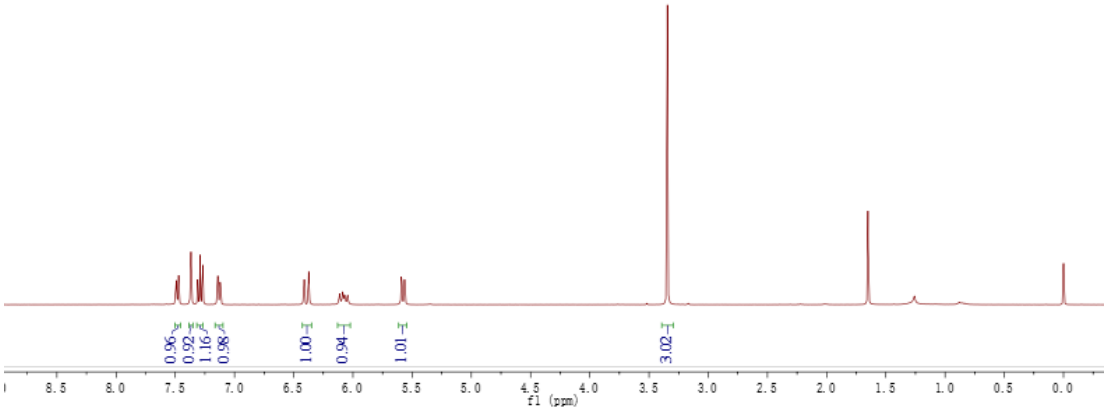

2.02
0.94
0.98
1.00
0.93
0.98
3.05
f1 (ppm)

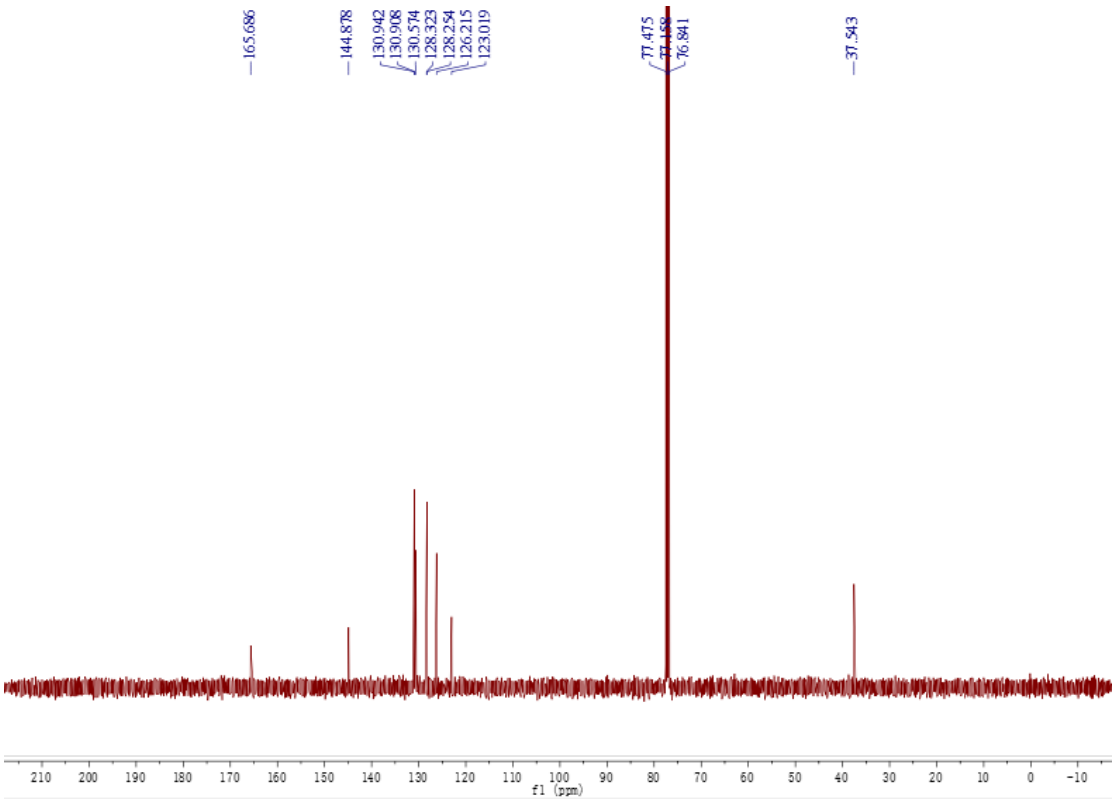

165.685
144.688
135.161
130.677
128.311
128.235
127.987
127.673
125.722
77.475
77.158
76.841
37.909
f1 (ppm)

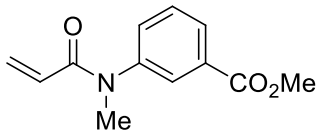

O
N
Me
Br

1f


7.492
7.472
7.368
7.311
7.291
7.267
7.141
7.121
6.416
6.412
6.374
6.370
6.112
6.086
6.071
6.045
5.592
5.588
5.566
5.562
3.346

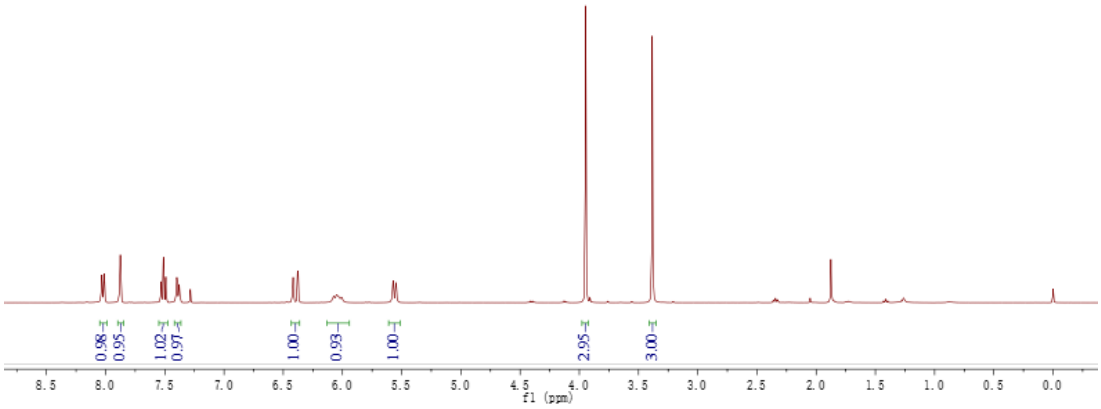

0.96
0.92
1.16
0.98
1.00
0.94
1.01
3.02
f1 (ppm)


165.686
144.878
130.942
130.908
130.574
128.323
128.254
126.215
123.019
77.475
77.158
76.841
37.543
f1 (ppm)

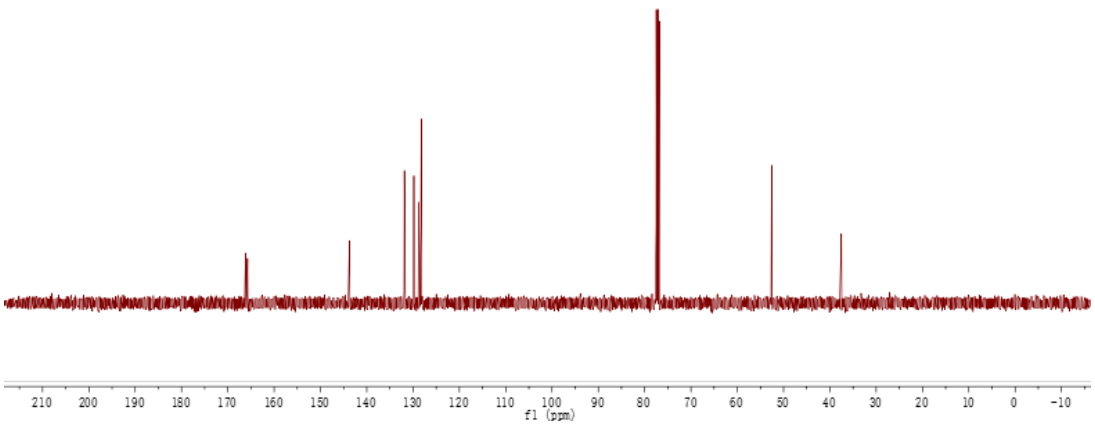

O
N
Me
CO2Me

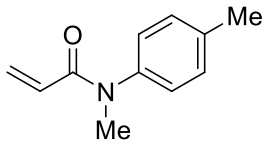
1g


8.031
8.012
7.876
7.531
7.512
7.492
7.399
7.379
7.284
6.421
6.417
6.379
6.375
6.075
6.049
6.008
5.575
5.572
5.547
3.947
3.384


0.98
0.95
1.02
0.97
1.00
0.93
1.00
2.95
3.00
f1 (ppm)

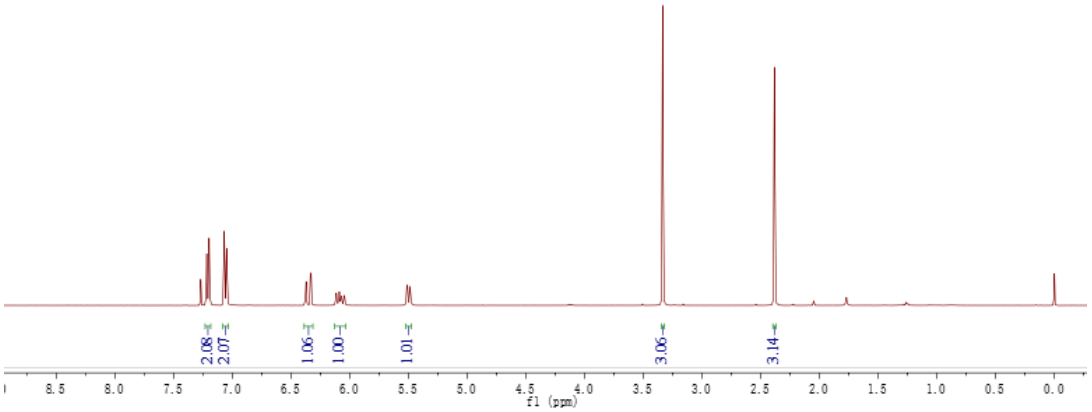

166.188
165.743
143.729
131.875
129.827
128.767
128.328
128.214
77.476
77.159
76.842
52.571
37.510


f1 (ppm)

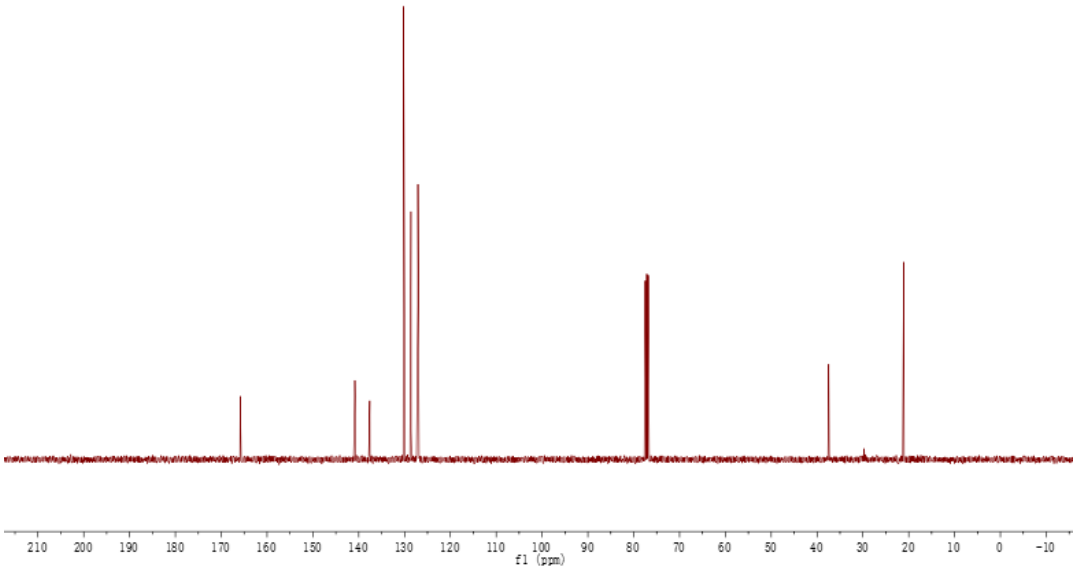

O
N
Me
Me

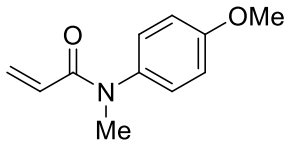
1h


7.269
7.218
7.198
7.069
7.048
6.376
6.371
6.334
6.329
6.115
6.089
6.073
6.047
5.513
5.509
5.487
5.483
3.335
2.384


2.08
2.07
1.06
1.00
1.01
3.06
3.14
f1 (ppm)

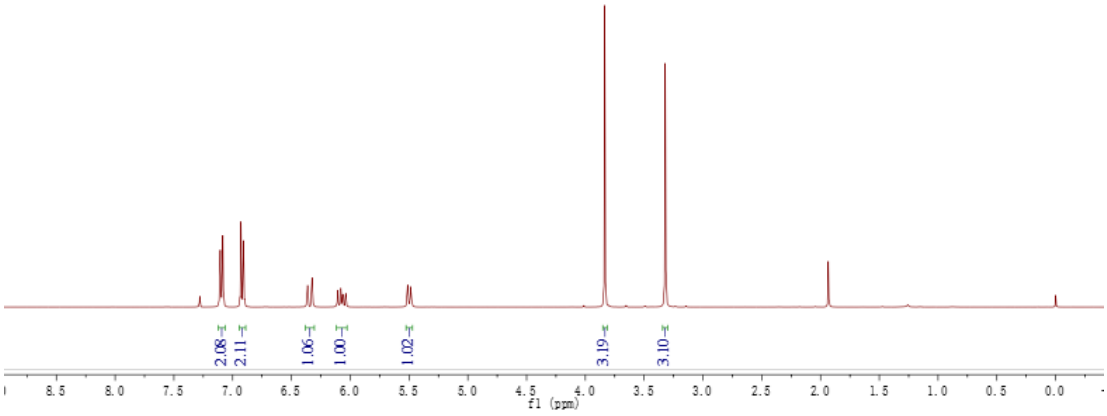

165.857
140.847
137.592
130.213
128.610
127.173
127.085
77.478
77.160
76.842
37.462
21.089


f1 (ppm)

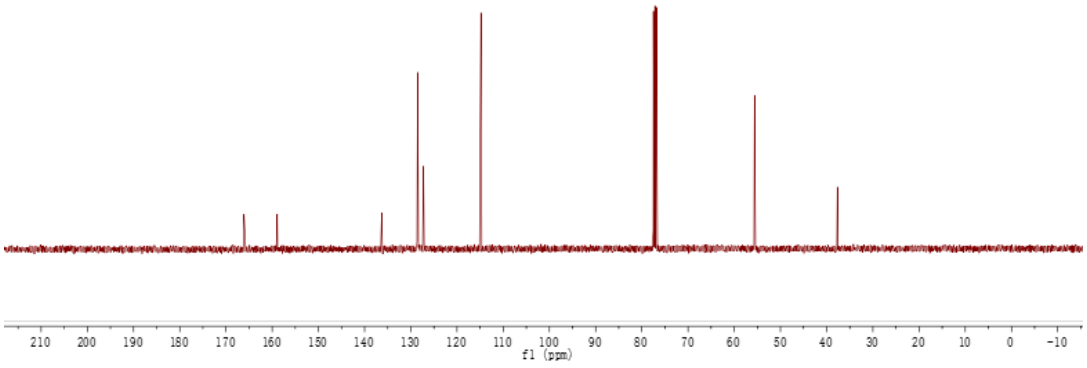

O
N
Me
OMe

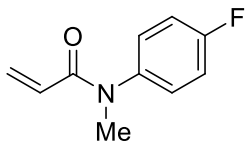
1i


7.280
7.106
7.084
6.929
6.924
6.912
6.907
6.368
6.363
6.325
6.321
6.106
6.080
6.064
6.038
5.512
5.508
5.487
5.482
3.835
3.321


2.08
2.11
1.06
1.00
1.02
3.19
3.10
f1 (ppm)

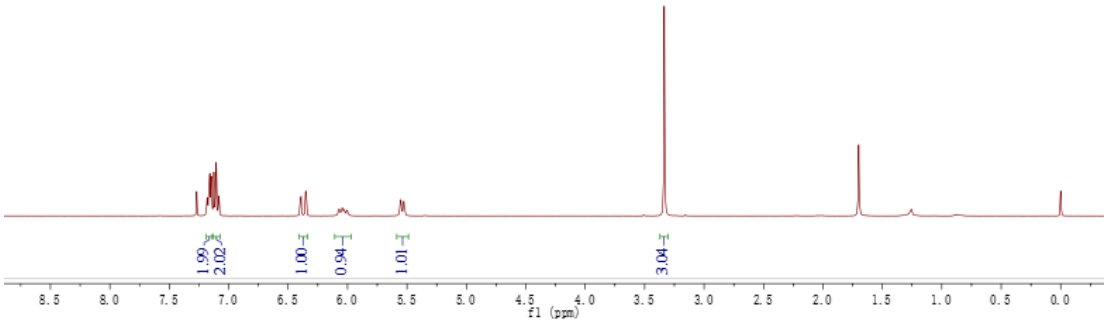

166.094
158.907
136.289
128.597
128.512
127.261
114.814
77.475
77.157
76.840
55.613
37.670


f1 (ppm)

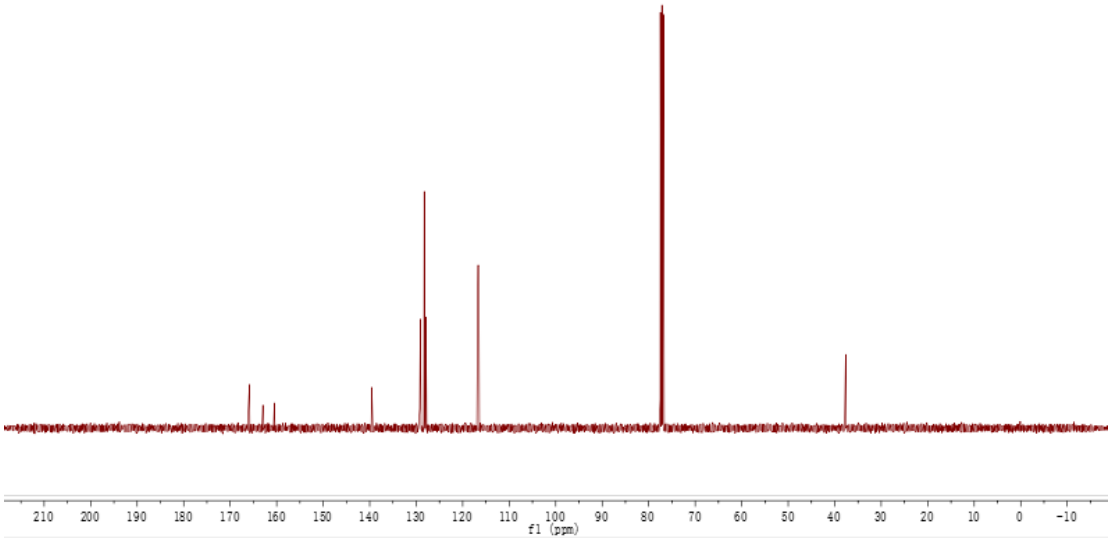

O
F
N
Me

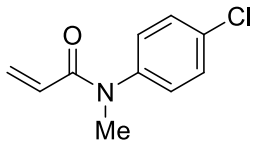
1j


7.269
7.181
7.176
7.169
7.159
7.152
7.147
7.132
7.125
7.119
7.105
7.088
7.083
6.396
6.391
6.354
6.349
6.071
6.045
6.030
6.004
5.552
5.527
3.335

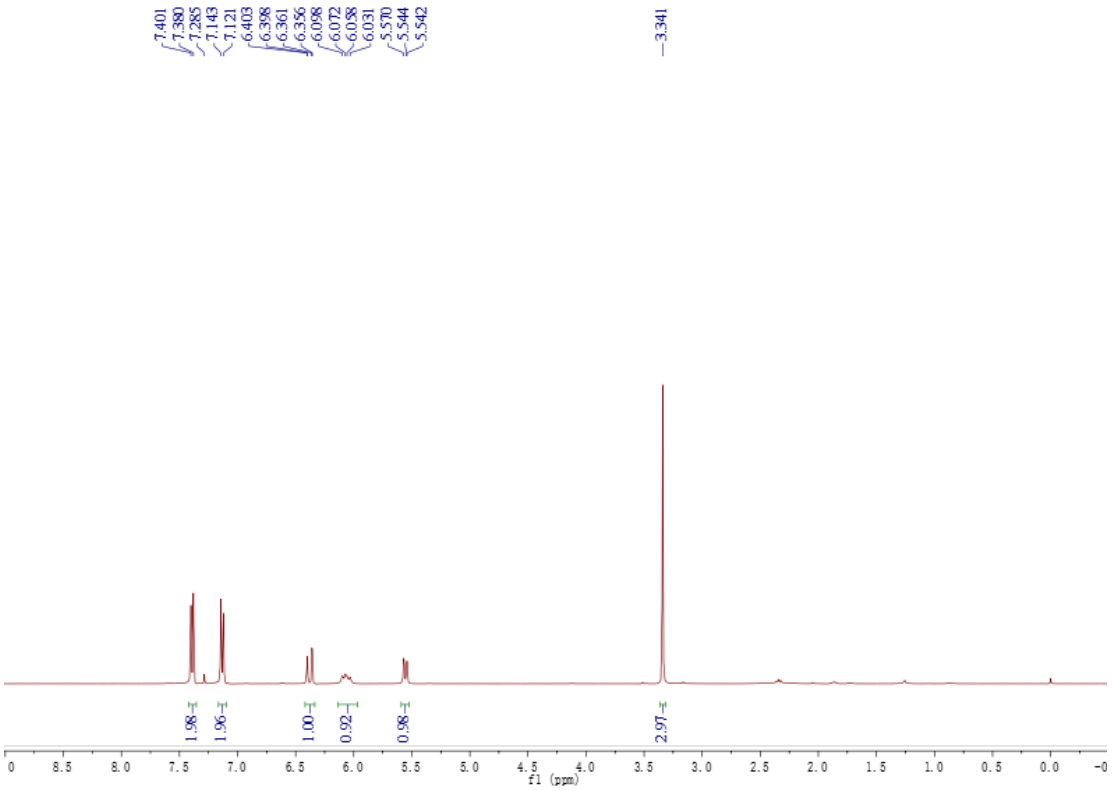

1.99
2.02
1.00
0.94
1.01
3.04
f1 (ppm)

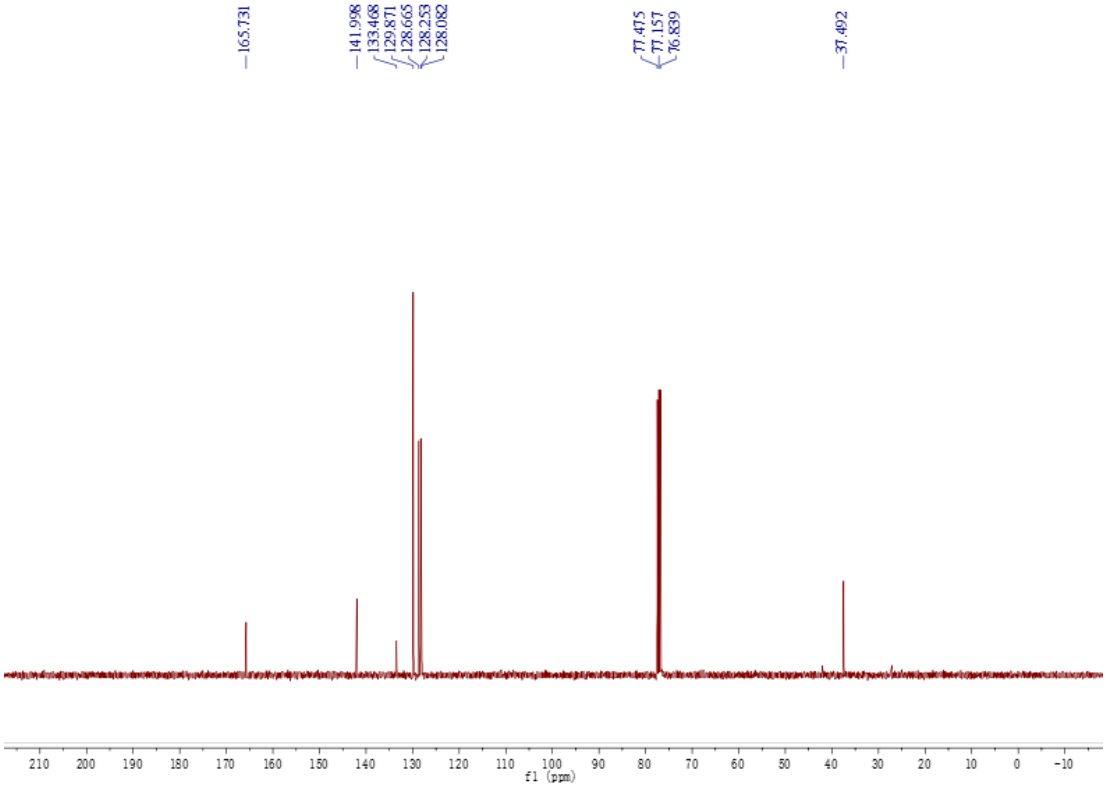

165.866
162.968
160.502
139.547
139.514
129.192
129.108
128.272
127.912
116.746
116.521
77.476
77.158
76.840
37.649

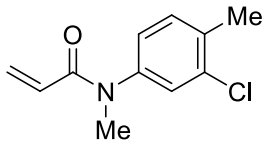

f1 (ppm)


O
N
Me
Cl

1k

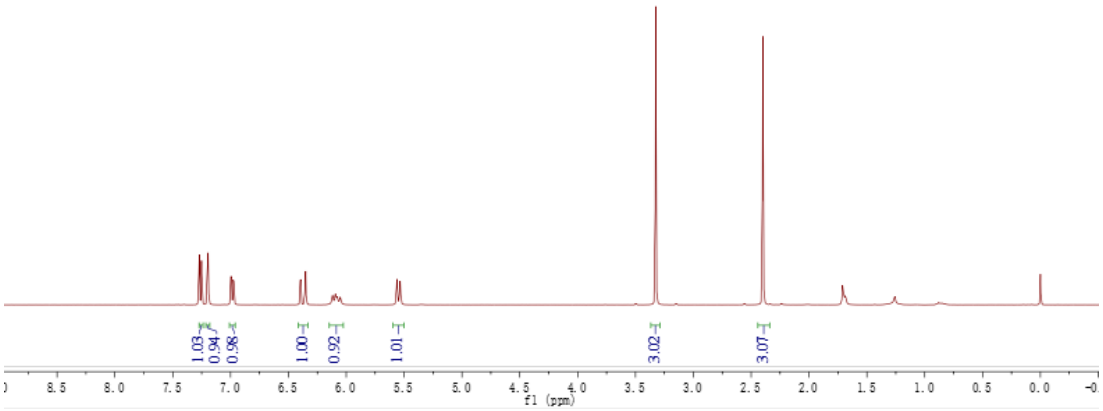

7.401
7.380
7.285
7.143
7.121
6.403
6.398
6.361
6.356
6.098
6.072
6.058
6.031
5.570
5.544
5.542
3.341
1.98
1.96
1.00
0.92
0.98
2.97
f1 (ppm)

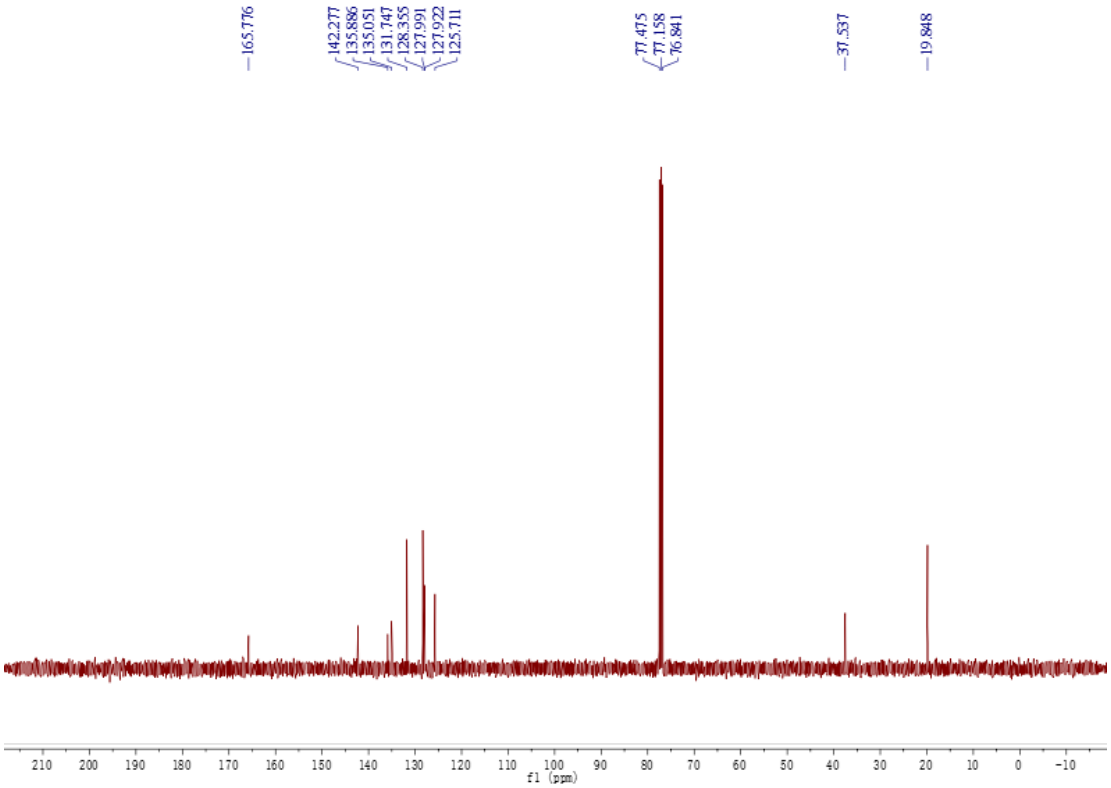

165.731
141.998
133.468
129.871
128.665
128.253
128.082
77.475
77.157
76.839
37.492
f1 (ppm)

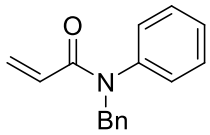

O
N
Me
Me
Cl

1l


7.270
7.252
7.199
7.194
6.998
6.993
6.978
6.973
6.397
6.393
6.356
6.351
6.120
6.094
6.079
6.052
5.563
5.560
5.534
3.325
2.399

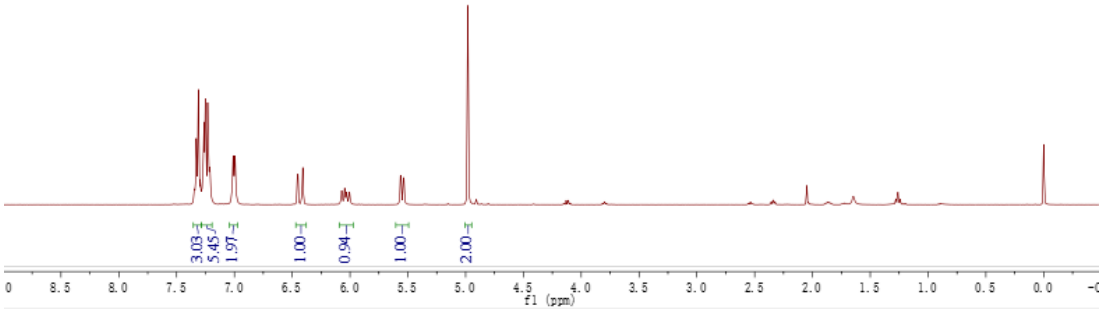

1.03
0.94
0.98
1.00
0.92
1.01
3.02
3.07
f1 (ppm)


165.776
142.277
135.886
135.051
131.747
128.355
127.991
127.922
125.711
77.475
77.158
76.841
37.537
19.848
f1 (ppm)

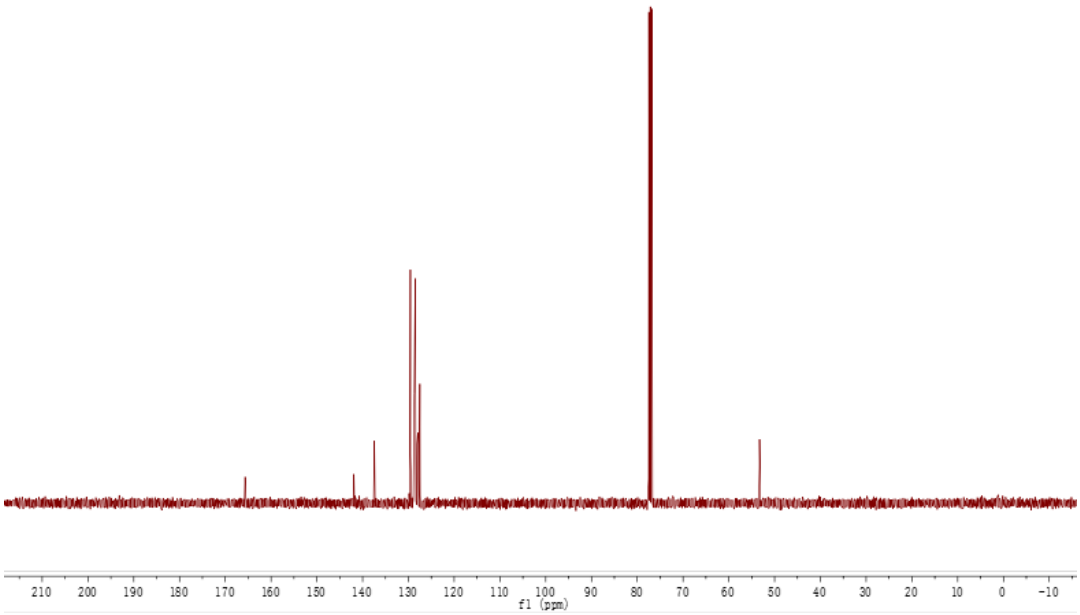

O
N
Bn

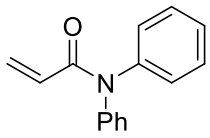
1m


7.330
7.311
7.297
7.267
7.262
7.251
7.232
7.212
7.011
6.995
6.455
6.430
6.413
6.408
6.072
6.047
6.031
6.005
5.564
5.560
5.538
5.534
4.981

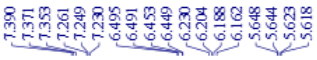

3.03
5.45
1.97
1.00
0.94
1.00
2.00
f1 (ppm)

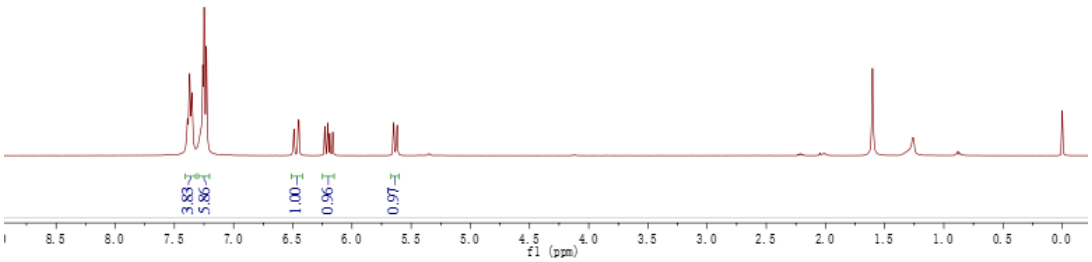

165.682
141.896
137.429
129.559
128.845
128.715
128.515
128.468
128.121
127.953
127.490
77.477
77.158
76.840
53.293

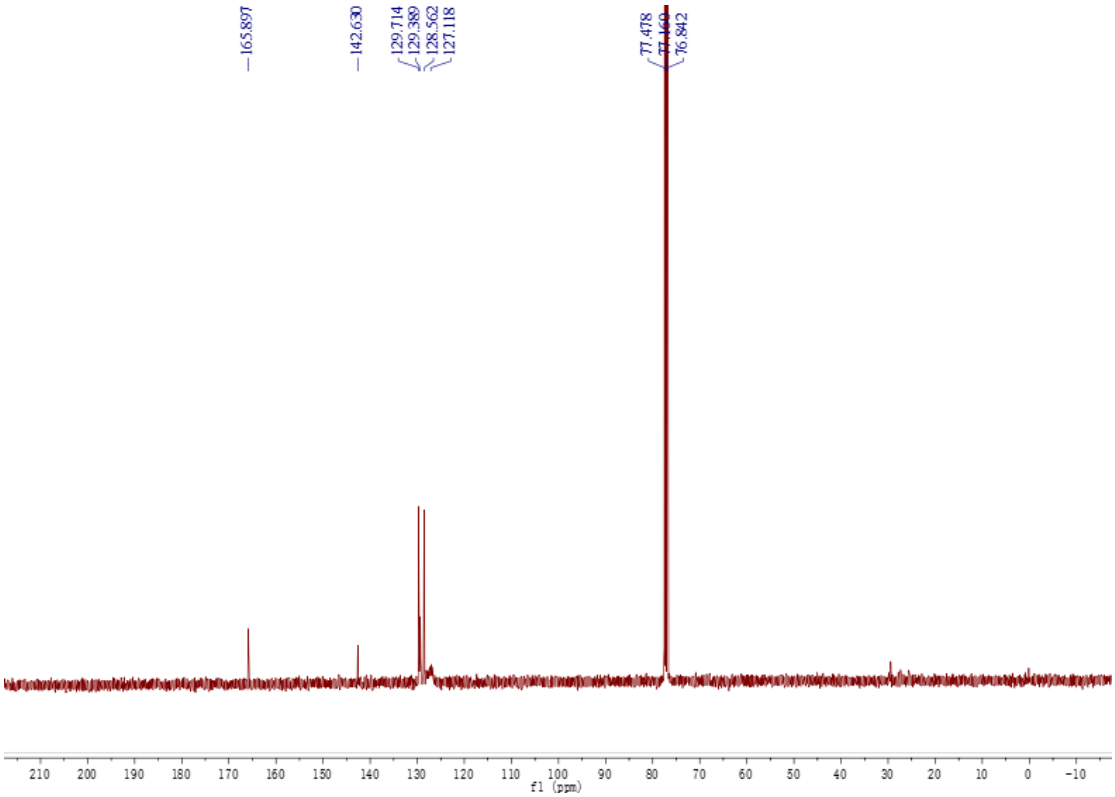

f1 (ppm)

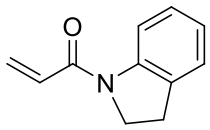

O
N
Ph

1n


7.390
7.371
7.353
7.261
7.249
7.230
6.495
6.491
6.453
6.449
6.230
6.204
6.188
6.162
5.648
5.644
5.623
5.618

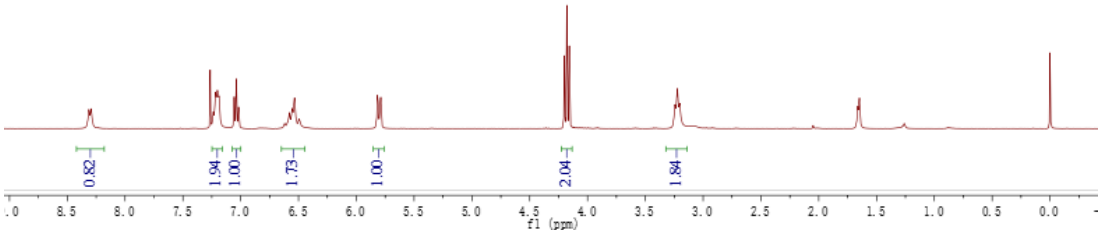

3.83
5.86
1.00
0.96
0.97
f1 (ppm)

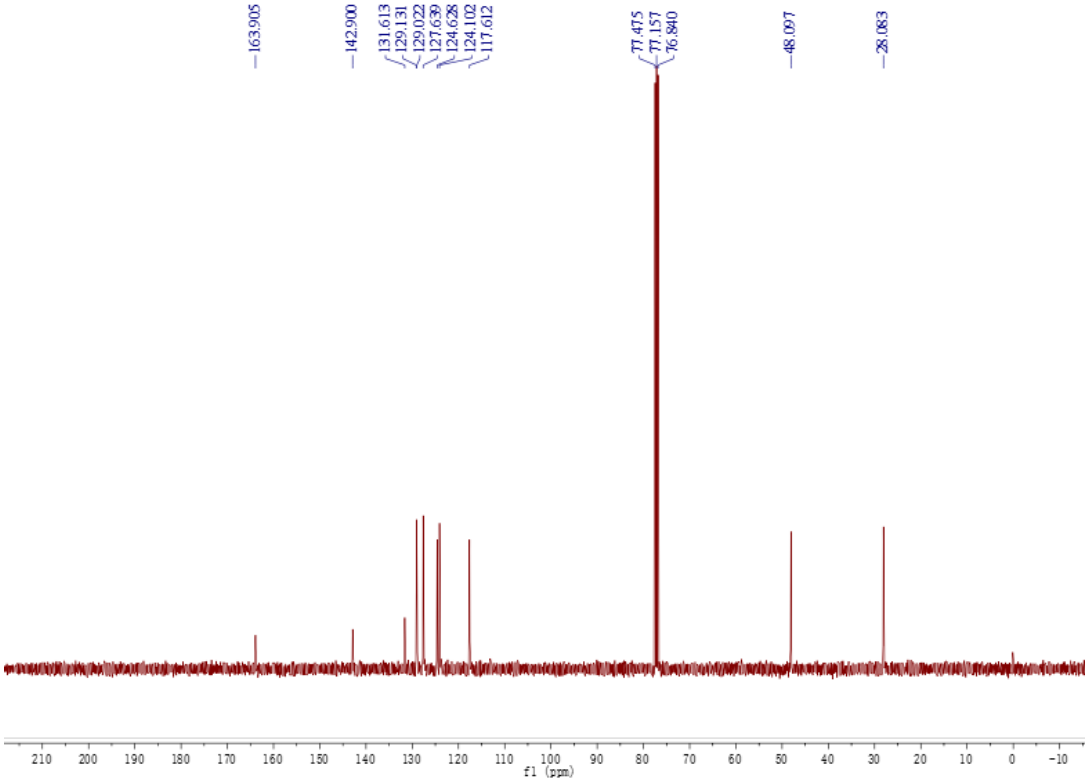

165.897
142.630
129.714
129.389
128.562
127.118
77.478
77.160
76.842
f1 (ppm)

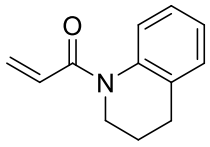


1o


8.313
8.293
7.263
7.188
7.056
7.037
7.019
6.620
6.579
6.554
6.534
6.495
5.818
5.812
5.794
5.788
4.201
4.180
4.158
3.243
3.223
3.203


0.82
1.94
1.00
1.73
1.00
2.04
1.84
f1 (ppm)


163.905
142.900
131.613
129.131
129.022
127.639
124.628
124.102
117.612
77.475
77.157
76.840
48.097
28.083
f1 (ppm)



1p


7.270
7.177
7.163
7.138
7.123
7.104
7.076
7.060
6.572
6.547
6.530
6.505
6.459
6.456
6.417
6.414
5.678
5.675
5.653
5.630
3.885
3.868
3.851
2.741
2.725
2.708
2.015
2.012
1.999
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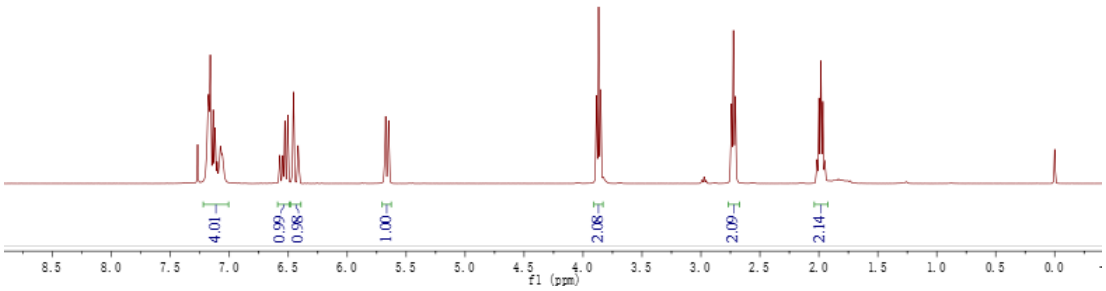
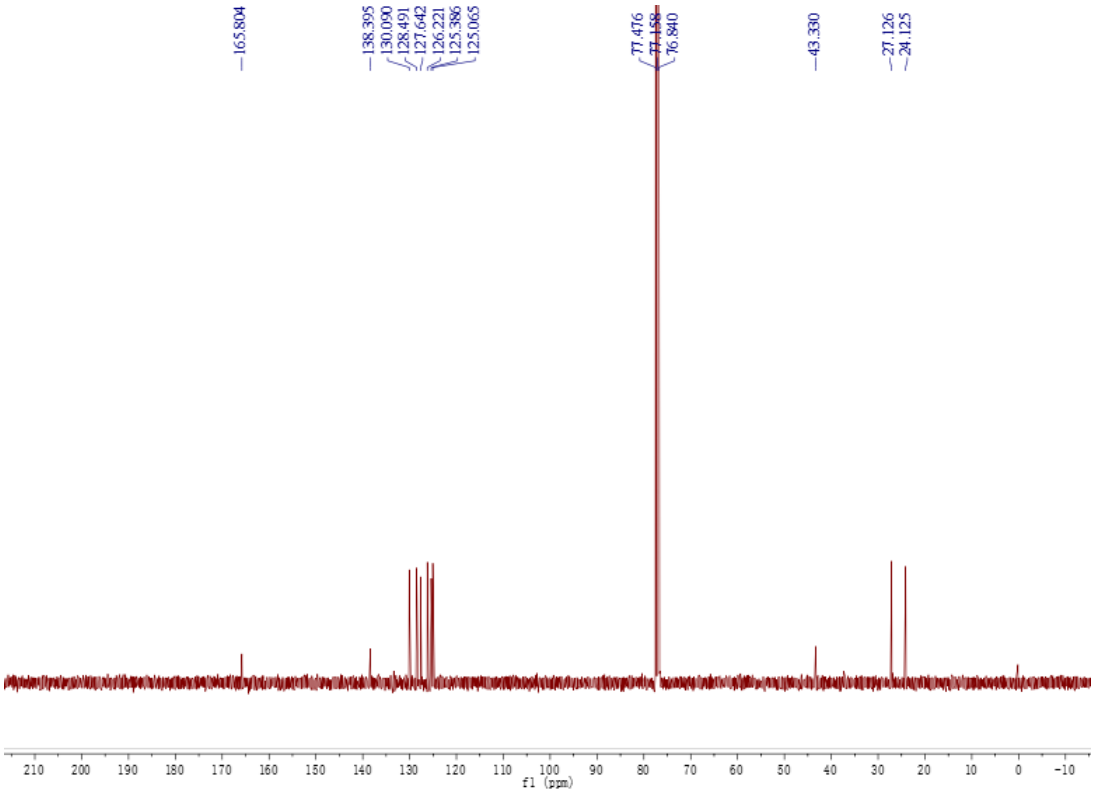
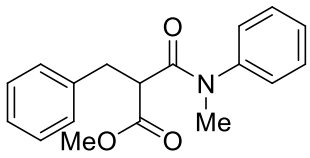
1.966
1.950

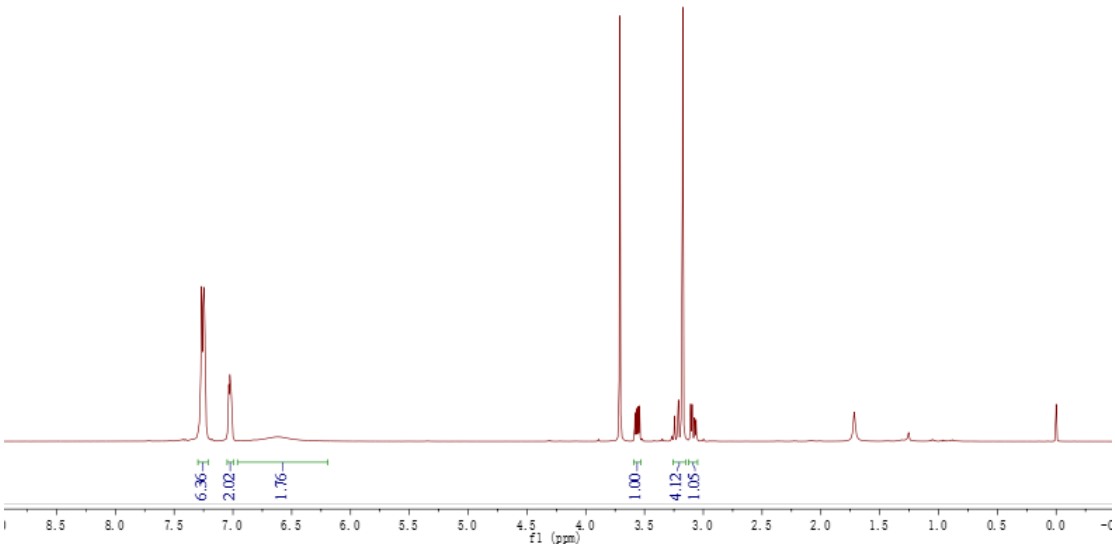

4.01
0.99
0.98
1.00
2.08
2.09
2.14
f1 (ppm)


165.804
138.395
130.090
128.491
127.642
126.221
125.386
125.065
77.476
77.158
76.840
43.330
27.126
24.125
f1 (ppm)

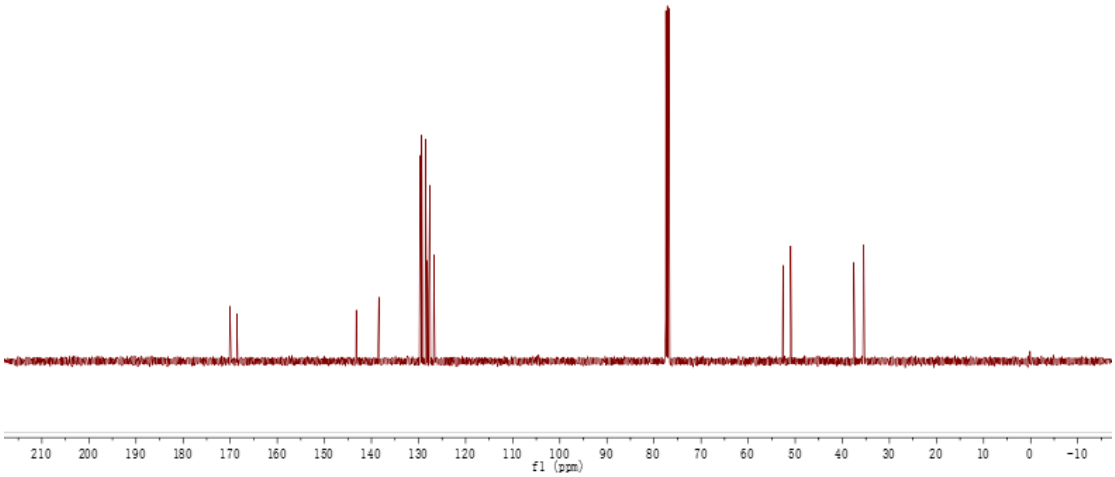

O
N
Me
MeO
O

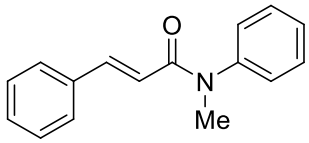
3a


7.266
7.255
7.246
7.240
7.035
7.027
7.017
7.012
6.617
3.710
3.581
3.568
3.556
3.543
3.245
3.220
3.212
3.186
3.176
3.108
3.096
3.075
3.062

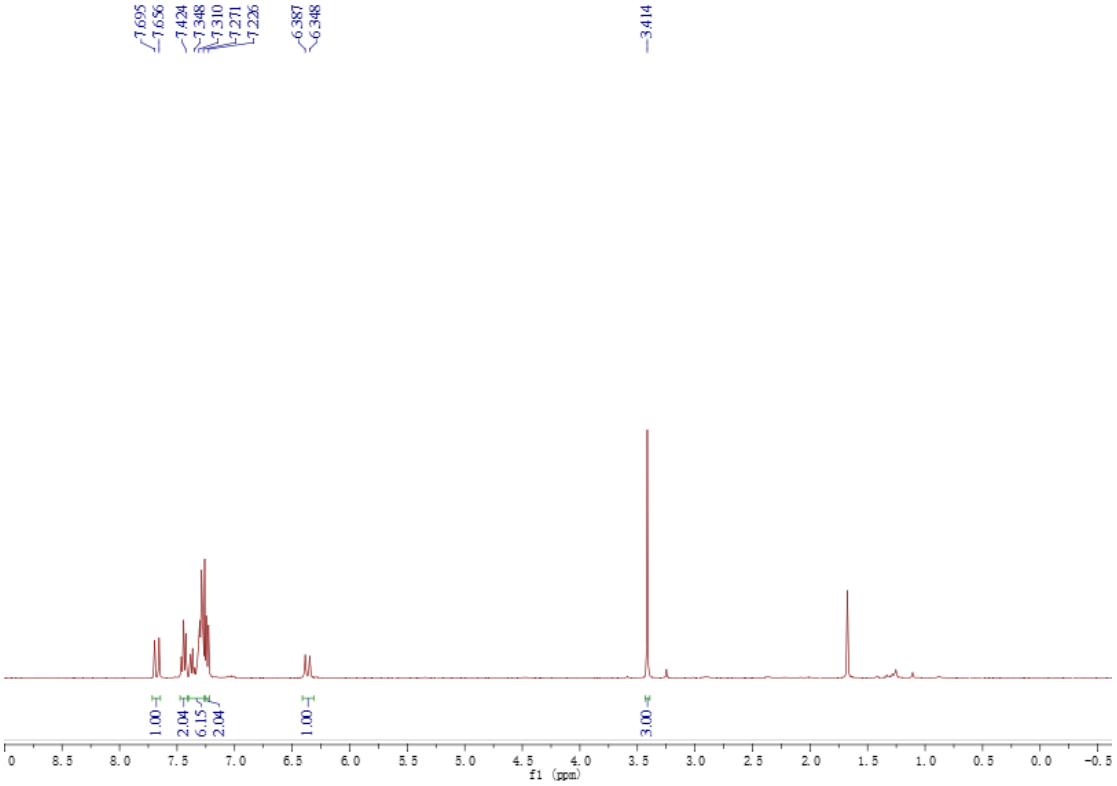

6.36
2.02
1.76
1.00
4.12
1.05
f1 (ppm)

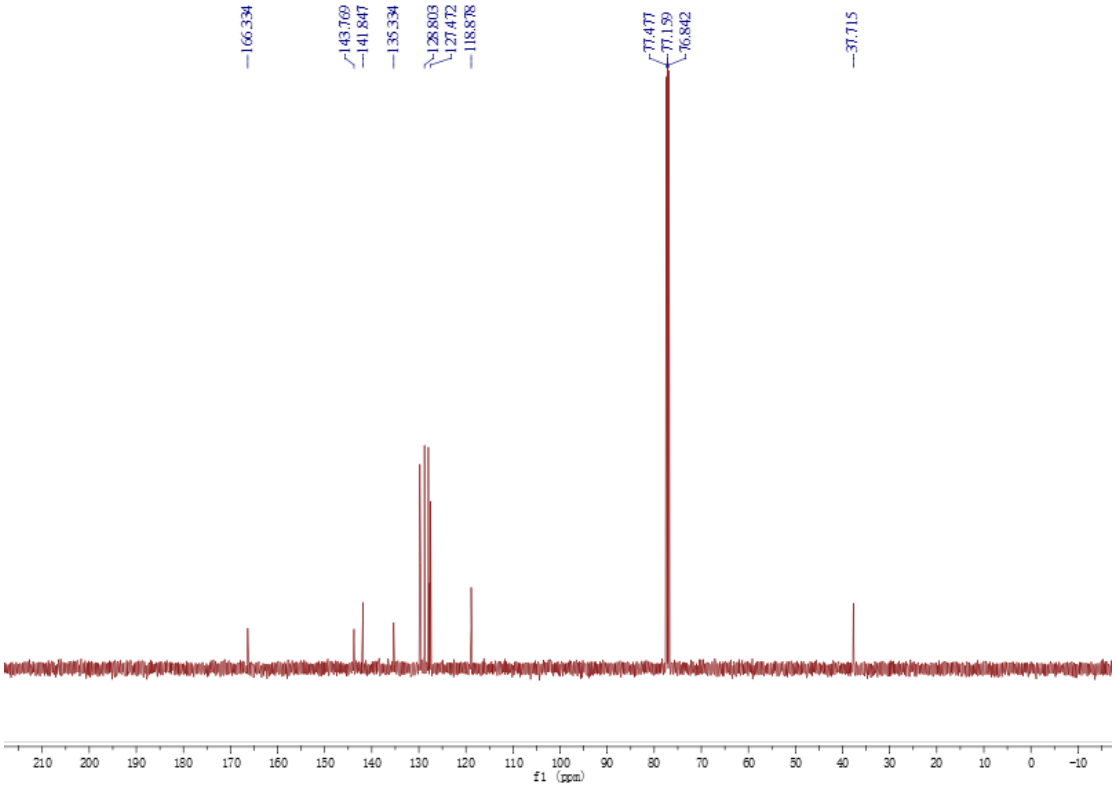

170.046
168.597
143.223
138.423
129.676
129.340
128.500
128.133
127.612
126.730
77.475
77.158
76.841
52.899
50.974
37.558
35.462

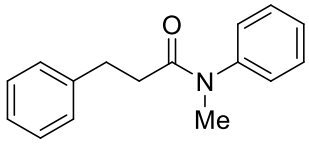

f1 (ppm)


O
N
Me

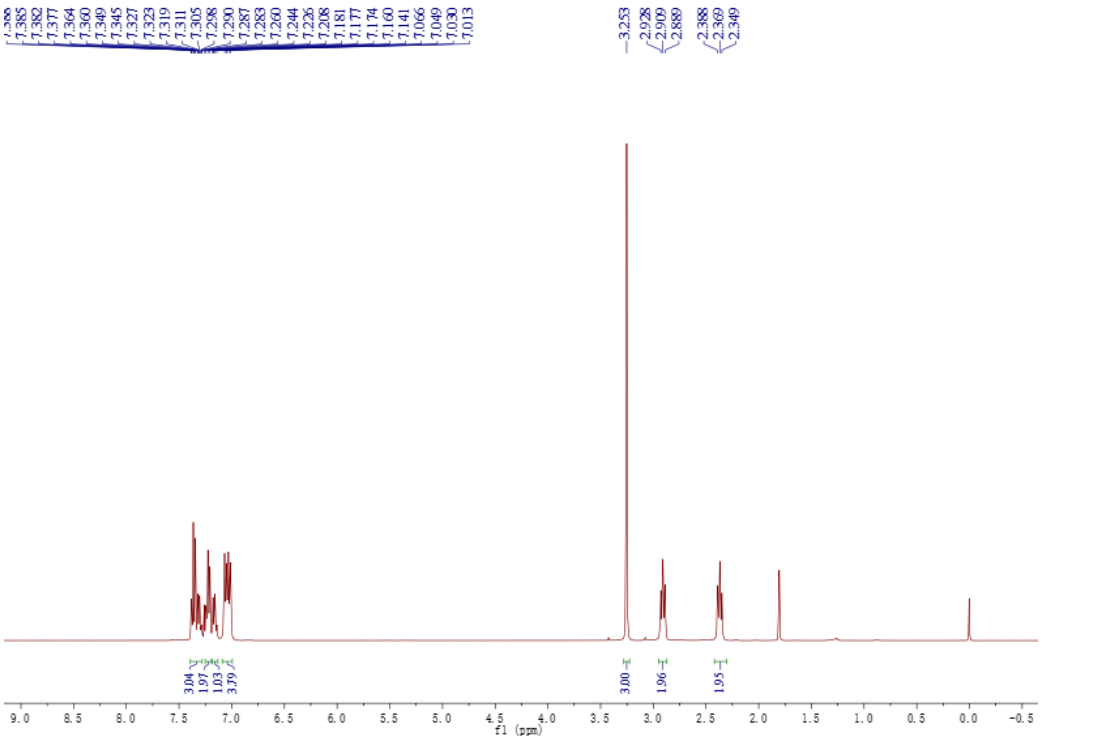
4

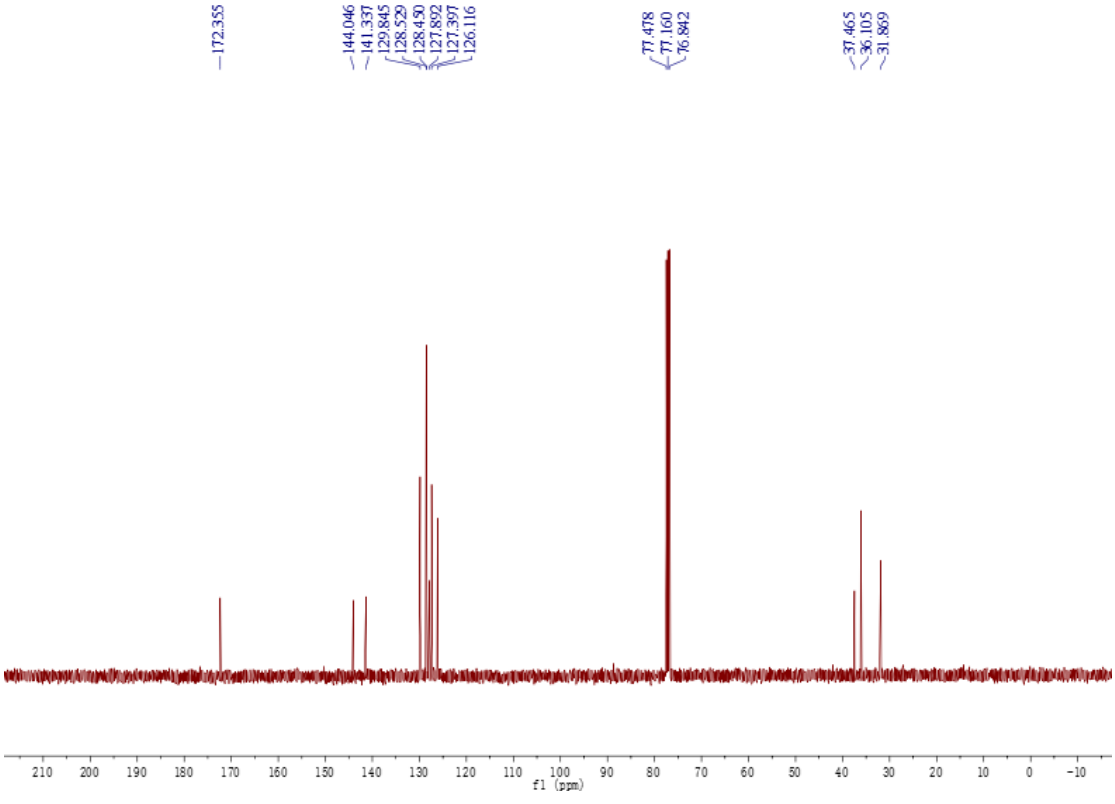

7.695
7.656
7.424
7.348
7.310
7.271
7.226
6.387
6.348
3.414
1.00
2.04
6.15
2.04
1.00
3.00
f1 (ppm)

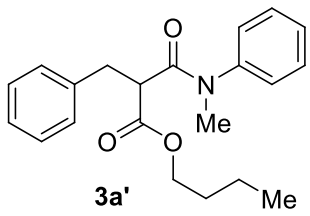

166.334
143.769
141.847
135.334
128.803
127.472
118.878
77.477
77.159
76.842
31.715
f1 (ppm)


O
N
Me

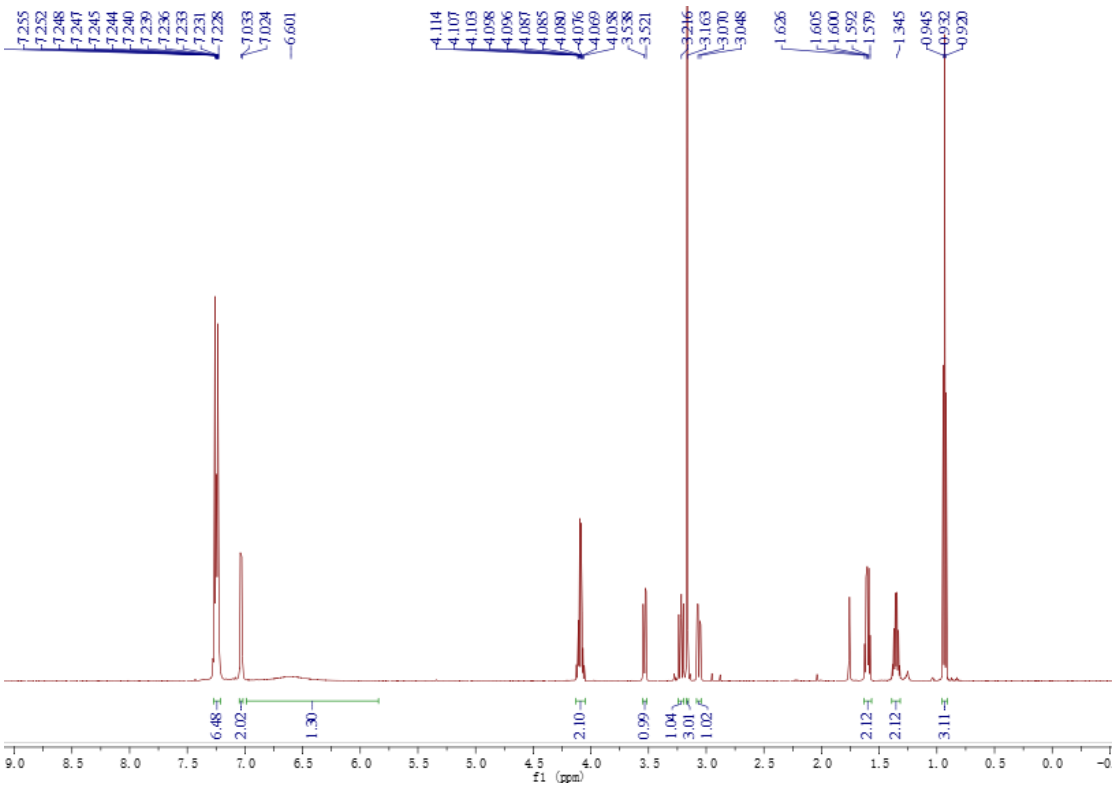
5

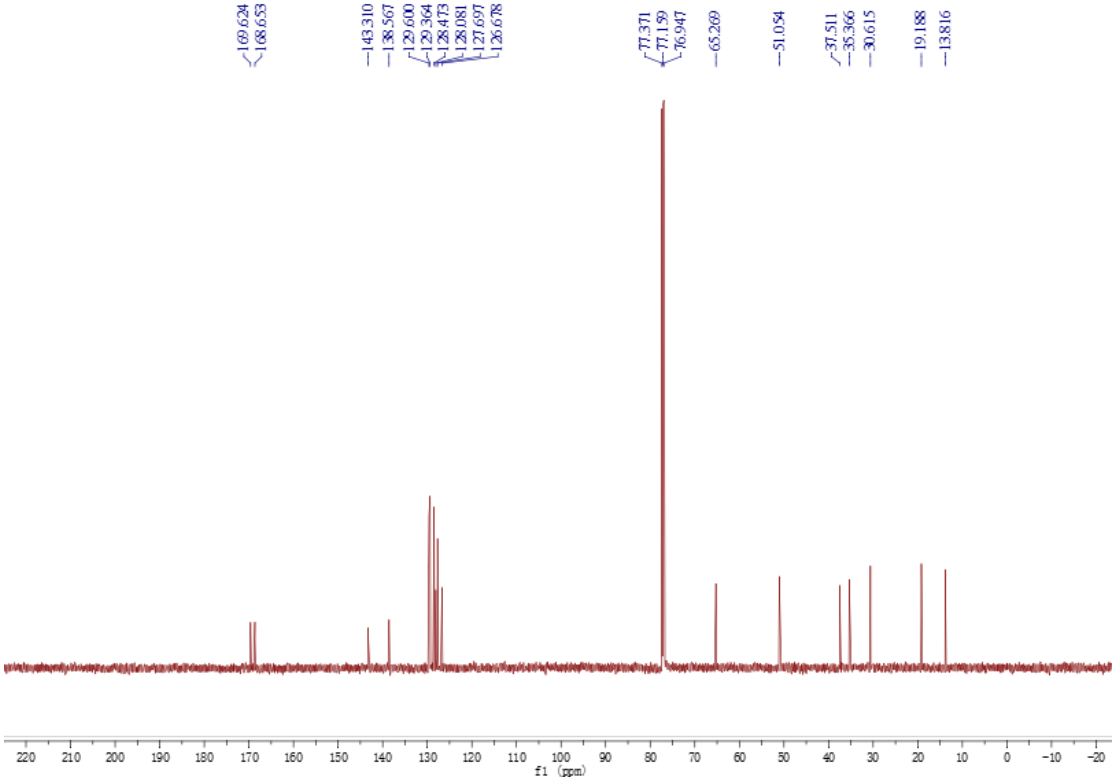

7.385
7.382
7.377
7.364
7.360
7.349
7.345
7.327
7.323
7.319
7.311
7.305
7.298
7.290
7.287
7.283
7.260
7.244
7.226
7.208
7.181
7.177
7.174
7.160
7.141
7.066
7.049
7.030
7.013
3.253
2.928
2.909
2.889
2.388
2.369
2.349
3.04
1.97
1.03
3.79
3.00
1.96
1.95
f1 (ppm)

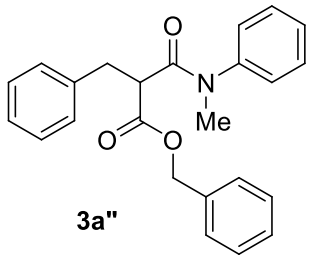

172.355
144.046
141.337
129.845
128.529
128.430
127.892
127.397
126.116
77.478
77.160
76.842
37.465
36.105
31.869
f1 (ppm)


O
N
Me
O
O
Me

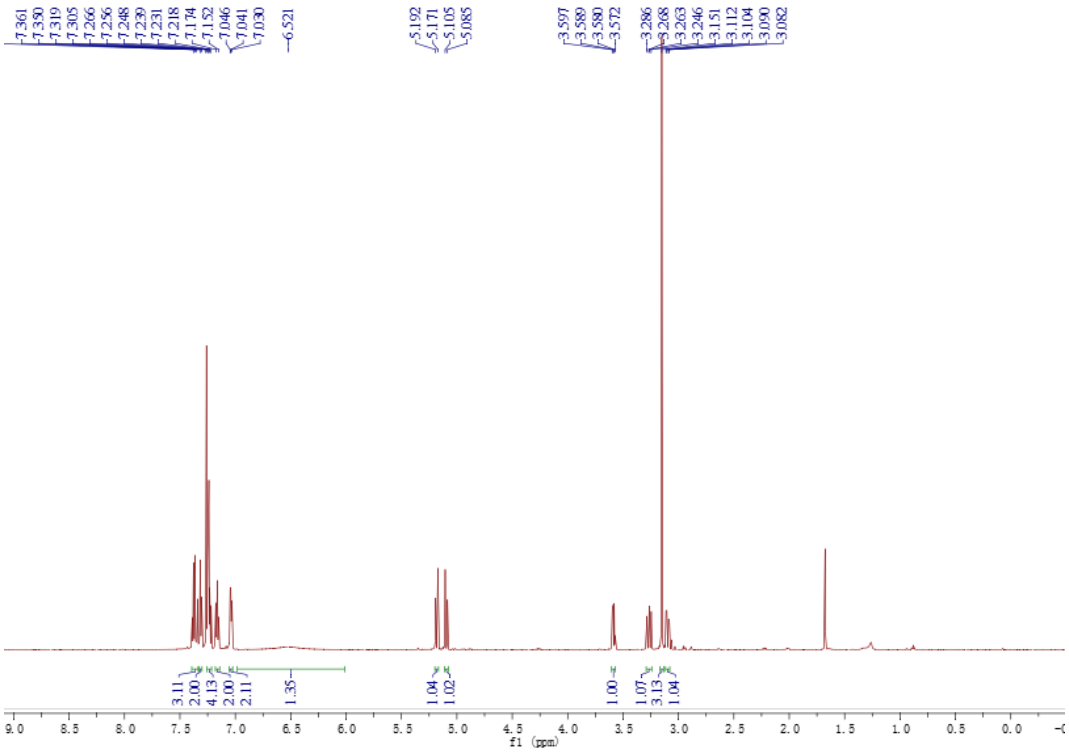
3a'

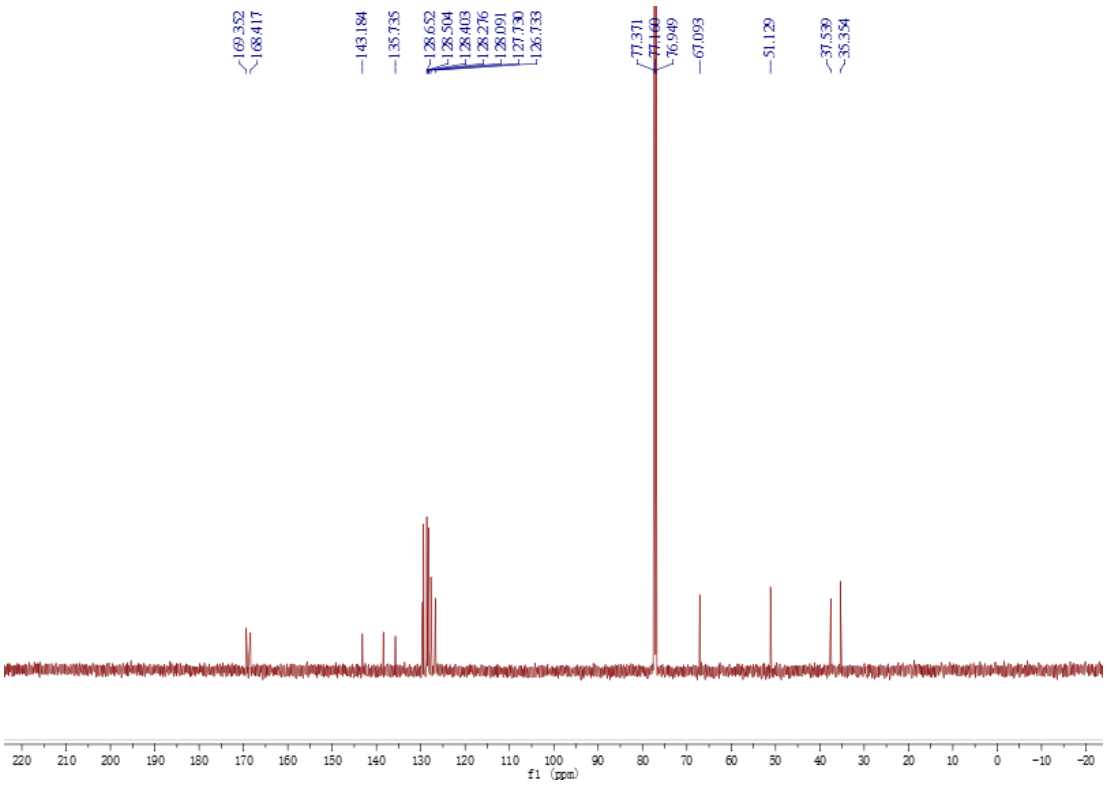

7.255
7.252
7.248
7.247
7.245
7.244
7.240
7.239
7.236
7.233
7.231
7.228
7.033
7.024
6.601
4.114
4.107
4.103
4.098
4.096
4.087
4.085
4.080
4.076
4.069
4.038
3.538
3.521
3.216
3.163
3.070
3.048
1.626
1.605
1.600
1.592
1.579
1.345
0.945
0.932
0.920
6.48
2.02
1.30
2.10
0.99
1.04
3.01
1.02
2.12
2.12
3.11
f1 (ppm)

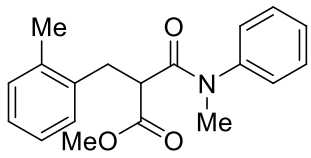

169.624
168.653
143.310
138.567
129.600
129.364
128.473
128.081
127.697
126.678
77.371
77.159
76.947
65.269
51.054
37.511
35.366
30.615
19.188
13.816
f1 (ppm)


O
N
Me
O
O

3a"


7.361
7.350
7.319
7.305
7.266
7.256
7.248
7.239
7.231
7.218
7.174
7.152
7.046
7.041
7.030
6.521
5.192
5.171
5.105
5.085
3.597
3.589
3.580
3.572
3.286
3.268
3.263
3.246
3.151
3.112
3.104
3.090
3.082
3.11
2.00
4.13
2.00
2.11
1.35
1.04
1.02
1.00
1.07
3.13
1.04
f1 (ppm)

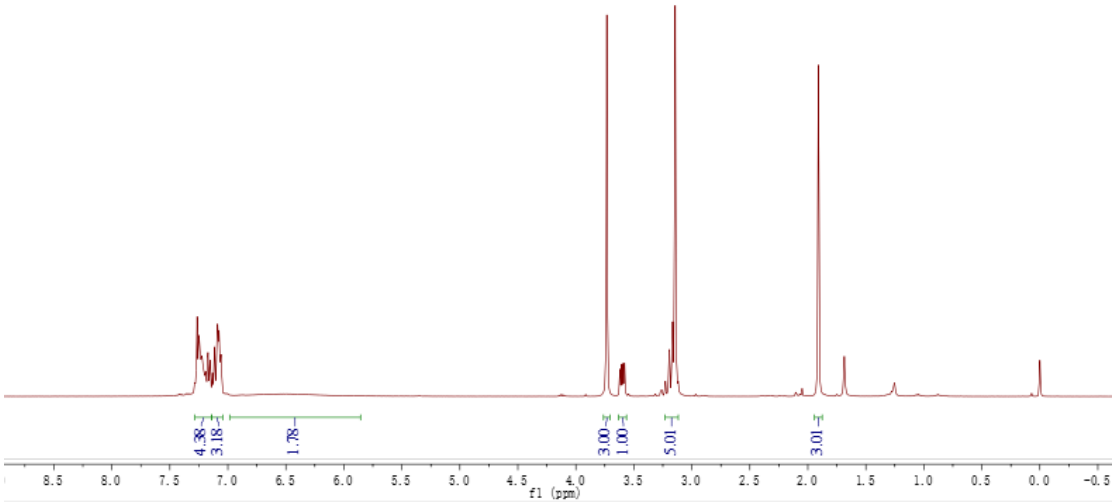

169.352
168.417
143.184
135.735
128.652
128.504
128.403
128.276
128.091
127.730
126.733
77.371
77.160
76.949
67.093
51.129
37.539
35.354
f1 (ppm)


Me
O
N
Me
MeO
O

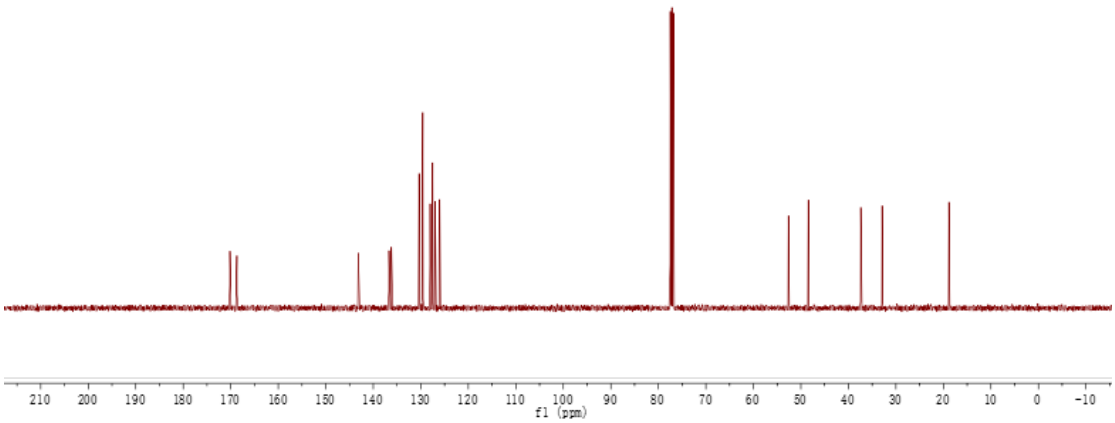
3b

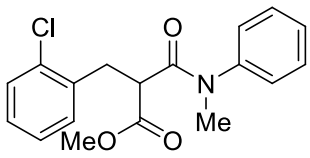

7.284
7.265
7.230
7.224
7.192
7.171
7.153
7.133
7.114
7.096
7.090
7.086
7.077
7.059
6.494


3.734
3.619
3.606
3.593
3.581
3.228
3.202
3.194
3.168
3.164
3.152
3.143
3.117
1.909

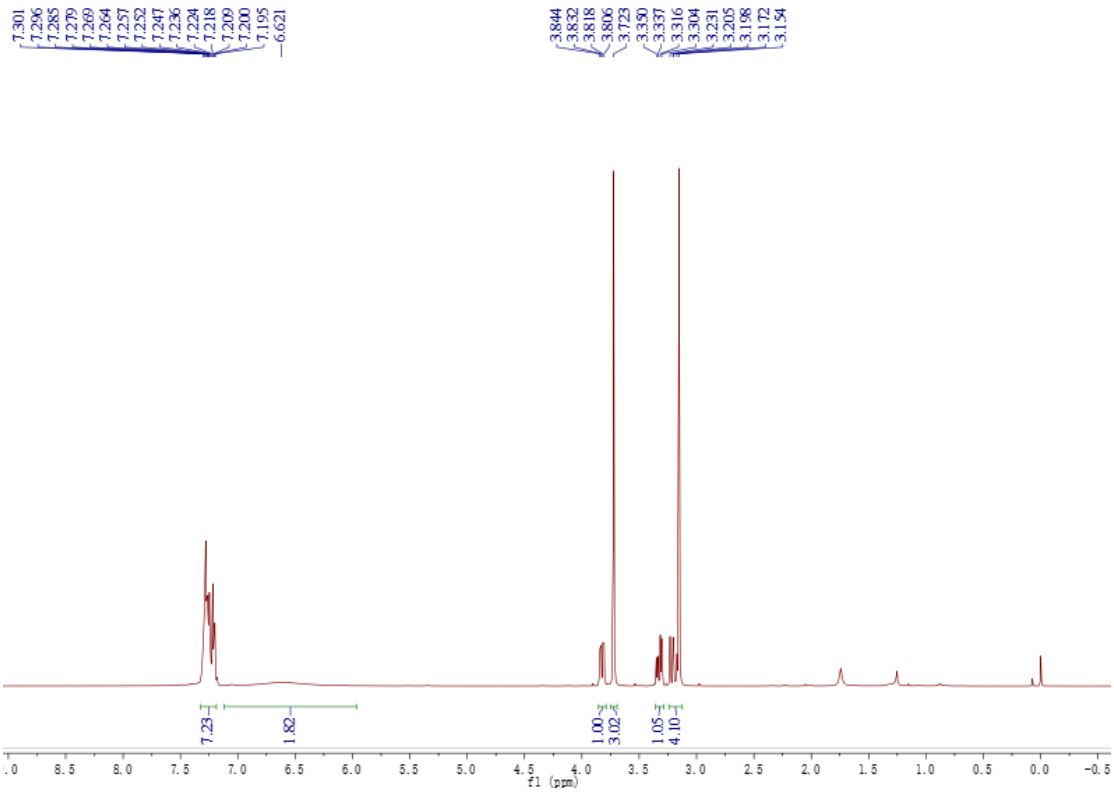

4.38
3.18
1.78
3.00
1.00
5.01
3.01
f1 (ppm)

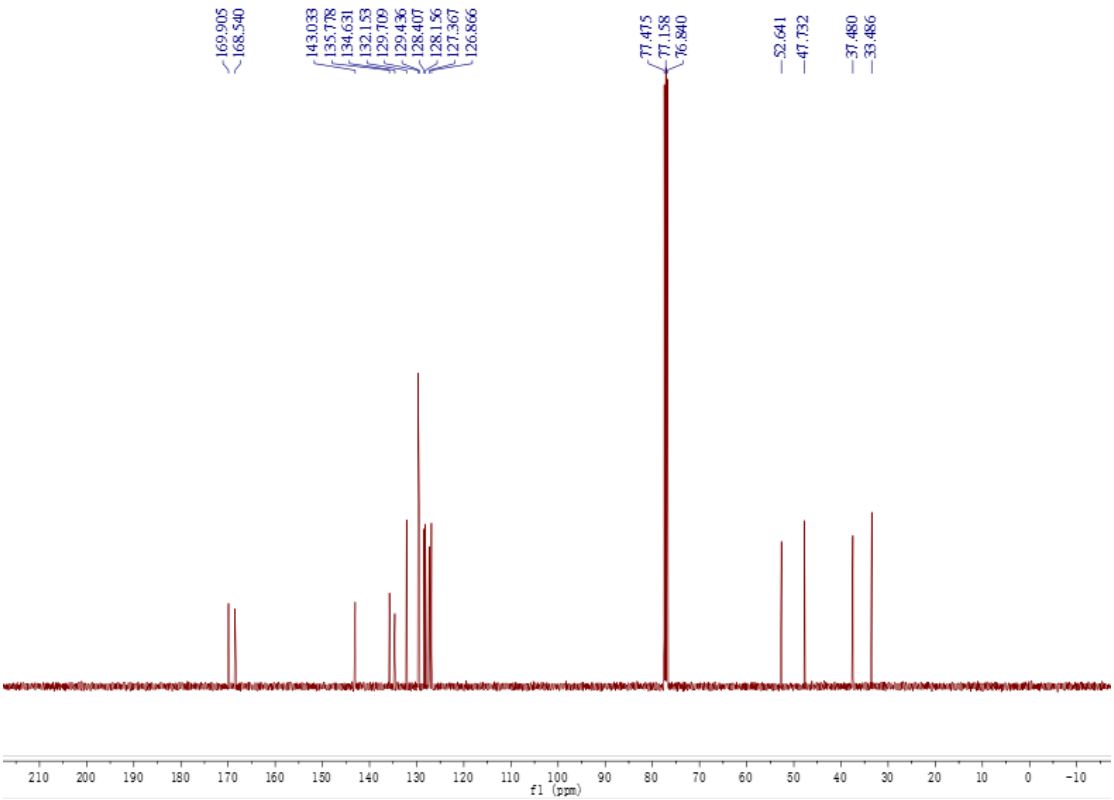

170.184
168.708
143.169
136.696
136.185
130.371
130.359
129.571
128.025
127.508
126.973
126.023
77.476
77.158
76.840
52.620
48.432
37.403
32.906
18.852

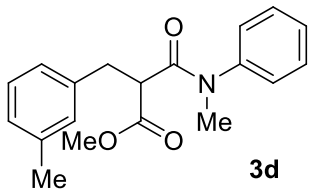

f1 (ppm)


Cl
O
N
Me
MeO
O

3c


7.301
7.296
7.285
7.279
7.269
7.264
7.257
7.252
7.247
7.236
7.224
7.218
7.209
7.200
7.195
6.621
3.844
3.832
3.818
3.806
3.723
3.350
3.337
3.316
3.304
3.231
3.205
3.198
3.172
3.154
7.23
1.82
1.00
3.02
1.05
4.10
f1 (ppm)

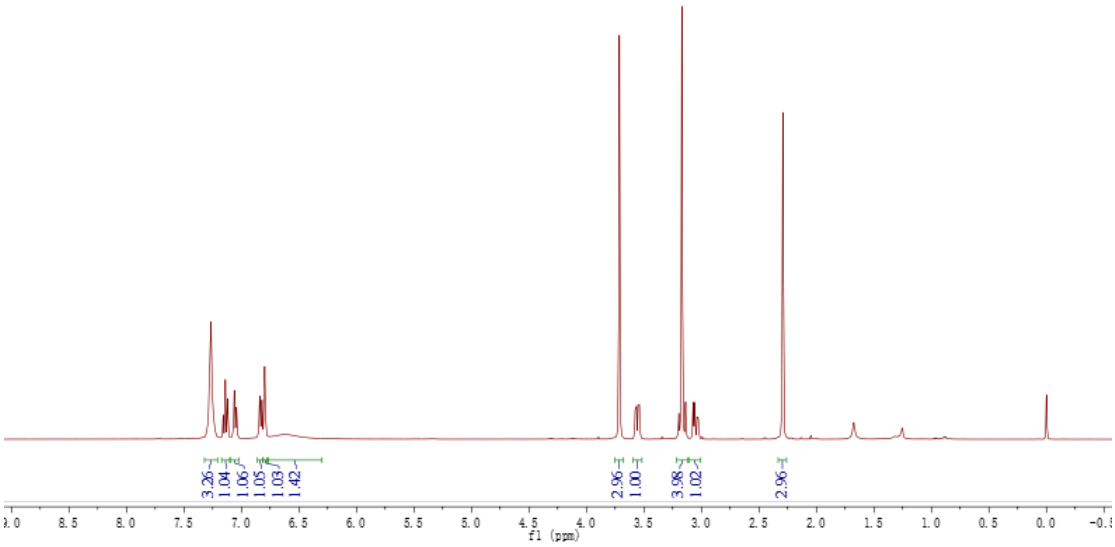

169.905
168.540
143.033
135.778
134.631
132.153
129.709
129.436
128.407
128.156
127.367
126.866
77.475
77.158
76.840
52.641
47.732
37.480
33.486
f1 (ppm)

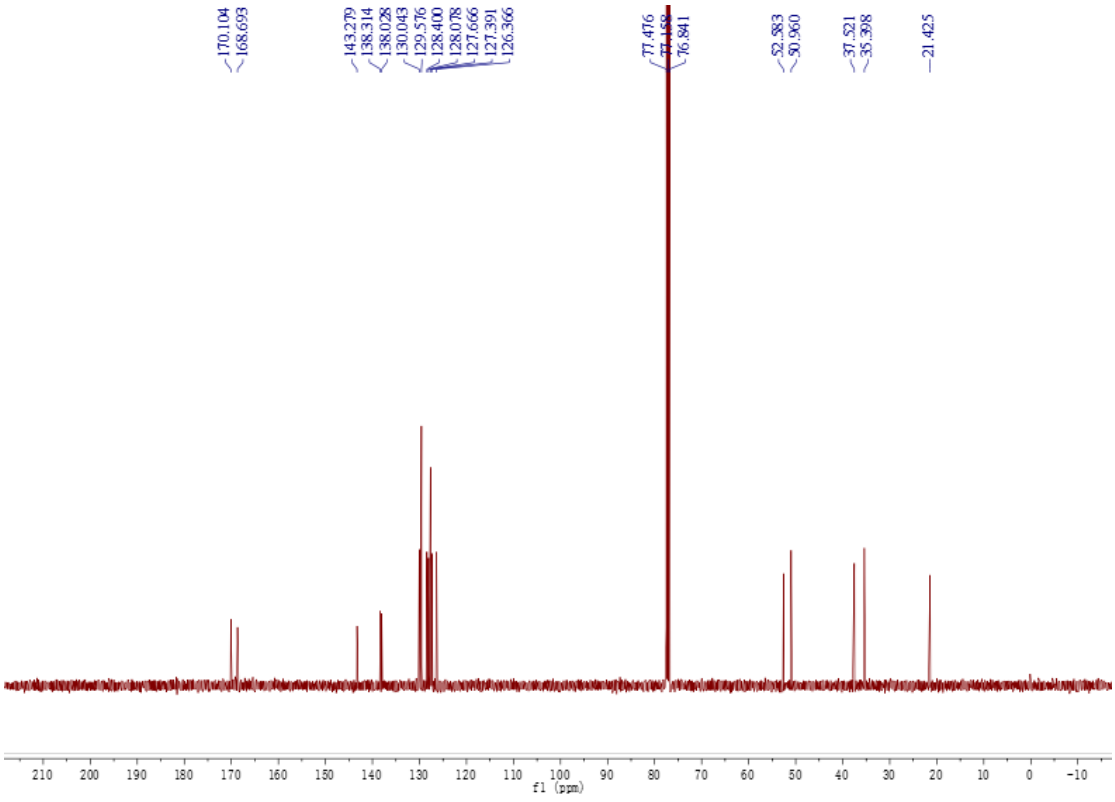

O
N
Me
MeO
O
Me

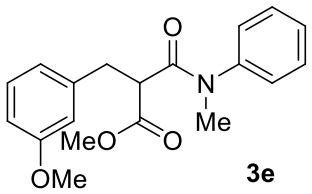
3d


7.295
7.295
7.285
7.276
7.271
7.265
7.255
7.241
7.158
7.140
7.121
7.062
7.043
6.841
6.822
6.798
6.601

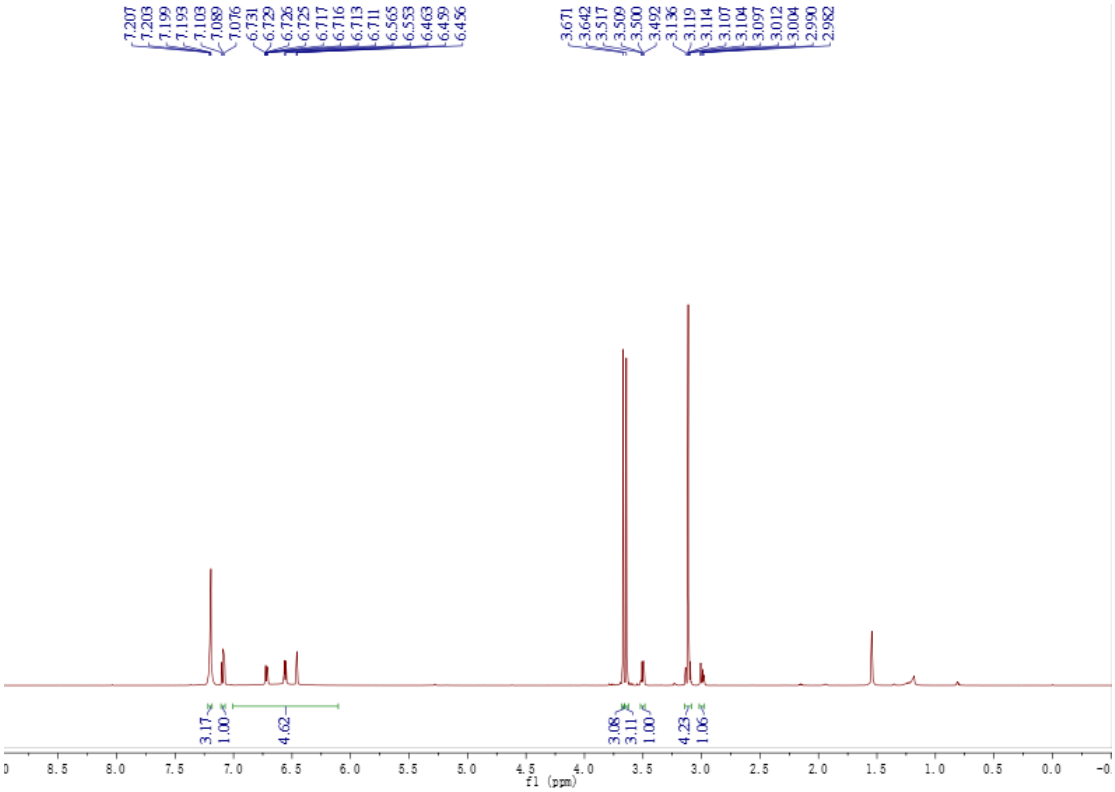

3.714
3.577
3.564
3.551
3.539
3.197
3.171
3.138
3.072
3.059
3.039
3.026
2.292


3.26
1.04
1.06
1.05
1.03
1.42
2.96
1.00
3.98
1.02
2.96
f1 (ppm)


170.104
168.693
143.279
138.314
138.028
130.043
129.576
128.400
128.078
127.666
127.391
126.366
77.476
77.158
76.841
52.583
50.960
37.521
35.398
21.425
f1 (ppm)


O
N
Me
MeO
O
OMe

3e


7.207
7.203
7.199
7.193
7.103
7.089
7.076
6.731
6.729
6.726
6.725
6.717
6.716
6.713
6.711
6.565
6.553
6.463
6.459
6.456
3.671
3.642
3.517
3.509
3.500
3.492
3.136
3.119
3.114
3.107
3.104
3.097
3.012
3.004
2.990
2.982
3.17
1.00
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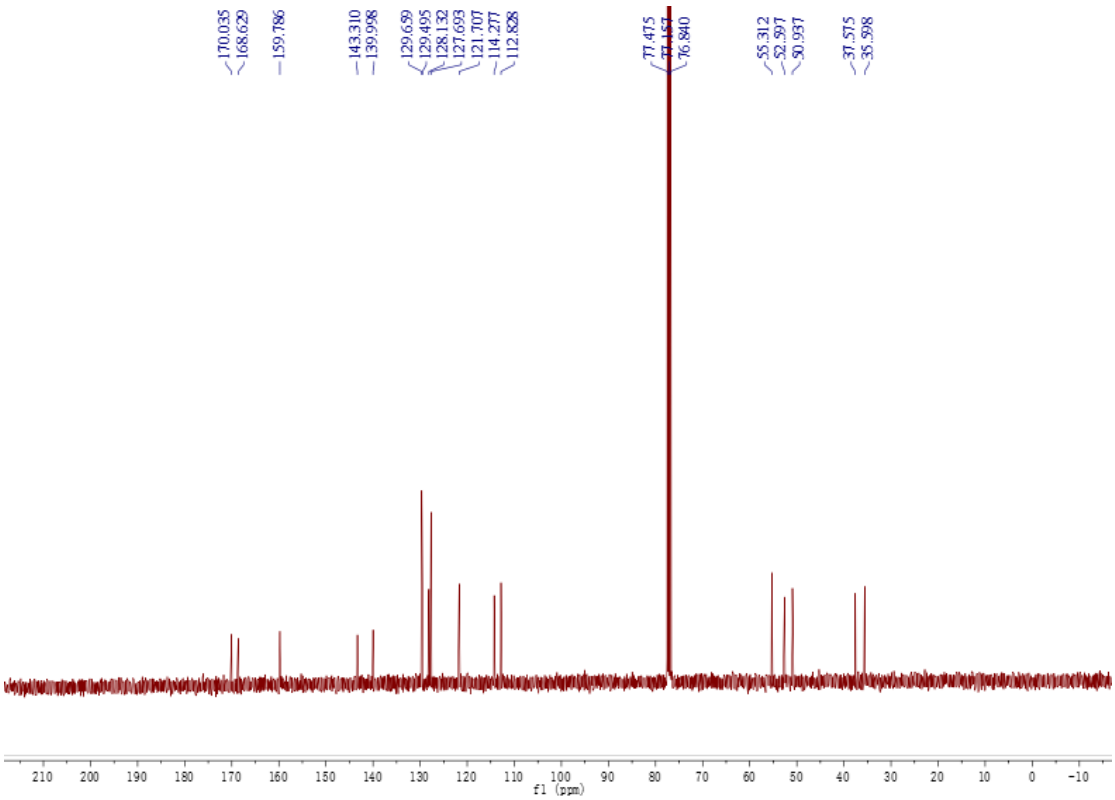
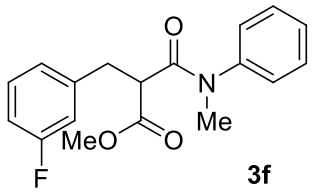
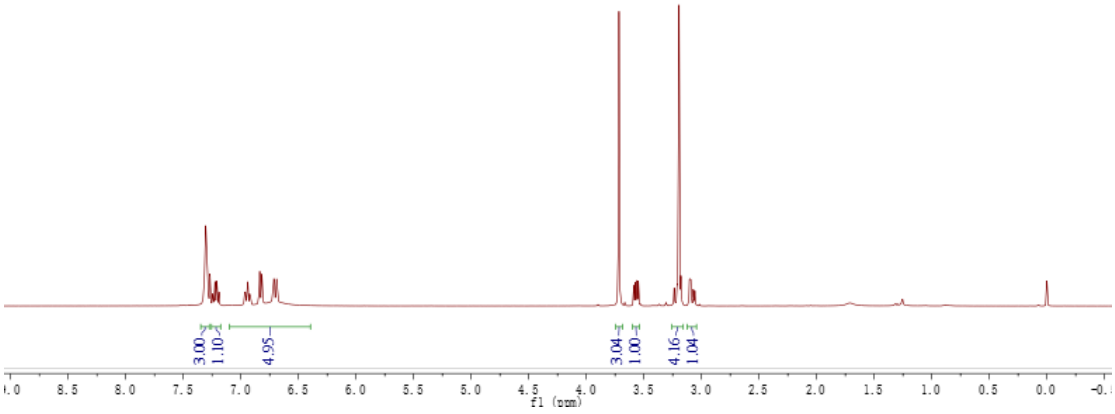
3.08
3.11
1.00
4.23
1.06
f1 (ppm)


170.035
168.629
159.786
143.310
139.998
129.689
129.495
128.132
127.693
121.707
114.277
112.828
77.475
77.157
76.840
55.312
52.597
50.937
37.575
35.998
f1 (ppm)


O
N
Me
MeO
O
F

3f


7.305
7.297
7.269
7.245
7.225
7.209
7.190
6.966
6.961
6.945
6.940
6.924
6.918
6.837
6.818
6.714
6.689
3.716
3.587
3.574
3.561
3.549
3.237
3.211
3.203
3.194
3.179
3.104
3.091
3.071
3.058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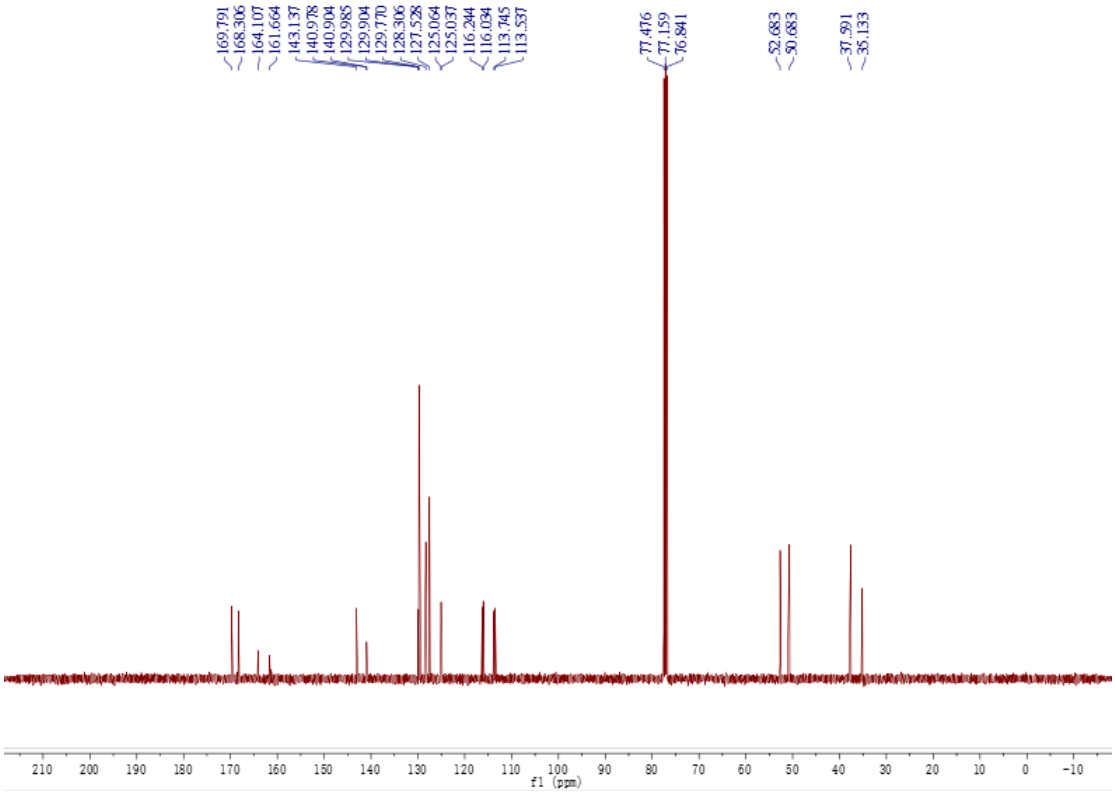
1.10
4.95
3.04
1.00
4.16
1.04
f1 (ppm)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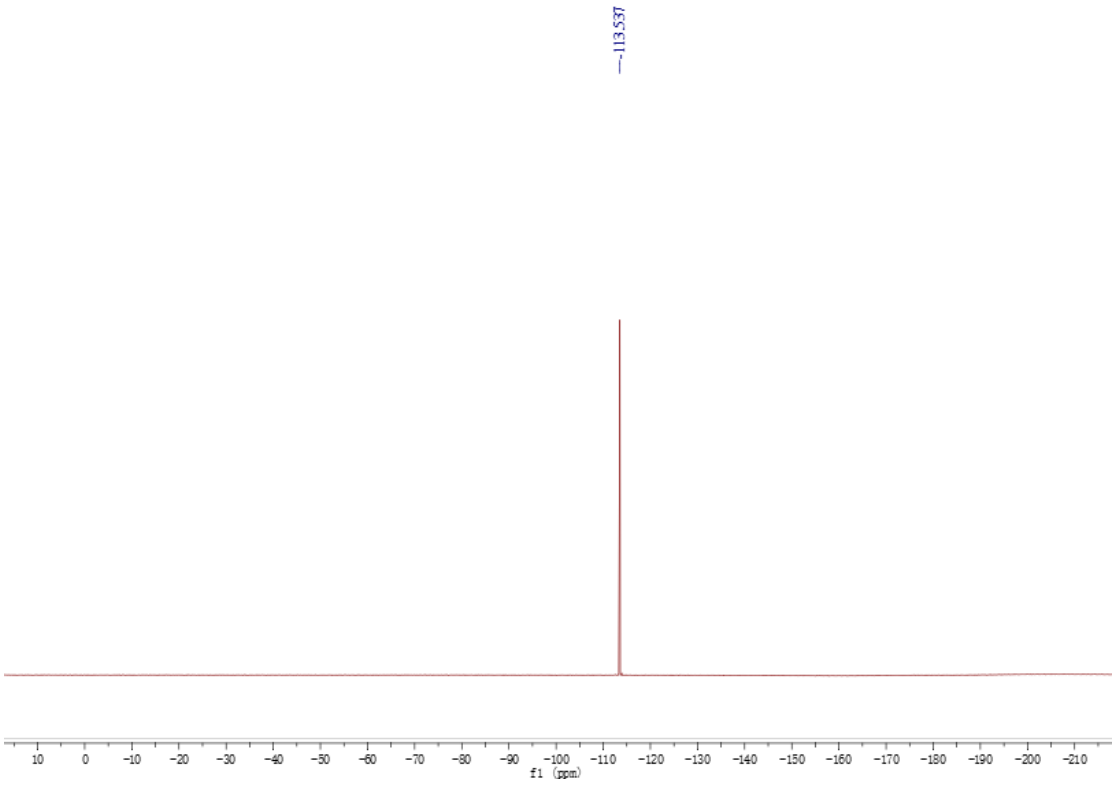
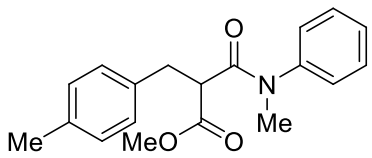
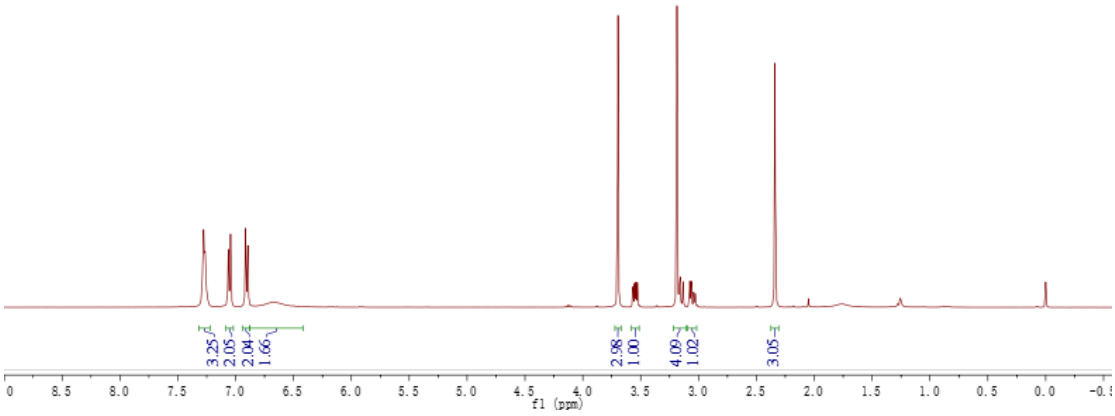
168.306
164.107
161.664
143.137
140.978
140.904
129.985
129.904
129.770
128.306
127.528
125.064
125.037
116.244
116.034
113.745
113.537
77.476
77.159
76.841
52.683
50.683
37.591
35.133
f1 (ppm)


-113.537
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
N
Me
Me
MeO
O

3g


7.290
7.282
7.276
7.266
7.252
7.063
7.044
6.914
6.895
6.669
3.696
3.566
3.553
3.542
3.528
3.187
3.168
3.159
3.134
3.076
3.062
2.340


3.25
2.05
2.04
1.66
2.98
1.00
4.09
1.02
3.05
f1 (ppm)


170.102
168.688

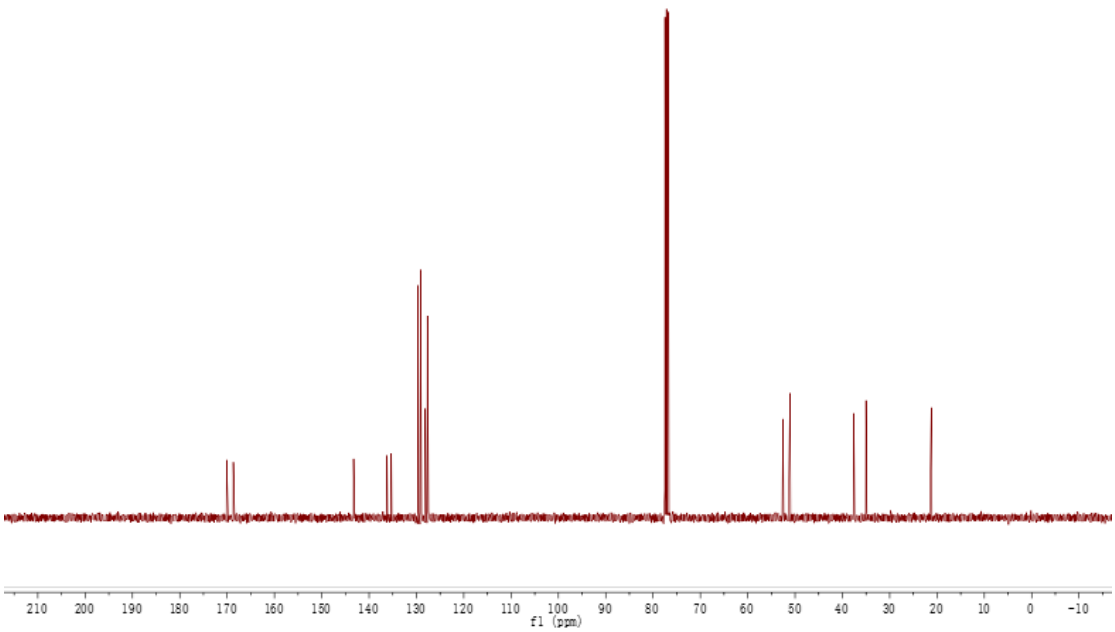
143.275
136.206
135.302
129.668
129.177
129.117
128.121
127.672

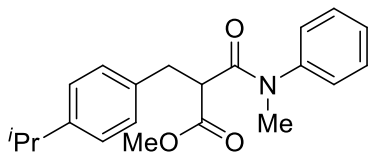

77.477
77.158
76.840


52.548
51.055


37.584
35.017

21.208

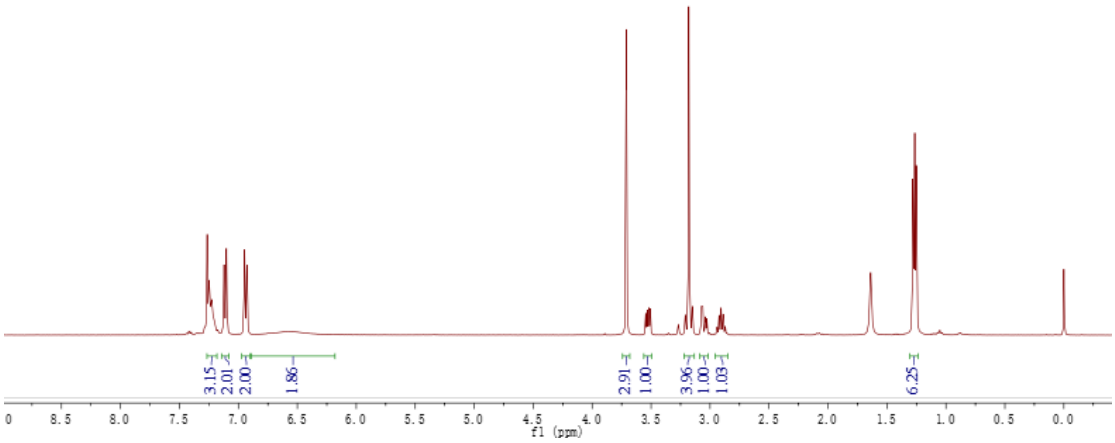

f1 (ppm)


O
N
Me
iPr
MeO
O

3h


7.265
7.249
7.226
7.204
7.122
7.102
6.948
6.928
6.563


3.711
3.545
3.533
3.520
3.508
3.210
3.181
3.151
3.074
3.062
3.040
3.028
2.958
2.941
2.924
2.906
2.889
2.872
2.855
1.281
1.269
1.264
1.252


3.15
2.01
2.00
1.86
2.91
1.00
3.06
1.00
1.03
6.25
f1 (ppm)


170.120
168.791

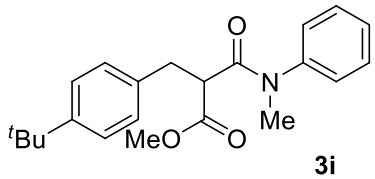
147.487
143.284
135.804
129.616
129.288
128.064
127.607
126.523


77.475
77.157
76.840

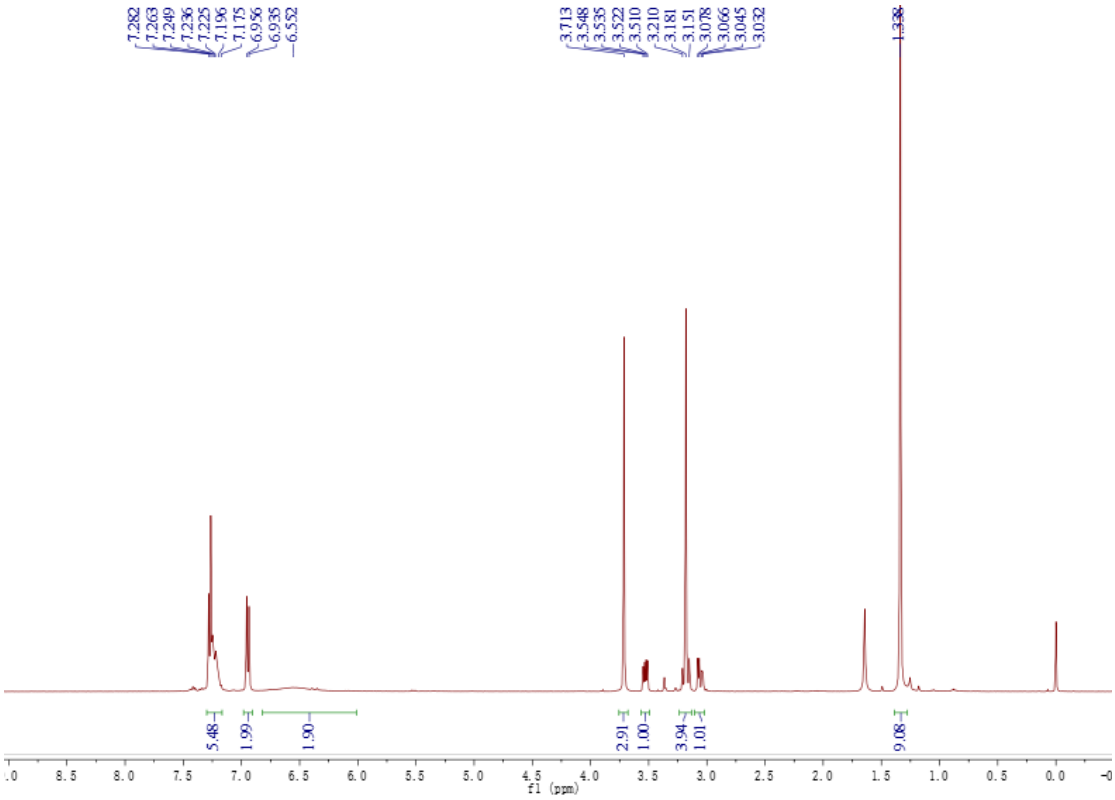

52.583
51.107

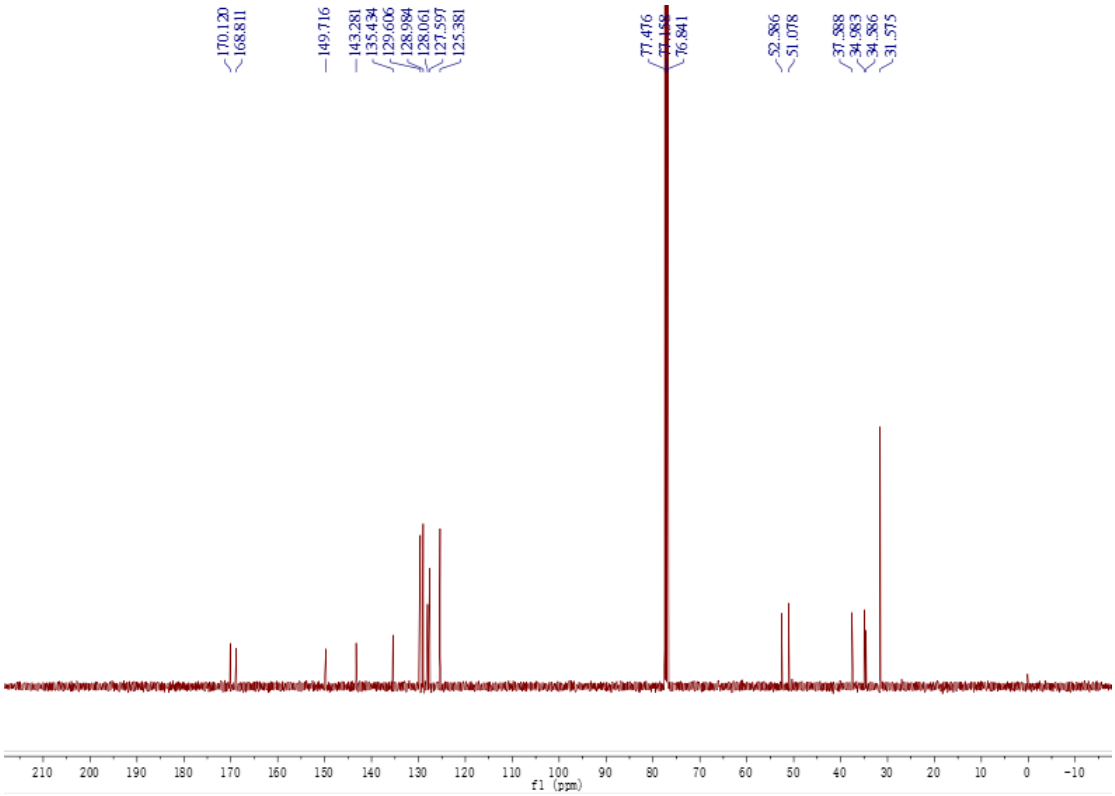

37.586
35.101
33.953
24.408
24.224

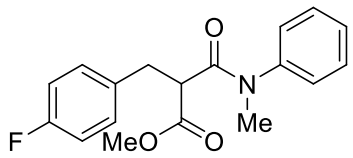
f1 (ppm)


O
N
Me
tBu
MeO
O

3i


7.282
7.263
7.249
7.236
7.225
7.196
7.175
6.956
6.935
6.552
3.713
3.548
3.535
3.522
3.510
3.210
3.181
3.151
3.078
3.066
3.045
3.032
1.388
5.48
1.99
1.90
2.91
1.00
3.94
1.01
9.08
f1 (ppm)

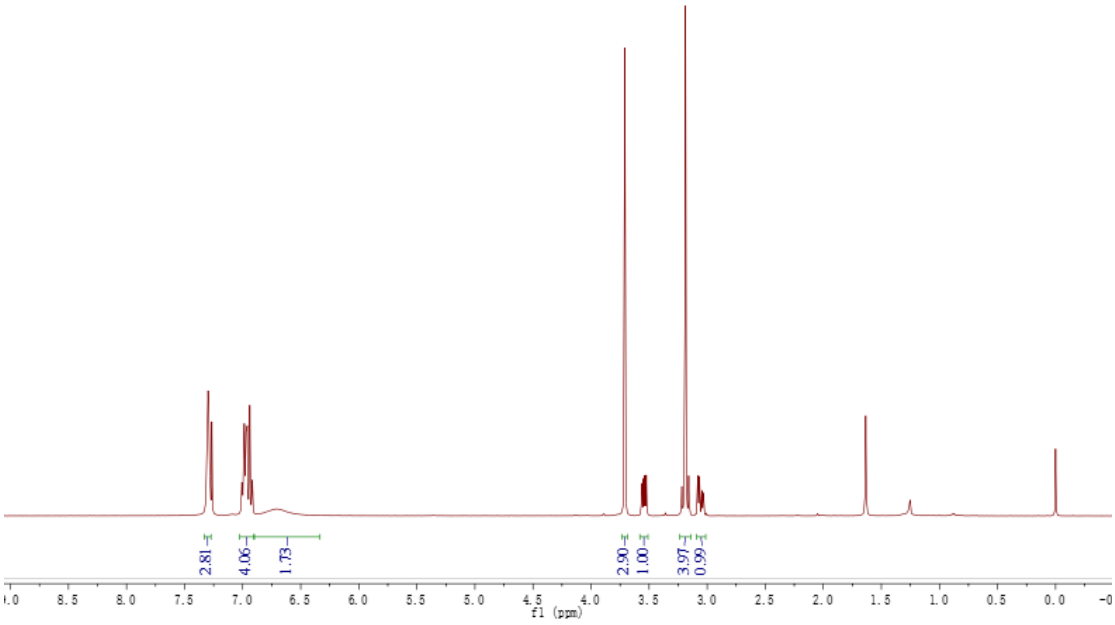

170.120
168.811
149.716
143.281
135.434
129.606
128.984
128.061
127.597
125.381
77.476
77.158
76.841
52.386
51.078
37.588
34.983
34.386
31.575
f1 (ppm)

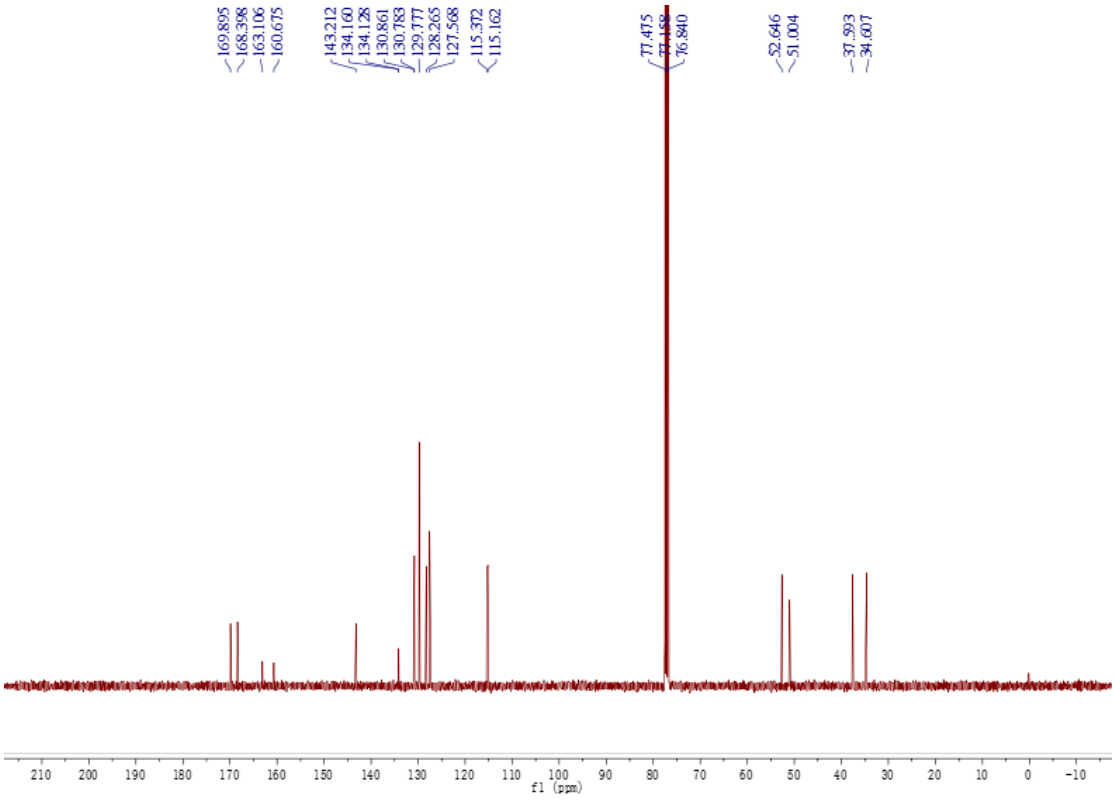

O
N
Me
F
MeO
O

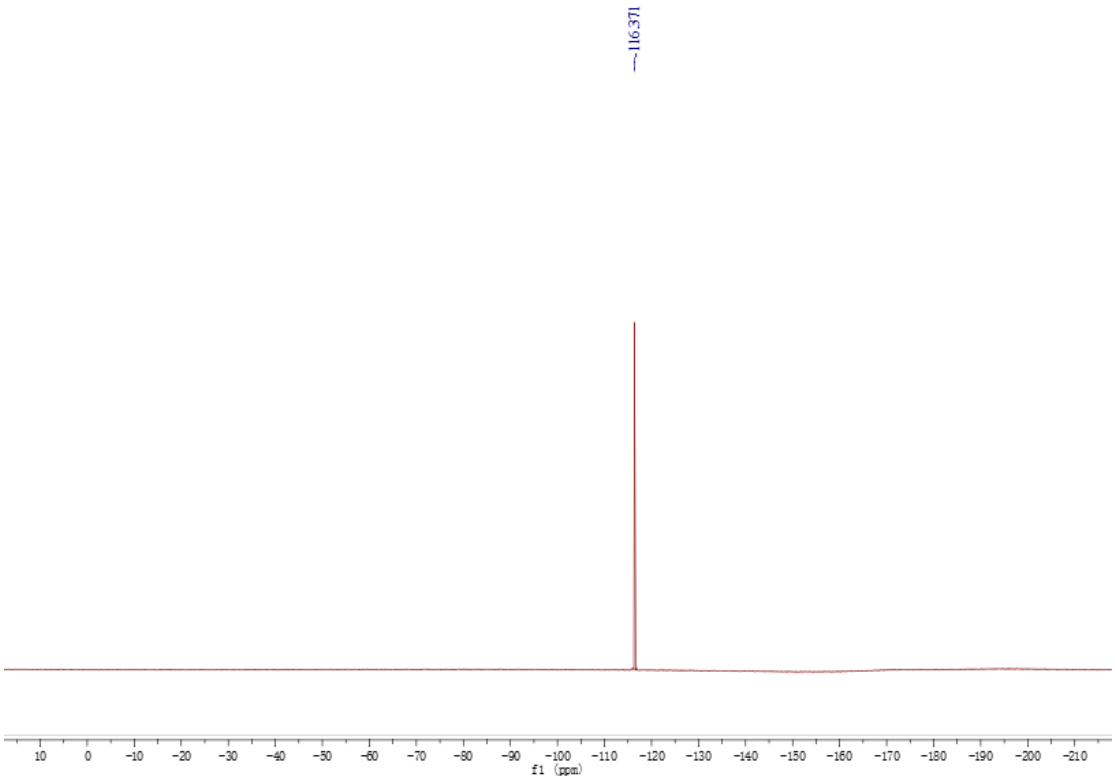
3j

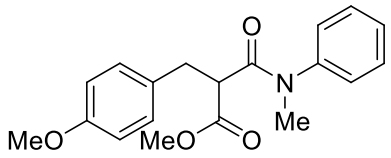

7.311
7.304
7.298
7.290
7.279
7.266
7.007
6.992
6.985
6.971
6.960
6.939
6.917
6.710


3.710
3.562
3.590
3.537
3.524
3.218
3.188
3.159
3.080
3.067
3.046
3.034


2.81
4.06
1.73
2.90
1.00
3.97
0.99
f1 (ppm)


169.895
168.398
163.106
160.675
143.212
134.160
134.128
130.861
130.783
129.777
128.265
127.568
115.372
115.162
77.475
77.158
76.840
52.646
51.004
37.593
34.607
f1 (ppm)

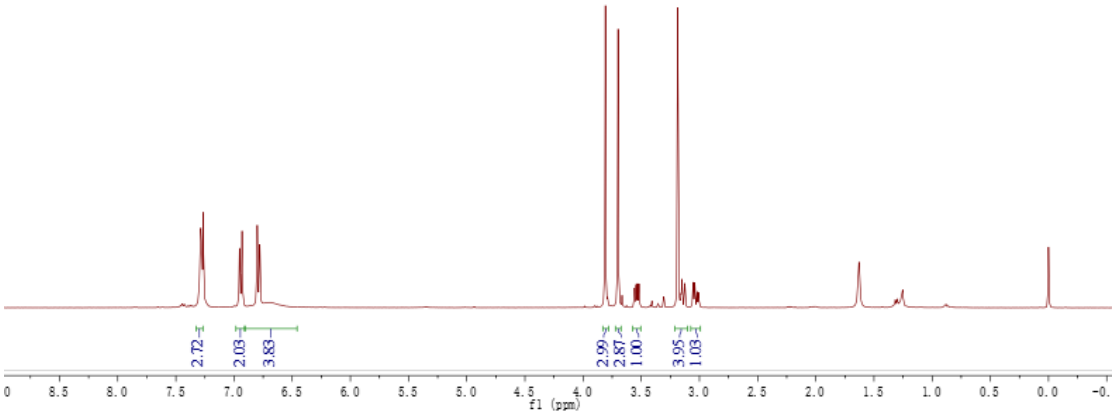

-116.371
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

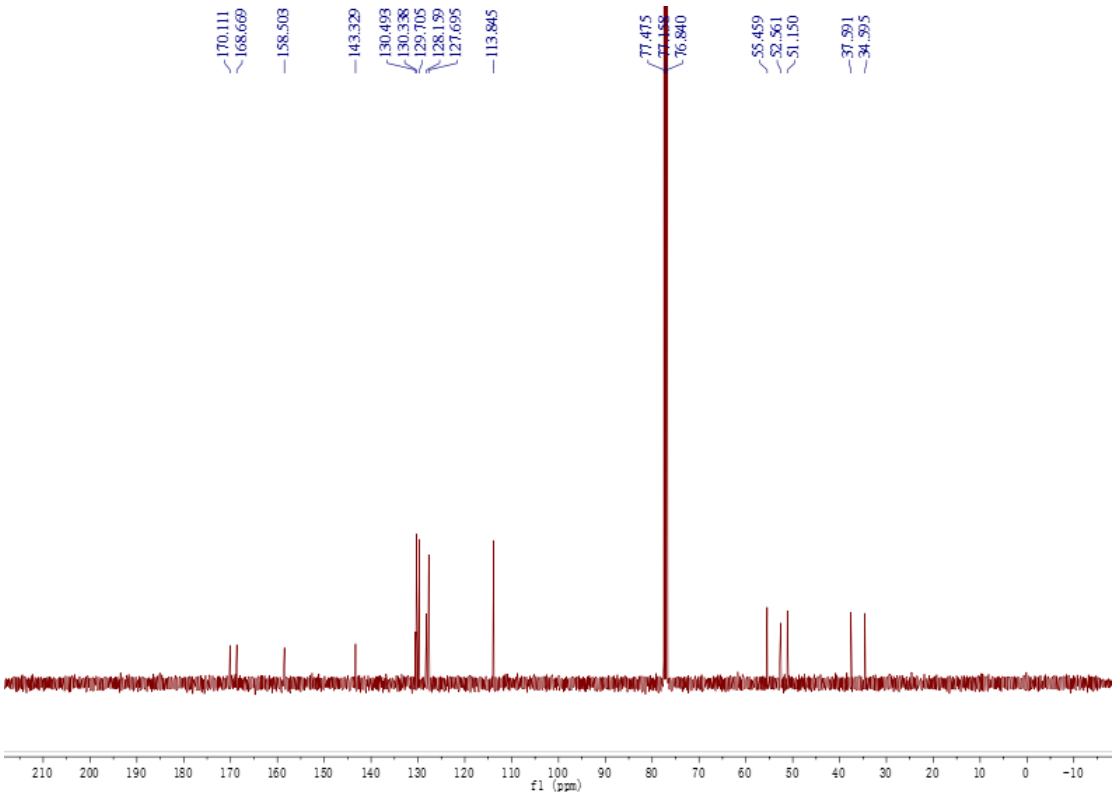

O
N
Me
MeO
MeO
O

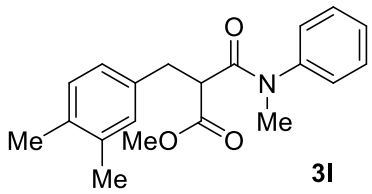
3k


7.290
7.287
7.285
7.277
7.265
6.953
6.932
6.800
6.779
6.689


3.809
3.700
3.558
3.545
3.533
3.520
3.187
3.159
3.151
3.126
3.054
3.041
3.020
3.007


2.72
2.03
3.83
2.99
2.87
1.00
3.95
1.03
f1 (ppm)

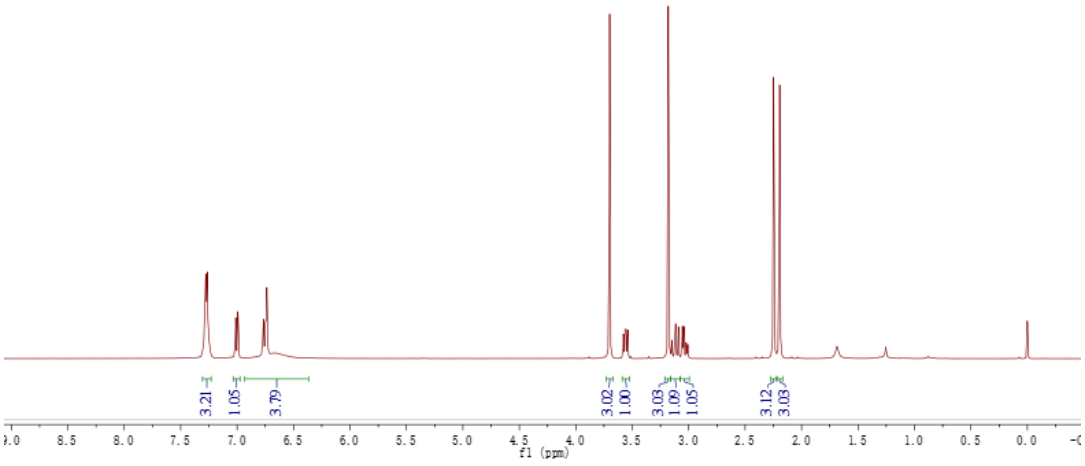

170.111
168.669
158.503
143.329
130.493
130.338
129.705
128.159
127.695
113.845
77.475
77.158
76.840
55.459
52.561
51.150
37.991
34.995
f1 (ppm)

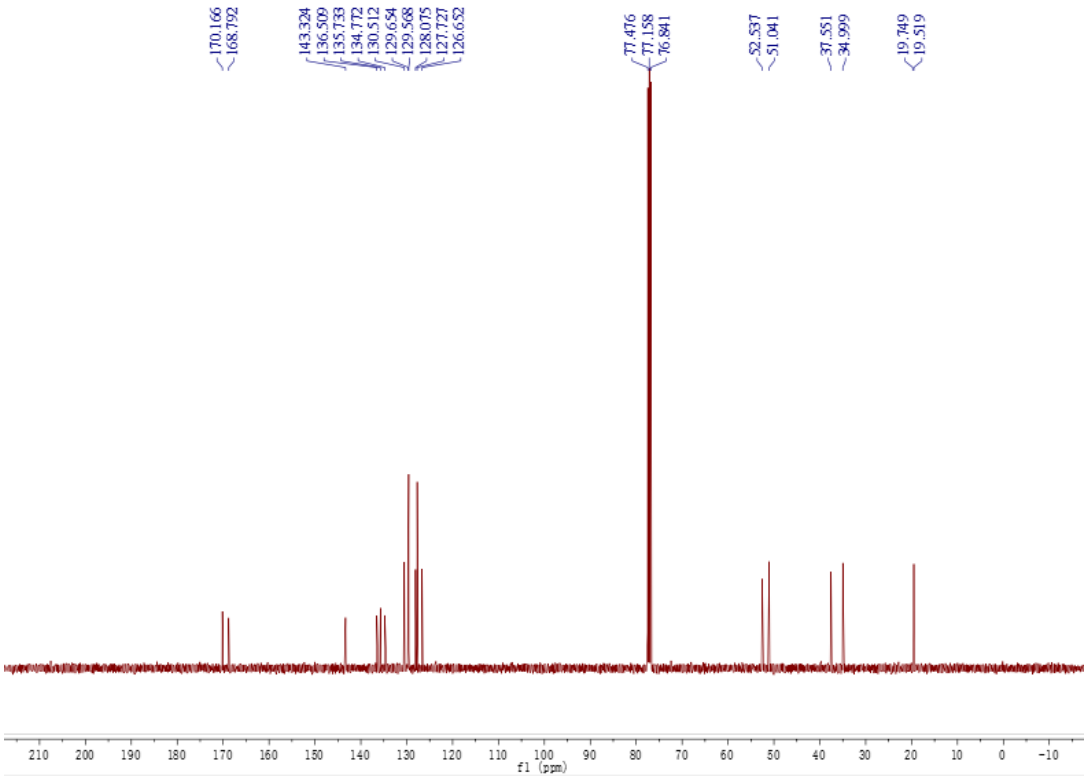

O
N
Me
Me
MeO
O
Me

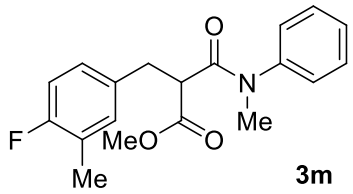
3l


7.291
7.283
7.277
7.272
7.264
7.248
7.239
7.012
6.993
6.766
6.746
6.737
6.665


3.700
3.578
3.564
3.554
3.540
3.181
3.149
3.125
3.116
3.092
3.056
3.042
3.022
3.009
2.248
2.194


3.21
1.05
3.79
3.02
1.00
3.03
1.09
1.05
3.12
3.03
f1 (ppm)

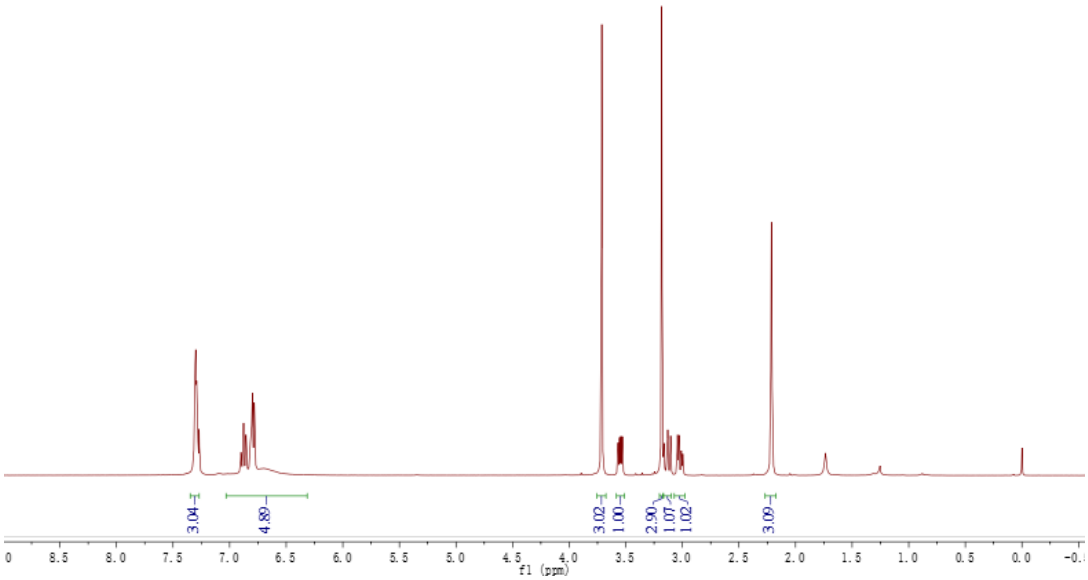

170.166
168.792
143.324
136.500
135.733
134.772
130.512
129.654
129.568
128.075
127.727
126.652
77.476
77.158
76.841
52.537
51.041
37.551
34.999
19.749
19.519
f1 (ppm)


O
N
Me
F
MeO
O
Me

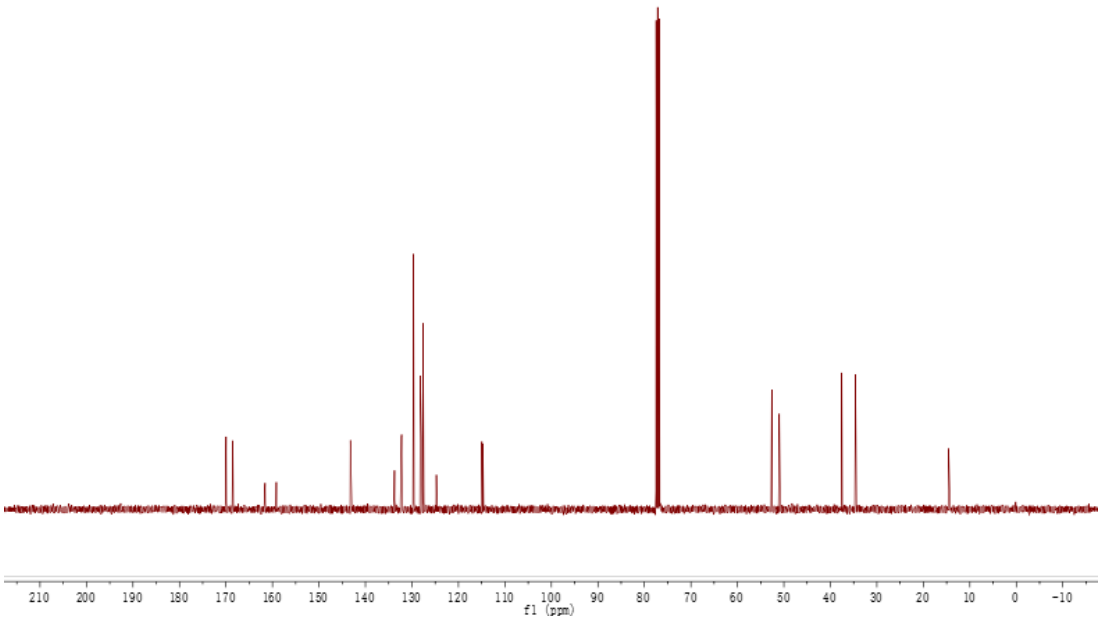
3m

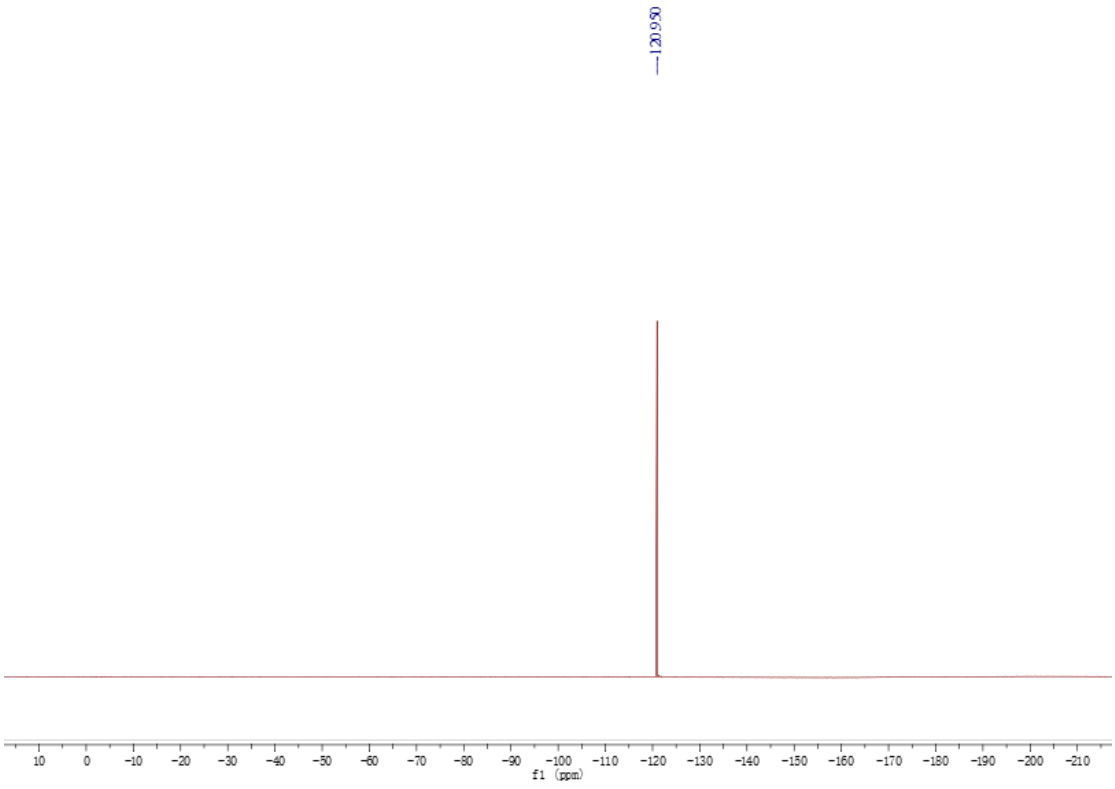

7.306
7.300
7.291
7.279
7.270
6.900
6.877
6.855
6.820
6.815
6.802
6.797
6.782
6.697

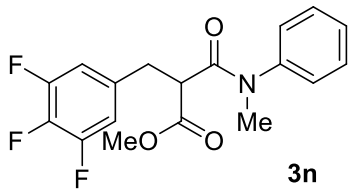

3.713
3.568
3.555
3.543
3.530
3.182
3.163
3.138
3.129
3.104
3.043
3.030
3.009
2.996
2.214


3.04
4.89
3.02
1.00
2.90
1.07
1.02
3.09
f1 (ppm)

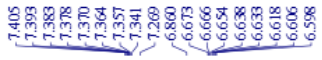

169.958
168.522
161.578
159.160
143.231
133.785
133.749
132.269
132.218
129.654
128.193
128.049
127.970
127.596
124.744
124.573
114.943
114.724
77.476
77.158
76.840
52.610
50.983
37.541
34.600
14.554
14.519


f1 (ppm)

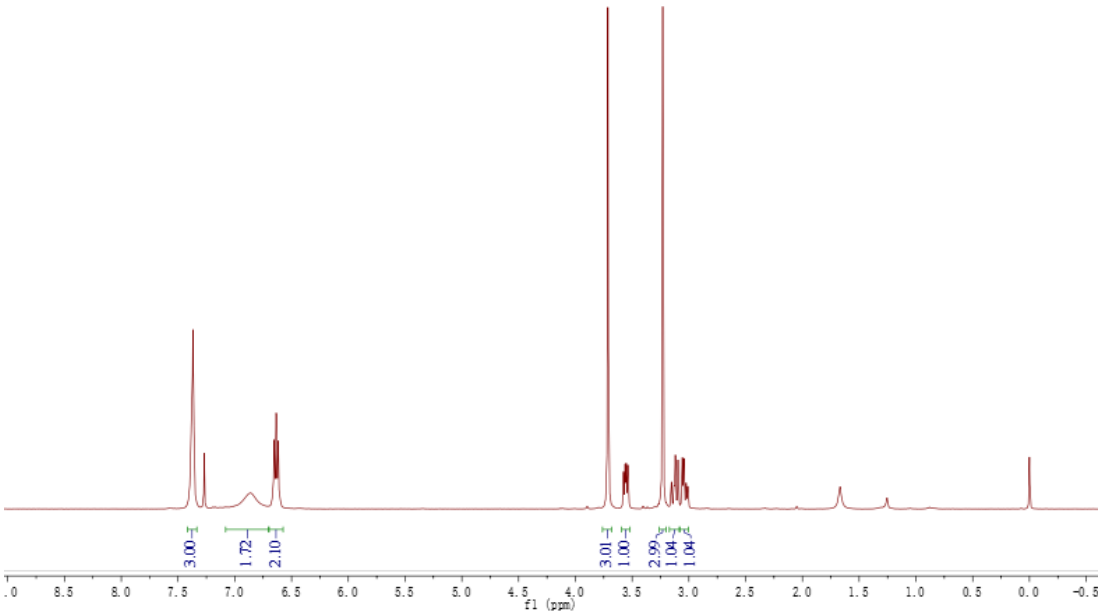

-120.950
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

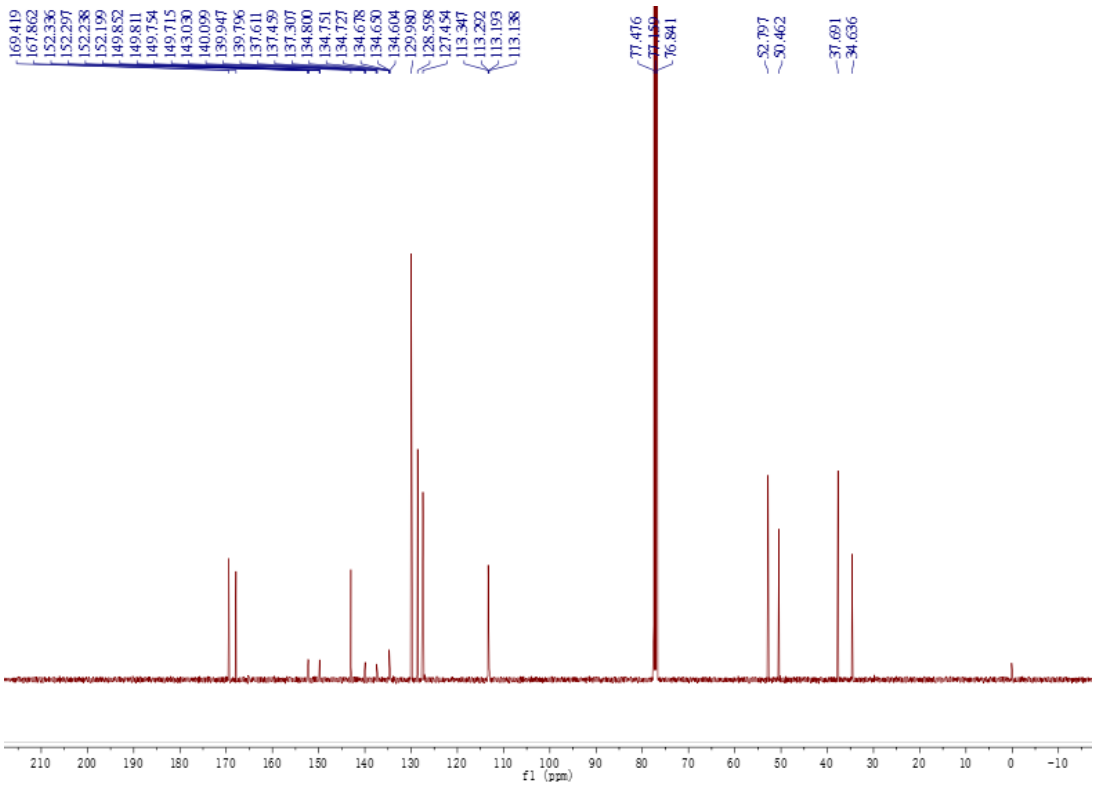

O
F
N
Me
F
MeO
O
F

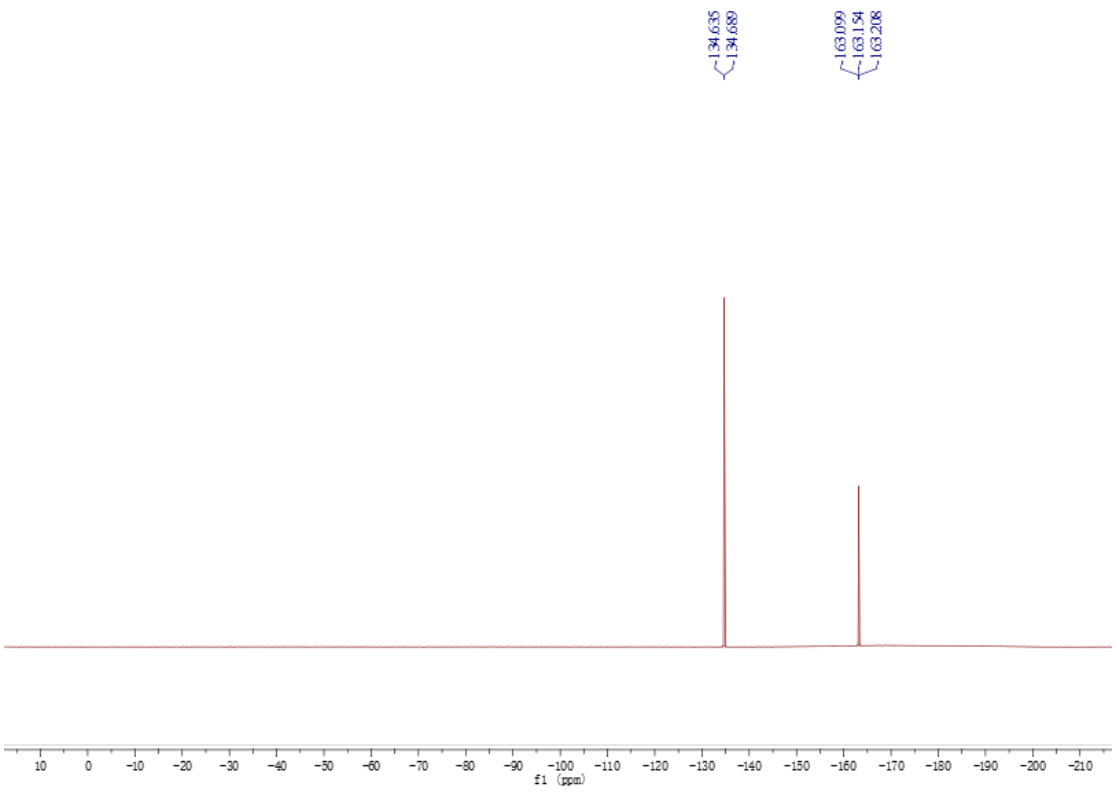
3n

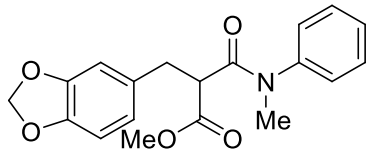

7.405
7.393
7.383
7.378
7.370
7.364
7.357
7.341
7.269
6.860
6.673
6.666
6.654
6.638
6.633
6.618
6.606
6.598


3.713
3.576
3.562
3.552
3.538
3.231
3.154
3.130
3.120
3.096
3.058
3.044
3.024
3.010

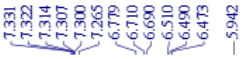

3.00
1.72
2.10
3.01
1.00
2.99
1.04
1.04
f1 (ppm)


169.419
167.862
152.336
152.297
152.238
152.199
149.852
149.811
149.754
149.715
143.030
140.099
139.947
139.796
137.611
137.459
137.307
134.800
134.751
134.727
134.678
134.650
134.604
129.980
128.598
127.454
113.347
113.292
113.193
113.138
77.476
77.160
76.841
52.797
50.462
37.691
34.636
f1 (ppm)

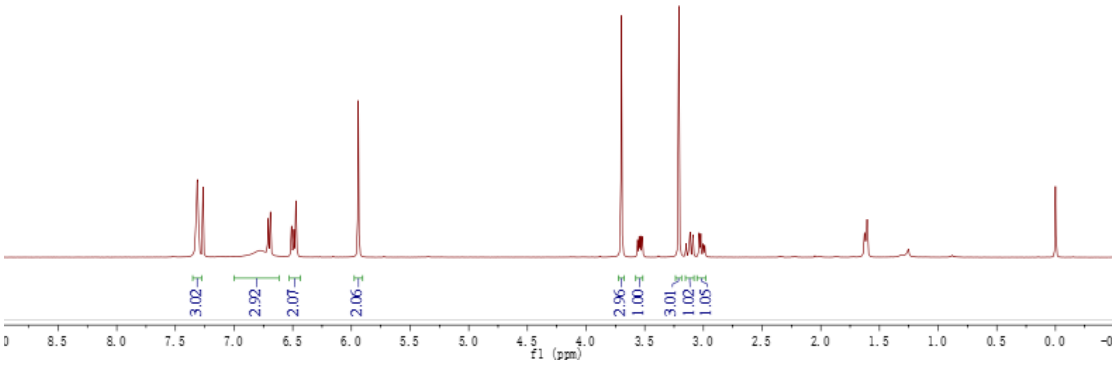

134.635
134.689
163.099
163.154
163.208
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
O
O
N
Me
MeO
O

3o

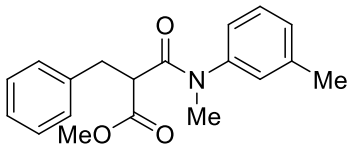

7.331
7.322
7.314
7.307
7.300
7.265
6.779
6.710
6.690
6.510
6.490
6.473
5.942


3.699
3.561
3.548
3.537
3.523
3.210
3.148
3.123
3.114
3.090
3.036
3.023
3.002
2.989


3.02
2.92
2.07
2.06
2.96
1.00
3.01
1.02
1.05
f1 (ppm)


169.992
168.562
147.613
146.304
143.297
132.145
129.732
128.254
127.661
122.287
109.748
108.289
100.978
77.476
77.160
76.840
52.597
51.126
37.633
35.162

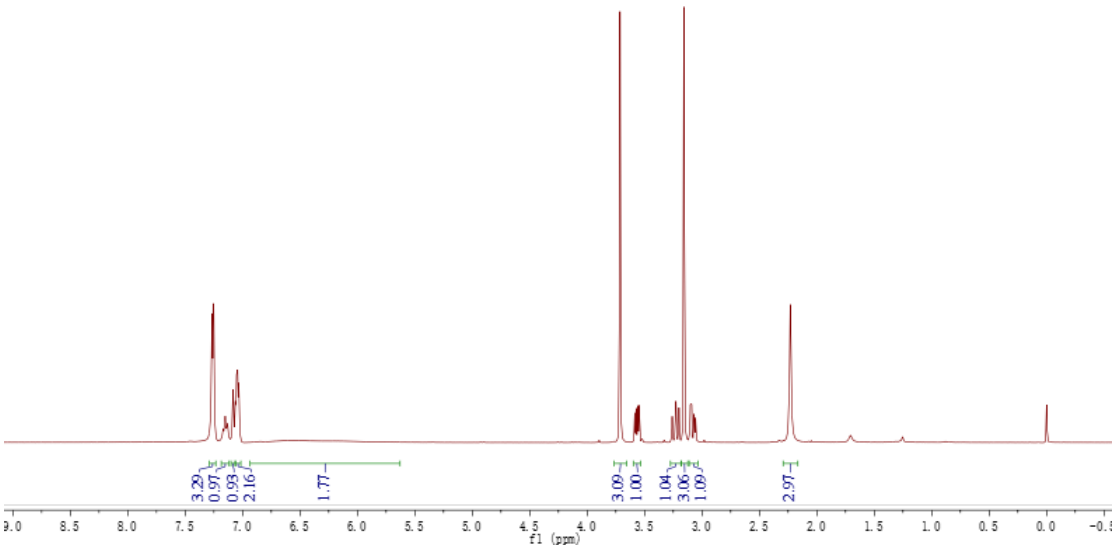
f1 (ppm)

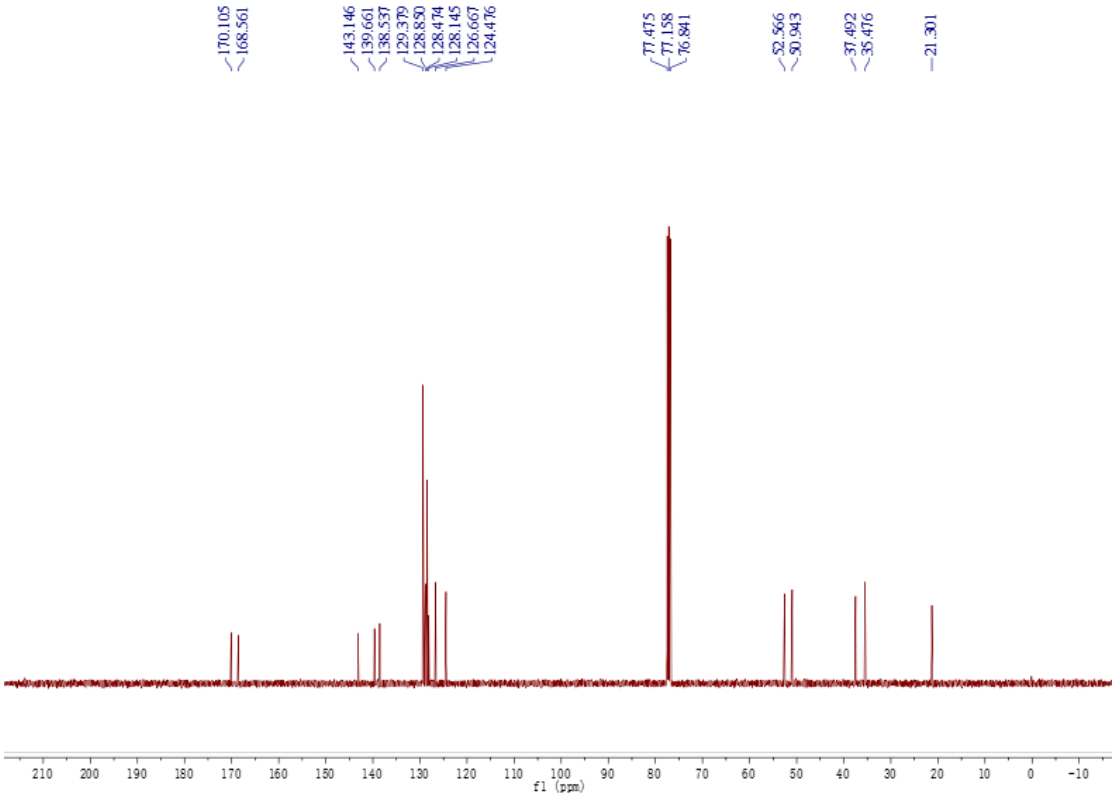

O
N
Me
Me
MeO
O

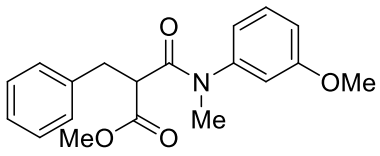
3ab


7.278
7.269
7.265
7.257
7.251
7.242
7.169
7.151
7.132
7.083
7.063
7.053
7.044
7.035
7.030
6.549


3.714
3.586
3.574
3.560
3.548
3.260
3.233
3.227
3.201
3.158
3.102
3.090
3.069
3.057
2.232


3.29
0.97
0.93
2.16
1.77
3.09
1.00
1.04
3.06
1.09
2.97
f1 (ppm)

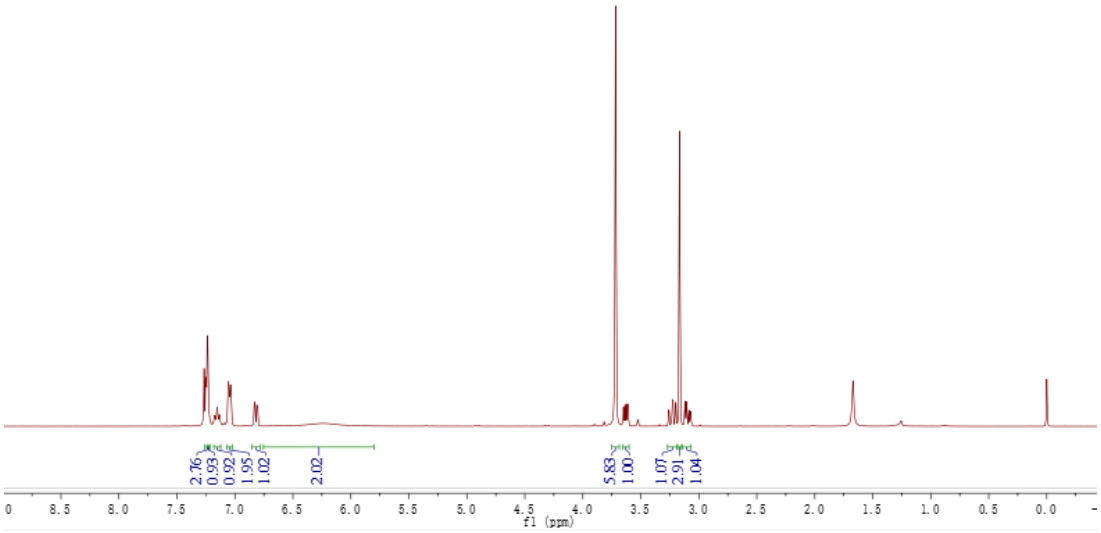

170.105
168.561
143.146
139.661
138.537
129.379
128.850
128.474
128.145
126.667
124.476
77.475
77.158
76.841
52.566
50.943
37.492
35.476
21.301
f1 (ppm)


O
N
Me
OMe
MeO
O

3ac

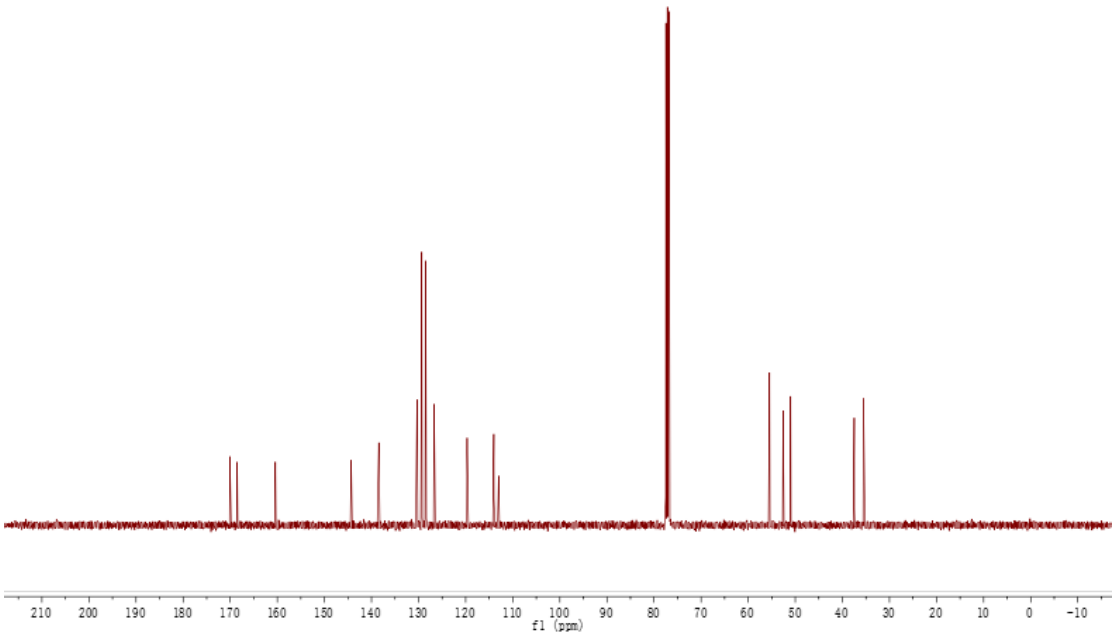

7.266
7.252
7.247
7.239
7.234
7.228
7.173
7.154
7.134
7.057
7.052
7.038
7.033
6.832
6.827
6.811
6.806
6.241

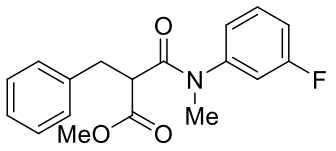

3.718
3.649
3.637
3.624
3.611
3.258
3.232
3.224
3.199
3.166
3.118
3.106
3.085
3.072


2.76
0.93
0.92
1.95
1.02
2.02
5.83
1.00
1.07
2.91
1.04
f1 (ppm)


170.078
168.521
160.405
144.315
138.447
130.326
129.318
128.481
126.700
119.683
114.015
113.000

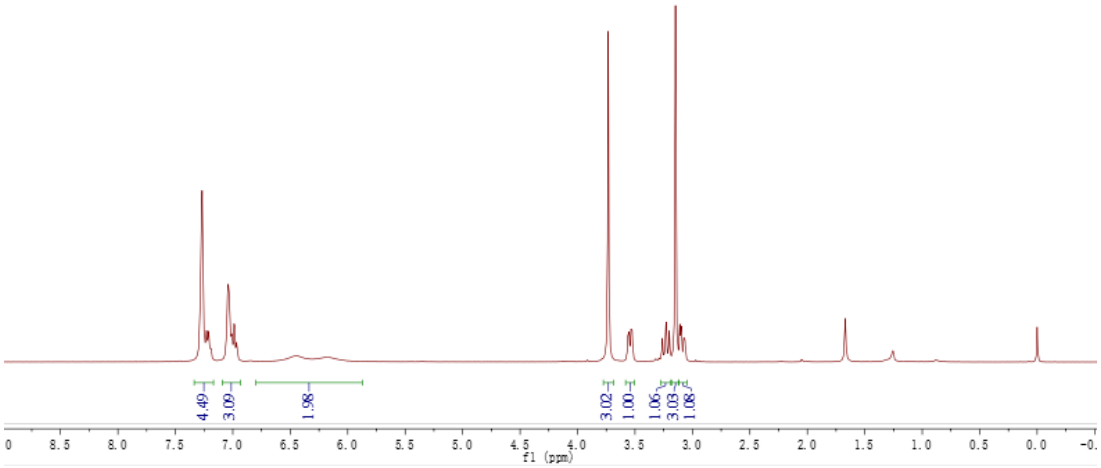

77.475
77.157
76.840
55.470
52.590
50.988
37.474
35.513

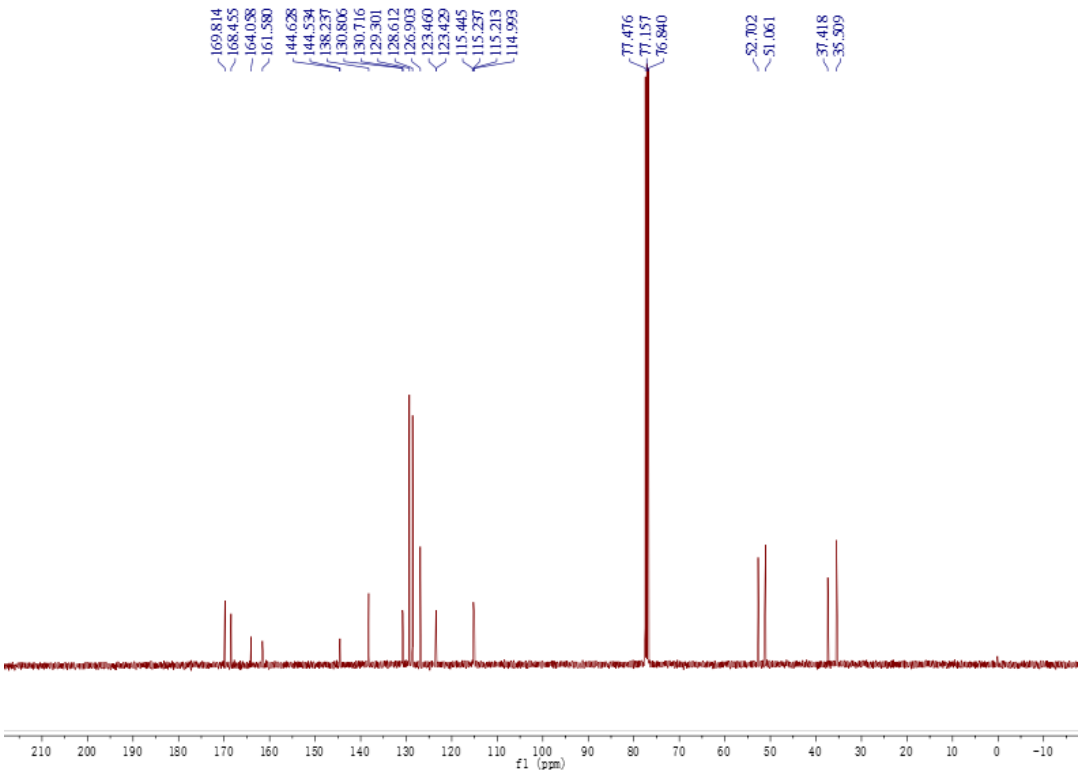

f1 (ppm)

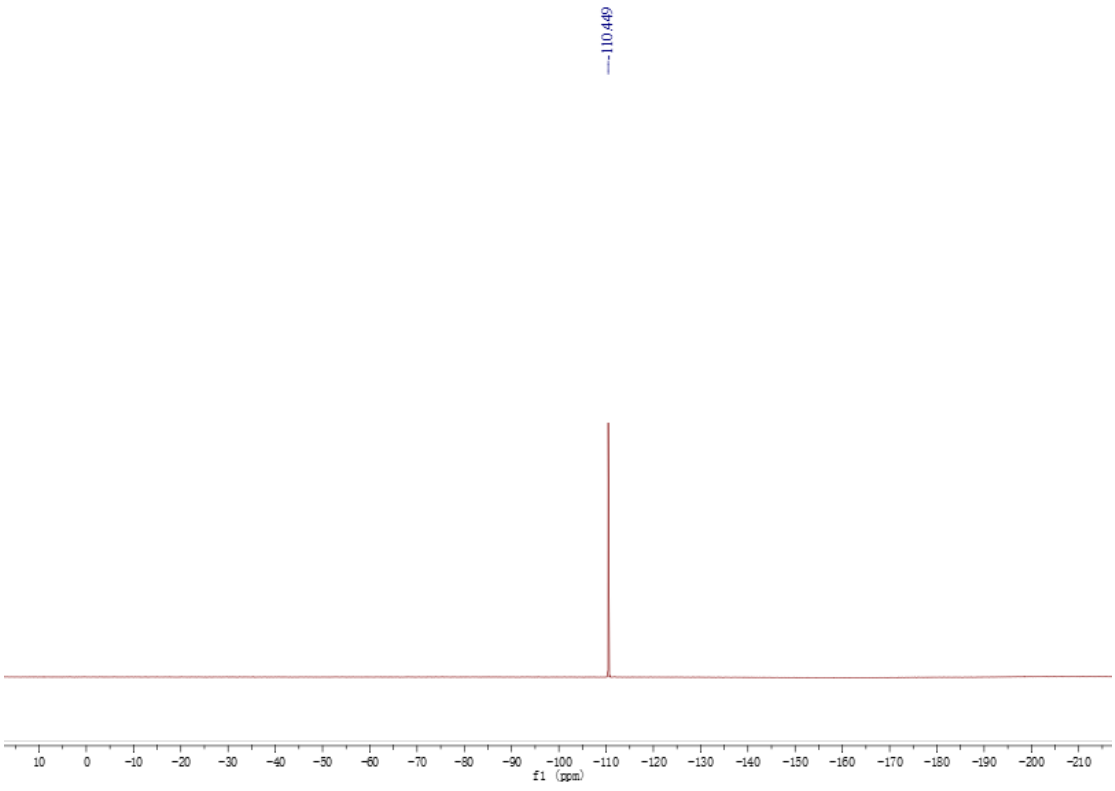

O
N
Me
F
MeO
O

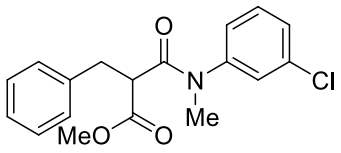
3ad


7.279
7.271
7.265
7.229
7.211
7.049
7.040
7.031
7.025
7.014
7.013
7.011
7.006
6.990
6.984
6.970
6.176
3.733
3.563
3.551
3.536
3.525
3.262
3.234
3.228
3.202
3.148
3.110
3.099
3.076
3.065


4.49
3.09
1.98
3.02
1.00
1.06
3.03
1.08
f1 (ppm)


169.814
168.455
164.038
161.580
144.628
144.534
138.237
130.806
130.716
129.301
128.612
126.903
123.460
123.429
115.445
115.237
115.213
114.993
77.476
77.157
76.840
52.702
51.061
37.418
35.509
f1 (ppm)

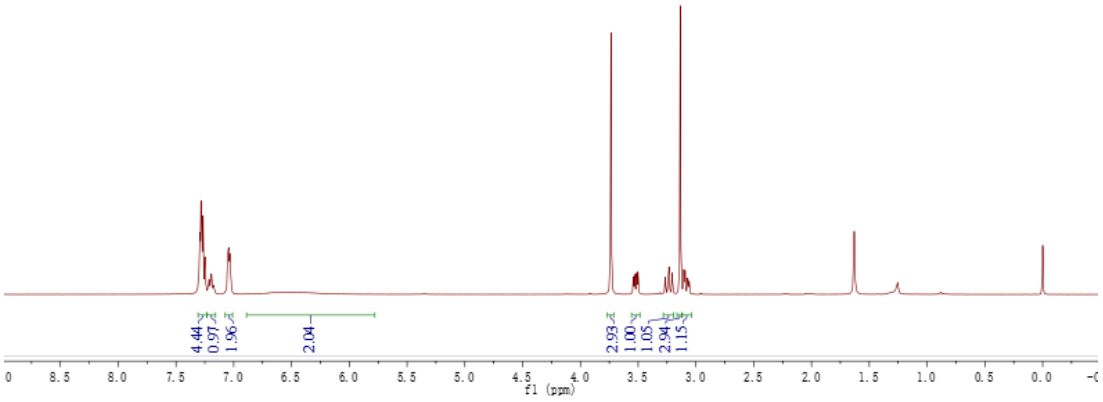

-110.449
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

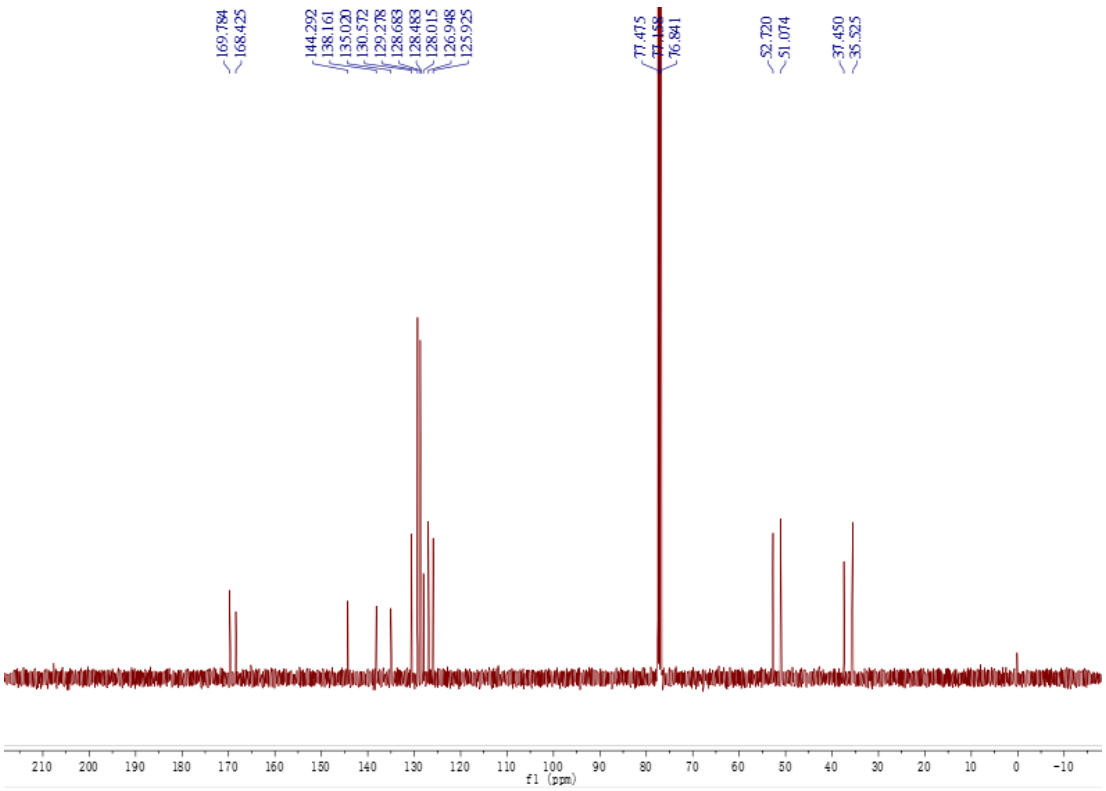

O
N
Me
Cl
MeO
O

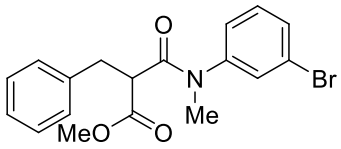
3ae


7.296
7.292
7.284
7.278
7.266
7.253
7.249
7.245
7.213
7.194
7.174
7.052
7.043
7.036
7.030
6.569

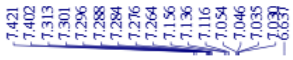

3.736
3.541
3.530
3.514
3.503
3.266
3.233
3.206
3.136
3.105
3.094
3.071
3.060


4.44
0.97
1.96
2.04
2.93
1.00
1.05
2.94
1.15
f1 (ppm)

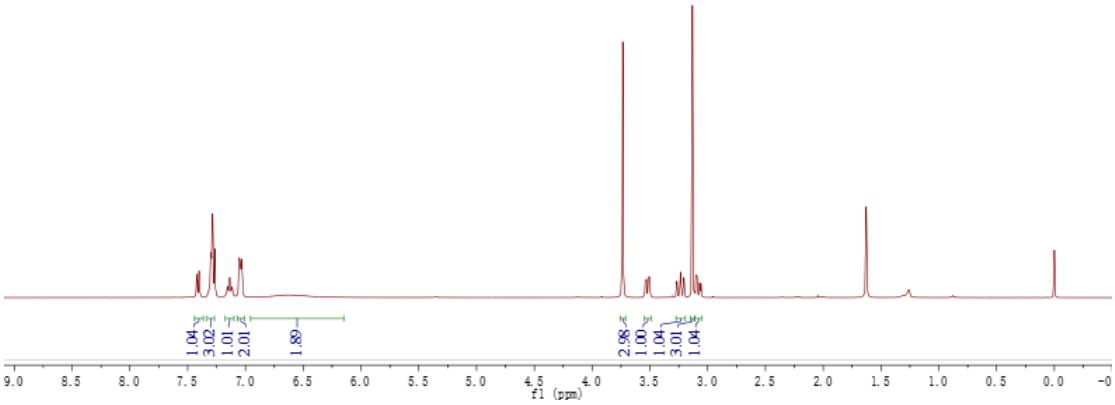

169.784
168.425
144.292
138.161
135.020
130.572
129.278
128.683
128.483
128.015
126.948
125.925
77.475
77.158
76.841
52.720
51.074
37.450
35.525
f1 (ppm)

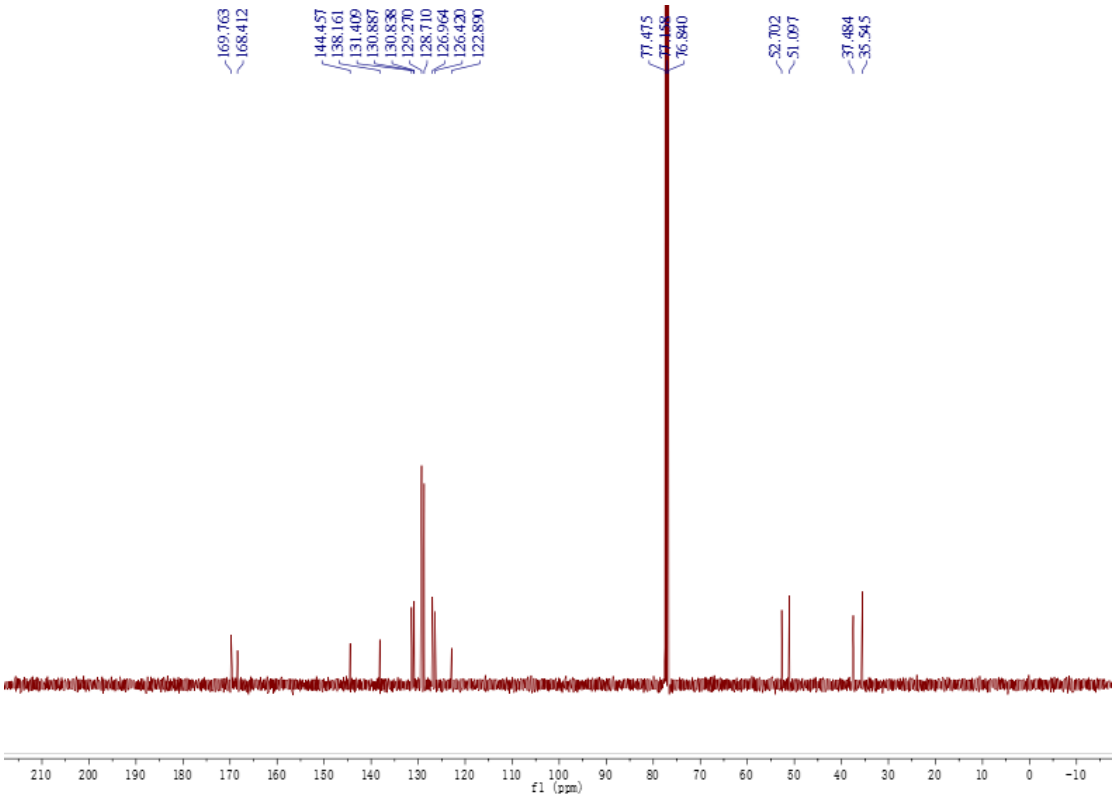

O
N
Me
Br
MeO
O

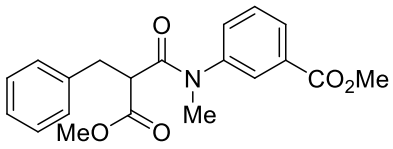
3af


7.421
7.402
7.313
7.301
7.296
7.288
7.284
7.276
7.264
7.156
7.136
7.116
7.054
7.046
7.035
7.030
6.637


3.735
3.541
3.530
3.514
3.502
3.267
3.239
3.233
3.206
3.132
3.103
3.092
3.070
3.059

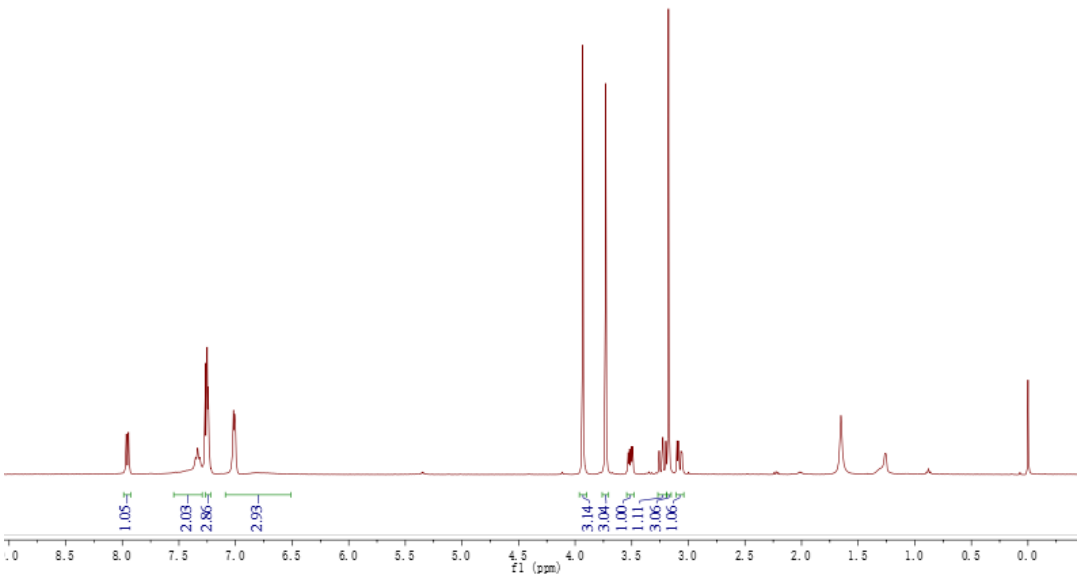

1.04
3.02
1.01
2.01
1.89
2.98
1.00
1.04
3.01
1.04
f1 (ppm)

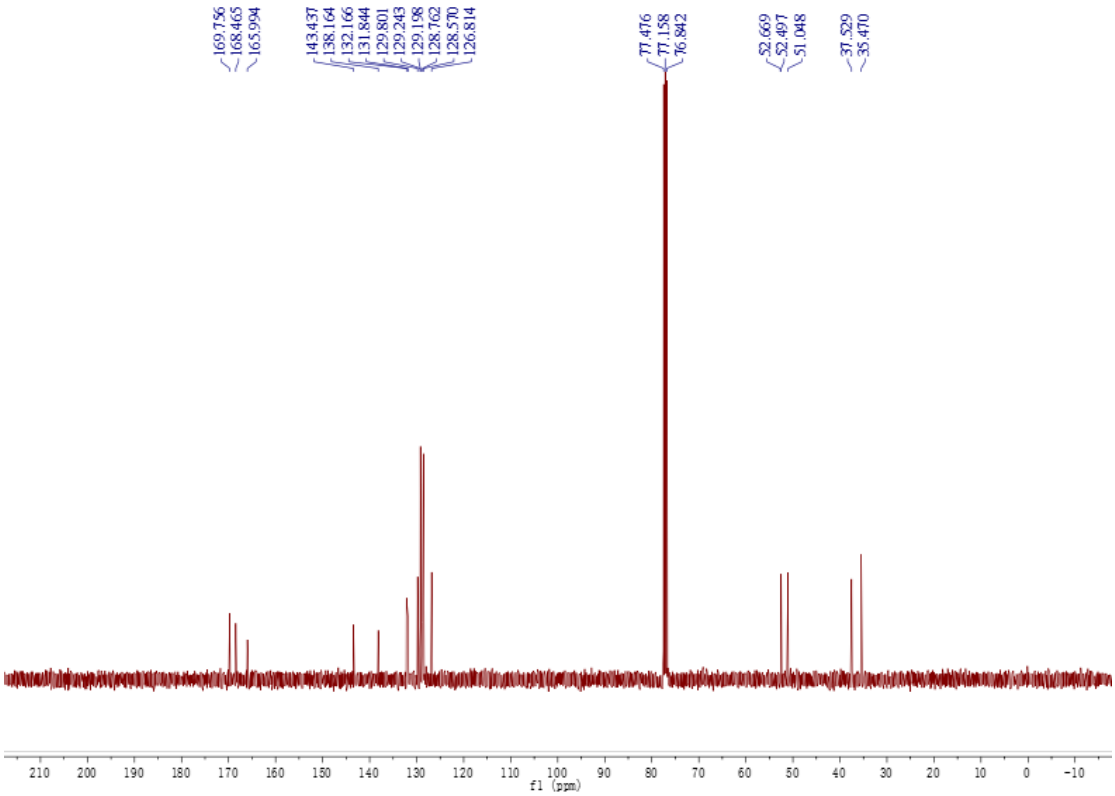

169.763
168.412
144.457
138.161
131.409
130.887
130.838
129.270
128.710
126.964
126.420
122.890
77.475
77.158
76.840
52.702
51.097
37.484
35.545
f1 (ppm)


O
N
Me
CO2Me
MeO
O

3ag


7.965
7.945
7.353
7.335
7.316
7.267
7.255
7.252
7.242
7.238
7.022
7.018
7.009
7.000
6.828
3.933
3.731
3.532
3.520
3.505
3.494
3.258
3.231
3.225
3.198
3.176
3.100
3.088
3.066
3.055


1.05
2.03
2.86
2.93
3.14
3.04
1.00
1.11
3.06
1.06
f1 (ppm)


169.736
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165.994
143.437
138.164
132.166
131.844
129.801
129.243
129.198
128.762
128.570
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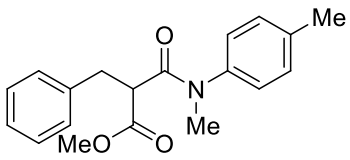
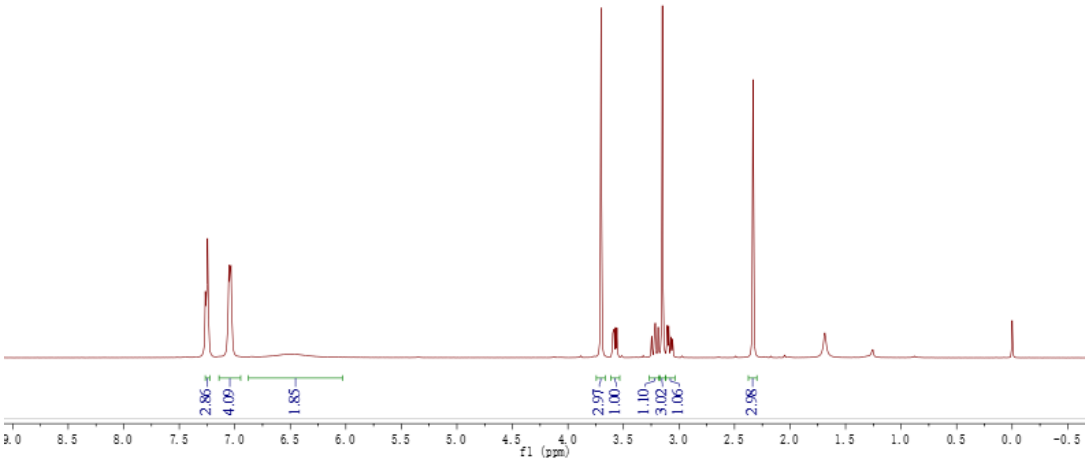
52.497
51.048
37.529
35.470
f1 (ppm)

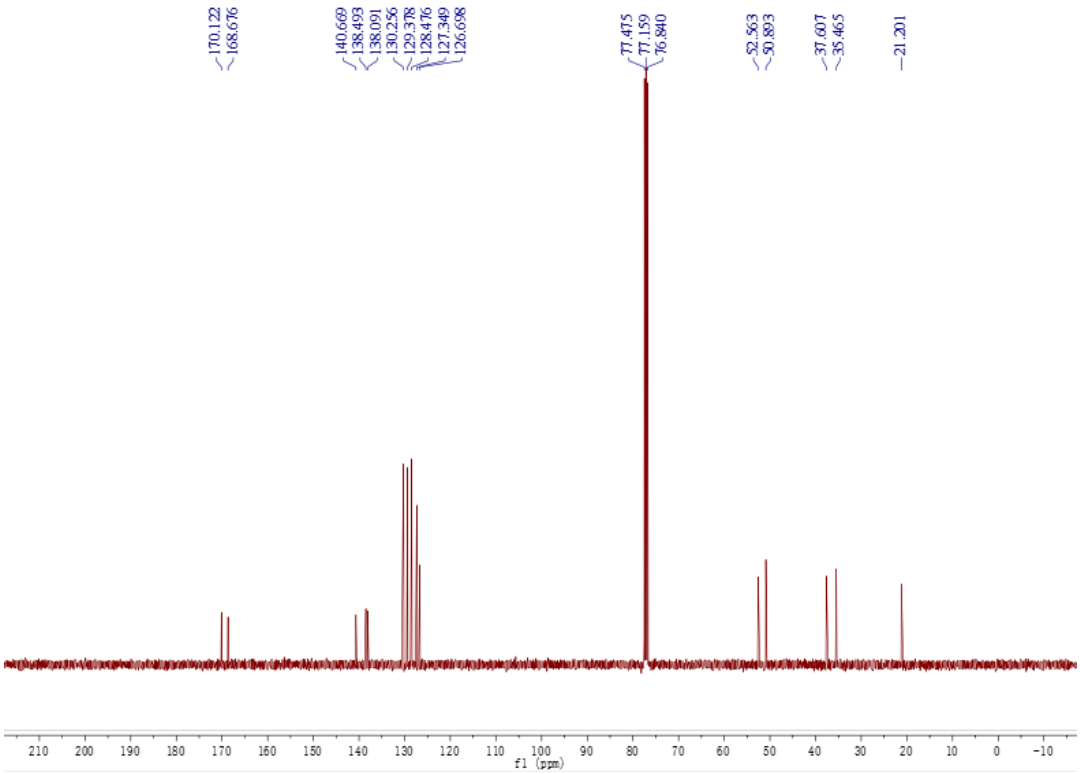

Me
O
N
Me
MeO
O

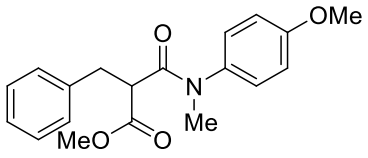
3ah


7.265
7.258
7.254
7.246
7.241
7.233
7.230
7.058
7.053
7.046
7.041
7.034
7.029
6.492


3.702
3.597
3.584
3.572
3.559
3.247
3.221
3.213
3.188
3.150
3.105
3.093
3.072
3.059
2.334

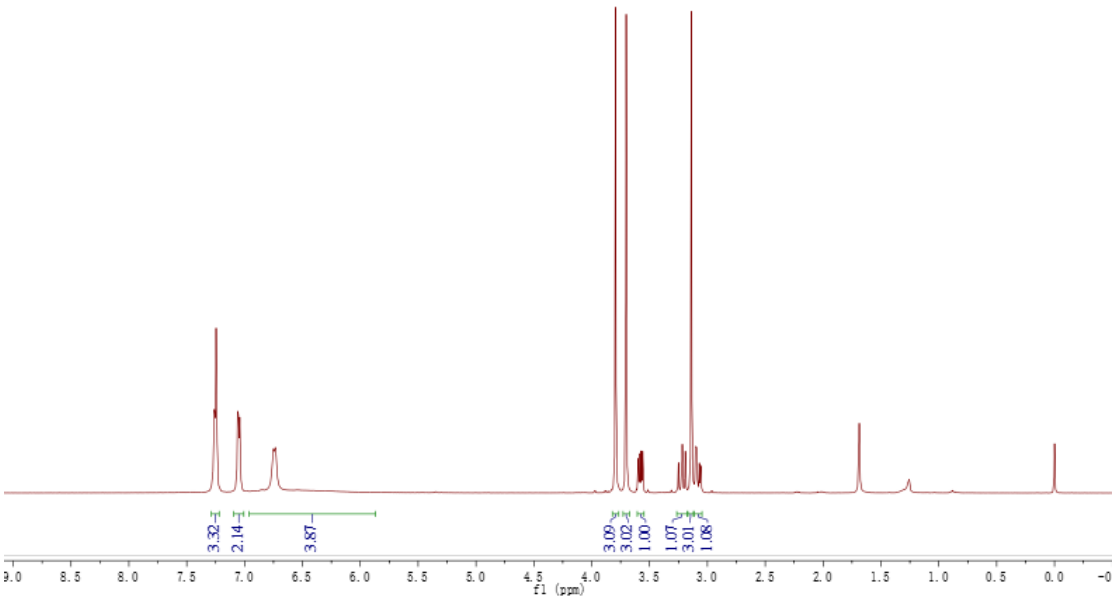

2.86
4.09
1.85
2.97
1.00
1.10
3.02
1.06
2.08
f1 (ppm)


170.122
168.676
140.669
138.493
138.091
130.256
129.378
128.476
127.349
126.698
77.475
77.159
76.840
52.563
50.893
37.607
35.465
21.201
f1 (ppm)

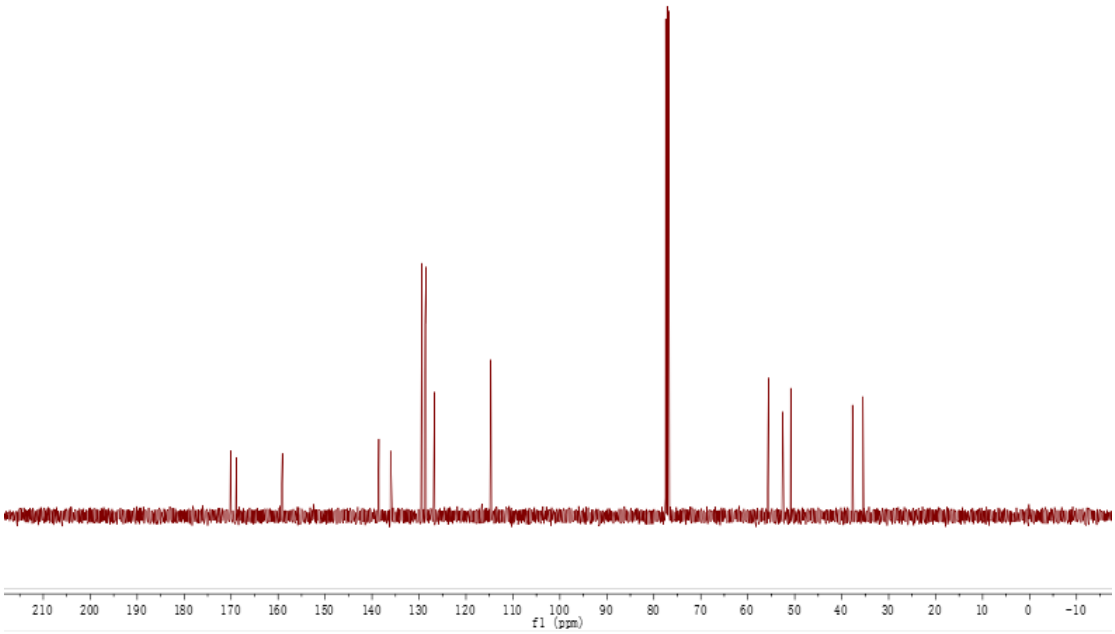

OMe
O
N
Me
MeO
O

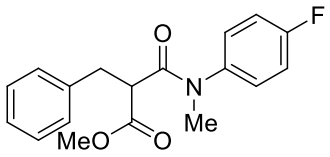
3ai


7.265
7.264
7.260
7.255
7.247
7.245
7.244
7.061
7.054
7.043
7.037
6.751
6.734
6.549
3.794
3.702
3.598
3.585
3.572
3.560
3.250
3.224
3.217
3.191
3.139
3.104
3.091
3.070
3.058


3.32
2.14
3.87
3.09
3.02
1.00
1.07
3.01
1.08
f1 (ppm)

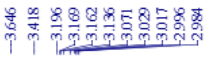

170.114
168.882
159.080
138.550
136.060
129.385
128.713
128.487
126.706
114.704
77.475
77.158
76.841
55.584
52.543
50.855
37.716
35.473

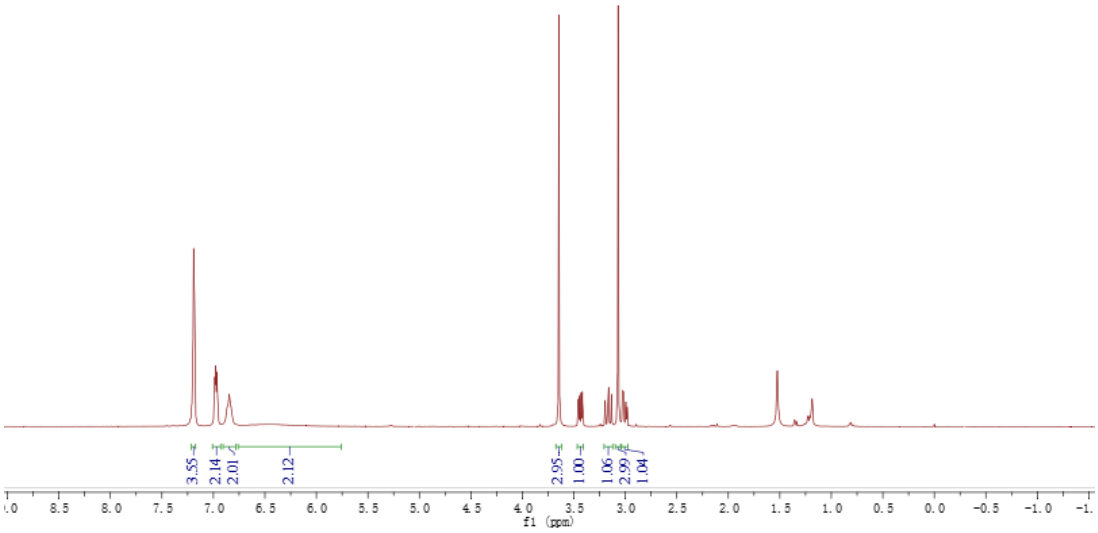

f1 (ppm)

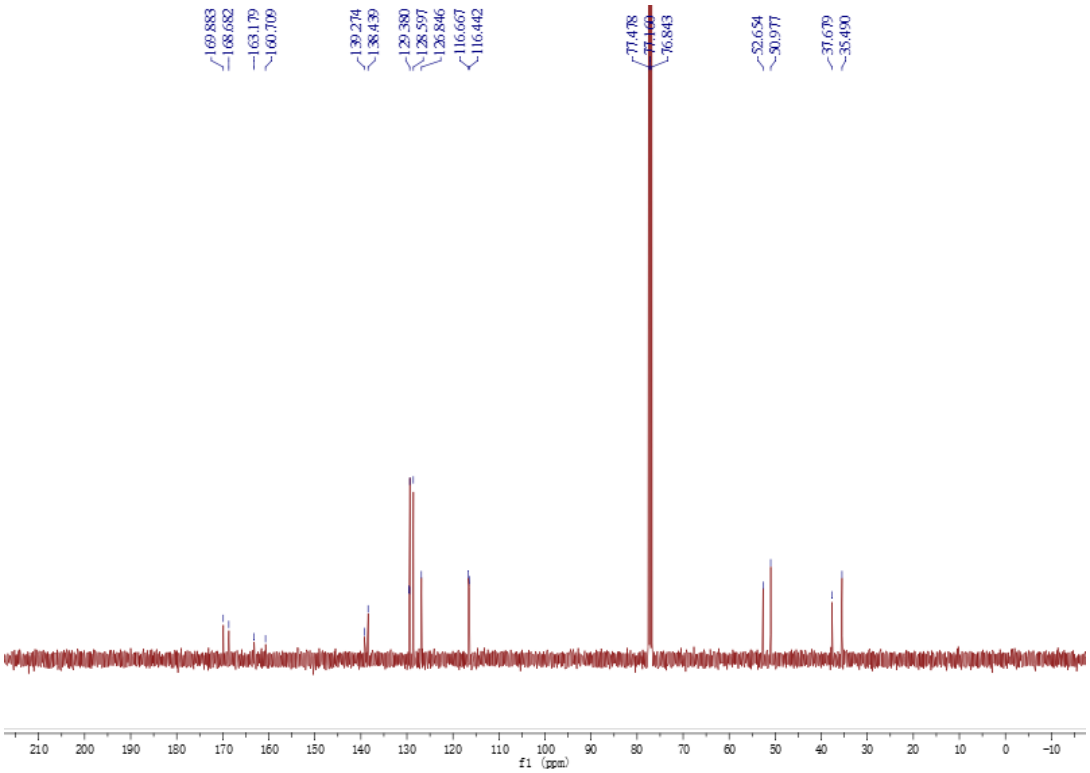

O
F
N
Me
MeO
O

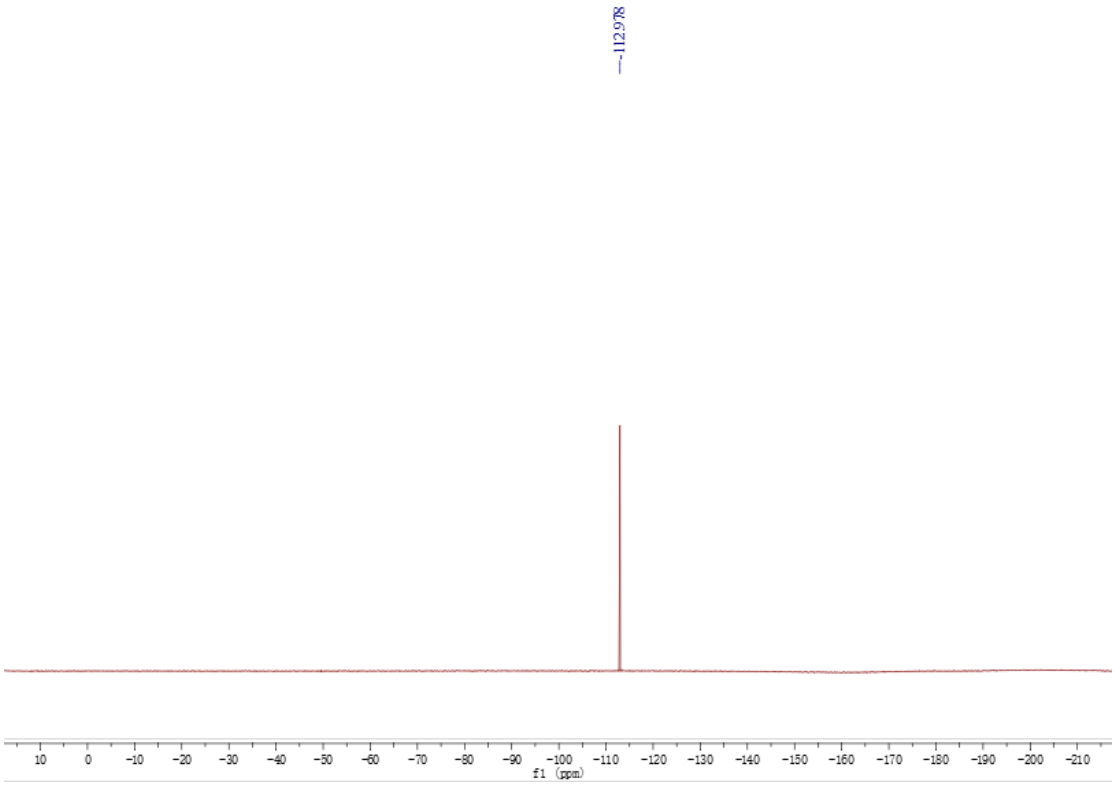
3aj

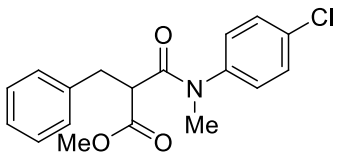

7.210
7.201
7.197
7.193
7.189
7.183
7.174
6.986
6.826
6.472


3.646
3.418
3.196
3.169
3.162
3.136
3.071
3.029
3.017
2.996
2.984


3.55
2.14
2.01
2.12
2.95
1.00
1.06
2.99
1.04
f1 (ppm)


169.883
168.682
163.179
160.709
139.274
138.439
129.380
128.597
126.846
116.667
116.442
77.478
77.160
76.843
52.654
50.977
37.679
35.490
f1 (ppm)

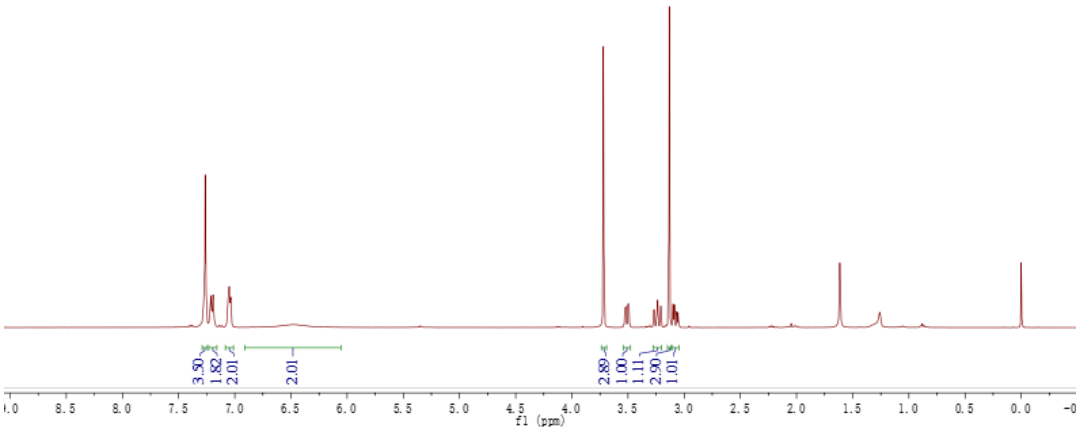

-112.978
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
Cl
N
Me
MeO
O

3ak


7.285
7.275
7.271
7.264
7.263
7.259
7.214
7.193
7.059
7.049
7.040
7.036
6.472


3.719
3.529
3.518
3.502
3.491
3.269
3.242
3.236
3.209
3.133
3.099
3.088
3.066
3.054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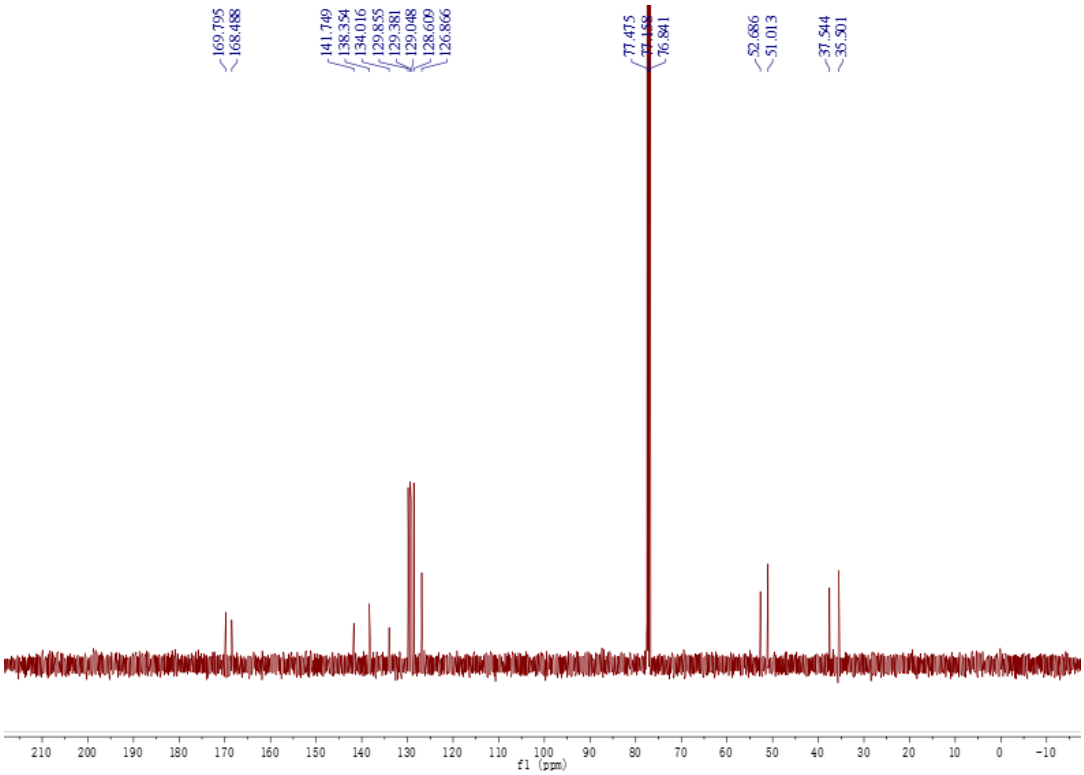
1.82
2.01
2.01
2.89
1.00
1.11
2.90
1.01
f1 (ppm)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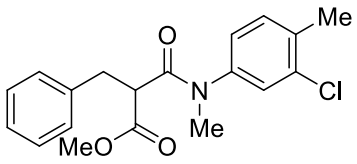
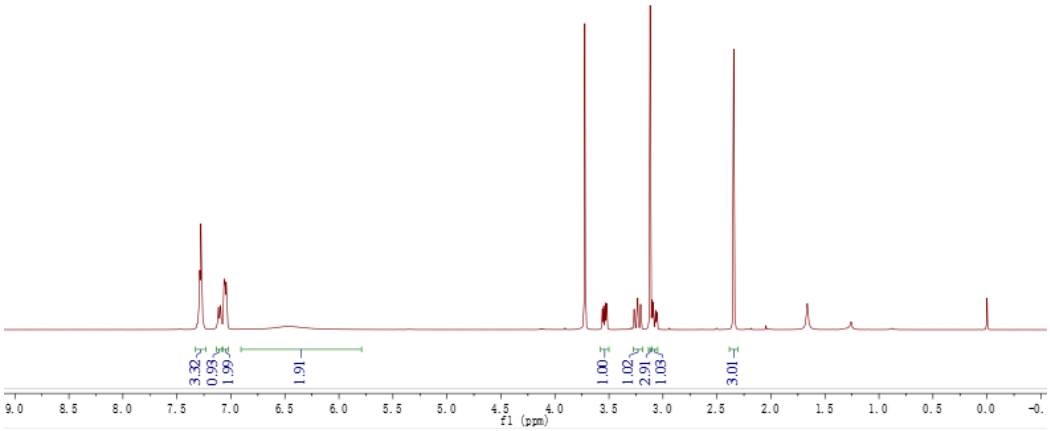
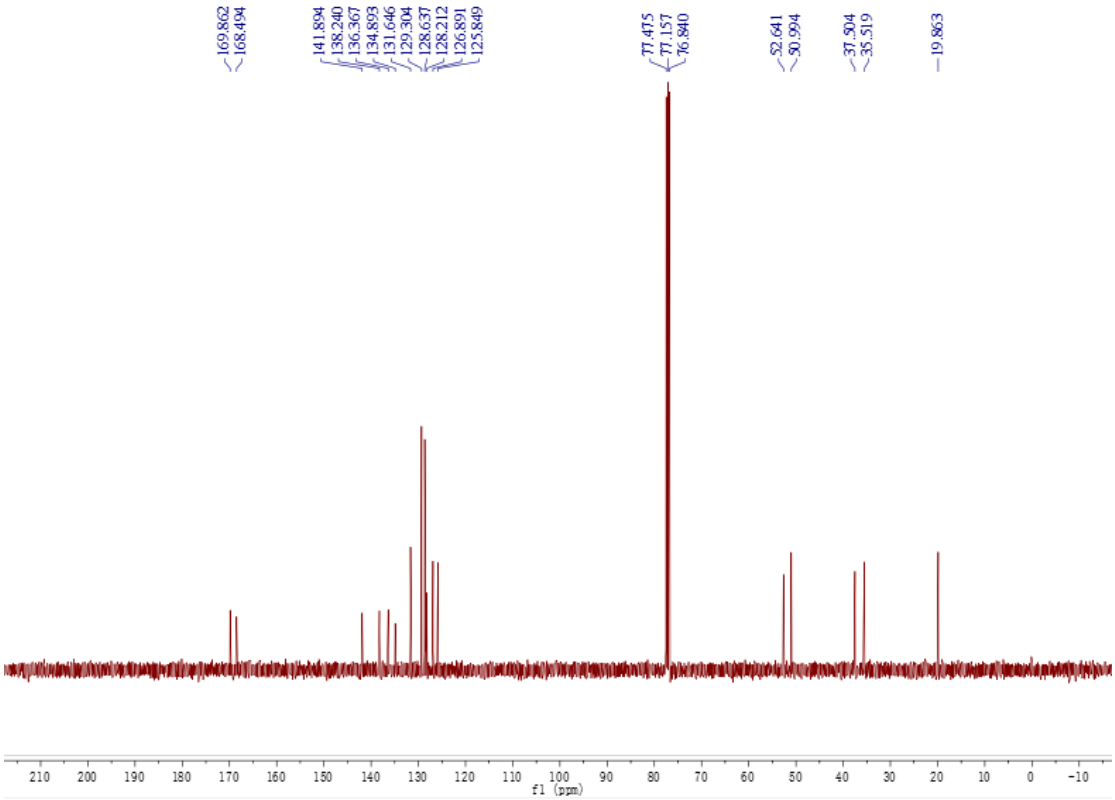
168.488
141.749
138.354
134.016
129.855
129.381
129.048
128.609
126.866
77.475
77.158
76.841
52.686
51.013
37.544
35.501
f1 (ppm)

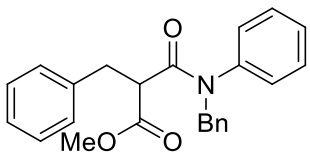

Me
O
N
Cl
Me
MeO
O

3al


7.314
7.301
7.291
7.289
7.279
7.275
7.265
7.116
7.096
7.063
7.055
7.045
7.040
6.469
3.724
3.561
3.549
3.534
3.522
3.267
3.240
3.233
3.206
3.119
3.101
3.089
3.067
3.056
2.345

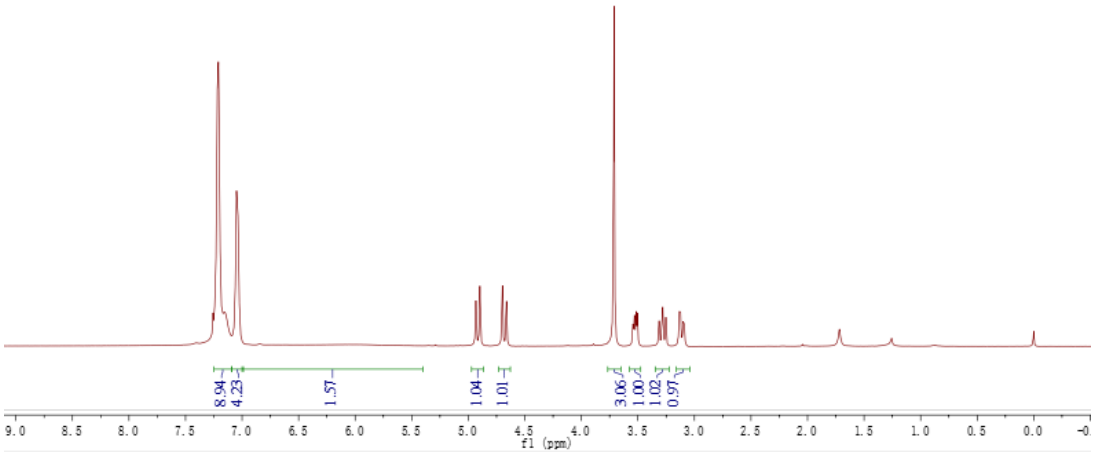

3.32
0.93
1.99
1.91
1.00
1.02
2.91
1.03
3.01
f1 (ppm)


169.862
168.494
141.894
138.240
136.367
134.893
131.646
129.304
128.637
128.212
126.891
125.849
77.475
77.157
76.840
52.641
50.994
37.504
35.519
19.863
f1 (ppm)

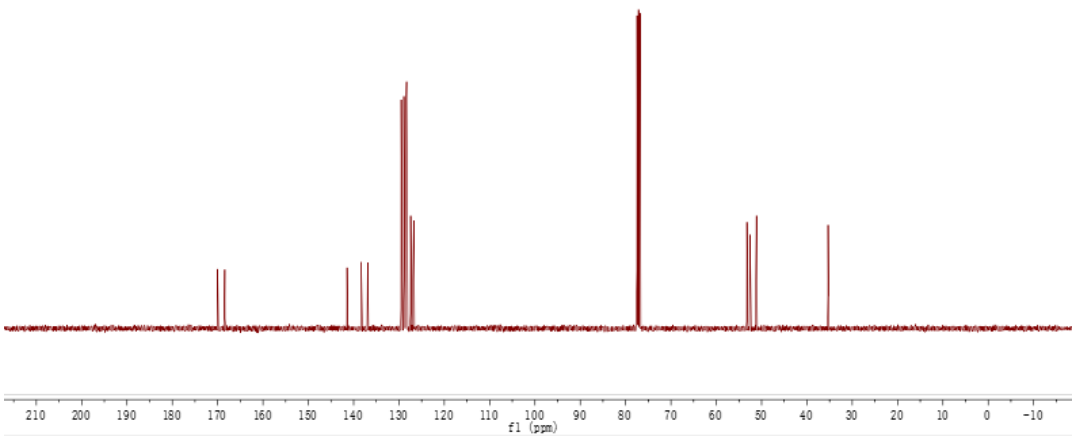

O
N
Bn
MeO
O

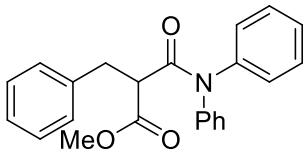
3am


7.257
7.244
7.223
7.216
7.209
7.204
7.199
7.178
7.150
7.054
7.049
7.039
7.030
6.049
4.933
4.897
4.698
4.662
3.711
3.542
3.530
3.516
3.504
3.313
3.286
3.279
3.253
3.134
3.123
3.101
3.090


8.94
4.23
1.57
1.04
1.01
3.06
1.00
1.02
0.97
f1 (ppm)


170.018
168.419
141.459
138.336
136.903
129.506
129.385
128.919
128.807
128.480
128.318
128.297
127.418
126.719
77.478
77.160
76.843
53.251
52.557
51.138
35.334


f1 (ppm)


O
N
Ph
MeO
O

3an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7.327
7.313
7.296
7.275
7.272
7.257
7.171
7.153
7.143
7.137
7.124
7.120
7.108
7.088
6.728


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3.741
3.367
3.340
3.334
3.307
3.207
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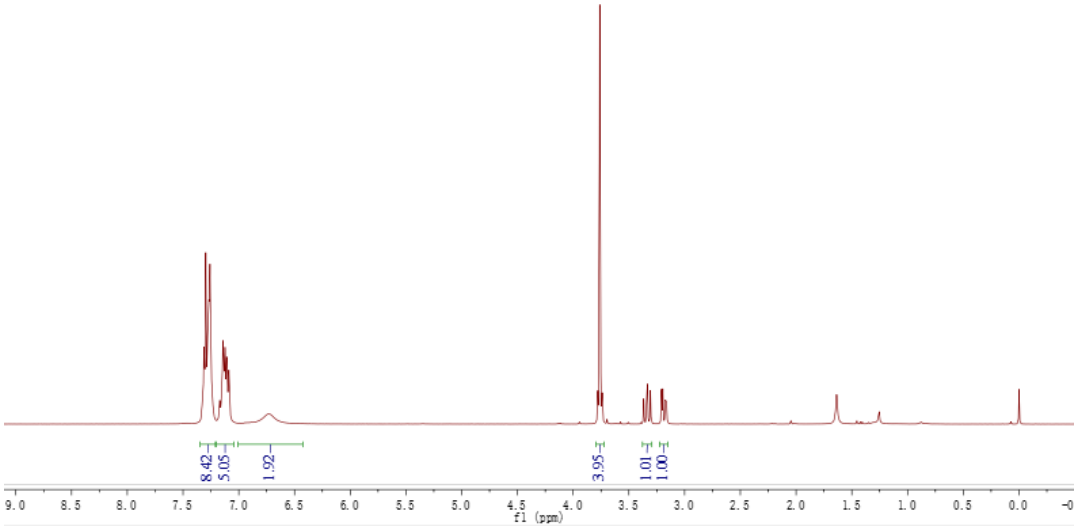
3.174
3.162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1.92
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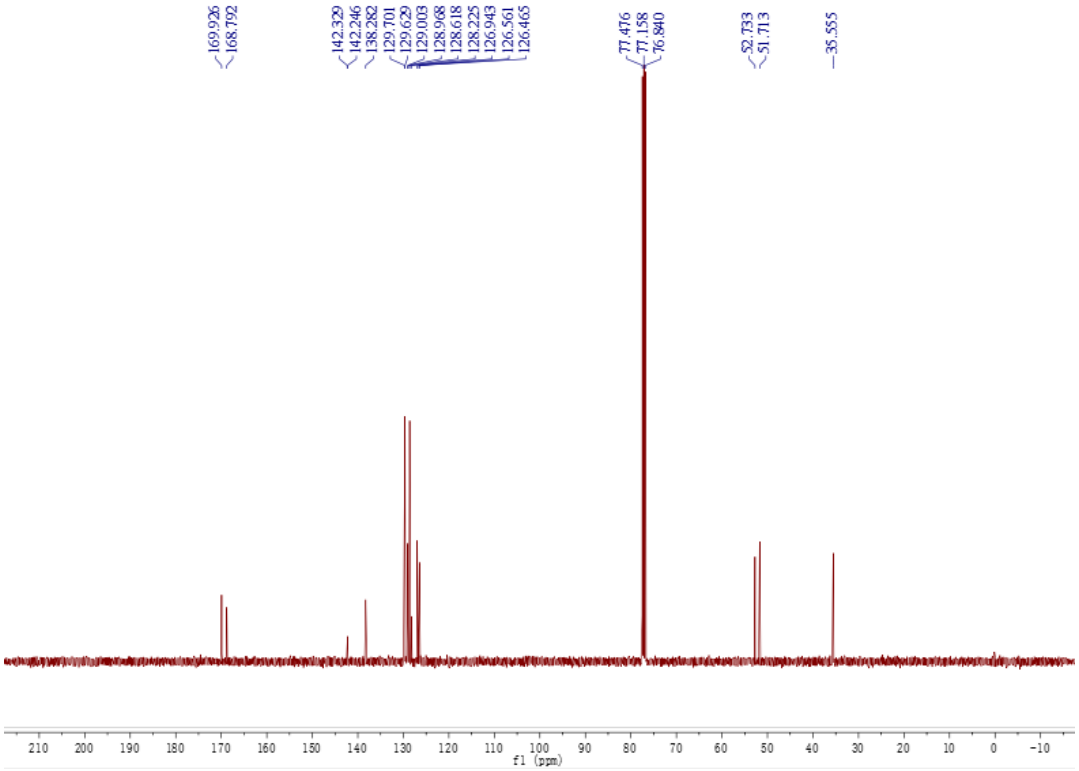
1.01
1.00
f1 (ppm)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142.329
142.246
138.282
129.701
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129.003
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128.618
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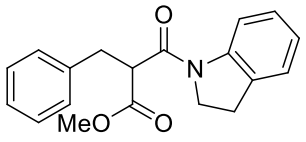
126.561
126.465
77.476
77.158
76.840
52.733
51.713
35.555
f1 (ppm)


O
N
MeO
O

3ao


8.271
8.251
7.255
7.247
7.239
7.225
7.218
7.199
7.187
7.178
7.166
7.152
7.133
7.044
7.026
7.007
4.160
4.143
4.135
4.119
4.110
4.093
3.887
3.871
3.866
3.850
3.729
3.708
3.691
3.682
3.666
3.657
3.641
3.409
3.387
3.375
3.353
3.339
3.324
3.305
3.289
3.157
3.140
3.131
3.116
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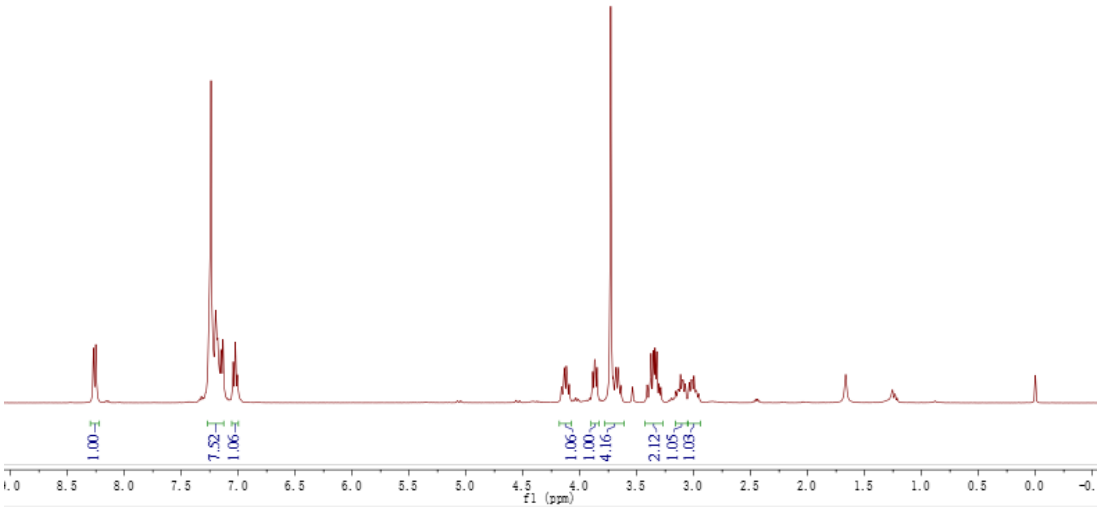
3.092
3.075
3.039
3.023
3.014
2.998
2.983
2.974
2.957


1.00
7.52
1.06
1.06
1.00
4.16
2.12
1.05
1.03
f1 (ppm)


169.591
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142.639
138.415
131.582
129.020
128.730
127.670
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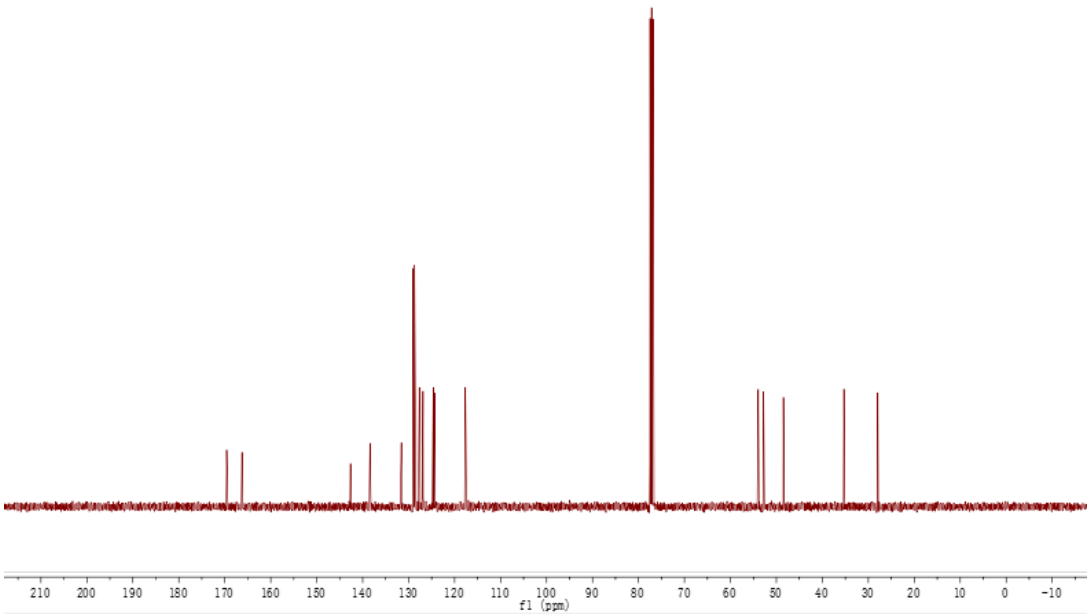
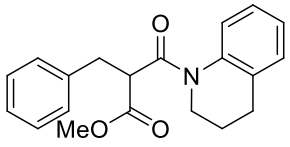
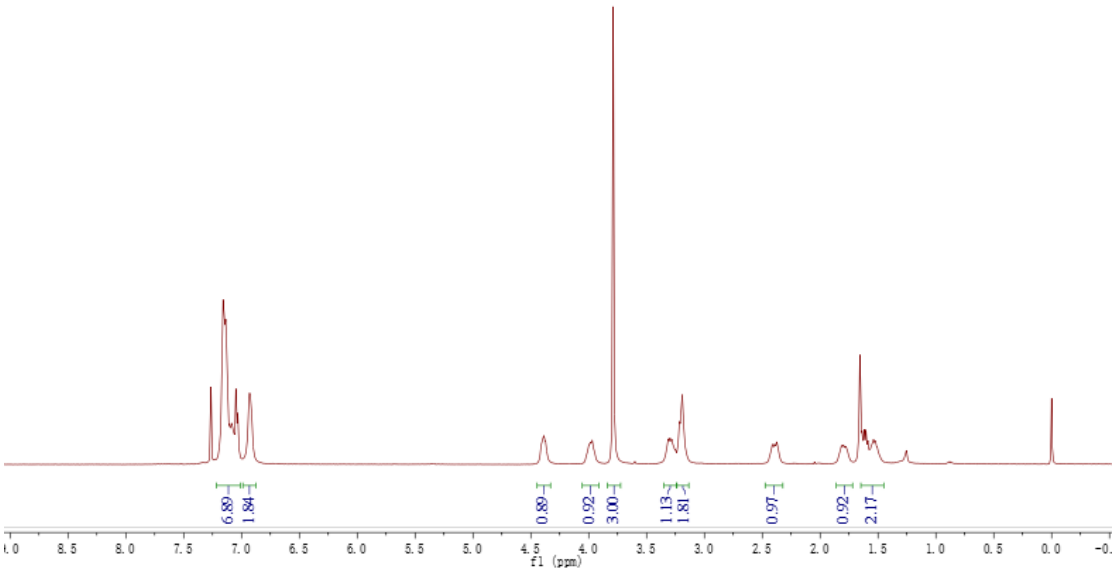
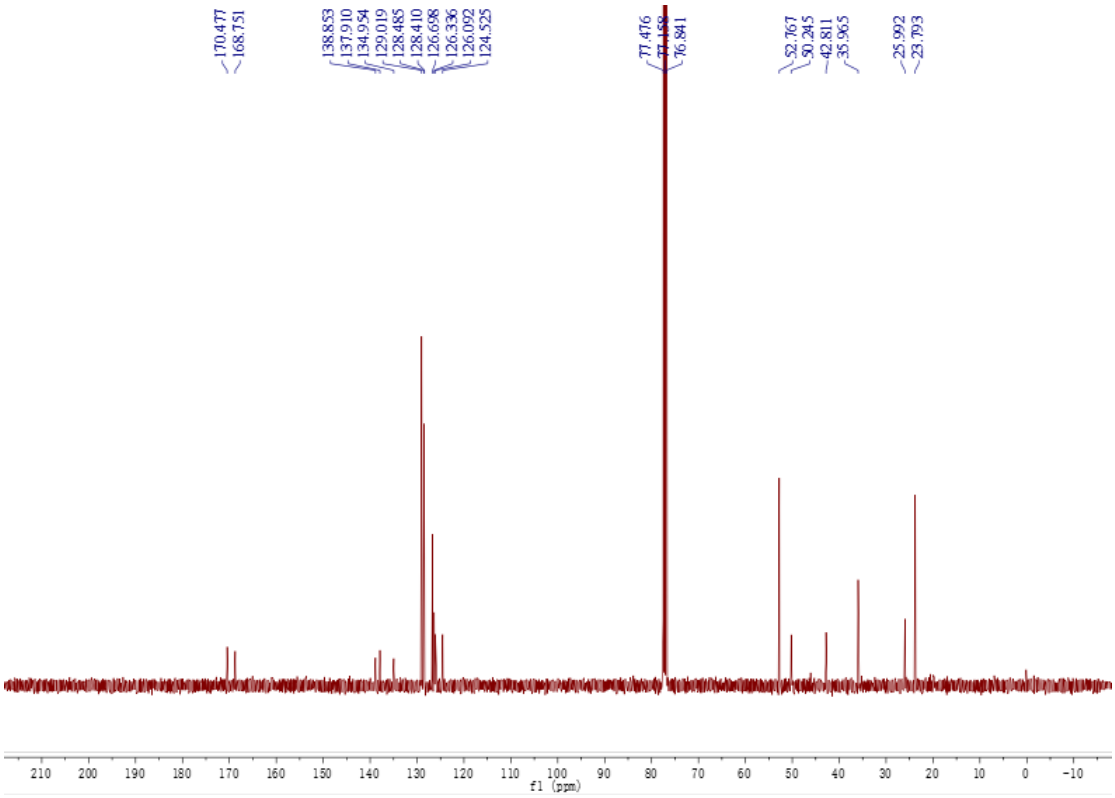
124.643
124.335
117.653
77.475
77.158
76.840
53.949
52.799
48.468
35.313
27.945

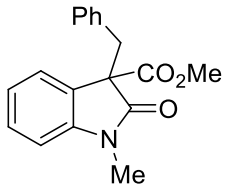

f1 (ppm)



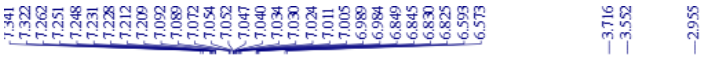
3ap






Ph
CO2Me
O
N
Me

6


7.341
7.322
7.262
7.251
7.248
7.231
7.228
7.212
7.209
7.092
7.089
7.072
7.054
7.052
7.047
7.040
7.034
7.030
7.024
7.011
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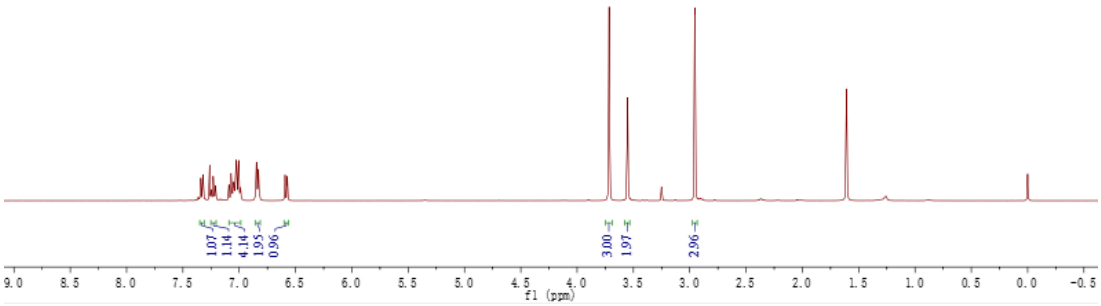
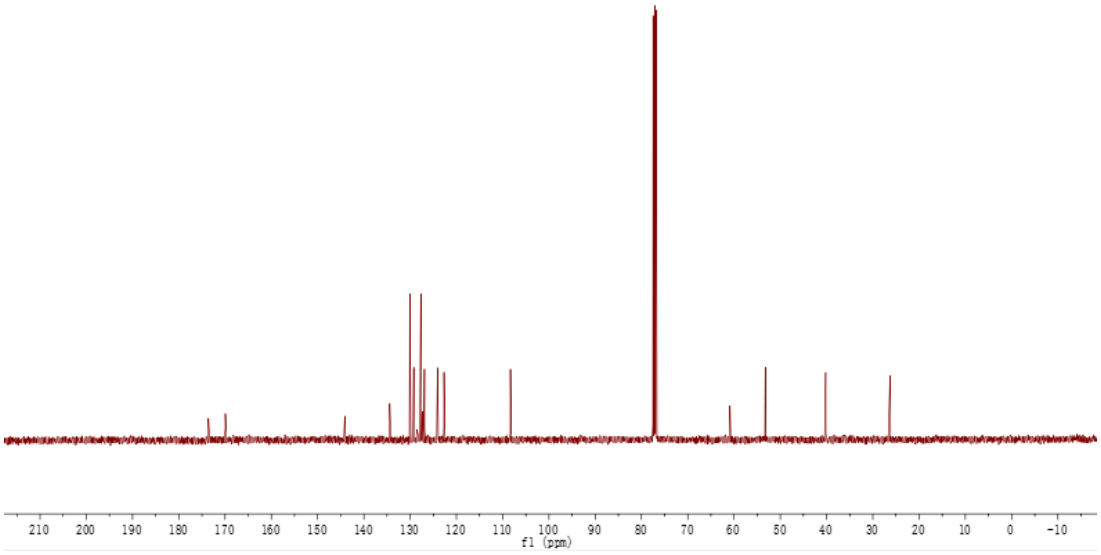
6.825
6.593
6.573
3.716
3.552
2.955


1.07
1.14
4.14
1.95
0.96
3.00
1.97
2.96
f1 (ppm)


173.596
169.932
144.125
134.412
130.071
129.227
127.691
127.384
126.896
124.071
122.680
108.320
77.477
77.160
76.842
60.878
53.236
40.189
26.276


f1 (ppm)