Supporting Information

Nickel-Catalyzed Reductive 1,2-Alkylarylation of Alkenes *via* a 1,5-Hydrogen Atom Transfer (HAT) Cascade

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1. General Information

Unless otherwise noted, all of these reactions were carried out under an argon atmosphere. For column chromatography, silica gel (200-300 mesh) was employed. Solvent was freshly distilled prior to use unless otherwise noted.

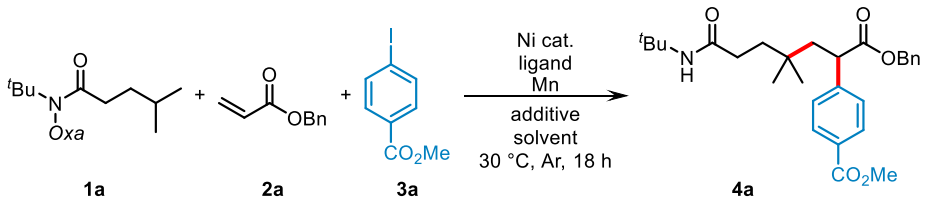
Instrumentation: ^{1}H NMR spectra were recorded on Bruker AVANCE NEO 600 or Bruker AVANCE NEO 400 with 600 MHz or 400 MHz frequencies. ^{13}C NMR spectra were recorded on Bruker AVANCE NEO 600 or Bruker AVANCE NEO 400 with 151 MHz or 101 MHz frequencies. ^{19}F NMR spectra were recorded on Bruker AVANCE NEO 600 or Bruker AVANCE NEO 400 with 565 MHz or 376 MHz frequencies. Chemical shifts (ppm) were recorded with TMS (tetramethylsilane) as the internal reference standard. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal (TMS $\delta = 0$ for ^{1}H NMR and $CDCl_3$ $\delta = 77.0$ for ^{13}C NMR). Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). Data collection for crystal structure was performed on a 'Rigaku XtaLAB Synergy-DW' diffractometer. HRMS obtained using a Q-TOF instrument equipped with an ESI source.

Materials: All solvents were dried according to standard procedure before use. The solvents DMA and THF used in the reaction were extra dry treated with commercially available molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Commercial reagents were used as received without further purification unless otherwise noted. Other commercially available reagents and solvents were used without further purification, like Adamas, Innochem, Leyan, Bide, and Laajoo. The *O*-oxalate hydroxamic acid esters compounds **1** used in the reaction are synthesized according to previously reported methods.

2. The optimization of the reaction

The investigation began with the selection of *O*-oxalate hydroxamic acid ester **1a**, benzyl acrylate **2a**, and 4-iodobenzoic acid methyl ester **3a** as model substrates. Using $NiCl_2$·DME as the catalyst, bipyridine ligand **L1**, and Mn powder as the reductant, we were pleased to obtain the desired product **4a** with a 13% yield (Table S1, entry 1). Given the critical role of solvents in cross-electrophile coupling, we initially tested several solvents (entries 2-6), discovering that a mixture of DMA/THF in a 2:1 ratio (v/v) was optimal. Screening of Ni salts revealed that the reactions could be catalyzed by both Ni(II) and Ni(0), with $NiCl_2$·DME proving to be the most effective (entries 7-14). Further optimization of the reactant ratios increased the yield to 36% (entry 15). We also explored various bidentate N-containing ligands (**L2**-**L10**), finding that **L2** provided the best efficiency, achieving a 45% yield of **4a** (entries 16-24). When Zn powder was used as the reductant, the yield decreased to 39% (entry 25). The yield was further improved to 78% with the addition of anhydrous $MgBr_2$, and we deduced that anhydrous $MgBr_2$ may accelerate reduction of the Ni^{II} intermediates or assist in activating the surface of the Mn^0,[1] while the use of LiCl, LiBr, or NaI resulted in only a trace yield (entries 26-33). Reducing the loadings of catalyst and ligand produced a 33% yield of **4a** (entry 34). Control experiments confirmed that the Ni salt, ligand, and reductant are all essential components for the successful transformation (entries 35-40).

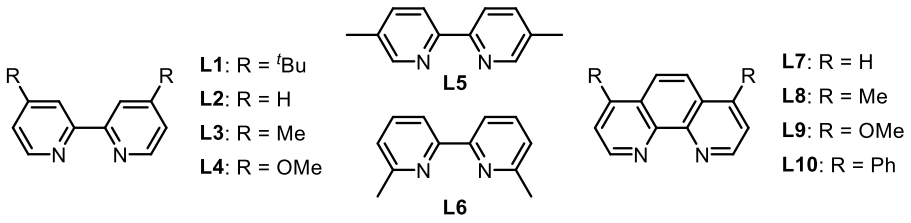
Table S1. Optimization of reaction conditions for alkylarylation of alkenes[a,b]



1a 2a 3a 4a

entry	catalyst	ligand	additive	solvent	yield(%)[c]
1	$NiCl_2$·DME	**L1**		THF	13
2	$NiCl_2$·DME	**L1**		DMA	20
3	$NiCl_2$·DME	**L1**		DMSO	11
4	$NiCl_2$·DME	**L1**		Et_2O	0
5	$NiCl_2$·DME	**L1**		1,4-dioxane	0
6	$NiCl_2$·DME	**L1**		DMA/THF = 2:1	27
7	$NiCl_2$	**L1**		DMA/THF = 2:1	0
8	$NiBr_2$	**L1**		DMA/THF = 2:1	0
9	NiI_2	**L1**		DMA/THF = 2:1	11
10	$NiCl_2·6H_2O$	**L1**		DMA/THF = 2:1	20
11	$NiBr_2$·DME	**L1**		DMA/THF = 2:1	19
12	$Ni(COD)_2$	**L1**		DMA/THF = 2:1	19
13	$Ni(acac)_2$	**L1**		DMA/THF = 2:1	0
14	$Ni(PPh_3)Cl_2$	**L1**		DMA/THF = 2:1	trace
15[d]	$NiCl_2$·DME	**L1**		DMA/THF = 2:1	36

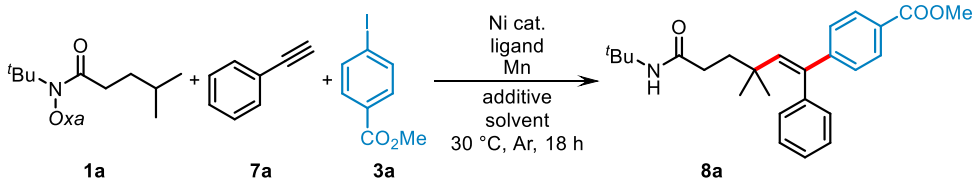
16[d]	$NiCl_2$·DME	**L2**		DMA/THF = 2:1	45
17[d]	$NiCl_2$·DME	**L3**		DMA/THF = 2:1	39
18[d]	$NiCl_2$·DME	**L4**		DMA/THF = 2:1	35
19[d]	$NiCl_2$·DME	**L5**		DMA/THF = 2:1	44
20[d]	$NiCl_2$·DME	**L6**		DMA/THF = 2:1	25
21[d]	$NiCl_2$·DME	**L7**		DMA/THF = 2:1	29
22[d]	$NiCl_2$·DME	**L8**		DMA/THF = 2:1	25
23[d]	$NiCl_2$·DME	**L9**		DMA/THF = 2:1	16
24[d]	$NiCl_2$·DME	**L10**		DMA/THF = 2:1	14
25[d,e]	$NiCl_2$·DME	**L2**		DMA/THF = 2:1	39
26[d]	$NiCl_2$·DME	**L2**	$MgCl_2$	DMA/THF = 2:1	65
27[d,e]	$NiCl_2$·DME	**L2**	$MgCl_2$	DMA/THF = 2:1	61
28[d]	$NiCl_2$·DME	**L2**	LiCl	DMA/THF = 2:1	trace
29[d]	$NiCl_2$·DME	**L2**	LiBr	DMA/THF = 2:1	trace
30[d]	$NiCl_2$·DME	**L2**	NaI	DMA/THF = 2:1	trace
31[d]	$NiCl_2$·DME	**L2**	$ZnCl_2$	DMA/THF = 2:1	11
32[d]	$NiCl_2$·DME	**L2**	$ZnBr_2$	DMA/THF = 2:1	13
33[d]	**$NiCl_2$·DME**	**L2**	**$MgBr_2$**	**DMA/THF = 2:1**	**78**
34[d,f]	$NiCl_2$·DME	**L2**	$MgBr_2$	DMA/THF = 2:1	33
35[d]	$CoCl_2$	**L2**	$MgBr_2$	DMA/THF = 2:1	0
36[d]	$PdCl_2$	**L2**	$MgBr_2$	DMA/THF = 2:1	0
37[d]	$CuCl_2$	**L2**	$MgBr_2$	DMA/THF = 2:1	0
38[d]		**L2**	$MgBr_2$	DMA/THF = 2:1	0
39[d]	$NiCl_2$·DME		$MgBr_2$	DMA/THF = 2:1	0
40[d,g]	$NiCl_2$·DME	**L2**	$MgBr_2$	DMA/THF = 2:1	0



[a]Reaction conditions: **1a** (0.2 mmol, 109.2 mg, 2.0 equiv.), **2a** (0.2 mmol, 30 μL), **3a** (0.3 mmol, 78.6 mg, 1.5 equiv.), Ni cat. (10 mol%), ligand (12 mol%), Mn (3.0 equiv.), additive (1.0 equiv.), solvent (1.5 mL), Ar, 30 °C, and 18 h. [b]*Oxa* = $OCOCO_2Me$. [c]Isolated yield. [d]**1a** (0.4 mmol) was used. [e]Zn as the reductant. [f]Ni cat. (5 mol%), ligand (6 mol%). [g]Without Mn.

Under the optimum conditions of alkylarylation of alkenes (Table S1, entry 33), using **7a** as model substrate (Table S2, entry 1), we obtained the target product **8a** in 15% yield. Similarly, we screened the reaction solvents and found that a mixture of DMA/THF in a 2:1 ratio (v/v) were still the best (entries 2-5). As the addition of additives during the screening of reaction conditions for the alkylarylation of alkenes led to a significant increase in yield, we gave priority to the screening of additives, and found that anhydrous $MgCl_2$ as an additive increased the yield to 26% (entries 6-11). The reaction yield was increased to 50% using the tridentate N-containing ligand **L12** as the ligand (entries 12-22). Screening of Ni salts showed that $Ni(PCy_3)Cl_2$ was the most effective (entries 23-29). Reducing the loadings of catalyst and ligand leads to a decrease in yield (entry 30). Control experiment demonstrated that no reaction occurred in the absence of ligand (entry 31), highlighting the critical role of the ligand in this reaction.

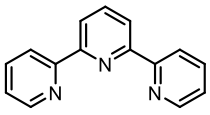
Table S2. Optimization of reaction conditions for alkylarylation of alkynes[a,b]



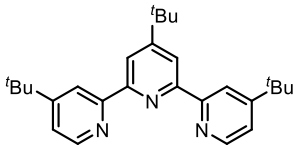
1a **7a** **3a** **8a**

entry	Ni cat.	ligand	additive	solvent	yield(%)[c]
1	$NiCl_2$·DME	**L2**	$MgBr_2$	DMA/THF = 2:1	15
2	$NiCl_2$·DME	**L2**	$MgBr_2$	THF	9
3	$NiCl_2$·DME	**L2**	$MgBr_2$	DMA	11
4	$NiCl_2$·DME	**L2**	$MgBr_2$	DMSO	7
5	$NiCl_2$·DME	**L2**	$MgBr_2$	DMF	10
6	$NiCl_2$·DME	**L2**	$MgCl_2$	DMA/THF = 2:1	26
7[d]	$NiCl_2$·DME	**L2**	$MgCl_2$	DMA/THF = 2:1	21
8	$NiCl_2$·DME	**L2**	$ZnCl_2$	DMA/THF = 2:1	12
9	$NiCl_2$·DME	**L2**	LiBr	DMA/THF = 2:1	0
10	$NiCl_2$·DME	**L2**	LiCl	DMA/THF = 2:1	trace
11	$NiCl_2$·DME	**L2**	NaI	DMA/THF = 2:1	trace
12	$NiCl_2$·DME	**L1**	$MgCl_2$	DMA/THF = 2:1	32
13	$NiCl_2$·DME	**L3**	$MgCl_2$	DMA/THF = 2:1	34
14	$NiCl_2$·DME	**L4**	$MgCl_2$	DMA/THF = 2:1	trace
15	$NiCl_2$·DME	**L5**	$MgCl_2$	DMA/THF = 2:1	35
16	$NiCl_2$·DME	**L6**	$MgCl_2$	DMA/THF = 2:1	40
17	$NiCl_2$·DME	**L7**	$MgCl_2$	DMA/THF = 2:1	0
18	$NiCl_2$·DME	**L8**	$MgCl_2$	DMA/THF = 2:1	trace
19	$NiCl_2$·DME	**L9**	$MgCl_2$	DMA/THF = 2:1	trace
20	$NiCl_2$·DME	**L10**	$MgCl_2$	DMA/THF = 2:1	trace
21	$NiCl_2$·DME	**L11**	$MgCl_2$	DMA/THF = 2:1	26
22	$NiCl_2$·DME	**L12**	$MgCl_2$	DMA/THF = 2:1	50
23	$NiCl_2$	**L12**	$MgCl_2$	DMA/THF = 2:1	48
24	$NiBr_2$	**L12**	$MgCl_2$	DMA/THF = 2:1	43

25	NiI_2	**L12**	$MgCl_2$	DMA/THF = 2:1	40
26	$Ni(acac)_2$	**L12**	$MgCl_2$	DMA/THF = 2:1	56
27	$Ni(COD)_2$	**L12**	$MgCl_2$	DMA/THF = 2:1	46
28	$Ni(PPh_3)Cl_2$	**L12**	$MgCl_2$	DMA/THF = 2:1	57
29	**$Ni(PCy_3)Cl_2$**	**L12**	**$MgCl_2$**	**DMA/THF = 2:1**	**62**
30[e]	$Ni(PCy_3)Cl_2$	**L12**	$MgCl_2$	DMA/THF = 2:1	57
31	$Ni(PCy_3)Cl_2$		$MgCl_2$	DMA/THF = 2:1	0



L11

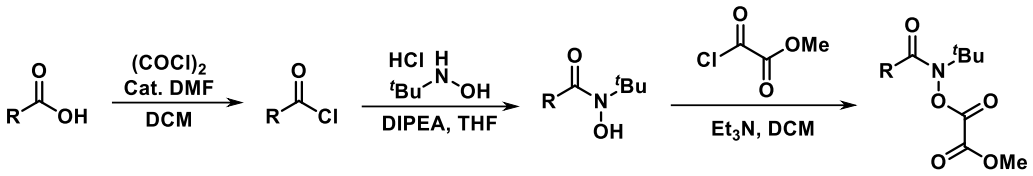


L12

[a]Reaction conditions: **1a** (0.2 mmol, 109.2 mg, 2.0 equiv.), **7a** (0.2 mmol, 22 μL), **3a** (0.3 mmol, 78.6 mg, 1.5 equiv.), Ni cat. (10 mol%), ligand (12 mol%), Mn (3.0 equiv.), additive (1.0 equiv.), solvent (1.5 mL), Ar, 30 °C, and 18 h. [b]*Oxa* = $OCOCO_2Me$. [c]Isolated yield. [d]Zn as the reductant. [e]Ni cat. (5 mol%), ligand (6 mol%).

3. General procedure

3.1 General procedure for preparation of *O*-oxalate hydroxamic acid esters compounds 1



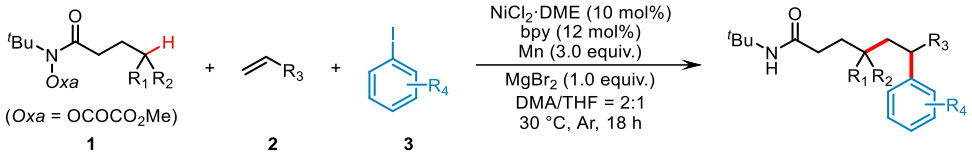
O-oxalate hydroxamic acid esters substrates were prepared by following the literature report[2]

Step 1: To a solution of carboxylic acid (1.0 equiv.) and 3-5 drops of anhydrous DMF in anhydrous CH_2Cl_2 (0.5 M) at 0 ℃, oxalyl chloride (1.5 equiv.) was added dropwise over 10 minutes. The reaction was vigorously stirred at room temperature for 3 h. The solvent was removed in vacuum. Anhydrous CH_2Cl_2 was added to remove the residual of oxalyl chloride in vacuum. Then the resulting acyl chloride was redissolved in anhydrous acetonitrile and used directly for the next step without further purification.

Step 2: A solution of the *N*-(*tert*-butyl)hydroxylamine hydrochloride in anhydrous THF (0.4 M) was cooled to 0 ℃, treated with DIPEA (2.0 equiv.) and stirred for 15 minutes. The acyl chloride (1.0 equiv.) in anhydrous acetonitrile was added dropwise over 15 minutes and the mixture was allowed to warm to room temperature overnight. The mixture was diluted with saturated $NaHCO_3$ and EtOAc and the layers were separated. The aqueous layer was extracted twice with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine, successively, and then evaporated. Purification by column chromatography on silica gel eluting with petroleum ether and EtOAc gave the hydroxylamine.

Step 3: To a solution of hydroxylamine in anhydrous CH_2Cl_2 (0.35 M) at 0 ℃, Et_3N (1.5 equiv.) was added dropwise. Methyl oxalyl chloride (1.5 equiv.) was then added dropwise over 10 minutes. The reaction was vigorously stirred at room temperature for 4 h. The mixture was diluted with saturated $NaHCO_3$ and CH_2Cl_2 and the layers were separated. The aqueous layer was extracted twice with CH_2Cl_2 and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine, successively, and then evaporated. Purification by column chromatography on silica gel eluting with petroleum ether and EtOAc gave the *O*-oxalate hydroxamic acid esters compounds **1**.

3.2 General procedure for nickel-catalyzed reductive alkylarylation of alkenes

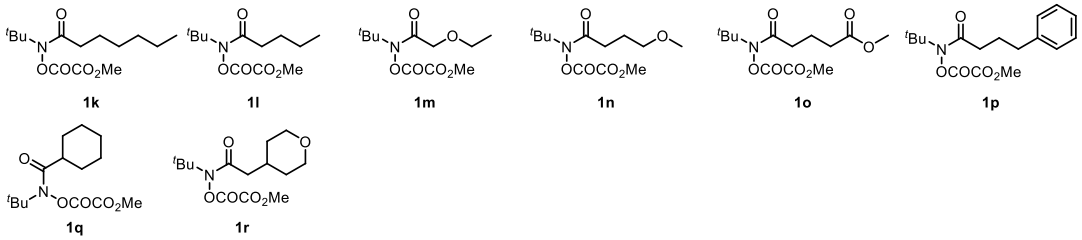


In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added aryl iodides **3** (0.3 mmol, 1.5 equiv.), $NiCl_2$·DME (10 mol%, 4.4 mg), bpy (12 mol%, 3.7 mg), Mn powder (0.6 mmol, 33 mg, 3.0 equiv.) and $MgBr_2$ (0.2 mmol, 36.8 mg, 1.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1) was injected via a syringe. The mixture was allowed to stirred (1000 rpm) at 30 ℃ for approximately 15 minute before *O*-oxalate hydroxamic acid esters **1** (0.4 mmol, 2.0 equiv.) and alkenes **2** (0.2 mmol) were added immediately. The reaction was stirred (1000 rpm) at 30 ℃ for 18 hours. After the reaction was complete as judged by TLC analysis, the mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. The filtrate was concentrated under reduced pressure. The resulting reaction mixture was purified by column chromatography on silica gel to afford the desired product.

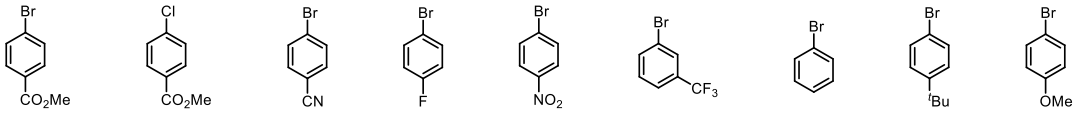
Note: *keeping a stirring speed at 1000 rpm and reaction temperature around 30 ℃ is necessary for reproducibility. In addition, pre-stirring must be carried out before adding **1** and **2**.*

Table S3. Unsuccessful or poor resultant substrates

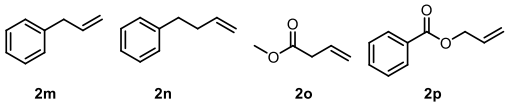
O-oxalate hydroxamic acid esters containing secondary carbon reactive sites were investigated and all showed worse results.



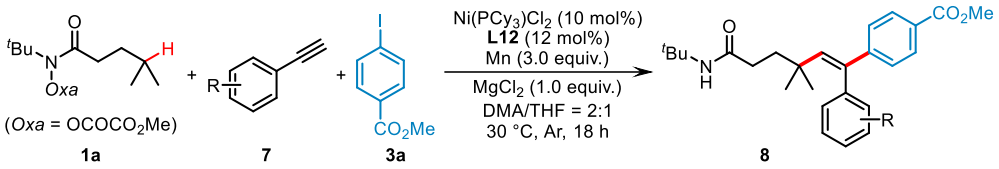
Unsuccessful aryl bromides and aryl chlorides



Unsuccessful unactivated alkenes acceptors



3.3 General procedure for nickel-catalyzed reductive alkylarylation of alkynes

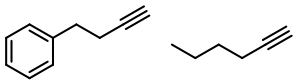


In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added methyl 4-iodobenzoate **3a** (0.3 mmol, 78.6 mg, 1.5 equiv.), $Ni(PCy_3)Cl_2$ (10 mol%, 13.8 mg), **L12** (12 mol%, 9.7 mg), Mn powder (0.6 mmol, 33 mg, 3.0 equiv.) and $MgCl_2$ (0.2 mmol, 19 mg, 1.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1) was injected via a syringe. The mixture was allowed to stirred (1000 rpm) at 30 ℃ for approximately 15 minute before *O*-oxalate hydroxamic acid esters **1a** (0.4 mmol, 109.2 mg, 2.0 equiv.) and alkynes **7** (0.2 mmol) were added. The reaction was stirred (1000 rpm) at 30 ℃ for 18 hours. After the reaction was complete as judged by TLC analysis, the mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. The filtrate was concentrated under reduced pressure. The resulting reaction mixture was purified by column chromatography on silica gel to afford the desired product.

Note: *keeping a stirring speed at 1000 rpm and reaction temperature around 30 ℃ is necessary for reproducibility. In addition, pre-stirring must be carried out before adding* ***1a*** *and* ***7****.*

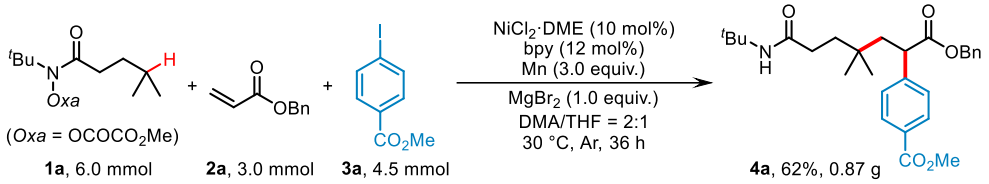
Table S4. Unsuccessful substrates

Unsuccessful unactivated alkynes acceptors



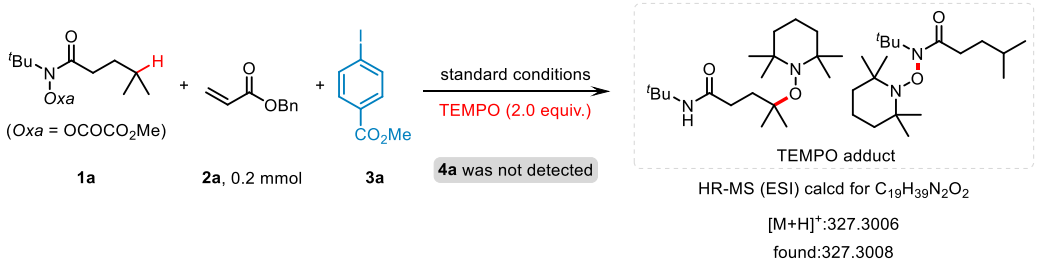
7l **7m**

3.4 General procedure for scale-up preparation



In an argon-filled glove box, to a 100 mL pre-dried round bottom flask equipped with a stir bar were added methyl 4-iodobenzoate **3a** (4.5 mmol, 1.179 g, 1.5 equiv.), $NiCl_2$·DME (10 mol%, 66 mg), bpy (12 mol%, 55.5 mg), Mn powder (9.0 mmol, 495 mg, 3.0 equiv.) and $MgBr_2$ (3.0 mmol, 552 mg, 1.0 equiv.). The flask was capped tightly with a rubber septum and taken out of the glovebox. Then, 22.5 mL anhydrous solvent (DMA/THF = 2/1) was injected via a syringe. The mixture was allowed to stirred (1000 rpm) at 30 ℃ for approximately 30 minute before *O*-oxalate hydroxamic acid esters **1a** (6.0 mmol, 1.638 mg, 2.0 equiv.) and benzyl acrylate **2a** (3.0 mmol, 450 μL) were added. The reaction was stirred (1000 rpm) at 30 ℃ for 36 hours. After the reaction was complete as judged by TLC analysis, the mixture was quenched by adding 100 mL of saturated aqueous NaCl and 100 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 100 mL) and dried. The filtrate was concentrated under reduced pressure. The resulting reaction mixture was purified by column chromatography on silica gel to afford the desired product **4a**.

3.5 General procedure for radical trapping experiments



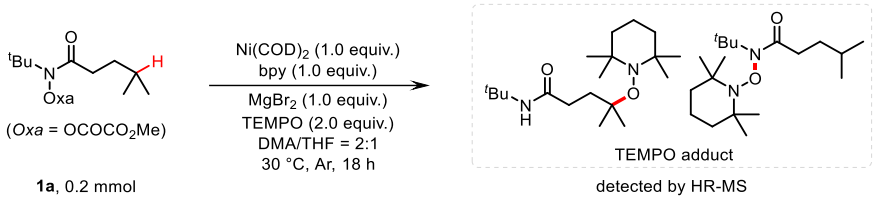
HR-MS (ESI) calcd for $C_{19}H_{39}N_2O_2$

$[M+H]^+$:327.3006

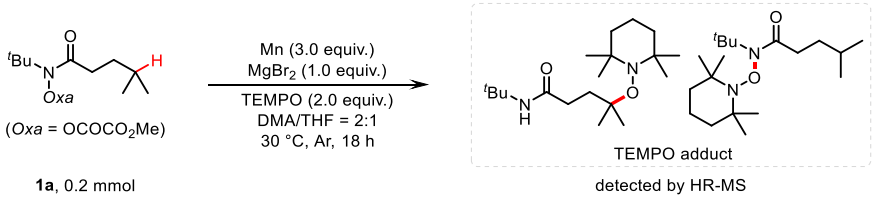
found:327.3008

In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added methyl 4-iodobenzoate **3a** (0.3 mmol, 78.6 mg, 1.5 equiv.), $NiCl_2$·DME (10 mol%, 4.4 mg), bpy (12 mol%, 3.7 mg), Mn powder (0.6 mmol, 33 mg, 3.0 equiv.), $MgBr_2$ (0.2 mmol, 36.8 mg, 1.0 equiv.) and TEMPO (0.4 mmol, 62.5 mg, 2.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1) was injected via a syringe. The mixture was allowed to stirred (1000 rpm) at 30 ℃ for approximately 15 minute before *O*-oxalate hydroxamic acid esters **1a** (0.4 mmol, 109.2 mg, 2.0 equiv.) and benzyl acrylate **2a** (0.2 mmol, 30 μL) were added immediately. The reaction was stirred (1000 rpm) at 30 ℃ for 18 hours. The mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. After concentration under reduced pressure, the mixture was analyzed by HR-MS. It was found that the reaction was completely suppressed by adding TEMPO and the TEMPO-adduct was detected by HR-MS.

3.6 General procedure for studying the generation of radical

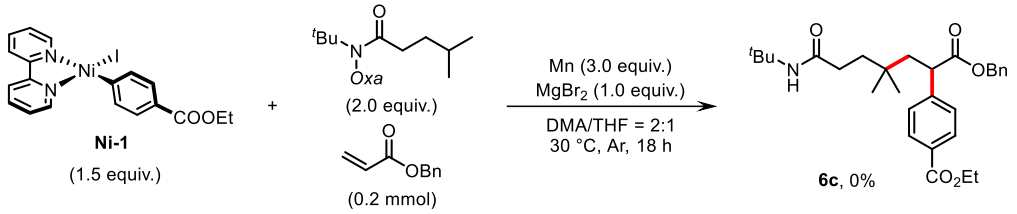


In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added $Ni(COD)_2$ (0.2 mmol, 55 mg, 1.0 equiv.), bpy (0.2 mmol, 31.3 mg, 1.0 equiv.), $MgBr_2$ (0.2 mmol, 36.8 mg, 1.0 equiv.) and TEMPO (0.4 mmol, 62.5 mg, 2.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1) and *O*-oxalate hydroxamic acid esters **1a** (0.2 mmol, 54.6 mg) was injected via a syringe. The mixture was stirred (1000 rpm) at 30 ℃ for 18 hours. The mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. After concentration under reduced pressure, the TEMPO-adduct was detected by HR-MS.

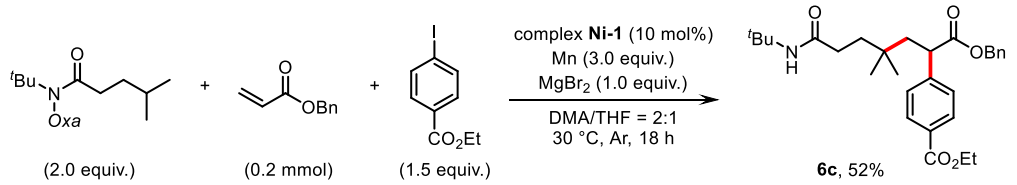


In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added Mn powder (0.6 mmol, 33 mg, 3.0 equiv.), $MgBr_2$ (0.2 mmol, 36.8 mg, 1.0 equiv.) and TEMPO (0.4 mmol, 62.5 mg, 2.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1) and *O*-oxalate hydroxamic acid esters **1a** (0.2 mmol, 54.6 mg) were injected via a syringe. The mixture was stirred (1000 rpm) at 30 ℃ for 18 hours. The mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. After concentration under reduced pressure, the TEMPO-adduct was detected by HR-MS.

3.7 General procedure for stoichiometric reactions of complex Ni-1



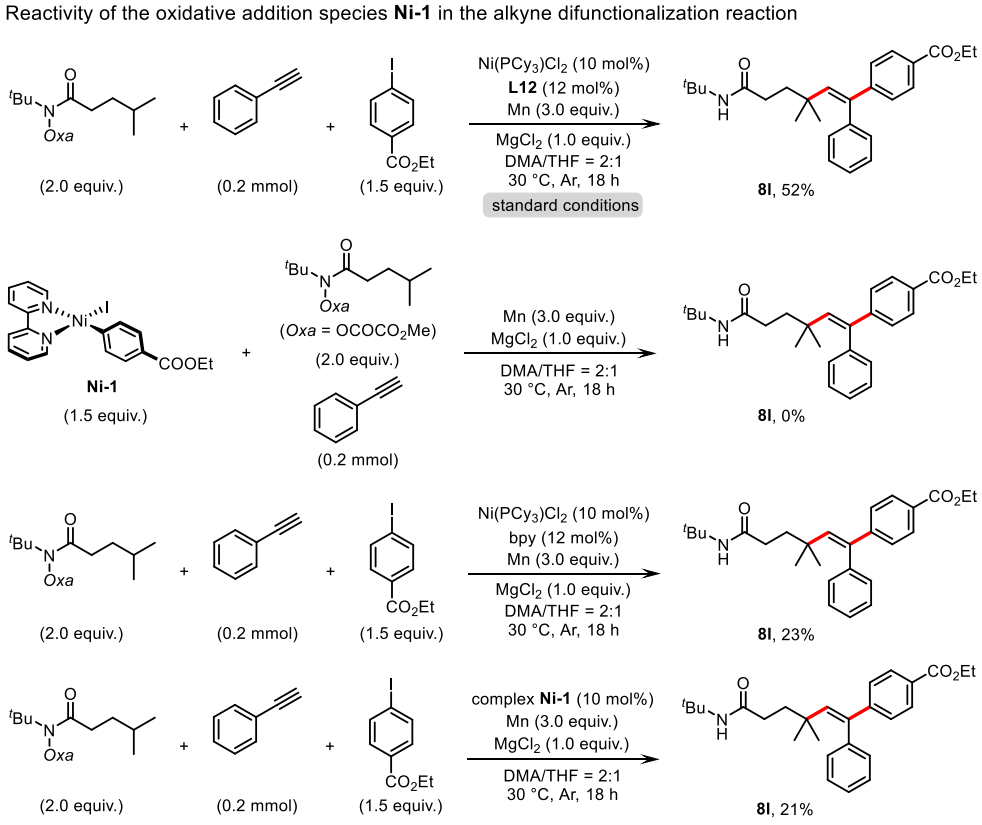
In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added complex **Ni-1** (0.3 mmol, 147.3 mg, 1.5 equiv.), Mn powder (0.6 mmol, 33 mg, 3.0 equiv.), and $MgBr_2$ (0.2 mmol, 36.8 mg, 1.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1), *O*-oxalate hydroxamic acid esters **1a** (0.4 mmol, 109.2 mg, 2.0 equiv.) and benzyl acrylate **2a** (0.2 mmol, 30 μL) were added via a syringe. The reaction was stirred (1000 rpm) at 30 ℃ for 18 hours. The mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. After concentration under reduced pressure, the mixture was analyzed by TLC, which revealed that the difunctionalization product **6c** was not formed.



In an argon-filled glove box, to a 10 mL pre-dried schlenk tube equipped with a stir bar were added complex **Ni-1** (10 mol%, 9.8 mg), Mn powder (0.6 mmol, 33 mg, 3.0 equiv.), and $MgBr_2$ (0.2 mmol, 36.8 mg, 1.0 equiv.). The vial was capped tightly with a rubber septum and taken out of the glovebox. Then, 1.5 mL anhydrous solvent (DMA/THF = 2/1) and ethyl 4-iodobenzoate (0.3 mmol, 51 μL, 1.5 equiv.) were injected via a syringe. The mixture was allowed to stirred (1000 rpm) at 30 ℃ for approximately 3 minute before *O*-oxalate hydroxamic acid esters **1a** (0.4 mmol, 109.2 mg, 2.0 equiv.) and benzyl acrylate **2a** (0.2 mmol, 30 μL) were added immediately. The reaction was stirred (1000 rpm) at 30 ℃ for 18 hours. The mixture was quenched by adding 20 mL of saturated aqueous NaCl and 20 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL) and dried. After concentration under reduced pressure, the residue was purified by chromatography on silica gel to give product **6c** in a yield of 52%.

Note: *The deep red complex **Ni-1** was synthesized according to the reported method.*[3] *It is unstable and quickly converted to the dimer, therefore it was generated and used immediately.*

3.8 The reactivity of complex Ni-1 in the alkyne difunctionalization reaction.



We investigated the reactivity of complex **Ni-1** in the alkyne bifunctionalization reaction and no detectable amount of **8l** was observed in the stoichiometric reaction of **Ni-1** with hydroxamic ester **1a** and phenylacetylene **7a**, which is similar to the results for the alkene difunctionalization reaction. Considering that 2,2'-bipyridine (bpy) was not the optimal ligand for the alkyne difunctionalization reaction, a control experiment was performed using catalytic $Ni(PCy_3)Cl_2$ and bpy as the ligand, and the product **8l** was isolated in 23% yield. When 10 mol% of **Ni-1** was used as the catalyst, the desired product **8l** was obtained in a 21% yield.

3.9 References

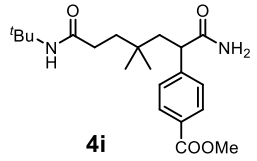
1 Z. Zhu, Y. Gong, W. Tong, W. Xue and H. Gong, *Org. Lett.*, 2021, **23**, 2158-2163.

2 Z.-Y. Liu and S. P. Cook, *Org. Lett.*, 2022, **24**, 3313-3318.

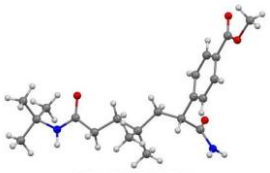
3 H. Chen, L. Hu, W. Ji, L. Yao and X. Liao, *ACS Catal.*, 2018, **8**, 10479-10485.

4. X-ray single crystal diffraction data of 4i

Sample preparation: The pure compound was dissolved in a vial (10 mL) containing MeOH and covered with a lid. Then put the vial in the freezer (2 - 8 ℃) for about a week, during which the crystal was formed. The X-ray was detected after the crystal was formed. The crystal was measured on a ' Rigaku XtaLAB Synergy-DW ' diffractometer.



4i



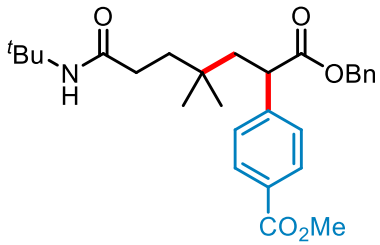
CCDC 2388081

Bond precision:	C-C = 0.0108 A		Wavelength= 0.71073
Cell:	a=6.815 (4)	b=9.609 (5)	c=33.961 (19)
	alpha=90.897(11)	beta=90.084 (10)	gamma=95.582 (11)
Temperature:	296 K		
	Calculated		Reported
Volume	2213 (2)		2213 (2)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C21 H32 N2 O4		?
Sum formula	C21 H32 N2 O4		C21 H32 N2 O4
Mr	376.49		376.48
Dx,g cm^{-3}	1.130		1.130
Z	4		4
Mu (mm-1)	0.078		0.078
F000	816.0		816.0
F000’	816.37		
h,k,lmax	8,11,40		8,11,40
Nref	7796		7646
Tmin,Tmax	0.981,0.985		0.482,0.746
Tmin’	0.977		

Correction method= # Reported T Limits: Tmin=0.482 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.981	Theta(max)= 25.000
R(reflections)= 0.1162(2855)	wR2(reflections)= 0.3174(7646)
S = 1.037	Npar= 500

5. Characterization Data



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4a)

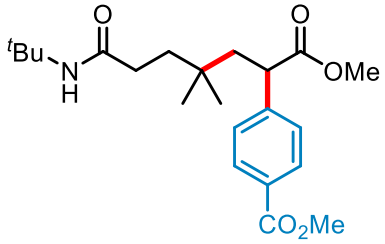
Colorless oil, yield: 78%, 72.9 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.21 (dd, *J* = 7.2, 2.2 Hz, 2H), 5.30 (s, 1H), 5.12 – 5.01 (m, 2H), 3.90 (s, 3H), 3.78 (dd, *J* = 8.8, 3.9 Hz, 1H), 2.33 (dd, *J* = 14.2, 8.8 Hz, 1H), 2.09 – 2.01 (m, 1H), 2.00 – 1.92 (m, 1H), 1.60 – 1.50 (m, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 172.4, 166.7, 145.6, 135.4, 129.9, 129.0, 128.4, 128.2, 128.0, 127.9, 66.9, 52.0, 50.9, 47.6, 44.5, 37.3, 33.2, 32.5, 28.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{38}NO_5^+$ 468.2744; found 468.2727.



methyl 4-(7-(*tert*-butylamino)-1-methoxy-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4b)

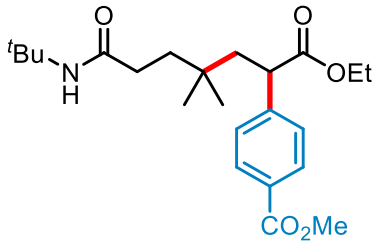
Colorless oil, yield: 74%, 57.9 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.37 (s, 1H), 3.90 (s, 3H), 3.74 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.65 (s, 3H), 2.32 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.10 – 2.04 (m, 1H), 2.02 – 1.94 (m, 1H), 1.58 – 1.49 (m, 3H), 1.33 (s, 9H), 0.87 (d, *J* = 5.1 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 172.4, 166.7, 145.7, 129.9, 129.0, 127.8, 52.2, 52.0, 50.9, 47.4, 44.6, 37.2, 33.2, 32.5, 28.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{34}NO_5^+$ 392.2431; found 392.2419.



methyl 4-(7-(*tert*-butylamino)-1-ethoxy-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4c)

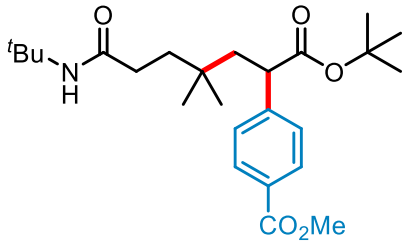
Colorless oil, yield: 74%, 60 mg

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 4.17 – 4.09 (m, 1H), 4.10 – 4.03 (m, 1H), 3.90 (s, 3H), 3.72 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.32 (dd, *J* = 14.2, 9.0

Hz, 1H), 2.11 – 2.03 (m, 1H), 2.02 – 1.95 (m, 1H), 1.57 – 1.49 (m, 3H), 1.33 (s, 9H), 1.19 (t, J = 7.1 Hz, 3H), 0.87 (d, J = 4.4 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 172.5, 166.7, 145.9, 129.8, 128.9, 127.7, 61.0, 52.0, 50.9, 47.6, 44.6, 37.2, 33.2, 32.5, 28.7, 26.9, 26.8, 13.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{36}NO_5^+$ 406.2588; found 406.2574.



methyl 4-(1-(*tert*-butoxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4d)

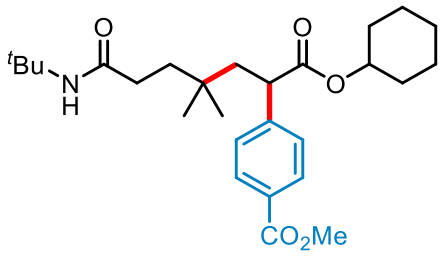
Colorless oil, yield: 72%, 62.4 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 5.33 (s, 1H), 3.90 (s, 3H), 3.61 (dd, J = 8.9, 3.6 Hz, 1H), 2.28 (dd, J = 14.2, 8.9 Hz, 1H), 2.11 – 2.04 (m, 1H), 2.02 – 1.94 (m, 1H), 1.58 – 1.54 (m, 2H), 1.51 – 1.48 (m, 1H), 1.35 (s, 9H), 1.32 (s, 9H), 0.88 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 172.5, 166.8, 146.6, 129.8, 128.7, 127.7, 80.8, 51.9, 50.9, 48.7, 44.4, 37.3, 33.2, 32.5, 28.7, 27.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{40}NO_5^+$ 434.2901; found 434.2887.



methyl 4-(7-(*tert*-butylamino)-1-(cyclohexyloxy)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4e)

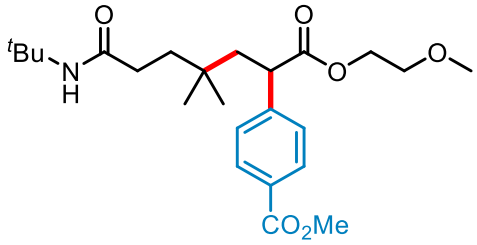
Colorless oil, yield: 77%, 70.8 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 5.39 (s, 1H), 4.70 (dt, J = 8.8, 4.7 Hz, 1H), 3.90 (s, 3H), 3.69 (dd, J = 9.1, 3.6 Hz, 1H), 2.33 (dd, J = 14.2, 9.1 Hz, 1H), 2.11 – 2.03 (m, 1H), 2.03 – 1.94 (m, 1H), 1.84 – 1.77 (m, 1H), 1.73 – 1.63 (m, 2H), 1.61 – 1.52 (m, 4H), 1.51 – 1.39 (m, 3H), 1.36 – 1.31 (m, 10H), 1.29 – 1.24 (m, 2H), 0.88 (d, J = 3.9 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 172.5, 166.7, 146.2, 129.8, 128.8, 127.7, 73.1, 51.9, 50.9, 47.9, 44.3, 37.3, 33.2, 32.5, 31.2, 31.0, 28.7, 26.9, 26.9, 25.2, 23.5, 23.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{42}NO_5^+$ 460.3057; found 460.3042.



methyl 4-(7-(*tert*-butylamino)-1-(2-methoxyethoxy)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate

(4f)

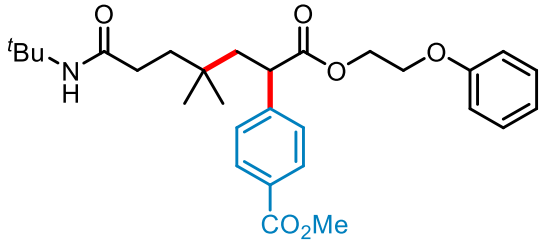
Colorless oil, yield: 68%, 59.2 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.32 (s, 1H), 4.32 – 4.23 (m, 1H), 4.20 – 4.05 (m, 1H), 3.90 (d, *J* = 1.3 Hz, 3H), 3.77 (dd, *J* = 8.9, 3.8 Hz, 1H), 3.54 – 3.44 (m, 2H), 3.29 (s, 3H), 2.32 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.15 – 2.01 (m, 1H), 2.01 – 1.93 (m, 1H), 1.59 – 1.45 (m, 3H), 1.32 (s, 9H), 0.87 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 172.5, 166.7, 145.7, 129.9, 129.0, 127.9, 70.2, 64.0, 58.8, 52.1, 51.0, 47.6, 44.6, 37.3, 33.3, 32.5, 28.7, 27.0, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{38}NO_6^+$ 436.2694; found 436.2677.



methyl 4-(7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxo-1-(2-phenoxyethoxy)heptan-2-yl)benzoate (4g)

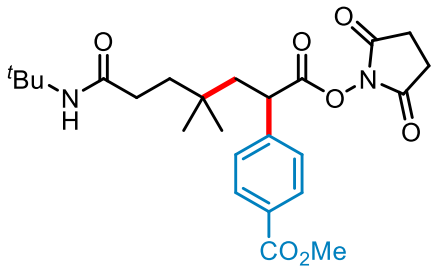
Yellow oil, yield: 55%, 54.8 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.01 – 6.89 (m, 1H), 6.82 (dt, *J* = 7.8, 1.0 Hz, 2H), 5.30 (s, 1H), 4.50 – 4.41 (m, 1H), 4.38 – 4.27 (m, 1H), 4.17 – 4.04 (m, 2H), 3.89 (s, 3H), 3.77 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.32 (dd, *J* = 14.2, 9.0 Hz, 1H), 2.11 – 2.02 (m, 1H), 2.01 – 1.89 (m, 1H), 1.58 – 1.45 (m, 3H), 1.31 (s, 9H), 0.86 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 172.4, 166.6, 158.2, 145.5, 129.9, 129.4, 129.0, 127.8, 121.1, 114.5, 65.4, 63.3, 52.0, 50.9, 47.6, 44.6, 37.3, 33.2, 32.4, 28.7, 26.9, 26.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{40}NO_6^+$ 498.2850; found 498.2832.



methyl 4-(7-(*tert*-butylamino)-1-((2,5-dioxopyrrolidin-1-yl)oxy)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4h)

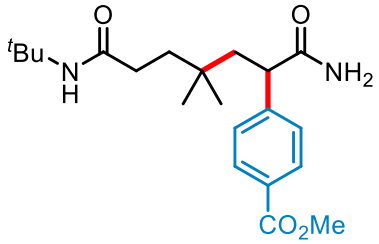
Yellow oil, yield: 31%, 29.4 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.34 (s, 1H), 4.02 (dd, *J* = 7.9, 4.4 Hz, 1H), 3.90 (s, 3H), 2.85 – 2.66 (m, 4H), 2.36 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.10 – 2.03 (m, 1H), 2.02 – 1.95 (m, 1H), 1.71 (dd, *J* = 14.4, 4.4 Hz, 1H), 1.64 – 1.51 (m, 2H), 1.32 (s, 9H), 0.92 (d, *J* = 9.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 169.5, 166.5, 143.4, 130.2, 129.7, 128.0, 52.1, 51.0, 45.1, 44.6, 37.2, 33.4, 32.5, 28.7, 26.9, 26.7, 25.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{35}N_2O_7^+$ 475.2439; found 475.2434.



methyl 4-(1-amino-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (4i)

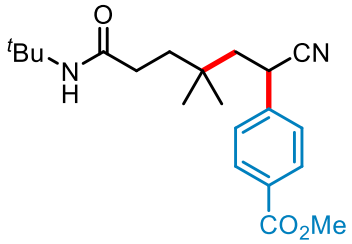
White solid (m. p. 232-234 ℃), yield: 63%, 47.4 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.93 (d, J = 8.3 Hz, 2H), 7.65 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.35 (s, 1H), 6.86 (s, 1H), 3.89 (s, 3H), 3.72 (dd, J = 8.8, 3.5 Hz, 1H), 2.25 (dd, J = 13.9, 8.8 Hz, 1H), 2.09 – 1.91 (m, 2H), 1.45 (t, J = 7.5, 6.9, 3.8 Hz, 2H), 1.38 (dd, J = 13.9, 3.6 Hz, 1H), 1.26 (s, 9H), 0.86 (s, 6H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 175.0, 172.6, 166.6, 149.2, 129.6, 128.3, 128.1, 52.5, 50.1, 47.6, 44.7, 38.0, 33.6, 31.8, 29.0, 27.1, 27.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{33}N_2O_4^+$ 377.2435; found 377.2422.



methyl 4-(6-(*tert*-butylamino)-1-cyano-3,3-dimethyl-6-oxohexyl)benzoate (4j)

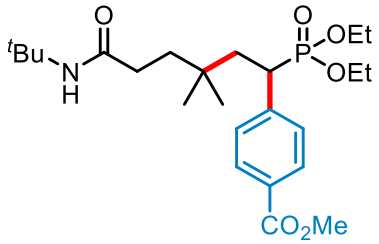
Colorless oil, yield: 51%, 36.6 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 5.50 (s, 1H), 3.93 (s, 3H), 3.86 (dd, J = 10.5, 3.2 Hz, 1H), 2.20 – 2.11 (m, 1H), 2.09 – 2.01 (m, 2H), 1.78 – 1.64 (m, 2H), 1.60 (dd, J = 14.5, 3.3 Hz, 1H), 1.33 (s, 9H), 1.04 (d, J = 12.1 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 166.3, 142.3, 130.5, 129.9, 127.2, 121.5, 52.2, 51.1, 47.6, 37.0, 33.5, 32.7, 32.6, 28.7, 27.2, 26.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{31}N_2O_3^+$ 359.2329; found 359.2317.



methyl 4-(6-(*tert*-butylamino)-1-(diethoxyphosphoryl)-3,3-dimethyl-6-oxohexyl)benzoate (4k)

Colorless oil, yield: 54%, 50.7 mg

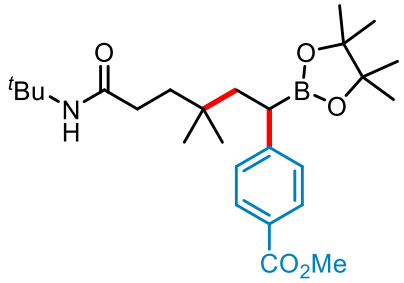
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 5.44 (s, 1H), 4.08 (qd, J = 7.3, 2.5 Hz, 4H), 3.90 (s, 3H), 3.33 (dd, J = 7.7, 4.4 Hz, 1H), 2.37 (dd, J = 14.3, 7.7 Hz, 1H), 1.72 – 1.51 (m, 4H), 1.47 (dd, J = 14.3, 4.4 Hz, 1H), 1.32 (td, J = 7.1, 4.9 Hz, 6H), 1.26 (s, 9H), 0.84 (d, J = 24.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 166.9, 147.6, 130.0, 128.7, 127.5, 61.5 (d, *J* = 6.5 Hz), 52.0, 51.3, 49.9, 44.1, 33.7 (d, *J* = 4.7 Hz), 33.5 (d, *J* = 16.6 Hz), 28.5, 26.8, 26.6, 20.5 (d, *J* = 141.1 Hz), 16.5 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{41}NO_6P^+$ 470.2666; found 470.2645.



methyl 4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzoate (4l)

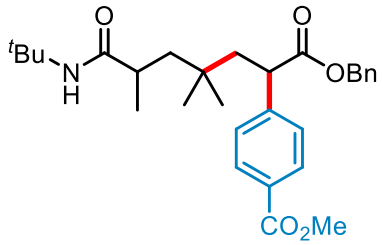
Colorless oil, yield: 67%, 61.6 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 6.5 Hz, 2H), 5.21 (s, 1H), 3.88 (s, 3H), 2.47 (dd, *J* = 8.8, 4.6 Hz, 1H), 2.05 – 1.99 (m, 2H), 1.98 – 1.91 (m, 1H), 1.58 – 1.51 (m, 3H), 1.31 (s, 9H), 1.13 (s, 12H), 0.86 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 167.1, 150.6, 129.6, 128.1, 127.0, 83.4, 51.8, 50.9, 43.7, 37.7, 33.7, 32.7, 28.7, 26.9, 26.9, 24.5, 24.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{43}BNO_5^+$ 460.3229; found 460.3217.



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4,6-trimethyl-1,7-dioxoheptan-2-yl)benzoate (5a)

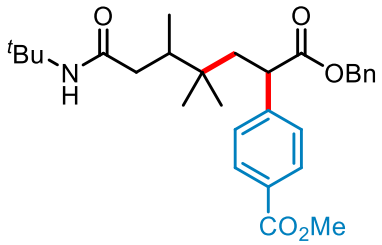
Colorless oil, yield: 57%, 54.9 mg, dr = 3:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.32 – 7.28 (m, 3H), 7.24 – 7.16 (m, 2H), 5.25 (d, *J* = 4.3 Hz, 1H), 5.10 (dd, *J* = 12.4, 2.2 Hz, 1H), 5.02 (dd, *J* = 12.4, 9.4 Hz, 1H), 3.90 (d, *J* = 2.2 Hz, 3H), 3.81 – 3.68 (m, 1H), 2.46 – 2.29 (m, 1H), 2.14 – 2.00 (m, 1H), 1.99 – 1.88 (m, 1H), 1.70 – 1.49 (m, 1H), 1.28 (d, *J* = 12.3 Hz, 9H), 1.15 – 0.99 (m, 4H), 0.89 – 0.76 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 173.9, 173.8, 166.8, 166.8, 145.8, 145.8, 135.5, 129.9, 129.8, 128.9, 128.9, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 66.8, 52.1, 52.0, 50.8, 47.7, 47.6, 45.6, 45.3, 45.1, 45.0, 38.1, 38.1, 33.9, 33.9, 28.6, 27.1, 26.9, 26.8, 26.5, 21.5, 21.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{40}NO_5^+$ 482.2901; found 482.2877.



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4,5-trimethyl-1,7-dioxoheptan-2-yl)benzoate (5b)

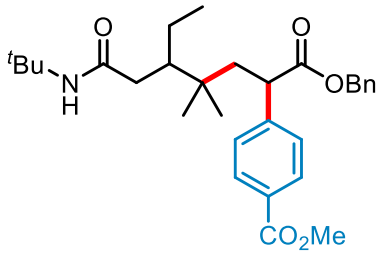
Colorless oil, yield: 55%, 52.9 mg, dr = 1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.39 (dd, *J* = 9.7, 8.3 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.23 – 7.19 (m, 2H), 5.46 – 5.22 (m, 1H), 5.13 – 5.08 (m, 1H), 5.06 – 4.99 (m, 1H), 3.90 (d, *J* = 1.3 Hz, 3H), 3.84 – 3.74 (m, 1H), 2.45 – 2.30 (m, 1.5H), 2.29 – 2.24 (m, 0.5H), 2.00 – 1.83 (m, 1H), 1.68 – 1.52 (m, 2H), 1.34 (d, *J* = 9.7 Hz, 9H), 0.86 (d, *J* = 6.7 Hz, 1.5H), 0.83 – 0.80 (m, 4.5H), 0.77 (d, *J* = 24.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 173.8, 172.3, 172.1, 166.8, 145.8, 145.8, 135.5, 135.4, 129.9, 128.9, 128.9, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 66.9, 66.8, 52.0, 51.1, 51.1, 47.4, 47.3, 43.0, 42.9, 40.0, 38.9, 38.5, 35.7, 35.7, 28.8, 28.7, 24.7, 24.5, 24.2, 23.7, 14.2, 14.1.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{40}NO_5^+$ 482.2901; found 482.2880.



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-5-ethyl-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (5c)

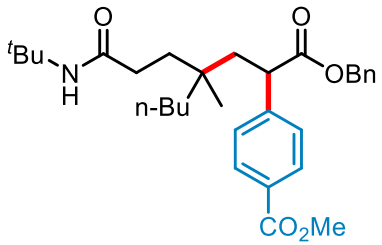
Colorless oil, yield: 49%, 48.6 mg, dr = 1.3:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (t, *J* = 8.7 Hz, 2H), 7.39 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.17 (m, 2H), 5.37 (d, *J* = 6.3 Hz, 0.5H), 5.27 (d, *J* = 6.8 Hz, 0.5H), 5.13 – 5.08 (m, 1H), 5.03 (d, *J* = 12.4 Hz, 1H), 3.90 (d, *J* = 2.4 Hz, 3H), 3.86 – 3.79 (m, 1H), 2.43 – 2.31 (m, 1H), 2.28 – 2.14 (m, 1H), 1.85 – 1.71 (m, 2H), 1.65 – 1.48 (m, 2H), 1.32 (d, *J* = 10.7 Hz, 9H), 1.09 – 0.97 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 1.8H), 0.87 – 0.82 (m, 4.2H), 0.78 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 173.9, 172.5, 172.3, 166.8, 166.8, 146.0, 145.9, 135.5, 135.5, 129.9, 129.9, 128.9, 128.8, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 66.8, 66.8, 52.0, 52.0, 51.0, 50.9, 47.4, 47.3, 45.2, 45.2, 43.2, 42.8, 38.5, 36.8, 36.7, 28.7, 28.7, 25.2, 25.1, 24.2, 24.0, 23.6, 23.4, 13.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{42}NO_5^+$ 496.3057; found 496.3038.



methyl 4-(1-(benzyloxy)-4-(3-(*tert*-butylamino)-3-oxopropyl)-4-methyl-1-oxooctan-2-yl)benzoate (5d)

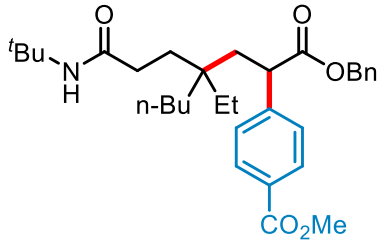
Colorless oil, yield: 58%, 59.1 mg, dr = 1.1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.24 – 7.15 (m, 2H), 5.29 (s, 1H), 5.13 – 4.95 (m, 2H), 3.90 (s, 3H), 3.75 (dd, *J* = 8.6, 3.8 Hz, 1H), 2.31 (dt, *J* = 14.3, 8.0 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.96 – 1.85 (m, 1H), 1.61 – 1.46 (m, 3H), 1.32 (s, 9H), 1.23 – 1.12 (m, 5H), 0.92 – 0.81 (m, 4H), 0.79 (d, *J* = 4.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 172.5, 166.7, 145.7, 135.3, 129.9, 129.0, 128.4, 128.2, 128.0, 127.9, 127.9, 66.9, 66.9, 52.0, 50.9, 47.2, 47.2, 42.4, 42.3, 39.2, 39.1, 35.6, 35.6, 34.7, 34.6, 32.1, 32.1, 28.7, 25.5, 25.5, 24.4, 23.4, 23.4, 14.0, 14.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{31}H_{44}NO_5^+$ 510.3214; found 510.3193.



methyl 4-(1-(benzyloxy)-4-(3-(*tert*-butylamino)-3-oxopropyl)-4-ethyl-1-oxooctan-2-yl)benzoate (5e)

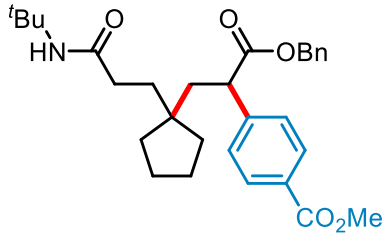
Colorless oil, yield: 46%, 48.2 mg, dr = 1.2:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 5.3, 1.8 Hz, 3H), 7.20 (dd, *J* = 7.0, 2.7 Hz, 2H), 5.29 (d, *J* = 18.7 Hz, 1H), 5.10 – 5.01 (m, 2H), 3.90 (s, 3H), 3.74 – 3.69 (m, 1H), 2.27 (dd, *J* = 14.7, 8.3 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.85 – 1.78 (m, 1H), 1.57 – 1.50 (m, 2H), 1.44 – 1.37 (m, 1H), 1.32 (s, 9H), 1.25 – 1.09 (m, 8H), 0.86 – 0.83 (m, 3H), 0.74 – 0.68 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 173.9, 172.7, 172.6, 166.7, 145.8, 145.8, 135.3, 135.3, 129.9, 129.0, 128.5, 128.2, 128.2, 128.0, 127.9, 66.9, 52.1, 50.9, 46.8, 46.8, 39.3, 39.3, 38.1, 35.3 (d, *J* = 2.1 Hz), 31.8, 31.7, 31.7, 31.7, 28.7, 28.2, 28.2, 24.9, 24.8, 23.4, 14.1, 14.0, 7.4, 7.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{46}NO_5^+$ 524.3370; found 524.3350.



methyl 4-(1-(benzyloxy)-3-(1-(3-(*tert*-butylamino)-3-oxopropyl)cyclopentyl)-1-oxopropan-2-yl)benzoate (5f)

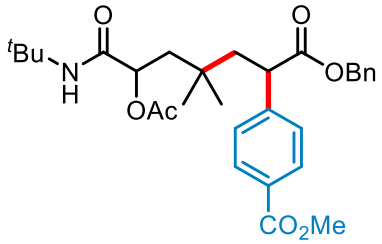
Yellow oil, yield: 66%, 65.2 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.20 (dd, *J* = 6.8, 2.9 Hz, 2H), 5.27 (s, 1H), 5.13 – 4.99 (m, 2H), 3.90 (s, 3H), 3.75 (dd, *J* = 8.1, 4.3 Hz, 1H), 2.44 – 2.31 (m, 1H), 2.12 – 2.00 (m, 1H), 1.91 – 1.82 (m, 1H), 1.68 – 1.51 (m, 7H), 1.40 – 1.24 (m, 13H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 172.5, 166.7, 145.6, 135.3, 129.9, 129.0, 128.4, 128.2, 128.0, 127.9, 66.9, 52.0, 50.9, 48.3, 45.3, 41.3, 37.6, 37.4, 33.3, 33.0, 28.7, 24.0, 23.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{40}NO_5^+$ 494.2901; found 494.2881.



methyl 4-(6-acetoxy-1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (5g)

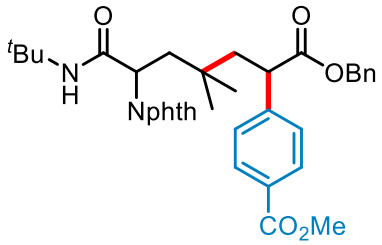
Yellow oil, yield: 45%, 47.3 mg, dr = 1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.21 (dt, *J* = 5.4, 2.7 Hz, 2H), 5.68 (d, *J* = 28.7 Hz, 1H), 5.11 – 5.07 (m, 1H), 5.04 – 4.98 (m, 2H), 3.91 (s, 3H), 3.82 – 3.77 (m, 1H), 2.43 – 2.33 (m, 1H), 2.05 (s, 1.5H), 1.95 (s, 1.5H), 1.79 – 1.69 (m, 2H), 1.67 – 1.58 (m, 1H), 1.32 (d, *J* = 3.1 Hz, 9H), 0.89 (d, *J* = 8.3 Hz, 3H), 0.86 (d, *J* = 2.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 173.6, 170.0, 169.9, 169.3, 169.3, 166.7, 166.7, 145.4, 135.4, 135.3, 130.0, 129.9, 129.1, 129.0, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 72.2, 72.1, 67.0, 66.9, 52.1, 52.1, 51.2, 47.6, 47.6, 45.3, 44.7, 43.2, 42.6, 33.4, 33.3, 28.5, 27.4, 27.2, 27.1, 26.8, 21.0, 20.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{40}NO_7^+$ 526.2799; found 526.2777.



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-6-(1,3-dioxoisoindolin-2-yl)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (5h)

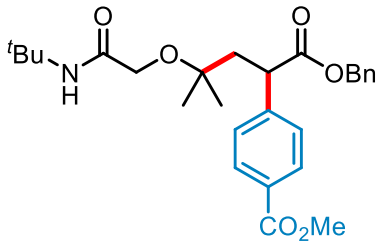
Yellow oil, yield: 38%, 46.6 mg, dr = 1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 1H), 7.85 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.25 (m, 4H), 7.21 – 7.15 (m, 2H), 5.99 (d, *J* = 18.3 Hz, 1H), 5.14 – 4.92 (m, 3H), 4.80 (dd, *J* = 9.4, 3.5 Hz, 0.5H), 4.76 – 4.70 (m, 0.5H), 3.90 (d, *J* = 6.2 Hz, 3H), 3.77 (dd, *J* = 8.7, 4.0 Hz, 0.5H), 3.72 (dd, *J* = 9.3, 3.4 Hz, 0.5H), 2.41 – 2.31 (m, 1.5H), 2.25 (dd, *J* = 14.9, 8.9 Hz, 0.5H), 2.12 (dd, *J* = 14.9, 4.0 Hz, 0.5H), 2.06 – 2.01 (m, 0.5H), 1.68 – 1.58 (m, 1H), 1.29 (d, *J* = 10.0 Hz, 9H), 0.90 (s, 1.5H), 0.87 (d, *J* = 5.6 Hz, 3H), 0.83 (s, 1.5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 173.5, 168.3, 168.3, 168.1, 168.1, 166.8, 166.6, 145.4, 145.0, 135.4, 135.3, 134.3, 134.2, 131.5, 131.4, 129.9, 129.8, 129.0, 128.9, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 67.0, 66.9, 52.6, 52.4, 52.1, 51.5, 51.5, 47.5, 47.5, 45.3, 44.0, 40.3, 39.3, 33.7, 33.6, 28.5, 28.5, 27.0, 26.9, 26.4, 26.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{37}H_{42}NO_7^+$ 613.2908; found 613.2886.



methyl 4-(1-(benzyloxy)-4-(2-(*tert*-butylamino)-2-oxoethoxy)-4-methyl-1-oxopentan-2-yl)benzoate (5i)

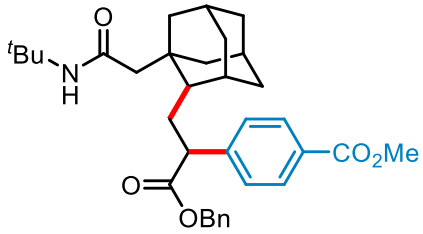
Colorless oil, yield: 51%, 47.9 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.23 – 7.18 (m, 2H), 6.51 (s, 1H), 5.14 – 5.01 (m, 2H), 3.92 – 3.85 (m, 4H), 3.77 – 3.63 (m, 2H), 2.70 (dd, *J* = 14.3, 10.5 Hz, 1H), 1.76 (dd, *J* = 14.3, 2.9 Hz, 1H), 1.39 (s, 9H), 1.21 (d, *J* = 8.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 169.5, 166.7, 144.7, 135.4, 130.0, 129.2, 128.5, 128.3, 127.9, 127.7, 75.7, 66.8, 62.3, 52.1, 50.8, 47.1, 45.2, 28.7, 25.4, 24.1.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_6^+$ 470.2537; found 470.2521.



methyl 4-(1-(benzyloxy)-3-((1S,2S,3R,5R,7S)-1-(2-(*tert*-butylamino)-2-oxoethyl)adamantan-2-yl)-1-oxopropan-2-yl)benzoate (5j)

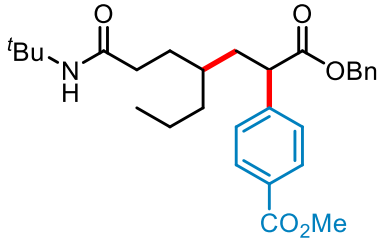
Colorless oil, yield: 47%, 51.3 mg, dr = 1.1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.19 (m, 2H), 5.29 (s, 0.5H), 5.18 – 5.02 (m, 2.5H), 3.91 (s, 3H), 3.78 (dd, *J* = 10.6, 4.7 Hz, 0.5H), 3.72 (dd, *J* = 8.8, 6.5 Hz, 0.5H), 2.17 – 2.06 (m, 1H), 1.97 – 1.83 (m, 4H), 1.80 – 1.66 (m, 6H), 1.65 – 1.49 (m, 6H), 1.44 – 1.42 (m, 1H), 1.35 (s, 4.5H), 1.30 (s, 4.5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 173.1, 170.6, 170.3, 166.9, 166.8, 144.8, 143.8, 135.7, 135.6, 129.9, 129.8, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 66.6, 66.6, 52.1, 52.0, 51.1, 51.1, 49.6, 49.3, 48.7, 48.6, 45.7, 45.0, 42.9, 42.7, 42.7, 38.3, 38.2, 37.2, 37.1, 36.9, 36.7, 35.3, 35.2, 32.4, 30.8, 30.7, 30.6, 30.4, 30.2, 28.8, 28.8, 28.3, 28.1, 28.1.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{34}H_{43}NO_5Na^+$ 568.3033; found 568.3012.



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-1,7-dioxo-4-propylheptan-2-yl)benzoate (5k)

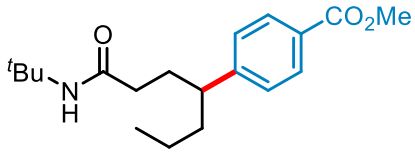
Colorless oil, dr = 1.1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 5.31 (s, 0.53H), 5.16 (s, 0.47H), 5.11 (dd, *J* = 12.4, 3.7 Hz, 1H), 5.06 (dd, *J* = 12.4, 7.9 Hz, 1H), 3.91 (s, 3H), 3.81 (dt, *J* = 10.6, 7.3 Hz, 1H), 2.11 – 2.02 (m, 2H), 2.01 – 1.90 (m, 1H), 1.82 – 1.68 (m, 1H), 1.67 – 1.47 (m, 3H), 1.31 (d, *J* = 17.4 Hz, 9H), 1.26 – 1.16 (m, 4H), 0.82 (dt, *J* = 17.6, 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 173.3, 172.3, 172.1, 166.8, 166.8, 144.3, 144.3, 135.6, 135.6, 129.9, 129.1, 129.1, 128.5, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 66.7, 66.7, 52.1, 51.0, 49.2, 49.2, 37.5, 37.4, 35.7, 35.3, 34.8, 34.7, 34.6, 34.4, 29.1, 29.0, 28.8, 28.7, 19.4, 19.2, 14.3, 14.2.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{40}NO_5^+$ 482.2901; found 482.2906.



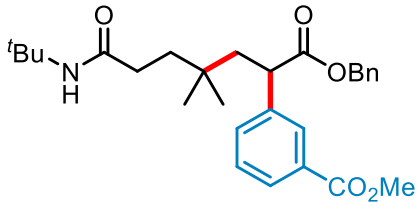
methyl 4-(1-(*tert*-butylamino)-1-oxoheptan-4-yl)benzoate (5k')

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.09 (s, 1H), 3.91 (s, 3H), 2.60 (dt, *J* = 9.7, 4.8 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.91 – 1.76 (m, 3H), 1.68 – 1.52 (m, 2H), 1.30 (s, 9H), 1.22 – 1.07 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 167.0, 150.8, 129.7, 128.1, 127.8, 52.0, 51.0, 45.2, 39.0, 35.3, 32.0, 28.7, 20.5, 14.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{30}NO_3^+$ 320.2220; found 320.2223.



methyl 3-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (6a)

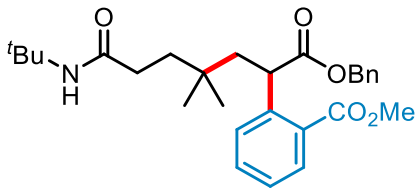
Colorless oil, yield: 77%, 72 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 5.4 Hz, 3H), 7.24 – 7.19 (m, 2H), 5.36 (s, 1H), 5.14 – 5.07 (m, 1H), 5.07 – 4.99 (m, 1H), 3.91 (s, 3H), 3.78 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.35 (dd, *J* = 14.2, 9.0 Hz, 1H), 2.09 – 2.02 (m, 1H), 2.01 – 1.93 (m, 1H), 1.59 – 1.50 (m, 3H), 1.32 (s, 9H), 0.85 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 172.4, 166.7, 140.8, 135.4, 132.4, 130.4, 128.9, 128.7, 128.4, 128.1, 128.0, 66.8, 52.0, 50.9, 47.3, 44.5, 37.3, 33.2, 32.5, 28.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{38}NO_5^+$ 468.2744; found 468.2726.



methyl 2-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (6b)

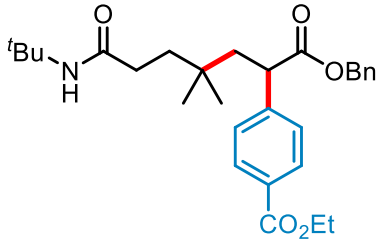
Colorless oil, yield: 31%, 29 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.16 (dd, *J* = 7.3, 2.3 Hz, 2H), 5.66 (s, 1H), 5.07 – 4.99 (m, 2H), 4.80 (dd, *J* = 8.7, 3.4 Hz, 1H), 3.84 (s, 3H), 2.36 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.06 – 1.94 (m, 2H), 1.65 – 1.57 (m, 1H), 1.57 – 1.51 (m, 2H), 1.33 (s, 9H), 0.86 (d, *J* = 10.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 173.1, 168.4, 141.3, 135.7, 132.1, 130.4, 129.6, 129.0, 128.3, 127.9, 127.7, 126.8, 66.6, 52.3, 50.8, 43.7, 42.2, 37.6, 33.5, 33.1, 28.8, 27.5, 27.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{38}NO_5^+$ 468.2744; found 468.2726.



ethyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (6c)

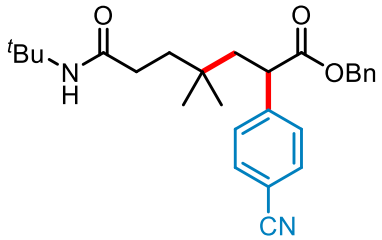
Colorless oil, yield: 82%, 78 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.21 (dd, *J* = 7.4, 2.1 Hz, 2H), 5.32 (s, 1H), 5.12 – 5.07 (m, 1H), 5.06 – 5.00 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.78 (dd, *J* = 8.7, 4.0 Hz, 1H), 2.33 (dd, *J* = 14.2, 8.7 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.99 – 1.93 (m, 1H), 1.60 – 1.46 (m, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 172.4, 166.2, 145.5, 135.3, 129.8, 129.3, 128.4, 128.1, 128.0, 127.8, 66.8, 60.8, 50.9, 47.6, 44.5, 37.2, 33.2, 32.4, 28.7, 26.9, 26.8, 14.2.

HRMS (ESI) *m/z*: [M + H]+ Calcd for $C_{29}H_{40}NO_5^+$ 482.2901; found 482.2882.



benzyl 7-(*tert*-butylamino)-2-(4-cyanophenyl)-4,4-dimethyl-7-oxoheptanoate (6d)

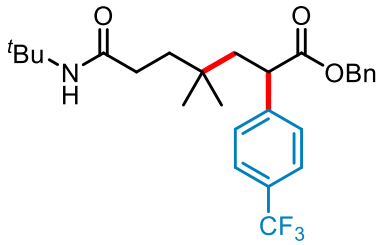
Colorless oil, yield: 71%, 61.7 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.46 – 7.40 (m, 2H), 7.34 – 7.29 (m, 3H), 7.21 (dd, *J* = 6.6, 2.9 Hz, 2H), 5.32 (s, 1H), 5.17 – 4.95 (m, 2H), 3.77 (dd, *J* = 9.0, 3.7 Hz, 1H), 2.32 (dd, *J* = 14.2, 9.0 Hz, 1H), 2.11 – 1.95 (m, 2H), 1.62 – 1.49 (m, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 172.2, 145.8, 135.1, 132.4, 128.6, 128.4, 128.3, 128.1, 118.6, 111.0, 67.1, 51.0, 47.7, 44.7, 37.1, 33.3, 32.4, 28.7, 26.8, 26.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{35}N_2O_3^+$ 435.2642; found 435.2626.



benzyl 7-(*tert*-butylamino)-4,4-dimethyl-7-oxo-2-(4-(trifluoromethyl)phenyl)heptanoate (6e)

Yellow solid (m. p. 66-68 ℃), yield: 81%, 77.4 mg

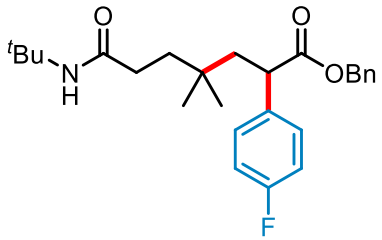
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.32 – 7.27 (m, 3H), 7.23 – 7.17 (m, 2H), 5.32 (s, 1H), 5.12 – 5.02 (m, 2H), 3.78 (dd, J = 9.1, 3.6 Hz, 1H), 2.35 (dd, J = 14.2, 9.1 Hz, 1H), 2.08 – 2.02 (m, 1H), 2.01 – 1.95 (m, 1H), 1.60 – 1.51 (m, 3H), 1.32 (s, 9H), 0.85 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 172.4, 144.5, 135.3, 129.4 (q, J = 32.4 Hz), 128.4, 128.2, 128.2, 128.0, 125.5 (q, J = 3.8 Hz), 124.0 (q, J = 272.0 Hz), 66.9, 51.0, 47.4, 44.7, 37.2, 33.2, 32.5, 28.7, 26.8, 26.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{35}F_3NO_3^+$ 478.2564; found 478.2545.



benzyl 7-(*tert*-butylamino)-2-(4-fluorophenyl)-4,4-dimethyl-7-oxoheptanoate (6f)

Colorless oil, yield: 41%, 35.1 mg

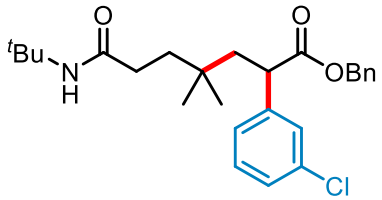
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 5H), 7.23 – 7.18 (m, 2H), 7.01 – 6.95 (m, 2H), 5.25 (s, 1H), 5.11 – 4.98 (m, 2H), 3.70 (dd, J = 8.9, 4.0 Hz, 1H), 2.28 (dd, J = 14.2, 8.9 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.98 – 1.92 (m, 1H), 1.56 – 1.48 (m, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 172.5, 161.9 (d, J = 245.5 Hz), 136.2 (d, J = 3.2 Hz), 135.5, 129.3 (d, J = 8.0 Hz), 128.4, 128.2, 128.0, 115.4 (d, J = 21.3 Hz), 66.7, 51.0, 46.8, 44.7, 37.3, 33.2, 32.6, 28.8, 26.9, 26.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{35}FNO_3^+$ 428.2595; found 428.2578.



benzyl 7-(*tert*-butylamino)-2-(3-chlorophenyl)-4,4-dimethyl-7-oxoheptanoate (6g)

Colorless oil, yield: 83%, 73.7 mg

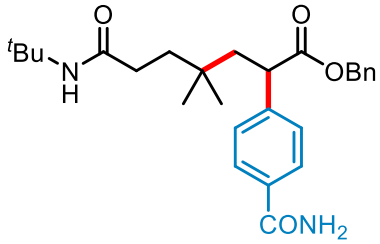
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.25 – 7.17 (m, 5H), 5.33 (s, 1H), 5.13 – 5.07 (m, 1H), 5.06 – 5.00 (m, 1H), 3.68 (dd, J = 9.1, 3.7 Hz, 1H), 2.29 (dd, J = 14.2, 9.1 Hz, 1H), 2.08 – 2.00 (m,

1H), 2.00 – 1.93 (m, 1H), 1.55 – 1.49 (m, 3H), 1.32 (s, 9H), 0.87 – 0.81 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 172.5, 142.4, 135.3, 134.3, 129.8, 128.4, 128.2, 128.0, 127.9, 127.3, 126.1, 66.9, 51.0, 47.2, 44.5, 37.3, 33.2, 32.5, 28.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{34}ClNO_3Na^+$ 466.2119; found 466.2104.



benzyl 7-(*tert*-butylamino)-2-(4-carbamoylphenyl)-4,4-dimethyl-7-oxoheptanoate (6h)

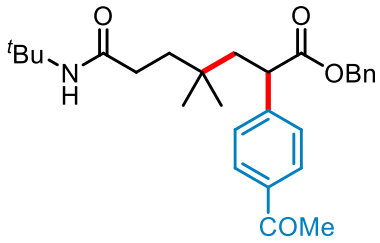
Colorless oil, yield: 43%, 38.9 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.24 – 7.20 (m, 2H), 6.36 (s, 1H), 6.03 (s, 1H), 5.33 (s, 1H), 5.11 – 5.07 (m, 1H), 5.05 – 4.99 (m, 1H), 3.77 (dd, *J* = 8.9, 3.9 Hz, 1H), 2.32 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.98 – 1.92 (m, 1H), 1.60 – 1.50 (m, 3H), 1.32 (s, 9H), 0.83 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 172.5, 169.0, 144.6, 135.3, 132.2, 128.5, 128.2, 128.1, 128.0, 127.8, 66.9, 51.0, 47.5, 44.6, 37.3, 33.2, 32.5, 28.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{37}N_2O_4^+$ 453.2748; found 453.2731.



benzyl 2-(4-acetylphenyl)-7-(*tert*-butylamino)-4,4-dimethyl-7-oxoheptanoate (6i)

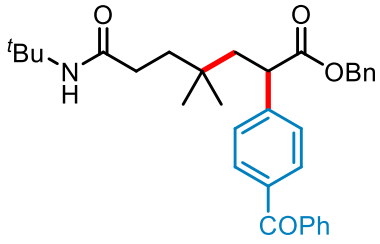
Colorless oil, yield: 82%, 74.1 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.24 – 7.19 (m, 2H), 5.36 (s, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.03 (d, *J* = 12.3 Hz, 1H), 3.79 (dd, *J* = 8.9, 3.8 Hz, 1H), 2.58 (s, 3H), 2.34 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.08 – 2.02 (m, 1H), 2.01 – 1.95 (m, 1H), 1.60 – 1.51 (m, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.5, 173.7, 172.4, 145.8, 135.9, 135.3, 128.7, 128.4, 128.2, 128.0, 128.0, 66.9, 50.9, 47.6, 44.6, 37.2, 33.2, 32.4, 28.7, 26.8, 26.8, 26.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{38}NO_4^+$ 452.2795; found 452.2779.



benzyl 2-(4-benzoylphenyl)-7-(*tert*-butylamino)-4,4-dimethyl-7-oxoheptanoate (6j)

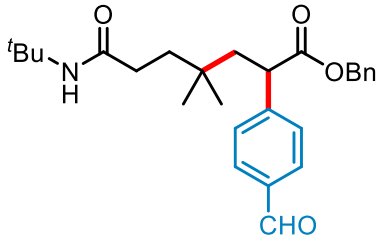
Colorless oil, yield: 90%, 92.5 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 5.35 (s, 1H), 5.14 – 5.10 (m, 1H), 5.09 – 5.04 (m, 1H), 3.81 (dd, *J* = 9.1, 3.7 Hz, 1H), 2.37 (dd, *J* = 14.2, 9.1 Hz, 1H), 2.09 – 2.03 (m, 1H), 2.02 – 1.96 (m, 1H), 1.62 – 1.54 (m, 3H), 1.32 (s, 9H), 0.86 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.1, 173.8, 172.4, 145.1, 137.4, 136.3, 135.3, 132.4, 130.4, 129.9, 128.4, 128.2, 128.2, 128.0, 127.7, 66.9, 50.9, 47.6, 44.6, 37.3, 33.2, 32.5, 28.7, 26.8, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{33}H_{40}NO_4^+$ 514.2952; found 514.2932.



benzyl 7-(*tert*-butylamino)-2-(4-formylphenyl)-4,4-dimethyl-7-oxoheptanoate (6k)

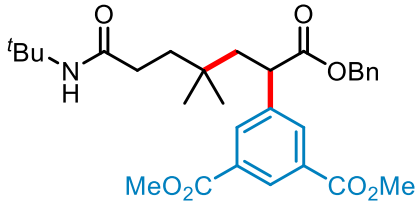
Colorless oil, yield: 71%, 62.1 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.24 – 7.20 (m, 2H), 5.34 (s, 1H), 5.13 – 5.08 (m, 1H), 5.07 – 5.00 (m, 1H), 3.81 (dd, *J* = 8.9, 3.8 Hz, 1H), 2.35 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.09 – 2.03 (m, 1H), 2.02 – 1.96 (m, 1H), 1.61 – 1.51 (m, 3H), 1.32 (s, 9H), 0.85 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.7, 173.5, 172.3, 147.3, 135.3, 135.2, 130.0, 128.5, 128.4, 128.2, 128.0, 67.0, 50.9, 47.8, 44.6, 37.2, 33.3, 32.4, 28.7, 26.8, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_4^+$ 438.2639; found 438.2622.



dimethyl 5-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)isophthalate (6l)

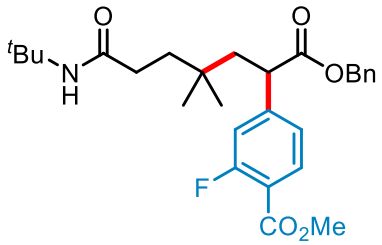
Colorless oil, yield: 36%, 37.8 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.19 (d, *J* = 1.6 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.25 – 7.20 (m, 2H), 5.30 (s, 1H), 5.14 – 5.09 (m, 1H), 5.05 – 5.00 (m, 1H), 3.94 (s, 6H), 3.84 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.38 (dd, *J* = 14.2, 9.0 Hz, 1H), 2.09 – 2.03 (m, 1H), 2.02 – 1.96 (m, 1H), 1.61 – 1.50 (m, 3H), 1.32 (s, 9H), 0.85 (d, *J* = 2.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 172.3, 165.9, 141.5, 135.2, 133.2, 131.0, 129.6, 128.4, 128.2, 128.2, 67.0, 52.4, 51.0, 47.3, 44.5, 37.4, 33.3, 32.5, 28.7, 26.9, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{40}NO_7^+$ 526.2799; found 526.2778.



methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)-2-fluorobenzoate (6m)

Colorless oil, yield: 65%, 63.1 mg

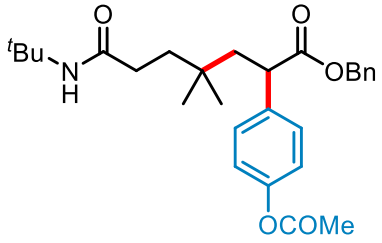
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 1H), 7.36 – 7.28 (m, 3H), 7.26 – 7.20 (m, 2H), 7.17 – 7.08 (m, 2H), 5.32 (s, 1H), 5.13 – 5.08 (m, 1H), 5.06 – 5.03 (m, 1H), 3.91 (s, 3H), 3.74 (dd, *J* = 9.1, 3.8 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.08 – 2.01 (m, 1H), 2.01 – 1.95 (m, 1H), 1.58 – 1.51 (m, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 172.3, 164.5 (d, *J* = 3.7 Hz), 161.8 (d, *J* = 260.8 Hz), 147.8 (d, *J* = 8.5 Hz), 135.2, 132.3, 128.5, 128.3, 128.1, 123.5 (d, *J* = 3.3 Hz), 117.2 (d, *J* = 10.0 Hz), 116.3 (d, *J* = 23.2 Hz), 67.1, 52.2, 51.0, 47.4, 44.5, 37.2, 33.2, 32.4, 28.7, 26.8, 26.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -108.7 (dd, *J* = 12.0, 7.1 Hz, 1F).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{37}FNO_5^+$ 486.2650; found 486.2633.



benzyl 2-(4-acetoxyphenyl)-7-(*tert*-butylamino)-4,4-dimethyl-7-oxoheptanoate (6n)

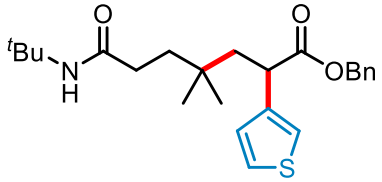
Colorless oil, yield: 30%, 28.1 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 5H), 7.25 – 7.20 (m, 2H), 7.04 – 6.98 (m, 2H), 5.27 (s, 1H), 5.12 – 5.07 (m, 1H), 5.04 – 5.00 (m, 1H), 3.70 (dd, *J* = 9.4, 3.4 Hz, 1H), 2.35 – 2.27 (m, 4H), 2.07 – 2.00 (m, 1H), 1.99 – 1.94 (m, 1H), 1.57 – 1.48 (m, 3H), 1.32 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 172.5, 169.4, 149.7, 138.1, 135.5, 128.8, 128.5, 128.2, 128.0, 121.7, 66.8, 51.0, 46.9, 44.7, 37.4, 33.2, 32.6, 28.8, 26.9, 26.9, 21.1.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{38}NO_5^+$ 468.2744; found 468.2726.



benzyl 7-(*tert*-butylamino)-4,4-dimethyl-7-oxo-2-(thiophen-3-yl)heptanoate (6o)

Colorless oil, yield: 77%, 64 mg

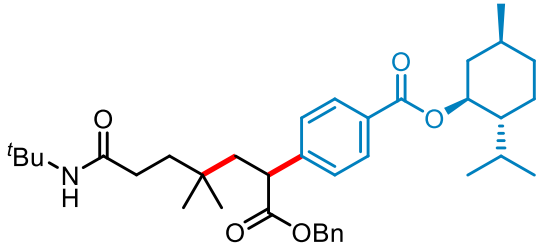
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 3H), 7.26 – 7.22 (m, 3H), 7.11 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.05 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.33 (s, 1H), 5.11 – 5.04 (m, 2H), 3.87 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.25 (dd,

J = 14.2, 9.0 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.99 – 1.93 (m, 1H), 1.62 – 1.57 (m, 1H), 1.54 – 1.49 (m, 2H), 1.32 (s, 9H), 0.85 (d, *J* = 2.8 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 172.6, 140.4, 135.5, 128.4, 128.1, 128.0, 127.1, 125.7, 121.4, 66.6, 50.9, 44.3, 43.0, 37.3, 33.1, 32.6, 28.7, 26.8, 26.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{34}NO_3S^+$ 416.2254; found 416.2239.



(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (6p)

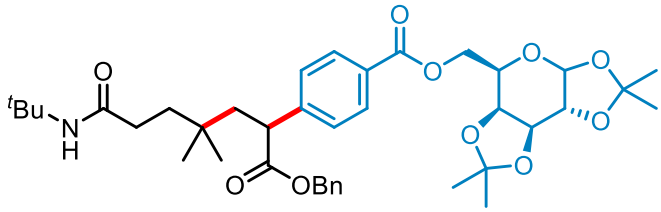
Colorless oil, yield: 59%, 69.8 mg, dr = 1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.33 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 5.30 (s, 1H), 5.13 – 5.07 (m, 1H), 5.05 – 4.99 (m, 1H), 4.92 (td, *J* = 10.8, 4.4 Hz, 1H), 3.78 (dd, *J* = 8.7, 3.8 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.15 – 2.07 (m, 1H), 2.03 – 1.91 (m, 3H), 1.77 – 1.67 (m, 2H), 1.60 – 1.50 (m, 5H), 1.32 (s, 9H), 0.92 (dd, *J* = 6.8, 4.0 Hz, 6H), 0.85 (s, 6H), 0.79 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 173.8, 172.4, 165.7, 145.4, 145.4, 135.4, 129.9, 129.7, 128.4, 128.2, 128.0, 127.8, 74.8, 66.9, 50.9, 47.6, 47.2, 44.5, 44.5, 40.9, 37.3, 34.2, 33.2, 32.5, 31.4, 28.7, 26.9, 26.9, 26.8, 26.4, 23.6, 22.0, 20.7, 16.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{37}H_{54}NO_5^+$ 592.3997; found 592.3973.



((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(1-(benzyloxy)-7-(*tert*-butylamino)-4,4-dimethyl-1,7-dioxoheptan-2-yl)benzoate (6q)

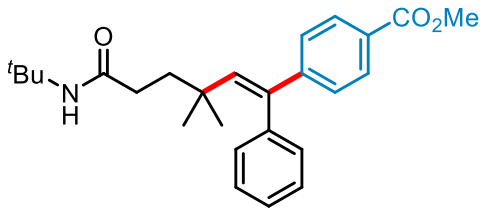
Colorless oil, yield: 52%, 72.4 mg, dr = 1:1

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.24 – 7.19 (m, 2H), 5.56 (d, *J* = 4.9 Hz, 1H), 5.27 (s, 1H), 5.09 (d, *J* = 12.3 Hz, 1H), 5.03 (d, *J* = 12.3 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.54 – 4.48 (m, 1H), 4.47 – 4.39 (m, 1H), 4.37 – 4.30 (m, 2H), 4.22 – 4.15 (m, 1H), 3.77 (dd, *J* = 8.9, 3.8 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.09 – 1.92 (m, 2H), 1.58 – 1.50 (m, 6H), 1.48 (s, 3H), 1.36 (s, 3H), 1.35 – 1.31 (m, 12H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 172.4, 166.0, 145.7, 135.4, 130.1, 128.9, 128.4, 128.2, 128.0, 127.9, 109.6, 108.7, 96.3, 71.1, 70.7, 70.5, 66.9, 66.1, 66.1, 63.8, 63.8, 51.0, 47.7, 44.5, 37.3, 33.3, 32.5, 28.7, 26.9, 26.8, 26.0, 25.9, 24.9, 24.4.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{39}H_{53}NO_{10}Na^+$ 718.3562; found 718.3534.



methyl (*E*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-phenylhex-1-en-1-yl)benzoate (8a)

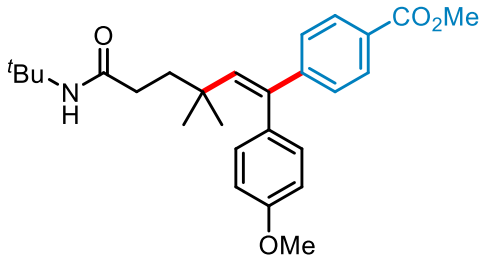
White solid (m. p. 106-108 ℃), yield: 62%, 50.5 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 6.07 (s, 1H), 5.25 (s, 1H), 3.88 (s, 3H), 2.16 – 2.06 (m, 2H), 1.69 – 1.60 (m, 2H), 1.31 (s, 9H), 0.92 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 166.9, 148.2, 140.0, 139.7, 139.6, 130.0, 129.3, 128.2, 128.0, 127.2, 126.7, 52.0, 51.0, 39.7, 37.0, 33.6, 28.8, 28.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{34}NO_3^+$ 408.2533; found 408.2518.



methyl (*Z*)-4-(6-(*tert*-butylamino)-1-(4-methoxyphenyl)-3,3-dimethyl-6-oxohex-1-en-1-yl)benzoate (8b)

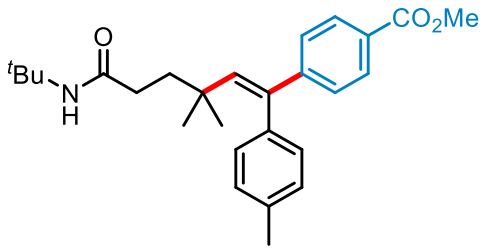
Colorless oil, yield: 66%, 57.8 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.05 (s, 1H), 5.25 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 2.16 – 2.06 (m, 2H), 1.69 – 1.60 (m, 2H), 1.31 (s, 9H), 0.93 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 166.9, 158.7, 148.7, 140.1, 139.3, 131.8, 131.1, 129.2, 128.1, 126.7, 113.4, 55.1, 51.9, 50.9, 39.7, 36.9, 33.5, 28.8, 28.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_4^+$ 438.2639; found 438.2622.



methyl (*E*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-(p-tolyl)hex-1-en-1-yl)benzoate (8c)

Colorless oil, yield: 63%, 53.1 mg

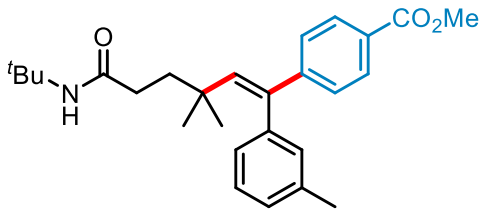
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.04 (s, 1H), 5.22 (s, 1H), 3.88 (s, 3H), 2.38 (s, 3H), 2.14 – 2.06 (m, 2H),

1.67 – 1.58 (m, 2H), 1.31 (s, 9H), 0.93 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.9, 148.5, 139.9, 139.7, 136.8, 136.7, 129.9, 129.3, 128.7, 128.1, 126.7, 51.9, 51.0, 39.6, 36.9, 33.6, 28.9, 28.7, 21.2.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_3^+$ 422.2690; found 422.2675.



methyl (*Z*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-(m-tolyl)hex-1-en-1-yl)benzoate (8d)

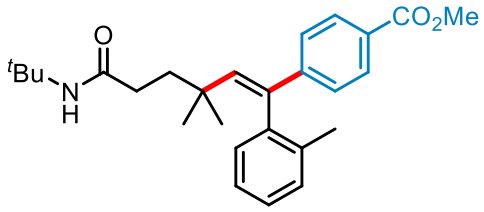
Colorless oil, yield: 67%, 56.5 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.15 – 7.09 (m, 1H), 7.02 – 6.90 (m, 2H), 6.04 (s, 1H), 5.23 (s, 1H), 3.88 (s, 3H), 2.35 (s, 3H), 2.15 – 2.06 (m, 2H), 1.69 – 1.59 (m, 2H), 1.32 (s, 9H), 0.92 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 166.9, 148.4, 139.8, 139.8, 139.6, 137.5, 130.7, 129.3, 128.1, 127.9, 127.8, 127.1, 126.7, 51.9, 51.0, 39.8, 37.0, 33.6, 28.8, 28.7, 21.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_3^+$ 422.2690; found 422.2674.



methyl (*Z*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-(o-tolyl)hex-1-en-1-yl)benzoate (8e)

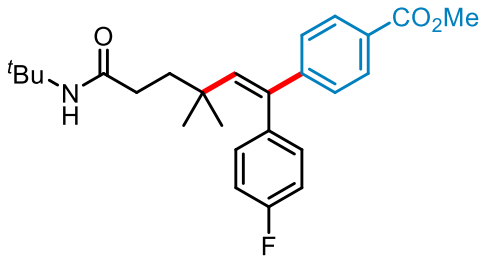
Colorless oil, yield: 67%, 56.5 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 6.12 (s, 1H), 5.30 (s, 1H), 3.88 (s, 3H), 2.17 – 2.08 (m, 2H), 2.03 (s, 3H), 1.76 – 1.69 (m, 1H), 1.68 – 1.62 (m, 1H), 1.33 (s, 9H), 0.88 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 166.9, 147.2, 139.9, 138.8, 138.7, 136.3, 130.6, 130.1, 129.4, 128.2, 127.6, 126.3, 125.1, 51.9, 51.0, 40.4, 37.1, 33.5, 28.7, 27.8, 27.5, 19.9.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_3^+$ 422.2690; found 422.2675.



methyl (*Z*)-4-(6-(*tert*-butylamino)-1-(4-fluorophenyl)-3,3-dimethyl-6-oxohex-1-en-1-yl)benzoate (8f)

Colorless oil, yield: 66%, 56.2 mg

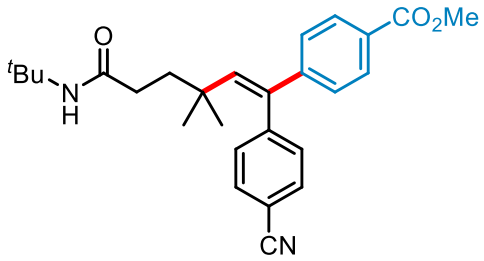
Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.14 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.09 – 7.00 (m, 2H), 6.09 (s, 1H), 5.25 (s, 1H), 3.88 (s, 3H), 2.14 – 2.06 (m, 2H), 1.71 – 1.62 (m, 2H), 1.32 (s, 9H), 0.91 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 166.8, 162.0 (d, *J* = 246.7 Hz), 148.0, 140.6, 138.6, 135.5 (d, *J* = 3.6 Hz), 131.6 (d, *J* = 7.8 Hz), 129.4, 128.4, 126.7, 115.0 (d, *J* = 21.3 Hz), 52.0, 51.0, 39.9, 37.0, 33.4, 28.7, 28.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.8 – -114.9 (m, 1F).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{33}FNO_3^+$ 426.2439; found 426.2423.



methyl (*E*)-4-(6-(*tert*-butylamino)-1-(4-cyanophenyl)-3,3-dimethyl-6-oxohex-1-en-1-yl)benzoate (8g)

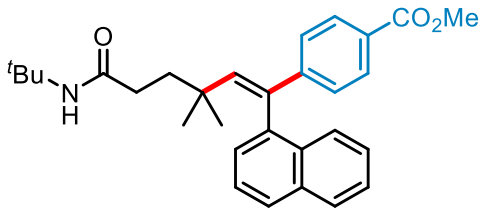
Colorless oil, yield: 33%, 28.6 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.13 (s, 1H), 5.26 (s, 1H), 3.89 (s, 3H), 2.15 – 2.07 (m, 2H), 1.71 – 1.64 (m, 2H), 1.33 (s, 9H), 0.89 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 166.7, 146.9, 145.1, 141.3, 138.1, 131.8, 130.9, 129.5, 128.8, 126.7, 118.6, 111.3, 52.1, 51.1, 40.0, 37.1, 33.3, 28.8, 28.6.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{33}N_2O_3^+$ 433.2486; found 433.2470.



methyl (*Z*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-1-(naphthalen-1-yl)-6-oxohex-1-en-1-yl)benzoate (8h)

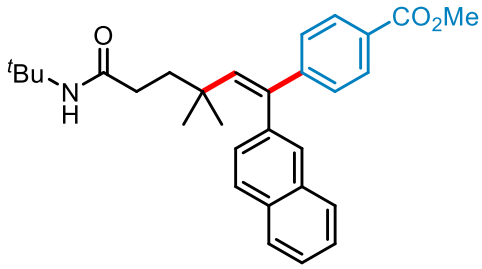
Deep red oil, yield: 58%, 53.1 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 4H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.45 – 7.33 (m, 3H), 7.31 – 7.24 (m, 2H), 6.37 (s, 1H), 5.14 (s, 1H), 3.84 (s, 3H), 2.17 – 2.01 (m, 2H), 1.74 – 1.55 (m, 2H), 1.29 (s, 9H), 0.78 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 166.8, 147.7, 141.9, 137.5, 136.9, 133.6, 132.4, 129.5, 128.3, 128.3, 128.0, 127.9, 126.2, 126.2, 126.1, 125.8, 125.0, 51.9, 51.0, 40.0, 37.3, 33.6, 28.7, 27.8, 27.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{36}NO_3^+$ 458.2690; found 458.2673.



methyl (*Z*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-1-(naphthalen-2-yl)-6-oxohex-1-en-1-yl)benzoate (8i)

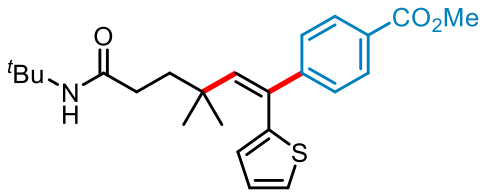
Colorless oil, yield: 68%, 62.2 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 5H), 7.68 (s, 1H), 7.53 – 7.47 (m, 2H), 7.29 – 7.22 (m, 3H), 6.16 (s, 1H), 5.20 (s, 1H), 3.86 (s, 3H), 2.17 – 2.09 (m, 2H), 1.70 – 1.61 (m, 2H), 1.27 (s, 9H), 0.93 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 166.9, 148.2, 140.4, 139.6, 137.2, 132.8, 132.4, 129.3, 128.8, 128.3, 128.2, 127.9, 127.7, 127.6, 126.9, 126.3, 126.0, 51.9, 50.9, 39.8, 37.1, 33.5, 28.9, 28.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{36}NO_3^+$ 458.2690; found 458.2673.



methyl (*Z*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-(thiophen-2-yl)hex-1-en-1-yl)benzoate (8j)

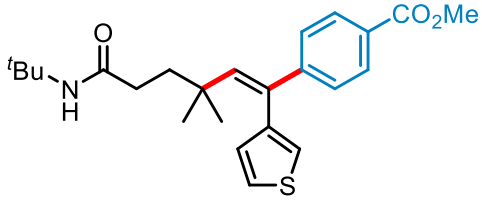
Colorless oil, yield: 48%, 39.7 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 2H), 7.35 (dd, J = 5.2, 1.2 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.08 – 7.01 (m, 1H), 6.98 – 6.91 (m, 1H), 6.18 (s, 1H), 5.25 (s, 1H), 3.89 (s, 3H), 2.17 – 2.06 (m, 2H), 1.74 – 1.64 (m, 2H), 1.32 (s, 9H), 1.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 166.9, 148.0, 144.2, 139.9, 132.5, 129.4, 128.6, 128.5, 126.6, 126.5, 126.1, 52.0, 51.0, 39.4, 37.3, 33.6, 28.8, 28.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{32}NO_3S^+$ 414.2097; found 414.2083.



methyl (*Z*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-(thiophen-3-yl)hex-1-en-1-yl)benzoate (8k)

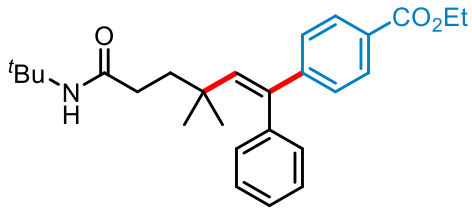
Colorless oil, yield: 63%, 52.1 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.33 (dd, J = 4.8, 3.0 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.14 – 7.10 (m, 1H), 6.91 – 6.84 (m, 1H), 6.12 (s, 1H), 5.24 (s, 1H), 3.89 (s, 3H), 2.16 – 2.05 (m, 2H), 1.72 – 1.61 (m, 2H), 1.32 (s, 9H), 0.96 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 166.9, 147.7, 141.6, 139.1, 134.7, 129.6, 129.3, 128.3, 126.5, 125.2, 123.9, 52.0, 51.0, 39.5, 36.9, 33.5, 28.8, 28.6.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{32}NO_3S^+$ 414.2097; found 414.2082.



ethyl (*E*)-4-(6-(*tert*-butylamino)-3,3-dimethyl-6-oxo-1-phenylhex-1-en-1-yl)benzoate (8l)

Colorless oil, yield: 52%, 43.8 mg

Purified by flash column chromatography through silica gel (petroleum ether/ethyl acetate = 5:1)

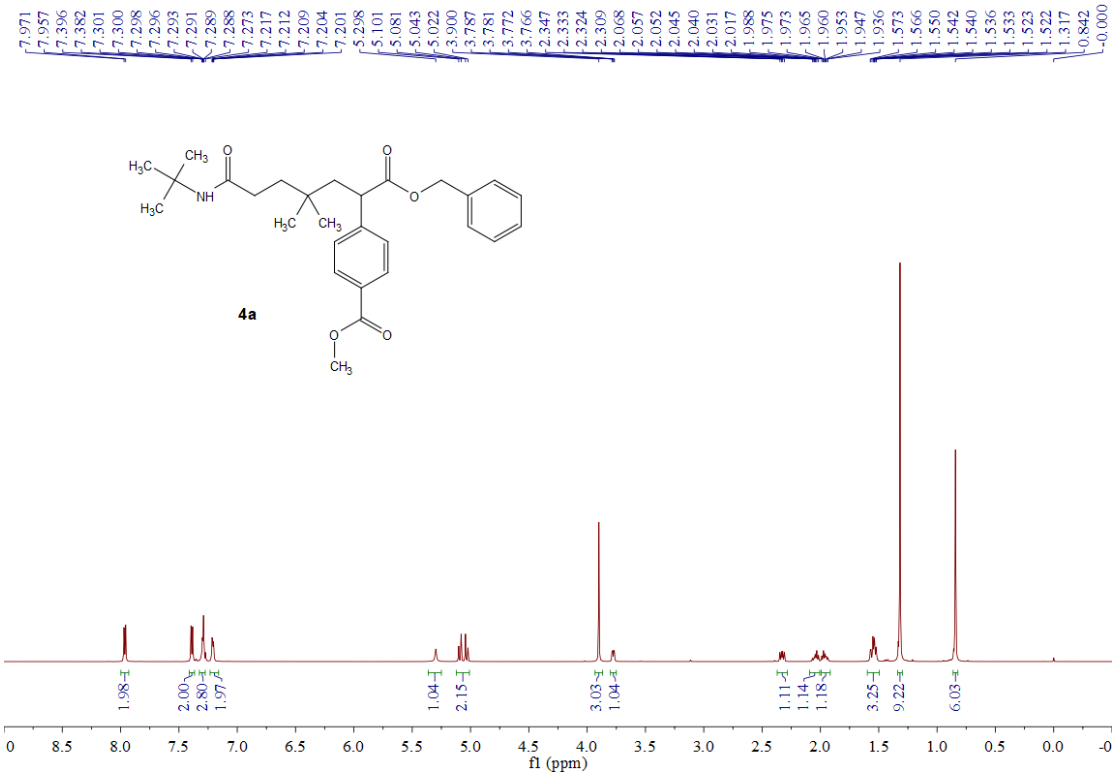
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.24 – 7.16 (m, 4H), 6.06 (s, 1H), 5.23 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.15 – 2.06 (m, 2H), 1.68 – 1.58 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.32 (s, 9H), 0.92 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 166.4, 148.2, 139.9, 139.7, 139.7, 130.0, 129.3, 128.6, 128.0, 127.2, 126.7, 60.8, 51.0, 39.7, 37.0, 33.5, 28.8, 28.7, 14.3.

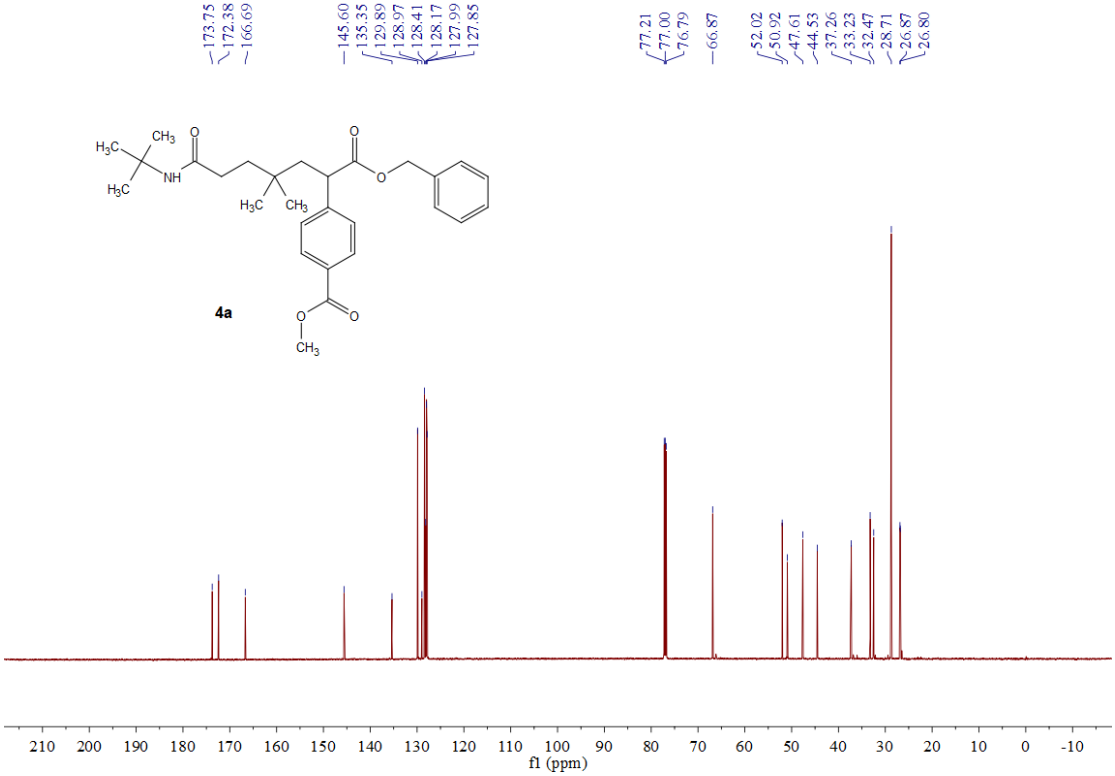
HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_3^+$ 422.2690; found 422.2695.

6. NMR Spectroscopic Data

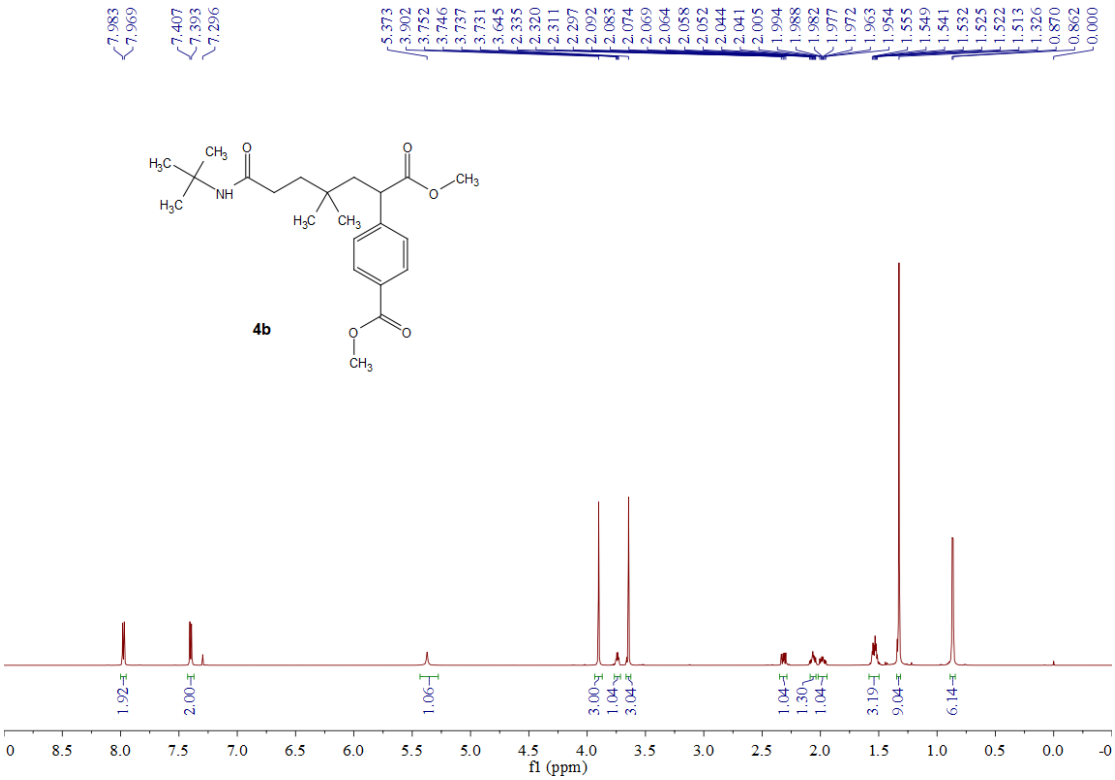
^{1}H NMR (600 MHz, $CDCl_3$) of 4a



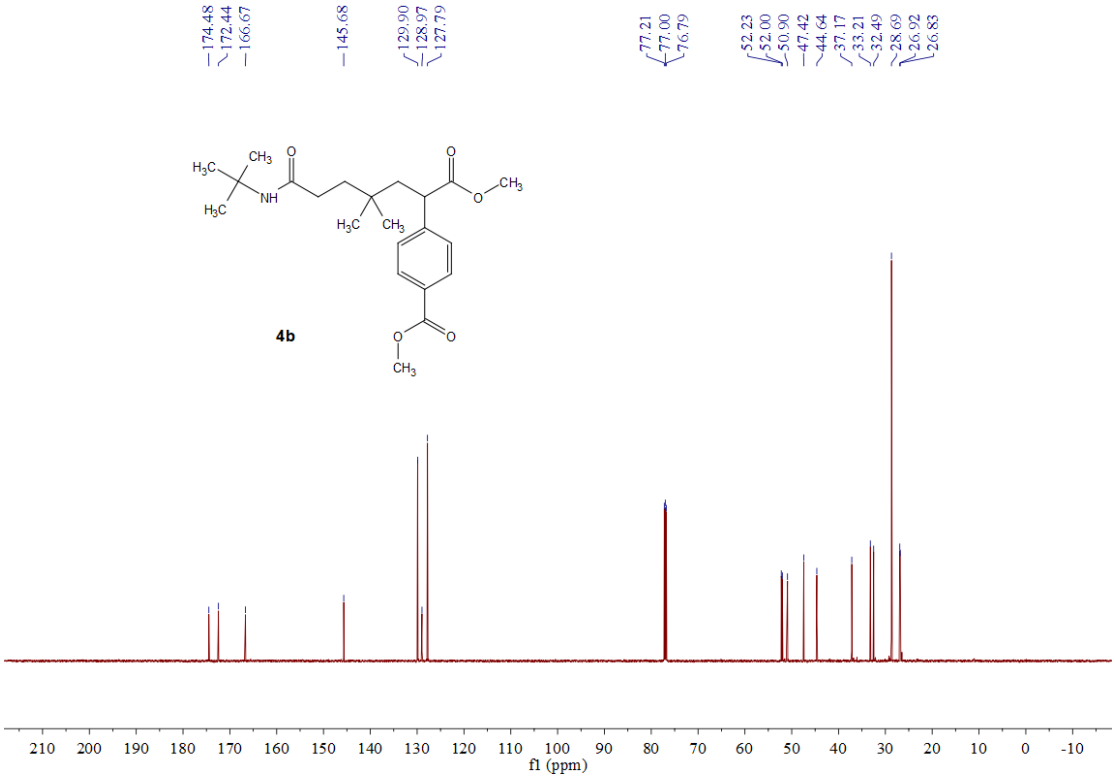
^{13}C NMR (151 MHz, $CDCl_3$) of 4a



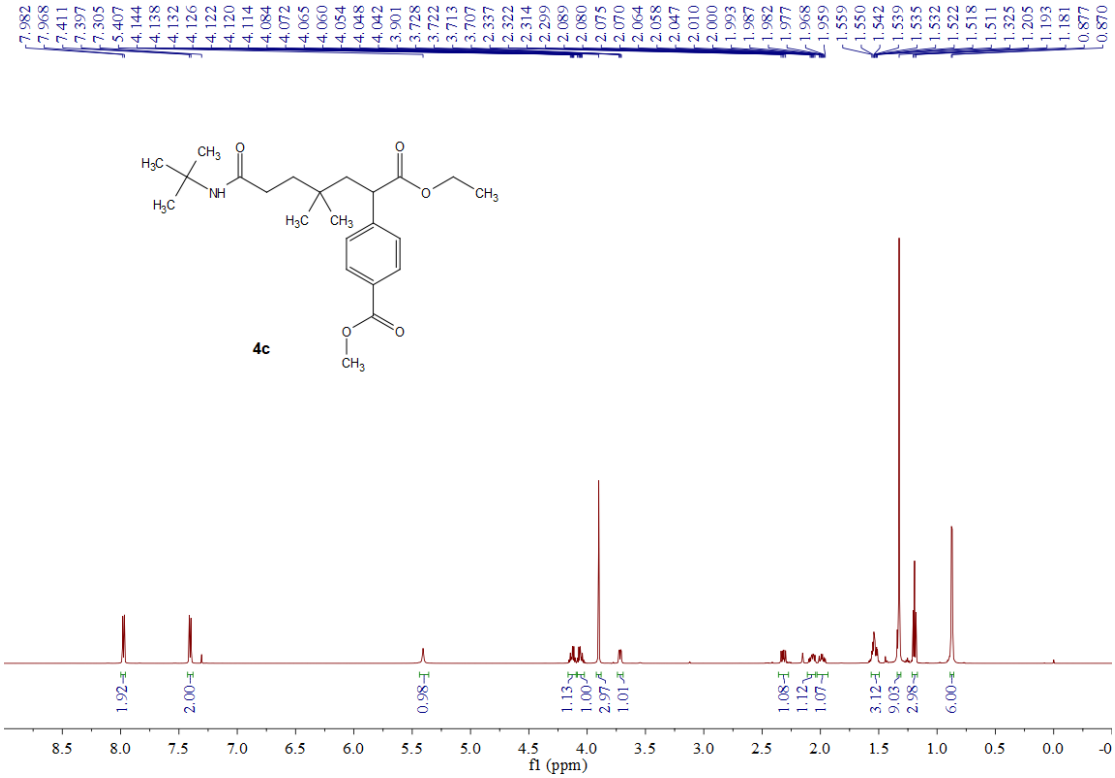
^{1}H NMR (600 MHz, $CDCl_3$) of 4b



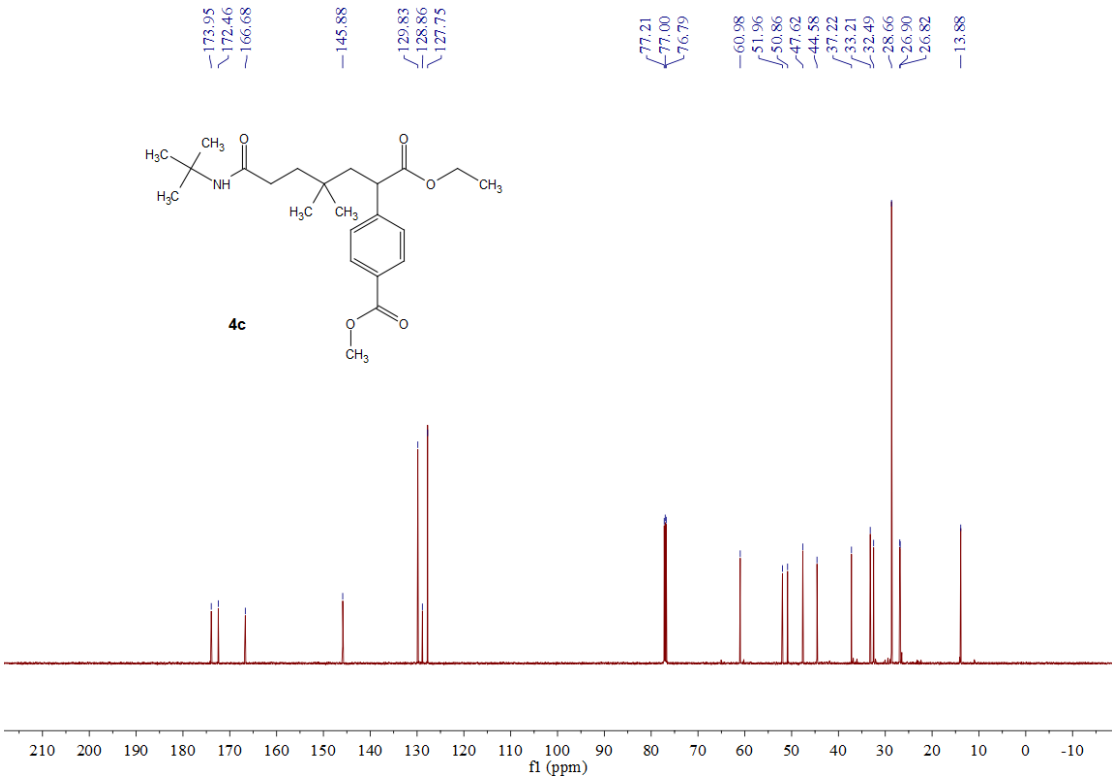
^{13}C NMR (151 MHz, $CDCl_3$) of 4b



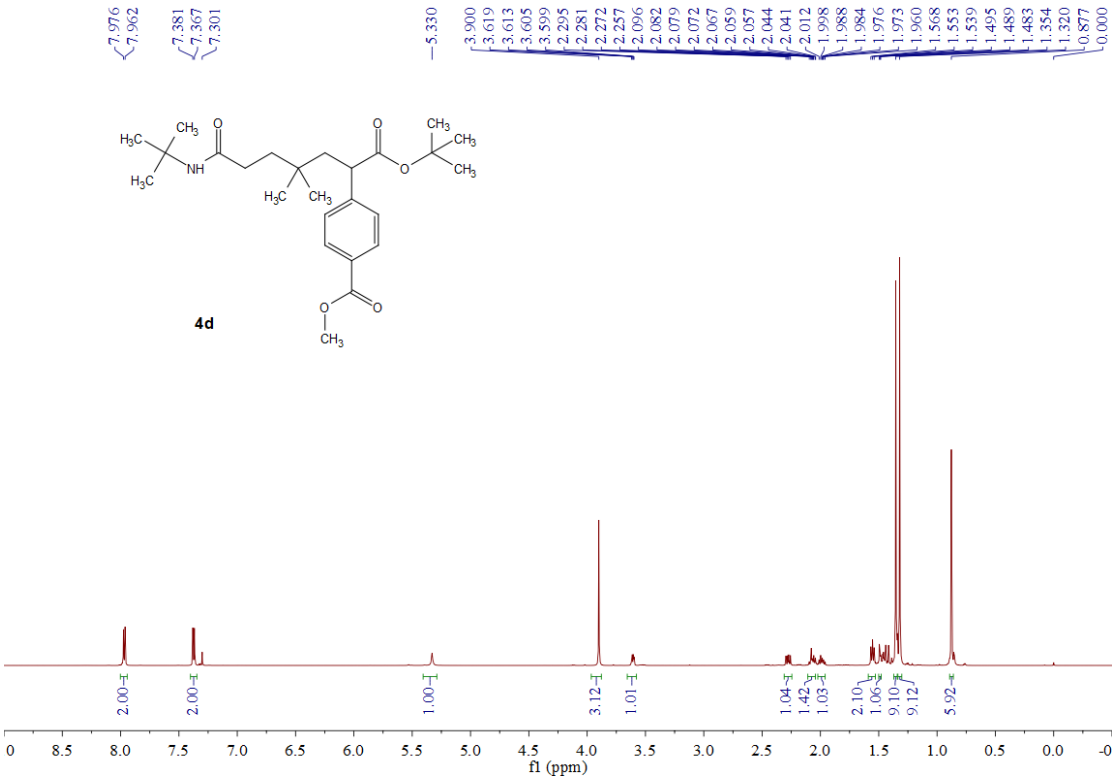
^{1}H NMR (600 MHz, $CDCl_3$) of 4c



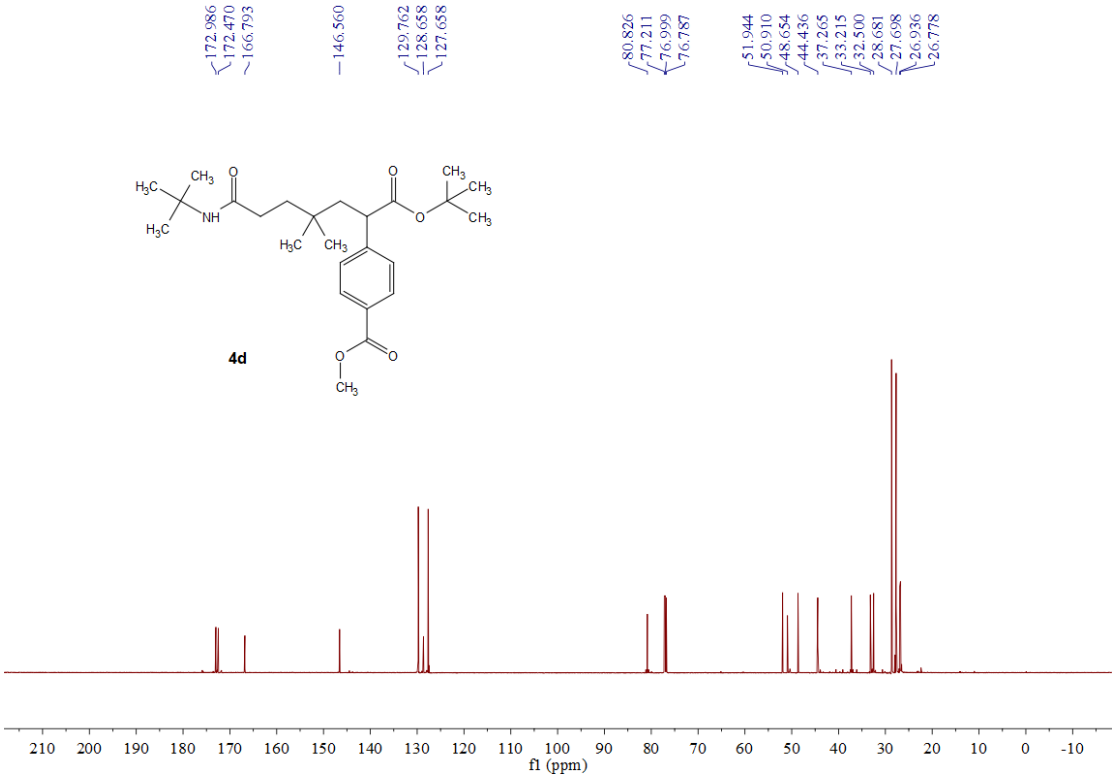
^{13}C NMR (151 MHz, $CDCl_3$) of 4c



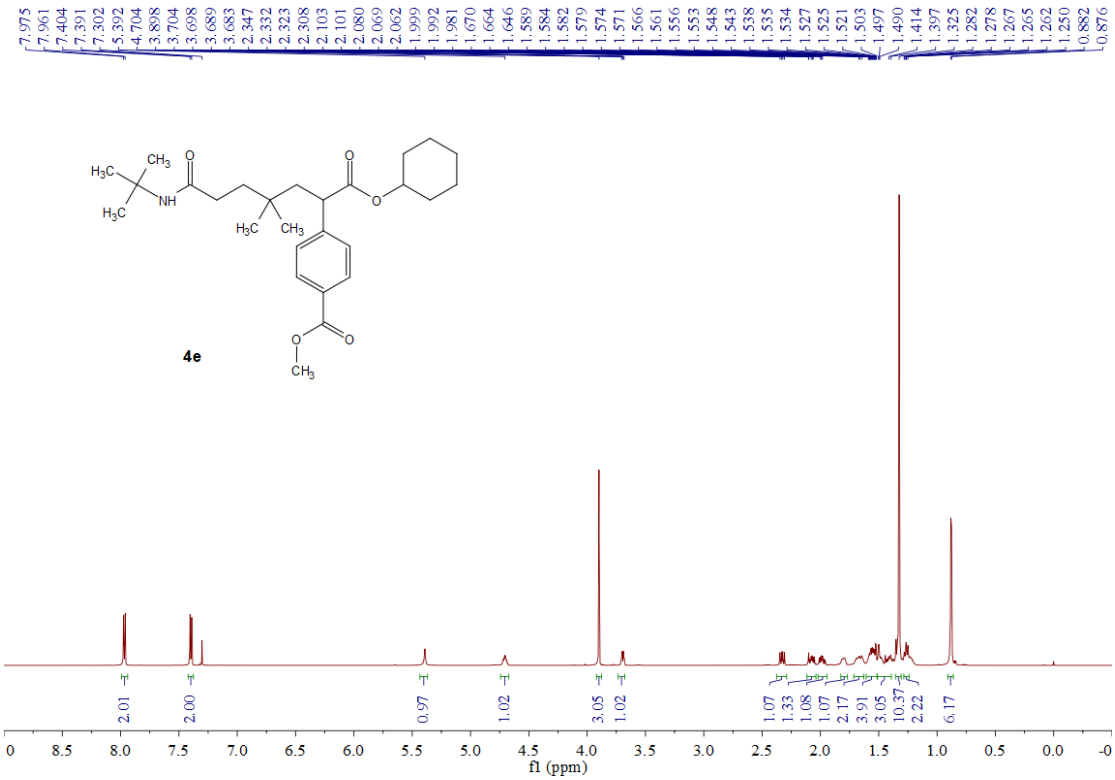
^{1}H NMR (600 MHz, $CDCl_3$) of 4d



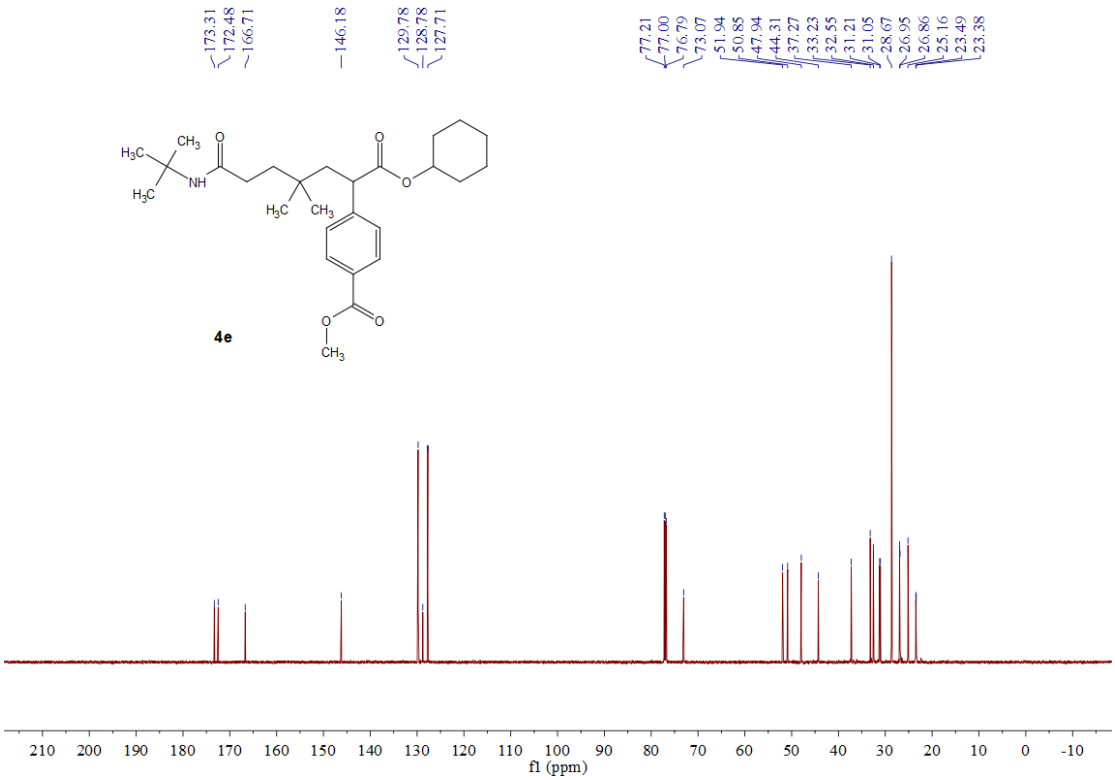
^{13}C NMR (151 MHz, $CDCl_3$) of 4d



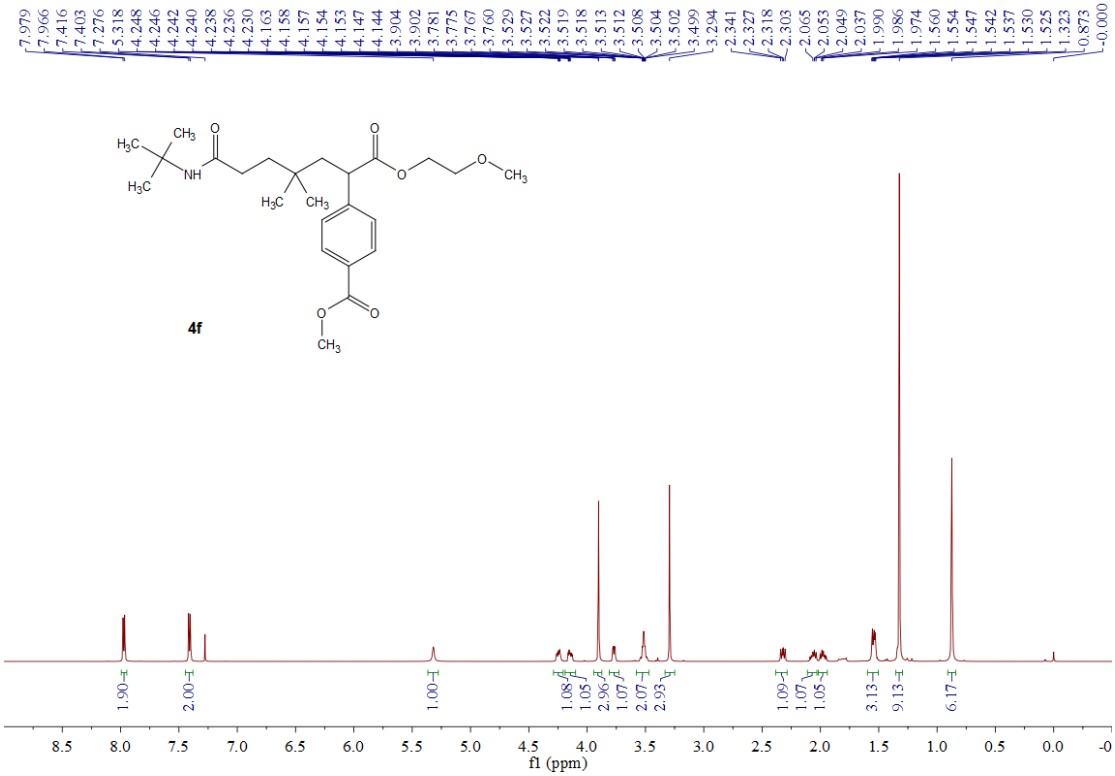
^{1}H NMR (600 MHz, $CDCl_3$) of 4e



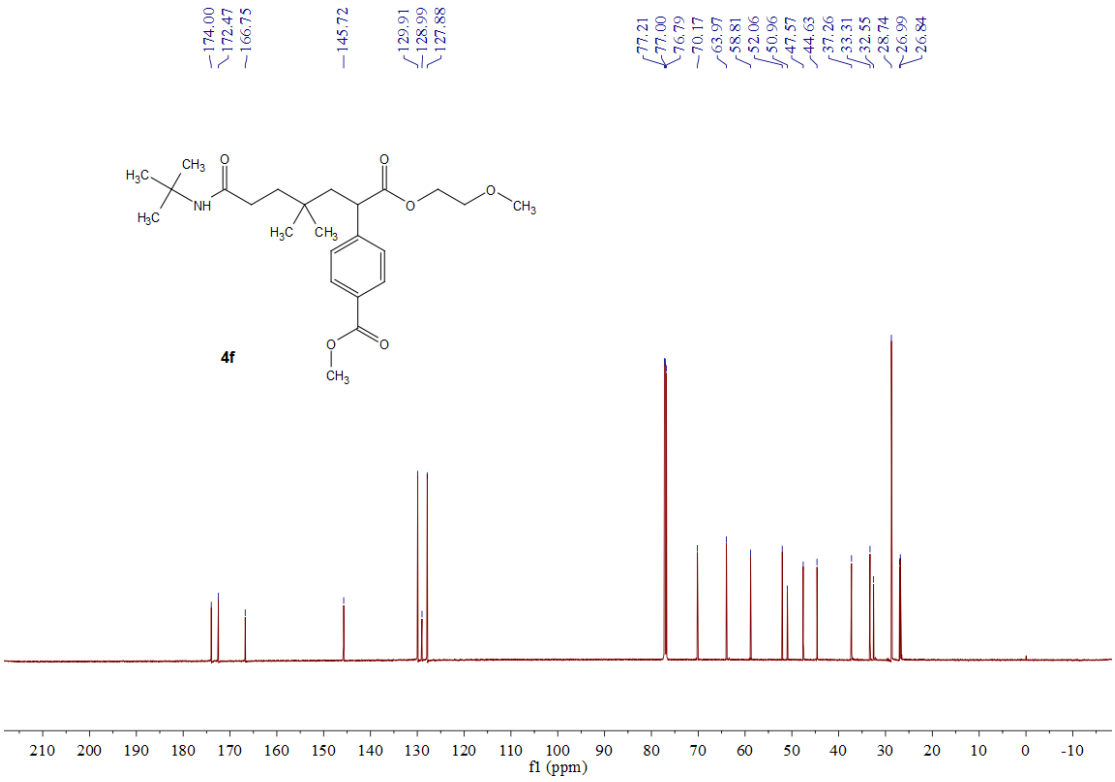
^{13}C NMR (151 MHz, $CDCl_3$) of 4e



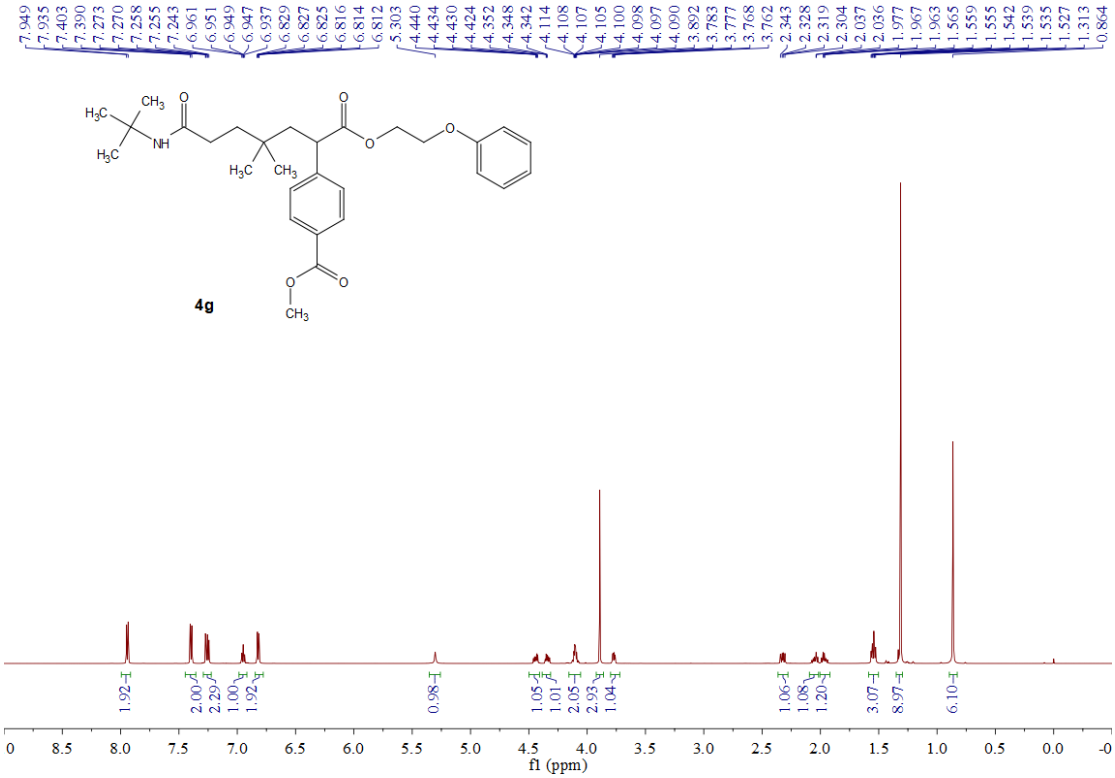
^{1}H NMR (600 MHz, $CDCl_3$) of 4f



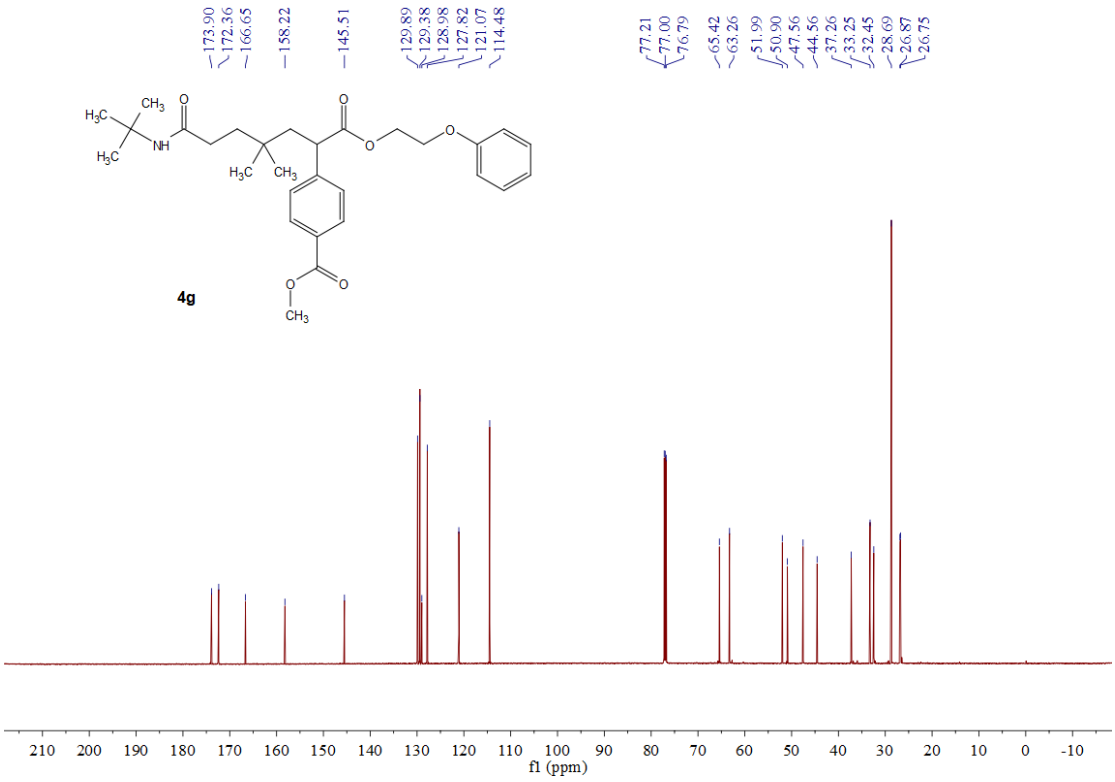
^{13}C NMR (151 MHz, $CDCl_3$) of 4f



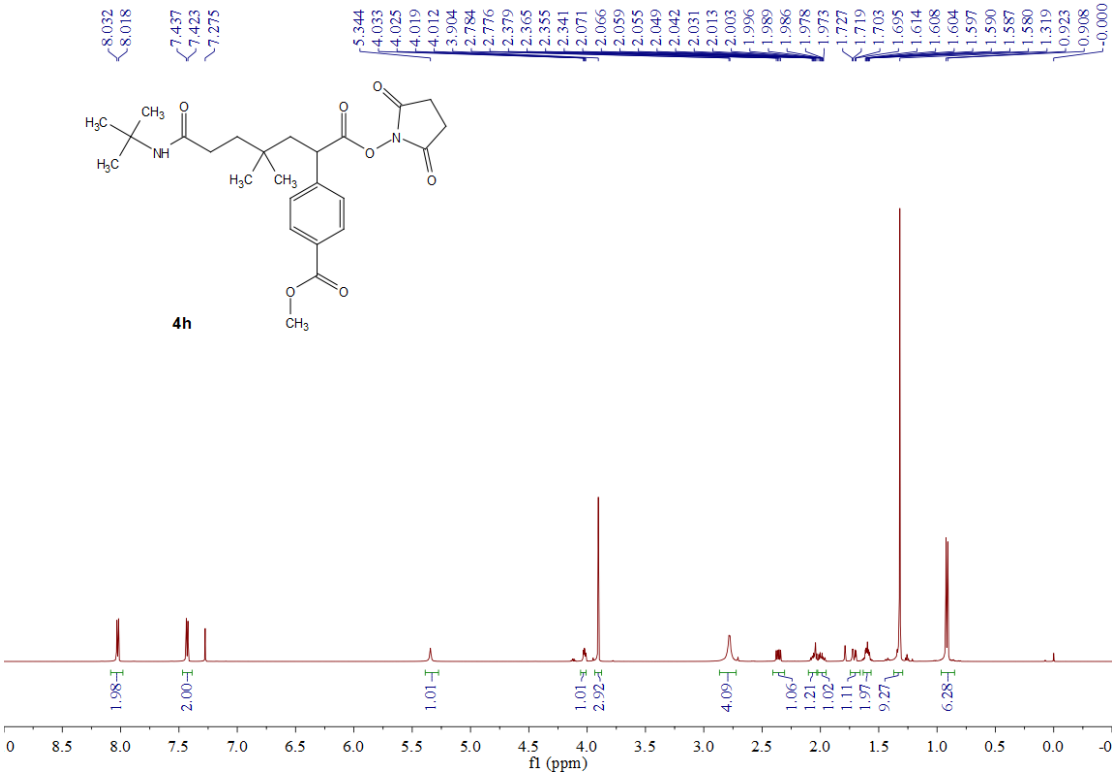
^{1}H NMR (600 MHz, $CDCl_3$) of 4g



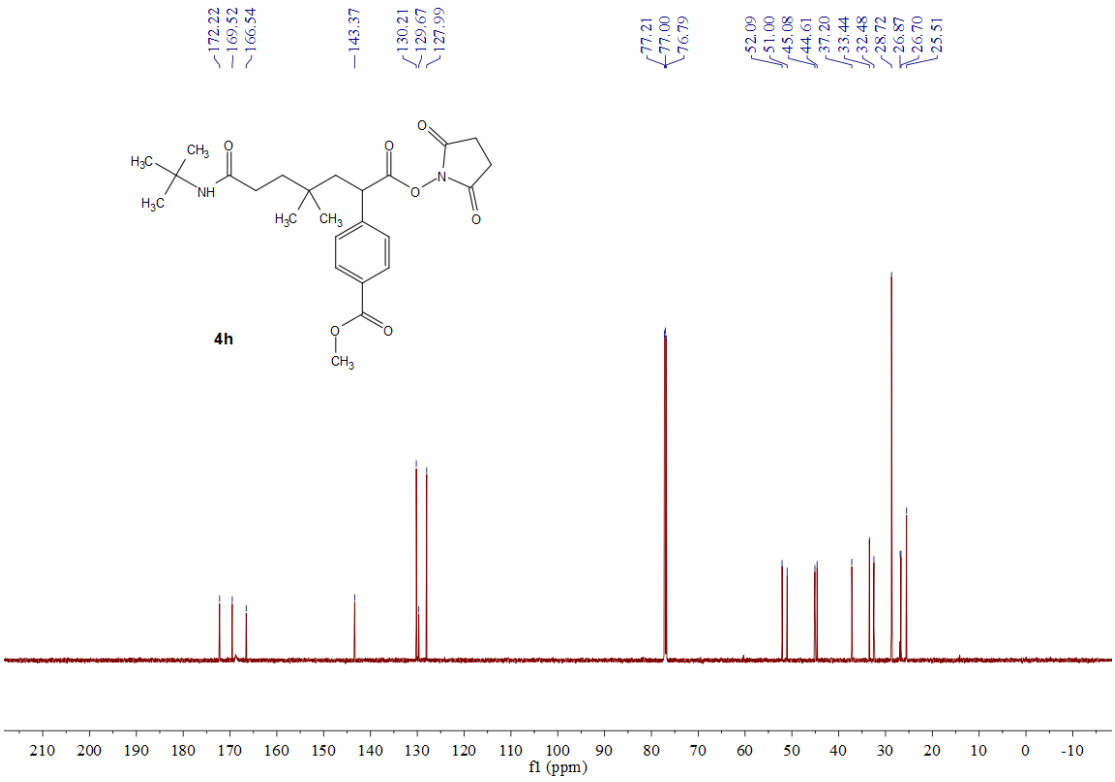
^{13}C NMR (151 MHz, $CDCl_3$) of 4g



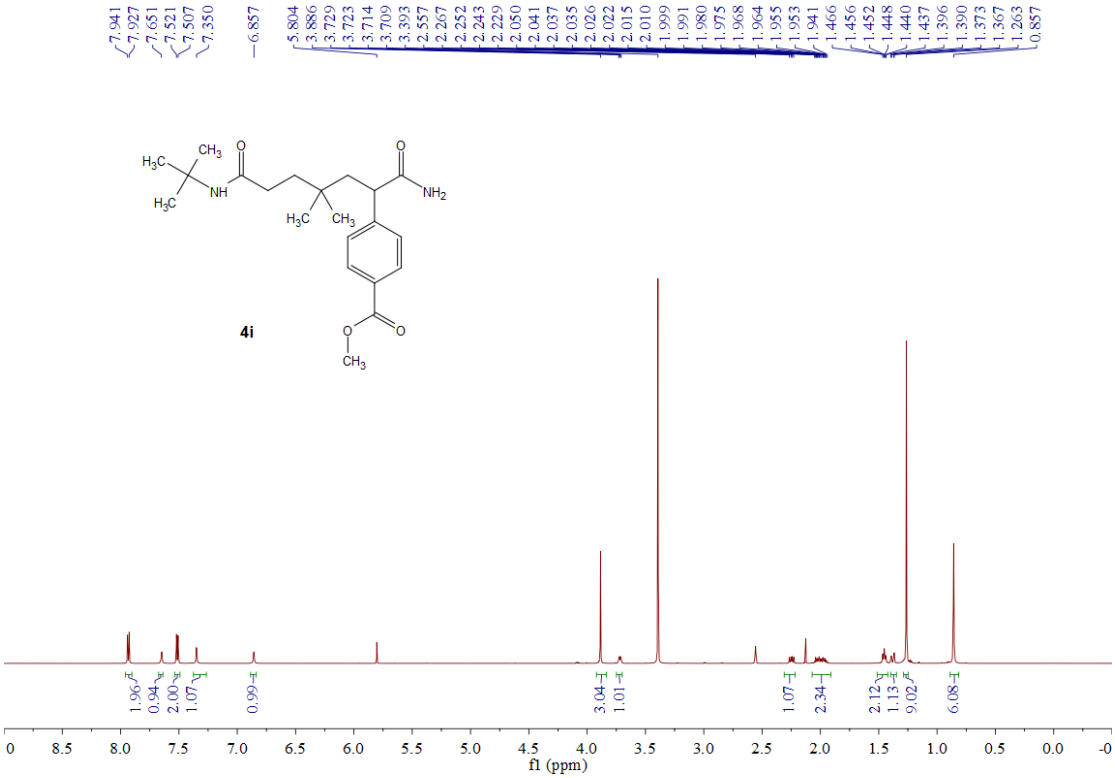
^{1}H NMR (600 MHz, $CDCl_3$) of 4h



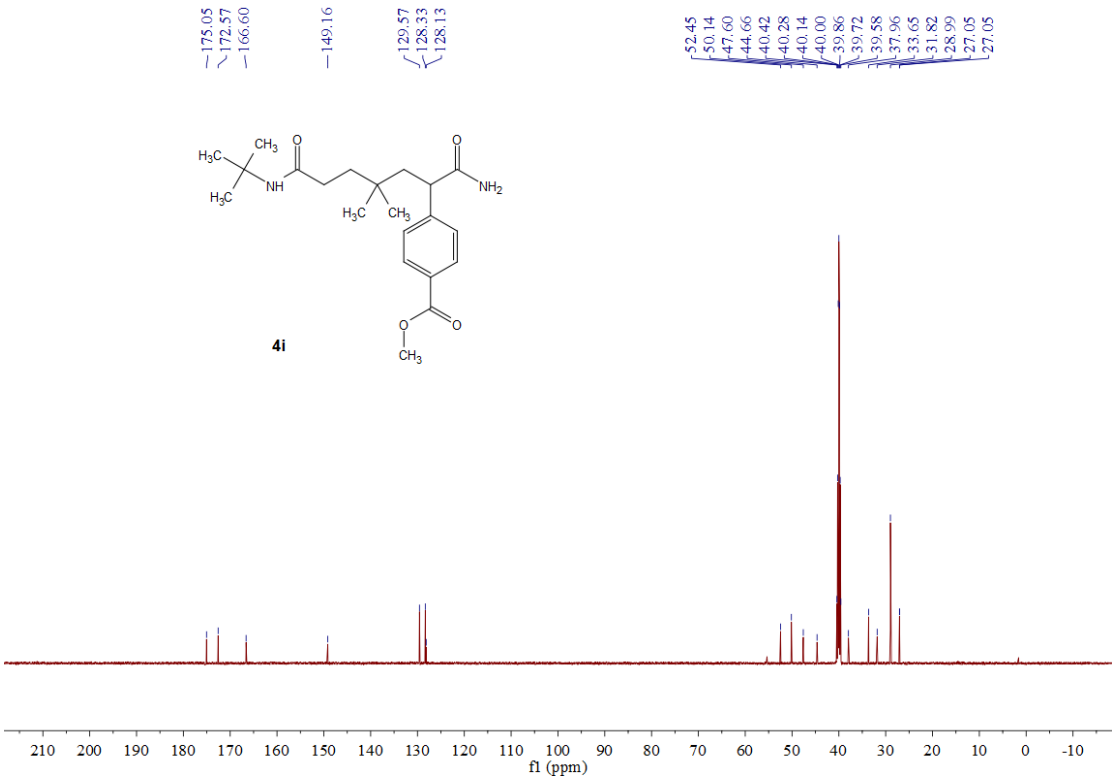
^{13}C NMR (151 MHz, $CDCl_3$) of 4h



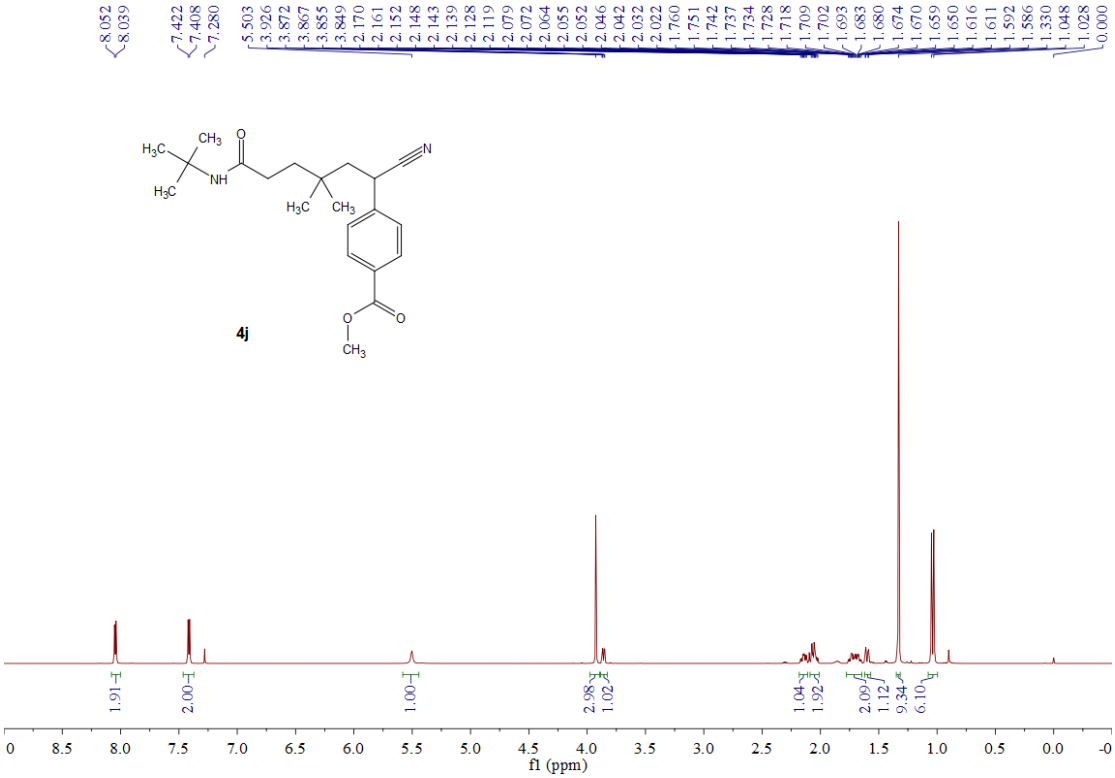
^{1}H NMR (600 MHz, $(CD_3)_2SO$) of 4i



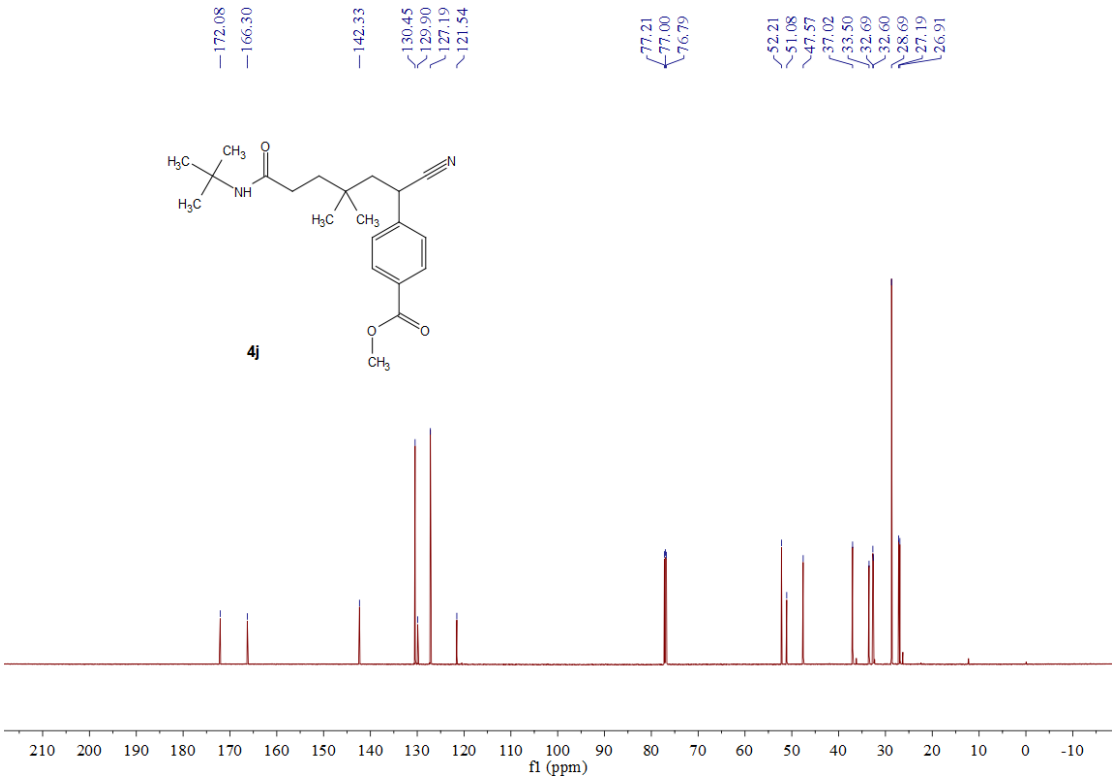
^{13}C NMR (151 MHz, $(CD_3)_2SO$) of 4i



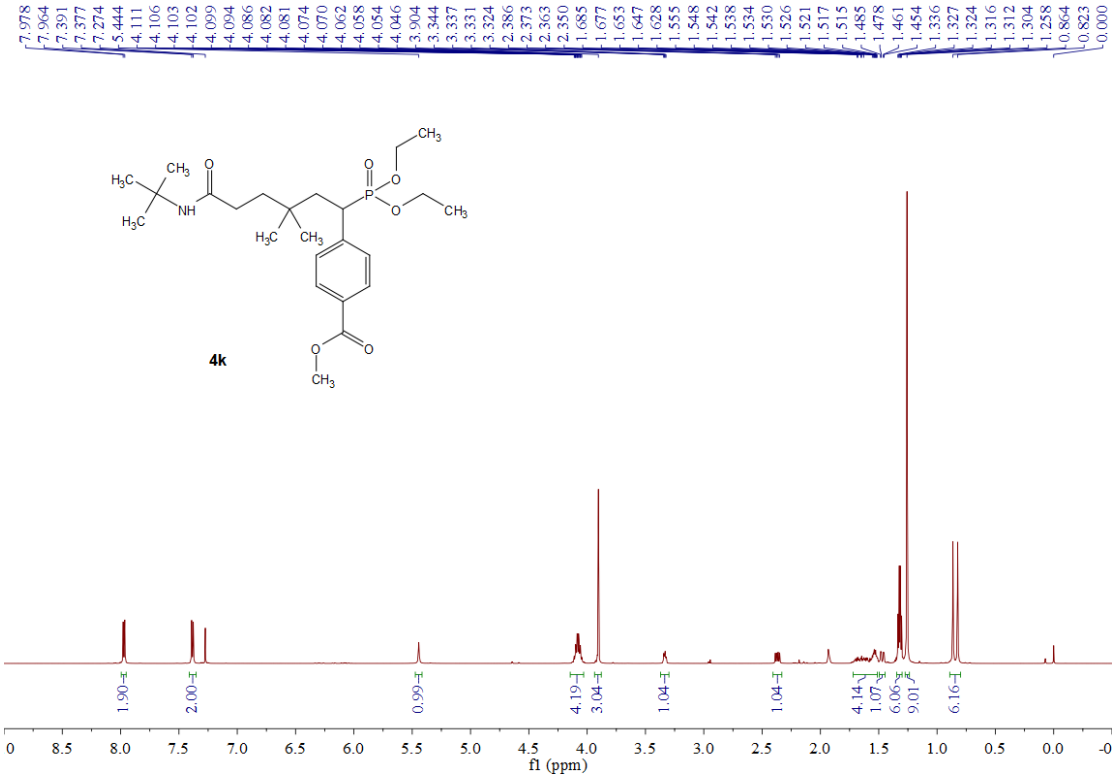
^{1}H NMR (600 MHz, $CDCl_3$) of 4j



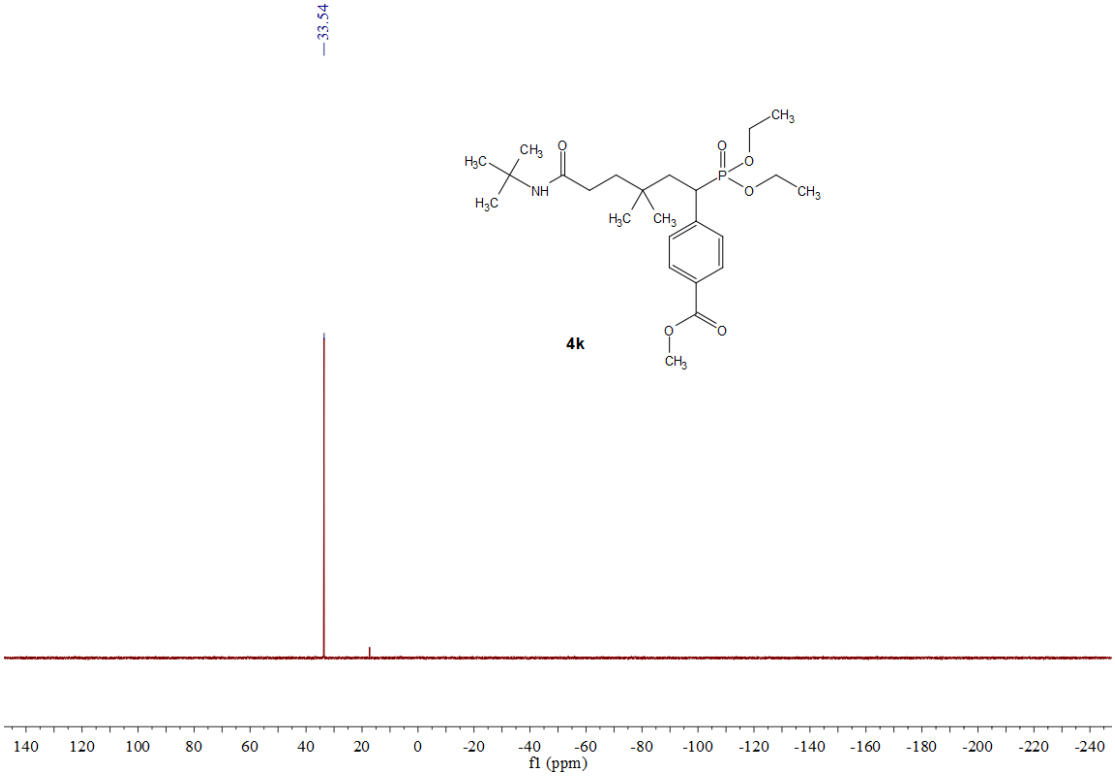
^{13}C NMR (151 MHz, $CDCl_3$) of 4j



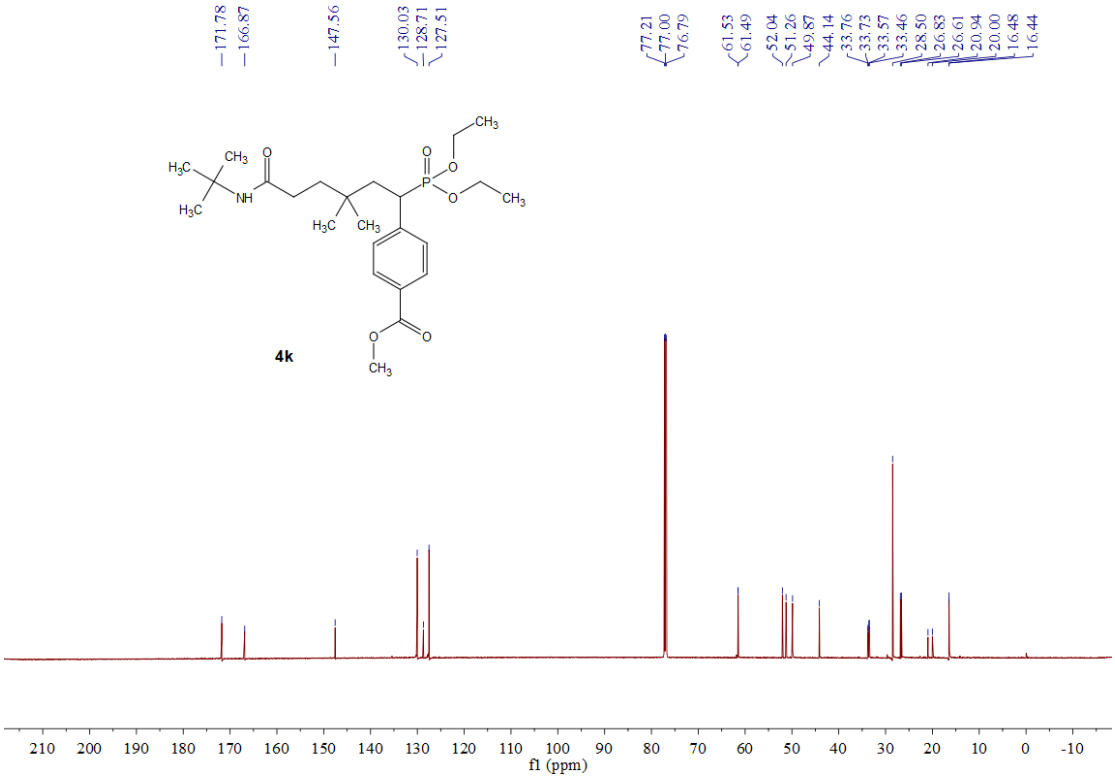
^{1}H NMR (600 MHz, $CDCl_3$) of 4k



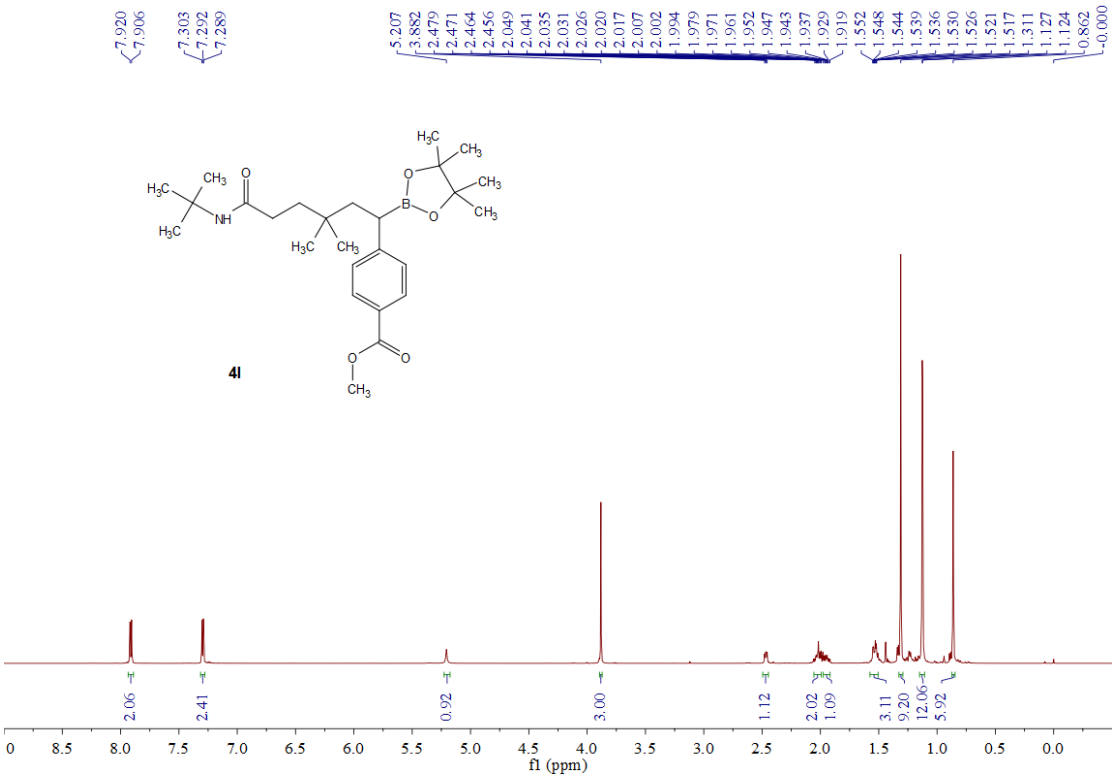
^{31}P NMR (162 MHz, $CDCl_3$) of 4k



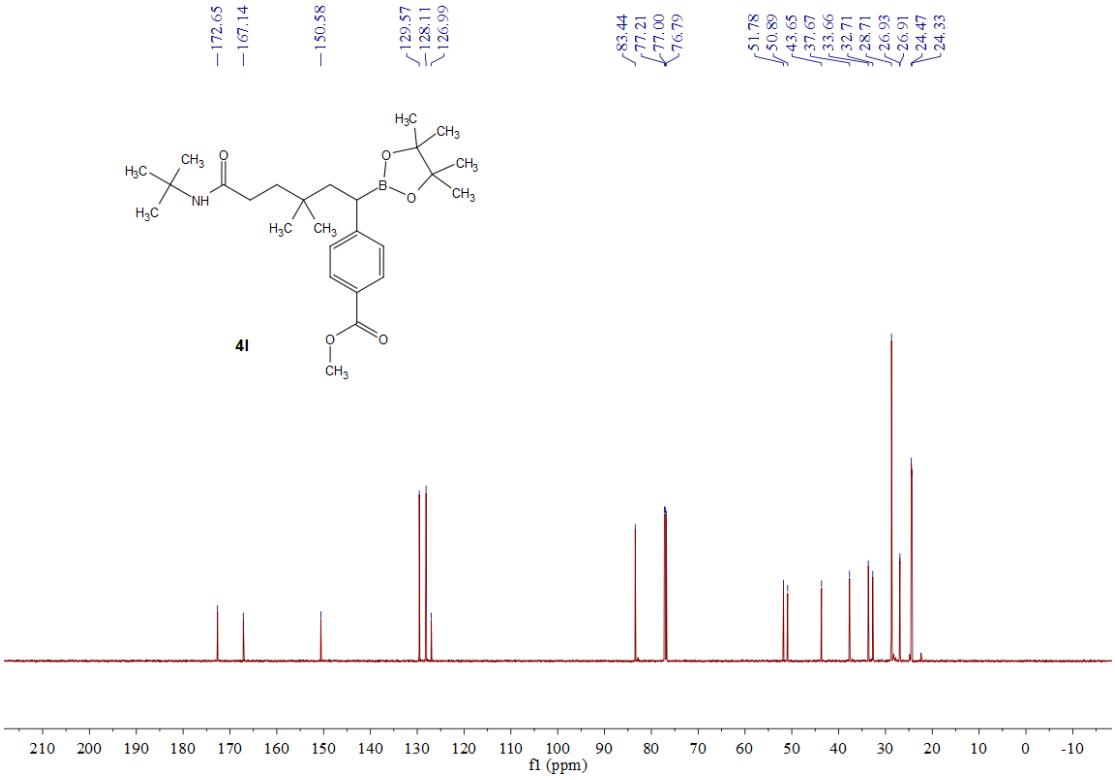
^{13}C NMR (151 MHz, $CDCl_3$) of 4k



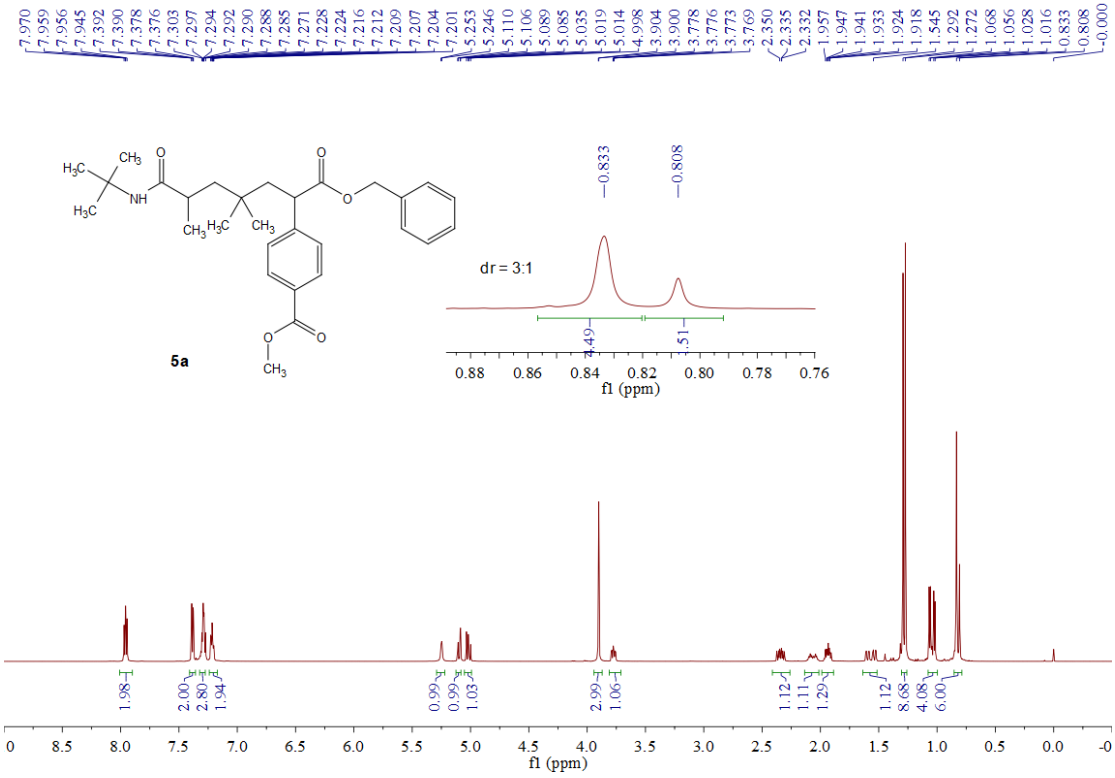
^{1}H NMR (600 MHz, $CDCl_3$) of 4l



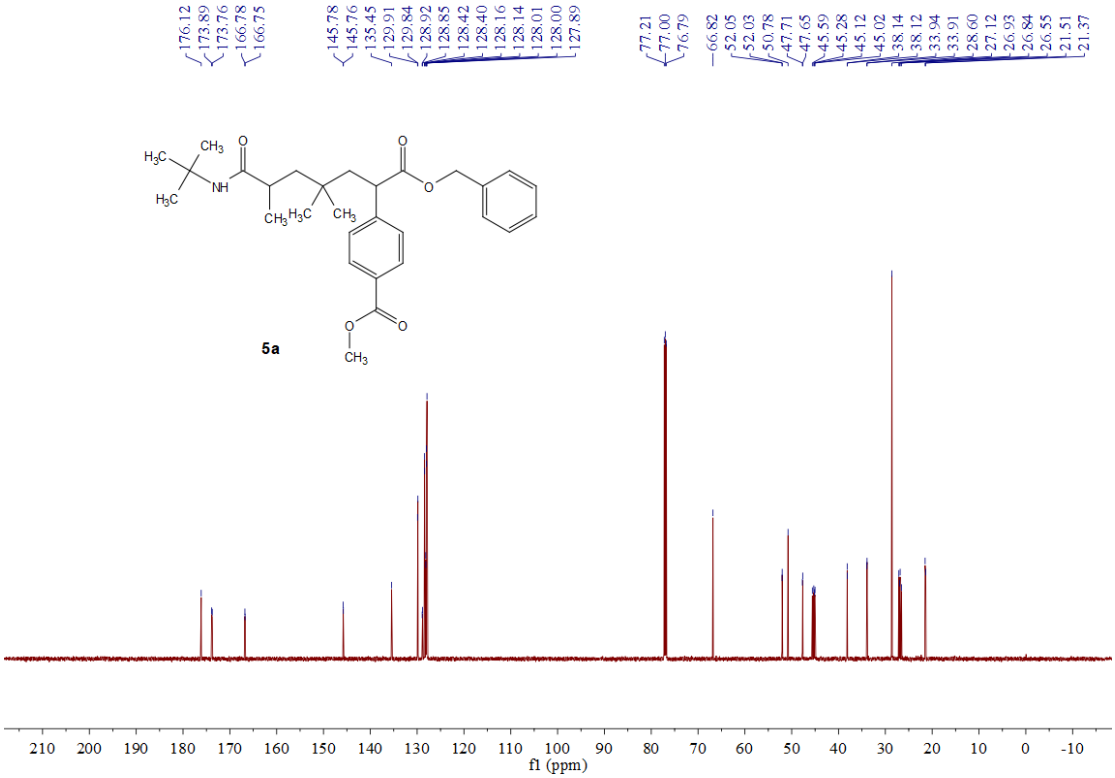
^{13}C NMR (151 MHz, $CDCl_3$) of 4l



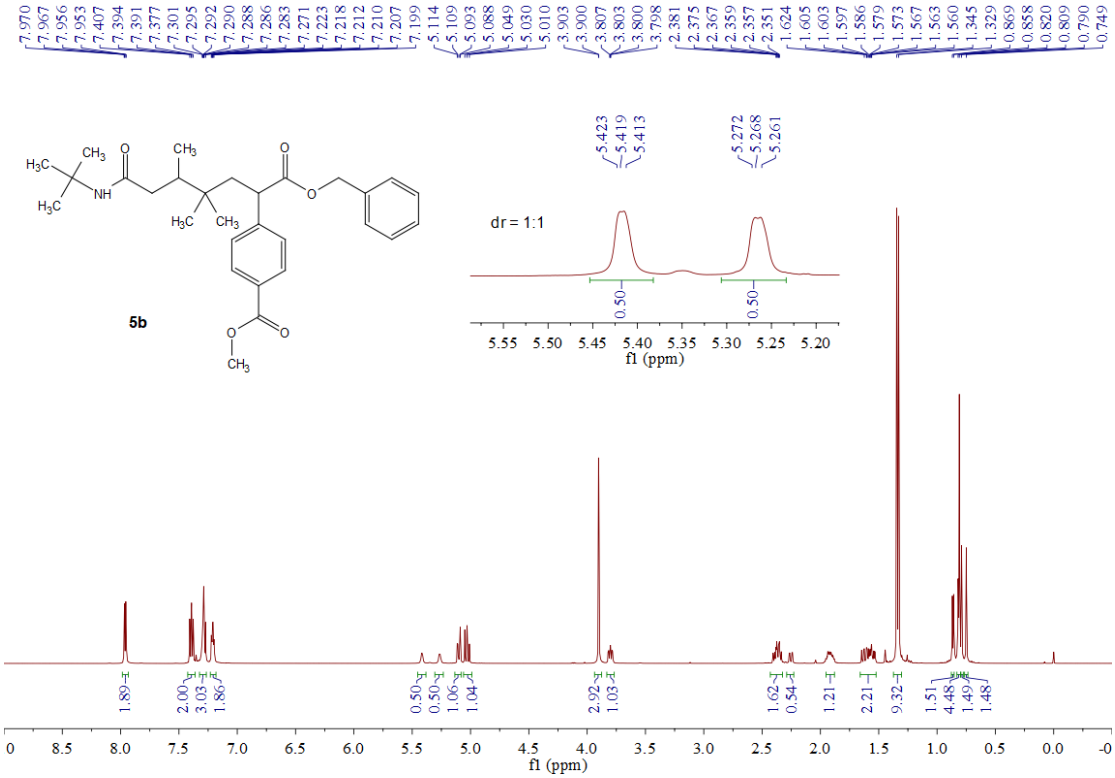
^{1}H NMR (600 MHz, $CDCl_3$) of 5a



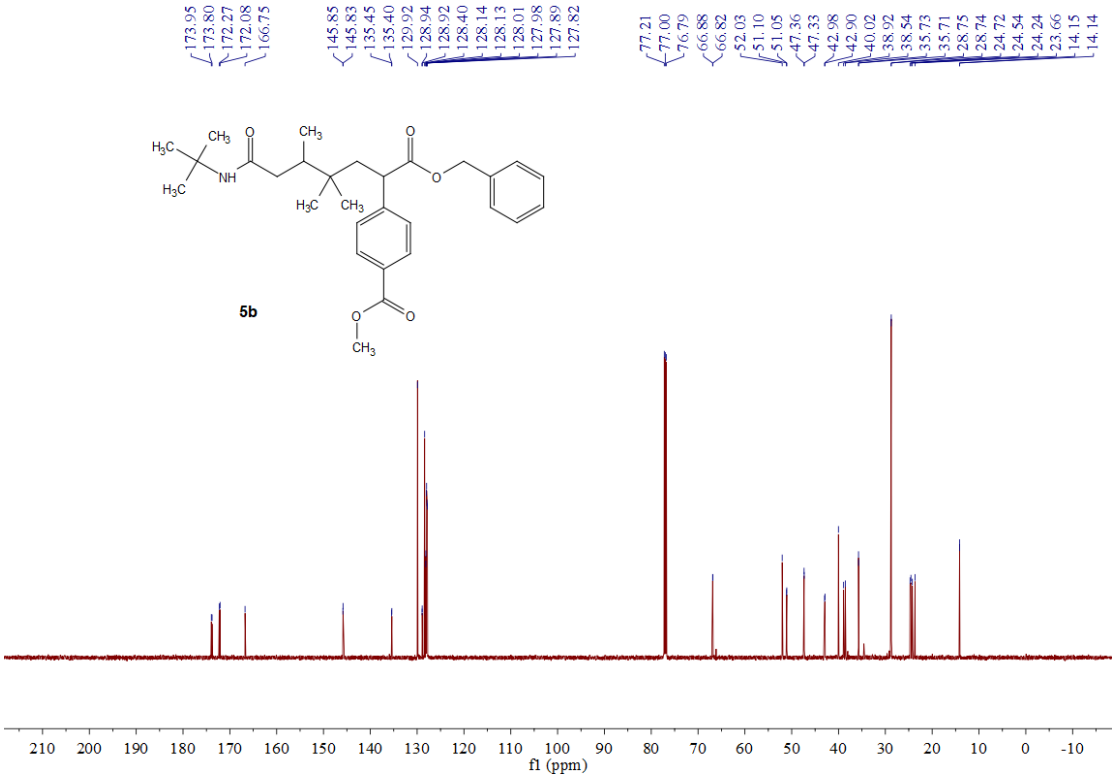
^{13}C NMR (151 MHz, $CDCl_3$) of 5a



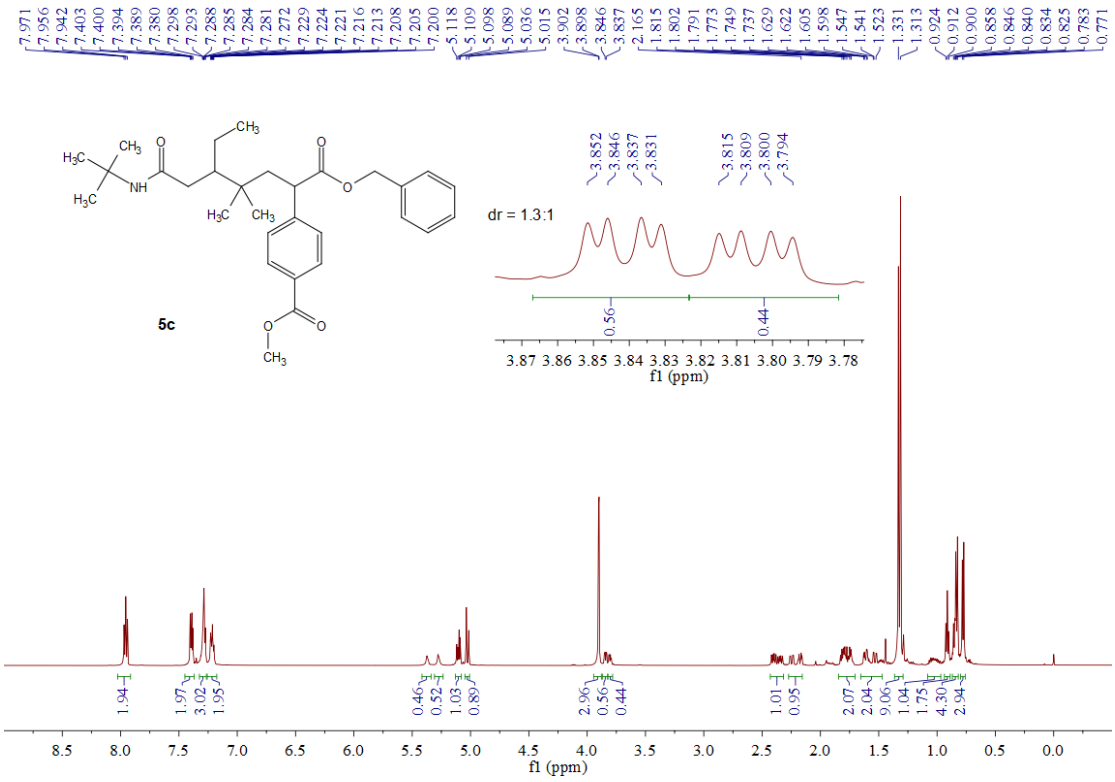
^{1}H NMR (600 MHz, $CDCl_3$) of 5b



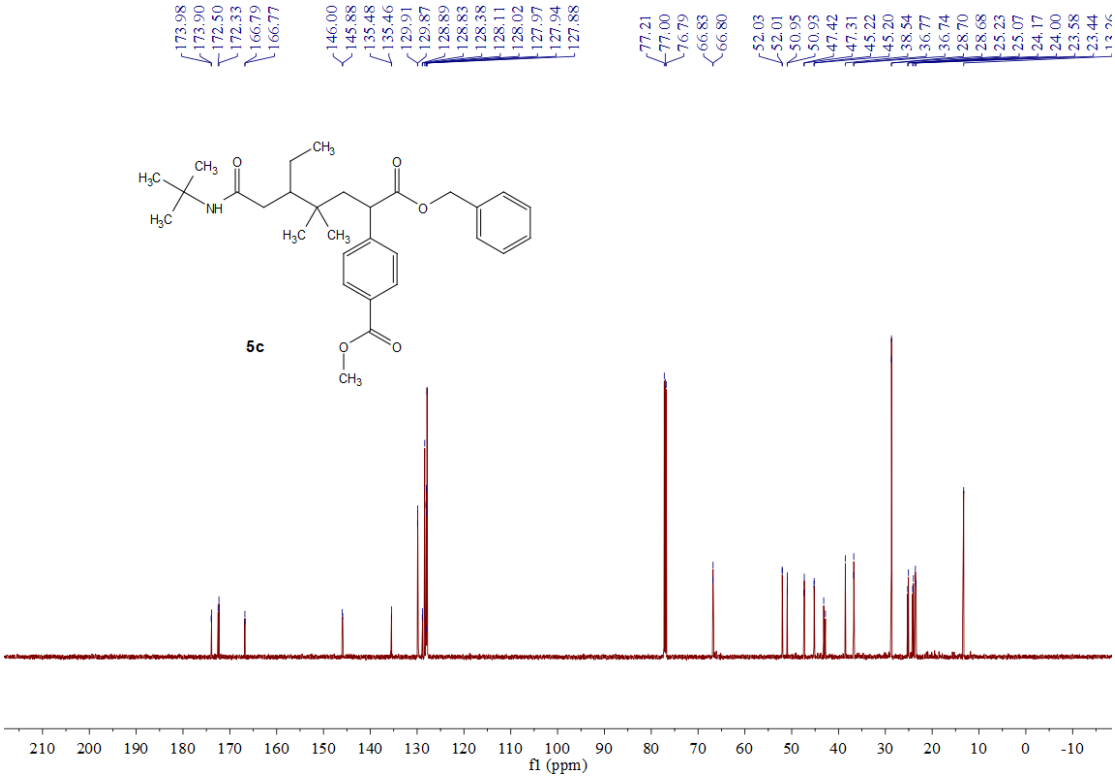
^{13}C NMR (151 MHz, $CDCl_3$) of 5b



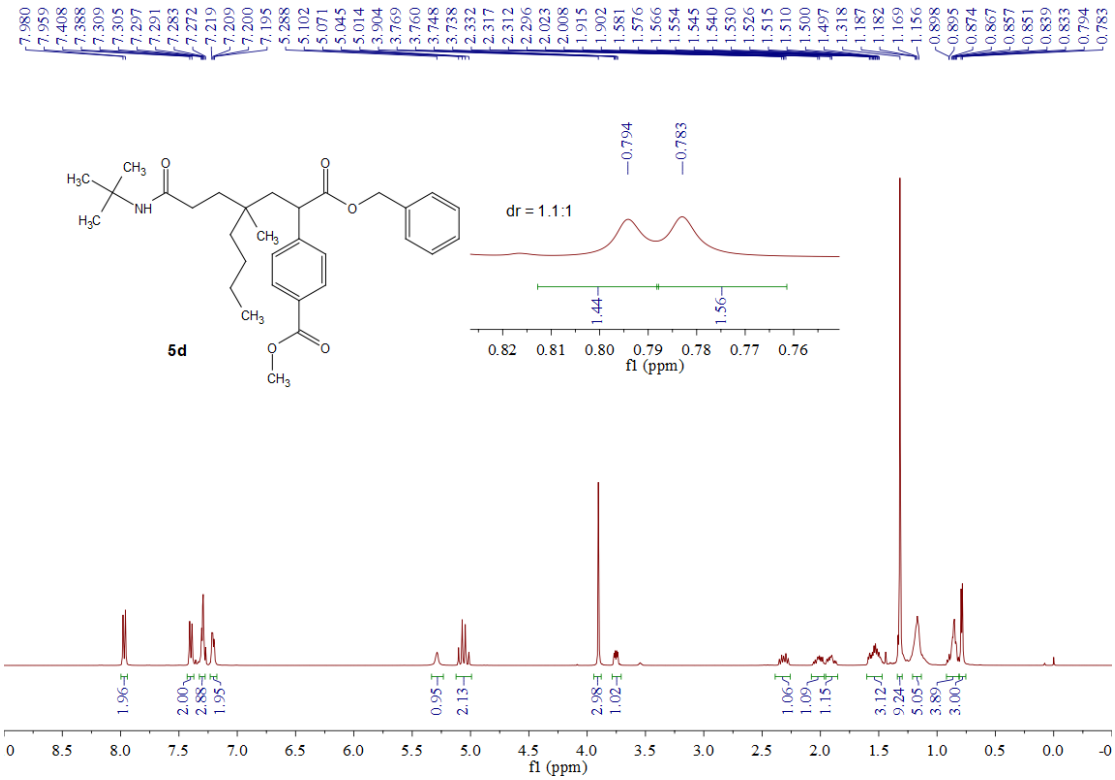
^{1}H NMR (600 MHz, $CDCl_3$) of 5c



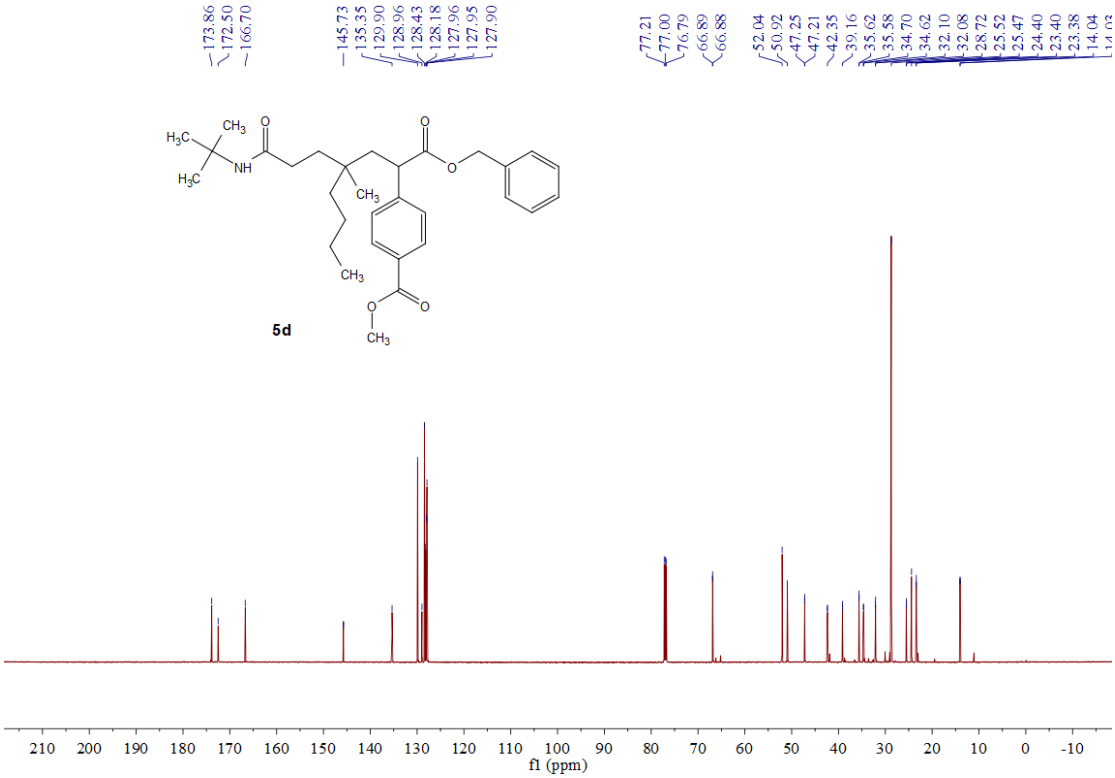
^{13}C NMR (151 MHz, $CDCl_3$) of 5c



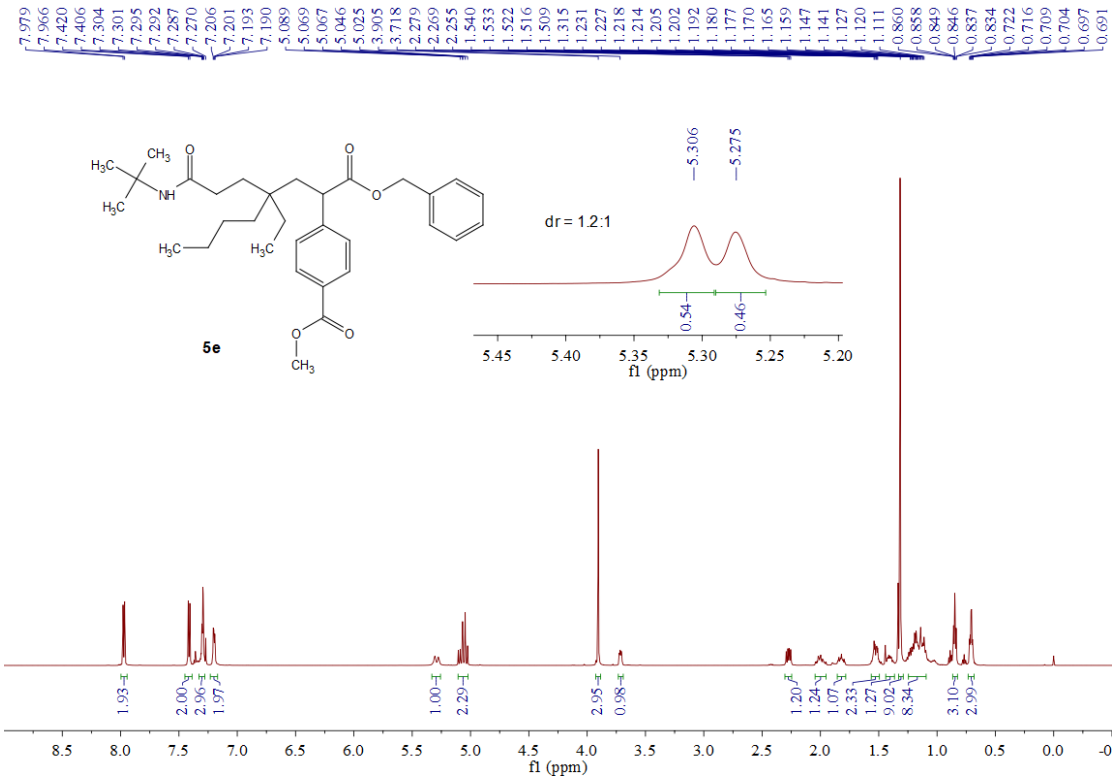
^{1}H NMR (400 MHz, $CDCl_3$) of 5d



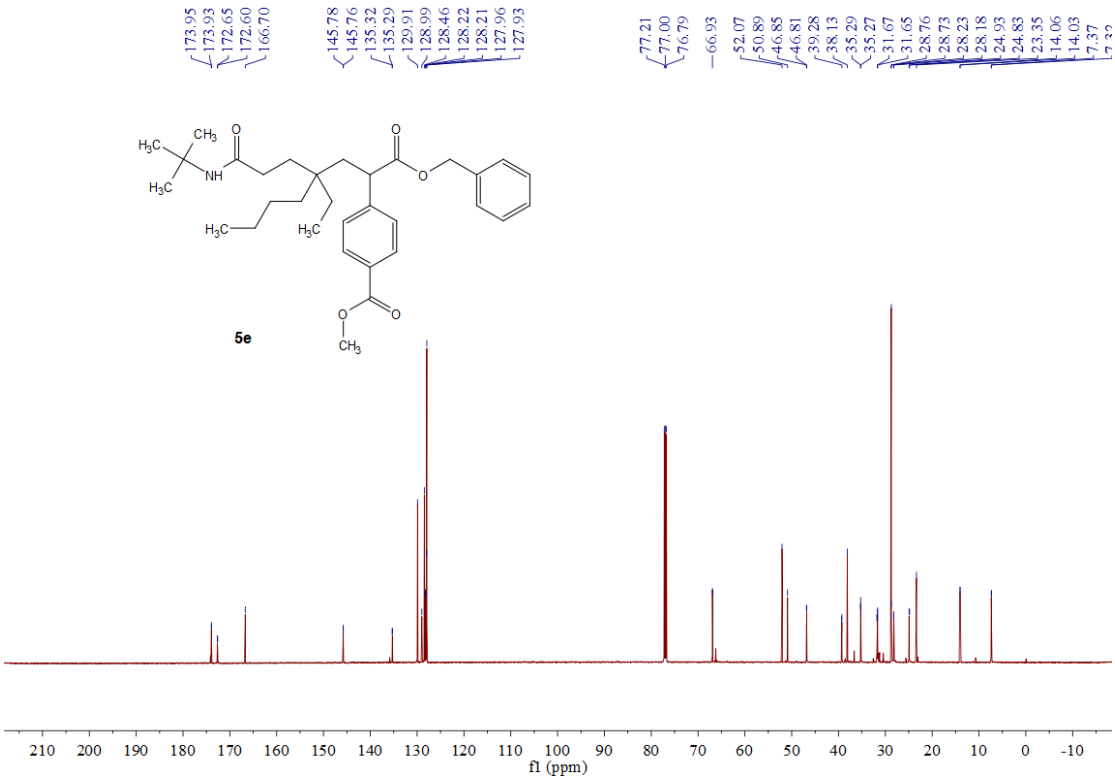
^{13}C NMR (151 MHz, $CDCl_3$) of 5d



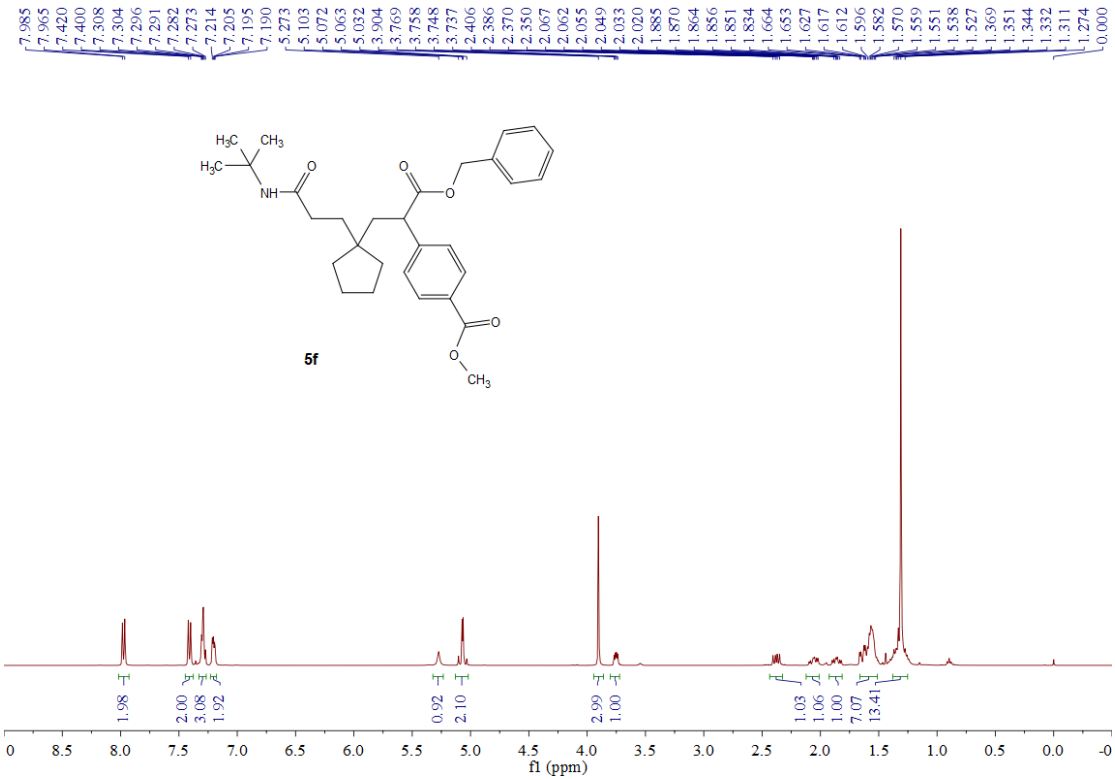
^{1}H NMR (600 MHz, $CDCl_3$) of 5e



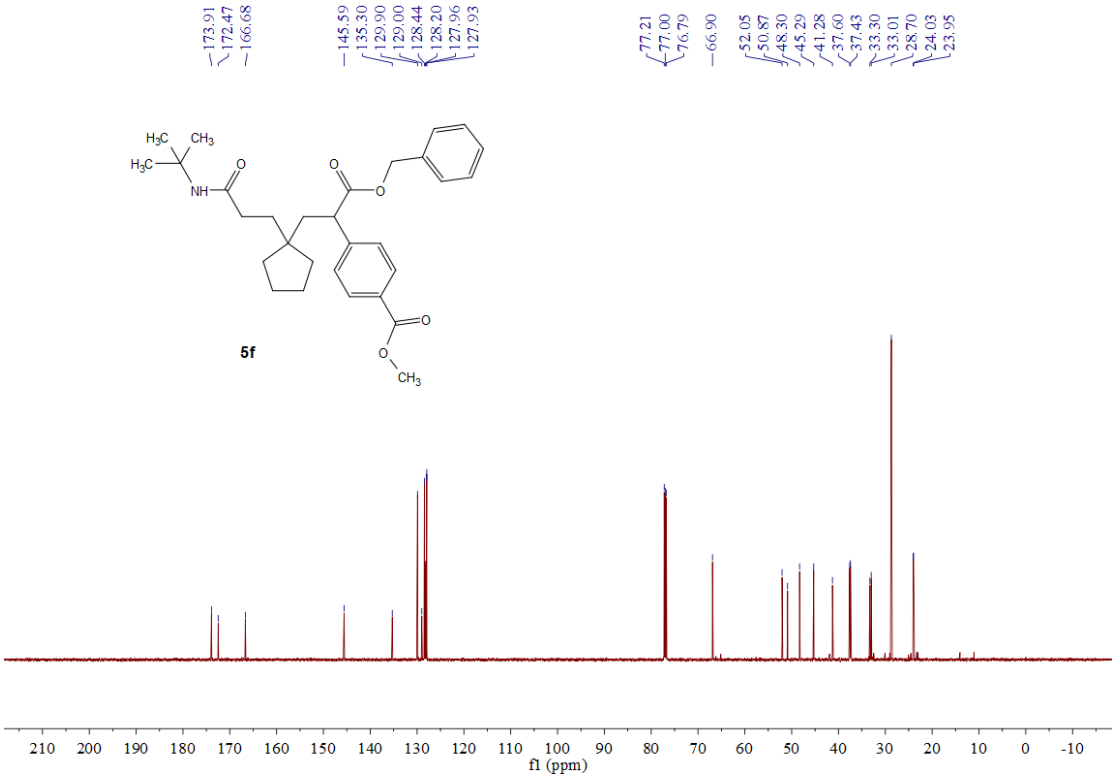
^{13}C NMR (151 MHz, $CDCl_3$) of 5e



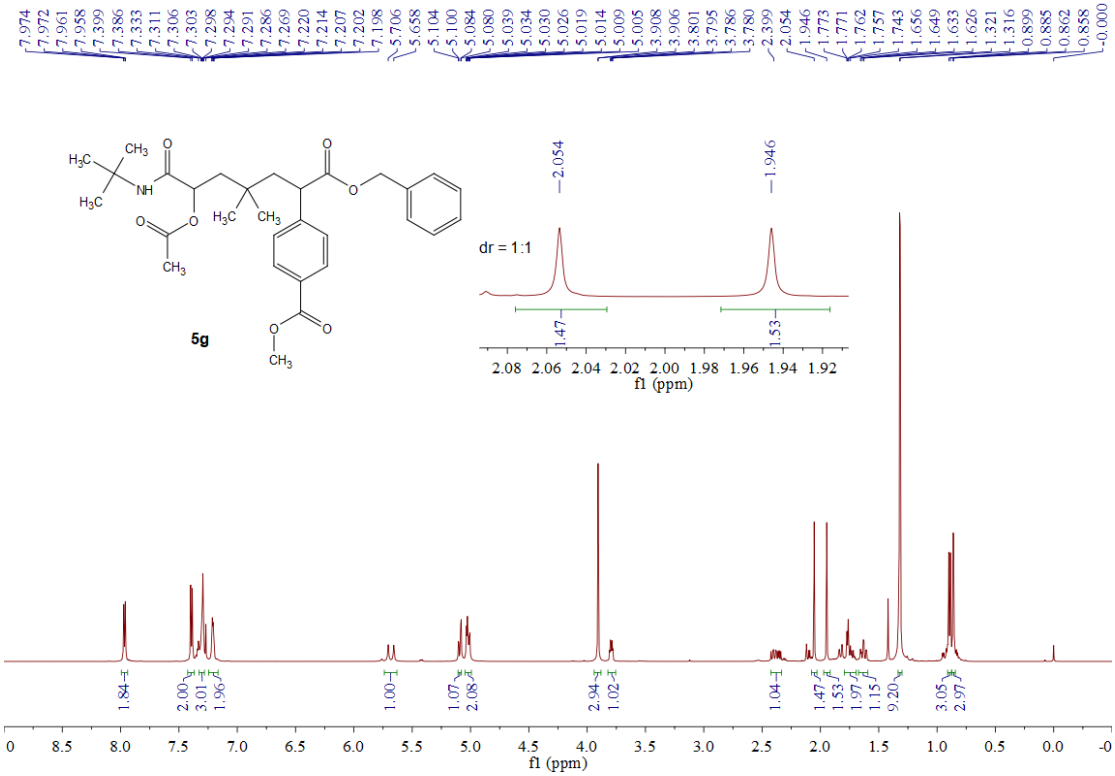
^{1}H NMR (400 MHz, $CDCl_3$) of 5f



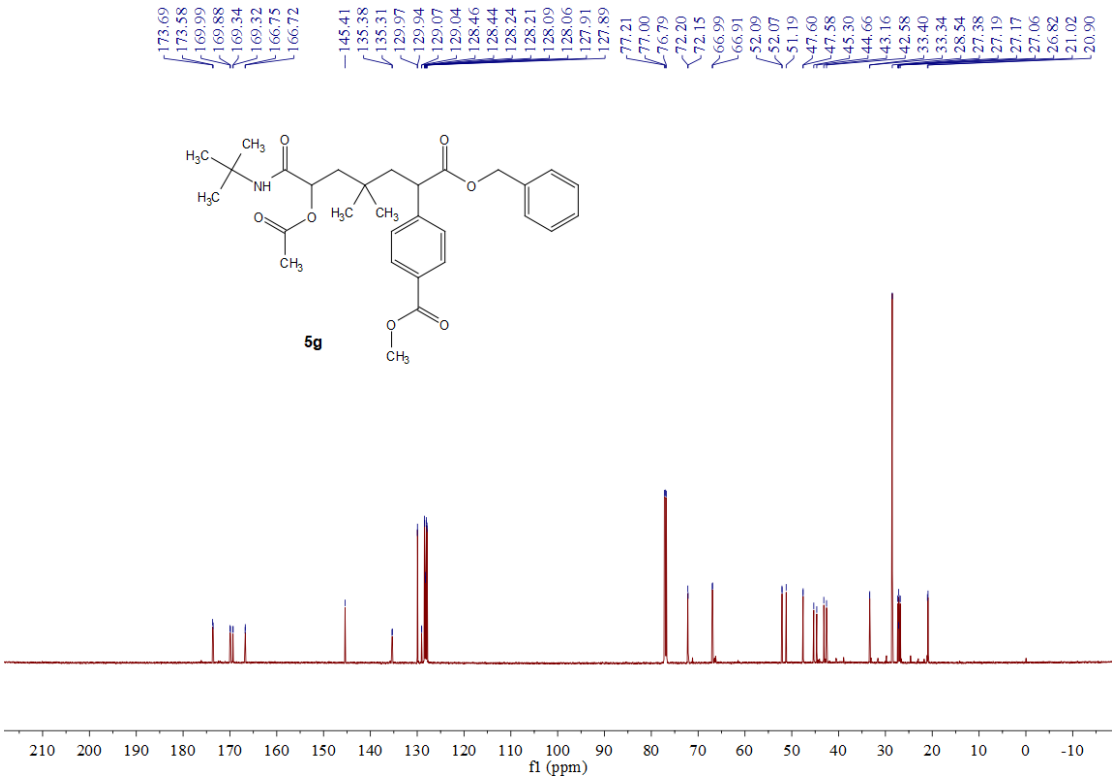
^{13}C NMR (151 MHz, $CDCl_3$) of 5f



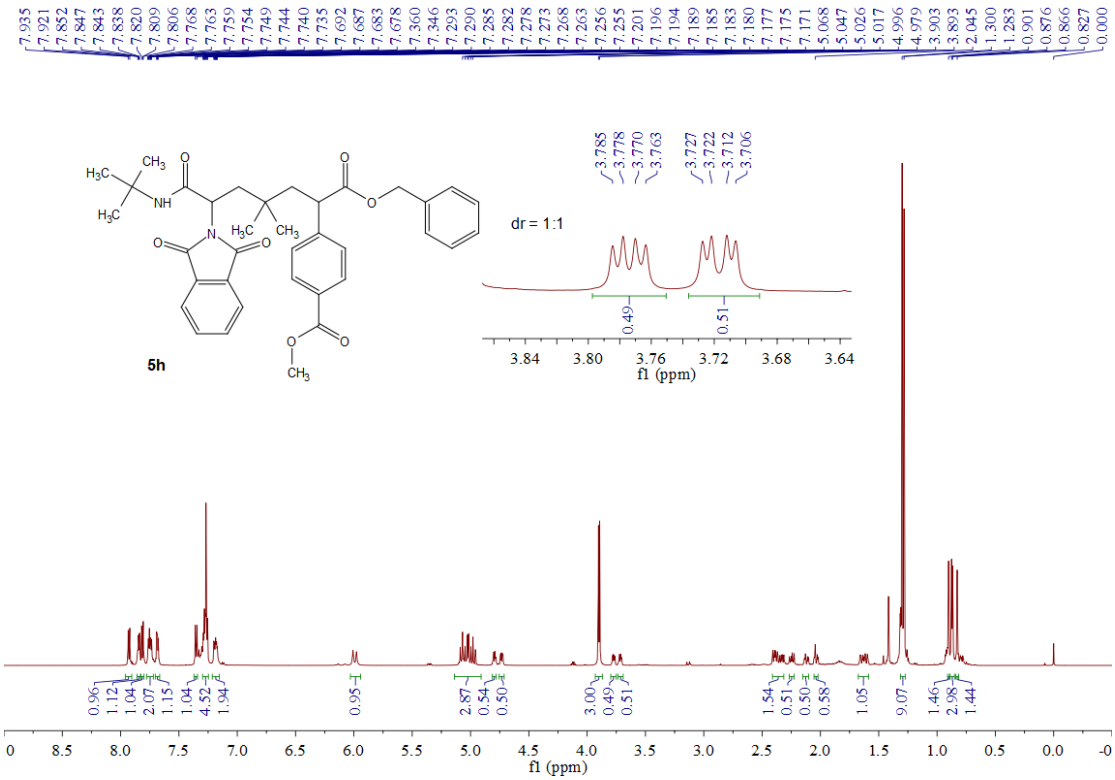
^{1}H NMR (600 MHz, $CDCl_3$) of 5g



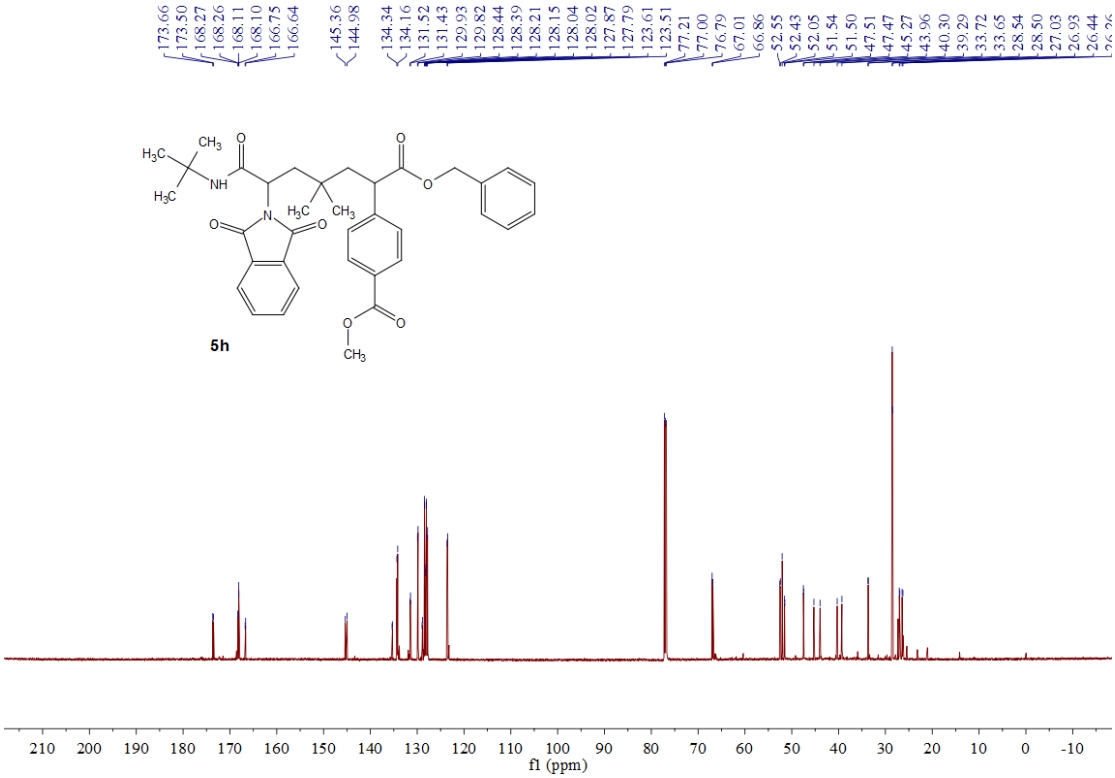
^{13}C NMR (151 MHz, $CDCl_3$) of 5g



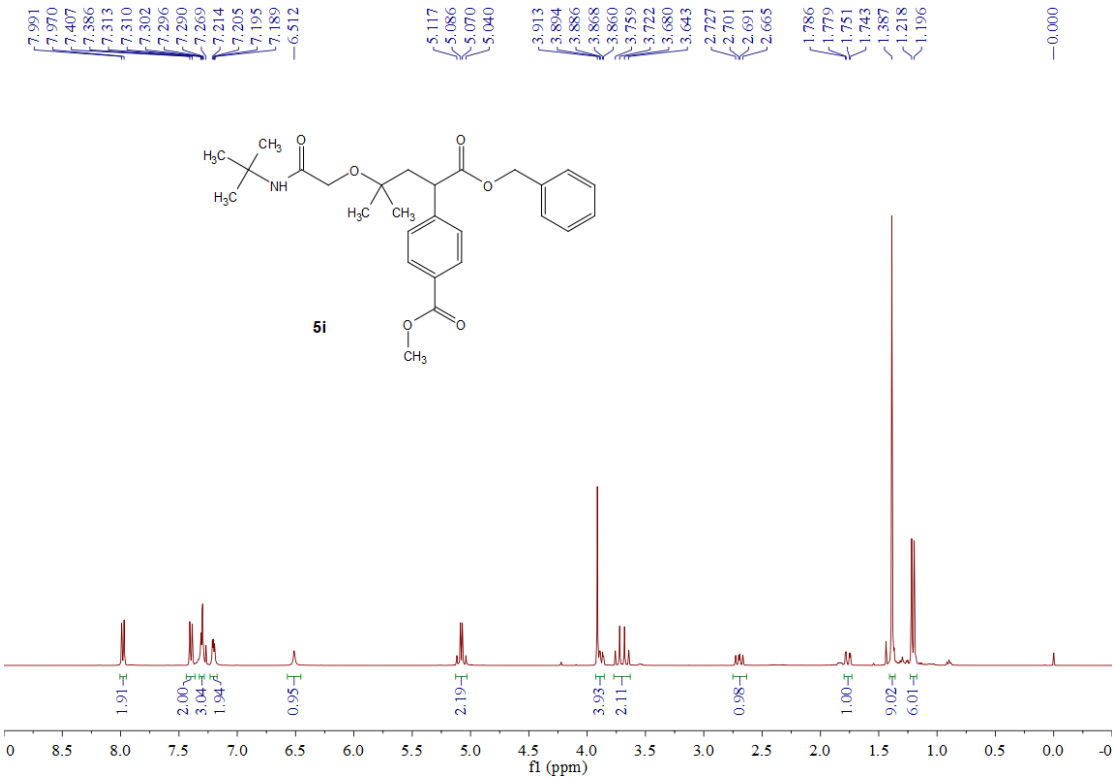
^{1}H NMR (600 MHz, $CDCl_3$) of 5h



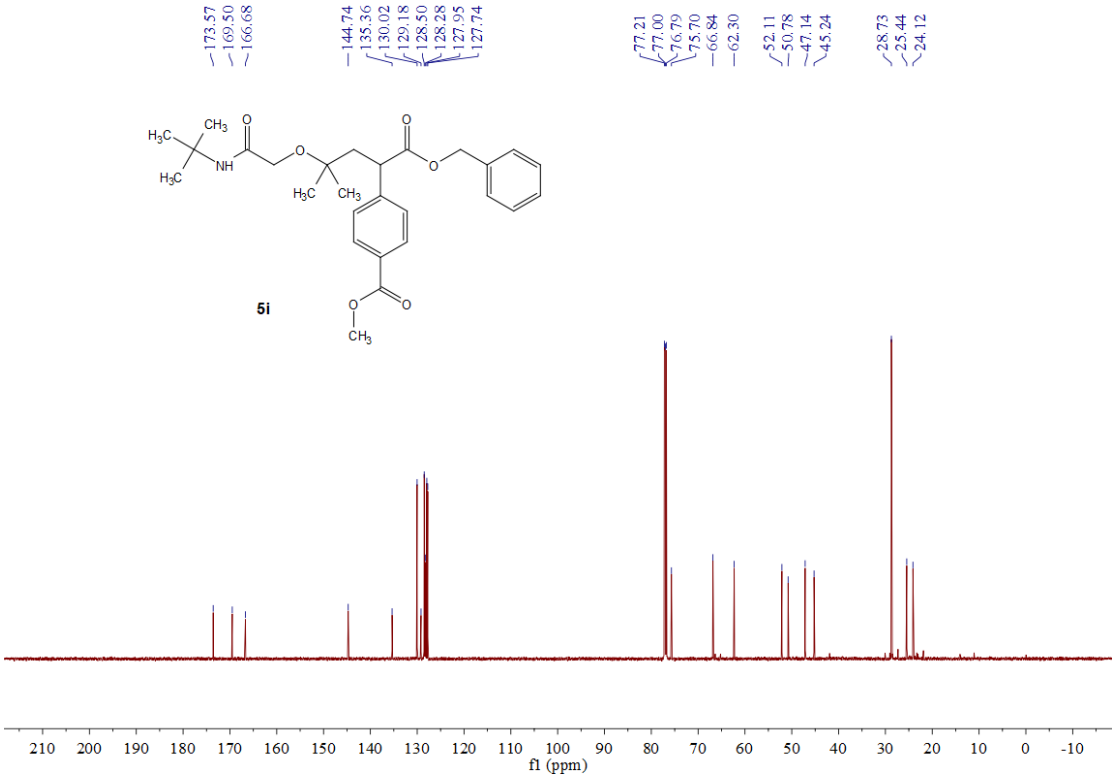
^{13}C NMR (151 MHz, $CDCl_3$) of 5h



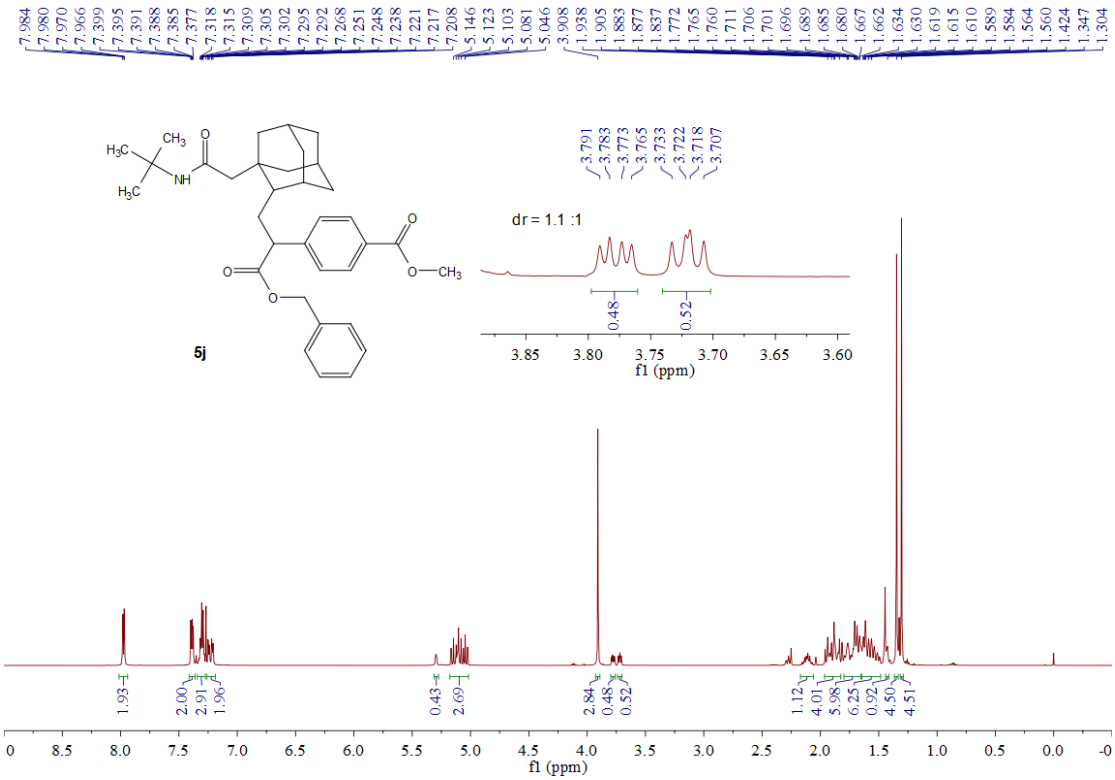
^{1}H NMR (400 MHz, $CDCl_3$) of 5i



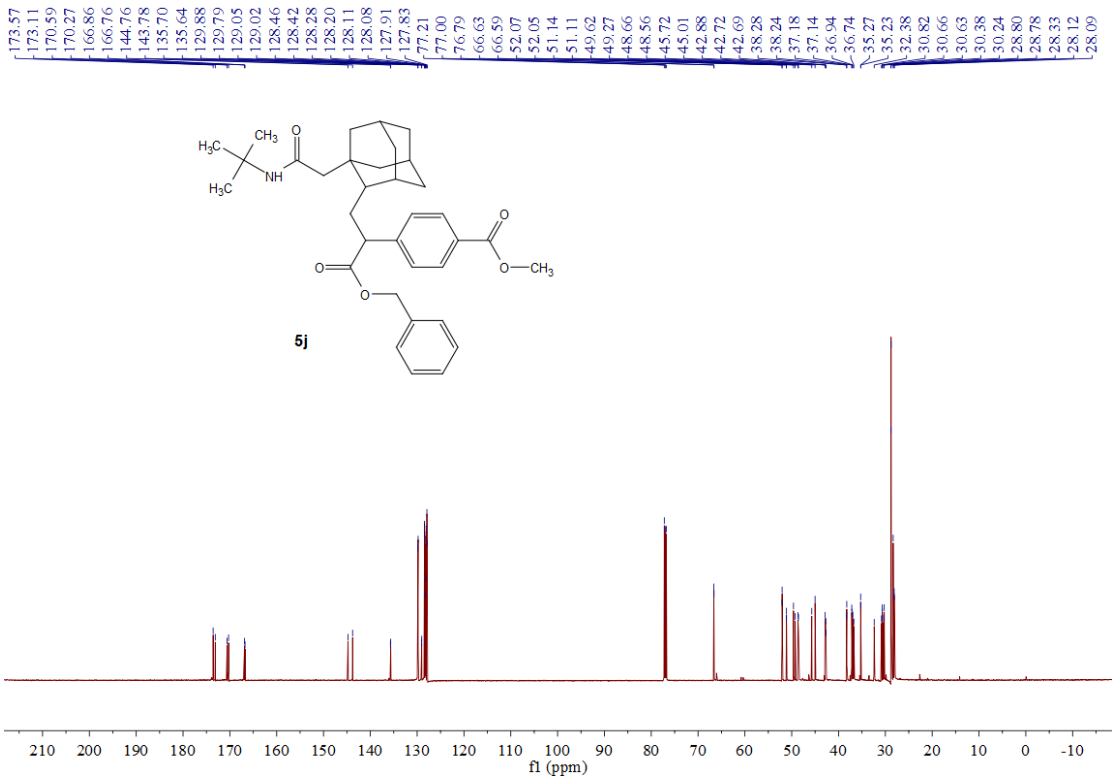
^{13}C NMR (151 MHz, $CDCl_3$) of 5i



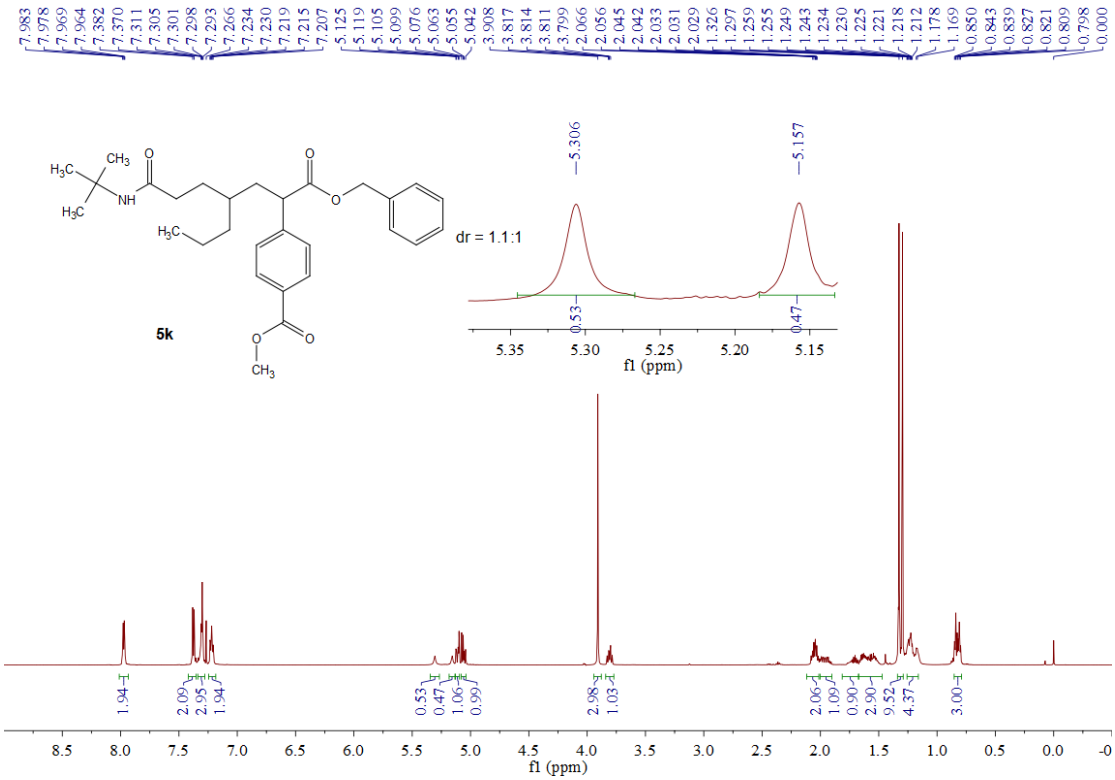
^{1}H NMR (600 MHz, $CDCl_3$) of 5j



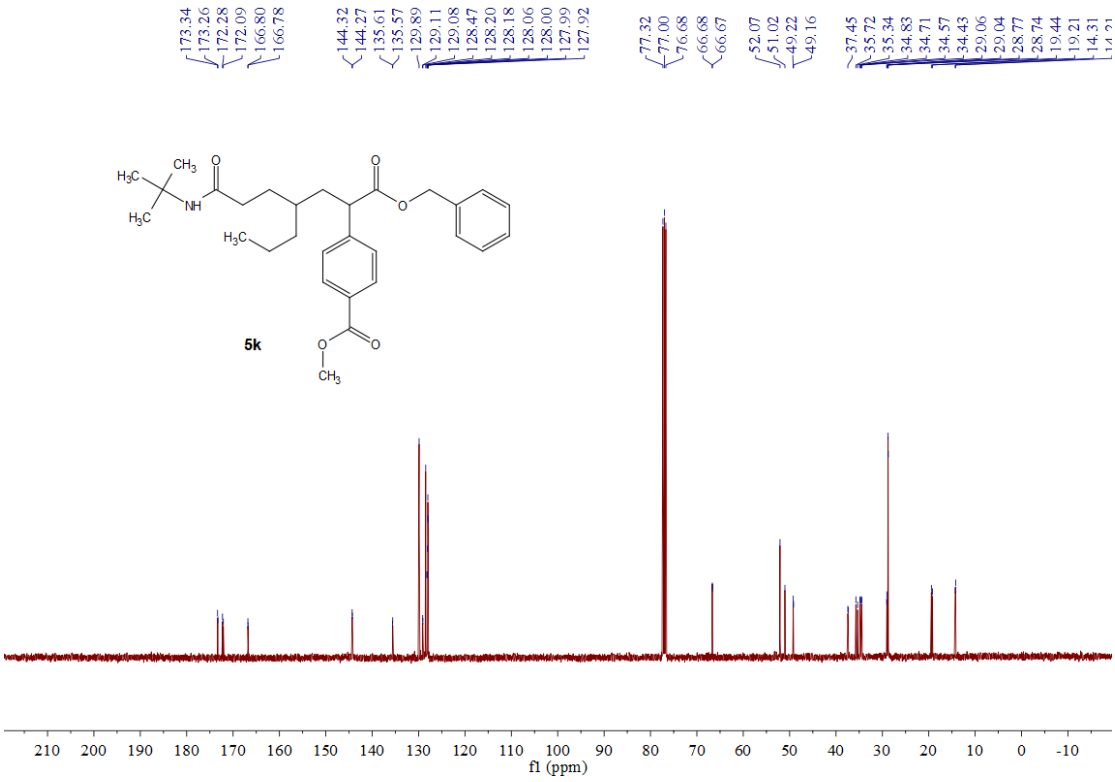
^{13}C NMR (151 MHz, $CDCl_3$) of 5j



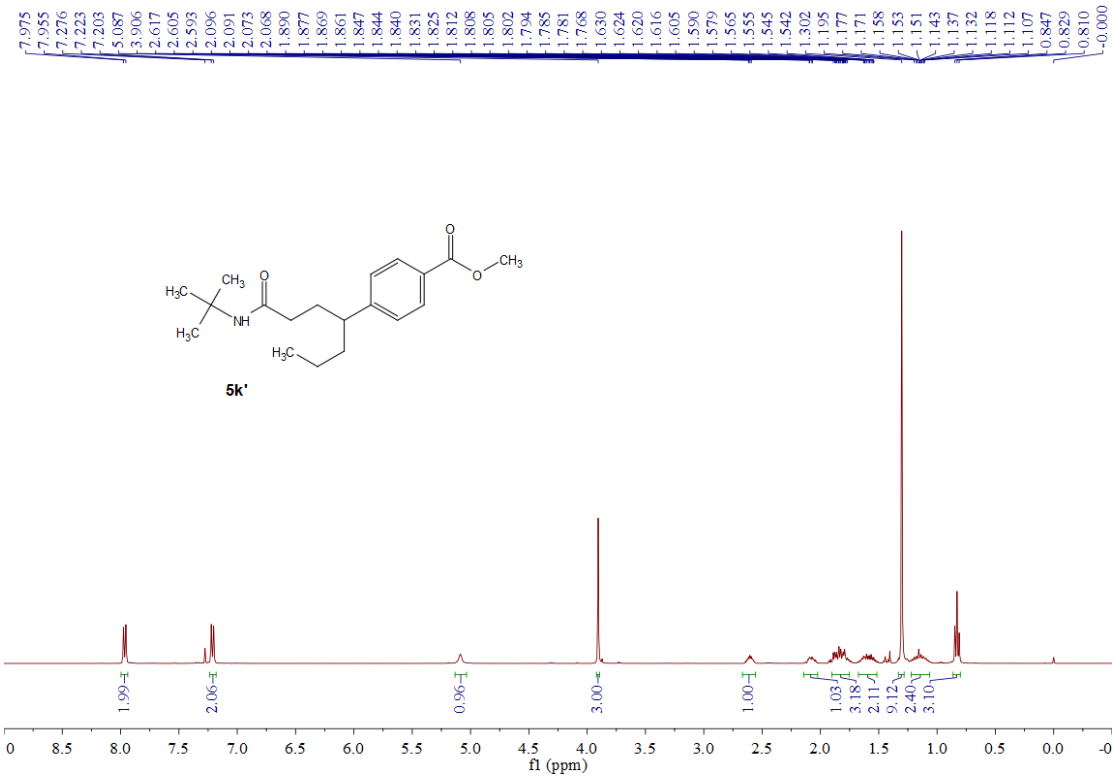
^{1}H NMR (600 MHz, $CDCl_3$) of 5k



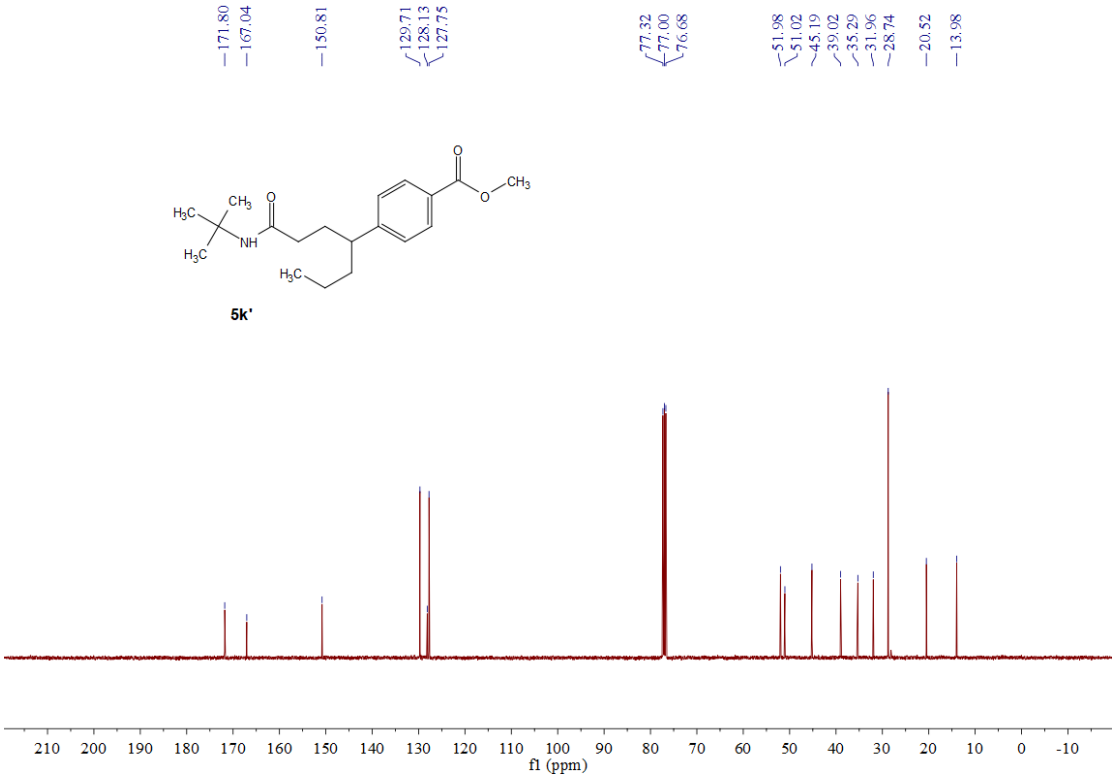
^{13}C NMR (101 MHz, $CDCl_3$) of 5k



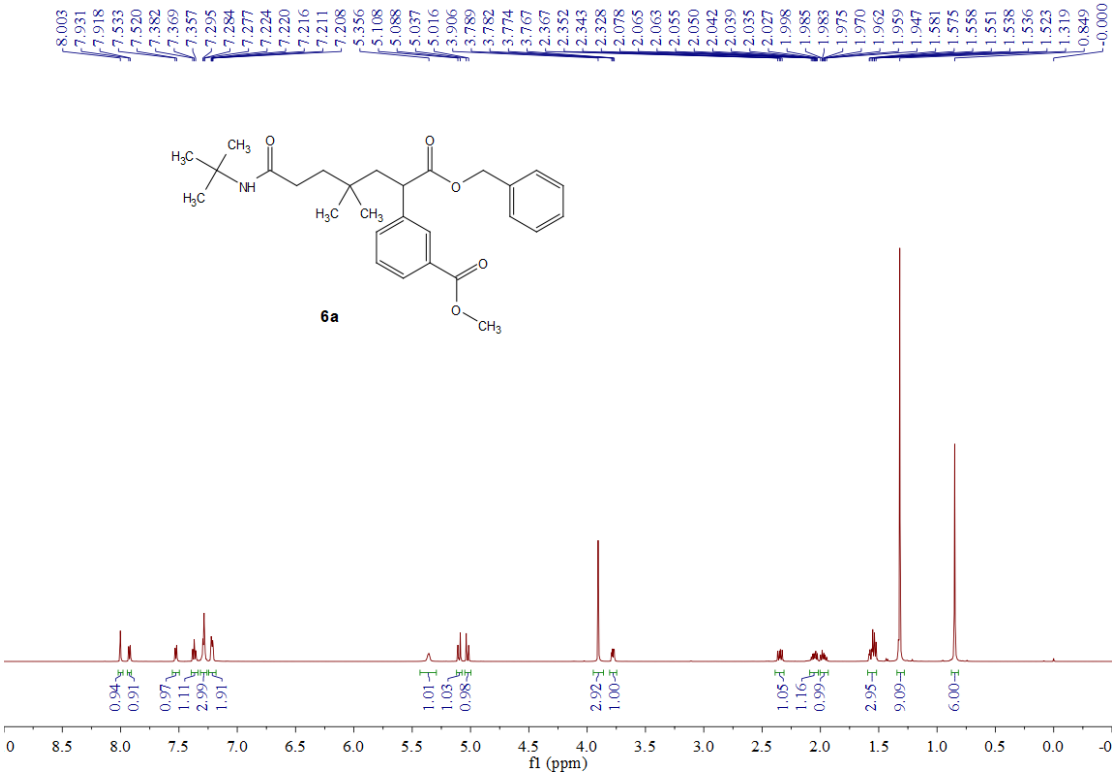
^{1}H NMR (400 MHz, $CDCl_3$) of 5k'



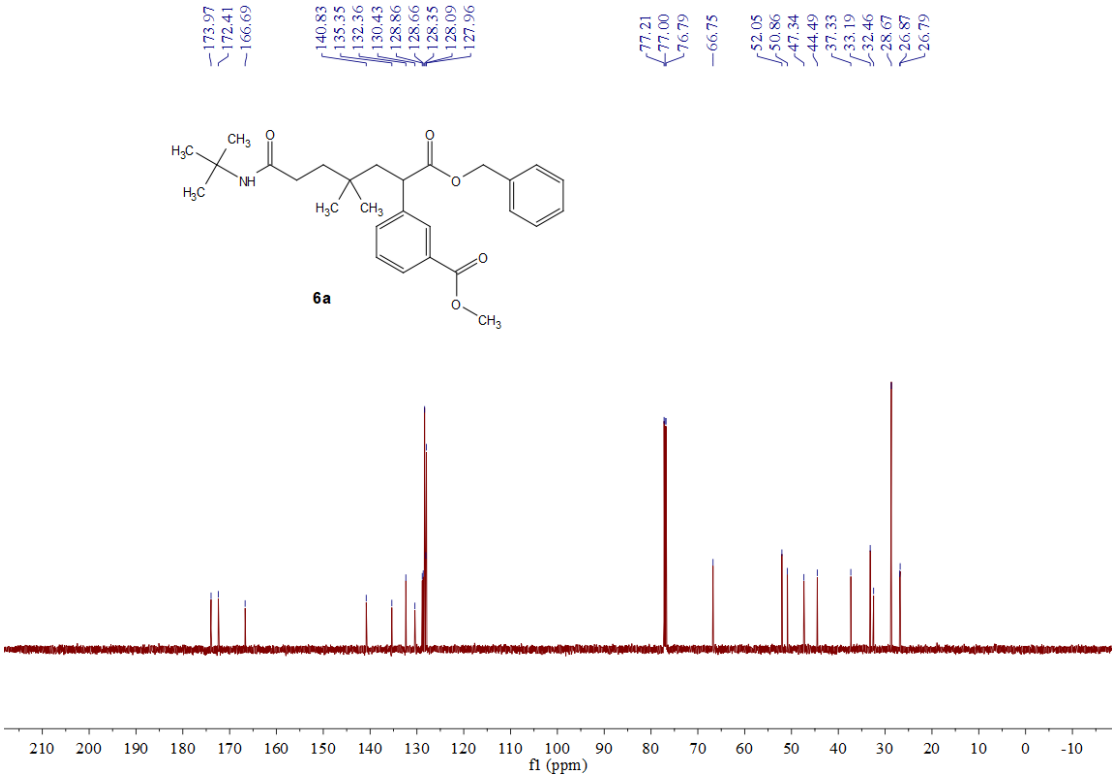
^{13}C NMR (101 MHz, $CDCl_3$) of 5k'



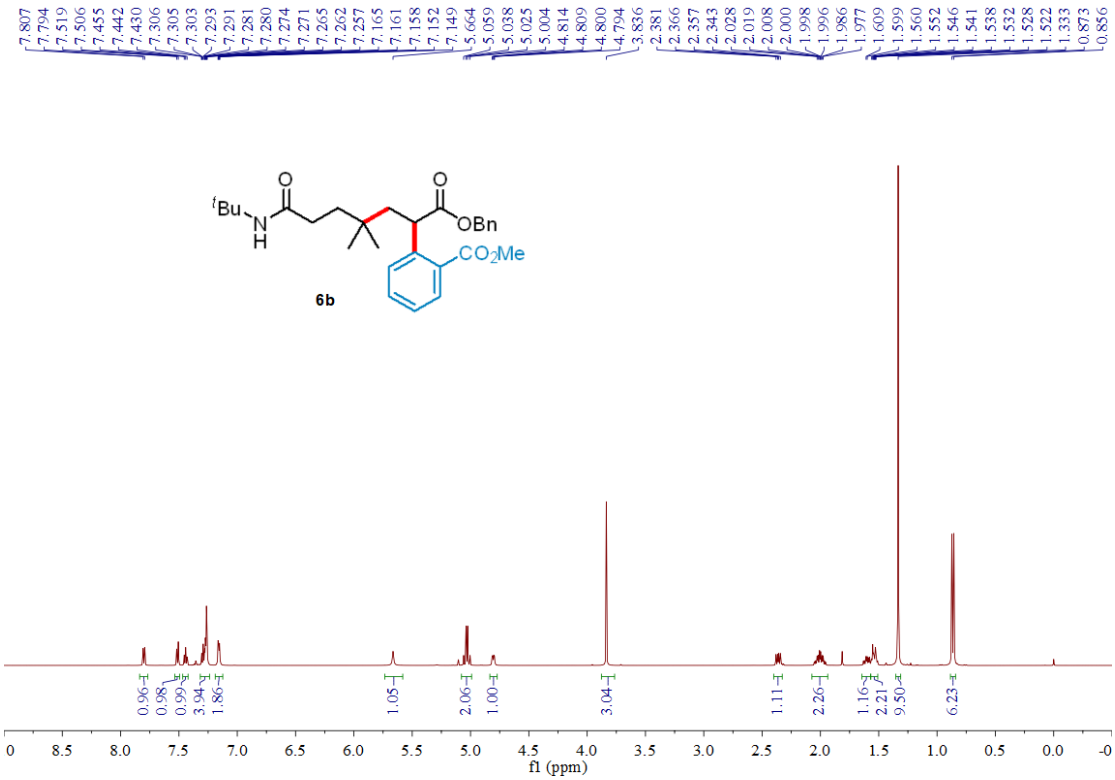
^{1}H NMR (600 MHz, $CDCl_3$) of 6a



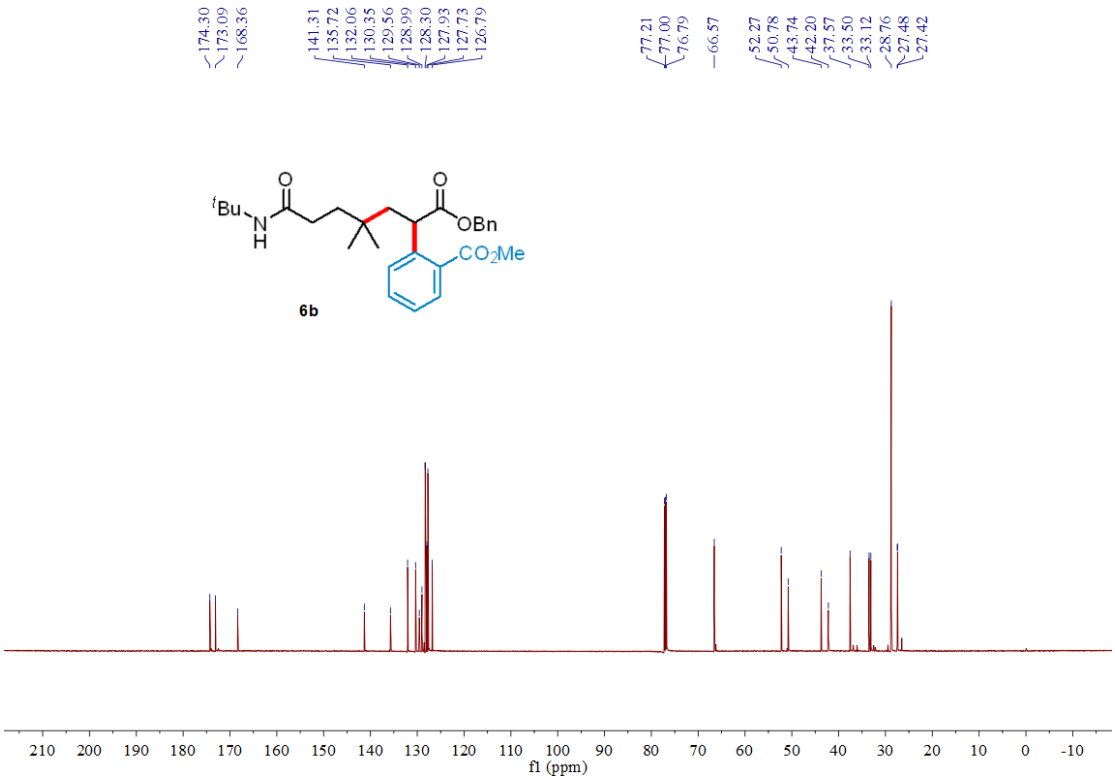
^{13}C NMR (151 MHz, $CDCl_3$) of 6a



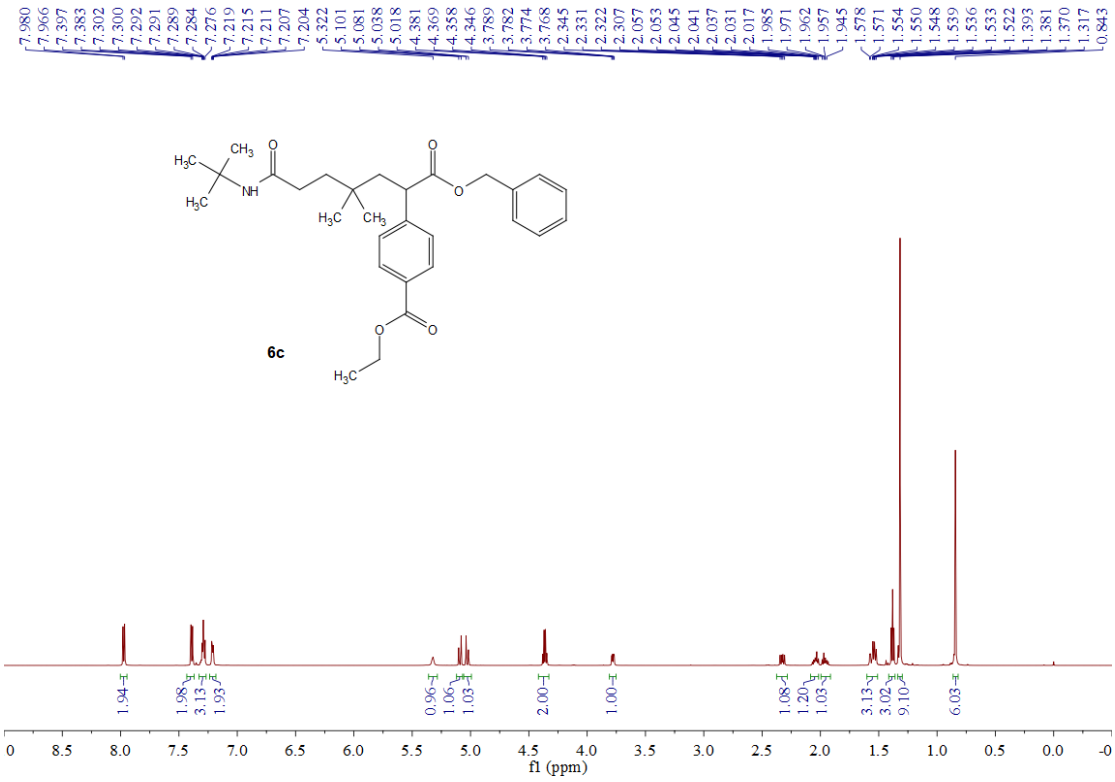
^{1}H NMR (600 MHz, $CDCl_3$) of 6b



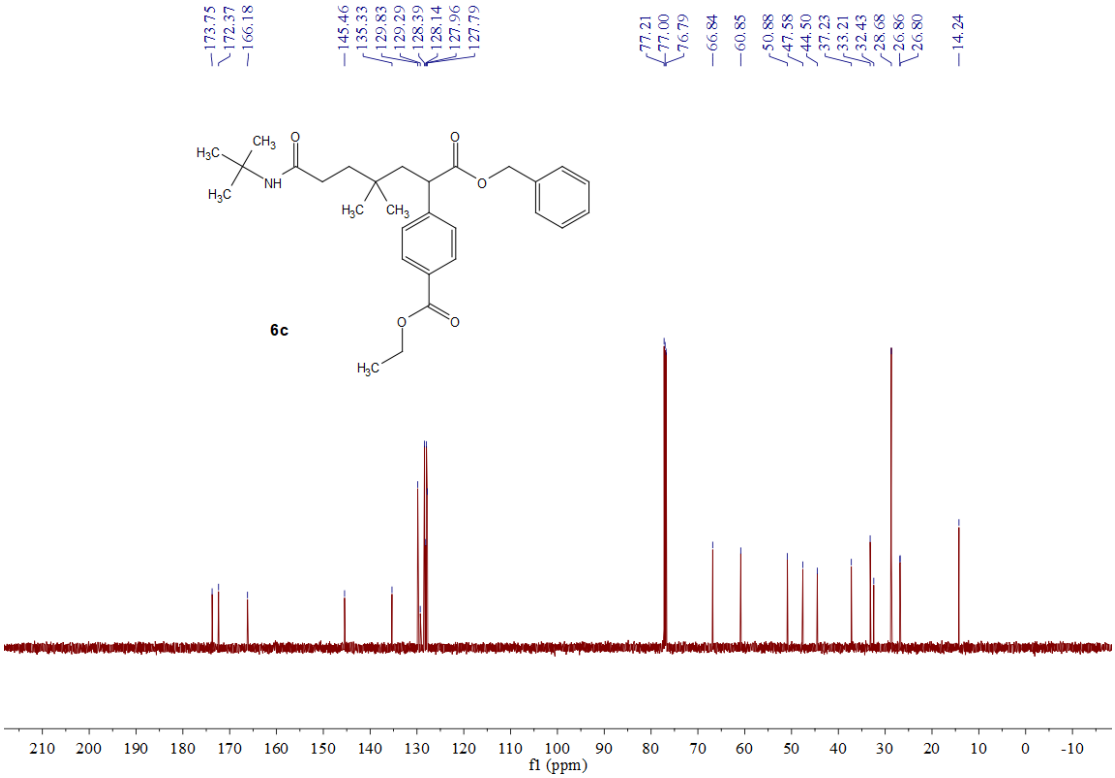
^{13}C NMR (151 MHz, $CDCl_3$) of 6b



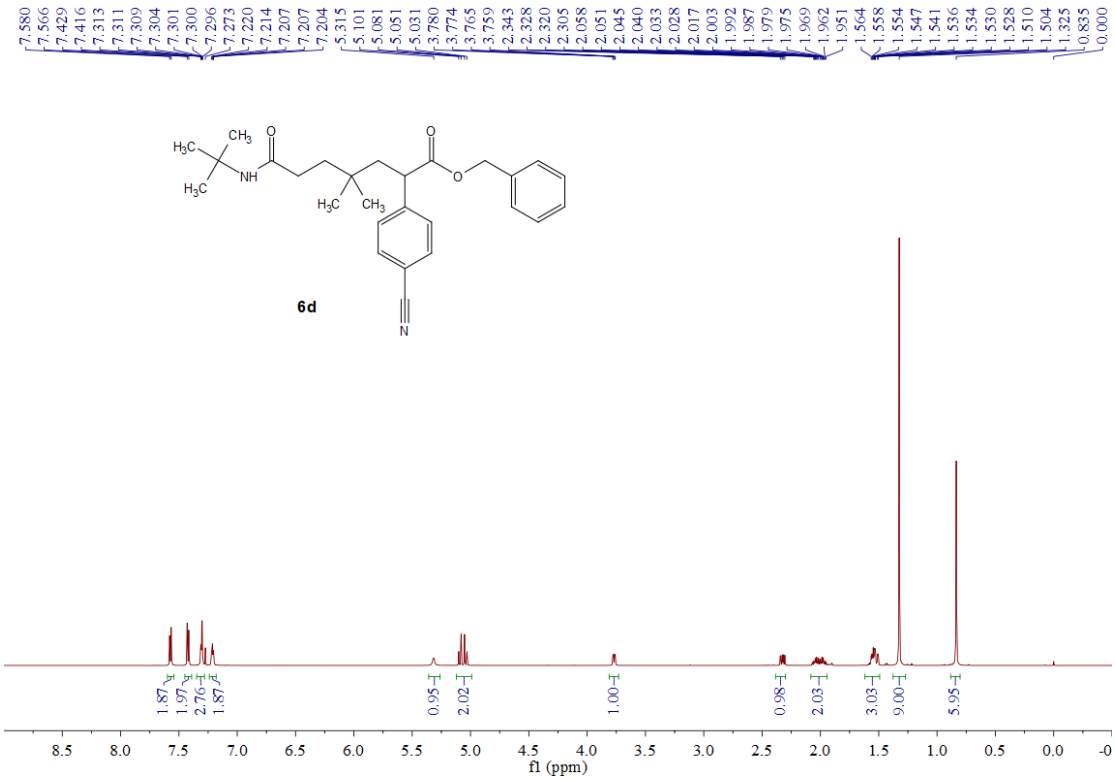
^{1}H NMR (600 MHz, $CDCl_3$) of 6c



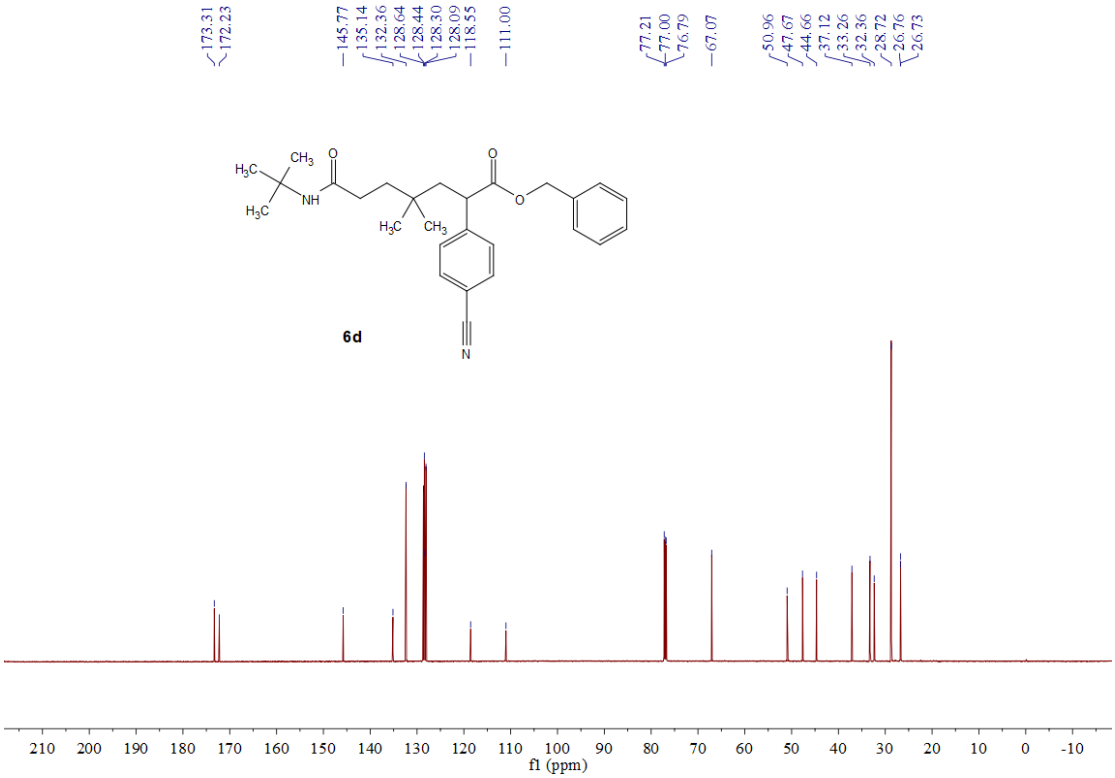
^{13}C NMR (151 MHz, $CDCl_3$) of 6c



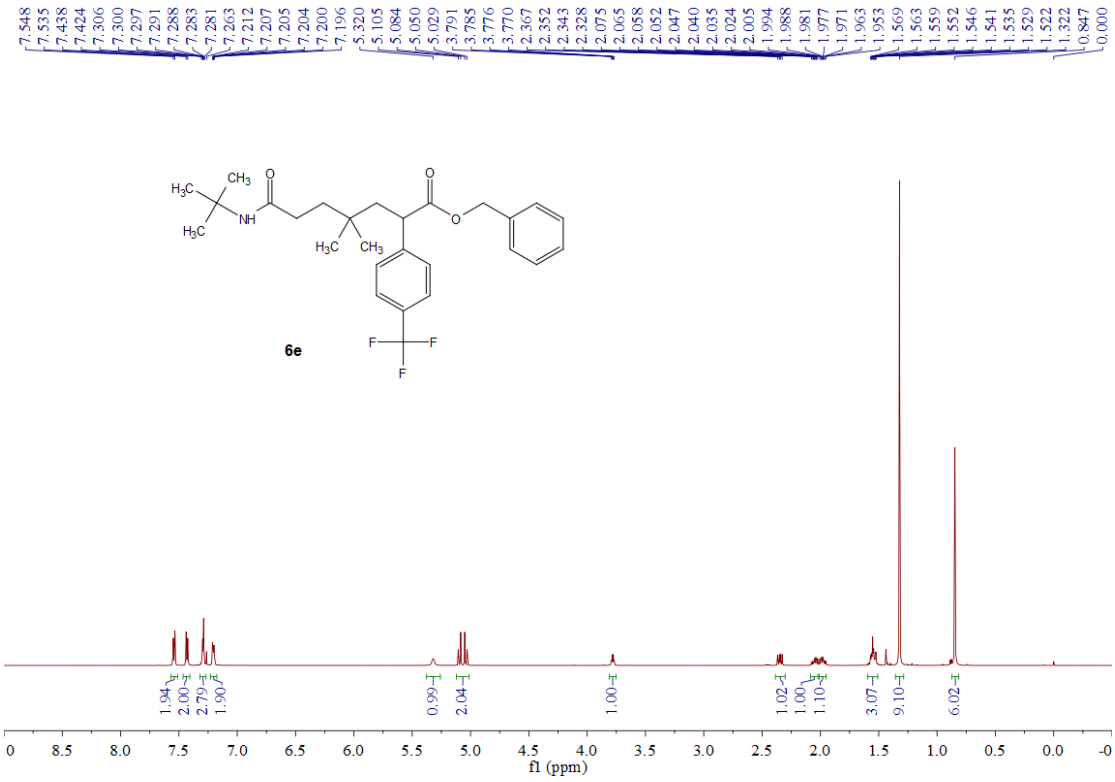
^{1}H NMR (600 MHz, $CDCl_3$) of 6d



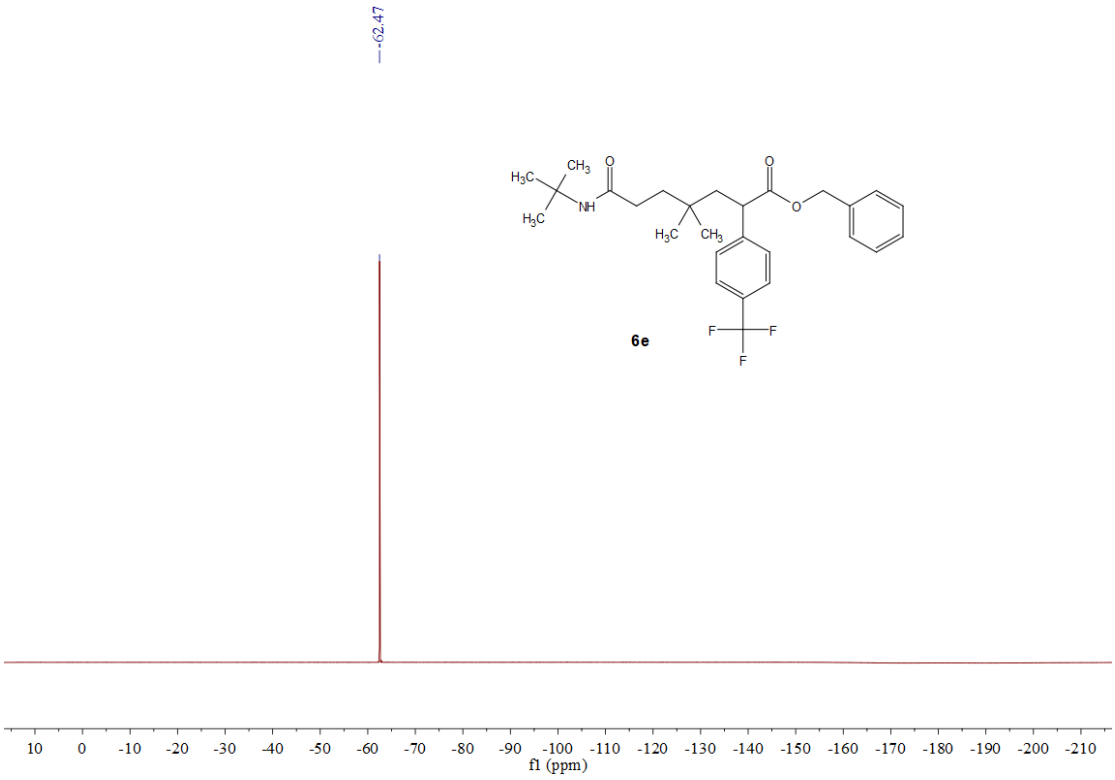
^{13}C NMR (151 MHz, $CDCl_3$) of 6d



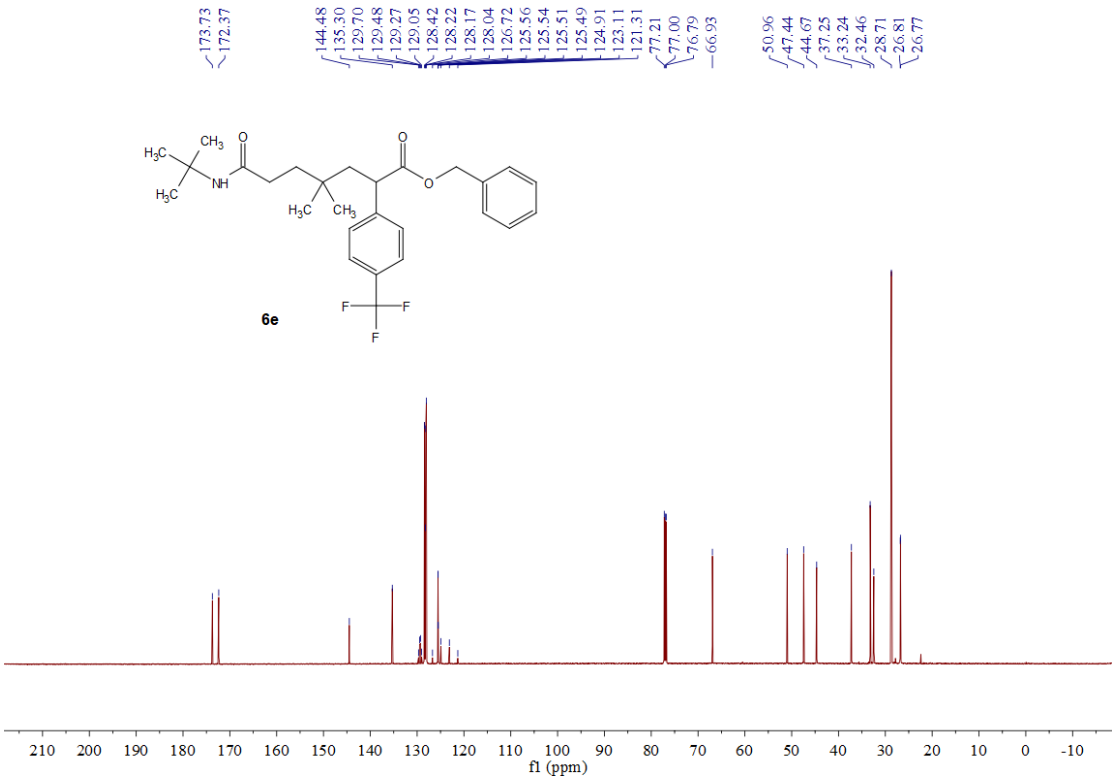
^{1}H NMR (600 MHz, $CDCl_3$) of 6e



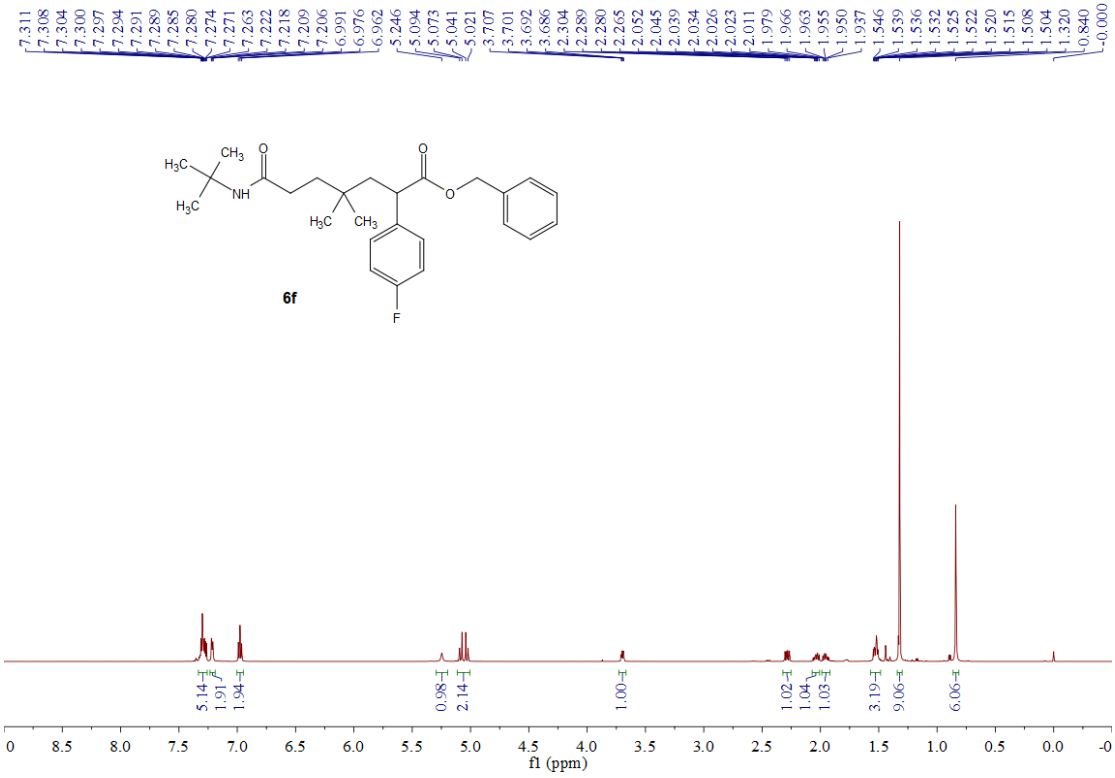
^{19}F NMR (376 MHz, $CDCl_3$) of 6e



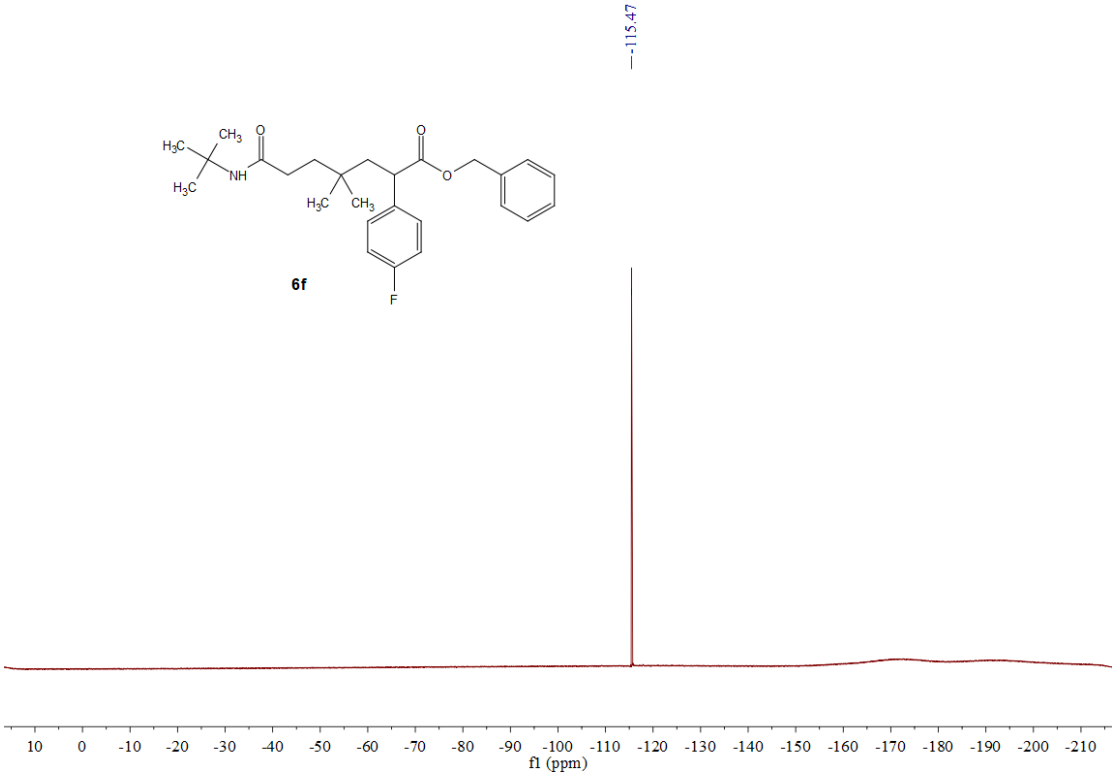
^{13}C NMR (151 MHz, $CDCl_3$) of 6e



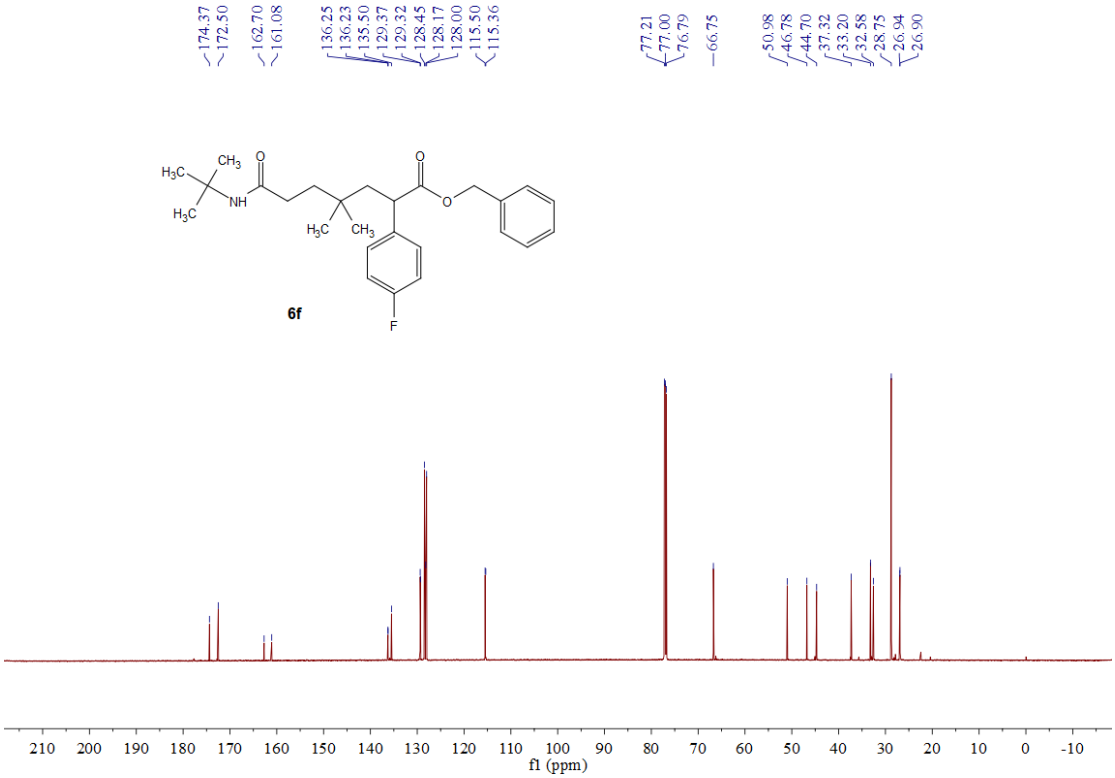
^{1}H NMR (600 MHz, $CDCl_3$) of 6f



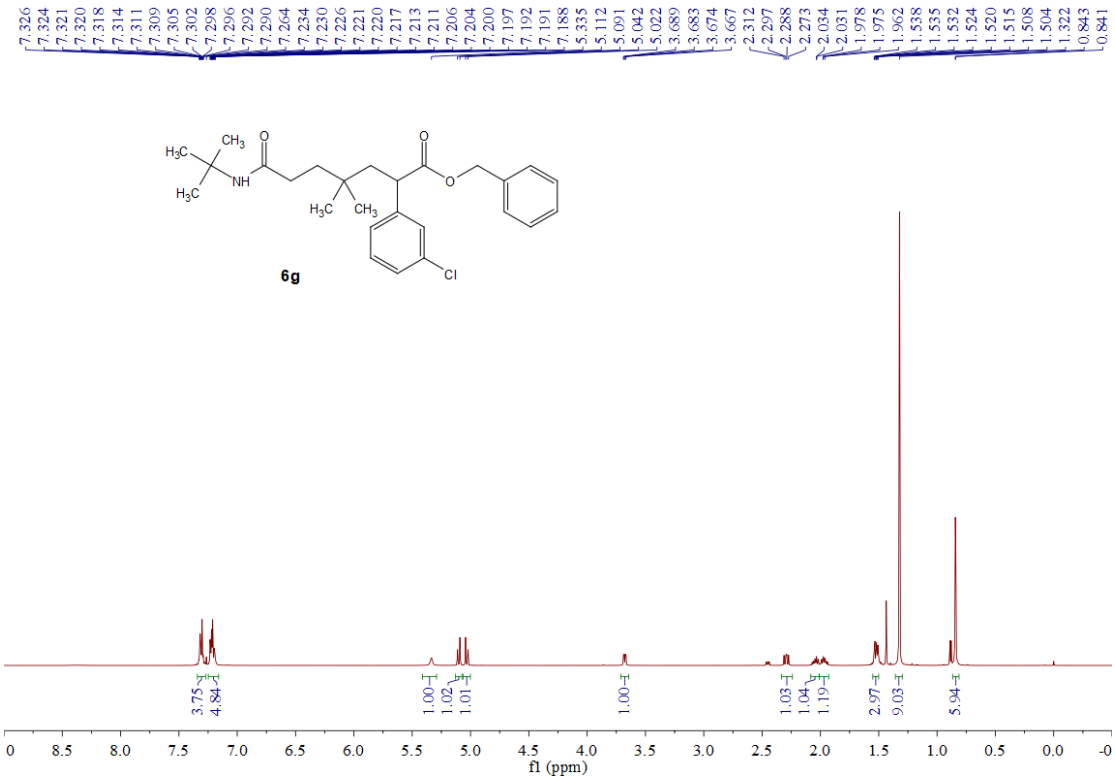
^{19}F NMR (376 MHz, $CDCl_3$) of 6f



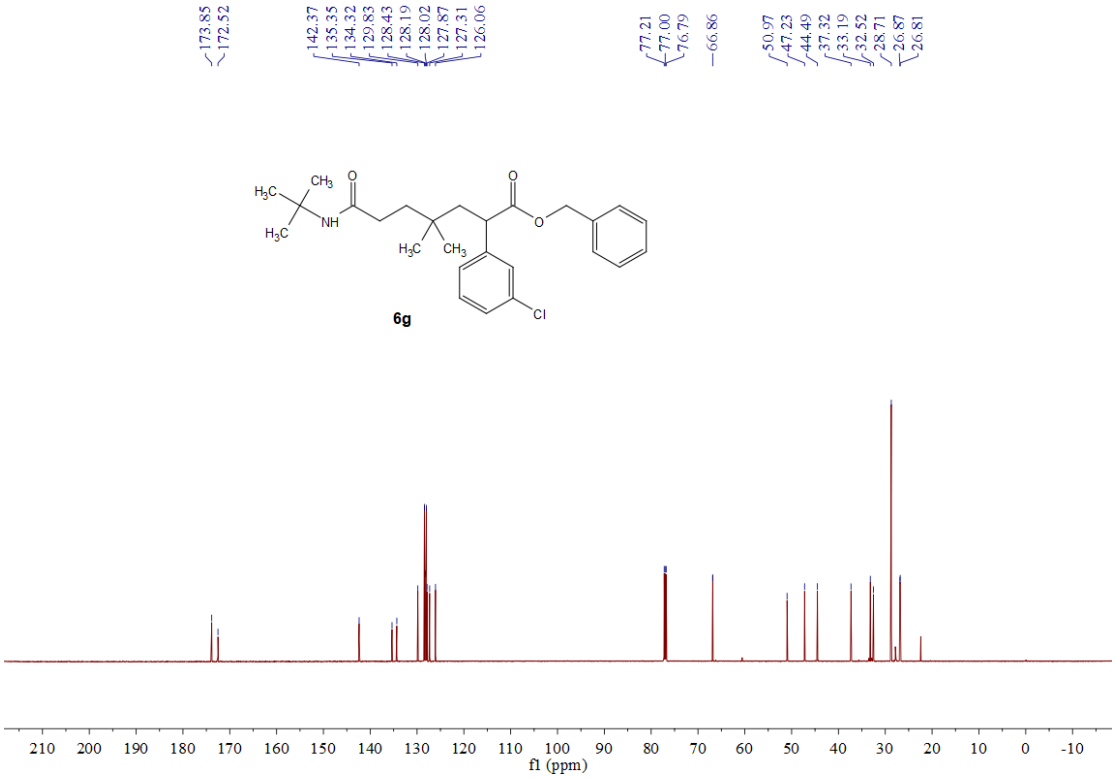
^{13}C NMR (151 MHz, $CDCl_3$) of 6f



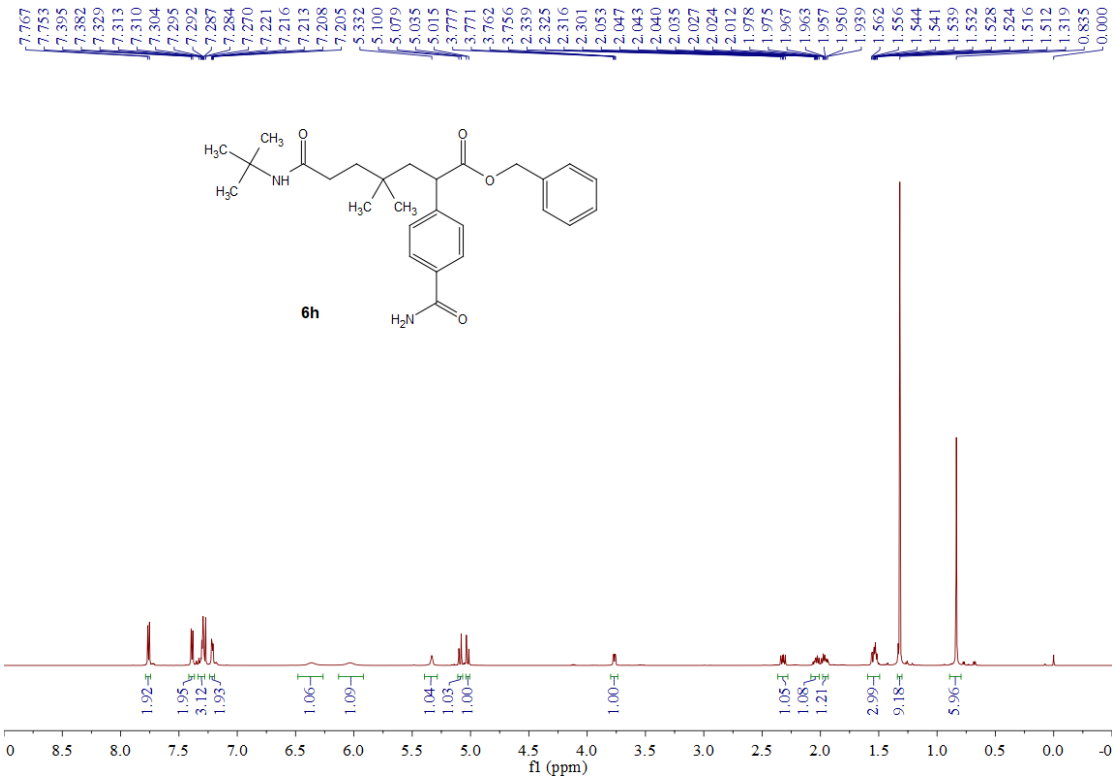
^{1}H NMR (600 MHz, $CDCl_3$) of 6g



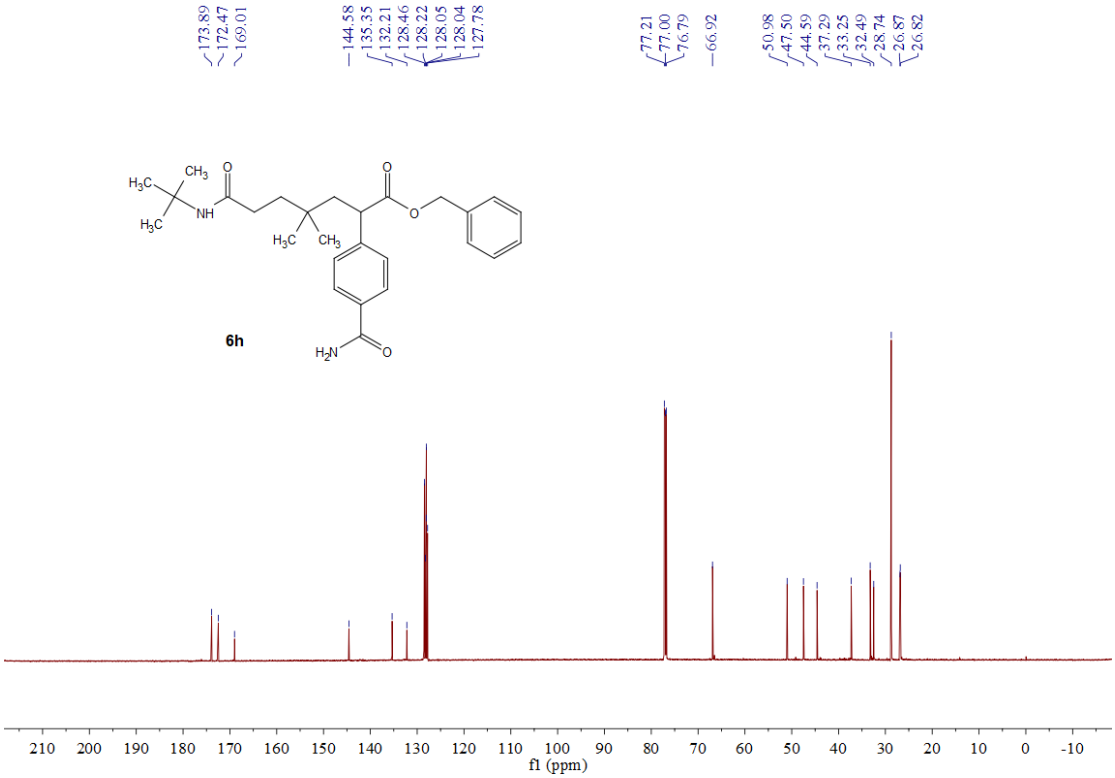
^{13}C NMR (151 MHz, $CDCl_3$) of 6g



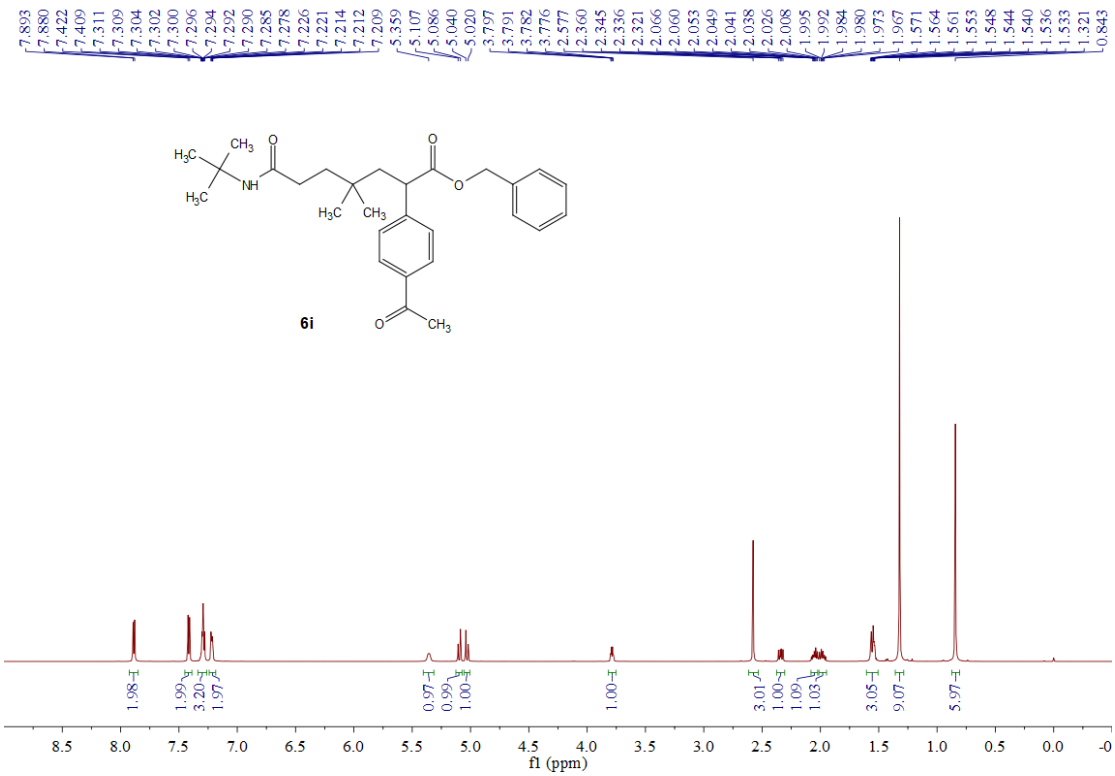
^{1}H NMR (600 MHz, $CDCl_3$) of 6h



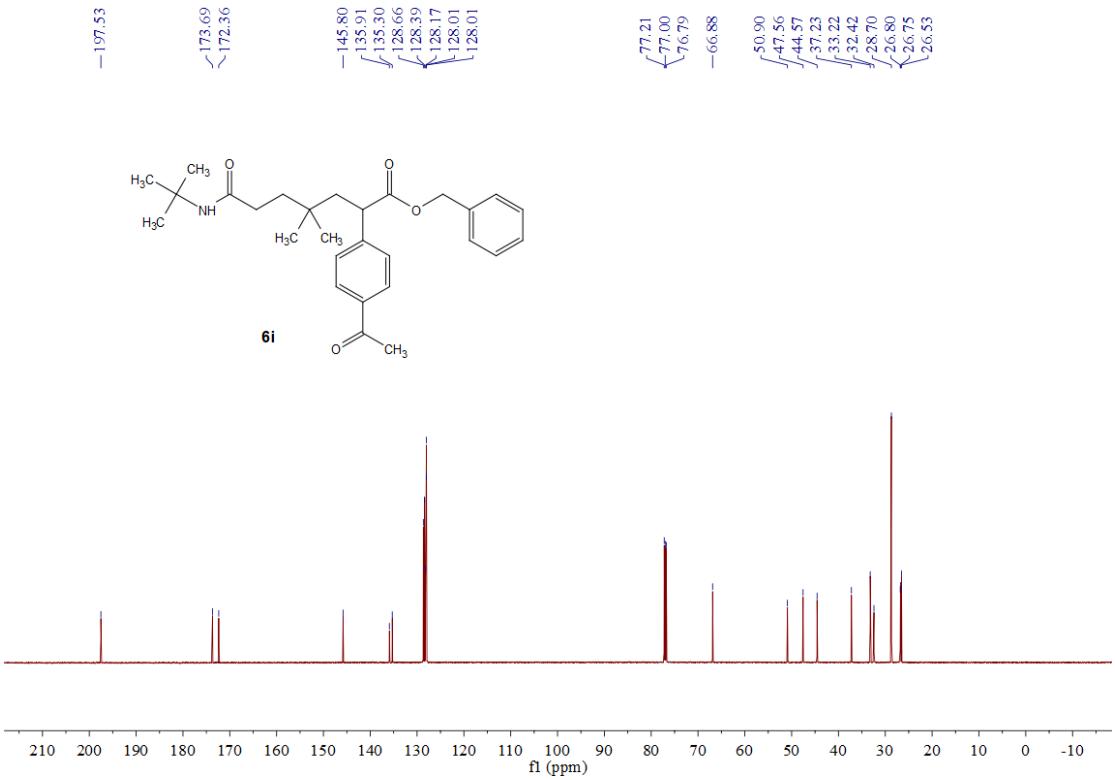
^{13}C NMR (151 MHz, $CDCl_3$) of 6h



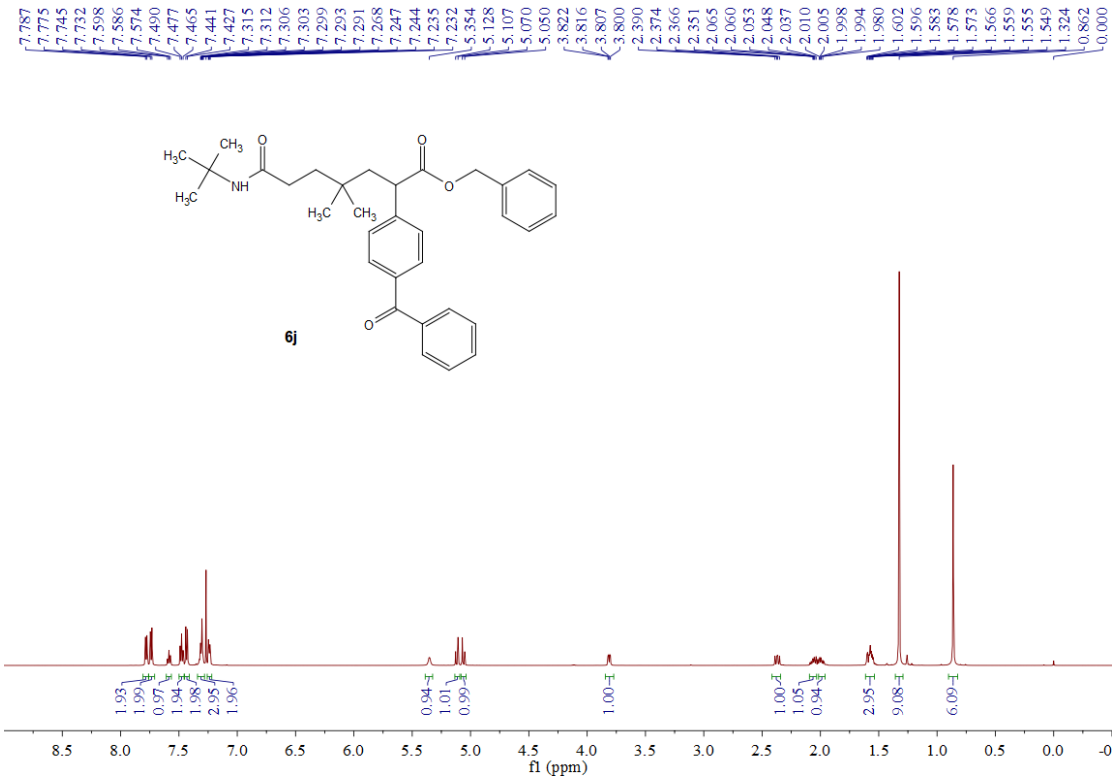
^{1}H NMR (600 MHz, $CDCl_3$) of 6i



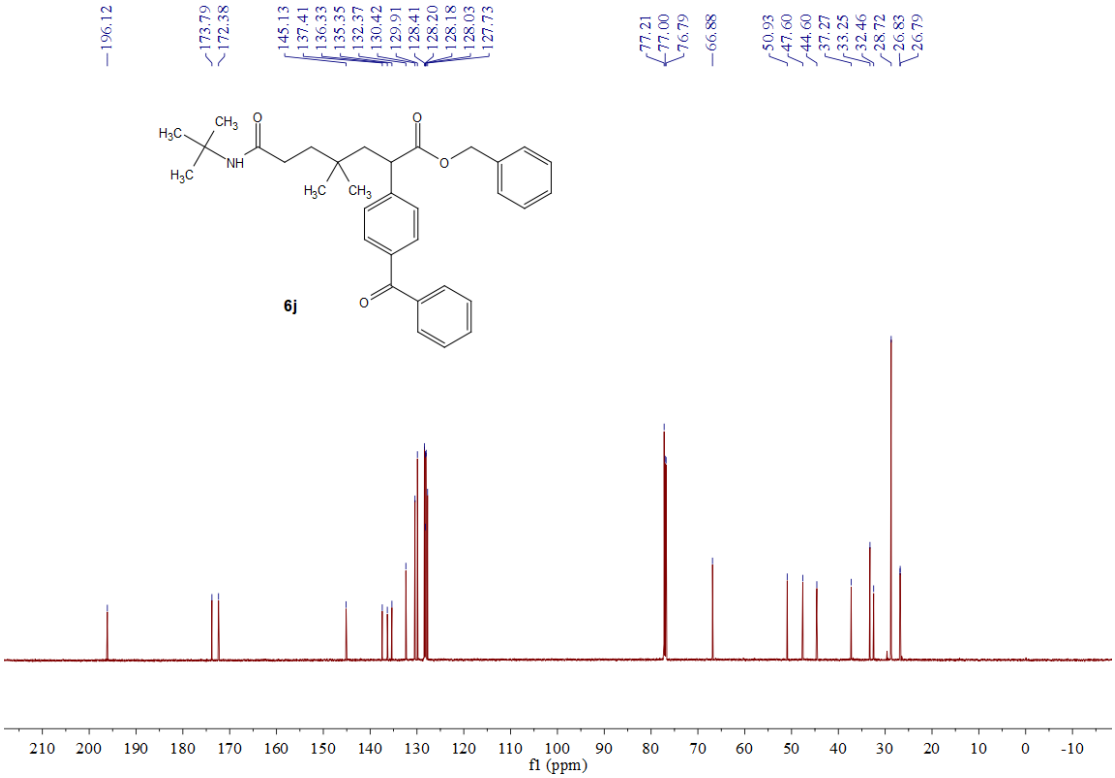
^{13}C NMR (151 MHz, $CDCl_3$) of 6i



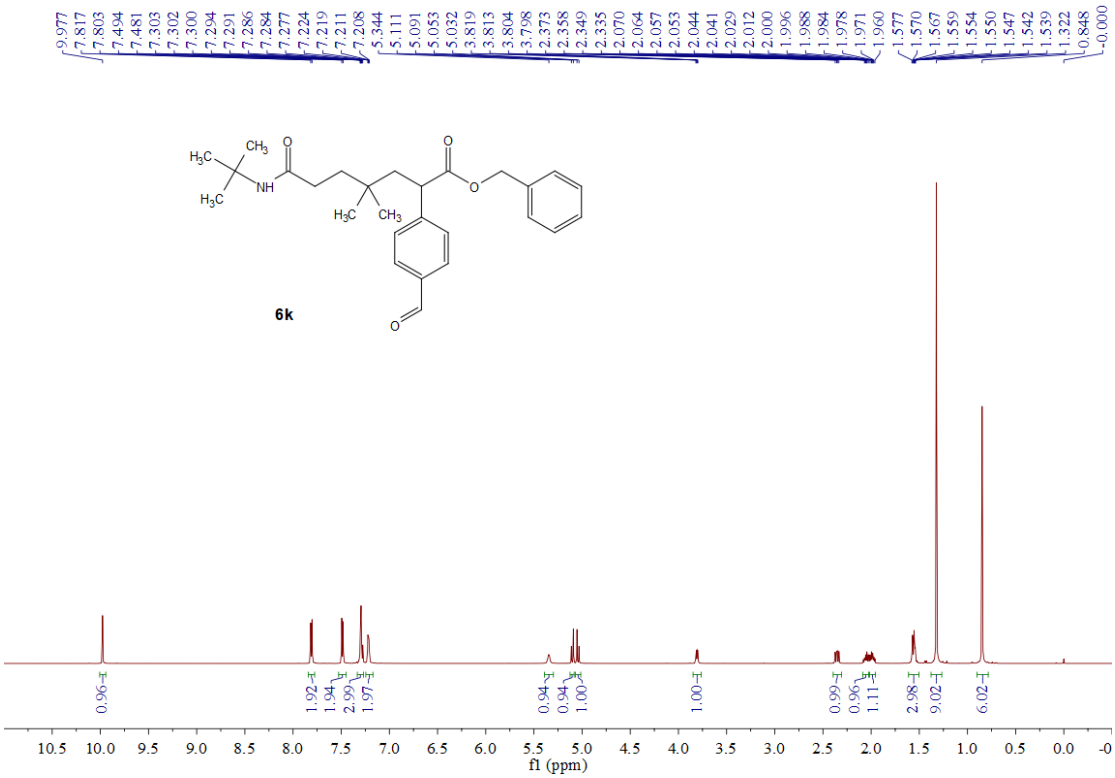
^{1}H NMR (600 MHz, $CDCl_3$) of 6j



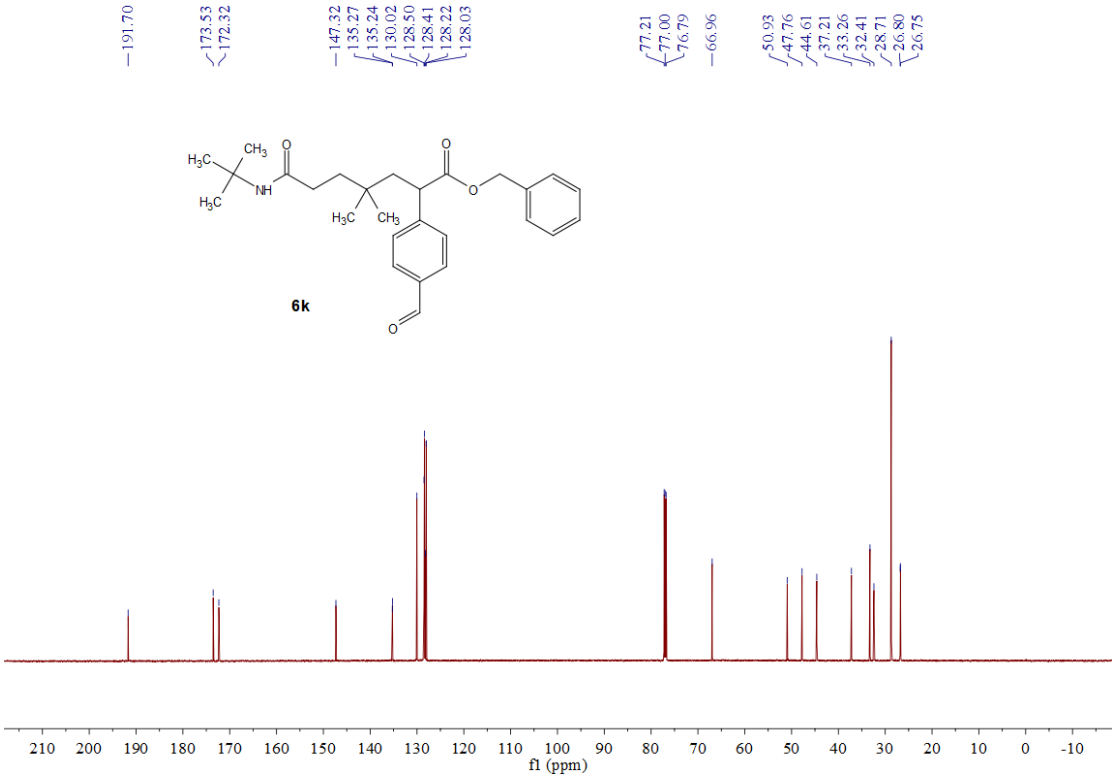
^{13}C NMR (151 MHz, $CDCl_3$) of 6j



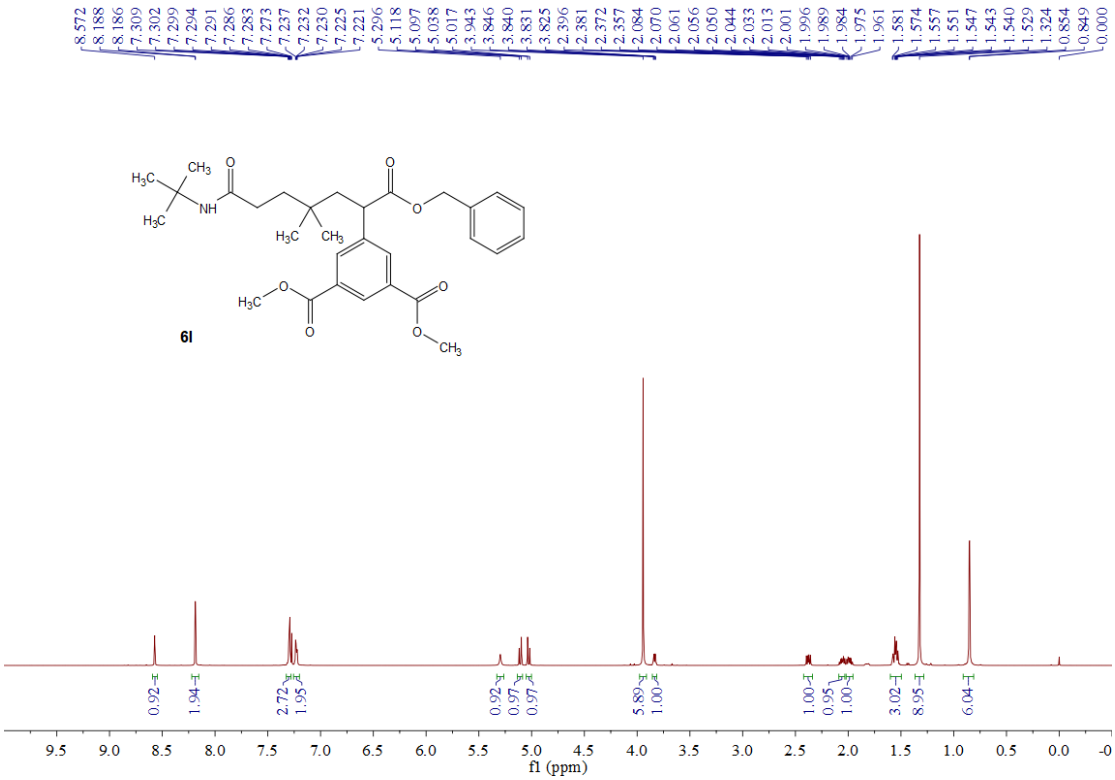
^{1}H NMR (600 MHz, $CDCl_3$) of 6k



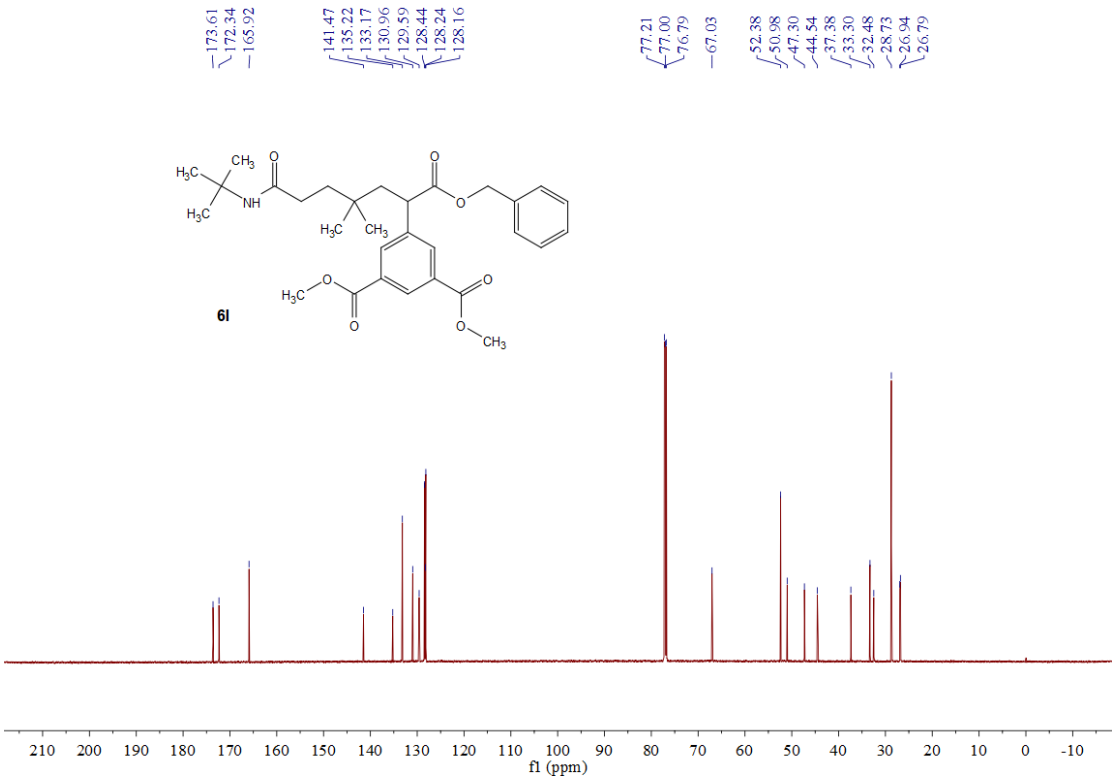
^{13}C NMR (151 MHz, $CDCl_3$) of 6k



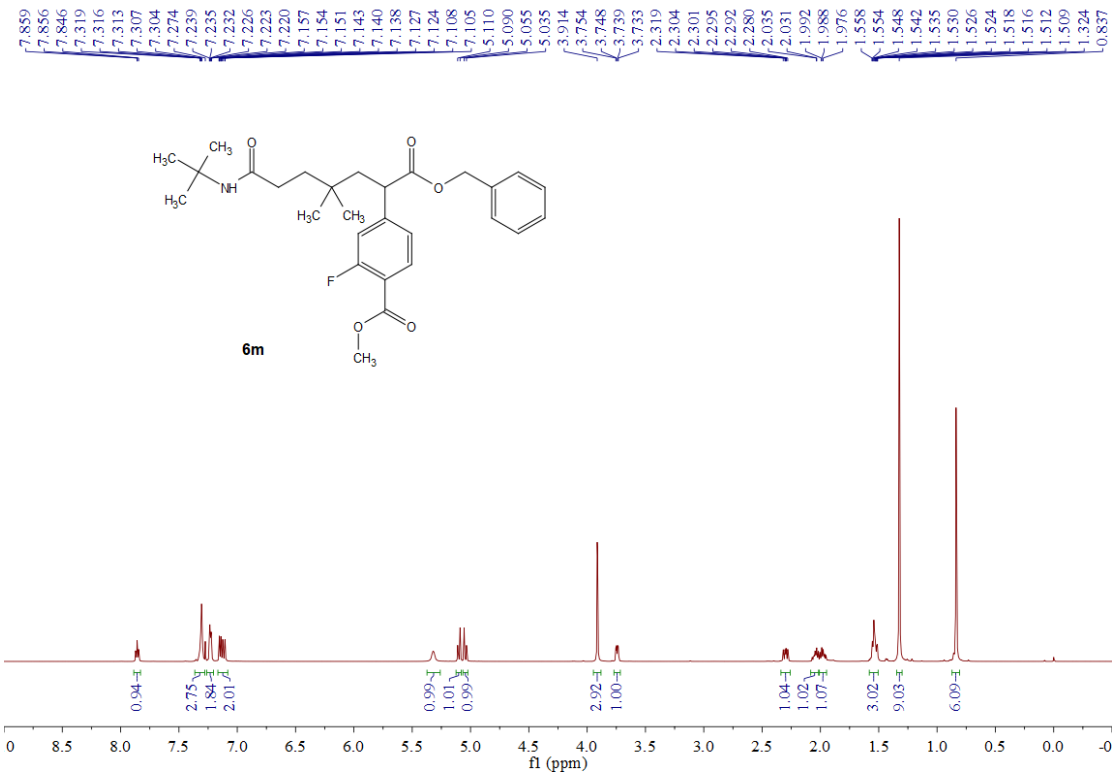
^{1}H NMR (600 MHz, $CDCl_3$) of 6l



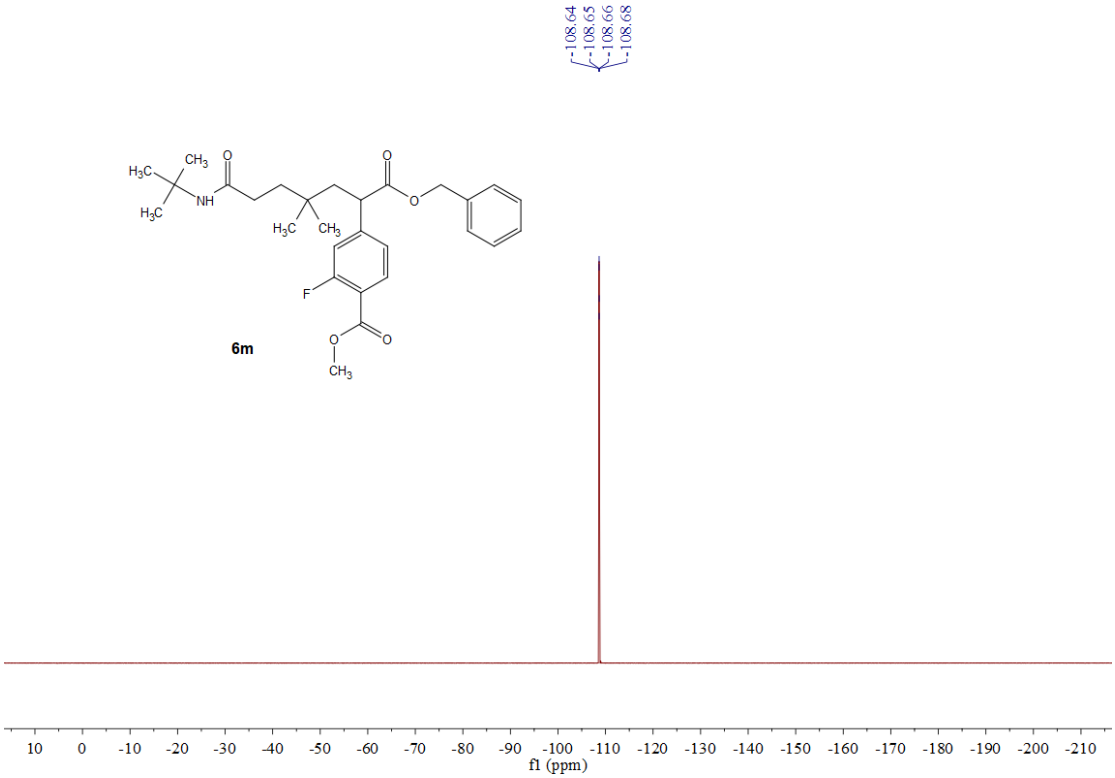
^{13}C NMR (151 MHz, $CDCl_3$) of 6l



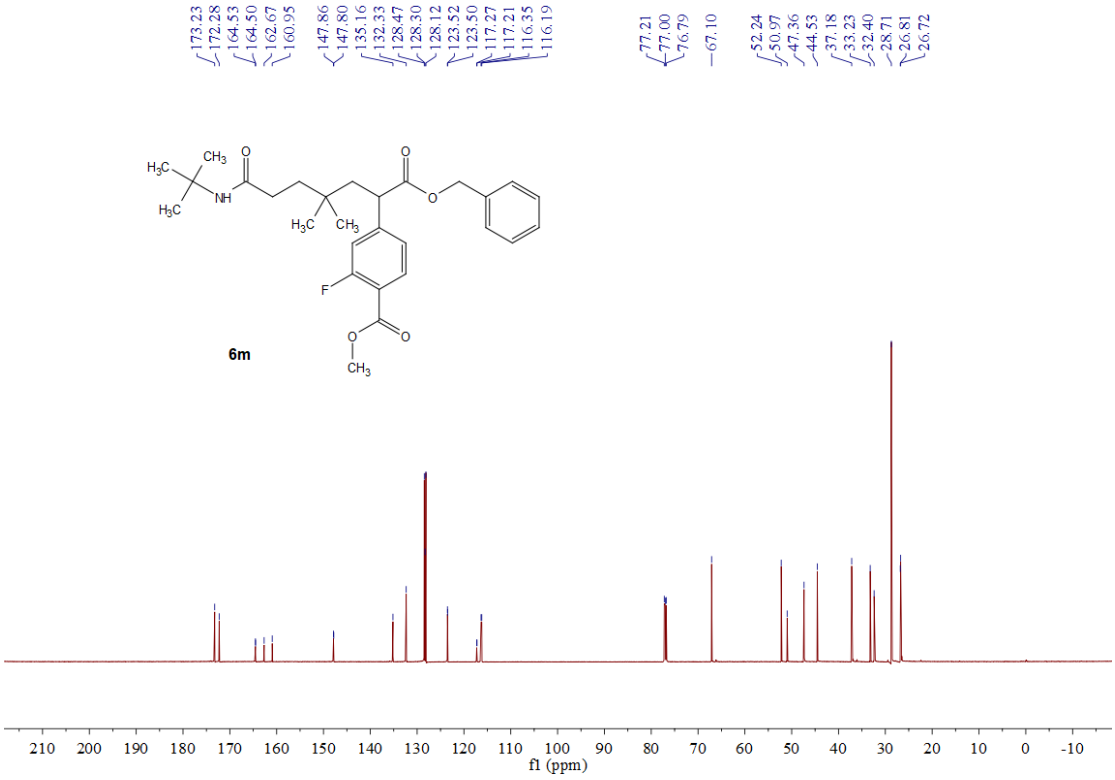
^{1}H NMR (600 MHz, $CDCl_3$) of 6m



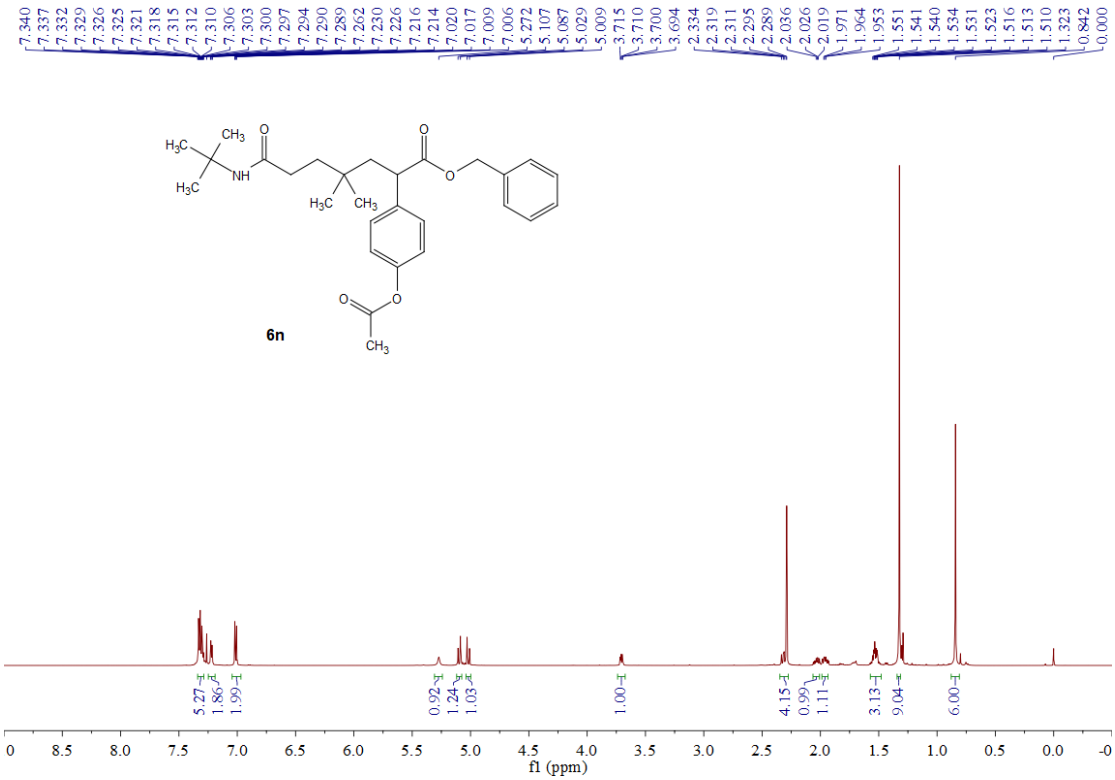
^{19}F NMR (565 MHz, $CDCl_3$) of 6m



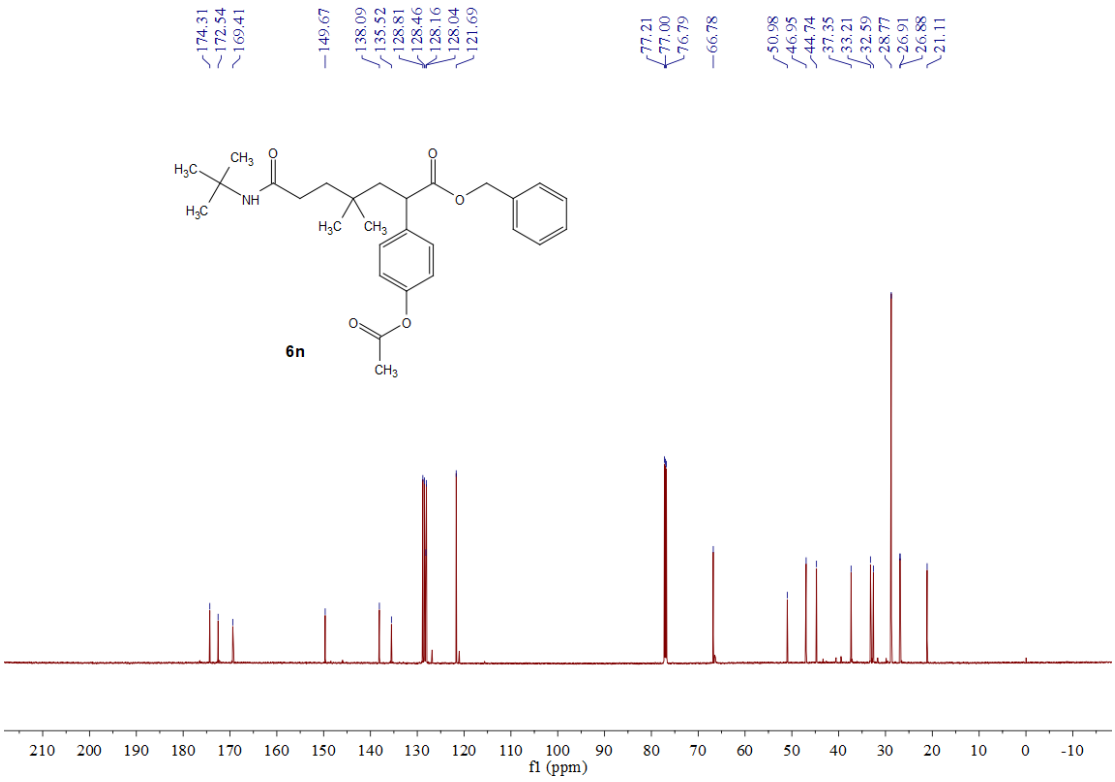
^{13}C NMR (151 MHz, $CDCl_3$) of 6m



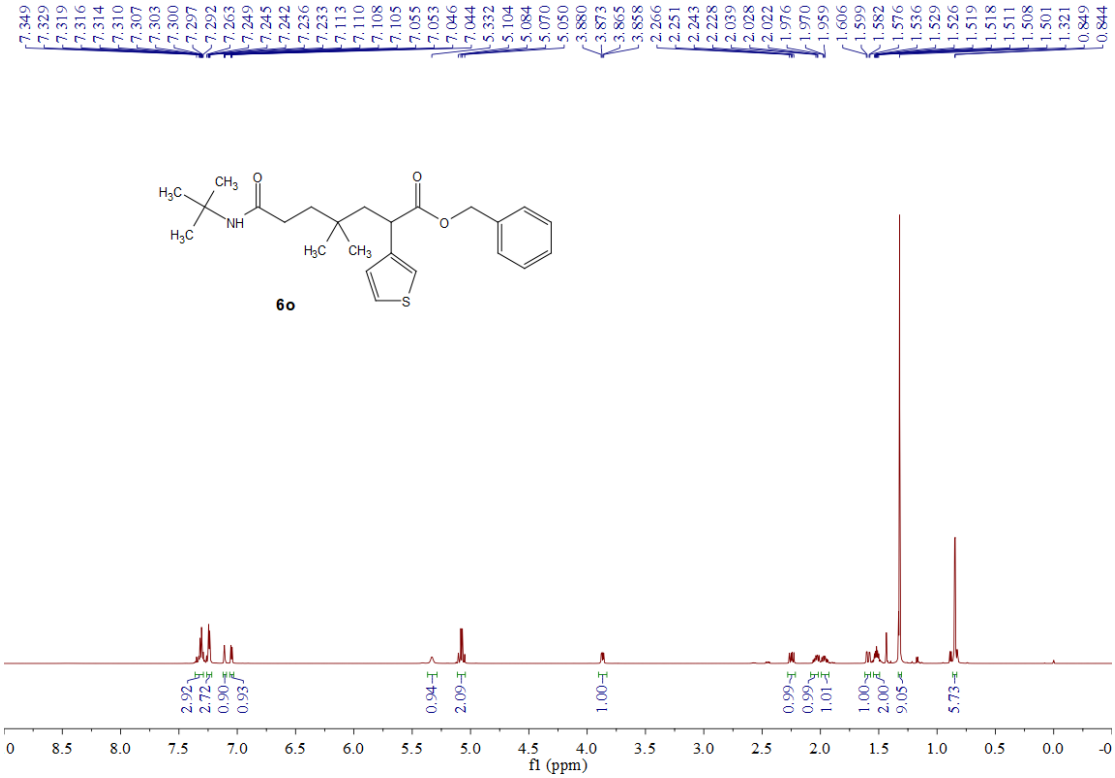
^{1}H NMR (600 MHz, $CDCl_3$) of 6n



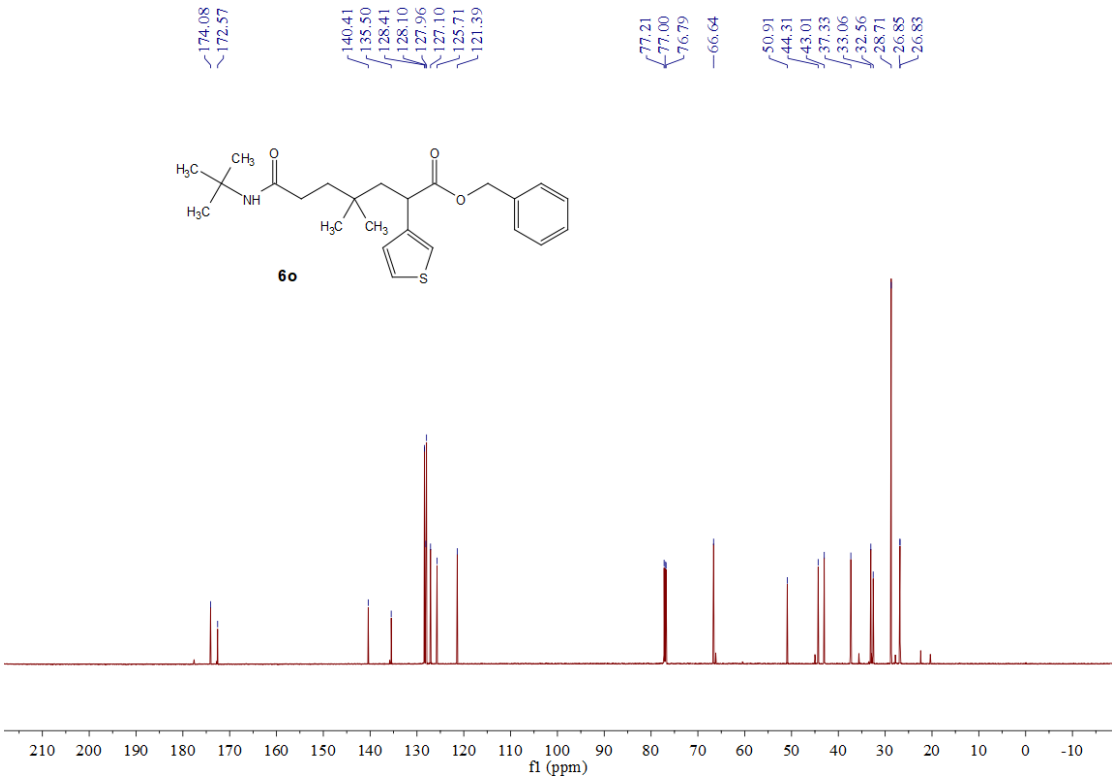
^{13}C NMR (151 MHz, $CDCl_3$) of 6n



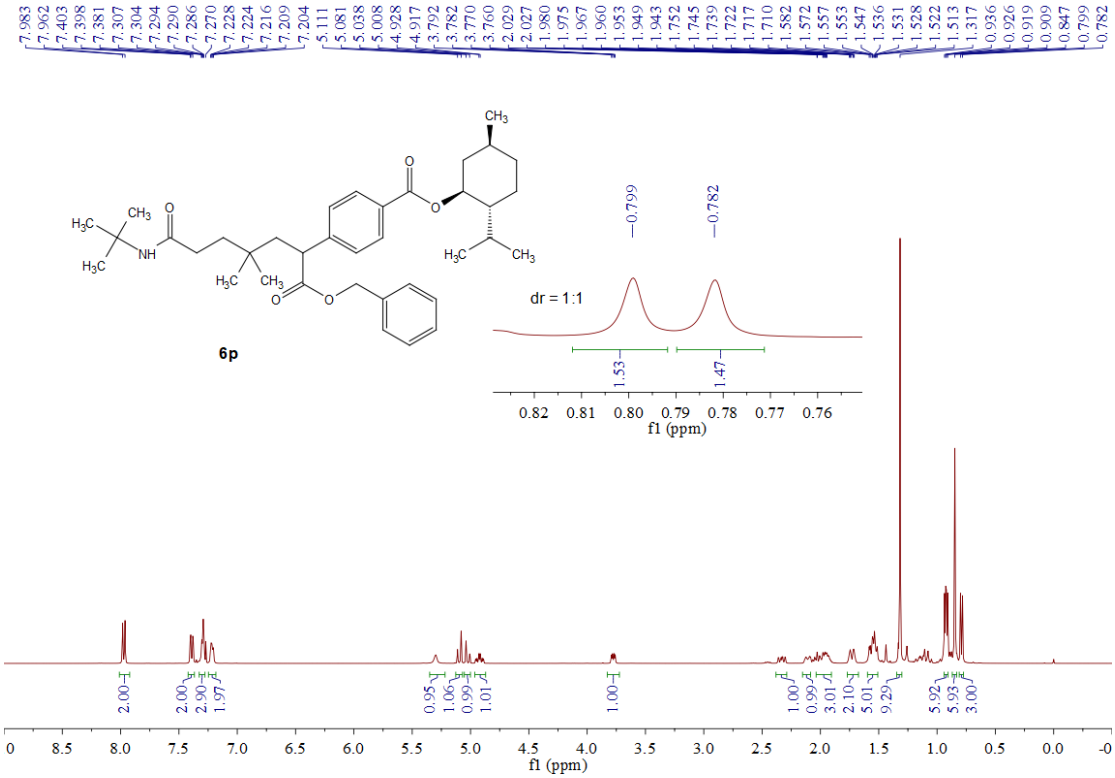
^{1}H NMR (600 MHz, $CDCl_3$) of 6o



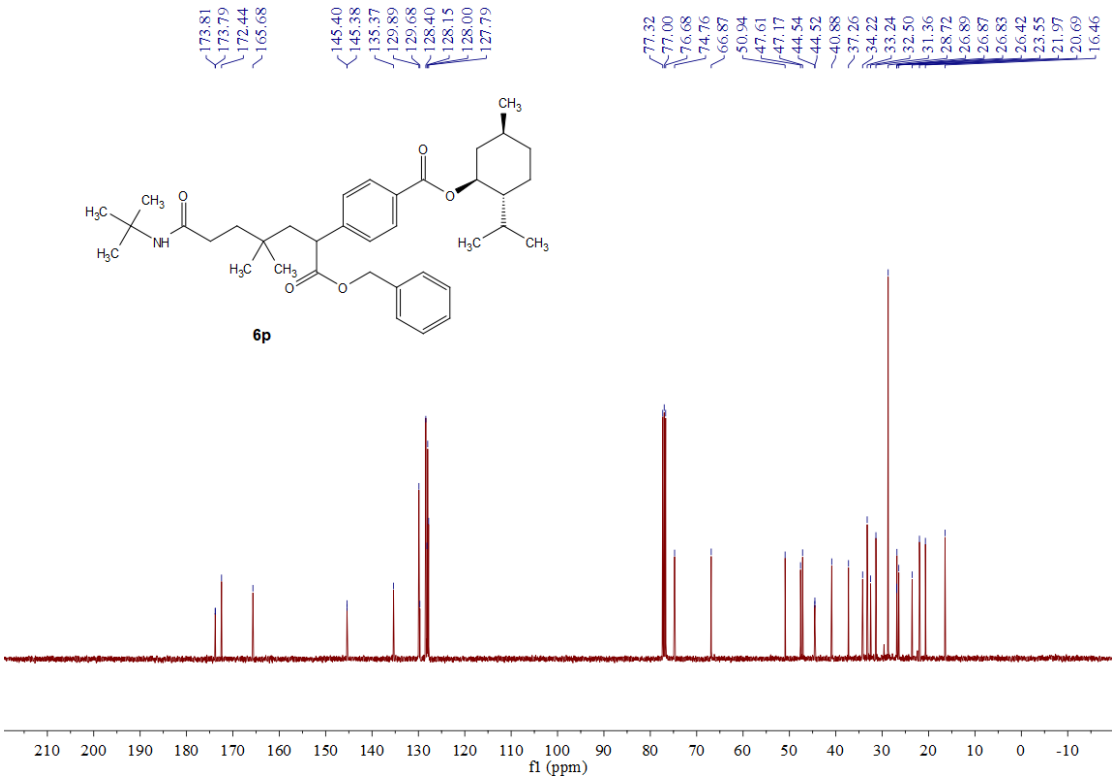
^{13}C NMR (151 MHz, $CDCl_3$) of 6o



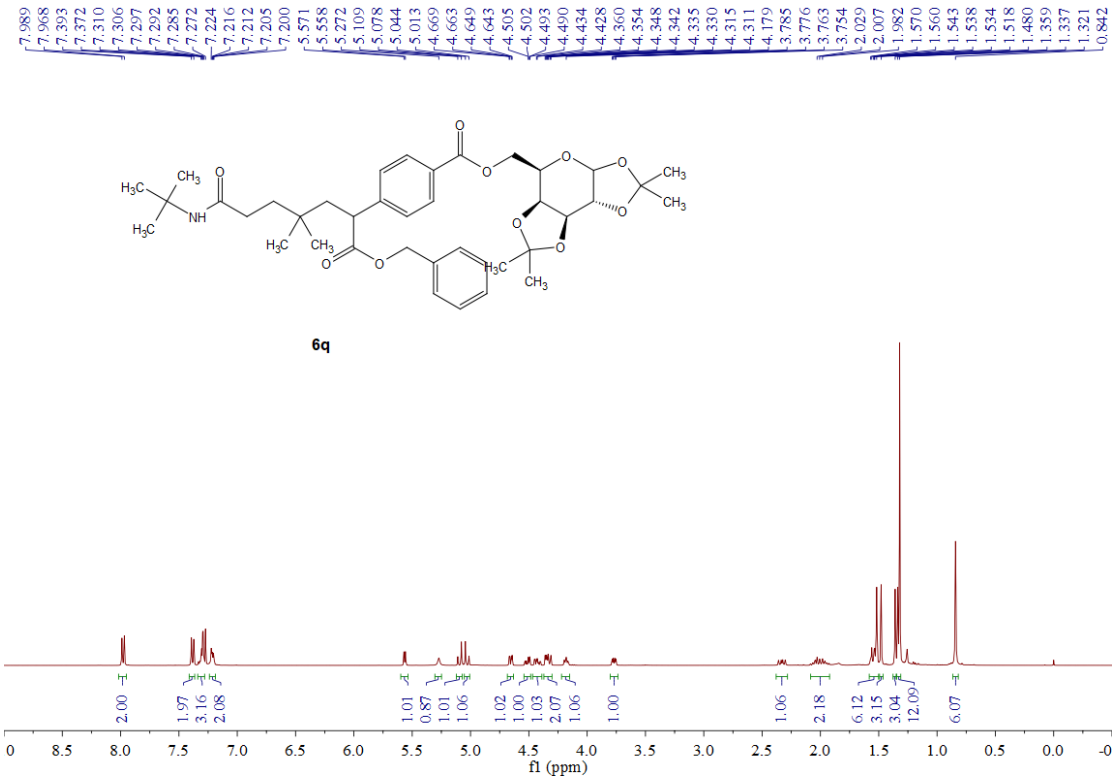
^{1}H NMR (400 MHz, $CDCl_3$) of 6p



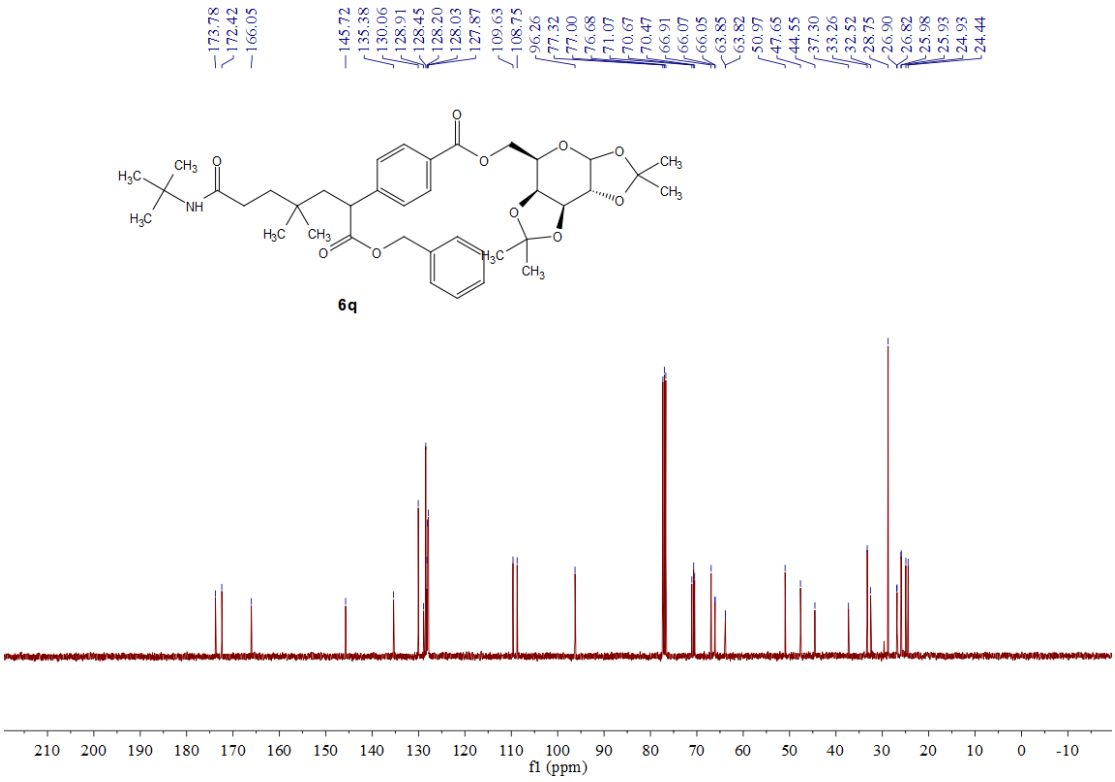
^{13}C NMR (101 MHz, $CDCl_3$) of 6p



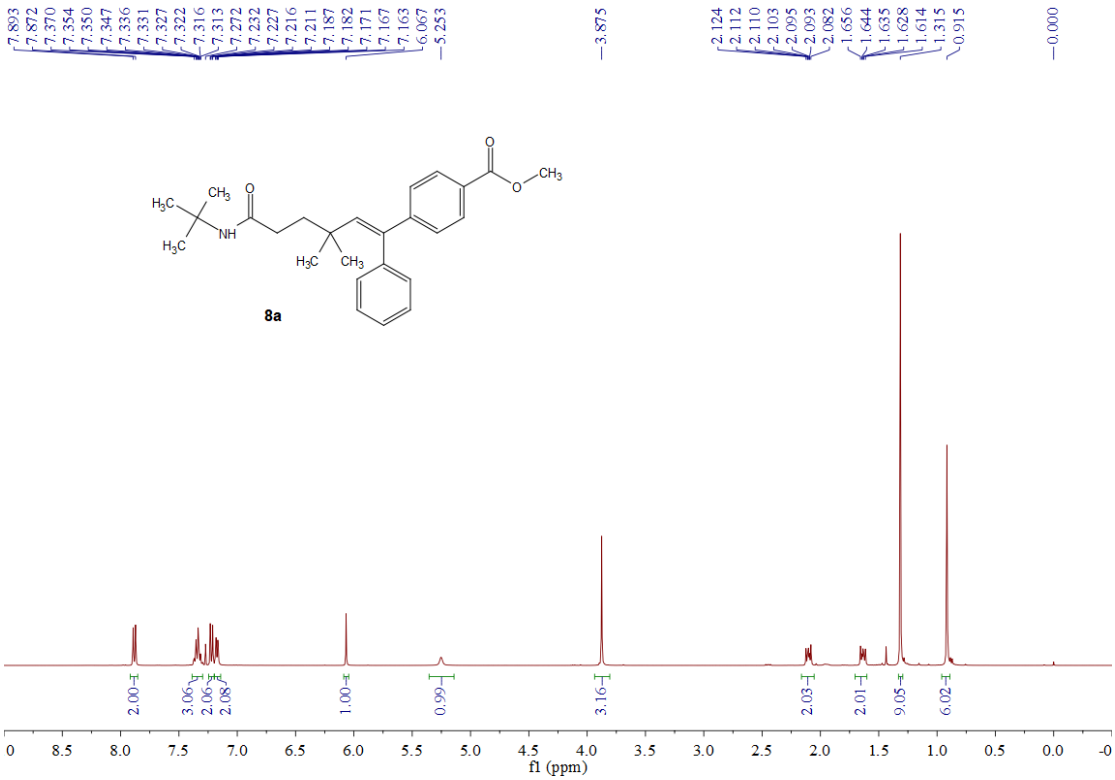
^{1}H NMR (400 MHz, $CDCl_3$) of 6q



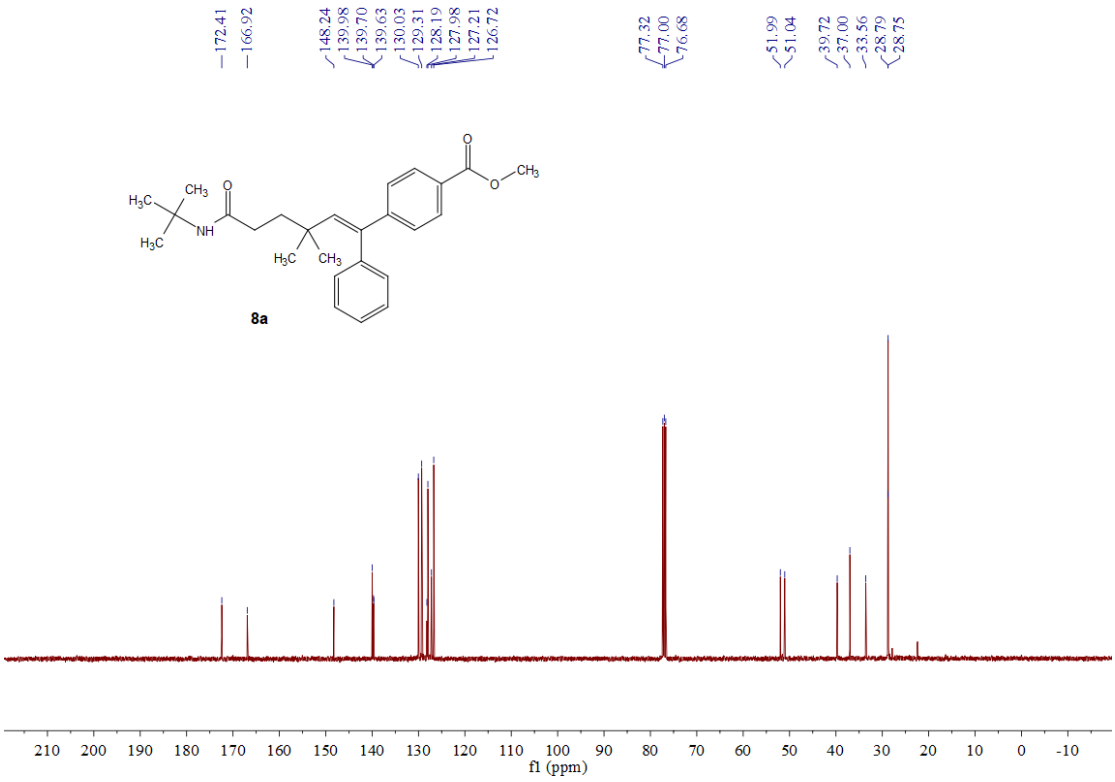
^{13}C NMR (101 MHz, $CDCl_3$) of 6q



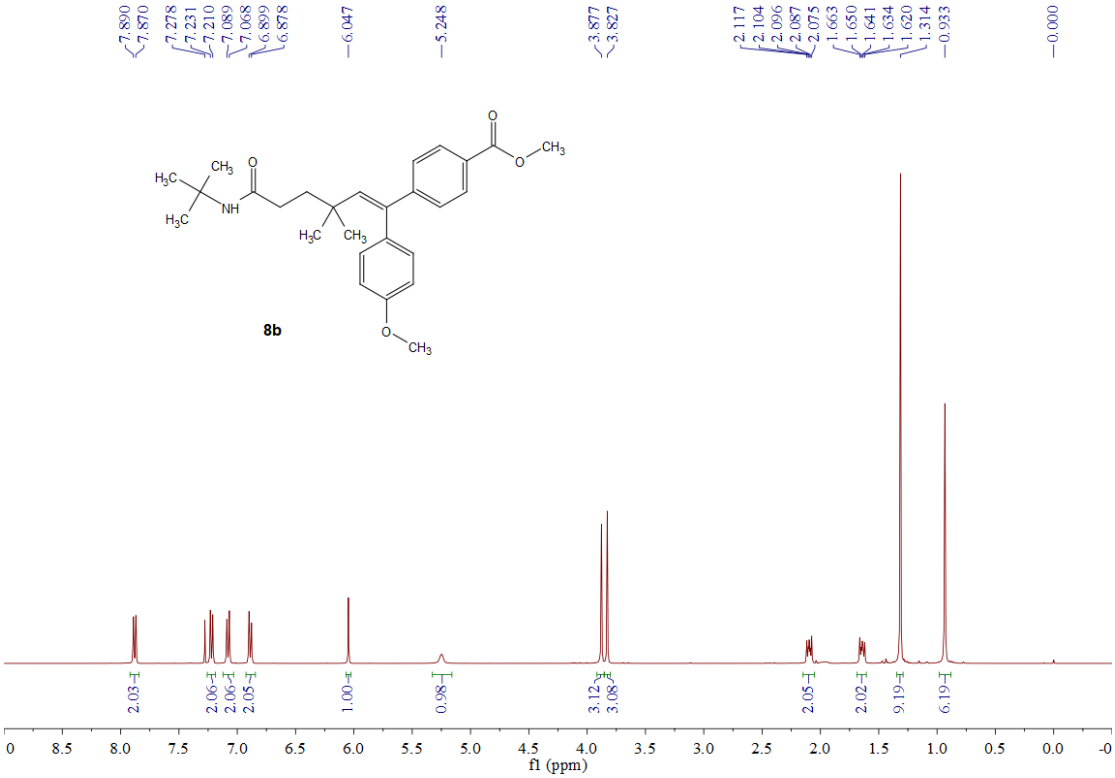
^{1}H NMR (400 MHz, $CDCl_3$) of 8a



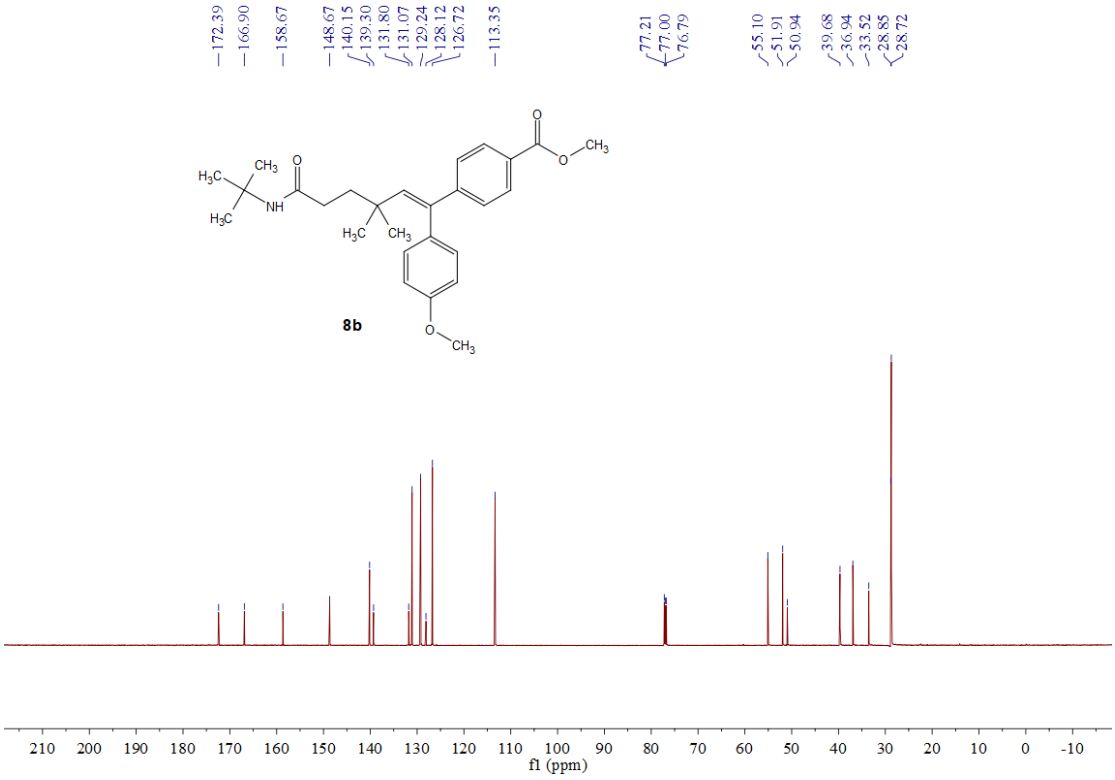
^{13}C NMR (101 MHz, $CDCl_3$) of 8a



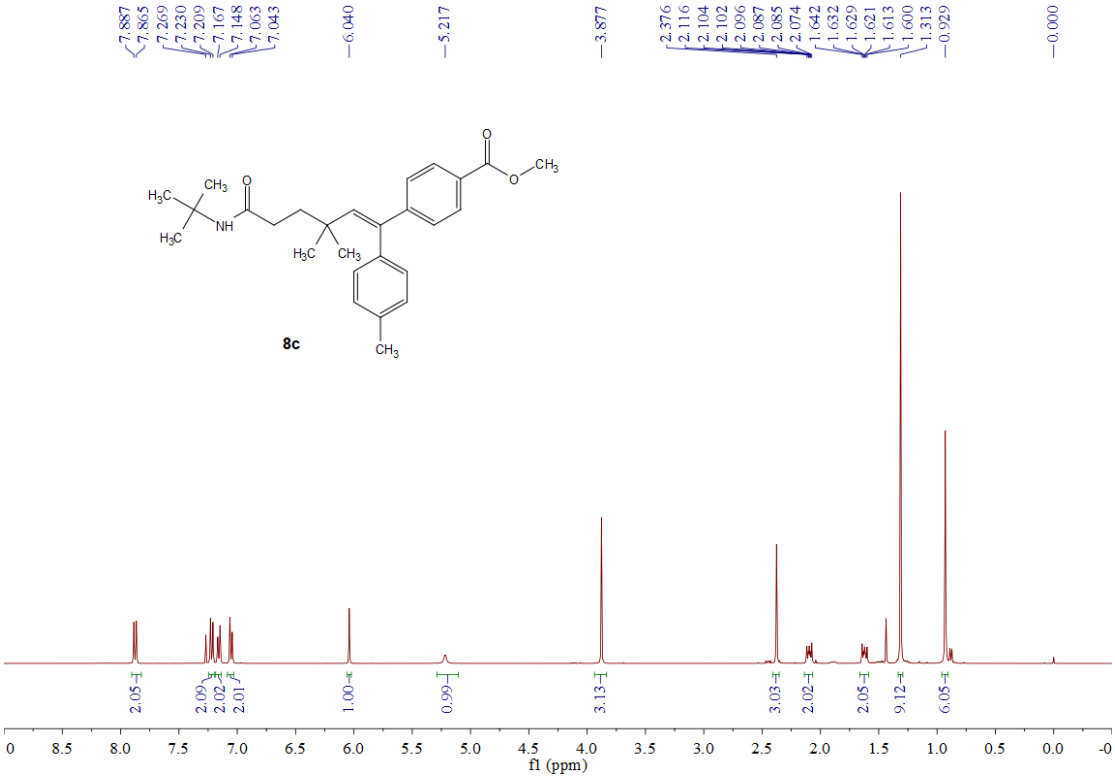
^{1}H NMR (400 MHz, $CDCl_3$) of 8b



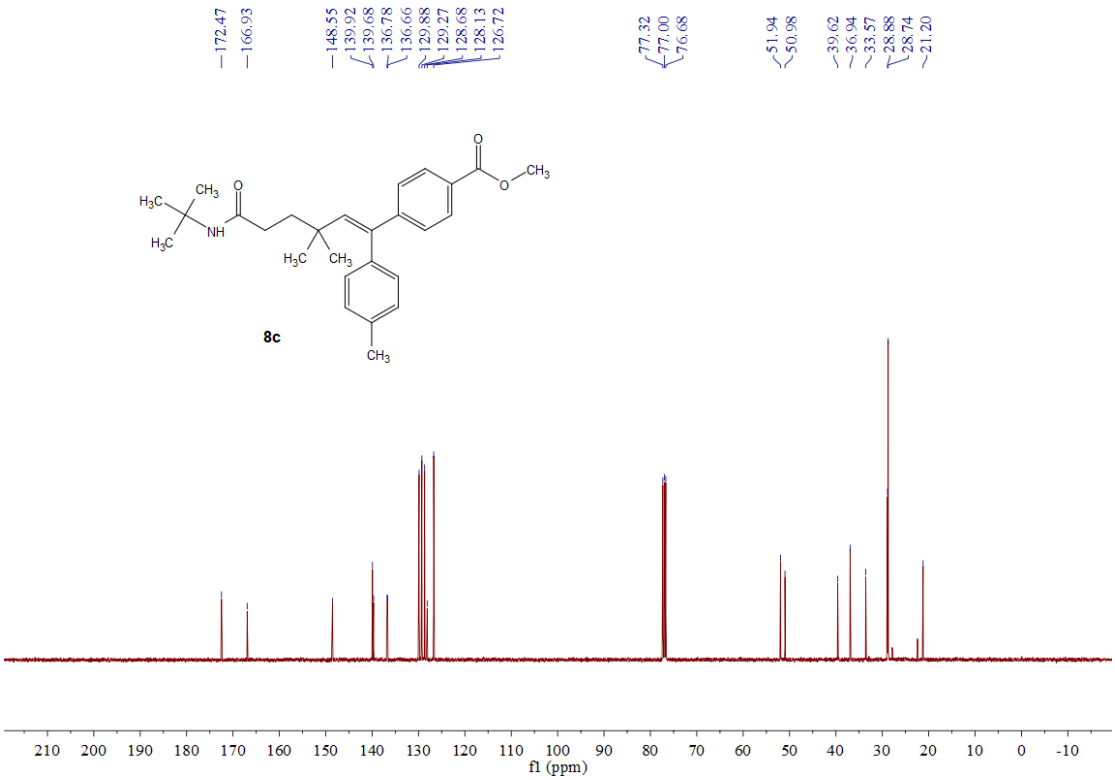
^{13}C NMR (151 MHz, $CDCl_3$) of 8b



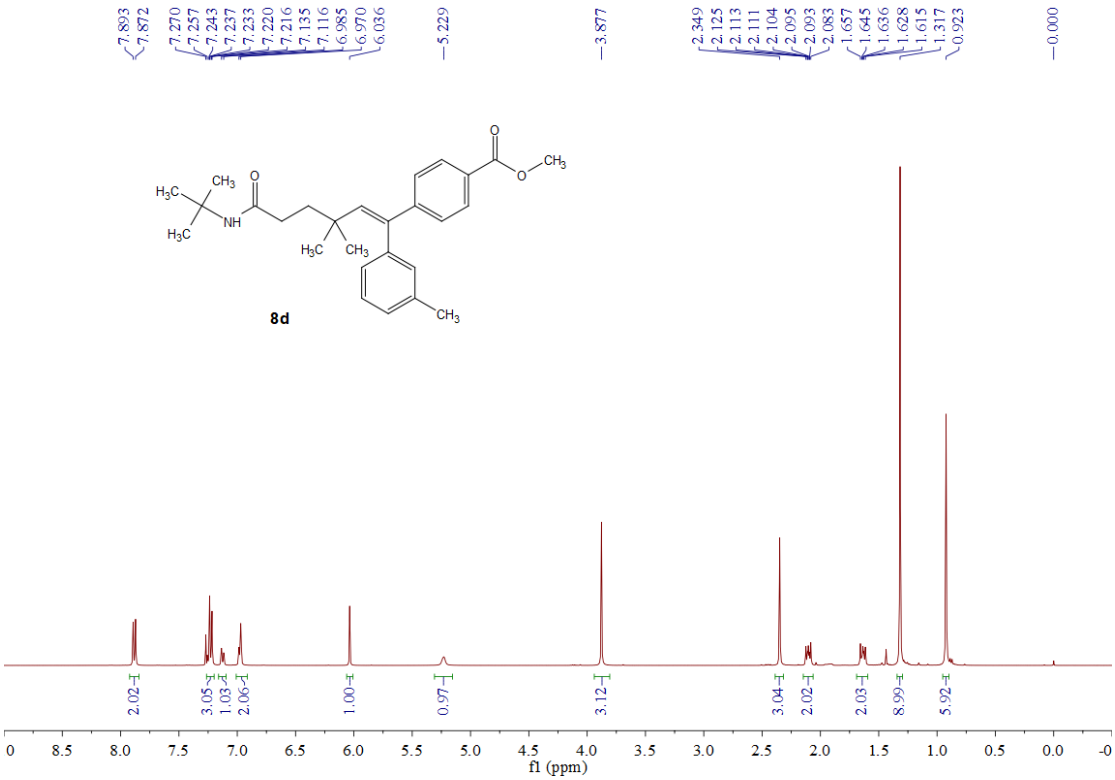
^{1}H NMR (400 MHz, $CDCl_3$) of 8c



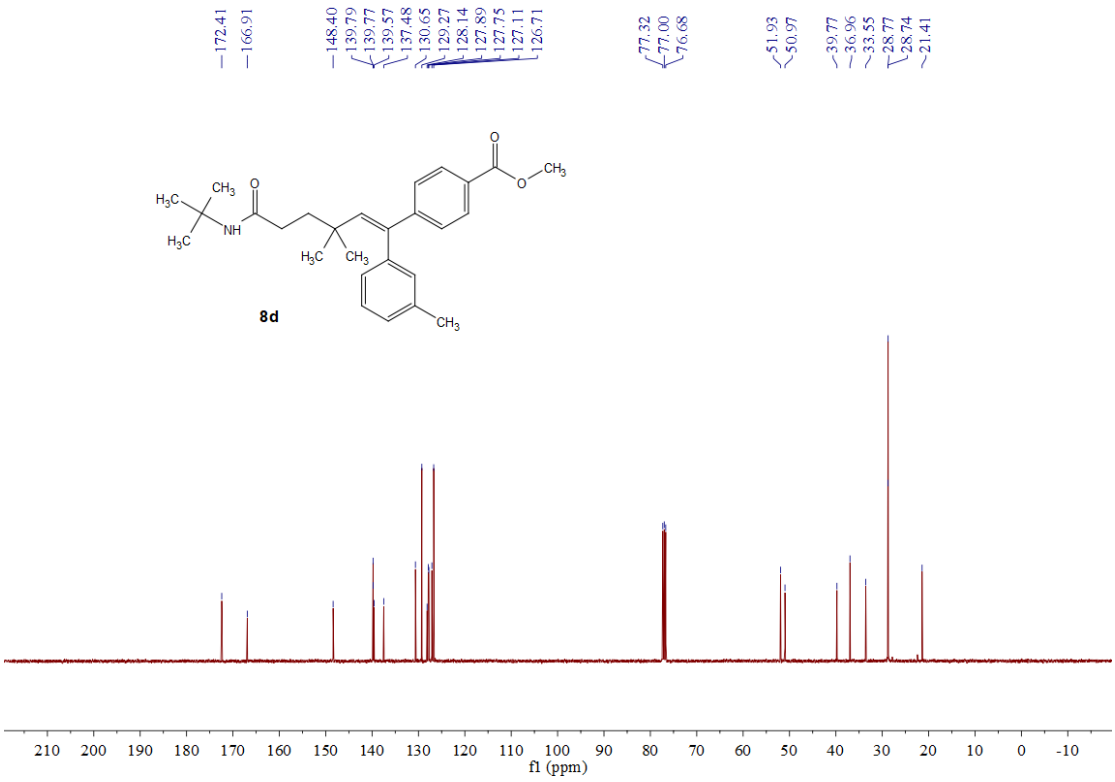
^{13}C NMR (101 MHz, $CDCl_3$) of 8c



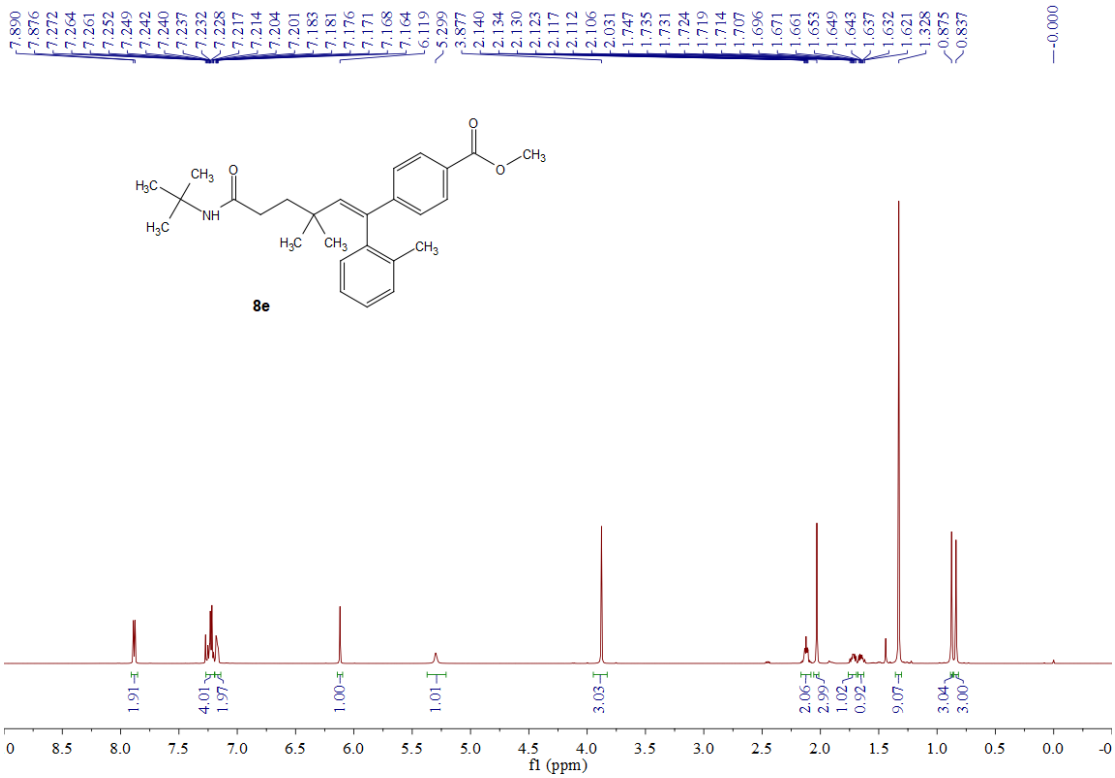
^{1}H NMR (400 MHz, $CDCl_3$) of 8d



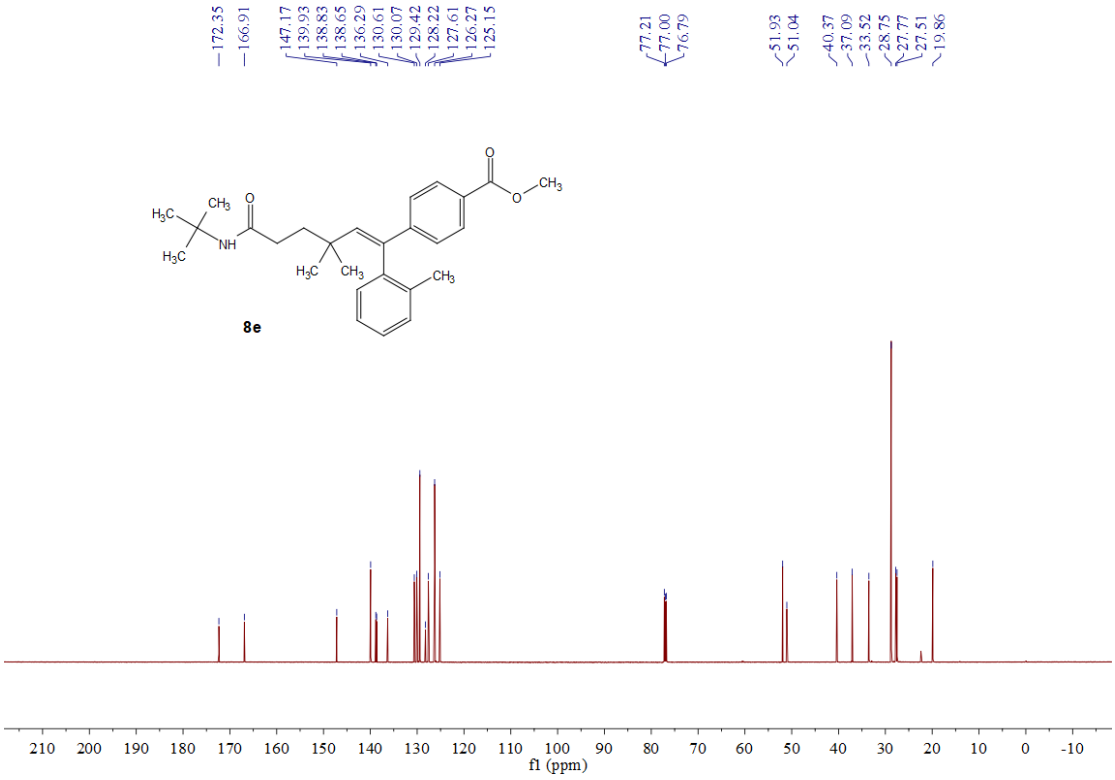
^{13}C NMR (101 MHz, $CDCl_3$) of 8d



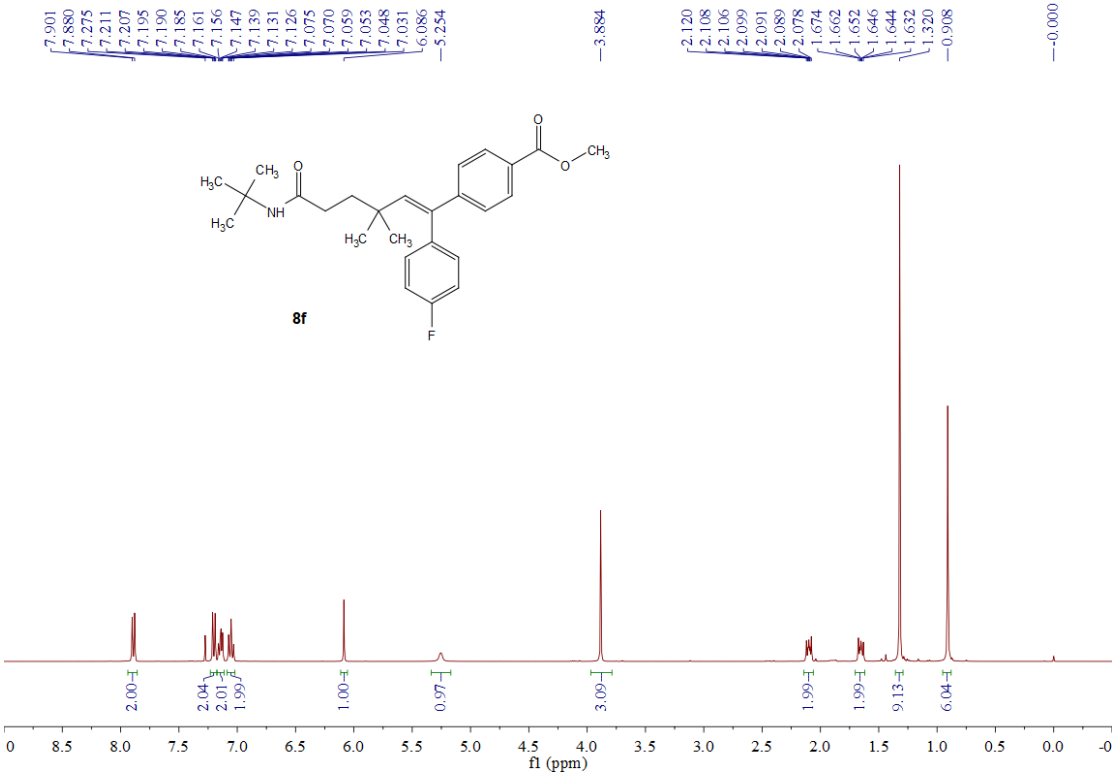
^{1}H NMR (600 MHz, $CDCl_3$) of 8e



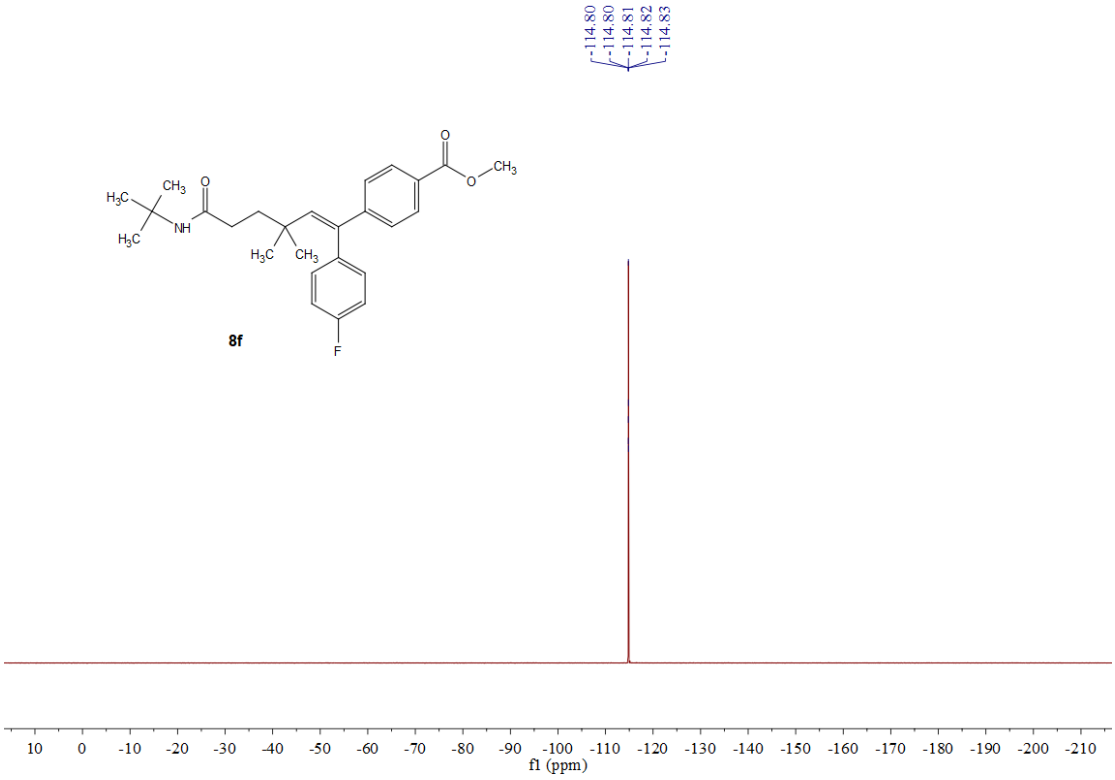
^{13}C NMR (151 MHz, $CDCl_3$) of 8e



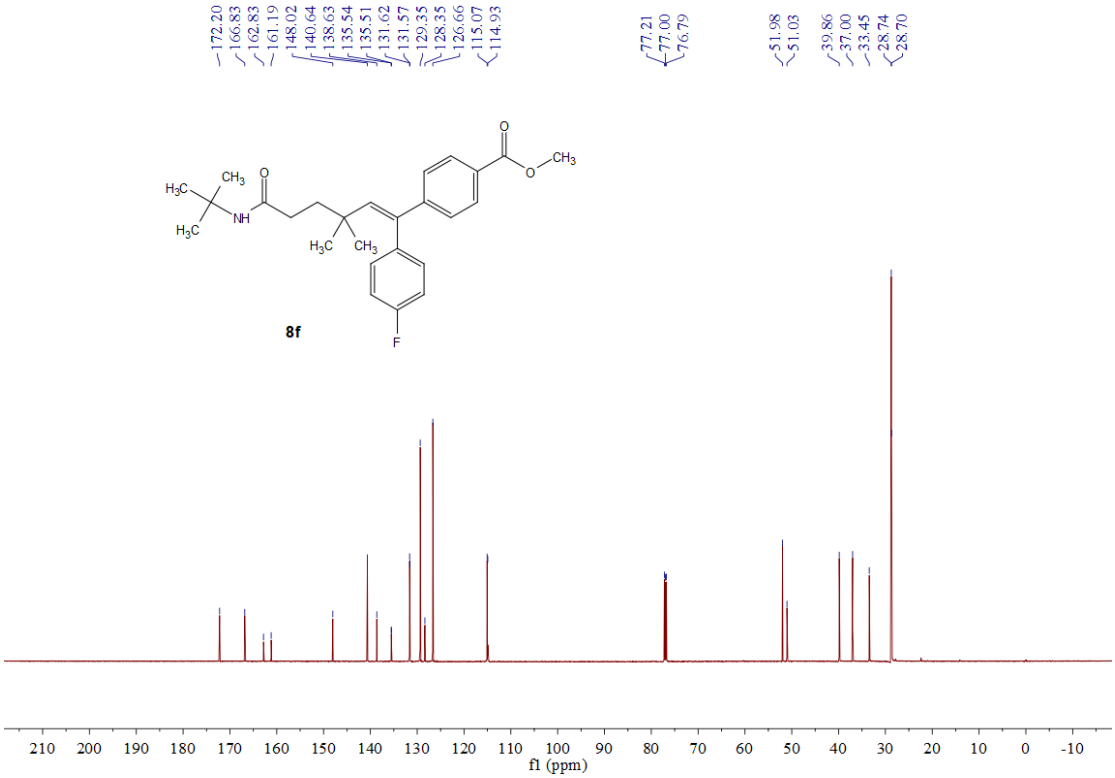
^{1}H NMR (400 MHz, $CDCl_3$) of 8f



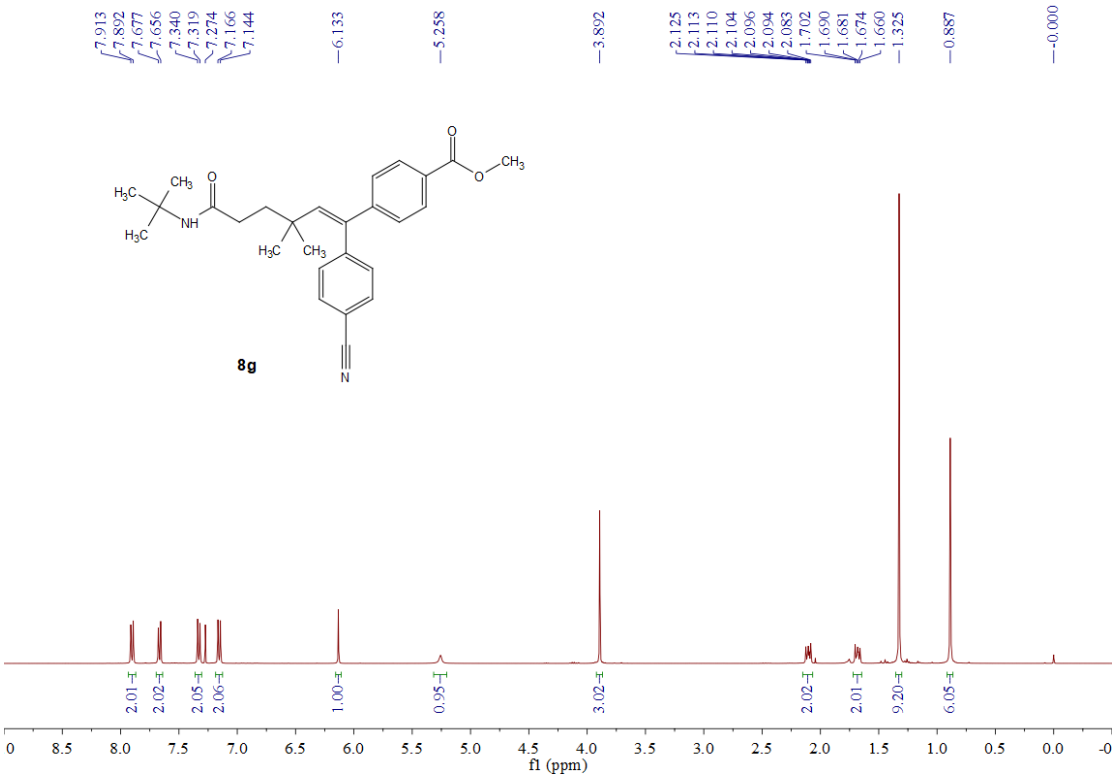
^{19}F NMR (565 MHz, $CDCl_3$) of 8f



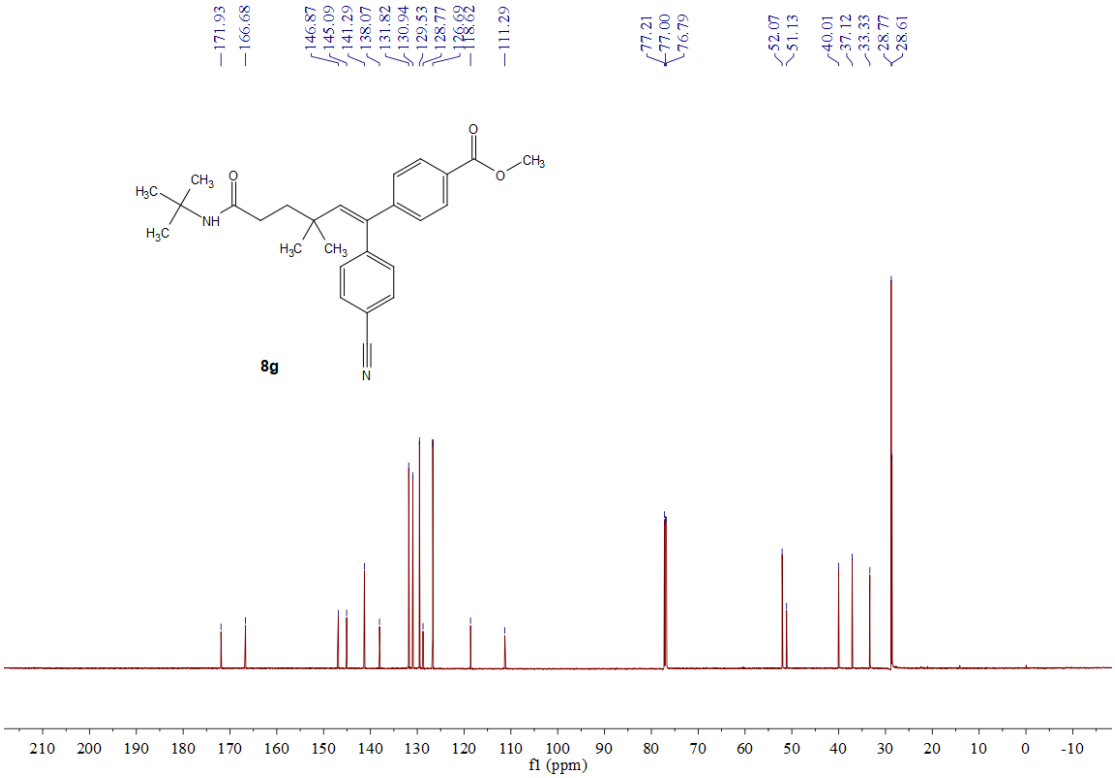
^{13}C NMR (151 MHz, $CDCl_3$) of 8f



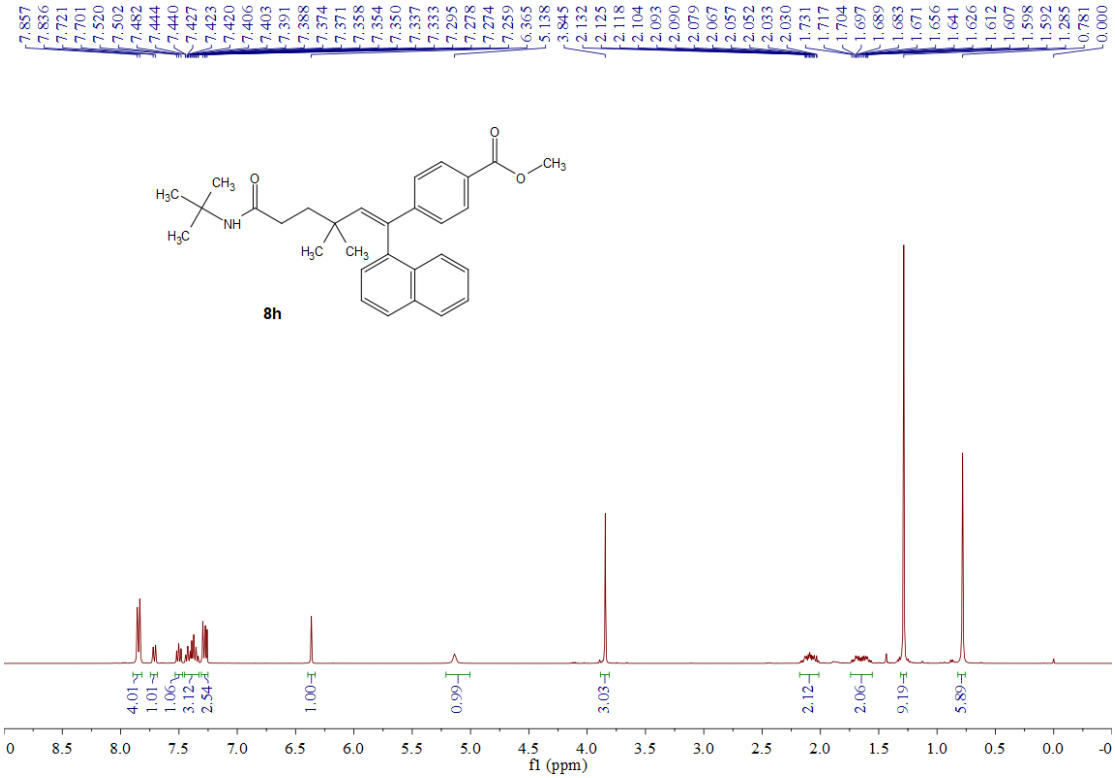
^{1}H NMR (400 MHz, $CDCl_3$) of 8g



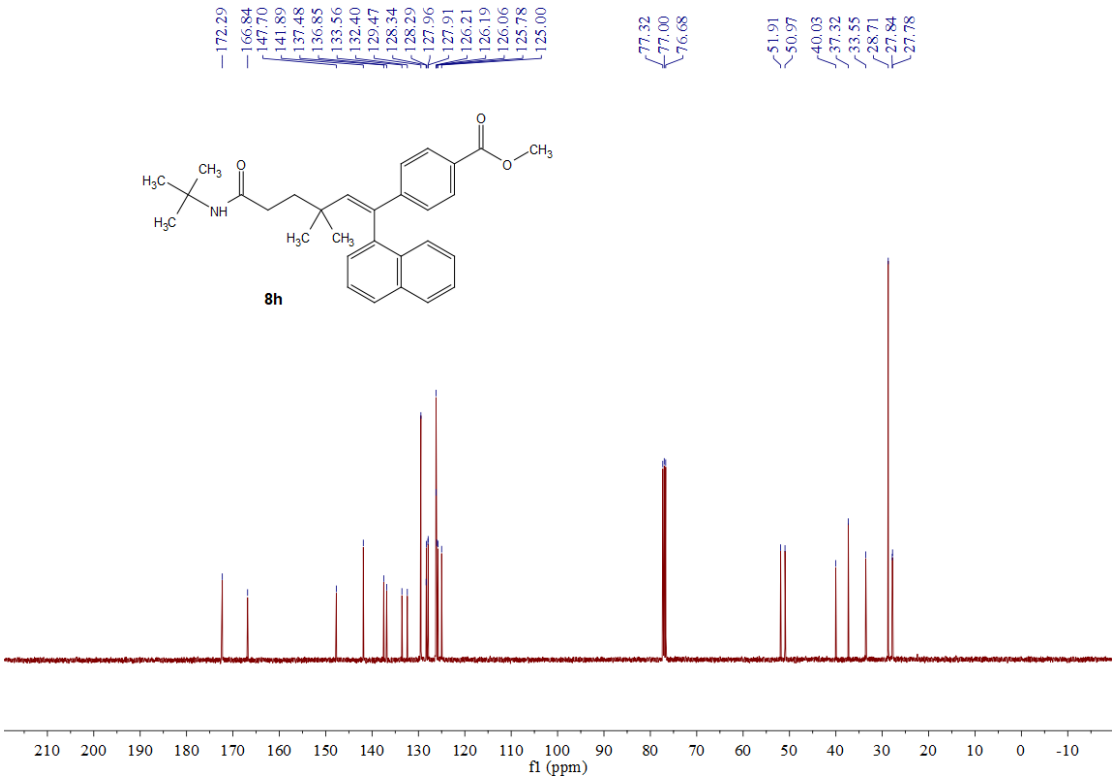
^{13}C NMR (151 MHz, $CDCl_3$) of 8g



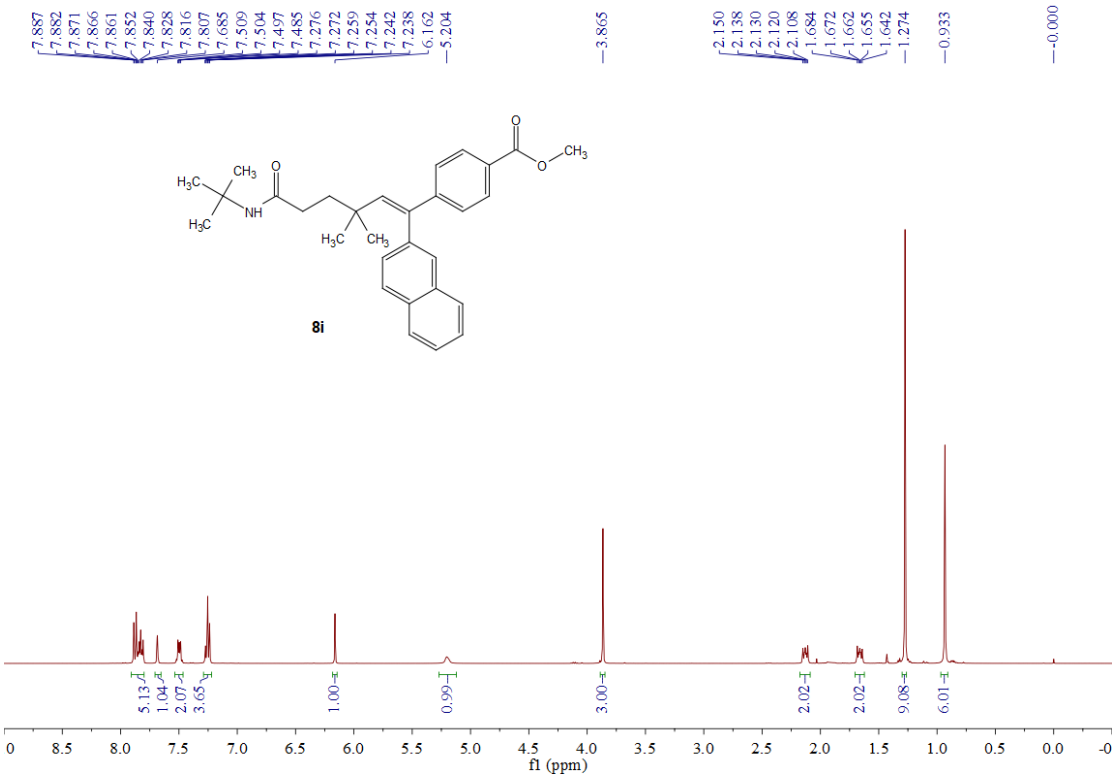
^{1}H NMR (400 MHz, $CDCl_3$) of 8h



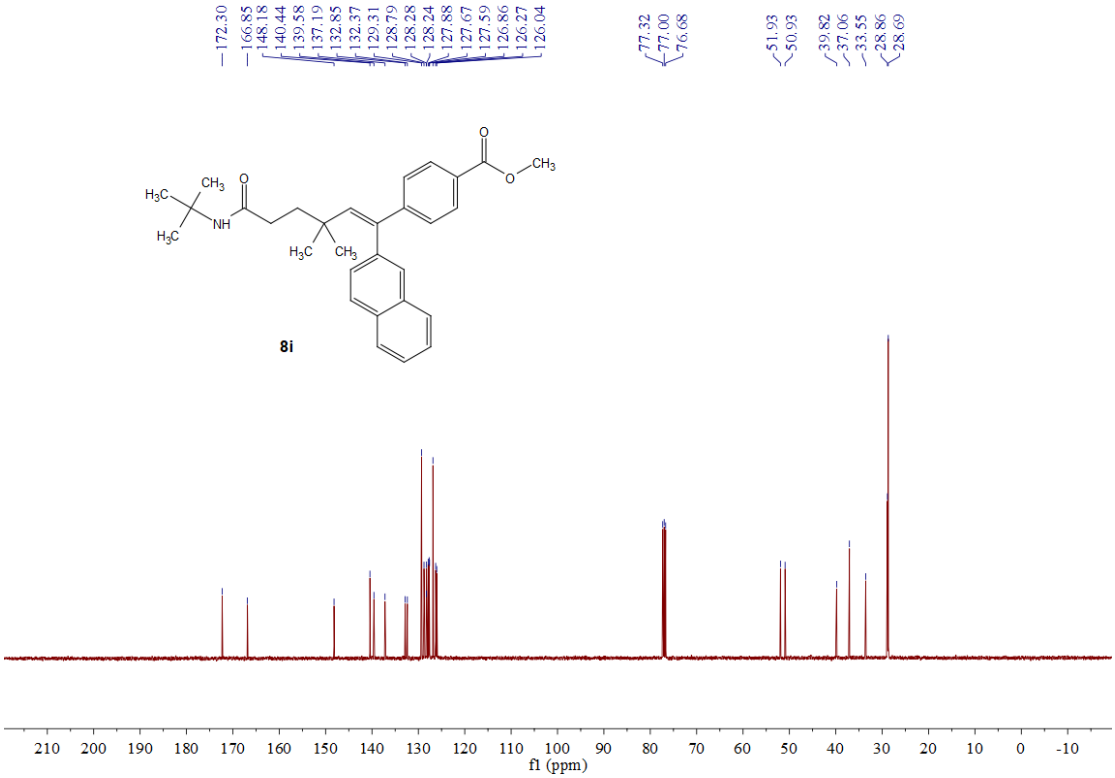
^{13}C NMR (101 MHz, $CDCl_3$) of 8h



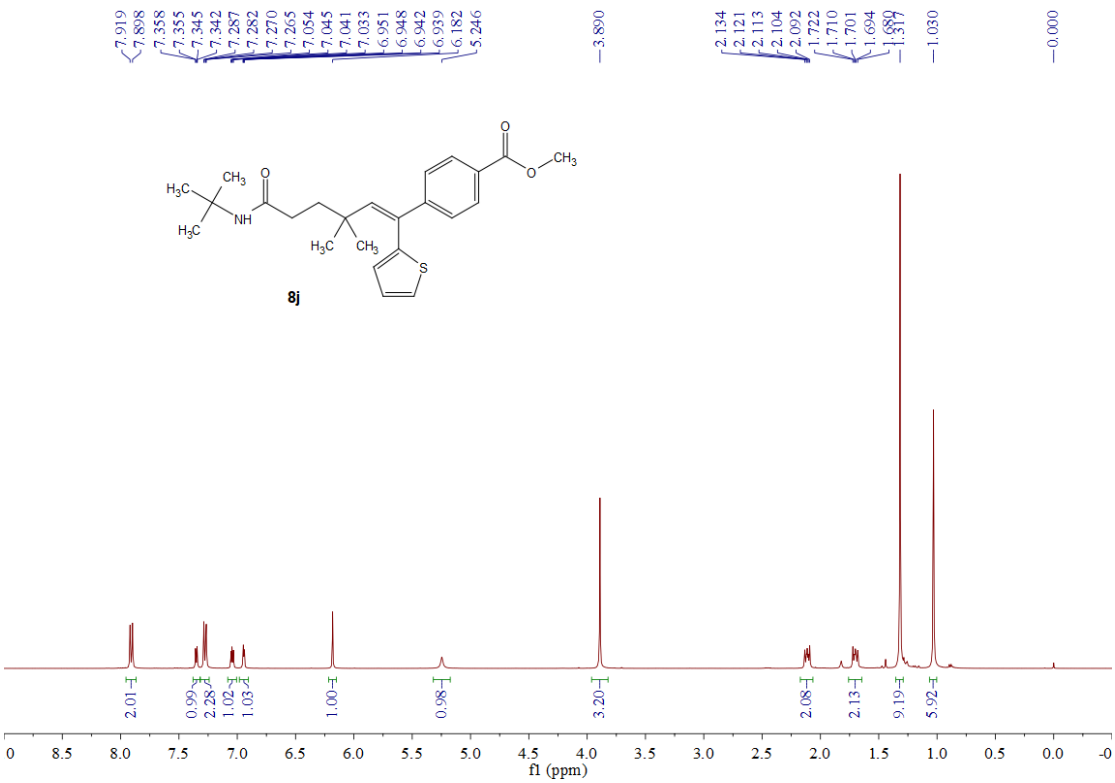
^{1}H NMR (400 MHz, $CDCl_3$) of 8i



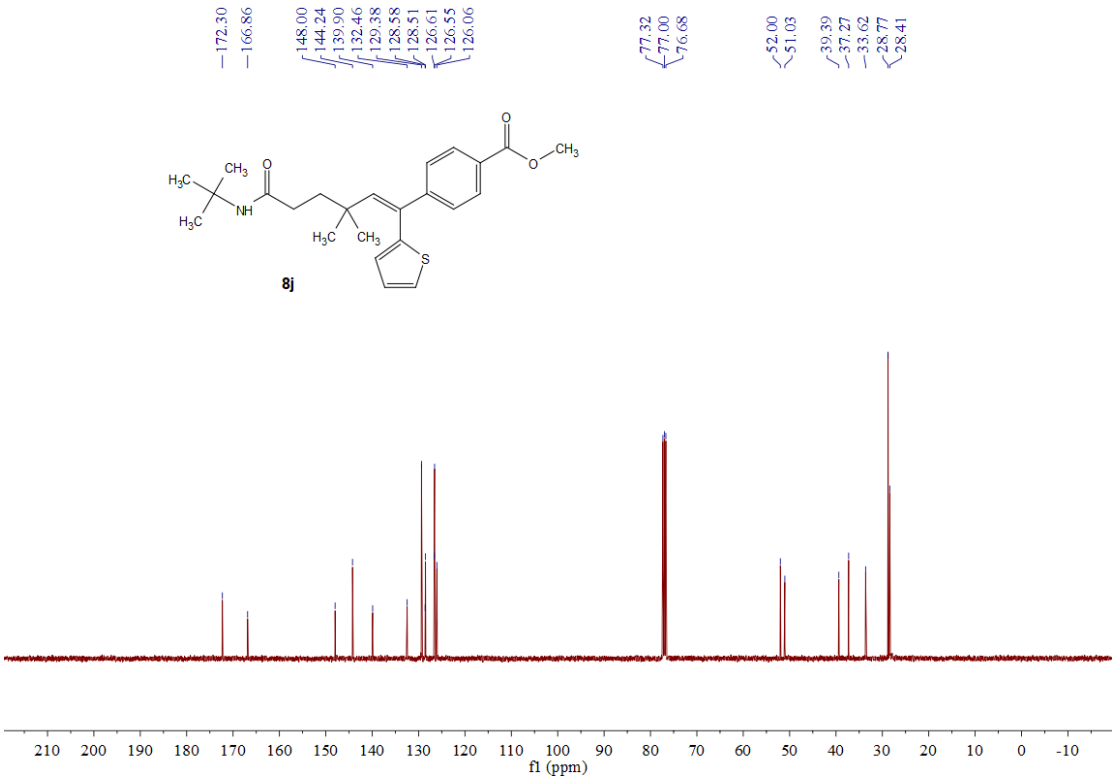
^{13}C NMR (101 MHz, $CDCl_3$) of 8i



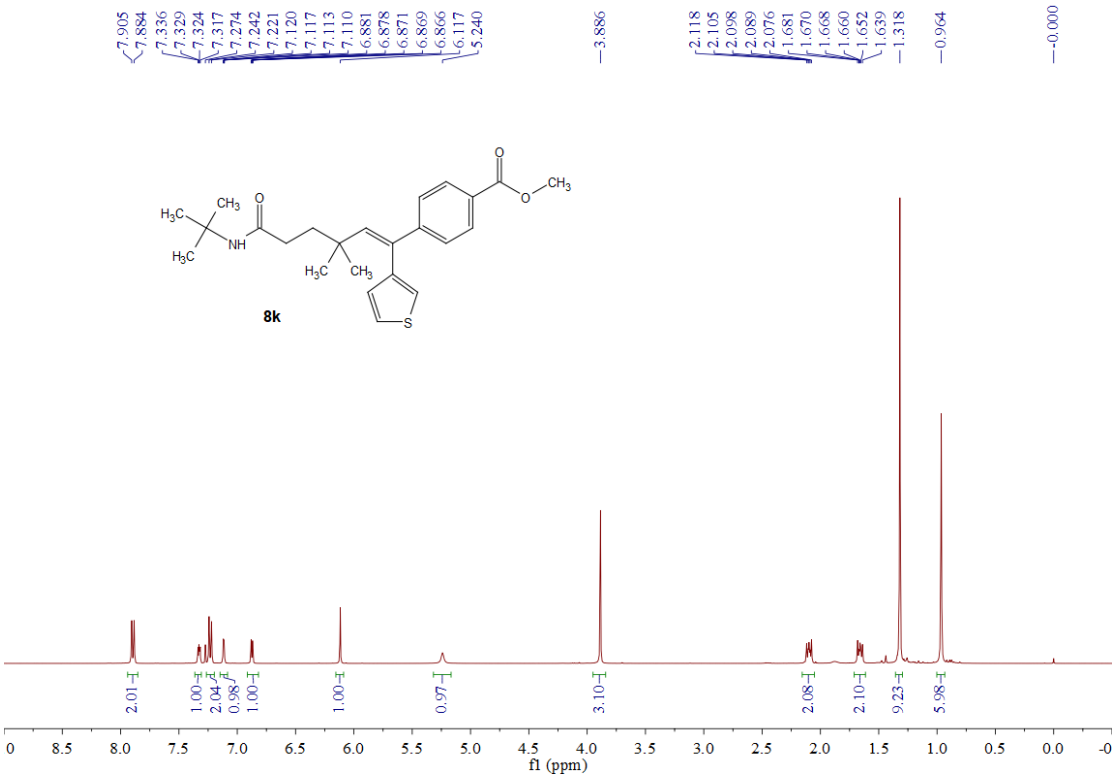
^{1}H NMR (400 MHz, $CDCl_3$) of 8j



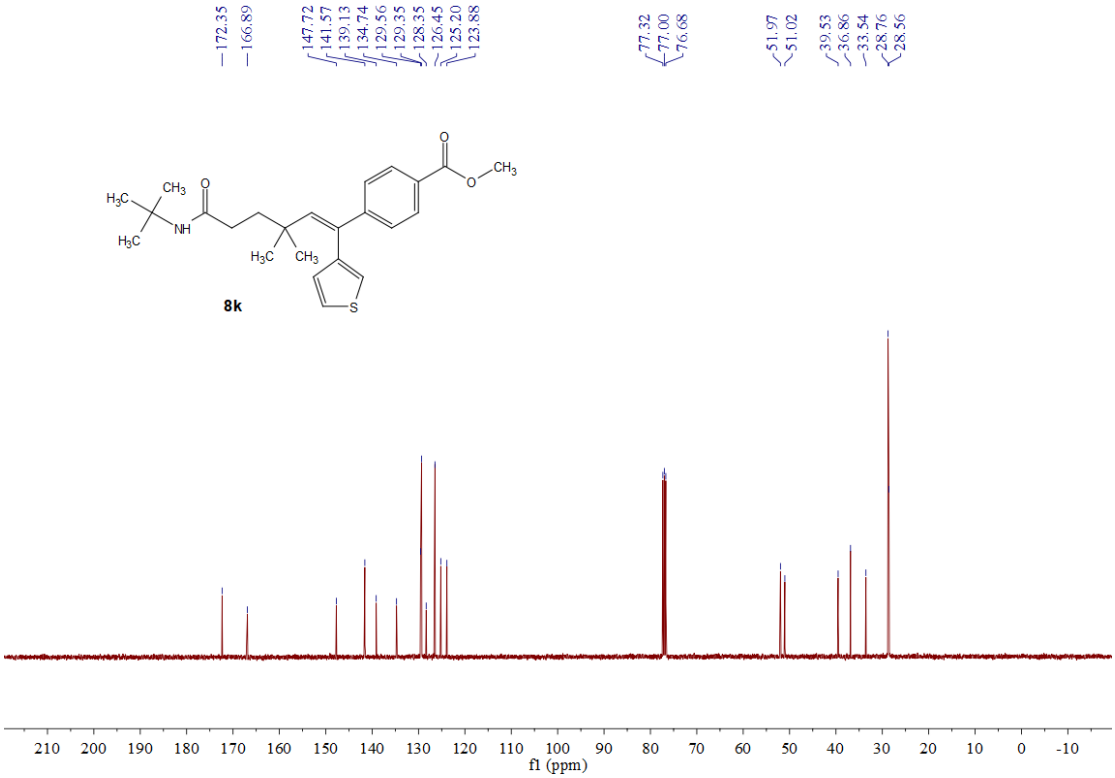
^{13}C NMR (101 MHz, $CDCl_3$) of 8j



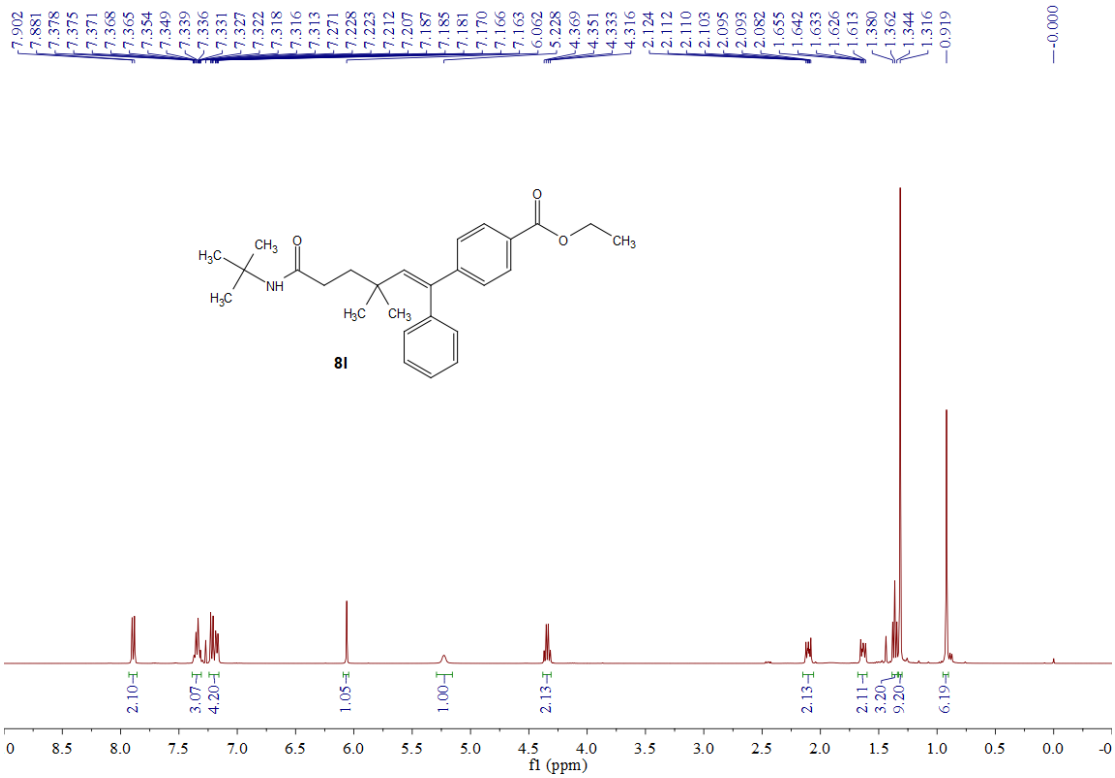
^{1}H NMR (400 MHz, $CDCl_3$) of 8k



^{13}C NMR (101 MHz, $CDCl_3$) of 8k



^{1}H NMR (400 MHz, $CDCl_3$) of 8l



^{13}C NMR (101 MHz, $CDCl_3$) of 8l