

Visible-light-induced synthesis of bibenzofuranones *via* a cerium-mediated energy transfer process

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I. General Method

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out under argon atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. ^1H and ^{13}C NMR spectra were taken on Bruker AV400 and Agilent INOVA 600 with TMS as an internal standard and CDCl_3 as solvent. ^{19}F NMR was recorded on Bruker Avance Neo 600 and Jeol Jnm-Ecs 400M. HRMS analyses were made by Lanzhou University by means of ESI. Melting points were measured using a micro melting point apparatus and are uncorrected. FT-IR spectra were recorded on an IR Tracer-100 spectrometer. The UV-Vis absorption experiments were conducted using SHIMADZU UV-2600.

II. Optimization of the Reaction Conditions

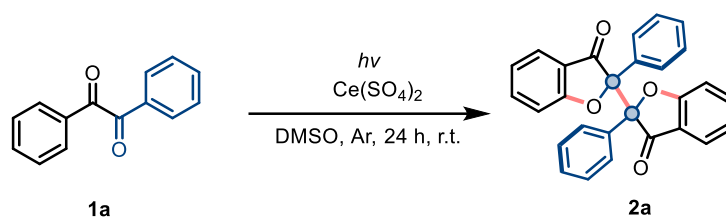
Table S1. Screening of oxidants^{a,b}

Entry	Oxidant	Yield (%) ^b
1	—	14
2 ^c	—	n.p.
3 ^{cd}	DMSO	15
4 ^e	O_2	14
5	TBHP	12
6	PIDA	28
7	m-CPBA	24
8	4-picoline-N-oxide	20
9	4-cyanopyridine-N-oxide	n.p.
10	NaIO_4	34
11	$\text{K}_2\text{S}_2\text{O}_8$	26
12	$\text{Ce}(\text{SO}_4)_2$	76
13	CAN	42
14	CeO_2	34
15	CeCl_3	40
16	$\text{Ce}(\text{SO}_4)_2$ (0.05 mmol)	64
17	$\text{Ce}(\text{SO}_4)_2$ (0.15 mmol)	74

^a Reaction conditions: benzil (0.1 mmol), DMSO (1.0 mL), oxidant (0.1 mmol), and H_2O (60 μL) were irradiated with 380 nm light for 24 h under argon atmosphere at room temperature. ^b Yields were determined by ^1H NMR with nitromethane as internal standard. ^c CH_3CN (1 mL), Ar. ^d

DMSO (0.5 mmol, 5.0 equiv.). ^e O₂ atmosphere. TBHP, *tert*-butyl hydroperoxide; PIDA, phenyliodine diacetate; *m*-CPBA, 3-chloroperoxybenzoic acid; CAN, ammonium ceric sulfate.

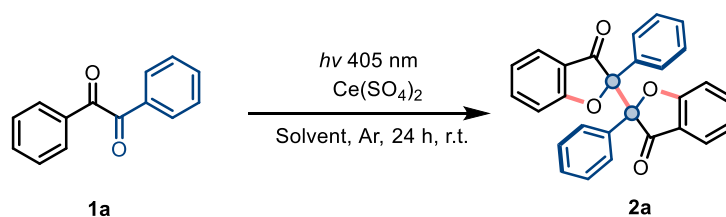
Table S2. Screening of the light sources^{a,b}



Entry	Light source	Yield (%) ^b
1	380 nm	76
2	405 nm	90 (82)
3	425 nm	62
4	465 nm	50

^a Reaction conditions: benzil (0.1 mmol), DMSO (1.0 mL), Ce(SO₄)₂ (0.1 mmol), and H₂O (60 μL) were irradiated with light for 24 h under argon atmosphere at room temperature. ^b Yields were determined by ¹H NMR with nitromethane as internal standard. Isolated yield in brackets.

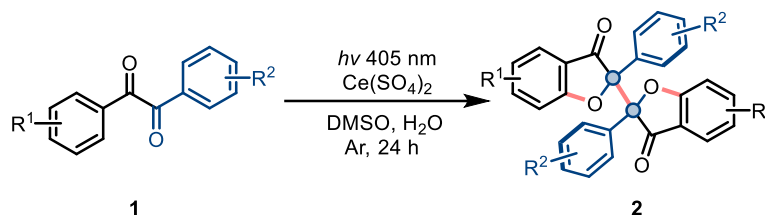
Table S3. Screening of the solvents^{a,b}



Entry	Solvent	Yield (%) ^b
1	DMSO	90 (82)
2	acetone	74
3	methanol	48
4	isopropyl alcohol	80
5	CH ₃ CN	70
6	EtOAc	48
7 ^c	DMSO	80

^a Reaction conditions: benzil (0.1 mmol), solvent (1.0 mL), Ce(SO₄)₂ (0.1 mmol), and H₂O (60 μL) were irradiated with 405 nm light for 24 h under argon atmosphere at room temperature. ^b Yields were determined by ¹H NMR with nitromethane as internal standard. ^c Without H₂O.

III. General Experimental Procedure



To a 20 mL dry glass tube with stirring bar were added **1** (0.1 mmol, 1.0 equiv.), $\text{Ce}(\text{SO}_4)_2$ (33.2 mg, 0.1 mmol, 1.0 equiv.), H_2O (60 μL), and DMSO (1 mL). The resulting mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon. The mixture was then stirred at room temperature and irradiated with 405 nm light for 24 h. After reaction, it was filtered with celite, and extracted with ethyl acetate (3 \times 5 mL). The combined organic phases were washed with brine (10 mL), and then dried over anhydrous Na_2SO_4 . The organic layers were concentrated in vacuo, and the crude product was purified by preparative TLC on silica gel to afford the product. SemiLEDs blue LEDs (405 nm, 3W \times 2).

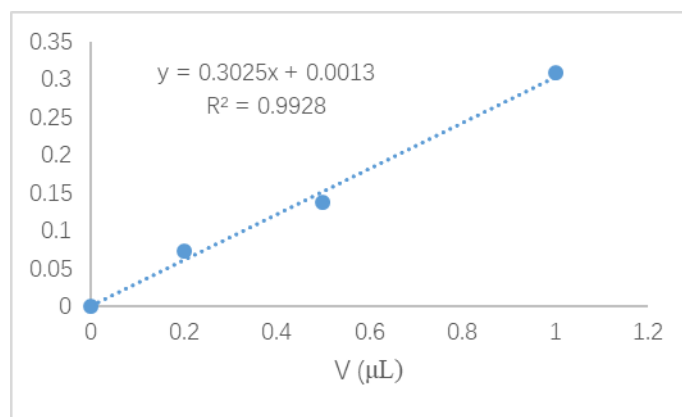


Figure S1. Photochemical reaction setup

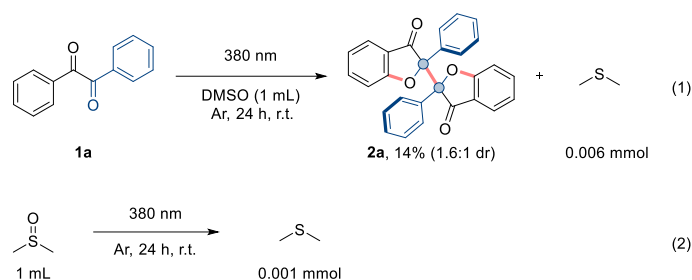
IV. Investigating the Role of DMSO under Oxidant-Free Conditions.

Under oxidant-free conditions, we attempted to use CH_3CN as the reaction solvent, and no product **2a** was found. However, when 5 equivalents of DMSO were added to the reaction system with CH_3CN as the solvent, product **2a** was obtained with 15% yield. Please see Supporting Information Table S1.

In addition, gas chromatography-mass spectrometry (GC-MS) analysis confirmed the formation of dimethyl sulfide in the reaction described in entry 1 of Table 1 (Equation 1). To further quantify the amount of dimethyl sulfide produced, gas chromatography (GC) was conducted. Furthermore, to exclude the possibility of DMSO undergoing self-reduction under light exposure, a blank control experiment (reaction 2) was designed and performed.



The standard curve is represented by the equation $y = 0.3025x + 0.0013$, with $R^2 = 0.9928$. The variable x denotes the volume of dimethyl sulfide (μL), whereas y represents the ratio of the peak area of dimethyl sulfide to that of diphenylmethane, which is used as the internal standard.



GC analysis confirmed the formation of 0.46 μL (0.006 mmol) of dimethyl sulfide under the conditions specified in entry 1 of Table 1 (reaction 1), whereas only 0.07 μL (0.001 mmol) was detected in the corresponding blank control experiment (reaction 2). These experimental results demonstrated that DMSO acts as an oxidant under the specified reaction conditions in entry 1 of Table 1.

V. X-Ray Crystallographic Data for 2p-1

The chloroform solution of **2p-1** was slowly evaporated at room temperature to give crystals. X-ray crystal structures of **2p-1** were determined at 293 K. Crystal structure information has been deposited at the Cambridge Crystallographic Data Centre, CCDC: 2068626.

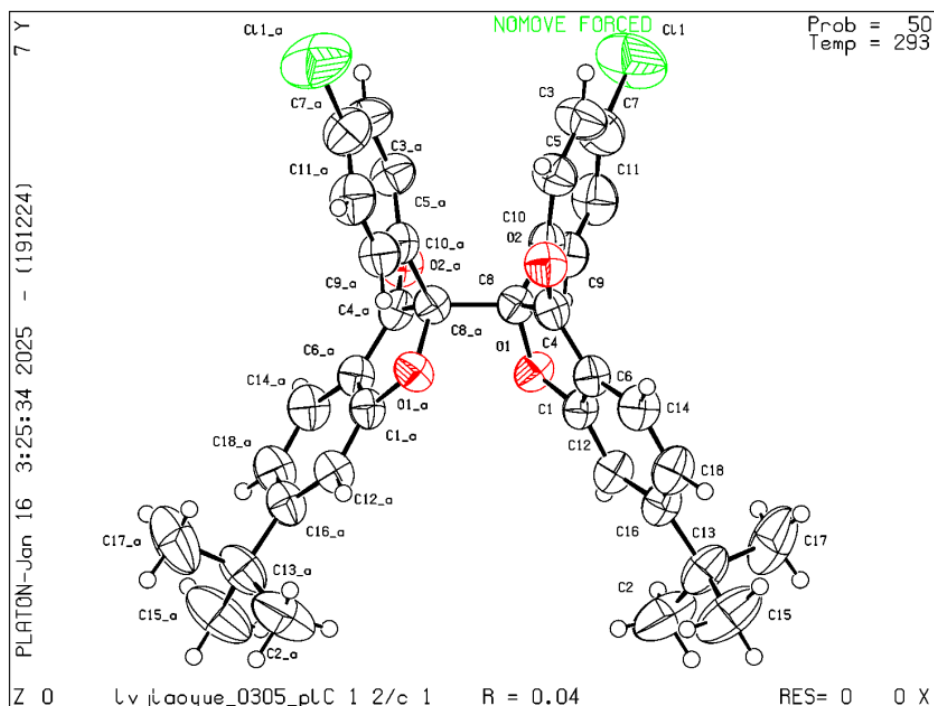


Figure S2. Crystal structure of compound **2p-1**

Table S4. X-ray crystallographic data of **2p-1**

Bond precision:	C-C = 0.0025 Å	Wavelength=1.54184
Cell:	a = 20.4876(3) b = 12.8985(4) c = 12.1074(2)	
	alpha = 90 beta = 102.608(1) gamma = 90	
Temperature:	293 K	
	Calculated	Reported
Volume	3122.34 (12)	3122.34 (12)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C ₃₆ H ₃₂ Cl ₂ O ₄	C ₃₆ H ₃₂ Cl ₂ O ₄
Sum formula	C ₃₆ H ₃₂ Cl ₂ O ₄	C ₃₆ H ₃₂ Cl ₂ O ₄
Mr	599.52	599.51
Dx, g cm ⁻³	1.275	1.275
Z	4	4
Mu (mm ⁻¹)	2.172	2.172
F000	1256.0	1256.0
F000'	1262.20	
h, k, lmax	25,16,15	25,16,14
Nref	3253	3093
Tmin, Tmax	0.925,0.957	0.588,1.000
Tmin'	0.897	
Correction method = # Reported T Limits:	Tmin = 0.588	
Tmax = 1.000 AbsCorr = MULTI-SCAN		
Data completeness = 0.951	Theta(max) = 75.615	
R(reflections) = 0.0421 (2597)	wR2(reflections) = 0.1250 (3093)	

Thermal ellipsoids are shown at 50% probability.

Table S5. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2p-1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	$U(\text{eq})$
C11	794.2(5)	9514.4(6)	-681.9(7)	137.8(4)
O1	402.0(5)	5039.8(8)	1775.0(8)	51.1(3)
O2	1005.2(5)	6582.0(9)	4209.7(9)	61.1(3)
C1	946.6(7)	4506.5(11)	2363.5(11)	48.3(3)
C2	1533.2(15)	1523.6(19)	1471(2)	114.5(10)
C3	744.4(12)	8681.9(16)	1339.6(19)	82.5(6)
C4	905.6(7)	5934.7(12)	3467.9(11)	49.0(3)
C5	647.4(9)	7877.4(13)	2043.9(15)	65.3(4)
C6	1254.7(7)	4978.7(12)	3367.1(11)	50.2(3)
C7	689.5(11)	8494.8(17)	205.7(18)	82.2(6)
C8	353.8(7)	6006.1(11)	2362.1(11)	47.4(3)
C9	446.9(8)	6725.3(14)	463.9(13)	61.9(4)
C10	487.4(7)	6892.1(12)	1612.7(12)	51.7(3)
C11	550.4(10)	7522.0(17)	-235.4(16)	77.2(5)
C12	1173.5(7)	3598.2(12)	1988.8(12)	54.4(4)
C13	2054.6(10)	2192.7(16)	2211.3(15)	74.4(5)
C14	1821.9(8)	4523.8(14)	4039.0(13)	60.9(4)
C15	2466.3(16)	1546(2)	3171(2)	114.7(10)
C16	1745.7(8)	3144.2(14)	2646.4(13)	58.6(4)
C17	2524.3(14)	2615(3)	1486(2)	122.2(10)
C18	2058.6(8)	3625.0(15)	3671.0(14)	66.1(4)

Table S6. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2p-1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U11	U22	U33	U23	U13	U12
C11	206.9(9)	110.9(5)	109.0(5)	40.6(4)	63.5(5)	-19.6(5)
O1	48.1(5)	56.6(6)	43.1(5)	-5.4(4)	-2.3(4)	7.2(4)
O2	59.8(6)	71.4(7)	48.2(6)	-11.4(5)	3.5(5)	-6.8(5)
C1	42.3(7)	59.4(8)	41.0(7)	4.8(6)	4.3(5)	3.7(6)
C2	125(2)	87.9(16)	116(2)	-27.6(14)	-4.4(16)	41.4(14)
C3	104.4(15)	64.6(11)	81.9(13)	5.2(9)	27.9(11)	-12.4(10)
C4	43.8(7)	61.2(8)	40.3(7)	-0.5(6)	5.2(5)	-7.0(6)
C5	75.7(11)	65.0(10)	56.5(9)	0.0(7)	17.5(8)	-7.2(8)
C6	45.2(7)	61.3(8)	41.4(7)	2.2(6)	3.6(6)	-0.8(6)
C7	95.2(14)	83.5(13)	74.2(12)	18.8(10)	32.1(11)	-3.6(11)
C8	45.1(7)	52.8(8)	41.6(7)	-3.5(6)	3.5(5)	0.5(6)
C9	64.1(9)	73.5(10)	49.8(8)	0.1(7)	15.9(7)	1.4(8)

C10	46.5(7)	61.8(8)	46.5(7)	1.8(6)	9.6(6)	1.4(6)
C11	85.1(12)	97.5(14)	53.6(9)	10.0(9)	25.2(9)	0.5(11)
C12	54.3(8)	65.9(9)	41.0(7)	0.9(6)	5.9(6)	8.7(7)
C13	78.8(11)	88.6(12)	53.7(9)	5.2(9)	9.6(8)	35.7(10)
C14	54.8(8)	75.6(10)	45.5(7)	2.7(7)	-4.1(6)	2.6(7)
C15	150(2)	118(2)	68.8(13)	12.0(12)	9.8(14)	76.8(18)
C16	56.3(8)	72.3(10)	46.7(8)	8.7(7)	10.5(6)	14.1(7)
C17	113.7(19)	169(3)	98.6(17)	17.4(18)	54.4(16)	59.9(19)
C18	55.9(9)	85.1(11)	51.6(8)	7.3(8)	-1.1(7)	15.8(8)

Table S7. Bond Lengths for **2p-1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C11	C7	1.741(2)	C6	C14	1.394(2)
O1	C1	1.3707(16)	C7	C11	1.369(3)
O1	C8	1.4489(16)	C8	C81	1.557(3)
O2	C4	1.2106(17)	C8	C10	1.521(2)
C1	C6	1.382(2)	C9	C10	1.392(2)
C1	C12	1.374(2)	C9	C11	1.377(3)
C2	C13	1.507(3)	C12	C16	1.394(2)
C3	C5	1.385(2)	C13	C15	1.526(3)
C3	C7	1.374(3)	C13	C16	1.526(2)
C4	C6	1.444(2)	C13	C17	1.537(3)
C4	C8	1.5550(19)	C14	C18	1.368(2)
C5	C10	1.386(2)	C16	C18	1.410(2)

Table S8. Bond Angles for **2p-1**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C8	108.16(10)	C10	C8	C4	111.50(11)
O1	C1	C6	113.54(13)	C10	C8	C81	115.16(10)
O1	C1	C12	123.52(12)	C11	C9	C10	121.03(17)
C12	C1	C6	122.93(13)	C5	C10	C8	121.53(13)
C7	C3	C5	119.49(19)	C5	C10	C9	118.40(15)
O2	C4	C6	130.20(13)	C9	C10	C8	120.06(14)
O2	C4	C8	124.81(13)	C7	C11	C9	119.41(17)
C6	C4	C8	104.97(11)	C1	C12	C16	118.21(14)
C3	C5	C10	120.61(17)	C2	C13	C15	110.0(2)
C1	C6	C4	108.12(12)	C2	C13	C16	111.86(16)
C1	C6	C14	119.34(14)	C2	C13	C17	108.3(2)
C14	C6	C4	132.47(14)	C15	C13	C16	112.27(15)
C3	C7	C11	119.33(17)	C15	C13	C17	108.5(2)
C11	C7	C11	119.65(16)	C16	C13	C17	105.70(18)
C11	C7	C3	121.02(18)	C18	C14	C6	118.43(14)

O1	C8	C4	104.88(11)	C12	C16	C13	120.06(14)
O1	C8	C81	105.75(8)	C12	C16	C18	118.81(15)
O1	C8	C10	108.26(11)	C18	C16	C13	120.95(14)
C4	C8	C81	110.57(14)	C14	C18	C16	122.27(14)

Table S9. Torsion Angles for **2p-1**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C11	C7	C11	C9	-177.94(15)	C5	C3	C7	C11	178.63(17)
O1	C1	C6	C4	-1.71(17)	C5	C3	C7	C11	-1.0(3)
O1	C1	C6	C14	-179.00(13)	C6	C1	C12	C16	-0.9(2)
O1	C1	C12	C16	178.03(14)	C6	C4	C8	O1	4.74(14)
O1	C8	C10	C5	-163.00(13)	C6	C4	C8	C8 ¹	118.31(9)
O1	C8	C10	C9	17.34(17)	C6	C4	C8	C10	-112.20(13)
O2	C4	C6	C1	179.69(15)	C6	C14	C18	C16	-0.5(3)
O2	C4	C6	C14	-3.5(3)	C7	C3	C5	C10	-0.9(3)
O2	C4	C8	O1	-176.84(13)	C8	O1	C1	C6	4.97(16)
O2	C4	C8	C8 ¹	-63.28(15)	C8	O1	C1	C12	-174.07(13)
O2	C4	C8	C10	66.21(18)	C8	C4	C6	C1	-2.01(15)
C1	O1	C8	C4	-5.80(14)	C8	C4	C6	C14	174.77(16)
C1	O1	C8	C8 ¹	-122.72(13)	C8 ¹	C8	C10	C5	78.92(19)
C1	O1	C8	C10	113.35(12)	C8 ¹	C8	C10	C9	-100.75(16)
C1	C6	C14	C18	0.7(2)	C10	C9	C11	C7	-0.6(3)
C1	C12	C16	C13	-174.19(15)	C11	C9	C10	C5	-1.2(2)
C1	C12	C16	C18	1.0(2)	C11	C9	C10	C8	178.45(15)
C2	C13	C16	C12	-31.6(3)	C12	C1	C6	C4	177.33(13)
C2	C13	C16	C18	153.3(2)	C12	C1	C6	C14	0.0(2)
C3	C5	C10	C8	-177.74(16)	C12	C16	C18	C14	-0.3(3)
C3	C5	C10	C9	1.9(3)	C13	C16	C18	C14	174.86(17)
C3	C7	C11	C9	1.7(3)	C15	C13	C16	C12	-155.8(2)
C4	C6	C14	C18	-175.81(16)	C15	C13	C16	C18	29.1(3)
C4	C8	C10	C5	-48.12(19)	C17	C13	C16	C12	86.1(2)
C4	C8	C10	C9	132.21(14)	C17	C13	C16	C18	-89.1(2)

Table S10. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2p-1**

Atom	x	y	z	U(eq)
H2A	1334.14	1897.35	795.4	172
H2B	1194.11	1344.23	1873.21	172
H2C	1739.37	903.02	1271.58	172
H3	845.79	9343.7	1631.68	99
H5	690.06	7999.45	2813.37	78
H9	348.56	6065.47	163.91	74
H11	525.86	7400.43	-1000.48	93

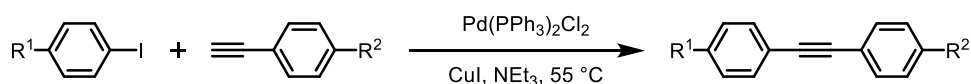
Atom	x	y	z	U(eq)
H12	951.46	3294.24	1314.55	65
H14	2034.3	4824.15	4721.29	73
H15A	2189.25	1337.06	3676.54	172
H15B	2834.1	1951.3	3576.59	172
H15C	2634.47	941.59	2861.97	172
H17A	2881.65	2996.6	1957.72	183
H17B	2278.38	3064.21	910.93	183
H17C	2706.42	2047.9	1137.15	183
H18	2438.98	3320.73	4112.02	79

VI. Preparation and Characterization of Starting Materials

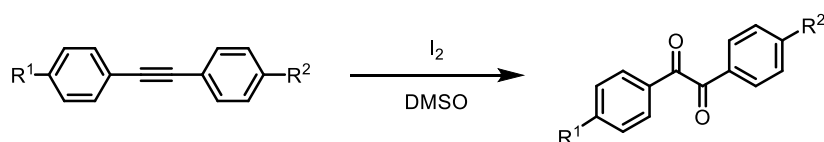
i. The preparation of the starting materials



Symmetric substrate synthesis:¹ bromocumene (20.0 mmol, 2.0 equiv.), acetylenedicarboxylic acid (1.14 g, 10.0 mmol, 1.0 equiv.), Pd(PPh₃)₂Cl₂ (426.8 mg, 1 mmol, 0.1 equiv.), 1,4-bis(diphenylphosphanyl)butane (350.9 mg, 0.5 mmol, 0.05 equiv.), 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepine (3.0 mL, 20 mmol, 1.0 equiv.) and DMSO (50 mL) were added into the flask under argon atmosphere, and then reacted in an oil bath at 80 °C for 3 h. The reaction was monitored by TLC. After the reaction was completed, water and ethyl acetate (3 × 35 mL) were added for extraction, the organic phases were mixed and then washed with brine, dried with anhydrous Na₂SO₄, and concentrated to remove the solvent. Purification was performed by silica gel chromatography using petroleum ether as the eluent.



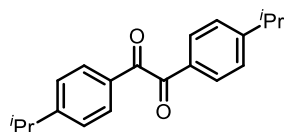
Asymmetric substrate synthesis: iodobenzene (10.0 mmol, 1.0 equiv.), phenylacetylene (11.0 mmol, 1.1 equiv.), Pd(PPh₃)₂Cl₂ (70.2 mg, 0.1 mmol, 0.01 equiv.), CuI (380 mg, 2.0 mmol, 0.2 equiv.) and triethylamine (50 mL) were added into the flask, and then stirred for 24 h in an oil bath at 55 °C under argon atmosphere. The reaction was monitored by TLC. After the reaction was completed, water and ethyl acetate (3 × 35 mL) were added for extraction, the organic phases were mixed, washed with brine, dried over anhydrous Na₂SO₄, and concentrated to remove the solvent. Purification was performed by silica gel chromatography using petroleum ether as the eluent.



Synthesis of diketone compounds:² alkynes (3 mmol, 1.0 equiv.), I₂ (1.5 g, 6 mmol, 2.0 equiv.), and DMSO (50 mL) were added to the flask and then stirred and refluxed for 3 h. The reaction was monitored by TLC. After the reaction was completed, water and ethyl acetate (3 × 35 mL) were added for extraction. The organic phases were mixed, washed with brine, dried over

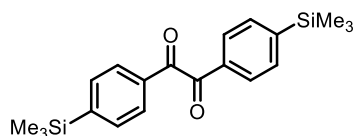
anhydrous Na₂SO₄, and concentrated to remove the solvent. Purification by silica gel chromatography (petroleum ether: ethyl acetate = 16:1).

ii. Characterization data of starting materials



1,2-Bis(4-isopropylphenyl)ethane-1,2-dione (**1c**). Yellow solid.

¹H NMR (600 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 2.98 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.7, 156.8, 131.1, 130.3, 127.3, 34.6, 23.7. ¹H and ¹³C NMR data agreed with literature.³

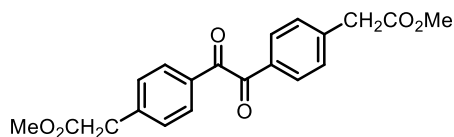


1,2-Bis(4-(trimethylsilyl)phenyl)ethane-1,2-dione (**1e**). Yellow solid. M.p. 74-76 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 8.1 Hz, 4H), 7.66 (d, *J* = 7.8 Hz, 4H), 0.29 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.2, 150.0, 134.0, 133.1, 128.8, -1.3.

IR (KBr, ν / cm⁻¹): 3449, 2956, 1674, 1593, 1388, 1250, 1214, 1179, 841, 749, 677.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₂₀H₂₇O₂Si₂]⁺: 355.1176, found: 355.1178.

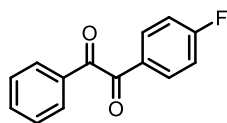


Dimethyl 2,2'-(oxalylbis(4,1-phenylene))diacetate (**1f**). Yellow solid. M.p. 57-59 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.91 (m, 4H), 7.43 (d, *J* = 8.4 Hz, 4H), 3.71 (s, 4H), 3.70 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.1, 171.0, 141.5, 131.9, 130.4, 130.2, 52.5, 41.4.

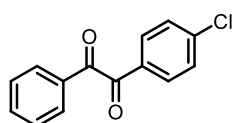
IR (KBr, ν / cm⁻¹): 2953, 1737, 1672, 1605, 1572, 1435, 1418, 1171, 1009, 886, 725, 578.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₂₀H₁₉O₆]⁺: 355.1544, found: 355.1545.



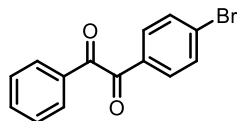
1-(4-Fluorophenyl)-2-phenylethane-1,2-dione (**1g**). Yellow solid.

¹H NMR (600 MHz, CDCl₃) δ 8.03 – 7.98 (m, 2H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.2, 192.8, 166.8 (d, *J* = 258.3 Hz), 135.1, 132.9, 132.8 (d, *J* = 9.9 Hz), 130.0, 129.6 (d, *J* = 2.9 Hz), 129.1, 116.5 (d, *J* = 22.2 Hz). **⁹F NMR** (565 MHz, CDCl₃) δ -101.16 – -101.22 (m). ¹H and ¹³C NMR data agreed with literature.⁴



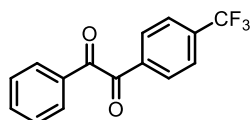
1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (**1h**). Yellow solid.

¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.46 (m, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ 194.0, 193.2, 141.7, 135.2, 133.0, 131.6, 131.4, 130.1, 129.6, 129.2. ¹H and ¹³C NMR data agreed with literature.⁵



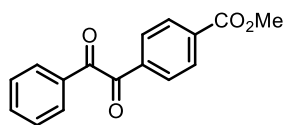
1-(4-Bromophenyl)-2-phenylethane-1,2-dione (**1i**). Yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.94 (m, 2H), 7.87 – 7.81 (m, 2H), 7.66 (d, *J* = 7.3 Hz, 3H), 7.52 (t, *J* = 7.7 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.0, 193.4, 135.2, 132.9, 132.6, 131.8, 131.4, 130.6, 130.1, 129.2. ¹H and ¹³C NMR data agreed with literature.⁵



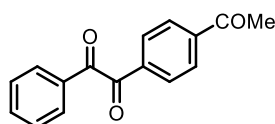
1-Phenyl-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (**1j**). Yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.2 Hz, 2H), 8.01 – 7.95 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.66 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 193.5, 193.0, 135.8 (d, *J* = 32.9 Hz), 135.6, 135.2, 132.6, 130.2, 130.0, 129.2, 126.0 (d, *J* = 3.7 Hz), 123.3 (q, *J* = 273.1 Hz). **¹⁹F NMR** (565 MHz, CDCl₃) δ -63.4. ¹H and ¹³C NMR data agreed with literature.⁶



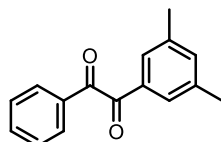
Methyl 4-(2-oxo-2-phenylacetyl)benzoate (**1k**). Yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.19 – 8.14 (m, 2H), 8.07 – 8.02 (m, 2H), 8.01 – 7.95 (m, 2H), 7.68 (tt, *J* = 7.0, 1.3 Hz, 1H), 7.58 – 7.50 (m, 2H), 3.96 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.0, 193.8, 166.1, 136.2, 135.5, 135.3, 132.8, 130.3, 130.1, 129.9, 129.3, 52.8. ¹H and ¹³C NMR data agreed with literature.⁷



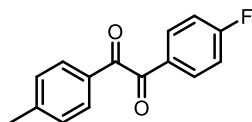
1-(4-Acetylphenyl)-2-phenylethane-1,2-dione (**1l**). Pale yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 4H), 8.00 – 7.94 (m, 2H), 7.72 – 7.64 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 2.66 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 197.4, 193.9, 193.8, 141.4, 136.1, 135.4, 132.7, 130.3, 130.1, 129.3, 128.9, 27.2. ¹H and ¹³C NMR data agreed with literature.⁵



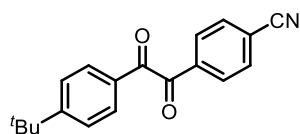
1-(3,5-Dimethylphenyl)-2-phenylethane-1,2-dione (**1m**). Pale yellow oil.

¹H NMR (600 MHz, CDCl₃) δ 7.97 – 7.92 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (s, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 195.2, 194.9, 138.9, 136.8, 134.9, 133.1, 130.0, 129.1, 127.6, 21.2. ¹H and ¹³C NMR data agreed with literature.⁸



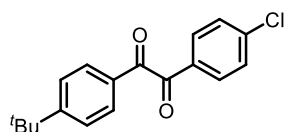
1-(4-Fluorophenyl)-2-(*p*-tolyl)ethane-1,2-dione (**1n**). Yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 – 7.98 (m, 2H), 7.86 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 8.6$ Hz, 2H), 2.44 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.0, 193.1, 166.8 (d, $J = 258.1$ Hz), 146.6, 132.9 (d, $J = 9.8$ Hz), 130.5, 130.2, 129.9, 129.7 (d, $J = 2.9$ Hz), 116.5 (d, $J = 22.1$ Hz), 22.1. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -97.4 – -106.8 (m). ^1H and ^{13}C NMR data agreed with literature.⁷



4-(2-(4-(*Tert*-butyl)phenyl)-2-oxoacetyl)benzonitrile (**1o**). Yellow solid.

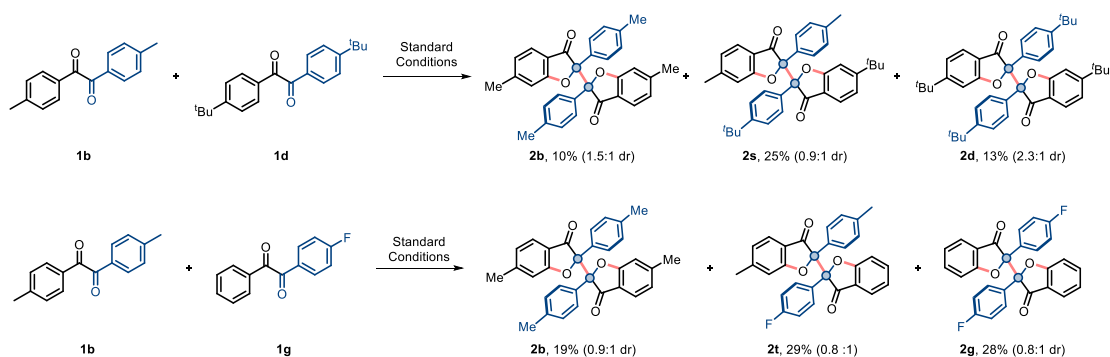
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.5$ Hz, 2H), 7.90 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.55 (d, $J = 8.6$ Hz, 2H), 1.34 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 192.8, 192.7, 159.8, 136.2, 132.8, 130.3, 130.2, 130.1, 126.4, 117.9, 117.7, 35.6, 31.1, 31.0. ^1H and ^{13}C NMR data agreed with literature.⁹



1-(4-(*Tert*-butyl)phenyl)-2-(4-chlorophenyl)ethane-1,2-dione (**1p**). Yellow solid.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.91 (dd, $J = 12.0, 8.1$ Hz, 4H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H), 1.34 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 193.7, 193.4, 159.4, 141.6, 131.7, 131.3, 130.5, 130.1, 129.5, 126.2, 35.6, 31.1. ^1H and ^{13}C NMR data agreed with literature.⁸

VII. Cross-coupling reaction of two different benzil derivatives

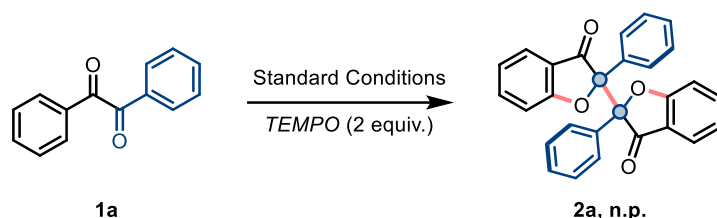


To a 20 mL dry glass tube with a stir bar were added **1b** (23.8 mg, 0.1 mmol, 1.0 equiv.), **1d** (32.2 mg, 0.1 mmol, 1.0 equiv.) or **1g** (22.8 mg, 0.1 mmol, 1.0 equiv.), $\text{Ce}(\text{SO}_4)_2$ (66.4 mg, 0.2 mmol, 2.0 equiv.), H_2O (60 μL), and DMSO (1 mL). The reaction mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon. Then mixture was then stirred

at room temperature and irradiated with 405 nm light for 24 h. After the reaction, the mixture was then filtered with celite, and extracted with ethyl acetate (3×5 mL). The combined organic phases were washed with brine (10 mL) and then dried over anhydrous Na₂SO₄. The organic layers were concentrated in vacuo, and the crude product was purified by preparative TLC on silica gel to afford the product (Petroleum ether/ethyl acetate = 8:1, then use CHCl₃ as eluent for separation). The dr value was determined based on the isolated yields. When **1b** and **1d** were used as substrates, products **2b**, **2s**, and **2d** were obtained with a total yield of 48%, in a ratio of 1:2.5:1.3. **2b-1** 1.5 mg, 6%; **2b-2** 1.0 mg, 4%; **2s-1** 3.3 mg, 12%; **2s-2** 3.5 mg, 13%; **2d-1** 3.2 mg, 9%; **2d-2** 1.4 mg, 4%. Similarly, using **1b** and **1g** as substrates resulted in the formation of **2b**, **2t**, and **2g** with a total yield of 76%, in a ratio of 1:1.5:1.5. **2b-1** 2.1 mg, 9%; **2b-2** 2.4 mg, 10%; **2t-1** 3.0 mg, 13%; **2t-2** 3.7 mg, 16%; **2g-1** 2.8 mg, 12%; **2g-2** 3.6 mg, 16%.

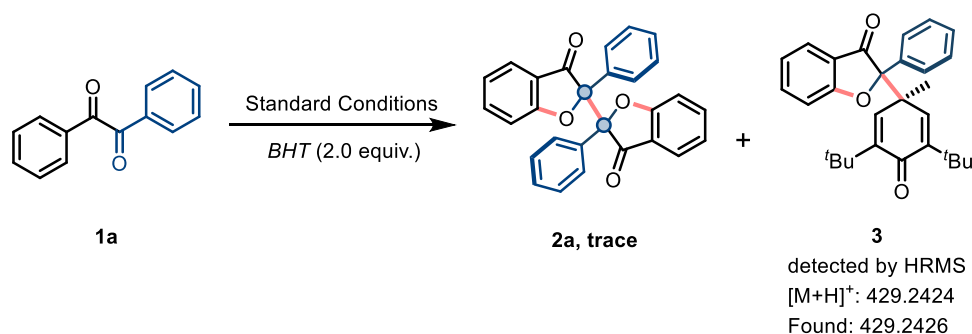
VIII. Investigation of the Mechanism

i. TEMPO was used as radical scavenger



To a 20 mL dry glass tube with a stir bar were added benzil (21.0 mg, 0.1 mmol, 1.0 equiv.), Ce(SO₄)₂ (33.2 mg, 0.1 mmol, 1.0 equiv.), 2,2,6,6-tetramethyl-1-piperidinyloxy (31.2 mg, 0.2 mmol, 2.0 equiv.), H₂O (60 μL), and DMSO (1 mL). The reaction mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon. Then mixture was then stirred at room temperature and irradiated with 405 nm light for 24 h. After the reaction, the mixture was then filtered with celite, and extracted with ethyl acetate (3×5 mL). The combined organic phases were washed with brine (10 mL) and then dried over anhydrous Na₂SO₄. The desired product **2a** was not observed, as determined by ¹H NMR analysis.

ii. BHT was used as radical scavenger



To a 20 mL dry glass tube with a stir bar were added benzil (21.0 mg, 0.1 mmol, 1.0 equiv.), Ce(SO₄)₂ (33.2 mg, 0.1 mmol, 1.0 equiv.), 2,6-di-*tert*-butyl-4-methylphenol (44.0 mg, 0.2 mmol, 2.0 equiv.), H₂O (60 μL), and DMSO (1 mL). The reaction mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon. The mixture was then stirred at room temperature and irradiated with 405 nm light for 24 h. After the reaction, it was filtered with celite and extracted with ethyl acetate (3×5 mL). The combined organic phases were washed with

brine (10 mL), and then dried over anhydrous Na_2SO_4 . Only trace amounts **2a** were observed on the ^1H NMR spectrum.

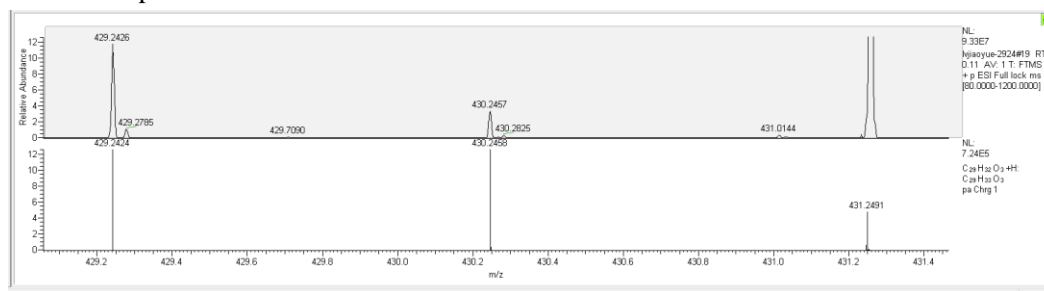


Figure S3. HRMS of reaction intermediates captured by TEMPO

iii. Investigate the role of $\text{Ce}(\text{SO}_4)_2$ in the reaction

Preparation of the mixture of cerium sulfate and benzil: benzil (210 mg, 1 mmol, 1.0 equiv.) and $\text{Ce}(\text{SO}_4)_2$ (332 mg, 1 mmol, 1.0 equiv.), and acetonitrile (10 mL) were stirred at room temperature for 2 h in the dark. Then the solvent was removed under vacuum.

The Raman spectrum was measured using HORIBA LaRAM HR Evolution with a 532 nm laser.¹⁰

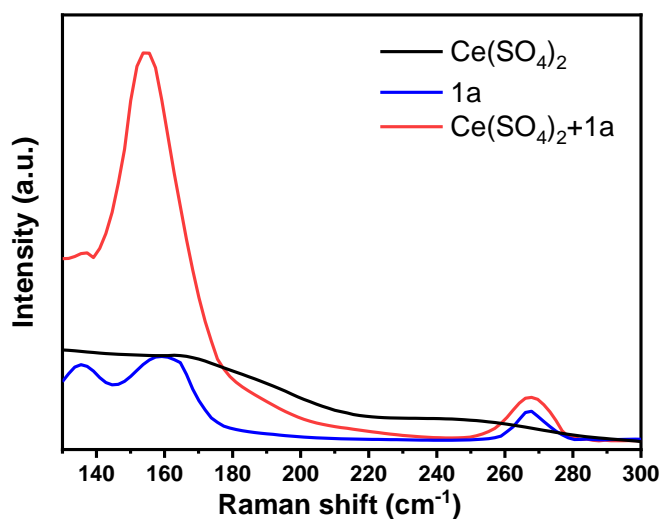


Figure S4. Raman spectrum of **1a**, $\text{Ce}(\text{SO}_4)_2$ and the mixture

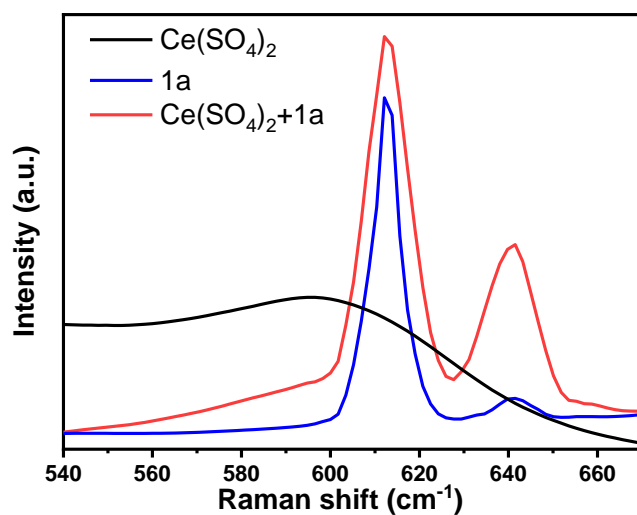


Figure S5. Raman spectrum of **1a**, Ce(SO₄)₂ and the mixture

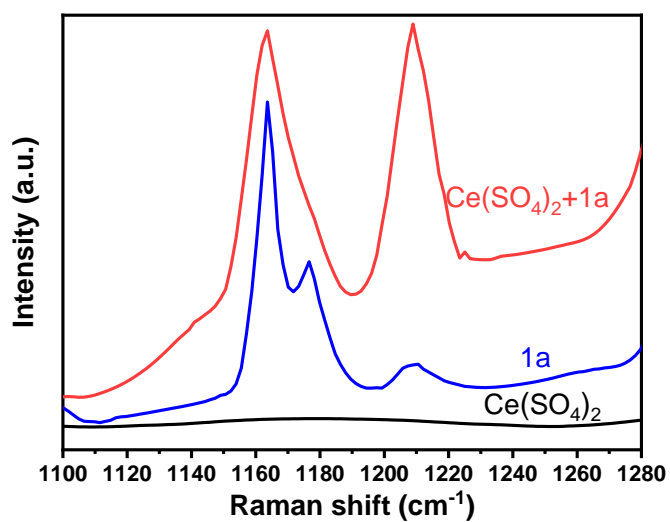


Figure S6. Raman spectrum of **1a**, Ce(SO₄)₂ and the mixture

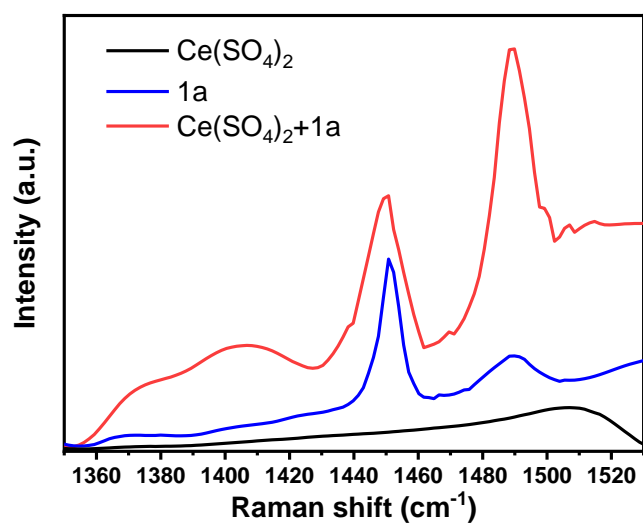


Figure S7. Raman spectrum of **1a**, $\text{Ce}(\text{SO}_4)_2$ and the mixture

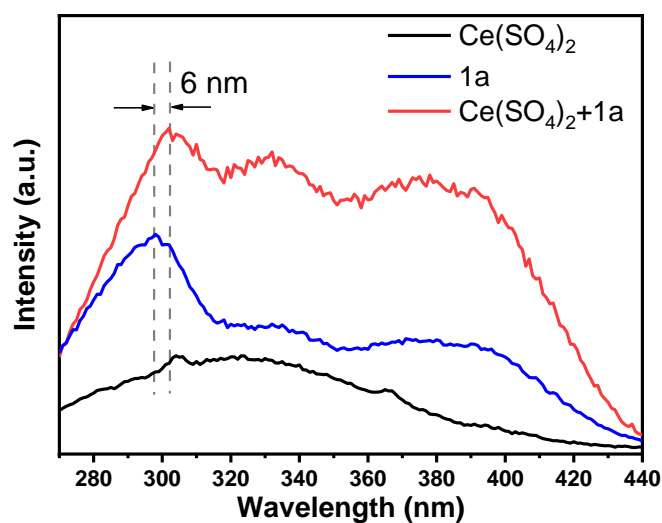


Figure S8. Excitation spectrum of **1a**, $\text{Ce}(\text{SO}_4)_2$ and the mixture

The excitation spectrum was measured using HORIBA Fluorolog TCSPC at a fixed emission wavelength of 488 nm with a 1nm slit. The excitation wavelength of **1a** red-shifted with the addition of $\text{Ce}(\text{SO}_4)_2$, and the energy decreased.

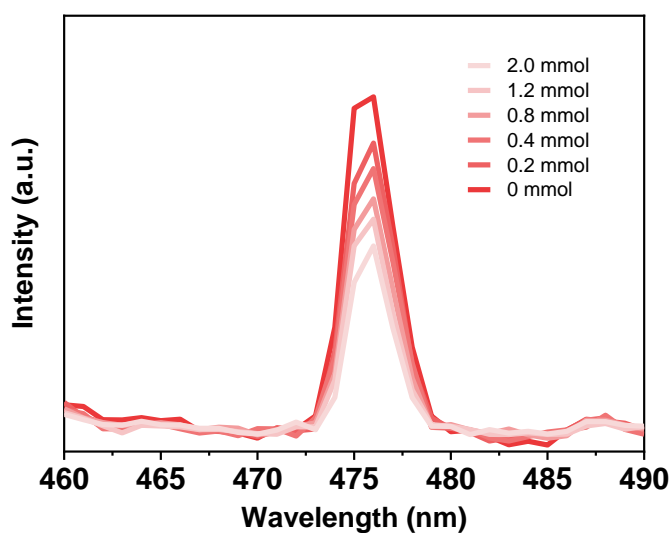


Figure S9. Quenching of the $\text{Ce}(\text{SO}_4)_2$ in the presence of **1a**

Fluorescence quenching experiments were performed using a HORIBA Instruments Incorporated spectrofluorometer. The excitation wavelength was fixed at 350 nm and the emission intensity was collected at 488 nm. Sample preparation: $\text{Ce}(\text{SO}_4)_2$ (1 mmol) and different amounts of **1a** (0.2, 0.4, 0.8, 1.2, and 2 mmol) were added to 10 mL of acetonitrile and stirred at room temperature for 2 h in the dark. The solvent was removed under vacuum, and the resulting solid mixture was tested for fluorescence.

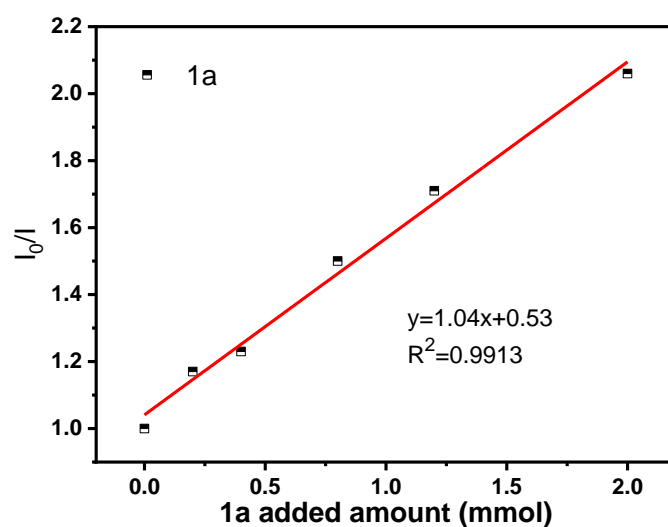


Figure S10. Stern-Volmer quenching plot

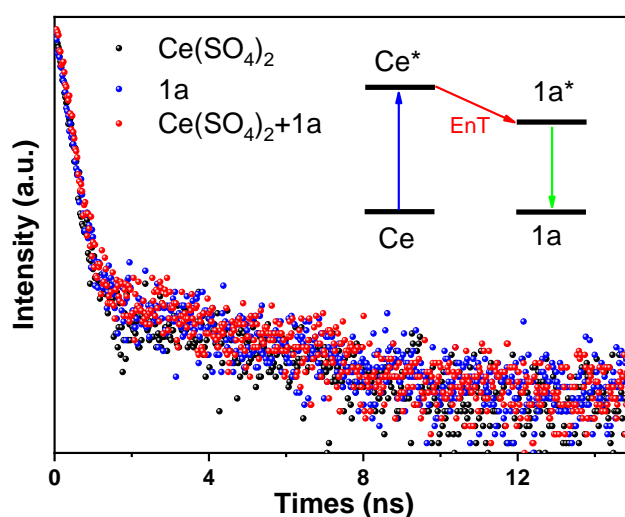


Figure S11. Fluorescence lifetime experiments of benzil, $\text{Ce}(\text{SO}_4)_2$ and the mixture

The data were fitted according to the following equation, where τ is the fluorescence lifetime. The results are shown in the table below:

$$Y = A \cdot \exp(-t/\tau) + Y_0$$

Table S11. Fluorescence lifetime fitting

	A	τ	Y_0
$\text{Ce}(\text{SO}_4)_2$	2071.44019	0.68747	16.04004
Benzil	2003.93199	0.69443	19.21576
the mixture	2187.39667	0.70916	18.3161

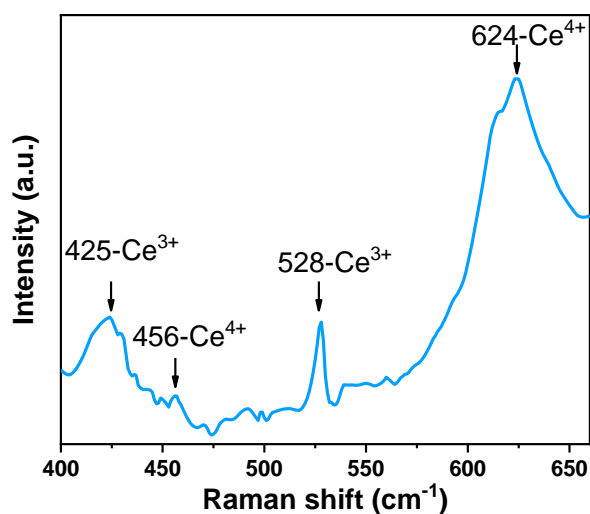


Figure S12. Raman spectrum of solid sample after reaction

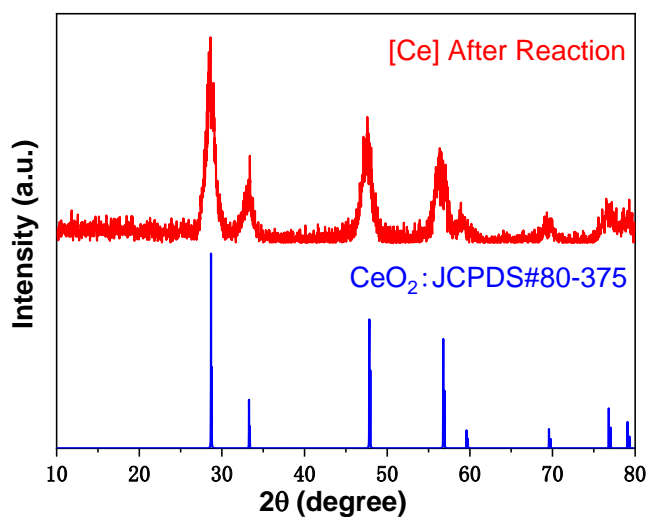


Figure S13. XRD of the solid sample after the reaction

XRD was tested on a Rigaku MiNiFlex600 using Cu K α rays ($\lambda = 0.1542$) from 10-80° at 40 kV. Sample preparation: After the reaction, the solid was isolated by centrifugation, then washed with water and oven dried.

XPS was tested on SHIMADZU Axis Supra. The XPS spectra demonstrate that the peak at 907.55 eV belongs to Ce³⁺,¹¹ confirming the presence of Ce³⁺ after the reaction.

Sample preparation for XPS: After the reaction, the solid was separated by centrifugation, washed with water and dried in a vacuum drying oven for 2 h, and then sent for testing under argon.

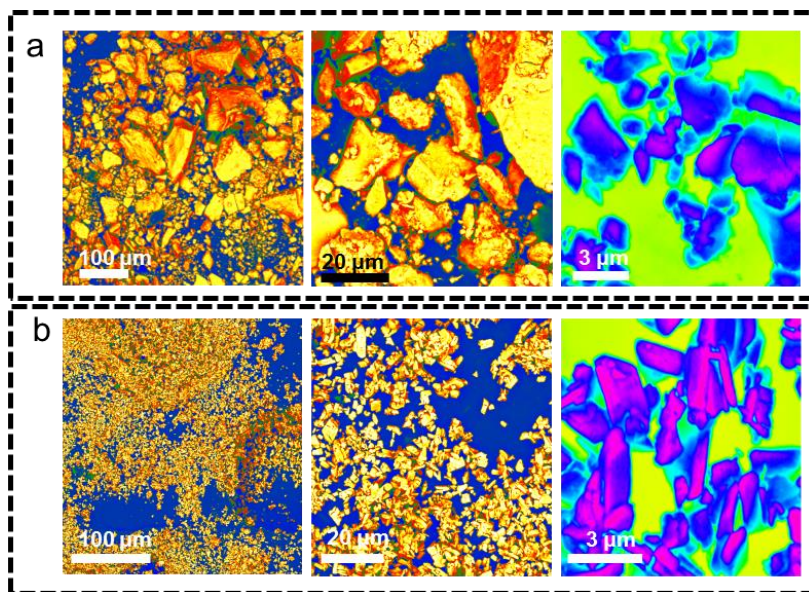
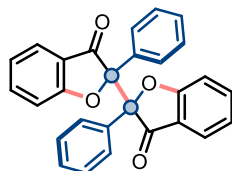


Figure S14. SEM of cerium sulfate before reaction (a) and solid samples after reaction (b)

SEM was tested on Phenom desktop scanning electron microscope. It is obvious that the particle size of cerium becomes smaller and more uniform in the SEM images before and after the reaction.

IX. Characterization Data for Products

2, 2'-Diphenyl-[2,2'-bibenzofuran]-3,3'(2*H*, 2'*H*)-dione (2a).



White solid, 17.1 mg, 82%. Eluent (Petroleum ether/ethyl acetate = 8:1). M.p. = 184 – 185 °C.

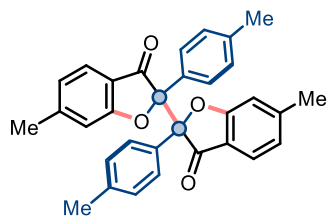
¹H NMR (600 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.58 – 7.52 (m, 5H), 7.50 – 7.48 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.22 (m, 4H), 7.13 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.06 – 6.99 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.7, 196.4, 171.2, 170.9, 138.1, 138.0, 131.3, 131.0, 129.0, 128.1, 128.0, 127.4, 127.3, 124.9, 124.7, 122.4, 122.3, 121.7, 121.3, 113.3, 112.9, 90.6, 90.0.

IR (KBr, *v* / cm⁻¹): 3070, 2562, 1720, 1611, 1463, 1198, 999, 760, 706.

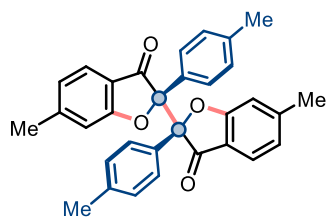
HRMS (ESI) *m/z*: [M+H]⁺calcd for [C₂₈H₁₉O₄]⁺: 419.1278, found: 419.1278.

6,6'-Dimethyl-2,2'-di-*p*-tolyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2b).



White solid, 14.1 mg, 60%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-6,6'-dimethyl-2,2'-di-*p*-tolyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2b-1).**



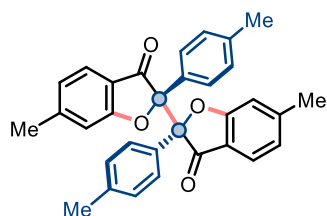
White solid. M.p. = 262 – 263 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 4H), 7.05 (d, *J* = 8.1 Hz, 4H), 6.83 (d, *J* = 7.5 Hz, 4H), 2.37 (s, 6H), 2.32 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.3, 171.8, 149.9, 138.6, 128.6, 128.0, 127.9, 124.5, 123.7, 119.0, 113.1, 90.3, 22.7, 21.3. ¹H and ¹³C NMR data have been reported in literature.¹²

IR (KBr, ν / cm⁻¹): 2918, 1717, 1617, 1327, 1142, 1026, 812, 514.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₂H₂₇O₄]⁺: 475.1904, found: 475.1904.

***Trans*-6,6'-dimethyl-2,2'-di-*p*-tolyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2b-2).**



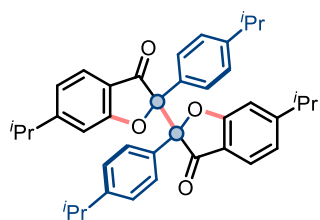
White solid. M.p. = 246 – 247 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.90 (s, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 6H), 2.30 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 195.8, 171.4, 149.8, 138.7, 128.8, 128.1, 128.0, 124.4, 123.8, 119.5, 113.3, 91.3, 22.7, 21.3. ¹H and ¹³C NMR data have been reported in literature.¹²

IR (KBr, ν / cm⁻¹): 2917, 1721, 1617, 1452, 1327, 1023, 812, 793, 755.

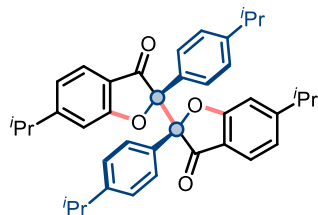
HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₂H₂₇O₄]⁺: 475.1904, found: 475.1904.

6,6'-Diisopropyl-2,2'-bis(4-isopropylphenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2c).



White solid, 19.5 mg, 67%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-6,6'-diisopropyl-2,2'-bis(4-isopropylphenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2c-1).**



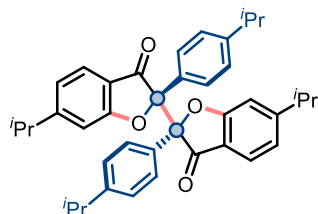
White solid, M.p. = 100 – 102 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 4H), 7.08 (d, *J* = 8.5 Hz, 4H), 6.90 – 6.82 (m, 4H), 2.88 (dp, *J* = 10.4, 6.9 Hz, 4H), 1.23 – 1.19 (m, 24H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.4, 172.0, 160.7, 149.5, 129.0, 128.1, 125.2, 124.6, 121.4, 119.5, 110.3, 90.5, 35.1, 33.9, 24.1, 24.0, 23.6, 23.6.

IR (KBr, *v* / cm⁻¹): 2961, 1720, 1618, 1437, 1119, 939, 825, 736.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₄₀H₄₃O₄]⁺: 587.3156, found: 587.3154.

***Trans*-6,6'-diisopropyl-2,2'-bis(4-isopropylphenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2c-2).**



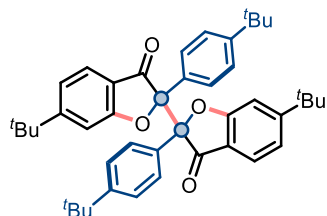
White solid, M.p. = 222 – 224 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 8.3, 2.4 Hz, 6H), 7.07 (d, *J* = 8.4 Hz, 4H), 6.97 (s, 2H), 6.85 (dd, *J* = 8.0, 1.3 Hz, 2H), 2.87 (dp, *J* = 24.6, 6.9 Hz, 4H), 1.23 (dd, *J* = 6.9, 3.5 Hz, 12H), 1.18 (dd, *J* = 6.9, 1.4 Hz, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.0, 171.6, 160.6, 149.5, 129.1, 128.1, 125.4, 124.4, 121.5, 119.8, 110.7, 91.2, 35.1, 33.9, 24.0, 23.6.

IR (KBr, *v* / cm⁻¹): 2960, 2925, 1721, 1617, 1509, 1436, 1326, 1117, 1005, 803, 768, 457.

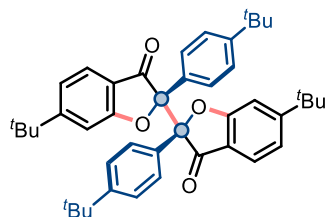
HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₄₀H₄₃O₄]⁺: 587.3156, found: 587.3154.

6,6'-Di-*tert*-butyl-2,2'-bis(4-(*tert*-butyl)phenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2d).



White solid, 17.6 mg, 55%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-6,6'-di-*tert*-butyl-2,2'-bis(4-(*tert*-butyl)phenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2d-1).**



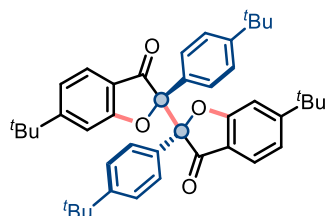
White solid, M.p. = 310 – 311 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.25 – 7.22 (m, 4H), 7.07 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.00 (d, *J* = 1.4 Hz, 2H), 1.27 (d, *J* = 4.1 Hz, 36H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.5, 172.0, 163.0, 151.7, 128.7, 127.7, 124.1, 124.1, 120.2, 119.0, 109.5, 90.4, 36.0, 34.6, 31.4, 31.1.

IR (KBr, *v* / cm⁻¹): 2963, 2869, 1723, 1619, 1597, 1428, 1273, 1197, 934, 825, 713, 558.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₄₄H₅₁O₄]⁺: 643.3782, found: 643.3779.

***Trans*-6,6'-di-*tert*-butyl-2,2'-bis(4-(*tert*-butyl)phenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2d-2).**



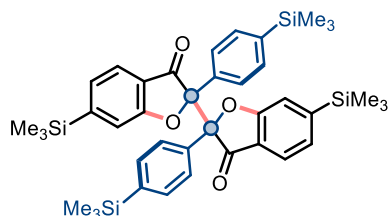
White solid, M.p. = 280 – 282 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.6 Hz, 4H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 4H), 7.13 (d, *J* = 1.5 Hz, 2H), 7.02 (dd, *J* = 8.2, 1.5 Hz, 2H), 1.29 (s, 18H), 1.25 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.2, 171.6, 162.9, 151.7, 128.8, 127.8, 124.2, 124.0, 120.3, 119.3, 109.9, 91.2, 36.0, 34.6, 31.4, 31.1.

IR (KBr, *v* / cm⁻¹): 2960, 2924, 2869, 1726, 1618, 1597, 1427, 1266, 1027, 934, 826, 713, 557.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₄₄H₅₁O₄]⁺: 643.3782, found: 643.3781.

6,6'-Bis(trimethylsilyl)-2,2'-bis(4-(trimethylsilyl)phenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2e).



White solid, 30.2 mg, 86%. Eluent (Petroleum ether/ethyl acetate = 64:1).

M.p. = 129 – 130 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.51 (dd, *J* = 15.3, 7.6 Hz, 2H), 7.46 (t, *J* = 8.6 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.24 – 7.10 (m, 4H), 0.25 – 0.18 (m, 36H). **¹³C NMR** (101 MHz, CDCl₃) δ 197.0,

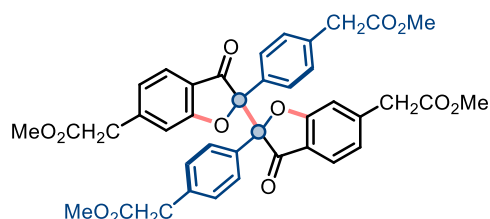
196.5, 170.8, 170.3, 154.2, 154.0, 141.3, 141.2, 132.4, 132.2, 131.9, 127.3, 127.3, 126.9, 126.8, 123.7, 123.6, 121.8, 121.5, 117.8, 117.5, 91.0, 89.9, -1.0, -1.3.

IR (KBr, ν / cm^{-1}): 2955, 2360, 1727, 1609, 1584, 1402, 1316, 1249, 1113, 840, 727.

HRMS (ESI) m/z : $[M+H]^+$ calcd for $[\text{C}_{40}\text{H}_{51}\text{O}_4\text{Si}_4]^+$: 707.2859, found: 707.2859.

Dimethyl

2,2'-((6,6'-bis(2-methoxy-2-oxoethyl)-3,3'-dioxo-[2,2'-bibenzofuran]-2,2'(3*H*,3'*H*)-diyl)bis(4,1-phenylene))diacetate (2f).



White solid, 27.2 mg, 77%. Eluent (Petroleum ether/ethyl acetate = 1:1).

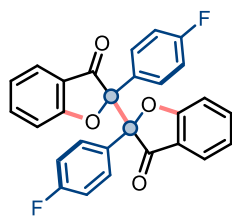
M.p. = 79 – 80 °C.

¹H NMR (400 MHz, CDCl_3) δ 7.53 (t, $J = 8.0$ Hz, 2H), 7.41 (dd, $J = 8.4, 1.8$ Hz, 4H), 7.15 (dd, $J = 8.3, 5.9$ Hz, 4H), 7.05 (s, 1H), 6.98 – 6.94 (m, 3H), 3.69 (d, $J = 7.5$ Hz, 6H), 3.65 (d, $J = 2.7$ Hz, 10H), 3.60 (d, $J = 2.9$ Hz, 4H). **¹³C NMR** (101 MHz, CDCl_3) δ 196.0, 195.5, 171.9, 171.4, 171.0, 170.8, 170.7, 145.0, 144.9, 134.9, 134.9, 130.0, 129.9, 128.4, 128.3, 128.2, 124.9, 124.8, 124.0, 123.9, 120.6, 120.2, 114.0, 113.8, 91.2, 90.1, 52.5, 52.5, 52.2, 41.8, 41.7, 41.0, 41.0.

IR (KBr, ν / cm^{-1}): 2953, 2848, 1735, 1618, 1599, 1439, 1328, 1262, 1143, 1011, 735.

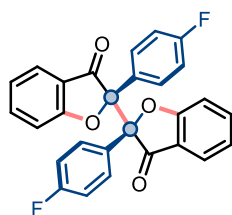
HRMS (ESI) m/z : $[M+H]^+$ calcd for $[\text{C}_{40}\text{H}_{35}\text{O}_{12}]^+$: 707.2123, found: 707.2123.

2,2'-Bis(4-fluorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2g).



White solid, 13.8 mg, 61%. Eluent (Petroleum ether/ethyl acetate = 8:1).

Cis-2,2'-bis(4-fluorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2g-1).



White solid. The melting point of this compound is above 300 °C, which cannot be measured by a micro melting point meter.

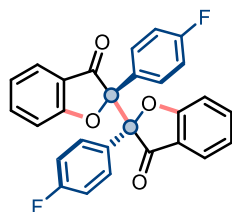
¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.55 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.09 – 7.04 (m, 2H), 7.01 – 6.92 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.5, 171.1, 163.4 (d, *J* = 248.7 Hz), 138.3, 130.0 (d, *J* = 8.4 Hz), 126.7 (d, *J* = 3.0 Hz), 125.0, 122.6, 121.2, 114.4 (d, *J* = 21.5 Hz), 112.9, 89.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.4.

IR (KBr, *v* / cm⁻¹): 2919, 2850, 1722, 1611, 1506, 1463, 1299, 1230, 1163, 1018, 755, 515.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₂₈H₁₇F₂O₄]⁺: 455.1089, found: 455.1089.

***Trans*-2,2'-bis(4-fluorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2g-2).**



White solid, M.p. = 210 – 211 °C.

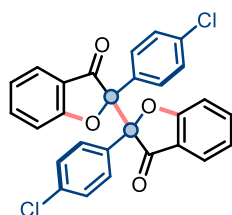
¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.51 (m, 8H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 2H), 6.94 (t, *J* = 8.8 Hz, 4H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.2, 170.8, 163.3 (d, *J* = 249.0 Hz), 138.3, 130.0 (d, *J* = 8.4 Hz), 126.9 (d, *J* = 2.8 Hz), 124.8, 122.7, 121.5, 114.5 (d, *J* = 21.6 Hz), 113.3, 90.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.4.

IR (KBr, *v* / cm⁻¹): 2922, 2851, 1722, 1611, 1507, 1476, 1300, 1232, 1015, 756, 516.

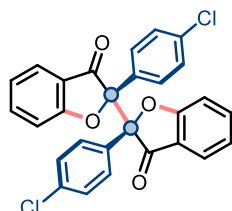
HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₂₈H₁₇F₂O₄]⁺: 455.1089, found: 455.1089.

2,2'-Bis(4-chlorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2h).



White solid, 12.5 mg, 52%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-2,2'-bis(4-chlorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2h-1).**



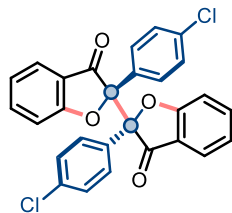
White solid, M.p. = 186 – 187 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 7.7 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 4H), 7.24 (d, *J* = 8.8 Hz, 4H), 7.07 (t, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.2, 171.1, 138.4, 135.5, 129.5, 129.4, 127.6, 125.0, 122.7, 121.1, 112.9, 89.3.

IR (KBr, ν / cm^{-1}): 2921, 2851, 1722, 1612, 1464, 1298, 1093, 1017, 901, 796, 753, 604, 469.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{28}\text{H}_{17}\text{Cl}_2\text{O}_4]^+$: 487.0498, found: 487.0500.

***Trans*-2,2'-bis(4-chlorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2h-2).**



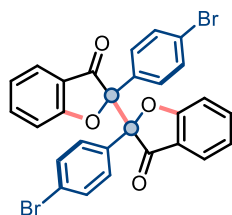
White solid, M.p. = 221– 222 °C.

¹H NMR (400 MHz, CDCl_3) δ 7.61 – 7.56 (m, 4H), 7.47 (d, $J = 8.7$ Hz, 4H), 7.24 (d, $J = 8.7$ Hz, 4H), 7.11 (d, $J = 8.7$ Hz, 2H), 7.05 (t, $J = 7.4$ Hz, 2H). **¹³C NMR** (101 MHz, CDCl_3) δ 195.9, 170.8, 138.4, 135.5, 129.6, 129.4, 127.8, 124.9, 122.8, 121.4, 113.3, 90.0.

IR (KBr, ν / cm^{-1}): 2922, 2851, 1722, 1611, 1401, 1299, 1095, 1014, 753, 461.

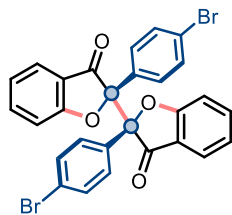
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{28}\text{H}_{17}\text{Cl}_2\text{O}_4]^+$: 487.0498, found: 487.0498.

2,2'-Bis(4-bromophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2i).



White solid, 17.5 mg, 61%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-2,2'-bis(4-bromophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2i-1).**



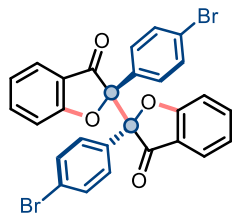
White solid, M.p. = 197– 198 °C.

¹H NMR (600 MHz, CDCl_3) δ 7.62 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 4H), 7.35 (d, $J = 8.6$ Hz, 4H), 7.07 (t, $J = 7.4$ Hz, 2H), 7.00 (d, $J = 8.4$ Hz, 2H). **¹³C NMR** (151 MHz, CDCl_3) δ 196.2, 171.1, 138.4, 130.6, 130.0, 129.8, 125.0, 124.0, 122.7, 121.1, 113.0, 89.3.

IR (KBr, ν / cm^{-1}): 2920, 2851, 1722, 1611, 1463, 1298, 1013, 901, 754, 514.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{28}\text{H}_{17}\text{Br}_2\text{O}_4]^+$: 576.9468, found: 576.9468.

***Trans*-2,2'-bis(4-bromophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2i-2).**



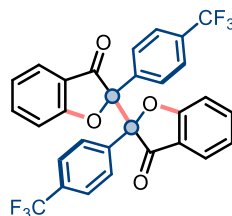
White solid, M.p. = 221– 222 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.58 (d, *J* = 6.8 Hz, 4H), 7.39 (s, 8H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.7, 170.7, 138.3, 130.6, 130.0, 129.6, 124.8, 123.8, 122.7, 121.3, 113.2, 89.9.

IR (KBr, ν / cm⁻¹): 2921, 2851, 1722, 1610, 1463, 1325, 1010, 752, 515.

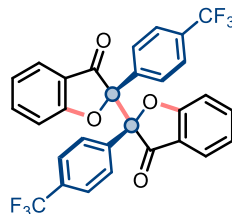
HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₂₈H₁₇Br₂O₄]⁺: 576.9468, found: 576.9468.

2,2'-Bis(4-(trifluoromethyl)phenyl)-[2,2'-bibenzofuran]-3,3'-(2H,2'H)-dione (2j).



White solid, 14.9 mg, 55%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-2,2'-bis(4-(trifluoromethyl)phenyl)-[2,2'-bibenzofuran]-3,3'-(2H,2'H)-dione (2j-1).**



White solid. The melting point of this compound is above 300 °C, which cannot be measured by a micro melting point meter.

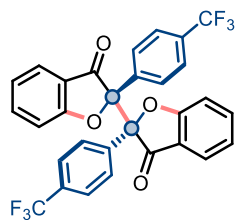
¹H NMR (600 MHz, CDCl₃) δ 7.68 – 7.57 (m, 8H), 7.53 (d, *J* = 8.0 Hz, 4H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 195.8, 171.2, 138.7, 134.8, 131.4 (q, *J* = 32.6 Hz), 128.5, 125.1, 124.4 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz), 122.9, 120.9, 113.0, 89.1.

¹⁹F NMR (565 MHz, CDCl₃) δ -62.7.

IR (KBr, ν / cm⁻¹): 2923, 2851, 1724, 1612, 1463, 1326, 1117, 759, 420.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₀H₁₇F₆O₄]⁺: 555.1026, found: 555.1026.

***Trans*-2,2'-bis(4-(trifluoromethyl)phenyl)-[2,2'-bibenzofuran]-3,3'-(2H,2'H)-dione (2j-2).**



White solid, M.p. = 220– 222 °C.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.67 (d, J = 8.2 Hz, 4H), 7.60 (ddd, J = 10.4, 7.2, 1.6 Hz, 4H), 7.53 (d, J = 8.3 Hz, 4H), 7.14 (d, J = 8.3 Hz, 2H), 7.08 (t, J = 7.4 Hz, 2H).

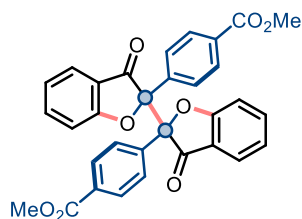
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 195.4, 170.8, 138.6, 134.9, 131.4 (q, J = 32.6 Hz), 128.5, 125.0, 124.5 (q, J = 3.7 Hz), 124.0 (q, J = 273.0, 272.2 Hz), 123.0, 121.3, 113.2, 89.9.

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -62.8.

IR (KBr, ν / cm^{-1}): 2919, 2850, 1724, 1613, 1325, 1118, 1017, 758.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{30}\text{H}_{17}\text{F}_6\text{O}_4]^+$: 555.1026, found: 555.1026.

Dimethyl 4,4'-(3,3'-dioxo-[2,2'-bibenzofuran]-2,2'(3*H*,3'*H*)-diyl)dibenzoate (2k).



White solid, 9.9 mg, 37%. Eluent (Petroleum ether/ethyl acetate = 4:1).

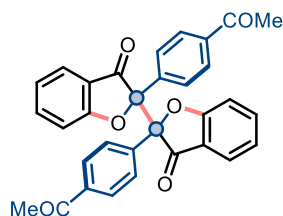
M.p. = 269 – 270 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (d, J = 8.7 Hz, 4H), 7.64 – 7.60 (m, 3H), 7.57 (dd, J = 7.9, 3.5 Hz, 5H), 7.15 (d, J = 8.2 Hz, 1H), 7.10 – 7.03 (m, 3H), 3.91 (s, 3H), 3.90 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 195.8, 195.5, 171.2, 170.9, 166.8, 166.8, 138.5, 138.5, 135.9, 135.8, 130.8, 130.8, 128.7, 128.6, 128.0, 125.0, 124.9, 122.8, 122.8, 121.4, 121.0, 113.3, 113.0, 90.2, 89.5, 52.4.

IR (KBr, ν / cm^{-1}): 2918, 2849, 1724, 1612, 1435, 1280, 1111, 1020, 765, 703.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{32}\text{H}_{23}\text{O}_8]^+$: 535.1387, found: 535.1387.

2,2'-Bis(4-acetylphenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2l).



White solid, 15.3 mg, 61%. Eluent (Petroleum ether/ethyl acetate = 4:1).

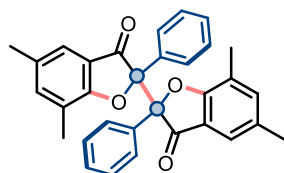
The melting point of this compound is above 300 °C, which cannot be measured by a micro melting point meter.

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.80 (m, 4H), 7.67 – 7.55 (m, 8H), 7.16 – 7.03 (m, 4H), 2.58 (d, *J* = 6.6 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 197.9, 197.9, 195.8, 195.4, 171.2, 170.8, 138.5, 138.5, 137.5, 136.0, 135.8, 128.3, 127.5, 127.3, 125.1, 124.9, 122.9, 122.8, 121.3, 121.0, 113.3, 113.0, 90.3, 89.6, 29.8, 26.9.

IR (KBr, *v* / cm⁻¹): 2918, 2850, 1722, 1686, 1608, 1425, 1198, 958, 736, 544, 468.

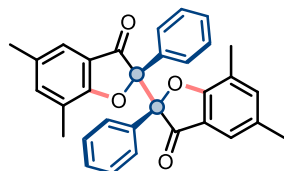
HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₂H₂₃O₆]⁺: 503.1489, found: 503.1488.

5,5',7,7'-Tetramethyl-2,2'-diphenyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2m).



White solid, 12.6 mg, 53%. Eluent (Petroleum ether/ethyl acetate = 8:1).

***Cis*-5,5',7,7'-tetramethyl-2,2'-diphenyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2m-1).**



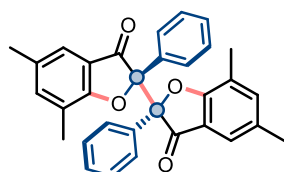
White solid, M.p. = 245 – 248 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 7.9 Hz, 4H), 7.30 (t, *J* = 7.1 Hz, 2H), 7.23 (dd, *J* = 15.6, 8.3 Hz, 6H), 7.16 (s, 2H), 2.27 (s, 6H), 2.04 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 197.2, 168.6, 139.6, 131.6, 131.5, 128.8, 128.0, 127.2, 122.6, 121.3, 121.0, 90.3, 20.8, 13.9.

IR (KBr, *v* / cm⁻¹): 2920, 2850, 1718, 1613, 1491, 1264, 1018, 747.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₂H₂₇O₄]⁺: 475.1904, found: 475.1903.

***Trans*-5,5',7,7'-tetramethyl-2,2'-diphenyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2m-2).**



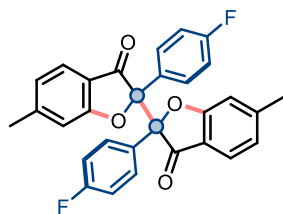
White solid, M.p. = 248 – 250 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.6 (d, *J* = 7.5 Hz, 4H), 7.3 – 7.2 (m, 2H), 7.2 (t, *J* = 7.3 Hz, 4H), 7.1 (d, *J* = 12.9 Hz, 4H), 2.2 (s, 6H), 2.2 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 196.9, 168.2, 139.7, 131.9, 131.7, 128.8, 127.9, 127.3, 127.2, 122.7, 121.1, 90.7, 20.7, 14.2.

IR (KBr, *v* / cm⁻¹): 2921, 2851, 1717, 1613, 1491, 1448, 1264, 1015, 746.

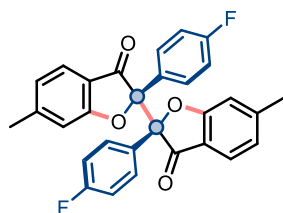
HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₂H₂₇O₄]⁺: 475.1904, found: 475.1904.

2,2'-Bis(4-fluorophenyl)-6,6'-dimethyl-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2n).



White solid, 9.4 mg, 39%. Eluent (Petroleum ether/ethyl acetate = 8:1).

Cis-2,2'-bis(4-fluorophenyl)-6,6'-dimethyl-[2,2'-bibenzofuran]-3,3'(2H,2'H)-dione(2n-1).



White solid. The melting point of this compound is above 300 °C, which cannot be measured by a micro melting point meter.

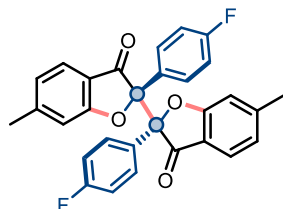
¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.44 (m, 6H), 6.93 (t, *J* = 8.8 Hz, 4H), 6.87 (d, *J* = 7.0 Hz, 4H), 2.39 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.0, 171.7, 163.3 (d, *J* = 248.5 Hz), 150.5, 129.9 (d, *J* = 8.5 Hz), 127.3 (d, *J* = 2.8 Hz), 124.5, 124.2, 118.8, 114.3 (d, *J* = 21.6 Hz), 113.1, 89.5, 22.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.8.

IR (KBr, *v* / cm⁻¹): 2921, 2850, 1719, 1618, 1507, 1204, 1121, 1020, 809, 756, 525.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₀H₂₁F₂O₄]⁺: 483.1402, found: 483.1402.

Trans-2,2'-bis(4-fluorophenyl)-6,6'-dimethyl-[2,2'-bibenzofuran]-3,3'(2H,2'H)-dione(2n-2).



White solid, M.p. = 228 – 229 °C.

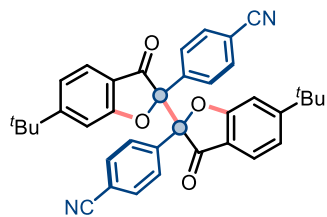
¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.47 (m, 4H), 7.45 (d, *J* = 7.9 Hz, 2H), 6.95 – 6.90 (m, 6H), 6.85 (d, *J* = 7.9 Hz, 2H), 2.39 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.5, 171.3, 163.3 (d, *J* = 248.6 Hz), 150.4, 130.0 (d, *J* = 8.3 Hz), 127.3 (d, *J* = 3.2 Hz), 124.4, 124.2, 119.2, 114.4 (d, *J* = 21.4 Hz), 113.3, 90.4, 22.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.7.

IR (KBr, *v* / cm⁻¹): 2921, 2851, 1720, 1618, 1507, 1230, 1024, 812, 536.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₀H₂₁F₂O₄]⁺: 483.1402, found: 483.1402.

4,4'-(6,6'-Di-tert-butyl-3,3'-dioxo-[2,2'-bibenzofuran]-2,2'(3H,3'H)-diyl)dibenzonitrile (2o).



White solid, 13.7 mg, 47%. Eluent (Petroleum ether/ethyl acetate = 32:1).

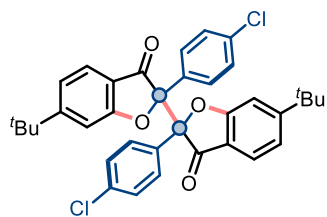
The melting point of this compound is above 300 °C, which cannot be measured by a micro melting point meter.

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.62 (m, 4H), 7.57 – 7.52 (m, 5H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.18 – 7.12 (m, 3H), 7.05 (s, 1H), 1.32 (s, 9H), 1.30 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.8, 194.4, 171.9, 171.4, 164.5, 164.4, 136.4, 131.3, 131.2, 128.7, 128.6, 124.5, 124.3, 121.4, 121.3, 118.6, 118.5, 118.5, 118.2, 113.1, 113.1, 109.9, 109.5, 89.6, 88.8, 36.2, 36.2, 31.1.

IR (KBr, *v* / cm⁻¹): 2963, 2923, 2858, 2230, 1722, 1617, 1426, 1022, 828, 553.

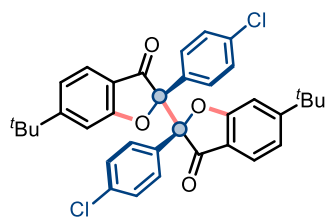
HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₈H₃₃N₂O₄]⁺: 581.2435, found: 581.2435.

6,6'-Di-*tert*-butyl-2,2'-bis(4-chlorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2p).



White solid, 25.8 mg, 86%. Eluent (Petroleum ether/ethyl acetate = 64:1).

***Cis*-6,6'-di-*tert*-butyl-2,2'-bis(4-chlorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2p-1).**



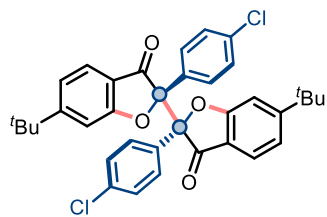
White solid, M.p. = 279 – 280 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 4H), 7.23 (d, *J* = 8.7 Hz, 4H), 7.12 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.00 (s, 2H), 1.29 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.7, 171.8, 163.6, 135.2, 129.9, 129.3, 127.4, 124.2, 120.6, 118.4, 109.4, 89.3, 36.0, 31.0.

IR (KBr, *v* / cm⁻¹): 2957, 2921, 2851, 1722, 1619, 1427, 1017, 823, 730.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for [C₃₆H₃₃Cl₂O₄]⁺: 599.1750, found: 599.1749.

***Trans*-6,6'-di-*tert*-butyl-2,2'-bis(4-chlorophenyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2p-2).**

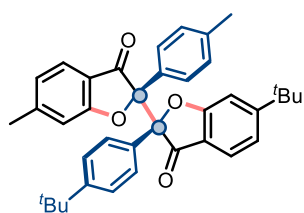


White solid, M.p. = 200 – 202 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, *J* = 13.8, 8.7 Hz, 6H), 7.23 (d, *J* = 8.8 Hz, 4H), 7.12 – 7.09 (m, 4H), 1.30 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.8, 171.9, 163.7, 135.3, 130.0, 129.4, 127.6, 124.3, 120.8, 118.5, 109.5, 89.4, 36.1, 31.1.

IR (KBr, ν / cm⁻¹): 2959, 2920, 2850, 1728, 1596, 1260, 1094, 1021, 800.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₆H₃₃Cl₂O₄]⁺: 599.1750, found: 599.1749.



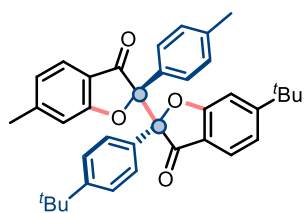
***Cis*-6-(*tert*-butyl)-2-(4-(*tert*-butyl)phenyl)-6'-methyl-2'-(*p*-tolyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2s-1).**

White solid, 3.3 mg, 12%, Eluent (Petroleum ether/ethyl acetate = 8:1), M.p. = 91 – 92 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.09 – 6.99 (m, 4H), 6.83 (d, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.28 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.3, 196.3, 171.8, 171.7, 162.9, 151.6, 149.7, 138.4, 128.6, 128.6, 127.8, 127.8, 127.7, 124.3, 124.0, 124.0, 123.5, 120.1, 119.0, 118.8, 112.9, 109.4, 90.2, 90.2, 35.9, 34.5, 31.3, 31.0, 22.5, 21.2.

IR (KBr, ν / cm⁻¹): 2962, 1721, 1618, 1597, 1428, 1327, 1267, 1199, 1121, 934, 812, 795, 489.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₈H₃₉O₄]⁺: 559.2843, found: 559.2843.



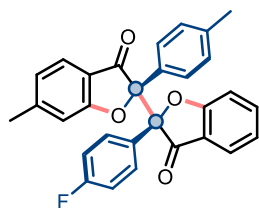
***Trans*-6-(*tert*-butyl)-2-(4-(*tert*-butyl)phenyl)-6'-methyl-2'-(*p*-tolyl)-[2,2'-bibenzofuran]-3,3'(2*H*,2'*H*)-dione (2s-2).**

White solid, 3.5 mg, 13%, Eluent (Petroleum ether/ethyl acetate = 8:1), M.p. = 67 – 68 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.41 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 3H), 6.92 (s, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 1.29 (s, 9H), 1.27 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.8, 195.7, 171.4, 171.2, 162.8, 151.6, 149.6, 138.5, 128.7, 128.5, 127.9, 127.8, 127.7, 124.2, 124.1, 123.9, 123.6, 120.2, 119.4, 119.0, 113.2, 109.7, 91.3, 91.1, 35.9, 34.5, 31.2, 31.0, 22.5, 21.2.

IR (KBr, ν / cm⁻¹): 2961, 2925, 1724, 1618, 1428, 1327, 1276, 1199, 934, 751, 489.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₈H₃₉O₄]⁺: 559.2843, found: 559.2844.



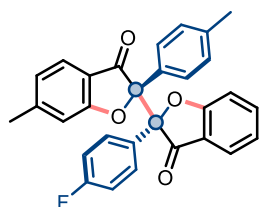
Cis-2'-(4-fluorophenyl)-6-methyl-2-(p-tolyl)-[2,2'-bibenzofuran]-3,3'(2H,2'H)-dione (2t-1).

White solid, 3.0 mg, 13%, Eluent (Petroleum ether/ethyl acetate = 8:1), M.p. = 74 – 75 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.60 (m, 1H), 7.58 – 7.53 (m, 1H), 7.50 – 7.45 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.08 – 7.02 (m, 4H), 6.95 – 6.90 (m, 2H), 6.86 – 6.79 (m, 2H), 2.36 (s, 3H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.6, 196.0, 171.5, 171.1, 163.2 (d, *J* = 247.9 Hz), 150.0, 138.8, 138.0, 129.9 (d, *J* = 8.2 Hz), 128.1, 127.9, 127.8, 127.0 (d, *J* = 3.0 Hz), 124.8, 124.3, 123.8, 122.2, 121.1, 118.8, 114.0 (d, *J* = 21.4 Hz), 112.8, 90.0, 89.6, 22.5, 21.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.0 – -113.2 (m).

IR (KBr, ν / cm⁻¹): 2924, 1721, 1616, 1508, 1463, 1326, 1299, 1231, 1163, 756, 512.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₀H₂₂FO₄]⁺: 465.1497, found: 465.1500.



Trans-2'-(4-fluorophenyl)-6-methyl-2-(p-tolyl)-[2,2'-bibenzofuran]-3,3'(2H,2'H)-dione (2t-2).

White solid, 3.7 mg, 16%, Eluent (Petroleum ether/ethyl acetate = 8:1), M.p. = 174 – 175 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.55 (m, 2H), 7.52 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.97 – 6.90 (m, 3H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.2, 195.5, 171.2, 170.7, 163.1 (d, *J* = 248.3 Hz), 150.0, 138.8, 137.9, 129.9 (d, *J* = 8.4 Hz), 128.2, 128.1, 127.8, 127.1 (d, *J* = 3.2 Hz), 124.6, 124.2, 123.9, 122.3, 121.5, 119.2, 114.2 (d, *J* = 21.5 Hz), 113.2, 113.1, 90.9, 90.3, 22.5, 21.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.9 – -113.0 (m).

IR (KBr, ν / cm⁻¹): 2924, 1722, 1615, 1507, 1463, 1326, 1299, 1230, 796, 755, 511.

HRMS (ESI) m/z: [M+H]⁺ calcd for [C₃₀H₂₂FO₄]⁺: 465.1497, found: 465.1499.

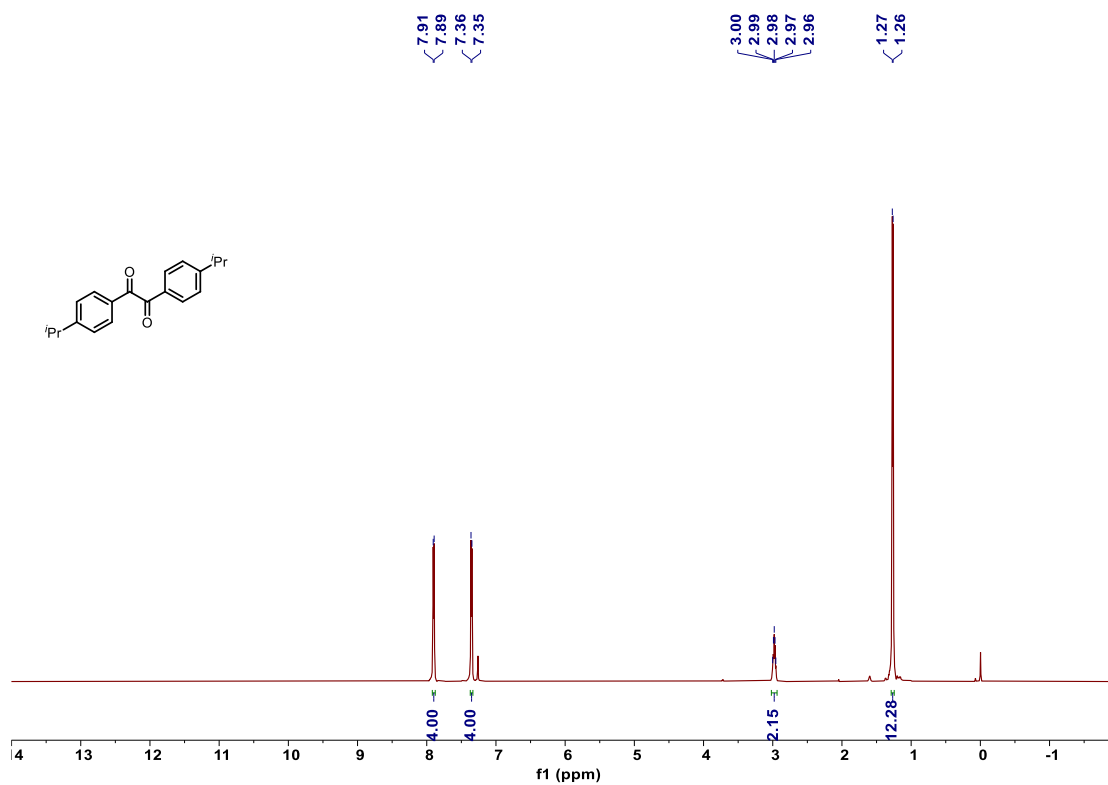
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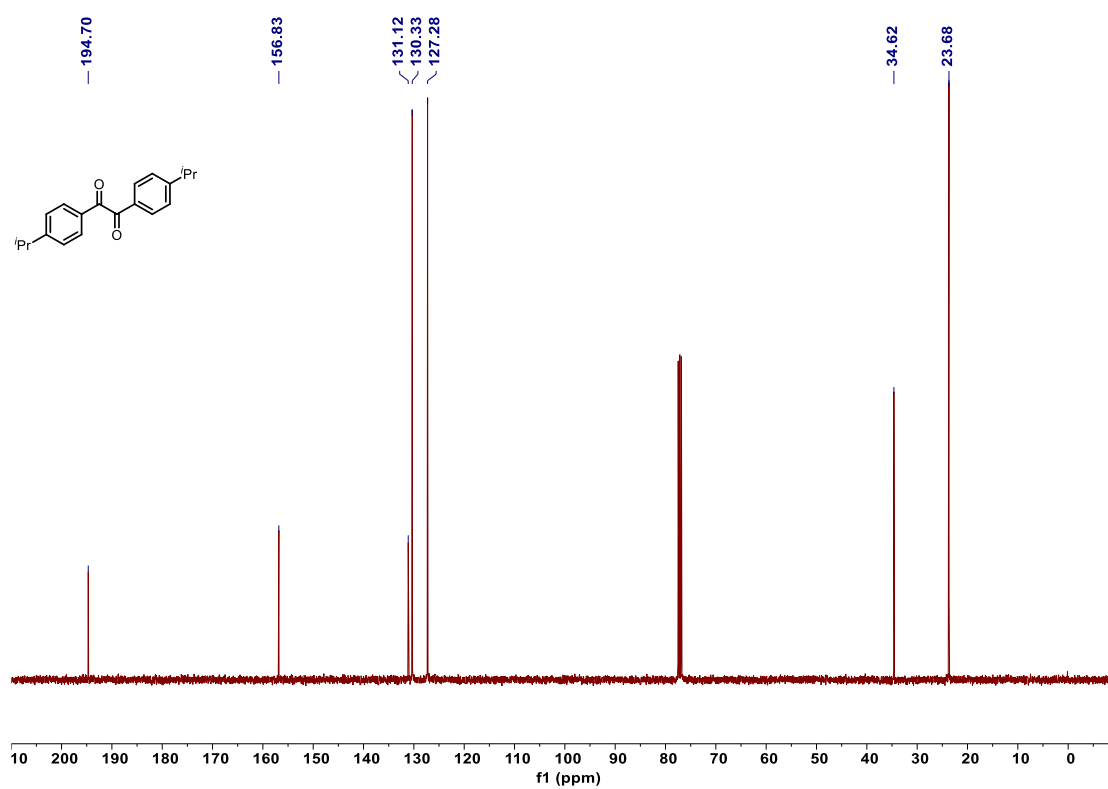
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XI. NMR Spectra

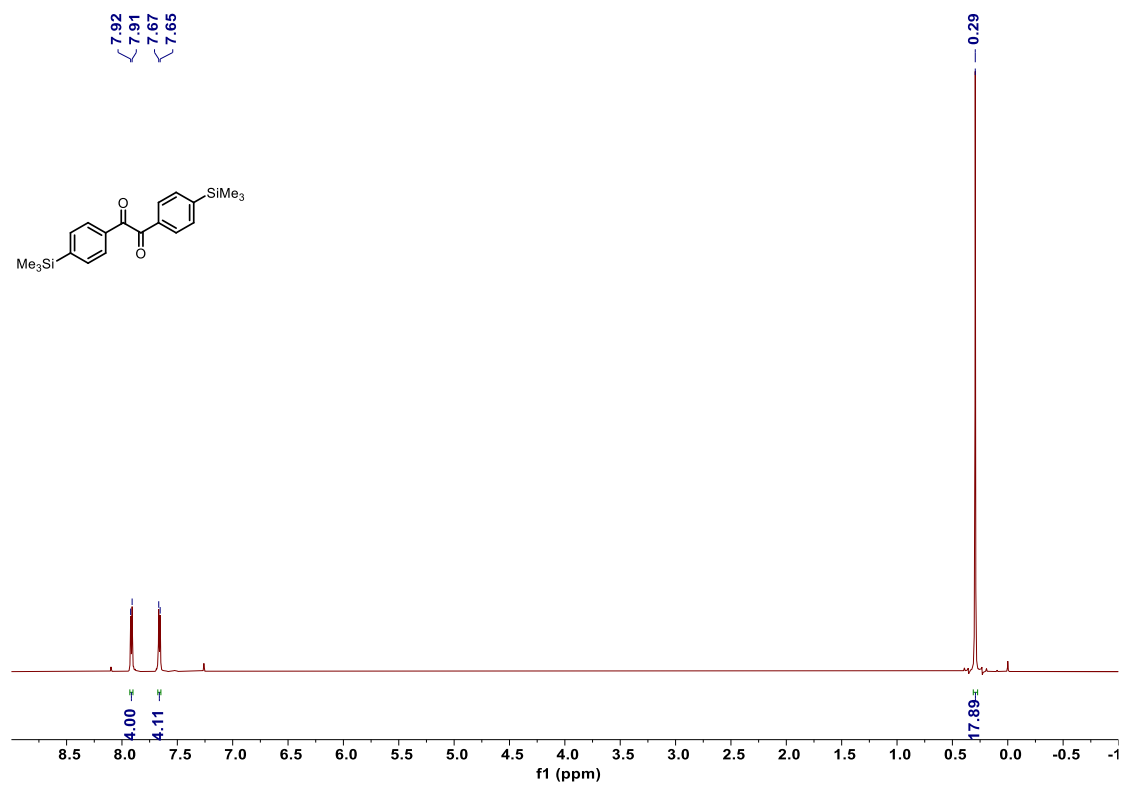
^1H NMR (600 MHz, CDCl_3) spectra of compound **1c**



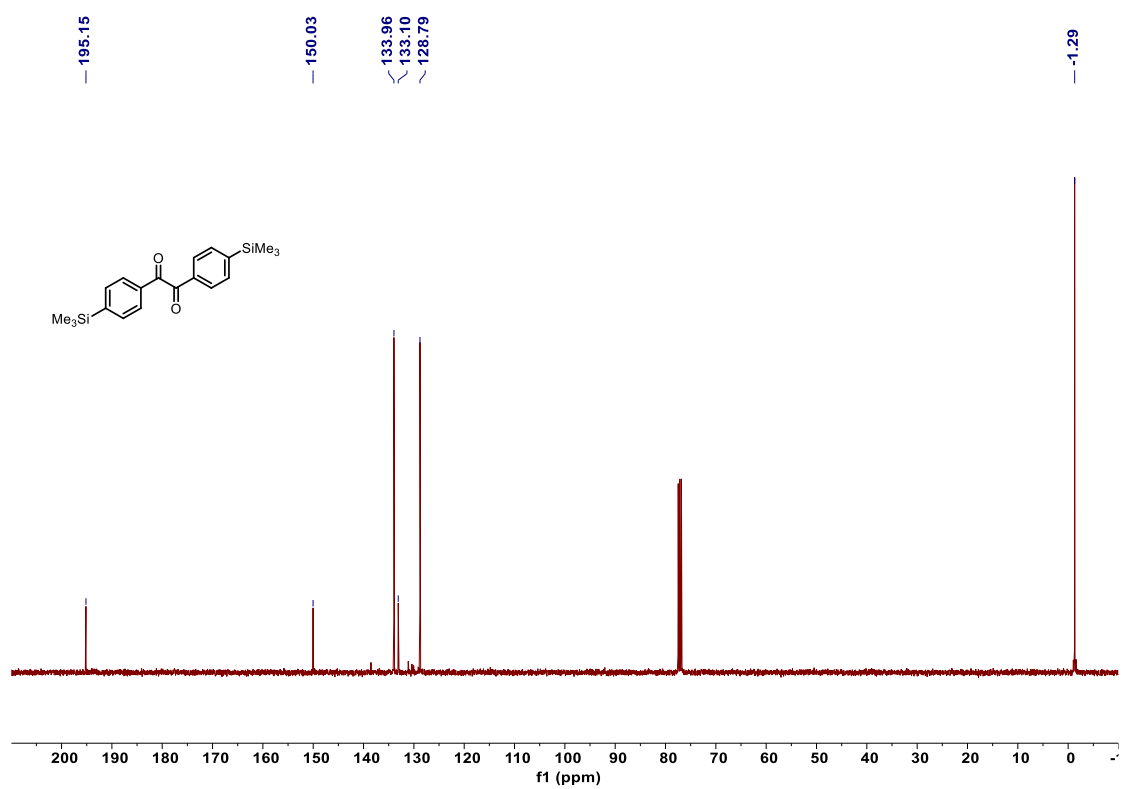
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1c**



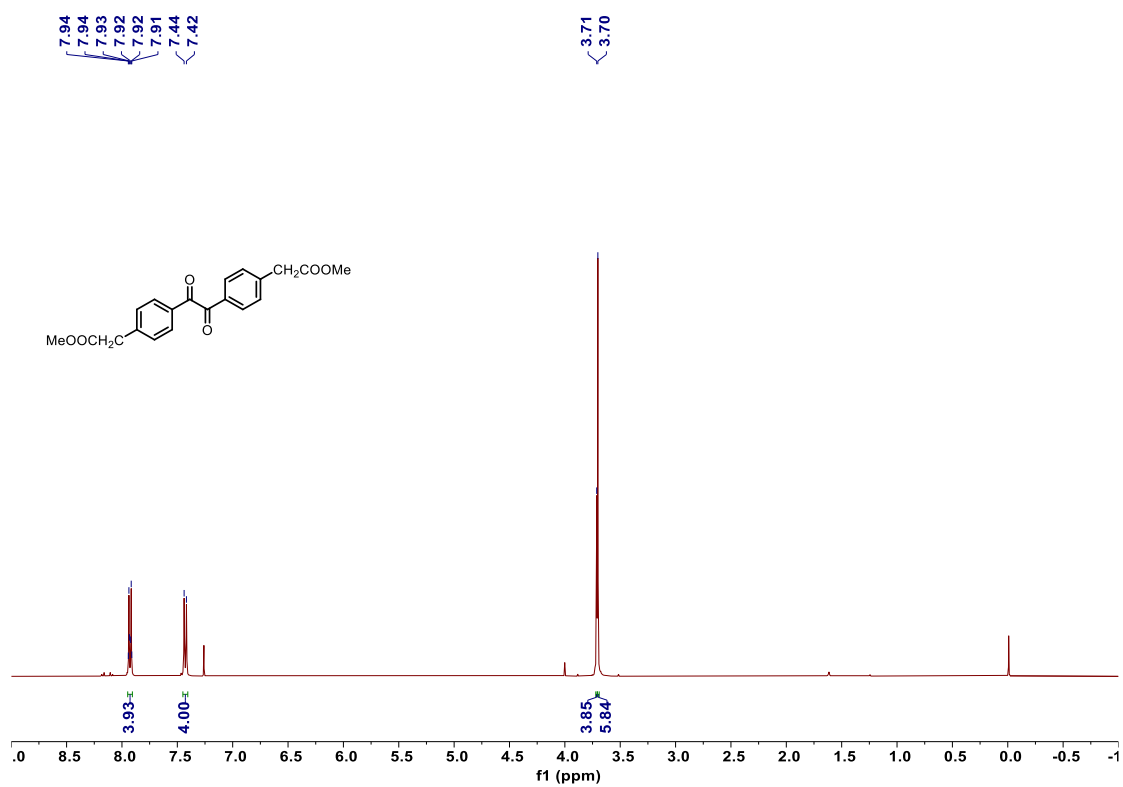
^1H NMR (600 MHz, CDCl_3) spectra of compound **1e**



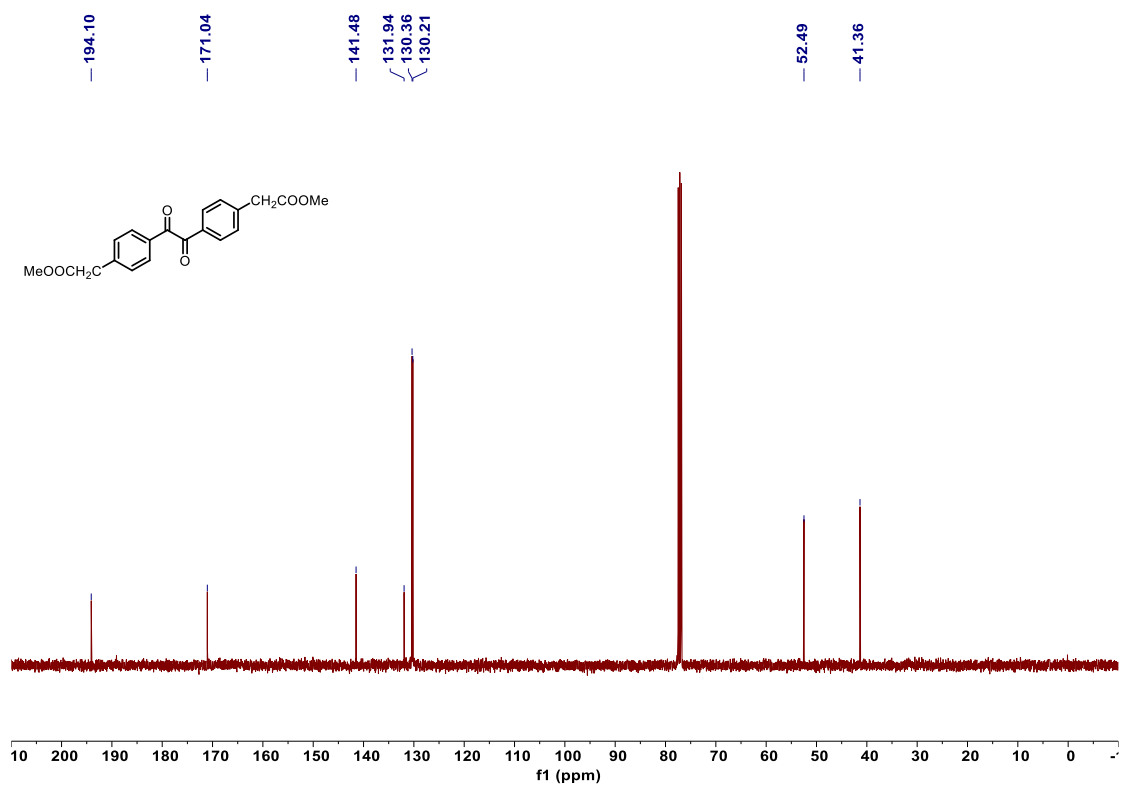
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1e**



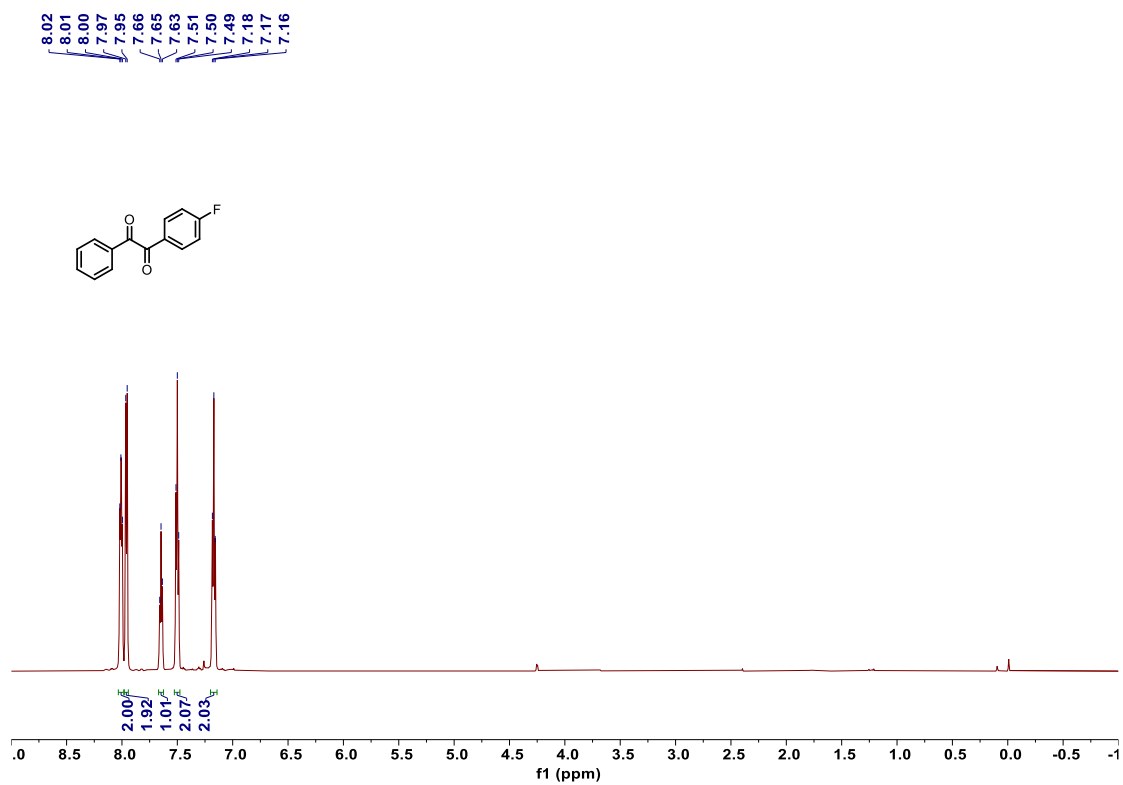
^1H NMR (400 MHz, CDCl_3) spectra of compound **1f**



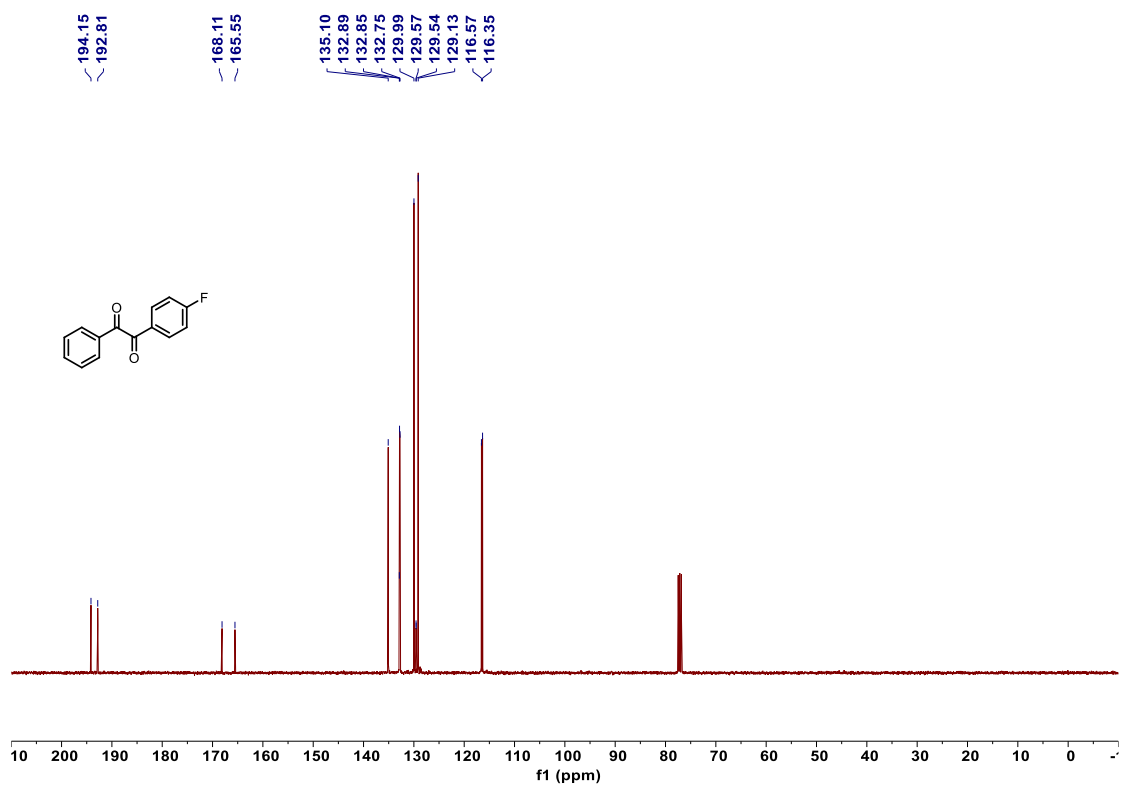
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1f**



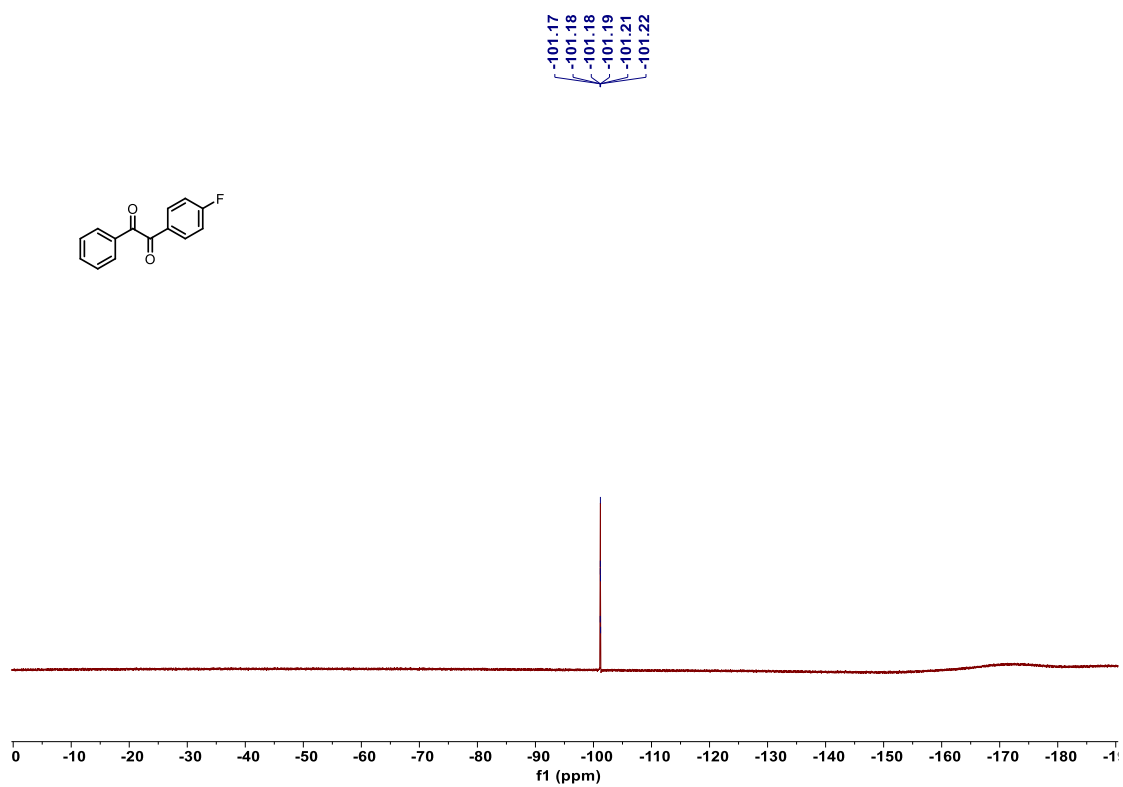
^1H NMR (600 MHz, CDCl_3) spectra of compound **1g**



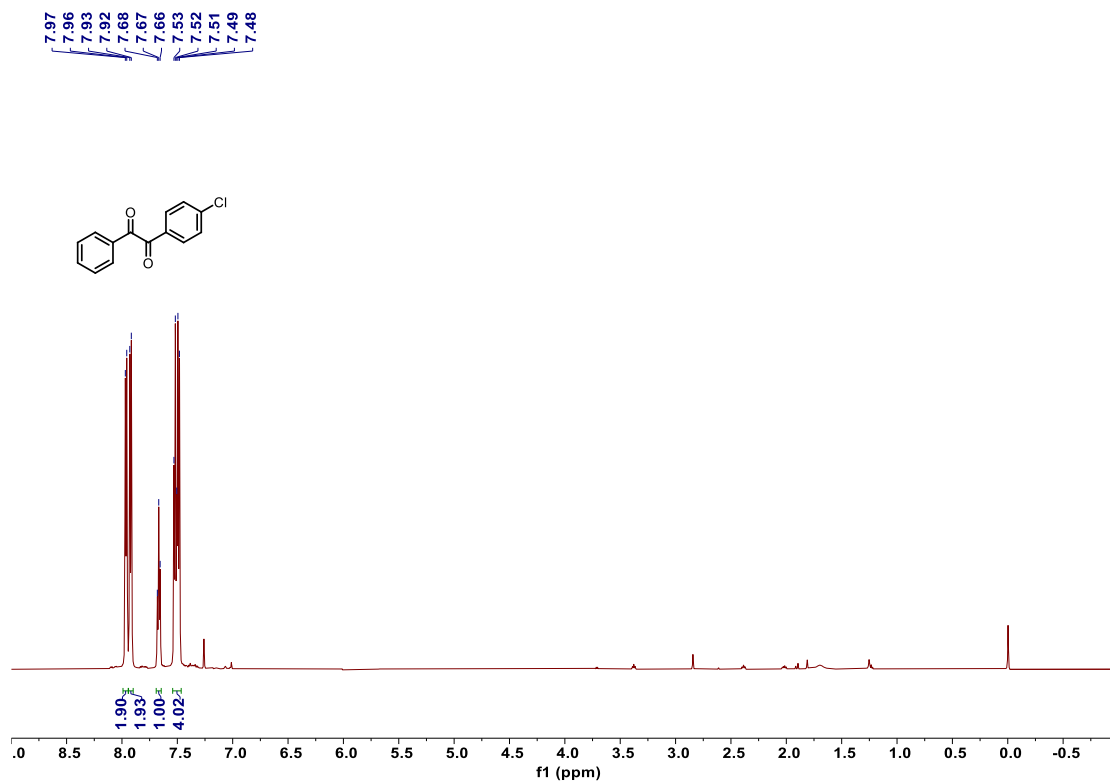
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1g**



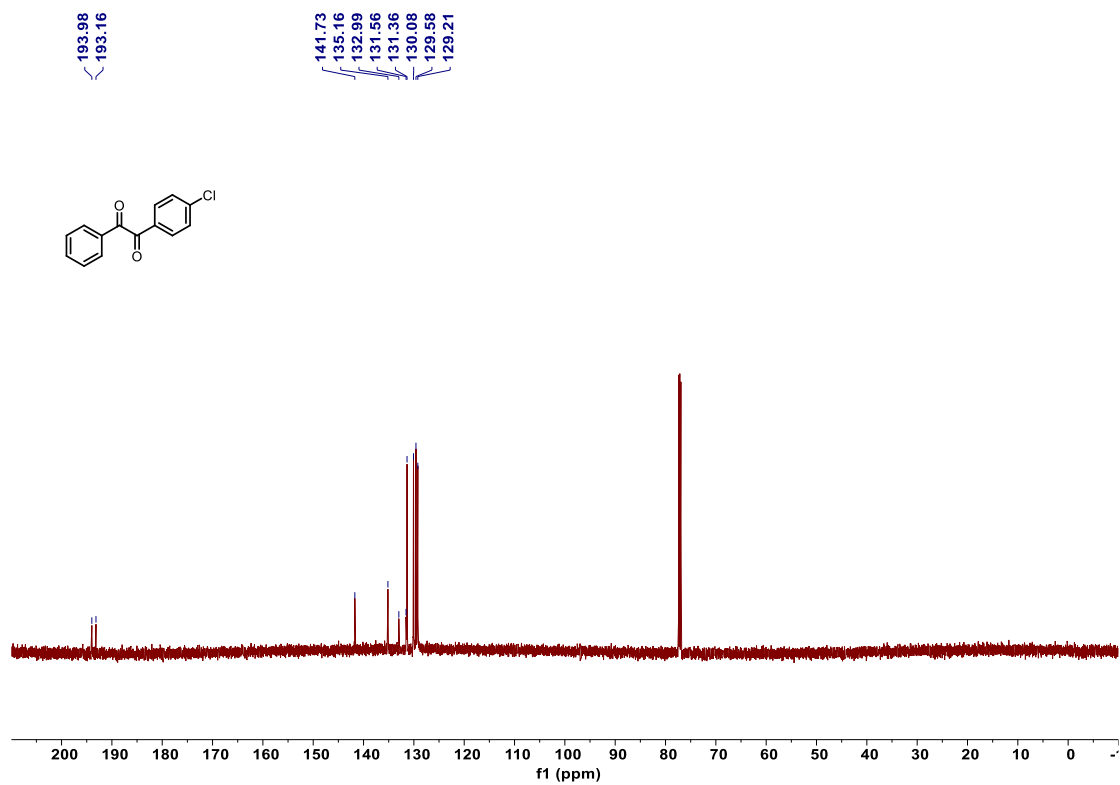
^{19}F NMR (565MHz, CDCl_3) spectra of compound **1g**



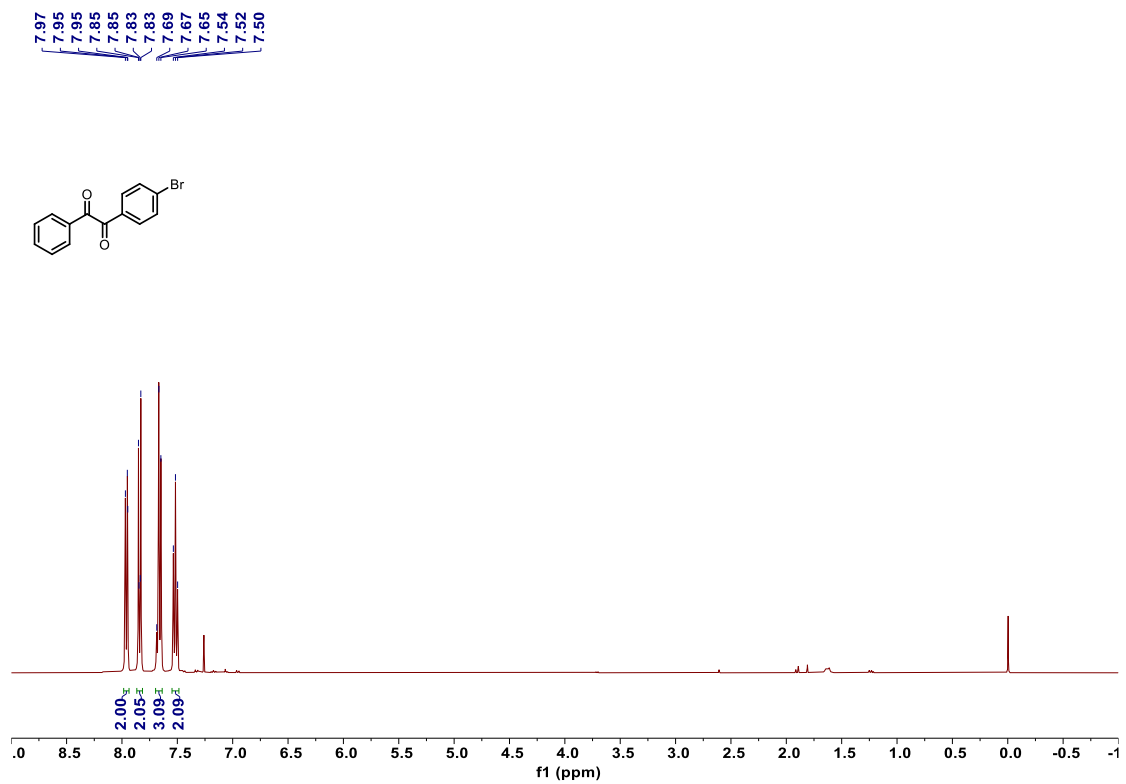
^1H NMR (600 MHz, CDCl_3) spectra of compound **1h**



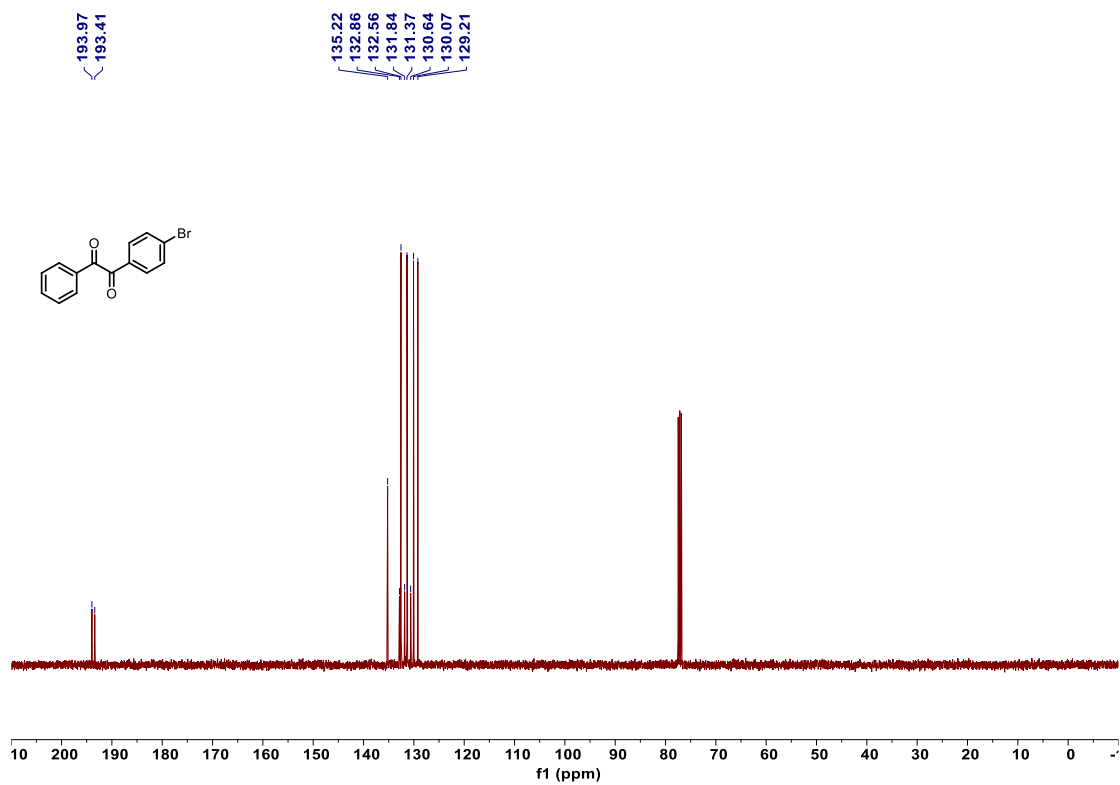
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **1h**



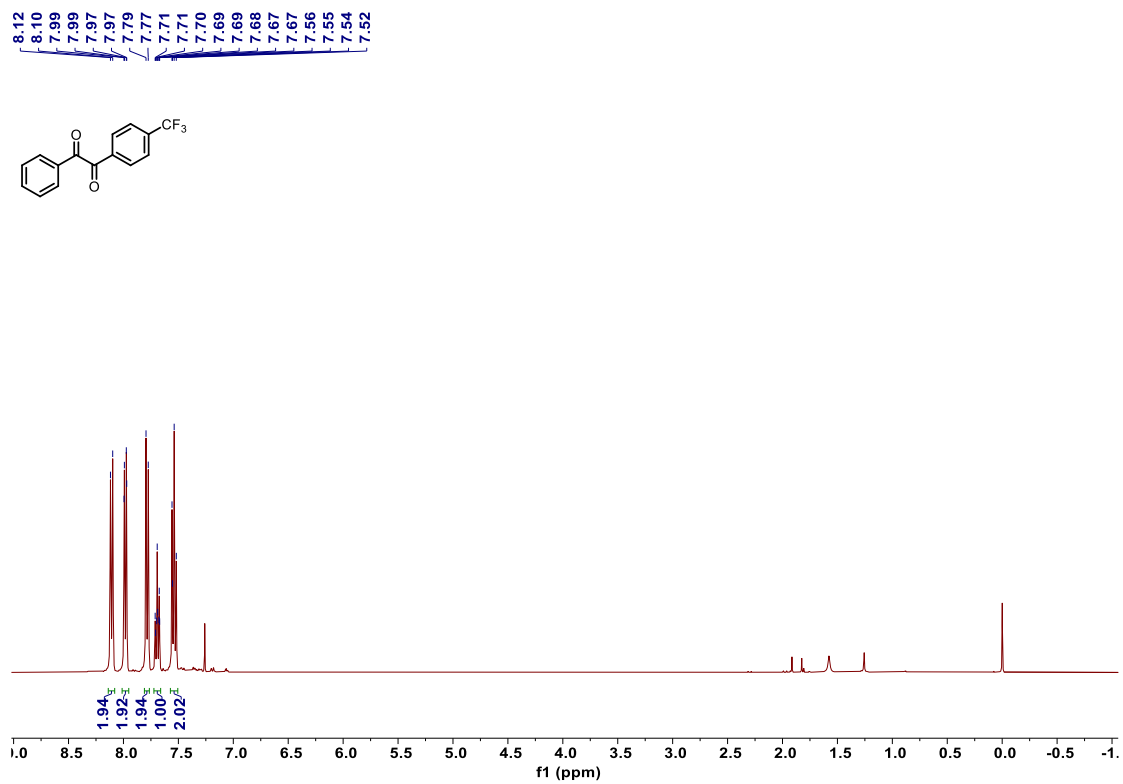
^1H NMR (400 MHz, CDCl_3) spectra of compound **1i**



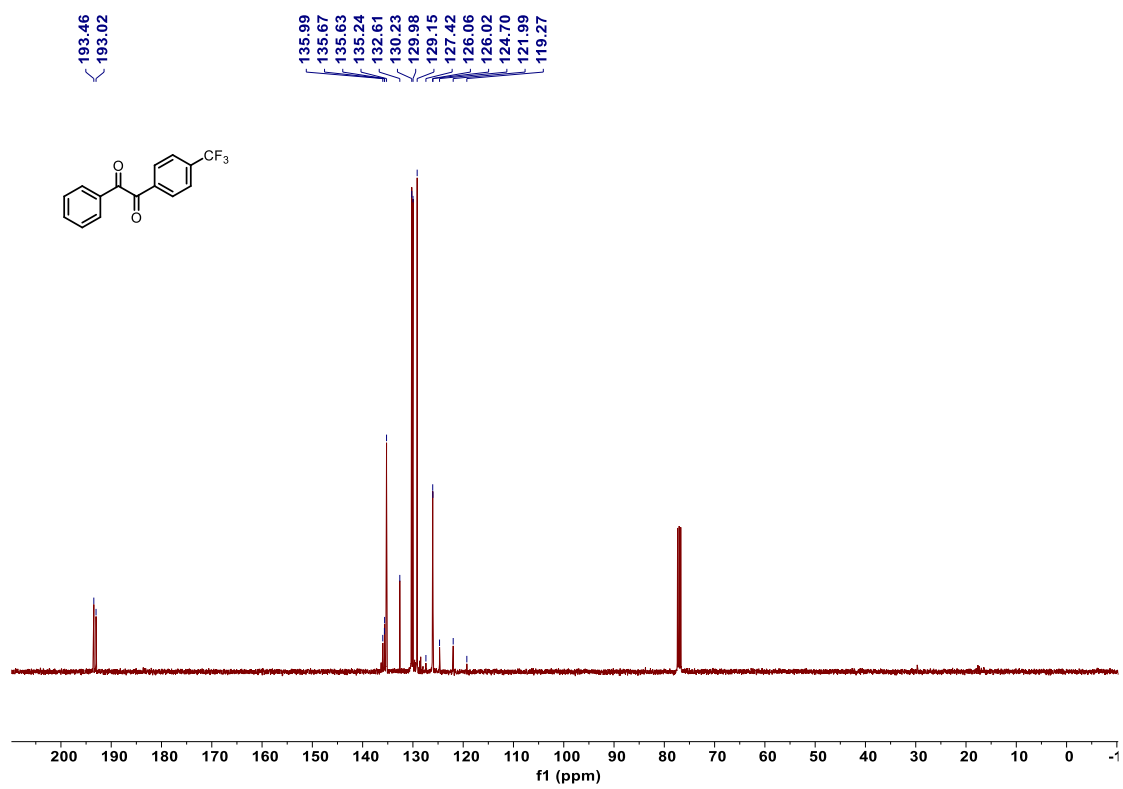
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1i**



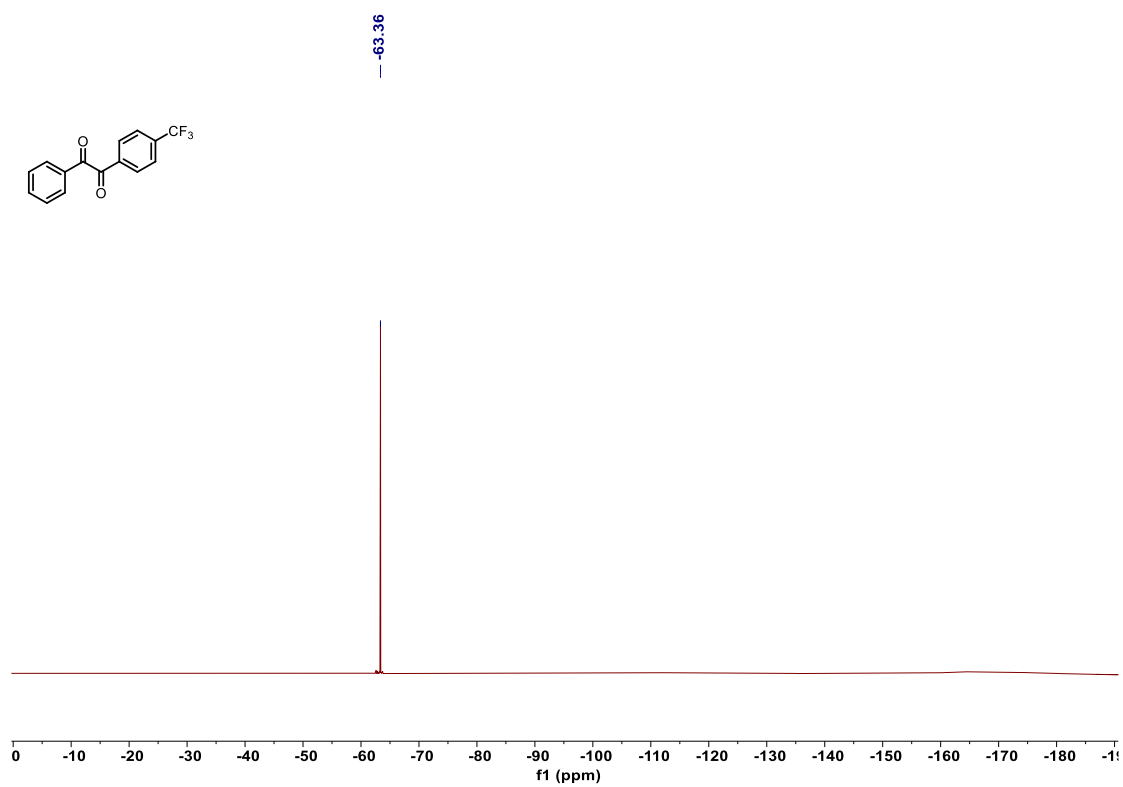
^1H NMR (400 MHz, CDCl_3) spectra of compound **1j**



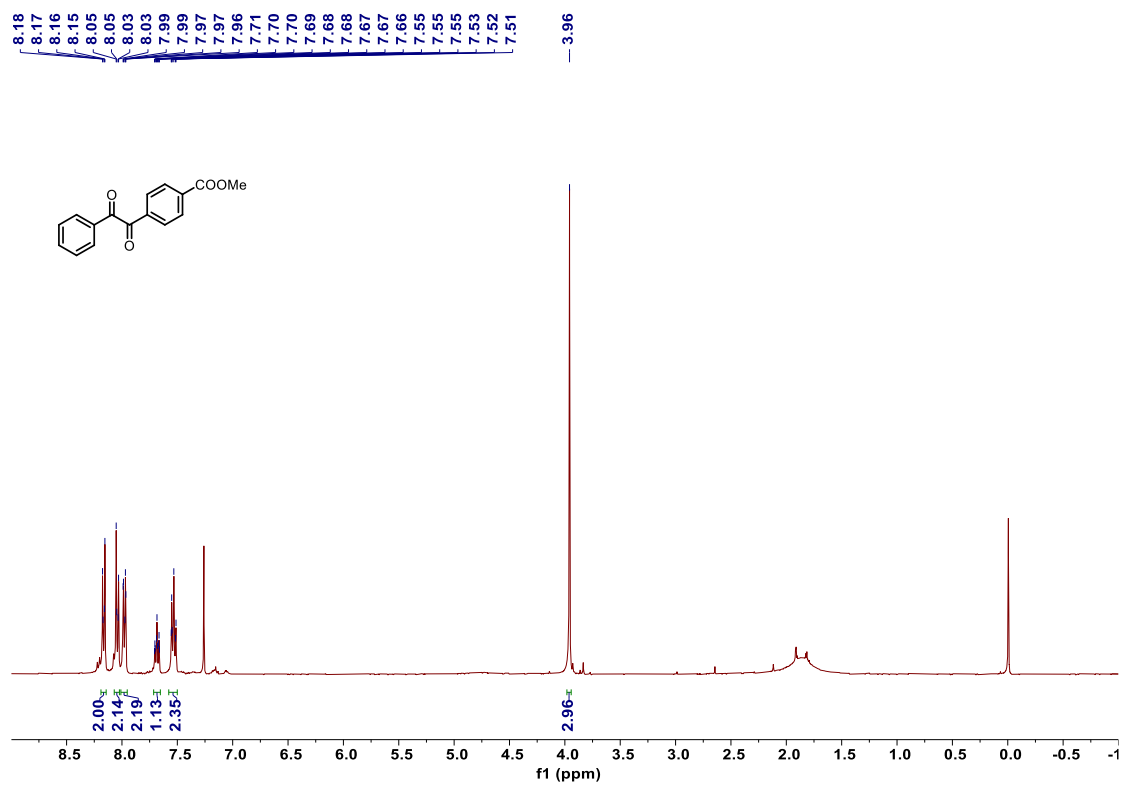
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1j**



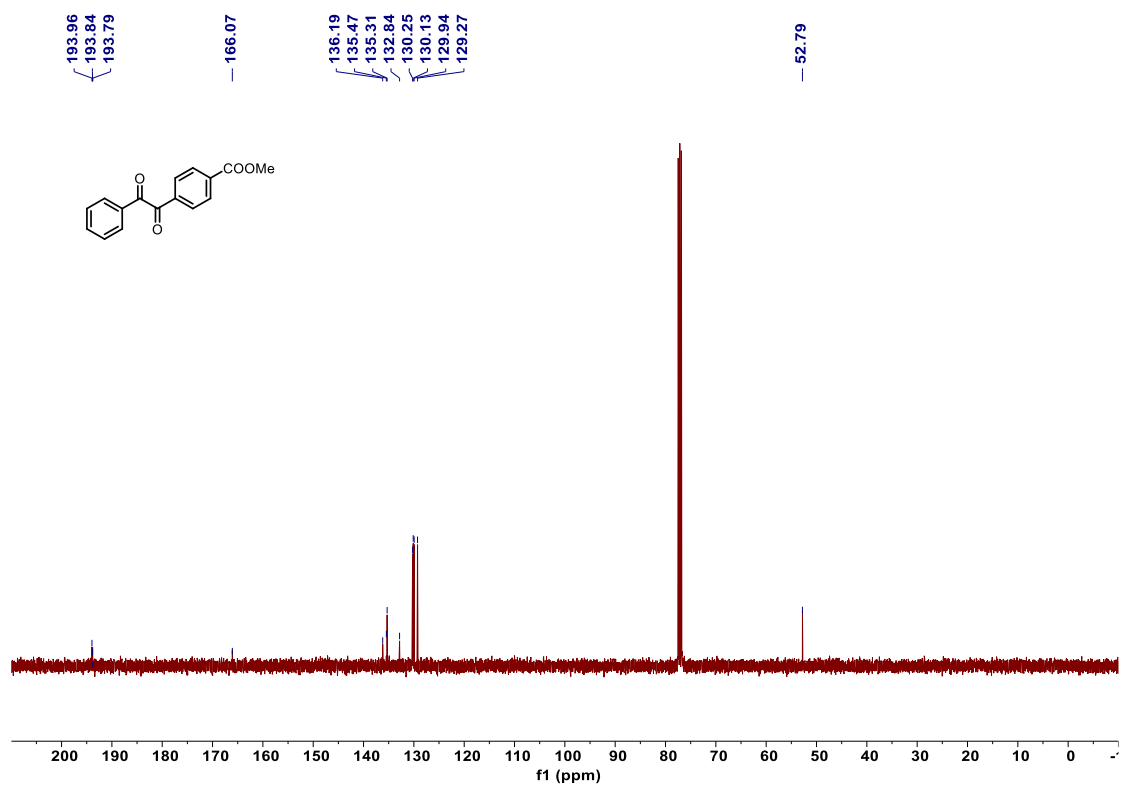
^{19}F NMR (565 MHz, CDCl_3) spectra of compound **1j**



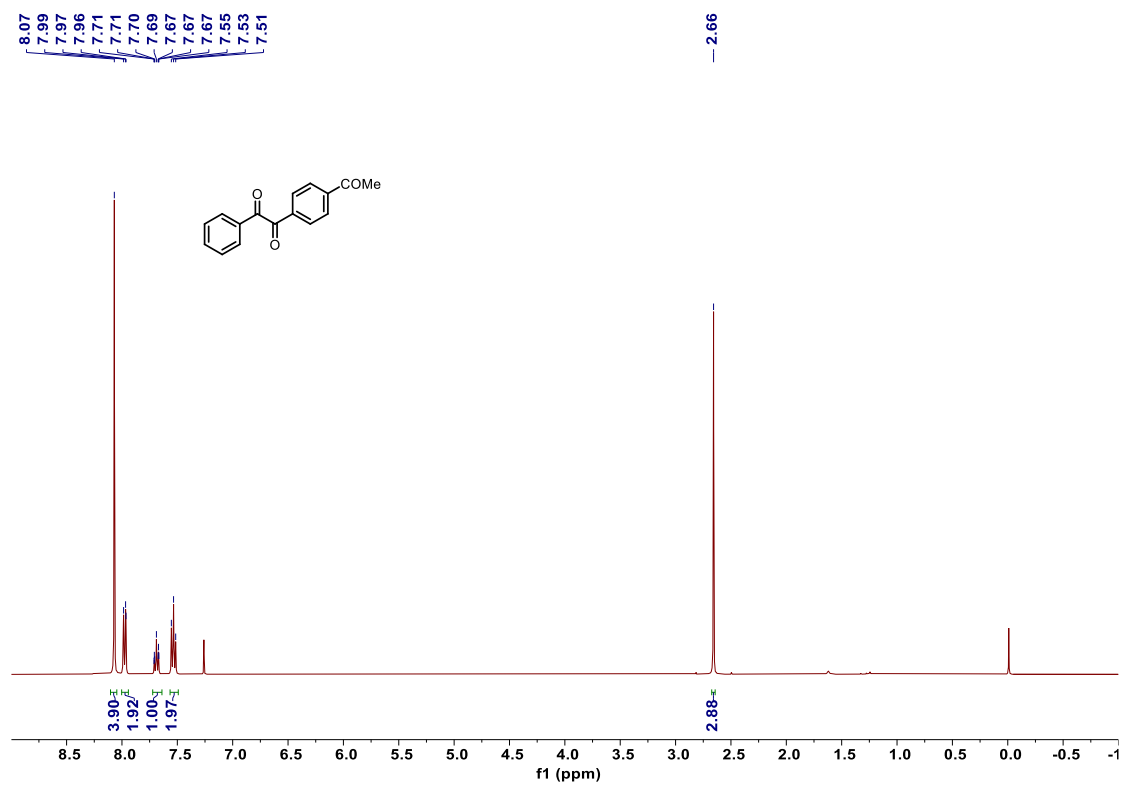
^1H NMR (400 MHz, CDCl_3) spectra of compound **1k**



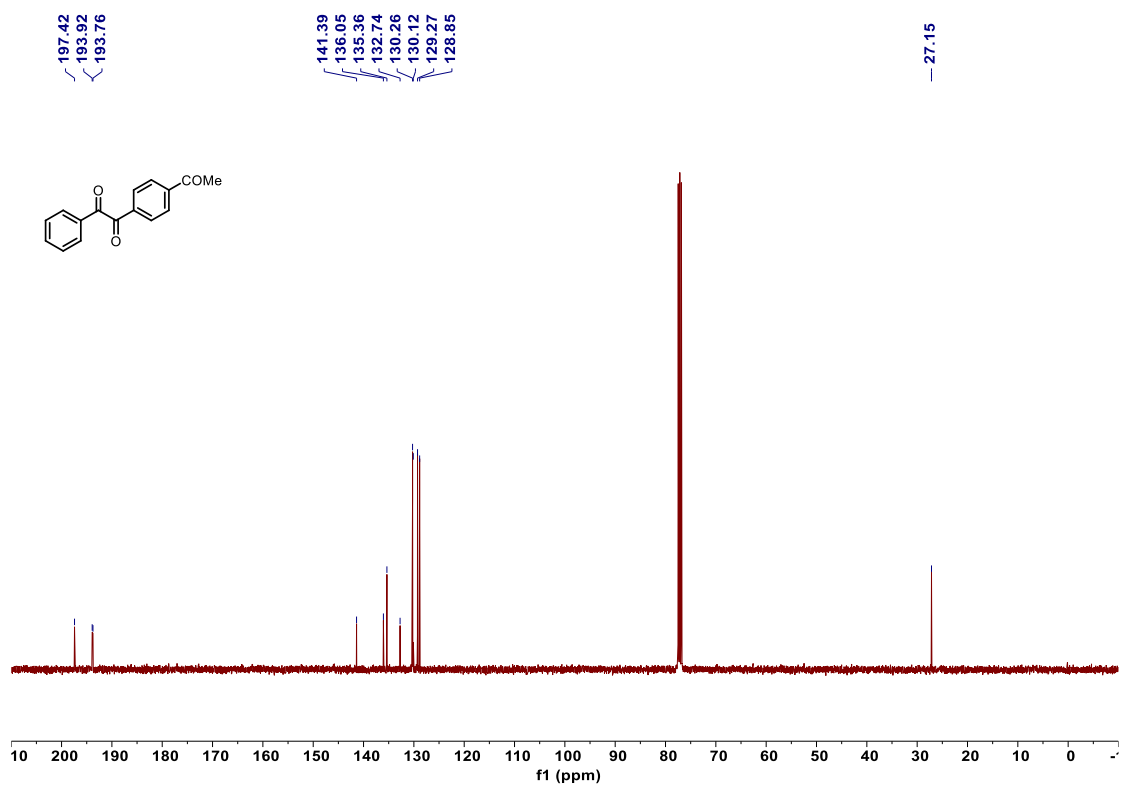
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **1k**



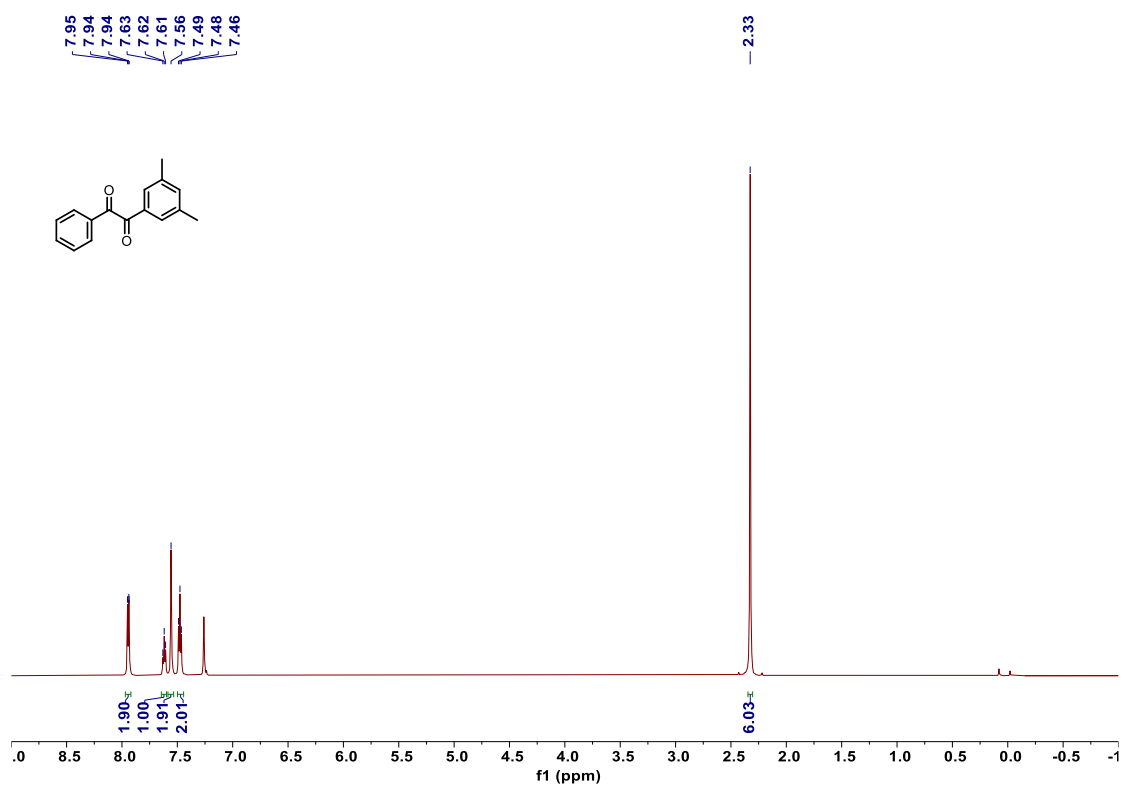
^1H NMR (400 MHz, CDCl_3) spectra of compound **11**



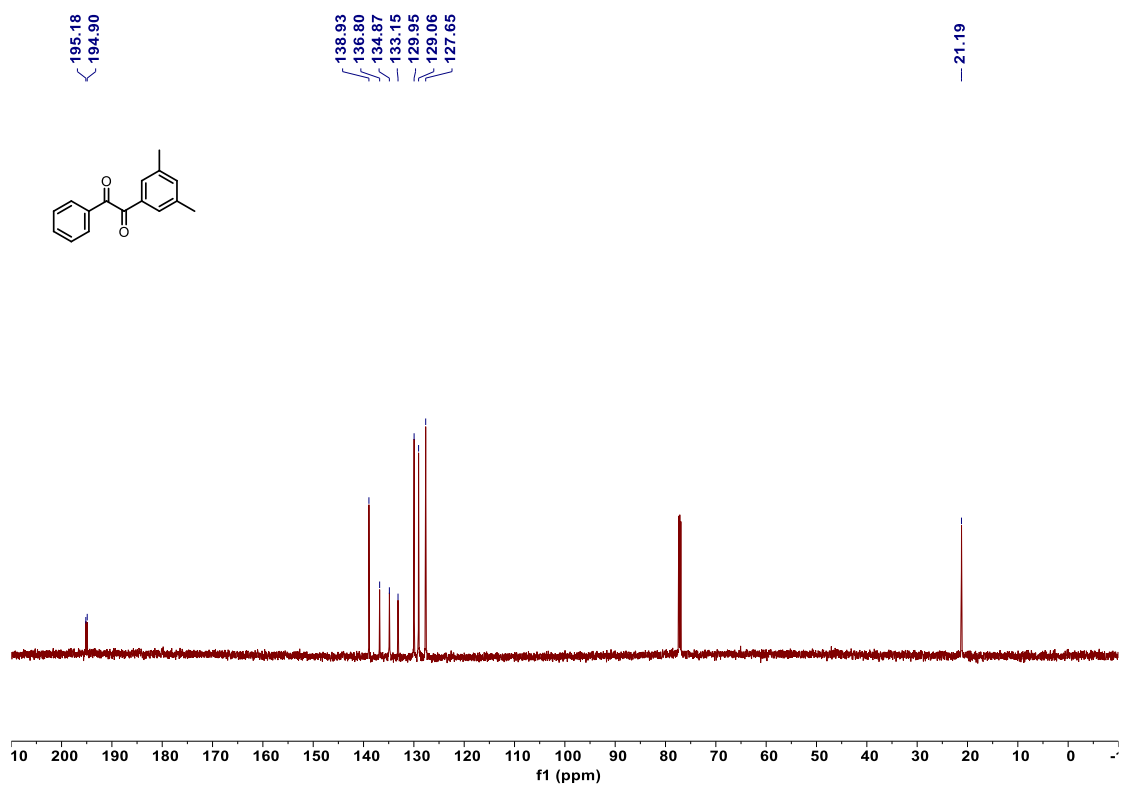
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **11**



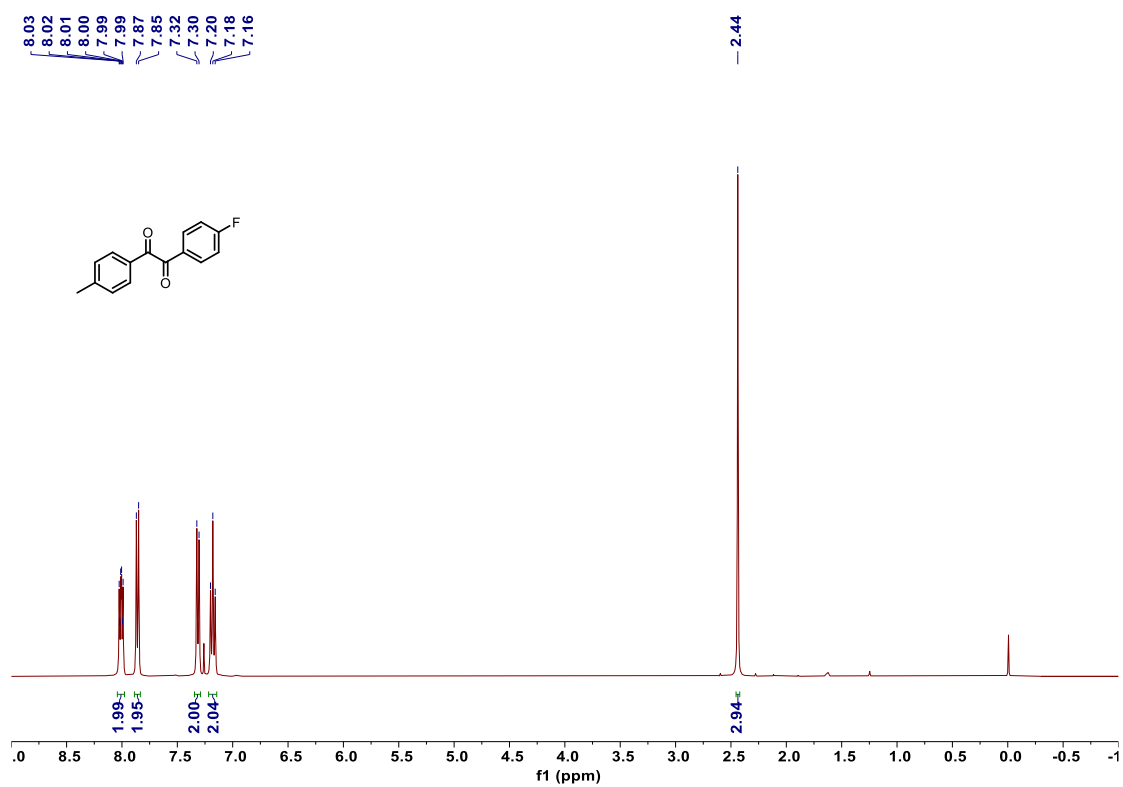
^1H NMR (600 MHz, CDCl_3) spectra of compound **1m**



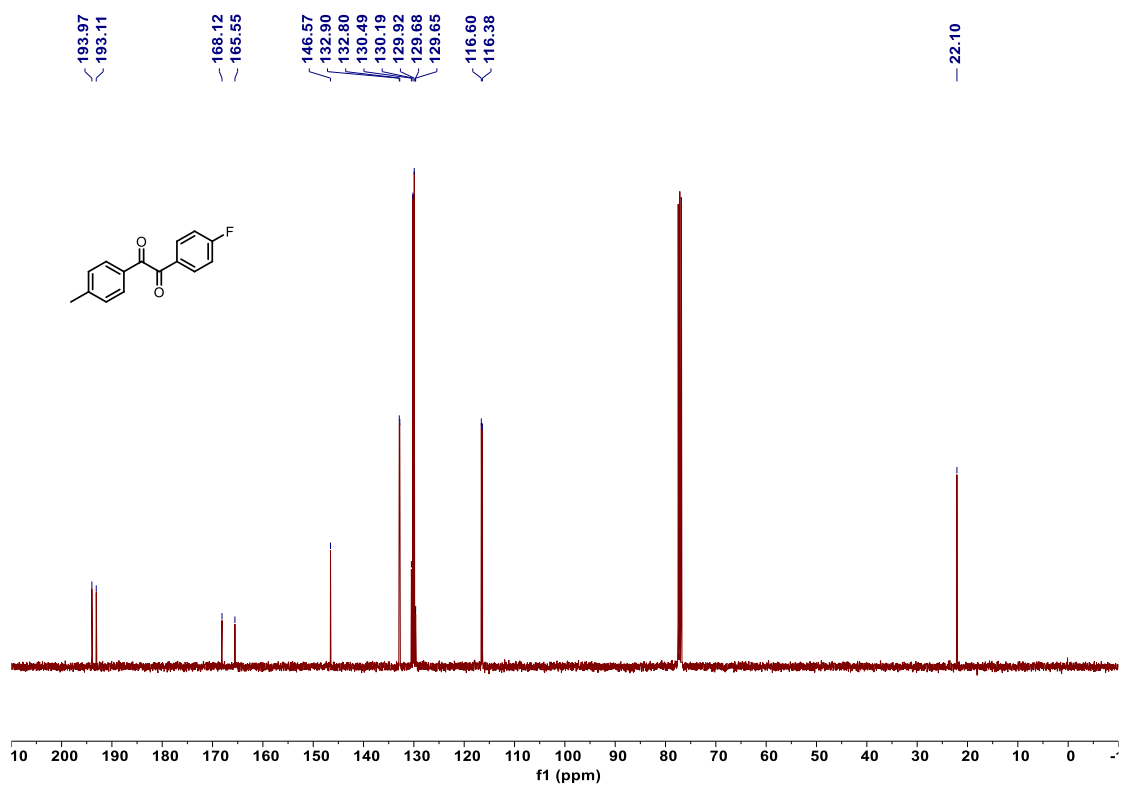
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **1m**



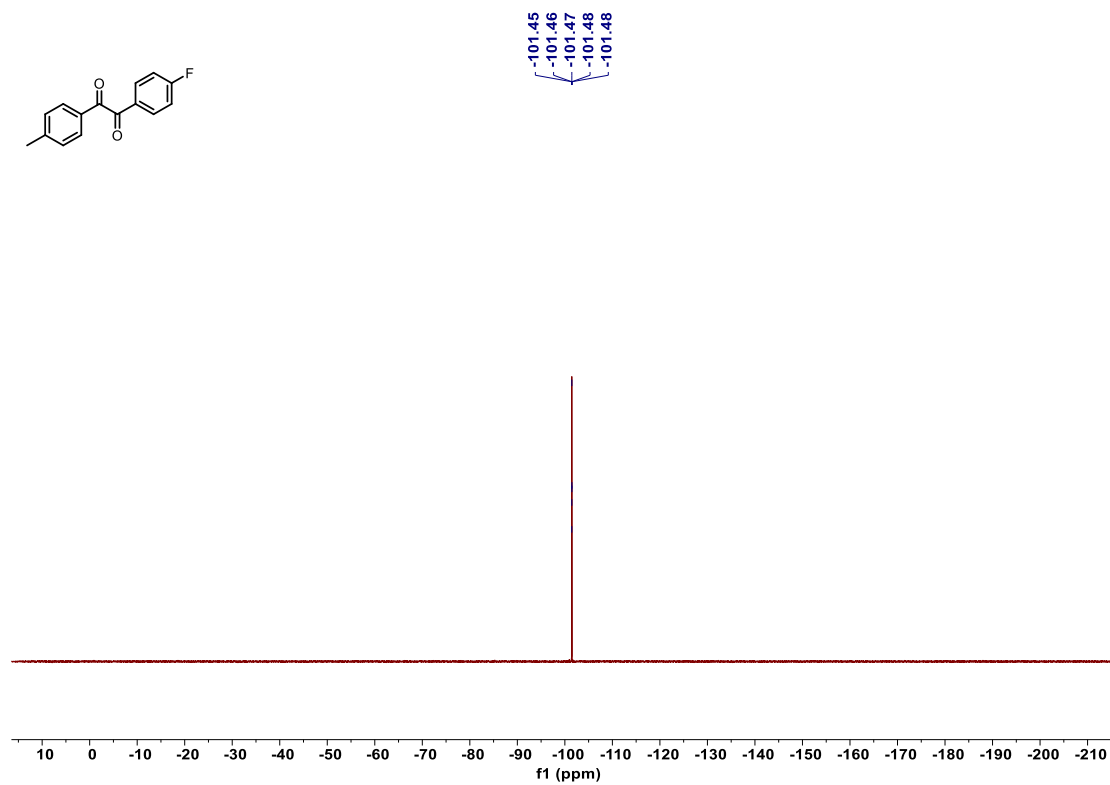
¹H NMR (400 MHz, CDCl₃) spectra of compound **1n**



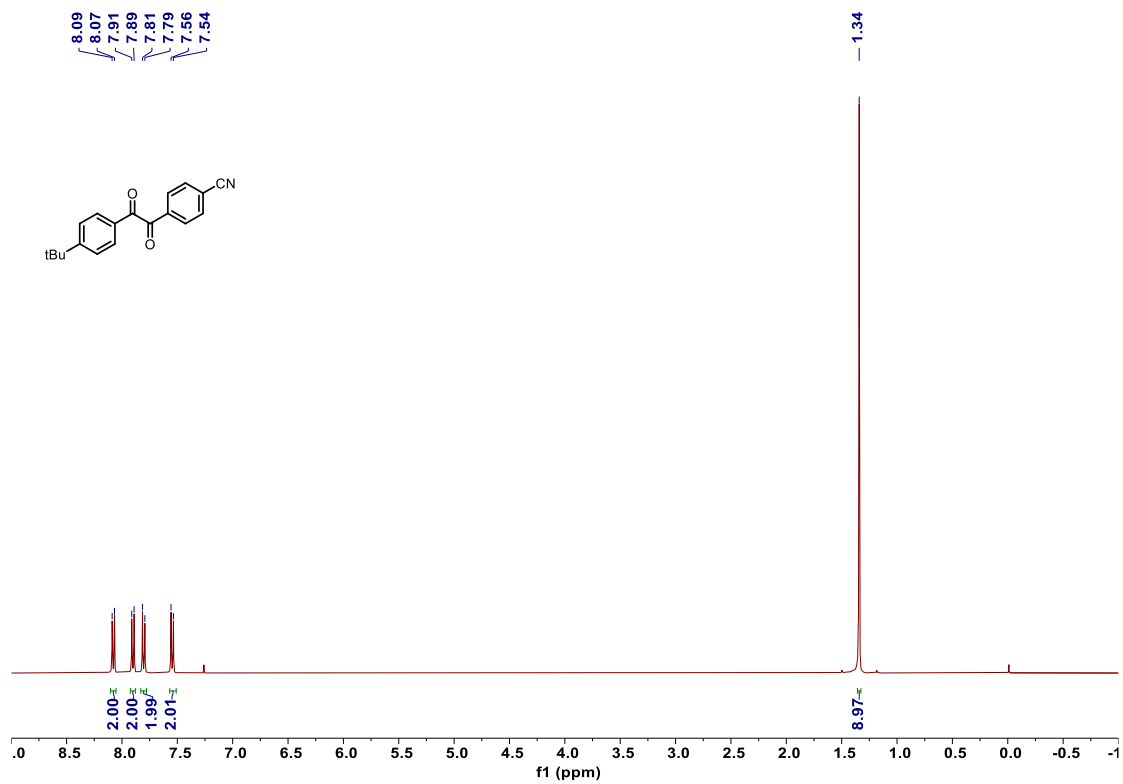
¹³C NMR (101 MHz, CDCl₃) spectra of compound **1n**



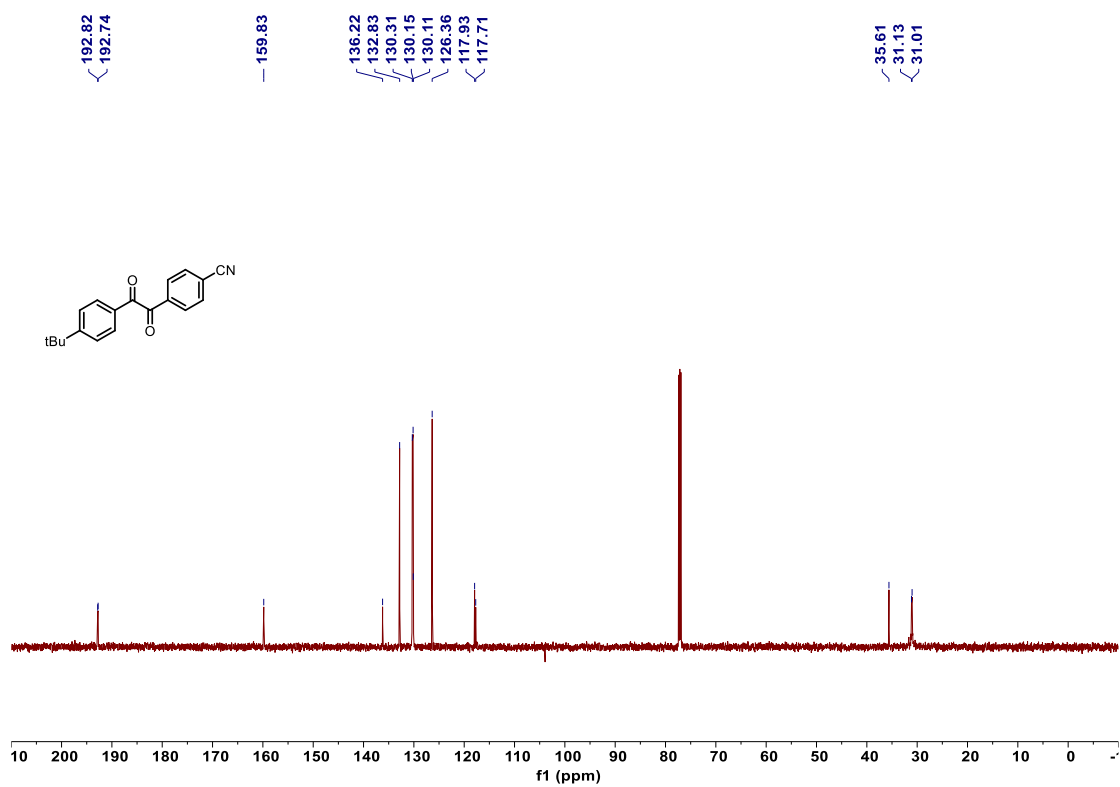
^{19}F NMR (565MHz, CDCl_3) spectra of compound **1n**



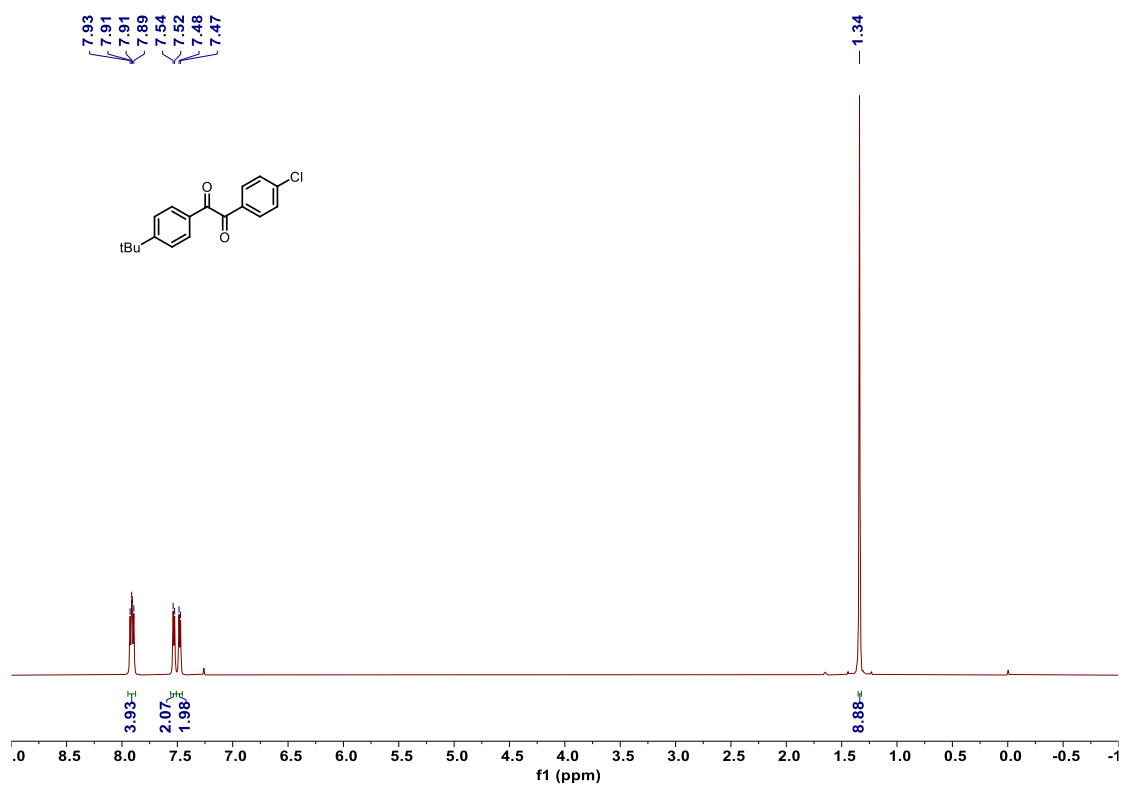
^1H NMR (400 MHz, CDCl_3) spectra of compound **1o**



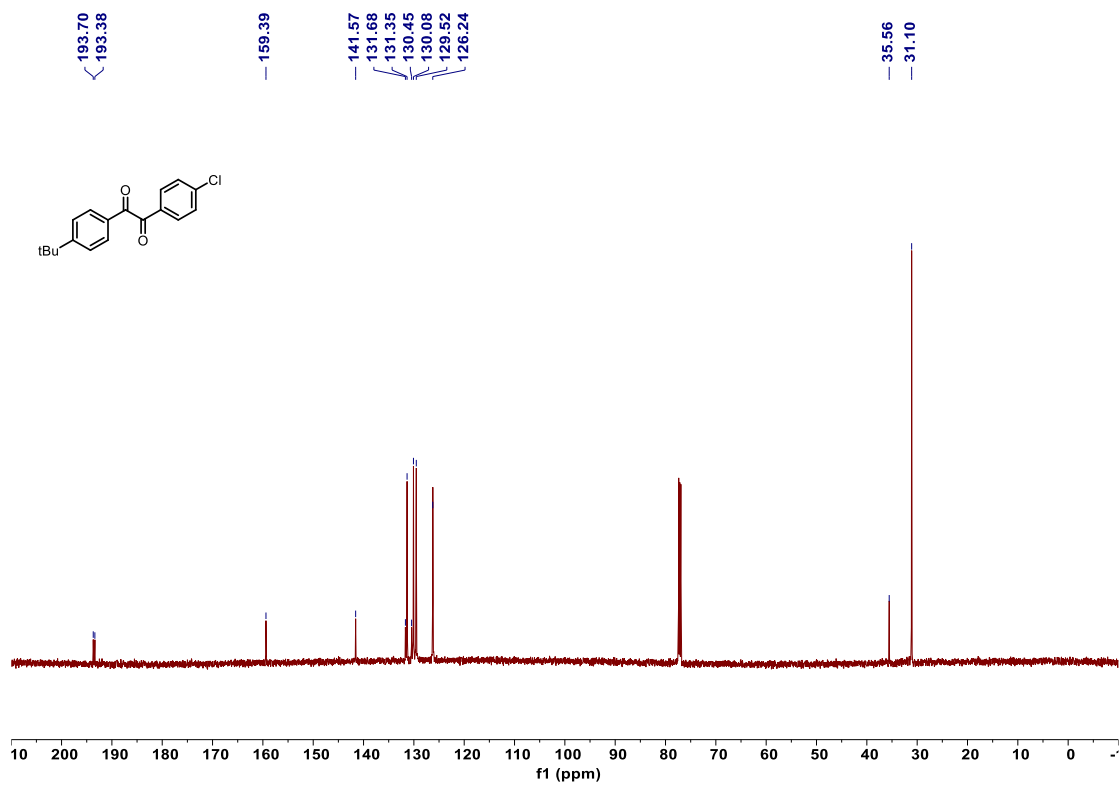
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **1o**



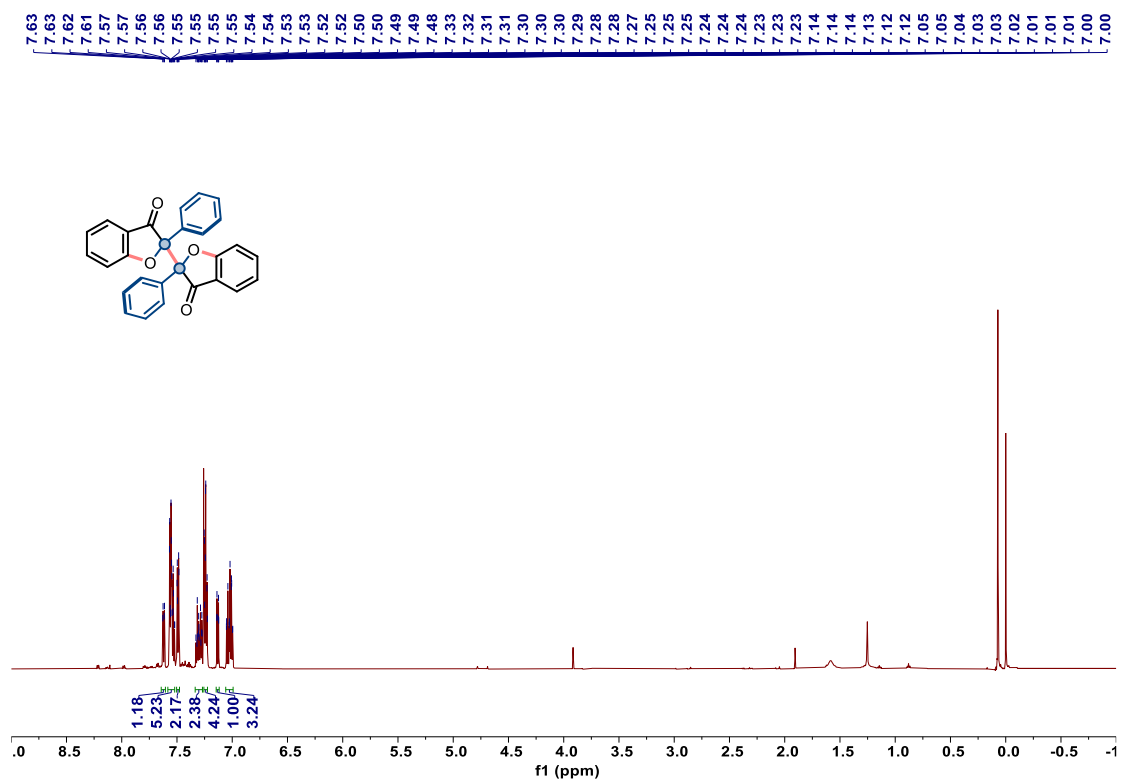
^1H NMR (600 MHz, CDCl_3) spectra of compound **1p**



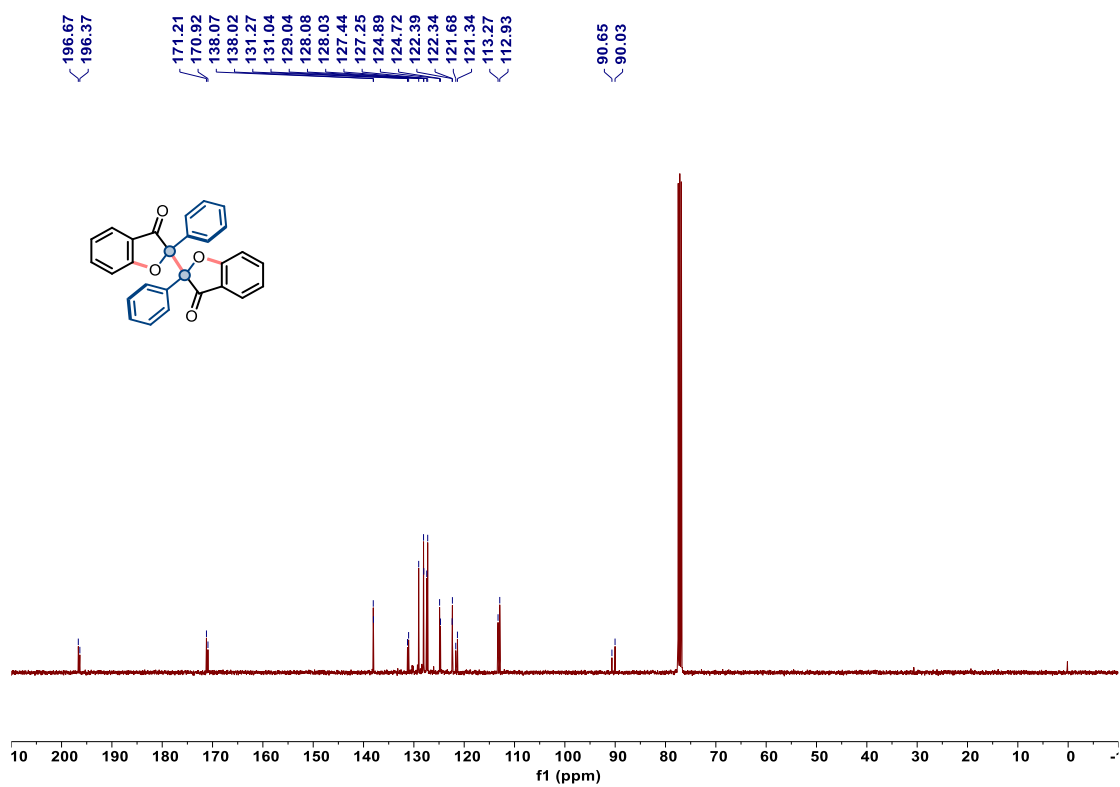
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **1p**



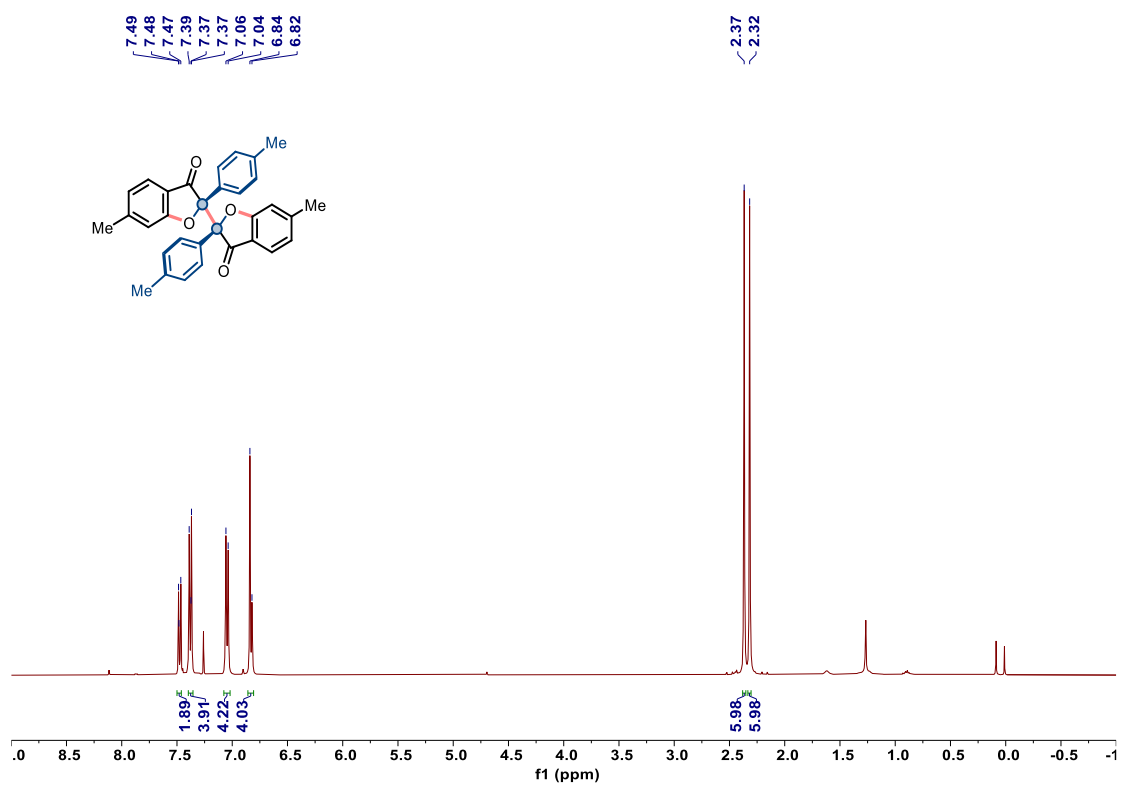
^1H NMR (600 MHz, CDCl_3) spectra of compound **2a**



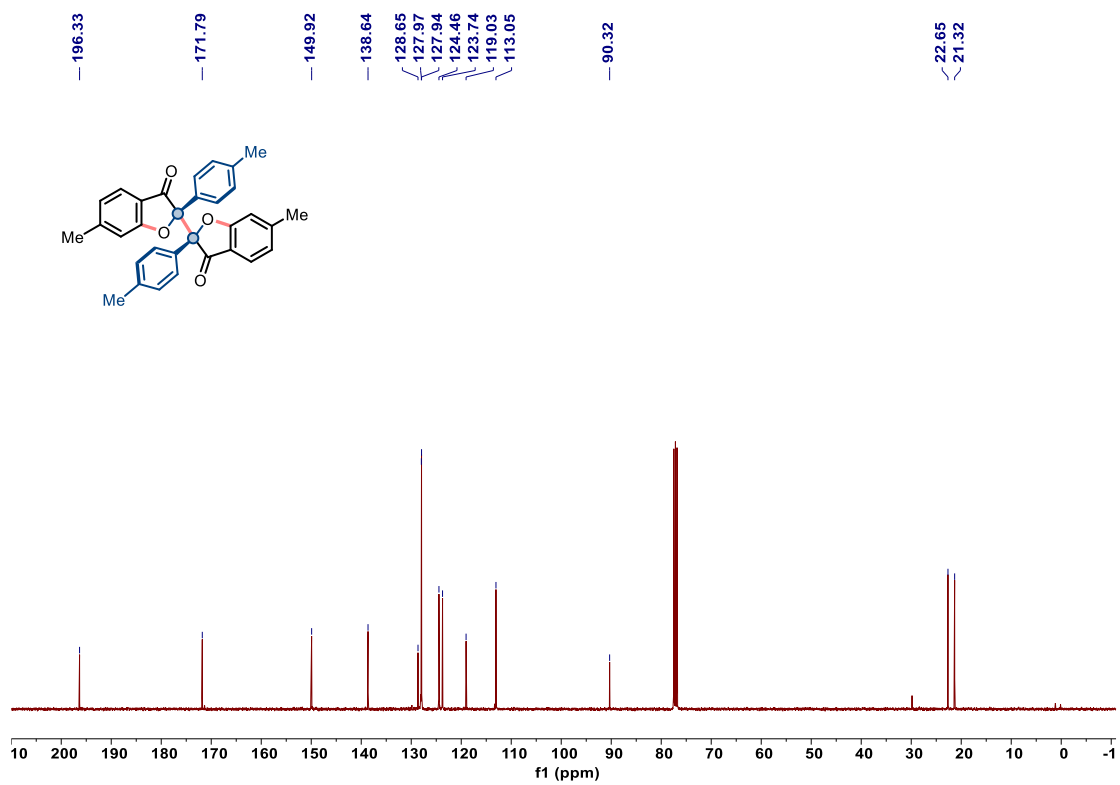
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2a**



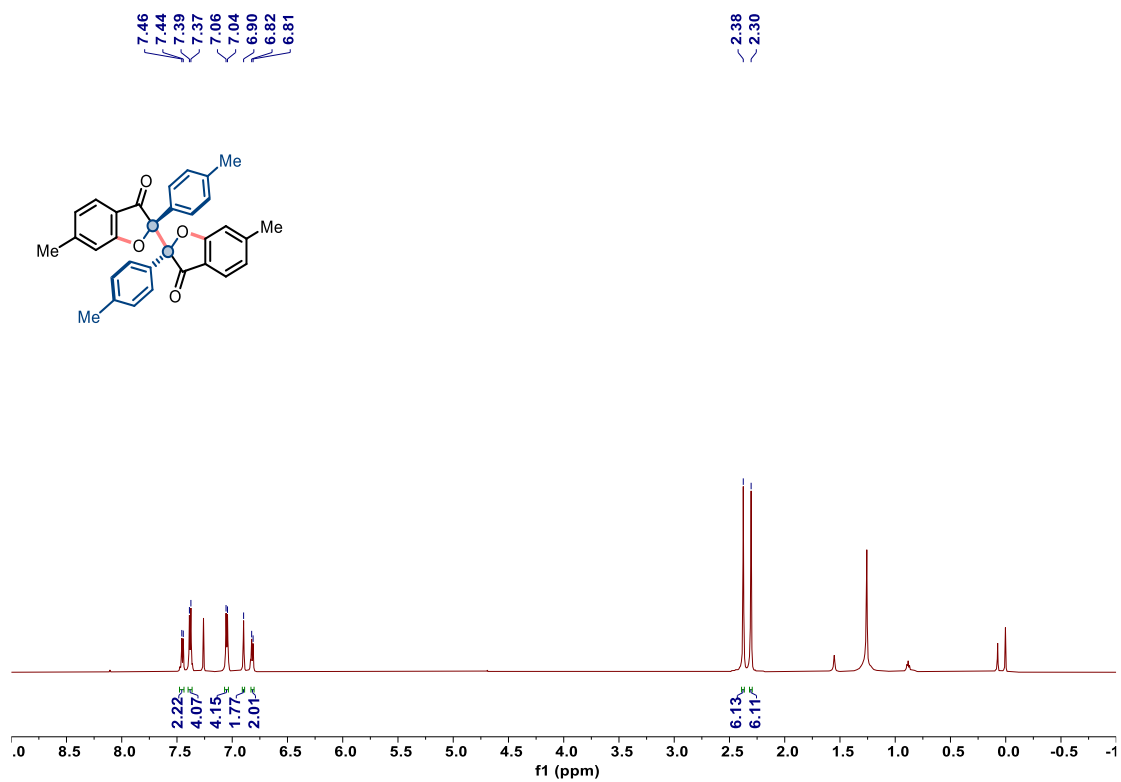
^1H NMR (400 MHz, CDCl_3) spectra of compound **2b-1**



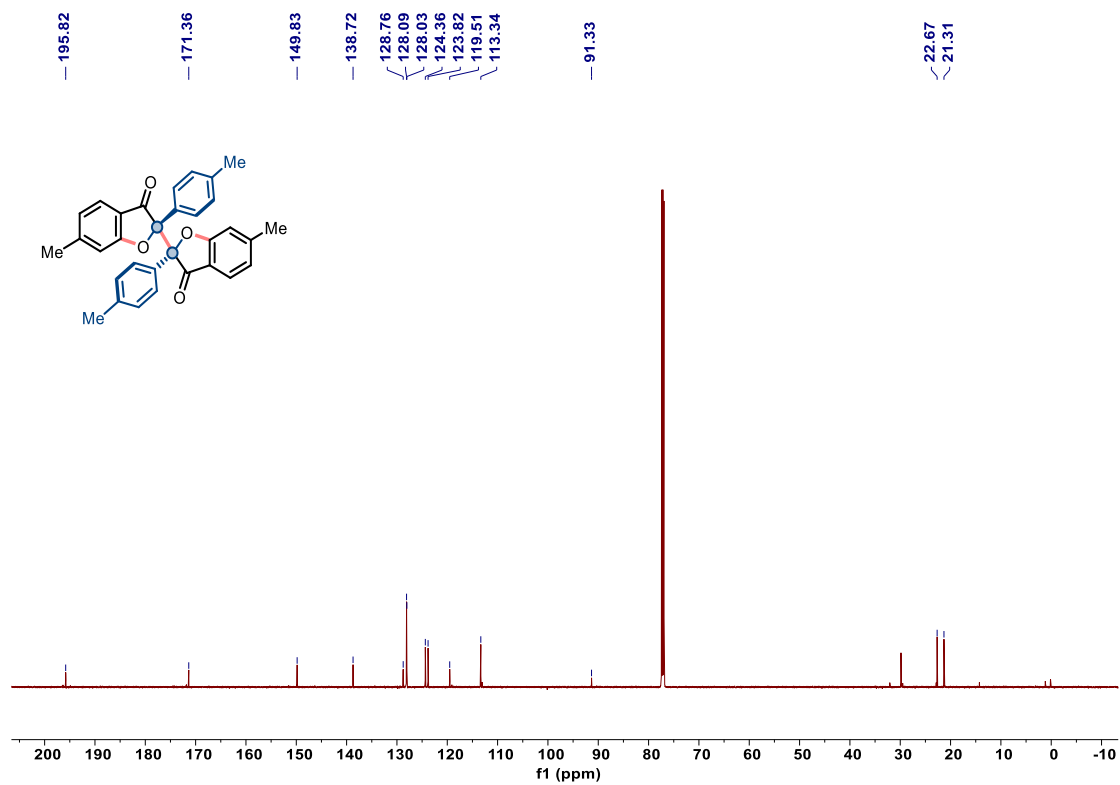
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2b-1**



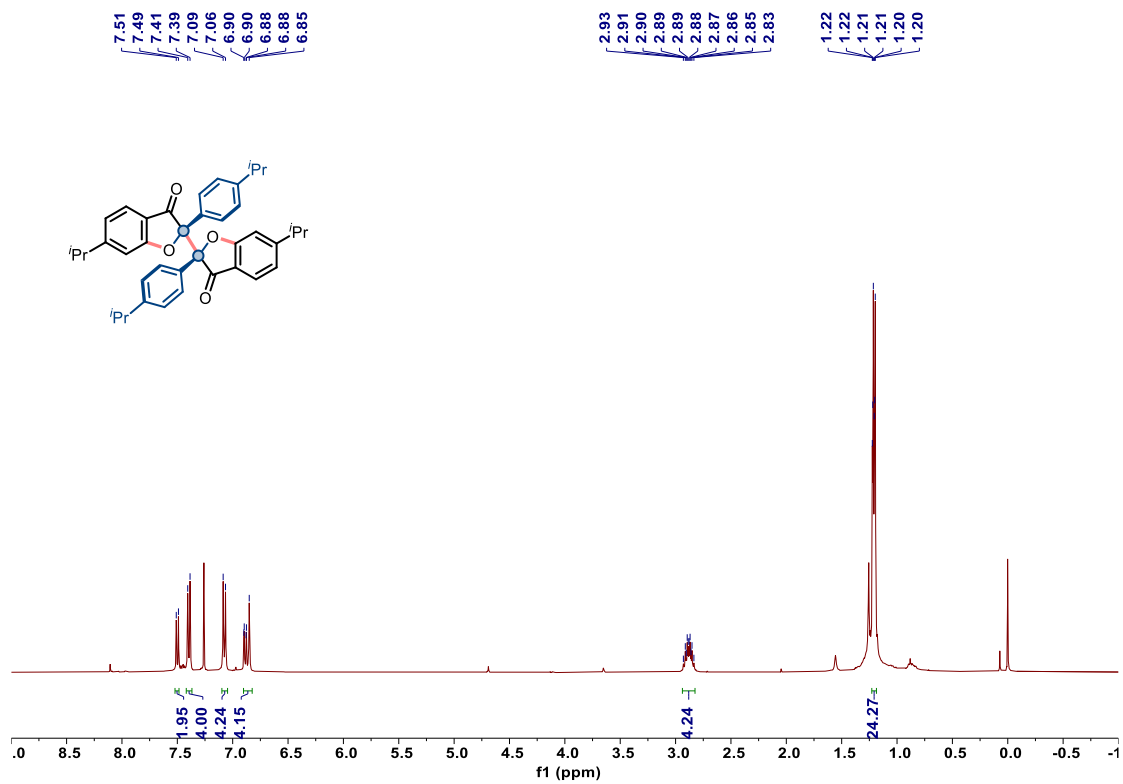
^1H NMR (600 MHz, CDCl_3) spectra of compound **2b-2**



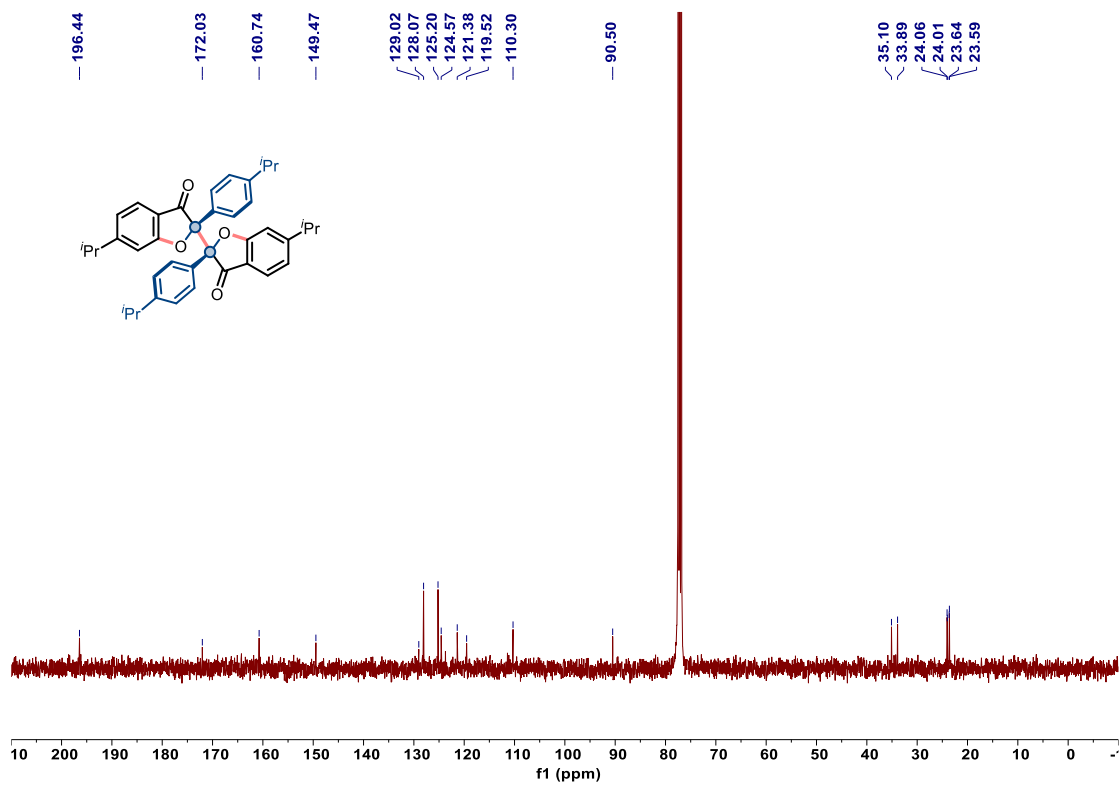
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **2b-2**



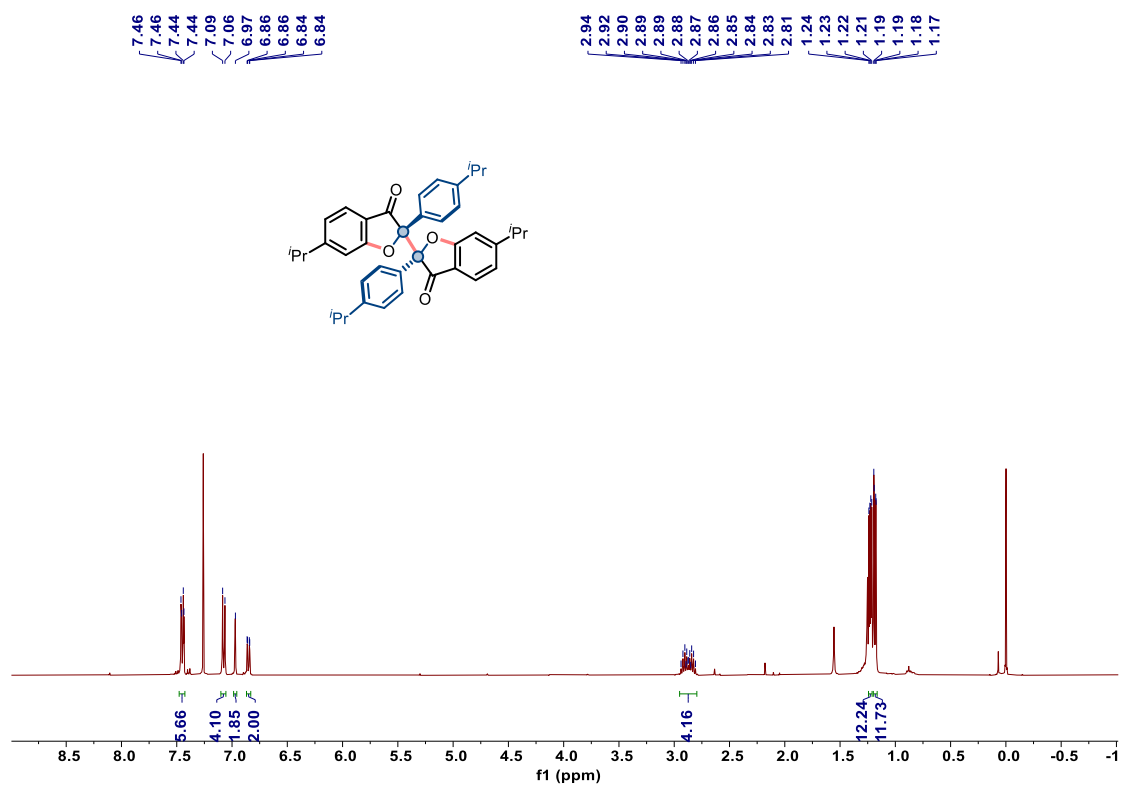
^1H NMR (400 MHz, CDCl_3) spectra of compound **2c-1**



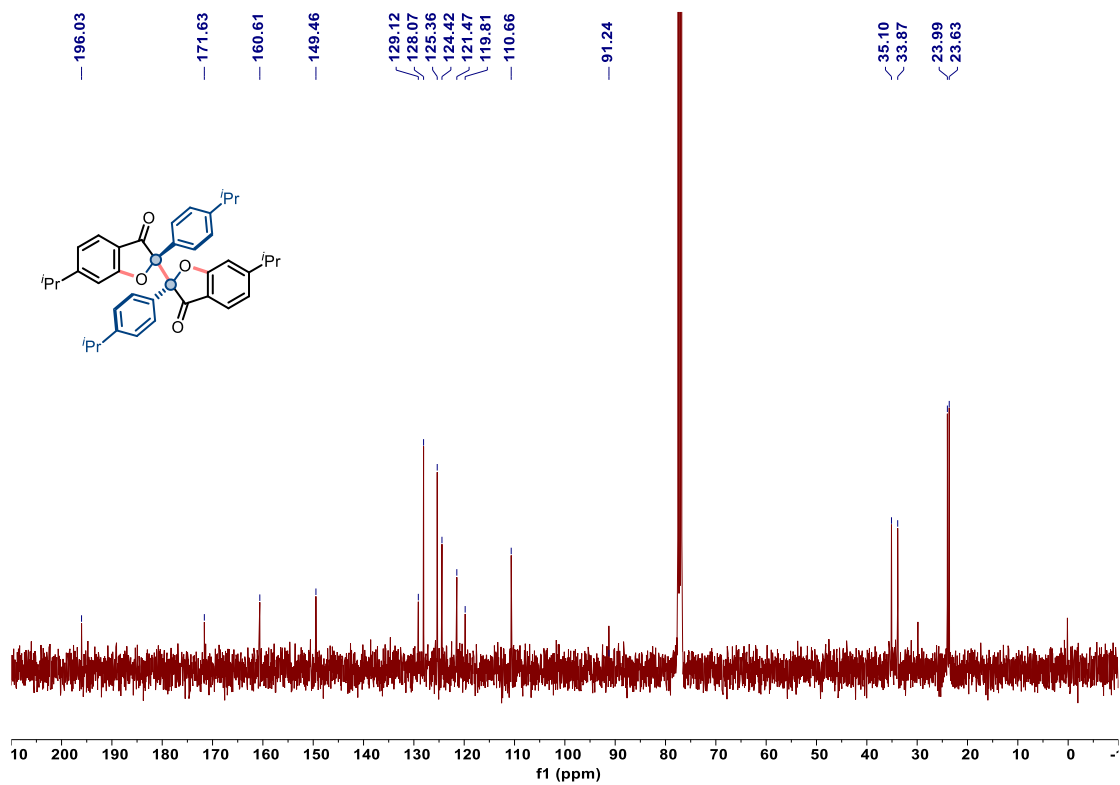
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2c-1**



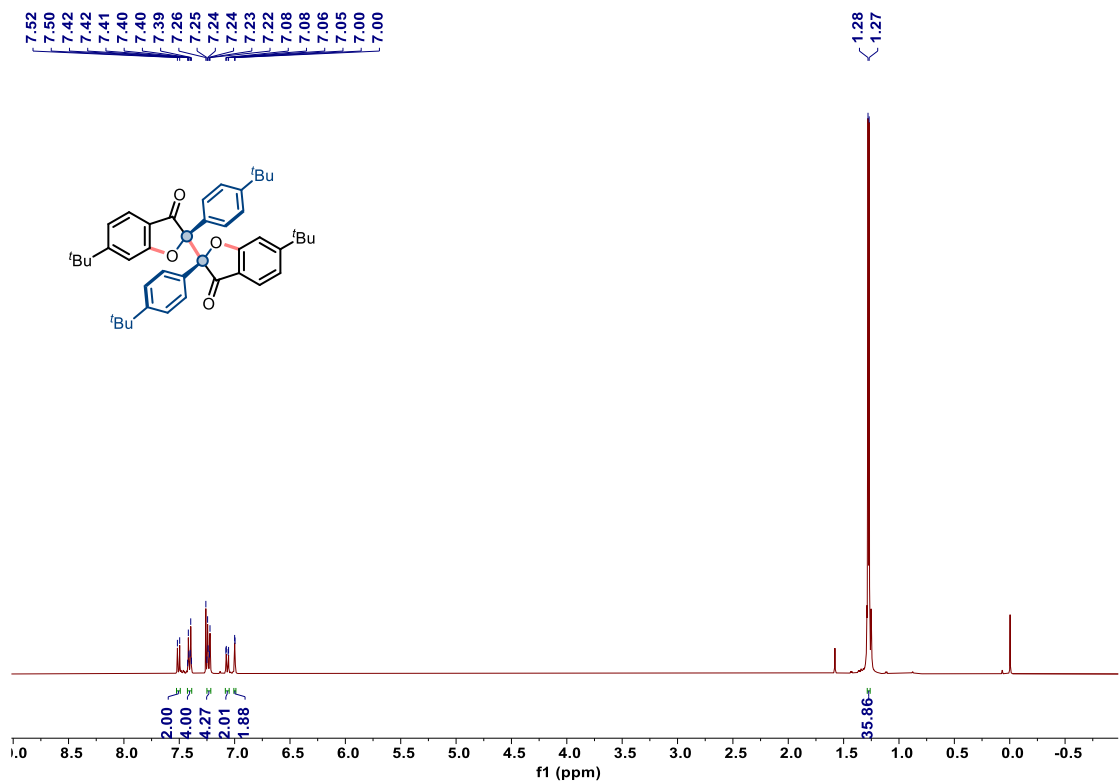
^1H NMR (400 MHz, CDCl_3) spectra of compound **2c-2**



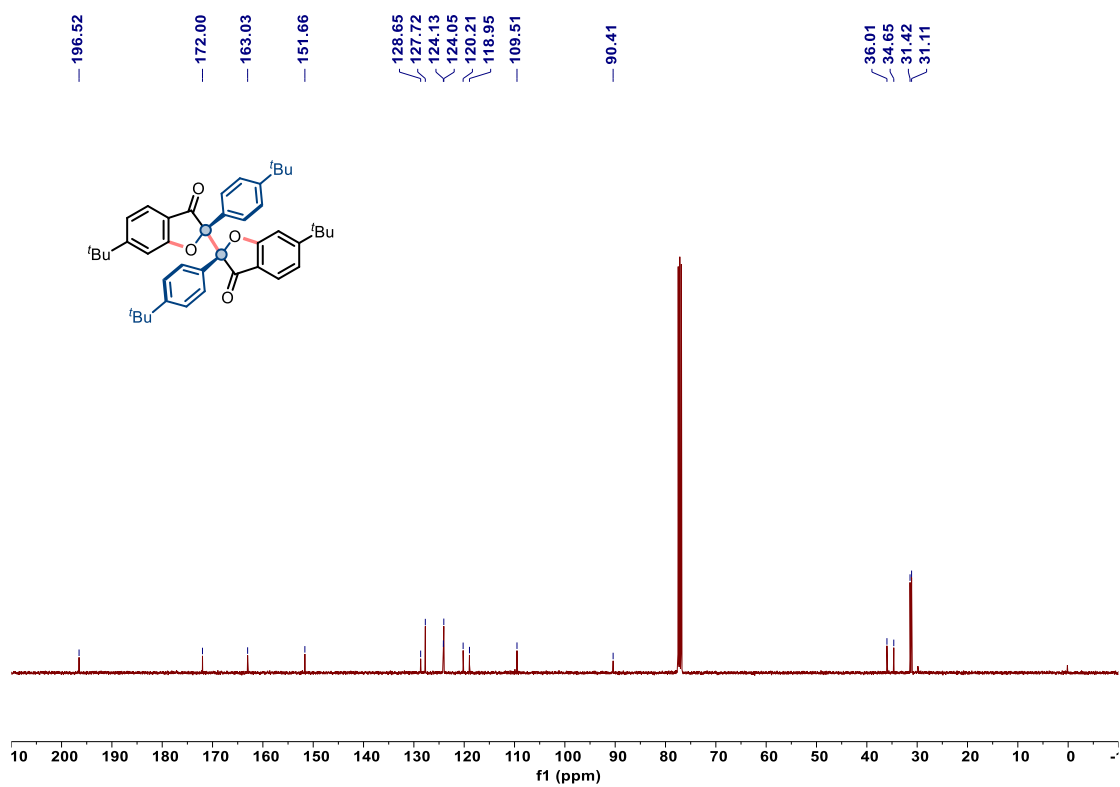
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2c-2**



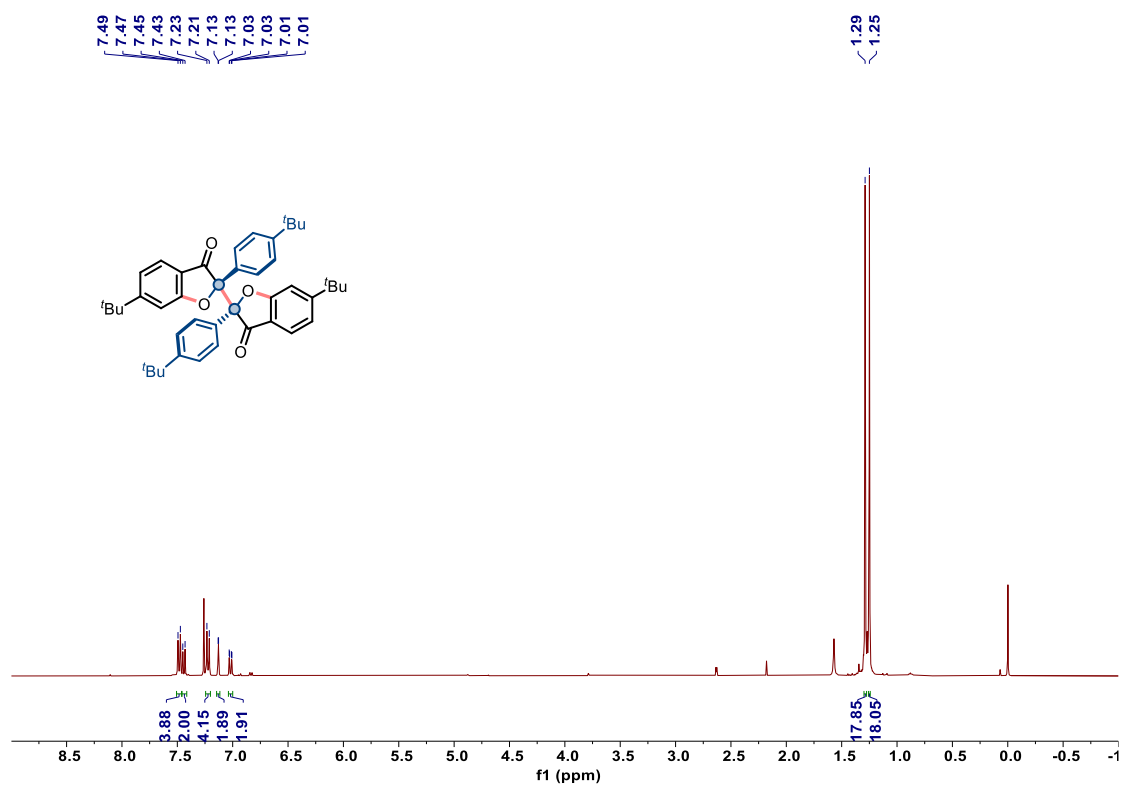
^1H NMR (400 MHz, CDCl_3) spectra of compound **2d-1**



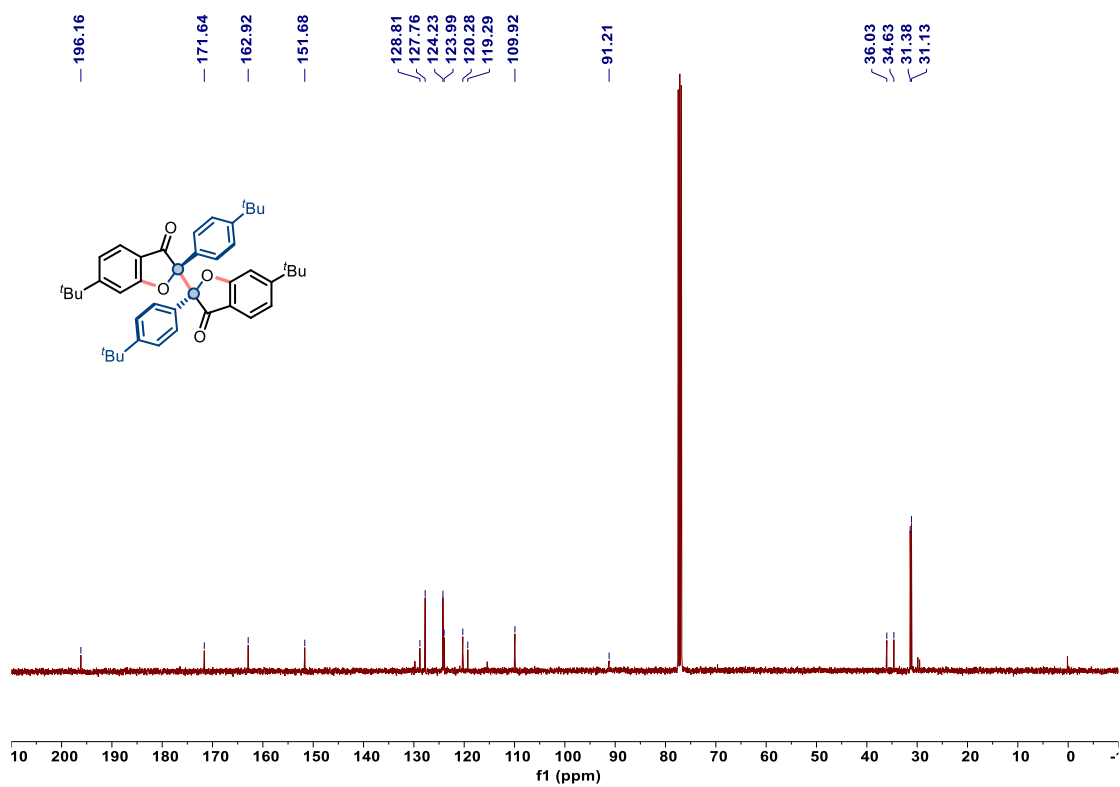
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2d-1**



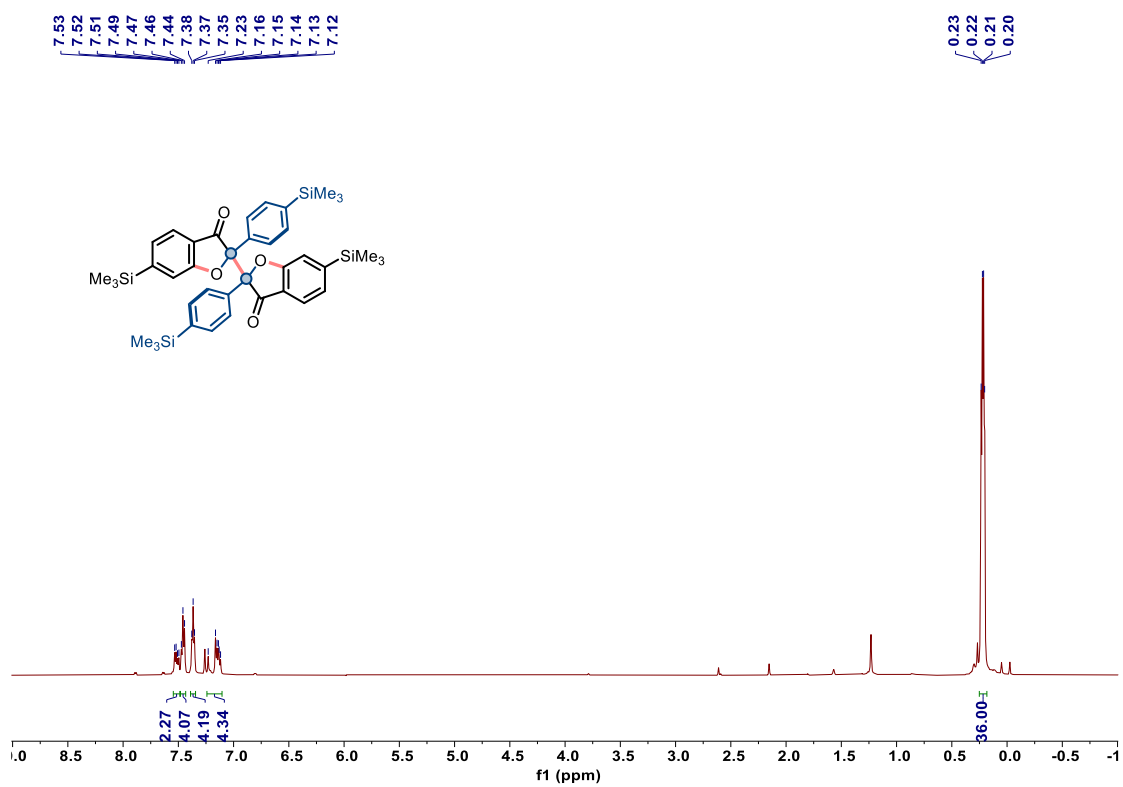
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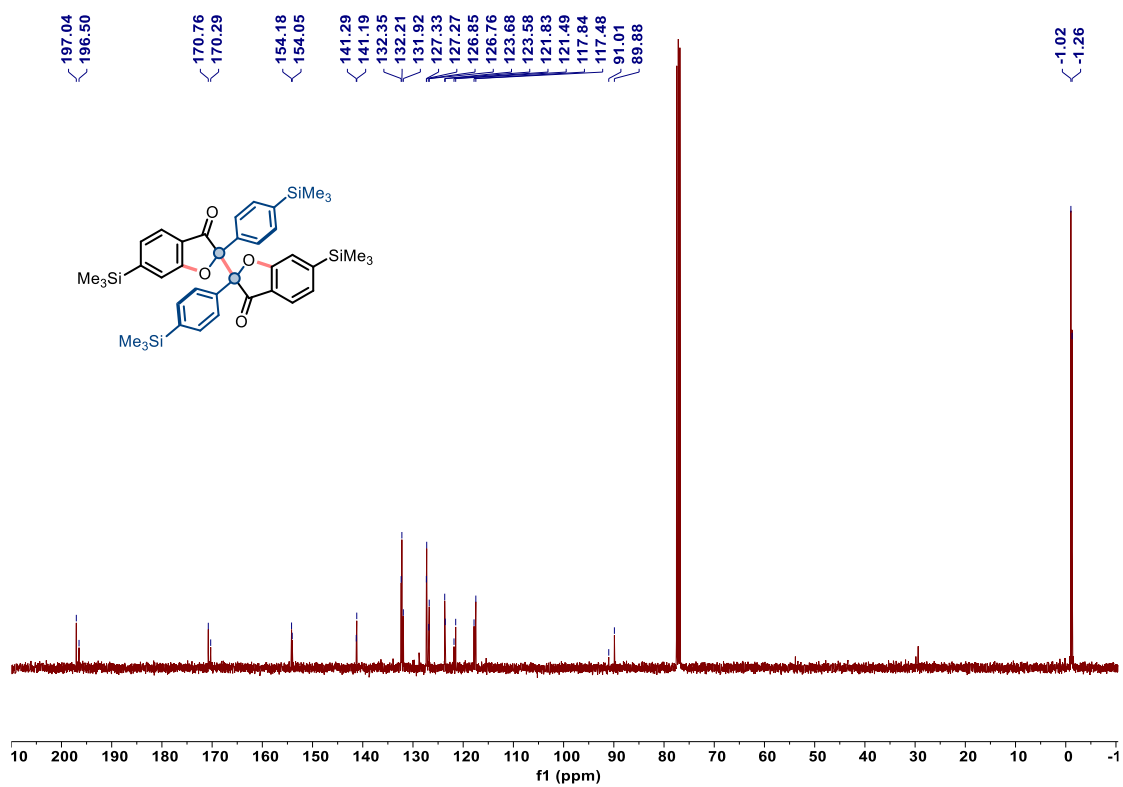
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2d-2**



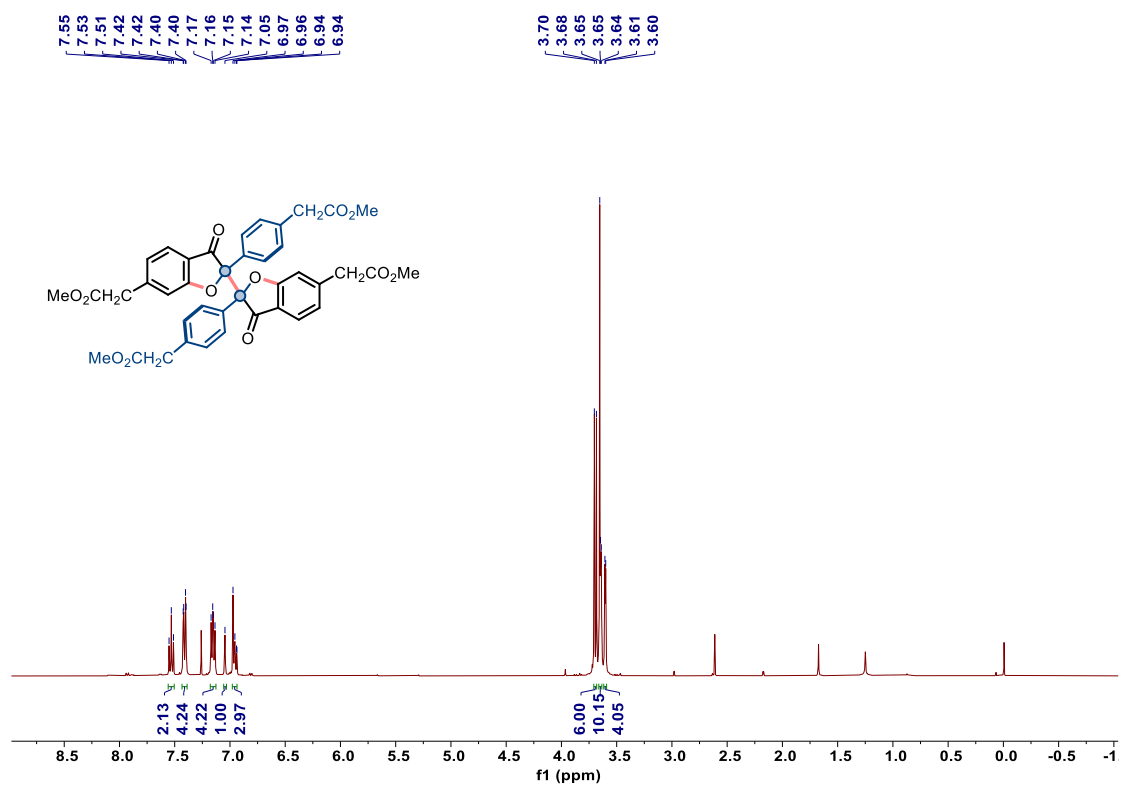
^1H NMR (600 MHz, CDCl_3) spectra of compound **2e**



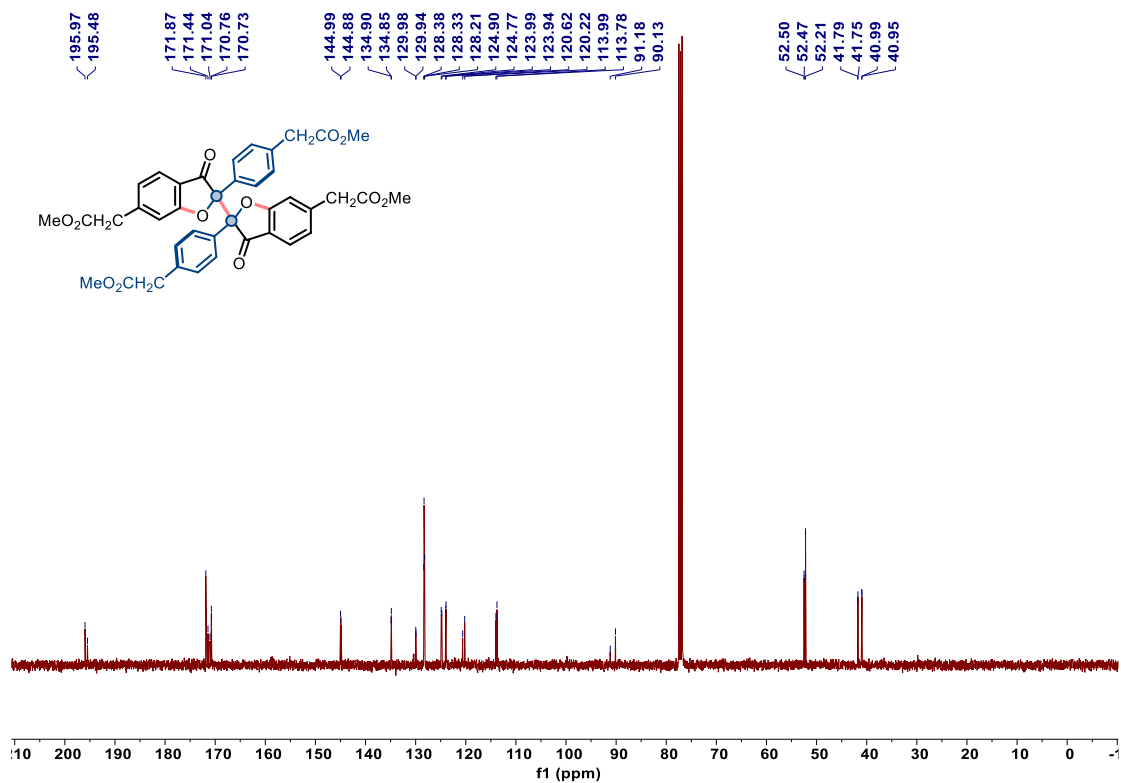
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2e**



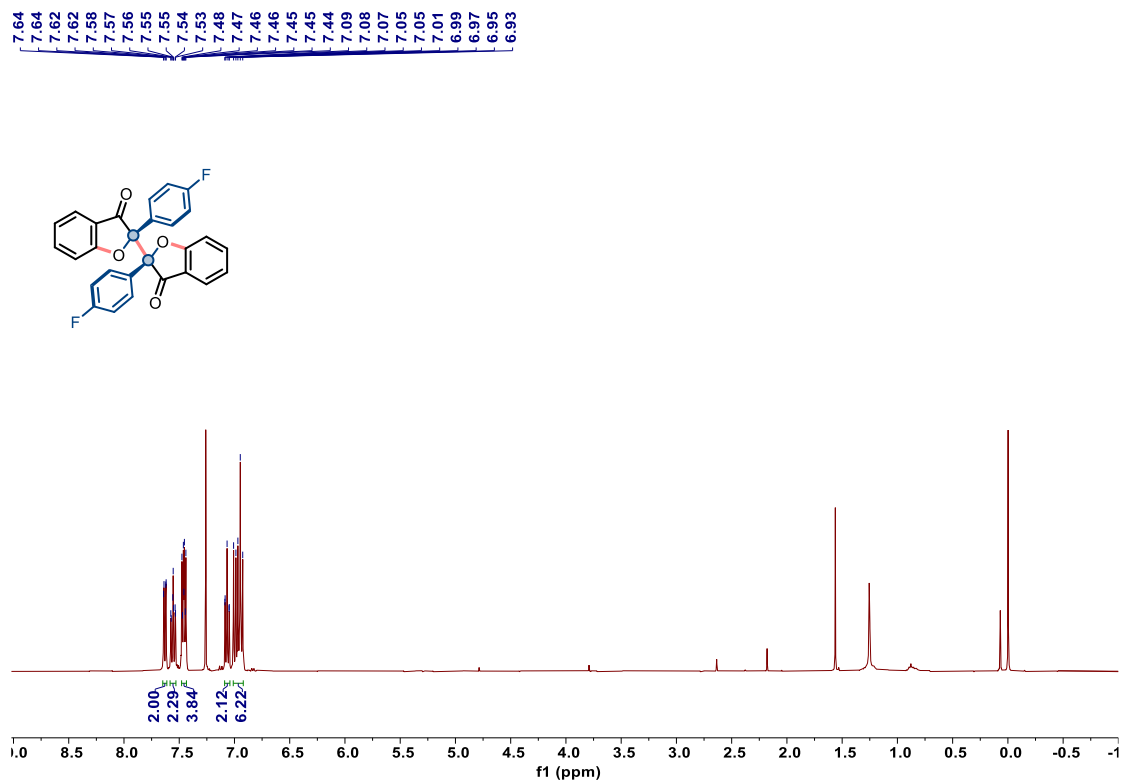
^1H NMR (400 MHz, CDCl_3) spectra of compound **2f**



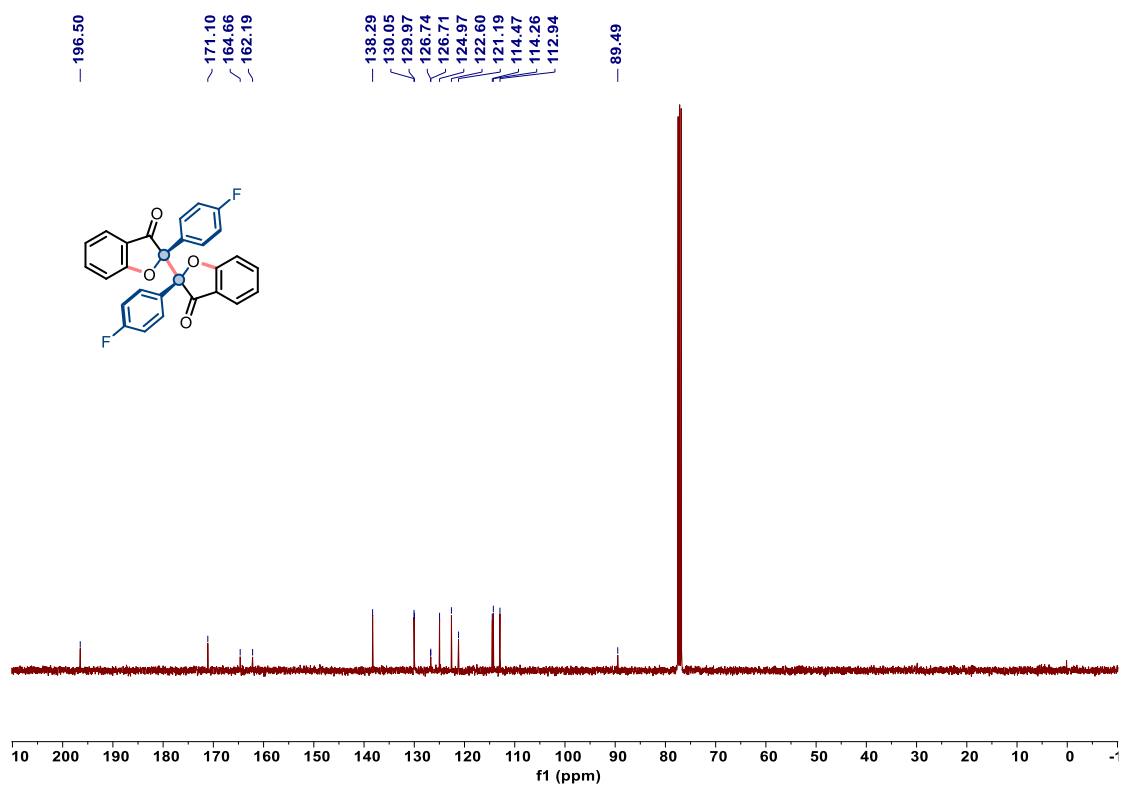
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2f**



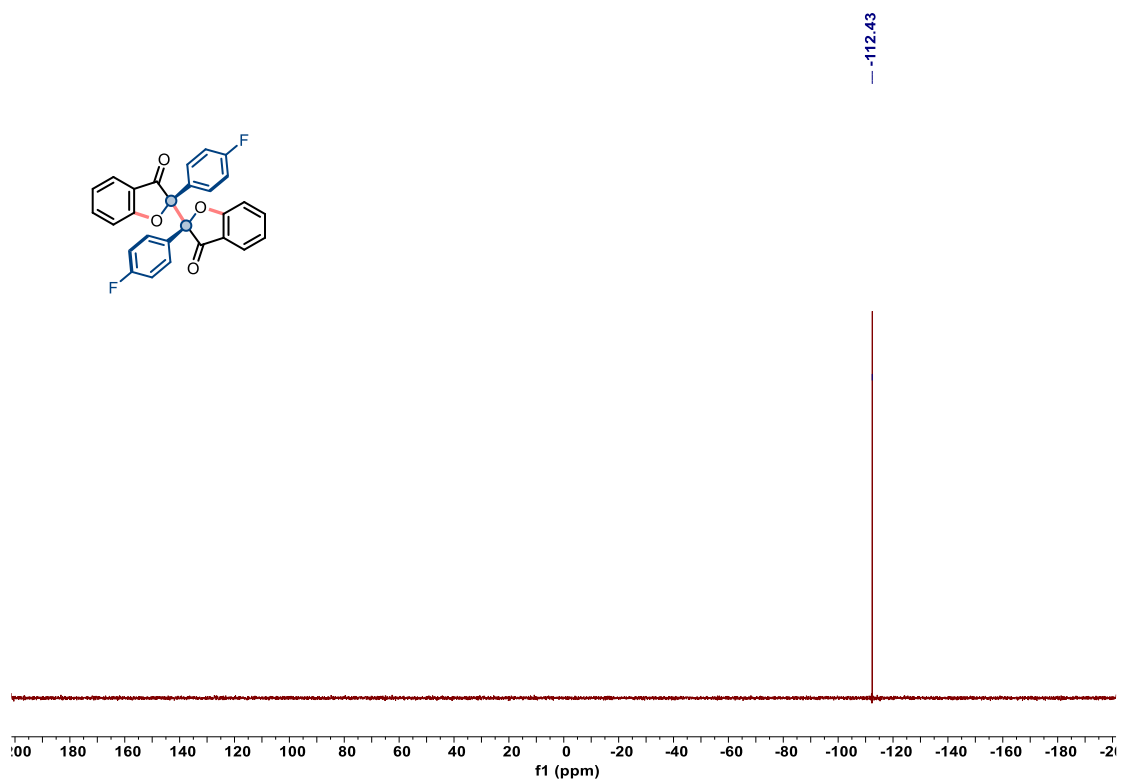
^1H NMR (400 MHz, CDCl_3) spectra of compound **2g-1**



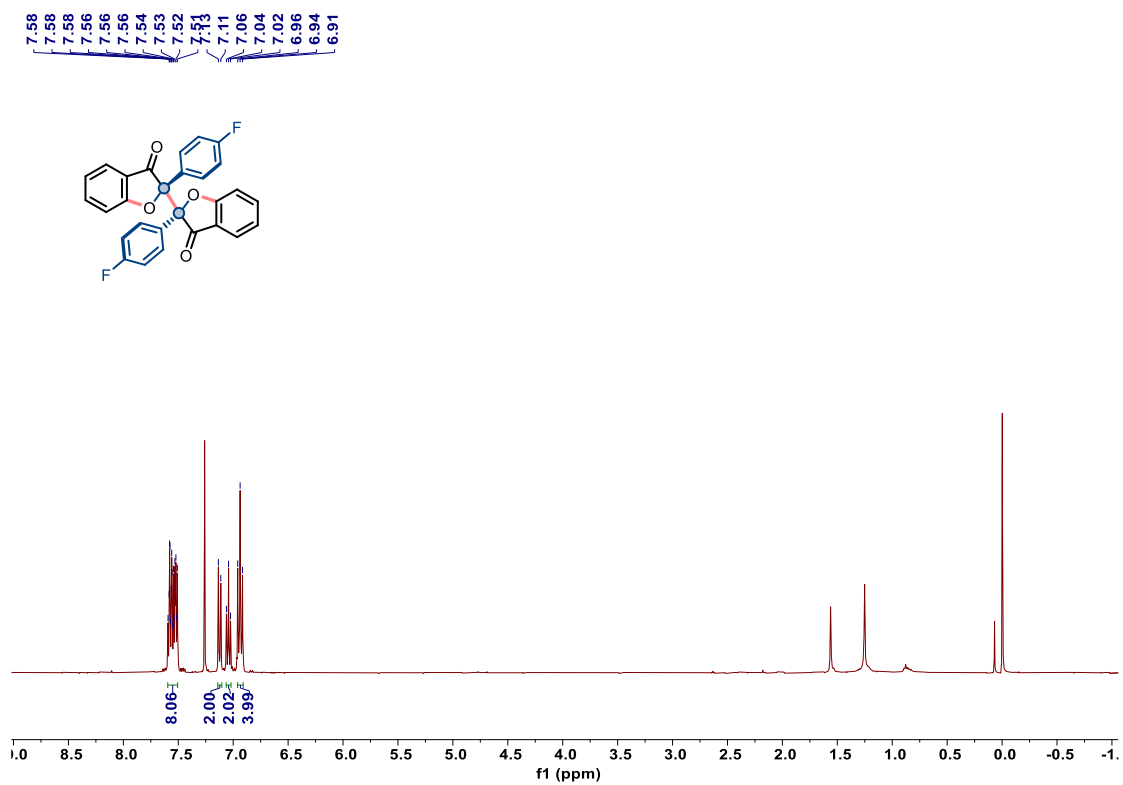
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2g-1**



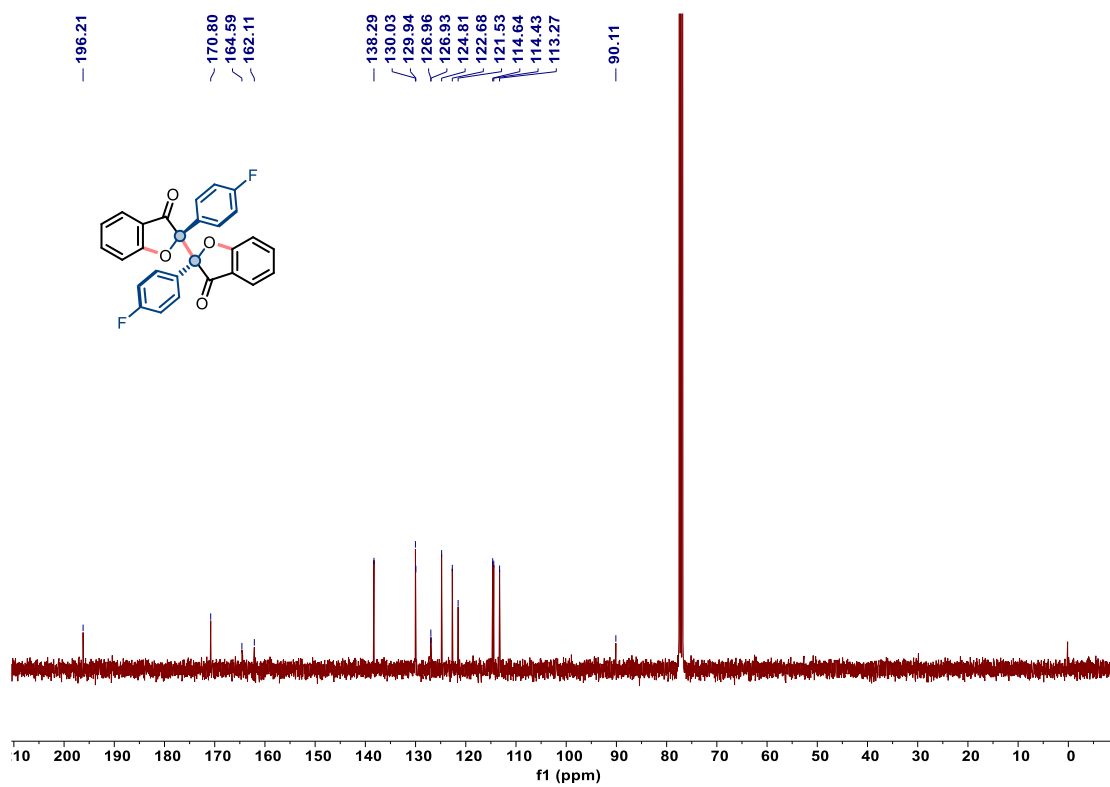
^{19}F NMR (376 MHz, CDCl_3) spectra of compound **2g-1**



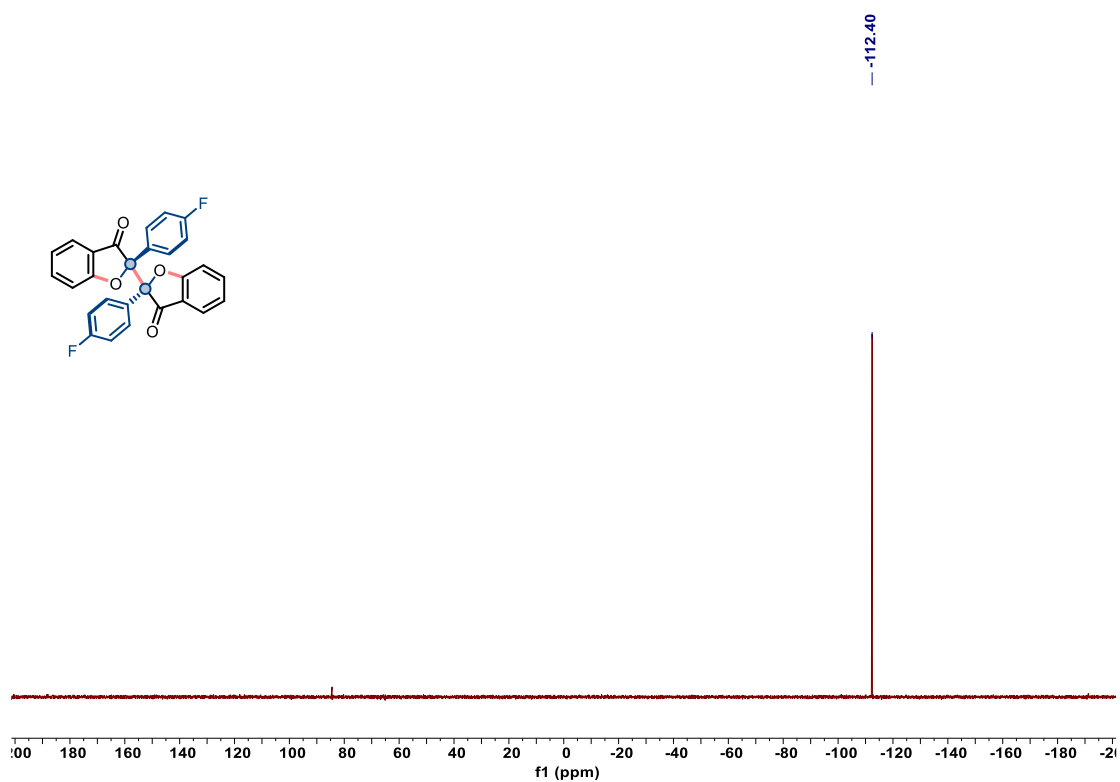
^1H NMR (400 MHz, CDCl_3) spectra of compound **2g-2**



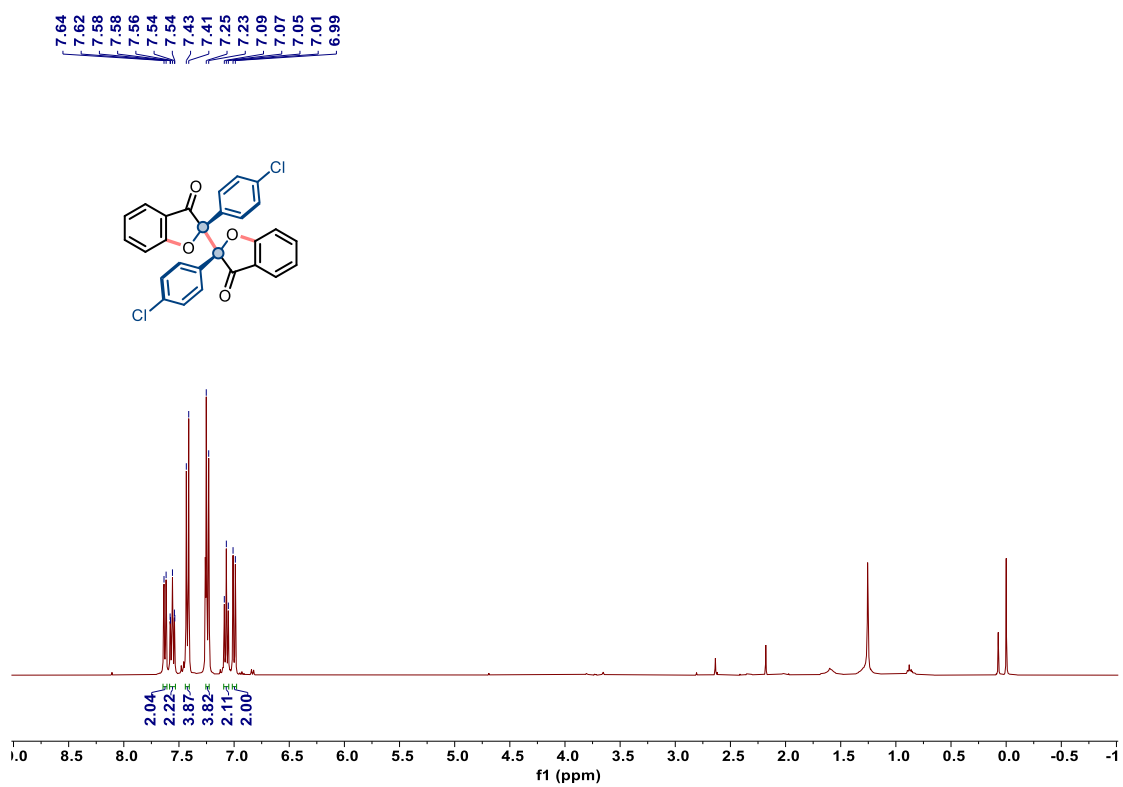
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2g-2**



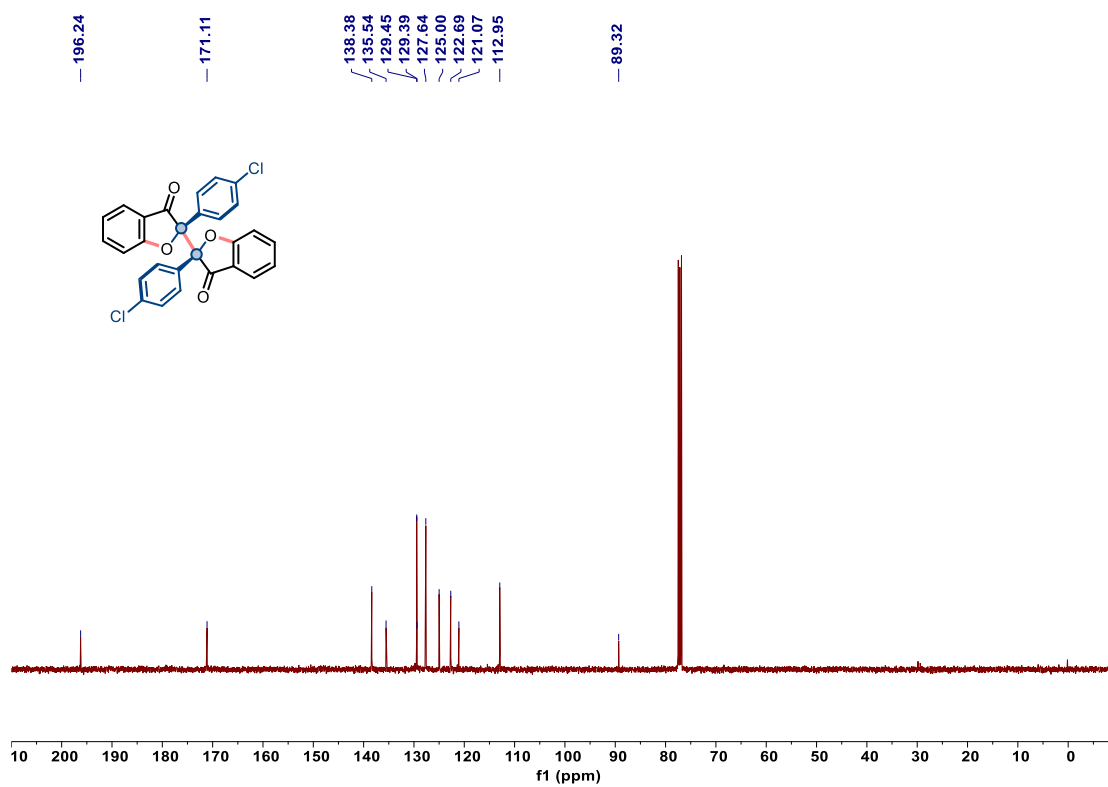
^{19}F NMR (376 MHz, CDCl_3) spectra of compound **2g-2**



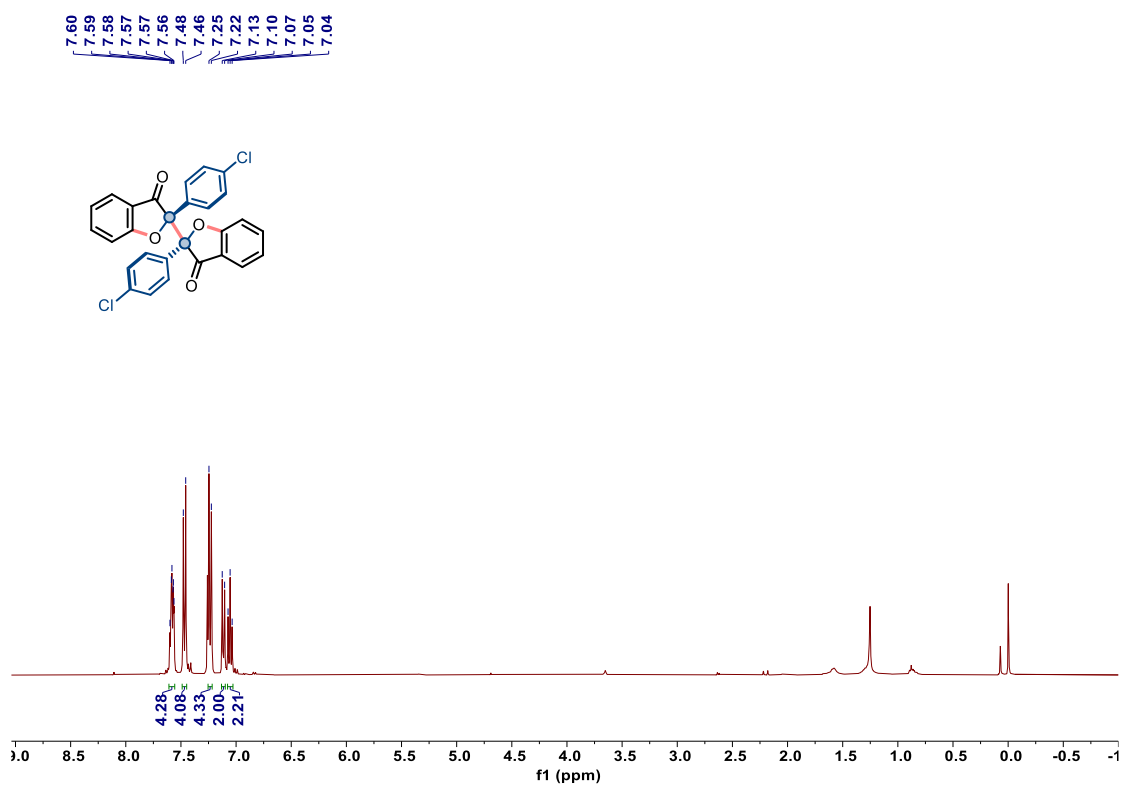
^1H NMR (400 MHz, CDCl_3) spectra of compound **2h-1**



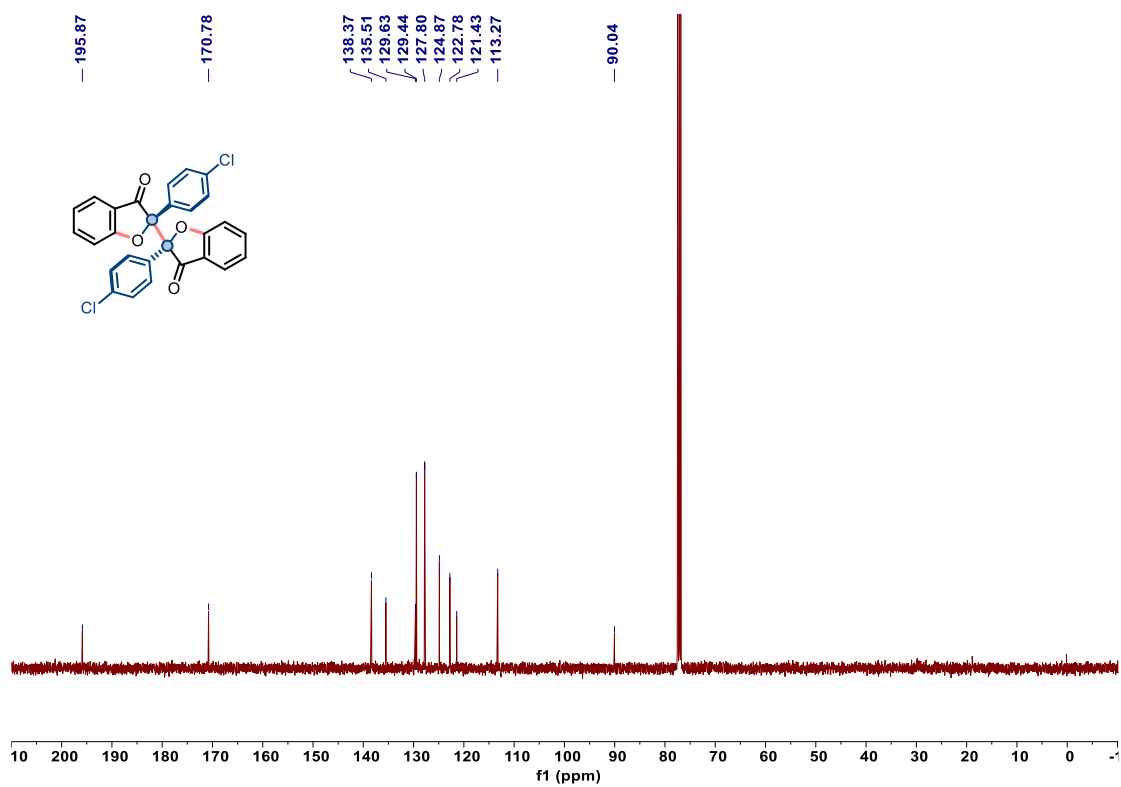
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2h-1**



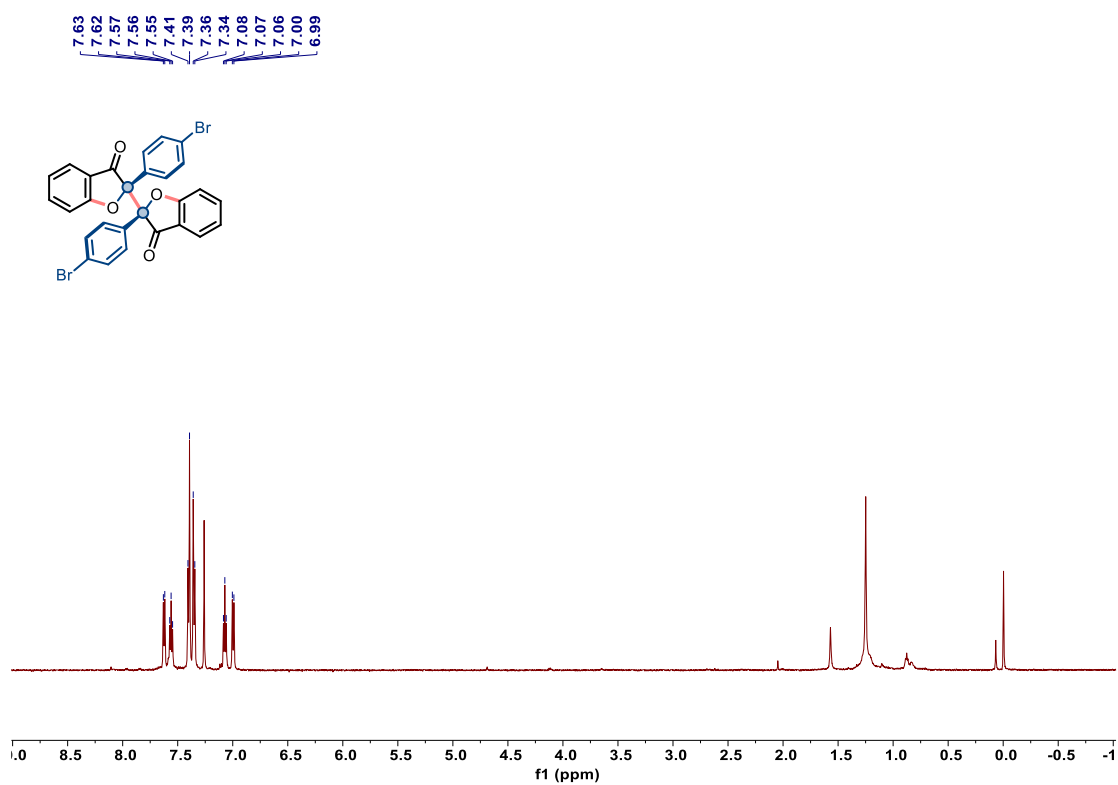
^1H NMR (400 MHz, CDCl_3) spectra of compound **2h-2**



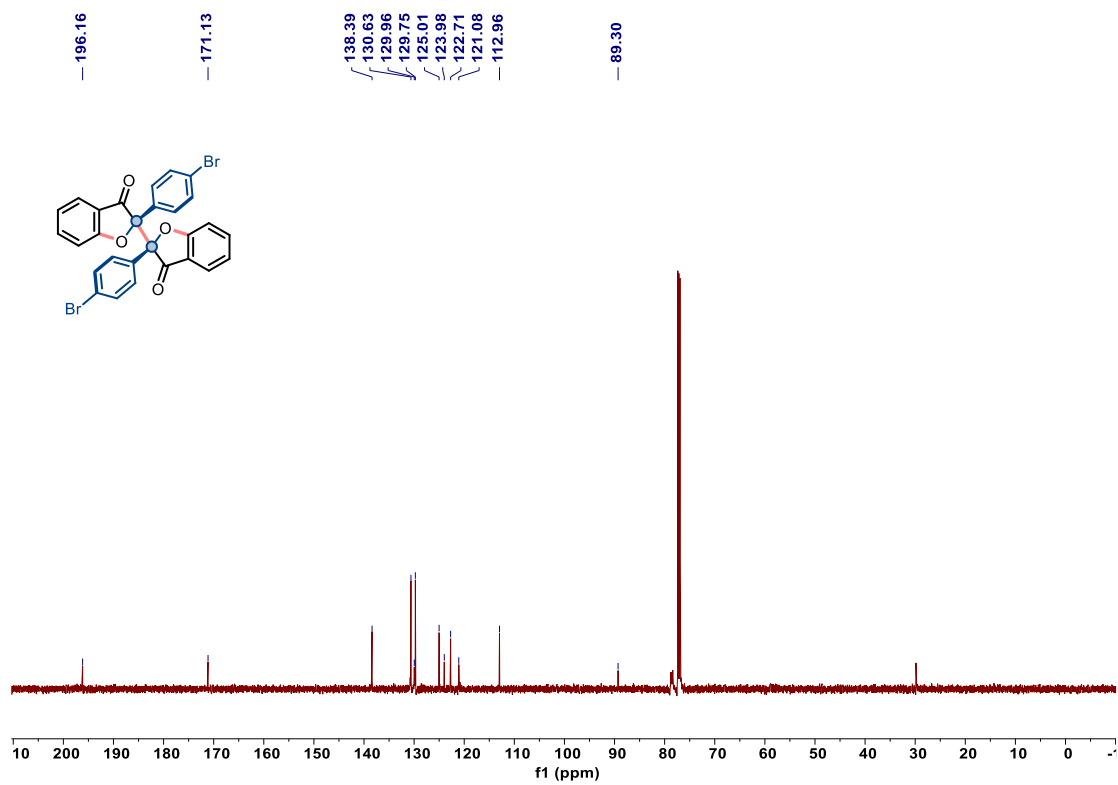
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2h-2**



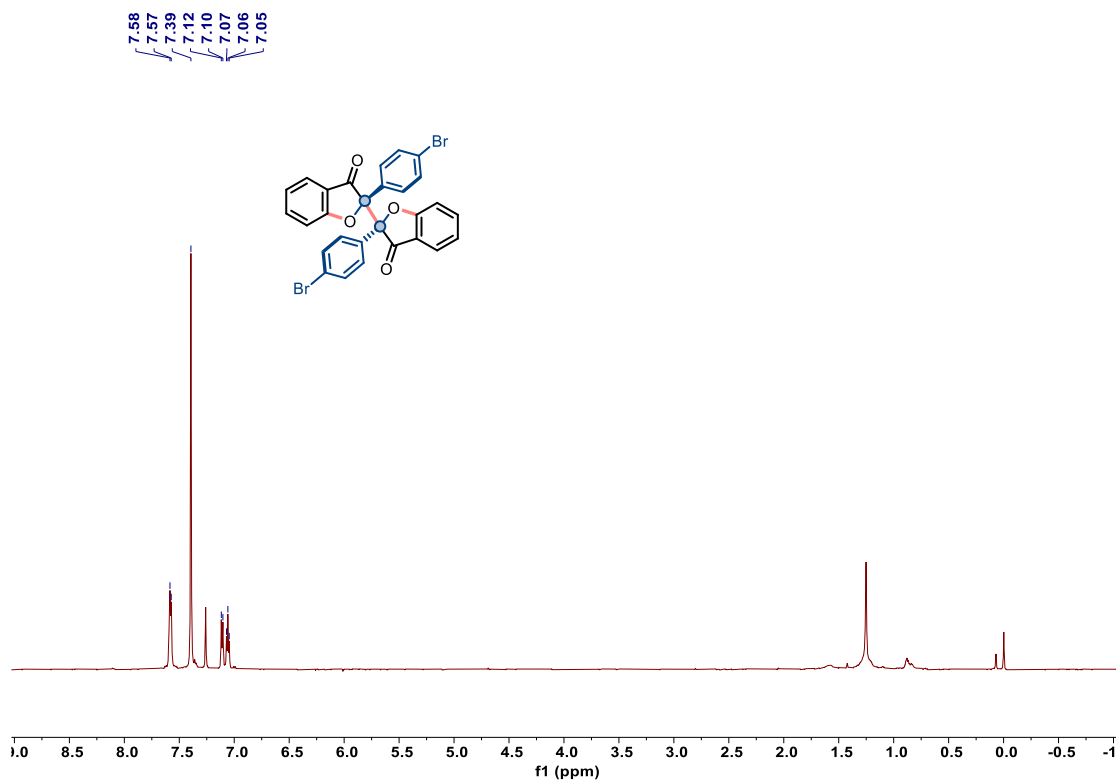
^1H NMR (600 MHz, CDCl_3) spectra of compound **2i-1**



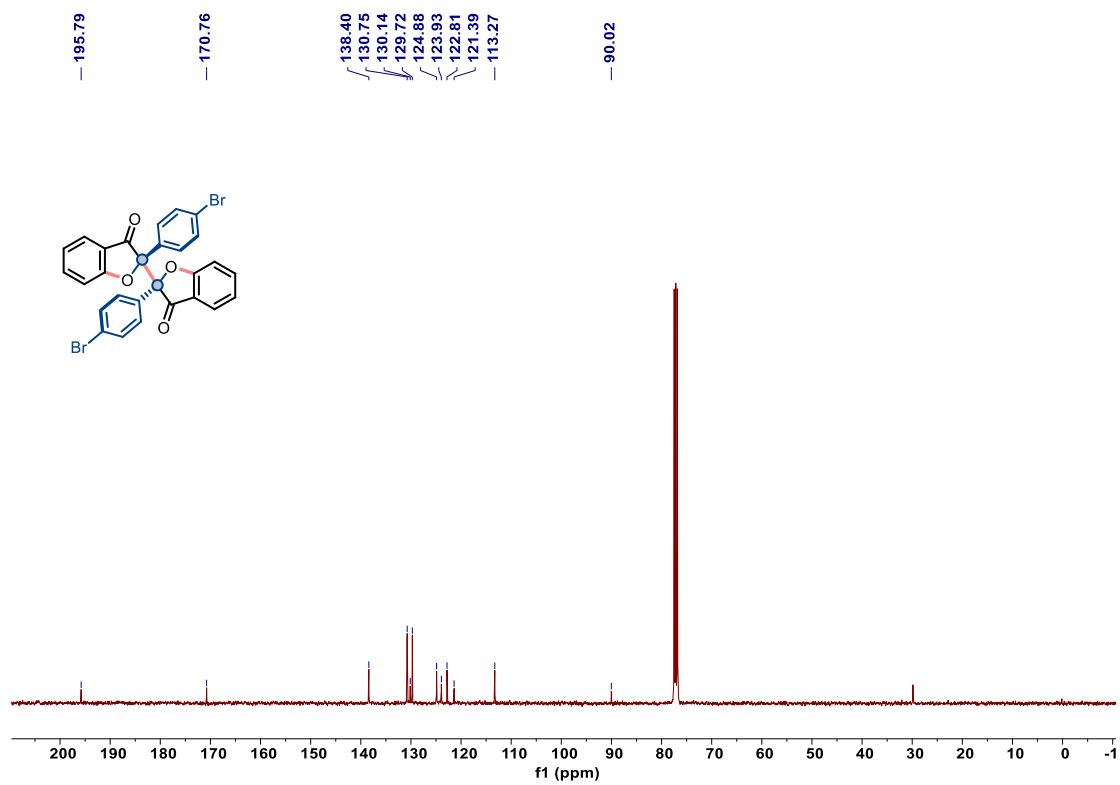
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **2i-1**



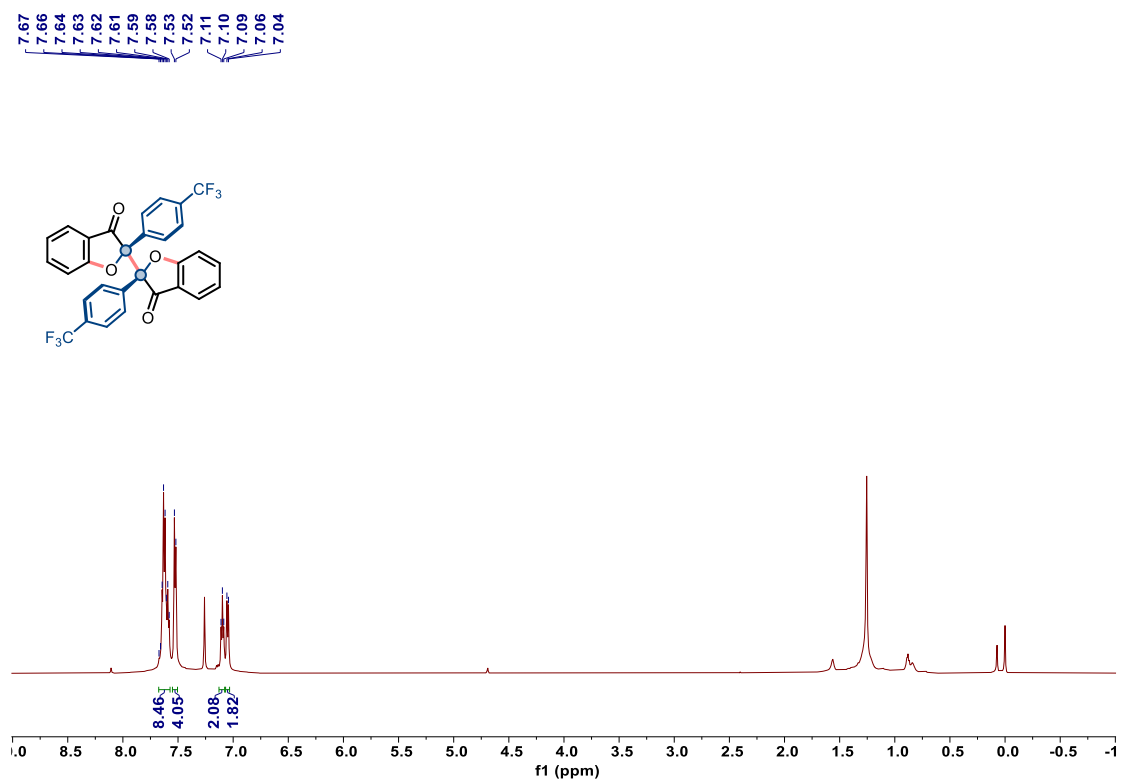
^1H NMR (600 MHz, CDCl_3) spectra of compound **2i-2**



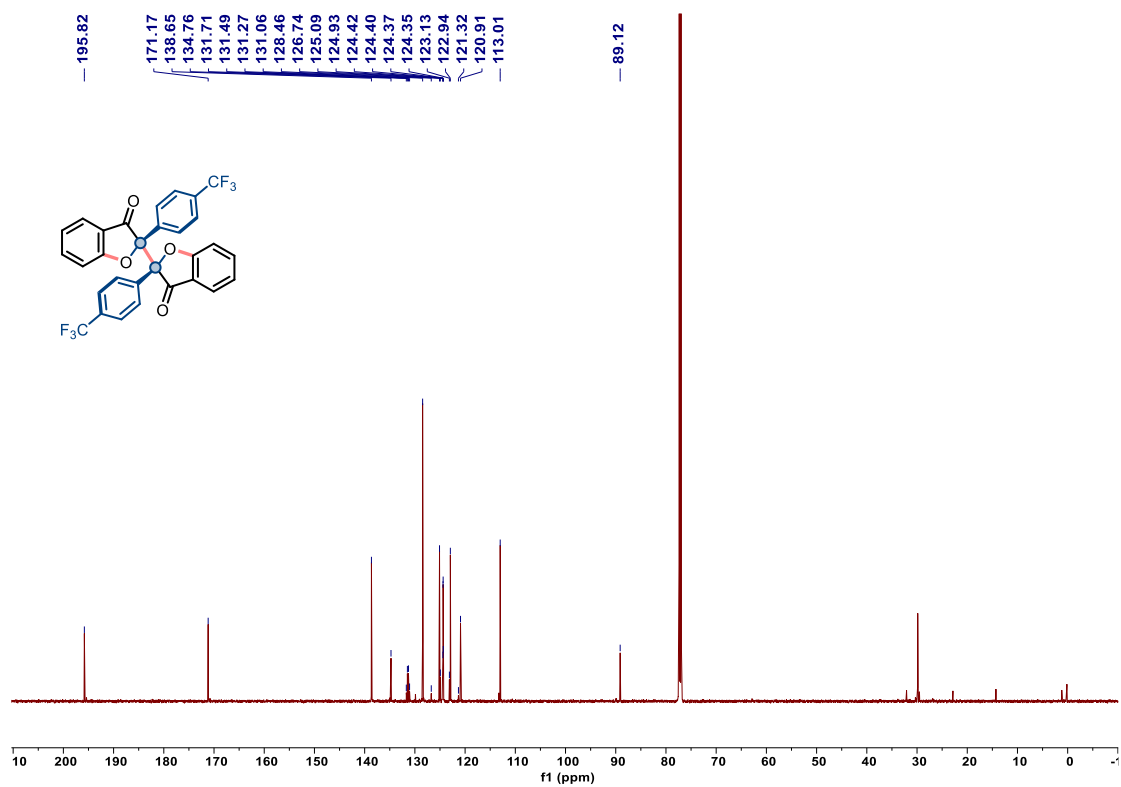
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2i-2**



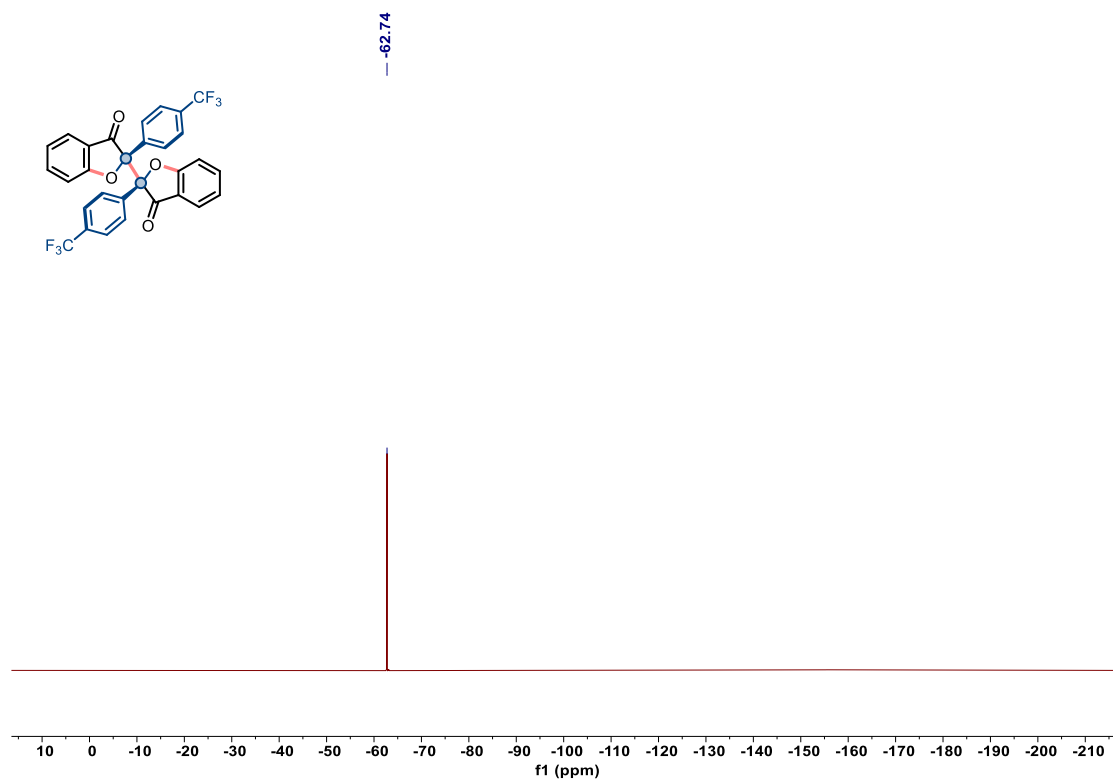
^1H NMR (600 MHz, CDCl_3) spectra of compound **2j-1**



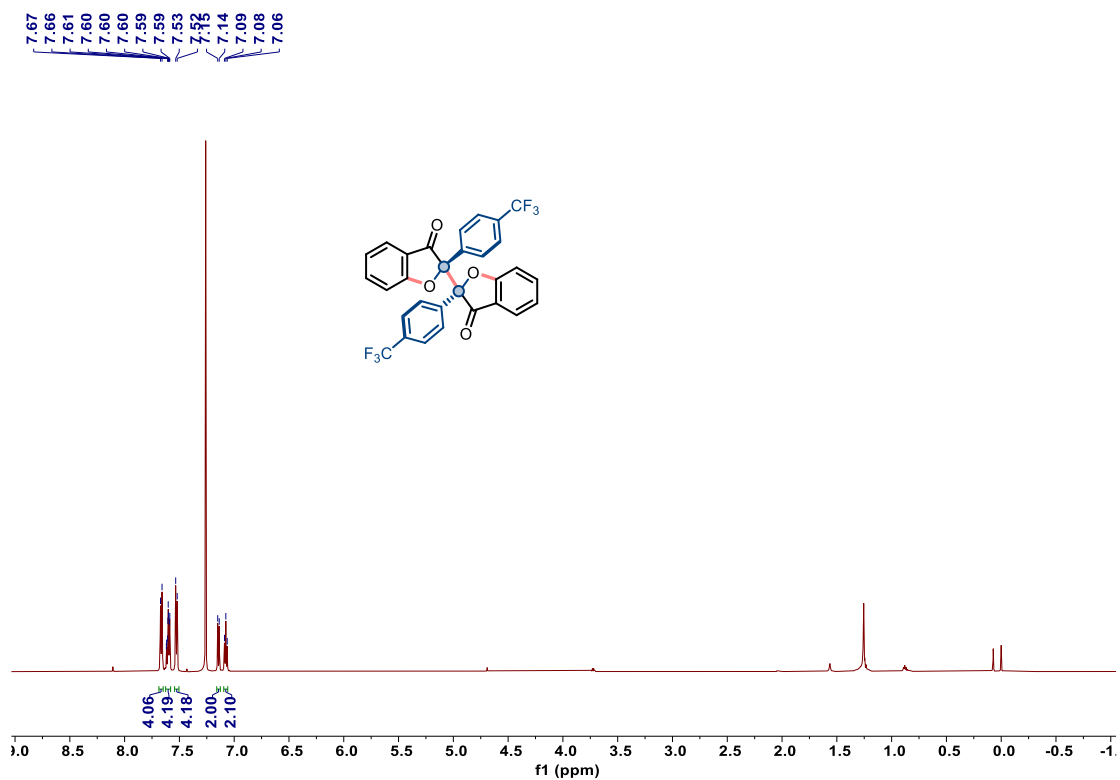
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **2j-1**



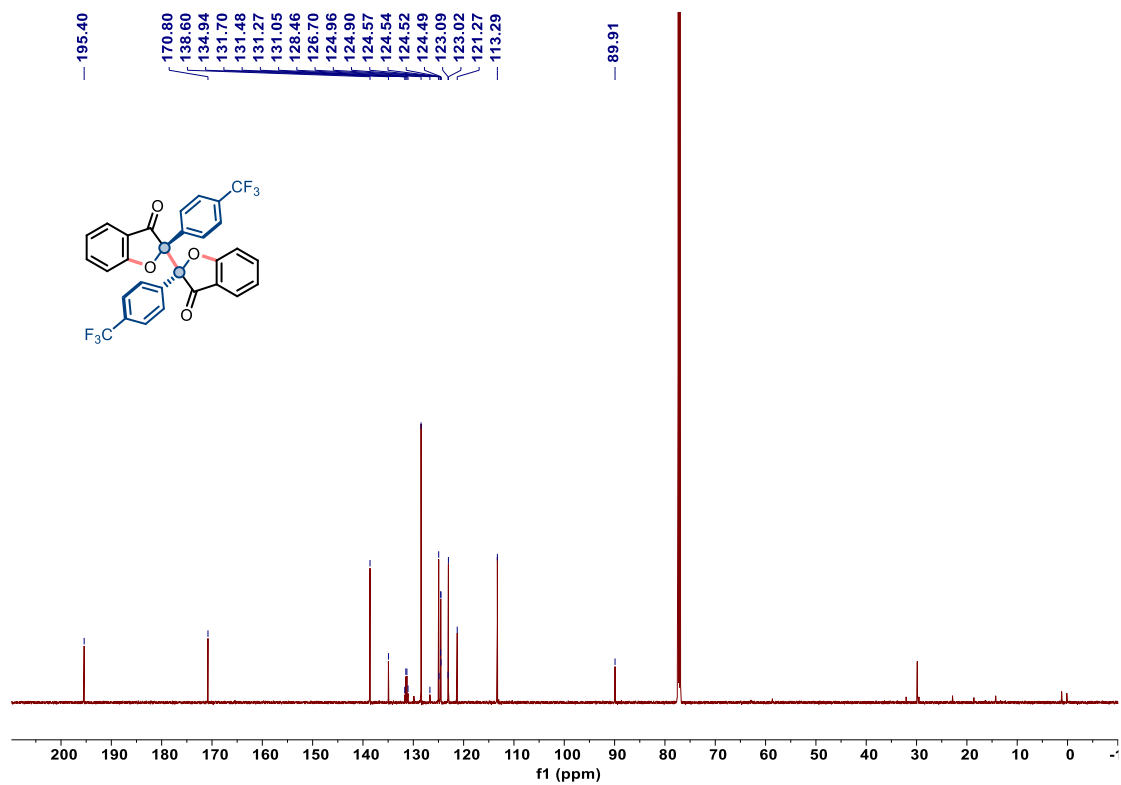
^{19}F NMR (565 MHz, CDCl_3) spectra of compound **2j-1**



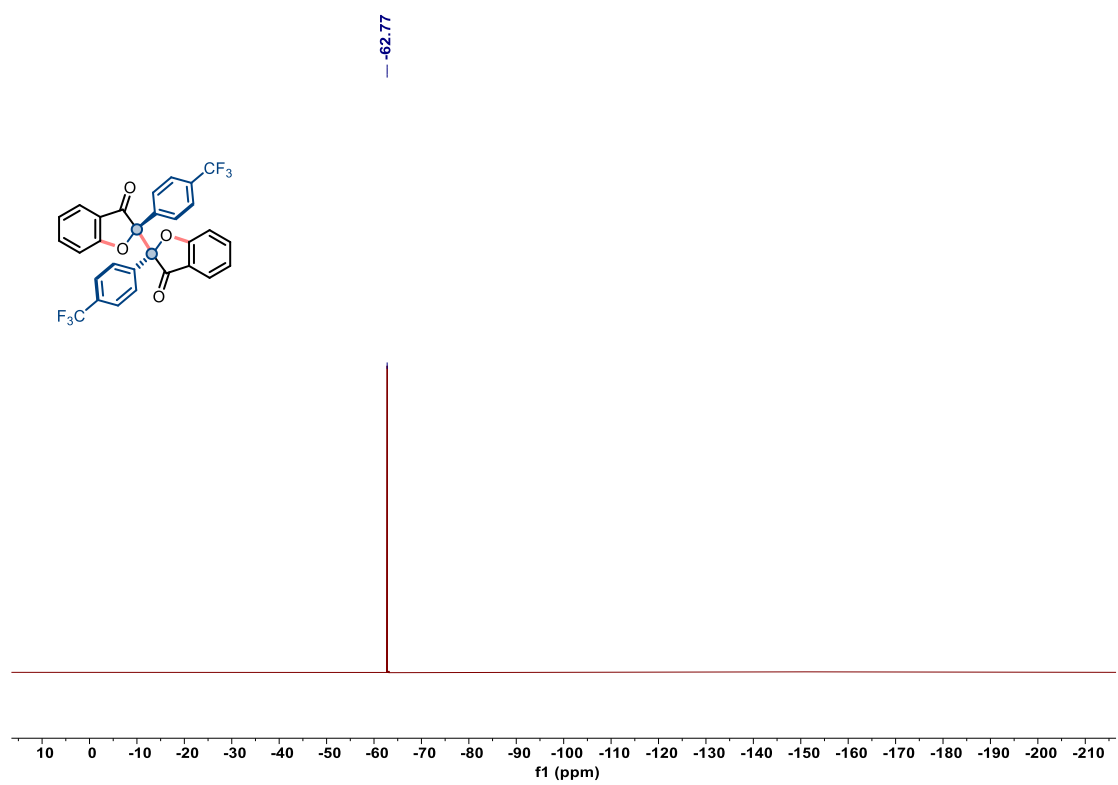
^1H NMR (600 MHz, CDCl_3) spectra of compound **2j-2**



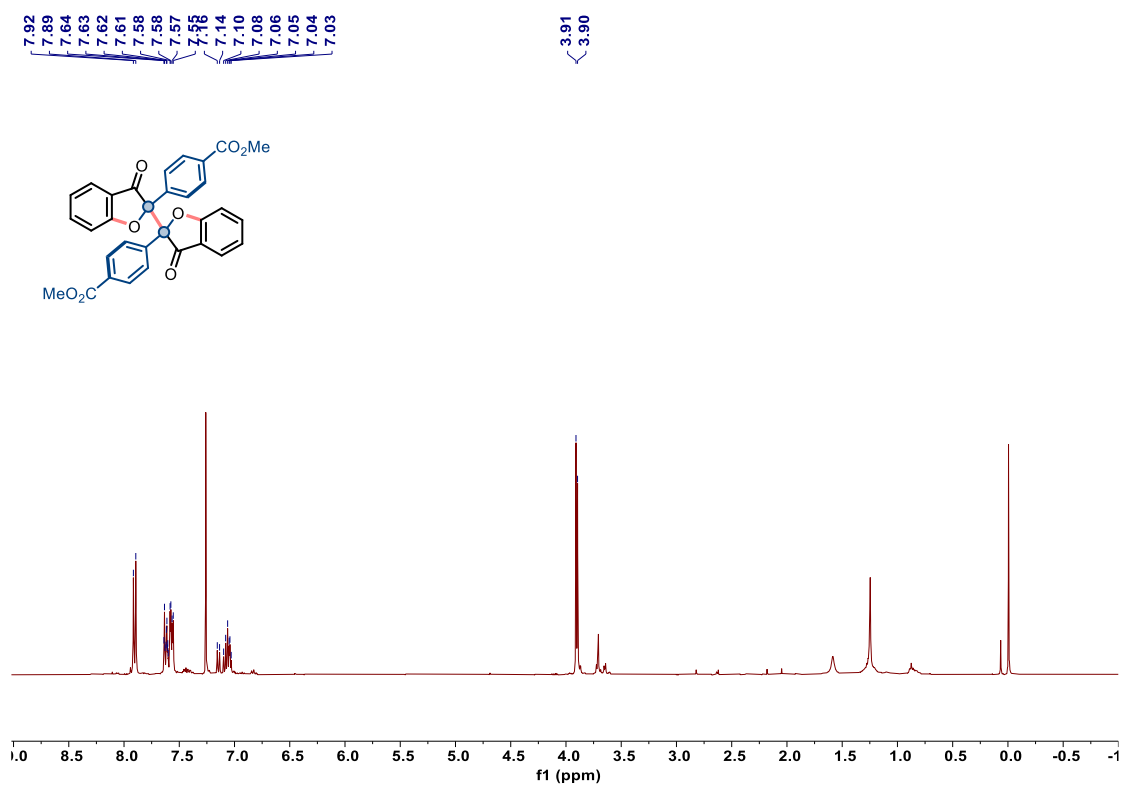
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **2j-2**



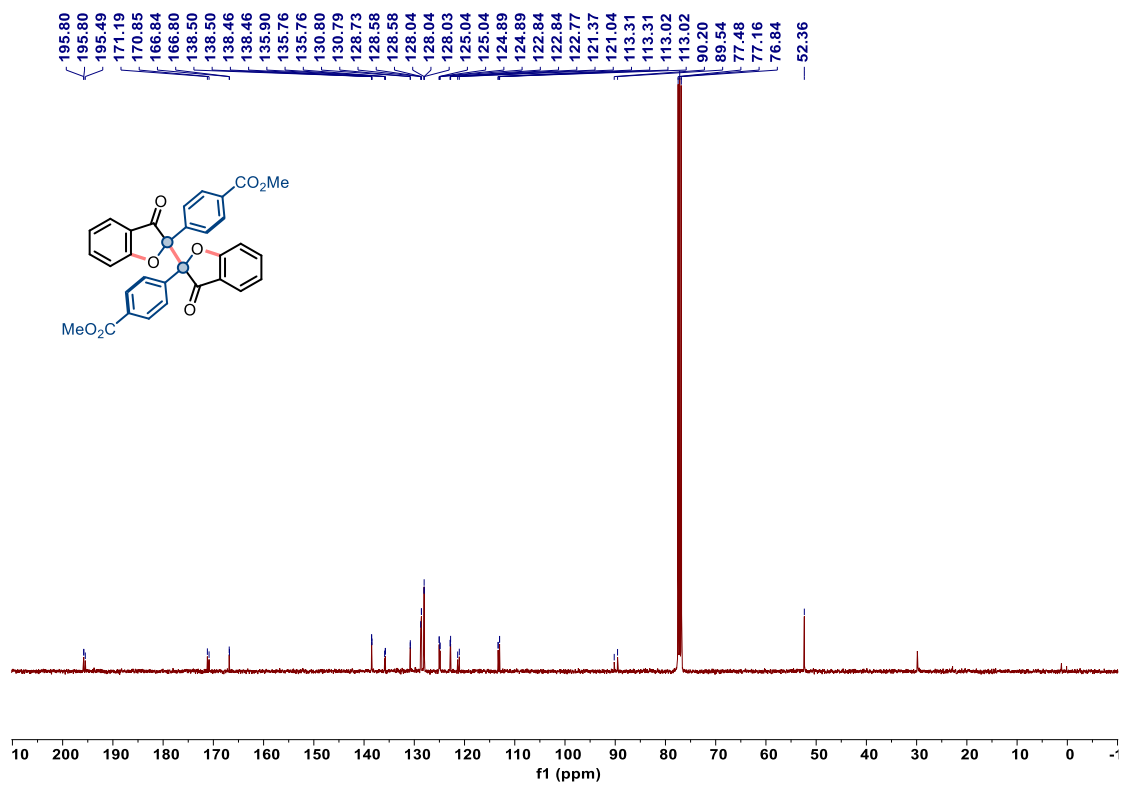
^{19}F NMR (565 MHz, CDCl_3) spectra of compound **2j-2**



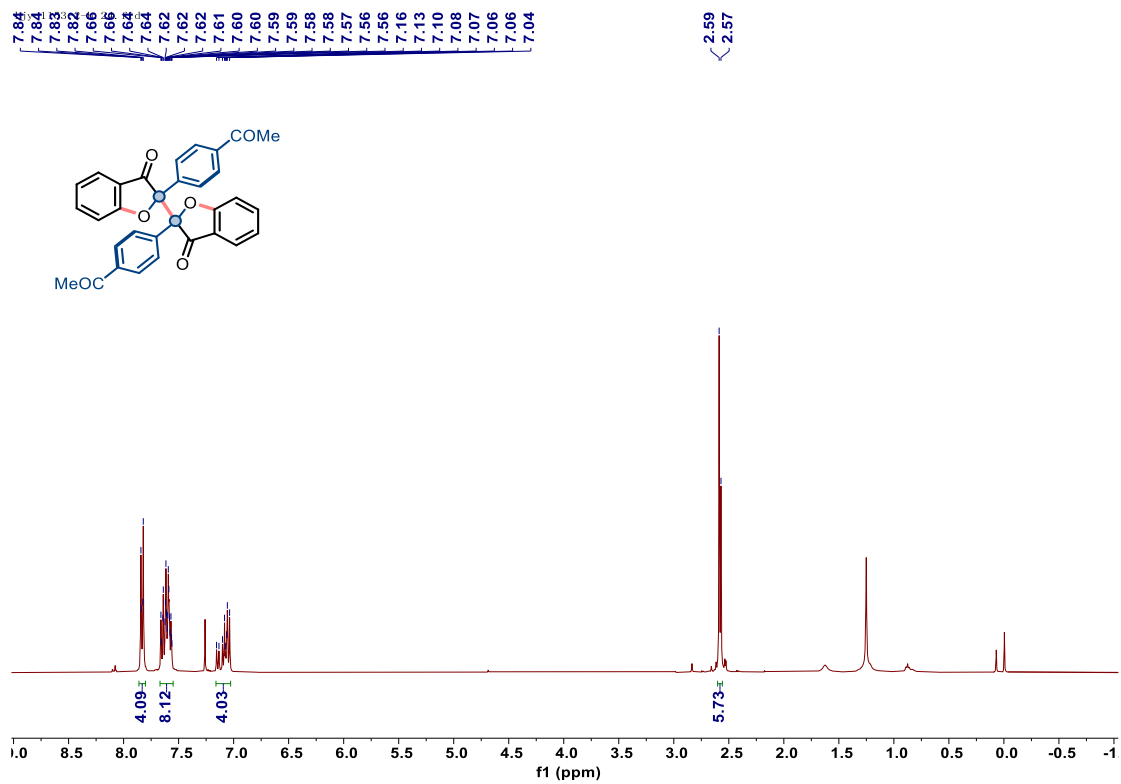
^1H NMR (400 MHz, CDCl_3) spectra of compound **2k**



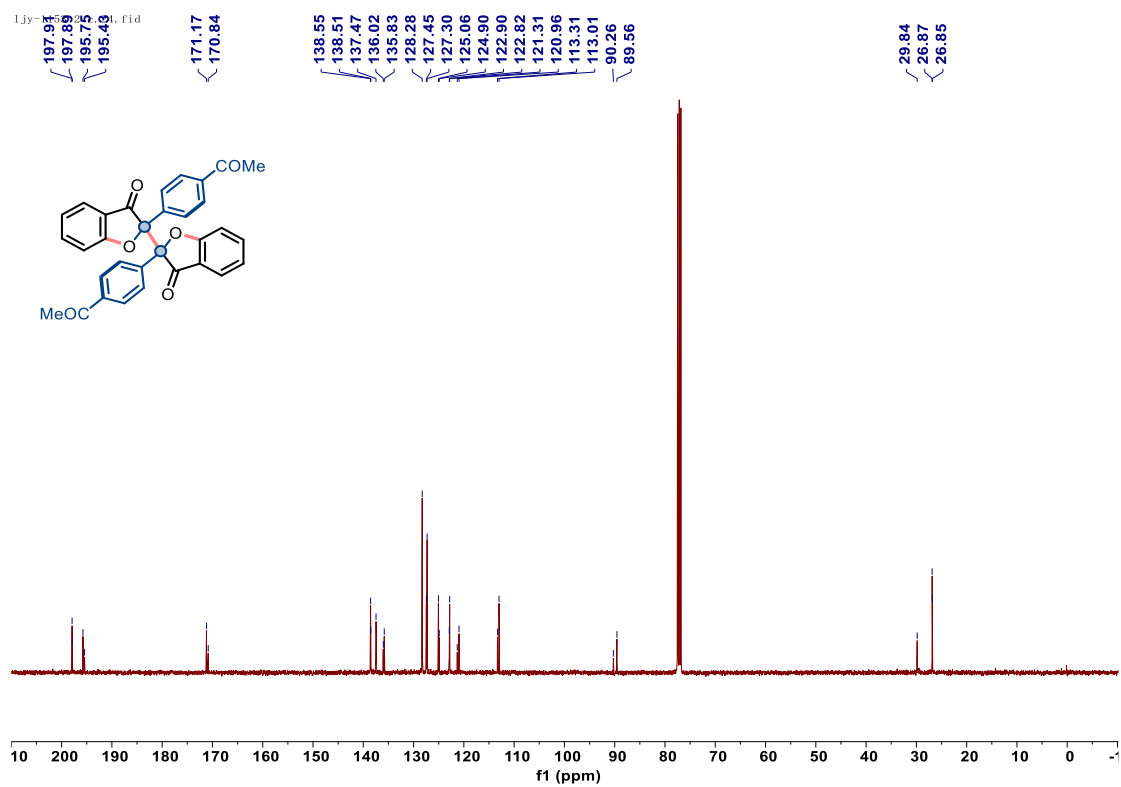
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2k**



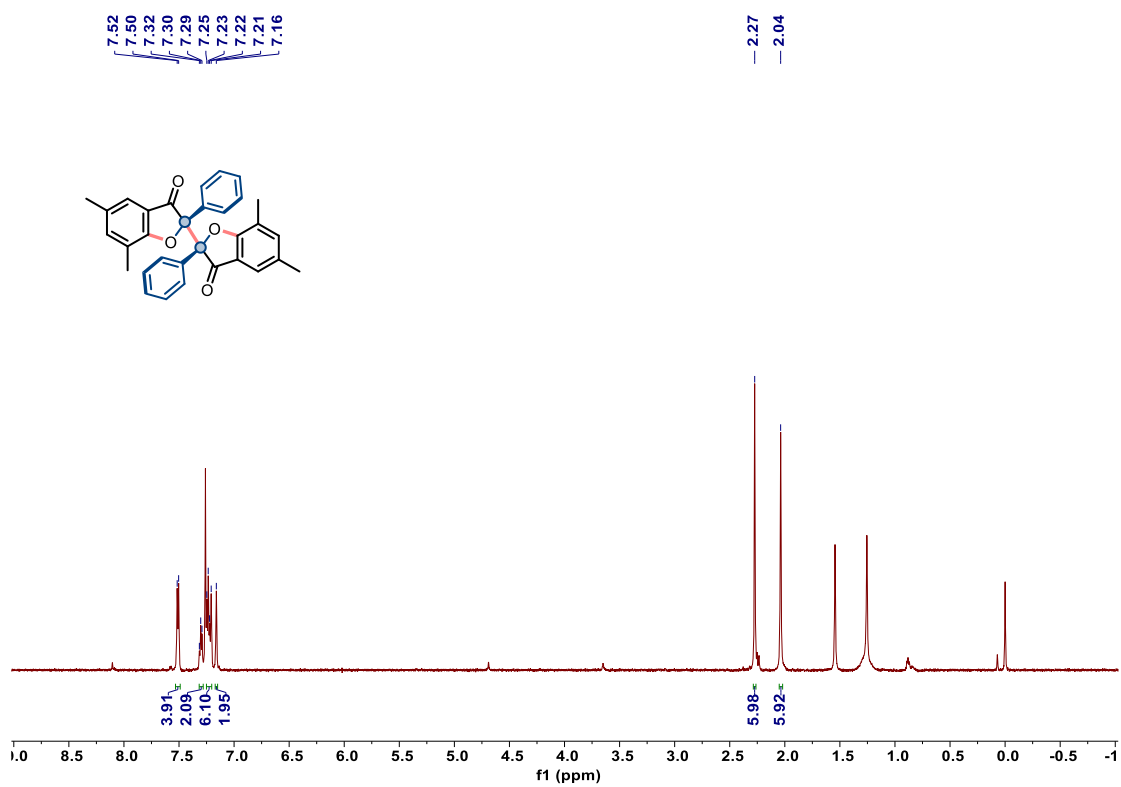
^1H NMR (400 MHz, CDCl_3) spectra of compound **2l**



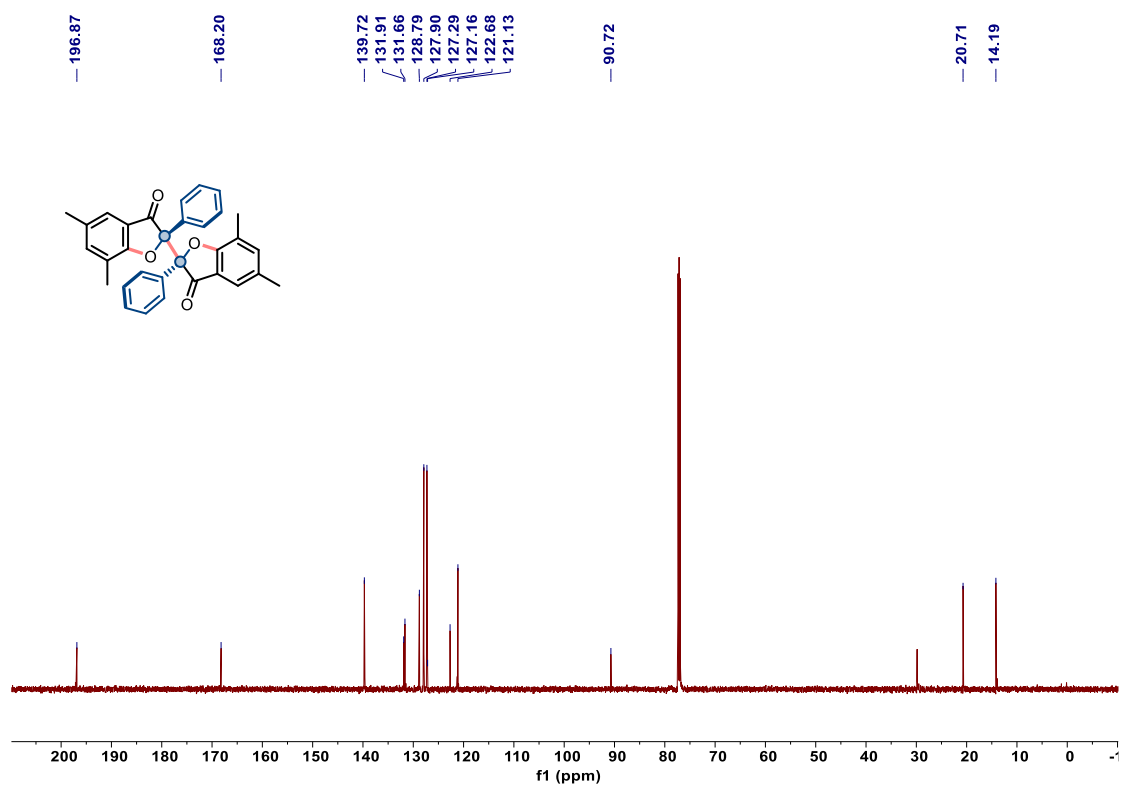
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2l**



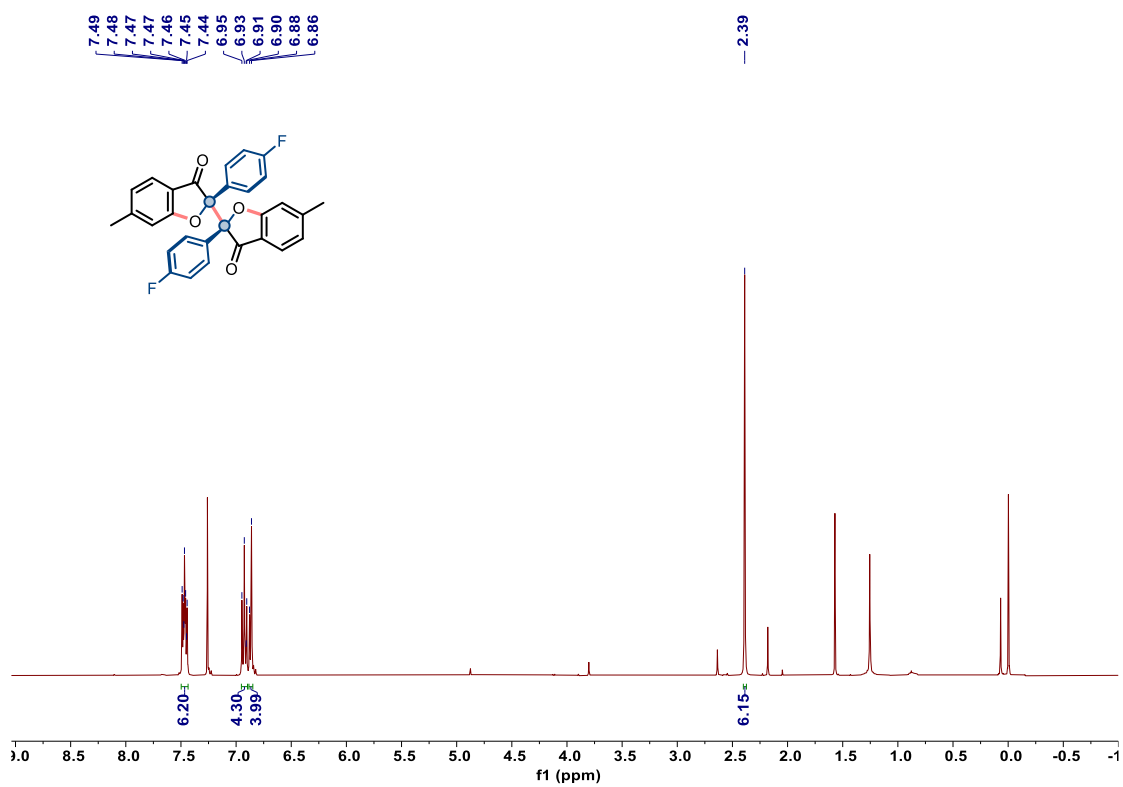
^1H NMR (600 MHz, CDCl_3) spectra of compound **2m-1**



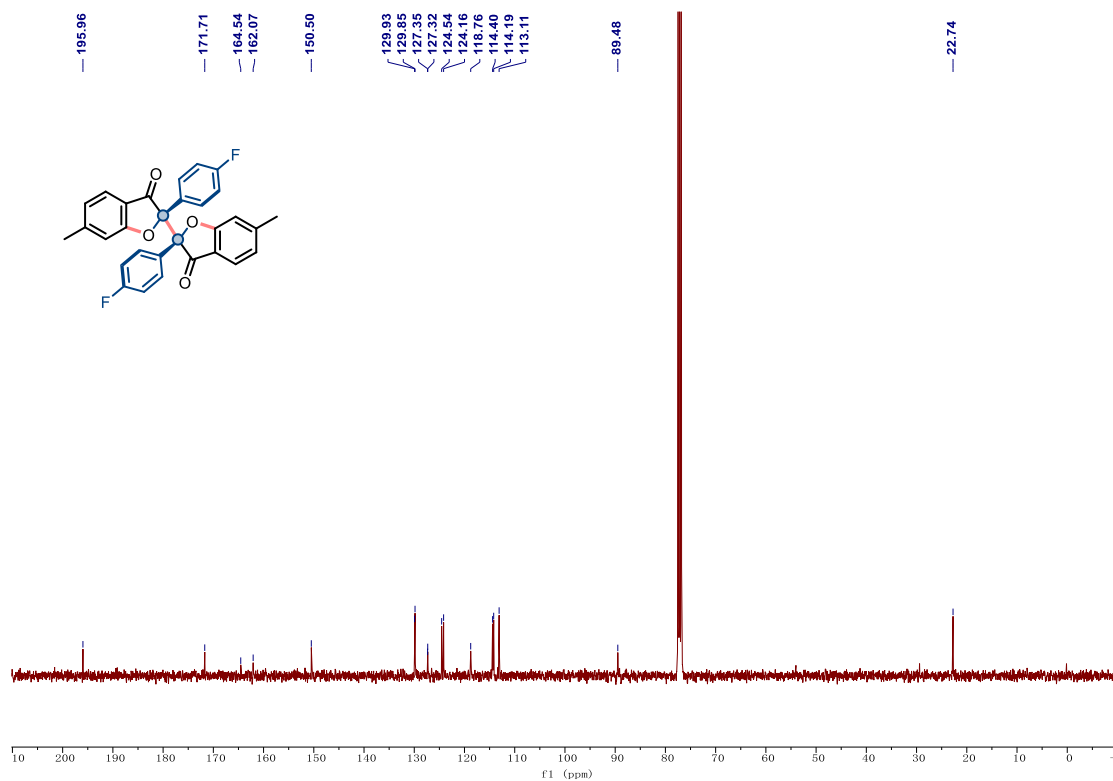
^{13}C NMR (151 MHz, CDCl_3) spectra of compound **2m-2**



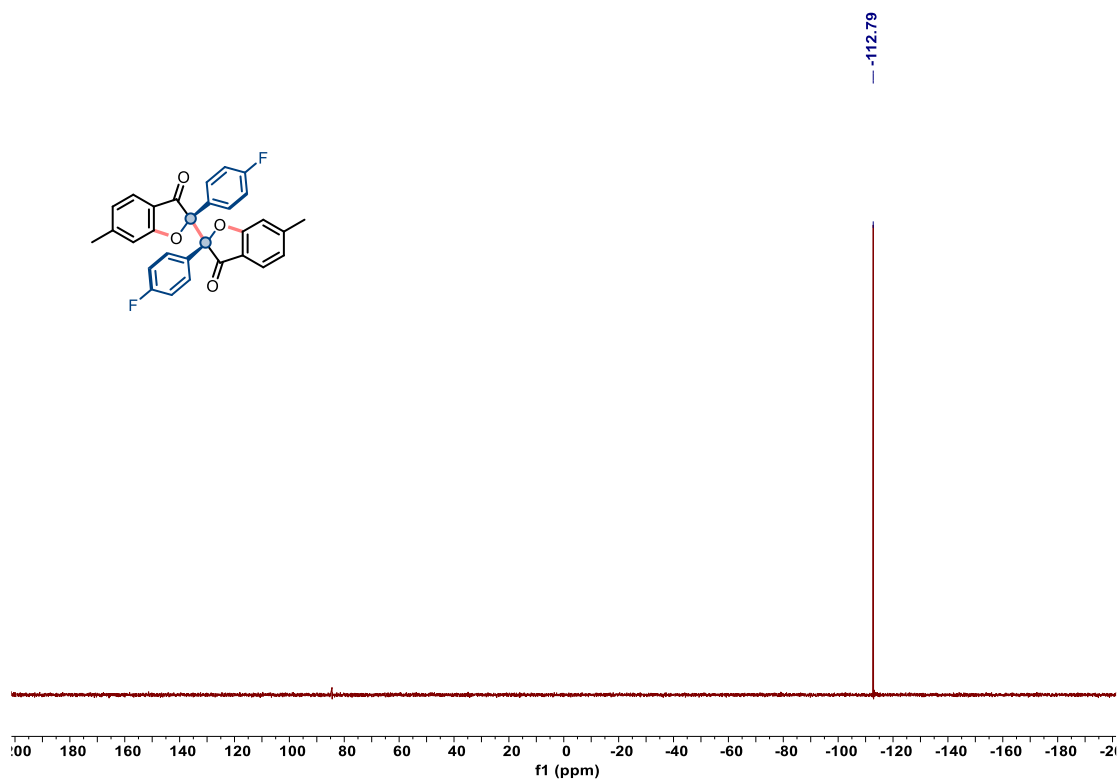
^1H NMR (400 MHz, CDCl_3) spectra of compound **2n-1**



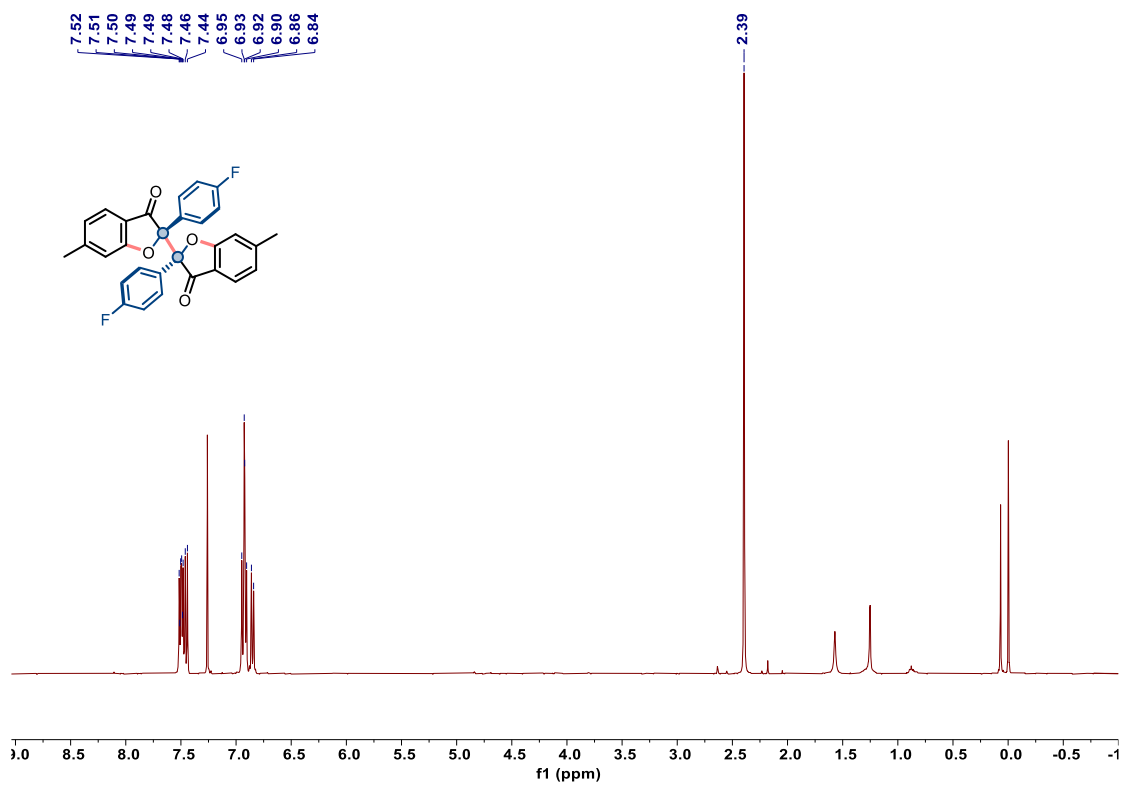
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2n-1**



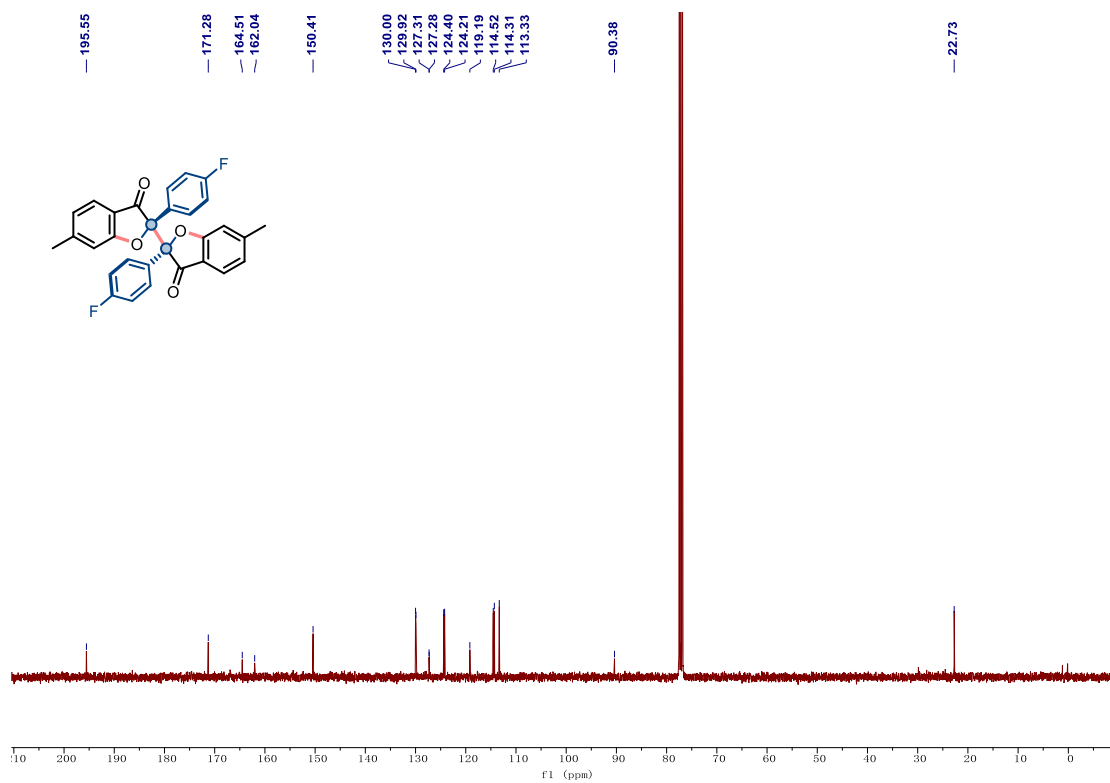
^{19}F NMR (376 MHz, CDCl_3) spectra of compound **2n-1**



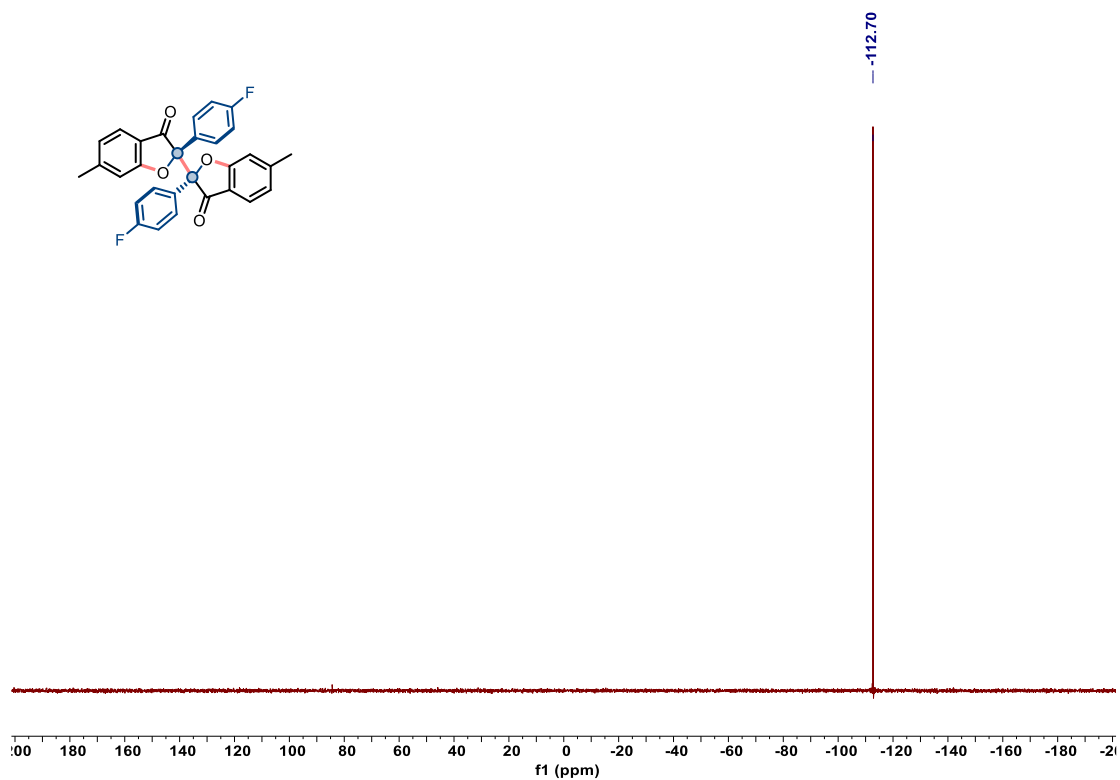
^1H NMR (400 MHz, CDCl_3) spectra of compound **2n-2**



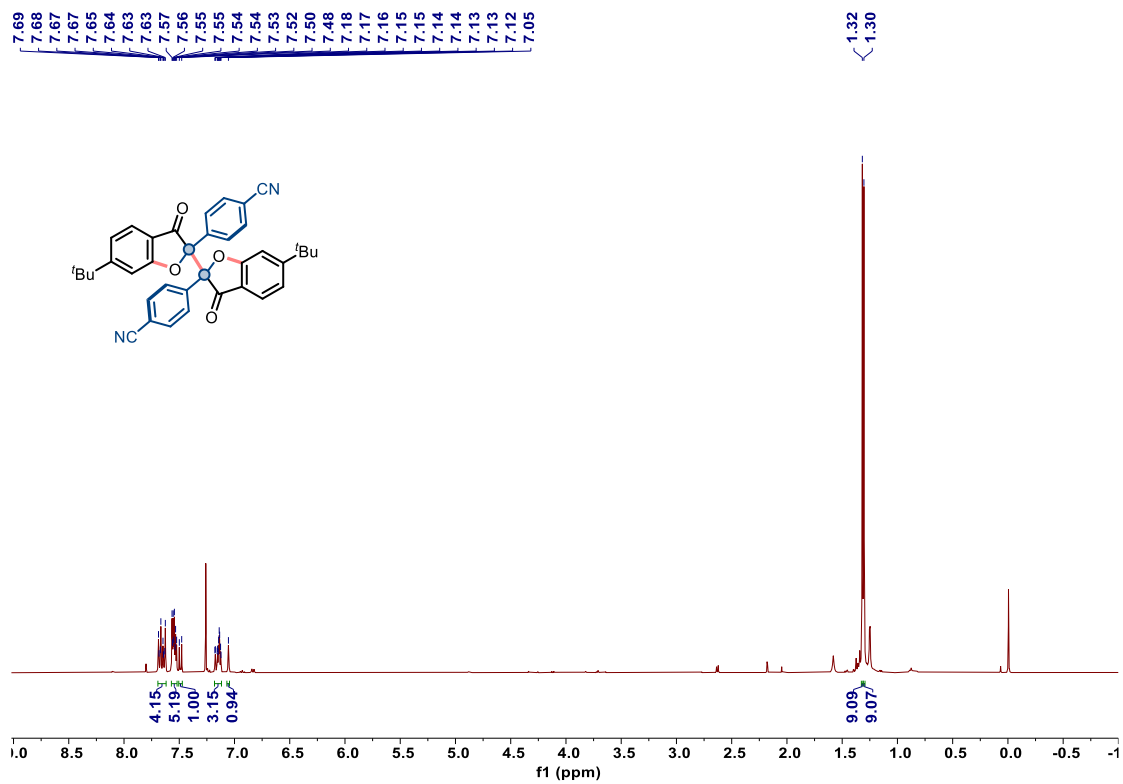
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2n-2**



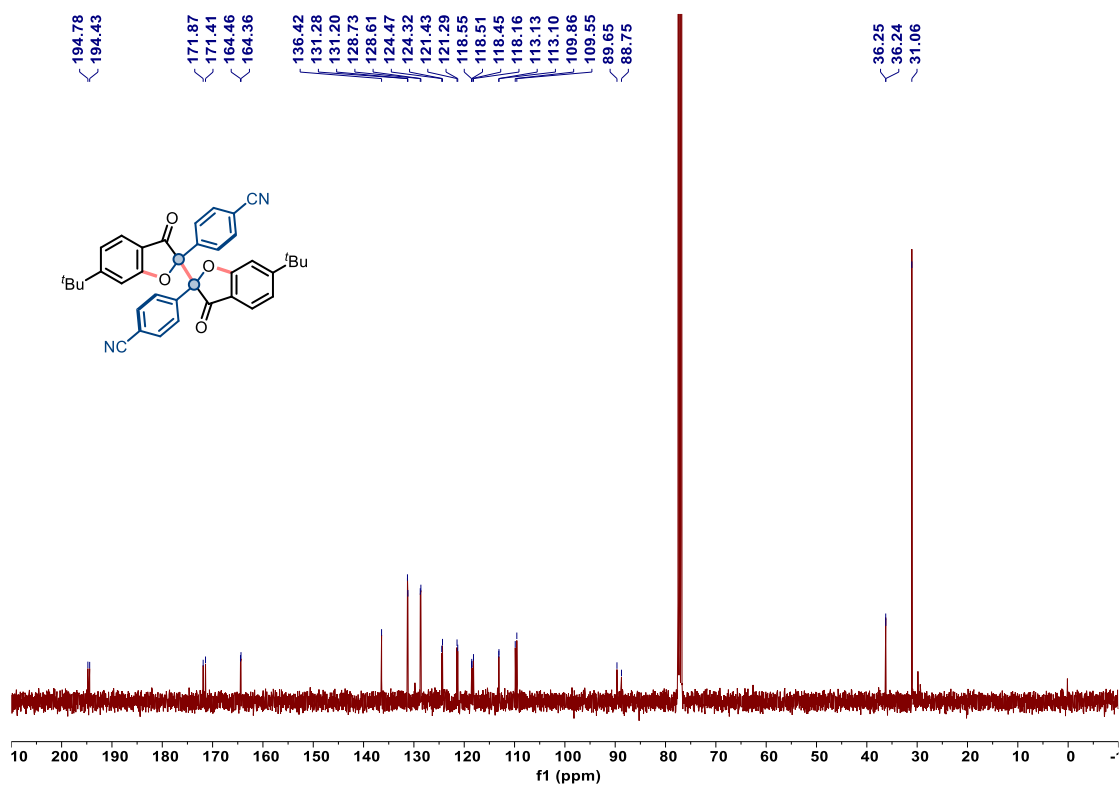
^{19}F NMR (376 MHz, CDCl_3) spectra of compound **2n-2**



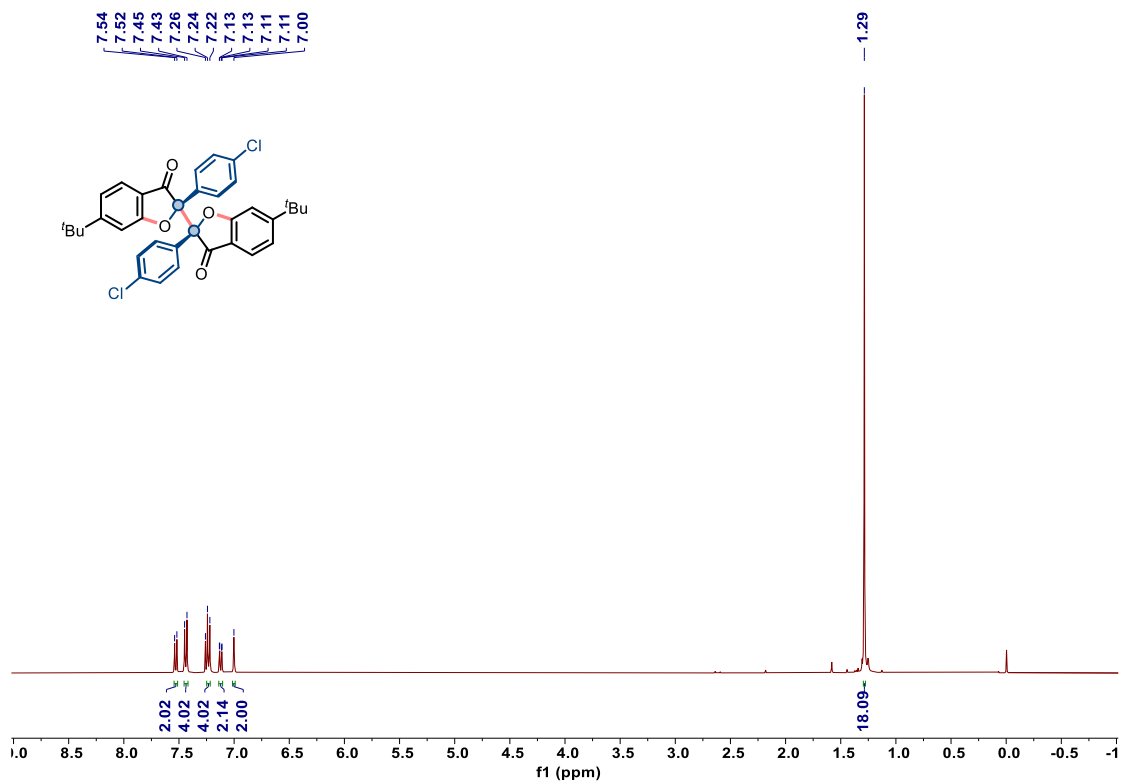
^1H NMR (400 MHz, CDCl_3) spectra of compound **2o**



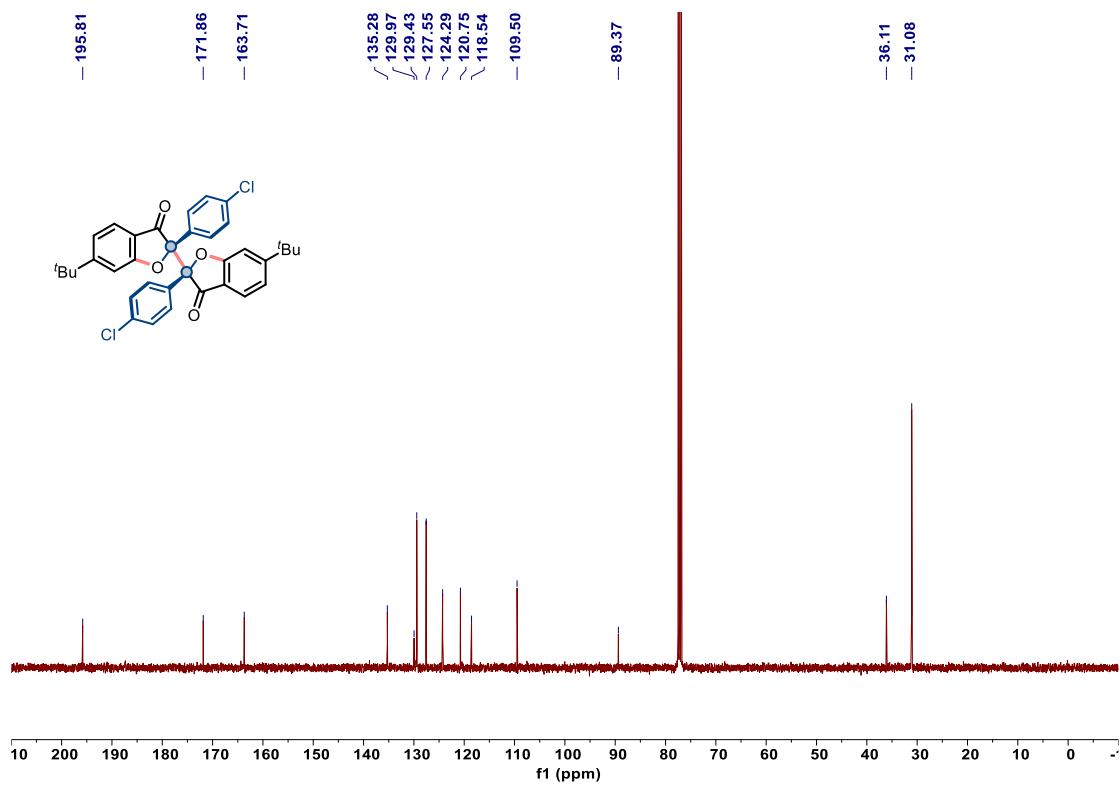
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2o**



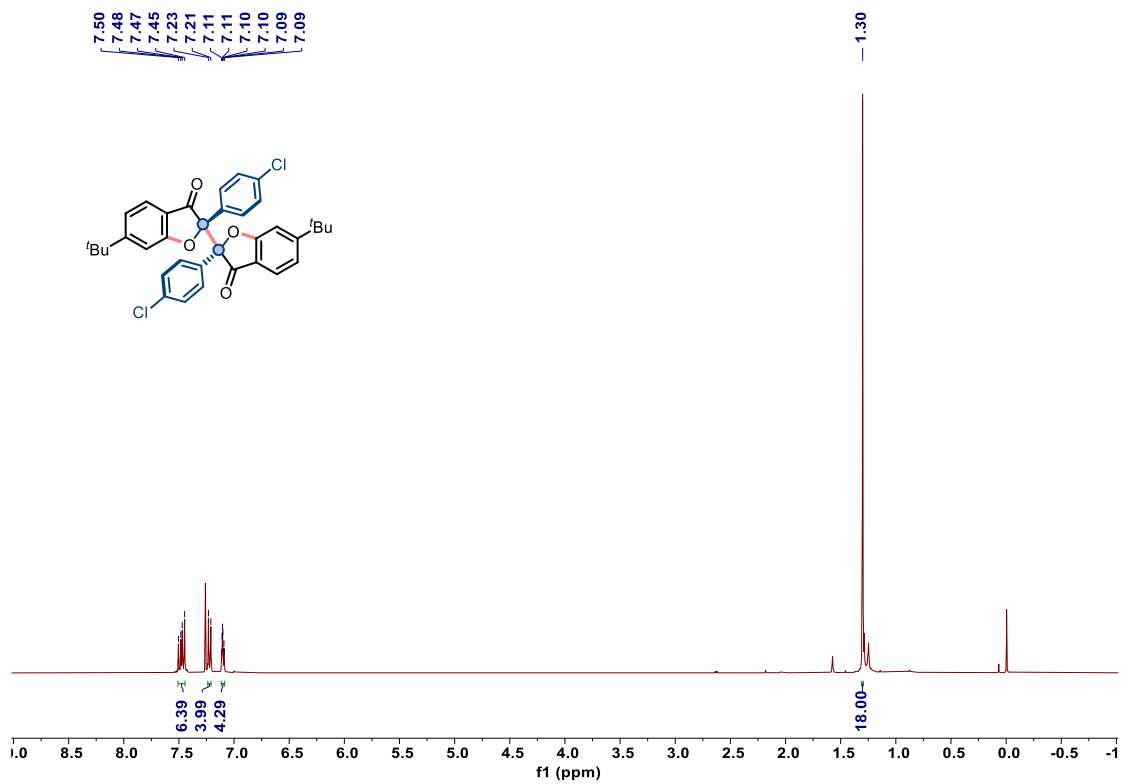
^1H NMR (400 MHz, CDCl_3) spectra of compound **2p-1**



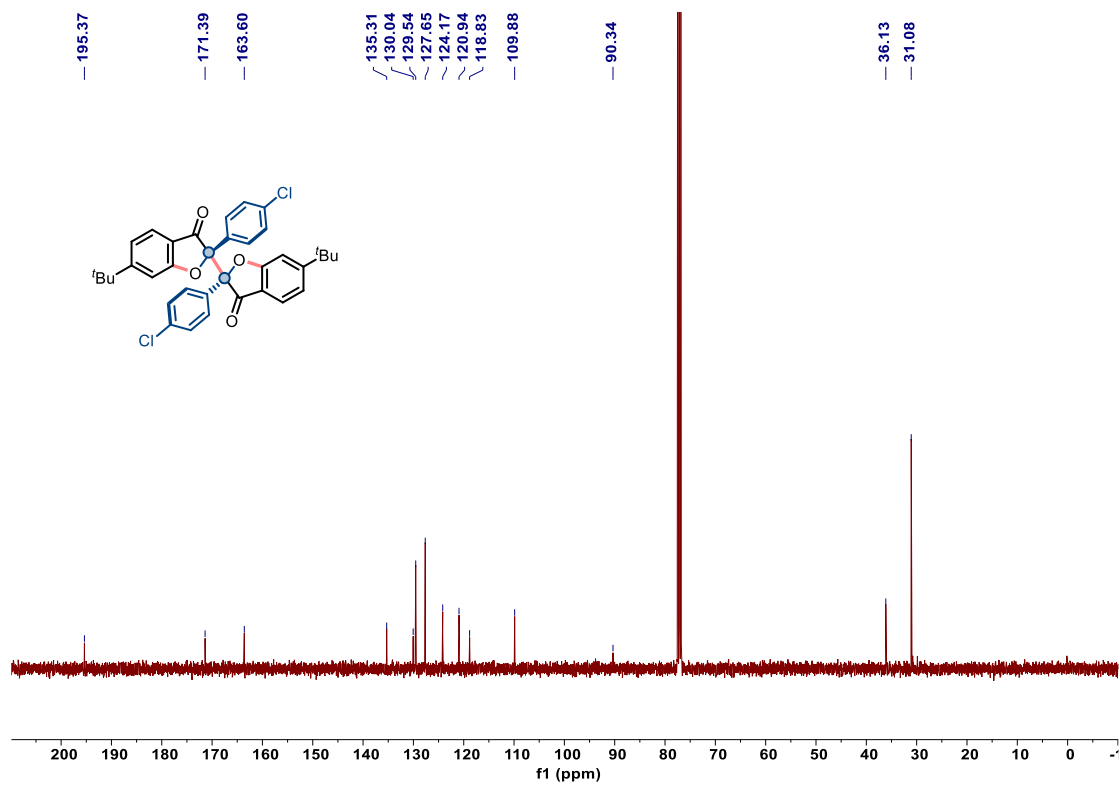
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2p-1**



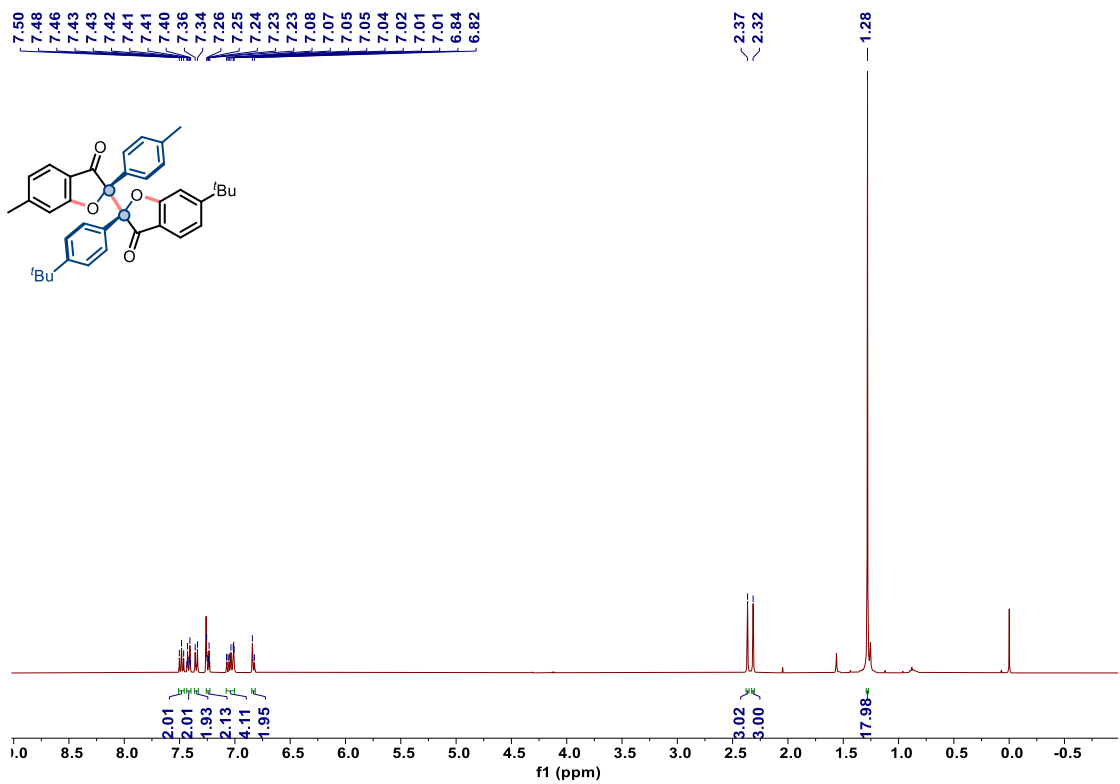
^1H NMR (400 MHz, CDCl_3) spectra of compound **2p-2**



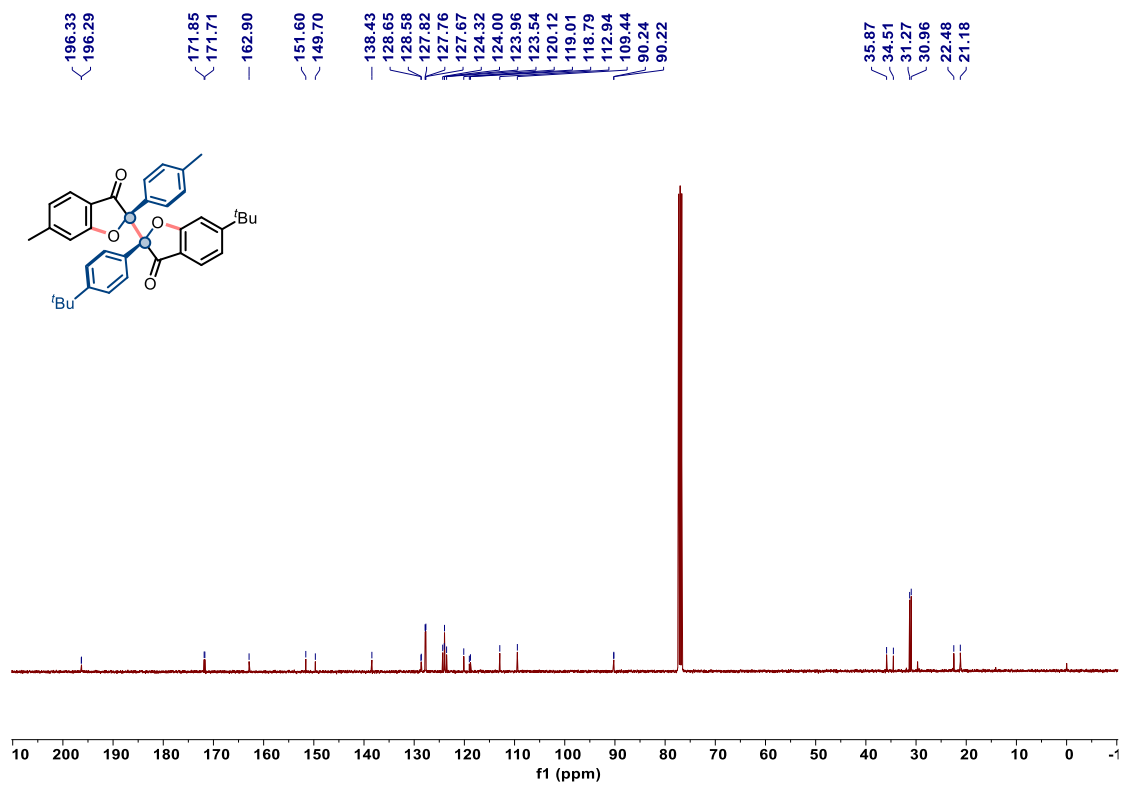
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2p-2**



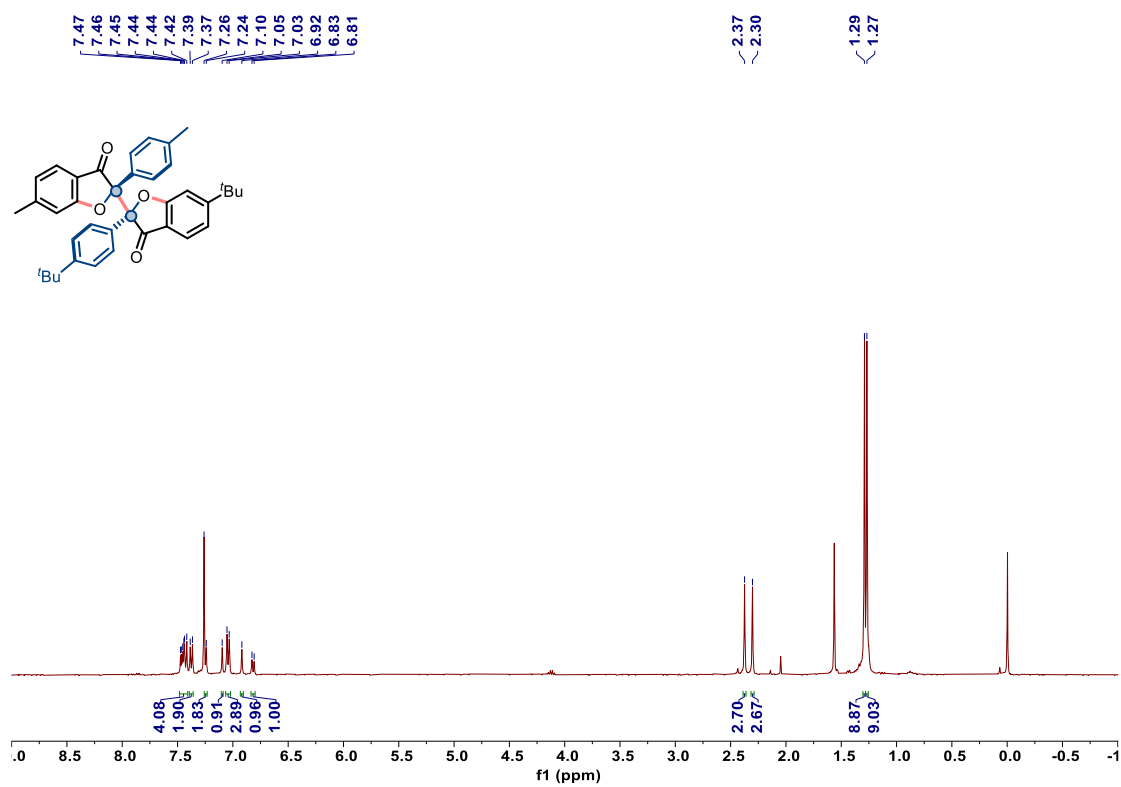
^1H NMR (400 MHz, CDCl_3) spectra of compound **2s-1**



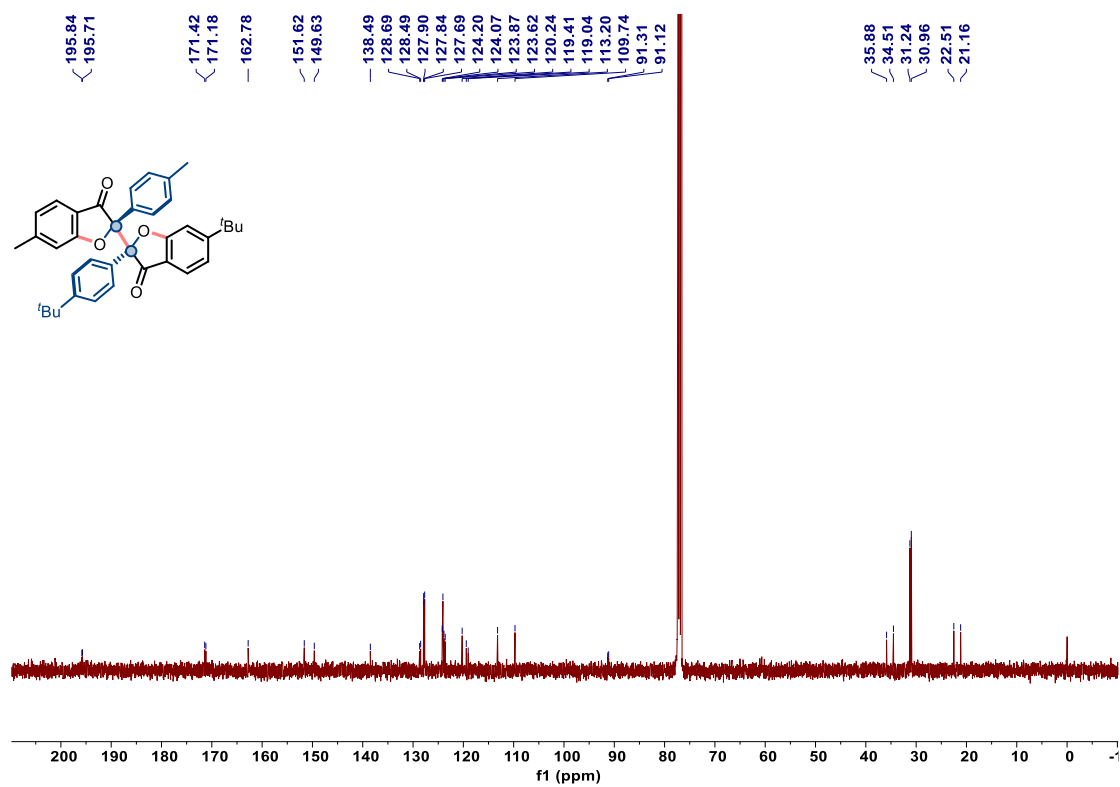
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2s-1**



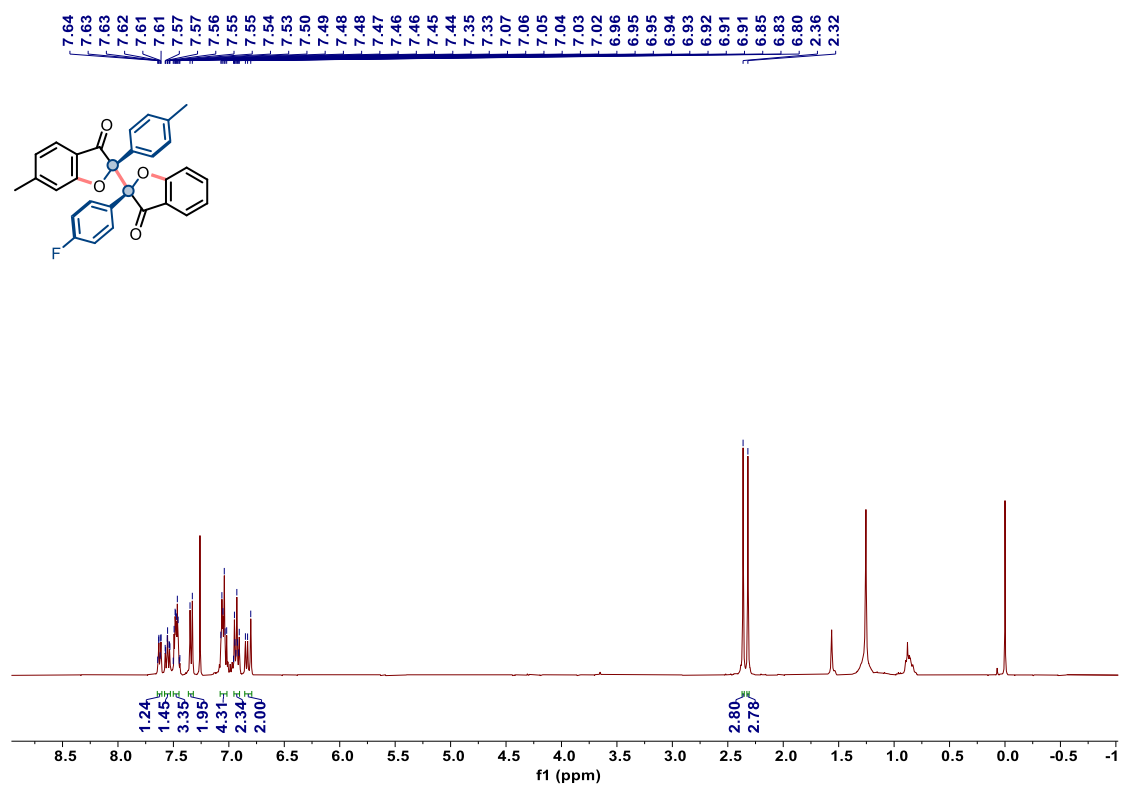
^1H NMR (400 MHz, CDCl_3) spectra of compound **2s-2**



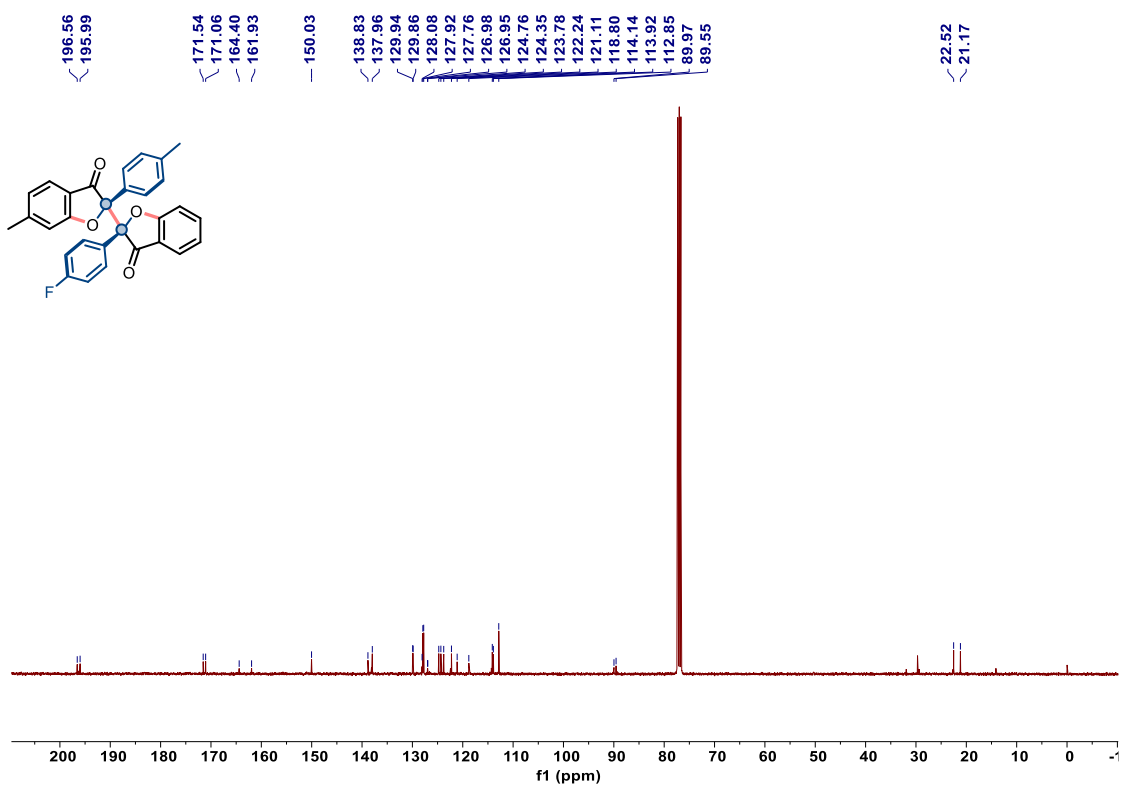
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2s-2**



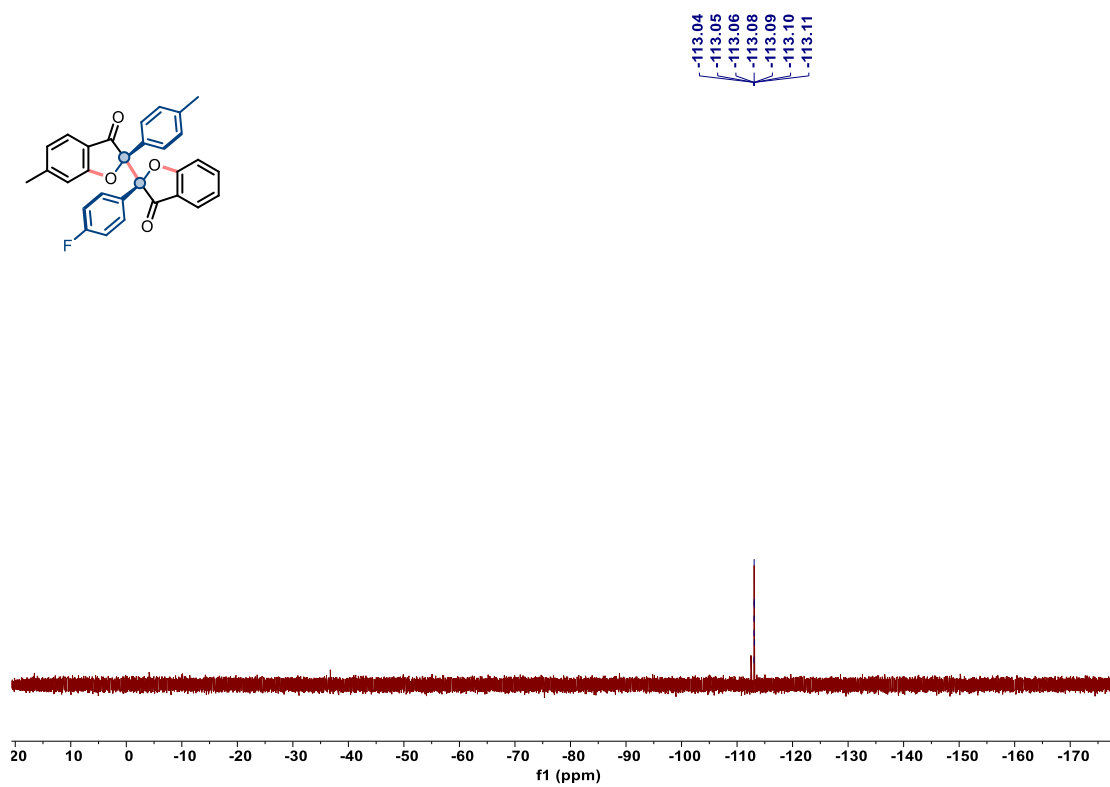
^1H NMR (400 MHz, CDCl_3) spectra of compound **2t-1**



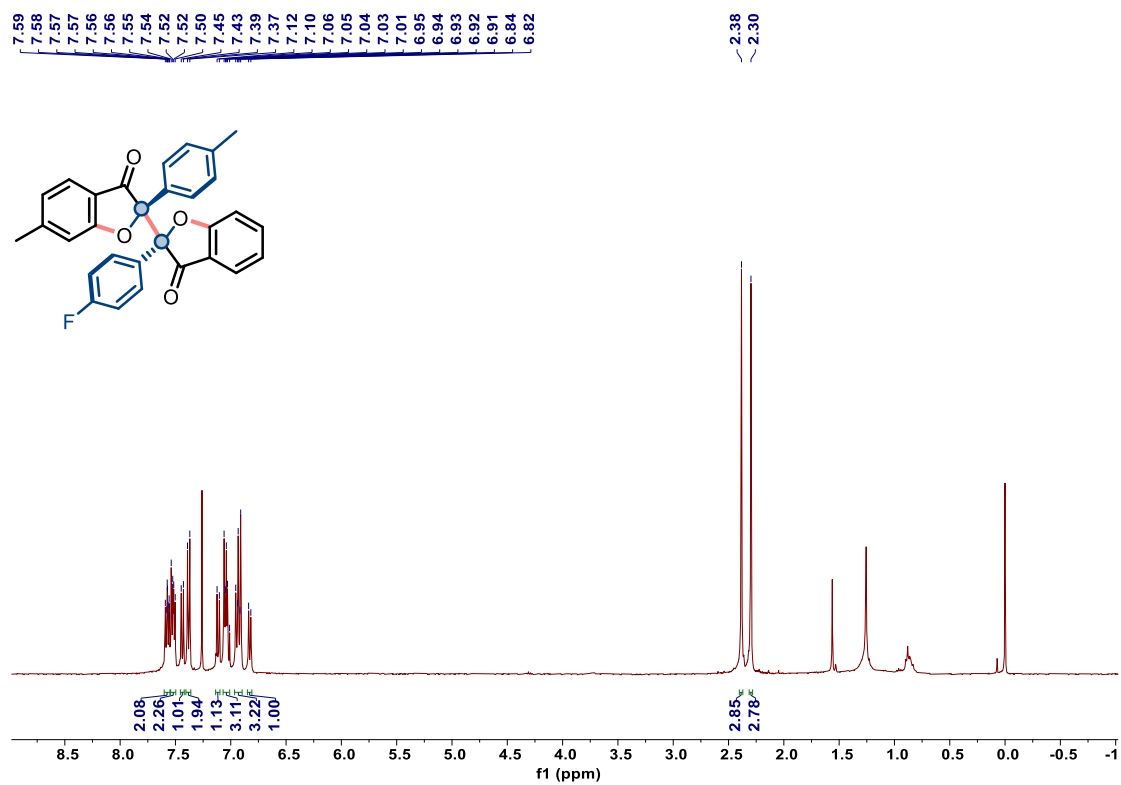
^{13}C NMR (101 MHz, CDCl_3) spectra of compound **2t-1**



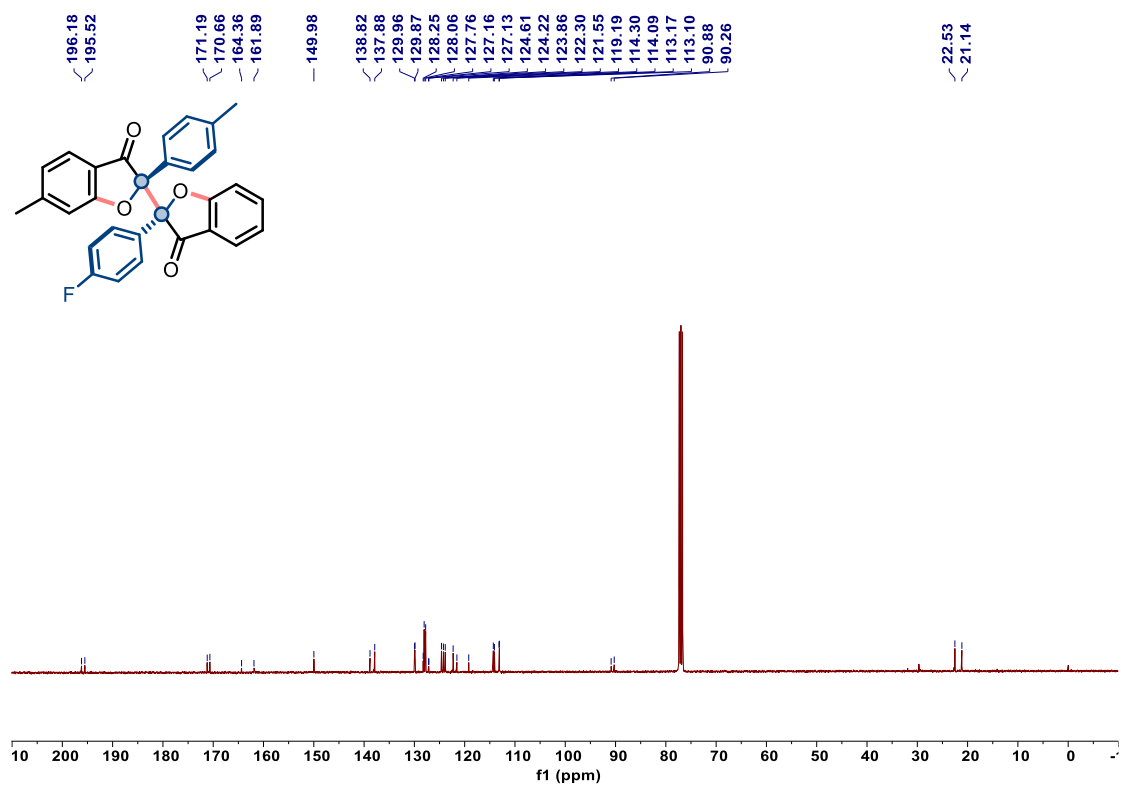
^{19}F NMR (376 MHz, CDCl_3) spectra of compound **2t-1**



¹H NMR (400 MHz, CDCl₃) spectra of compound **2t-2**



¹³C NMR (101 MHz, CDCl₃) spectra of compound **2t-2**



^{19}F NMR (376 MHz, CDCl_3) spectra of compound **2t-2**

