

Supporting information

Ag₂O Nanoparticle-Catalyzed Substrate-Controlled Regioselectivities: Direct Access to 3-Ylideneephthalides and Isocoumarins

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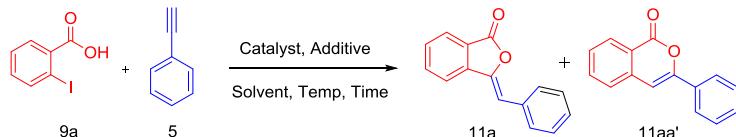
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To be published on Web.

I. Table 1. Detailed Optimization study.



Entry.	Metal.	Additive.	Solvent.	Temp. (°C).	Time (hr.)	Yield. (%)
1	CuI	--	DMF	80	3	10 ^b
2	Ag ₂ O	--	DMF	80	3	45
3	Ag ₂ O	PivOH	DMF	80	3	75
4	AgOAc	PivOH	DMF	80	3	43
5	AgCl	PivOH	DMF	80	3	Nil
6	AgNO ₃	PivOH	DMF	80	3	Nil
Screening of other metal oxides						
6a	ZnO	-----	DMF	80	3	traces
6b	CuO	-----	DMF	80	3	traces
6c	CdO	-----	DMF	80	3	traces
6d	PbO	-----	DMF	80	3	No reaction
6e	Al ₂ O ₃	-----	DMF	80	3	No reaction
6f	CrO ₃	-----	DMF	80	3	No reaction
6g	NiO	-----	DMF	80	3	No reaction
6h	MnO ₂	-----	DMF	80	3	No reaction
6i	Fe ₂ O ₃	-----	DMF	80	3	No reaction
Optimization with Ag ₂ ONPs						
7	Ag₂ONPs	PivOH	DMF	80	3	83
8	Ag ₂ ONPs	AcOH	DMF	80	3	46
9	Ag ₂ ONPs	PivOH	DMF	80	24	59
10	Ag ₂ ONPs	PivOH	DMF	100	3	90
11	Ag₂ONPs	PivOH	DMF	120	3	95
12	Ag ₂ ONPs	PivOH	DMF	130	3	88
13	Ag ₂ ONPs	PivOH	DMF	120	1.5	88
14	Ag ₂ ONPs	PivOH	DMF	120	2	88
Screening of Solvents						
15.	Ag ₂ ONPs	PivOH	DMSO	80	3	55
16	Ag ₂ ONPs	PivOH	O-xylene	80	3	17
17.	Ag ₂ ONPs	PivOH	Toluene	80	3	25
18.	Ag ₂ ONPs	PivOH	DCE	80	3	30
19.	Ag ₂ ONPs	PivOH	1,4-Dioxane	80	3	27
20.	Ag ₂ ONPs	PivOH	PEG	80	3	No Reaction
21.	Ag ₂ ONPs	PivOH	H ₂ O	80	3	No Reaction
Screening of basic additives						
22.	Ag ₂ ONPs	Na ₂ CO ₃	DMF	80	3	No reaction
23.	Ag ₂ ONPs	Cs ₂ CO ₃	DMF	80	3	No reaction
24.	Ag ₂ ONPs	NaOH	DMF	80	3	No reaction
25.	Ag ₂ ONPs	1,10-phenanthroline	DMF	80	3	No reaction
Catalytic loading of Ag ₂ ONPs (in equiv.)						
26.	0.2	DMF	PivOH	80	3	8
27.	0.5	DMF	PivOH	80	3	20
28.	0.75	DMF	PivOH	80	3	56
29.	1	DMF	PivOH	80	3	83
30.	-----	DMF	PivOH	80	3	No Reaction

II. ^1H NMR and ^{13}C NMR Spectral Data of all synthesized compounds 11-21.

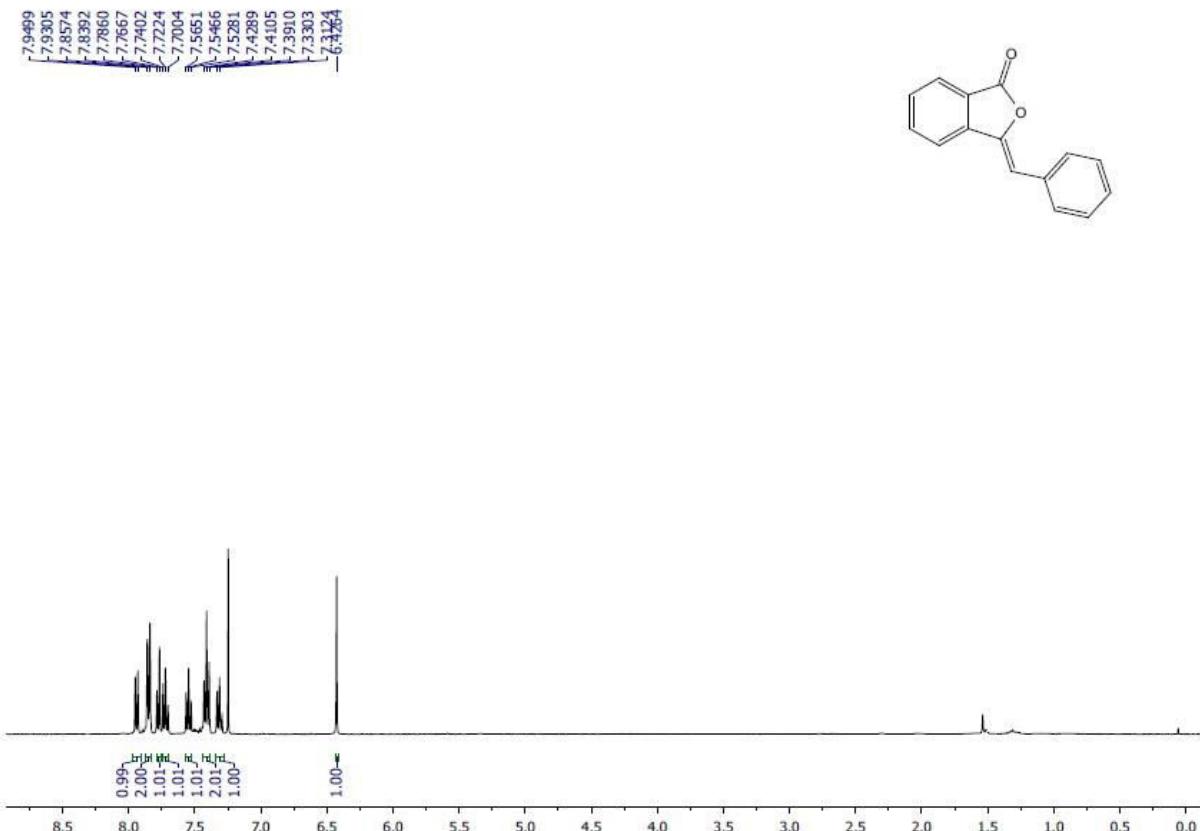


Figure 1: ^1H -NMR spectral data of 11a.

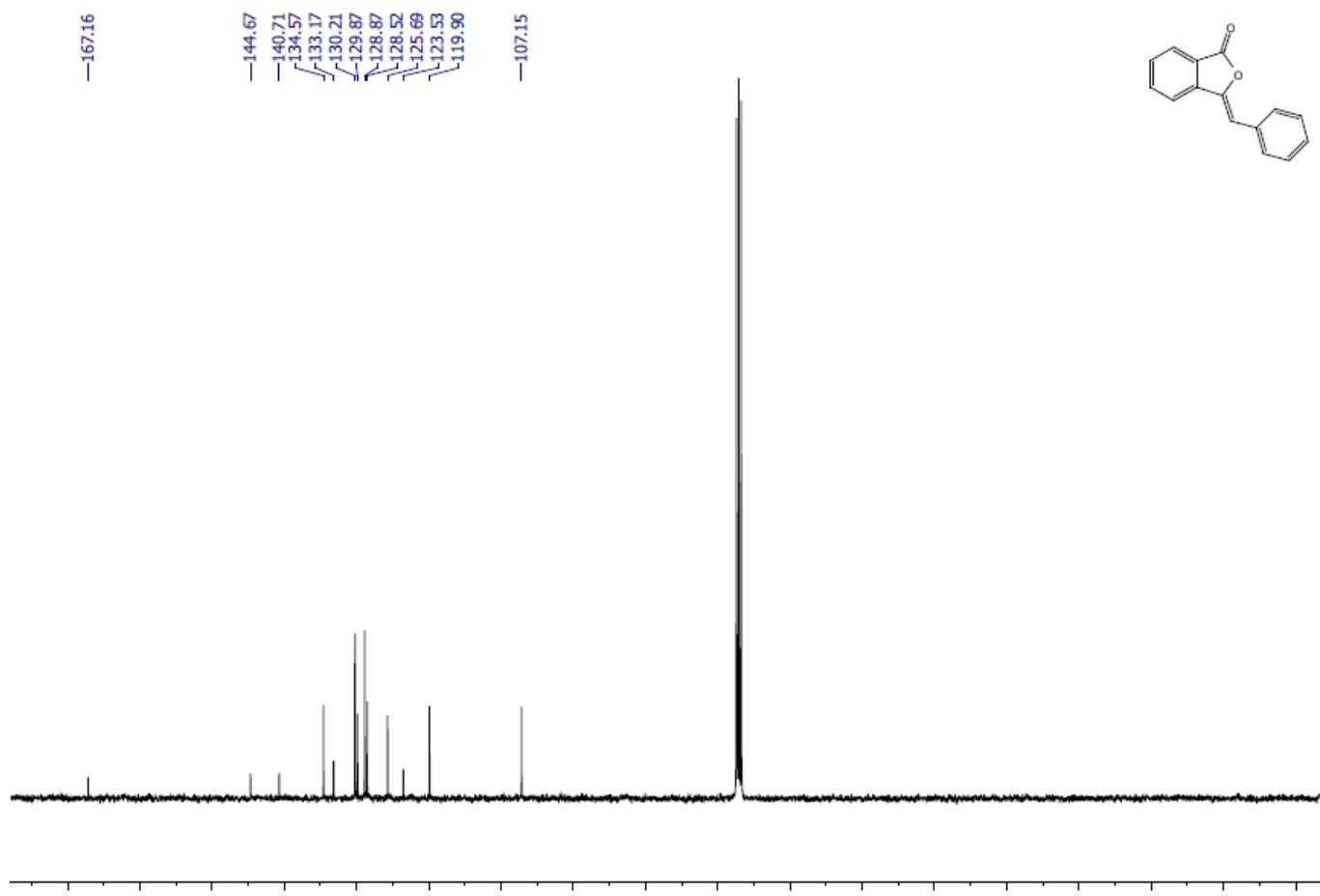


Figure 2: ^{13}C -NMR spectral data of 11a.

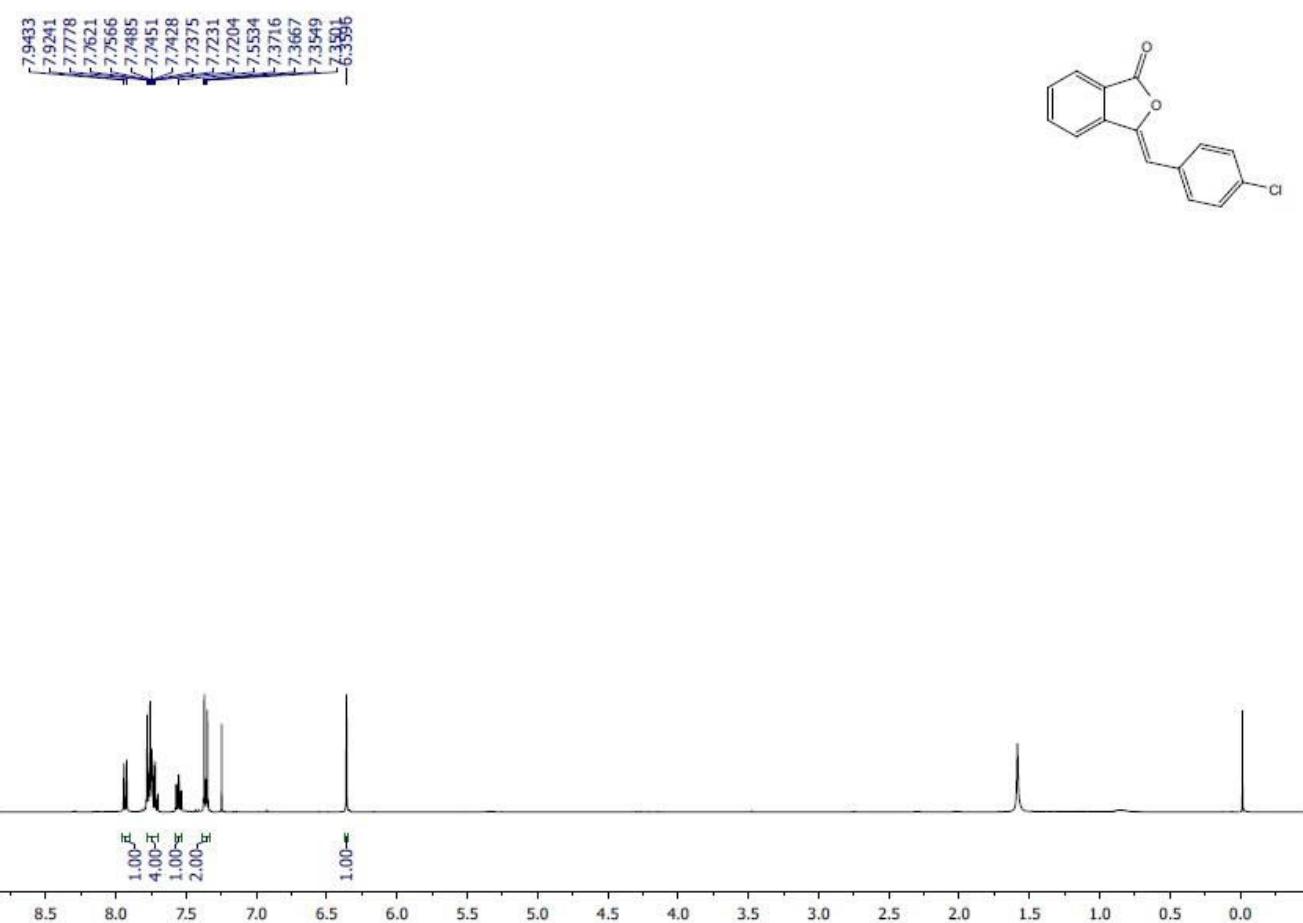


Figure 3: ^1H -NMR spectral data **11b**.

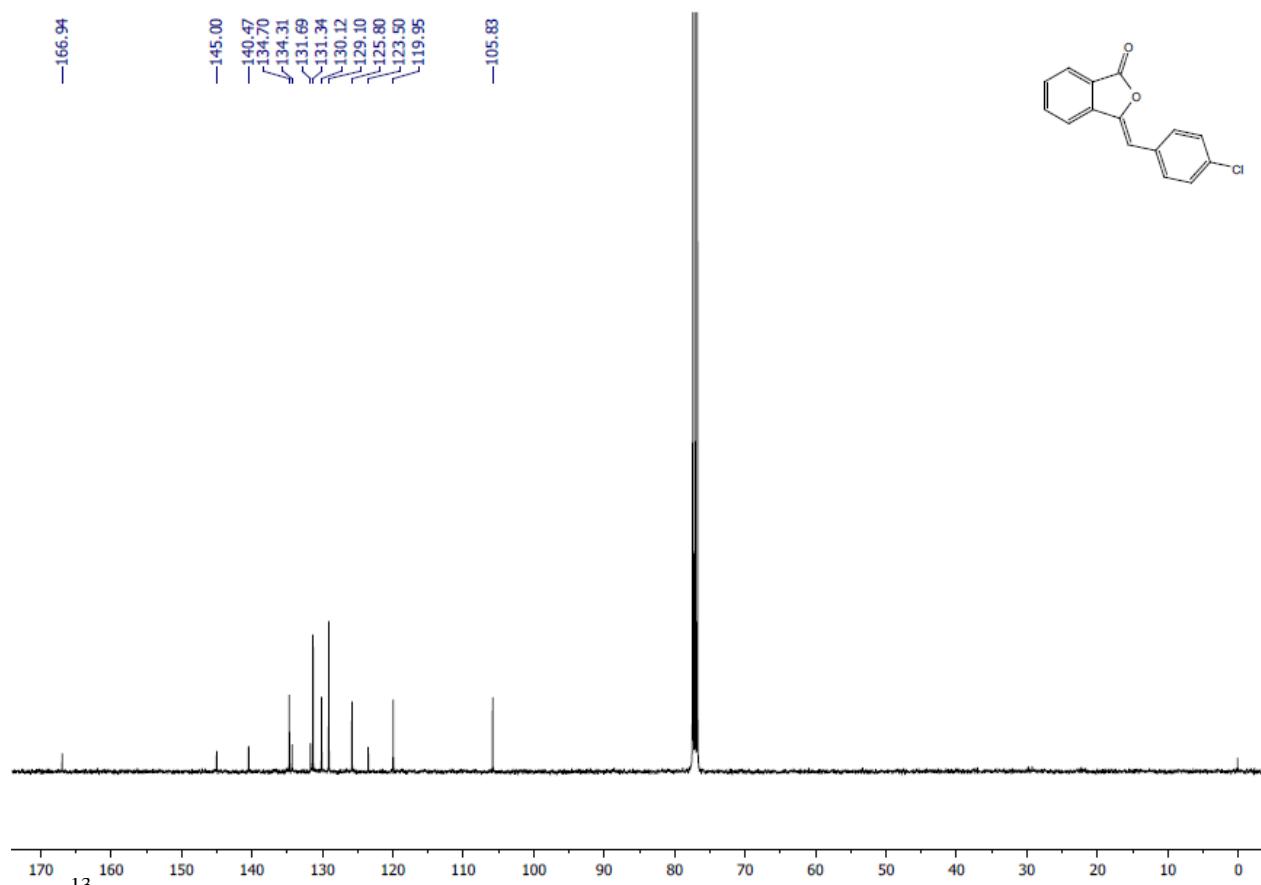


Figure 4: ^{13}C -NMR spectral data of **11b**.

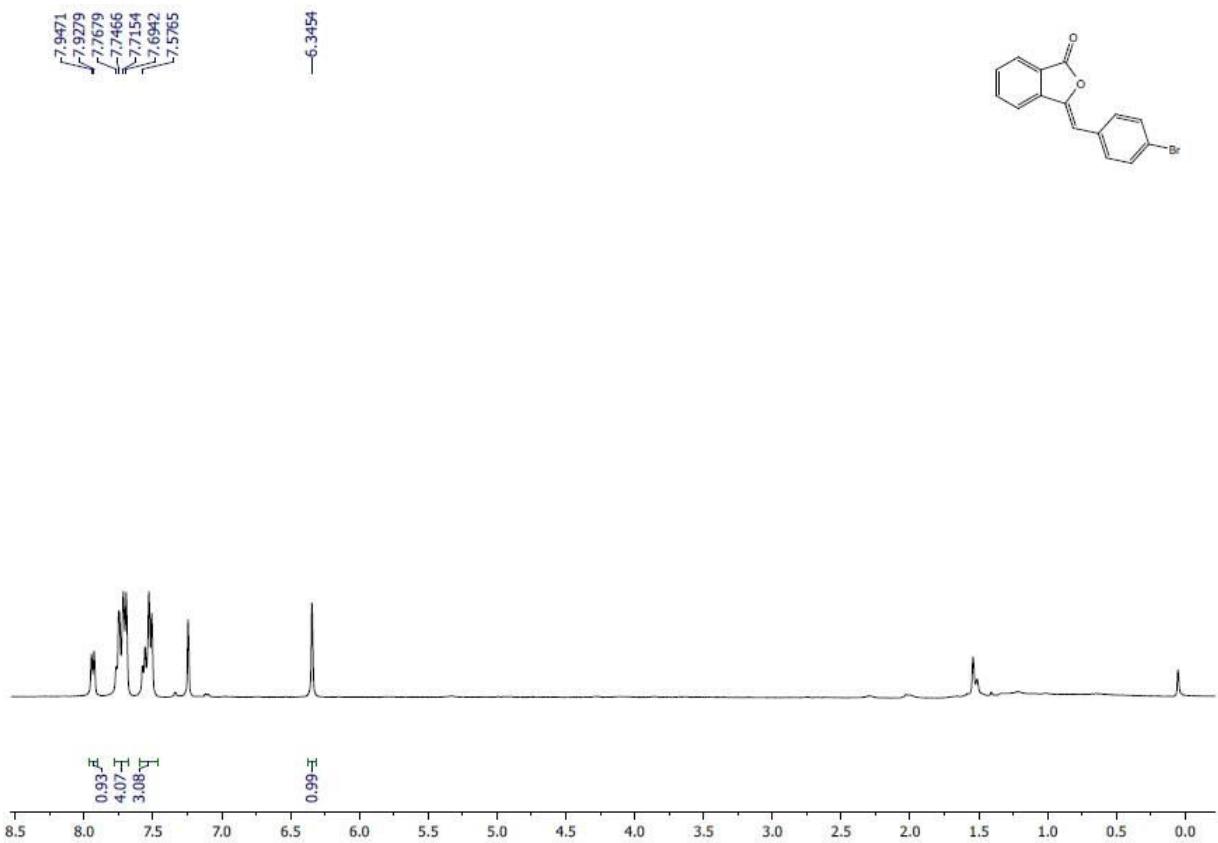


Figure 5: ¹H-NMR spectral data of 11c.

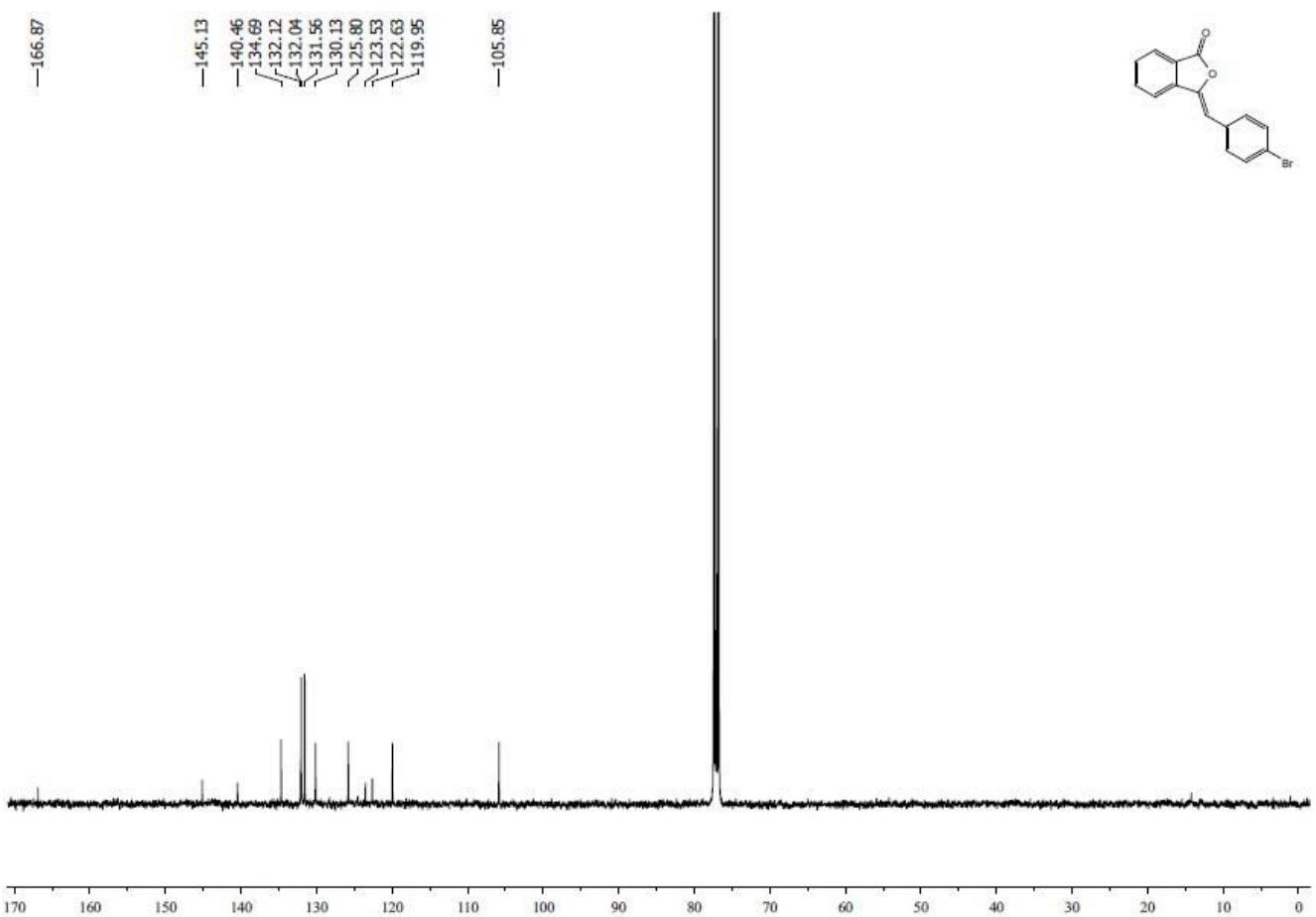


Figure 6: ¹³C-NMR spectral data of 11c.

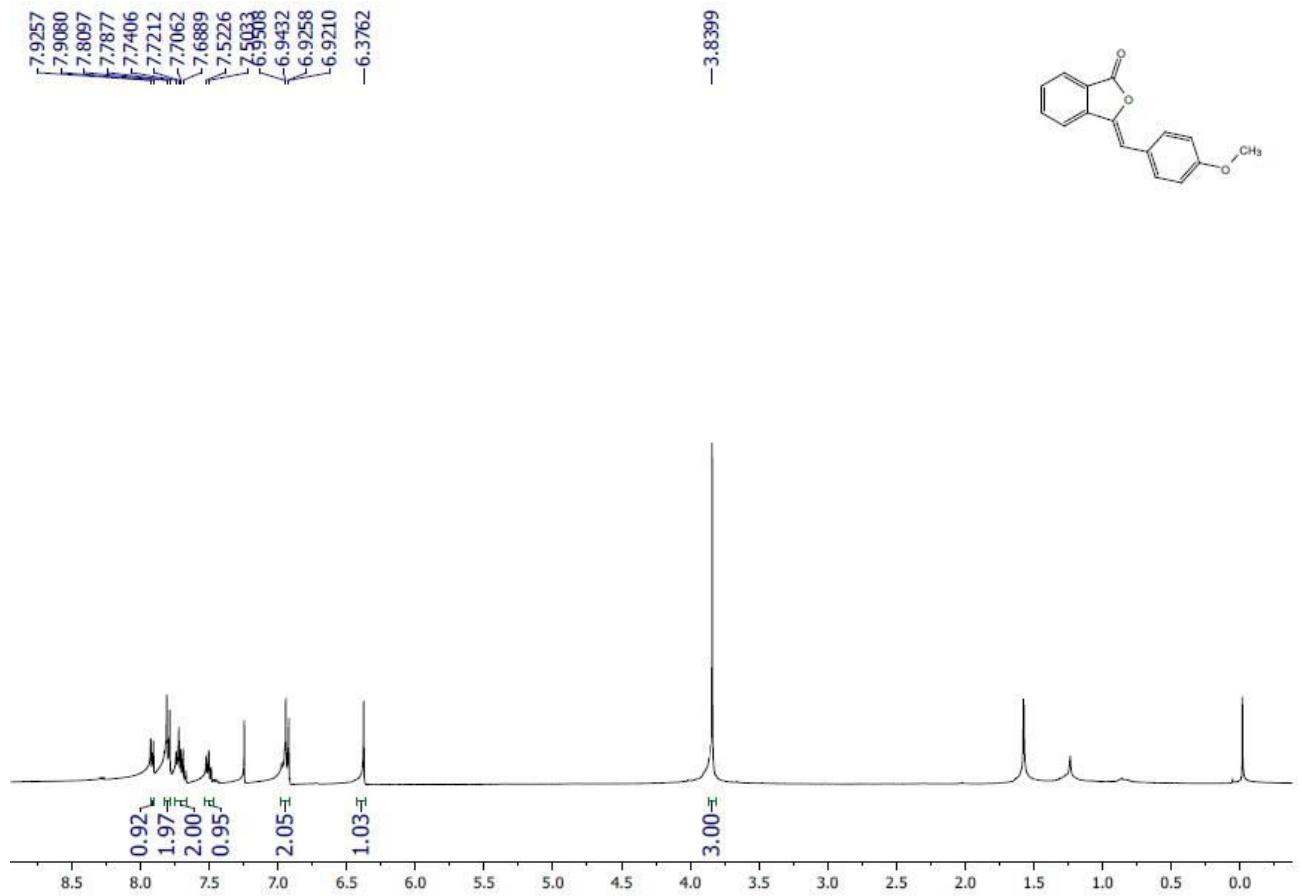


Figure 7: ^1H -NMR spectral data of **11d**.

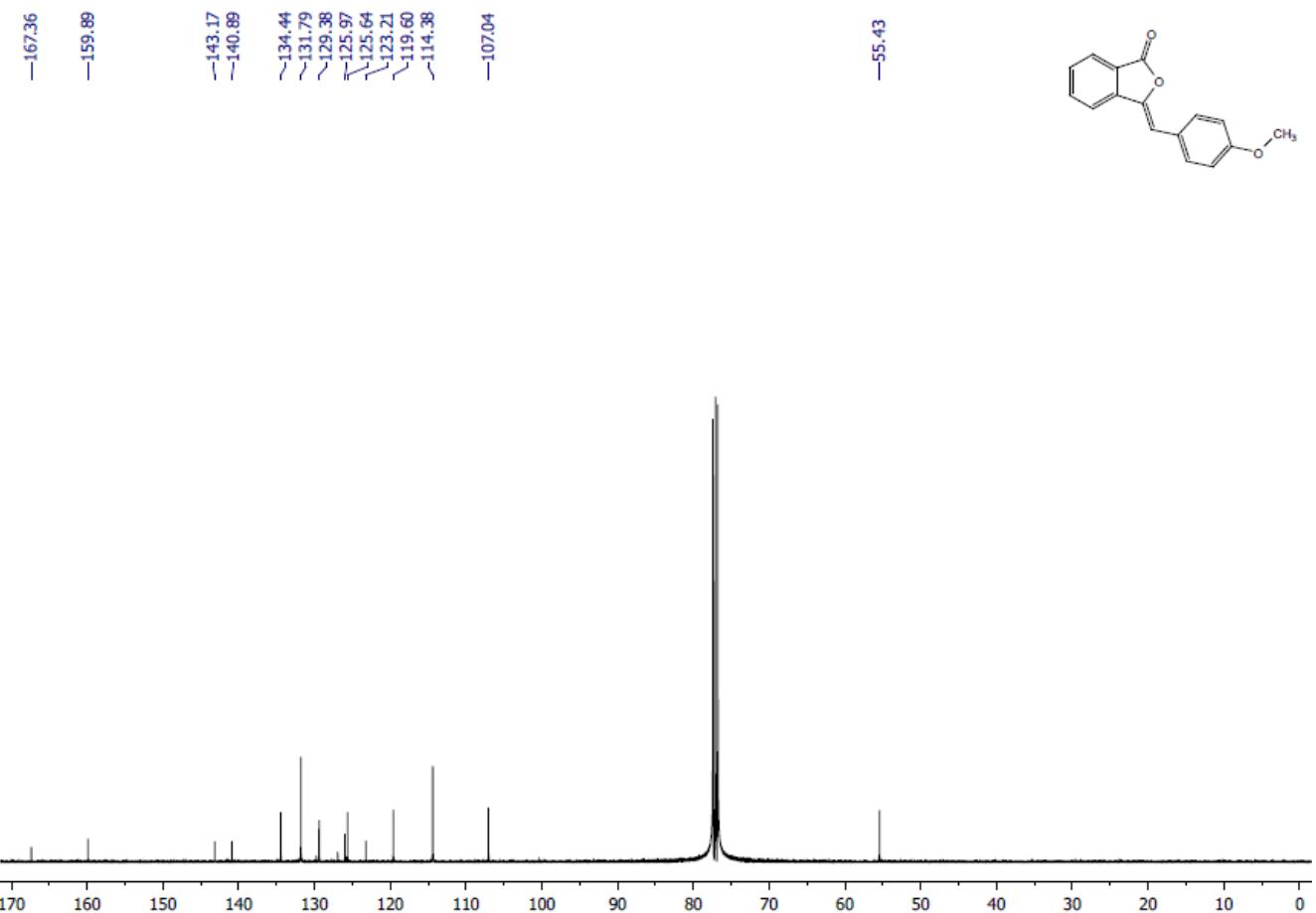


Figure 8: ^{13}C -NMR spectral data of **11d**.

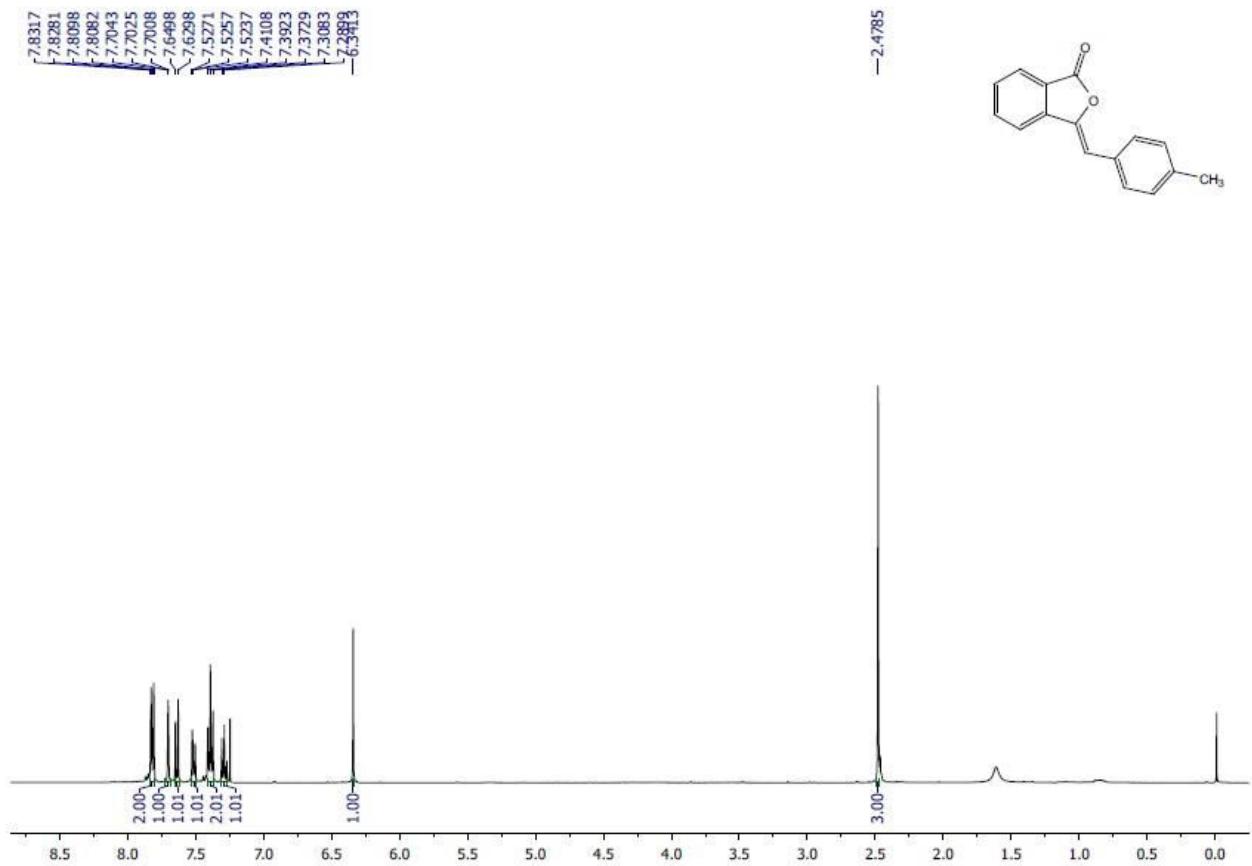


Figure 9: ^1H -NMR spectral data of **11e**.

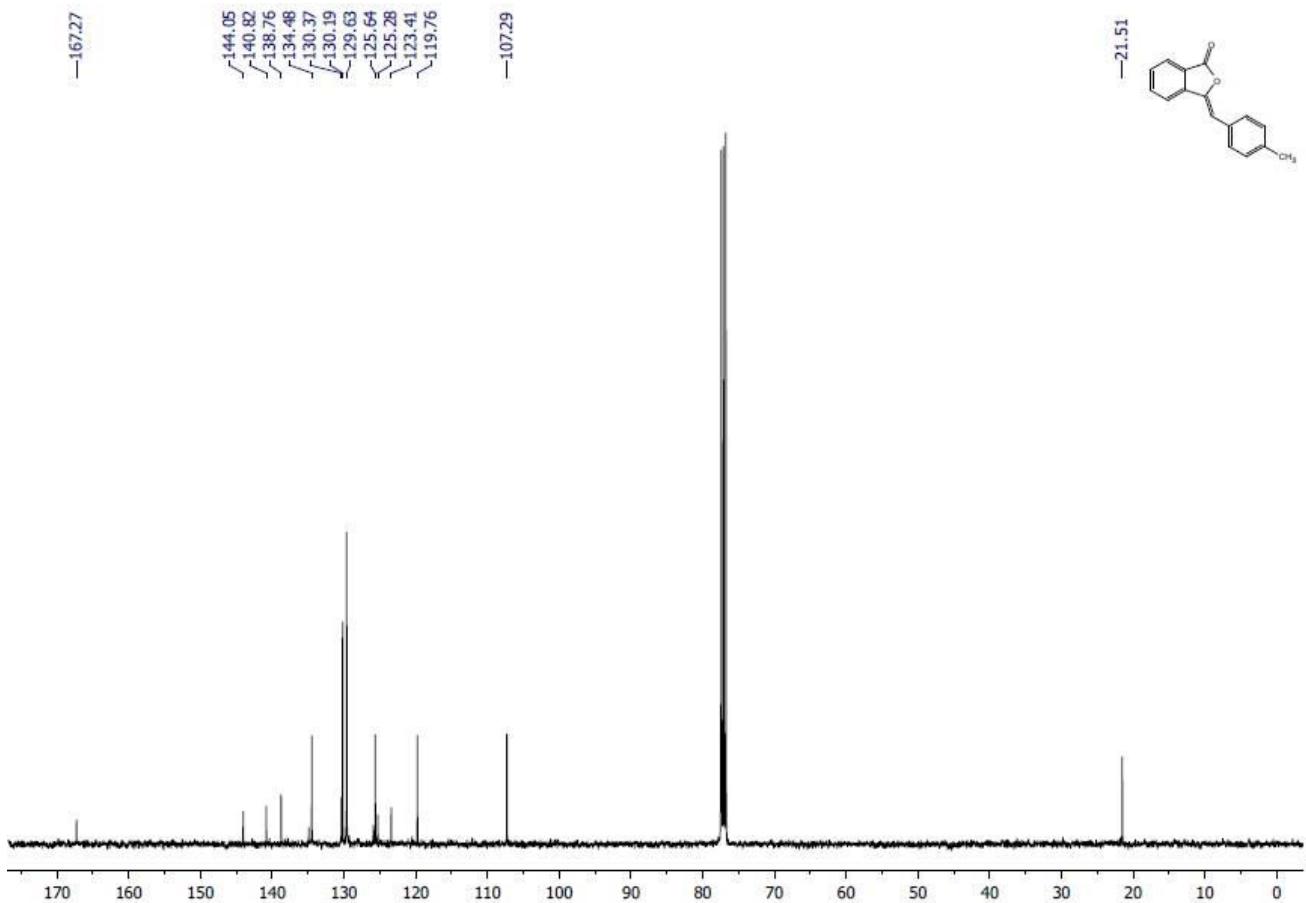


Figure 10: ^{13}C -NMR spectral data of **11e**.

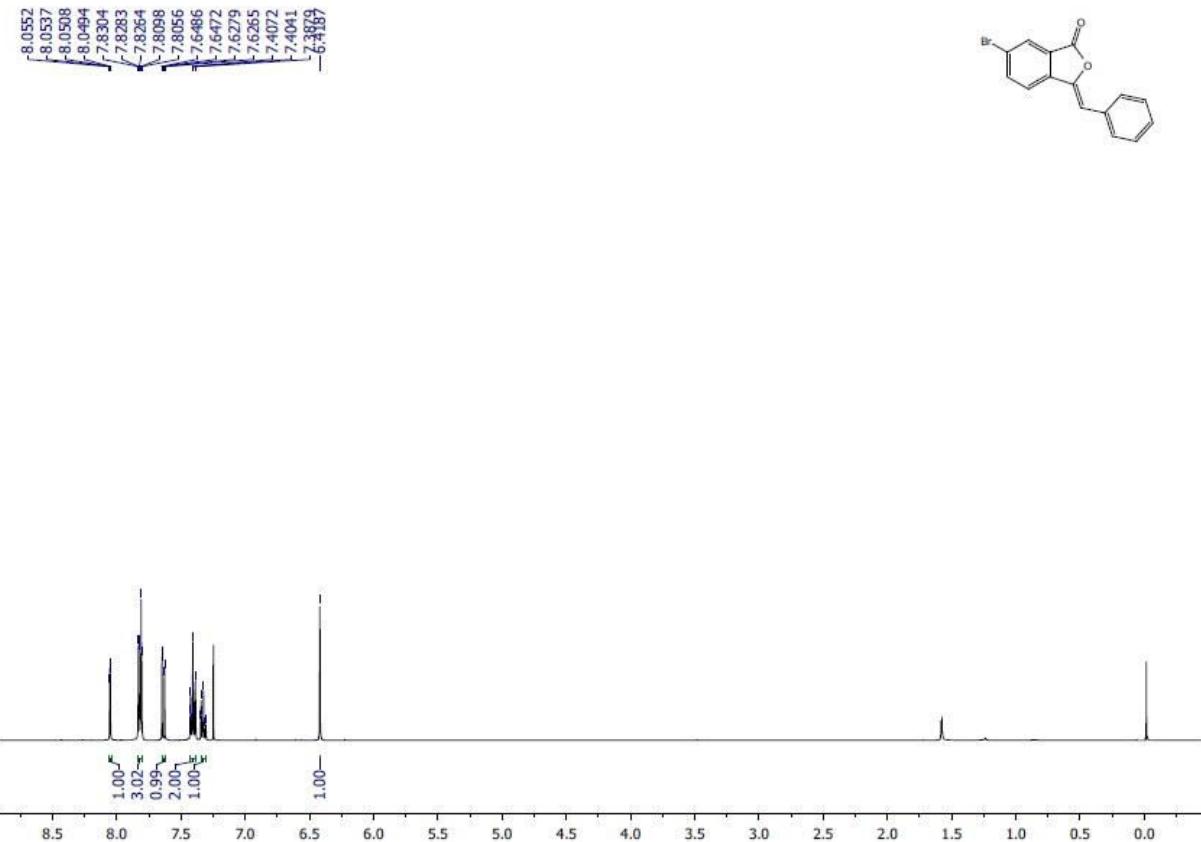


Figure 11: ¹H-NMR spectral data of **12a**.

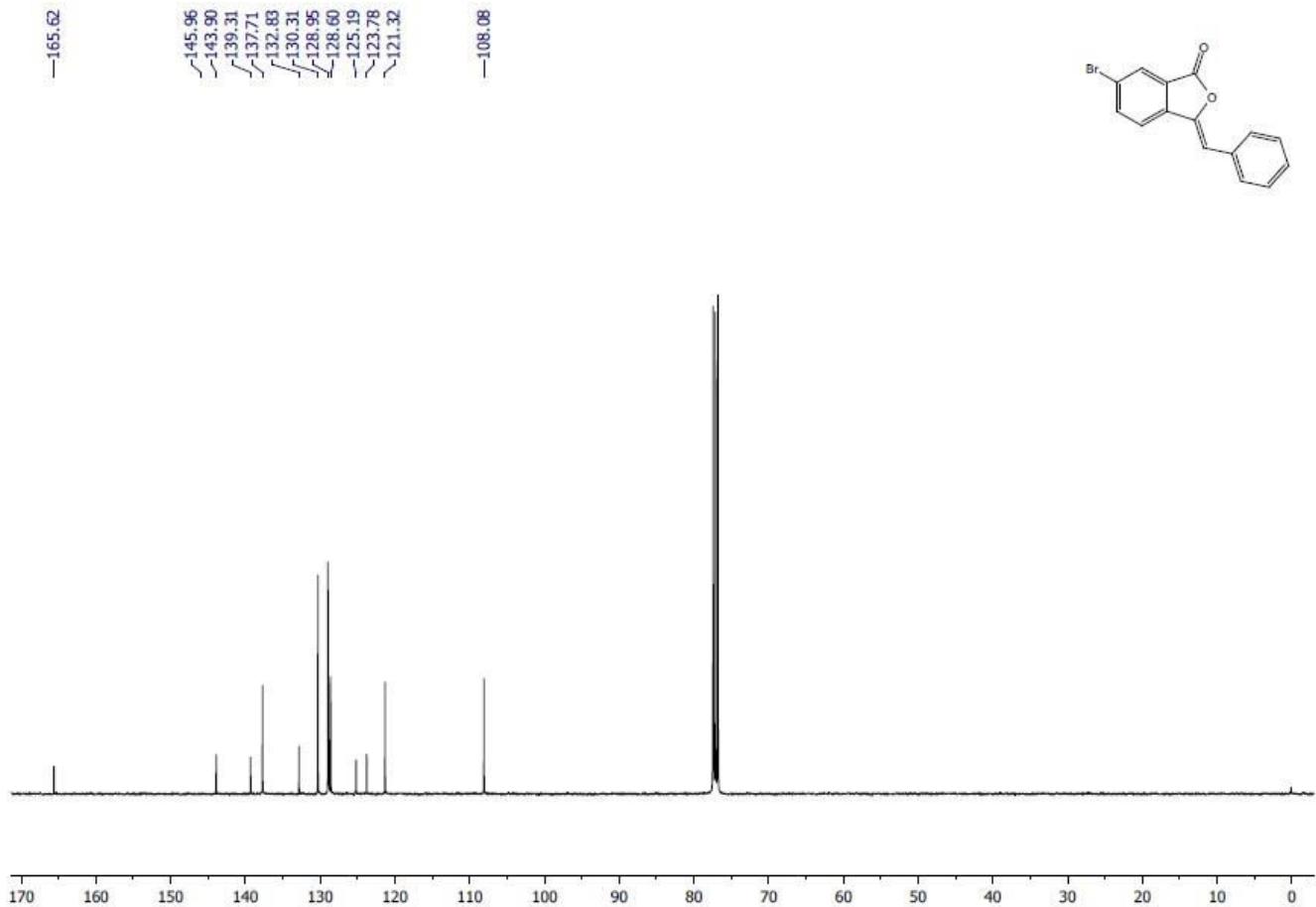


Figure 12: ¹³C-NMR spectral data of **12a**.

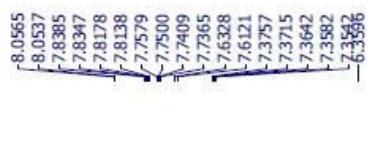


Figure 13: ¹H-NMR spectral data of **12b**.

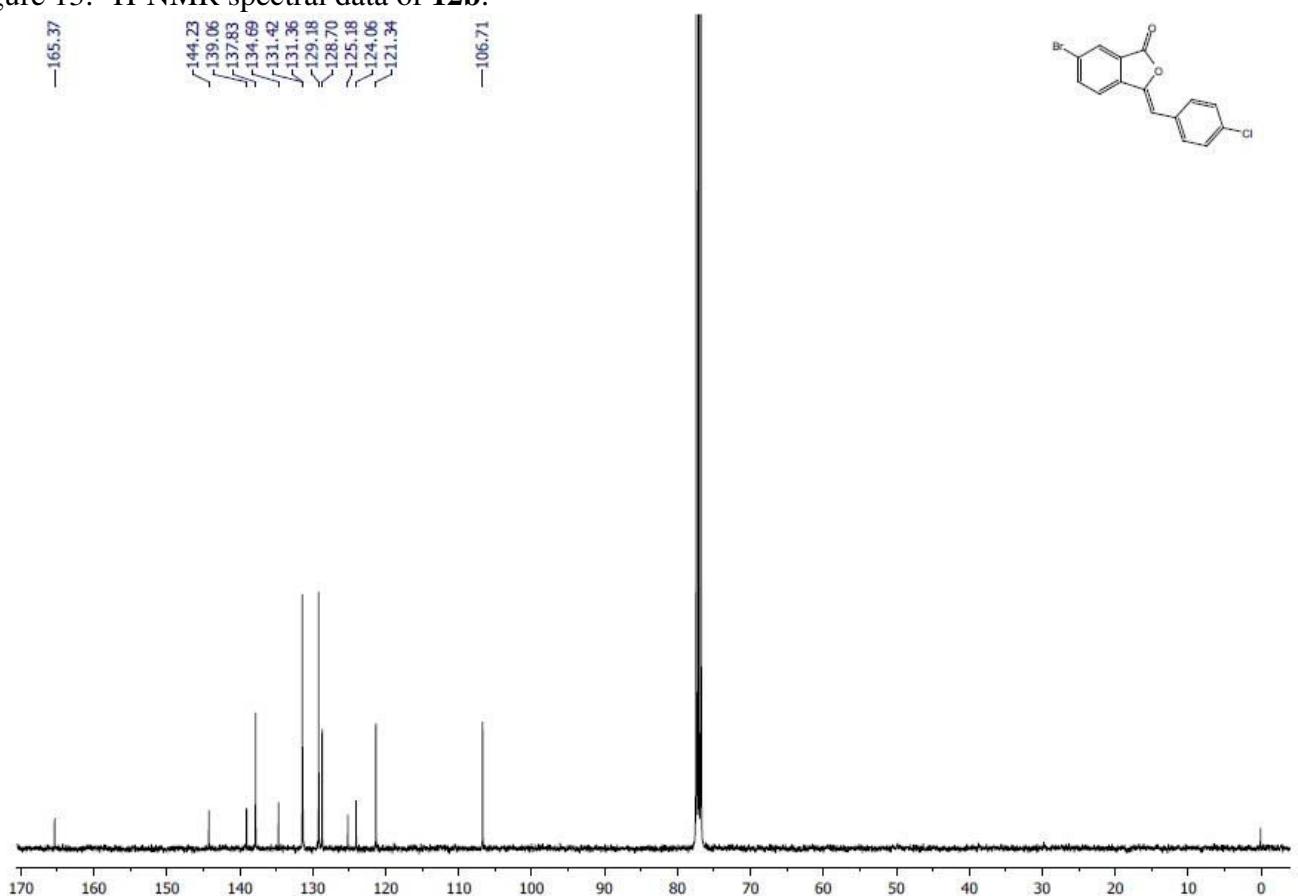


Figure 14: ¹³C-NMR spectral data of **12b**.

8.0668
8.0645
7.8461
7.8420
7.8256
7.8237
7.8213
7.6982
7.6795
7.6771
7.6418
7.6211
7.5387
7.5172
7.5186
-6.3511

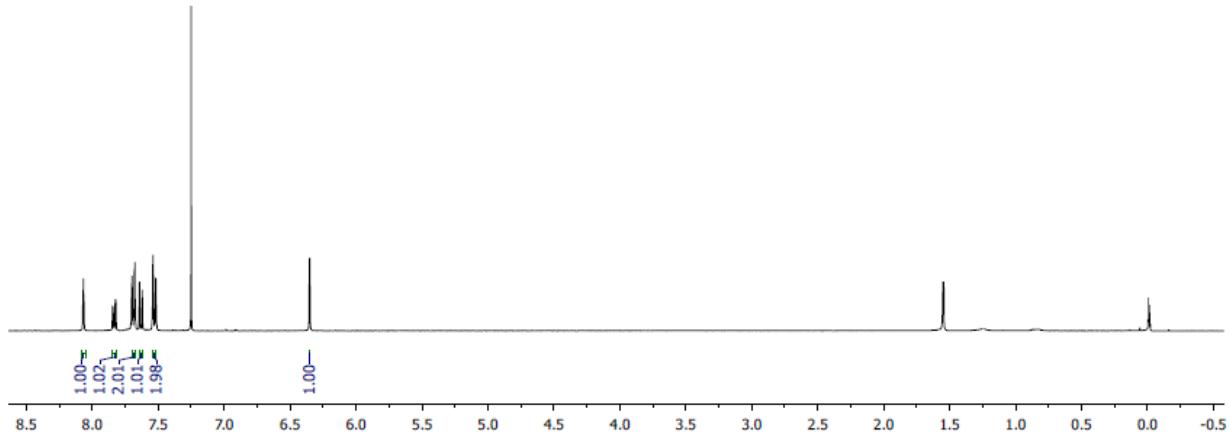
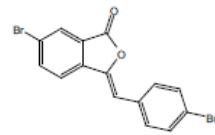


Figure 15: ^1H -NMR spectral data of **12c**.

-165.35
~144.46
~139.07
~137.85
~132.15
~131.78
~131.64
~128.73
~125.21
~124.10
~123.04
~121.36

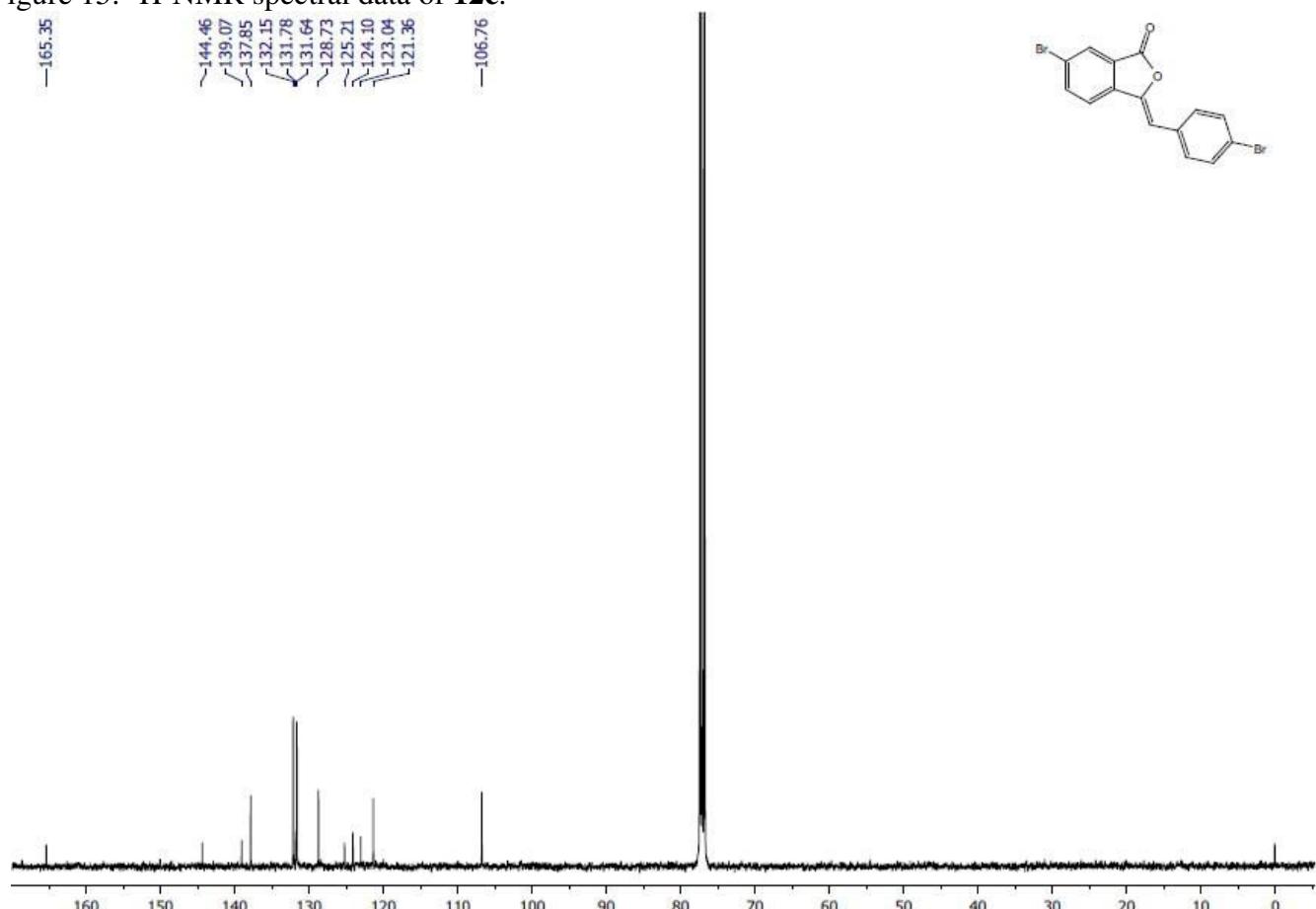
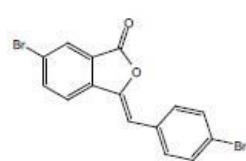


Figure 16: ^{13}C -NMR spectral data of **12c**.

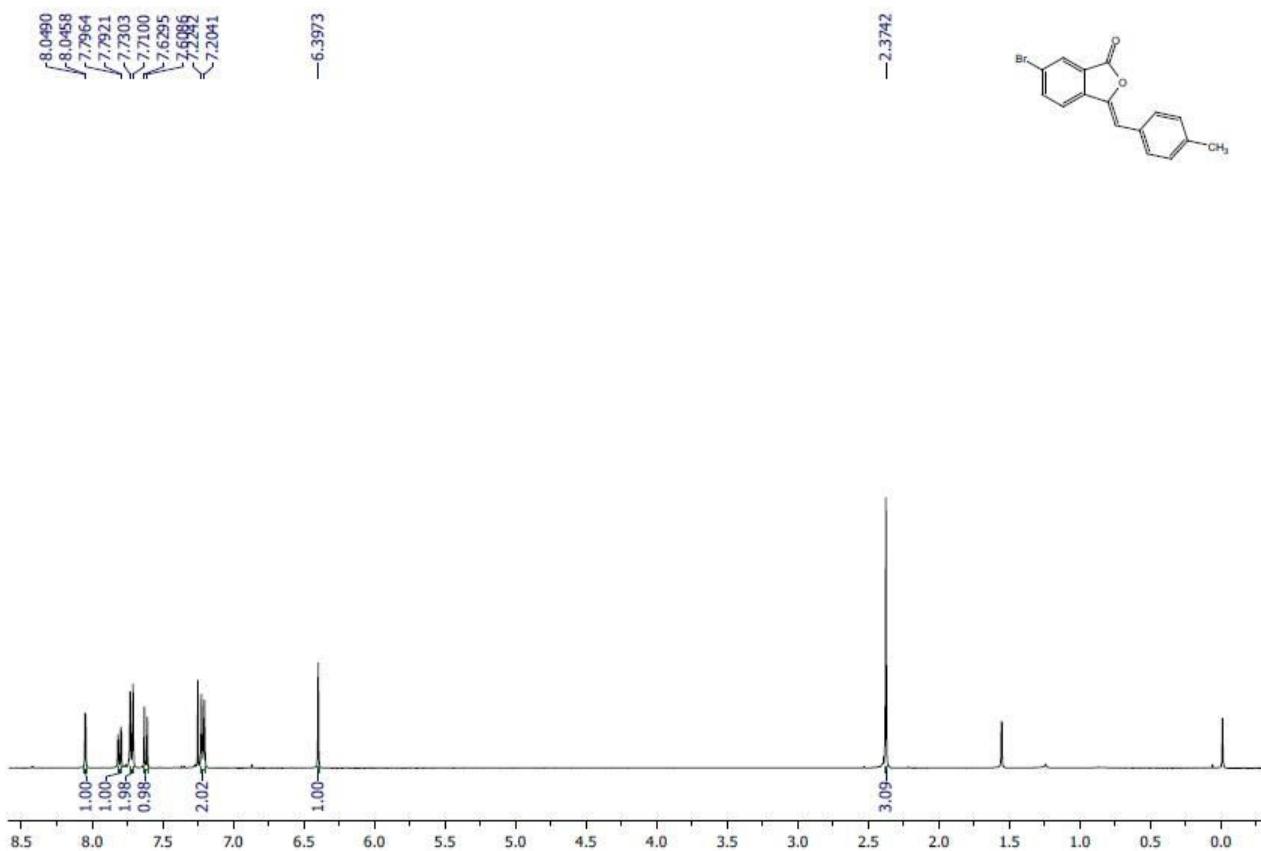


Figure 17: ¹H-NMR spectral data of **12d**.

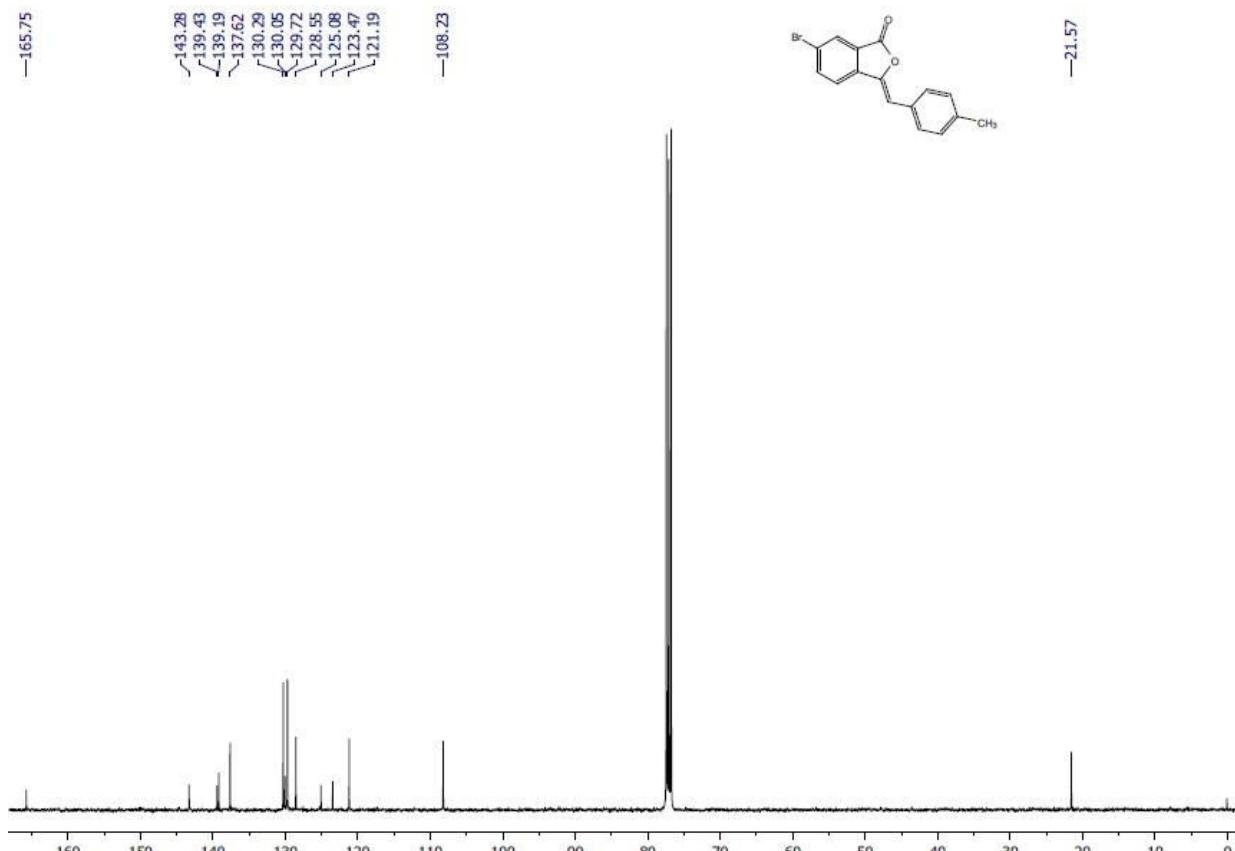


Figure 18: ¹³C-NMR spectral data of **12d**.

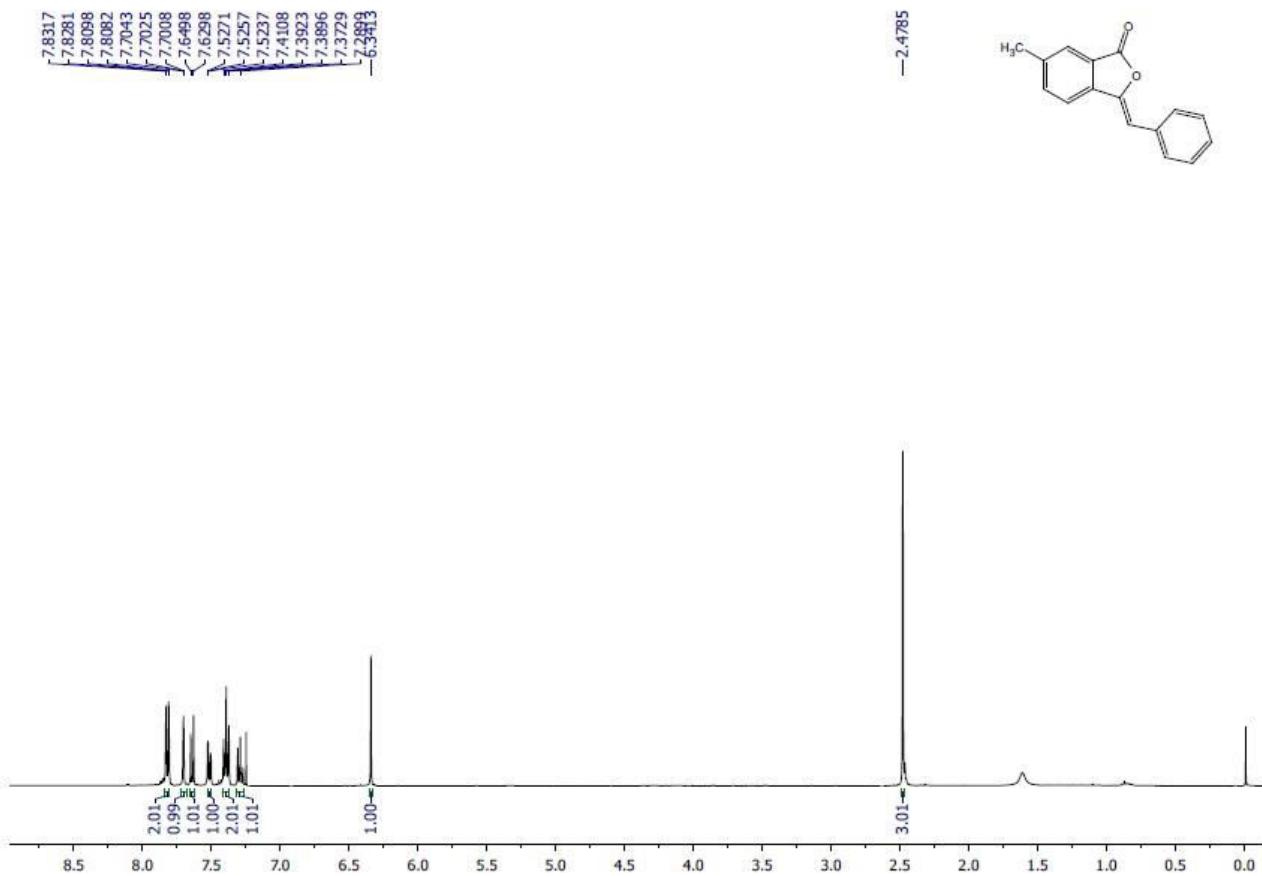


Figure 19: ^1H -NMR spectral data of **13a**.

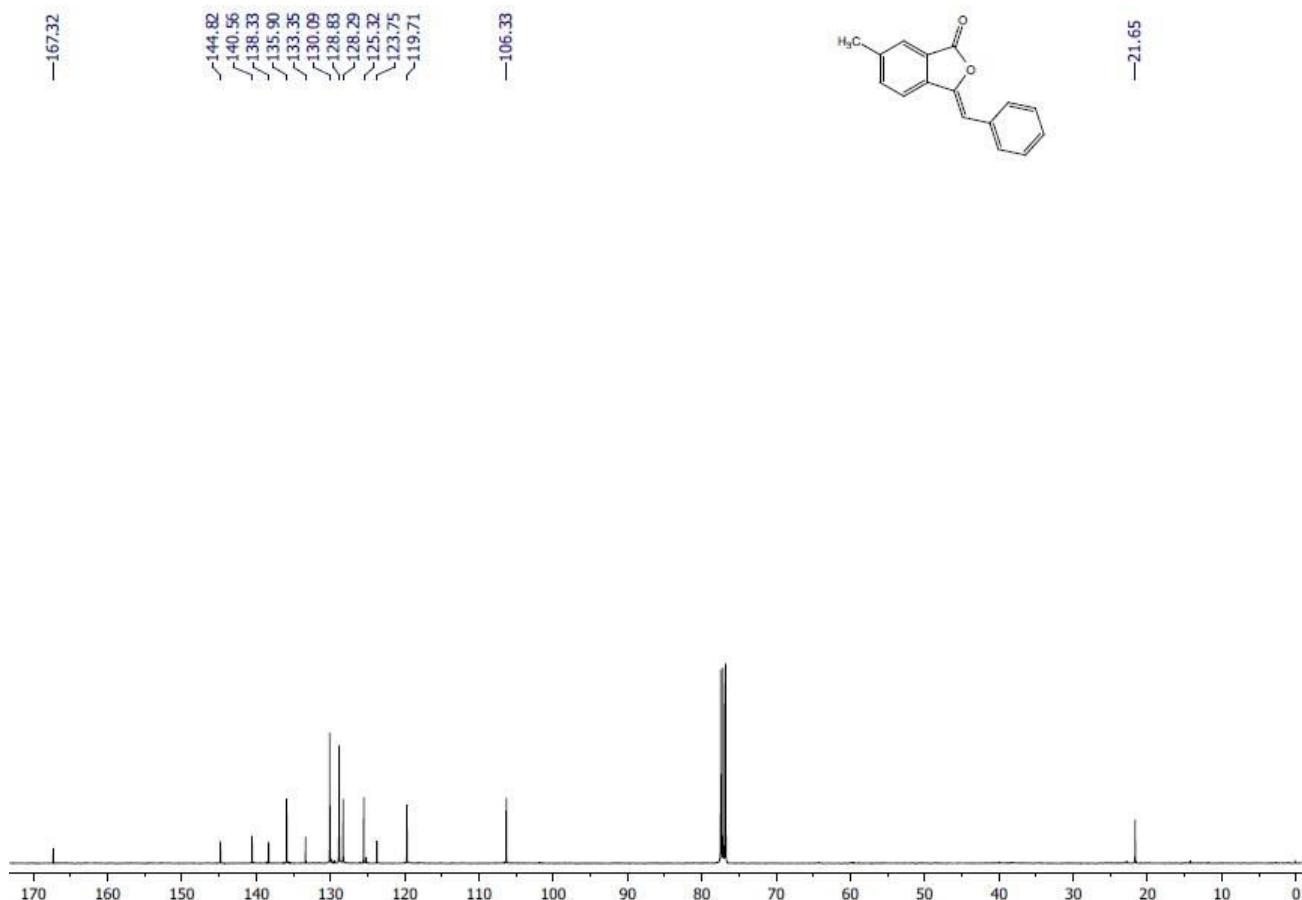


Figure 20: ^{13}C -NMR spectral data of **13a**.

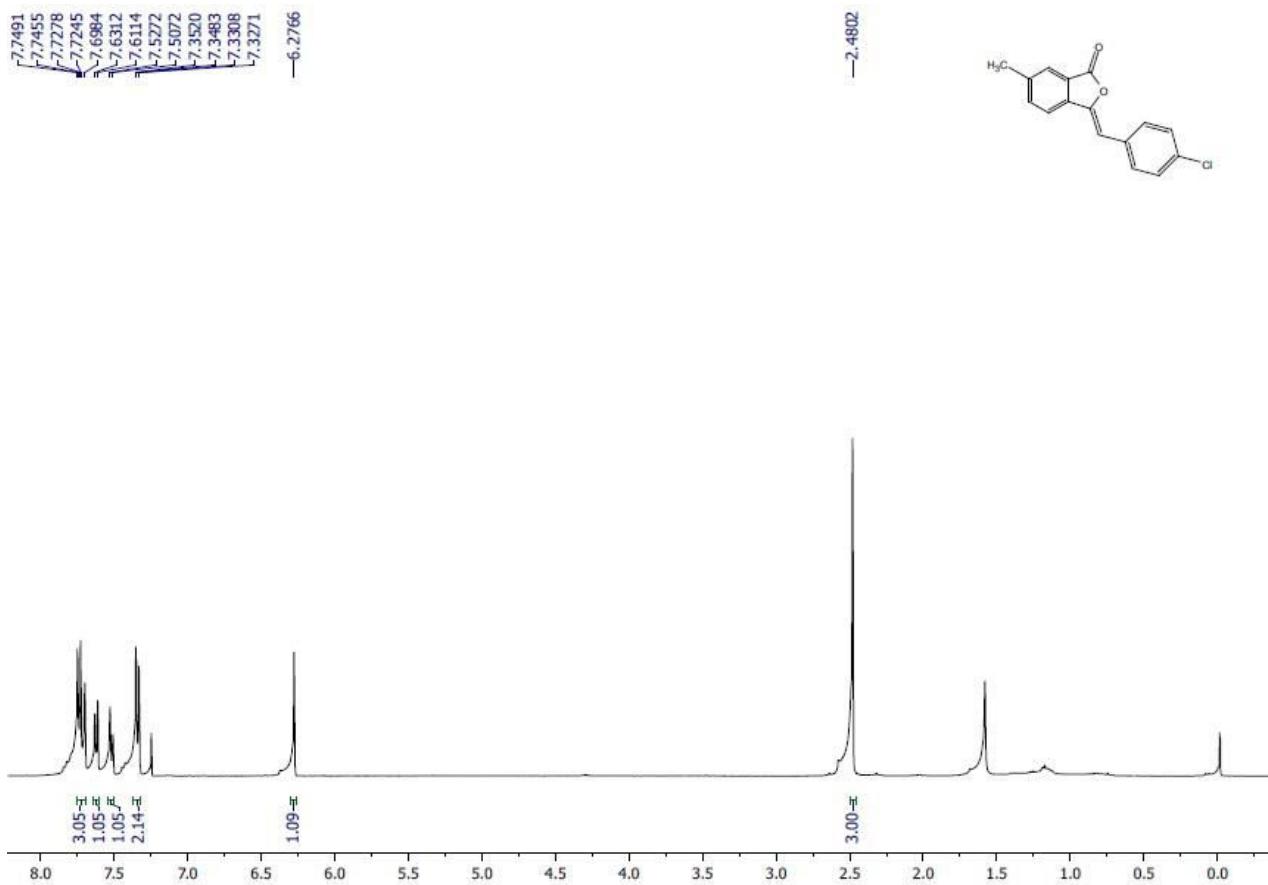


Figure 21: ^1H -NMR spectral data of **13b**.

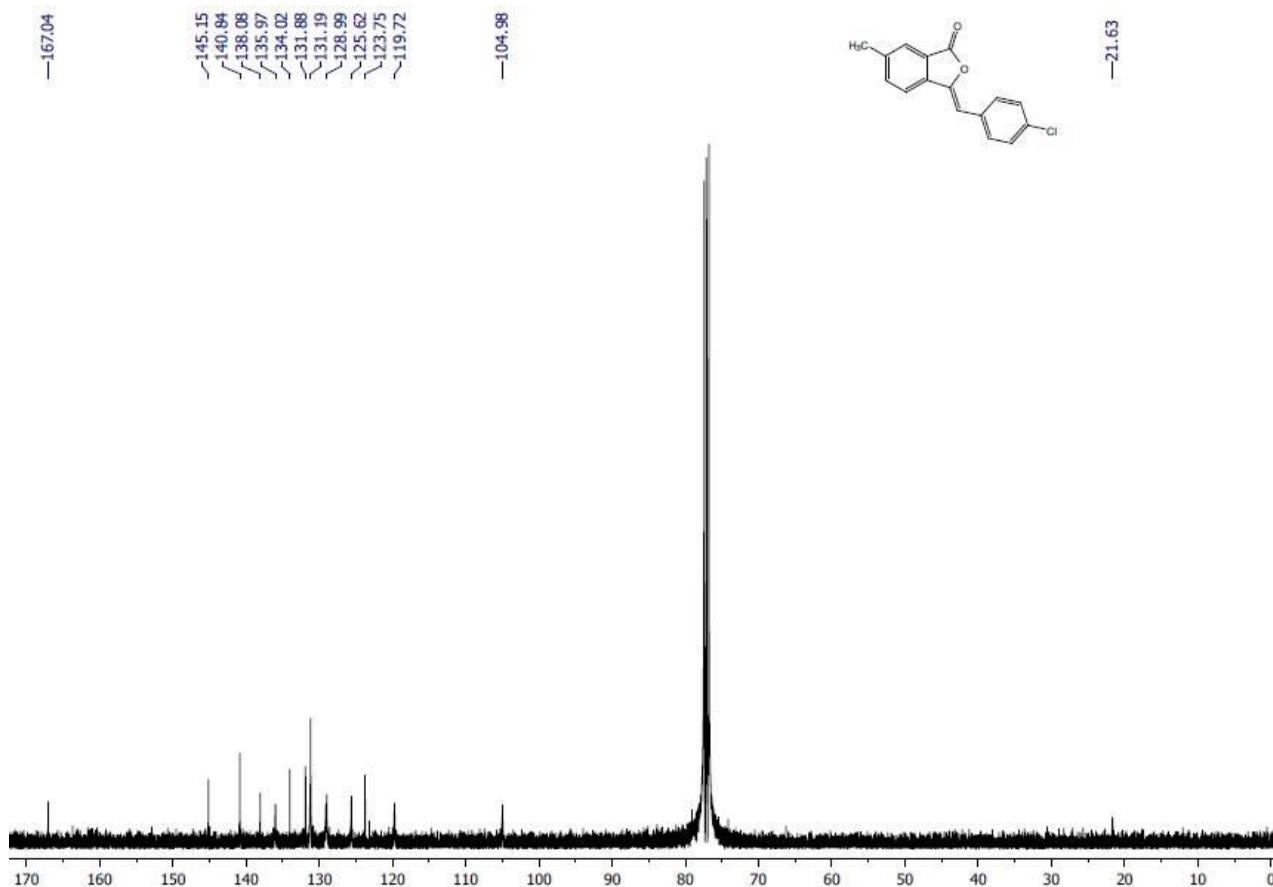


Figure 22: ^{13}C -NMR spectral data of **13b**.

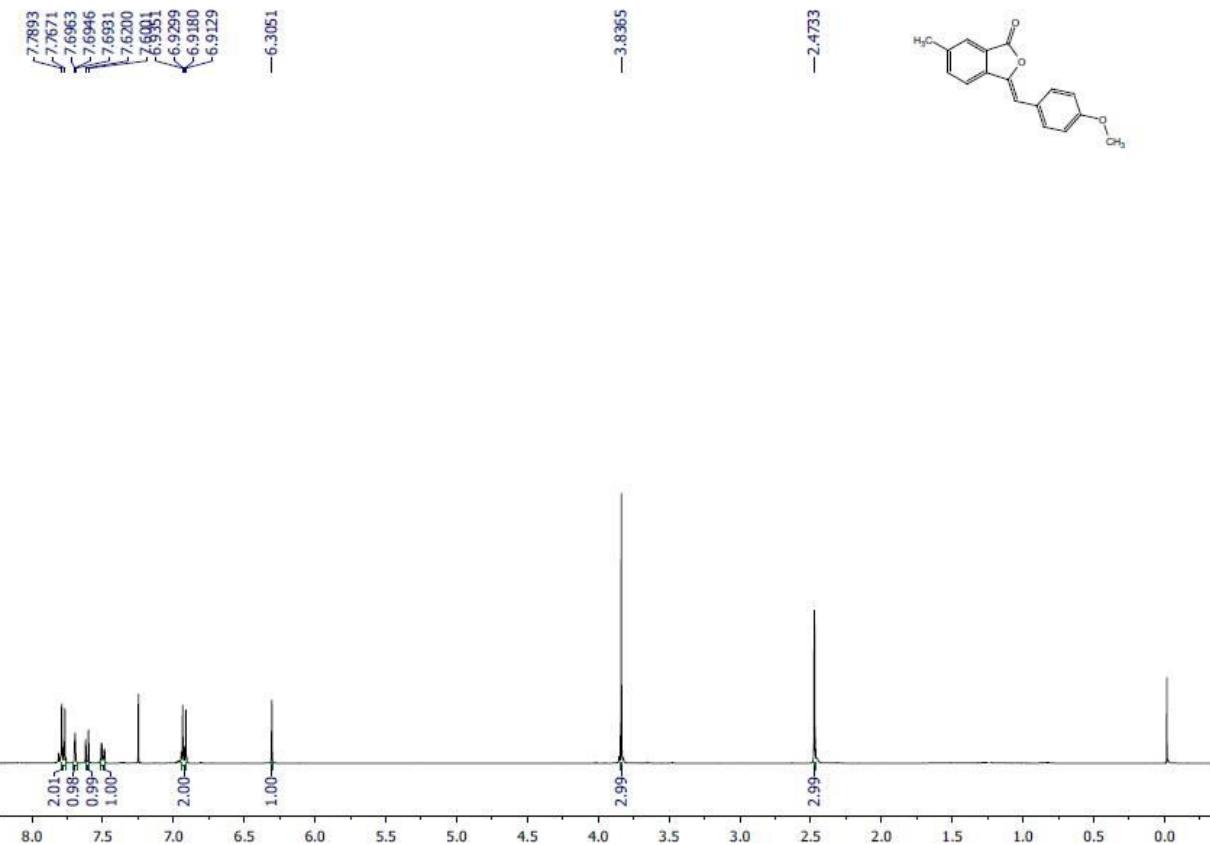


Figure 23: ^1H -NMR spectral data of **13c**.

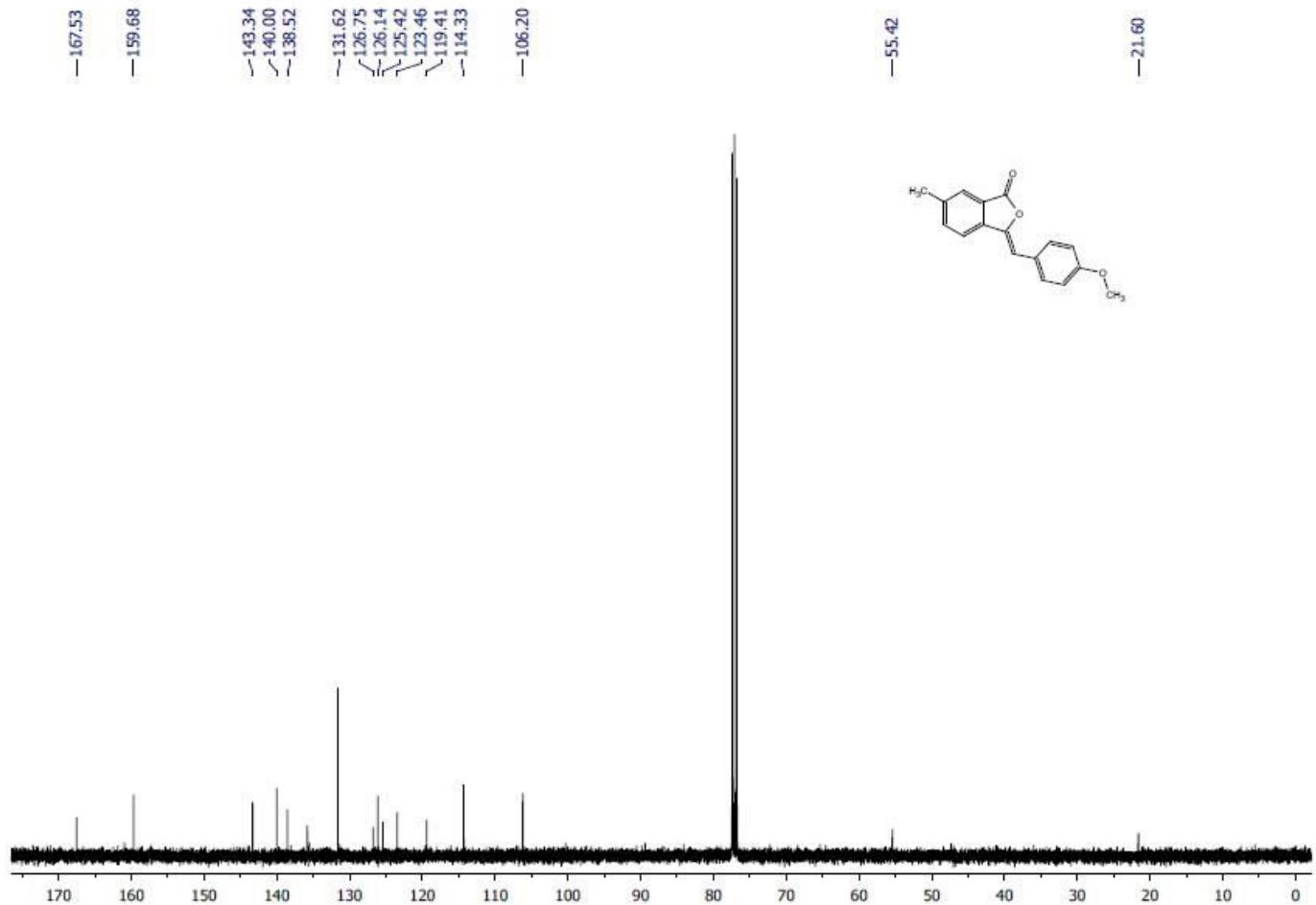


Figure 24: ^{13}C -NMR spectral data of **13c**.

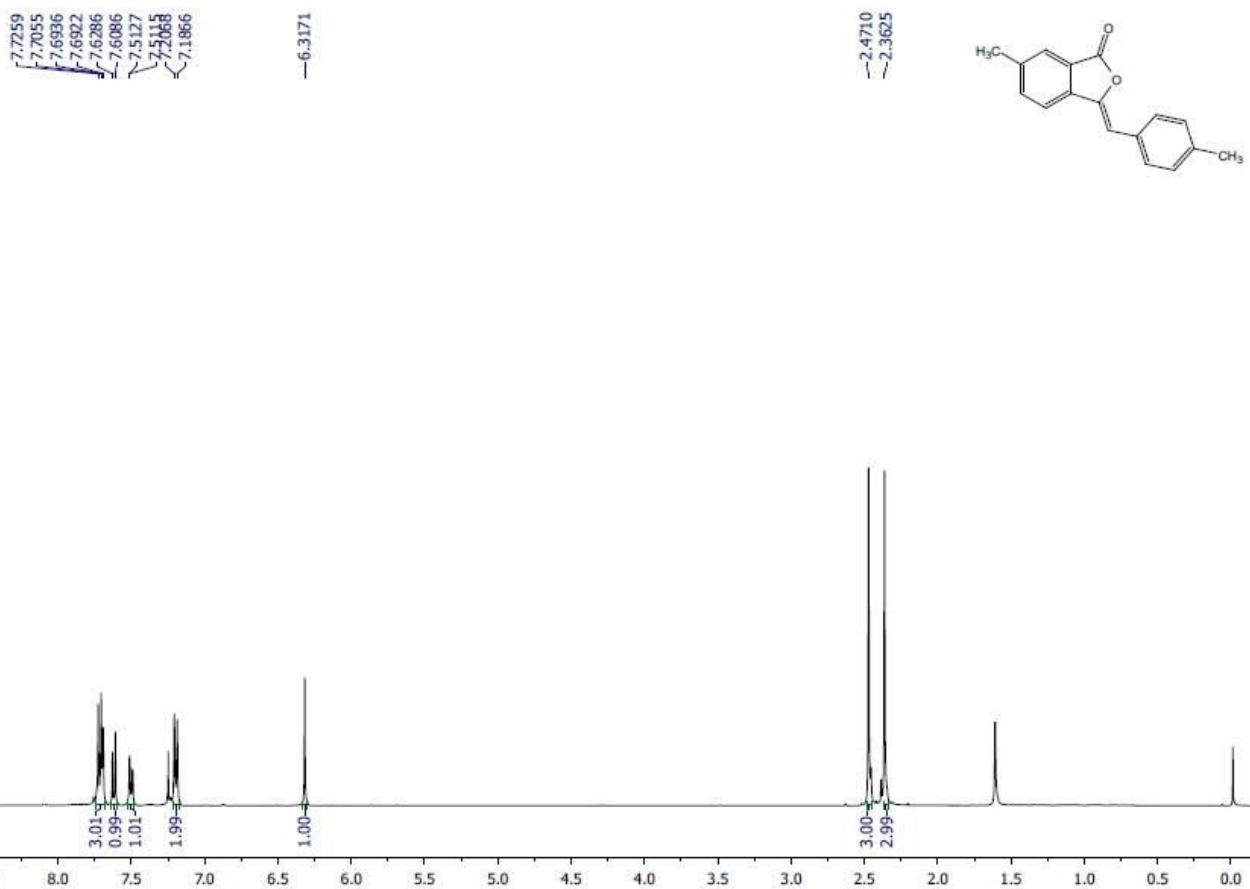


Figure 25: ^1H -NMR spectral data of **13d**.

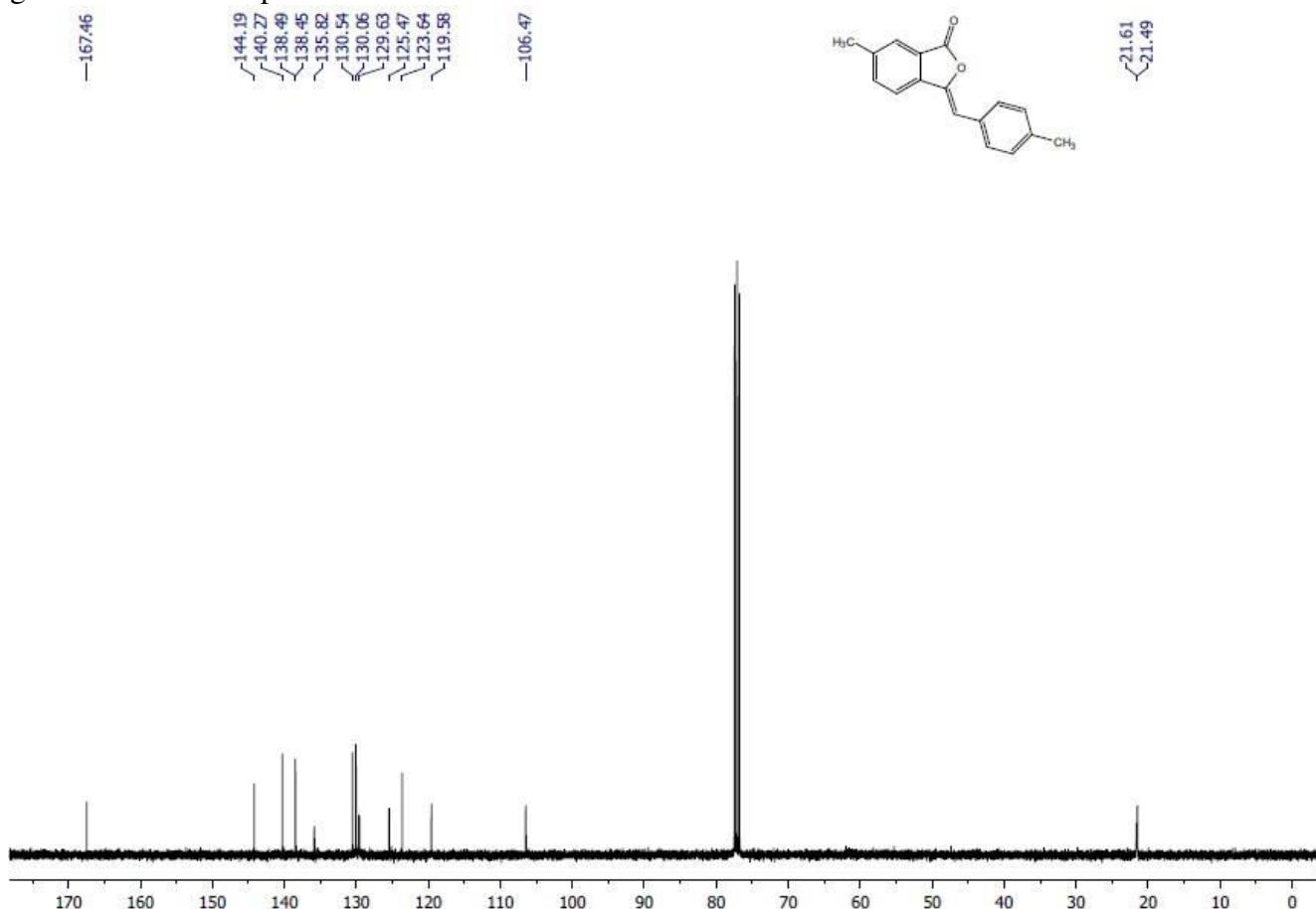


Figure 26: ^{13}C -NMR spectral data of **13d**.

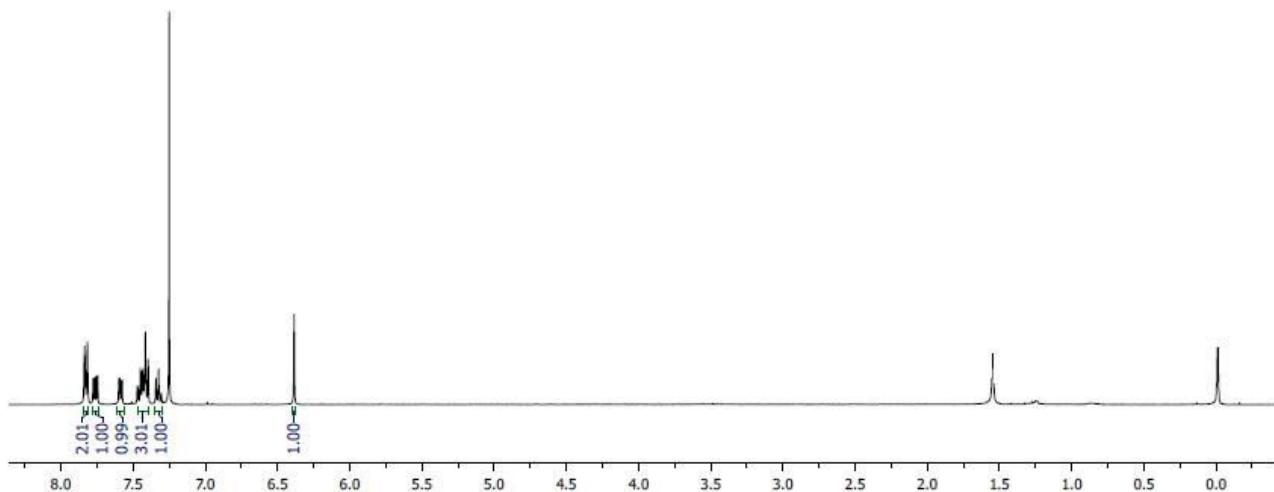
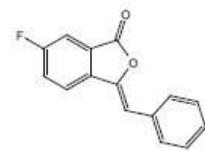


Figure 27: ¹H-NMR spectral data of **14a**.

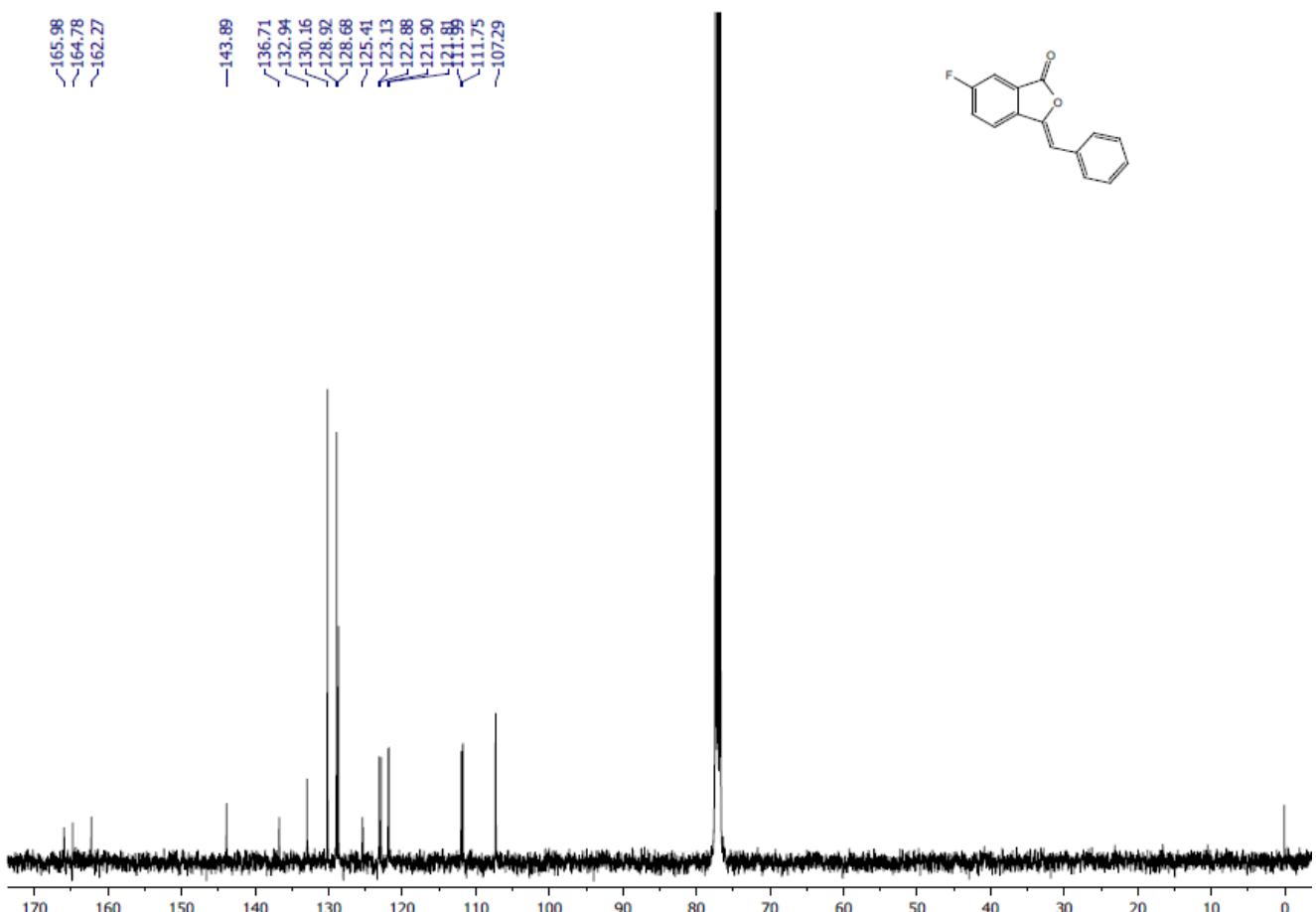
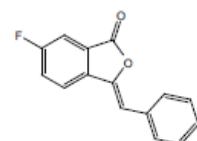
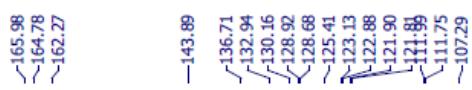


Figure 28: ¹³C-NMR spectral data of **14a**.

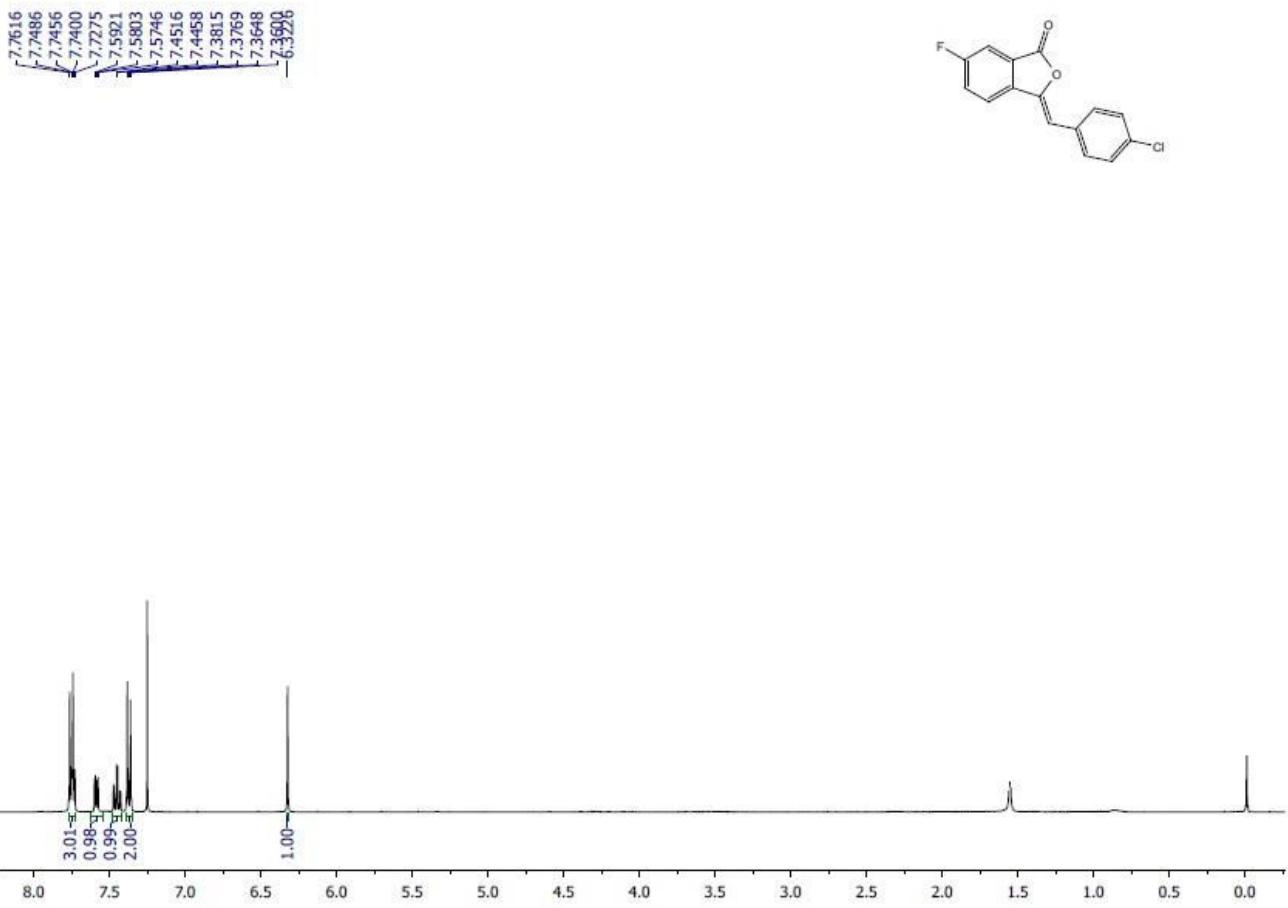


Figure 29: ^1H -NMR spectral data of **14b**.

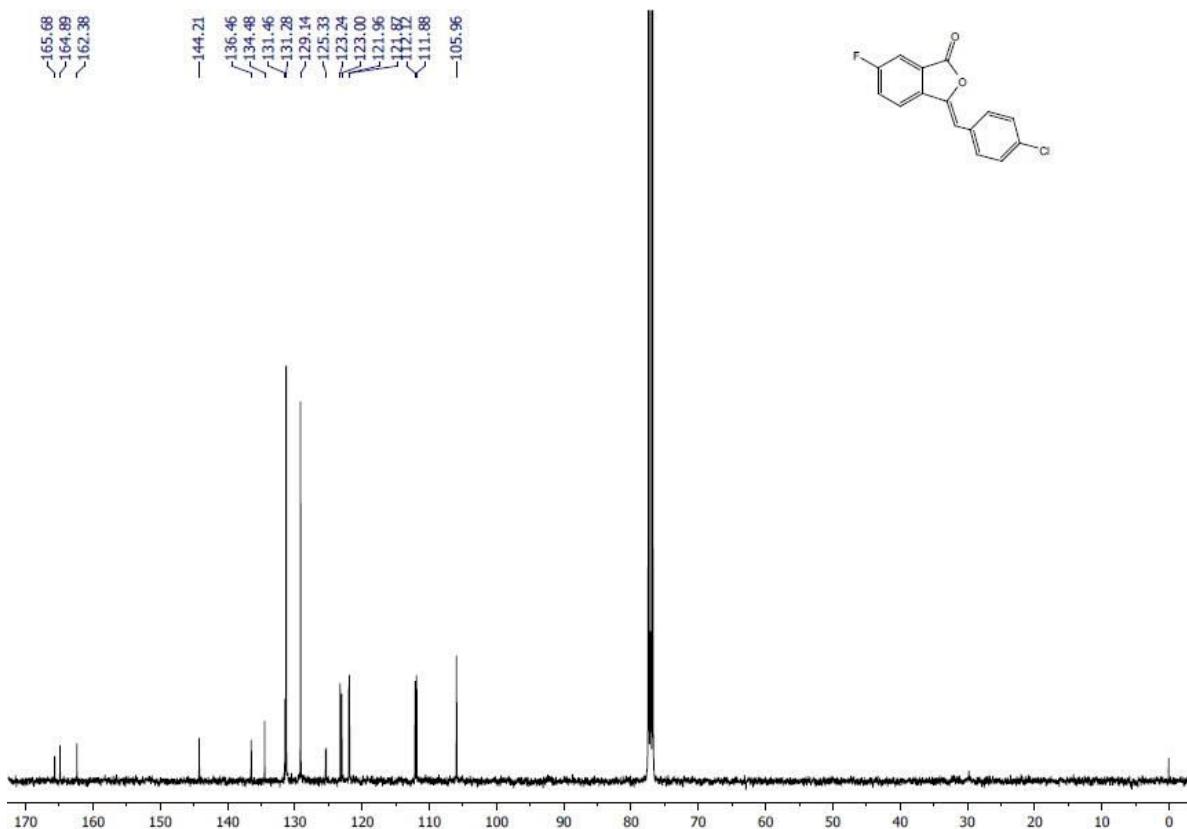


Figure 30: ^{13}C -NMR spectral data of **14b**.

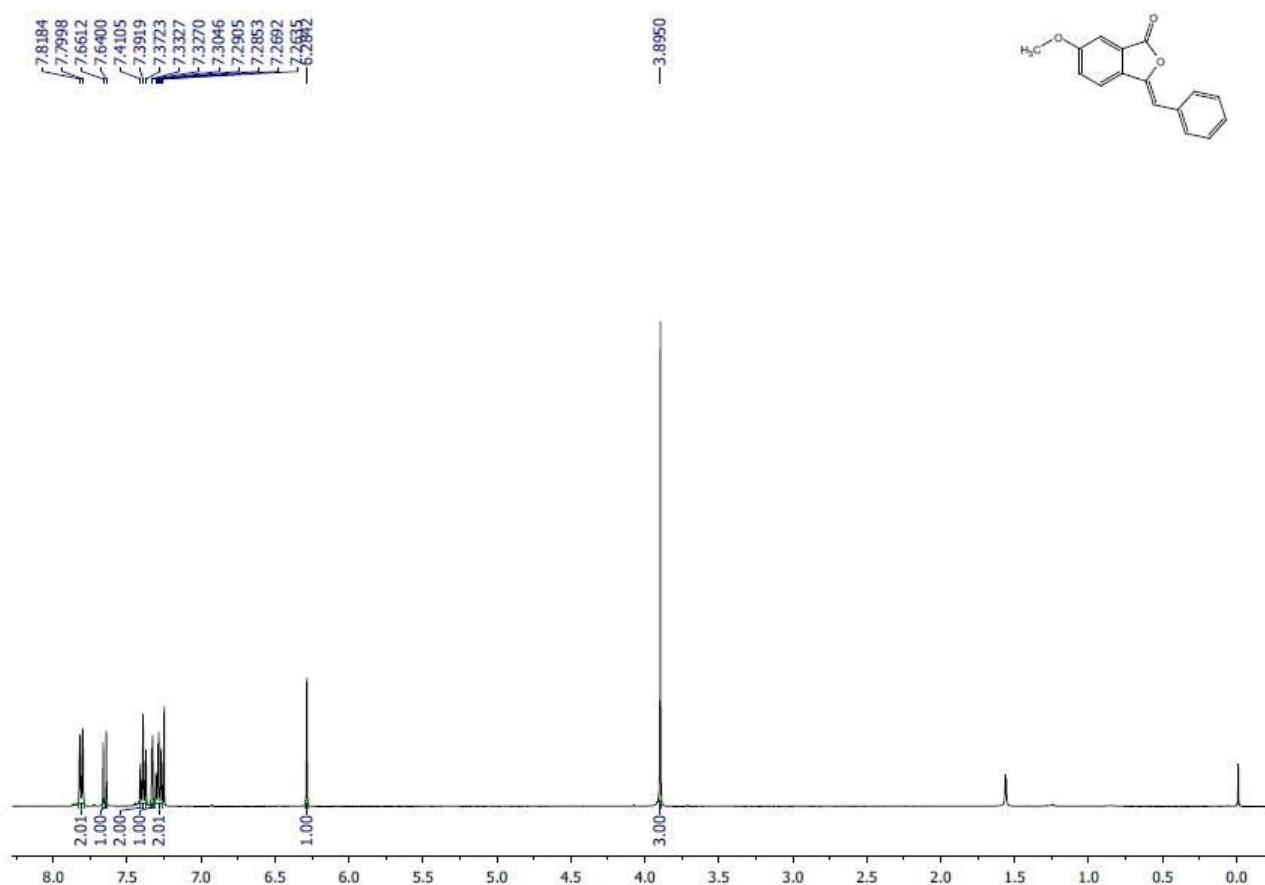


Figure 31: ^1H -NMR spectral data of **15a**.

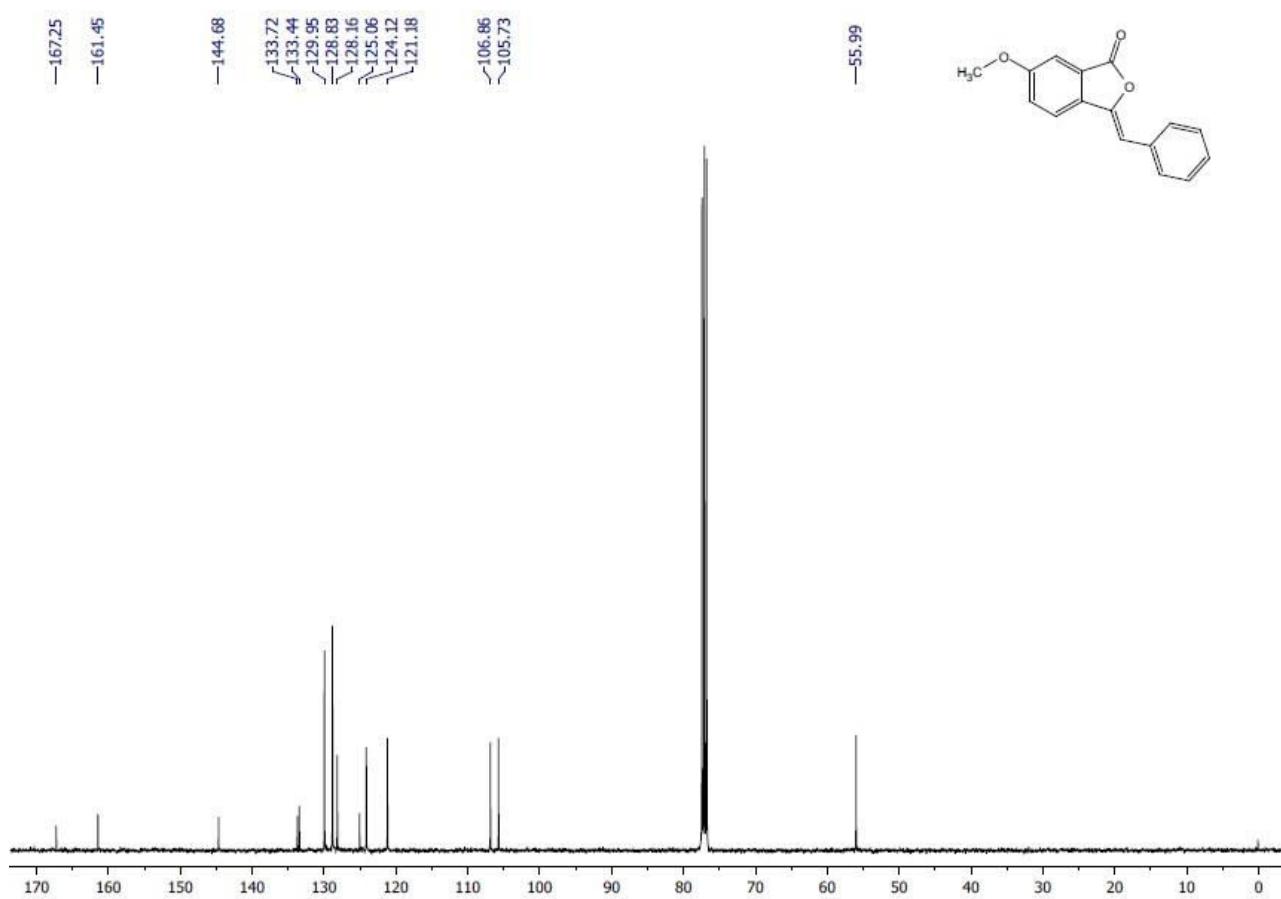


Figure 32: ^{13}C -NMR spectral data of **15a**.

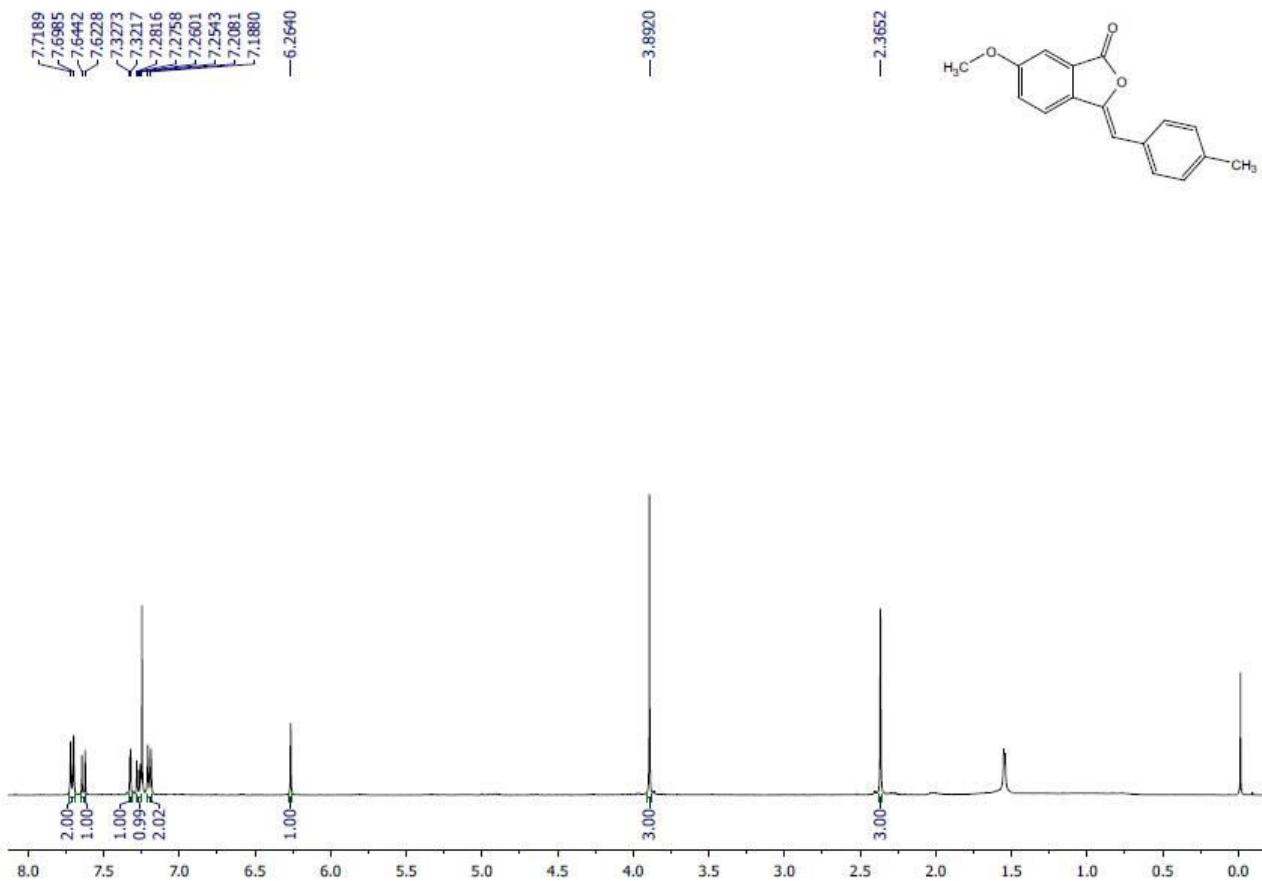


Figure 33: ^1H -NMR spectral data of **15b**.

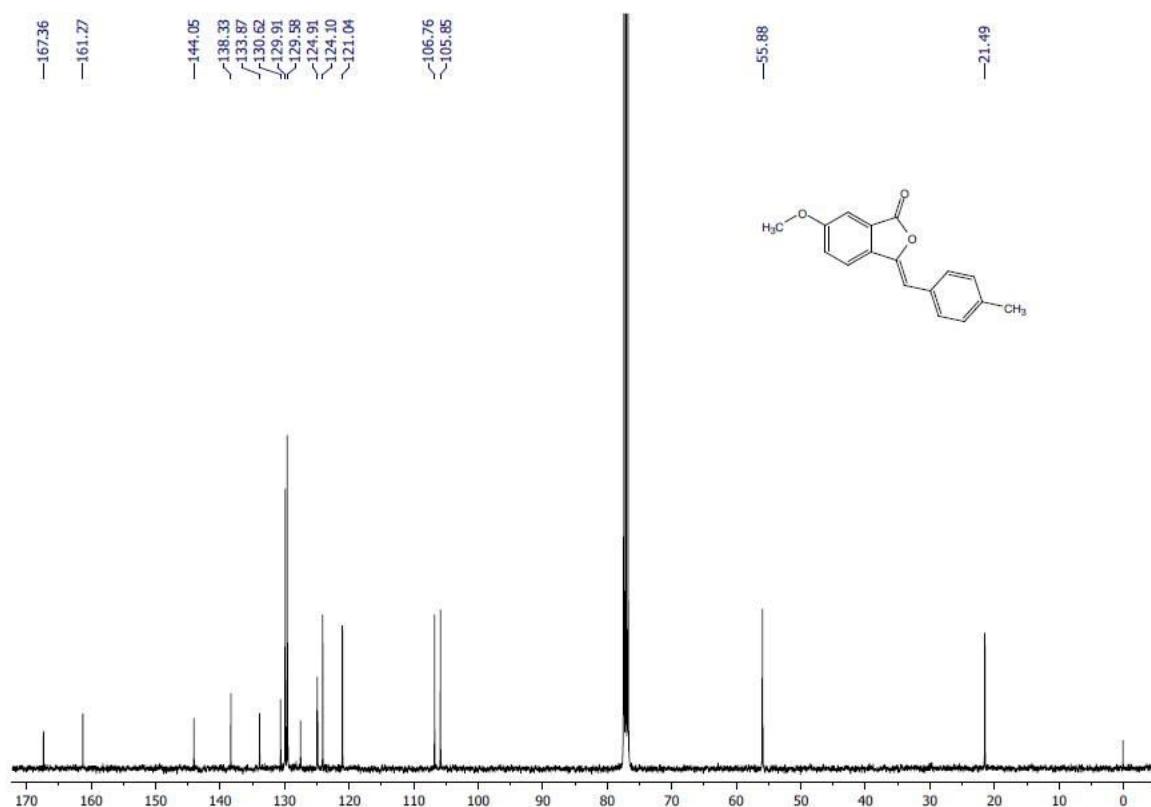


Figure 34: ^{13}C -NMR spectral data of **15b**.

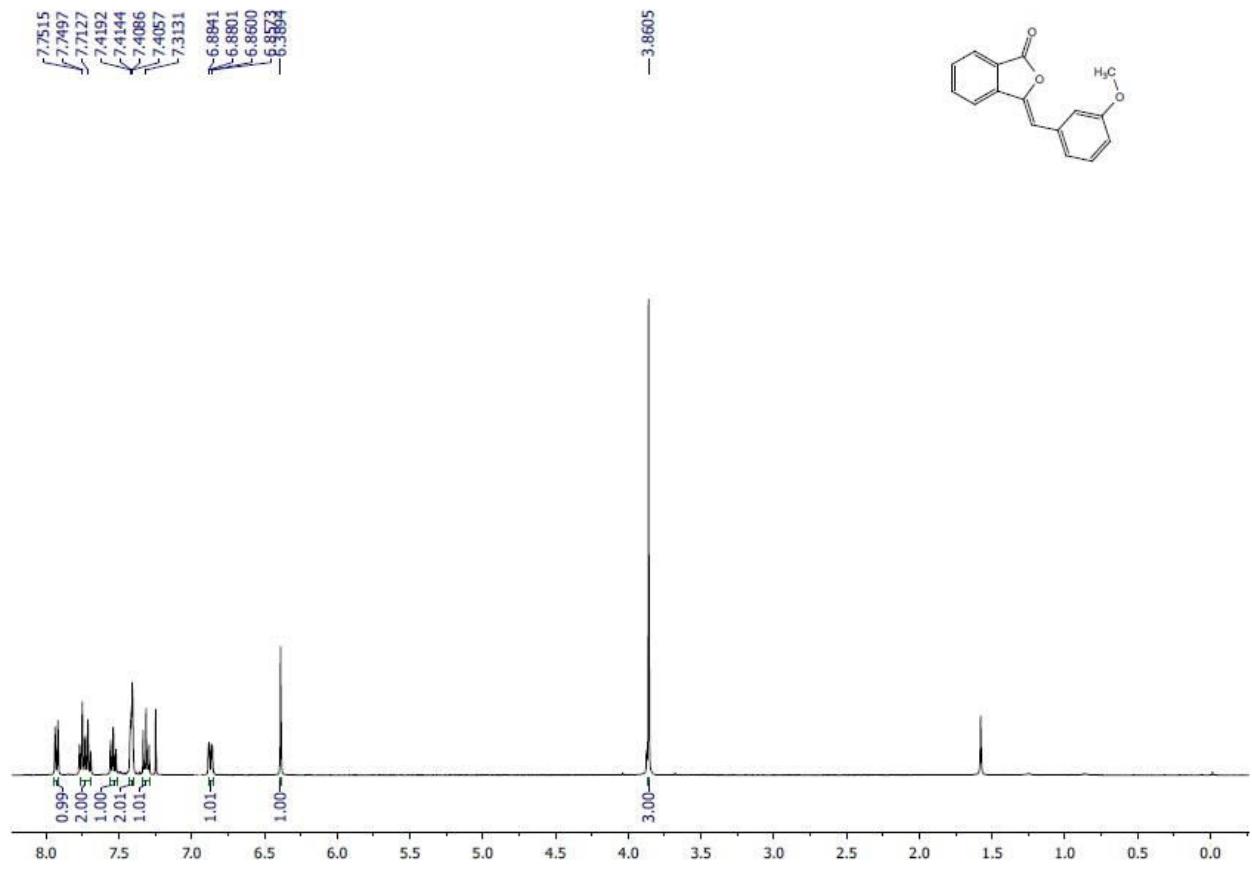


Figure 35: ^1H -NMR spectral data of **16a**.

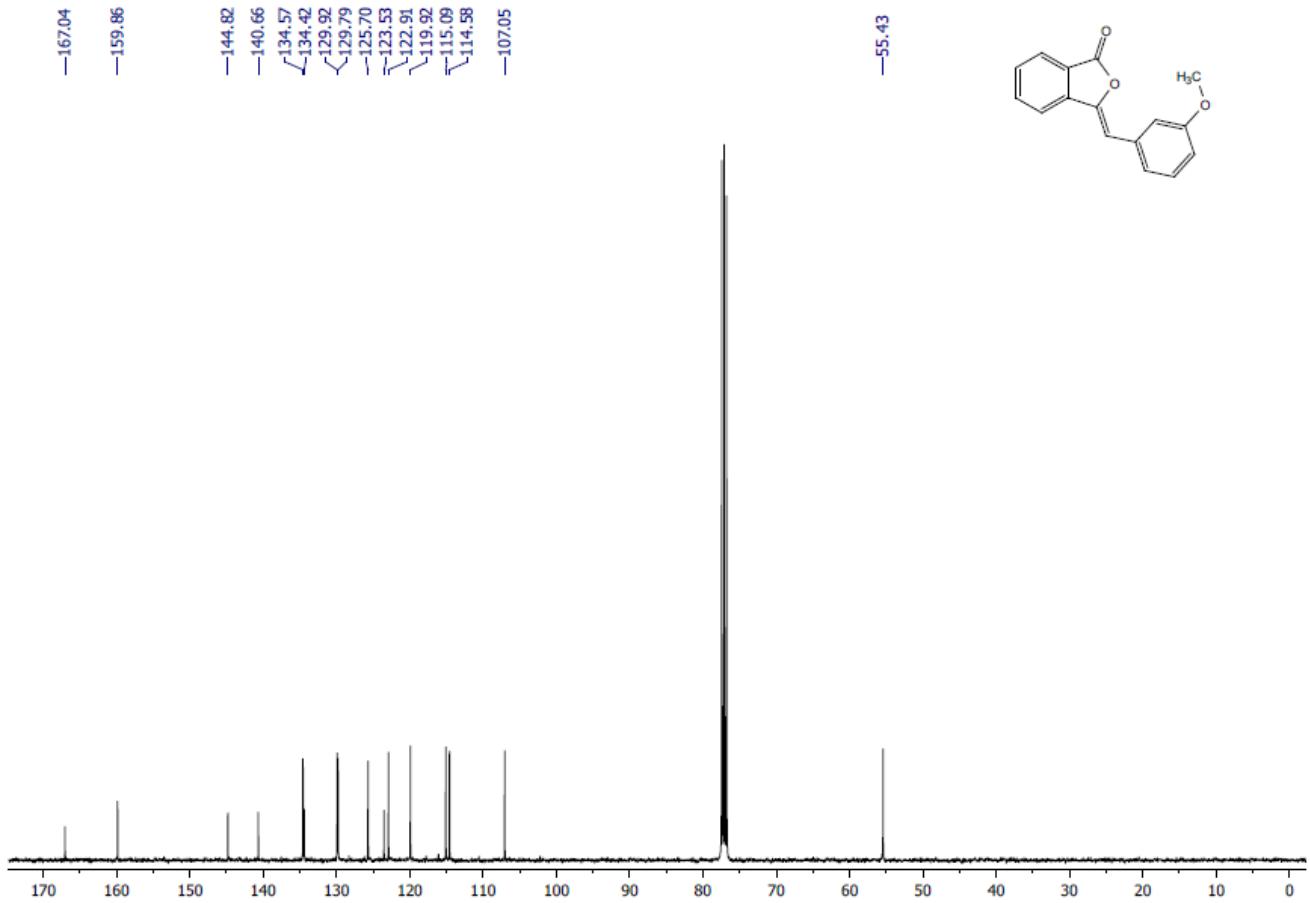


Figure 36: ^{13}C -NMR spectral data of **16a**.

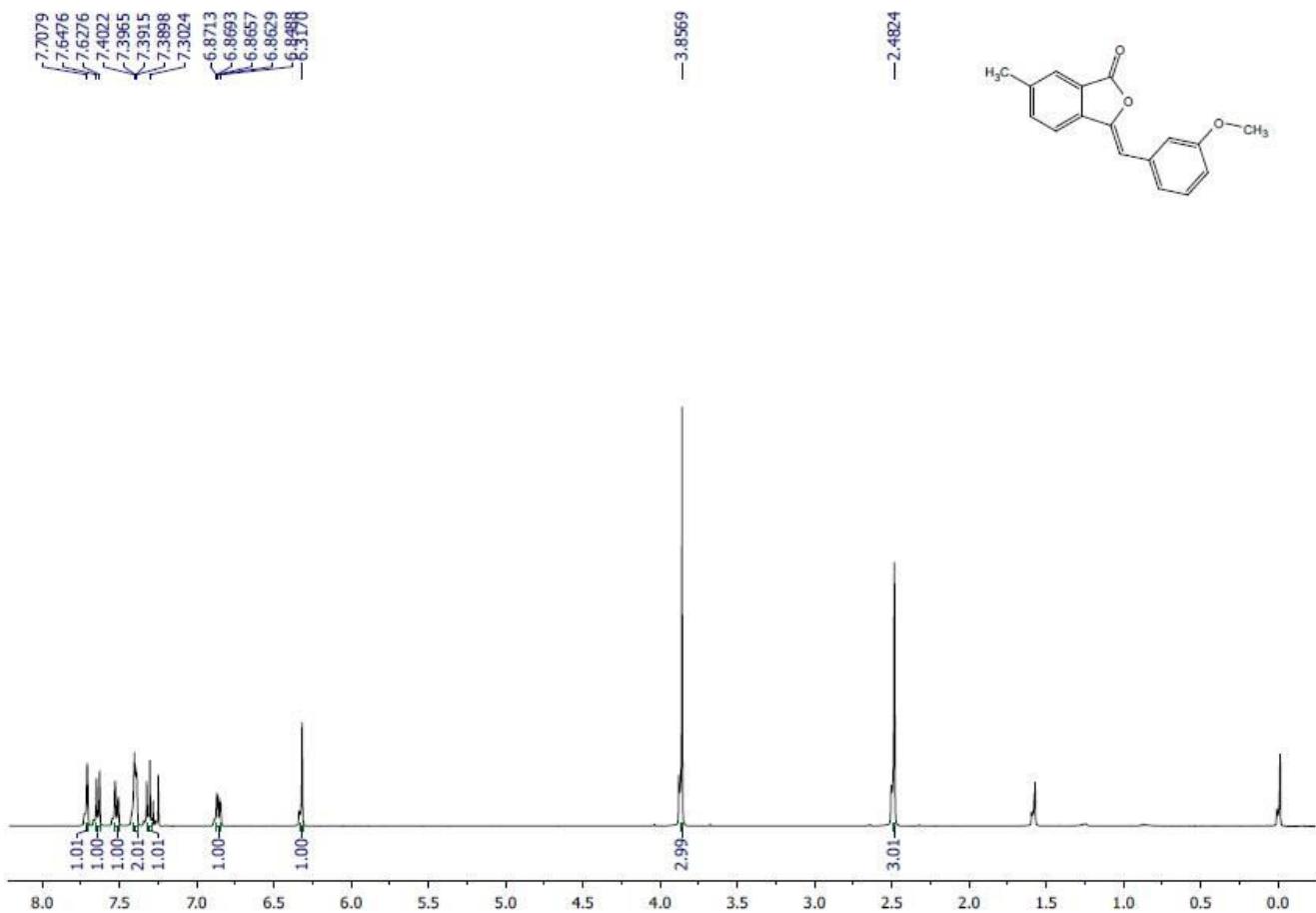


Figure 37: ^1H -NMR spectral data of **16b**.

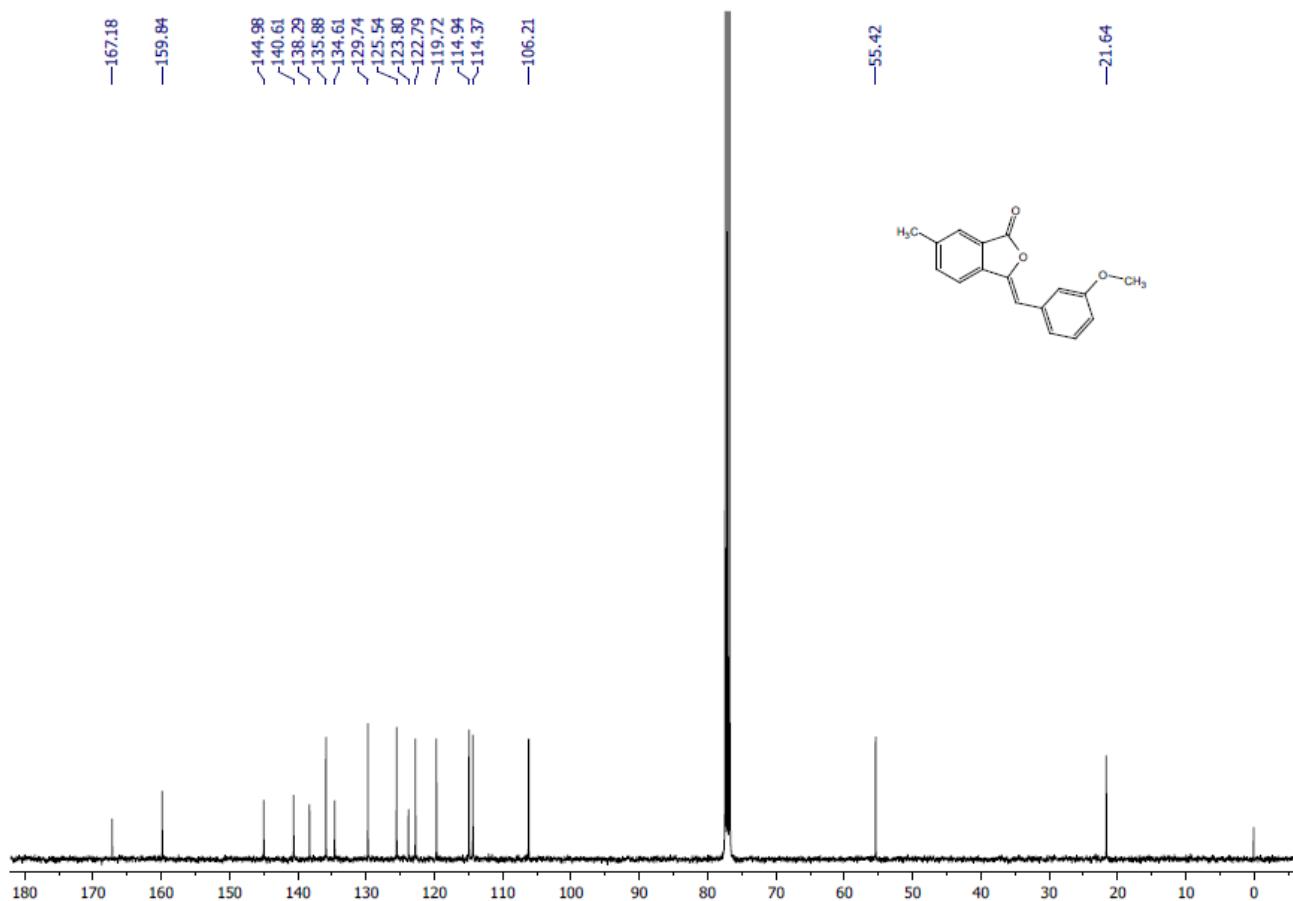


Figure 38: ^{13}C -NMR spectral data of **16b**.

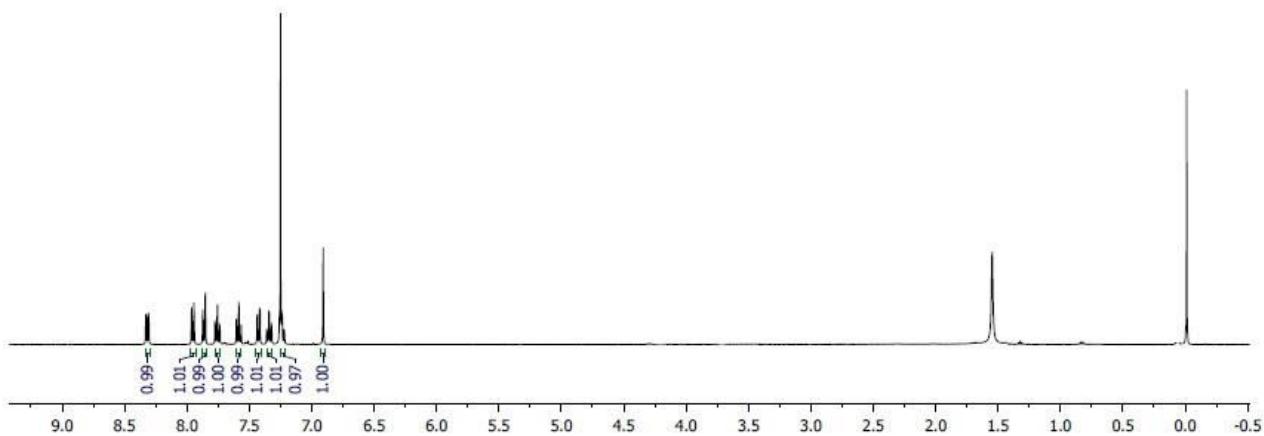


Figure 39: ^1H -NMR spectral data of **17a**.

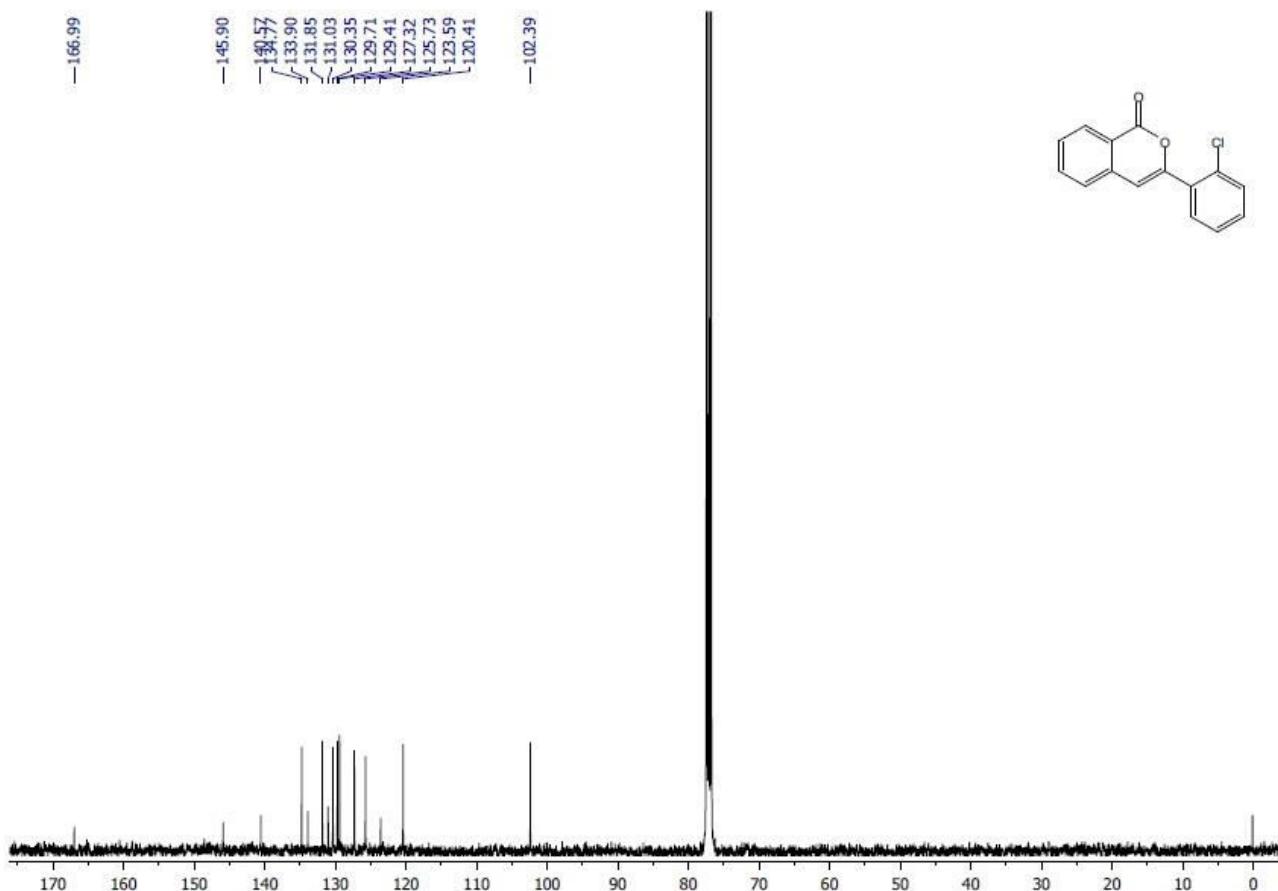


Figure 40: ^{13}C -NMR spectral data of **17a**.

-8.2969
-8.2771
-7.9559
-7.9366
-7.8714
-7.8519
-7.7727
-7.7540
-7.7348
-7.6258
-7.6030
-7.5818
-7.5630
-7.3992
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-7.3610
-7.1724
-7.1528
-7.1340
-6.8745

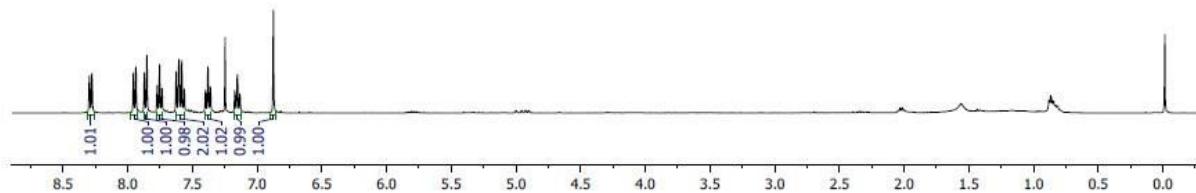
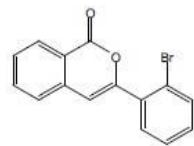


Figure 41: ^1H -NMR spectral data of **17b**.

-166.96

-145.76

-134.58

-133.05

-132.65

-131.98

-131.37

-130.37

-129.62

-127.92

-125.77

-124.71

-123.56

-120.41

-105.15

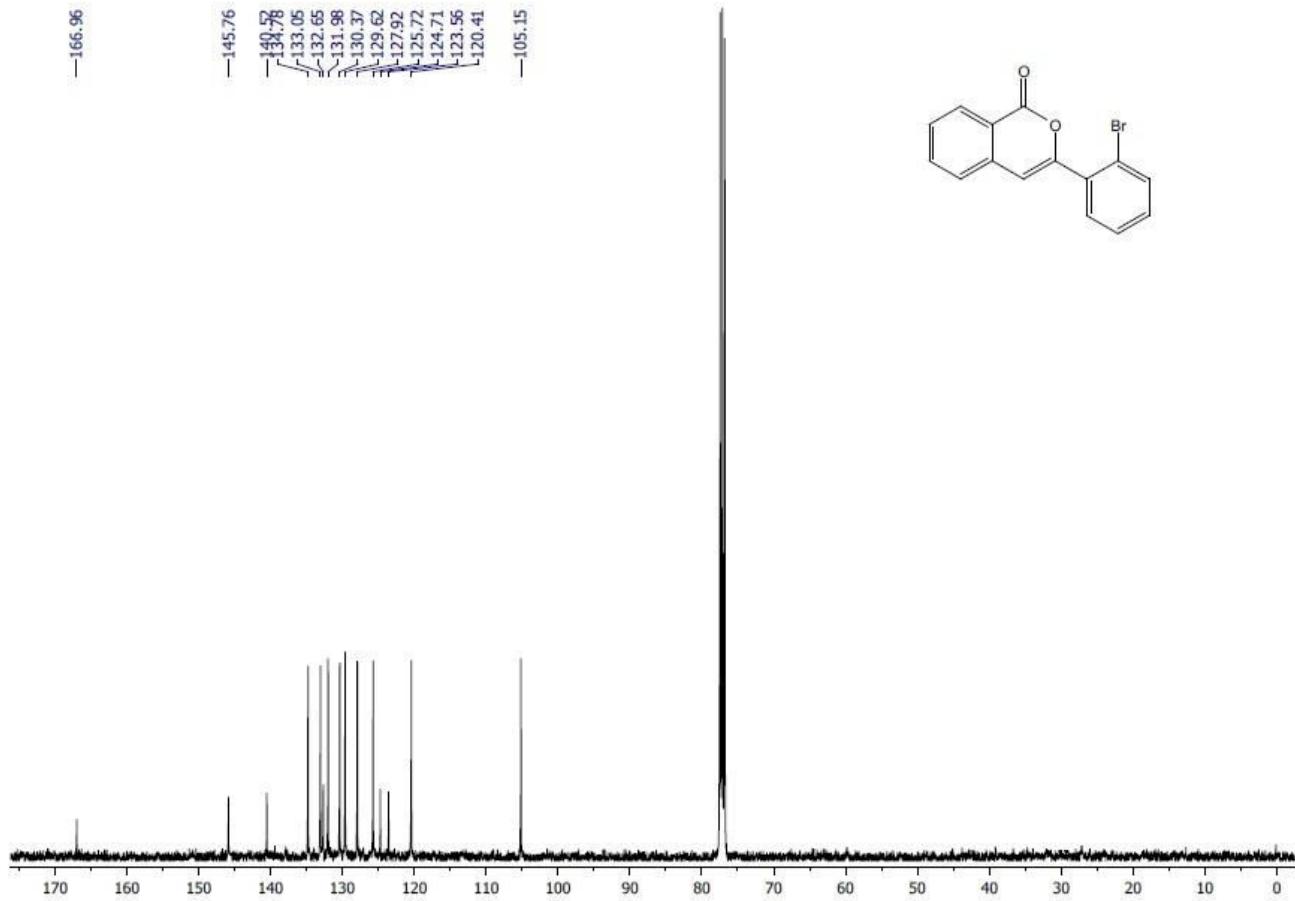
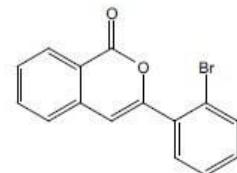


Figure 42: ^{13}C -NMR spectral data of **17b**.

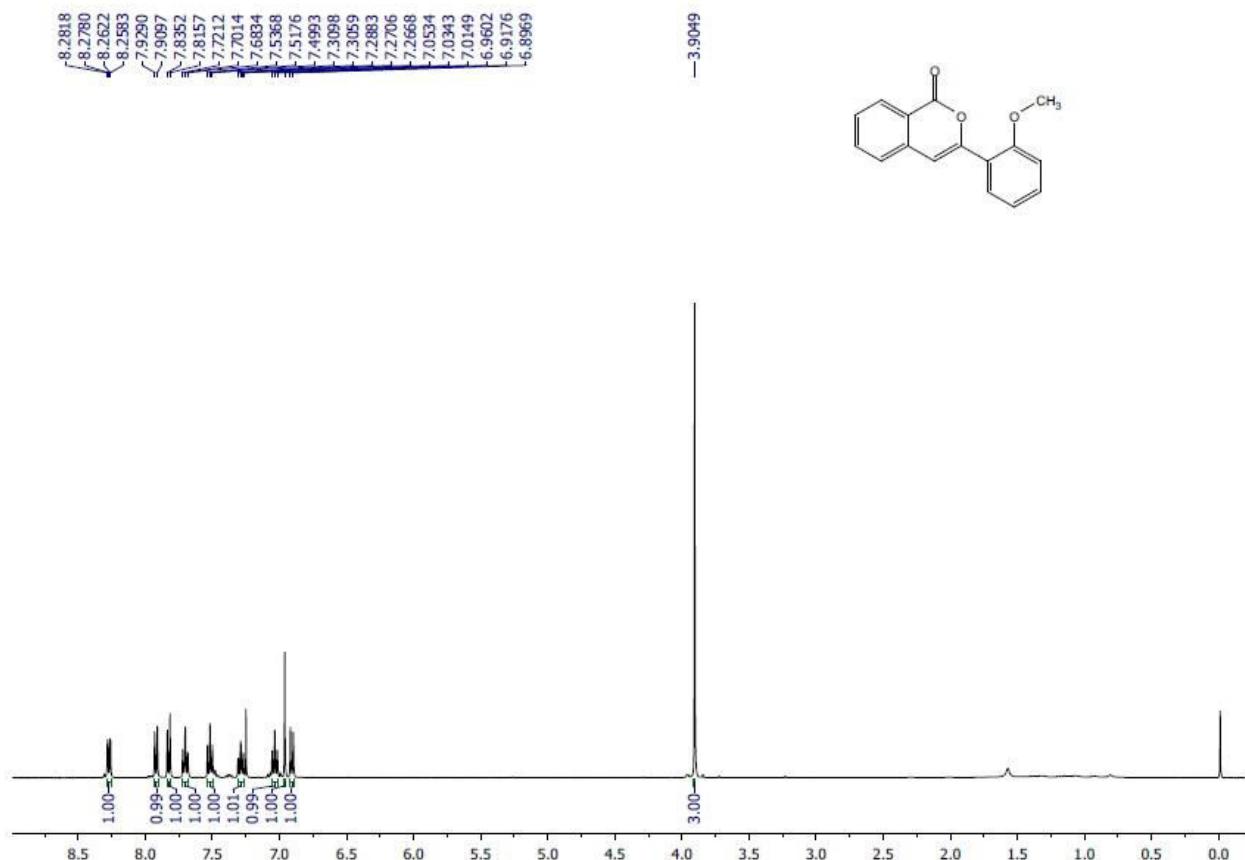


Figure 43: ^1H -NMR spectral data of **17c**.

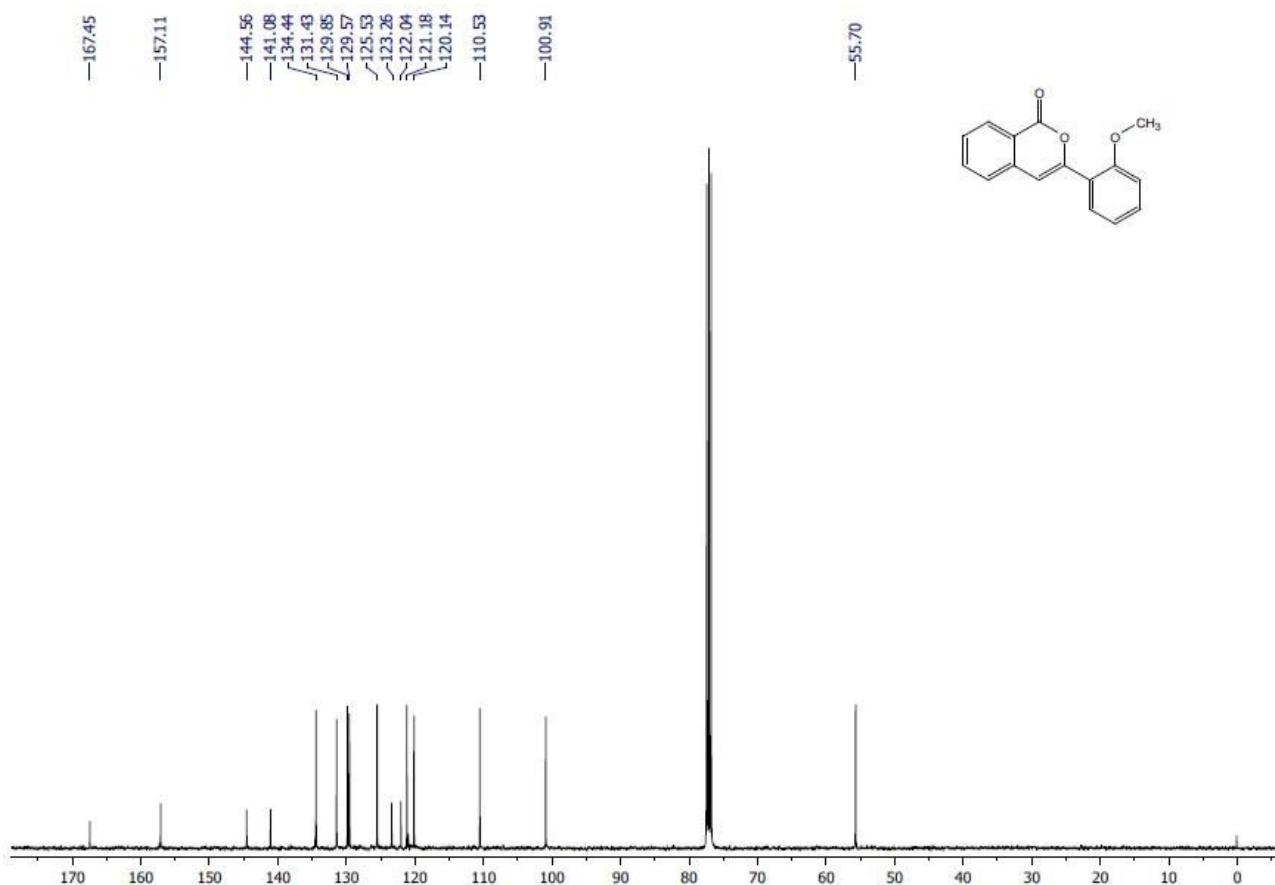


Figure 44: ^{13}C -NMR spectral data of **17c**.

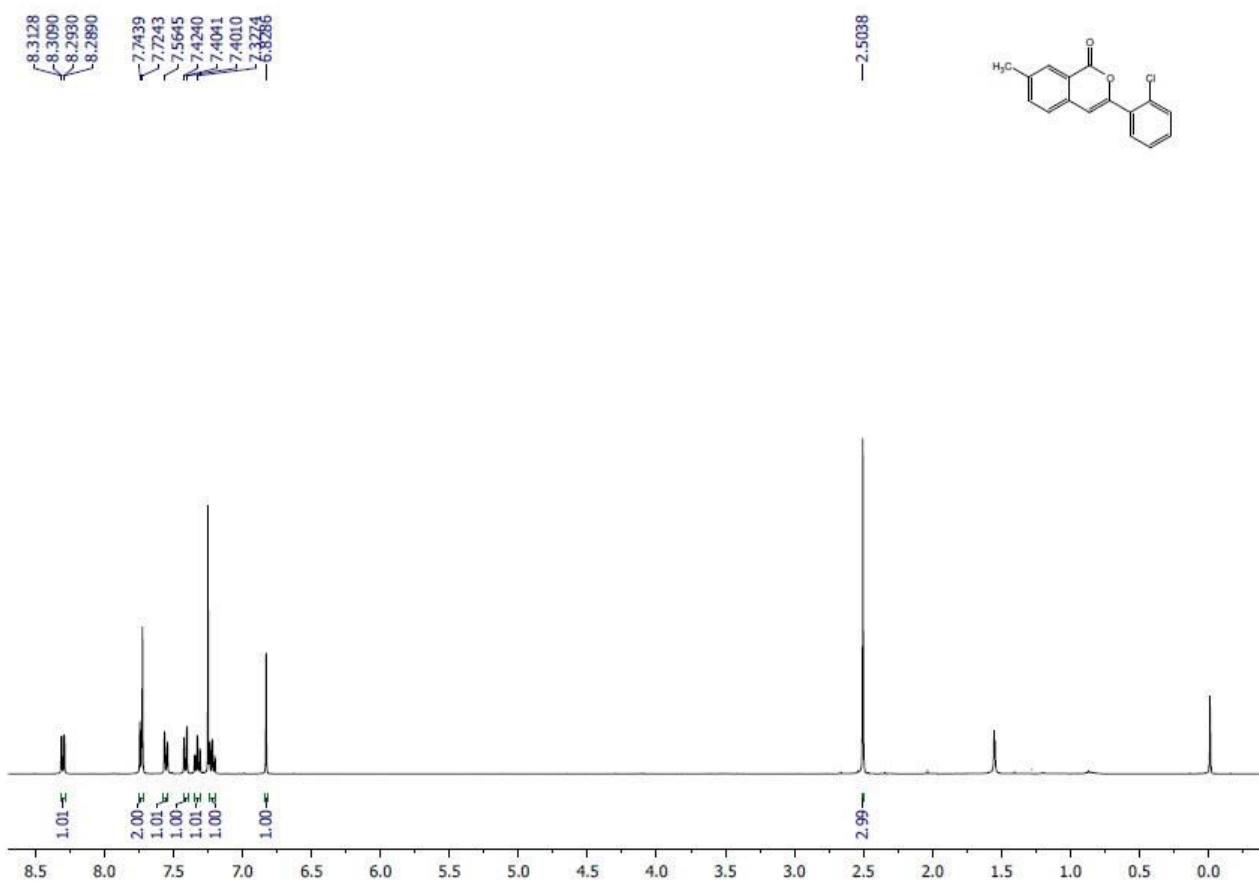


Figure 45: ^1H -NMR spectral data of **18a**.

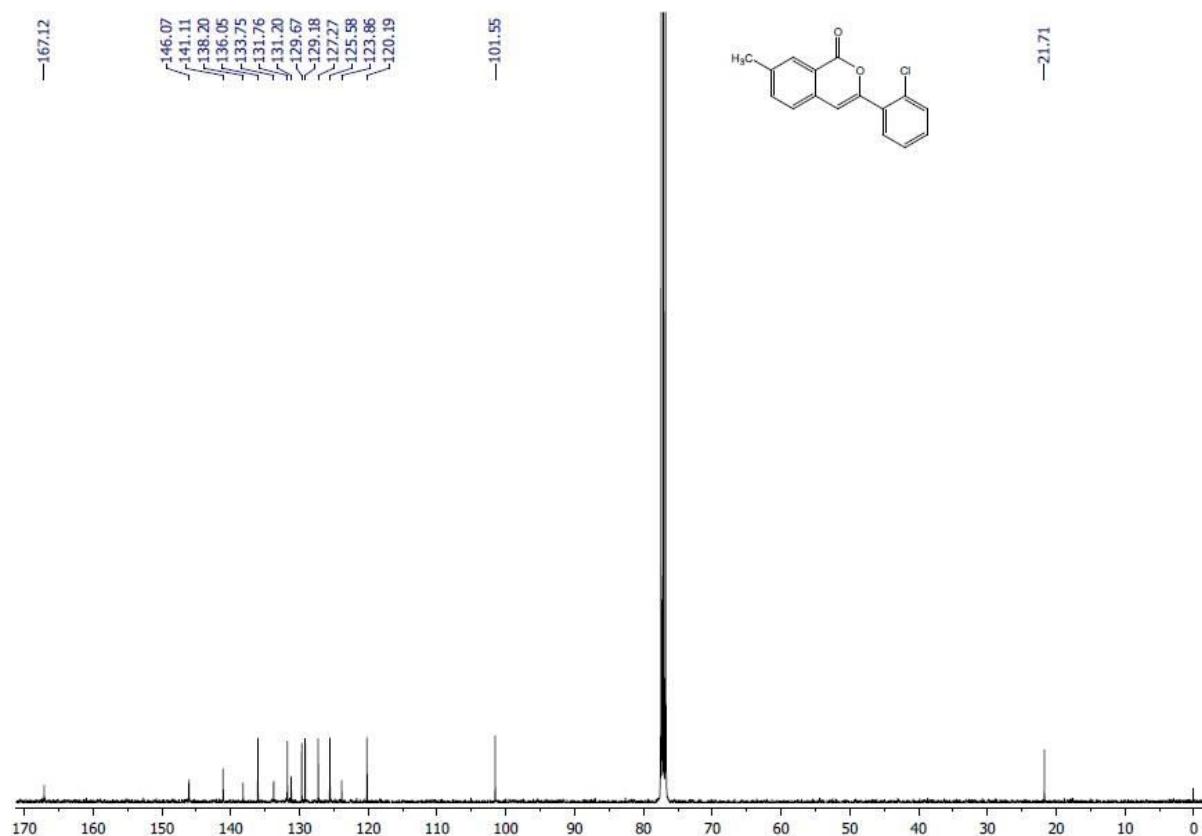
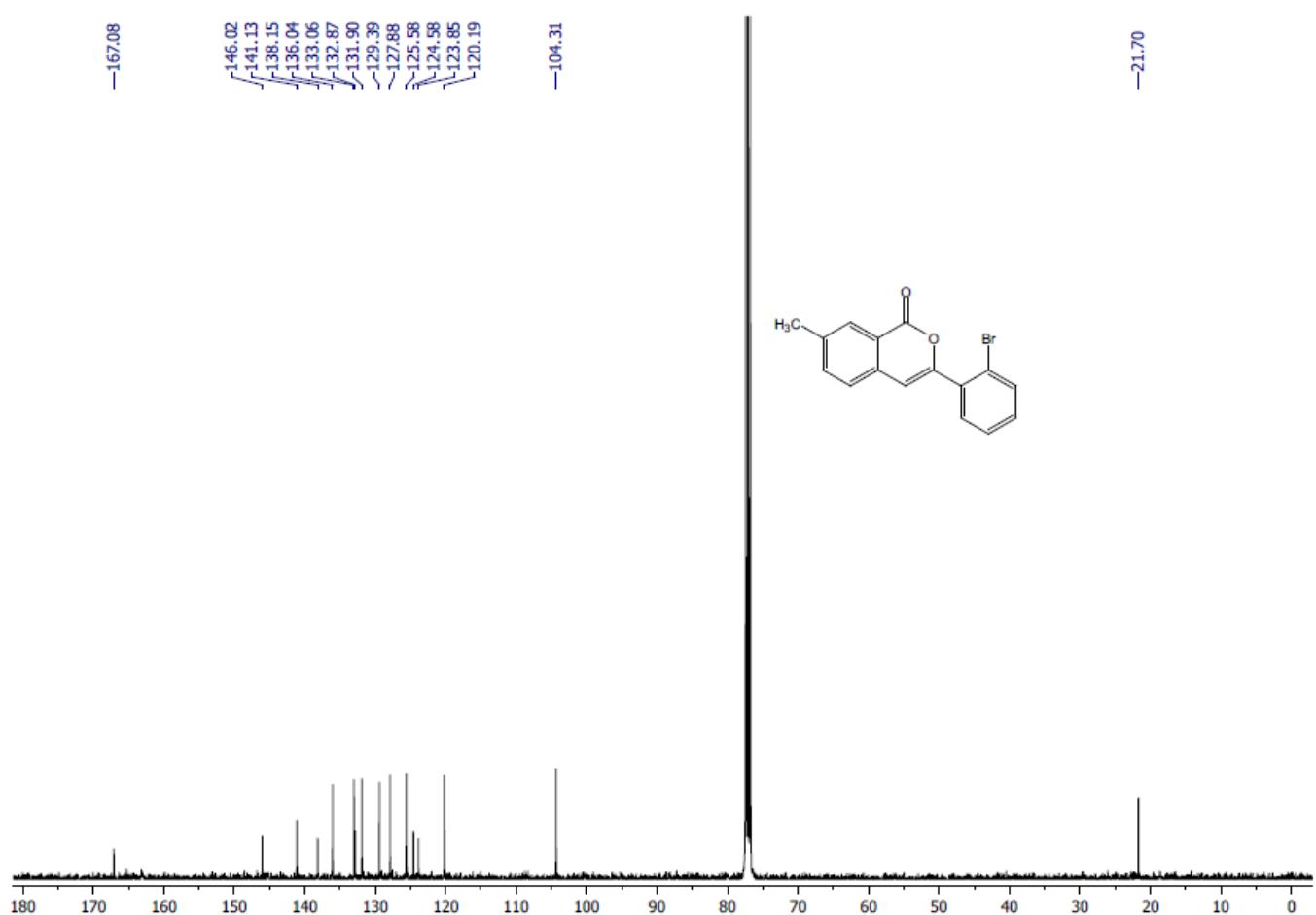
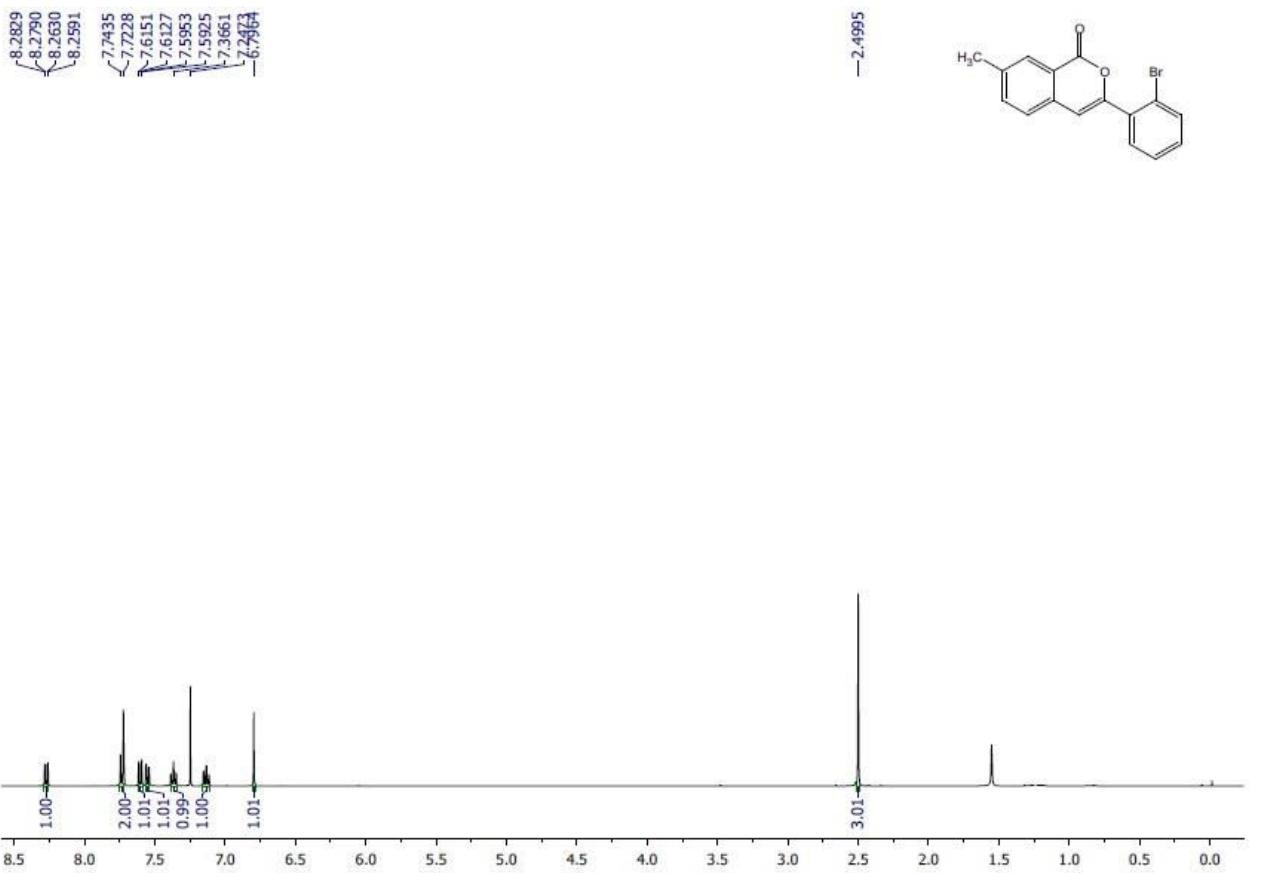


Figure 46: ^{13}C -NMR spectral data of **18a**.



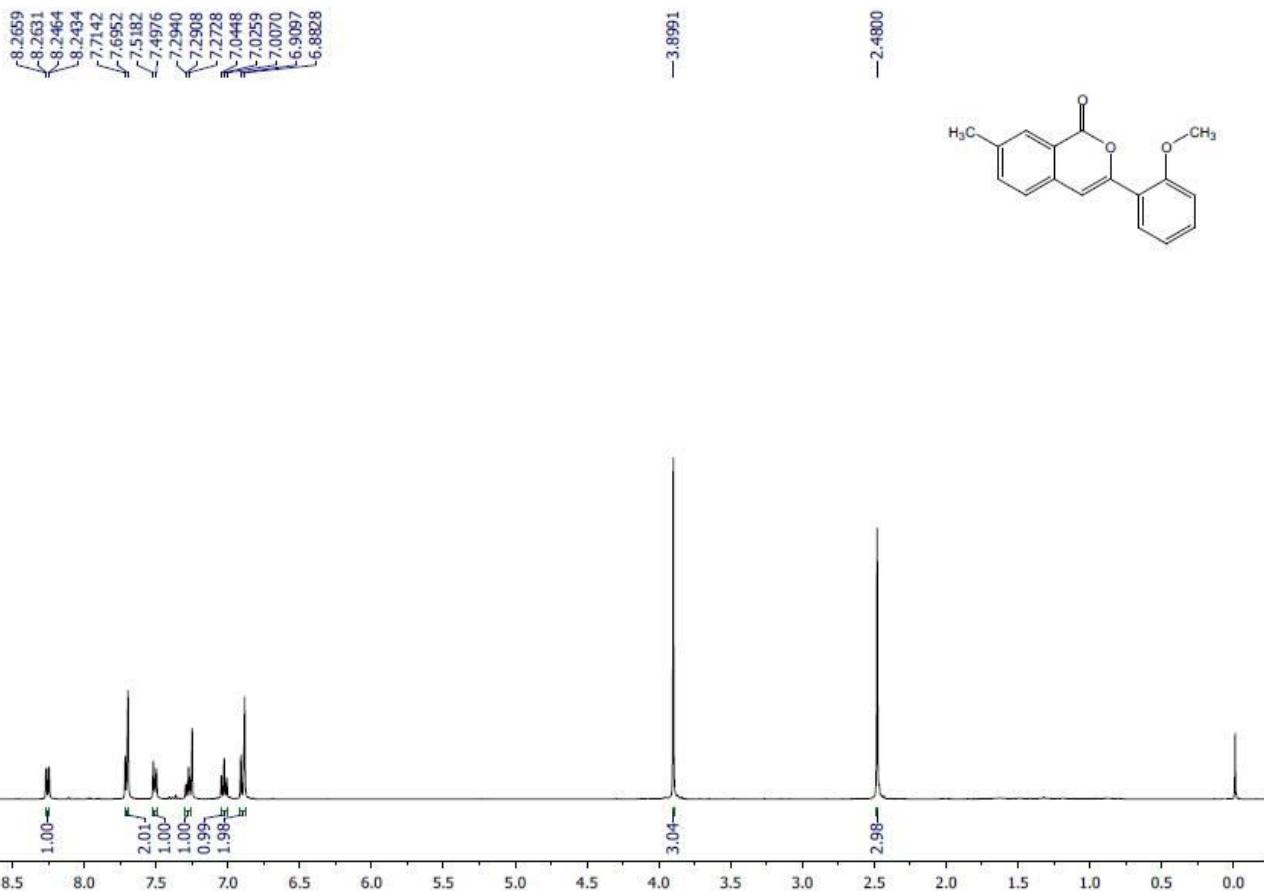


Figure 49: ^1H -NMR spectral data of **18c**.

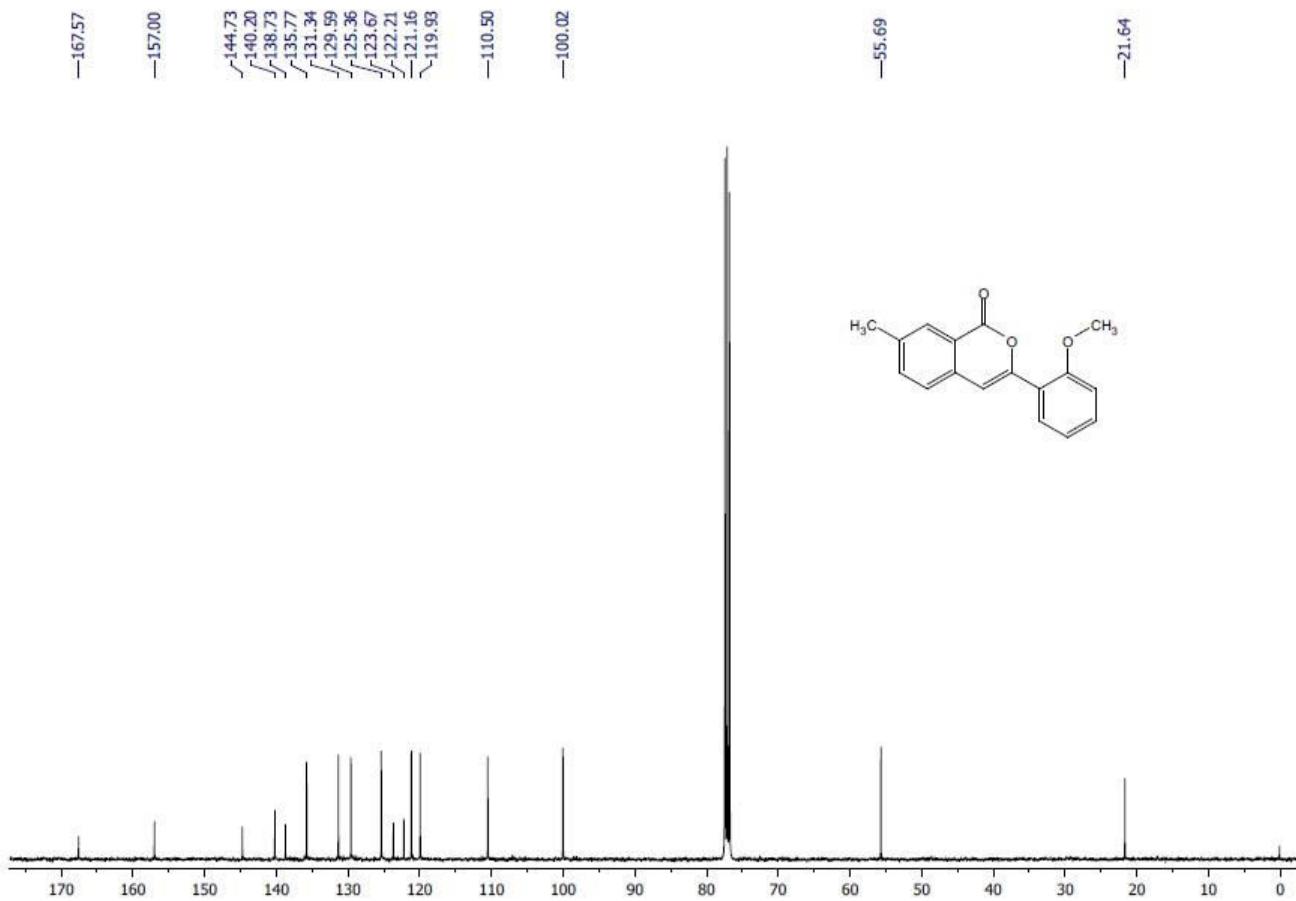


Figure 50: ^{13}C -NMR spectral data of **18c**.

8.0752
8.0701
7.8456
7.8412
7.8378
7.7374
7.7297
7.7168
7.7090
7.4137
7.4087
7.3341
6.9053

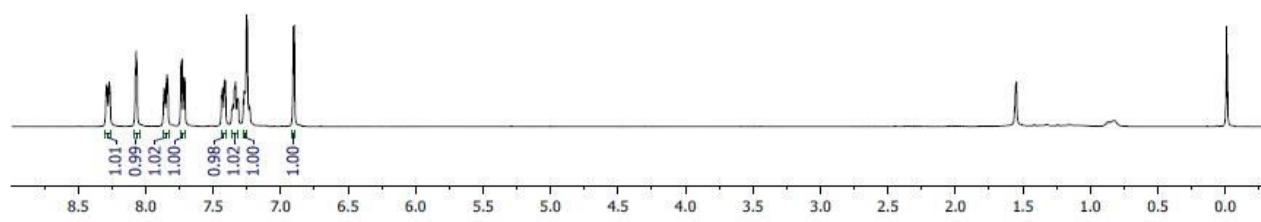
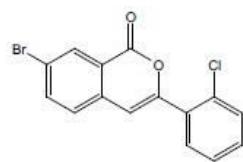


Figure 51: ^1H -NMR spectral data of **19a**.

-165.40

-139.17
-137.88
-134.03
-131.83
-130.72
-129.79
-129.71
-128.64
-127.38
-125.29
-124.32
-121.79

-103.23

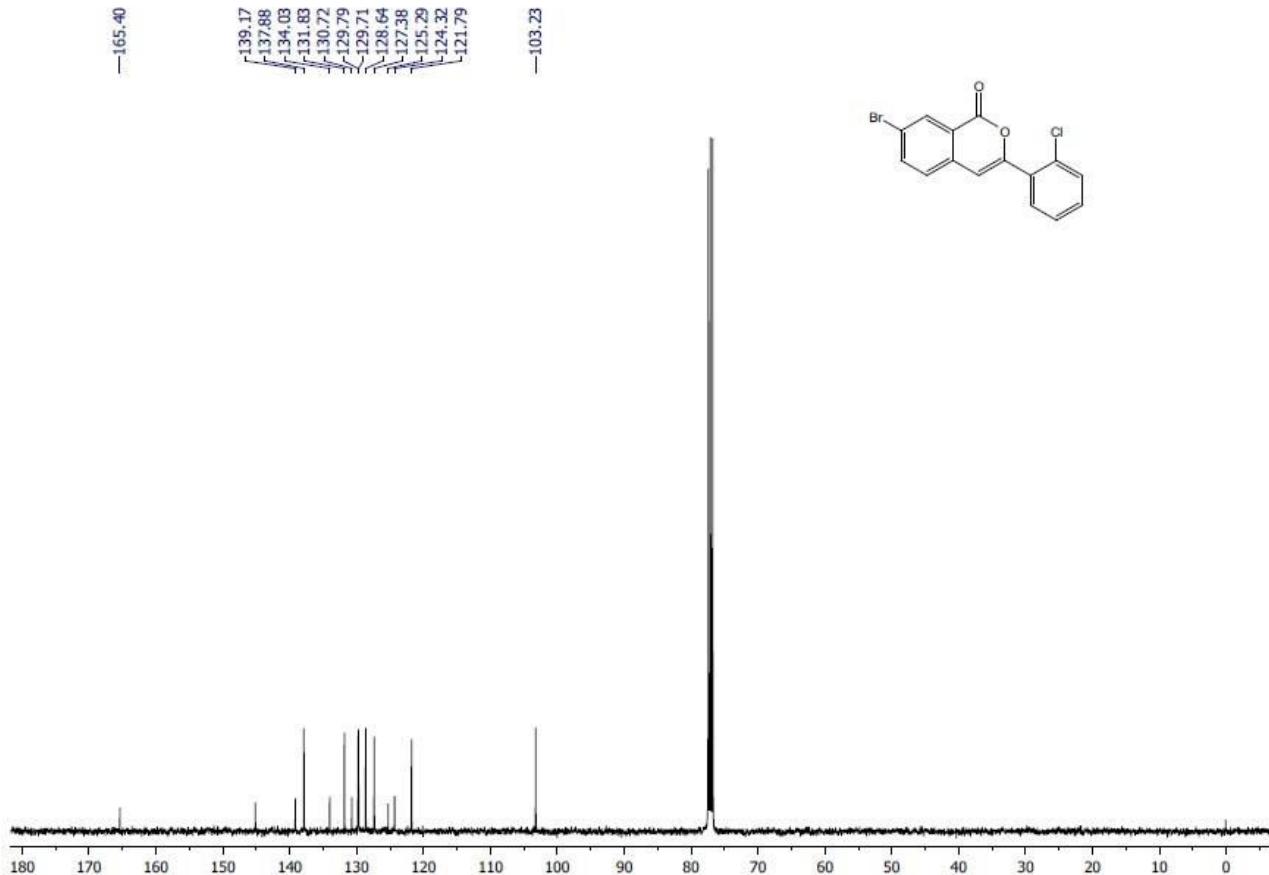
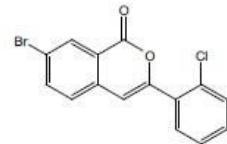


Figure 52: ^{13}C -NMR spectral data of **19a**.

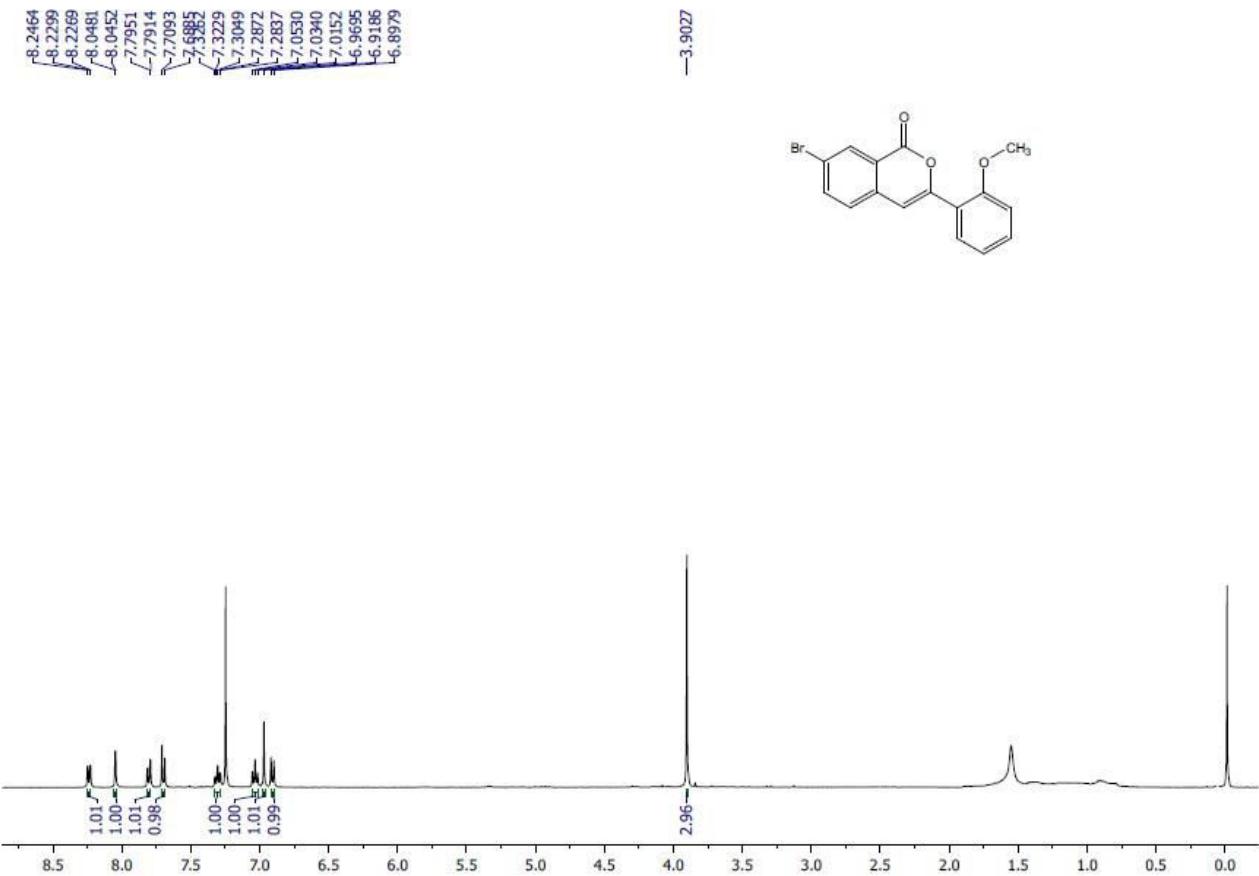


Figure 53: ^1H -NMR spectral data of **19b**.

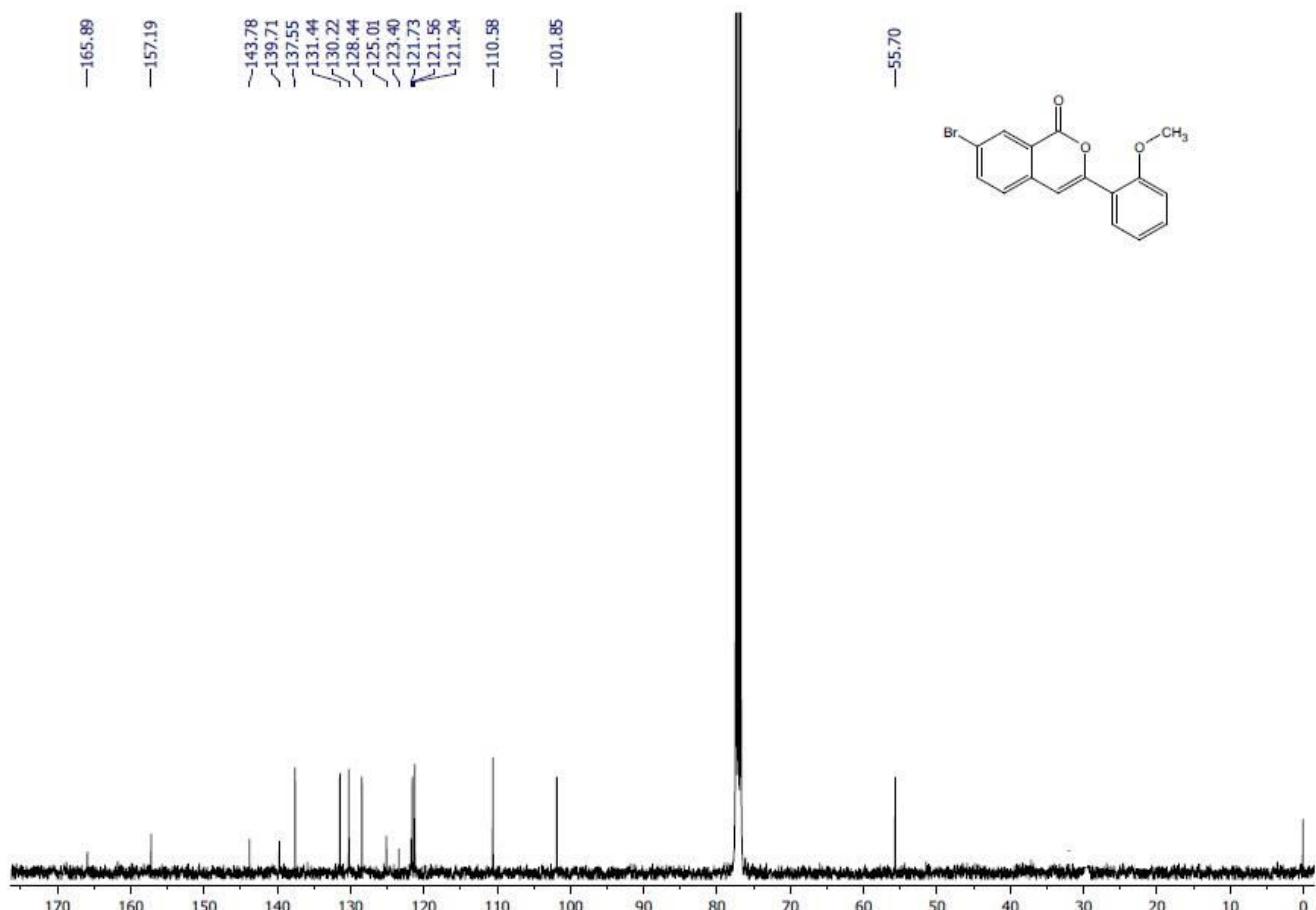


Figure 54: ^{13}C -NMR spectral data of **19b**.

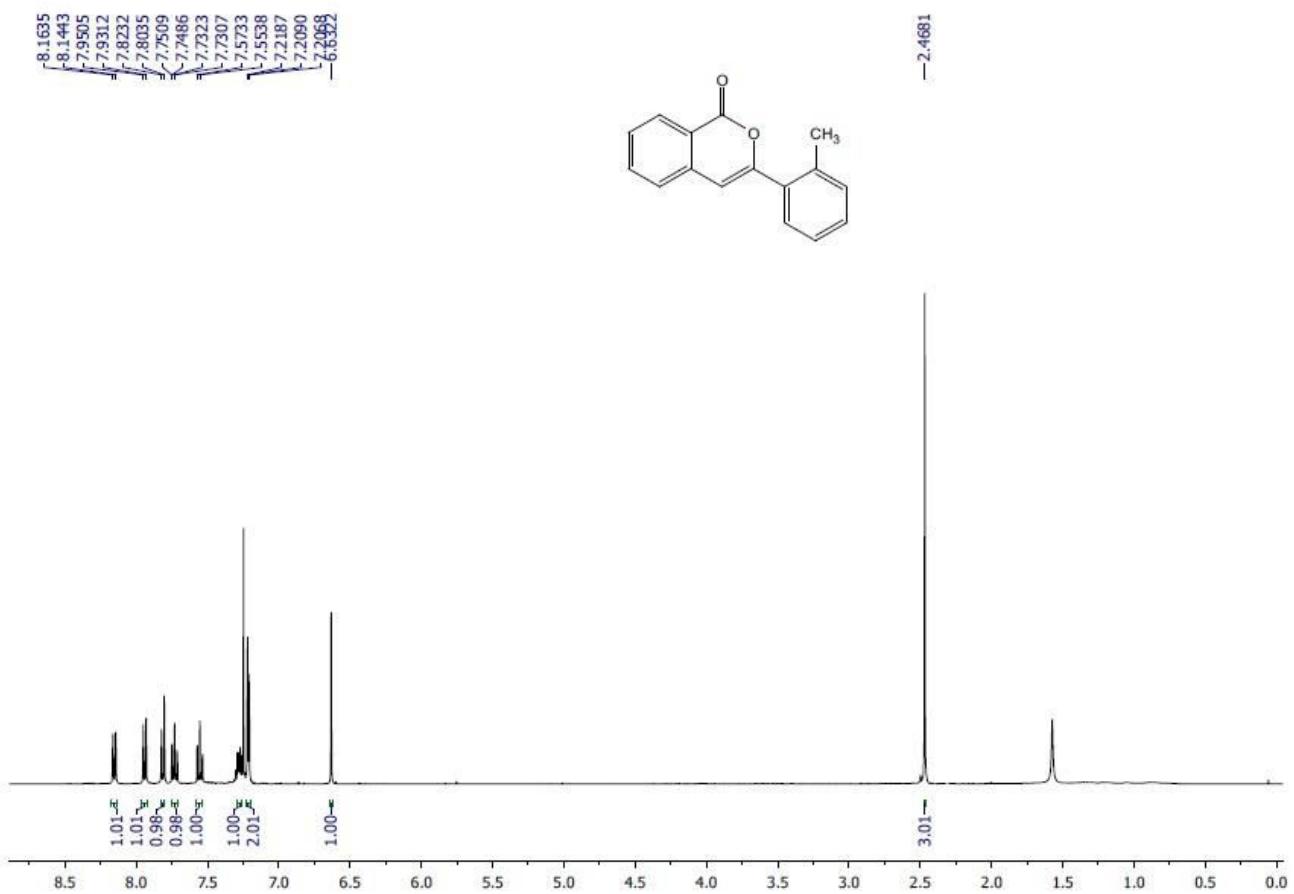


Figure 55: ^1H -NMR spectral data of 20a.

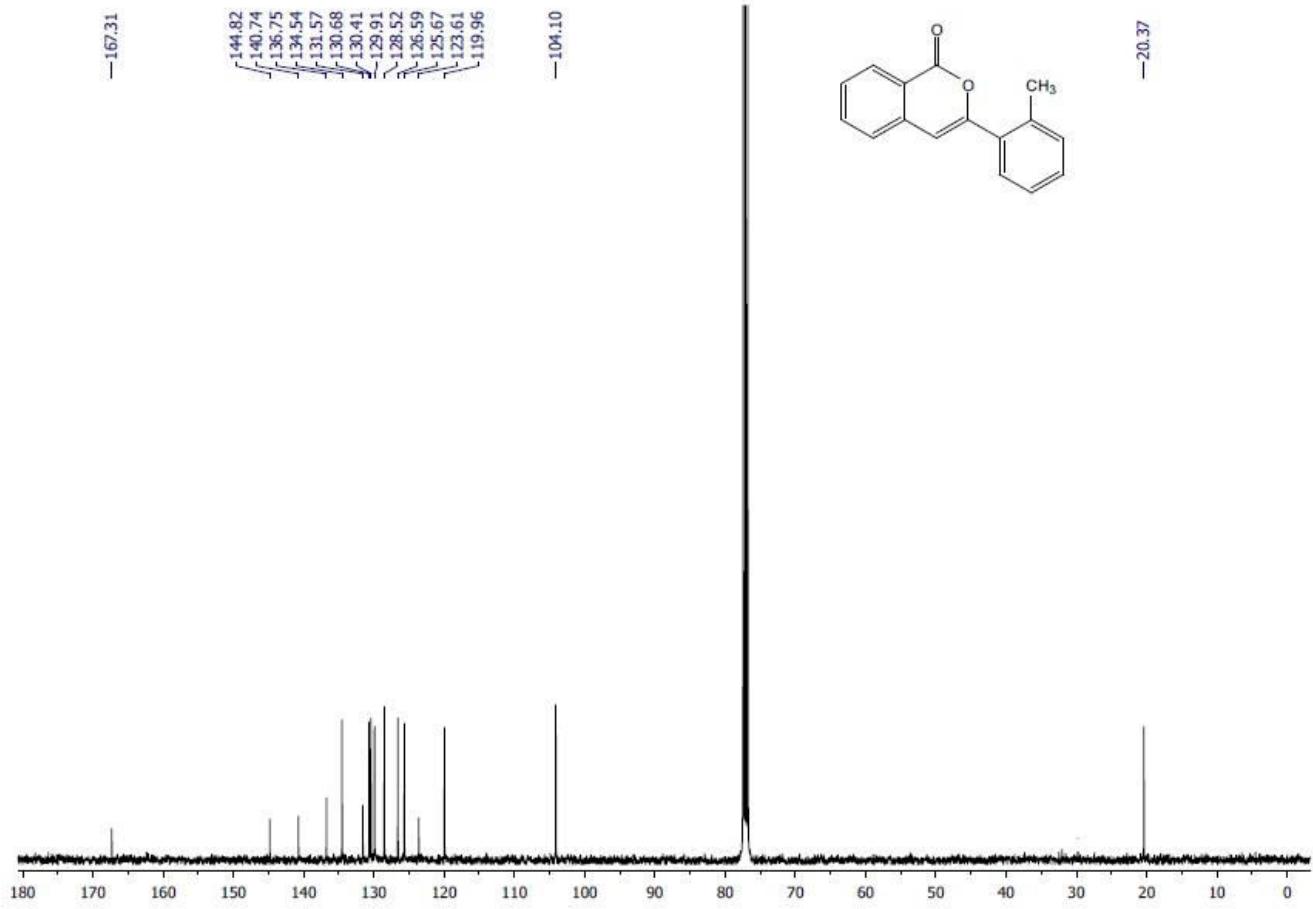
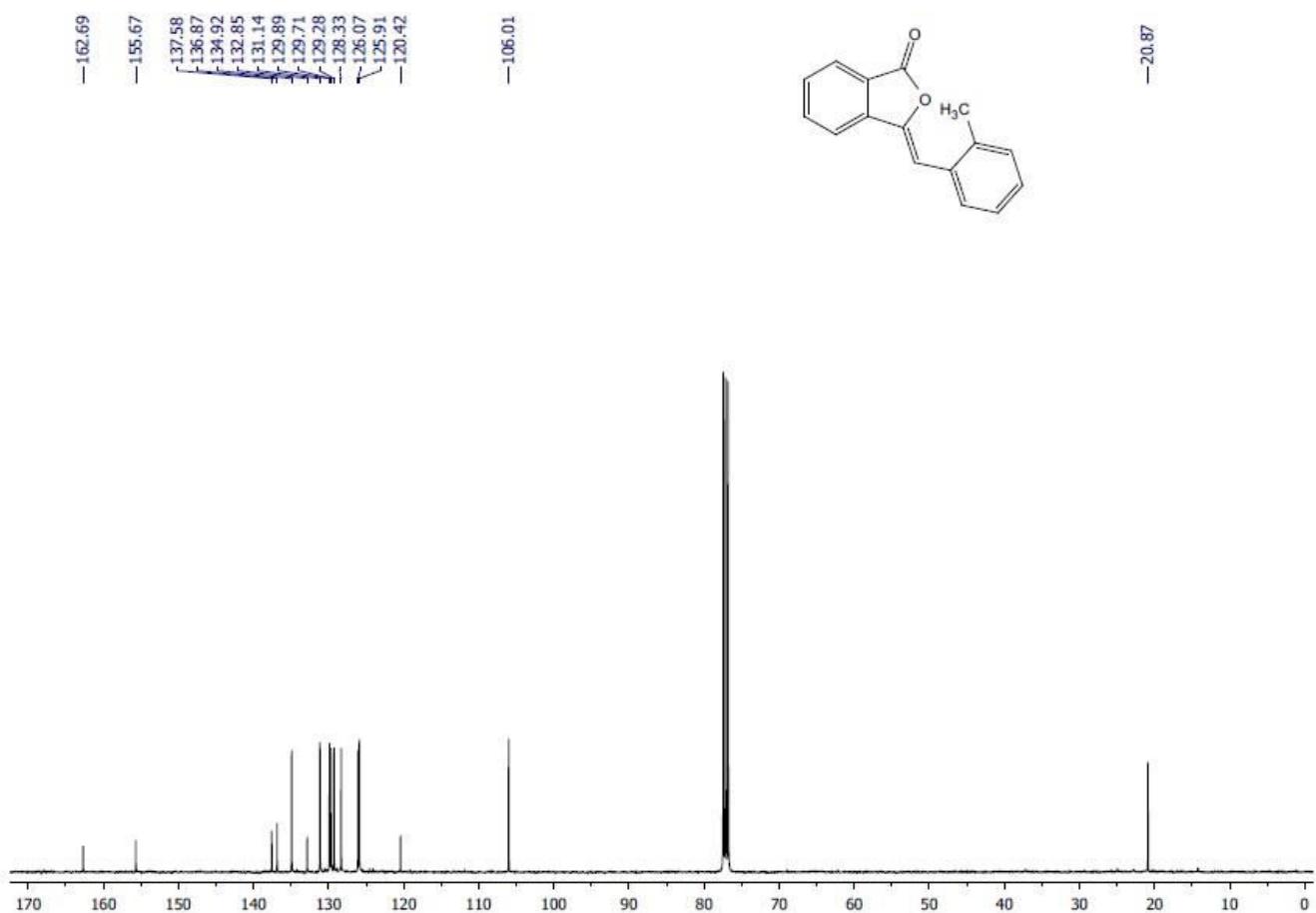
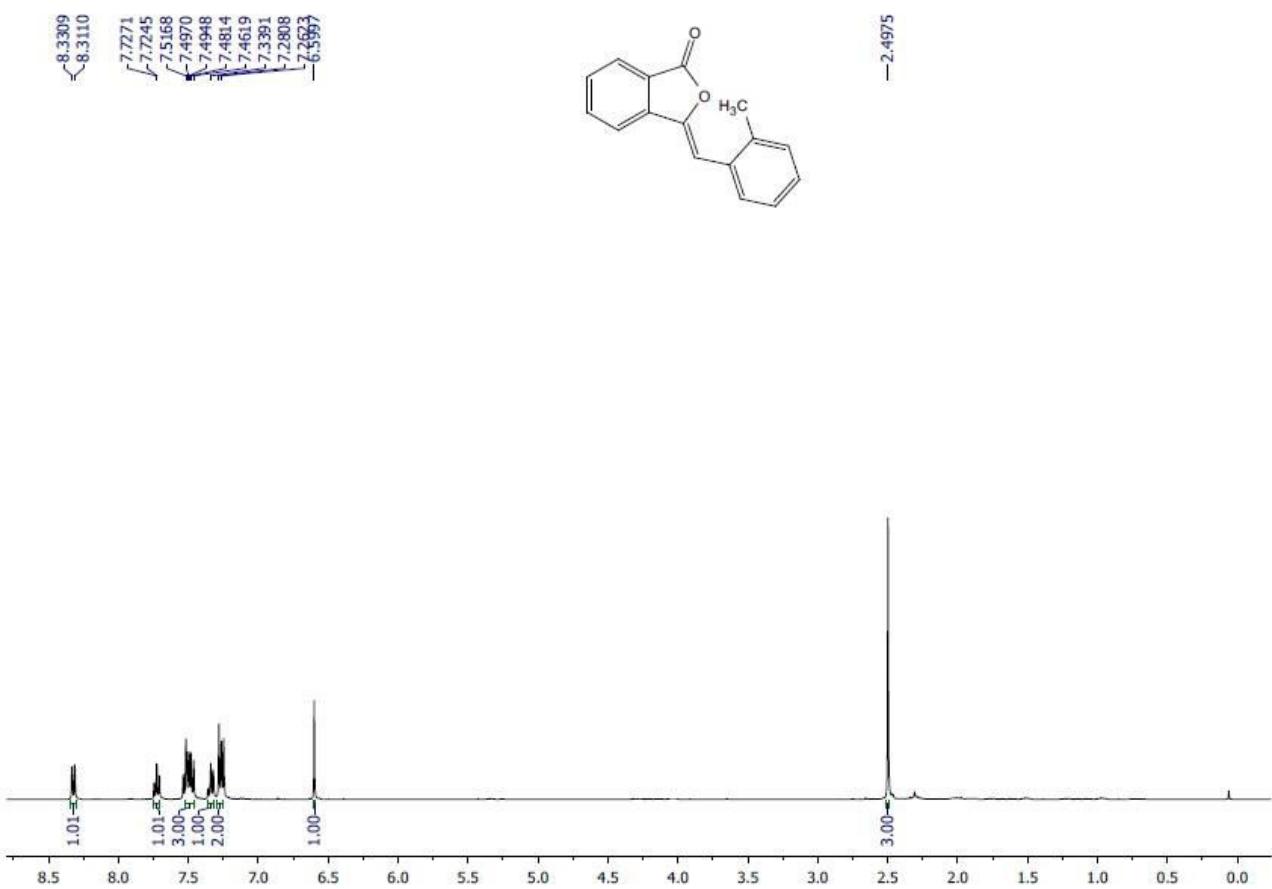


Figure 56: ^{13}C -NMR spectral data of 20a.



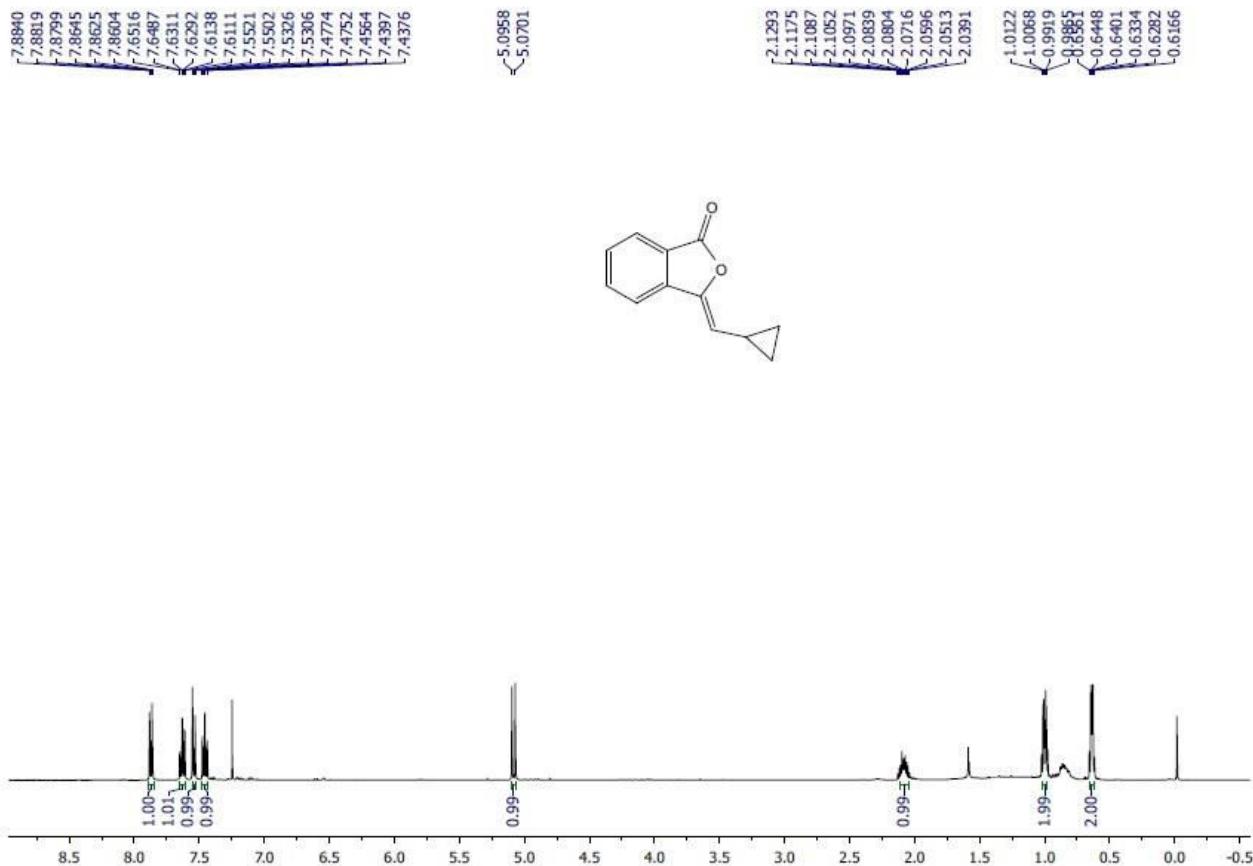


Figure 59: ^1H -NMR spectral data of **21a**.

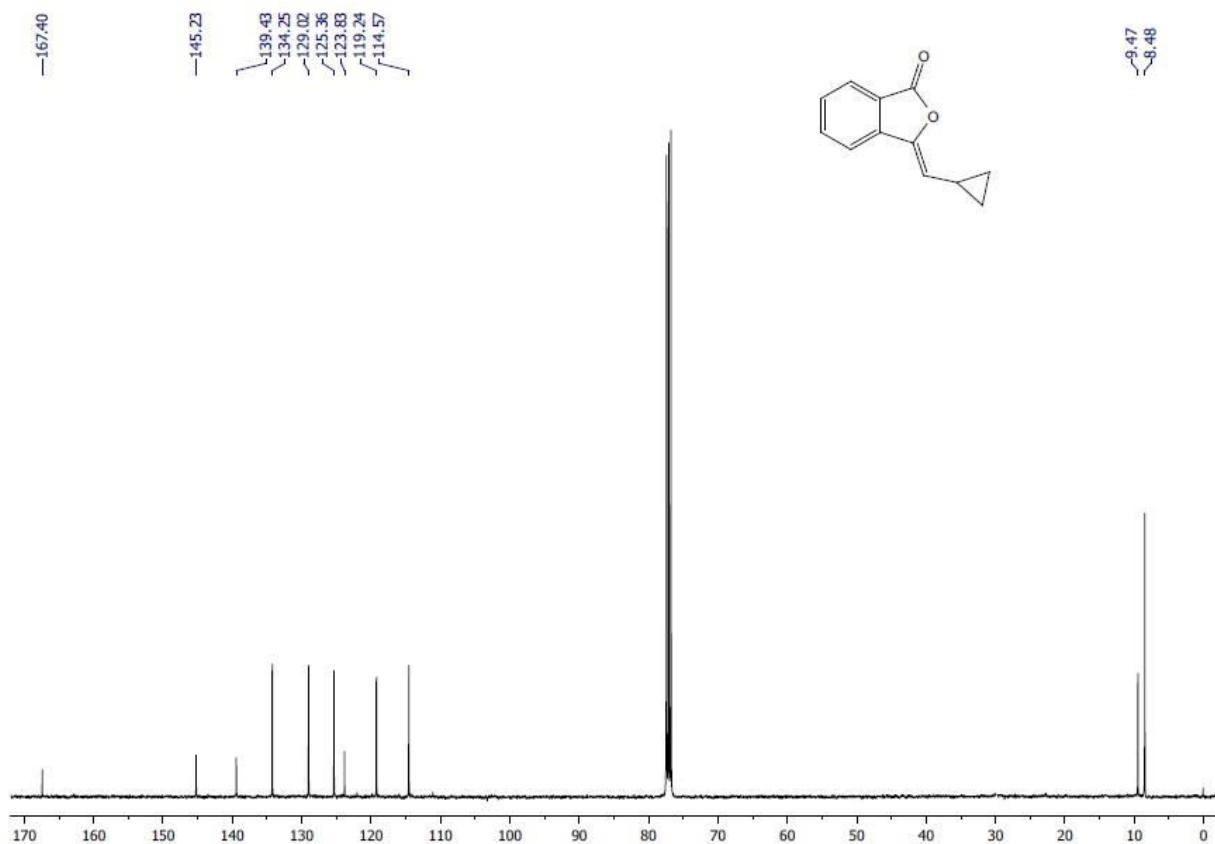
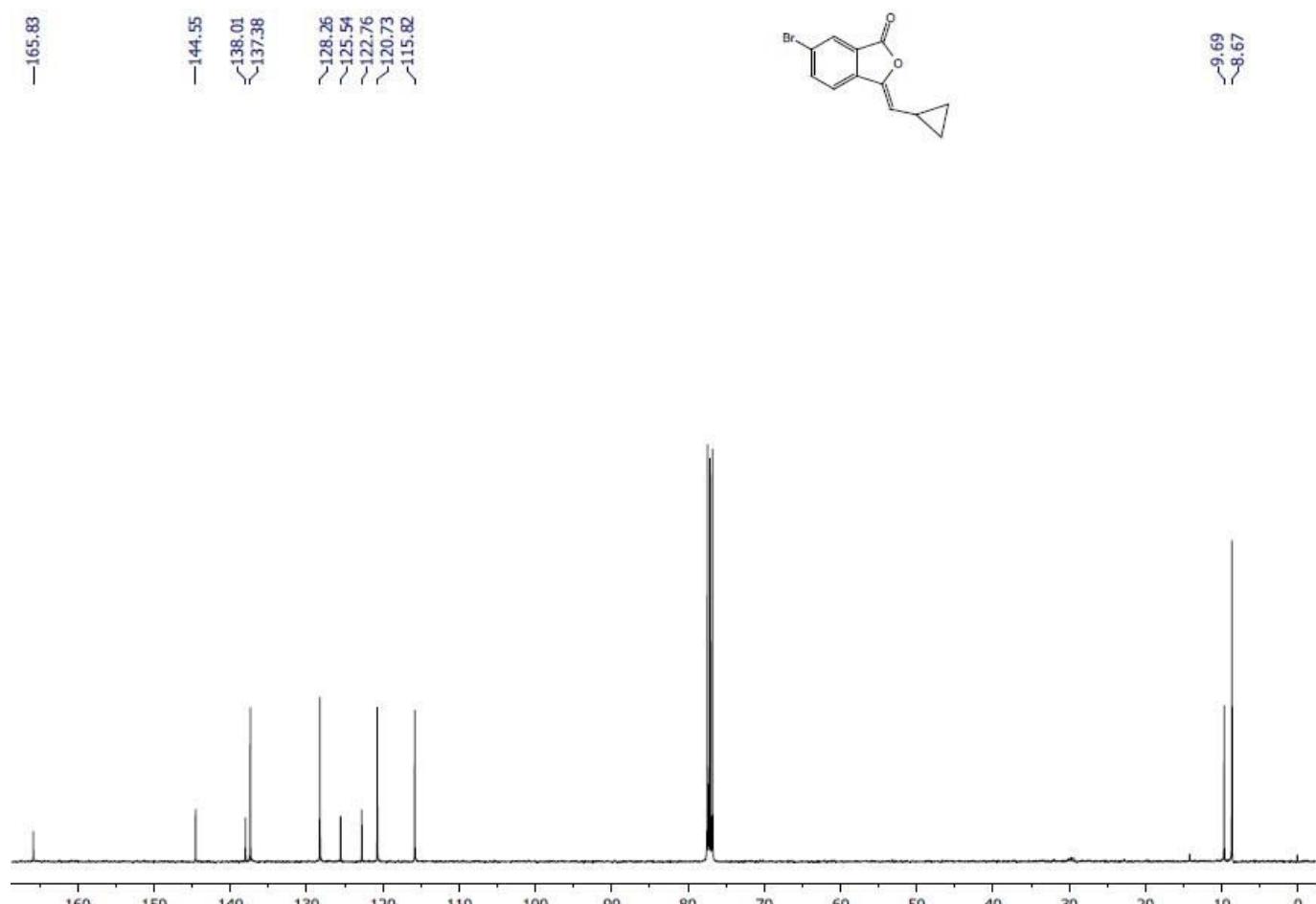
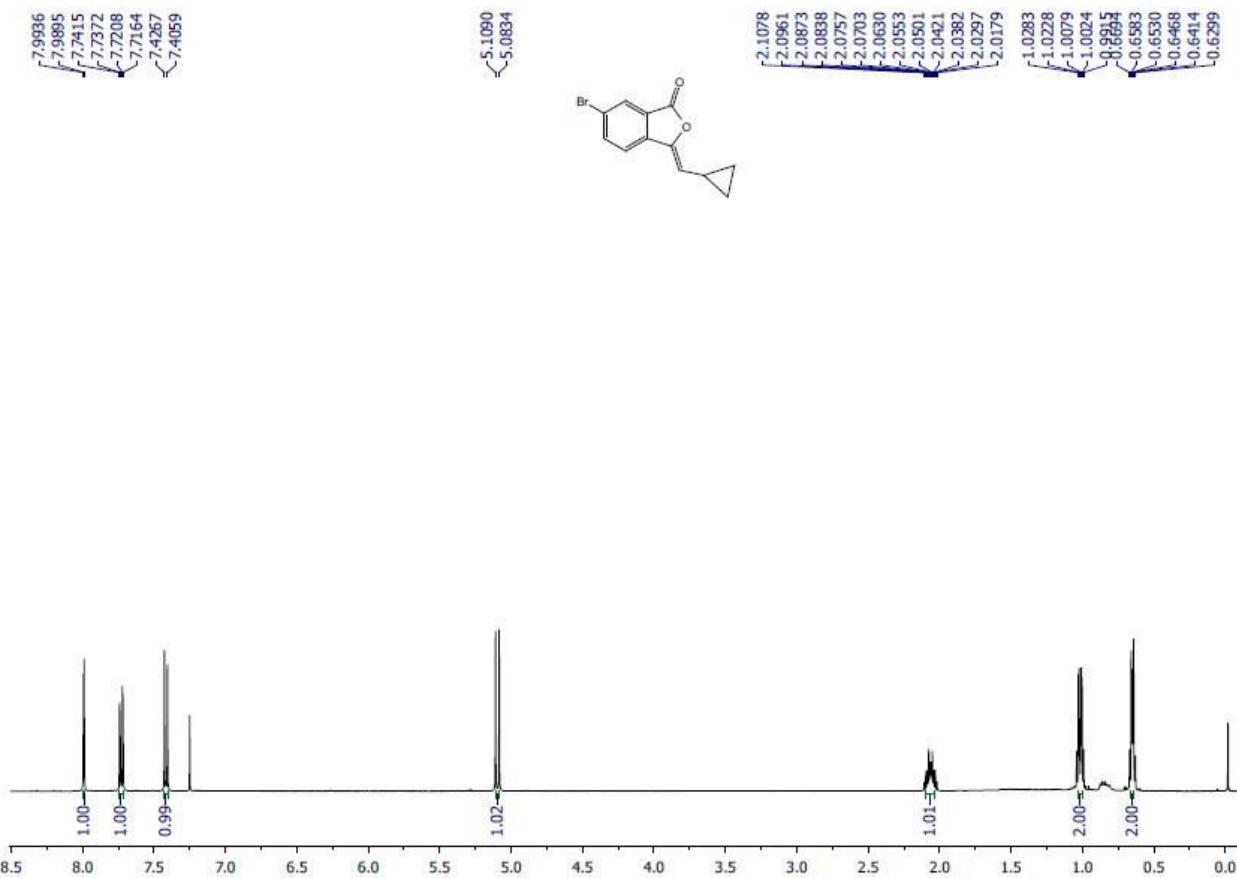


Figure 60: ^{13}C -NMR spectral data of **21a**.



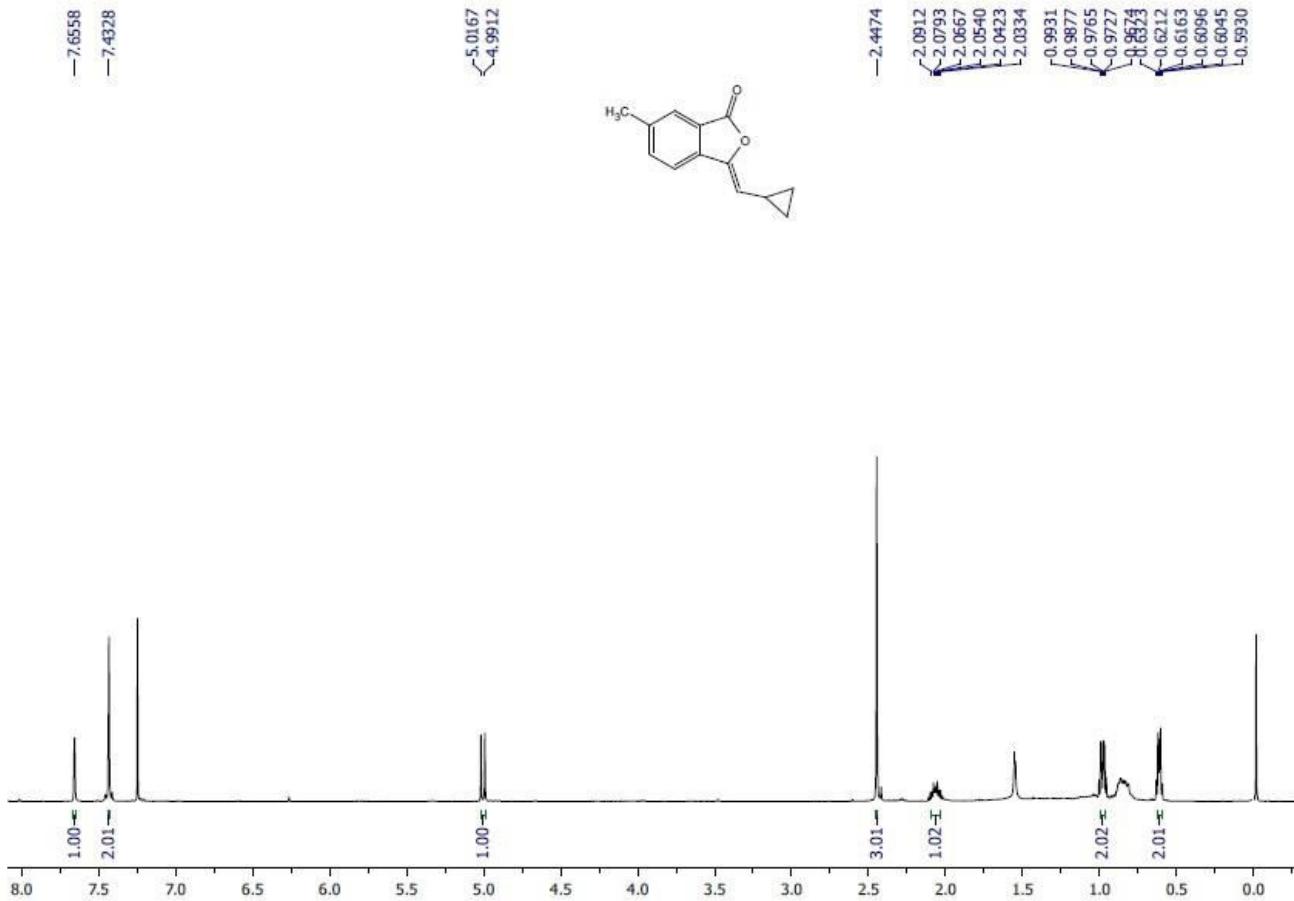


Figure 63: ^1H -NMR spectral data of **21c**.

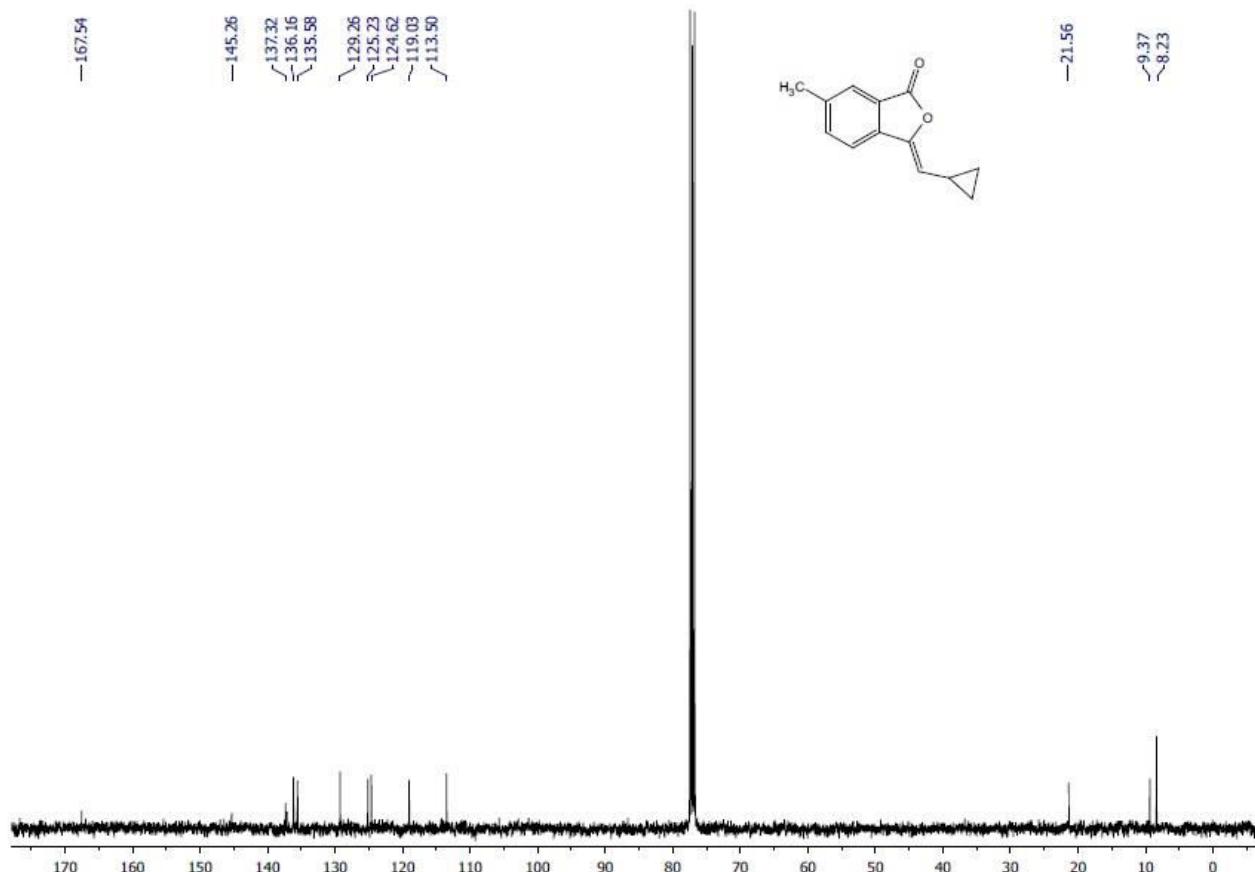


Figure 64: ^{13}C -NMR spectral data of **21c**.