Palladium-Catalyzed Oxidative Cycloaddition of 1-Indanones and Internal Aryl Alkynes toward Benzo[c]fluorenone Derivatives

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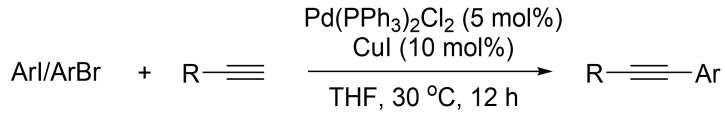
General Methods and Materials

$Pd(OAc)_2$, $Pd(TFA)_2$, $Pd(PPh_3)_4$, $Pd(acac)_2$, $Pd(dba)_2$, $Pd_2(dba)_3$, $PdCl_2$, $Cu(OAc)_2 \cdot H_2O$, BQ, TEMPO, Ag_2CO_3, $AgSbF_6$, AgOTf, $AgNTf_2$, PPh_3, PCy_3, ^{t}BuXphos, Ruphos, Xphos, BINAP, Xantphos, DPPE, 1-indanones **1**, and 1-indenone were purchased from Energy Chemical and used without further purification. The synthesis of alkynes **2** used in this work were prepared according to the methods reported in literature.[1] Other chemicals were purchased from commercial suppliers, further dried and purified if necessary. The water used was re-distillated and ion-free. ^{1}H and ^{13}C NMR spectra were achieved on a Bruker AVANCE 400 MHz spectrometer (^{1}H 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. The X-ray diffraction data were collected on Xcalibur, Eos diffractometer.

Preparation of Internal Alkynes

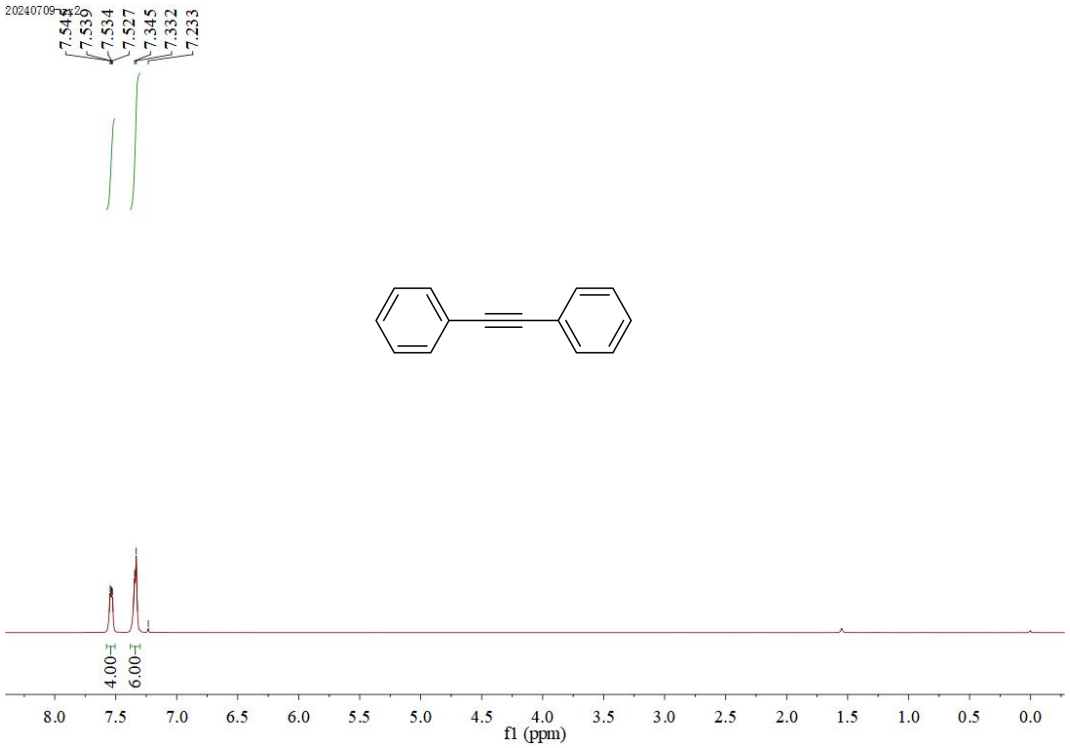
preparation of internal aryl alkynes via Sonogashira coupling. [1]

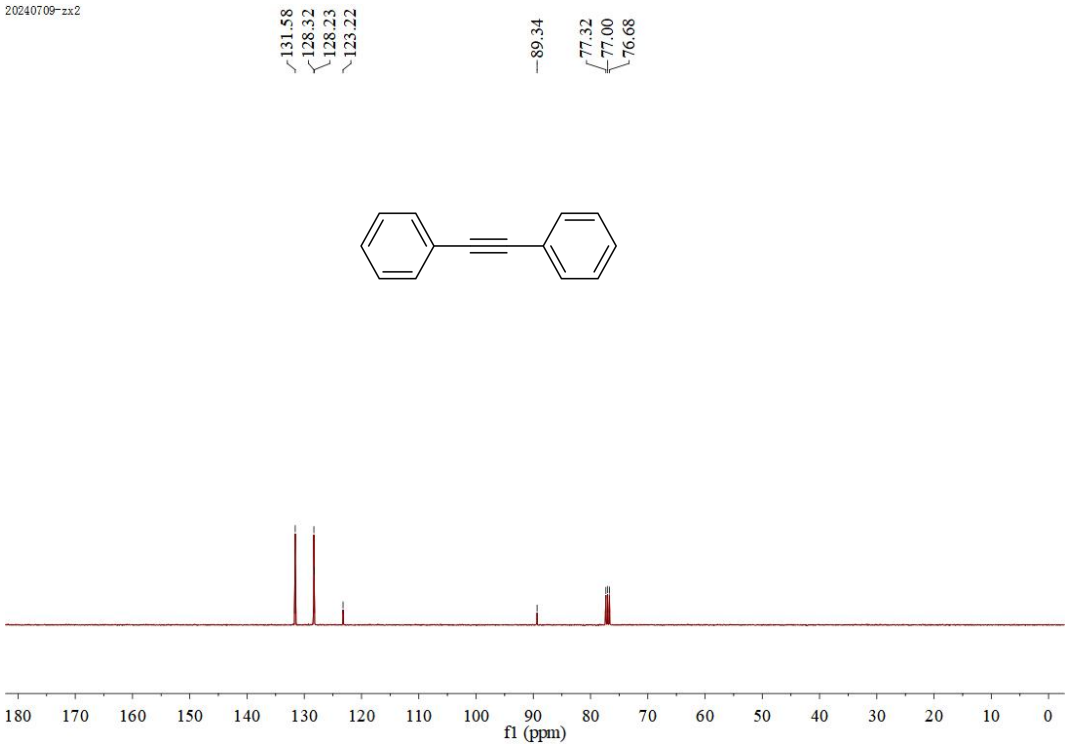


A typical operation: a dry schlenk flask was charged with aryl halide or vinyl halide (10.0 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%). The mixture was degassed under argon for three times. Et_3N (20 mL) and the terminal alkyne (1.2 equiv) was then added. The mixture was stirred at 30 °C until all the aryl halide or vinyl halide was consumed. The reaction mixture was diluted with diethyl ether, washed with water and brine, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography.

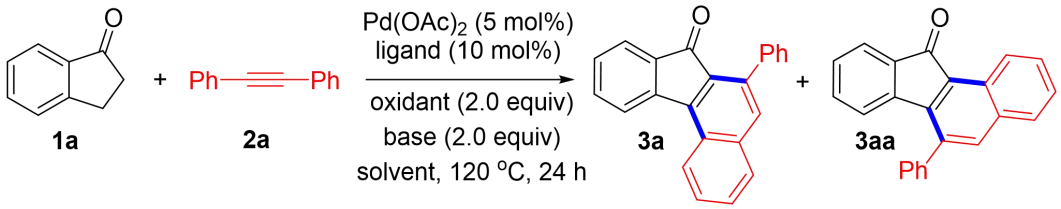
1,2-Diphenylethyne (**2a**)[1]: a dry schlenk flask was charged with iodobenzene (10.0 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%). The mixture was degassed under argon for three times. Et_3N (20 mL) and the ethynylbenzene (12.0 mmol, 1.2 equiv) was then added. The mixture was stirred at 30 °C until all the iodobenzene was consumed. The reaction mixture was diluted with diethyl ether, washed with water and brine, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography. Obtained as a gray solid (1673.2 mg, 94% yield), eluting with 1% EtOAc in PE (elution gradient); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.55 (m, 4H), 7.30 - 7.37 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.32, 128.23, 123.2, 89.3.

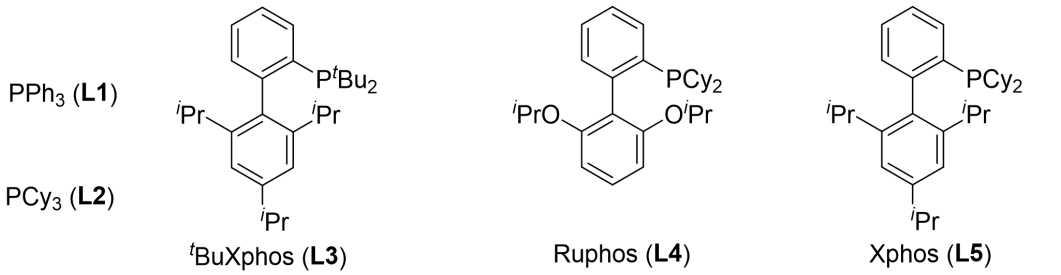
^{1}H NMR ($CDCl_3$, 400 MHz) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectrum of **2a**

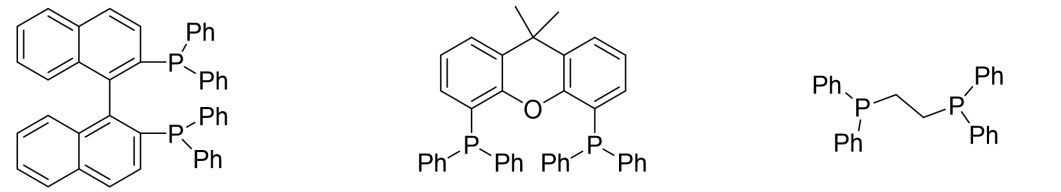




Screening of Reaction Conditions[a]





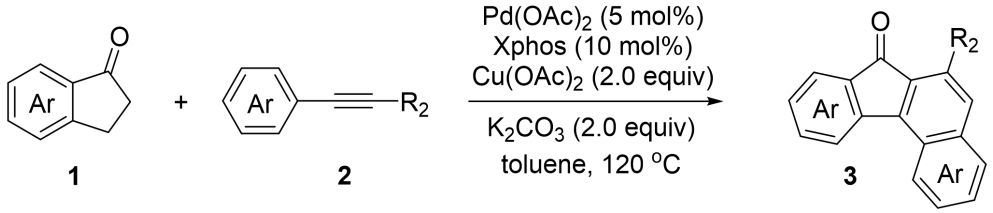


entry	catalyst	Ligand	oxidant	base	solvent	yield(%)[b] (3a/3aa)
1	$Pd(OAc)_2$	L1	$Cu(OAc)_2$	K_2CO_3	toluene	41 (3/1)
2	$Pd(OAc)_2$	L2	$Cu(OAc)_2$	K_2CO_3	toluene	62 (>10/1)
3	$Pd(OAc)_2$	L3	$Cu(OAc)_2$	K_2CO_3	toluene	52 (>5/1)
4	$Pd(OAc)_2$	L4	$Cu(OAc)_2$	K_2CO_3	toluene	39 (>10/1)
5	**$Pd(OAc)_2$**	**L5**	**$Cu(OAc)_2$**	**K_2CO_3**	**toluene**	**71 (>20/1)**
6	$Pd(OAc)_2$	L6	$Cu(OAc)_2$	K_2CO_3	toluene	trace
7	$Pd(OAc)_2$	L7	$Cu(OAc)_2$	K_2CO_3	toluene	trace
8	$Pd(OAc)_2$	L8	$Cu(OAc)_2$	K_2CO_3	toluene	trace
9	$Pd(OAc)_2$	L5	$Cu(OAc)_2{\cdot}H_2O$	K_2CO_3	toluene	70 (>20/1)
10	$Pd(OAc)_2$	L5	BQ	K_2CO_3	toluene	0
11	$Pd(OAc)_2$	L5	TEMPO	K_2CO_3	toluene	50 (2/1)
12	$Pd(OAc)_2$	L5	Ag_2CO_3	K_2CO_3	toluene	trace
13	$Pd(OAc)_2$	L5	$AgSbF_6$	K_2CO_3	toluene	trace
14	$Pd(OAc)_2$	L5	AgOTf	K_2CO_3	toluene	trace
15	$Pd(OAc)_2$	L5	$AgNTf_2$	K_2CO_3	toluene	trace
16[c]	$Pd(OAc)_2$	L5	$Cu(OAc)_2$ (1.0)	K_2CO_3	toluene	44 (>10/1)
17[d]	$Pd(OAc)_2$	L5	$Cu(OAc)_2$ (3.0)	K_2CO_3	toluene	32 (>10/1)
18	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	CS_2CO_3	toluene	61 (>20/1)
19	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	Na_2CO_3	toluene	32 (>10/1)
20	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	NaOAc	toluene	37 (>10/1)

21	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_3PO_4	toluene	62 (>10/1)
22	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2HPO_4	toluene	trace
23	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	NaH	toluene	trace
24	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	LiO^tBu	toluene	trace
25	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	DMF	0
26	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	DMSO	0
27	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	CH_3CN	0
28	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	DCE	0
29	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	THF	trace
30	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	dioxane	trace
31	$Pd(OAc)_2$	L5	$Cu(OAc)_2$	K_2CO_3	MeOH	0
32[e]		L5	$Cu(OAc)_2$	K_2CO_3	toluene	0
33[f]	$Pd(OAc)_2$		$Cu(OAc)_2$	K_2CO_3	toluene	0
34[g]	$Pd(OAc)_2$	L5		K_2CO_3	toluene	0
35[h]	$Pd(OAc)_2$	L5	$Cu(OAc)_2$		toluene	trace
36	$Pd(TFA)_2$	L5	$Cu(OAc)_2$	K_2CO_3	toluene	66 (>10/1)
37	$Pd(PPh_3)_4$	L5	$Cu(OAc)_2$	K_2CO_3	toluene	trace
38	$Pd(acac)_2$	L5	$Cu(OAc)_2$	K_2CO_3	toluene	trace
39	$Pd(dba)_2$	L5	$Cu(OAc)_2$	K_2CO_3	toluene	trace
40	$Pd_2(dba)_3$	L5	$Cu(OAc)_2$	K_2CO_3	toluene	trace
41	$PdCl_2$	L5	$Cu(OAc)_2$	K_2CO_3	toluene	trace

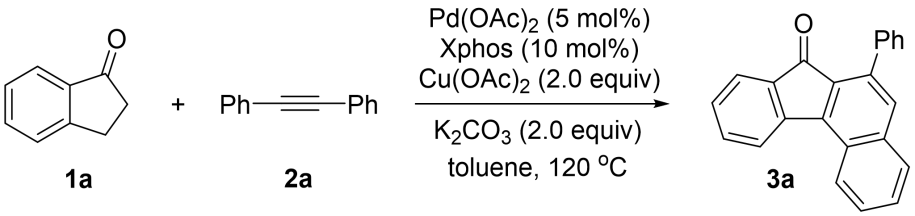
[a]Reaction conditions: 1-indanone **1a** (0.2 mmol), diphenylacetylene **2a** (0.3 mmol, 1.5 equiv), palladium catalyst (5 mol%), ligand (10 mol%), oxidant (2.0 equiv), base (2.0 equiv), solvent (3 mL) at 120 °C for 24 h under air atmosphere. [b]Isolated yield. [c]Reaction carried out in the presence of 1.0 equiv $Cu(OAc)_2$. [d]Reaction carried out in the presence of 3.0 equiv $Cu(OAc)_2$. [e]Reaction carried out in the absence of $Pd(OAc)_2$. [f]Reaction carried out in the absence of **L5**. [g]Reaction carried out in the absence of $Cu(OAc)_2$. [h]Reaction carried out in the absence of K_2CO_3.

General Catalytic Procedure for Palladium-Catalyzed Oxidative Cycloaddition of 1-Indanones and Internal Aryl Alkynes toward Benzofluorenone Derivatives



To a dry thick walled pressure resistant tube (25 mL) was charged with 2,3-dihydro-1H-inden-1-ones **1** (0.2 mmol), alkynes **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. 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 = 20 : 1) to yield product.

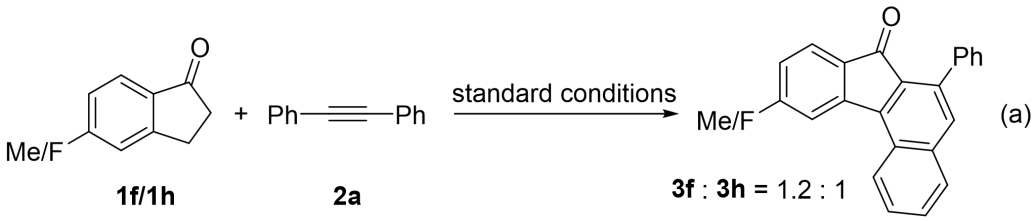
Procedure Gram-scale for the Synthesis of 3a.



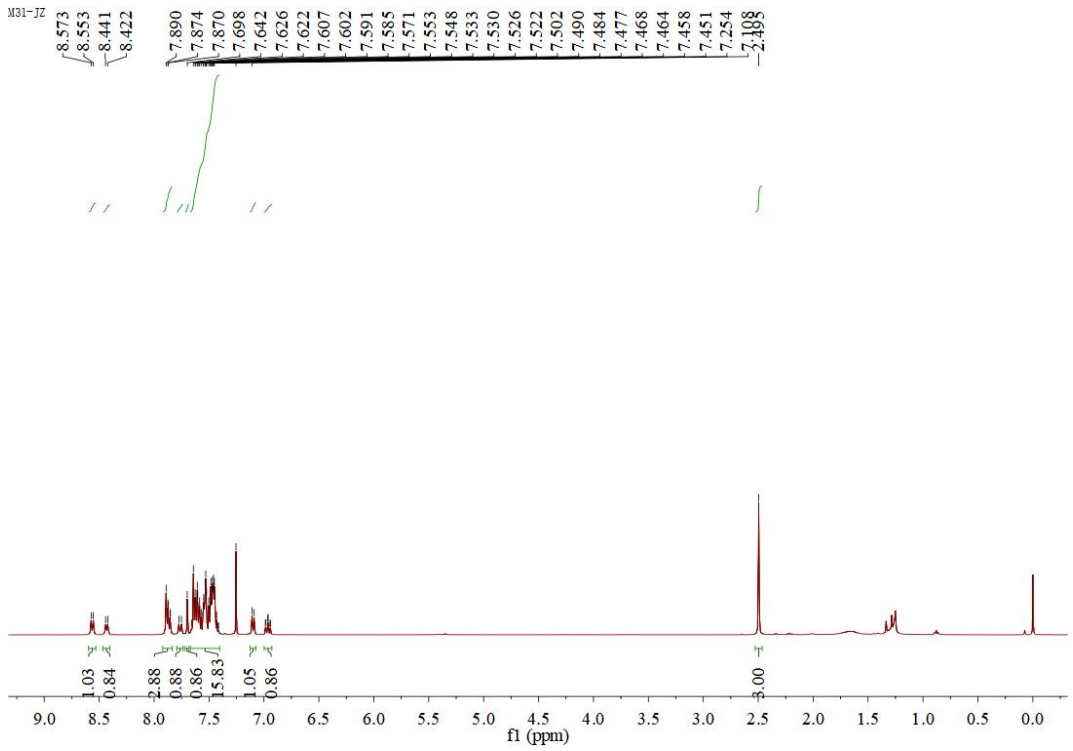
1a **2a** **3a**

To a dry thick walled pressure resistant tube (250 mL) was charged with 2,3-dihydro-1H-inden-1-one **1a** (5 mmol), 1,2-diphenylethyne **2a** (7.5 mmol, 1.5 equiv), $Pd(OAc)_2$ (57.2 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 1997.5 mg, 2.0 equiv), Xphos (238.7 mg, 10 mol%), K_2CO_3 (0.4 mmol, 1380.0 mg), then the toluene (50 mL) was added. 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 200 mL of dichloromethane and washed with 200 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 = 20 : 1) to yield product **3a** (64% yield, 979.2 mg).

Mechanistic Study



To a dry thick walled pressure resistant tube (25 mL) was charged with 5-methyl-2,3-dihydro-1H-inden-1-one **1b** (0.1 mmol), 5-fluoro-2,3-dihydro-1*H*-inden-1-one **1d** (0.1 mmol), 1,2-diphenylethyne **2a** (0.3 mmol), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 ^oC 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 = 20 : 1) to yield product.


M31-JZ
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8.553
8.441
8.422
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7.870
7.698
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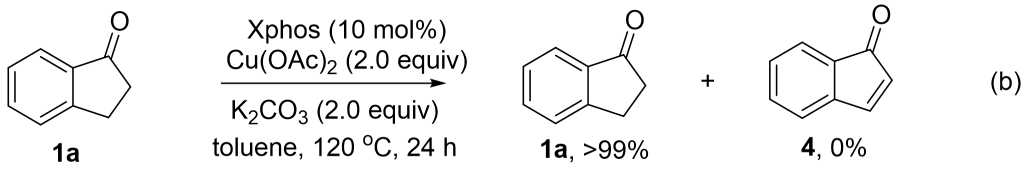
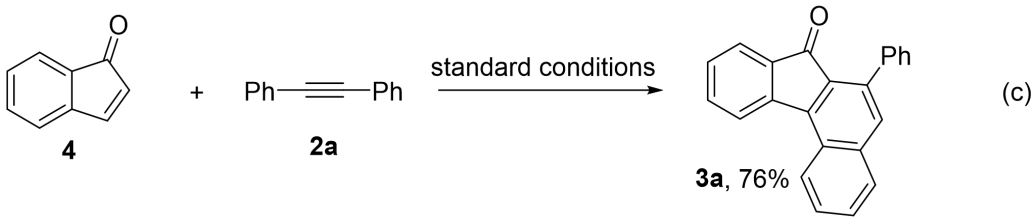
7.607
7.602
7.591
7.585
7.571
7.553
7.548
7.533
7.530
7.526
7.522
7.502
7.490
7.484
7.477
7.468
7.464
7.458
7.451
7.254
2.108
2.495
1.03
0.84
2.88
0.88
0.86
15.83
1.05
0.86
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



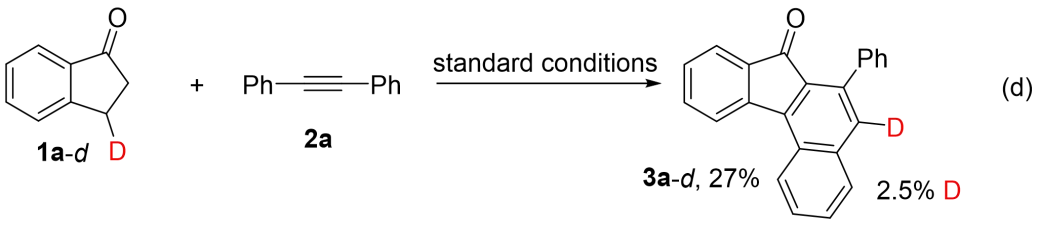
1a **1a**, >99% **4**, 0%

To a dry thick walled pressure resistant tube (25 mL) was charged with 2,3-dihydro-1H-inden-1-one **1a** (0.2 mmol), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. 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. No indenone **4** was found, and and the recovery rate of 1-indanone **1a** was almost 100%.

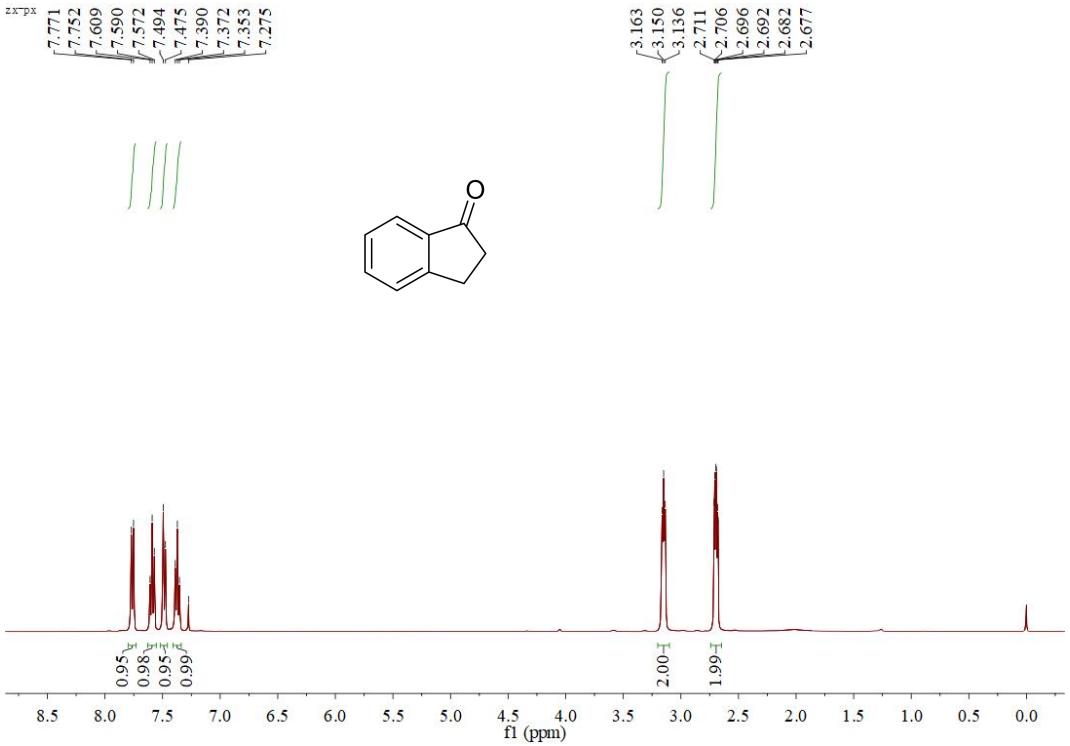


(c)

To a dry thick walled pressure resistant tube (25 mL) was charged with 1H-inden-1-one **4** (0.2 mmol), 1,2-diphenylethyne **2a** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 ^oC 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 = 20 : 1) to yield product **3a** (76% yield, 46.5 mg).



To a dry thick walled pressure resistant tube (25 mL) was charged with 2,3-dihydro-1H-inden-1-one **1a**-*d* (0.2 mmol), 1,2-diphenylethyne **2a** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. 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 = 20 : 1) to yield product.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7.590
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7.353
7.275
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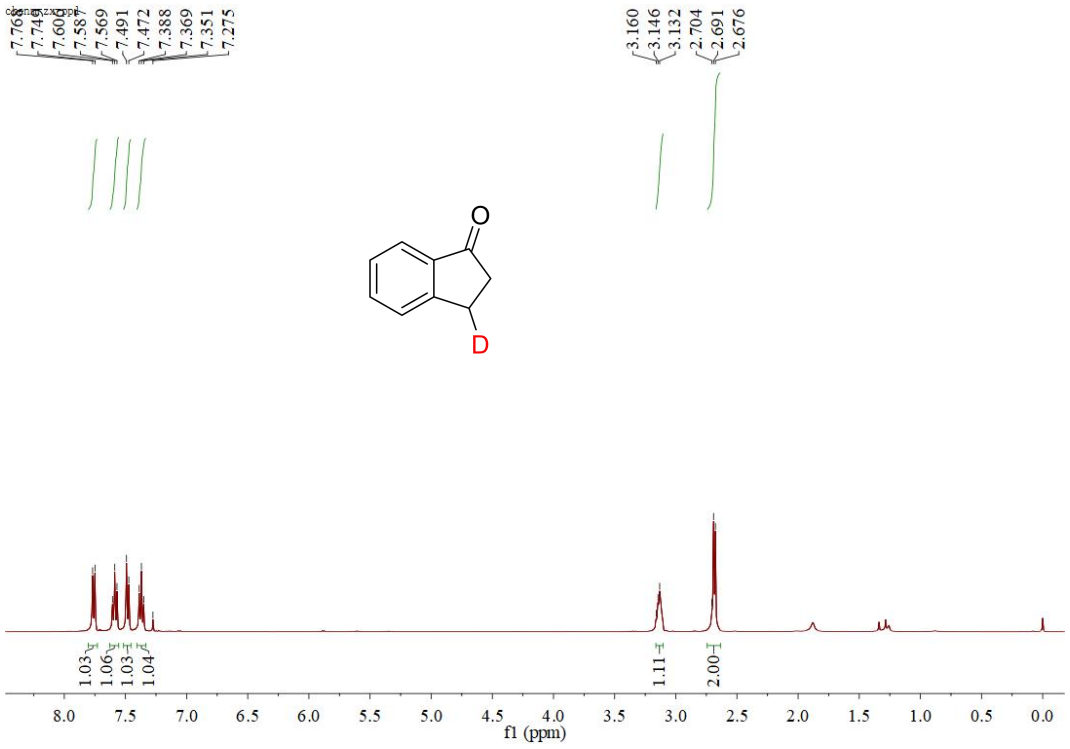
3.150
3.136
2.711
2.706
2.696
2.692
2.682
2.677
O
0.95
0.98
0.95
0.99
2.00
1.99
f1 (ppm)


7.768
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7.569
7.491
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7.275
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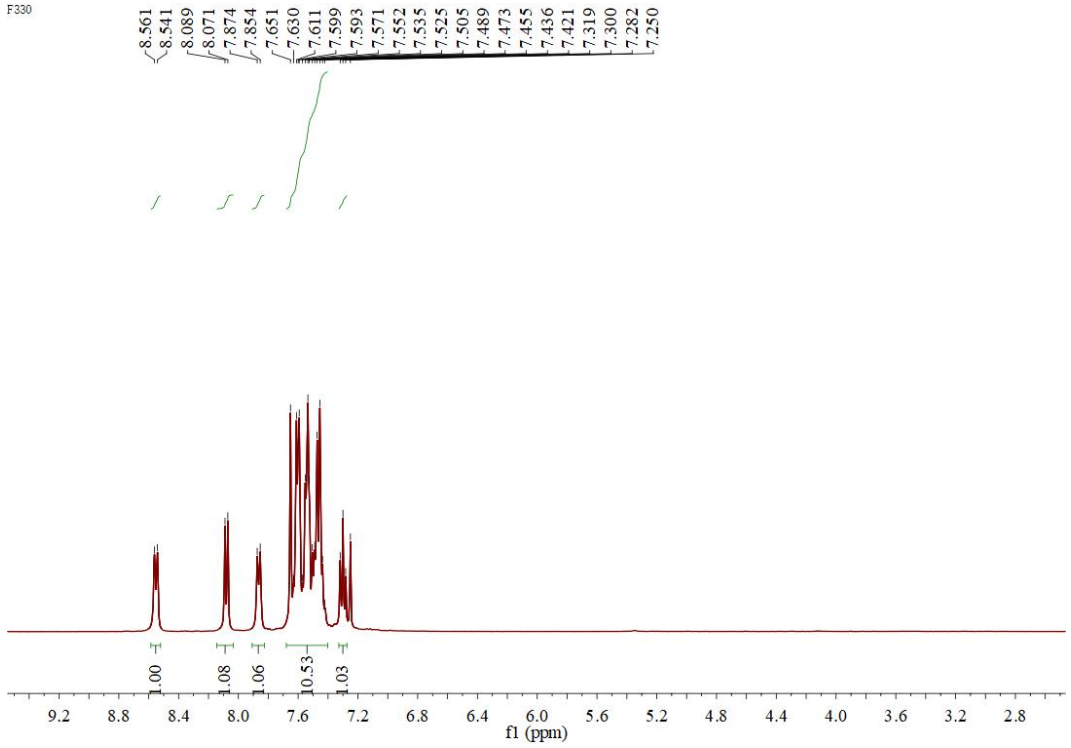
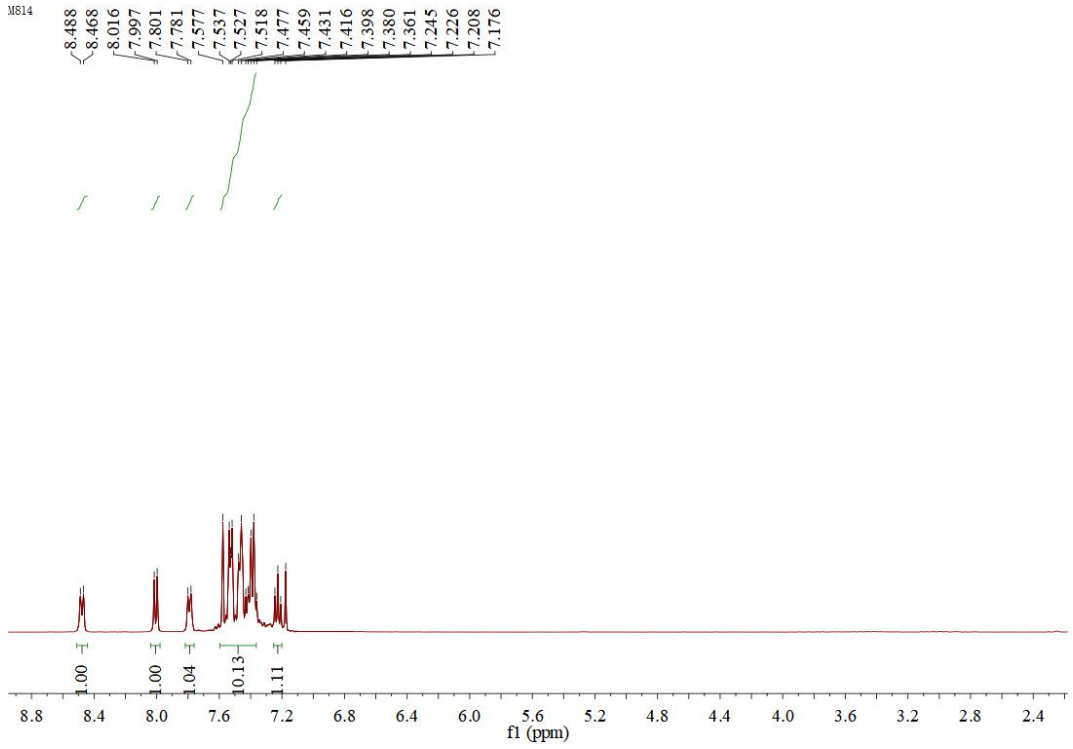
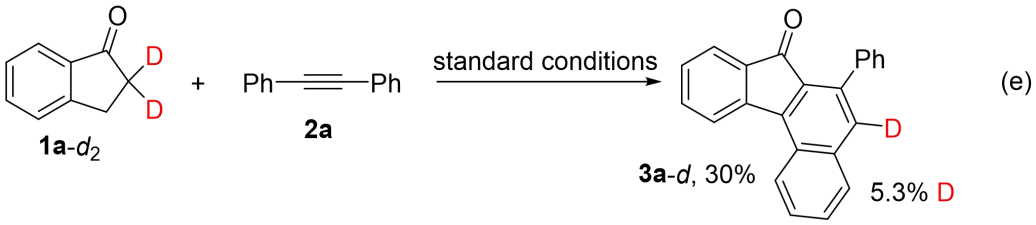
1.03
1.04
1.11
2.00
f1 (ppm)

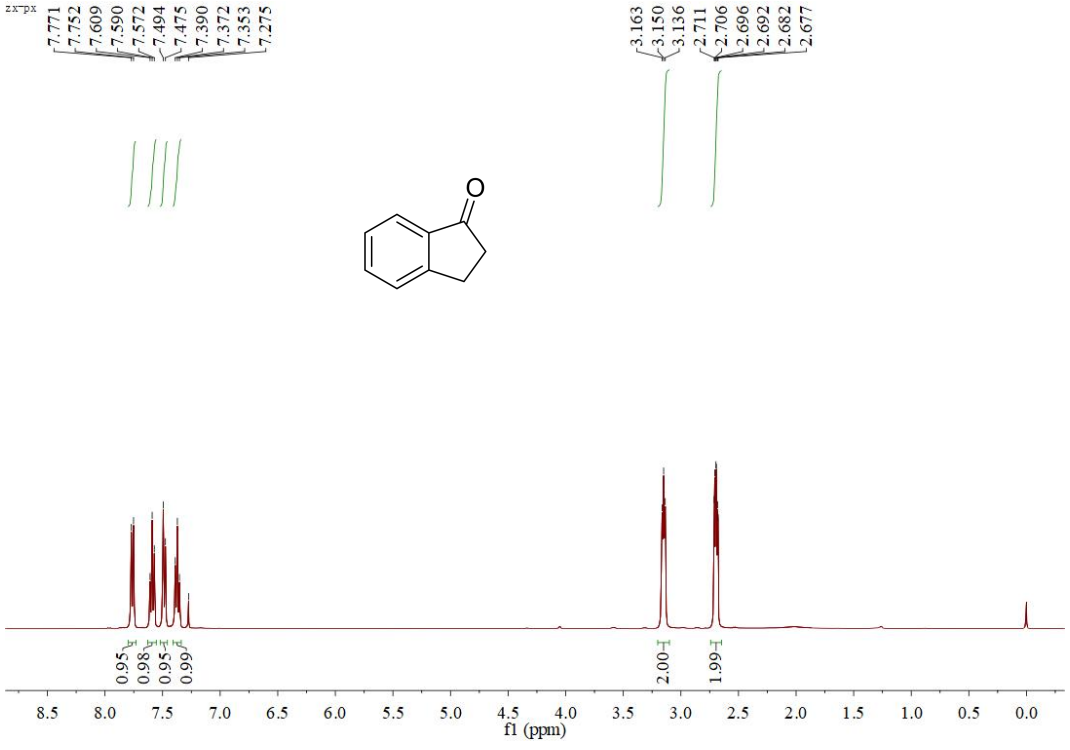


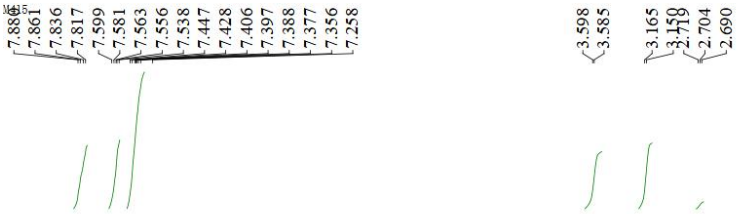


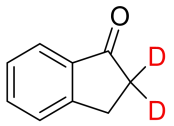
10.53-10.13/10.53*100% = 3.8%

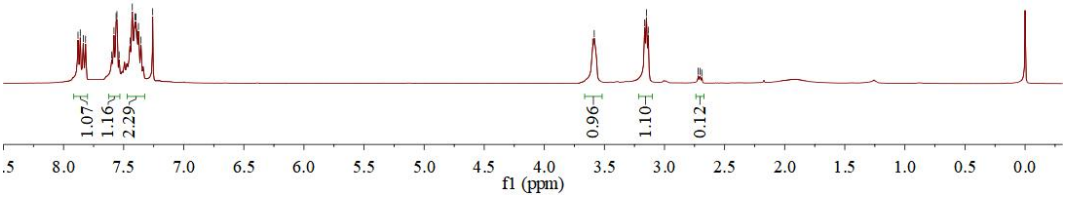


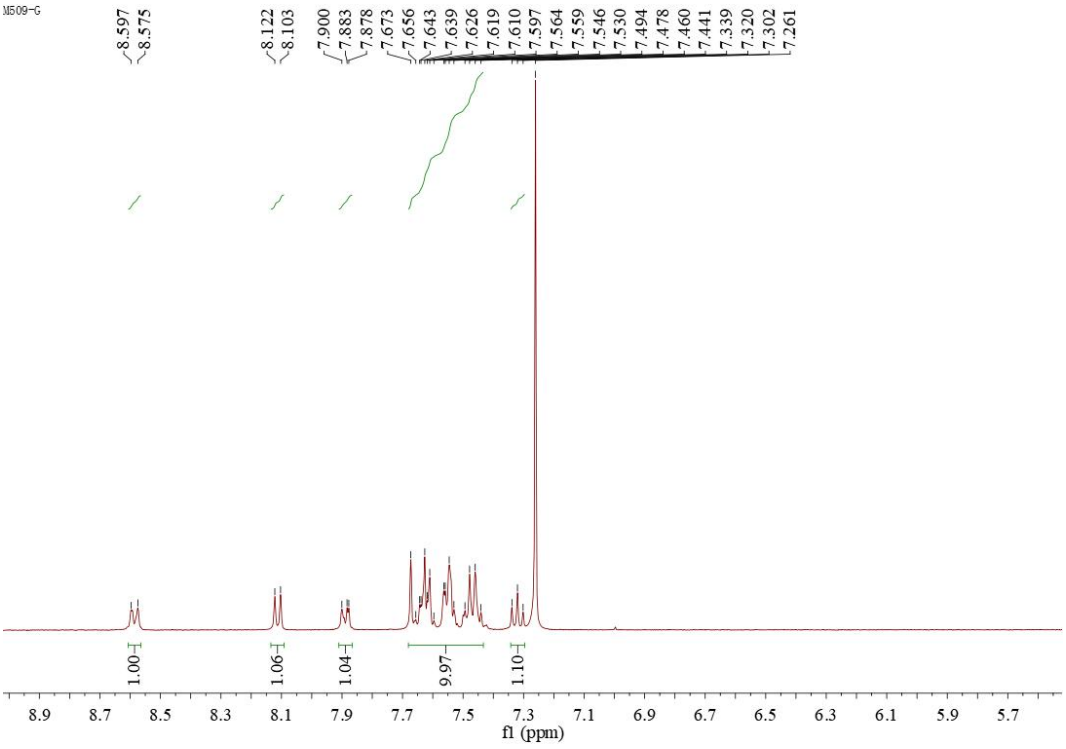
To a dry thick walled pressure resistant tube (25 mL) was charged with 2,3-dihydro-1H-inden-1-one **1a**-d_2 (0.2 mmol), 1,2-diphenylethyne **2a** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. 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 = 20 : 1) to yield product.



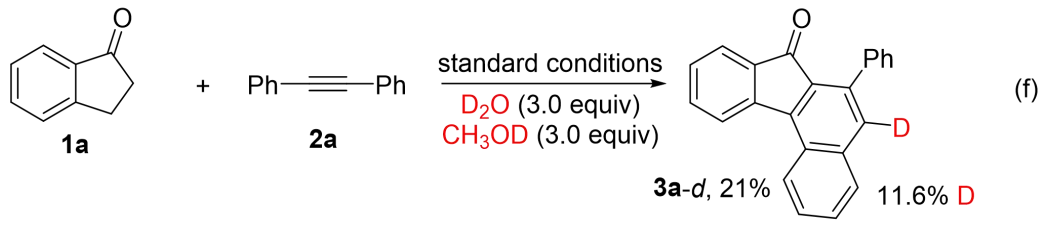




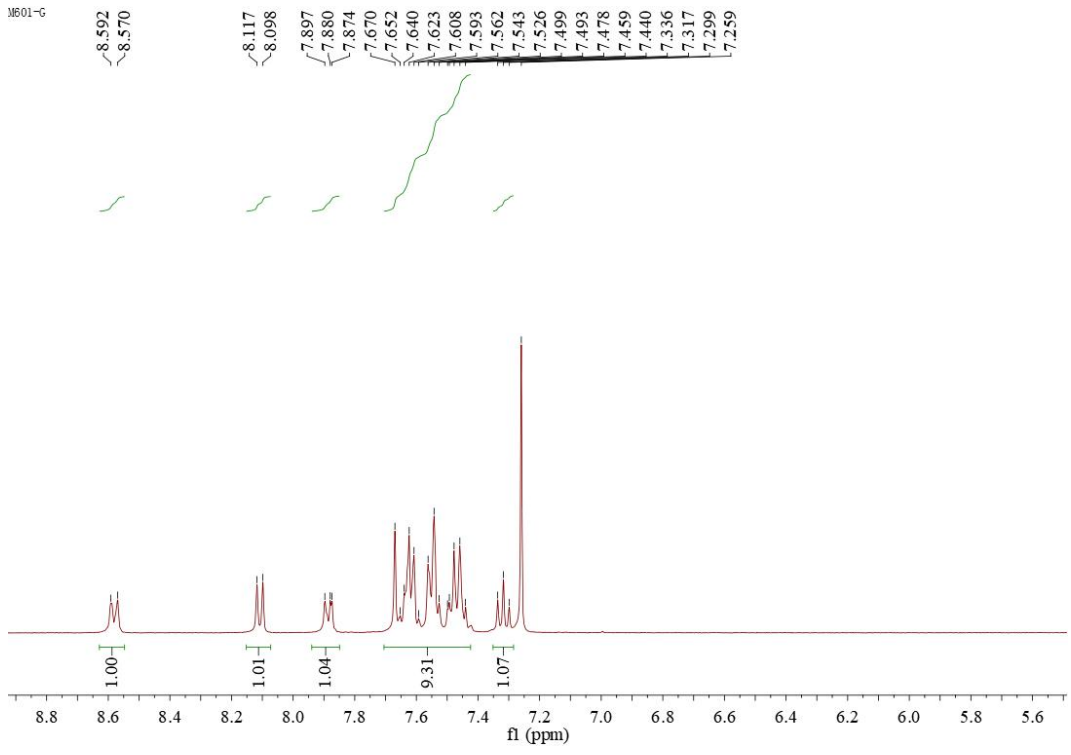




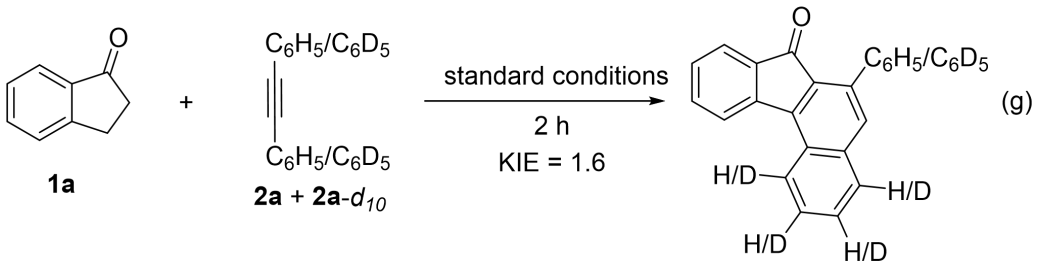
10.53-9.97/10.53*100% = 5.3%



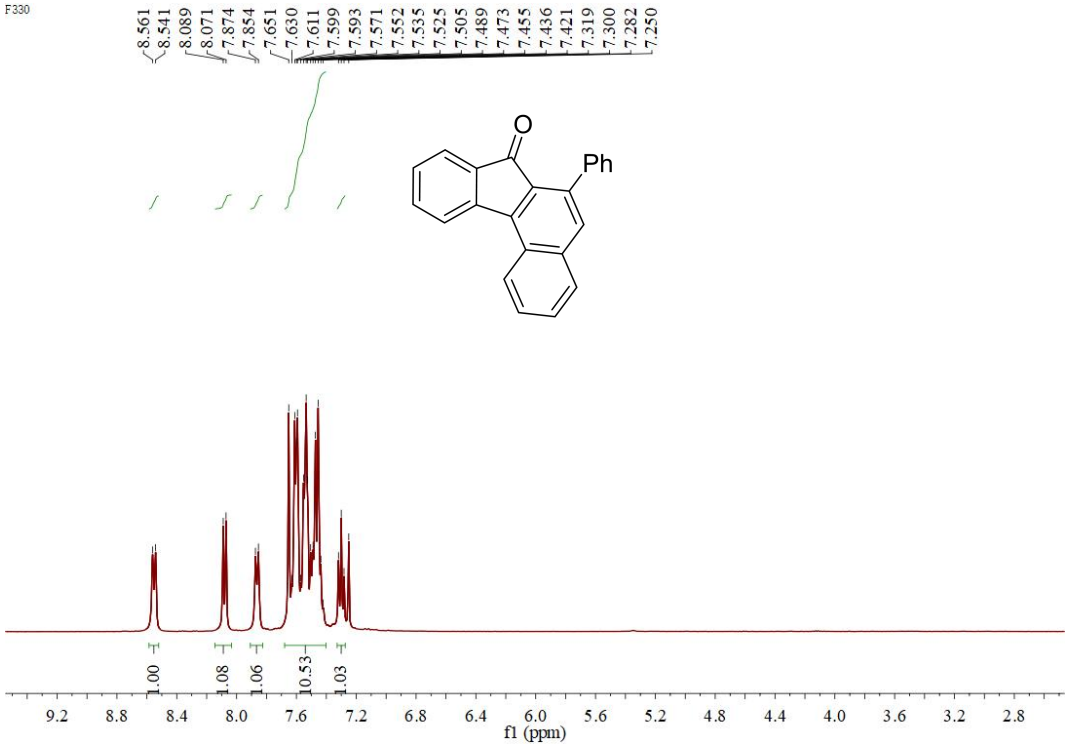
To a dry thick walled pressure resistant tube (25 mL) was charged with 2,3-dihydro-1H-inden-1-one **1a** (0.2 mmol), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), toluene (3 mL), then the D_2O (10.8 mg, 0.6 mmol), and CD_3OD (21.6 mg, 0.6 mmol) were added. 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 = 20 : 1) to yield product.

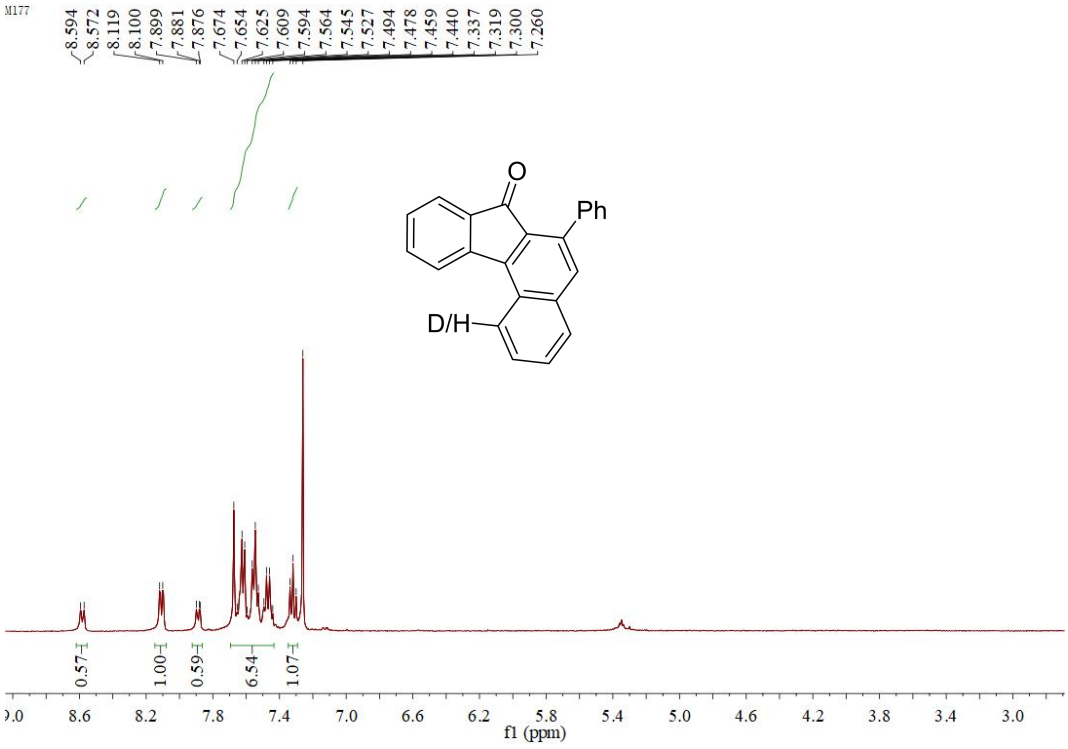


10.53-9.31/10.53*100% = 11.6%



To a dry thick walled pressure resistant tube (25 mL) was charged with 2,3-dihydro-1H-inden-1-one **1a** (0.2 mmol), 1,2-diphenylethyne **2a** (0.15 mmol), 1,2-diphenylethyne-d_{10} **2a**-d_{10} (0.15 mmol), $Pd(OAc)_2$ (2.3 mg, 5 mol%), $Cu(OAc)_2$ (0.4 mmol, 79.9 mg, 2.0 equiv), Xphos (9.6 mg, 10 mol%), K_2CO_3 (0.4 mmol, 55.2 mg), then the toluene (3 mL) was added. The tube was closed with a PTFE thread sealing cap. The mixture was stirred at 120 °C in oil bath for 1 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.



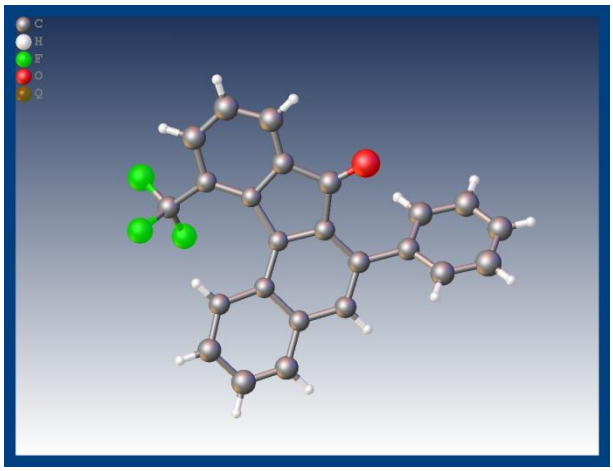


6.54/(10.53-6.54) = 6.54/3.99 = 1.6

X-Ray Crystallographic Data

Crystal Structure Details for Product 3m (CCDC: 2312081)

A pale yellow solid crystal of **3m** ($C_{24}H_{13}F_3O$)was grown by the vapor diffusion method (hexane and EtOAc). X-Ray diffraction data of one these crystals were collected on a Xcalibur, Eos diffractometer. The measurements were performed with Mo-Kα radiation (λ =0.71073 Å). The crystal was kept at 296.15 K during data collection.



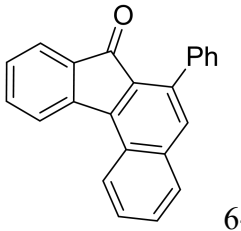
Perspective thermal ellipsoid view of the single-crystal structures at 50% probability

Table 1 Crystal data and structure refinement for 1.

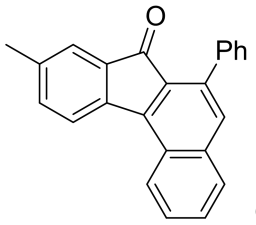
Identification code	1
Empirical formula	$C_{24}H_{13}F_3O$
Formula weight	374.34
Temperature/K	296.15
Crystal system	Orthorhombic
Space group	Pca21 (No. 29)
a/Å	14.865(2)
b/Å	12.8982(19)
c/Å	9.3217(14)
α/°	90.00
β/°	106.415(4)
γ/°	90.00
Volume/Å^3	1787.3(4)
Z	4
ρ_{calc}g/cm^3	1.391
μ/mm^{-1}	0.105
F(000)	768.0

Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.1 to 27.6
Index ranges	-19 ≤ h ≤ 13, -15 ≤ k ≤ 16, -11 ≤ l ≤ 12
Reflections collected	9588
Independent reflections	3757 [R_{int} = 0.0520, R_{sigma} = 0.1233]
Data/restraints/parameters	3757/0/227
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0523, wR_2 = 0.1309
Final R indexes [all data]	R_1 = 0.0961, wR_2 = 0.1552
Largest diff. peak/hole / e Å^{-3}	-0.23/0.18

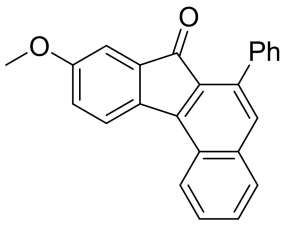
Characterization data for the products



6-Phenyl-7H-benzo[c]fluoren-7-one (**3a**): Obtained as a yellow solid (43.5 mg, 71% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.42 - 7.65 (m, 10H), 7.28 - 7.32 (t, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 144.3, 144.0, 138.1, 137.7, 137.5, 134.6, 134.2, 131.4, 129.5, 129.4, 128.9, 128.7, 128.5, 128.2, 127.8, 127.8, 127.6, 124.7, 123.9, 123.3; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{15}O$ $[M + H]^+$ 307.1117, found 307.1115.

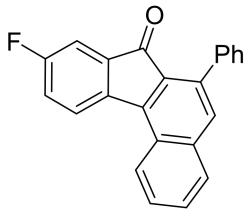


9-Methyl-6-phenyl-7H-benzo[c]fluoren-7-one (**3b**): Obtained as a yellow solid (47.4 mg, 74% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 - 8.50 (t, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.82 - 7.84 (t, 1H), 7.53 - 7.60 (m, 5H), 7.41 - 7.48 (m, 3H), 7.38 (s, 1H), 7.28 (d, J = 7.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 144.6, 141.2, 139.1, 138.1, 137.6, 137.4, 134.8, 134.5, 130.9, 129.4, 128.6, 128.4, 128.0, 127.8, 127.4, 124.8, 124.6, 123.1, 21.2; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O$ $[M + H]^+$ 321.1274, found 321.1273.

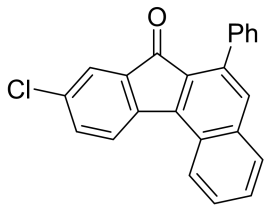


9-Methoxy-6-phenyl-7H-benzo[c]fluoren-7-one (**3c**): Obtained as a yellow solid (46.4 mg, 69% yield), eluting with 7% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 - 8.49 (t, 1H), 7.96 (d, J = 8.0 Hz, 1H),

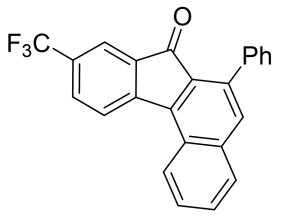
7.83 - 7.85 (t, 1H), 7.53 - 7.59 (m, 5H), 7.43 - 7.48 (m, 3H), 7.16 (d, J = 2.4 Hz, 1H), 6.97 - 7.00 (q, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 160.6, 145.1, 138.1, 137.7, 137.6, 136.7, 136.2, 130.1, 129.4, 129.3, 128.8, 128.3, 127.8, 127.7, 127.4, 124.8, 124.3, 118.6, 109.9, 55.7; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O_2$ [M + H] $^+$ 337.1223, found 337.1224.



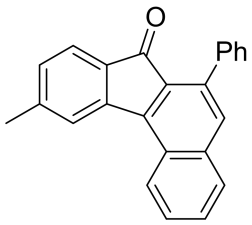
9-Fluoro-6-phenyl-7H-benzo[c]fluoren-7-one (**3d**): Obtained as a yellow solid (41.5 mg, 64% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 6.8 Hz, 1H), 7.72 (d, J = 9.2 Hz, 1H), 7.67 (s, 1H), 7.45 - 7.60 (m, 8H), 6.92 - 6.96 (t, J = 8.4, 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.7 (d, J = 251.6 Hz), 146.6 (d, J = 9.8 Hz), 142.2 (d, J = 1.8 Hz), 137.8, 137.6, 137.3, 132.1, 130.5 (d, J = 2.8 Hz), 129.6, 129.4, 129.1, 128.8, 127.9, 127.9, 127.8, 125.6 (d, J = 10.1 Hz), 124.1, 114.8 (d, J = 22.9 Hz), 111.8 (d, J = 25.9 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -103.4; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}FO$ [M + H] $^+$ 325.1023, found 325.1021.



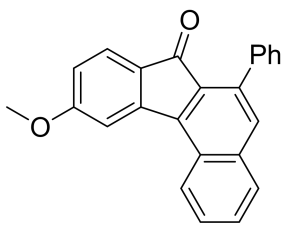
9-Chloro-6-phenyl-7H-benzo[c]fluoren-7-one (**3e**): Obtained as a yellow solid (44.9 mg, 66% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.31 - 7.35 (m, 1H), 7.06 - 7.14 (m, 4H), 6.96 - 7.00 (m, 2H), 6.78 (t, J = 8.4 Hz, 1H), 6.63 - 7.64 (m, 1H), 6.47 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 145.5, 142.3, 140.0, 138.9, 136.6, 135.9, 134.3, 133.0, 129.5, 129.3, 129.1, 128.8, 128.5, 128.3, 127.8, 127.2, 124.4, 124.3, 123.7; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}ClO$ [M + H] $^+$ 341.0728, found 341.0725.



6-Phenyl-9-(trifluoromethyl)-7H-benzo[c]fluoren-7-one (**3f**): Obtained as a yellow solid (45.6 mg, 61% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.81 - 7.83 (m, 2H), 7.75 (s, 1H), 7.64 - 7.70 (m, 2H), 7.45 - 7.55 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 147.1, 142.9, 137.8 (q, J = 5.4, 9.9 Hz), 137.6, 137.5, 135.0, 132.60, 131.2 (q, J = 3.8, 7.6 Hz), 131.1, 130.8, 129.7, 129.3, 128.7 (q, J = 6.4, 94.9 Hz), 128.1, 127.9, 125.0, 124.4, 123.2, 122.3, 120.5 (q, J = 3.7, 7.1 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -63.0; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{14}F_3O$ $[M + H]^+$ 375.0991, found 375.0987.

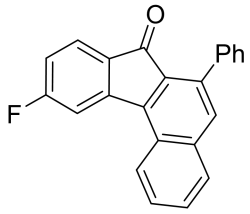


10-Methyl-6-phenyl-7H-benzo[c]fluoren-7-one (**3g**): Obtained as a yellow solid (49.3 mg, 77% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.63 (s, 1H), 7.58 - 7.61 (m, 2H), 7.53 - 7.55 (m, 2H), 7.41 - 7.50 (m, 4H), 7.09 (d, J = 7.2 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 145.1, 144.4, 144.0, 138.1, 137.7, 137.3, 132.3, 131.3, 129.5, 129.4, 129.2, 128.6, 128.1, 127.7, 127.5, 124.7, 124.5, 123.8, 22.4; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O$ $[M + H]^+$ 321.1274, found 321.1277.

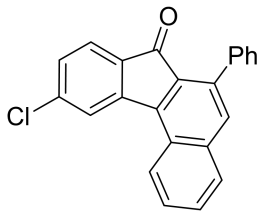


10-Methoxy-6-phenyl-7H-benzo[c]fluoren-7-one (**3h**): Obtained as a yellow solid (47.0 mg, 70% yield), eluting with 7% EtOAc in PE

(elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.8 Hz, 1H), 7.84 - 7.86 (m, 1H), 7.65 (s, 1H), 7.53 - 7.60 (m, 6H), 7.43 - 7.49 (m, 3H), 6.70 - 6.73 (q, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.7, 146.1, 142.7, 138.1, 137.5, 137.2, 131.6, 129.8, 129.5, 129.4, 128.5, 128.1, 127.7, 127.6, 127.6, 125.6, 124.4, 112.2, 110.7, 55.8; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O_2$ [M + H] $^{+}$ 337.1223, found 337.1225.

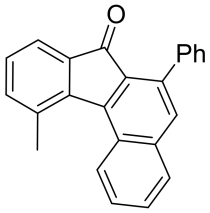


10-Fluoro-6-phenyl-7H-benzo[c]fluoren-7-one (**3i**): Obtained as a yellow solid (39.5 mg, 61% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 7.6 Hz, 1H), 7.87 - 7.89 (m, 1H), 7.74 - 7.77 (dd, J = 2.0, 9.6 Hz, 1H), 7.70 (s, 1H), 7.57 - 7.66 (m, 3H), 7.52 - 7.54 (m, 2H), 7.42 - 7.50 (m, 3H), 6.94 - 6.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 166.7 (d, J = 151.7 Hz), 146.6 (d, J = 9.6 Hz), 142.3 (d, J = 2.3 Hz), 137.8, 137.6, 137.3, 132.1, 130.5 (d, J = 2.6 Hz), 129.6, 129.4, 129.1, 128.9, 128.0, 127.9, 127.8, 125.6, 125.5, 124.1, 114.8 (d, J = 22.8 Hz), 111.8 (d, J = 25.9 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -103.4; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}FO$ [M + H] $^{+}$ 325.1023, found 325.1025.

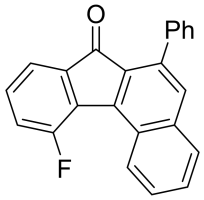


10-Chloro-6-phenyl-7H-benzo[c]fluoren-7-one (**3j**): Obtained as a yellow solid (42.2 mg, 62% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.69 (s, 1H), 7.59 - 7.66 (m, 2H), 7.44 - 7.54 (m, 6H), 7.25 - 7.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 145.6, 142.8, 140.3, 137.7, 137.7, 137.4, 132.7, 132.1, 129.6, 129.3, 129.0, 128.9, 128.6, 128.0, 128.0, 127.9, 127.8, 124.7, 124.3,

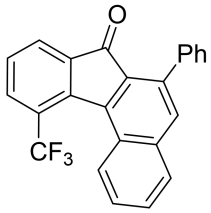
123.9; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}ClO$ [M + H] $^+$ 341.0728, found 341.0725.



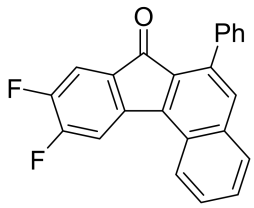
11-Methyl-6-phenyl-7H-benzo[c]fluoren-7-one (**3k**): Obtained as a yellow solid (41.6 mg, 65% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.68 (s, 1H), 7.52 - 7.59 (m, 4H), 7.43 - 7.51 (m, 4H), 7.35 (d, J = 7.6 Hz, 1H), 7.21 - 7.24 (t, 1H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 148.7, 143.4, 138.4, 138.1, 137.74, 137.71, 136.2, 132.7, 131.1, 130.6, 129.5, 128.9, 128.8, 128.7, 127.8, 127.3, 126.6, 125.9, 121.8, 24.0; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O$ [M + H] $^+$ 321.1274, found 321.1272.



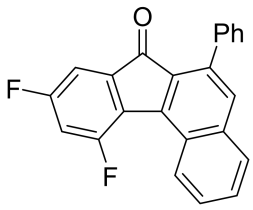
11-fluoro-6-phenyl-7H-benzo[c]fluoren-7-one (**3l**): Obtained as a yellow solid (33.7 mg, 52% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.36 (m, 1H), 7.89 - 7.92 (m, 1H), 7.75 - 7.77 (m, 1H), 7.49 - 7.53 (m, 3H), 7.34 - 7.44 (m, 5H), 7.16 - 7.18 (m, 1H), 7.07 (t, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 163.3 (d, J = 249.7 Hz), 143.9, 139.7, 139.6, 137.8, 137.7, 137.6, 137.1 (d, J = 7.1 Hz), 131.1, 129.5, 129.3, 129.0, 128.7 (d, J = 3.1 Hz), 127.9, 127.8, 127.7, 127.7, 124.5, 124.4 (d, J = 7.5 Hz), 119.9 (d, J = 22.6 Hz), 111.7 (d, J = 23.6 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -111.7; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}FO$ [M + H] $^+$ 325.1023, found 325.1026.



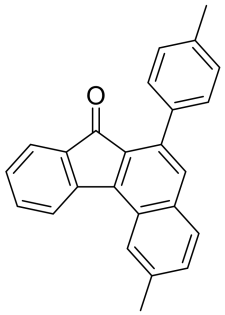
6-Phenyl-11-(trifluoromethyl)-7H-benzo[c]fluoren-7-one (**3m**): Obtained as a yellow solid (32.2 mg, 43% yield), eluting with 20% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.78 - 7.82 (t, 3H), 7.54 - 7.64 (m, 4H), 7.45 - 7.51 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 146.9, 142.4, 137.6, 137.6, 137.5, 137.3, 132.5, 132.4 (q, J = 4.9, 9.6 Hz), 131.0, 129.5, 128.7, 128.3, 128.2, 128.1, 127.9 (q, J = 7.9, 267.2 Hz), 126.2, 125.7 (q, J = 7.5, 13.4 Hz), 125.5, 125.4, 122.7; ^{19}F NMR (400 MHz, $CDCl_3$) δ -55.7; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{14}F_3O$ [M + H] $^{+}$ 375.0991, found 375.0993.



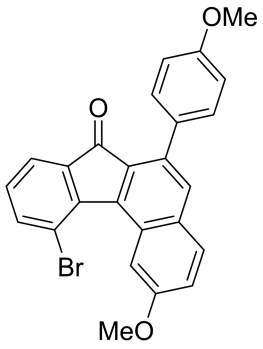
9,10-Difluoro-6-phenyl-7H-benzo[c]fluoren-7-one (**3n**): Obtained as a yellow solid (34.2 mg, 50% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 - 8.24 (m, 1H), 7.84 - 7.86 (m, 1H), 7.68 (s, 1H), 7.59 - 7.63 (m, 2H), 7.46 - 7.49 (m, 5H), 7.17 - 7.19 (m, 1H), 6.96 - 7.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 153.7 (dd, J = 253.3, 13.6 Hz), 150.6 (dd, J = 251.8, 13.7 Hz), 147.7, 147.6, 147.1, 142.1 (t, J = 1.8 Hz), 140.6 (dd, J = 7.5, 3.8 Hz), 139.3, 138.5, 138.4, 137.7, 137.5 (d, J = 5.8 Hz), 131.8, 131.1 (dd, J = 4.6, 3.4 Hz), 129.6, 129.3, 129.1, 128.8 (dd, J = 3.4 Hz), 128.1, 128.0, 127.9, 127.6, 124.4, 124.0, 123.9, 119.1 (dd, J = 1.8 Hz), 113.5 (dd, J = 18.9, 1.5 Hz), 113.3(d, J = 21.5 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -127.9 (d, J = 4.9 Hz), -136.2 (d, J = 4.9 Hz); HRMS (ESI-TOF) m/z calcd for $C_{23}H_{13}F_2O$ [M + H] $^{+}$ 343.0929, found 343.0927.



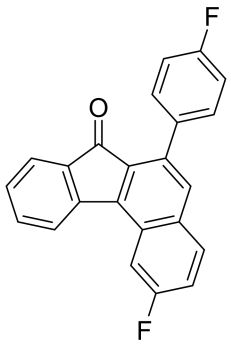
9,11-Difluoro-6-phenyl-7H-benzo[c]fluoren-7-one (**3o**): Obtained as a yellow solid (31.5 mg, 46% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.54 - 7.61 (m, 3H), 7.38 - 7.46 (m, 5H), 7.19 (s, 1H), 6.60 - 6.65 (t, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 163.8 (d, J = 253.6 Hz), 163.7 (d, J = 253.6 Hz), 155.7 (d, J = 254.7 Hz), 155.6 (d, J = 254.7 Hz), 144.2 (dd, J = 3.9 Hz), 138.9 (dd, J = 7.7, 5.1 Hz), 137.8, 137.7, 132.0, 129.3 (dd, J = 7.6, 11.1 Hz), 128.7 (dd, J = 3.1, 1.7 Hz), 128.0, 127.9, 127.6 (d, J = 3.2 Hz), 127.4, 127.0, 126.7, 124.3 (dd, J = 14.8, 4.2 Hz), 124.0, 110.2 (dd, J = 31.7, 25.8 Hz), 108.6 (dd, J = 23.3, 2.7 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -108.2 (d, J = 5.1 Hz), -120.9 (d, J = 5.1 Hz); HRMS (ESI-TOF) m/z calcd for $C_{23}H_{13}F_2O$ $[M + H]^+$ 343.0929, found 343.0932.



2-Methyl-6-(p-tolyl)-7H-benzo[c]fluoren-7-one (**3p**): Obtained as a yellow solid (50.8 mg, 76% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.58 - 7.59 (m, 2H), 7.50 - 7.53 (m, 1H), 7.40 - 7.45 (m, 3H), 7.25 - 7.30 (m, 3H), 2.59 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 144.2, 143.3, 137.5, 137.4, 136.8, 135.8, 135.2, 134.6, 134.1, 131.1, 131.0, 129.2, 129.2, 128.6, 128.5, 128.3, 123.7, 123.5, 123.2, 22.2, 21.4; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}O$ $[M + H]^+$ 335.1430, found 335.1432.

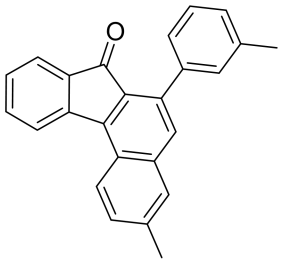


11-Bromo-2-methoxy-6-(4-methoxyphenyl)-7H-benzo[c]fluoren-7-one (**3q**): Obtained as a yellow solid (60.4 mg, 68% yield), eluting with 10% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 3.0 Hz, 1H), 7.70 - 7.74 (m, 2H), 7.65 (s, 1H), 7.59 (d, J = 6.8 Hz, 1H), 7.46 - 7.48 (m, 2H), 7.24 - 7.27 (m, 1H), 7.13 - 7.17 (m, 1H), 6.98 - 7.00 (m, 2H), 4.02 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 159.4, 157.5, 145.4, 144.7, 140.4, 138.9, 135.3, 133.7, 132.0, 131.3, 130.6, 130.2, 130.1, 129.9, 127.7, 122.8, 122.5, 116.7, 113.3, 106.7, 55.7, 55.3; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{18}BrO_3$ $[M + H]^+$ 445.0434, found 445.0432.

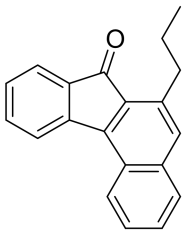


2-Fluoro-6-(4-fluorophenyl)-7H-benzo[c]fluoren-7-one (**3r**): Obtained as a yellow solid (43.8 mg, 64% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 - 8.70 (dd, J = 2.4, 10.8 Hz, 1H), 7.78 (s, 1H), 7.73 - 7.77 (dd, J = 2.0, 9.2 Hz, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.45 - 7.49 (m, 2H), 7.12 - 7.26 (m, 5H), 6.57 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 163.3 (d, J = 249.1 Hz), 162.8 (d, J = 246.2 Hz), 144.5, 143.3, 136.6, 135.2, 134.8, 134.1 (d, J = 2.3 Hz), 134.0, 132.8 (d, J = 9.7 Hz), 131.1, 130.9 (d, J = 8.0 Hz), 130.7 (d, J = 9.7 Hz), 130.3 (d, J = 11.3 Hz), 129.8, 129.2, 127.0, 123.8, 123.1, 117.7 (d, J = 26.0 Hz), 115.7 (d, J = 21.3 Hz), 108.0 (d, J = 22.7 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -114.1, -118.6; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{13}F_2O$ [M +

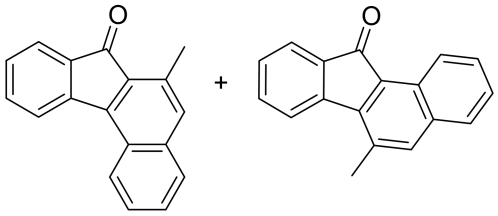
H] $^{+}$ 343.0929, found 343.0932.



3-Methyl-6-(*m*-tolyl)-7H-benzo[c]fluoren-7-one (**3s**): Obtained as a yellow solid (46.1 mg, 69% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.55 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.35 - 7.38 (m, 3H), 7.31 (d, J = 7.6 Hz, 1H), 7.26 (s, 1H), 2.55 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 144.1, 144.1, 139.0, 138.2, 138.0, 137.8, 137.3, 135.1, 134.8, 134.6, 134.1, 130.6, 130.0, 129.5, 128.8, 128.5, 128.4, 127.6, 126.6, 124.5, 123.7, 123.2, 21.8, 21.5; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}O$ [M + H] $^{+}$ 335.1430, found 335.1431.



6-propyl-7H-benzo[c]fluoren-7-one (**3t**): Obtained as a yellow liquid (39.2 mg, 72% yield), eluting with 20% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 - 8.48 (m, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.78 - 7.80 (m, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.48 - 7.55 (m, 4H), 7.26 - 7.31 (m, 1H), 3.13 - 3.17 (t, 2H), 1.69 - 1.78 (m, 2H), 1.02 - 1.05 (t, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 144.4, 143.8, 139.2, 137.7, 134.6, 134.2, 130.2, 129.4, 128.9, 128.6, 128.3, 127.7, 126.8, 124.6, 123.6, 123.2, 33.8, 24.0, 14.1; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{17}O$ [M + H] $^{+}$ 273.1279, found 273.1276.



6-Methyl-7H-benzo[a]fluoren-7-one (**3u**), 6-Methyl-11H-benzo[c]fluoren-11-one (**3u'**). Mixture cannot seperate. Obtained as a yellow liquid (37.1 mg, 76% yield), eluting with 5% EtOAc in PE (elution gradient); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.4 Hz, 1.0H), 8.40 - 8.43 (m, 2.3H), 7.98 (d, J = 7.6 Hz, 2.4H), 7.73 - 7.75 (m, 2.3H), 7.57 - 7.68 (m, 7.4H), 7.50 - 7.53 (m, 6.0H), 7.47 - 7.48 (m, 4.7H), 7.36 - 7.41 (m, 3.1H), 7.28 (d, J = 7.2 Hz, 2.4H), 7.23 - 7.26 (m, 2.9H), 2.73 (s, 6.5H), 2.70 (s, 3.0H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 195.4, 145.2, 144.5, 144.3, 143.4, 137.7, 136.6, 134.9, 134.6, 134.3, 134.2, 134.2, 134.1, 131.2, 130.8, 129.7, 129.5, 128.7, 128.7, 128.6, 128.5, 128.3, 127.6, 127.5, 126.8, 126.5, 124.6, 124.2, 123.7, 123.6, 123.2, 123.1, 20.9, 18.5; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{13}O$ $[M + H]^+$ 245.0961, found 245.0963.

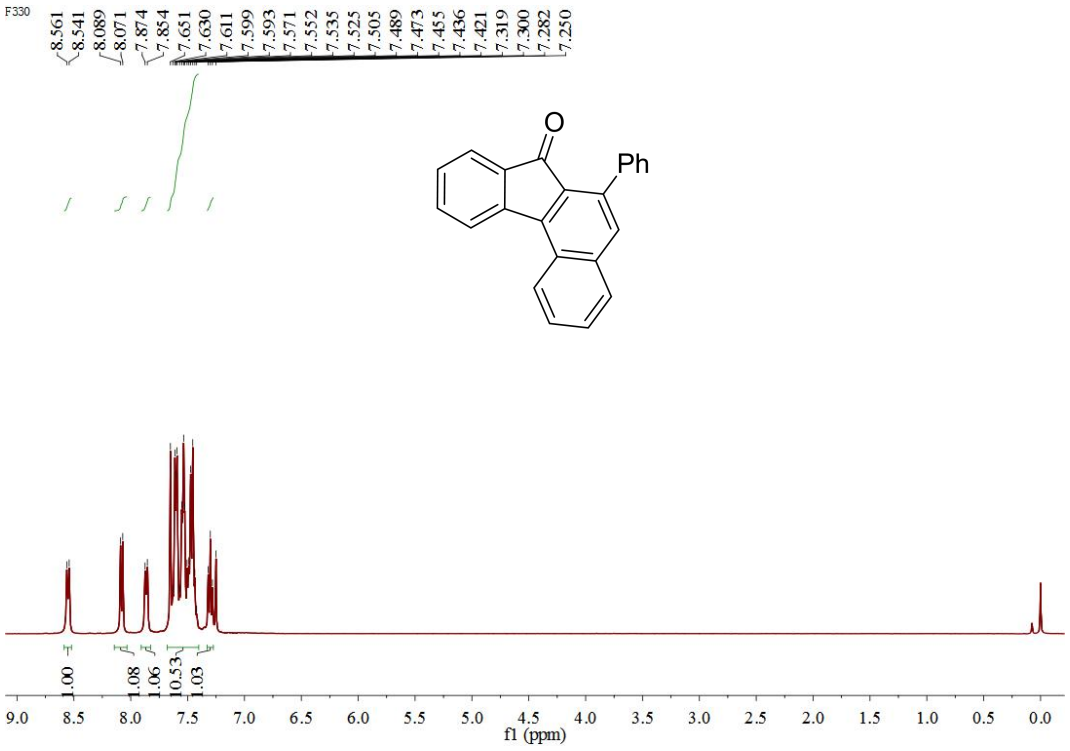
References

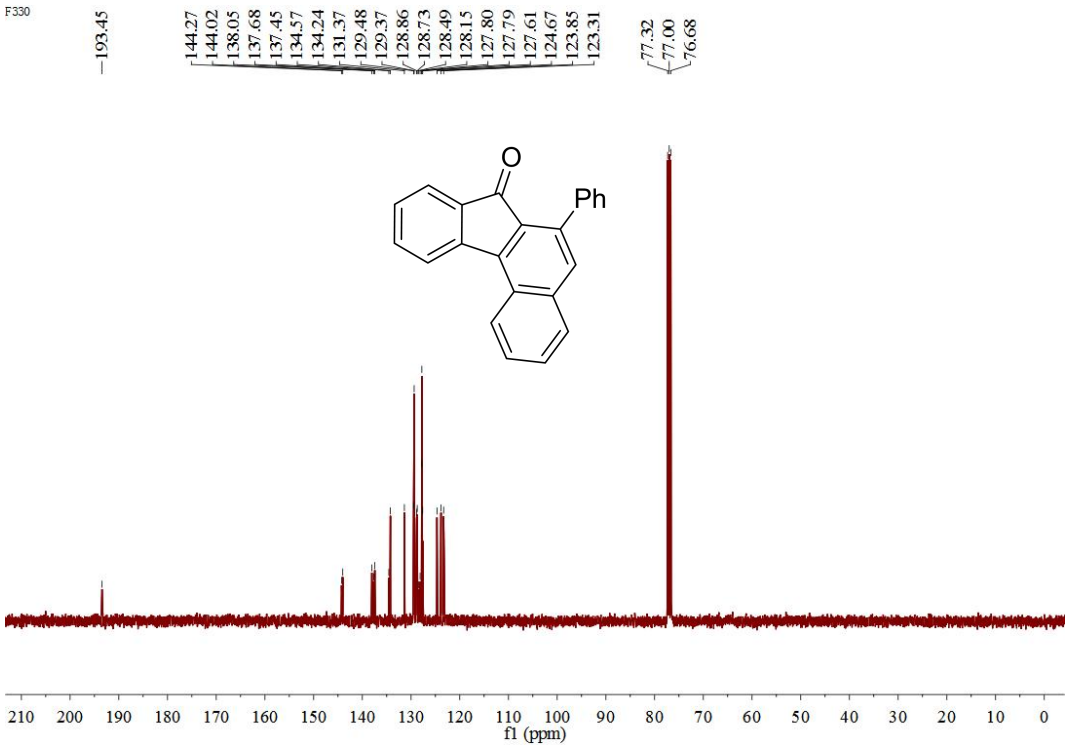
(1) (a) Zeng, Q.; Gao, F.; Benet-Buchholz, J.; Kleij, A. W. Stereoselective ThreeComponent Allylic Alkylation Enabled by Dual Photoredox/Ni Catalysis. *ACS Catal*. **2023**, *13*, 7514. (b) Cheng, Y. Y.; Yu, J. X.; Lei, T.; Hou, H. Y.; Chen, B.; Tung, C. H.; Wu, L. Z. Direct 1, 2-Dicarbonylation of Alkenes towards 1, 4-Diketones via Photocatalysis. *Angewandte Chemie.* **2021**, *133*, 27026. (c) Tong, X.; Wu, Z.; Wu, Z.; Ang, H. T.; Miao, Y.; Lu, Y.; Wu, J. Photocatalytic Reductive Functionalization of Aryl Alkynes via Alkyne Radical Anions. *ACS Catal*. **2024**, *14*, 9283-9293. (d) Kaper, T.; Fischer, M.; Thye, H.; Geik, D.; Schmidtmann, M.; Beckhaus, R.; Doye, S. Intermolecular Hydroaminoalkylation of Alkynes. *Chem. Eur. J*. **2021**, *27*, 6899-6903. (d) Till, N. A.; Smith, T. R.; Smith, T. R.; MacMillan, D. W. C. Decarboxylative Hydroalkylation of Alkynes. *J. Am. Chem. Soc*. **2018**, *140*, 5701-5705. (e) Sakabe, K.; Tsurugi, H.; Hirano, K.; Satoh, T.; Miura, M. Rhodium/Phosphine/Amine·HBr Catalyst System for Highly Selective Cross Cyclodimerization of Aryl- and

Alkylalkynes: Efficient Access to Multisubstituted Naphthalene Derivatives. *Chem. Eur. J*. **2010**, *16*, 445-449. (f) Huang, L.-Y.; Aulwurm, U. R.; Heinemann, F. W.; Kisch, H. Rhodium-Catalyzed Synthesis of Naphthalene Derivatives Through Cyclodimerization of Arylalkynes. *Eur. J. Inorg. Chem*. **1998**, 1998, 1951- 1957.

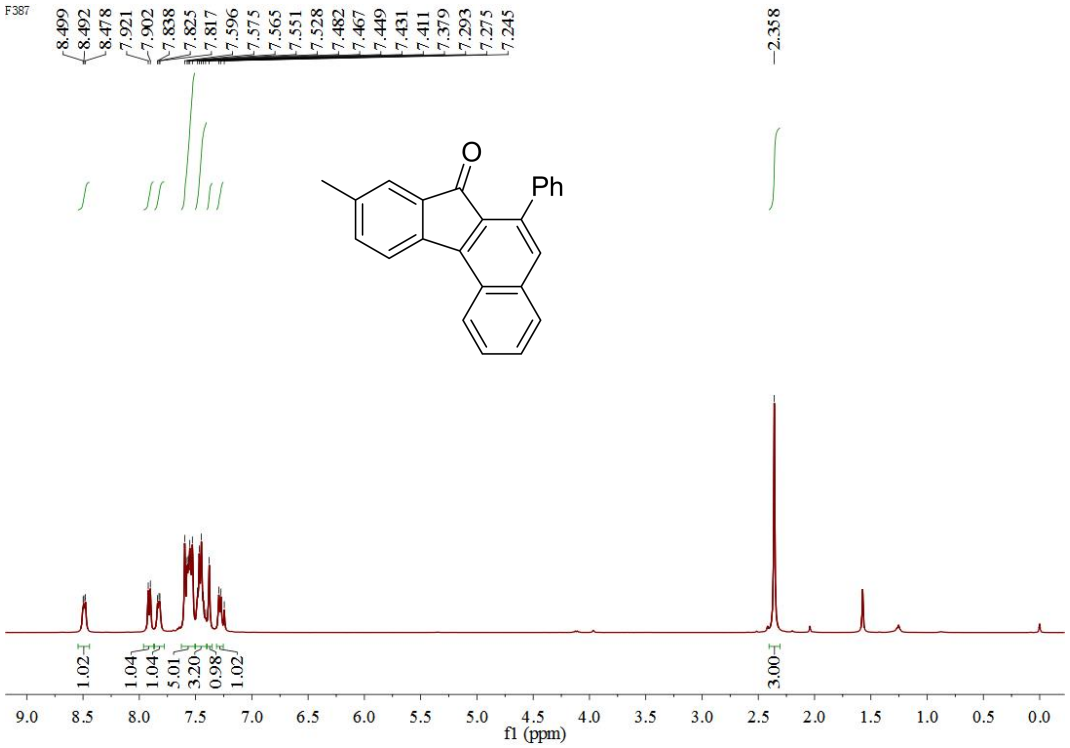
Copies of ^{1}H and ^{13}C NMR spectra of products

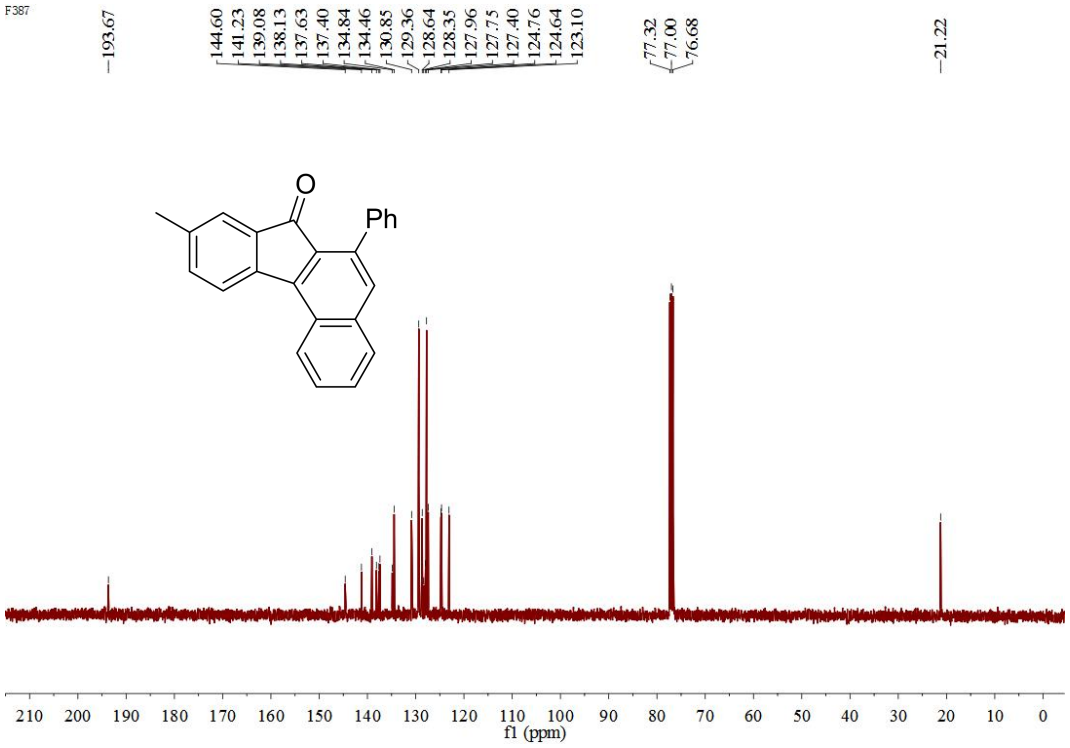
^{1}H NMR and ^{13}C NMR of 3a





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





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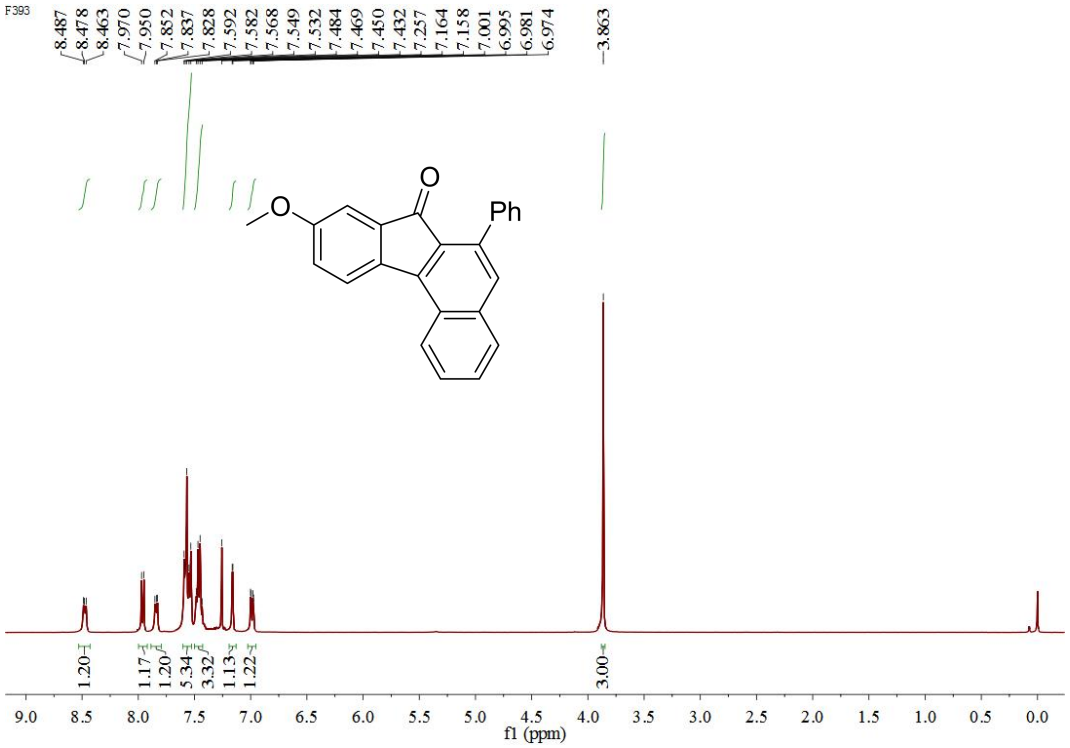
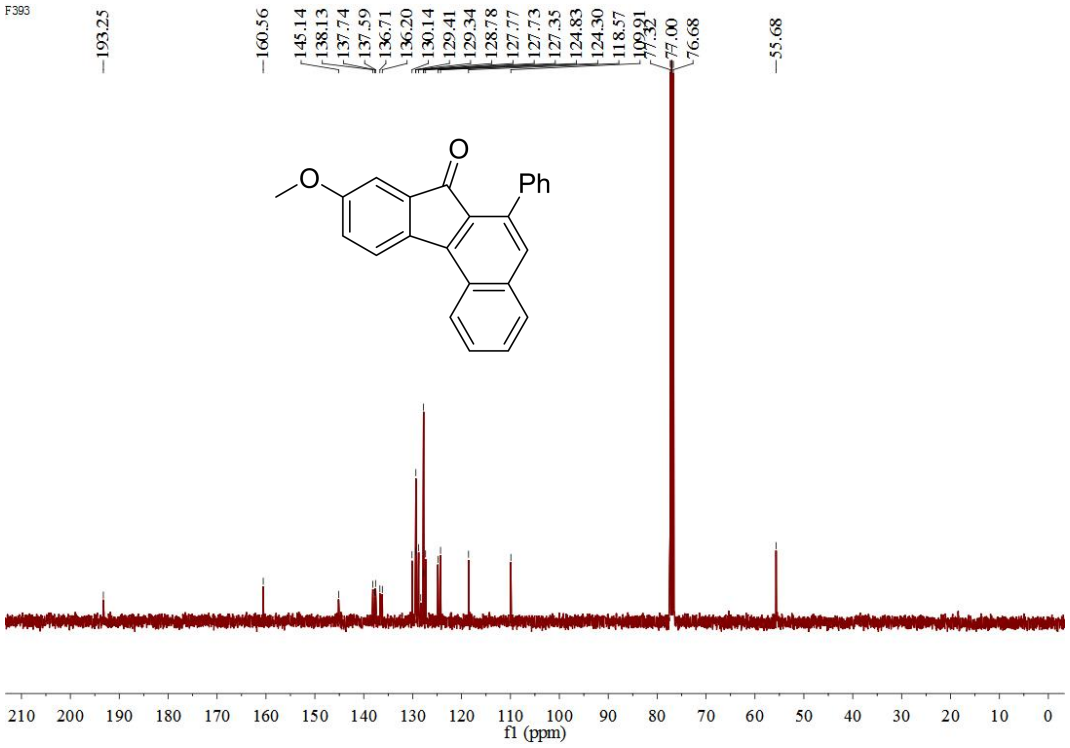
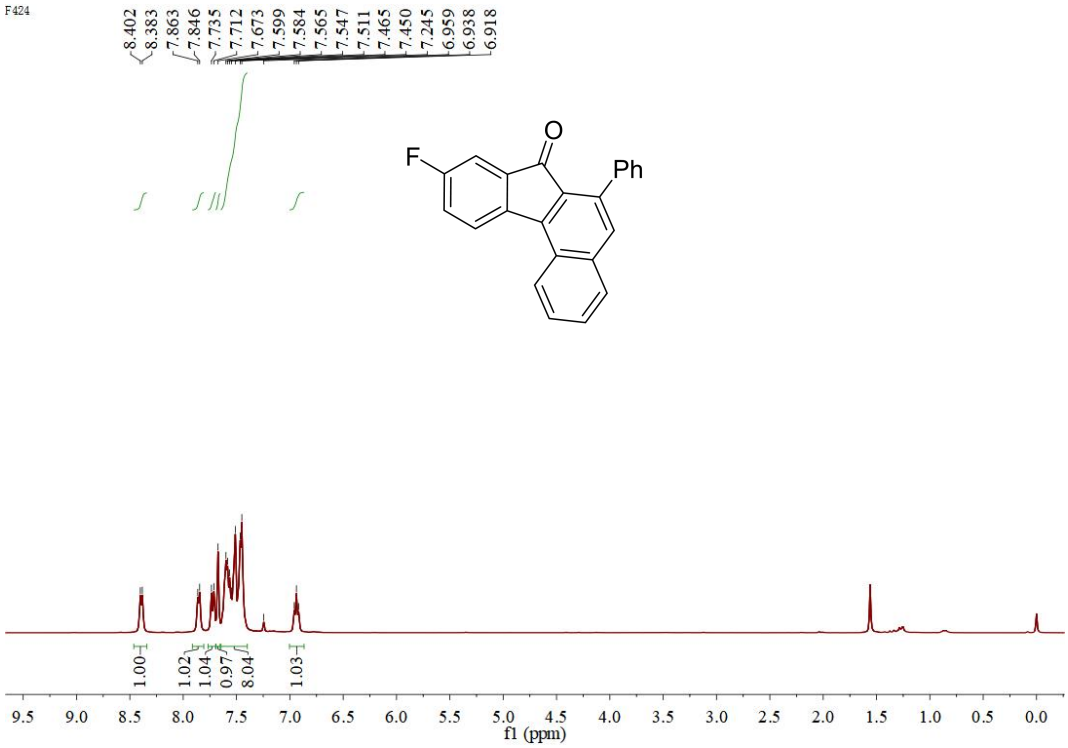
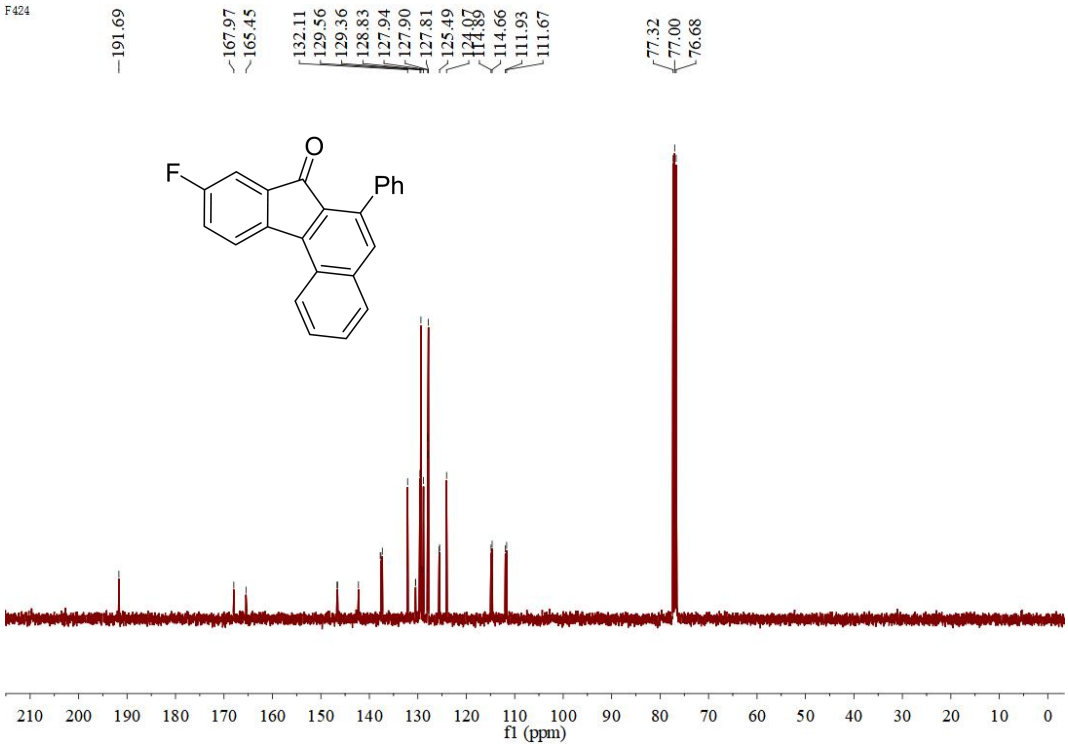
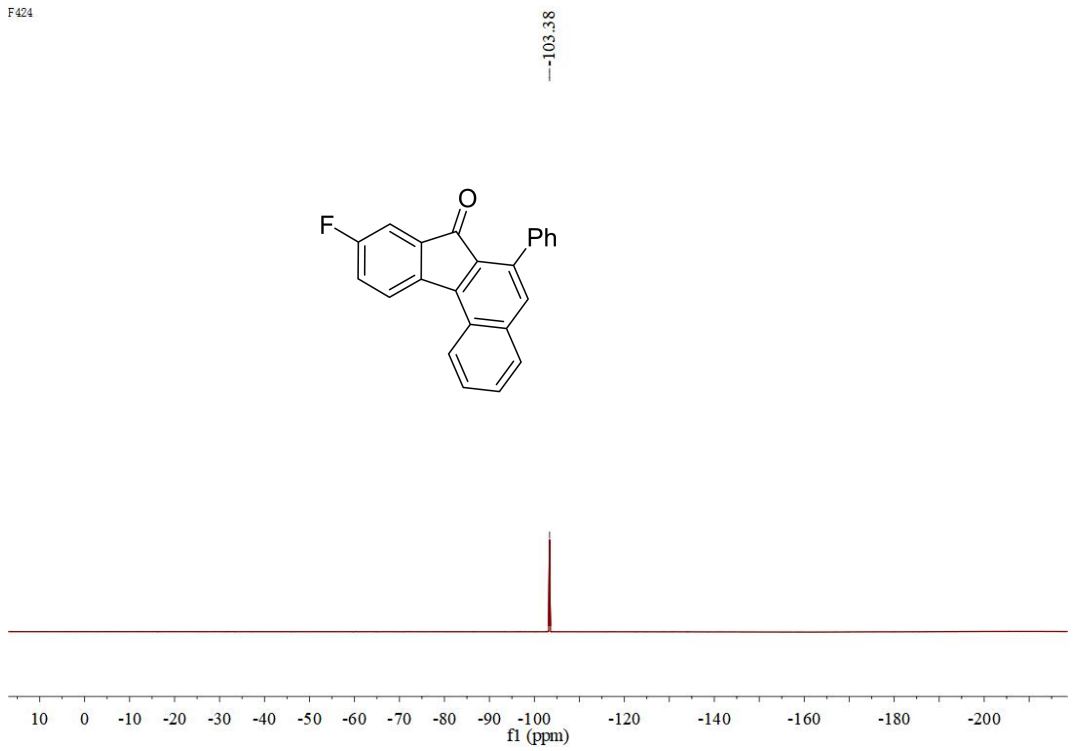




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3d



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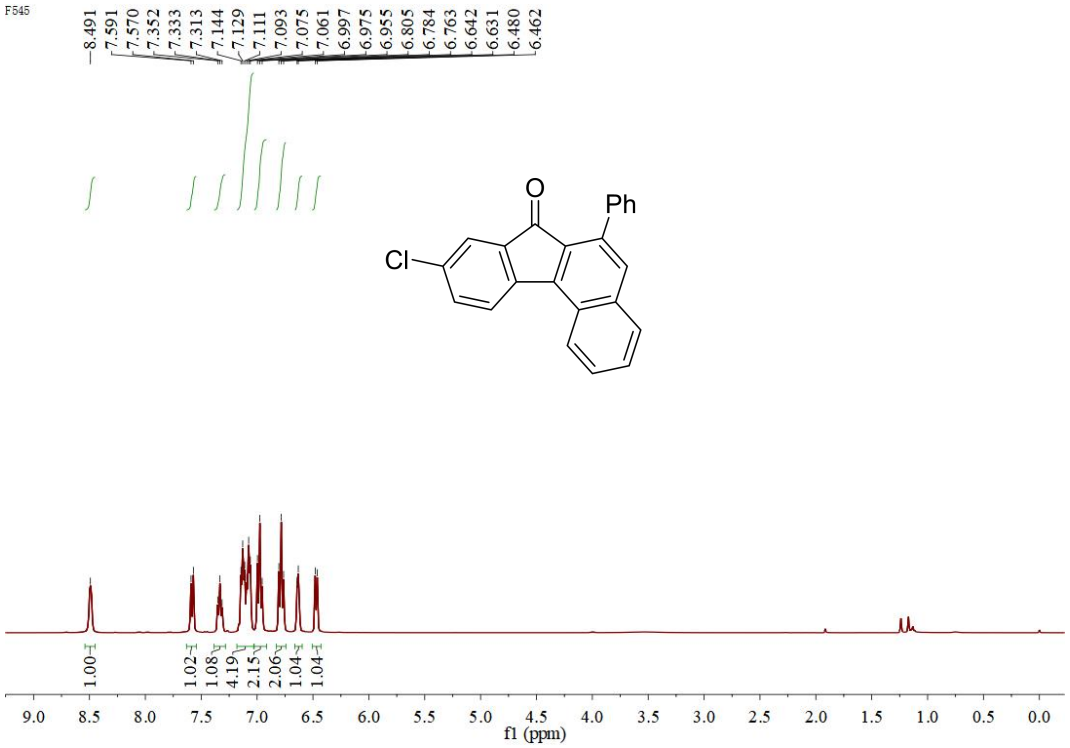
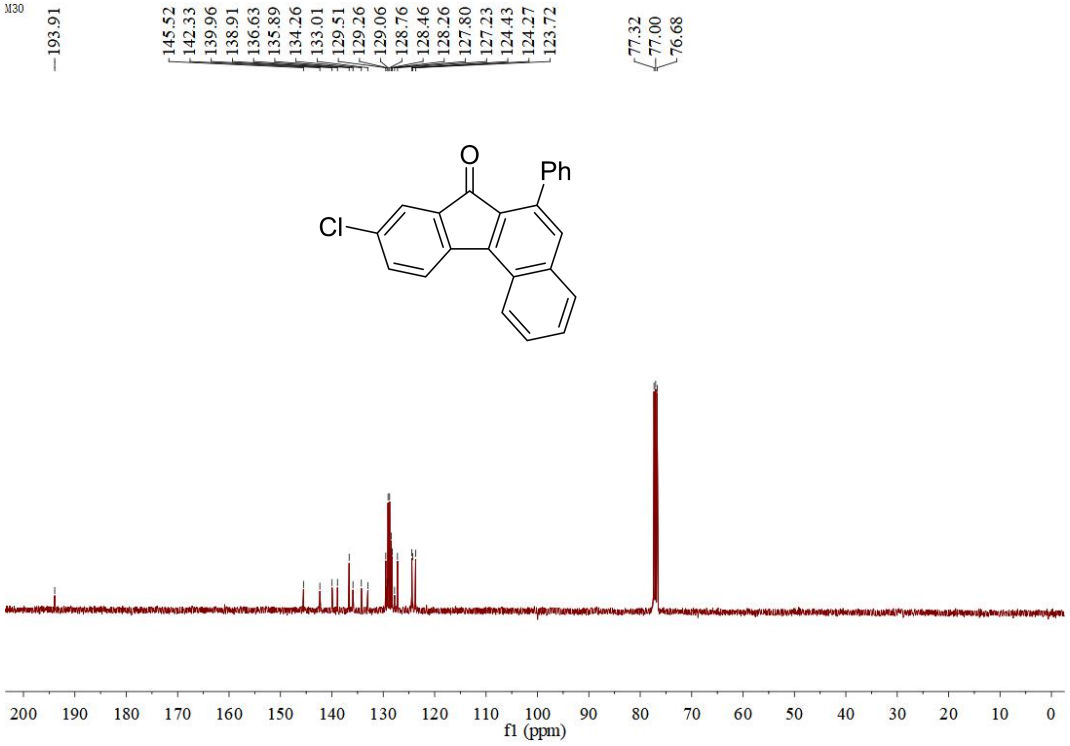
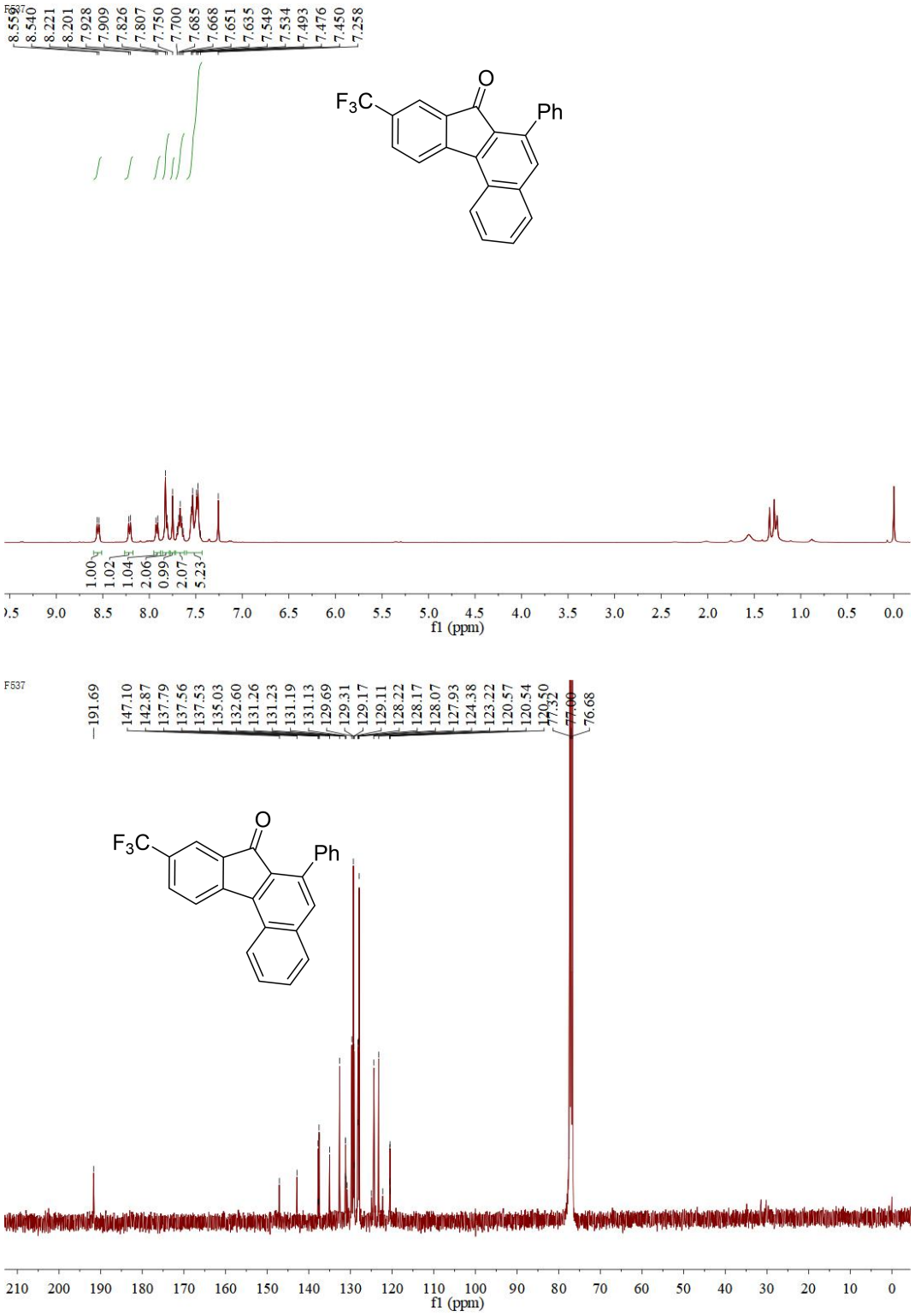
f1 (ppm)

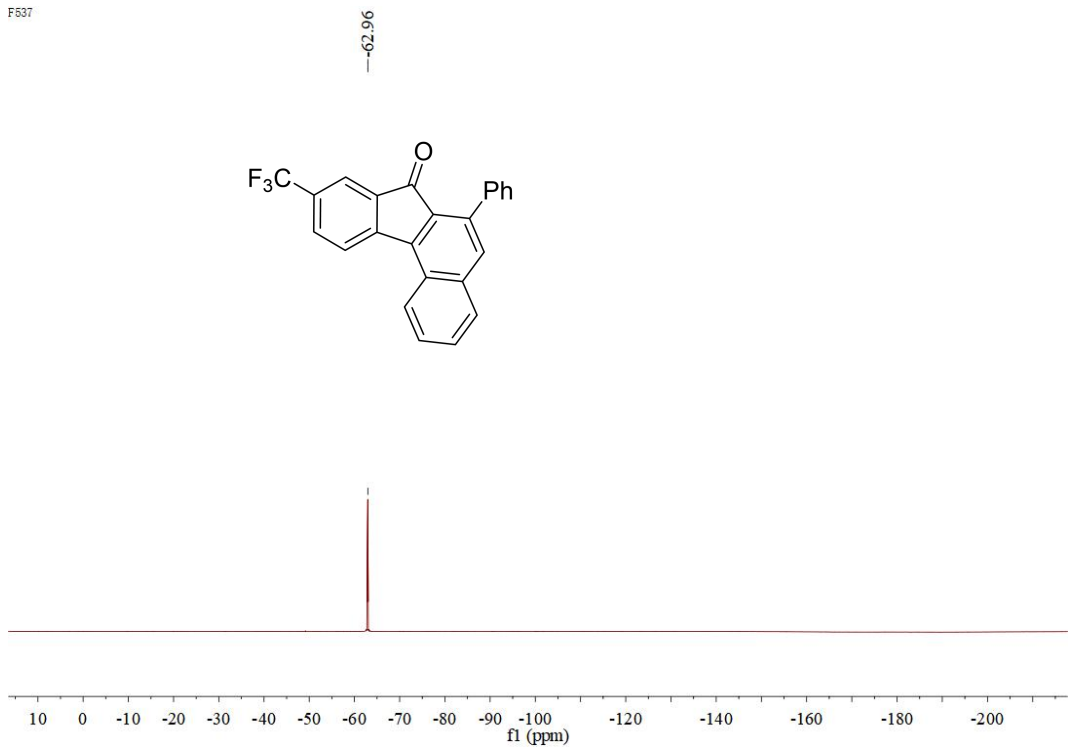
^{1}H NMR and ^{13}C NMR of 3e



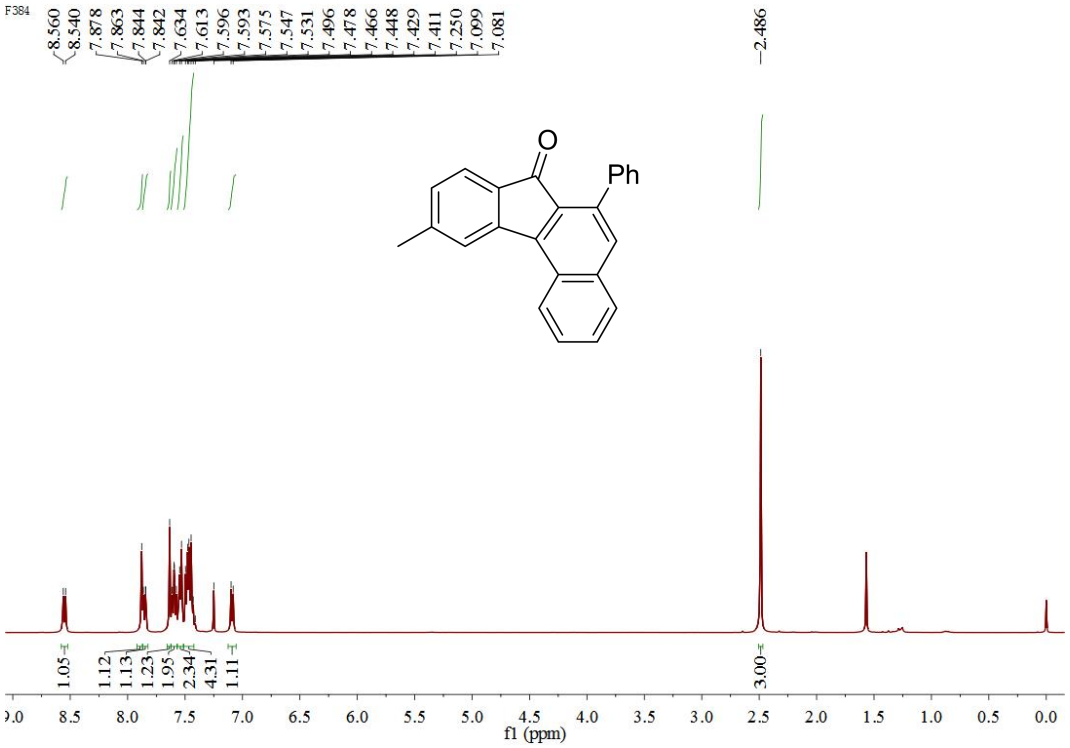


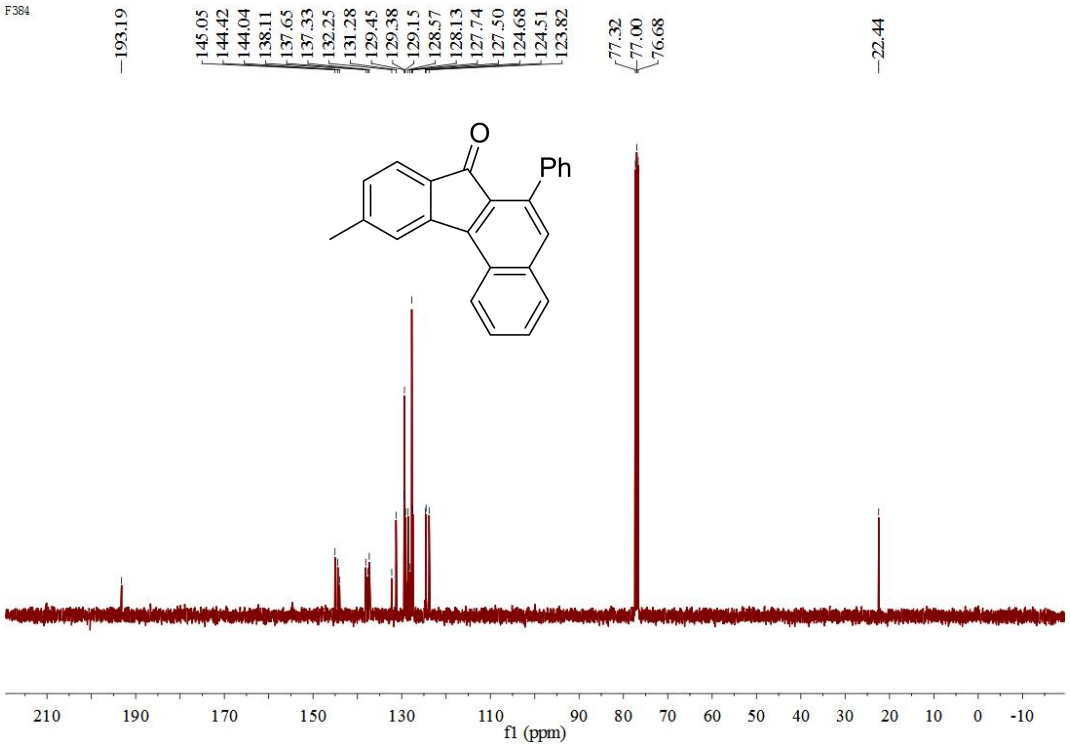
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3f



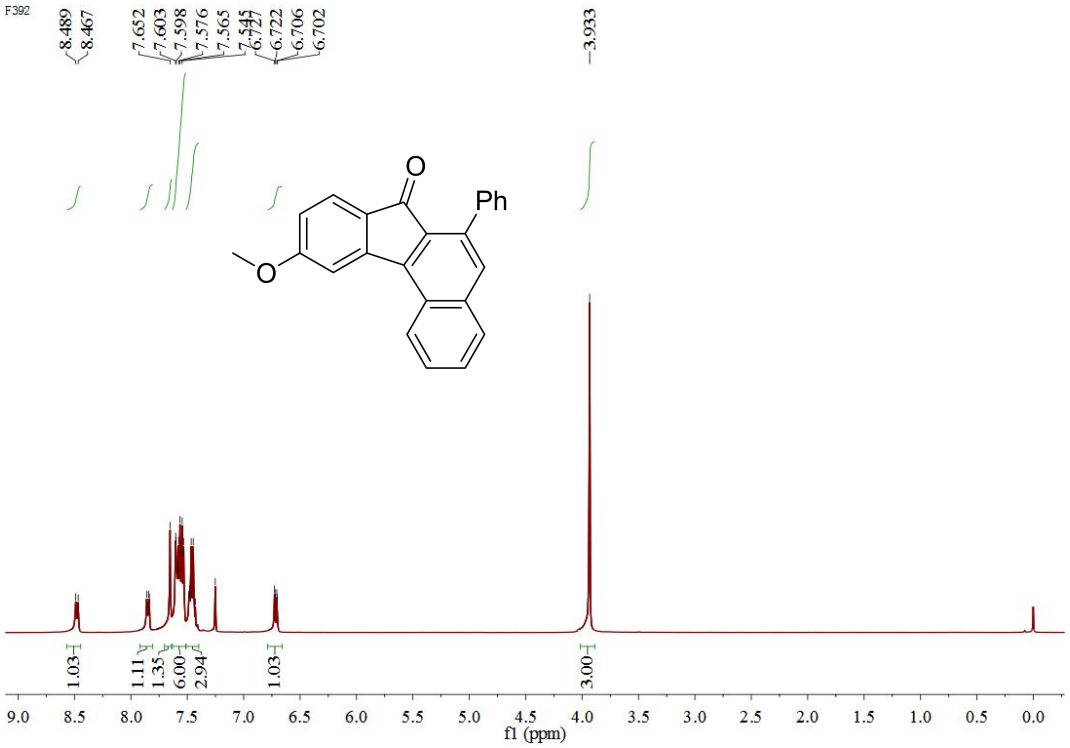

F537
-62.96
F3C
O
Ph
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

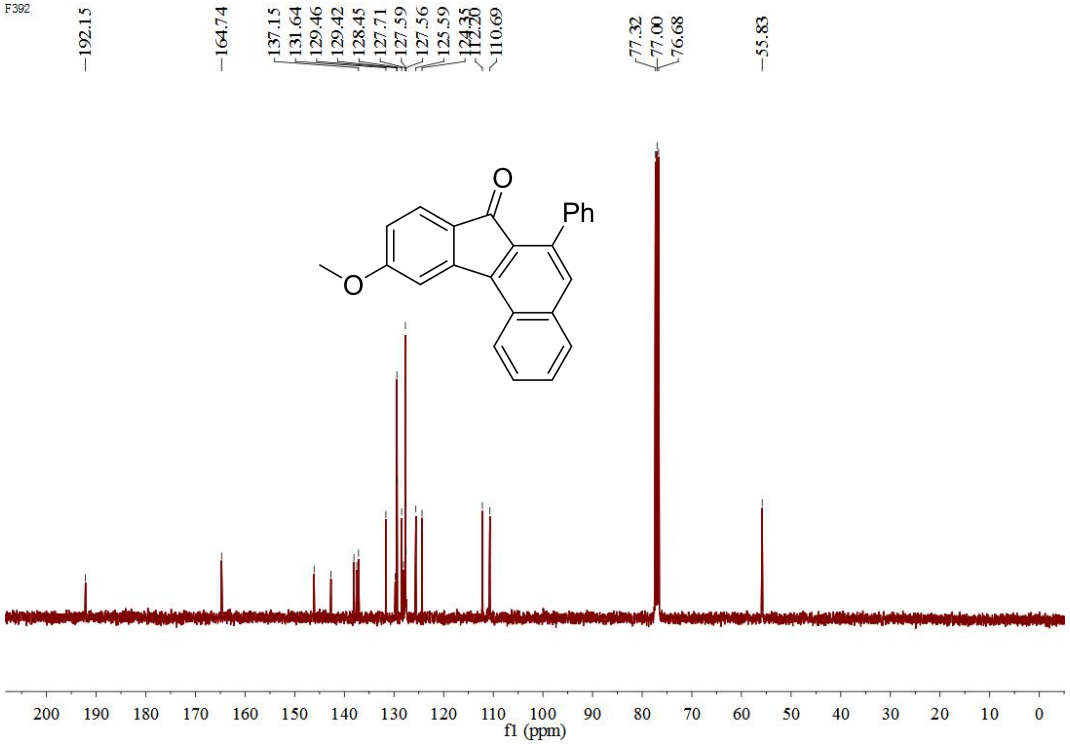
^{1}H NMR, and ^{13}C NMR of 3g



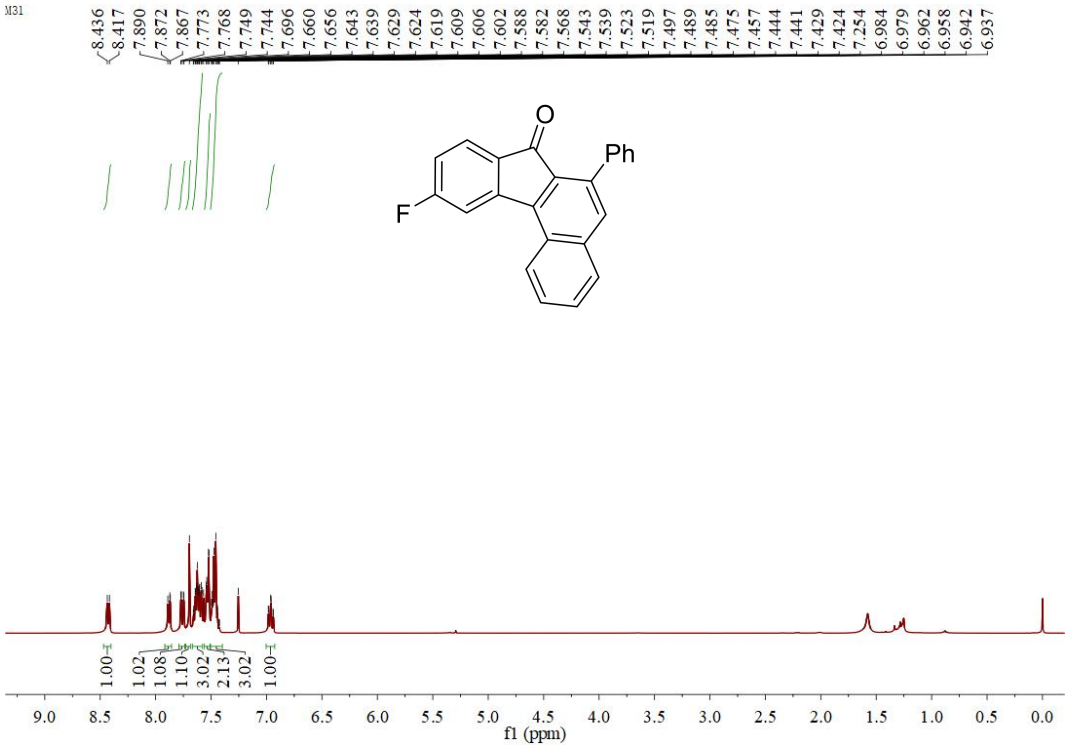


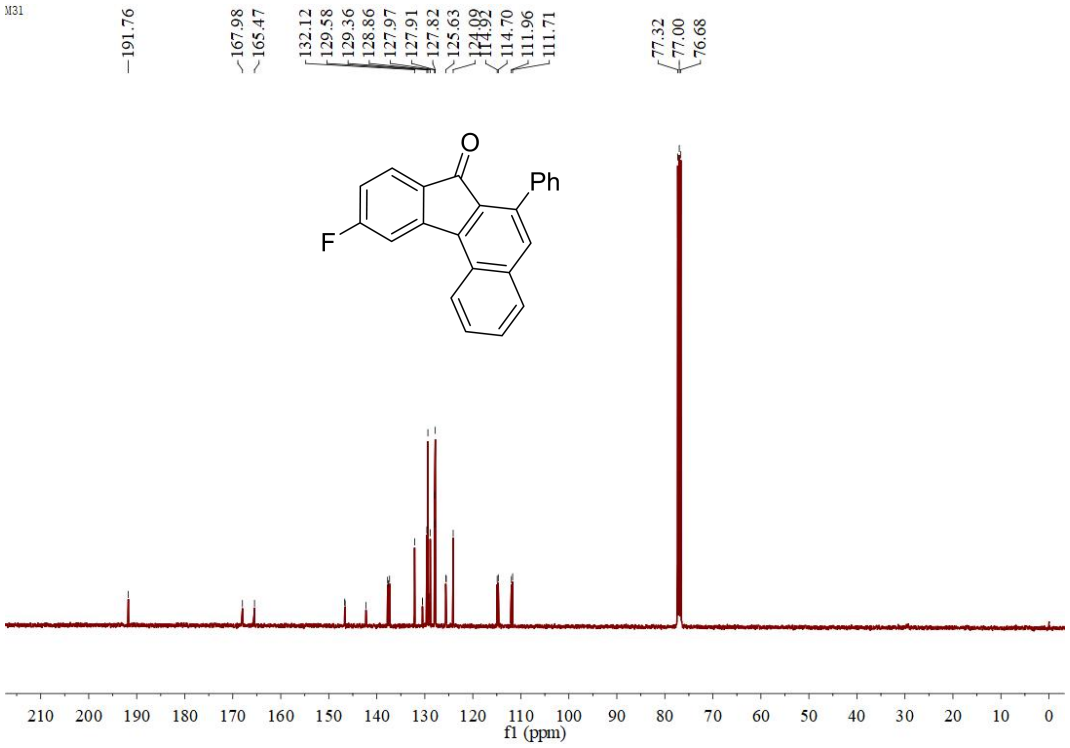
^{1}H NMR, and ^{13}C NMR of 3h

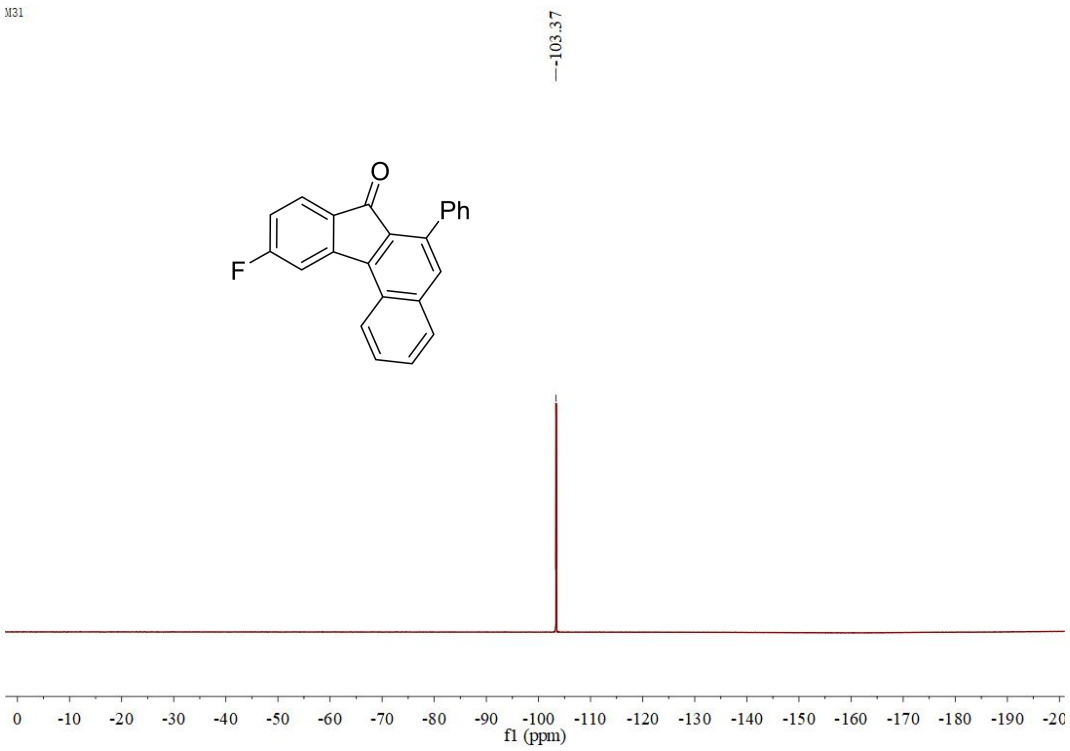




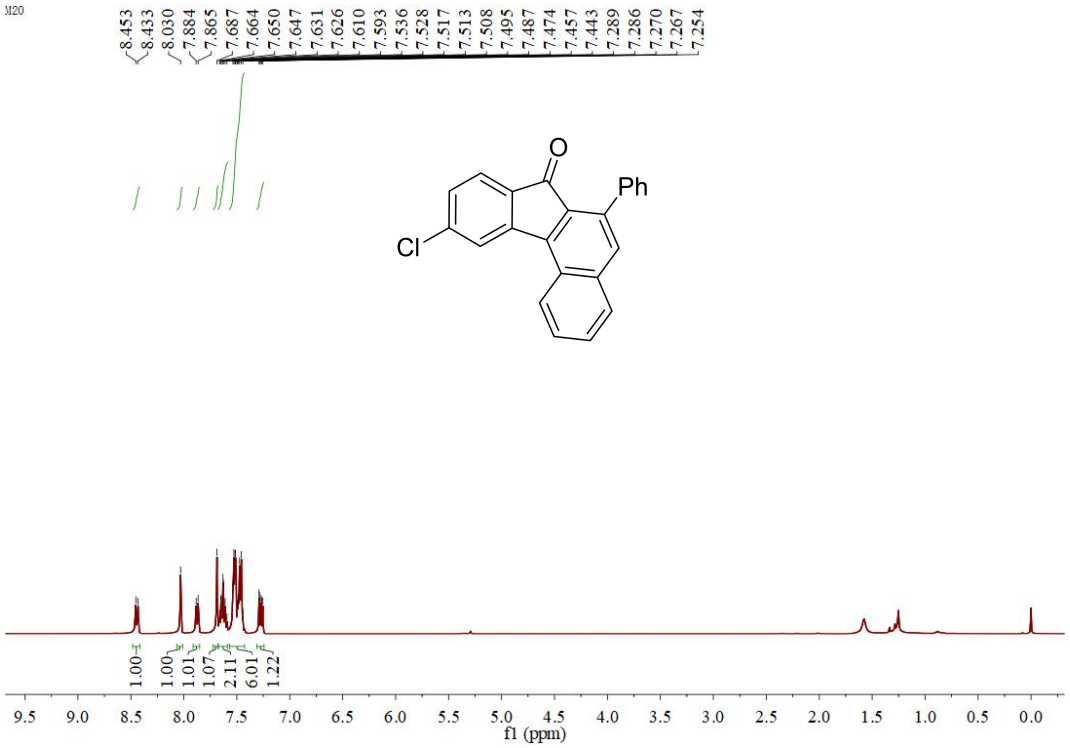
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3i

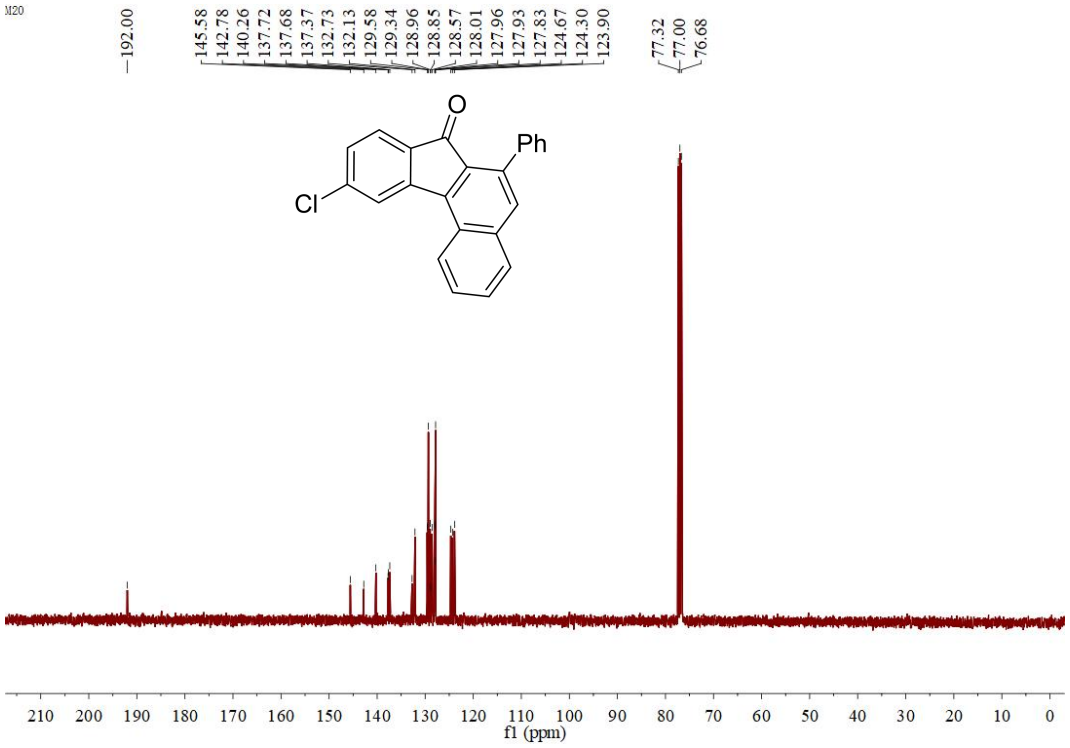




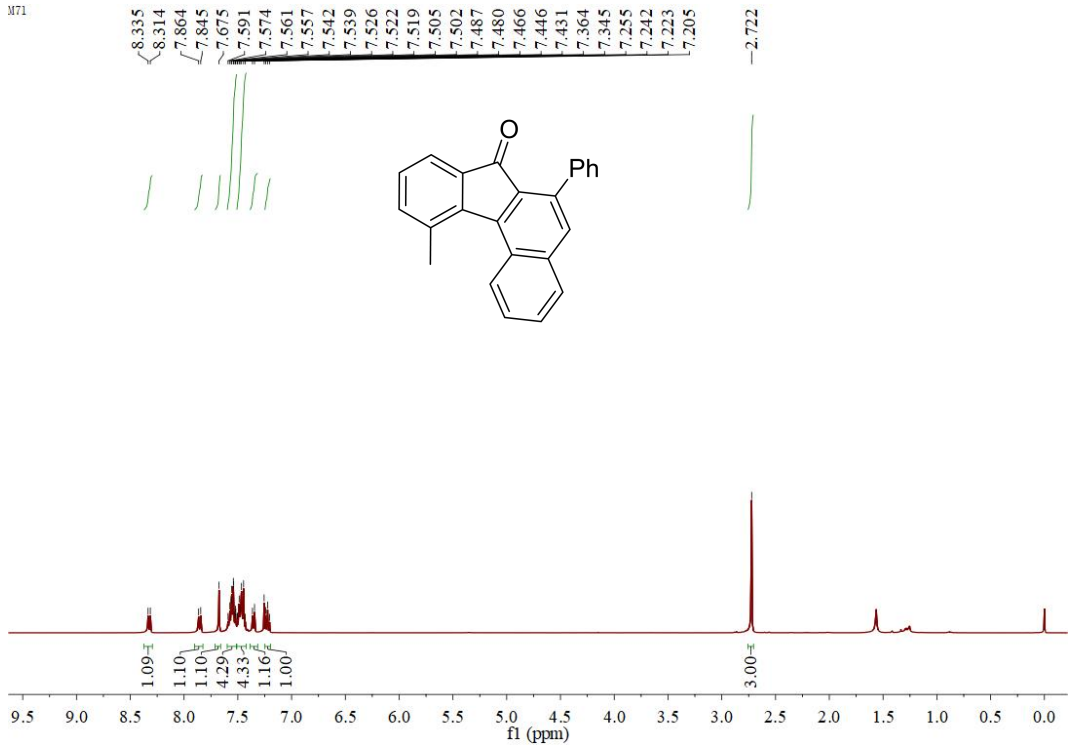

M31
-103.37
O
Ph
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

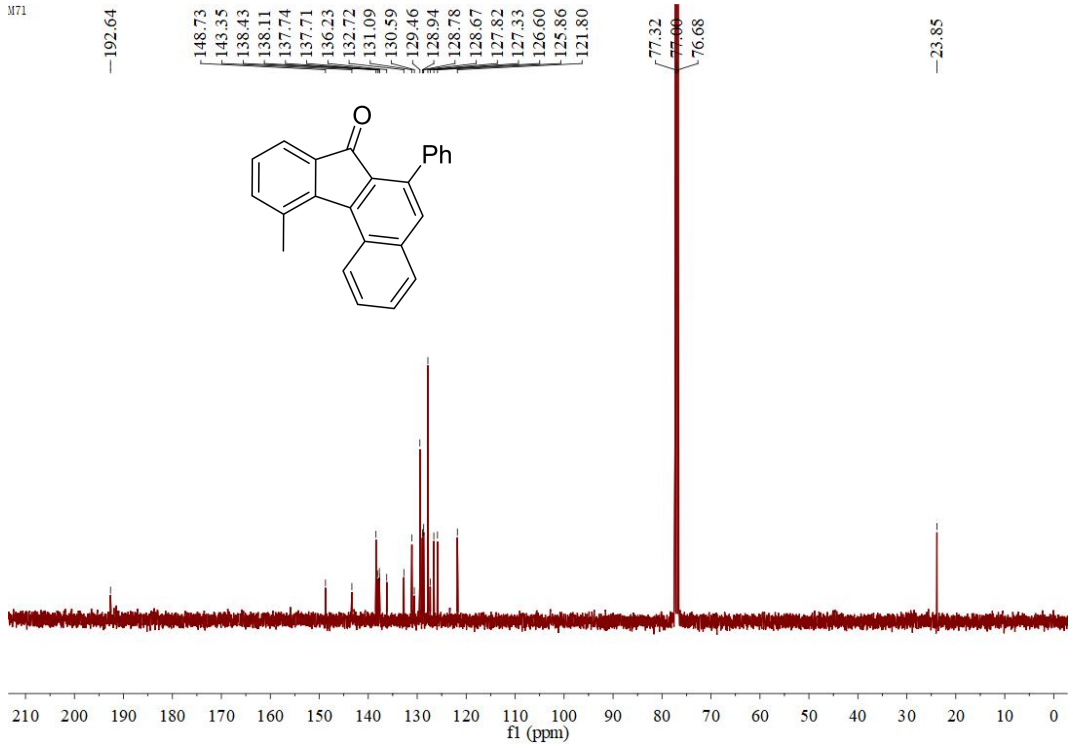
^{1}H NMR, and ^{13}C NMR of 3j



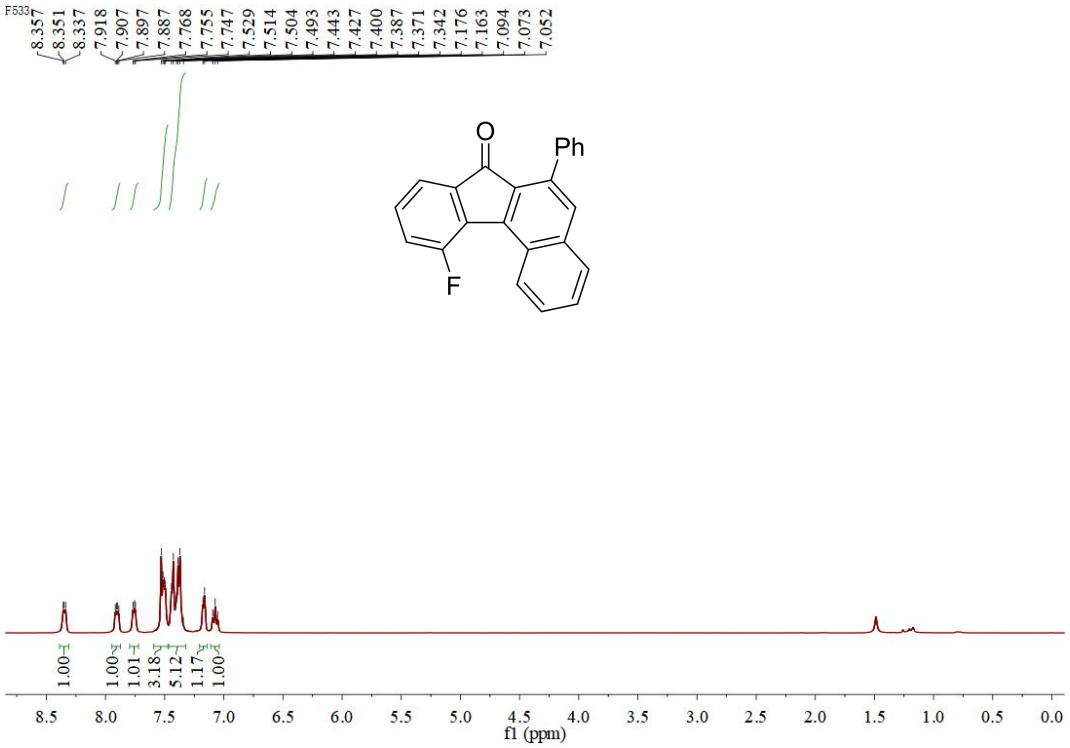


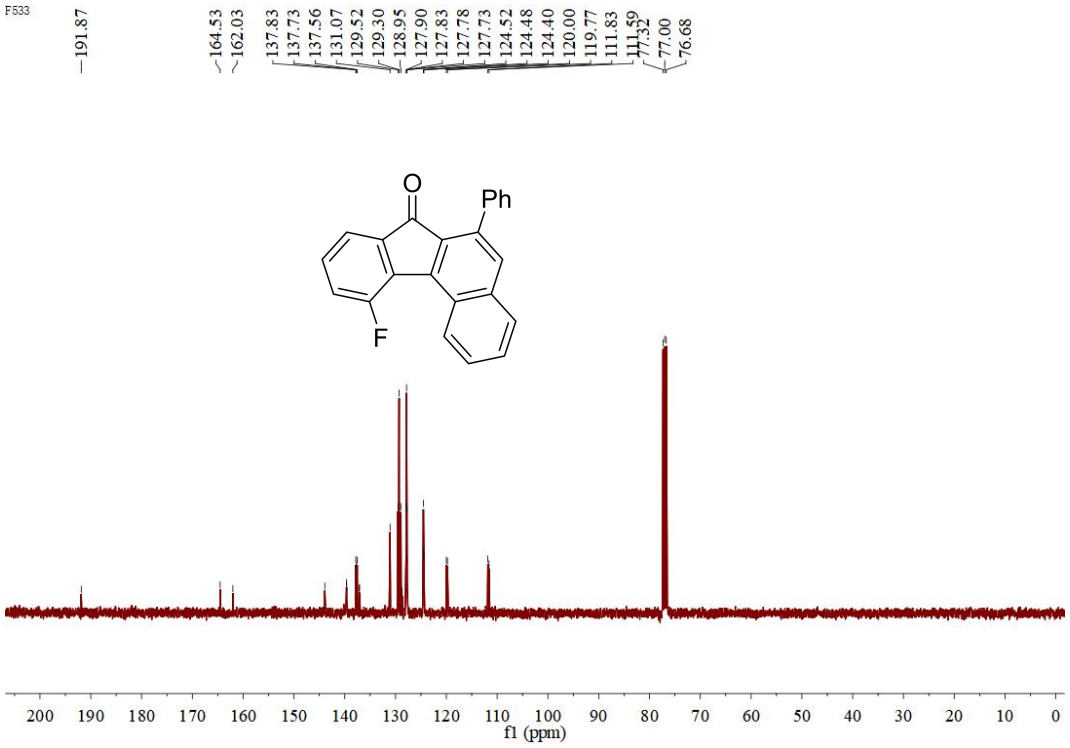
^{1}H NMR, and ^{13}C NMR of 3k

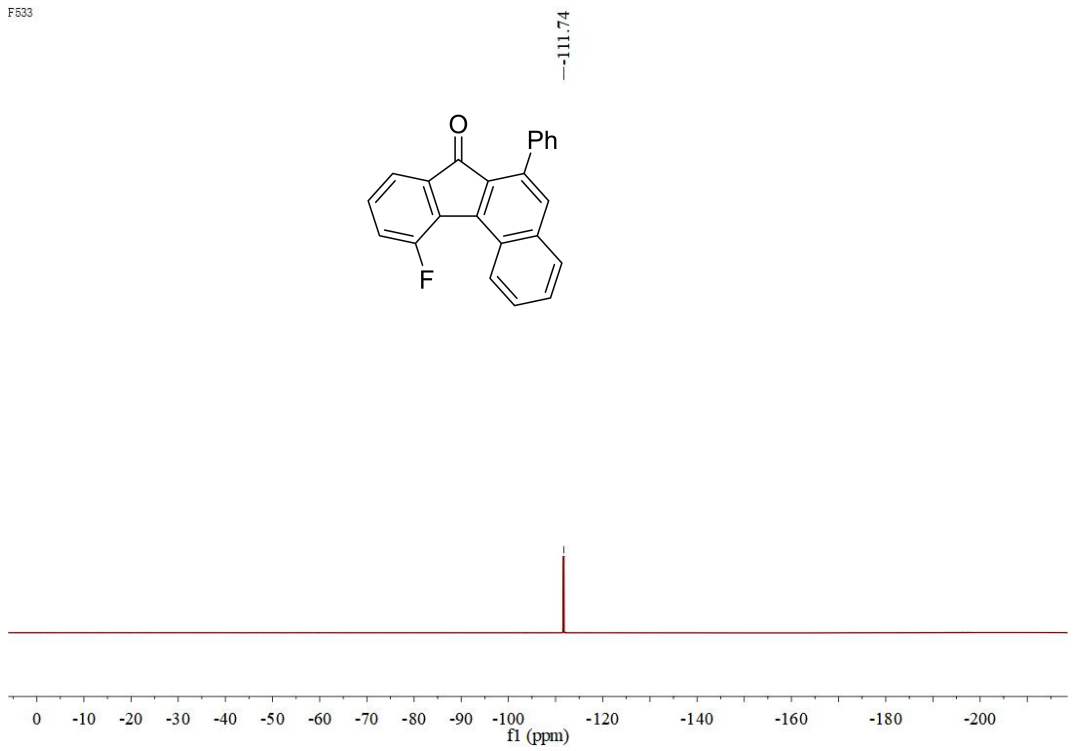




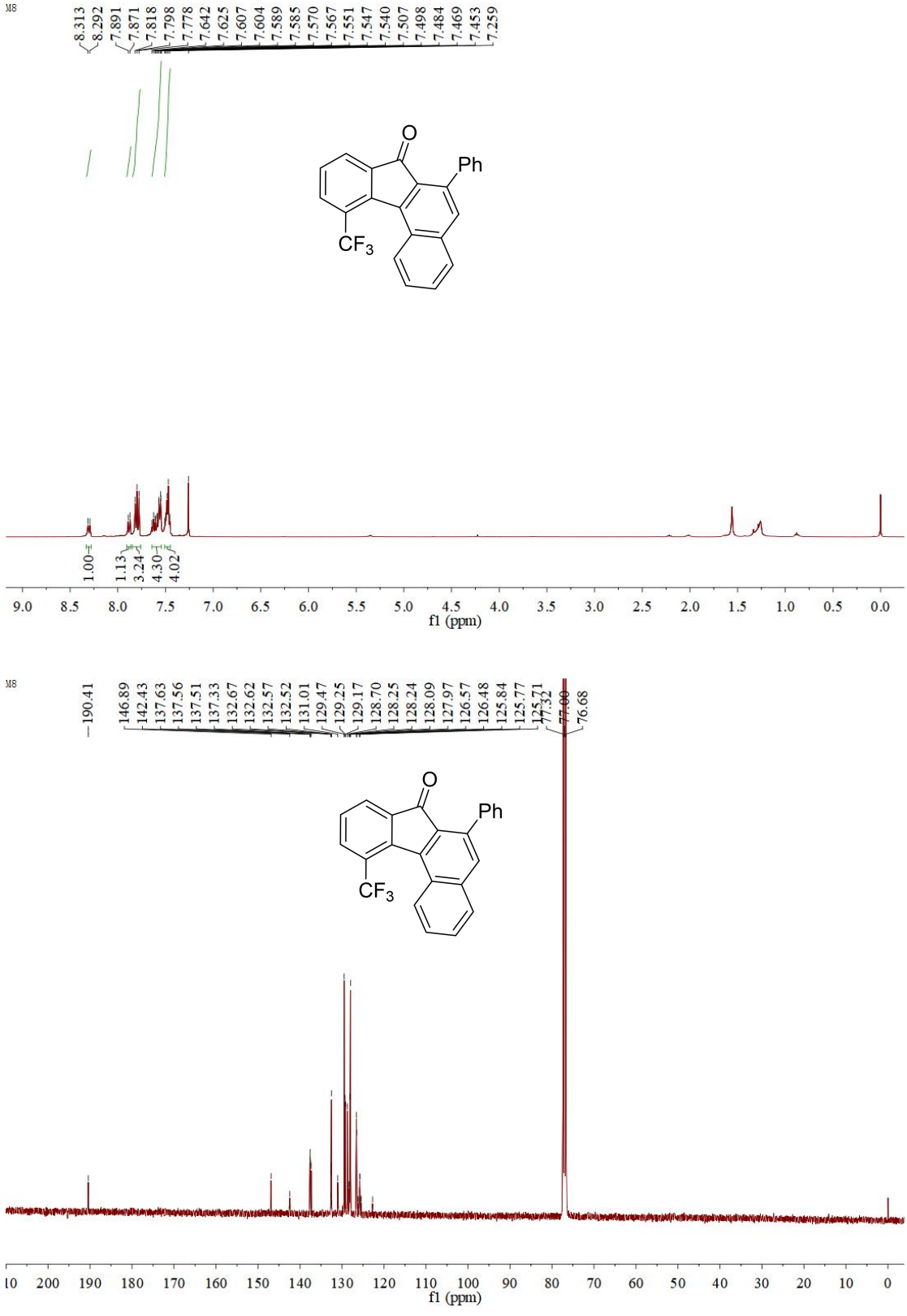
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3l



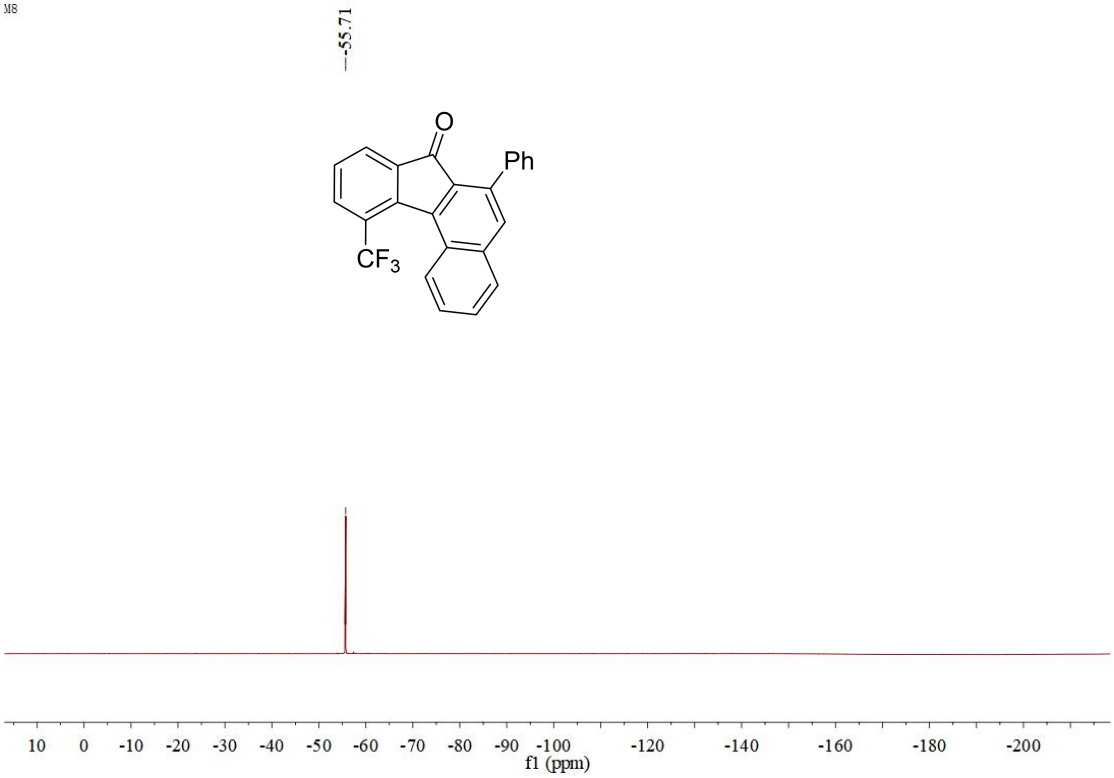



F533
-111.74
O
Ph
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

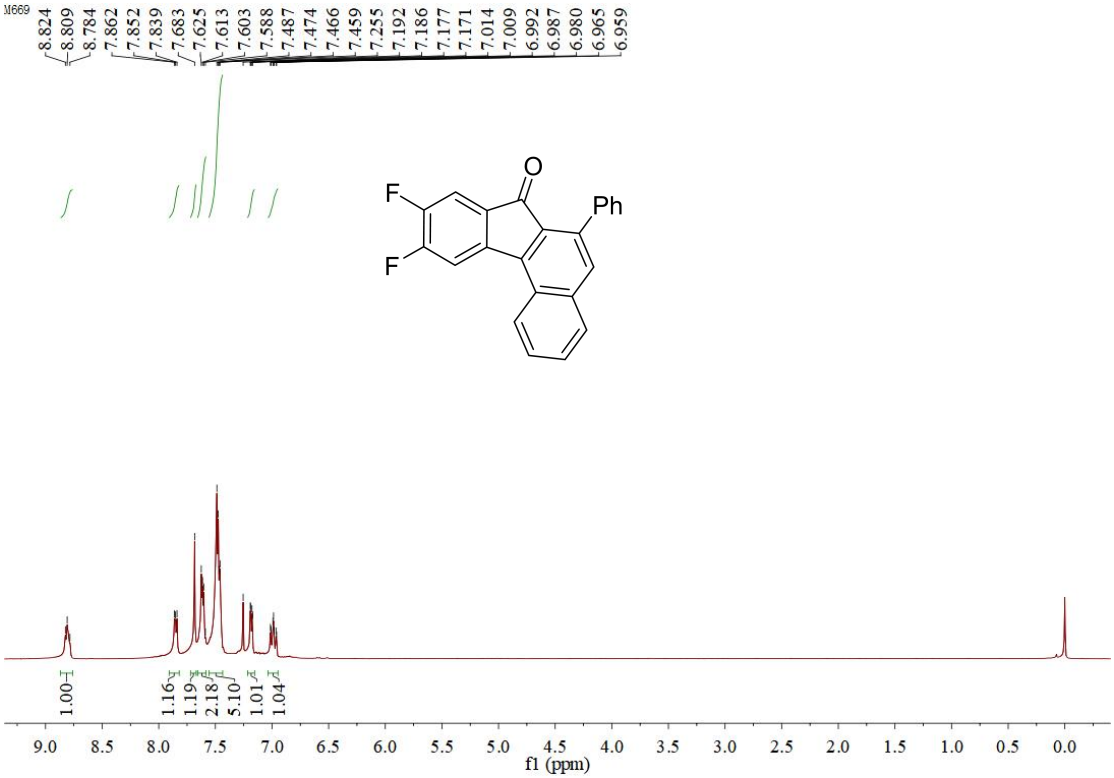
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3m

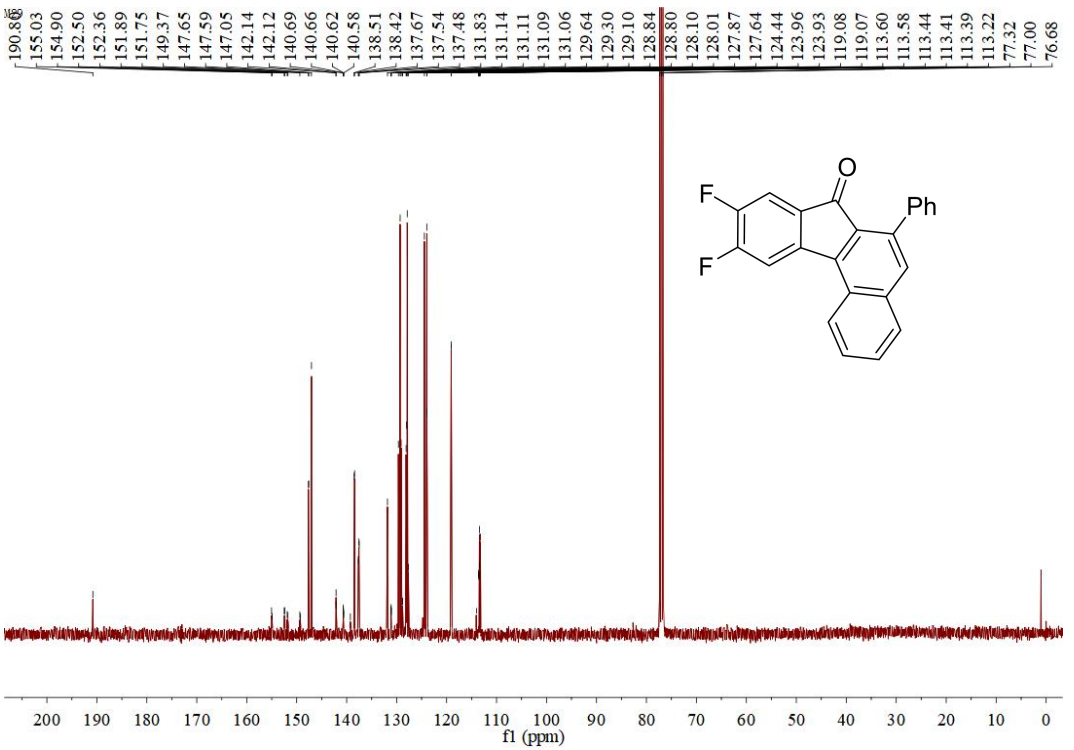


M8


-55.71
O
Ph
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

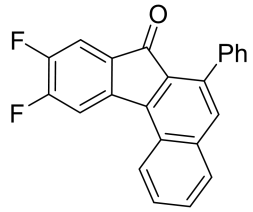
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3n

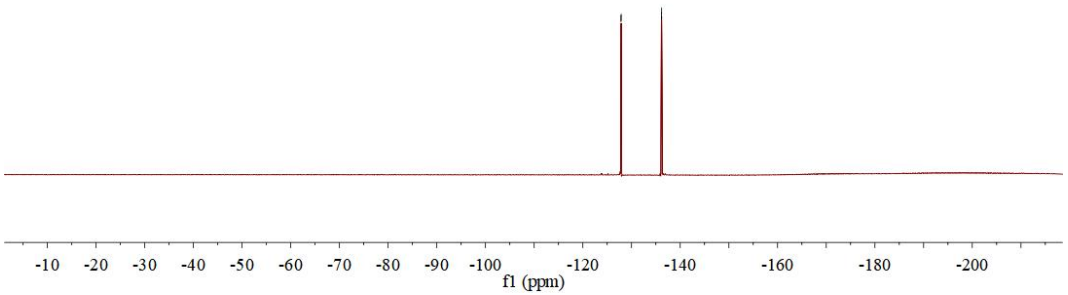




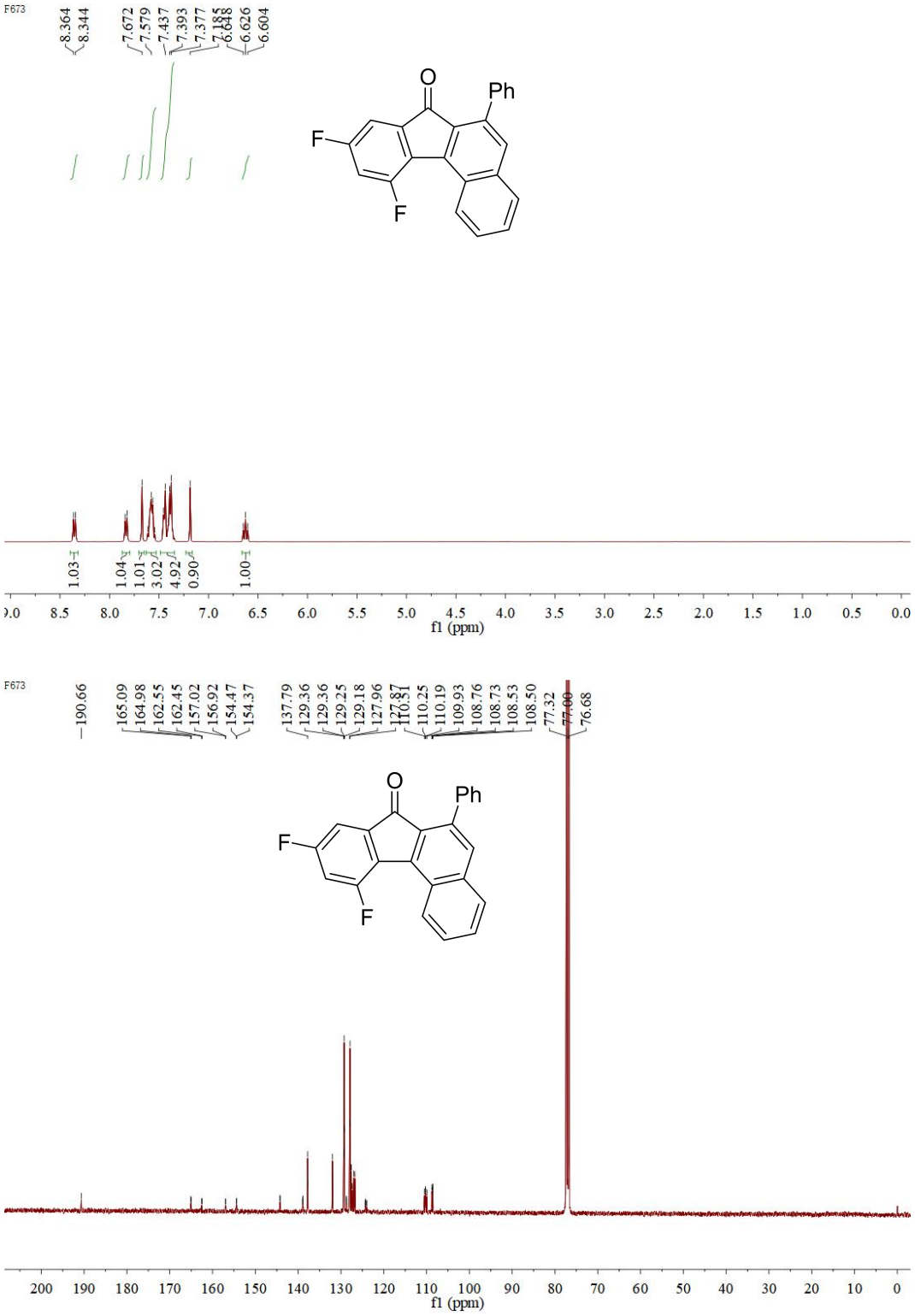
M29

-127.83
-127.88
-136.14
-136.19

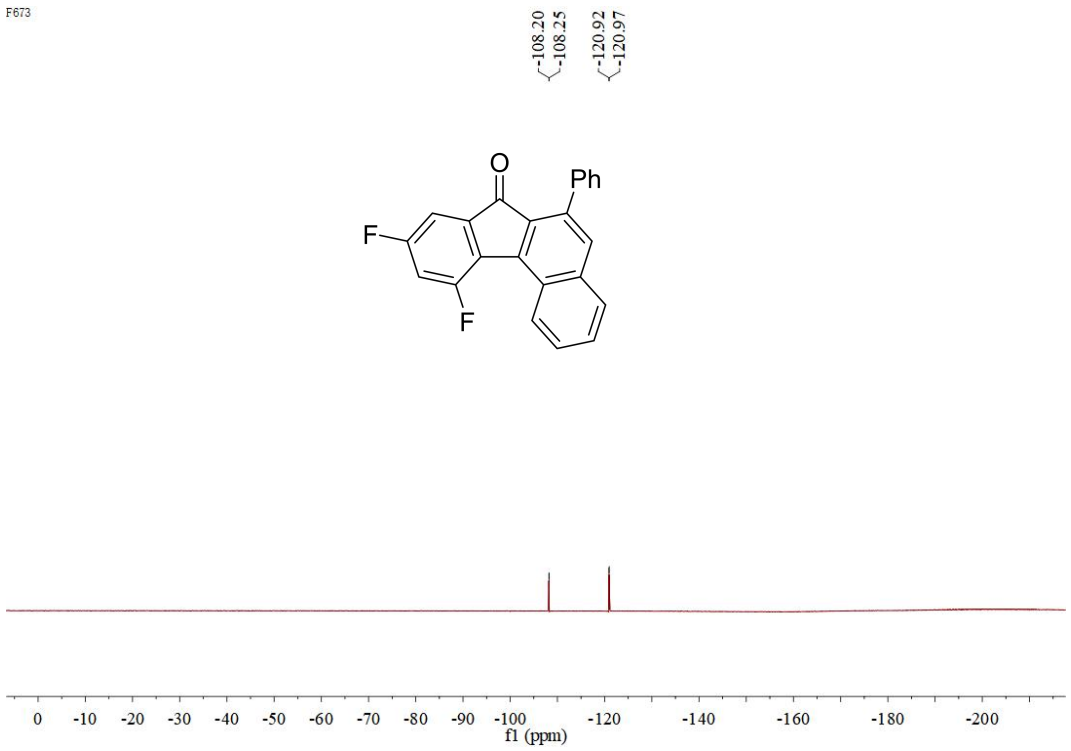




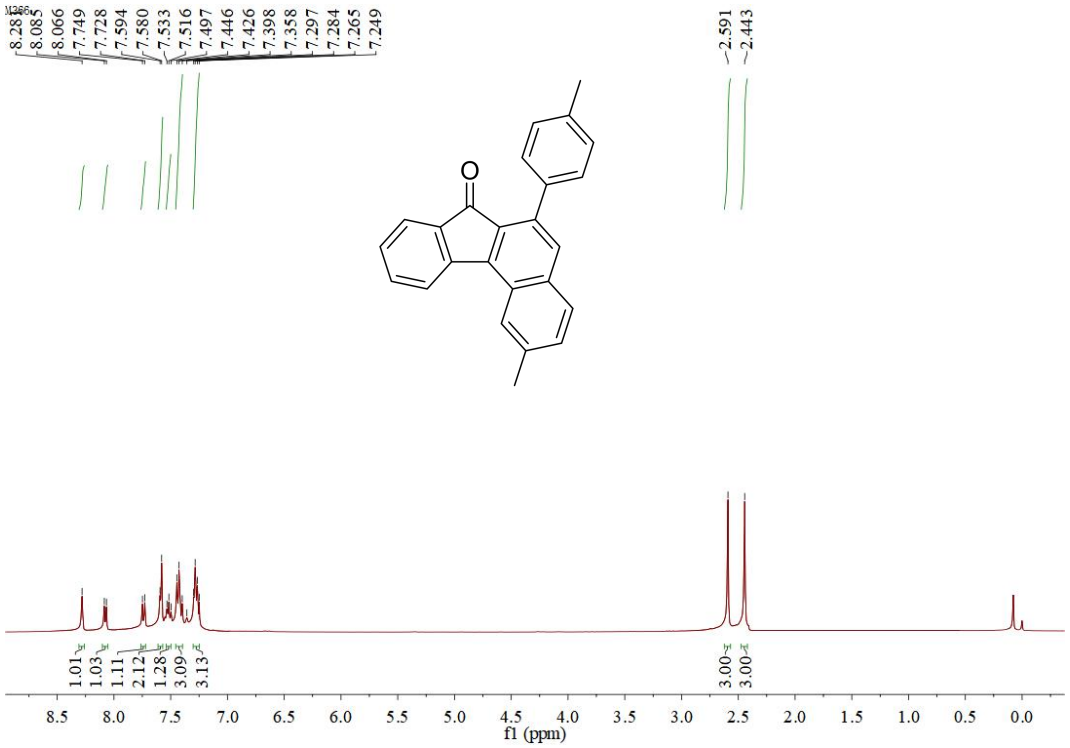
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3o

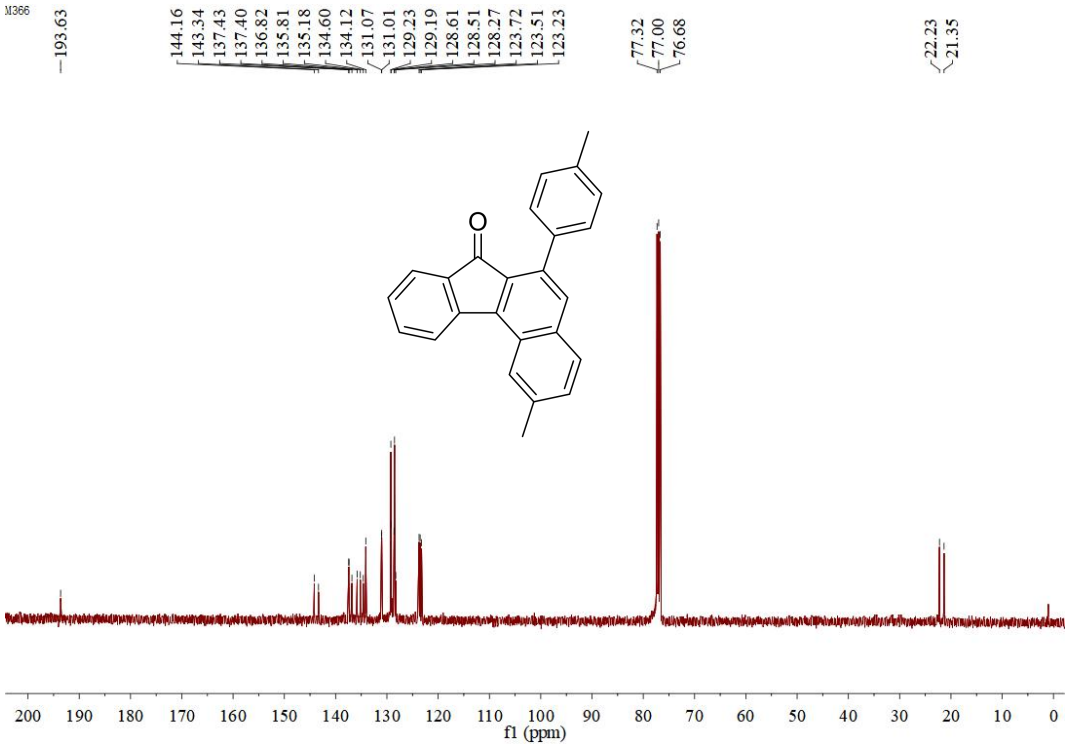


F673

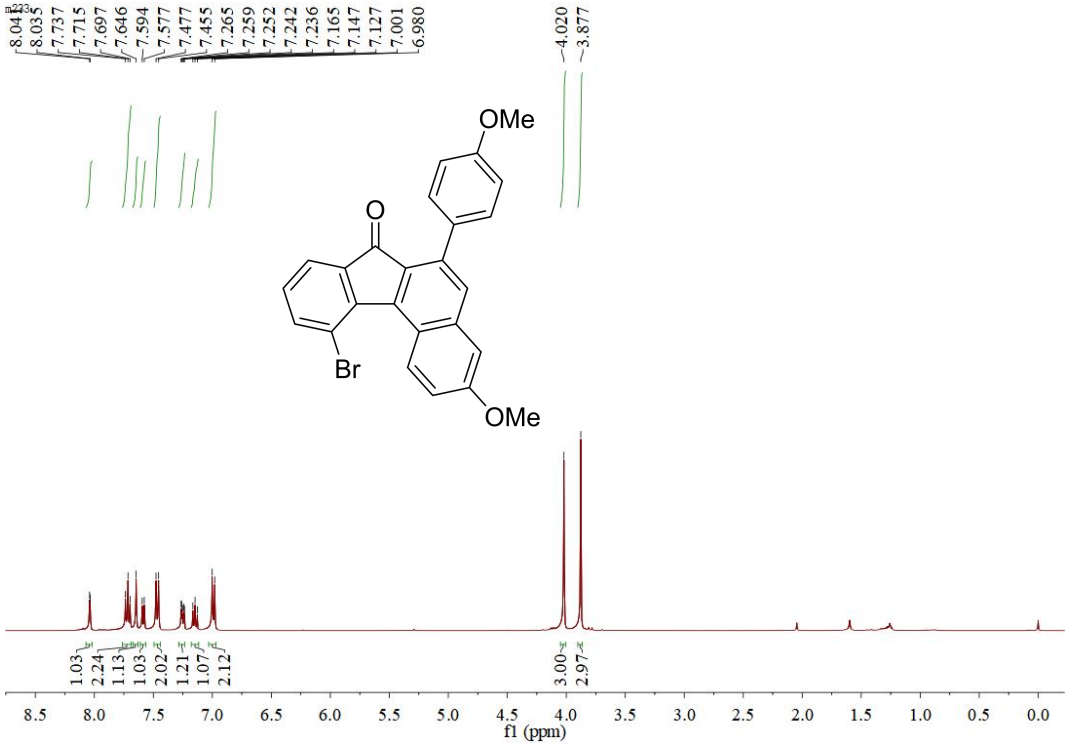

-108.20
-108.25
-120.92
-120.97
O
Ph
F
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

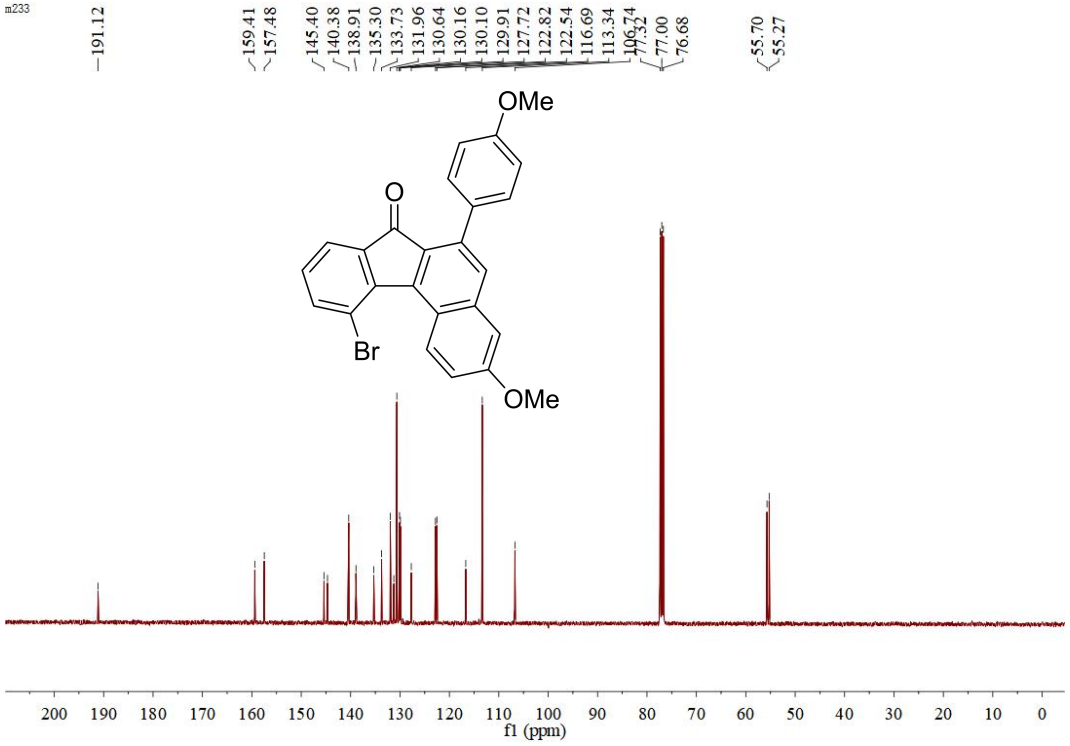
^{1}H NMR and ^{13}C NMR of 3p



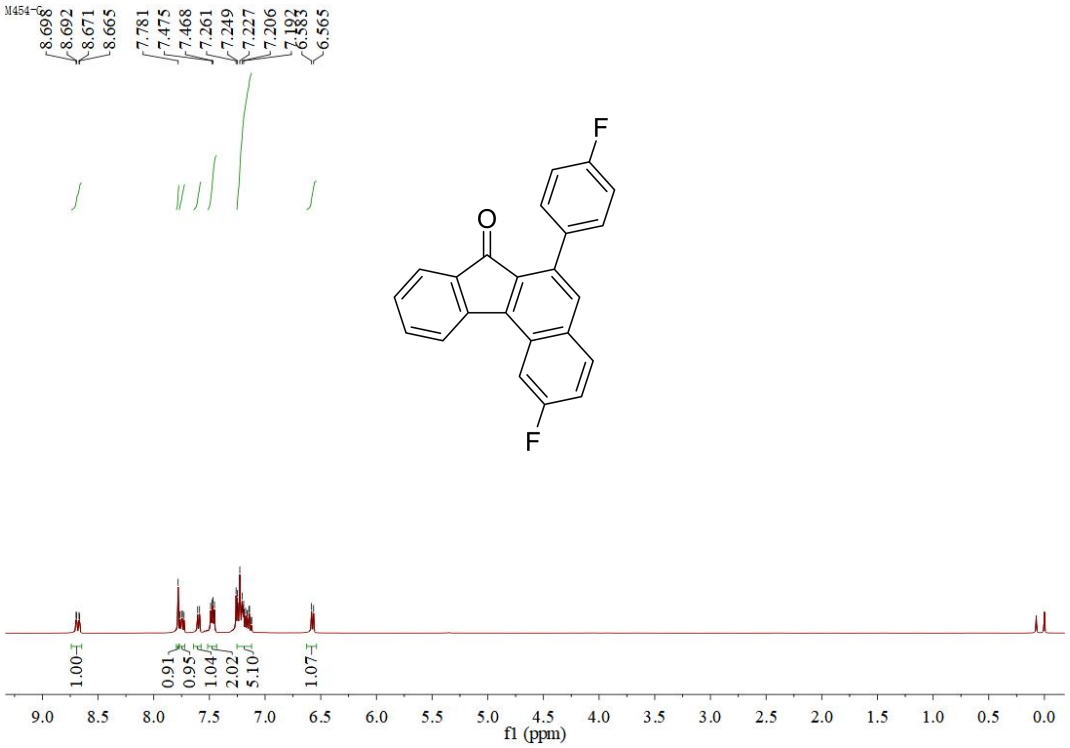


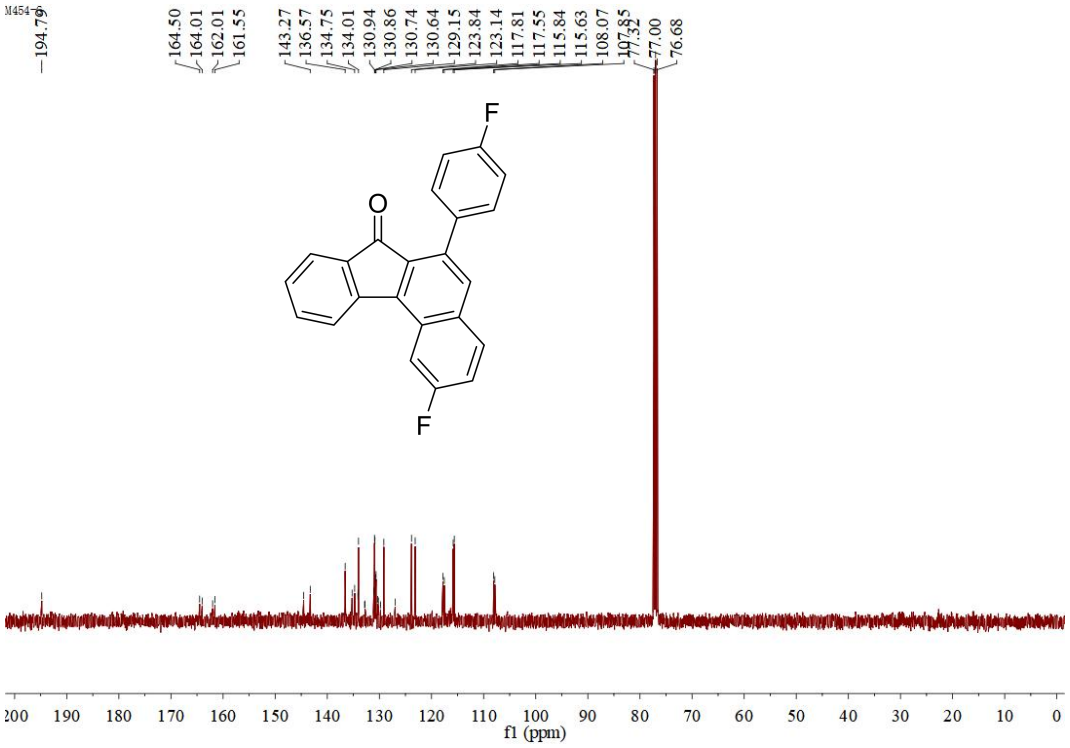
^{1}H NMR and ^{13}C NMR of 3q

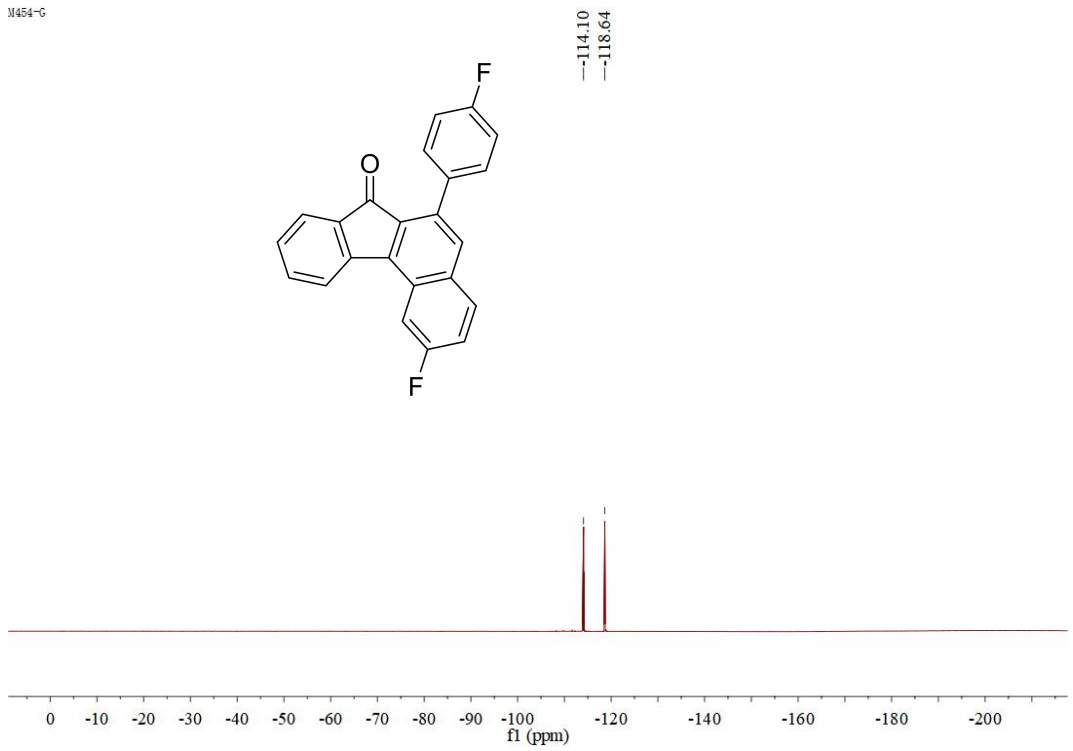




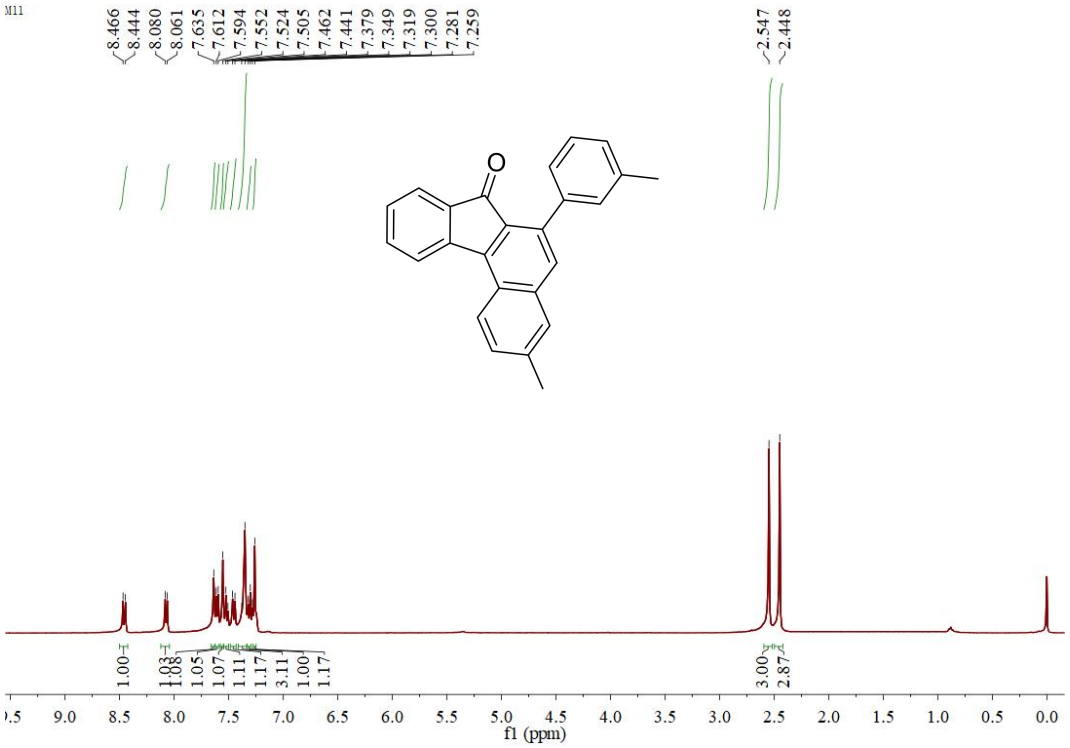
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 3r

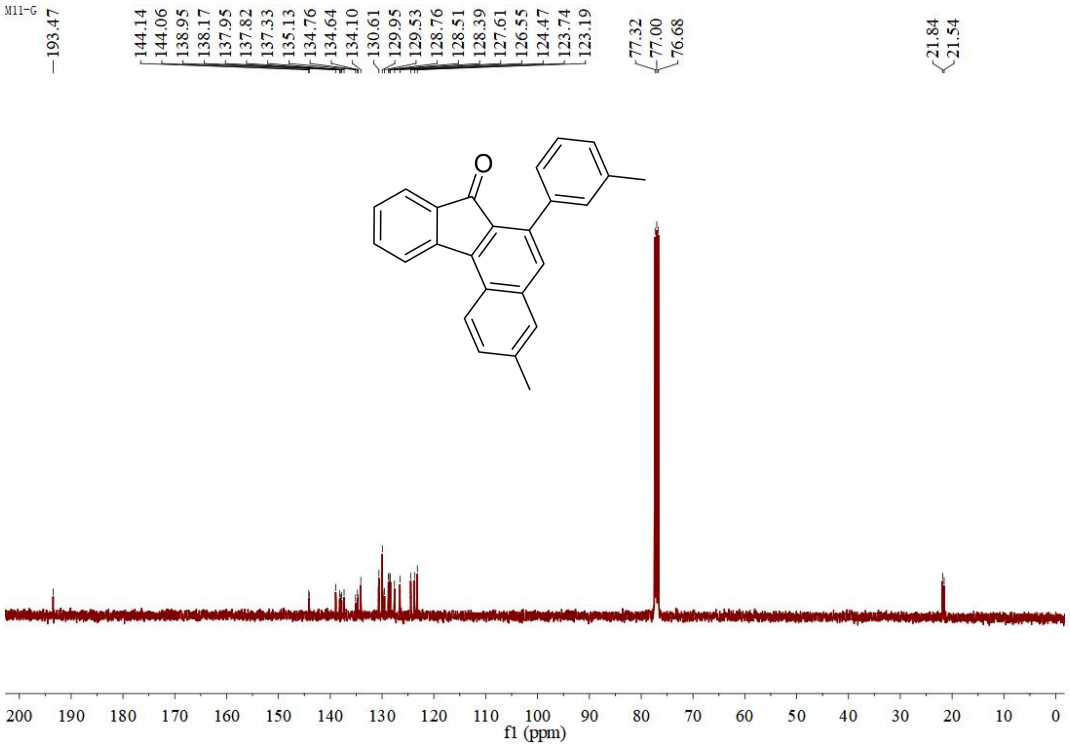




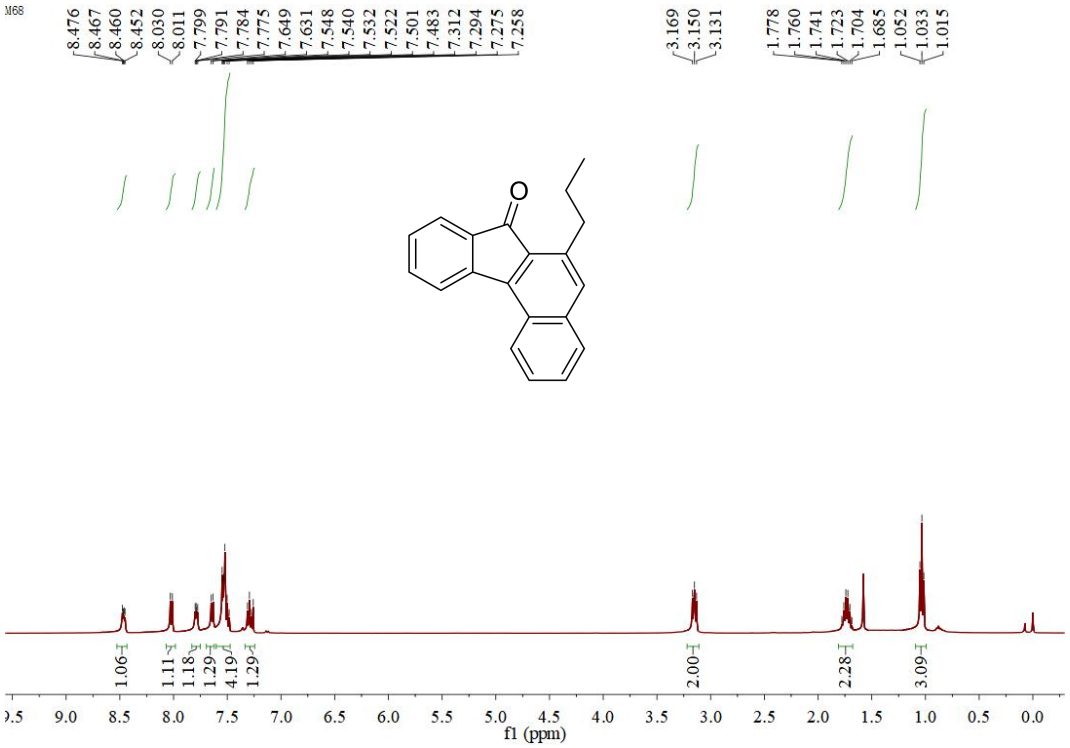

M454-G
-114.10
-118.64
F
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

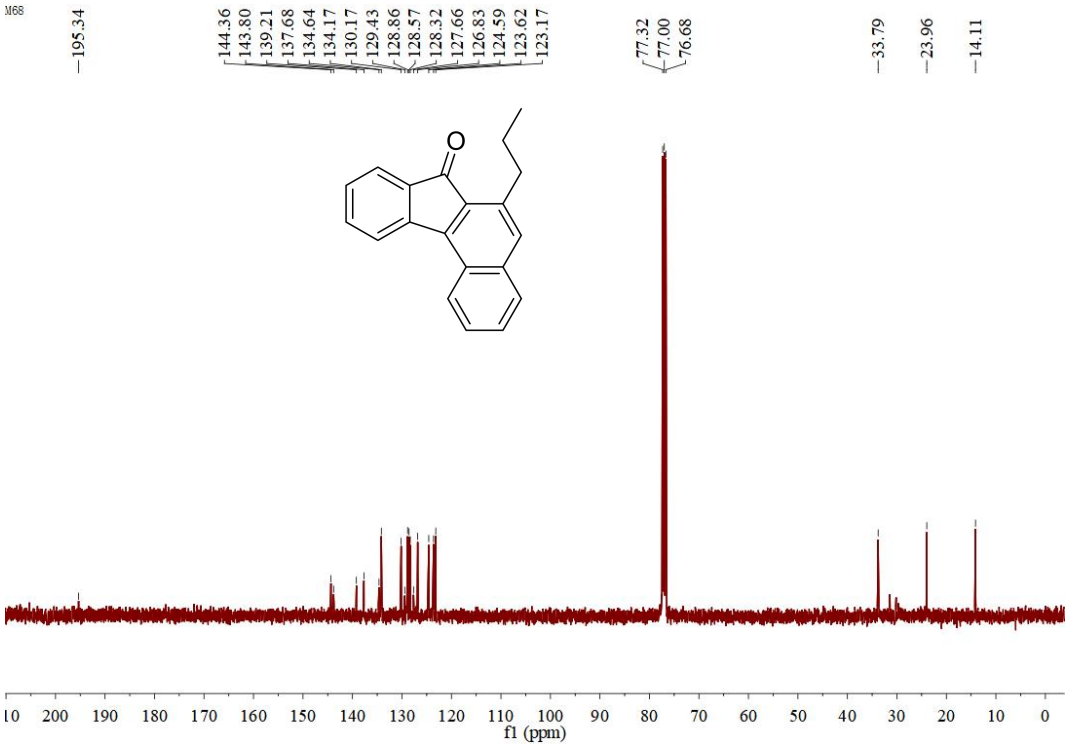
^{1}H NMR and ^{13}C NMR of 3s





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





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