

ELECTRONIC SUPPORTING INFORMATION FOR

Imines with rare α -heteroatom substituted amine component generated in situ via Staudinger/aza-Wittig tandem and their application in multicomponent reactions

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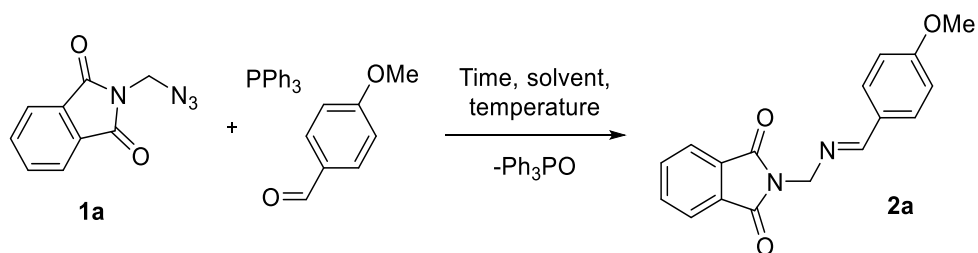
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Table S1

Reaction conditions optimization for *in situ* imine generation from azide **1a** and *p*-anisaldehyde in presence of triphenylphosphine. Dibromomethane was used as internal standard for ¹H NMR spectra.



Entry	Solvent	Temperature, °C	Time, h	Yield, % (NMR)
1	toluene	60	16	70
2	toluene	80	16	81
3	toluene	110	16	67
4	toluene	130	16	68
5	toluene	80	3	69
6	toluene	80	6	68
7	MeCN	80	16	77
8	DMSO	80	16	34
9	DCE	80	16	26
10	DMF	80	16	69

Crystallographic data

Single crystal X-ray data were obtained using an Agilent Technologies SuperNova Atlas diffractometer. Crystals were kept at 100(2) K during data collection. Using Olex2¹, the structure was solved with the SHELXT² structure solution program using Intrinsic Phasing and refined with the SHELXL³ refinement package using Least Squares minimisation. Deposition number 2261122 (**6a**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

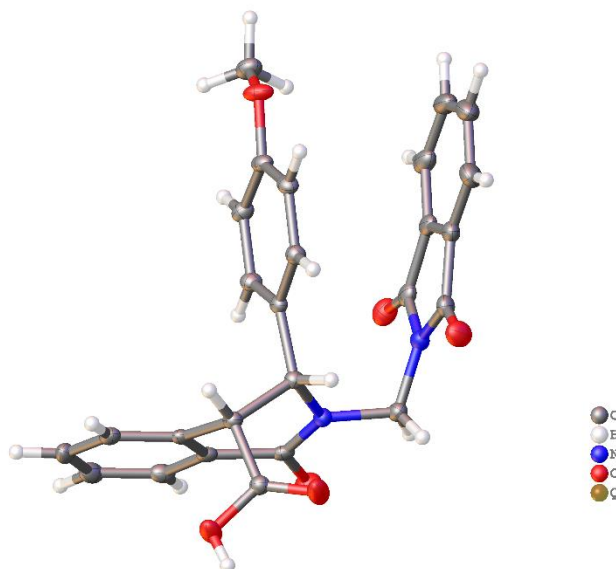


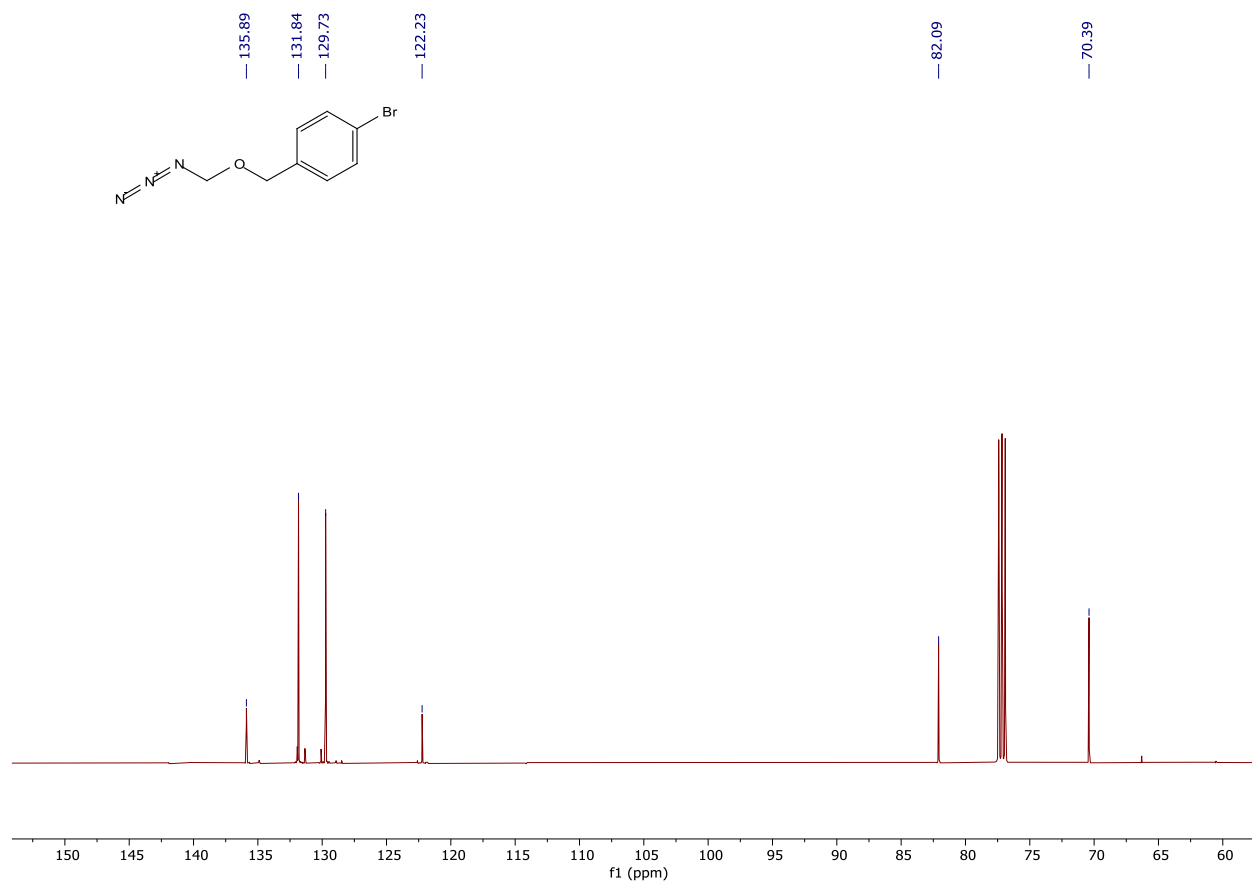
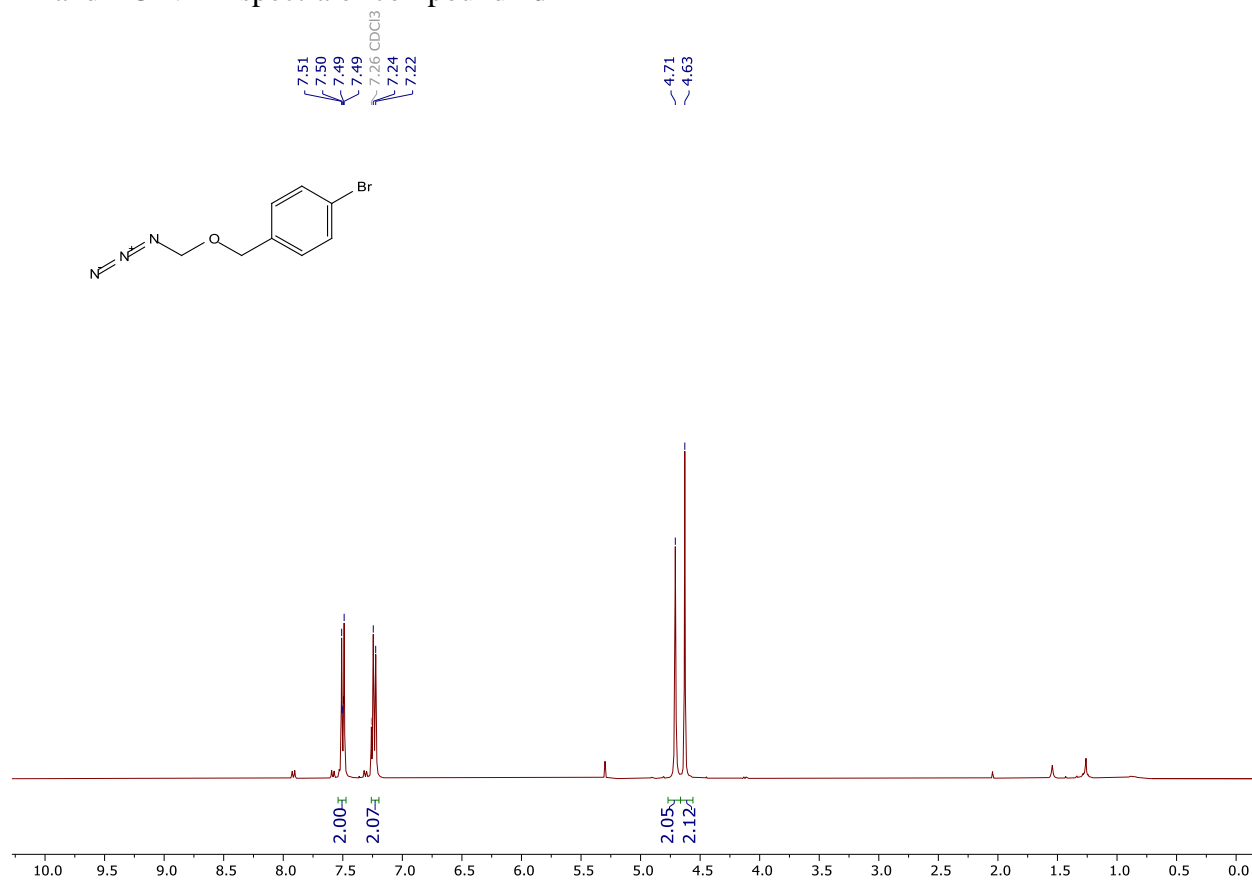
Figure S1. ORTEP representation of compound **6a** drawn at 50% probability level.

Table S2. Crystal data and structure refinement for **6a**.

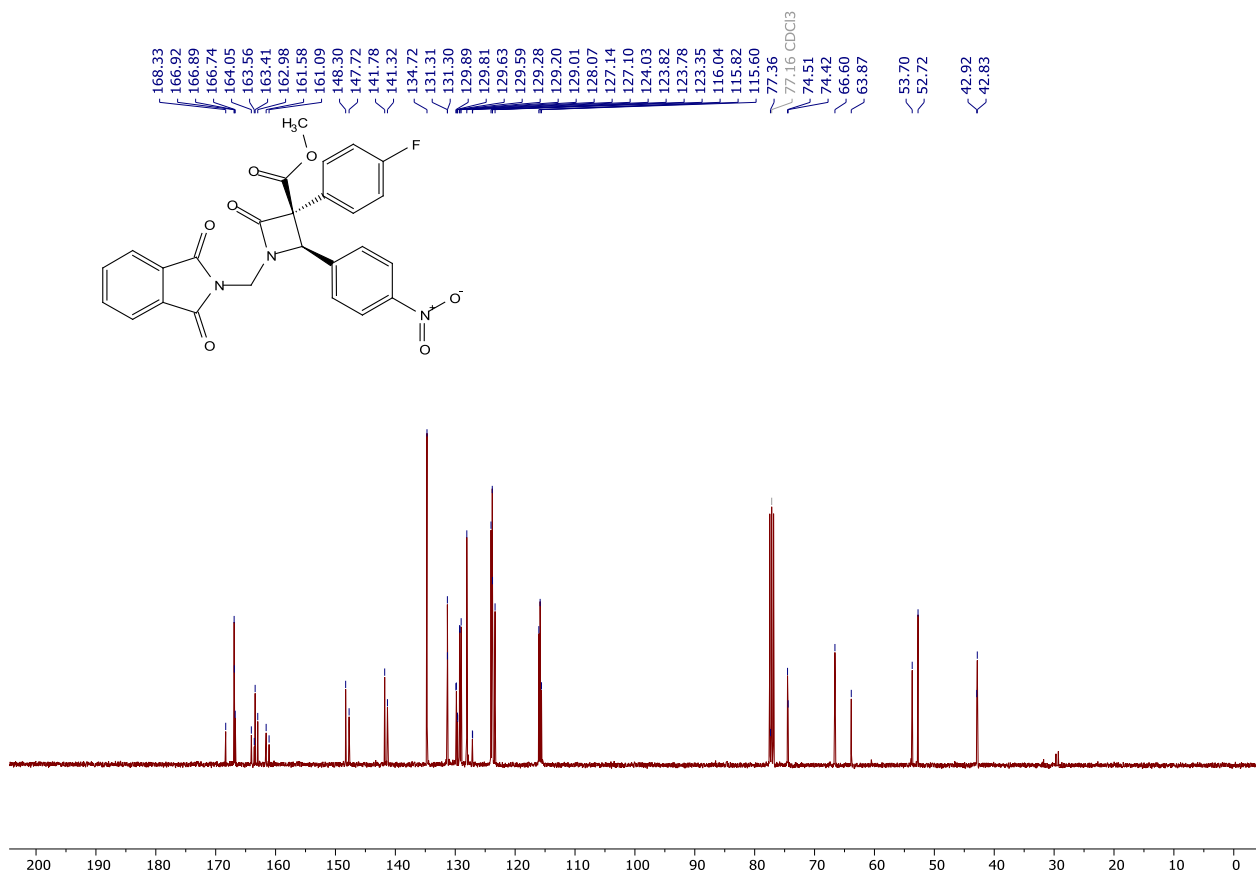
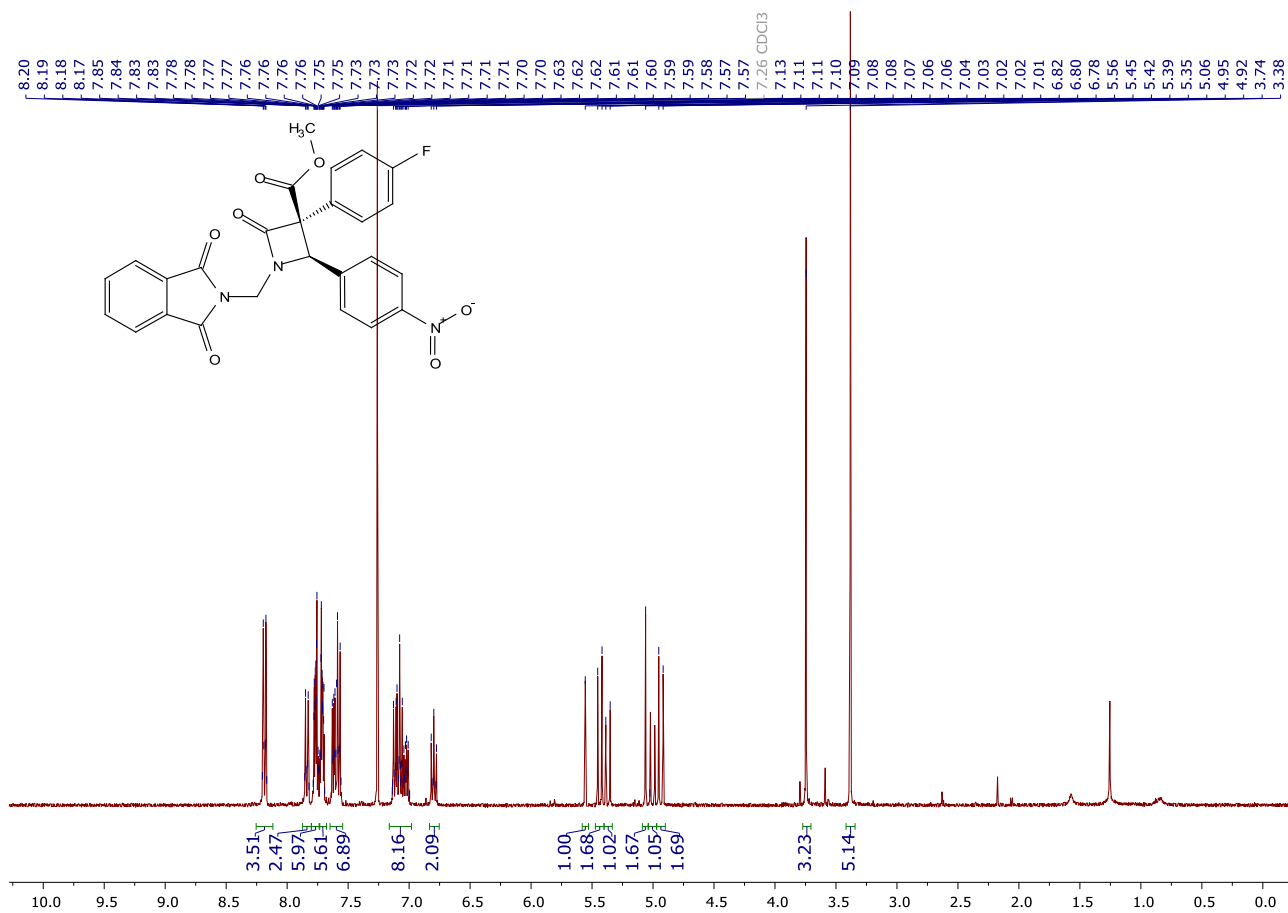
Identification code	1ver0-23431_PPS-376_auto
Empirical formula	C ₂₆ H ₂₀ N ₂ O ₆
Formula weight	456.458
Temperature/K	100.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.3756(1)
b/Å	10.9149(2)
c/Å	23.5070(4)
α/°	90
β/°	95.279(2)
γ/°	90
Volume/Å³	2139.87(6)
Z	4
ρ_{calc}/cm³	1.417
μ/mm⁻¹	0.845
F(000)	955.4
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.56 to 152.48
Index ranges	-10 ≤ h ≤ 9, -9 ≤ k ≤ 13, -29 ≤ l ≤ 27
Reflections collected	10915
Independent reflections	4377 [R _{int} = 0.0413, R _{sigma} = 0.0390]

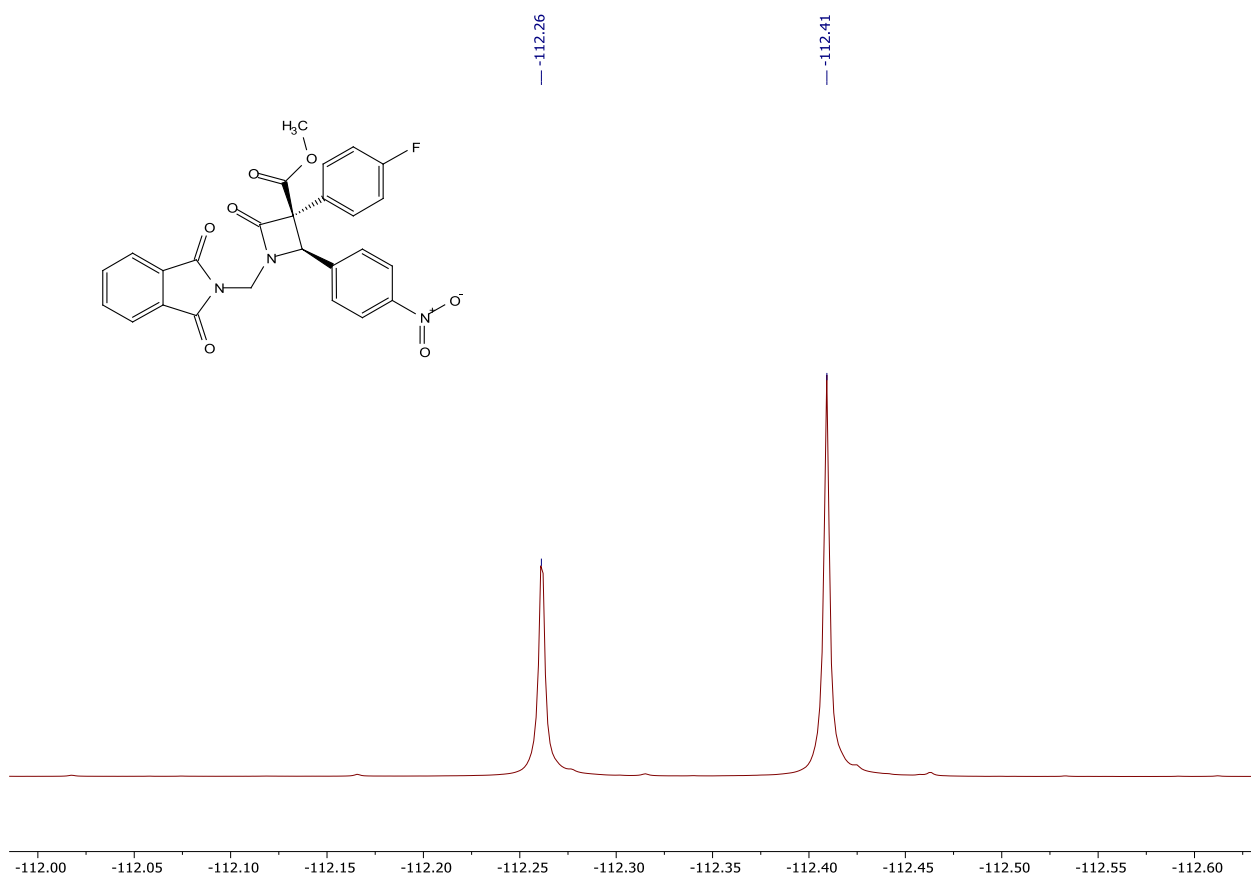
Data/restraints/parameters	4377/0/309
Goodness-of-fit on F²	1.058
Final R indexes [I>2σ (I)]	R ₁ = 0.0434, wR ₂ = 0.1147
Final R indexes [all data]	R ₁ = 0.0534, wR ₂ = 0.1225
Largest diff. peak/hole / e Å⁻³	0.41/-0.32

Copies of ^1H , ^{13}C and ^{19}F NMR spectra
 ^1H and ^{13}C NMR spectra of compound **1d**

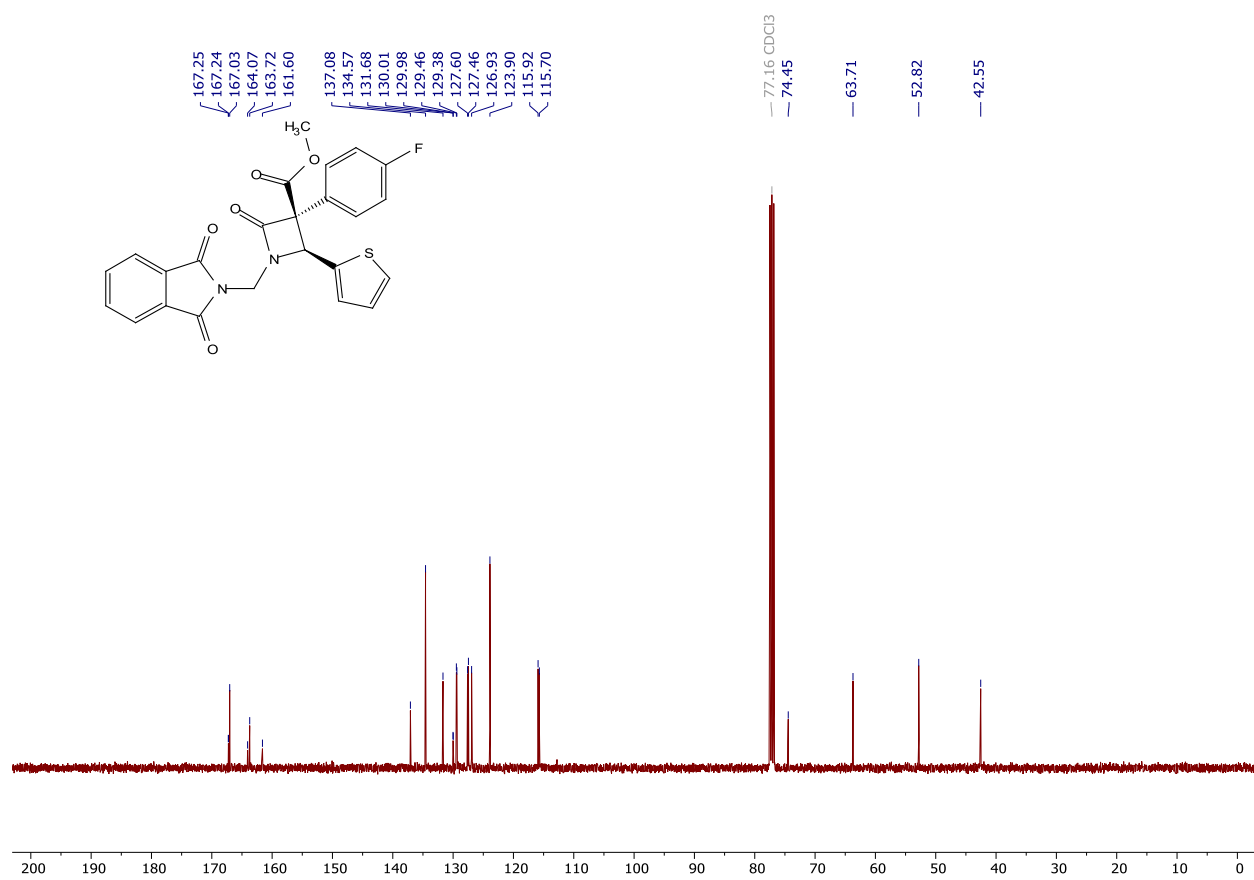
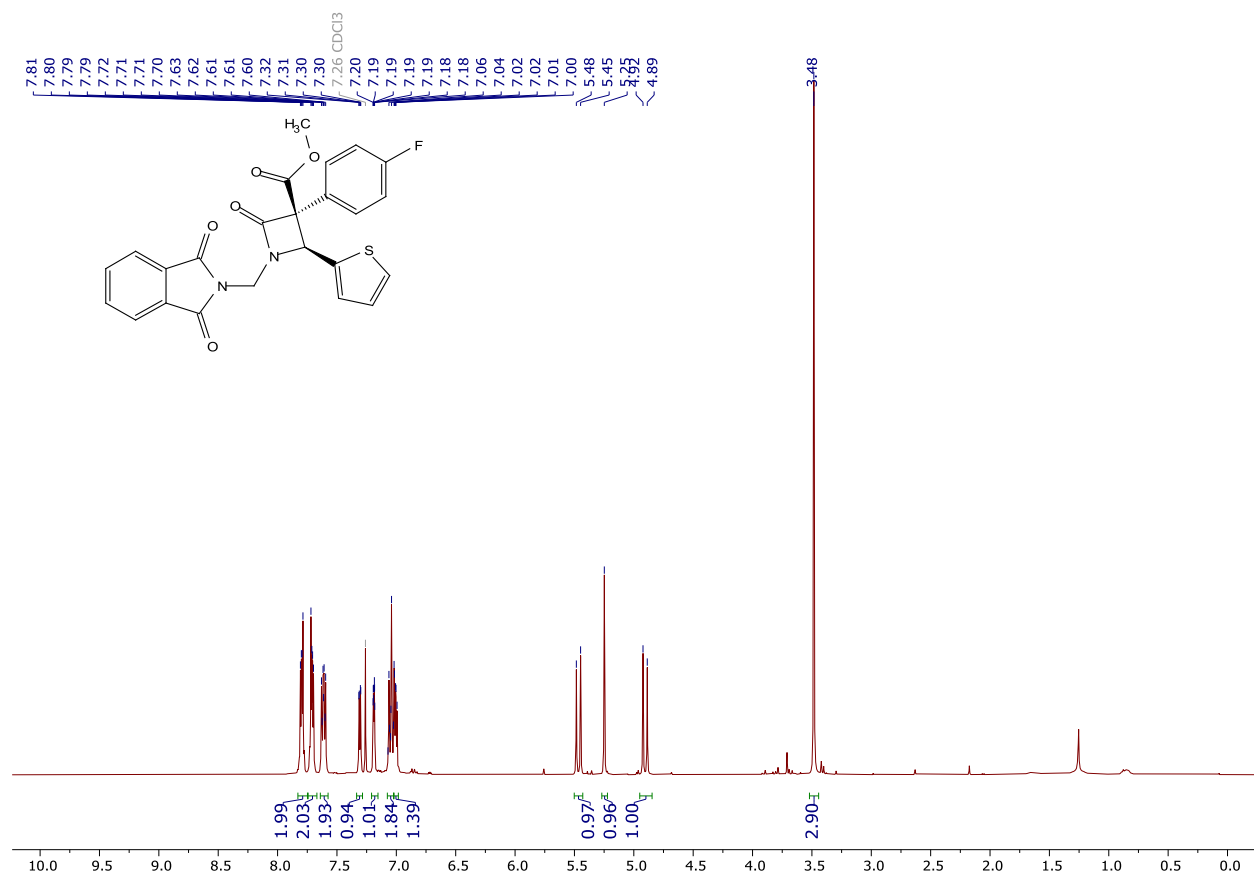


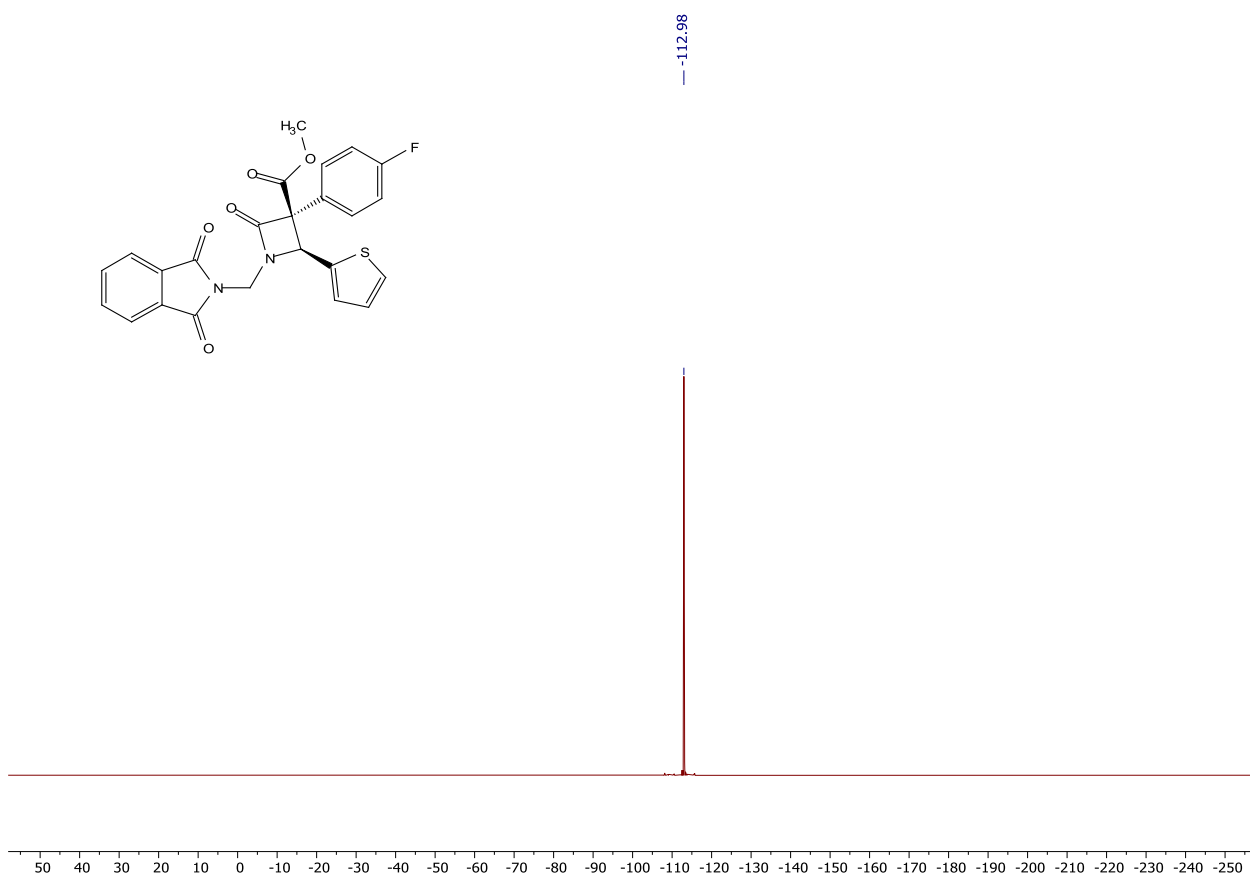
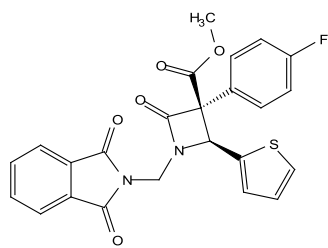
^1H , ^{13}C and ^{19}F NMR spectra of compound **4a**



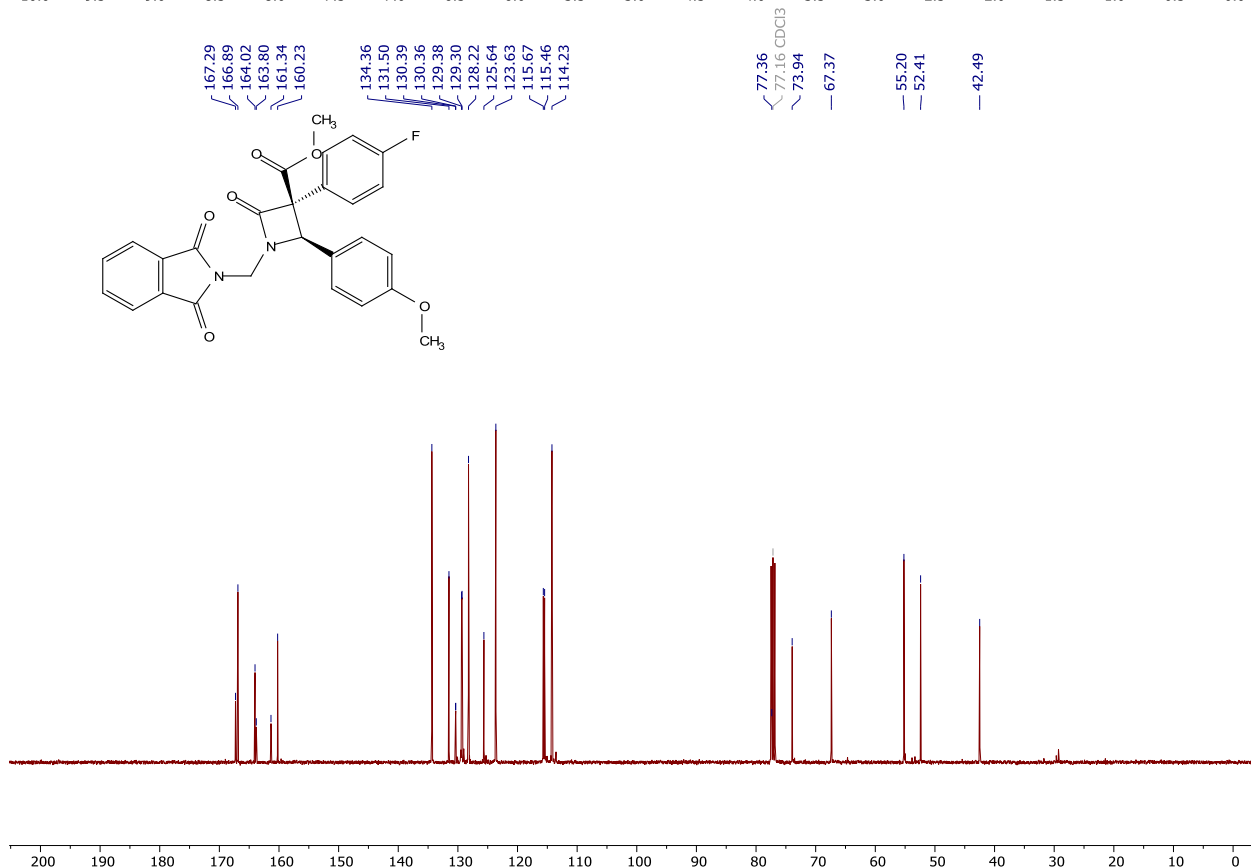
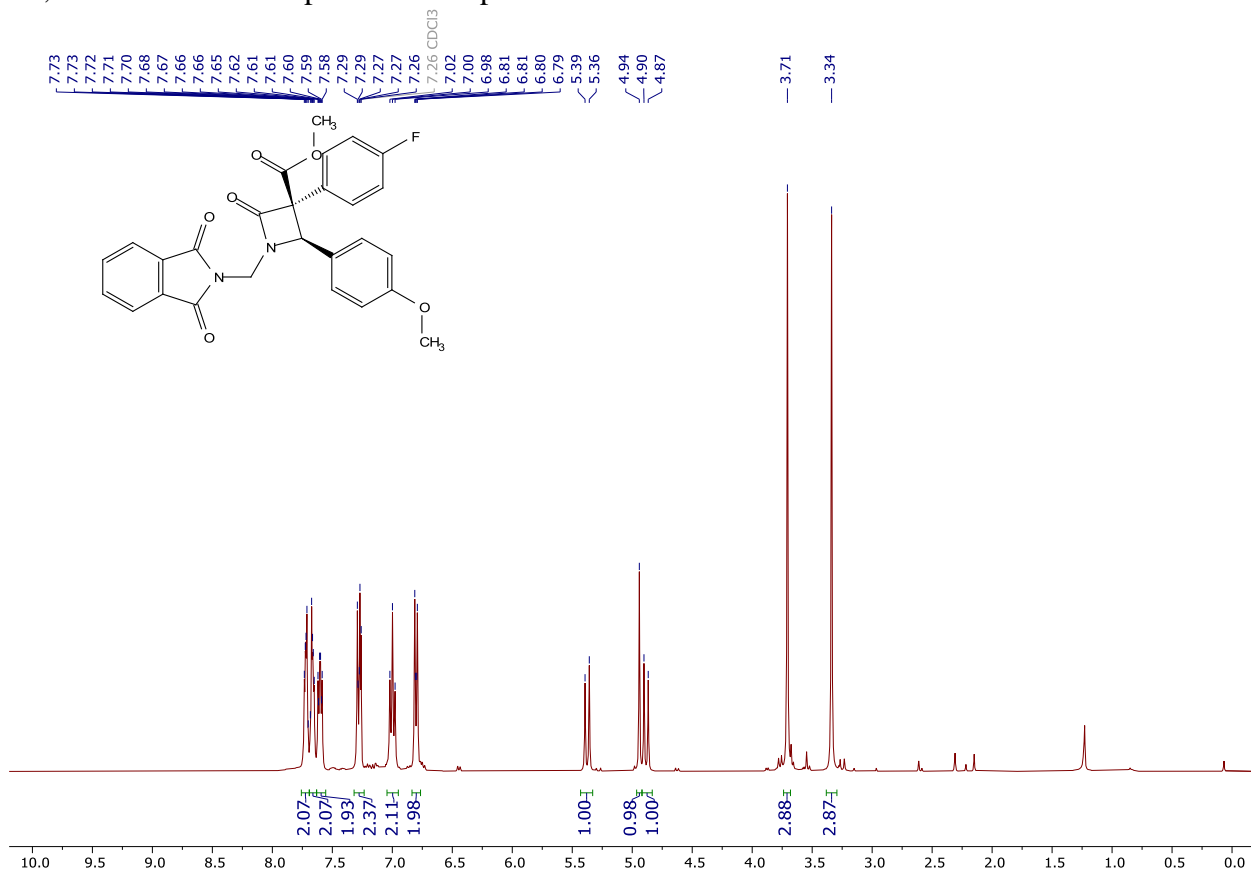


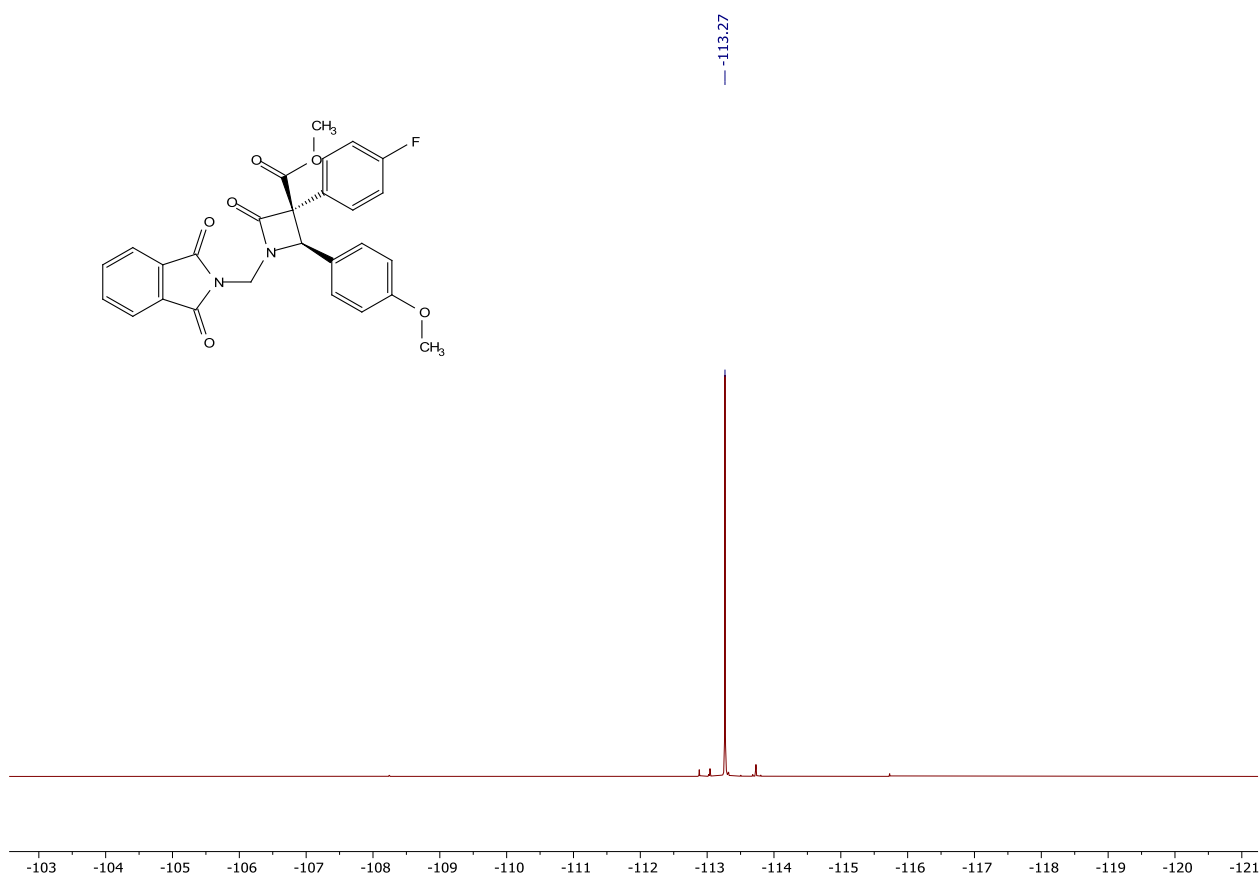
^1H , ^{13}C and ^{19}F NMR spectra of compound **4b**



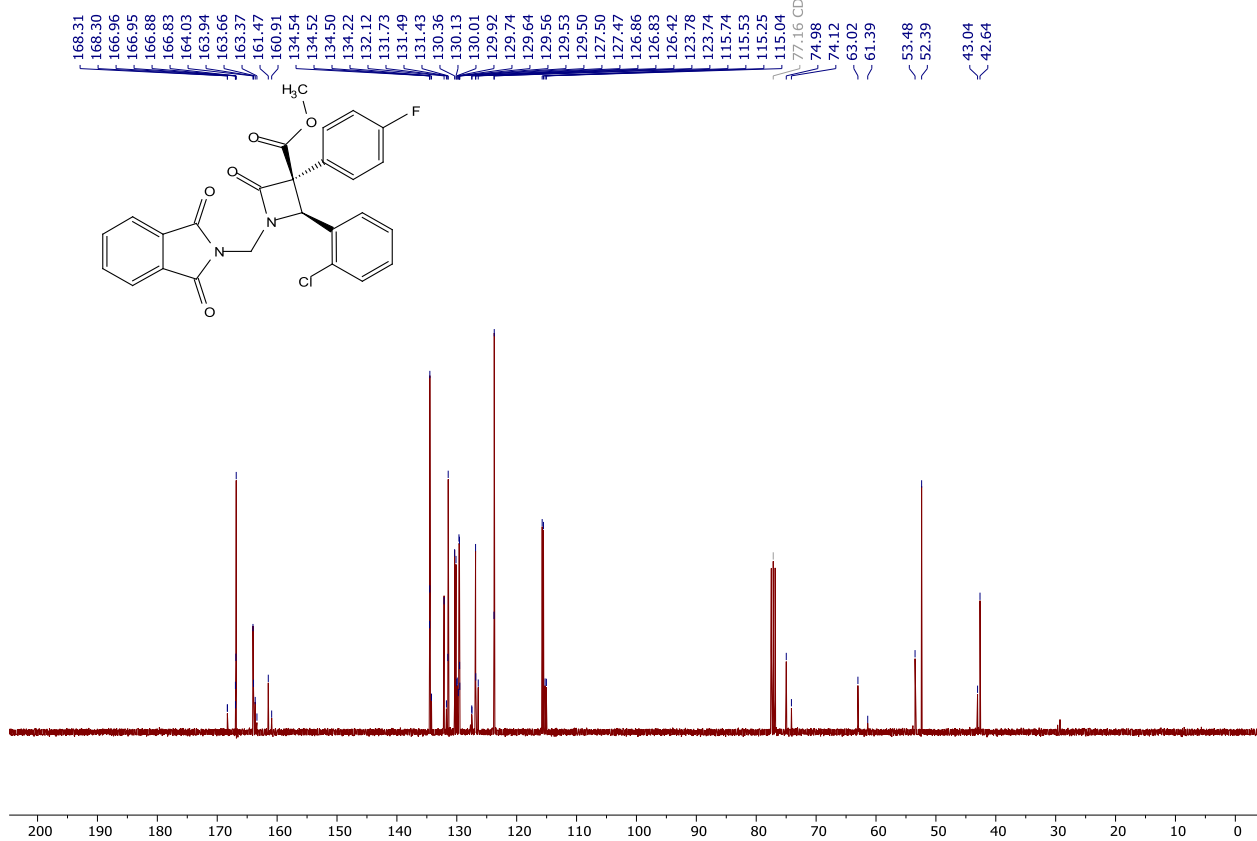
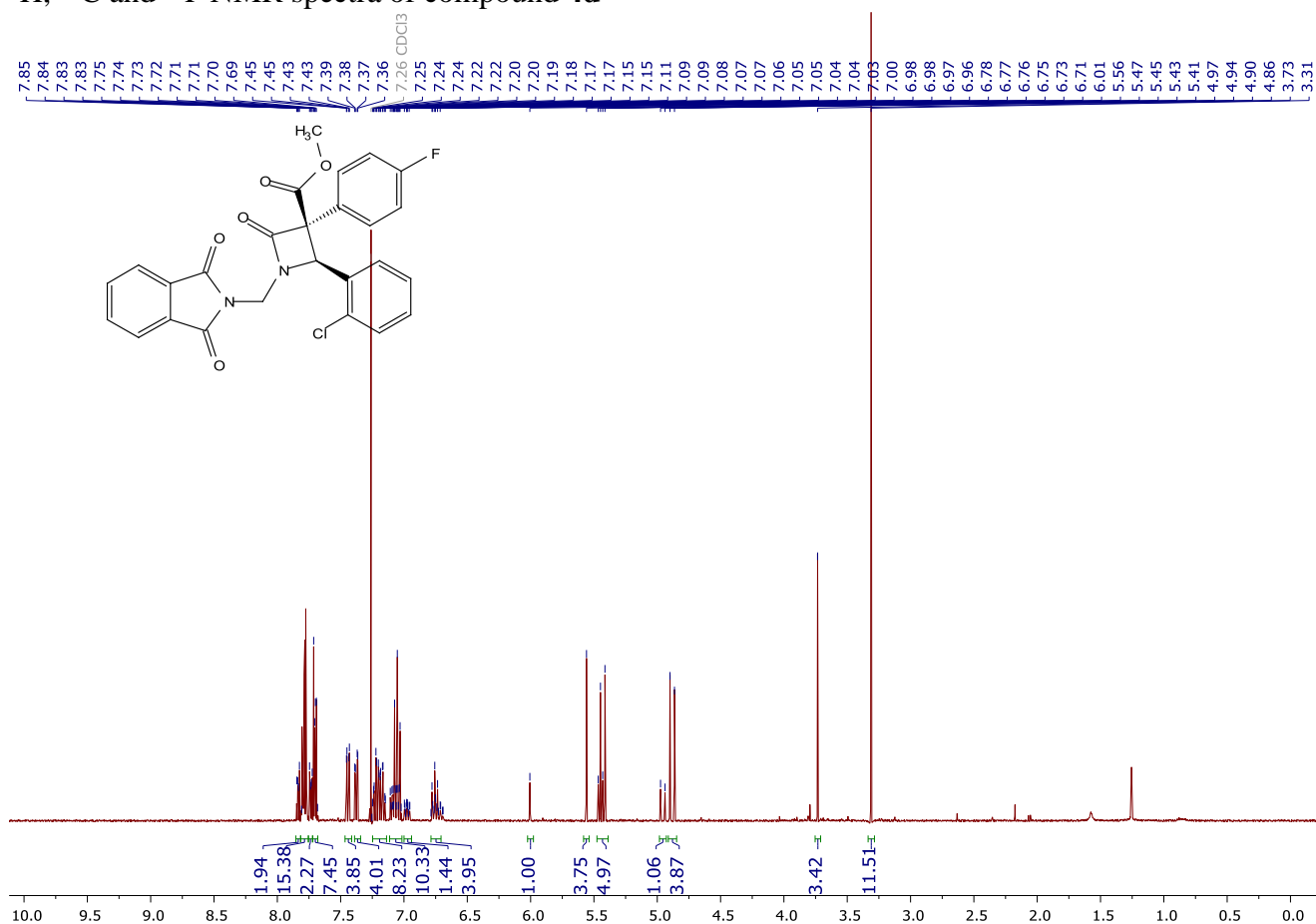


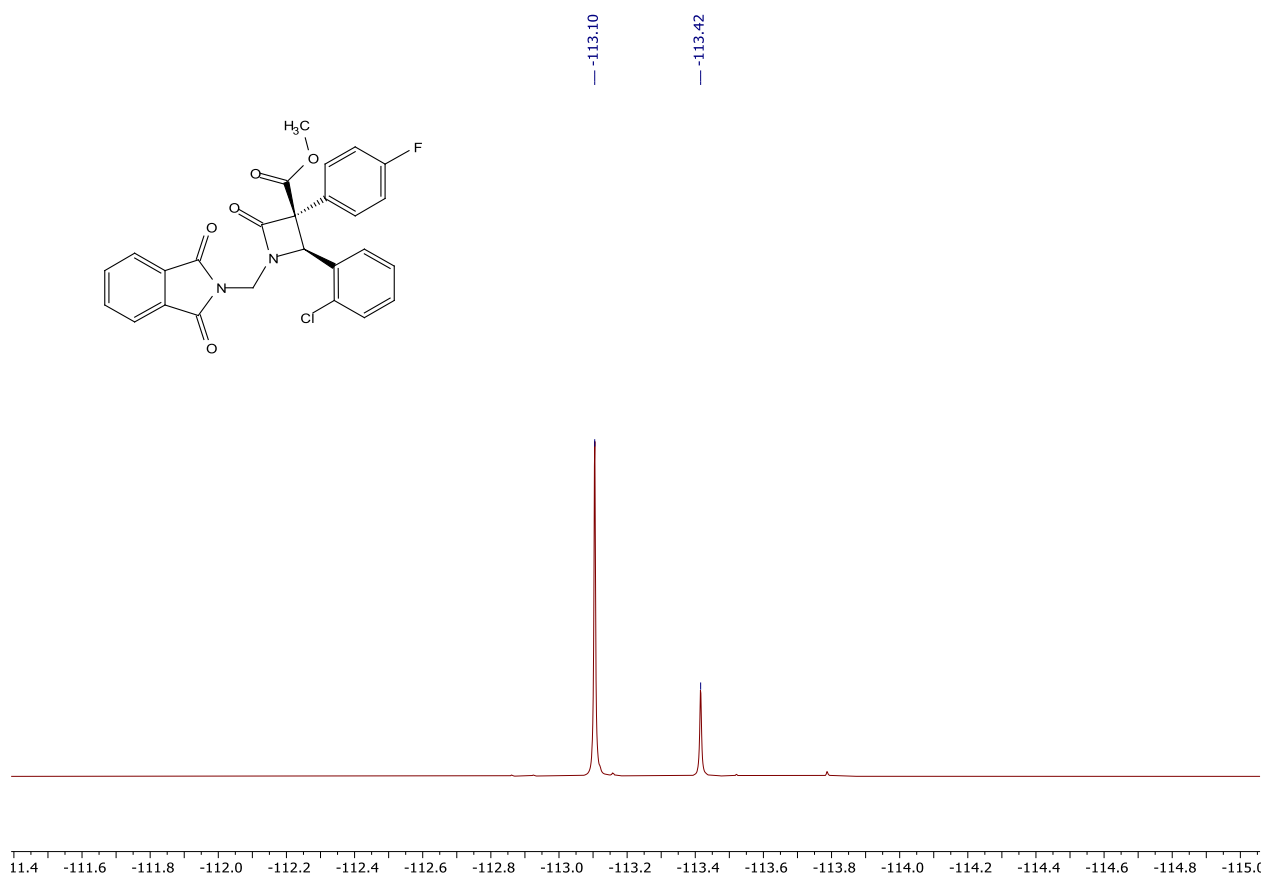
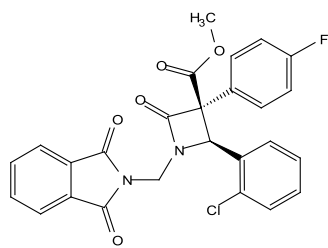
^1H , ^{13}C and ^{19}F NMR spectra of compound **4c**



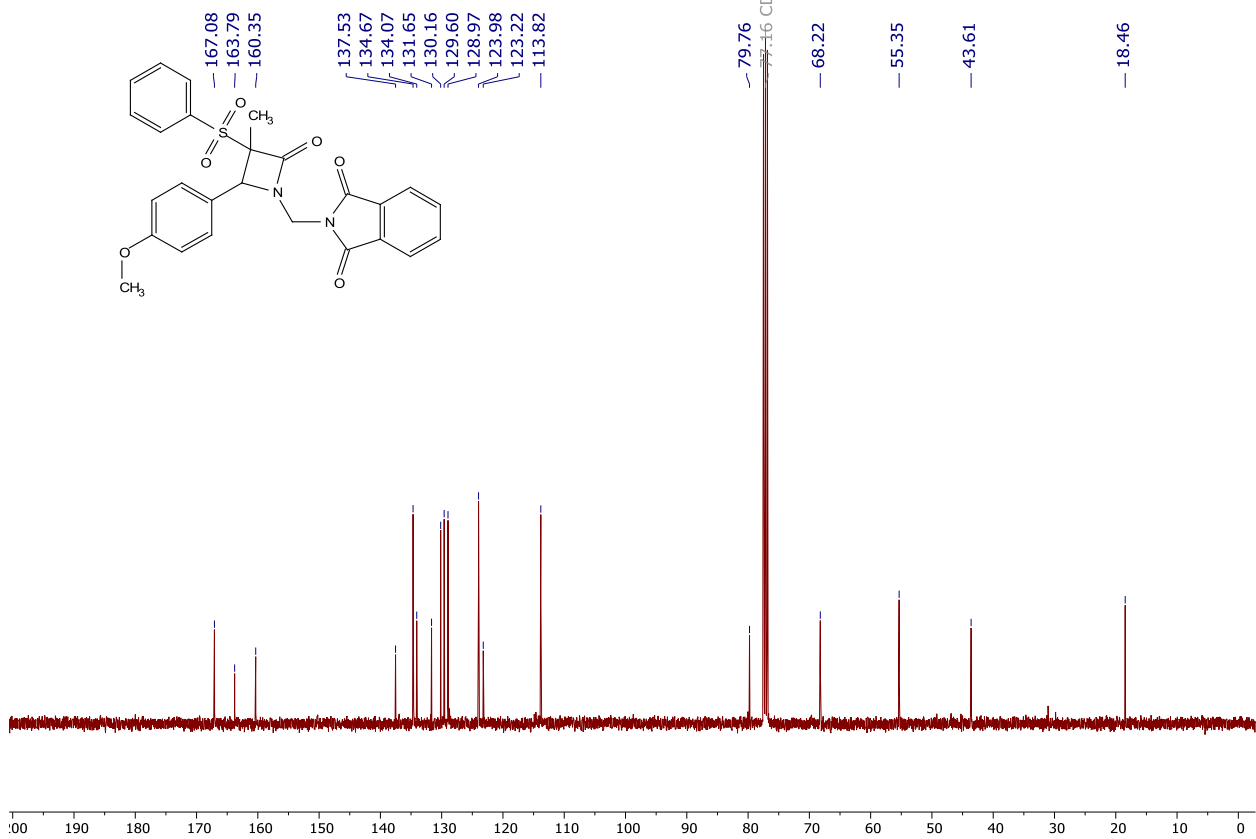
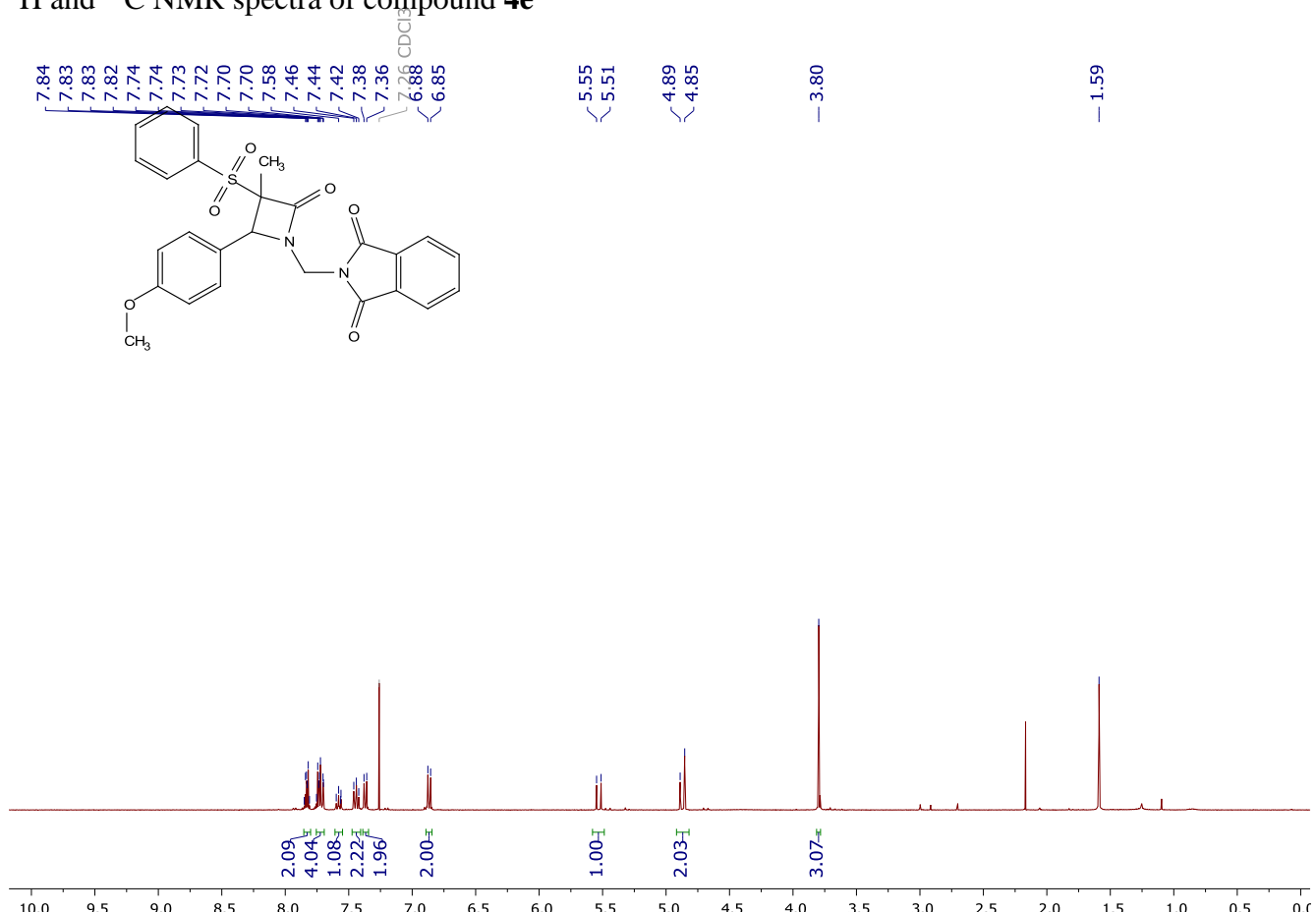


^1H , ^{13}C and ^{19}F NMR spectra of compound **4d**

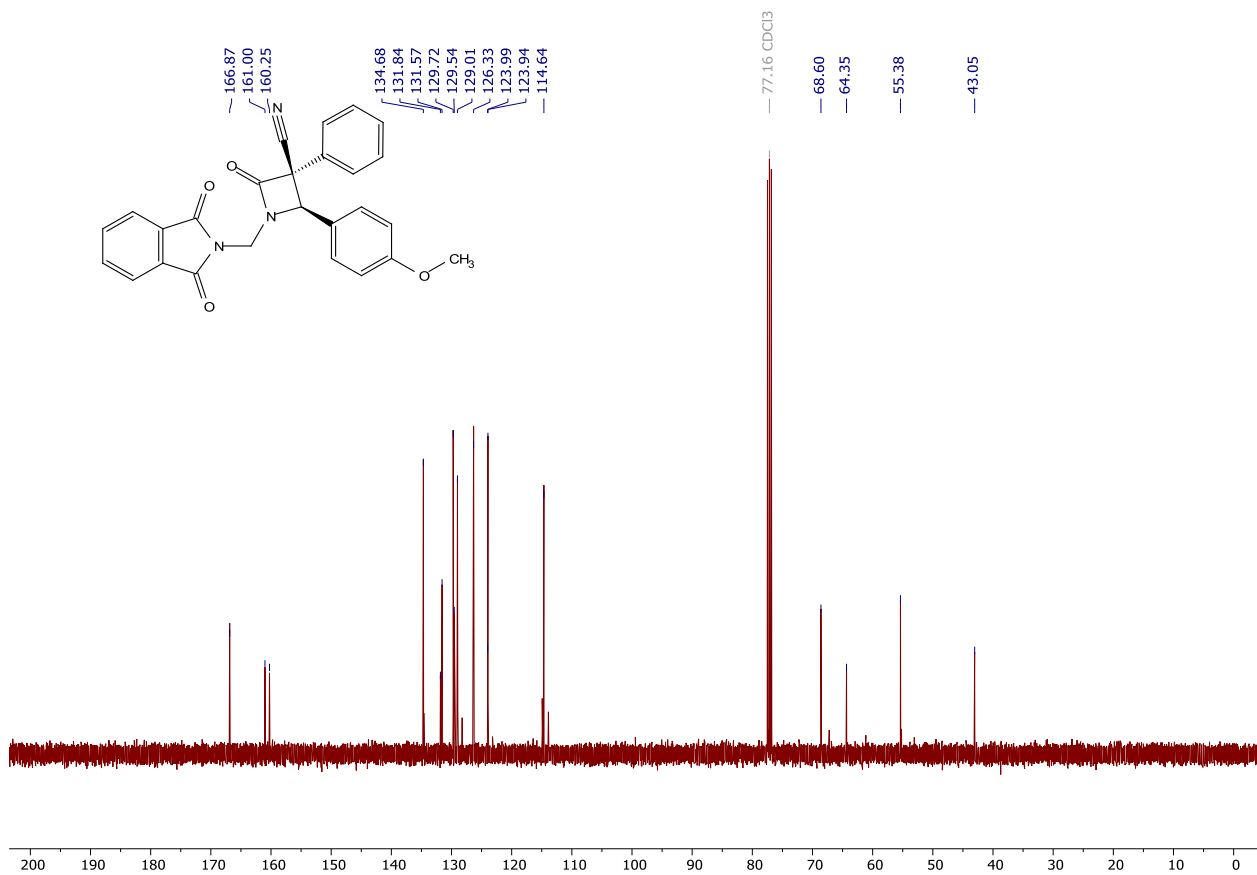
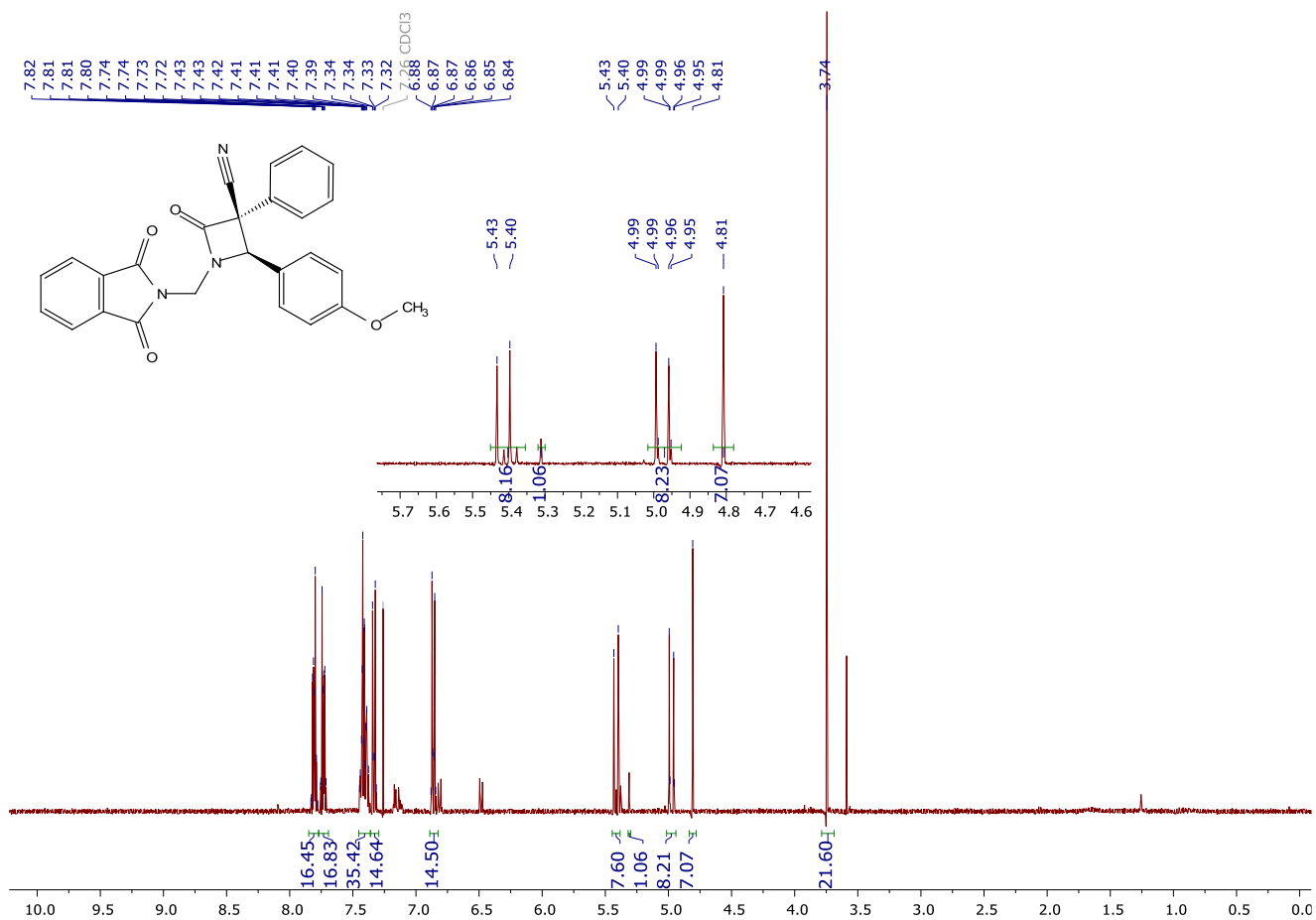




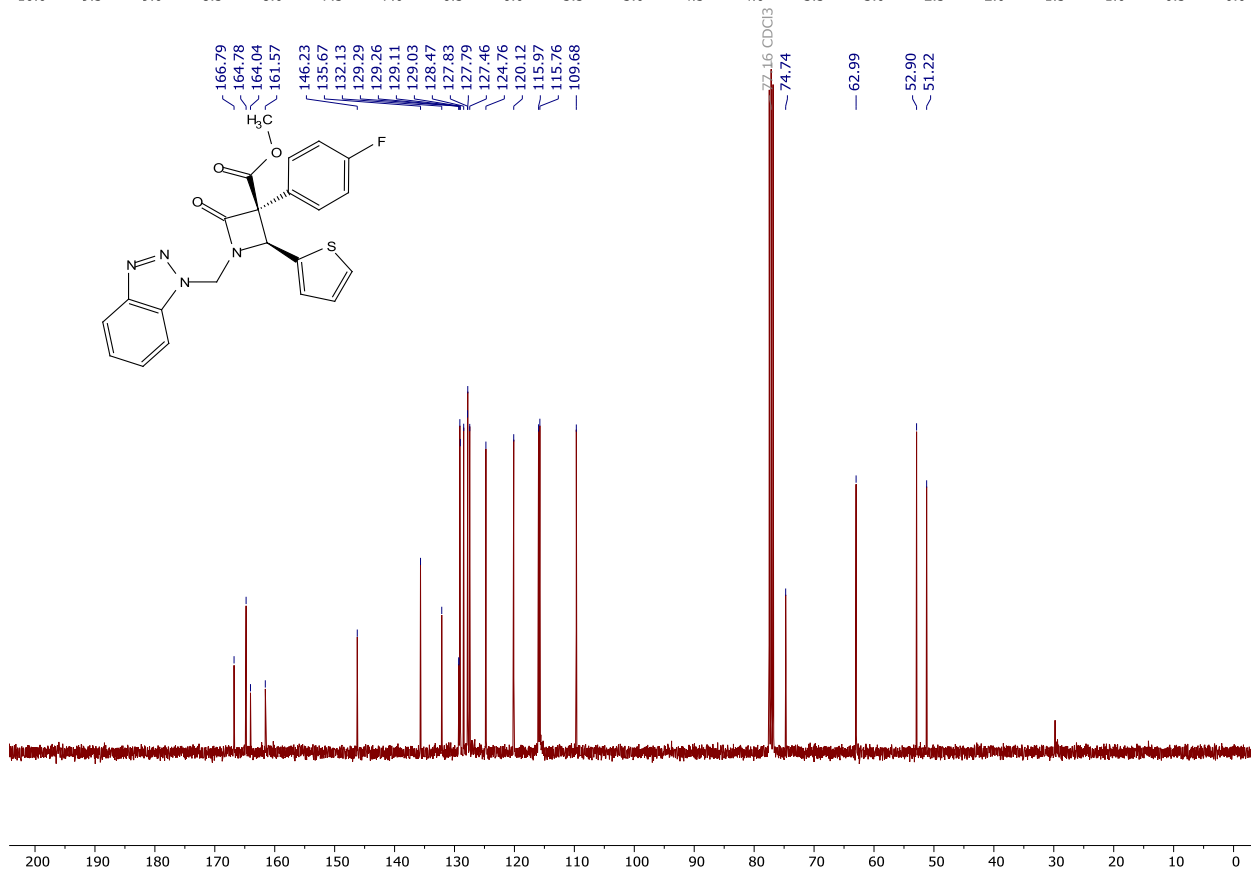
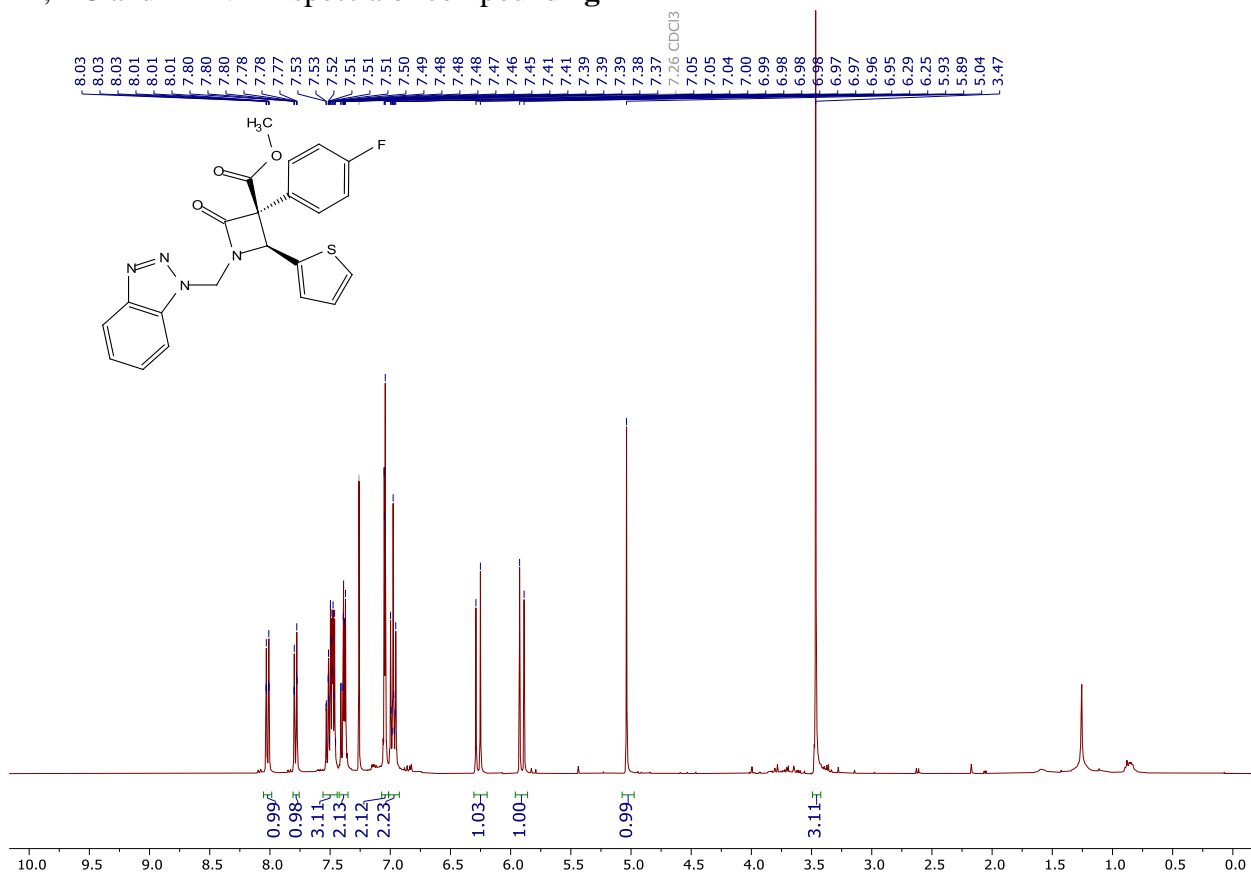
^1H and ^{13}C NMR spectra of compound **4e**

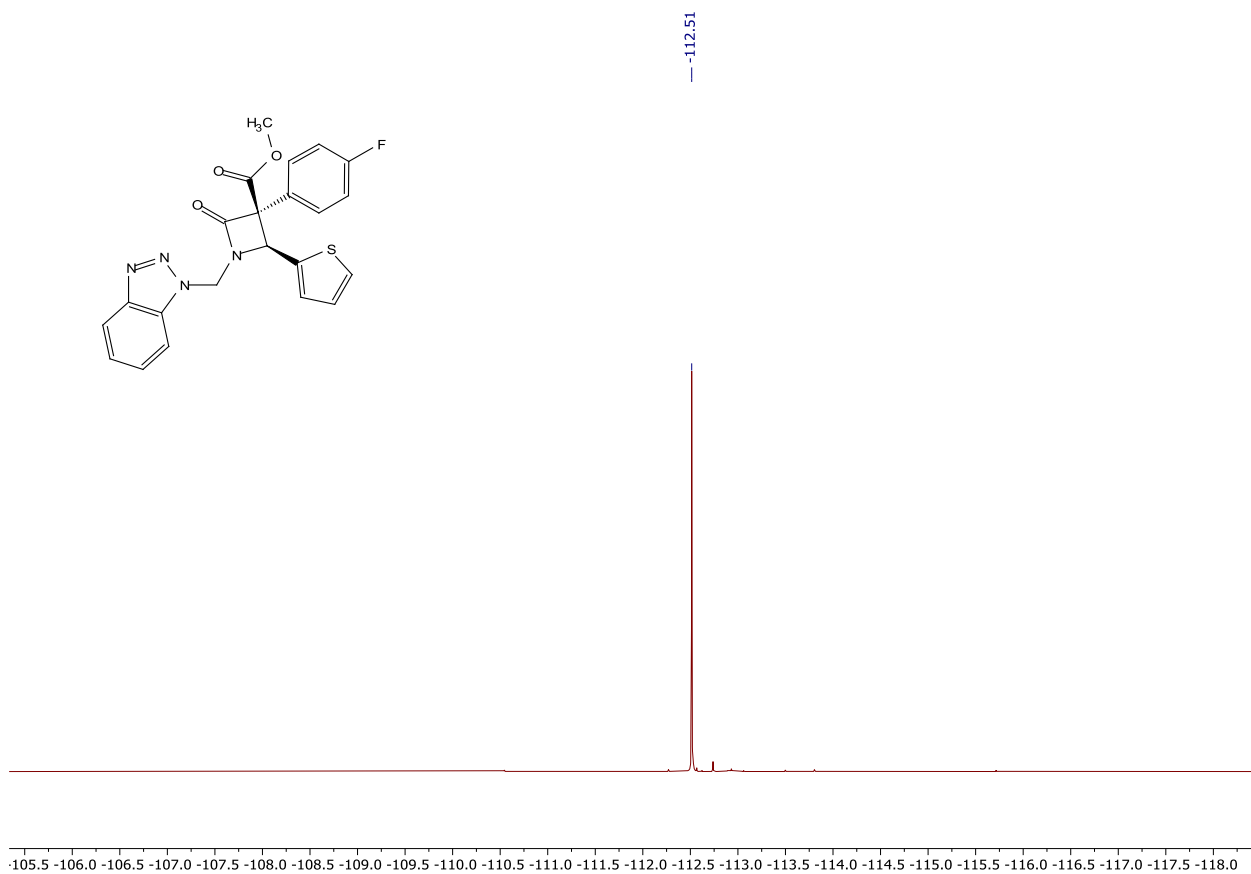


^1H and ^{13}C NMR spectra of compound **4f**

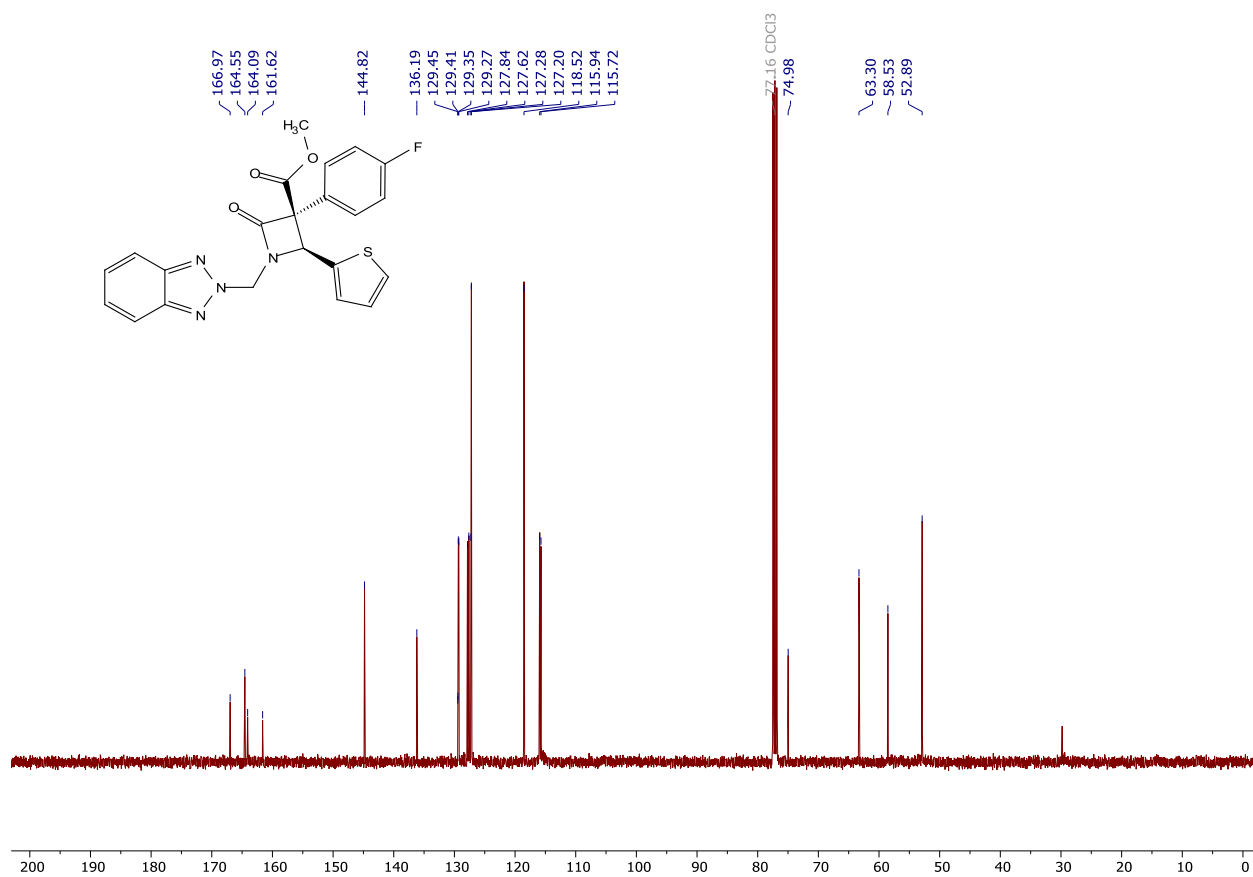
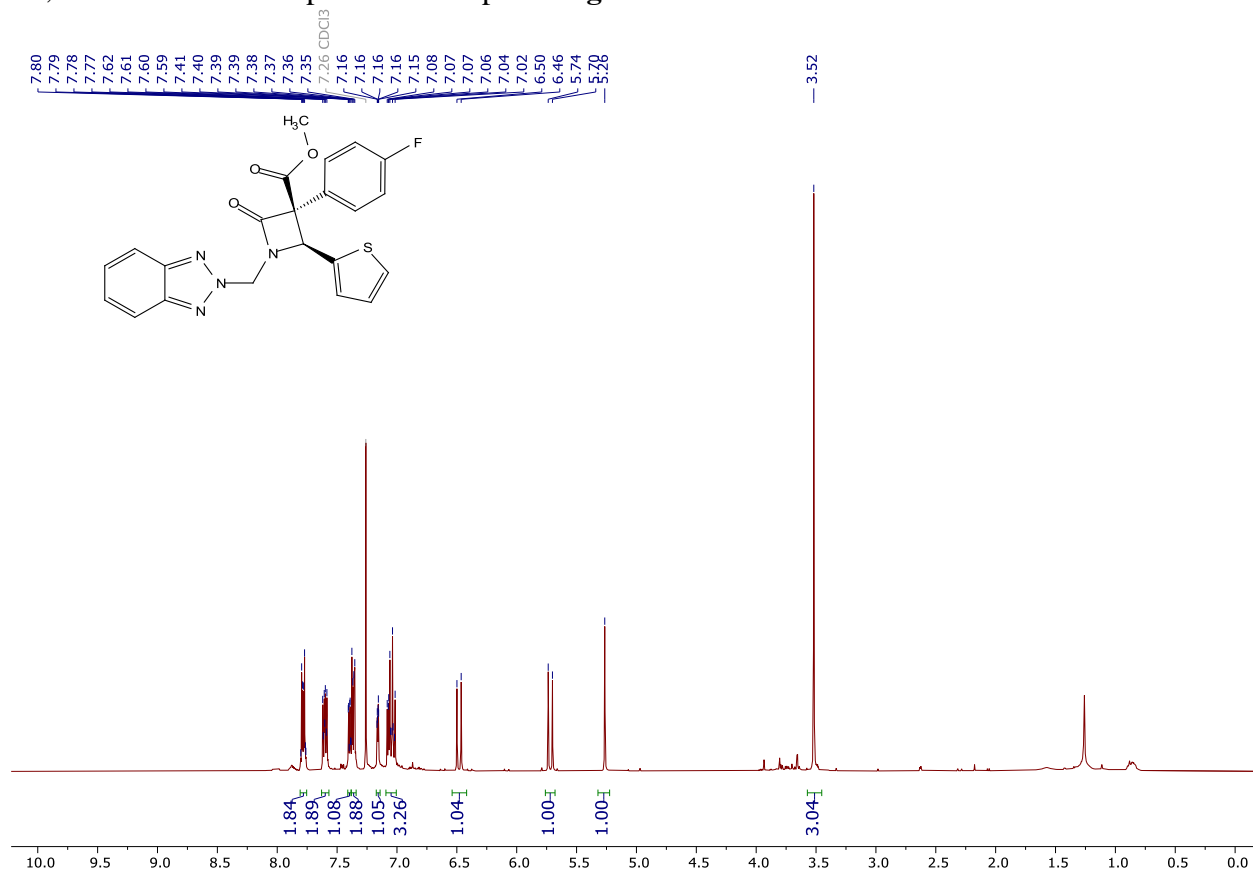


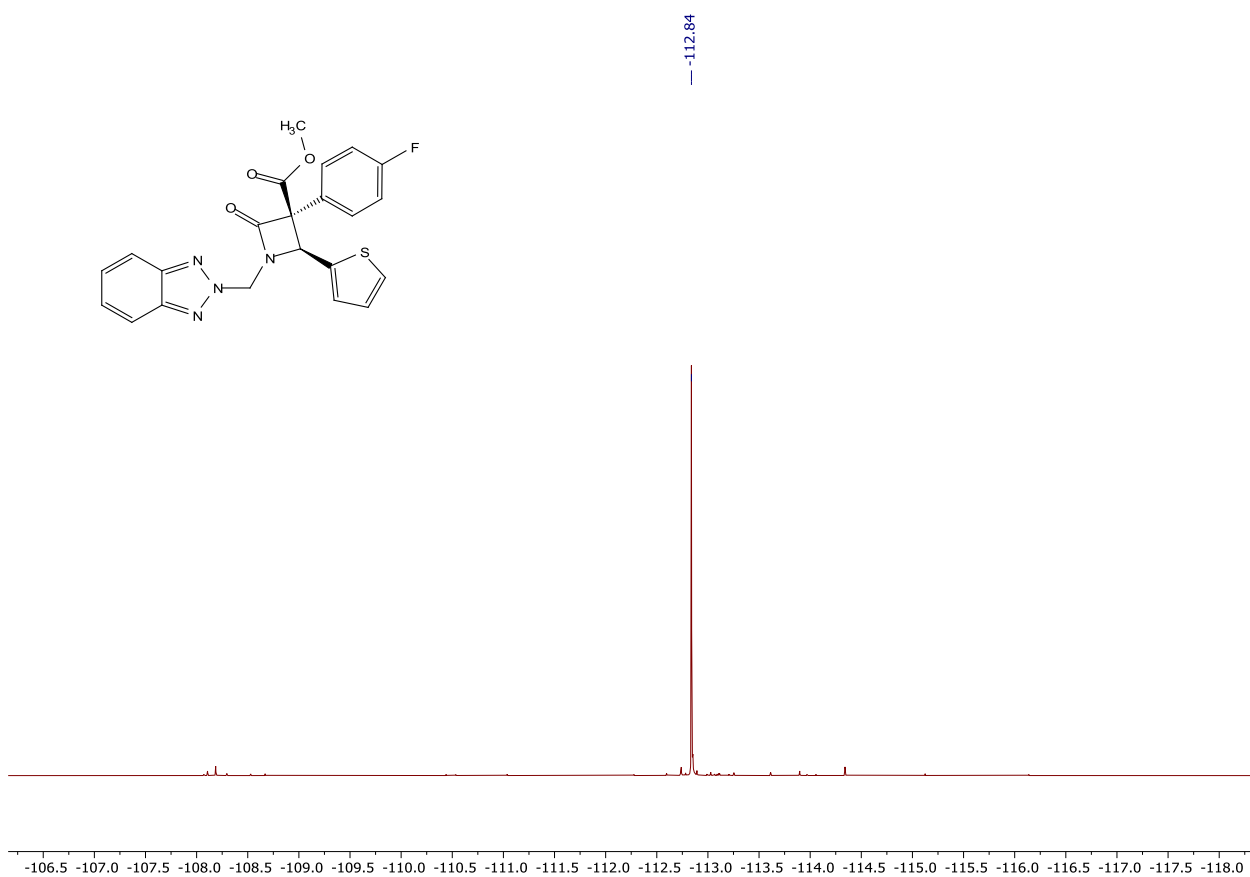
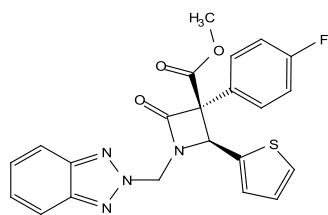
^1H , ^{13}C and ^{19}F NMR spectra of compound **4g**



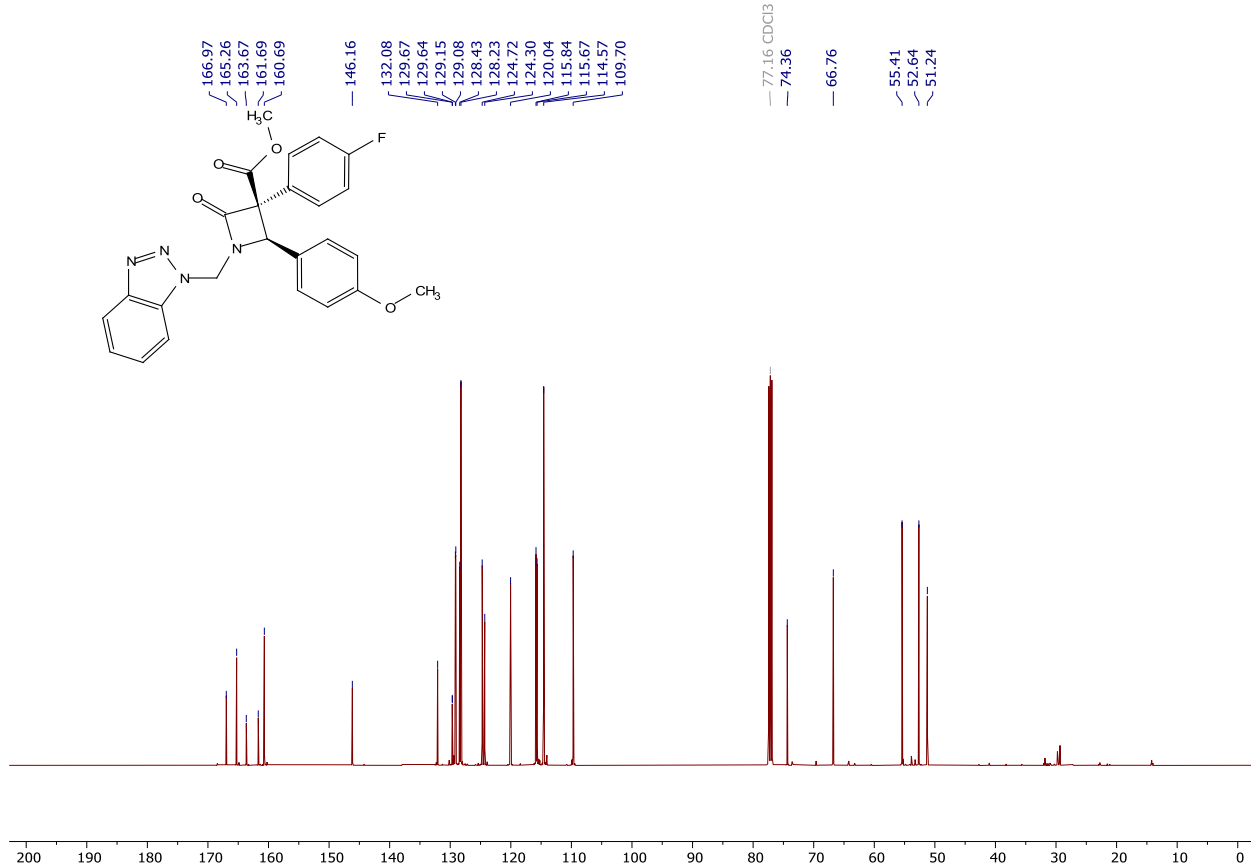
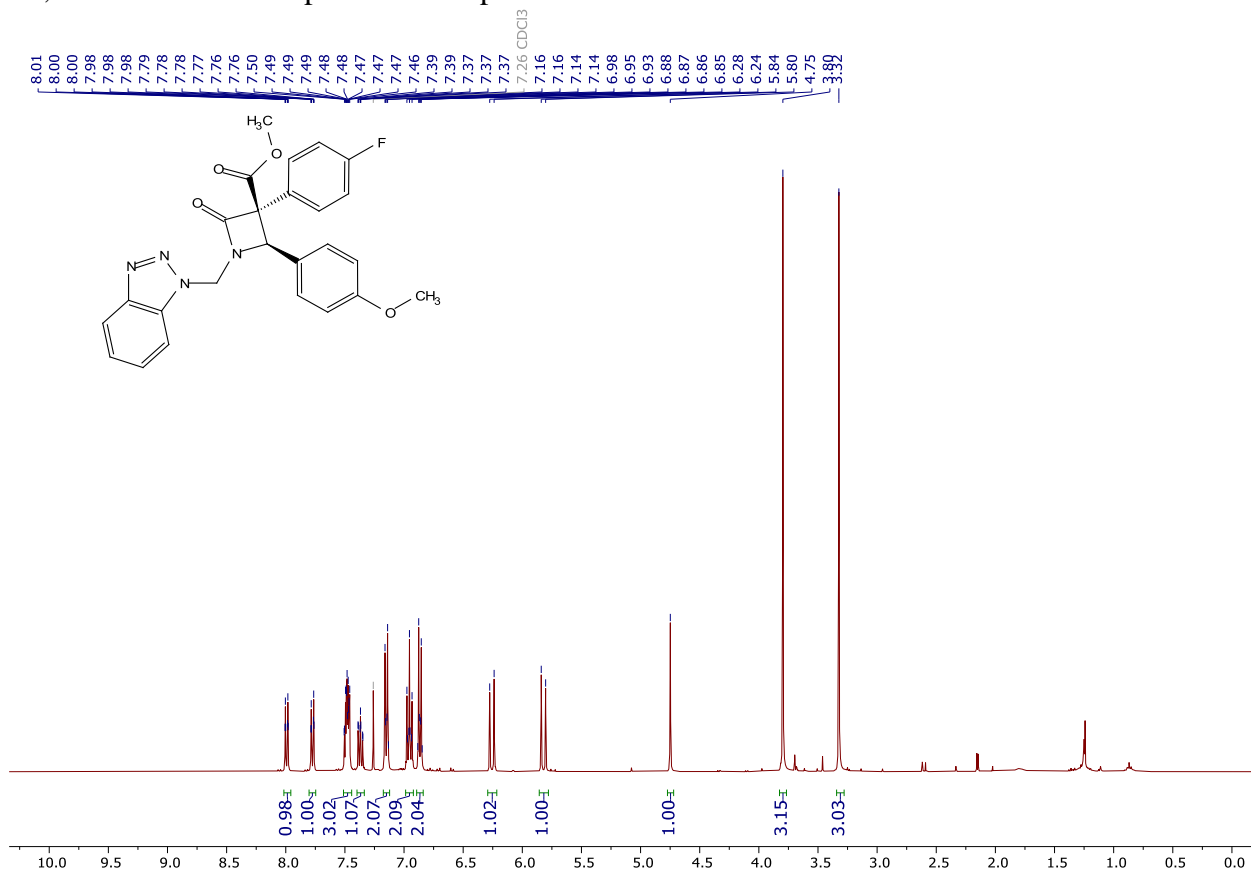


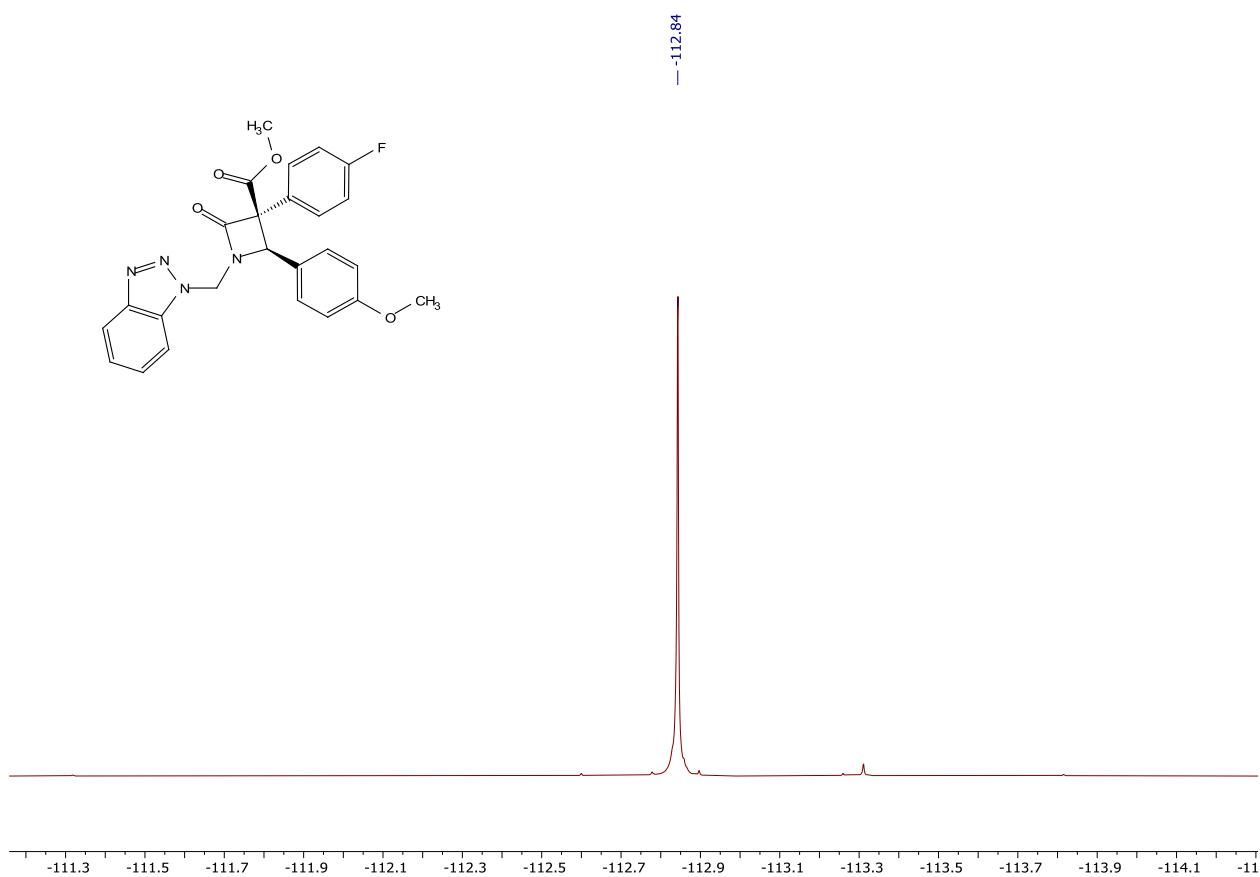
^1H , ^{13}C and ^{19}F NMR spectra of compound **4g**



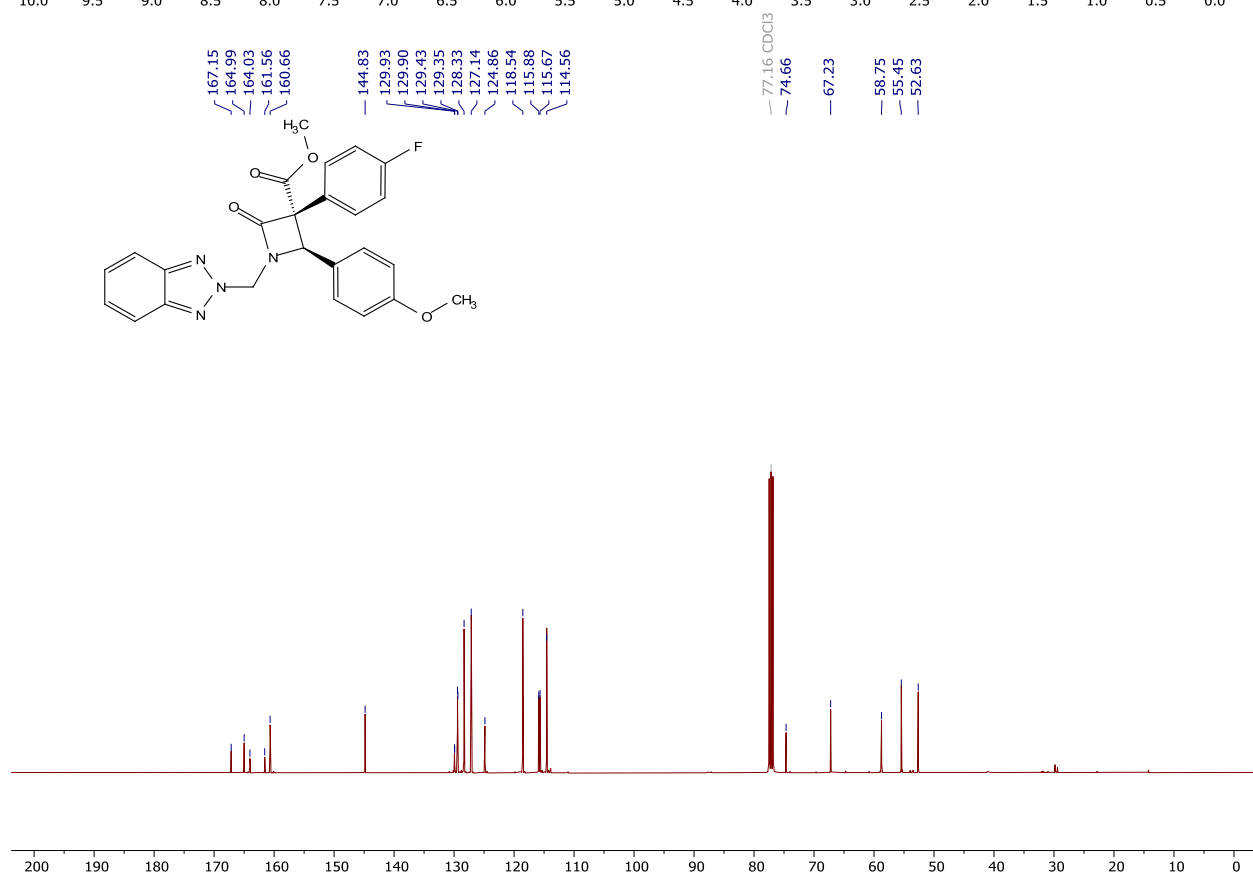
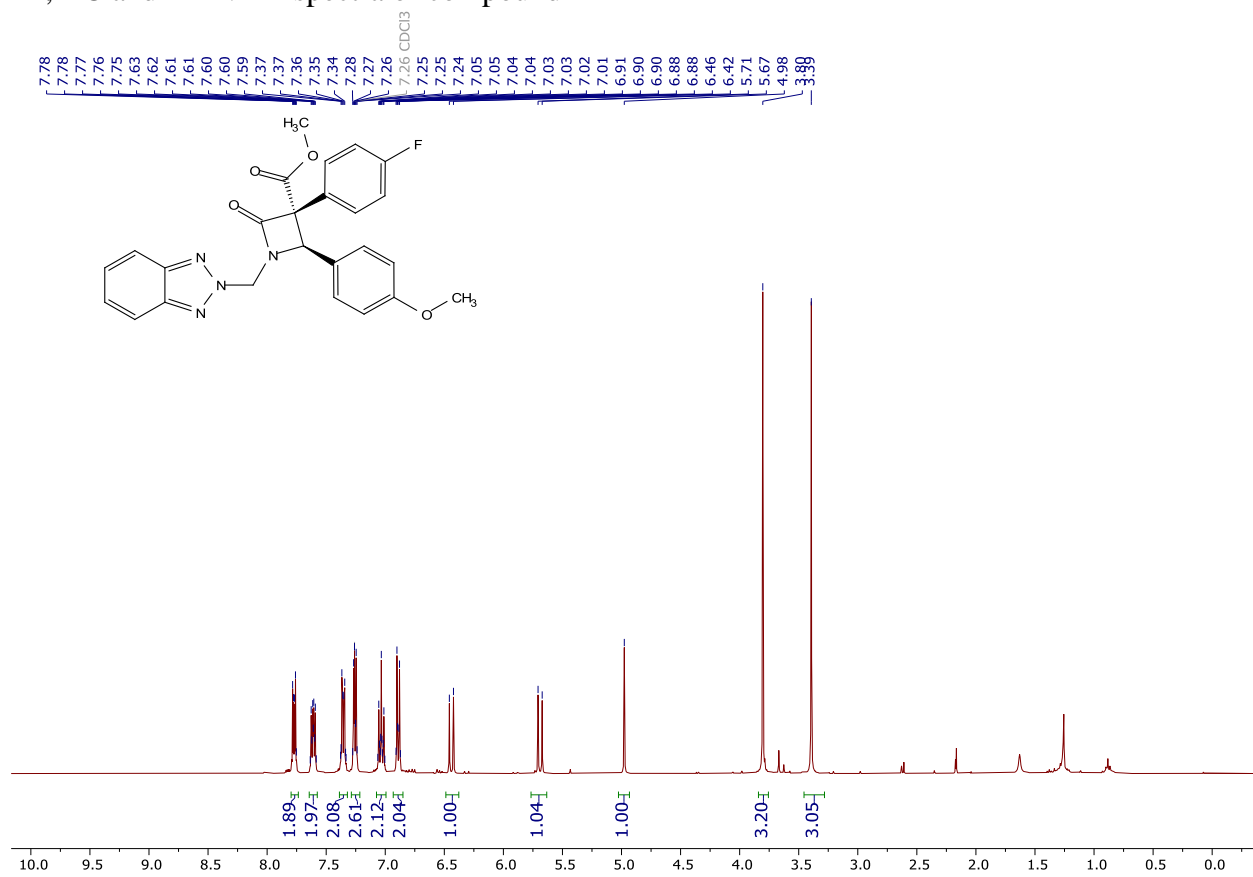


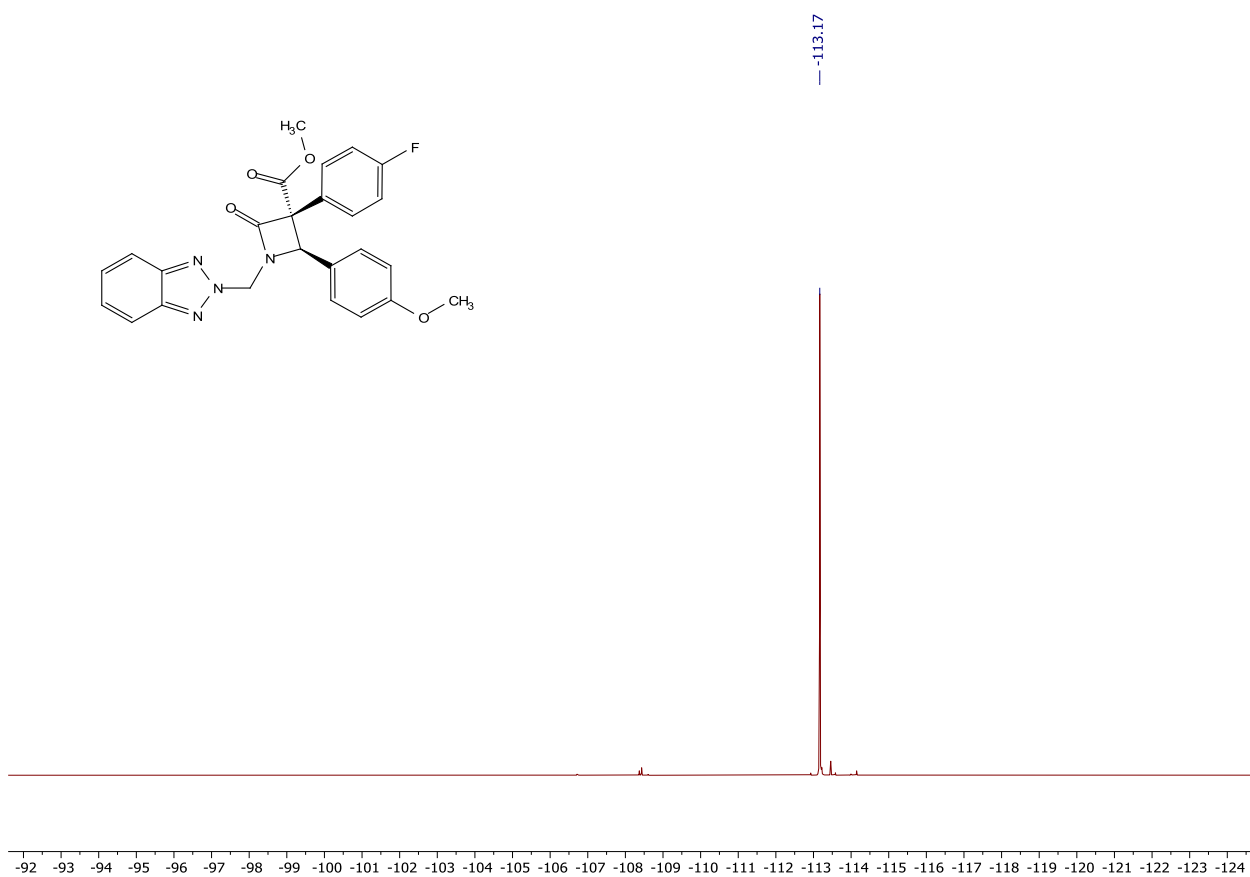
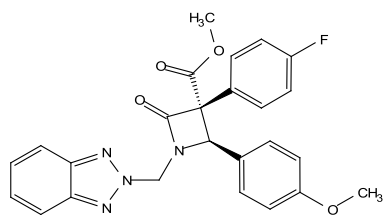
^1H , ^{13}C and ^{19}F NMR spectra of compound **4h**



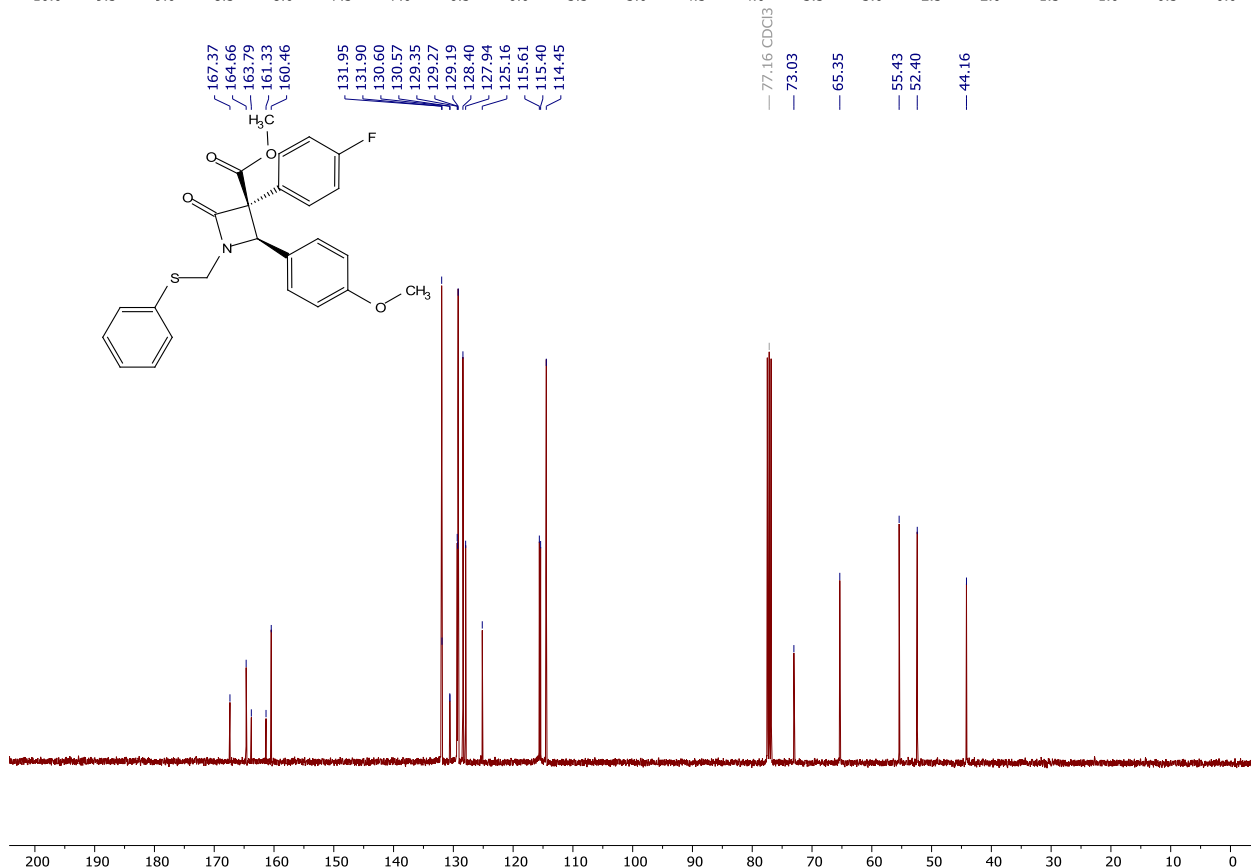
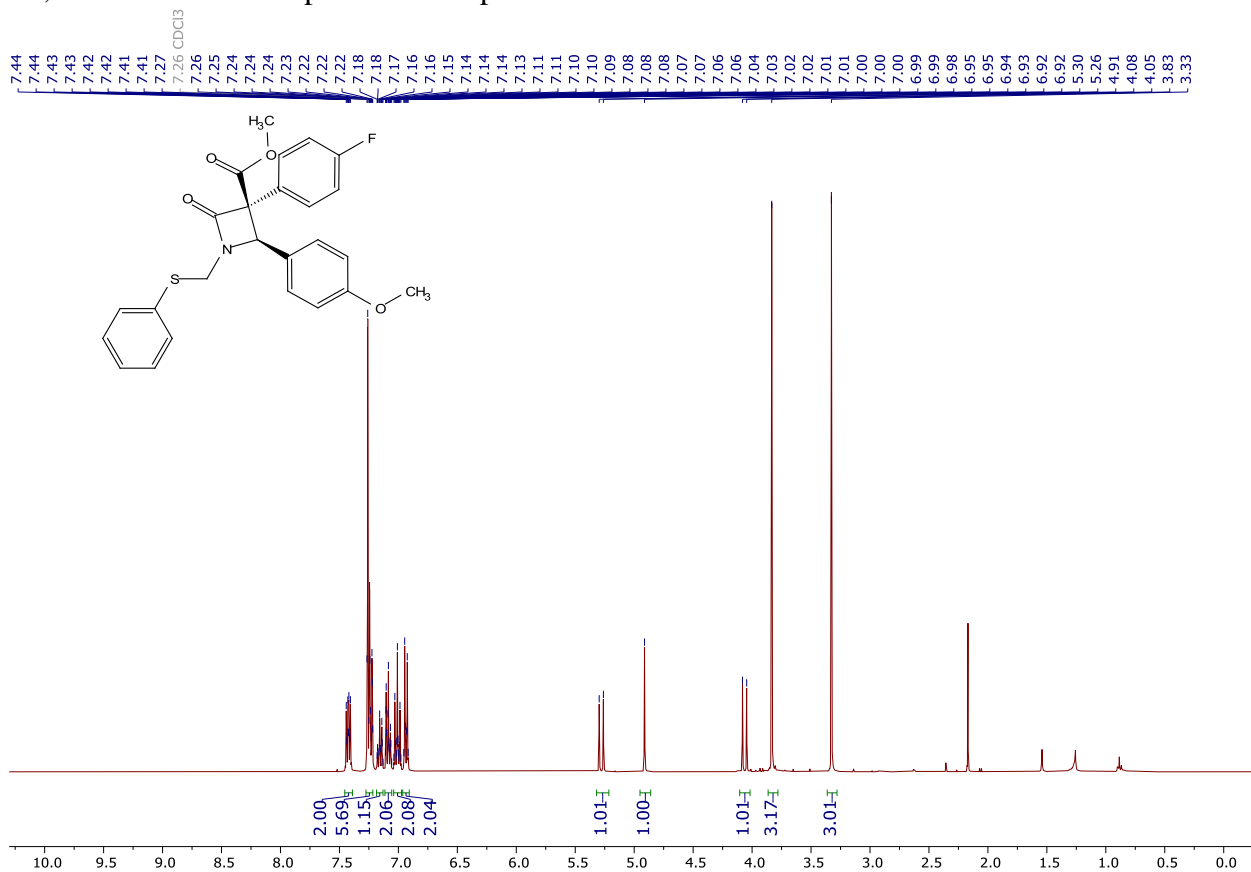


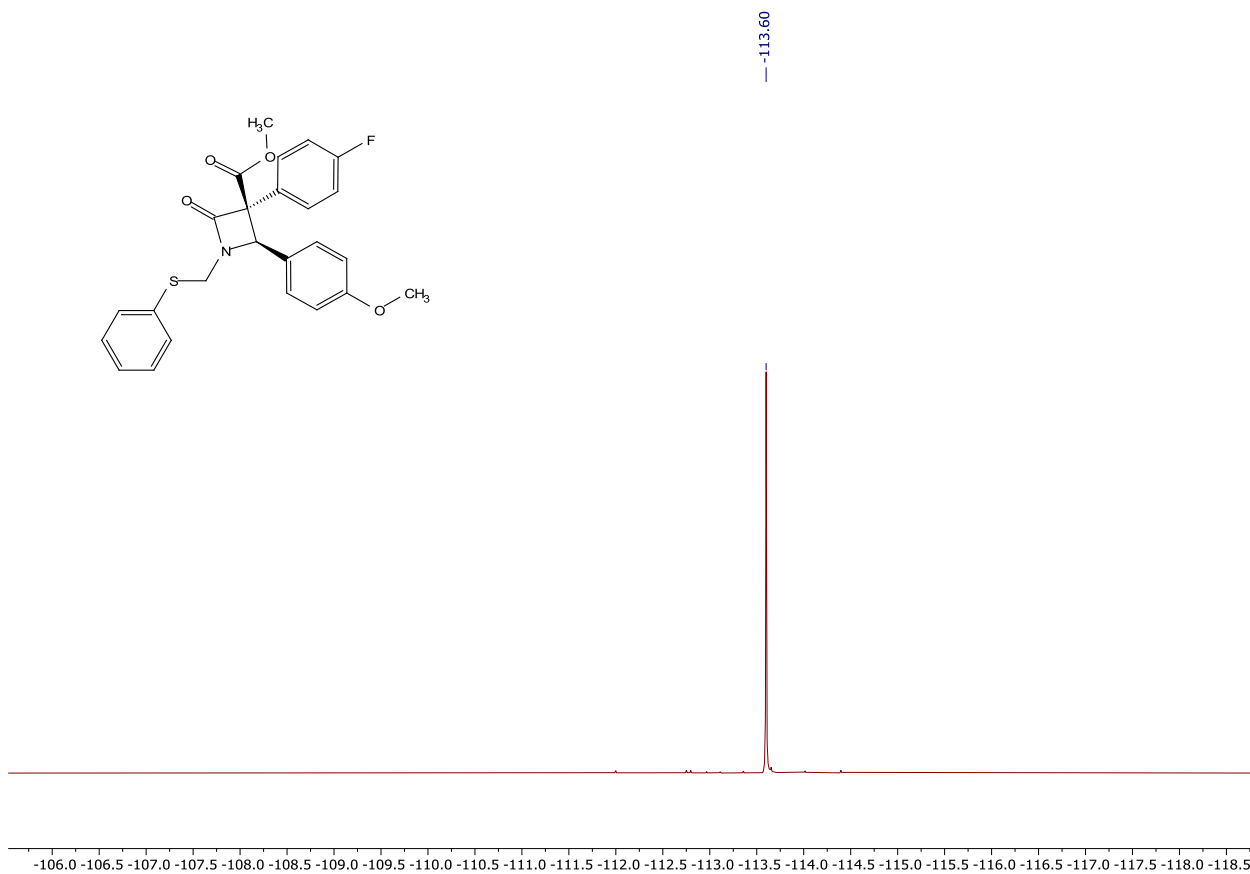
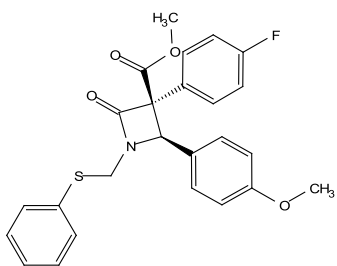
^1H , ^{13}C and ^{19}F NMR spectra of compound **4h**



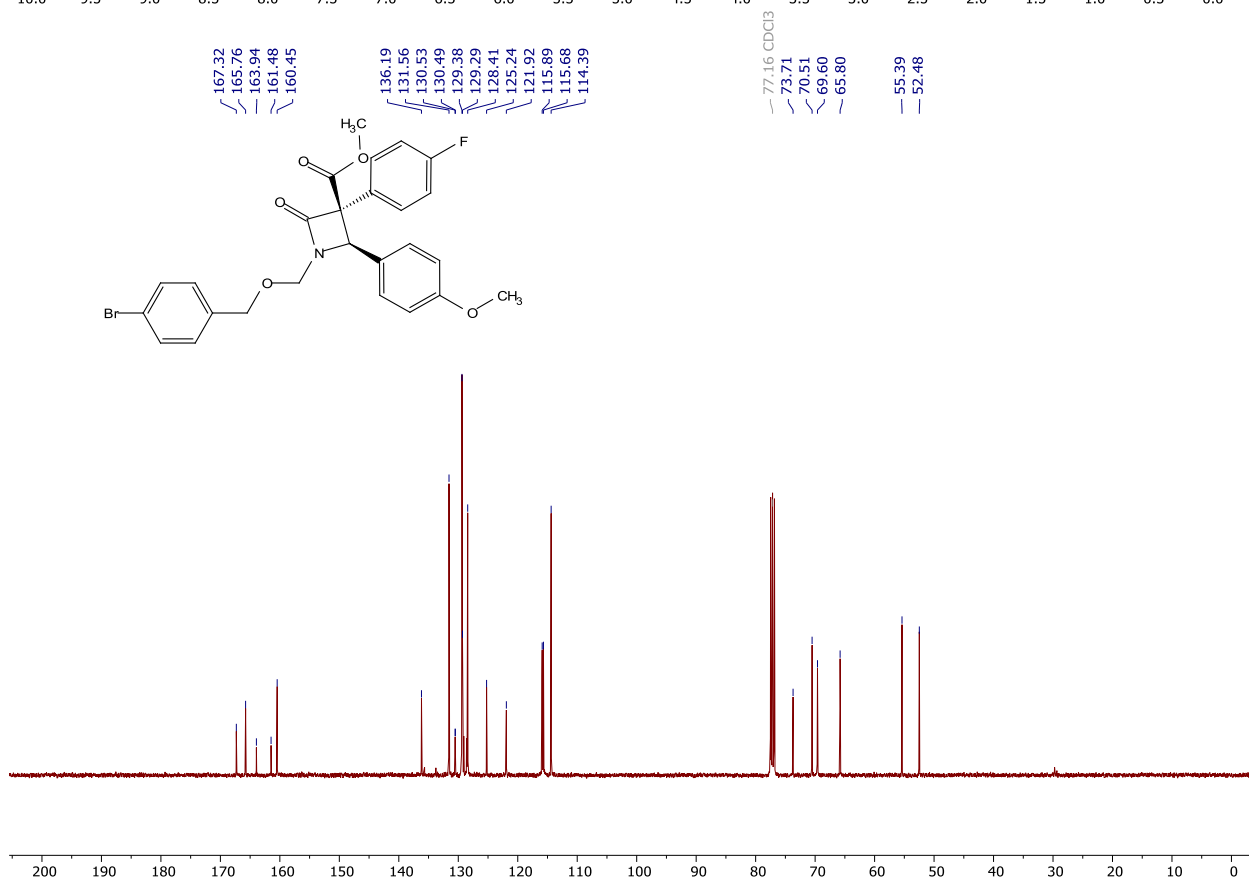
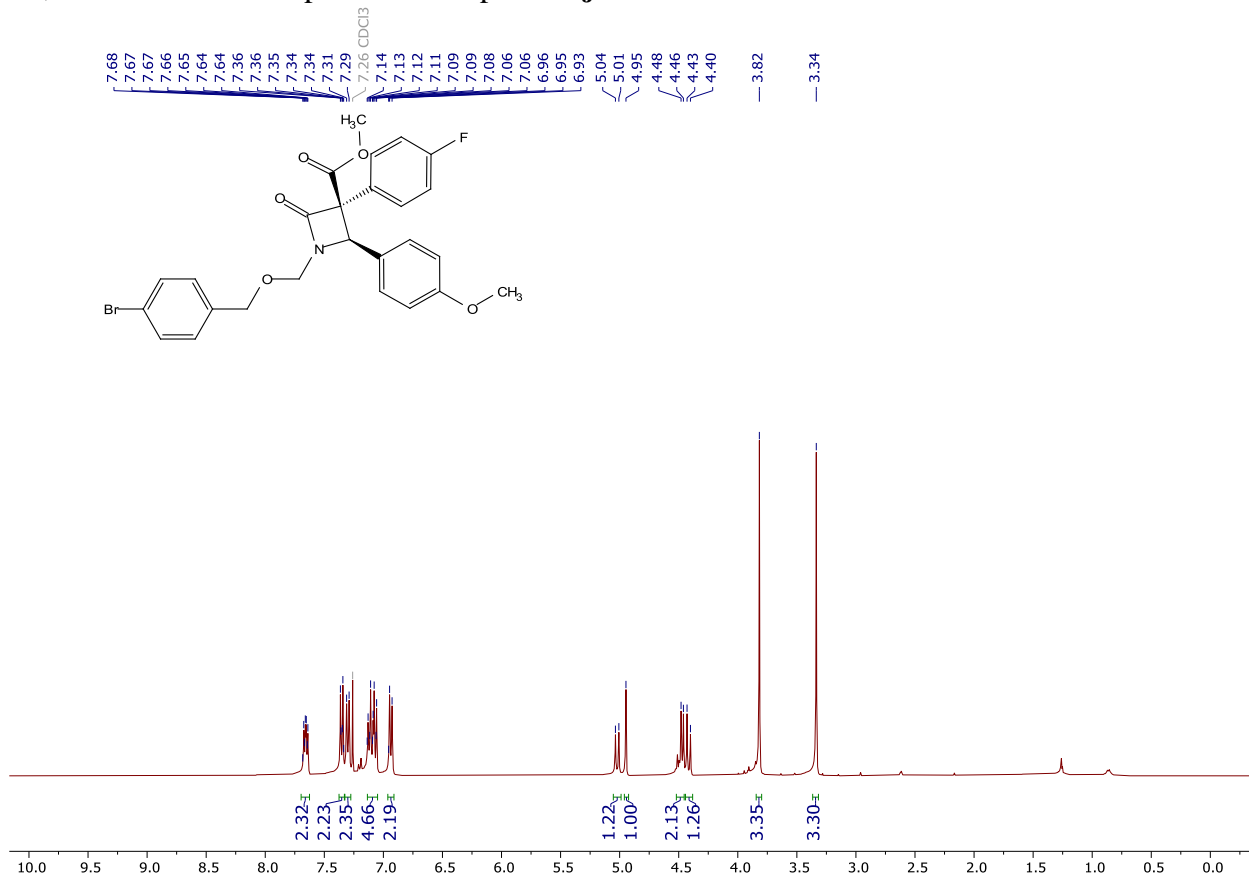


^1H , ^{13}C and ^{19}F NMR spectra of compound **4i**

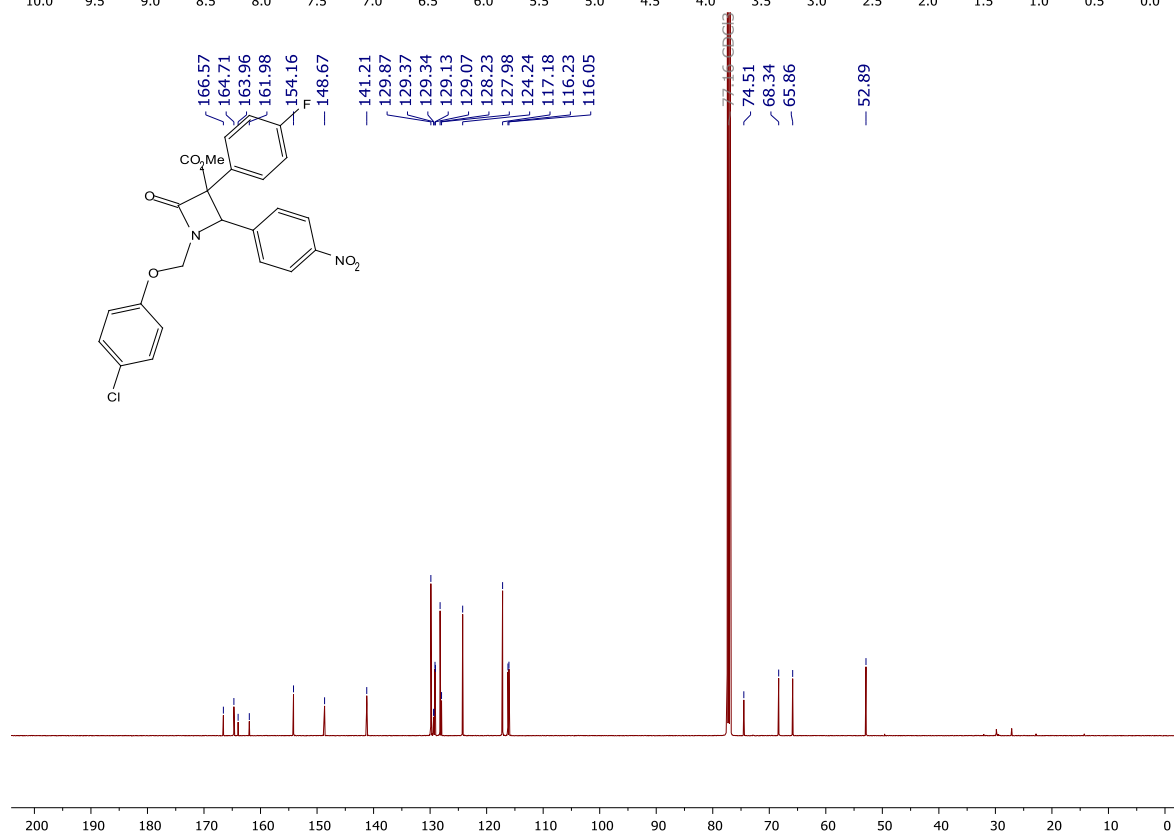
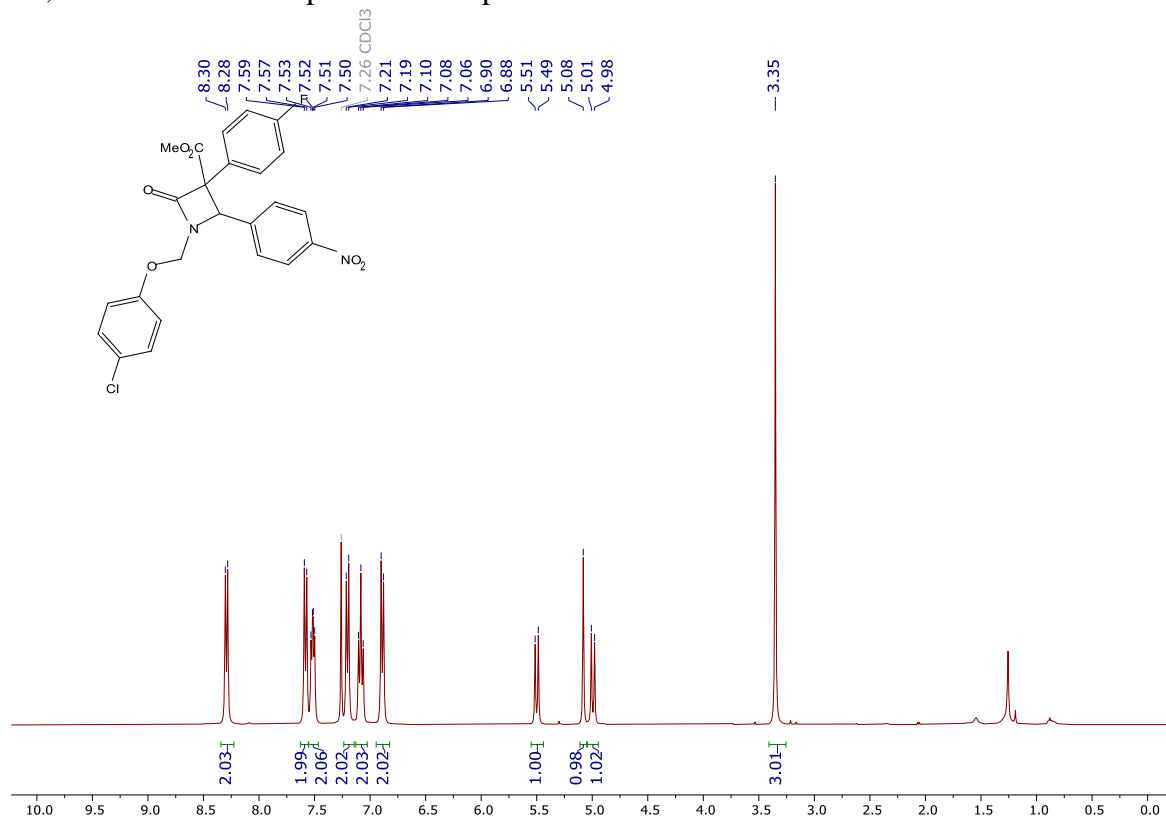


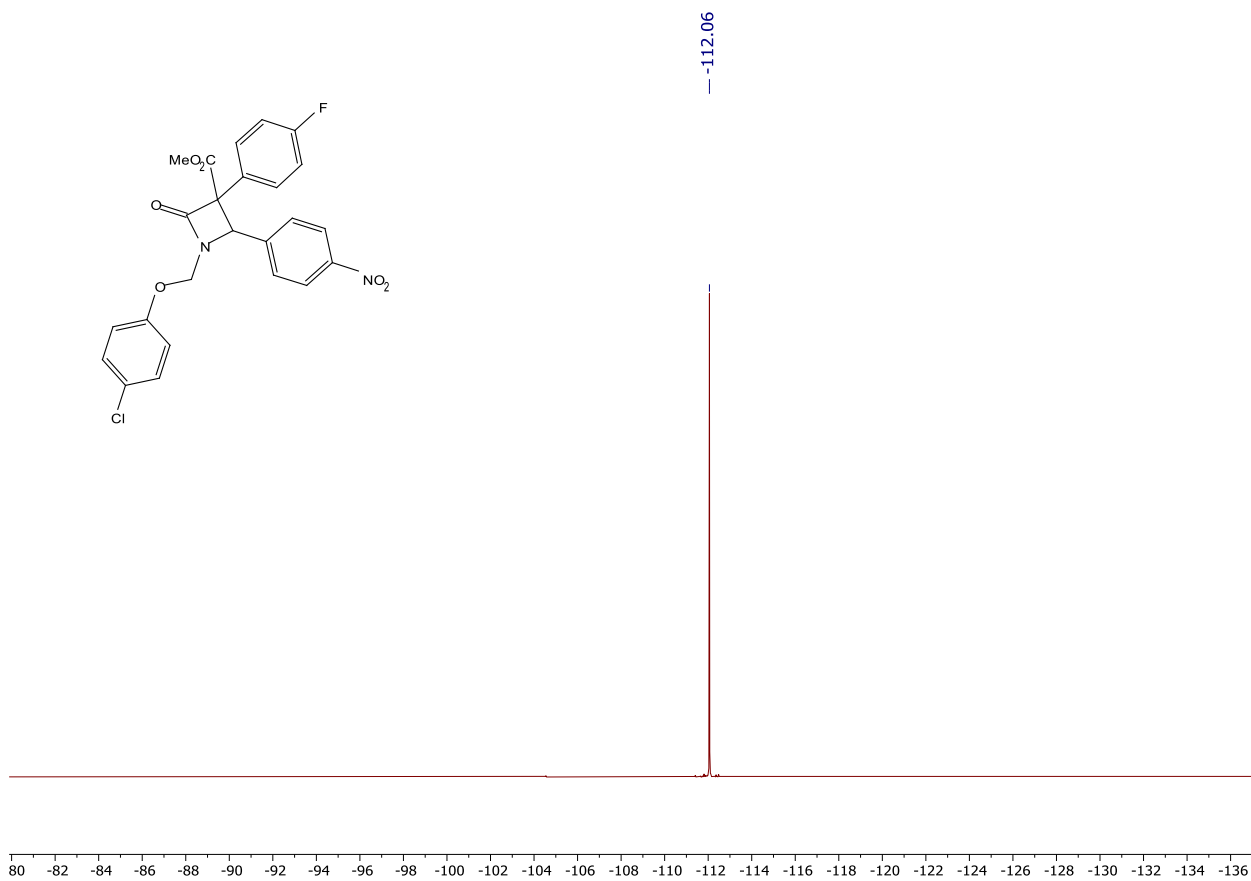
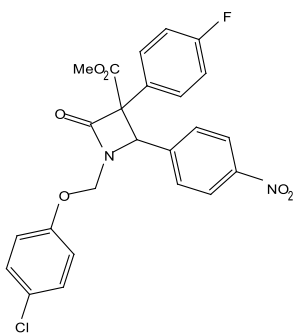


^1H , ^{13}C and ^{19}F NMR spectra of compound **4j**

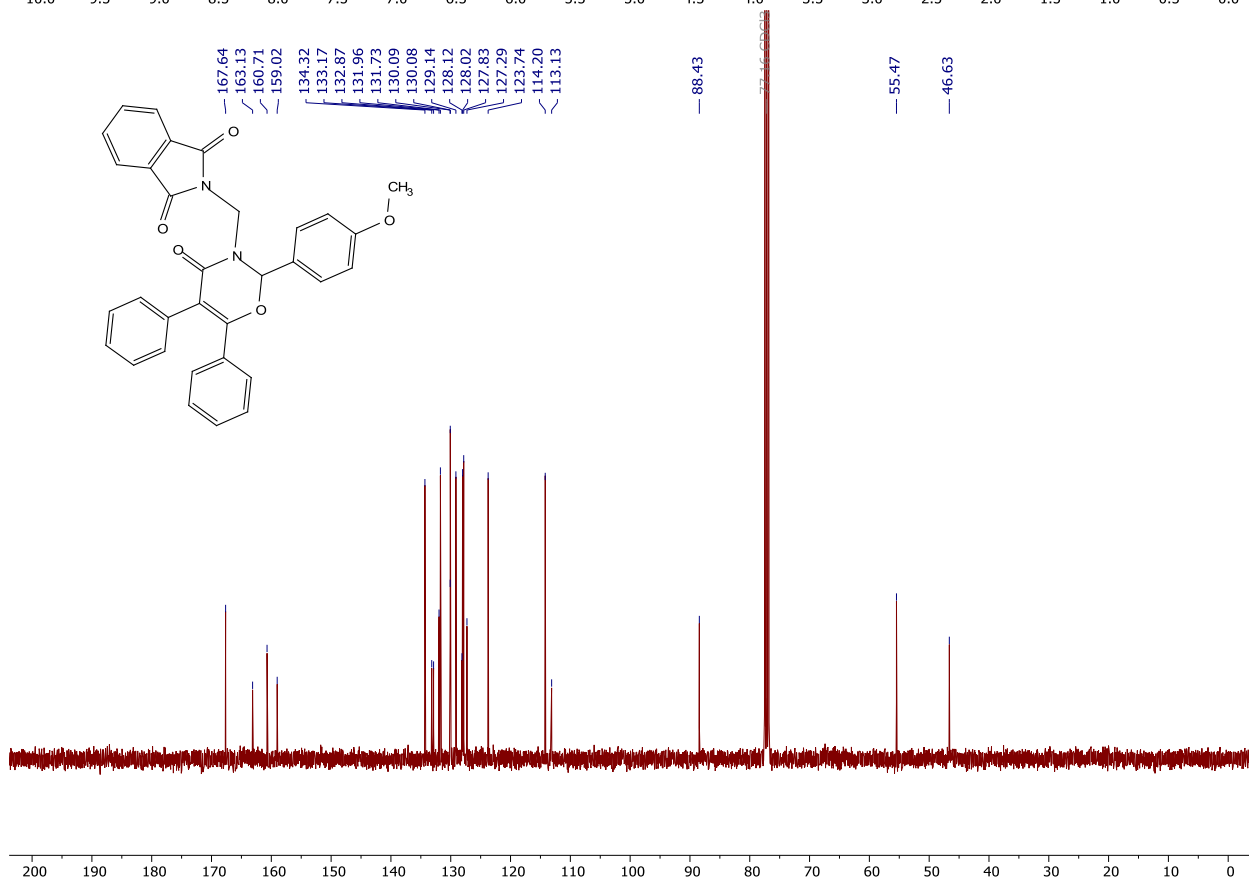
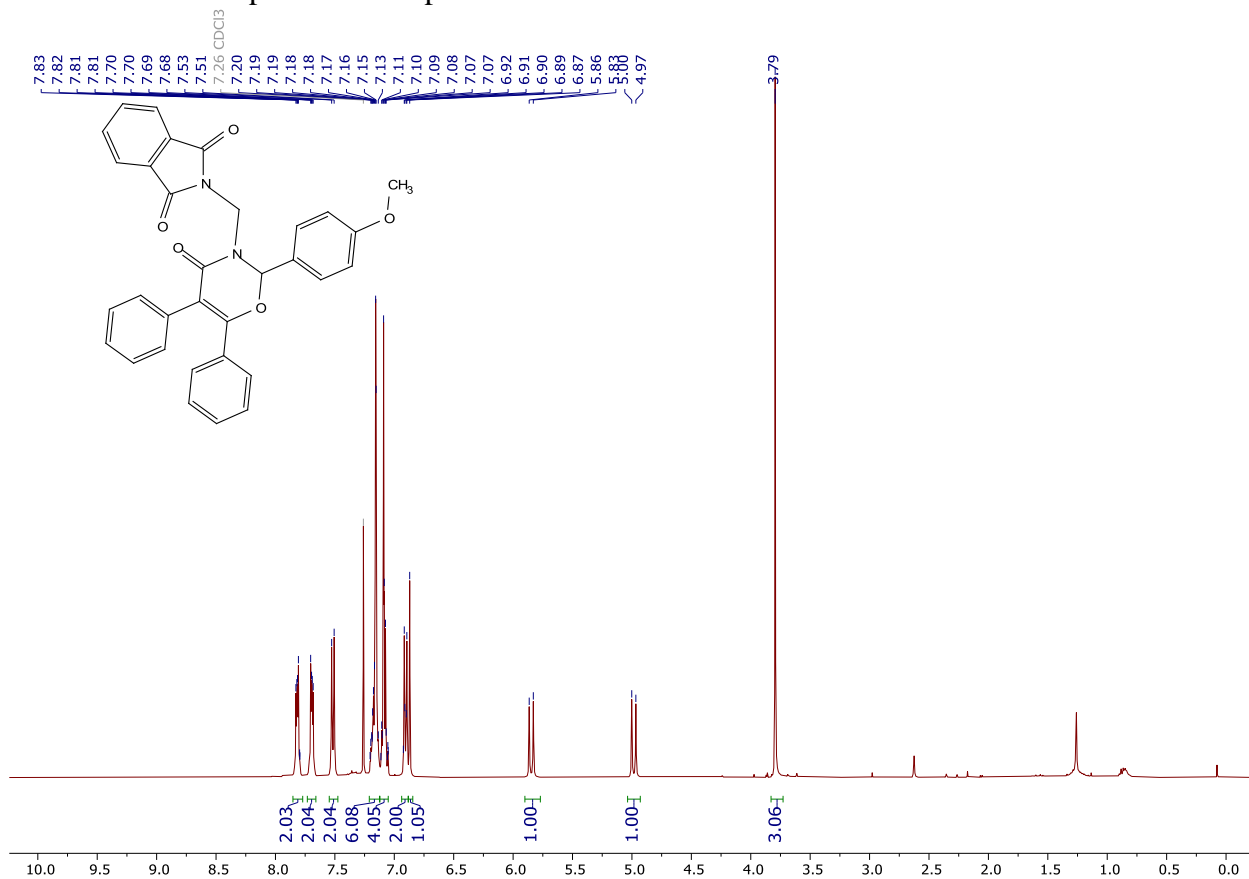


^1H , ^{13}C and ^{19}F NMR spectra of compound **4k**

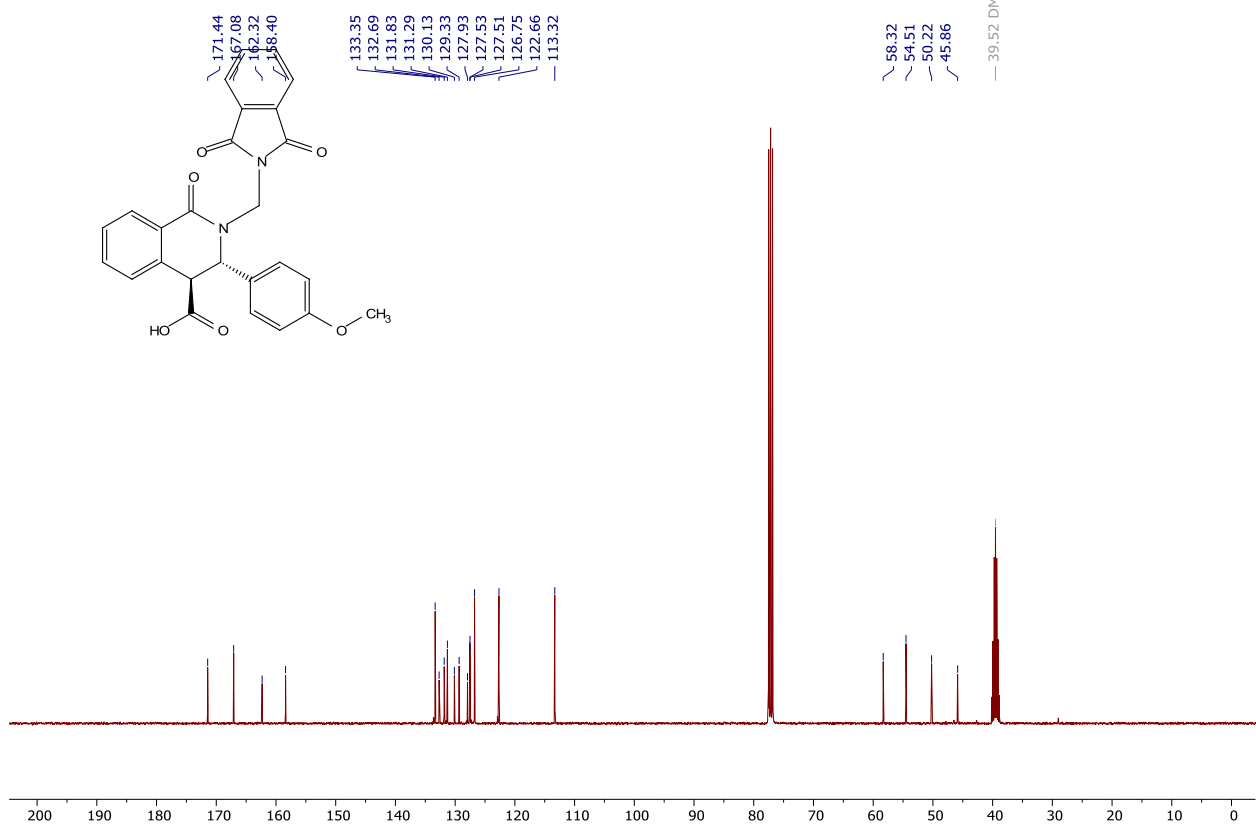
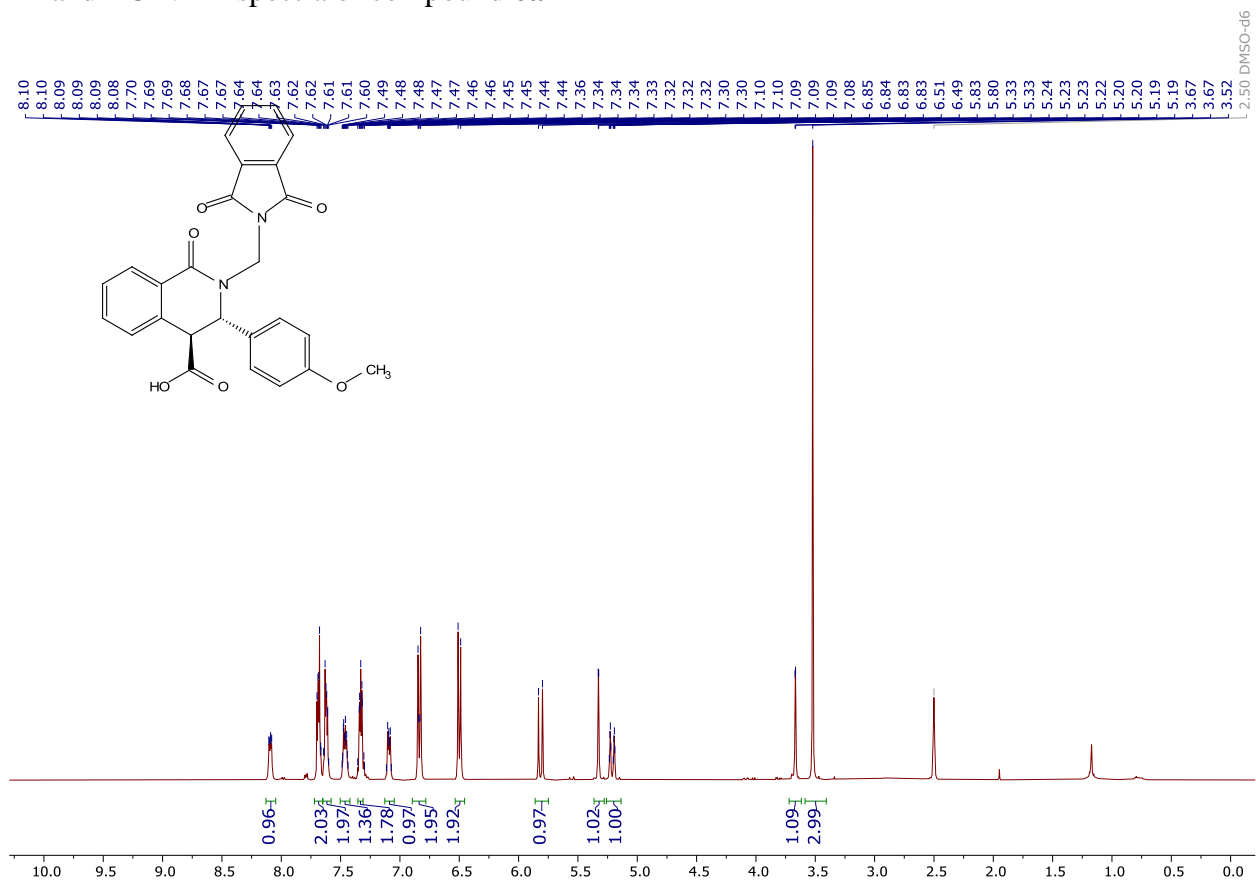




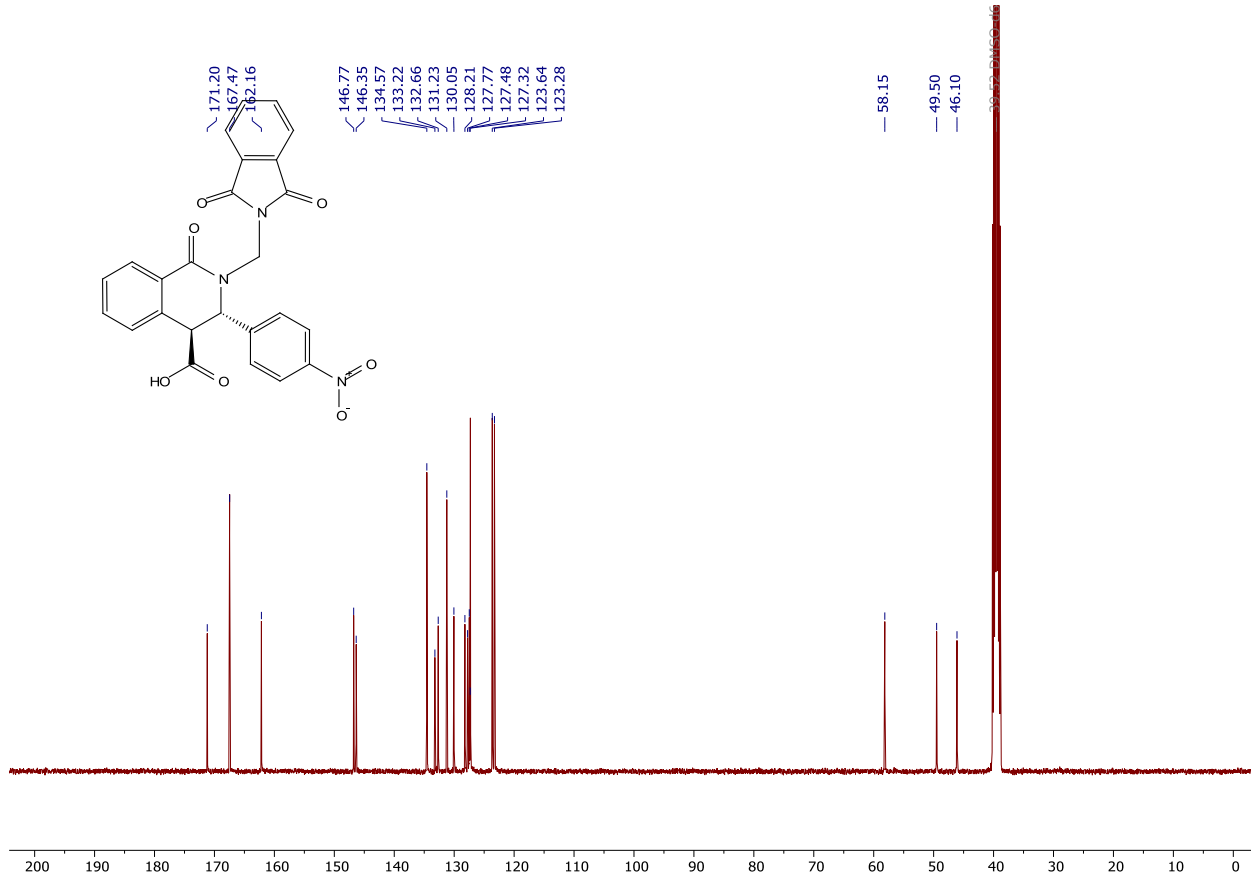
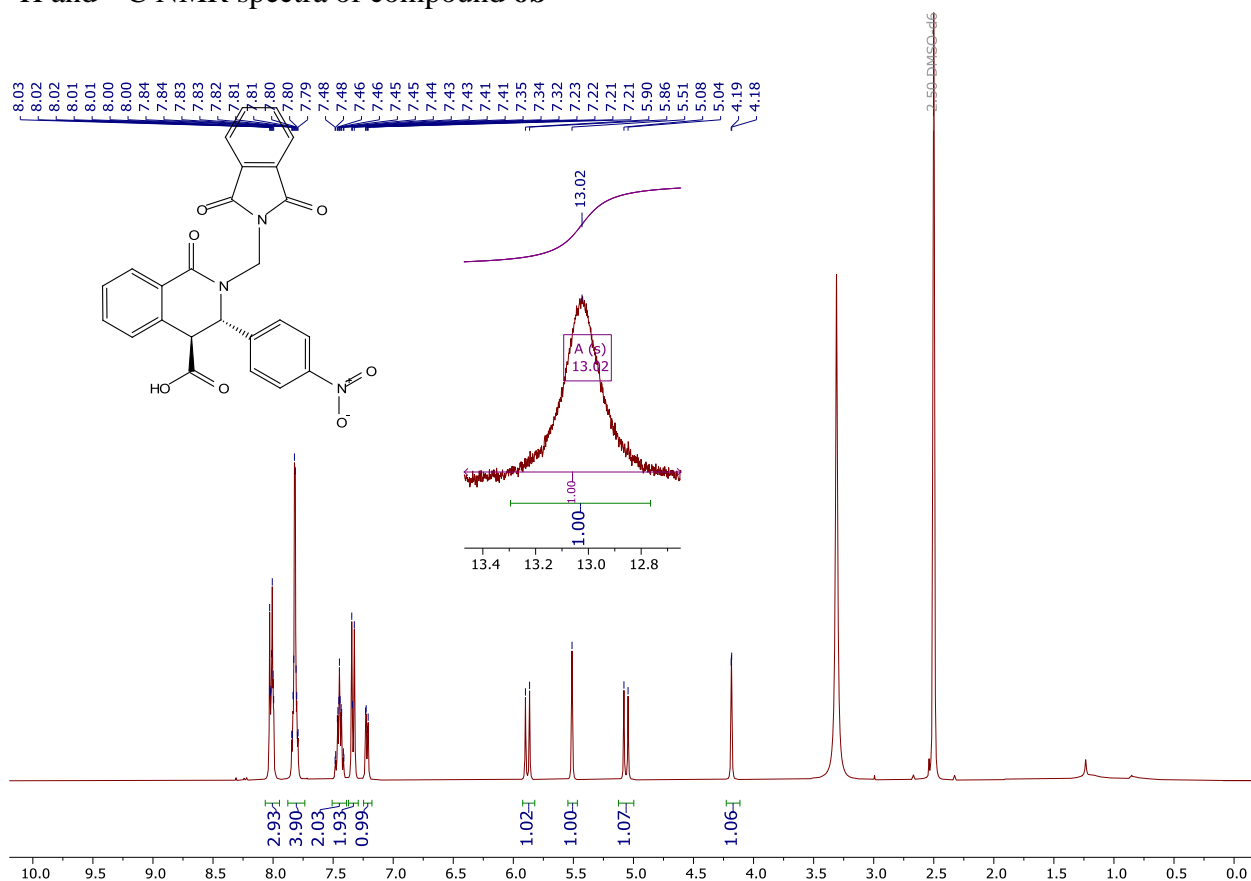
^1H and ^{13}C NMR spectra of compound 5



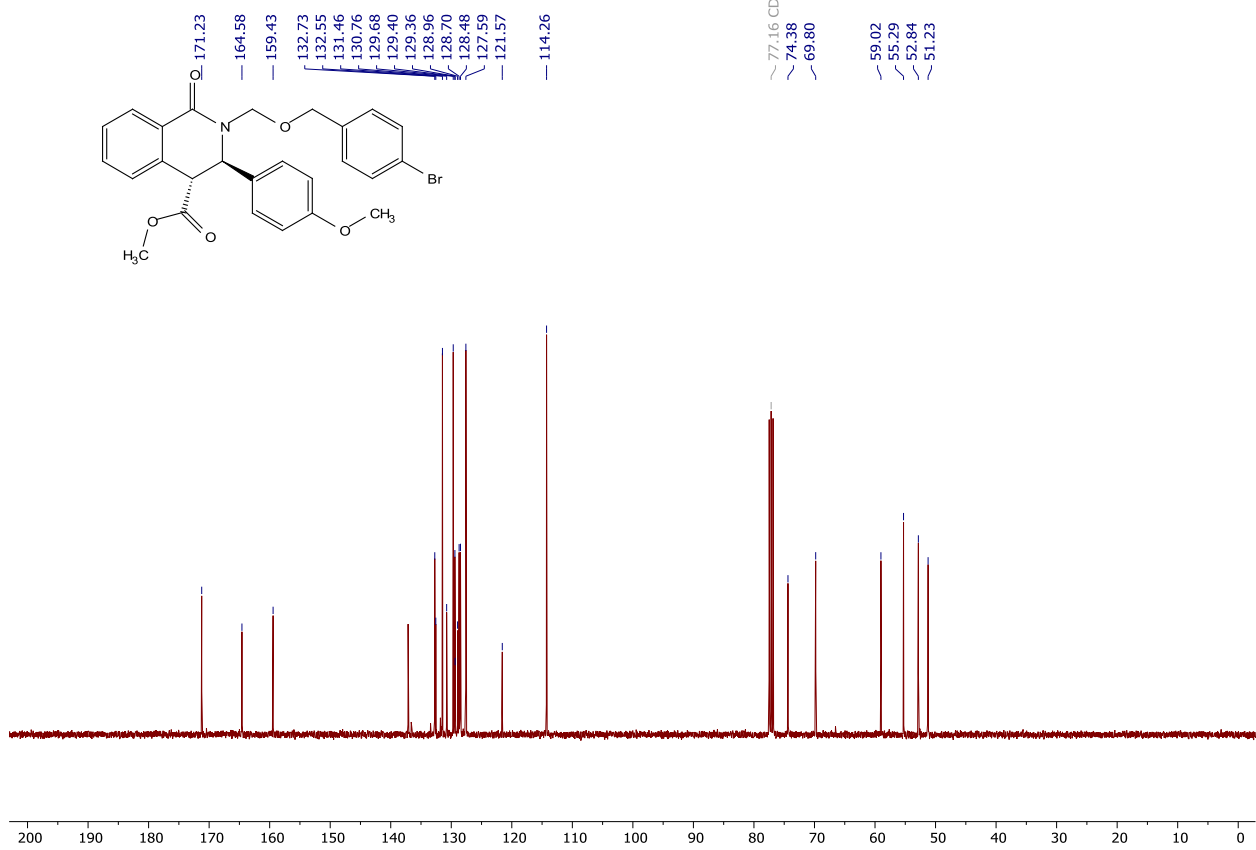
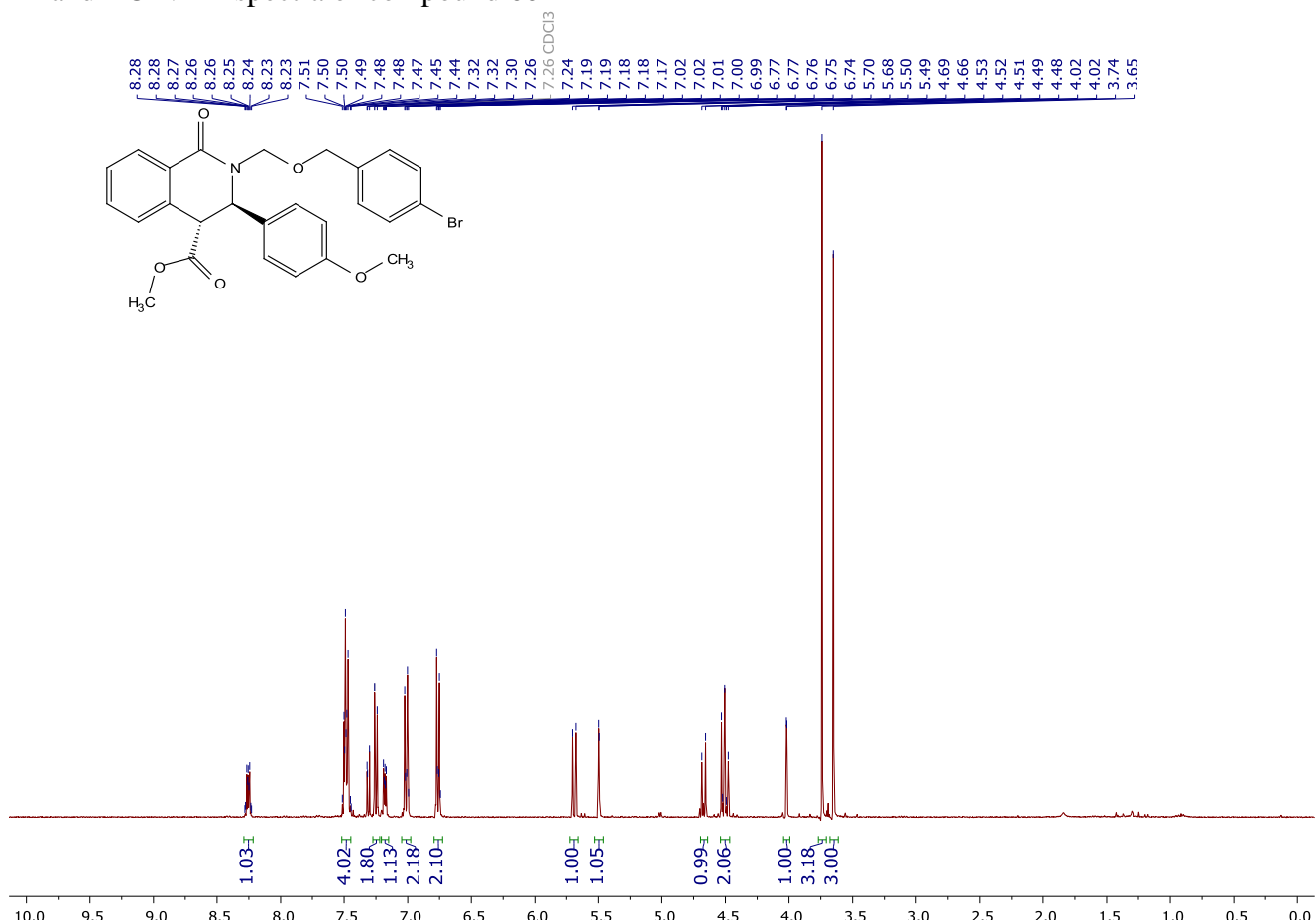
^1H and ^{13}C NMR spectra of compound **6a**



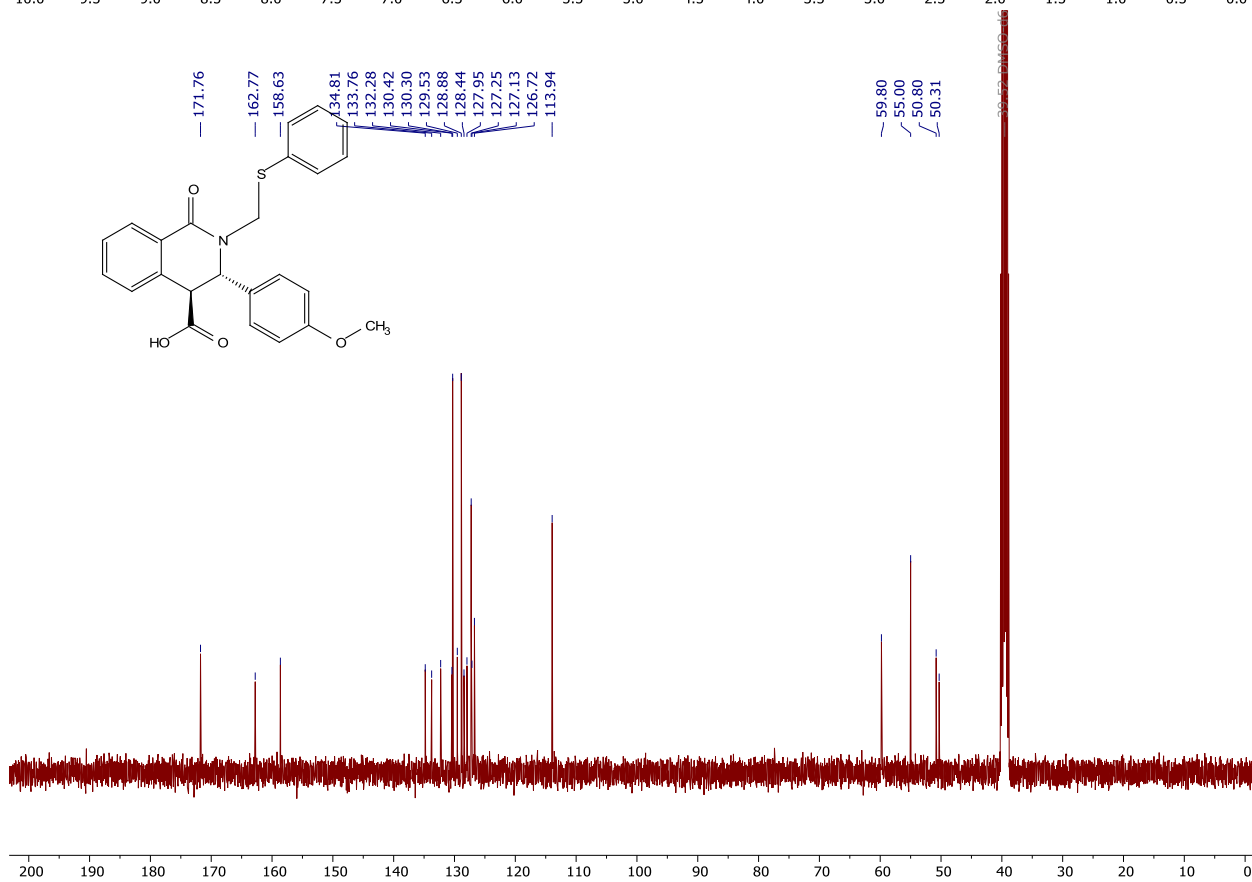
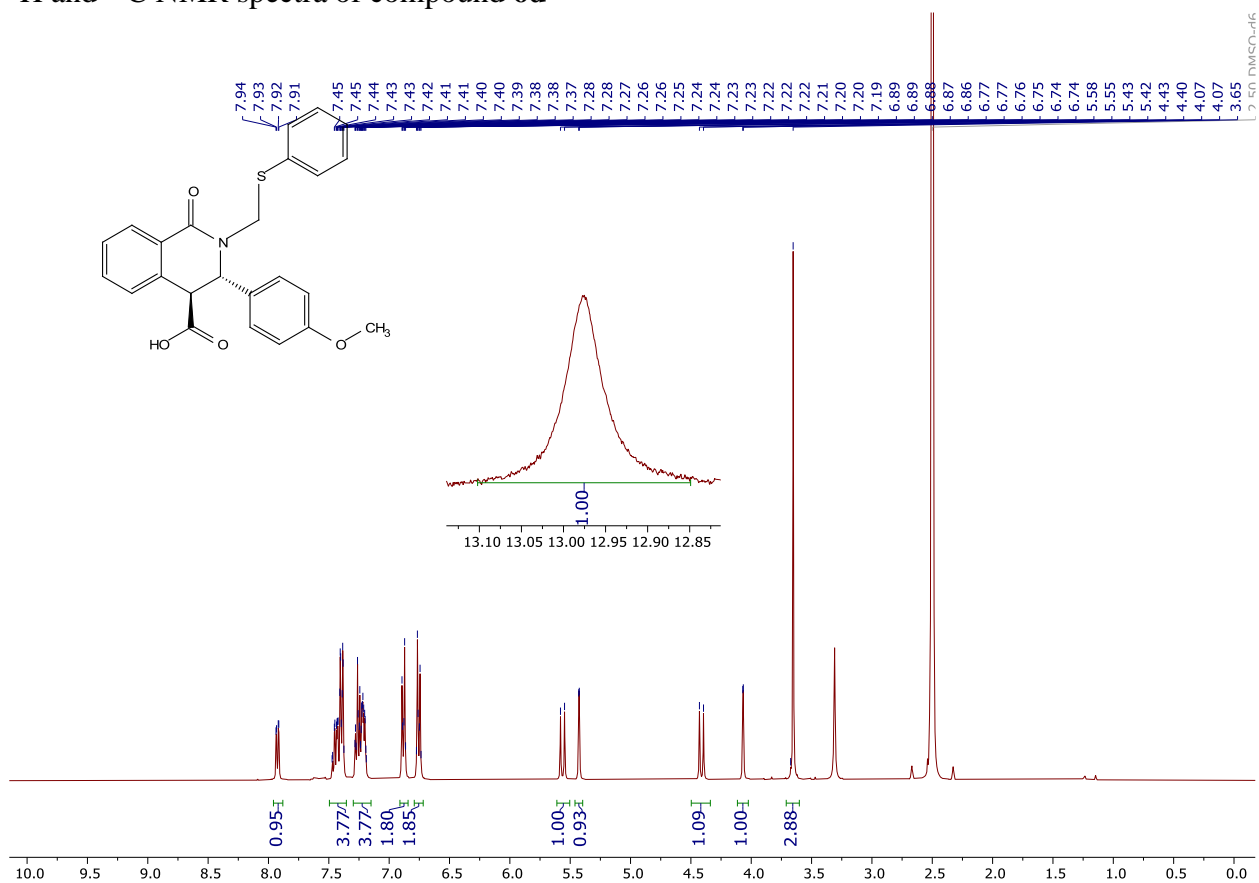
^1H and ^{13}C NMR spectra of compound **6b**



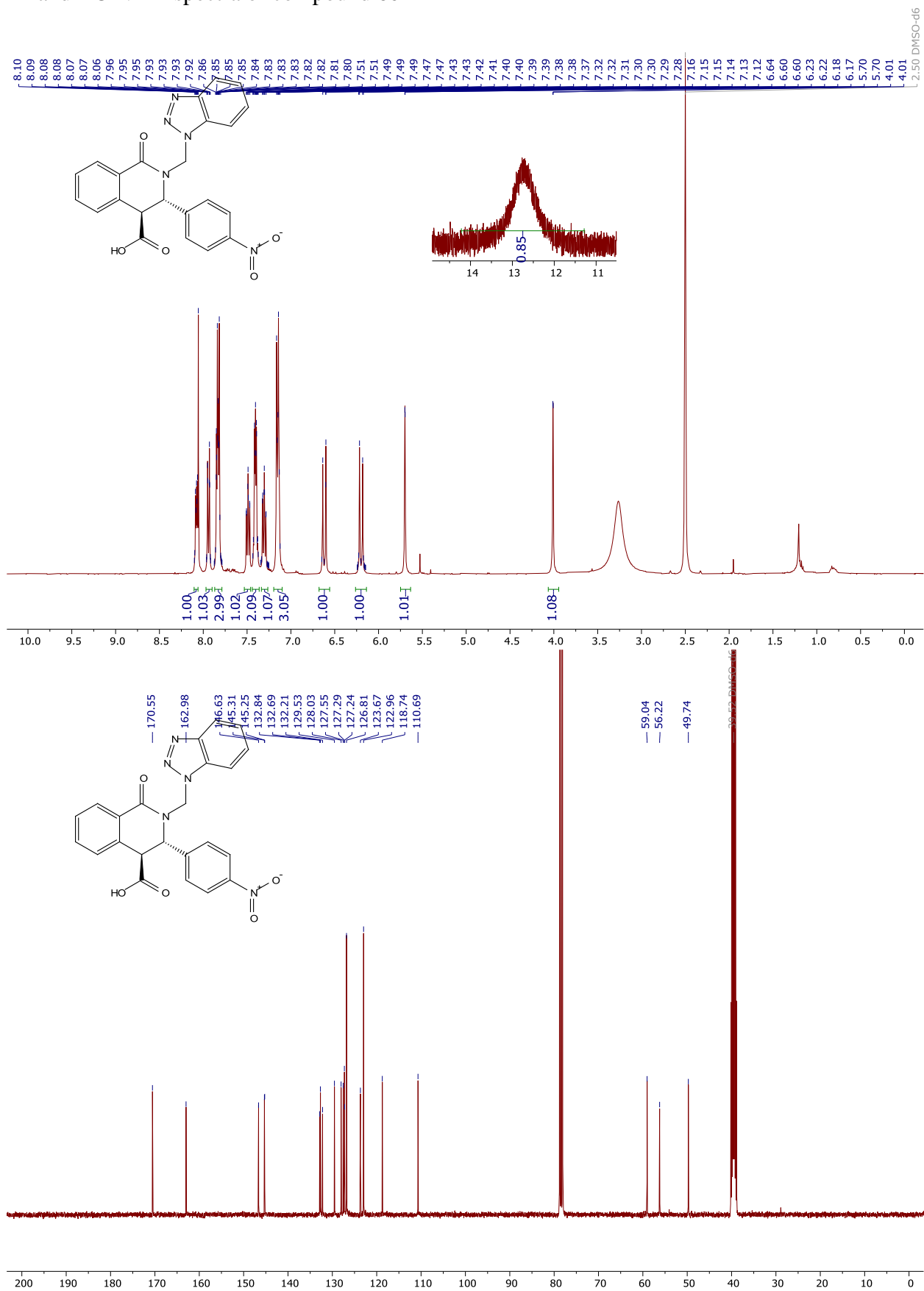
^1H and ^{13}C NMR spectra of compound **6c**



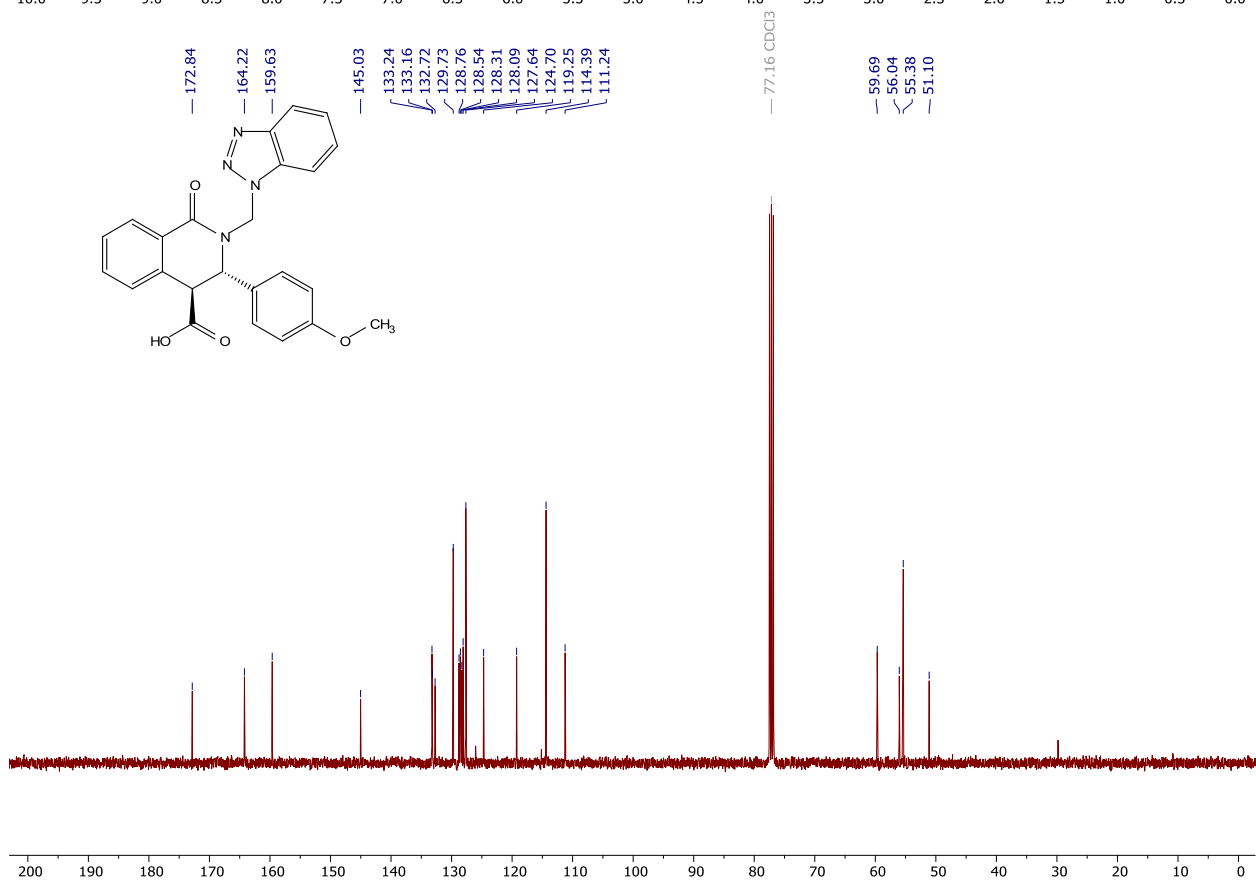
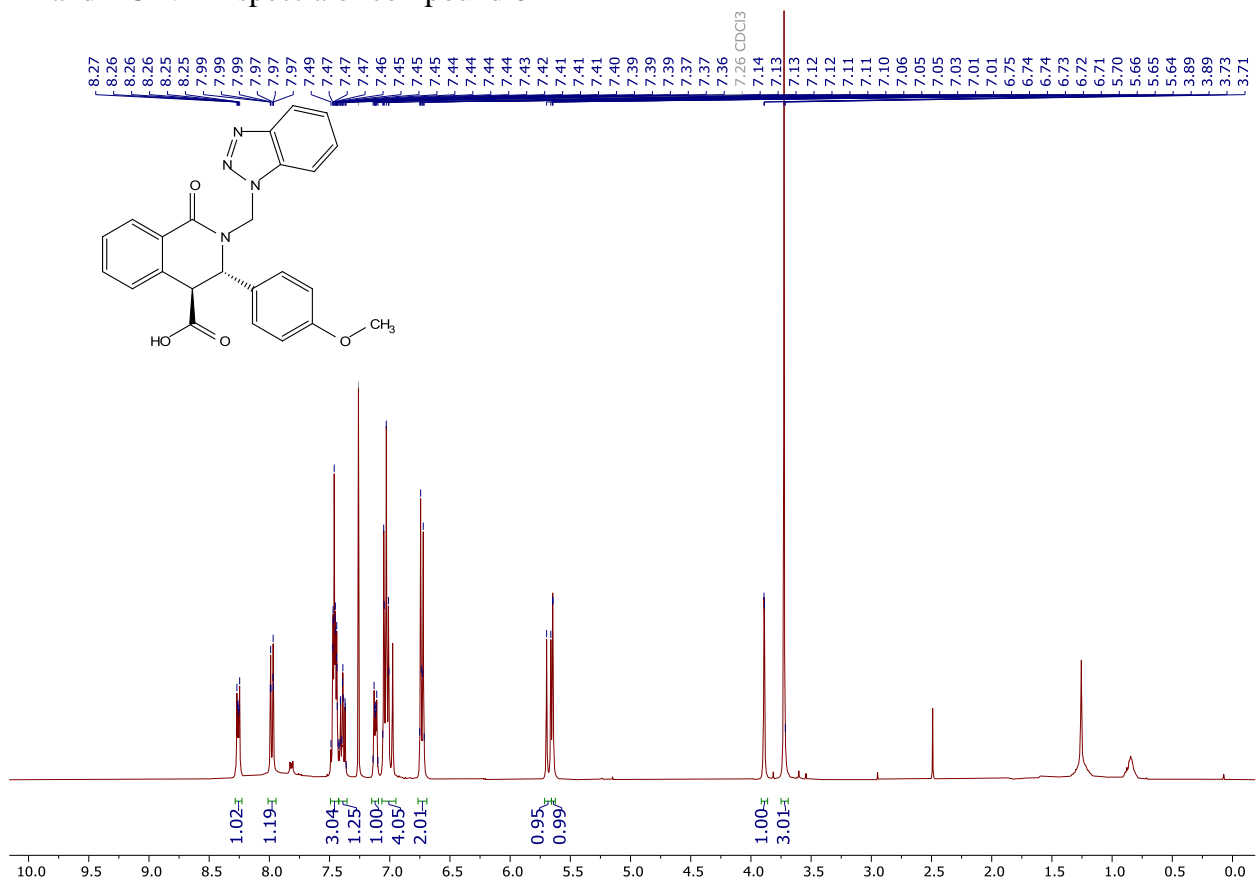
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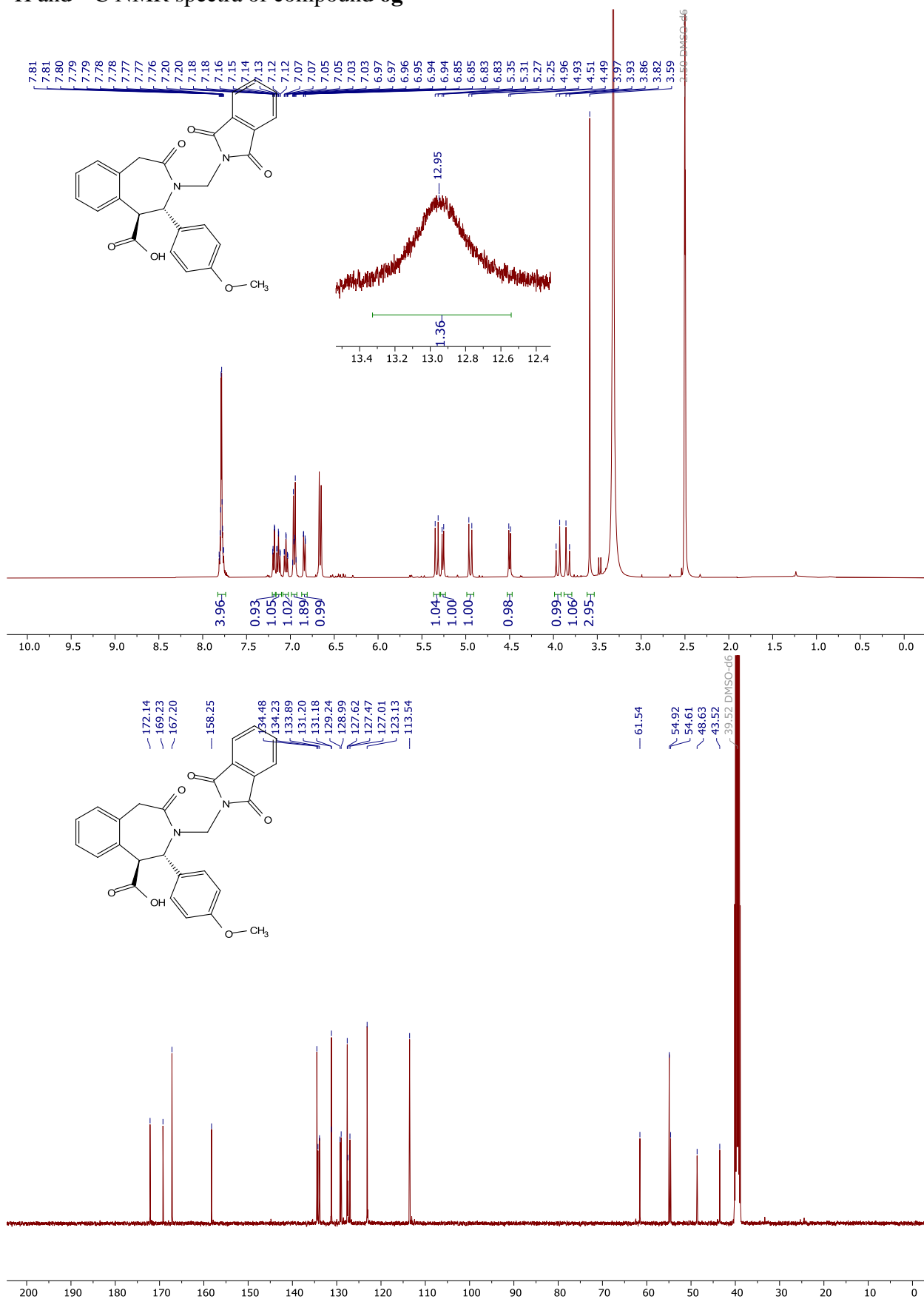
^1H and ^{13}C NMR spectra of compound **6e**



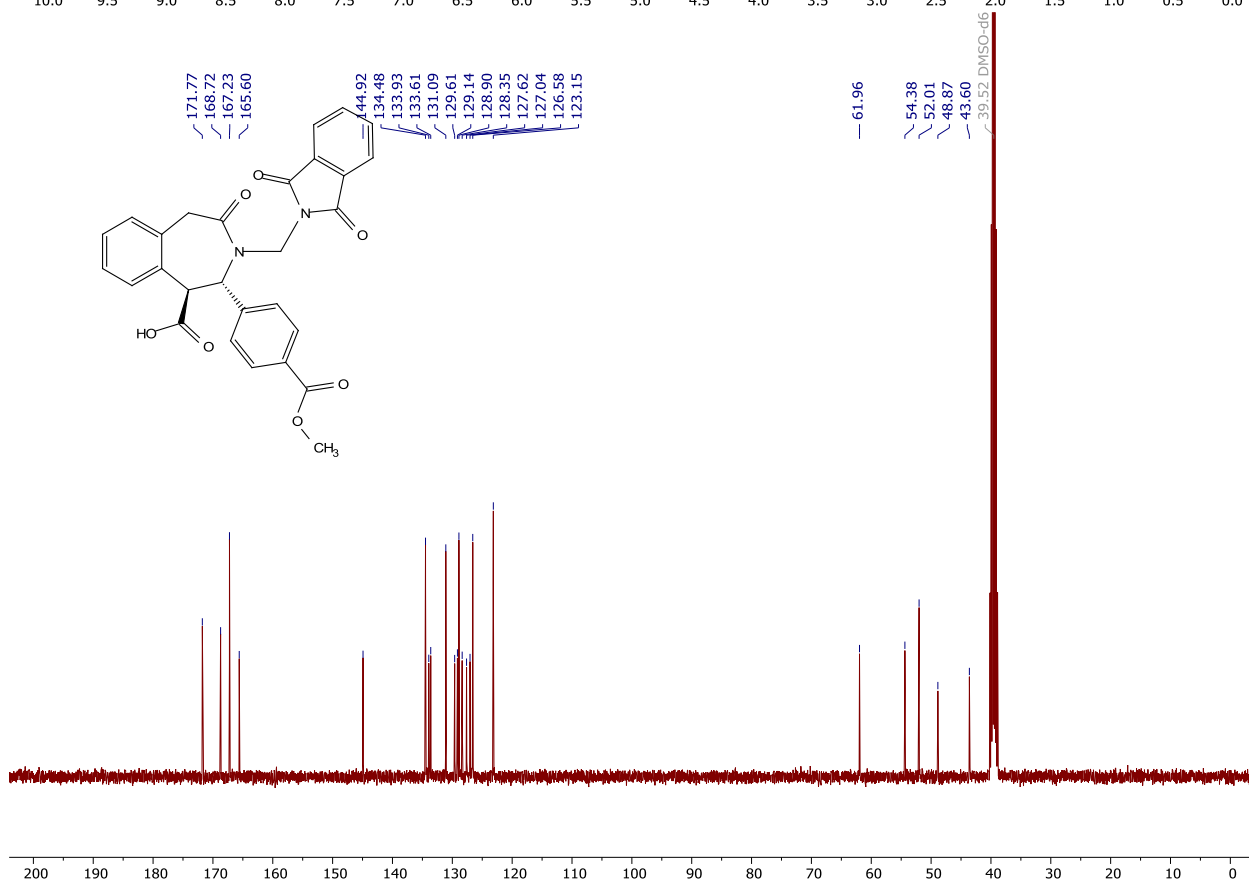
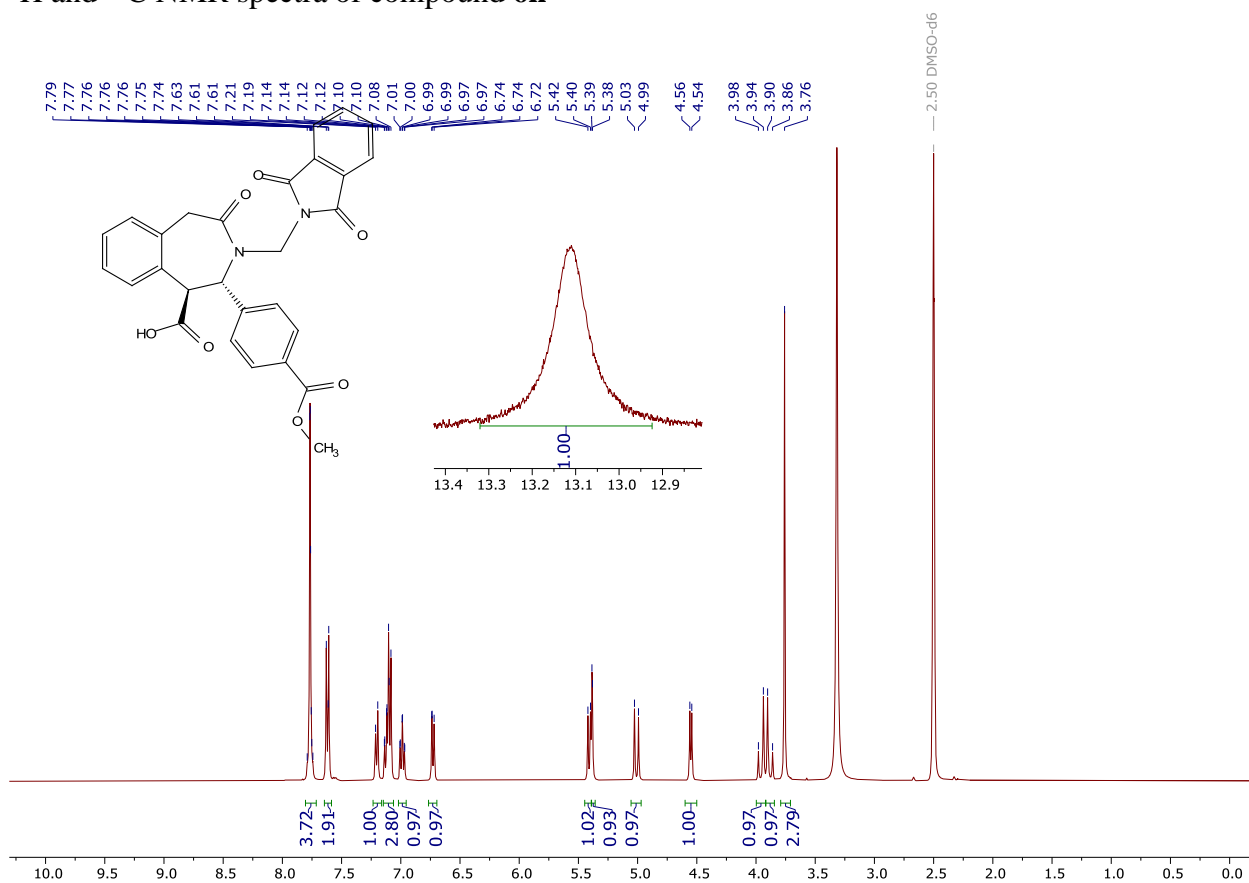
^1H and ^{13}C NMR spectra of compound **6f**



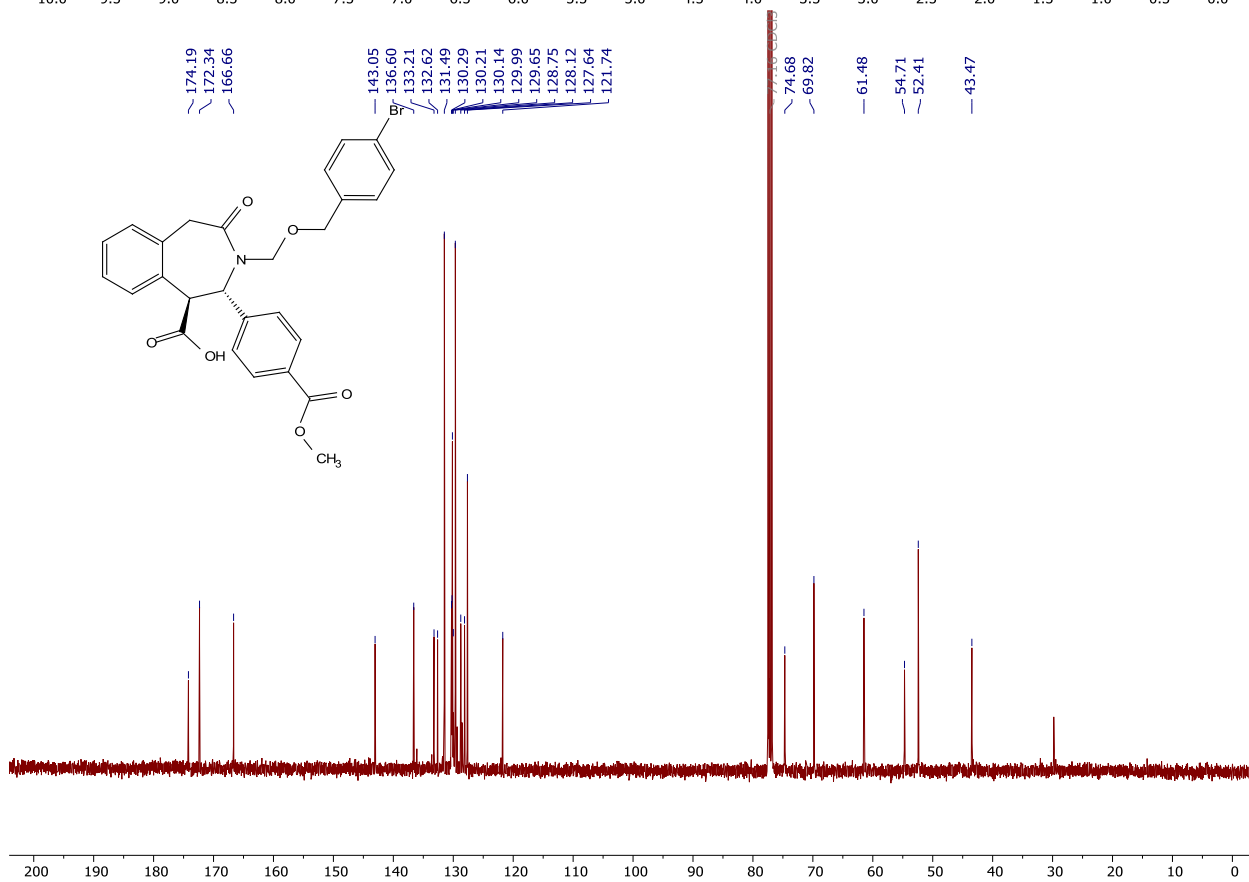
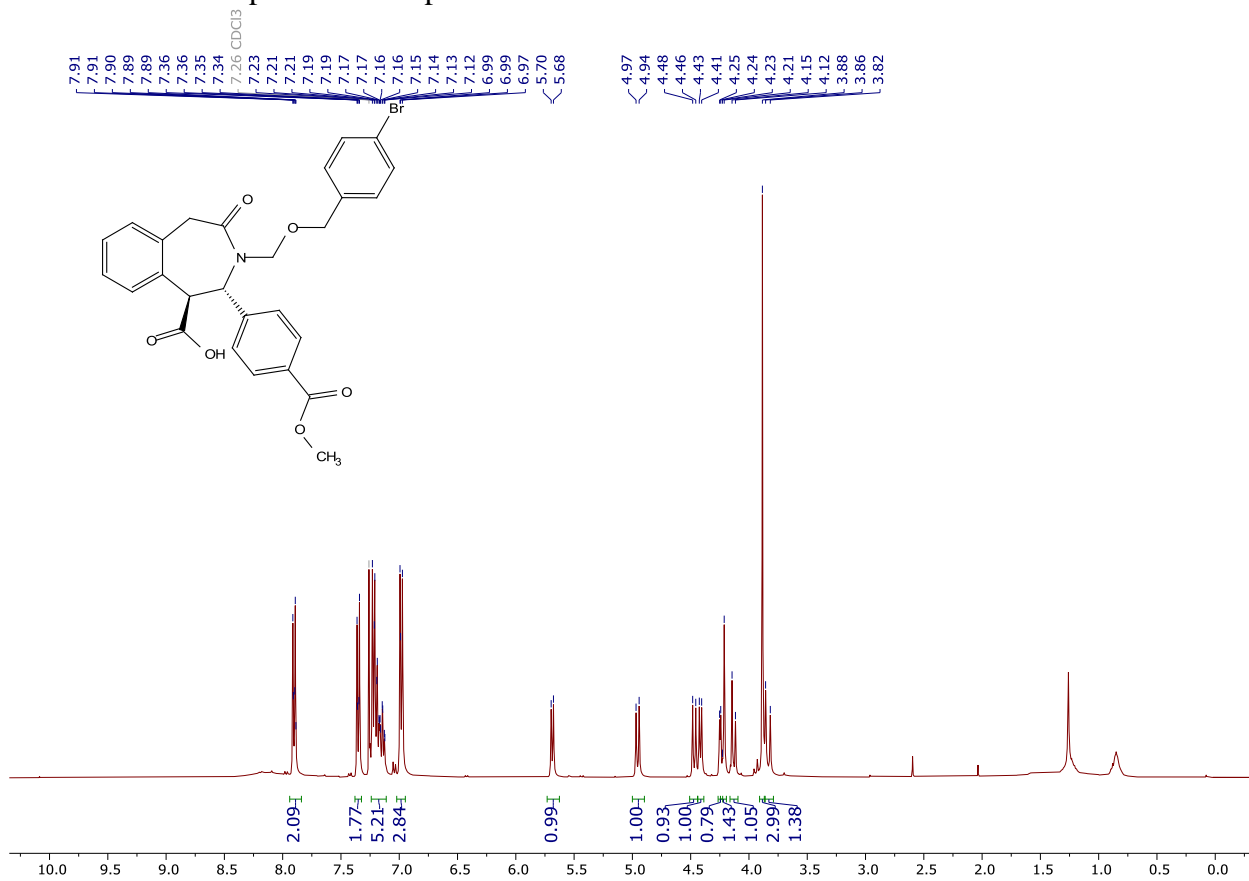
^1H and ^{13}C NMR spectra of compound **6g**



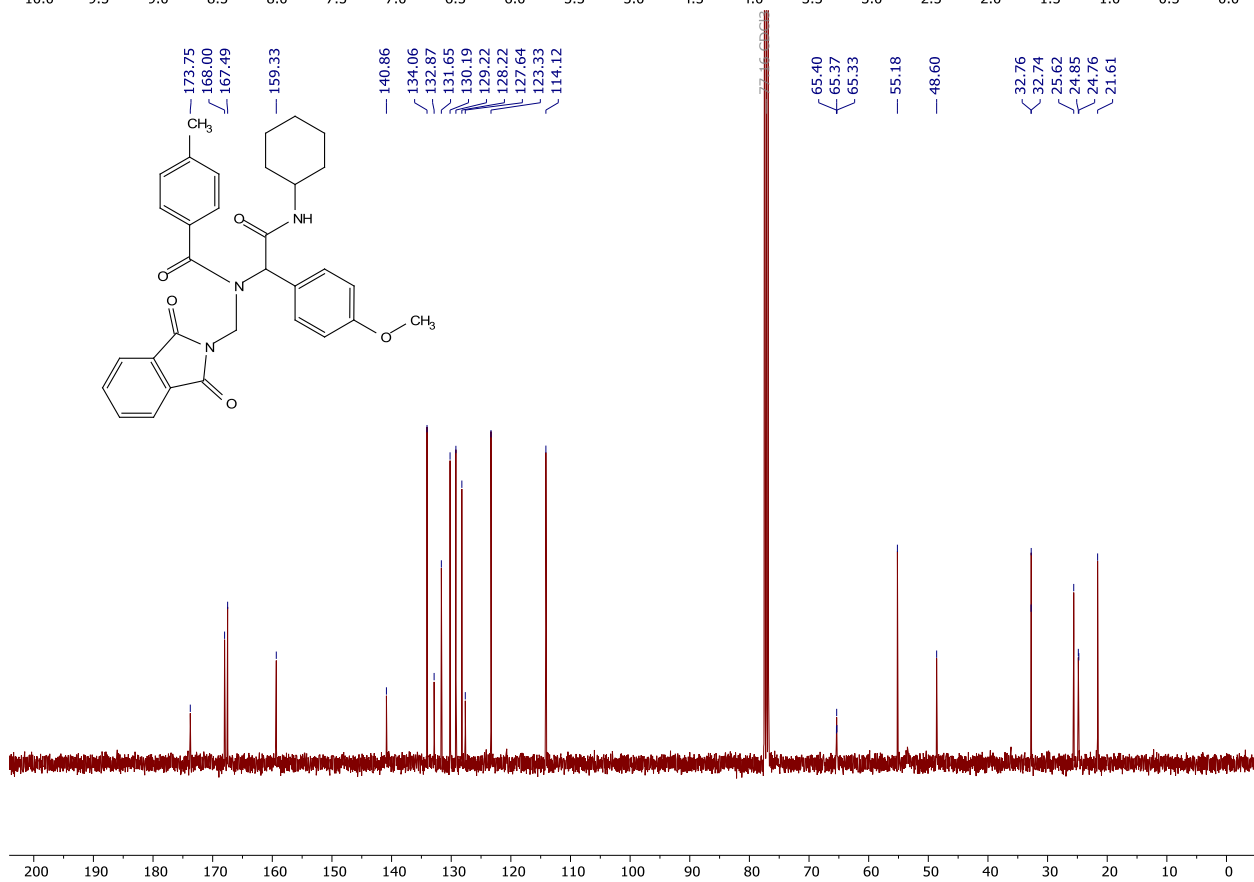
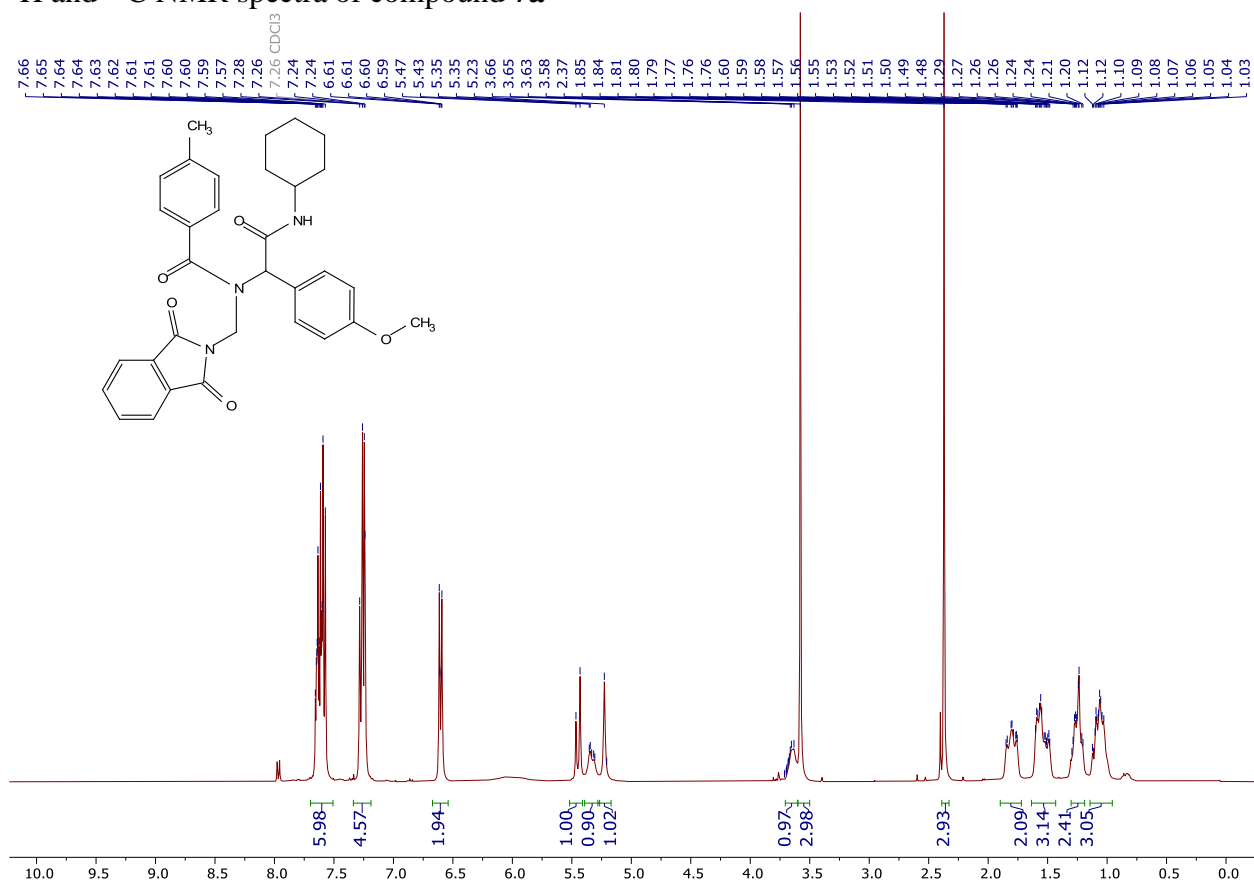
^1H and ^{13}C NMR spectra of compound **6h**



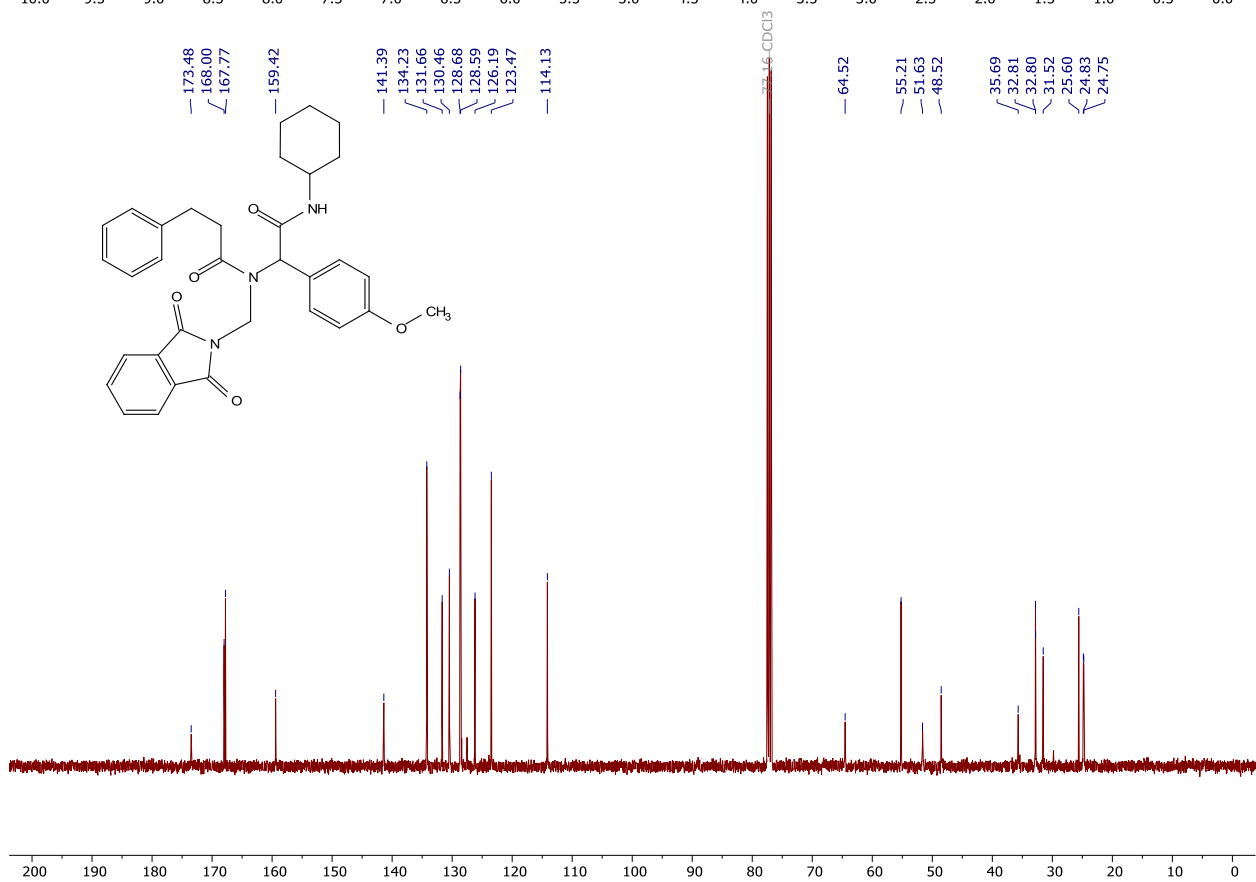
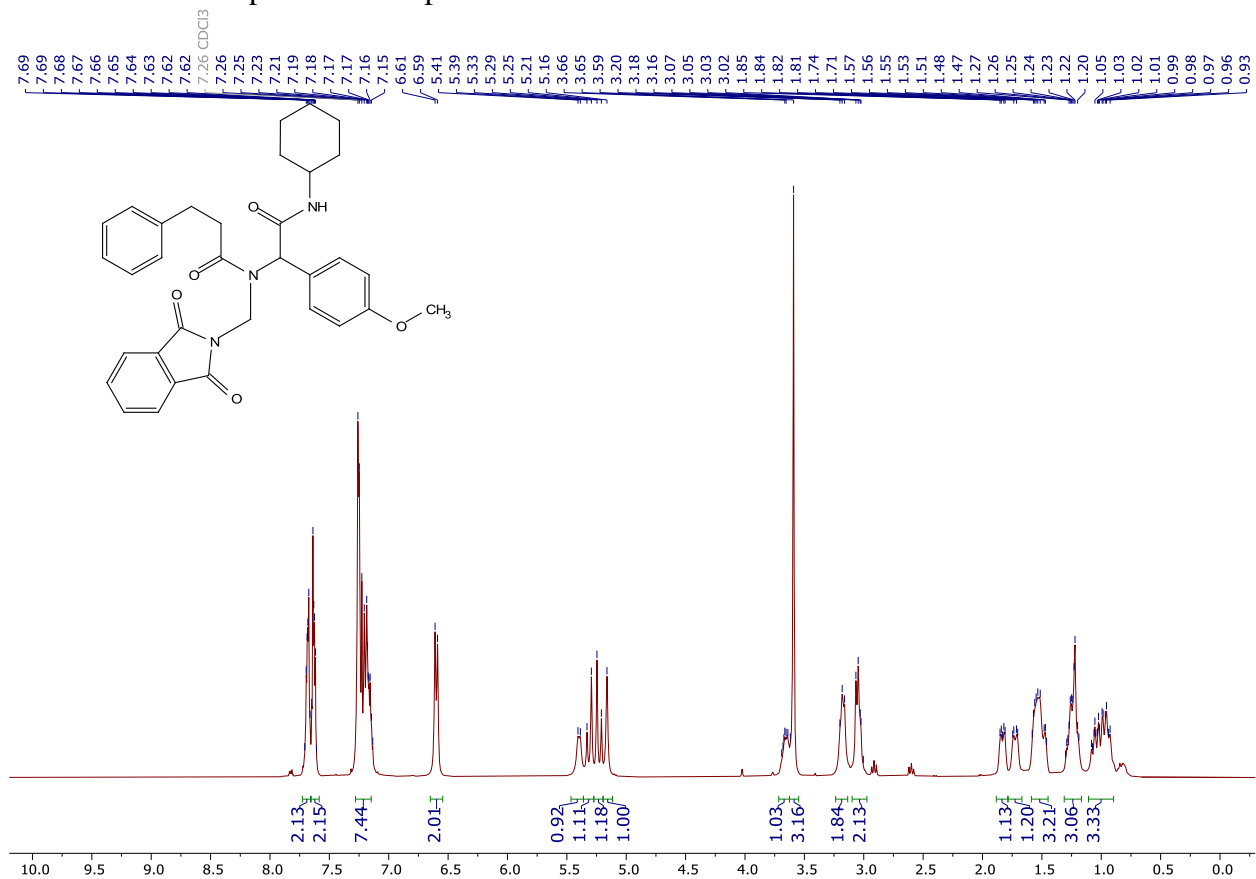
^1H and ^{13}C NMR spectra of compound **6i**



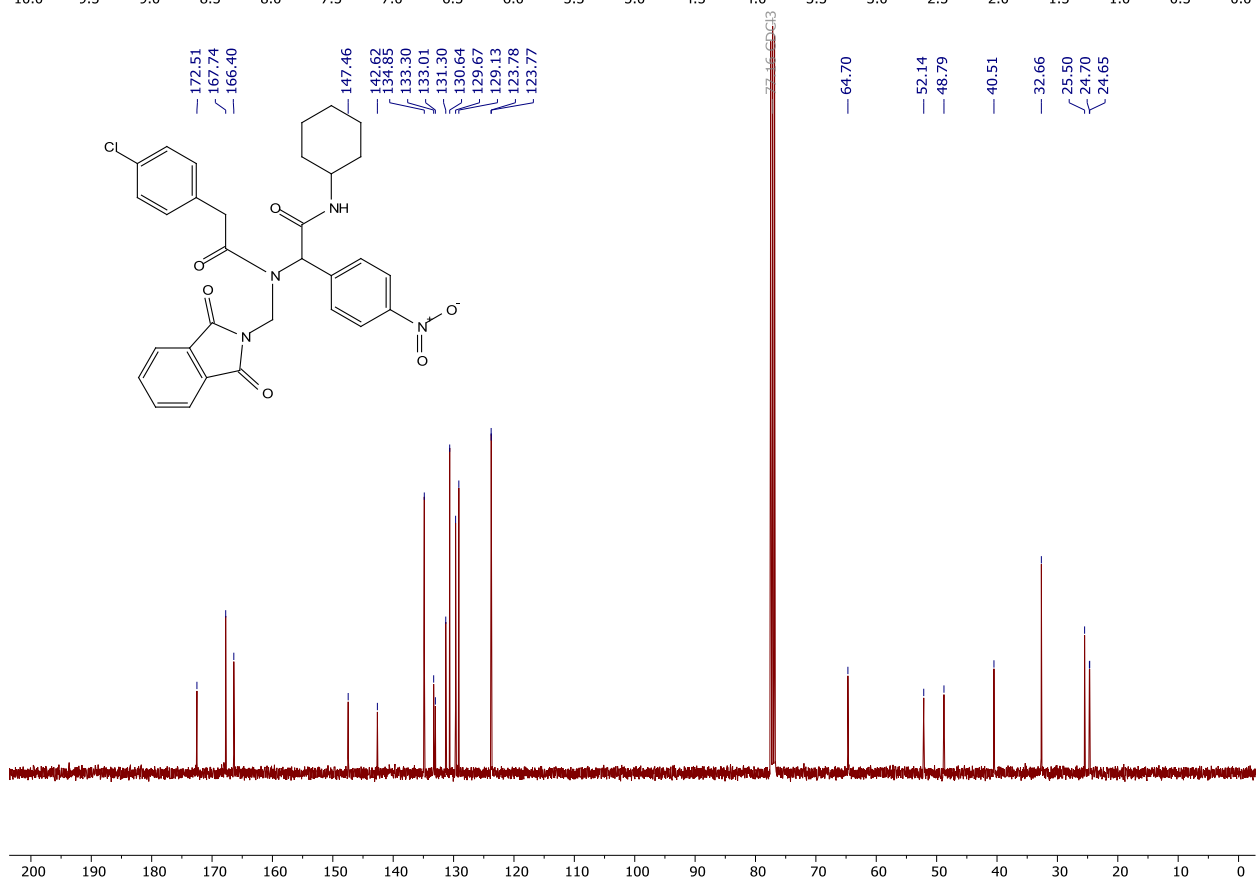
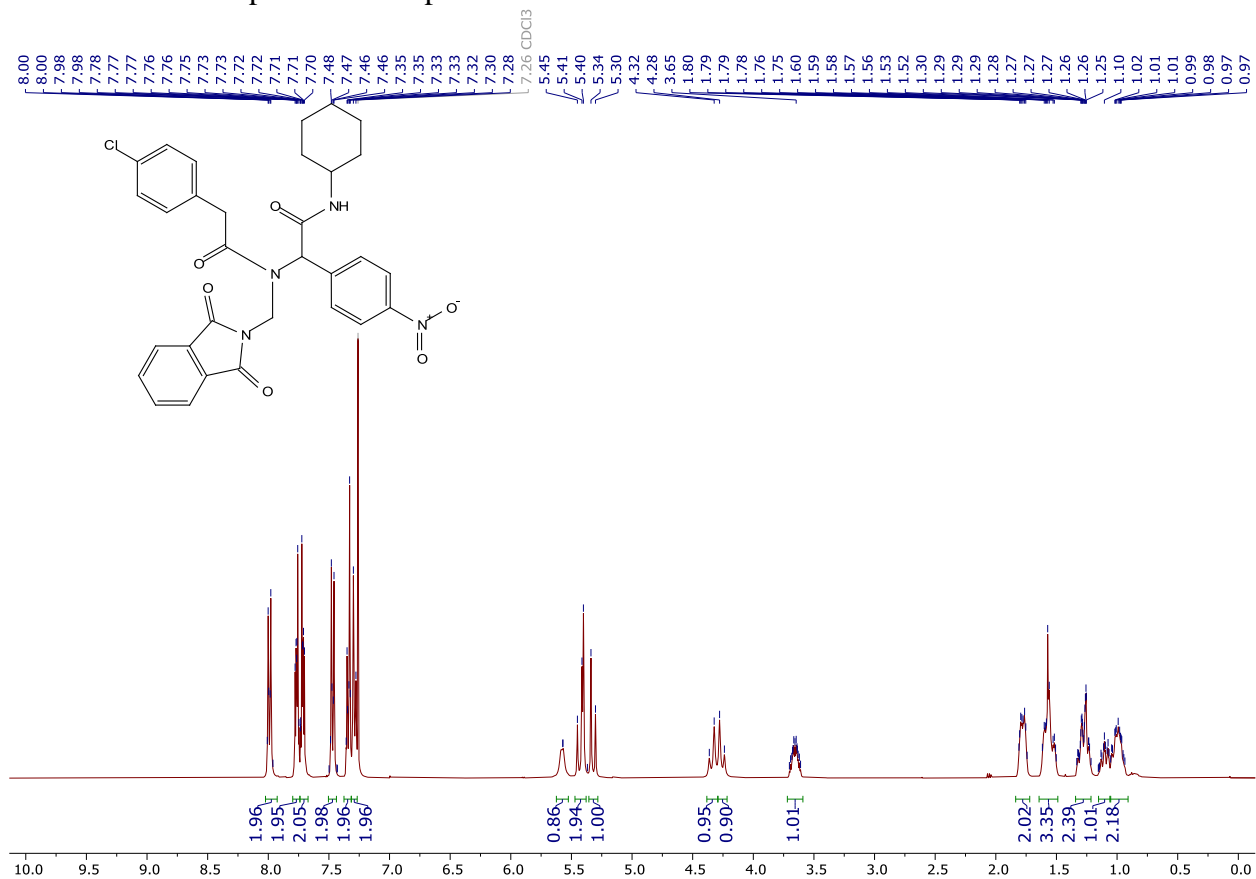
^1H and ^{13}C NMR spectra of compound **7a**



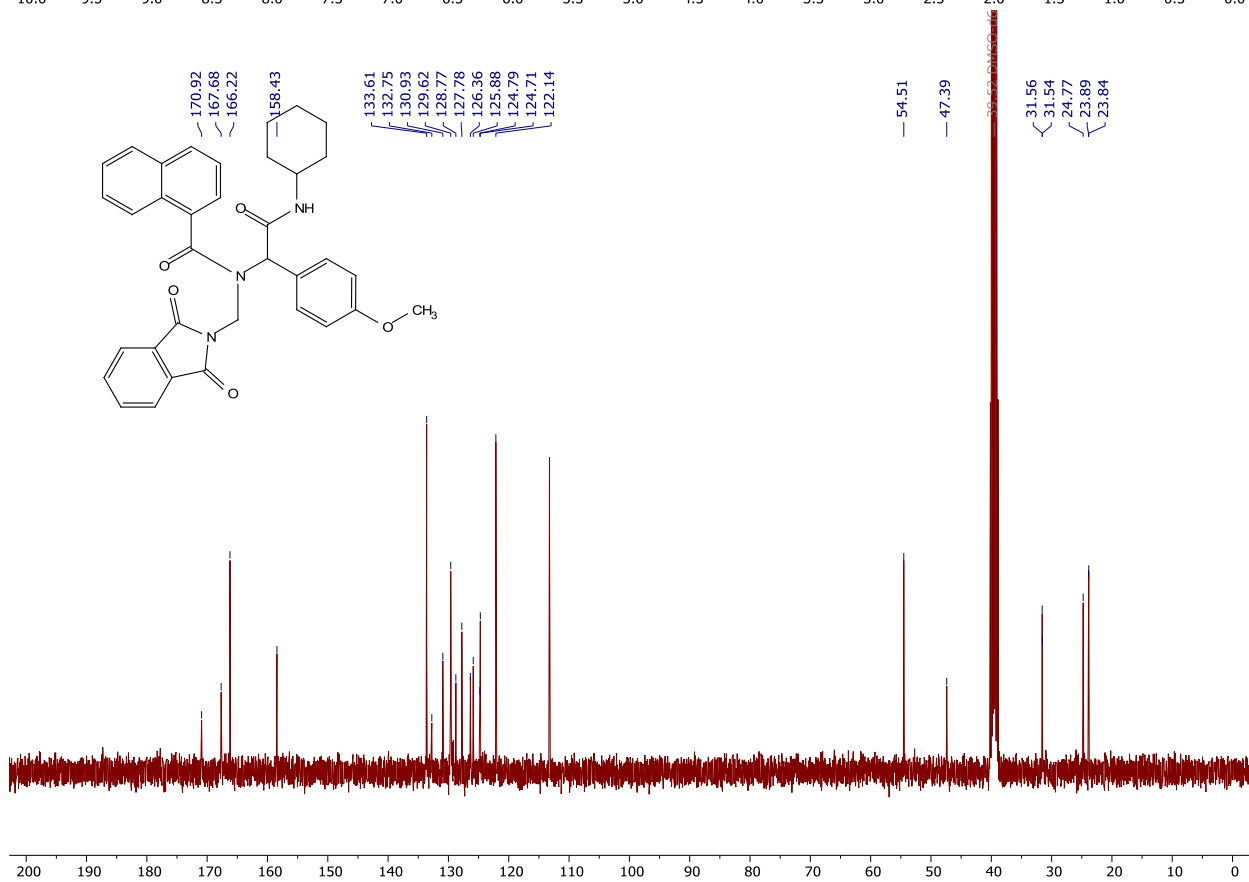
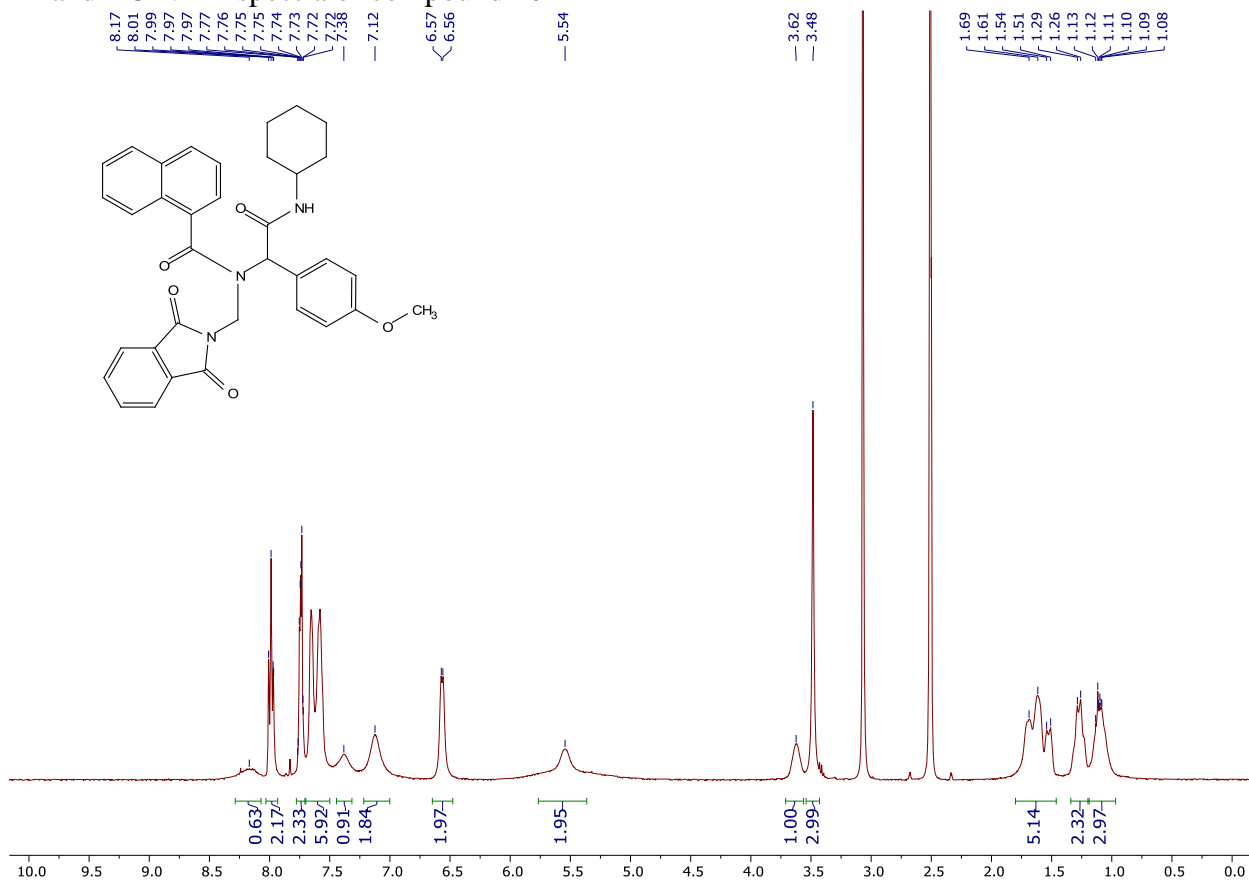
¹H and ¹³C NMR spectra of compound **7b**



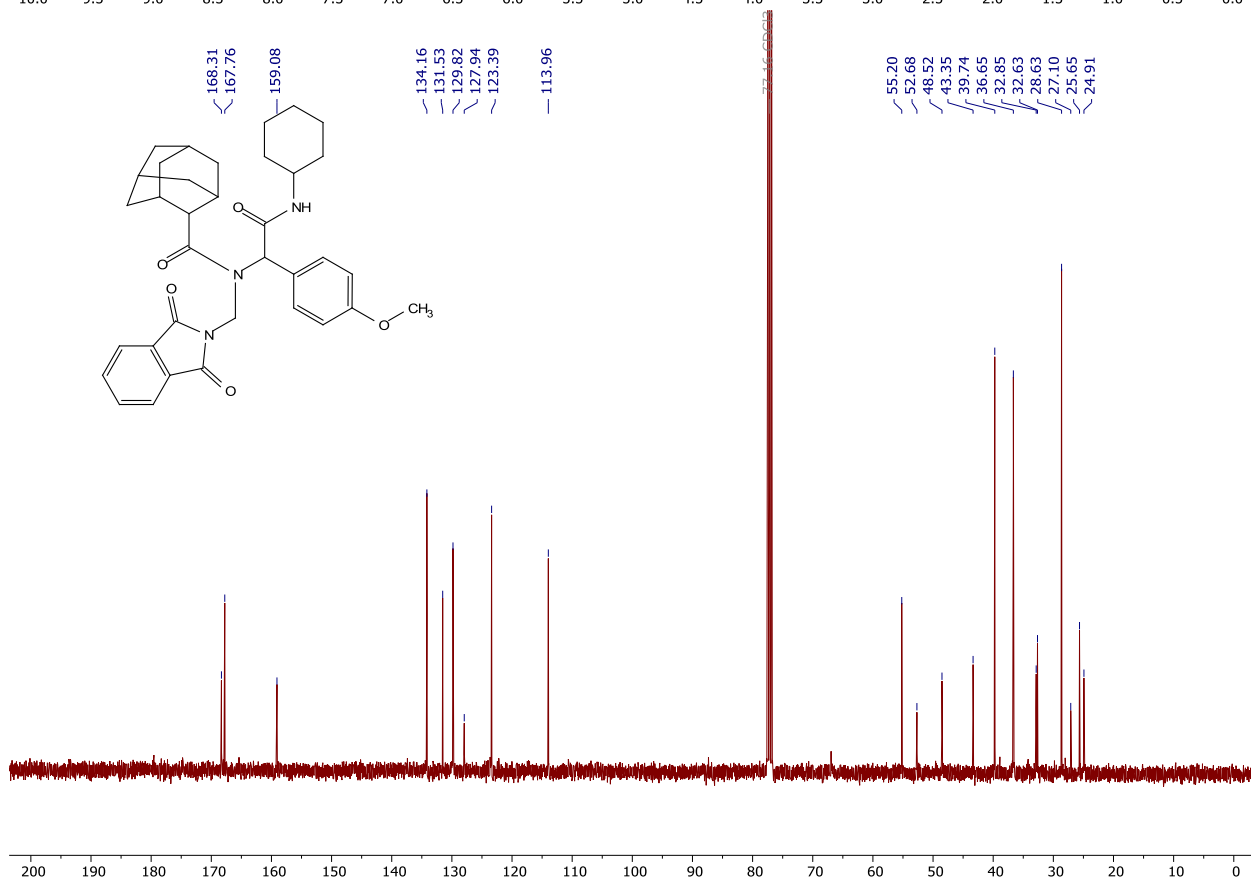
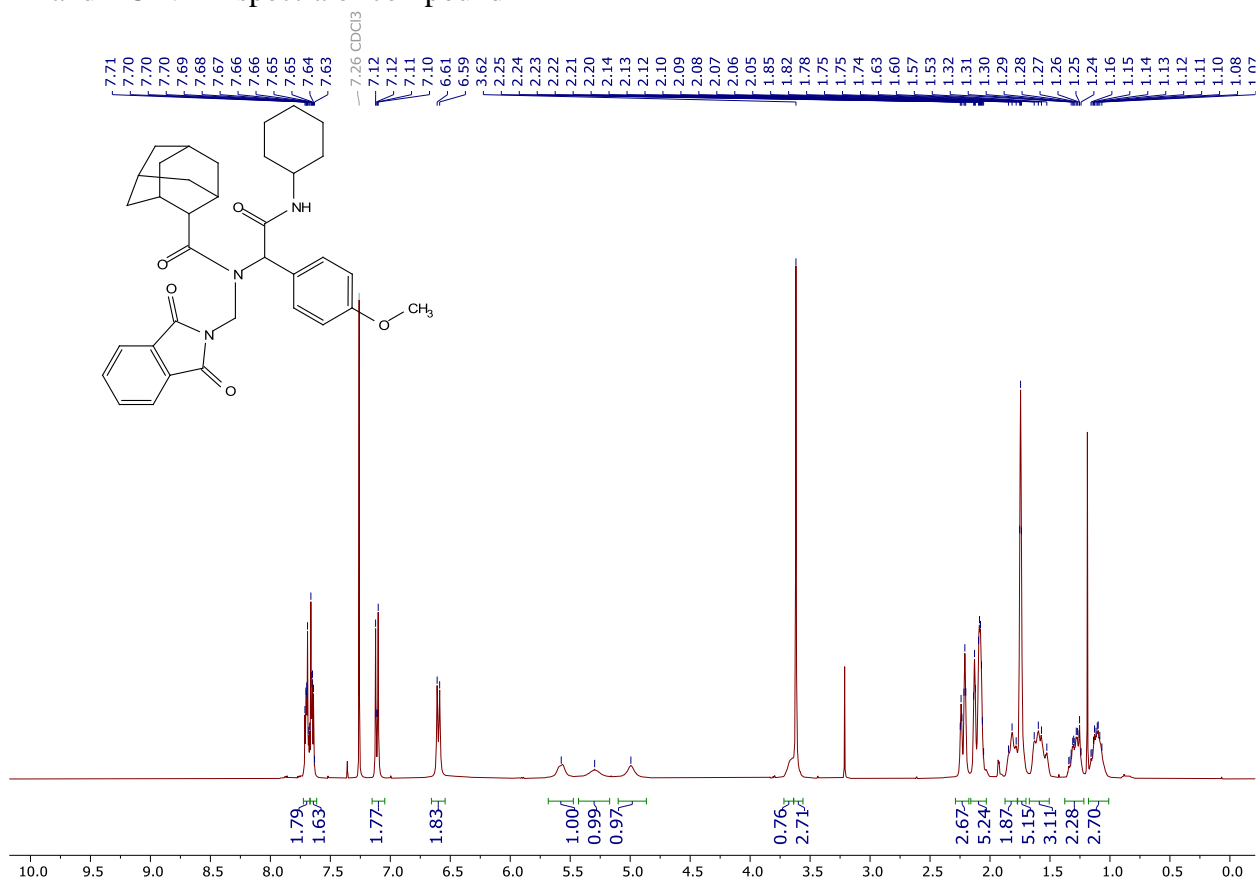
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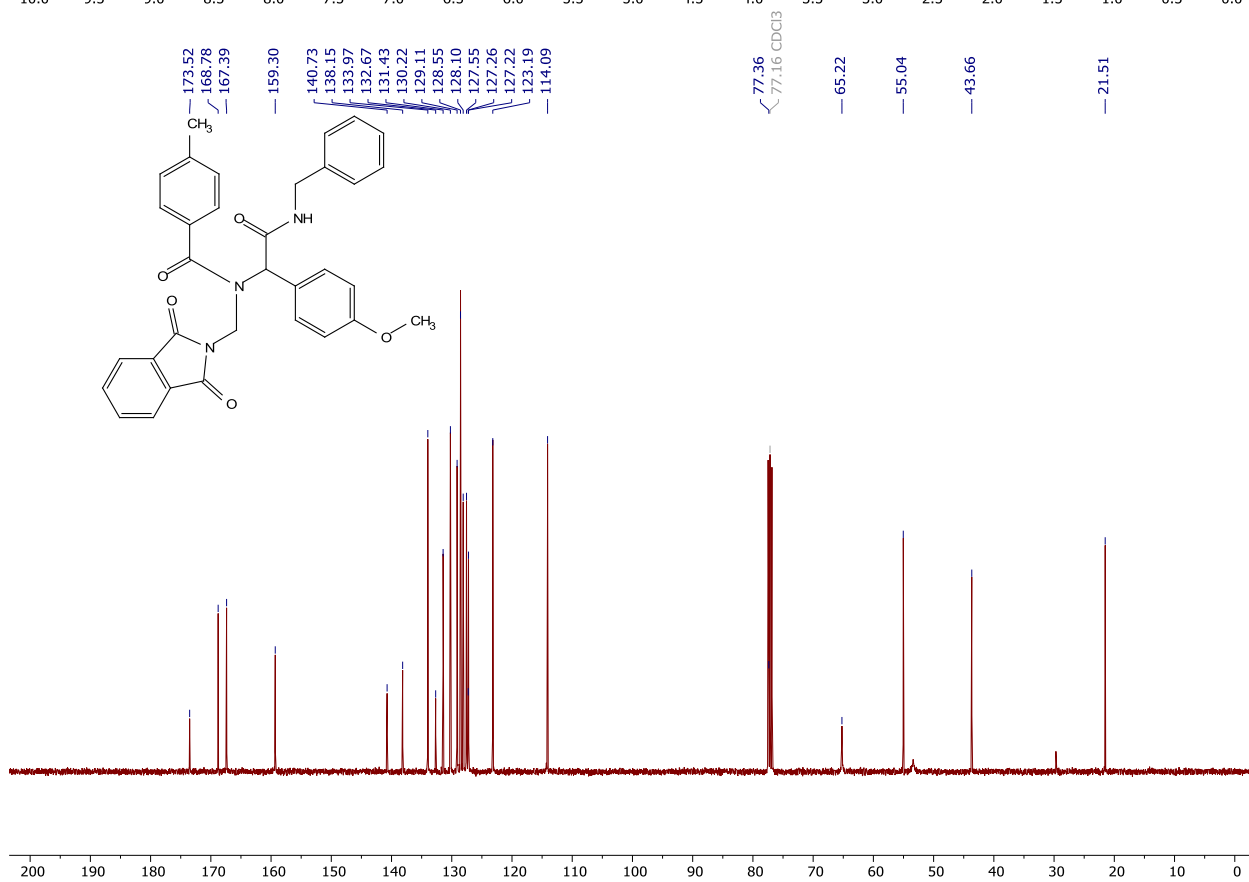
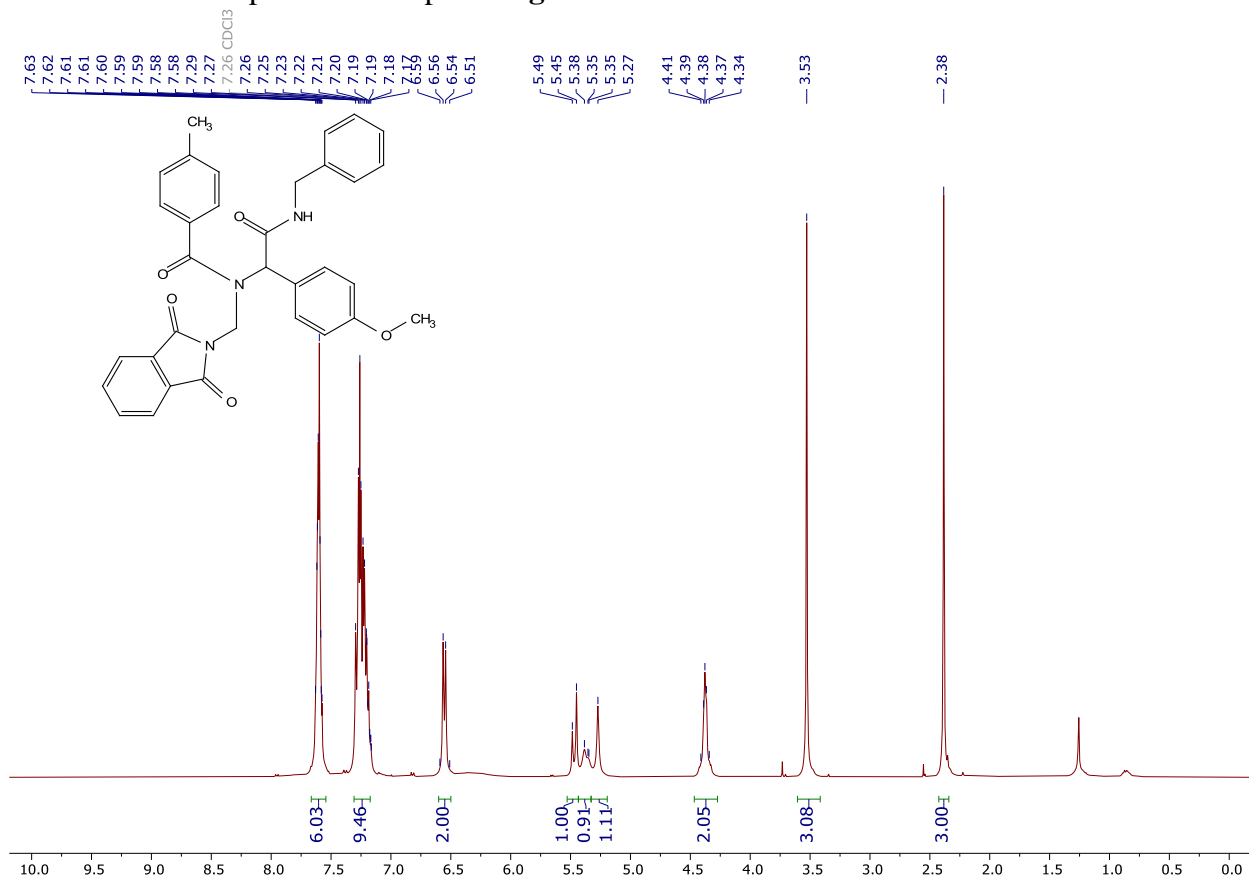
^1H and ^{13}C NMR spectra of compound **7e**



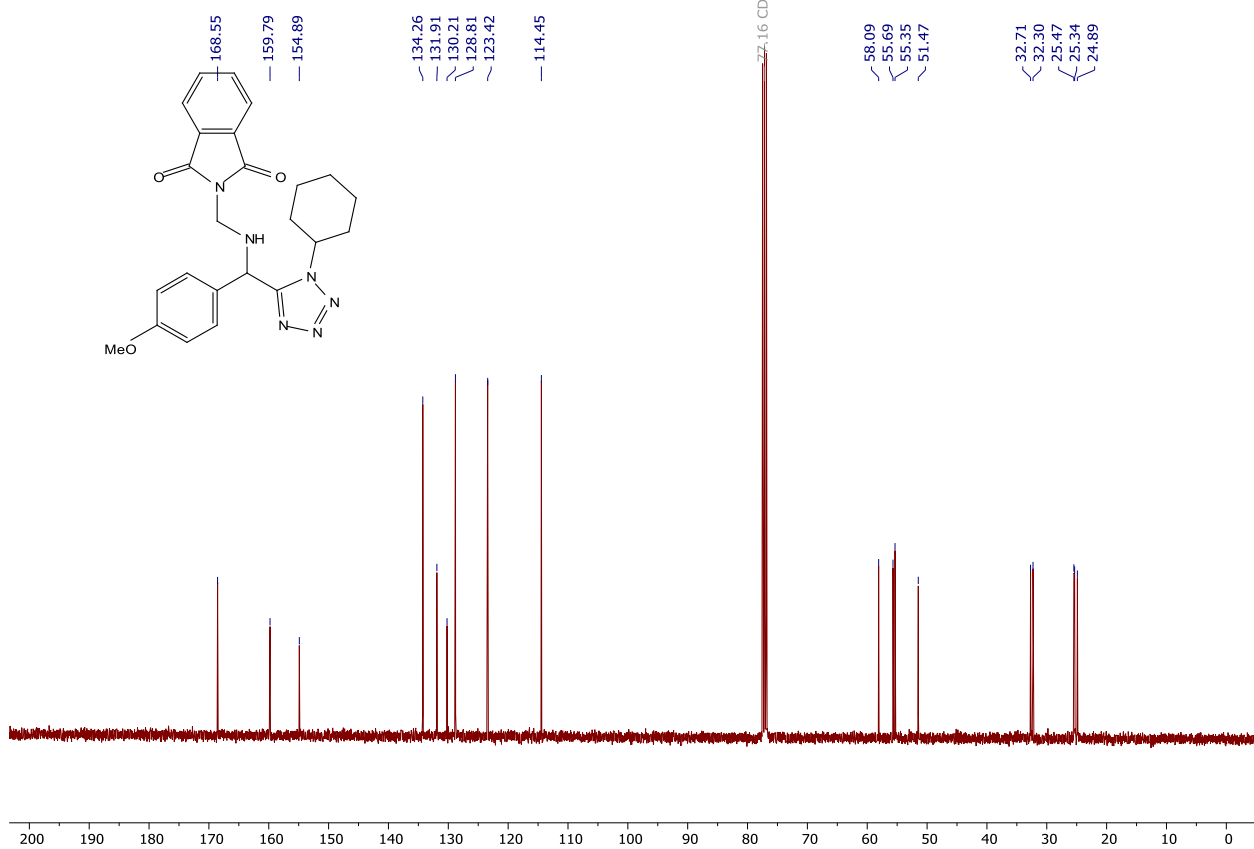
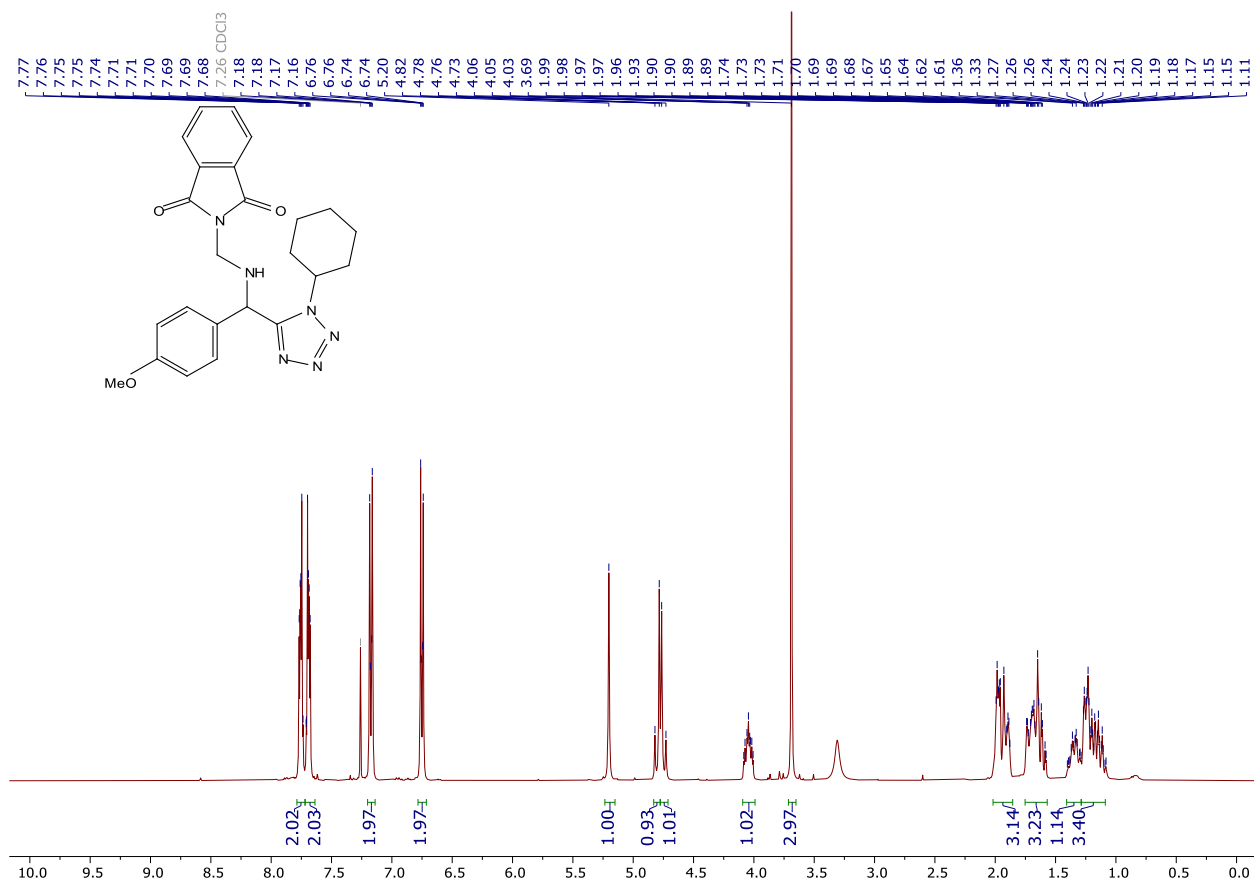
^1H and ^{13}C NMR spectra of compound **7f**



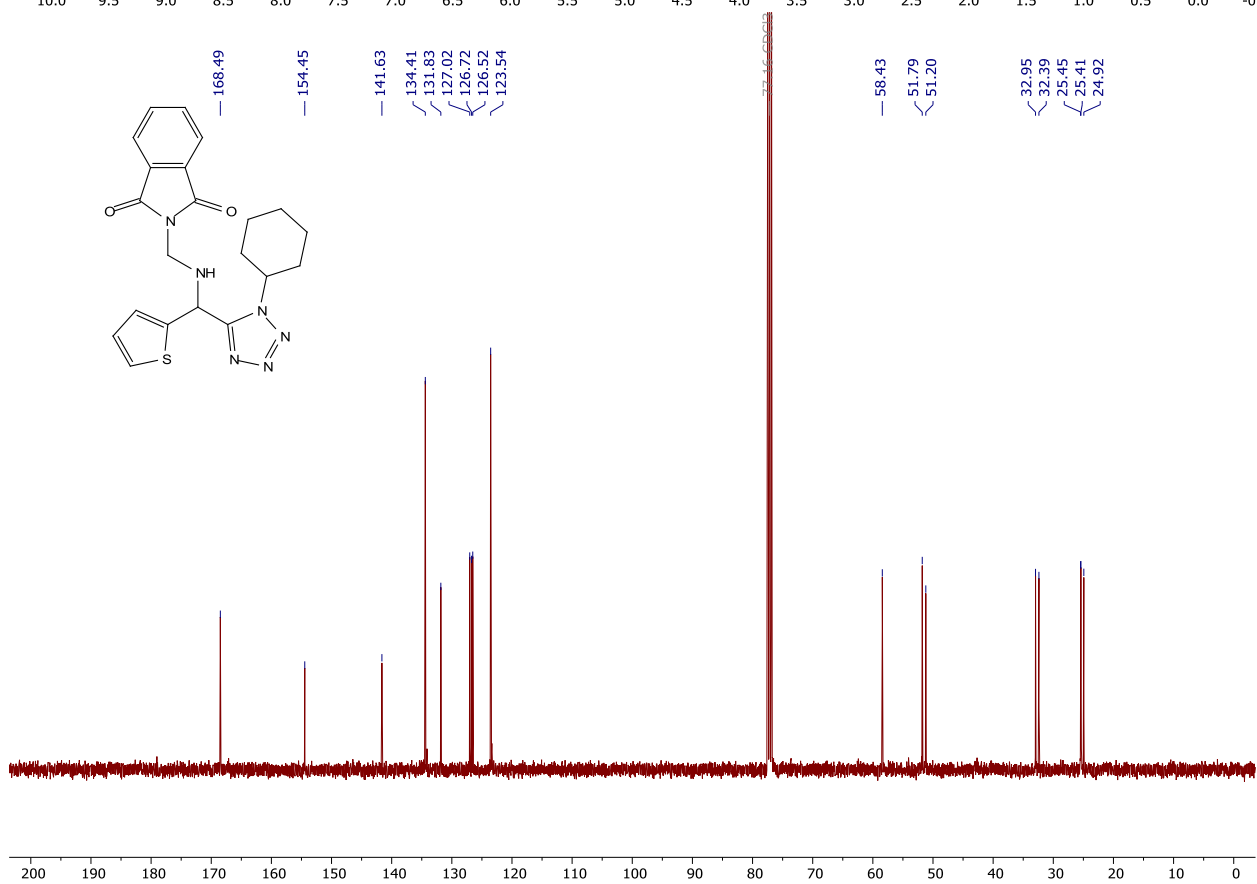
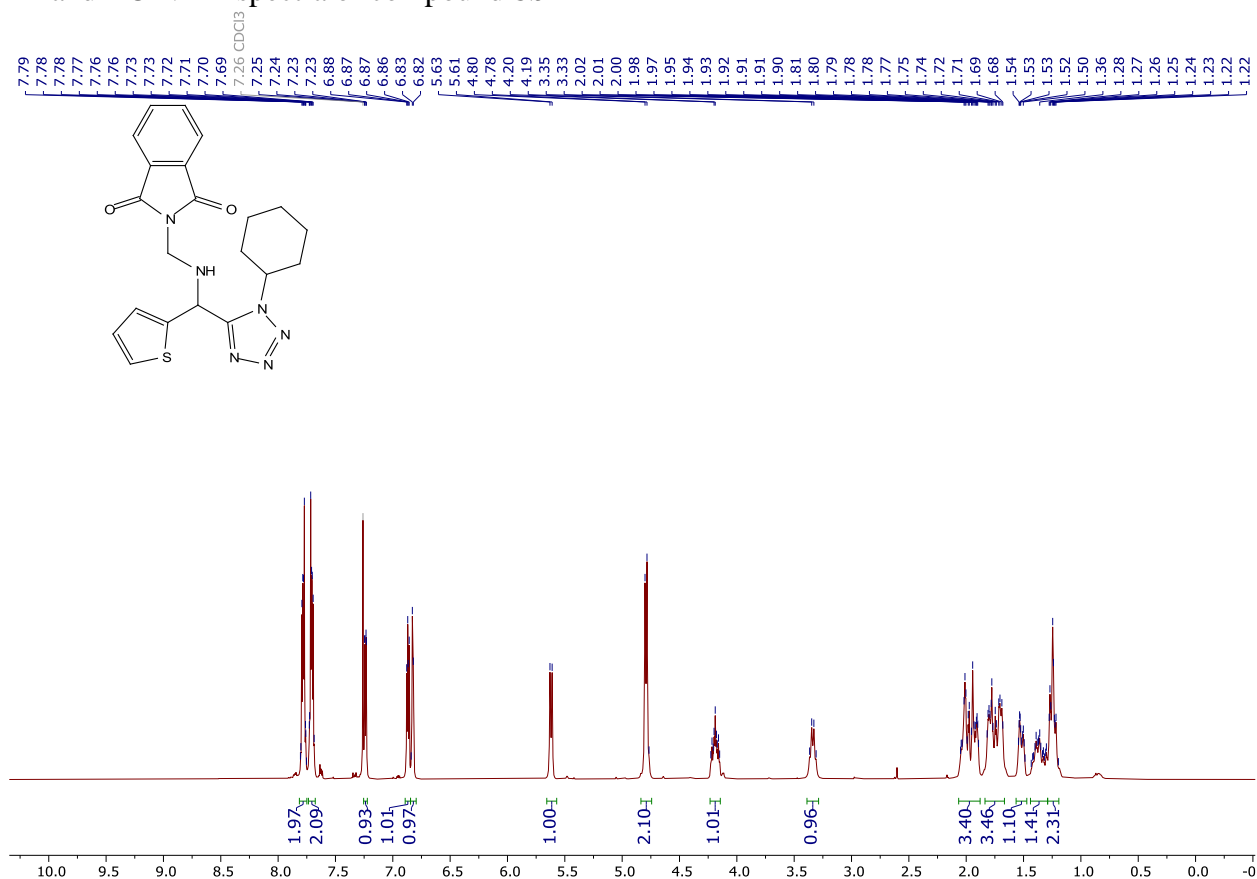
^1H and ^{13}C NMR spectra of compound **7g**



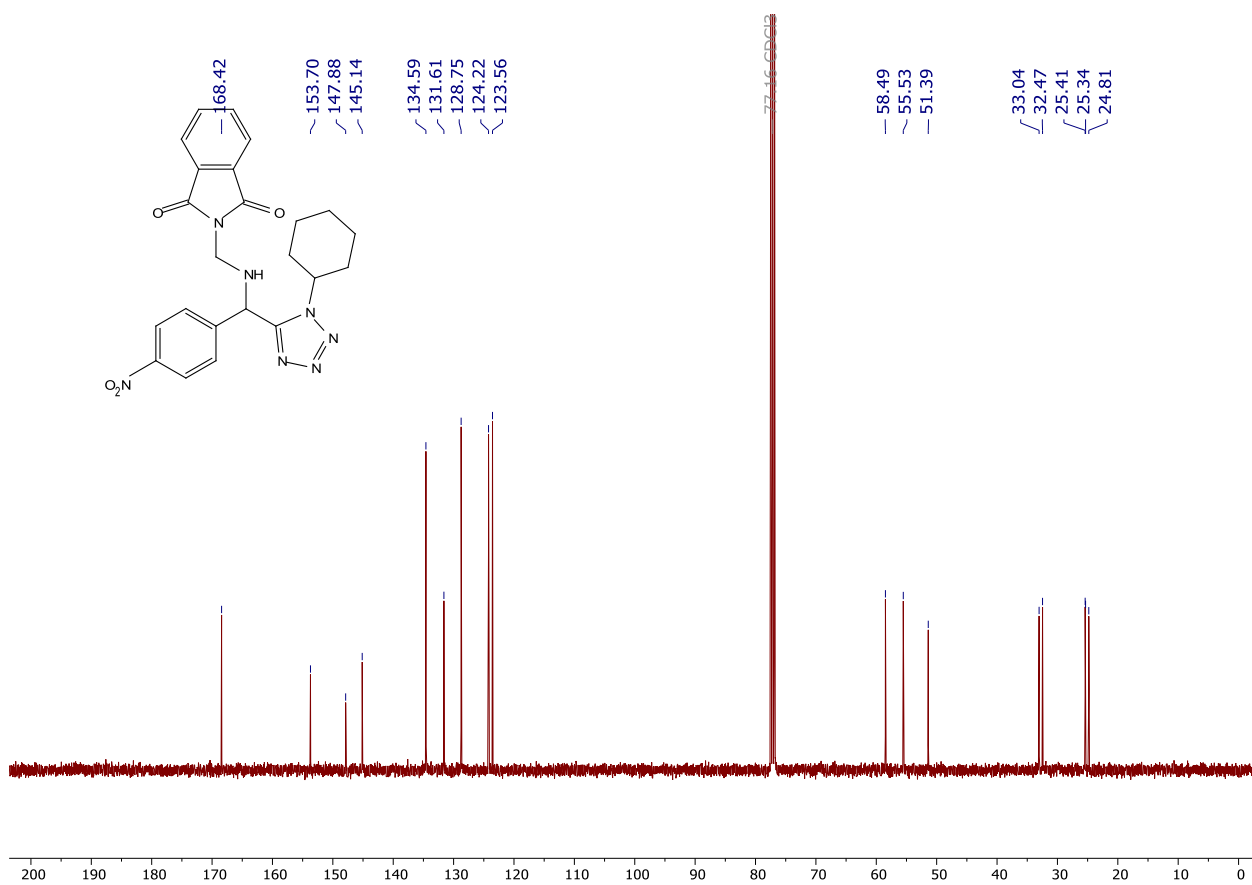
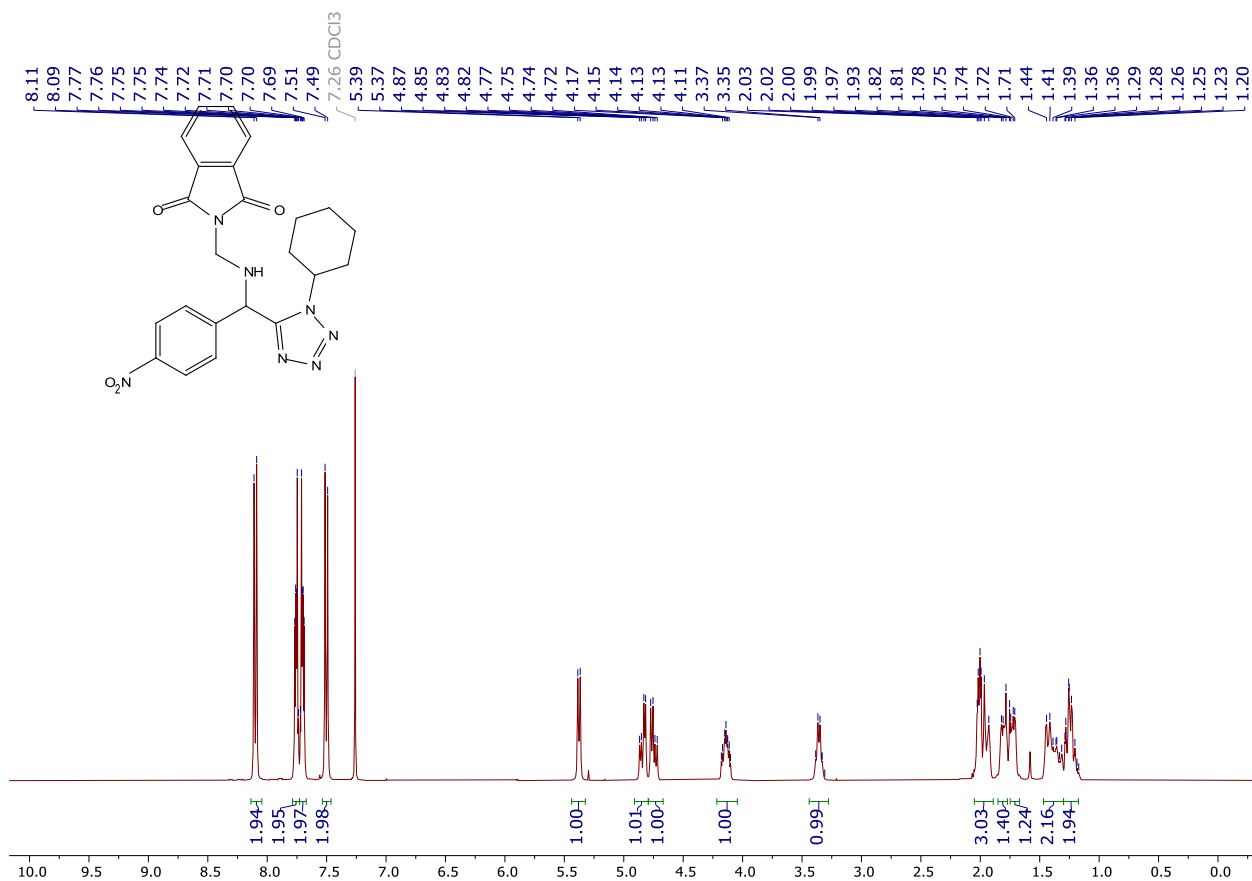
^1H and ^{13}C NMR spectra of compound **8a**



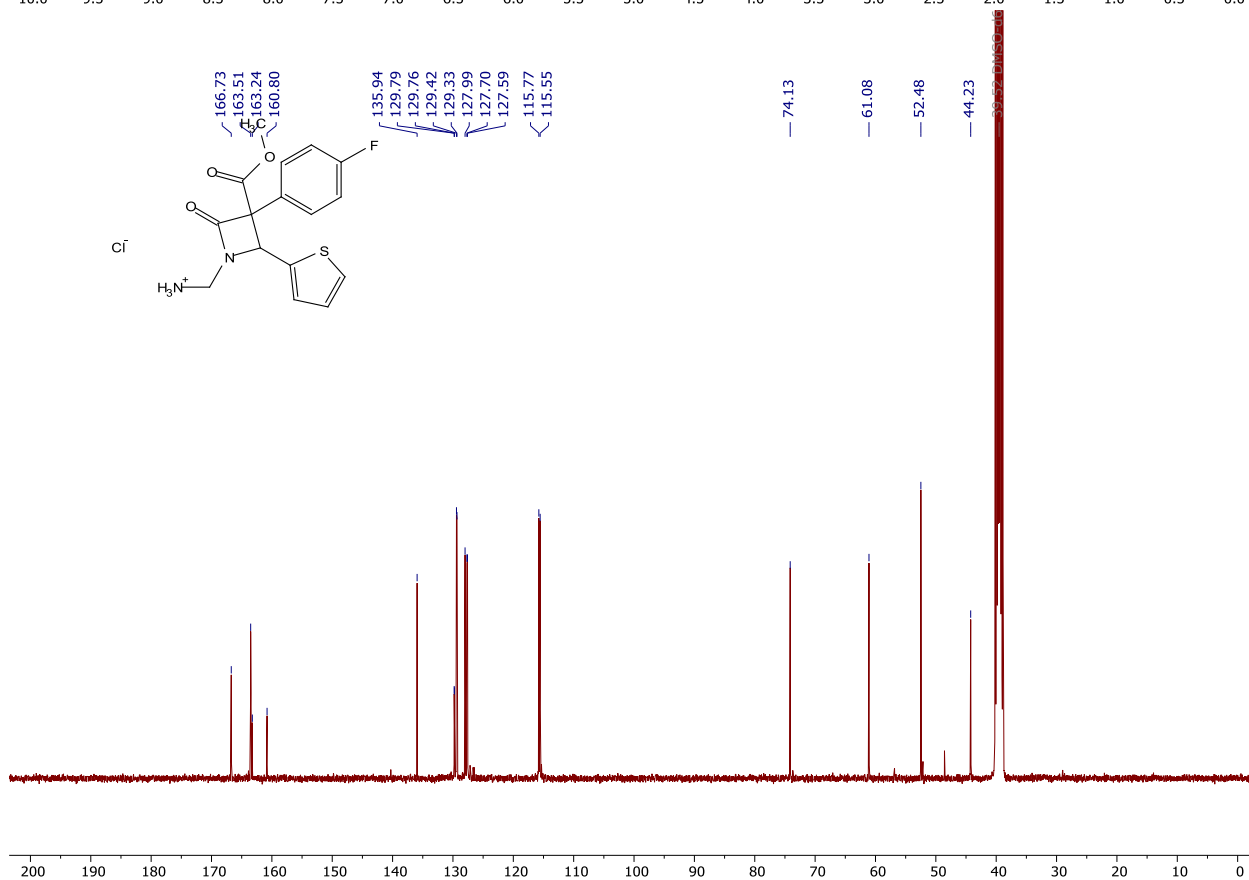
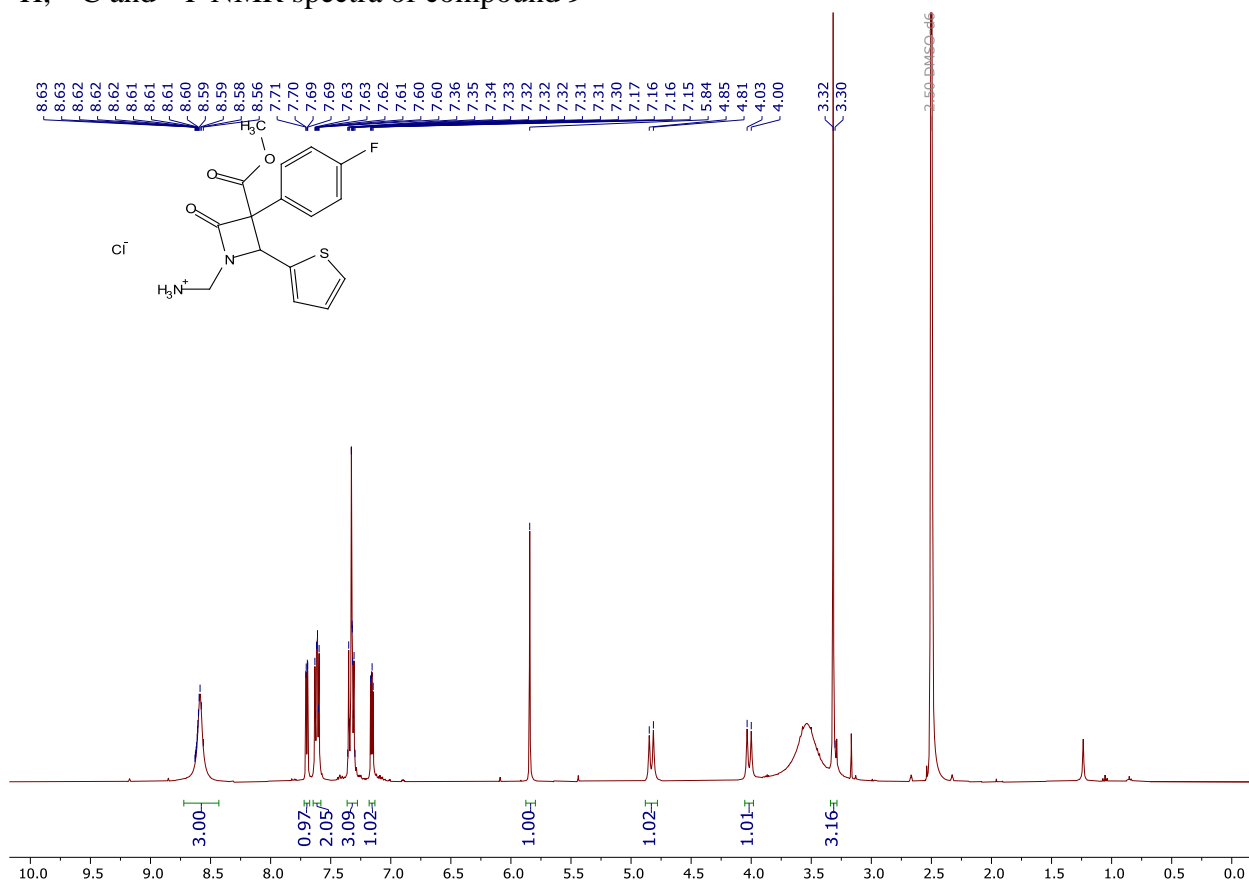
^1H and ^{13}C NMR spectra of compound **8b**

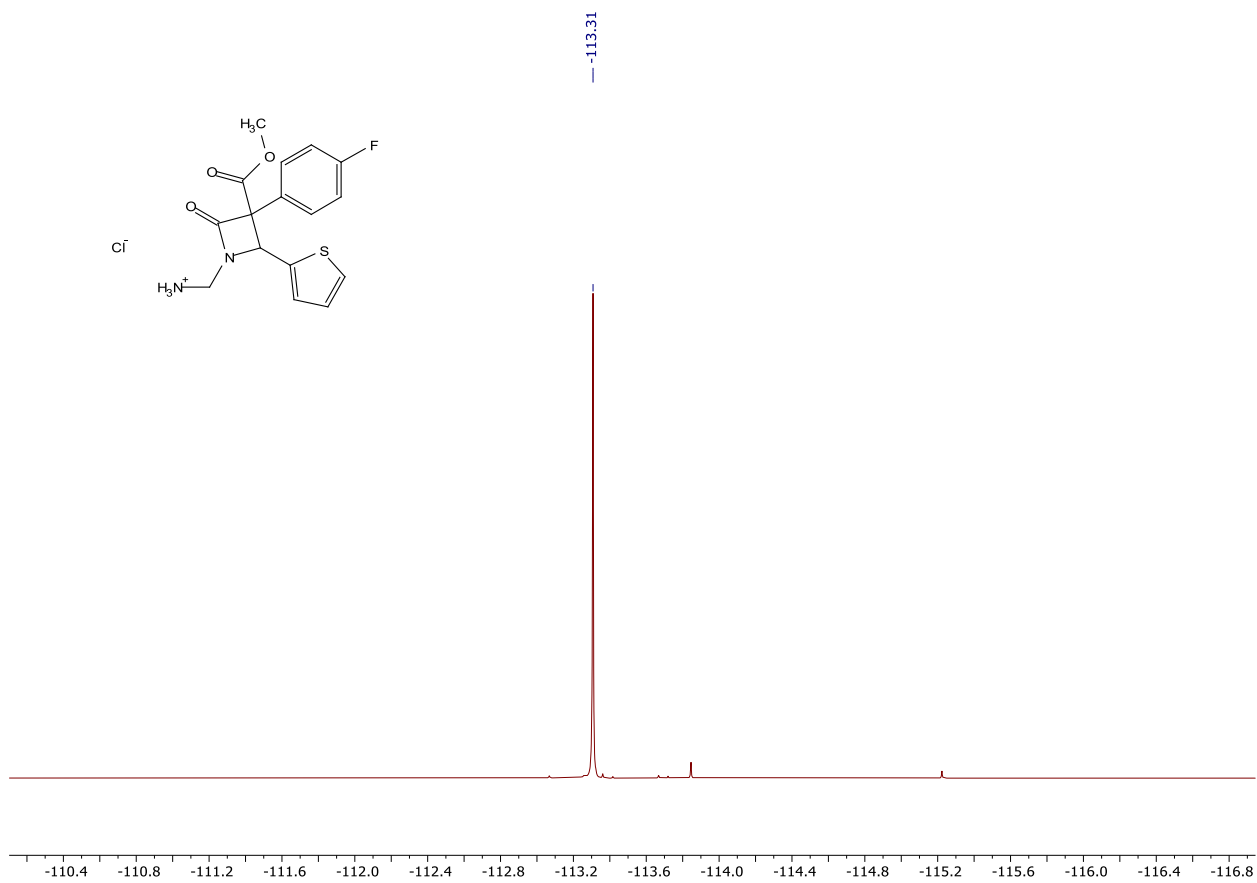


^1H and ^{13}C NMR spectra of compound **8c**

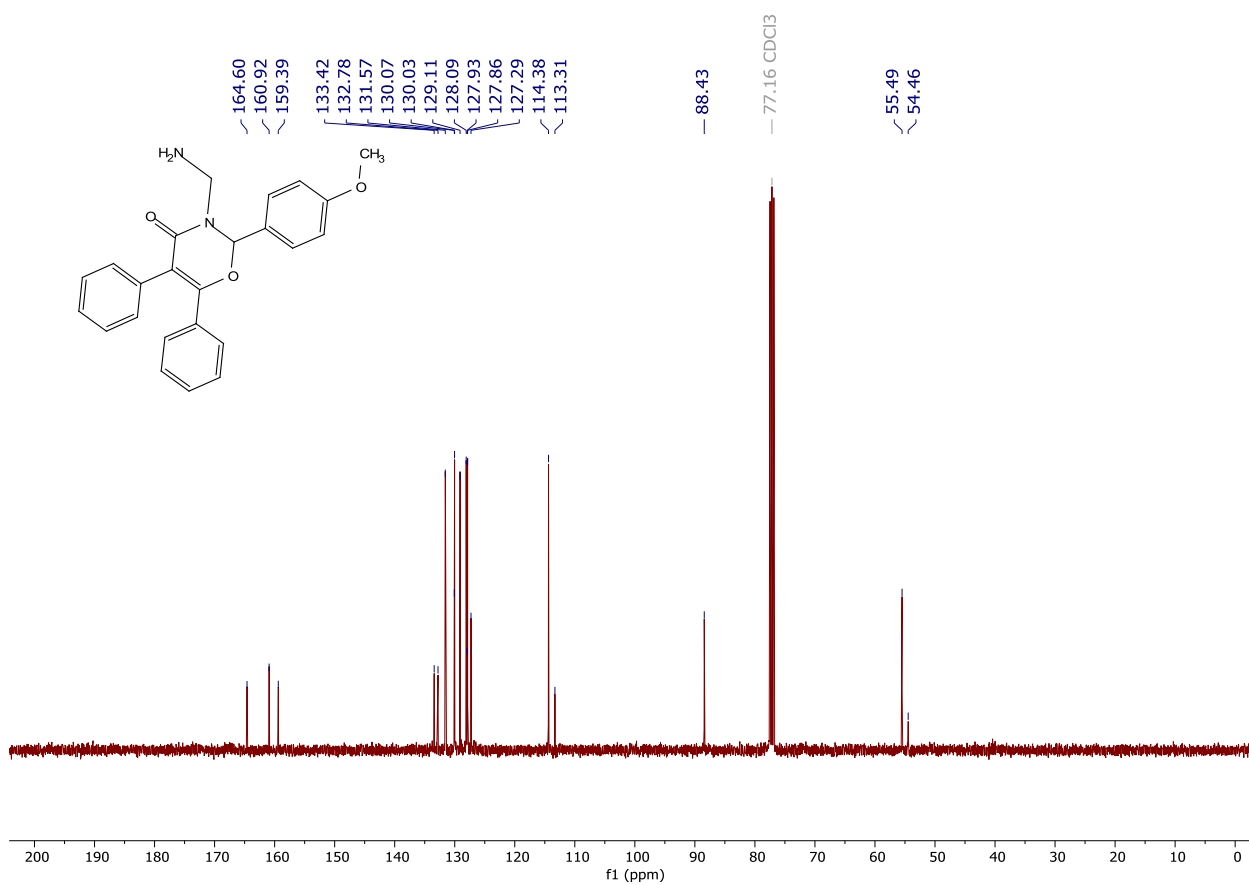
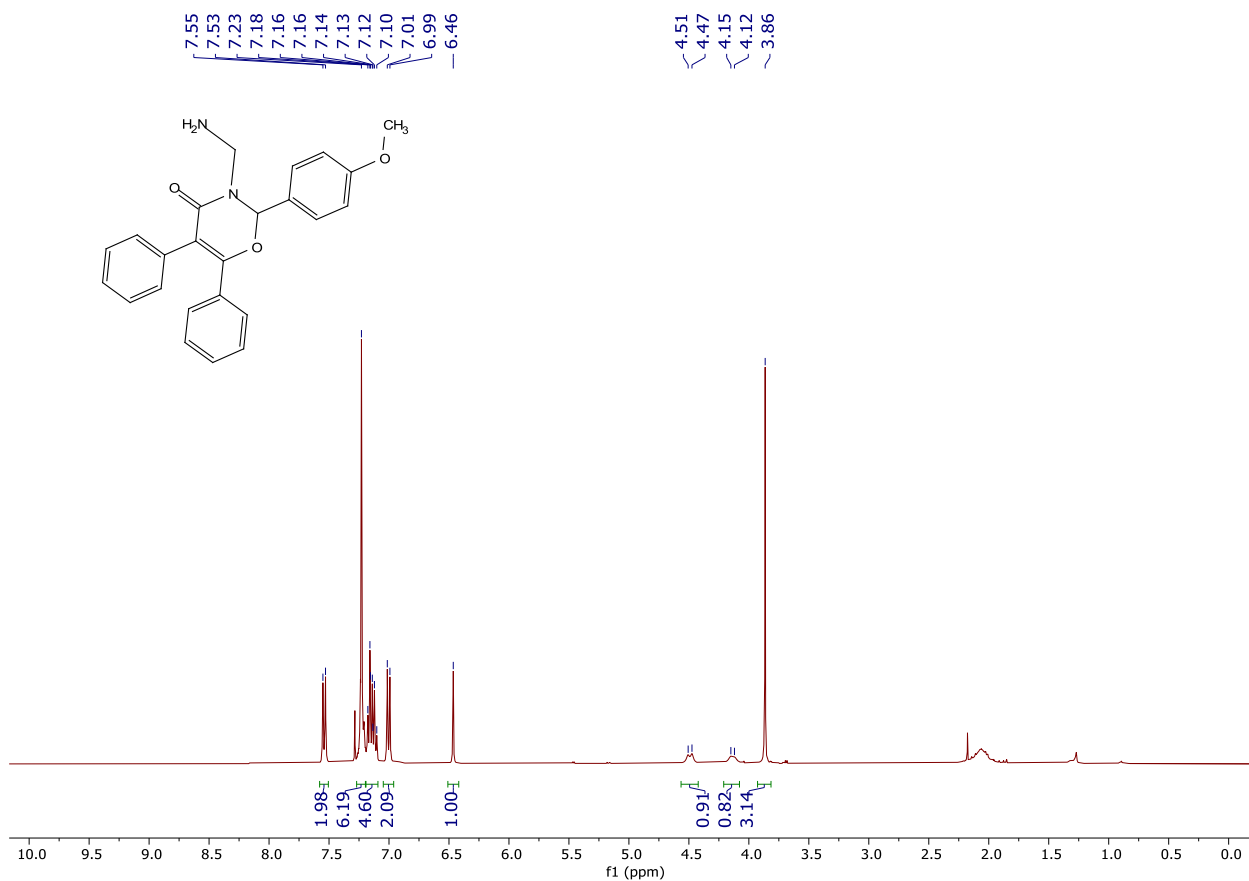


^1H , ^{13}C and ^{19}F NMR spectra of compound **9**

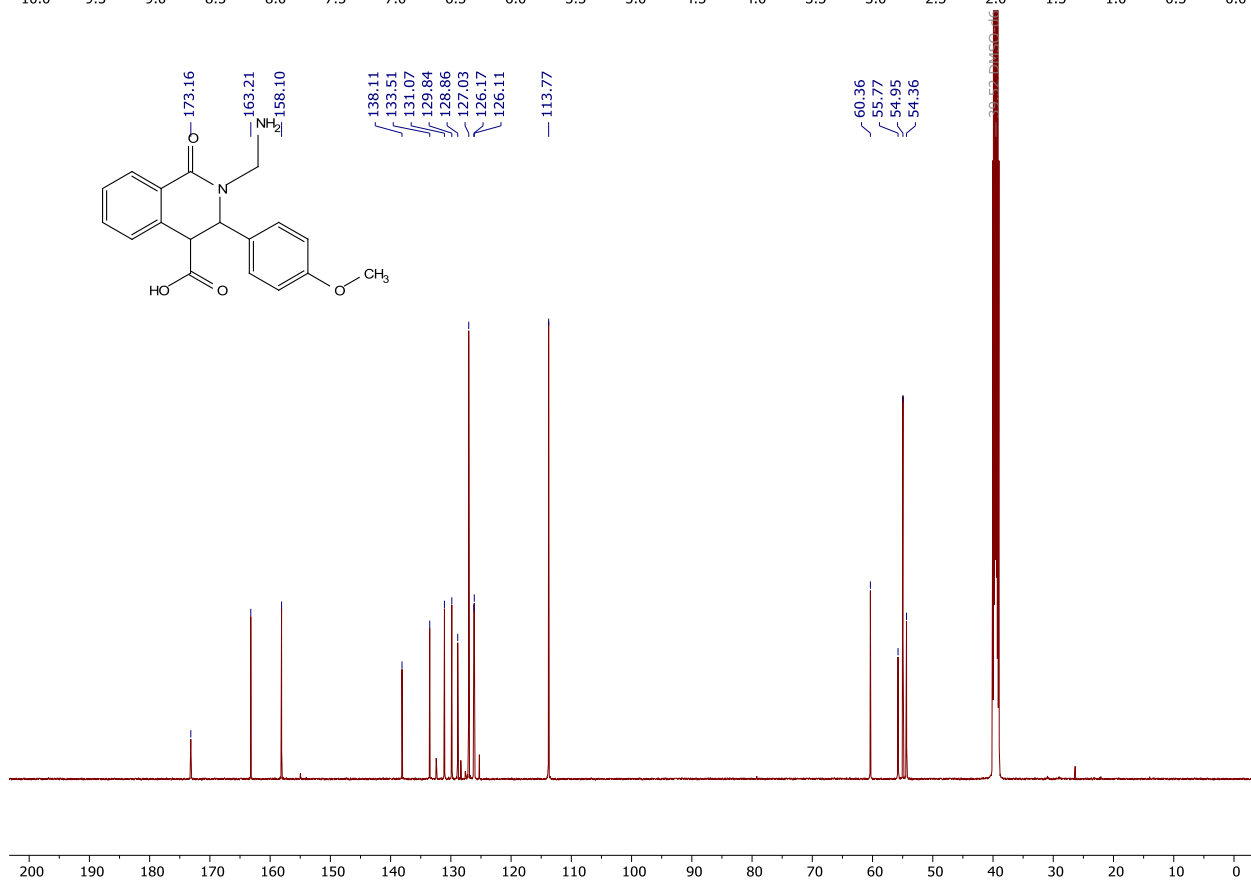
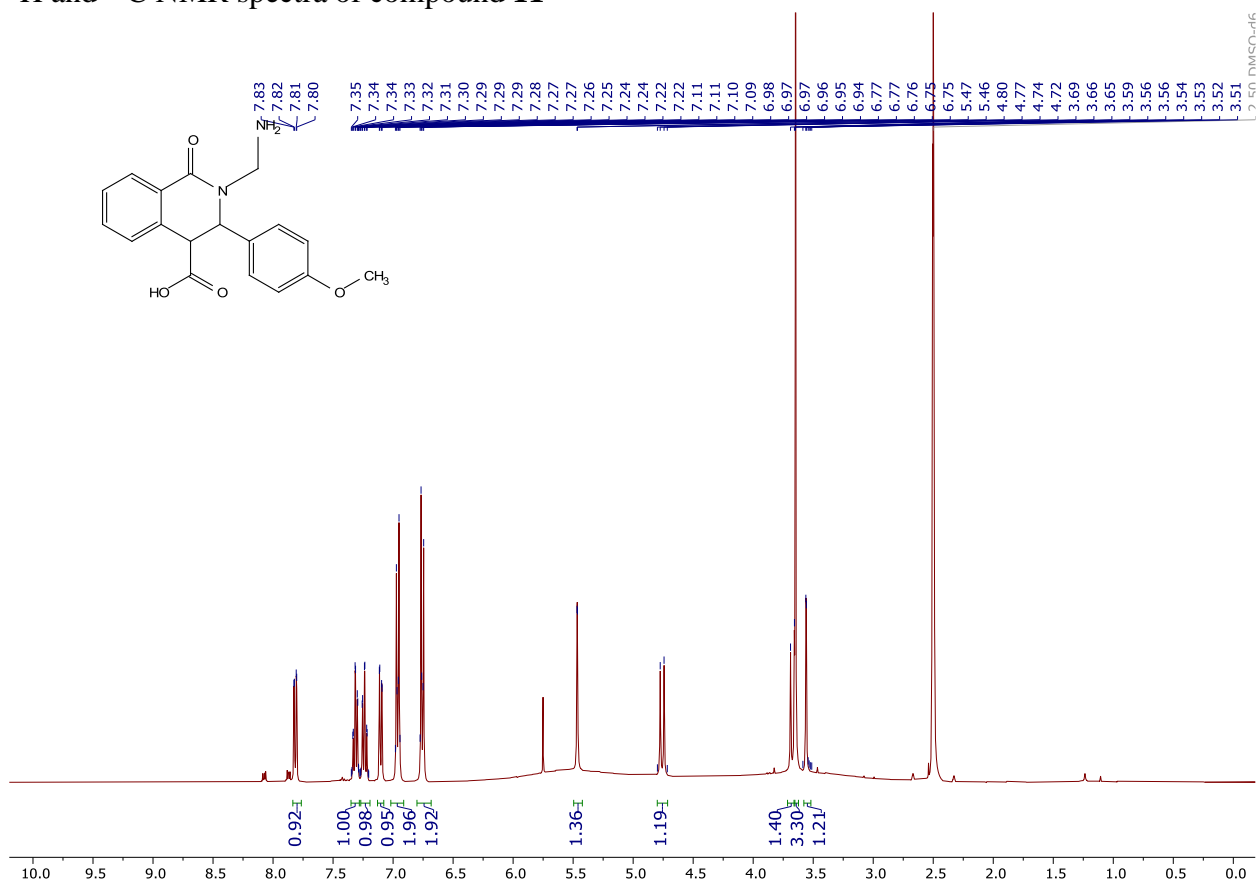




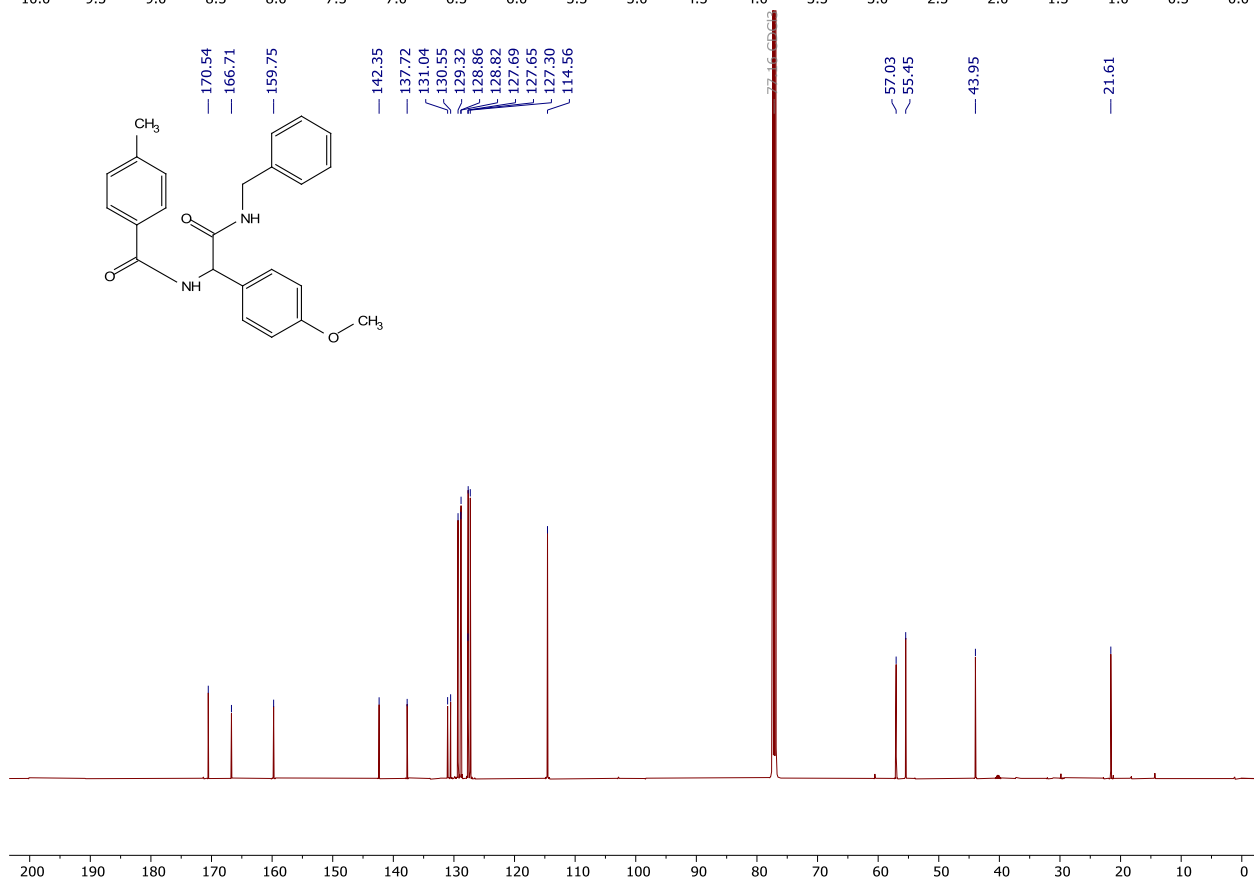
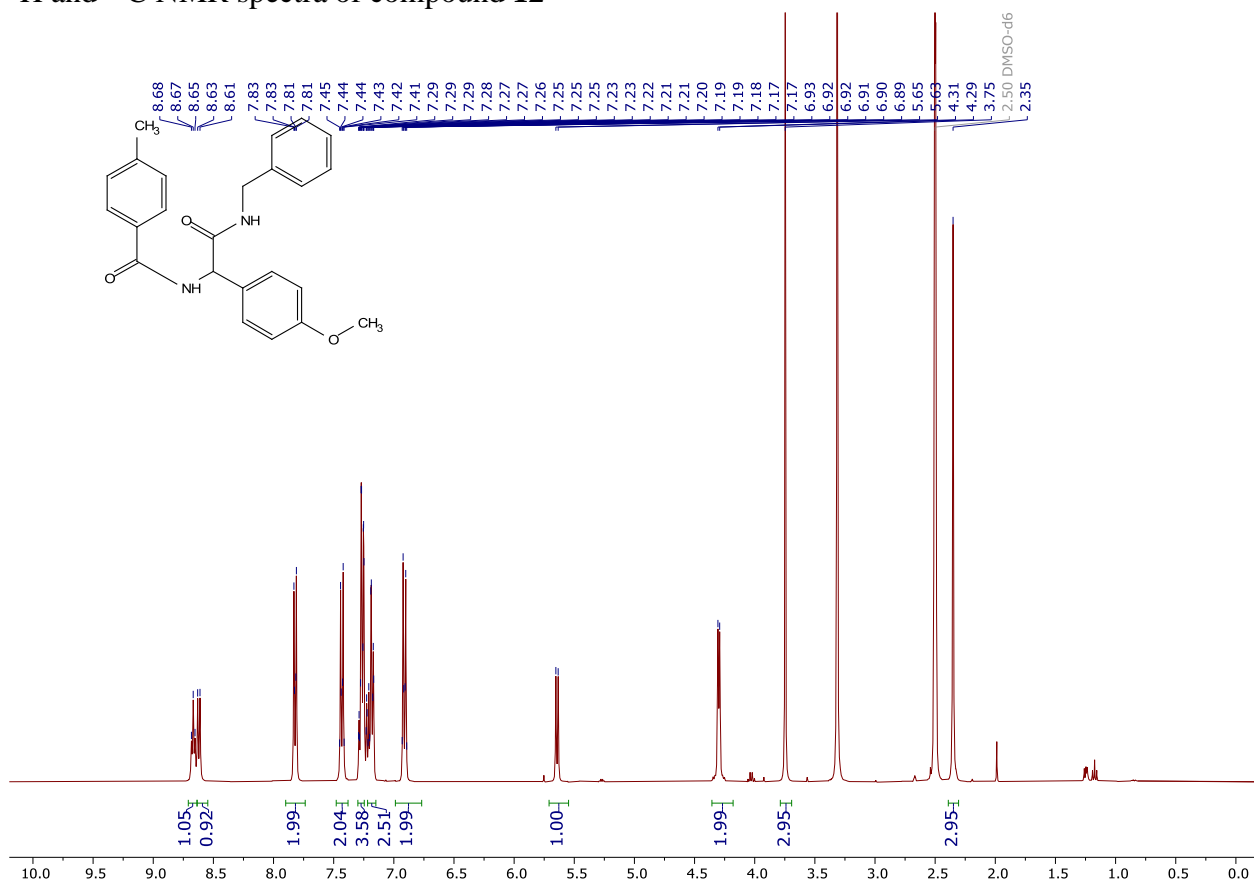
^1H and ^{13}C NMR spectra of compound **10**



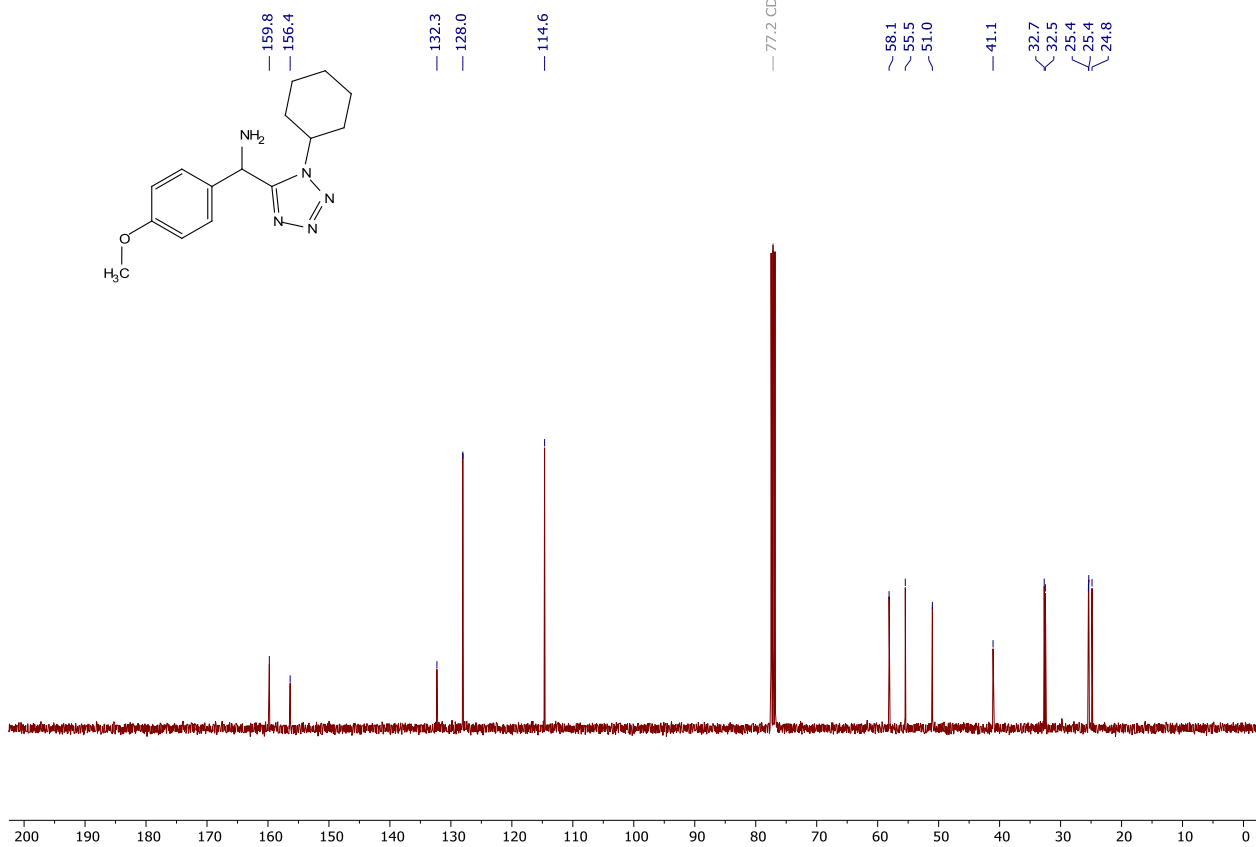
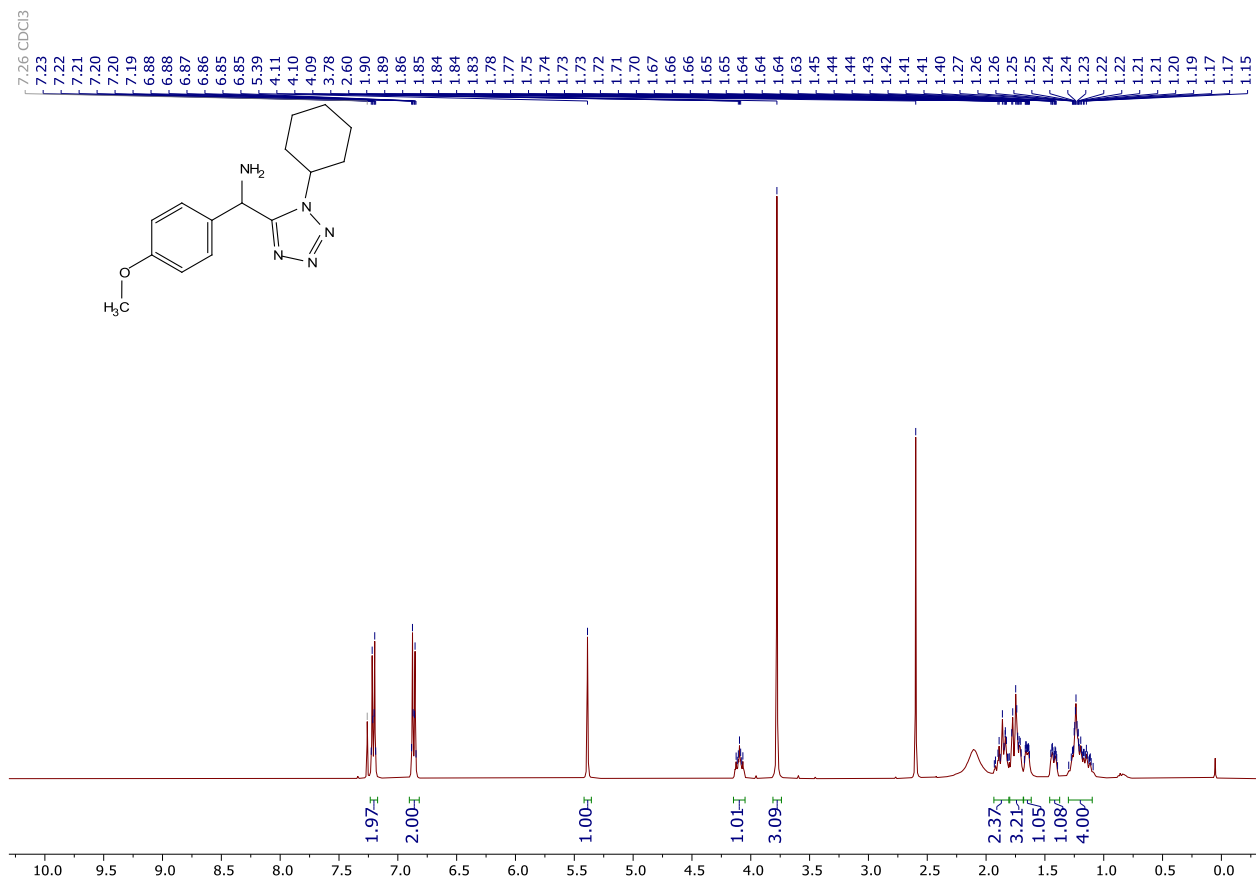
^1H and ^{13}C NMR spectra of compound **11**



^1H and ^{13}C NMR spectra of compound **12**



^1H and ^{13}C NMR spectra of compound **13**



References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009**, *42* (2), 339-341.
2. Sheldrick, G. M., SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr A Found Adv* **2015**, *71* (Pt 1), 3-8.
3. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr C Struct Chem* **2015**, *71* (Pt 1), 3-8.