Supporting Information

Divergent Syntheses of Spiroindanones and 2-Substituted 1-Indanones by Ruthenium-Catalyzed Tandem Coupling and Cyclization of Aromatic Acids with *α,β*-Unsaturated Ketones

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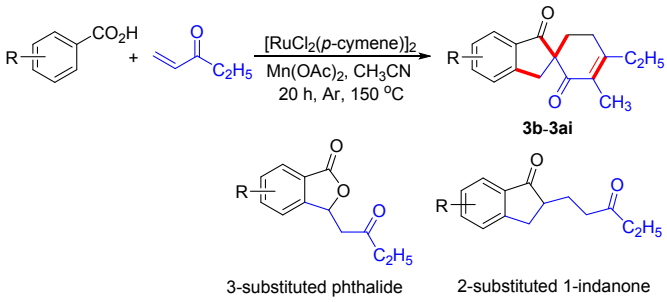
1. The conversions of aromatic acids and the yields of byproducts

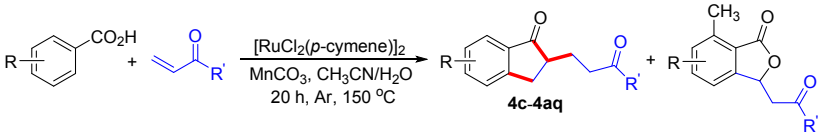
Table S1 The conversions of aromatic acids and the yields of byproducts in Table 2



Entry	Product	Conversion of acid	Yield (%)[a]		Entry	Product	Conversion of acid	Yield (%)[a]	
			phthalide	1-indanone				phthalide	1-indanone
1	**3a**	100	4	18	19	**3s**	100	11	16
2	**3b**	100	3	16	20	**3t**	100	7	14
3	**3c**	100	5	19	21	**3u**	100	7	15
4	**3d**	100	trace	ND	22	**3v**	100	trace	12
5	**3e**	95	6	13	23	**3w**	100	trace	23
6	**3f**	96	5	11	24	**3x**	100	trace	23
7	**3g**	97	8	9	25	**3y**	100	trace	19
8	**3h**	98	7	14	26	**3z**	100	6	6
9	**3i**	96	12	14	27	**3aa**	97	8	6
10	**3j**	100	3	19	28	**3ab**	100	4	12
11	**3k**	100	trace	19	29	**3ac**	100	4	8
12	**3l**	100	7	15	30	**3ad**	92	12	7
13	**3m**	100	4	16	31	**3ae**	93	7	12
14	**3n**	100	5	17	32	**3af**	100	3	ND
15	**3o**	100	8	14	33	**3ag**	100	2	ND
16	**3p**	100	11	14	34	**3ah**	97	4	8
17	**3q**	100	7	17	35	**3ai**	83	2	4
18	**3r**	100	9	9					

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Table S2 The conversions of aromatic acids and the yields of byproducts in Table 4

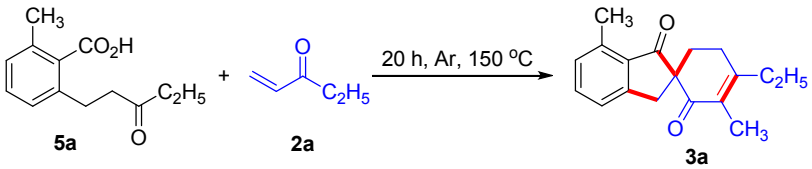


Entry	Product	Conversion of acid (%)[a]	Yield of phthalide (%)[a]	Entry	Product	Conversion of acid (%)	Yield of phthalide (%)[a]
1	**4a**	100	6	23	**4w**	100	6
2	**4b**	96	4	24	**4x**	100	ND
3	**4c**	96	4	25	**4y**	91	ND
4	**4d**	98	2	26	**4z**	85	ND
5	**4e**	97	6	27	**4aa**	96	6
6	**4f**	93	5	28	**4ab**	94	6
7	**4g**	89	4	29	**4ac**	96	6
8	**4h**	88	5	30	**4ad**	94	5
9	**4i**	100	6	31	**4ae**	95	5
10	**4j**	100	4	32	**4af**	100	8
11	**4k**	100	2	33	**4ag**	100	3
12	**4l**	99	5	34	**4ah**	100	2
13	**4m**	96	2	35	**4ai**	100	ND
14	**4n**	97	7	36	**4aj**	100	ND
15	**4o**	97	3	37	**4ak**	100	ND
16	**4p**	100	10	38	**4al**	100	ND
17	**4q**	100	4	39	**4am**	100	ND
18	**4r**	100	6	40	**4an**	100	ND
19	**4s**	96	8	41	**4ao**	100	ND
20	**4t**	93	5	42	**4ap**	100	ND
21	**4u**	93	11	43	**4aq**	100	ND
22	**4v**	97	7				

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

2. Mechanistic studies

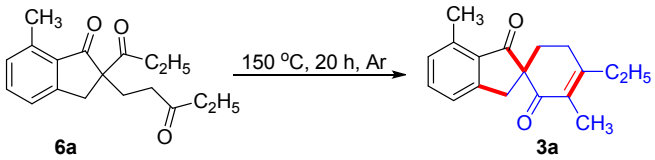
Table S3. Experimental results using **5a** as a reactant for the synthesis of **3a**



Entry	Conditions	Yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $Mn(OAc)_2$ (0.75 equiv), CH_3CN (0.6 mL)	65%
2	$Mn(OAc)_2$ (0.75 equiv), CH_3CN (0.6 mL)	61%
3	CH_3CN (0.6 mL)	ND

[a] Reaction conditions: **5a** (0.1 mmol), **2a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] ND = not detected.

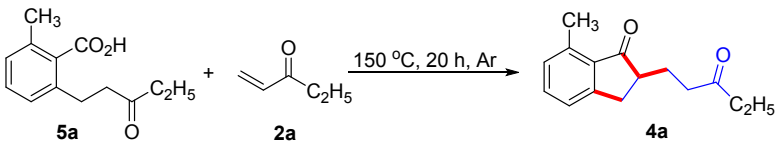
Table S4. Experimental results using **6a** as a reactant for the synthesis of **3a**



Entry	Conditions	Yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $Mn(OAc)_2$ (0.75 equiv), CH_3CN (0.6 mL)	56%
2	$Mn(OAc)_2$ (0.75 equiv), CH_3CN (0.6 mL)	43%
3	CH_3CN (0.6 mL)	ND

[a]Reaction conditions: **6a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] ND = not detected.

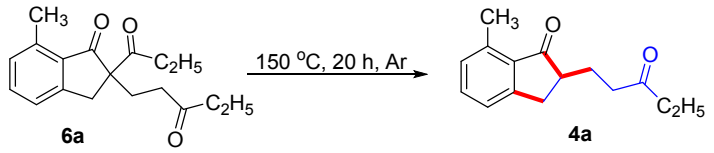
Table S5. Experimental results using **5a** as a reactant for the synthesis of **4a**



Entry	Conditions	Yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $MnCO_3$ (1.0 equiv), H_2O (38 μL), CH_3CN (0.6 mL)	61
2	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $MnCO_3$ (1.0 equiv), H_2O (0.6 mL)	21
3	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), H_2O (0.6 mL)	ND
4	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), H_2O (38 μL), CH_3CN (0.6 mL)	ND
5	$MnCO_3$ (1.0 equiv), H_2O (38 μL), CH_3CN (0.6 mL)	56
6	$MnCO_3$ (1.0 equiv), H_2O (0.6 mL)	29
7	$MnCO_3$ (1.0 equiv), CH_3CN (0.6 mL)	trace
8	H_2O (38 μL), CH_3CN (0.6 mL)	ND

[a] Reaction conditions: **5a** (0.1 mmol), **2a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] ND = not detected.

Table S6. Experimental results using **6a** as a reactant for the synthesis of **4a**



Entry	Conditions	Yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $MnCO_3$ (1.0 equiv), H_2O (38 μL), CH_3CN (0.6 mL)	68
2	$MnCO_3$ (1.0 equiv), H_2O (38 μL), CH_3CN (0.6 mL)	30
3	$MnCO_3$ (1.0 equiv), H_2O (0.6 mL)	42
4	$MnCO_3$ (1.0 equiv), CH_3CN (0.6 mL)	ND
5	H_2O (0.6 mL)	ND

[a] Reaction conditions: **6a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

3. Single crystal X-ray diffraction results

3.1 Single crystal X-ray diffraction result of 3q

The single crystal was obtained from n-hexane and ethyl acetate. Using Olex2,[1] the structure was solved with the XT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimisation.[2-3]

Figure S1. Crystal structure of 3q

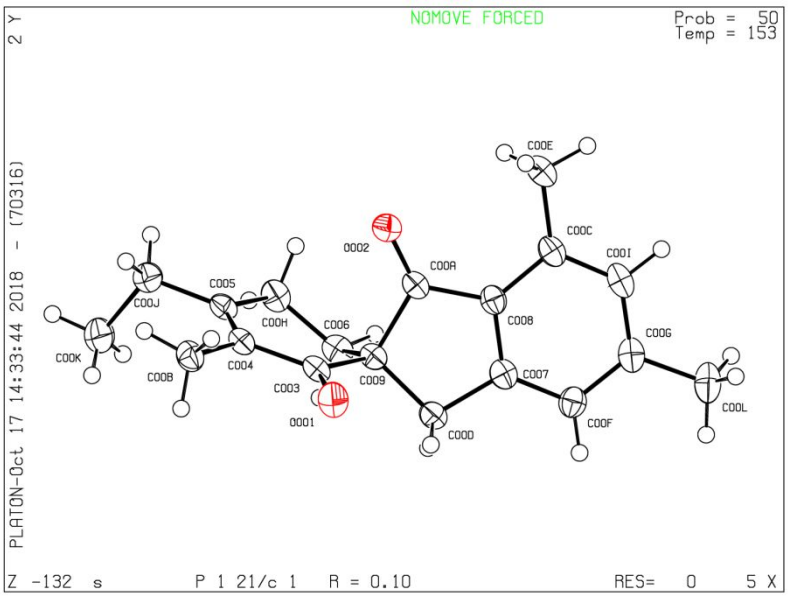


Table S7. Crystal data and structure refinement for **3q**.

Compound Number	**3q**
Empirical formula	$C_{19}H_{22}O_2$
Formula weight	282.36
Temperature/K	153.08
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.8547(16)
b/Å	16.926(2)
c/Å	7.0925(9)
α/°	90
β/°	102.502(3)
γ/°	90
Volume/Å^3	1506.6(3)
Z	4
ρcalcg/cm3	1.245
μ/mm^{-1}	0.619
F(000)	608.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.22 to 136.704
Index ranges	$-15 \leq h \leq 15$, $-20 \leq k \leq 20$, $-7 \leq l \leq 8$
Reflections collected	20710
Independent reflections	2719 [R_{int} = 0.0534, R_{sigma} = 0.0324]
Data/restraints/parameters	2719/0/195
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0989, wR_2 = 0.2813
Final R indexes [all data]	R_1 = 0.0998, wR_2 = 0.2819
Largest diff. peak/hole / e Å^{-3}	0.79/-0.36

3.2 Single crystal X-ray diffraction result of 4a

The single crystal was obtained from n-hexane and ethyl acetate. Using Olex2,[1] the structure was solved with the XTstructure solution program using Intrinsic Phasing and refined with the XLrefinement package using Least Squares minimisation.[2-3]

Figure S2. Crystal structure of **4a**

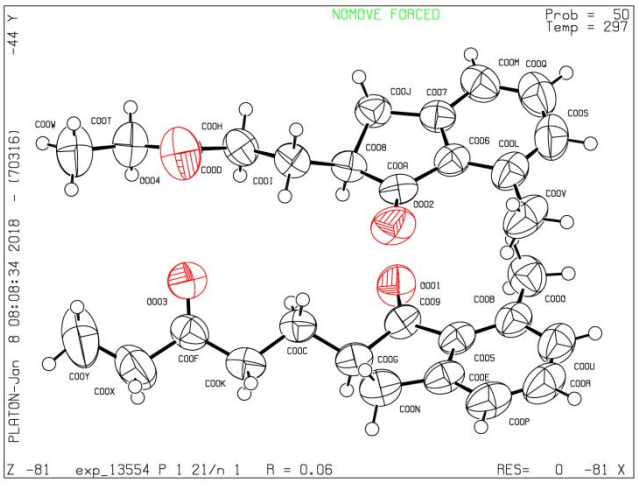


Table S8. Crystal data and structure refinement for **4a**.

Compound Number	**4a**
Empirical formula	$C_{15}H_{18}O_2$
Formula weight	230.29
Temperature/K	297
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.6874(3)
b/Å	7.3742(2)
c/Å	27.9567(7)
α/°	90
β/°	98.825(2)
γ/°	90
Volume/Å^3	2584.65(11)
Z	8
ρ_{calc}g/cm^3	1.184
μ/mm^{-1}	0.609
F(000)	992.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.014 to 144.306
Index ranges	$-15 \leq h \leq 15$, $-6 \leq k \leq 8$, $-34 \leq l \leq 34$
Reflections collected	29206
Independent reflections	4984 [R_{int} = 0.0306, R_{sigma} = 0.0155]
Data/restraints/parameters	4984/0/311
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1687
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1789
Largest diff. peak/hole / e Å^{-3}	0.15/-0.15

3.3 References

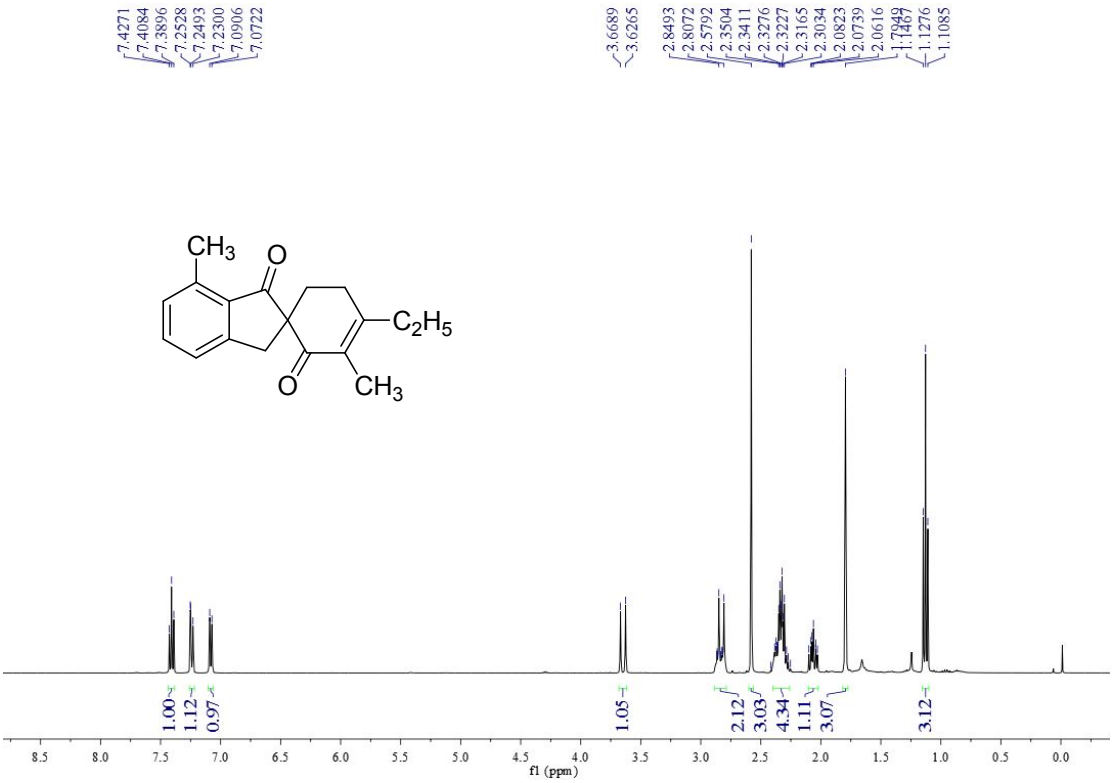
(1) Dolomanov, O.V.; Bourhis, L.J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*. **2009**, *42*, 339−341.

(2) Sheldrick, G. M. SHELXT – Integrated space-group and crystal structure determination. *Acta Crystallogr. A* **2015**, *71*, 3−8.

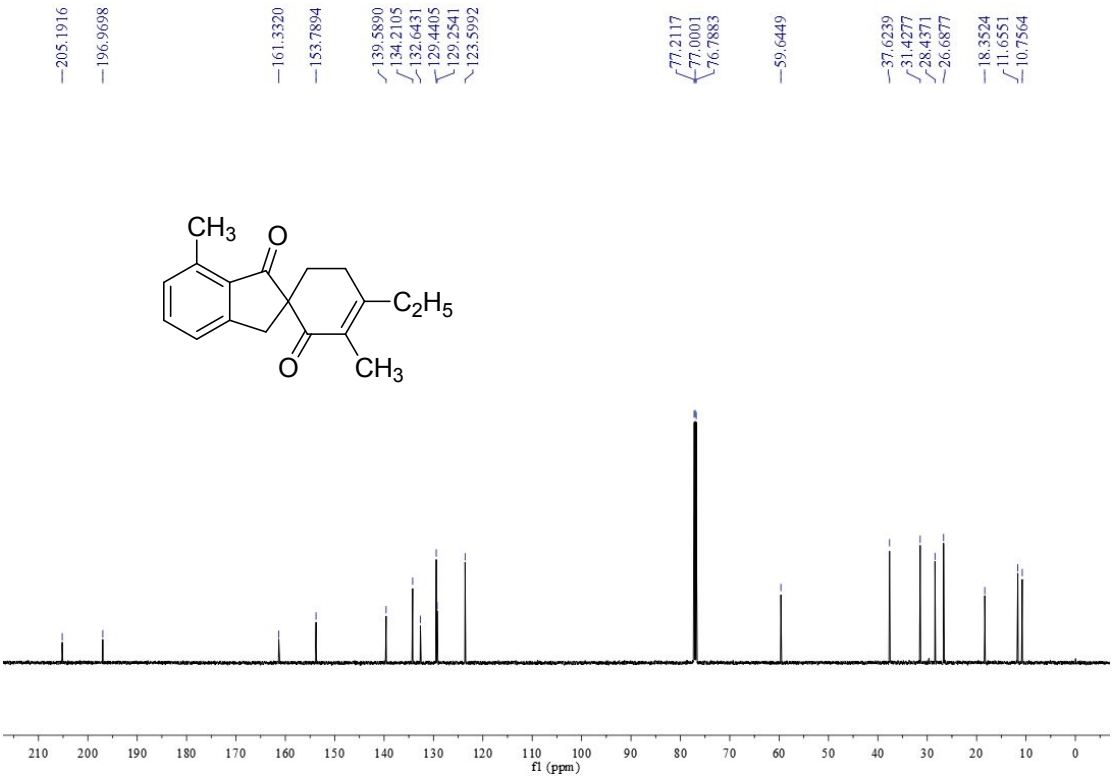
(3) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112−122.

4. Copies of NMR spectra

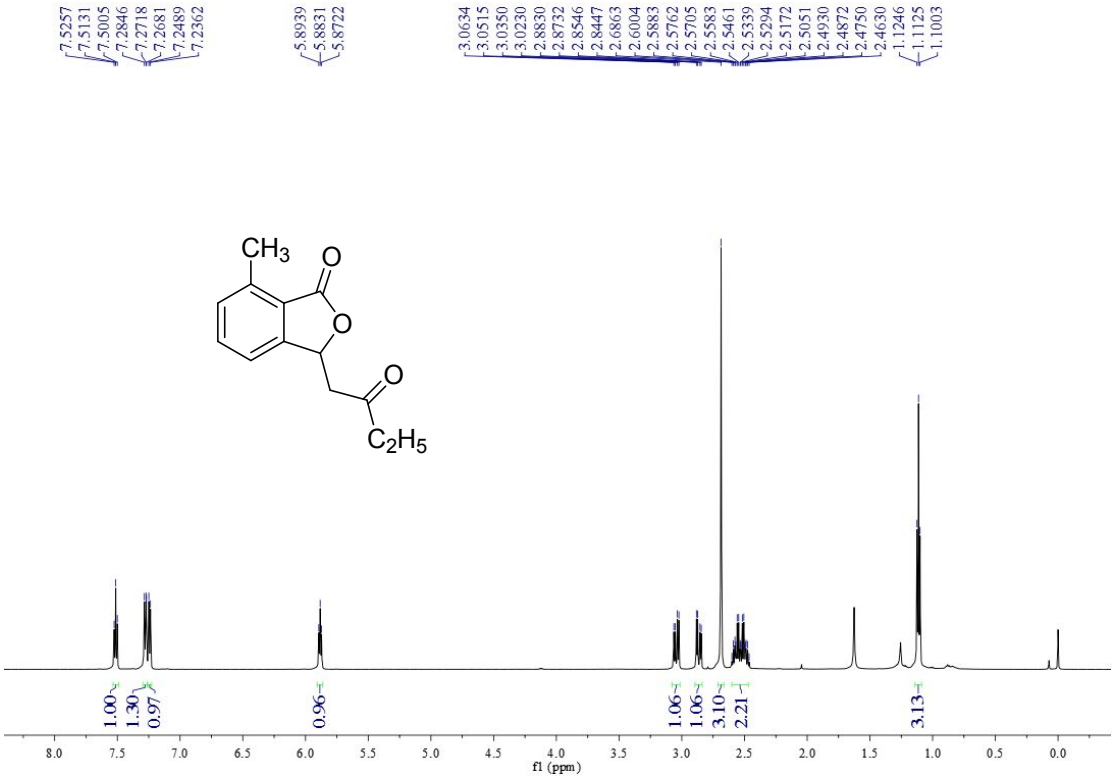
^{1}H NMR spectra of compound 3a



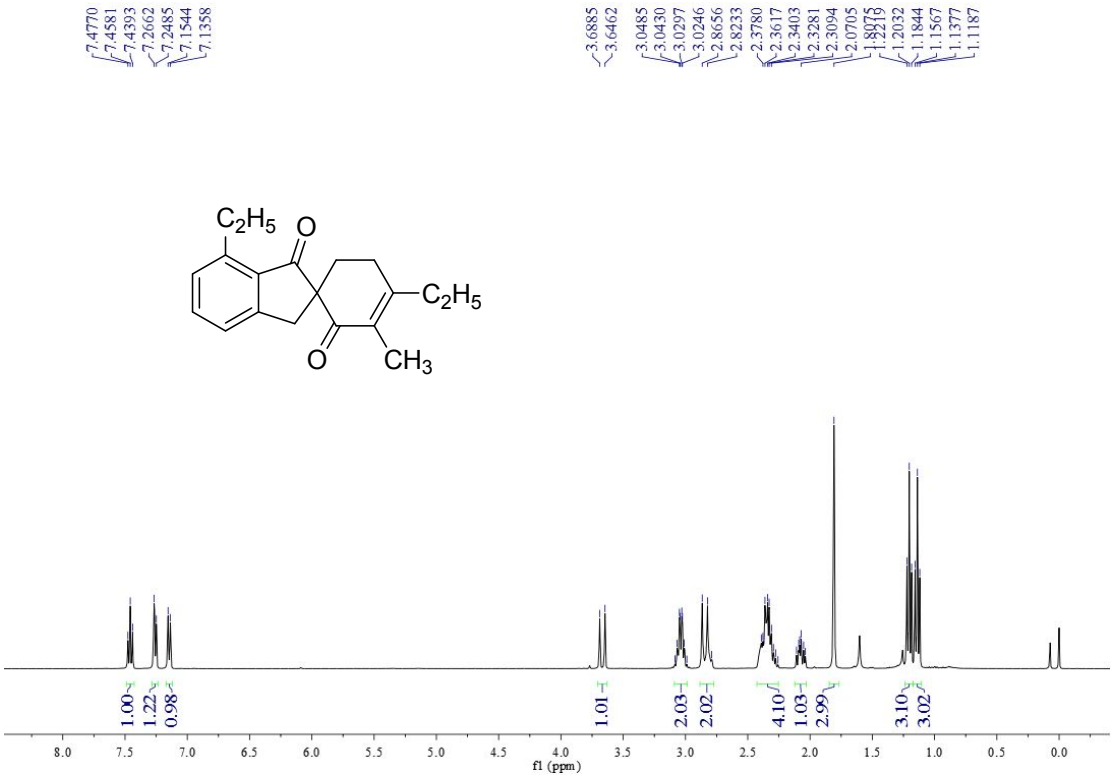
^{13}C NMR spectra of compound 3a



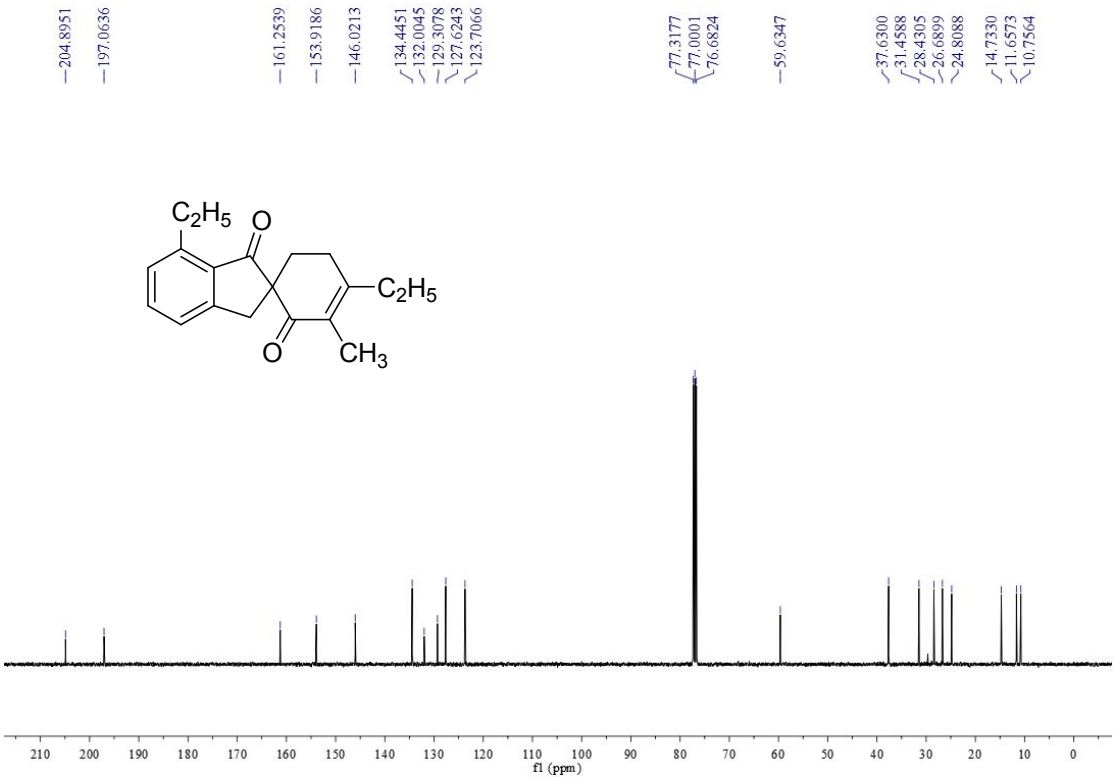
^{1}H NMR spectra of compound 3a'



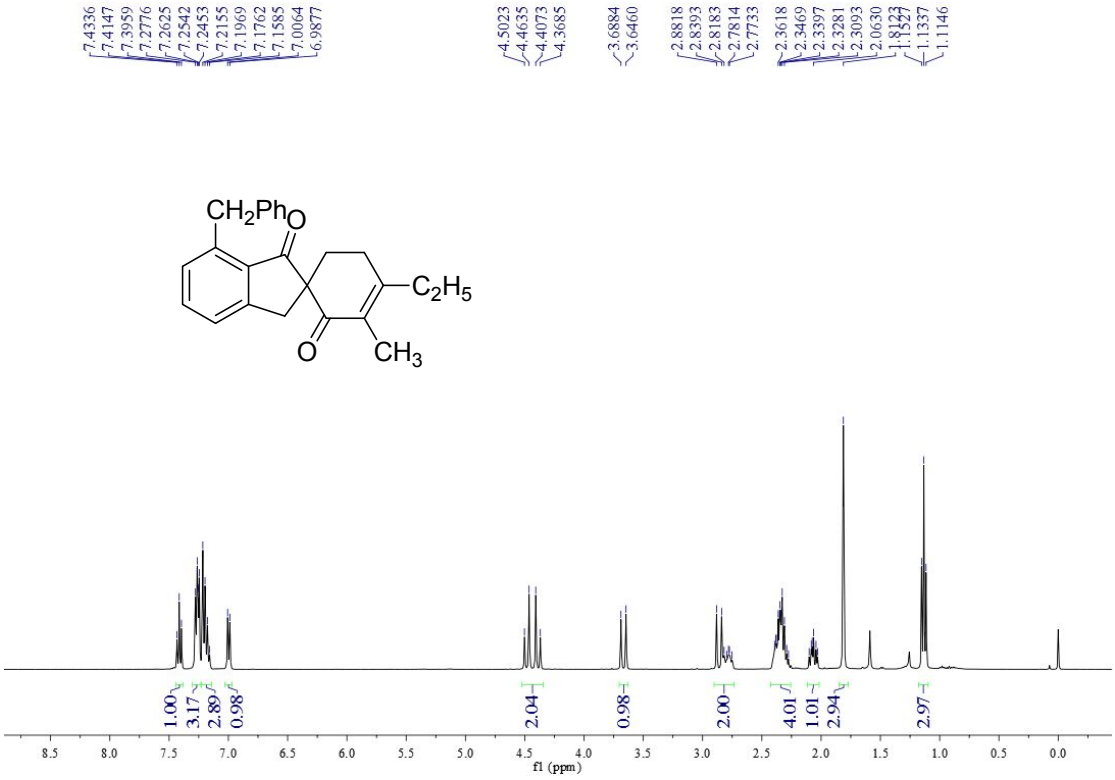
^{1}H NMR spectra of compound 3b



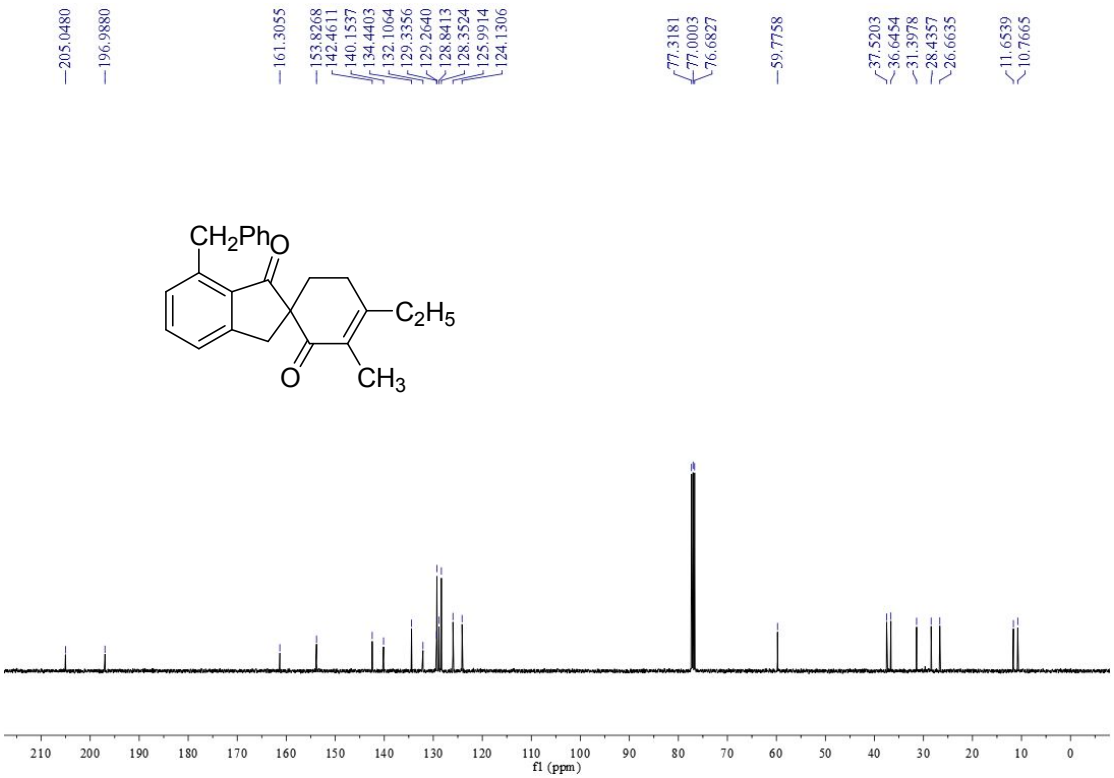
^{13}C NMR spectra of compound 3b



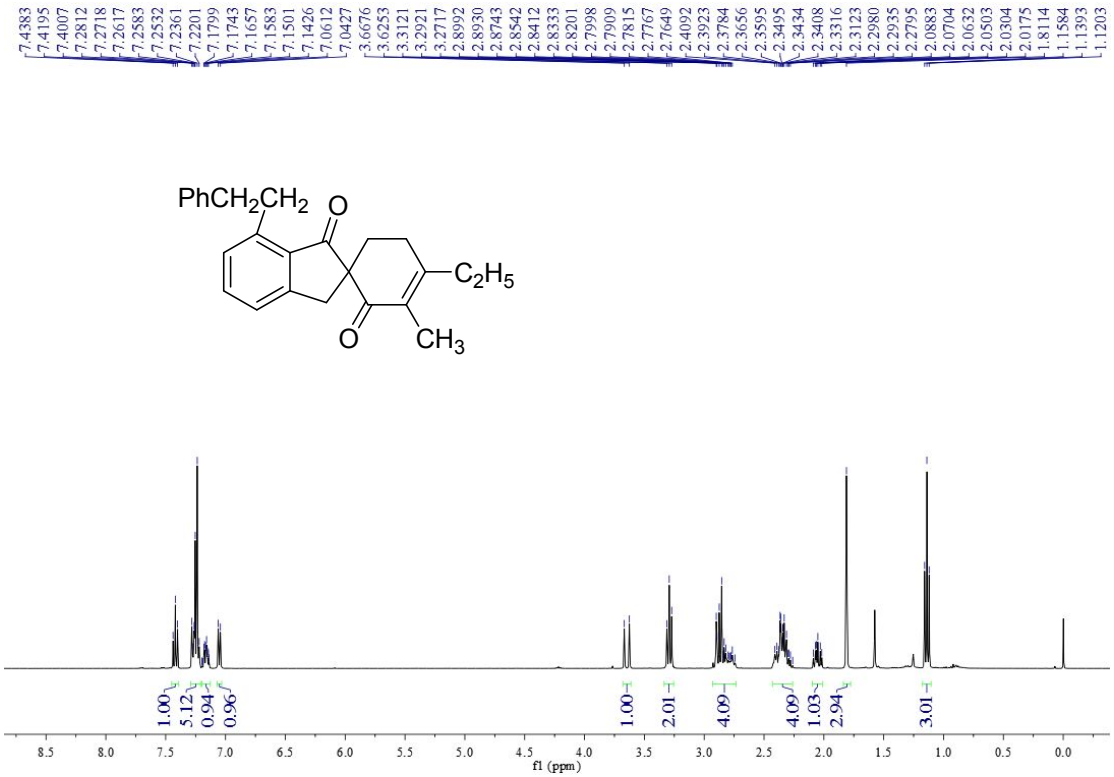
^{1}H NMR spectra of compound 3c



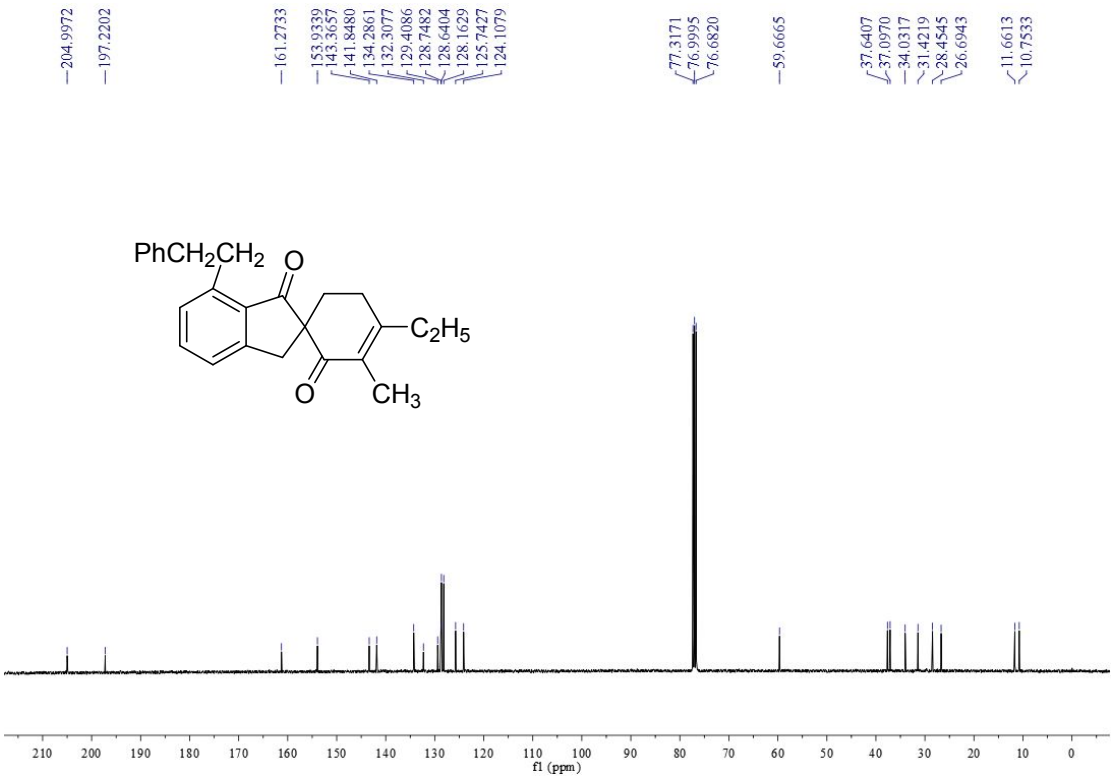
^{13}C NMR spectra of compound 3c



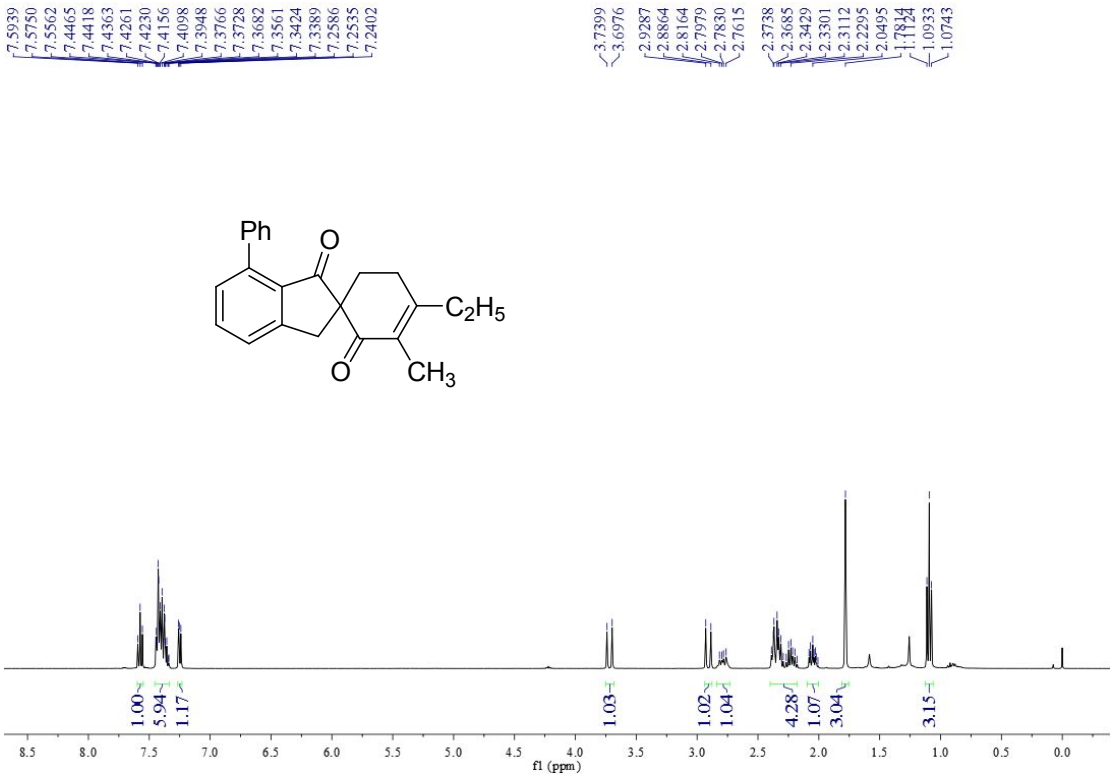
^{1}H NMR spectra of compound 3d



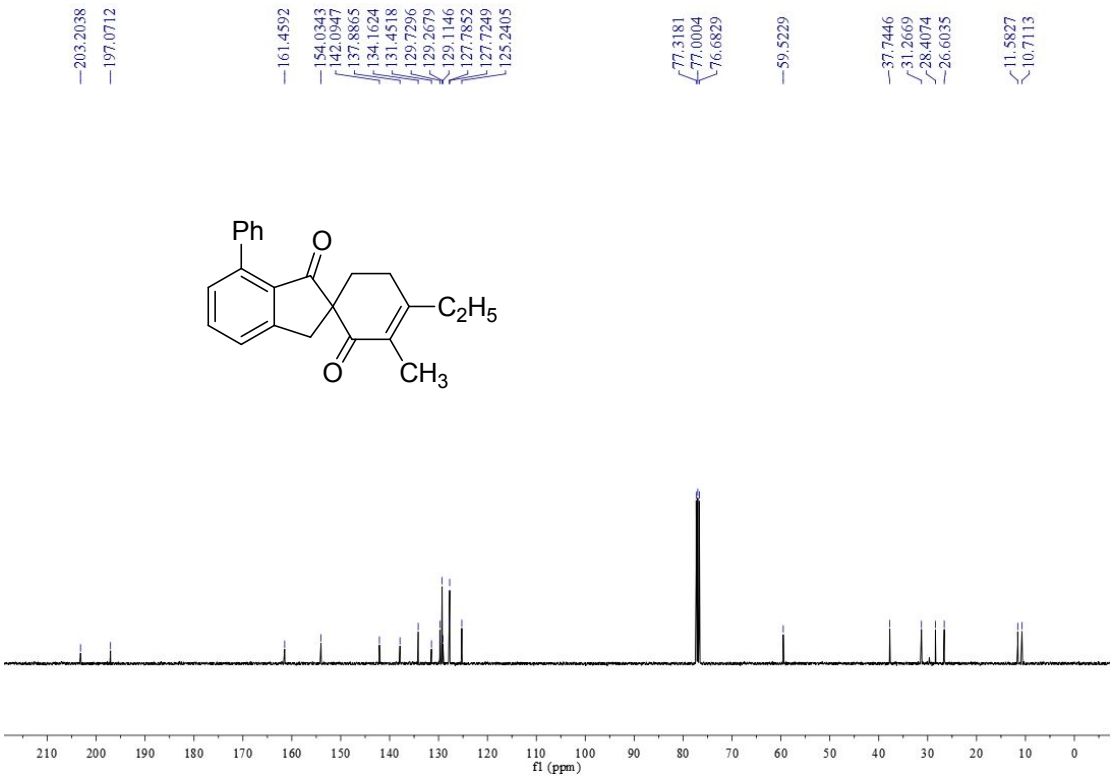
^{13}C NMR spectra of compound 3d



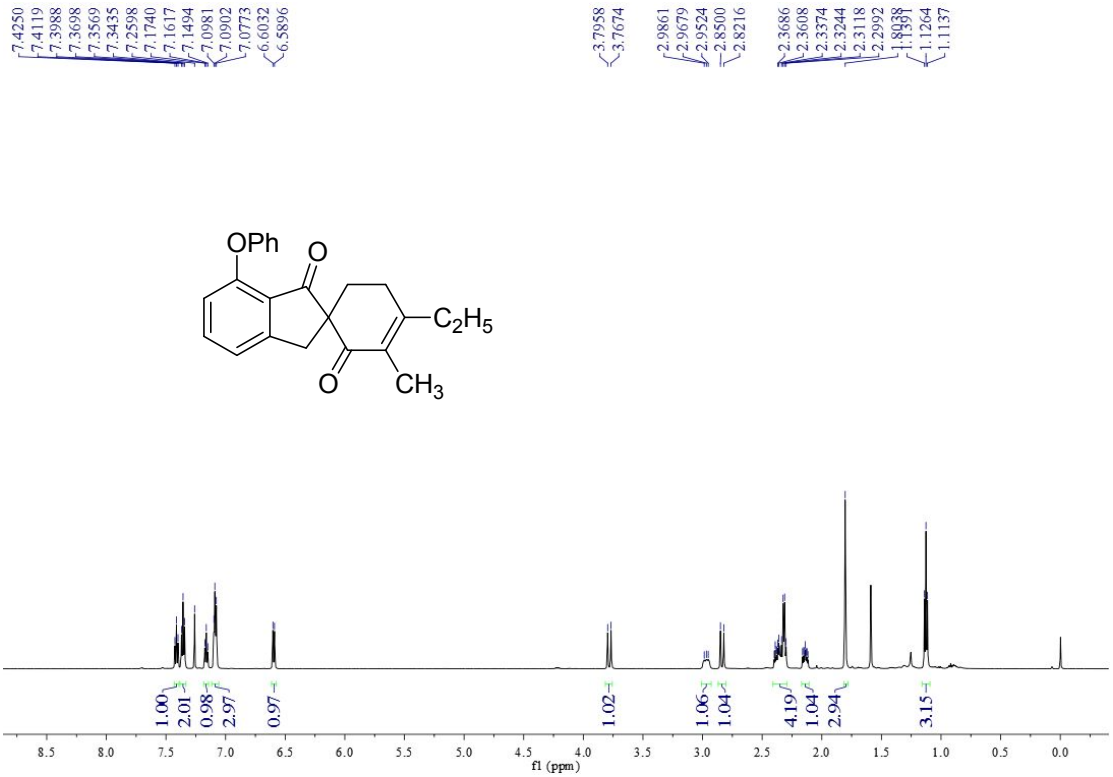
^{1}H NMR spectra of compound 3e



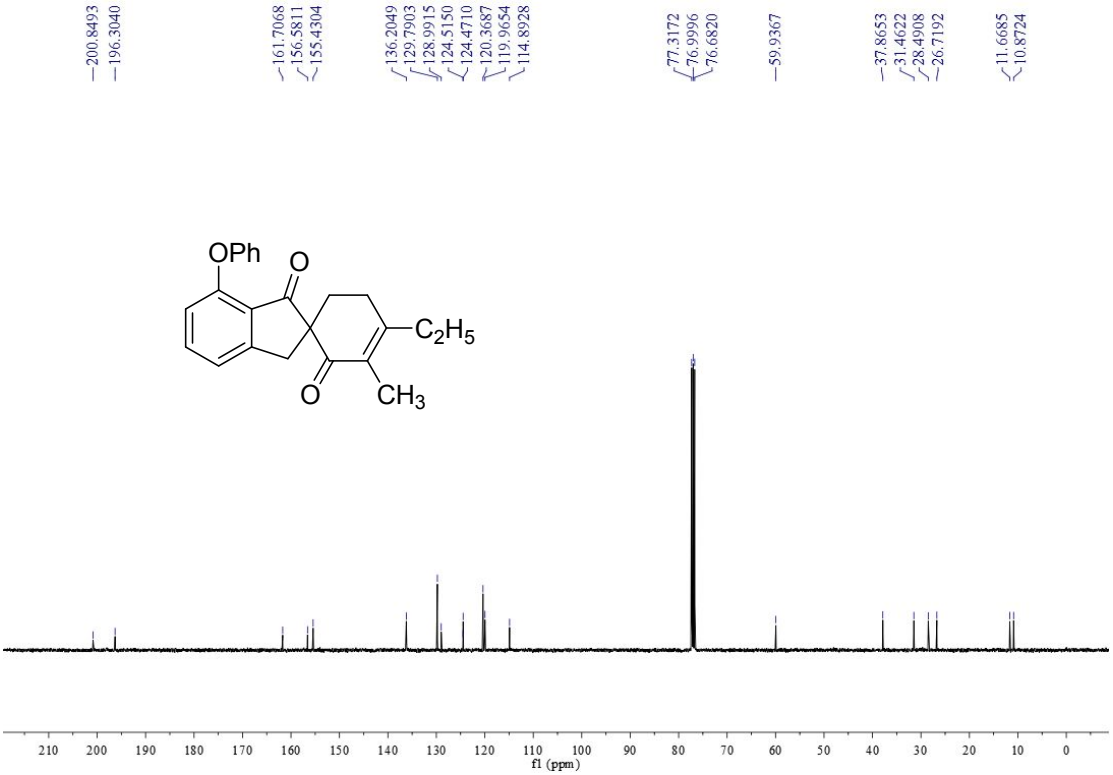
^{13}C NMR spectra of compound 3e



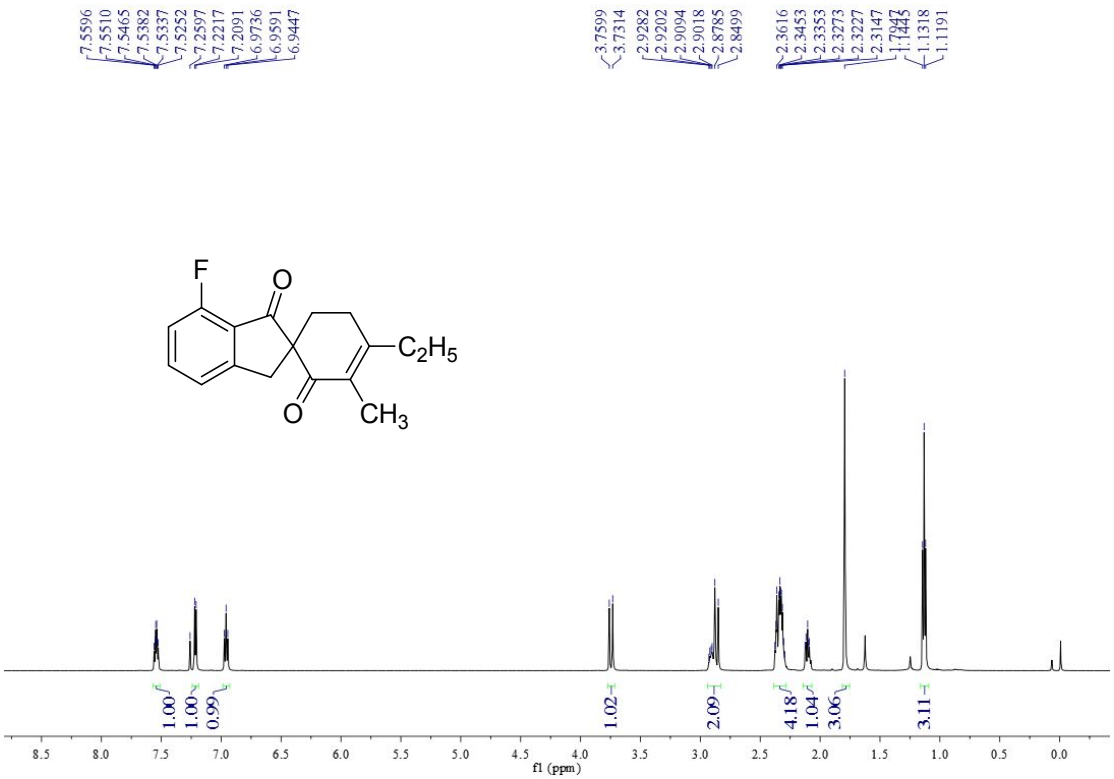
^{1}H NMR spectra of compound 3f



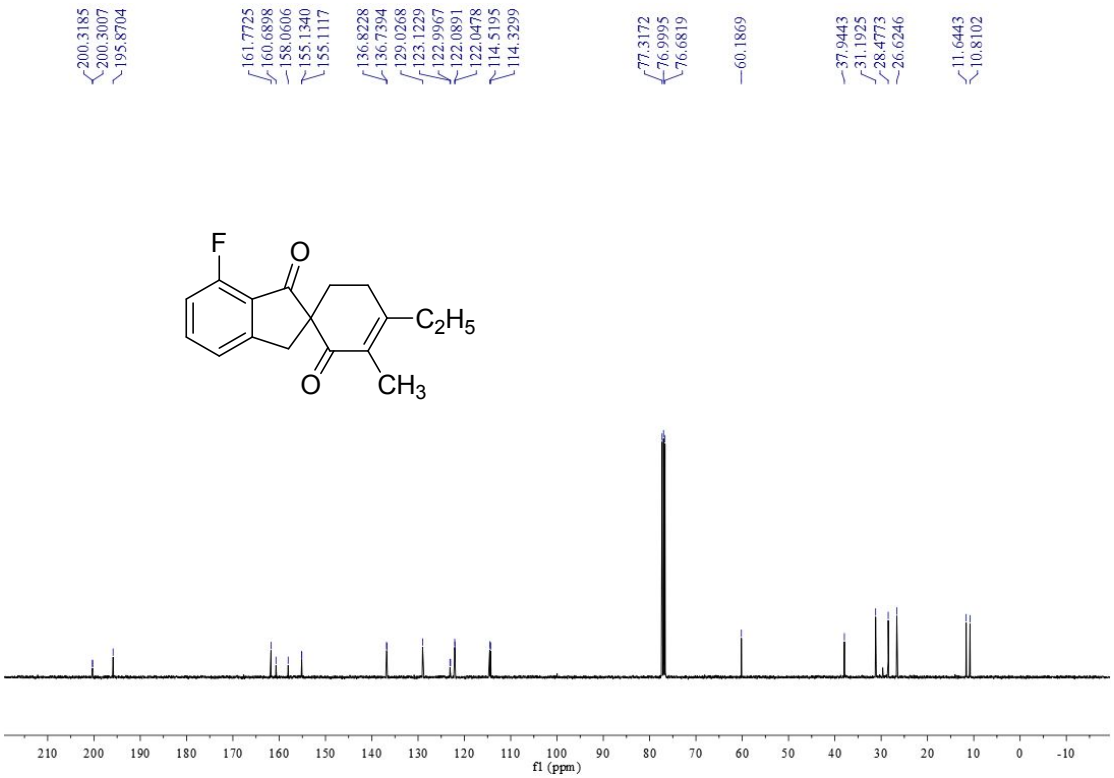
^{13}C NMR spectra of compound 3f



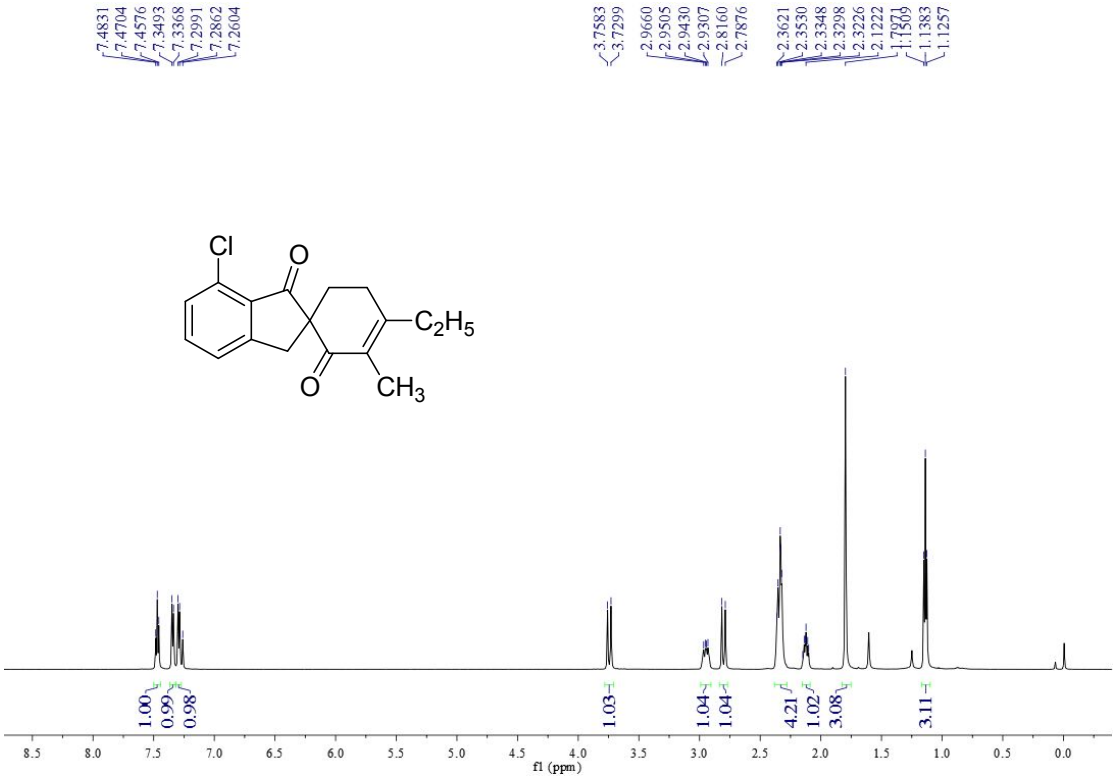
^{1}H NMR spectra of compound 3g



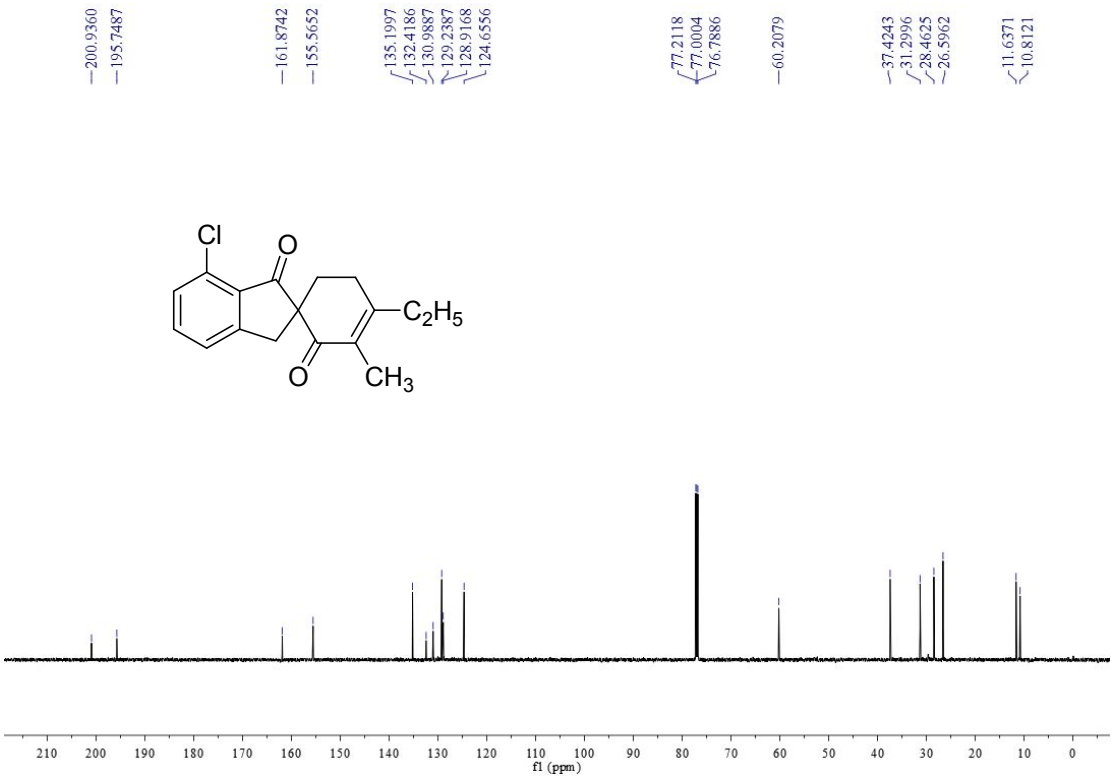
^{13}C NMR spectra of compound 3g



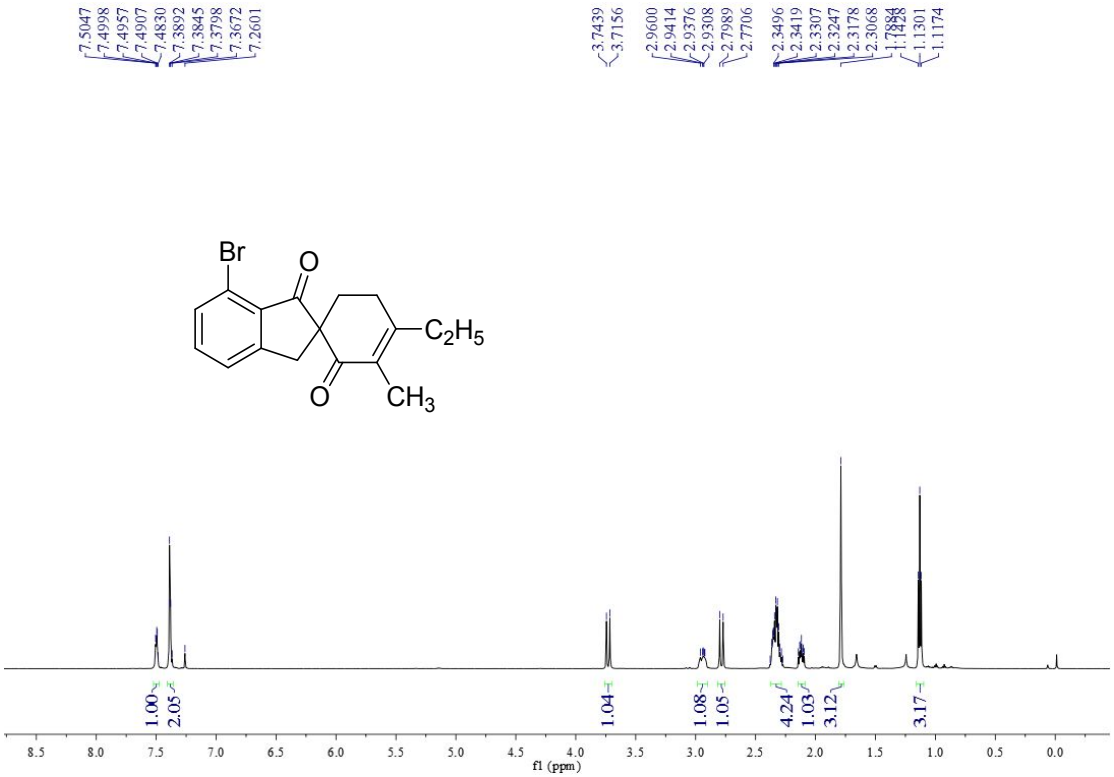
^{1}H NMR spectra of compound 3h



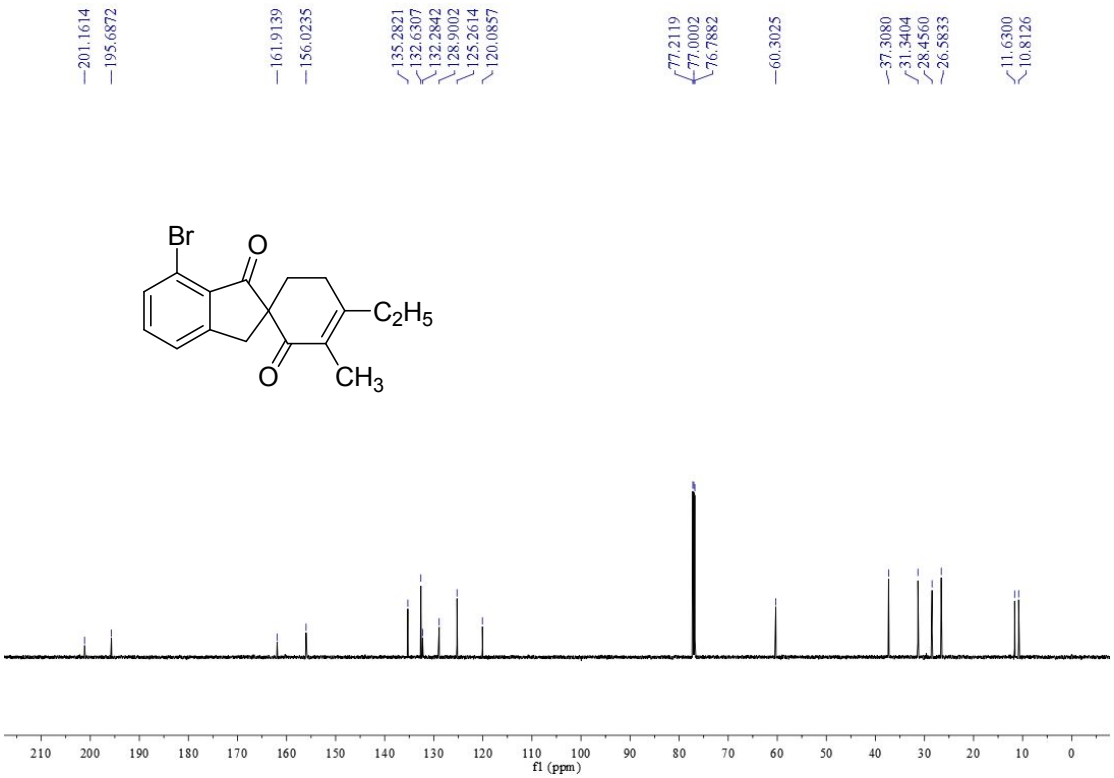
^{13}C NMR spectra of compound 3h



^{1}H NMR spectra of compound 3i



^{13}C NMR spectra of compound 3i



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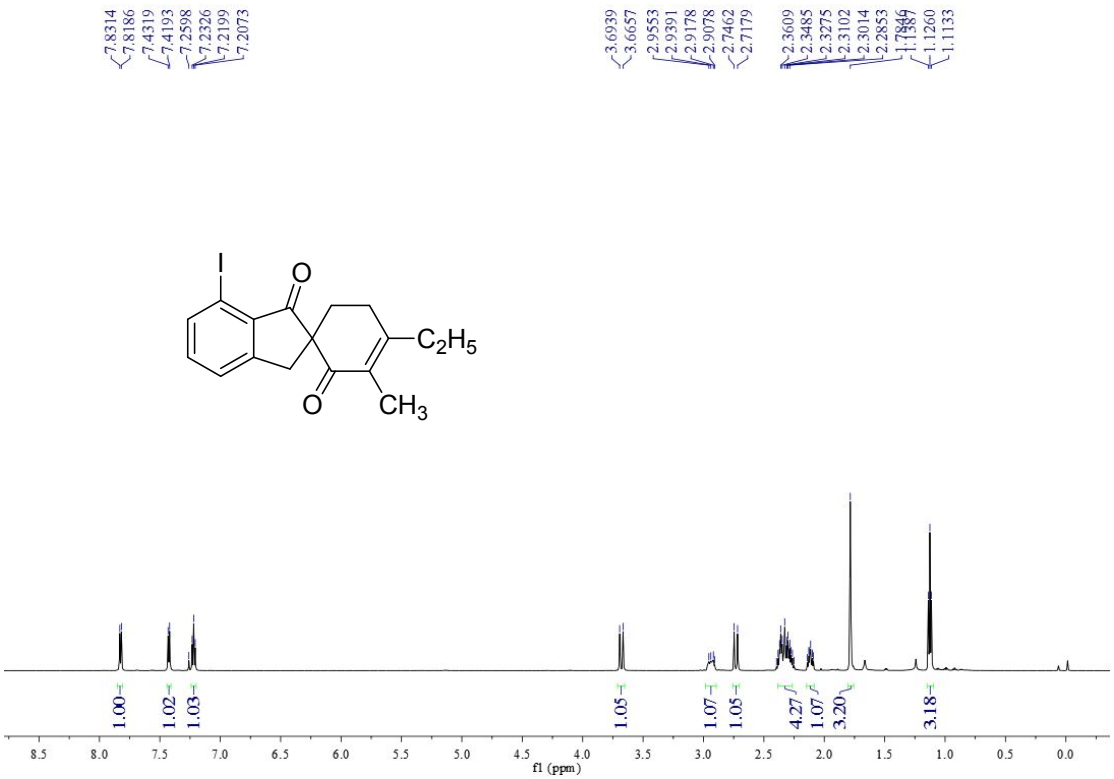
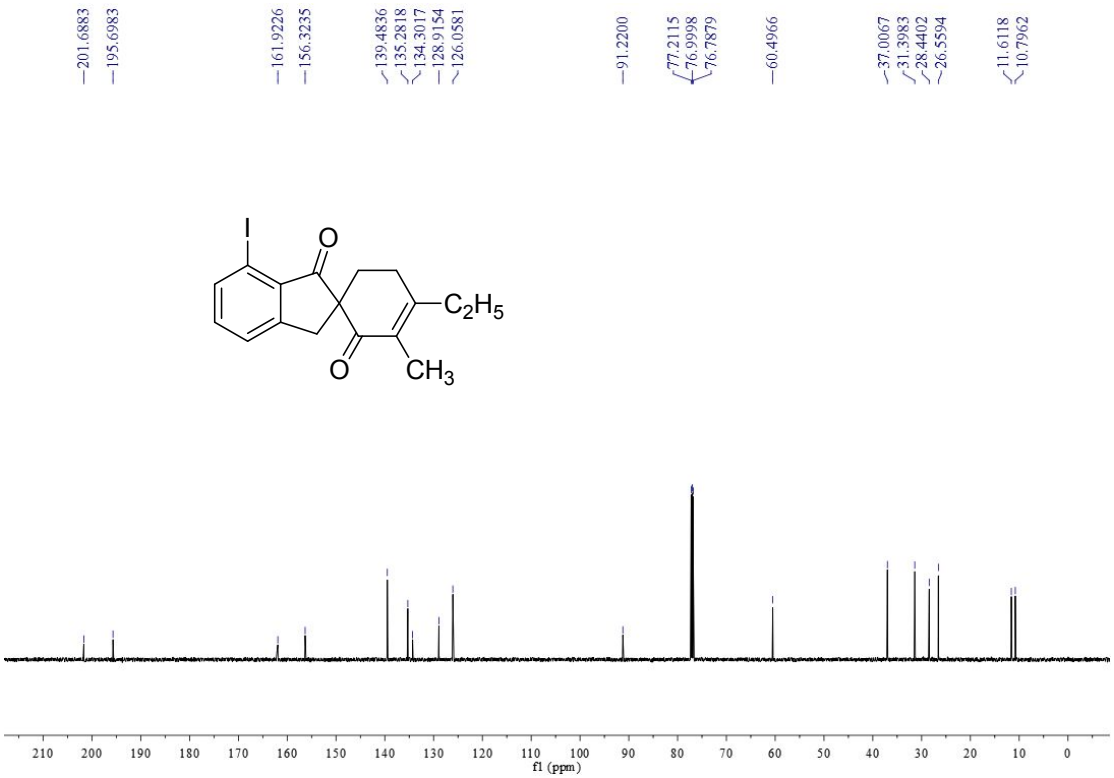
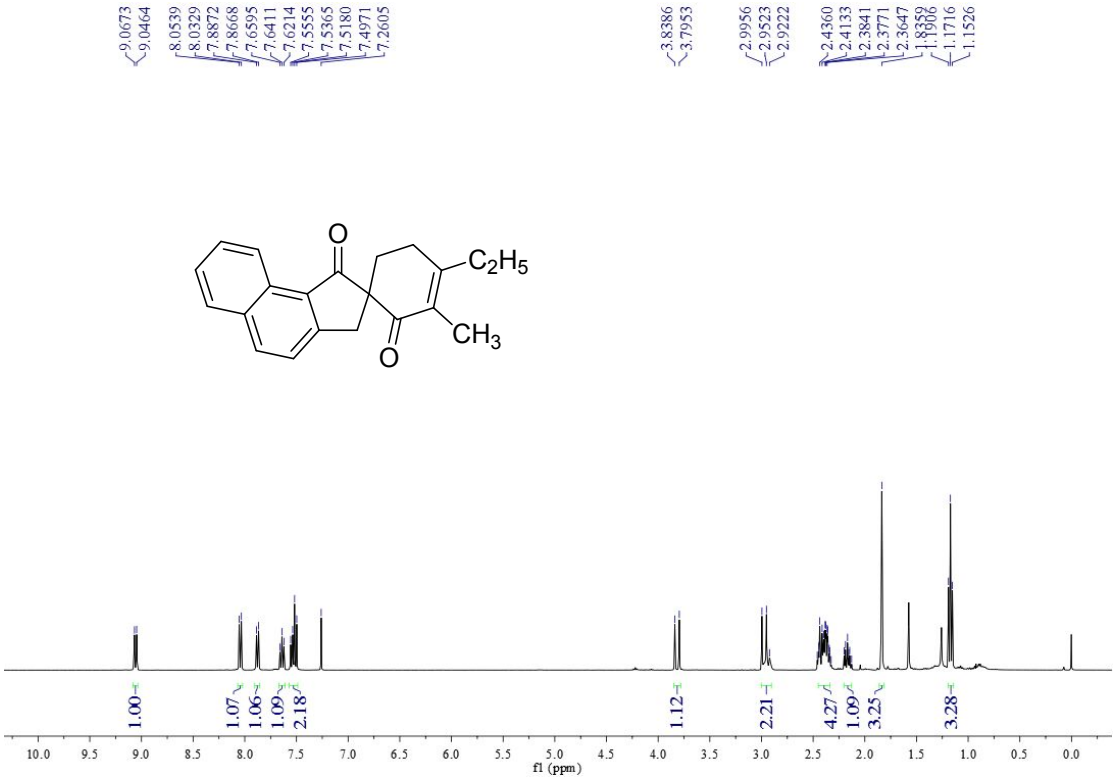


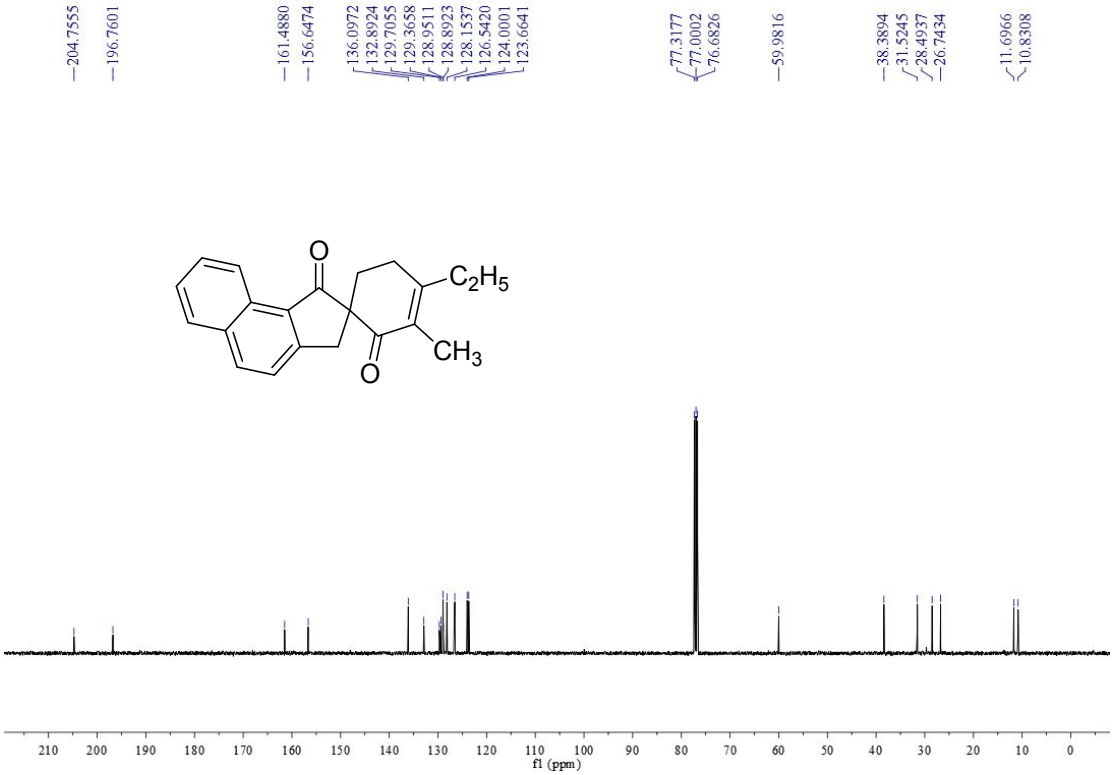
^{13}C NMR spectra of compound 3j



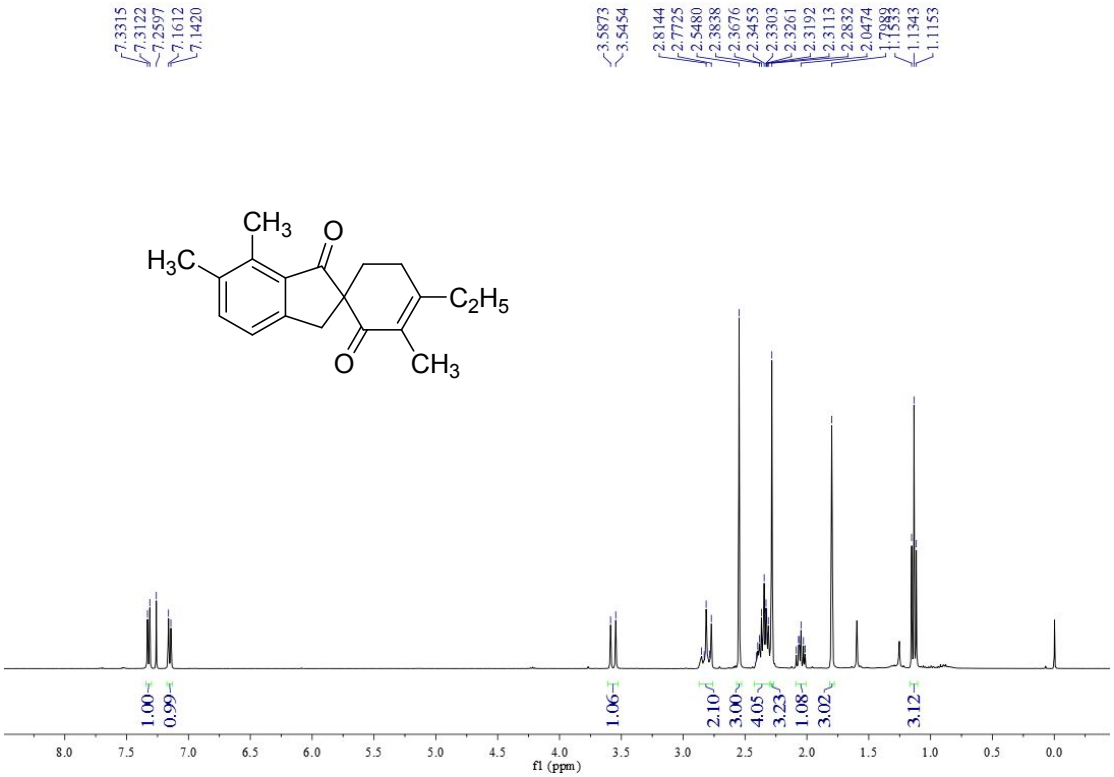
^{1}H NMR spectra of compound 3k



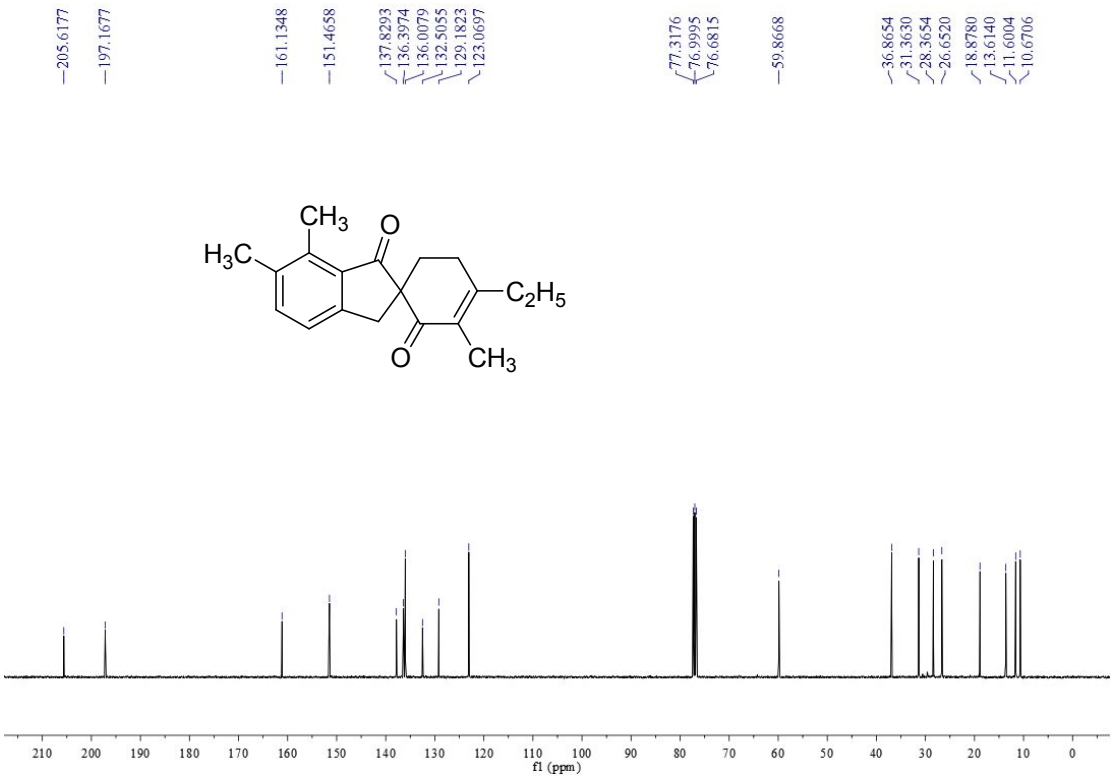
^{13}C NMR spectra of compound 3k



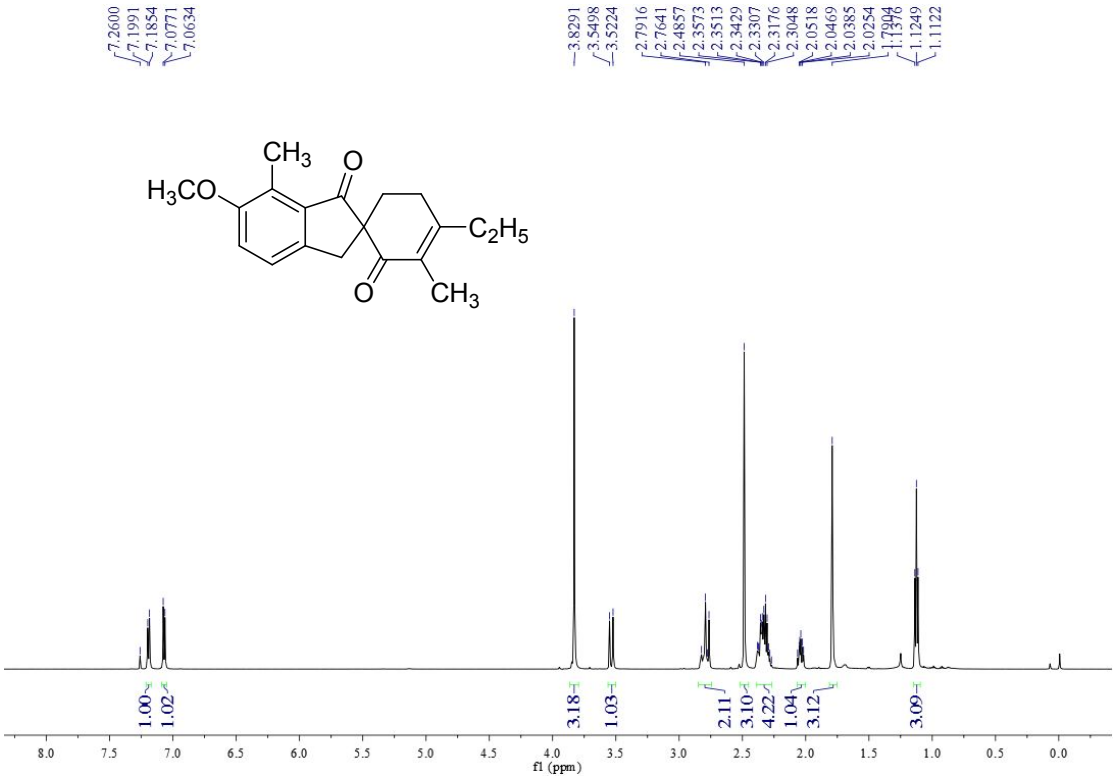
^{1}H NMR spectra of compound 3l



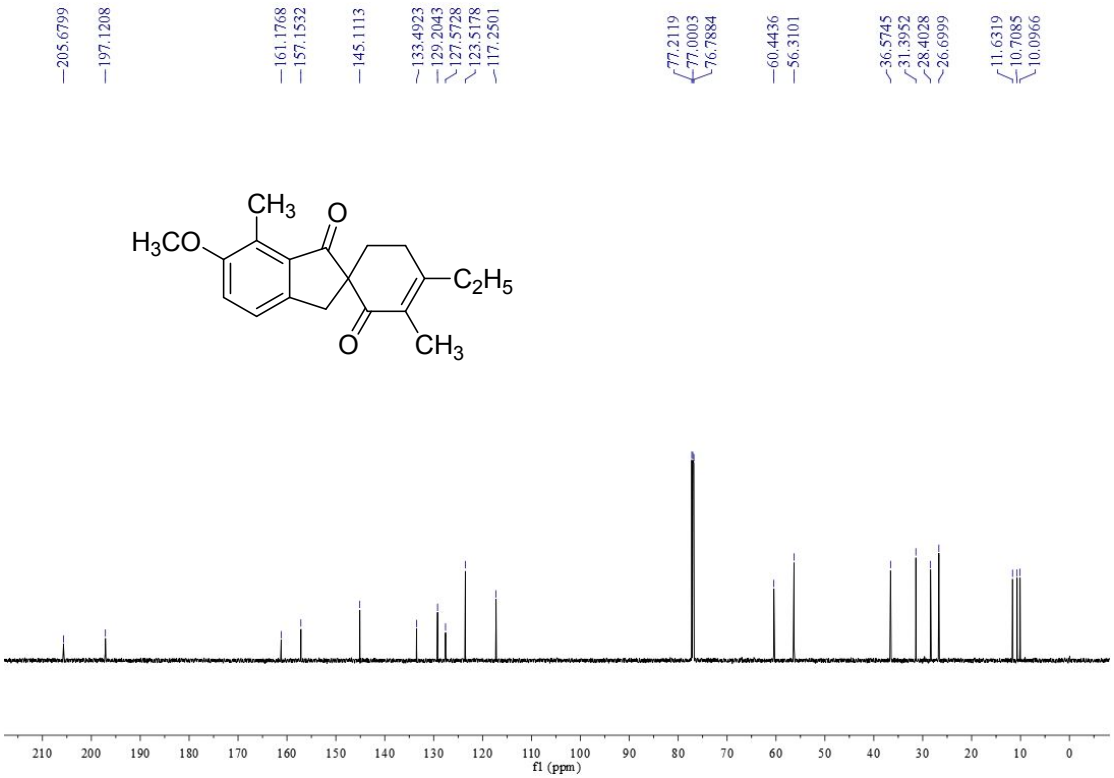
^{13}C NMR spectra of compound 3l



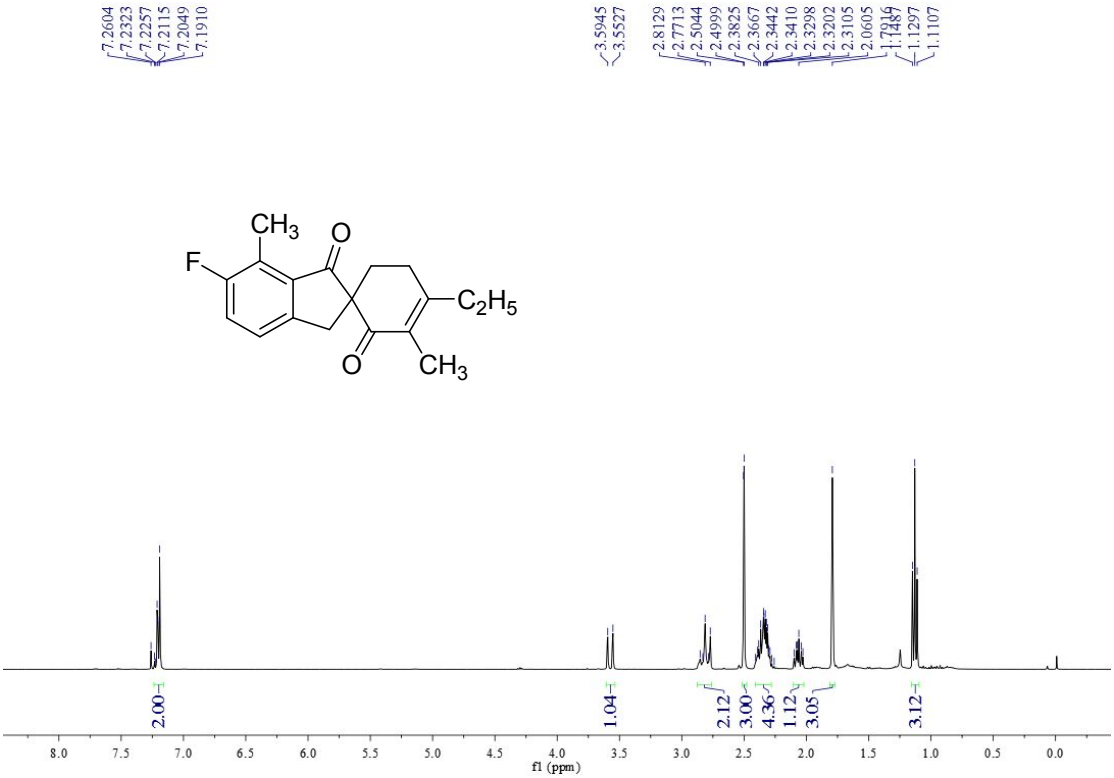
^{1}H NMR spectra of compound 3m



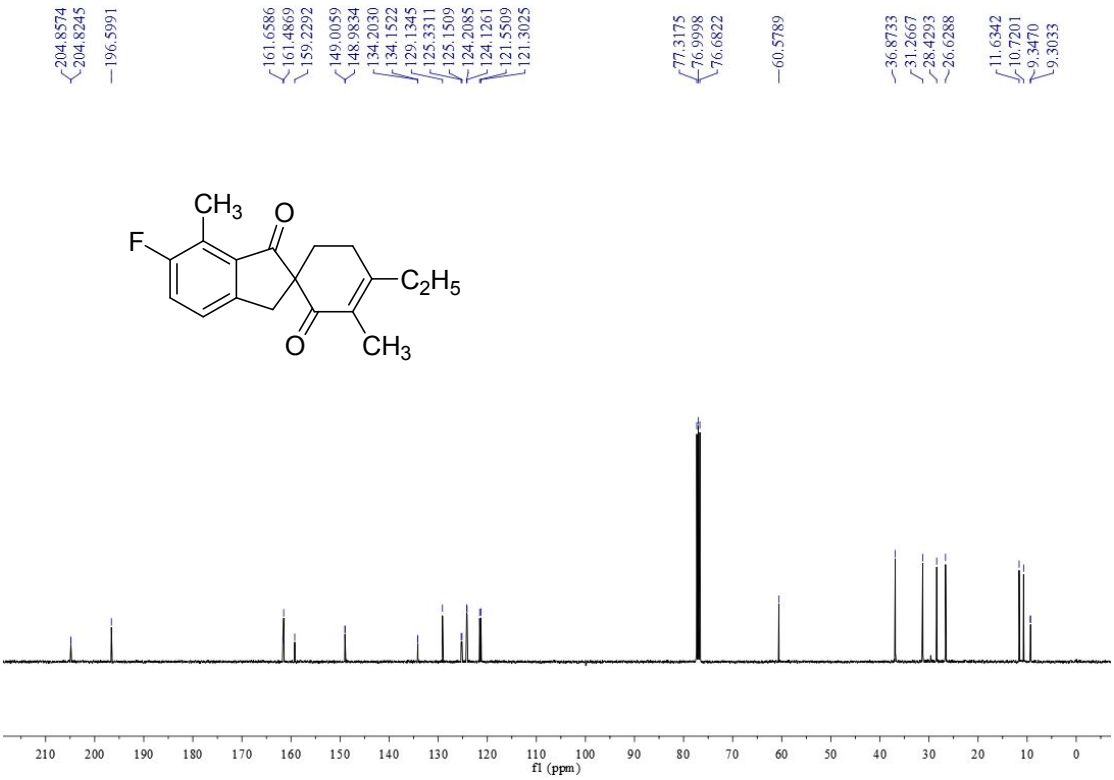
^{13}C NMR spectra of compound 3m



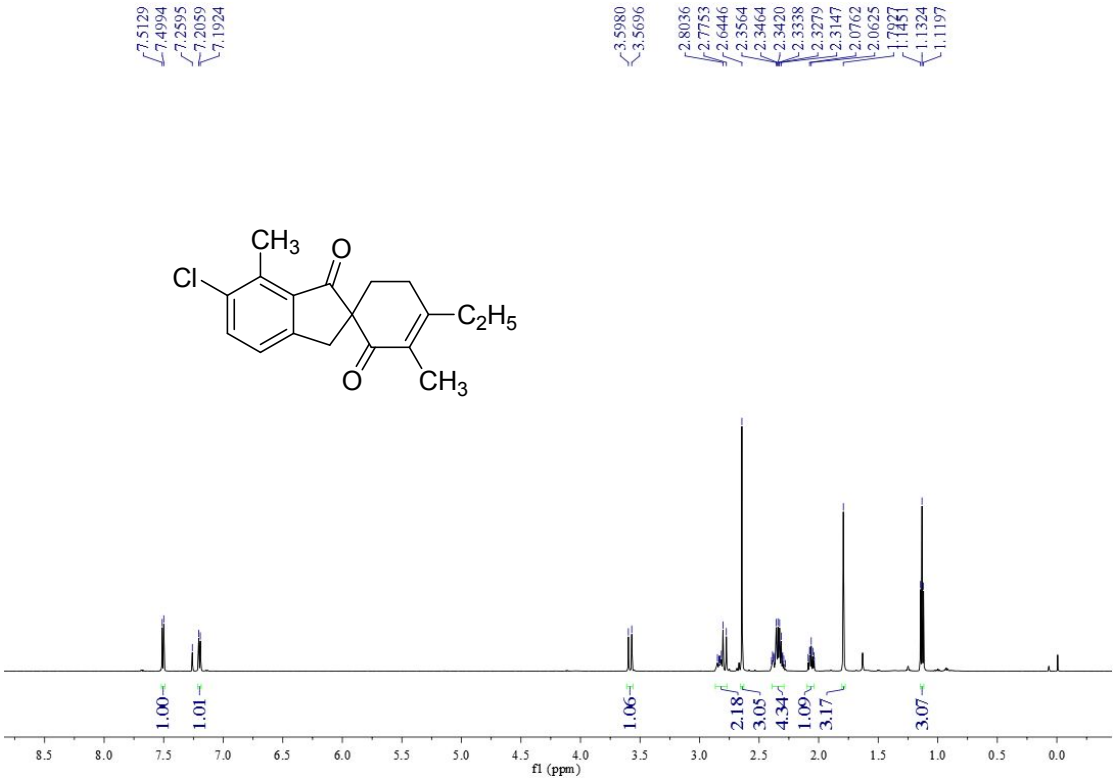
^{1}H NMR spectra of compound 3n



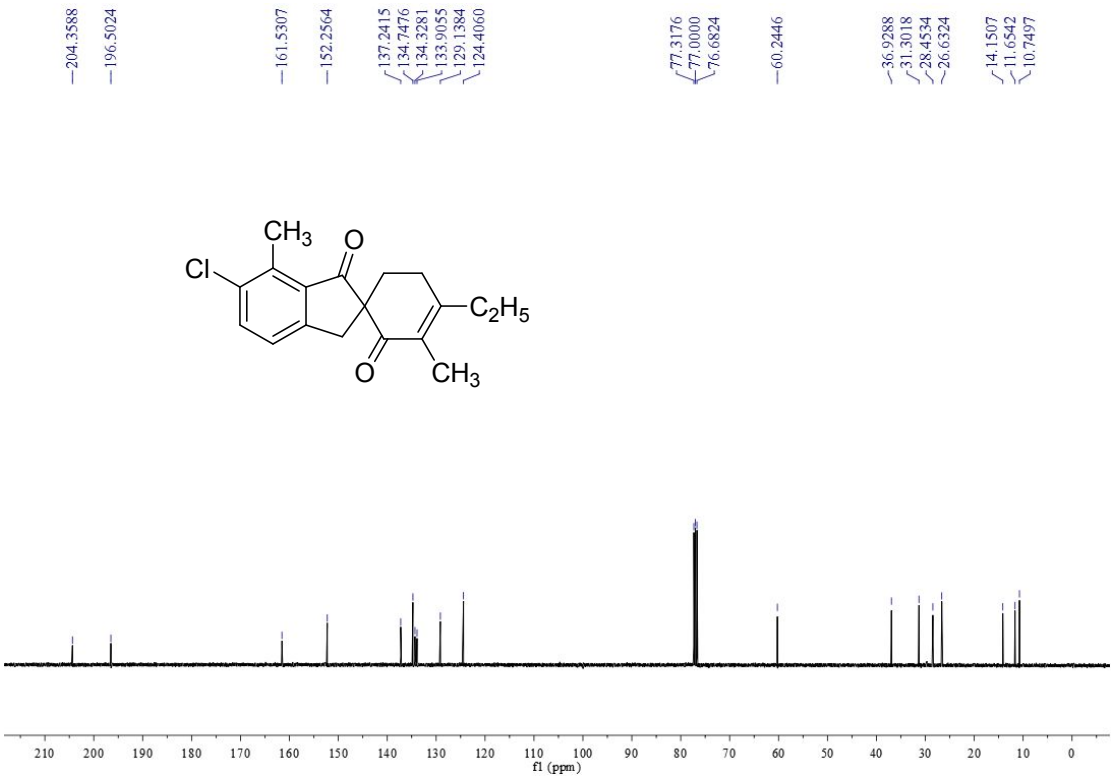
^{13}C NMR spectra of compound 3n



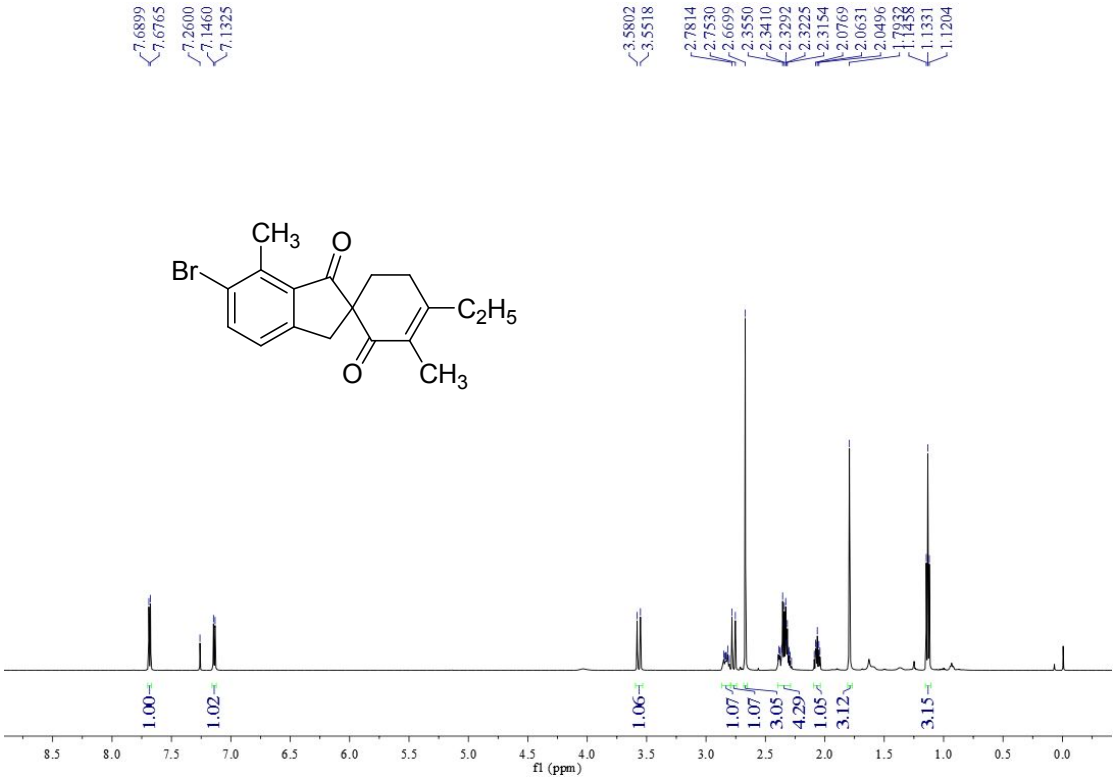
^{1}H NMR spectra of compound 3o



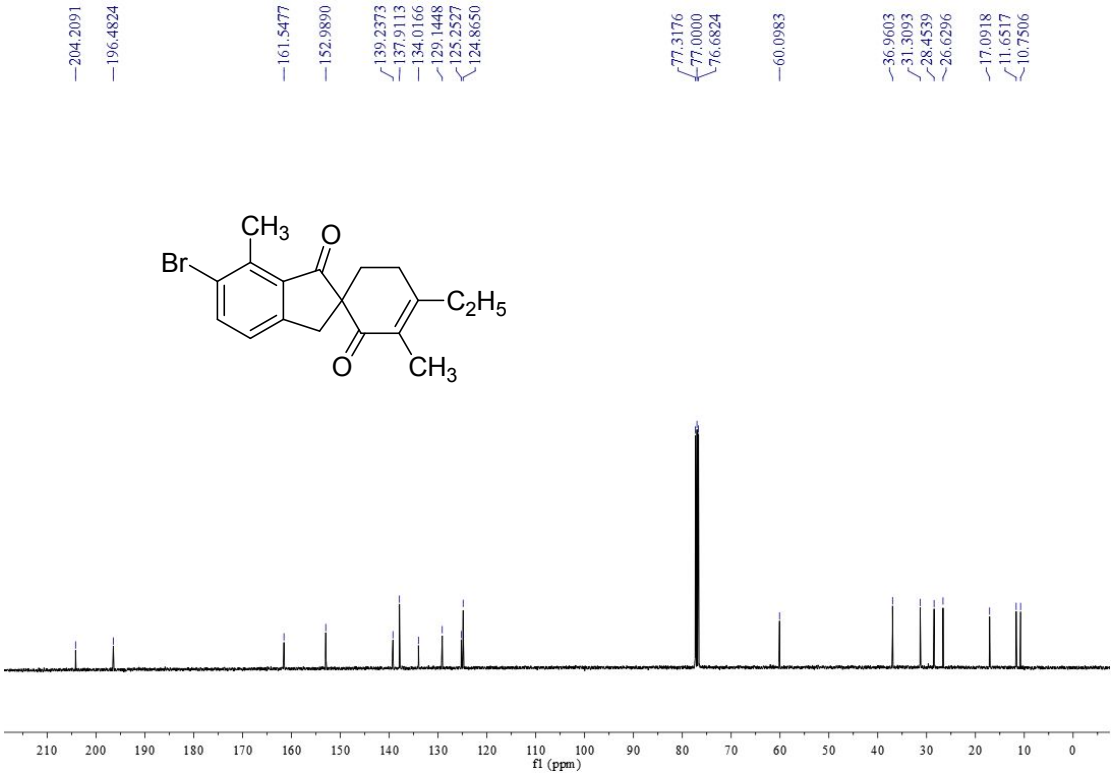
^{13}C NMR spectra of compound 3o



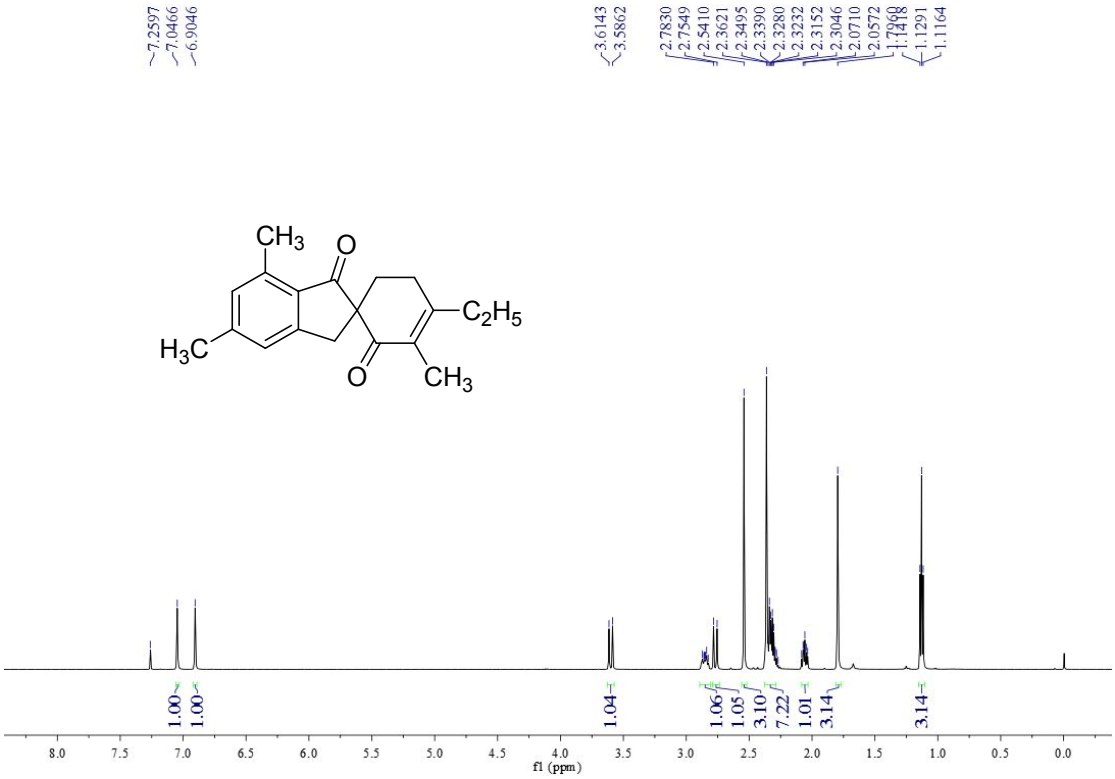
^{1}H NMR spectra of compound 3p



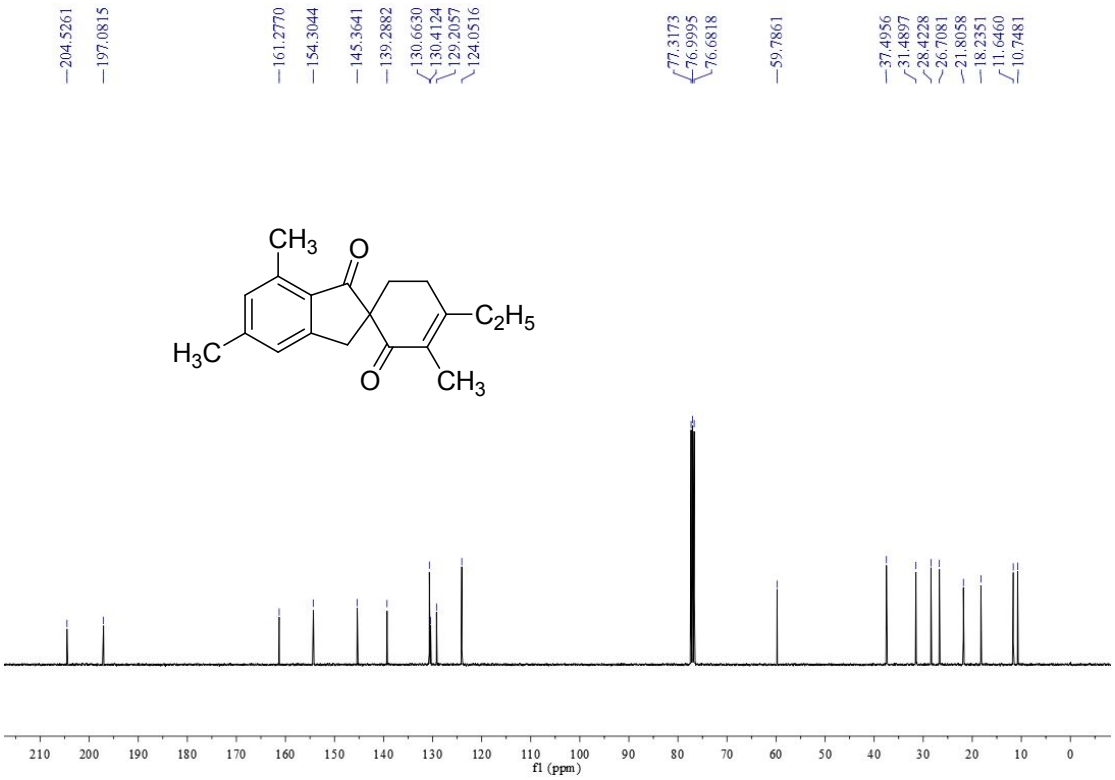
^{13}C NMR spectra of compound 3p



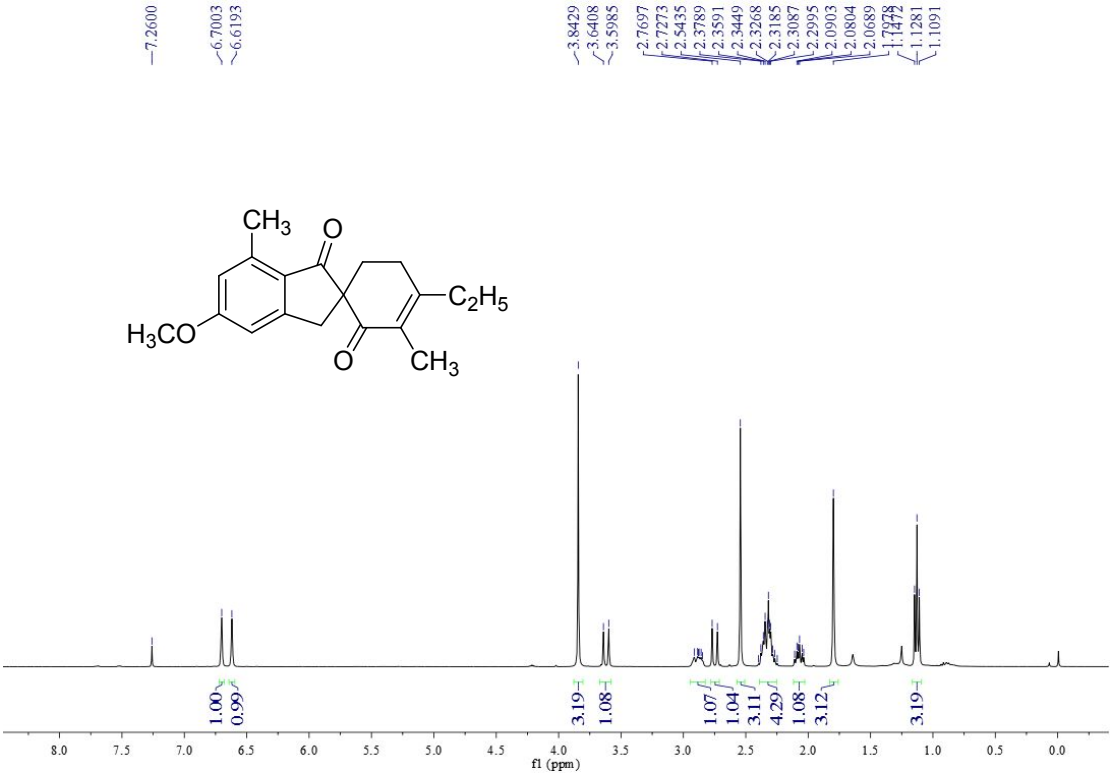
^{1}H NMR spectra of compound 3q



^{13}C NMR spectra of compound 3q



^{1}H NMR spectra of compound 3r



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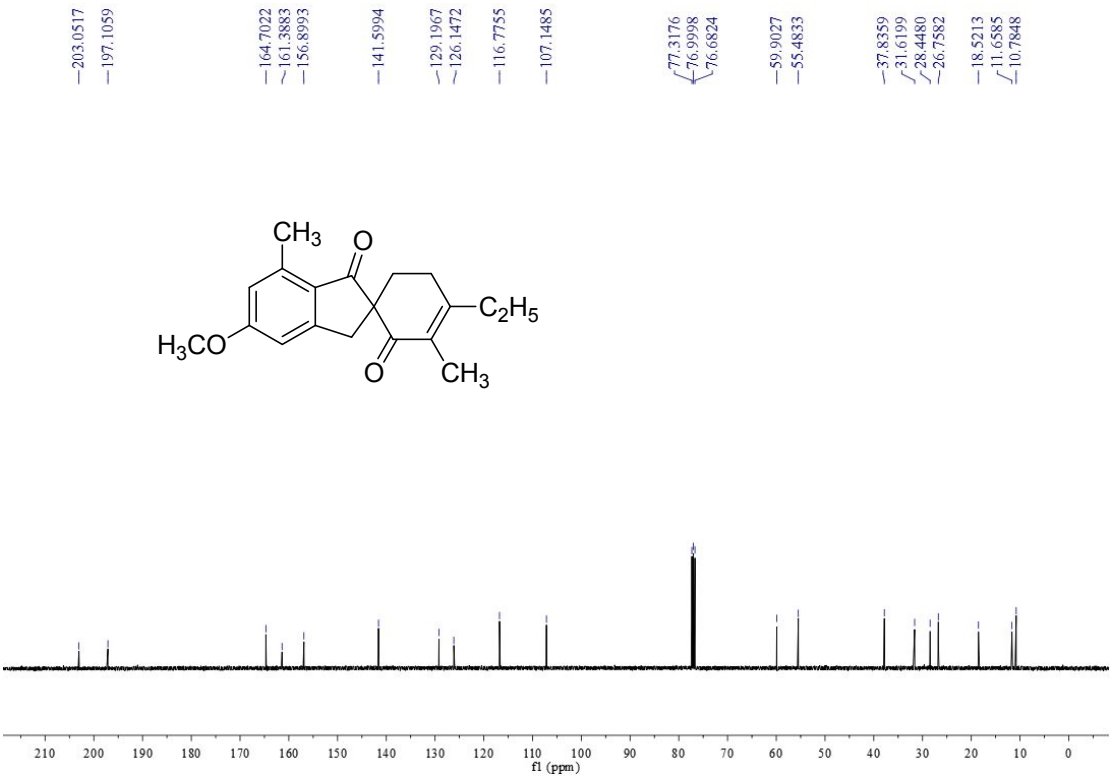
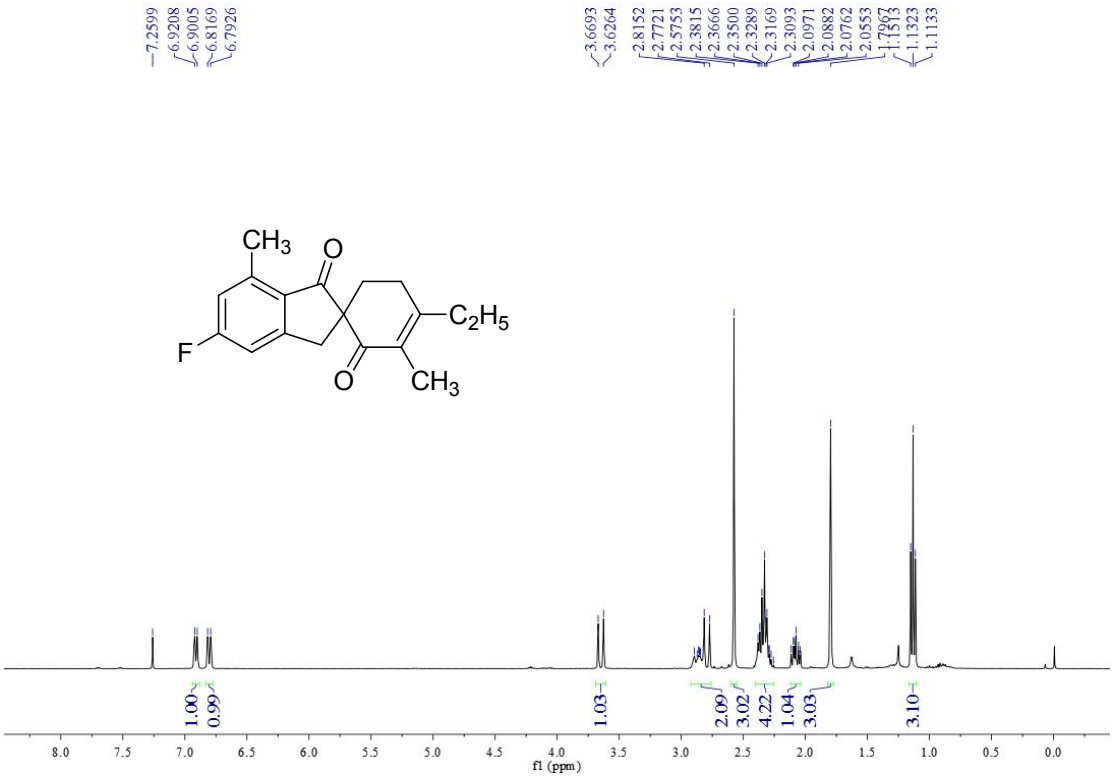
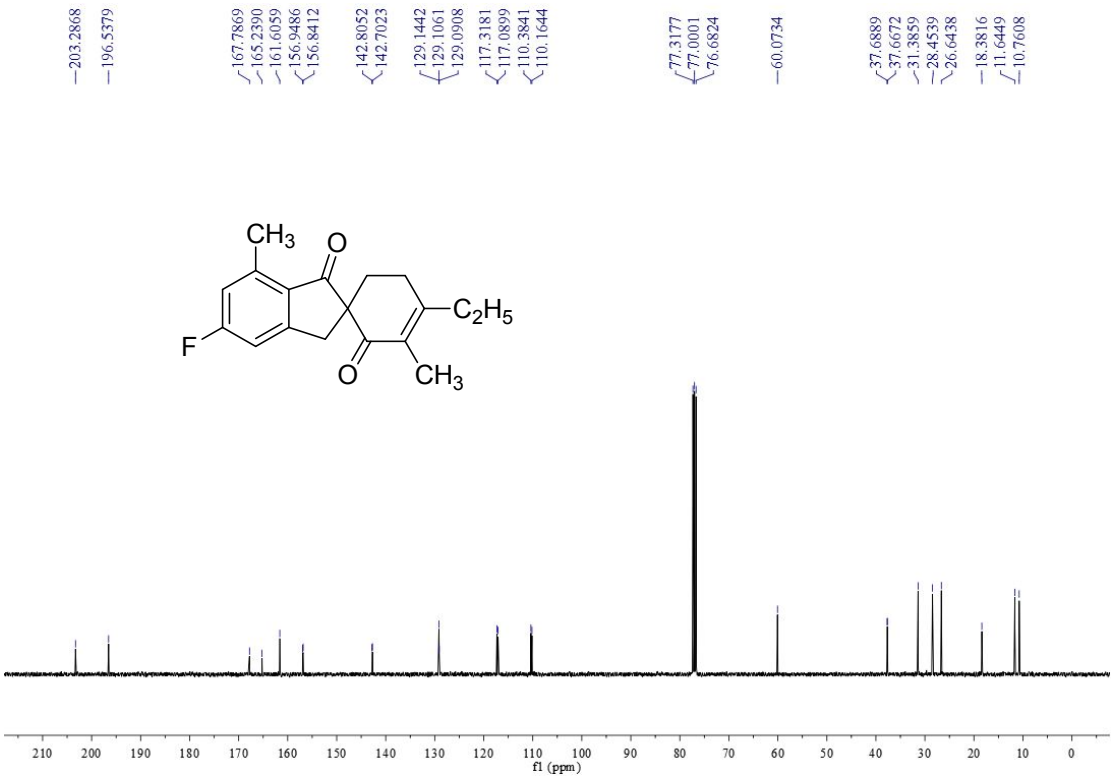


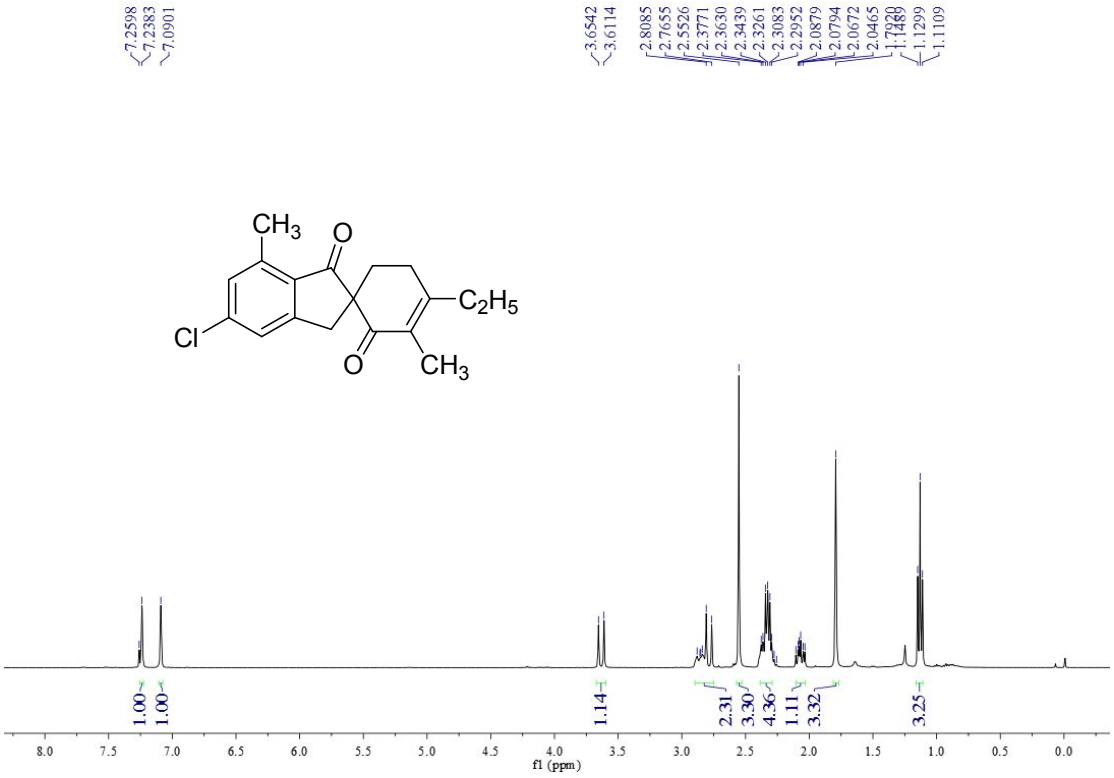
^{1}H NMR spectra of compound 3s



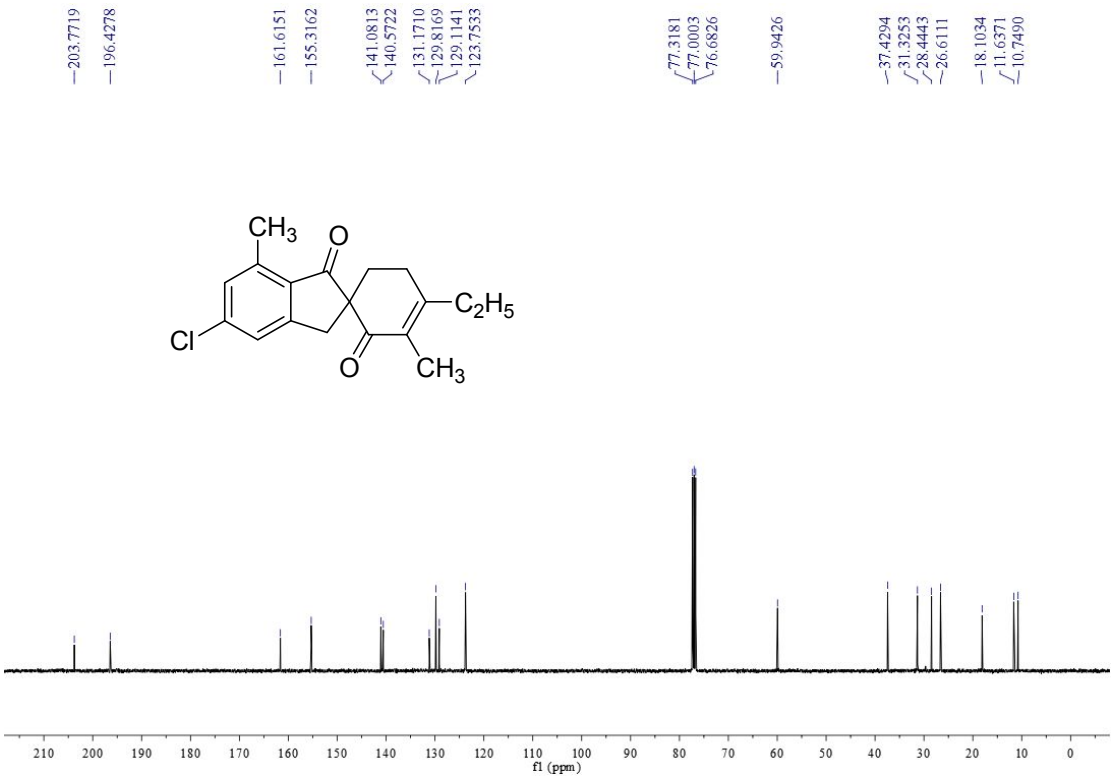
^{13}C NMR spectra of compound 3s



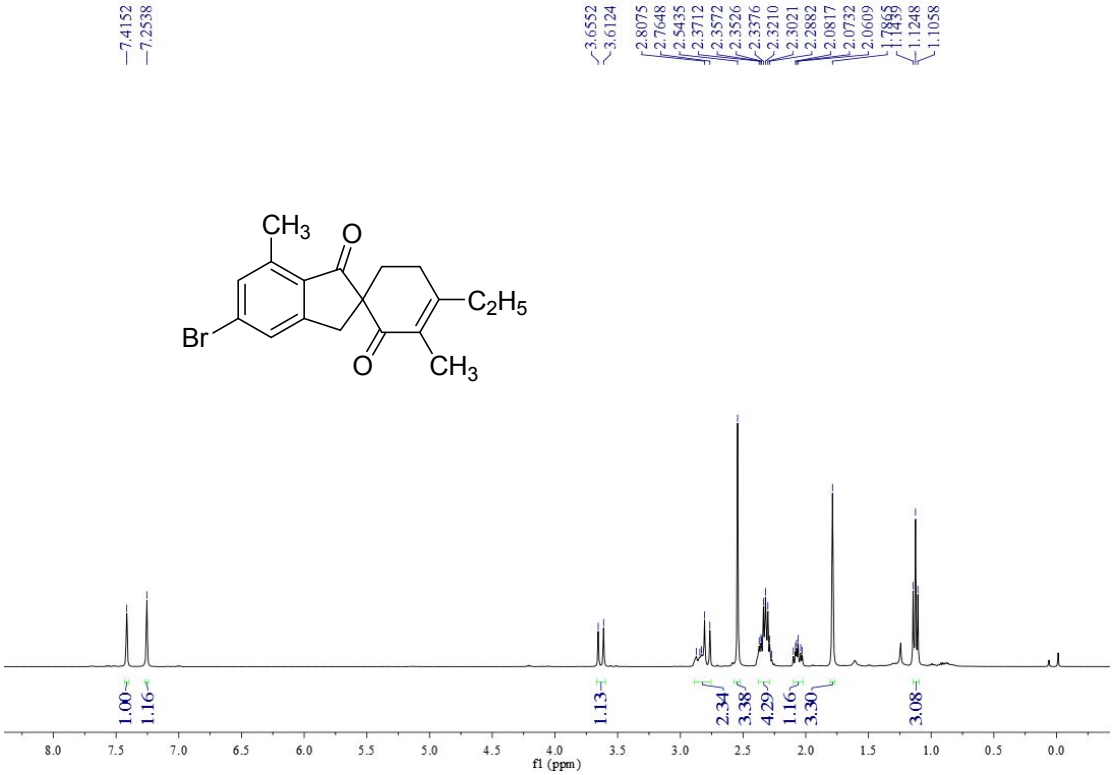
^{1}H NMR spectra of compound 3t



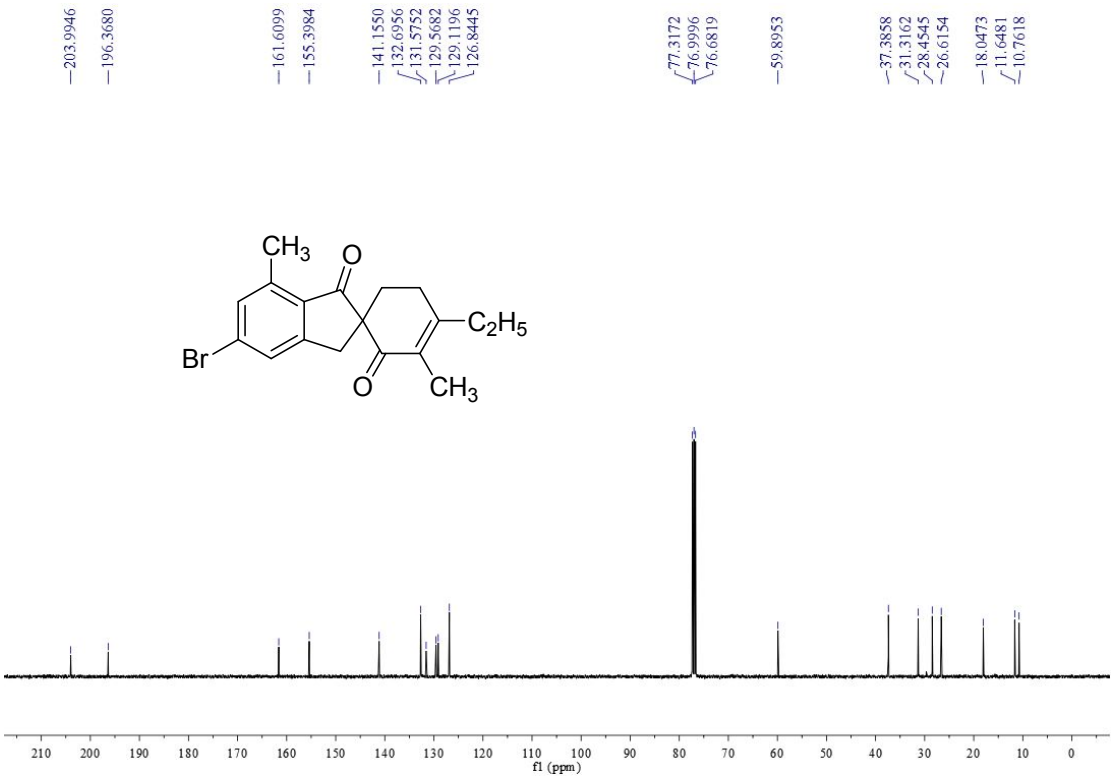
^{13}C NMR spectra of compound 3t



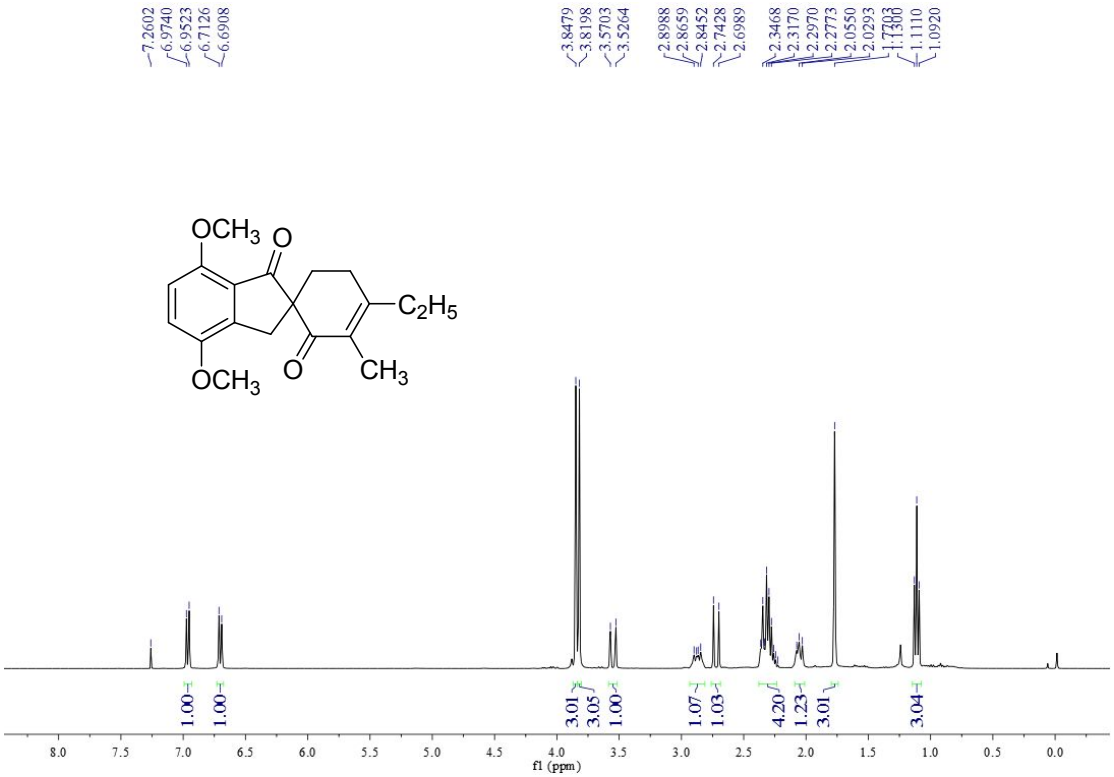
^{1}H NMR spectra of compound 3u



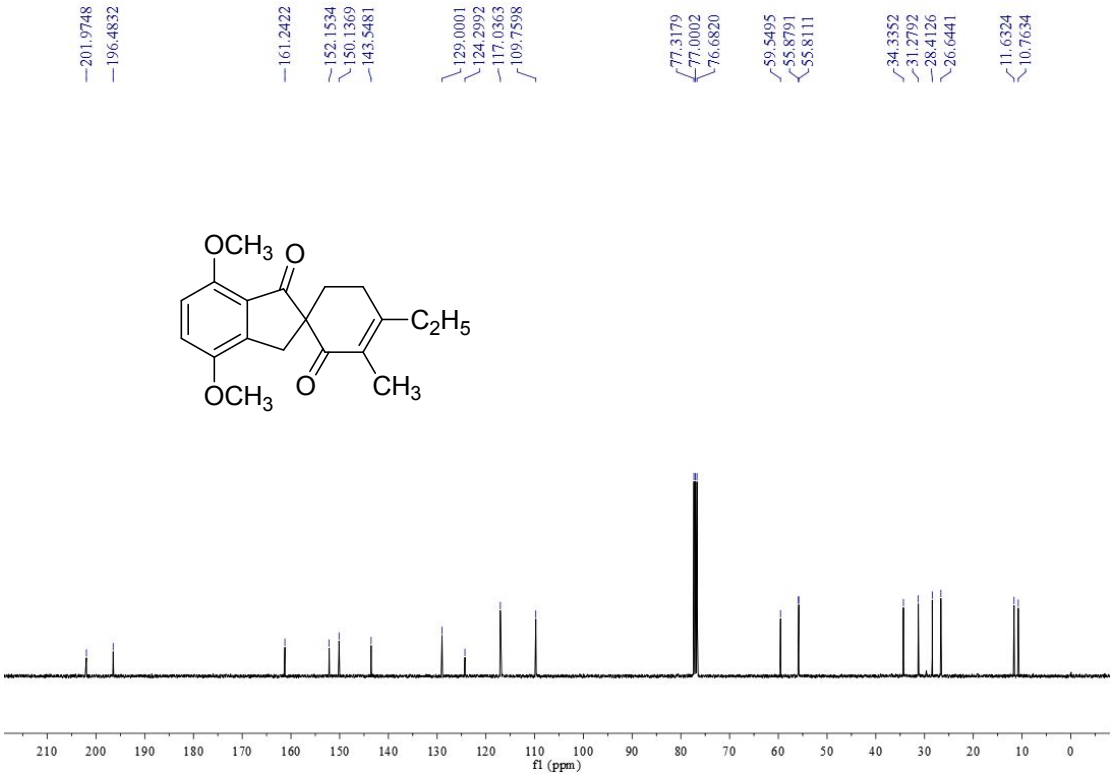
^{13}C NMR spectra of compound 3u



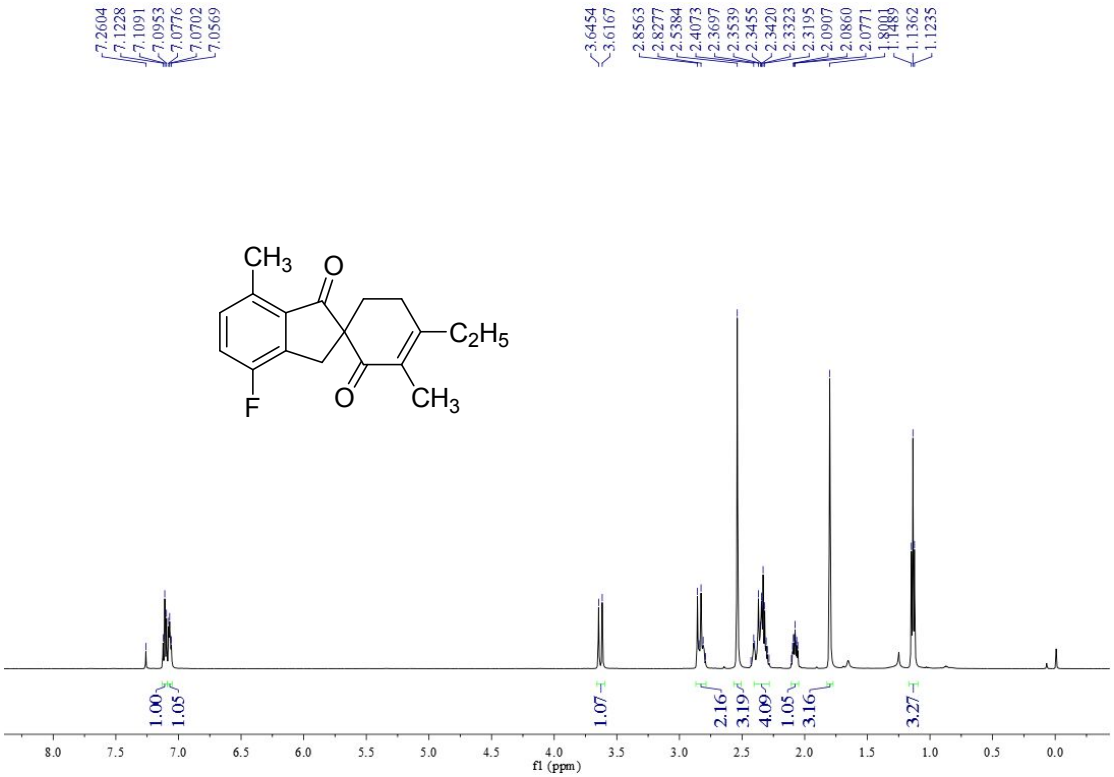
^{1}H NMR spectra of compound 3v



^{13}C NMR spectra of compound 3v



^{1}H NMR spectra of compound 3w



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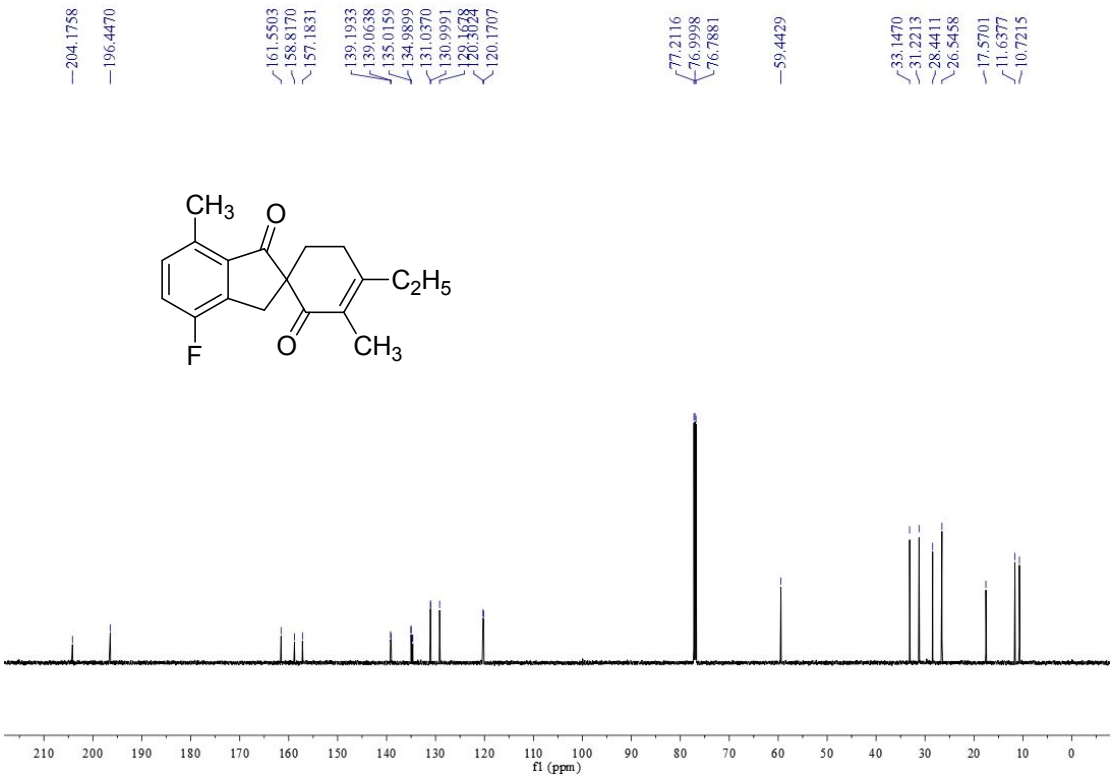
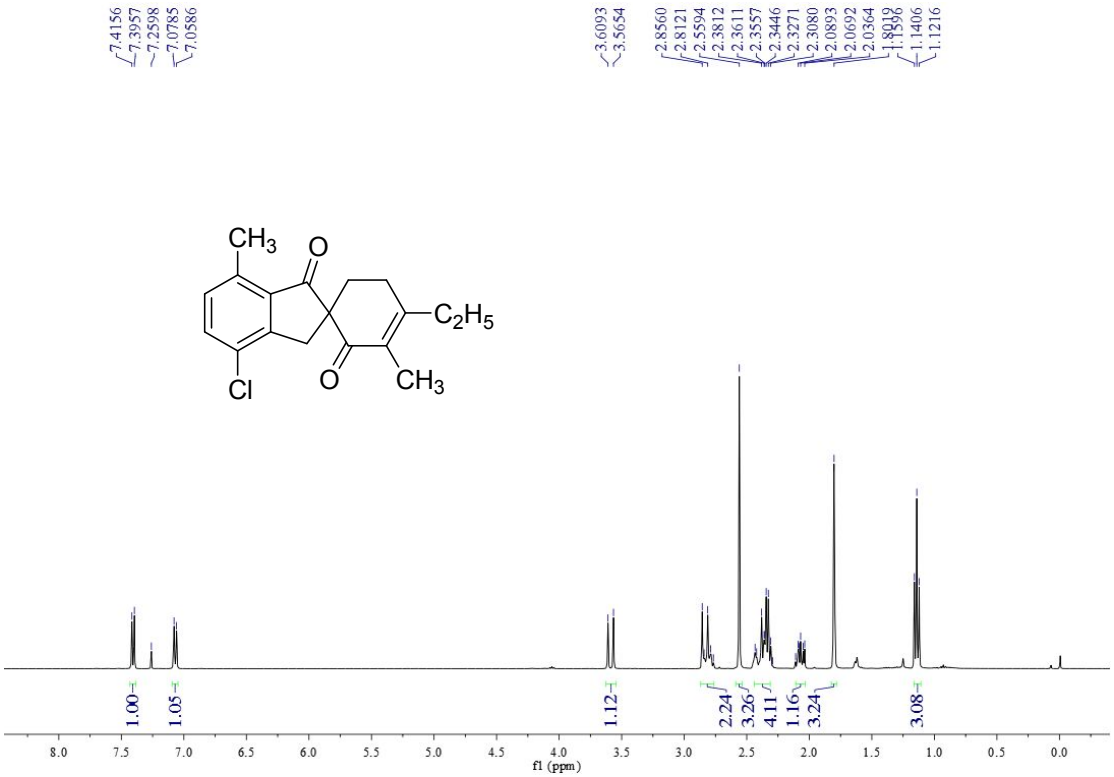
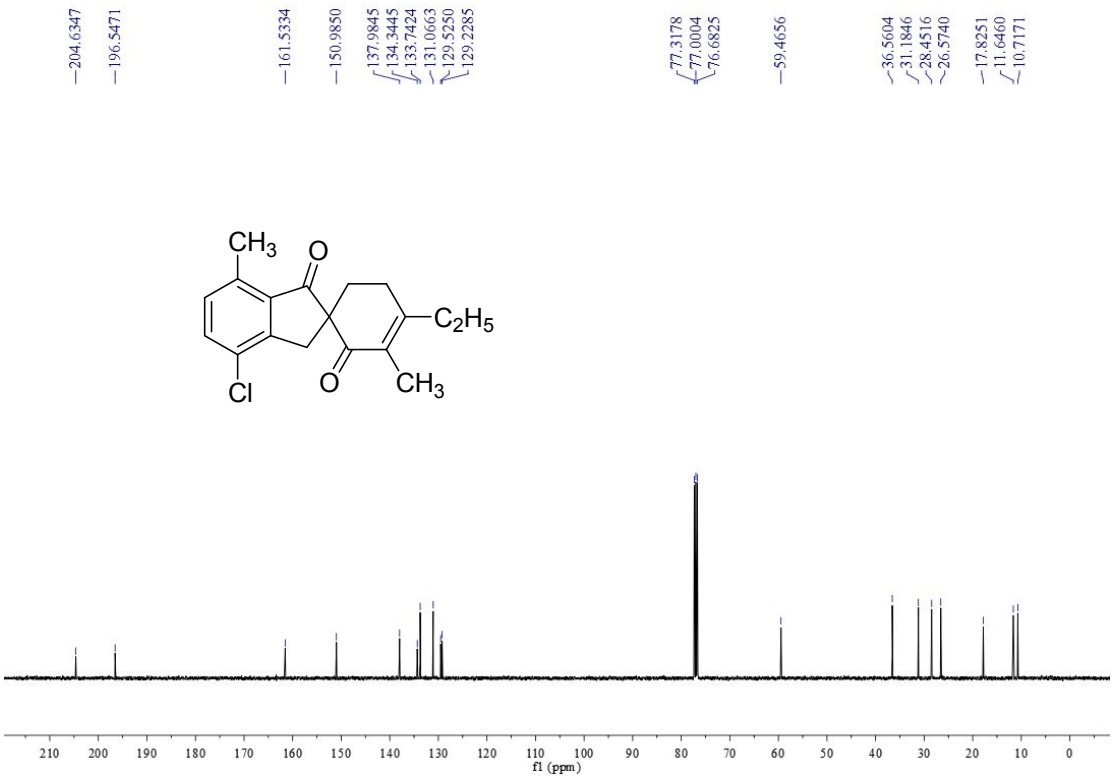


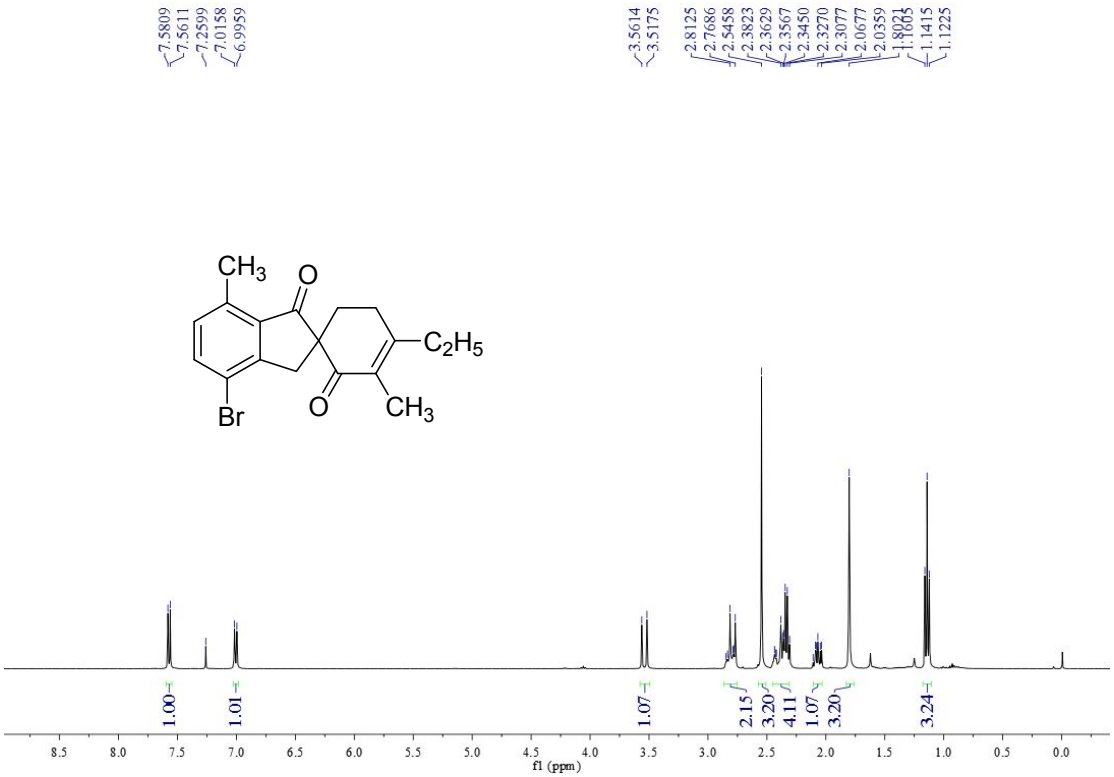
^{1}H NMR spectra of compound 3x



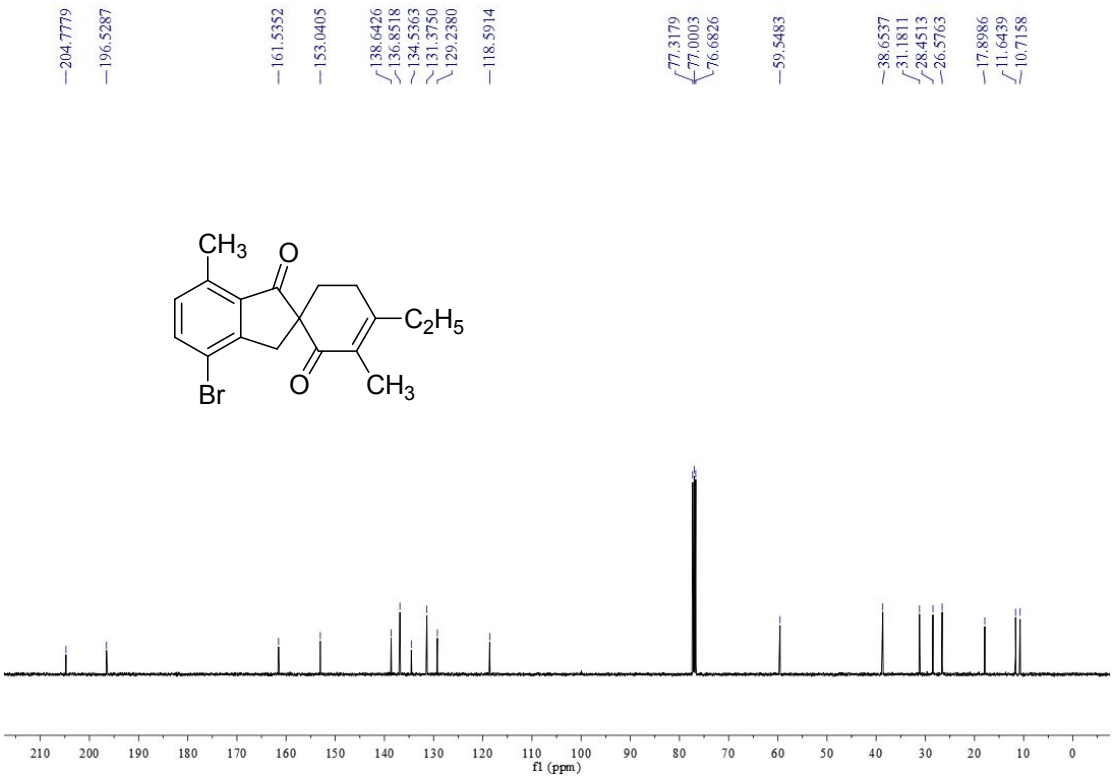
^{13}C NMR spectra of compound 3x



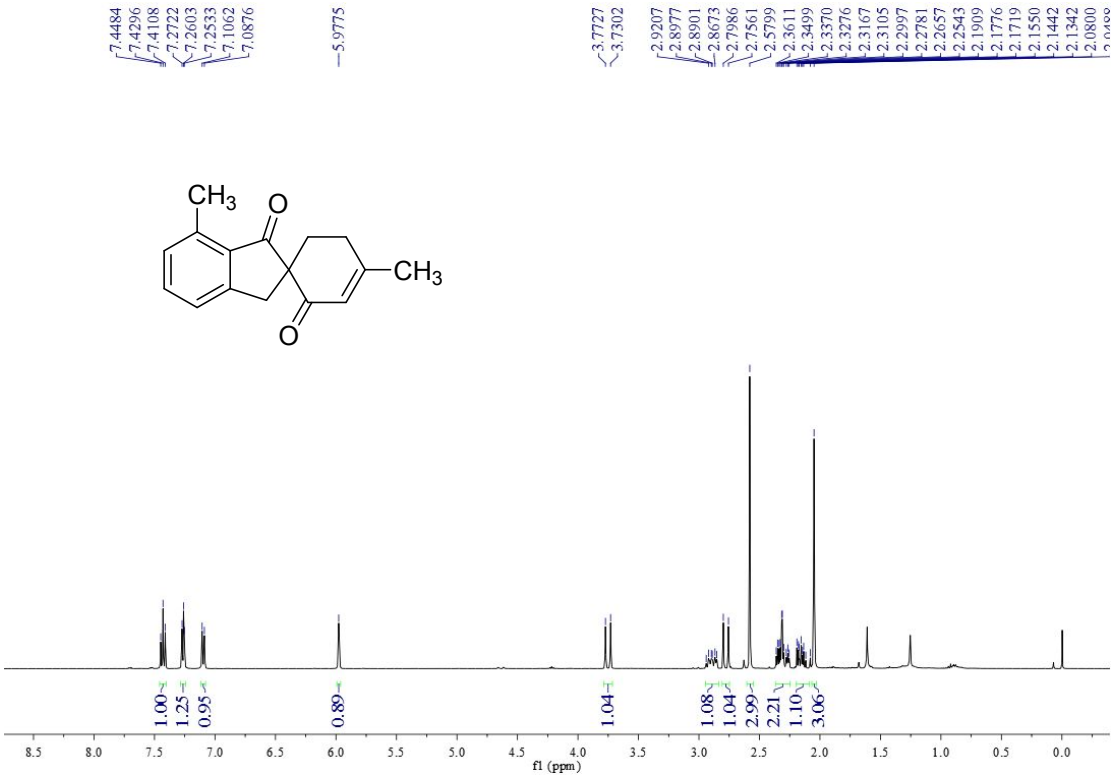
^{1}H NMR spectra of compound 3y



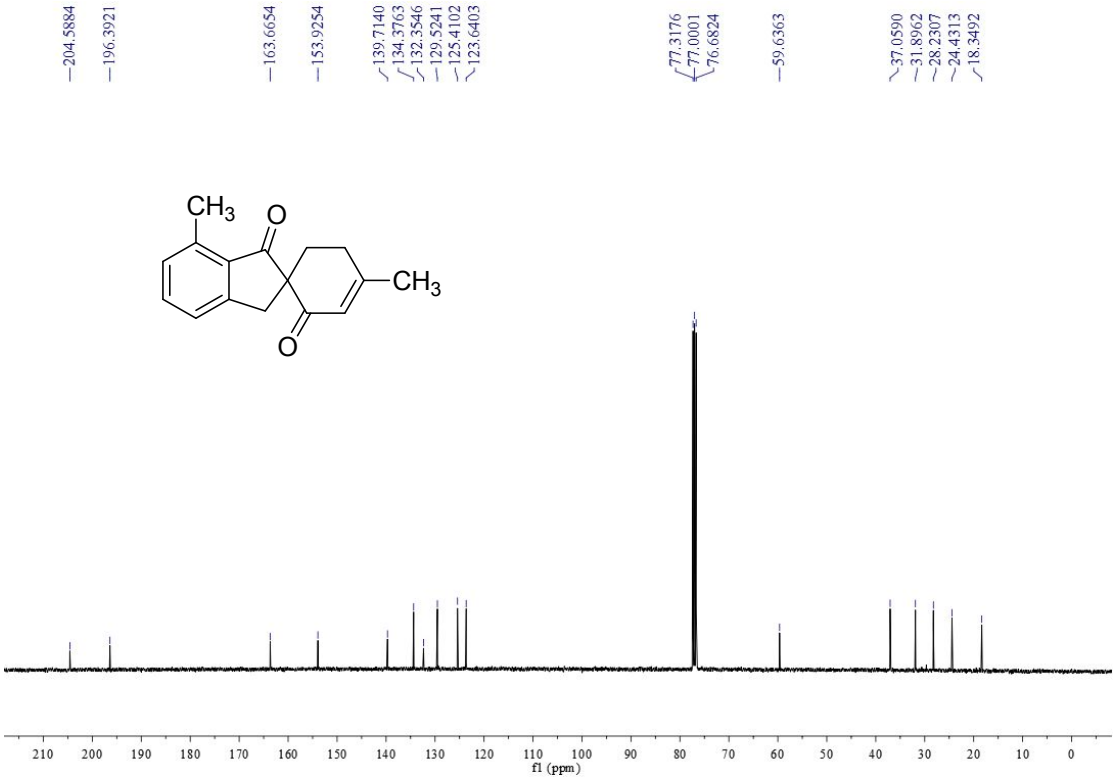
^{13}C NMR spectra of compound 3y



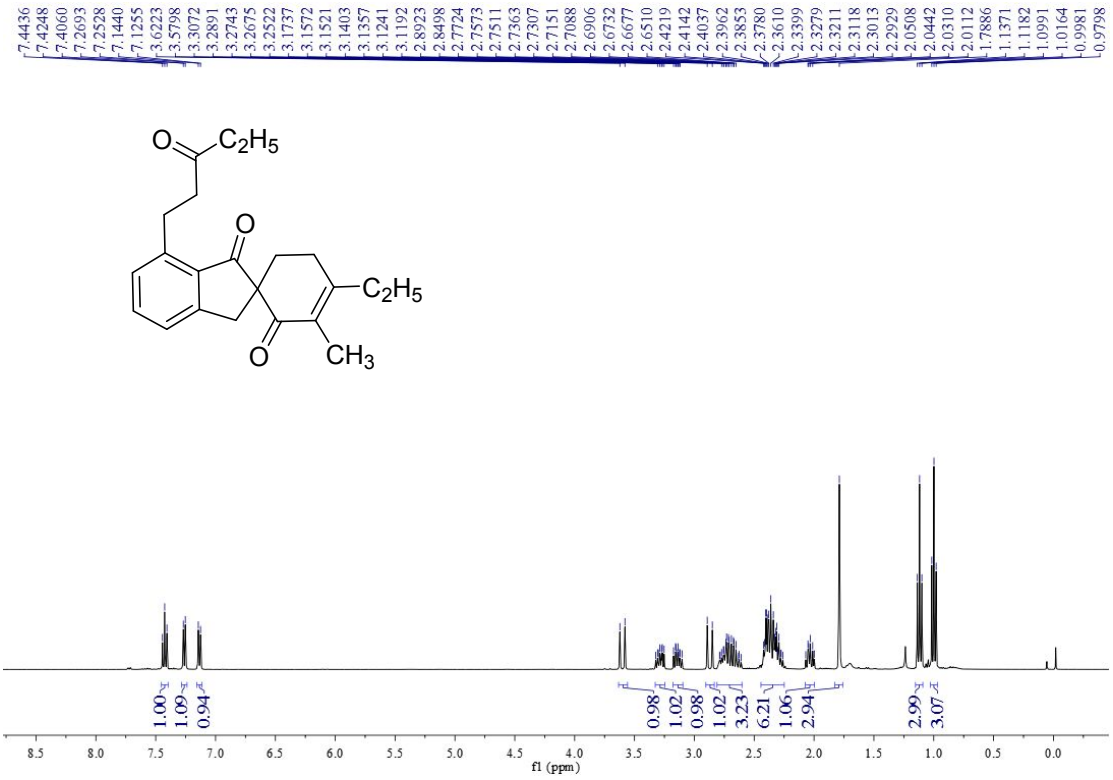
^{1}H NMR spectra of compound 3z



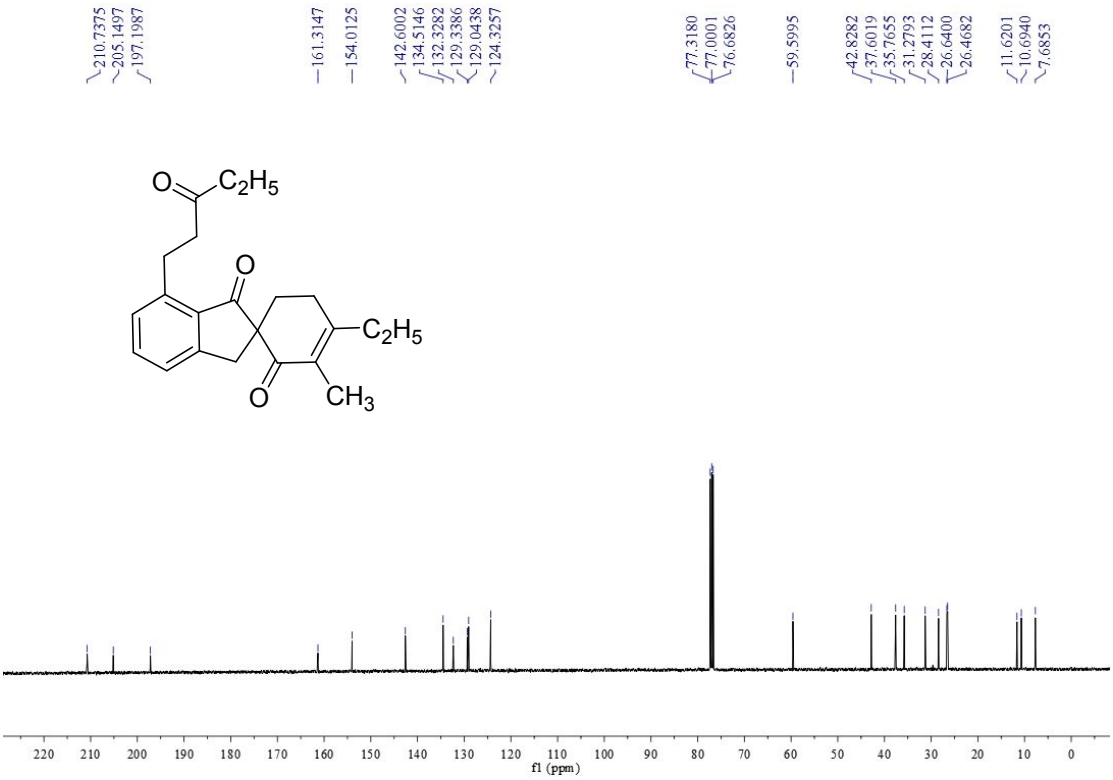
^{13}C NMR spectra of compound 3z



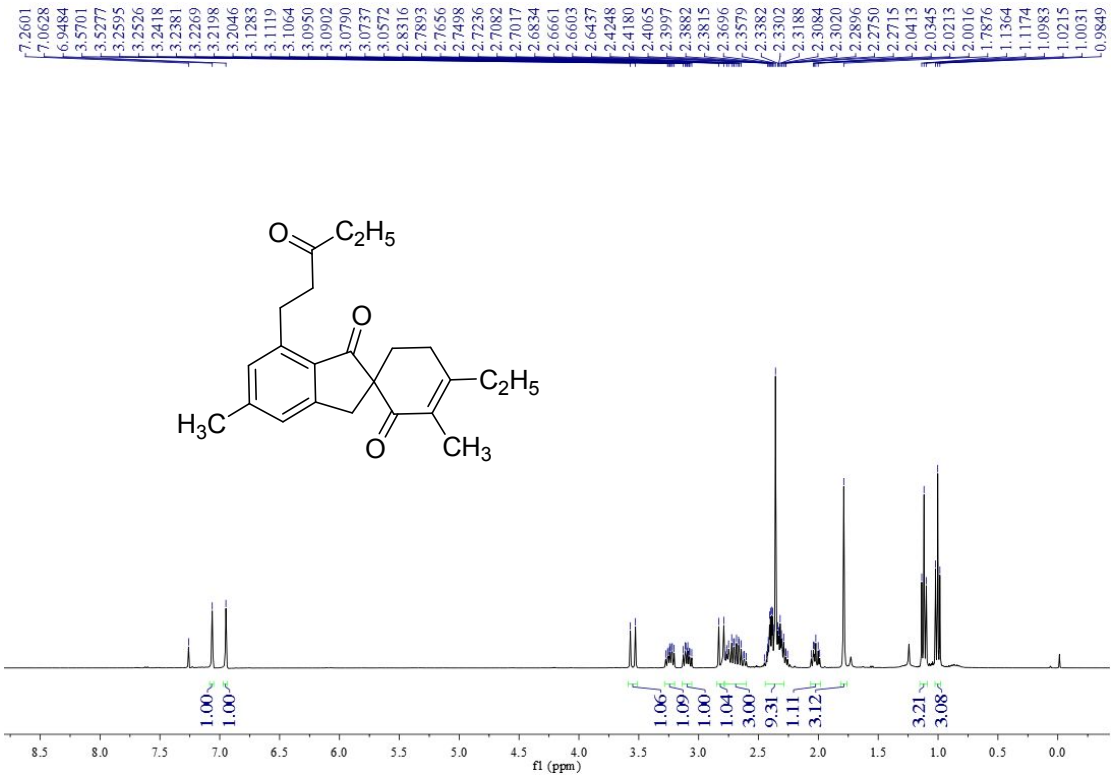
^{1}H NMR spectra of compound 3aa



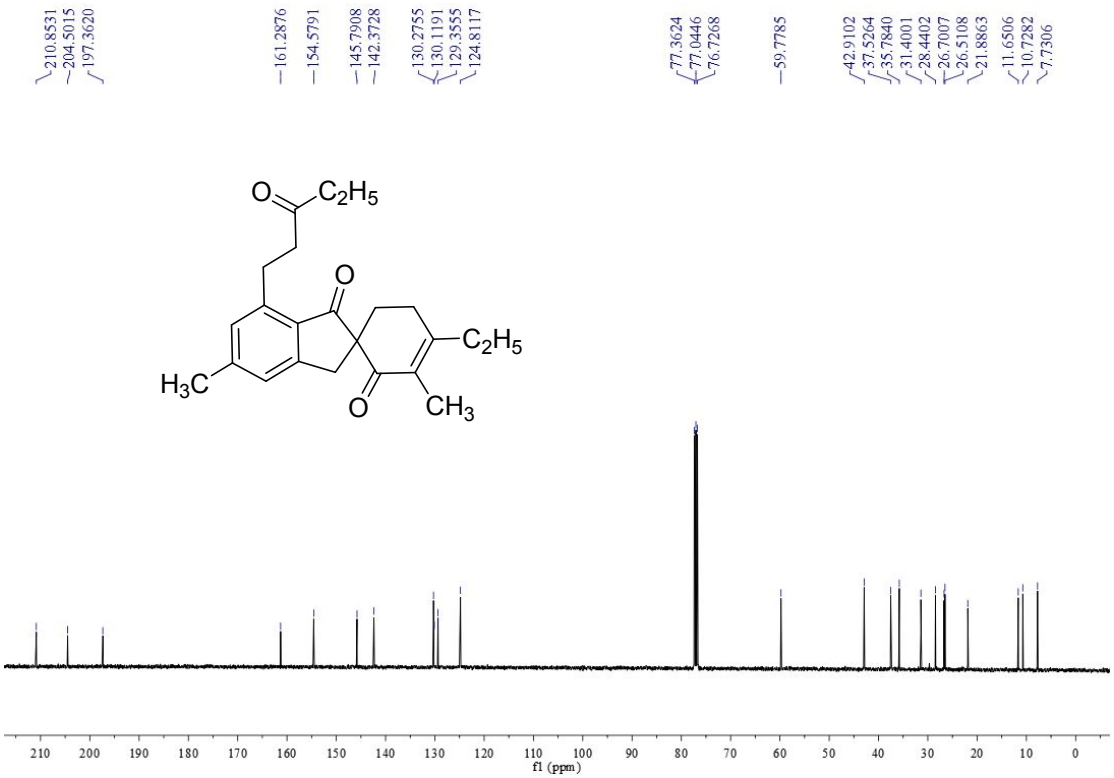
^{13}C NMR spectra of compound 3aa



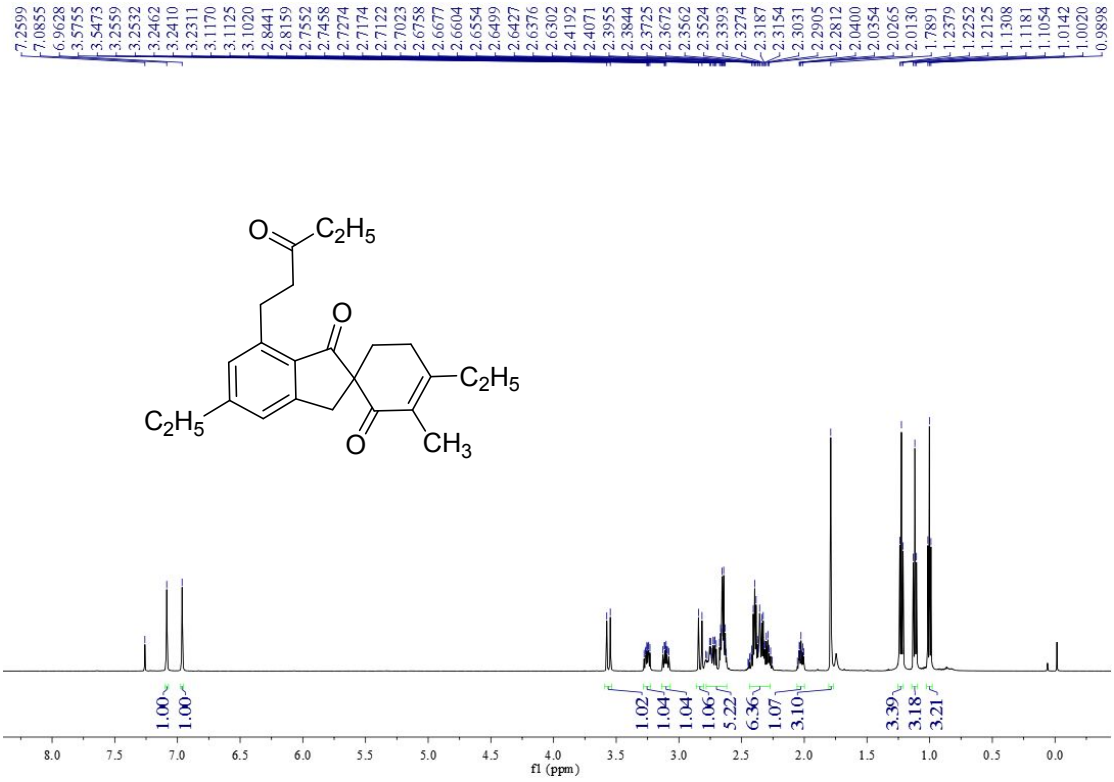
^{1}H NMR spectra of compound 3ab



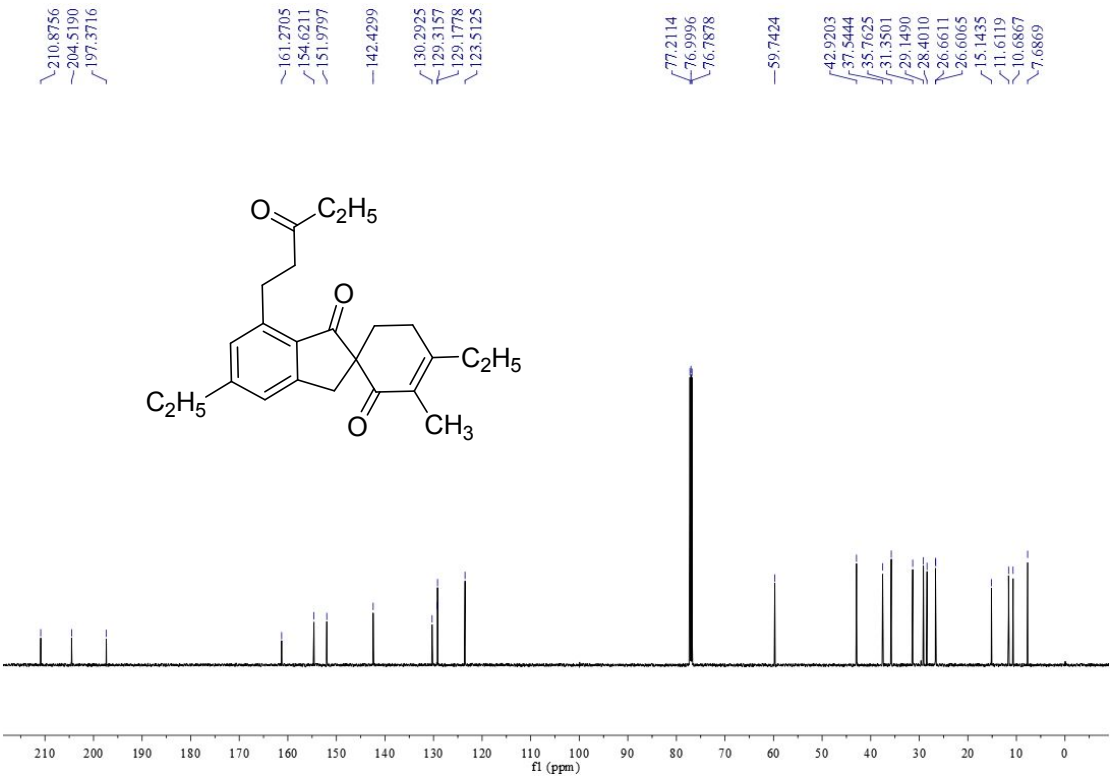
^{13}C NMR spectra of compound 3ab



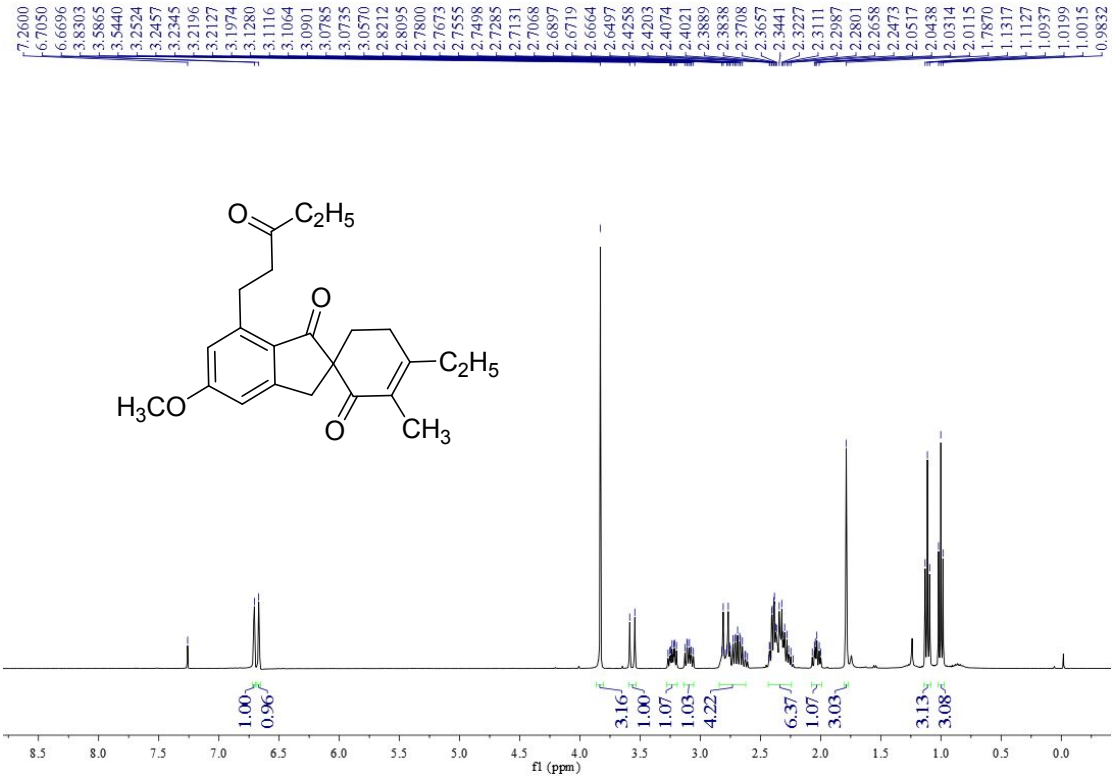
^{1}H NMR spectra of compound 3ac



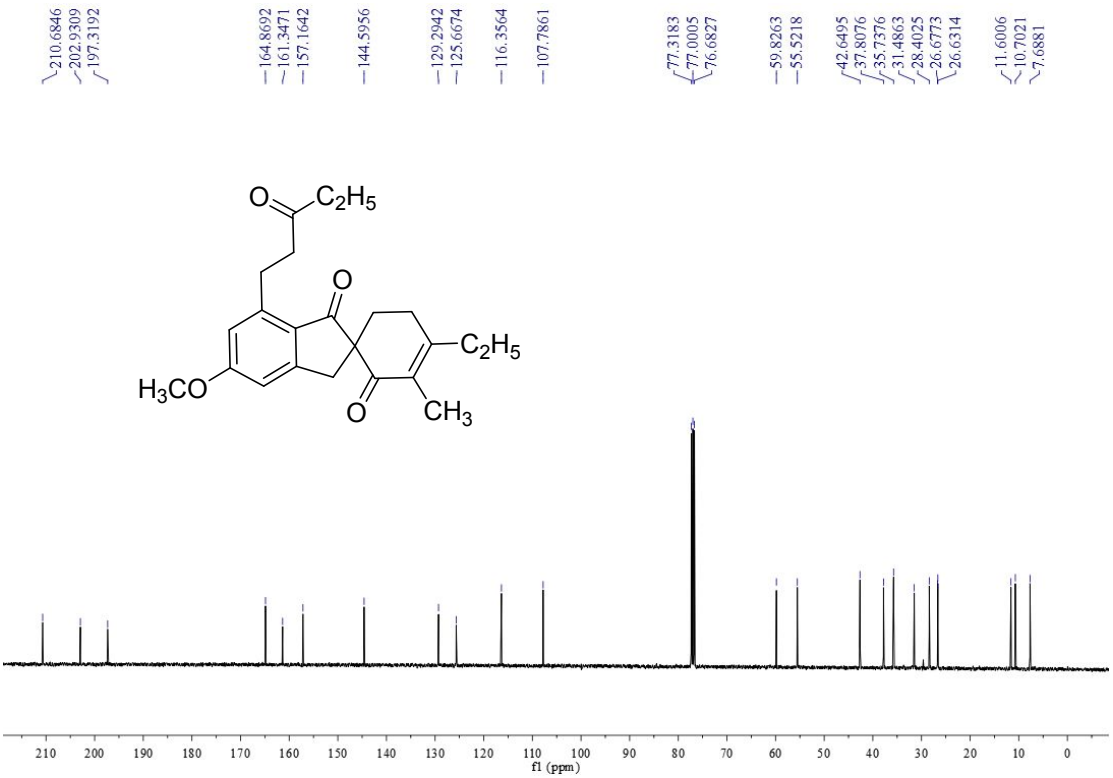
^{13}C NMR spectra of compound 3ac



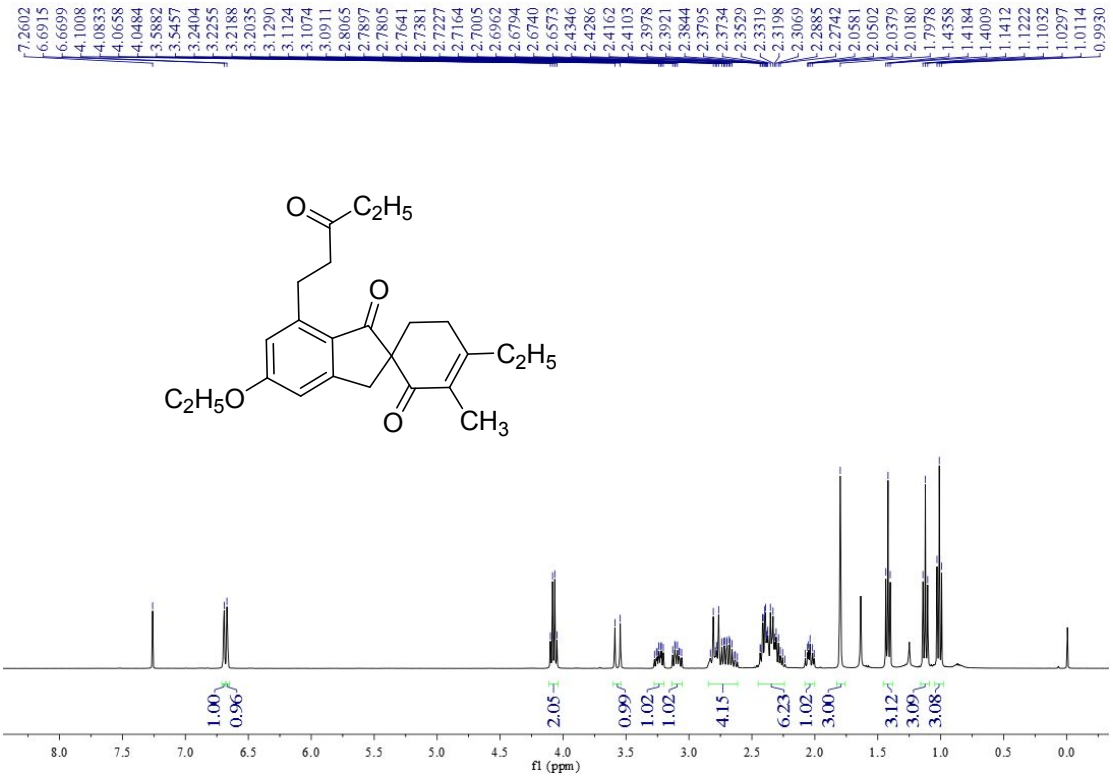
^{1}H NMR spectra of compound 3ad



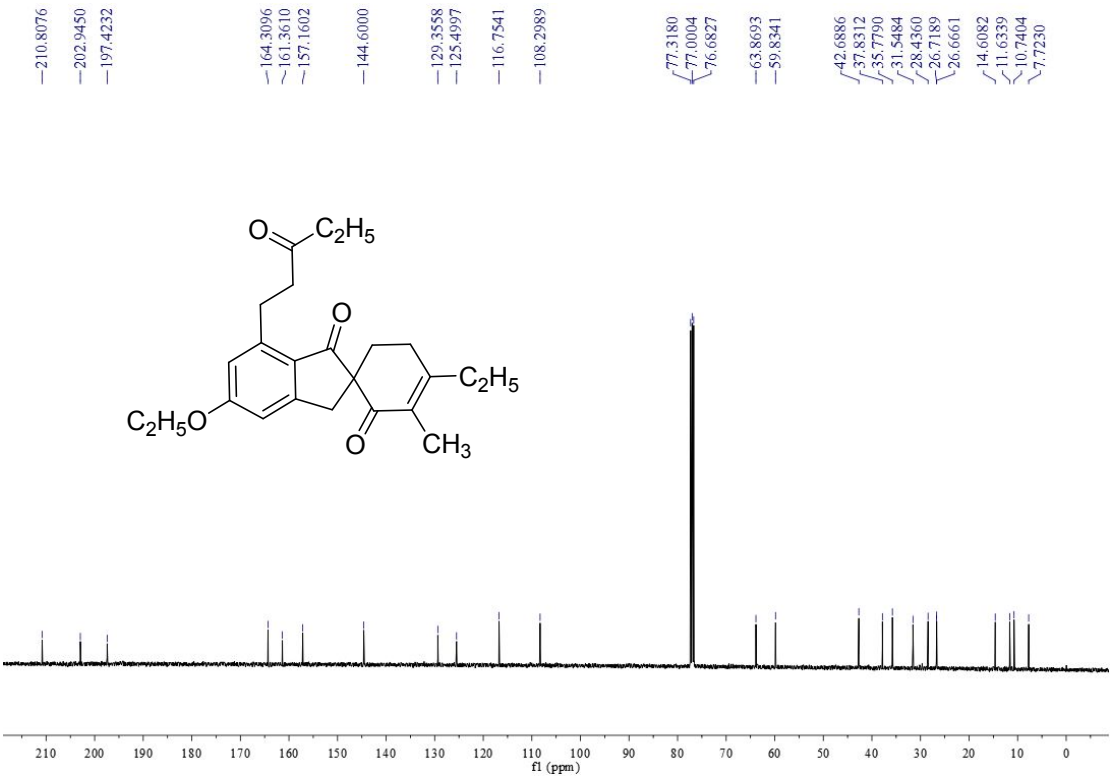
^{13}C NMR spectra of compound 3ad



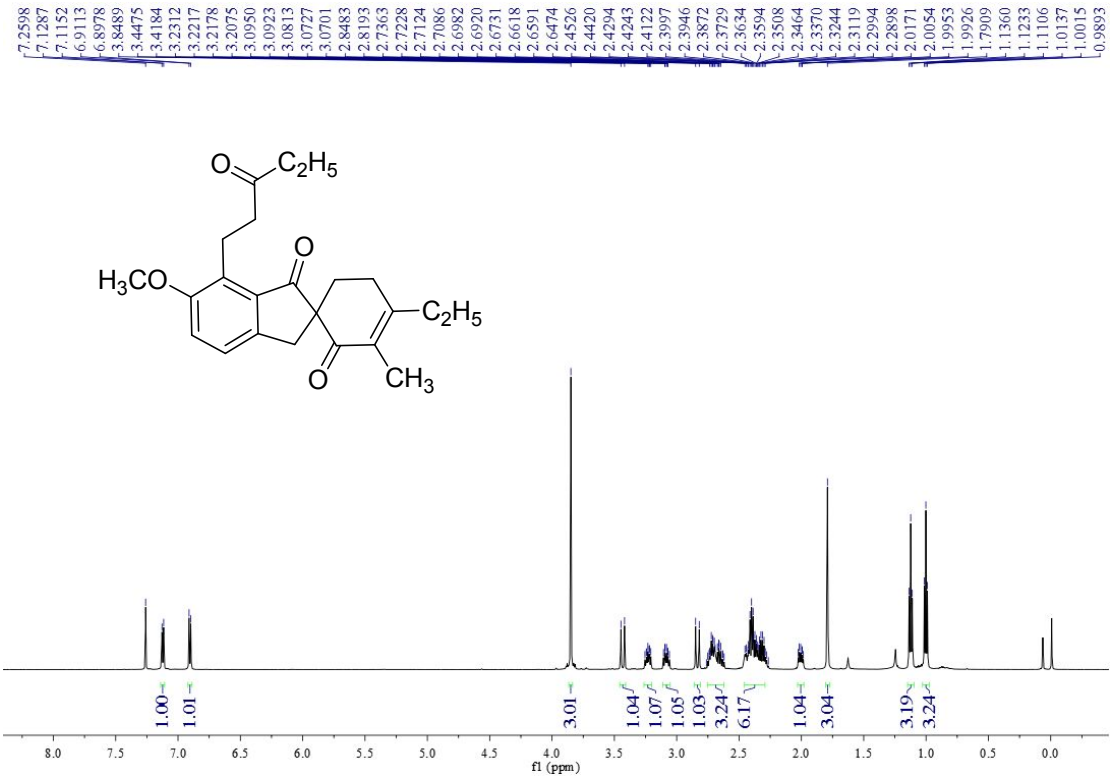
^{1}H NMR spectra of compound 3ae



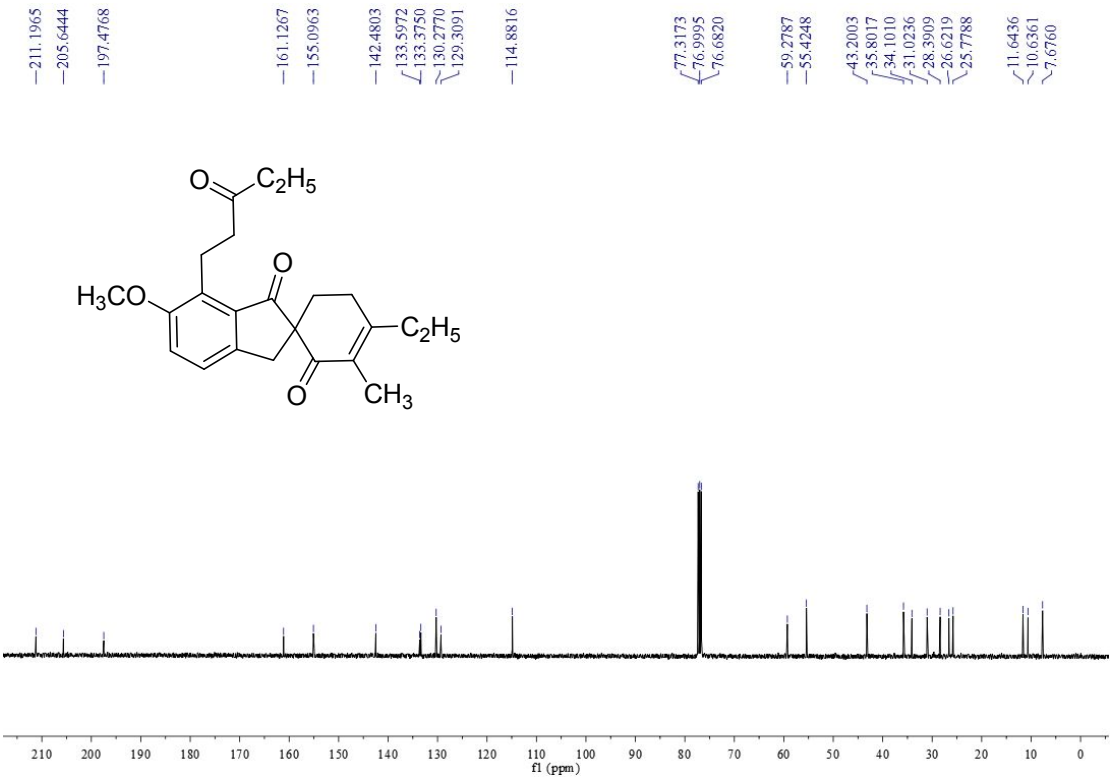
^{13}C NMR spectra of compound 3ae



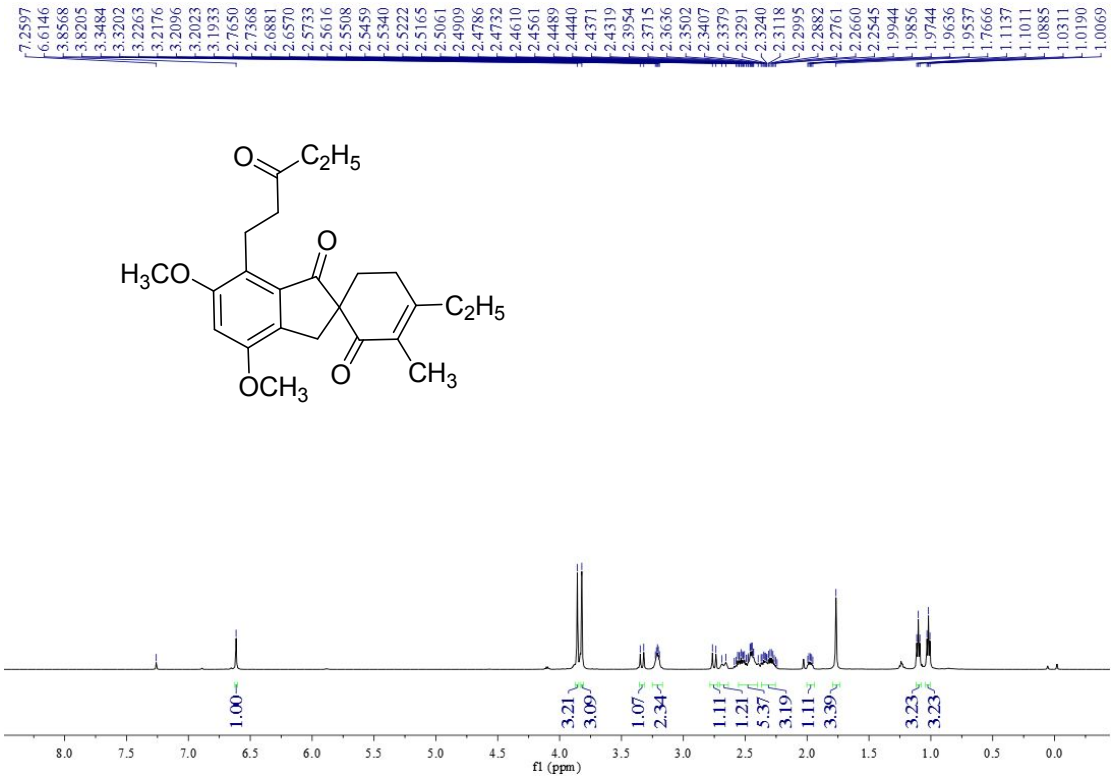
^{1}H NMR spectra of compound 3af



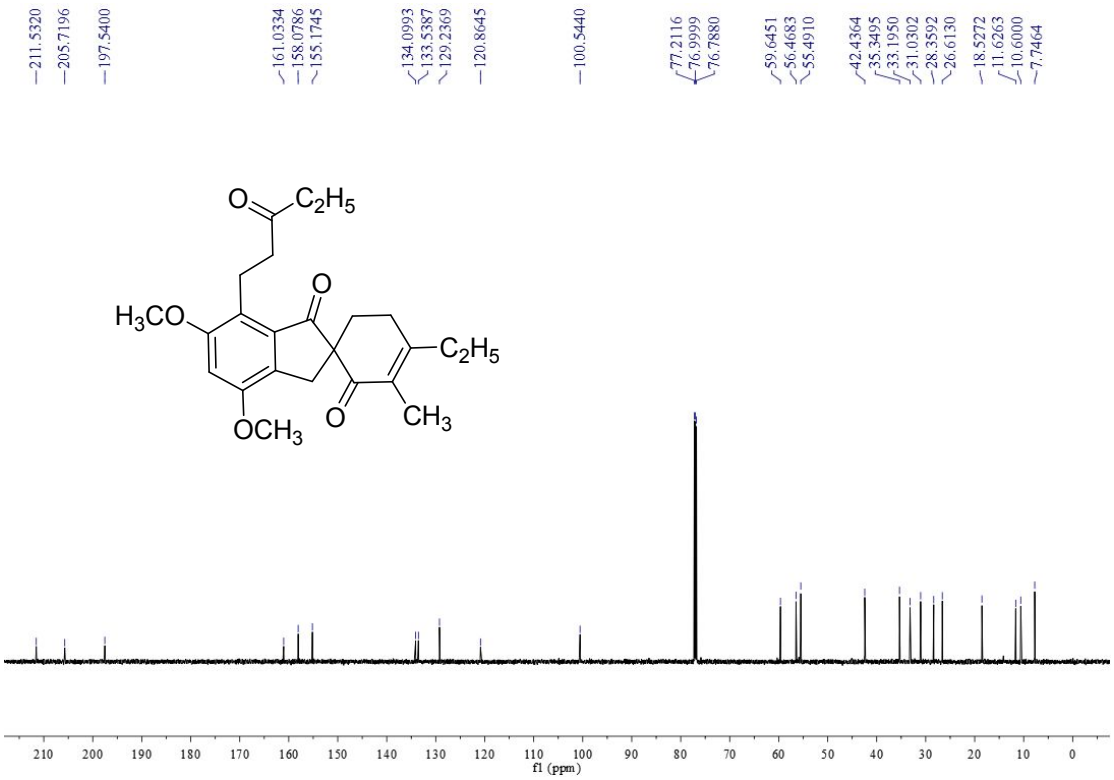
^{13}C NMR spectra of compound 3af



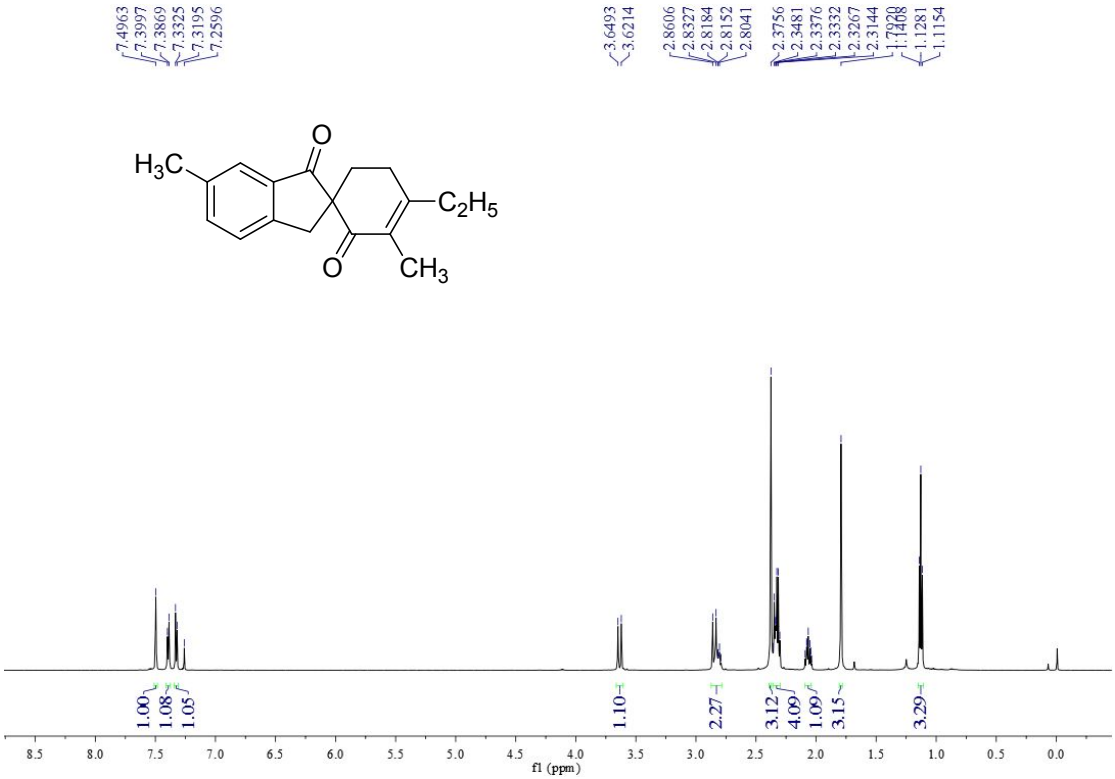
^{1}H NMR spectra of compound 3ag



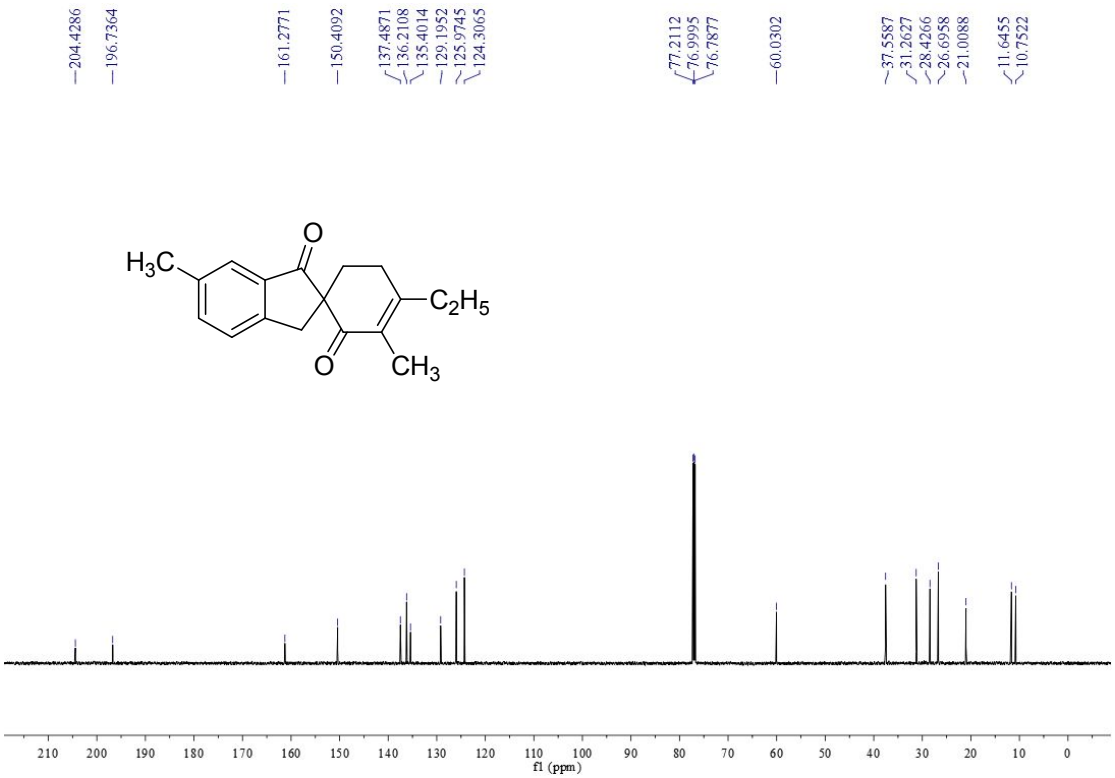
^{13}C NMR spectra of compound 3ag



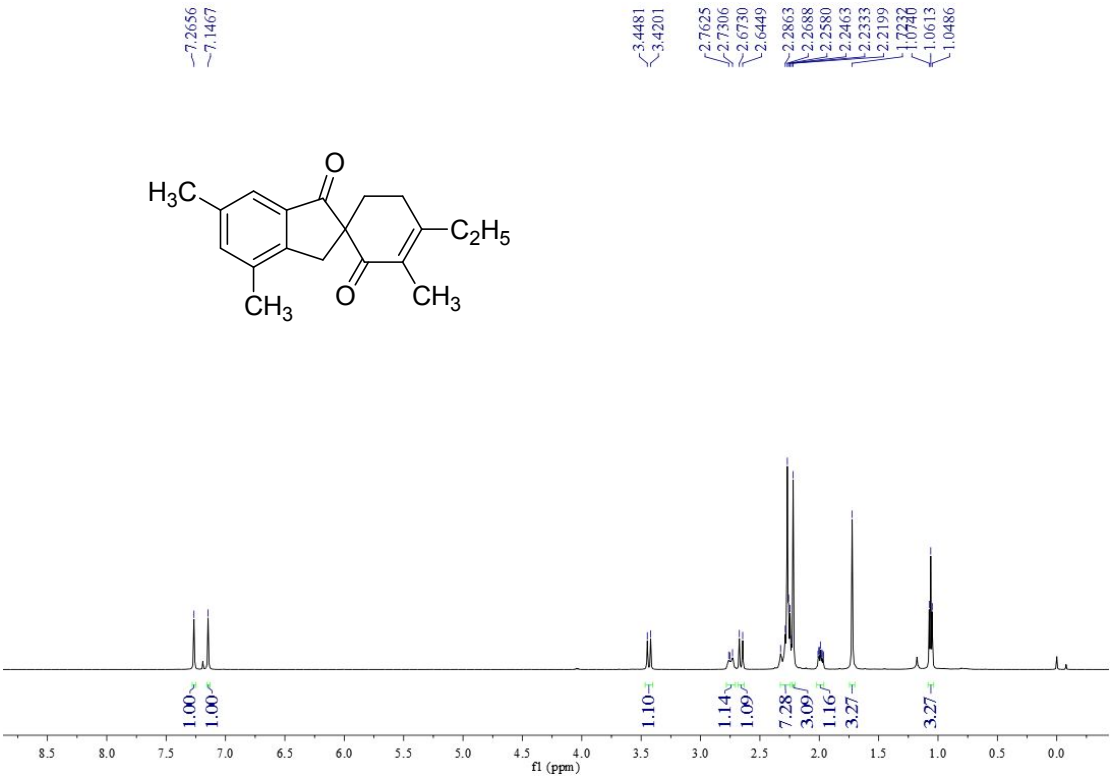
^{1}H NMR spectra of compound 3ah



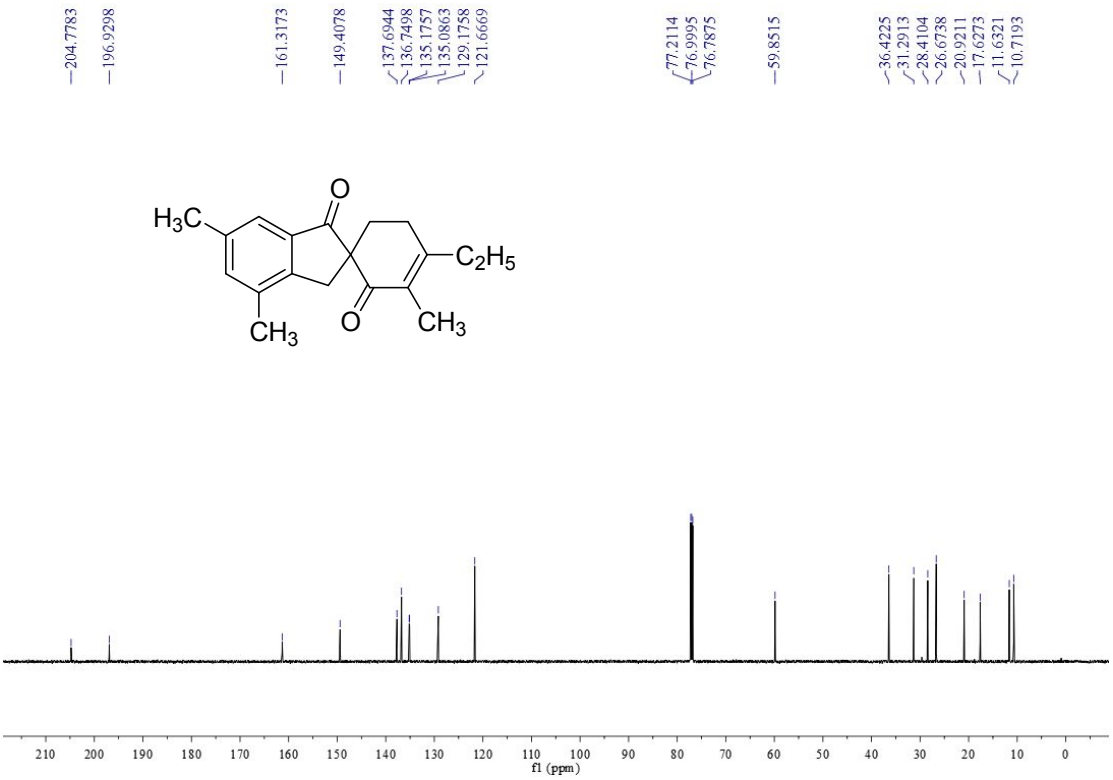
^{13}C NMR spectra of compound 3ah



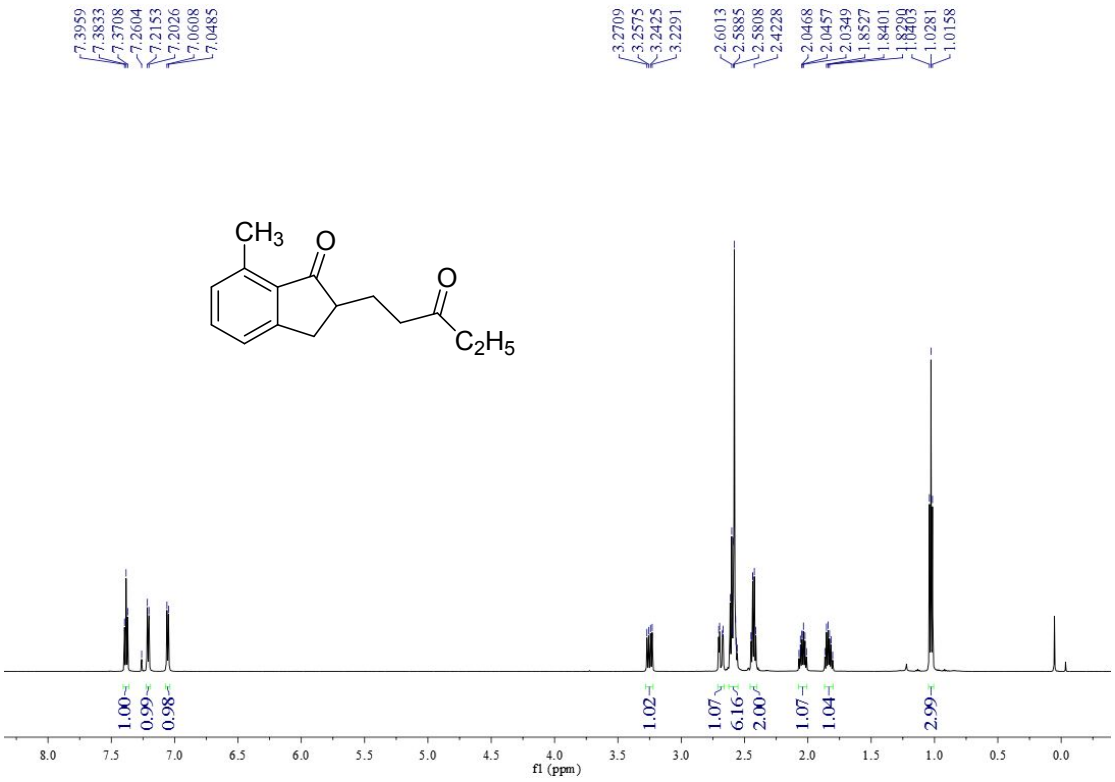
^{1}H NMR spectra of compound 3ai



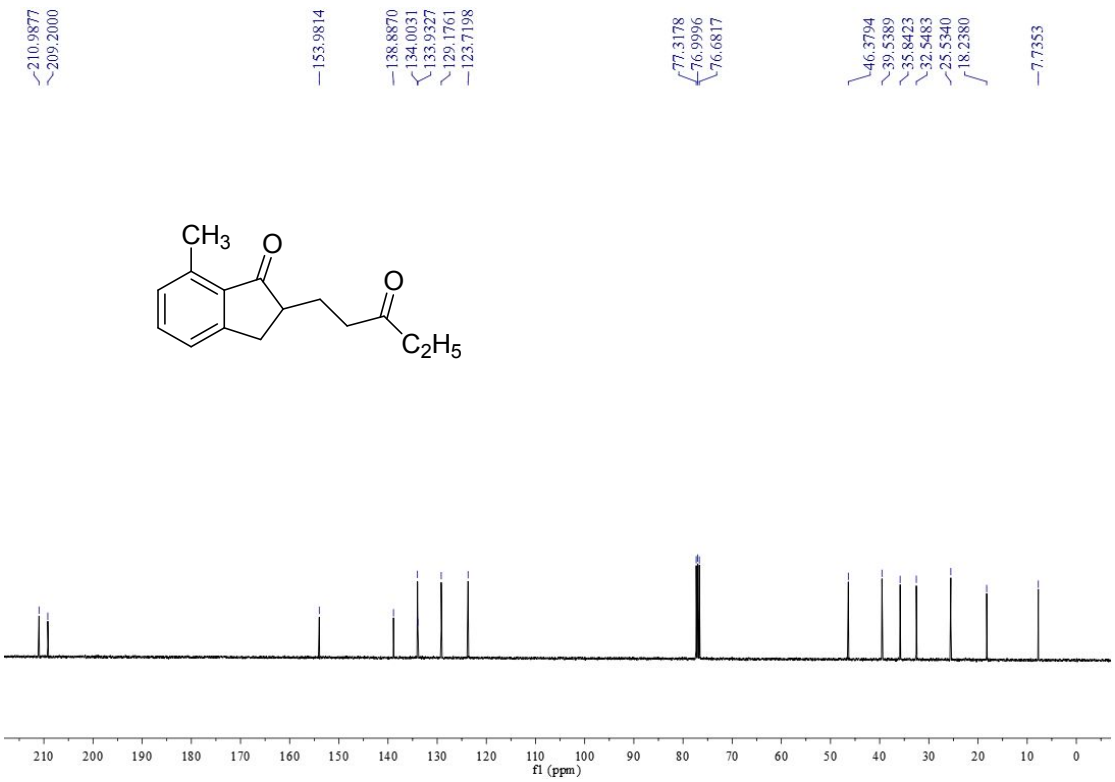
^{13}C NMR spectra of compound 3ai



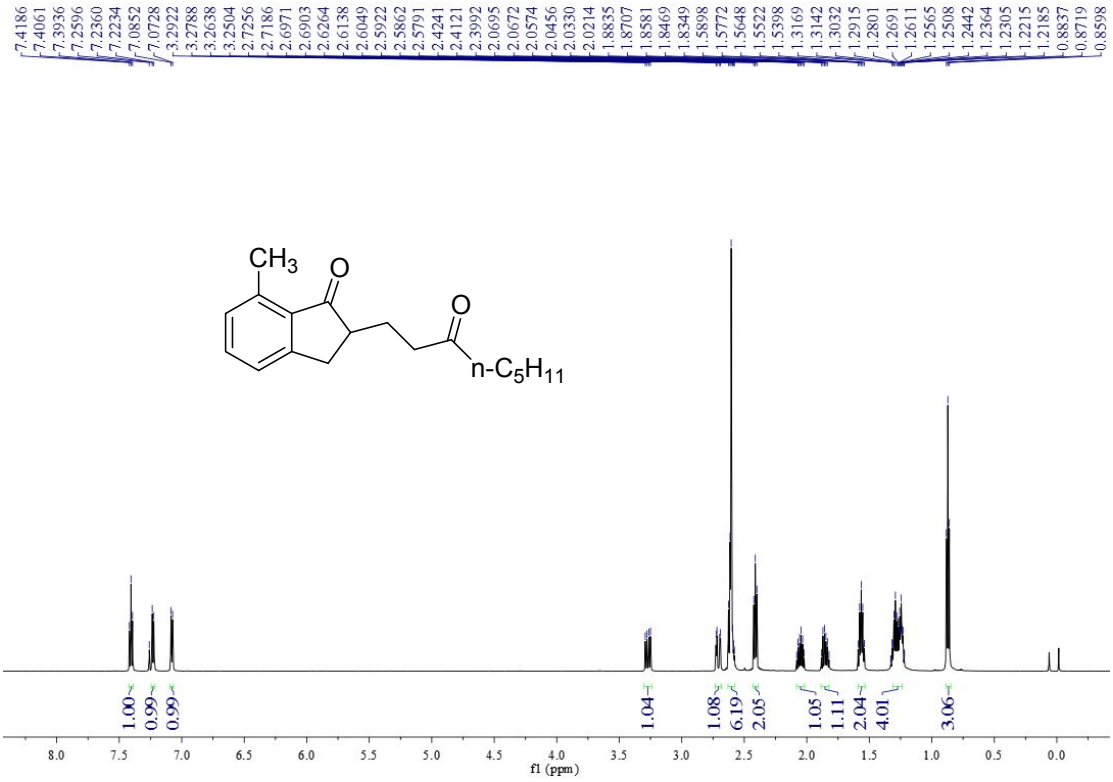
^{1}H NMR spectra of compound 4a



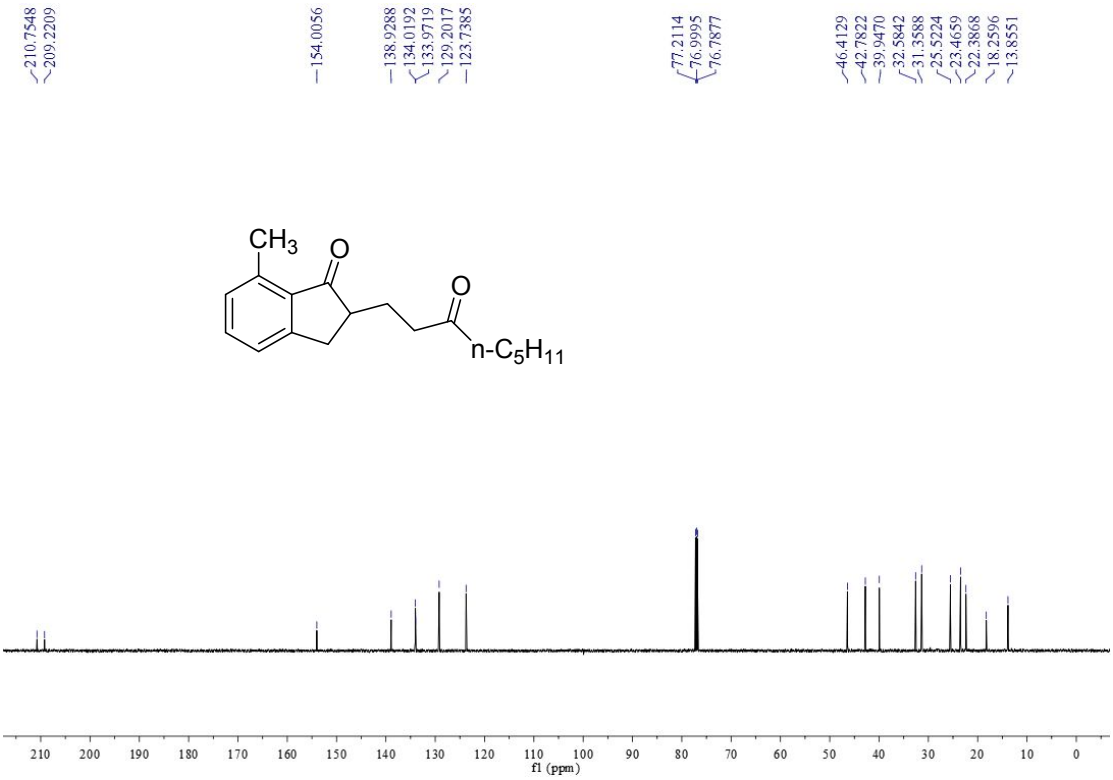
^{13}C NMR spectra of compound 4a



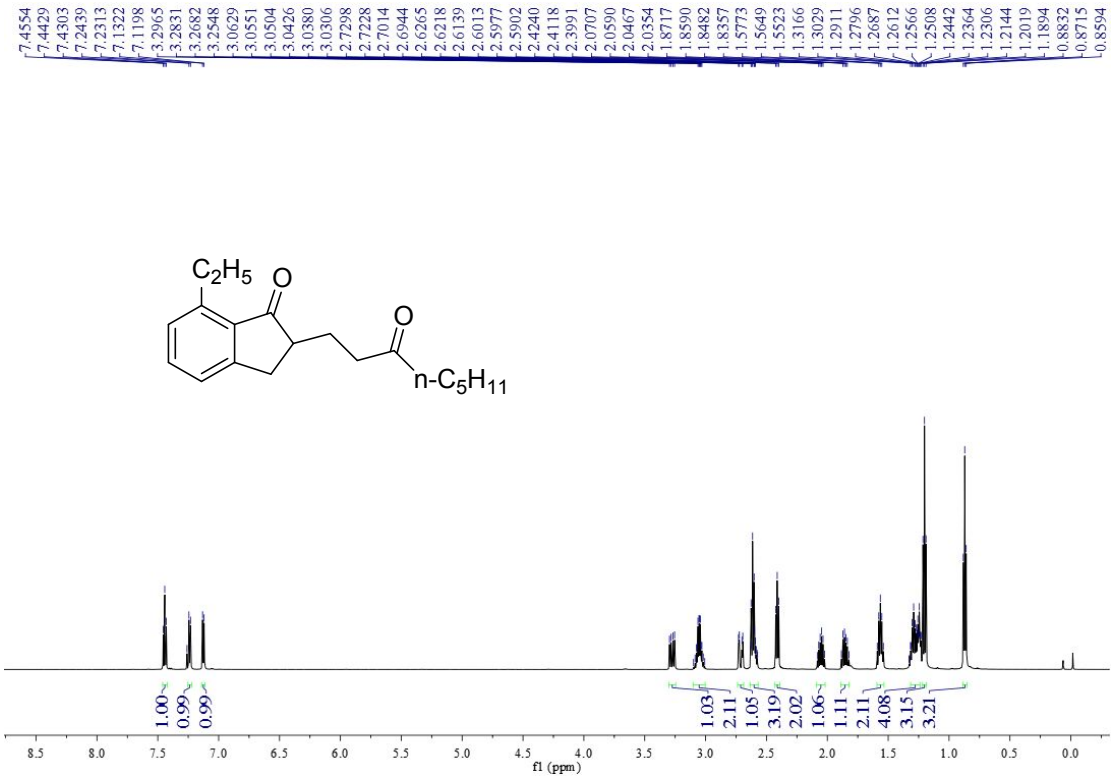
^{1}H NMR spectra of compound 4b



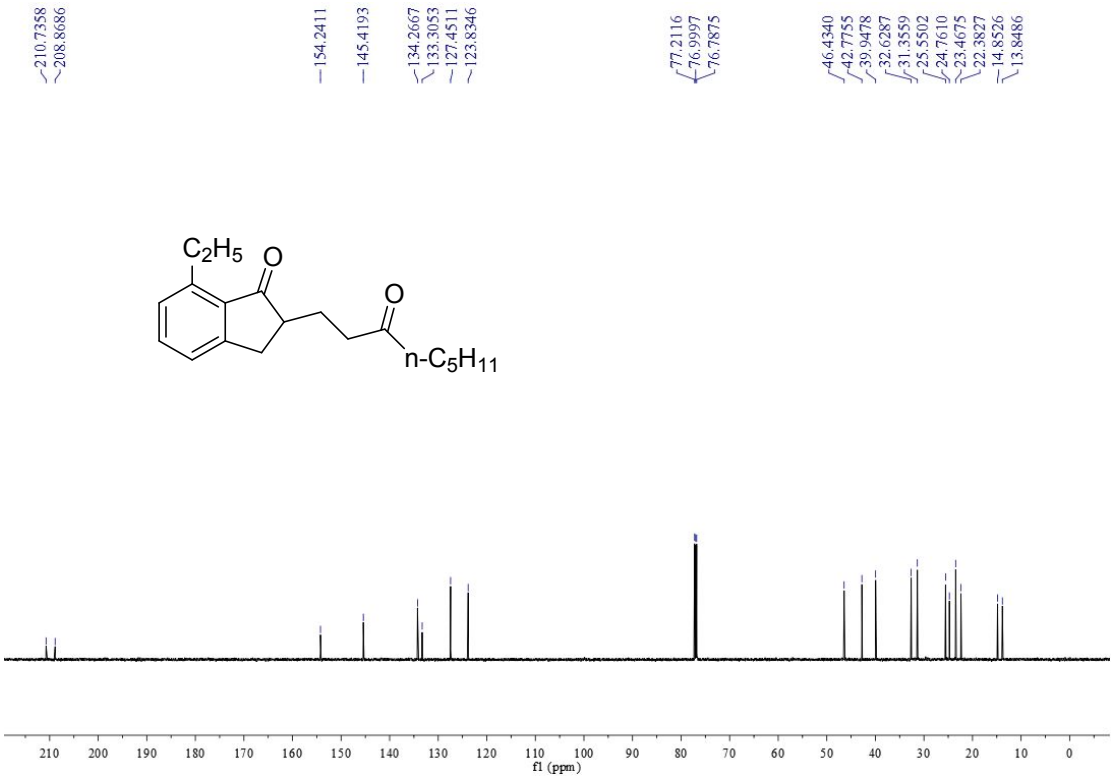
^{13}C NMR spectra of compound 4b



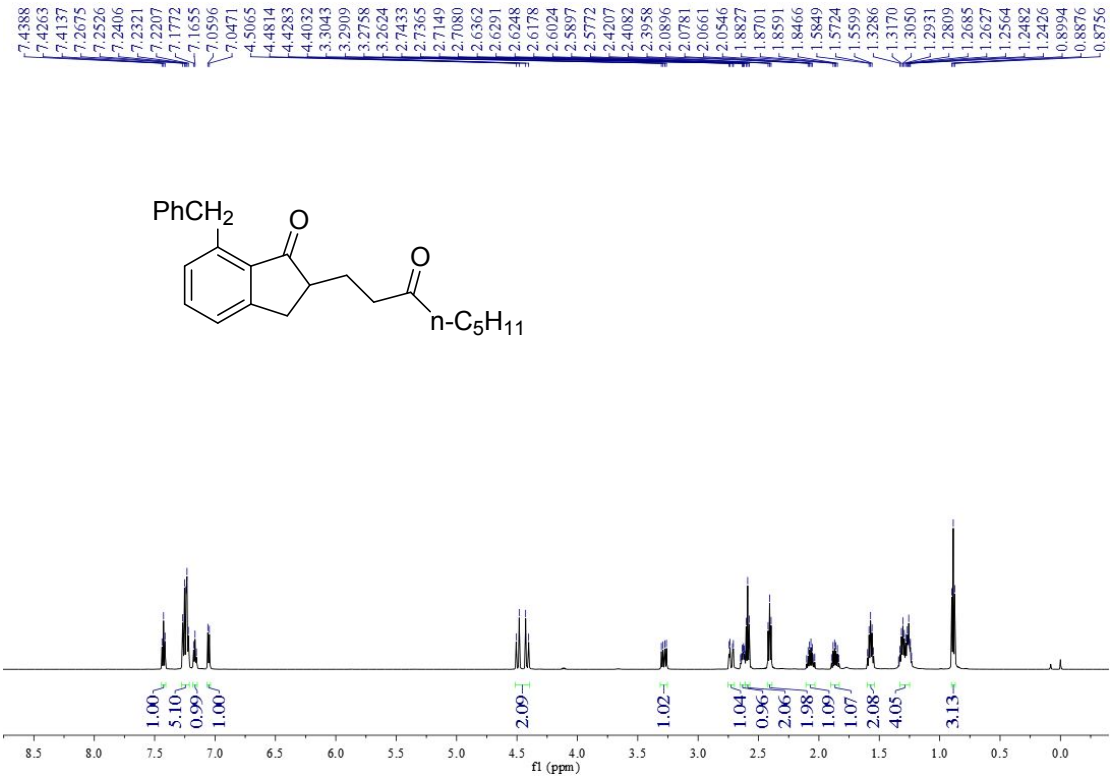
^{1}H NMR spectra of compound 4c



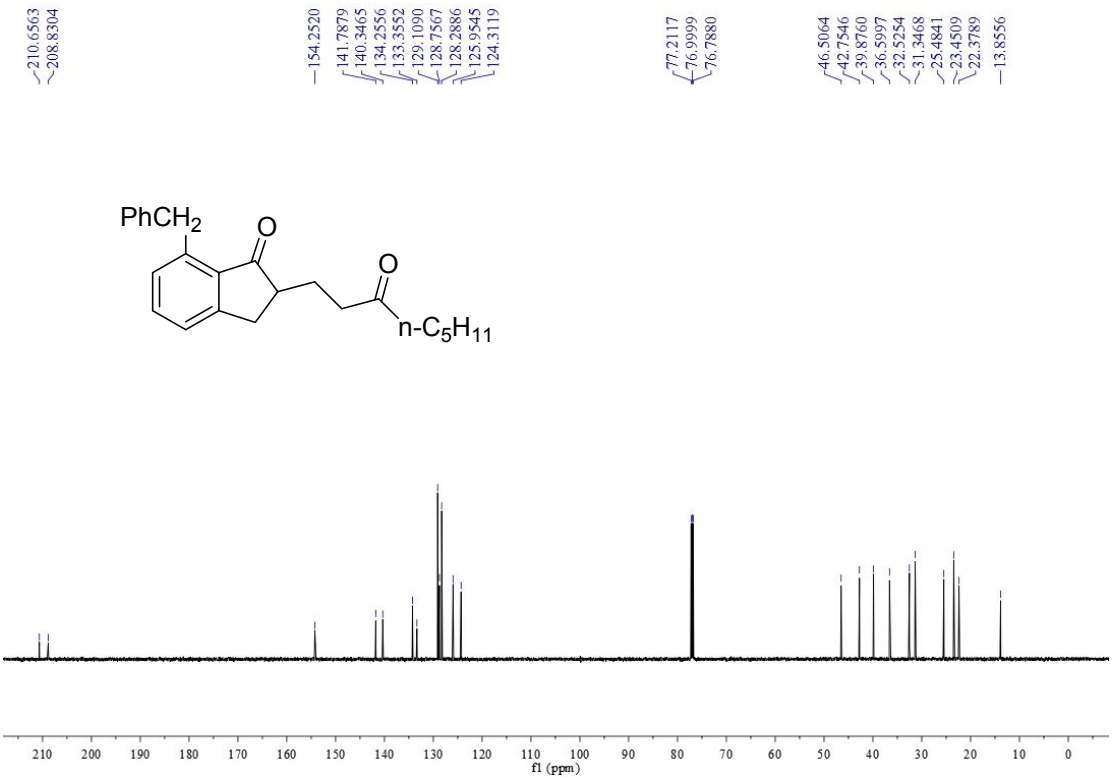
^{13}C NMR spectra of compound 4c



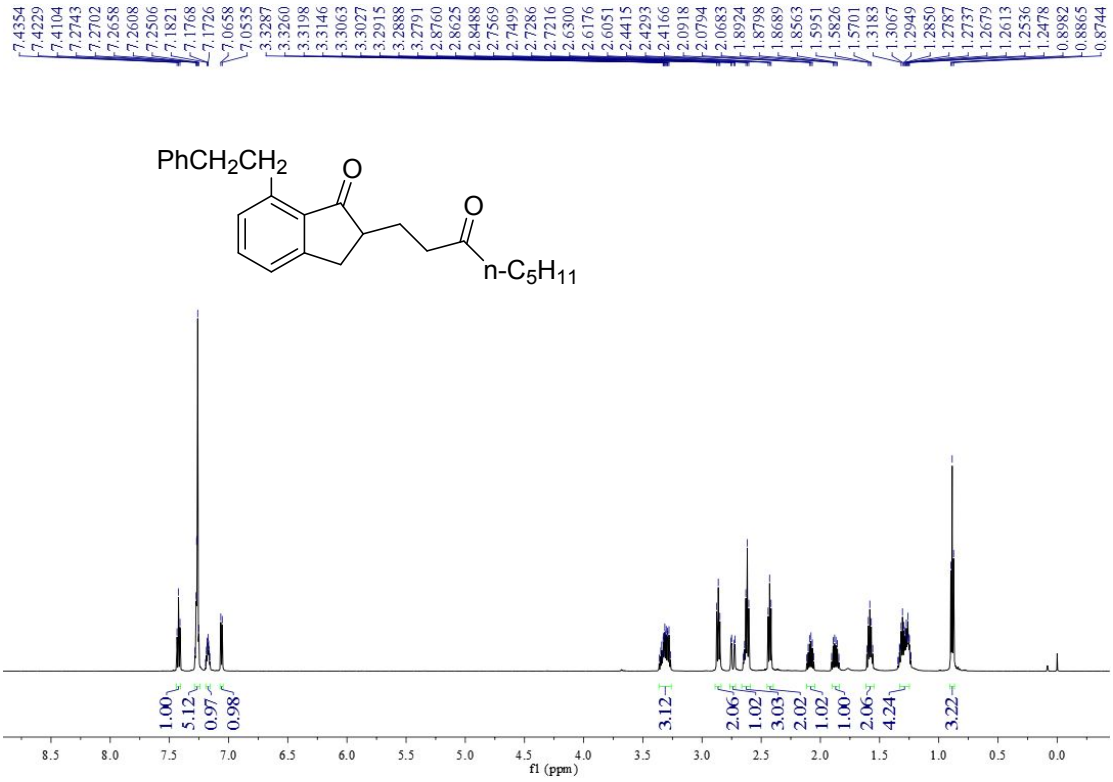
^{1}H NMR spectra of compound 4d



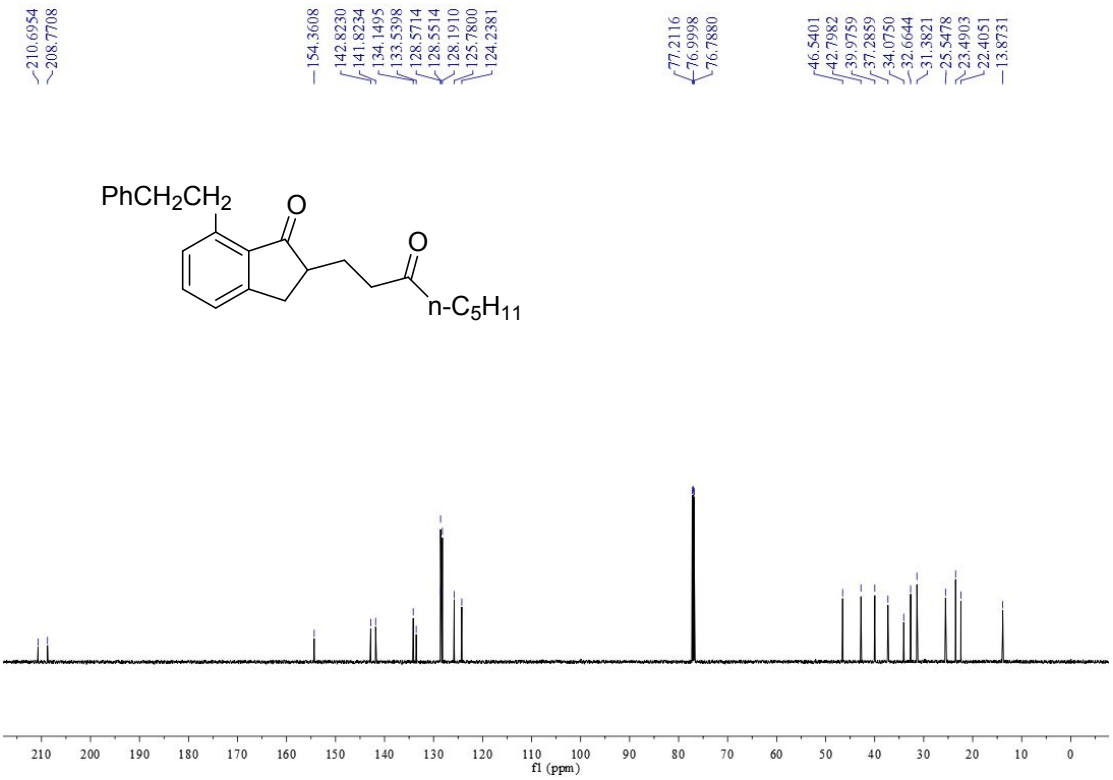
^{13}C NMR spectra of compound 4d



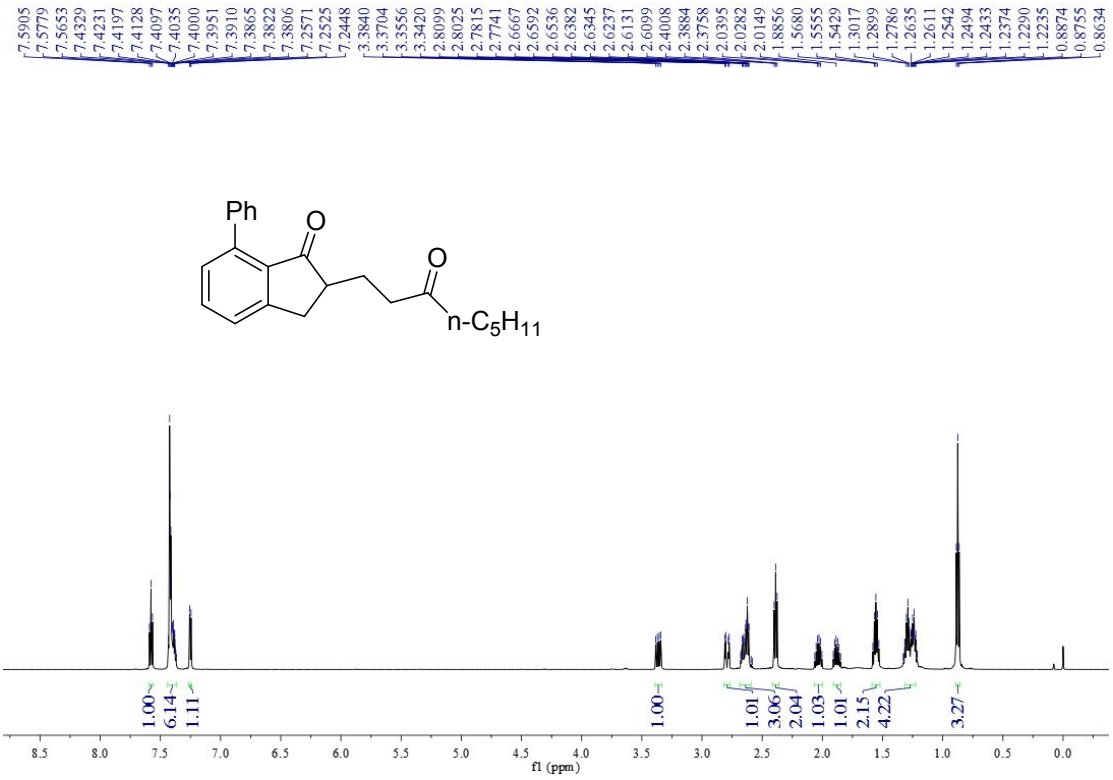
^{1}H NMR spectra of compound 4e



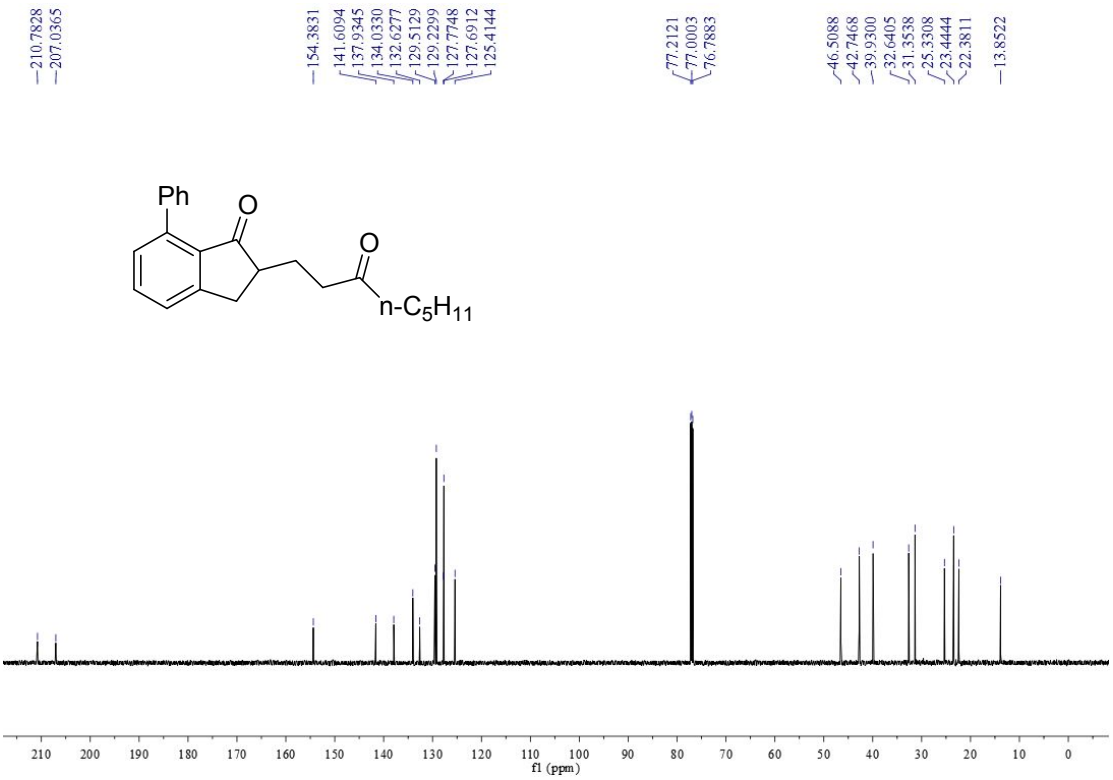
^{13}C NMR spectra of compound 4e



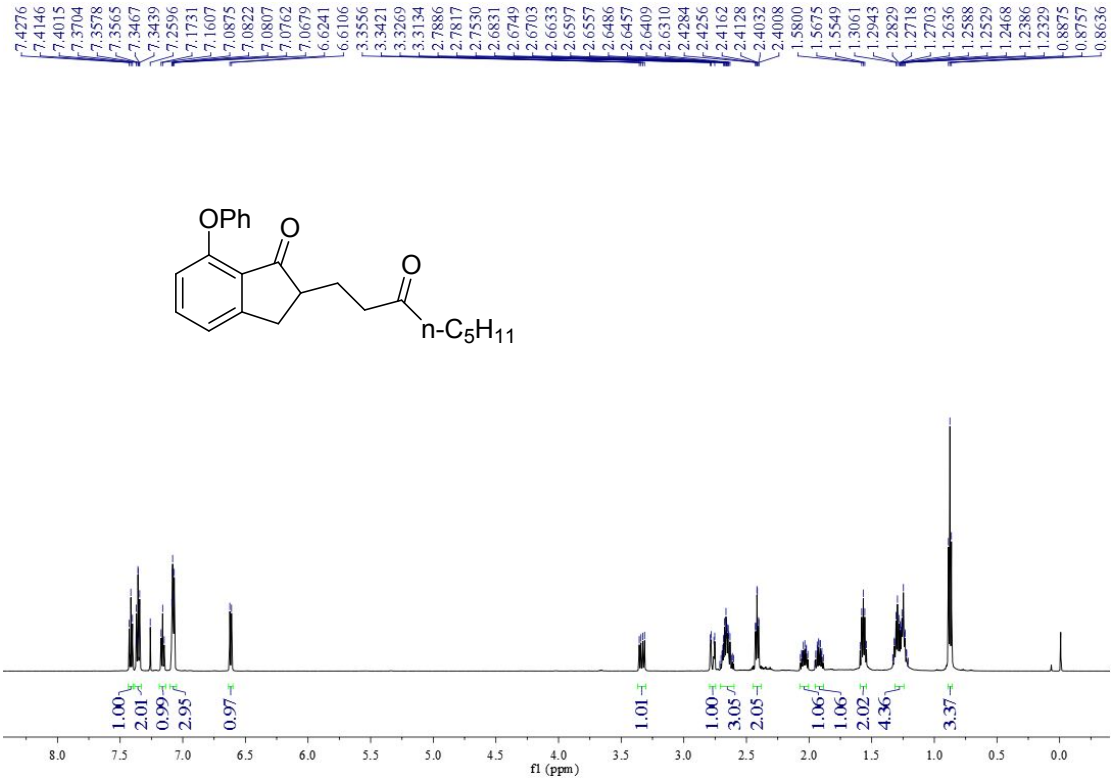
^{1}H NMR spectra of compound 4f



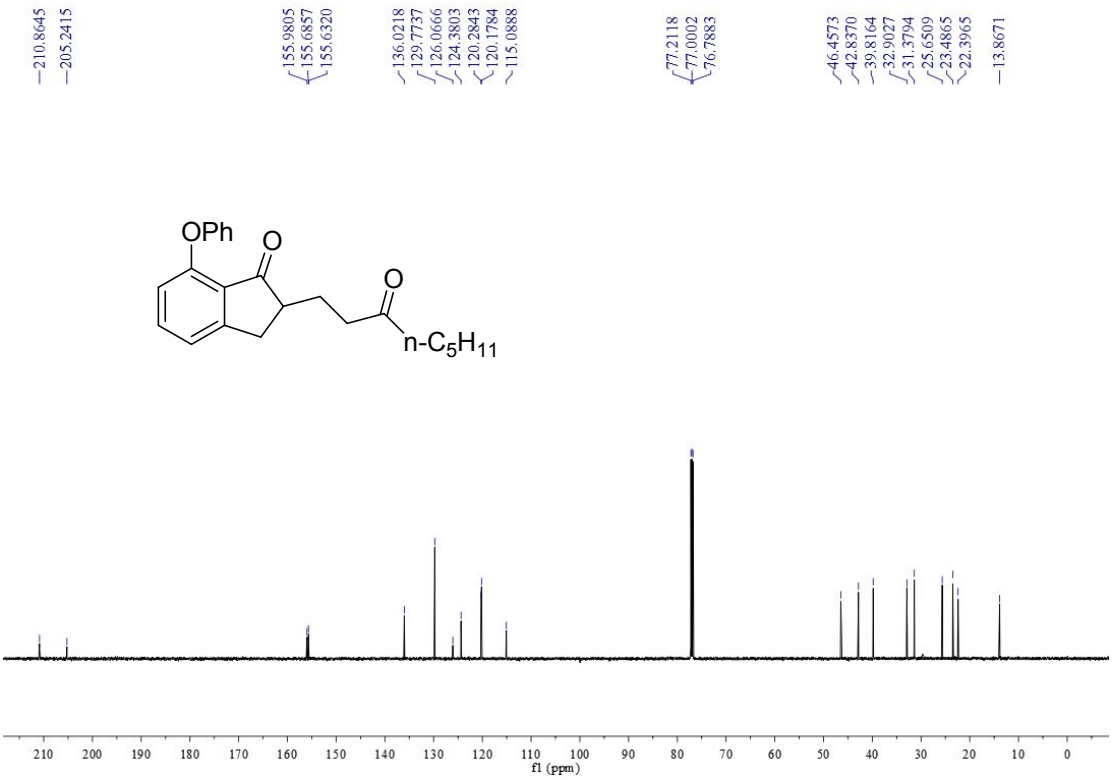
^{13}C NMR spectra of compound 4f



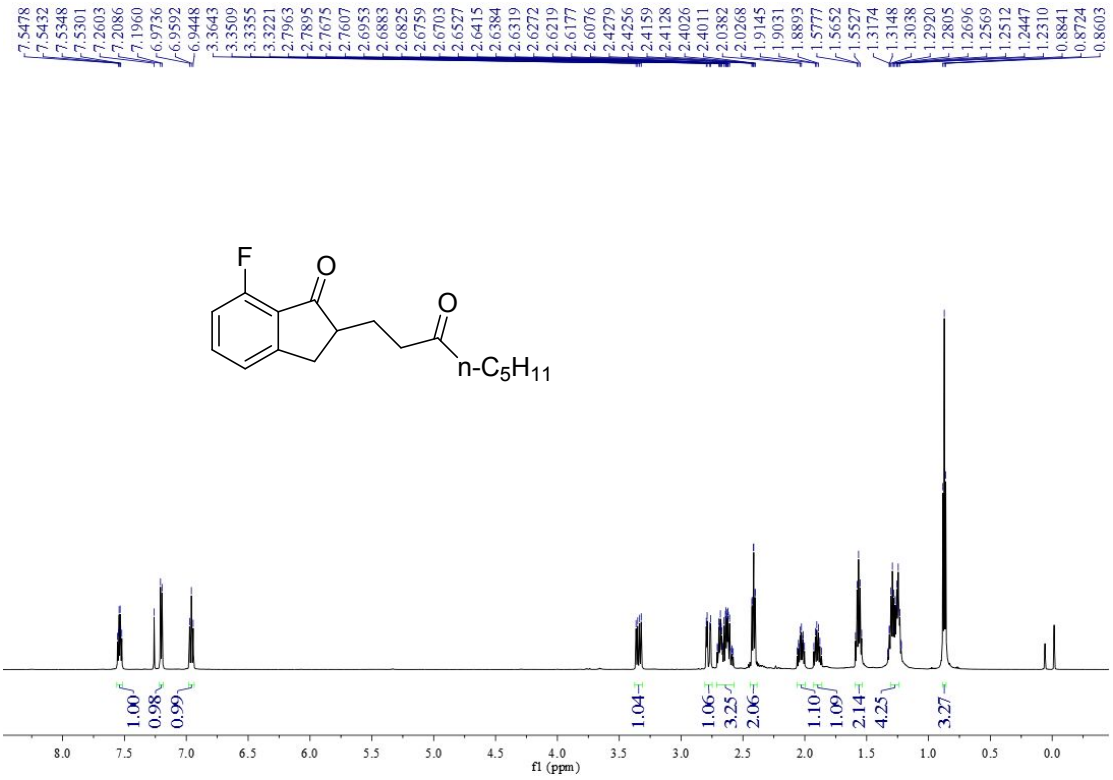
^{1}H NMR spectra of compound 4g



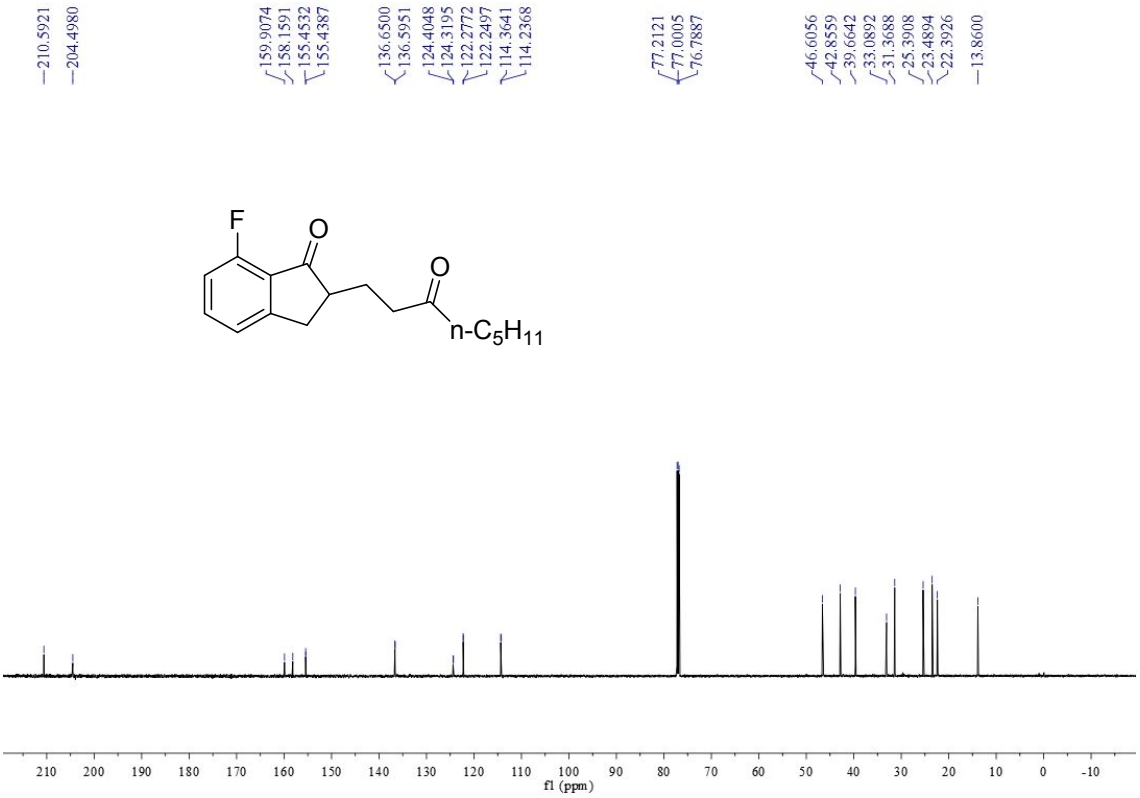
^{13}C NMR spectra of compound 4g



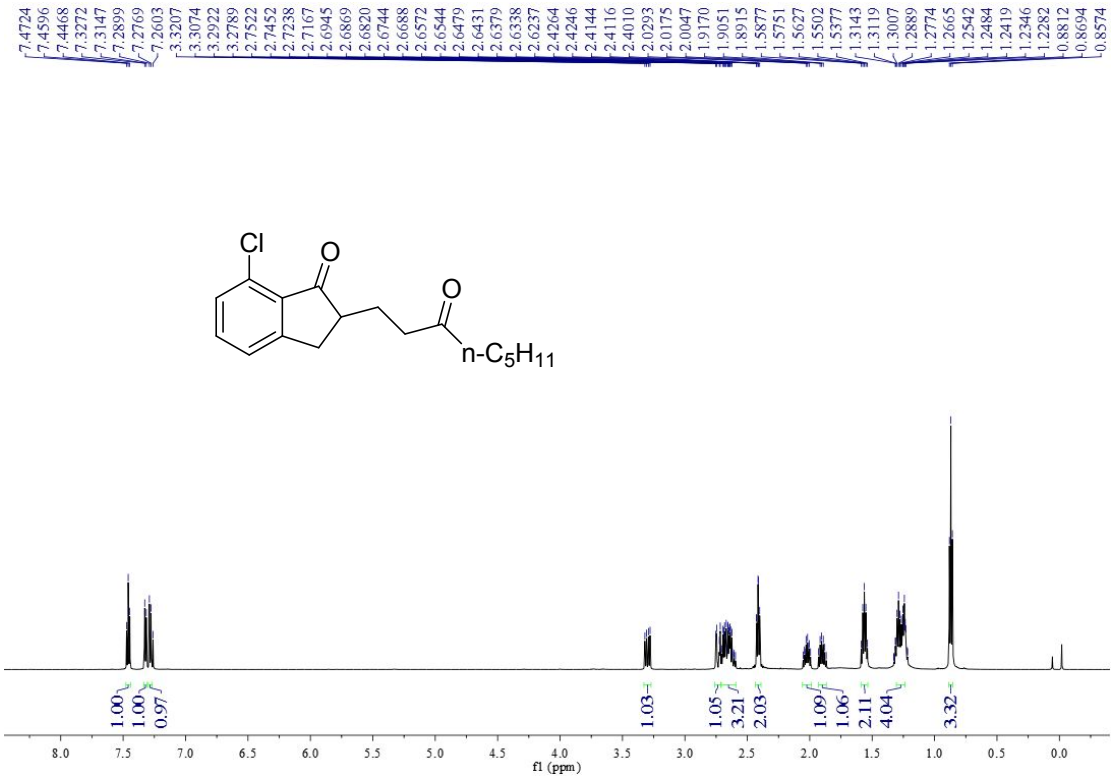
^{1}H NMR spectra of compound 4h



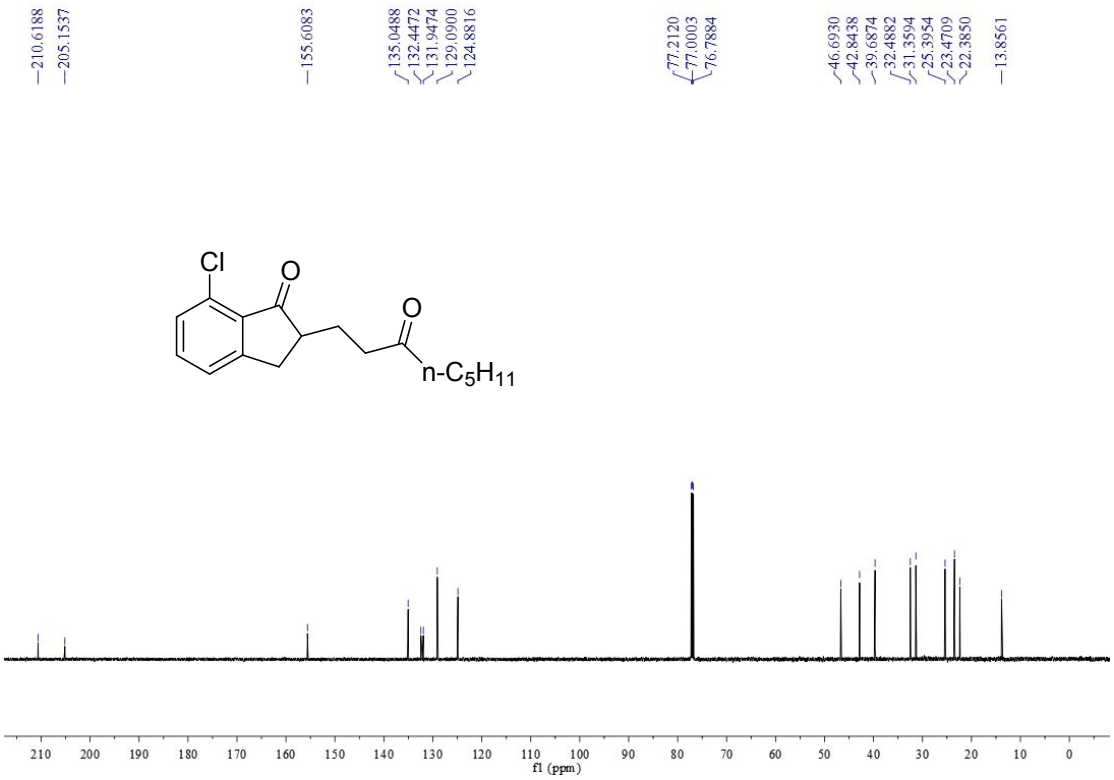
^{13}C NMR spectra of compound 4h



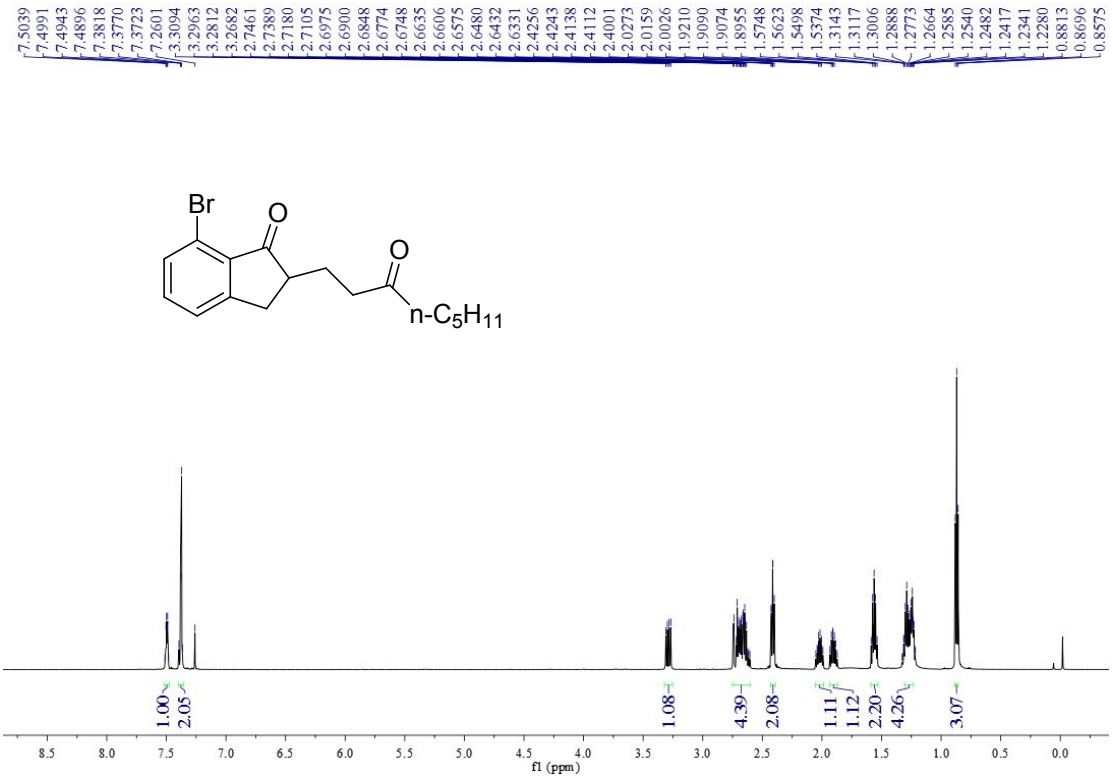
^{1}H NMR spectra of compound 4i



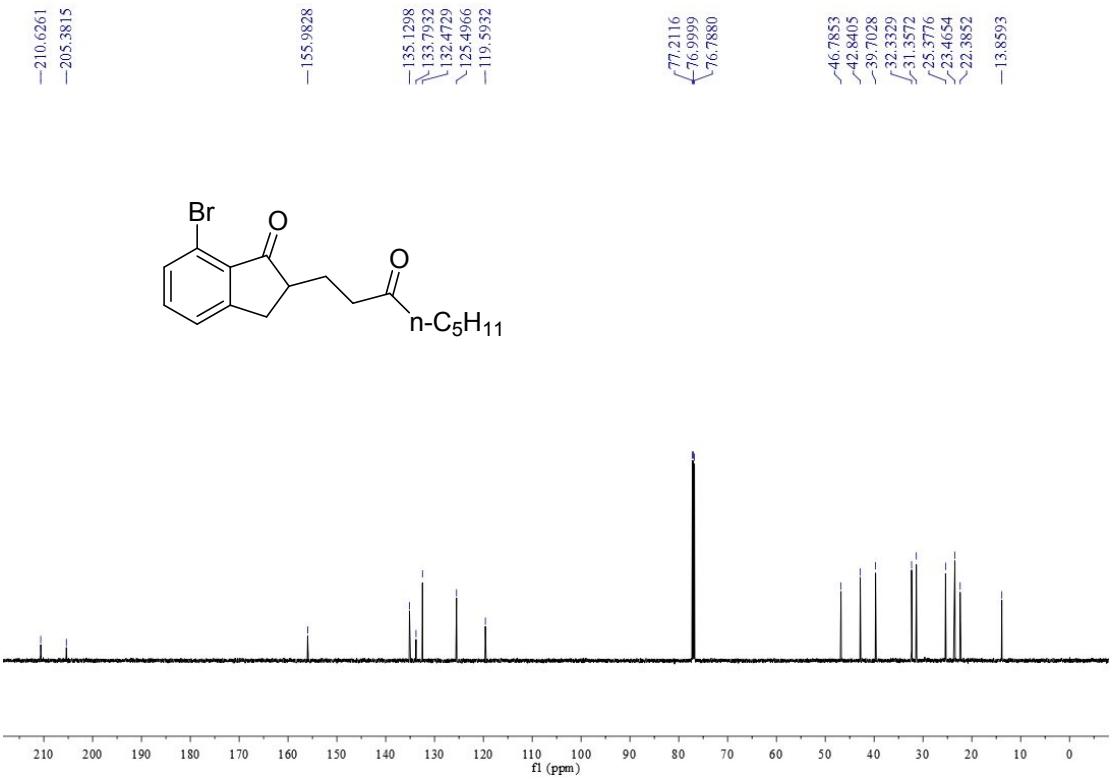
^{13}C NMR spectra of compound 4i



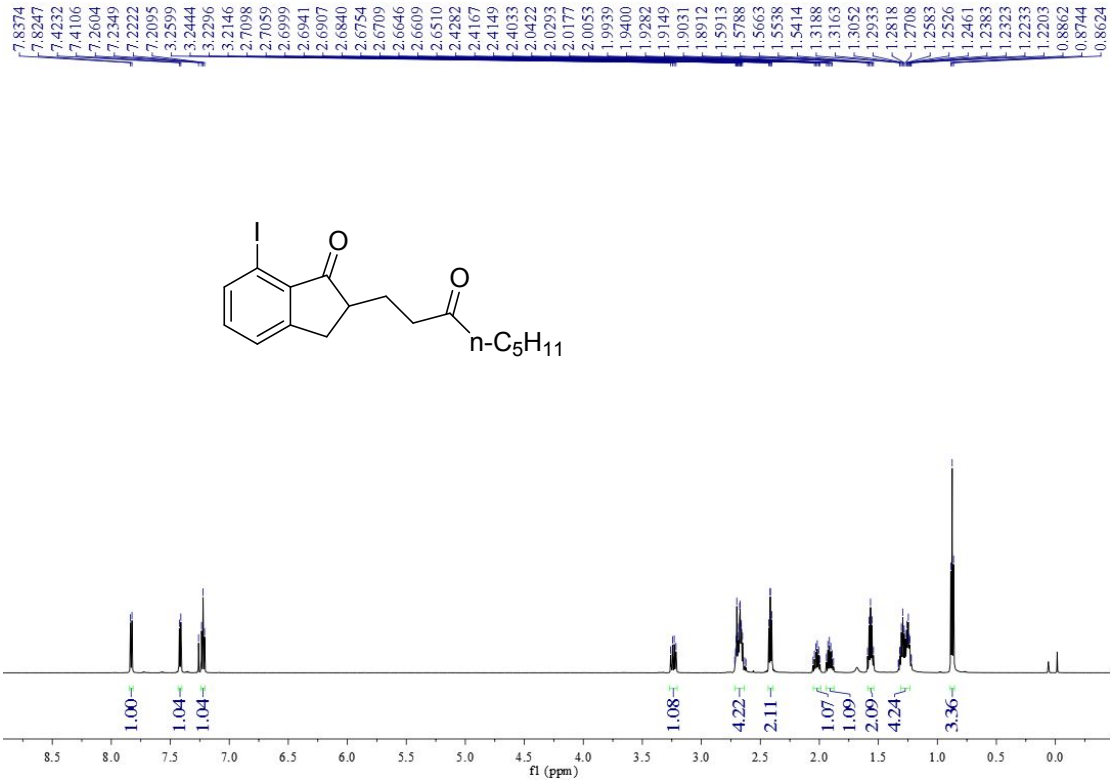
^{1}H NMR spectra of compound 4j



^{13}C NMR spectra of compound 4j



^{1}H NMR spectra of compound 4k



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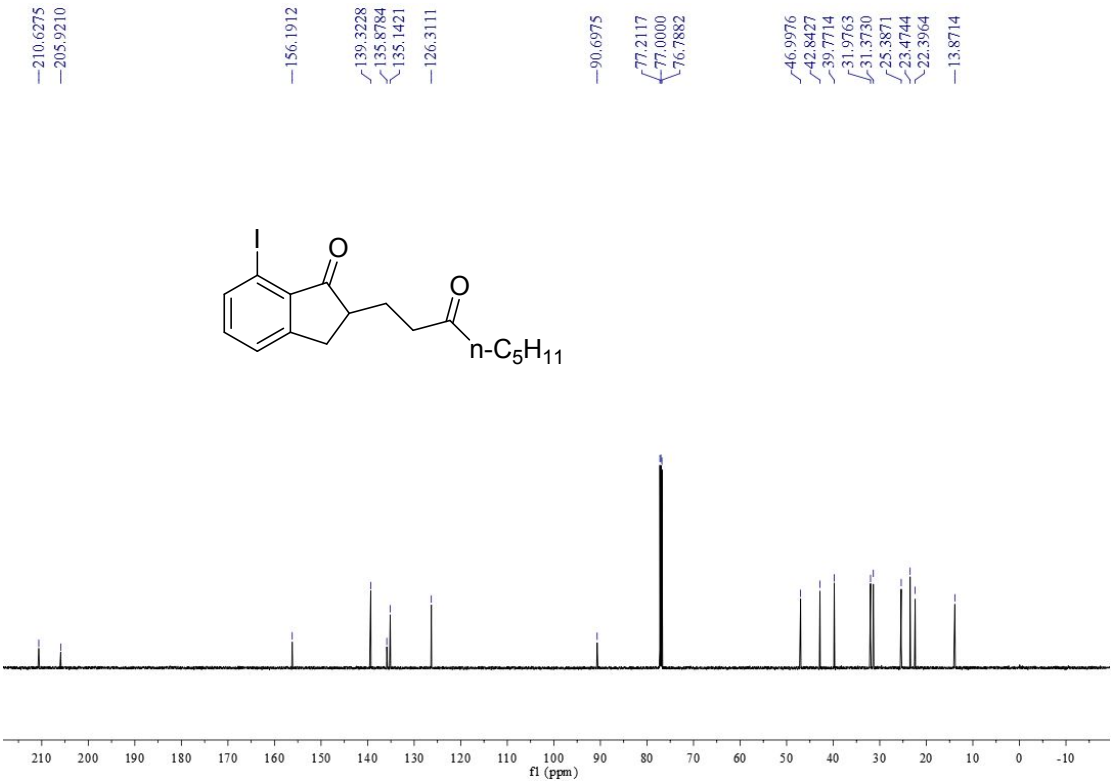
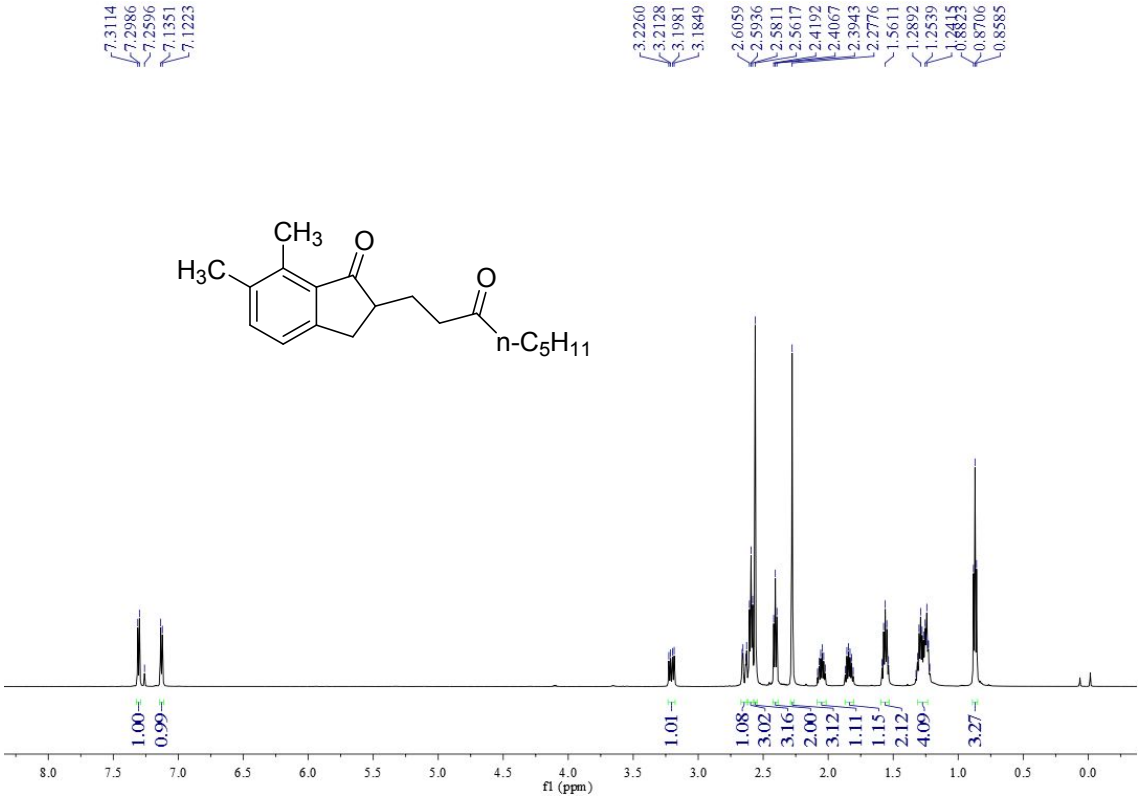


^{1}H NMR spectra of compound 4l



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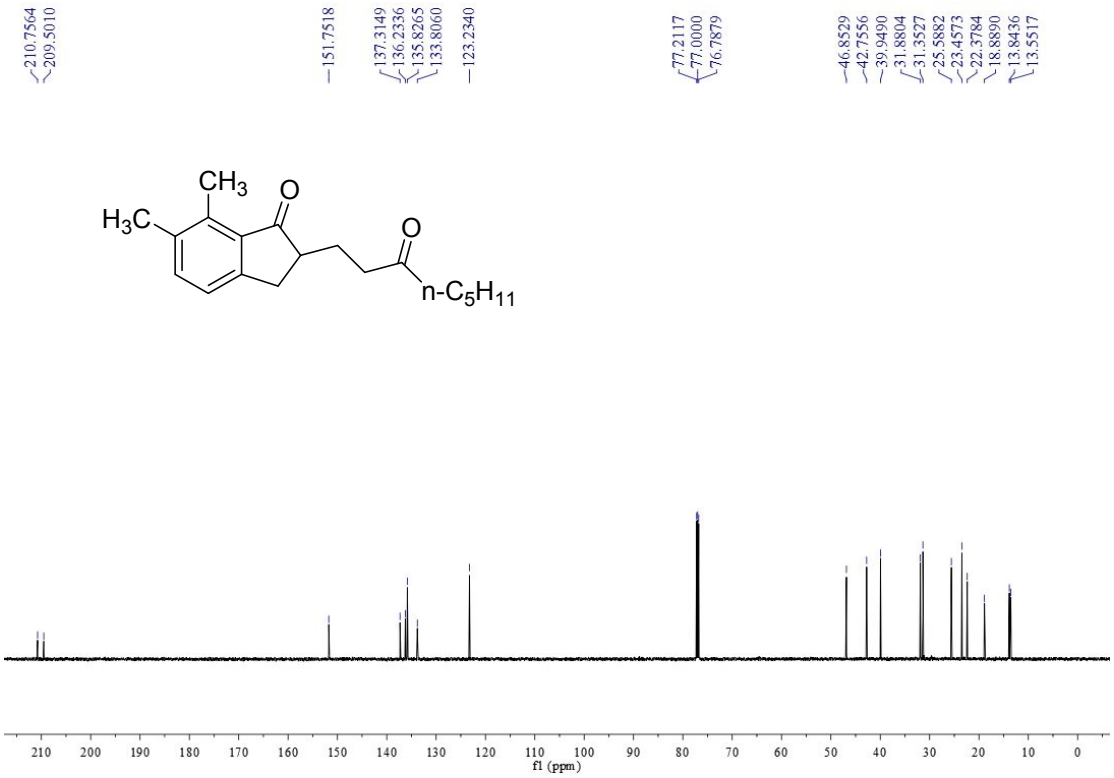
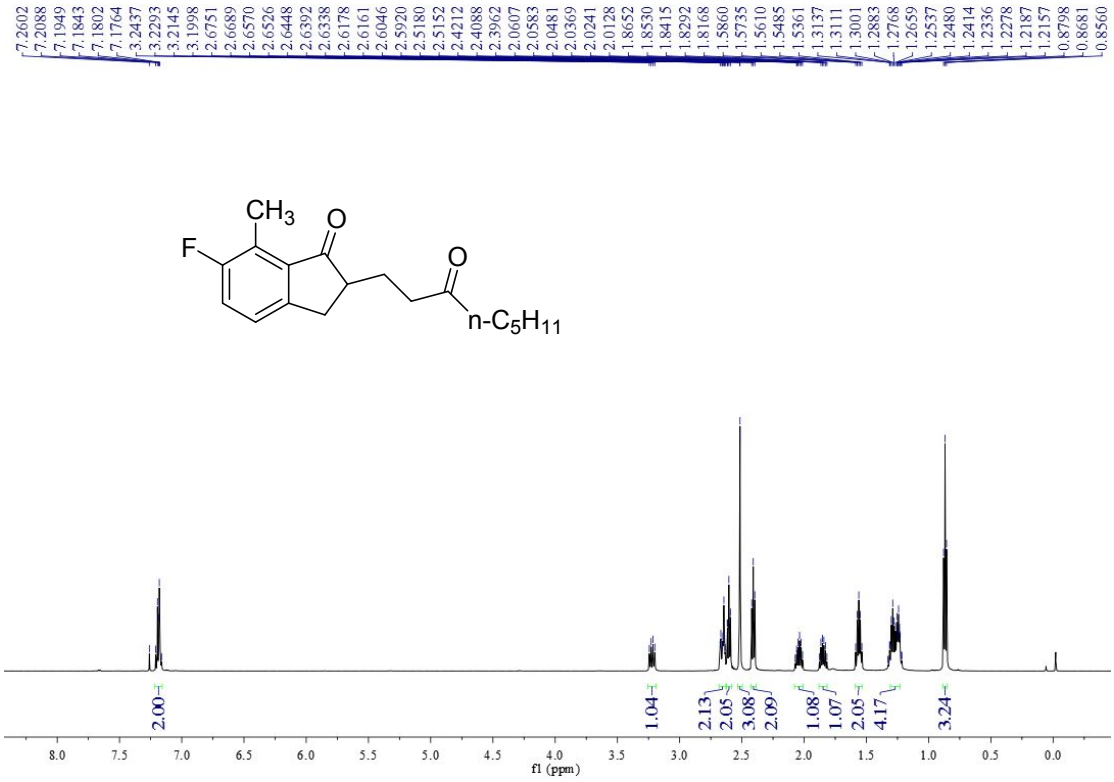
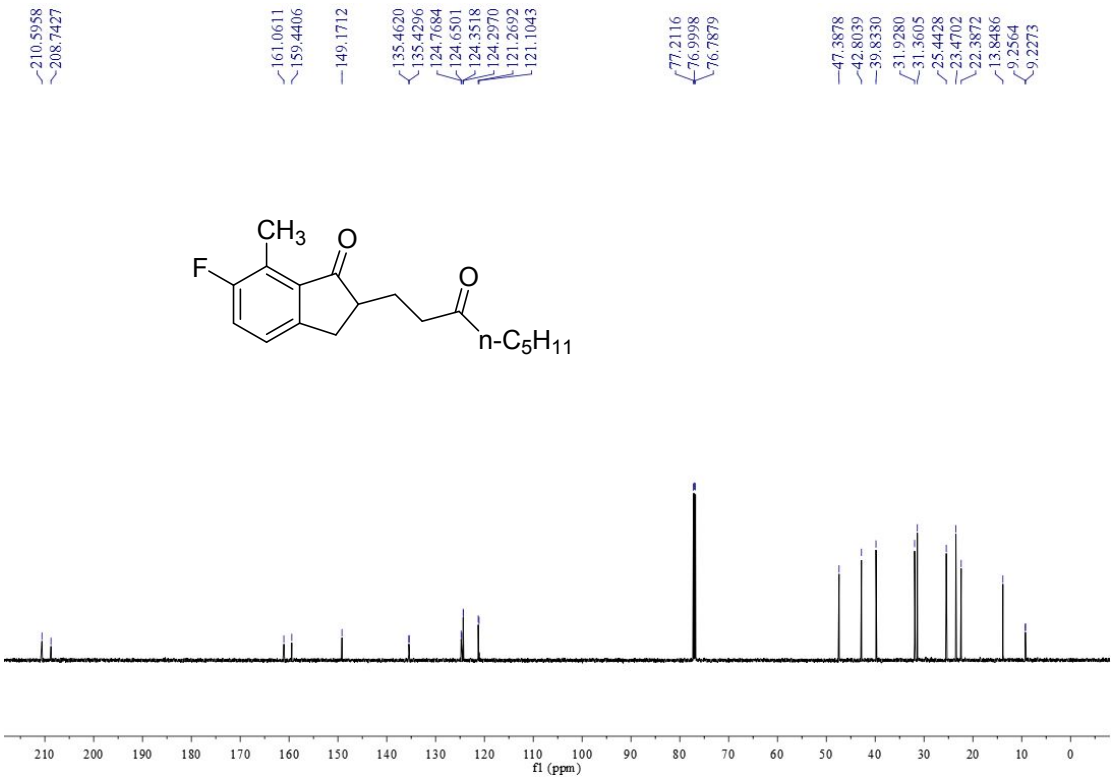


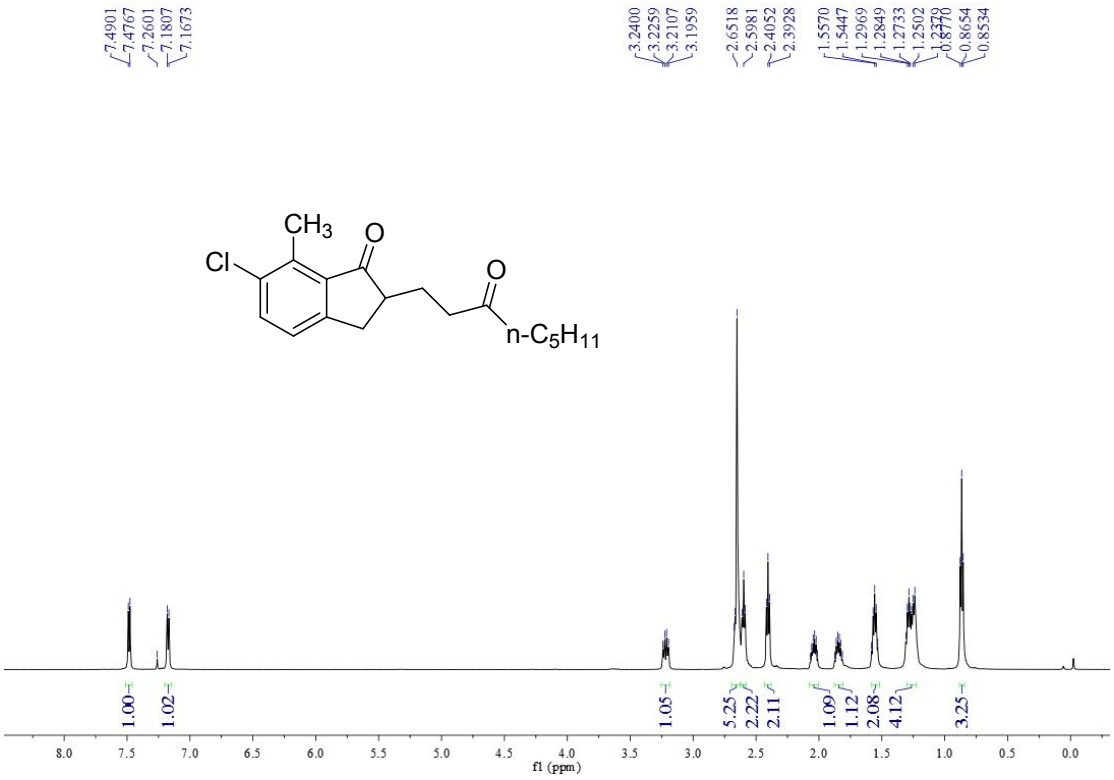
^{1}H NMR spectra of compound 4m



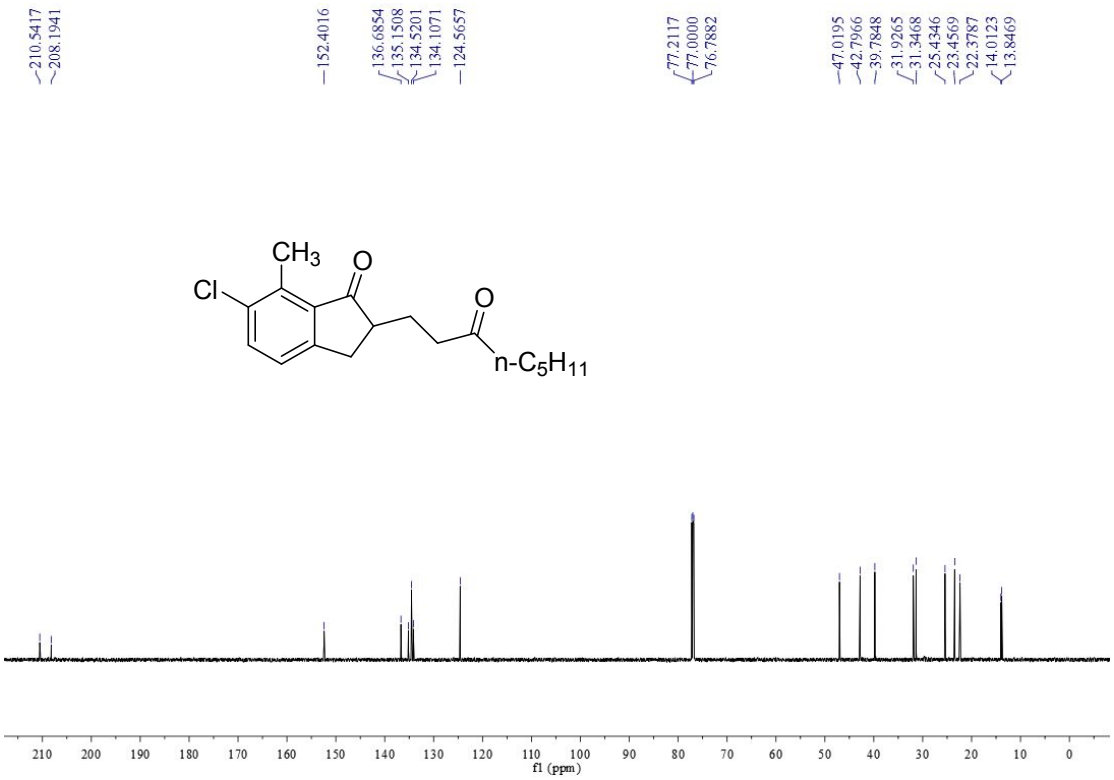
^{13}C NMR spectra of compound 4m



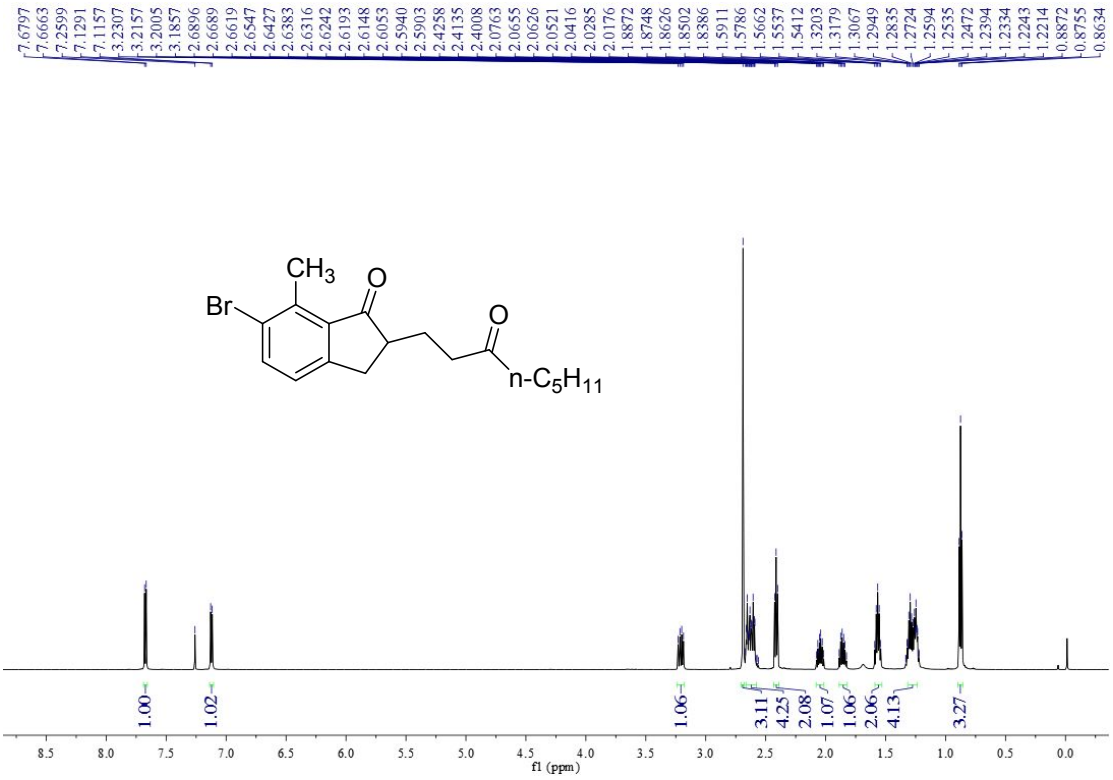
^{1}H NMR spectra of compound 4n



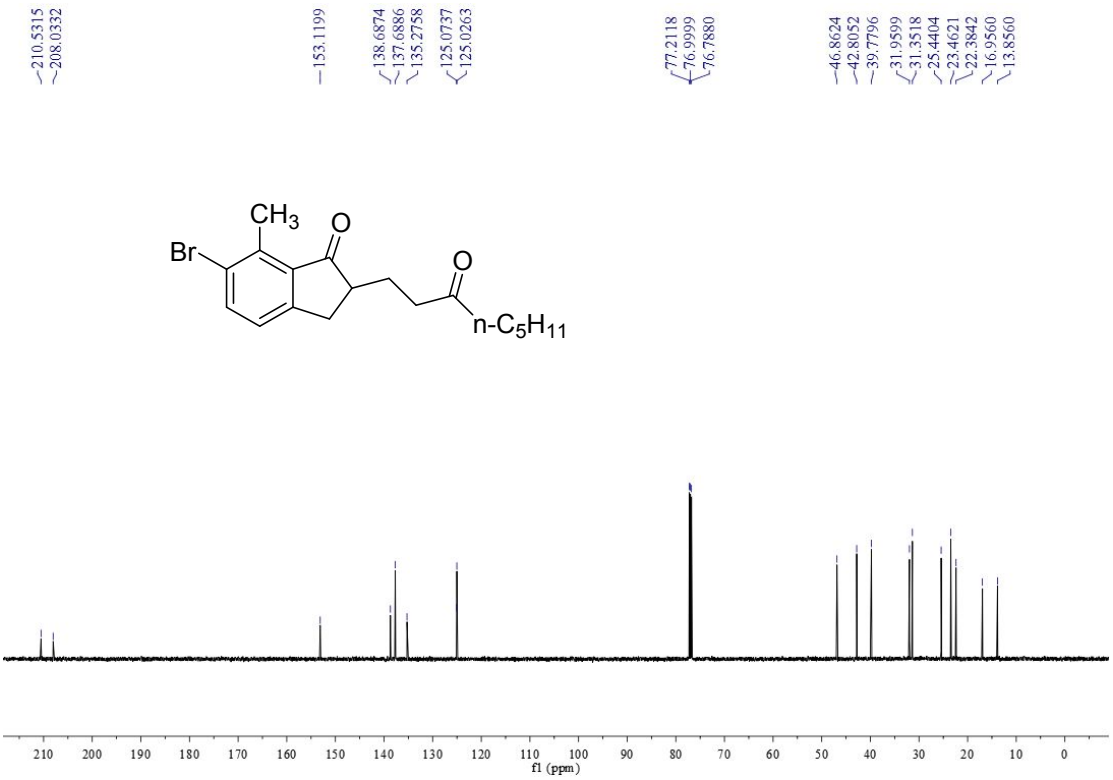
^{13}C NMR spectra of compound 4n



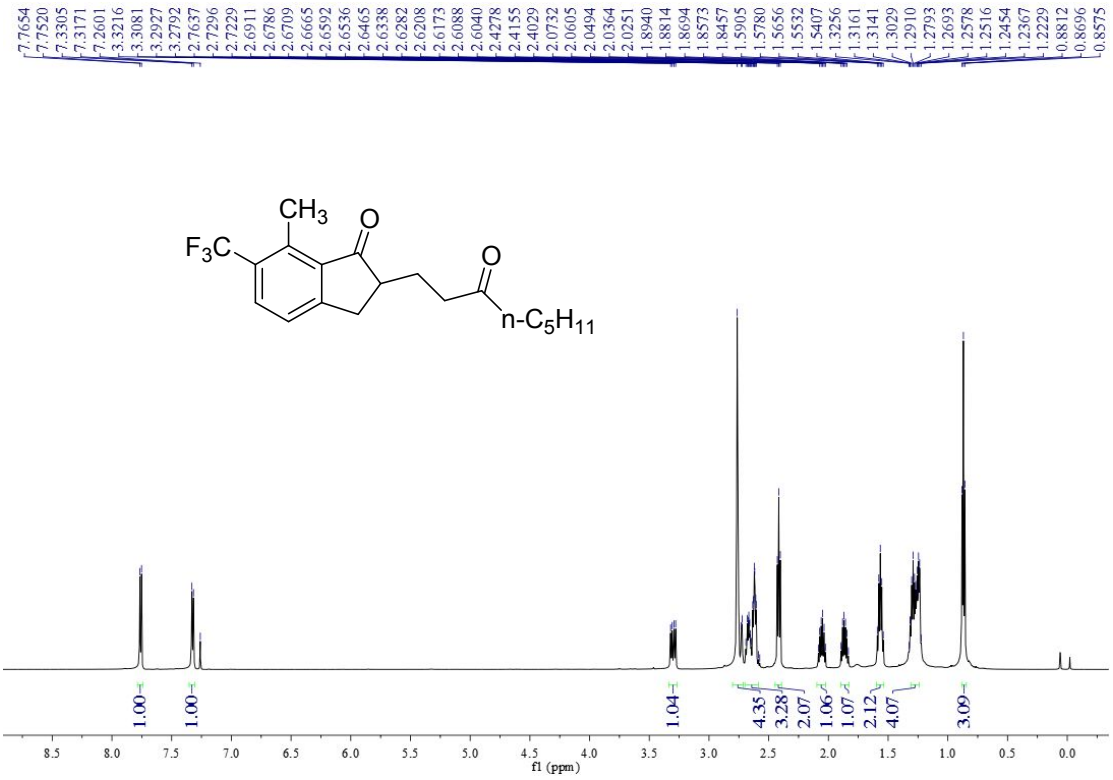
^{1}H NMR spectra of compound 4o



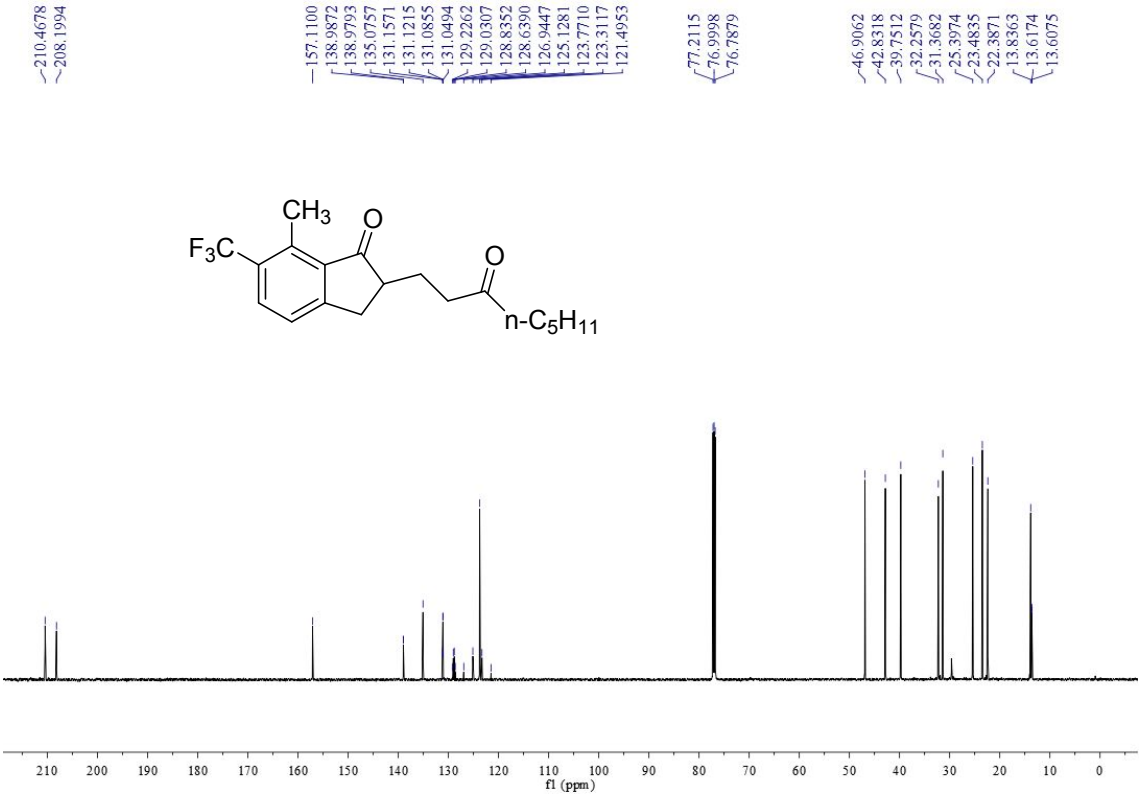
^{13}C NMR spectra of compound 4o



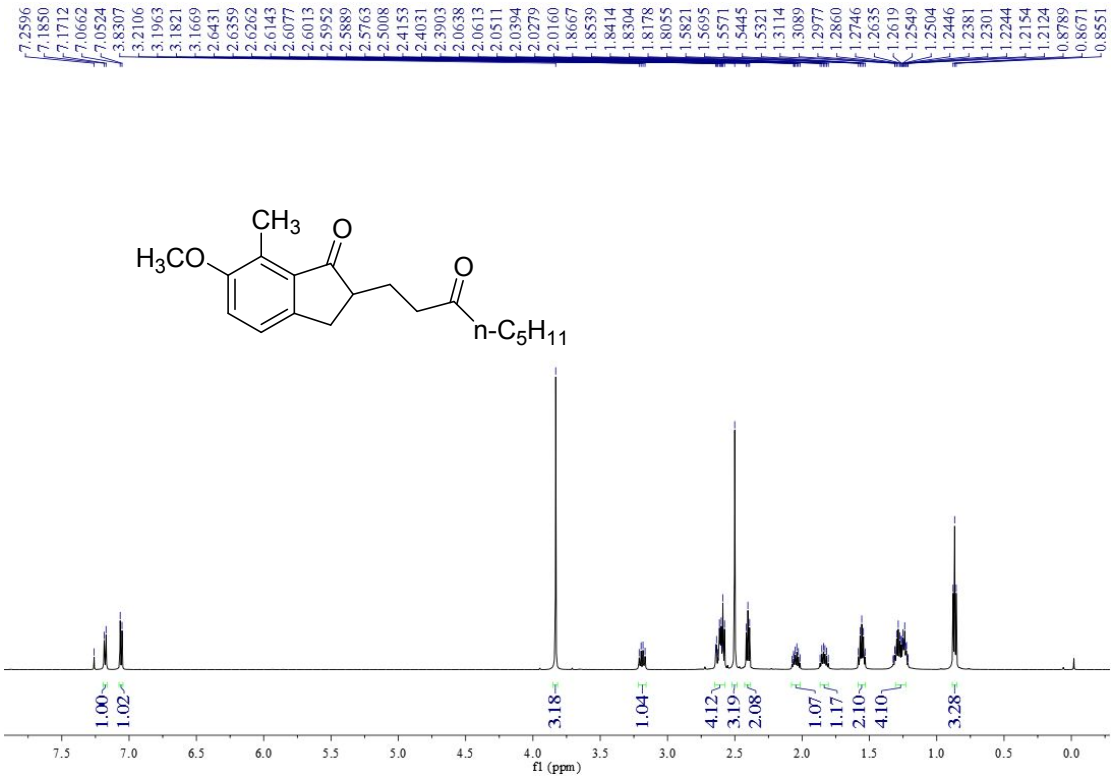
^{1}H NMR spectra of compound 4p



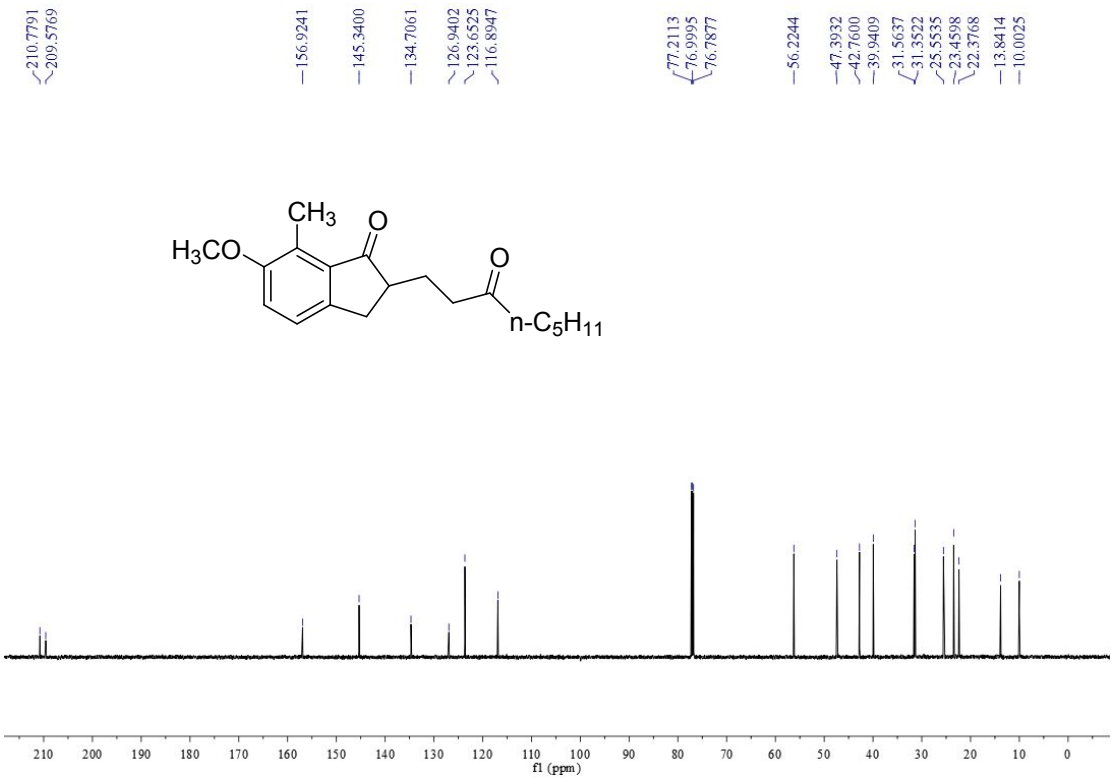
^{13}C NMR spectra of compound 4p



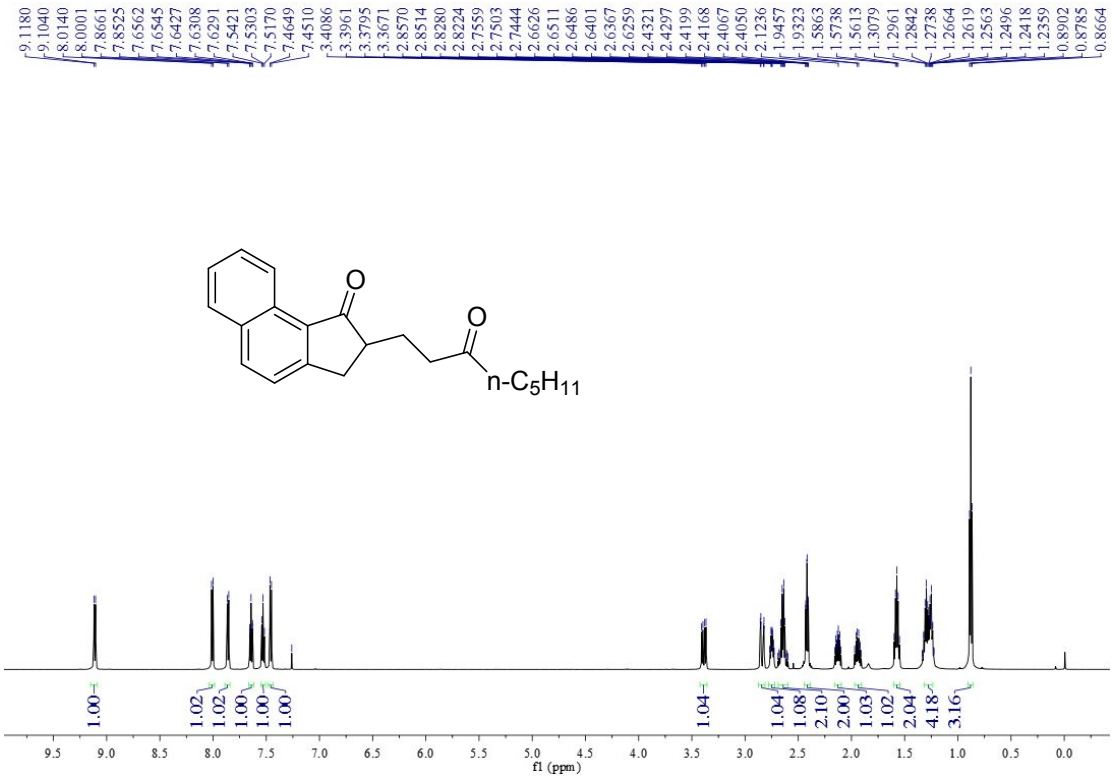
^{1}H NMR spectra of compound 4q



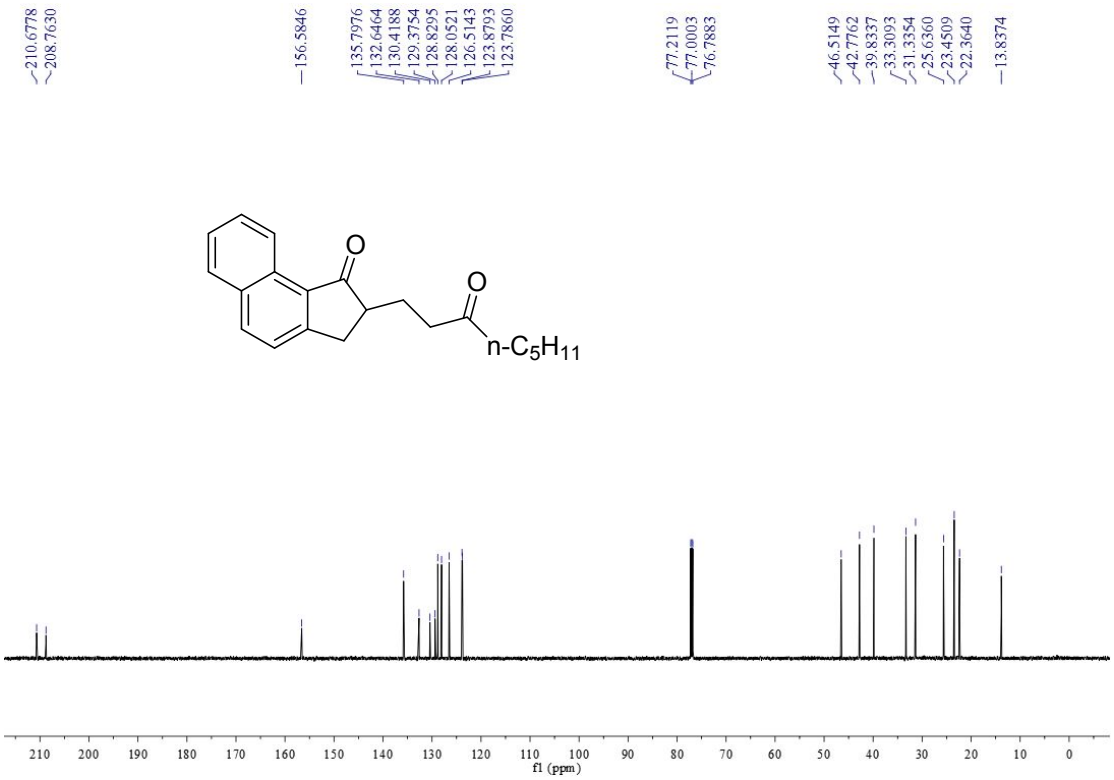
^{13}C NMR spectra of compound 4q



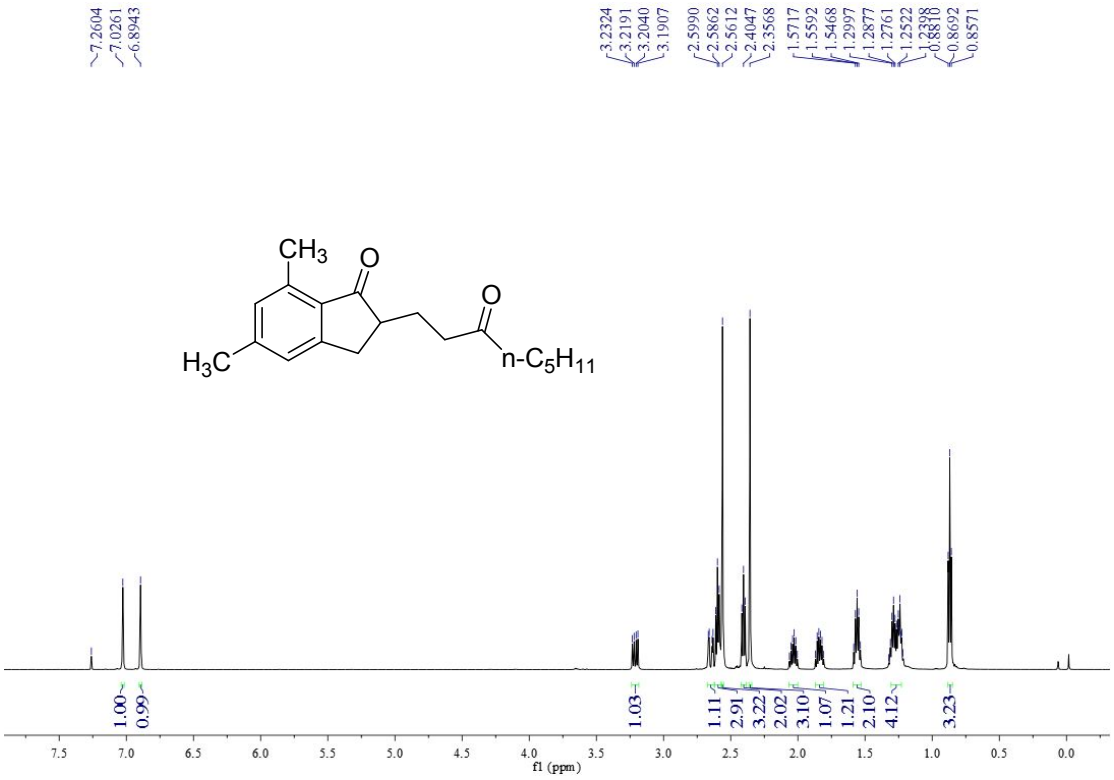
^{1}H NMR spectra of compound 4r



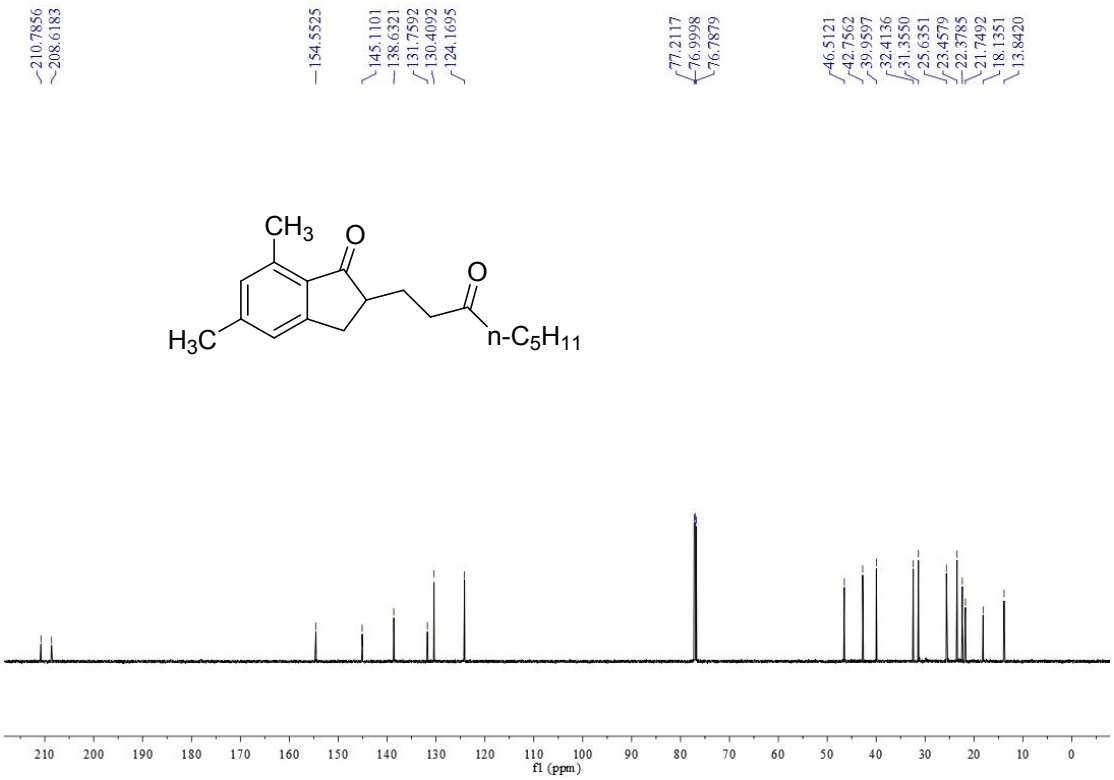
^{13}C NMR spectra of compound 4r



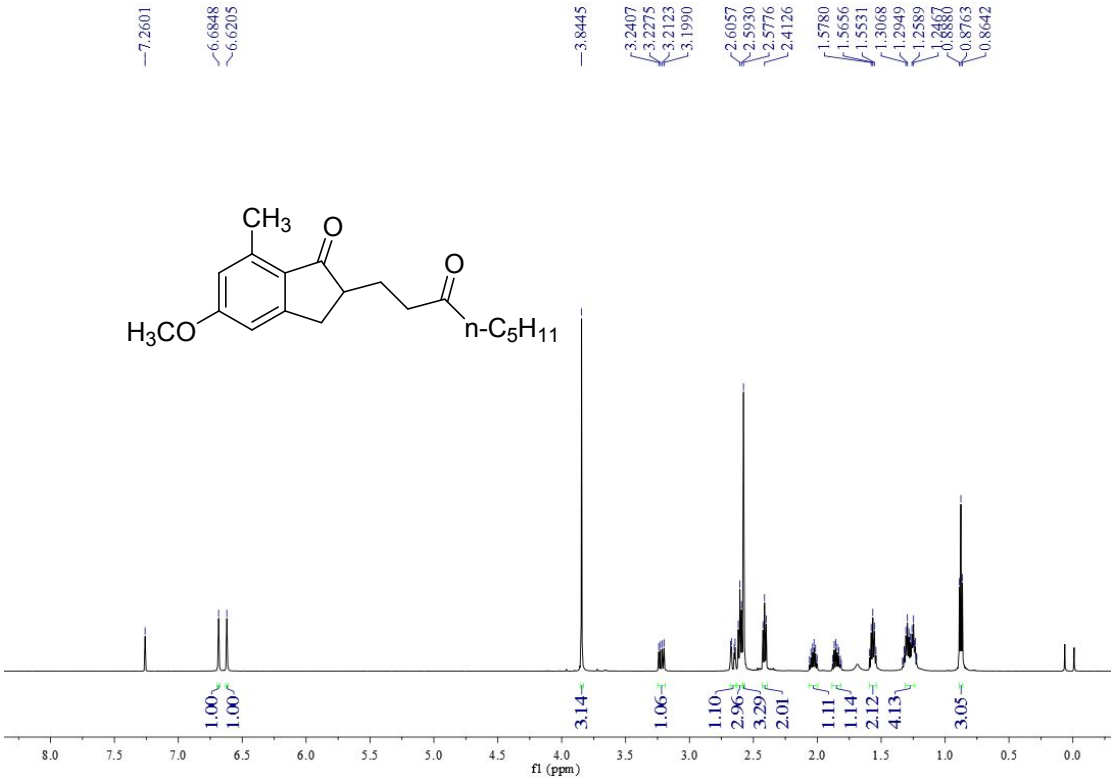
^{1}H NMR spectra of compound 4s



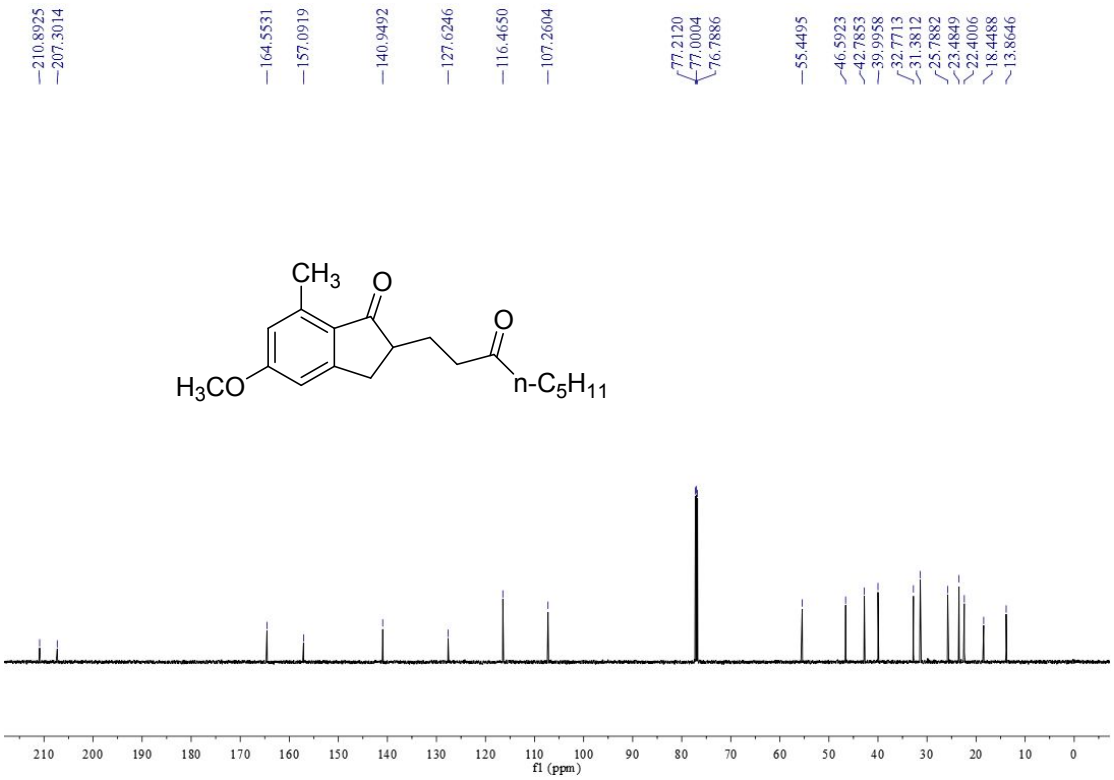
^{13}C NMR spectra of compound 4s



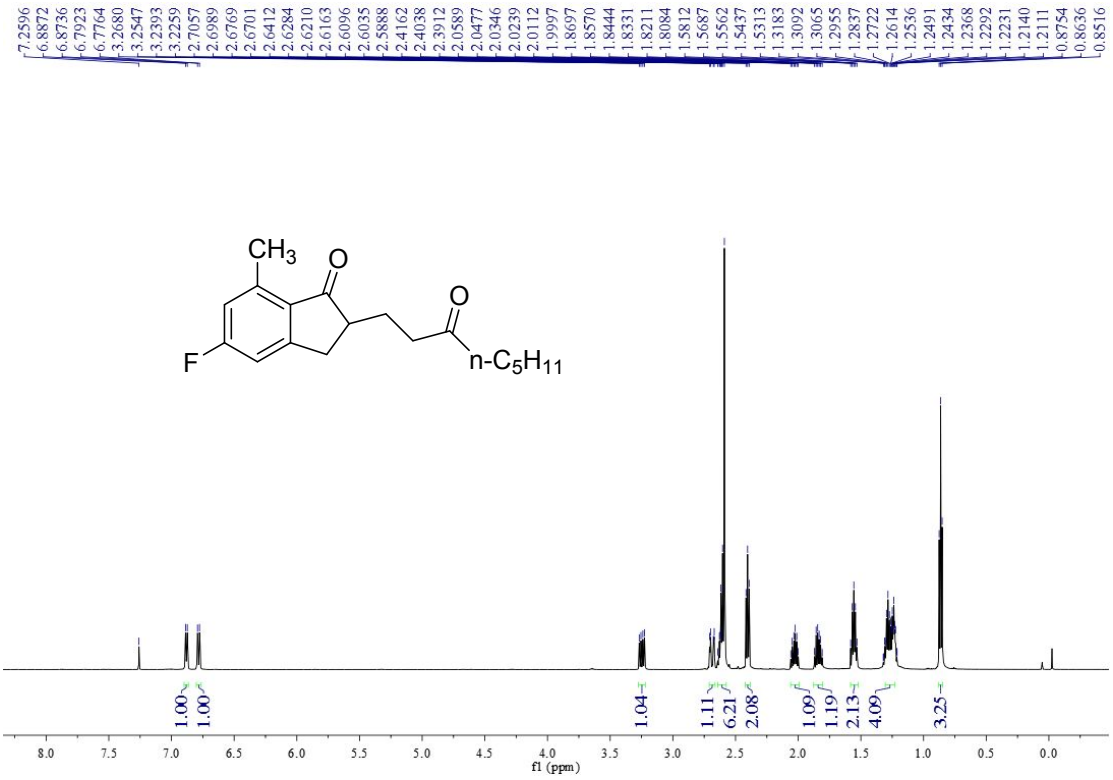
^{1}H NMR spectra of compound 4t



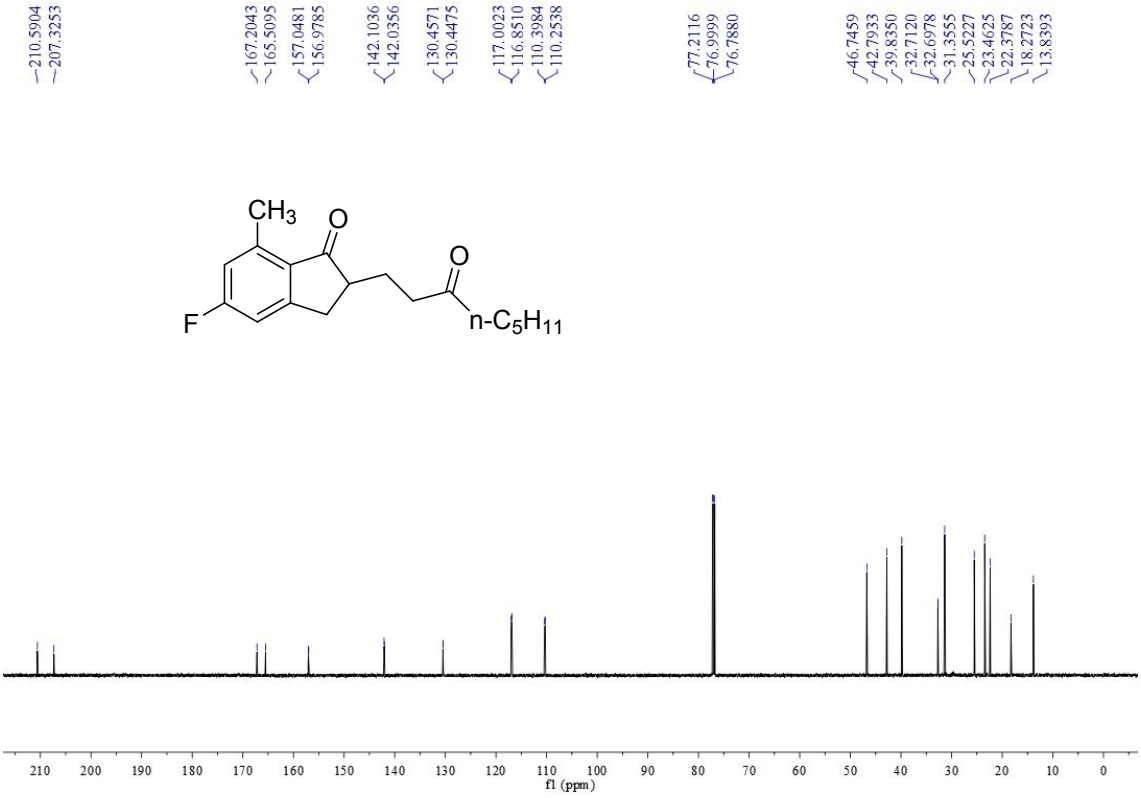
^{13}C NMR spectra of compound 4t



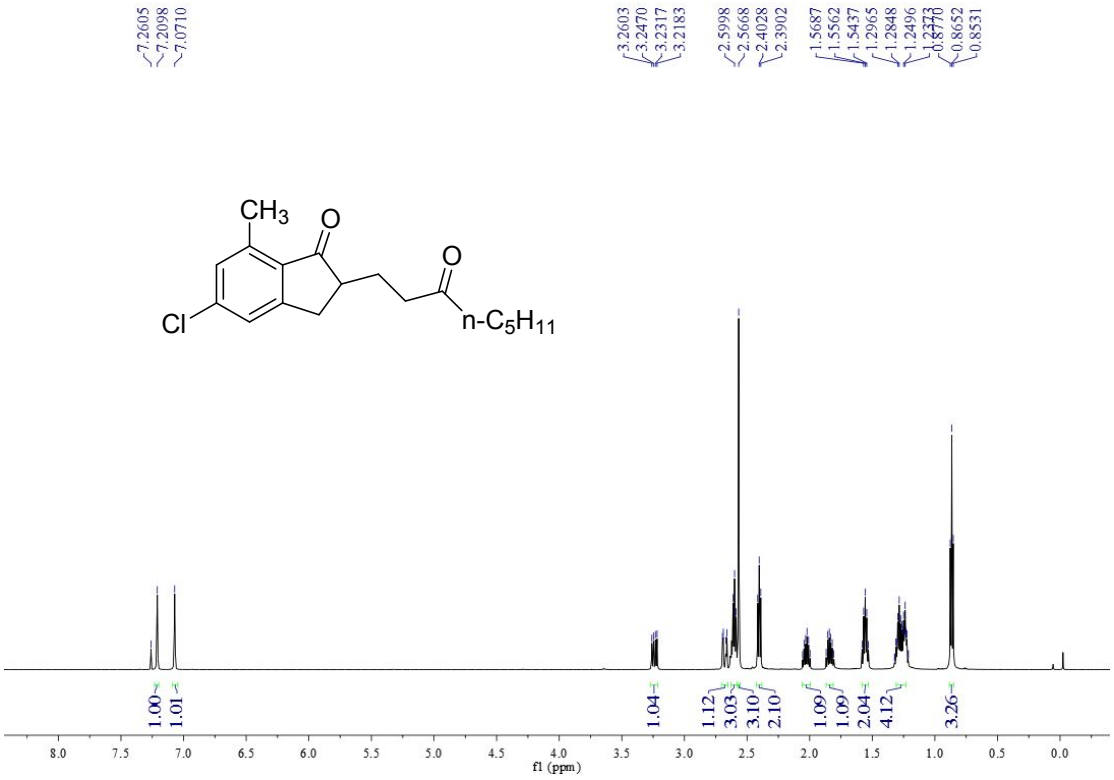
^{1}H NMR spectra of compound 4u



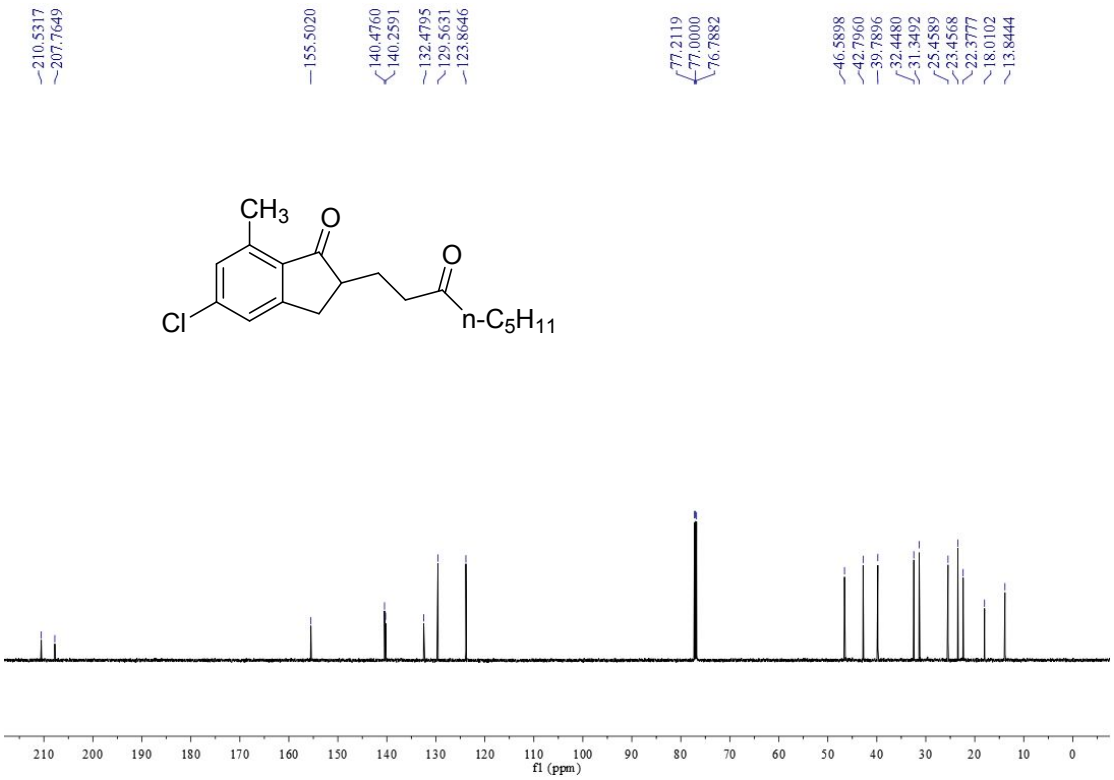
^{13}C NMR spectra of compound 4u



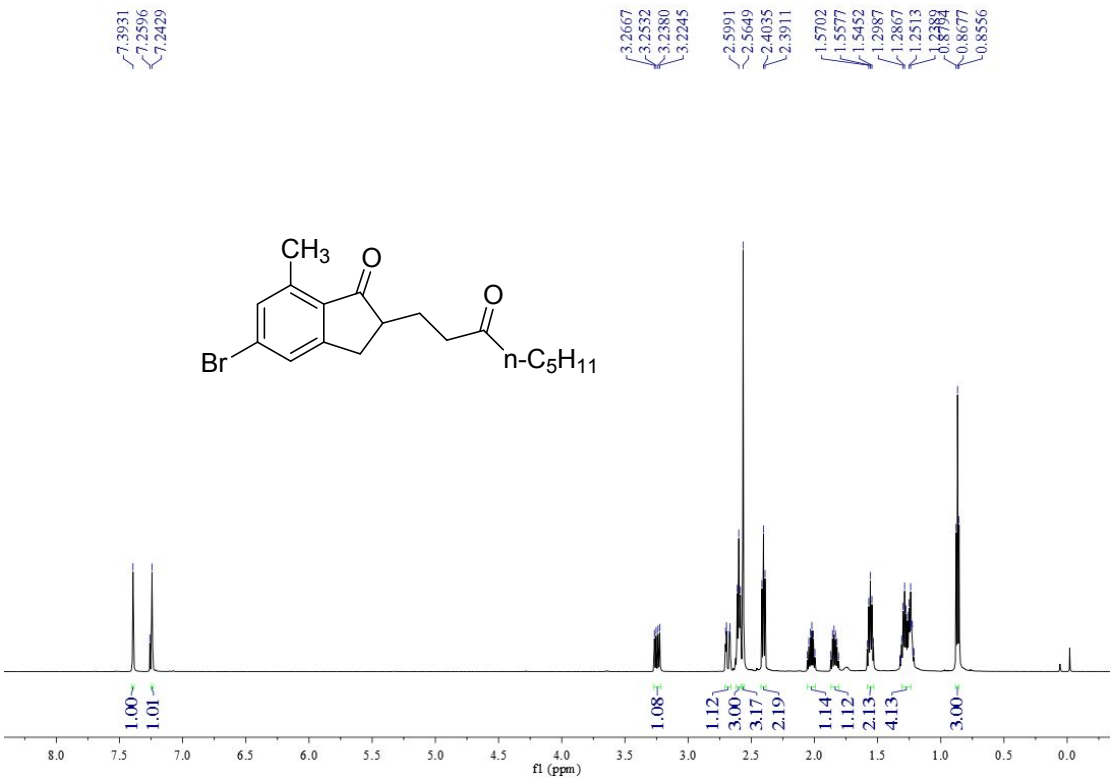
^{1}H NMR spectra of compound 4v



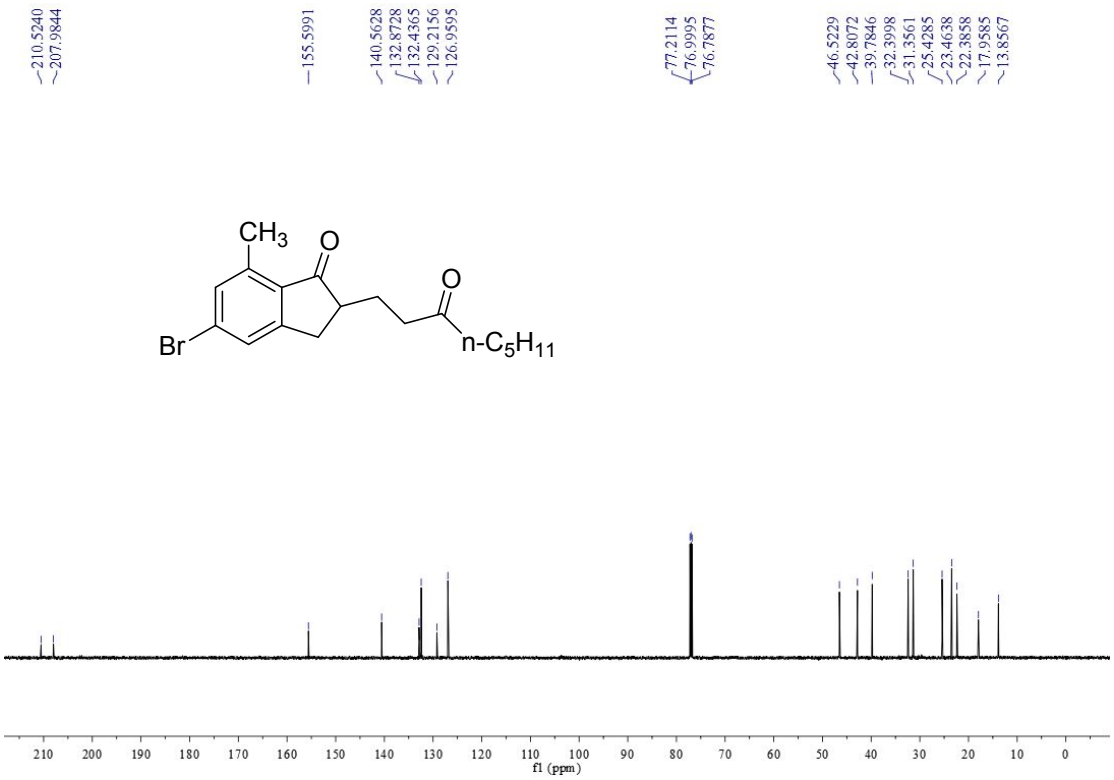
^{13}C NMR spectra of compound 4v



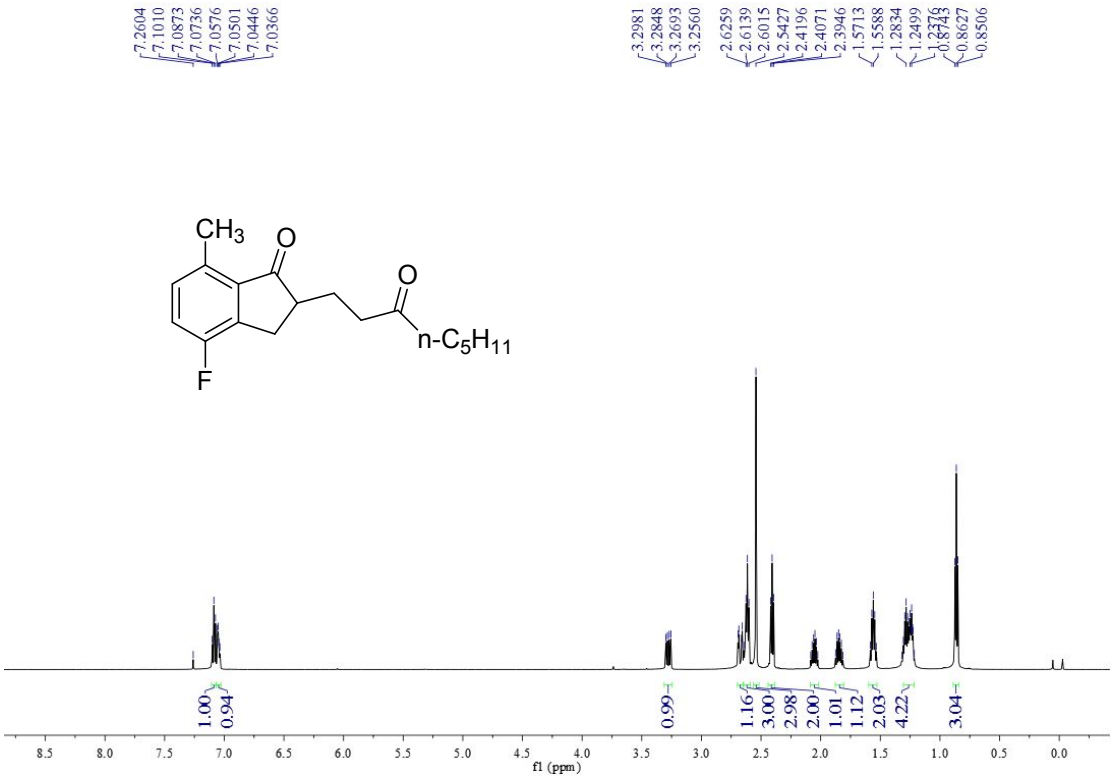
^{1}H NMR spectra of compound 4w



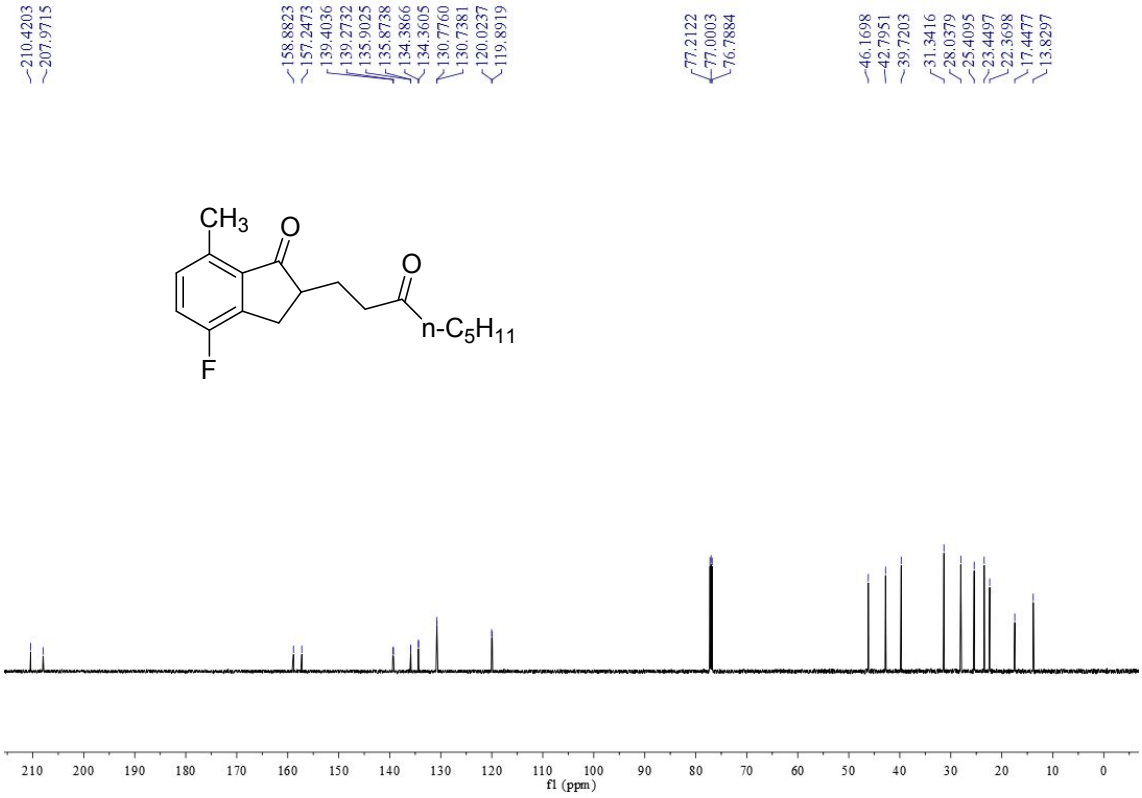
^{13}C NMR spectra of compound 4w



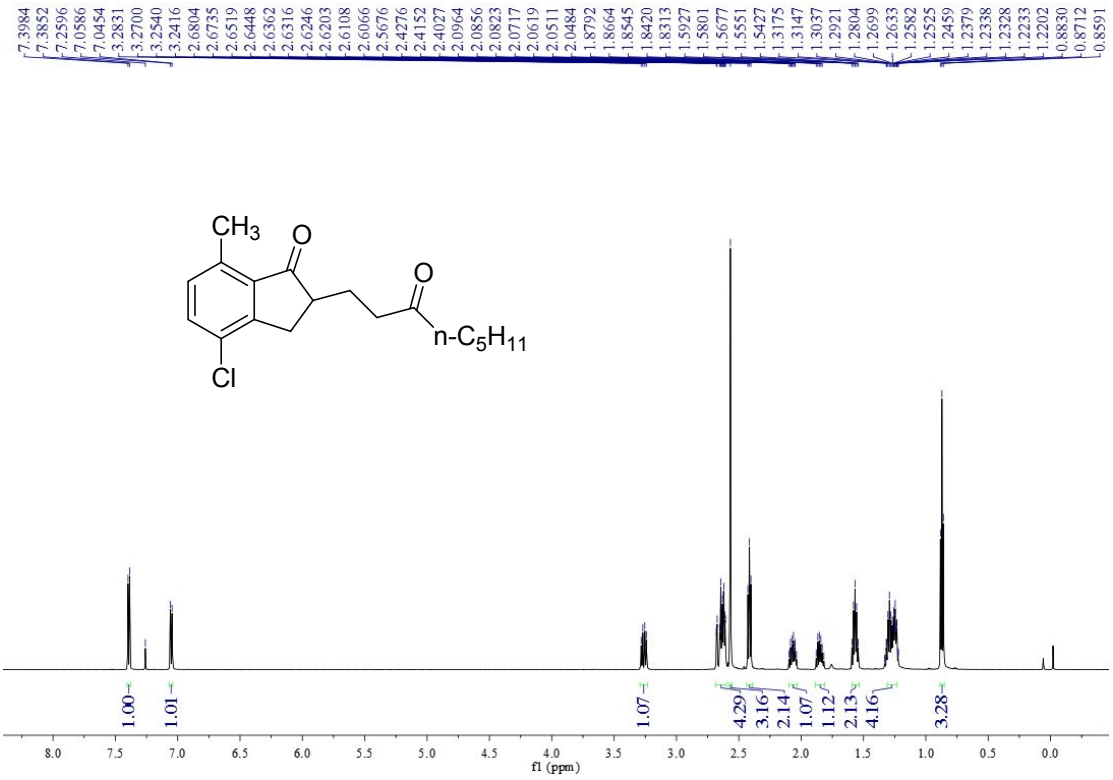
^{1}H NMR spectra of compound 4x



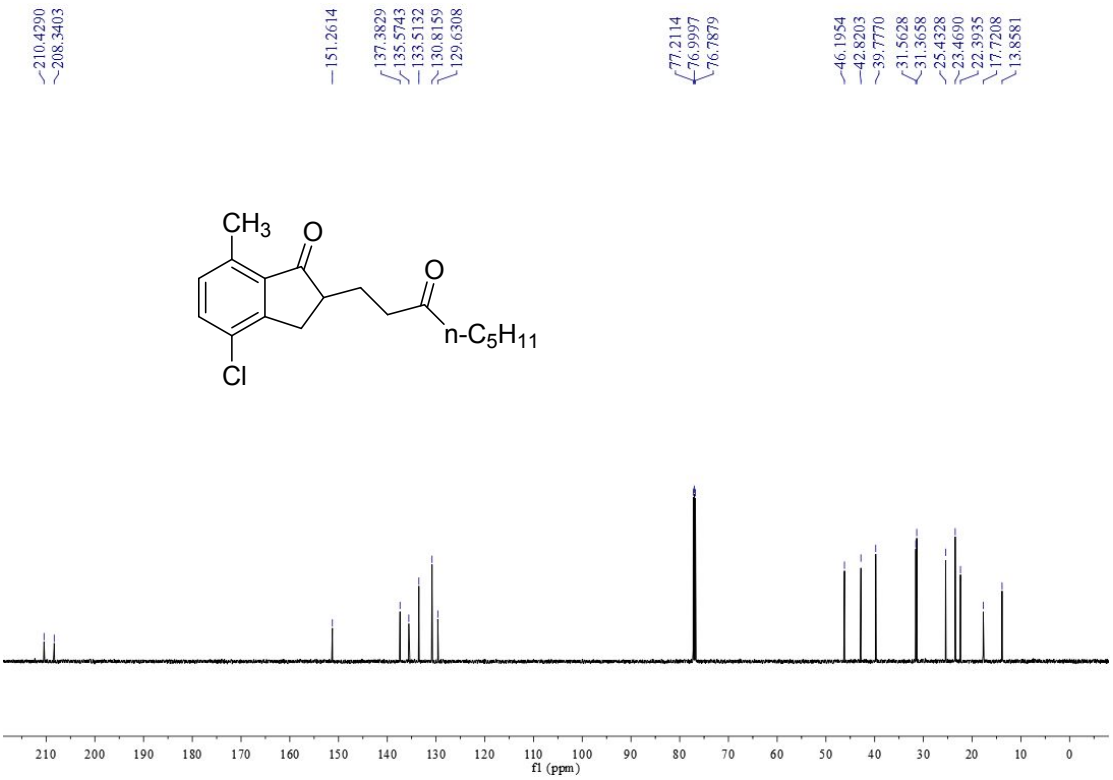
^{13}C NMR spectra of compound 4x



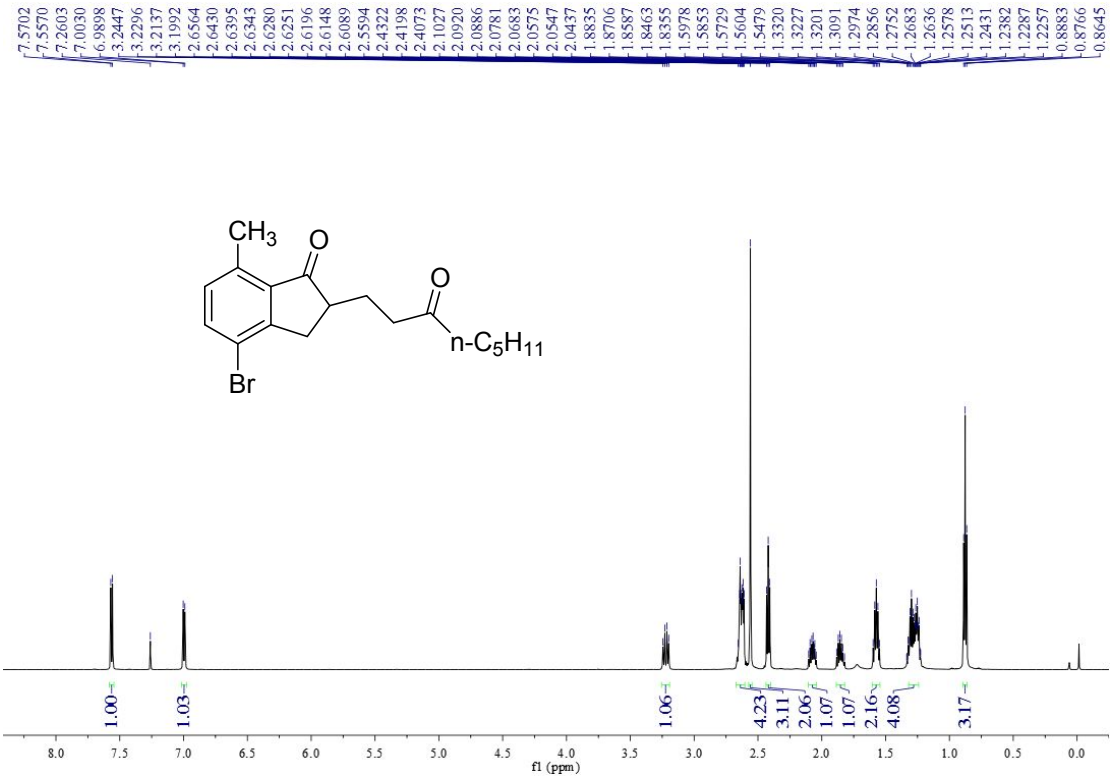
^{1}H NMR spectra of compound 4y



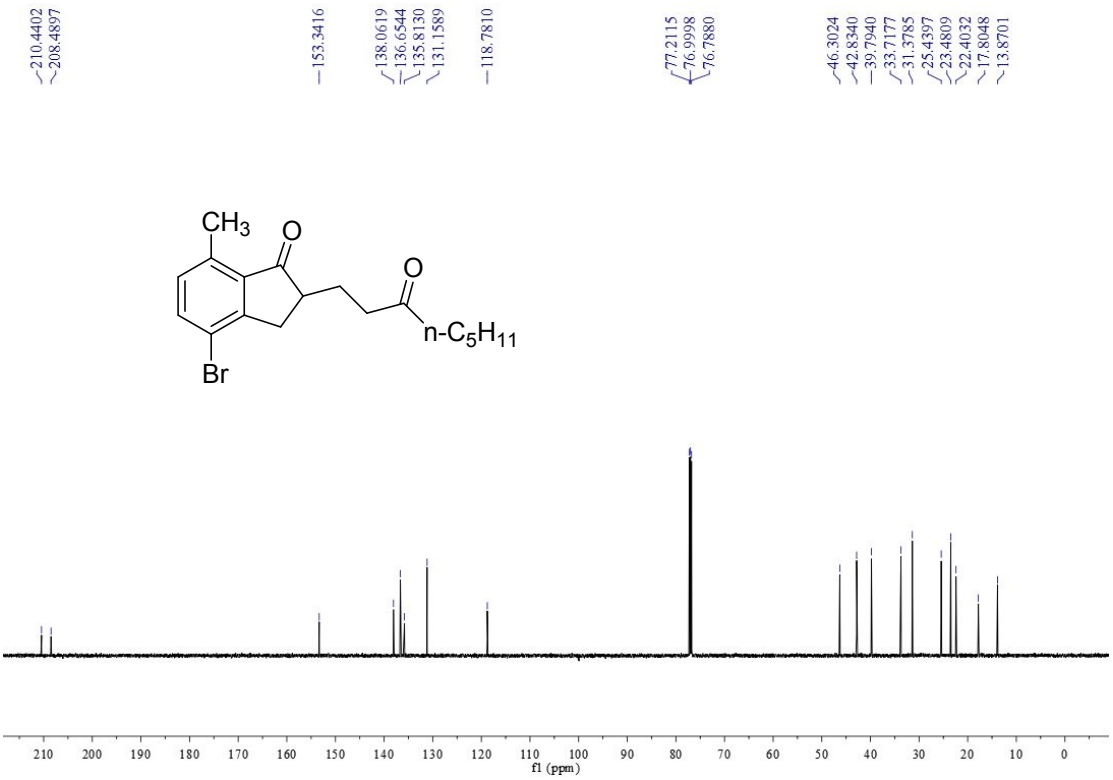
^{13}C NMR spectra of compound 4y



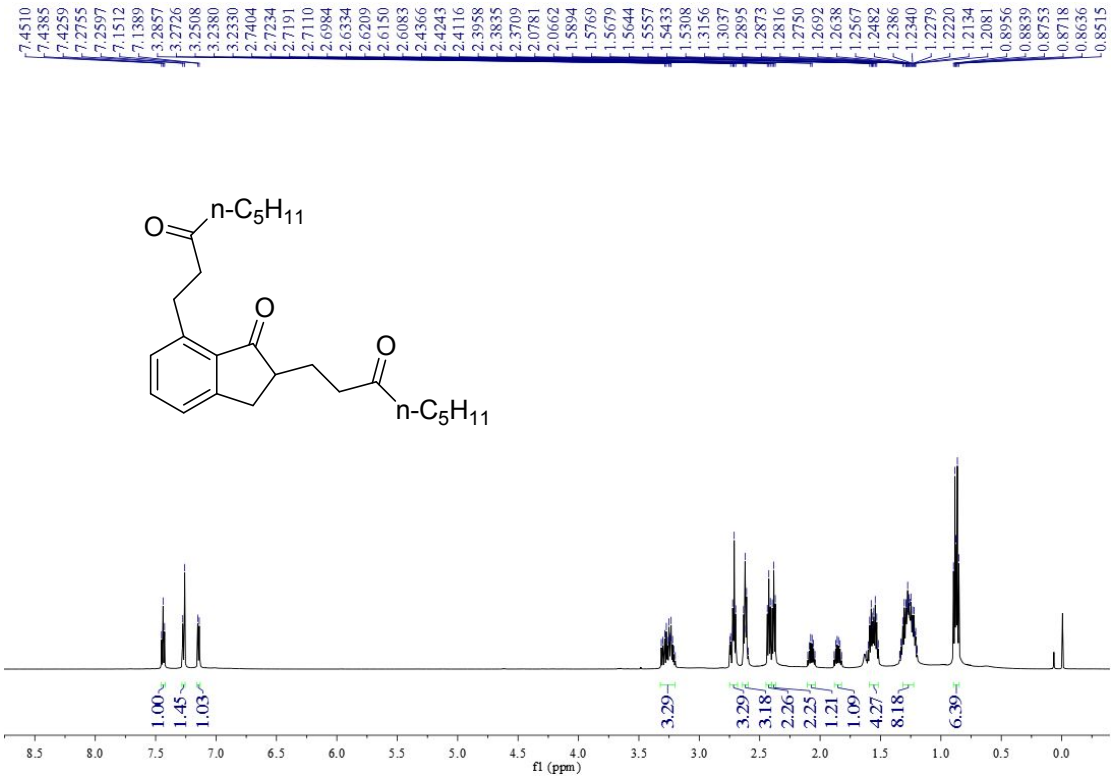
^{1}H NMR spectra of compound 4z



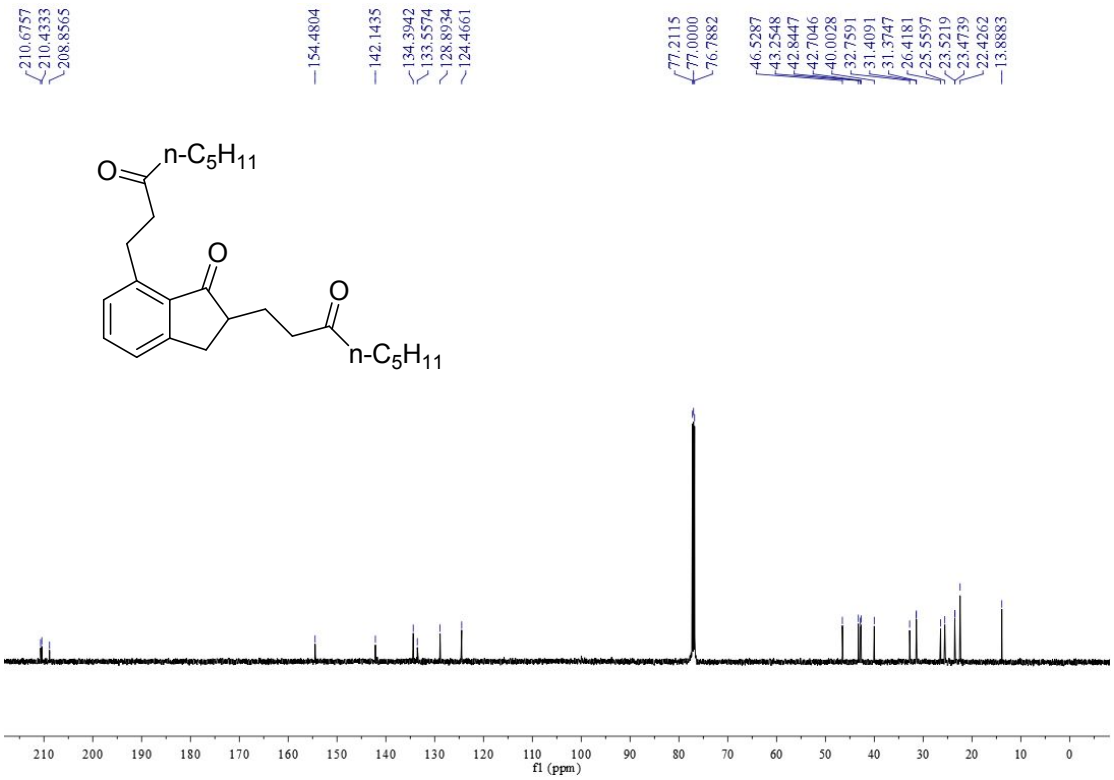
^{13}C NMR spectra of compound 4z



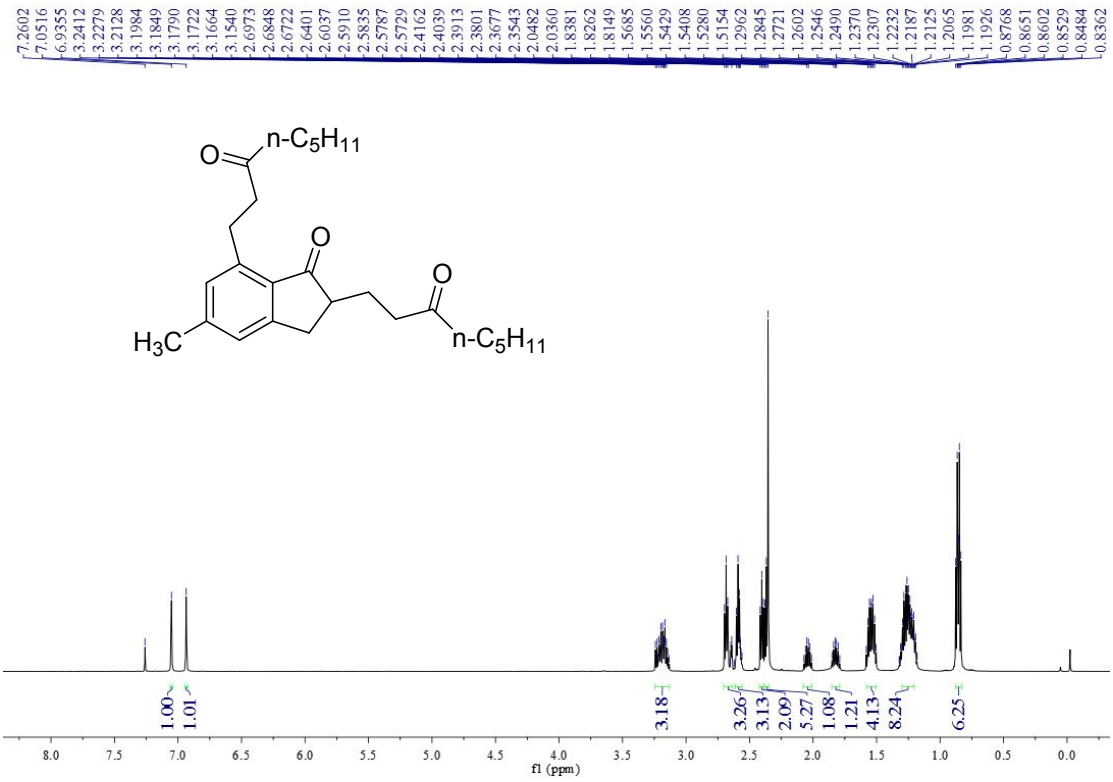
^{1}H NMR spectra of compound 4aa



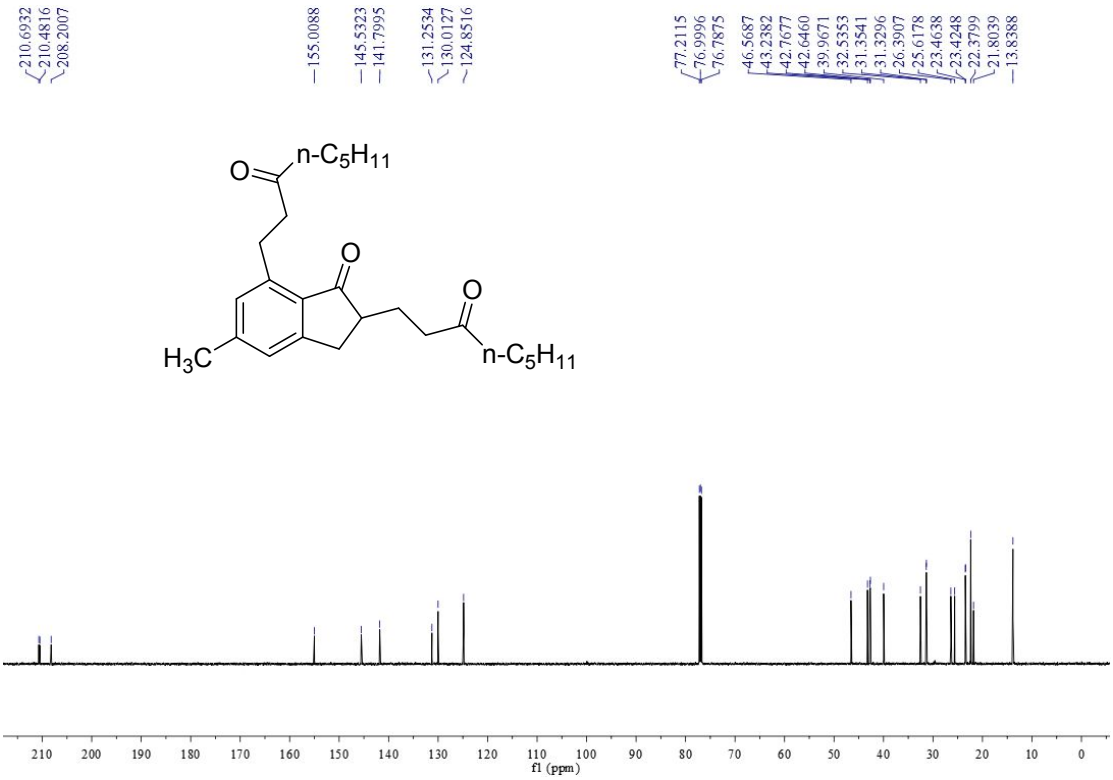
^{13}C NMR spectra of compound 4aa



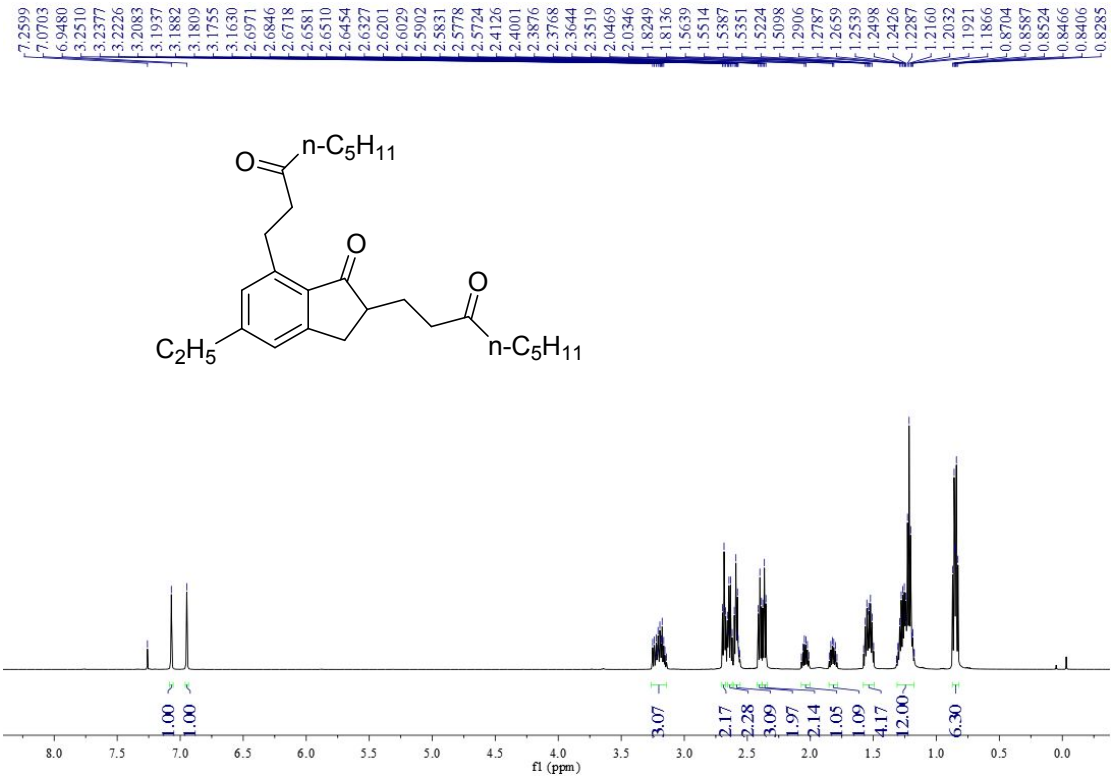
^{1}H NMR spectra of compound 4ab



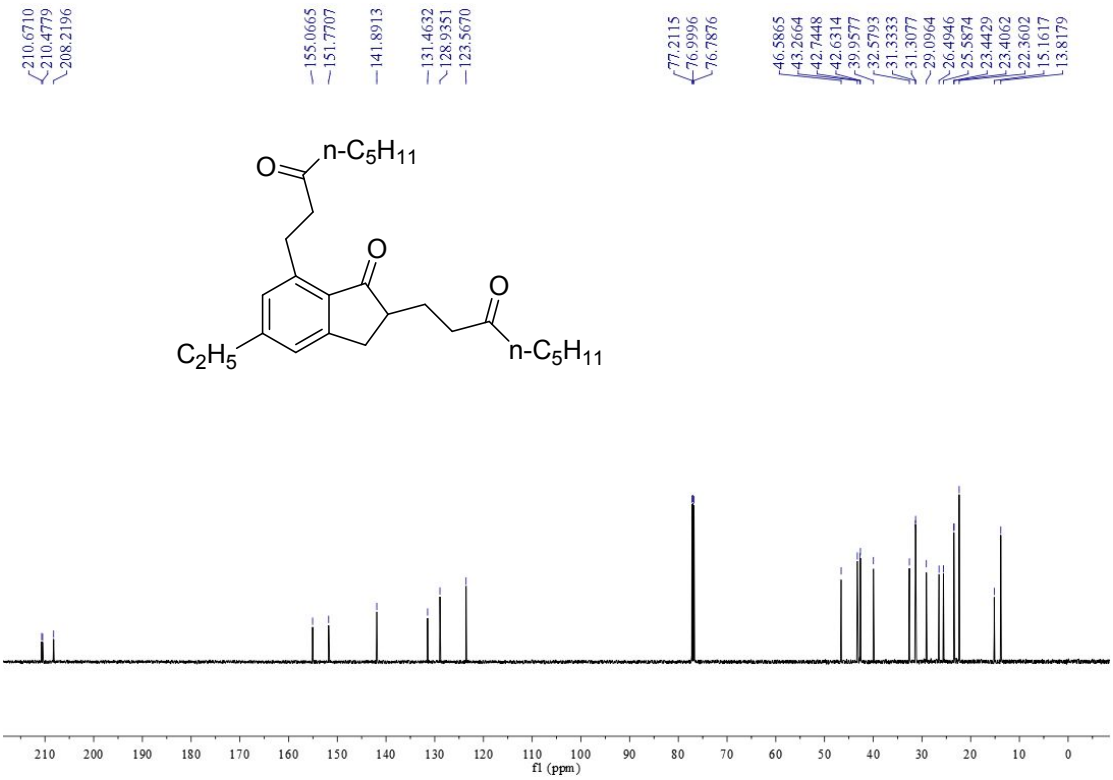
^{13}C NMR spectra of compound 4ab



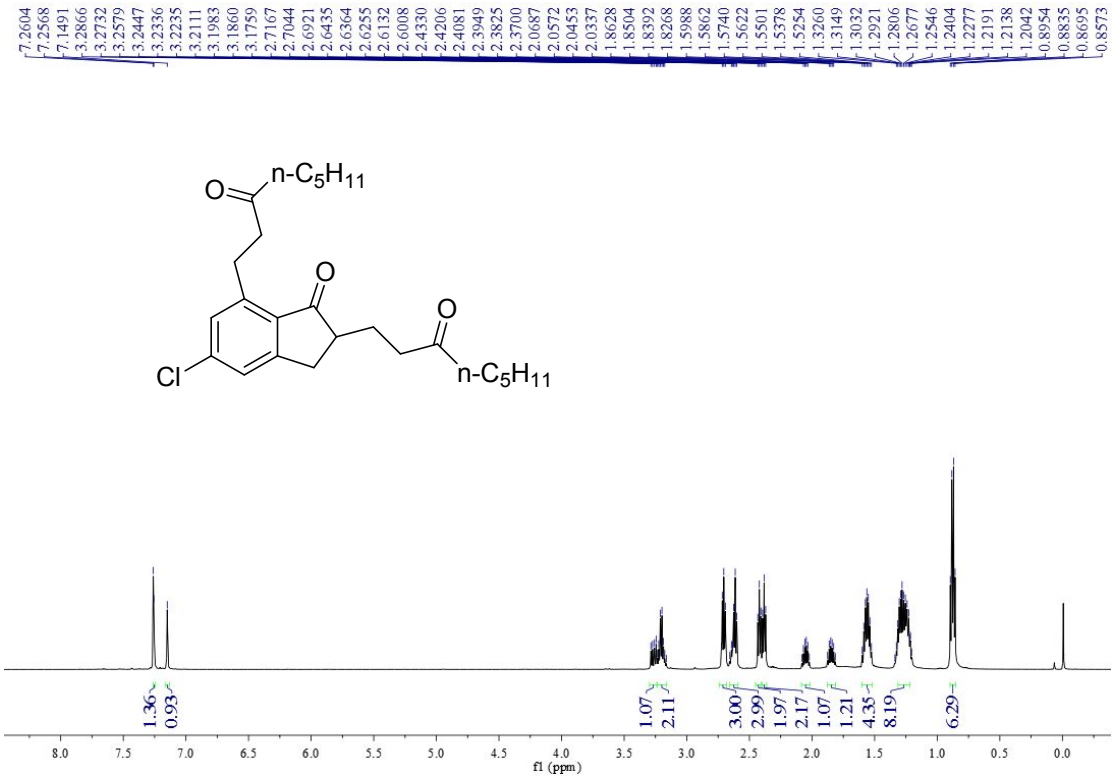
^{1}H NMR spectra of compound 4ac



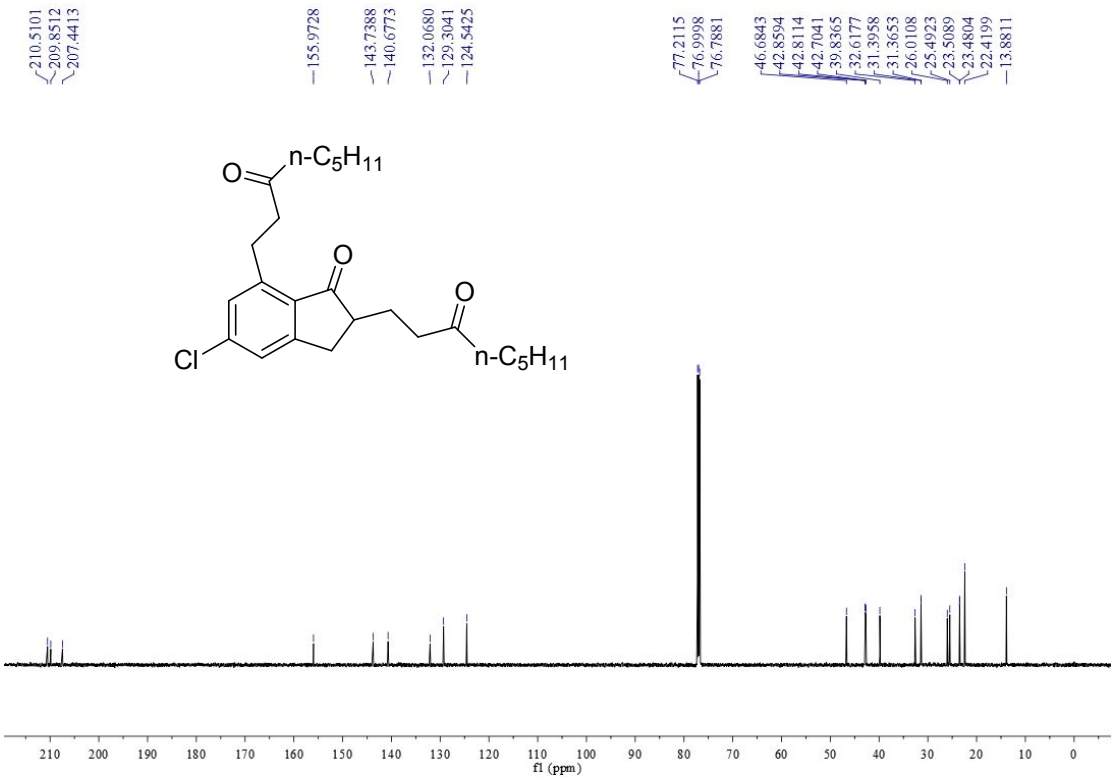
^{13}C NMR spectra of compound 4ac



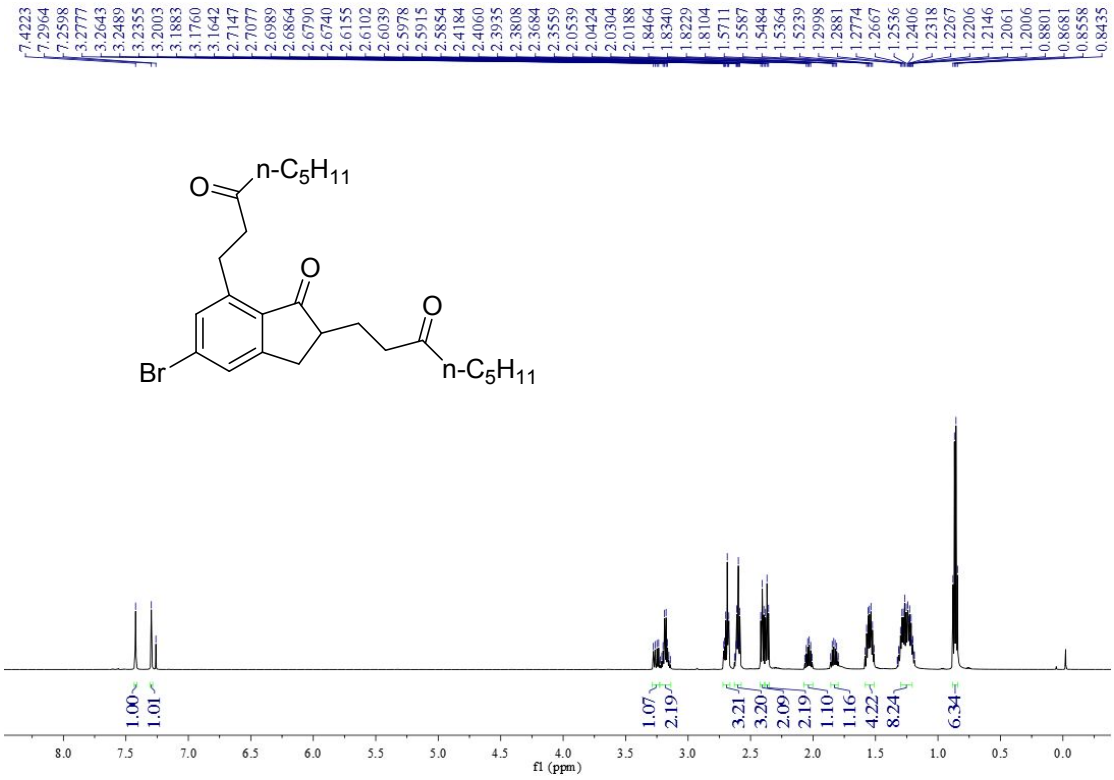
^{1}H NMR spectra of compound 4ad



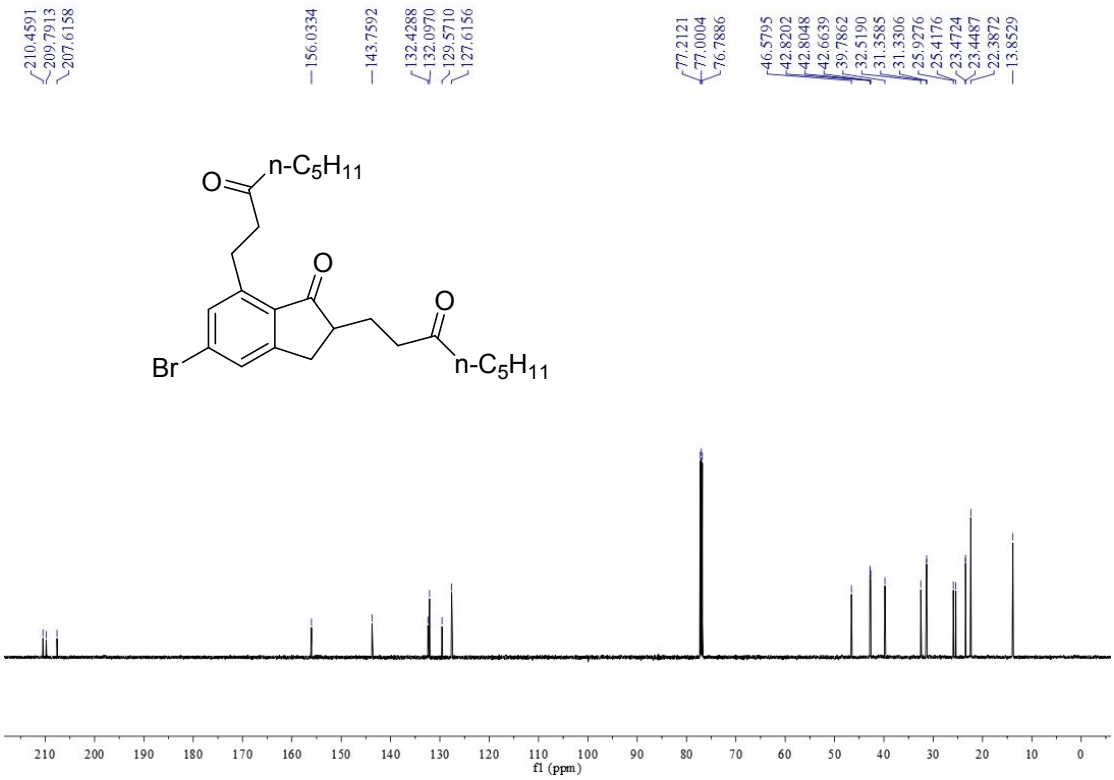
^{13}C NMR spectra of compound 4ad



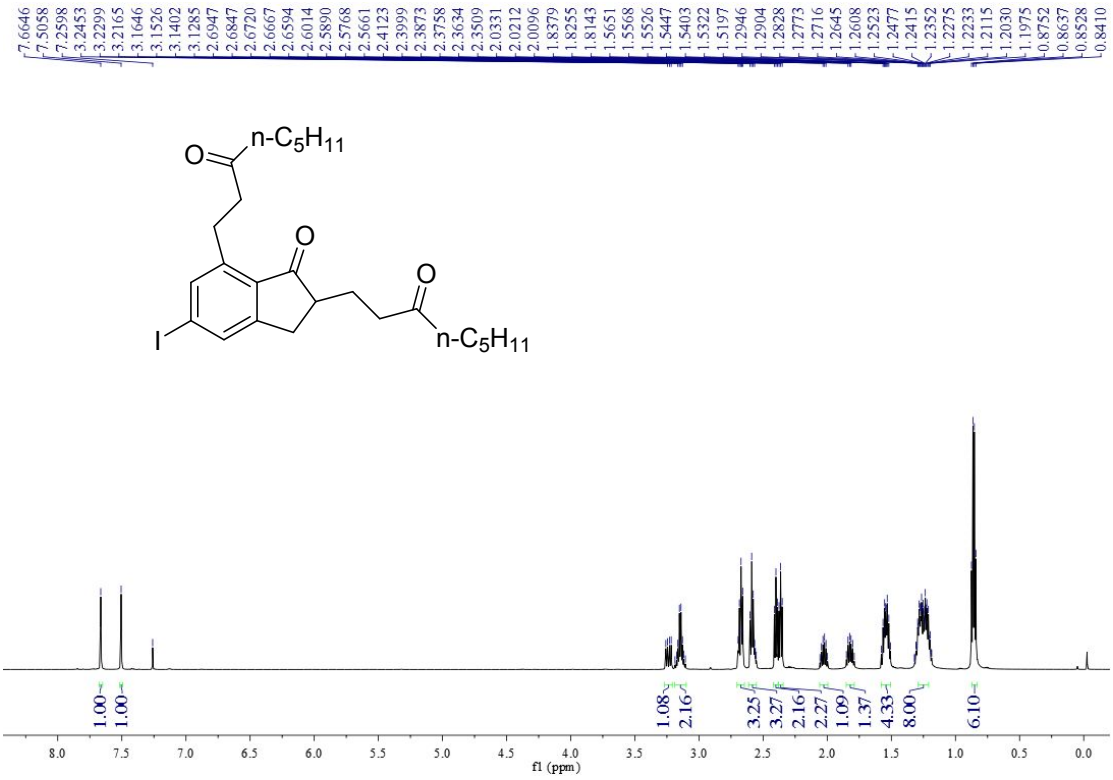
^{1}H NMR spectra of compound 4ae



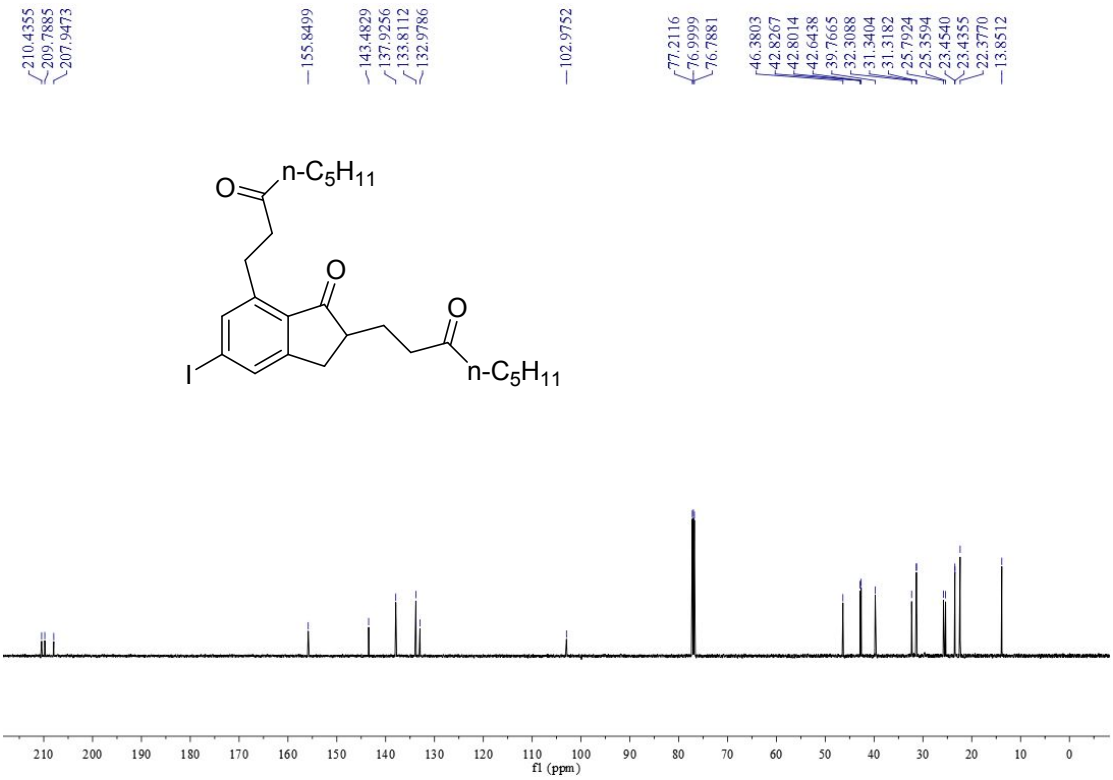
^{13}C NMR spectra of compound 4ae



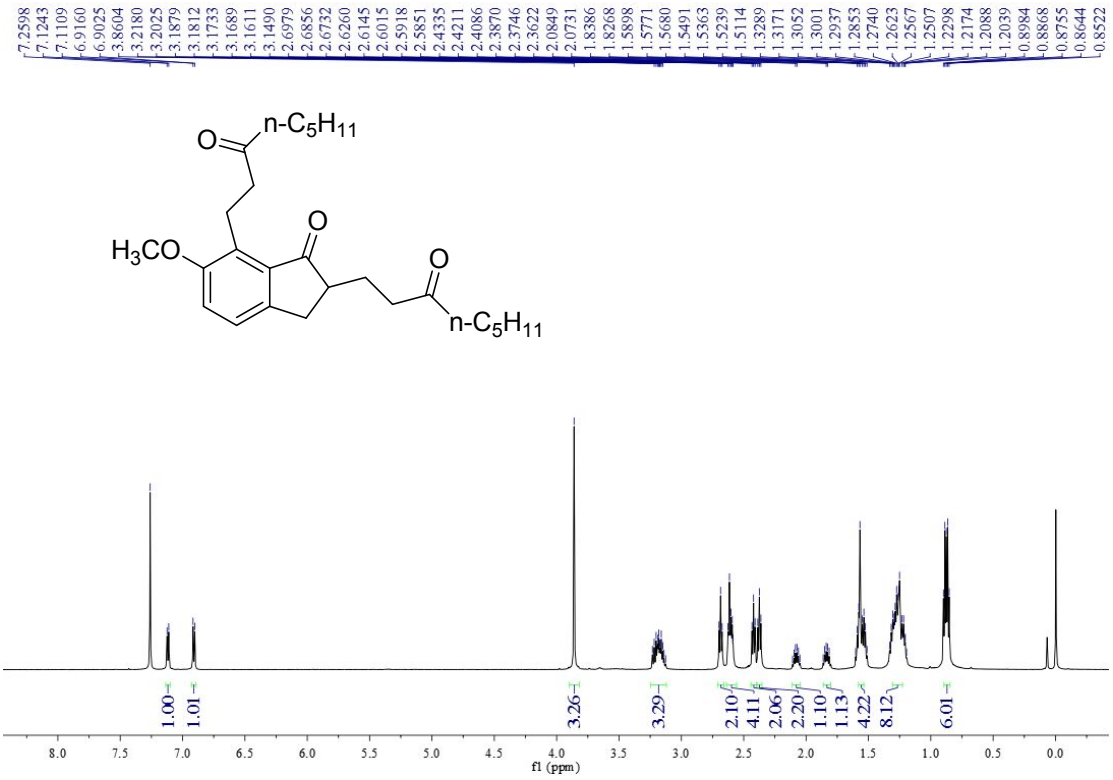
^{1}H NMR spectra of compound 4af



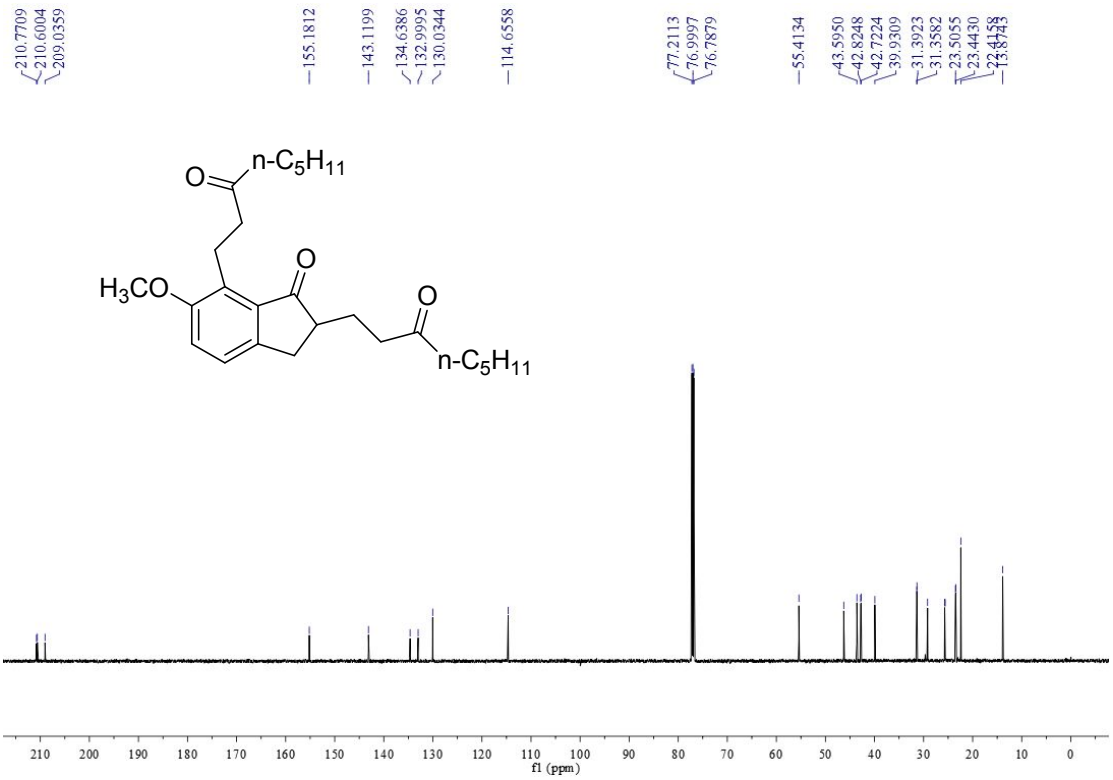
^{13}C NMR spectra of compound 4af



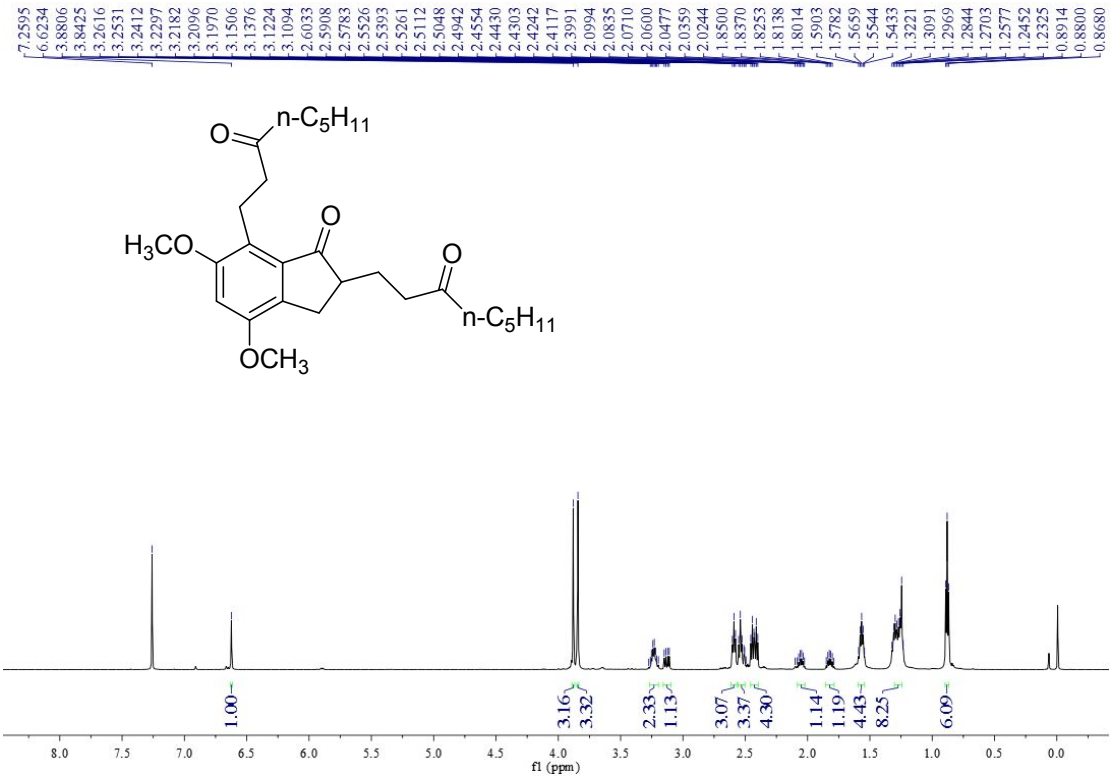
^{1}H NMR spectra of compound 4ag



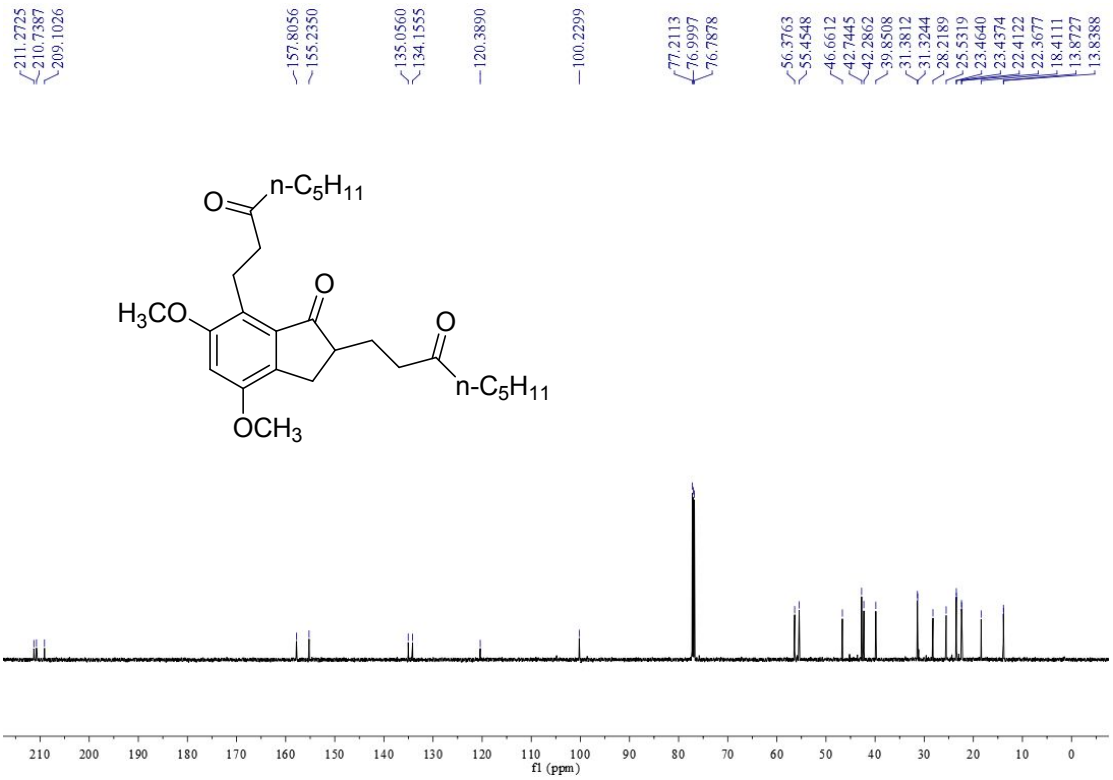
^{13}C NMR spectra of compound 4ag



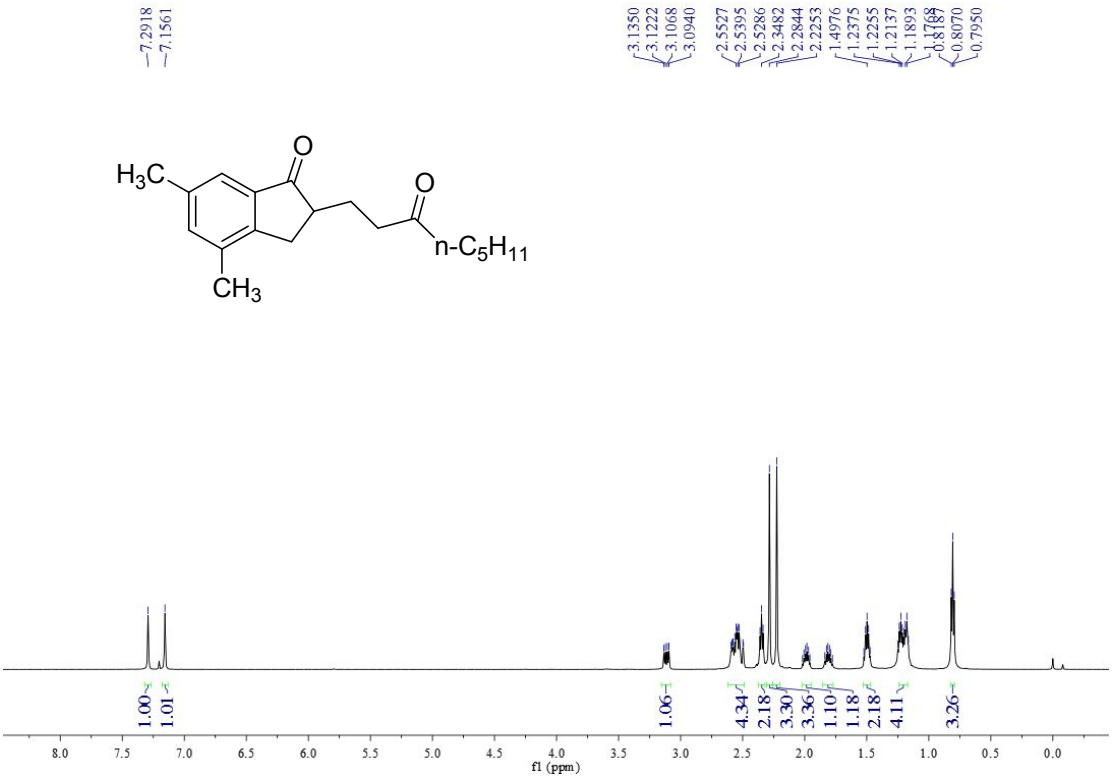
^{1}H NMR spectra of compound 4ah



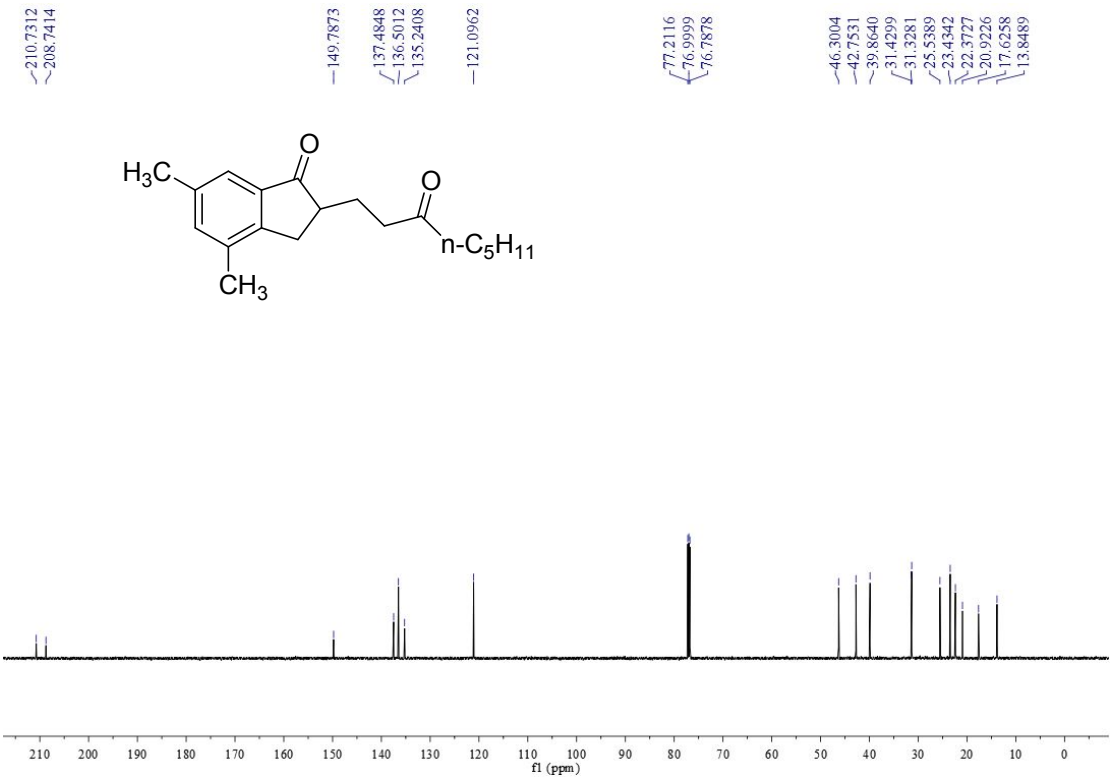
^{13}C NMR spectra of compound 4ah



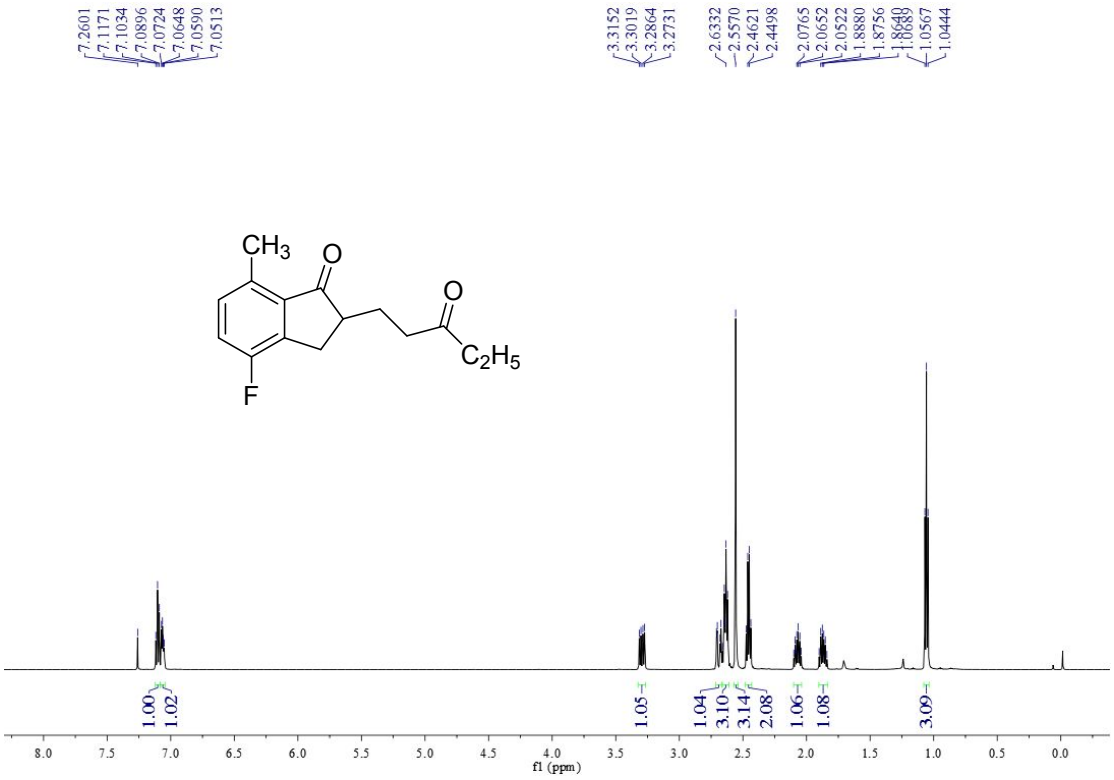
^{1}H NMR spectra of compound 4ai



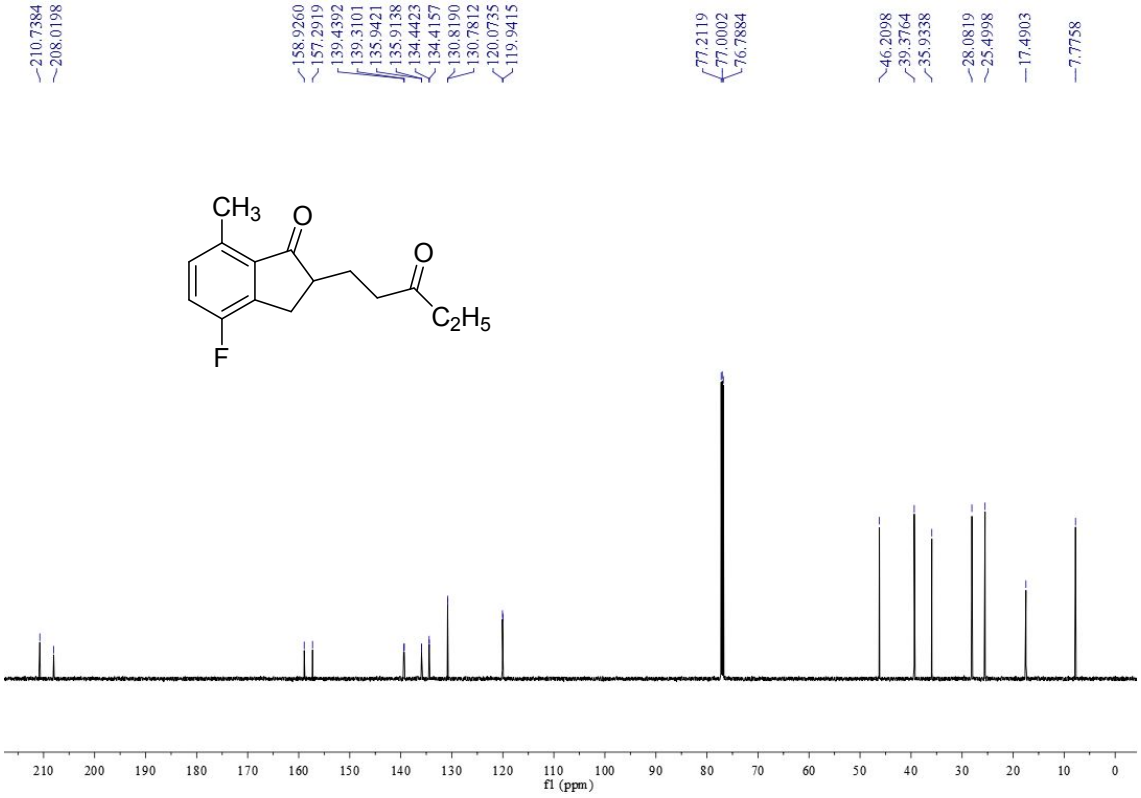
^{13}C NMR spectra of compound 4ai



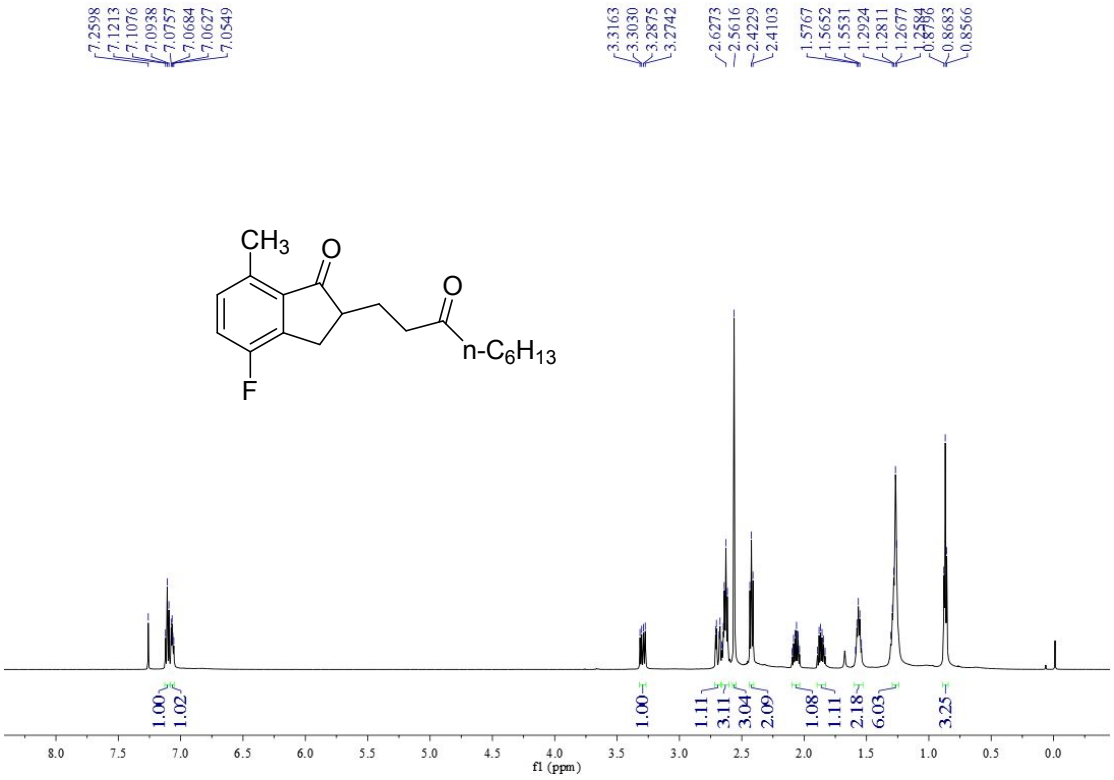
^{1}H NMR spectra of compound 4aj



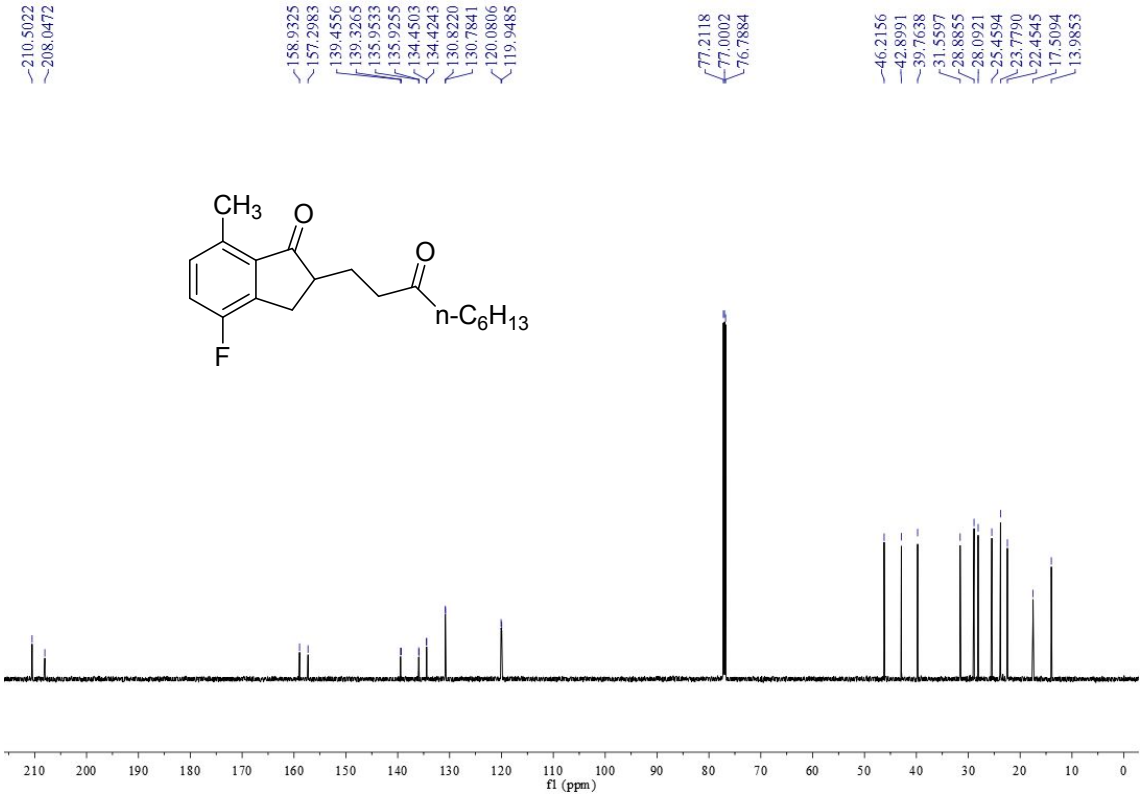
^{13}C NMR spectra of compound 4aj



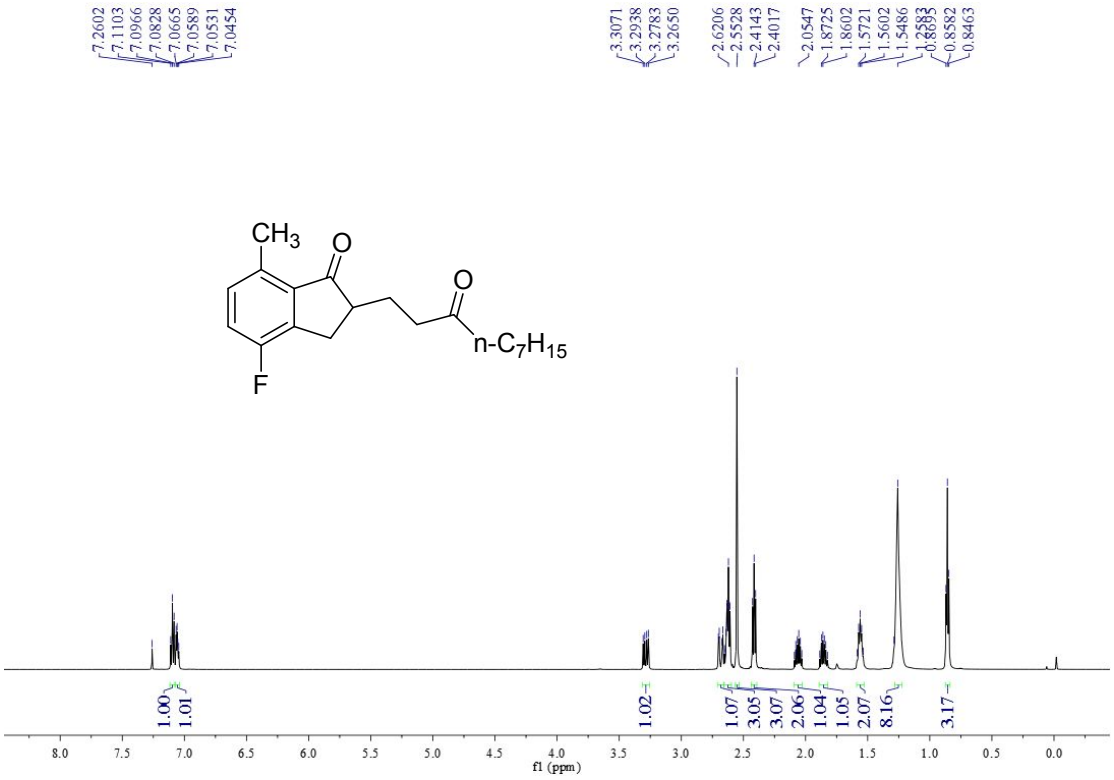
^{1}H NMR spectra of compound 4ak



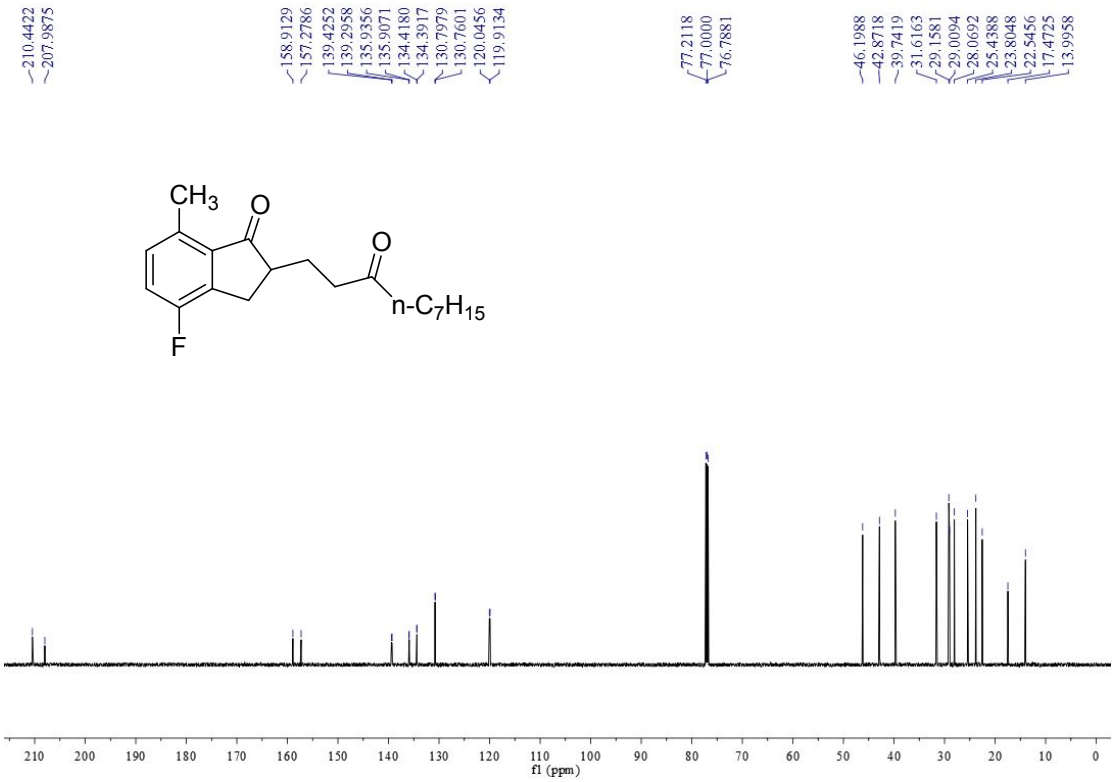
^{13}C NMR spectra of compound 4ak



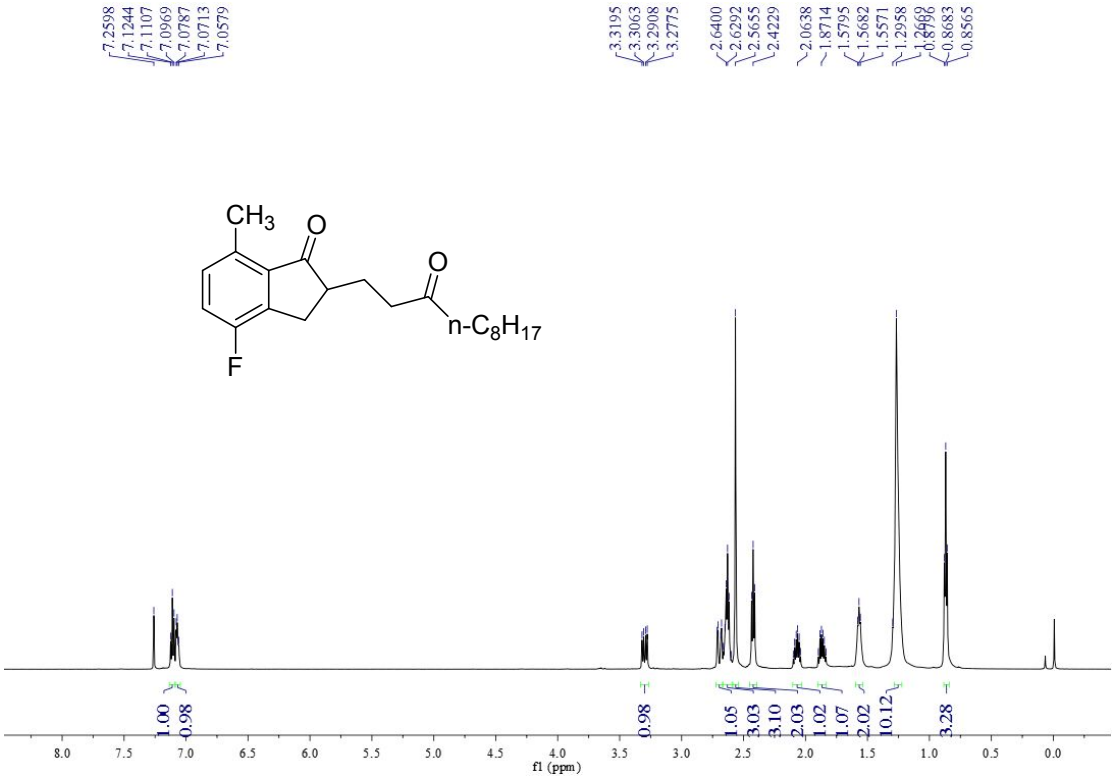
^{1}H NMR spectra of compound 4al



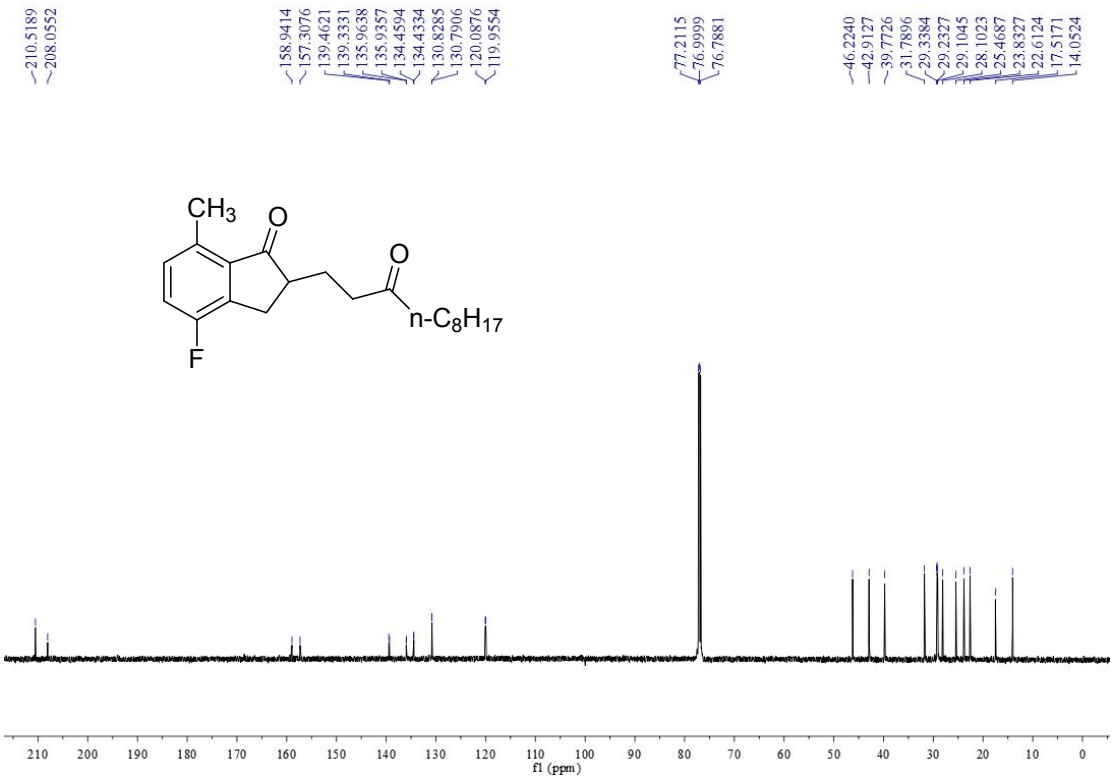
^{13}C NMR spectra of compound 4al



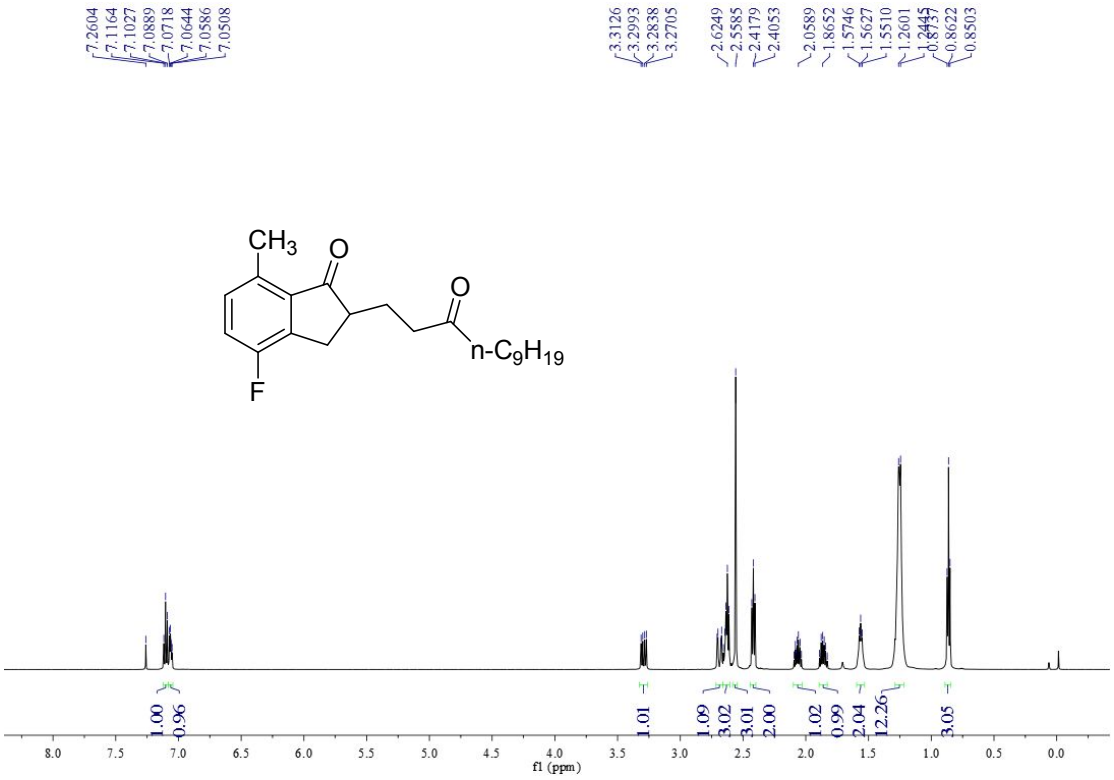
^{1}H NMR spectra of compound 4am



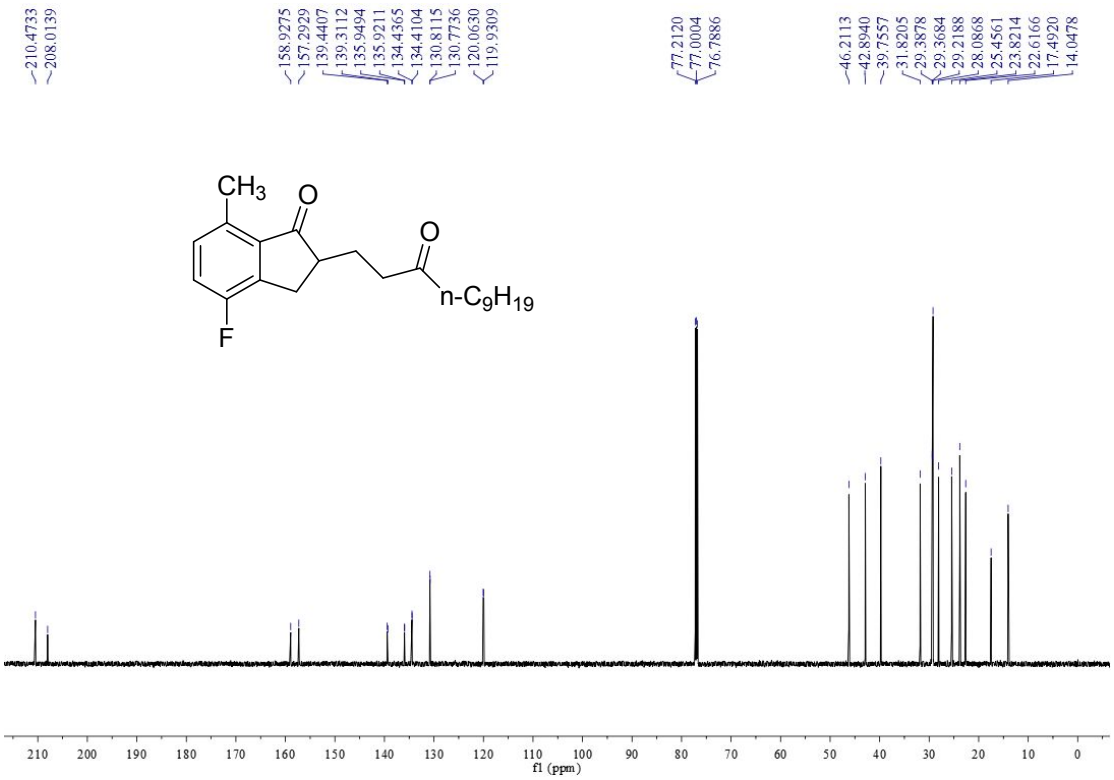
^{13}C NMR spectra of compound 4am



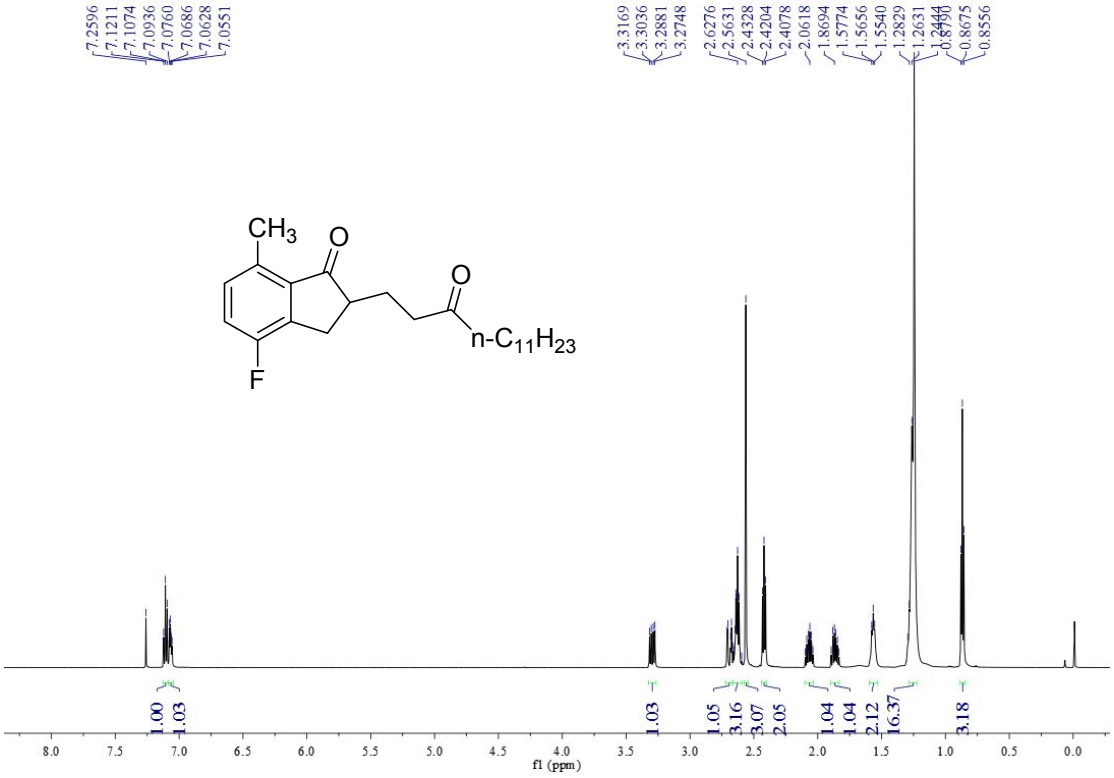
^{1}H NMR spectra of compound 4an



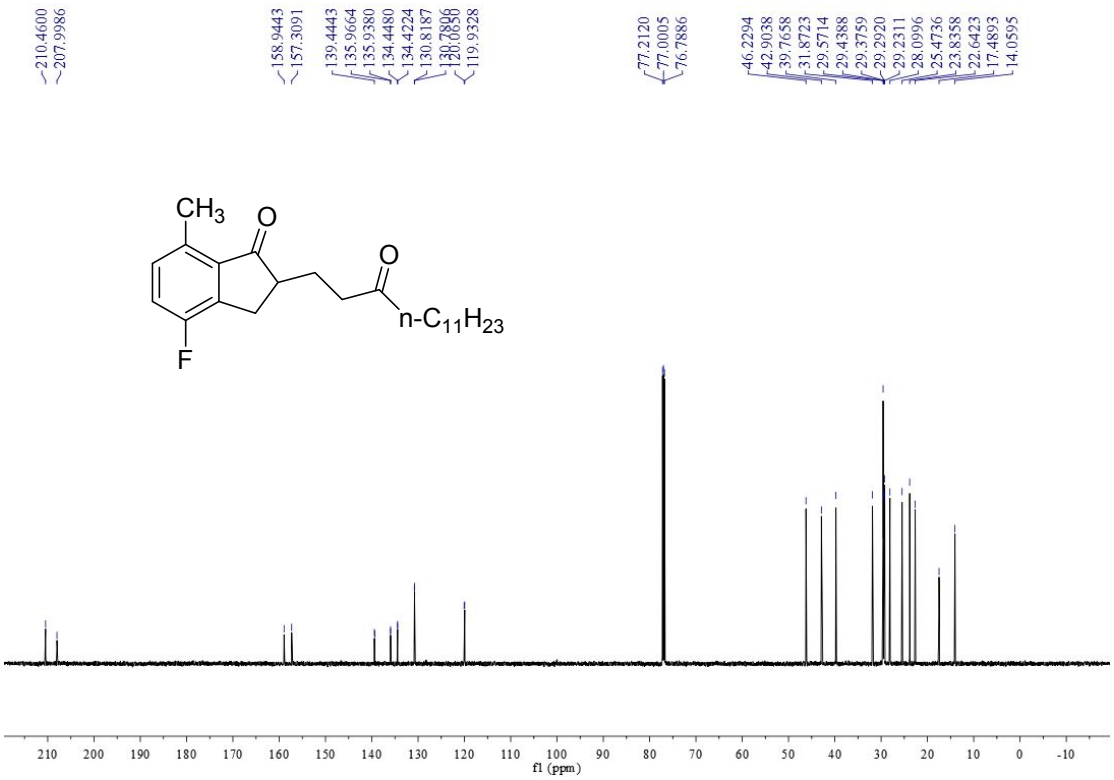
^{13}C NMR spectra of compound 4an



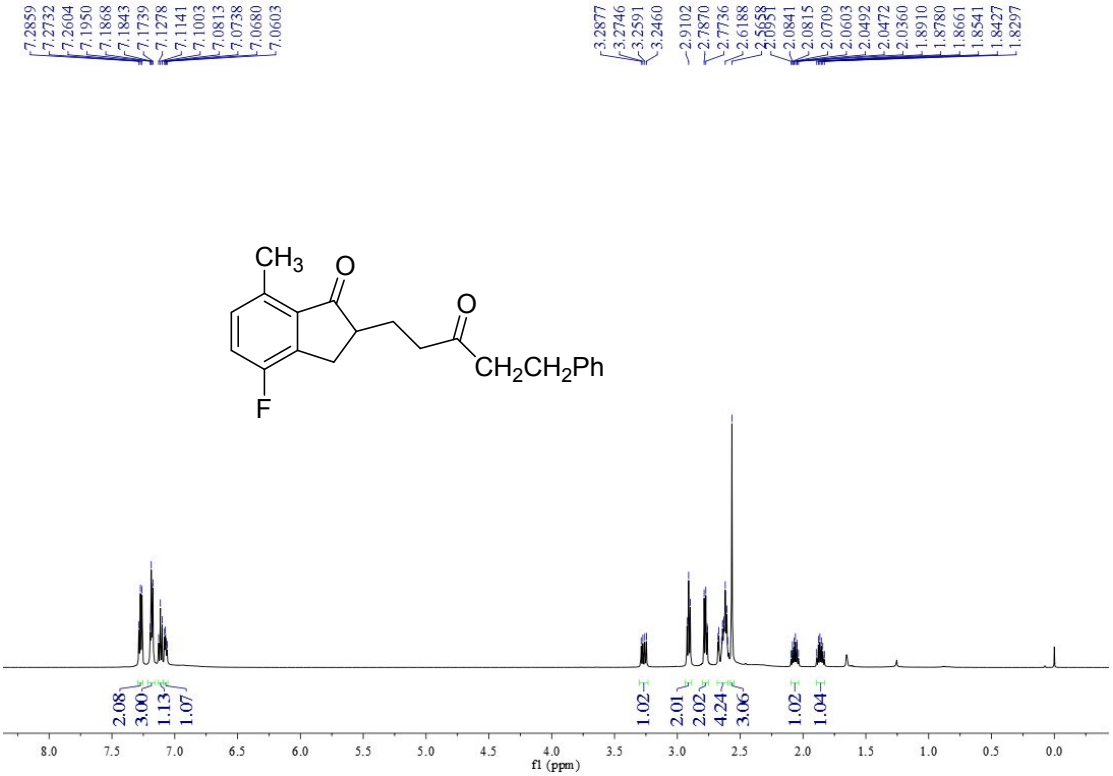
^{1}H NMR spectra of compound 4ao



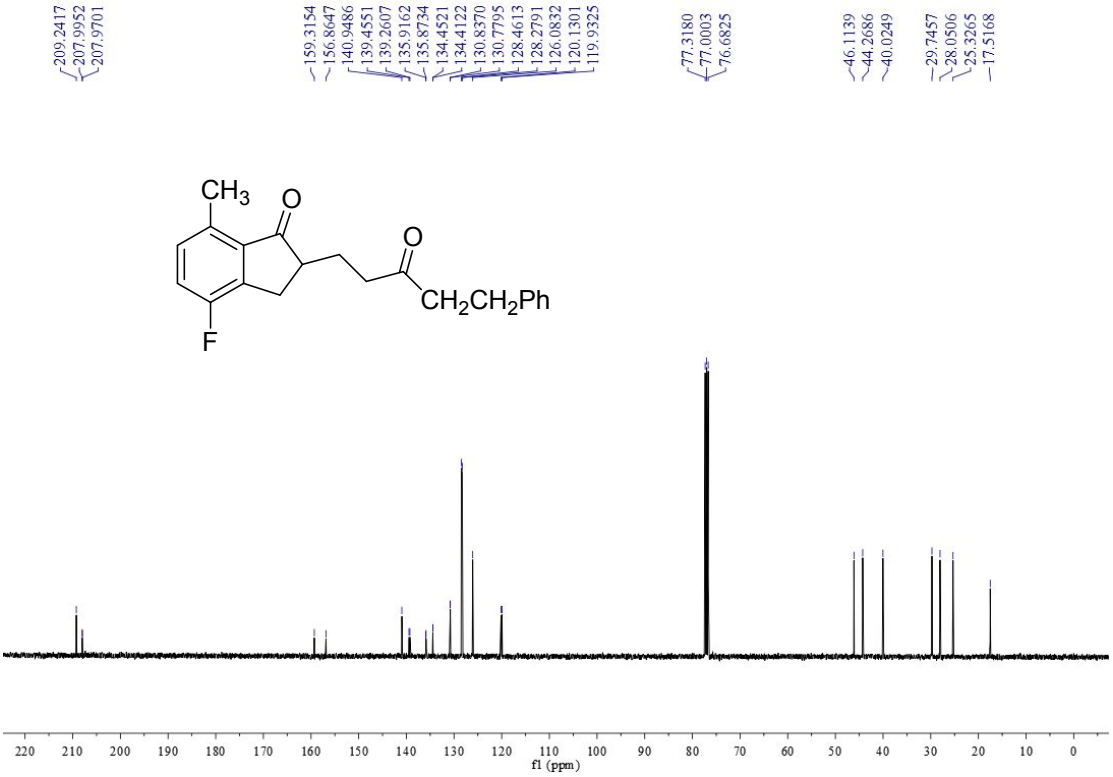
^{13}C NMR spectra of compound 4ao



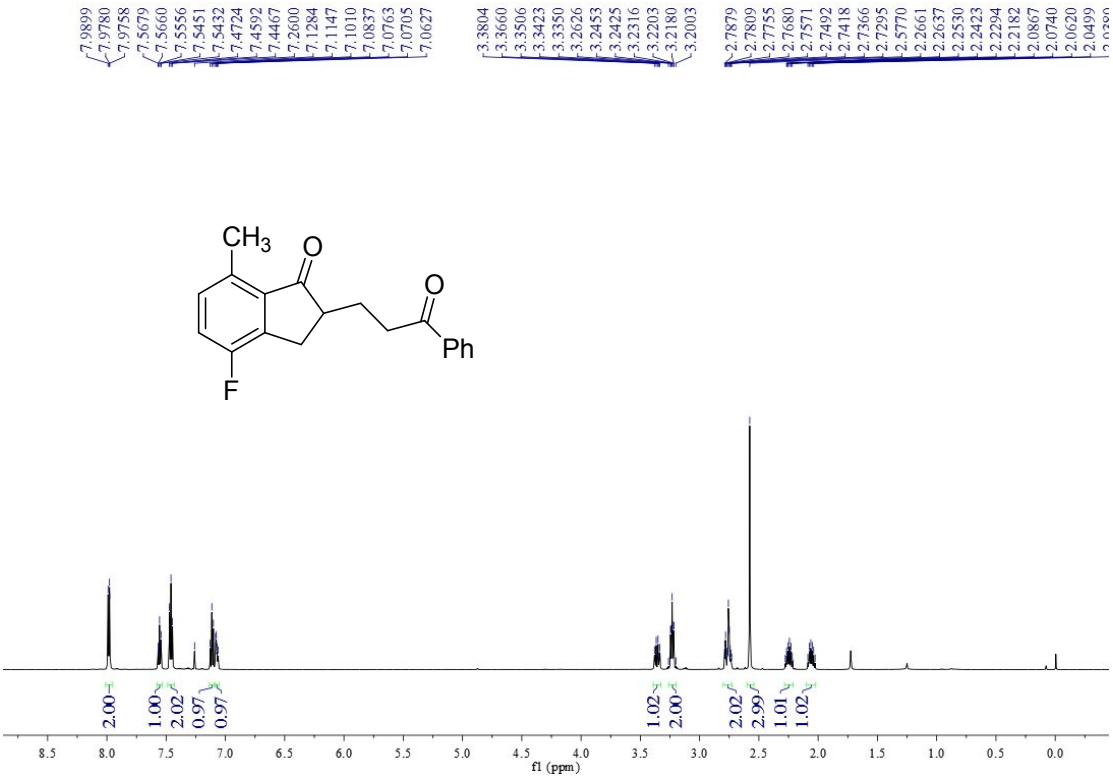
^{1}H NMR spectra of compound 4ap



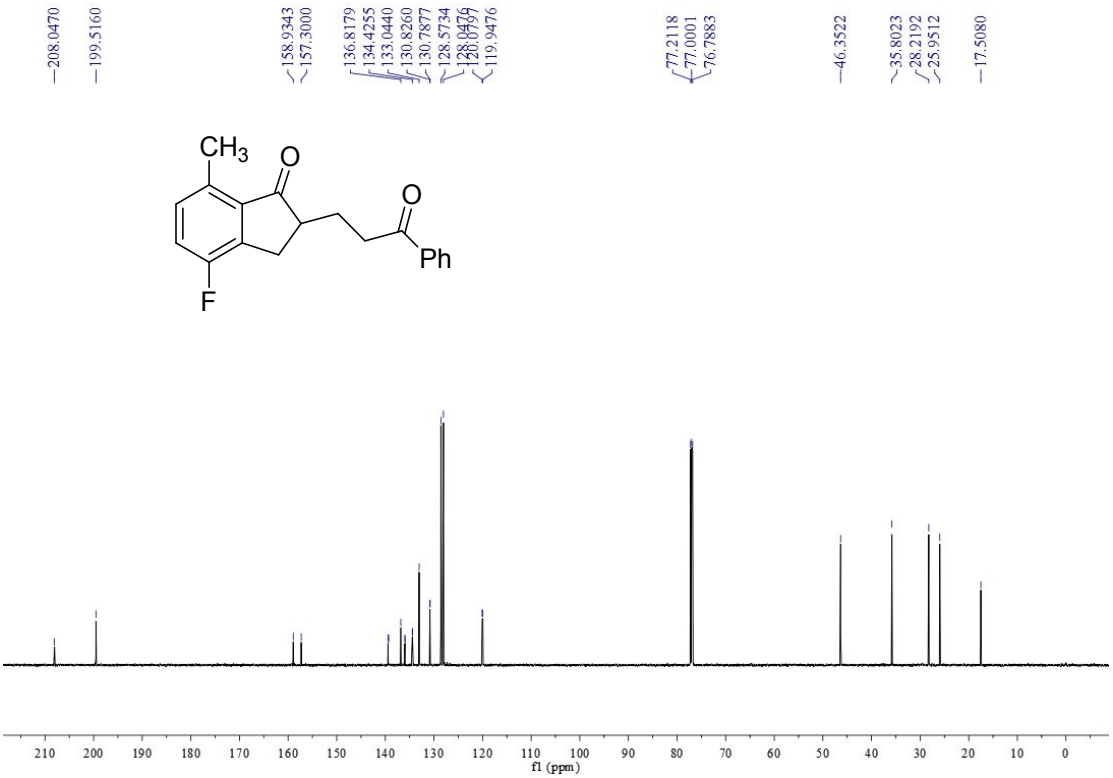
^{13}C NMR spectra of compound 4ap



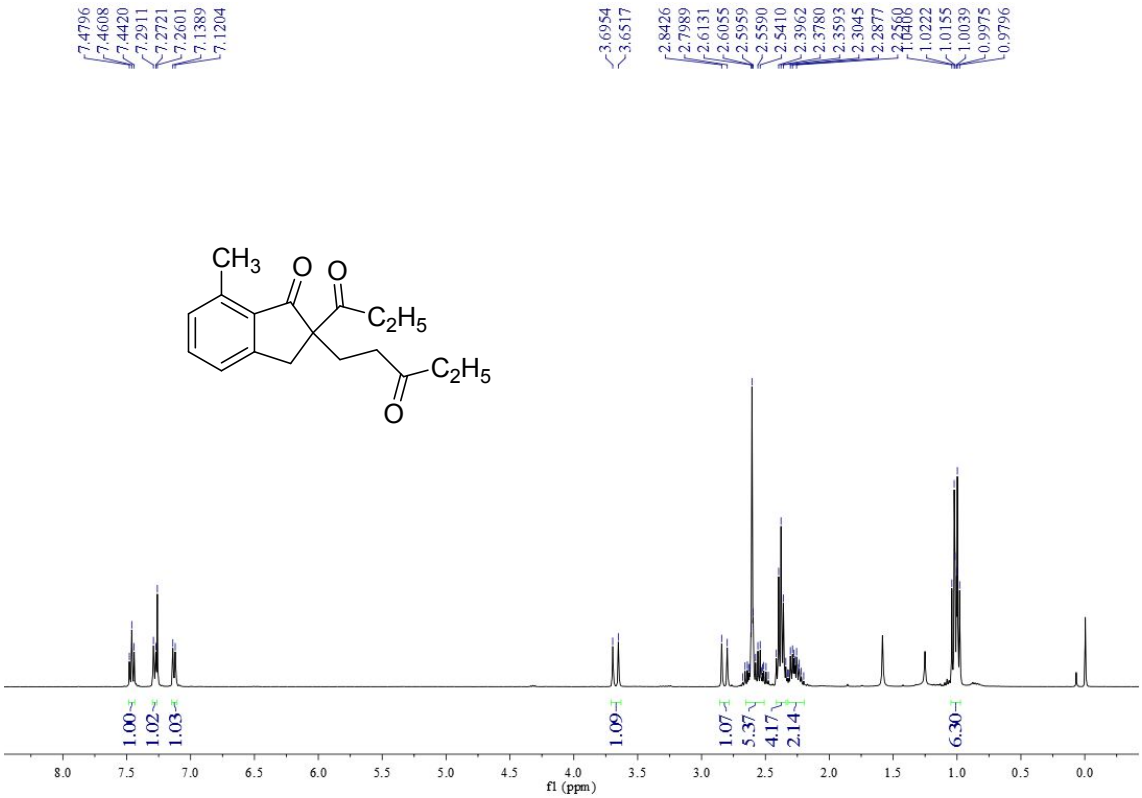
^{1}H NMR spectra of compound 4aq



^{13}C NMR spectra of compound 4aq



^{1}H NMR spectra of compound 6a



^{13}C NMR spectra of compound 6a