Direct Access to Furan and Cyclopropane Derivatives by Palladium-Catalyzed C-H Activation/Alkenes Insertion/Annulation

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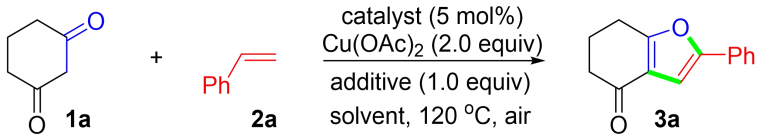
General Methods and Materials

$Pd(OAc)_2$, $Pd(TFA)_2$, $Pd(PPh_3)_4$, $Pd(acac)_2$, $Pd(dba)_2$, $[RhCp^*Cl_2]_2$, $[IrCp^*Cl_2]_2$, $[RuCl_2(p\text{-cymene})]_2$, $Cp^*CoI_2(CO)$, $Cu(OAc)_2$, TFA, HOTf, and PivOH were purchased from Energy Chemical and used without further purification. Other chemicals were purchased from commercial suppliers, further dried and purified if necessary. The water used was re-distillated and ion-free. ^1H and ^{13}C NMR spectra were achieved on a Bruker AVANCE 400 MHz spectrometer (^1H 400 MHz; ^{13}C 100 MHz) in $CDCl_3$. Abbreviations for data quoted are *s*-singlet; *brs*-broad singlet; *d*-doublet; *t*-triplet; *dd*-doublet of doublets; m-multiplet. High-resolution mass spectra were measured on a Waters Micromass GCT facility. Thin-layer chromatographies were done on pre-coated silica gel 60F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

Screening of Reaction Conditions[a]

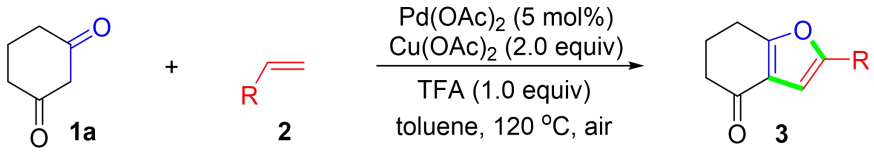


entry	catalyst	additive	solvent	yield (%)[b]
1	$Pd(OAc)_2$	HOAc	toluene	15
2	$Pd(OAc)_2$	PivOH	toluene	64
3	$Pd(OAc)_2$	TFA	toluene	77
4	$Pd(OAc)_2$	HOTf	toluene	23
5	$Pd(OAc)_2$	TFA	DMF	trace
6	$Pd(OAc)_2$	TFA	DMSO	NR
7	$Pd(OAc)_2$	TFA	TEF	NR
8	$Pd(OAc)_2$	TFA	CH_3CN	NR
9	$Pd(OAc)_2$	TFA	DCE	NR
10	$Pd(OAc)_2$	TFA	THF	NR
11	$Pd(OAc)_2$	TFA	dioxane	NR
12[c]	$Pd(OAc)_2$	TFA	toluene	26
13[d]	$Pd(OAc)_2$		toluene	0
14[e]		TFA	dioxane	0
15[f]	$Pd(OAc)_2$	TFA	toluene	64
16[g]	$Pd(OAc)_2$	TFA	toluene	71
17[h]	$Pd(OAc)_2$	TFA	toluene	34
18[i]	$Pd(OAc)_2$	TFA	toluene	51
19	$Pd(TFA)_2$	TFA	toluene	72
20	$Pd(acac)_2$	TFA	toluene	NR
21	$Pd(PPh_3)_4$	TFA	toluene	NR
22	$Pd(dba)_2$	TFA	toluene	NR
23	$[RhCp^*Cl_2]_2$	TFA	toluene	NR
24	$[IrCp^*Cl_2]_2$	TFA	toluene	NR
25	$[RuCl_2(p\text{-cymene})]_2$	TFA	Toluene	NR
26	$Cp^*CoI_2(CO)$	TFA	Toluene	14

[a]Reaction conditions: 1.3-cyclohexanedione **1a** (0.2 mmol), styrene **2a** (0.3 mmol, 1.5 equiv), catalyst (5 mol%), $Cu(OAc)_2$ (2.0 equiv), additive (1.0 equiv), solvent (2 mL) at 120 °C for 12 h under air atmosphere. [b]Isolated yield; [c]Reaction carried out in the absence of $Cu(OAc)_2$; [d]Reaction carried out in the absence of TFA; [e]Reaction carried out in the absence of $Pd(OAc)_2$; [e]Reaction carried out in the absence of catalyst $Pd(OAc)_2$; [f]Reaction carried out in the presence of 0.5 equiv TFA; [g]Reaction carried out in the presence of 2.0 equiv TFA; [h]Reaction carried out in the presence of 0.5 equiv $Cu(OAc)_2$; [i]Reaction carried out in the presence of 2.0 equiv $Cu(OAc)_2$.

Thus, we commenced our investigation with the treatment of 1.3-cyclohexanedione (**1a**) with styrene (**2a**) in the presence of $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (2.0 equiv), and HOAc (1.0 equiv) in toluene at 120 °C, and annulation product 2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (**3a**) was observed in 15% yield with good regioselectivity (Table 1, entry 1). Based on this finding, a variety of acid additives, such as PivOH, TFA, and HOTf, were examined, and TFA was found to be the best choice (Table 1, entries 2-4). Further, the screening of common organic solvents revealed that toluene is the best choice for this transformation (entries 5-11). Subsequently, control experiments proved that $Pd(OAc)_2$, $Cu(OAc)_2$, and PivOH were necessary for promoting higher product yield (entries 12-14). Furthermore, variations in the loading of $Cu(OAc)_2$, and PivOH did not provide an improvement in yield of product **3a** (entries 15-18). Finally, changing $Pd(OAc)_2$ to other well-known palladium species (entries 19-22) and common high-efficiency oxidative annulations catalysts (entries 23-26) also obviously reduced yield or completely inhibited the reaction for the generation of **3a**.

General Catalytic Procedure for the Synthesis of 3



To a dry thick walled pressure resistant tube (25 mL) was charged with 1,3-cyclohexanedione **1a** (0.2 mmol, 1.0 equiv), olefines **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5.0 mol%), $Cu(OAc)_2$ (0.4 mmol, 72.4 mg, 2.0 equiv), toluene (2 mL), then the TFA (0.2 mmol) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product.

Procedure Gram-scale for the Synthesis of 3a

To a dry thick walled pressure resistant tube (250 mL) was charged with 1,3-cyclohexanedione **1a** (5 mmol, 1.0 equiv), styrene **2** (7.5 mmol, 1.5 equiv), $Pd(OAc)_2$ (57.5 mg, 5 mol%), $Cu(OAc)_2$ (10 mmol, 1810 mg, 2.0 equiv), toluene (50 mL), then the TFA (5 mmol) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 ^oC in oil bath for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (100 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product **3a** (61% yield, 646.6 mg).

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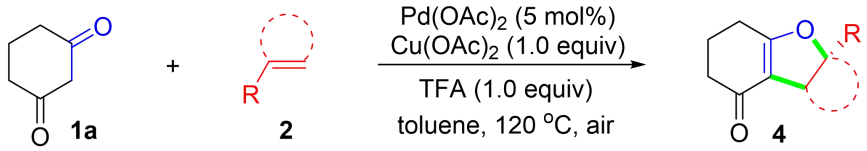
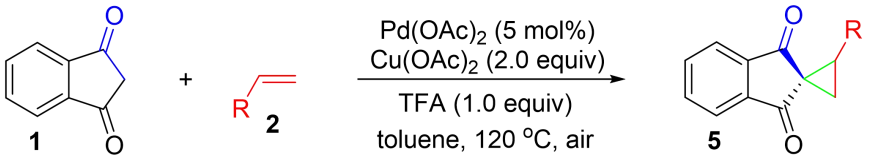
General Catalytic Procedure for the Synthesis of 4



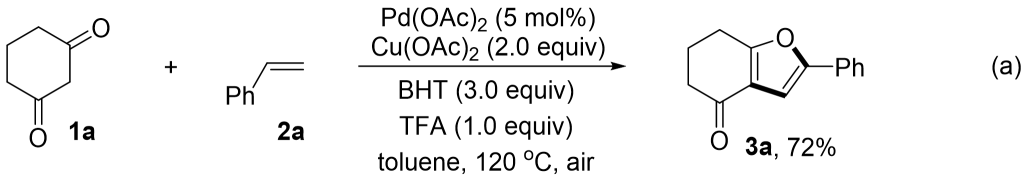
To a dry thick walled pressure resistant tube (25 mL) was charged with 1,3-cyclohexanedione **1a** (0.2 mmol, 1.0 equiv), olefines **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5.0 mol%), $Cu(OAc)_2$ (0.4 mmol, 72.4 mg, 2.0 equiv), toluene (2 mL), then the TFA (0.2 mmol) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product.

General Catalytic Procedure for for the Synthesis of 5



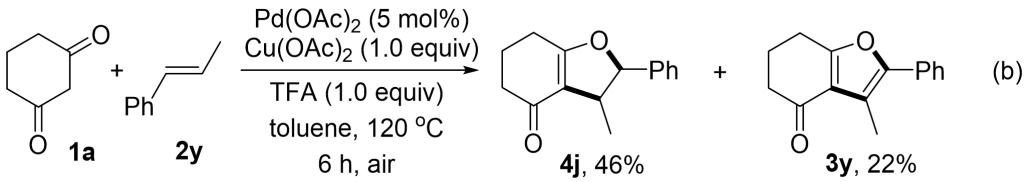
To a dry thick walled pressure resistant tube (25 mL) was charged with 1,3-indindanone **1a** (0.2 mmol, 1.0 equiv), olefines **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5.0 mol%), $Cu(OAc)_2$ (0.4 mmol, 72.4 mg, 2.0 equiv), toluene (2 mL), then the TFA (0.2 mmol) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 20 : 1) to yield product.

Mechanistic Study

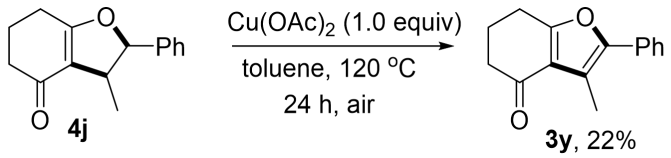


(a)

To a dry thick walled pressure resistant tube (25 mL) was charged with cyclopentane-1,3-dione (0.2 mmol, 1.0 equiv), styrene (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5.0 mol%), $Cu(OAc)_2$ (0.4 mmol, 72.4 mg, 2.0 equiv), BHT (3.0 mmol), toluene (2 mL), then the TFA (0.2 mmol) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 12 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product.



To a dry thick walled pressure resistant tube (25 mL) was charged with cyclopentane-1,3-dione (0.2 mmol, 1.0 equiv), prop-1-en-1-ylbenzene (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5.0 mol%), $Cu(OAc)_2$ (0.4 mmol, 72.4 mg, 2.0 equiv), toluene (2 mL), then the TFA (0.2 mmol) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 6 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product.



(c)

To a dry thick walled pressure resistant tube (25 mL) was charged with 3-methyl-2-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2*H*)-one (0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (0.2 mmol, 1.0 equiv), toluene (2 mL). The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 24 hours under an atmosphere of air. After the reaction finished, the resulted mixtures were diluted with 20 mL of dichloromethane and washed with 20 mL of H_2O. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10 : 1) to yield product **3y**.

X-Ray Crystallographic Data

Crystal Structure Details for Product 4g (CCDC 2350852)

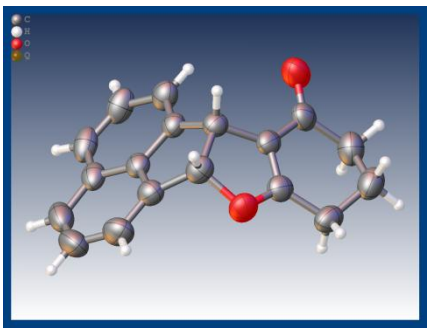
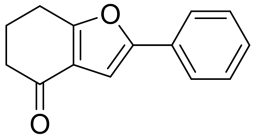


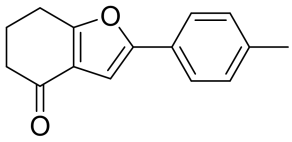
Table 1 Crystal data and structure refinement for 1

Identification code	1
Empirical formula	$C_{18}H_{14}O_2$
Formula weight	262.29
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2312(4)
b/Å	14.7726(6)
c/Å	8.2671(3)
α/°	90
β/°	109.0620(10)
γ/°	90
Volume/Å^3	1296.42(8)
Z	4
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	0.087
F(000)	552.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/	4.726 to 50.014
Index ranges	$-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-9 \leq l \leq 9$
Reflections collected	25739
Independent reflections	2275 [R_{int} = 0.0584, R_{sigma} = 0.0234]
Data/restraints/parameters	2275/0/181
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1149
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1233
Largest diff. peak/hole / e Å^{-3}	0.29/-0.16

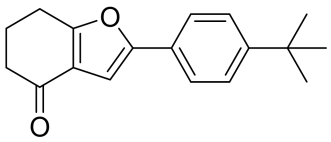
Characterization data for the products



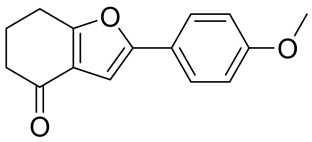
2-Phenyl-6,7-dihydrobenzofuran-4(5H)-one (**3a**):[1] Obtained as a pale yellow liquid (32.6 mg, 77% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.27 - 7.33 (m, 2H), 7.18 - 7.21 (t, 1H), 6.79 (s, 1H), 2.82 - 2.85 (t, 2H), 2.41 - 2.44 (t, 2H), 2.07 - 2.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 166.6, 154.1, 129.7, 128.7, 128.0, 123.9, 122.8, 100.8, 37.5, 23.3, 22.4; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{13}O_2$ $[M + H]^+$ 213.0910, found 213.0913.



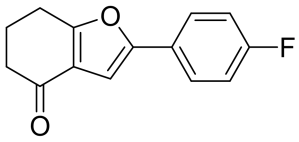
2-(*p*-Tolyl)-6,7-dihydrobenzofuran-4(5H)-one (**3b**): Obtained as a pale yellow liquid (36.6 mg, 81% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 6.73 (s, 1H), 2.82 - 2.85 (t, 2H), 2.40 - 2.43 (t, 2H), 2.27 (s, 3H), 2.07 - 2.13 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 166.3, 154.4, 138.0, 129.4, 127.0, 123.8, 122.8, 100.0, 37.5, 23.3, 22.5, 21.2; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067, found 227.1069.



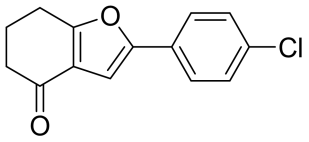
2-(4-(Tert-butyl)phenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3c**): Obtained as a pale yellow liquid (42.3 mg, 79% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 2.82 - 2.85 (t, 2H), 2.40 - 2.43 (t, 2H), 2.09 - 2.12 (t, 2H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 166.4, 154.3, 151.2, 127.0, 125.6, 123.7, 122.8, 100.1, 37.5, 34.6, 31.1, 23.3, 22.5; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{21}O_2$ $[M + H]^+$ 269.1536, found 269.1535.



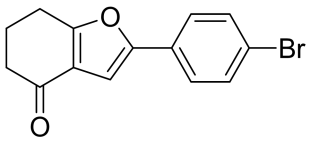
2-(4-Methoxyphenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3d**):[1] Obtained as a pale yellow liquid (36.8 mg, 76% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.65 (s, 1H), 3.74 (s, 3H), 2.83 - 2.86 (t, 2H), 2.41 - 2.44 (t, 2H), 2.10 - 2.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 166.1, 159.5, 154.2, 125.4, 122.8, 122.7, 114.2, 99.1, 55.3, 37.5, 23.3, 22.5; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}O_3$ $[M + H]^+$ 243.1016, found 243.1014.



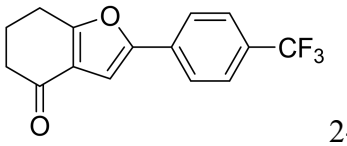
2-(4-Fluorophenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3e**): Obtained as a pale yellow liquid (33.6 mg, 73% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.53 (t, 2H), 6.96 - 7.00 (t, 2H), 6.71 (s, 1H), 2.82 - 2.86 (t, 2H), 2.41 - 2.44 (t, 2H), 2.08 - 2.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 166.5, 162.4 (d, J = 246.6 Hz), 153.2, 125.7 (d, J = 8.1 Hz), 122.8, 115.8 (d, J = 21.9 Hz), 100.5 (d, J = 1.3 Hz), 37.5, 23.3, 22.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -113.0; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{12}FO_2$ $[M + H]^+$ 231.0816, found 231.0818.



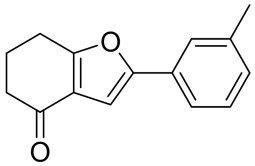
2-(4-Chlorophenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3f**): Obtained as a pale yellow liquid (36.9 mg, 75% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.77 (s, 1H), 2.84 - 2.87 (t, 2H), 2.42 - 2.45 (t, 2H), 2.09 - 2.15 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 166.8, 153.0, 133.7, 128.9, 128.2, 125.1, 122.9, 101.3, 37.5, 23.3, 22.4; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{12}ClO_2$ $[M + H]^+$ 247.0520, found 247.0521.



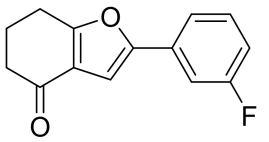
2-(4-Bromophenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3g**):[1] Obtained as a pale yellow liquid (42.9 mg, 74% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 4H), 6.80 (s, 1H), 2.84 - 2.88 (t, 2H), 2.43 - 2.46 (t, 2H), 2.10 - 2.16 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 166.8, 153.1, 131.9, 128.7, 125.4, 122.9, 121.9, 101.4, 37.5, 23.4, 22.4; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{12}BrO_2$ $[M + H]^+$ 291.0015, found 291.0014.



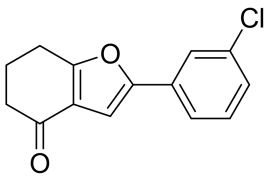
2-(4-(Trifluoromethyl)phenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3h**): Obtained as a pale yellow liquid (38.6 mg, 69% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 6.91 (s, 1H), 2.87 - 2.90 (t, 2H), 2.44 - 2.47 (t, 2H), 2.12 - 2.18 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 167.4, 152.6, 132.9, 129.6 (q, J = 32.3, 64.9 Hz), 125.8 (q, J = 3.7, 7.5 Hz), 125.71, 125.5 (q, J = 270.4, 501.6 Hz), 123.0, 102.9, 37.5, 23.4, 22.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.7; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{12}F_3O_2$ $[M + H]^+$ 281.0784, found 281.0782.



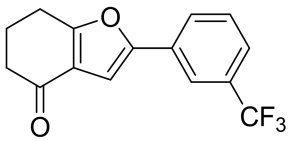
2-(*m*-Tolyl)-6,7-dihydrobenzofuran-4(5H)-one (**3i**): Obtained as a pale yellow liquid (36.2 mg, 80% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.37 (m, 2H), 7.16 - 7.20 (t, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.77 (s, 1H), 2.82 - 2.85 (t, 2H), 2.40 - 2.43 (t, 2H), 2.28 (s, 3H), 2.07 - 2.11 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 166.5, 154.3, 138.3, 129.6, 128.8, 128.6, 124.5, 122.8, 121.1, 100.6, 37.5, 23.3, 22.5, 21.4; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067, found 227.1066.



2-(3-Fluorophenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3j**): Obtained as a pale yellow liquid (32.2 mg, 70% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.71 (t, 1H), 7.15 - 7.20 (q, 1H), 7.00 - 7.12 (m, 3H), 2.86 - 2.89 (t, 2H), 2.44 - 2.47 (t, 2H), 2.11 - 2.17 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 166.4, 158.7 (d, J = 250.3 Hz), 148.3 (d, J = 2.9 Hz), 129.0 (d, J = 2.8 Hz), 124.2 (d, J = 3.5 Hz), 123.1, 118.1 (d, J = 11.8 Hz), 116.0 (d, J = 18.2 Hz), 105.9 (d, J = 12.0 Hz), 37.6, 23.3, 22.5; ^{19}F NMR (400 MHz, $CDCl_3$) δ -113.1; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{12}FO_2$ $[M + H]^+$ 231.0816, found 231.0818.

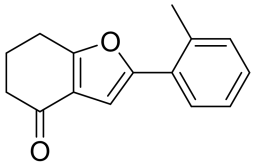


2-(3-Chlorophenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3k**): Obtained as a pale yellow liquid (34.9 mg, 71% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.15 - 7.24 (m, 2H), 6.81 (s, 1H), 2.84 - 2.87 (t, 2H), 2.42 - 2.45 (t, 2H), 2.10 - 2.16 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 167.0, 152.6, 134.8, 131.4, 130.0, 127.9, 123.8, 122.9, 121.9, 101.9, 37.5, 23.3, 22.4; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{12}ClO_2$ $[M + H]^+$ 247.0520, found 247.0522.

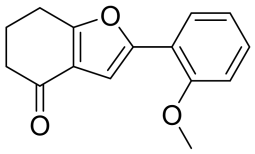


2-(3-(Trifluoromethyl)phenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3l**): Obtained as a pale yellow liquid (35.8 mg, 64% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.38 - 7.44 (m, 2H), 6.87 (s, 1H), 2.86 - 2.89 (t, 2H), 2.43 - 2.46 (t, 2H), 2.10 - 2.16 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 167.1, 152.5, 131.2 (q, J = 32.3, 64.6 Hz), 130.4, 129.3, 128.1 (t, J = 42.5 Hz), 126.9, 125.2, 124.4 (q, J = 3.5, 7.2 Hz), 122.9, 122.5, 120.5 (q, J = 3.8, 7.7 Hz), 102.2, 37.5, 23.3, 22.4; ^{19}F NMR

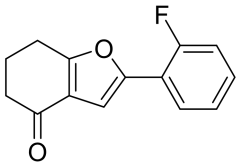
(400 MHz, $CDCl_3$) δ -62.9; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{12}F_3O_2$ $[M + H]^+$ 281.0784, found 281.0787.



2-(*o*-Tolyl)-6,7-dihydrobenzofuran-4(5H)-one (**3m**): Obtained as a pale yellow liquid (34.4 mg, 76% yield), eluting with 10% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, CDCl3) δ 7.60 (d, J = 6.8 Hz, 1H), 7.15 - 7.18 (m, 3H), 6.69 (s, 1H), 2.84 - 2.87 (t, 2H), 2.43 - 2.46 (t, 2H), 2.39 (s, 3H), 2.11 - 2.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 166.3, 153.5, 134.8, 131.2, 129.0, 128.0, 126.9, 126.0, 122.7, 104.5, 37.5, 23.3, 22.5, 21.8; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067, found 227.1068.

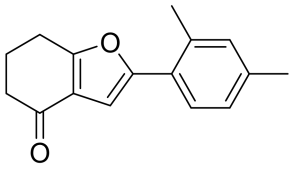


2-(2-Methoxyphenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3n**): Obtained as a pale yellow liquid (33.9 mg, 70% yield), eluting with 10% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 1H), 7.17 - 7.21 (t, 1H), 7.11 (s, 1H), 6.87 -6.95 (m, 2H), 3.85 (s, 3H), 2.85 - 2.88 (t, 2H), 2.43 - 2.46 (t, 2H), 2.09 - 2.16 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 165.9, 155.6, 150.5, 128.7, 125.8, 123.0, 120.5, 118.7, 110.9, 105.7, 55.3, 37.6, 23.4, 22.5; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}O_3$ $[M + H]^+$ 243.1016, found 243.1017.

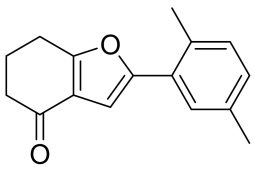


2-(2-Fluorophenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3o**): Obtained as a pale yellow liquid (30.4 mg, 66% yield), eluting with 10% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.6 Hz, 1H), 7.23 - 7.28 (t, 2H), 6.87 - 6.91 (t, 1H), 6.81 (s, 1H), 2.84 - 2.87 (t, 2H), 2.42 - 2.45 (t, 2H), 2.10 - 2.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 166.9, 163.0 (d, J = 244.3 Hz),

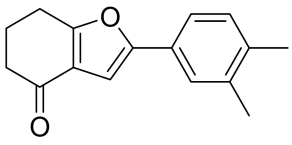
152.8 (d, J = 3.0 Hz), 131.7 (d, J = 8.5 Hz), 130.4 (d, J = 8.4 Hz), 122.9, 119.5 (d, J = 2.9 Hz), 114.8 (d, J = 21.2 Hz), 110.8 (d, J = 23.6 Hz), 101.9, 37.5, 23.3, 22.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -112.4; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{12}FO_2$ [M + H] $^+$ 231.0816, found 231.0815.



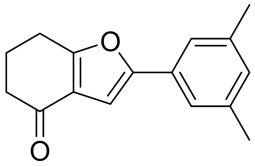
2-(2,4-Dimethylphenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3p**): Obtained as a pale yellow liquid (39.4 mg, 82% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 2.87 - 2.90 (t, 2H), 2.45 - 2.48 (t, 2H), 2.36 (s, 3H), 2.29 (s, 3H), 2.13 - 2.19 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 166.2, 153.7, 135.5, 131.9, 131.2, 128.9, 128.8, 127.5, 122.8, 104.4, 37.6, 23.4, 22.6, 21.4, 21.0; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O_2$ [M + H] $^+$ 241.1223, found 241.1225.



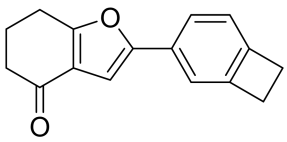
2-(2,5-Dimethylphenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3q**): Obtained as a pale yellow liquid (40.3 mg, 84% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.80 (s, 1H), 2.96 - 2.99 (t, 2H), 2.54 - 2.58 (t, 2H), 2.46 (s, 3H), 2.39 (s, 3H), 2.23 - 2.26 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 166.1, 153.6, 135.4, 131.7, 131.1, 128.8, 128.7, 127.4, 122.7, 104.3, 37.5, 23.3, 22.5, 21.3, 20.9; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O_2$ [M + H] $^+$ 241.1223, found 241.1222.



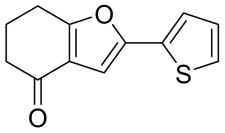
2-(3,4-Dimethylphenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3r**): Obtained as a pale yellow liquid (40.8 mg, 85% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.72 (s, 1H), 2.83 - 2.86 (t, 2H), 2.41 - 2.44 (t, 2H), 2.20 (s, 3H), 2.18 (s, 3H), 2.09 - 2.12 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 166.3, 154.5, 136.9, 136.7, 130.0, 127.4, 125.1, 122.8, 121.4, 99.9, 37.6, 23.4, 22.5, 19.8, 19.5; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1223, found 241.1223.



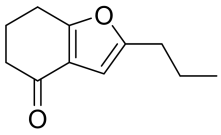
2-(3,5-Dimethylphenyl)-6,7-dihydrobenzofuran-4(5H)-one (**3s**): Obtained as a pale yellow liquid (42.7 mg, 89% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 6.84 (s, 1H), 6.75 (s, 1H), 2.82 - 2.85 (t, 2H), 2.40 - 2.43 (t, 2H), 2.25 (s, 3H), 2.07 - 2.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 166.4, 154.5, 138.2, 129.8, 129.5, 122.8, 121.7, 100.5, 37.5, 23.3, 22.5, 21.2; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1223, found 241.1224.



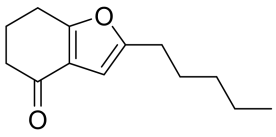
2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-6,7-dihydrobenzofuran-4(5H)-one (**3t**): Obtained as a pale yellow liquid (40.5 mg, 85% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (d, J = 7.6 Hz, 1H), 7.26 (s, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.72 (s, 1H), 3.12 (s, 4H), 2.85 - 2.88 (t, 2H), 2.43 - 2.46 (t, 2H), 2.12 - 2.15 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 166.3, 155.2, 146.3, 146.1, 128.6, 122.9, 122.9, 122.8, 118.2, 99.9, 37.6, 29.6, 29.4, 23.4, 22.6; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{15}O_2$ $[M + H]^+$ 239.1067, found 239.1065.



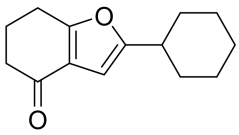
2-(Thiophen-2-yl)-6,7-dihydrobenzofuran-4(5H)-one (**3u**): Obtained as a pale yellow liquid (31.0 mg, 71% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 - 7.20 (m, 2H), 6.96 - 6.98 (t, 1H), 6.65 (s, 1H), 2.84 - 2.87 (t, 2H), 2.43 - 2.46 (t, 2H), 2.10 - 2.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 166.3, 149.7, 132.4, 127.7, 125.1, 123.6, 122.8, 100.7, 37.6, 23.4, 22.5; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{11}O_2S$ $[M + H]^+$ 219.0474, found 219.0476.



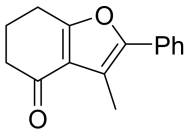
2-Propyl-6,7-dihydrobenzofuran-4(5H)-one (**3v**): Obtained as a pale yellow liquid (31.0 mg, 87% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 2.82 - 2.85 (t, 2H), 2.56 - 2.60 (t, 2H), 2.45 - 2.49 (t, 2H), 2.13 - 2.19 (m, 2H), 1.61 - 1.70 (m, 2H), 0.95 - 0.98 (t, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 165.9, 156.8, 121.8, 101.2, 37.5, 29.7, 23.3, 22.6, 21.0, 13.6; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{15}O_2$ $[M + H]^+$ 179.1067, found 179.1069.



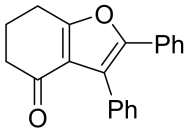
2-Pentyl-6,7-dihydrobenzofuran-4(5H)-one (**3w**): Obtained as a pale yellow liquid (26.4 mg, 64% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 1H), 2.82 - 2.85 (t, 2H), 2.57 - 2.61 (t, 2H), 2.46 - 2.49 (t, 2H), 2.13 - 2.19 (m, 2H), 1.59 - 1.67 (m, 2H), 1.31 - 1.35 (m, 4H), 0.88 - 0.92 (t, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 165.9, 157.1, 121.8, 101.1, 37.5, 31.2, 27.7, 27.3, 23.3, 22.6, 22.3, 13.9; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{19}O_2$ $[M + H]^+$ 207.1380, found 207.1381.



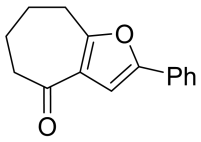
2-Cyclohexyl-6,7-dihydrobenzofuran-4(5H)-one (**3x**): Obtained as a pale yellow liquid (28.3 mg, 65% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (s, 1H), 2.82 - 2.85 (t, 2H), 2.56 - 2.59 (m, 1H), 2.45 - 2.48 (t, 2H), 2.13 - 2.19 (m, 2H), 1.99 - 2.01 (m, 2H), 1.79 - 1.81 (m, 2H), 1.69 - 1.72 (m, 1H), 1.21 - 1.41 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 165.7, 161.4, 121.6, 99.2, 37.5, 36.9, 31.2, 25.9, 25.7, 23.3, 22.6; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1381.



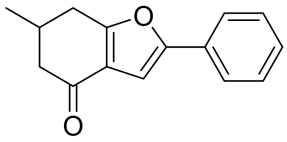
3-Methyl-2-phenyl-6,7-dihydrobenzofuran-4(5H)-one (**3y**):[1] Obtained as a pale yellow liquid (27.1 mg, 60% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 2H), 7.43 - 7.47 (t, 2H), 7.31 - 7.35 (t, 1H), 2.92 - 2.95 (t, 2H), 2.52 - 2.55 (t, 2H), 2.51 (s, 3H), 2.18 - 2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 165.9, 148.9, 130.6, 128.6, 127.4, 125.8, 121.9, 114.7, 38.4, 23.6, 22.5, 10.2; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067, found 227.1068.



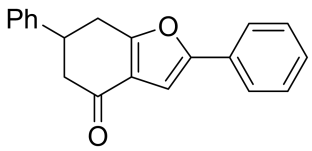
2,3-Diphenyl-6,7-dihydrobenzofuran-4(5H)-one (**3z**): Obtained as a pale yellow liquid (28.2 mg, 49% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.35 (m, 7H), 7.15 - 7.18 (t, 3H), 2.91 - 2.94 (t, 2H), 2.42 - 2.45 (t, 2H), 2.12 - 2.18 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 166.1, 149.0, 131.9, 130.1, 130.0, 128.3, 128.2, 127.8, 127.6, 126.1, 121.3, 119.8, 38.6, 23.8, 22.4; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{17}O_2$ $[M + H]^+$ 289.1223, found 289.1222.



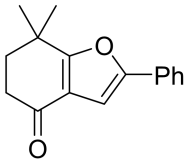
2-Phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-one (**3aa**):[1] Obtained as a pale yellow liquid (30.3 mg, 67% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 - 7.64 (m, 2H), 7.36 - 7.39 (m, 2H), 7.25 - 7.29 (m, 1H), 6.96 (s, 1H), 3.07 - 3.10 (t, 2H), 2.75 - 2.78 (m, 2H), 2.01 - 2.07 (m, 2H), 1.91 - 1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 161.2, 152.3, 129.7, 128.7, 127.8, 125.3, 123.7, 105.0, 44.4, 29.7, 24.8, 22.8; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067, found 227.1069.



6-Methyl-2-phenyl-6,7-dihydrobenzofuran-4(5H)-one (**3ab**): Obtained as a pale yellow liquid (36.2 mg, 80% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.6 Hz, 2H), 7.26 - 7.30 (t, 2H), 7.17 - 7.20 (t, 1H), 6.77 (s, 1H), 2.88 - 2.94 (t, 2H), 2.43 - 2.52 (t, 2H), 2.12 - 2.19 (t, 2H), 2.28 (d, J = 7.2 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 166.3, 154.3, 130.1, 129.7, 128.76, 128.6, 127.9, 127.9, 126.4, 123.8, 122.4, 100.7, 46.0, 31.4, 30.6, 21.0; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067, found 227.1069.

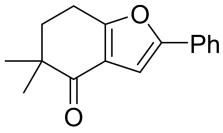


2,6-Diphenyl-6,7-dihydrobenzofuran-4(5H)-one (**3ac**): Obtained as a pale yellow liquid (49.0 mg, 85% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 2H), 7.27 - 7.33 (m, 4H), 7.19 - 7.22 (t, 4H), 6.84 (s, 1H), 3.47 - 3.55 (t, 1H), 3.14 - 3.19 (q, 1H), 3.00 - 3.07 (q, 1H), 2.71 (d, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 165.7, 154.7, 142.4, 129.7, 128.9, 128.8, 128.2, 127.2, 126.7, 124.0, 122.8, 100.8, 44.9, 41.2, 31.2; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{17}O_2$ $[M + H]^+$ 289.1223, found 289.1224.



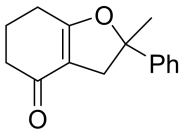
7,7-Dimethyl-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (**3ad'**):[1]

Obtained as a pale yellow liquid, eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 2H), 7.36 - 7.47 (m, 2H), 7.26 - 7.33 (m, 1H), 6.85 (s, 1H), 2.58 - 2.61 (t, 2H), 2.00 - 2.04 (t, 2H), 1.44 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 172.4, 154.0, 129.8, 128.7, 128.0, 123.9, 120.6, 100.7, 37.8, 35.3, 32.8, 26.0; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1223, found 241.1223.



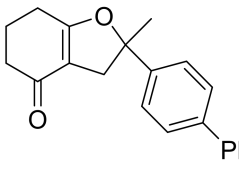
5,5-Dimethyl-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (**3ad''**):[1]

Obtained as a pale yellow liquid, eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.40 - 7.50 (m, 2H), 7.25 - 7.36 (m, 1H), 6.91 (s, 1H), 2.97 - 3.00 (t, 2H), 2.04 - 2.08 (t, 2H), 1.23 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 164.7, 154.4, 129.9, 128.7, 127.9, 123.8, 121.2, 101.6, 42.0, 36.4, 24.1, 21.0; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1223, found 241.1223.

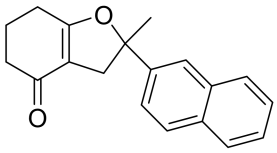


2-Methyl-2-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4a**):

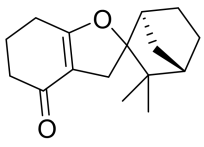
Obtained as a pale yellow liquid (32.8 mg, 72% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.27 (m, 5H), 2.42 - 2.46 (m, 2H), 2.22 - 2.28 (m, 2H), 2.14 - 2.20 (m, 1H), 1.87 - 1.94 (m, 2H), 1.80 - 1.84 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 170.2, 144.5, 128.4, 127.1, 124.1, 111.3, 80.5, 36.6, 32.4, 28.9, 28.8, 20.9, 15.7; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}O_2$ $[M + H]^+$ 229.1223, found 229.1221.



2-([1,1'-Biphenyl]-4-yl)-2-methyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4b**): Obtained as a pale yellow liquid (45.6 mg, 75% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.60 (m, 4H), 7.42 - 7.46 (m, 4H), 7.33 - 7.37 (t, 1H), 3.14 (d, J = 14.4 Hz, 1H), 3.03 (d, J = 14.0 Hz, 1H), 2.53 - 2.56 (t, 2H), 2.36 - 2.40 (m, 2H), 2.05 - 2.12 (t, 2H),1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 175.9, 144.5, 140.5, 140.4, 128.8, 127.4, 127.2, 127.0, 124.7, 92.5, 40.5, 36.4, 29.7, 24.1, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{21}O_2$ [M + H] $^+$ 305.1536, found 305.1535.

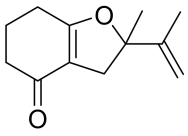


2-Methyl-2-(naphthalen-2-yl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4c**): Obtained as a pale yellow liquid (40.6 mg, 73% yield), eluting with 20% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 -7.86 (m, 4H), 7.43 - 7.52 (m, 3H), 3.20 (d, J = 14.4 Hz, 1H), 3.07 (d, J = 14.4 Hz, 1H), 2.56 - 2.59 (m, 2H), 2.36 - 2.41 (m, 2H), 2.08 - 2.13 (m, 2H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 183.3, 141.1, 133.0, 132.4, 128.4, 128.0, 127.4, 126.2, 126.1, 123.0, 122.4, 114.6, 83.6, 33.2, 32.1, 28.3, 26.6, 14.7; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}O_2$ [M + H] $^+$ 279.1380, found 279.1381.

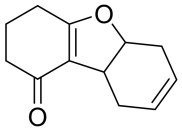


3',3'-Dimethyl-3,5,6,7-tetrahydro-4H-spiro[benzofuran-2,2'-bicyclo[2.2.1]heptan]-4-one (**4d**): Obtained as a pale yellow liquid (20.7 mg, 42% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 - 2.28 (m, 5H), 2.08 (d, J = 4.0 Hz, 1H), 1.84 - 1.97 (m, 5H), 1.73 (s, 1H), 1.43 - 1.54 (m, 2H), 1.30 - 1.38 (m, 1H), 1.04 (d, J = 9.2 Hz, 1H), 0.95 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 171.2, 111.0, 89.1, 49.5, 45.3, 44.3, 36.7, 34.3,

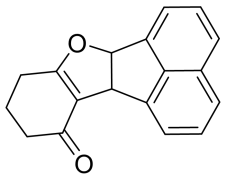
28.9, 25.1, 23.6, 23.2, 22.4, 22.1, 21.0, 16.6; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{23}O_2$ $[M + H]^+$ 247.1693, found 247.1692.



2-Methyl-2-(prop-1-en-2-yl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4e**): Obtained as a pale yellow liquid (28.0 mg, 73% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (s, 1H), 4.80 - 4.81 (t, 1H), 2.79 - 2.83 (m, 1H), 2.58 - 2.62 (m, 1H), 2.40 - 2.44 (t, 2H), 2.30 - 2.34 (m, 2H), 1.99 - 2.05 (m, 2H), 1.74 (d, J = 0.4 Hz, 3H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 176.0, 146.4, 112.4, 110.0, 93.2, 37.3, 36.2, 26.0, 23.9, 21.6, 18.3.; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{17}O_2$ $[M + H]^+$ 193.1223, found 193.1224.

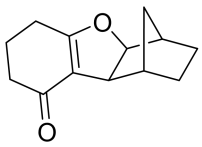


3,4,5a,6,9,9a-Hexahydrodibenzo[b,d]furan-1(2H)-one (**4f**): Obtained as a pale yellow liquid (23.6 mg, 62% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 - 6.01 (m, 1H), 5.77 - 5.80 (m, 1H), 4.78 - 4.79 (m, 1H), 3.05 (s, 1H), 2.31 - 2.42 (m, 4H), 2.27 - 2.29 (m, 1H), 2.14 - 2.20 (m, 1H), 1.92 - 1.98 (m, 2H), 1.77 - 1.78 (t, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 169.4, 133.5, 123.4, 115.6, 68.6, 36.8, 32.2, 28.4, 27.2, 22.0, 20.8; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1067, found 191.1066.

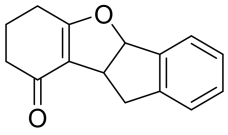


8,9,10,11b-Tetrahydroacenaphtho[1,2-b]benzofuran-11(6bH)-one (**4g**): Obtained as a pale yellow liquid (29.9 mg, 57% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.71 (dd, J = 8.0, 7.2 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.39 - 7.44 (m, 1H), 6.43 (d, J = 8.0 Hz, 1H), 5.04 (d, J = 8.0 Hz, 1H), 2.13 - 2.38 (m, 4H), 1.86 - 1.94 (m, 1H), 1.75 - 1.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0,

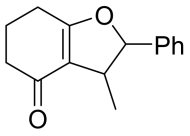
177.3, 143.6, 140.1, 137.1, 131.5, 128.7, 127.7, 126.1, 123.1, 121.8, 121.7, 115.3, 90.8, 49.5, 36.6, 24.0, 21.4; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{15}O_2$ [M + H] $^+$ 263.1067, found 263.1066.



2,3,4,4a,6,7,8,9b-Octahydro-1,4-methanodibenzo[b,d]furan-9(1H)-one (**4h**): Obtained as a pale yellow liquid (26.9 mg, 66% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (d, J = 7.6 Hz, 1H), 2.93 (d, J = 7.2 Hz, 1H), 2.37 - 2.40 (m, 1H), 2.30 - 2.35 (m, 2H), 2.22 - 2.25 (t, 2H), 1.91 - 1.96 (m, 2H), 1.39 - 1.49 (m, 2H), 1.34 (d, J = 8.8 Hz, 1H), 1.18 - 1.26 (m, 3H), 1.05 - 1.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 179.4, 115.2, 91.7, 48.5, 42.0, 39.0, 36.5, 31.6, 27.3, 23.6, 23.2, 21.6; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{17}O_2$ [M + H] $^+$ 205.1223, found 205.1225.

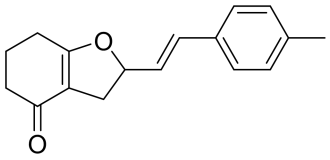


4b,6,7,8,9b,10-Hexahydro-9H-indeno[1,2-b]benzofuran-9-one (**4i**): Obtained as a pale yellow liquid (24.2 mg, 53% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 1H), 7.19 - 7.28 (m, 3H), 6.12 (d, J = 8.4 Hz, 1H), 3.93 - 3.97 (t, 1H), 3.25 - 3.31 (m, 1H), 3.10 (d, J = 16.8 Hz, 1H), 2.18 - 2.38 (m, 4H), 1.85 - 1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 176.5, 143.4, 139.4, 129.8, 127.0, 125.8, 125.6, 116.8, 93.3, 41.8, 37.5, 36.7, 24.0, 21.6; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}O_2$ [M + H] $^+$ 229.1223, found 229.1221.

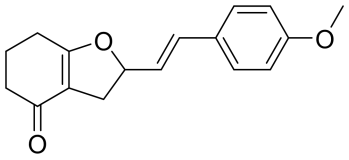


3-Methyl-2-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4j**): Obtained as a pale yellow liquid (14.6 mg, 32% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.41 (m, 3H), 7.26 - 7.32 (m, 2H), 5.16 (d, J = 6.8 Hz, 1H), 3.26 - 3.31 (m, 1H), 2.51 - 2.54 (t, 2H), 2.35 - 2.41 (m,

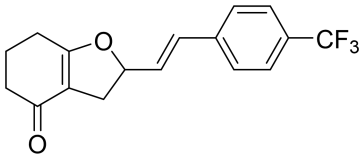
2H), 2.07 - 2.12 (m, 2H), 1.39 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 176.5, 140.2, 128.7, 128.5, 125.6, 117.37, 93.7, 43.0, 37.0, 24.0, 21.9, 19.4; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}O_2$ $[M + H]^+$ 229.1223, found 229.1222.



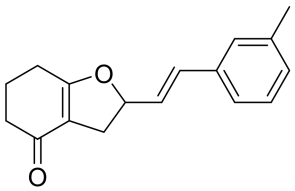
(*E*)-2-(4-Methylstyryl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4k**): Obtained as a pale yellow liquid (28.4 mg, 56% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 6.63 (d, J = 15.6 Hz, 1H), 6.18 - 6.24 (q, 1H), 5.34 - 5.41 (m, 1H), 3.05 - 3.12 (m, 1H), 2.68 - 2.74 (t, 1H), 2.45 - 2.48 (t, 2H), 2.36 - 2.39 (t, 2H), 2.34 (s, 3H), 2.03 - 2.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 177.1, 138.3, 133.2, 132.9, 129.3, 126.6, 126.0, 113.1, 86.2, 36.4, 32.1, 24.0, 21.7, 21.2; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380, found 255.1379.



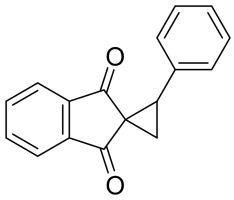
(*E*)-2-(4-Methoxystyryl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4l**): Obtained as a pale yellow liquid (27.5 mg, 51% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.93 - 6.95 (m, 1H), 6.82 - 6.86 (m, 1H), 6.93 (d, J = 16.0 Hz, 1H), 6.23 - 6.29 (q, 1H), 5.35 - 5.41 (m, 1H), 3.82 (s, 3H), 3.06 - 3.12 (m, 1H), 2.69 - 2.74 (m, 1H), 2.46 - 2.49 (t, 2H), 2.36 - 2.39 (t, 2H), 2.03 - 2.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 177.1, 159.7, 137.2, 132.9, 129.6, 127.3, 119.4, 114.0, 113.0, 111.9, 85.9, 55.2, 36.4, 32.1, 24.0, 21.6; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{19}O_3$ $[M + H]^+$ 271.1329, found 271.1325.



(*E*)-2-(4-(Trifluoromethyl)styryl)-3,5,6,7-tetrahydrobenzo furan-4(2H)-one (**4m**): Obtained as a pale yellow liquid (28.3 mg, 46% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 16.0 Hz, 1H), 6.33 - 6.39 (q, 1H), 5.38 - 5.44 (m, 1H), 3.09 - 3.15 (m, 1H), 2.70 - 2.75 (t, 1H), 2.47 - 2.50 (t, 2H), 2.37 - 2.40 (t, 2H), 2.05 - 2.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 177.0, 139.3, 131.3, 130.2, 129.8, 126.9, 125.63 (q, J = 3.8, 7.6 Hz), 125.4, 113.0, 85.3, 36.5, 32.2, 24.0, 21.7; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.6; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}F_3O_2$ $[M + H]^+$ 309.1097, found 309.1096.

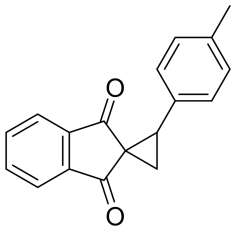


(*E*)-2-(3-Methylstyryl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-on e (**4n**): Obtained as a pale yellow liquid (31.5 mg, 62% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 - 7.26 (m, 3H), 7.07 - 7.10 (m, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.22 - 6.28 (q, 1H), 5.34 - 5.41 (m, 1H), 3.06 - 3.12 (m, 1H), 2.68 - 2.74 (m, 1H), 2.45 - 2.48 (t, 2H), 2.35 - 2.39 (t, 2H), 2.34 (s, 3H), 2.02 - 2.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 177.1, 138.2, 135.6, 133.2, 129.1, 128.5, 127.3, 126.8, 123.9, 113.0, 86.0, 36.4, 32.1, 29.6, 23.9, 21.6, 21.3; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380, found 255.1381.

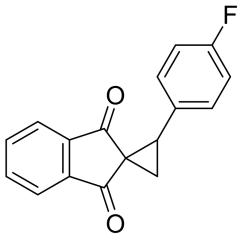


2-Phenylspiro[cyclopropane-1,2'-indene]-1',3'-dione (**5a**): Obtained as a pale yellow liquid (37.7 mg, 76% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 6.8 Hz, 1H), 7.73 - 7.82 (m, 3H),

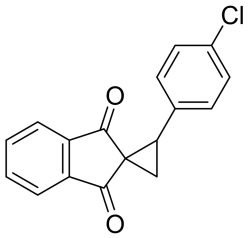
7.25 - 7.33 (m, 5H), 3.43 - 3.48 (t, 1H), 2.47 - 2.50 (q, 1H), 2.29 - 2.32 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 195.8, 142.6, 141.5, 134.8, 134.6, 133.5, 129.2, 128.1, 127.8, 122.5, 122.4, 42.6, 41.2, 22.2; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{13}O_2$ $[M + H]^+$ 249.0910, found 249.0911.



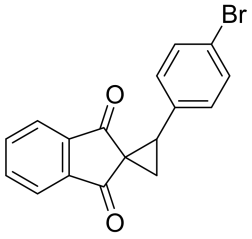
2-(*p*-Tolyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5b**): Obtained as a pale yellow liquid (44.0 mg, 84% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 1H), 7.71 - 7.81 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.41 - 3.45 (t, 1H), 2.45 - 2.48 (q, 1H), 2.27 - 2.31 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 195.9, 142.6, 141.5, 137.5, 134.7, 134.5, 130.4, 129.0, 128.8, 122.39, 122.35, 42.8, 41.3, 22.2, 21.2; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{15}O_2$ $[M + H]^+$ 263.1067, found 263.1068.



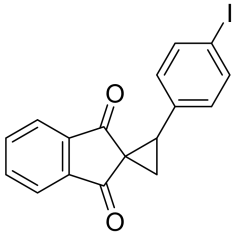
2-(4-Fluorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5c**): Obtained as a pale yellow liquid (38.3 mg, 72% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 6.8 Hz, 1H), 7.74 - 7.82 (m, 3H), 7.25 - 7.28 (t, 2H), 6.96 - 7.00 (t, 2H), 3.39 - 3.43 (t, 1H), 2.41 - 2.44 (q, 1H), 2.28 - 2.32 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 195.8, 162.2 (d, J = 245.3 Hz), 142.6, 141.6, 134.9, 134.7, 130.8, 130.7, 129.3 (d, J = 3.2 Hz), 122.5 (d, J = 1.5 Hz), 115.1 (d, J = 21.5 Hz), 42.5, 40.1, 22.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -114.1; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}FO_2$ $[M + H]^+$ 267.0816, found 267.0815.



2-(4-Chlorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5d**): Obtained as a pale yellow liquid (41.7 mg, 74% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 6.8 Hz, 1H), 7.74 - 7.82 (m, 3H), 7.21 - 7.27 (m, 4H), 3.36 - 3.41 (t, 1H), 2.40 - 2.43 (q, 1H), 2.28 - 2.31 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 195.7, 142.5, 141.5, 134.9, 134.7, 133.6, 132.1, 130.5, 128.3, 122.49, 122.48, 42.4, 40.0, 22.1; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}ClO_2$ $[M + H]^+$ 283.0520, found 283.0522.

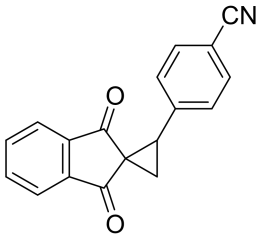


2-(4-Bromophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5e**): Obtained as a pale yellow liquid (45.6 mg, 70% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.2 Hz, 1H), 7.78 - 7.83 (m, 3H), 7.48 (d, J = 8.0 Hz, 2H), 3.44 - 3.48 (t, 1H), 2.47 - 2.50 (q, 1H), 2.34 - 2.38 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 195.4, 147.2, 142.4, 141.5, 141.2, 135.2, 135.1, 130.1, 123.2, 122.7, 122.6, 42.2, 38.8, 22.1; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}BrO_2$ $[M + H]^+$ 327.0015, found 327.0012.

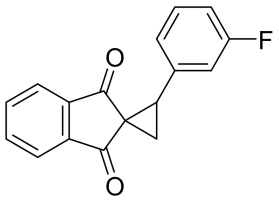


2-(4-Iodophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5f**): Obtained as a pale yellow liquid (57.4 mg, 77% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 6.8 Hz, 1H), 7.74 - 7.83 (m, 3H), 7.42 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.35 - 3.39 (t, 1H), 2.40 - 2.43 (q, 1H), 2.28 - 2.31 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 195.7, 142.6,

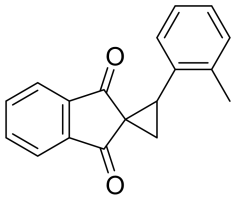
141.5, 135.0, 134.8, 132.6, 131.2, 130.8, 122.5, 121.8, 42.4, 40.0, 22.1; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}IO_2$ $[M + H]^+$ 374.9876, found 374.9878.



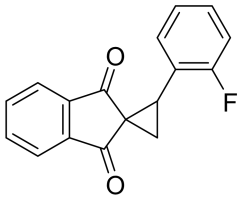
4-(1',3'-Dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-2-yl)benzonitrile (**5g**): Obtained as a pale yellow liquid (38.8 mg, 71% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.2 Hz, 1H), 7.79 - 7.84 (m, 3H), 7.60 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 3.40 - 3.44 (t, 1H), 2.43 - 2.46 (q, 1H), 2.31 - 2.35 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 195.5, 142.4, 141.5, 139.1, 135.2, 135.0, 131.8, 129.9, 122.7, 122.6, 118.6, 111.5, 42.2, 39.3, 22.0; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{12}NO_2$ $[M + H]^+$ 274.0863, found 274.0861.



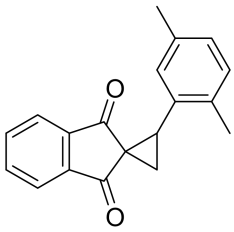
2-(3-Fluorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5h**): Obtained as a pale yellow liquid (34.6 mg, 65% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 6.8 Hz, 1H), 7.75 - 7.84 (m, 3H), 7.23 - 7.28 (q, 1H), 7.07 (d, J = 7.6 Hz, 1H),7.01 (d, J = 10.0 Hz, 1H), 6.93 - 6.97 (t, 1H), 3.38 - 3.43 (t, 1H), 2.41 - 2.44 (q, 1H), 2.27 - 2.30 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 195.8, 162.2 (d, J = 245.3 Hz), 142.6, 141.6, 134.9, 134.7, 130.8, 130.7, 129.3 (d, J = 3.2 Hz), 122.5 (d, J = 1.5 Hz), 115.1 (d, J = 21.5 Hz), 42.5, 40.1, 22.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -113.3; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}FO_2$ $[M + H]^+$ 267.0816, found 267.0817.



2-(*o*-Tolyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5i**): Obtained as a pale yellow liquid (41.4 mg, 79% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.2 Hz, 1H), 7.73 - 7.81 (m, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.18 - 7.26 (m, 2H), 7.07 (d, J = 6.8 Hz, 1H), 3.31 - 3.35 (t, 1H), 2.47 - 2.50 (q, 1H), 2.29 - 2.32 (q, 1H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 195.5, 142.2, 141.3, 137.8, 134.9, 134.6, 132.6, 129.7, 128.8, 127.9, 125.7, 122.4, 41.8, 39.4, 22.4, 19.5; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{15}O_2$ $[M + H]^+$ 263.1067, found 263.1065.

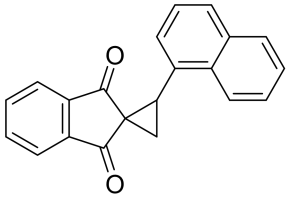


2-(2-Fluorophenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5j**): Obtained as a pale yellow liquid (37.2 mg, 70% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 6.8 Hz, 1H), 7.74 - 7.84 (m, 3H), 7.36 - 7.40 (t, 1H), 7.24 - 7.29 (q, 1H), 7.13 - 7.17 (t, 1H), 6.91 - 6.96 (t, 1H), 3.34 - 3.37 (t, 1H), 2.34 - 2.37 (q, 1H), 2.27 - 2.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 195.8, 161.9 (d, J = 245.9 Hz), 142.4, 141.6, 134.8, 134.6, 130.5 (d, J = 3.2 Hz), 129.6, 129.5, 123.8 (d, J = 3.6 Hz), 122.5 (d, J = 7.7 Hz), 121.7 (d, J = 14.5 Hz), 114.9 (d, J = 21.1 Hz), 40.9, 33.6 (d, J = 3.4 Hz), 21.5; ^{19}F NMR (400 MHz, $CDCl_3$) δ -115.7; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{12}FO_2$ $[M + H]^+$ 267.0816, found 267.0813.

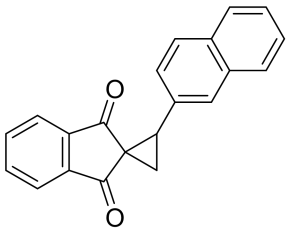


2-(2,5-Dimethylphenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5k**): Obtained as a pale yellow liquid (48.6 mg, 88% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 6.8 Hz, 1H), 7.73

- 7.81 (m, 3H), 7.16 (s, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 3.28 - 3.32 (t, 1H), 2.46 - 2.49 (q, 1H), 2.36 (s, 3H), 2.27 - 2.30 (q, 1H), 1.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 195.5, 142.2, 141.3, 135.1, 134.8, 134.7, 134.6, 132.3, 129.6, 128.7, 122.39, 122.35, 41.9, 39.6, 22.4, 21.1, 19.0; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{17}O_2$ $[M + H]^+$ 277.1223, found 277.1225.



2-(Naphthalen-1-yl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5l**): Obtained as a pale yellow liquid (42.3 mg, 71% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.74 - 7.80 (m, 3H), 7.65 - 7.69 (t, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.55 - 7.57 (m, 2H), 7.47 - 7.51 (t, 1H), 7.33 - 7.36 (m, 1H), 7.19 - 7.23 (t, 1H), 3.77 - 3.81 (t, 1H), 2.60 - 2.64 (q, 1H), 2.41 - 2.44 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 195.2, 142.3, 141.4, 134.9, 134.5, 133.3, 132.8, 130.1, 128.8, 128.7, 126.8, 126.4, 125.6, 125.1, 122.6, 122.4, 122.4, 42.1, 38.2, 22.2; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{15}O_2$ $[M + H]^+$ 299.1067, found 299.1065.



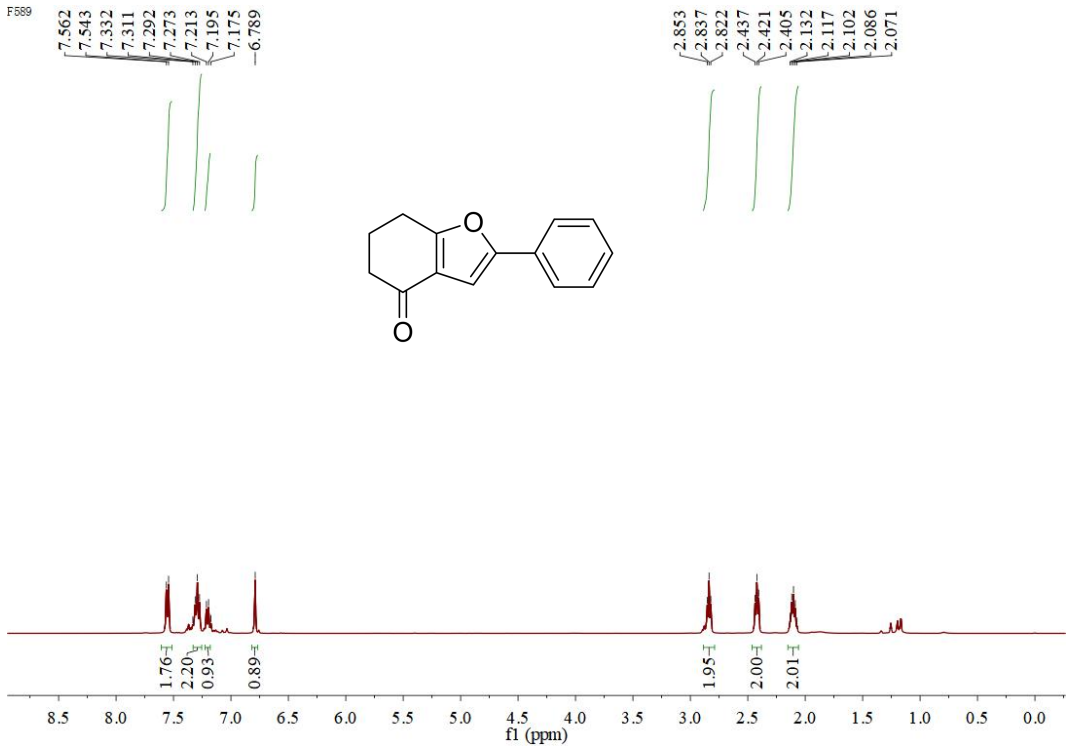
2-(Naphthalen-2-yl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (**5m**): Obtained as a pale yellow liquid (48.3 mg, 81% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 1H), 7.69 - 7.78 (m, 7H), 7.43 - 7.44 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 3.58 - 3.62 (t, 1H), 2.60 - 2.63 (q, 1H), 2.36 - 2.39 (q, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 195.7, 142.6, 141.6, 134.8, 134.6, 133.0, 132.8, 131.1, 128.4, 127.8, 127.6, 126.8, 126.1, 126.0, 122.4, 42.8, 41.4, 22.3; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{15}O_2$ $[M + H]^+$ 299.1067, found 299.1068.

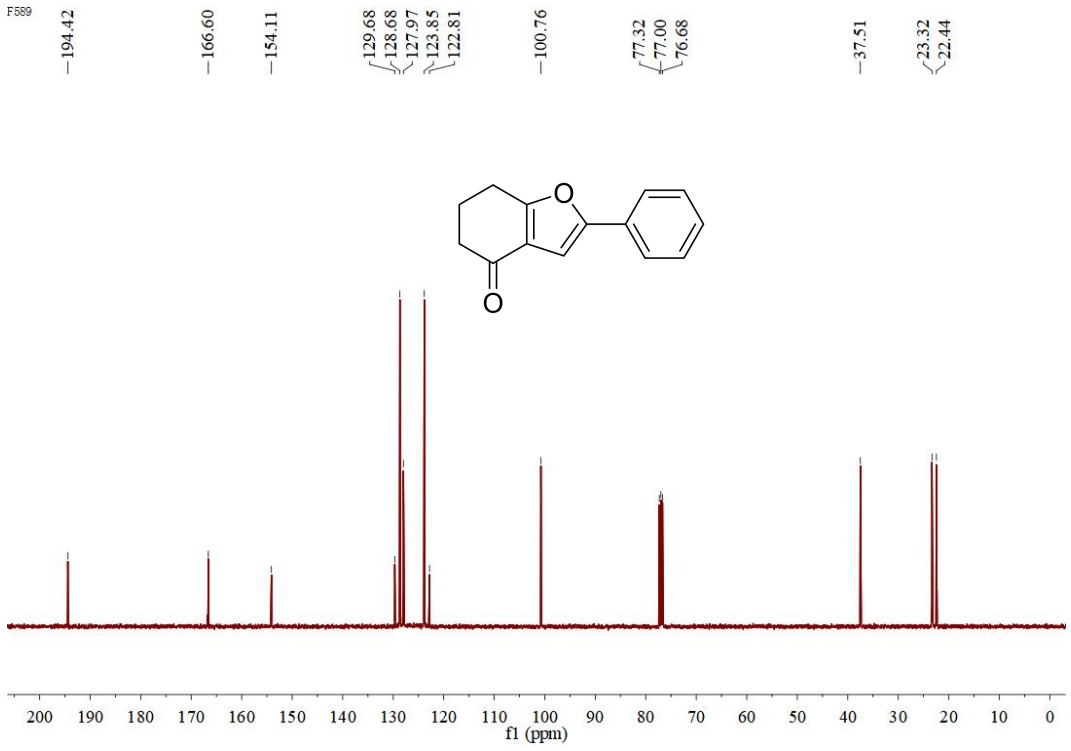
References

1. (a) A. Shao, X. Luo, C.-W. Chiang, M. Gao and A. Lei, *Chem. Eur. J*. **2017**, *23*, 17874-17878; (b) L. Xia and Y. R. Lee, *Eur. J. Org. Chem*. **2014**, 3430-3442; (c) L. Xia and Y. R. Lee, *Adv. Synth. Catal*. **2013**, *355*, 2361-2374; (d) Y.-Y. Han, Y.-Y. Jiao, D. Ren, Z. Hu, S. Shen and S. Yu, *Asian J. Org. Chem*. **2017**, *6*, 414-417; (e) S. Agasti, T. Pal, T. K. Achar, S. Maiti, D. Pal, S. Mandal, K. Daud, G. K. Lahiri and D. Maiti, *Angew. Chem. Int. Ed*. **2019**, *58*, 1-6.

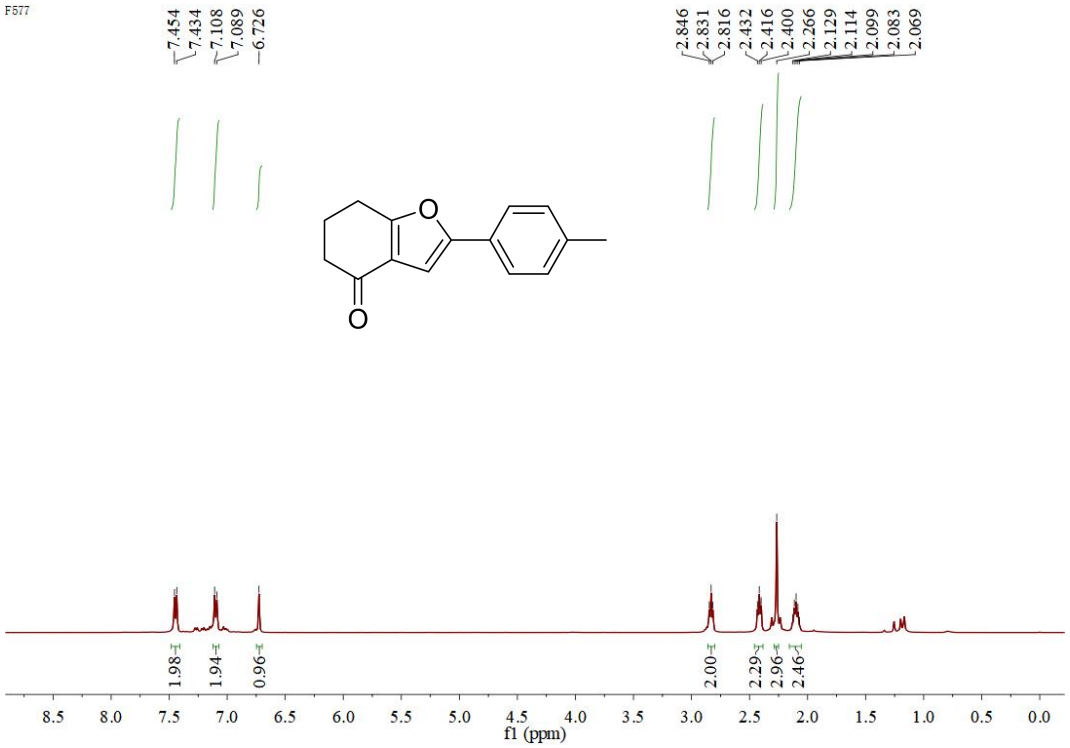
Copies of ^{1}H and ^{13}C NMR spectra of products

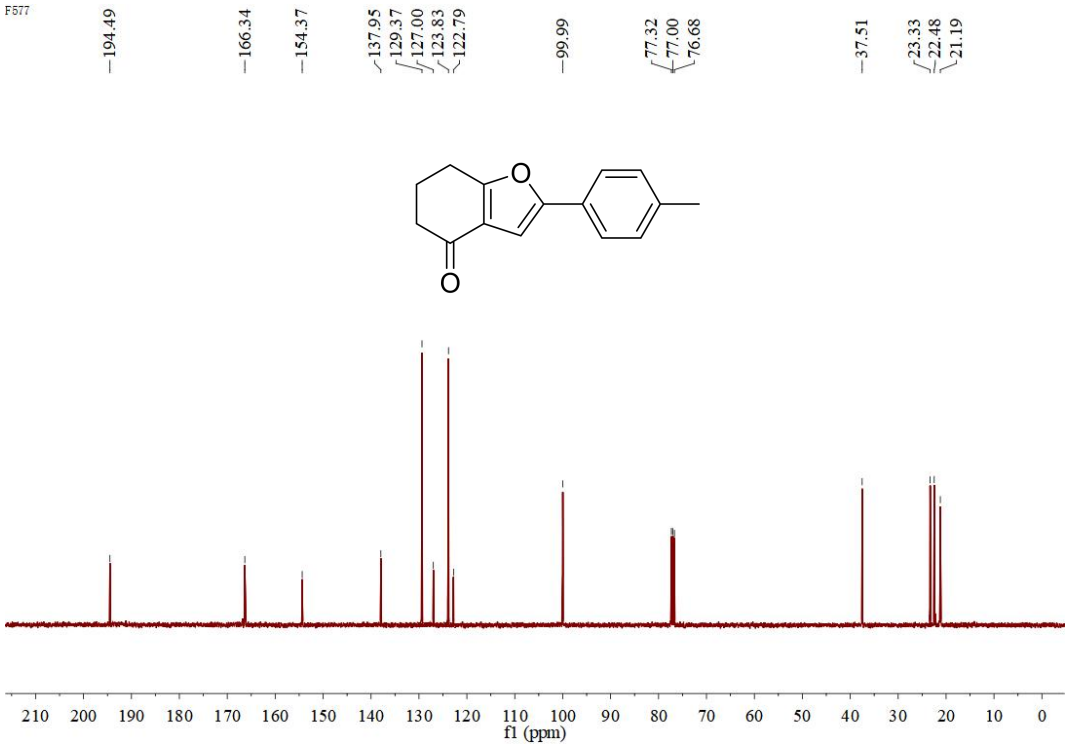
^{1}H NMR and ^{13}C NMR of 3a



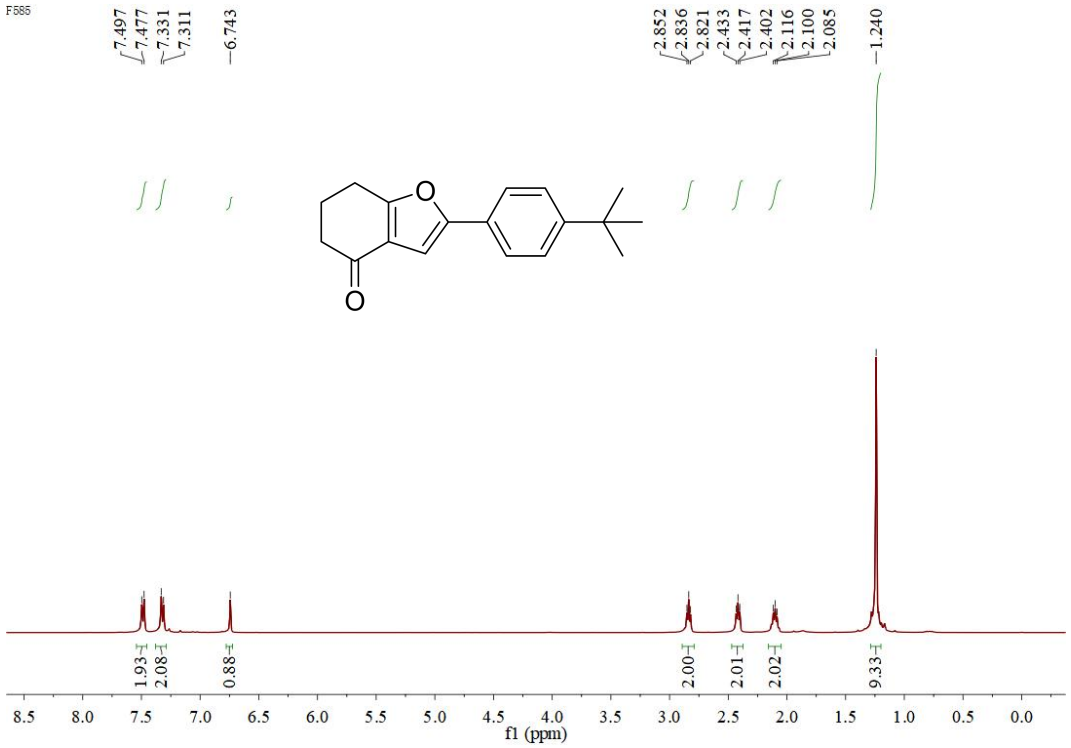


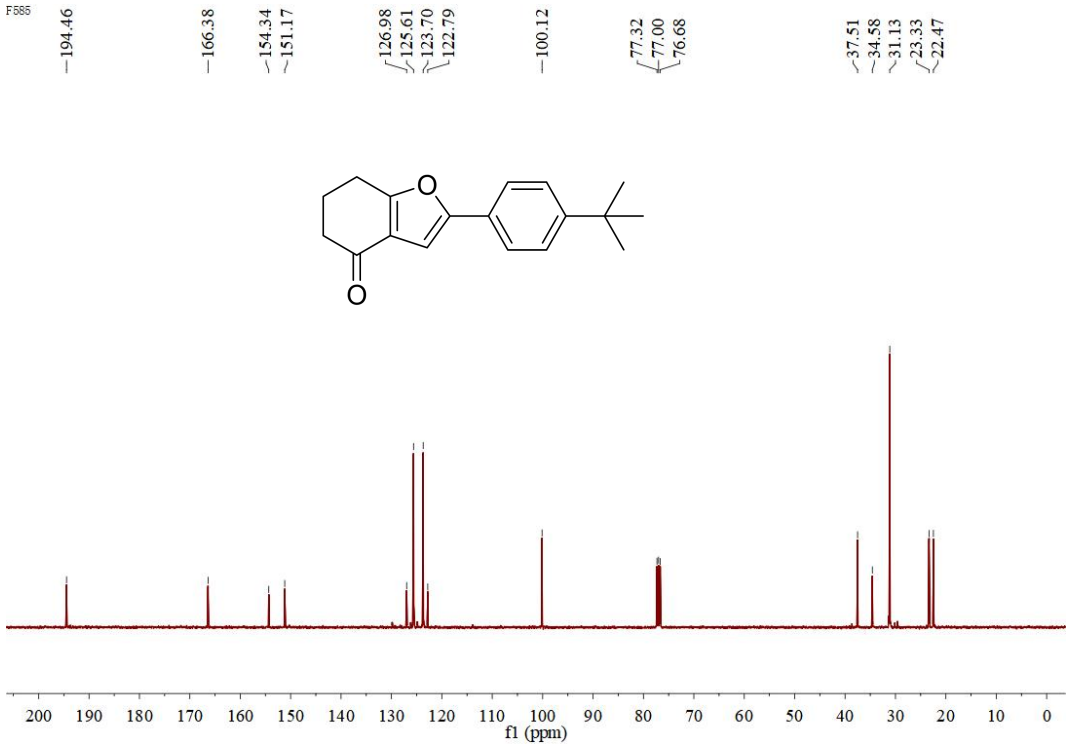
^{1}H NMR and ^{13}C NMR of 3b



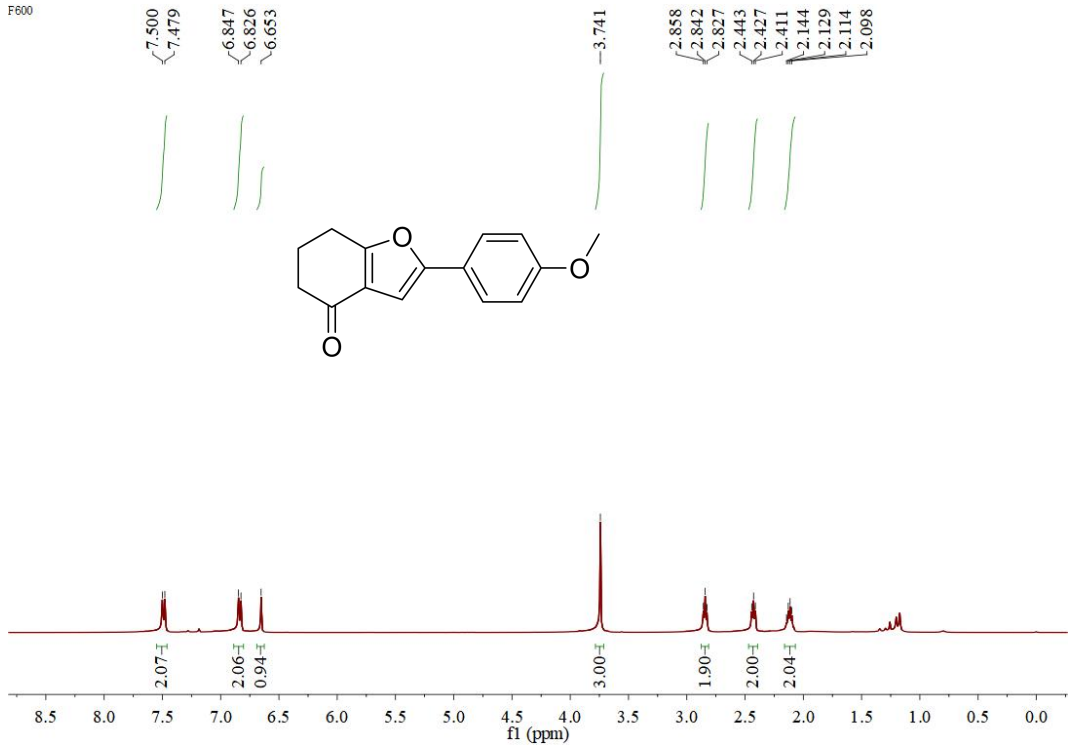


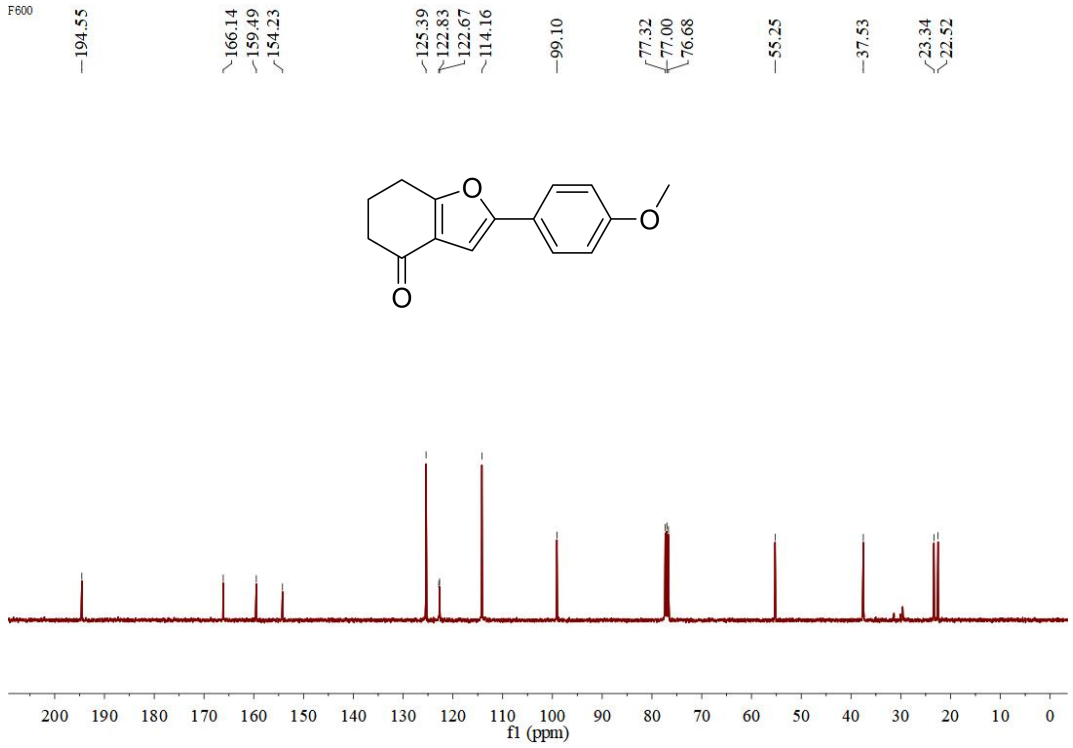
^{1}H NMR and ^{13}C NMR of 3c



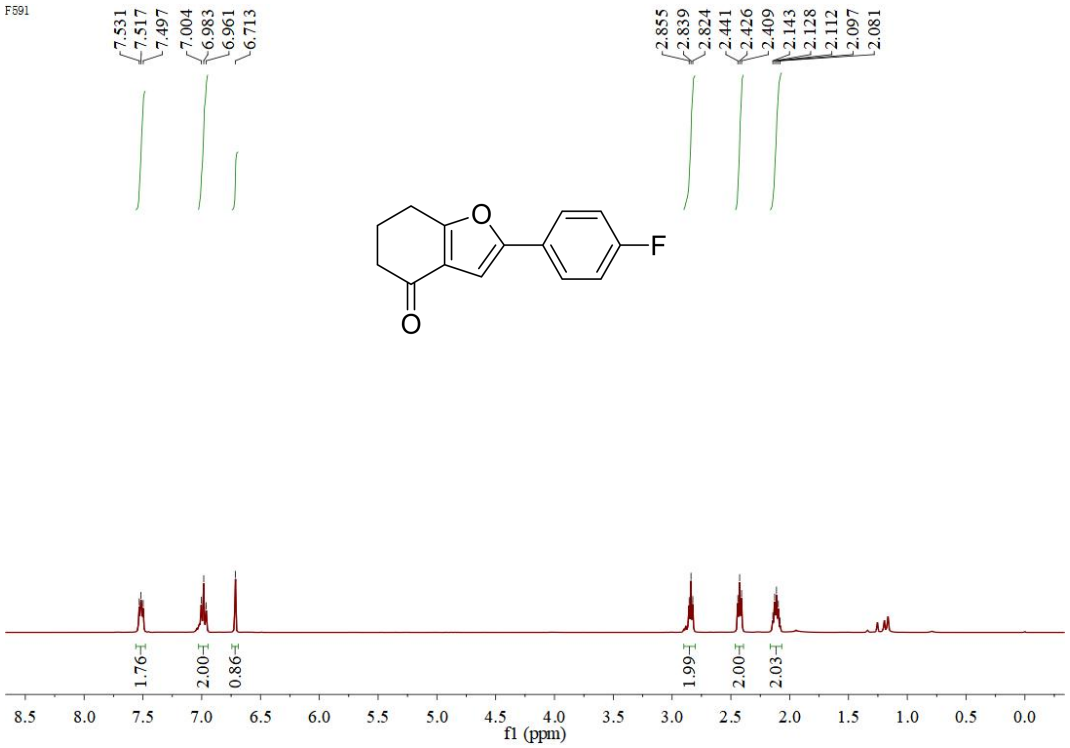


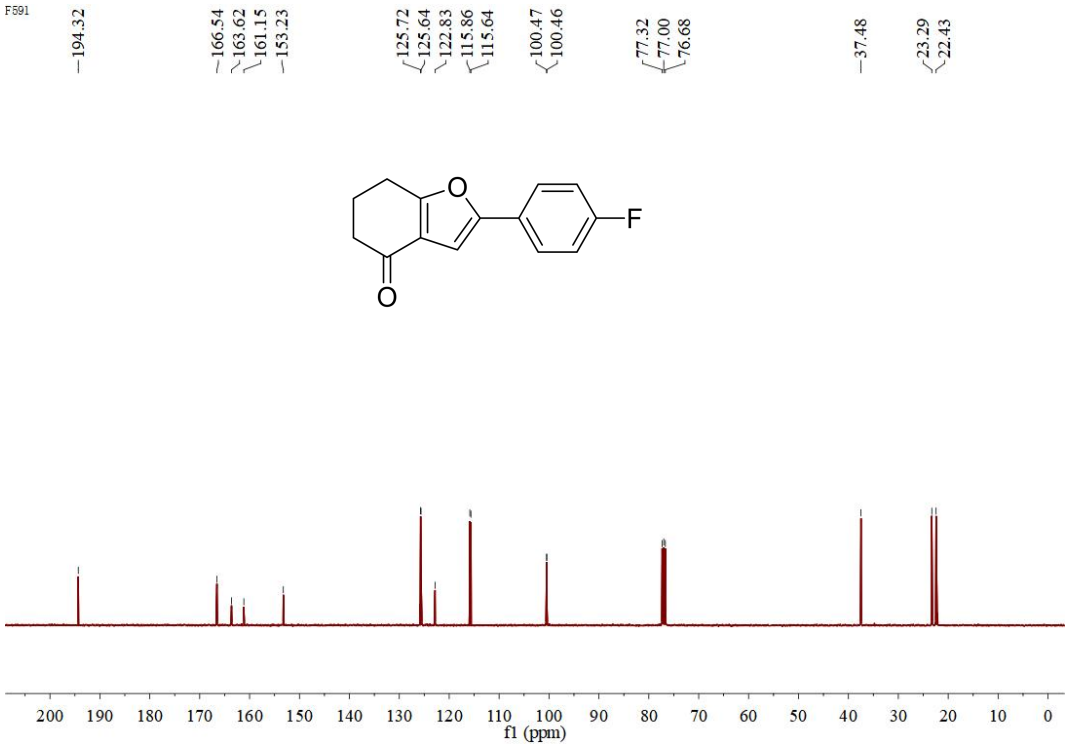
^{1}H NMR and ^{13}C NMR of 3d

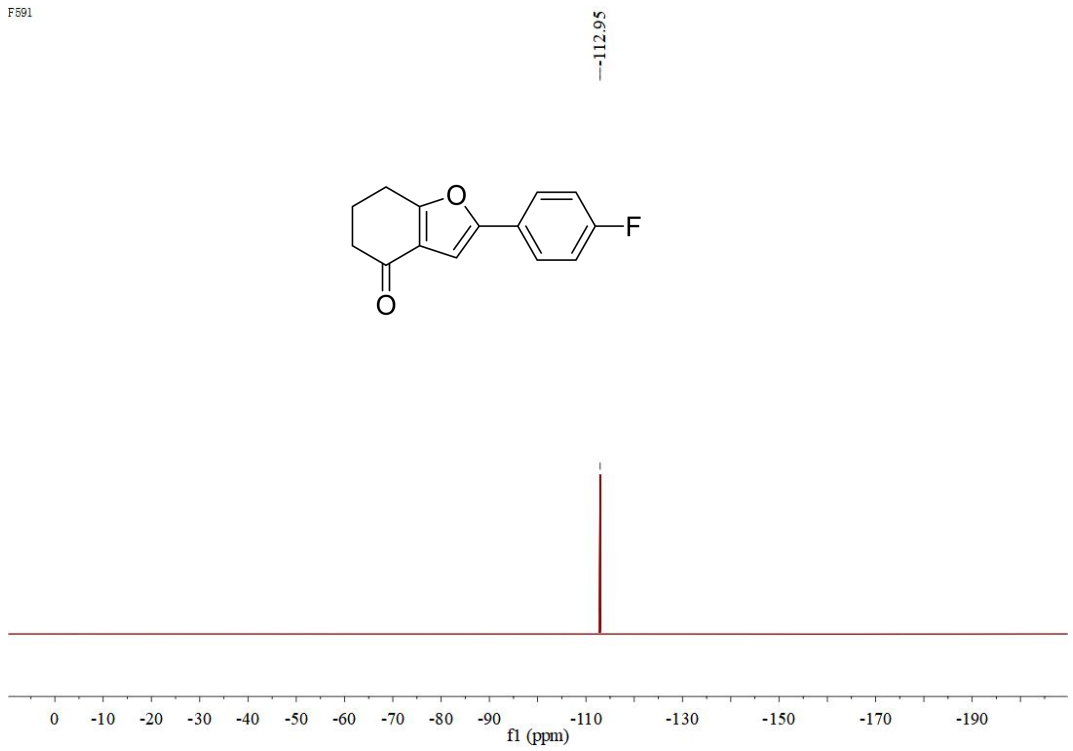




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3e



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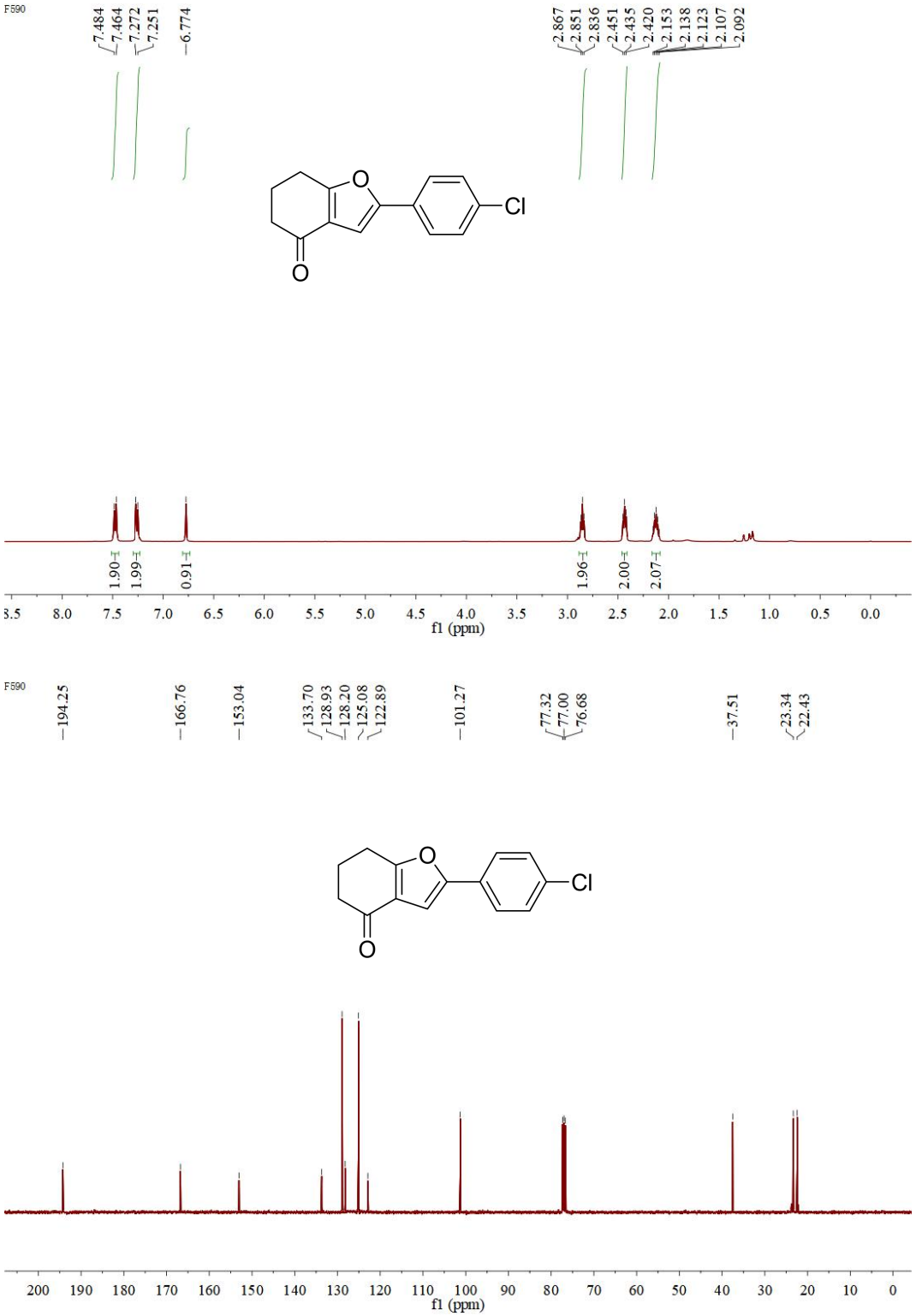
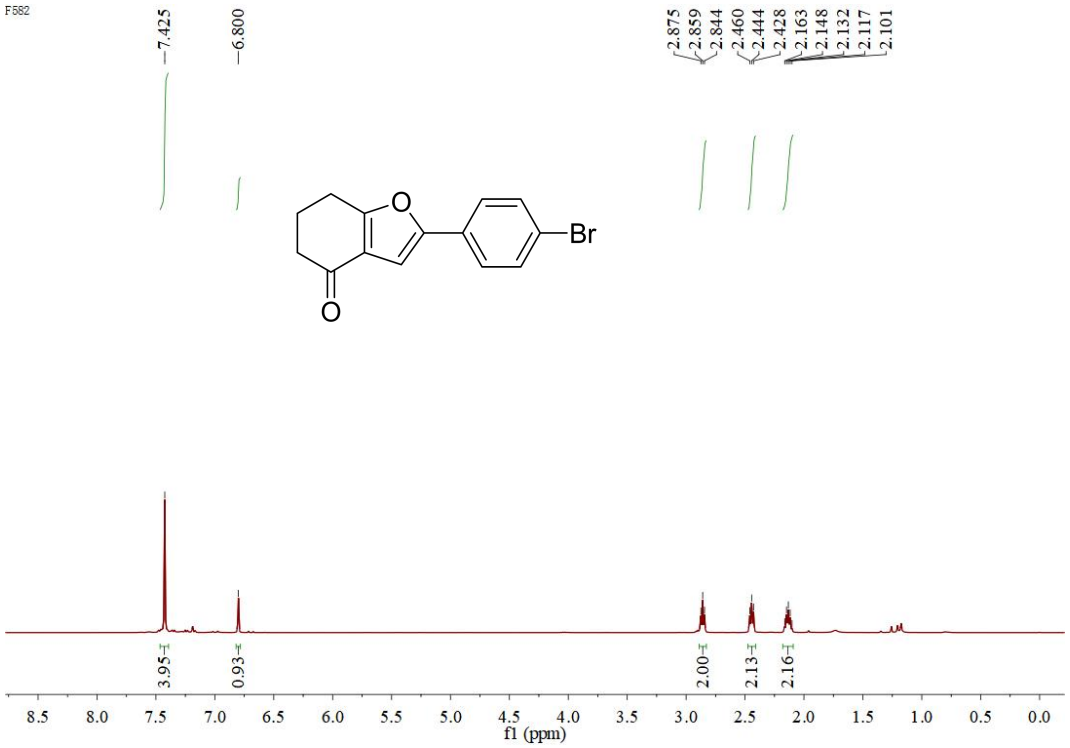
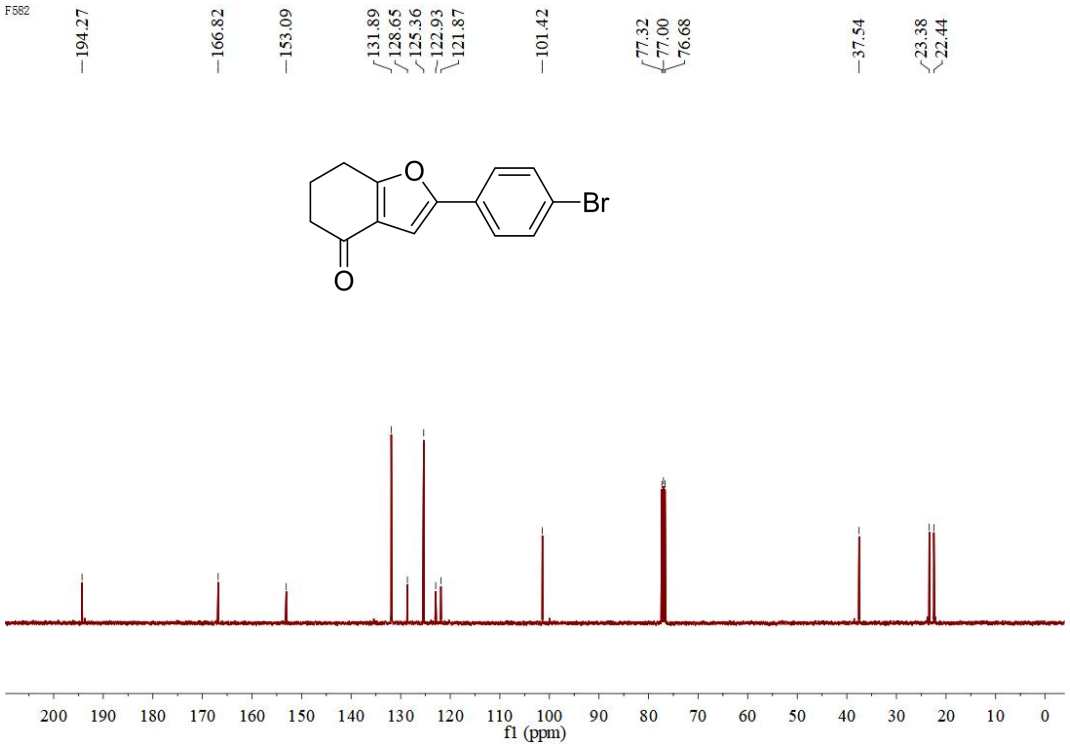
O
F
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)

^{1}H NMR and ^{13}C NMR of 3f

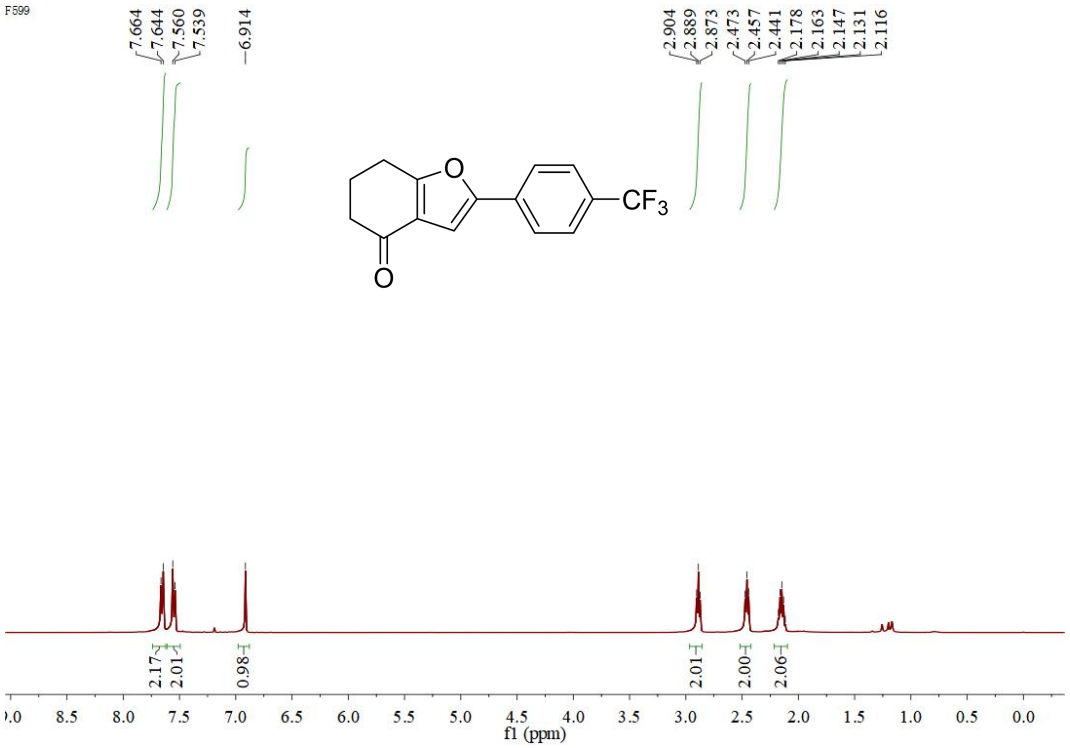


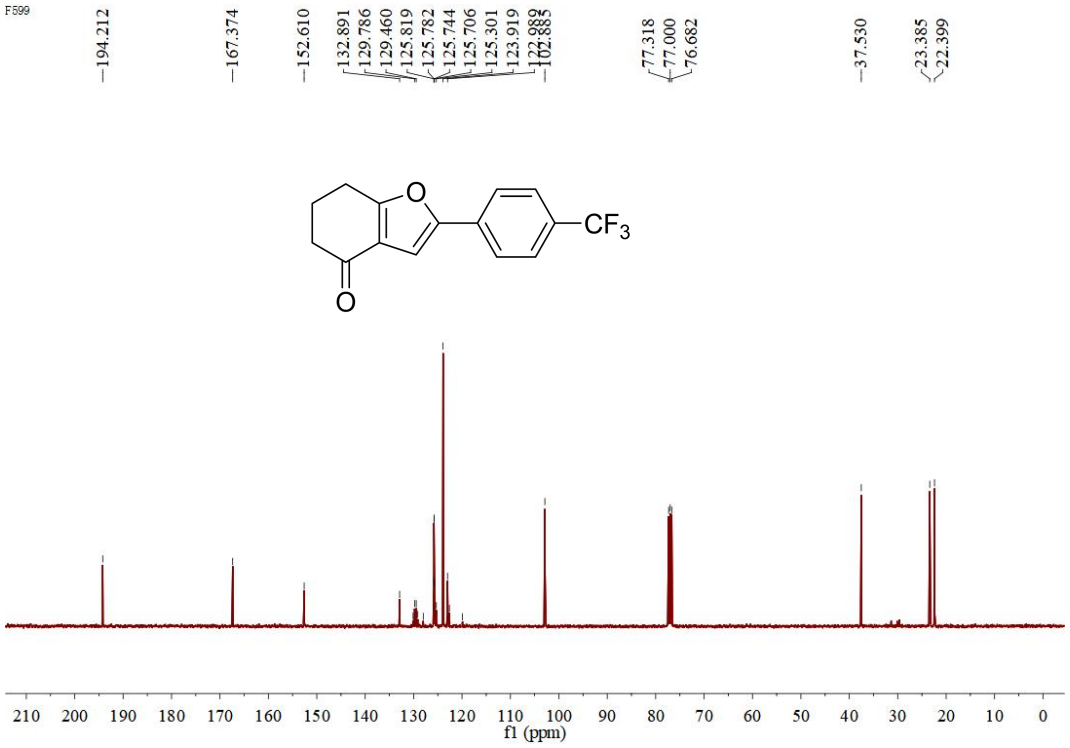
^{1}H NMR and ^{13}C NMR of 3g

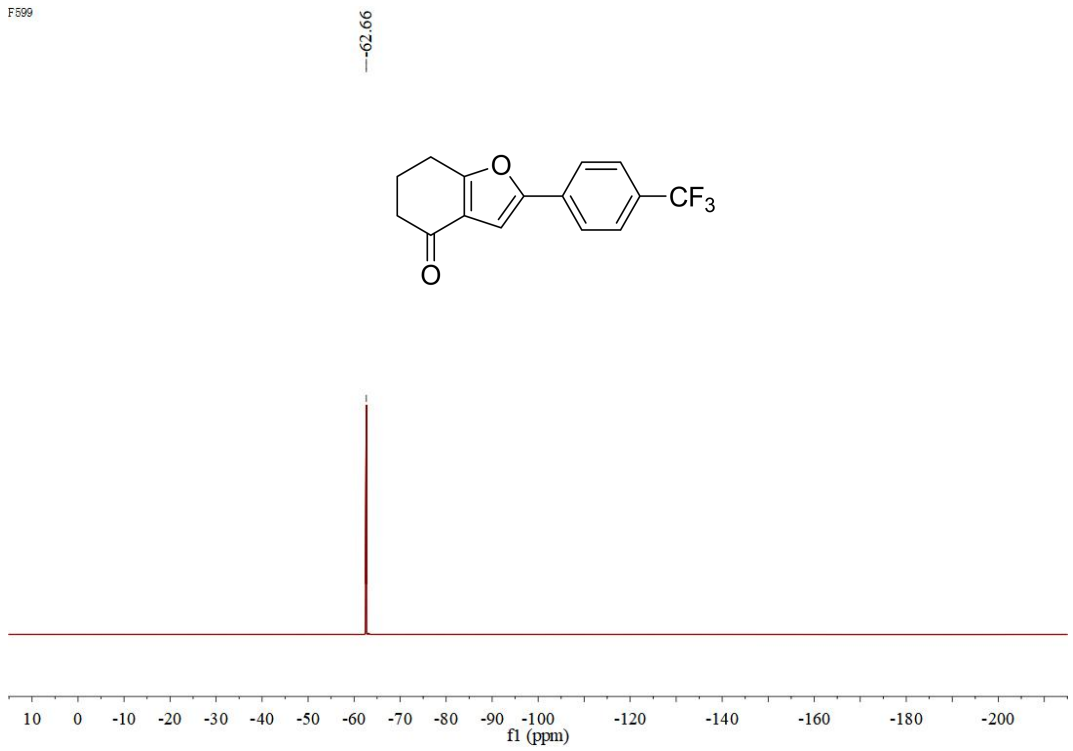




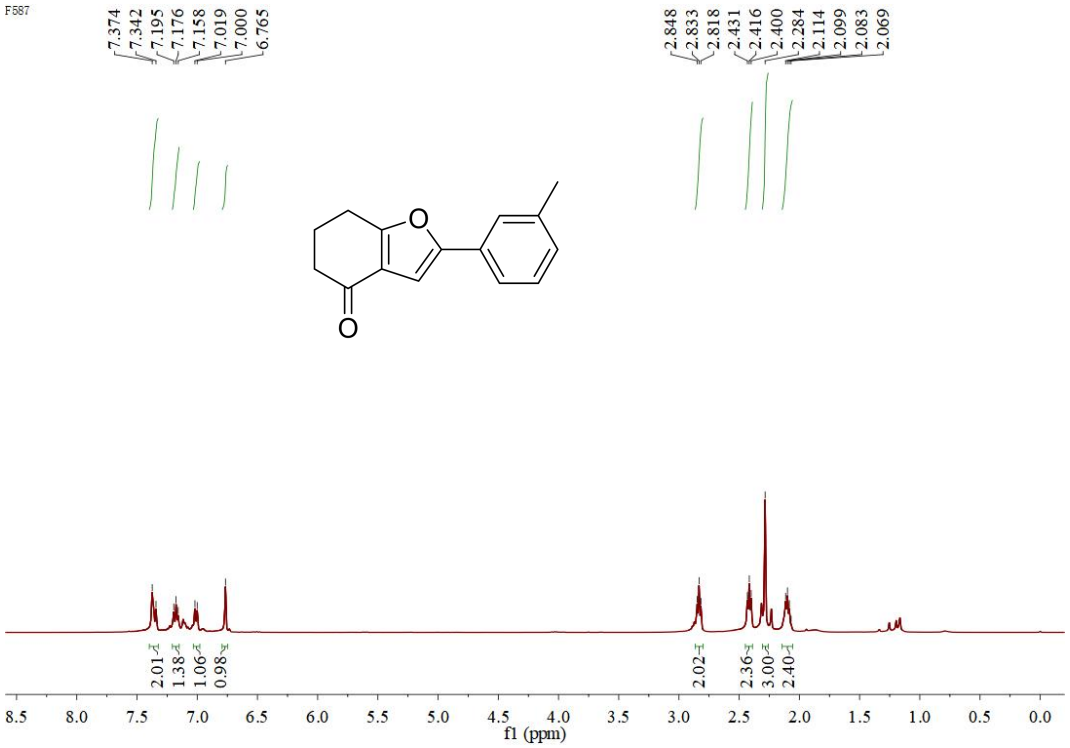
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3h

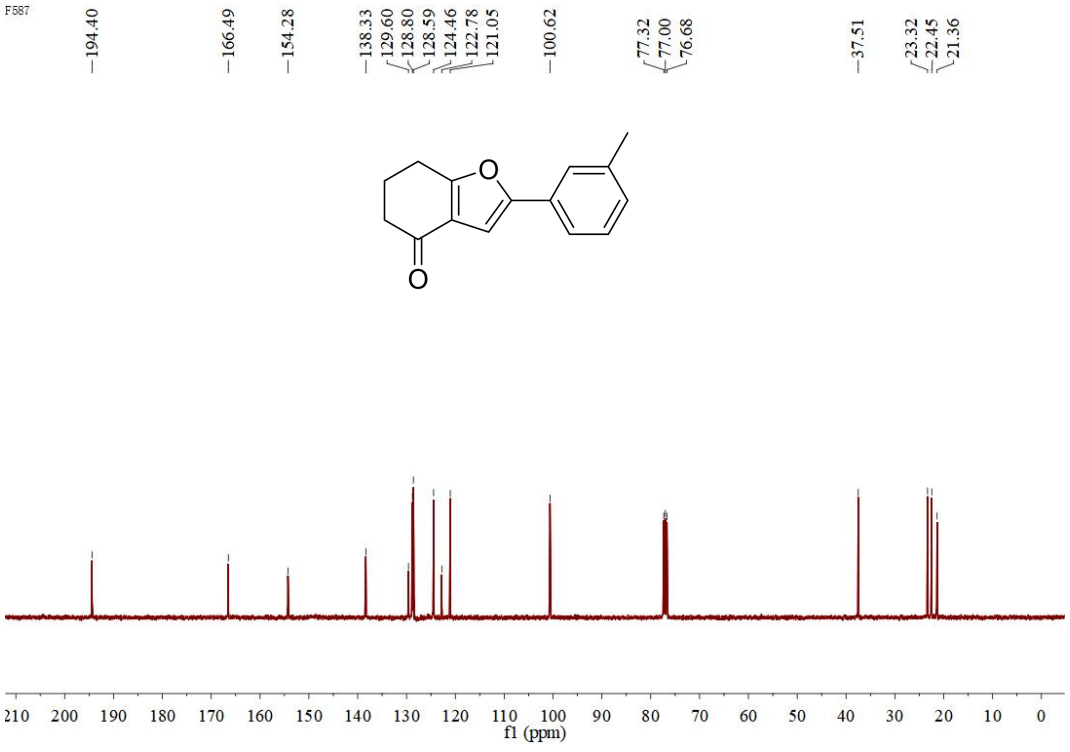




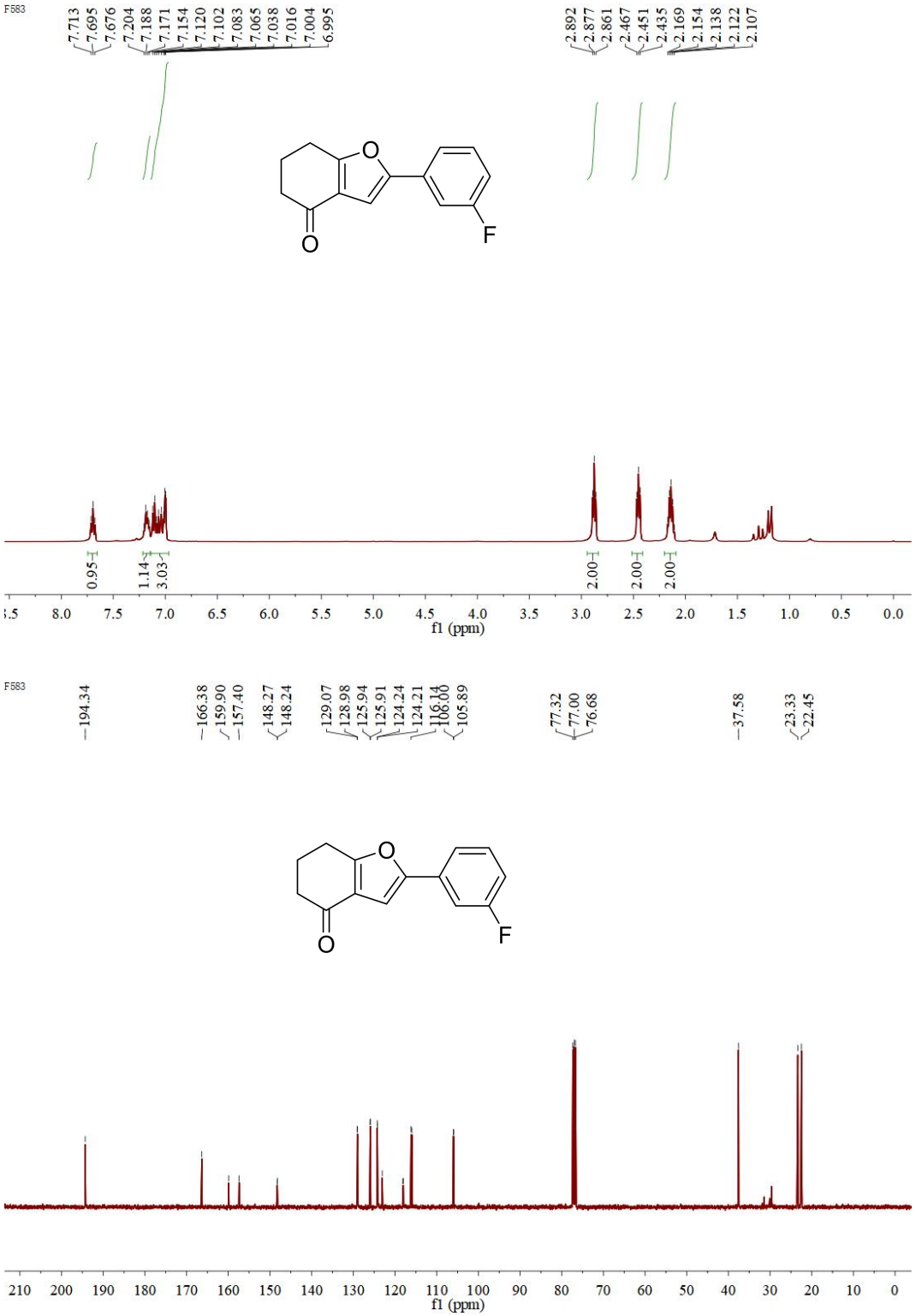

F599
-62.66
O
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

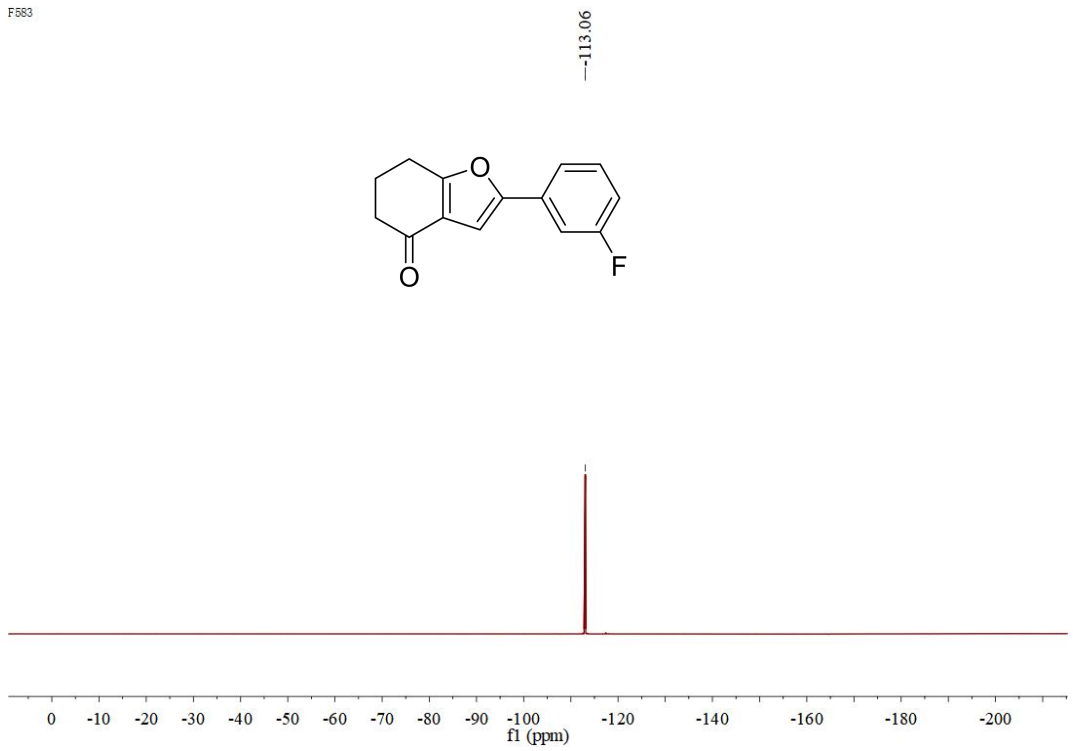
^{1}H NMR and ^{13}C NMR of 3i





^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3j




F583
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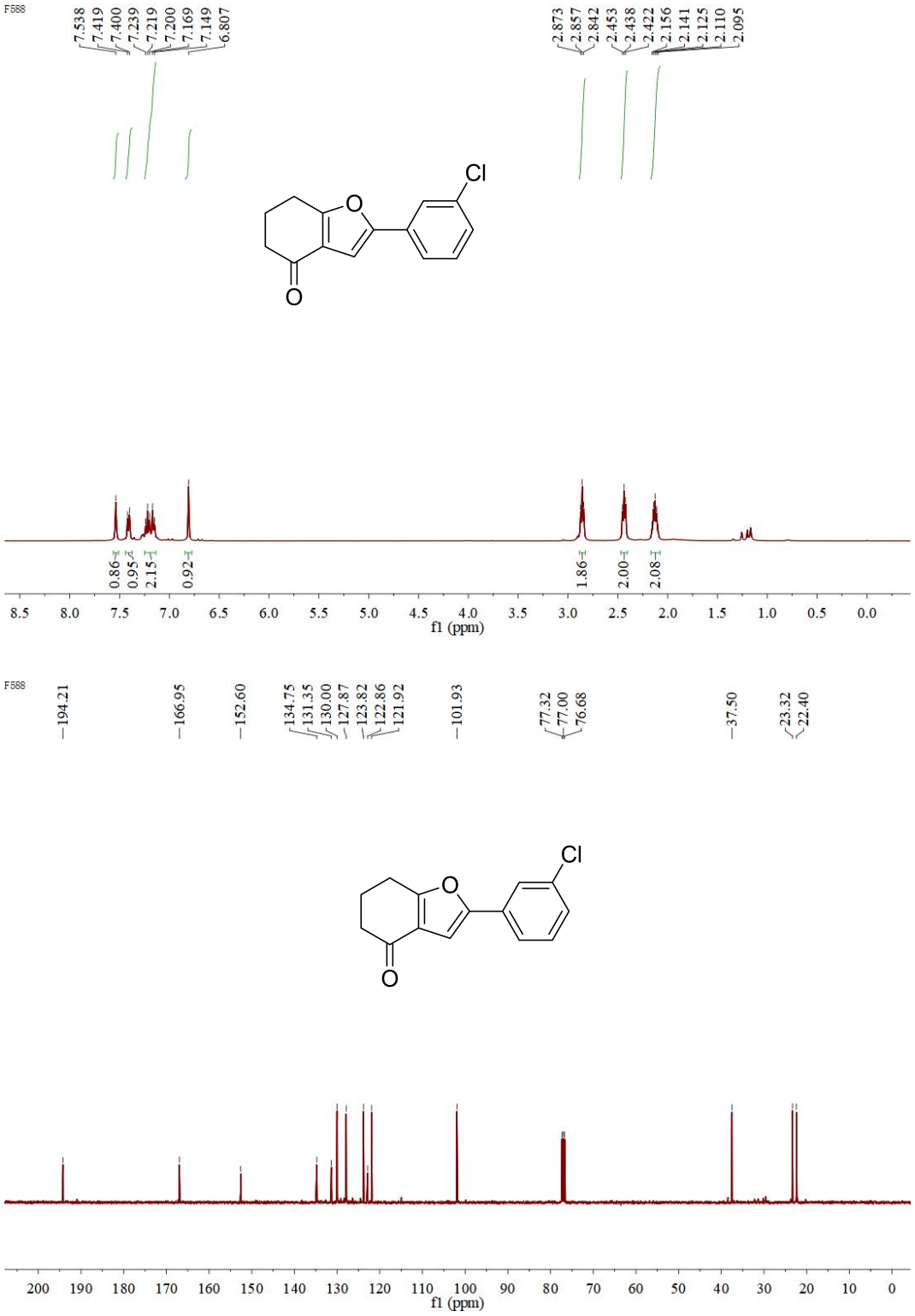
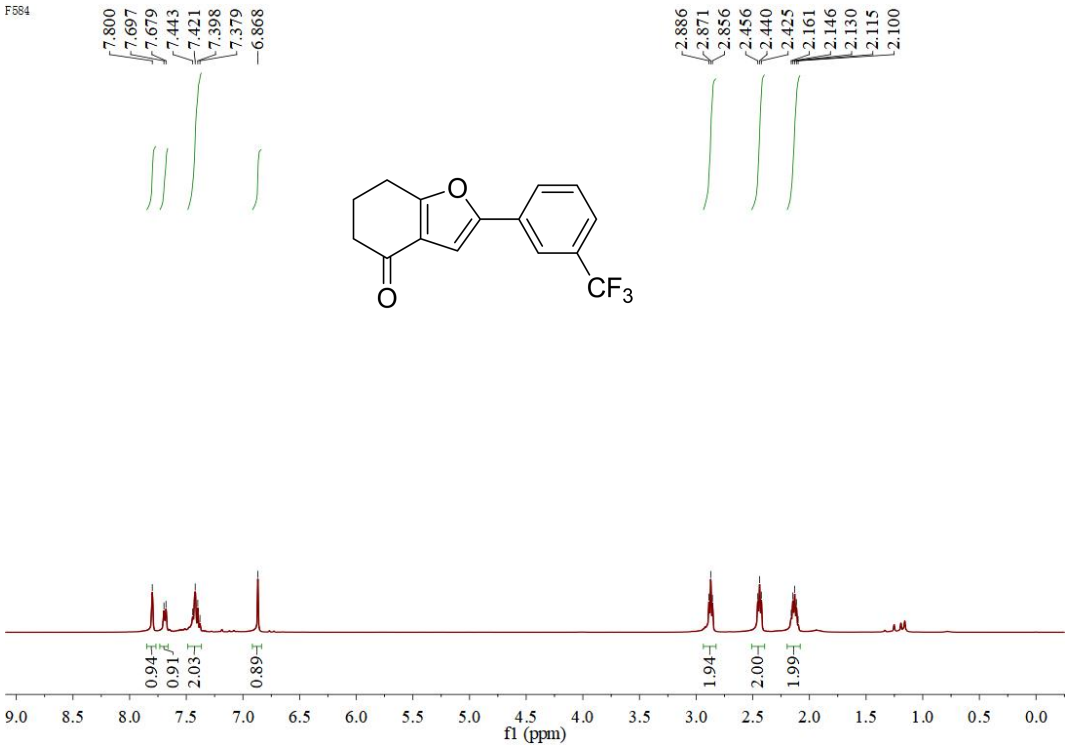
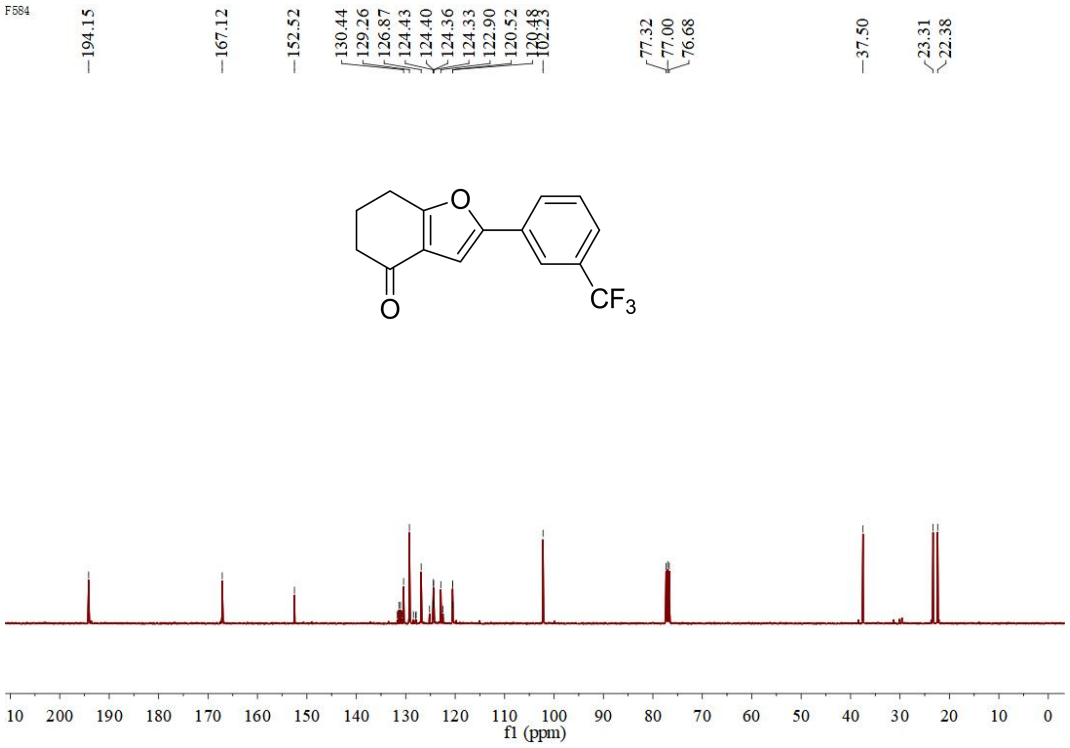
O
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

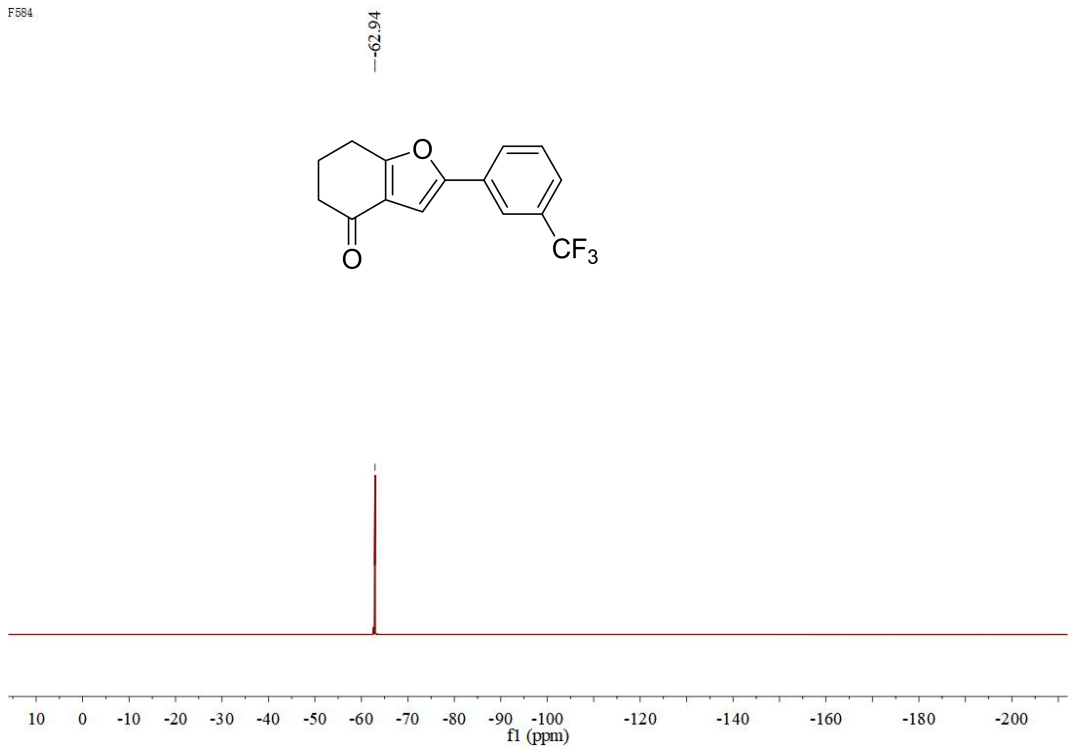
^{1}H NMR and ^{13}C NMR of 3k



^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3l



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O
CF3
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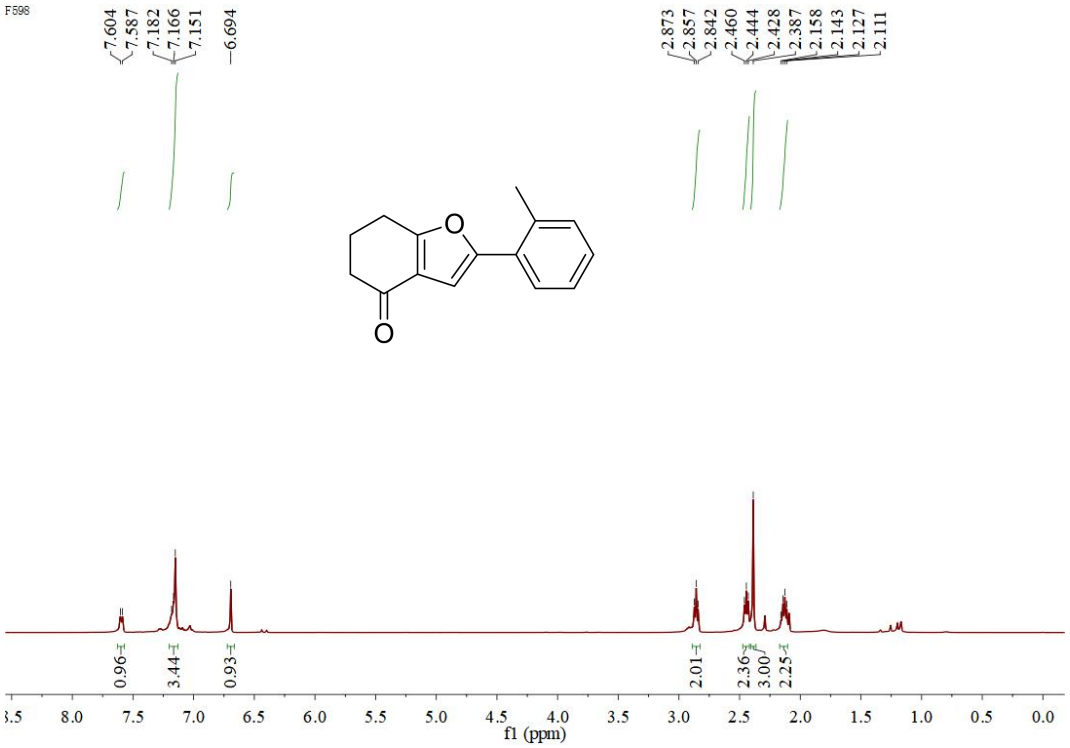
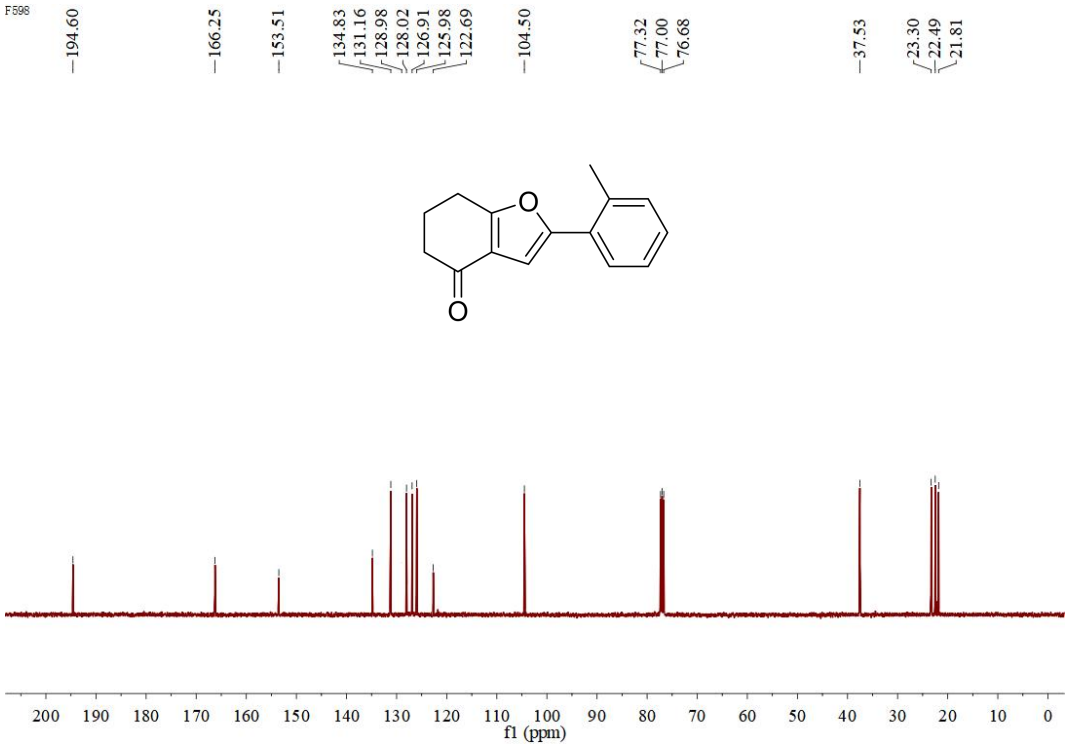
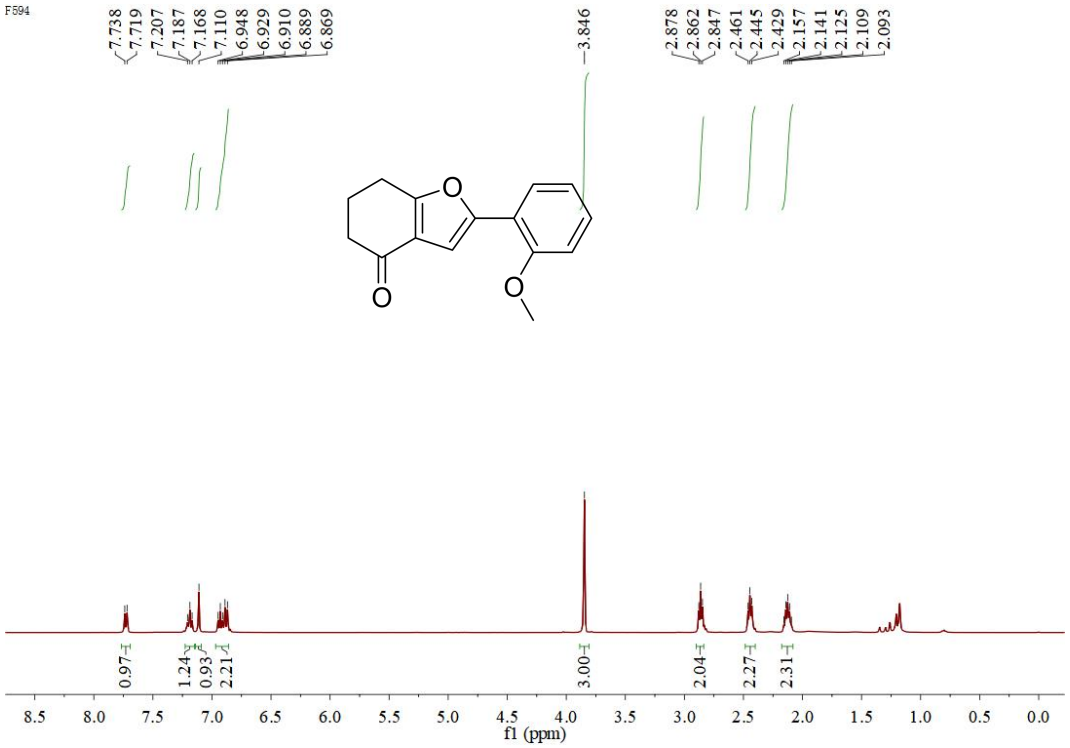
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

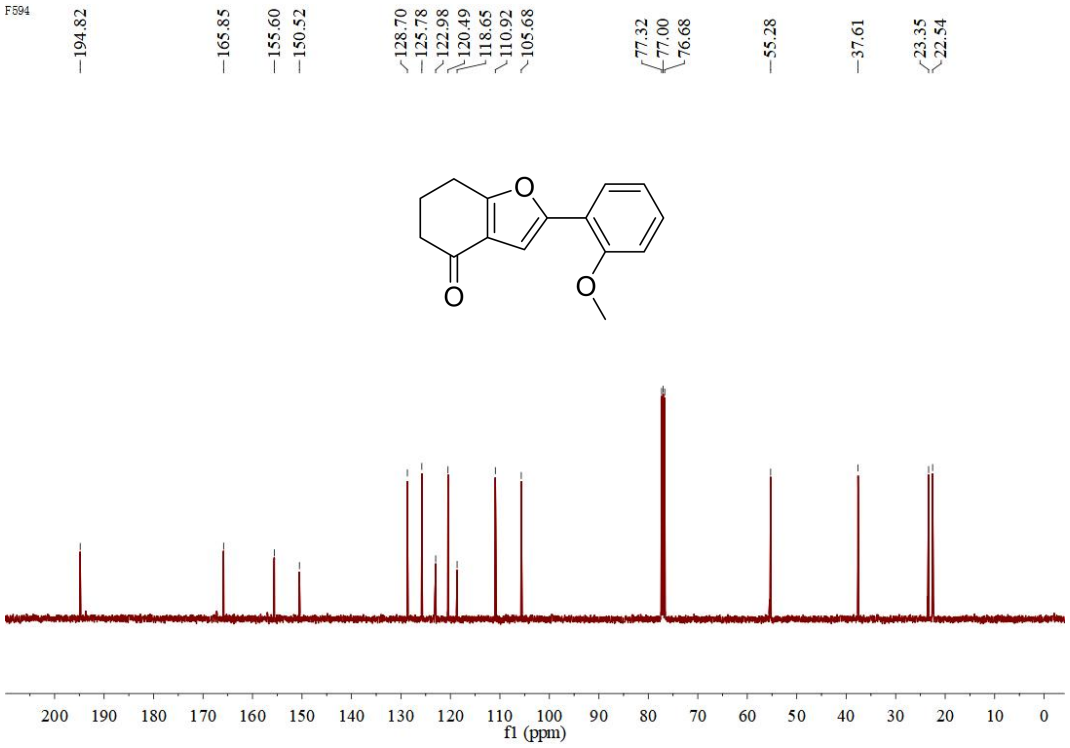
^{1}H NMR and ^{13}C NMR of 3m



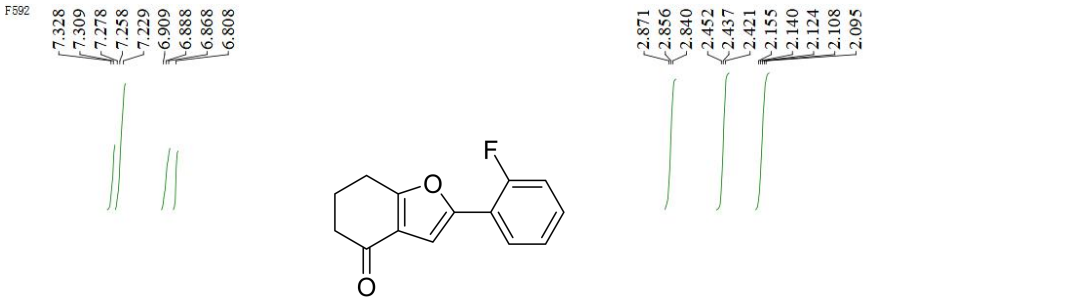


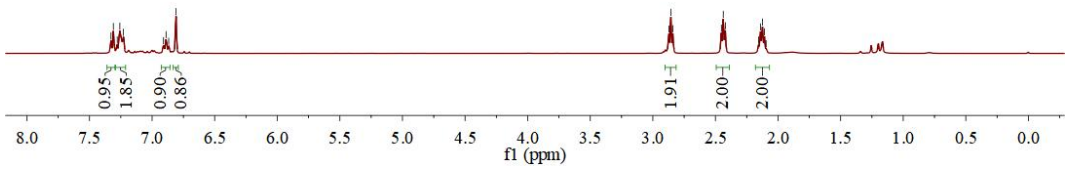
^{1}H NMR and ^{13}C NMR of 3n

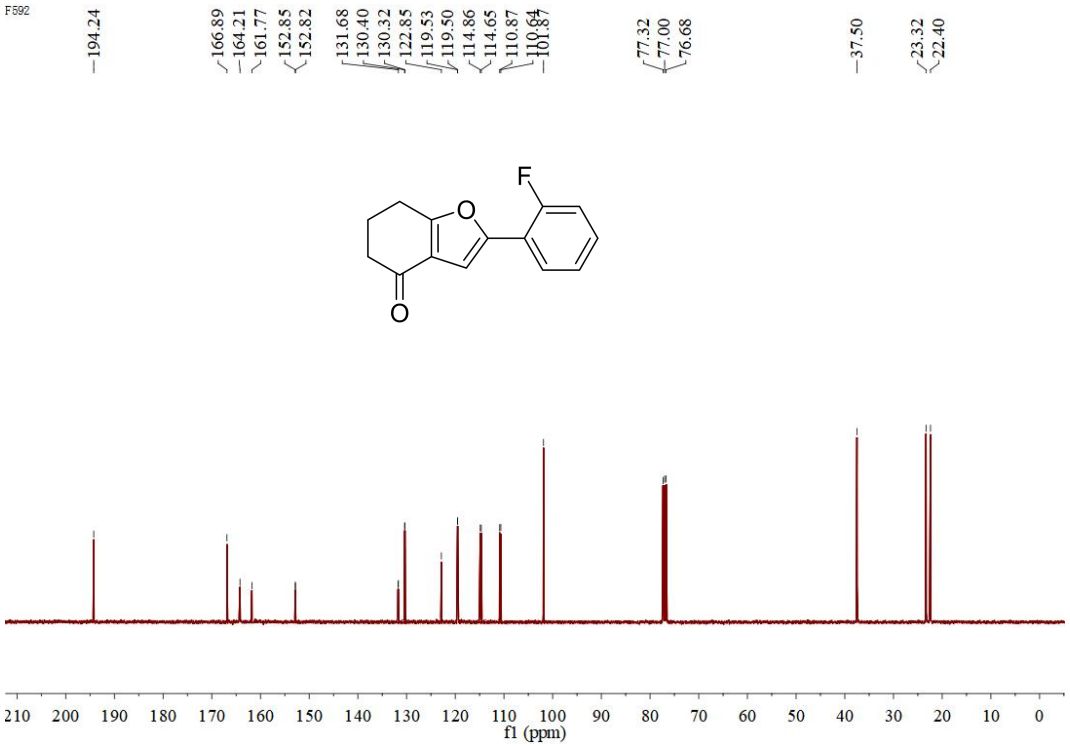


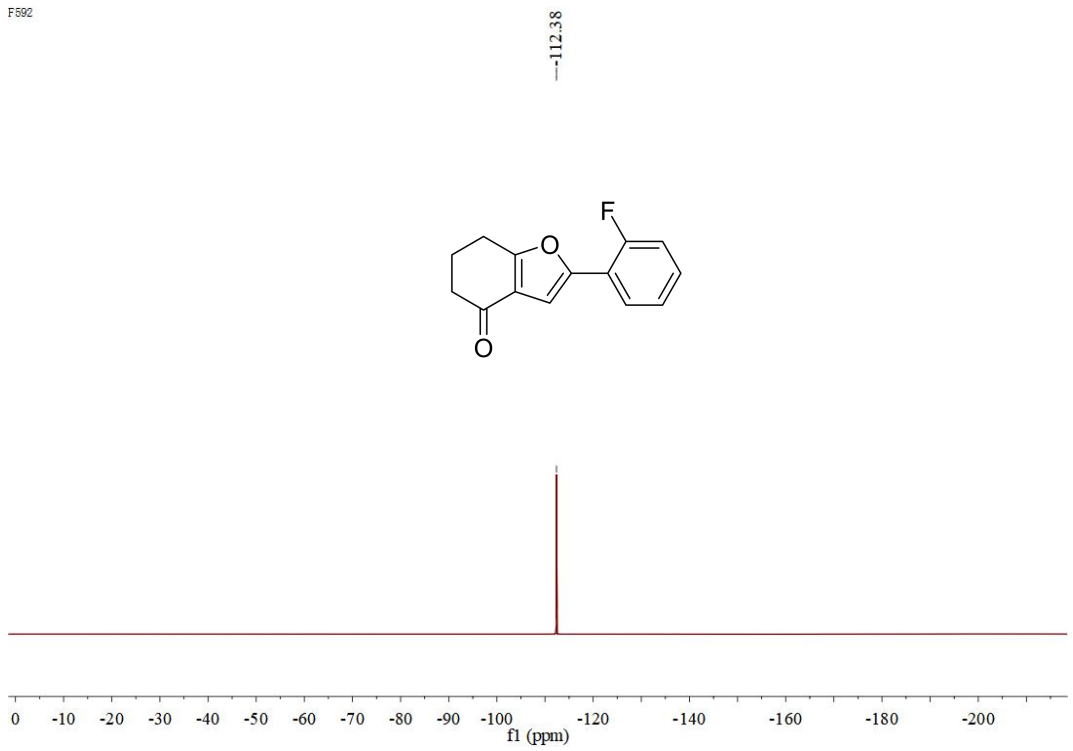


^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3o





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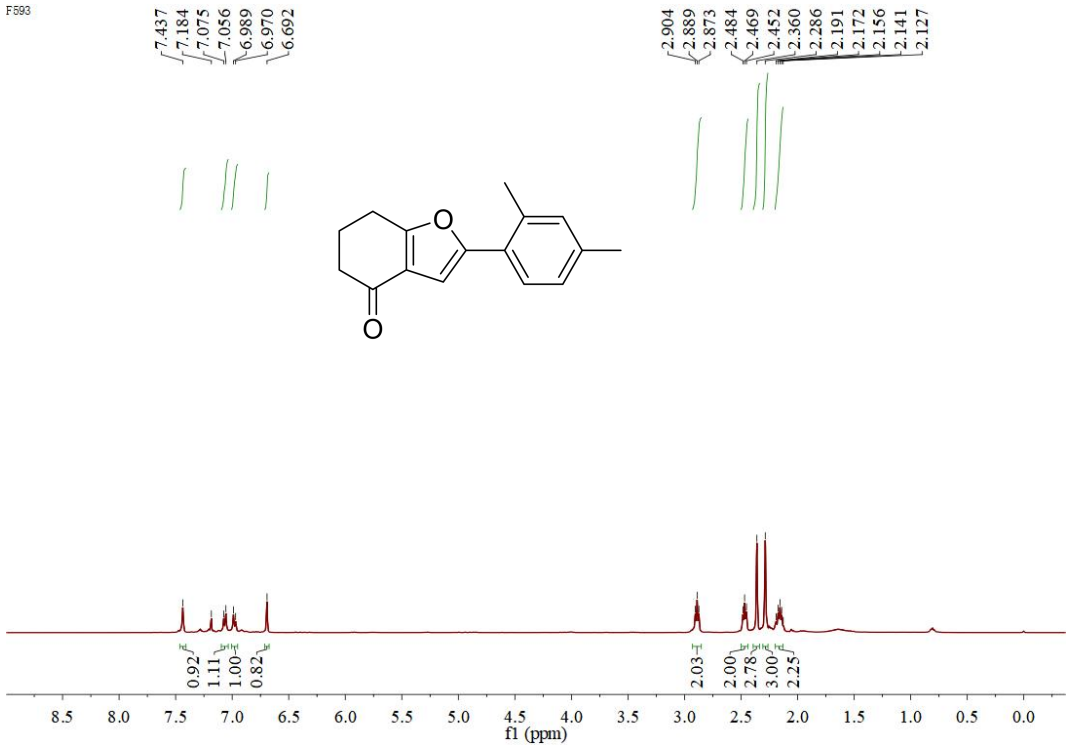
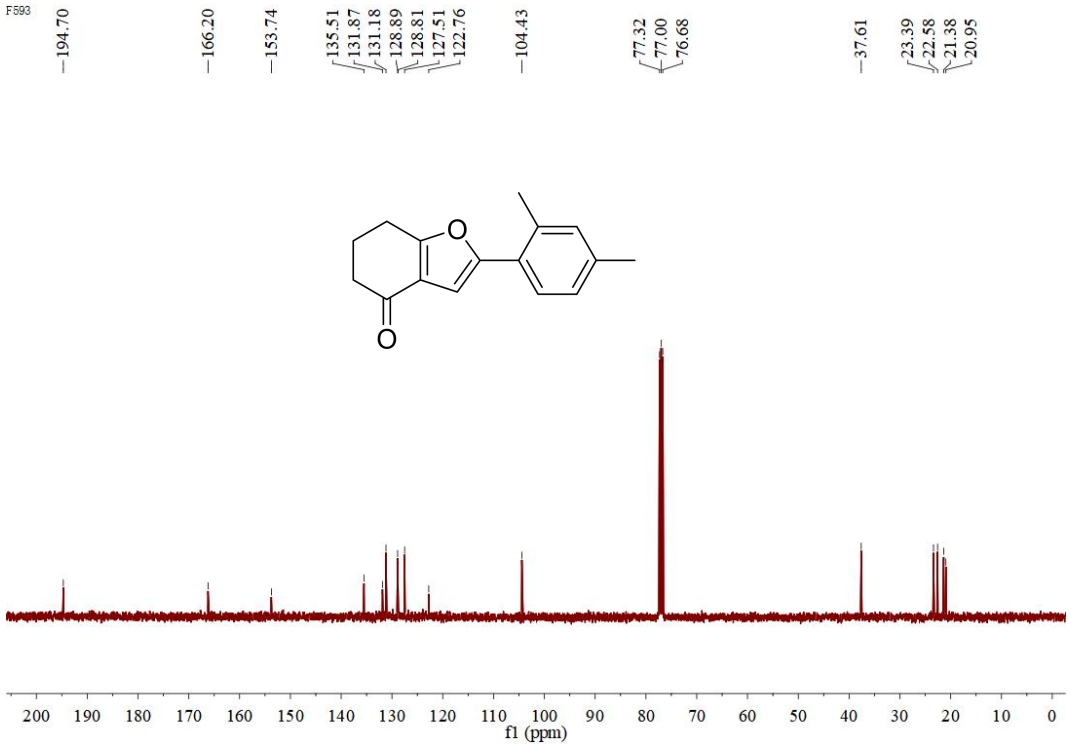
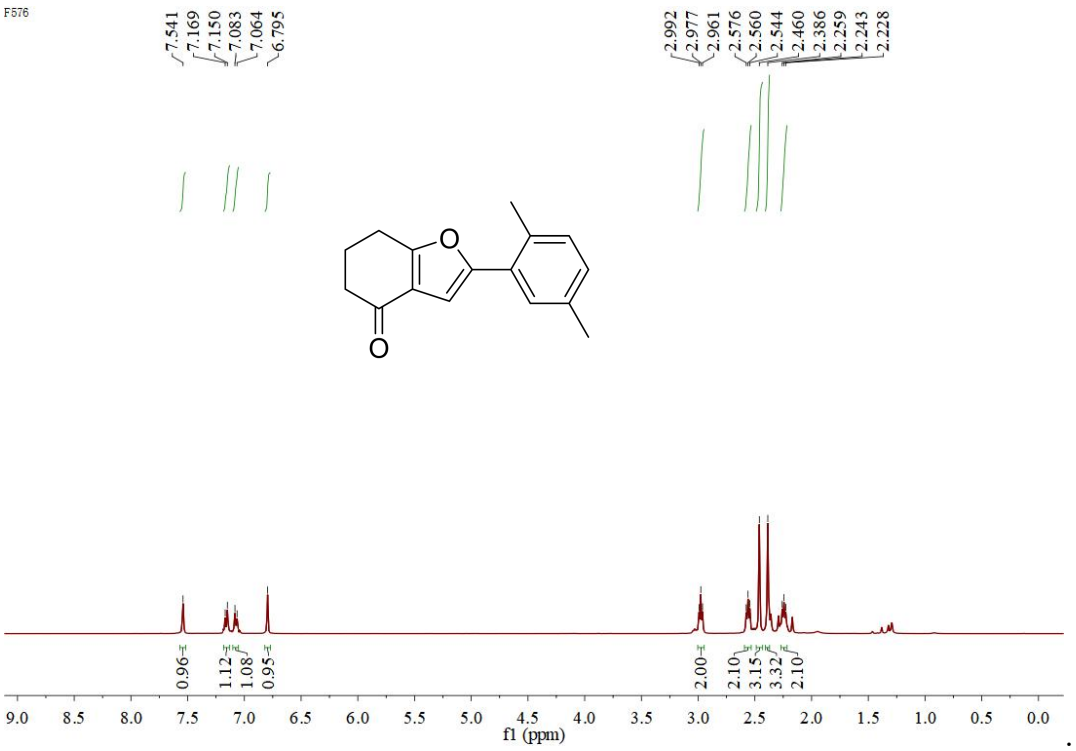
F
O
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

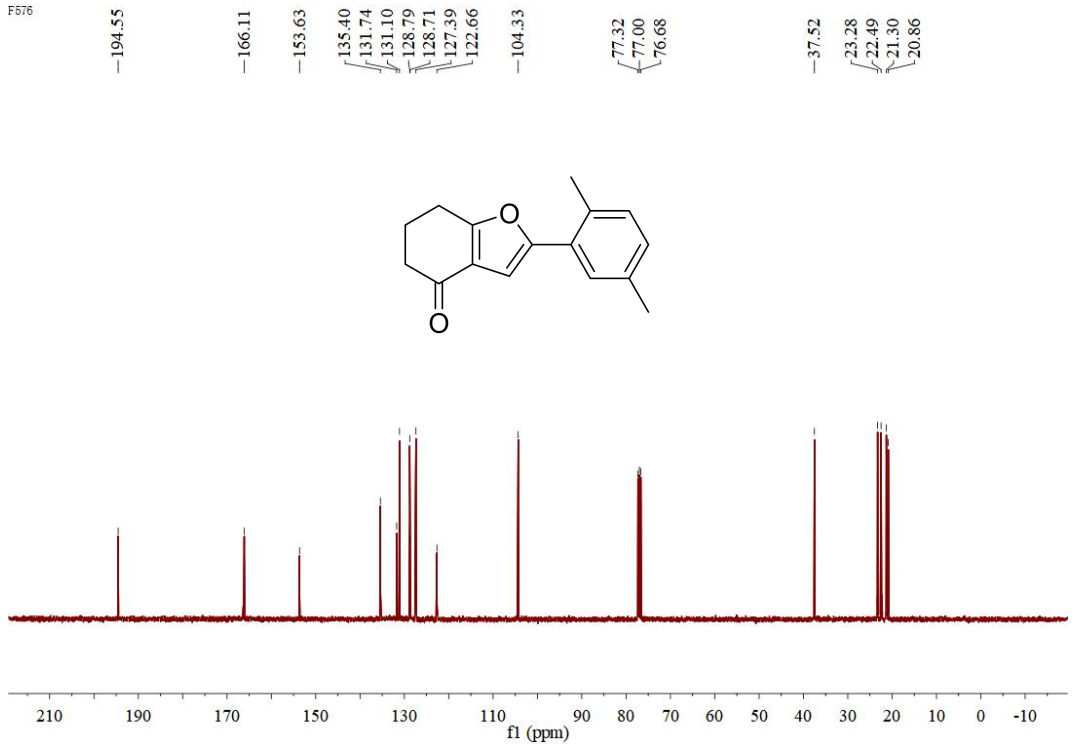
^{1}H NMR and ^{13}C NMR of 3p



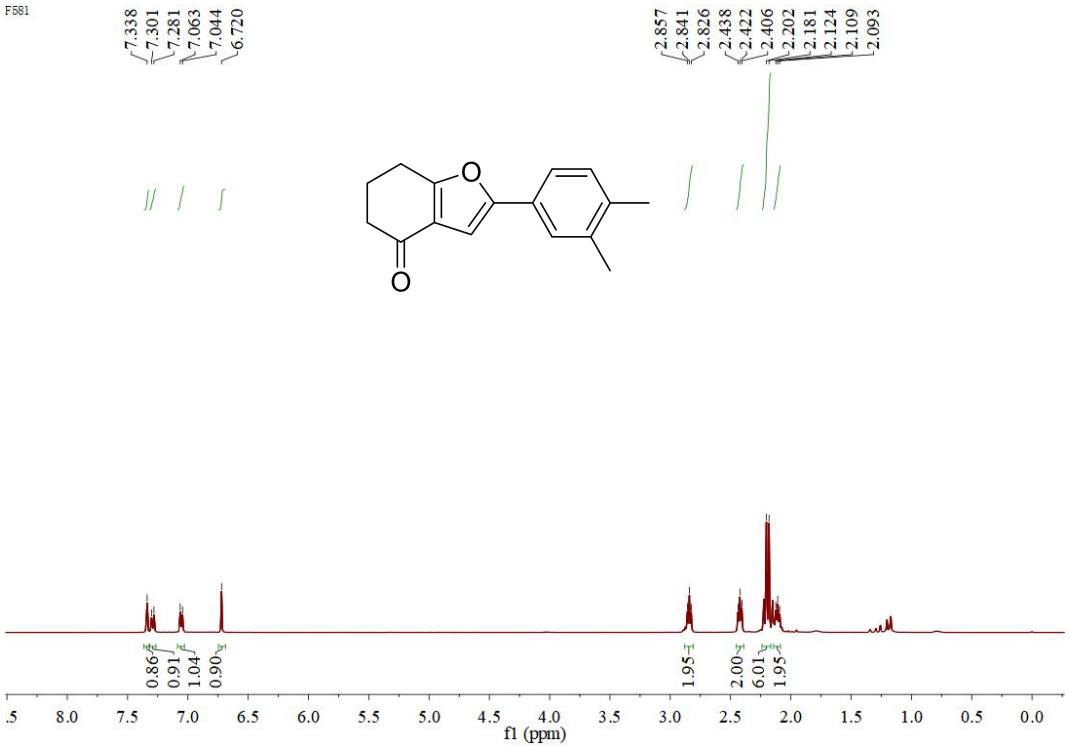


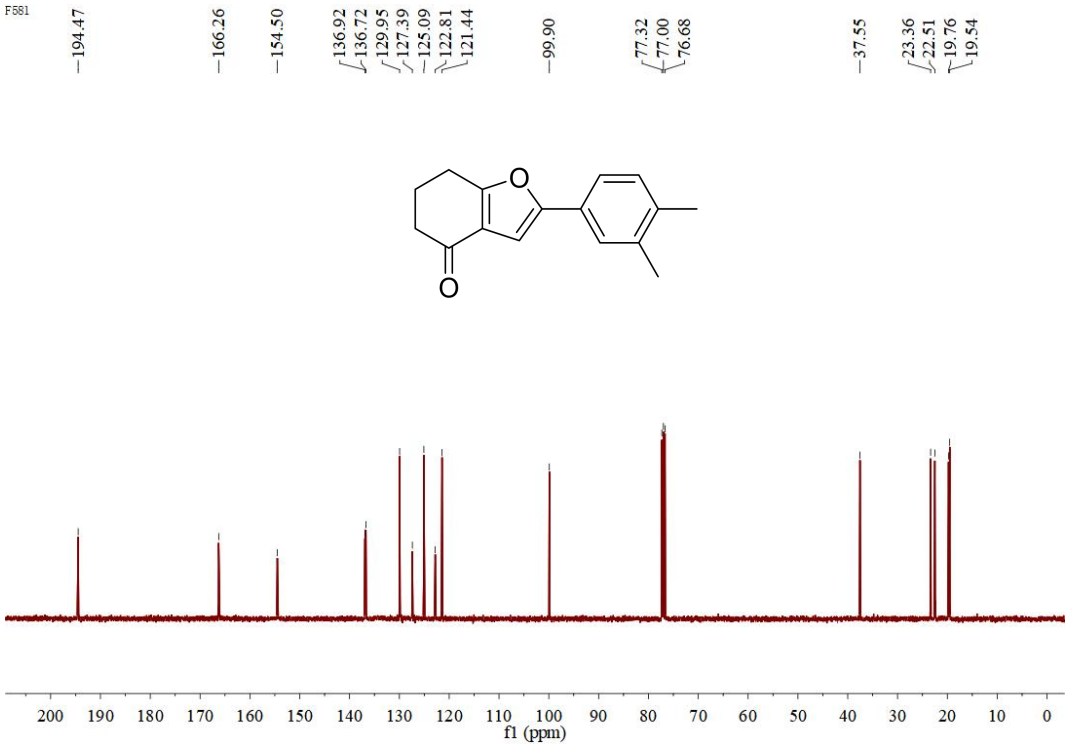
^{1}H NMR and ^{13}C NMR of 3q



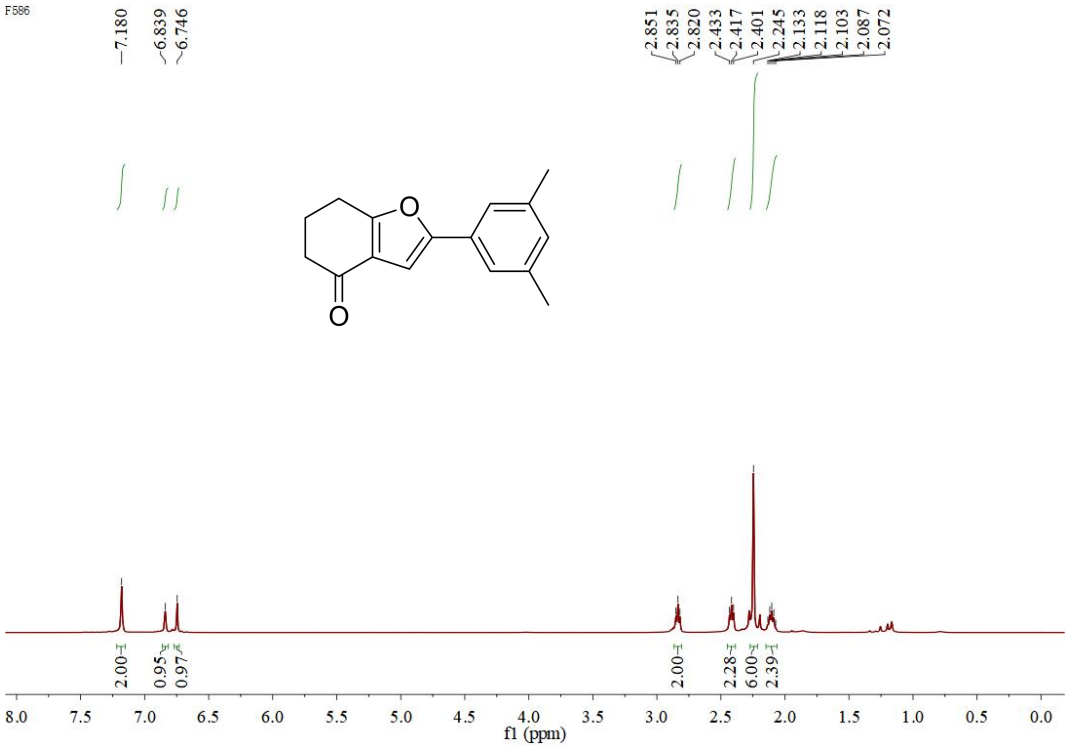


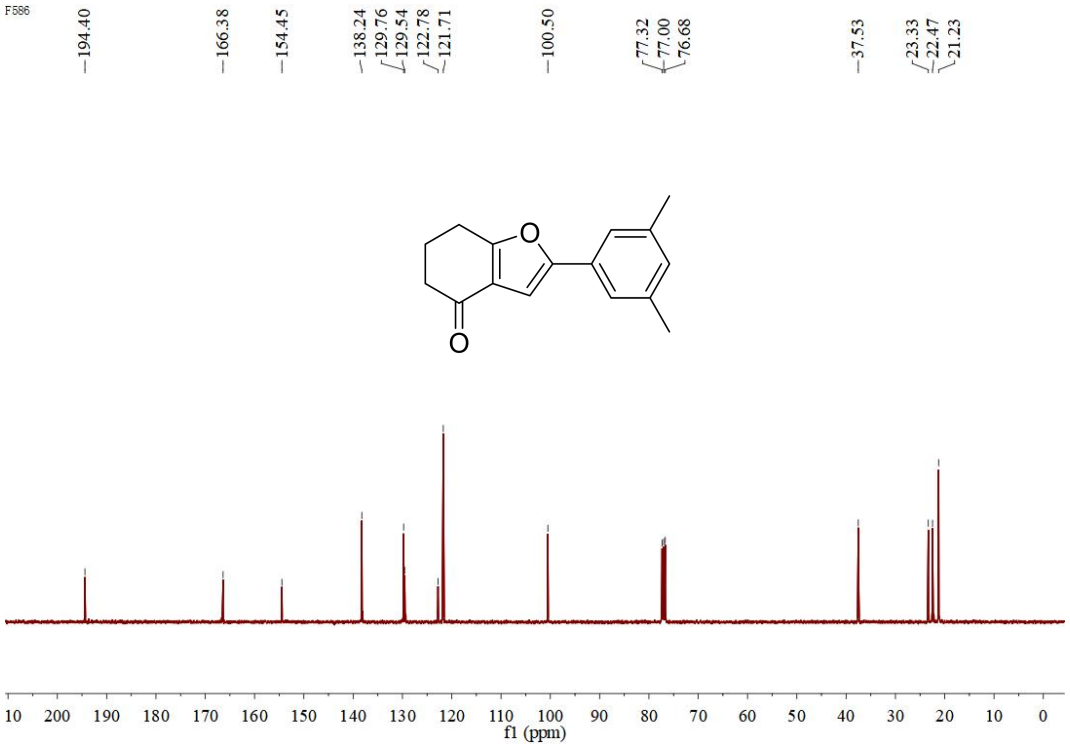
^{1}H NMR and ^{13}C NMR of 3r



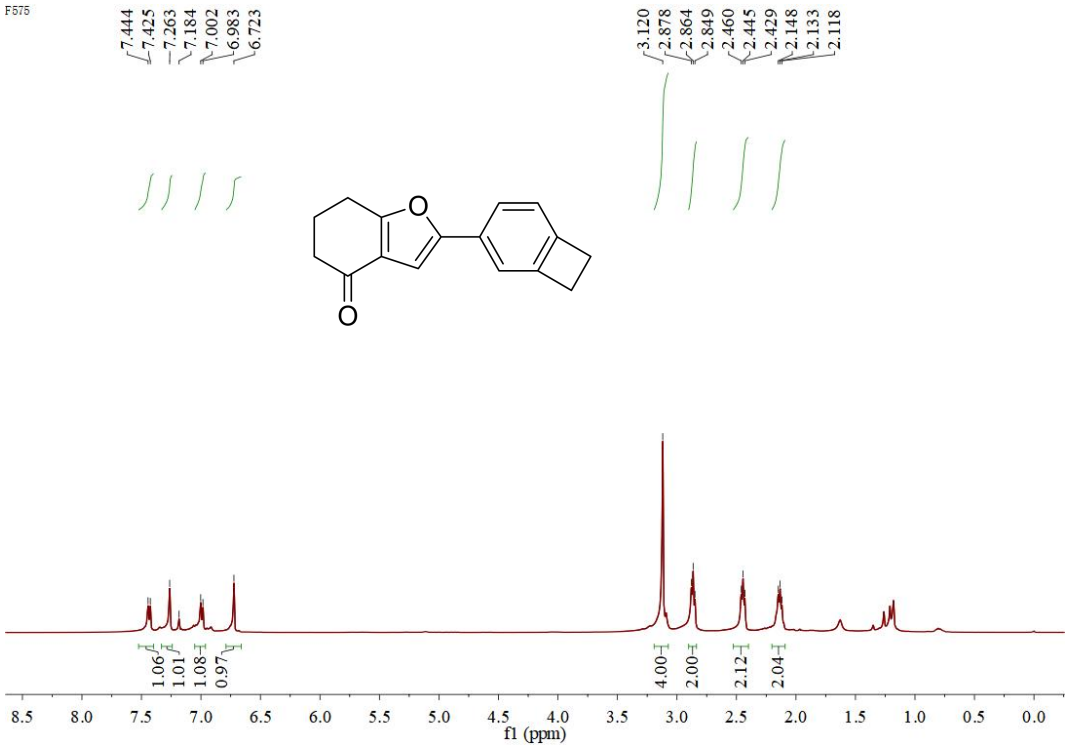


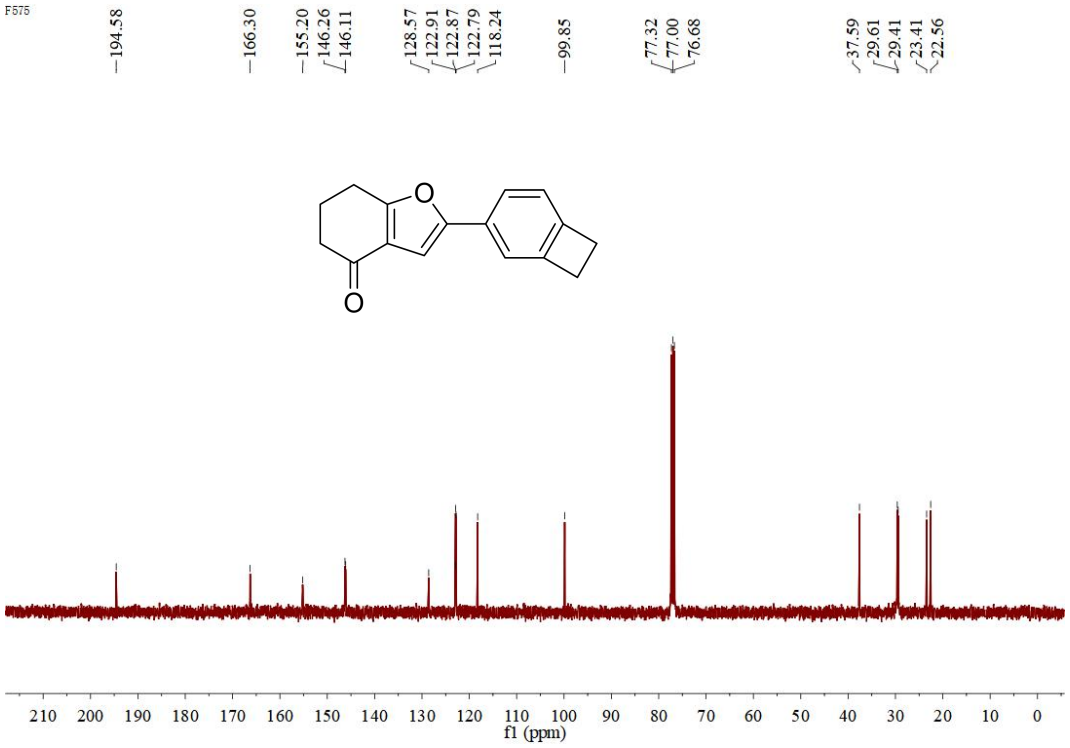
^{1}H NMR and ^{13}C NMR of 3s



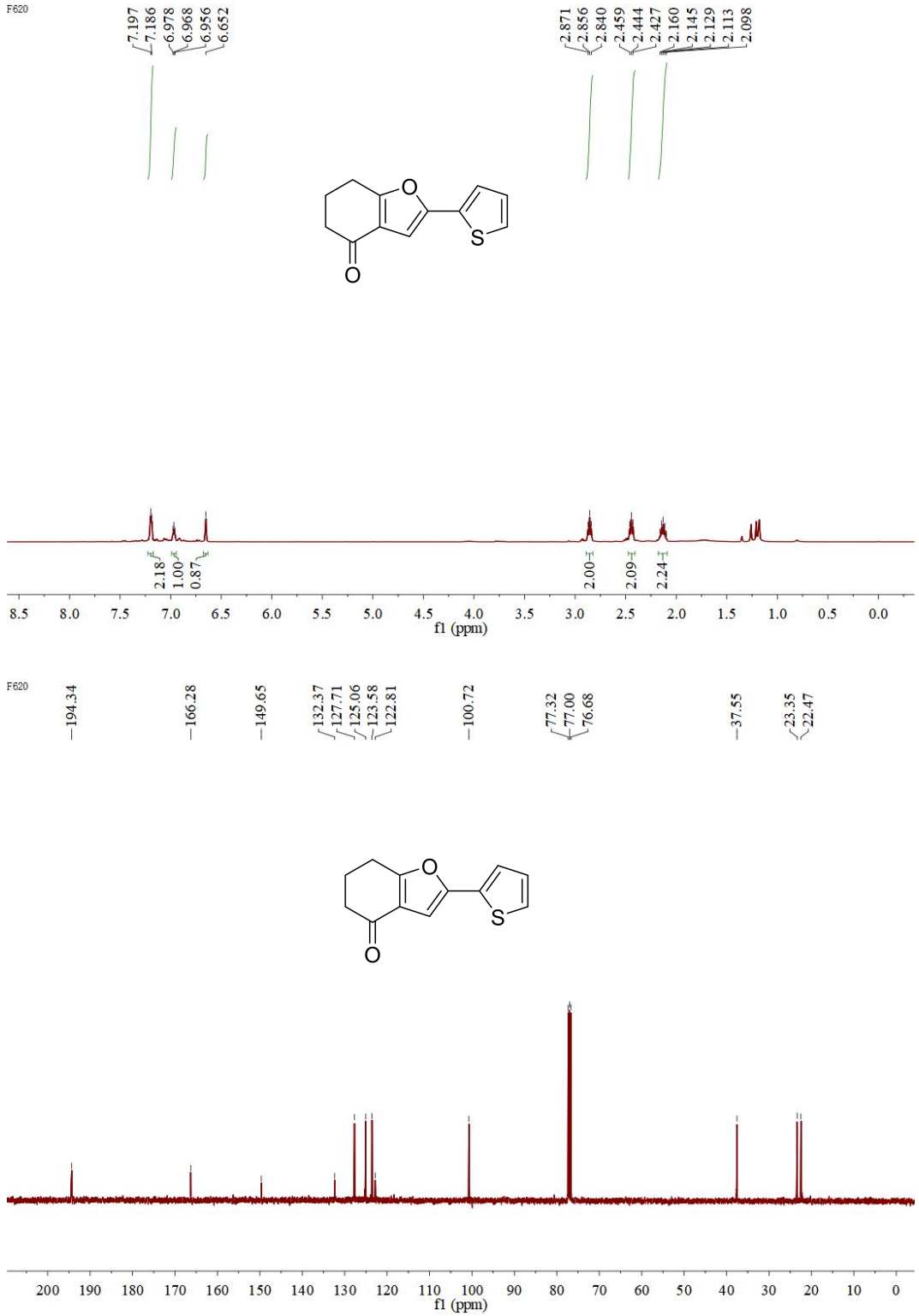


^{1}H NMR and ^{13}C NMR of 3t

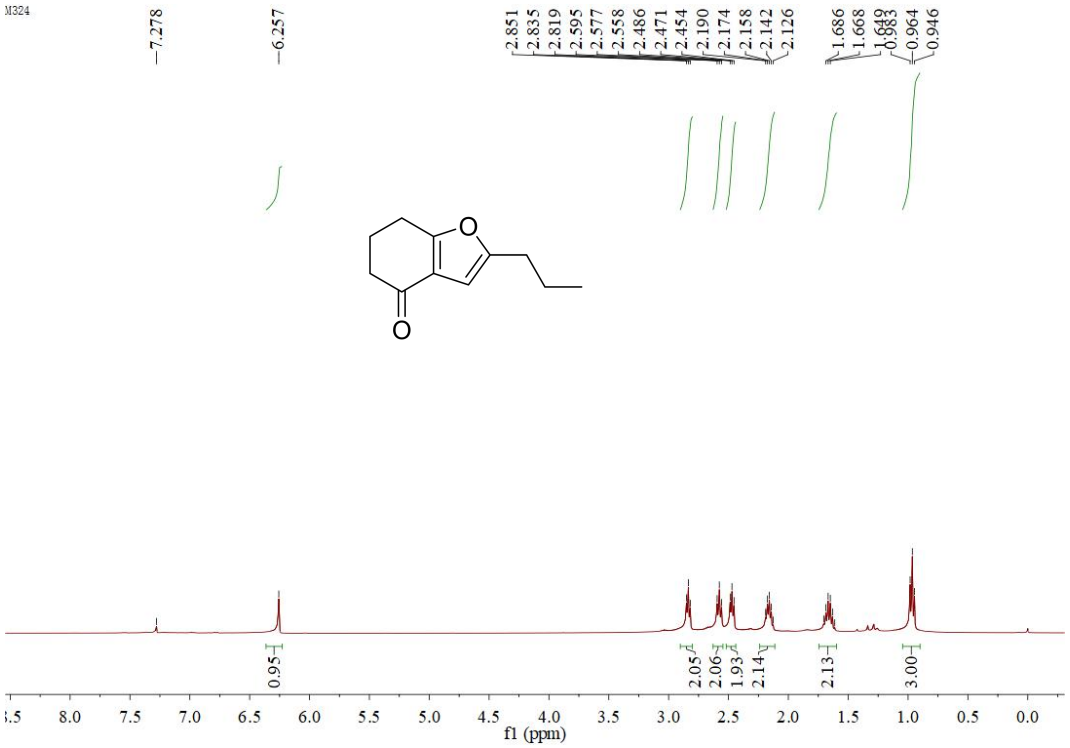


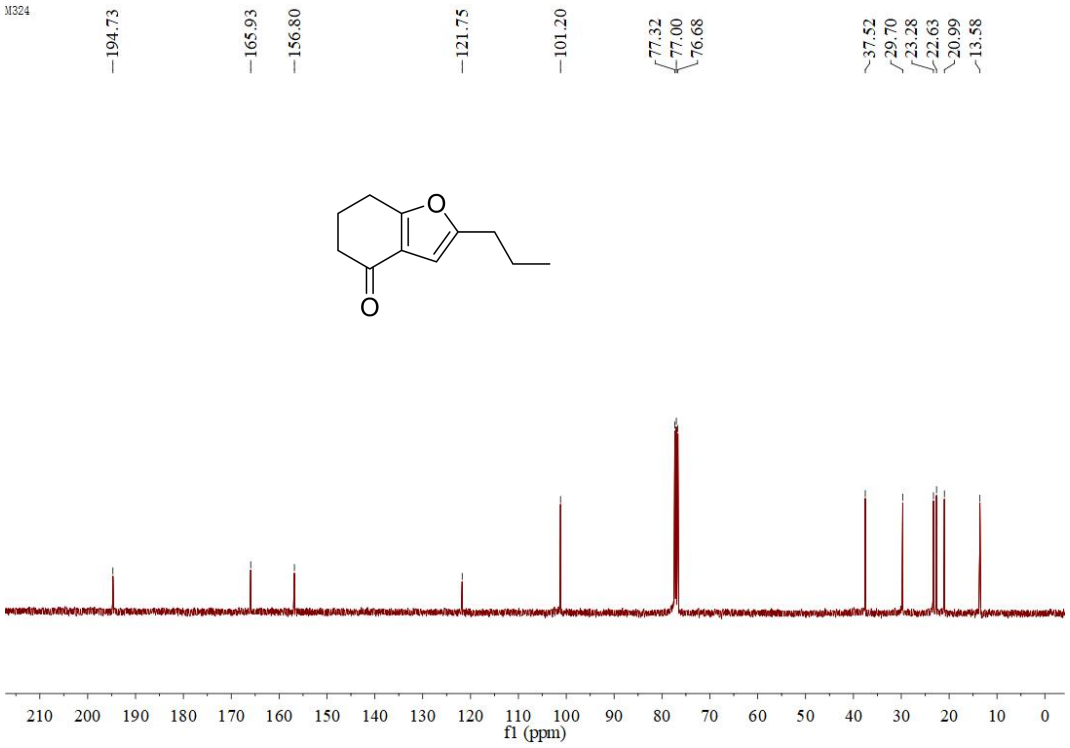


^{1}H NMR and ^{13}C NMR of 3u

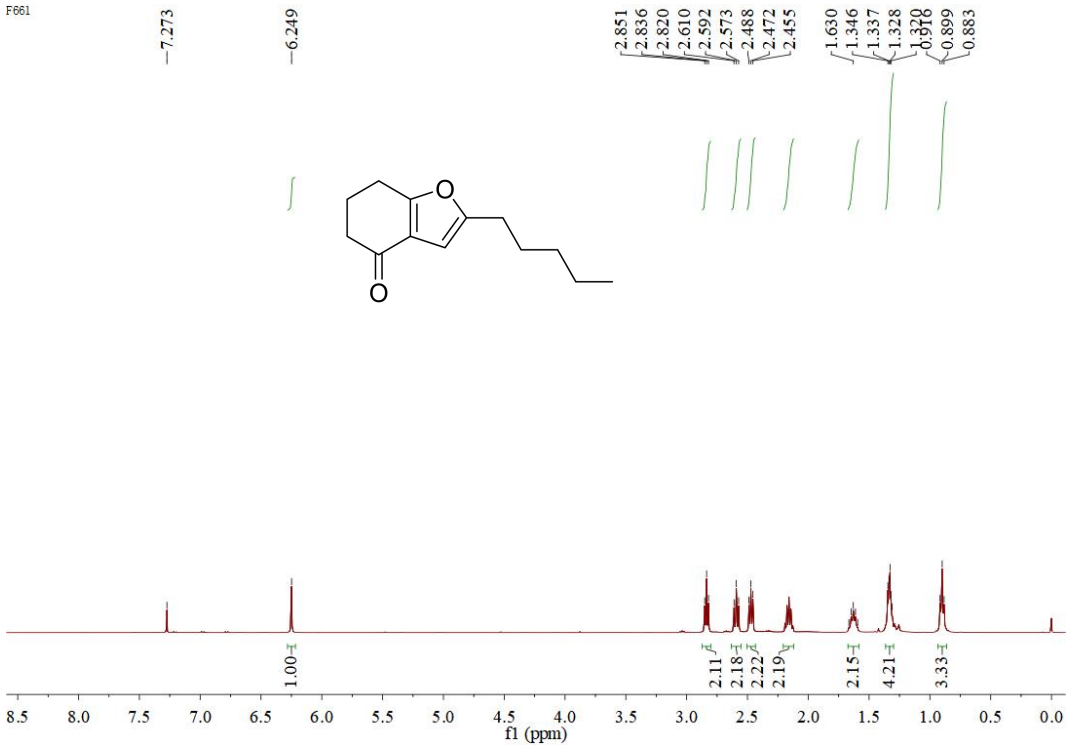


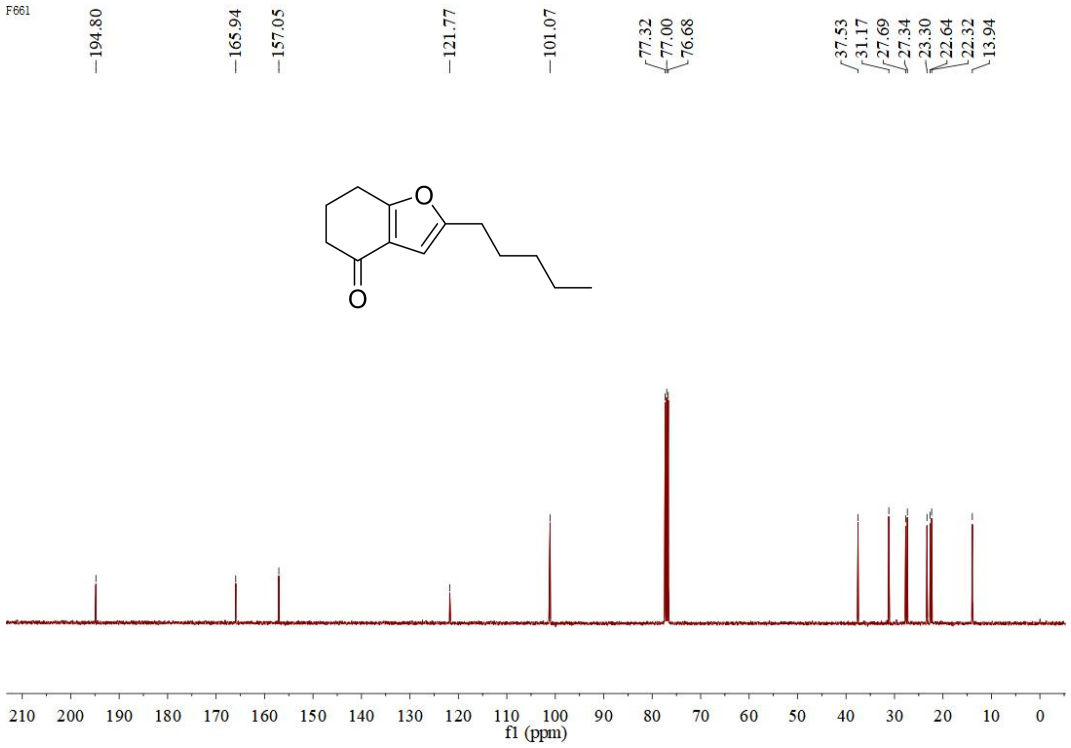
^{1}H NMR and ^{13}C NMR of 3v



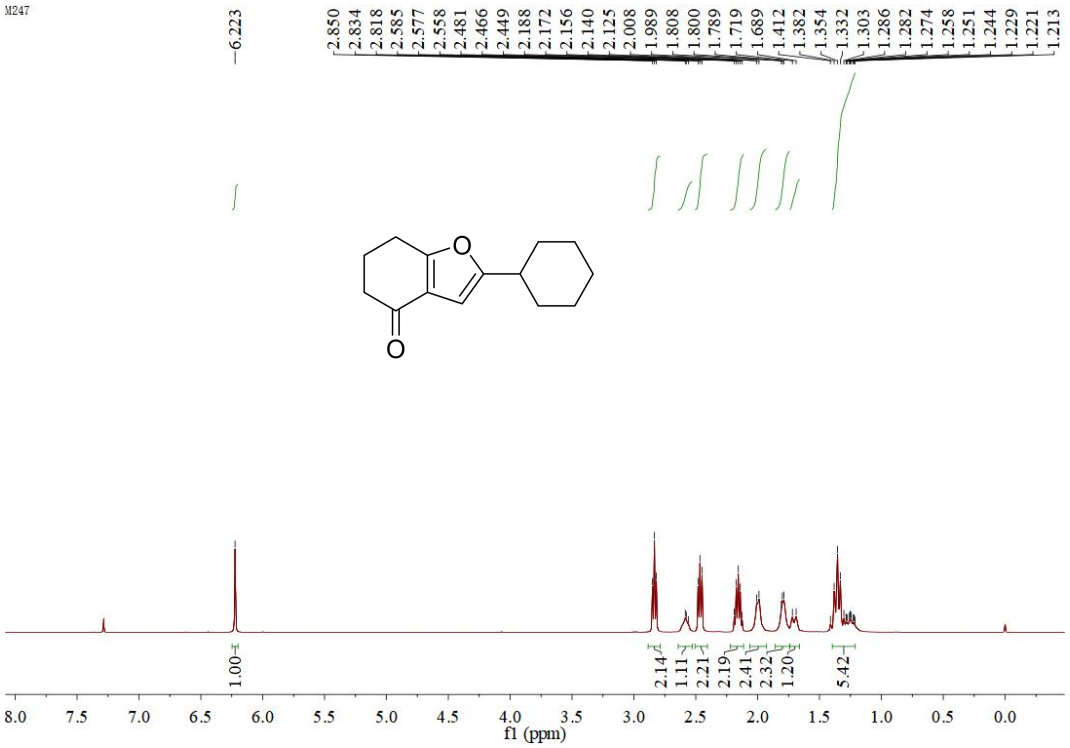


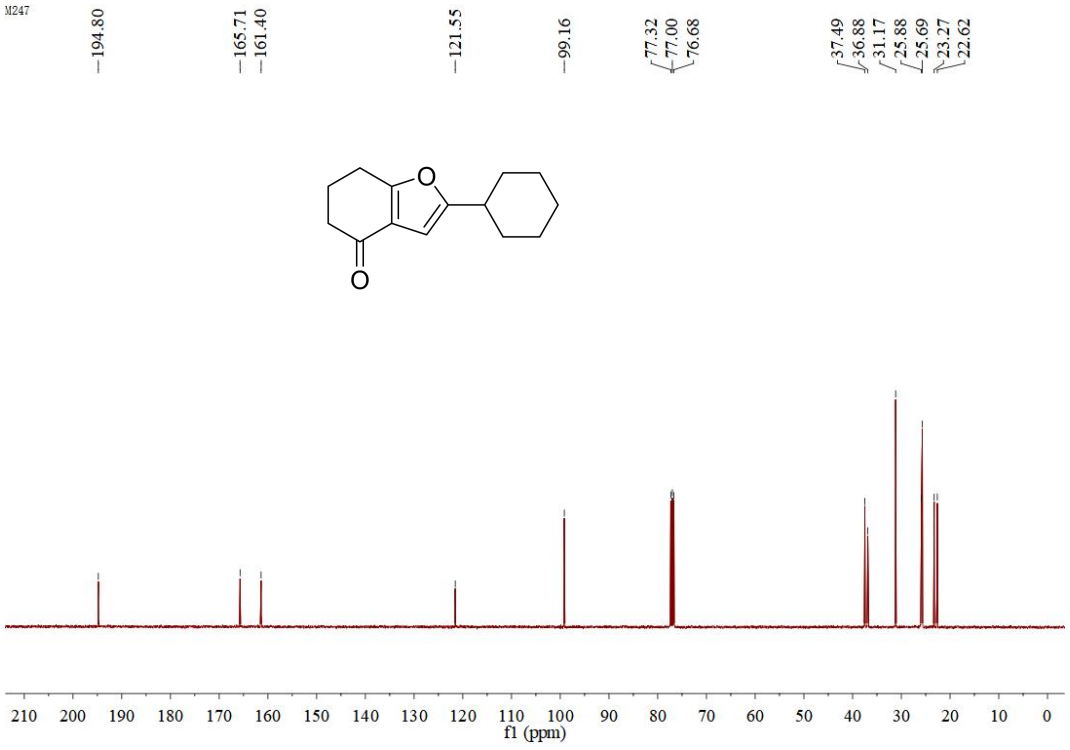
^{1}H NMR and ^{13}C NMR of 3w



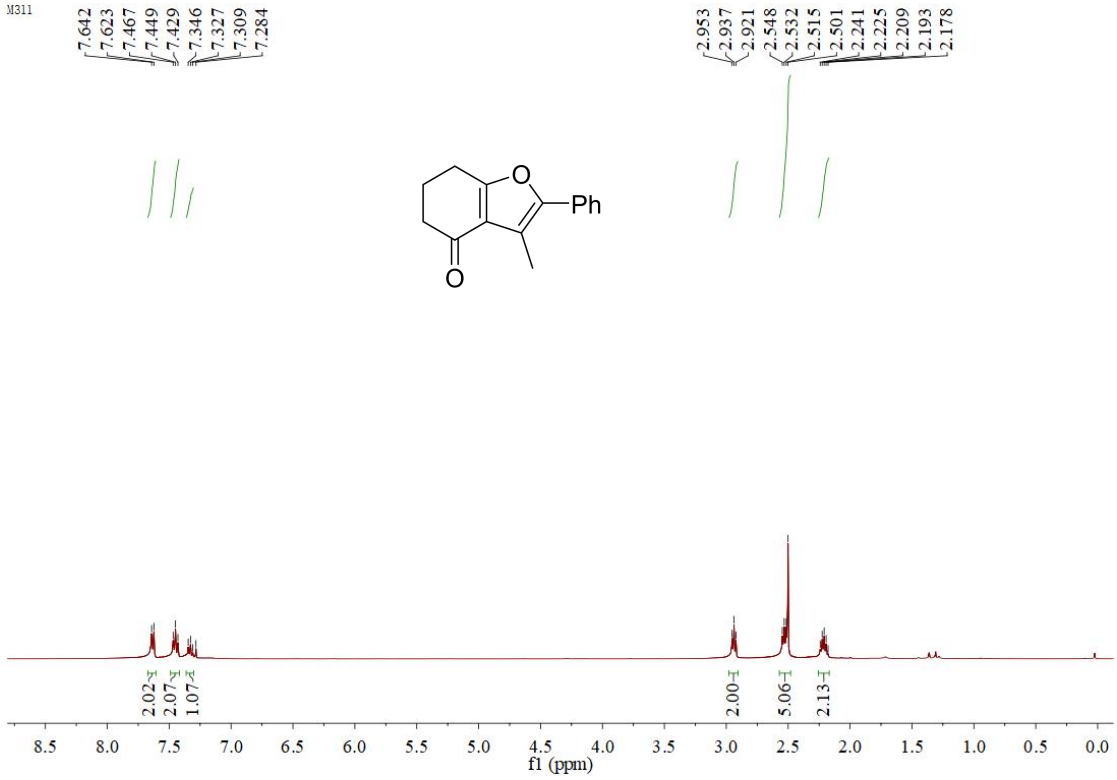


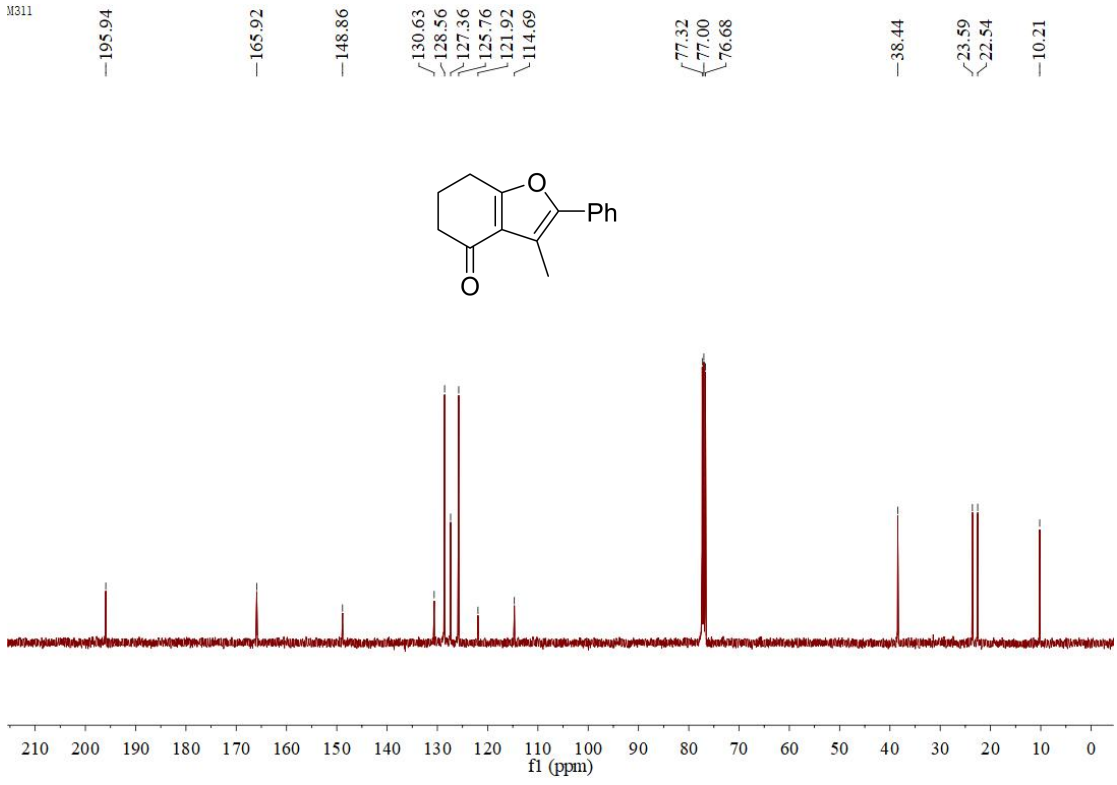
^{1}H NMR and ^{13}C NMR of 3x



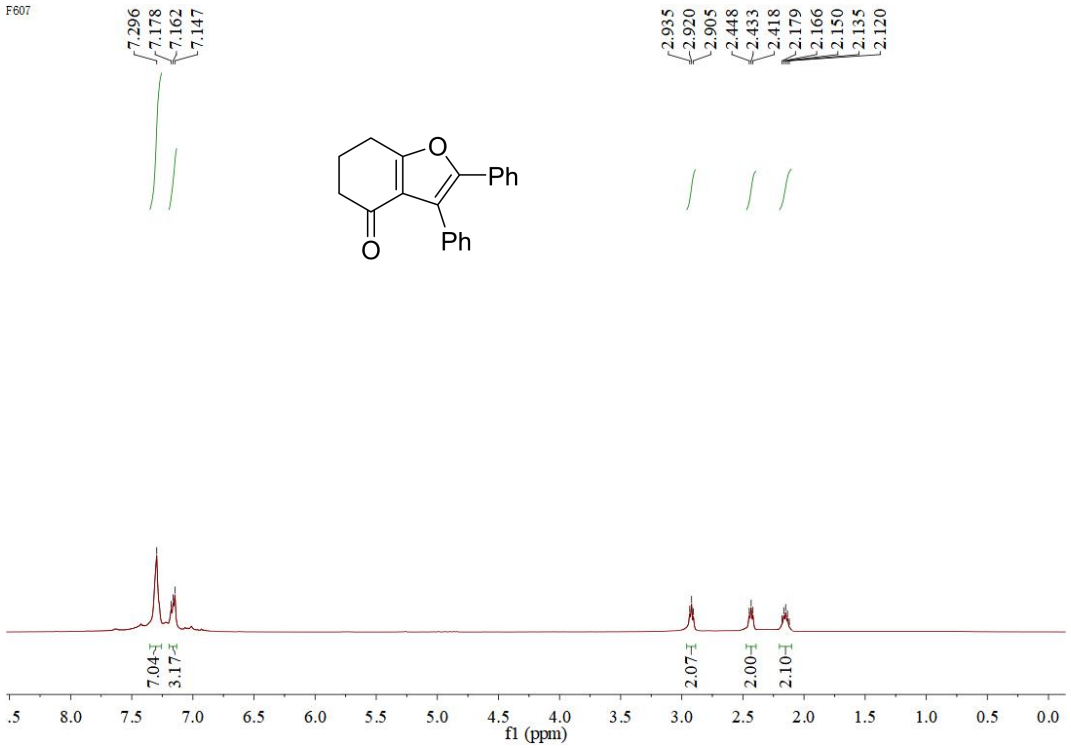


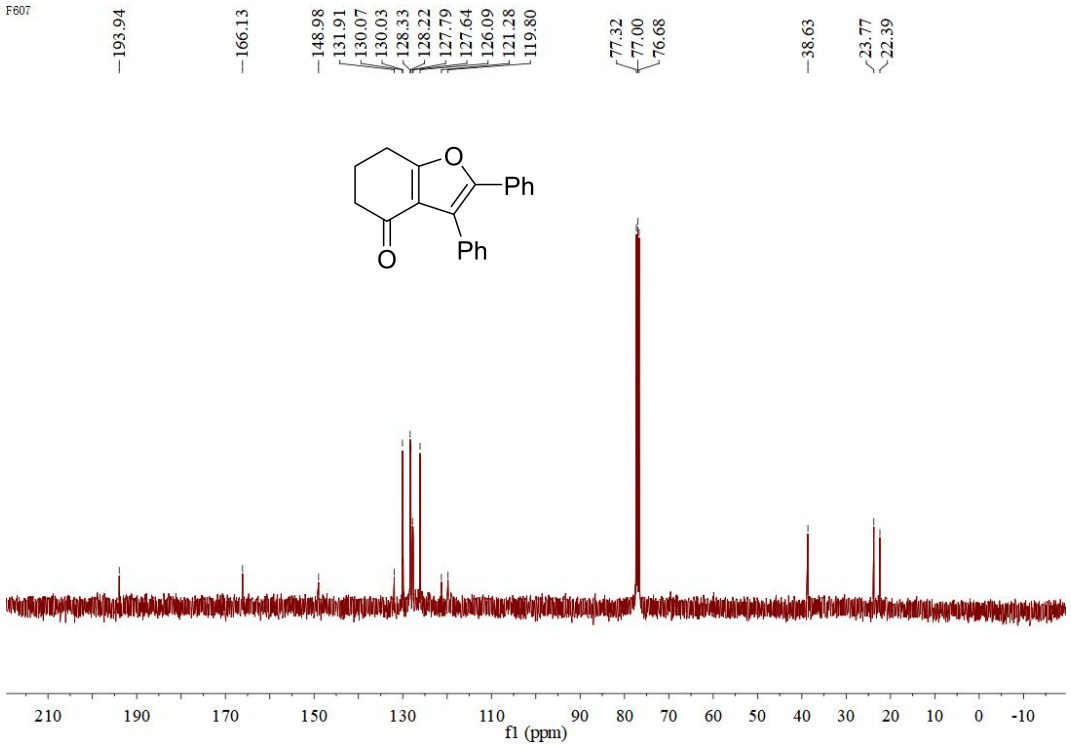
^{1}H NMR and ^{13}C NMR of 3y



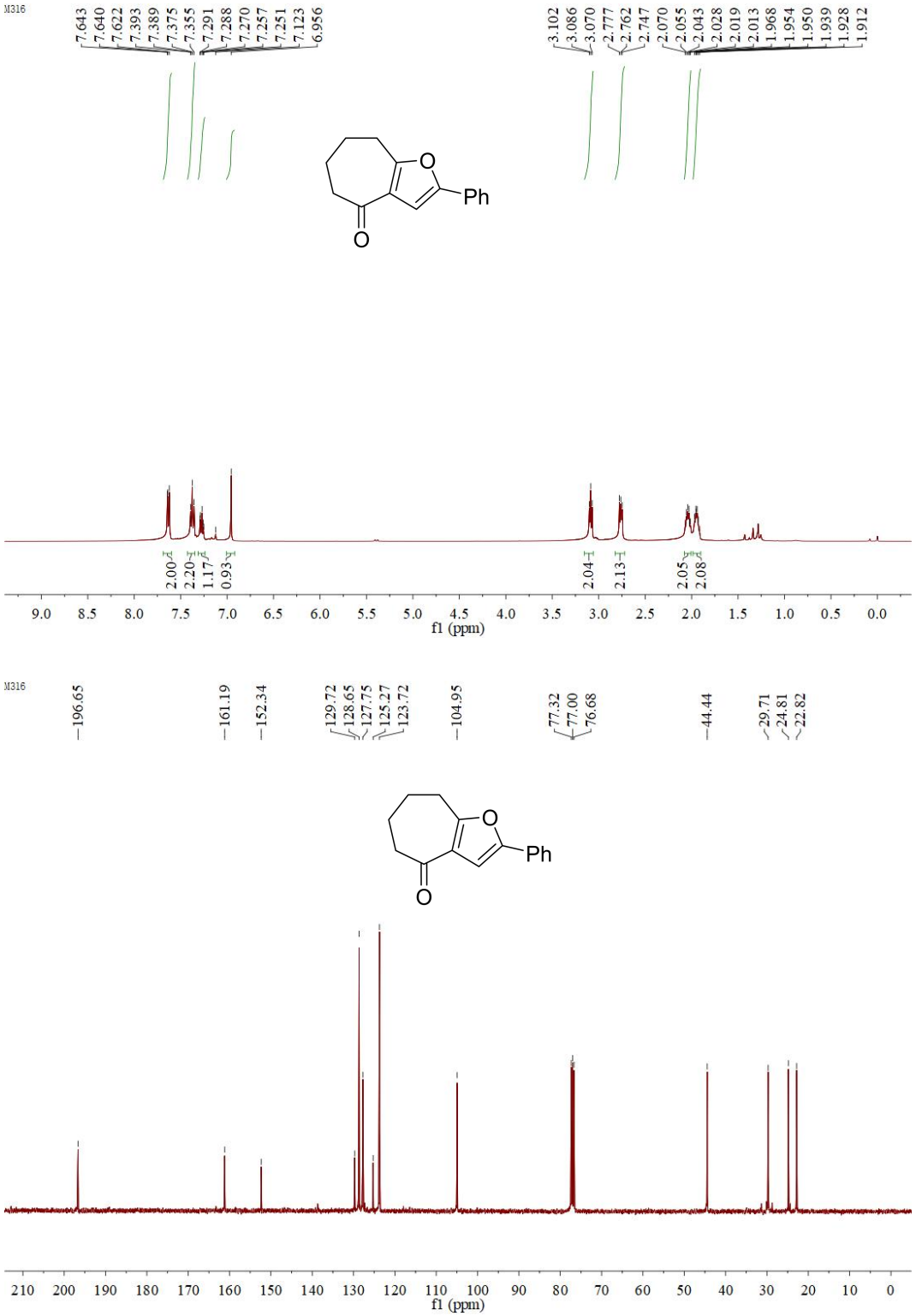


^{1}H NMR and ^{13}C NMR of 3z

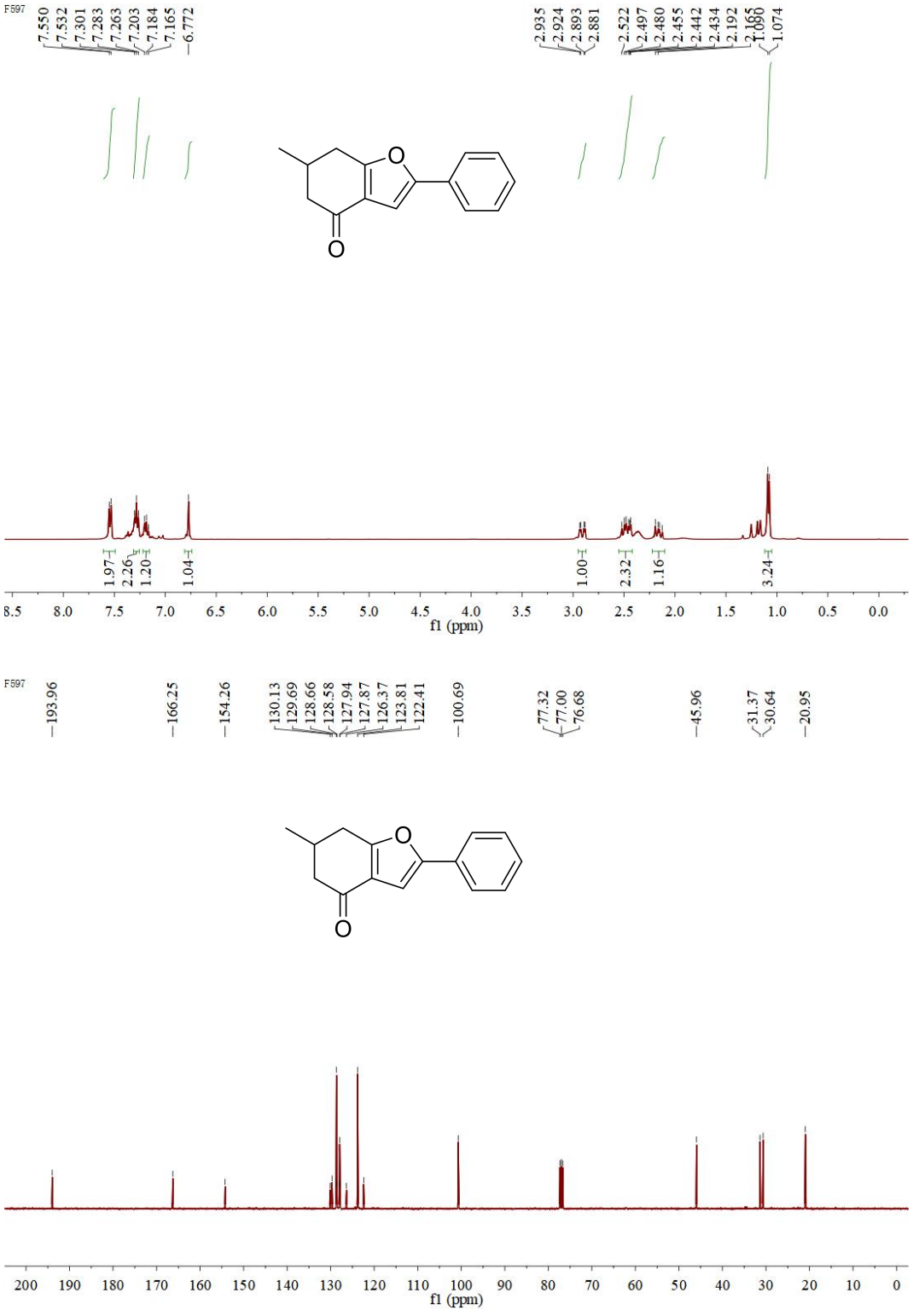




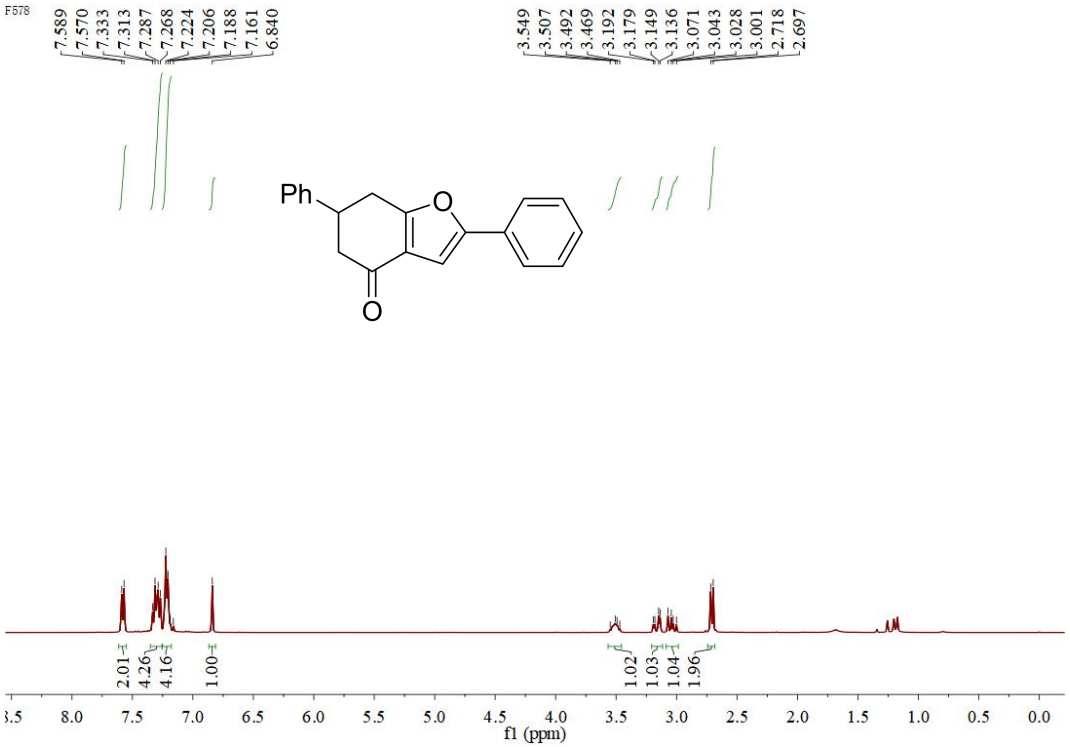
^{1}H NMR and ^{13}C NMR of 3aa

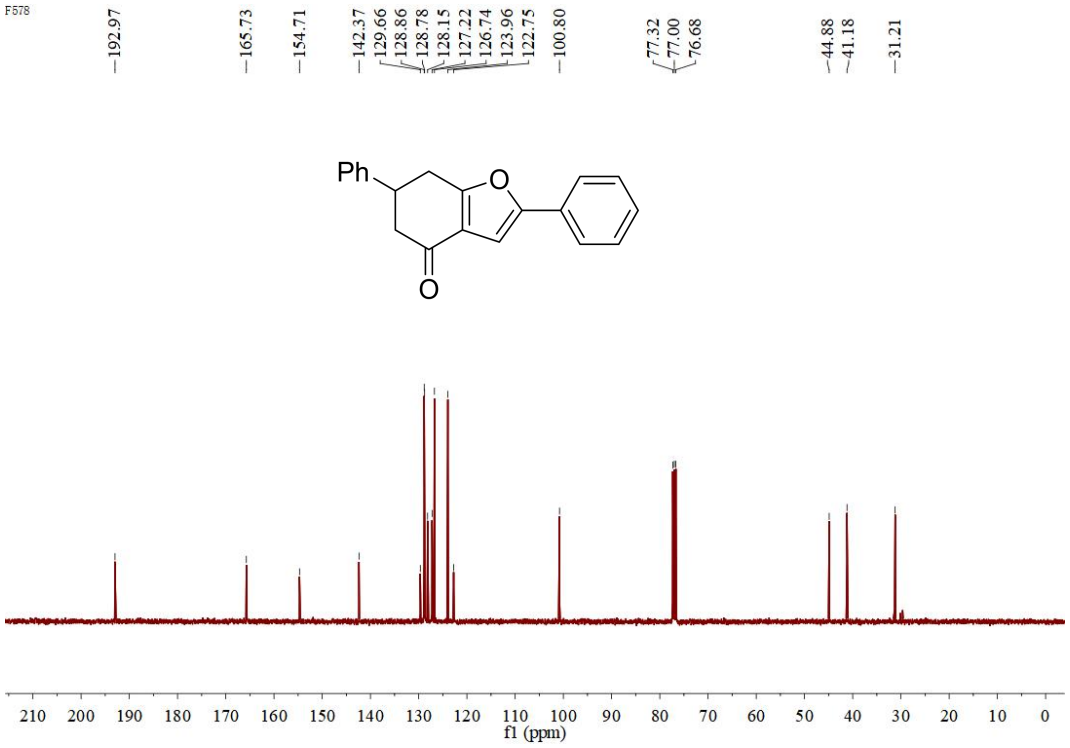


^{1}H NMR and ^{13}C NMR of 3ab

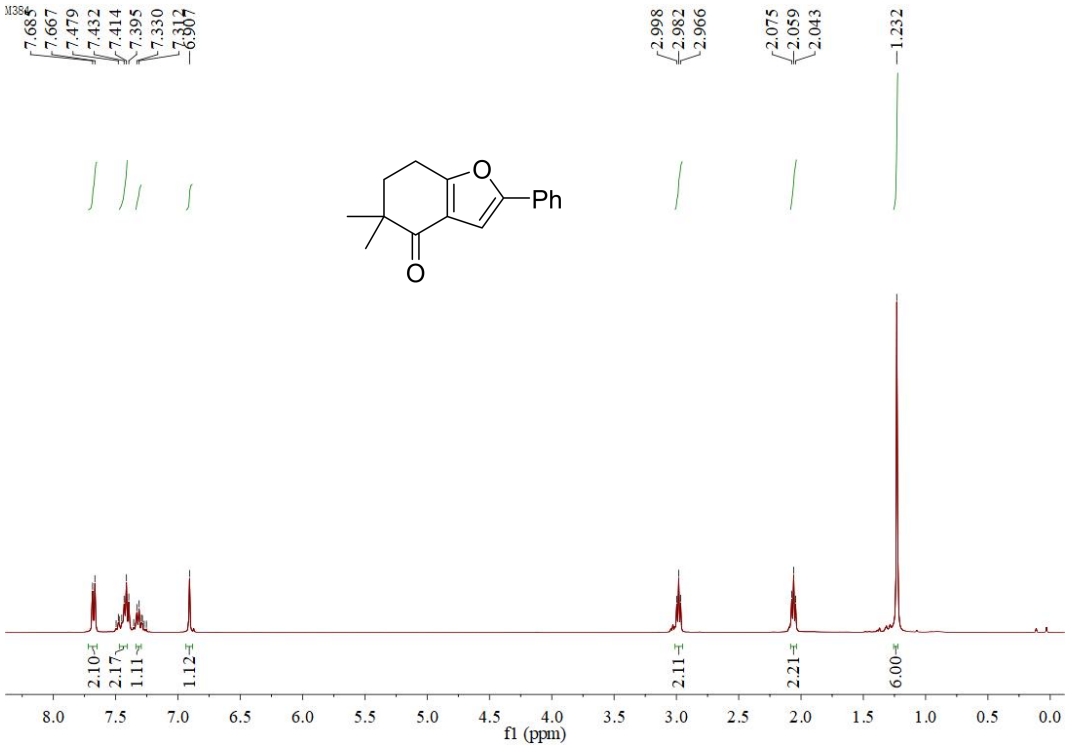


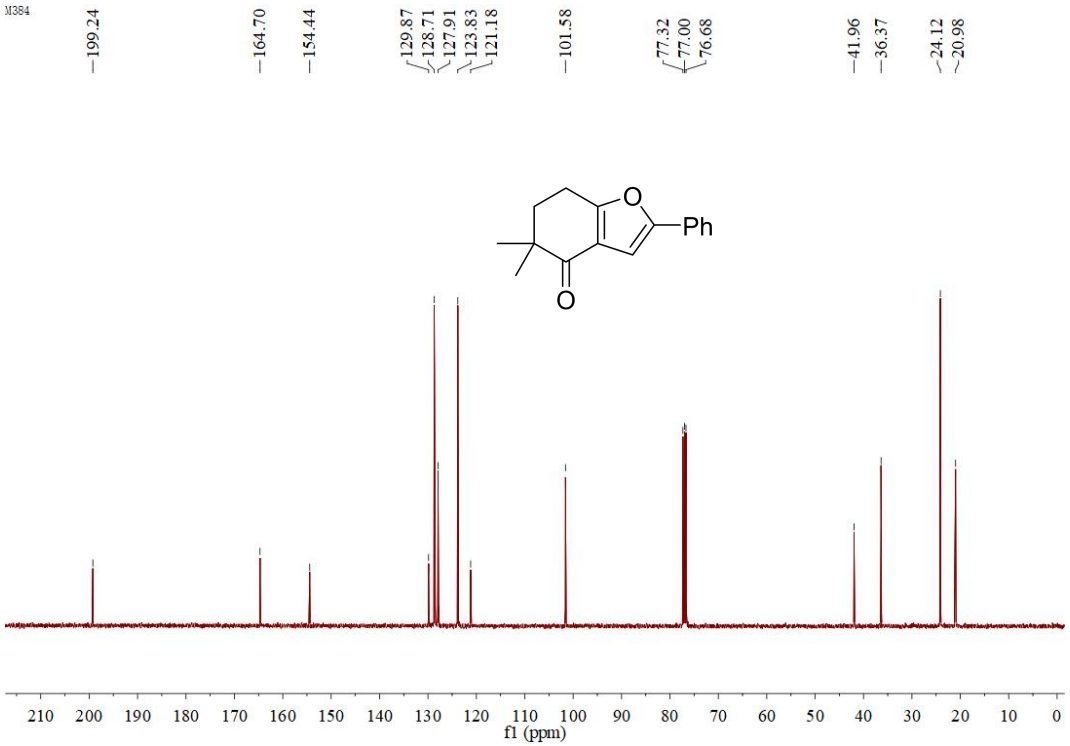
^{1}H NMR and ^{13}C NMR of 3ac



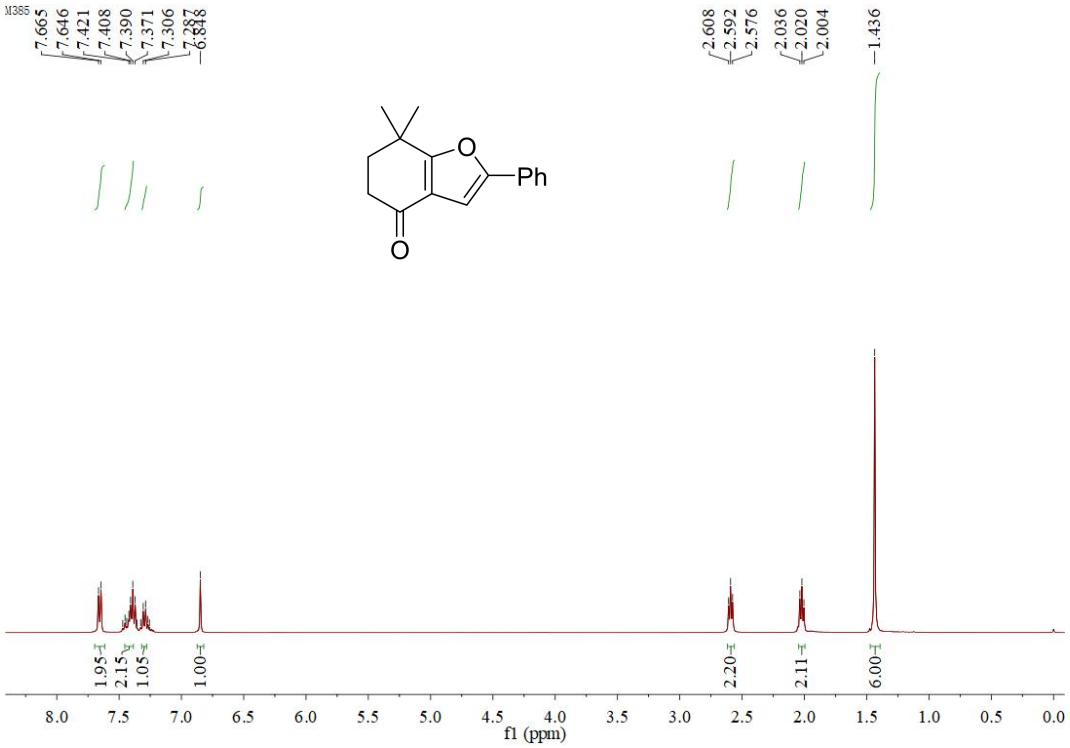


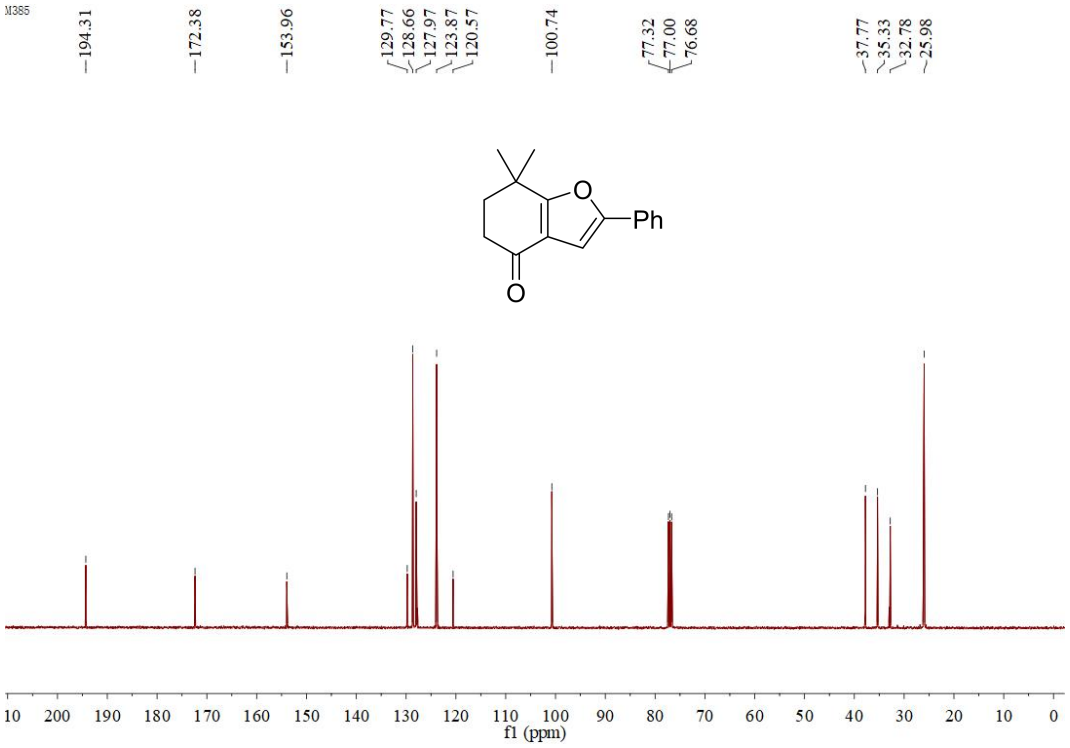
^{1}H NMR and ^{13}C NMR of 3ad'



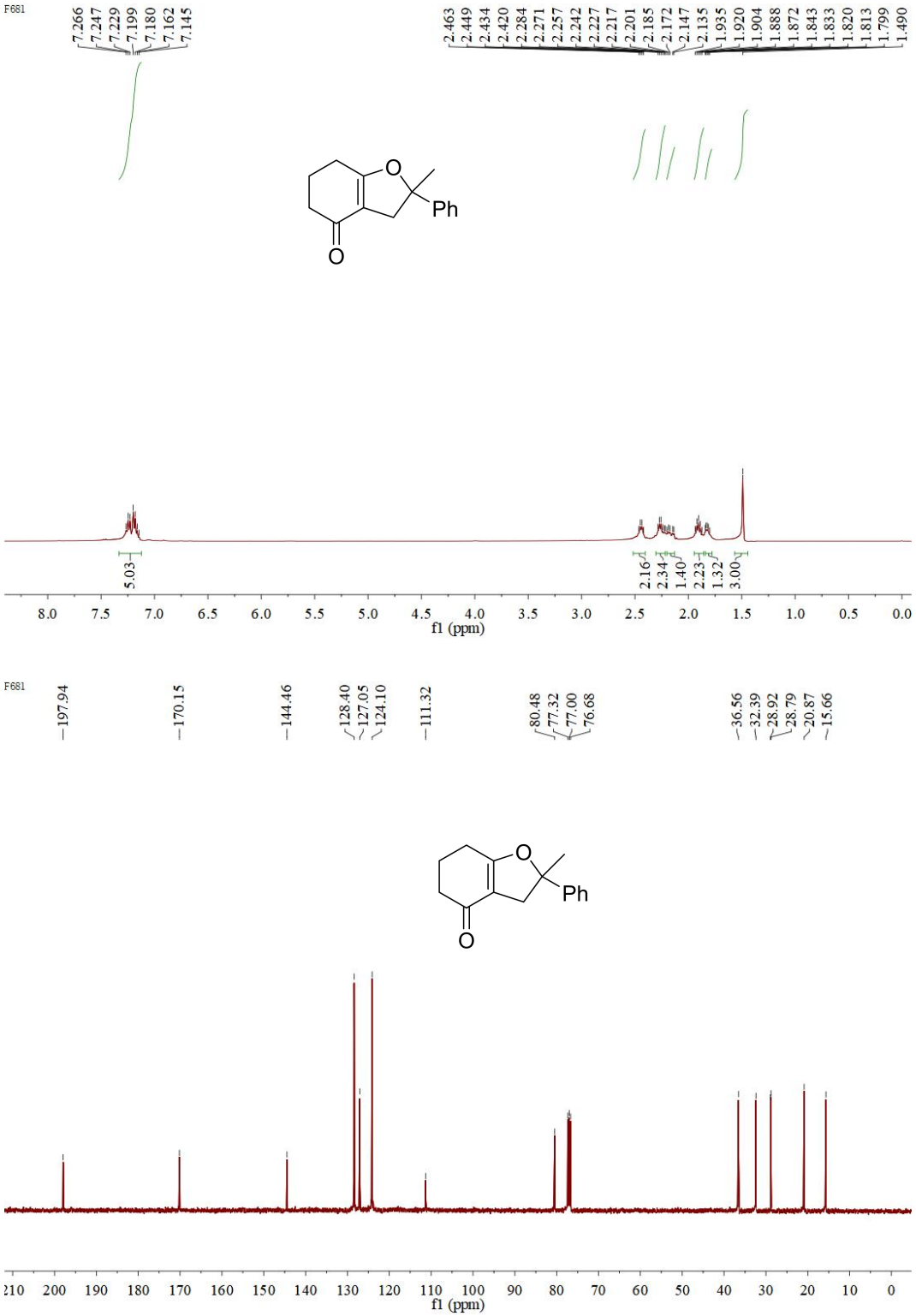


^{1}H NMR and ^{13}C NMR of 3ad''

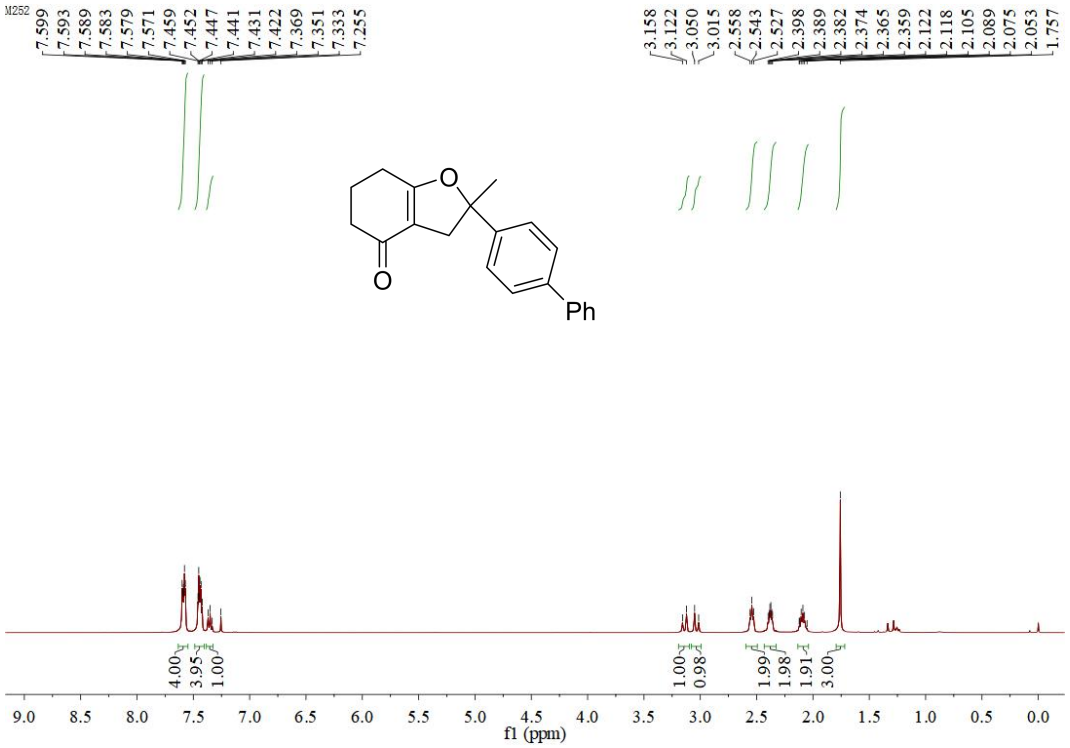


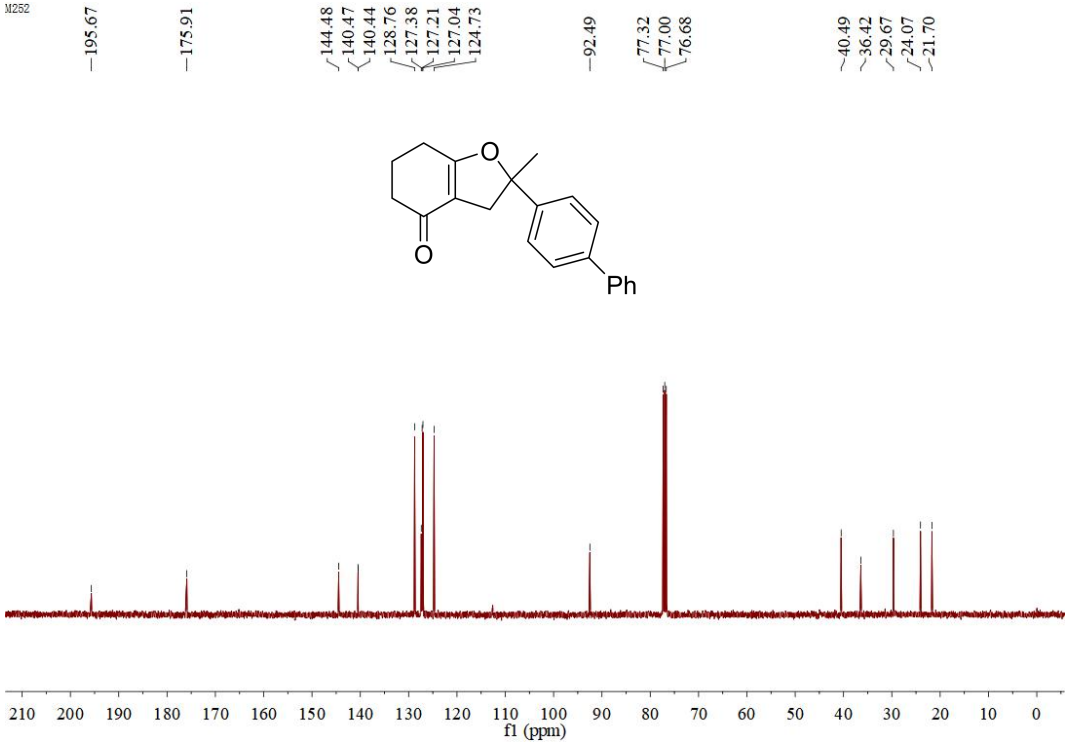


^{1}H NMR and ^{13}C NMR of 4a

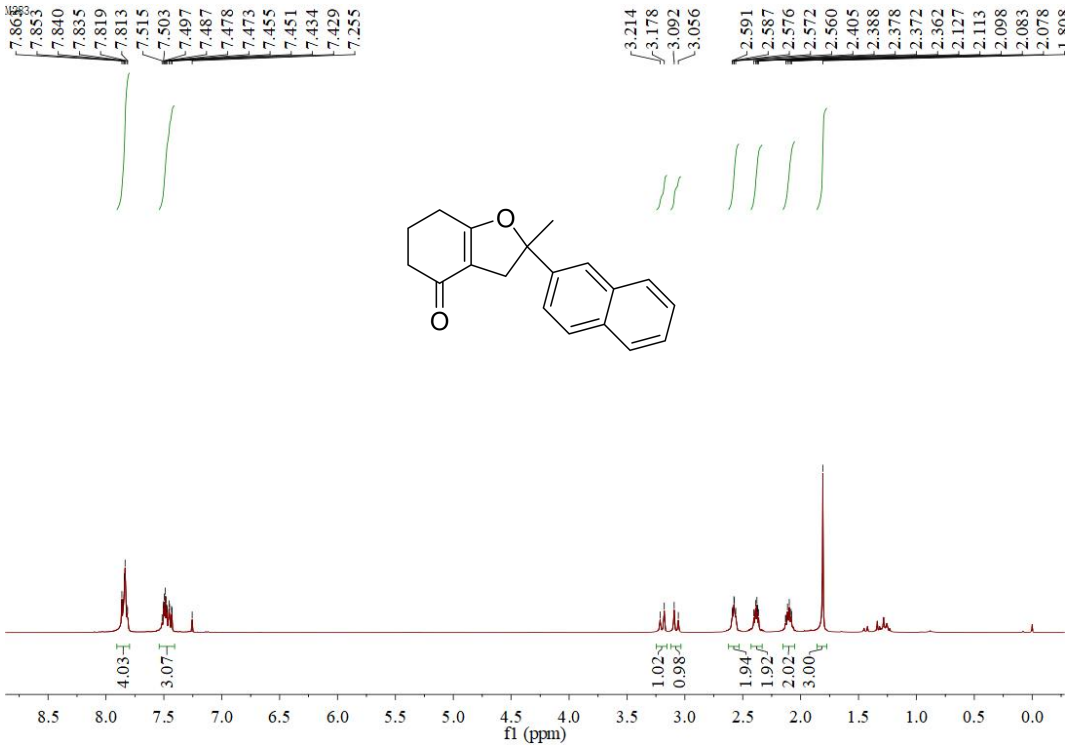


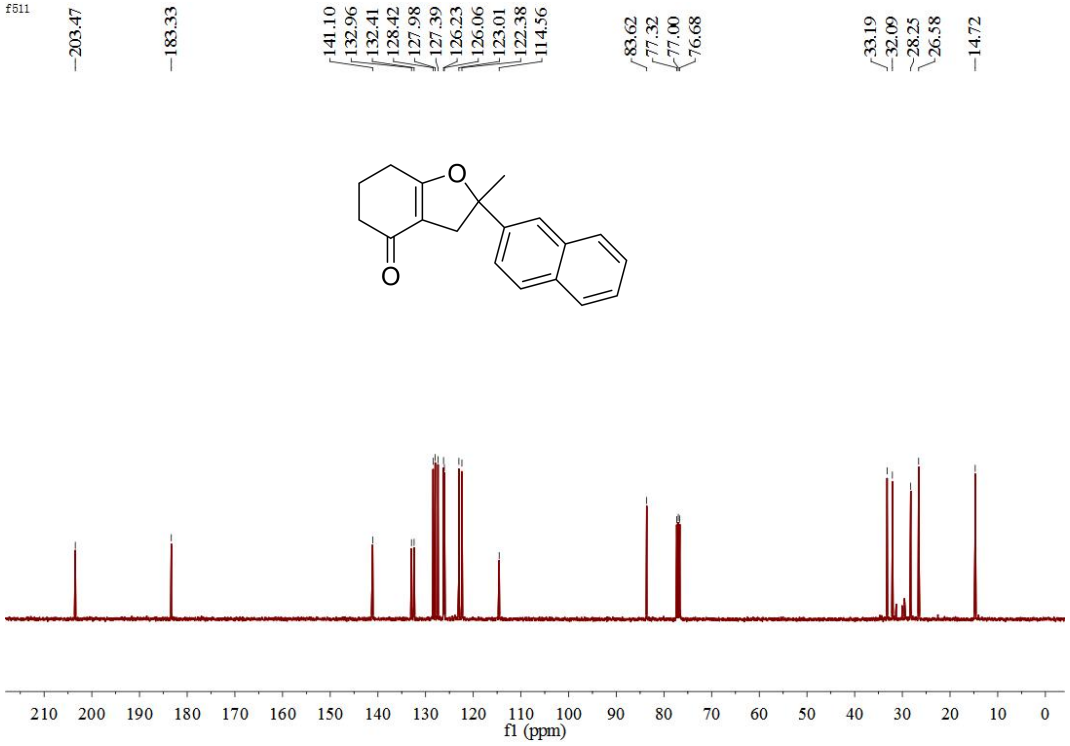
^{1}H NMR and ^{13}C NMR of 4b



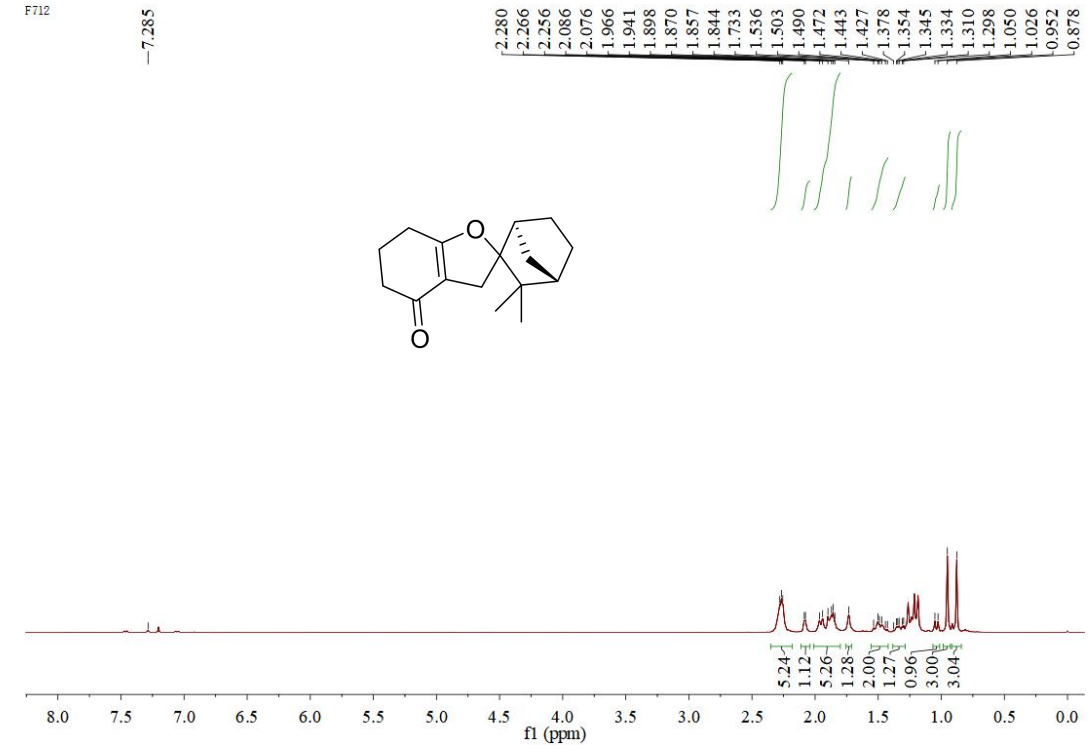


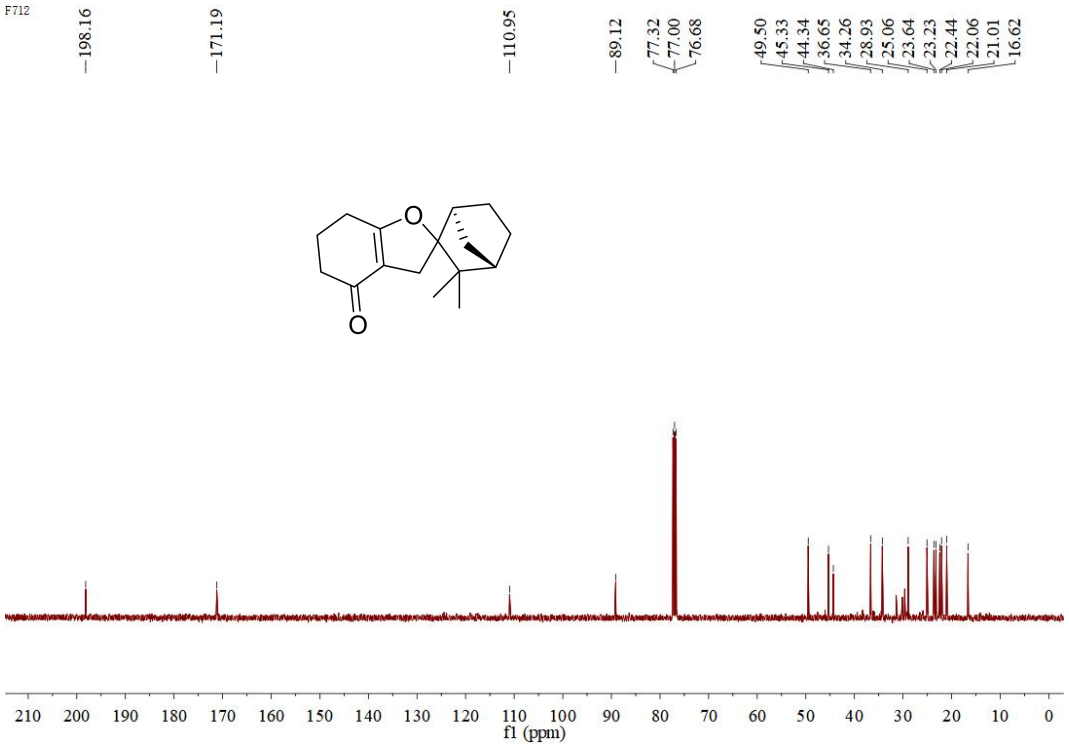
^{1}H NMR and ^{13}C NMR of 4c



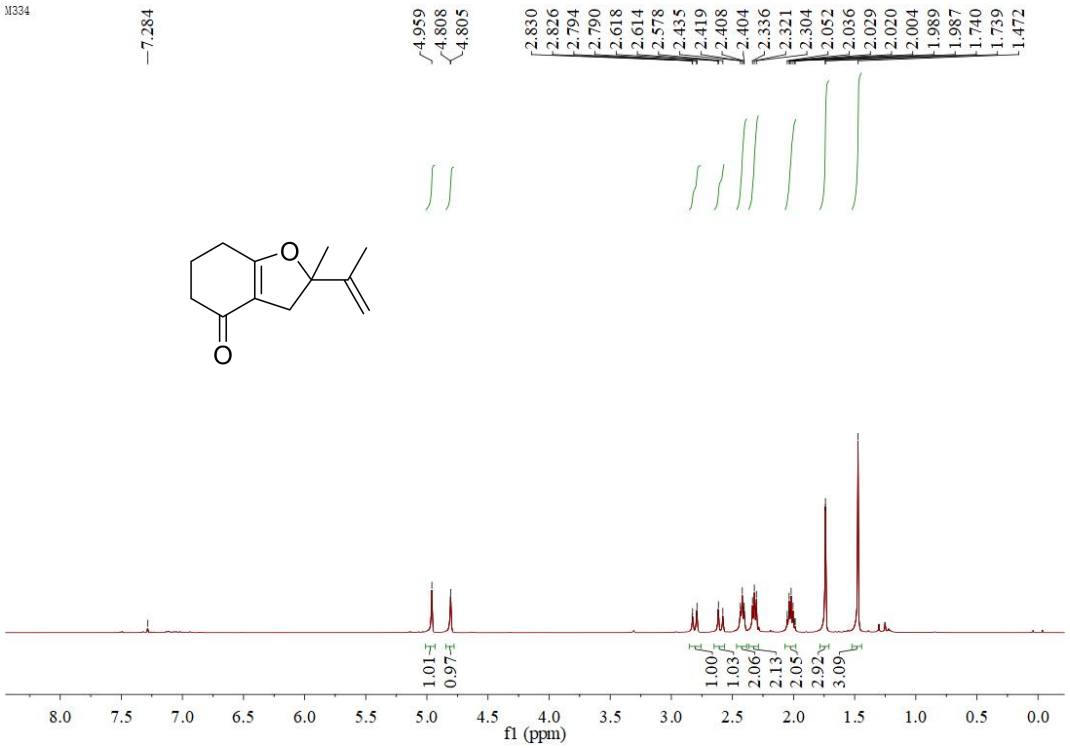


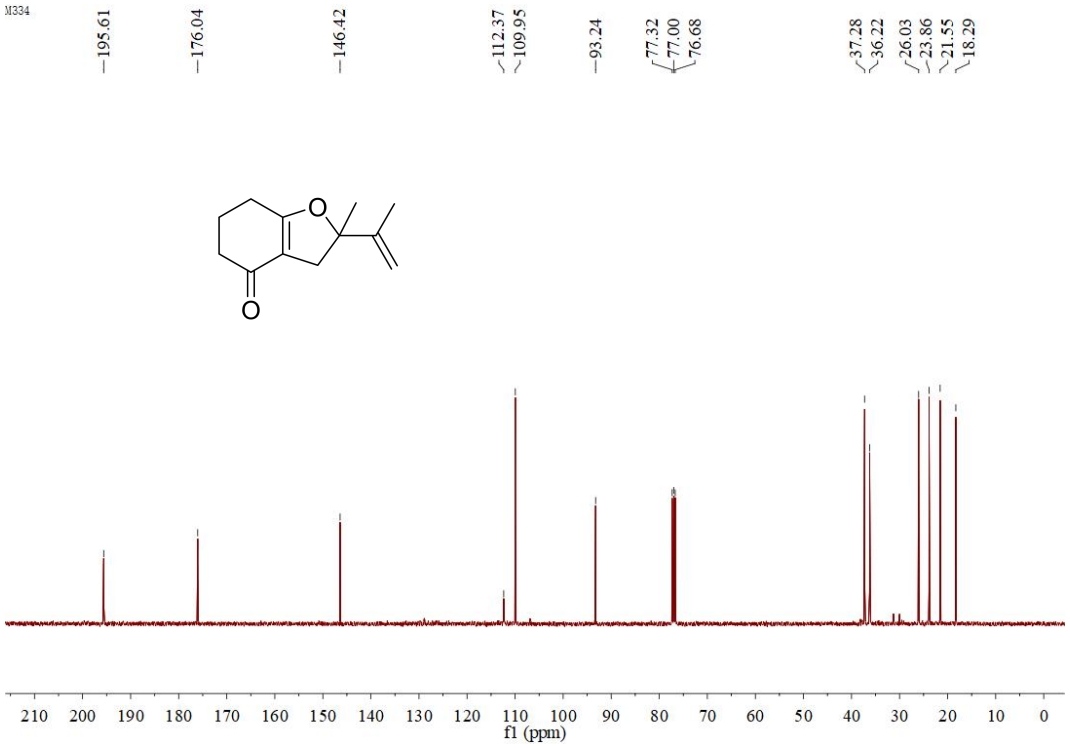
^{1}H NMR and ^{13}C NMR of 4d



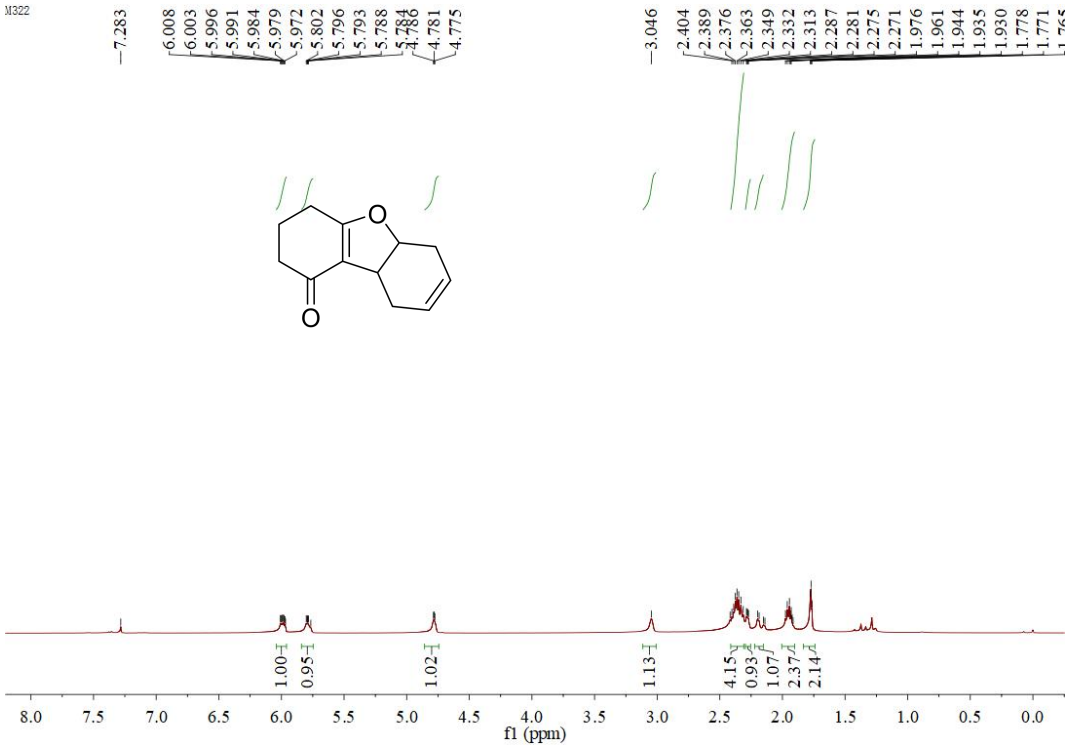


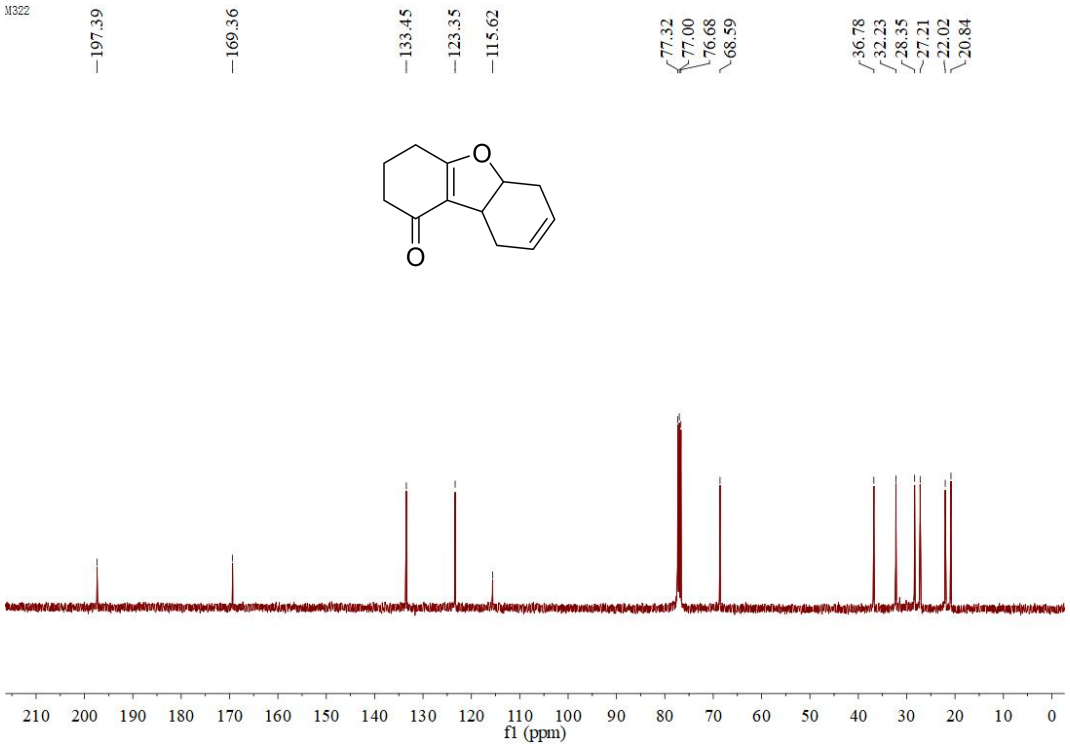
^{1}H NMR and ^{13}C NMR of 4e



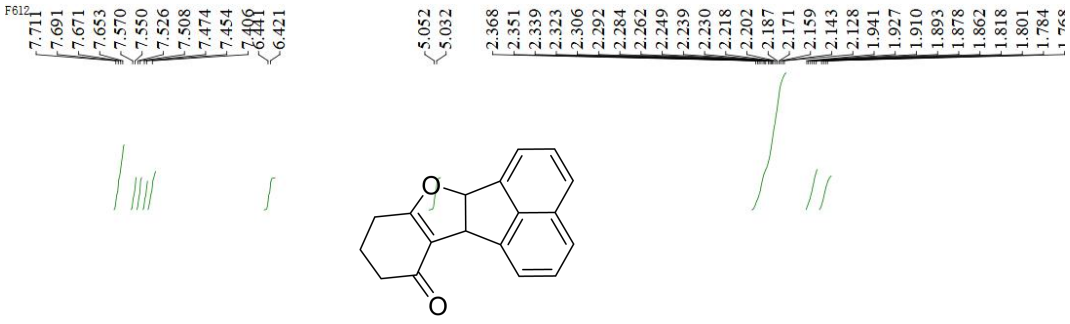


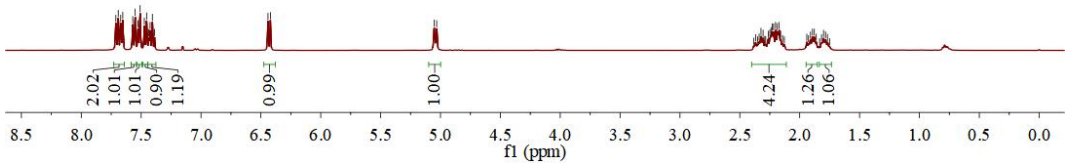
^{1}H NMR and ^{13}C NMR of 4f

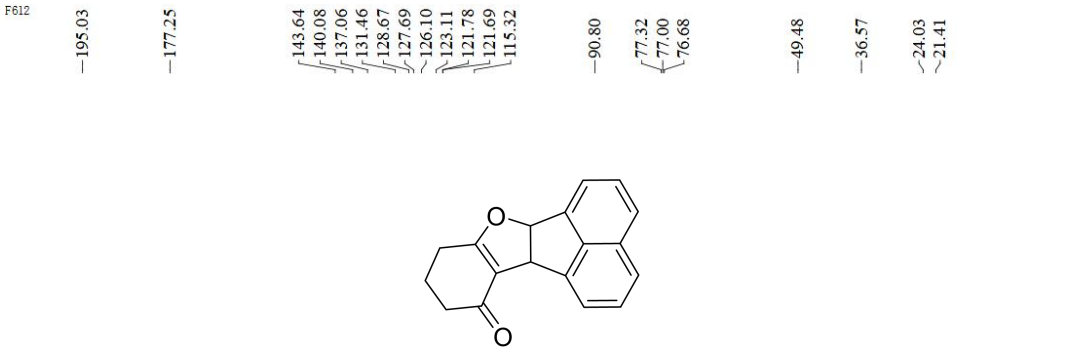


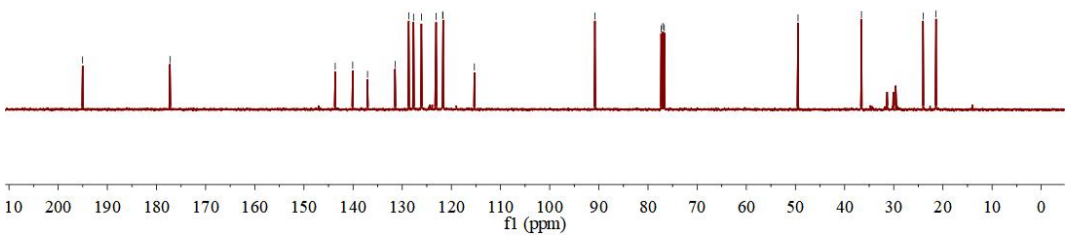


^{1}H NMR and ^{13}C NMR of 4g

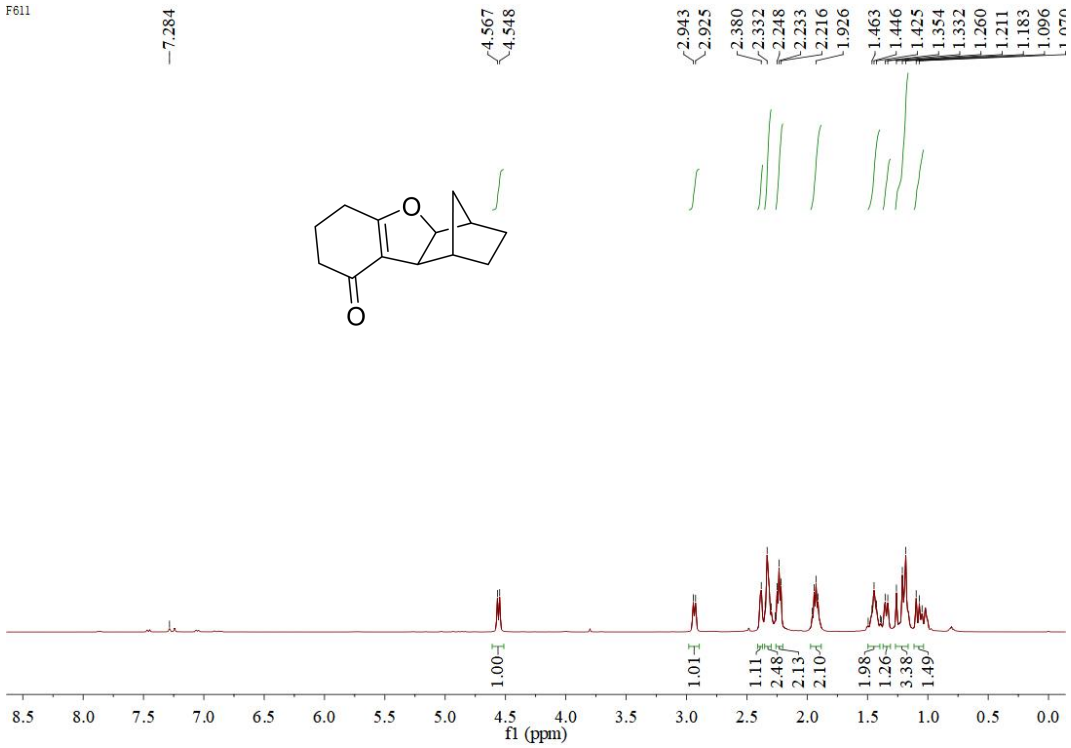


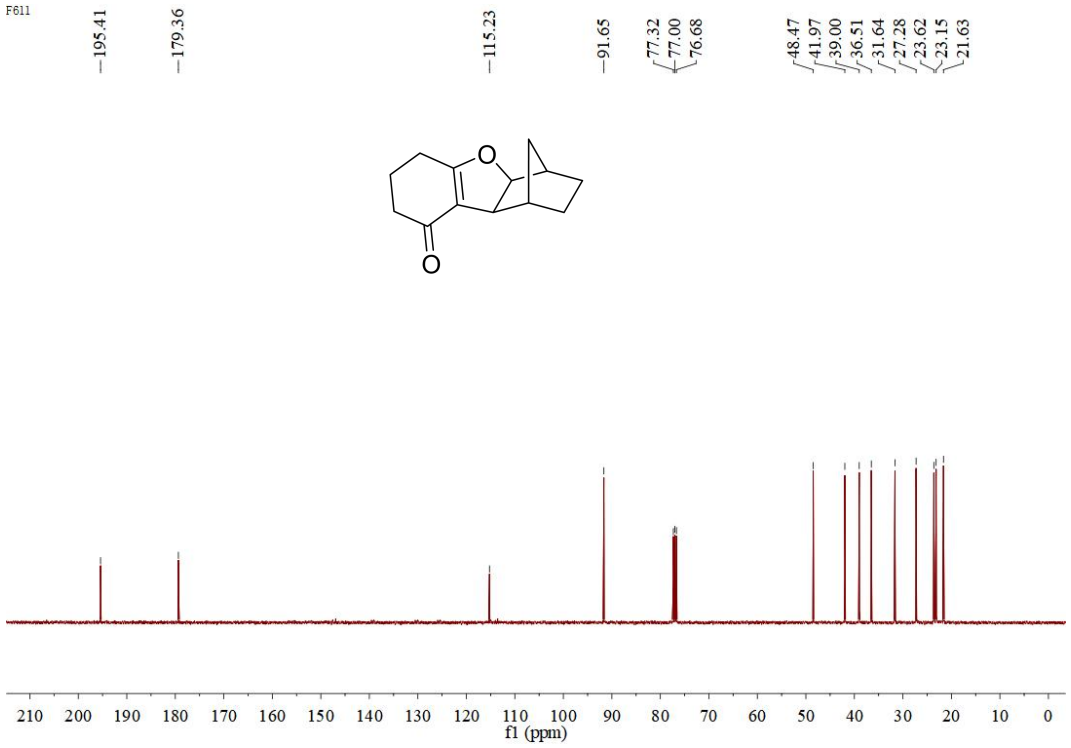




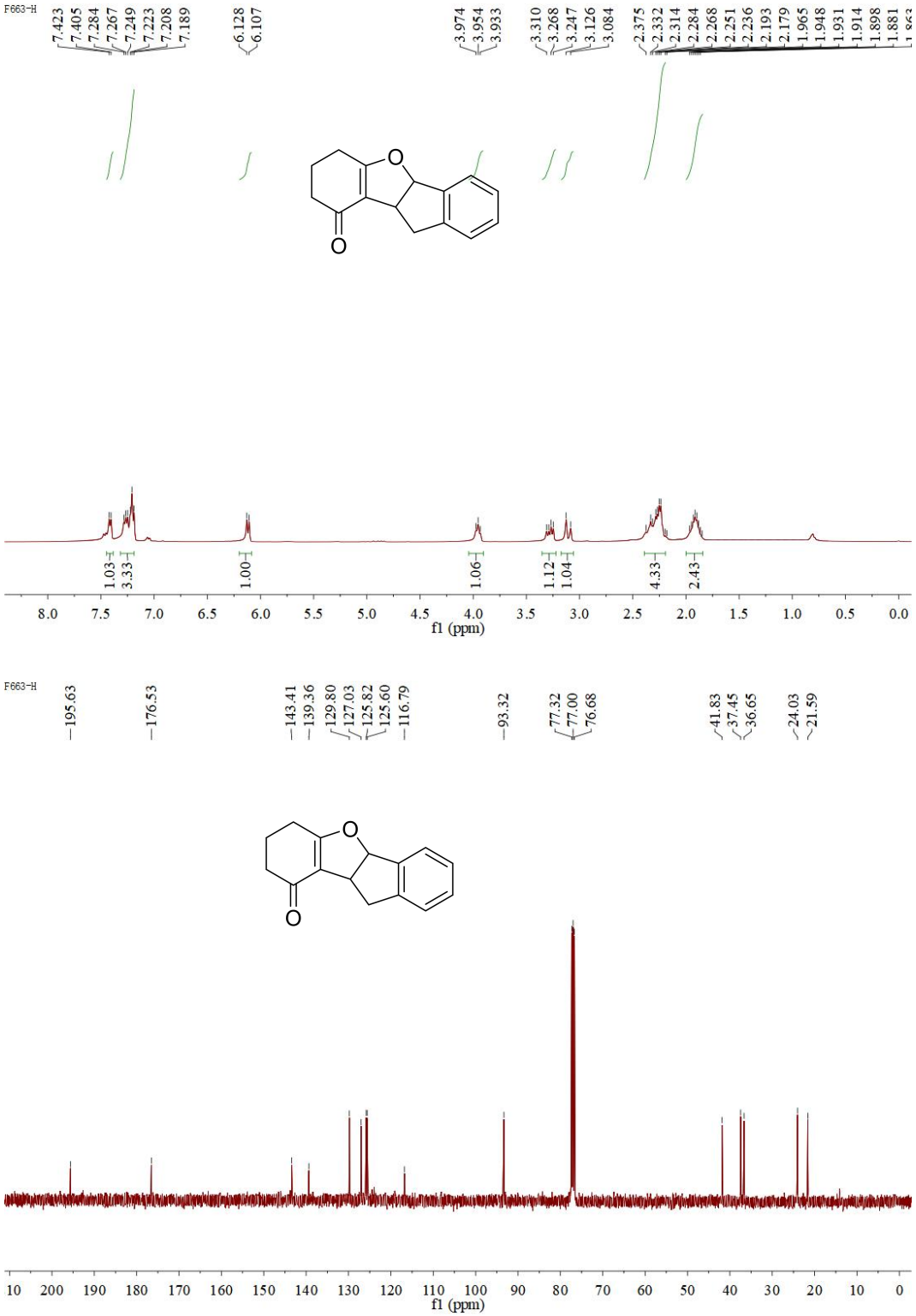


^{1}H NMR and ^{13}C NMR of 4h

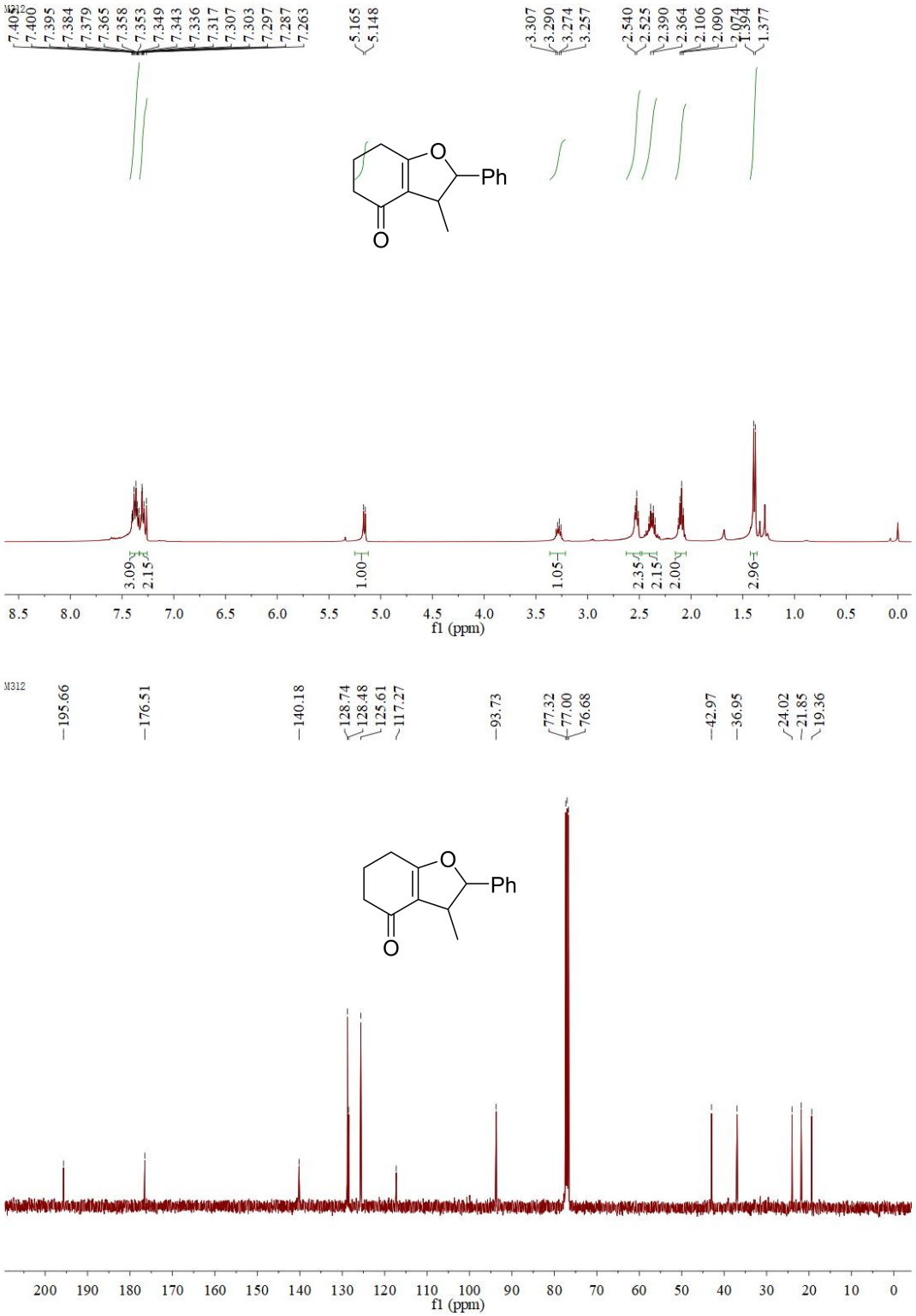




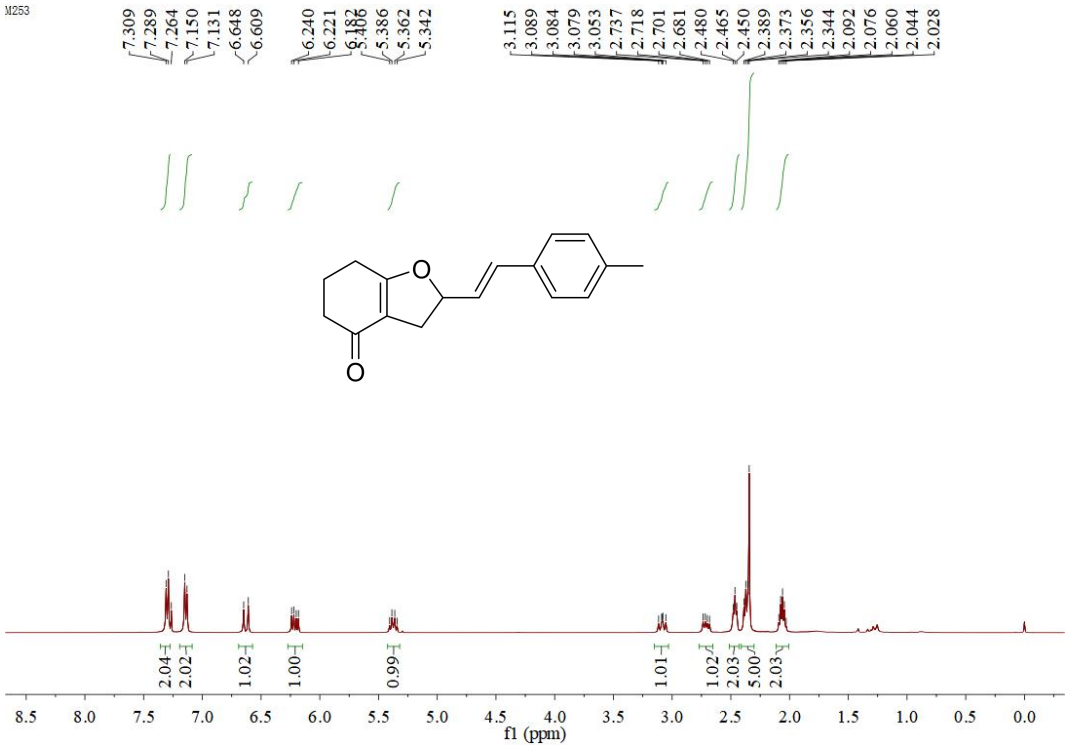
^{1}H NMR and ^{13}C NMR of 4i

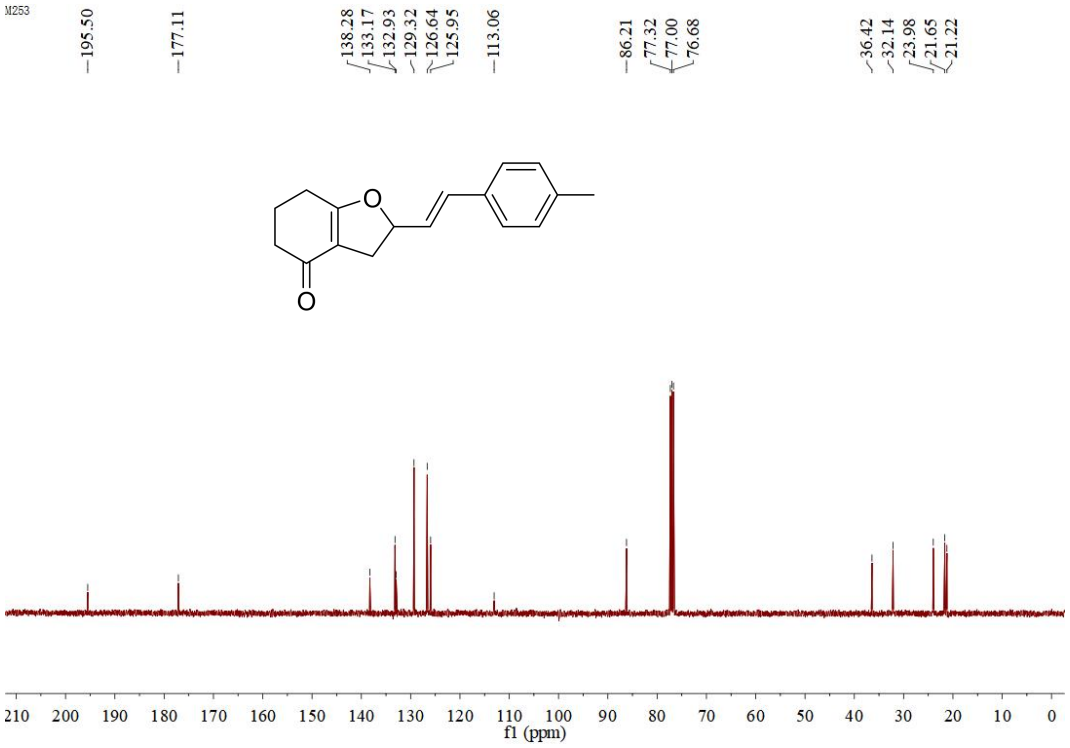


^{1}H NMR and ^{13}C NMR of 4j

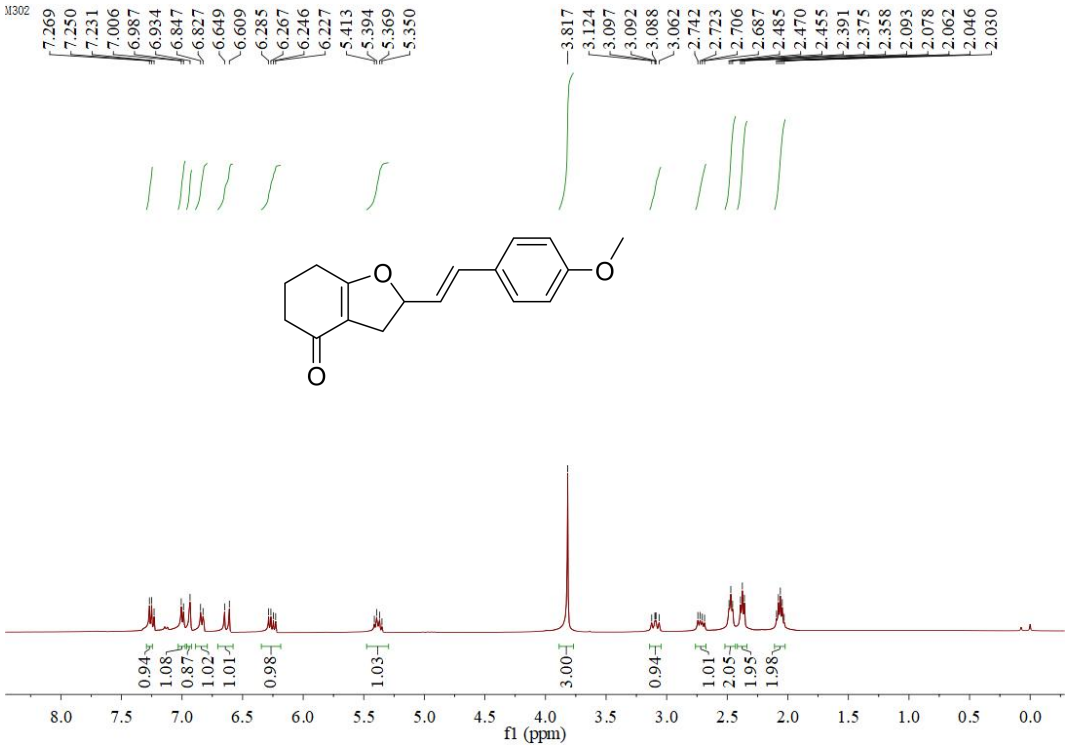


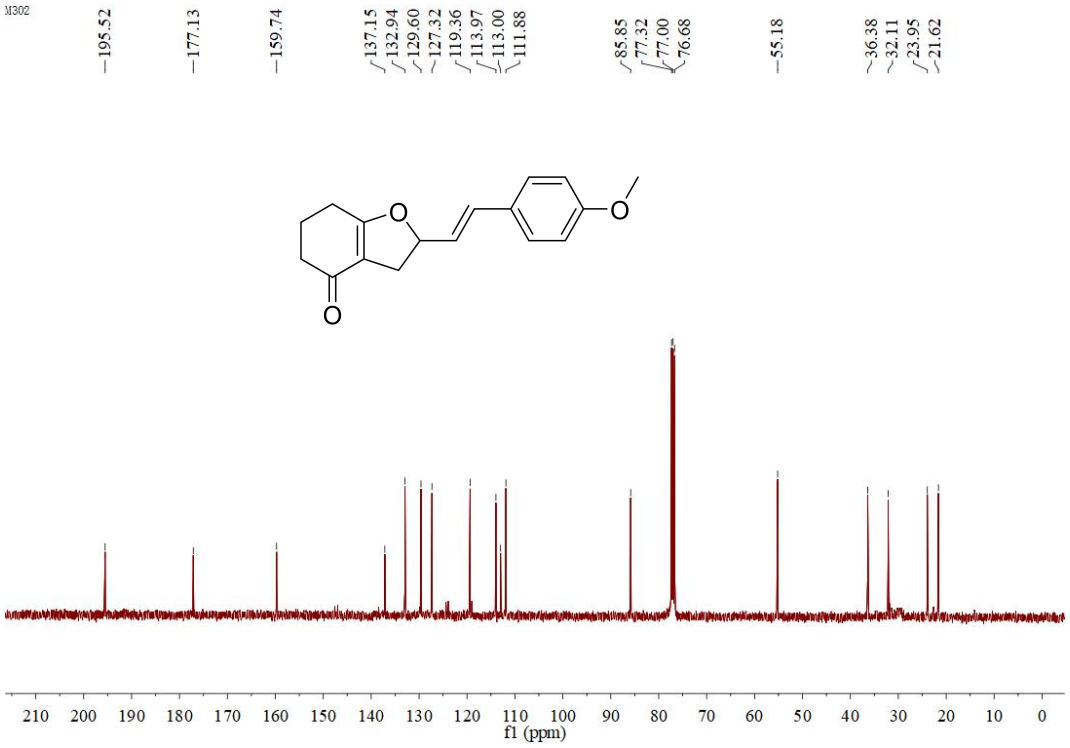
^{1}H NMR and ^{13}C NMR of 4k



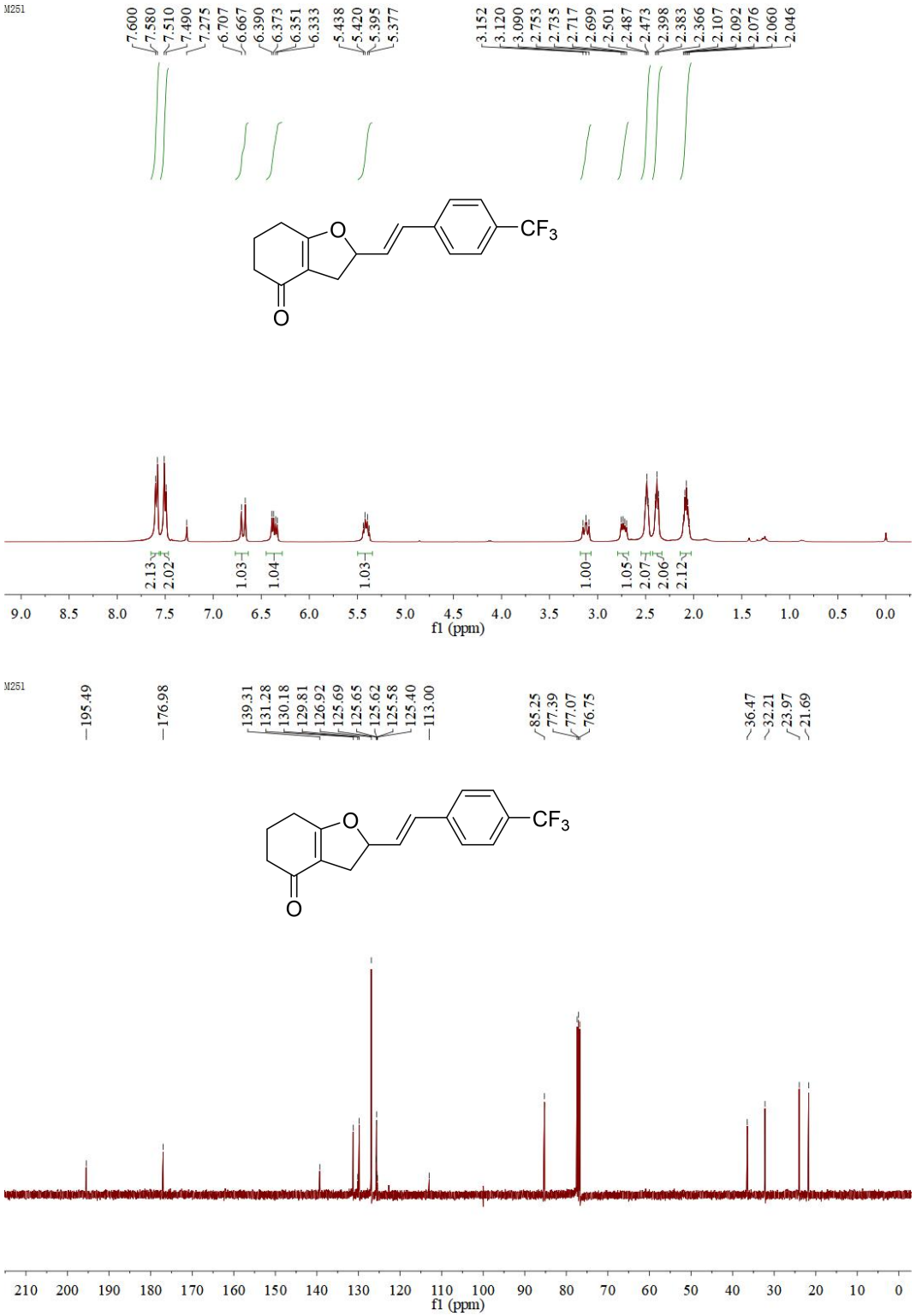


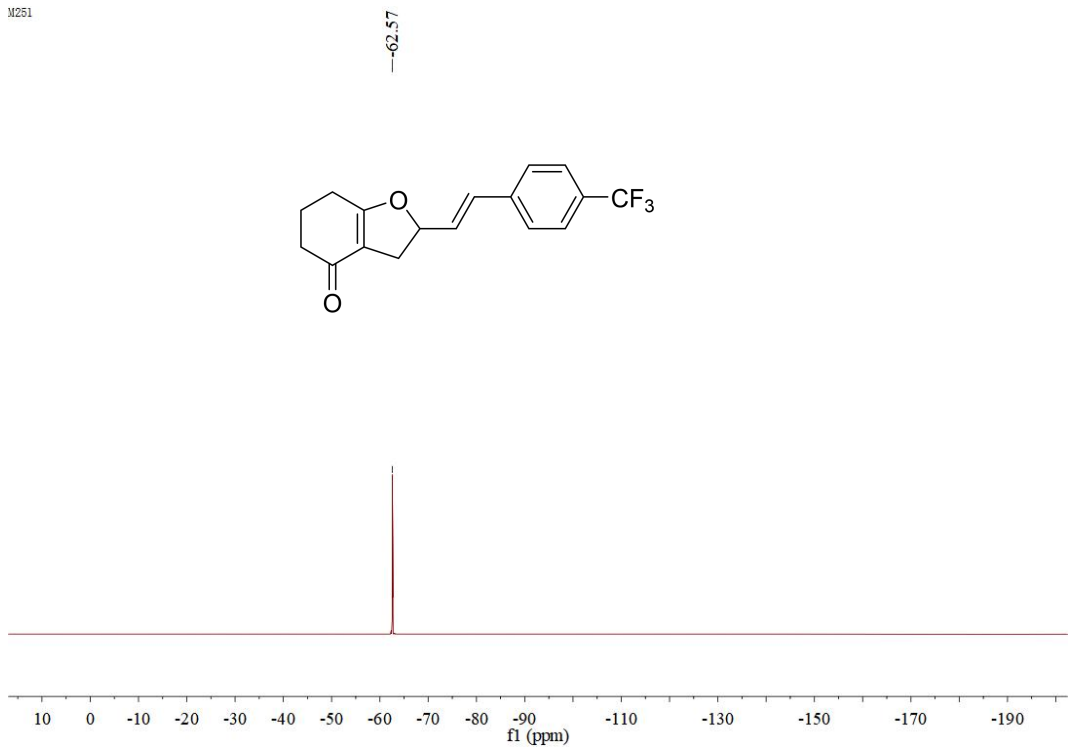
^{1}H NMR and ^{13}C NMR of 4l





^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 4m

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O
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-10
-20
-30
-40
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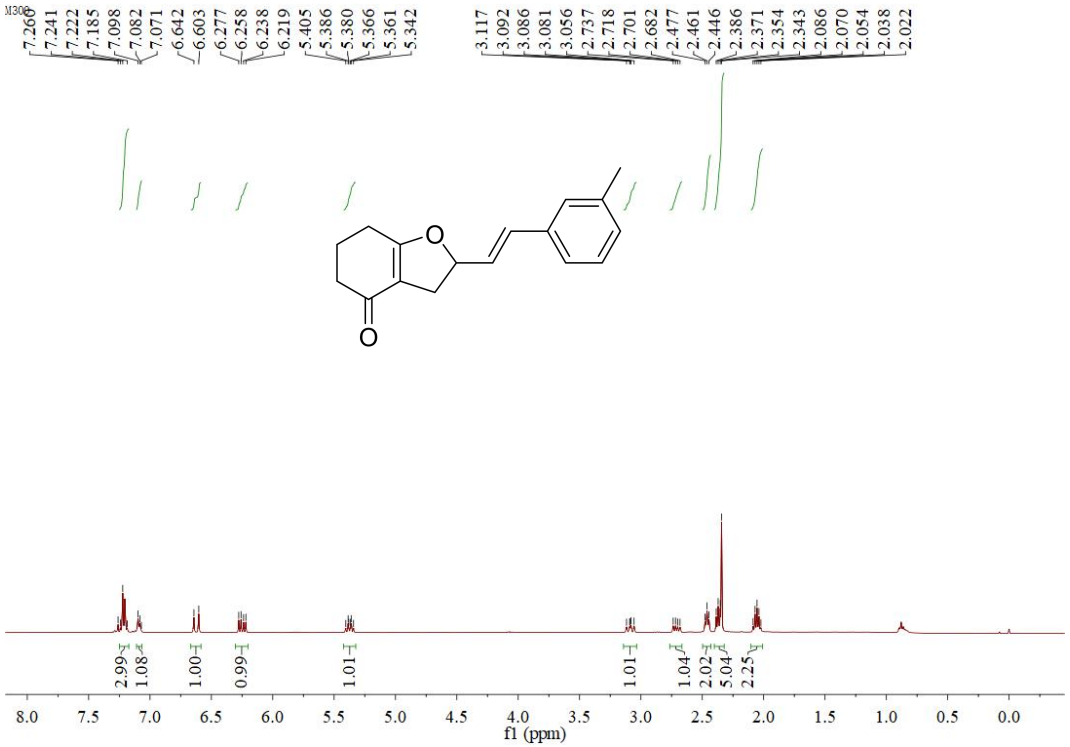
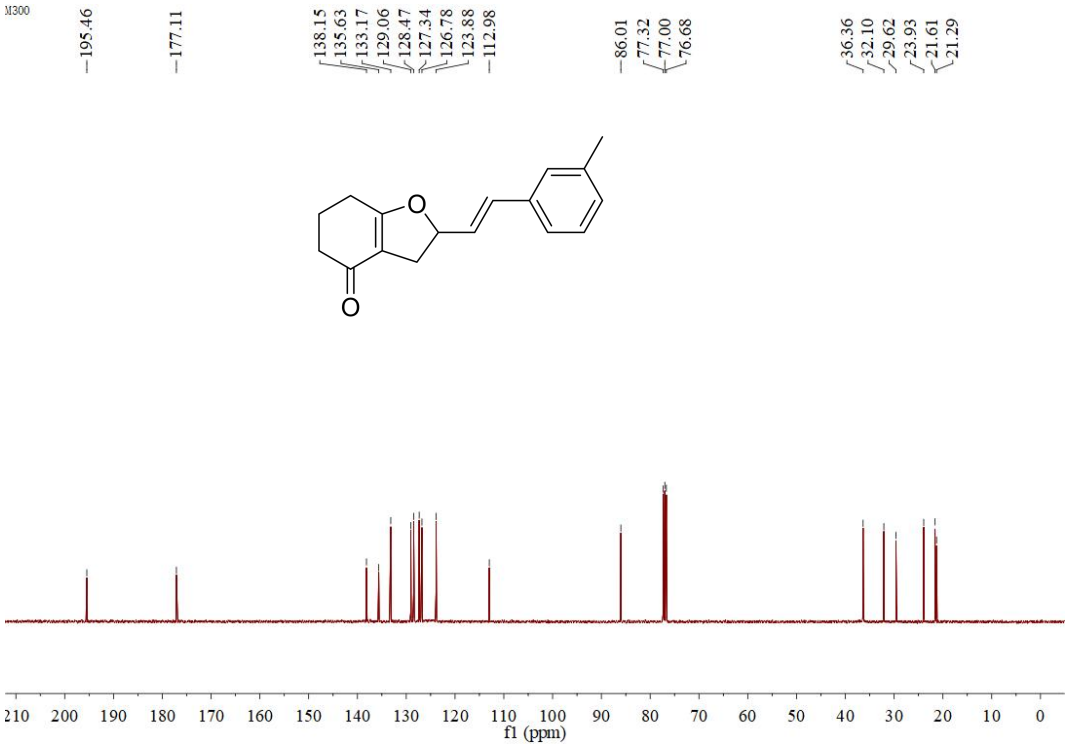
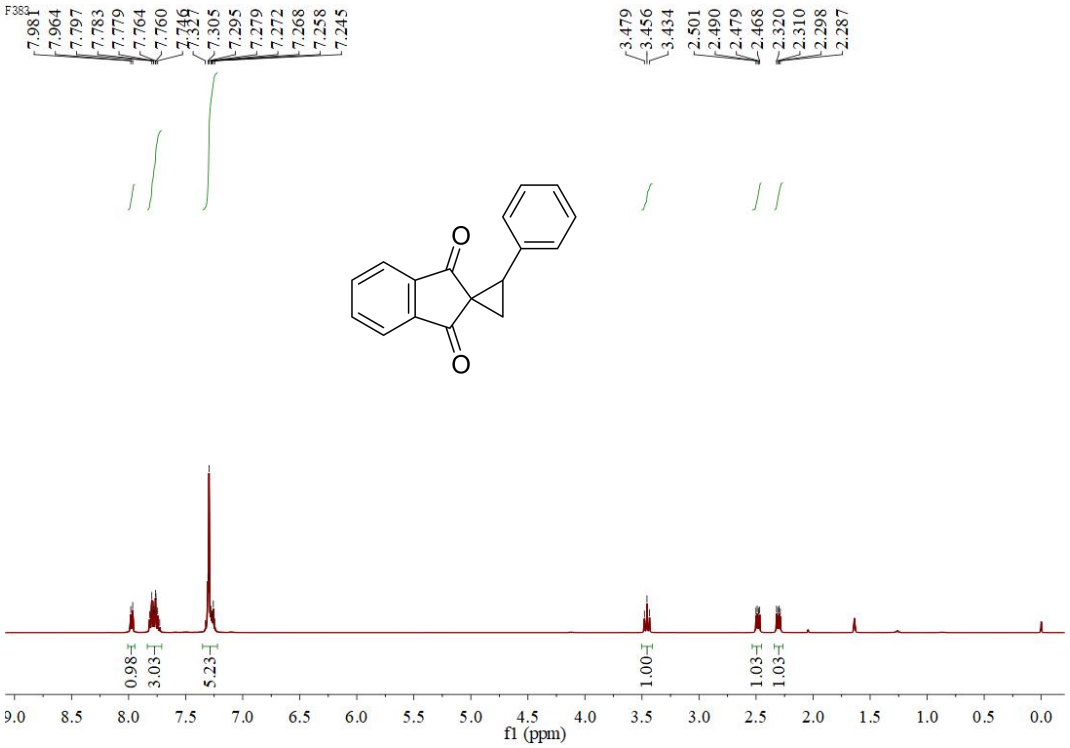
-90
-110
-130
-150
-170
-190
f1 (ppm)

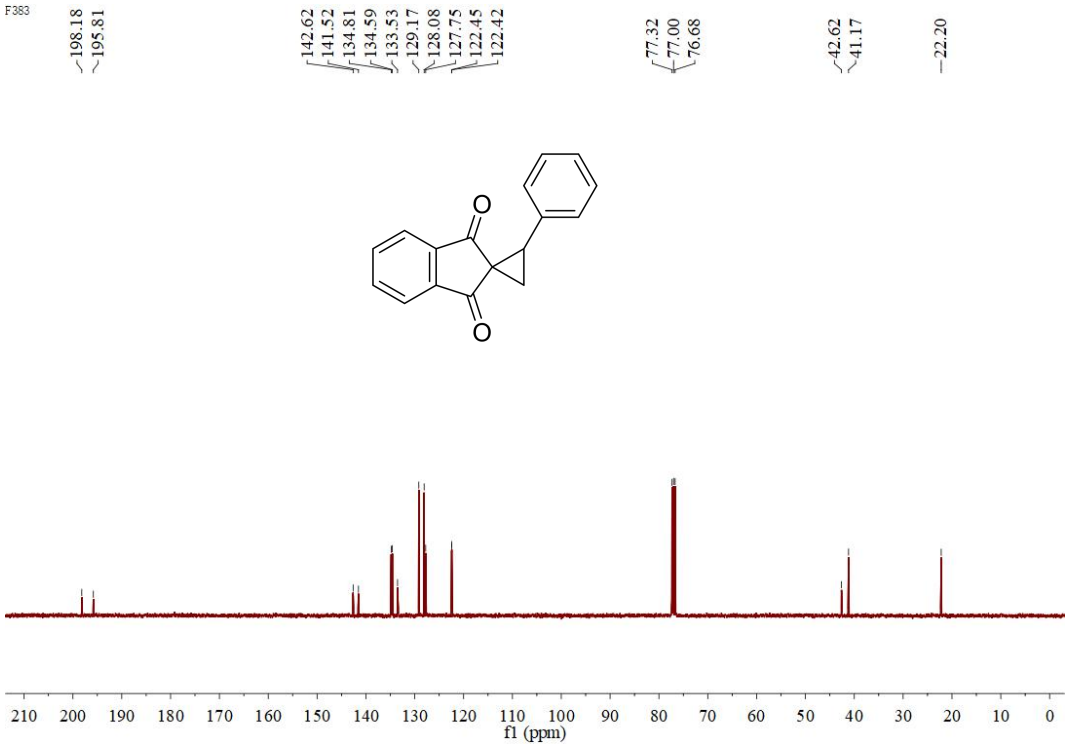
^{1}H NMR and ^{13}C NMR of 4n



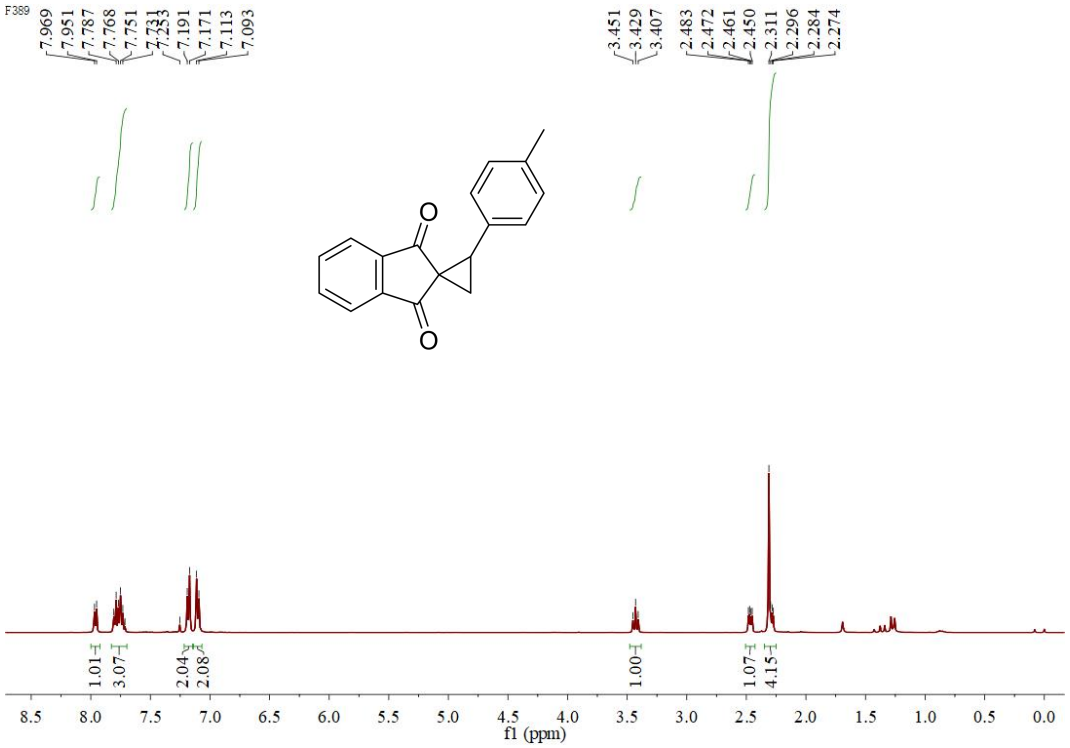


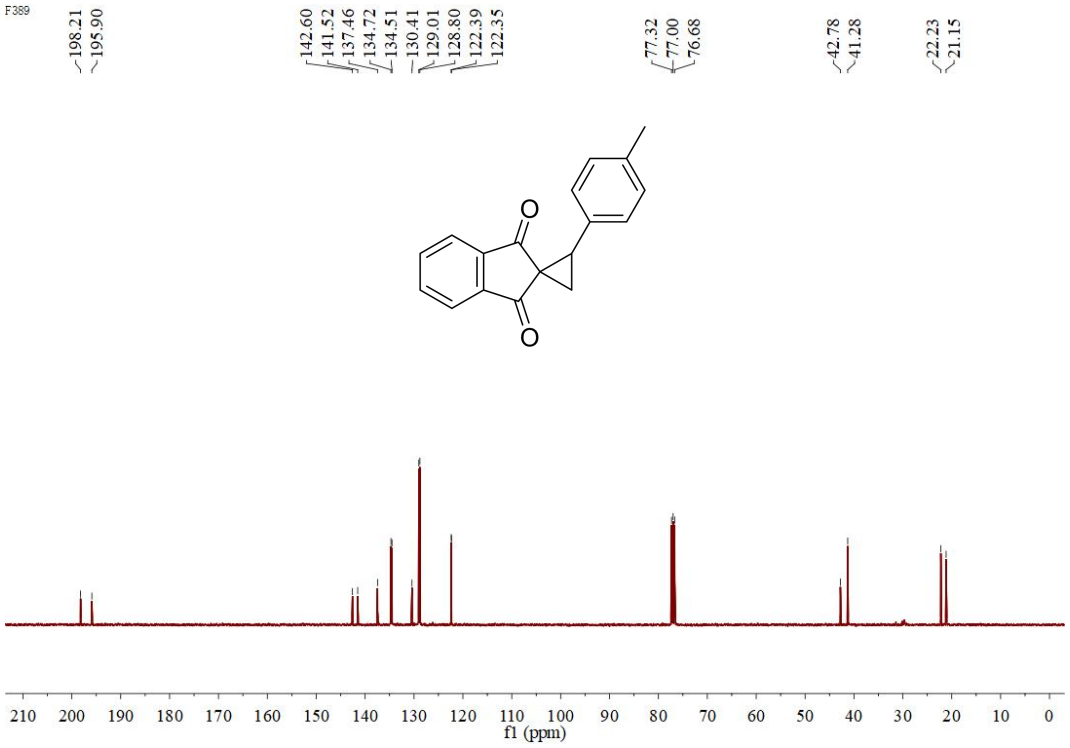
^{1}H NMR and ^{13}C NMR of 5a



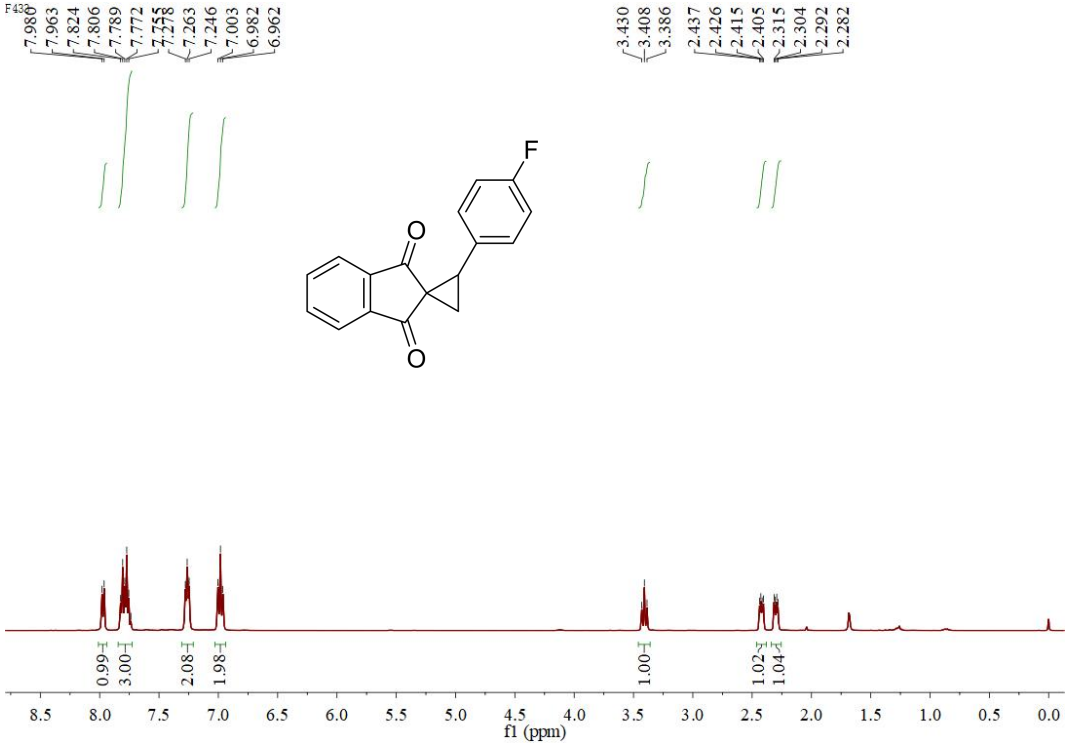


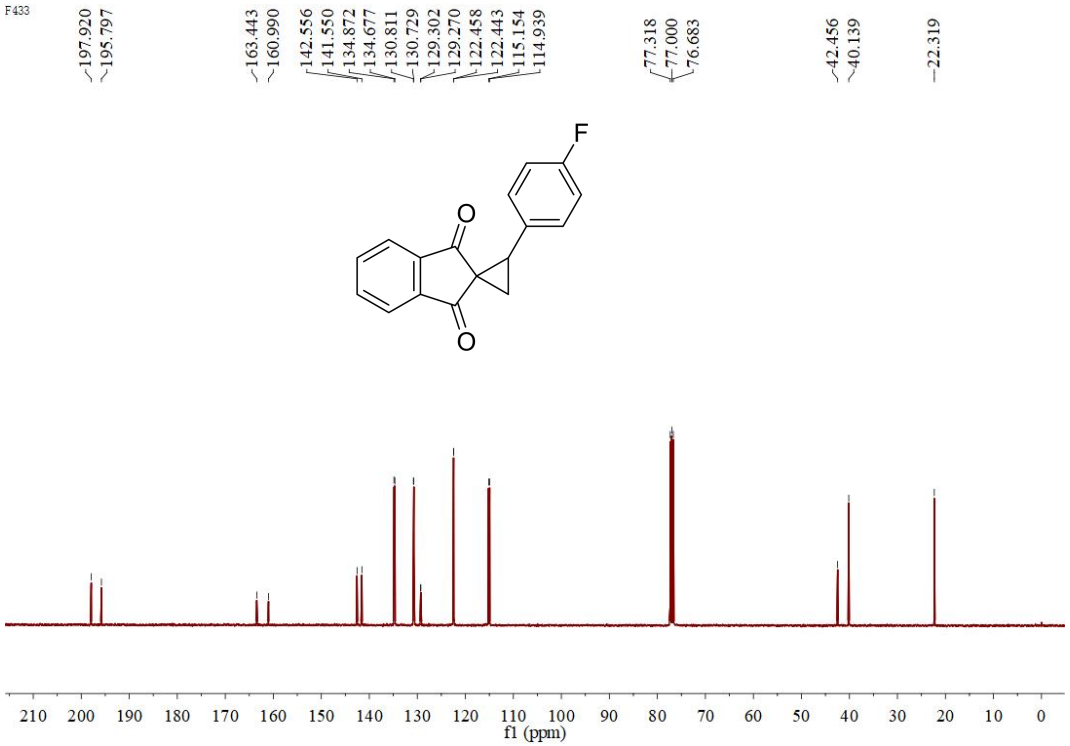
^{1}H NMR and ^{13}C NMR of 5b

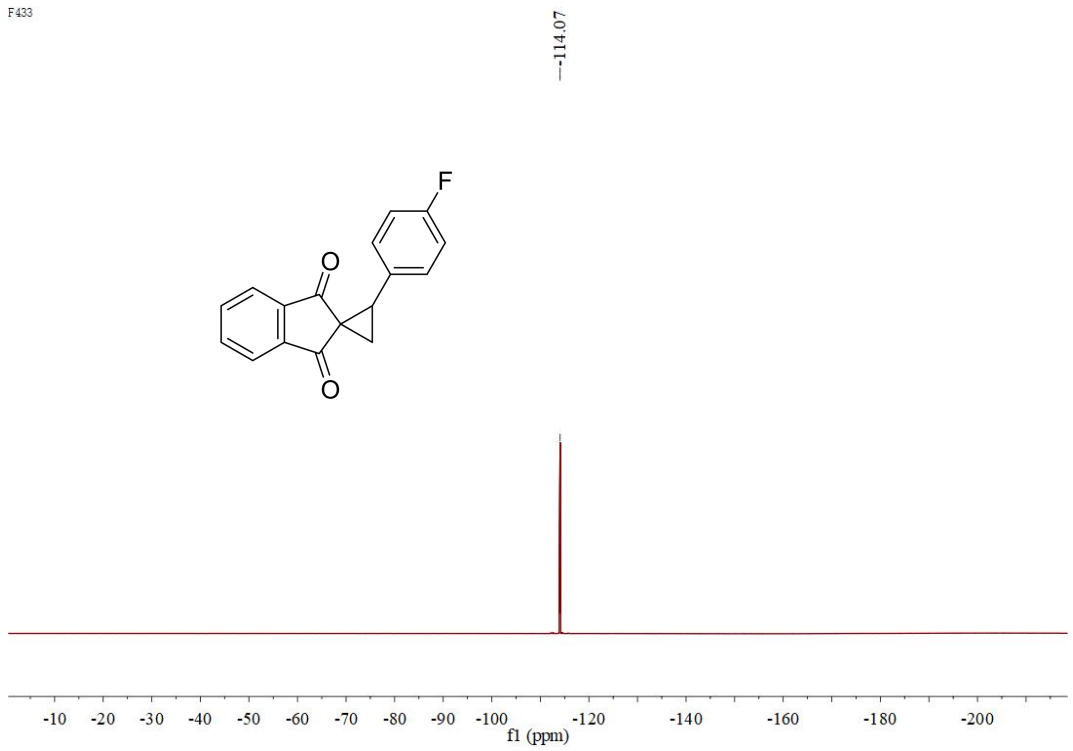




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 5c






F433
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F
O
O
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-20
-30
-40
-50
-60
-70
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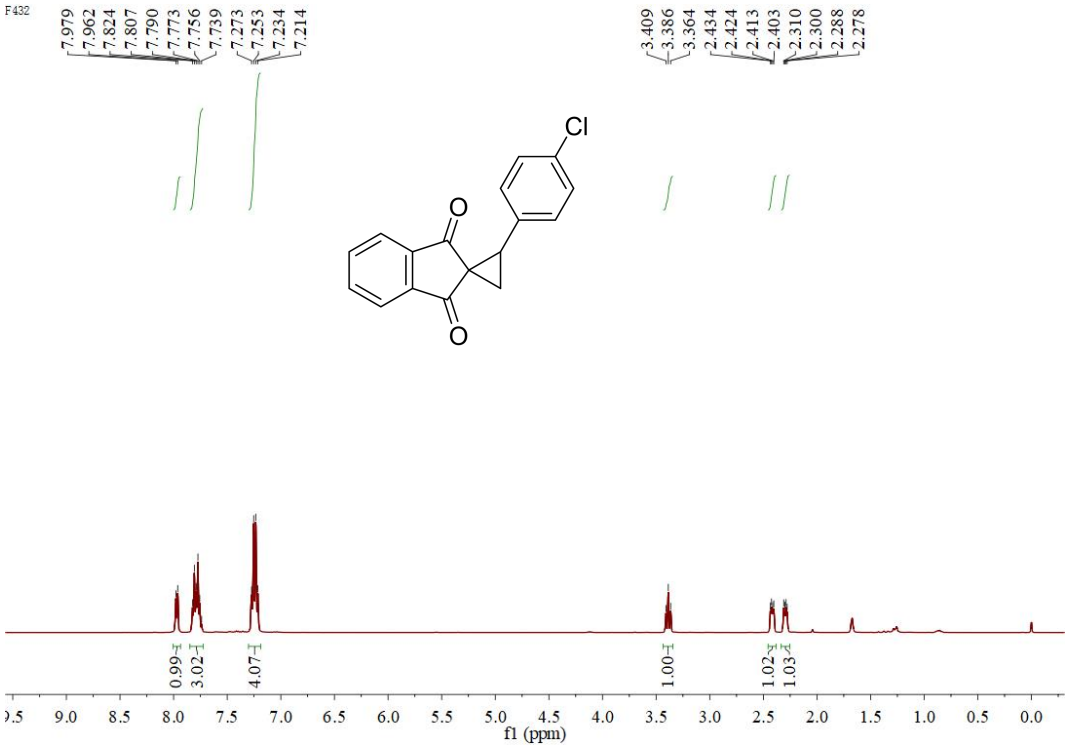
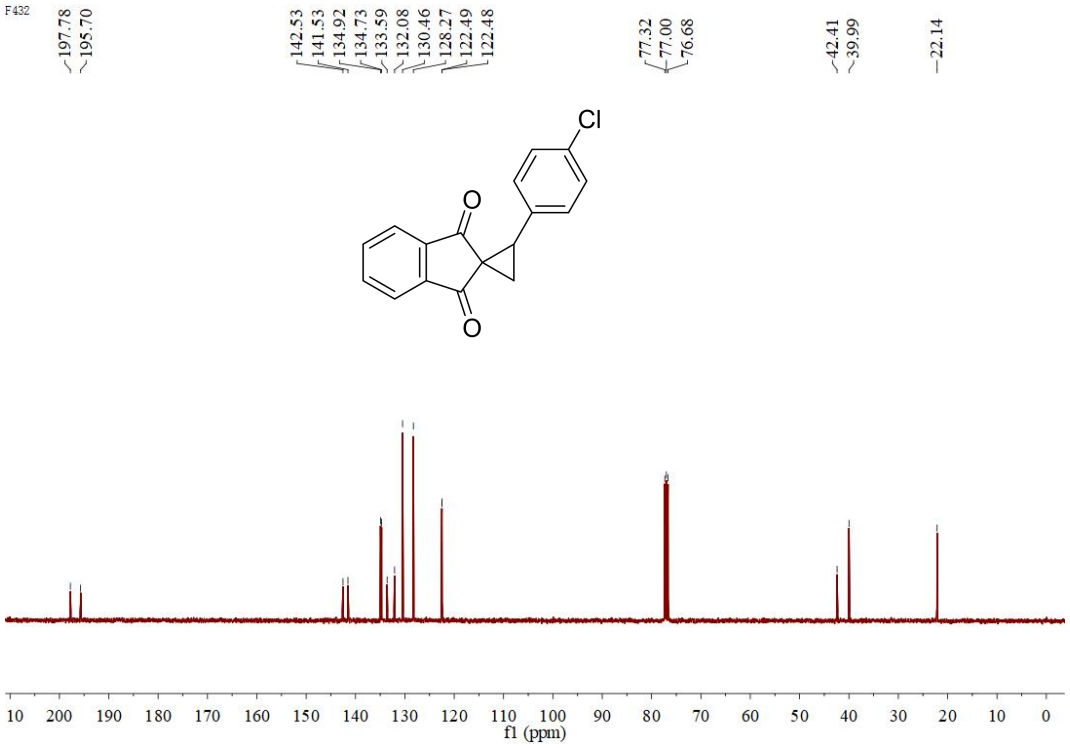
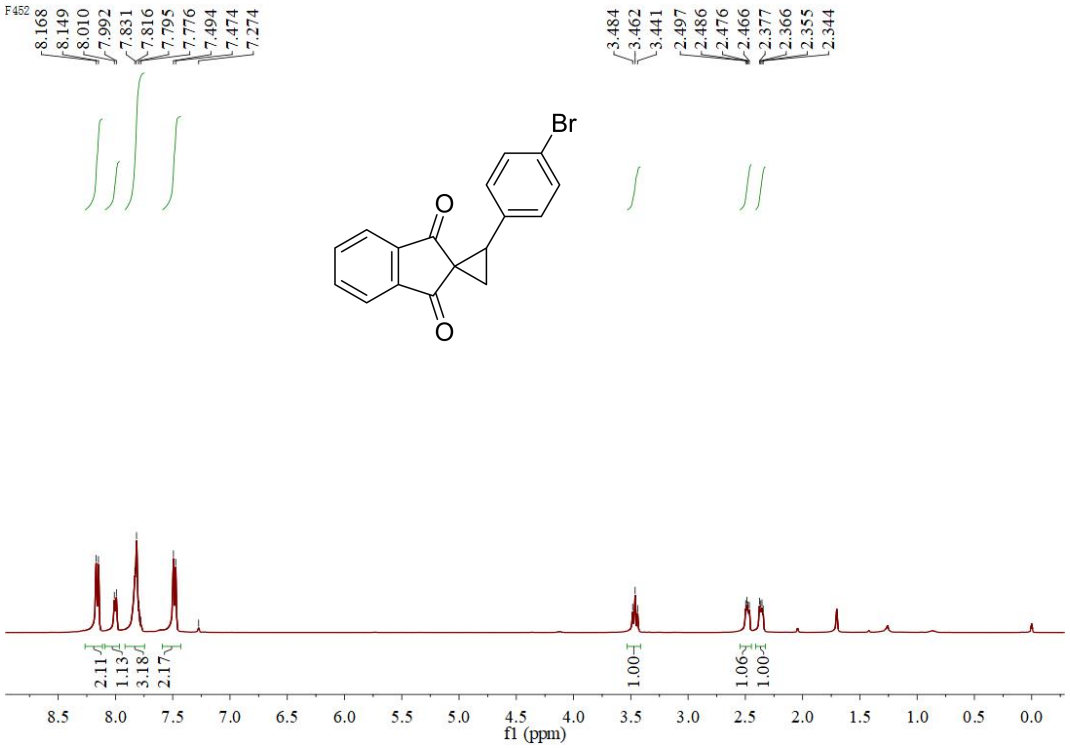
-100
-120
-140
-160
-180
-200
f1 (ppm)

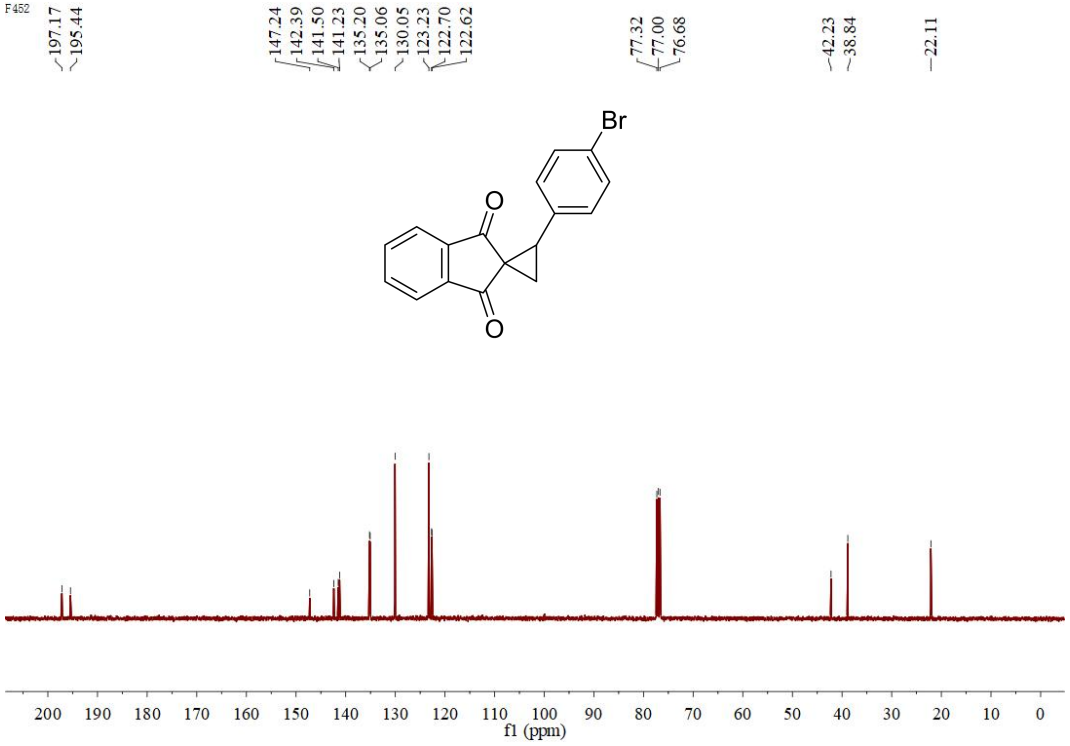
^{1}H NMR and ^{13}C NMR of 5d



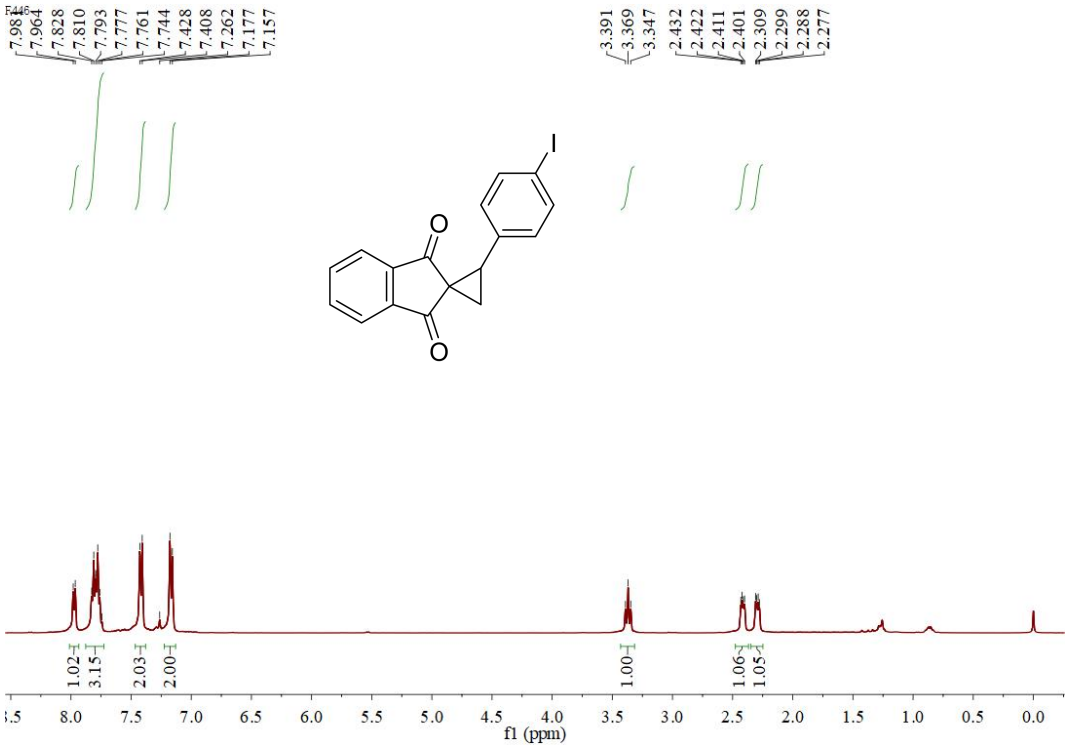


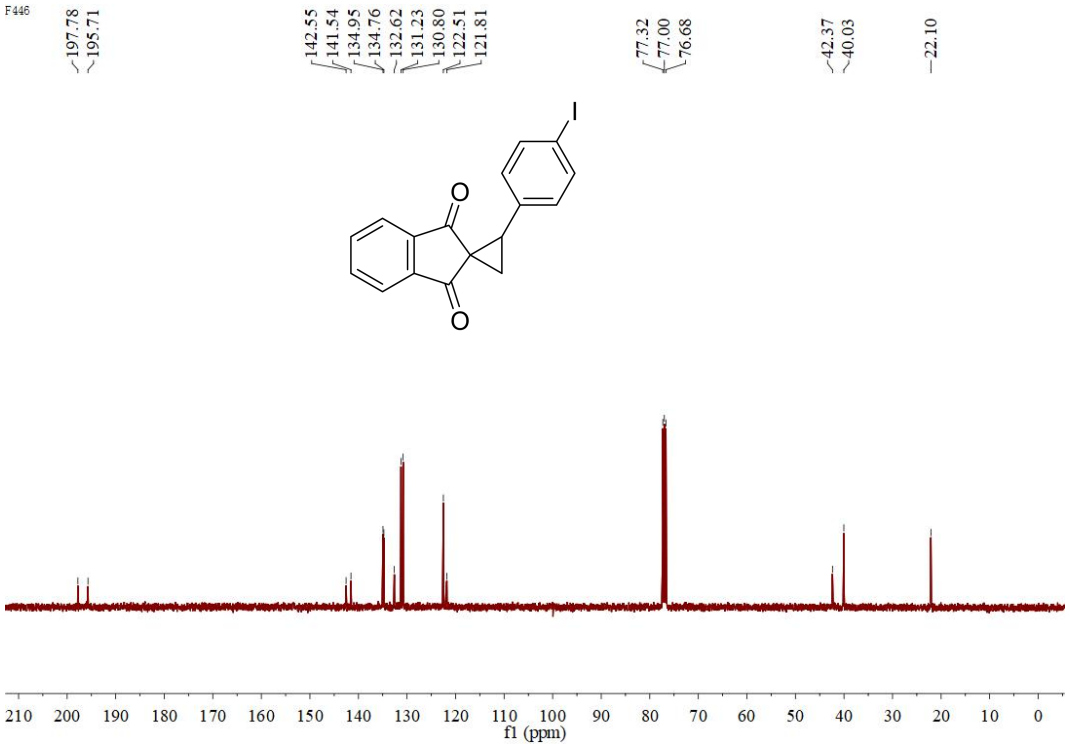
^{1}H NMR and ^{13}C NMR of 5e



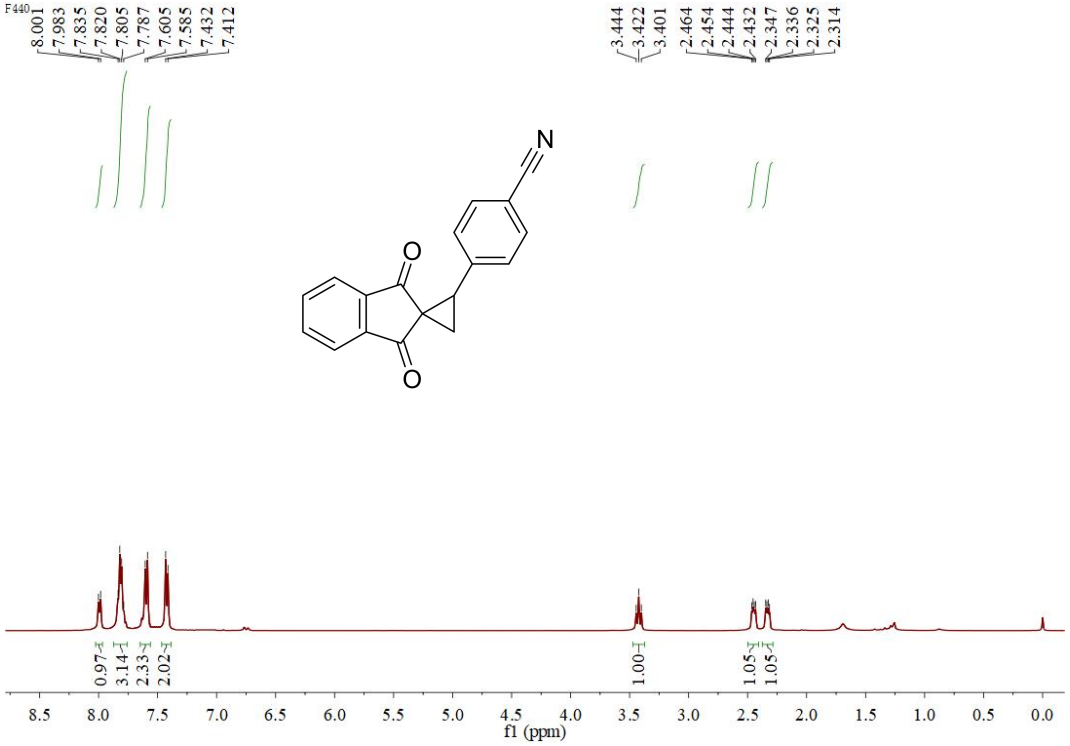


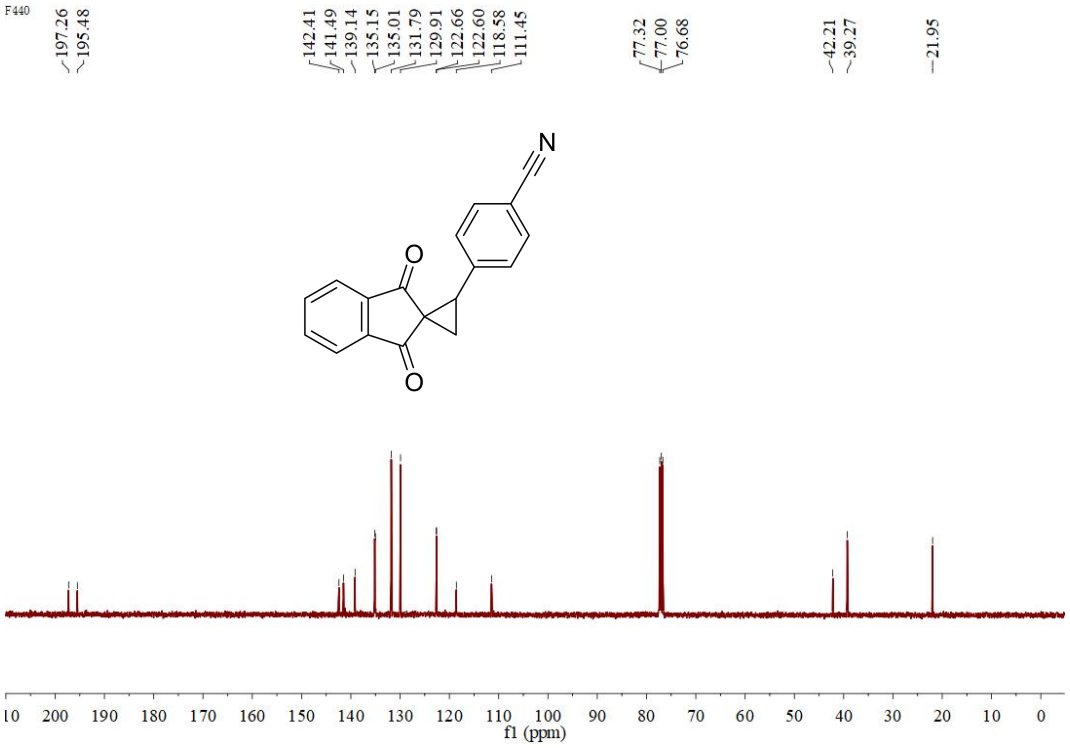
^{1}H NMR and ^{13}C NMR of 5f



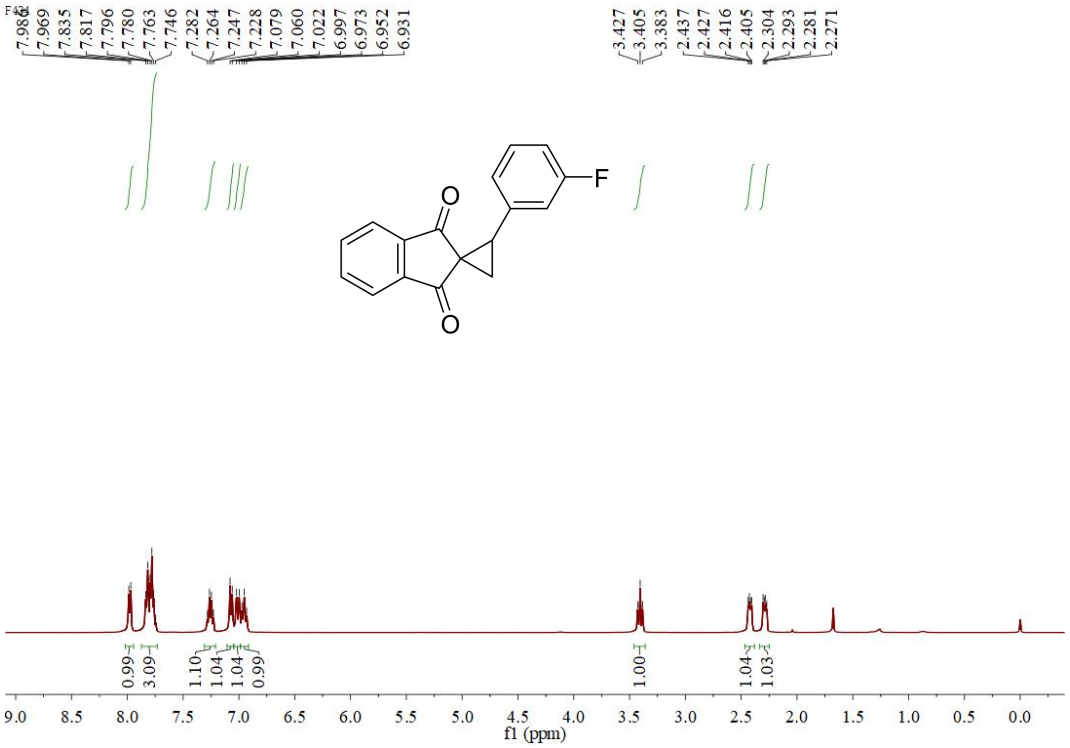


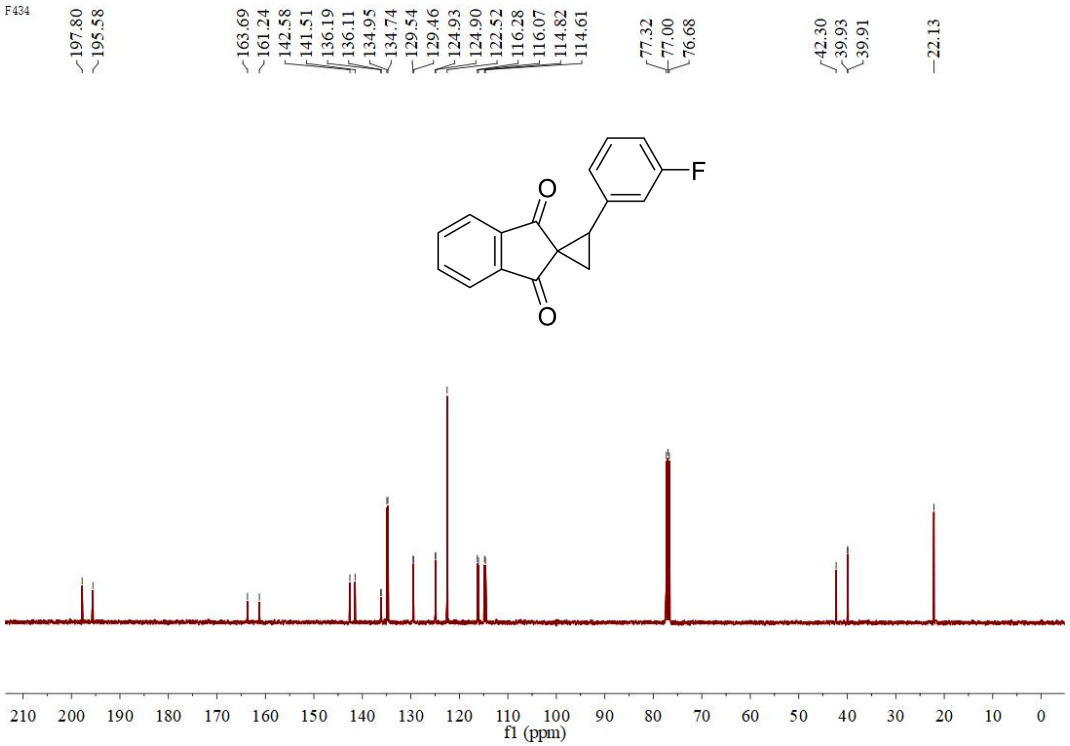
^{1}H NMR and ^{13}C NMR of 5g

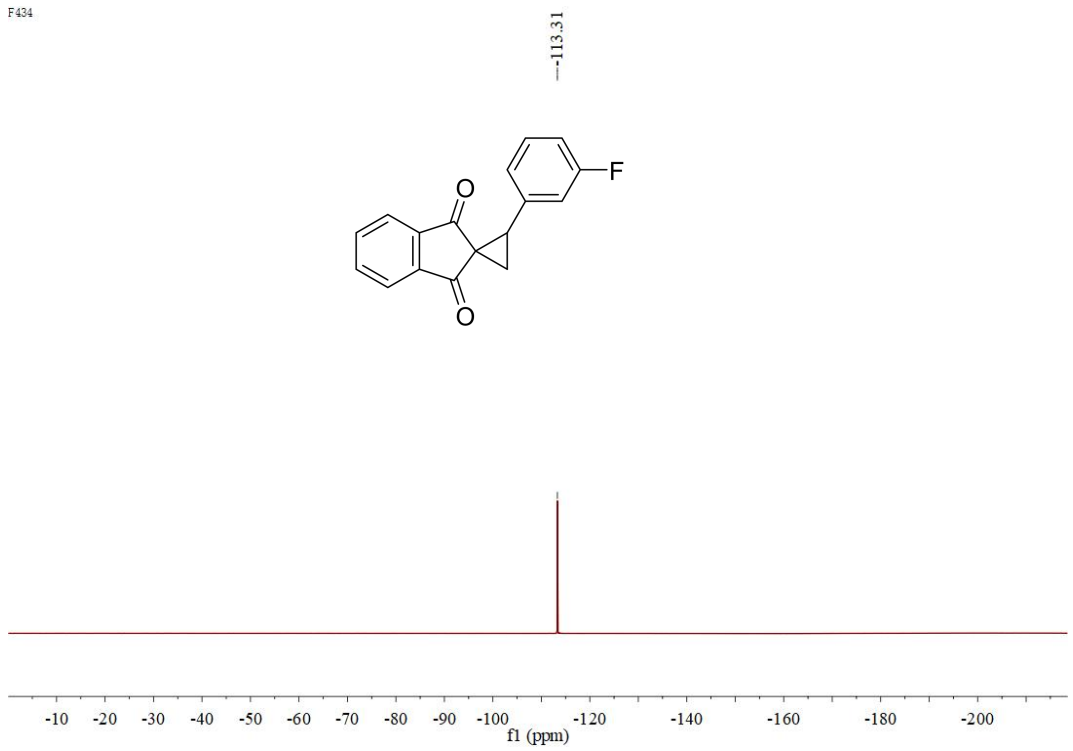




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 5h



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-20
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-40
-50
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-140
-160
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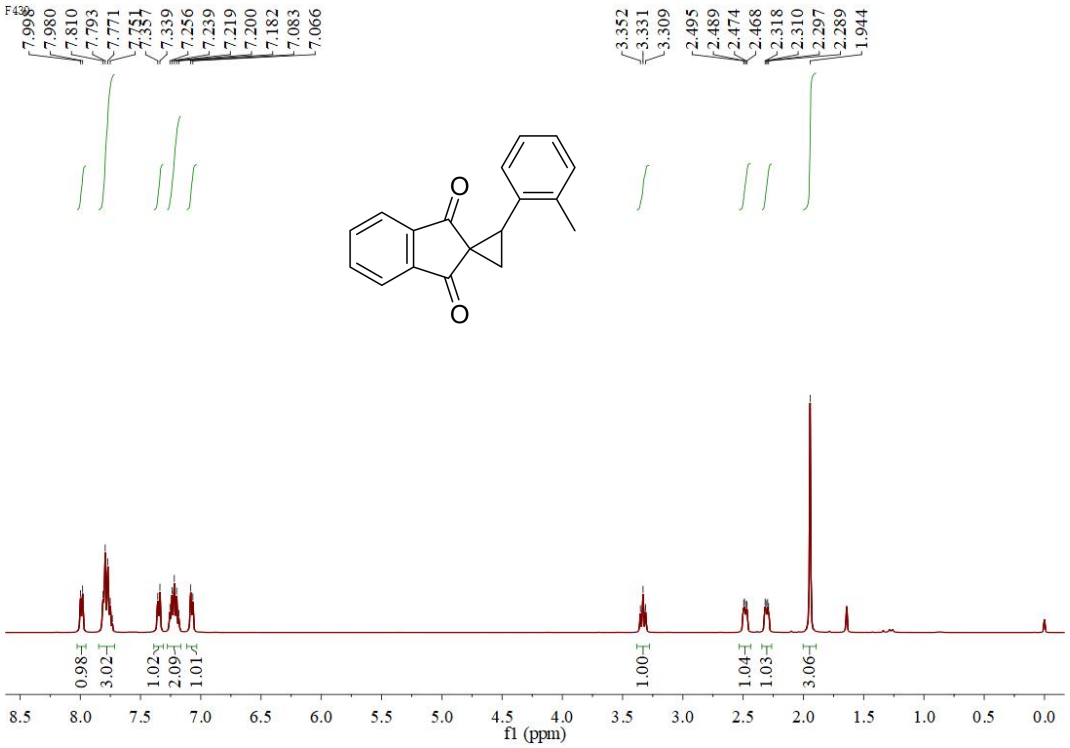
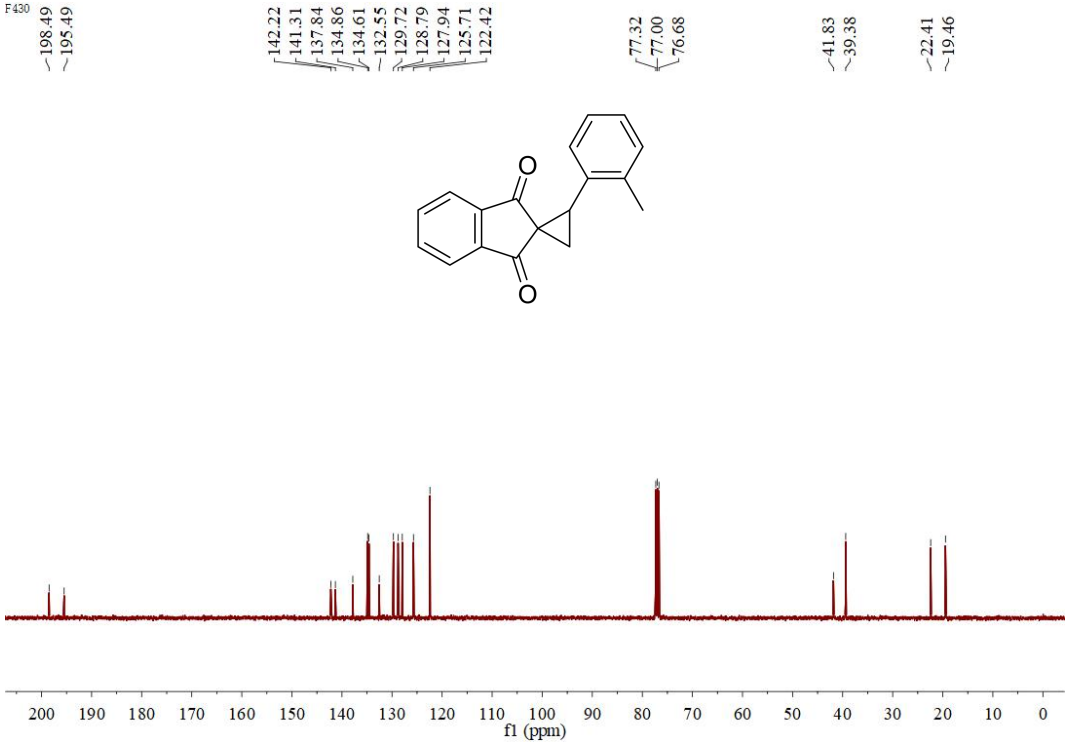
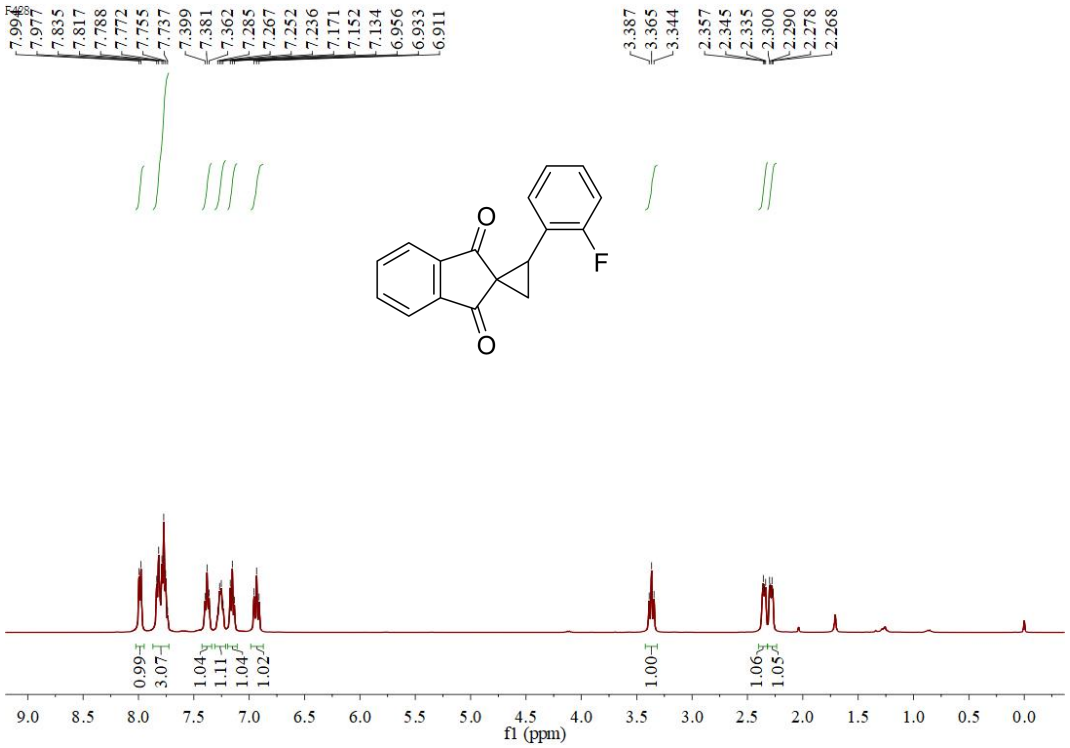
-200
f1 (ppm)

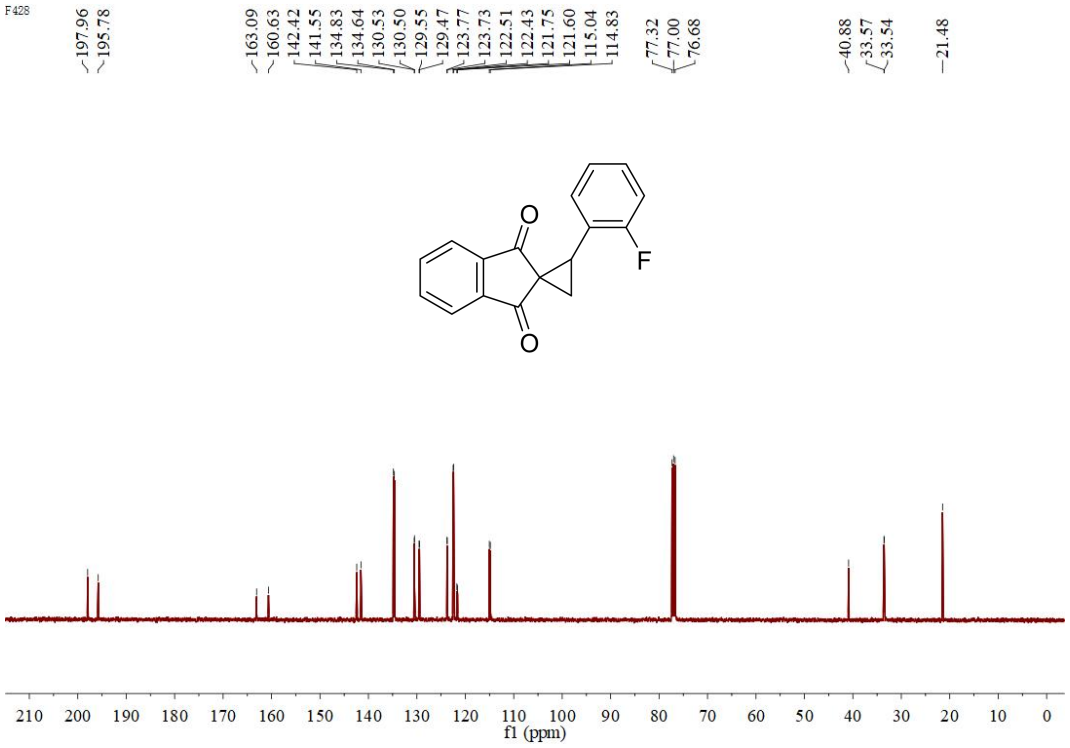
^{1}H NMR and ^{13}C NMR of 5i

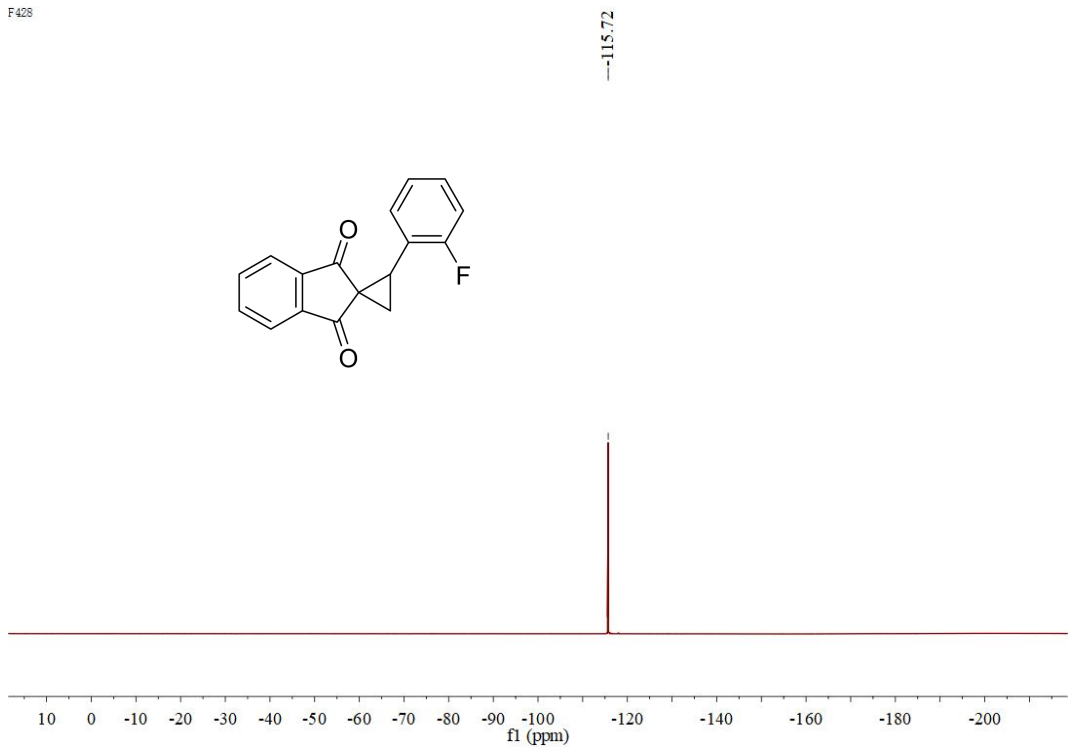




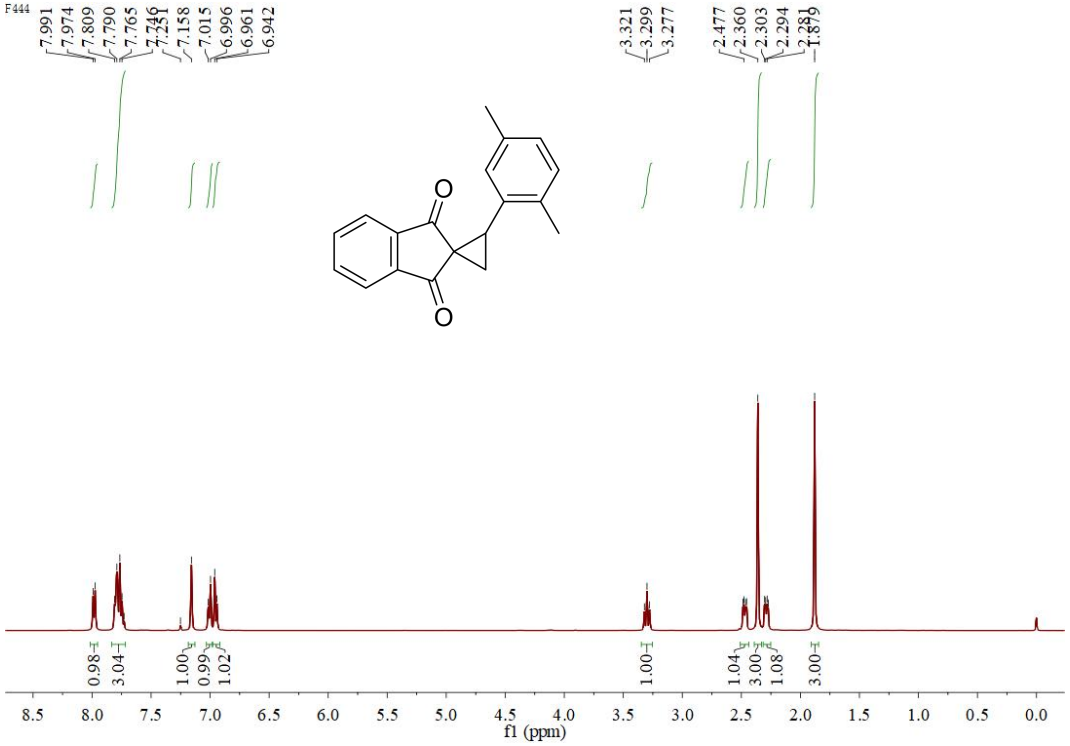
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 5j

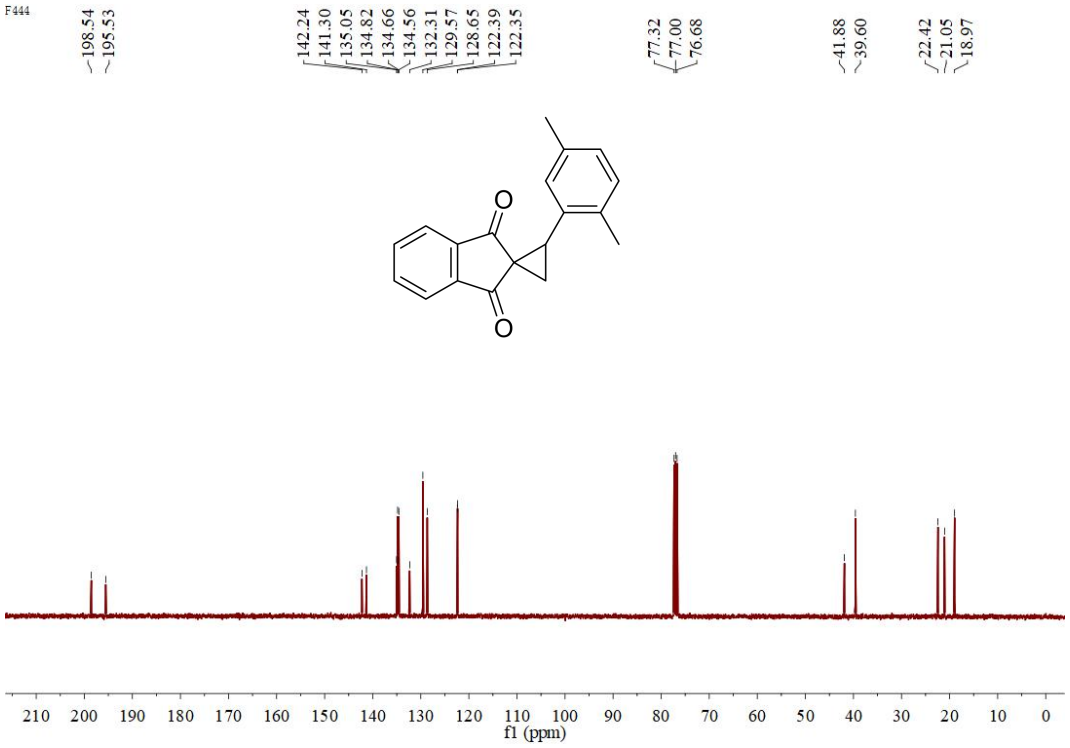




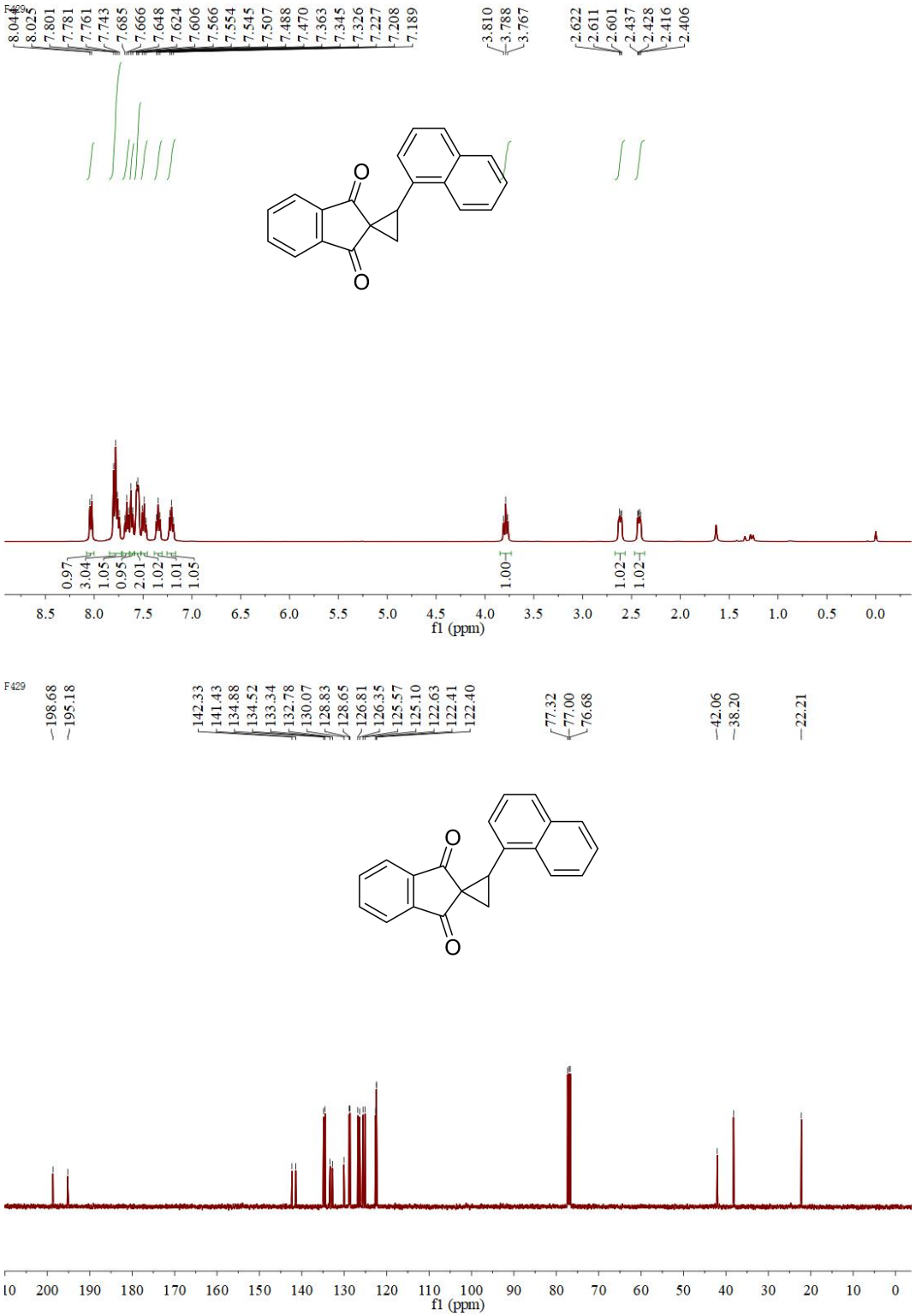

F428
-115.72
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

^{1}H NMR and ^{13}C NMR of 5k





^{1}H NMR and ^{13}C NMR of 5l



^{1}H NMR and ^{13}C NMR of 5m