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One-pot Synthesis of Multi-substituted Conjugated Dienones by Trapping Allene Carbocation with Active Ylides

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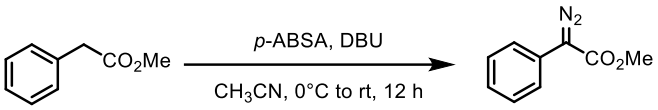
Table of Contents

1. General Information

All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Brucker spectrometers in $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High-resolution mass spectrometry (HRMS) was performed on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High Definition Mass Spectrometer. Yields for all compounds were combined yields for all isomers unless otherwise indicated. All reactions and manipulations were carried out under an N_2 atmosphere. All commercial anhydrous solvents were purchased from Alfa Aesar and used as such unless stated otherwise. 4 Å molecular sieves was dried in a Muffle furnace at 260 ºC for 5 h.

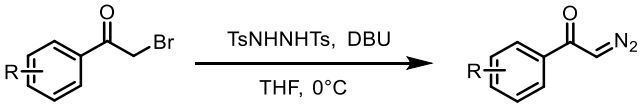
2. General Procedure

General procedure for the preparation of phenyl diazoester.[1]



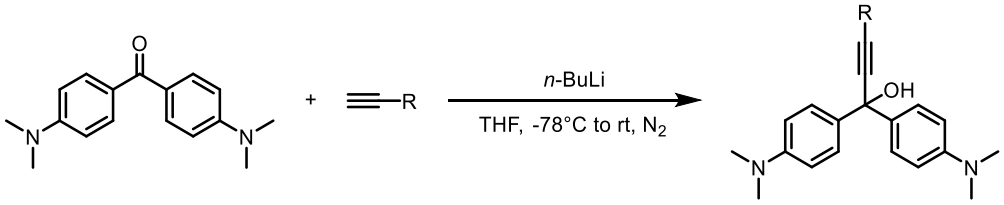
To a mixture of methyl phenylacetate (20 mmol) and tosyl azide (30 mmol) in anhydrous MeCN (15 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (30 mmol) was added slowly. The reaction mixture was stirred at room temperature for 12 h. Upon complete consumption of the starting materials, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (3 × 30 mL), washed by brine. The combined extracts were dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography (PE/EA, 50 :1) to afford the phenyl diazoester (3.1 g, 88% yield).

General procedure for the preparation of α-diazo ketone.[2]



To a mixture of 2-bromoacetophenones (5 mmol, 1.0 equiv) and *N*, *N*'-ditosylhydrazine (5.5 mmol, 1.1 equiv) in THF (30 mL) under N_2. This suspension was cooled to 0°C and DBU (7.5 mmol, 1.5 equiv) was added dropwise. After 30 minutes, the reaction mixture was poured into saturated aqueous sodium hydrogen carbonate solution, extracted with EA. The combined extracts were combined, washed with brine, dried with Na_2SO_4 and concentrated, then purified by flash chromatography to afford α-diazo ketones.

General procedure for Propargylic alcohols.[3]

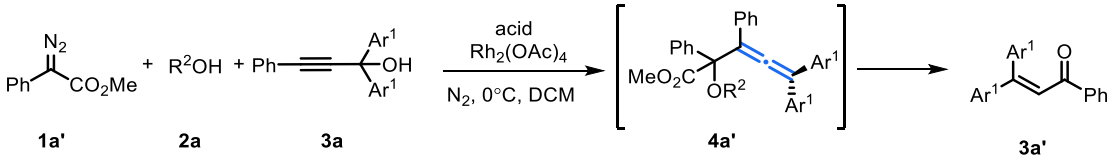


To the mixture of corresponding terminal alkyne1 (10 mmol) in THF (15 mL), *n*-BuLi (13 mmol, 6 mL, 2.5M in hexanes) was added dropwise at –78 °C. After 30 minutes, aromatic benzophenone (8 mmol) in THF (20 mL) was added at the same temperature and the mixture was slowly warmed to

room temperature stirred for 16 h. Checking the consumption of raw material, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (4 mL), extracted with EA (3 × 30 mL) The combined extracts were washed with brine, dried with Na_2SO_4. After evaporation of the solvent under the reduced pressure, the residue was resolved in DCM and PE by stirred it at 25 ℃ for 3 h after being filtered to give the propargylic alcohols.

3. Optimization of the reaction conditions

(a) Table S1. Screen of reaction with phenyl diazoester.



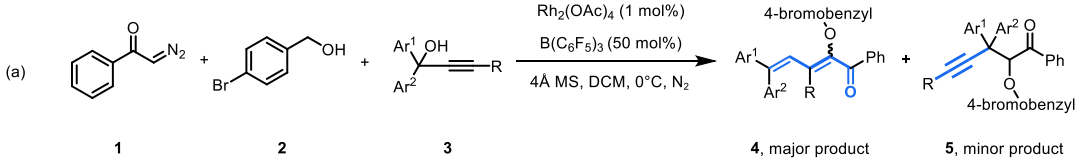
1a' **2a** **3a** **4a'** **3a'**

Ar^1 = *p*-(*N*,*N*-dimethylamino)phenyl
R^2=*p*-bromobenzyl

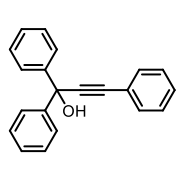
entry	acid	acid (xmol%)	**4a'** conv. (%)	**4a'** yield (%)	**3a'** yield (%) [d]
1	$Sc(OTf)_3$	10	<10	<10	_
2	TsOH	10	<10	<10	_
3	rac-PA	10	14	<10	_
4	*p*-FPhB$(OH)_2$	10	20	<10	_
5	*p*-FPhB$(OH)_2$	50	36	<10	_
6	*p*-FPhB$(OH)_2$	80	48	<10	_
7	*p*-FPhB$(OH)_2$	100	62	<10	_
8	*p*-FPhB$(OH)_2$	120	71	<10	_
9	*p*-FPhB$(OH)_2$	150	77	<10	_
10	*p*-FPhB$(OH)_2$	180	77	<10	_
11[c]	*p*-FPhB$(OH)_2$	150	80	<10	72

[a] The reaction was carried out on a 0.2 mmol scale. To a mixture of propargylic alcohols **3a** (0.2 mmol) and benzyl alcohols **2a** (0.3 mmol) in 1.5 mL of solvent and phenyl diazoester **1a** (0.3 mmol) in 1.5 mL of solvent was added via a syringe pump at room temperature stirred for 4 h. [b]Used 1 mol% catalyst. [c]Used 4Å molecular sieves as additive. [d]**3a'** convert from the decomposition of **4a'** during the process of column chromatography.

(b) Table S2. Screen the scope of propargylic alcohol.

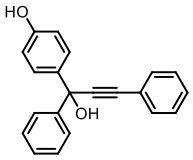


1 **2** **3** **4**, major product **5**, minor product



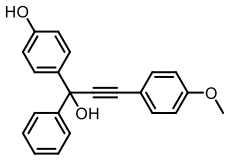
3a

trace



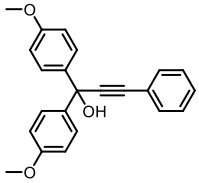
3b

<10% yield



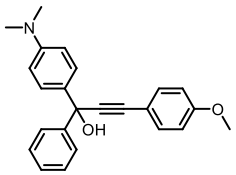
3c

<10% yield



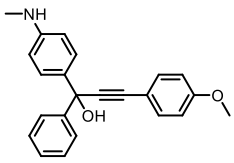
3d

<10% yield



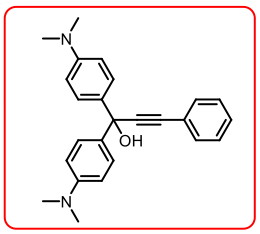
3e

<20% yield



3f

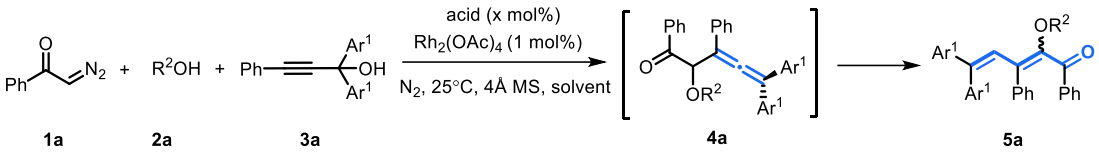
trace



3g

82% yield of **4**, ~10% yield of **5**

(c) Table S3. Screen of reaction with *α*-diazo ketone.



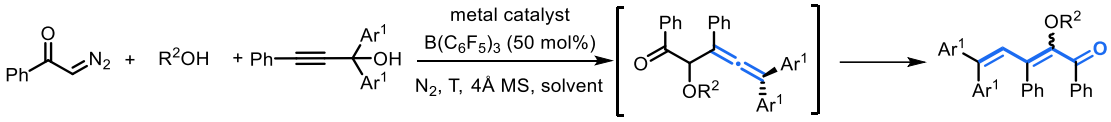
1a **2a** **3a** **4a** **5a**

Ar^1 = *p*-(*N*,*N*-dimethylamino)phenyl
R^2=*p*-bromobenzyl

entry	acid	acid (x mol%)	**4a** yield (%)	**5a** yield (%) [b]
1	$Sc(OTf)_3$	50	<10	<10
2	$Zn(OTf)_2$	50	<10	<10
3	$Yb(OTf)_3$	50	<10	<10
4	proline	50	N.R.	N.R.
5	TsOH	50	<10	<10
6	L-tartaric acid	50	<10	27
7	rac-PA	50	<10	18
8	$PhB(OH)_2$	50	<10	30
9	*p*-$FPhB(OH)_2$	50	<10	33
10	*p*-$FPhB(OH)_2$	150	<10	58
11	$B(C_6F_5)_3$	50	<10	66
12	$B(C_6F_5)_3$	20	<10	29
13	$B(C_6F_5)_3$	40	<10	50
14	$B(C_6F_5)_3$	60	<10	65

[a] The reaction was carried out on a 0.2 mmol scale. To a mixture of propargylic alcohols **3a** (0.2 mmol) and benzyl alcohols **2a** (0.3 mmol) in 1.5 mL of solvent and *α*-diazo ketone **1a** (0.3 mmol) in 1.5 mL of solvent was added *via* a syringe pump at room temperature stirred for 4 h. The solvent is anhydrous, and 4Å molecular sieve was used as an additive. [b] **4a** is not stable and the yield was determined by LC-MS.

(d) Table S3. Screen of reaction with *α*-diazo ketone.



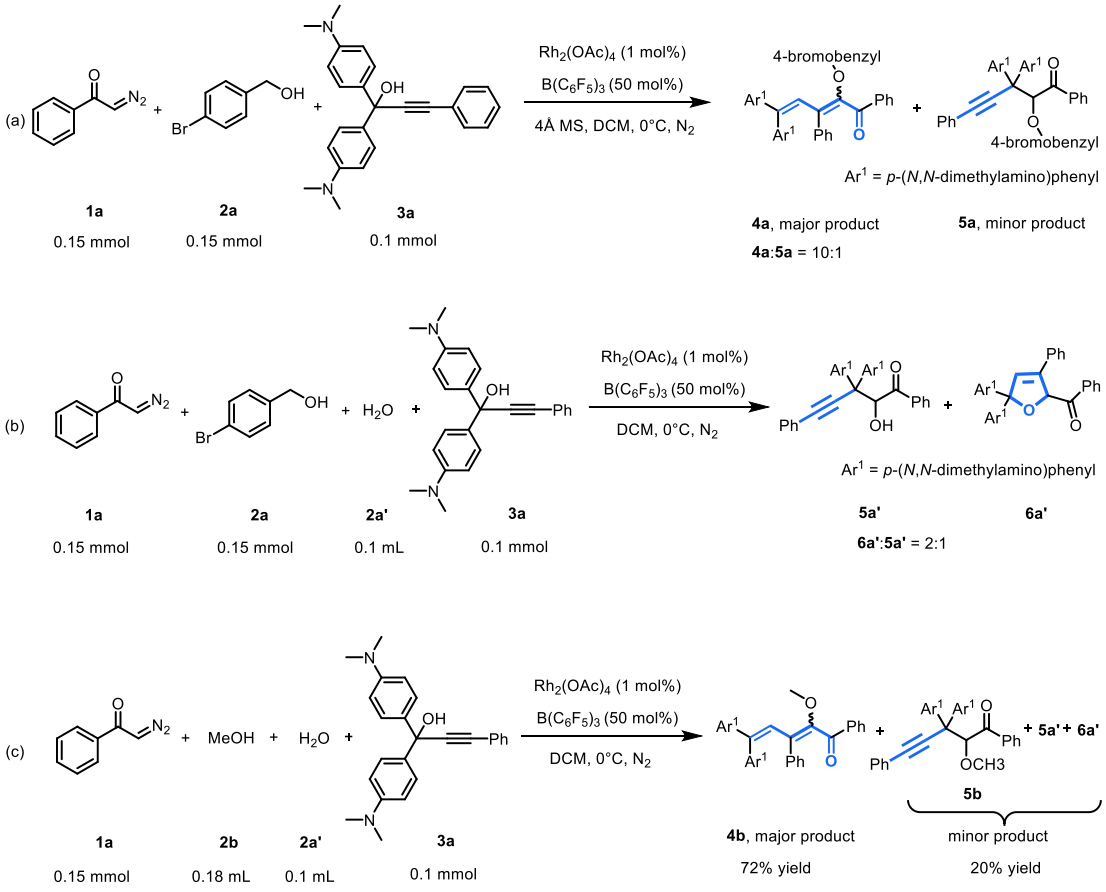
1a **2a** **3a** **4a** **5a**

Ar^1 = *p*-(*N*,*N*-dimethylamino)phenyl
R^2=*p*-bromobenzyl

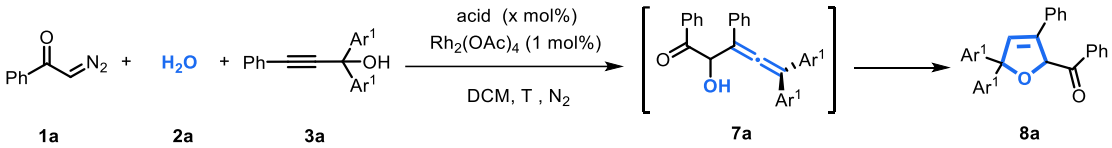
entry	metal catalyst	T (°C)	solvent	**4a** yield (%)	**5a** yield (%)
1	$Rh_2(OAc)_4$	25	DCM	<10	66
2	$Rh_2(OAc)_4$	10	DCM	<10	73
3	$Rh_2(OAc)_4$	0	DCM	<10	82
4	$Rh_2(OAc)_4$	-10	DCM	<10	79
5	$Rh_2(OAc)_4$	0	DCE	<10	74
6	$Rh_2(OAc)_4$	0	THF	<10	51
7	$Rh_2(OAc)_4$	0	Toluene	<10	43
8	$[Rh(COD)Cl]_2$	0	DCM	trace	trace
9	$[Pd(allyl)Cl]_2$	0	DCM	<10	34
10	$Rh_2(esp)_2$	0	DCM	<10	80

[a] The reaction was carried out on a 0.2 mmol scale. To a mixture of propargylic alcohols **3a** (0.2 mmol) and benzyl alcohols **2a** (0.3 mmol) in 1.5 mL of solvent and *α*-diazo ketones **1a** (0.3 mmol) in 1.5 mL of solvent was added *via* a syringe pump stirred for 4 h. [b] Used 1 mol % catalyst.

(e) Table S4. Test the effect of water on the reaction.



(f) Table S5. Screen of reaction with water.



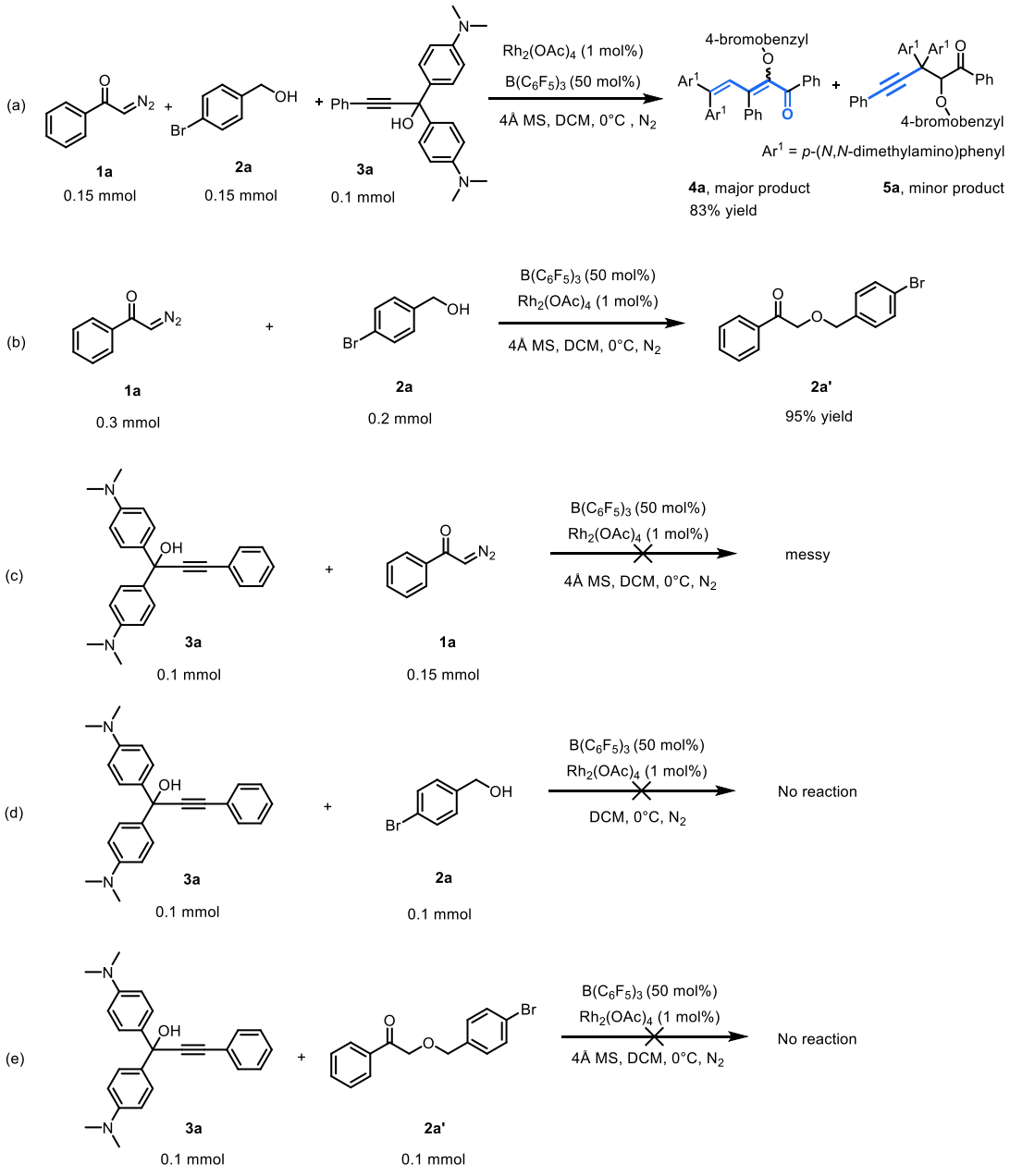
Ar^1 = *p*-(*N*,*N*-dimethylamino)phenyl

entry	acid (x mol%)	T (°C)	**7a** yield (%)	**8a** yield (%)
1	rac-PA (50)	0	<10	22
2	$B(C_6F_5)_3$ (50)	0	<10	77
3	$PhB(OH)_2$ (150)	0	<10	83
4	*p*-$FPhB(OH)_2$ (150)	0	<10	91
5	*p*-$FPhB(OH)_2$ (150)	-10	<10	74
6	*p*-$FPhB(OH)_2$ (150)	10	<10	82
7	*p*-$FPhB(OH)_2$ (150)	25	<10	75

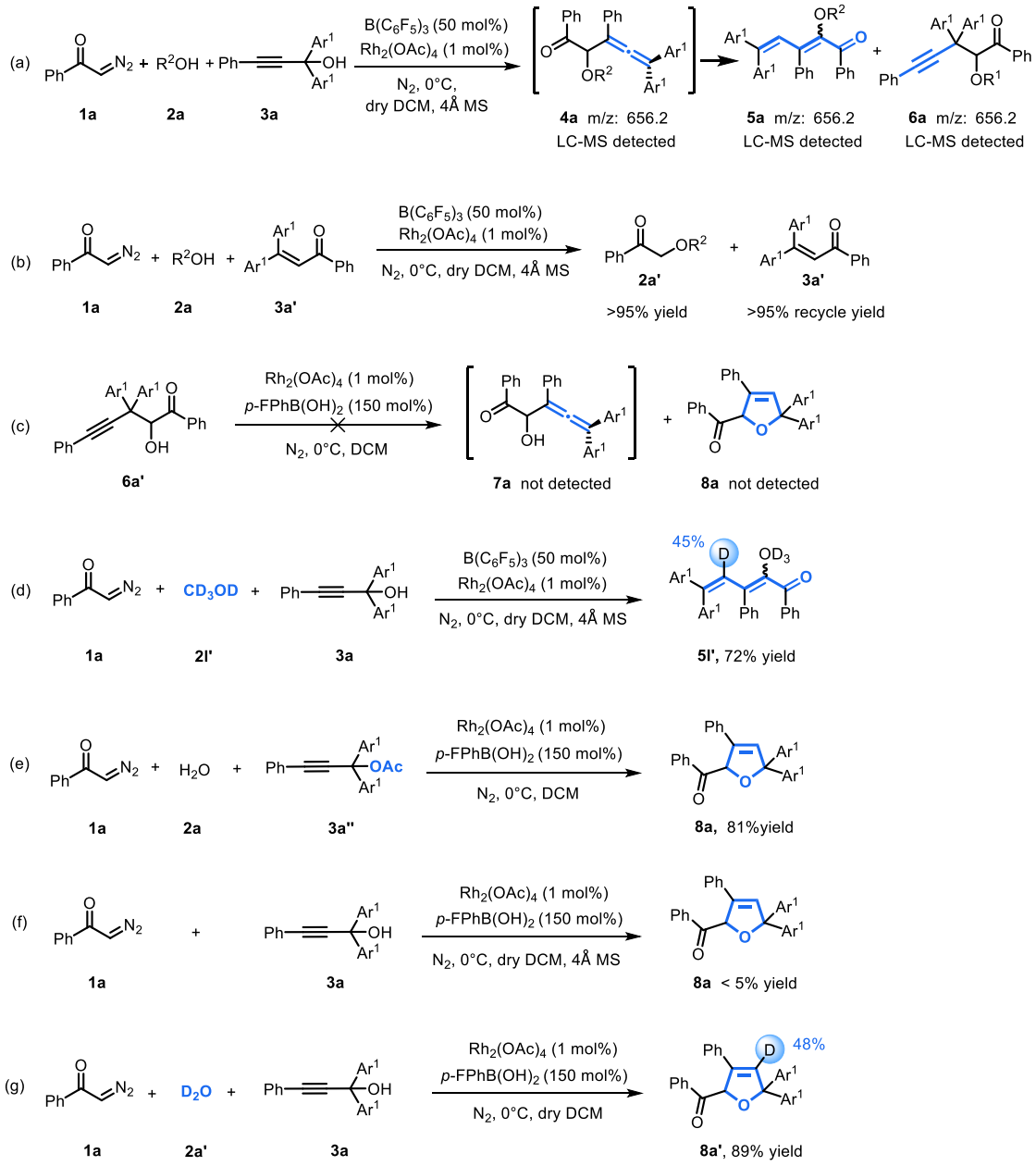
[a]The reaction was carried out on a 0.2 mmol scale. To a mixture of propargyl alcohols **3a** (0.2 mmol) and benzyl alcohols **2a** (0.3 mmol) in 1.5 mL of solvent and *α*-diazo ketones **1a** (0.3 mmol) in 1 mL of solvent was added *via* a syringe pump stirred for 4 h.

4.1 Control experiment

Scheme S1.

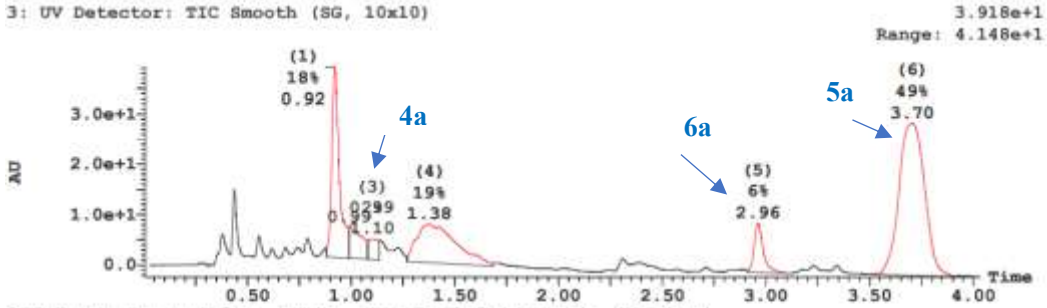


Scheme S2.



Ar^1 = *p*-(*N*,*N*-dimethylamino)phenyl; R^2=*p*-bromobenzyl

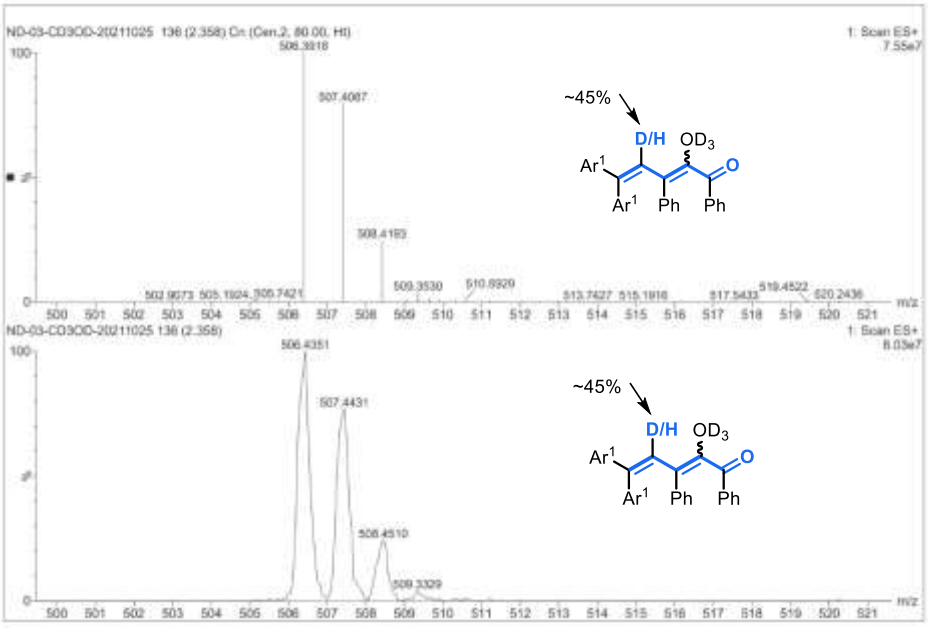
4.2 Figure S1.



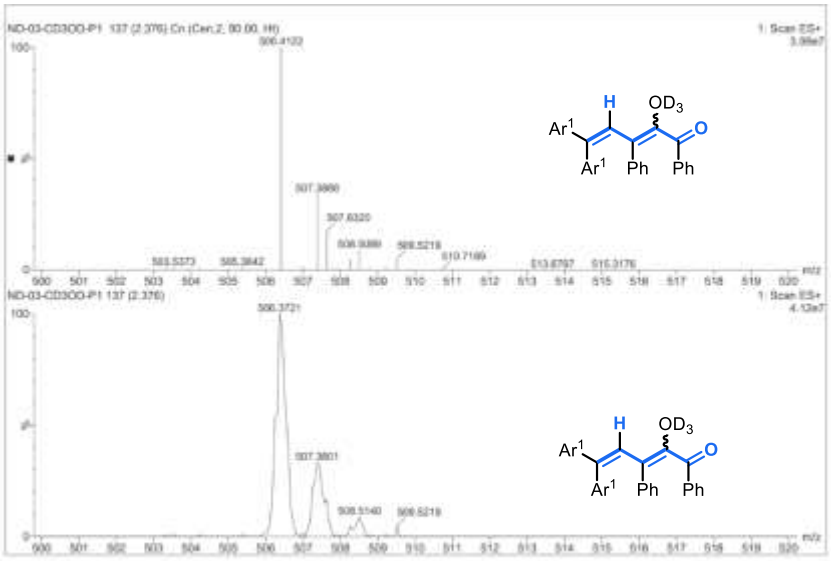
Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		0.92	2e+006	18.48	0	4e+007	
2		0.99	4e+005	4.95	0	6e+006	
3		1.10	2e+005	2.44	0	4e+006	
4		1.38	2e+006	19.42	0	8e+006	
5		2.96	5e+005	5.75	0	1e+007	
6		3.70	4e+006	48.96	0	3e+007	

4.3 Figure S2.

LC-MS spectra of CD_3OD experiment.

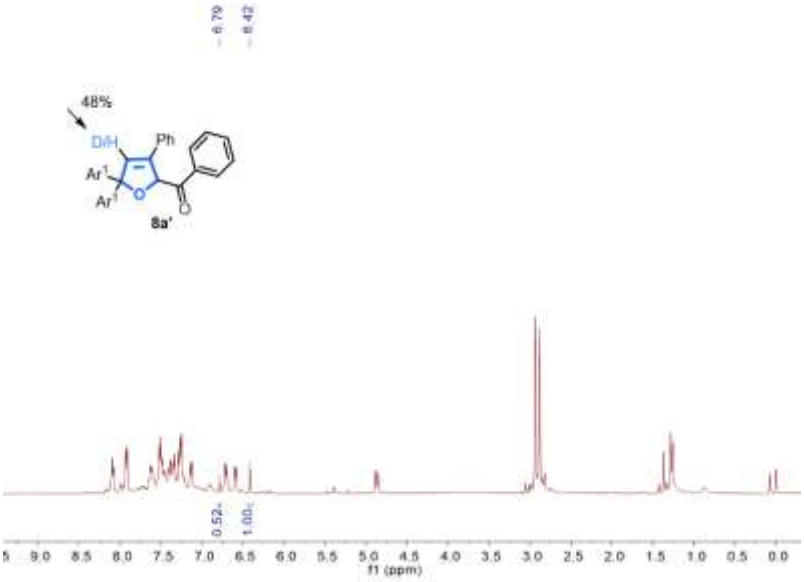


LC-MS spectra of CD_3OH experiment.



4.4 Figure S3.

^1H NMR spectra of D_2O experiment.



5. References.

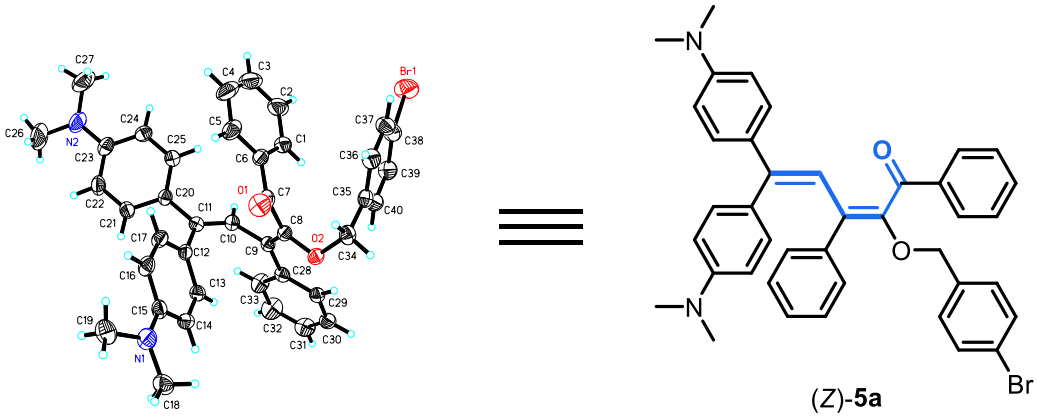
(1) H. Keipour, A. Jalba, L. Delage-Laurin and T. Ollevier, *J. Org. Chem.* 2017, **82**, 3000–3010.

(2) Z. L. Xia, J. D. Hu, Y. Q. Gao, Q. Z. Yao and W. Q. Xie, *Chem. Commun.* 2017, **53**, 7485–7488.

(3) H. Zhang, H. Tanimoto, T. Morimoto, Y. Nishiyama and K. Kakiuchi, *Org. Lett.* 2013, **15**, 5222–5225.

6. X-ray Diffraction Parameters and Data

Figure S4.



Bond precision: C-C = 0.0044 A Wavelength=0.71073

Cell: a=9.9024(2) b=10.9990(3) c=16.8991(5)
alpha=107.609(1) beta=96.177(1) gamma=104.848(1)

Temperature: 293 K

	Calculated	Reported
Volume	1661.18(8)	1661.18(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C40 H37 Br N2 O2	C40 H37 Br N2 O2
Sum formula	C40 H37 Br N2 O2	C40 H37 Br N2 O2
Mr	657.62	657.62
Dx,g cm-3	1.315	1.315
Z	2	2
Mu (mm-1)	1.275	1.275
F000	684.0	684.0
F000'	683.66	
h,k,lmax	12,13,20	12,13,20
Nref	6541	6520
Tmin,Tmax	0.858,0.926	0.607,0.746
Tmin'	0.858	

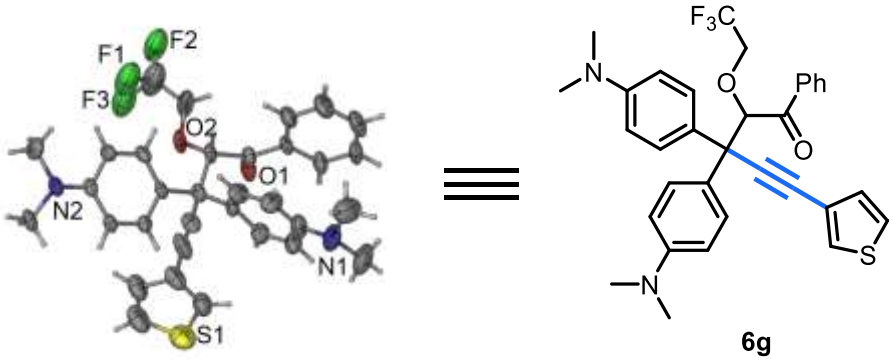
Correction method= # Reported T Limits: Tmin=0.607 Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.999

R(reflections)= 0.0456(4465) wR2(reflections)= 0.1191(6520)

S = 1.013 Npar= 410

Figure S5.



CCDC No.: 2110702

Bond precision: C-C = 0.0086 A Wavelength=1.54184

Cell: a=22.6154(10) b=11.0222(3) c=25.2859(12)
alpha=90 beta=109.234(5) gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	5951.2(5)	5951.2(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C33 H28 F3 N2 O2 S, C33 H30 F3 N2 O2 S [+ solvent]	0.5(C33 H28 F3 N2 O2 S), 0.5(C33 H30 F3 N2 O2 S)
Sum formula	C66 H58 F6 N4 O4 S2 [+ solvent]	C33 H29 F3 N2 O2 S
Mr	1149.28	574.64
Dx,g cm-3	1.283	1.283
Z	4	8
Mu (mm-1)	1.399	1.399
F000	2400.0	2400.0
F000'	2410.15	
h,k,lmax	27,13,30	27,13,30
Nref	10615	10529
Tmin,Tmax	0.831,0.882	0.400,1.000
Tmin'	0.556	

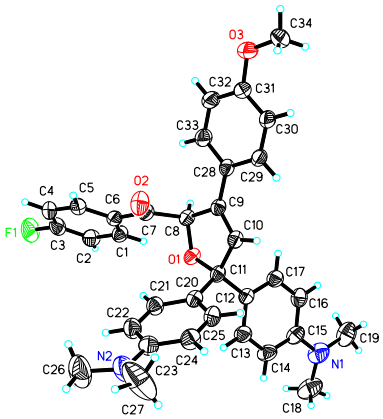
Correction method= # Reported T Limits: Tmin=0.400 Tmax=1.000 AbsCorr = MULTI-SCAN

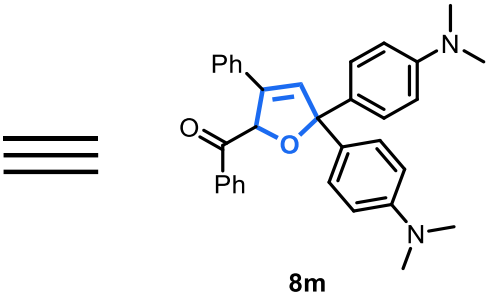
Data completeness= 0.992 Theta(max)= 67.077

R(reflections)= 0.1198(7586) wR2(reflections)= 0.2966(10529)

S = 1.099 Npar= 747

Figure S6.





8m

CCDC No.: 2064278

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=20.3167(8) b=11.1475(5) c=13.7918(6)
alpha=90 beta=109.564(1) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2943.2(2)	2943.2(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C34 H33 F N2 O3	C34 H33 F N2 O3
Sum formula	C34 H33 F N2 O3	C34 H33 F N2 O3
Mr	536.62	536.62
Dx,g cm-3	1.211	1.211
Z	4	4
Mu (mm-1)	0.082	0.082
F000	1136.0	1136.0
F000'	1136.52	
h,k,lmax	24,13,16	24,13,16
Nref	5490	5479
Tmin,Tmax	0.986,0.991	0.652,0.746
Tmin'	0.985	

Correction method= # Reported T Limits: Tmin=0.652 Tmax=0.746 AbsCorr = MULTI-SCAN

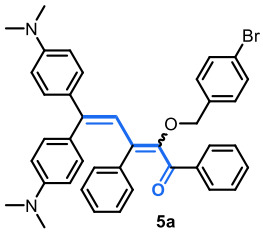
Data completeness= 0.998 Theta(max)= 25.494

R(reflections)= 0.0516(3286) wR2(reflections)= 0.1329(5479)

S = 1.023 Npar= 367

7. Characterization Data of Compounds[a]

2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-1,3-diphenylpenta-2,4-dien-1-one (5a)

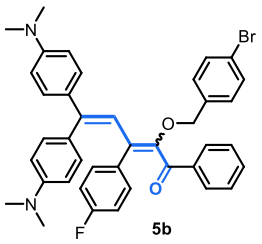


5a

Orange solid, 82% yield, *Z*/*E* isomer (50:50) ratio. (*Z*)-**5a**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.29 (d, 1H), 7.25 – 7.12 (m, 6H), 6.89 – 6.83 (m, 2H), 6.82 – 6.76 (m, 3H), 6.74 – 6.63 (m, 5H), 6.31 (d, *J* = 8.3 Hz, 2H), 4.73 (s, 2H), 2.99 (s, 6H), 2.80 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.3, 149.8, 148.5, 147.7, 137.9, 137.2, 136.4, 133.7, 132.4, 131.8, 131.6, 131.5, 131.3, 130.8, 130.3, 130.3, 130.1, 129.6, 129.4, 129.3, 128.7, 128.3, 128.0, 127.8, 127.1, 126.7, 122.1, 120.4, 111.8, 111.6, 71.7, 40.6, 40.5.

Mixture of (*Z*/*E*) isomers of **5a**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.1 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.34 (m, 5H), 7.33 – 7.28 (m, 3H), 7.24 – 7.15 (m, 6H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.80 (t, 3H), 6.73 – 6.69 (m, 4H), 6.67 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.48 (dd, *J* = 15.0, 8.5 Hz, 4H), 6.32 (d, *J* = 8.4 Hz, 2H), 5.96 (s, 1H), 4.74 (s, 2H), 4.62 (s, 2H), 3.00 (s, 6H), 2.92 (d, *J* = 3.9 Hz, 12H), 2.81 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1, 193.3, 150.3, 150.1, 149.8, 148.5, 148.4, 147.9, 147.7, 139.1, 138.0, 137.7, 137.3, 136.4, 136.0, 133.7, 132.4, 132.1, 131.8, 131.6, 131.5, 131.3, 130.8, 130.4, 130.3, 130.1, 129.6, 129.4, 129.4, 128.7, 128.4, 128.0, 127.9, 127.8, 127.4, 127.1, 126.8, 122.1, 121.9, 121.9, 120.4, 111.8, 111.6, 111.4, 72.5, 71.7, 40.7, 40.5, 40.4, 40.4. HRMS(ESI) Calcd. for $C_{40}H_{38}BrN_2O_2$ $(M+H)^+$ 657.2111, found 657.2107.

2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-3-(4-fluorophenyl)-1-phenylpenta-2,4-dien-1-one (5b)



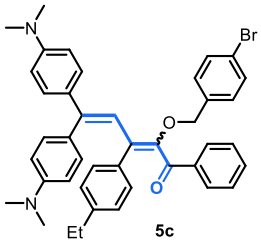
5b

Orange solid, 77% yield, *Z*/*E* isomer (56:44) ratio. (*Z*)-(**5b**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (s, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.21 – 7.13 (m, 4H), 6.85 (s, 1H), 6.76 (t, *J* = 6.8 Hz, 2H), 6.69 (dd, *J* = 16.0, 8.2 Hz, 4H), 6.34 (t, *J* = 8.5 Hz, 2H), 6.28 (d, *J* = 8.2 Hz, 2H), 4.79 (s, 2H), 2.99 (s, 6H), 2.80 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.9, 162.6, 160.1, 150.4, 149.9, 148.7, 148.1, 137.9, 136.2, 133.2 (d, *J* = 3.1 Hz), 133.0, 132.5, 132.0, 132.0, 131.6, 130.3, 129.4, 129.3, 128.4, 127.9, 122.2, 120.2, 114.0, 113.7, 111.8, 111.5, 71.8, 40.6, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.01 – -116.23 (m).

(*E*)-(**5b**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 6.6 Hz, 2H), 7.50 (d, J = 7.4 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.01 – 6.91 (m, 4H), 6.85 (d, J = 7.7 Hz, 2H), 6.65 (d, J = 7.3 Hz, 2H), 6.47 (d, J = 8.2 Hz, 4H), 6.03 (s, 1H), 4.58 (s, 2H), 2.91 (s, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.3, 163.4, 160.9, 150.2, 149.8, 148.4, 147.8, 138.8, 135.7, 133.6 (d, J = 3.3 Hz), 132.3, 131.6, 131.4, 131.3, 130.8, 130.4, 130.1, 129.3, 128.8, 128.4, 127.4, 122.0, 121.3, 114.8, 114.6, 111.6, 111.4, 72.4, 40.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.94 – -114.12 (m).

Mixture of (*Z*/*E*) isomers of **5b**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 7.6 Hz, 1.6H), 7.61 – 7.52 (m, 4H), 7.50 (d, J = 7.5 Hz, 0.8H), 7.44 (d, J = 6.3 Hz, 2H), 7.40 – 7.33 (m, 3.5H), 7.31 (d, J = 7.4 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.21 – 7.14 (m, 4H), 6.98 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.8 Hz, 1H), 6.88 – 6.82 (m, 2.6H), 6.80 – 6.73 (m, 2.3H), 6.71 (d, J = 6.6 Hz, 2H), 6.66 (t, J = 7.1 Hz, 3.5H), 6.46 (d, J = 7.3 Hz, 3H), 6.34 (t, J = 8.3 Hz, 2H), 6.29 (d, J = 7.3 Hz, 2H), 6.03 (s, 0.8H), 4.79 (s, 2H), 4.58 (s, 1.6H), 2.99 (s, 6H), 2.90 (s, 9.6H), 2.79 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.9, 193.3, 163.4, 162.6, 160.9, 160.2, 150.4, 150.2, 149.9, 149.8, 148.7, 148.4, 148.1, 147.8, 138.8, 137.9, 136.2, 135.7, 133.6 (d, J = 3.3 Hz), 133.2 (d, J = 3.3 Hz), 133.0, 132.5, 132.3, 132.1, 132.0, 131.6, 131.4, 131.3, 130.8, 130.4, 130.4, 130.1, 129.4, 129.3, 129.3, 128.8, 128.4, 128.4, 127.9, 127.4, 122.2, 122.0, 121.3, 120.2, 114.8, 114.6, 114.0, 113.8, 111.8, 111.6, 111.5, 111.4, 72.4, 71.9, 40.6, 40.5, 40.4, 40.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.91 – -114.09 (m), -115.99 – -116.13 (m). HRMS(ESI) Calcd. for $C_{40}H_{37}BrFN_2O_2$ $(M+H)^+$ 675.2017, found 675.2001.

2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-3-(4-ethylphenyl)-1-phenylpenta-2,4-dien-1-one (5c)

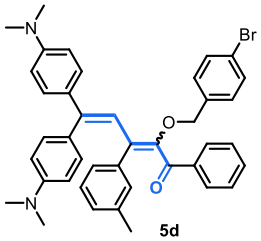


5c

Orange solid, 80% yield, *Z*/*E* isomer (46:54) ratio. Mixture of (*Z*/*E*) isomers of **5c**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1.7H), 7.48 (t, J = 7.3 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1.8H), 7.35 (d, J = 7.8 Hz, 4H), 7.27 (t, J = 7.4 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.16 (d, J = 8.7 Hz, 4H), 7.04 (d, J = 7.3 Hz, 2H), 6.92 (d, J = 7.5 Hz, 2H), 6.81 – 6.72 (m, 4H), 6.66 (d, J = 7.6 Hz, 1.7H), 6.56 (d, J = 7.7 Hz, 2H), 6.49 (t, J = 6.8 Hz, 3.5H), 6.44 (d, J = 7.6 Hz, 2H), 6.28 (d, J = 7.5 Hz, 1.7H), 5.91 (s, 1H), 4.71 (s, 1.7H), 4.61 (s, 2H), 2.97 (s, 5H), 2.89 (d, J = 2.6 Hz, 12H), 2.79 (s, 5H), 2.66 (q, J = 7.6 Hz, 2H), 2.25 (q, J = 7.6 Hz, 1.7H), 1.25 (t, J = 7.4 Hz, 3.2H), 0.92 (t, J = 7.6 Hz, 2.5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3, 193.4, 150.3, 150.1, 149.8, 149.6, 148.4, 148.2, 147.7, 147.7, 144.3, 142.6, 139.4, 138.2, 136.5, 136.1, 134.9, 134.4, 134.0, 132.2, 132.0, 131.9, 131.8, 131.6, 131.5, 131.4, 131.3, 130.8, 130.5, 130.3, 130.1, 129.7, 129.5, 129.4, 129.3, 128.7, 128.7,

128.3, 127.8, 127.6, 127.5, 126.6, 122.2, 122.1, 121.8, 120.5, 111.8, 111.6, 111.4, 72.5, 71.7, 40.5, 40.5, 40.4, 40.4, 28.8, 28.5, 15.6, 15.5. HRMS(ESI) Calcd. for $C_{42}H_{41}BrN_2O_2Na$ $(M+Na)^+$ 707.2244, found 707.2219.

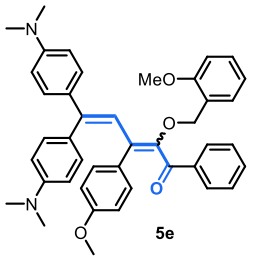
2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-1-phenyl-3-(m-tolyl)penta-2,4-dien-1-one (5d)



5d

Orange solid, 83% yield, *Z*/*E* isomer (44:56) ratio. Mixture of (*Z*/*E*) isomers of **5d**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.7 Hz, 1.6H), 7.49 (t, J = 8.1 Hz, 2.4H), 7.43 (d, J = 7.0 Hz, 3H), 7.39 – 7.32 (m, 4H), 7.29 (d, J = 7.8 Hz, 1H), 7.21 (t, J = 9.0 Hz, 4H), 7.15 (t, J = 7.5 Hz, 2H), 7.08 (d, J = 7.7 Hz, 1H), 7.03 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 10.0 Hz, 2.4H), 6.67 (d, J = 8.2 Hz, 2.4H), 6.59 (d, J = 8.7 Hz, 3.5H), 6.47 (dd, J = 14.5, 8.3 Hz, 4.8H), 6.30 (d, J = 8.2 Hz, 1.6H), 5.93 (s, 1H), 4.73 (s, 1.6H), 4.60 (s, 2H), 2.99 (s, 5H), 2.91 (d, J = 4.2 Hz, 12H), 2.80 (s, 5H), 2.30 (s, 3H), 1.91 (s, 2.5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1, 193.4, 150.3, 150.1, 149.7, 149.7, 148.4, 148.3, 147.9, 147.6, 139.2, 138.2, 137.5, 137.4, 136.9, 136.4, 136.1, 136.0, 134.1, 132.2, 132.0, 131.8, 131.5, 131.5, 131.5, 131.3, 130.8, 130.2, 130.1, 129.4, 129.3, 129.2, 128.8, 128.7, 128.7, 128.3, 127.9, 127.7, 127.4, 127.4, 127.0, 126.7, 122.1, 121.9, 120.4, 111.8, 111.6, 111.5, 111.4, 72.5, 71.7, 40.6, 40.5, 40.4, 40.4, 21.5, 20.8. HRMS(ESI) Calcd. for $C_{41}H_{40}BrN_2O_2$ $(M+H)^+$ 671.2268, found 671.2258.

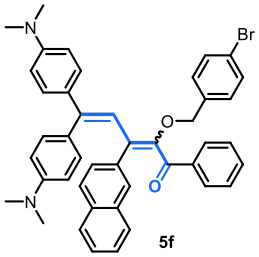
5,5-bis(4-(dimethylamino)phenyl)-2-((2-methoxybenzyl)oxy)-3-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (5e)



5e

Orange solid, 84% yield, *Z*/*E* isomer (45:55) ratio. Mixture of (*Z*/*E*) isomers of **5e**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 4H), 7.66 (d, J = 6.8 Hz, 1.6H), 7.45 (t, J = 7.3 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.30 (q, J = 7.3 Hz, 4H), 7.23 – 7.18 (m, 3H), 7.15 (d, J = 8.1 Hz, 2H), 6.99 (s, 1H), 6.90 (d, J = 8.1 Hz, 3H), 6.84 – 6.76 (m, 5H), 6.71 (d, J = 8.4 Hz, 3.3H), 6.63 (t, J = 7.9 Hz, 4H), 6.46 (d, J = 9.3 Hz, 4H), 6.26 (d, J = 8.6 Hz, 1.7H), 6.19 (d, J = 8.4 Hz, 1.6H), 5.92 (s, 1H), 4.89 (s, 1.6H), 4.75 (s, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 3.64 (s, 2.4H), 3.51 (s, 2.4H), 2.97 (s, 5H), 2.90 (s, 12H), 2.77 (s, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.2, 193.3, 159.1, 158.0, 157.6, 157.3, 150.2, 150.0, 149.6, 149.6, 148.8, 147.8, 147.4, 147.1, 139.3, 138.3, 133.6, 132.4, 132.2, 132.1, 131.7, 131.6, 131.1, 130.7, 130.6, 130.5, 130.2, 129.8, 129.6, 129.4, 129.4, 129.4, 129.3, 128.8, 128.1, 127.7, 127.6, 125.7, 125.3, 122.5, 121.1, 120.3, 120.3, 113.3, 112.6, 111.8, 111.6, 111.6, 111.5, 110.2, 110.0, 67.7, 67.6, 55.3, 55.1, 55.1, 55.0, 40.7, 40.6, 40.5, 40.4. HRMS(ESI) Calcd. for $C_{42}H_{42}N_2O_4$ $(M+H)^+$ 639.3217, found 639.3208.

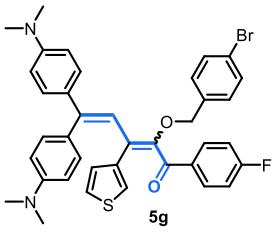
2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-3-(naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-one (5f)



Orange solid, 85% yield, *Z*/*E* isomer (50:50) ratio. (*E*)-(**5f**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.86 – 7.77 (m, 4H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.52 (t, 1H), 7.48 – 7.43 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 8.3 Hz, 2H), 6.42 (d, *J* = 8.2 Hz, 2H), 6.10 (s, 1H), 4.63 (s, 2H), 2.91 (s, 6H), 2.84 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.5, 150.2, 149.8, 148.6, 148.4, 139.1, 135.9, 135.2, 133.2, 132.9, 132.2, 131.6, 131.5, 131.3, 130.8, 130.1, 129.4, 129.0, 128.8, 128.4, 128.3, 127.6, 127.4, 127.3, 126.1, 125.9, 121.9, 121.8, 111.6, 111.4, 72.7, 40.4, 40.3.

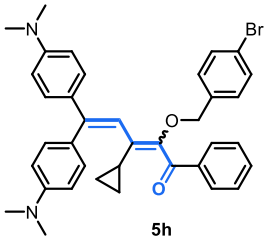
Mixture of (*Z*/*E*) isomers of **5f**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.86 – 7.77 (m, 4H), 7.77 – 7.71 (m, 2H), 7.59 – 7.51 (m, 3H), 7.46 (d, *J* = 7.7 Hz, 4H), 7.42 – 7.35 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 10.6 Hz, 4H), 7.25 – 7.19 (m, 4H), 7.15 (s, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 4H), 6.94 (t, 4H), 6.68 (d, *J* = 7.2 Hz, 4H), 6.65 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 8.3 Hz, 2H), 6.09 (s, 1H), 6.00 (d, *J* = 8.2 Hz, 2H), 4.85 (s, 2H), 4.63 (s, 2H), 2.99 (s, 6H), 2.91 (s, 6H), 2.84 (s, 6H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1, 193.4, 150.4, 150.2, 149.8, 149.5, 149.0, 148.6, 148.4, 148.1, 139.1, 138.1, 136.4, 135.9, 135.2, 134.8, 133.9, 133.2, 132.9, 132.5, 132.1, 132.1, 131.6, 131.6, 131.5, 131.3, 130.8, 130.3, 130.1, 129.4, 128.9, 128.9, 128.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.4, 127.4, 127.3, 126.8, 126.6, 126.1, 125.9, 125.1, 125.0, 122.2, 121.9, 121.8, 120.1, 111.8, 111.5, 111.4, 111.2, 72.7, 71.9, 40.5, 40.4, 40.3, 40.2. HRMS(ESI) Calcd. for $C_{44}H_{40}BrN_2O_2$ $(M+H)^+$ 707.2268, found 707.2234.

2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-1-(4-fluorophenyl)-3-(thiophen-3-yl)penta-2,4-dien-1-one (5g)



Orange solid, 76% yield, *Z*/*E* isomer (26:74) ratio. (*E*)-(**5g**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 2.9 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 4.2 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 8.3 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 8.3 Hz, 2H), 6.01 (s, 1H), 4.65 (s, 2H), 2.92 (d, *J* = 3.9 Hz, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.5, 166.3, 163.8, 150.2, 149.7, 147.6, 146.8, 138.7, 135.7, 135.0, 135.0, 131.6, 131.3, 131.2, 130.7, 130.2, 129.3, 128.5, 127.2, 125.9, 125.4, 124.9, 122.2, 120.5, 115.3, 115.1, 111.5, 111.5, 72.0, 40.4, 40.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.8 – -106.9 (m). HRMS(ESI) Calcd. for $C_{38}H_{34}BrFN_2O_2SNa$ $(M+Na)^+$ 703.1401, found 703.1378.

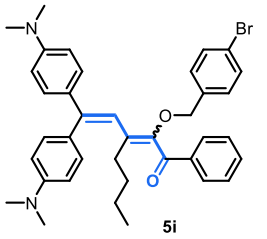
2-((4-bromobenzyl)oxy)-3-cyclopropyl-5,5-bis(4-(dimethylamino)phenyl)-1-phenylpenta-2,4-dien-1-one (5h)



5h

Orange solid, 73% yield, *Z*/*E* isomer (25:75) ratio. Mixture of (*Z*/*E*) isomers of **5h**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, J = 7.5 Hz, 0.9H), 7.45 (d, J = 8.0 Hz, 2.4H), 7.40 (d, J = 7.5 Hz, 2.8H), 7.37 – 7.31 (m, 1.3H), 7.29 (d, J = 6.8 Hz, 1H), 7.25 (d, J = 6.8 Hz, 1.8H), 7.18 (d, J = 7.7 Hz, 0.9H), 7.13 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 7.5 Hz, 0.7H), 6.99 (d, J = 7.5 Hz, 0.8H), 6.88 (d, J = 7.6 Hz, 2H), 6.65 (t, J = 6.7 Hz, 1.6H), 6.58 (d, J = 8.5 Hz, 2H), 6.50 (d, J = 7.8 Hz, 2H), 6.45 (d, J = 7.8 Hz, 1.8H), 6.25 (s, 0.3H), 5.41 (s, 1H), 4.61 (s, 2H), 4.43 (s, 0.7H), 2.98 (d, J = 3.1 Hz, 4H), 2.93 (s, 6H), 2.88 (s, 6H), 2.28 (p, J = 7.2 Hz, 1H), 1.38 (t, J = 7.1 Hz, 0.3H), 0.80 (d, J = 6.9 Hz, 4H), 0.34 (dd, J = 24.5, 6.9 Hz, 1.3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5, 192.4, 150.2, 150.0, 149.9, 149.6, 148.5, 148.1, 147.9, 146.7, 139.2, 137.9, 136.6, 136.5, 136.3, 135.1, 132.7, 132.2, 131.8, 131.6, 131.5, 131.4, 131.2, 130.9, 130.3, 129.9, 129.8, 129.7, 129.3, 129.2, 128.9, 128.1, 128.0, 127.3, 122.0, 121.7, 117.8, 116.7, 111.8, 111.5, 111.4, 111.4, 72.1, 72.0, 40.5, 40.5, 40.4, 13.5, 13.0, 7.8, 6.1. HRMS(ESI) Calcd. for $C_{37}H_{37}BrN_2O_2Na$ $(M+Na)^+$ 621.2111, found 621.2090.

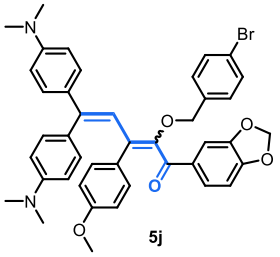
3-(2,2-bis(4-(dimethylamino)phenyl)vinyl)-2-((4-bromobenzyl)oxy)-1-phenylhept-2-en-1-one (5i)



5i

Orange solid, 75% yield, *Z*/*E* isomer (33:67) ratio. Mixture of (*Z*/*E*) isomers of **5i**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 7.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 9.6 Hz, 3H), 7.05 (d, J = 8.3 Hz, 1.2H), 6.99 (d, J = 7.9 Hz, 2H), 6.94 (t, J = 7.3 Hz, 2H), 6.81 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.2 Hz, 2H), 6.58 (t, J = 7.6 Hz, 2H), 6.46 (d, J = 8.3 Hz, 2H), 6.41 (d, J = 8.2 Hz, 2H), 6.34 (s, 0.5H), 5.99 (s, 1H), 4.40 (s, 1.9H), 4.38 (s, 0.9H), 2.91 (s, 6H), 2.87 (s, 6H), 2.84 (s, 6H), 2.14 (t, J = 7.8 Hz, 2H), 1.83 (t, J = 7.7 Hz, 1H), 1.40 – 1.29 (m, 3H), 1.18 – 1.12 (m, 2H), 0.97 – 0.90 (m, 1H), 0.79 (t, J = 7.2 Hz, 3.2H), 0.61 (t, J = 7.3 Hz, 1.6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.6, 191.6, 150.2, 150.1, 150.0, 149.5, 147.4, 147.3, 146.0, 145.4, 139.1, 138.5, 136.3, 136.2, 136.1, 136.0, 135.8, 132.2, 131.9, 131.5, 131.4, 131.1, 131.1, 130.7, 130.3, 129.3, 129.1, 128.9, 128.6, 128.3, 127.8, 122.2, 122.1, 120.9, 119.6, 111.8, 111.7, 111.7, 111.5, 72.7, 72.3, 40.5, 40.5, 40.3, 32.0, 30.7, 30.2, 29.0, 23.0, 22.4, 14.0, 13.8. HRMS(ESI) Calcd. for $C_{38}H_{42}BrN_2O_2$ $(M+H)^+$ 637.2261, found: 637.2243.

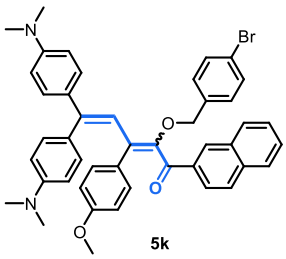
1-(benzo[d][1,3]dioxol-5-yl)-2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-3-(4-methoxypheny-l)penta-2,4-dien-1-one (5j)



5j

Orange solid, 81% yield, *Z*/*E* isomer (53:47) ratio. Mixture of (*Z*/*E*) isomers of **5j**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, J = 8.9 Hz, 1.8H), 7.40 (d, J = 8.5 Hz, 2H), 7.34 (dd, J = 8.1, 2.7 Hz, 3H), 7.25 – 7.12 (m, 8H), 7.02 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.3 Hz, 2H), 6.83 – 6.78 (m, 5H), 6.76 (s, 2H), 6.73 – 6.69 (m, 2H), 6.64 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.1 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1.8H), 6.42 (d, J = 8.3 Hz, 1.8H), 6.30 (dd, J = 13.5, 8.3 Hz, 4H), 6.02 (s, 1H), 5.97 (s, 1.8H), 5.90 (s, 2H), 4.67 (s, 2H), 4.57 (s, 1.8H), 3.79 (s, 2.7H), 3.54 (s, 3H), 2.96 (s, 6H), 2.88 (d, J = 7.1 Hz, 11H), 2.79 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.4, 191.7, 159.2, 158.2, 151.3, 151.0, 150.3, 150.2, 149.7, 149.7, 147.8, 147.7, 147.5, 147.3, 147.3, 147.1, 136.5, 136.0, 133.2, 132.7, 132.0, 131.9, 131.8, 131.5, 131.4, 131.4, 131.0, 130.8, 130.2, 130.0, 130.0, 129.8, 129.4, 129.3, 128.8, 127.6, 126.4, 125.3, 122.0, 121.9, 121.7, 120.5, 113.4, 112.8, 111.8, 111.6, 111.6, 111.6, 108.8, 108.8, 107.7, 107.5, 101.7, 101.6, 72.3, 71.6, 55.3, 55.0, 40.6, 40.5, 40.5, 40.4. HRMS(ESI) Calcd. for $C_{42}H_{39}BrN_2O_5Na$ $(M+Na)^+$ 753.1935, found 753.1911.

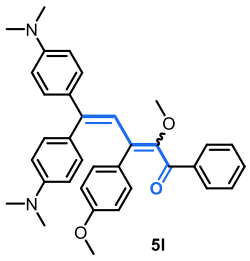
2-((4-bromobenzyl)oxy)-5,5-bis(4-(dimethylamino)phenyl)-3-(4-methoxyphenyl)-1-(naphthalen-2-yl)penta-2,4-dien-1-one (5k)



5k

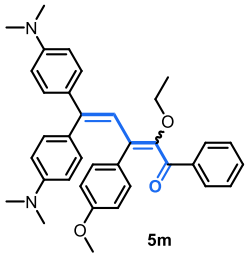
Orange solid, 83% yield, *Z*/*E* isomer (47:53) ratio. Mixture of (*Z*/*E*) isomers of **5k**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, J = 9.5 Hz, 2H), 7.85 (d, J = 8.3 Hz, 1H), 7.83 – 7.76 (m, 4H), 7.73 (d, J = 9.0 Hz, 3.7H), 7.64 (d, J = 8.7 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.53 – 7.45 (m, 2.8H), 7.42 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 7.4 Hz, 3.6H), 7.04 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 7.2 Hz, 4H), 6.87 (s, 0.9H), 6.85 – 6.77 (m, 3.6H), 6.70 (d, J = 8.8 Hz, 1.8H), 6.60 (d, J = 8.0 Hz, 2H), 6.42 – 6.29 (m, 5.8H), 6.18 (d, J = 8.5 Hz, 1.8H), 6.03 (s, 1H), 4.79 (s, 1.8H), 4.65 (s, 2H), 3.85 (s, 3H), 3.41 (s, 2.7H), 3.00 (s, 5.4H), 2.85 (s, 6H), 2.81 (s, 5.4H), 2.78 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.2, 193.4, 159.4, 158.2, 150.3, 150.1, 149.7, 149.5, 148.2, 147.7, 147.7, 147.5, 136.5, 135.9, 135.9, 135.4, 135.3, 135.2, 133.5, 132.7, 132.2, 132.0, 131.8, 131.6, 131.5, 131.5, 131.4, 131.0, 130.9, 130.8, 130.4, 130.3, 130.1, 130.1, 129.8, 129.7, 129.5, 129.3, 128.7, 128.1, 127.9, 127.9, 127.7, 127.6, 127.4, 126.3, 126.3, 124.8, 124.8, 122.1, 122.0, 121.8, 120.6, 113.6, 112.9, 111.8, 111.6, 111.5, 111.3, 72.4, 71.7, 55.4, 55.0, 40.6, 40.5, 40.4, 40.1. HRMS(ESI) Calcd. for $C_{45}H_{42}BrN_2O_3$ $(M+H)^+$ 737.2373, found 737.2330.

5,5-bis(4-(dimethylamino)phenyl)-2-methoxy-3-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (5l)



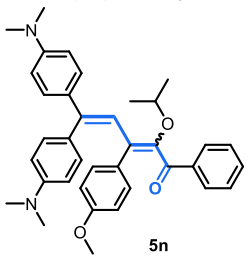
Orange solid, 72% yield, *Z*/*E* isomer (43:57) ratio. Mixture of (*Z*/*E*) isomers of **5l**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.7 Hz, 3.6H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.49 (t, 1H), 7.35 (q, *J* = 7.1 Hz, 3H), 7.30 (d, *J* = 6.8 Hz, 1.5H), 7.26 – 7.19 (m, 2H), 6.96 – 6.88 (m, 5.6H), 6.85 (d, *J* = 6.6 Hz, 1.5H), 6.79 (s, 0.7H), 6.68 (d, *J* = 6.9 Hz, 1.6H), 6.61 (d, *J* = 6.8 Hz, 2H), 6.52 – 6.45 (m, 4H), 6.42 (d, *J* = 6.7 Hz, 1.5H), 6.31 (d, *J* = 6.6 Hz, 1.5H), 5.89 (s, 1H), 3.84 (s, 3H), 3.56 (s, 2.2H), 3.52 (s, 3H), 3.49 (s, 2.1H), 2.98 (s, 4.7H), 2.92 (s, 12H), 2.83 (s, 4.4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3, 193.3, 159.4, 158.3, 150.3, 150.1, 149.8, 149.7, 149.2, 148.5, 147.9, 147.1, 139.6, 138.3, 132.4, 132.0, 131.8, 131.5, 131.4, 131.0, 130.9, 130.7, 130.1, 130.1, 129.9, 129.4, 129.4, 129.2, 129.1, 128.6, 128.3, 128.0, 127.4, 122.2, 120.5, 113.6, 112.9, 111.8, 111.7, 111.6, 111.4, 58.4, 58.0, 55.3, 55.0, 40.6, 40.5, 40.5, 40.4. HRMS(ESI) Calcd. for $C_{35}H_{36}N_2O_3$ $(M+H)^+$ 532.2799, found 533.2767.

5,5-bis(4-(dimethylamino)phenyl)-2-ethoxy-3-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (5m)



Orange solid, 68% yield, *Z*/*E* isomer (40:60) ratio. Mixture of (*Z*/*E*) isomers of **5m**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.71 (m, 5.3H), 7.47 (t, *J* = 7.1 Hz, 1H), 7.38 – 7.30 (m, 3.5H), 7.29 (s, 0.7H), 7.26 – 7.21 (m, 1.5H), 6.93 (s, 0.7H), 6.90 (d, *J* = 8.1 Hz, 4H), 6.84 (d, *J* = 8.0 Hz, 1.5H), 6.79 (d, *J* = 7.9 Hz, 1.4H), 6.68 (d, *J* = 8.3 Hz, 1.5H), 6.64 (d, *J* = 8.1 Hz, 2H), 6.53 – 6.44 (m, 4H), 6.35 (d, *J* = 8.0 Hz, 1.4H), 6.26 (d, *J* = 8.0 Hz, 1.4H), 5.93 (s, 1H), 3.84 (s, 3H), 3.79 (q, 1.4H), 3.72 (q, 2H), 3.54 (s, 2H), 2.98 (s, 4.5H), 2.91 (s, 12H), 2.81 (s, 4.3H), 1.27 (t, *J* = 6.8 Hz, 2H), 1.17 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.6, 193.6, 159.2, 158.1, 150.2, 150.1, 149.7, 149.6, 148.9, 147.9, 147.5, 146.9, 139.2, 138.1, 132.4, 132.2, 132.1, 131.8, 131.6, 131.5, 130.9, 130.7, 130.2, 130.0, 129.5, 129.4, 129.3, 129.3, 129.0, 128.7, 128.2, 128.0, 127.5, 122.3, 120.7, 113.5, 112.8, 111.9, 111.6, 111.6, 111.5, 66.8, 66.4, 55.3, 55.0, 40.7, 40.5, 40.5, 40.4, 15.8, 15.4. HRMS(ESI) Calcd. for $C_{36}H_{39}N_2O_3$ $(M+H)^+$ 547.2955, found 547.2924.

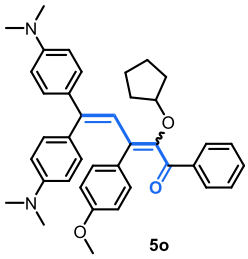
5,5-bis(4-(dimethylamino)phenyl)-2-isopropoxy-3-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (5n)



Orange solid, 70% yield, *Z*/*E* isomer (67:33) ratio. Mixture of (*Z*/*E*) isomers of **5n**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.9 Hz, 3H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 0.6H), 7.38 – 7.30 (m, 2H), 7.28 – 7.21 (m, 4H), 7.05 (s, 1H), 6.85 (t, *J* = 7.9 Hz, 2H), 6.78 – 6.70 (m, 4H), 6.70 – 6.64 (m, 3H), 6.48 (d, *J* = 8.3 Hz, 1H), 6.43 (d, *J* = 8.2 Hz, 1H), 6.28 (d, *J* = 8.3 Hz, 2H), 6.21 (d, *J* = 8.7 Hz, 2H), 6.04 (s, 0.5H), 4.11 – 4.01 (m, 1H), 4.00

– 3.91 (m, 0.5H), 3.81 (s, 1.5H), 3.51 (s, 3H), 2.96 (s, 6H), 2.89 (s, 6H), 2.78 (s, 6H), 1.28 (d, J = 6.0 Hz, 6H), 1.10 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5, 193.5, 158.9, 157.9, 150.2, 150.0, 149.6, 148.6, 147.2, 146.9, 146.8, 138.8, 138.0, 132.7, 132.5, 132.4, 132.2, 131.9, 131.6, 131.6, 130.9, 130.7, 130.5, 129.9, 129.4, 129.3, 129.0, 128.9, 128.5, 128.3, 128.0, 127.9, 122.6, 121.2, 113.3, 112.7, 111.9, 111.7, 111.6, 111.5, 73.3, 73.2, 55.3, 55.0, 40.7, 40.5, 40.5, 40.5, 22.9, 22.9. HRMS(ESI) Calcd. for $C_{37}H_{41}N_2O_3$ $(M+H)^+$ 561.3112, found 561.3106.

2-(cyclopentyloxy)-5,5-bis(4-(dimethylamino)phenyl)-3-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (5o)

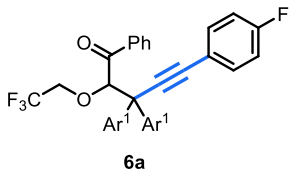


5o

Orange solid, 76% yield, *Z*/*E* isomer (56:44) ratio. Mixture of (*Z*/*E*) isomers of **5o**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.67 (m, 5H), 7.47 (t, J = 7.3 Hz, 1H), 7.39 – 7.30 (m, 2.7H), 7.29 – 7.19 (m, 4.5H), 7.01 (s, 1H), 6.85 (t, J = 7.2 Hz, 3H), 6.73 (t, 4H), 6.67 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.1 Hz, 1.6H), 6.46 (t, J = 6.9 Hz, 3H), 6.28 (d, J = 8.2 Hz, 2H), 6.21 (d, J = 8.2 Hz, 2H), 6.04 (s, 0.8H), 4.41 (s, 1H), 4.26 (s, 0.8H), 3.82 (s, 2.4H), 3.52 (s, 3H), 2.97 (s, 6H), 2.90 (s, 9.4H), 2.79 (s, 6H), 1.99 – 1.83 (m, 4H), 1.75 – 1.64 (m, 4H), 1.63 – 1.54 (m, 4H), 1.53 – 1.46 (m, 1.5H), 1.43 – 1.39 (m, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5, 193.5, 158.8, 157.9, 150.1, 150.0, 149.6, 149.5, 148.4, 147.1, 146.9, 146.5, 139.1, 138.0, 132.4, 132.3, 132.3, 132.2, 131.9, 131.6, 130.8, 130.7, 130.6, 129.8, 129.4, 129.2, 129.0, 128.9, 128.4, 128.3, 127.9, 122.5, 120.8, 113.2, 112.7, 111.9, 111.7, 111.6, 111.5, 82.6, 82.1, 55.3, 55.0, 40.7, 40.5, 40.5, 40.5, 33.1, 33.0, 23.9, 23.6. HRMS(ESI) Calcd. for $C_{39}H_{43}N_2O_3$ $(M+H)^+$ 587.3268, found 587.3246.

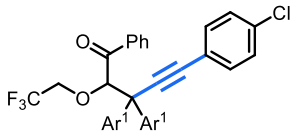
3,3-bis(4-(dimethylamino)phenyl)-5-(4-fluorophenyl)-1-phenyl-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6a)



6a

Gray-green oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.29 – 7.21 (m, 4H), 7.15 (t, J = 6.8 Hz, 2H), 6.90 (t, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 8.3 Hz, 2H), 5.70 (s, 1H), 3.90 (dq, J = 12.2, 9.6 Hz, 1H), 3.76 (dq, J = 13.5, 8.3 Hz, 1H), 2.93 (s, 6H), 2.86 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 163.6 (d, J = 250.3 Hz), 149.5, 138.1, 133.4, 133.4, 132.5, 129.9, 129.6, 129.1, 129.0, 128.9, 128.0, 123.6 (q, J = 279.9 Hz), 119.4 (d, J = 3.6 Hz), 115.2 (d, J = 21.7 Hz), 112.0, 111.8, 91.4, 87.6, 86.5, 67.3 (d, J = 34.6 Hz), 52.1, 40.5, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.18 (t, J = 8.7 Hz), -111.58 – -111.72 (m). HRMS(ESI) Calcd. for $C_{35}H_{32}F_4N_2O_2Na$ $(M+Na)^+$ 611.2292, found 611.2250.

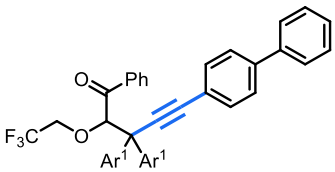
5-(4-chlorophenyl)-3,3-bis(4-(dimethylamino)phenyl)-1-phenyl-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6b)



6b

Gray-green oil, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.16 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 6.64 (d, J = 8.1 Hz, 2H), 6.51 (d, J = 8.1 Hz, 2H), 5.67 (s, 1H), 3.90 (dq, J = 13.1, 8.6 Hz, 1H), 3.57 (dq, J = 13.1, 8.6 Hz, 1H), 2.91 (s, 6H), 2.83 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 149.5, 138.1, 133.9, 132.8, 132.6, 129.7, 129.6, 129.0, 128.8, 128.3, 128.0, 123.6 (q, J = 279.2 Hz), 121.8, 112.0, 111.8, 92.8, 87.5, 86.4, 67.2 (q, J = 34.9 Hz), 52.1, 40.5, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.17 (t, J = 8.6 Hz). HRMS(ESI) Calcd. for $C_{35}H_{32}ClF_3N_2O_2Na$ $(M+Na)^+$ 627.1997, found 627.1956.

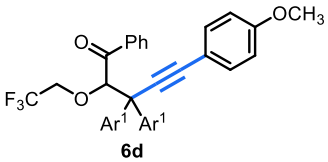
5-([1,1'-biphenyl]-4-yl)-3,3-bis(4-(dimethylamino)phenyl)-1-phenyl-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6c)



6c

Gray-green oil, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, J = 7.7 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.50 -7.46 (m, 3H), 7.46 – 7.38 (m, 4H), 7.38 – 7.28 (m, 4H), 7.28 - 7.22 (m, 3H), 6.68 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 8.4 Hz, 2H), 5.72 (s, 1H), 4.01 – 3.89 (m, 1H), 3.86 – 3.75 (m, 1H), 2.94 (s, 6H), 2.87 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.2, 149.5, 140.6, 140.5, 138.1, 132.6, 132.0, 130.0, 129.7, 129.1, 129.0, 128.8, 128.0, 127.5, 127.0, 126.7, 123.6 (q, J = 276.1 Hz), 122.3, 112.1, 111.8, 92.5, 88.6, 86.7, 67.2 (q, J = 35.0 Hz), 52.2, 40.6, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.2 (t, J = 8.7 Hz). HRMS(ESI) Calcd. for $C_{41}H_{37}F_3N_2O_2Na$ $(M+Na)^+$ 669.2699, found 669.2647.

3,3-bis(4-(dimethylamino)phenyl)-5-(4-methoxyphenyl)-1-phenyl-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6d)

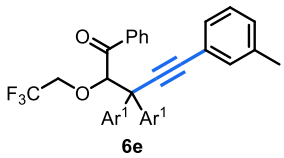


6d

Gray-green oil, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 8.5 Hz, 2H), 7.18 (t, J = 7.3 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.3 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 6.48 (d, J = 8.4 Hz, 2H), 5.62 (s, 1H), 3.85 (dq, J = 13.2, 8.7 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.69 (s, 3H), 2.85 (s, 6H), 2.79 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.3, 159.3, 149.4, 138.1, 132.9, 132.5, 130.4, 129.7, 129.2, 129.1, 129.0, 128.0, 123.6 (q, J = 280.2 Hz), 115.5, 113.6, 112.0, 111.8, 90.2, 88.7, 86.8, 67.4 (q, J = 35.0 Hz), 55.3, 52.0, 40.6, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.20 (t, J = 8.6 Hz). HRMS(ESI)

Calcd. for $C_{36}H_{35}F_3N_2O_3Na$ $(M+Na)^+$ 623.2504, found 623.2481.

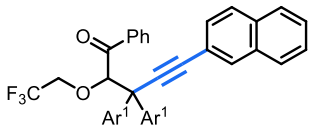
3,3-bis(4-(dimethylamino)phenyl)-1-phenyl-5-(m-tolyl)-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6e)



6e

Gray-green oil, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 7.7 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.64 (d, J = 7.7 Hz, 2H), 6.53 (d, J = 7.7 Hz, 2H), 5.68 (s, 1H), 3.90 (dq, J = 12.6, 9.6 Hz, 1H), 3.75 (dq, J = 12.6, 9.6 Hz, 1H), 2.91 (s, 6H), 2.84 (s, 6H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 149.4, 138.1, 137.6, 132.5, 132.1, 130.2, 129.7, 129.1, 129.0, 129.0, 128.8, 128.6, 128.0, 127.8, 123.6 (q, J = 280.8 Hz), 123.1, 112.0, 111.8, 91.3, 86.7, 67.4 (q, J = 34.6 Hz), 52.0, 40.6, 40.5, 21.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.22 (t, J = 8.6 Hz). HRMS(ESI) Calcd. for $C_{36}H_{35}F_3N_2O_2Na$ $(M+Na)^+$ 607.2543, found 607.2517.

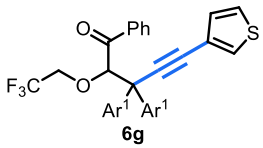
3,3-bis(4-(dimethylamino)phenyl)-5-(naphthalen-2-yl)-1-phenyl-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6f)



6f

Gray-green oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, J = 7.6 Hz, 2H), 7.76 (dd, J = 7.7 Hz, 2.4 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.60 (s, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.30 -7.21 (m, 3H), 6.69 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 8.5 Hz, 2H), 5.75 (s, 1H), 3.95 (dq, J = 12.9, 8.9 Hz, 1H), 3.81 (dq, J = 15.8, 8.3 Hz, 1H), 2.94 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.2, 149.5, 138.2, 132.9, 132.7, 132.6, 131.3, 130.1, 129.7, 129.1, 129.0, 128.9, 128.5, 128.1, 127.7, 127.6, 127.5, 126.4, 126.3, 123.6 (q, J = 279.4 Hz), 120.6, 112.1, 111.8, 92.1, 89.1, 86.7, 67.4 (q, J = 34.5 Hz), 52.2, 40.6, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.17 (t, J = 8.5 Hz). HRMS(ESI) Calcd. for $C_{39}H_{35}F_3N_2O_2Na$ $(M+Na)^+$ 643.2543, found 643.2519.

3,3-bis(4-(dimethylamino)phenyl)-1-phenyl-5-(thiophen-3-yl)-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6g)

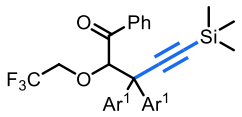


6g

Gray-green solid, 79% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 7.7 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 7.32 -7.24 (m, 4H), 7.17 – 7.14 (m, 1H), 7.11 (s, 1H), 6.84 (d, J = 4.9 Hz , 1H), 6.67 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 5.70 (s, 1H), 3.92 (dq, J = 12.5, 8.7 Hz, 1H), 3.78 (dq, J = 12.5, 8.7 Hz, 1H), 2.93 (s, 6H), 2.87 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.2, 149.4, 138.1, 132.6, 130.0, 129.9, 129.7, 129.1, 129.0, 128.9, 128.3, 128.0, 124.7, 123.6 (q, J = 279.5 Hz), 122.3, 112.0, 111.8, 91.1, 86.7, 84.0, 67.4 (q, J = 34.5 Hz), 52.1, 40.6, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.20 (t, J = 8.6 Hz). HRMS(ESI) Calcd. for $C_{33}H_{31}F_3N_2O_2SNa$

$(M+Na)^+$ 599.1951, found 599.1922.

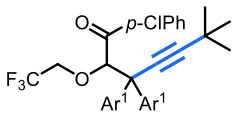
3-bis(4-(dimethylamino)phenyl)-1-phenyl-2-(2,2,2-trifluoroethoxy)-5-(trimethylsilyl)pent-4-yn-1-one (6h)



6h

Gray-green oil, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, J = 7.7 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 9.8 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 5.57 (s, 1H), 3.85 (dq, J = 13.1, 9.2 Hz, 1H), 3.74 (dq, J = 13.4, 8.6 Hz, 1H), 2.91 (s, 6H), 2.87 (s, 6H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.3, 150.8, 139.5, 134.1, 131.5, 131.2, 130.7, 130.4, 130.1, 129.4, 125.0 (q, J = 279.3 Hz), 113.4, 113.2, 109.0, 94.8, 88.0, 68.8 (q, J = 34.5 Hz), 53.8, 42.0, 42.0, 1.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.38 (t, J = 8.7 Hz). HRMS(ESI) Calcd. for $C_{32}H_{37}F_3N_2O_2SiNa$ $(M+Na)^+$ 589.2407, found 589.2369.

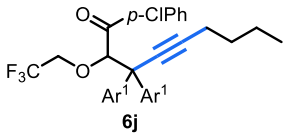
1-(4-chlorophenyl)-3,3-bis(4-(dimethylamino)phenyl)-6,6-dimethyl-2-(2,2,2-trifluoroethoxy)hept-4-yn-1-one (6i)



6i

Gray-green oil, 76% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.29 – 7.20 (m, 4H), 6.63 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 8.3 Hz, 2H), 5.44 (s, 1H), 3.89 – 3.74 (m, 2H), 2.92 (s, 6H), 2.87 (s, 6H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.2, 149.3, 138.8, 136.1, 130.7, 129.6, 129.5, 128.8, 128.2, 128.1, 123.6 (q, J = 277.6 Hz), 111.9, 111.7, 97.4, 87.7, 80.4, 67.5 (q, J = 34.4 Hz), 51.3, 40.6, 40.5, 30.7, 27.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.39 (t, J = 8.6 Hz). HRMS(ESI) Calcd. for $C_{33}H_{36}ClF_3N_2O_2Na$ $(M+Na)^+$ 607.2310, found 607.2287.

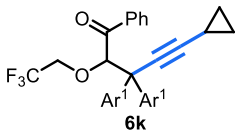
1-(4-chlorophenyl)-3,3-bis(4-(dimethylamino)phenyl)-2-(2,2,2-trifluoroethoxy)non-4-yn-1-one (6j)



6j

Gray-green oil, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 8.4 Hz, 2H), 5.46 (s, 1H), 3.93 – 3.83 (m, 1H), 3.82 – 3.72 (m, 1H), 2.92 (s, 6H), 2.87 (s, 6H), 2.10 (t, J = 6.6 Hz, 2H), 1.41 – 1.31 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.4, 149.4, 138.7, 136.2, 130.6, 130.2, 129.5, 129.4, 128.9, 127.9, 123.6 (q, J = 279.7 Hz), 111.9, 111.8, 89.5, 87.9, 81.7, 67.6 (q, J = 35.4 Hz), 51.7, 40.6, 40.5, 30.7, 22.1, 18.7, 13.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.26 (t, J = 8.6 Hz). HRMS(ESI) Calcd. for $C_{33}H_{36}ClF_3N_2O_2Na$ $(M+Na)^+$ 607.2310, found 607.2281.

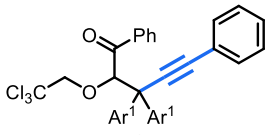
5-cyclopropyl-3,3-bis(4-(dimethylamino)phenyl)-1-phenyl-2-(2,2,2-trifluoroethoxy)pent-4-yn-1-one (6k)



6k

Gray-green oil, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 8.3 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 5.60 (s, 1H), 3.87 (dq, J = 13.0, 9.1 Hz, 1H), 3.73 (dq, J = 13.2, 8.2 Hz, 1H), 2.92 (s, 6H), 2.86 (s, 6H), 1.15 – 1.04 (m, 1H), 0.63 – 0.54 (m, 2H), 0.45 – 0.33 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.7, 149.7, 138.6, 132.9, 131.3, 130.1, 129.8, 129.4, 129.2, 128.3, 124.1 (q, J = 279.7 Hz), 112.4, 112.1, 92.6, 87.1, 67.7 (q, J = 34.4 Hz), 51.7, 41.0, 40.9, 8.2, 8.2, 0.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.25 (t, J = 8.5 Hz). HRMS(ESI) Calcd. for $C_{32}H_{33}F_3N_2O_2Na$ $(M+Na)^+$ 557.2386, found 557.2343.

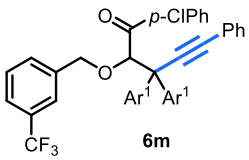
3,3-bis(4-(dimethylamino)phenyl)-1,5-diphenyl-2-(2,2,2-trichloroethoxy)pent-4-yn-1-one (6l)



6l

Gray-green oil, 69% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.28 (d, J = 7.5 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.17 (d, J = 6.7 Hz, 2H), 6.68 (d, J = 8.3 Hz, 2H), 6.61 (d, J = 8.3 Hz, 2H), 5.81 (s, 1H), 4.18 (d, J = 11.1 Hz, 1H), 4.08 (d, J = 11.1 Hz, 1H), 2.95 (s, 6H), 2.90 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 149.4, 138.0, 132.6, 131.5, 130.4, 130.1, 129.4, 129.2, 129.0, 128.0, 127.9, 123.4, 112.0, 111.7, 96.1, 92.1, 88.9, 87.8, 82.3, 52.2, 40.6, 40.6. HRMS(ESI) Calcd. for $C_{35}H_{33}Cl_3N_2O_2Na$ $(M+Na)^+$ 641.1500, found 641.1473.

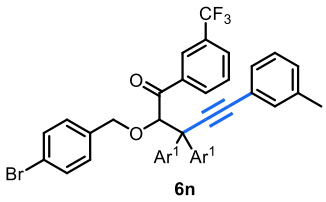
1-(4-chlorophenyl)-3,3-bis(4-(dimethylamino)phenyl)-5-phenyl-2-((3-(trifluoromethyl)benzyl)oxy)pent-4-yn-1-one (6m)



6m

Gray-green oil, 64% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.1 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.44 – 7.36 (m, 4H), 7.29 – 7.14 (m, 9H), 6.64 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 5.42 (s, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 2.93 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.8, 149.5, 149.4, 138.8, 138.1, 136.3, 131.5, 131.2, 130.7 (q, J = 32.5 Hz), 130.6, 130.1, 129.5, 129.4, 128.9, 128.8, 127.9, 128.0, 128.0, 124.8 (q, J = 3.7 Hz), 124.6 (q, J = 3.7 Hz), 123.3, 111.9, 111.8, 92.1, 88.7, 87.1, 71.6, 52.1, 40.5, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.50. HRMS(ESI) Calcd. for $C_{41}H_{36}ClF_3N_2O_2Na$ $(M+Na)^+$ 703.2310, found 703.2282.

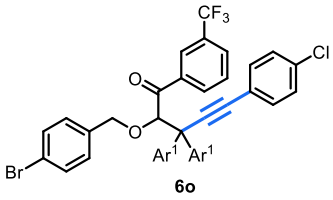
2-((4-bromobenzyl)oxy)-3,3-bis(4-(dimethylamino)phenyl)-5-(m-tolyl)-1-(3-(trifluoromethyl)phenyl)pent-4-yn-1-one (6n)



6n

Gray-green oil, 50% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, J = 8.0 Hz, 1H), 7.97 (s, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.32 (t, J = 7.9 Hz, 1H), 7.24 (d, J = 7.8 Hz, 2H), 7.14 – 7.02 (m, 5H), 6.99 (s, 1H), 6.62 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 8.5 Hz, 2H), 5.41 (s, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 2.92 (s, 6H), 2.87 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.2, 149.4, 149.3, 138.6, 137.6, 135.9, 132.3, 132.1, 131.4, 130.2 (q, J = 32.9 Hz), 130.0, 129.8, 129.5, 129.4, 129.0, 128.8, 128.6, 128.5 (q, J = 3.8 Hz), 128.3, 127.9, 126.0 (q, J = 3.9 Hz), 123.6 (q, J = 274.4 Hz), 123.0, 121.9, 111.9, 111.8, 91.5, 87.2, 71.9, 52.1, 40.5, 40.4, 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.69. HRMS(ESI) Calcd. for $C_{42}H_{38}BrF_3N_2O_2Na$ $(M+Na)^+$ 761.1961, found 761.1923.

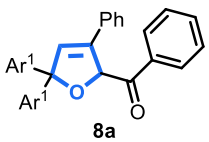
2-((4-bromobenzyl)oxy)-5-(4-chlorophenyl)-3,3-bis(4-(dimethylamino)phenyl)-1-(3-(trifluoromethyl)phenyl)-pent-4-yn-1-one (6o)



6o

Gray-green oil, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 8.0 Hz, 1H), 7.92 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.32 (t, J = 7.9 Hz, 1H), 7.24 – 7.15 (m, 6H), 7.08 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 8.1 Hz, 2H), 6.51 (d, J = 8.1 Hz, 2H), 5.40 (s, 1H), 4.57 (d, J = 11.8 Hz, 1H), 4.49 (d, J = 11.8 Hz, 1H), 2.93 (s, 6H), 2.86 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.1, 149.5, 149.4, 138.5, 135.8, 133.9, 132.8, 132.2, 131.5, 130.3 (q, J = 32.2 Hz), 129.8, 129.4, 129.2, 129.0, 128.6 (q, J = 3.8 Hz), 128.3, 125.9 (q, J = 4.1 Hz), 123.5 (q, J = 272.9 Hz), 122.0, 121.8, 111.9, 111.8, 92.9, 87.4, 86.8, 71.9, 52.1, 40.5, 40.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.69. HRMS(ESI) Calcd. for $C_{41}H_{35}BrClF_3N_2O_2Na$ $(M+Na)^+$ 781.1415, found 781.1395.

(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(phenyl)methanone (8a)

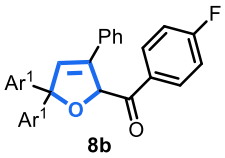


8a

Green oil, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 10.3 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.29 – 7.25 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 6.79 (s, 1H), 6.70 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 8.3 Hz, 2H), 6.42 (s, 1H), 2.94 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.5, 149.9, 149.7, 137.3, 136.1, 133.1, 132.9, 132.2, 131.2, 129.6, 128.5, 128.4, 127.9, 127.9, 127.6, 126.5, 112.1, 112.0, 96.2, 86.4, 40.6. HRMS(ESI)

Calcd. for $C_{33}H_{33}N_2O_2$ $(M+H)^+$ 489.2537, found 489.2519.

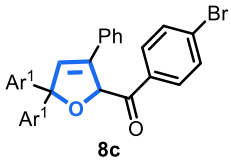
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(4-fluorophenyl)methanone (8b)



8b

Green oil, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.05 (m, 2H), 7.35 (d, J = 6.7 Hz, 2H), 7.32 – 7.22 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 7.03 (t, J = 8.6 Hz, 2H), 6.79 (s, 1H), 6.69 (d, J = 7.3 Hz, 2H), 6.58 (d, J = 7.2 Hz, 2H), 6.35 (s, 1H), 2.93 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.2, 167.0, 165.6 (d, J = 255.2 Hz), 149.9, 149.8, 137.3, 133.0, 132.4, 132.4 (d, J = 2.4 Hz), 132.3 (d, J = 9.5 Hz), 132.0, 131.1, 128.5, 128.1, 127.8, 127.6, 126.5, 115.5, 115.3, 112.1, 112.0, 96.2, 87.0, 40.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.16. HRMS(ESI) Calcd. for $C_{33}H_{32}FN_2O_2$ $(M+H)^+$ 507.2442, found 507.2431.

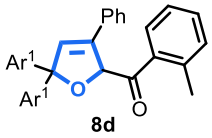
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(4-bromophenyl)methanone (8c)



8c

Green oil, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 6.8 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.09 (d, J = 8.7 Hz, 2H), 6.79 (s, 1H), 6.69 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 6.32 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.1, 149.9, 149.8, 137.2, 134.8, 133.0, 132.7, 131.9, 131.6, 131.2, 131.1, 128.6, 128.1, 127.8, 127.6, 126.5, 112.1, 112.0, 96.3, 87.1, 40.6. HRMS(ESI) Calcd. for $C_{33}H_{32}BrN_2O_2$ $(M+H)^+$ 567.1642, found 567.1621.

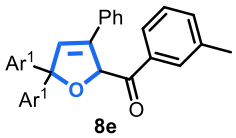
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(o-tolyl)methanone (8d)



8d

Green oil, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 7.1 Hz, 2H), 7.30 – 7.21 (m, 6H), 7.10 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 6.72 (s, 1H), 6.68 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 8.2 Hz, 2H), 6.29 (s, 1H), 2.91 (s, 6H), 2.89 (s, 6H), 2.20 (s, 3H). ^{13}C NMR (100MHz, Chloroform-*d*) δ 201.8, 149.8, 149.7, 138.5, 137.4, 137.2, 133.2, 132.6, 132.4, 131.5, 131.3, 130.9, 128.9, 128.5, 128.1, 128.0, 127.6, 126.6, 125.1, 112.1, 112.1, 96.2, 88.6, 40.7, 40.6, 20.5. HRMS(ESI) Calcd. for $C_{34}H_{35}N_2O_2$ $(M+H)^+$ 503.2687, found 503.2658.

(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(m-tolyl)methanone (8e)

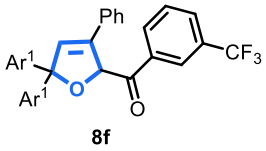


8e

Green oil, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.84 (m, 2H), 7.38 – 7.31 (m, 3H), 7.31 – 7.25 (m, 4H), 7.25 – 7.20 (m, 2H), 7.15 (d, J = 7.1 Hz, 2H), 6.79 (s, 1H), 6.70 (d, J = 8.1 Hz, 2H), 6.59 (d, J = 7.3 Hz, 2H), 6.40 (s, 1H), 2.93 (s, 6H), 2.88 (s,

6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.7, 149.9, 149.7, 138.1, 137.4, 136.2, 133.9, 133.2, 132.9, 132.3, 131.1, 130.0, 128.5, 128.3, 128.0, 127.9, 127.7, 126.9, 126.5, 112.2, 112.1, 96.2, 86.6, 40.7, 40.6, 21.4. HRMS(ESI) Calcd. for $C_{34}H_{35}N_2O_2$ $(M+H)^+$ 503.2693, found 503.2681.

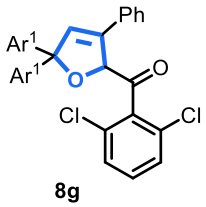
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(3-(trifluoromethyl)phenyl)methanone (8f)



8f

Green oil, 79% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.17 (m, 2H), 7.73 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 8.1 Hz, 1H), 7.37 (d, J = 7.6 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H), 7.07 (d, J = 8.3 Hz, 2H), 6.81 (s, 1H), 6.70 (d, J = 8.3 Hz, 2H), 6.55 (d, J = 8.3 Hz, 2H), 6.35 (s, 1H), 2.93 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.8, 149.9, 149.8, 137.1, 136.6, 132.8, 132.7, 132.6, 131.7, 131.4, 130.8 (q, J = 32.8 Hz), 129.3 (q, J = 3.6 Hz), 128.9, 128.6, 128.2, 127.8, 127.5, 126.5, 126.2 (q, J = 4.0 Hz), 123.6 (q, J = 279.9 Hz), 112.1, 112.0, 96.4, 87.0, 40.6, 40.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.71. HRMS(ESI) Calcd. for $C_{34}H_{32}F_3N_2O_2$ $(M+H)^+$ 557.2410, found 557.2391.

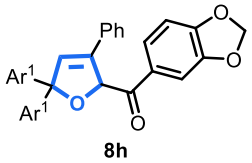
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(2,6-dichlorophenyl)methanone (8g)



8g

Green oil, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 7.5 Hz, 2H), 7.32 (t, 2H), 7.27 (t, J = 6.8 Hz, 1H), 7.16 – 7.10 (m, 3H), 6.89 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.6 Hz, 1H), 6.80 (d, 1H), 6.69 (s, 1H), 6.63 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 8.3 Hz, 2H), 6.20 (s, 1H), 2.93 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.1, 149.8, 149.6, 136.1, 135.9, 135.7, 133.5, 132.0, 132.0, 131.9, 129.6, 129.4, 128.6, 128.5, 127.7, 127.2, 126.9, 125.9, 112.1, 111.7, 96.8, 90.9, 40.6, 40.6. HRMS(ESI) Calcd. for $C_{33}H_{31}Cl_2N_2O_2$ $(M+H)^+$ 557.1684, found 557.1653.

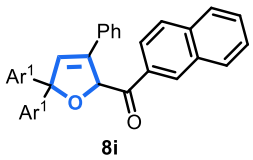
benzo[d][1,3]dioxol-5-yl(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)methanone (8h)



8h

Green oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.1 Hz, 1H), 7.53 (s, 1H), 7.33 (d, J = 7.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.27 – 7.19 (m, 3H), 7.15 (d, J = 8.7 Hz, 2H), 6.82 – 6.75 (m, 2H), 6.70 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 6.35 (s, 1H), 6.00 (s, 2H), 2.93 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3, 151.8, 149.9, 149.7, 147.9, 137.4, 133.1, 132.9, 132.2, 131.0, 130.9, 128.5, 127.9, 127.9, 127.6, 126.4, 126.3, 112.1, 112.1, 109.2, 107.8, 101.7, 96.1, 86.3, 40.6. HRMS(ESI) Calcd. for $C_{34}H_{33}N_2O_4$ $(M+H)^+$ 533.2435, found 533.2412.

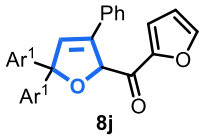
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(naphthalen-2-yl)methanone (8i)



8i

Green oil, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.75 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.46 (t, J = 7.0 Hz, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.30 (d, J = 6.7 Hz, 2H), 7.26 (d, 2H), 7.22 (s, 1H), 7.21 – 7.16 (m, 2H), 6.84 (s, 1H), 6.71 (d, J = 7.8 Hz, 2H), 6.61 – 6.52 (m, 3H), 2.93 (s, 6H), 2.86 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.7, 149.9, 149.7, 137.7, 135.6, 133.3, 133.2, 132.8, 132.4, 132.2, 131.8, 131.0, 130.0, 128.6, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 126.6, 126.4, 125.0, 112.2, 96.3, 87.2, 40.6. HRMS(ESI) Calcd. for $C_{37}H_{35}N_2O_2$ $(M+H)^+$ 539.2693, found 539.2684.

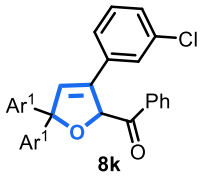
(5,5-bis(4-(dimethylamino)phenyl)-3-phenyl-2,5-dihydrofuran-2-yl)(furan-2-yl)methanone (8j)



8j

Green oil, 76% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.65 (m, 1H), 7.52 (s, 1H), 7.37 (d, J = 7.3 Hz, 2H), 7.26 – 7.13 (m, 6H), 7.06 – 6.99 (m, 1H), 6.78 (s, 1H), 6.74 – 6.61 (m, 4H), 6.39 (s, 1H), 6.22 (s, 1H), 2.91 (s, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.5, 151.3, 149.8, 149.8, 147.1, 137.3, 133.1, 132.4, 132.2, 131.4, 128.5, 128.1, 128.1, 127.4, 126.5, 120.5, 112.2, 112.1, 96.3, 86.9, 40.7. HRMS(ESI) Calcd. for $C_{31}H_{31}N_2O_3$ $(M+H)^+$ 479.2329, found 479.2314.

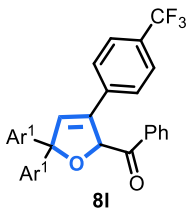
(3-(3-chlorophenyl)-5,5-bis(4-(dimethylamino)phenyl)-2,5-dihydrofuran-2-yl)(phenyl)methanone (8k)



8k

Green oil, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.27 (d, J = 7.4 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.10 (d, J = 7.1 Hz, 2H), 6.80 (s, 1H), 6.70 (d, J = 7.5 Hz, 2H), 6.57 (d, J = 7.4 Hz, 2H), 6.39 (s, 1H), 2.94 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.1, 149.9, 149.8, 136.1, 135.9, 134.9, 134.4, 133.2, 132.7, 132.6, 131.8, 129.8, 129.6, 128.4, 127.9, 127.8, 127.6, 126.6, 124.6, 112.1, 112.0, 96.2, 86.2, 40.6. HRMS(ESI) Calcd. for $C_{33}H_{32}ClN_2O_2$ $(M+H)^+$ 523.2147, found 523.2134.

(5,5-bis(4-(dimethylamino)phenyl)-3-(4-(trifluoromethyl)phenyl)-2,5-dihydrofuran-2-yl)(phenyl)methanone (8l)

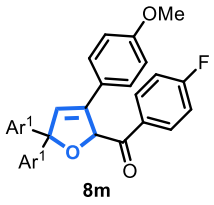


8l

Green oil, 82% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, J = 6.9 Hz, 2H), 7.56 – 7.50 (m, 3H), 7.46 – 7.38 (m, 4H), 7.28 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 6.88 (s, 1H), 6.71 (d, J = 7.5 Hz, 2H), 6.57 (d, J = 7.4 Hz, 2H), 6.44 (s, 1H), 2.94 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.1, 150.0, 149.8, 136.6, 136.1, 135.8, 133.6, 133.3,

132.4, 131.6, 129.7 (q, J = 30.8 Hz), 128.5, 127.9, 127.6, 126.7, 125.5 (q, J = 3.9 Hz), 124.1 (q, J = 280.0 Hz), 112.1, 112.0, 96.3, 86.1, 40.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.61. HRMS(ESI) Calcd. for $C_{34}H_{32}F_3N_2O_2$ $(M+H)^+$ 557.2410, found 557.2398.

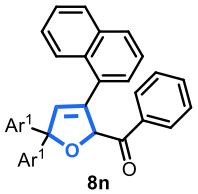
(5,5-bis(4-(dimethylamino)phenyl)-3-(4-methoxyphenyl)-2,5-dihydrofuran-2-yl)(4-fluorophenyl)methanone (8m)



8m

Light green solid, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.94 (m, 2H), 7.24 – 7.14 (m, 4H), 7.03 (d, J = 7.1 Hz, 2H), 6.90 (t, J = 7.7 Hz, 2H), 6.72 (d, J = 7.2 Hz, 2H), 6.60 (d, J = 9.0 Hz, 3H), 6.49 (d, J = 7.3 Hz, 2H), 6.20 (s, 1H), 3.67 (s, 3H), 2.83 (s, 6H), 2.80 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.5, 165.6 (d, J = 257.2 Hz), 159.4, 149.9, 149.7, 136.9, 133.3, 132.5 (d, J = 3.0 Hz), 132.3 (d, J = 9.2 Hz), 132.2, 129.1, 127.8, 127.5, 125.4, 115.3 (d, J = 22.3 Hz), 114.0, 112.1, 112.0, 96.2, 87.3, 55.3, 40.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.61. HRMS(ESI) Calcd. for $C_{34}H_{34}FN_2O_3$ $(M+H)^+$ 537.2548, found 537.2521.

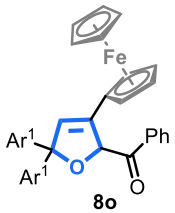
(5,5-bis(4-(dimethylamino)phenyl)-3-(naphthalen-1-yl)-2,5-dihydrofuran-2-yl)(phenyl)methanone (8n)



8n

Green oil, 89% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 7.7 Hz, 2H), 7.68 (d, J = 6.5 Hz, 2H), 7.60 (d, J = 5.9 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.44 (t, J = 7.7 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.84 (s, 1H), 6.63 (d, J = 8.2 Hz, 2H), 6.52 (d, J = 8.2 Hz, 2H), 6.46 (s, 1H), 2.86 (s, 6H), 2.81 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.6, 149.9, 149.7, 137.3, 136.2, 133.3, 133.1, 132.9, 132.1, 131.8, 130.3, 129.6, 128.4, 128.2, 128.2, 127.9, 127.7, 127.6, 126.3, 126.1, 125.5, 124.5, 112.1, 112.1, 96.3, 86.6, 40.6. HRMS(ESI) Calcd. for $C_{37}H_{35}N_2O_2$ $(M+H)^+$ 539.2693, found 539.2667.

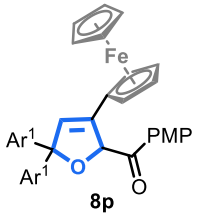
(5,5-bis(4-(dimethylamino)phenyl)-3-(ferrocene)-2,5-dihydrofuran-2-yl)(phenyl)methanone (8o)



8o

Red oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, J = 7.63 Hz, 2H), 7.49 (t, J = 8.00 Hz, 1H), 7.36 (d, J = 8.75 Hz, 2H), 7.24 (d, J = 8.13 Hz, 2H), 7.16 (d, J = 8.82 Hz, 2H), 6.70 (d, J = 7.62 Hz, 2H), 6.60 (d, J = 7.64 Hz, 2H), 6.47 (s, 1H), 6.12 (s, 1H), 4.47 (s, 1H), 4.22 (s, 1H), 4.14 (s, 1H), 4.12 (s, 1H), 4.09 – 4.01 (m, 5H), 2.93 (s, 6H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.5, 149.8, 149.7, 136.4, 136.1, 133.6, 133.1, 132.2, 129.7, 128.3, 128.0, 127.9, 127.5, 112.2, 112.1, 96.0, 87.9, 69.4, 69.0, 68.9, 67.6, 67.2, 40.7, 40.7. HRMS(ESI) Calcd. for $C_{37}H_{37}FeN_2O_2$ $(M+H)^+$ 597.2199, found 597.2174.

(5,5-bis(4-(dimethylamino)phenyl)-3-(ferrocene)-2,5-dihydrofuran-2-yl)(3-methoxyphenyl)methanone (8p)

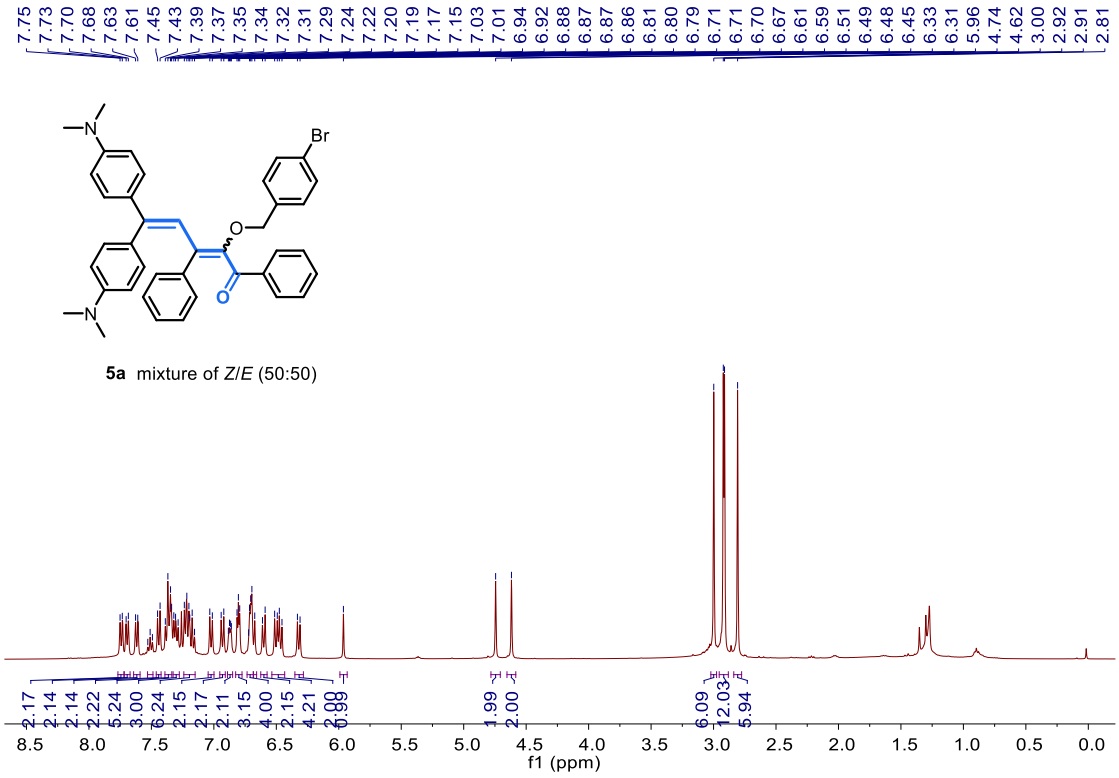


8p

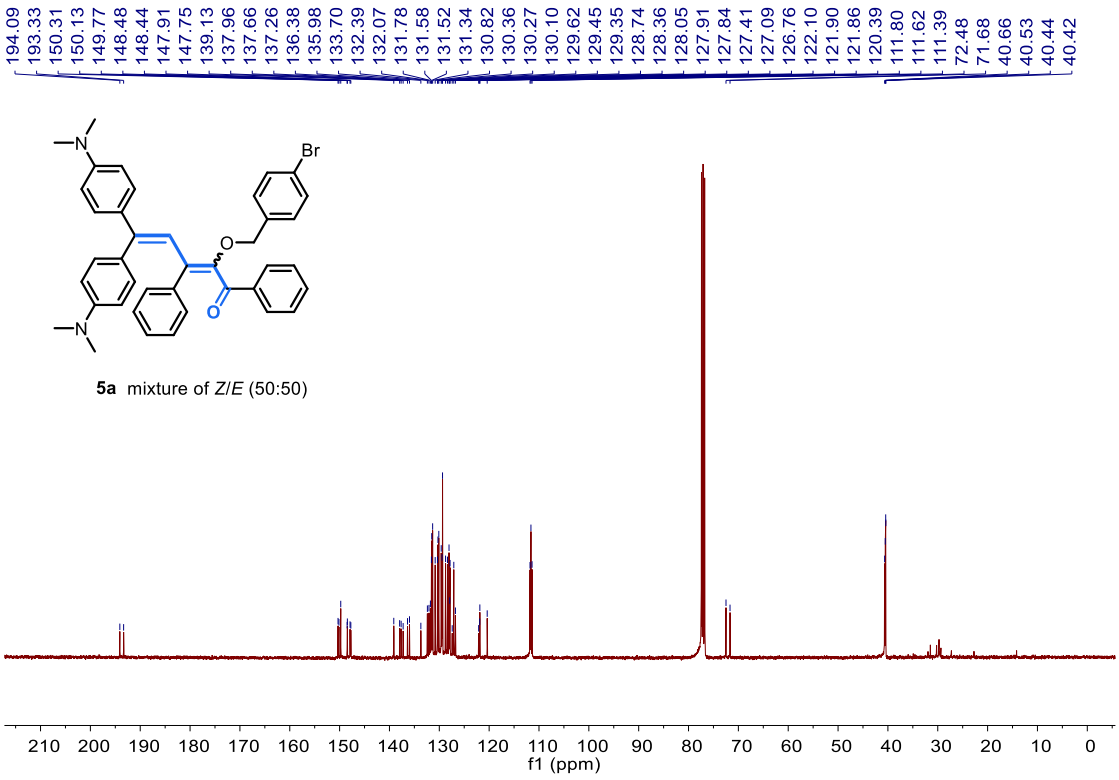
Red oil, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.10 (d, *J* = 2.1 Hz,1H), 4.46 (s, 1H), 4.20 (s, 1H), 4.16 – 4.10 (m, 2H), 4.09 – 4.00 (m, 5H), 3.8 (s, 3H), 2.9 (s, 6H), 2.9 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.8, 163.5, 149.8, 149.7, 136.7, 133.7, 132.3, 132.1, 129.2, 128.0, 127.7, 127.4, 113.5, 112.2, 112.1, 95.9, 87.8, 69.4, 69.0, 68.9, 67.5, 67.2, 55.4, 40.7, 40.7. HRMS(ESI) Calcd. for $C_{38}H_{39}FeN_2O_3$ $(M+H)^+$ 627.2305, found: 627.2279.

[a]Ar^1 =*p*-(*N*, *N*-dimethylamino) phenyl.

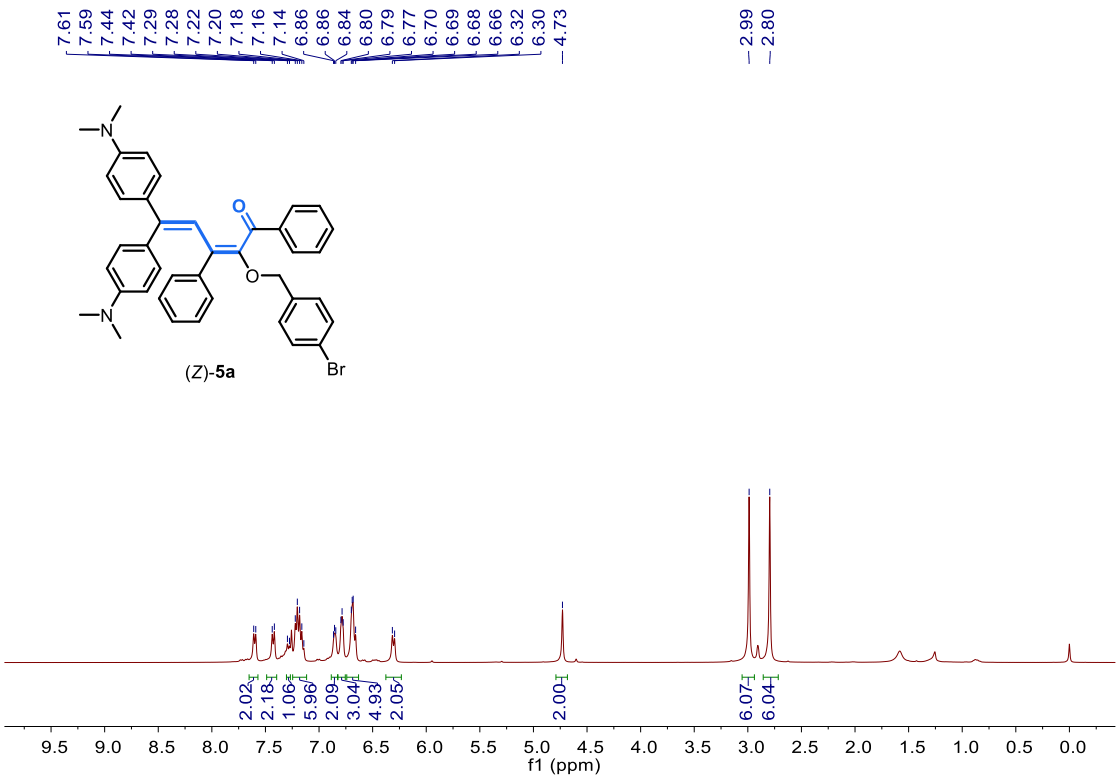
NMR Spectra of Compounds



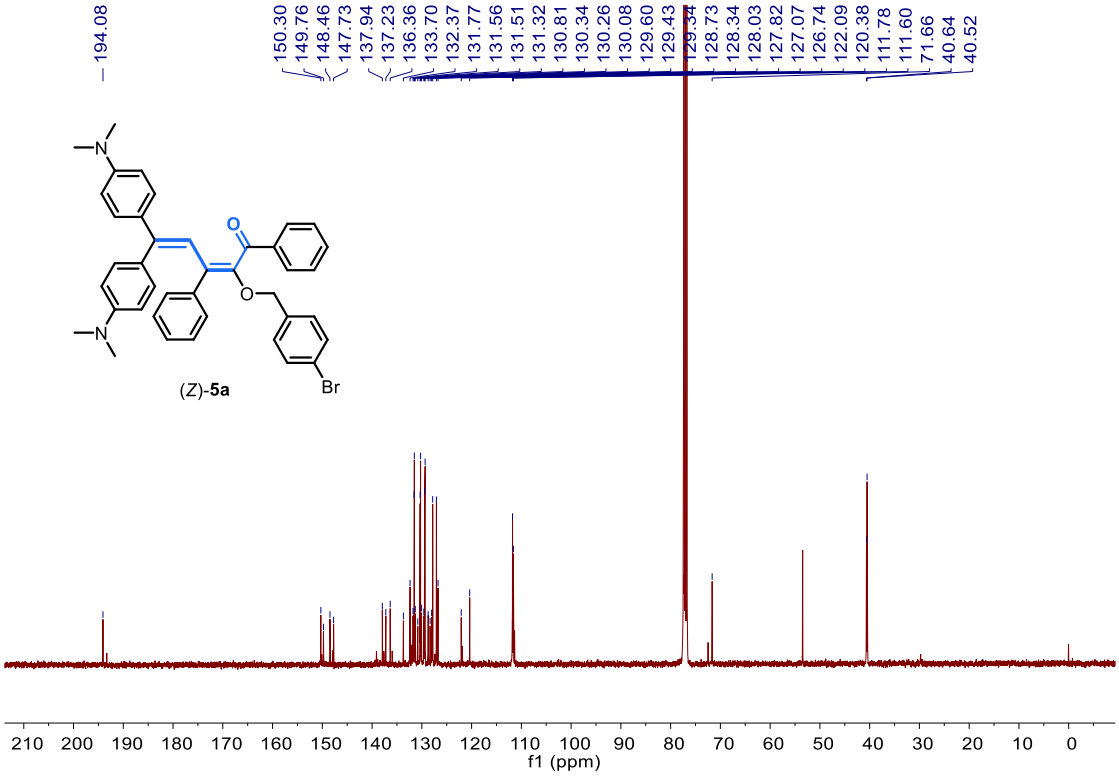
^{1}H NMR Spectrum of **5a** isomers mixture (400MHz, CDCl3)



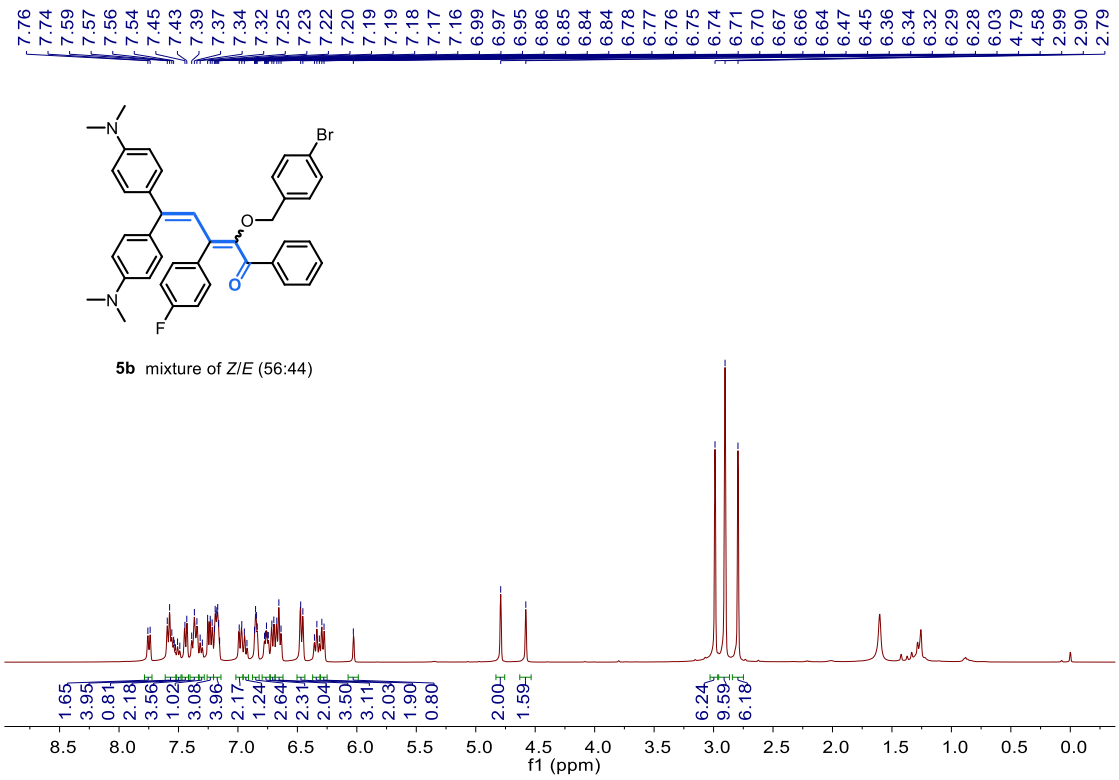
^{13}C NMR Spectrum of Compound **5a** isomers mixture (100MHz, CDCl3)



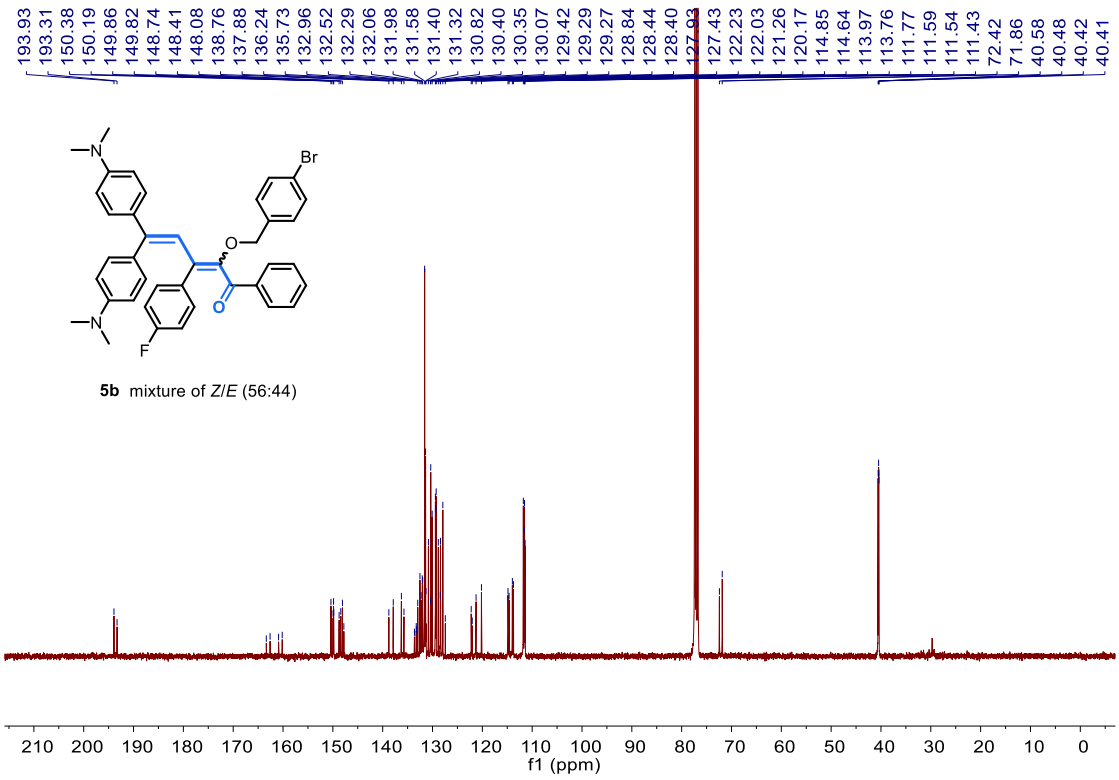
^{1}H NMR Spectrum of Compound (*Z*)-**5a** (400MHz, CDCl3)



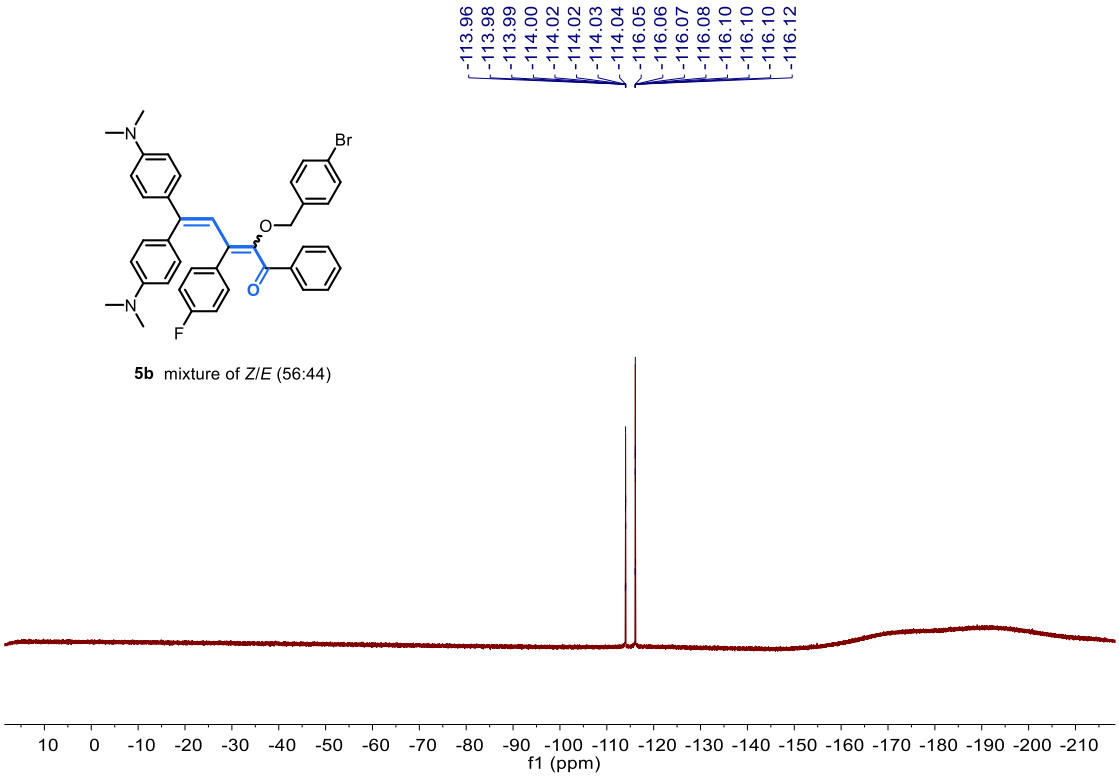
^{13}C NMR Spectrum of Compound (*Z*)-**5a** (100MHz, CDCl3)



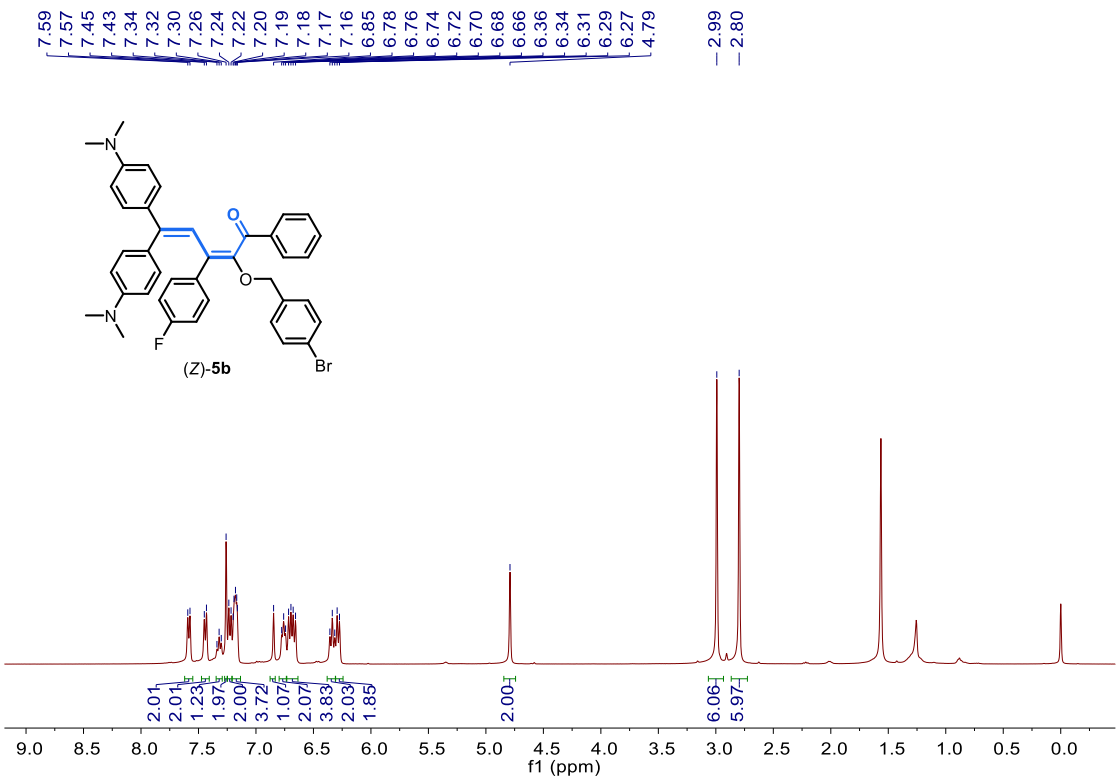
^{1}H NMR Spectrum of Compound **5b** isomers mixture (400MHz, CDCl3)



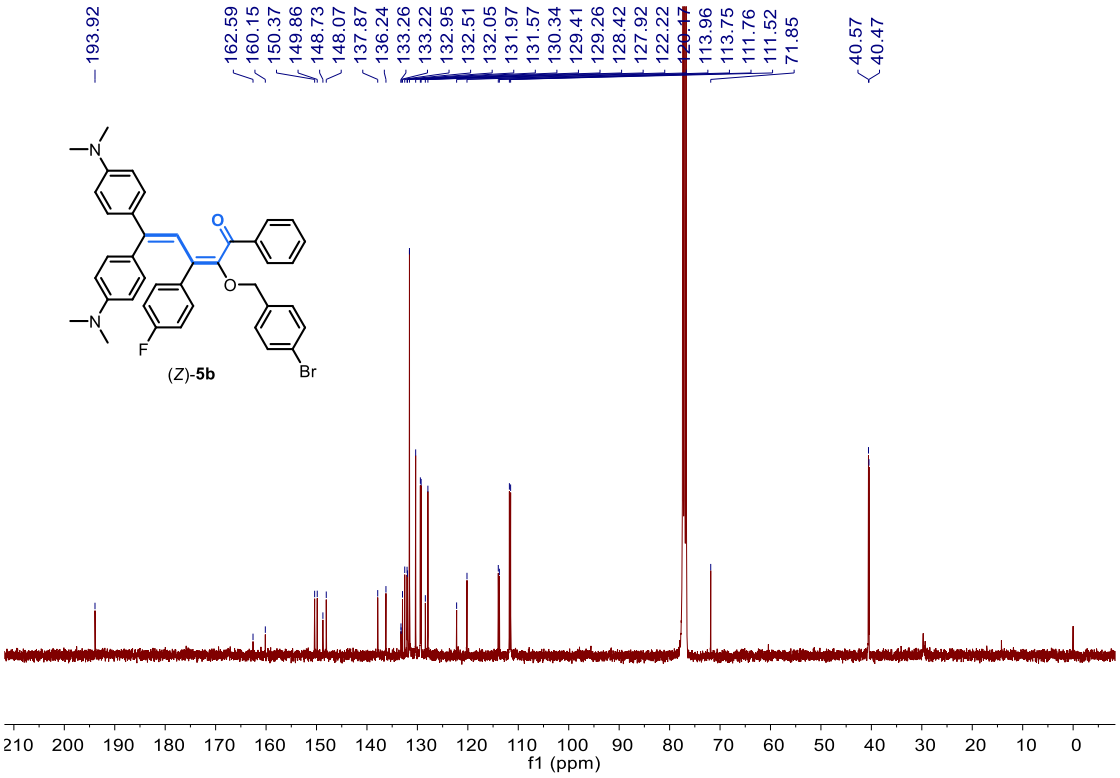
^{13}C NMR Spectrum of Compound **5b** isomers mixture (100MHz, CDCl3)



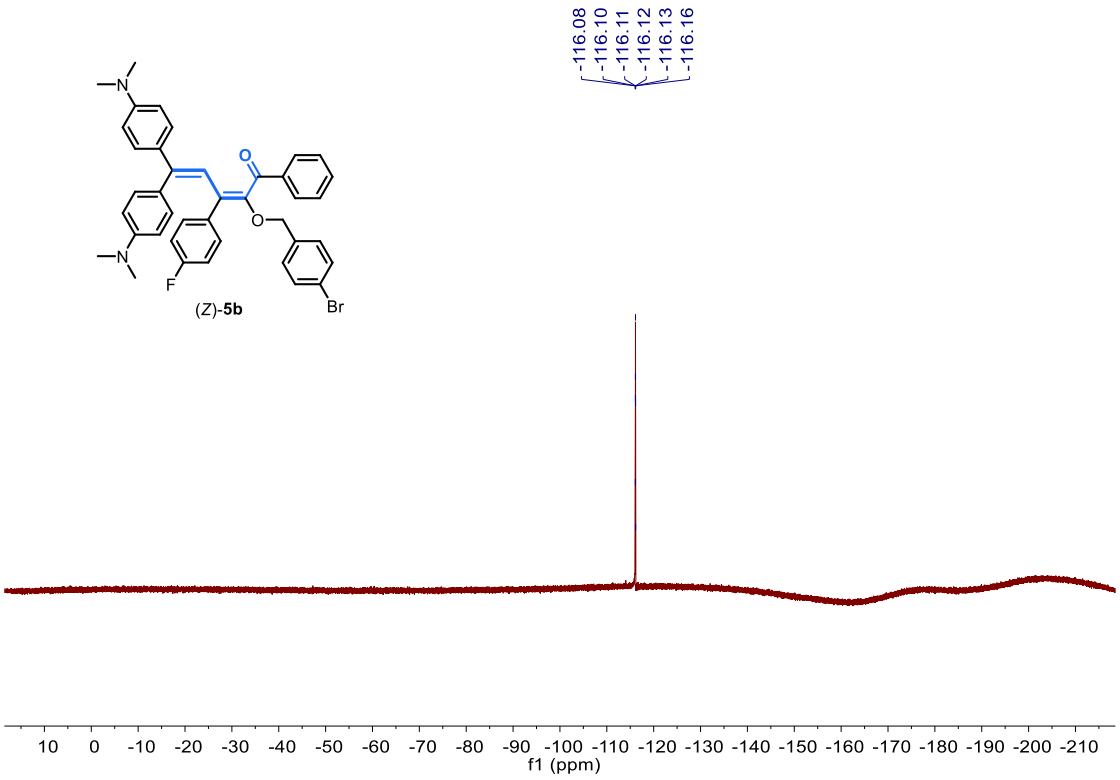
^{19}F NMR Spectrum of Compound **5b** isomers mixture (376 MHz, CDCl3)



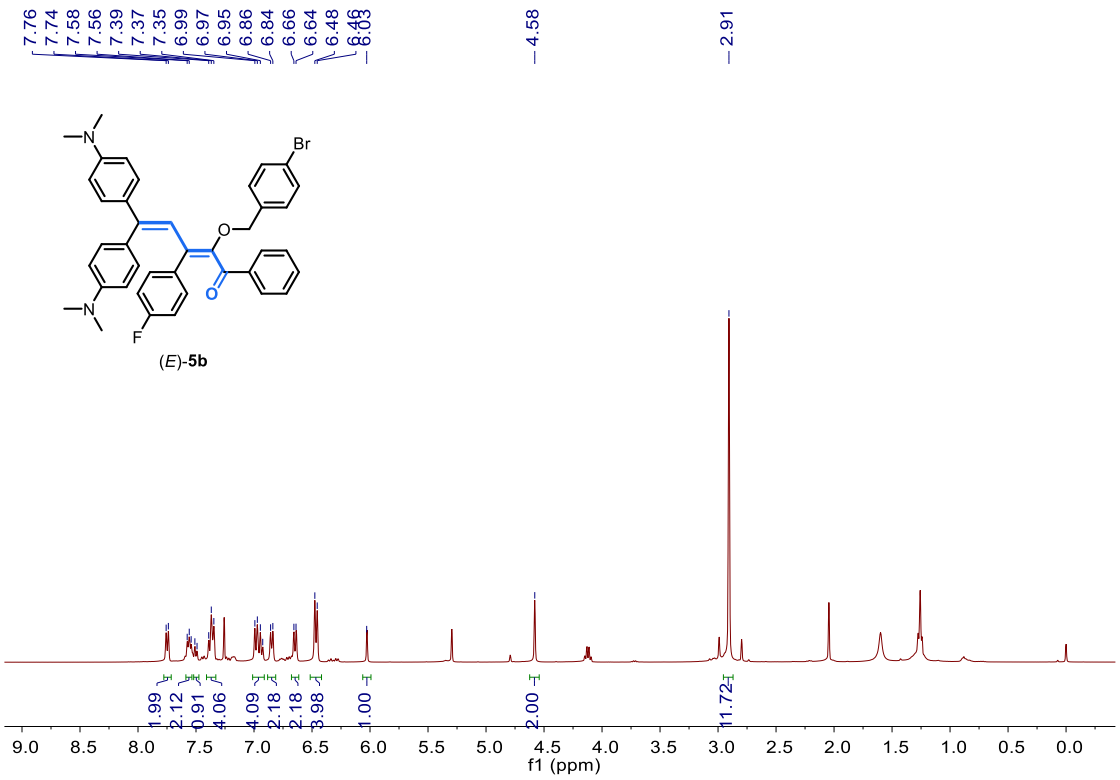
^{1}H NMR Spectrum of Compound (*Z*)-**5b** (400MHz, CDCl3)



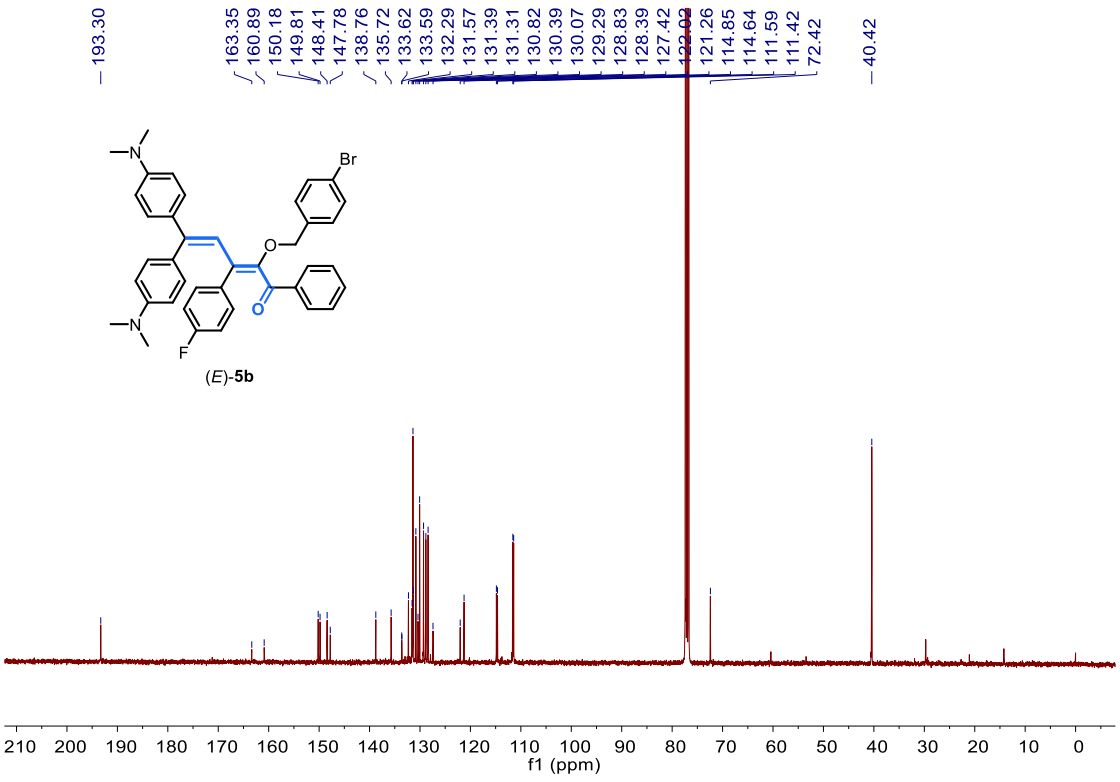
^{13}C NMR Spectrum of Compound (*Z*)-**5b** (100MHz, CDCl3)



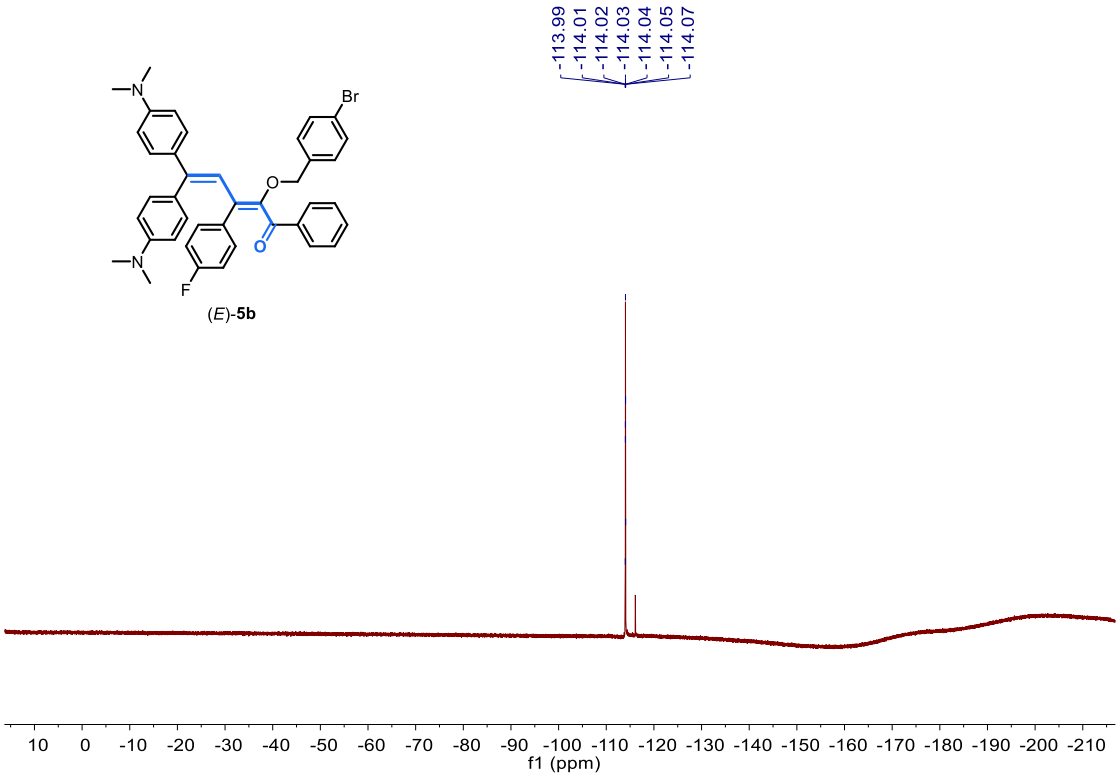
^{19}F NMR Spectrum of Compound (*Z*)-**5b** (376 MHz, CDCl3)



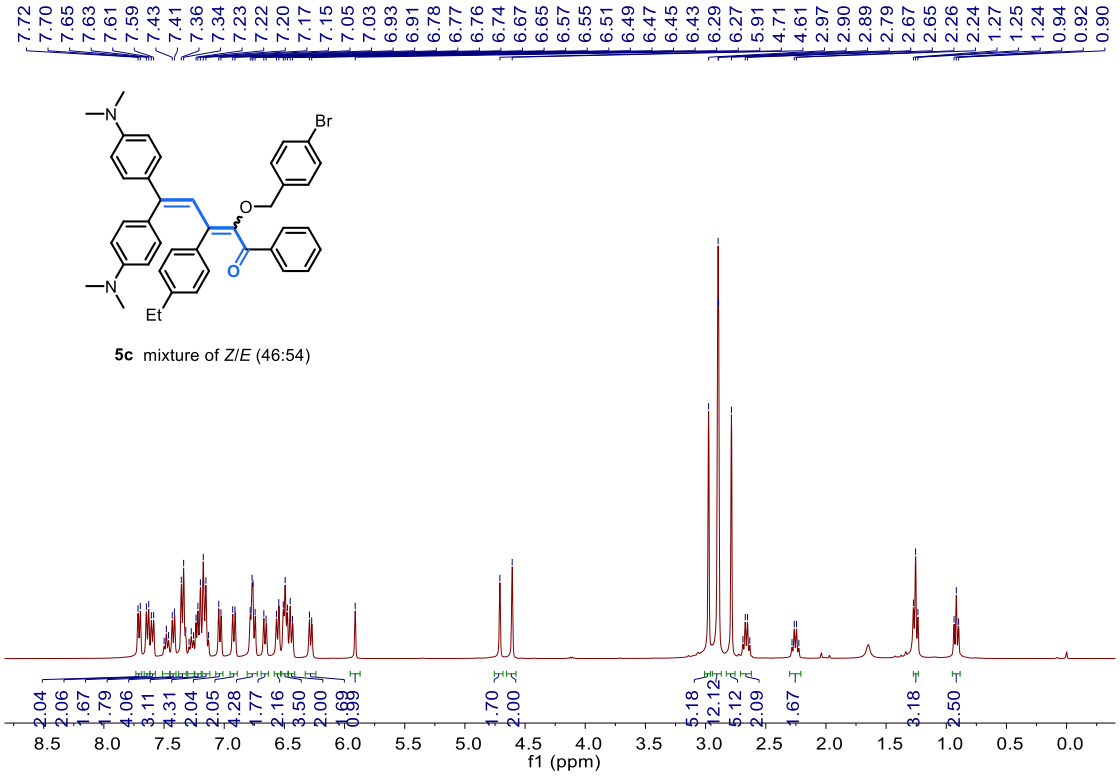
^{1}H NMR Spectrum of Compound (*E*)-**5b** (400MHz, CDCl3)



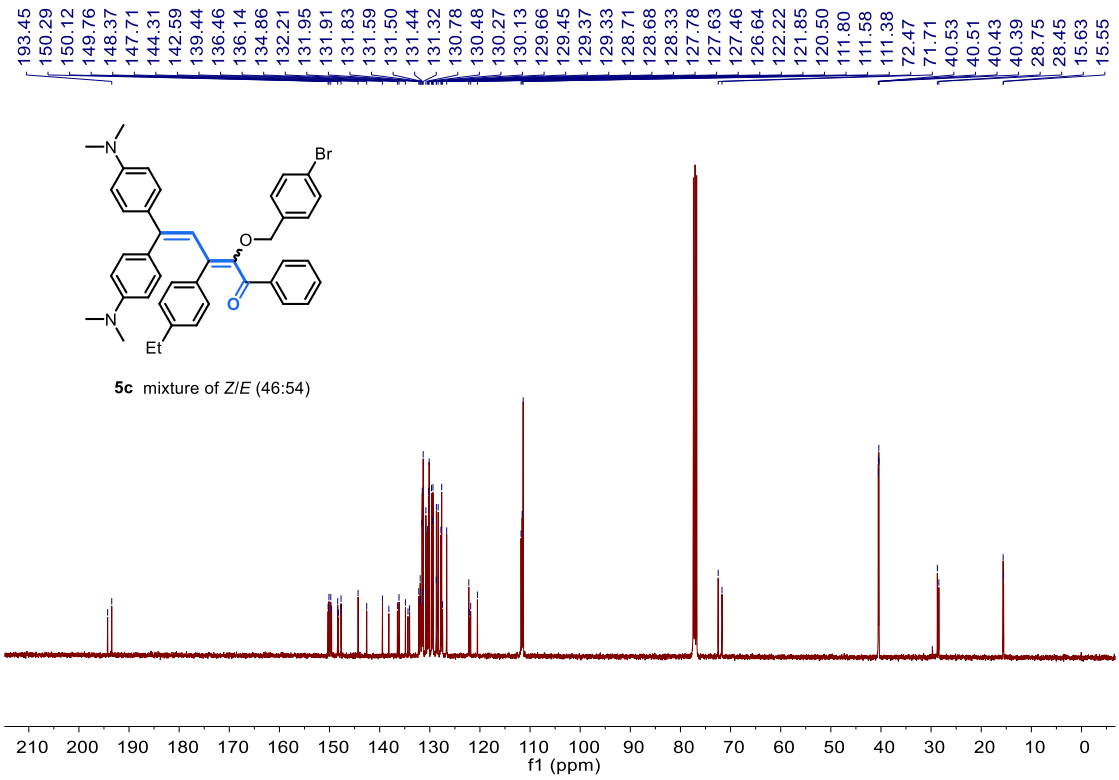
^{13}C NMR Spectrum of Compound (*E*)-**5b** (100MHz, CDCl3)



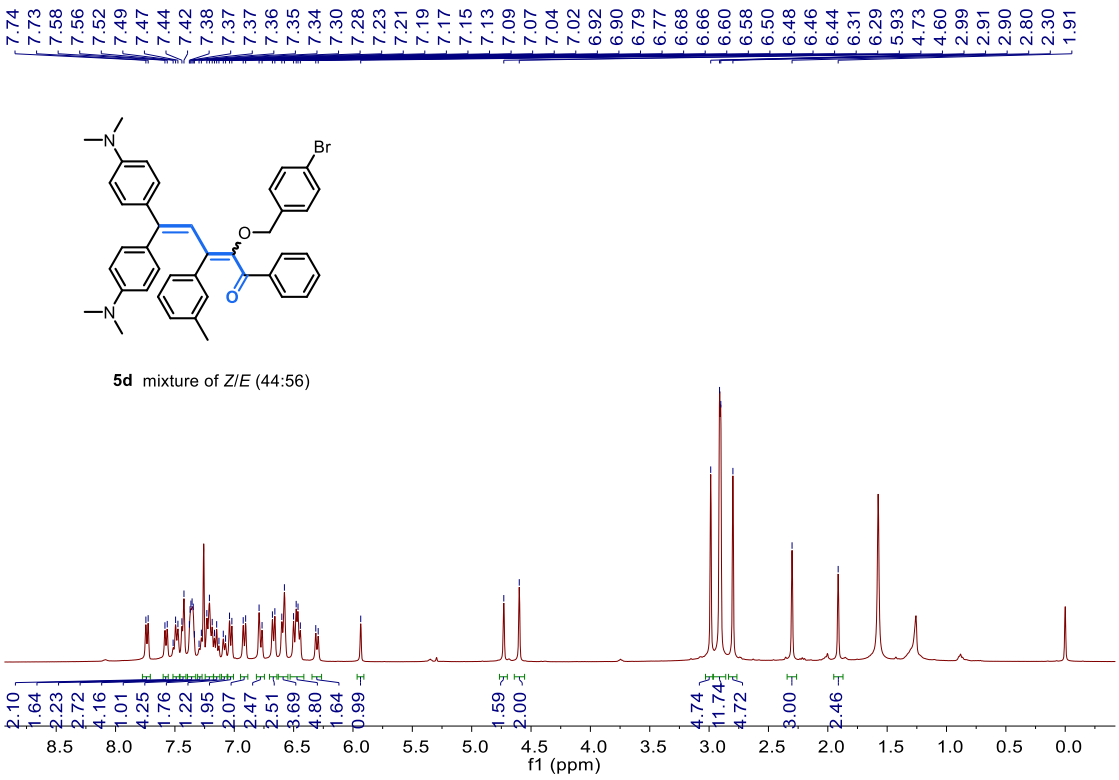
^{19}F NMR Spectrum of Compound (*E*)-**5b** (376 MHz, CDCl3)



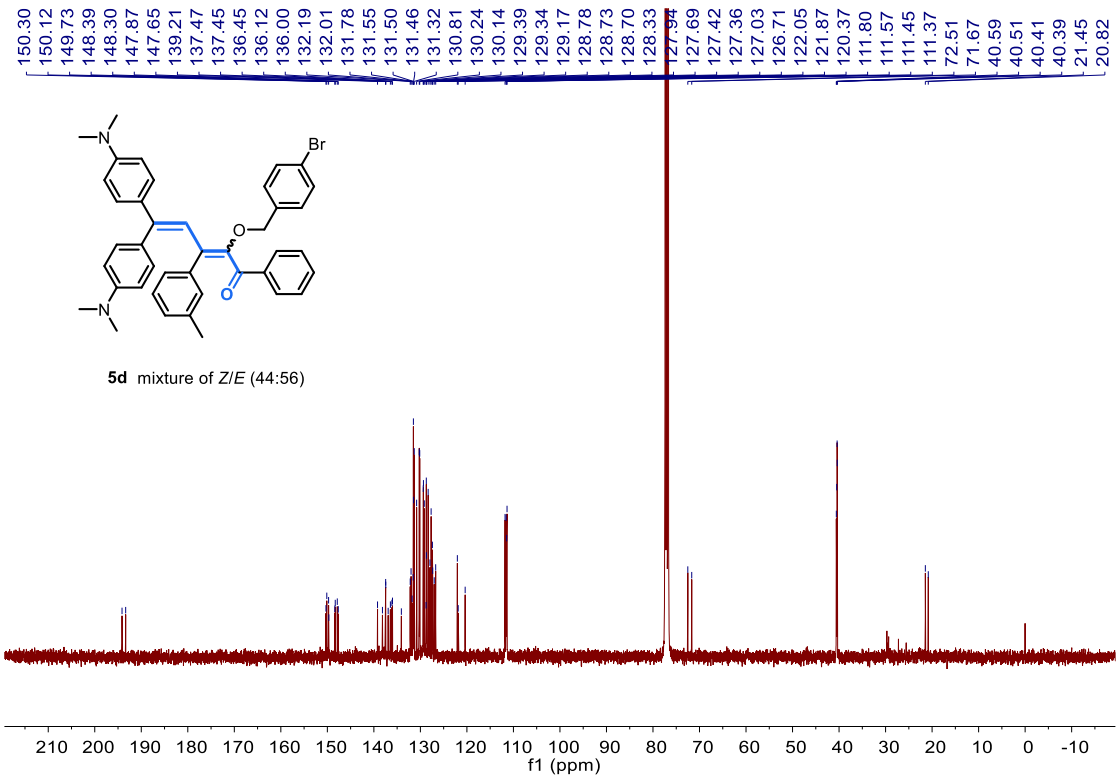
^{1}H NMR Spectrum of Compound **5c** isomers mixture (400MHz, CDCl3)



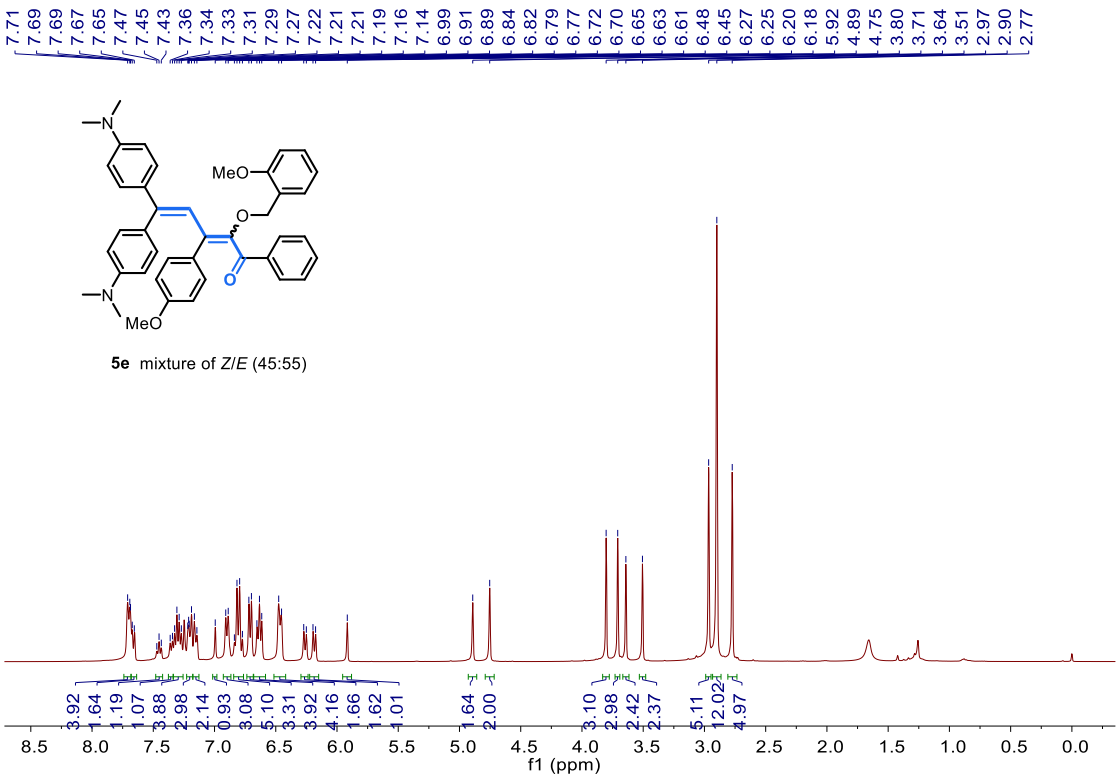
^{13}C NMR Spectrum of Compound **5c** isomers mixture (100MHz, CDCl3)



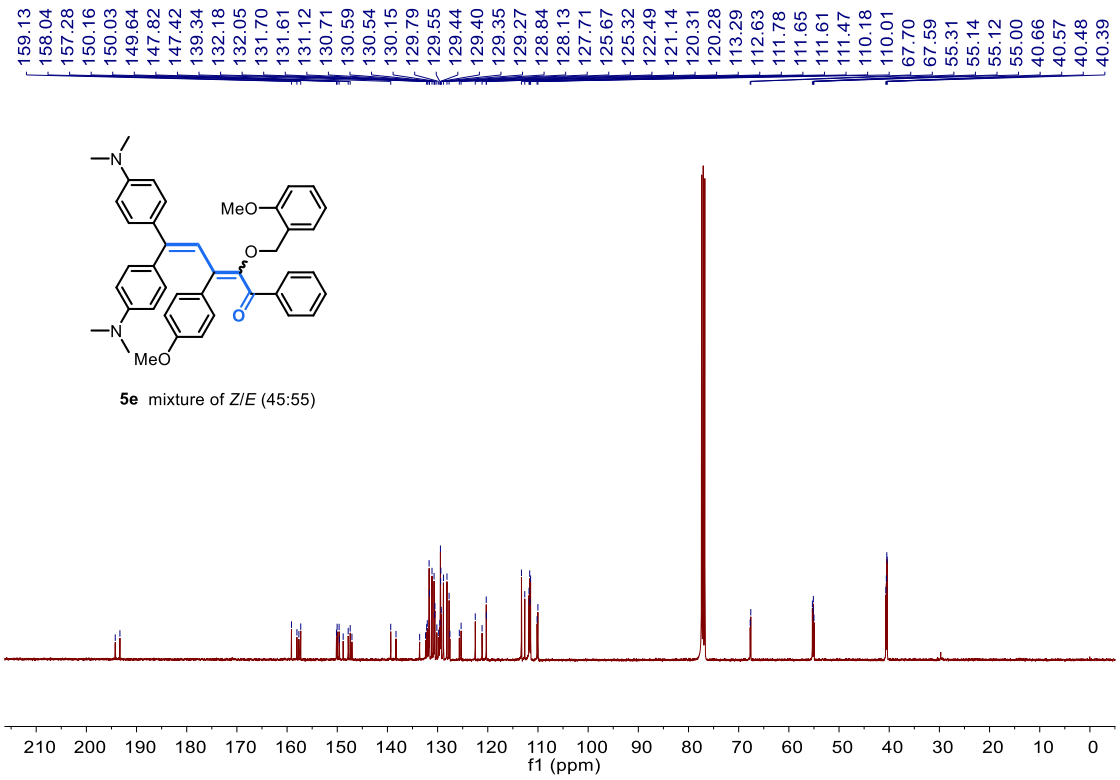
^{1}H NMR Spectrum of Compound **5d** isomers mixture (400MHz, CDCl3)



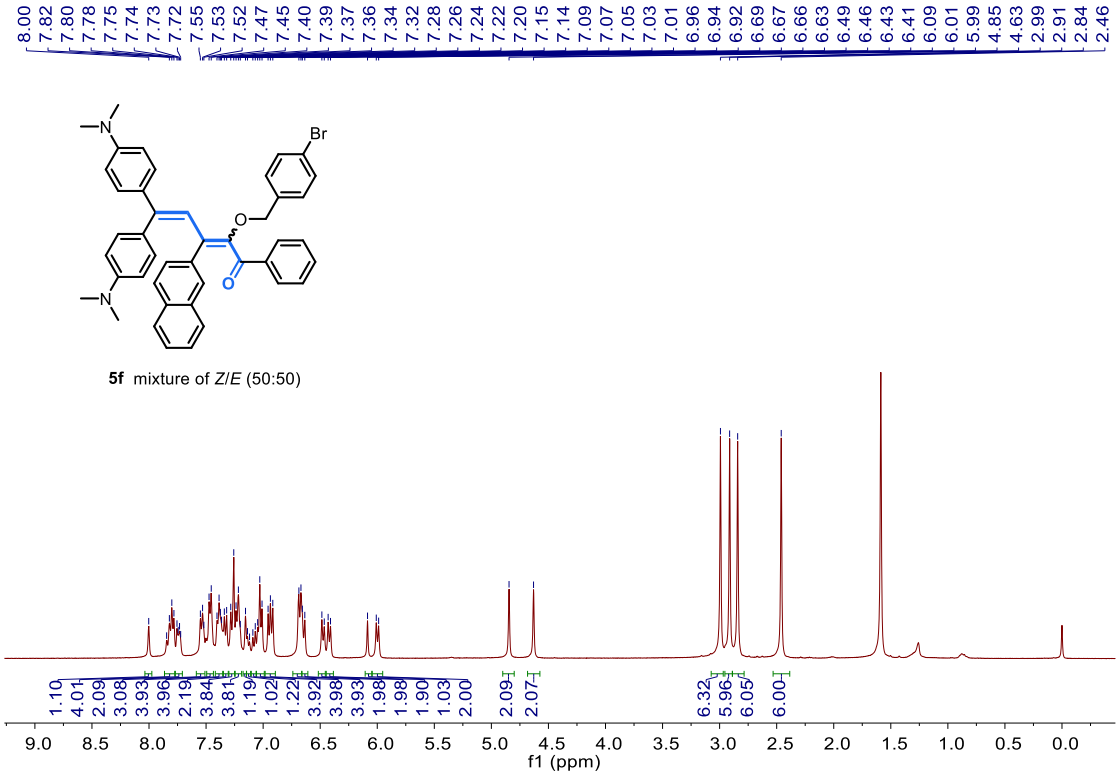
^{13}C NMR Spectrum of Compound **5d** isomers mixture (100MHz, CDCl3)



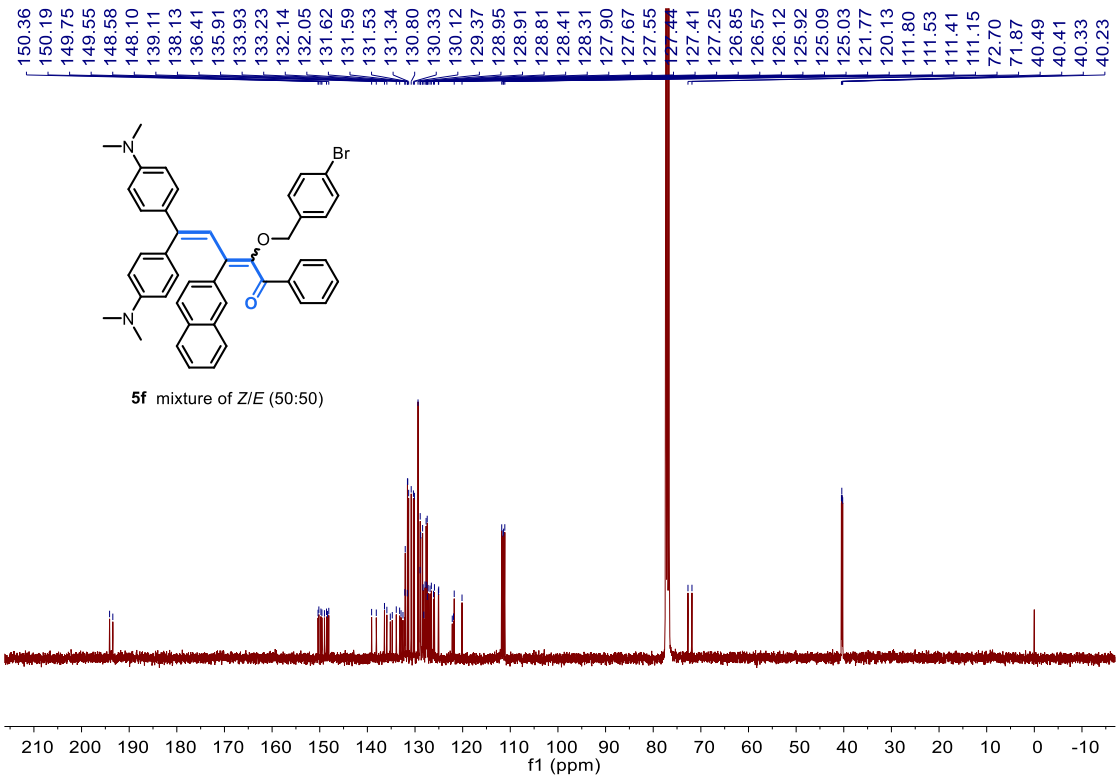
^{1}H NMR Spectrum of Compound **5e** isomers mixture (400MHz, CDCl3)



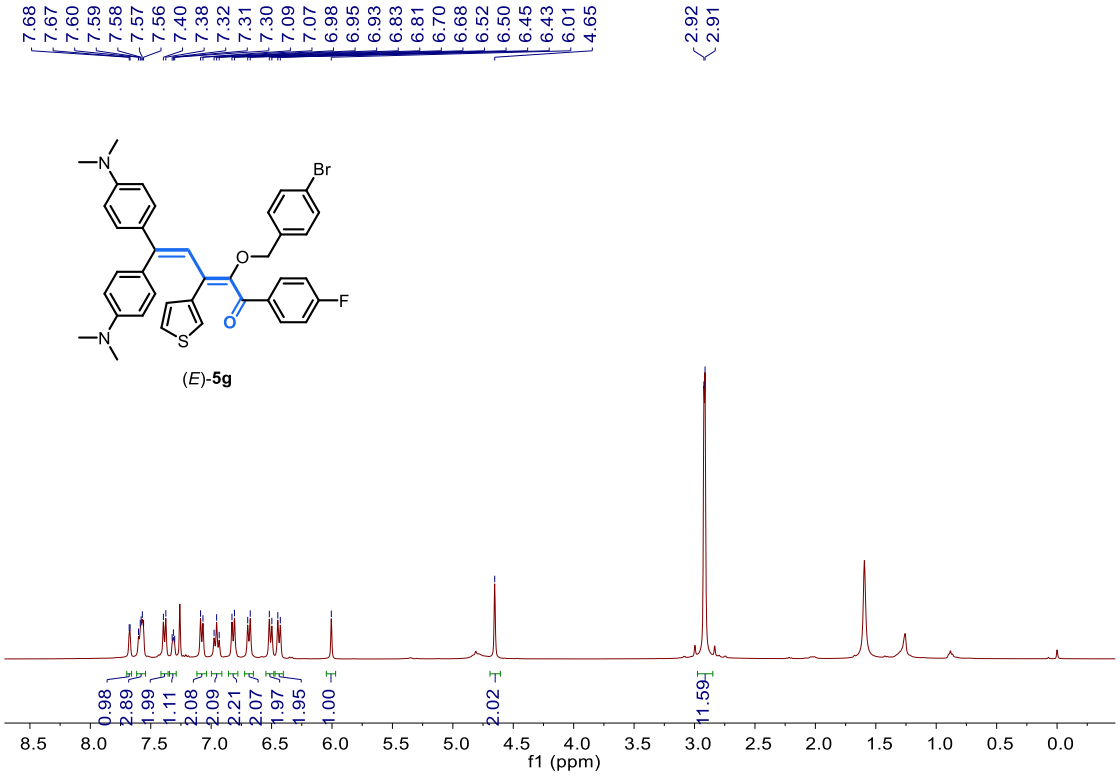
^{13}C NMR Spectrum of Compound **5e** isomers mixture (100MHz, CDCl3)



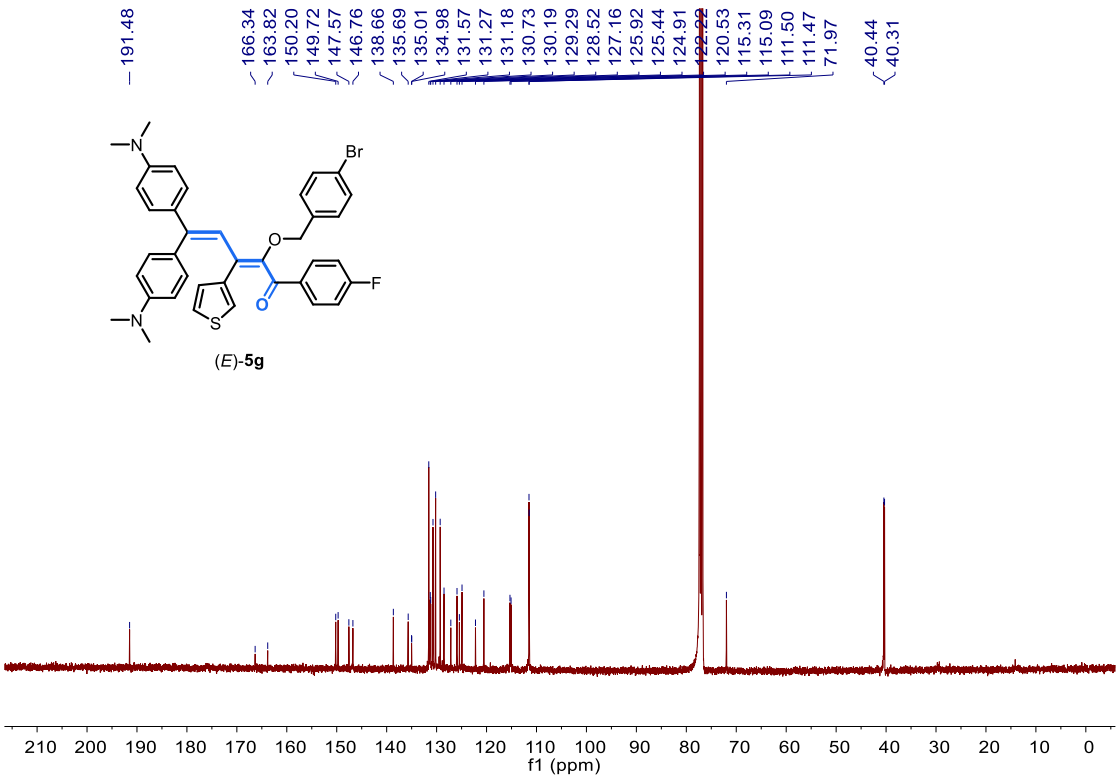
^{1}H NMR Spectrum of Compound **5f** isomers mixture (400MHz, CDCl3)



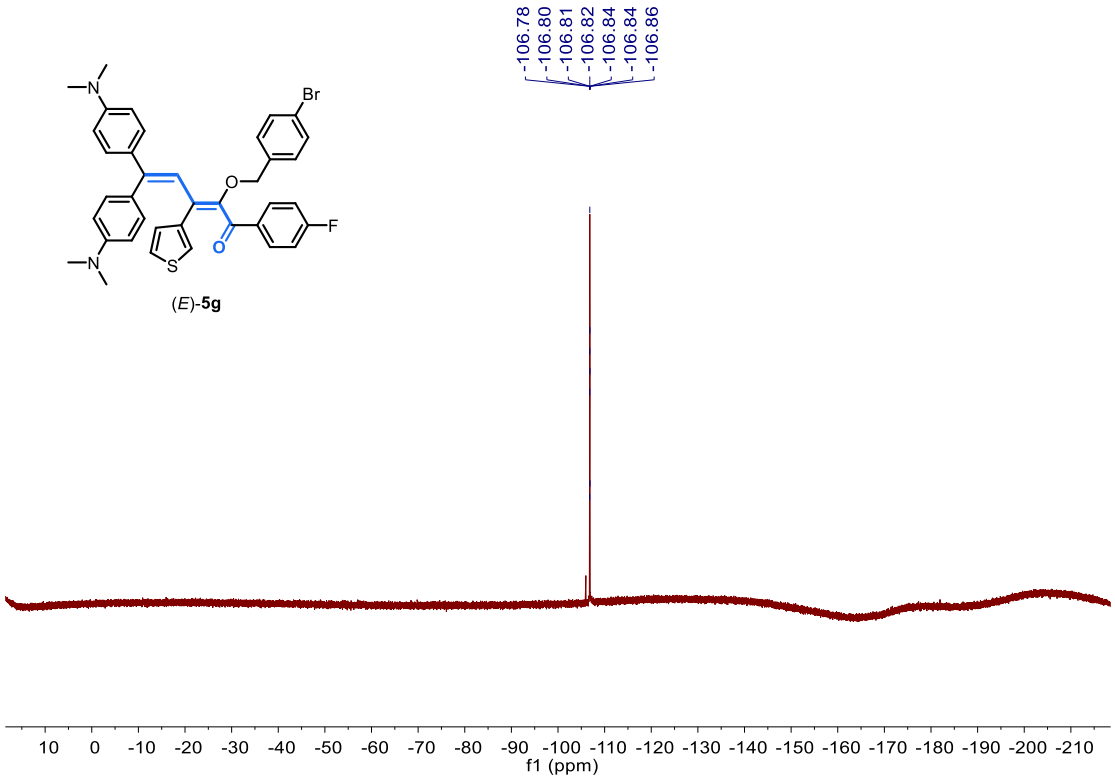
^{13}C NMR Spectrum of Compound **5f** isomers mixture (100MHz, CDCl3)



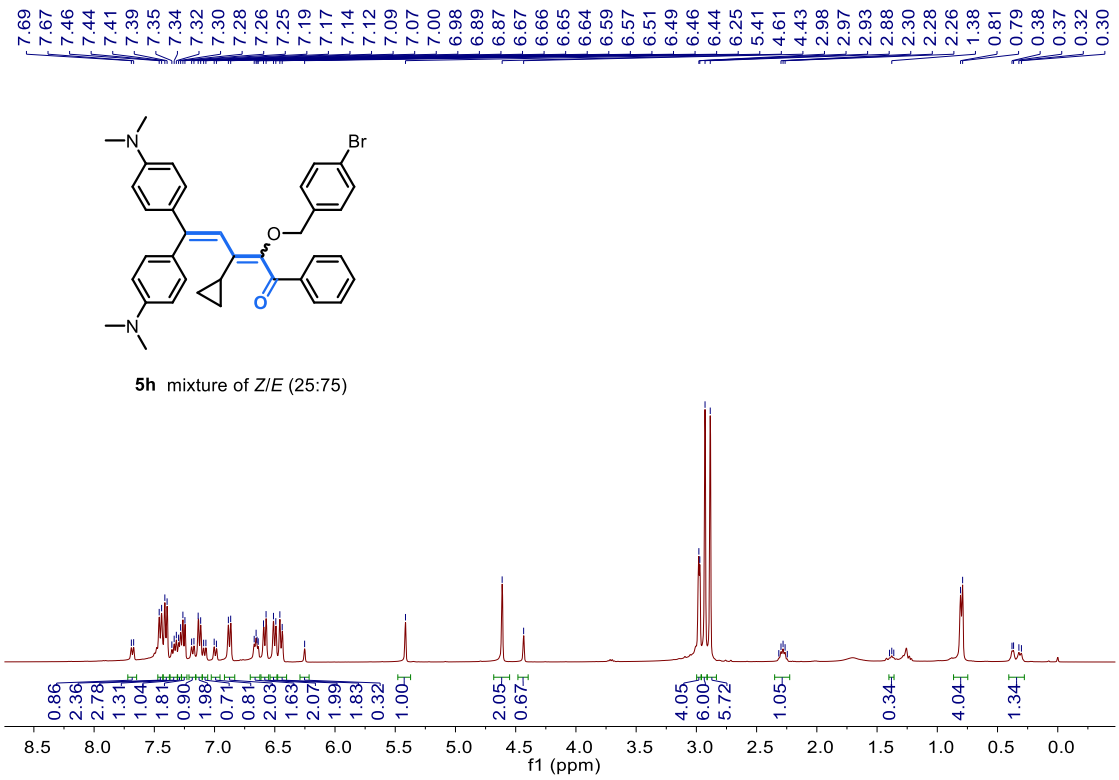
^{1}H NMR Spectrum of Compound (*E*)-**5g** (400MHz, CDCl3)



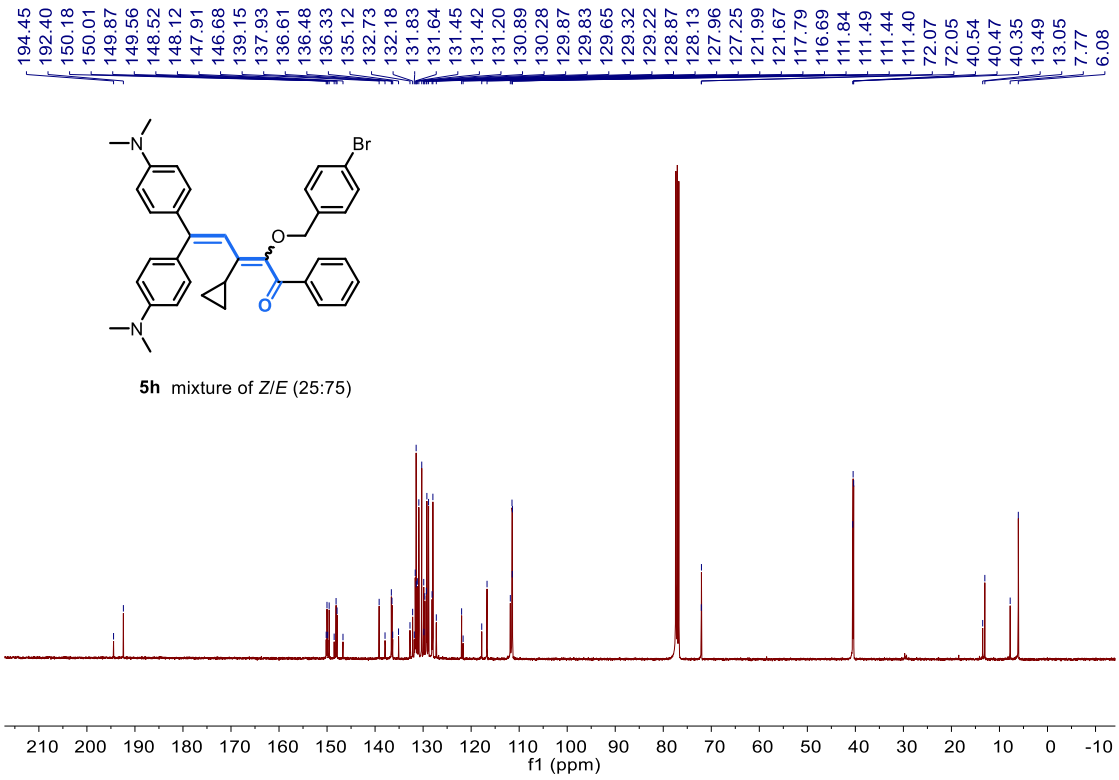
^{13}C NMR Spectrum of Compound (*E*)-**5g** (100MHz, CDCl3)



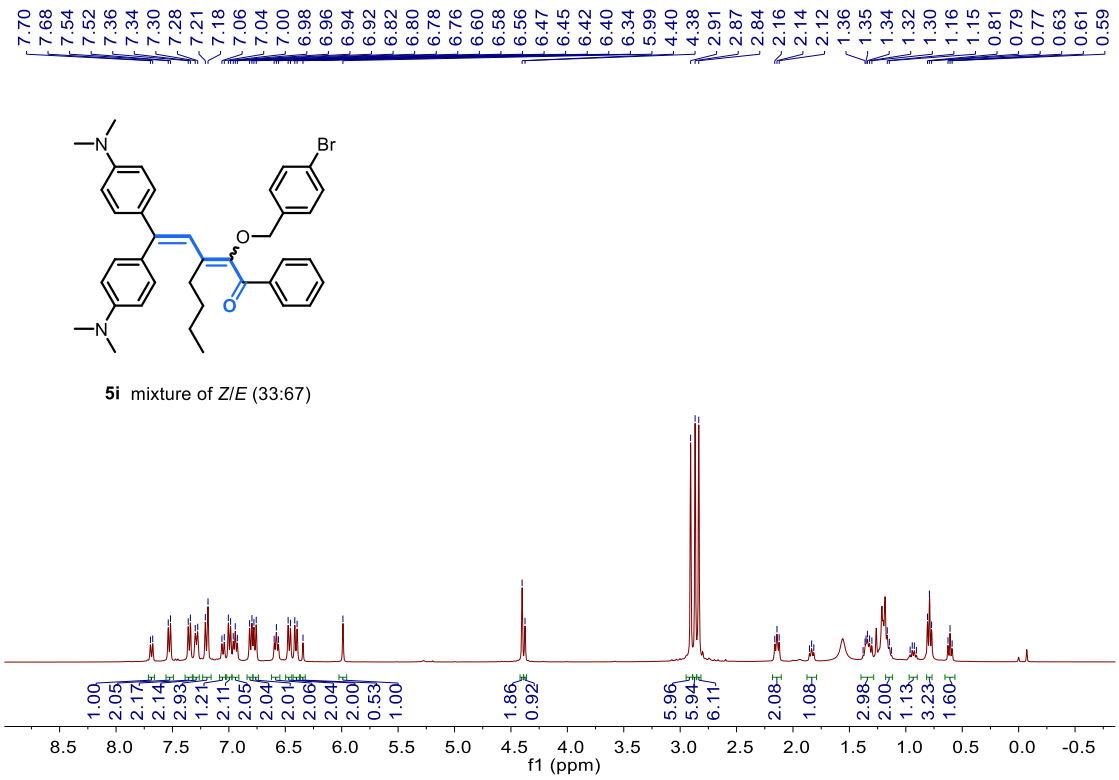
^{19}F NMR Spectrum of Compound (*E*)-**5g** (376 MHz, CDCl3)



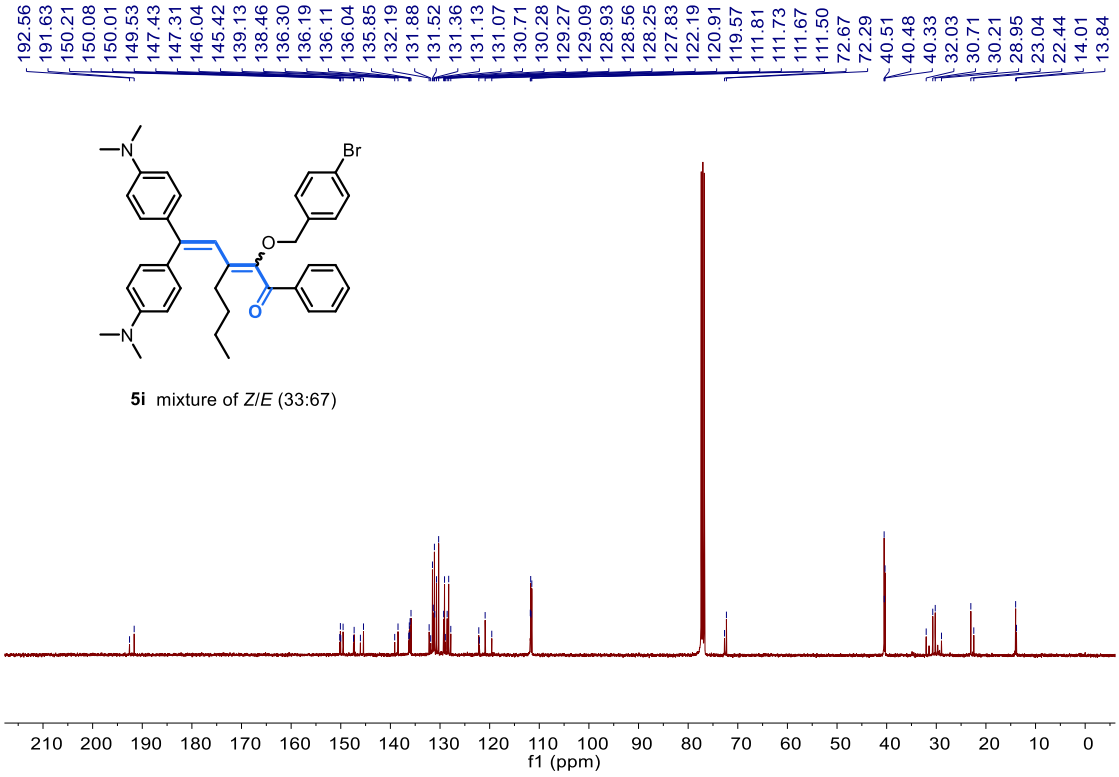
^{1}H NMR Spectrum of Compound **5h** isomers mixture (400MHz, CDCl3)



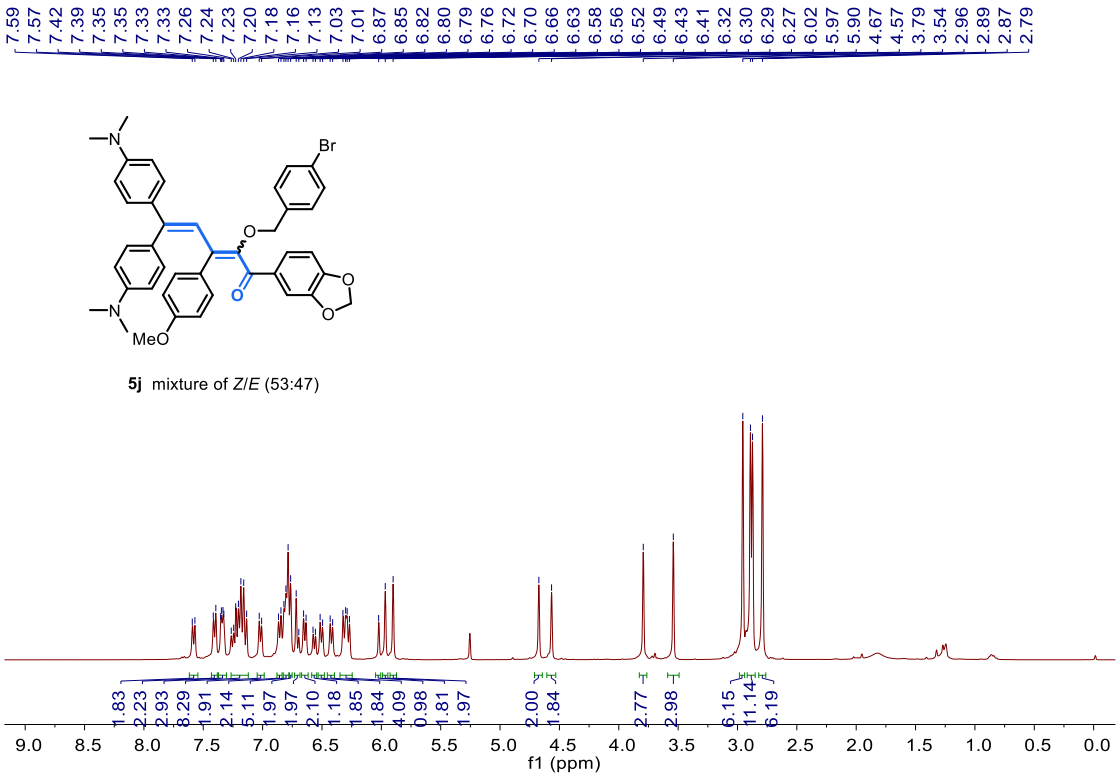
^{13}C NMR Spectrum of Compound **5h** isomers mixture (100MHz, CDCl3)



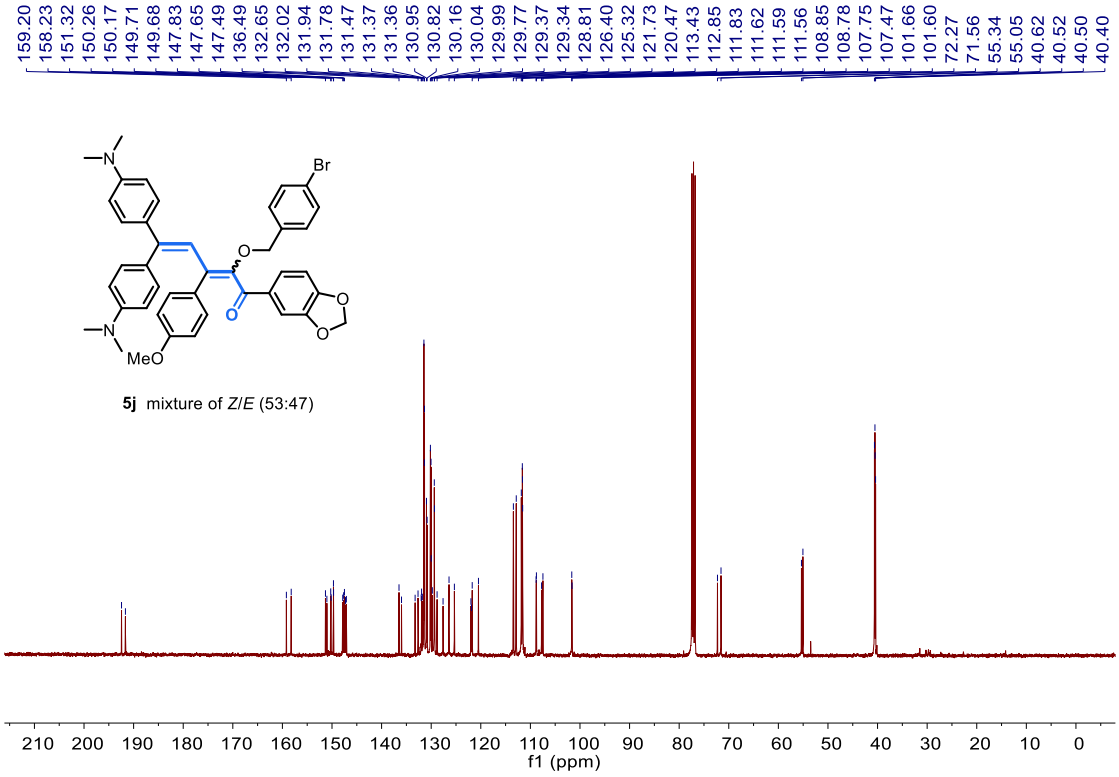
^{1}H NMR Spectrum of Compound **5i** isomers mixture (400MHz, CDCl3)



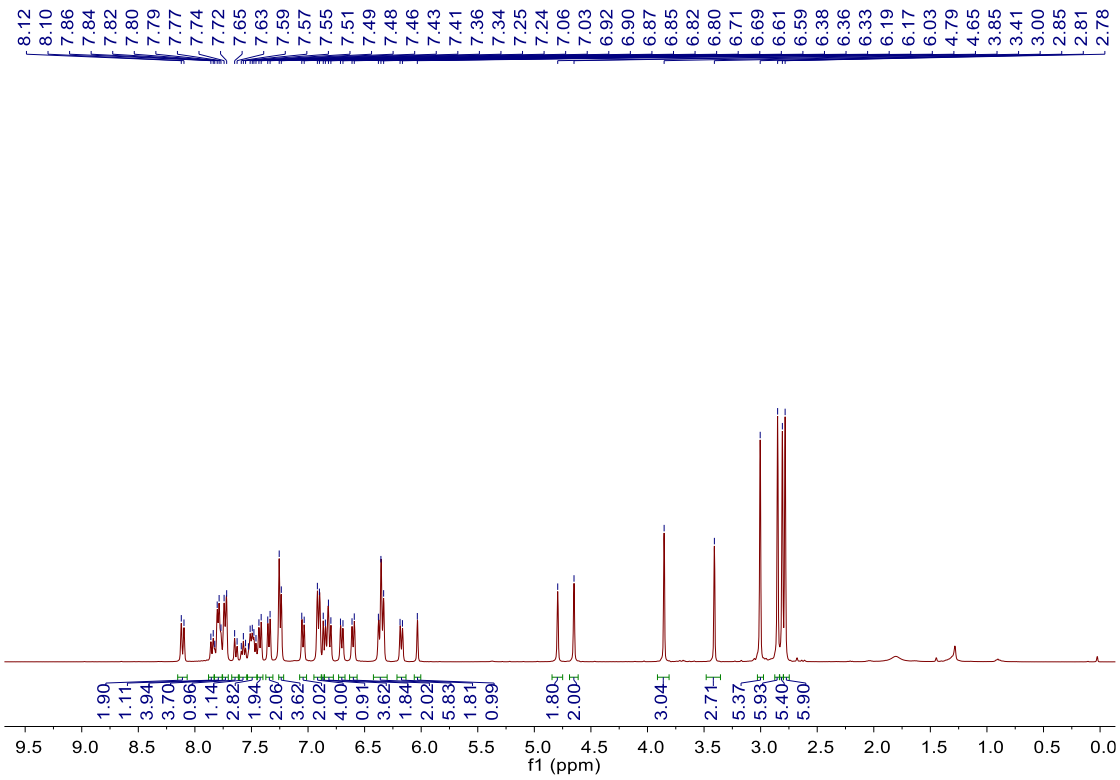
^{13}C NMR Spectrum of Compound **5i** isomers mixture (100MHz, CDCl3)



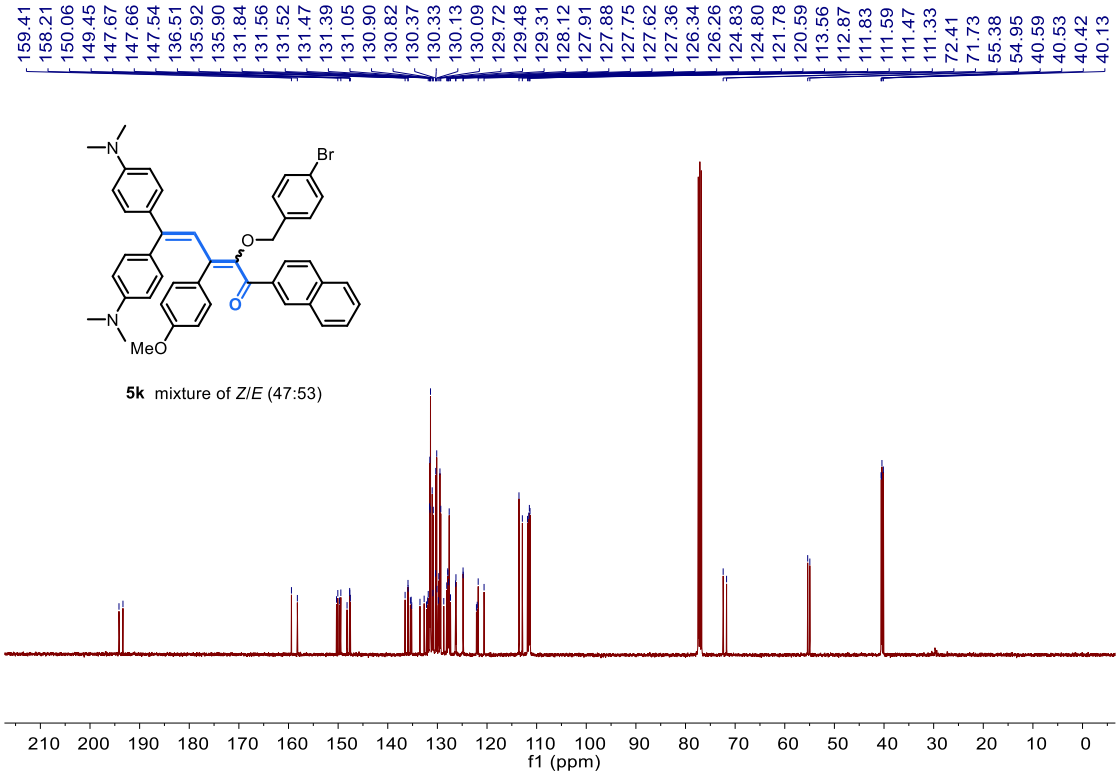
^{1}H NMR Spectrum of Compound **5j** isomers mixture (400MHz, CDCl3)



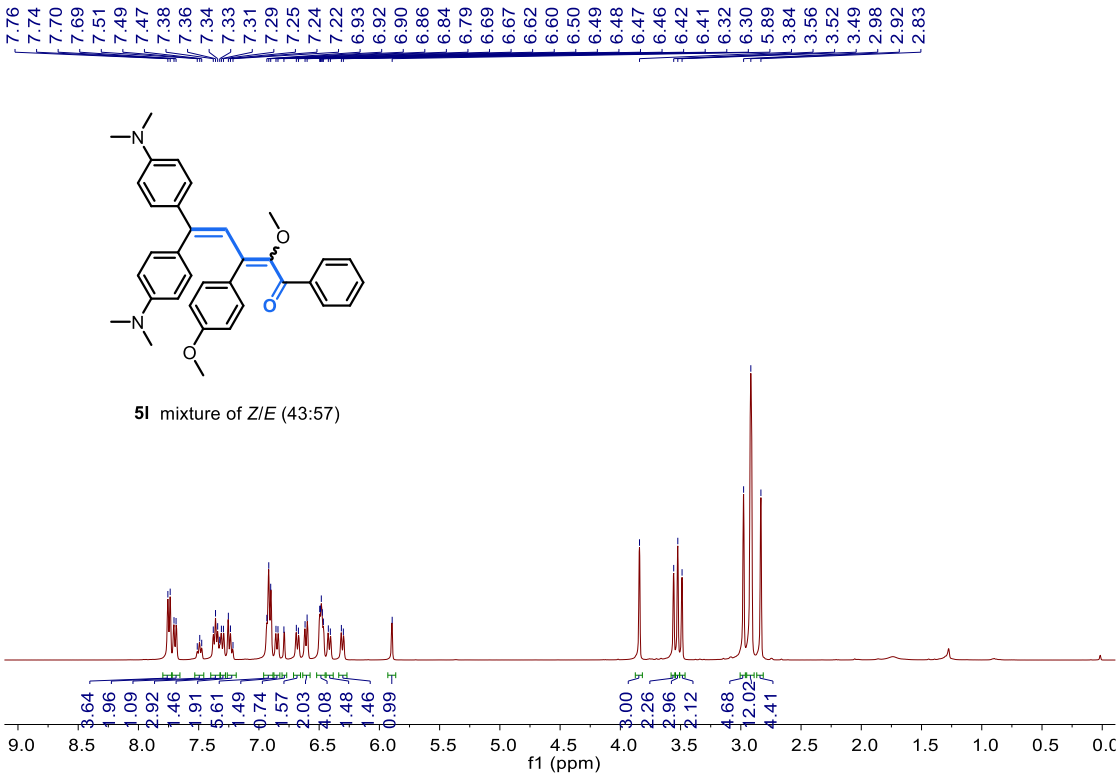
^{13}C NMR Spectrum of Compound **5j** isomers mixture (100MHz, CDCl3)



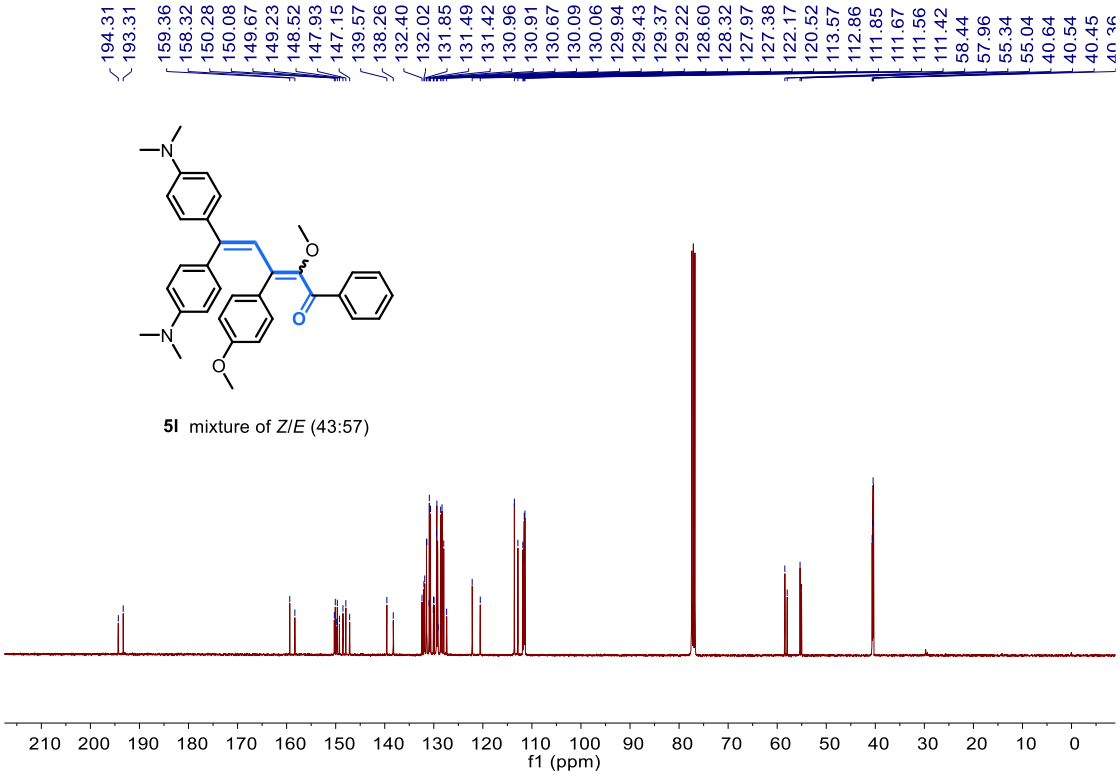
[1]H NMR Spectrum of Compound **5k** isomers mixture (400MHz, CDCl3)



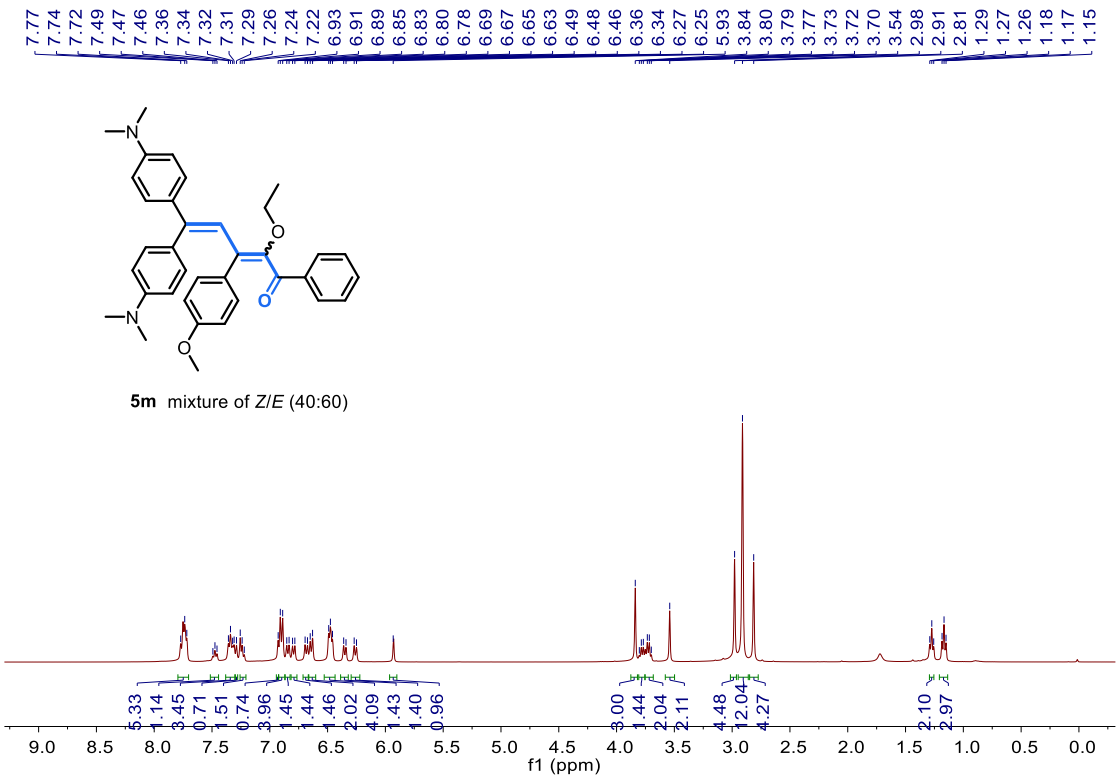
[13]C NMR Spectrum of Compound **5k** isomers mixture (100MHz, CDCl3)



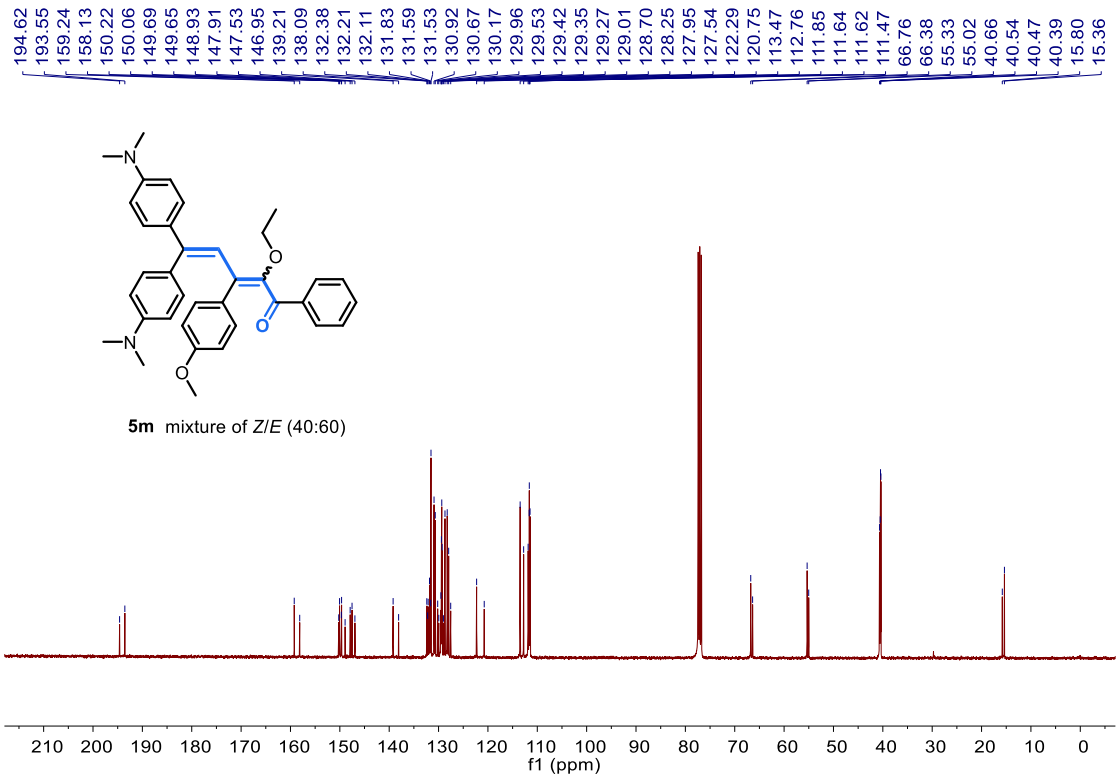
^{1}H NMR Spectrum of Compound **5l** isomers mixture (400MHz, CDCl3)



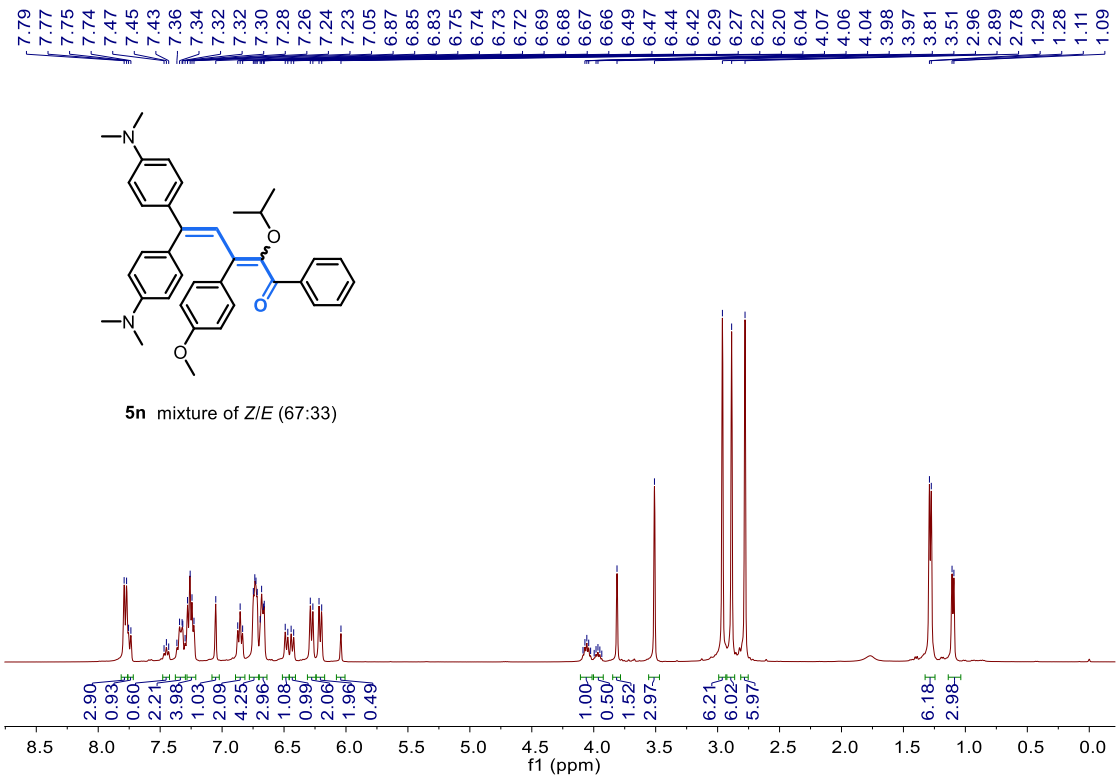
^{13}C NMR Spectrum of Compound **5l** isomers mixture (100MHz, CDCl3)



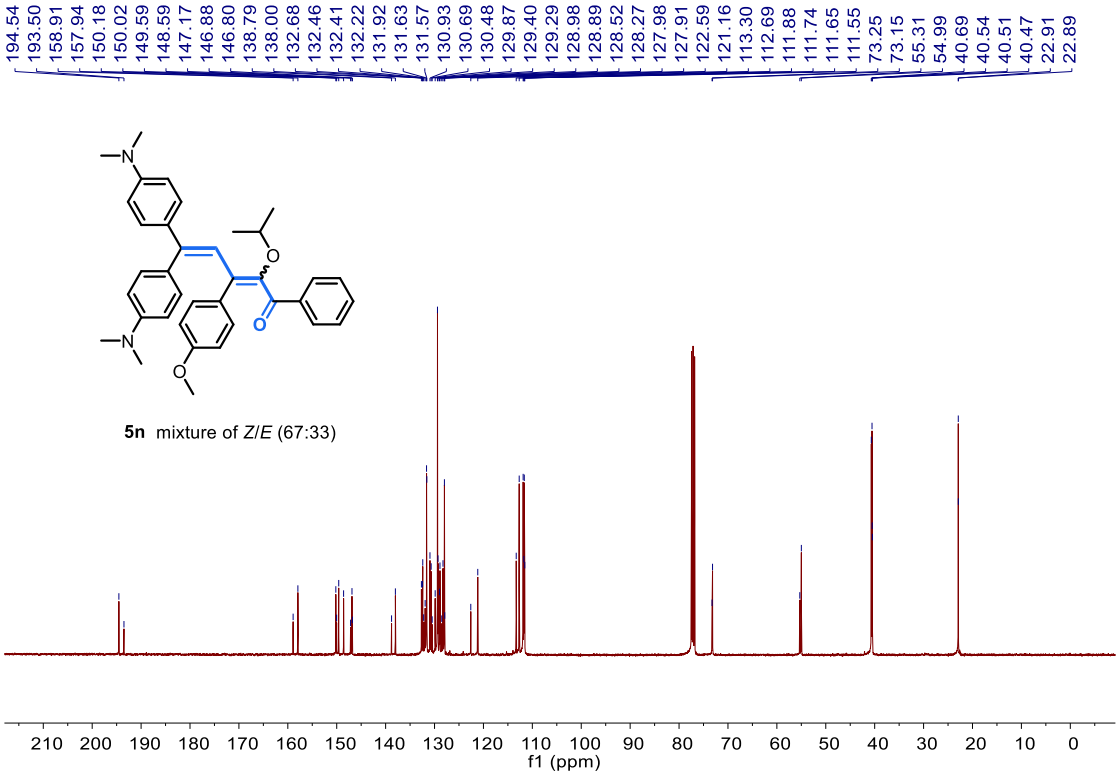
^{1}H NMR Spectrum of Compound **5m** isomers mixture (400MHz, CDCl3)



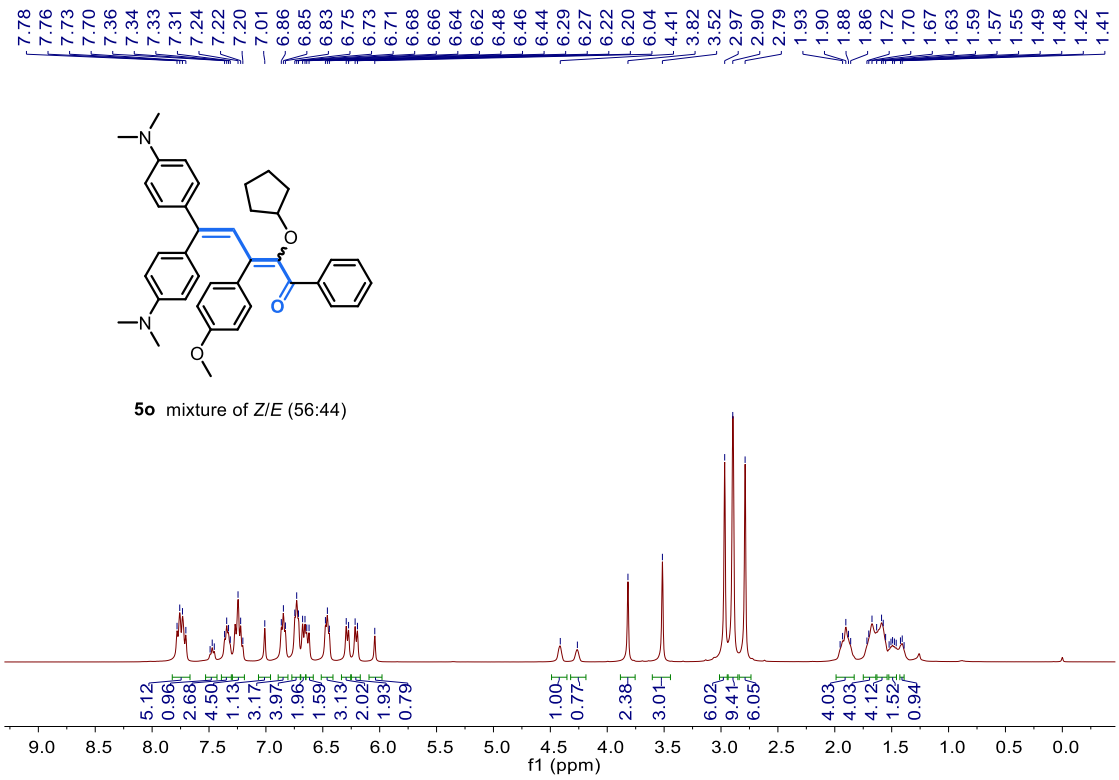
^{13}C NMR Spectrum of Compound **5m** isomers mixture (100MHz, CDCl3)



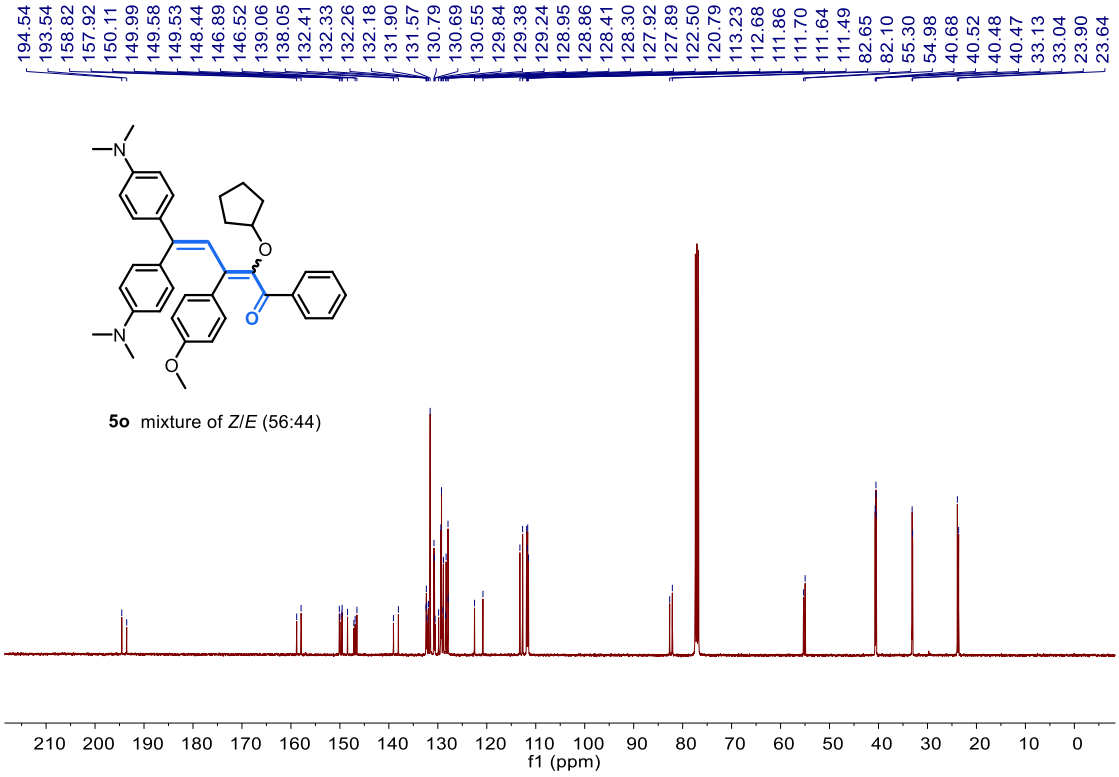
^{1}H NMR Spectrum of Compound **5n** isomers mixture (400MHz, CDCl3)



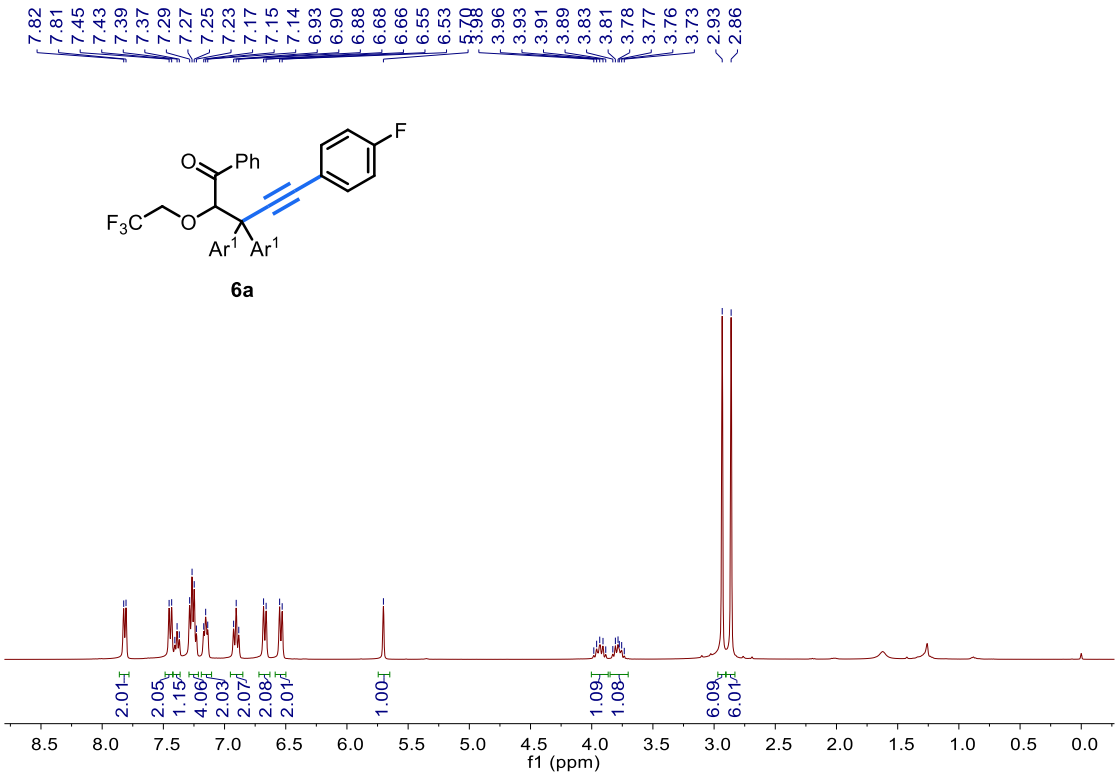
^{13}C NMR Spectrum of Compound **5n** isomers mixture (100MHz, CDCl3)



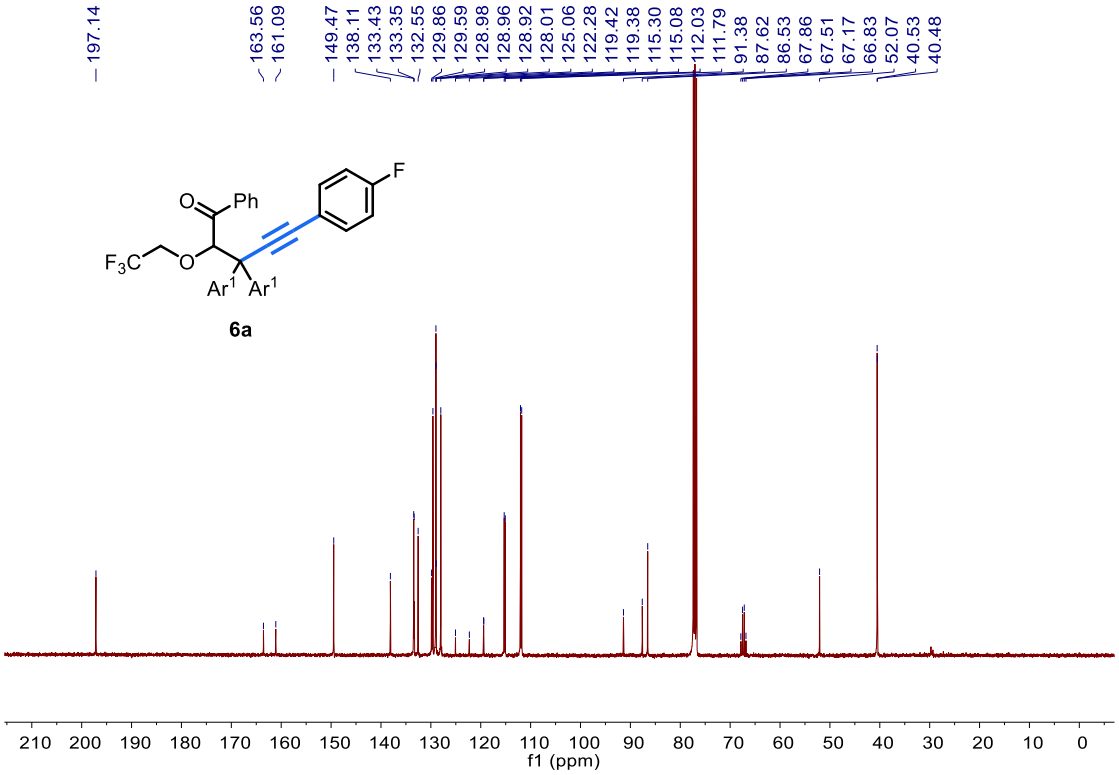
^{1}H NMR Spectrum of Compound **5o** isomers mixture (400MHz, CDCl3)



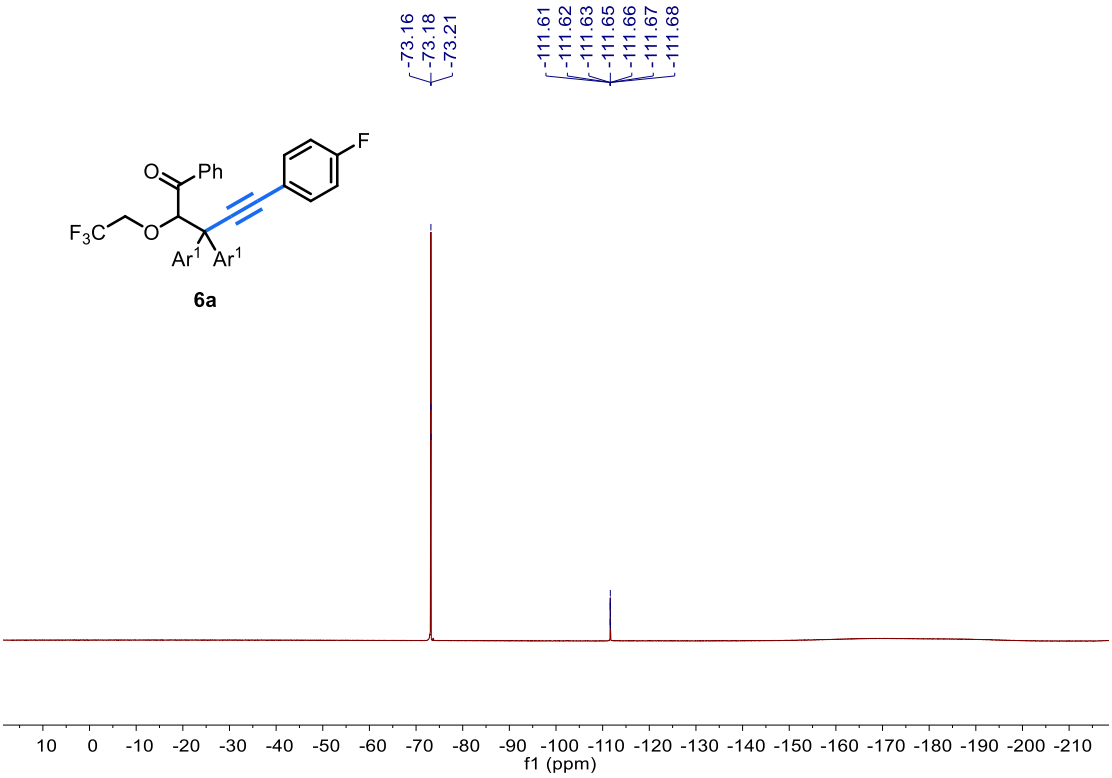
^{13}C NMR Spectrum of Compound **5o** isomers mixture (100MHz, CDCl3)



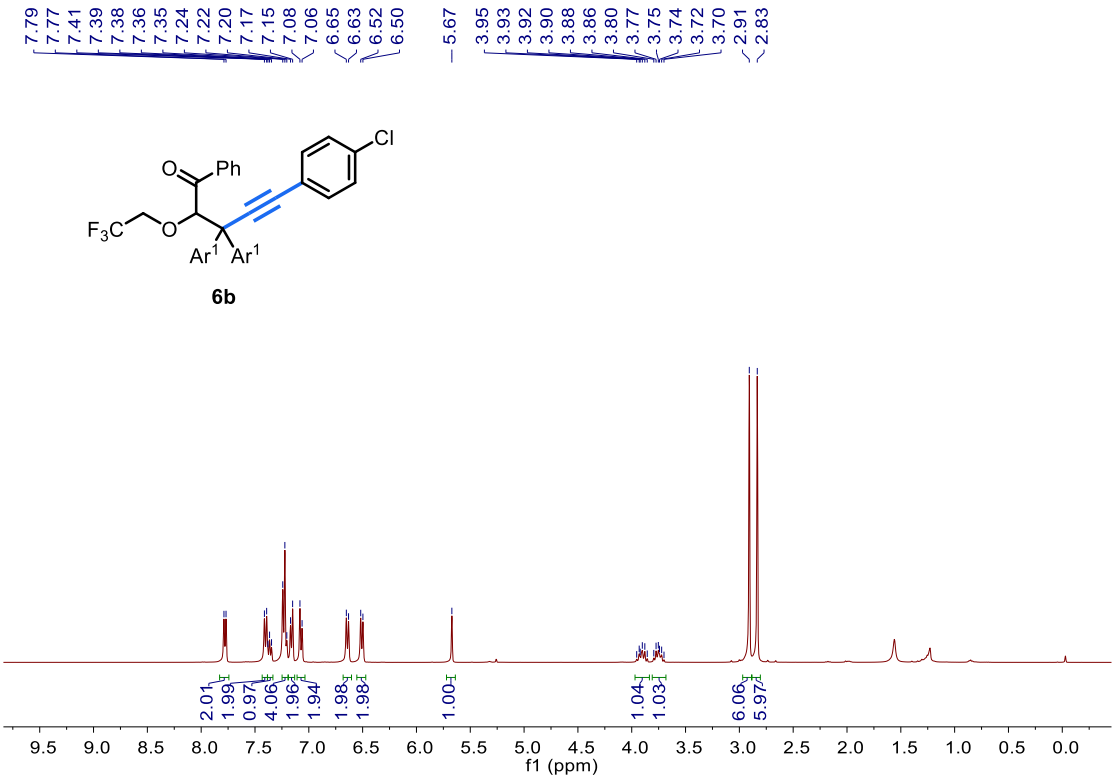
^{1}H NMR Spectrum of Compound **6a** (400MHz, CDCl3)



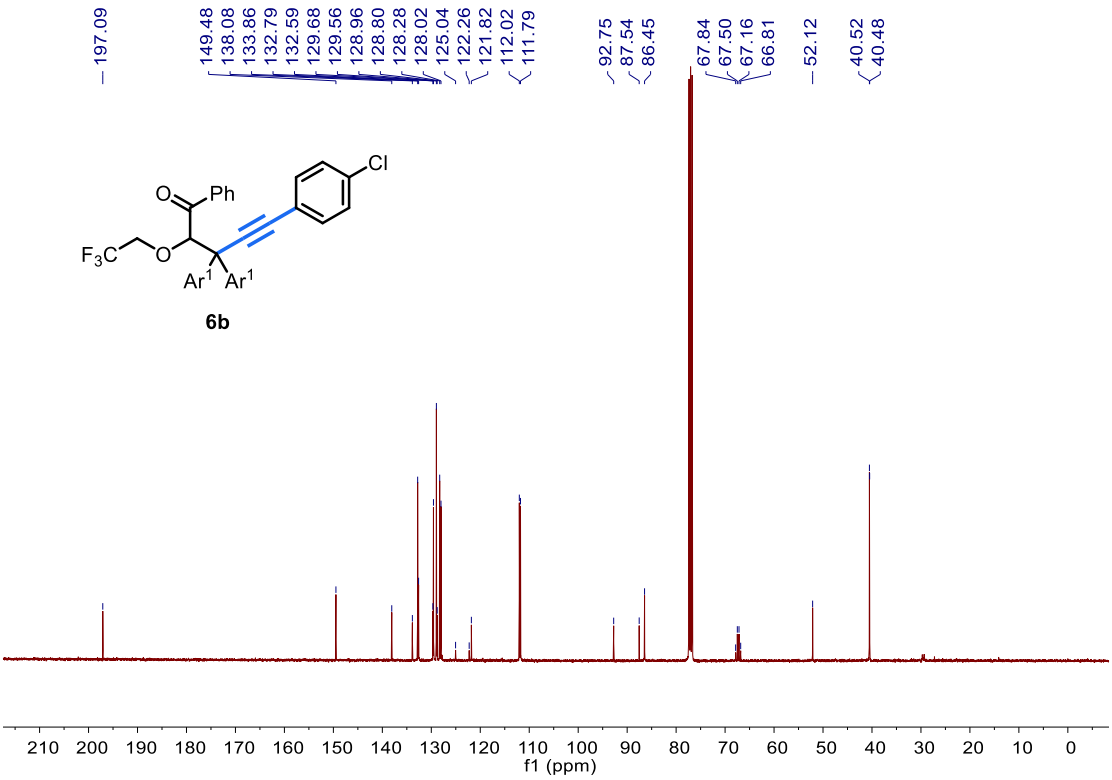
^{13}C NMR Spectrum of Compound **5o** (100MHz, CDCl3)



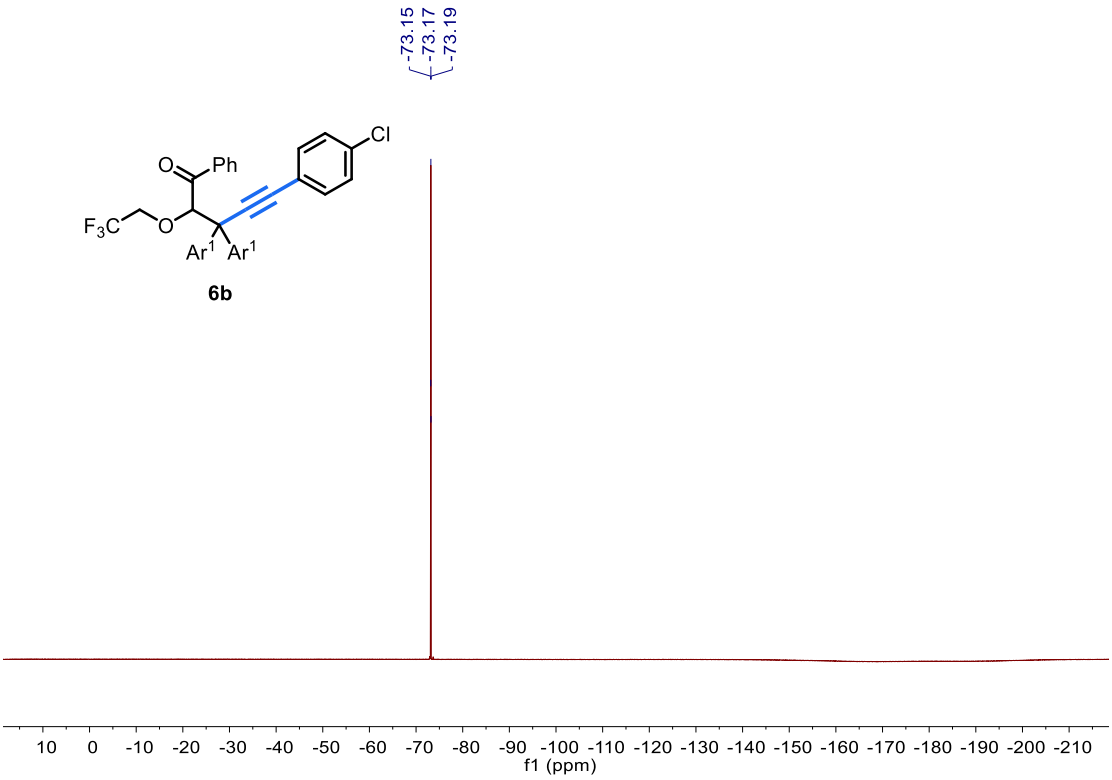
^{19}F NMR Spectrum of Compound **6a** (376 MHz, CDCl3)



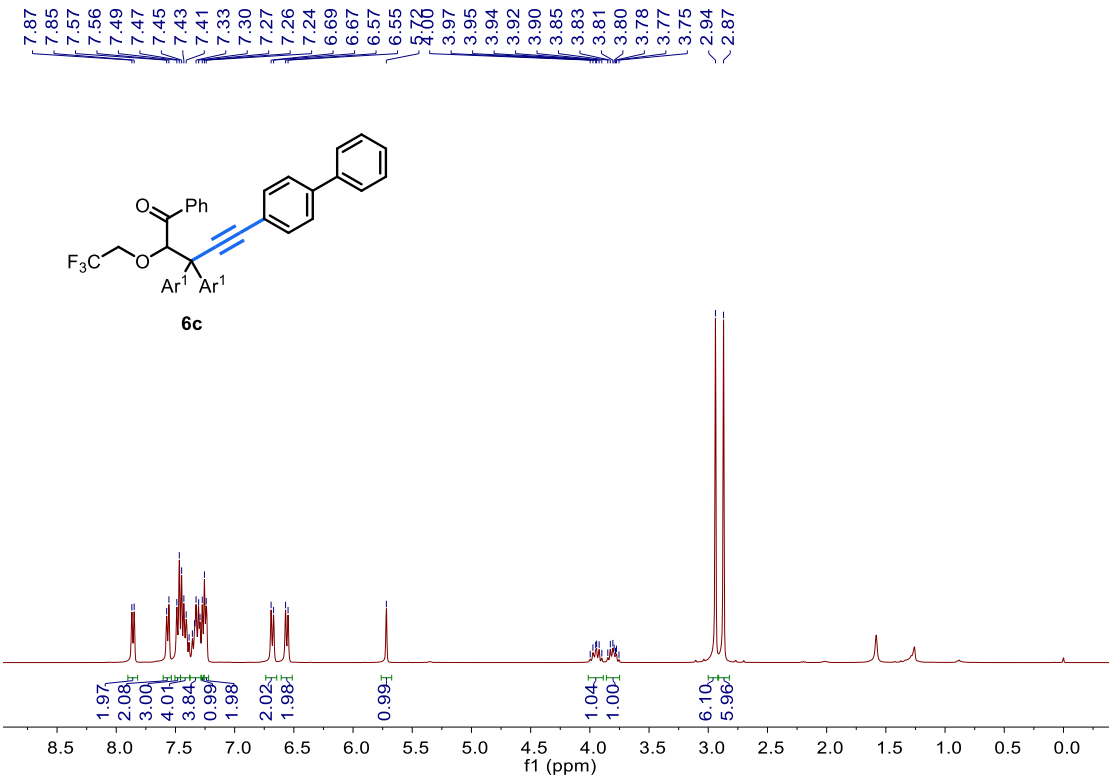
^{1}H NMR Spectrum of Compound **6b** (400MHz, CDCl3)



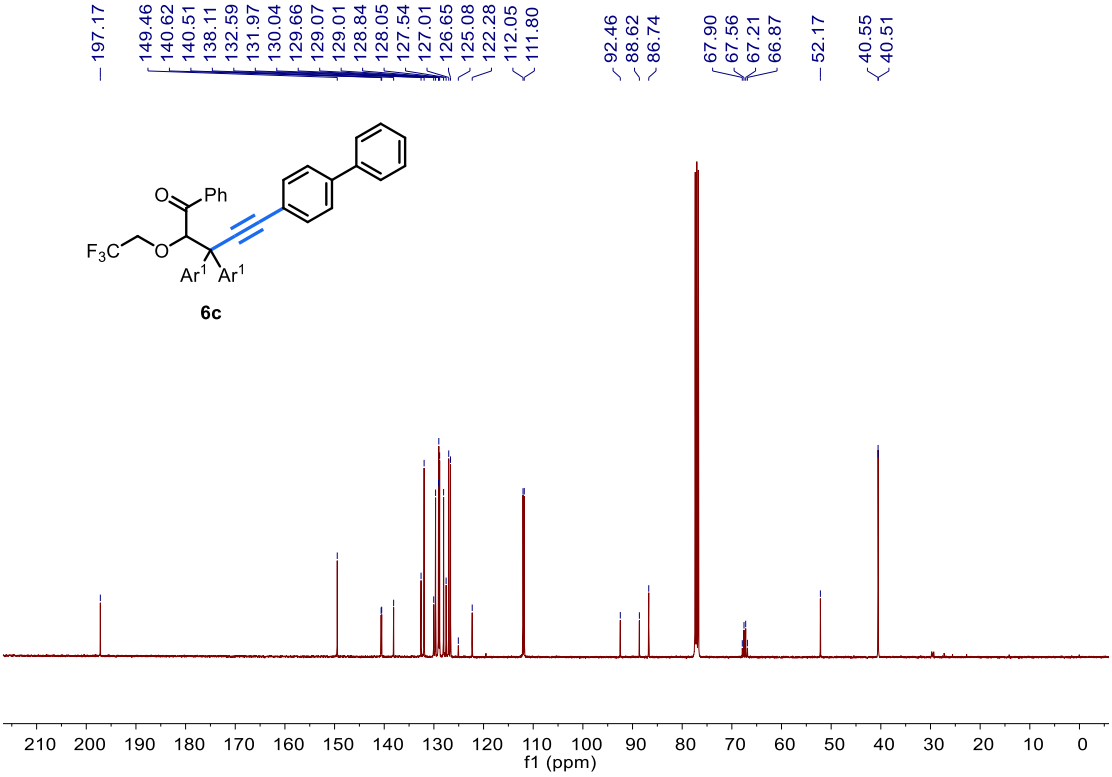
^{13}C NMR Spectrum of Compound **6b** (100MHz, CDCl3)



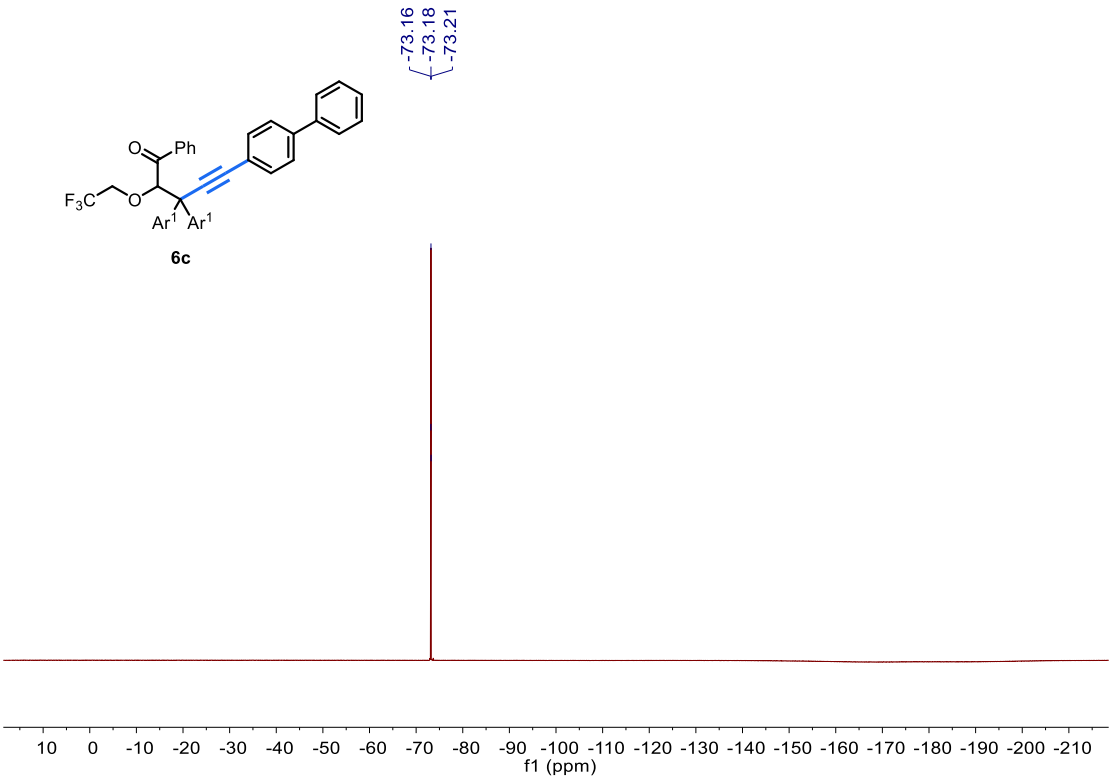
^{19}F NMR Spectrum of Compound **6b** (376 MHz, CDCl3)



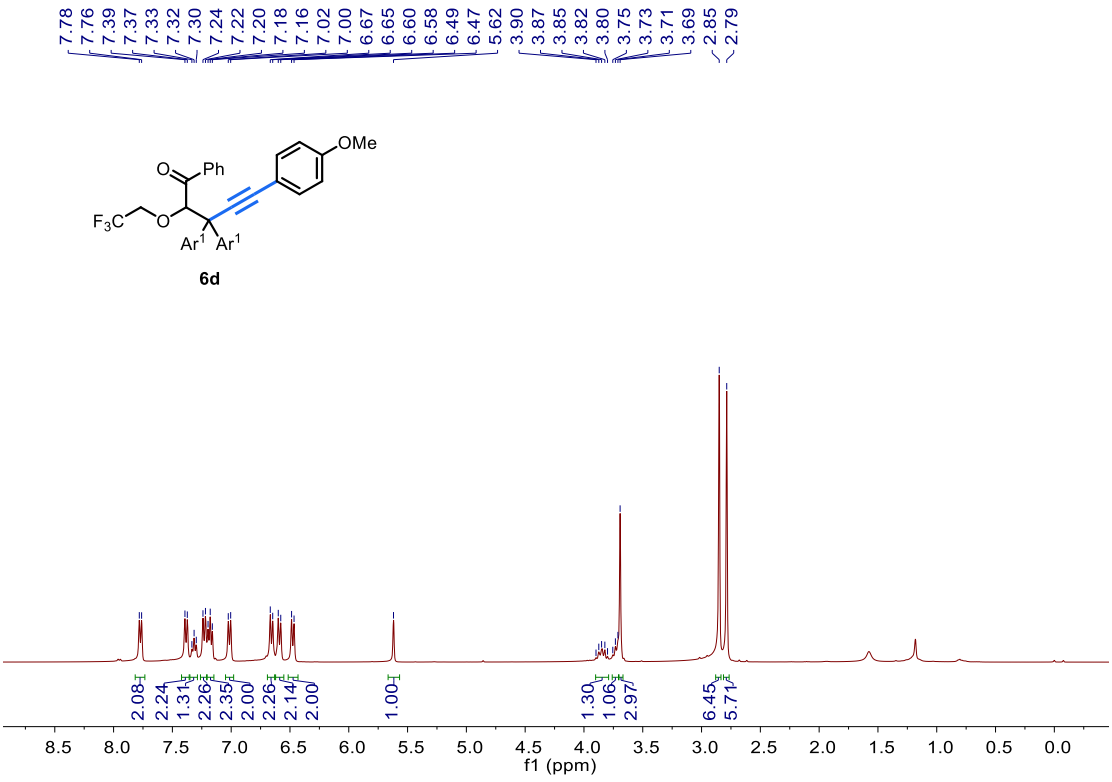
^{1}H NMR Spectrum of Compound **6c** (400MHz, CDCl3)



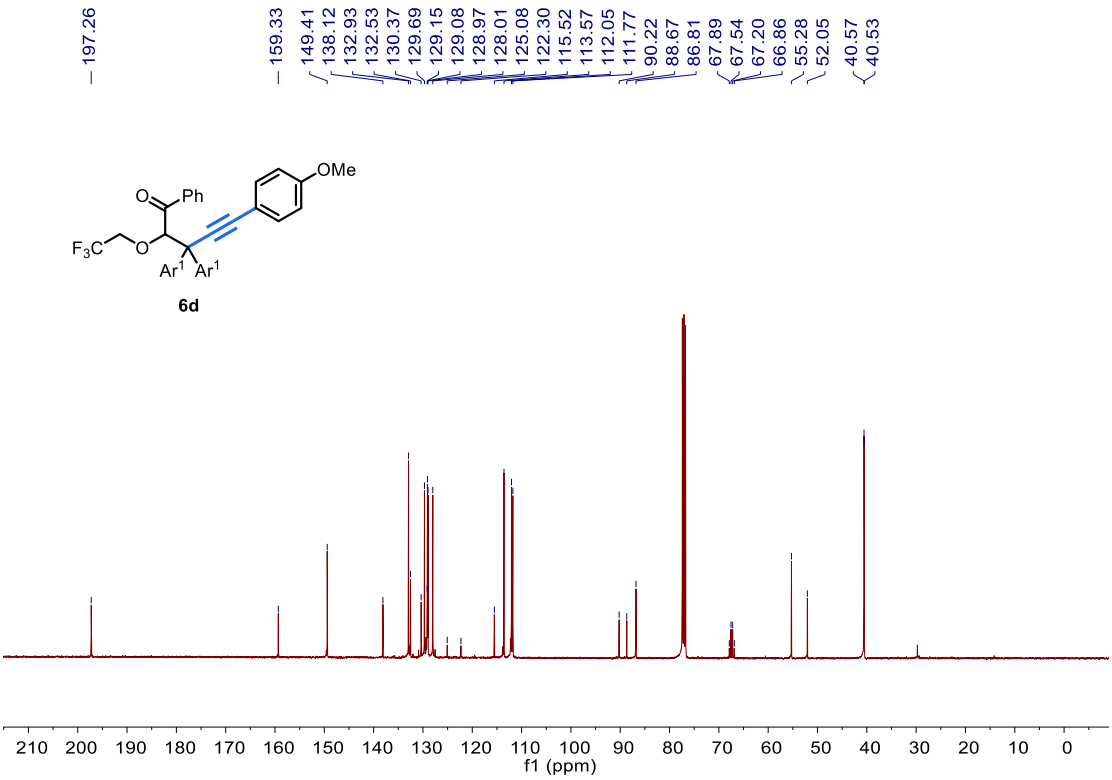
^{13}C NMR Spectrum of Compound **6c** (100MHz, CDCl3)



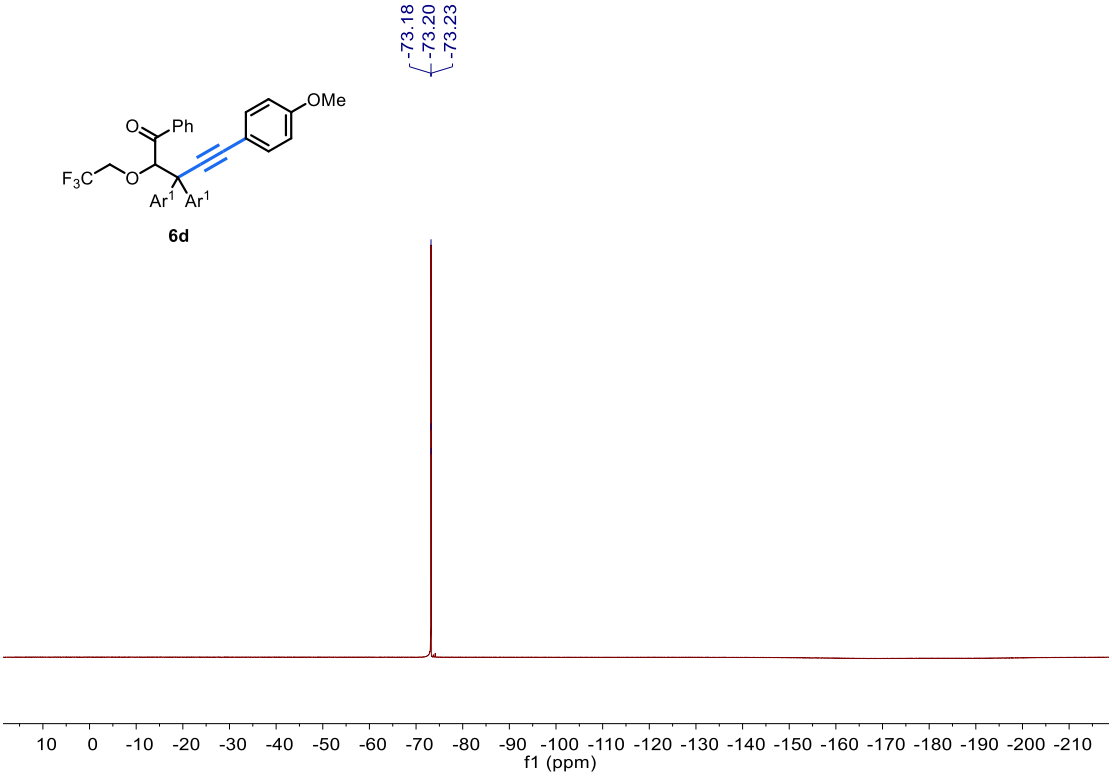
^{19}F NMR Spectrum of Compound **6c** (376 MHz, CDCl3)



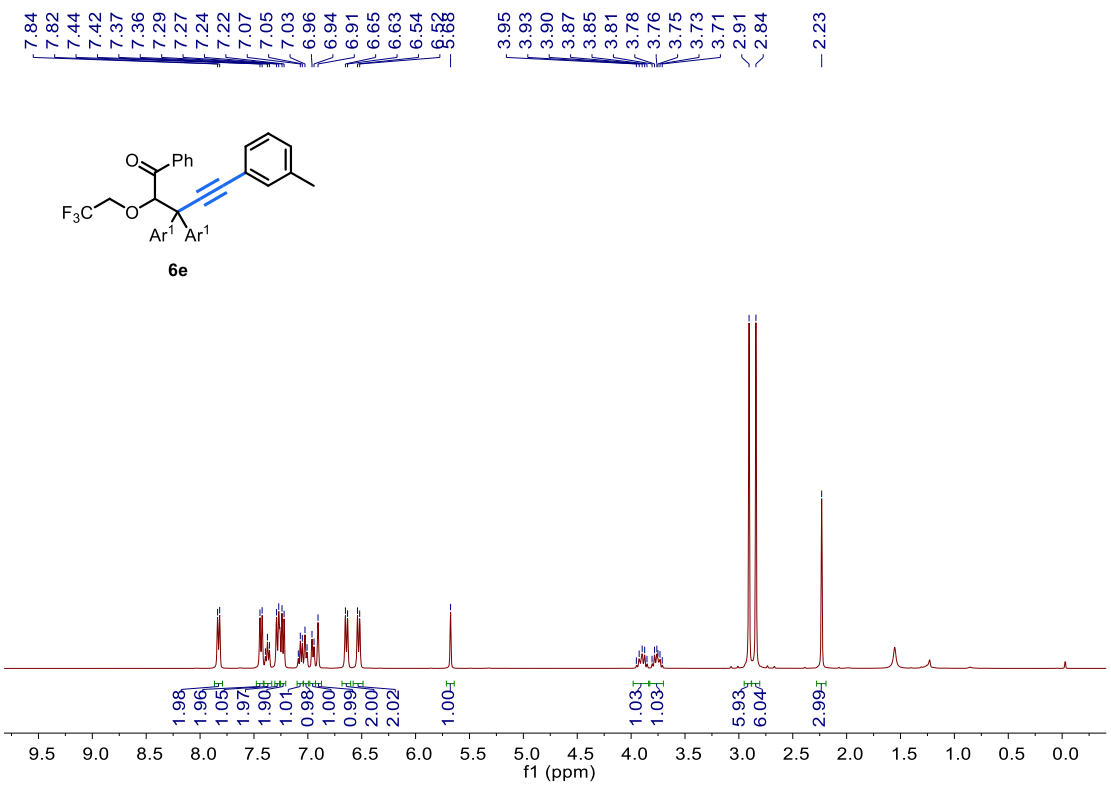
^{1}H NMR Spectrum of Compound **6d** (400MHz, CDCl3)



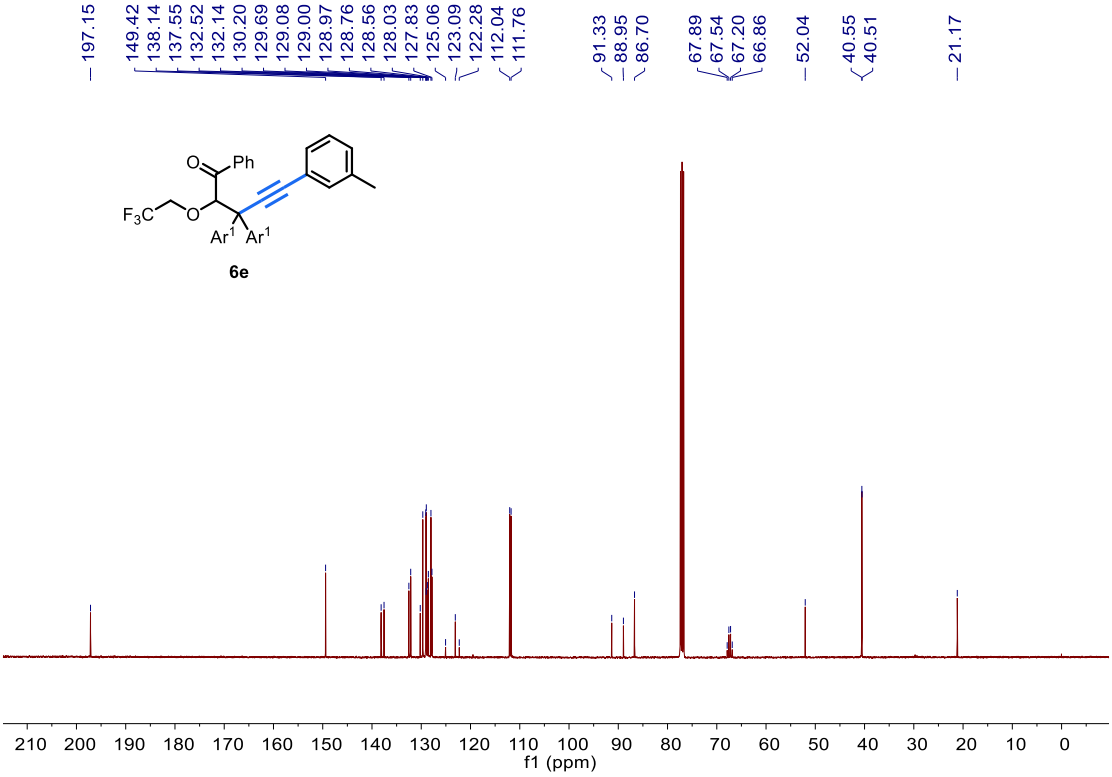
^{13}C NMR Spectrum of Compound **6d** (100MHz, CDCl3)



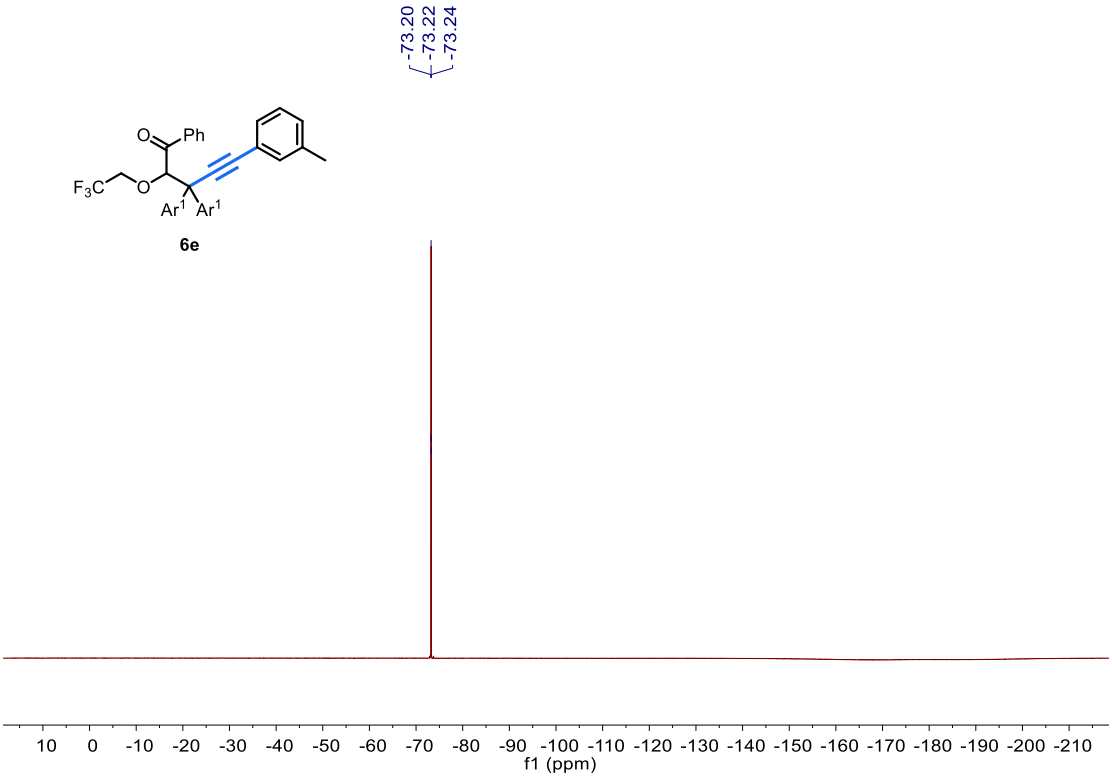
^{19}F NMR Spectrum of Compound **6d** (376 MHz, CDCl3)



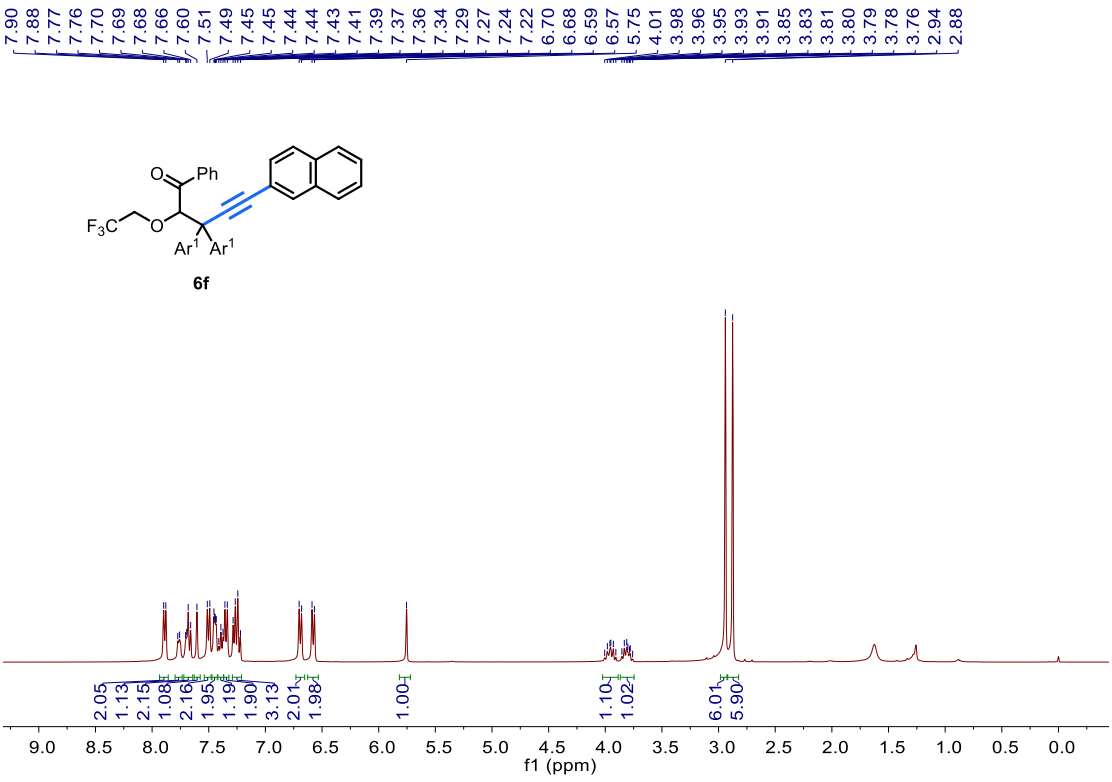
[1]H NMR Spectrum of Compound **6e** (400MHz, CDCl3)



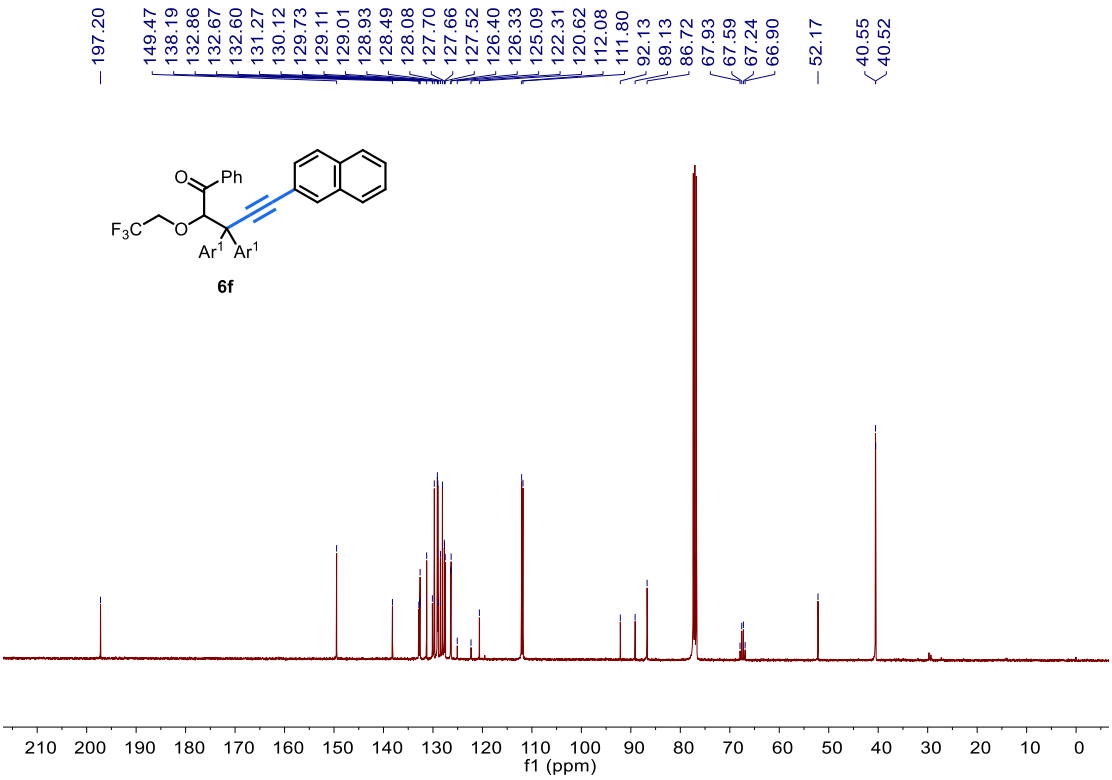
[13]C NMR Spectrum of Compound **6e** (100MHz, CDCl3)



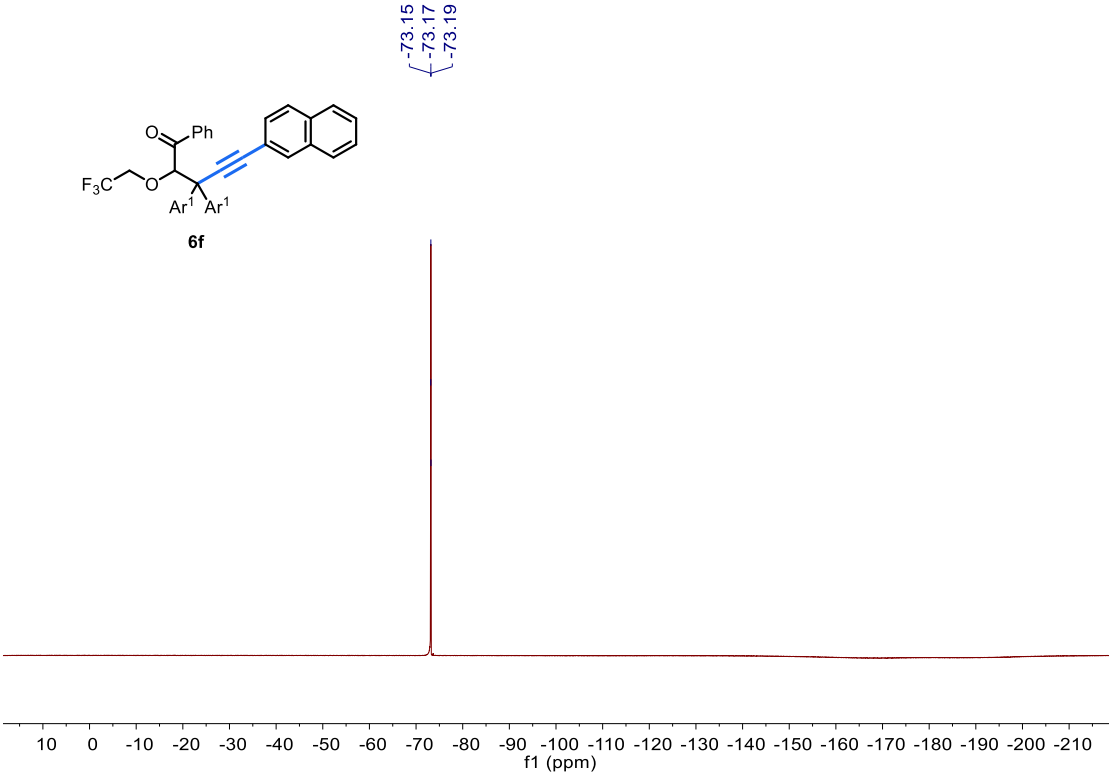
^{19}F NMR Spectrum of Compound **6e** (376 MHz, CDCl3)



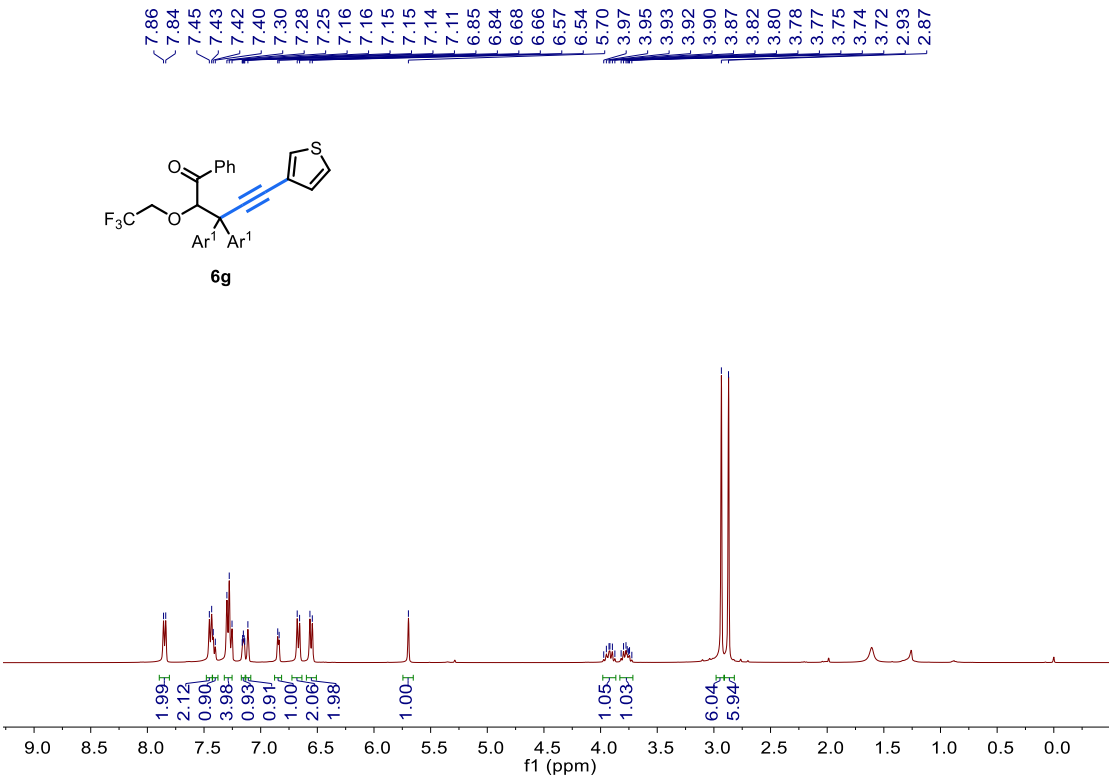
^{1}H NMR Spectrum of Compound **6f** (400MHz, CDCl3)



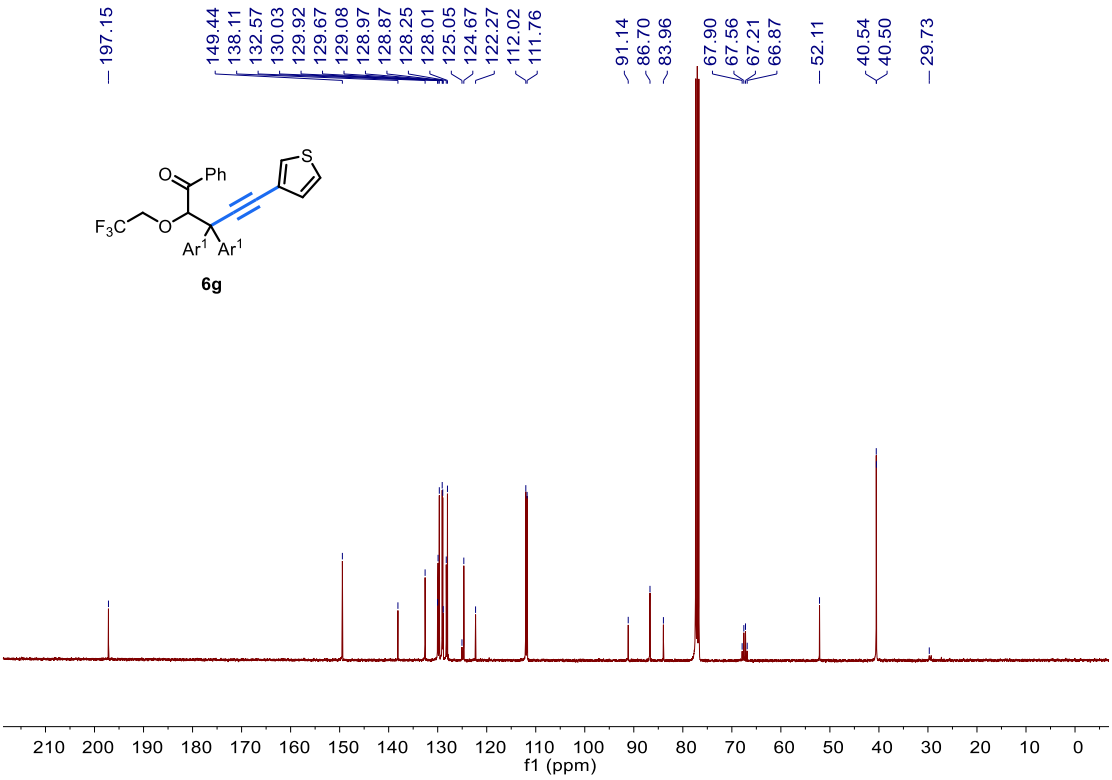
^{13}C NMR Spectrum of Compound **6f** (100MHz, CDCl3)



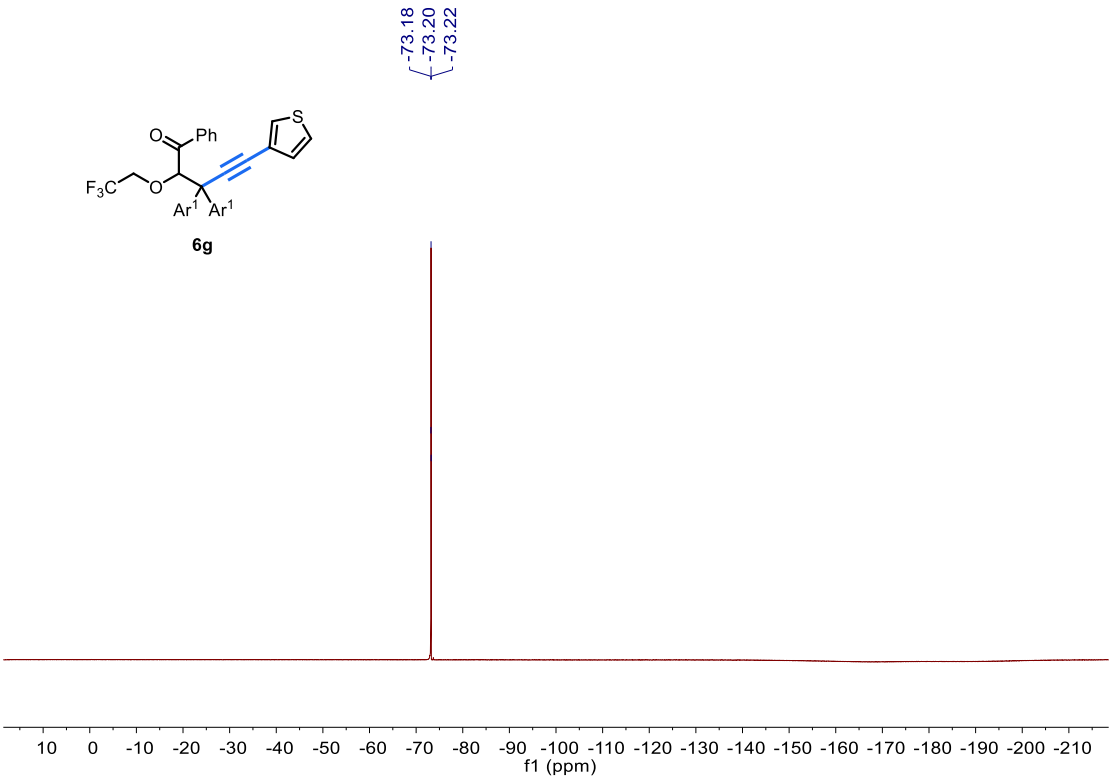
^{19}F NMR Spectrum of Compound **6f** (376 MHz, CDCl3)



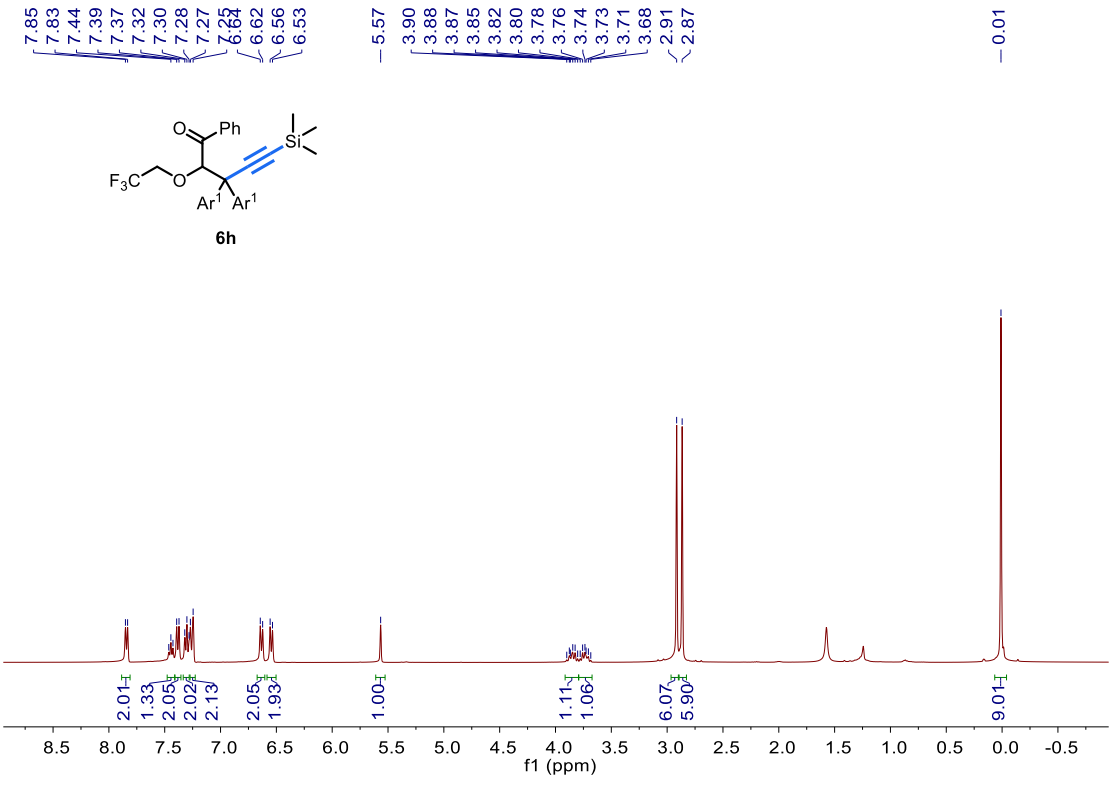
^{1}H NMR Spectrum of Compound **6g** (400MHz, CDCl3)



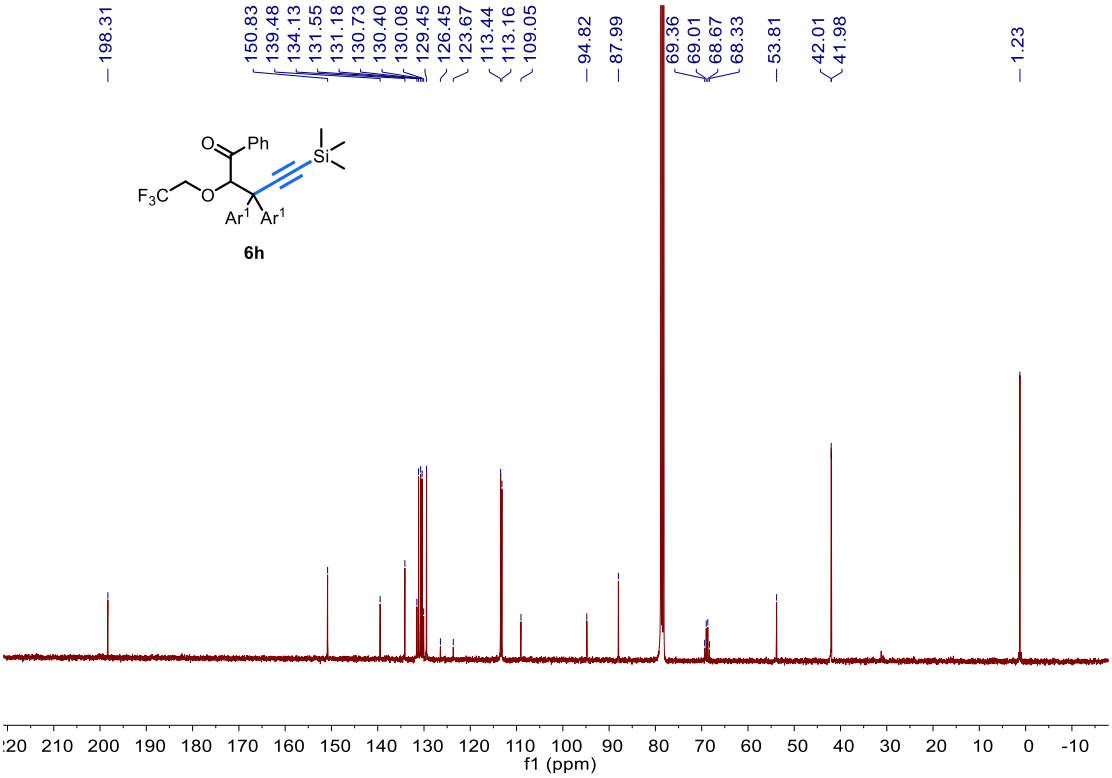
^{13}C NMR Spectrum of Compound **6g** (100MHz, CDCl3)



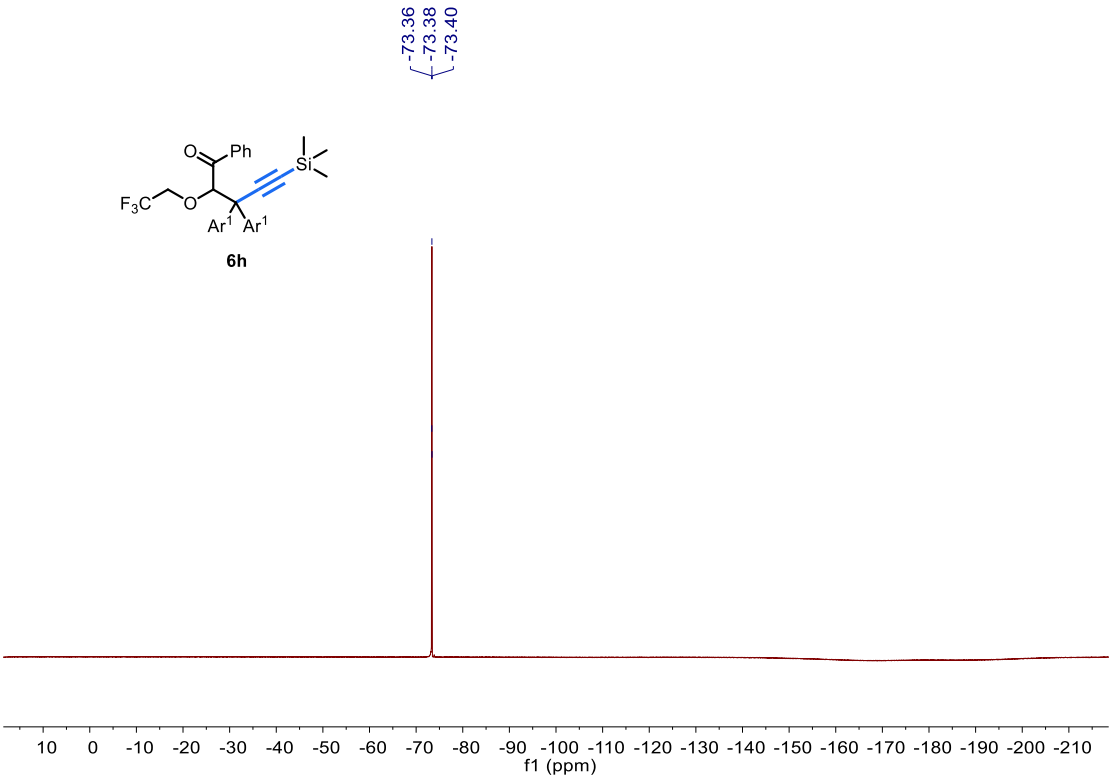
^{19}F NMR Spectrum of Compound **6g** (376 MHz, CDCl3)



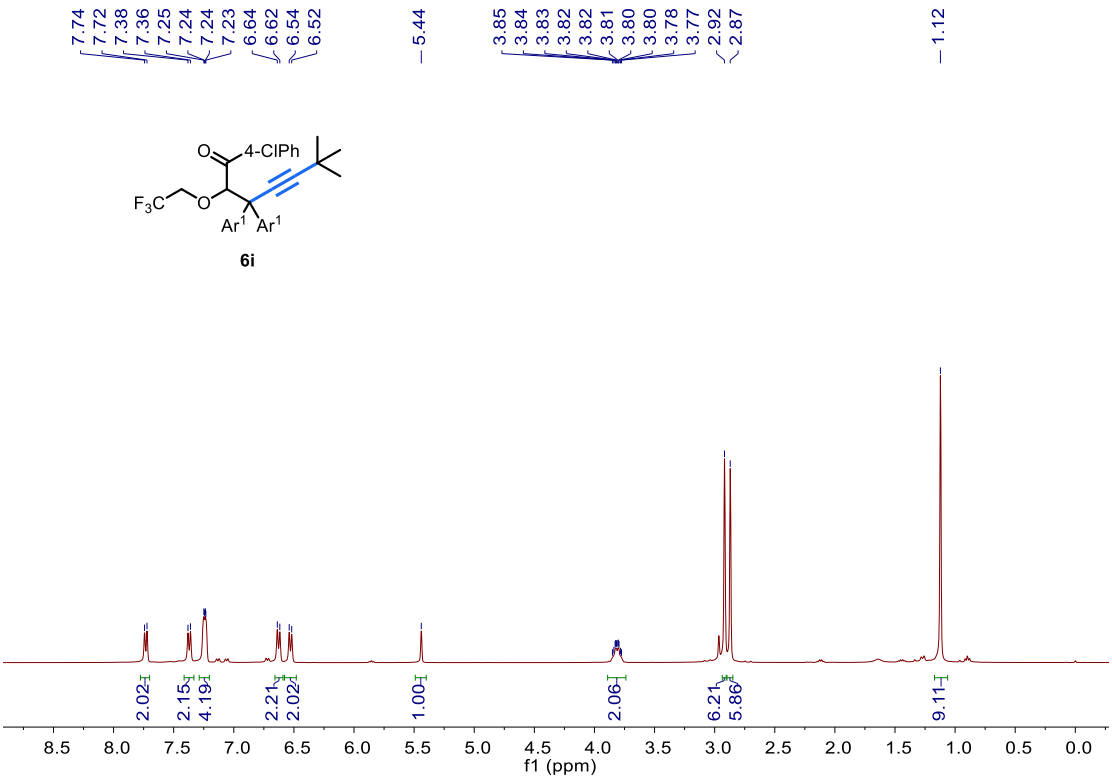
^{1}H NMR Spectrum of Compound **6h** (400MHz, CDCl3)



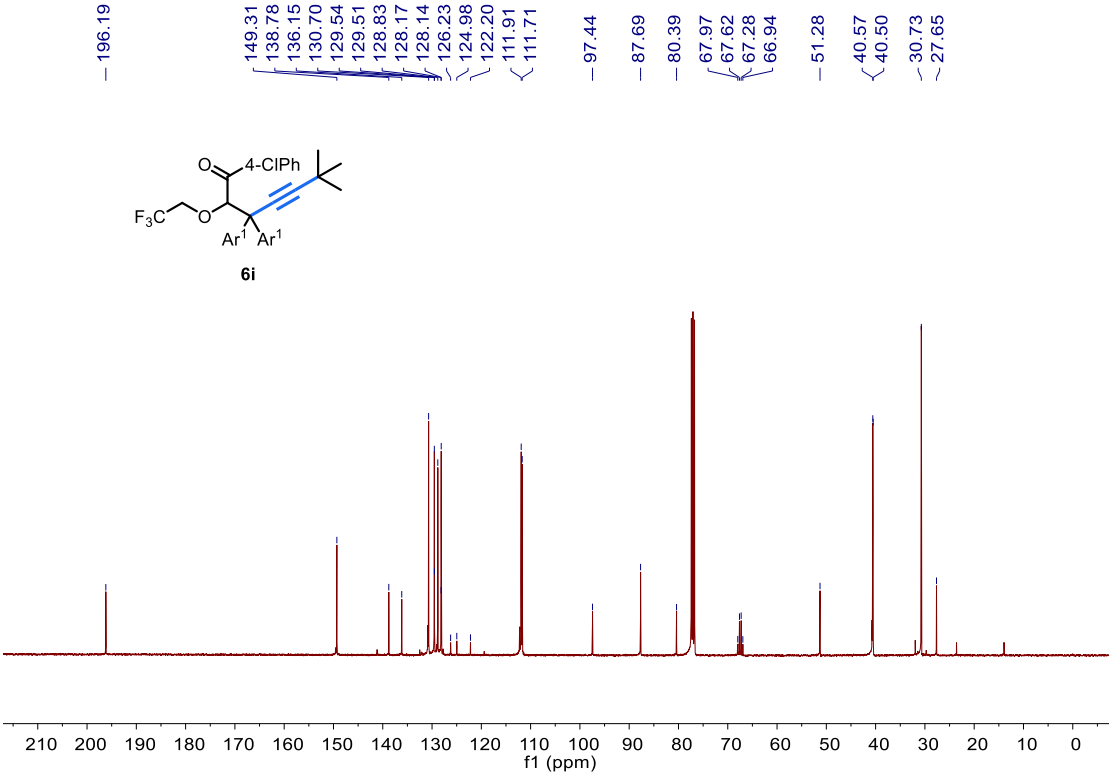
^{13}C NMR Spectrum of Compound **6h** (100MHz, CDCl3)



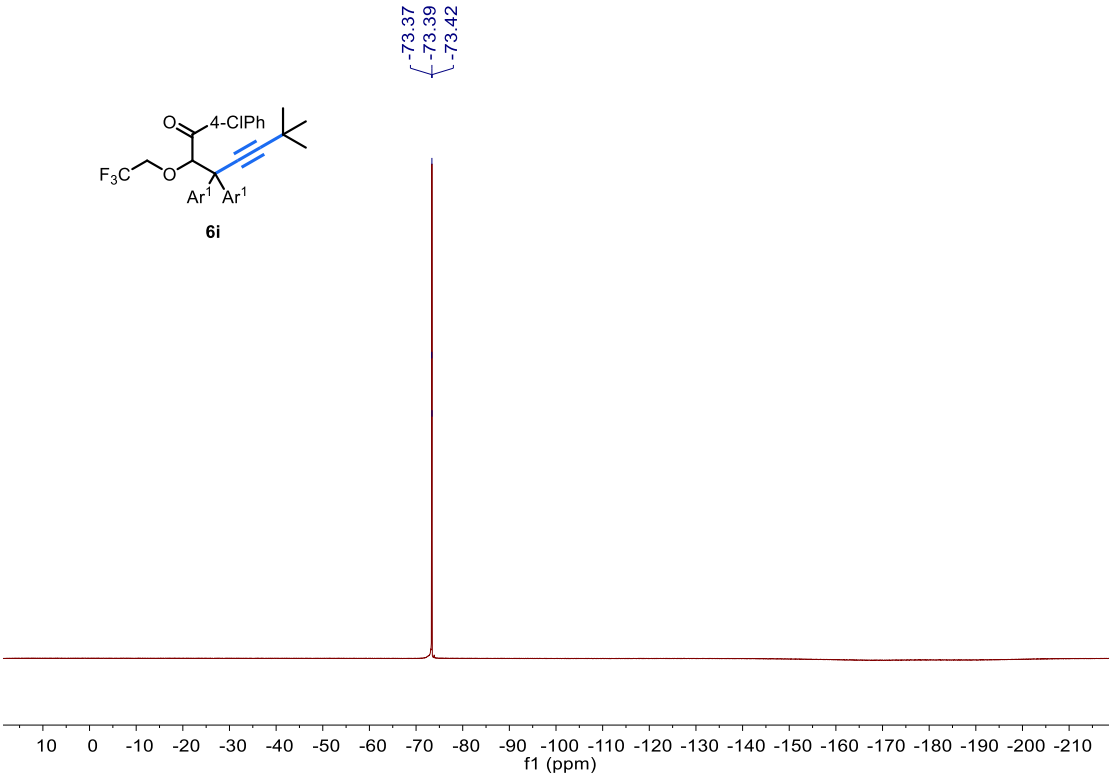
^{19}F NMR Spectrum of Compound **6h** (376 MHz, CDCl3)



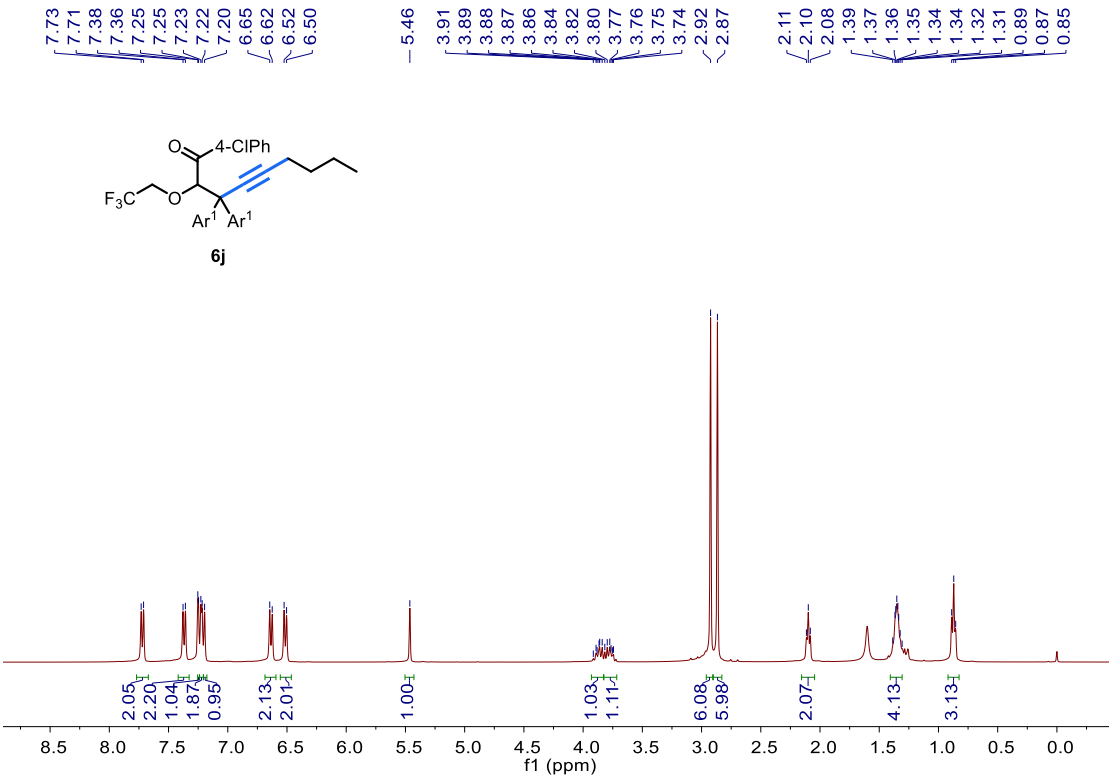
^{1}H NMR Spectrum of Compound **6i** (400MHz, CDCl3)



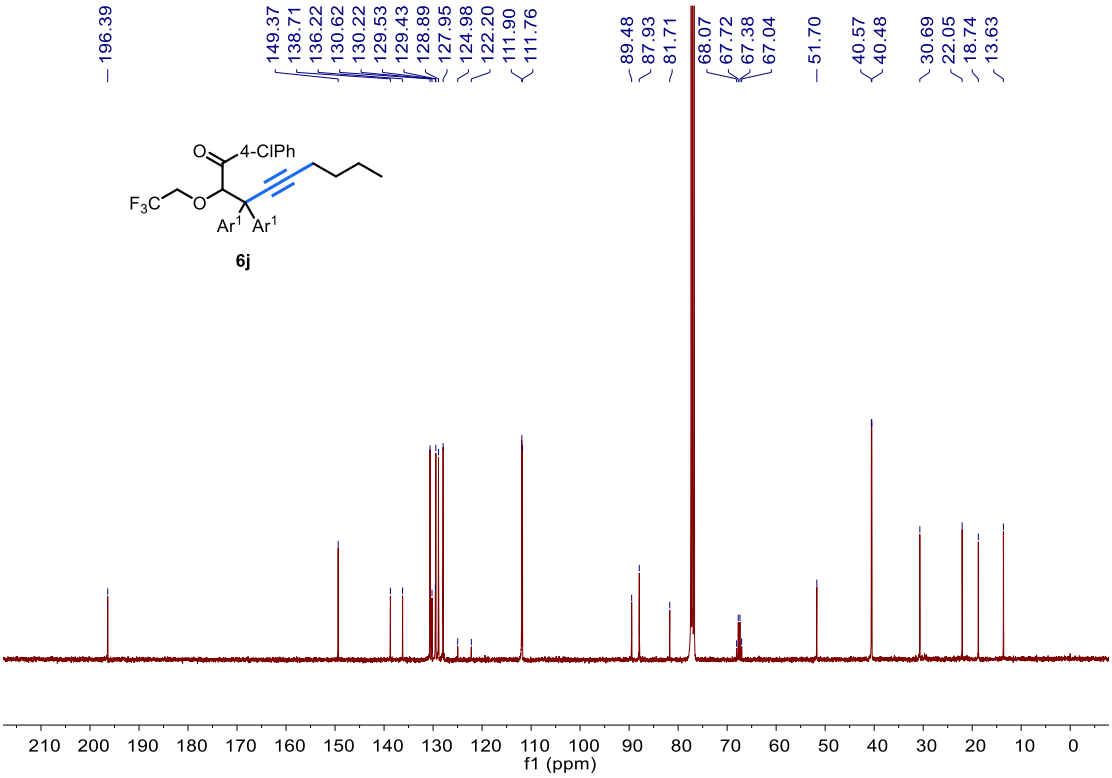
^{13}C NMR Spectrum of Compound **6i** (100MHz, CDCl3)



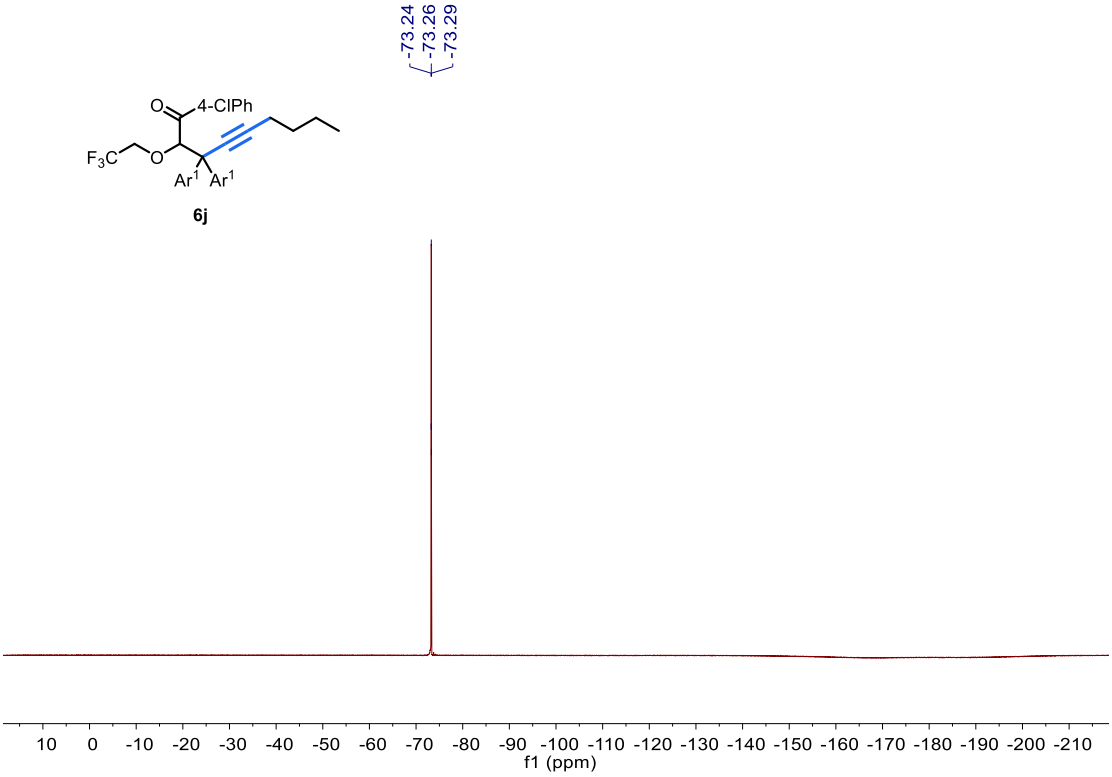
^{19}F NMR Spectrum of Compound **6i** (376 MHz, CDCl3)



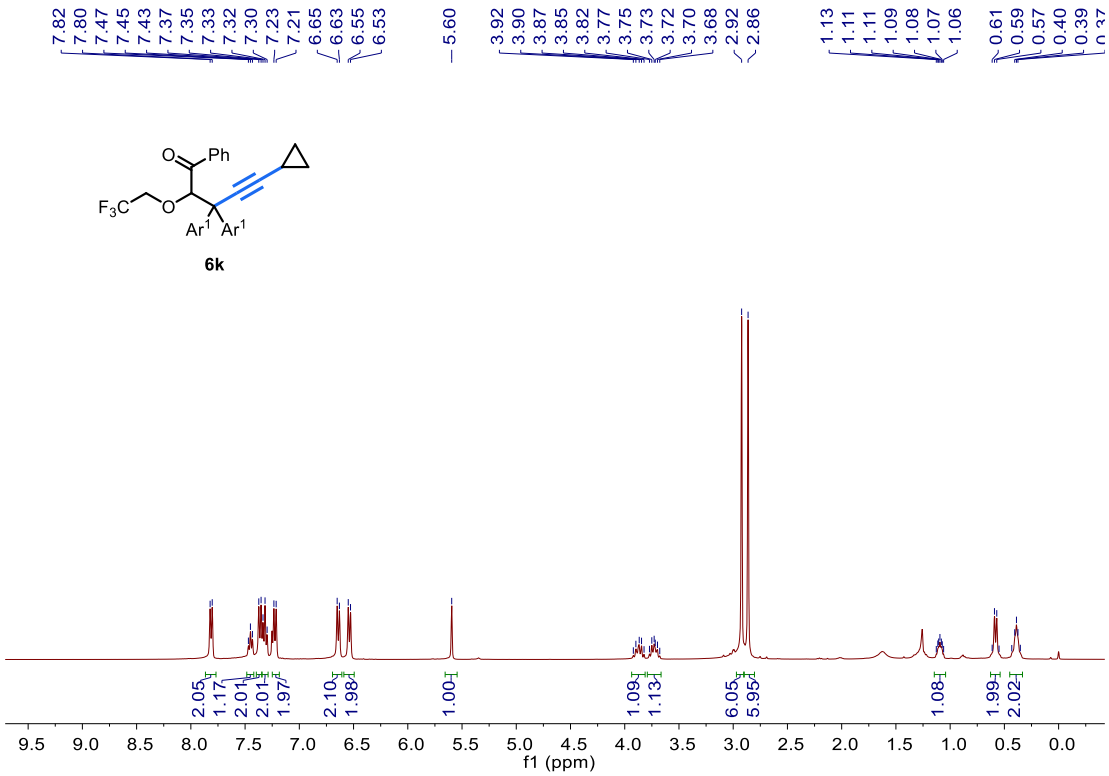
^{1}H NMR Spectrum of Compound **6j** (400MHz, CDCl3)



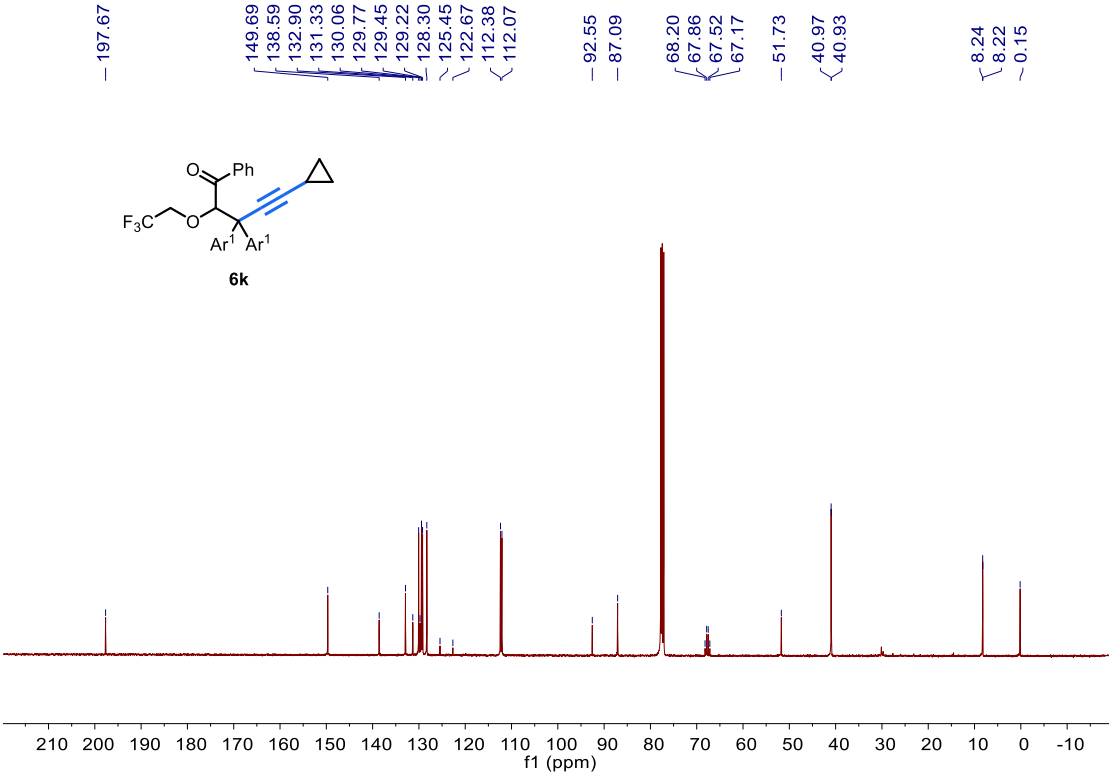
^{13}C NMR Spectrum of Compound **6j** (100MHz, CDCl3)



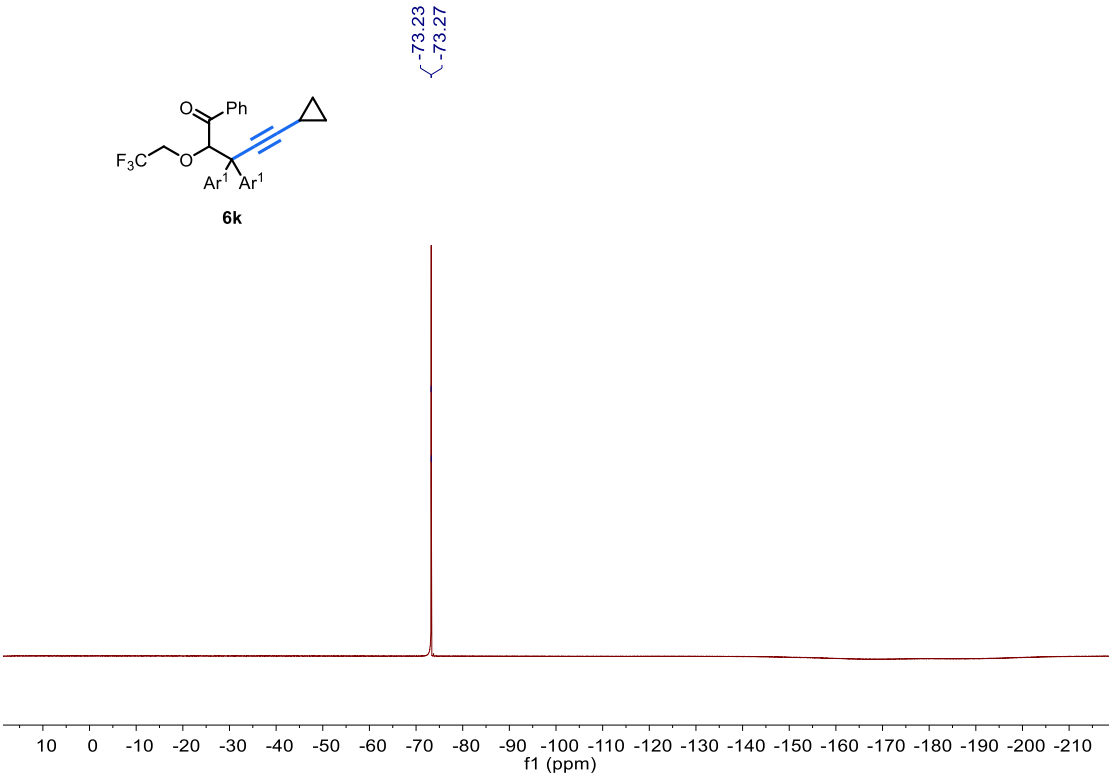
^{19}F NMR Spectrum of Compound **6j** (376 MHz, CDCl3)



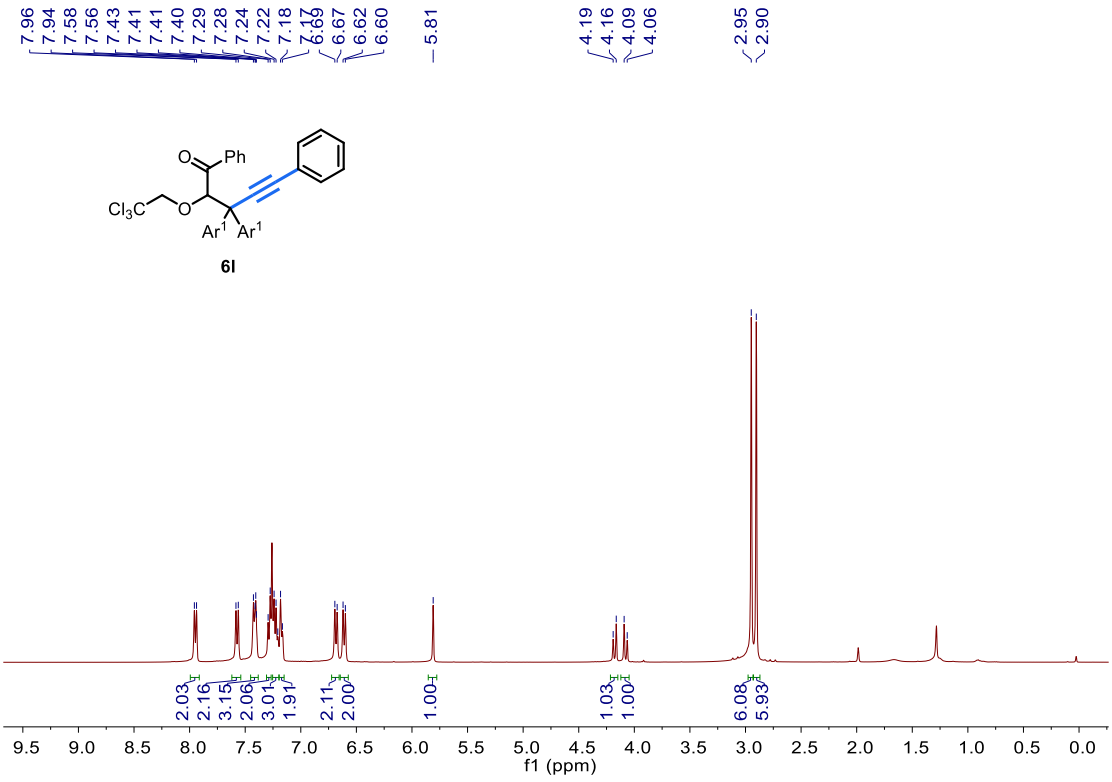
^{1}H NMR Spectrum of Compound **6k** (400MHz, CDCl3)



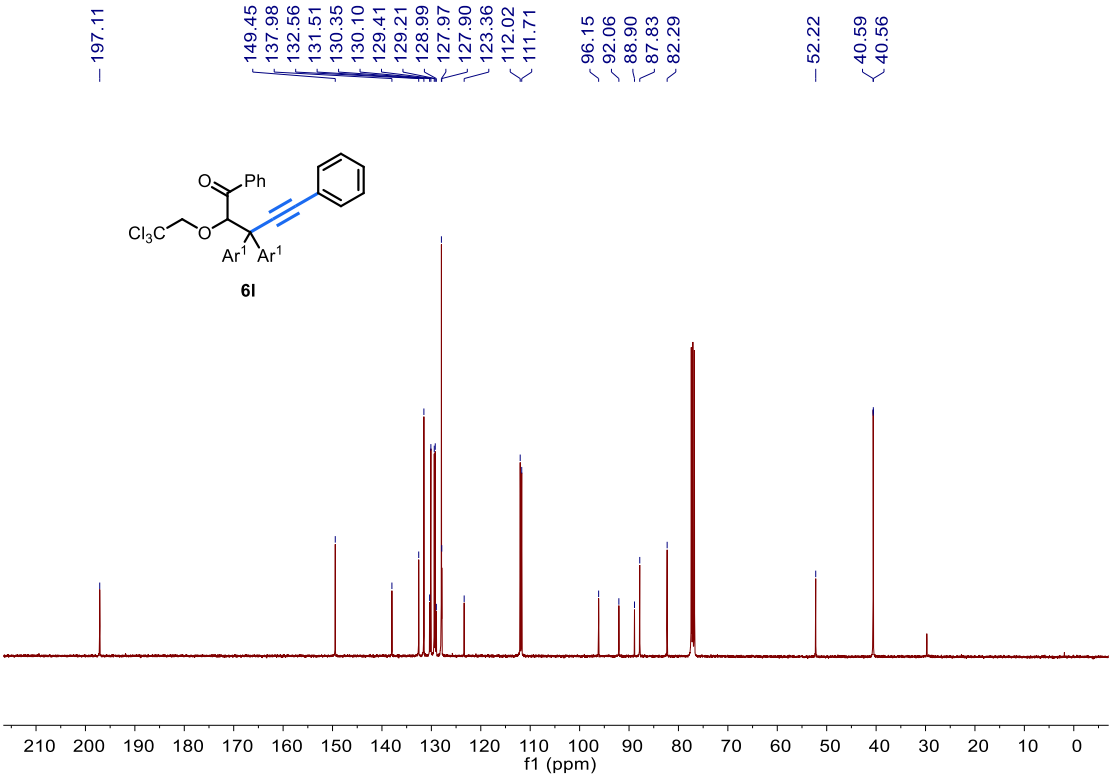
^{13}C NMR Spectrum of Compound **6k** (100MHz, CDCl3)



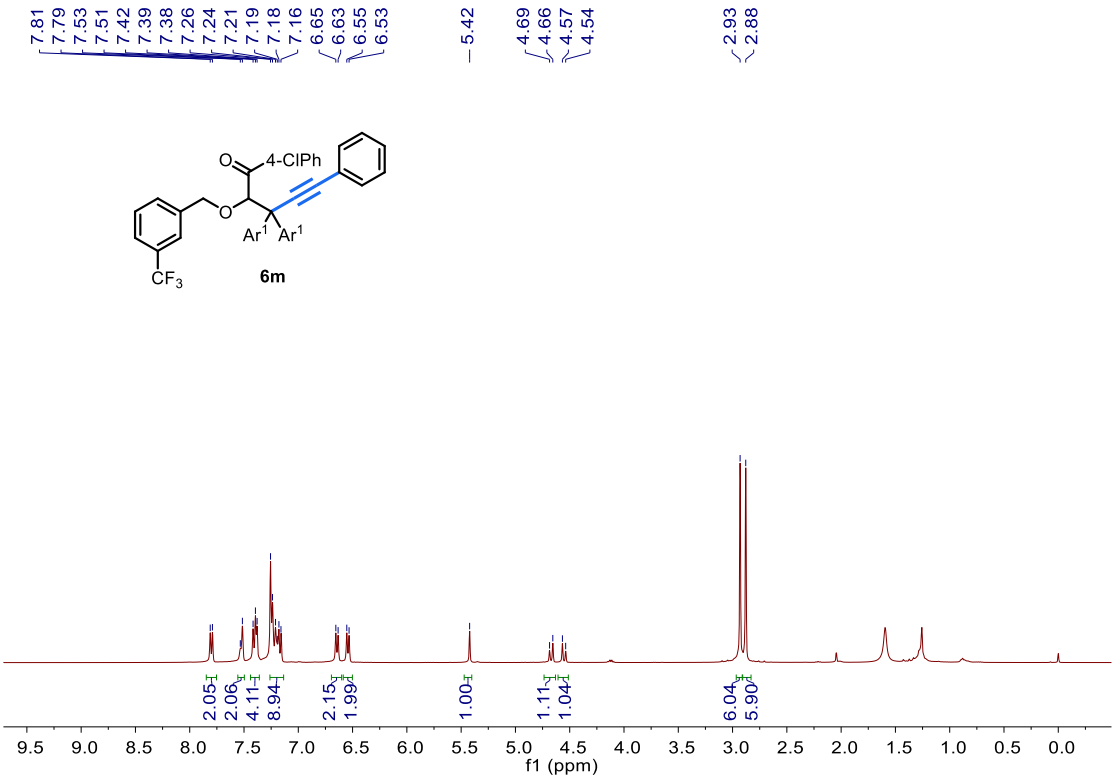
^{19}F NMR Spectrum of Compound **6k** (376 MHz, CDCl3)



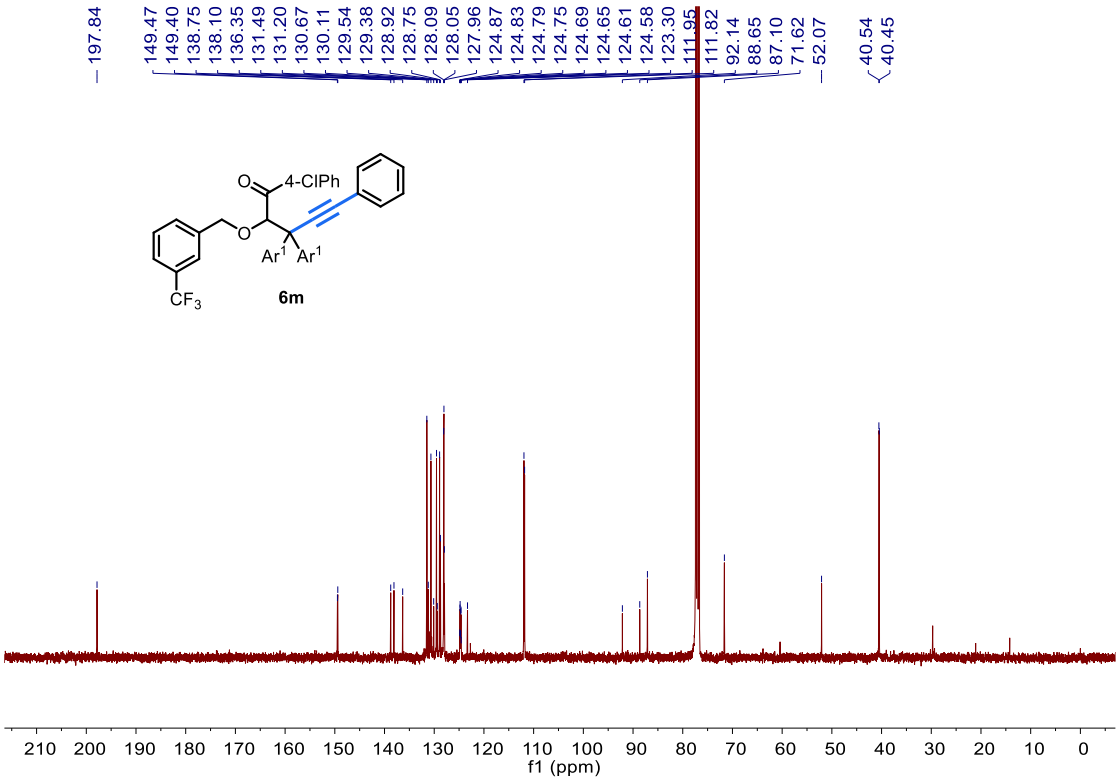
^{1}H NMR Spectrum of Compound **6l** (400MHz, CDCl3)



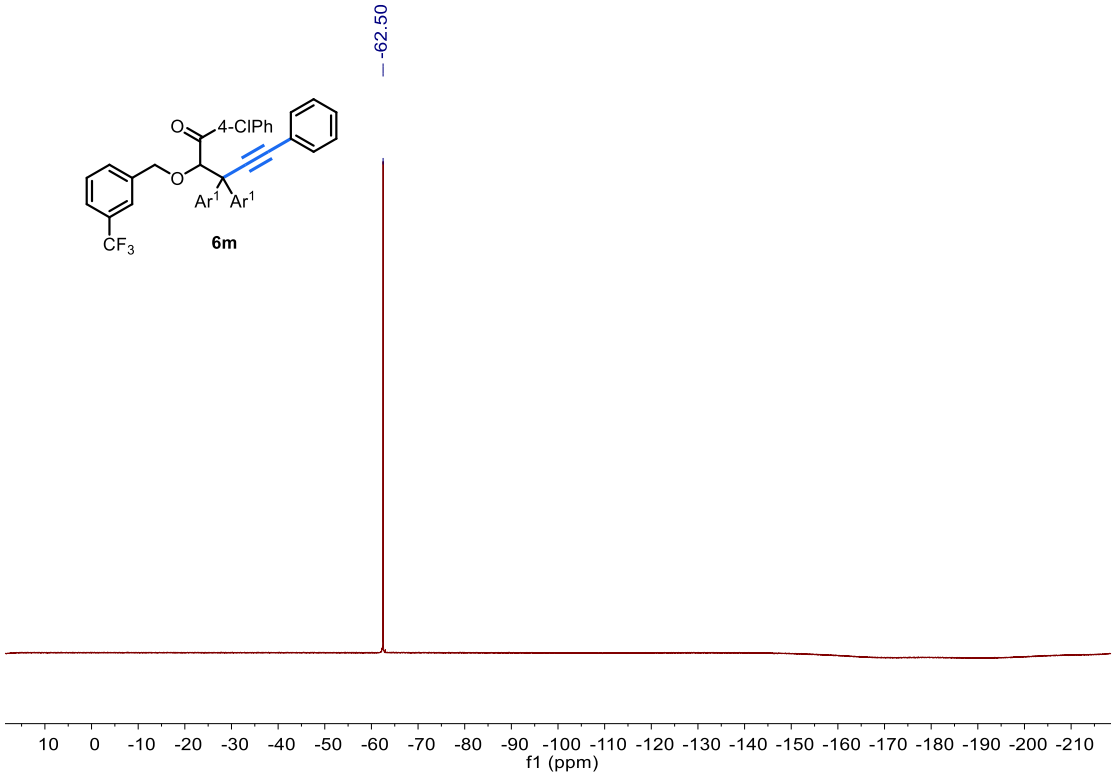
^{13}C NMR Spectrum of Compound **6l** (100MHz, CDCl3)



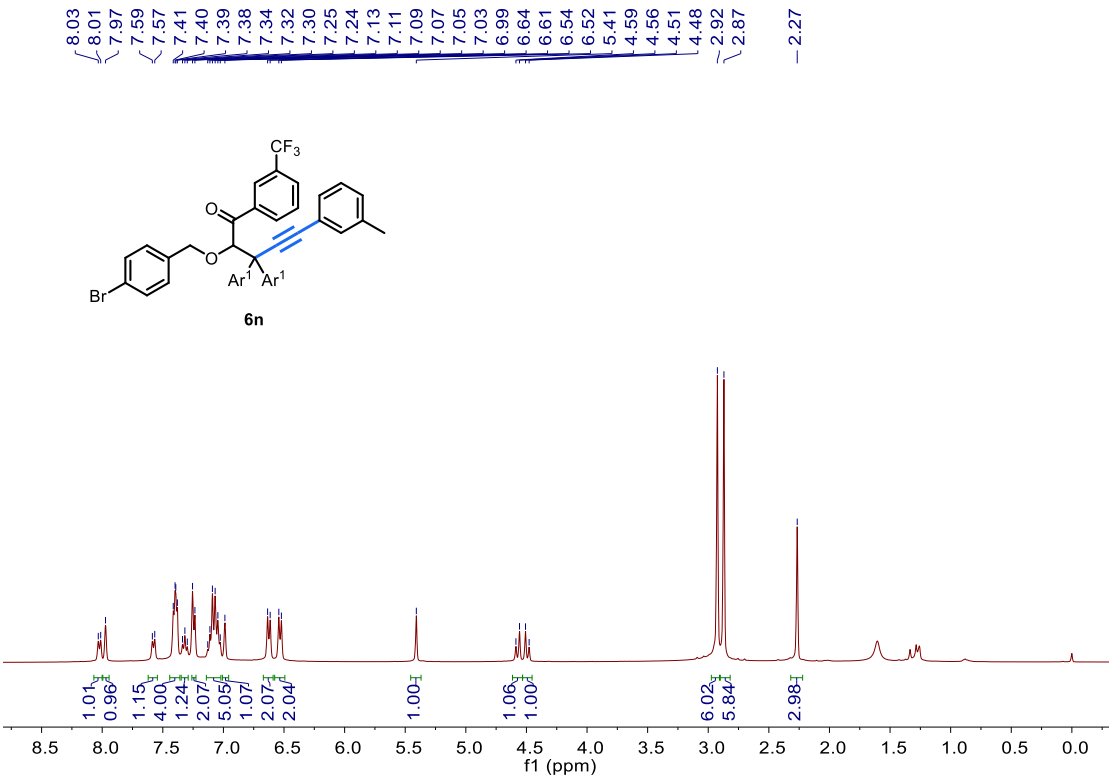
^{1}H NMR Spectrum of Compound **6m** (400MHz, CDCl3)



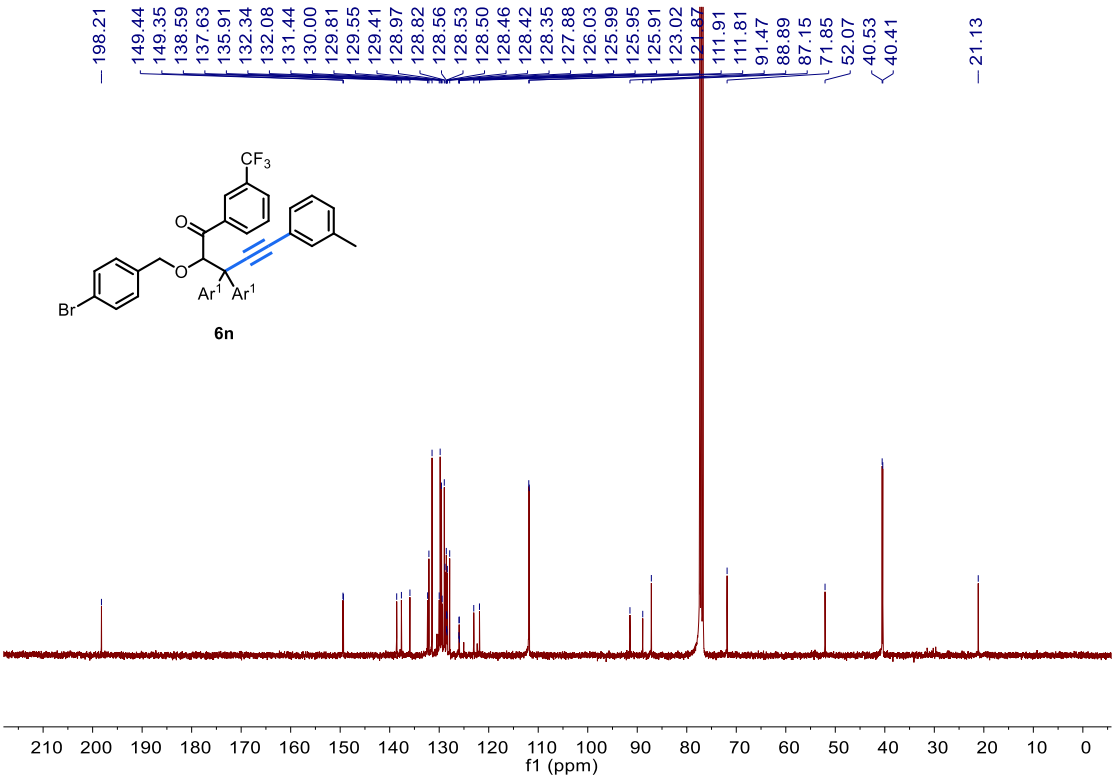
^{13}C NMR Spectrum of Compound **6m** (100MHz, CDCl3)



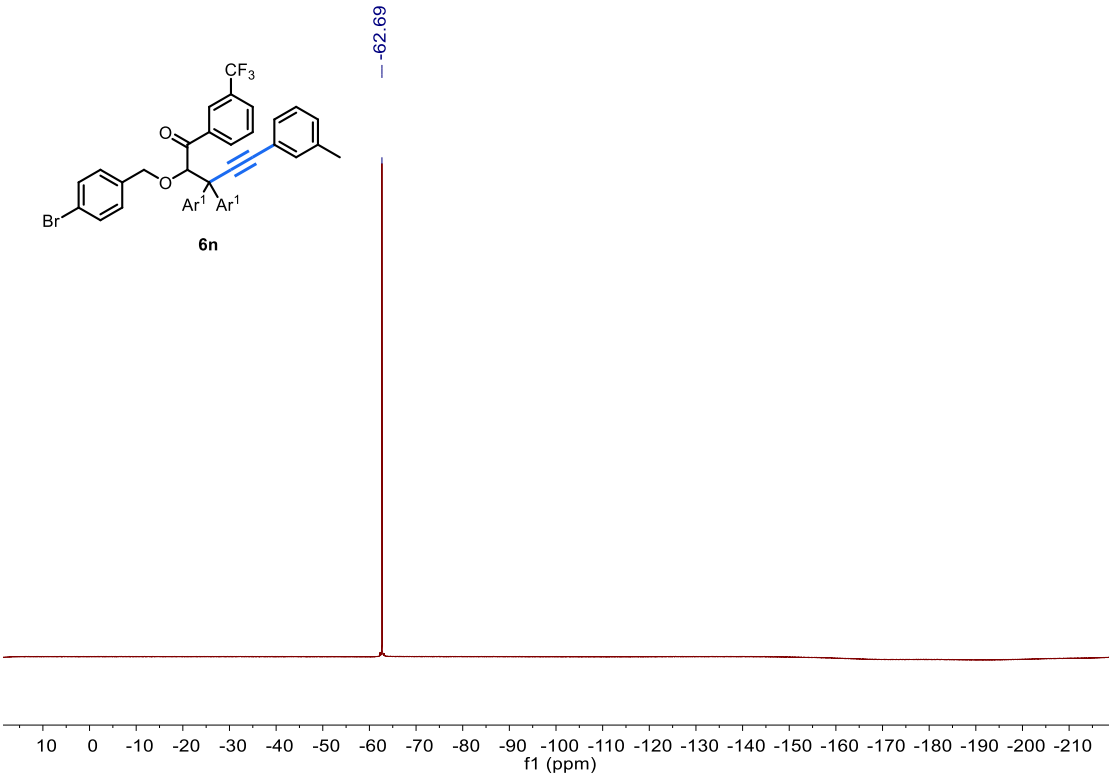
^{19}F NMR Spectrum of Compound **6m** (376 MHz, CDCl3)



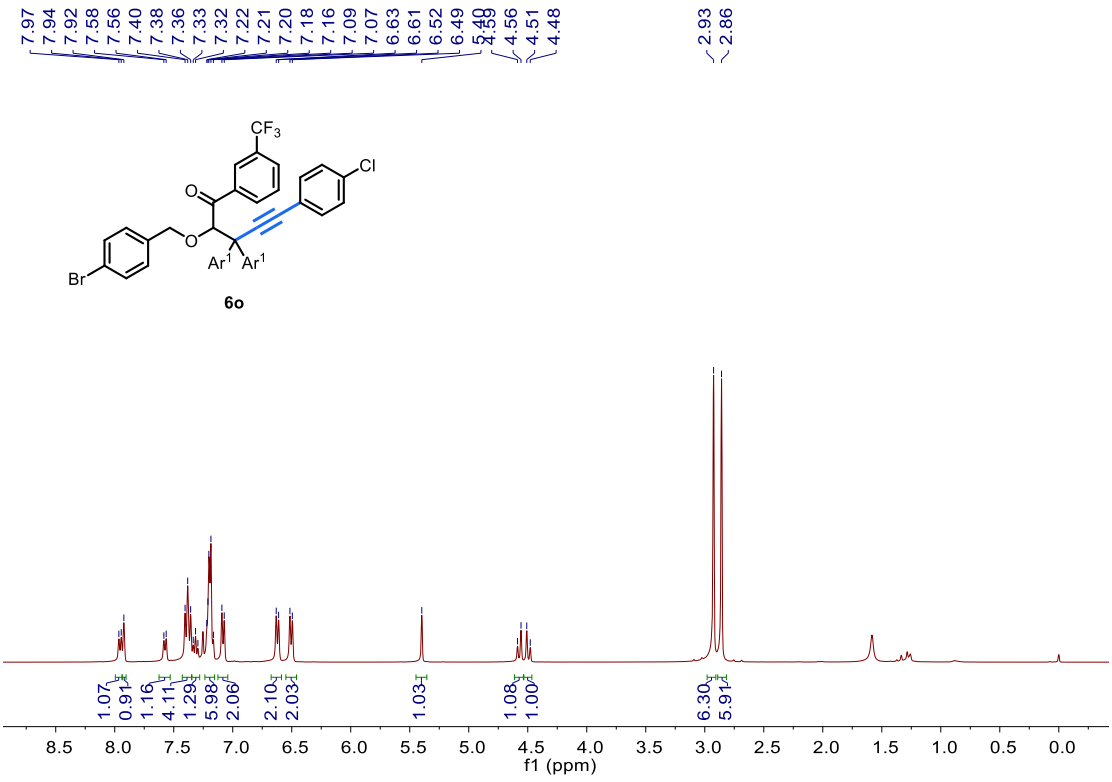
^{1}H NMR Spectrum of Compound **6n** (400MHz, CDCl3)



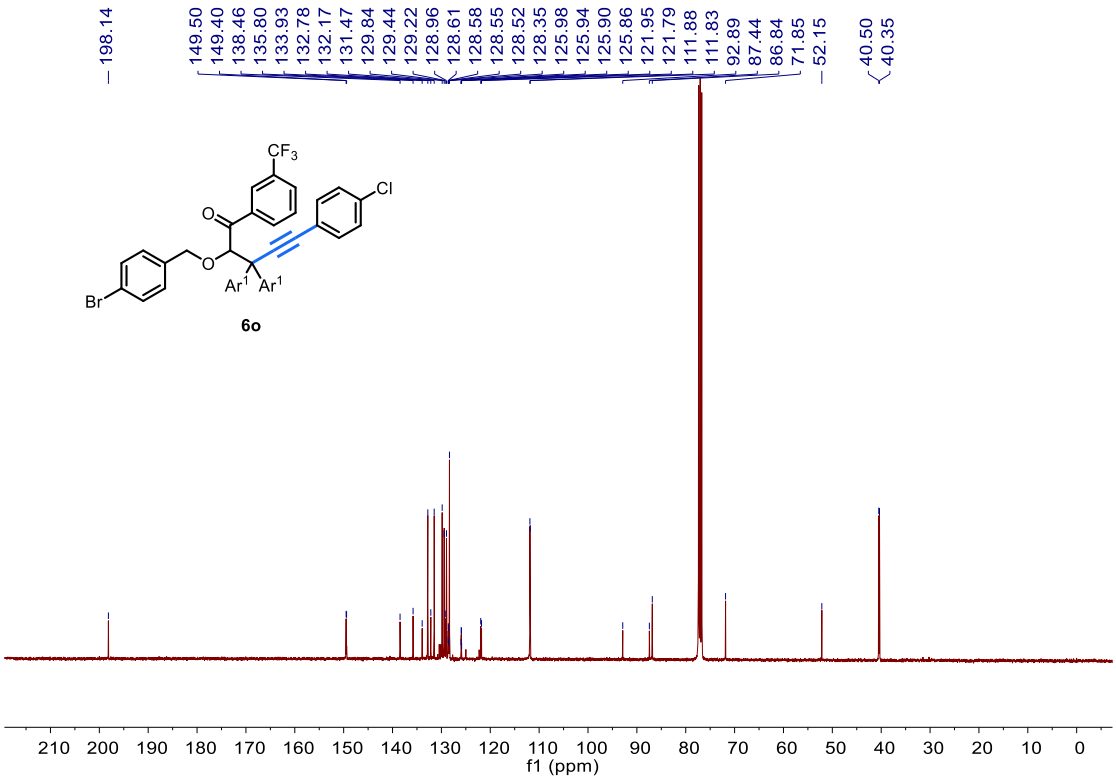
^{13}C NMR Spectrum of Compound **6n** (100MHz, CDCl3)



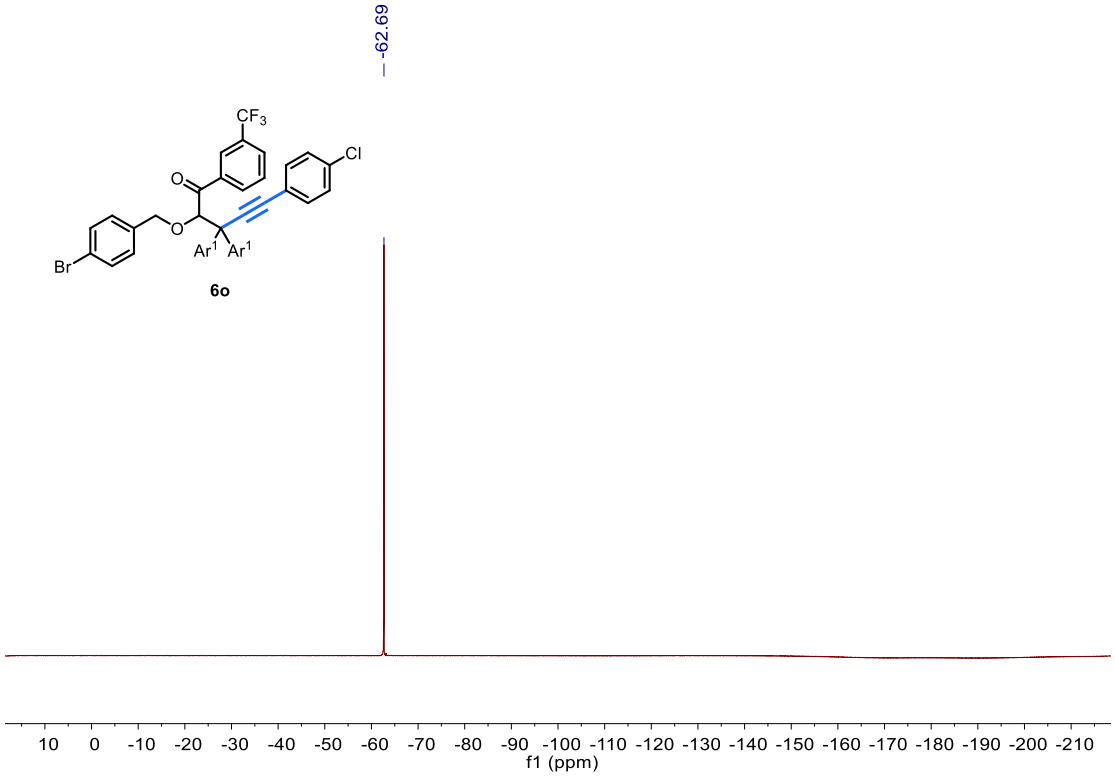
^{19}F NMR Spectrum of Compound **6n** (376 MHz, CDCl3)



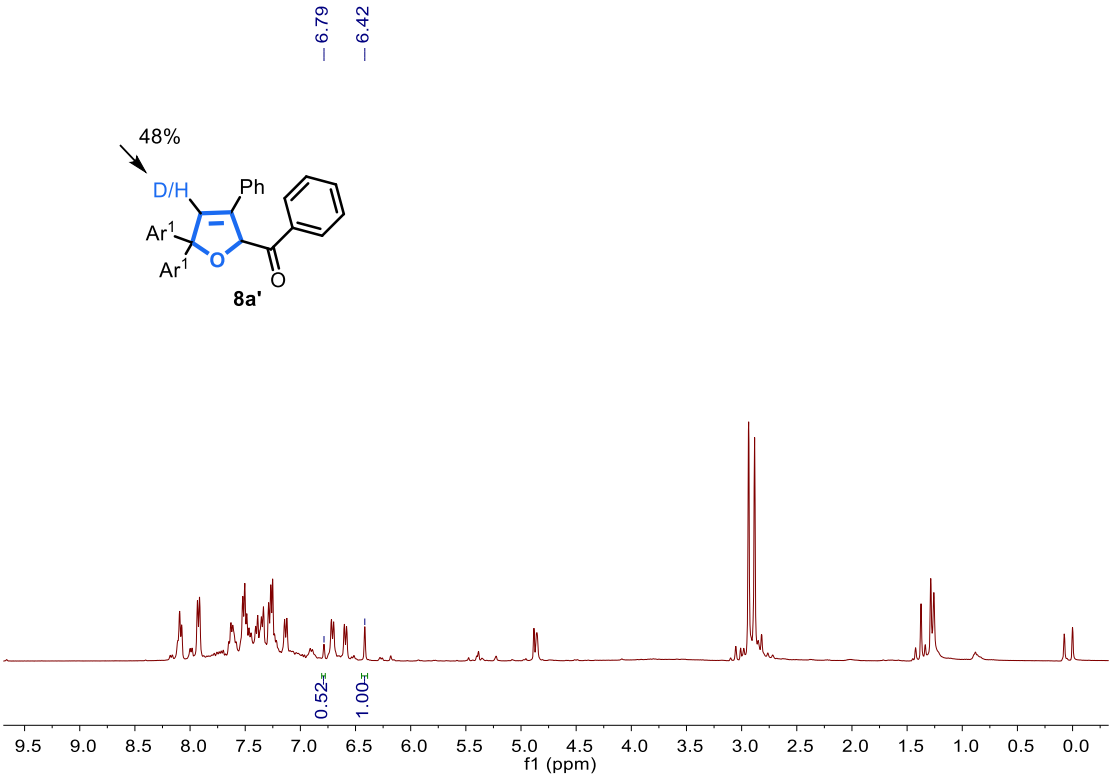
^{1}H NMR Spectrum of Compound **6o** (400MHz, CDCl3)



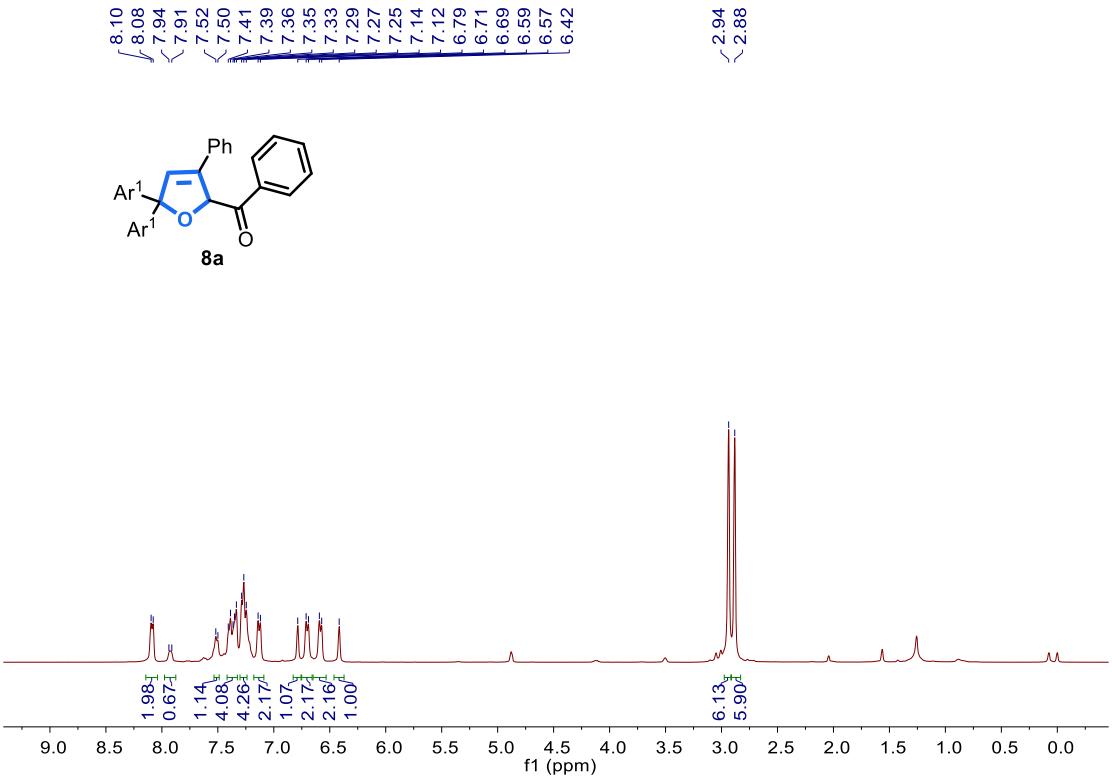
^{13}C NMR Spectrum of Compound **6o** (100MHz, CDCl3)



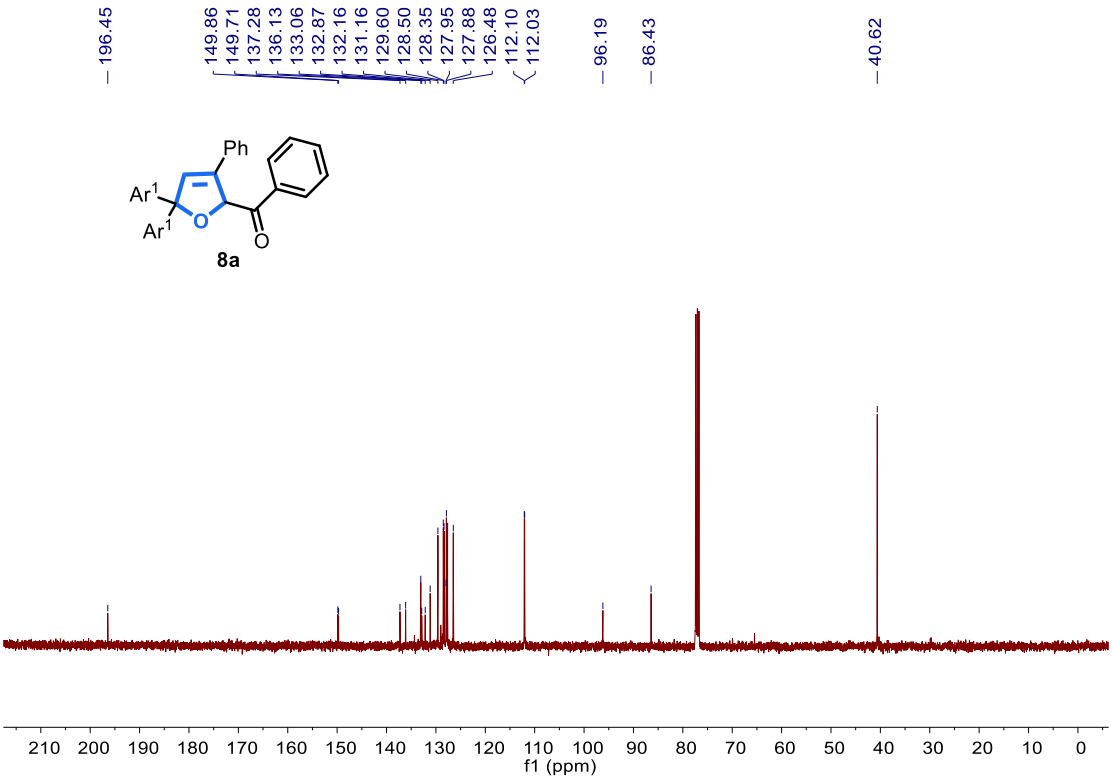
^{19}F NMR Spectrum of Compound **6o** (376 MHz, CDCl3)



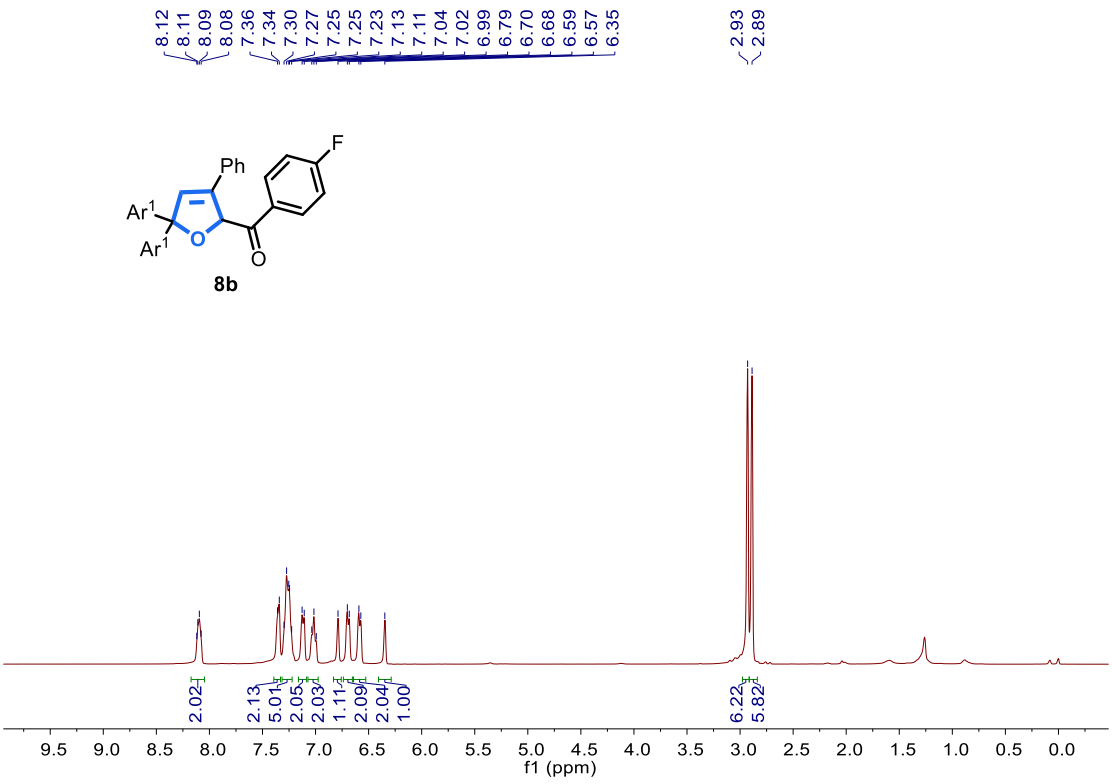
^{1}H NMR Spectrum of Compound **8a'** (400MHz, CDCl3)



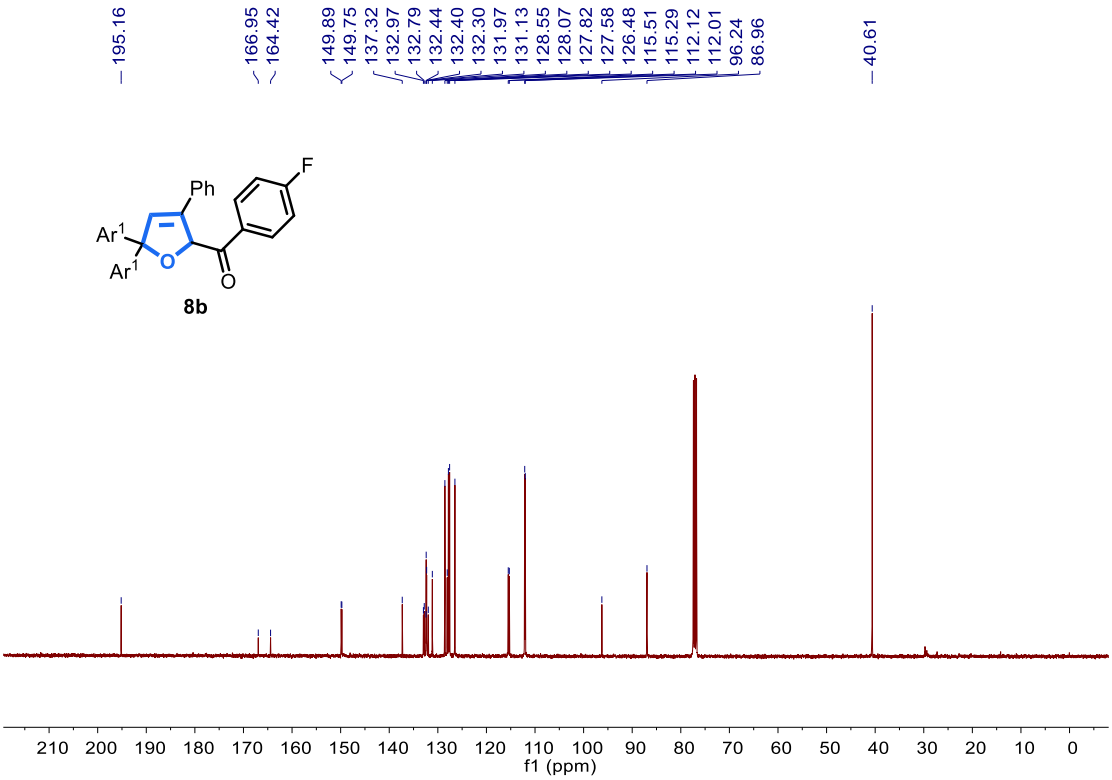
^{1}H NMR Spectrum of Compound **8a** (400MHz, CDCl3)



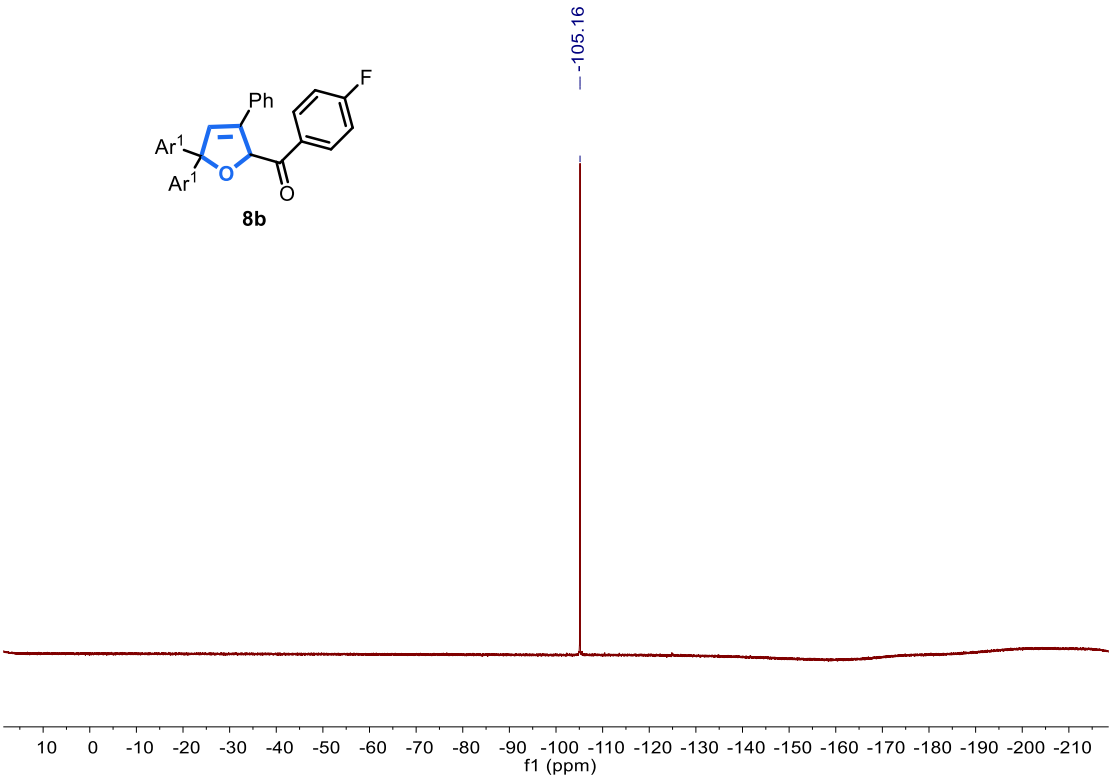
^{13}C NMR Spectrum of Compound **8a** (100MHz, CDCl3)



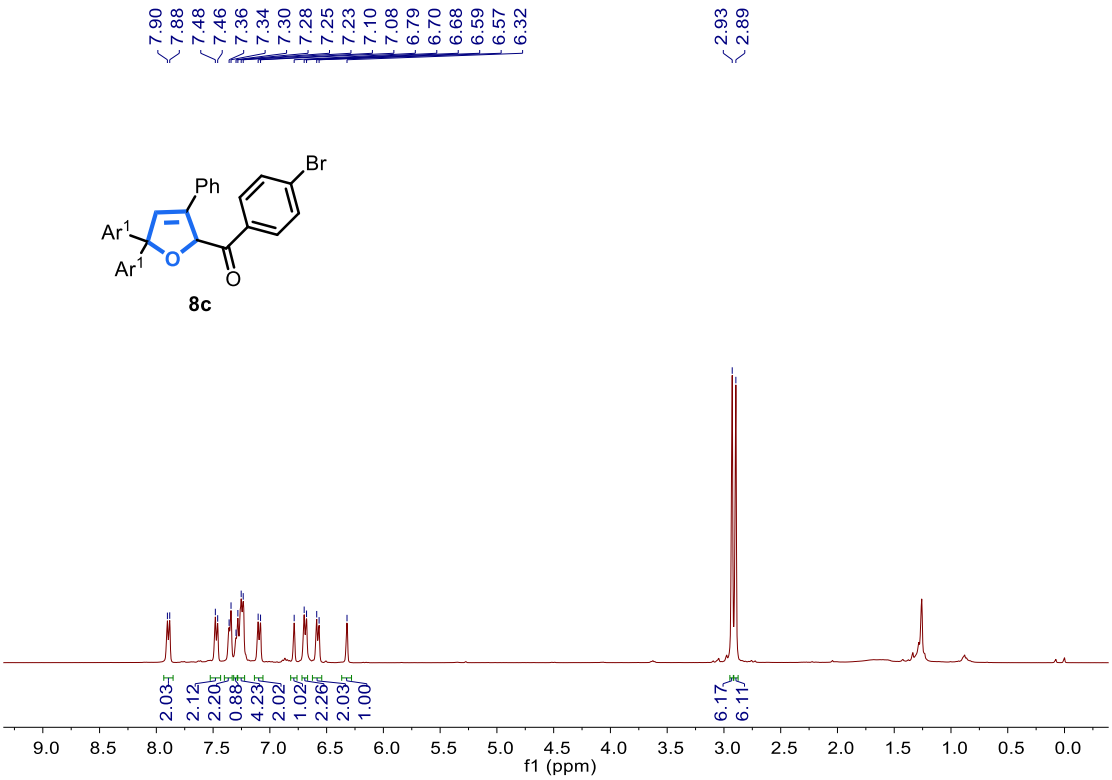
^{1}H NMR Spectrum of Compound **8b** (400MHz, CDCl3)



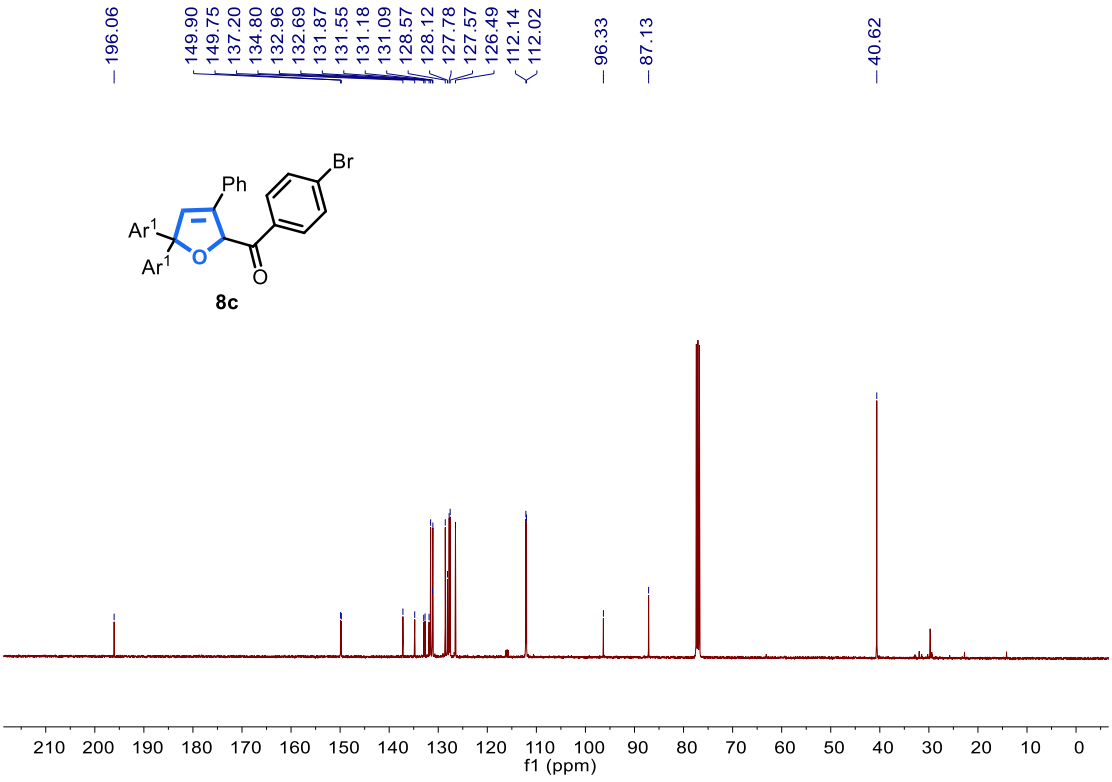
^{13}C NMR Spectrum of Compound **8b** (100MHz, CDCl3)



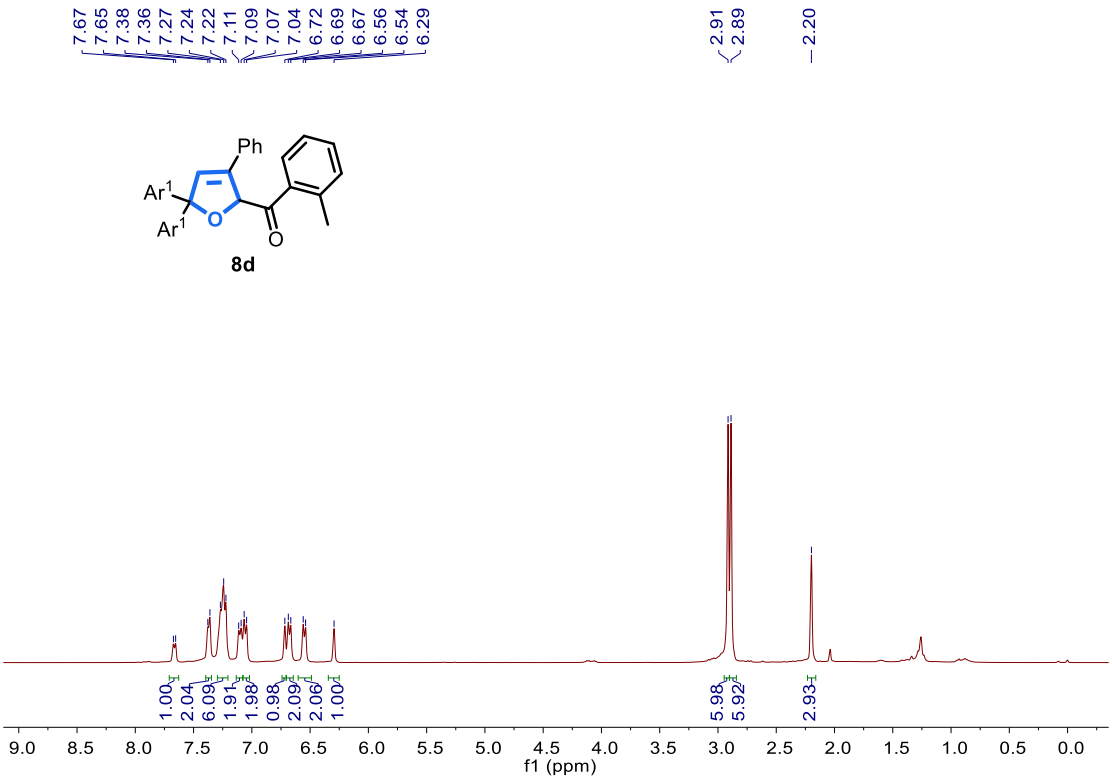
^{19}F NMR Spectrum of Compound **8b** (376 MHz, CDCl3)



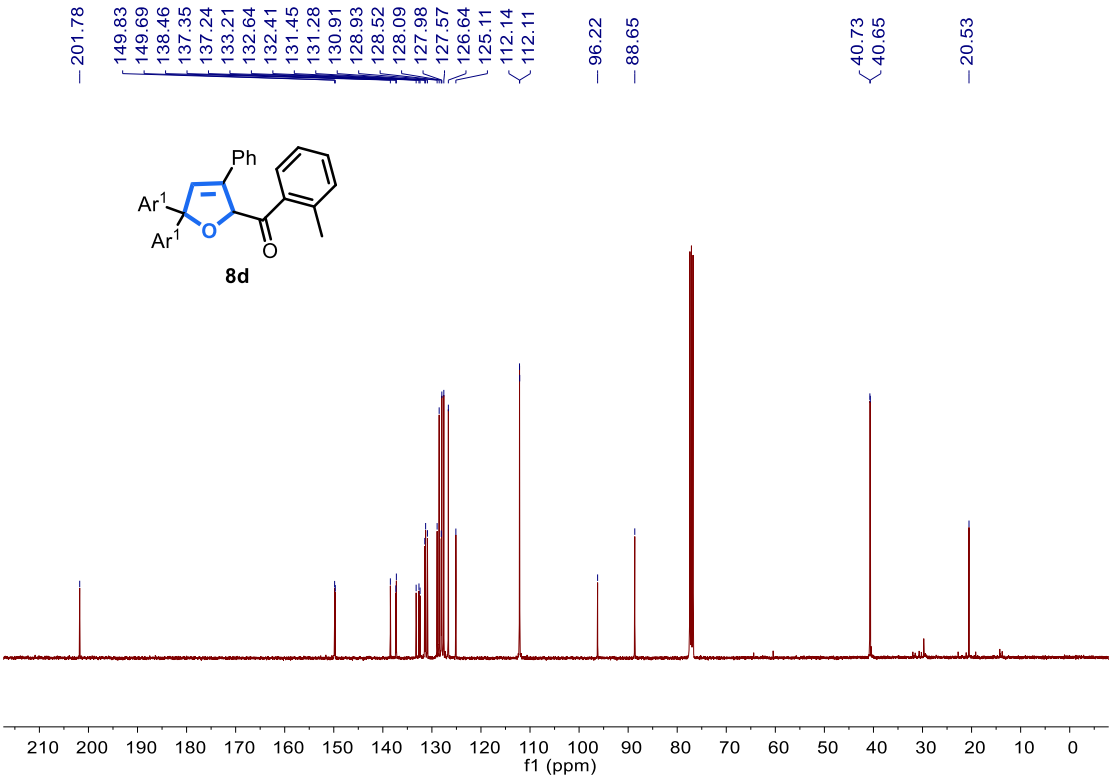
^{1}H NMR Spectrum of Compound **8c** (400MHz, CDCl3)



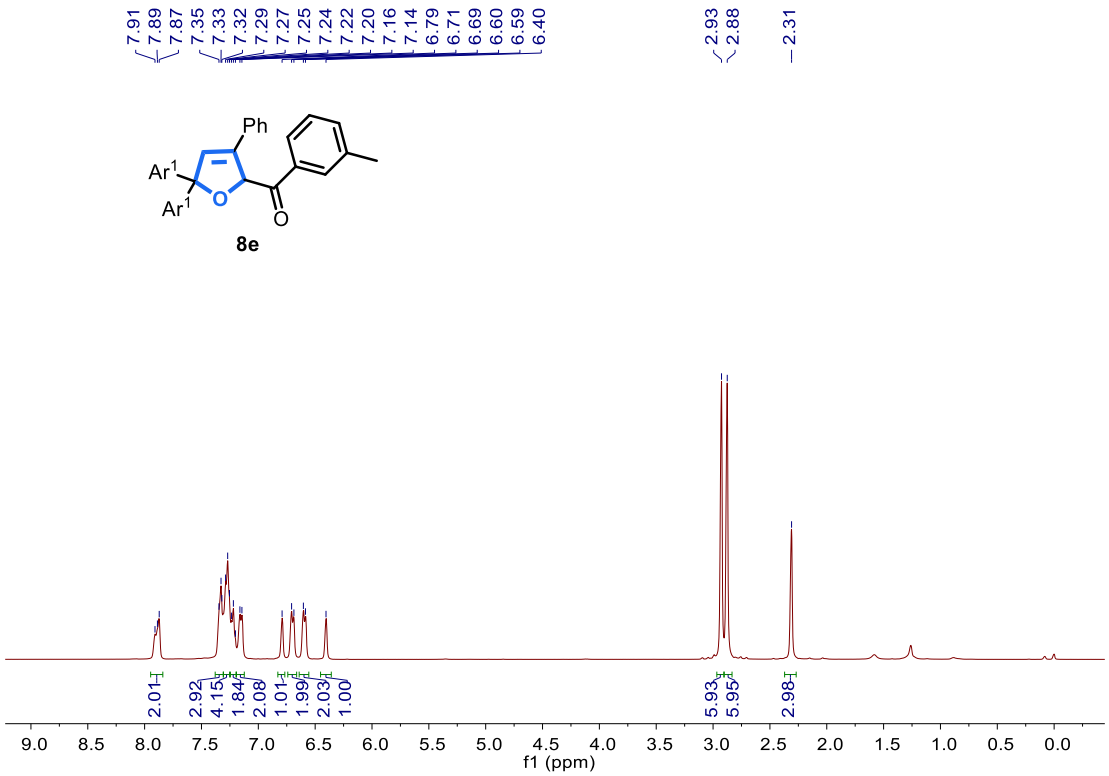
^{13}C NMR Spectrum of Compound **8c** (100MHz, CDCl3)



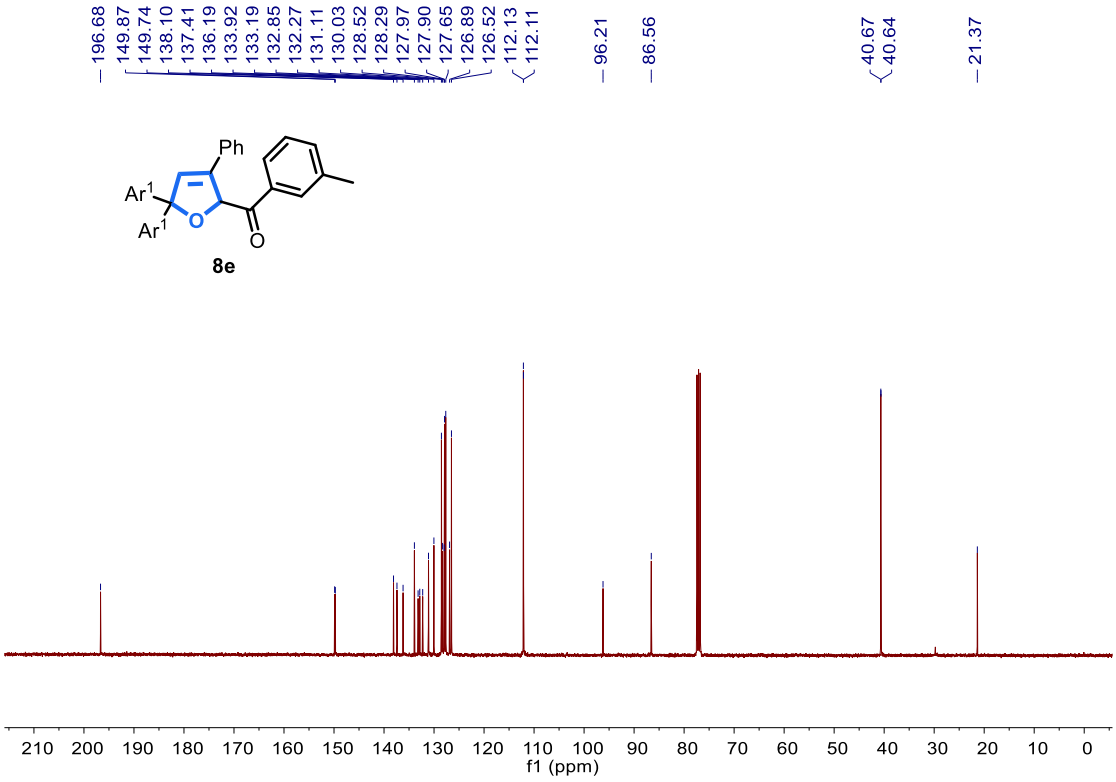
^{1}H NMR Spectrum of Compound **8d** (400MHz, CDCl3)



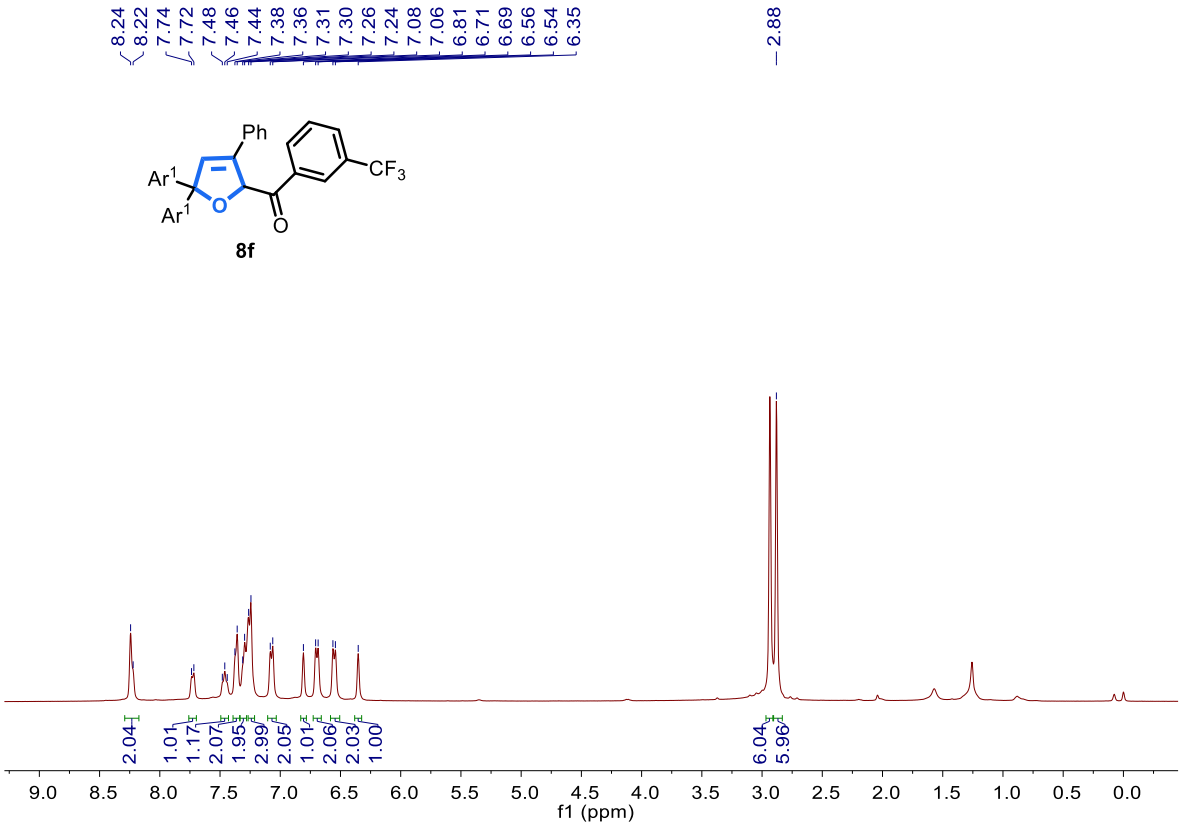
^{13}C NMR Spectrum of Compound **8d** (100MHz, CDCl3)



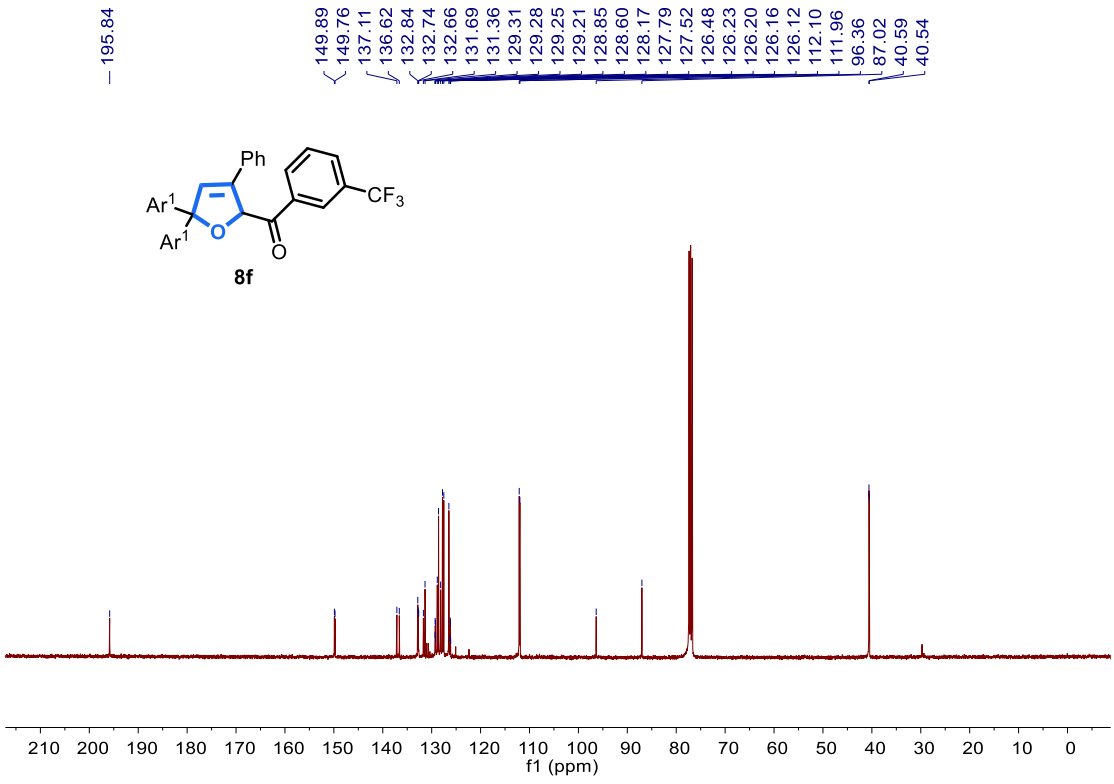
^{1}H NMR Spectrum of Compound **8e** (400MHz, CDCl3)



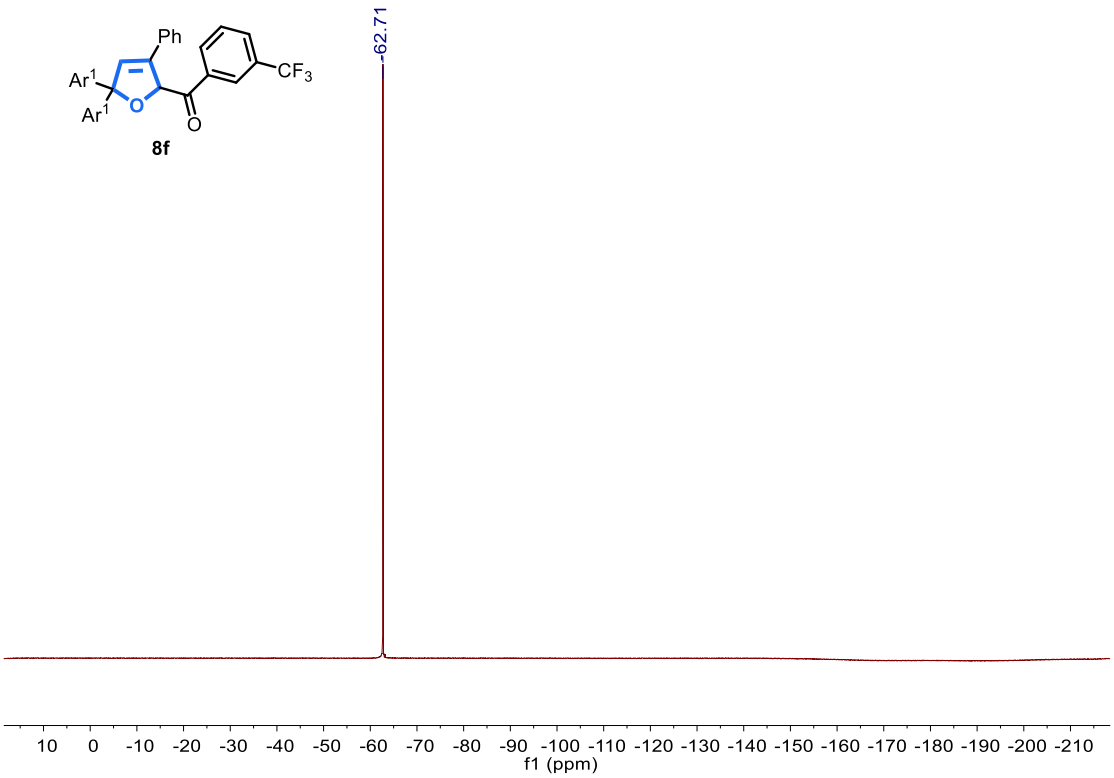
^{13}C NMR Spectrum of Compound **8e** (100MHz, CDCl3)



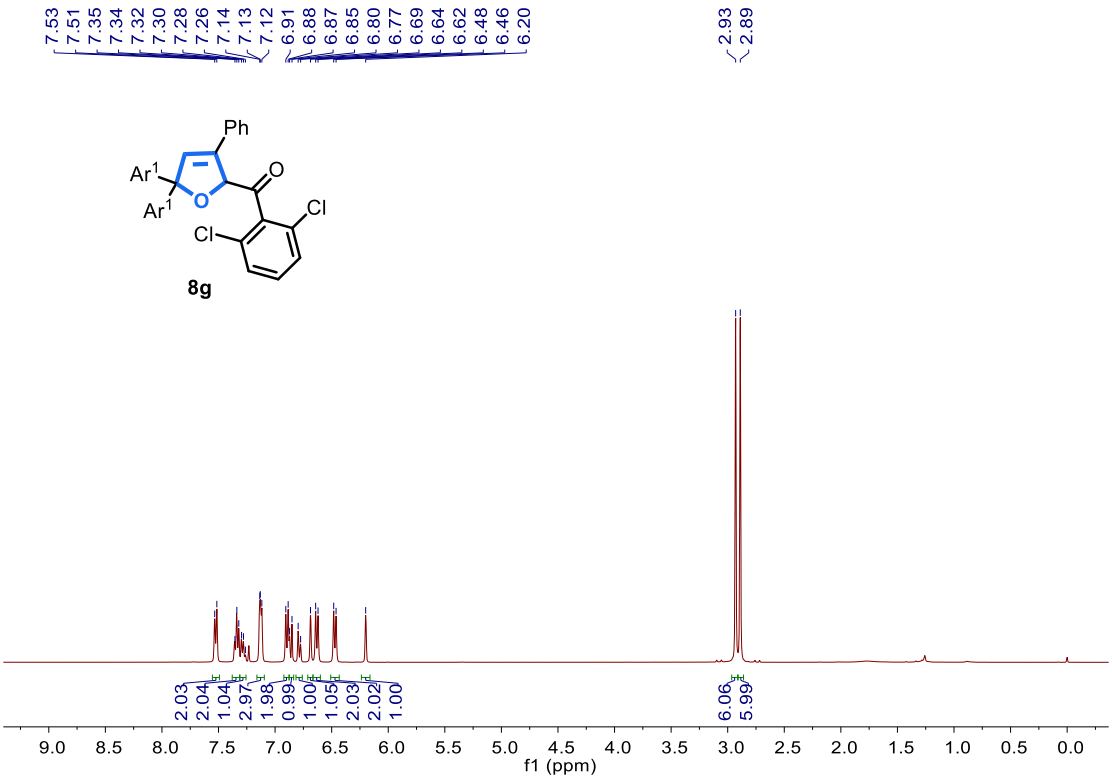
^{1}H NMR Spectrum of Compound **8f** (400MHz, CDCl3)



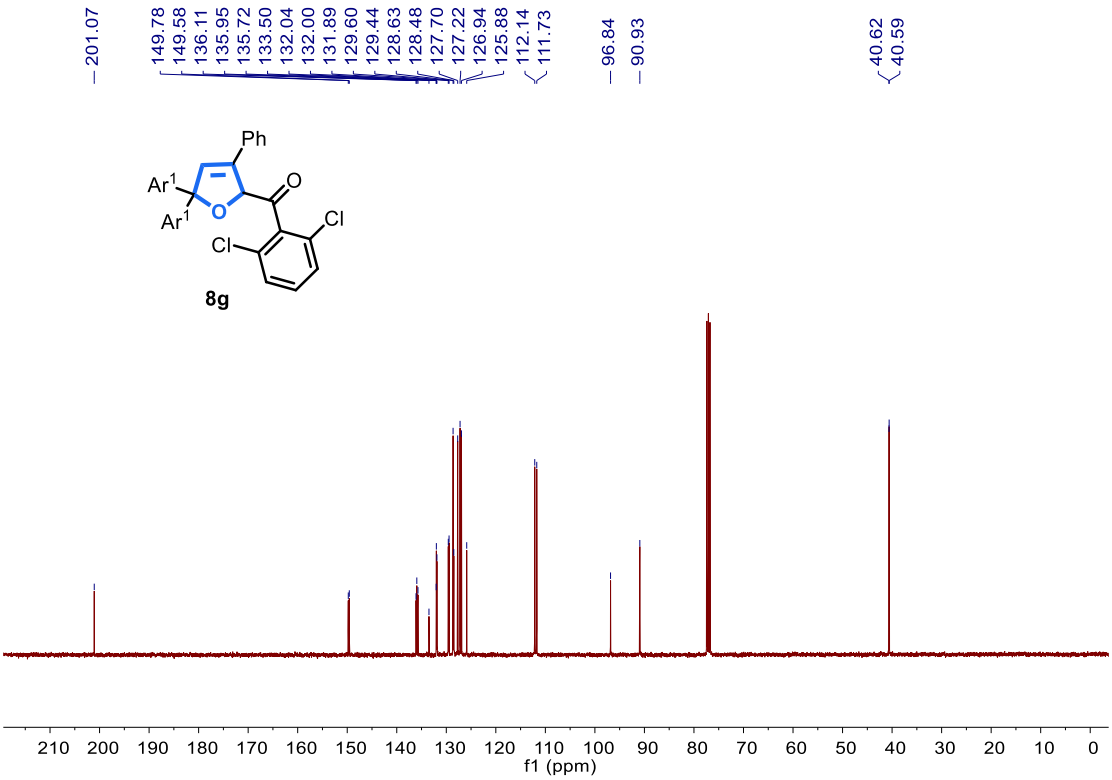
^{13}C NMR Spectrum of Compound **8f** (100MHz, CDCl3)



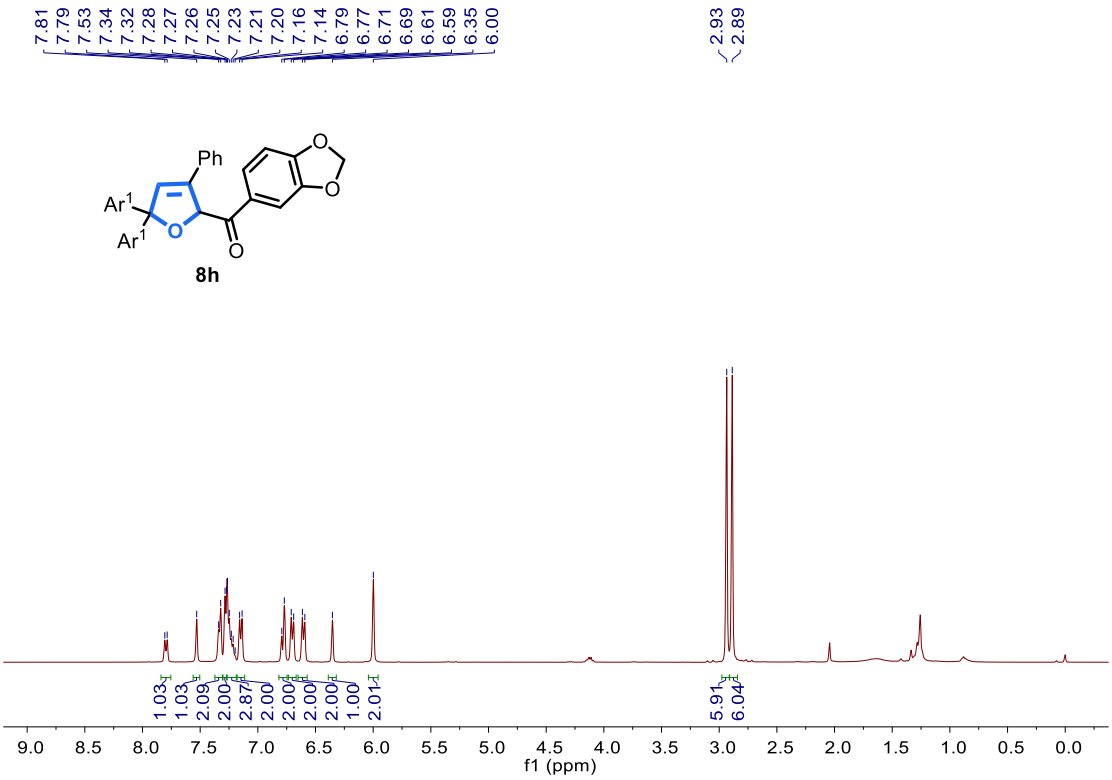
^{19}F NMR Spectrum of Compound **8f** (376 MHz, CDCl3)



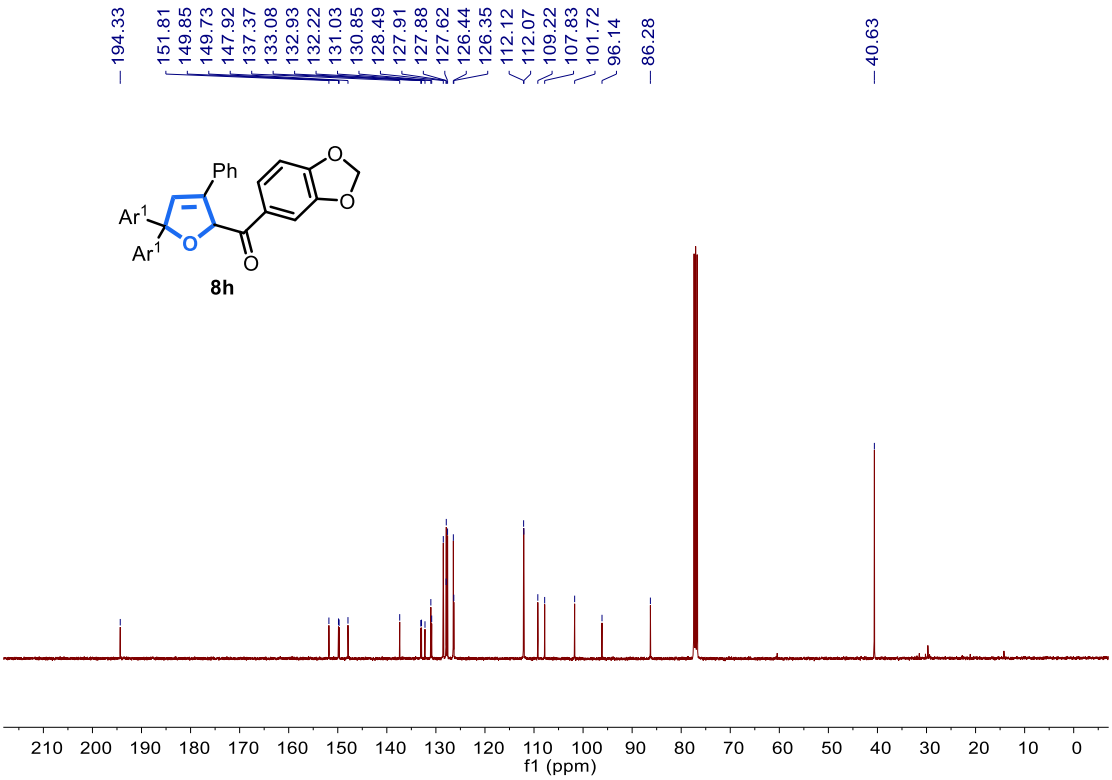
^{1}H NMR Spectrum of Compound **8g** (400MHz, CDCl3)



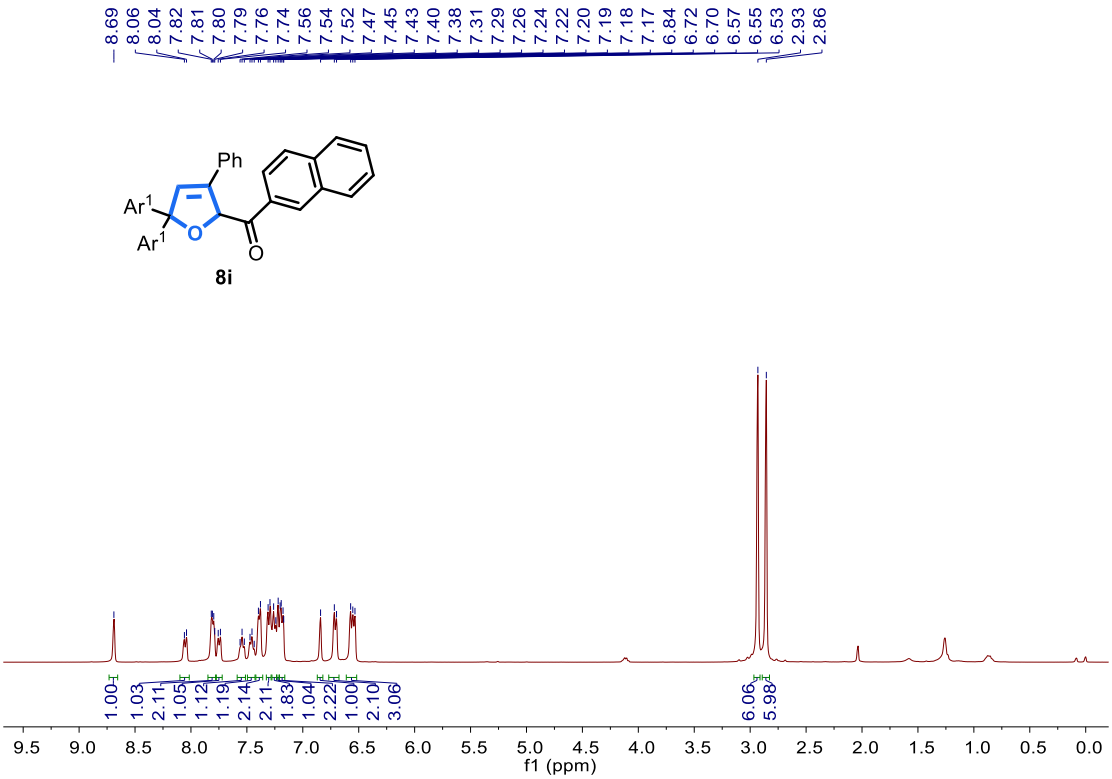
^{13}C NMR Spectrum of Compound **8g** (100MHz, CDCl3)



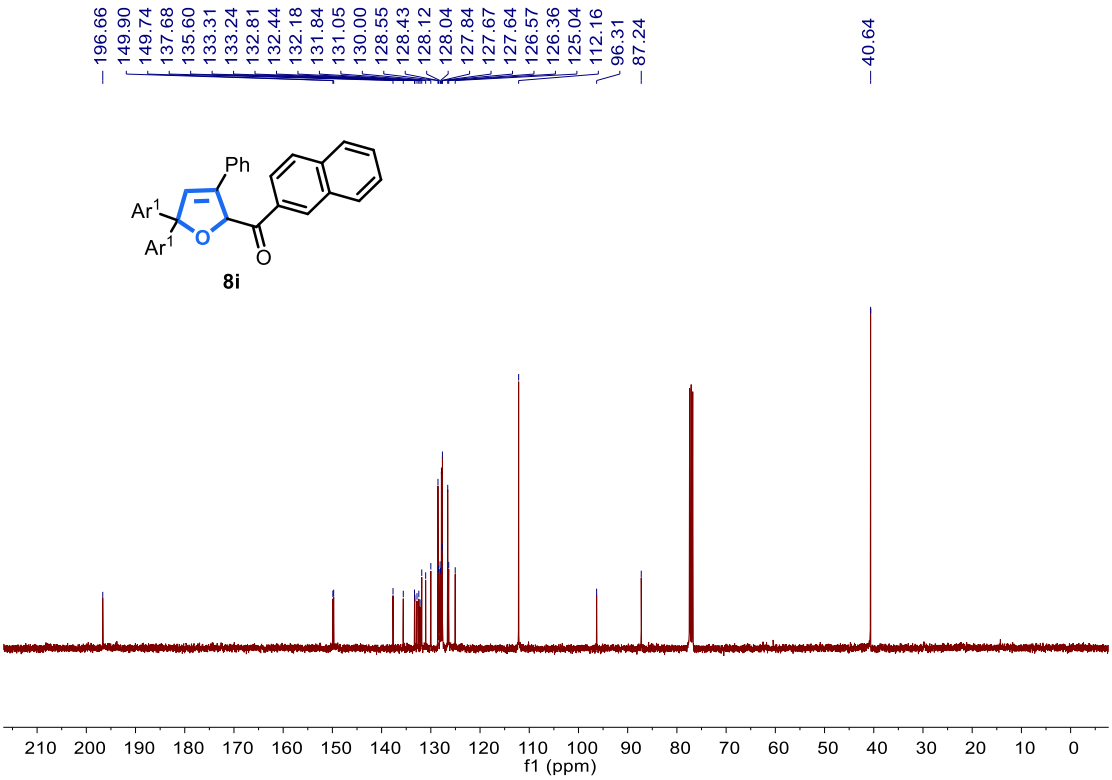
^{1}H NMR Spectrum of Compound **8h** (400MHz, CDCl3)



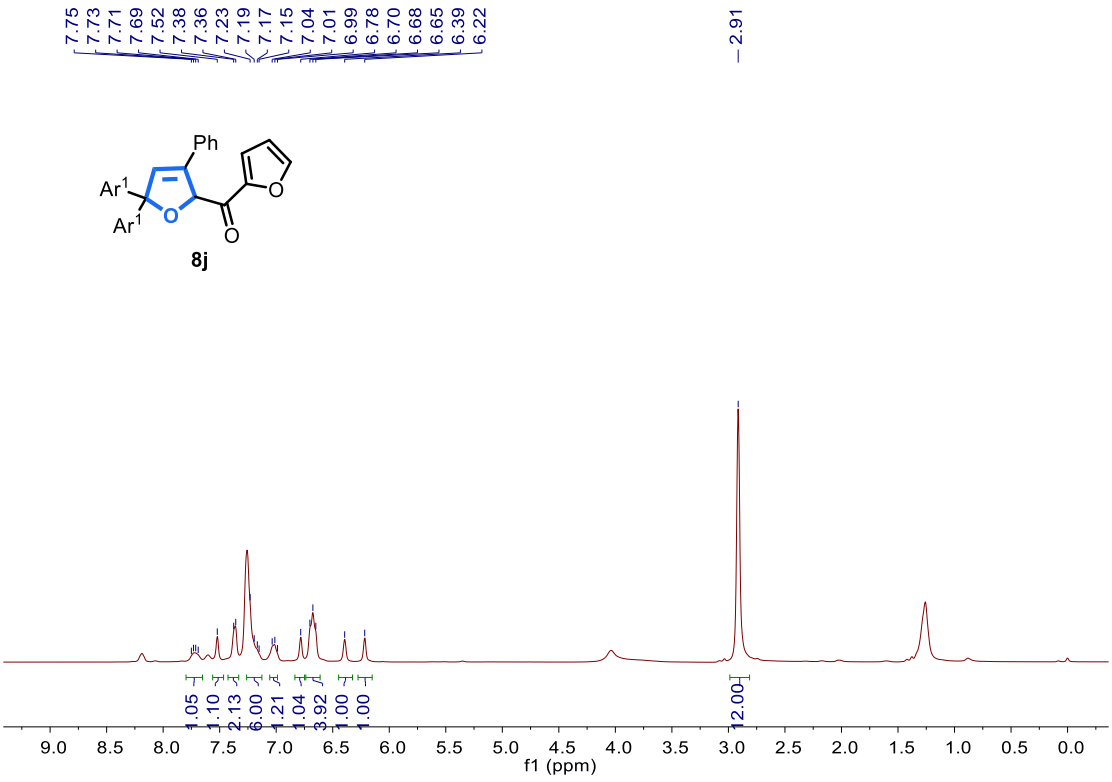
^{13}C NMR Spectrum of Compound **8h** (100MHz, CDCl3)



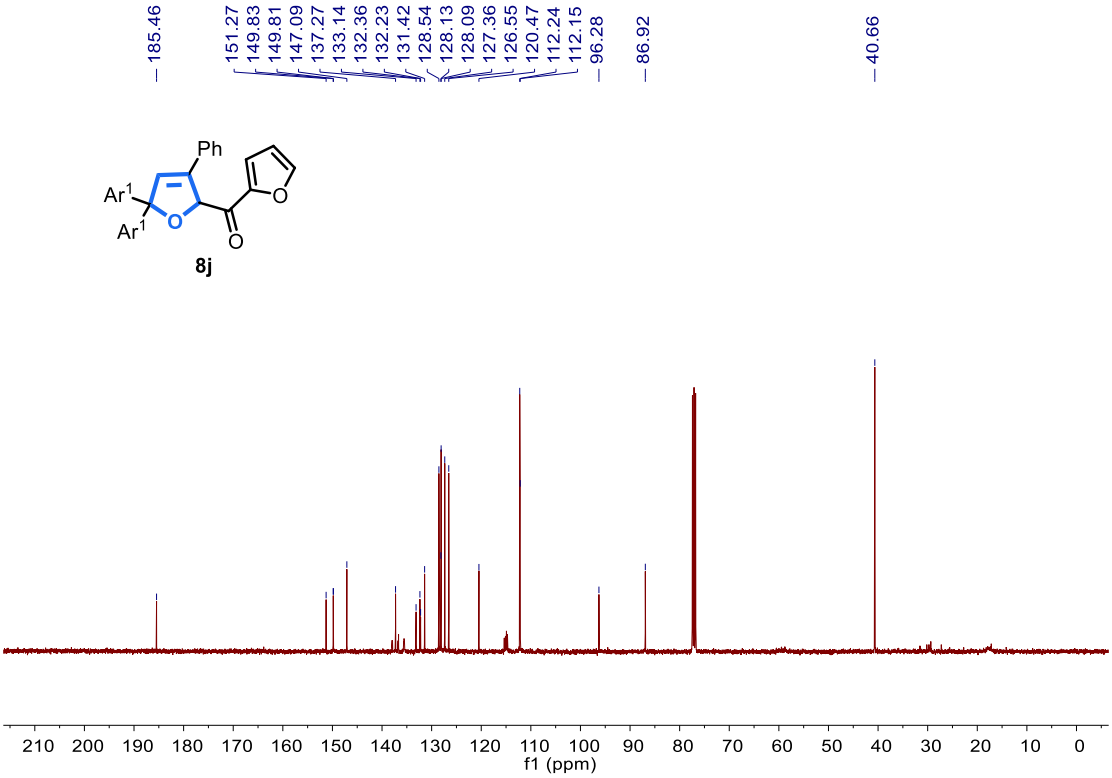
^{1}H NMR Spectrum of Compound **8i** (400MHz, CDCl3)



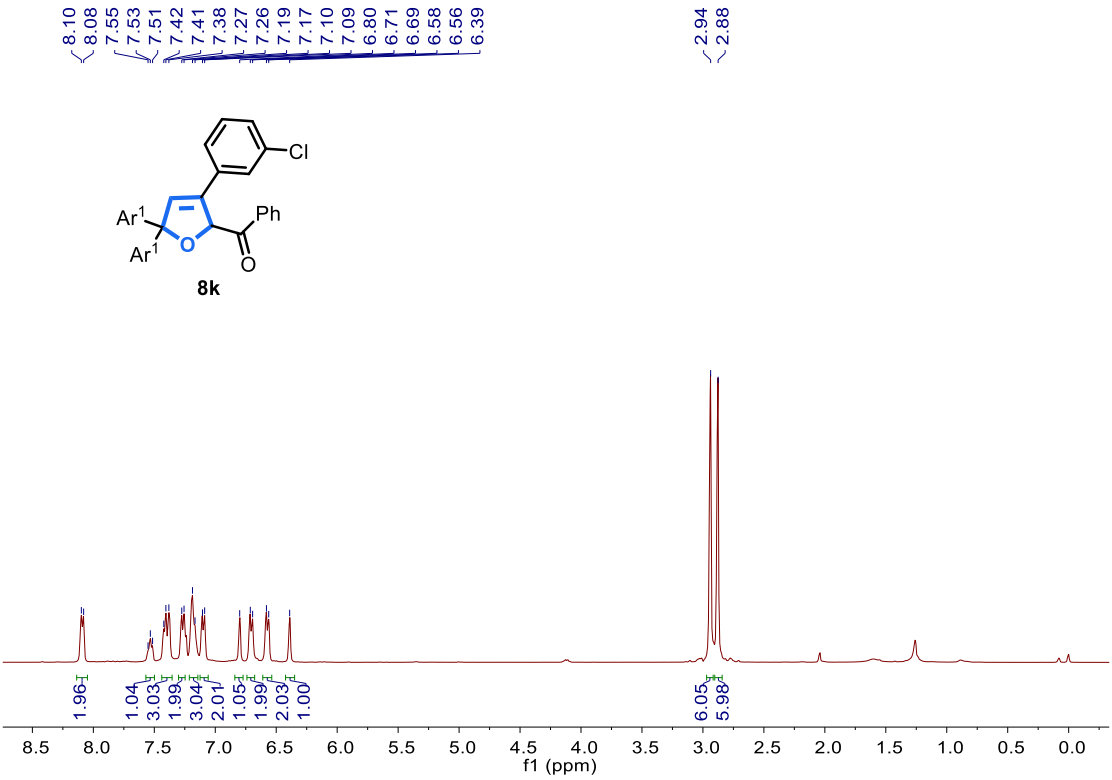
^{13}C NMR Spectrum of Compound **8i** (100MHz, CDCl3)



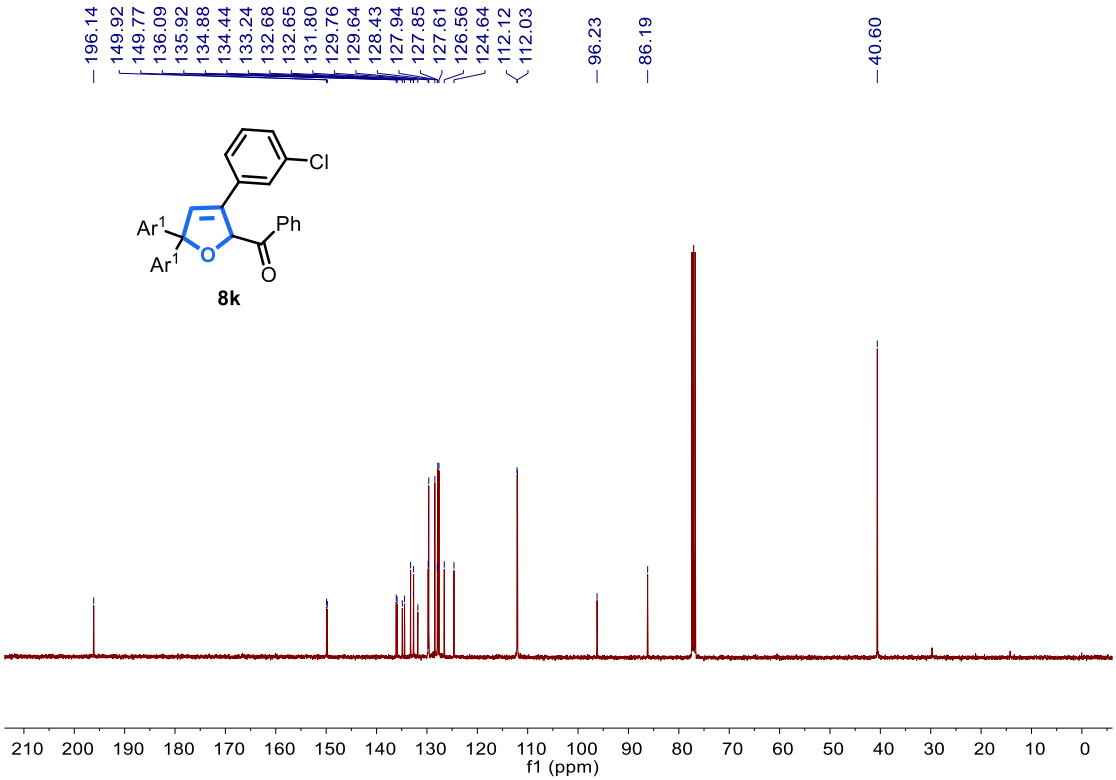
^{1}H NMR Spectrum of Compound **8j** (400MHz, CDCl3)



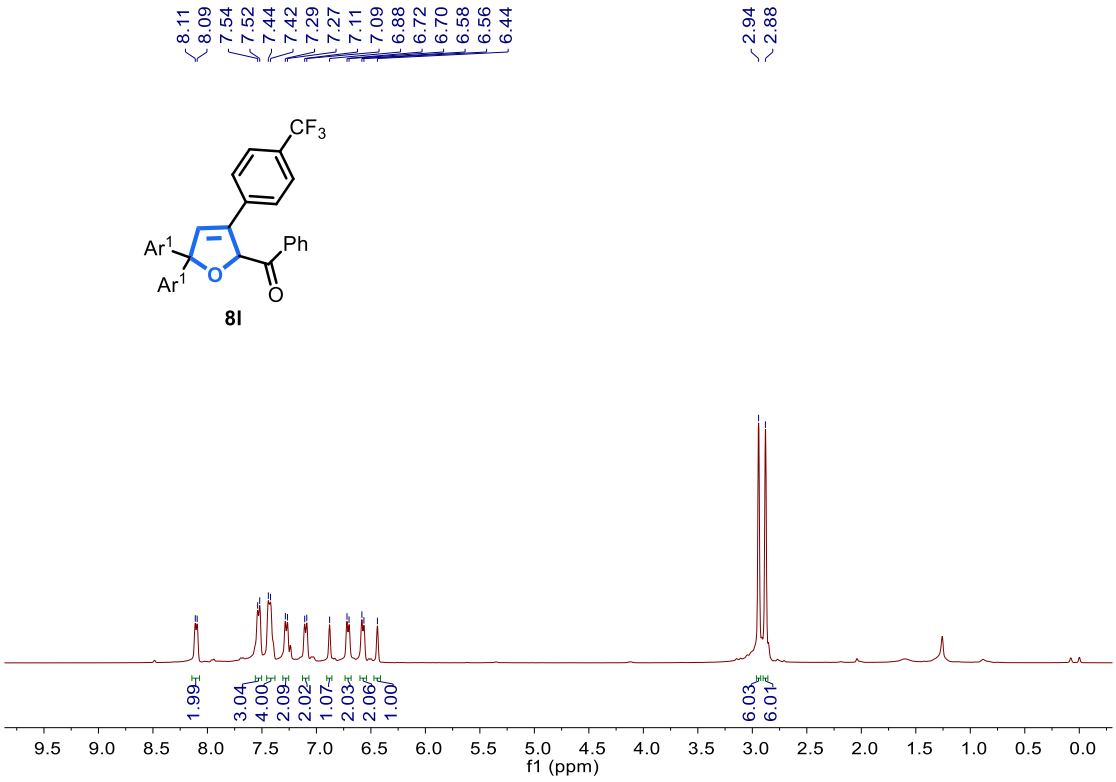
^{13}C NMR Spectrum of Compound **8j** (100MHz, CDCl3)



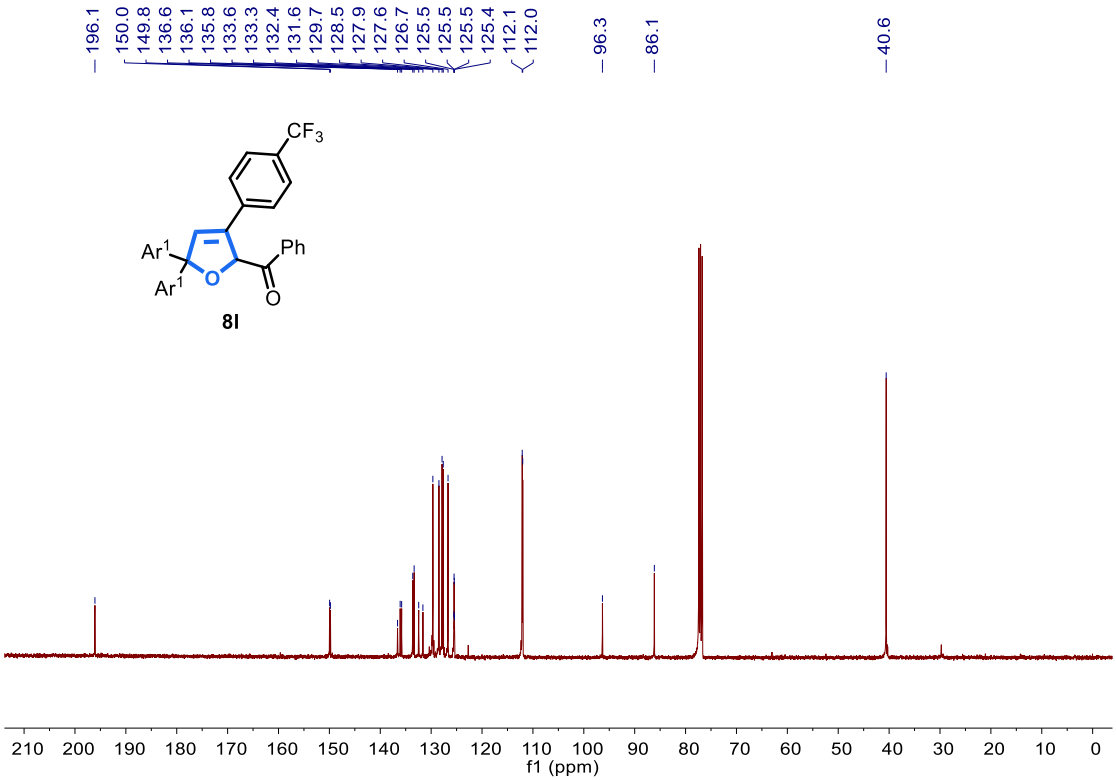
^{1}H NMR Spectrum of Compound **8k** (400MHz, CDCl3)



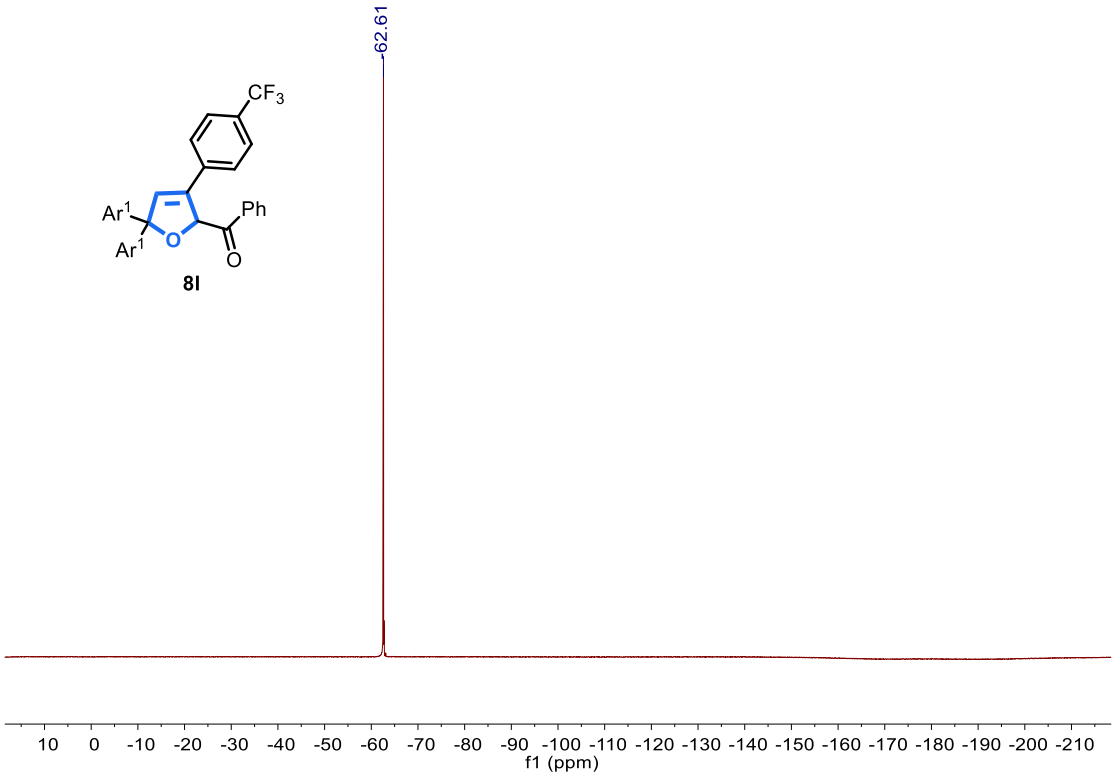
^{13}C NMR Spectrum of Compound **8k** (100MHz, CDCl3)



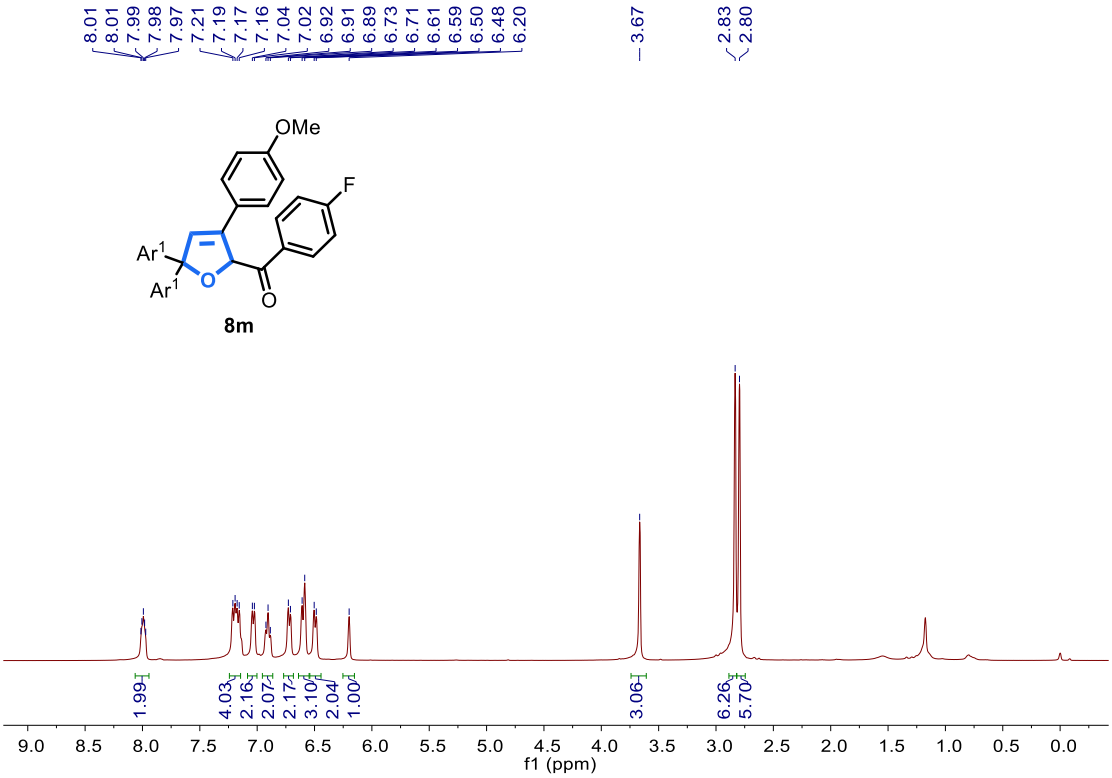
^{1}H NMR Spectrum of Compound **8l** (400MHz, CDCl3)



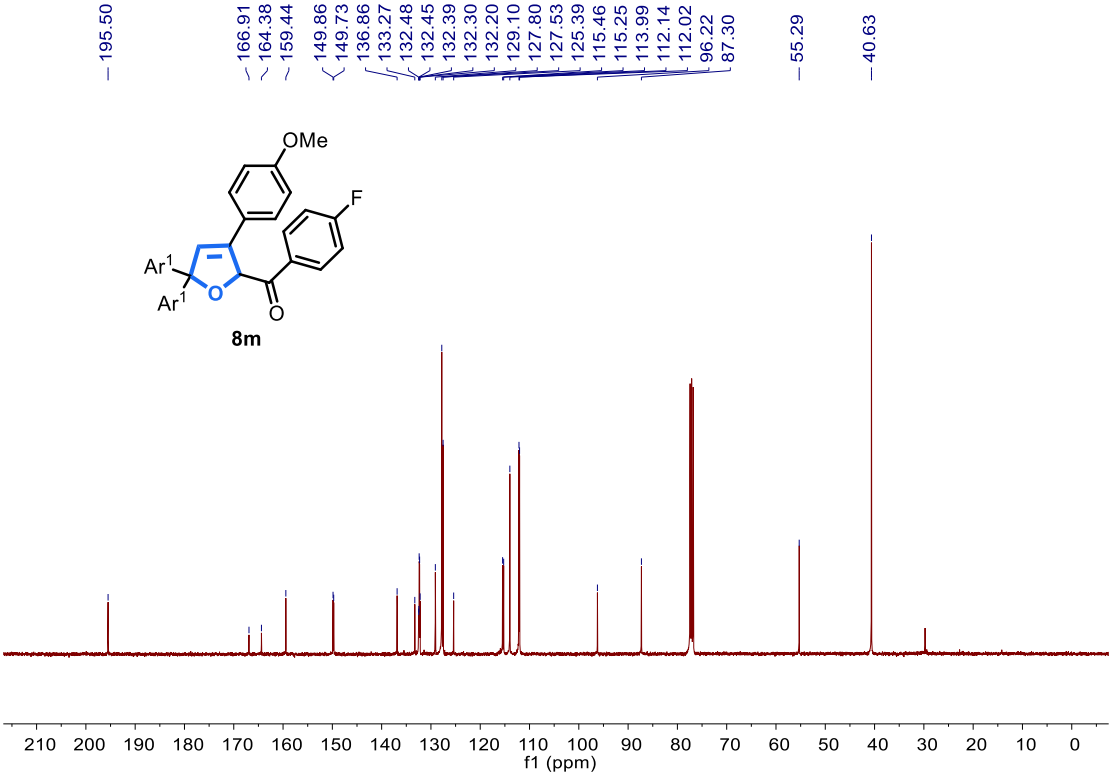
^{13}C NMR Spectrum of Compound **8l** (100MHz, CDCl3)



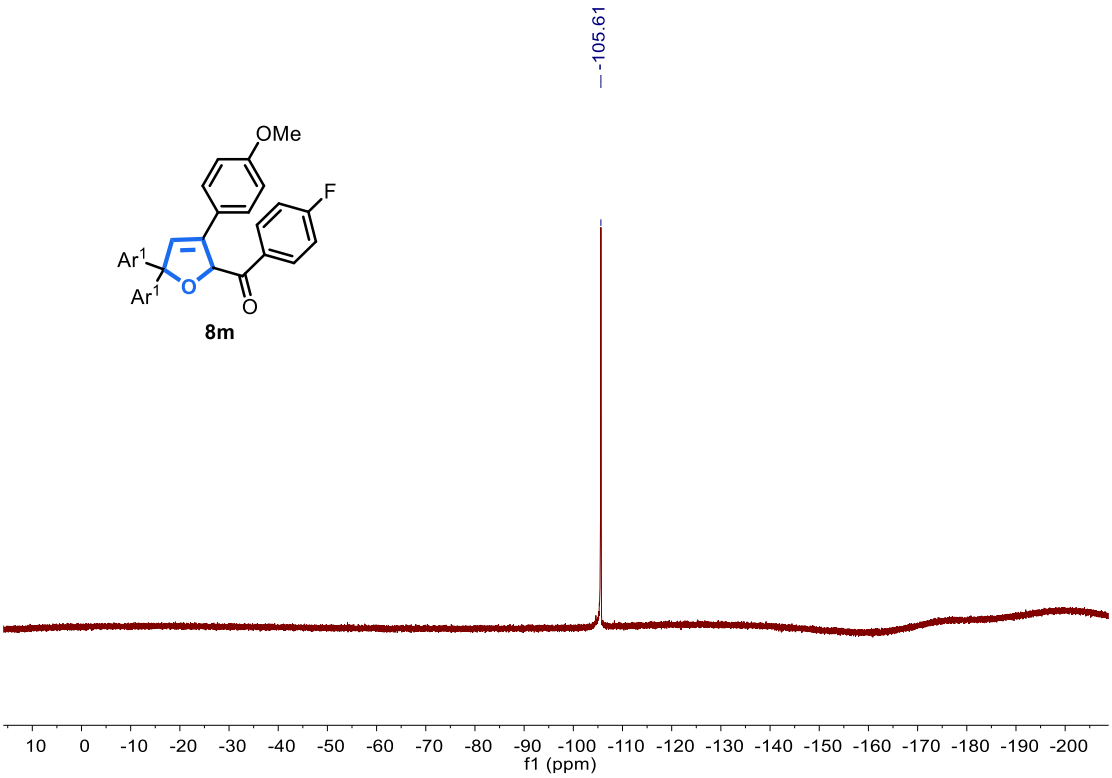
^{19}F NMR Spectrum of Compound **8l** (376 MHz, CDCl3)



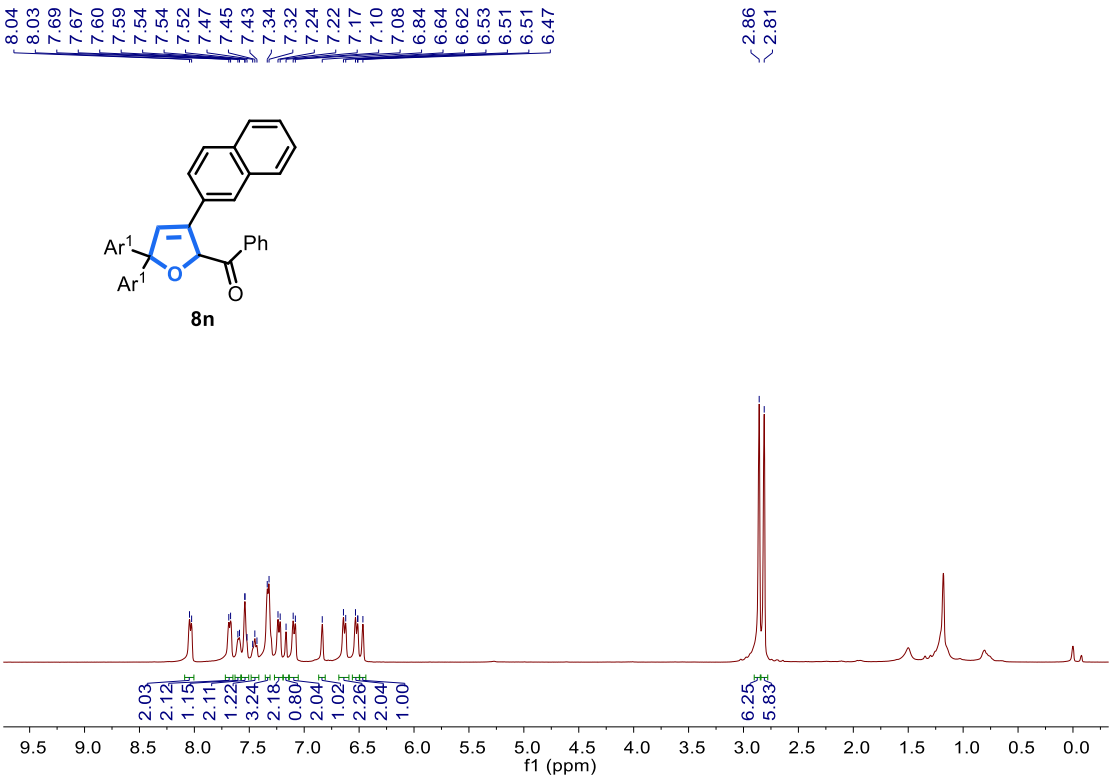
^{1}H NMR Spectrum of Compound **8m** (400MHz, CDCl3)



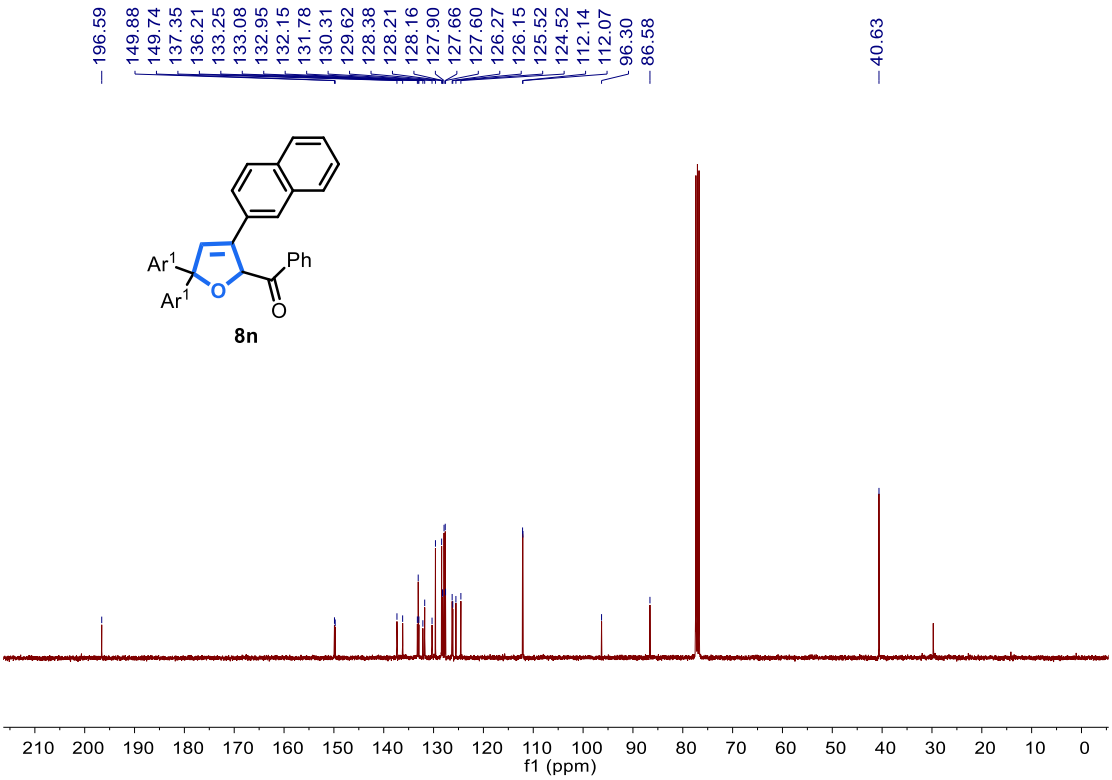
^{13}C NMR Spectrum of Compound **8m** (100MHz, CDCl3)



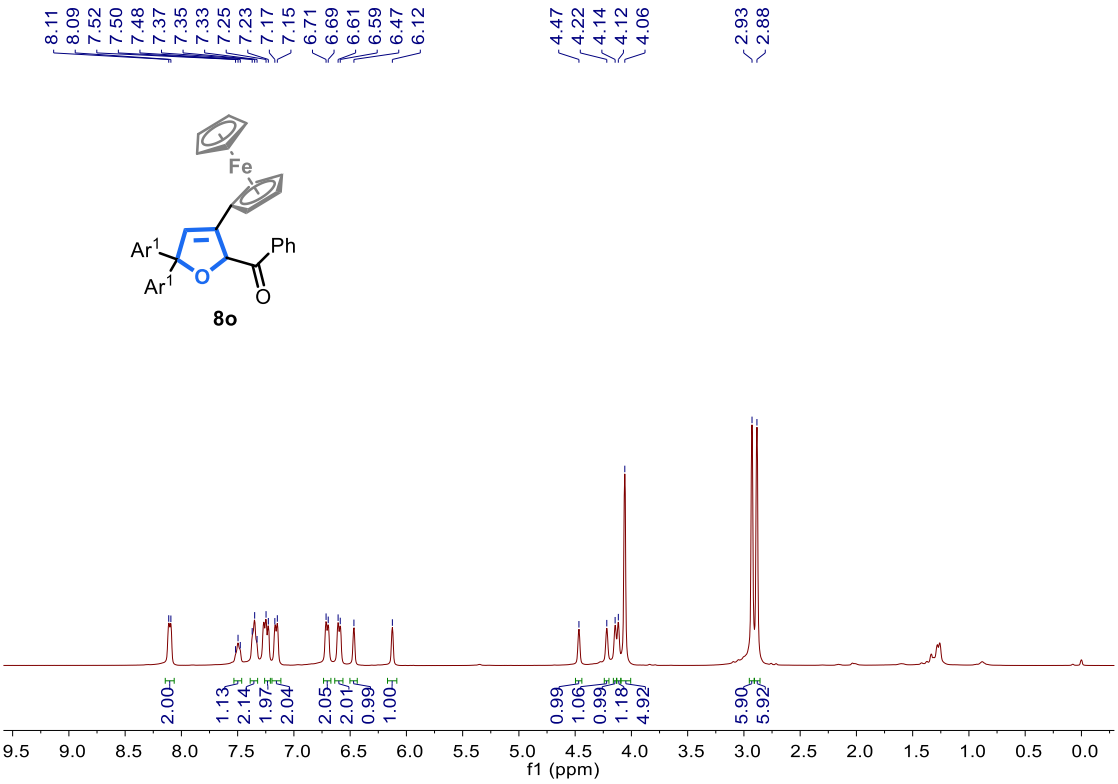
^{19}F NMR Spectrum of Compound **8m** (376 MHz, CDCl3)



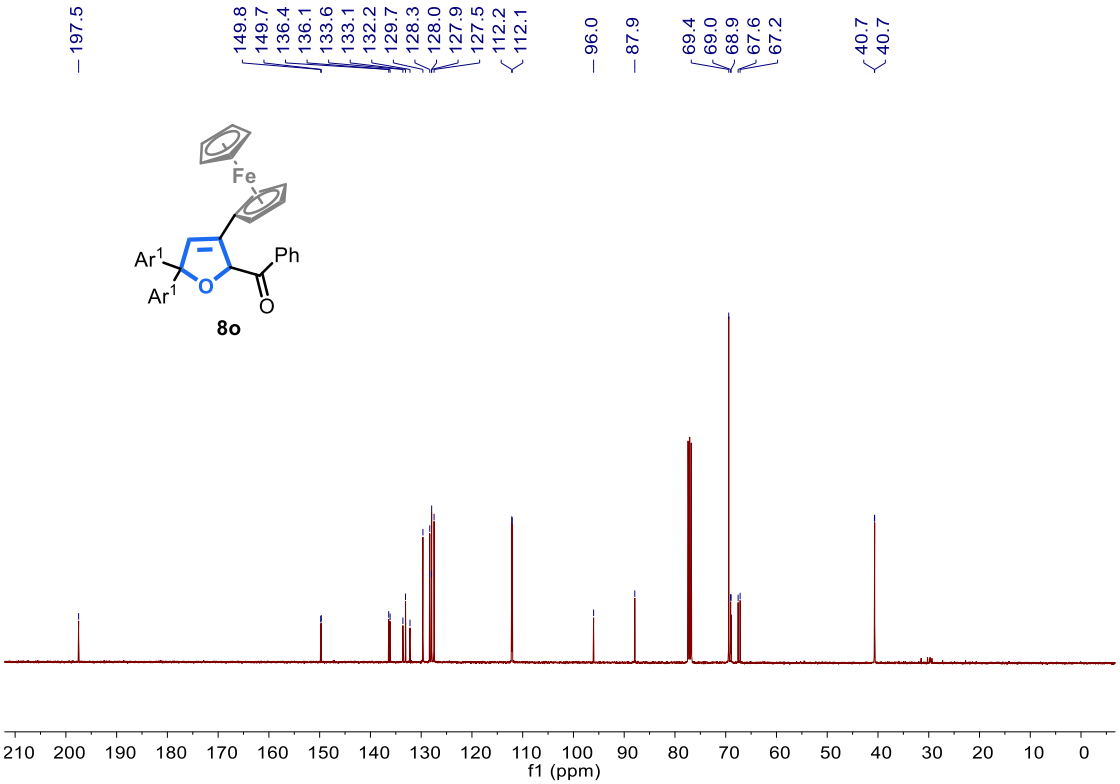
^{1}H NMR Spectrum of Compound **8n** (400MHz, CDCl3)



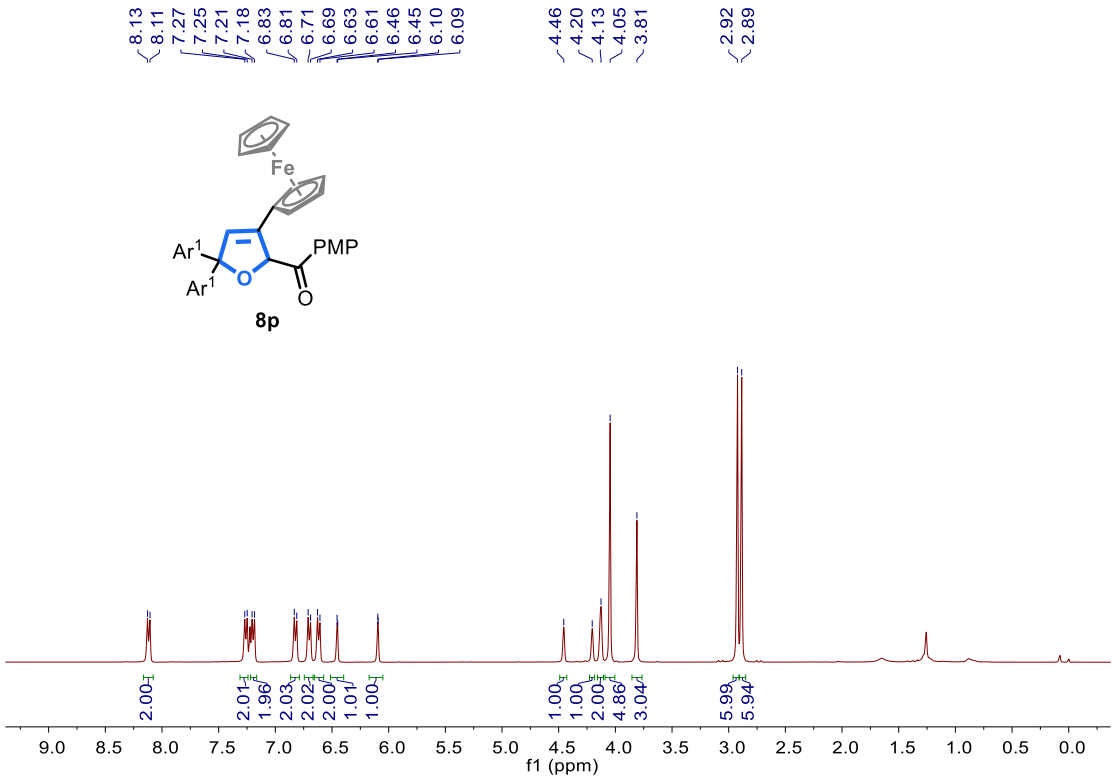
^{13}C NMR Spectrum of Compound **8n** (100MHz, CDCl3)



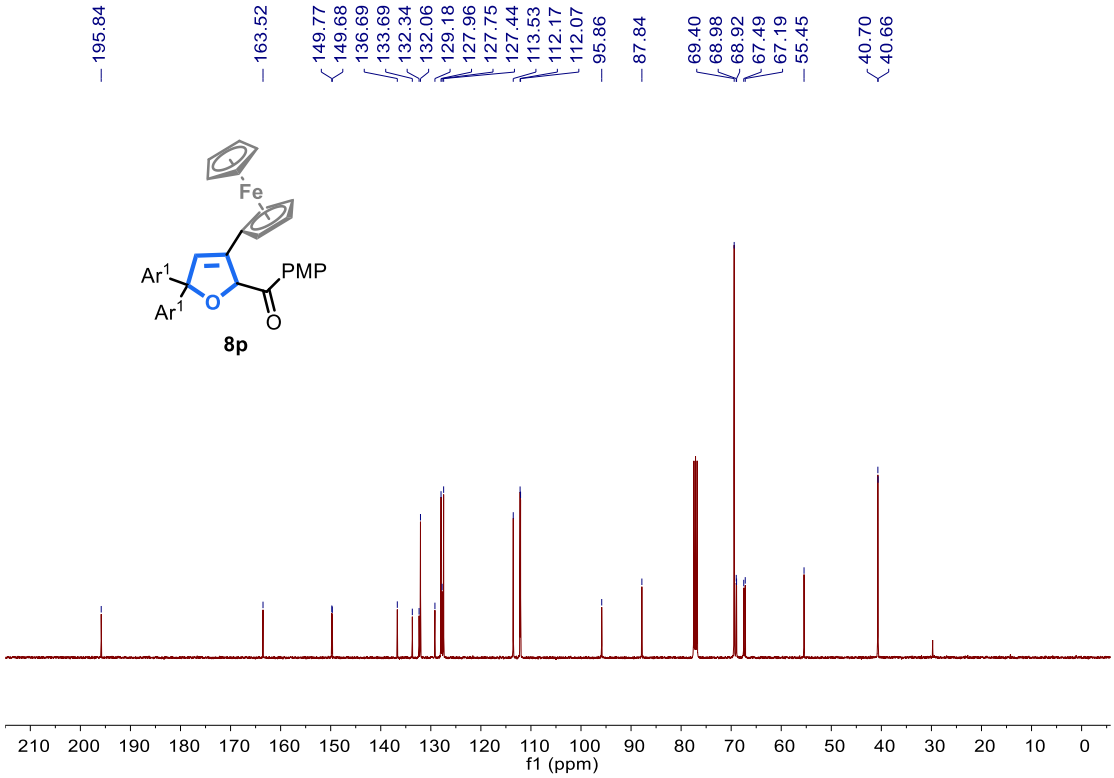
^{1}H NMR Spectrum of Compound **8o** (400MHz, CDCl3)



^{13}C NMR Spectrum of Compound **8o** (100MHz, CDCl3)



^{1}H NMR Spectrum of Compound **8p** (400MHz, CDCl3)



^{13}C NMR Spectrum of Compound **8p** (100MHz, CDCl3)