Supporting Information

Copper-catalyzed radical cascade reaction of cyclobutanes: synthesis of highly functionalized cyclobutene derivatives

Chunyang Liu, Xiaoyan Shangguan, Yan Li, and Qian Zhang**

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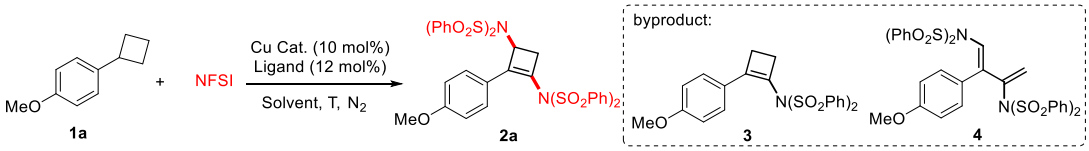
1. General Information

General All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV- 500/600 NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for ^{1}H) and $CHCl_3$ (77.0 ppm for ^{13}C), respectively. High-resolution mass spectra (HRMS) were recorded on Bruck microtof.

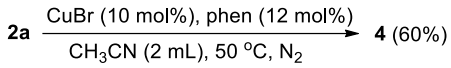
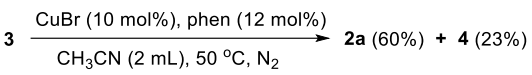
Materials Unless otherwise noted, commercial reagents were purchased from Energy-Chemical Limited, Alfa Aesar, and other commercial suppliers and were used as received. Cyclobutane substrates were synthesized according to procedures described in the literature.THF was distilled over sodium and stored under nitrogen atmosphere. CH_3CN, DCM and DCE were distilled over CaH_2 and stored under nitrogen atmosphere.

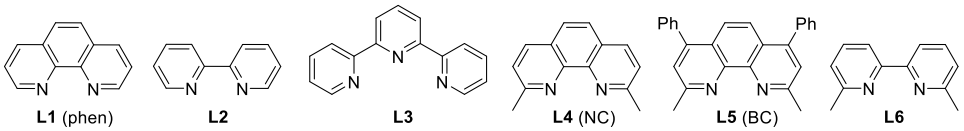
2. Detailed optimization of Reaction Conditions

Table S1. Optimization of conditions for 1,3-diaminocyclobutene synthesis[a]



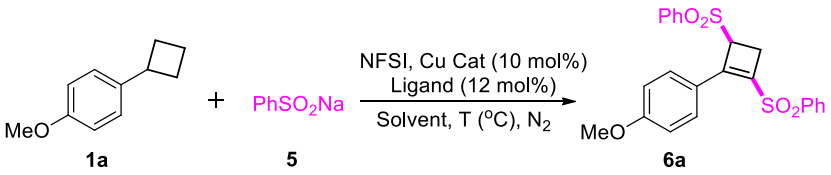
Entry	Cu Cat.	Ligand	Solvent	T (°C)	Yield (%)[b]
1	CuBr	**L1**	CH_3CN	50	15
2	CuBr	**L2**	CH_3CN	50	8
3	CuBr	**L3**	CH_3CN	50	16
4	CuBr	**L4**	CH_3CN	50	28
5	CuBr	**L5**	CH_3CN	50	42
6	CuBr	**L6**	CH_3CN	50	21
7	CuBr	--	CH_3CN	50	86
8	CuBr	--	CH_3CN	20	52
9	CuBr	--	CH_3CN	30	75
10	CuBr	--	CH_3CN	40	93
11	CuCl	--	CH_3CN	40	65
12	$Cu(CH_3CN)_4PF_6$	--	CH_3CN	40	45

13	CuOAc	--	CH_3CN	40	44
14	$CuBr_2$	--	CH_3CN	40	51
15	CuBr	--	THF	40	trace
16	CuBr	--	$PhCF_3$	40	0
17	CuBr	--	DCM	40	0
18	CuBr	--	DCE	40	0
19[c]	CuBr	--	CH_3CN	40	77
20[d]	CuBr	--	CH_3CN	40	61
21[e]	CuBr	--	CH_3CN	40	47
22[f]	CuBr	--	CH_3CN	40	31
23	CuBr (5 mol%)	--	CH_3CN	40	93
24	CuBr (2 mol%)	--	CH_3CN	40	76
25					
26					



[a] Reaction conditions: **1a** (0.2 mmol), NFSI (0.6 mmol, 3 equiv), catalyst (10 mol%) in 2 mL anhydrous solvent at 50 °C for 4 h under N_2 atmosphere. [b] Yield was determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] NFSI (0.5 mmol, 2.5 equiv). [d] NFSI (0.4 mmol, 2 equiv). [e] NFSI (0.3 mmol, 1.5 equiv). [f] NFSI (0.2 mmol, 1 equiv).

Table S2. Optimization of conditions for 1,3-disulfonylcyclobutene synthesis[a]

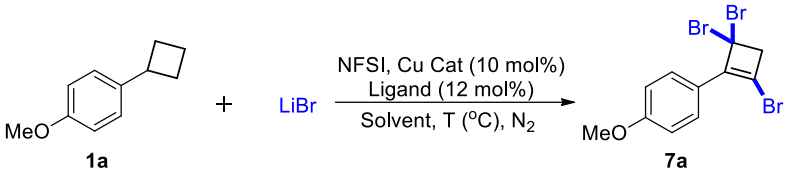


Entry	Cu Cat.	Ligand	Solvent	T (°C)	Yield (%)[b]
1	CuBr	**L1**	CH_3CN	40	6
2	CuBr	**L2**	CH_3CN	40	4
3	CuBr	**L3**	CH_3CN	40	7
4	CuBr	**L4**	CH_3CN	40	9
5	CuBr	**L5**	CH_3CN	40	12
6	CuBr	**L6**	CH_3CN	40	trace

7	CuBr	--	CH_3CN	40	0
8	CuCl	**L5**	CH_3CN	40	11
9	$Cu(CH_3CN)_4PF_6$	**L5**	CH_3CN	40	26
10	CuOAc	**L5**	CH_3CN	40	5
11	CuOTf	**L5**	CH_3CN	40	8
12	$Cu(CH_3CN)_4PF_6$	**L5**	CH_3CN	30	21
13	$Cu(CH_3CN)_4PF_6$	**L5**	CH_3CN	50	29
14	$Cu(CH_3CN)_4PF_6$	**L5**	CH_3CN	60	28
15	$Cu(CH_3CN)_4PF_6$	**L5**	THF	50	trace
16	$Cu(CH_3CN)_4PF_6$	**L5**	Toluene	50	7
17	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	50	48
18	$Cu(CH_3CN)_4PF_6$	**L5**	DCE	50	42
19[c]	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	50	59
20[d]	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	50	64
21[d,e]	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	50	78
22[d,f]	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	50	83
23[d,g]	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	50	81

[a] Reaction conditions: **1a** (0.2 mmol), NFSI (0.7 mmol, 3.5 equiv), $PhSO_2Na$ (0.5 mmol, 2.5 equiv), catalyst (10 mol%) and ligand (12 mol%) in 2 mL anhydrous solvent at 40 °C for 20 h under N_2 atmosphere. [b] Yield was determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] $PhSO_2Na$ (0.7 mmol, 3.5 equiv). [d] NFSI (0.8 mmol, 4 equiv), $PhSO_2Na$ (0.8 mmol, 4 equiv). [e] DCM (4 mL). [f] DCM (6 mL). [g] DCM (8 mL).

Table S3. Optimization of conditions for 1,3,3-tribromocyclobutene synthesis[a]

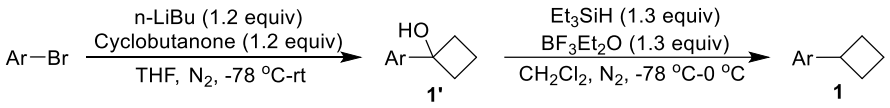


Entry	Cu Cat.	Ligand	Solvent	T (°C)	Yield (%)[b]
1	CuBr	--	DCE	50	48
2[c]	CuBr	--	DCE	50	65
3[c]	CuBr	**L1**	DCE	50	9
4[c]	CuBr	**L2**	DCE	50	30
5[c]	CuBr	**L3**	DCE	50	60
6[c]	CuBr	**L4**	DCE	50	18

7[c]	CuBr	**L5**	DCE	50	12
8[c]	CuBr	**L6**	DCE	50	45
9[c]	CuBr	--	DCE	60	84
10[c]	CuBr	--	DCE	70	94
11[c]	CuBr	--	DCE	80	92
12[c]	CuCl	--	DCE	70	68
13[c]	$Cu(CH_3CN)_4PF_6$	--	DCE	70	80
14[c]	CuOAc	--	DCE	70	76
15[c]	$CuBr_2$	--	DCE	70	78
16[c]	CuBr	--	CH_3CN	50	0
17[c]	CuBr	--	$PhCF_3$	70	0
18[c]	CuBr	--	DCM	70	81
19[c]	CuBr	--	Toluene	70	trace
20[c]	CuBr (5 mol%)	--	DCE	70	88
21[c, d]	CuBr	--	DCE	70	80
22[c, e]	CuBr	--	DCE	70	87

[a] Reaction conditions: **1a** (0.2 mmol), NFSI (0.70 mmol, 3.5 equiv), LiBr (0.5 mmol, 2.5 equiv), catalyst (10 mol%) in 2 mL dry solvent at 50 °C for 4 h under N_2 atmosphere. [b] Yield was determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] NFSI (0.86 mmol, 4.3 equiv), LiBr (0.66 mmol, 3.3 equiv) [d] KBr (0.66 mmol, 3.3 equiv) instead of LiBr. [e] TMSBr (0.66 mmol, 3.3 equiv) instead of LiBr.

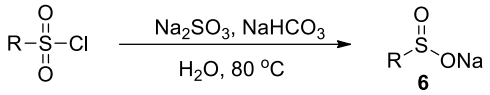
3. Cyclobutane and Sodium Sulfonate Substrates Synthesis



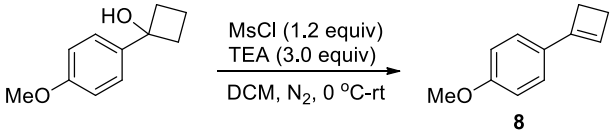
Following the literature procedure, a flame-dried round bottom flask charged with 10 mmol of aryl bromide in 25 mL THF was cooled to -78 °C and 4.8 mL of n-BuLi (2.5 M in hexane, 12 mmol, 1.2 equiv) was added dropwise via syringe. The mixture was stirred for 1.5 h at -78 ℃ before the addition of 841 mg of cyclobutanone (12.0 mmol, 1.2 equiv), then the mixture was warmed to room temperature and stirred over 3 h. After ammonium chloride solution quenching, the precipitated solid was removed by filtration. The filtrate was extracted with ethyl acetate (3×30 mL), washed with sodium chloride solution, and dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography.[1]

Following the literature procedure, a solution of 755 mg of Et_3SiH (6.5 mmol, 1.3 equiv) and 5 mmol of aryl cyclobutanol **1'** in 15 mL of CH_2Cl_2 was cooled to -78 °C and a solution of 923 mg

of boron trifluoride diethyl etherate (6.5 mmol, 1.3 equiv) in 5 mL of CH_2Cl_2 was added dropwise over 5 min. The mixture was warmed slowly to 0 °C and 1.59 g of K_2CO_3 (11.5 mmol, 2.3 equiv) was added followed by 10 mL of water. The solution was transferred with ether to a separator funnel and the aqueous phase was separated. The organic phase was washed with water and saturated NaCl solution, then dried over Na_2SO_4. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether) to obtain product **1**.[2]

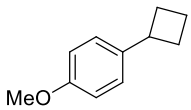


Following the literature procedure, Sulfonyl chlorides (10 mmol) were added to a solution of sodium sulfites (20 mmol) and sodium bicarbonate (1.68 g, 20 mmol) in water (10 mL, 1 M) and heated at 80 ℃ for 3 h, after cooling to room temperature the volatiles were removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates **6** as an amorphous solid.[3]



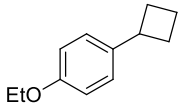
A solution of 1-(4-methoxyphenyl)cyclobutanol (5.0 mmol) in dry DCM (10 mL) was cooled to 0 ℃ followed by a dropwise addition of Et_3N (1.52 g, 15 mmol) and methanesulfonyl chloride (0.69 g, 6 mmol). The reaction mixture was stirred for 15 min at 0 ℃ and for 2 h at room temperature. The reaction was diluted with ether (20 mL) and quenched with water (10 mL). Organic phase was washed with 2 M HCl (10 mL), saturated solution of $NaHCO_3$ (5 mL), water (10 mL) and brine (10 mL) and dried over Na_2SO_4. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether) to obtain product **8**.[4]

1-cyclobutyl-4-methoxybenzene 1a



The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.4, 1.8 Hz, 2H), 6.84 (dd, *J* = 8.4, 1.8 Hz, 2H), 3.78 (s, 3H), 3.48 (p, *J* = 9.0 Hz, 1H), 2.34 – 2.27 (m, 2H), 2.14 – 2.06 (m, 2H), 2.02 – 1.94 (m, 1H), 1.87 – 1.80 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.7, 138.5, 127.2, 113.6, 55.3, 39.8, 30.1, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{15}O$ ($[M+H]^+$), 163.1120, found 163.1118. This compound is known.[5]

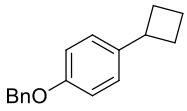
1-cyclobutyl-4-ethoxybenzene 1b



The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 – 7.11 (m, 2H), 6.85 – 6.81 (m, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.48 (p, *J* = 9.0 Hz, 1H), 2.34 – 2.27

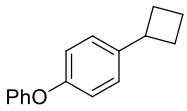
(m, 2H), 2.13 – 2.06 (m, 2H), 2.02 – 1.94 (m, 1H), 1.86 – 1.80 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.0, 138.4, 127.2, 114.2, 63.4, 39.8, 30.1, 18.2, 14.9. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{17}O$ ($[M+H]^+$), 177.1275, found 177.1276.

1-(benzyloxy)-4-cyclobutylbenzene 1c



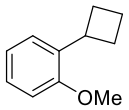
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (t, *J* = 5.4 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 7.14 – 7.11 (m, 2H), 6.92 – 6.88 (m, 2H), 5.01 (d, *J* = 3.6 Hz, 2H), 3.51 – 3.42 (m, 1H), 2.33 – 2.26 (m, 2H), 2.13 – 2.06 (m, 2H), 2.01 – 1.93 (m, 1H), 1.86 – 1.79 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 138.7, 137.3, 128.5, 127.8, 127.4, 127.2, 114.6, 114.6, 70.0, 39.7, 30.0, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{19}O$ ($[M+H]^+$), 239.1435, found 239.1431.

1-cyclobutyl-4-phenoxybenzene 1d



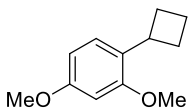
The title compound was isolated by column chromatography with petroleum ether as a white solid. **m.p.** 38 - 39 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.17 (t, *J* = 5.4 Hz, 2H), 7.08 – 7.04 (m, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.96 – 6.92 (m, 2H), 3.52 (p, *J* = 9.0 Hz, 1H), 2.36 – 2.30 (m, 2H), 2.16 – 2.09 (m, 2H), 2.04 – 1.96 (m, 1H), 1.88 – 1.82 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.7, 154.9, 141.3, 129.6, 127.5, 122.8, 118.9, 118.5, 39.8, 30.0, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{17}O$ ($[M+H]^+$), 225.1276, found 225.1279.

1-cyclobutyl-2-methoxybenzene 1e



The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.8, 1.6 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 3.77 – 3.70 (m, 1H), 2.34 – 2.29 (m, 2H), 2.14 – 2.07 (m, 2H), 2.04 – 1.96 (m, 1H), 1.85 – 1.78 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.2, 134.1, 126.7, 126.6, 120.3, 110.1, 55.2, 35.5, 28.9, 18.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{15}O$ ($[M+H]^+$), 163.1121, found 163.1124.

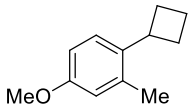
1-cyclobutyl-2,4-dimethoxybenzene 1f



The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 1H), 6.44 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.69 – 3.62 (m, 1H), 2.30 – 2.25 (m, 2H), 2.10 – 2.02 (m, 2H), 2.01 – 1.95 (m, 1H), 1.82 – 1.78 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.9, 158.0, 126.8, 126.7, 103.5, 98.3, 55.2, 55.1,

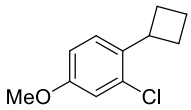
34.9, 29.0, 18.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{17}O_2$ ($[M+H]^+$), 193.1228, found 193.1226.

1-cyclobutyl-4-methoxy-2-methylbenzene 1g



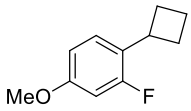
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4 Hz, 1H), 6.72 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H), 3.60 – 3.53 (m, 1H), 2.34 – 2.29 (m, 2H), 2.22 (s, 3H), 2.13 – 2.06 (m, 2H), 2.03 – 1.95 (m, 1H), 1.85 – 1.79 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 137.1, 136.0, 126.3, 115.8, 110.5, 55.2, 37.9, 29.0, 19.7, 18.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{17}O$ ($[M+H]^+$), 177.1279, found 177.1276.

2-chloro-1-cyclobutyl-4-methoxybenzene 1h



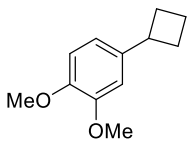
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.76 (s, 3H), 3.71 (p, *J* = 9.0 Hz, 1H), 2.40 – 2.33 (m, 2H), 2.11 – 2.04 (m, 2H), 2.03 – 1.97 (m, 1H), 1.85 – 1.78 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.1, 134.9, 133.8, 127.6, 114.7, 112.5, 55.4, 37.6, 28.8, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{14}ClO$ ($[M+H]^+$), 197.0731, found 197.0729.

1-cyclobutyl-2-fluoro-4-methoxybenzene 1i



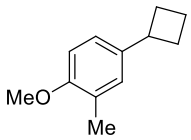
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 12.0 Hz, 1H), 3.76 (s, 3H), 3.65 (p, *J* = 9.0 Hz, 1H), 2.31 (q, *J* = 9.0 Hz, 2H), 2.13 (p, *J* = 9.6 Hz, 2H), 2.05 – 1.97 (m, 1H), 1.84 (q, *J* = 9.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.1, 158.9, 128.0, 124.6, 109.3, 101.4, 55.5, 33.9, 29.1, 18.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -115.85, -115.85, -115.86, -115.87, -115.87, -115.89, -115.90. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{14}FO$ ($[M+H]^+$), 181.1028, found 181.1030.

4-cyclobutyl-1,2-dimethoxybenzene 1j



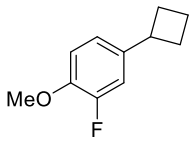
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.74 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.49 (p, *J* = 9.0 Hz, 1H), 2.35 – 2.28 (m, 2H), 2.15 – 2.07 (m, 2H), 2.03 – 1.95 (m, 1H), 1.87 – 1.81 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.8, 147.1, 139.1, 118.0, 111.1, 109.8, 56.0, 55.8, 40.1, 30.0, 18.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{17}O_2$ ($[M+H]^+$), 193.1227, found 193.1230.

4-cyclobutyl-1-methoxy-2-methylbenzene 1k



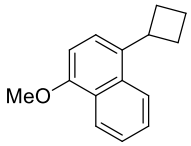
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.00 (d, *J* = 6.6 Hz, 2H), 6.77 – 6.74 (m, 1H), 3.80 (s, 3H), 3.45 (p, *J* = 9.0 Hz, 1H), 2.32 – 2.27 (m, 2H), 2.21 (s, 3H), 2.13 – 2.06 (m, 2H), 2.01 – 1.93 (m, 1H), 1.85 – 1.79 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.9, 138.1, 128.8, 126.3, 124.3, 109.8, 55.4, 39.8, 30.1, 18.2, 16.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{17}O$ ($[M+H]^+$), 177.1278, found 177.1280.

4-cyclobutyl-2-fluoro-1-methoxybenzene 1l



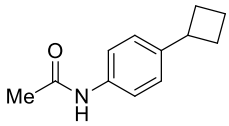
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.96 – 6.92 (m, 1H), 6.90 – 6.85 (m, 2H), 3.85 (s, 3H), 3.45 (p, *J* = 9.0 Hz, 1H), 2.34 – 2.27 (m, 2H), 2.11 – 2.04 (m, 2H), 2.02 – 1.94 (m, 1H), 1.86 – 1.80 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.3, 145.5, 139.7, 121.7, 114.1, 113.3, 56.4, 39.5, 29.9, 18.0. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -135.72, -135.75, -135.77, -135.78, -135.79. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{14}FO$ ($[M+H]^+$), 181.1029, found 181.1026.

1-cyclobutyl-4-methoxynaphthalene 1m



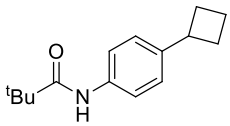
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 – 8.26 (m, 1H), 7.90 – 7.85 (m, 1H), 7.46 (dd, *J* = 18.6, 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.07 – 4.01 (m, 1H), 3.95 (s, 3H), 2.52 – 2.45 (m, 2H), 2.27 – 2.20 (m, 2H), 2.16 – 2.07 (m, 1H), 1.91 – 1.86 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.9, 133.7, 132.3, 126.0, 125.8, 124.8, 124.0, 122.5, 122.1, 103.2, 55.4, 37.6, 29.2, 18.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{17}O$ ($[M+H]^+$), 213.1277, found 213.1279.

***N*-(4-cyclobutylphenyl)acetamide 1n**



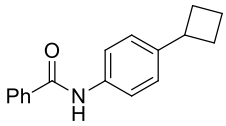
The title compound was isolated by column chromatography with ethyl acetate and petroleum ether (EA/PE = 1:10) as a white solid. **m.p.** 78 - 79 ^{o}C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 26.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.49 (p, *J* = 9.0 Hz, 1H), 2.35 – 2.28 (m, 2H), 2.14 (s, 3H), 2.12 – 2.07 (m, 2H), 2.03 – 1.97 (m, 1H), 1.86 – 1.81 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.5, 142.4, 135.5, 126.7, 120.0, 39.9, 29.8, 24.4, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{15}NNaO$ ($[M+Na]^+$), 212.1046, found 212.1042.

***N*-(4-cyclobutylphenyl)pivalamide 1o**



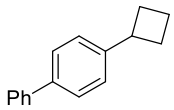
The title compound was isolated by column chromatography with ethyl acetate and petroleum ether (EA/PE = 1:10) as a white solid. **m.p.** 152 - 153 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 3.50 (p, *J* = 9.0 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.14 – 2.07 (m, 2H), 2.05 – 1.96 (m, 1H), 1.87 – 1.81 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 176.4, 142.3, 135.7, 126.7, 119.9, 39.9, 39.5, 29.8, 27.6, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{21}NNaO$ ($[M+Na]^+$), 254.1515, found 254.1525.

_N_-(4-cyclobutylphenyl)benzamide 1p



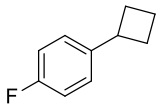
The title compound was isolated by column chromatography with ethyl acetate and petroleum ether (EA/PE = 1:10) as a white solid. **m.p.** 162 - 163 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.53 (p, *J* = 9.0 Hz, 1H), 2.36 – 2.31 (m, 2H), 2.17 – 2.09 (m, 2H), 2.05 – 1.97 (m, 1H), 1.85 (dd, *J* = 19.2, 9.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.7, 142.7, 135.6, 135.1, 131.7, 128.7, 127.0, 126.9, 120.3, 39.9, 29.8, 18.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{17}NNaO$ ($[M+Na]^+$), 274.1202, found 274.1206.

4-cyclobutyl-1,1'-biphenyl 1q



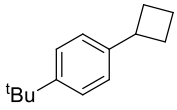
The title compound was isolated by column chromatography with petroleum ether as a white solid. **m.p.** 37 - 38 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 6.0 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 3.53 (p, *J* = 9.0 Hz, 1H), 2.32 (m, 2H), 2.19 – 2.11 (m, 2H), 2.03 – 1.95 (m, 1H), 1.84 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.3, 141.1, 138.6, 128.7, 126.9, 126.9, 126.7, 40.1, 29.8, 18.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{18}$ ($[M+H]^+$), 209.1325, found 209.1326. This compound is known.[5]

1-cyclobutyl-4-fluorobenzene 1r



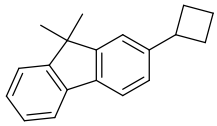
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 2H), 6.99 – 6.94 (m, 2H), 3.50 (p, *J* = 9.0 Hz, 1H), 2.36 – 2.30 (m, 2H), 2.14 – 2.06 (m, 2H), 2.04 – 1.96 (m, 1H), 1.89 – 1.81 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.1, 141.9, 127.6, 114.8, 39.7, 29.9, 18.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -117.95, -117.97, -117.97, -117.98, -118.00, -118.00, -118.01. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_{12}F$ ($[M+H]^+$), 151.0922, found 151.0921.

1-(tert-butyl)-4-cyclobutylbenzene 1s



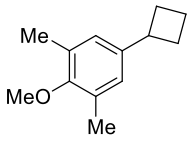
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.18 – 7.15 (m, 2H), 3.51 (p, *J* = 9.0 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.20 – 2.10 (m, 2H), 2.05 – 1.96 (m, 1H), 1.89 – 1.81 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.5, 143.2, 126.0, 125.1, 40.0, 34.4, 31.4, 29.9, 18.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{21}$ ($[M+H]^+$), 189.1643, found 189.1642. This compound is known.[6]

2-cyclobutyl-9,9-dimethyl-9H-fluorene 1t



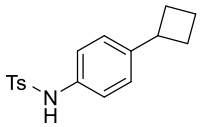
The title compound was isolated by column chromatography with petroleum ether as a white solid. **m.p.** 67 - 68 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 3.96 (p, *J* = 9.0 Hz, 1H), 2.78 – 2.69 (m, 2H), 2.62 – 2.53 (m, 2H), 2.43 – 2.33 (m, 1H), 2.26 – 2.21 (m, 1H), 1.83 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.6, 153.5, 145.5, 139.2, 136.9, 126.8, 126.7, 125.1, 122.4, 120.3, 119.7, 119.6, 46.6, 40.7, 30.1, 27.2, 18.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{21}$ ($[M+H]^+$), 249.1641, found 249.1643.

5-cyclobutyl-2-methoxy-1,3-dimethylbenzene 1u



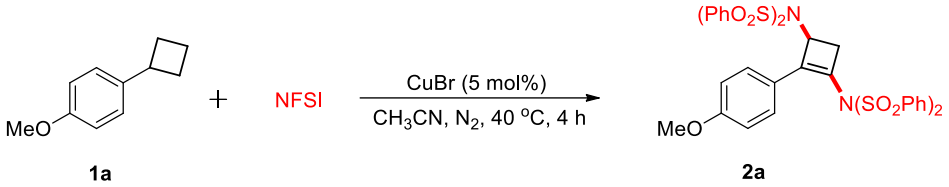
The title compound was isolated by column chromatography with petroleum ether as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 (s, 2H), 3.68 (s, 3H), 3.41 (p, *J* = 9.0 Hz, 1H), 2.31 – 2.27 (m, 2H), 2.26 (s, 6H), 2.13 – 2.06 (m, 2H), 2.00 – 1.92 (m, 1H), 1.84 – 1.79 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.9, 141.4, 130.3, 126.6, 59.5, 39.9, 29.9, 18.1, 16.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{19}O$ ($[M+H]^+$), 191.1435, found 191.1433.

***N*-(4-cyclobutylphenyl)-4-methylbenzenesulfonamide 1v**

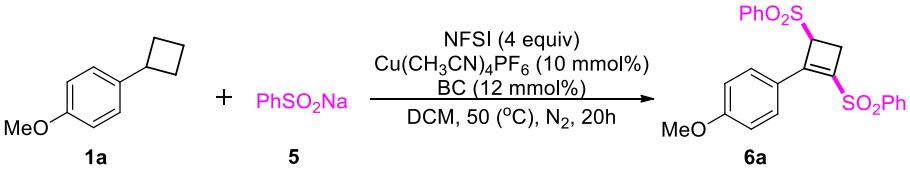


The title compound was isolated by column chromatography with ethyl acetate and petroleum ether (EA/PE = 1:10) as a white solid. **m.p.** 115 - 116 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 1H), 3.50 – 3.42 (m, 1H), 2.38 (s, 3H), 2.29 (dd, *J* = 16.8, 8.4 Hz, 2H), 2.09 – 2.02 (m, 2H), 2.02 – 1.96 (m, 1H), 1.82 (dd, *J* = 18.6, 9.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.7, 143.7, 136.3, 133.9, 129.6, 127.3, 127.1, 122.1, 39.8, 29.7, 21.5, 18.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{19}NNaO_2S$ ($[M+Na]^+$), 324.1029, found 324.1037.

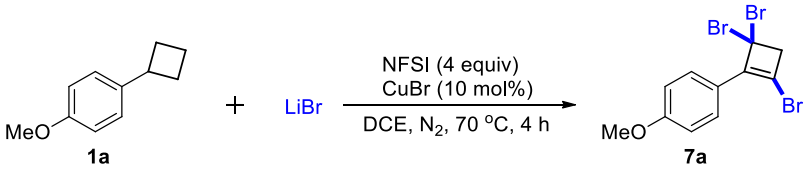
4. General Procedure and Spectral Data of Products



Take 2a as an example: In a nitrogen-filled glovebox, a mixture of CuBr (1.4 mg, 10 μmol), CH_3CN (2 mL) and Cyclobutane **1a** (32.4 mg, 0.2 mmol) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 min and adding NFSI (189.2 mg, 0.6 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at 40 °C for 4 h. After 4 h the reaction was quenched with water, extracted with DCM (3×5 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:6) to obtain product **2a**. The details and characterization data of the products are stated below.

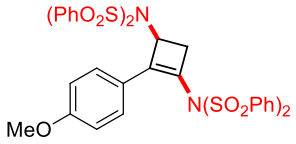


Take 6a as an example: In a nitrogen-filled glovebox, a mixture of $Cu(CH_3CN)_4PF_6$ (7.5 mg, 10 μmol), BC (**L5**) (8.6 mg, 12 μmol)and DCM (6 mL) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 10 min and adding Cyclobutane **1a** (32.4 mg, 0.2 mmol), $PhSO_2Na$ (131.2 mg, 0.8 mmol) and NFSI (252.3 mg, 0.8 mmol) successively. The vial was removed from the glovebox, and the mixture was stirred at 50 °C for 20 h. After 20 h the reaction was quenched with water, extracted with DCM (3×5 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:3) to obtain product **6a**. The details and characterization data of the products are stated below.



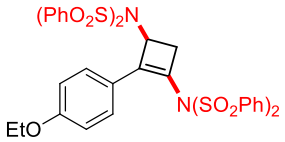
Take 7a as an example: In a nitrogen-filled glovebox, a mixture of CuBr (1.4 mg, 10 μmol), DCE (2 mL), Cyclobutane **1a** (32.4 mg, 0.2 mmol) and LiBr (57.3 mg, 0.66 mmol) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 5 min and adding NFSI (271.2 mg, 0.86 mmol) successively. The vial was removed from the glovebox, and the mixture was stirred at 70 °C for 4 h. After 4 h the reaction was quenched with water, extracted with DCM (3×5 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether) to obtain product **7a**.The details and characterization data of the products are stated below.

***N,N'*-(2-(4-methoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2a**



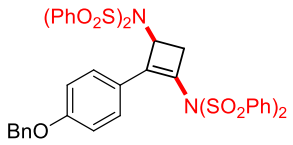
This compound was obtained in 92% (138.2 mg) yield as a white solid by the general procedure after 4 h. **m.p.** 108 - 109 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 – 7.96 (m, 4H), 7.94 (d, *J* = 6.0 Hz, 4H), 7.61 – 7.53 (m, 2H), 7.49 – 7.44 (m, 6H), 7.34 – 7.20 (m, 4H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 2H), 5.62 – 5.60 (m, 1H), 3.70 (s, 3H), 3.32 (d, *J* = 12.6 Hz, 1H), 2.90 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.2, 146.6, 139.7, 134.0, 133.6, 129.0, 128.7, 128.4, 128.1, 128.0, 123.2, 121.8, 113.5, 55.2, 52.9, 42.4. **IR** (in KBr): 3066, 2930, 1606, 1510, 1449, 1380, 1171, 1086, 855, 754, 722, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{35}H_{30}N_2NaO_9S_4$ ($[M+Na]^+$), 773.0726, found 773.0747.

***N,N'*-(2-(4-ethoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2b**



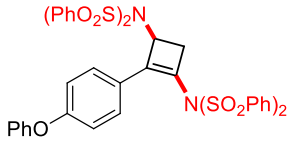
This compound was obtained in 86% (131.6 mg) yield as a white solid by the general procedure after 5 h. **m.p.** 96 - 97 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 – 7.97 (m, 4H), 7.94 (d, *J* = 4.2 Hz, 4H), 7.57 – 7.54 (m, 2H), 7.49 – 7.45 (m, 6H), 7.44 – 7.35 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 2.4 Hz, 1H), 3.97 – 3.88 (m, 2H), 3.31 (d, *J* = 12.6 Hz, 1H), 2.89 (dd, *J* = 12.6, 4.8 Hz, 1H), 1.39 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 146.7, 139.7, 134.0, 133.6, 129.0, 128.8, 128.6, 128.1, 128.0, 127.9, 123.0, 121.6, 114.0, 63.4, 52.9, 42.3, 14.7. **IR** (in KBr): 3066, 2930, 1605, 1508, 1448, 1378, 1313, 1170, 1086, 858, 757, 721, 686 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{36}H_{32}N_2NaO_9S_4$ ($[M+Na]^+$), 787.0883, found 787.0850.

***N,N'*-(2-(4-(benzyloxy)phenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2c**



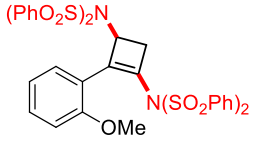
This compound was obtained in 66% (109.2 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 170 - 171 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 – 7.95 (m, 4H), 7.92 (d, *J* = 7.5 Hz, 4H), 7.52 – 7.50 (m, 2H), 7.44 – 7.40 (m, 8H), 7.39 – 7.34 (m, 3H), 7.34 – 7.25 (m, 4H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 8.5 Hz, 2H), 5.60 (dd, *J* = 4.5, 2.0 Hz, 1H), 4.99 (q, *J* = 12.5 Hz, 2H), 3.31 (dd, *J* = 13.0, 2.0 Hz 1H), 2.89 (dd, *J* = 13.0, 5.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.1, 146.5, 139.7, 136.6, 134.0, 133.6, 128.9, 128.6, 128.4, 128.1, 127.3, 123.3, 121.9, 114.4, 69.6, 52.8, 42.3. **IR** (in KBr): 3065, 1605, 1509, 1449, 1381, 1314, 1171, 1085, 857, 753, 720, 684 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{41}H_{34}N_2NaO_9S_4$ ($[M+Na]^+$), 849.1039, found 849.1035.

***N,N'*-(2-(4-phenoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2d**



This compound was obtained in 65% (105.7 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 142 - 143 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 4H), 7.97 (d, *J* = 7.2 Hz, 4H), 7.57 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.39 (m, 4H), 7.38 – 7.32 (m, 6H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.97 – 6.93 (m, 4H), 6.48 (d, *J* = 8.4 Hz, 2H), 5.66 – 5.63 (m, 1H), 3.38 (d, *J* = 12.6 Hz, 1H), 2.94 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.1, 156.0, 146.2, 139.6, 134.0, 133.6, 129.8, 129.1, 128.8, 128.4, 128.2, 128.0, 125.1, 124.0, 123.2, 119.3, 117.7, 52.8, 42.4. **IR** (in KBr): 3066, 1606, 1505, 1449, 1384, 1317, 1168, 1085, 855, 753, 721, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{40}H_{32}N_2O_9S_4$ ($[M+Na]^+$), 835.0883, found 835.0848.

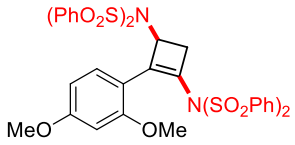
***N,N'*-(2-(2-methoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2e**



This compound was obtained in 68% (102.1 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 130 - 131 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 – 7.88 (m, 4H), 7.89 (d, *J* = 7.8 Hz, 4H), 7.59 – 7.50 (m, 2H), 7.49 – 7.42 (m, 6H), 7.38 – 7.29 (m, 4H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.46 (t, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 5.88 (d, *J* = 3.0 Hz, 1H), 3.43 (s, 3H), 3.37 (d, *J* = 12.6 Hz, 1H), 2.98 (dd, *J* = 12.6, 4.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 144.2, 140.1, 139.8, 133.8, 133.4, 130.4, 128.7, 128.5, 128.0, 124.4, 119.8, 110.1, 54.6, 54.4, 43.6.

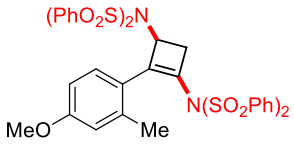
IR (in KBr): 3065, 2933, 1598, 1507, 1448, 1383, 1319, 1171, 1086, 858, 751, 720, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{40}H_{32}N_2NaO_8S_4$ ($[M+Na]^+$), 773.0726, found 773.0741.

***N,N'*-(2-(2,4-dimethoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2f**



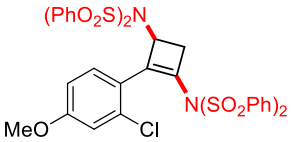
This compound was obtained in 82% (128.1 mg) yield as a white solid by the general procedure after 4 h. **m.p.** 146 - 147 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 – 7.95 (m, 4H), 7.90 (d, *J* = 7.8 Hz, 4H), 7.62 – 7.55 (m, 2H), 7.52 – 7.44 (m, 6H), 7.37 – 7.31 (m, 4H), 7.01 (d, *J* = 9.0 Hz, 1H), 6.01 (d, *J* = 8.4 Hz, 1H), 5.88 (s, 1H), 5.84 (d, *J* = 1.8 Hz, 1H), 3.71 (s, 3H), 3.39 (s, 3H), 3.33 (d, *J* = 12.0 Hz, 1H), 2.95 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.7, 158.4, 143.8, 140.3, 140.0, 133.7, 133.3, 129.7, 128.8, 128.5, 128.0, 121.9, 113.3, 104.3, 97.5, 55.3, 54.5, 54.4, 43.5. **IR** (in KBr): 3068, 2939, 1602, 1511, 1449, 1380, 1306, 1172, 1086, 852, 757, 720, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{36}H_{32}N_2NaO_{10}S_4$ ($[M+Na]^+$), 803.0832, found 803.0814.

***N,N'*-(2-(4-methoxy-2-methylphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2g**



This compound was obtained in 90% (137.7 mg) yield as a white solid by the general procedure after 4 h. **m.p.** 147 - 148 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 4H), 7.75 (d, *J* = 7.8 Hz, 4H), 7.54 (m, 4H), 7.38 (m, 8H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 2H), 5.48 (s, 1H), 3.76 (s, 3H), 3.23 (d, *J* = 12.6 Hz, 1H), 2.65 (dd, *J* = 12.6, 4.2 Hz, 1H), 2.11 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.1, 146.1, 139.9, 139.3, 133.9, 133.6, 130.4, 128.7, 128.4, 128.0, 123.2, 123.0, 116.1, 111.0, 55.2, 54.7, 42.9, 20.6. **IR** (in KBr): 3065, 2930, 1606, 1497, 1448, 1376, 1314, 1169, 1086, 855, 754, 720, 686 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{36}H_{32}N_2NaO_9S_4$ ($[M+Na]^+$), 787.0883, found 787.0859.

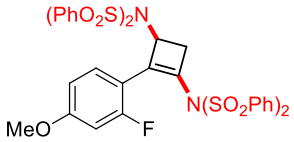
***N,N'*-(2-(2-chloro-4-methoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2h**



This compound was obtained in 78% (122.5 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 145 - 146 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 4H), 7.88 (d, *J* = 7.8 Hz, 4H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.38 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.86 (d, *J* = 2.4 Hz, 1H), 3.71 (s, 3H), 3.28 (d, *J* = 12.6 Hz, 1H), 2.91 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR**

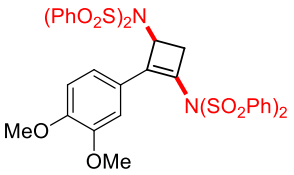
(150 MHz, $CDCl_3$) δ 160.2, 144.2, 140.0, 139.4, 133.9, 133.4, 131.25 (s), 128.9, 128.7, 128.3, 128.0, 125.3, 122.3, 115.0, 112.5, 55.5, 55.0, 43.5. **IR** (in KBr): 3064, 2934, 1596, 1448, 1378, 1316, 1170, 1087, 856, 753, 721, 686 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{35}H_{29}ClN_2NaO_8S_4$ ($[M+Na]^+$), 807.0337, found 807.0310.

***N,N'*-(2-(2-fluoro-4-methoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2i**



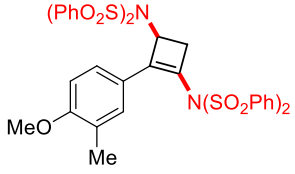
This compound was obtained in 90% (138.4 mg) yield as a white solid by the general procedure after 5 h. **m.p.** 145 - 146 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 4H), 7.95 – 7.92 (m, 4H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.50 – 7.45 (m, 6H), 7.35 (t, *J* = 7.8 Hz, 4H), 6.96 (t, *J* = 8.4 Hz, 1H), 6.21 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.13 (dd, *J* = 12.0, 2.4 Hz, 1H), 5.72 (dd, *J* = 4.8, 1.8 Hz, 1H), 3.70 (s, 3H), 3.44 (dd, *J* = 13.2, 2.4 Hz, 1H), 2.96 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.5, 160.6, 140.9, 140.1, 139.8, 133.9, 133.5, 129.2, 128.9, 128.7, 128.5, 128.1, 124.2, 111.8, 109.8, 101.4, 55.6, 53.6, 43.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -107.16. **IR** (in KBr): 3065, 2930, 1617, 1504, 1447, 1378, 1326, 1171, 1086, 854, 754, 721, 686 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{35}H_{29}FN_2NaO_8S_4$ ($[M+Na]^+$), 791.0631, found 791.0616.

***N,N'*-(2-(3,4-dimethoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2j**



This compound was obtained in 78% (121.8 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 125 - 126 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 – 7.97 (m, 4H), 7.94 (t, *J* = 12.6 Hz, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.40 (m, 6H), 7.39 – 7.29 (m, 4H), 6.73 (d, *J* = 1.2 Hz, 1H), 6.65 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.40 (d, *J* = 8.4 Hz, 1H), 5.66 (dd, *J* = 4.8, 1.8 Hz, 1H), 3.80 (s, 3H), 3.48 (s, 3H), 3.36 (dd, *J* = 12.6, 1.8 Hz, 1H), 2.93 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.8, 148.2, 146.4, 139.7, 134.0, 133.6, 129.5, 128.6, 128.5, 128.1, 123.3, 122.3, 119.8, 110.3, 109.1, 55.8, 55.4, 52.8, 42.5. **IR** (in KBr): 3068, 2938, 1610, 1500, 1448, 1375, 1303, 1166, 1086, 862, 751, 720, 683 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{36}H_{32}N_2NaO_{10}S_4$ ($[M+Na]^+$), 803.0831, found 803.0816.

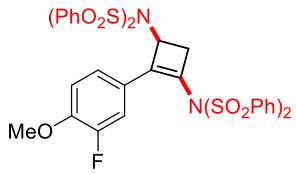
***N,N'*-(2-(4-methoxy-3-methylphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2k**



This compound was obtained in 77% (117.8 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 151 - 152 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 – 7.96 (m, 4H), 7.94 (d, *J* = 4.8 Hz, 4H),

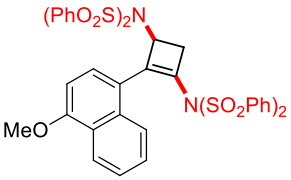
7.57 – 7.53 (m, 2H), 7.52 – 7.40 (m, 6H), 7.34 – 7.27 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.66 (s, 1H), 6.32 (d, *J* = 8.4 Hz, 1H), 5.59 (d, *J* = 4.2 Hz, 1H), 3.73 (s, 3H), 3.32 (d, *J* = 12.6 Hz, 1H), 2.89 (dd, *J* = 12.6, 4.8 Hz, 1H), 1.83 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.6, 146.8, 139.8, 133.9, 133.5, 129.2, 129.0, 128.6, 128.5, 128.2, 126.1, 125.8, 122.8, 121.2, 109.2, 55.3, 52.9, 42.5, 15.9. **IR** (in KBr): 3066, 2924, 1603, 1504, 1448, 1377, 1336, 1171, 1085, 854, 753, 721, 686 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{40}H_{32}N_2NaO_8S_4$ ([M+Na]$^+$), 787.0881, found 787.0846.

***N,N'*-(2-(3-fluoro-4-methoxyphenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2l**



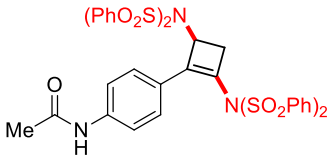
This compound was obtained in 66% (101.5 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 134 - 135 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 – 8.01 (m, 4H), 7.96 (d, *J* = 7.5 Hz, 4H), 7.61 – 7.56 (m, 2H), 7.54 – 7.42 (m, 6H), 7.41 – 7.33 (m, 4H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.59 – 6.52 (m, 1H), 6.43 (t, *J* = 8.5 Hz, 1H), 5.59 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H), 3.36 (d, *J* = 13.5 Hz, 1H), 2.92 (dd, *J* = 13.5, 5.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.3, 148.3, 145.4, 139.6, 139.5, 134.1, 133.7, 129.0, 128.8, 128.3, 128.1, 123.4, 123.4, 122.9, 113.7, 112.4, 56.1, 52.7, 42.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -134.37, -134.39, -134.40, -134.40, -134.41, -134.42. **IR** (in KBr): 3067, 2939, 1615, 1513, 1449, 1379, 1306, 1172, 1086, 858, 755, 721, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{35}H_{29}FN_2NaO_8S_4$ ([M+Na]$^+$), 791.0627, found 791.0611.

***N,N'*-(2-(4-methoxynaphthalen-1-yl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2m**



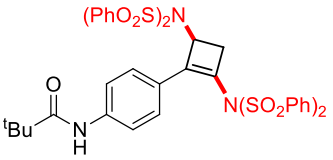
This compound was obtained in 52% (83.3 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 116 - 117 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.75 (m, 8H), 7.40 – 7.34 (m, 5H), 7.33 – 7.30 (m, 1H), 7.22 – 7.15 (m, 9H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.81 (d, *J* = 2.4 Hz, 1H), 3.95 (s, 3H), 3.59 (d, *J* = 12.0 Hz, 1H), 2.90 (dd, *J* = 12.0, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 144.2, 139.9, 138.9, 133.6, 133.3, 131.0, 128.5, 128.3, 128.2, 127.8, 127.3, 127.2, 125.6, 125.4, 125.2, 124.0, 121.8, 121.1, 103.1, 55.6, 53.6, 42.9. **IR** (in KBr): 3065, 2935, 1618, 1513, 1449, 1379, 1322, 1170, 1085, 852, 753, 720, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{39}H_{32}N_2NaO_9S_4$ ([M+Na]$^+$), 823.0883, found 823.0872.

***N*-(4-(2,4-bis(*N*-(phenylsulfonyl)phenylsulfonamido)cyclobut-1-en-1-yl)phenyl)acetamide 2n**



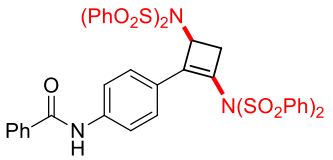
This compound was obtained in 56% (87.1 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 134 - 135 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 – 7.94 (m, 4H), 7.90 (d, *J* = 7.8 Hz, 4H), 7.72 (s, 1H), 7.61 – 7.56 (m, 2H), 7.55 – 7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.37 – 7.29 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 5.58 (dd, *J* = 4.8, 2.4 Hz, 1H), 3.34 (dd, *J* = 12.6, 1.8 Hz, 1H), 2.90 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.4 , 146.7 , 139.5 , 139.4 , 139.0 , 134.2 , 133.8 , 129.0 , 128.8 , 128.3 , 128.1 , 127.1 , 125.7 , 122.6 , 118.9 , 52.8 , 42.4 , 24.4. **IR** (in KBr): 3388, 3065, 2926, 1733, 1589, 1520, 1448, 1384, 1312, 1170, 1086, 855, 754, 720, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{36}H_{31}N_3NaO_9S_4$ ($[M+Na]^+$), 800.0835, found 800.0821.

***N*-(4-(2,4-bis(*N*-(phenylsulfonyl)phenylsulfonamido)cyclobut-1-en-1-yl)phenyl)pivalamide 2o**



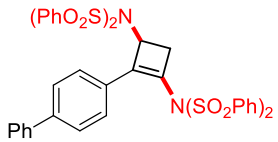
This compound was obtained in 58% (95.1 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 132 - 133 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 4H), 7.92 (d, *J* = 8.0 Hz, 4H), 7.62 – 7.56 (m, 2H), 7.50 – 7.44 (m, 6H), 7.40 – 7.32 (m, 4H), 7.30 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.56 (dd, *J* = 4.5, 2.0 Hz, 1H), 3.35 (dd, *J* = 13.0, 2.0 Hz, 1H), 2.90 (dd, *J* = 13.0, 5.0 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.5 , 146.5 , 139.5 , 139.5 , 138.9 , 134.1 , 133.7 , 129.0 , 128.8 , 128.3 , 128.1 , 127.1 , 125.9 , 122.6 , 119.1 , 52.8 , 42.5 , 39.6 , 27.4. **IR** (in KBr): 3401, 3068, 2927, 1812, 1606, 1516, 1449, 1378, 1313, 1169, 1086, 859, 755, 721, 686 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{39}H_{37}N_3NaO_9S_4$ ($[M+Na]^+$), 842.1303, found 842.1317.

***N*-(4-(2,4-bis(*N*-(phenylsulfonyl)phenylsulfonamido)cyclobut-1-en-1-yl)phenyl)benzamide 2p**



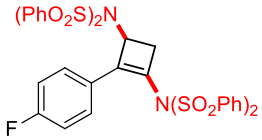
This compound was obtained in 62% (104.2 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 125 - 126 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 4H), 7.95 – 7.90 (m, 5H), 7.89 – 7.87 (m, 2H), 7.63 – 7.57 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.48 (s, 1H), 7.47 – 7.43 (m, 4H), 7.39 – 7.32 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.60 (dd, *J* = 4.8, 1.8 Hz, 1H), 3.35 (dd, *J* = 12.6, 1.8 Hz, 1H), 2.91 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.5, 146.5, 139.6, 139.6, 138.9, 134.6, 134.2, 133.8, 132.0, 129.1, 128.8, 128.8, 128.4, 128.2, 127.3, 127.1, 126.3, 123.2, 119.4, 52.9, 42.6. **IR** (in KBr): 3385, 3063, 2924, 1733, 1601, 1519, 1449, 1380, 1316, 1170, 1086, 855, 753, 720, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{41}H_{33}N_3NaO_9S_4$ ($[M+Na]^+$), 862.0991, found 862.0979.

***N*,*N*'-(2-([1,1'-biphenyl]-4-yl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2q**



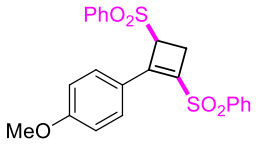
This compound was obtained in 54% (86.1 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 163 - 164 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 4H), 7.95 (d, *J* = 6.6 Hz, 4H), 7.61 – 7.56 (m, 2H), 7.51 – 7.46 (m, 10H), 7.40 – 7.39 (m, 1H), 7.33– 7.27 (m, 3H), 7.25 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 5.71 (s, 1H), 3.40 (d, *J* = 12.6 Hz, 1H), 2.96 (dd, *J* = 12.6, 4.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.6, 141.6, 140.3, 139.8, 134.0, 133.6, 129.2, 129.0, 128.8, 128.5, 128.2, 127.7, 126.8, 126.6, 124.5, 52.8, 42.7. **IR** (in KBr): 3065, 2925, 1581, 1518, 1448, 1381, 1315, 1170, 1086, 854, 753, 720, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{40}H_{32}N_2NaO_8S_4$ ([M+Na]$^+$), 819.0934, found 819.0901.

***N*,*N*'-(2-(4-fluorophenyl)cyclobut-1-ene-1,3-diyl)bis(*N*-(phenylsulfonyl)benzenesulfonamide) 2r**



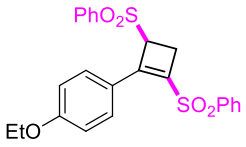
This compound was obtained in 52% (76.8 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 97 - 98 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 – 7.99 (m, 4H), 7.95 (d, *J* = 7.2 Hz, 4H), 7.58 (t, *J* = 6.6 Hz, 2H), 7.50 (d, *J* = 6.6 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.36 – 7.31 (m, 4H), 6.98 – 6.95 (m, 2H), 6.56 (t, *J* = 8.4 Hz, 2H), 5.65 – 5.62 (m, 1H), 3.37 (d, *J* = 12.6 Hz, 1H), 2.93 (dd, *J* = 12.6, 4.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.8, 145.8, 139.7, 134.1, 133.8, 129.0, 128.8, 128.4, 128.4, 128.2, 127.5, 126.6, 124.3, 115.2, 52.7, 42.5. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -110.02, -110.03, -110.04, -110.05, -110.06, -110.07, -110.08. **IR** (in KBr): 3065, 2929, 1588, 1521, 1448, 1384, 1316, 1170, 1086, 855, 754, 722, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{34}H_{27}FN_2NaO_8S_4$ ([M+Na]$^+$), 761.0532, found 761.0526.

(2-(4-methoxyphenyl)cyclobut-1-enedisulfonyl)dibenzene 6a



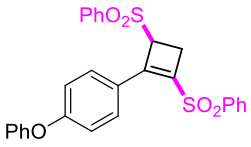
This compound was obtained in 80% (70.4 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 127 – 128 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.63 – 7.55 (m, 4H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.65 (dd, *J* = 5.0, 1.5 Hz, 1H), 3.87 (s, 3H), 2.97 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.64 (dd, *J* = 14.0, 1.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.1, 147.5, 139.3, 135.5, 134.3, 133.8, 132.8, 131.9, 129.4, 128.9, 128.8, 127.3, 121.9, 114.0, 59.8, 55.4, 30.8. **IR** (in KBr): 3064, 2935, 1774, 1604, 1508, 1445, 1382, 1148, 1078, 930, 727, 687 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}NaO_5S_2$ ([M+Na]$^+$), 463.0644, found 463.0646.

(2-(4-ethoxyphenyl)cyclobut-1-enedisulfonyl)dibenzene 6b



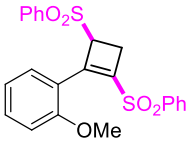
This compound was obtained in 68% (61.8 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 120 – 121 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.65 (dd, *J* = 5.0, 1.5 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.97 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.64 (dd, *J* = 14.0, 1.5 Hz, 1H), 1.44 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.5, 147.5, 139.3, 135.5, 134.2, 133.7, 132.5, 131.9, 129.3, 128.9, 128.8, 127.3, 121.7, 114.4, 63.7, 59.7, 30.7, 14.6. **IR** (in KBr): 3066, 2923, 1772, 1604, 1508, 1446, 1395, 1150, 1077, 922, 724, 687 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}NaO_5S_2$ ([M+Na]$^+$), 477.0801, found 477.0790.

(2-(4-phenoxyphenyl)cyclobut-1-enedisulfonyl)dibenzene 6c



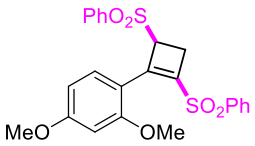
This compound was obtained in 53% (53.3 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 146 – 147 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.64 – 7.57 (m, 4H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.65 (dd, *J* = 5.0, 1.5 Hz, 1H), 2.97 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.65 (dd, *J* = 14.0, 1.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.5, 155.3, 147.1, 139.1, 135.7, 134.3, 134.2, 133.9, 131.9, 130.0, 129.4, 128.9, 127.4, 124.6, 123.6, 120.2, 117.5, 59.8, 30.8. **IR** (in KBr): 3074, 2935, 1772, 1614, 1506, 1447, 1396, 1151, 1082, 923, 726, 683 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}NaO_5S_2$ ([M+Na]$^+$), 525.0801, found 525.0792.

(2-(2-methoxyphenyl)cyclobut-1-enedisulfonyl)dibenzene 6d



This compound was obtained in 62% (54.6 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 133 – 134 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.45 (m, 3H), 7.31 – 7.25 (m, 3H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 4.90 (t, *J* = 3.0 Hz, 1H), 3.39 (s, 3H), 3.06 (d, *J* = 3.0 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 147.5, 139.3, 138.3, 137.2, 133.9, 133.7, 132.4, 132.0, 129.4, 128.7, 128.5, 127.7, 120.4, 117.9, 110.4, 61.3, 54.9, 30.8. **IR** (in KBr): 3065, 2942, 1774, 1622, 1528, 1455, 1396, 1138, 1058, 912, 744, cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}NaO_5S_2$ ([M+Na]$^+$), 463.0644, found 463.0639.

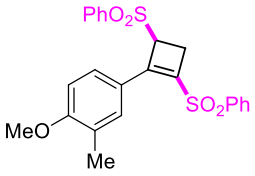
(2-(2,4-dimethoxyphenyl)cyclobut-1-enedisulfonyl)dibenzene 6e



This compound was obtained in 73% (68.6 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 166 - 167 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.49 (m, 5H), 7.32 (t, *J* = 8.0 Hz, 2H), 6.52 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.11 (d, *J* = 2.0 Hz, 1H), 4.87 (dd, *J* = 4.5, 2.0 Hz, 1H), 3.83 (s, 3H), 3.41 (s, 3H), 3.02 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.97 (dd, *J* = 13.5, 2.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.4, 159.2, 147.3, 139.6, 137.1, 135.5, 133.7, 133.3, 129.3, 128.8, 128.5, 127.5, 111.1, 104.8, 97.9, 61.3, 55.5, 54.9, 30.8. **IR** (in KBr): 3064, 2935, 1774, 1604, 1508, 1445, 1382, 1148, 1078, 930, 727, 687 cm^{-1}**. IR** (in KBr): 3068, 2937, 1771, 1611, 1505, 1446, 1375, 1148, 1078, 937, 722,

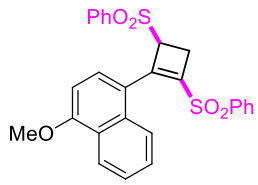
687 cm^{-1}. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}NaO_6S_2$ ($[M+Na]^+$), 493.0746, found 493.0741.

(2-(4-methoxy-3-methylphenyl)cyclobut-1-enedisulfonyl)dibenzene 6f



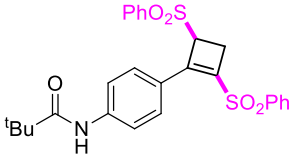
This compound was obtained in 77% (70.1 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 180 – 181 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.55 (m, 5H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.65 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H), 2.96 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.68 (d, *J* = 14.0 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.4, 147.8, 139.4, 135.8, 134.2, 133.7, 132.5, 132.0, 129.8, 129.3, 128.9, 128.8, 127.2, 126.8, 121.4, 109.6, 59.7, 55.4, 30.6, 16.1. **IR** (in KBr): 3069, 2945, 1772, 1606, 1504, 1448, 1377, 1140, 1085, 929, 731, 685 cm^{-1}. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}NaO_5S_2$ ($[M+Na]^+$), 477.0801, found 477.0799.

1-(2,4-bis(phenylsulfonyl)cyclobut-1-en-1-yl)-4-methoxynaphthalene 6g



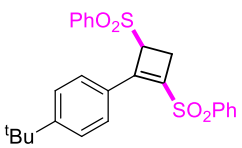
This compound was obtained in 55% (53.9 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 131 – 132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.29 (t, *J* = 7.0 Hz, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.90 – 4.85 (m, 1H), 4.00 (s, 3H), 3.31 (dd, *J* = 13.5, 1.5 Hz, 1H), 3.19 (dd, *J* = 13.5, 4.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.4, 148.5, 139.9, 138.8, 136.9, 133.8, 133.4, 131.2, 129.9, 129.1, 128.3, 128.0, 127.9, 127.1, 125.4, 125.0, 124.2, 122.2, 119.0, 102.9, 62.1, 55.7, 30.0. **IR** (in KBr): 3066, 2925, 1772, 1634, 1518, 1458, 1375, 1150, 1083, 911, 720, 687 cm^{-1}. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{22}NaO_5S_2$ ($[M+Na]^+$), 513.0801, found 513.0793.

***N*-(4-(2,4-bis(phenylsulfonyl)cyclobut-1-en-1-yl)phenyl)pivalamide 6h**



This compound was obtained in 43% (43.8 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 183 – 184 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.71 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.63 – 7.56 (m, 6H), 7.51 (s, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.36 (m, 2H), 4.67 (dd, *J* = 4.8, 1.8 Hz, 1H), 2.99 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.68 (dd, *J* = 14.4, 1.8 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 176.8, 147.2, 140.9, 139.1, 135.5, 134.6, 134.4, 133.9, 131.0, 129.4, 128.9, 128.9, 127.4, 124.7, 119.3, 59.7, 39.9, 30.9, 27.6. **IR** (in KBr): 3387, 3066, 2926, 1686, 1582, 1509, 1447, 1367, 1155, 1079, 915, 733, 687 cm^{-1}. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{27}NNaO_5S_2$ ($[M+Na]^+$), 532.1223, found 532.1231.

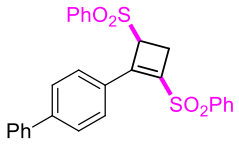
(2-(4-(tert-butyl)phenyl)cyclobut-1-enedisulfonyl)dibenzene 6i



This compound was obtained in 47% (43.8 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 102 – 103 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.75 (dd, *J*= 8.4, 1.2 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.59 – 7.55 (m, 3H), 7.51 – 7.48 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.34 (m, 2H), 4.68 (dd, *J* = 4.8, 1.8 Hz, 1H), 2.98 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.68 (dd, *J* = 14.4, 1.8 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.0, 147.9, 139.2, 135.8,

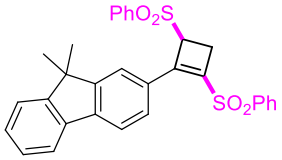
135.1, 134.2, 133.8, 129.6, 129.4, 128.9, 128.8, 127.5, 126.2, 125.6, 59.7, 35.0, 31.0, 30.8. **IR** (in KBr): 3066, 2961, 1772, 1608, 1507, 1447, 1364, 1151, 1080, 912, 726, 687 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{26}H_{26}NaO_4S_2$ ($[M+Na]^+$), 489.1165, found 489.1159.

4-(2,4-bis(phenylsulfonyl)cyclobut-1-en-1-yl)-1,1'-biphenyl 6j



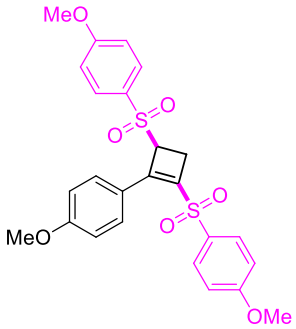
This compound was obtained in 48% (46.7 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 201 – 202 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.57 (m, 8H), 7.49 (dd, *J* = 18.0, 8.0 Hz, 4H), 7.39 (dt, *J* = 15.5, 7.5 Hz, 3H), 4.74 – 4.70 (m, 1H), 3.01 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.72 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 147.4, 143.9, 139.8, 139.0, 136.2, 135.7, 134.3, 134.0, 130.3, 129.5, 129.0, 128.9, 128.2, 127.9, 127.5, 127.1, 59.8, 31.0. **IR** (in KBr): 3067, 2935, 1734, 1616, 1511, 1446, 1374, 1154, 1080, 911, 731, 688 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}NaO_4S_2$ ($[M+Na]^+$), 509.0852, found 509.0857.

2-(2,4-bis(phenylsulfonyl)cyclobut-1-en-1-yl)-9,9-dimethyl-9H-fluorene 6k



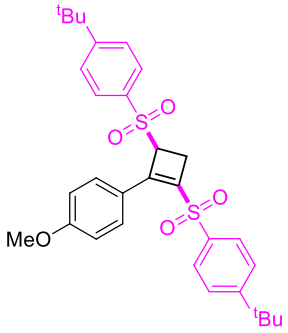
This compound was obtained in 67% (70.5 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 175 – 176 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.2 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.78 – 7.75 (m, 3H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.55 (m, 4H), 7.51 – 7.46 (m, 3H), 7.41 – 7.37 (m, 2H), 7.35 (t, *J*= 7.8 Hz, 2H), 4.75 (dd, *J* = 4.8, 1.8 Hz, 1H), 3.04 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.76 (dd, *J* = 14.4, 1.8 Hz, 1H), 1.54 (s, 3H), 1.51 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.6, 153.7, 148.3, 142.5, 139.3, 138.0, 135.6, 135.0, 134.3, 133.9, 129.4, 129.1, 128.9, 128.8, 128.5, 127.9, 127.4, 127.2, 124.4, 122.8, 120.8, 120.0, 60.0, 47.0, 31.1, 27.0, 26.8. **IR** (in KBr): 3065, 2925, 1772, 1592, 1508, 1448, 1362, 1157, 1080, 910, 736, 687 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{31}H_{26}NaO_4S_2$ ($[M+Na]^+$), 549.1165, found 549.1149.

4,4'-(2-(4-methoxyphenyl)cyclobut-1-enedisulfonyl)bis(methoxybenzene) 6l



This compound was obtained in 67% (67.2 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 151 – 152 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 6.92 (dd, *J* = 11.0, 9.0 Hz, 4H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.62 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84 (s, 3H), 3.00 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.57 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.0, 163.8, 161.9, 146.4, 133.5, 131.8, 131.2, 130.8, 129.5, 126.6, 122.1, 114.5, 114.0, 59.8, 55.6, 55.6, 55.4, 30.7. **IR** (in KBr): 3064, 2924, 1772, 1605, 1508, 1446, 1375, 1149, 1077, 929, 723, 689 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}NaO_7S_2$ ($[M+Na]^+$), 523.0853, found 523.0847.

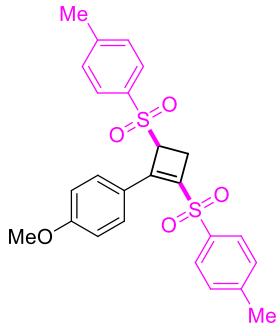
4,4'-(2-(4-methoxyphenyl)cyclobut-1-enedisulfonyl)bis(tert-butylbenzene) 6m



This compound was obtained in 64% (70.8 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 151 - 152 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J*

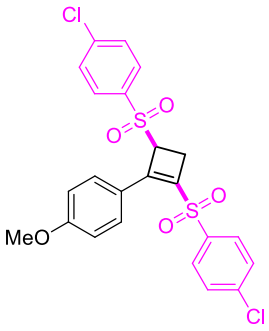
= 8.5 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.60 (dd, *J* = 5.0, 1.5 Hz, 1H), 3.86 (s, 3H), 2.88 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.77 (dd, *J* = 14.0, 1.5 Hz, 1H), 1.35 (s, 9H), 1.33 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.8, 158.3, 157.8, 147.1, 136.3, 133.6, 133.2, 131.8, 128.8, 127.3, 126.4, 126.0, 122.2, 113.9, 59.8, 55.4, 35.3, 35.3, 31.0, 31.0, 30.7. **IR** (in KBr): 2955, 2597, 1800, 1623, 1515, 1466, 1336, 1155, 1063, 911, 744, 677 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{31}H_{36}NaO_5S_2$ ([M+Na]$^+$), 575.1896, found 575.1888.

4,4'-(2-(4-methoxyphenyl)cyclobut-1-enedisulfonyl)bis(methylbenzene) 6n



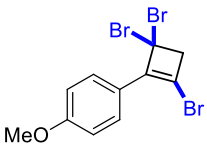
This compound was obtained in 76% (71.2 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 146 - 147 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.63 – 4.60 (m, 1H), 3.86 (s, 3H), 2.94 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.63 (d, *J* = 14.0 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (125MHz, $CDCl_3$) δ 161.9, 147.0, 145.2, 144.8, 136.3, 133.1, 132.5, 131.8, 129.9, 129.4, 128.9, 127.4, 122.0, 113.9, 59.8, 55.4, 30.7, 21.7, 21.6. **IR** (in KBr): 3027, 2915, 1772, 1654, 1508, 1453, 1376, 1160, 1079, 945, 725, 682 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}NaO_5S_2$ ([M+Na]$^+$), 491.0958, found 491.0953.

4,4'-(2-(4-methoxyphenyl)cyclobut-1-enedisulfonyl)bis(chlorobenzene) 6o



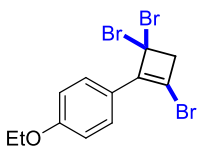
This compound was obtained in 56% (56.8 mg) yield as a white solid by the general procedure after 20 h. **m.p.** 138 – 139 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 15.0, 8.5 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 4.66 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 3.04 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.58 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.4, 147.7, 141.3, 140.8, 137.7, 133.8, 132.4, 131.9, 130.4, 129.8, 129.2, 128.7, 121.6, 114.2, 59.9, 55.5, 30.7. **IR** (in KBr): 3086, 2924, 1772, 1606, 1508, 1448, 1395, 1148, 1085, 910, 730, 667 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{18}Cl_2NaO_5S_2$ ([M+Na]$^+$), 530.9867, found 530.9861.

1-methoxy-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7a



This compound was obtained in 92% (73.0 mg) yield as a white solid by the general procedure after 4 h. **m.p.** 96 - 97 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.93 (s, 2H), 3.85 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.7, 148.2, 127.7, 121.1, 114.1, 107.8, 62.2, 55.3, 46.3. **IR** (in KBr): 2928, 2839, 1746, 1623, 1507, 1457, 1310, 1178, 1060, 829, 657 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_9Br_3NaO$ ([M+Na]$^+$), 416.8101, found 416.8092.

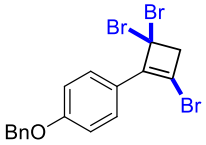
1-ethoxy-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7b



This compound was obtained in 82% (67.4 mg) yield as a white solid by the

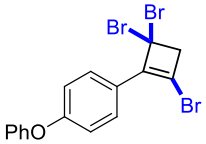
general procedure after 5 h. **m.p.** 92 - 93 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.01 – 6.97 (m, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.1, 148.2, 127.7, 121.0, 114.6, 107.6, 63.6, 62.3, 46.3, 14.7. **IR** (in KBr): 2926, 2835, 1747, 1623, 1507, 1457, 1315, 1178, 1061, 829, 658 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{11}Br_3NaO$ ($[M+Na]^+$), 430.8255, found 430.8248.

1-(benzyloxy)-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7c



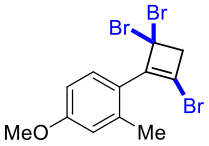
This compound was obtained in 53% (50.0 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 125 – 126 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 2H), 7.46 – 7.43 (m, 2H), 7.41 – 7.39 (m, 2H), 7.36 – 7.32 (m, 1H), 7.10 – 7.05 (m, 2H), 5.12 (s, 2H), 3.93 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.9, 148.2 , 136.5, 128.7, 128.1, 127.8, 127.5, 121.4, 115.0, 70.1, 62.3, 46.2. **IR** (in KBr): 2930, 1716, 1629, 1502, 1457, 1310, 1168, 1070, 834, 691 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}Br_3NaO$ ($[M+Na]^+$), 492.8409, found 492.8401.

1-phenoxy-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7d



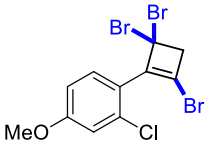
This compound was obtained in 71% (65.2 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 121 - 122 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.41 – 7.35 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.10 – 7.04 (m, 4H), 3.94 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.0, 156.0, 148.0, 129.9, 127.9, 124.2, 123.1, 119.8, 118.1, 109.1, 62.3, 46.0. **IR** (in KBr): 2930, 1716, 1629, 1502, 1457, 1374, 1168, 1070, 834, 691 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{11}Br_3NaO$ ($[M+Na]^+$), 478.8249, found 478.8254.

4-methoxy-2-methyl-1-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7e



This compound was obtained in 48% (39.4 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 87 - 88 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 1H), 6.82 – 6.80 (m, 2H), 3.92 (s, 2H), 3.83 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.6, 151.7, 139.5, 128.8, 121.5, 116.2, 115.8, 111.1, 61.9, 55.2, 51.3, 20.6. **IR** (in KBr): 2924, 2869, 1735, 1628, 1505, 1454, 1310, 1176, 1079, 832, 697 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{11}Br_3NaO$ ($[M+Na]^+$), 430.8247, found 430.8255.

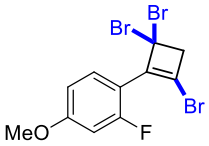
2-chloro-4-methoxy-1-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7f



This compound was obtained in 70% (57.9 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 97 - 98 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.0 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.4 Hz,

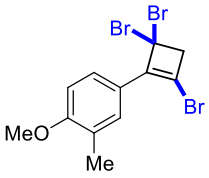
1H), 3.94 (s, 2H), 3.84 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.2, 148.6, 134.9, 129.6, 120.9, 118.4, 115.4, 112.8, 62.1, 55.6, 50.1. **IR** (in KBr): 2938, 2837, 1746, 1643, 1458, 1297, 1192, 1073, 839, 677 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_8Br_3ClNaO$ ($[M+Na]^+$), 450.7702, found 450.7707.

2-fluoro-4-methoxy-1-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7g



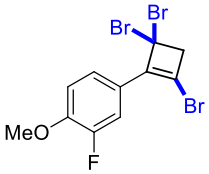
This compound was obtained in 80% (66.4 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 90 - 91 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (t, *J* = 8.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.68 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.94 (s, 2H), 3.84 (s, 3H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 162.2, 161.4, 145.4, 128.5, 113.1, 110.1, 109.3, 102.4, 62.9, 55.7, 47.5. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -102.49, -102.49, -102.50, -102.51, -102.52, -102.54. **IR** (in KBr): 2935, 2839, 1716, 1626, 1504, 1464, 1330, 1165, 1080, 836, 670 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_8Br_3FNaO$ ($[M+Na]^+$), 434.8001, found 434.8792.

1-methoxy-2-methyl-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7h



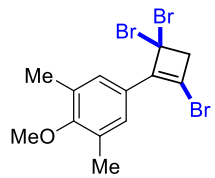
This compound was obtained in 78% (64.1 mg) yield as a white solid by the general procedure after 5 h. **m.p.** 71 - 72 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 1H), 7.81 – 7.77 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 2H), 3.87 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (150 MHz, C DCl_3) δ 159.0, 148.3, 128.3, 127.1, 125.4, 120.69, 109.8, 107.4, 62.3, 55.4, 46.5, 16.4, 16.4. **IR** (in KBr): 2916, 2830, 1716, 1628, 1498, 1457, 1330, 1168, 1078, 846, 667 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{11}Br_3NaO$ ($[M+Na]^+$), 430.8249, found 430.8242.

2-fluoro-1-methoxy-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7i



This compound was obtained in 93% (77.2 mg) yield as a white solid by the general procedure after 4 h. **m.p.** 82 - 83 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.1, 149.0, 147.2, 122.8, 121.4, 113.8, 113.2, 109.6, 62.2, 56.2, 45.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -133.60, -133.60, -133.62, -133.62, -133.62, -133.64, -133.64. **IR** (in KBr): 2936, 2840, 1716, 1632, 1510, 1473, 1318, 1168, 1061, 849, 674 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_8Br_3FNaO$ ($[M+Na]^+$),434.8798, found 434.8791.

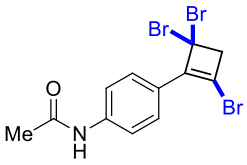
2-methoxy-1,3-dimethyl-5-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7j



This compound was obtained in 67% (56.9 mg) yield as a white solid by the

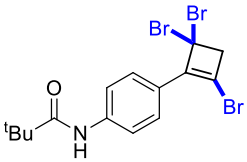
general procedure after 5 h. **m.p.** 65 - 66 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (s, 2H), 3.92 (s, 2H), 3.75 (s, 3H), 2.36 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.4, 148.2, 131.4, 126.7, 124.0, 109.2, 62.3, 59.6, 46.3, 16.3. **IR** (in KBr): 2934, 2855, 1716, 1631, 1507, 1457, 1317, 1161, 1086, 837, 687 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{13}Br_3NaO$ ($[M+Na]^+$), 444.8405, found 444.8411.

***N*-(4-(2,4,4-tribromocyclobut-1-en-1-yl)phenyl)acetamide 7k**



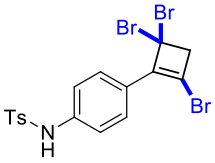
This compound was obtained in 45% (38.2 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 151 - 152 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 3.94 (s, 2H), 2.21 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.4, 148.0, 139.2, 127.1, 124.3, 119.5, 109.6, 62.3, 45.9, 24.7. **IR** (in KBr): 3239, 2929, 2849, 1628, 1509, 1321, 1182, 1077, 829, 697 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}Br_3NNaO$ ($[M+Na]^+$), 443.8205, found 443.8200.

***N*-(4-(2,4,4-tribromocyclobut-1-en-1-yl)phenyl)pivalamide 7l**



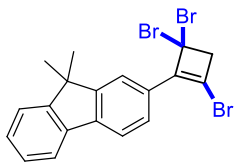
This compound was obtained in 55% (51.3 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 155 - 156 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (s, 1H), 3.94 (s, 2H), 1.33 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 176.6, 148.0, 139.4, 127.0, 124.1, 119.6, 109.5, 62.3, 46.0, 39.8, 27.6. **IR** (in KBr): 3307, 2932, 2869, 1666, 1509, 1320, 1187, 1082, 837, 669 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{16}Br_3NNaO$ ($[M+Na]^+$), 485.8674, found 485.8685.

4-methyl-N-(4-(2,4,4-tribromocyclobut-1-en-1-yl)phenyl)benzenesulfonamide 7m



This compound was obtained in 80% (85.8 mg) yield as a white solid by the general procedure after 6 h. **m.p.** 175 - 176 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 – 7.88 (m, 2H), 7.75 – 7.74 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.18 (m, 2H), 6.96 (s, 1H), 3.92 (s, 2H), 2.40 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.6, 144.3, 137.9, 136.1, 129.9, 127.3, 127.3, 124.9, 120.1, 110.3, 62.3, 45.7, 21.6. **IR** (in KBr): 3231, 2924, 2852, 1634, 1504, 1304, 1184, 1086, 839, 667 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}Br_3NNaO_2S$ ($[M+Na]^+$), 555.8188, found 555.8179.

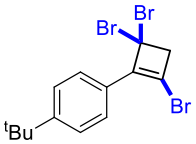
9,9-dimethyl-2-(2,4,4-tribromocyclobut-1-en-1-yl)-9H-fluorene 7n



This compound was obtained in 55% (53.1 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 144 - 145 °C. **^{1}H NMR** (600 MHz,

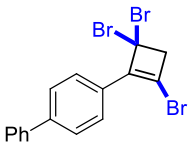
$CDCl_3$) δ 8.08 (d, *J* = 1.8 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.75 (m, 1H), 7.46 – 7.45 (m, 1H), 7.36 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.98 (s, 2H), 1.54 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.2, 153.8, 148.8, 140.9, 138.4, 128.0, 127.2, 127.1, 125.2, 122.7, 120.5, 120.3, 120.1, 109.8, 62.3, 47.0, 46.2, 27.1. **IR** (in KBr): 2923, 2865, 1716, 1616, 1507, 1457, 1312, 1170, 1079, 833, 689 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{15}Br_3Na$ ($[M+Na]^+$), 502.8614, found 502.8606.

1-(tert-butyl)-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7o



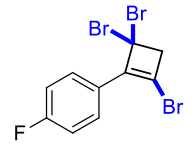
This compound was obtained in 42% (35.5 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 64 - 65 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 2H), 1.35 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.2, 148.5, 125.9, 125.6, 125.6, 109.8, 62.4, 46.1, 35.0, 31.1. **IR** (in KBr): 2927, 2861, 1716, 1631, 1507, 1459, 1319, 1161, 1081, 839, 667 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{15}Br_3Na$ ($[M+Na]^+$), 442.8617, found 442.8611.

4-(2,4,4-tribromocyclobut-1-en-1-yl)-1,1'-biphenyl 7p



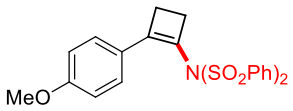
This compound was obtained in 66% (58.5 mg) yield as a white solid by the general procedure after 8 h. **m.p.** 71 - 72 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 7.73 – 7.70 (m, 2H), 7.64 – 7.61 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.37 (m, 1H), 3.98 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.3, 142.5, 140.3, 128.9, 127.8, 127.3, 127.3, 127.1, 126.5, 110.9, 62.4, 45.9. **IR** (in KBr): 2934, 1716, 1625, 1507, 1457, 1319, 1080, 840, 685 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{11}Br_3Na$ ($[M+Na]^+$), 462.8302, found 462.8311.

1-fluoro-4-(2,4,4-tribromocyclobut-1-en-1-yl)benzene 7q



This compound was obtained in 36% (27.7 mg) yield as a white solid by the general procedure after 9 h. **m.p.** 77 - 78 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 – 7.80 (m, 2H), 7.26 – 7.17 (m, 2H), 3.95 (s, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.4, 147.6, 128.2, 124.7, 115.9, 110.4, 62.3, 45.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -108.96, -108.96, -108.97, -108.98, -108.99, -109.00, -109.01, -109.02. **IR** (in KBr): 2923, 1716, 1619, 1503, 1457, 1376, 1157, 1081, 829, 657 cm^{-1}**. HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_6Br_3FNa$ ($[M+Na]^+$), 404.7895, found 404.7889.

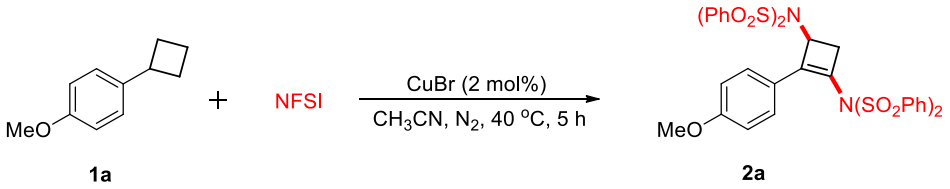
***N*-(2-(4-methoxyphenyl)cyclobut-1-en-1-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3**



The title compound was isolated by column chromatography with ethyl acetate and petroleum ether (EA/PE = 1:15) as a white solid in 8% (10.9 mg) yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.99 (m,

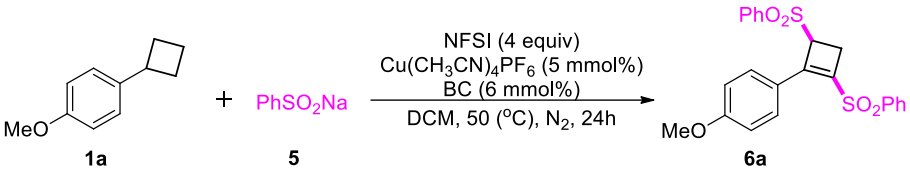
4H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 4H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 3.76 (s, 3H), 2.69 – 2.66 (m, 2H), 2.59 – 2.56 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.1, 149.4, 140.1, 133.8, 128.9, 128.4, 128.0, 124.9, 119.3, 113.4, 55.2, 31.1, 24.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}NNaO_5S_2$ ([M+Na]$^+$), 478.0752, found 478.0759.

5. Gram-scale Reactions



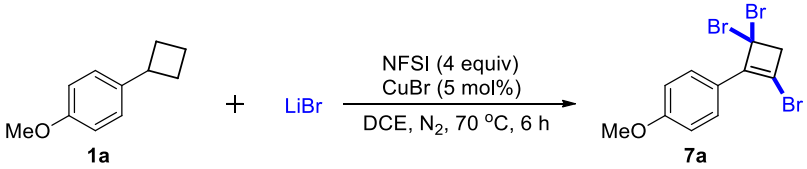
1a **2a**

In a nitrogen-filled glovebox, a mixture of CuBr (20.0 mg, 0.14 mmol), CH_3CN (20 mL) and Cyclobutane**1a** (1.14 g, 7 mmol) was added into a 50 mL flame-dried reaction tube containing a magnetic stirring bar. The resulting mixture was stirred for 5 min and adding NFSI (6.62 g, 21 mmol) successively. The tube was removed from the glovebox, and the mixture was stirred at 40 °C for 5 h. After 5 h the reaction was quenched with water, extracted with DCM (3×30 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:6) to obtain product **2a** (4.46 g, 85%).



1a **5** **6a**

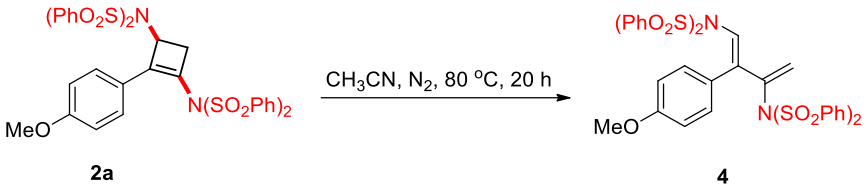
In a nitrogen-filled glovebox, a mixture of $Cu(CH_3CN)_4PF_6$ (93.2 mg, 0.25 mmol), **L2** (108 mg, 0.3 mmol)and DCM (100 mL) was added into a 250 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 10 min and adding Cyclobutane **1a** (0.81 g, 5 mmol), $PhSO_2Na$ (3.28 g, 20 mmol) and NFSI (6.31 g, 20 mmol) successively. The vial was removed from the glovebox, and the mixture was stirred at 50 °C for 24 h. After 24 h the reaction was quenched with water, extracted with DCM (3×100 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:3) to obtain product **6a** (1.50 g, 68%).



1a **7a**

In a nitrogen-filled glovebox, a mixture of CuBr (50.1 mg, 0.35 mmol), DCE (20 mL), Cyclobutane**1a** (1.14 g, 7 mmol) and LiBr (1.82 g, 21 mmol) was added into a 50 mL flame-dried reaction tube containing a magnetic stirring bar. The resulting mixture was stirred for 10 min and adding NFSI (8.83 g, 28 mmol) successively. The tube was removed from the glovebox, and the mixture was stirred at 70 °C for 6 h. After 6 h the reaction was quenched with water, extracted with DCM (3×30 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether) to obtain product **7a** (2.44 g, 88%).

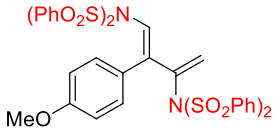
6. Synthetic Application of highly Functionalized Cyclobutene Derivatives



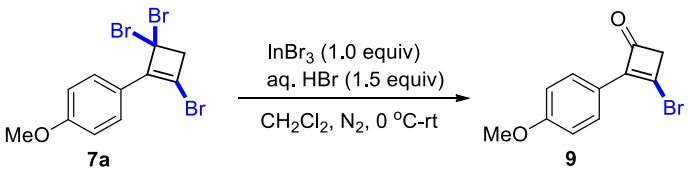
2a **4**

In a nitrogen-filled glovebox, a mixture ofcyclobutene **2a** (0.1 mmol) and CH_3CN (1 mL) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. The reaction mixture was stirred at 80 °C for 20 h. Finally, the residue was directly purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:6) to afford the desired product **4** (67.5 mg, 90%).[7]

(*E*)-N,N'-(2-(4-methoxyphenyl)buta-1,3-diene-1,3-diyl)bis(N-(phenylsulfonyl)benzenesulfonamide) 4



The title compound was isolated by column chromatography with ethyl acetate and petroleum ether (EA/PE = 1:6) as a white solid in 90% (67.5 mg) yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 4H), 7.60 – 7.52 (m, 8H), 7.45 (t, *J* = 7.8 Hz, 4H), 7.36 (t, *J* = 7.8 Hz, 4H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.85 (s, 1H), 5.42 (s, 1H), 4.98 (s, 1H), 3.86 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.8, 146.9, 141.1, 138.2, 137.9, 134.1, 133.7, 131.5, 129.3, 129.1, 128.8, 128.5, 126.2, 121.3, 113.9, 55.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{35}H_{30}N_2NaO_9S_4$ ([M+Na]$^+$), 773.0728, found 773.0741.

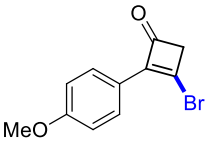


7a **9**

In a nitrogen-filled glovebox, a mixture of cyclobutene **7a** (0.1 mmol), $InBr_3$ (35.5mg, 0.1 mmol) and CH_2Cl_2 (1 mL) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. 48%

hydrobromic acid (25 mg, 0.15 mmol,) was added at 0 °C and the reaction mixture was stirred at room temperature for 36 h. Finally, the residue was directly purified by flash column chromatography on silica gel (petroleum ether) to afford the desired product **9** (16.4 mg, 65%).[8]

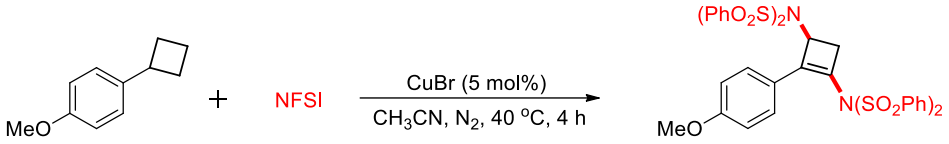
3-bromo-2-(4-methoxyphenyl)cyclobut-2-enone 9



The title compound was isolated by column chromatography with petroleum etheras a colorless oil in 65% (16.4 mg) yield. **^{1}H NMR** (500 MHz, CDCl3) δ 7.92 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H), 3.65 (s, 2H). **^{13}C NMR** (150 MHz, CDCl3) δ 186.6, 160.6, 147.6, 140.7, 128.2, 121.0, 114.1, 55.4, 55.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_9BrNaO_2$ ([M+Na]$^+$), 274.9678, found 274.9670.

7. Mechanism Study

(1) Radical inhibitor experiments

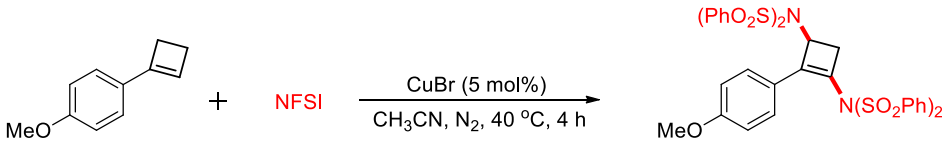


1a **2a**

Radical inhibitors (3.0 equiv)	Yield (%) of **2a**
TEMPO	not detected
BHT	not detected

In a nitrogen-filled glovebox, a mixture of CuBr (1.4 mg, 10 μmol), CH_3CN (2 mL) and Cyclobutane **1a** (32.4 mg, 0.2 mmol) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 min and adding NFSI (189.2 mg, 0.6 mmol) successively. Then BHT (0.6 mmol, 3 equiv) or TEMPO (0.6 mmol, 3 equiv) was added. The vial was removed from the glovebox, and the mixture was stirred at 40 °C for 4 h.

(2) Transformation of 8 to 2a.



8a **2a**

In a nitrogen-filled glovebox, a mixture of CuBr (1.4 mg, 10 μmol), CH_3CN (2 mL) and 1-(cyclobut-1-en-1-yl)-4-methoxybenzene **8a** (32 mg, 0.2 mmol) was added into a 10 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 min and adding NFSI (189.2 mg, 0.6 mmol) successively. The vial was removed from the glovebox,

and the mixture was stirred at 40 °C for 4 h. After 4 h the reaction was quenched with water, extracted with DCM (3×5 mL), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:6) to obtain product **2a** (42 mg, 28%).

(3) A possible mechanism of the formation of 1,3-disulfonylcyclobutene derivatives 6.

As depicted in Supplementary Fig. S1, initially, the oxidation of Cu^{I} and NFSI formed Cu^{II}-coordinated nitrogen-centered radical species **A** or Cu^{III} species **A'**. **A'** selectively abstracted the benzylic hydrogen atom from cyclobutane **1** followed by β-H elimination to generate cyclobutene **8**. Alternatively, **B** might rebound with Cu^{II} species to generate Cu^{III} species followed by β-Cu-H elimination to generate **8**.[9,10] Meanwhile, the oxidation of RSO_2Na and nitrogen-centered radical species **A** produced sulfonyl radical, which added to **8** followed by β-H elimination afforded 1-sulfonylcyclobutene derivative **10**. Then, the highly regio-selective allylic hydrogen atom abstraction form allylic radical **H** and Cu^{II} species **C** or **C'**. Subsequently, the ligand exchange between RSO_2Na and **C** or **C'** led Cu^{II}-SO_2R species **I**. The combination of **H** and **I** resulted in Cu^{III} species **J**, which underwent a reductive elimination to afford 1,3-disulfonylcyclobutene **6**, along with the regeneration of Cu^{I} catalyst. An alternative out-sphere direct ligand-transfer between **H** and **I** could not be exclude at the current stage.[11, 12]

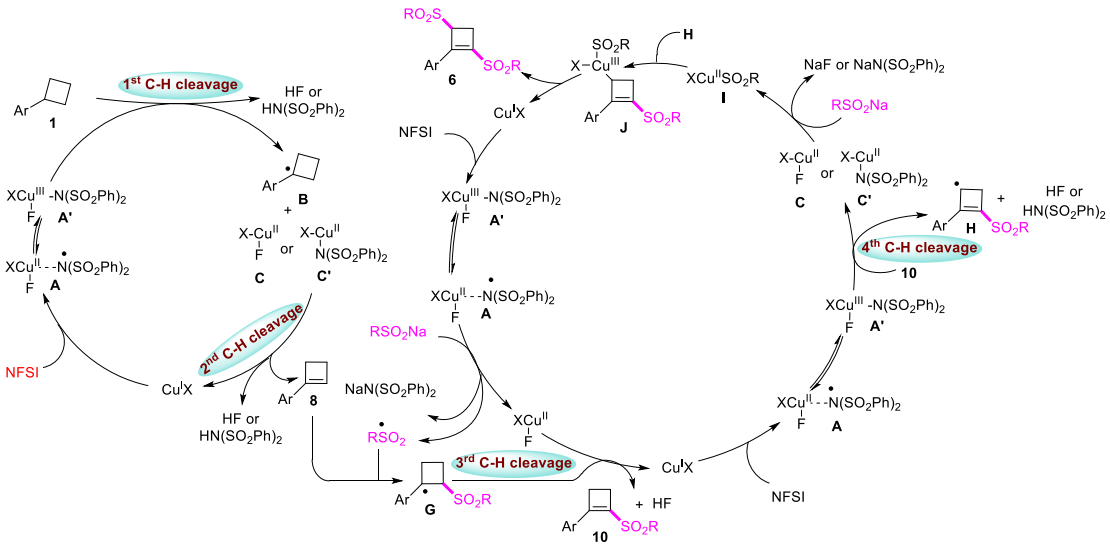


Figure S1. A proposed mechanism of the formation of **6**.

(4) A possible mechanism of the formation of 1,3,3-tribromocyclobutene derivatives 7.

As depicted in Supplementary Fig. S2, initially, the oxidation of Cu^{I} and NFSI formed Cu^{II}-coordinated nitrogen-centered radical species **A** or Cu^{III} species **A'**. **A'** selectively abstracted the benzylic hydrogen atom from cyclobutane **1** followed by β-H elimination to generate cyclobutene **8**. Alternatively, **B** might rebound with Cu^{II} species to generate Cu^{III} species followed by β-Cu-H elimination to generate **8**.[9,10] Meanwhile, the oxidation of LiBr and nitrogen-centered radical species **A** produced bromine radical, which added to **8** followed by β-H elimination afforded 1-bromocyclobutene derivative **11**. Then, the highly regio-selective allylic hydrogen atom abstraction form allylic radical **L** and Cu^{II} species **C** or **C'**. Subsequently, the ligand exchange between LiBr and **C** or **C'** led Cu^{II}-Br species **M**. The combination of **L** and **M** resulted in Cu^{III} species **N**, which underwent a reductive elimination to afford 1,3-dibromocyclobutene **12**, along with the regeneration of Cu^{I} catalyst. An alternative out-sphere direct ligand-transfer between **L** and **M** could not be exclude at the current stage.[13] Next, the highly selective allylic C–H bromination of **12** occurred, affording the desired product **7**.

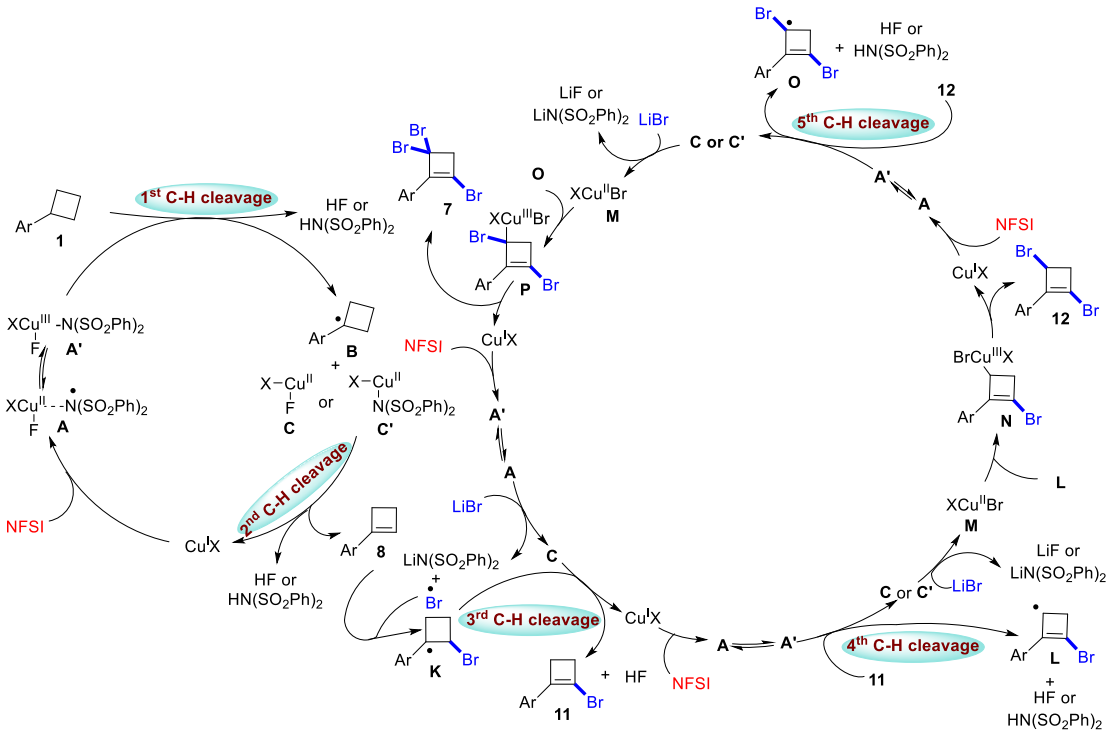


Figure S2. A proposed mechanism of the formation of 7.

8. Single Crystal Structure and Data

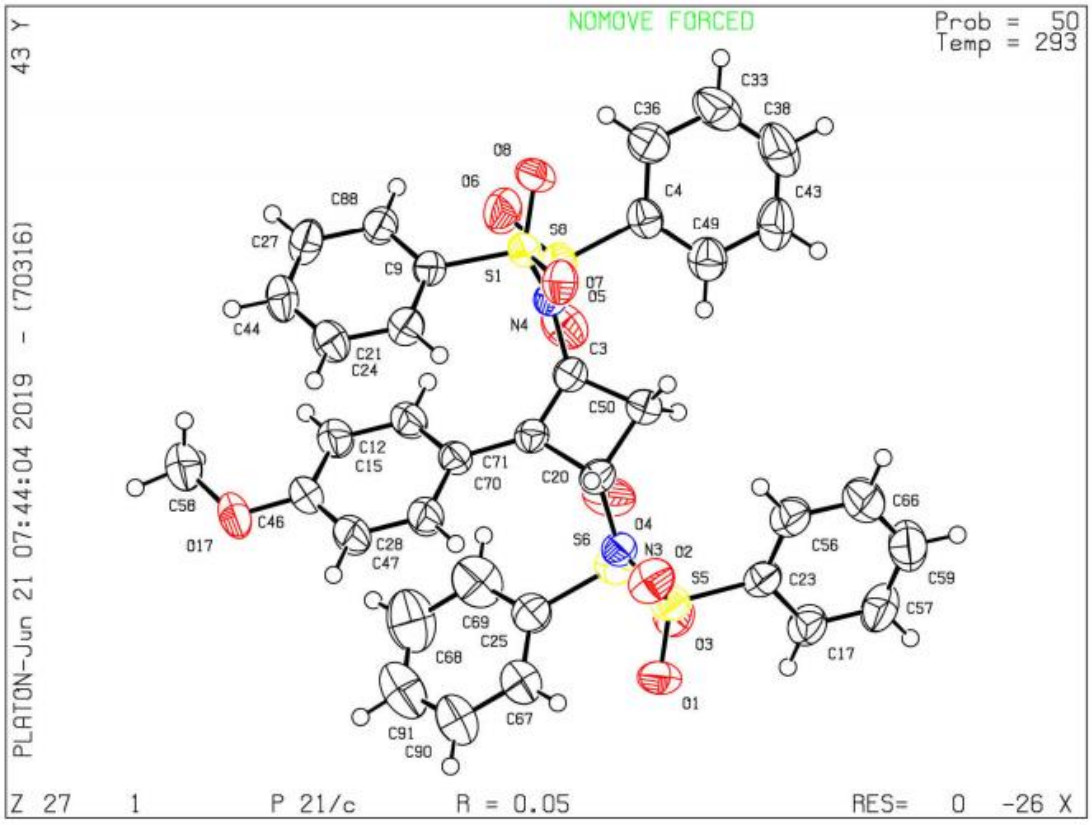


Figure S3. Crystal structure of **2a** (CCDC 1935659).

Table S4. Crystal data of 2a

CCDC number	1935659
Empirical formula	$C_{35}H_{24}N_3O_9S_4$
Formula weight	744.65
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, Space group	Monoclinic, P 21/C
Unit cell dimensions	a = 12.807 A alpha = 90 deg. b = 13.731 A beta = 110.60 deg. c = 20.965 A gamma = 90 deg.
Volume	3450.9 A^3
Z, Calculated density	4, 1.433 Mg/m^3
Reflections collected / unique	26169 / 6432 [R(int) = 0.0404]

F(000)	1536
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6432 / 0 / 451
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1255
R indices (all data)	R1 = 0.0743, wR2 = 0.1402
Largest diff. peak and hole	0.437 and -0.408 e.A^-3
$^{a}R_1 = \Sigma\|\|F_o\|-\|Fc\|\|/\Sigma\|Fo\|$; $^{b}wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$	

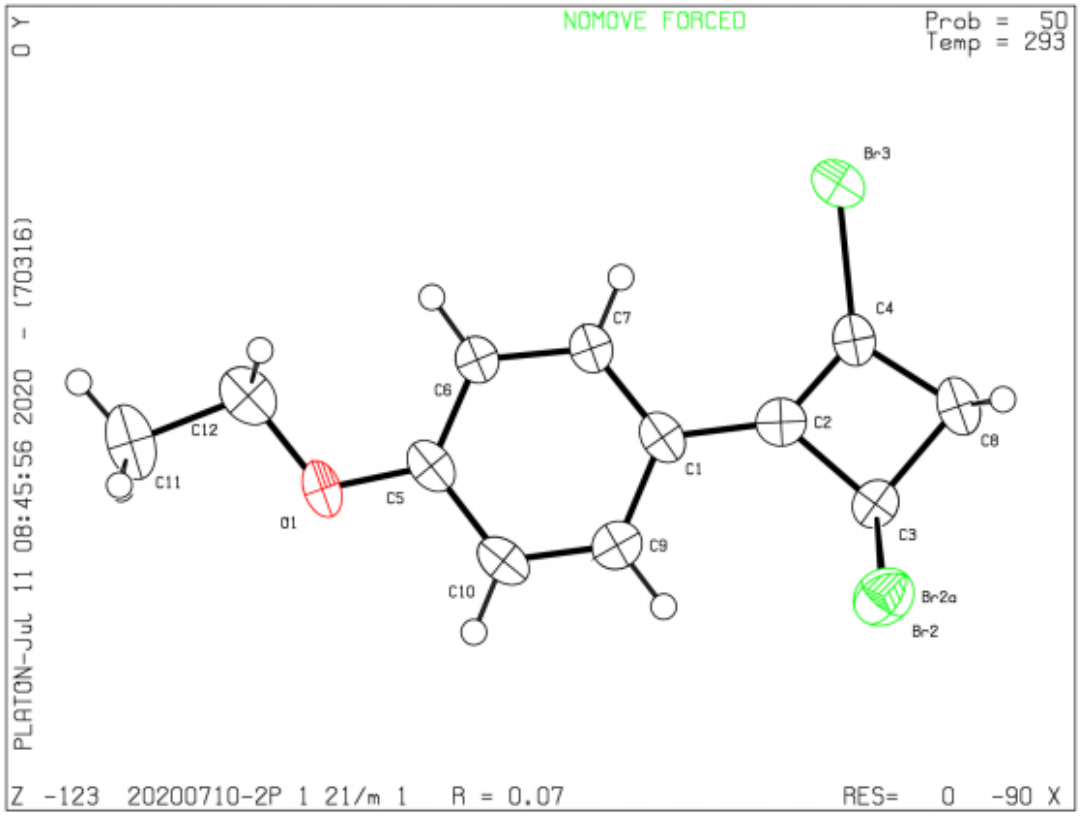


Figure S4. Crystal structure of **7b** (CCDC 2039202).

Table S5. Crystal data of 7b

CCDC number	2039202
Empirical formula	$C_{12}H_{11}Br_3O$
Formula weight	410.94
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, Space group	Monoclinic, P 1 21/m 1
Unit cell dimensions	a = 7.6142 A alpha = 90 deg. b = 7.1461 A beta = 106.526 deg. c = 12.6645 A gamma = 90 deg.
Volume	660.63 A^3
Z, Calculated density	2, 2.066 Mg/m^3
Reflections collected / unique	2611 / 1269 [R(int) = 0.0714]
F(000)	392
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.09601
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1269 / 0 / 95
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0747, wR2 = 0.1920
R indices (all data)	R1 = 0.0801, wR2 = 0.2058
Largest diff. peak and hole	1.249 and -1.334 e.A^-3

$^{a}R_1 = \Sigma||F_o|-|Fc||/\Sigma|Fo|$; $^{b}wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

9. NMR Spectra

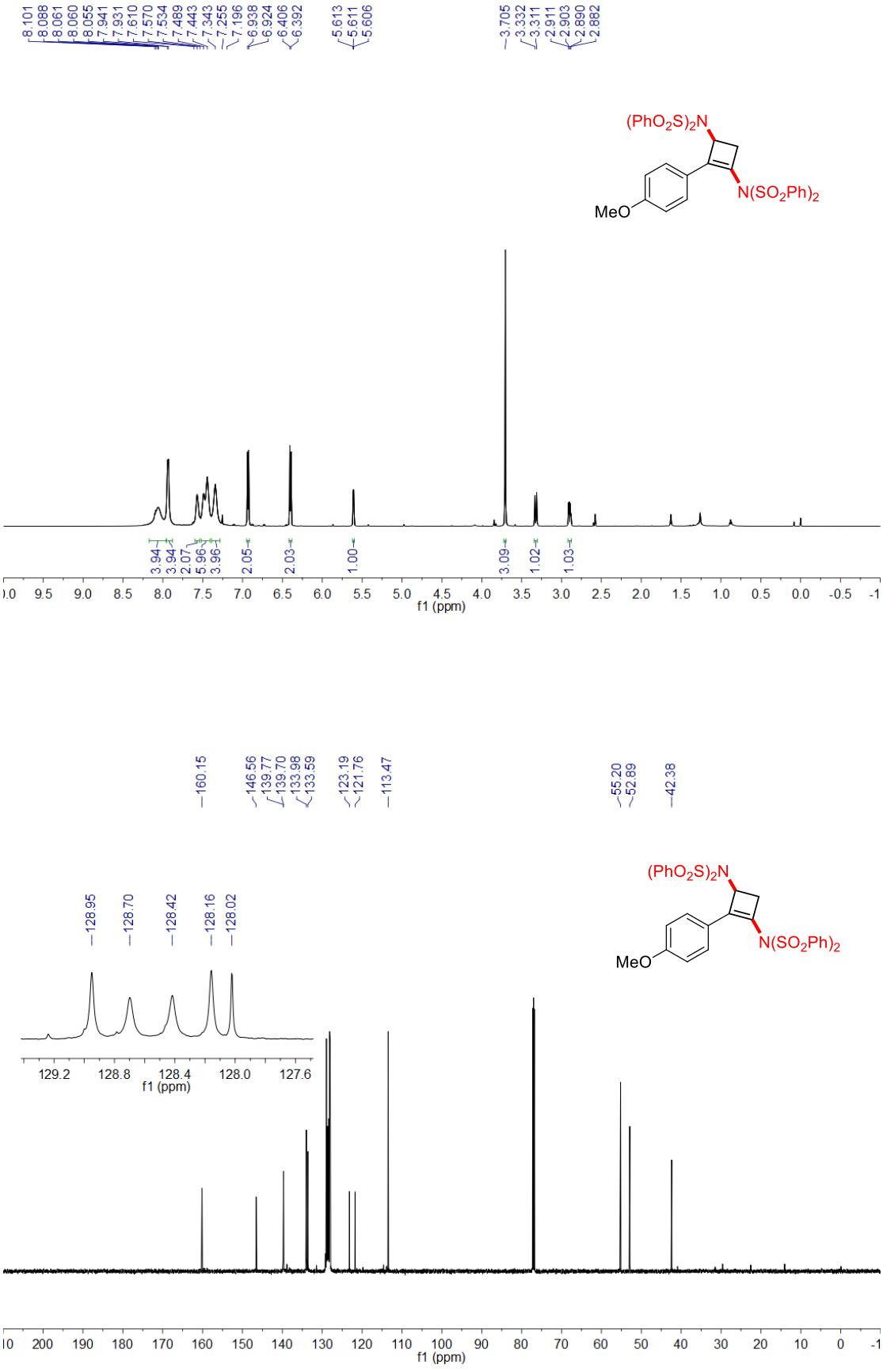


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of compound **2a.**

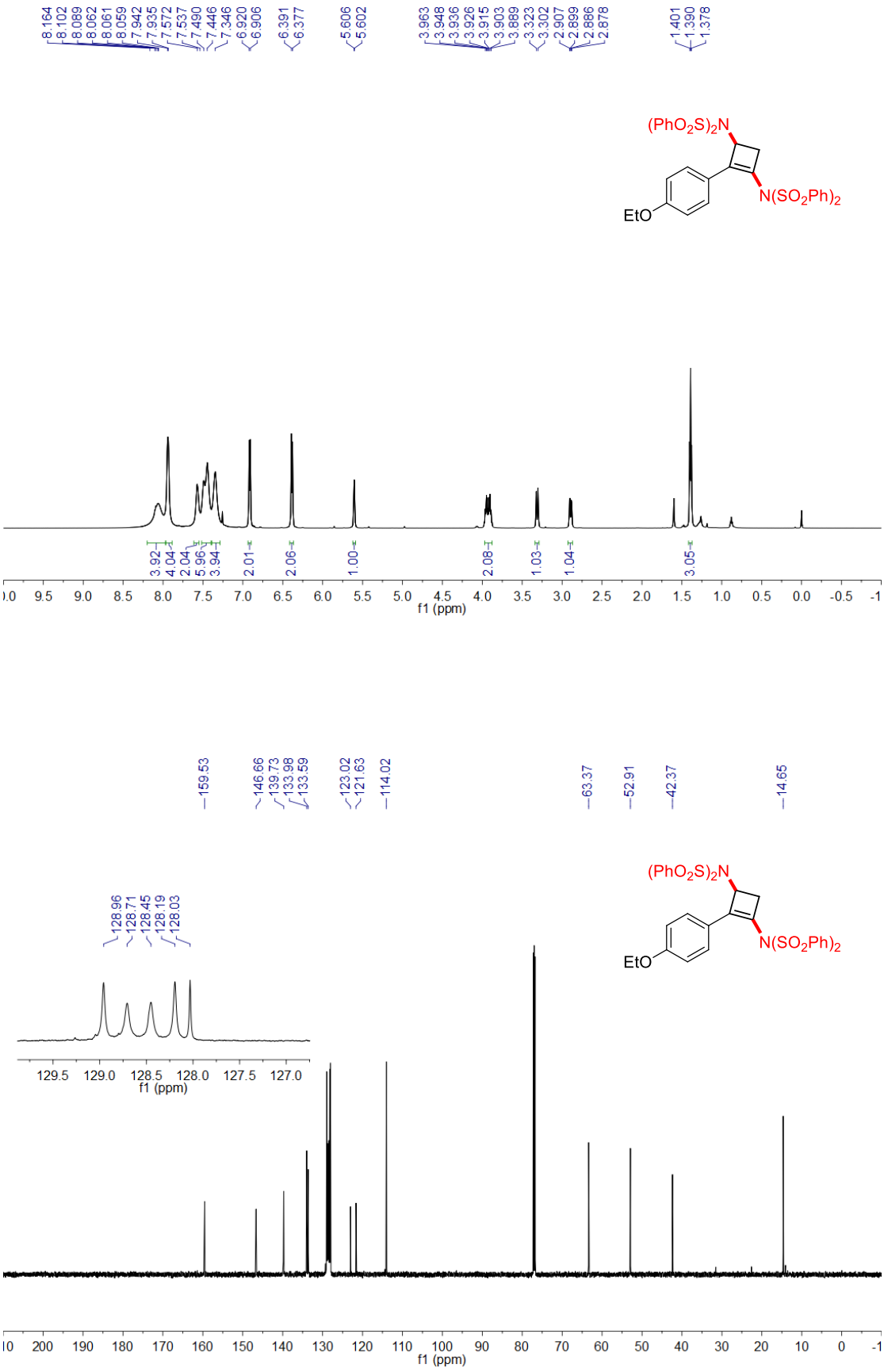


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of compound **2b**.

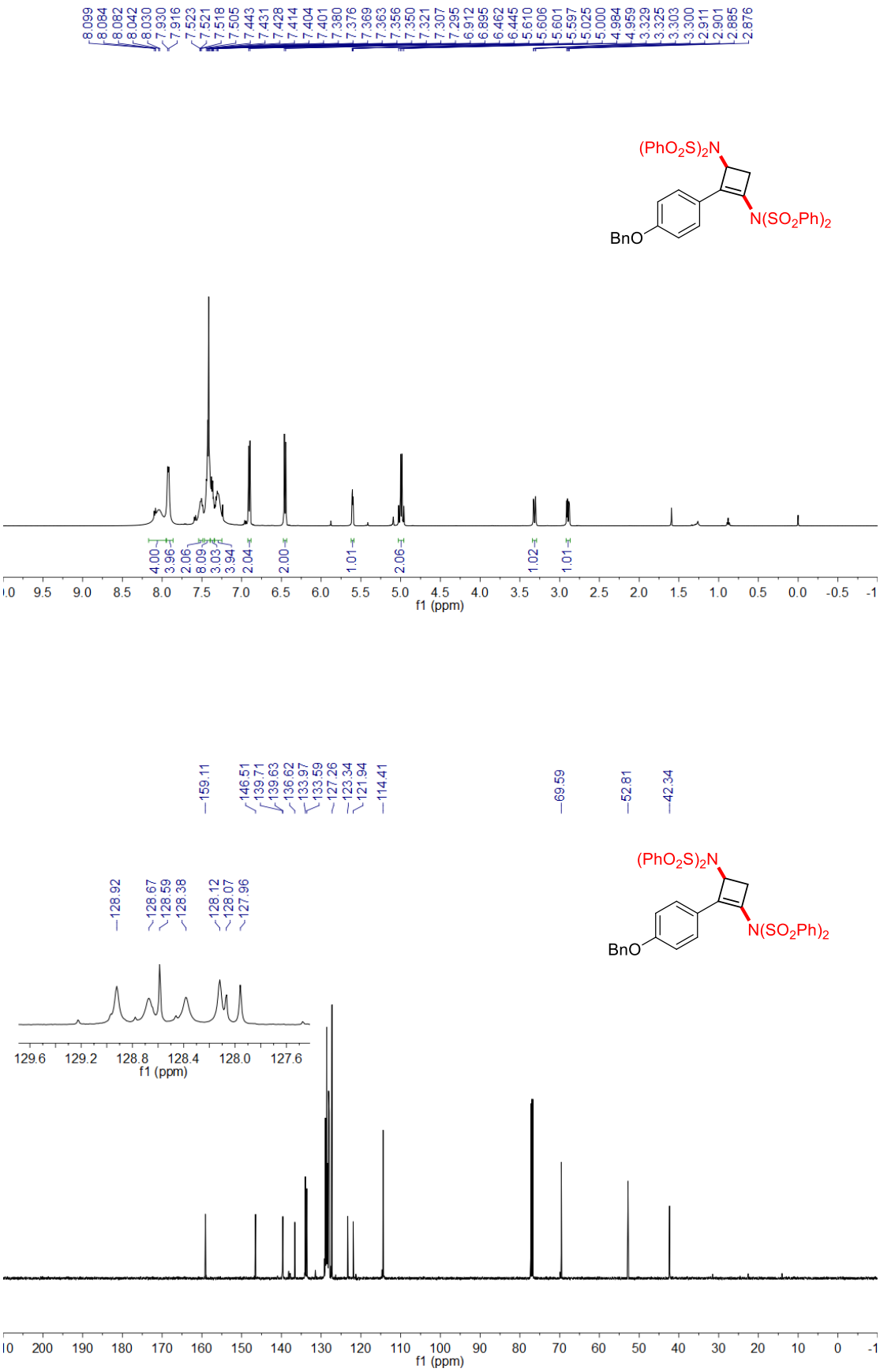


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of compound **2c**.

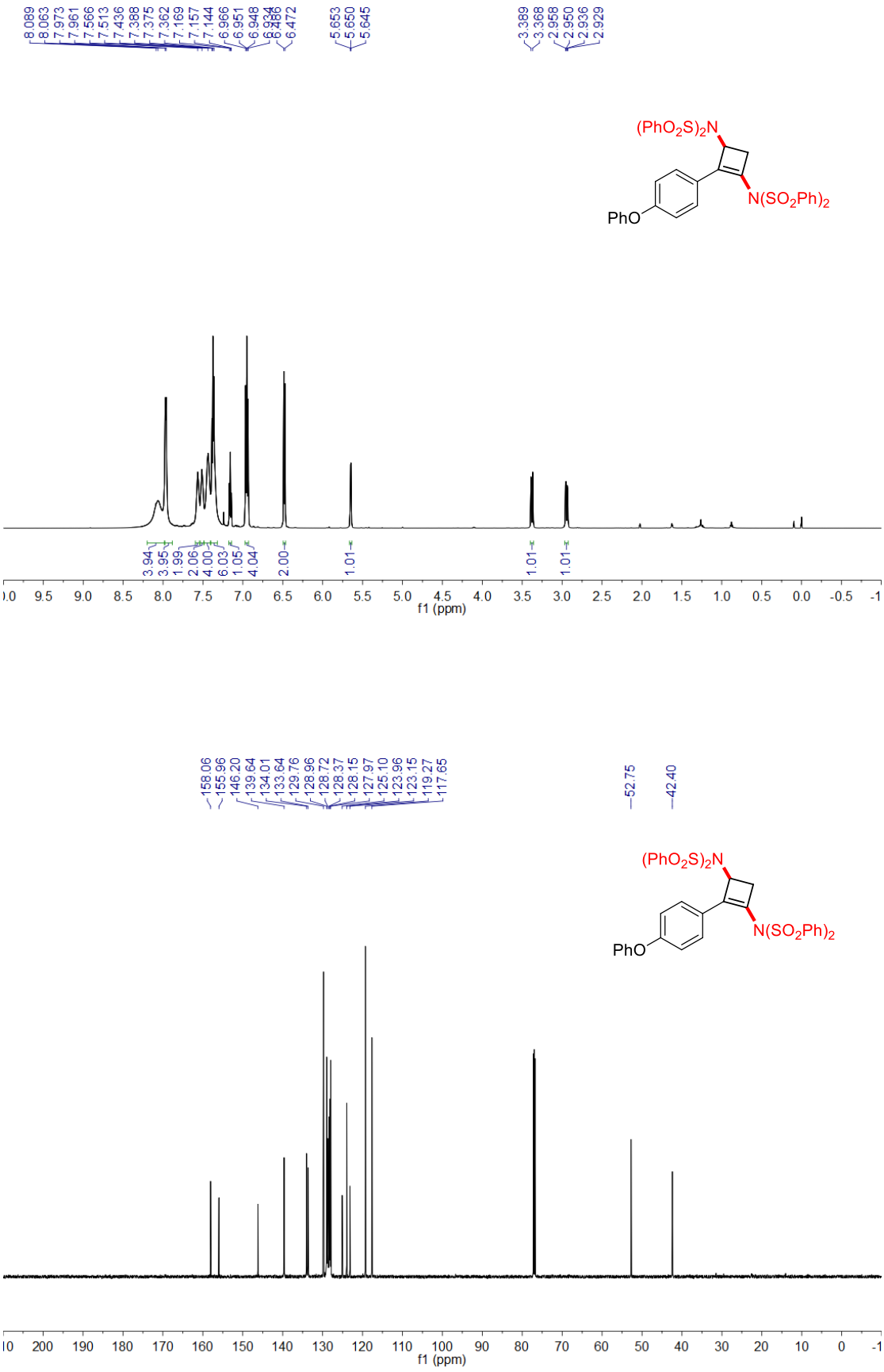


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound **2d**.

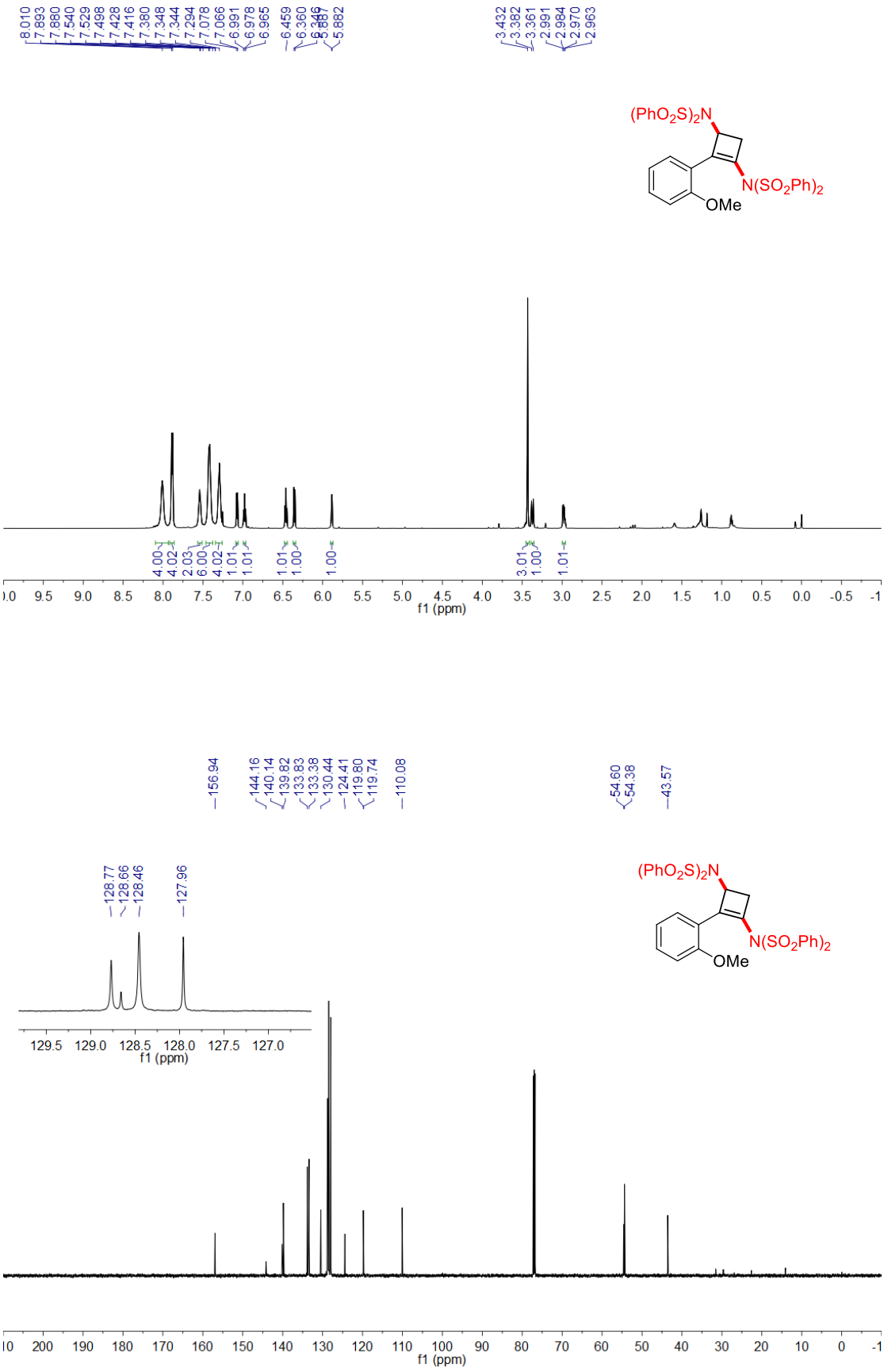


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of compound **2e**.

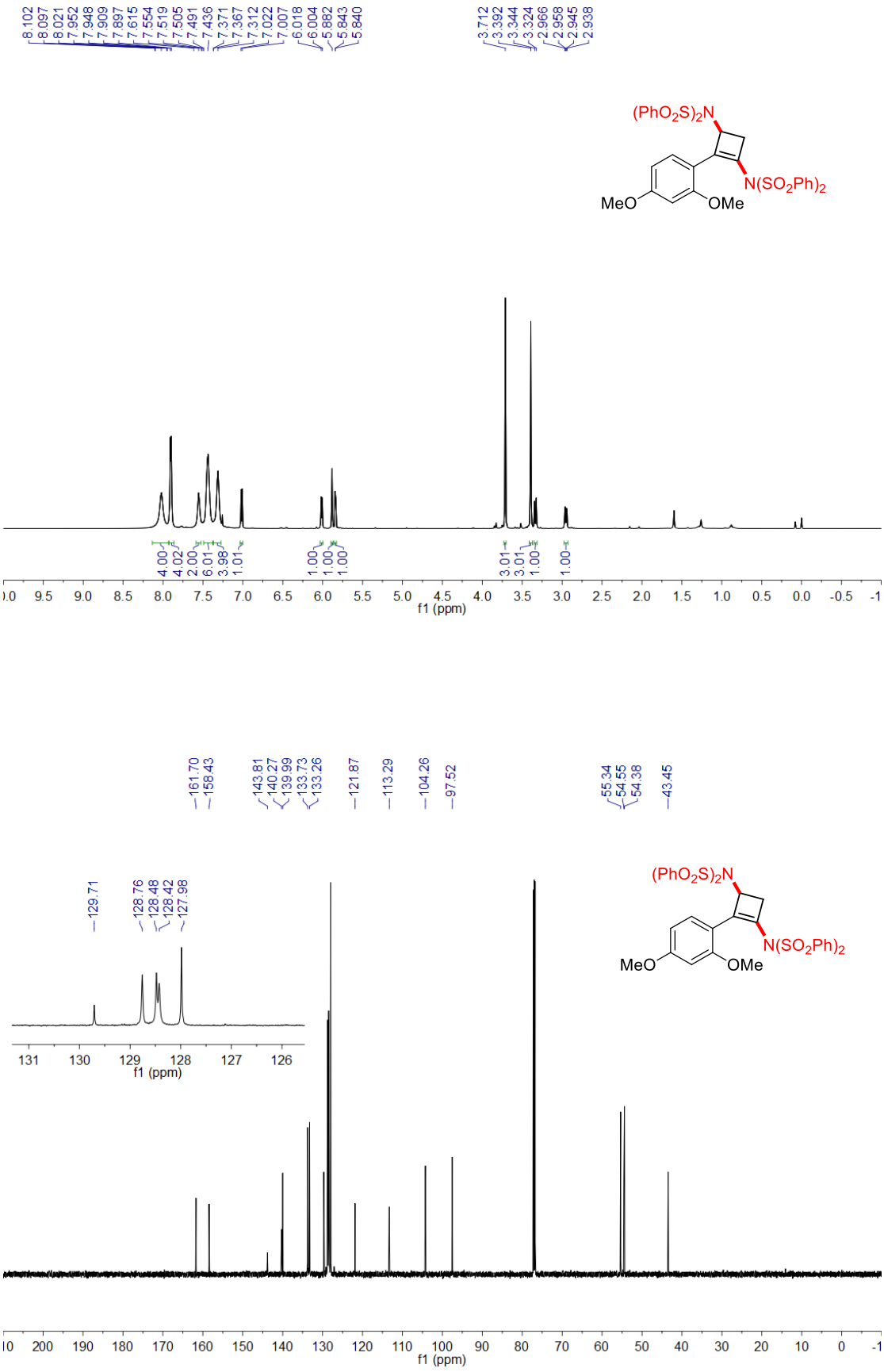


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of compound **2f**.

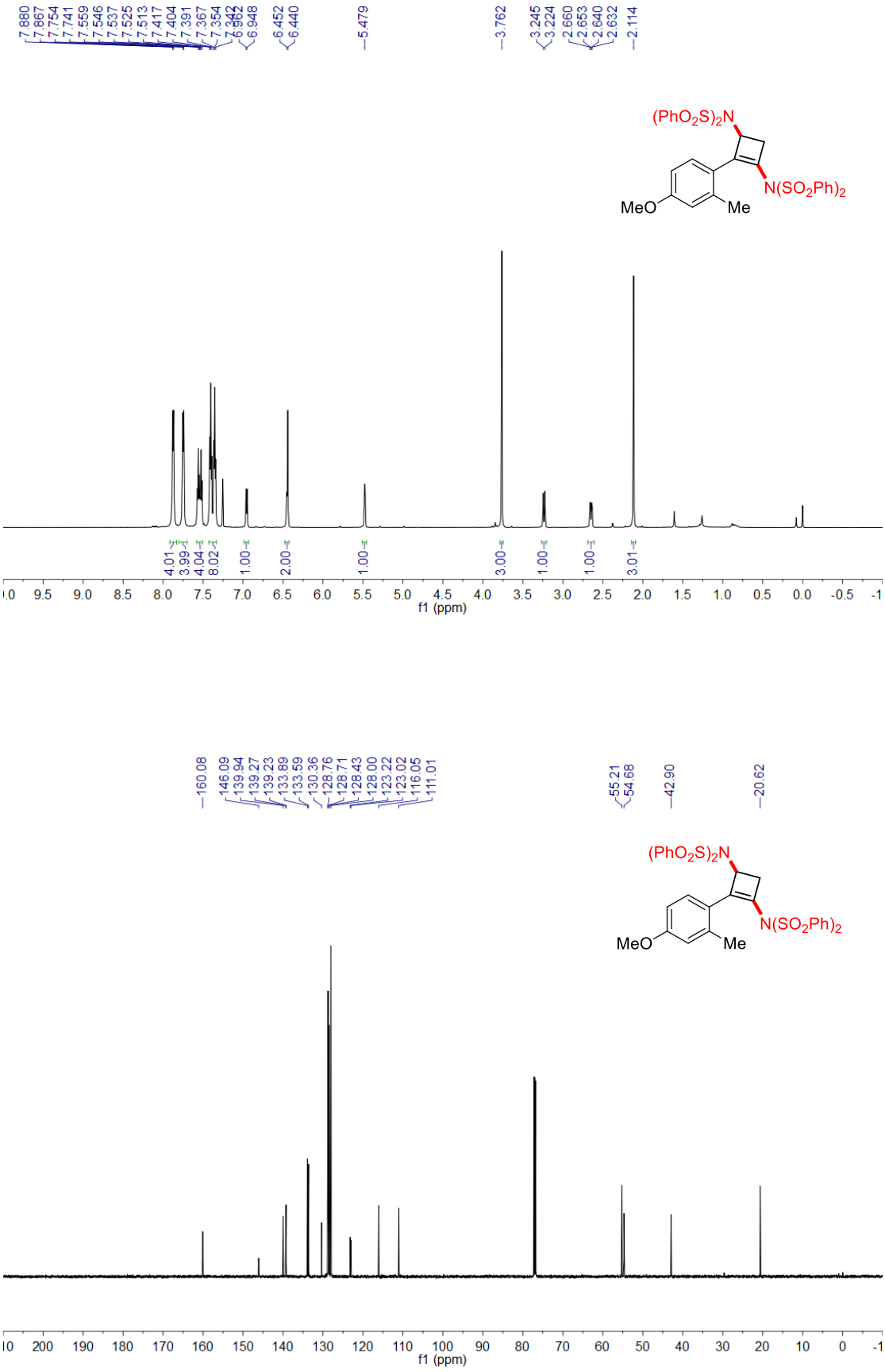


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of compound **2g**.

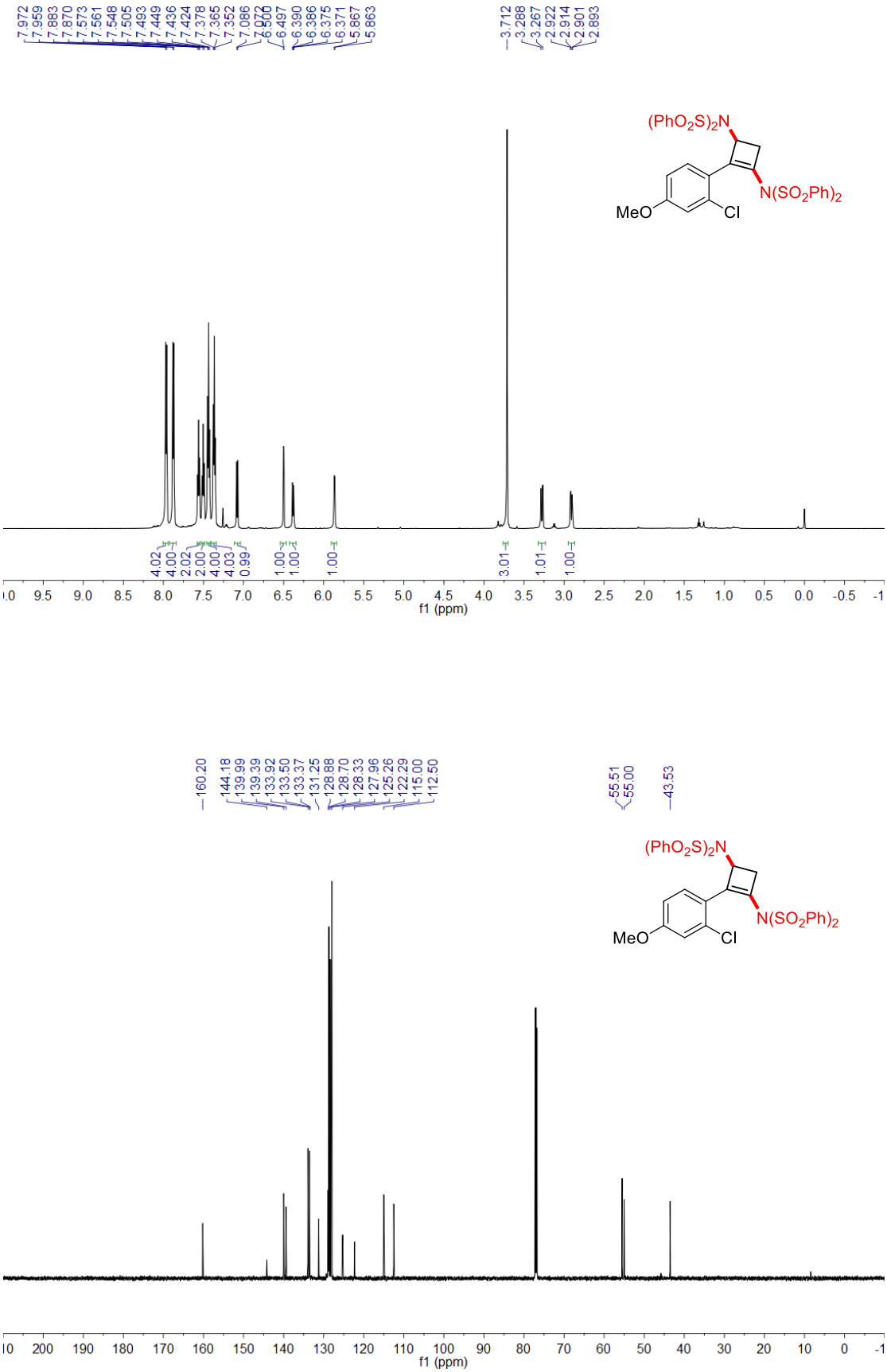
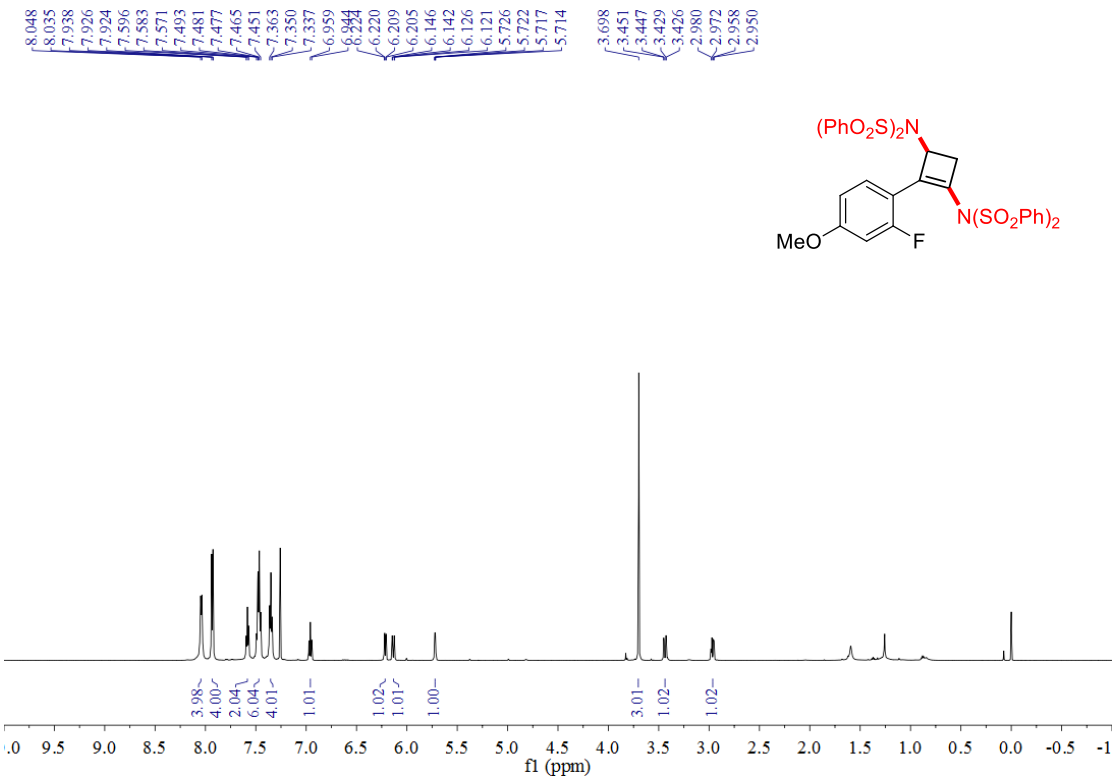


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of compound **2h**.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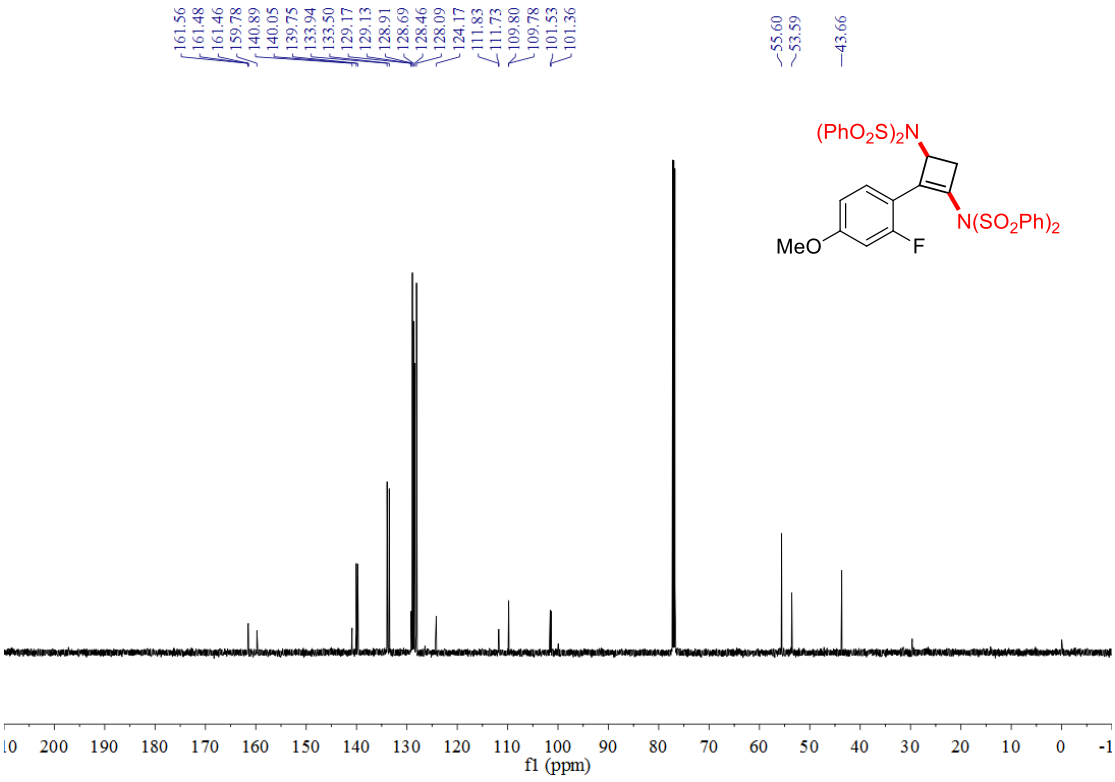
7.938
7.926
7.924
7.596
7.583
7.571
7.493
7.481
7.477
7.465
7.451
7.363
7.350
7.337
6.959
6.944
6.224
6.220
6.209
6.205
6.146
6.142
6.126
6.121
5.726
5.722
5.717
5.714
3.698
3.451
3.447
3.429
3.426
2.980
2.972
2.958
2.950
(PhO2S)2N
N(SO2Ph)2
MeO
F
3.98
4.00
2.04
6.04
4.01
1.01
1.02
1.01
1.00
3.01
1.02
1.02
f1 (ppm)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159.78
140.89
140.05
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133.94
133.50
129.17
129.13
128.91
128.69
128.46
128.09
124.17
111.83
111.73
109.80
109.78
101.53
101.36
55.60
53.59
43.66
(PhO2S)2N
N(SO2Ph)2
MeO
F
f1 (ppm)

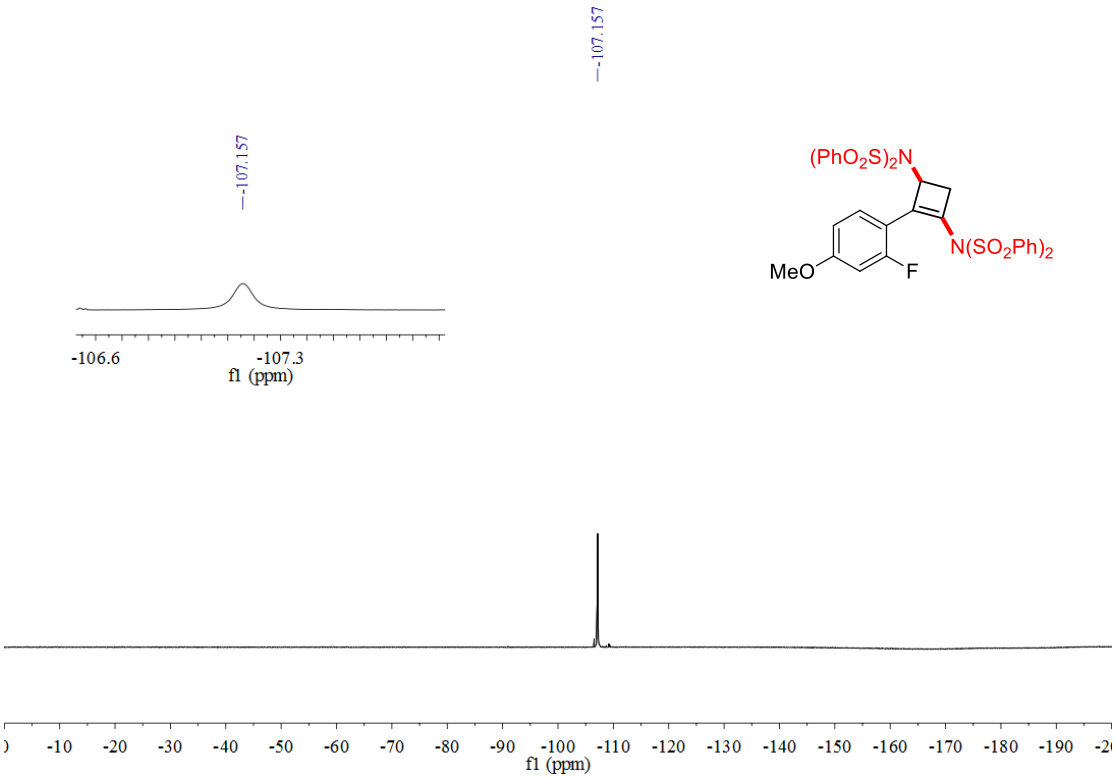
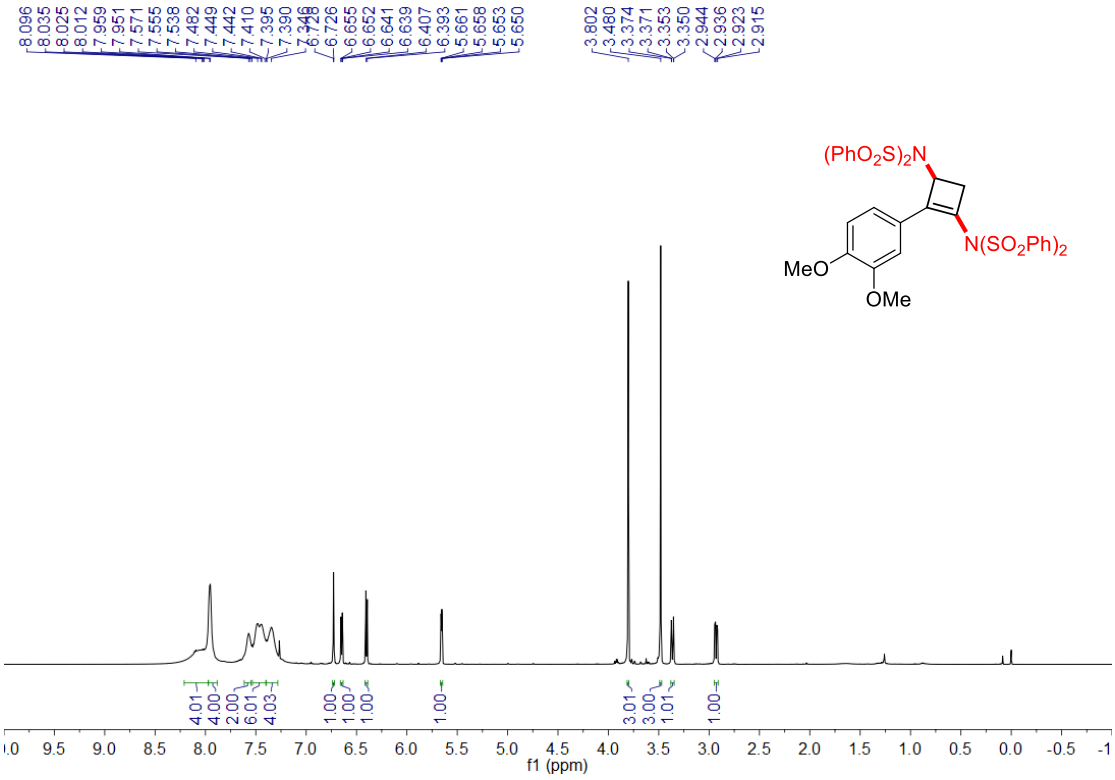


Figure S13. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **2i**.



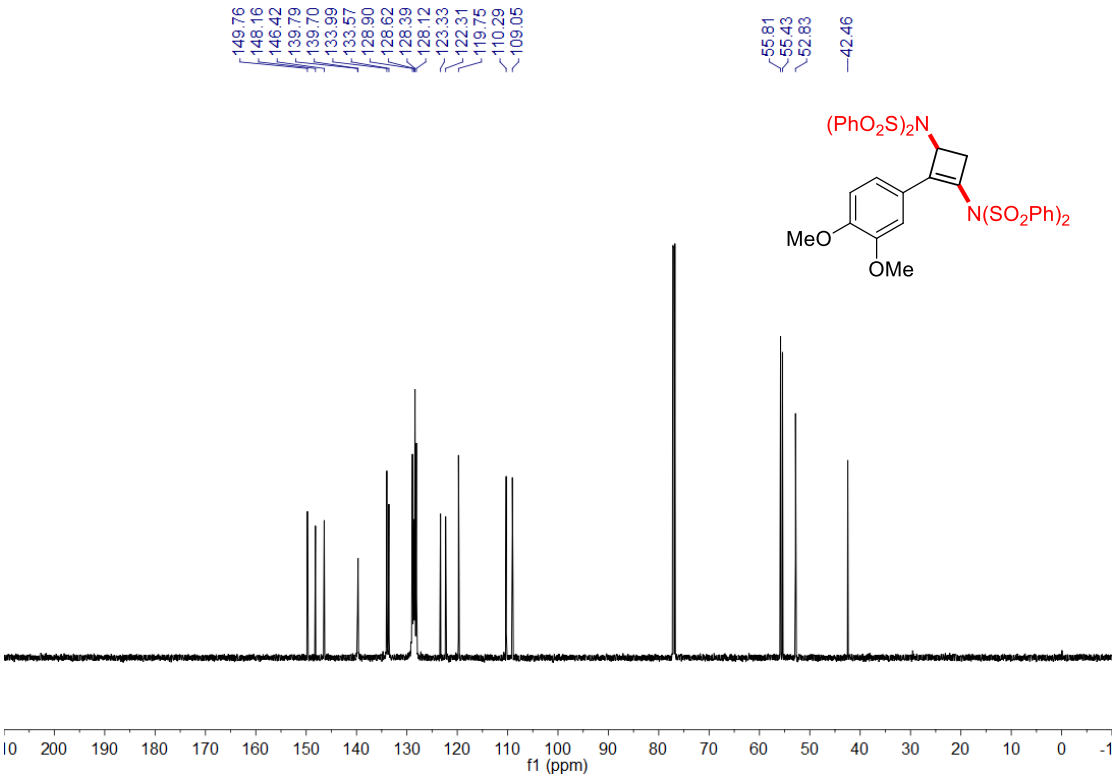
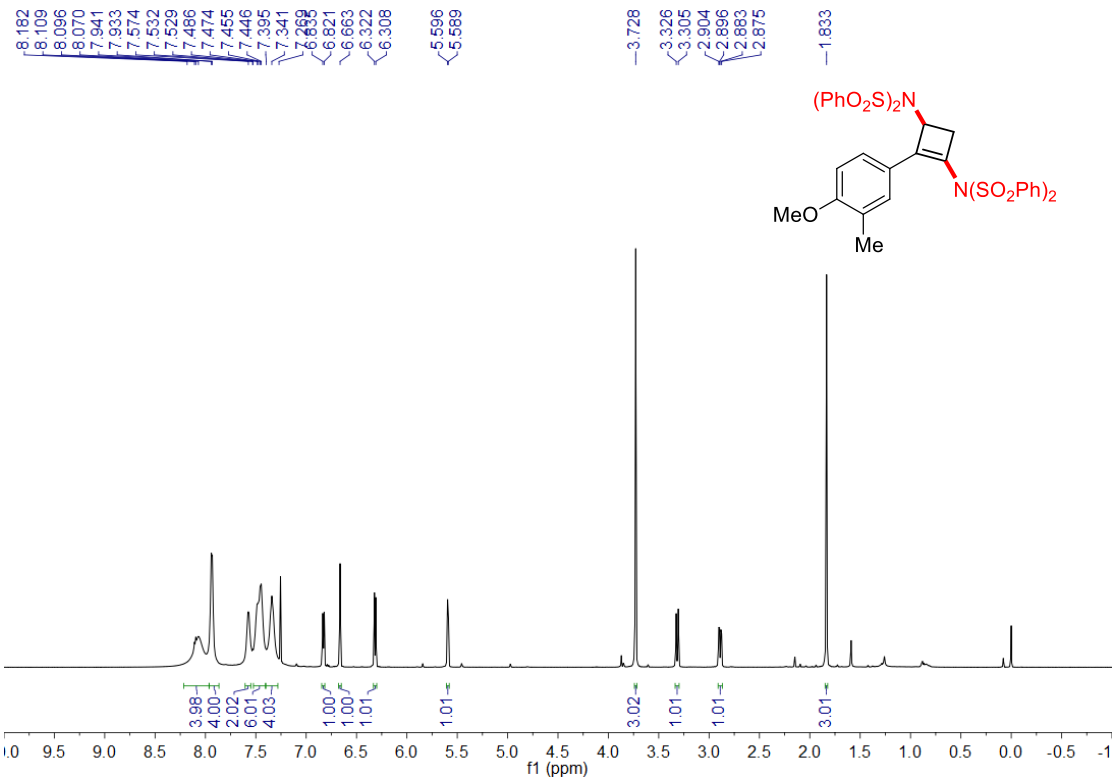


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of compound **2j**.



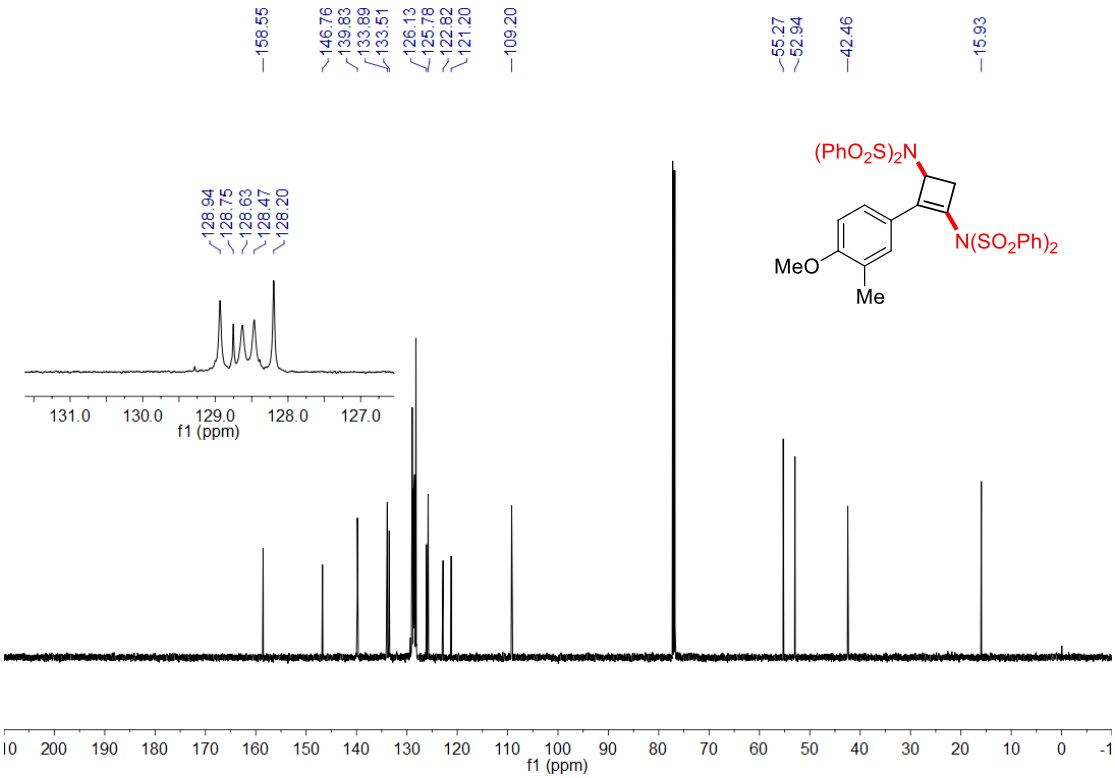
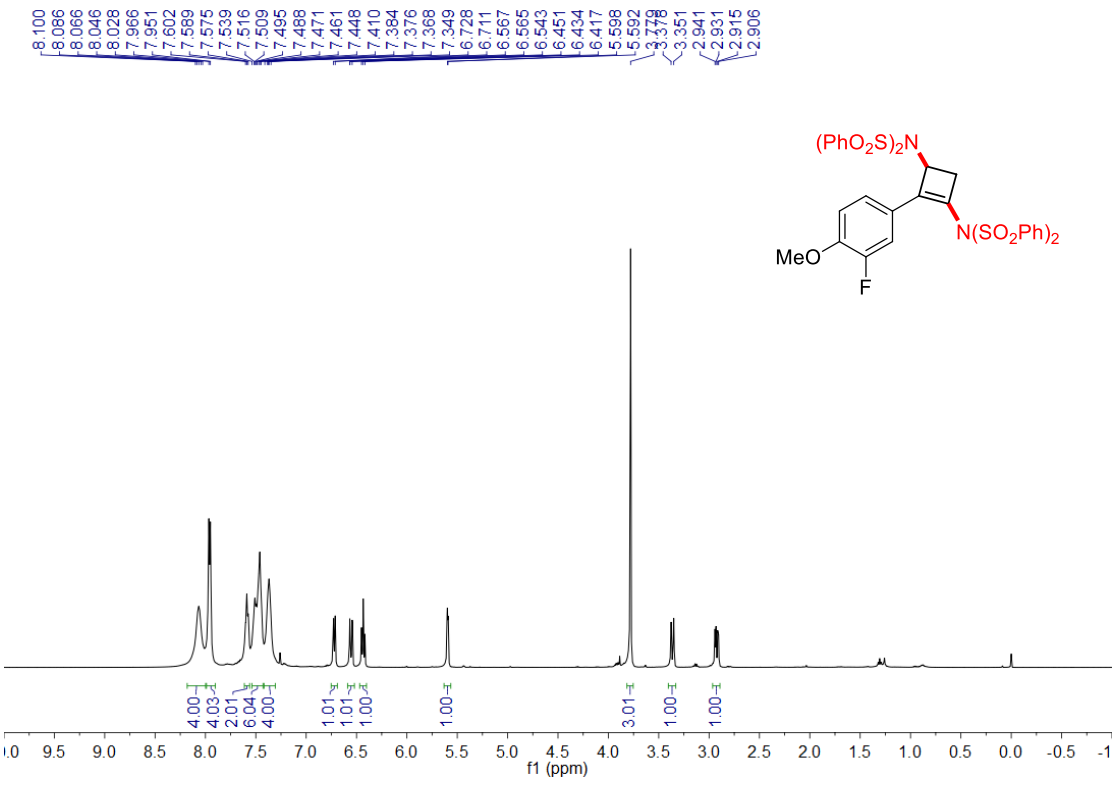


Figure S15. ^{1}H NMR and ^{13}C NMR spectra of compound **2k**.



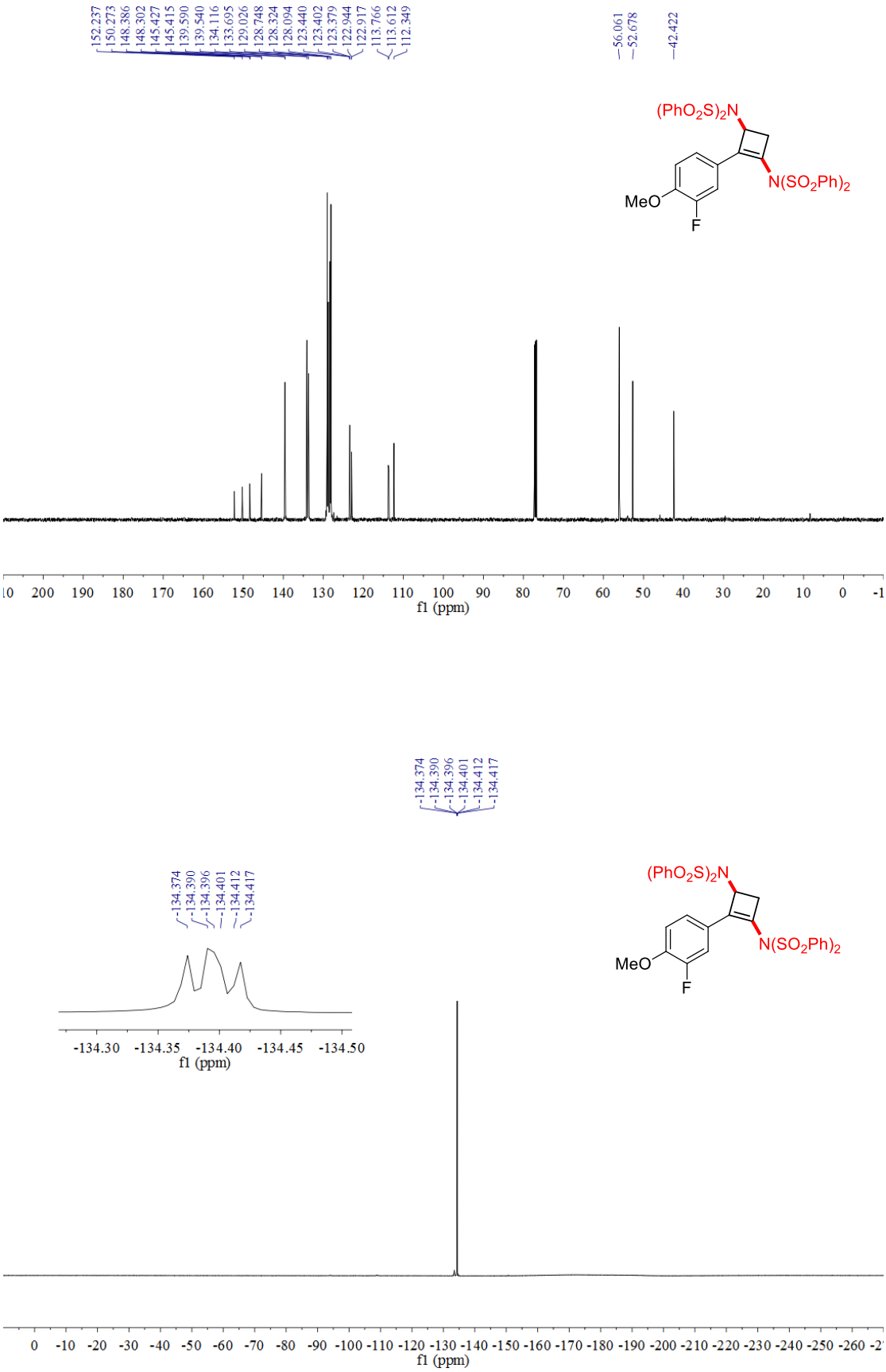


Figure S16. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **2l**.

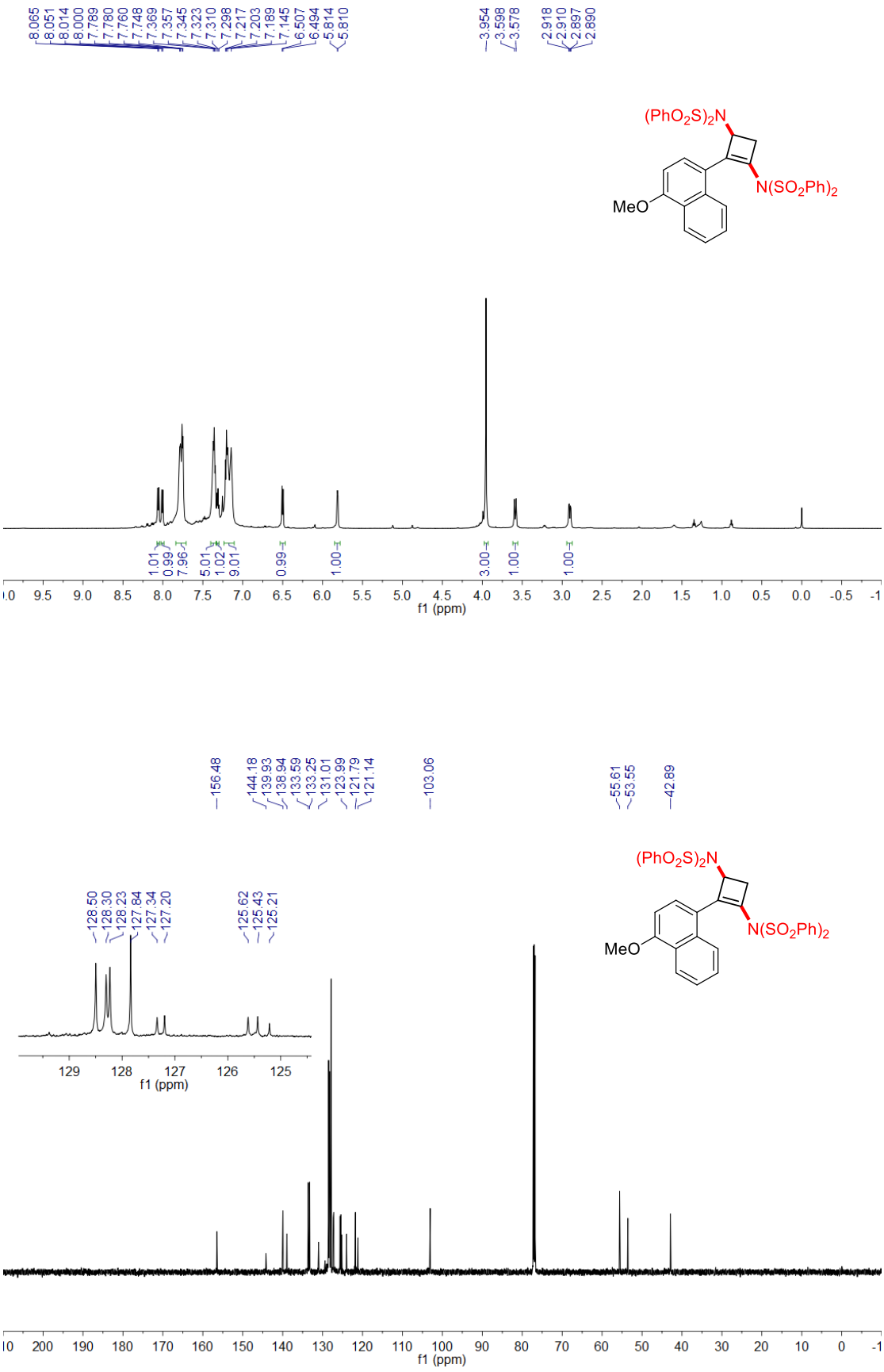


Figure S17. ^{1}H NMR and ^{13}C NMR spectra of compound **2m**.

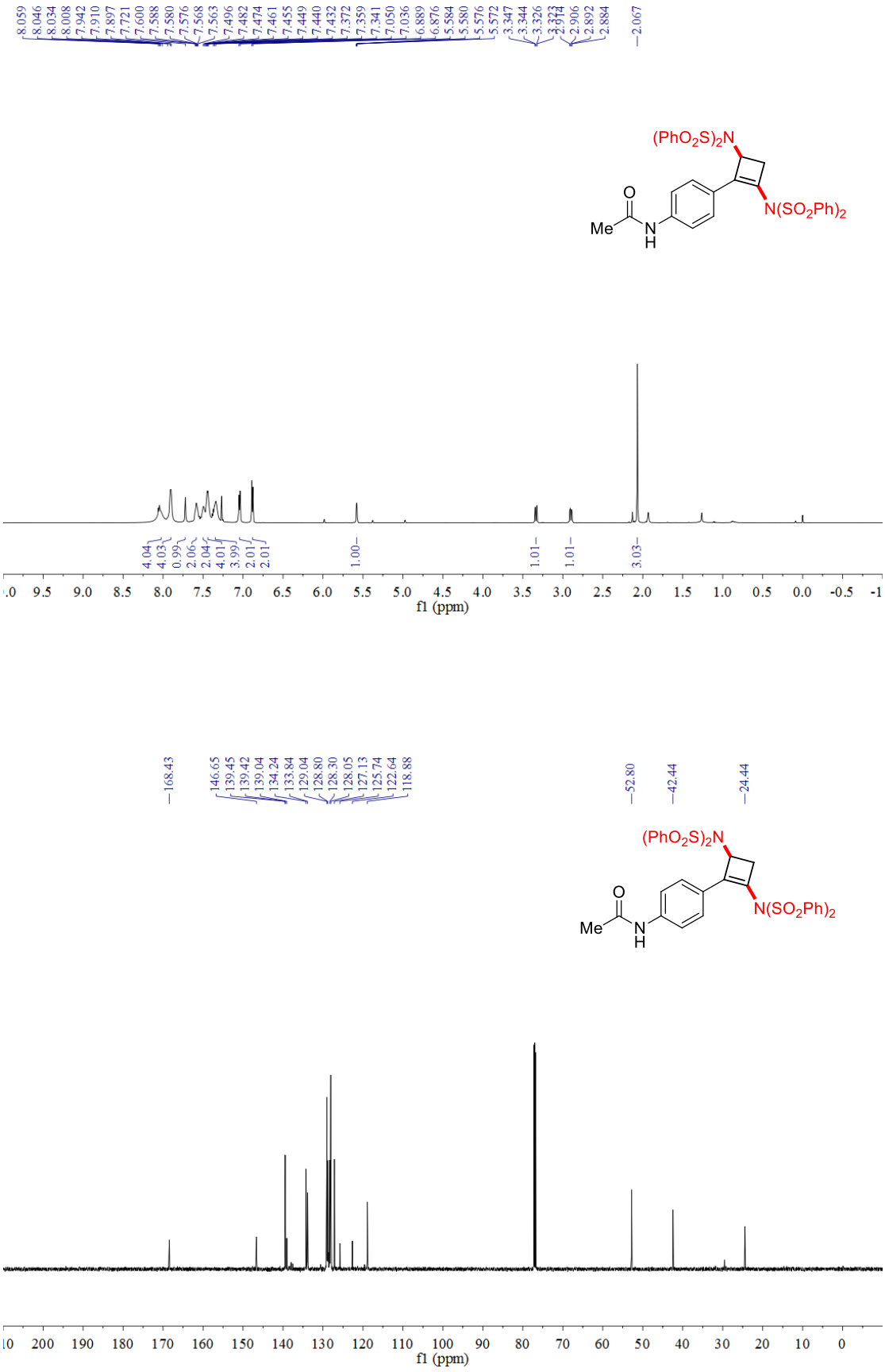
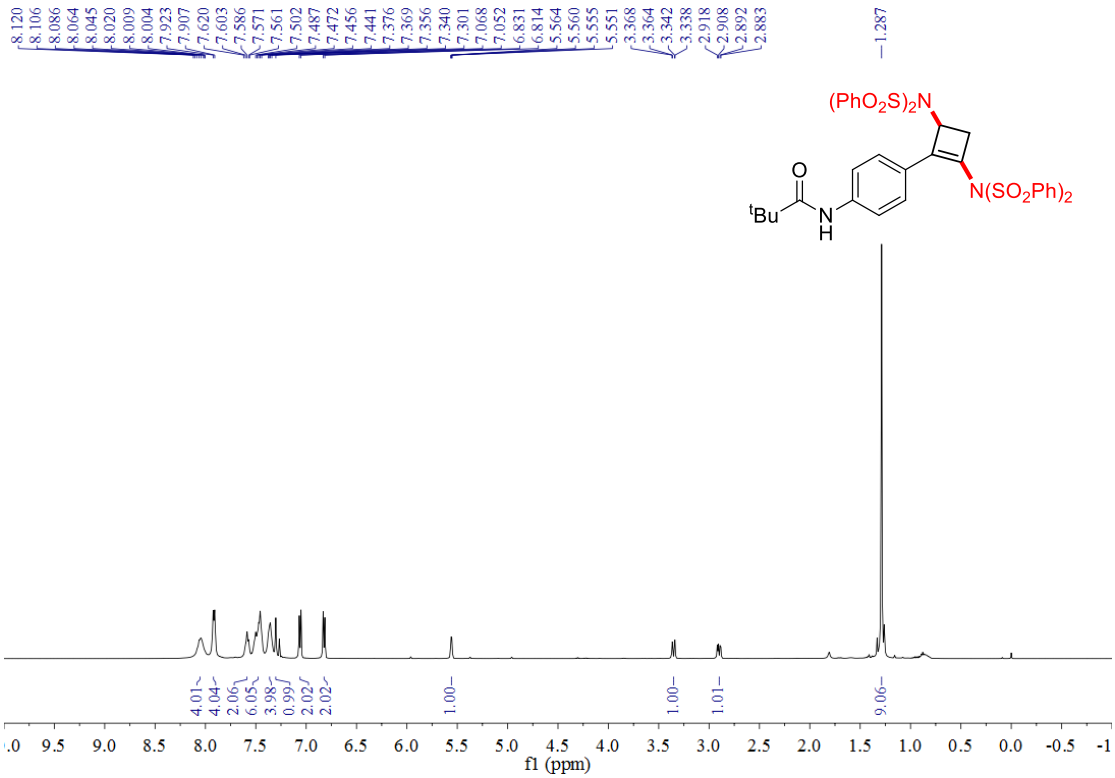


Figure S18. ^{1}H NMR and ^{13}C NMR spectra of compound **2n**.



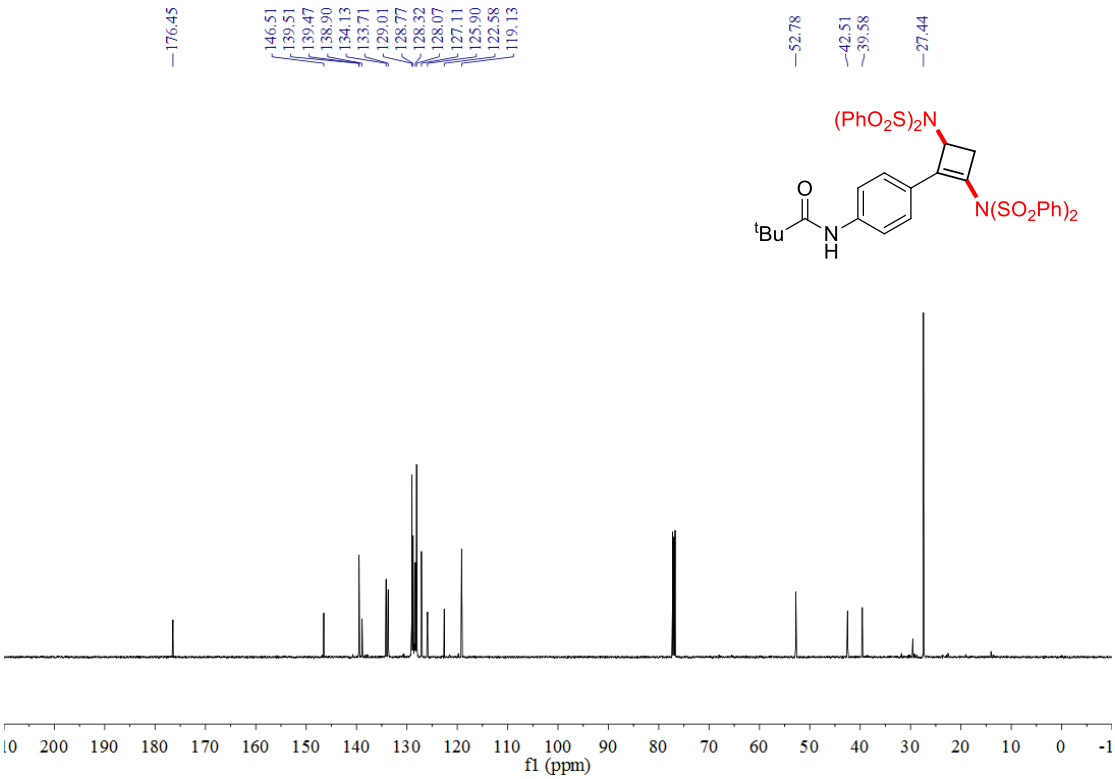


Figure S19. ^{1}H NMR and ^{13}C NMR spectra of compound **2o**.

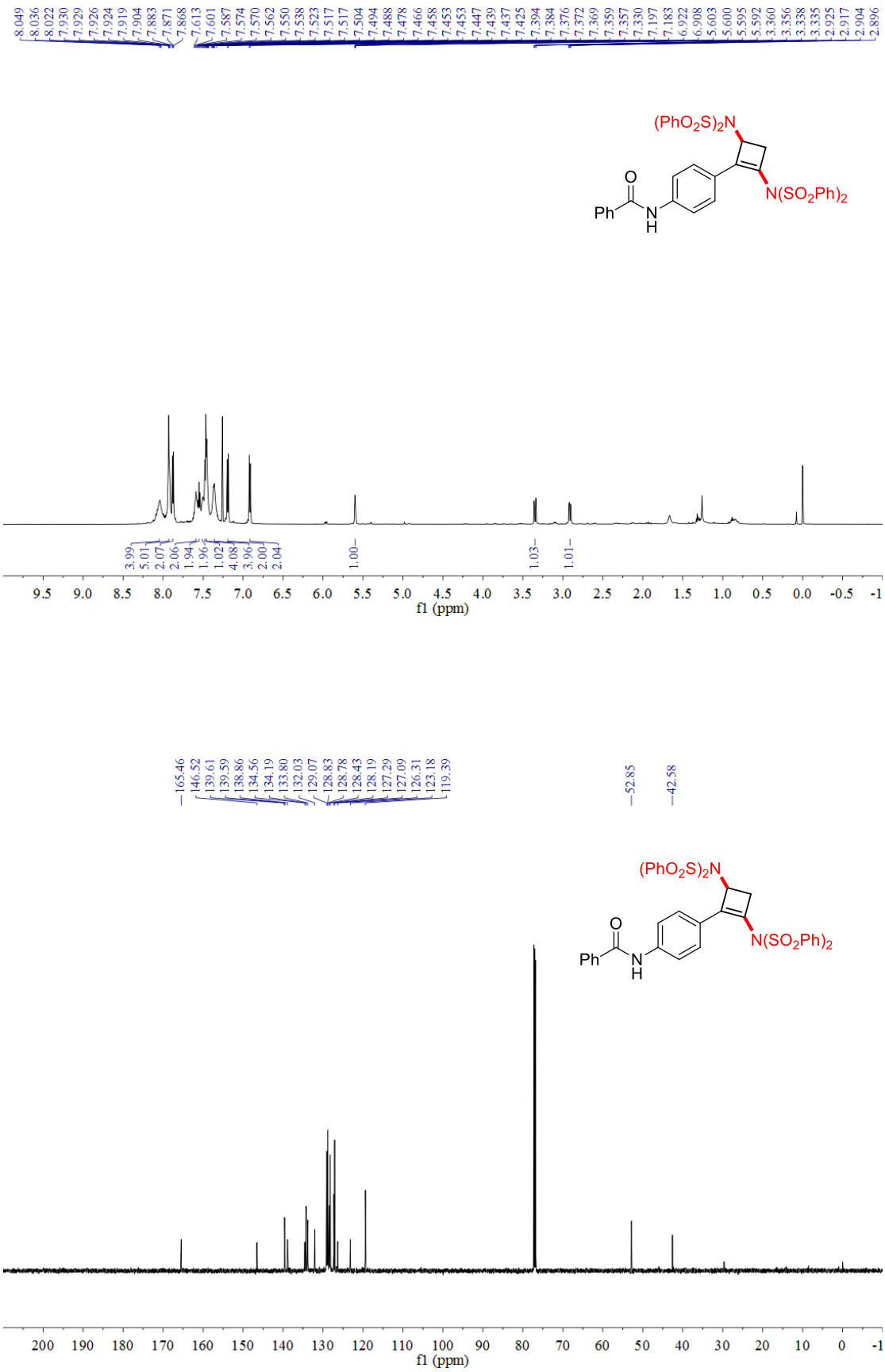


Figure S20. ^{1}H NMR and ^{13}C NMR spectra of compound **2p**.

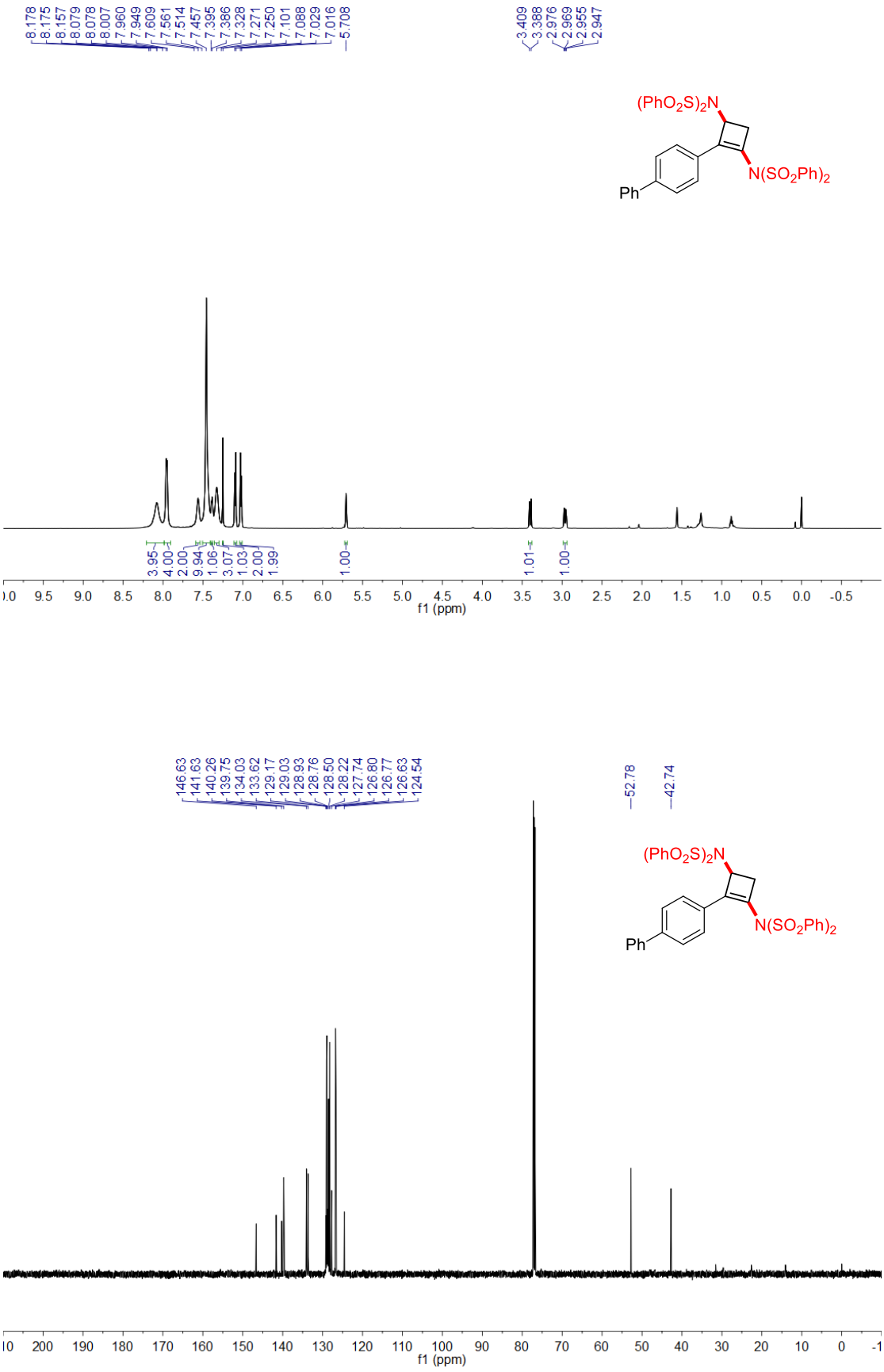
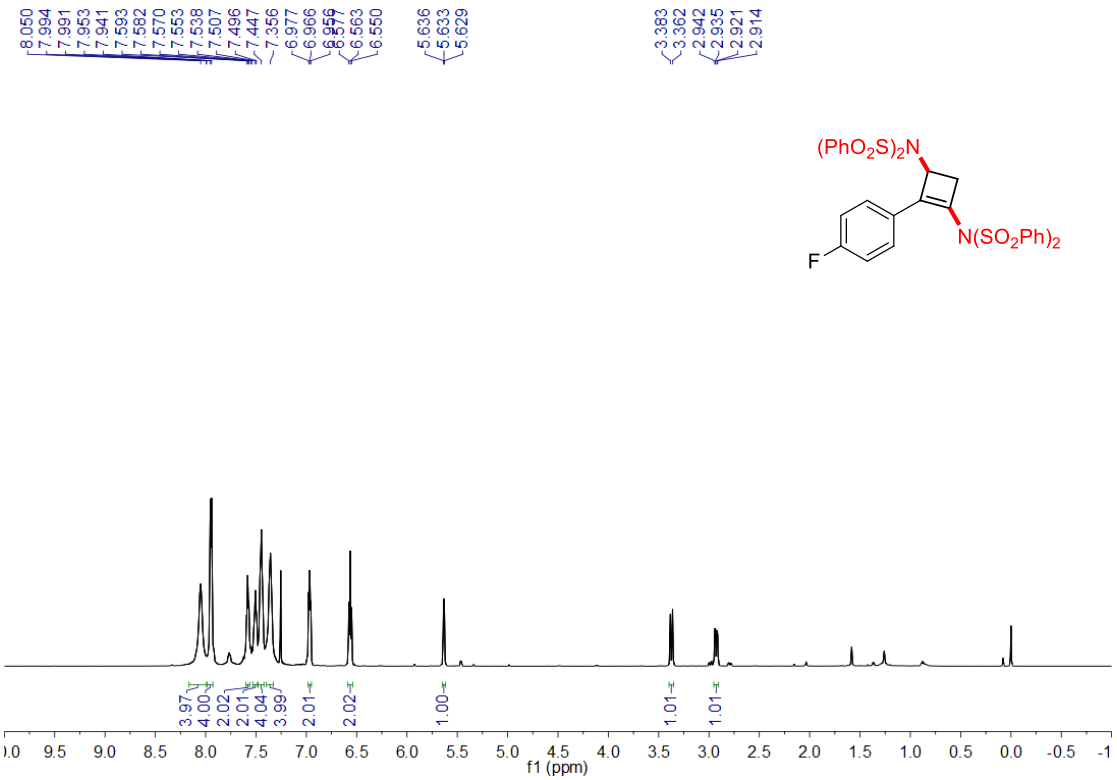


Figure S21. ^{1}H NMR and ^{13}C NMR spectra of compound **2q**.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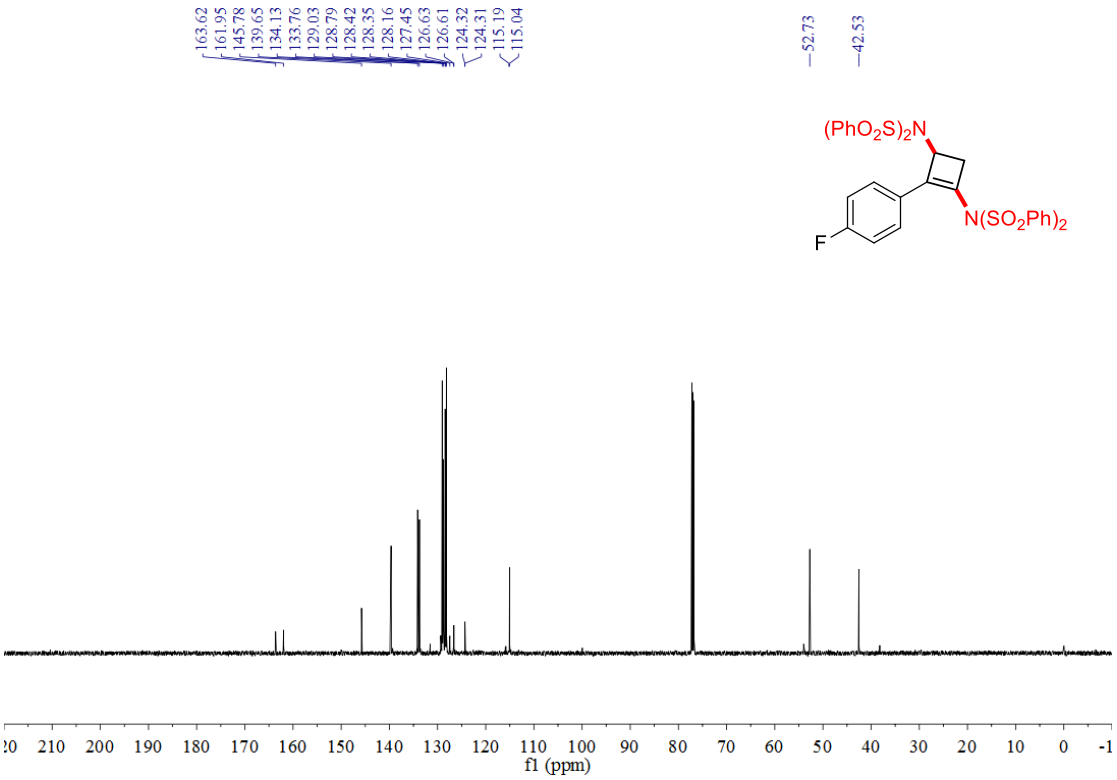
7.356
6.977
6.966
6.577
6.563
6.550
5.636
5.633
5.629
3.383
3.362
2.942
2.935
2.921
2.914
(PhO2S)2N
N(SO2Ph)2
F
3.97
4.00
2.02
2.01
4.04
3.99
2.01
2.02
1.00
1.01
1.01
f1 (ppm)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126.61
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124.31
115.19
115.04
52.73
42.53
(PhO2S)2N
N(SO2Ph)2
F
f1 (ppm)

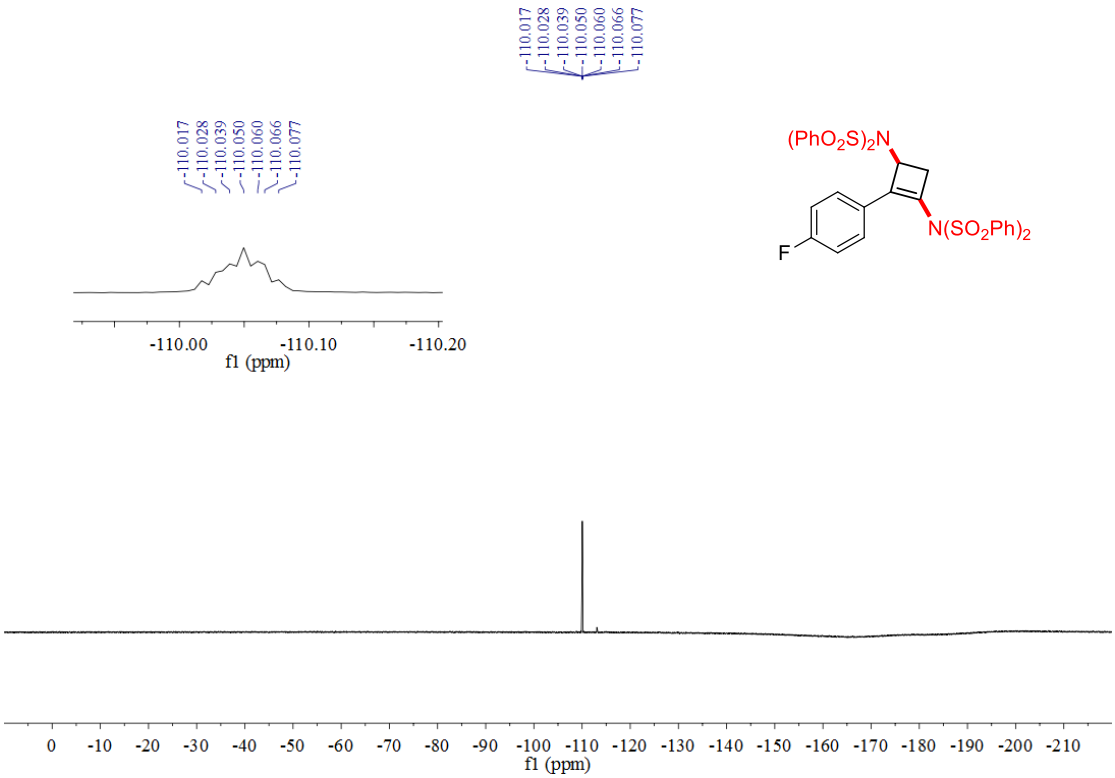
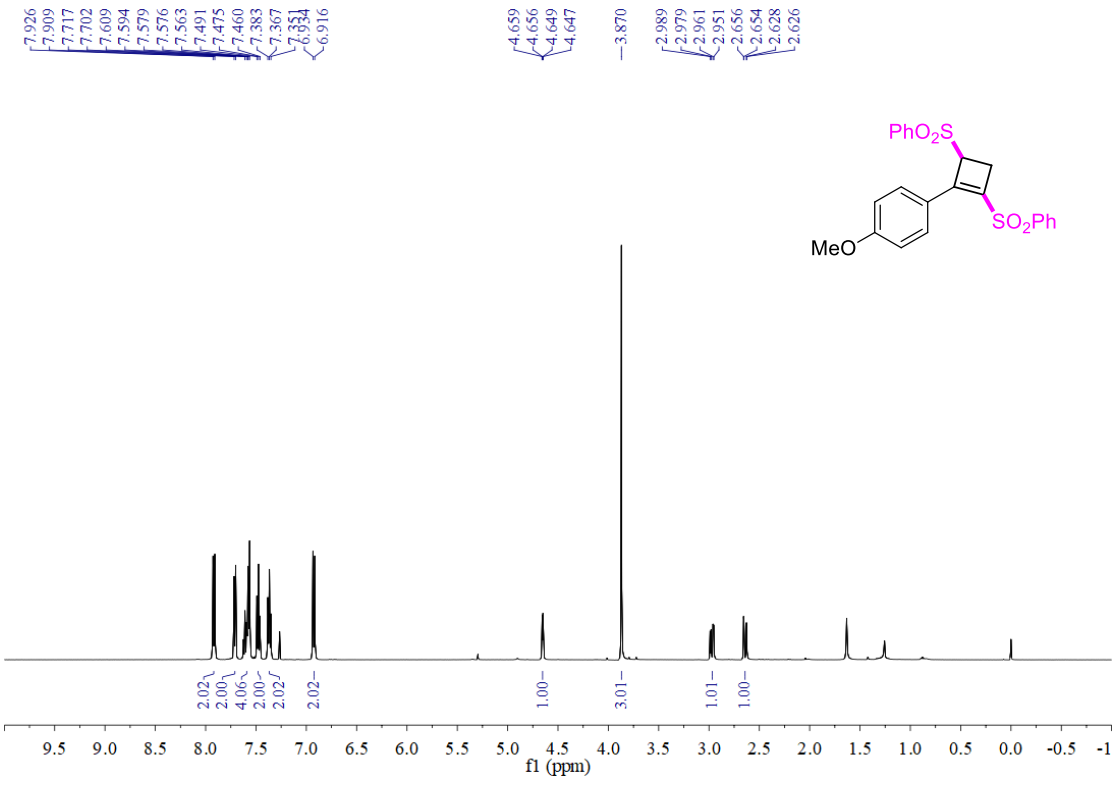


Figure S22. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **2r**.



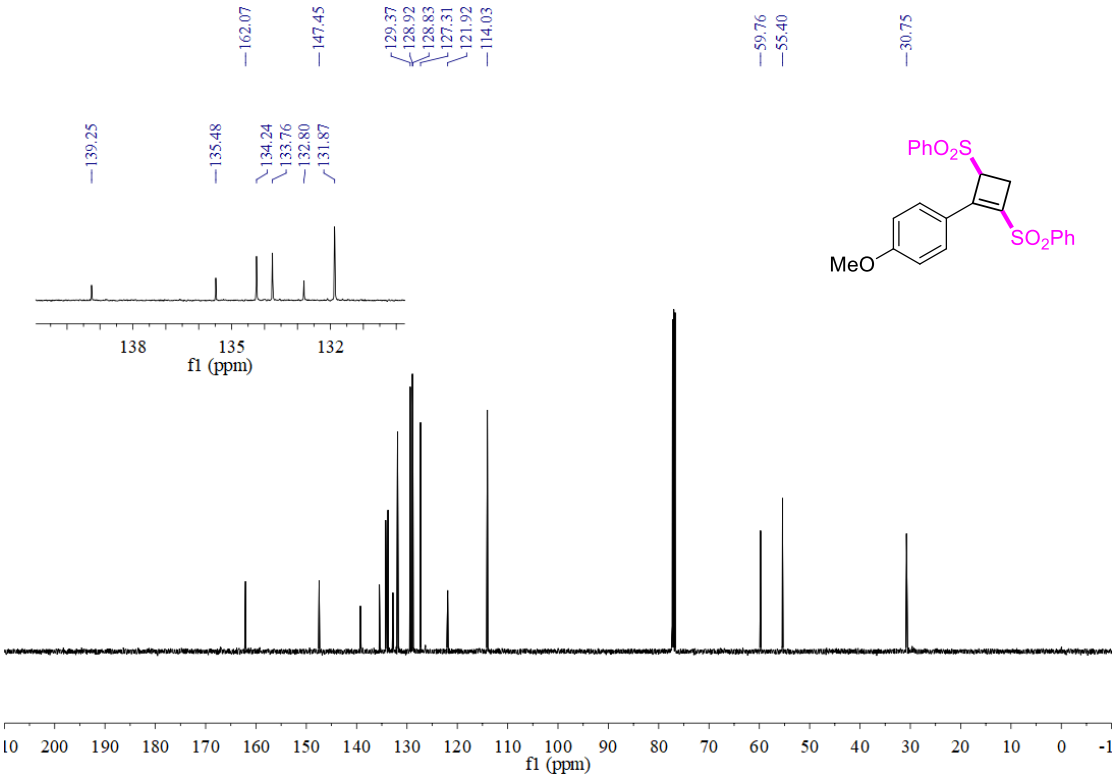
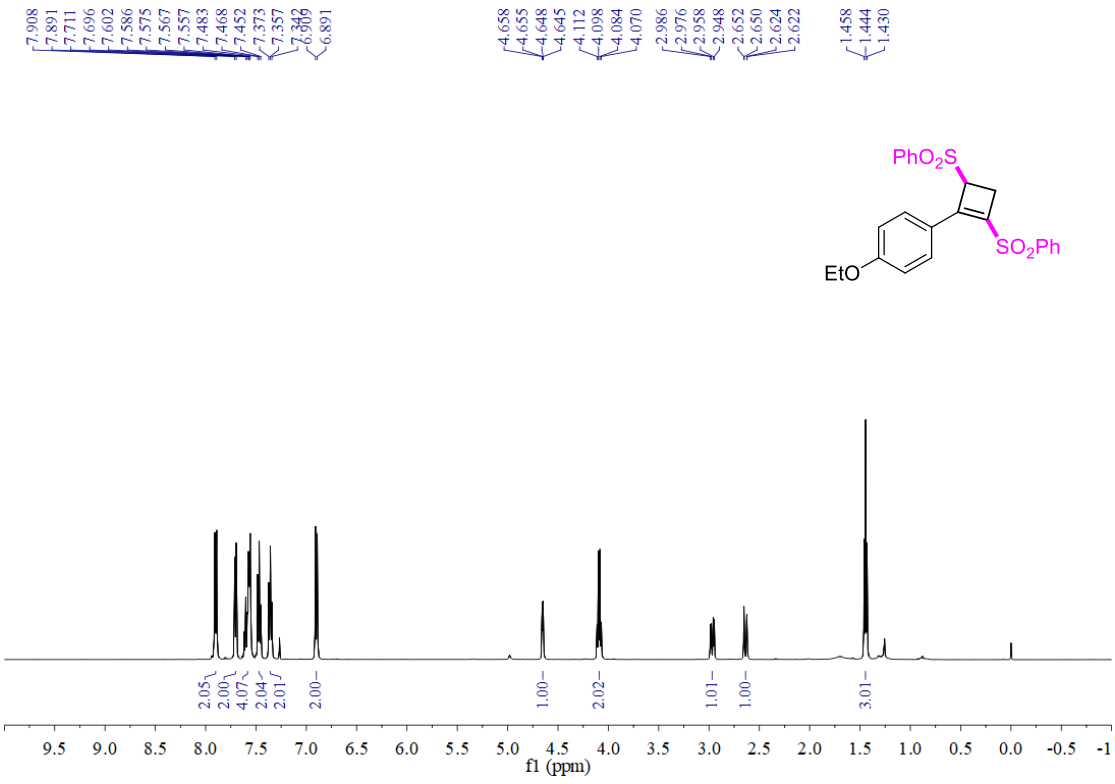


Figure S23. ^{1}H NMR and ^{13}C NMR spectra of compound **6a**.



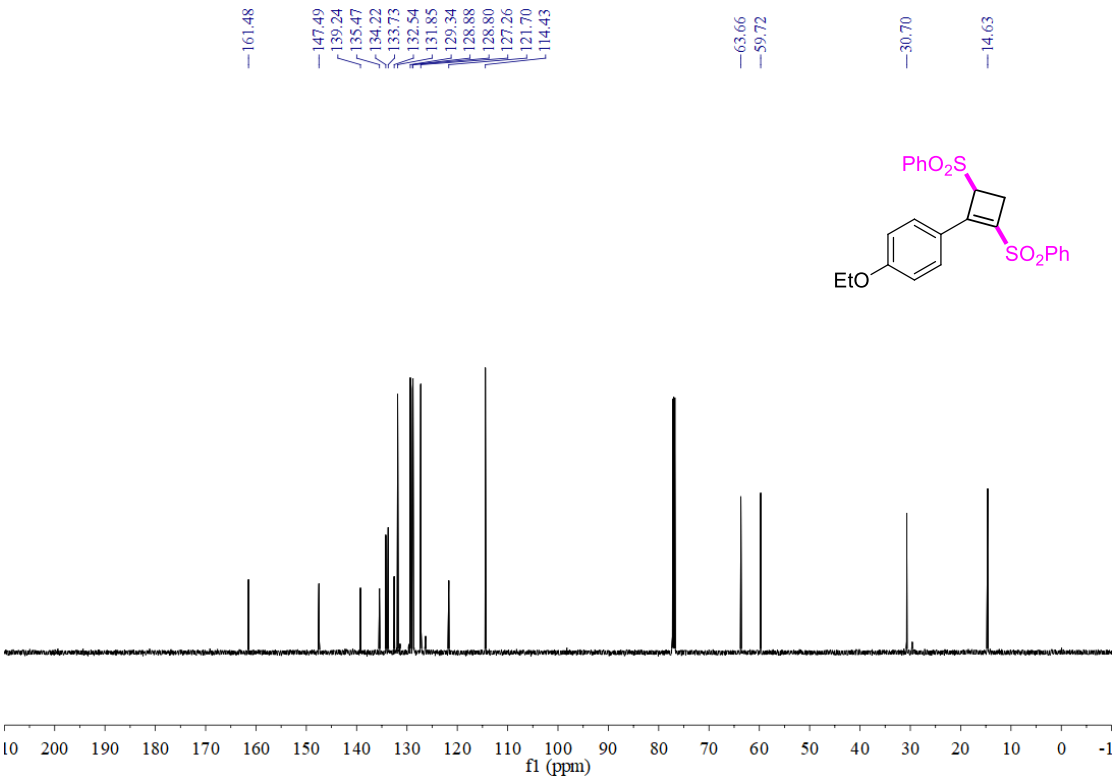
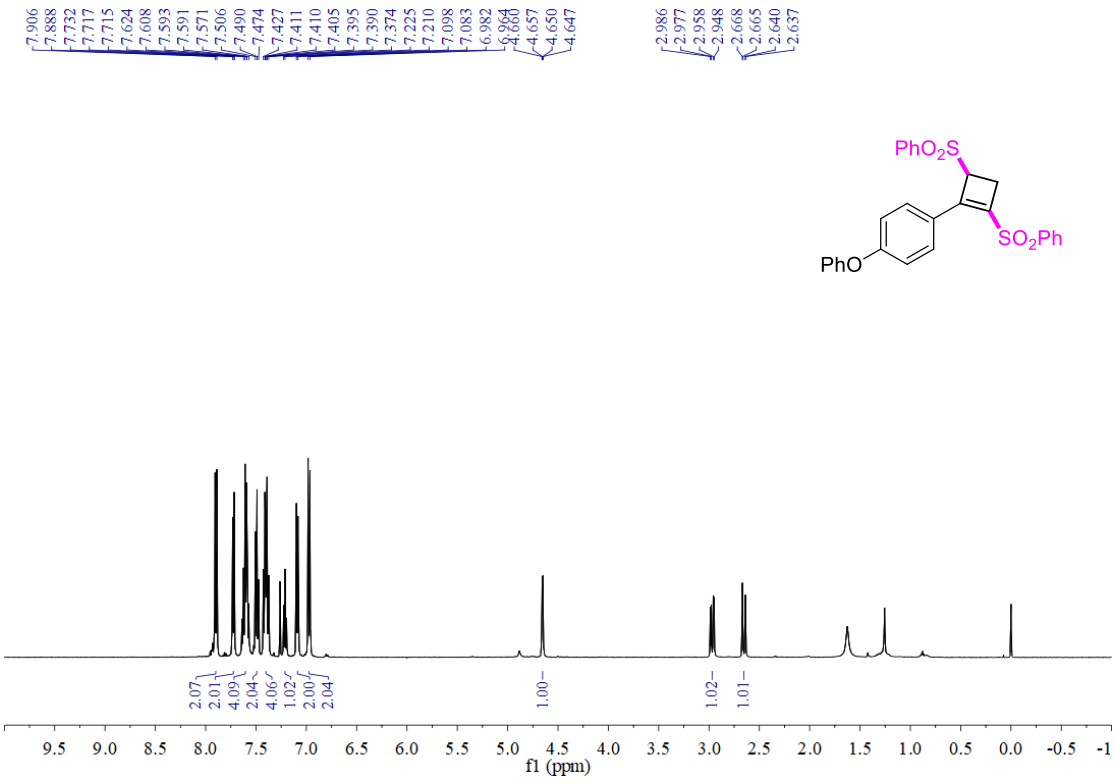


Figure S24. ^{1}H NMR and ^{13}C NMR spectra of compound **6b**.



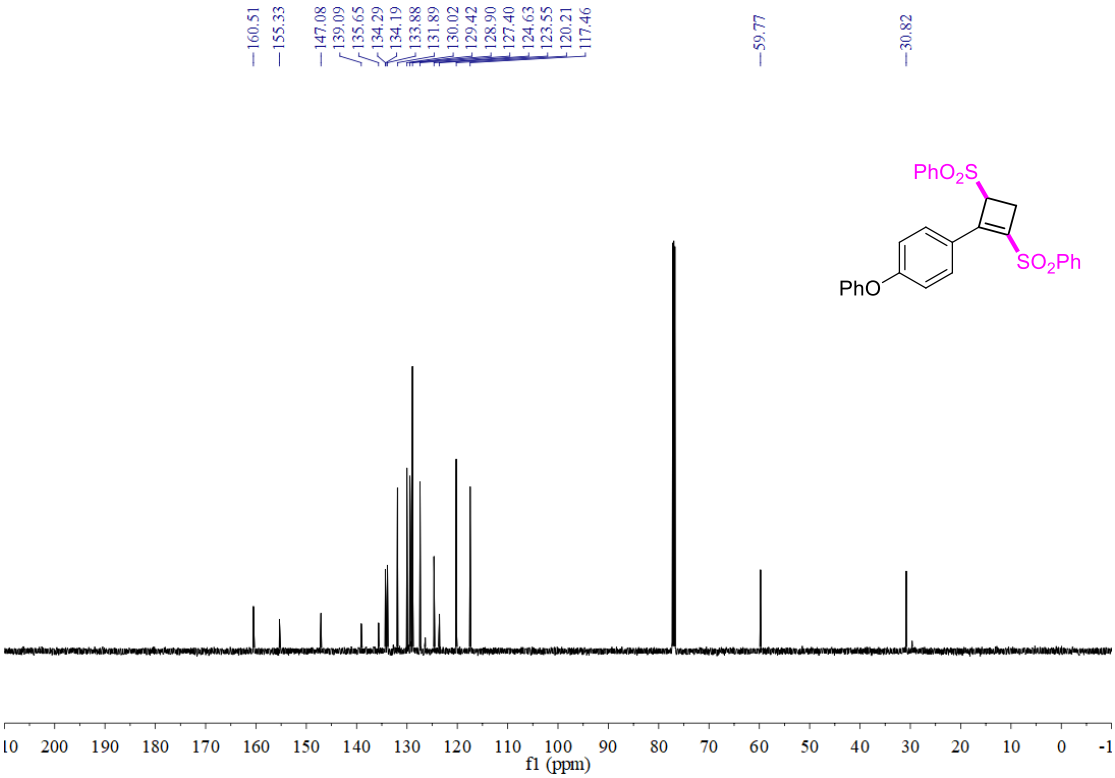
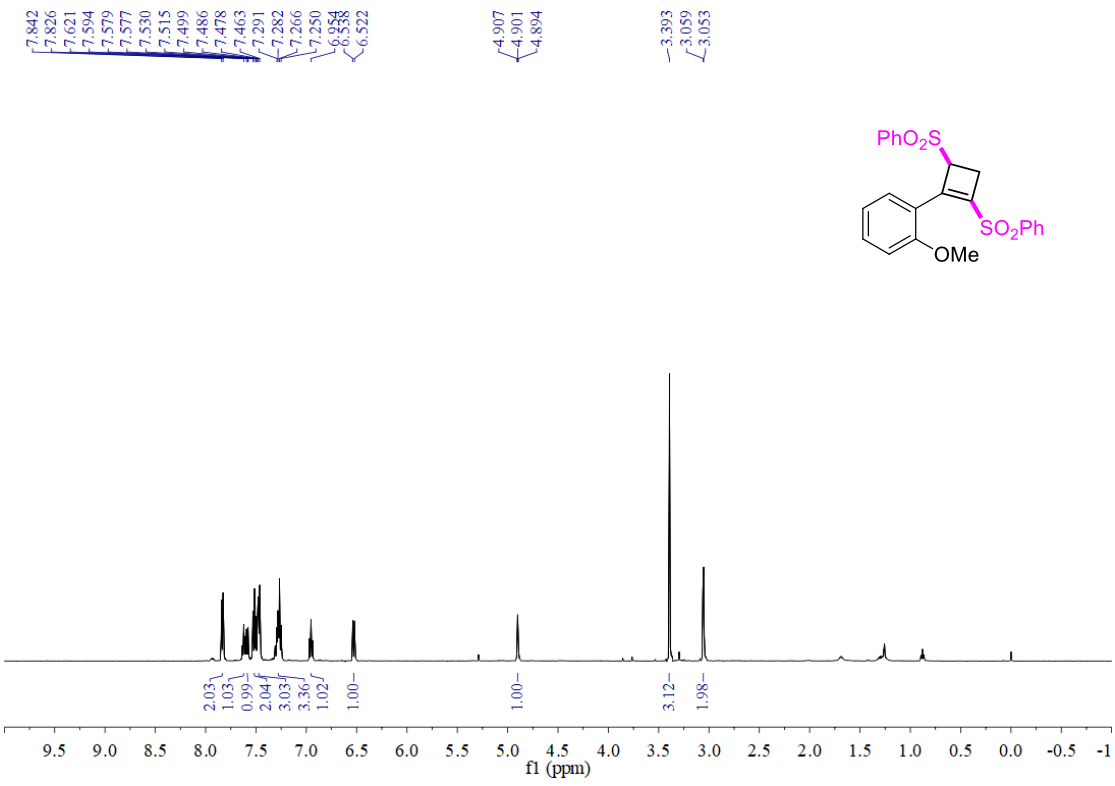


Figure S25. ^{1}H NMR and ^{13}C NMR spectra of compound **6c**.



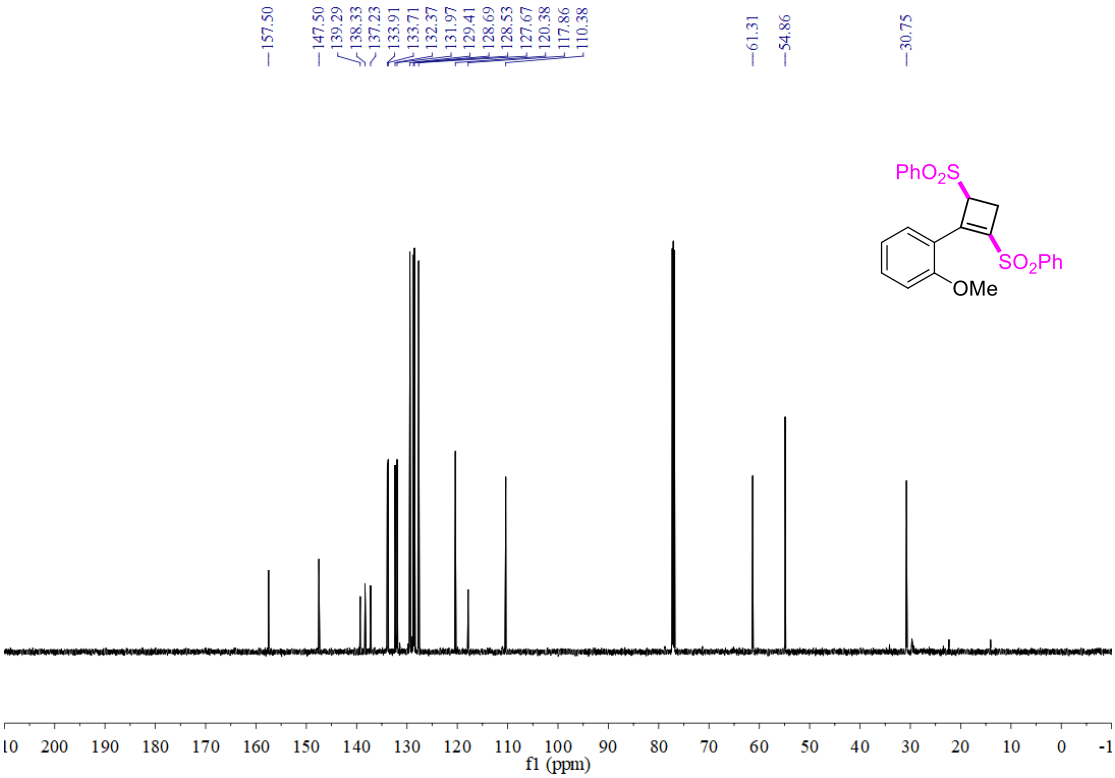
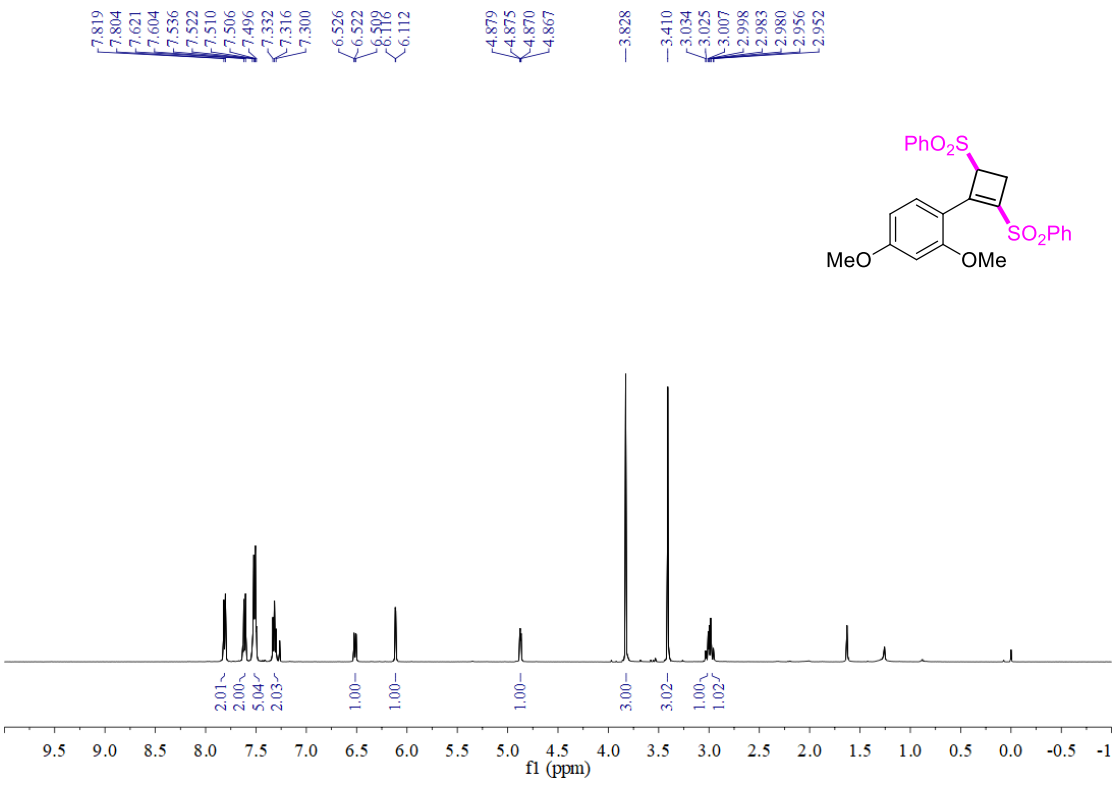


Figure S26. ^{1}H NMR and ^{13}C NMR spectra of compound **6d**.



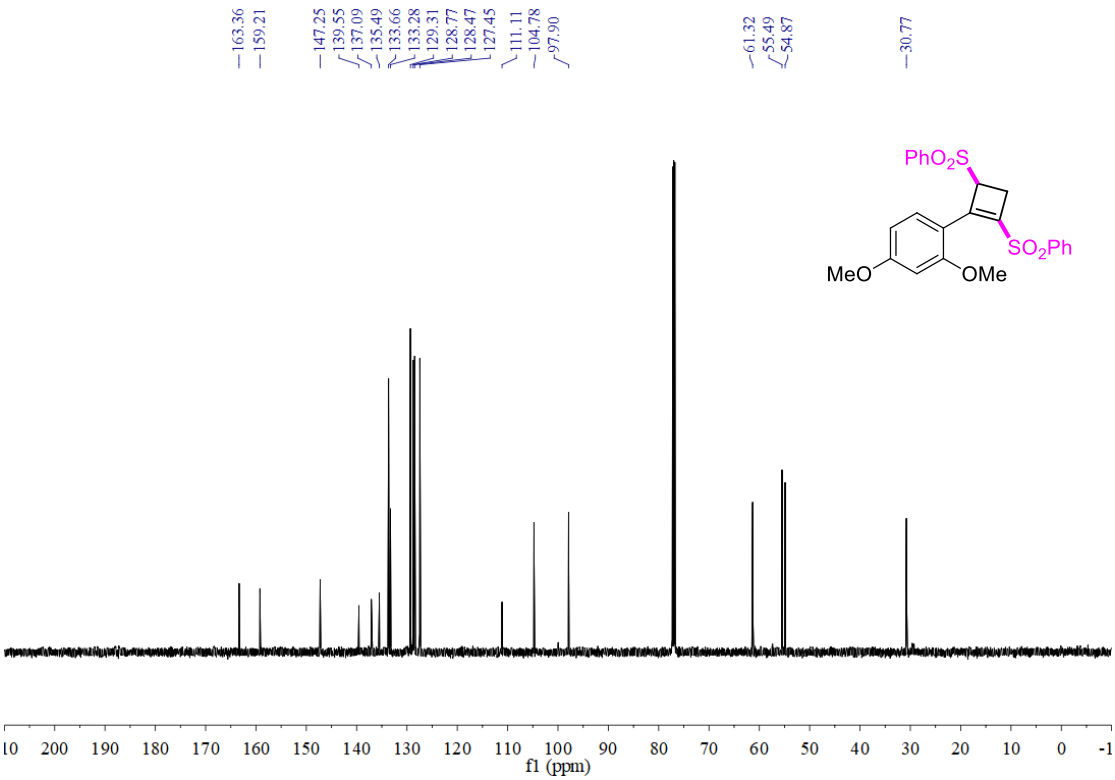
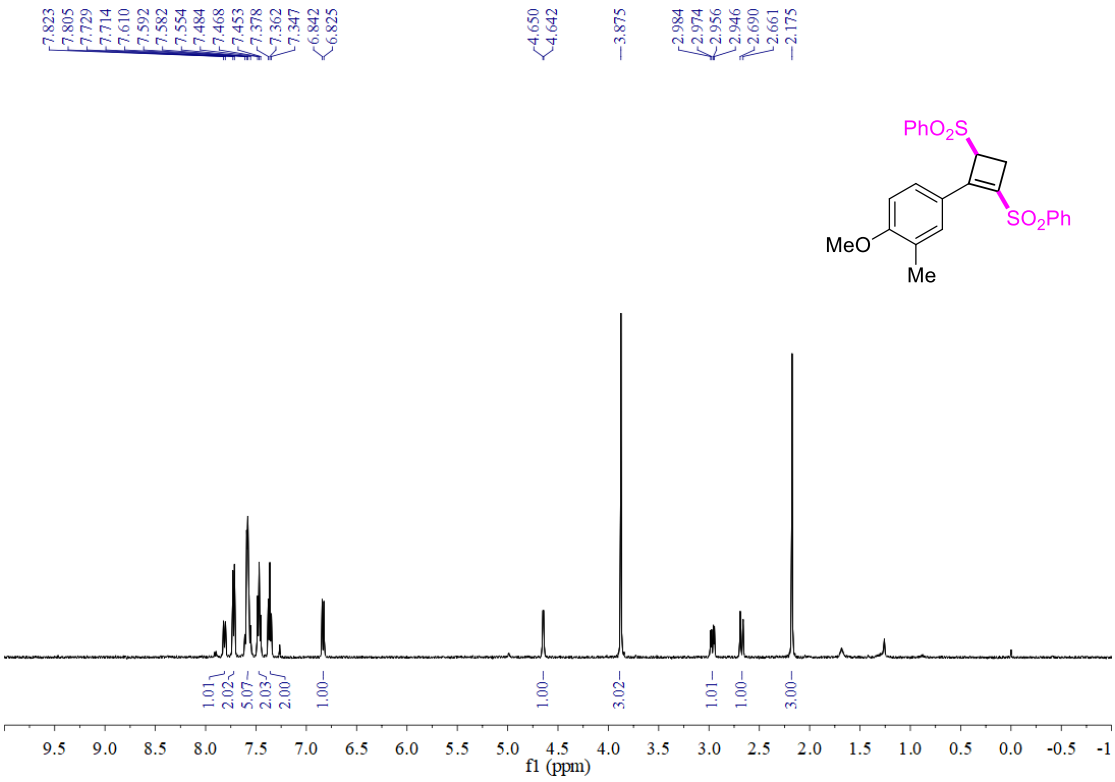


Figure S27. ^{1}H NMR and ^{13}C NMR spectra of compound **6e**.



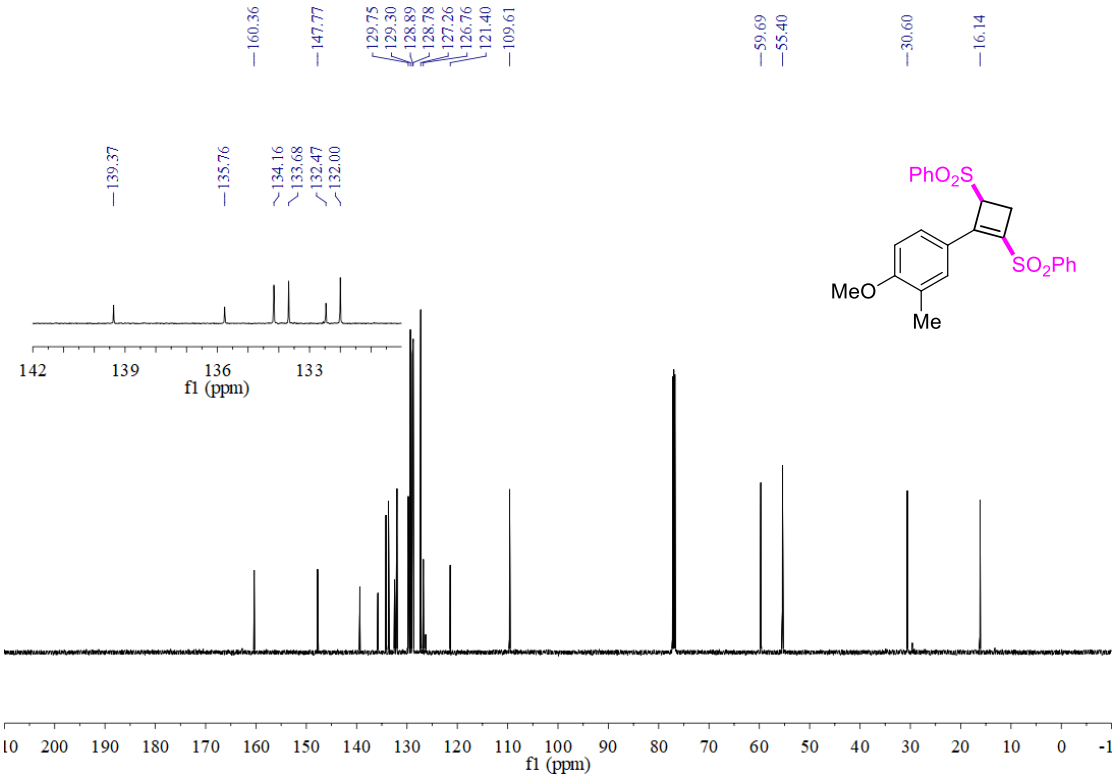
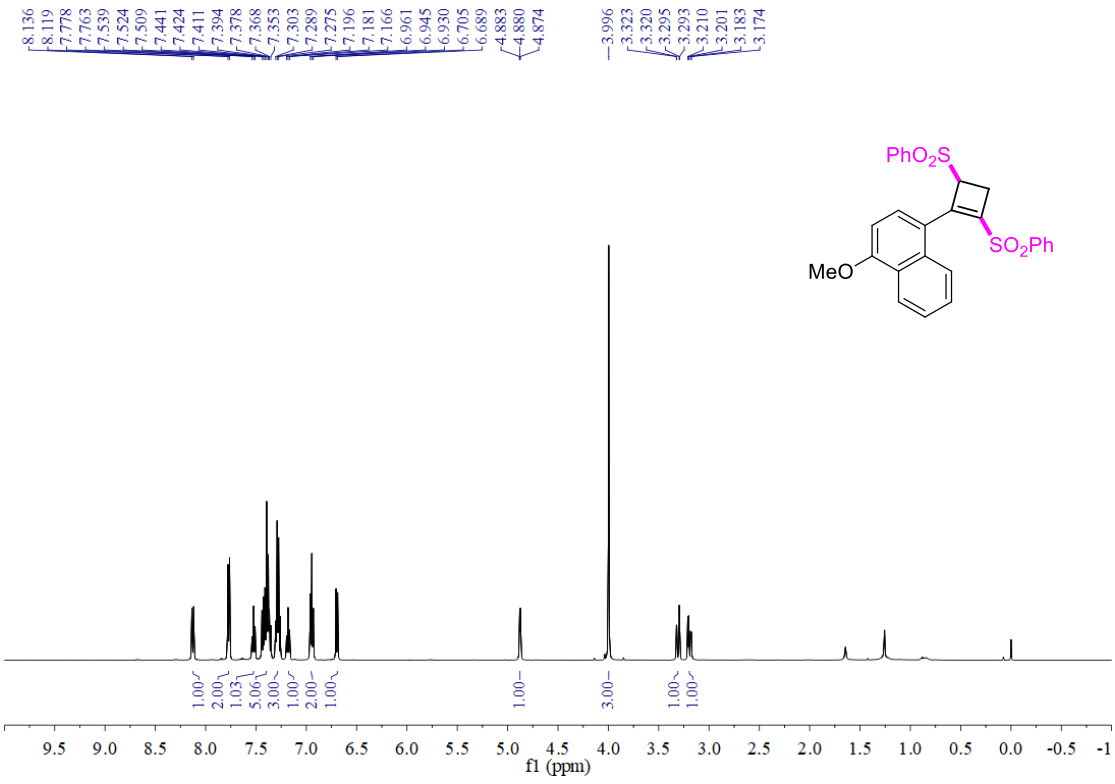


Figure S28. ^{1}H NMR and ^{13}C NMR spectra of compound **6f**.



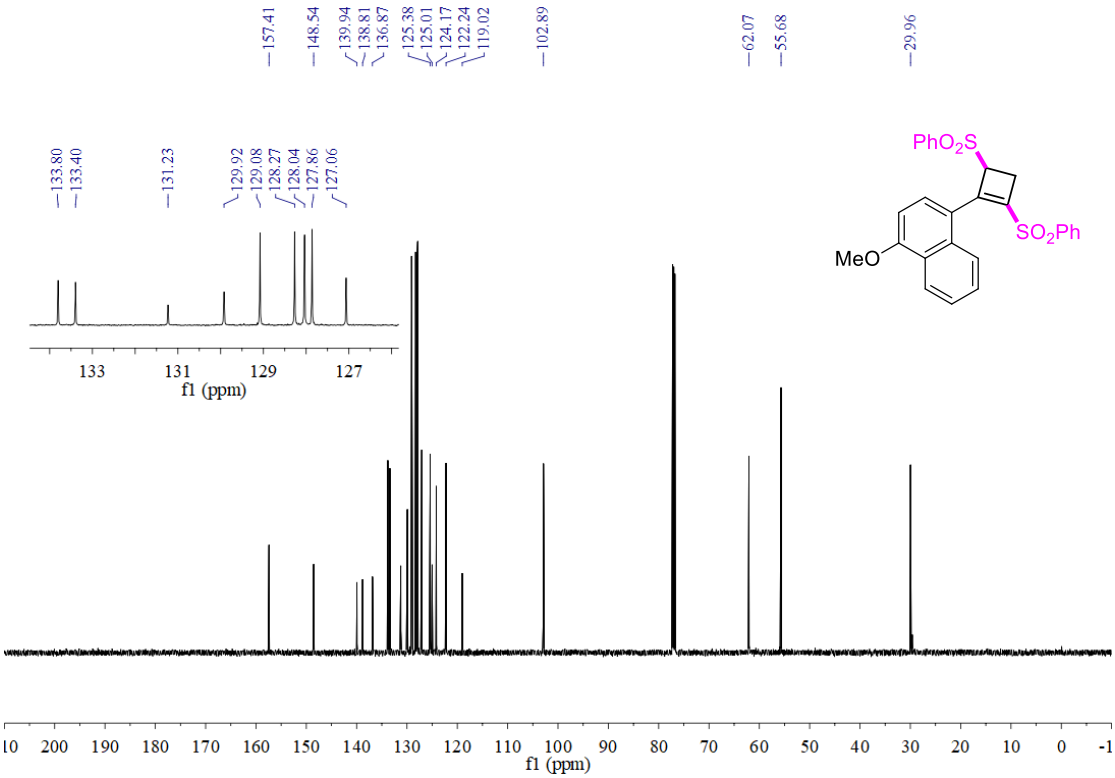
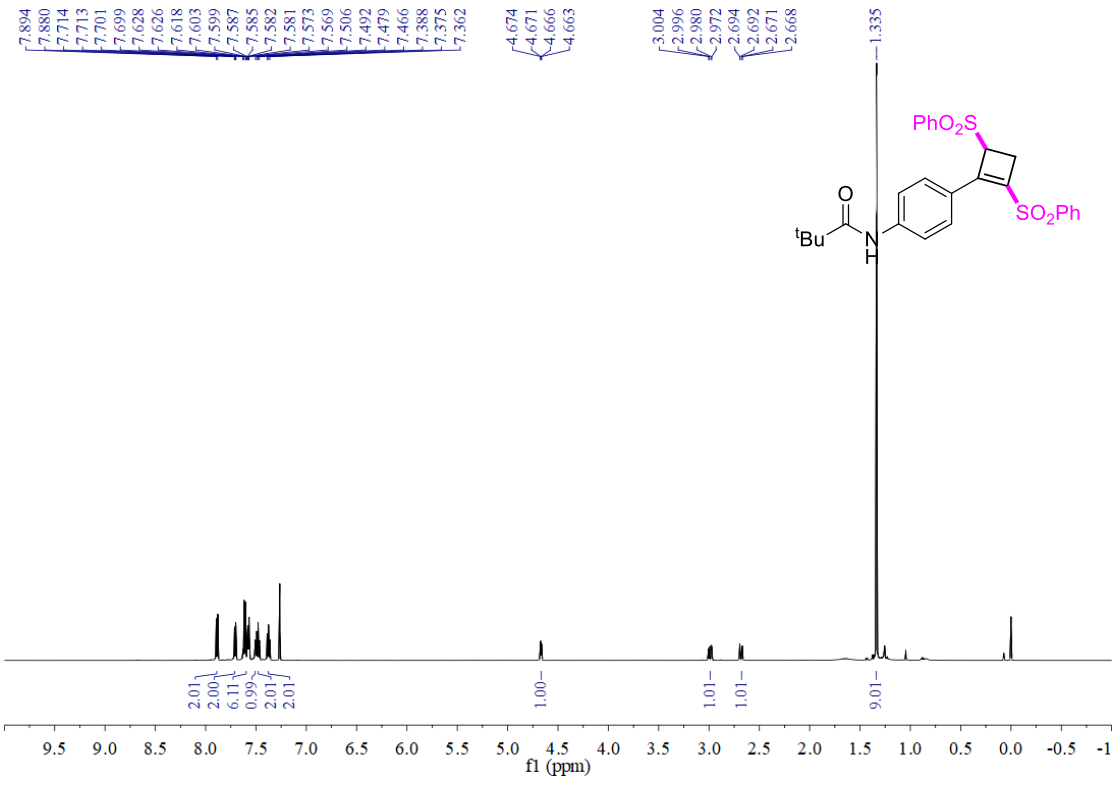


Figure S29. ^{1}H NMR and ^{13}C NMR spectra of compound **6g**.



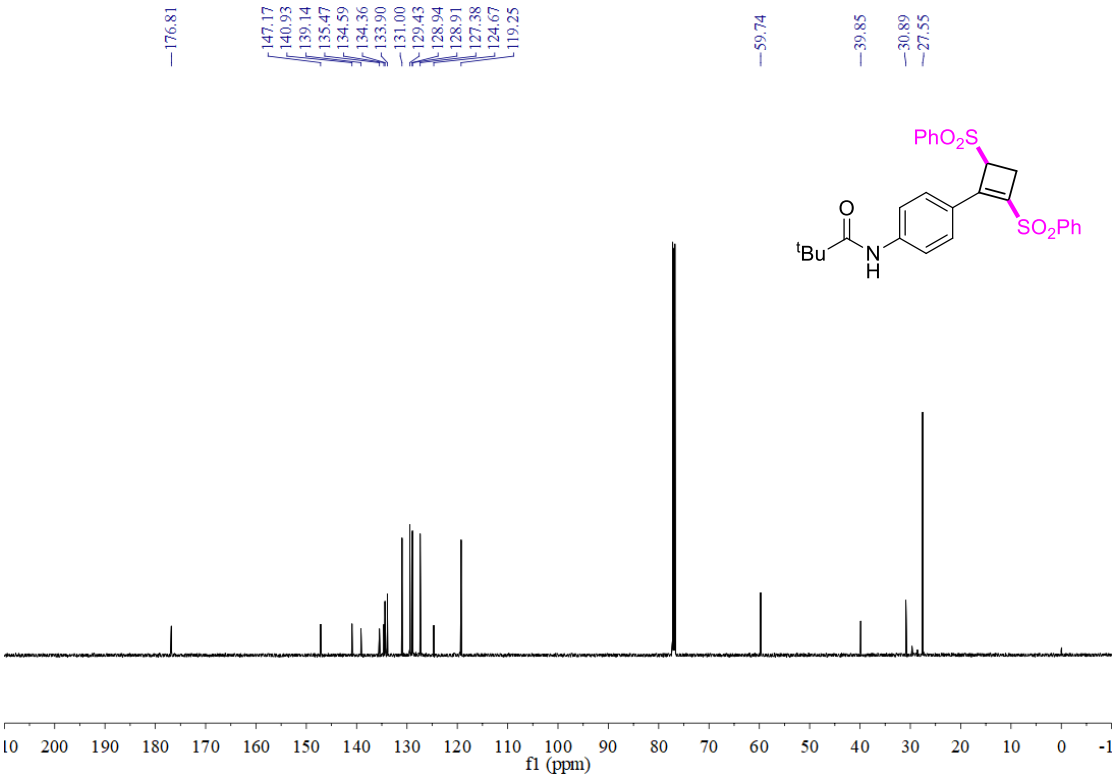
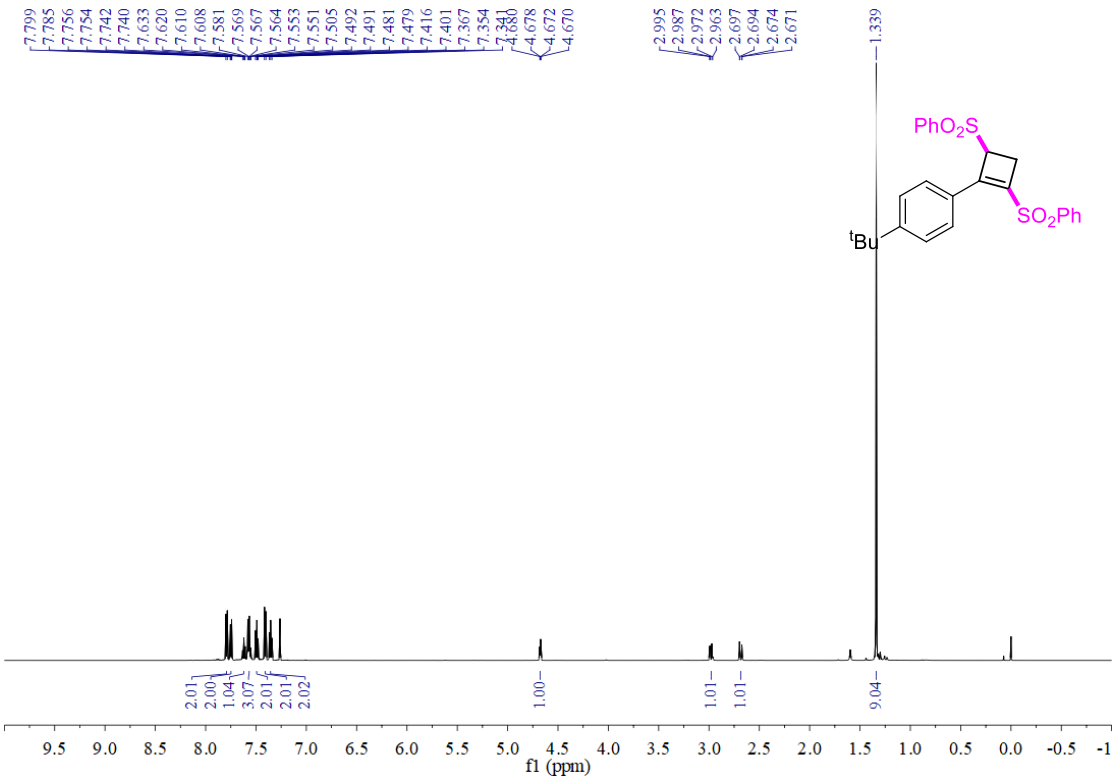


Figure S30. ^{1}H NMR and ^{13}C NMR spectra of compound **6h**.



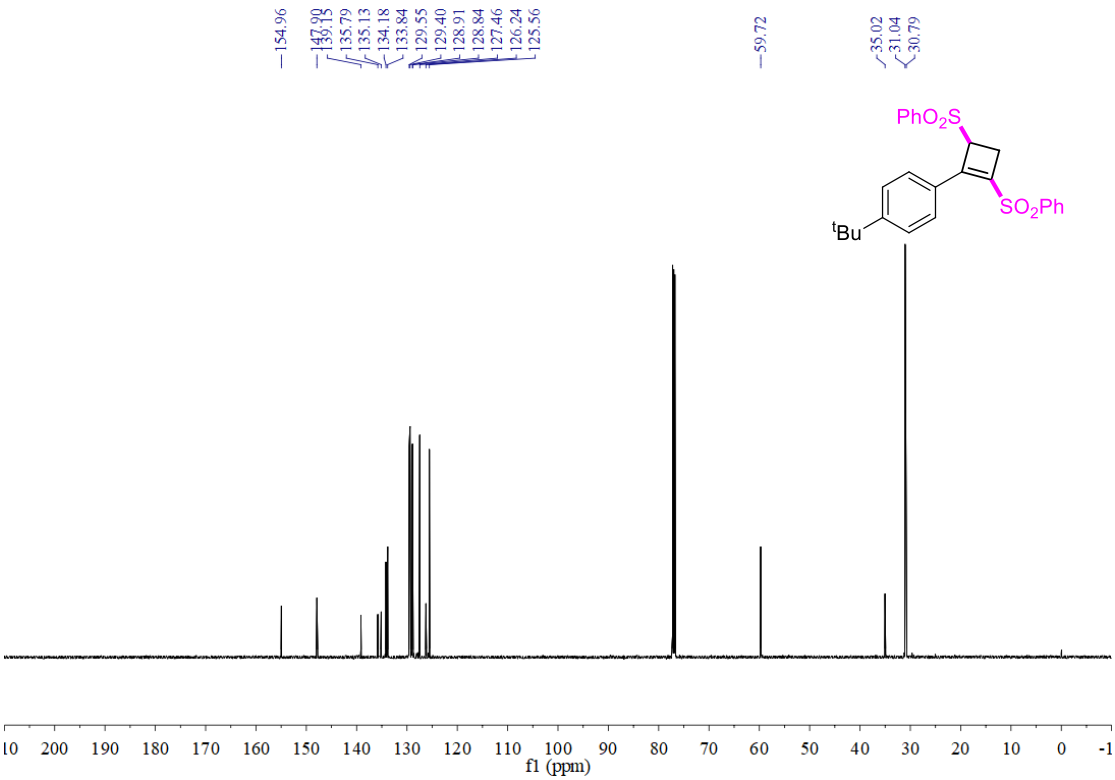
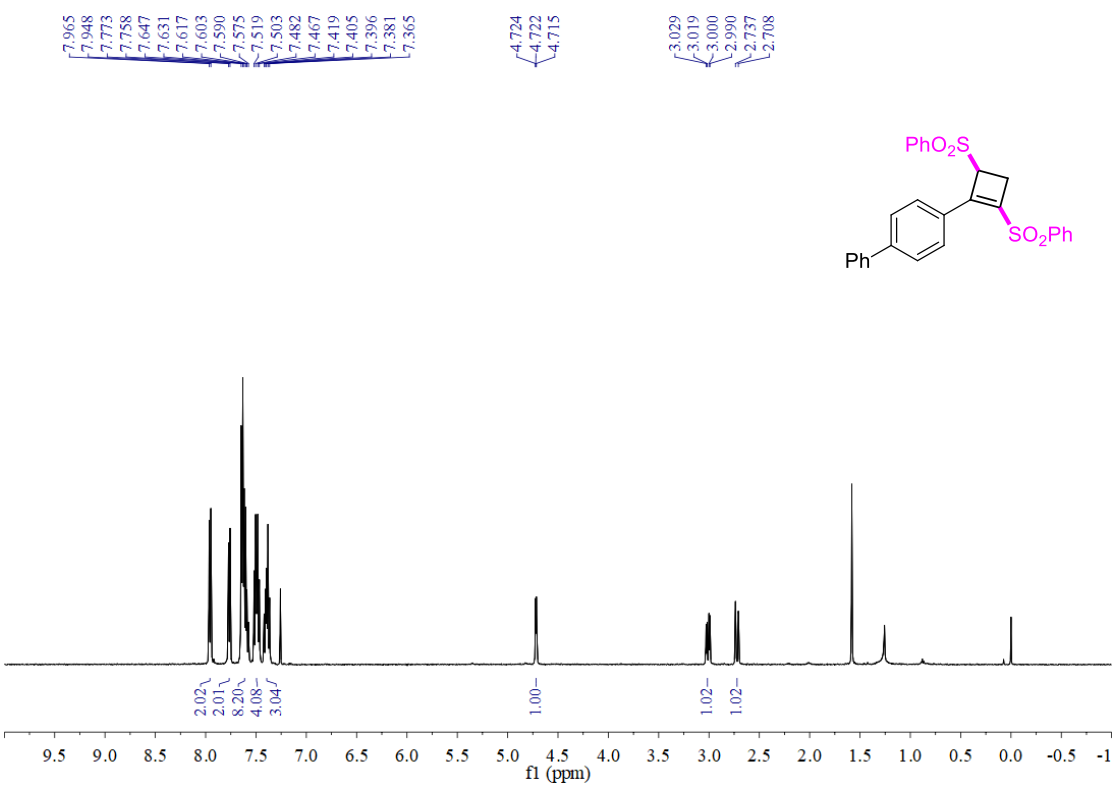


Figure S31. ^{1}H NMR and ^{13}C NMR spectra of compound **6i**.



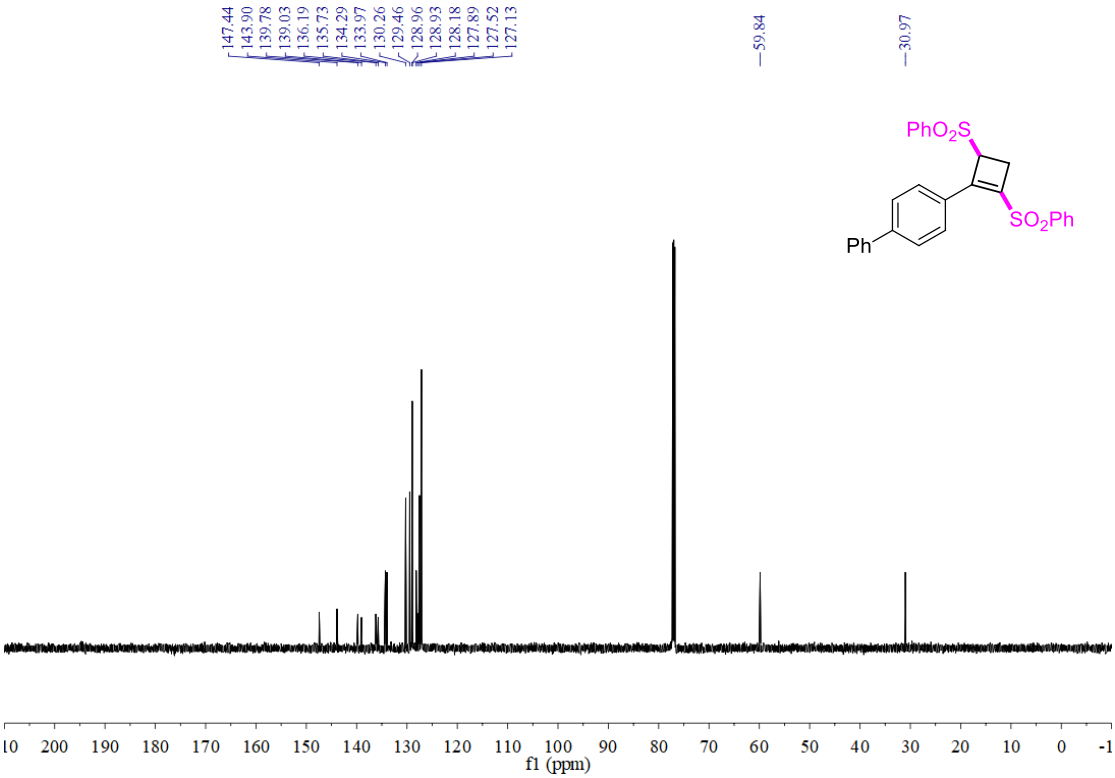
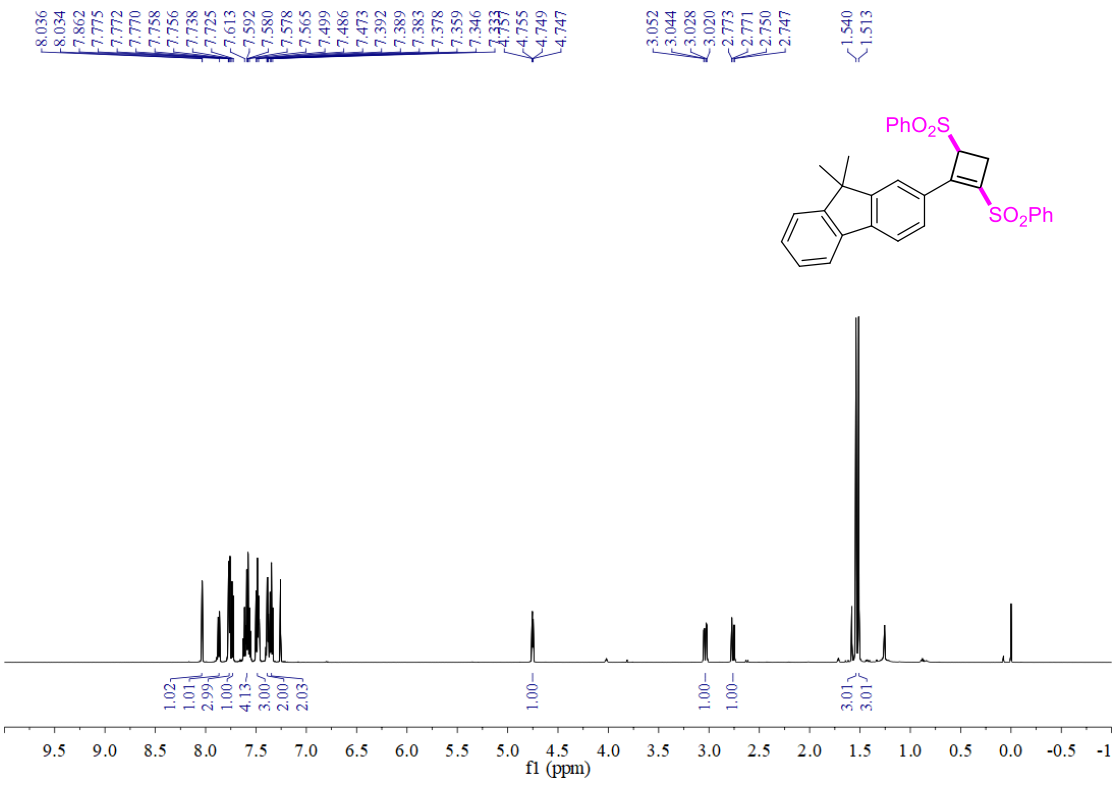


Figure S32. ^{1}H NMR and ^{13}C NMR spectra of compound **6j**.



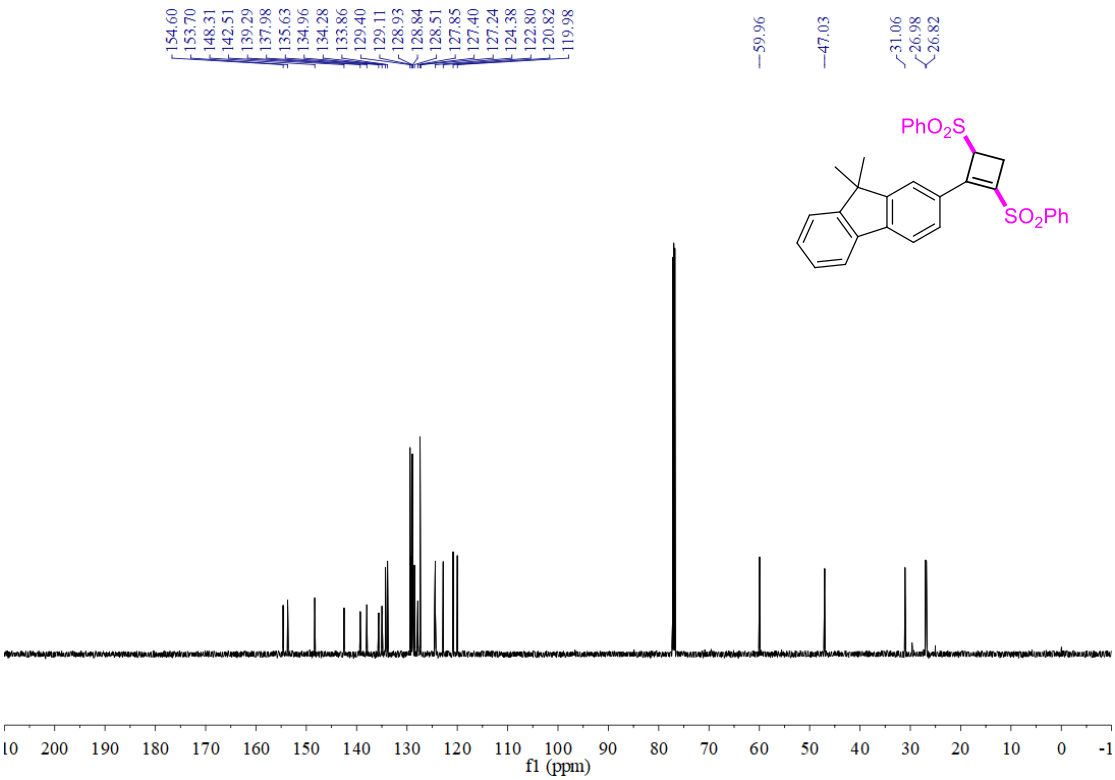
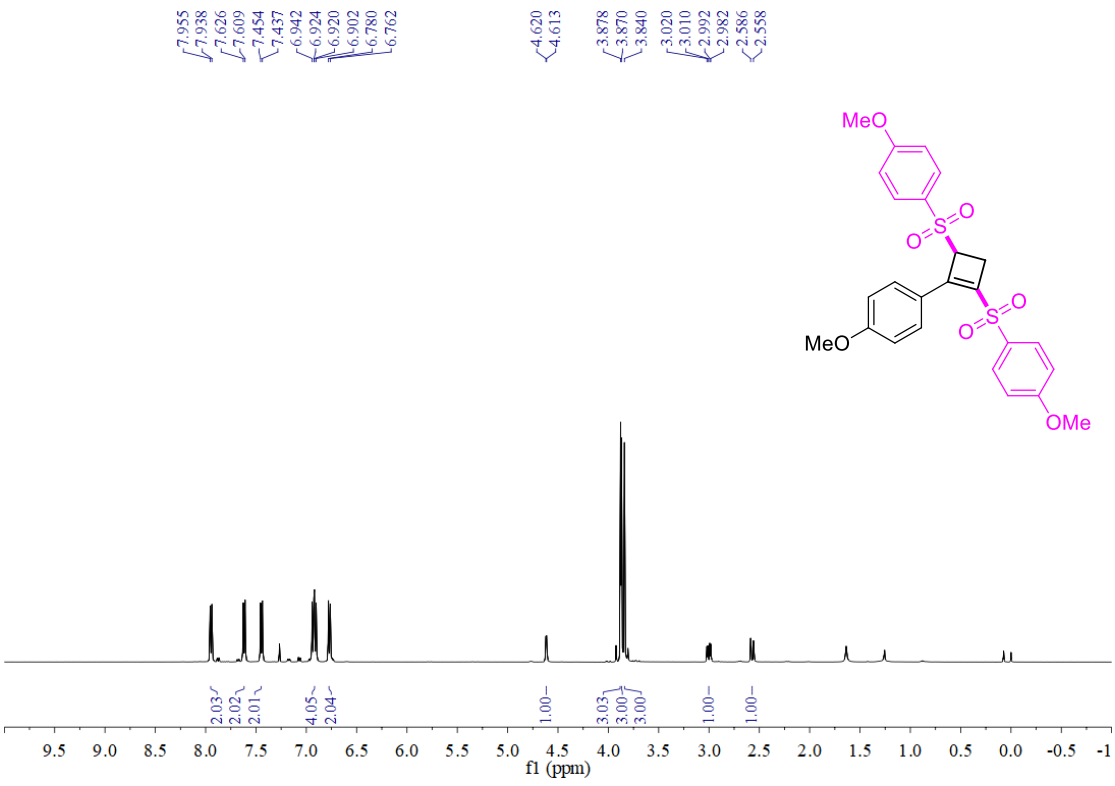


Figure S33. ^{1}H NMR and ^{13}C NMR spectra of compound **6k**.



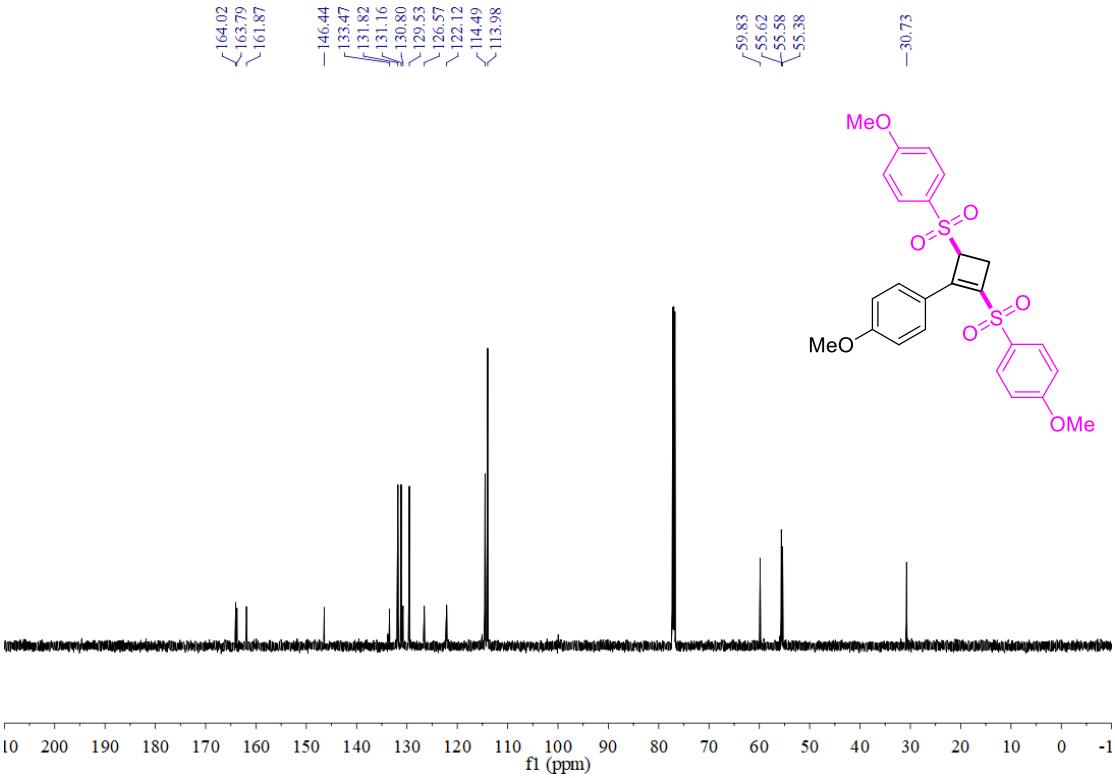
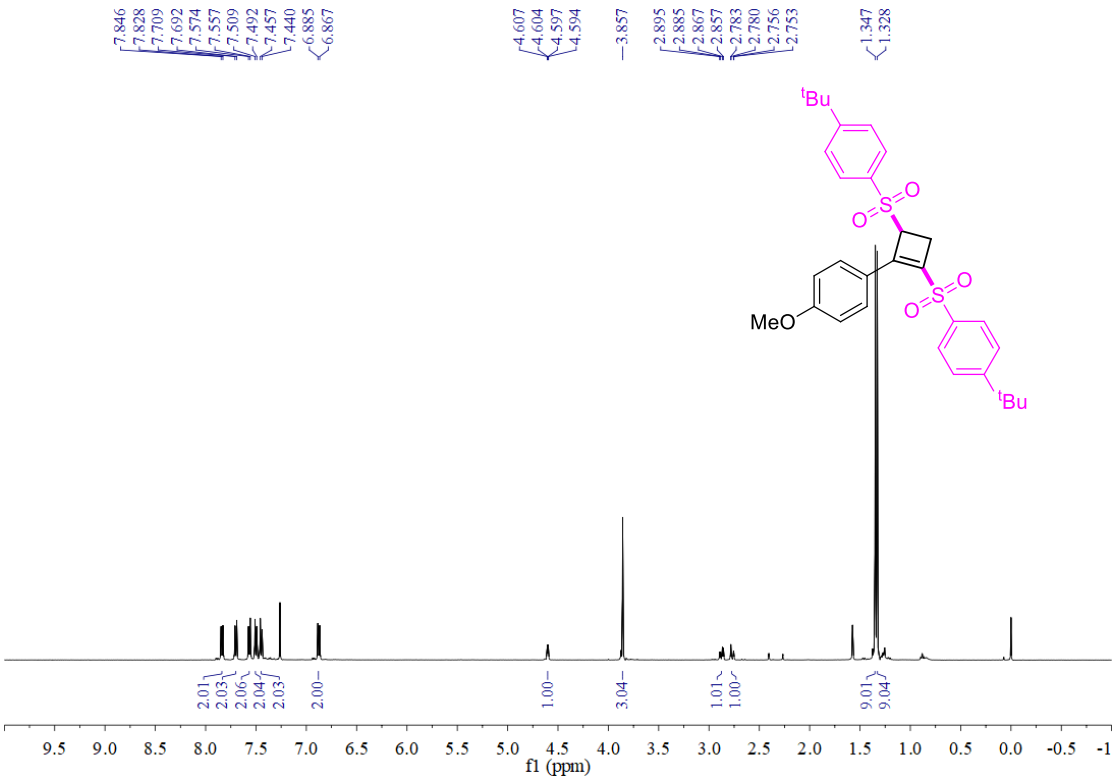


Figure S34. ^{1}H NMR and ^{13}C NMR spectra of compound **6l**.



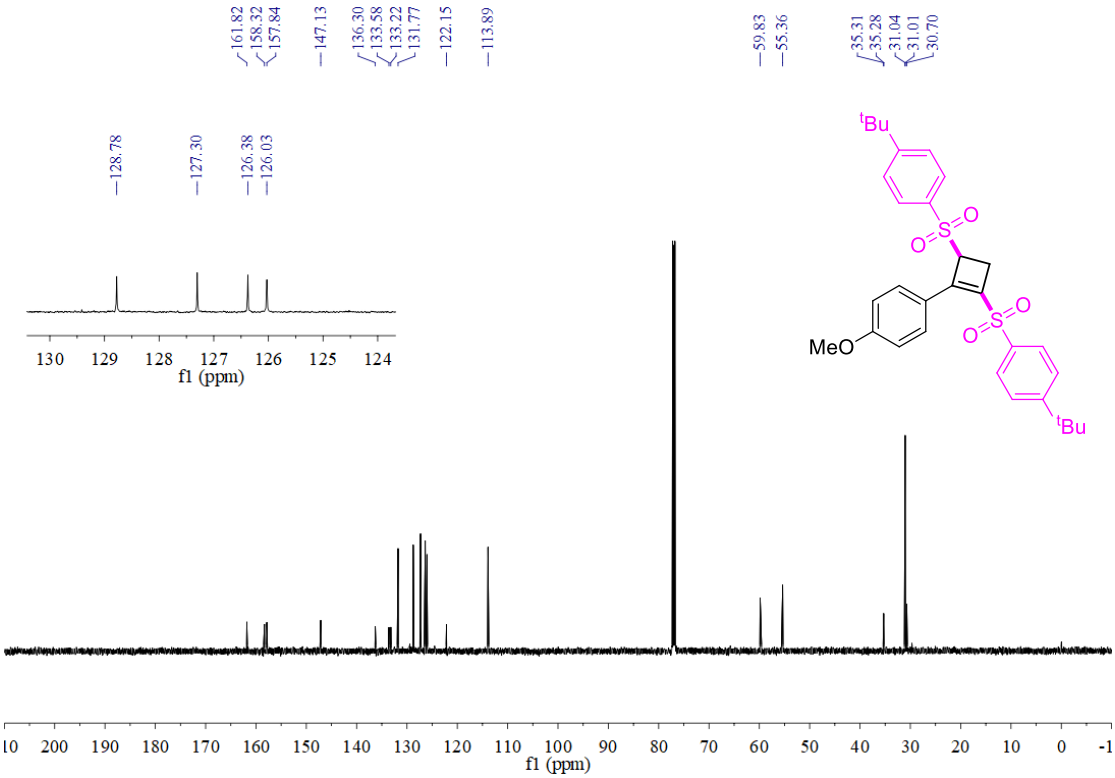
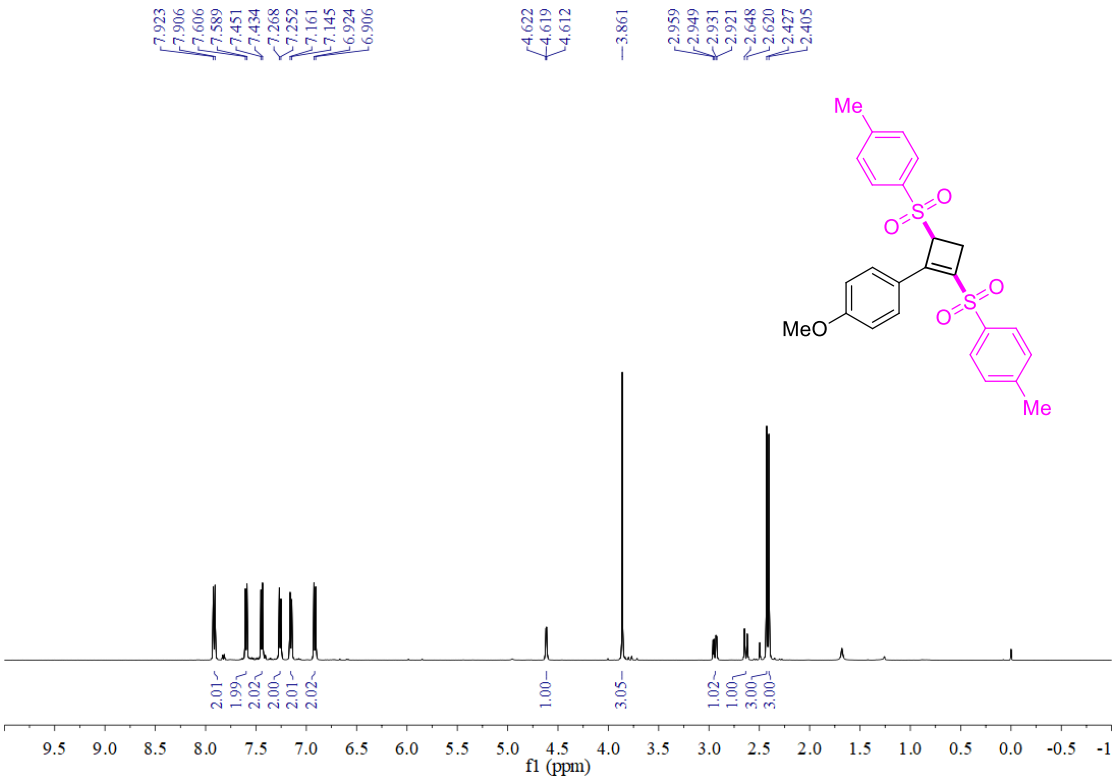


Figure S35. ^{1}H NMR and ^{13}C NMR spectra of compound **6m**.



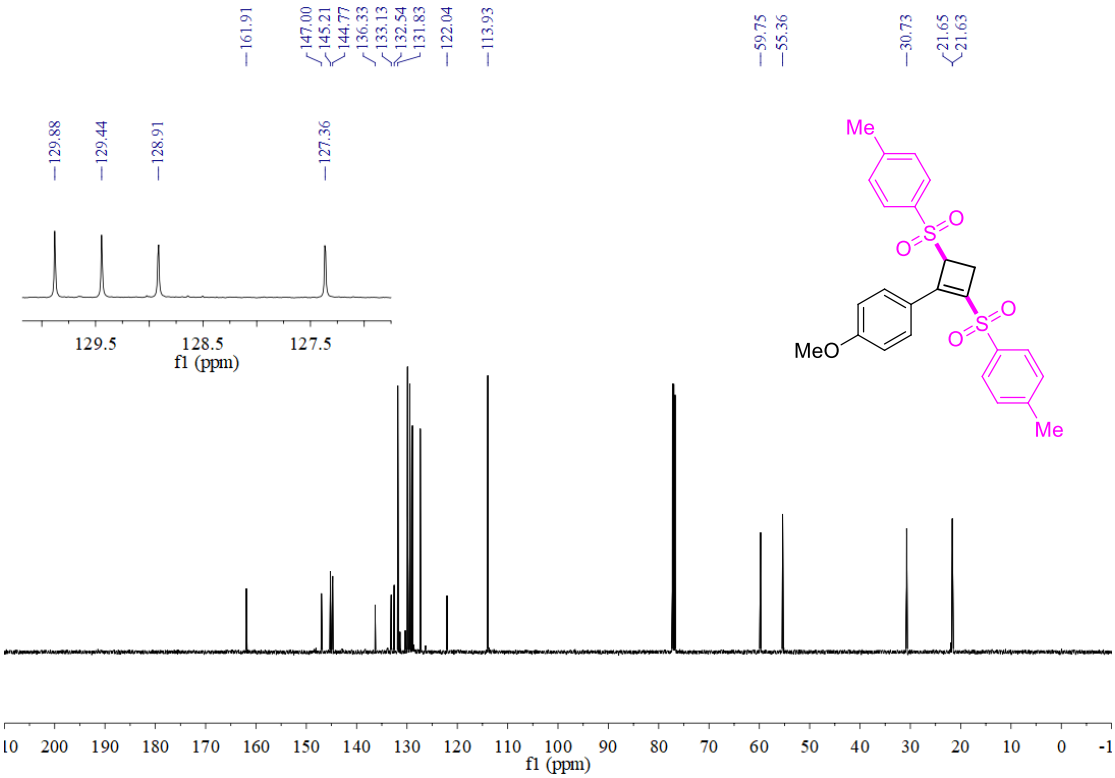
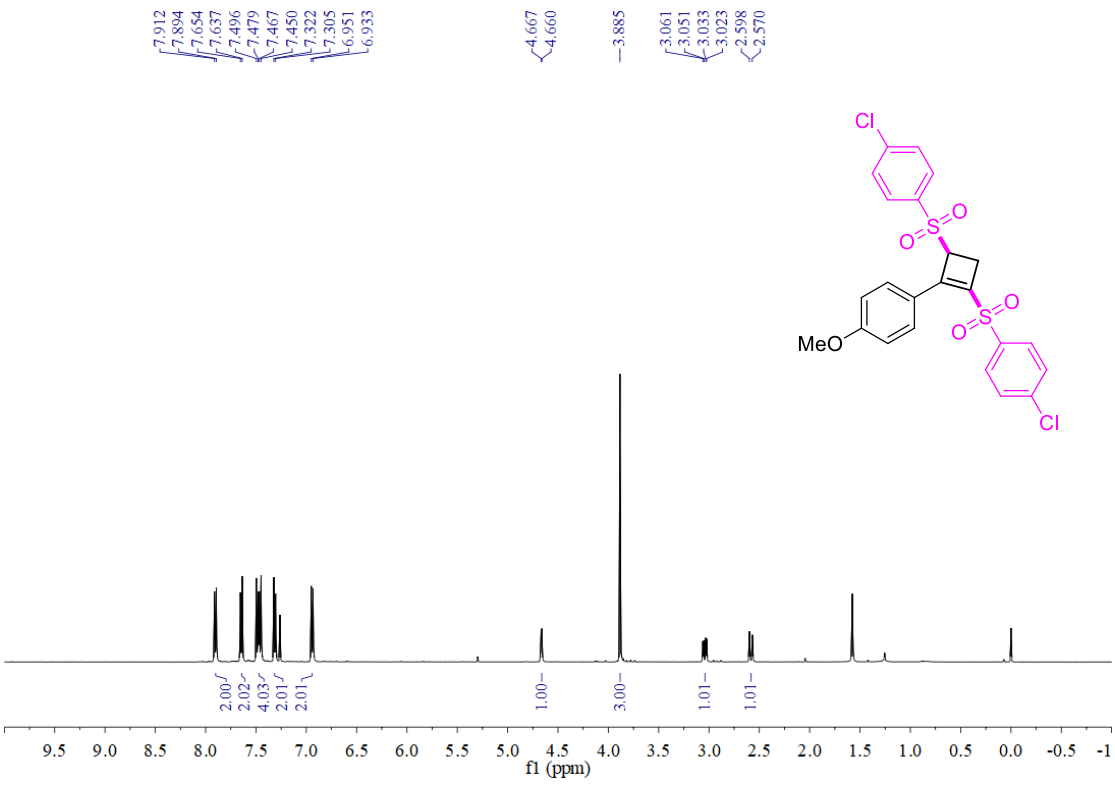


Figure S36. ^{1}H NMR and ^{13}C NMR spectra of compound **6n**.



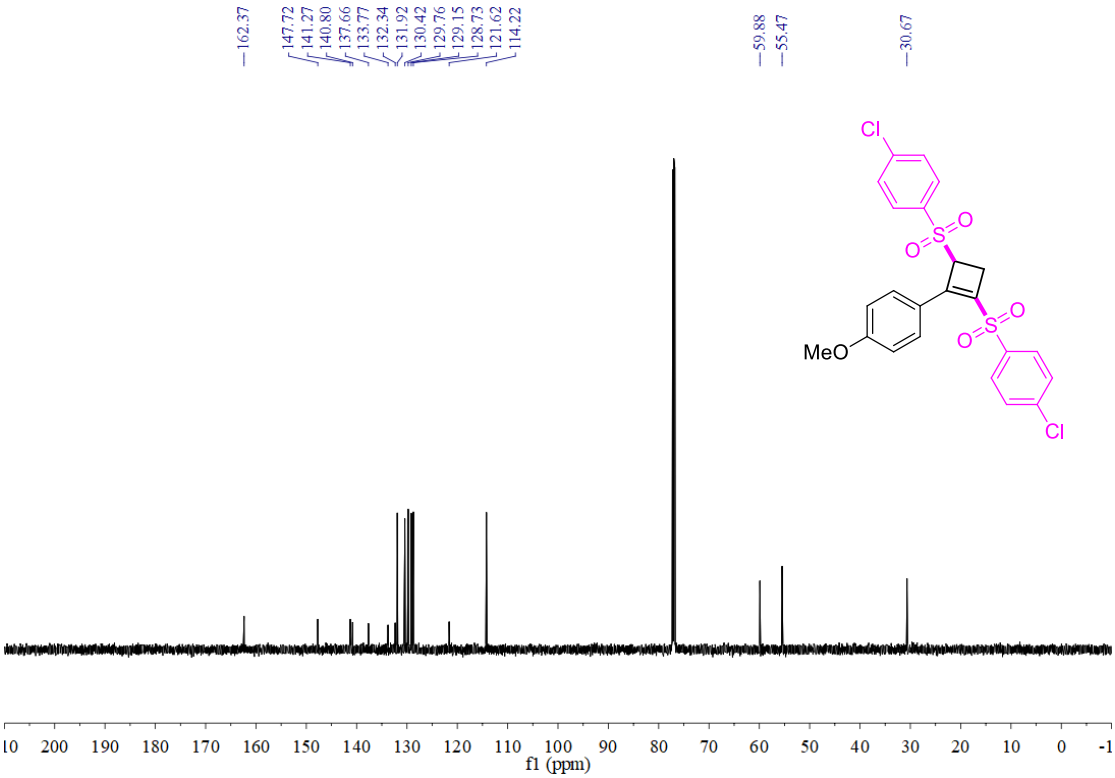
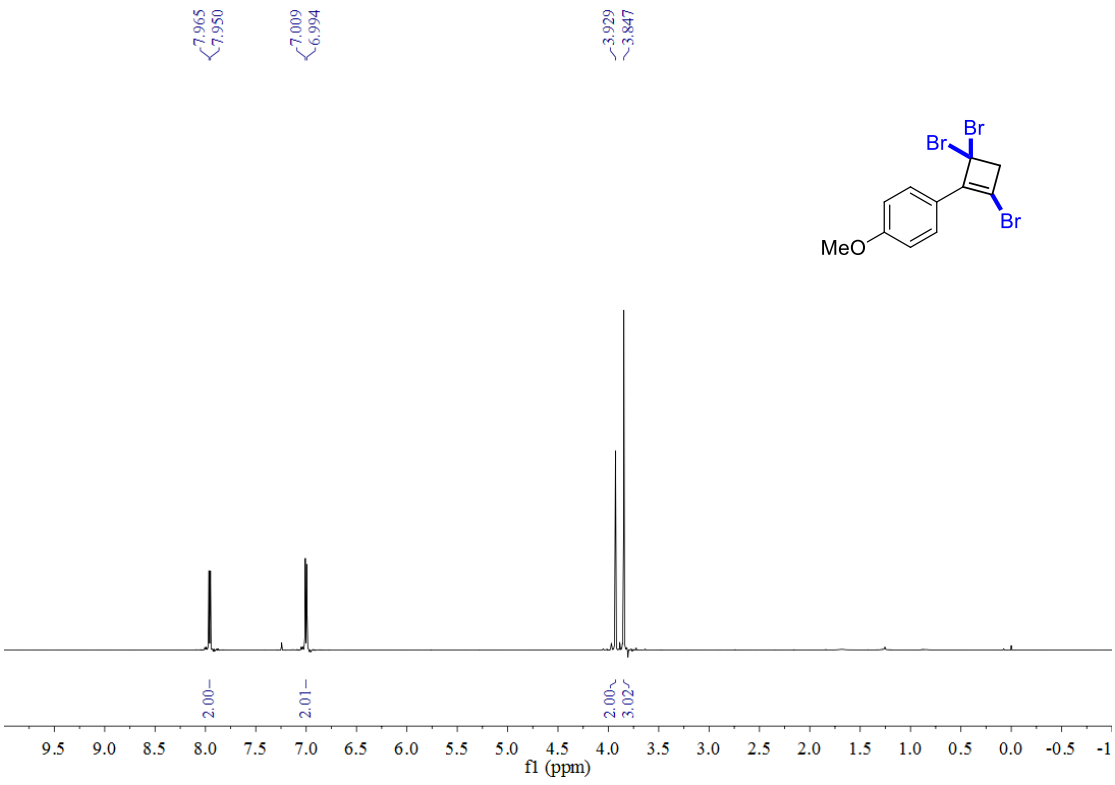


Figure S37. ^{1}H NMR and ^{13}C NMR spectra of compound **6o**.



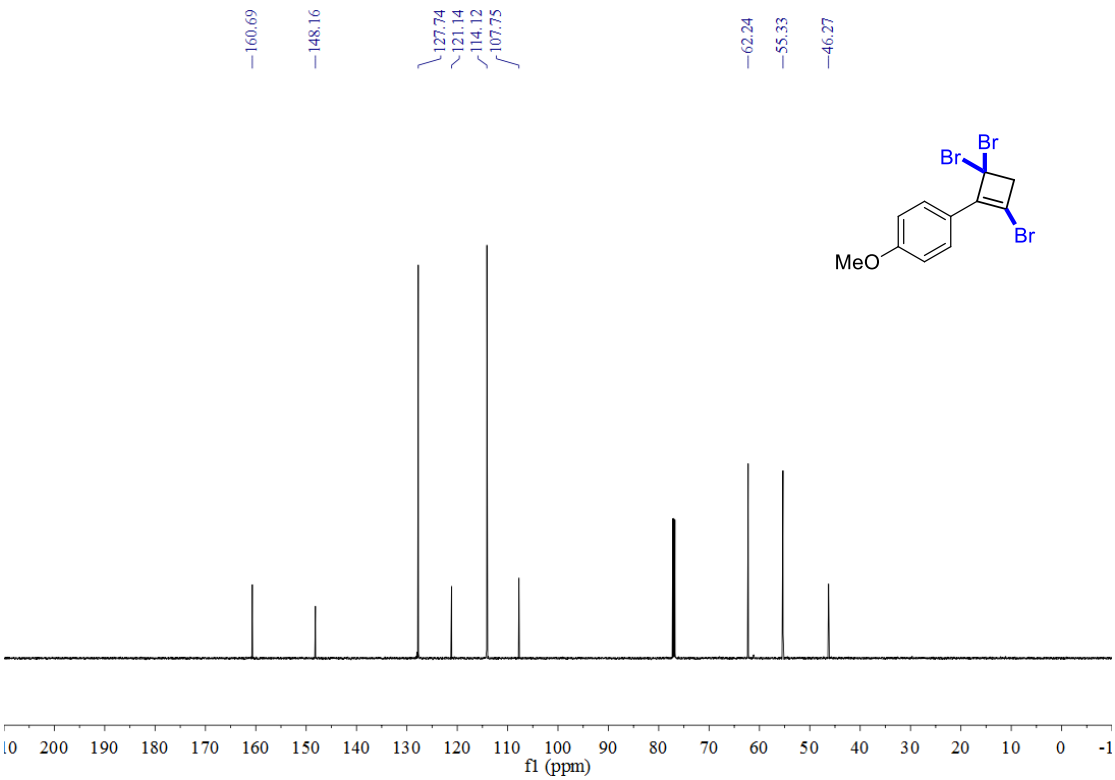
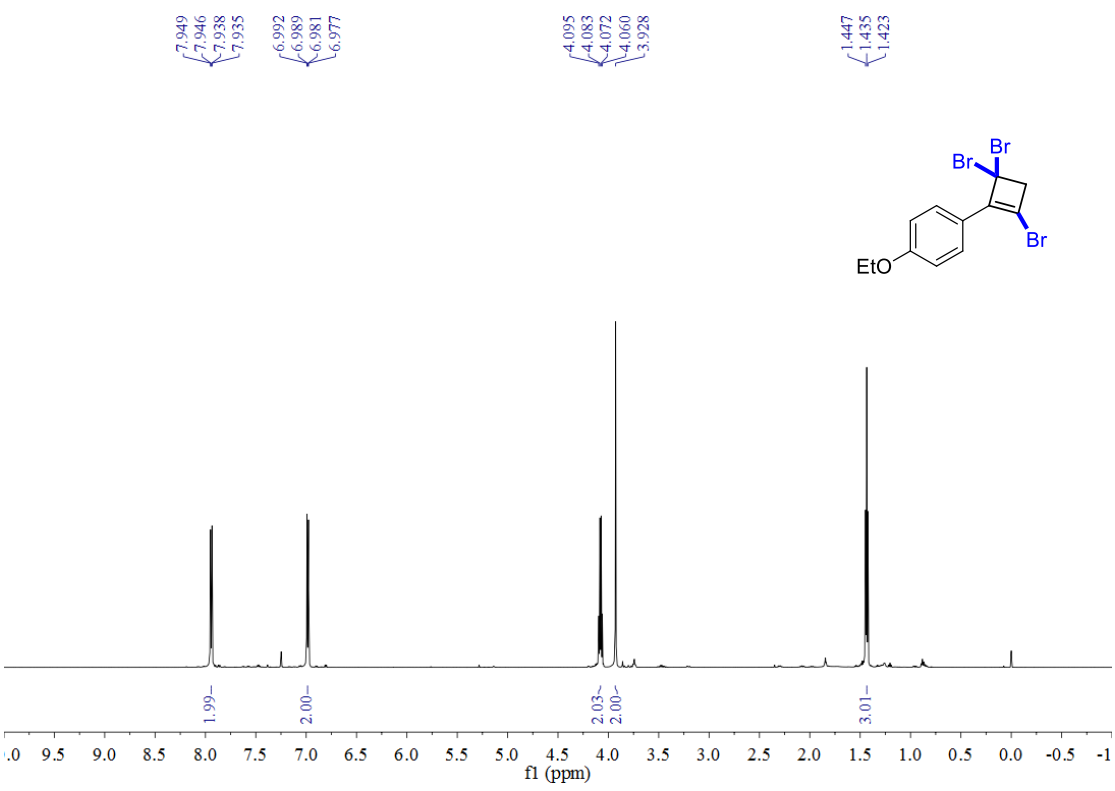


Figure S38. ^{1}H NMR and ^{13}C NMR spectra of compound **7a**.



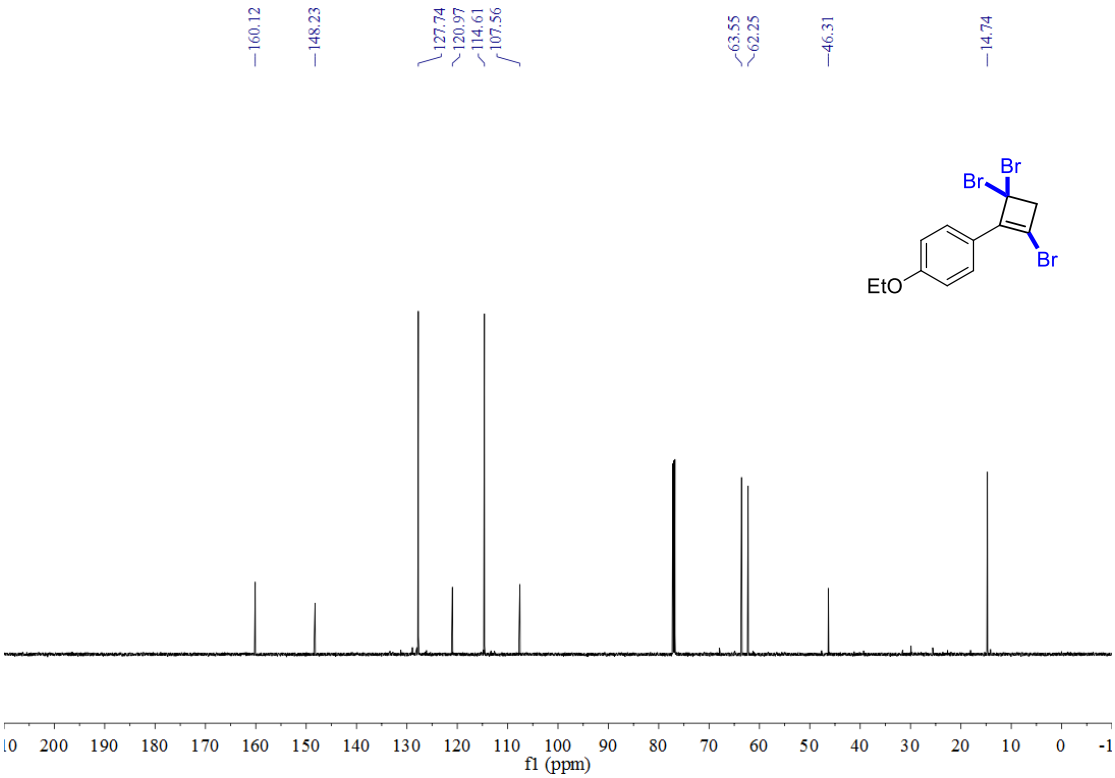
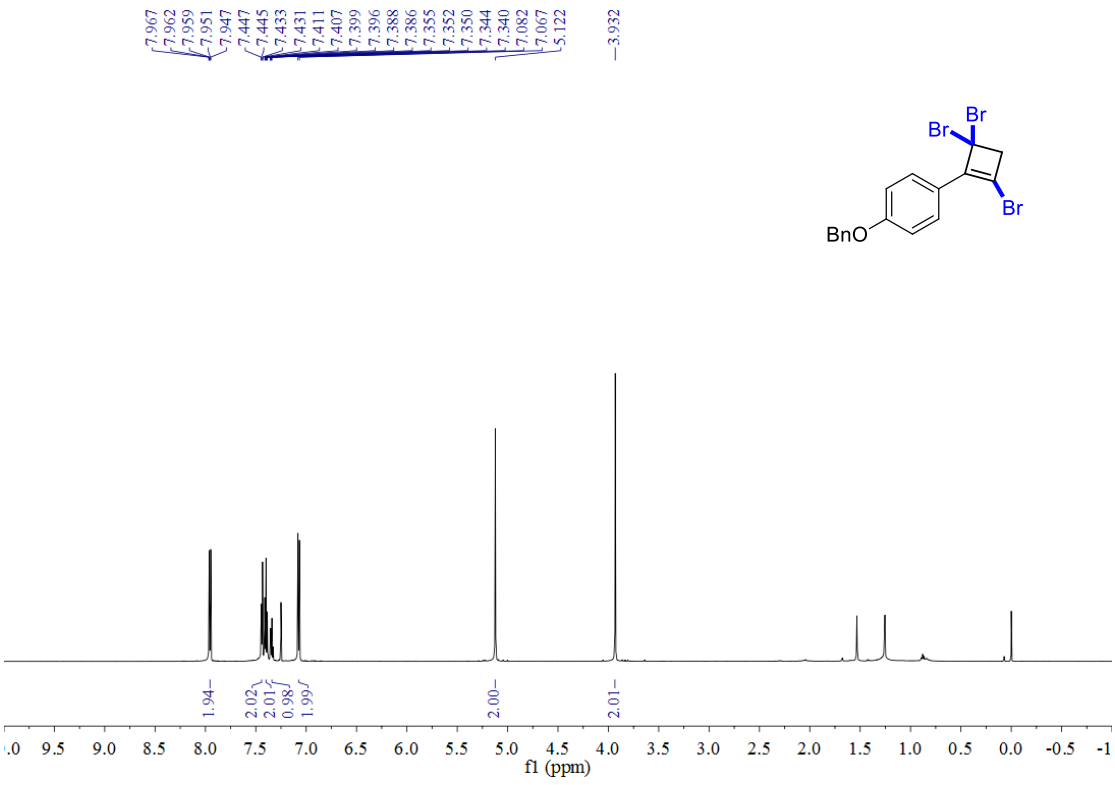


Figure S39. ^{1}H NMR and ^{13}C NMR spectra of compound **7b**.



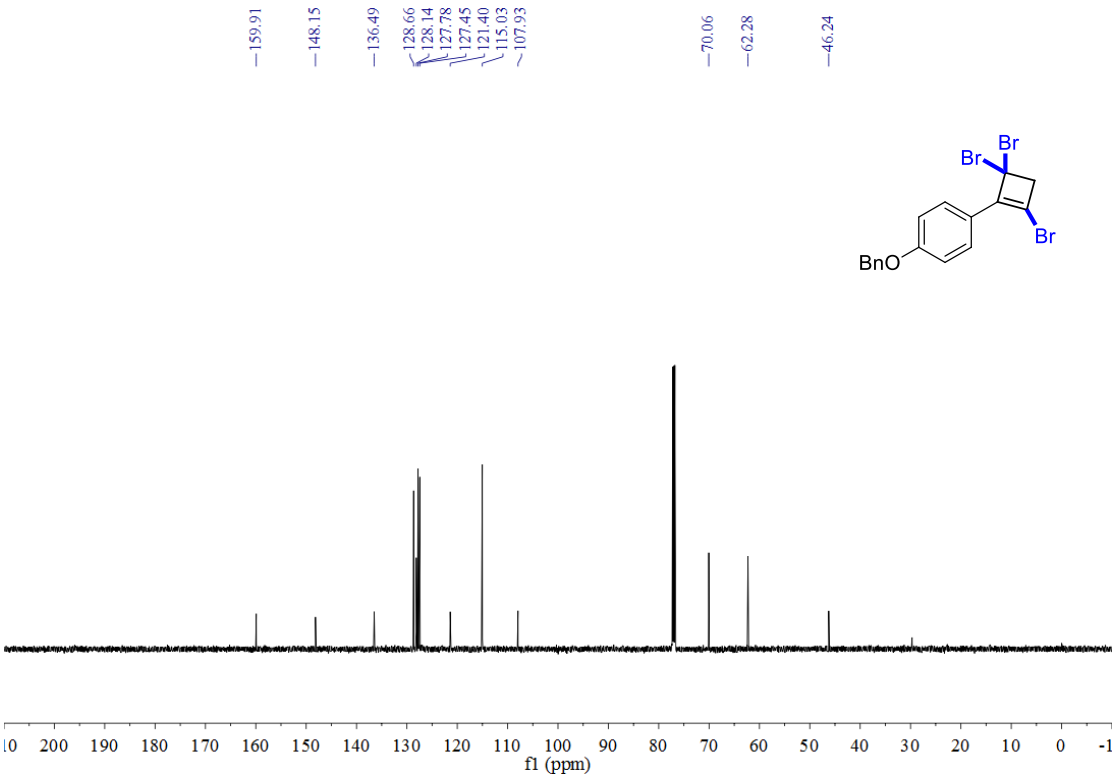
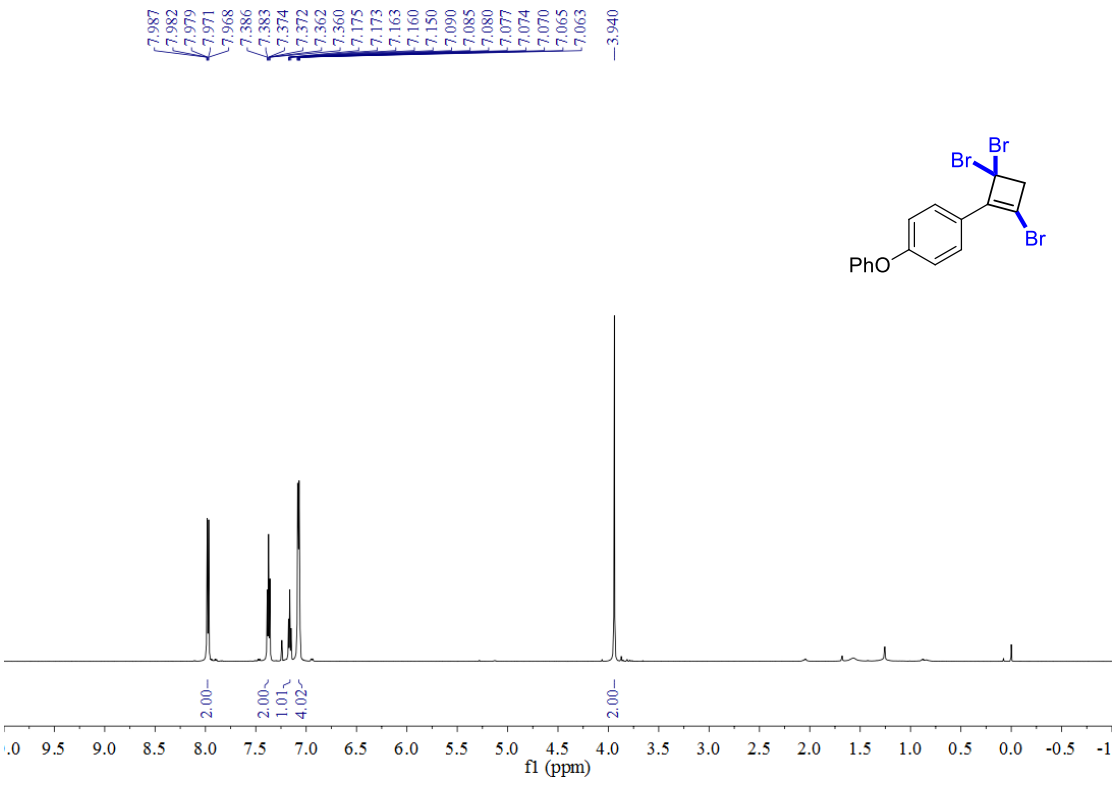


Figure S40. ^{1}H NMR and ^{13}C NMR spectra of compound **7c**.



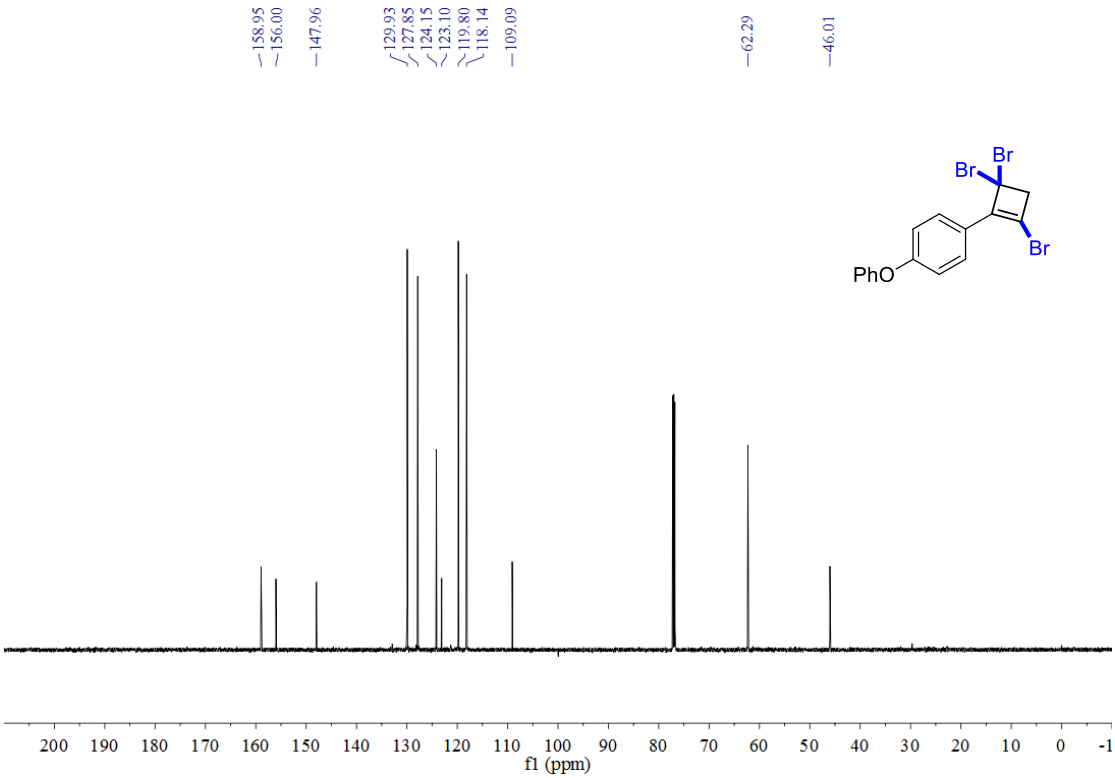
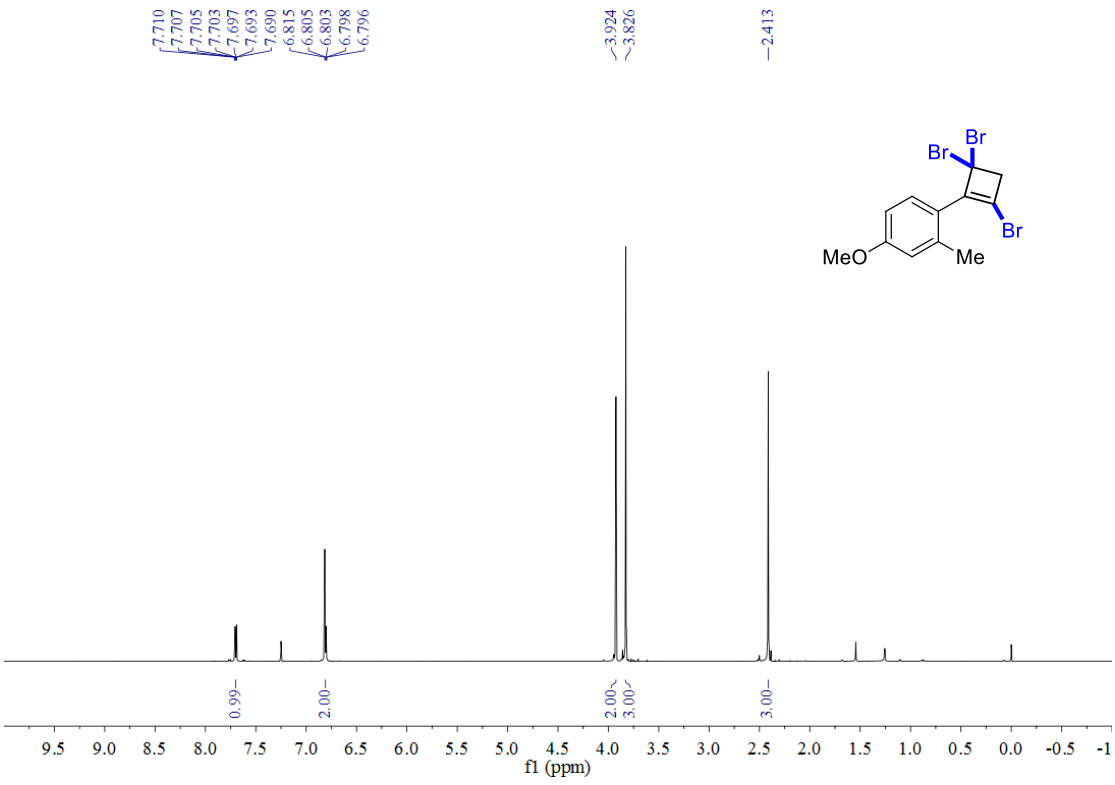


Figure S41. ^{1}H NMR and ^{13}C NMR spectra of compound **7d**.



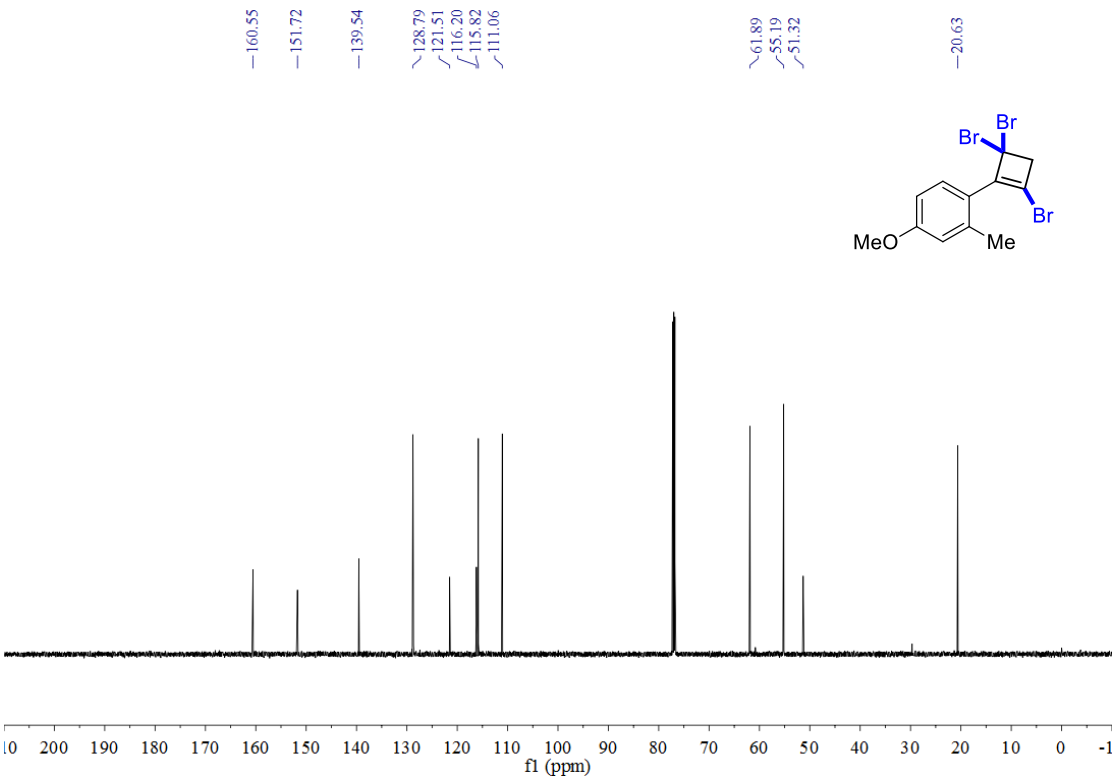
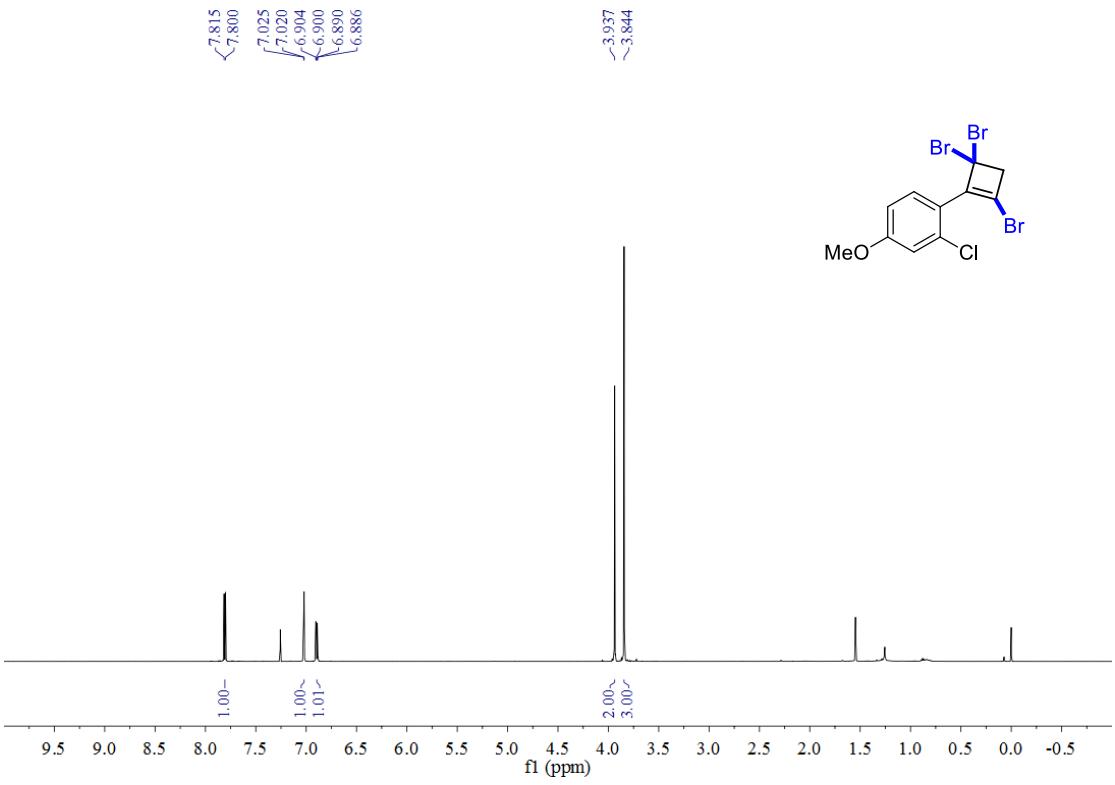


Figure S42. ^{1}H NMR and ^{13}C NMR spectra of compound **7e**.



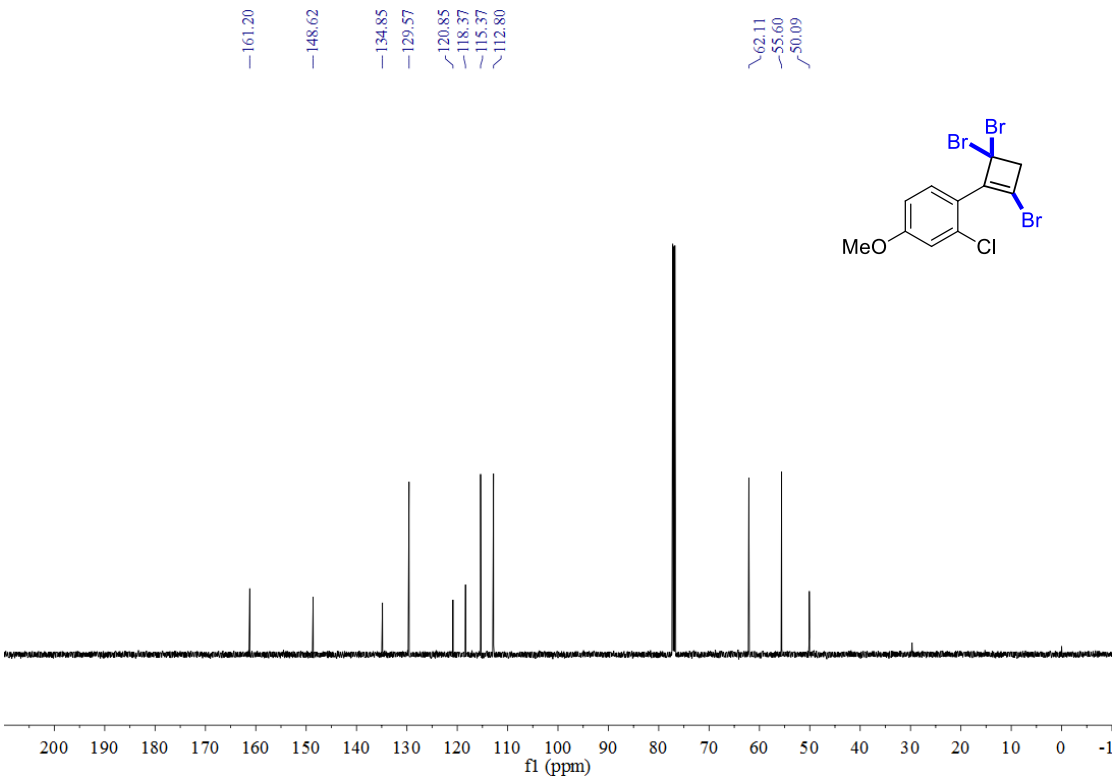
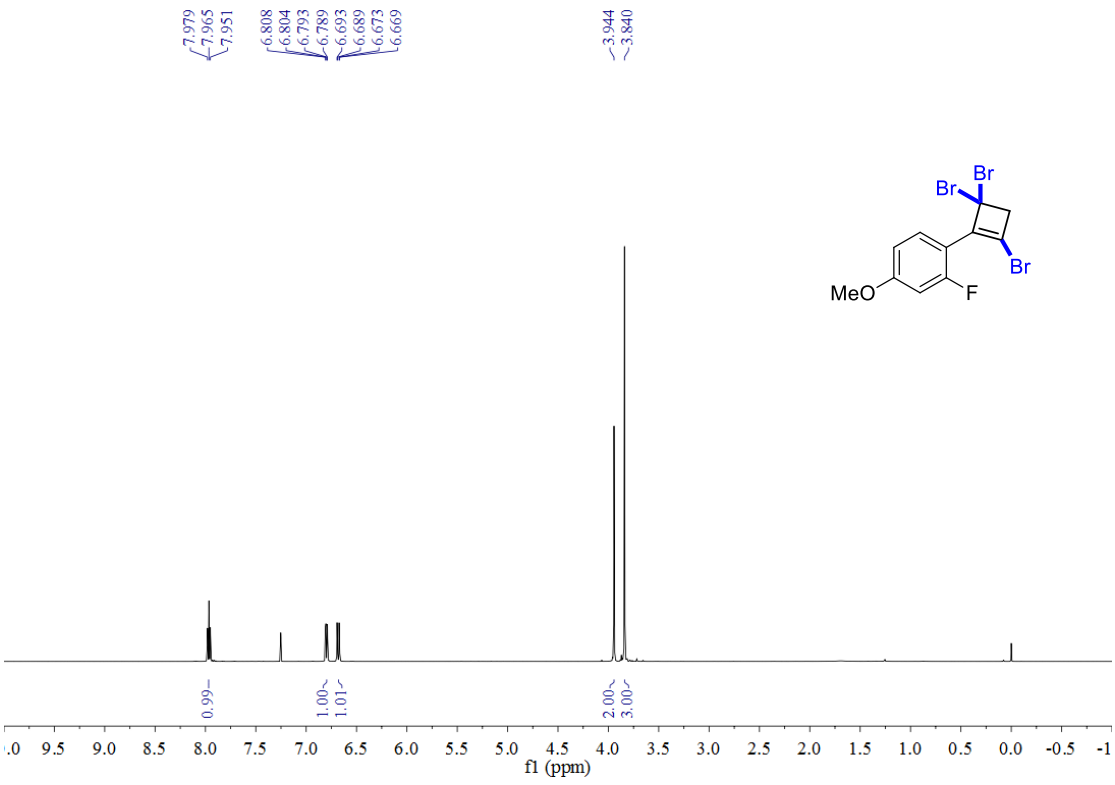


Figure S43. ^{1}H NMR and ^{13}C NMR spectra of compound **7f**.



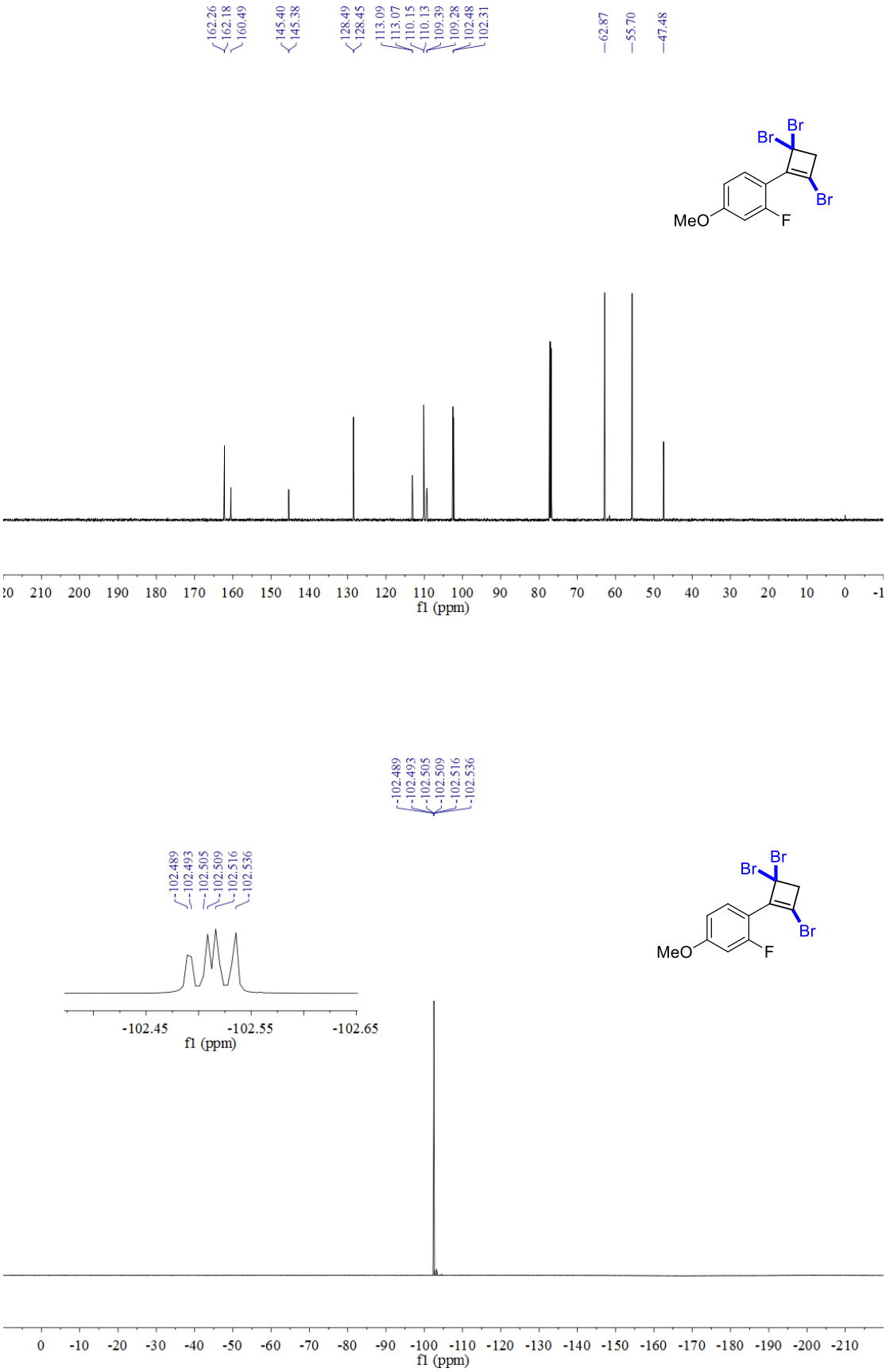


Figure S44. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **7g**.

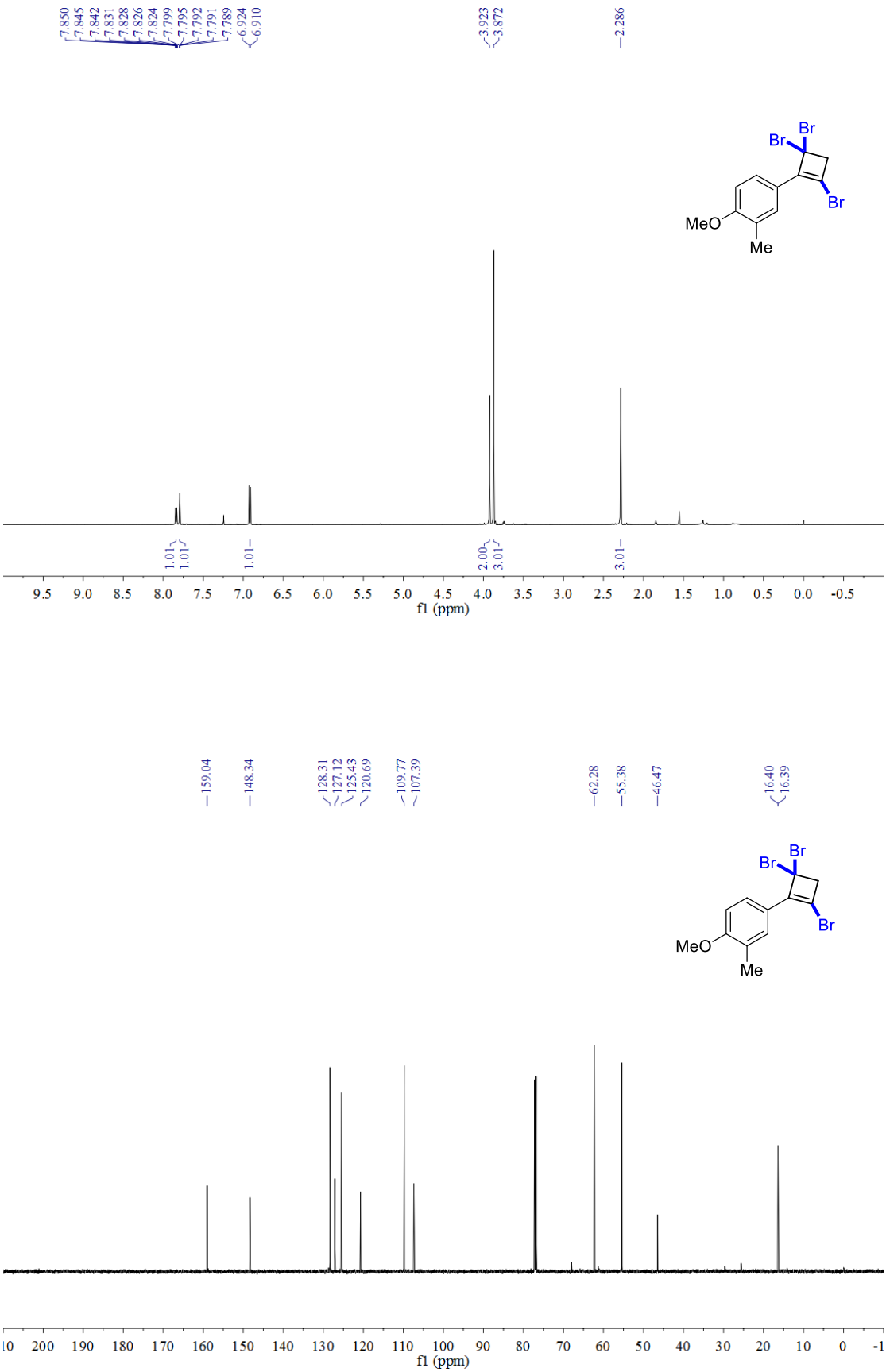
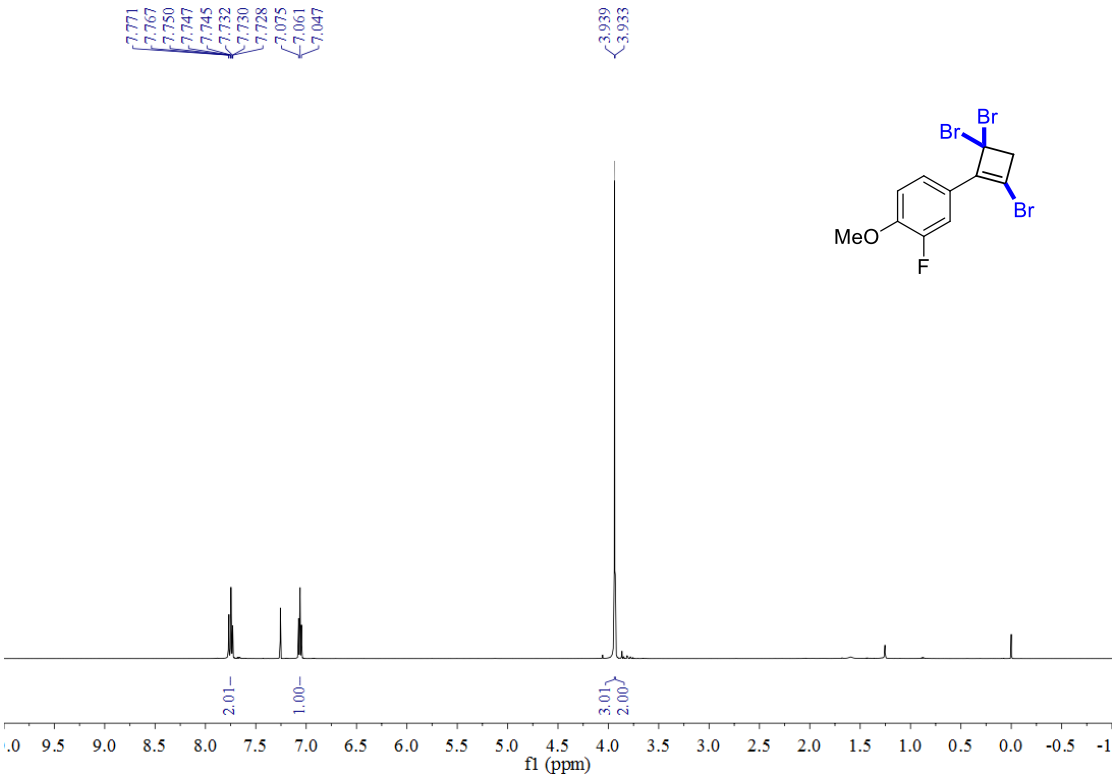
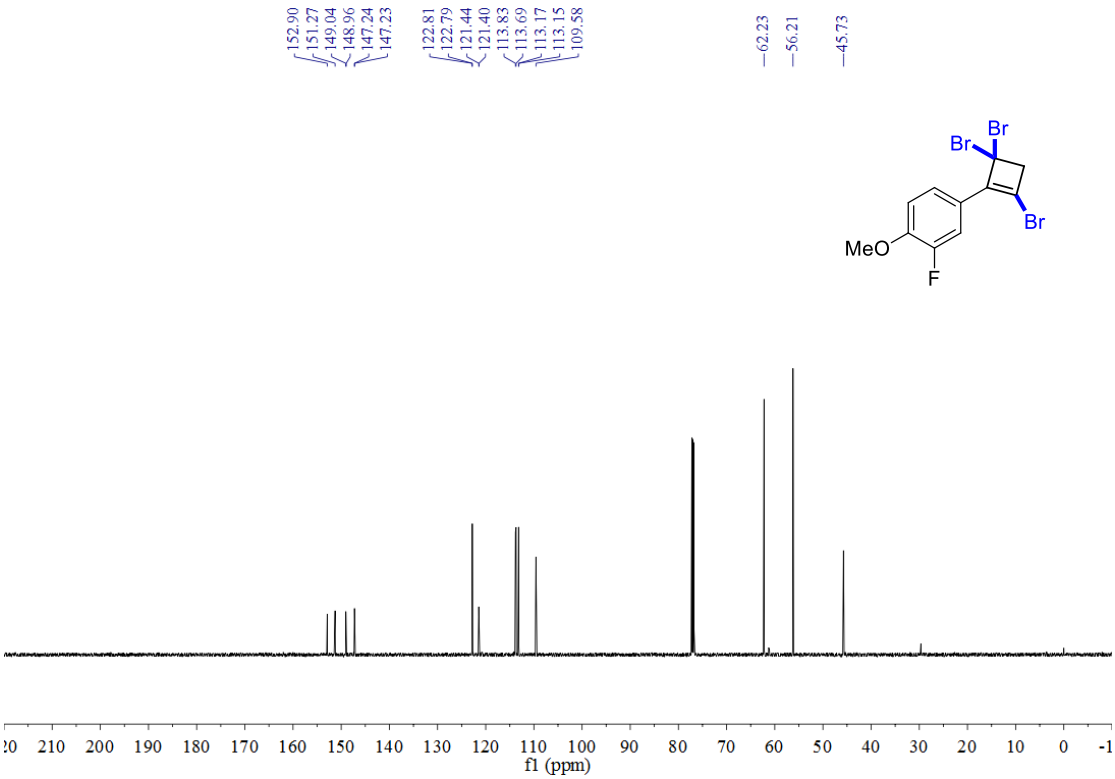


Figure S45. ^{1}H NMR and ^{13}C NMR spectra of compound **7h**.


7.771
7.767
7.750
7.747
7.745
7.732
7.730
7.728
7.075
7.061
7.047
3.939
3.933
Br
Br
Br
MeO
F
2.01
1.00
3.01
2.00
f1 (ppm)


152.90
151.27
149.04
148.96
147.24
147.23
122.81
122.79
121.44
121.40
113.83
113.69
113.17
113.15
109.58
62.23
56.21
45.73
Br
Br
Br
MeO
F
f1 (ppm)

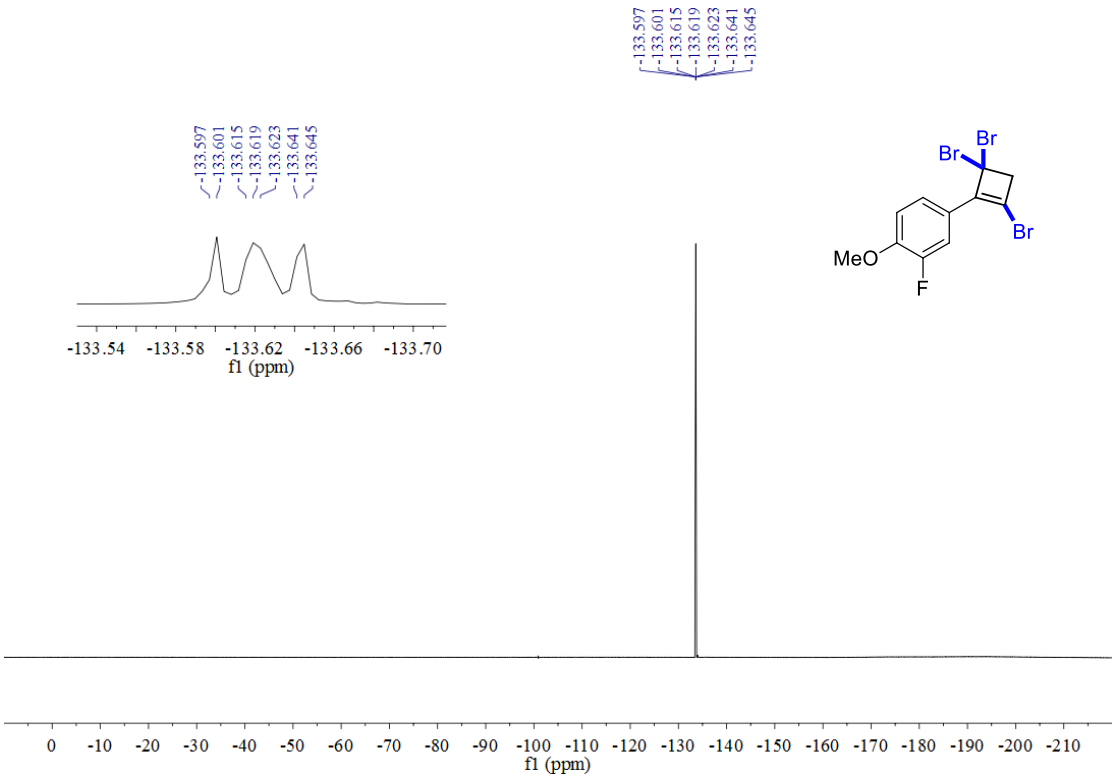
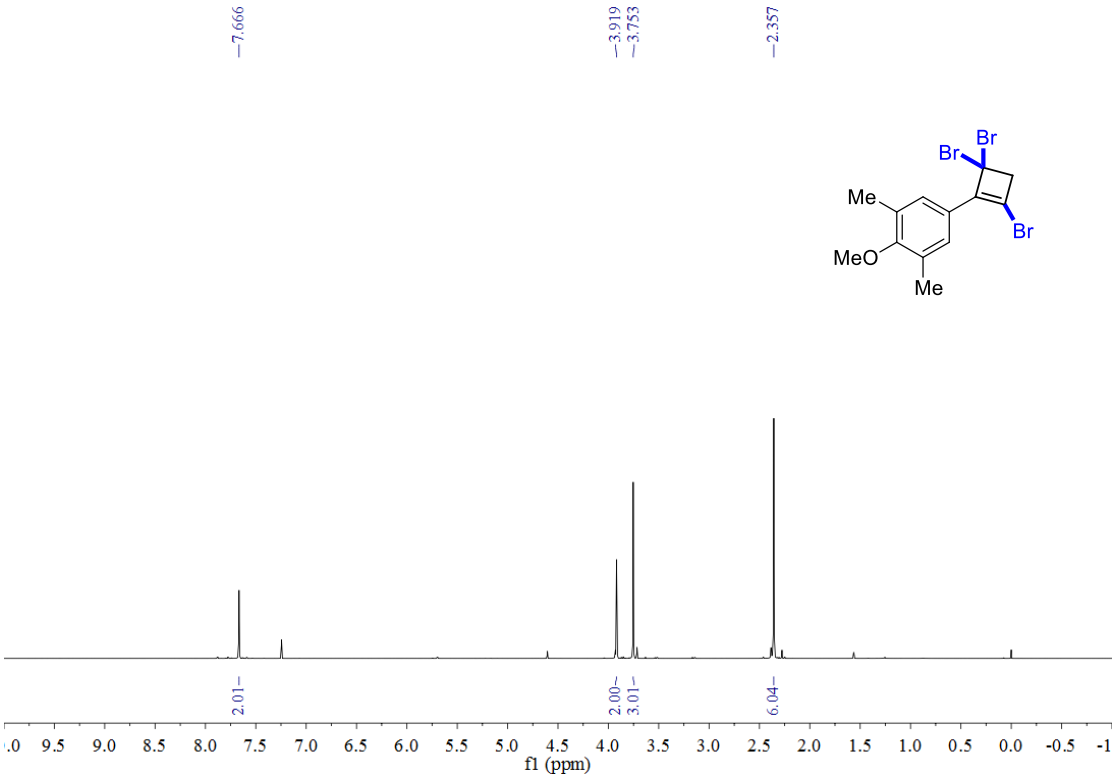


Figure S46. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **7i**.



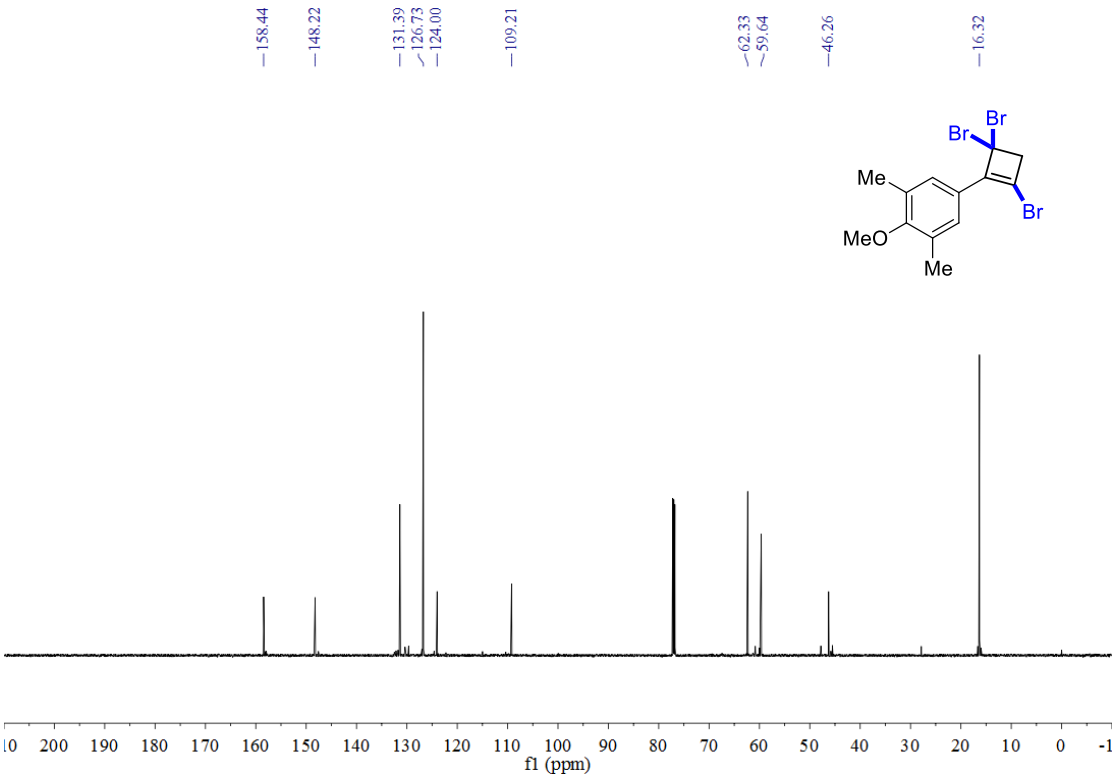
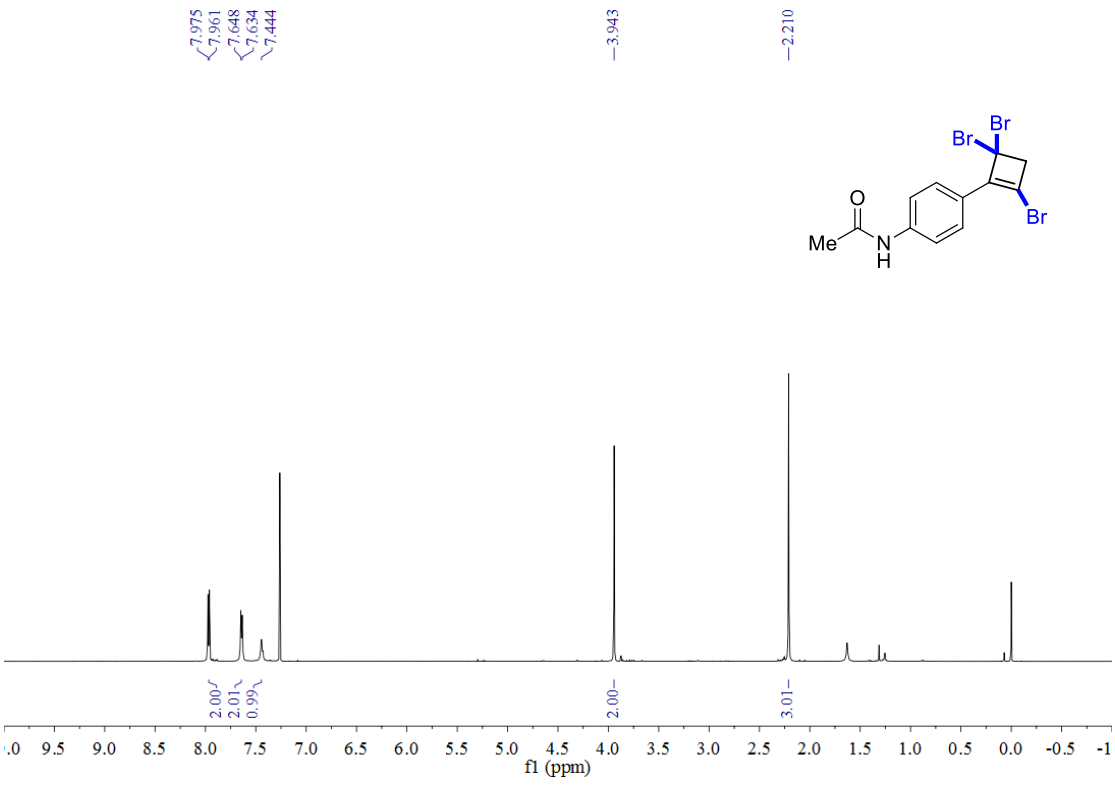


Figure S47. ^{1}H NMR and ^{13}C NMR spectra of compound **7j**.



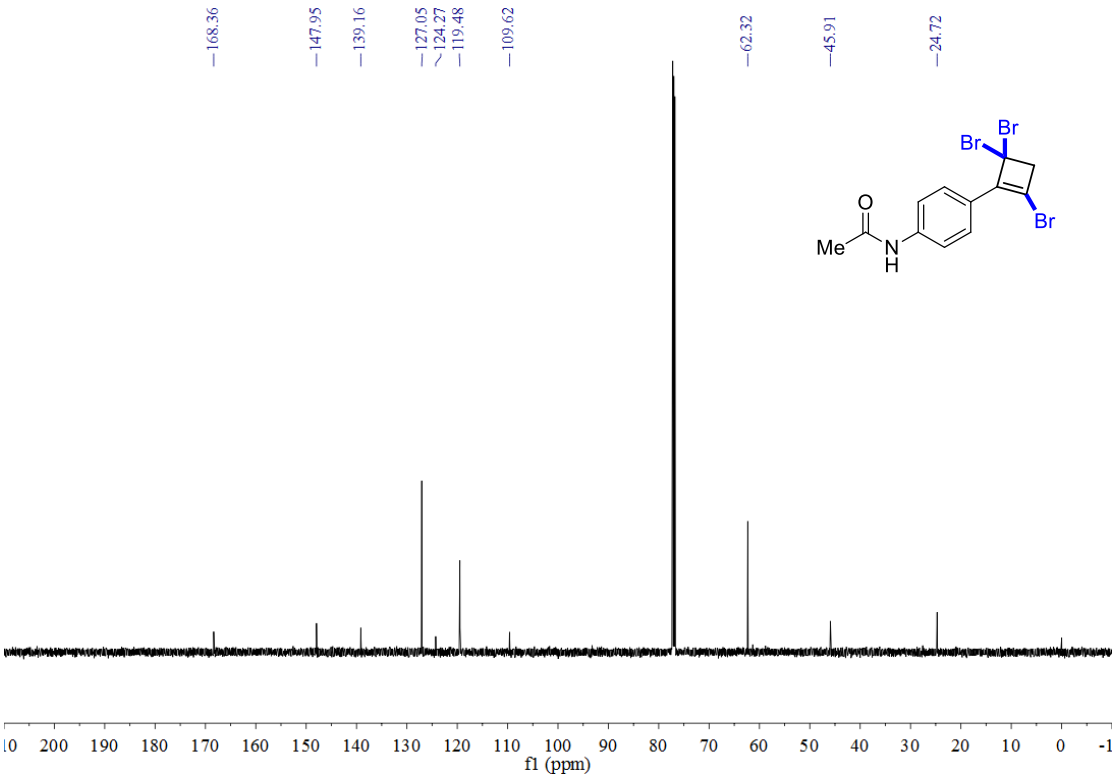
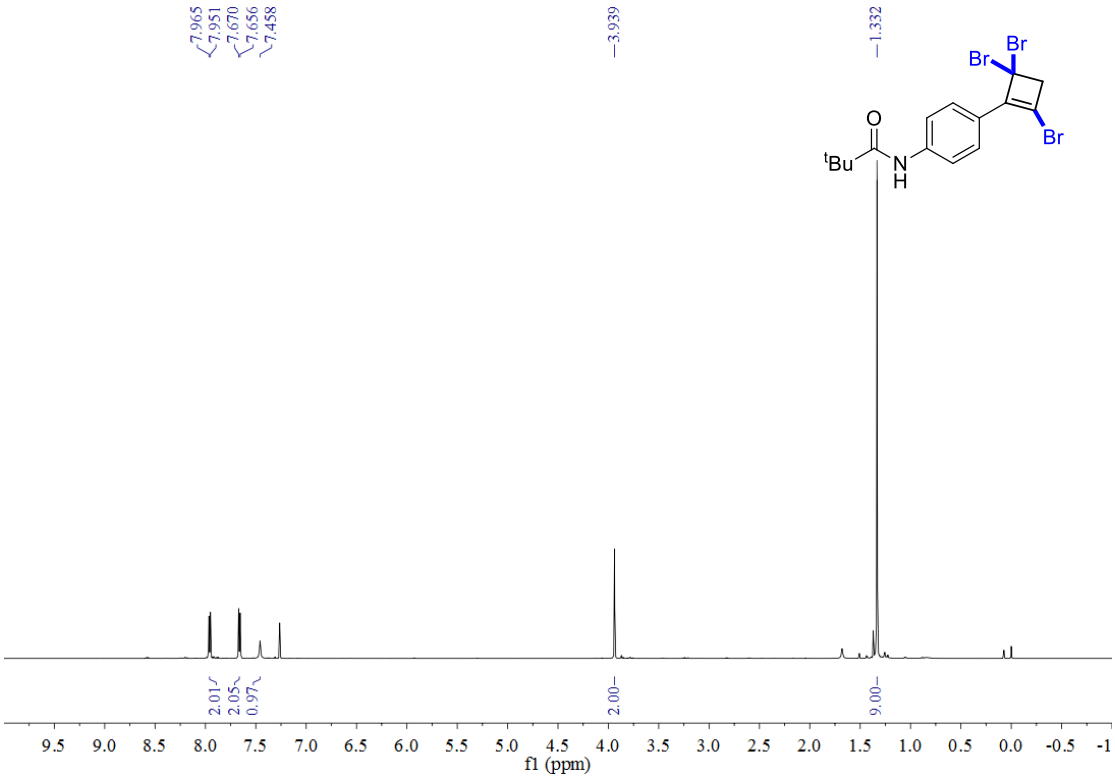


Figure S48. ^{1}H NMR and ^{13}C NMR spectra of compound **7k**.



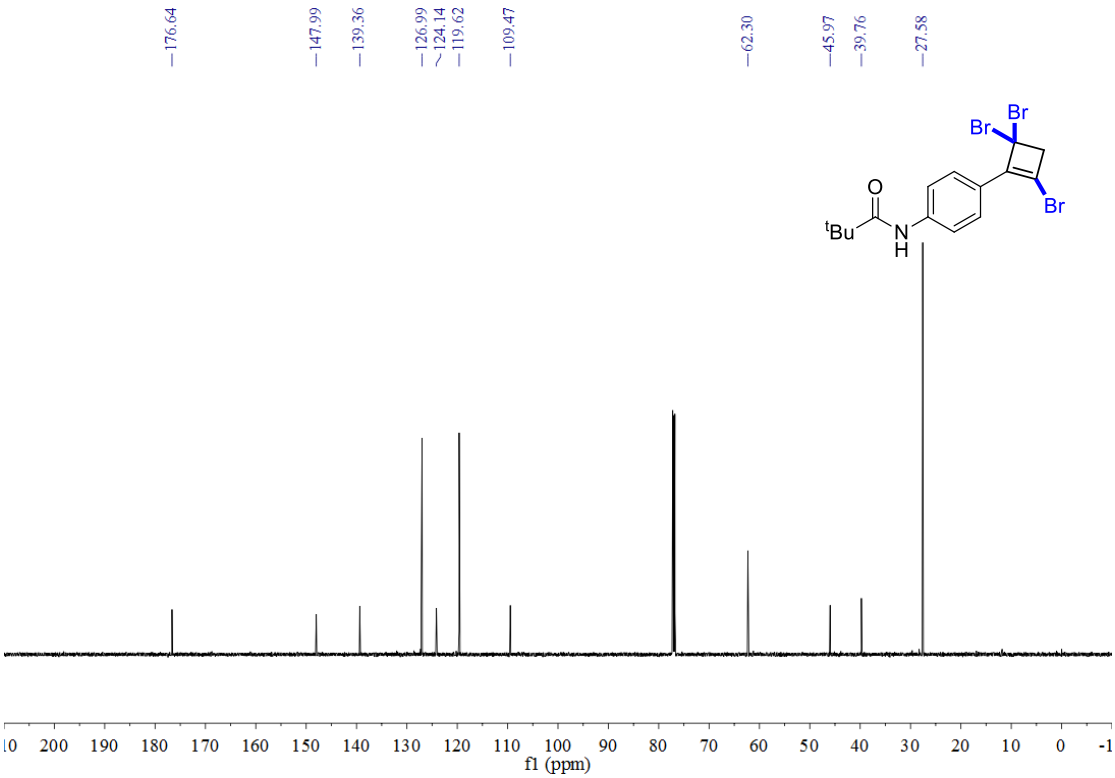
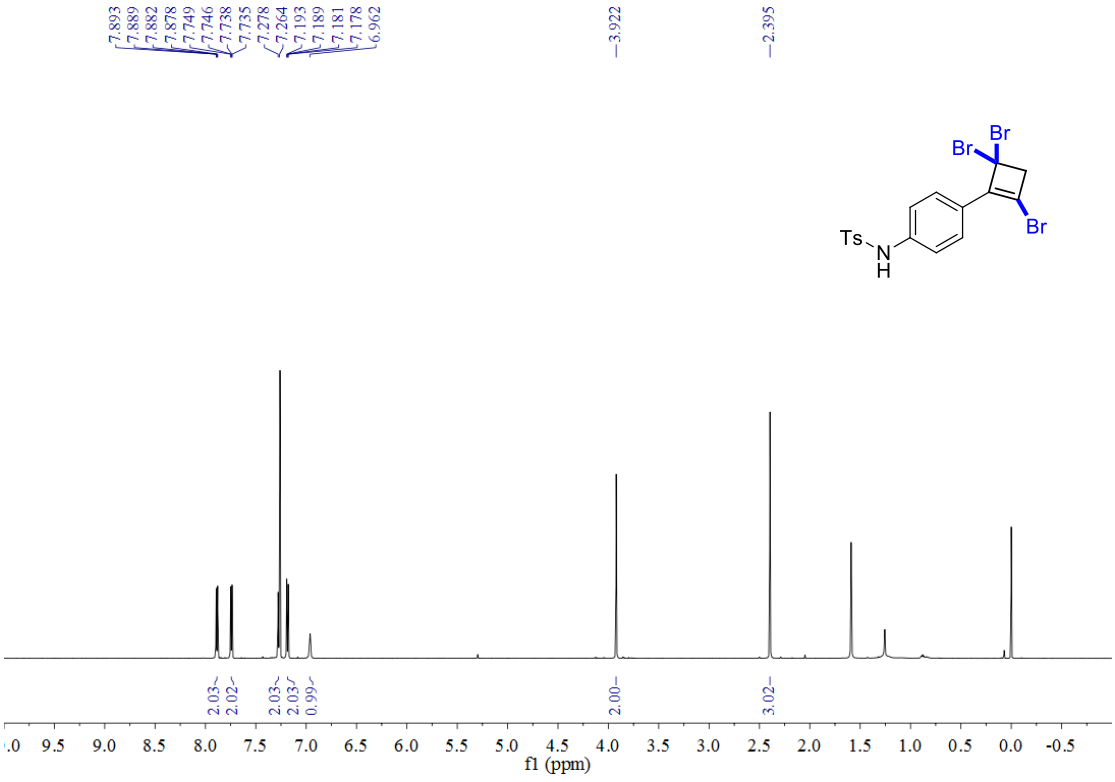


Figure S49. ^{1}H NMR and ^{13}C NMR spectra of compound **7l**.



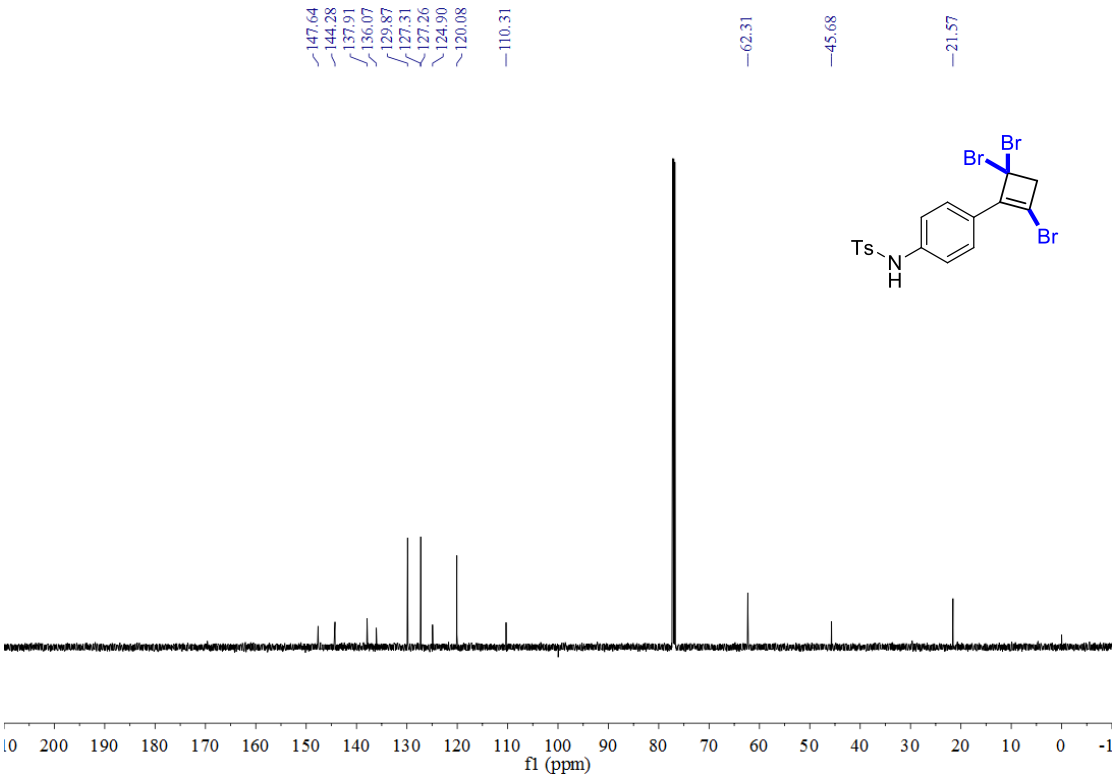
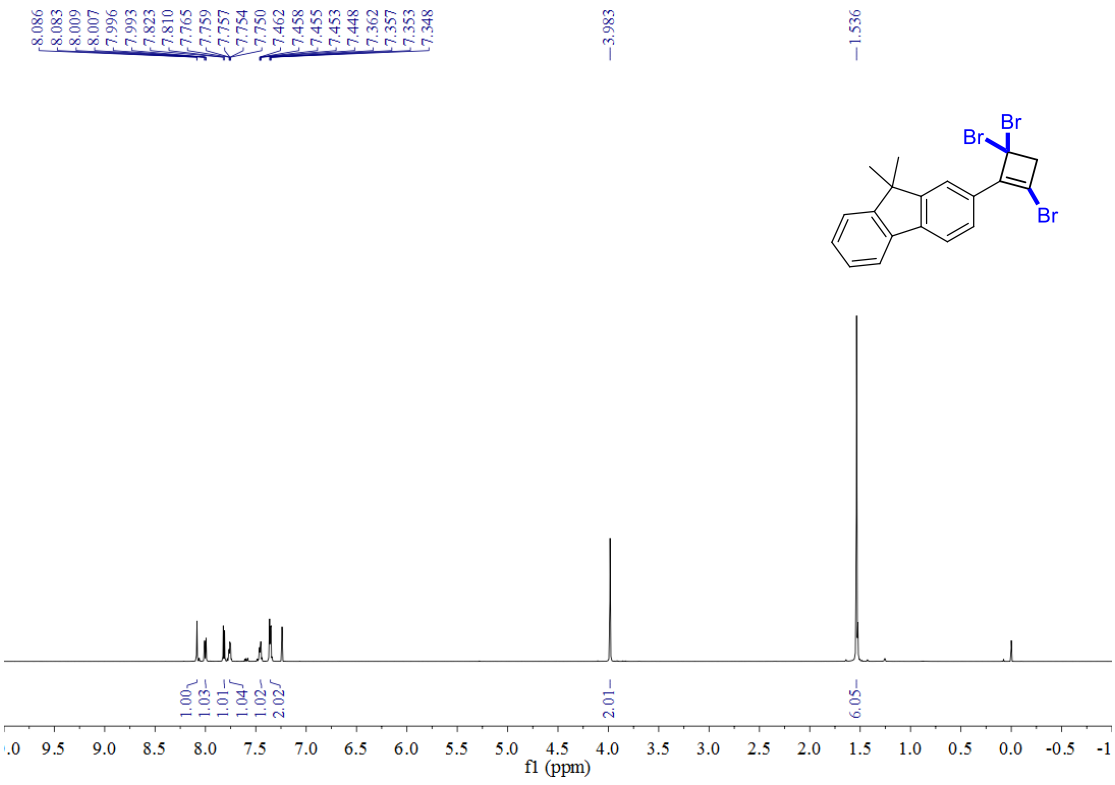


Figure S50. ^{1}H NMR and ^{13}C NMR spectra of compound **7m**.



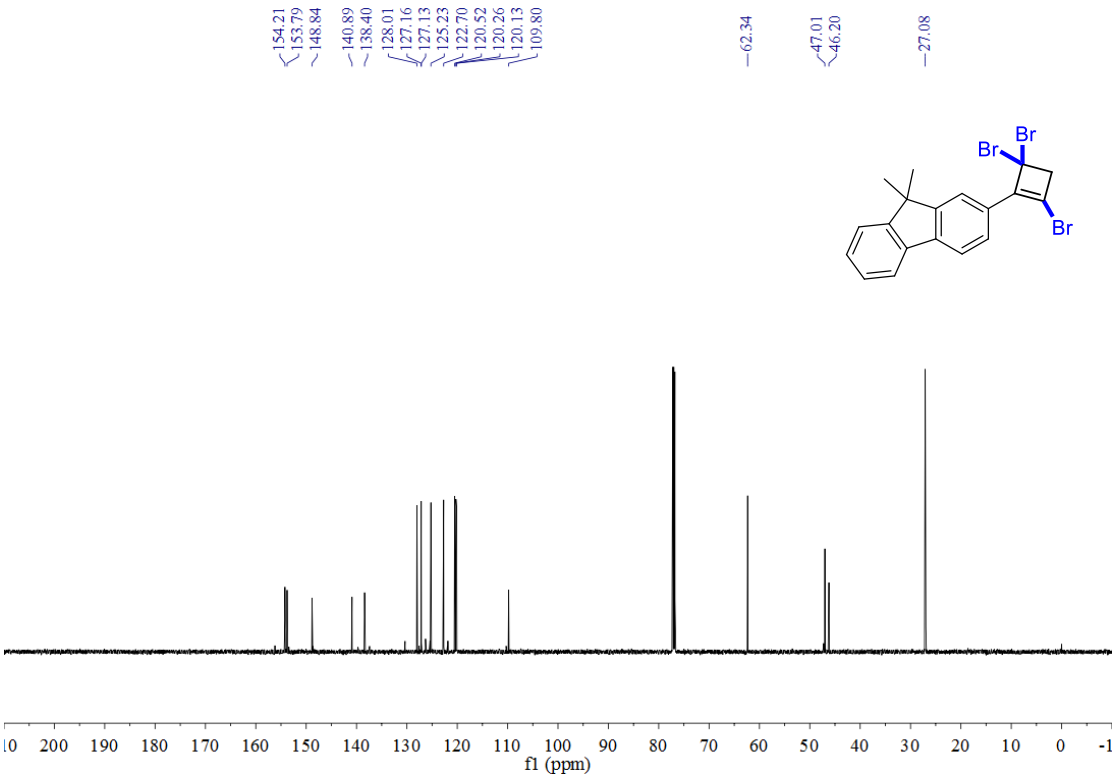
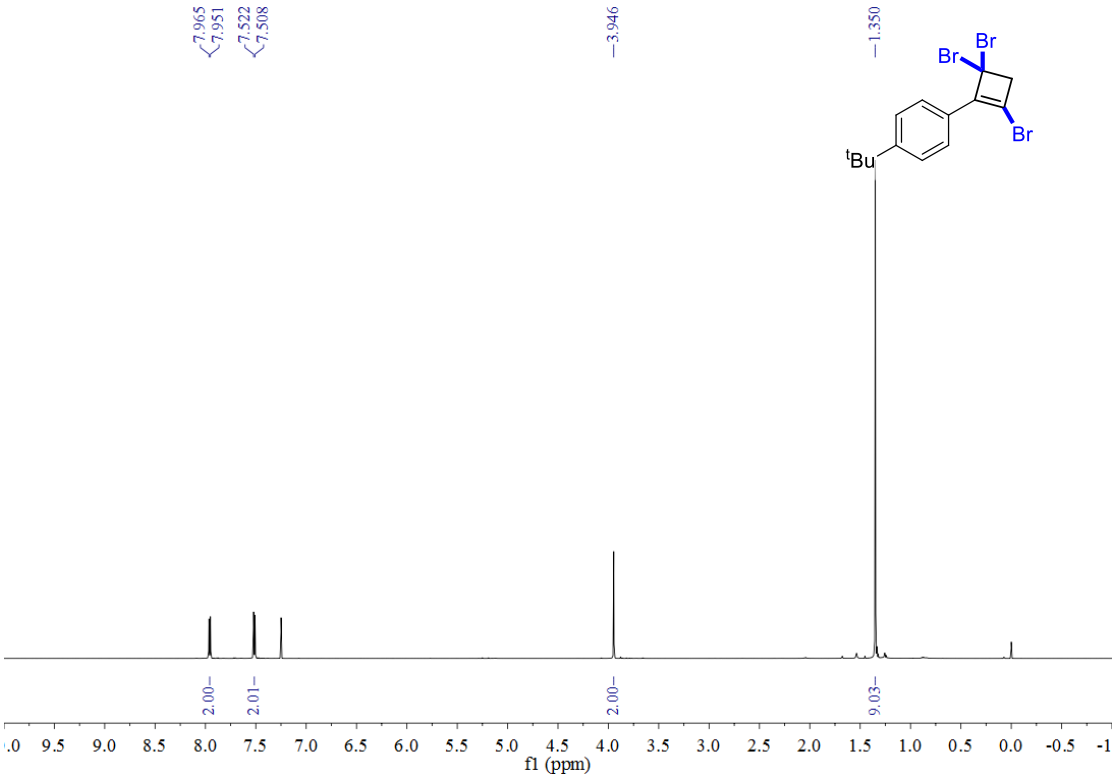


Figure S51. ^{1}H NMR and ^{13}C NMR spectra of compound **7n**.



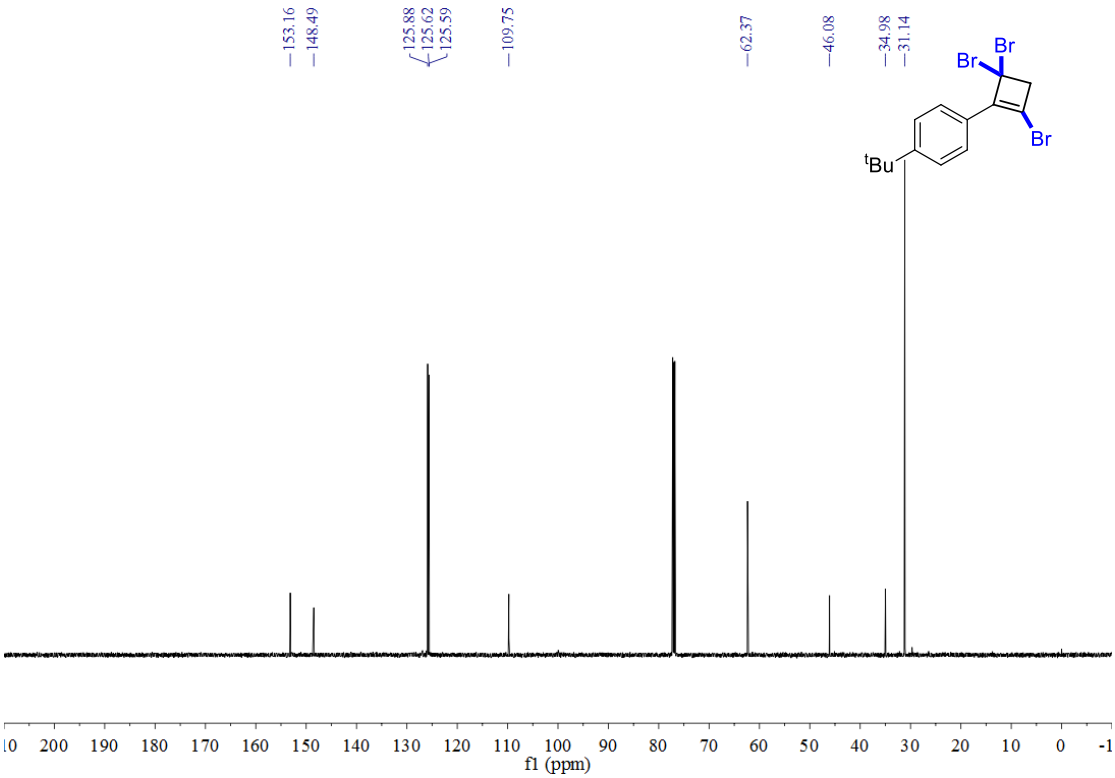
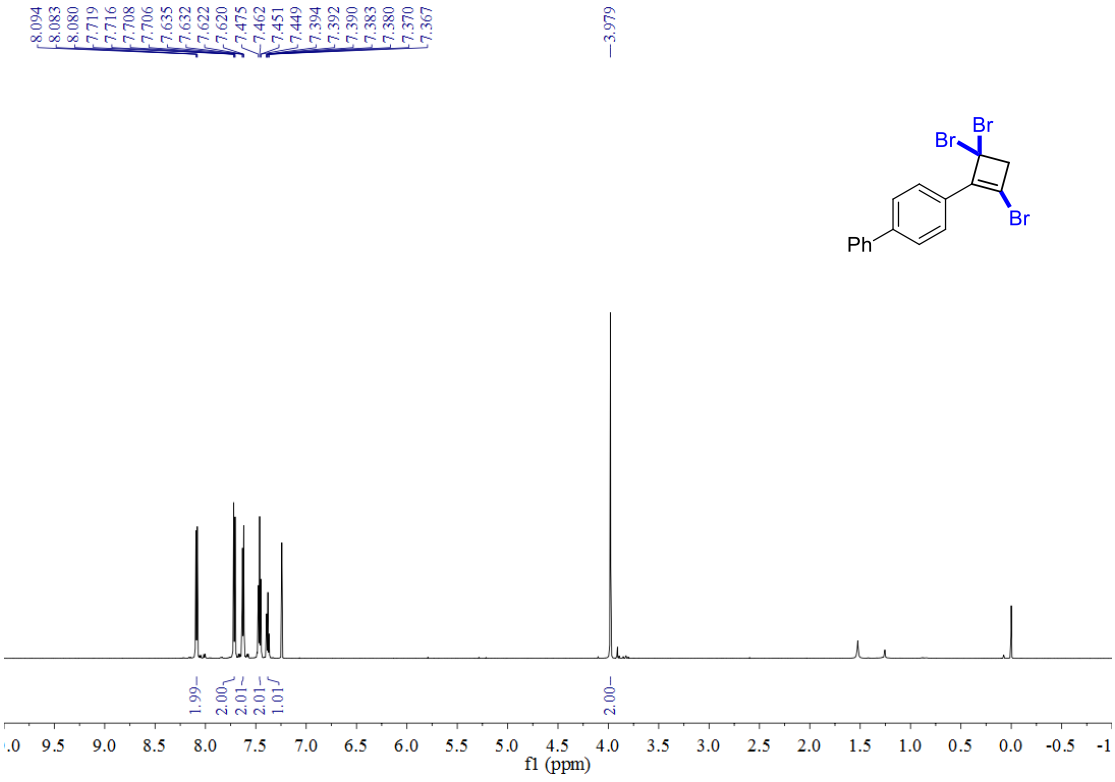


Figure S52. ^{1}H NMR and ^{13}C NMR spectra of compound **7o**.



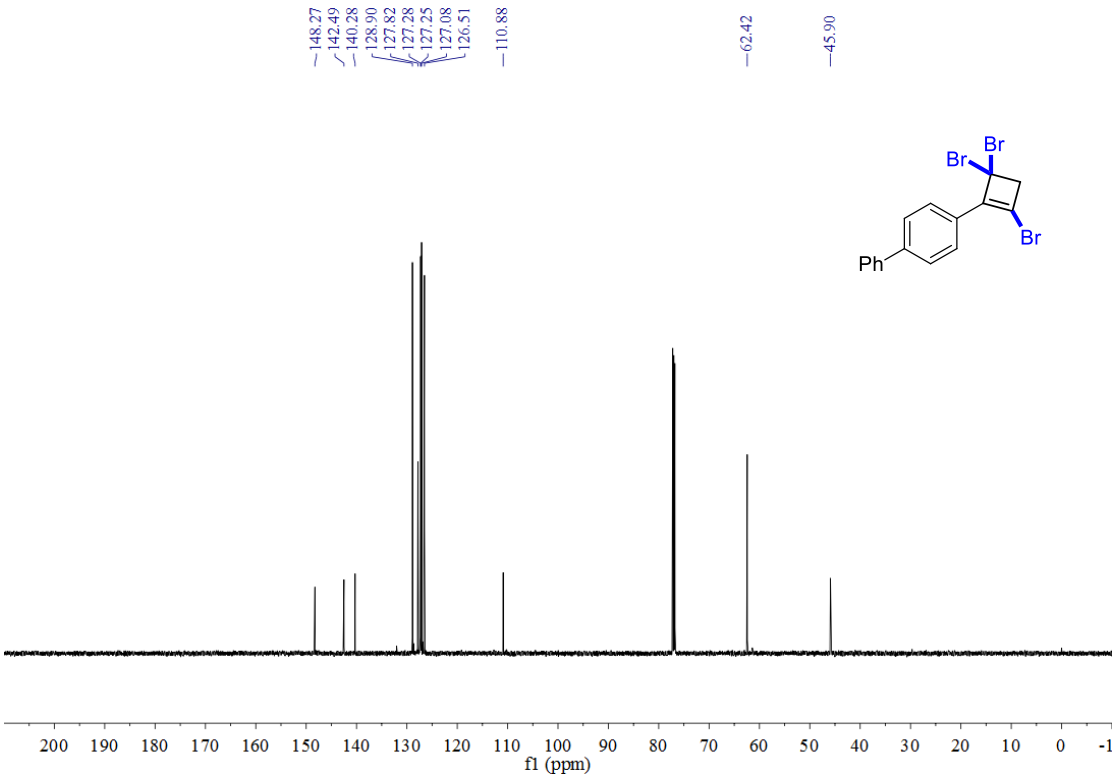
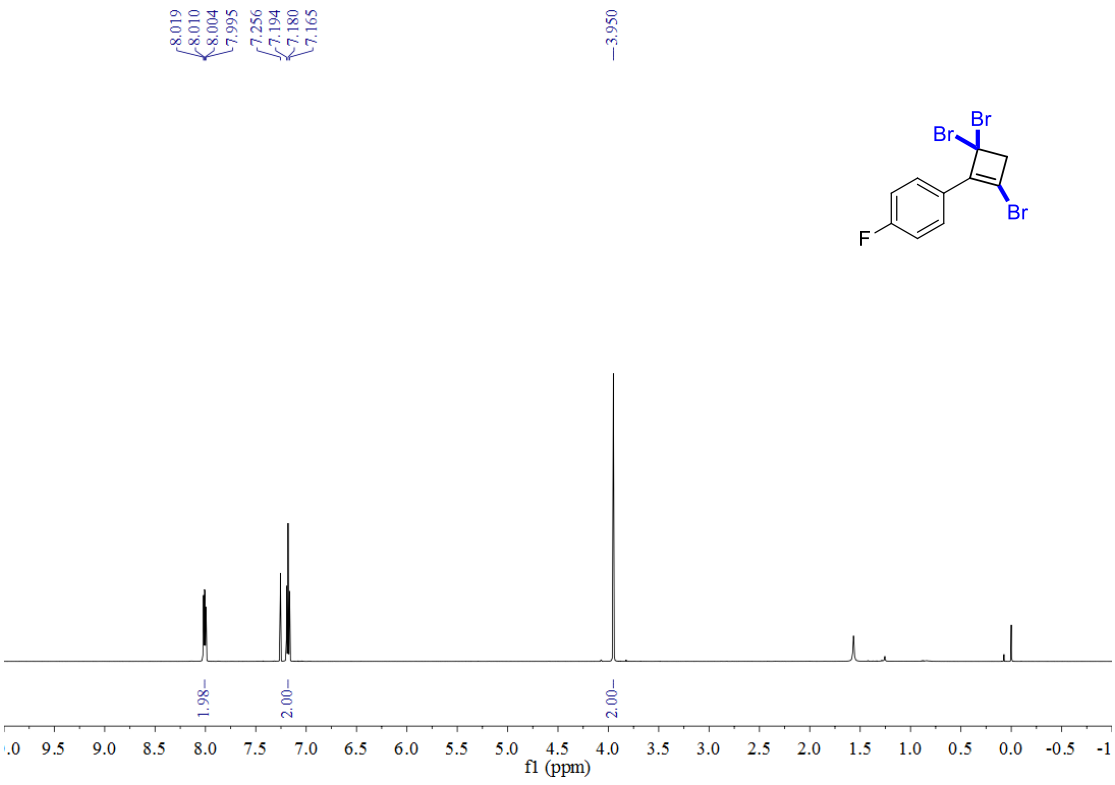


Figure S53. ^{1}H NMR and ^{13}C NMR spectra of compound **7p**.



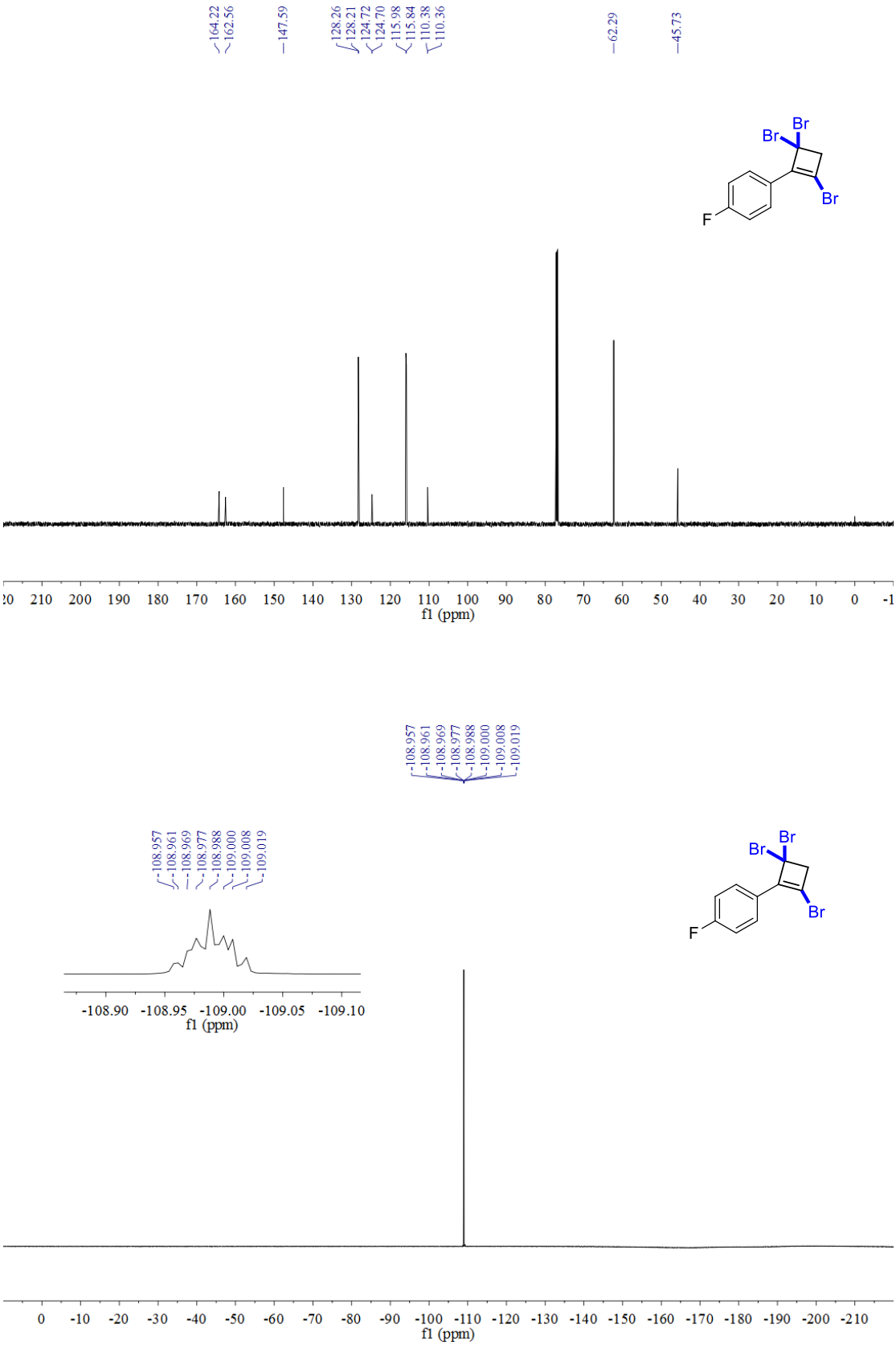


Figure S54. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **7q**.

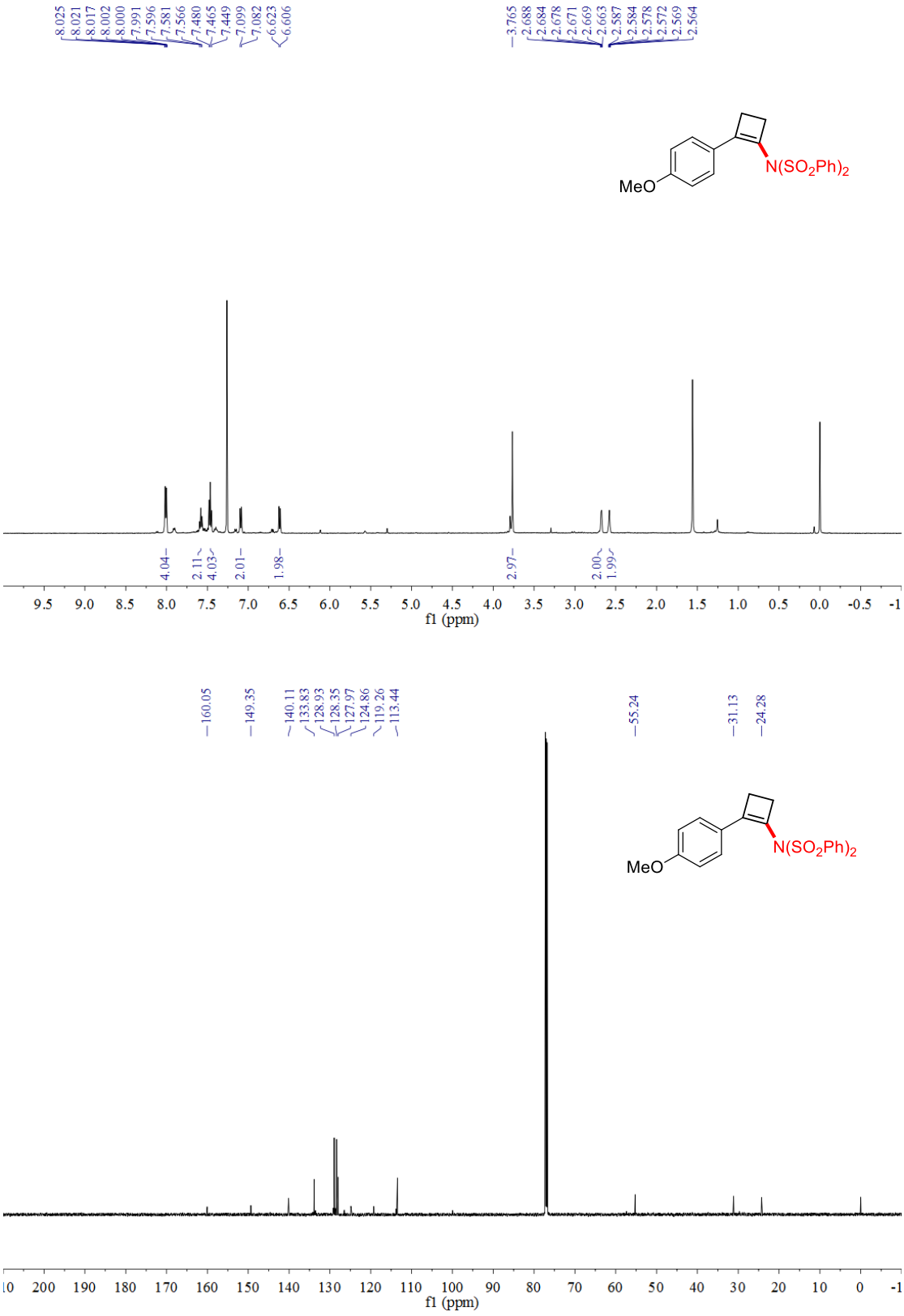


Figure S55. ^{1}H NMR and ^{13}C NMR spectra of compound **3**.

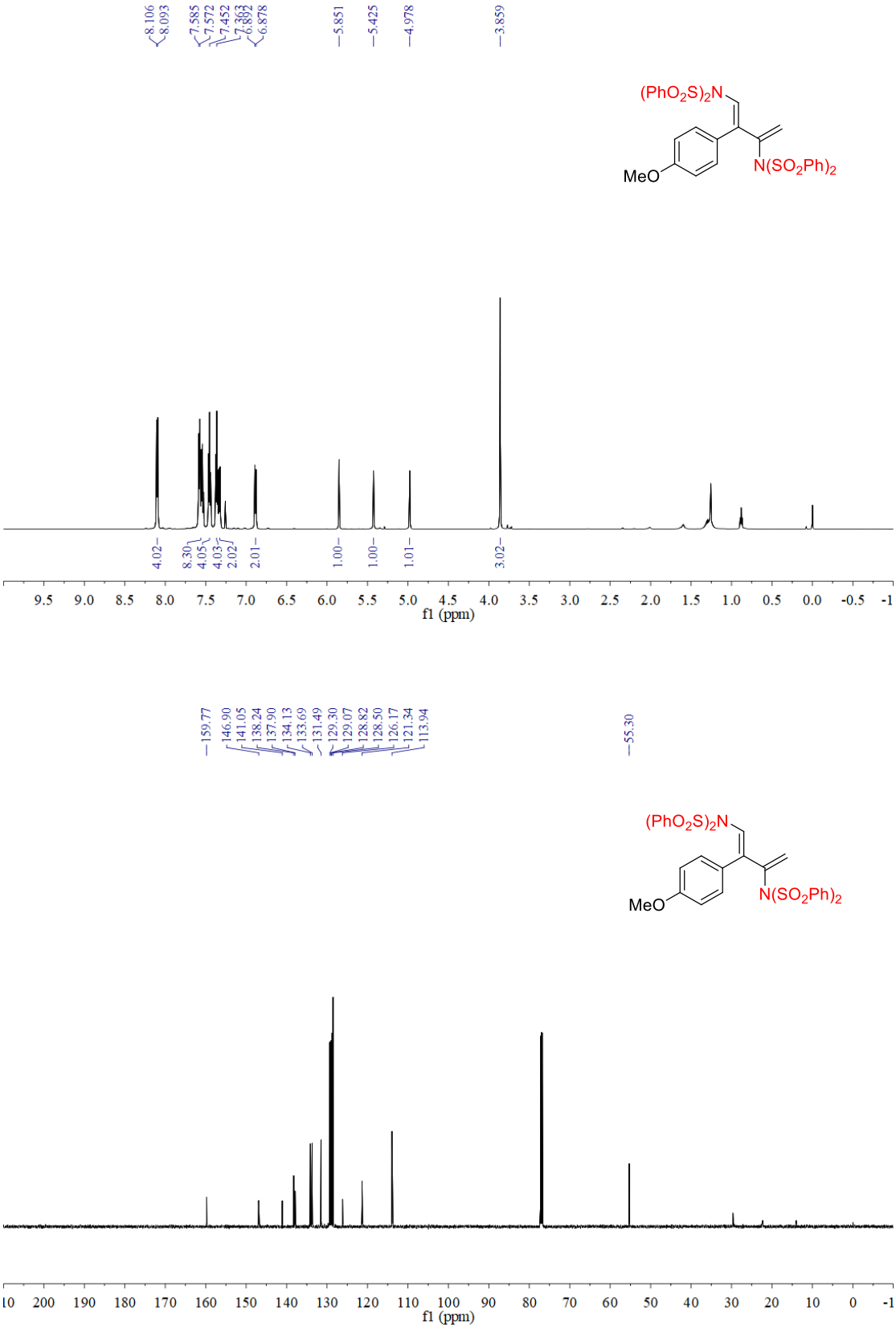


Figure S56. ^{1}H NMR and ^{13}C NMR spectra of compound **4**.

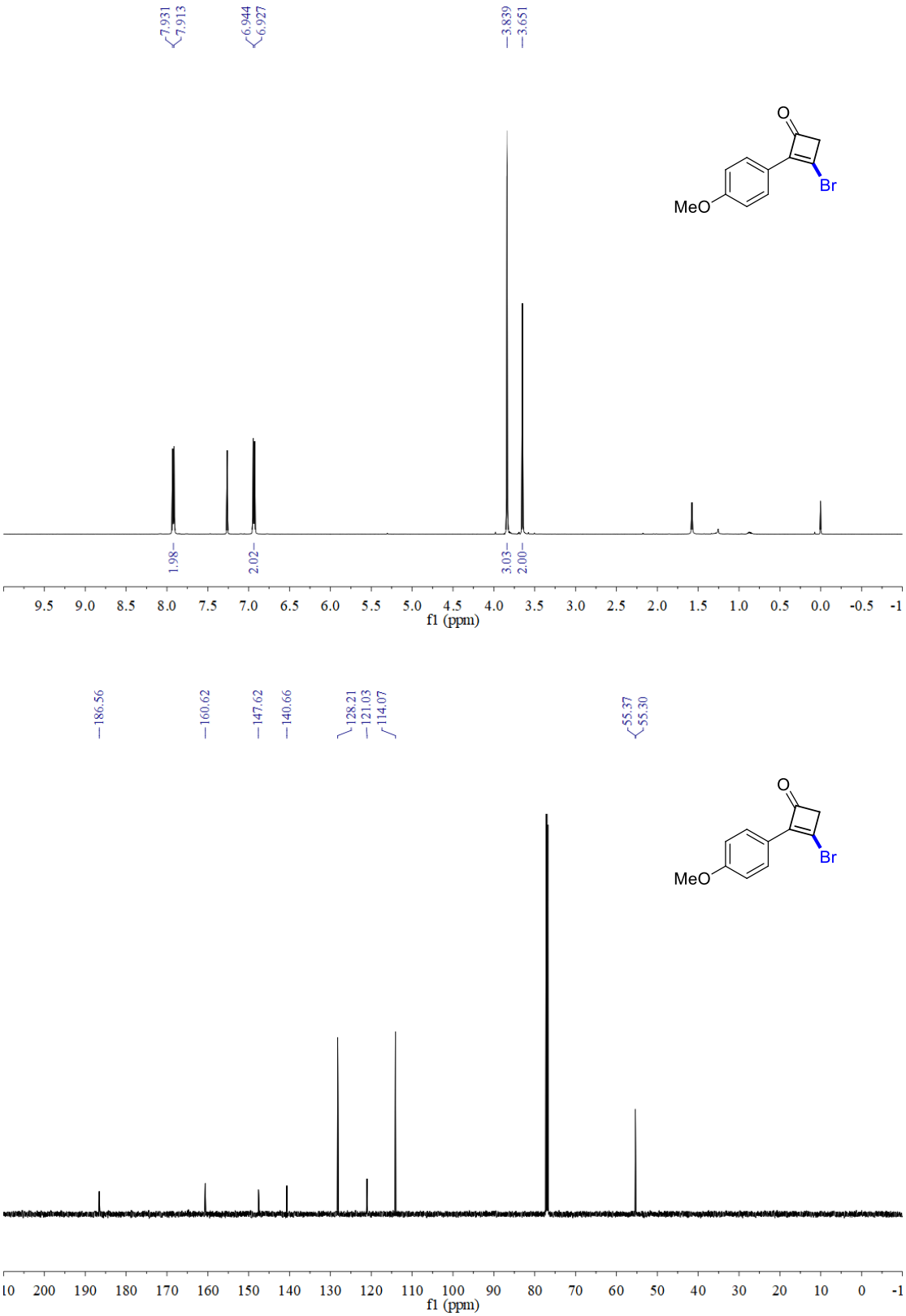


Figure S57. ^{1}H NMR and ^{13}C NMR spectra of compound **9**.

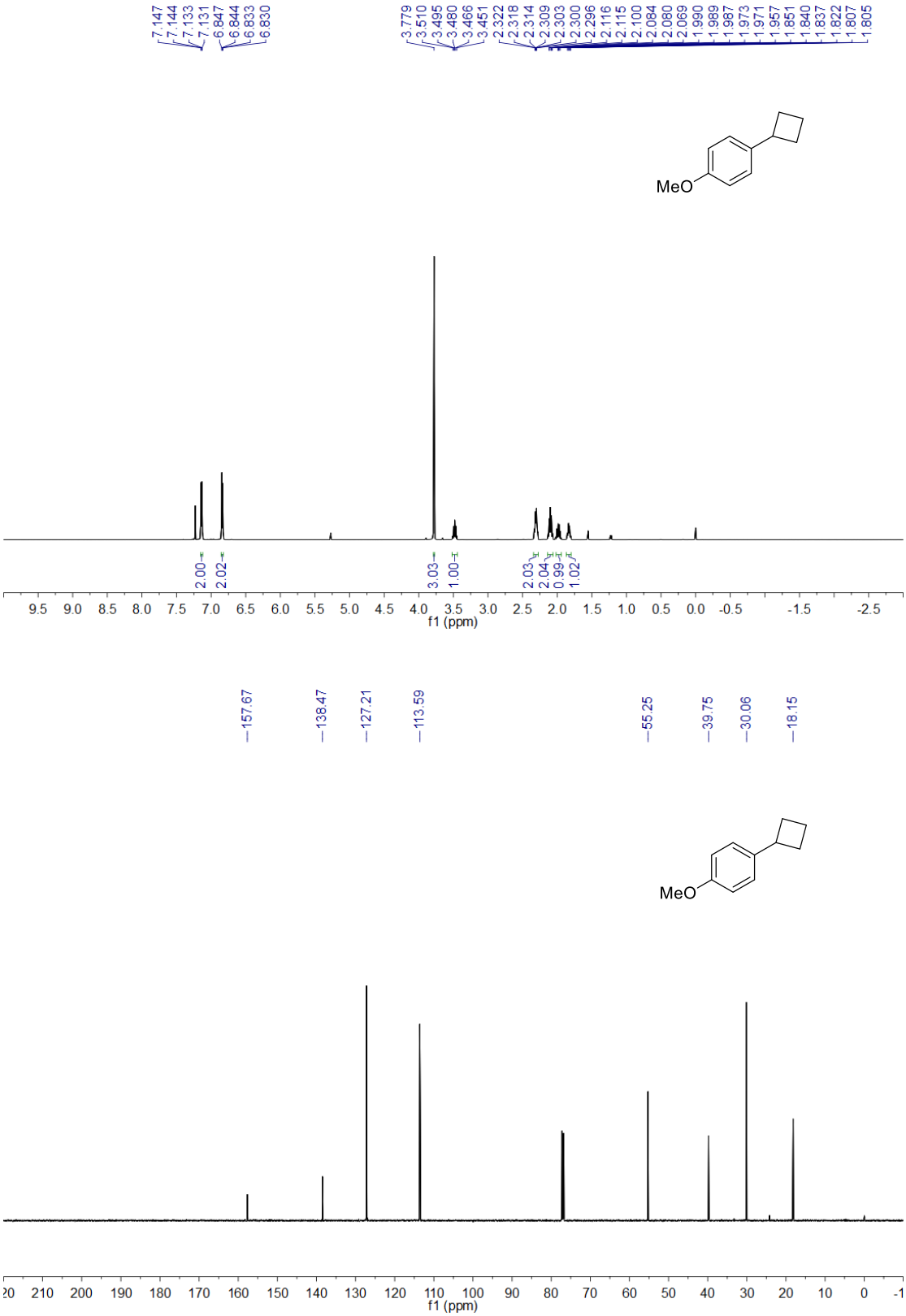


Figure S58. ^{1}H NMR and ^{13}C NMR spectra of compound **1a**.

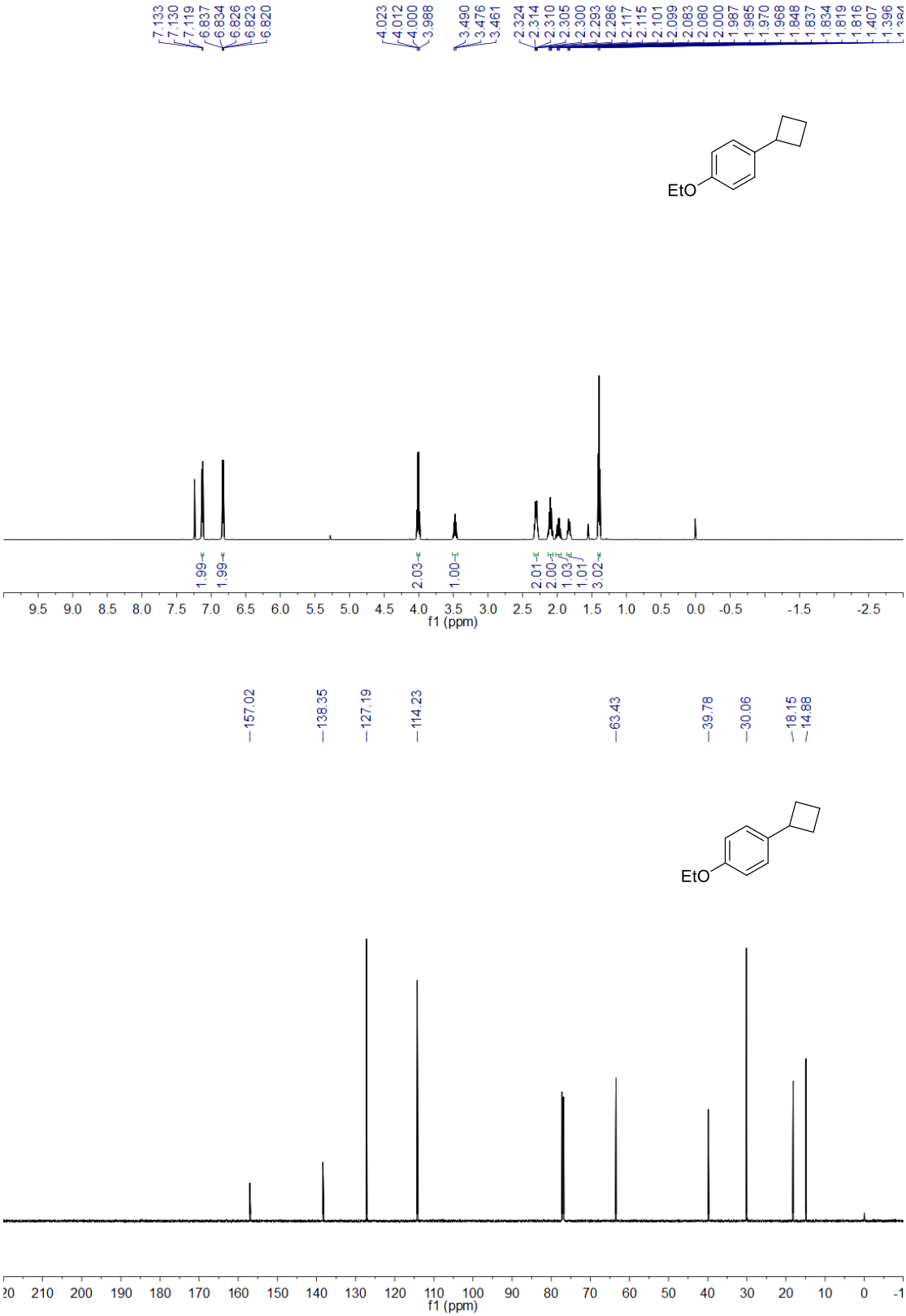


Figure S59. ^{1}H NMR and ^{13}C NMR spectra of compound **1b**.

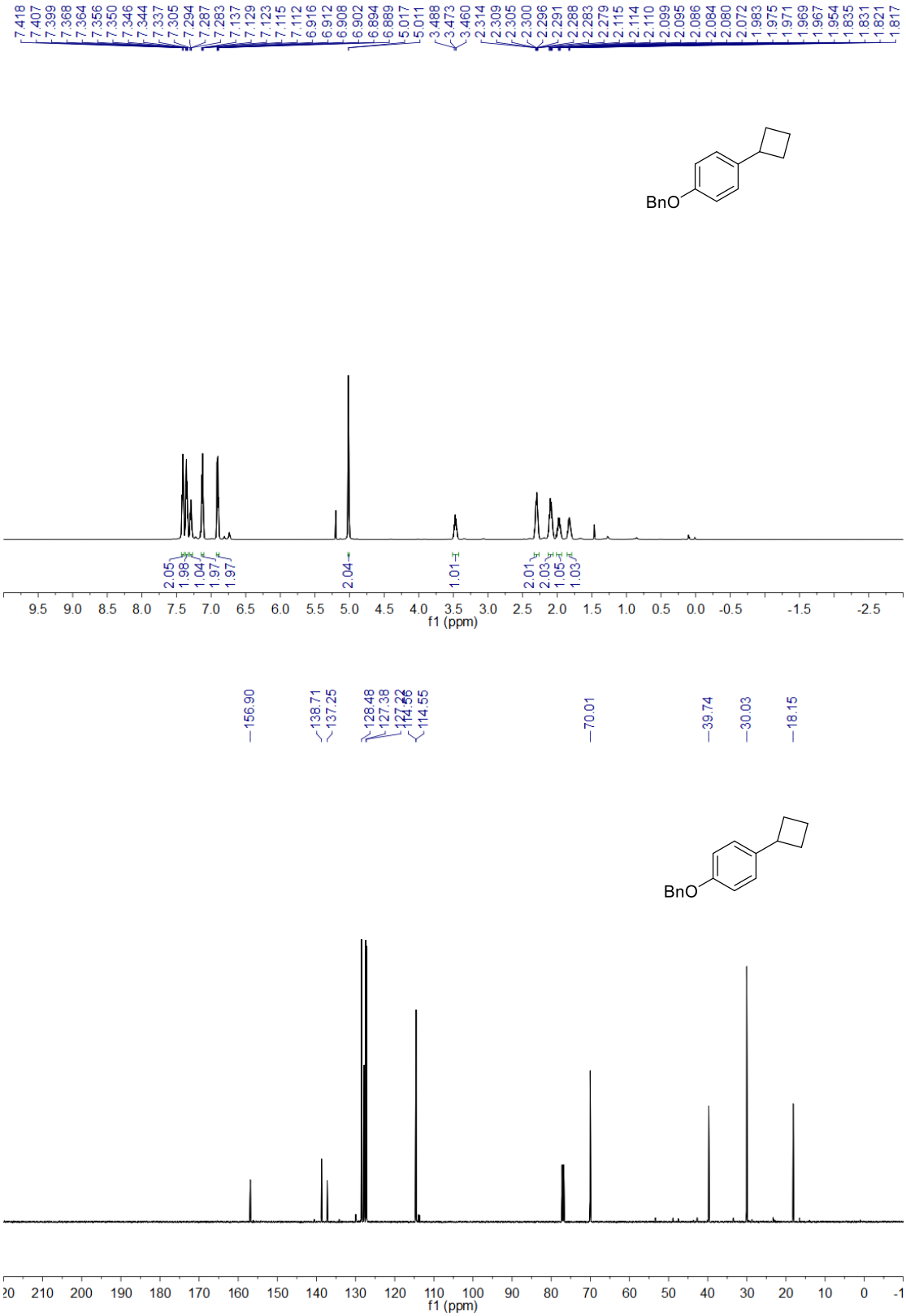


Figure S60. ^{1}H NMR and ^{13}C NMR spectra of compound **1c**.

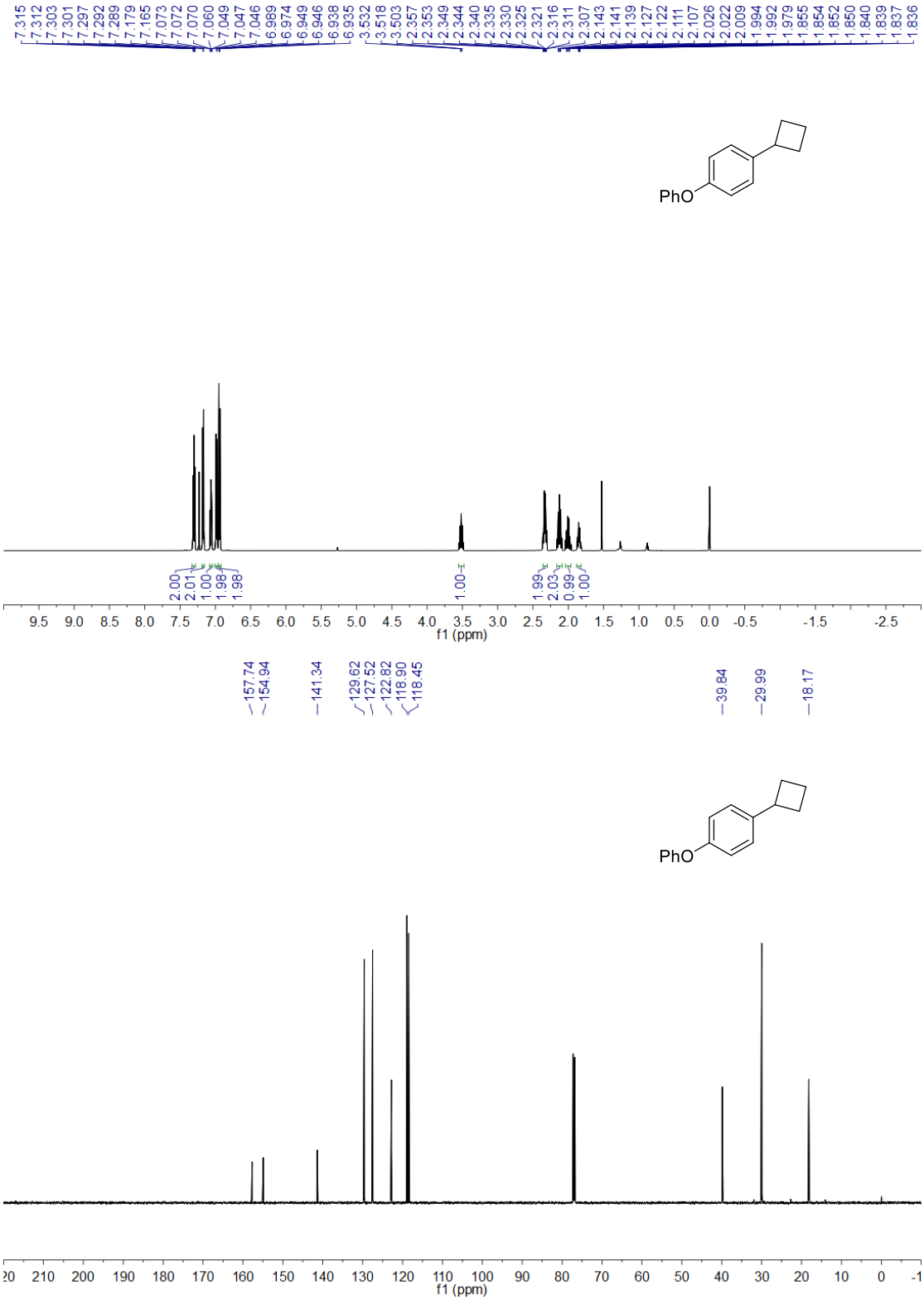


Figure S61. ^{1}H NMR and ^{13}C NMR spectra of compound **1d**.

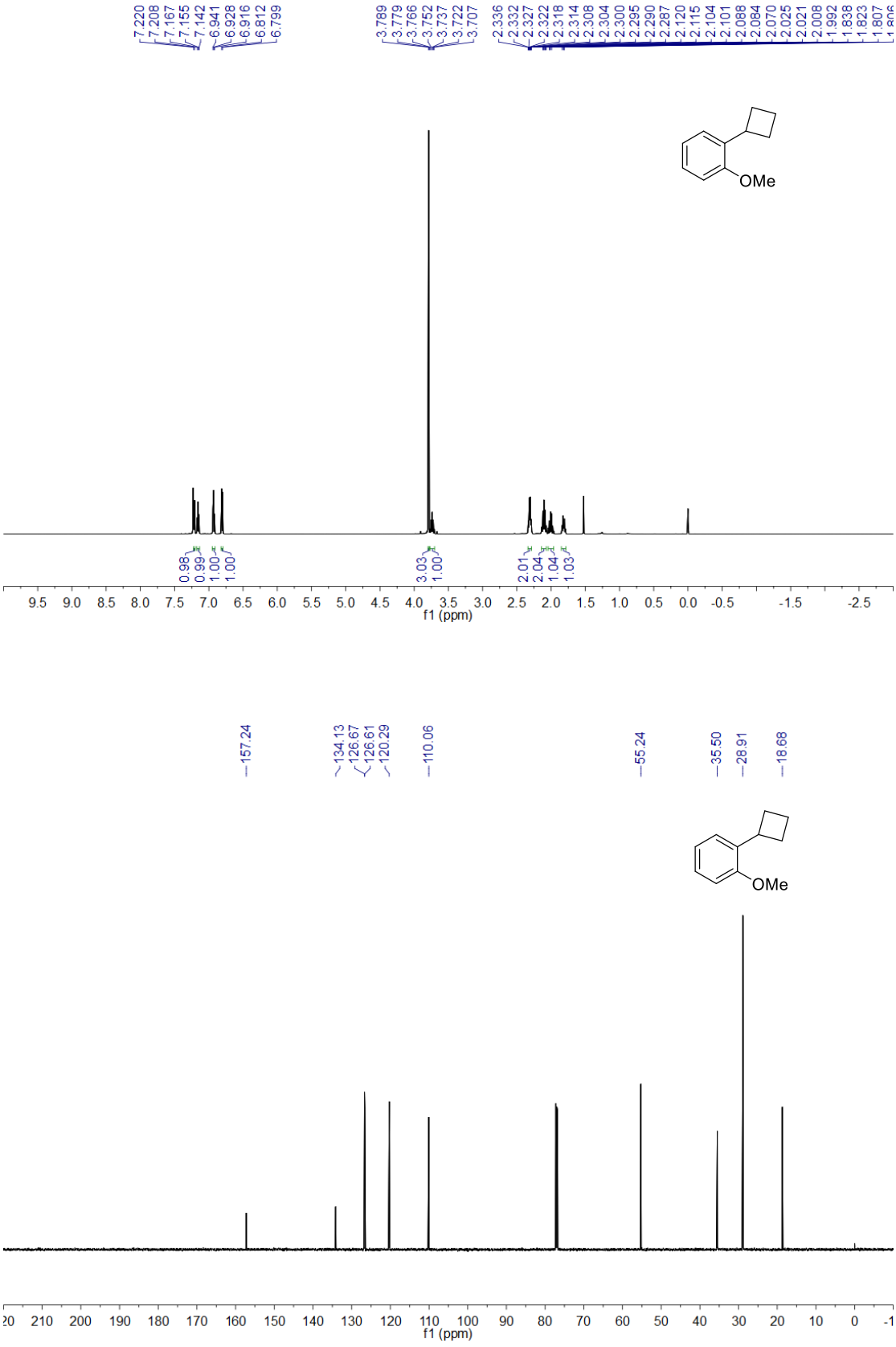


Figure S62. ^{1}H NMR and ^{13}C NMR spectra of compound **1e**.

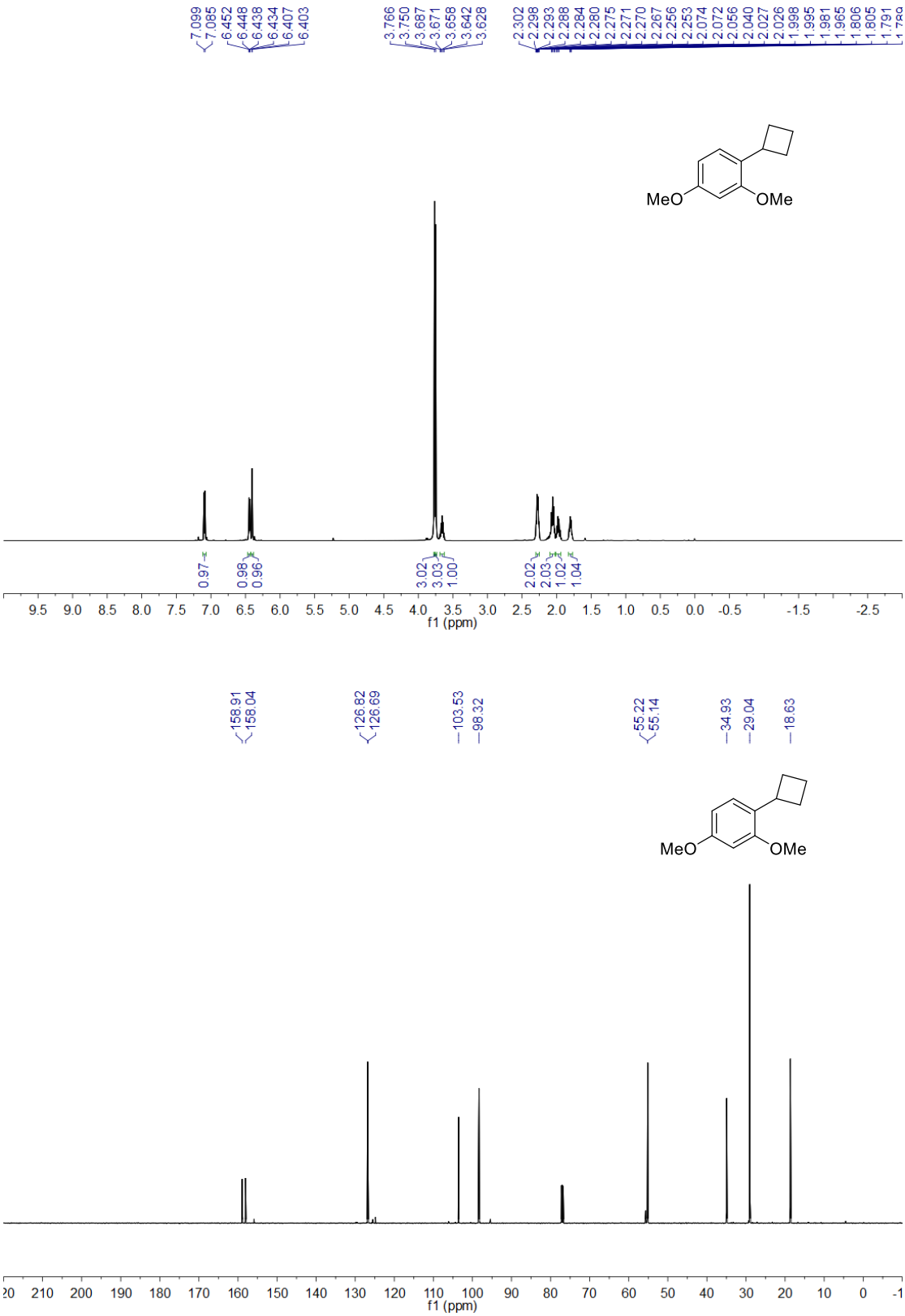


Figure S63. ^{1}H NMR and ^{13}C NMR spectra of compound **1f**.

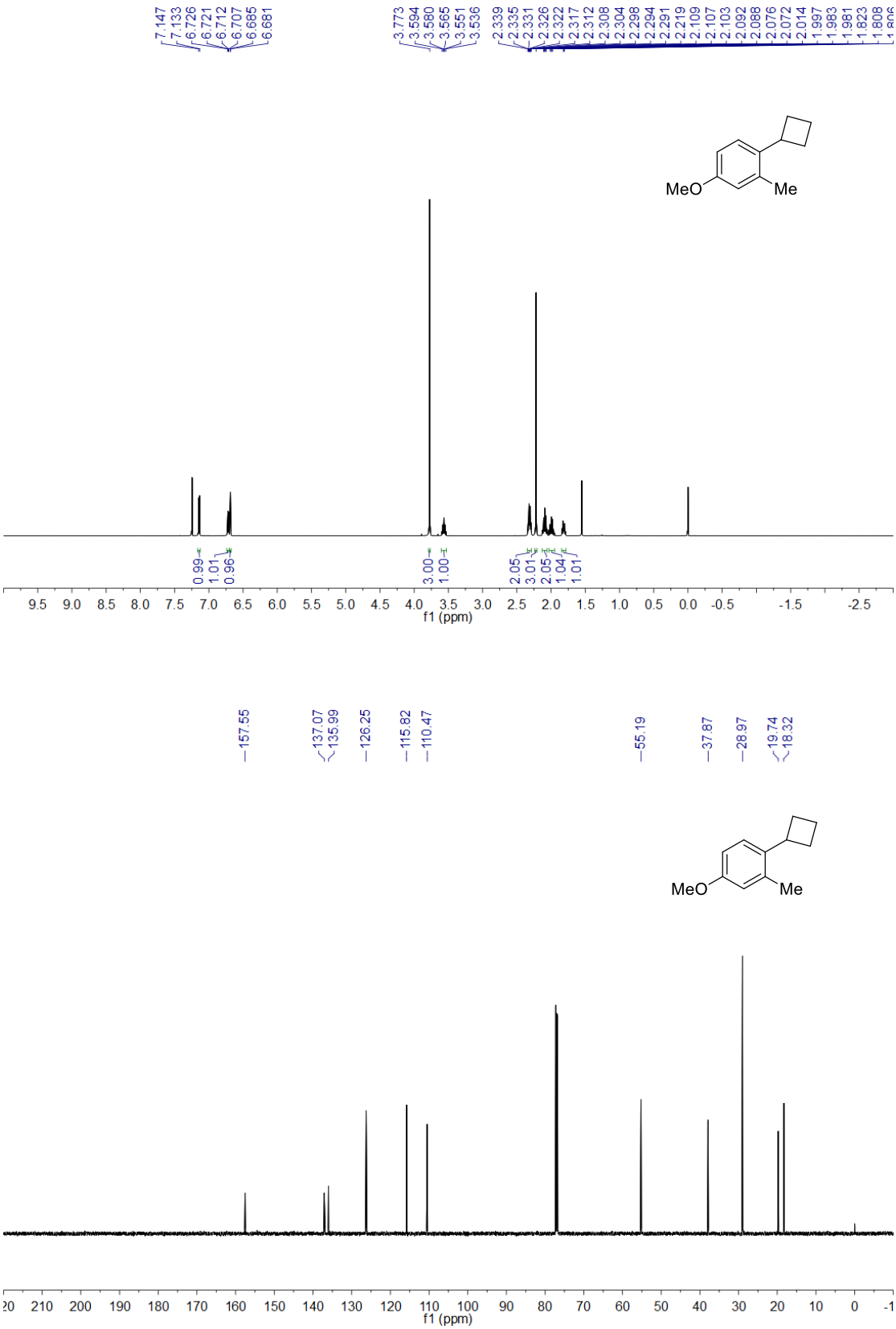


Figure S64. ^{1}H NMR and ^{13}C NMR spectra of compound **1g**.

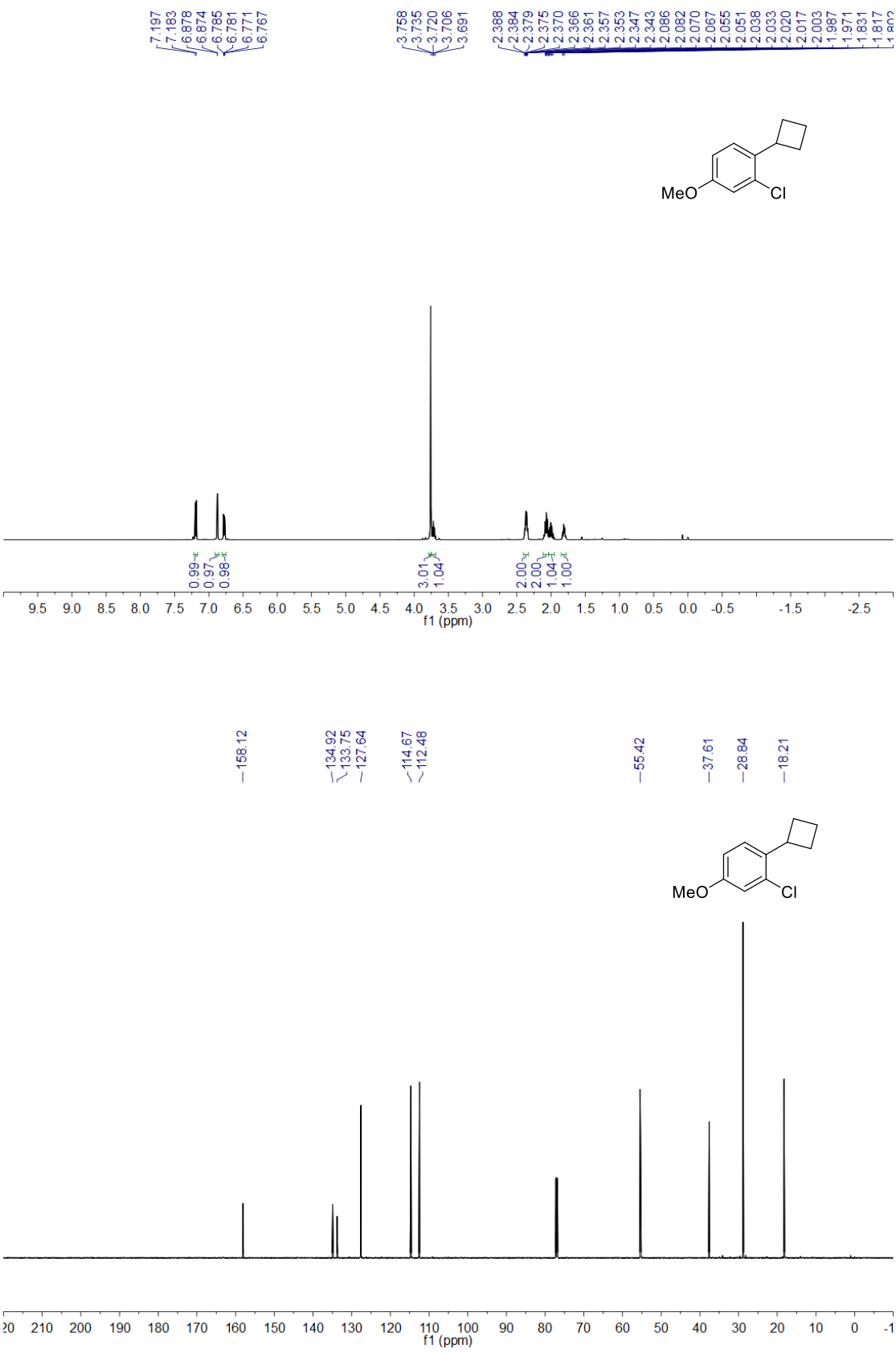
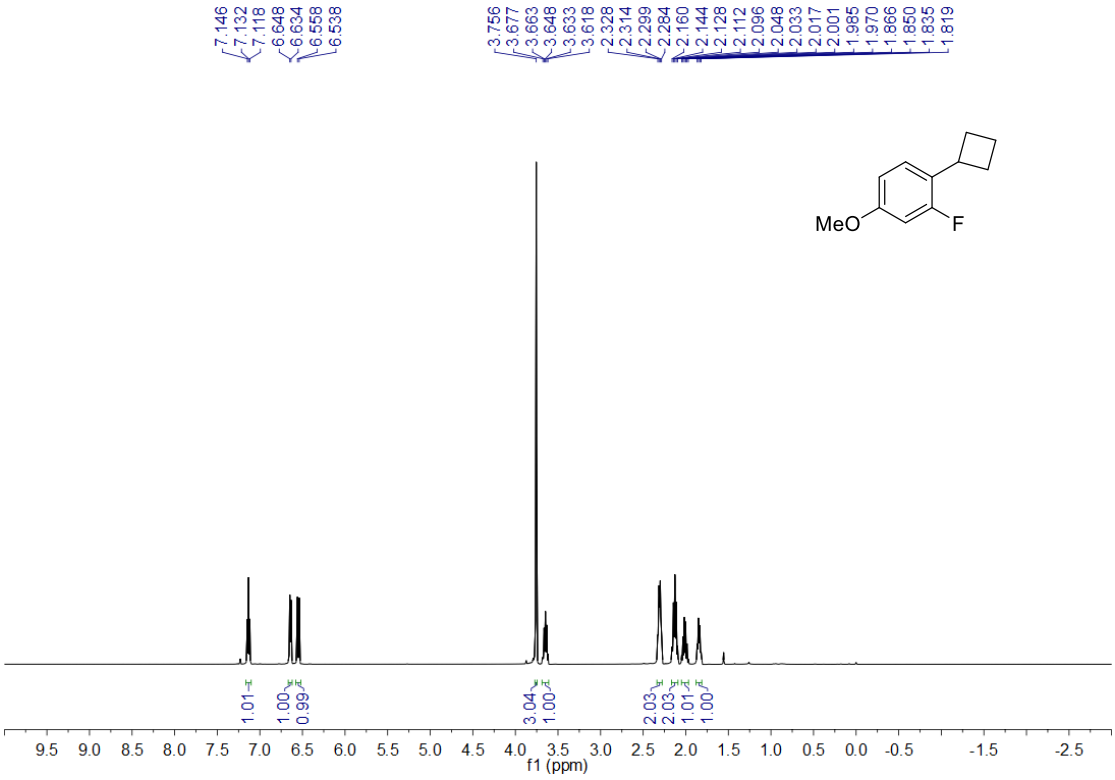
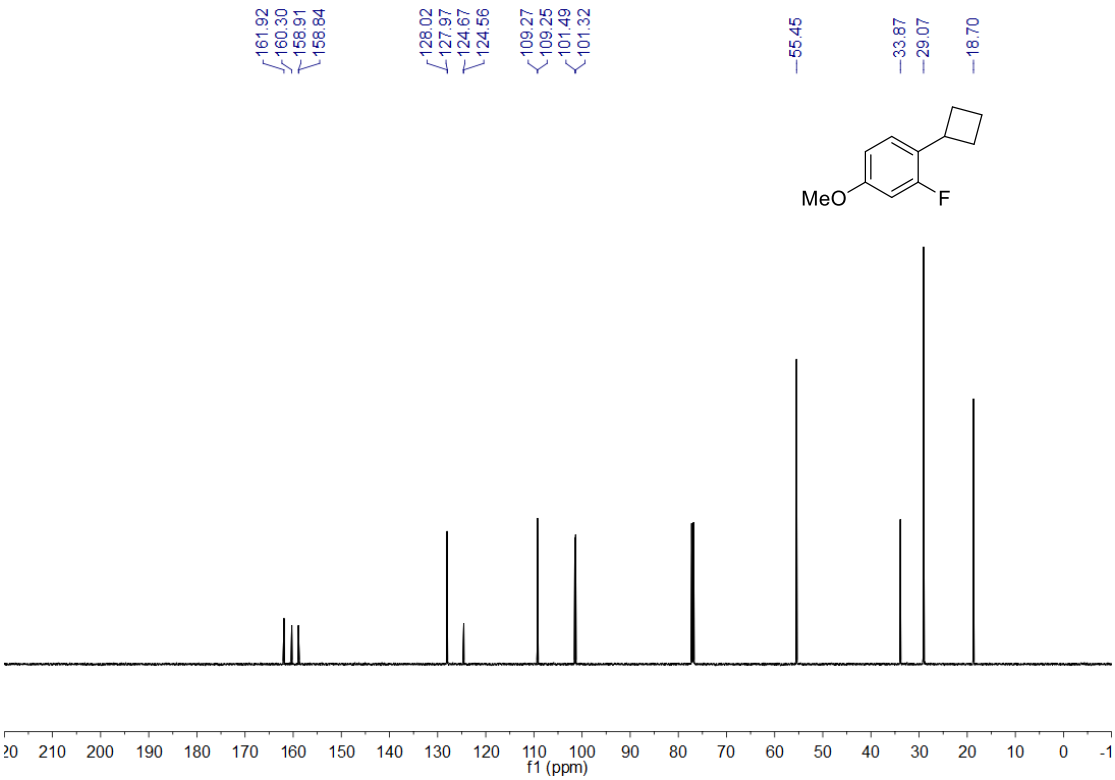


Figure S65. ^{1}H NMR and ^{13}C NMR spectra of compound **1h**.


7.146
7.132
7.118
6.648
6.634
6.558
6.538
3.756
3.677
3.663
3.648
3.633
3.618
2.328
2.314
2.299
2.284
2.160
2.144
2.128
2.112
2.096
2.048
2.033
2.017
2.001
1.985
1.970
1.866
1.850
1.835
1.819
MeO
F
1.01
1.00
0.99
3.04
1.00
2.03
2.03
1.01
1.00
f1 (ppm)


161.92
160.30
158.91
158.84
128.02
127.97
124.67
124.56
109.27
109.25
101.49
101.32
55.45
33.87
29.07
18.70
MeO
F
f1 (ppm)

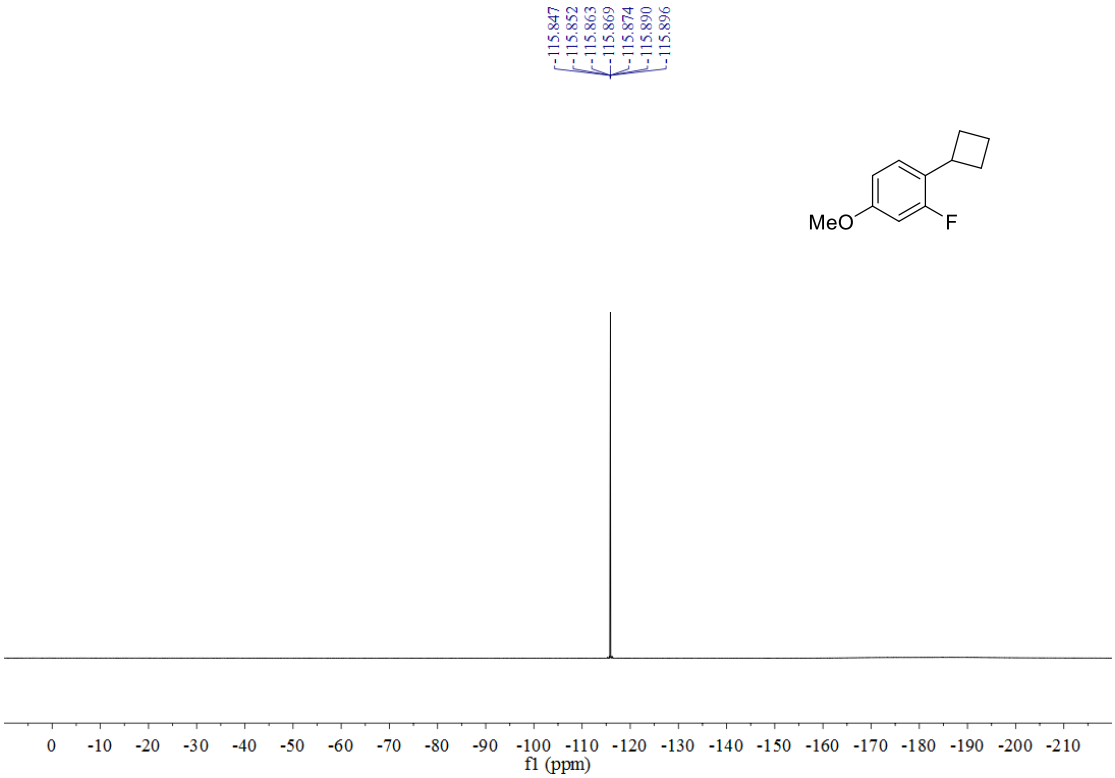
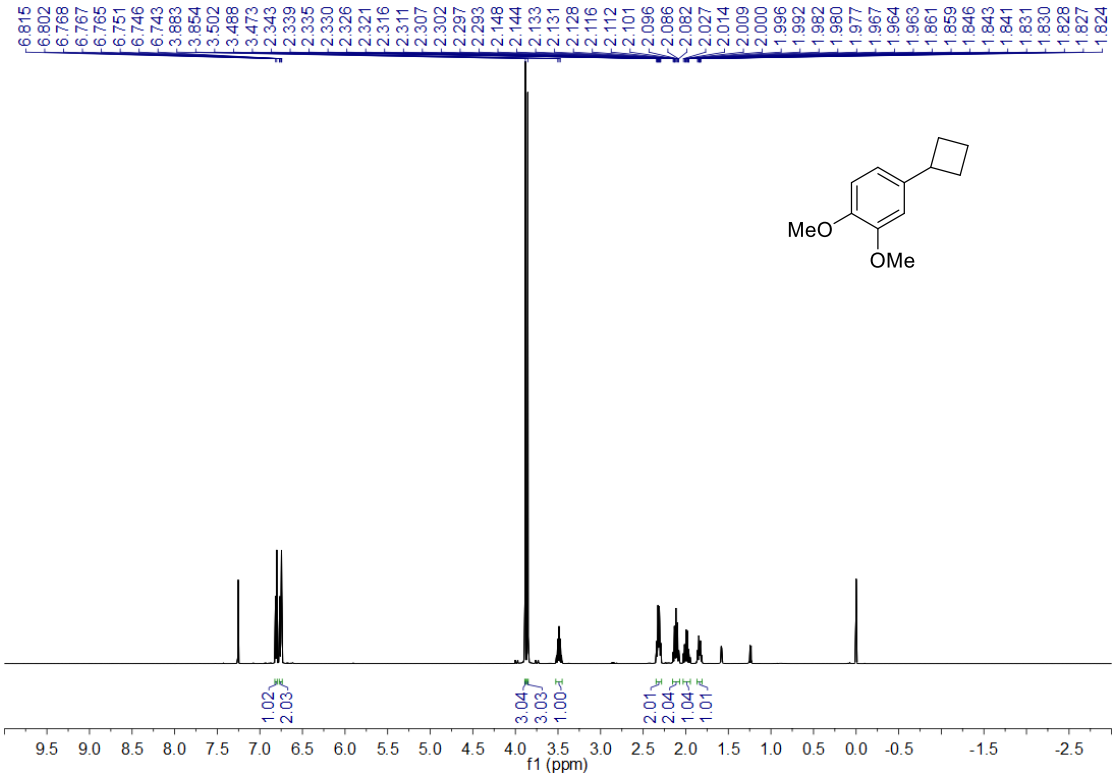


Figure S66. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **1i**.



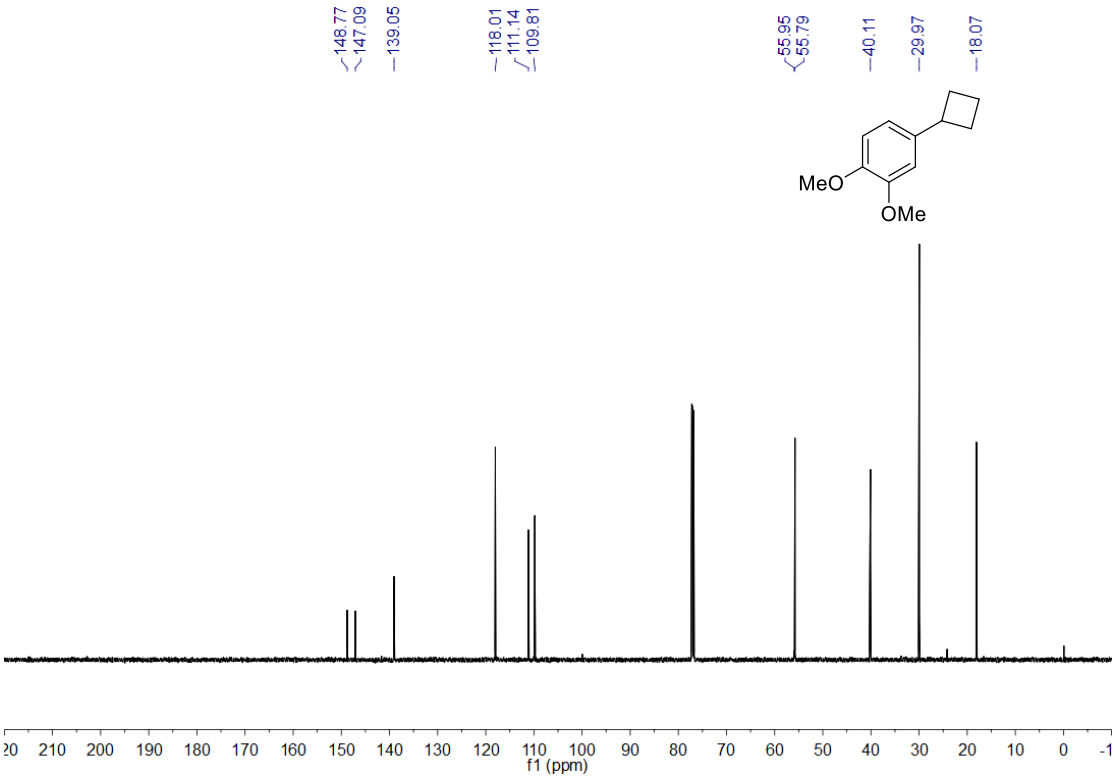
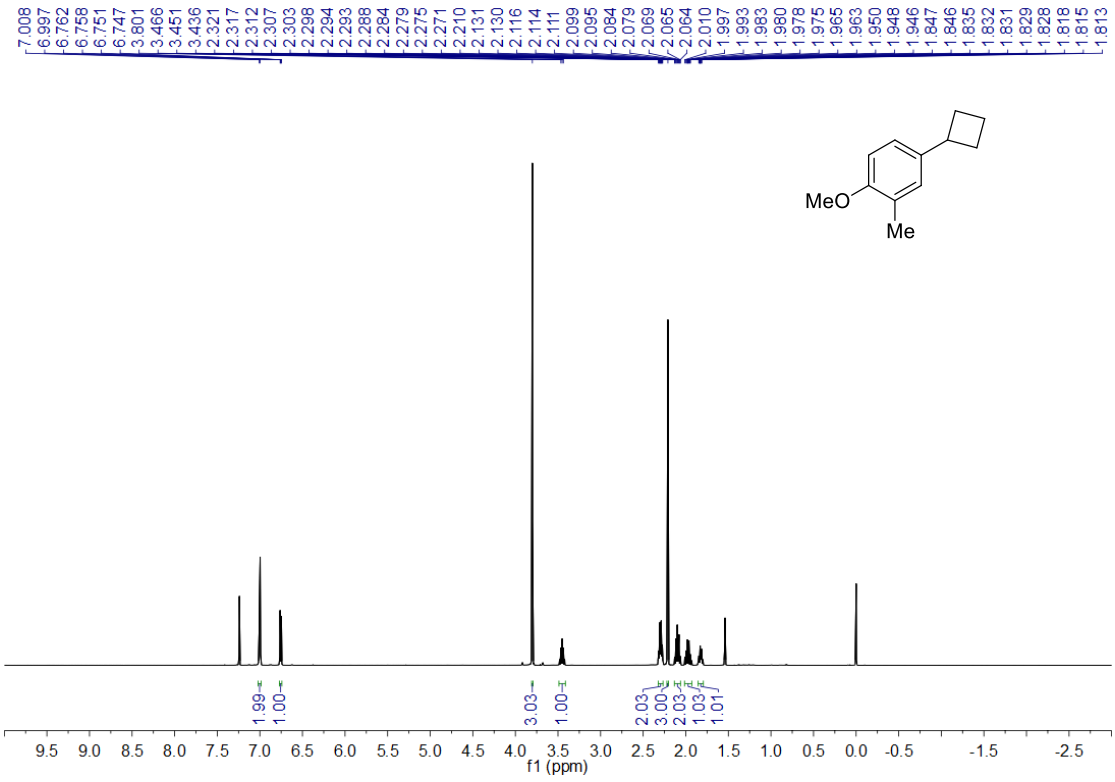


Figure S67. ^{1}H NMR and ^{13}C NMR spectra of compound **1j**.



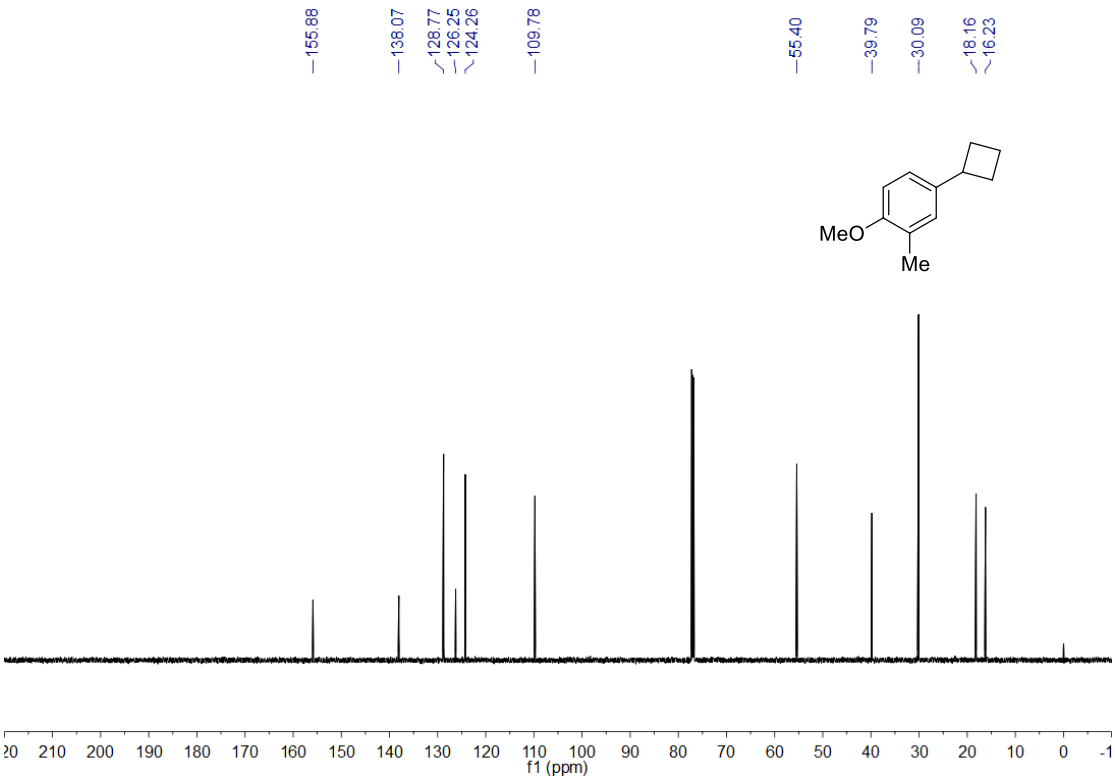
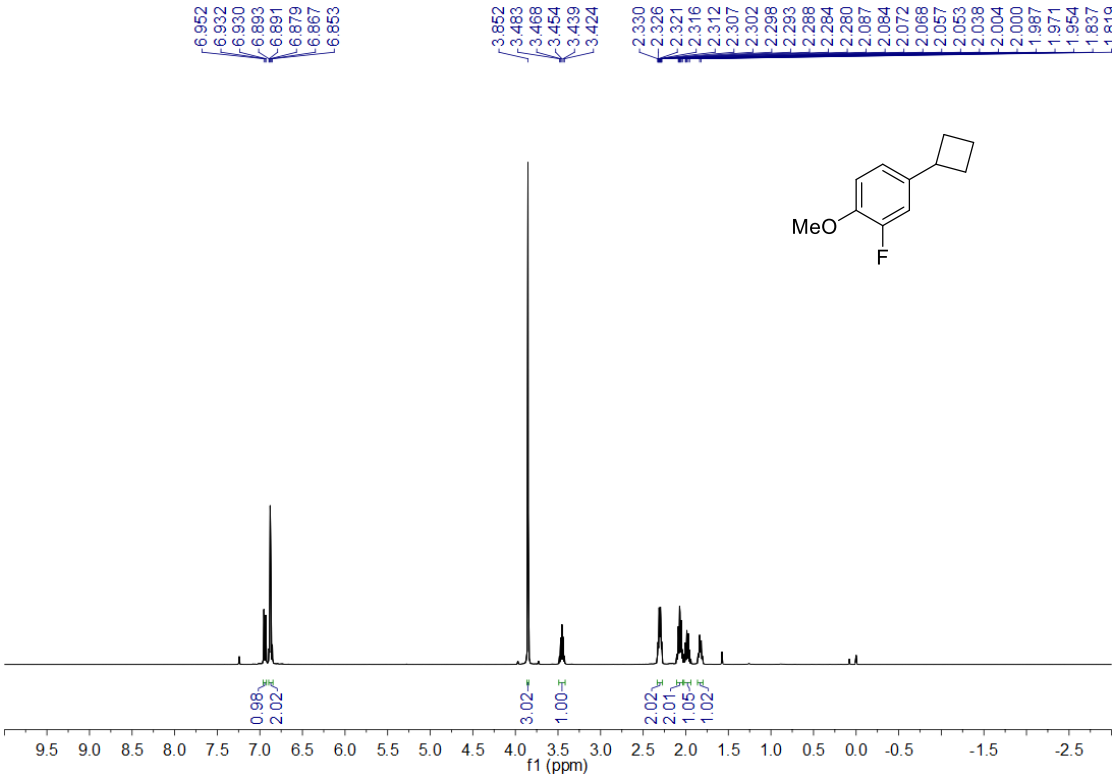


Figure S68. ^{1}H NMR and ^{13}C NMR spectra of compound **1k**.



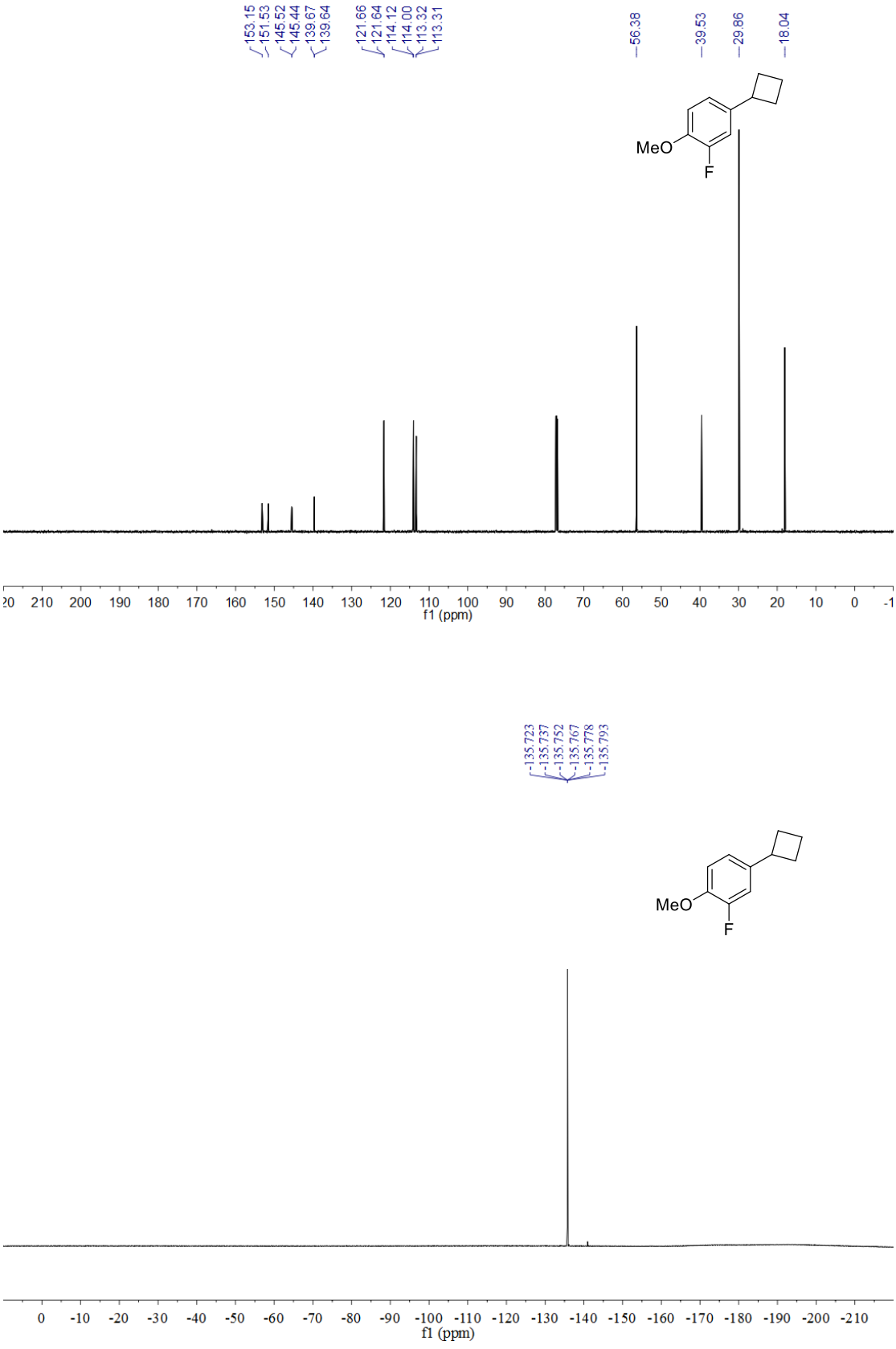


Figure S69. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **1l**.

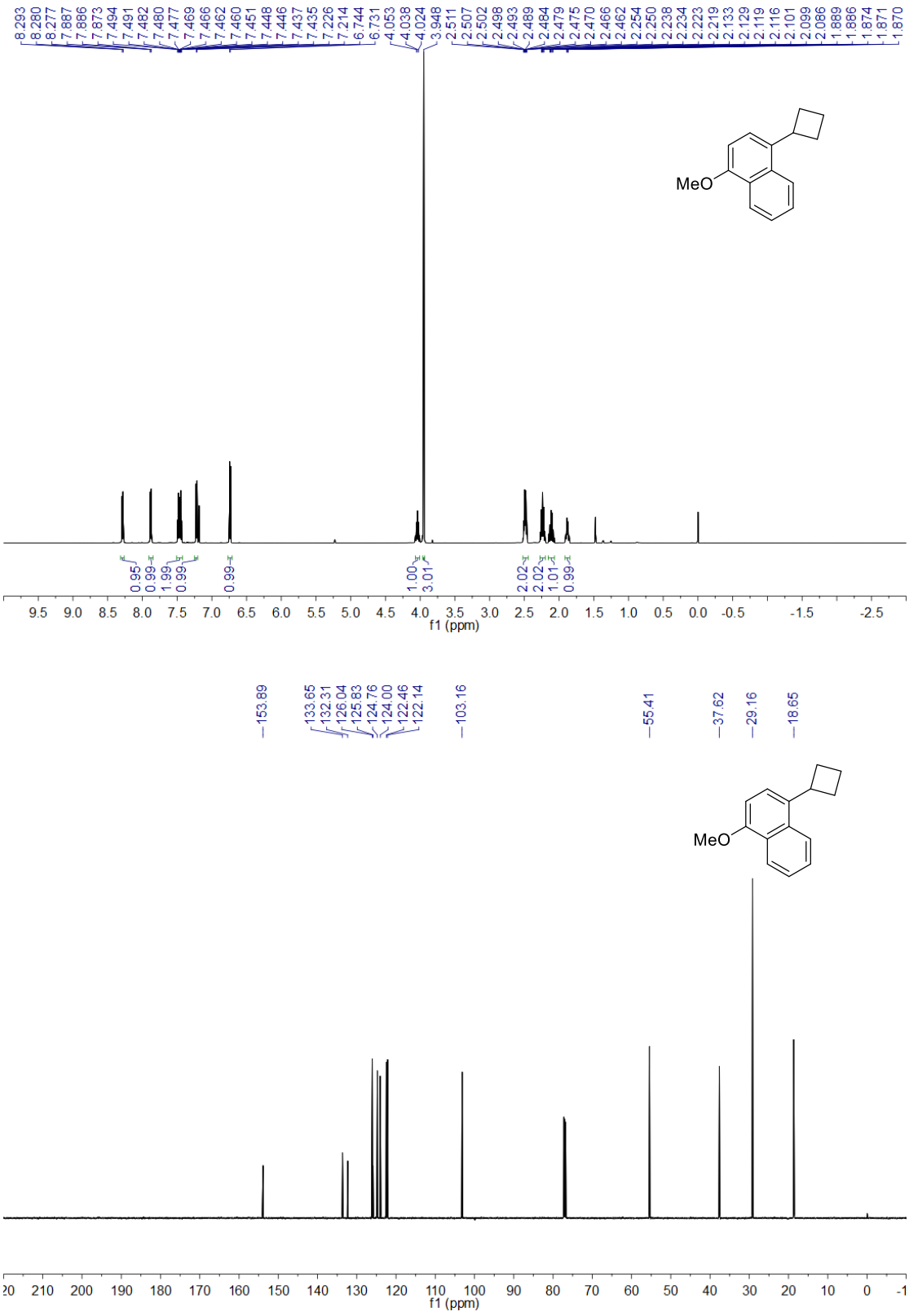


Figure S70. ^{1}H NMR and ^{13}C NMR spectra of compound **1m**.

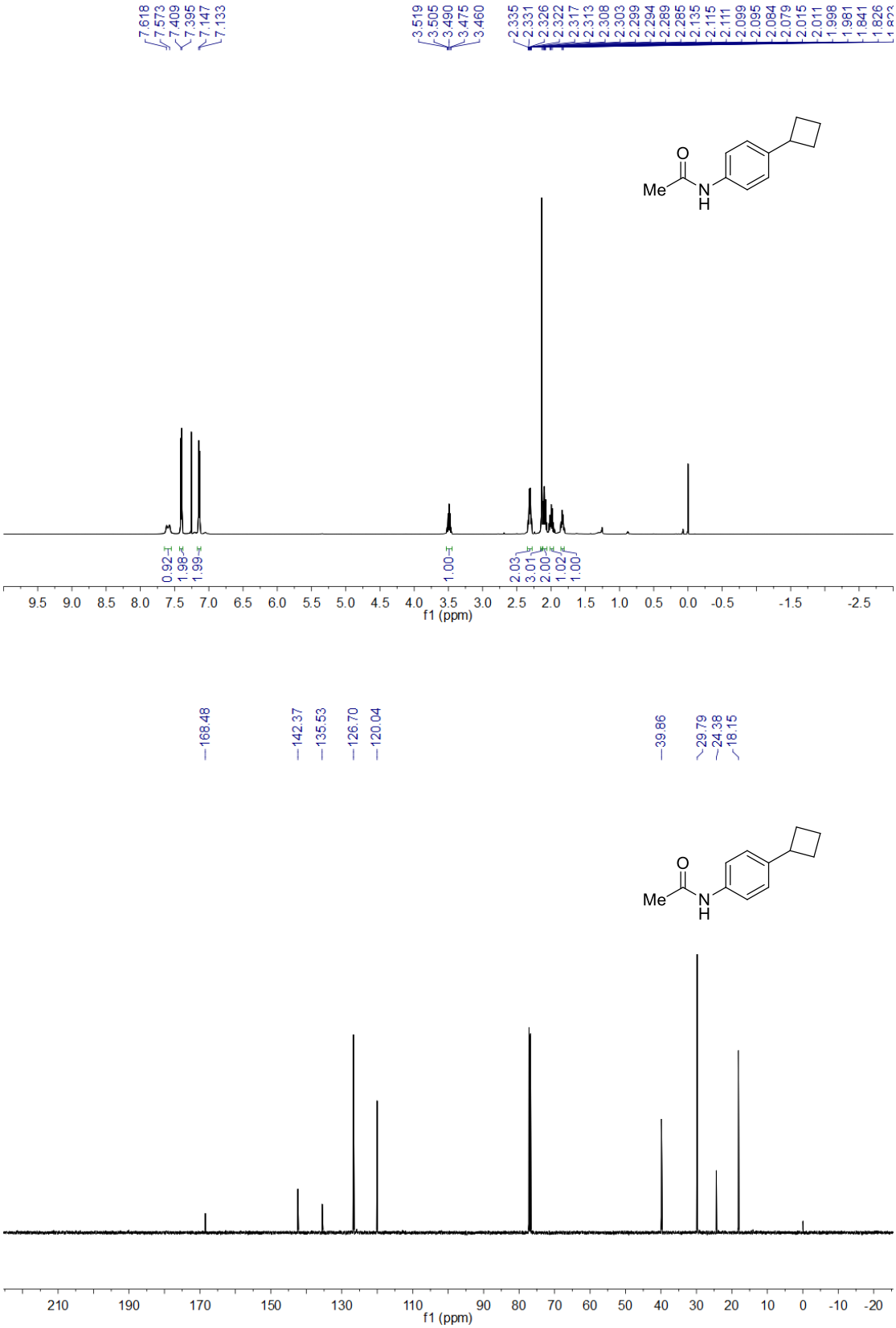


Figure S71. ^{1}H NMR and ^{13}C NMR spectra of compound **1n**.

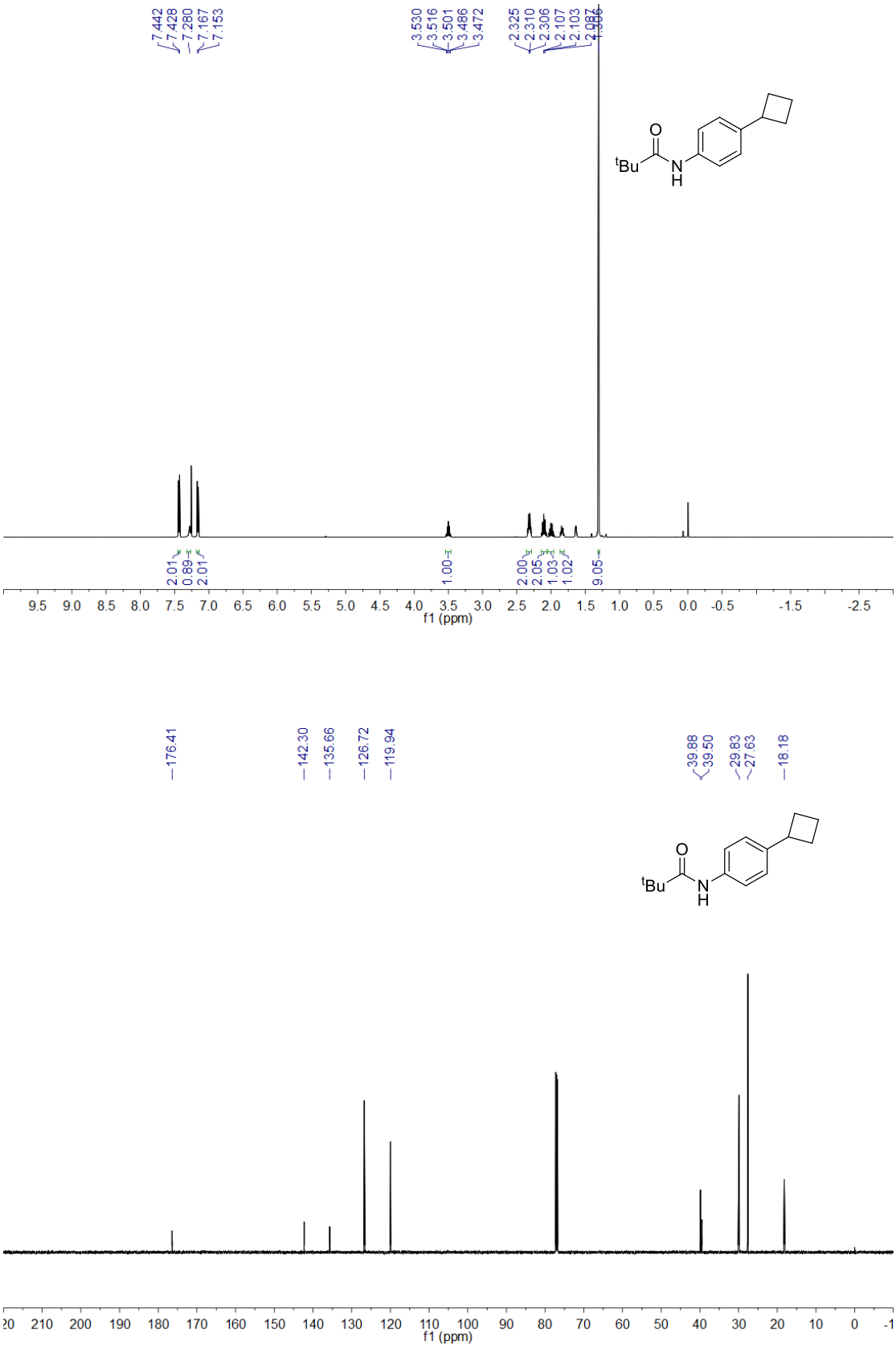


Figure S72. ^{1}H NMR and ^{13}C NMR spectra of compound **1o**.

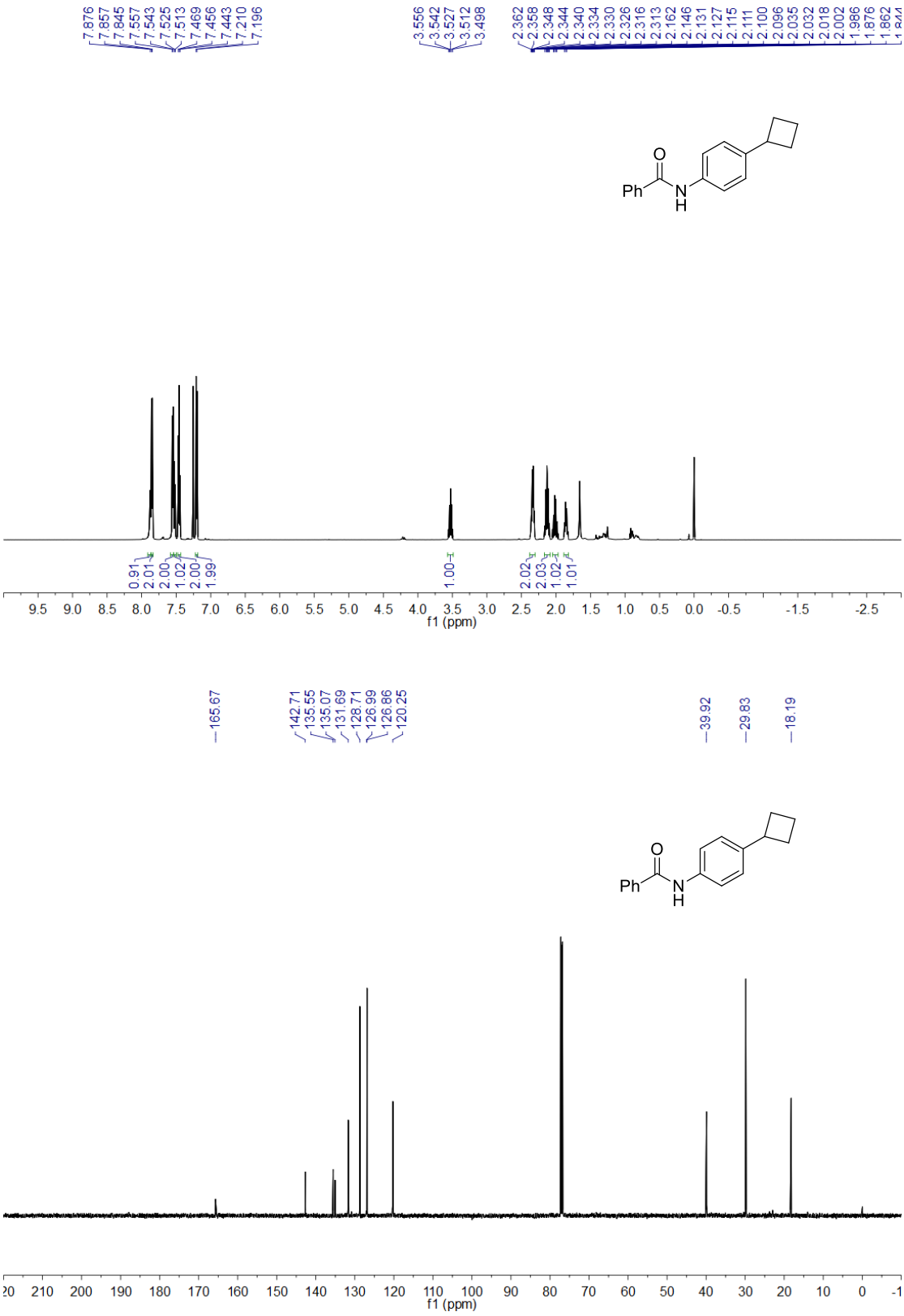


Figure S73. ^{1}H NMR and ^{13}C NMR spectra of compound **1p**.

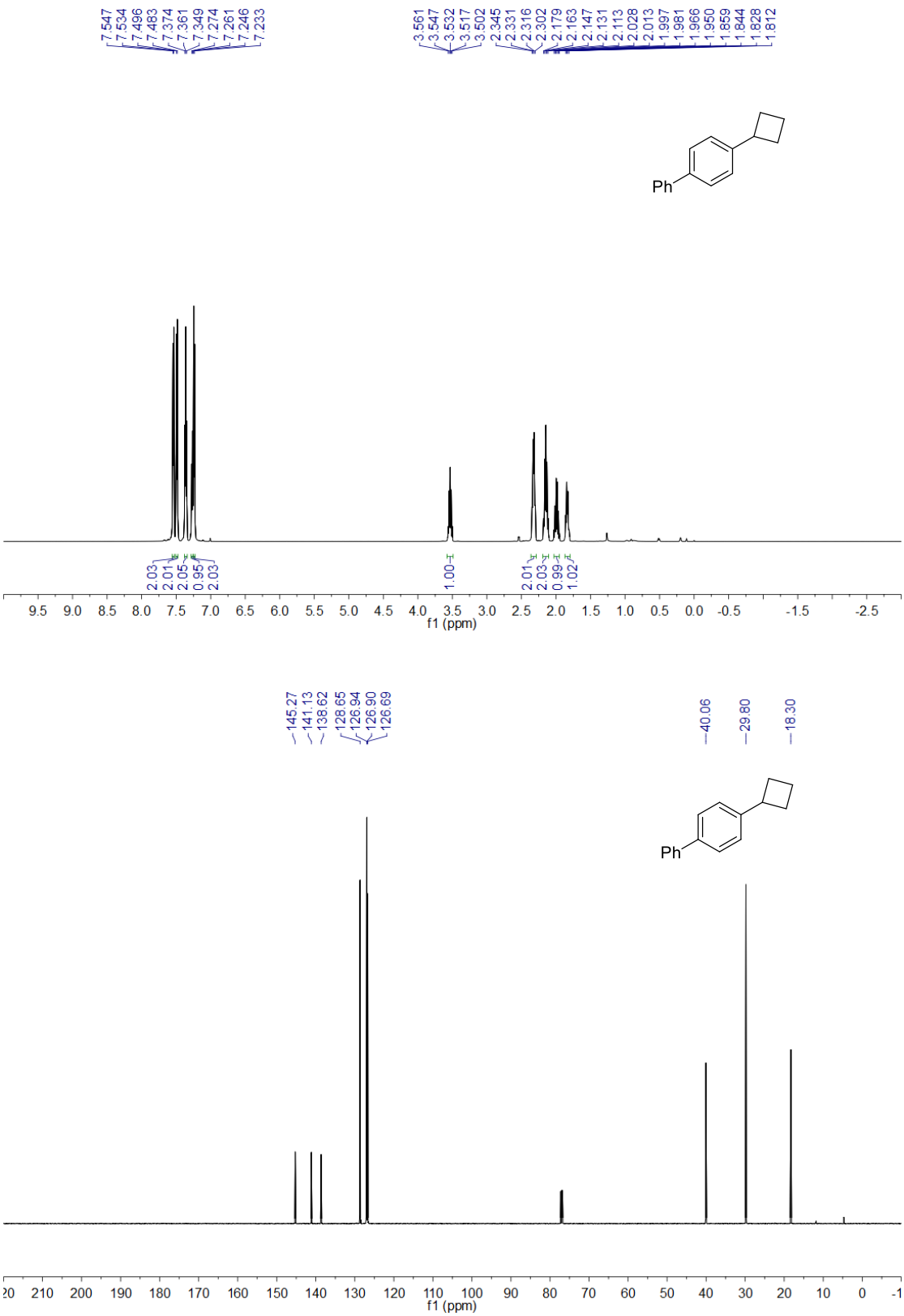
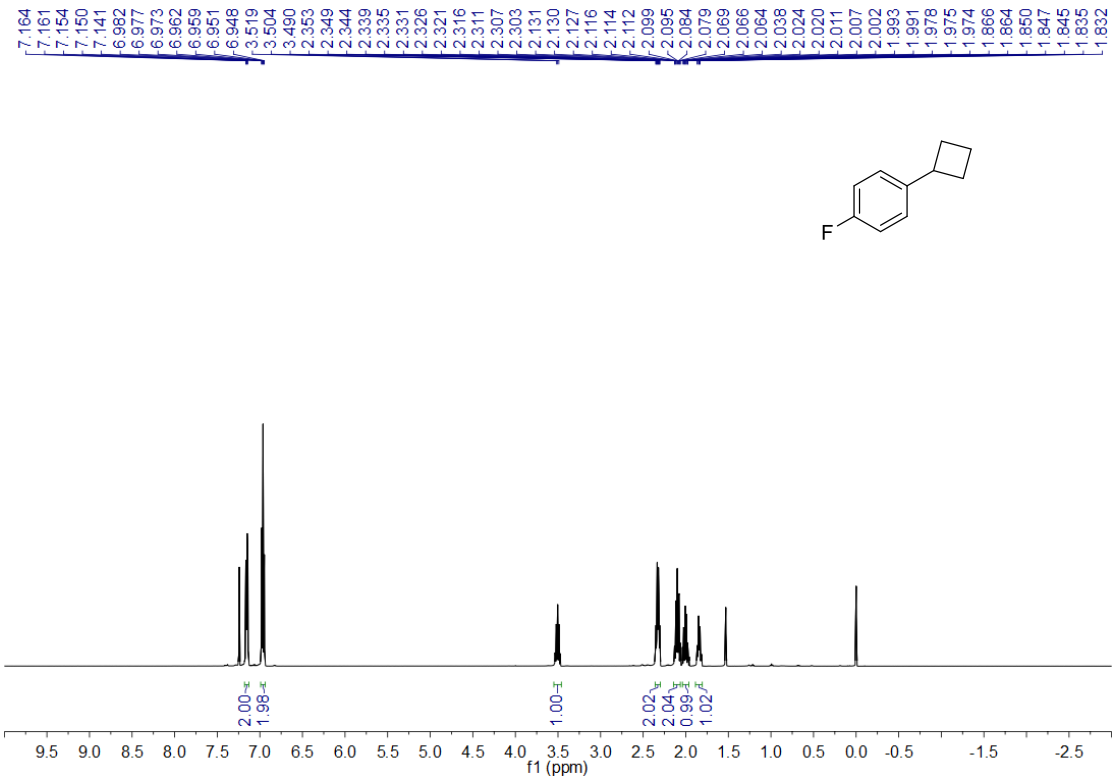
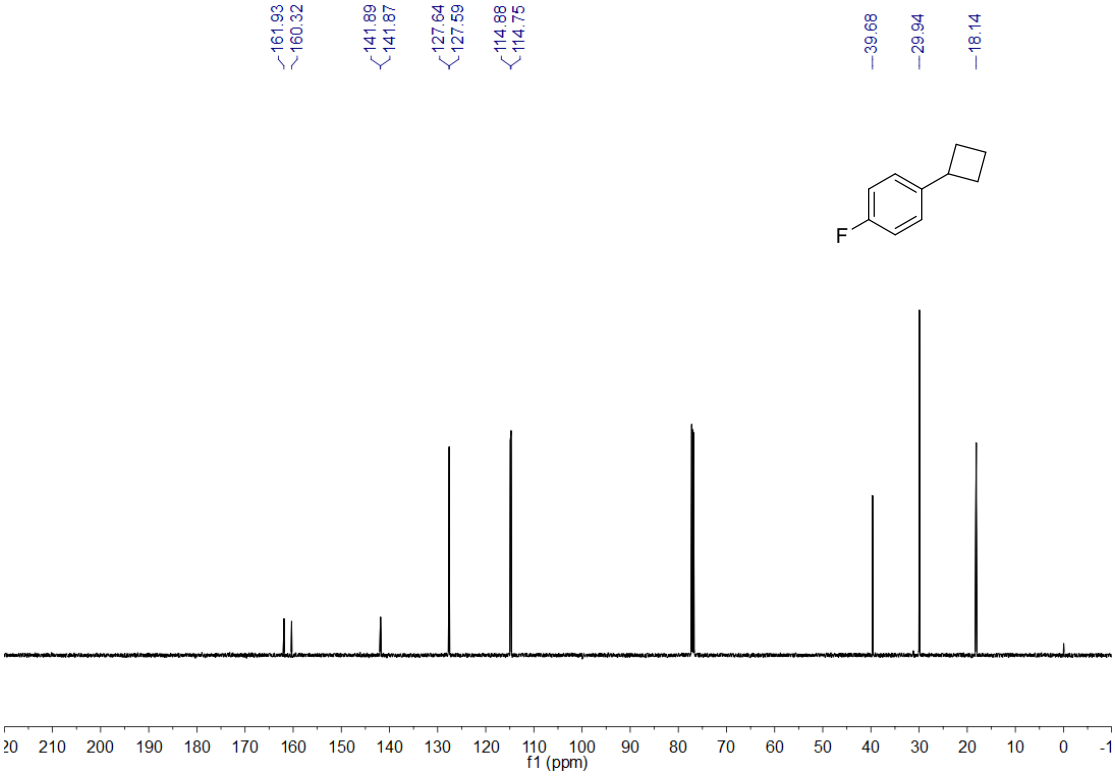


Figure S74. ^{1}H NMR and ^{13}C NMR spectra of compound **1q**.


7.164
7.161
7.154
7.150
7.141
6.982
6.977
6.973
6.962
6.959
6.951
6.948
3.519
3.504
3.490
2.353
2.349
2.344
2.339
2.335
2.331
2.326
2.321
2.316
2.311
2.307
2.303
2.131
2.130
2.127
2.116
2.114
2.112
2.099
2.095
2.084
2.079
2.069
2.066
2.064
2.038
2.024
2.020
2.011
2.007
2.002
1.993
1.991
1.978
1.975
1.974
1.866
1.864
1.850
1.847
1.845
1.835
1.832
F
2.00
1.98
1.00
2.02
2.04
0.99
1.02
f1 (ppm)


161.93
160.32
141.89
141.87
127.64
127.59
114.88
114.75
39.68
29.94
18.14
F
f1 (ppm)

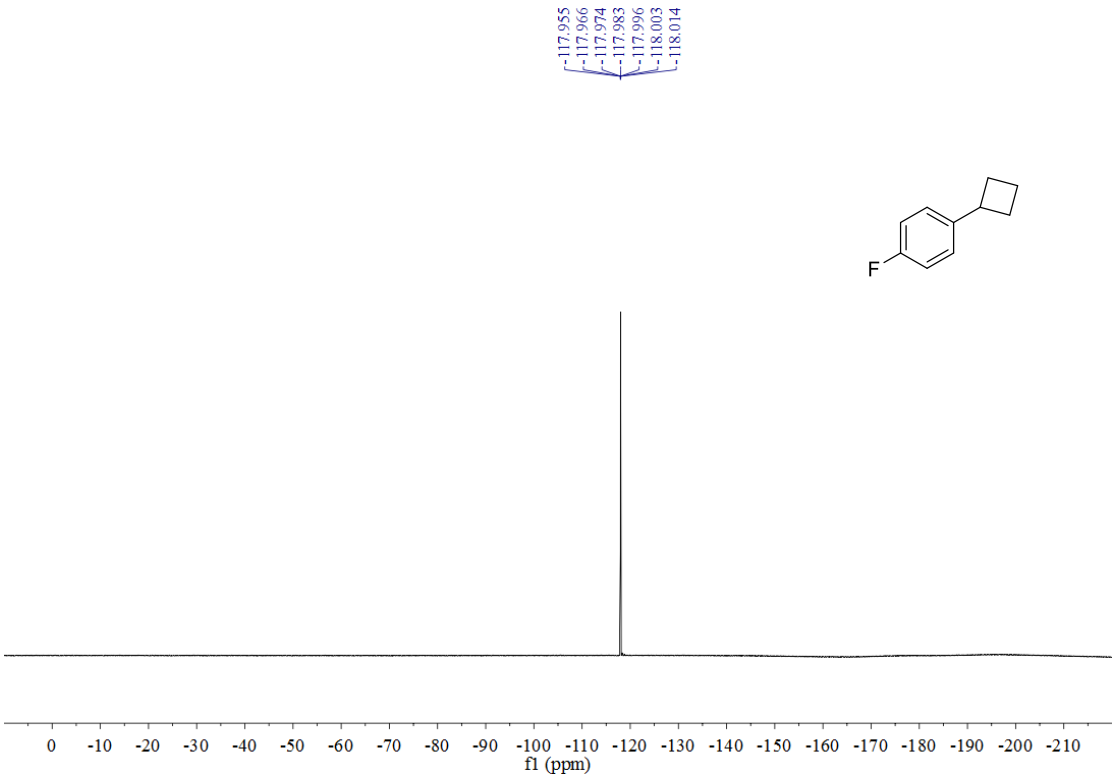
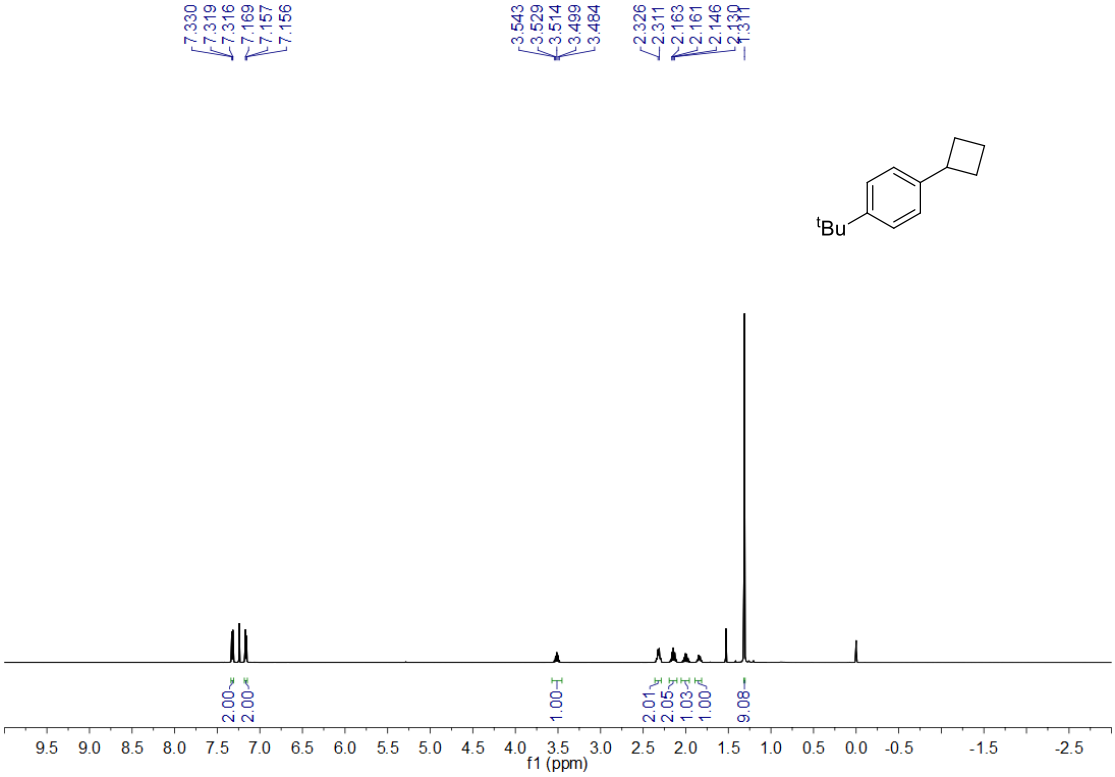


Figure S75. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **1r**.



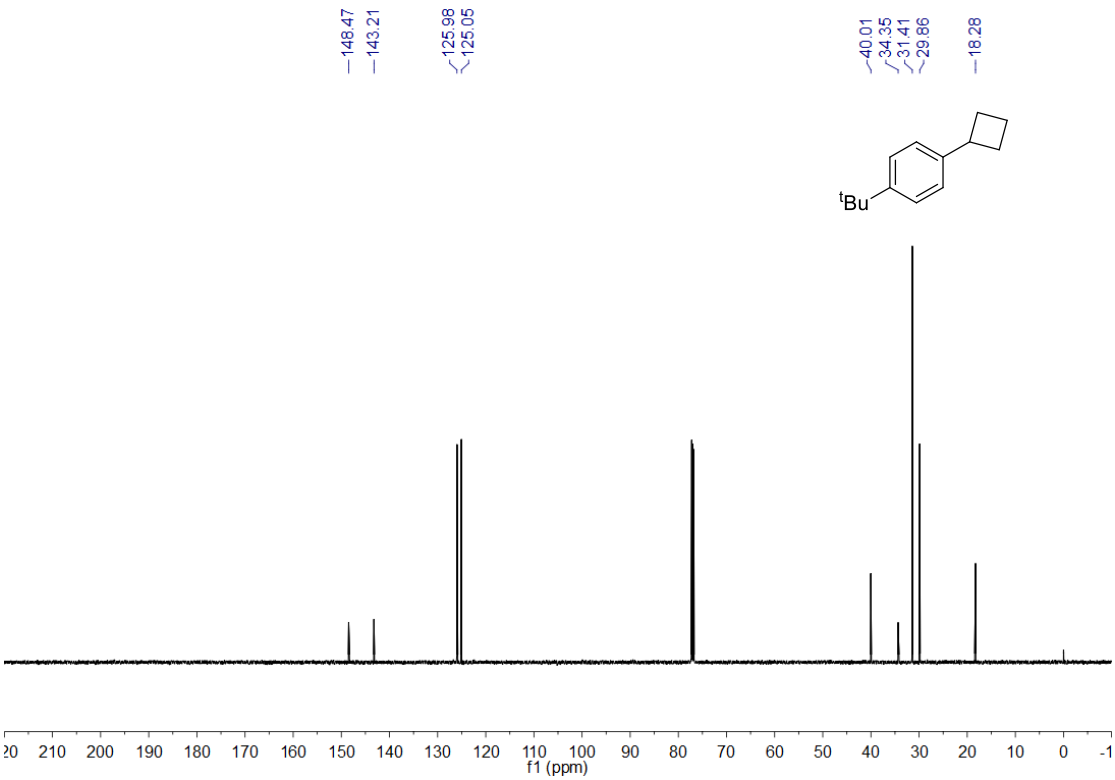
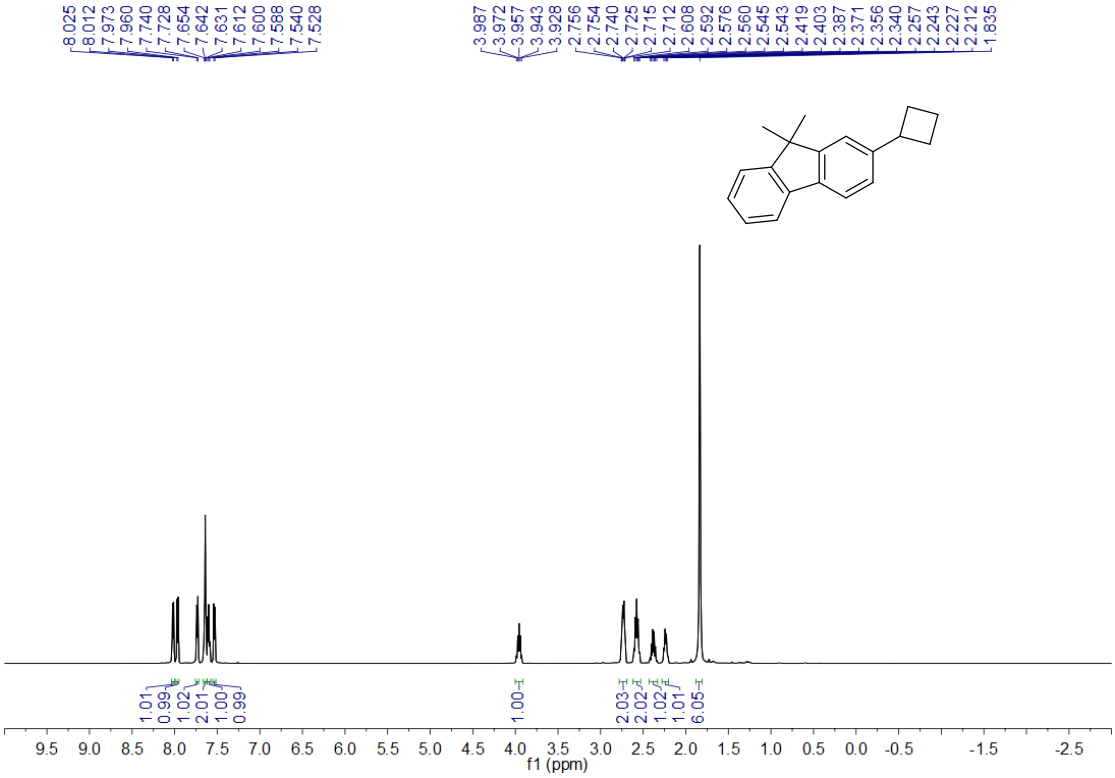


Figure S76. ^{1}H NMR and ^{13}C NMR spectra of compound **1s**.



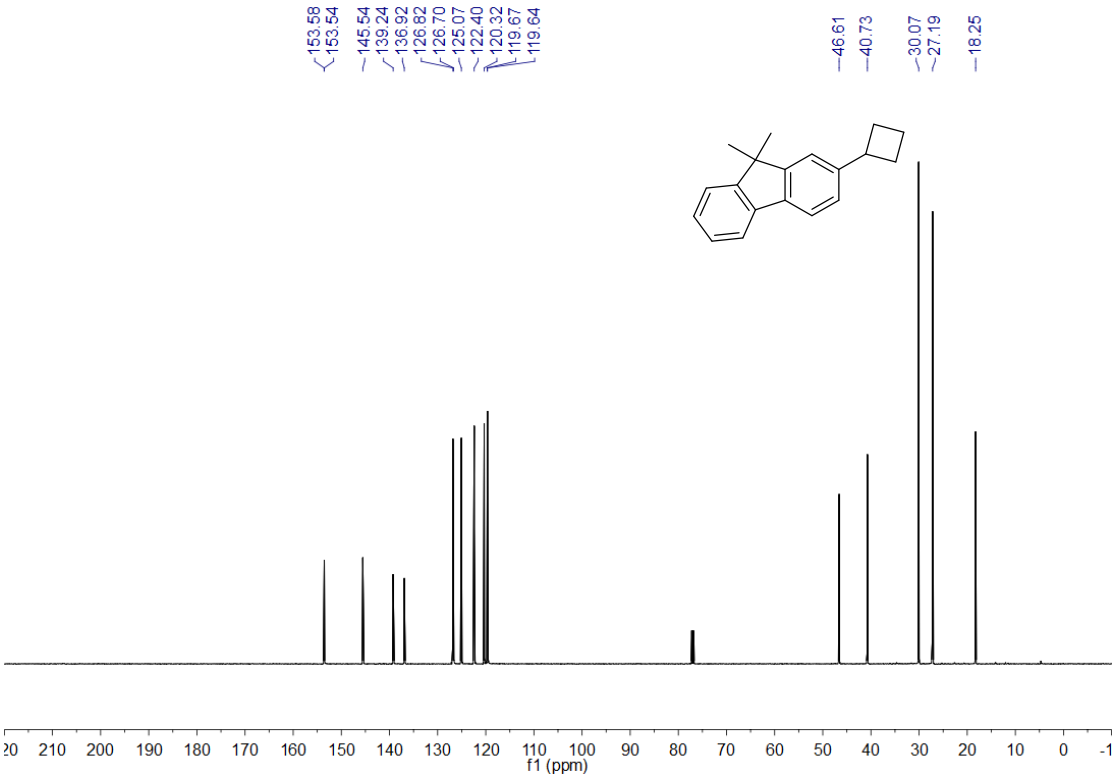
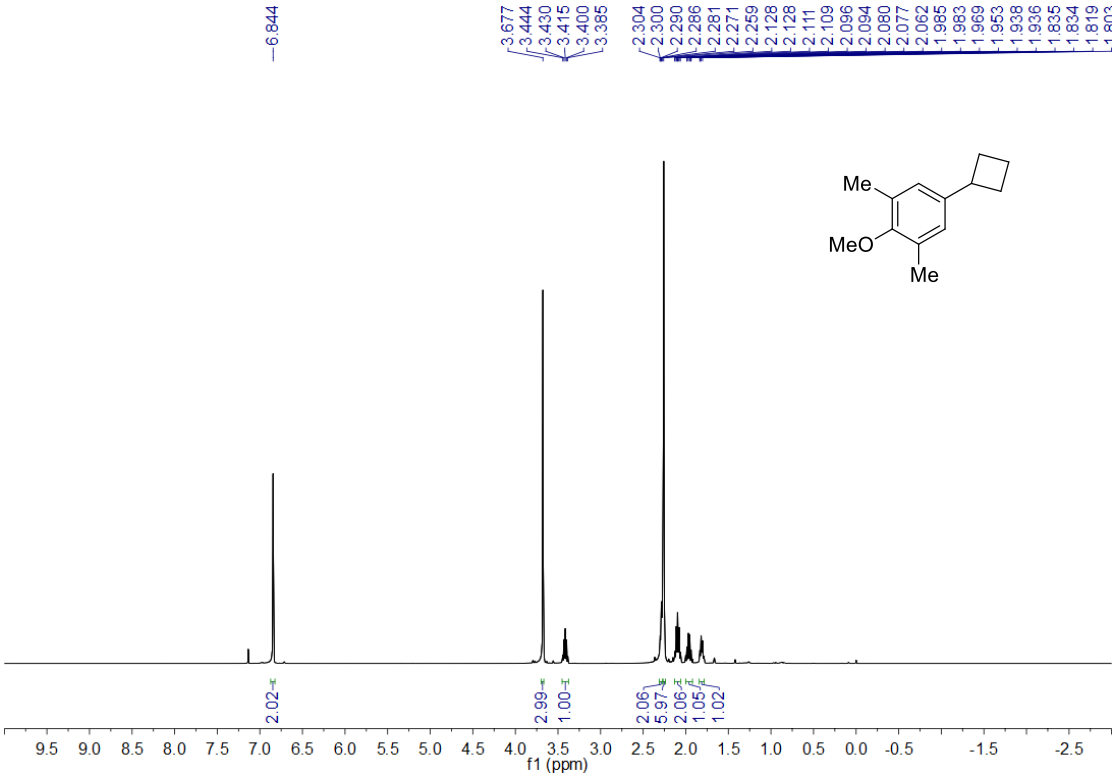


Figure S77. ^{1}H NMR and ^{13}C NMR spectra of compound **1t**.



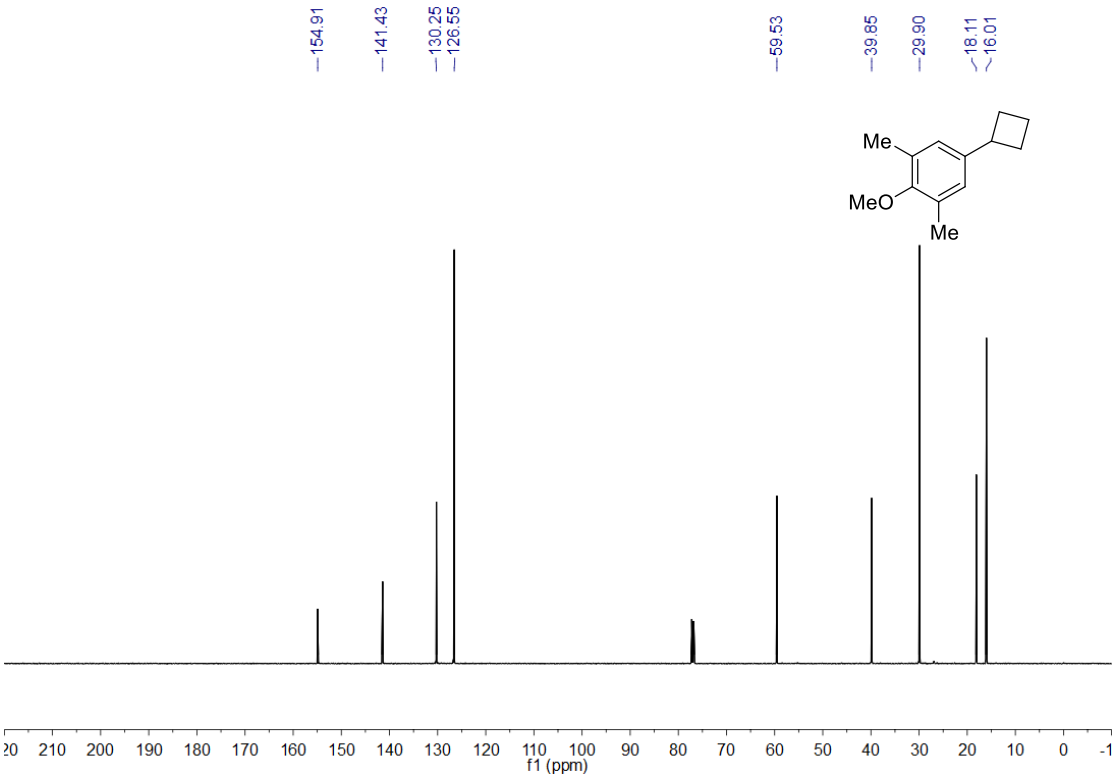
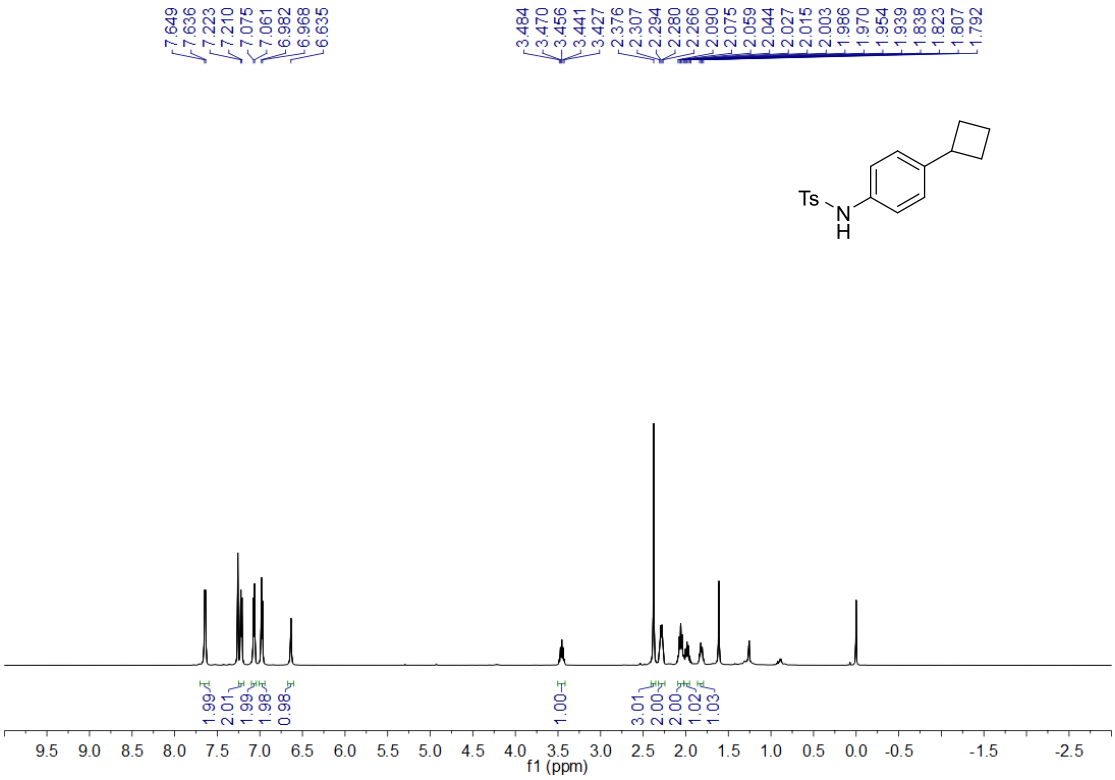


Figure S78. ^{1}H NMR and ^{13}C NMR spectra of compound **1u**.



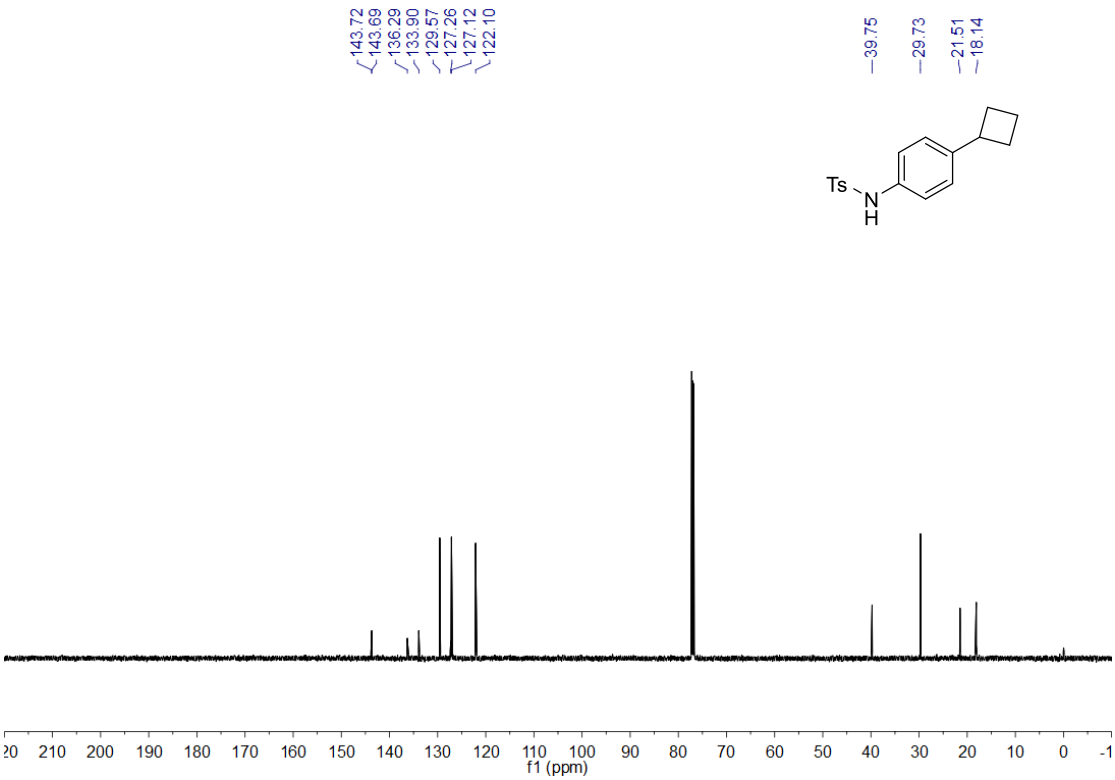


Figure S79. ^{1}H NMR and ^{13}C NMR spectra of compound **1v**.

10. References

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