

Supporting Information

Palladium-Catalyzed Cascade Carboesterification of Norbornene with Alkynes

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China*

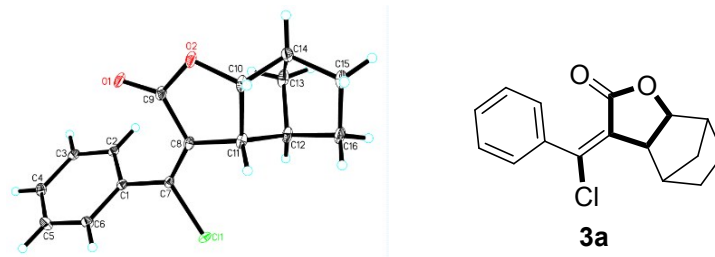
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X-ray Crystallographic Analysis for Product 3a

The CCDC number of compound **3a** is 1814490.

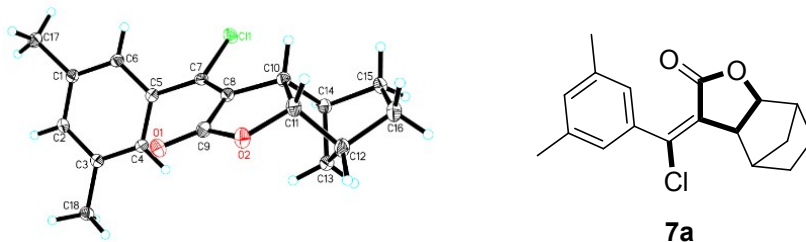


Crystal Data and Structure Refinement for Product **3a**

| | |
|-----------------------------------|--|
| Empirical formula | C ₁₆ H ₁₅ ClO ₂ |
| Formula weight | 274.73 |
| Temperature | 100.00(10) K |
| Wavelength | 1.54184 Å |
| Crystal system | monoclinic |
| Space group | P 1 21/c 1 |
| Unit cell dimensions | a= 6.07129(17) Å, α= 90.00° |
| | b= 18.3833(5) Å, β= 101.880(3) ° |
| | c= 12.0370(3) Å, γ= 90.00° |
| Density (calculated) | 1.388 Mg/m ³ |
| Absorption coefficient | 2524 mm ⁻¹ |
| F (000) | 576.0 |
| Crystal size | 0.21 × 0.16 × 0.15 mm |
| Theta range for data collection | 8.916 to 146.522 deg. |
| Index ranges | -6 ≤ h ≤ 7, -15 ≤ k ≤ 22, -14 ≤ l ≤ 13 |
| Reflections collected | 4776 |
| Independent reflections | 2576 |
| Completeness to theta = 29.55° | 99.88% |
| Absorption correction | multi-scan |
| Refinement method | Full-matrix least-squares on F ² |
| Data/restraints/parameters | 2576 / 0 / 173 |
| Goodness-of-fit on F ² | 1.034 |
| Final R indices [I>2sigma(I)] | R1 = 0.0815, wR2 = 0.2215 |
| R indices (all data) | R1 = 0.0825, wR2 = 0.2230 |

X-ray Crystallographic Analysis for Product 7a

The CCDC number of compound **7a** is 1838810.

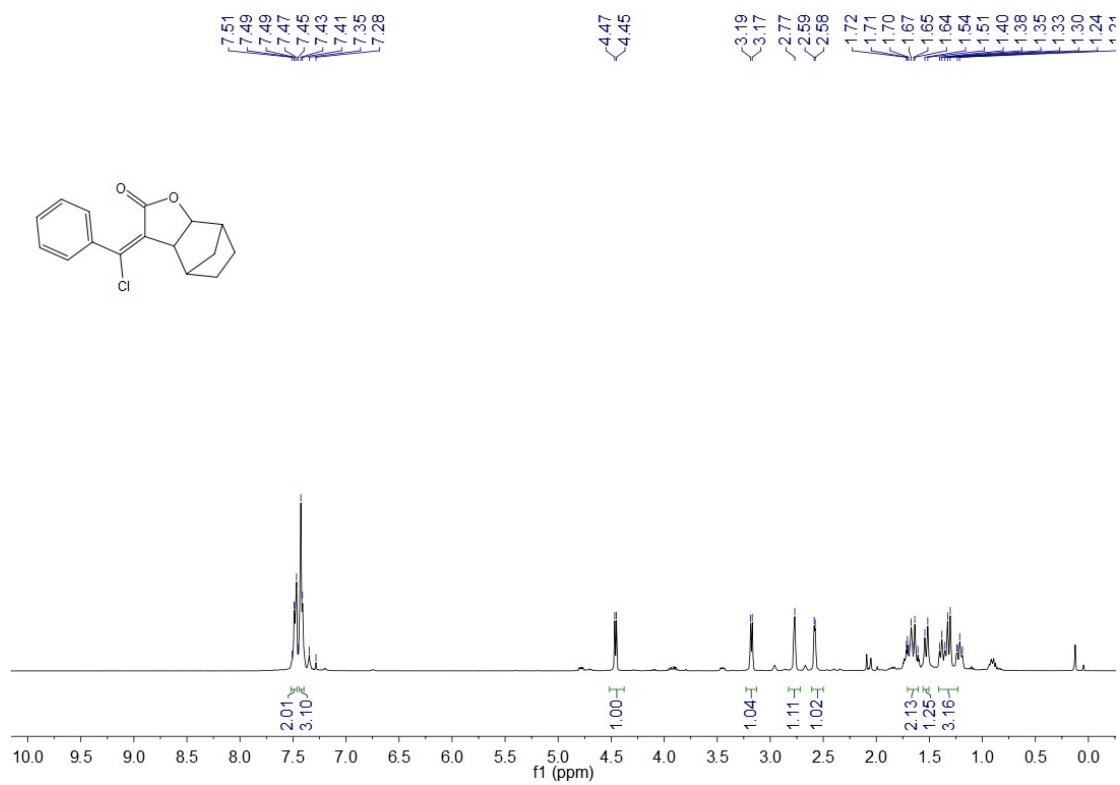


Crystal Data and Structure Refinement for Product **3a**

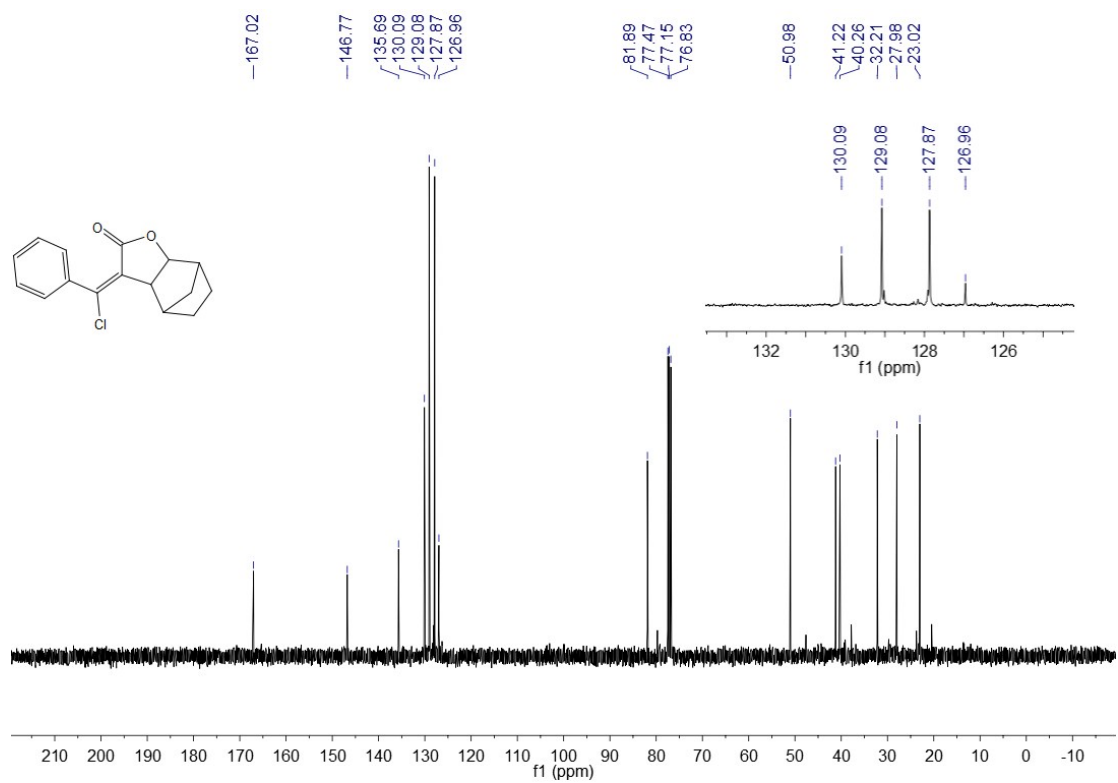
| | |
|-----------------------------------|--|
| Empirical formula | C ₁₈ H ₁₉ ClO ₂ |
| Formula weight | 302.78 |
| Temperature | 100.01(10) K |
| Wavelength | 1.54184 Å |
| Crystal system | monoclinic |
| Space group | P2 ₁ /n |
| Unit cell dimensions | a= 10.9261(3) Å, α= 90.00° |
| | b= 10.6284(3) Å, β= 90.813(3) ° |
| | c= 12.9254(4) Å, γ= 90.00° |
| Density (calculated) | 1.340 Mg/m ³ |
| Absorption coefficient | 2260 mm ⁻¹ |
| F(000) | 640.0 |
| Crystal size | 0.13 × 0.12 × 0.11 mm |
| Theta range for data collection | 10.528 to 148.364 deg. |
| Index ranges | -12 ≤ h ≤ 13, -10 ≤ k ≤ 13, -10 ≤ l ≤ 16 |
| Reflections collected | 6356 |
| Independent reflections | 2939 |
| Completeness to theta = 29.55° | 99.88% |
| Absorption correction | multi-scan |
| Refinement method | Full-matrix least-squares on F ² |
| Data/restraints/parameters | 2939 / 0 / 192 |
| Goodness-of-fit on F ² | 1.042 |
| Final R indices [I>2sigma(I)] | R1 = 0.0561, wR2 = 0.1542 |
| R indices (all data) | R1 = 0.0590, wR2 = 0.1588 |

NMR Spectra for All the Products

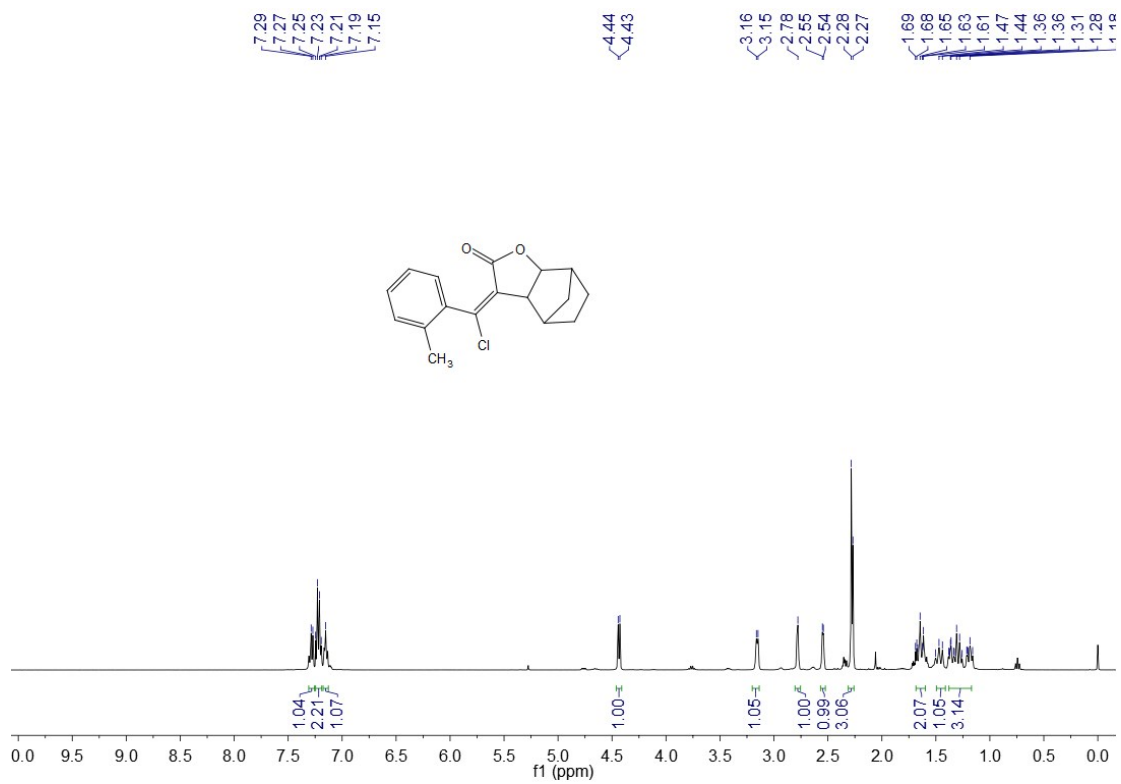
^1H NMR of Compound **3a**



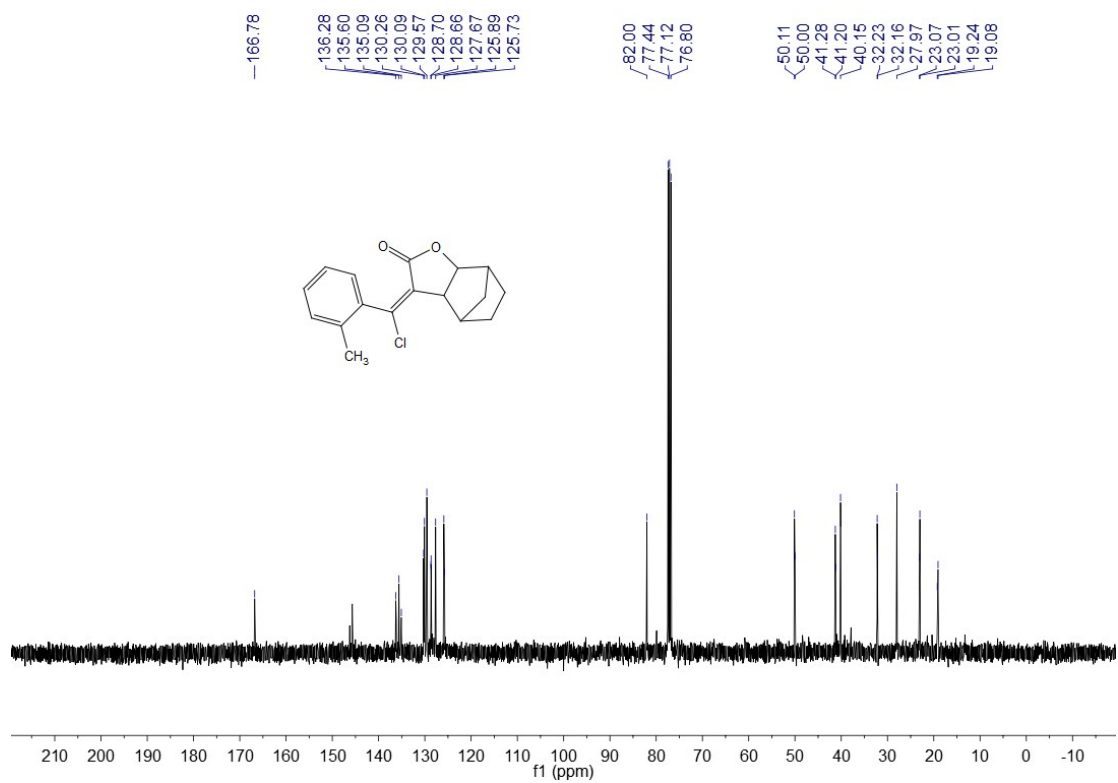
^{13}C NMR of Compound **3a**



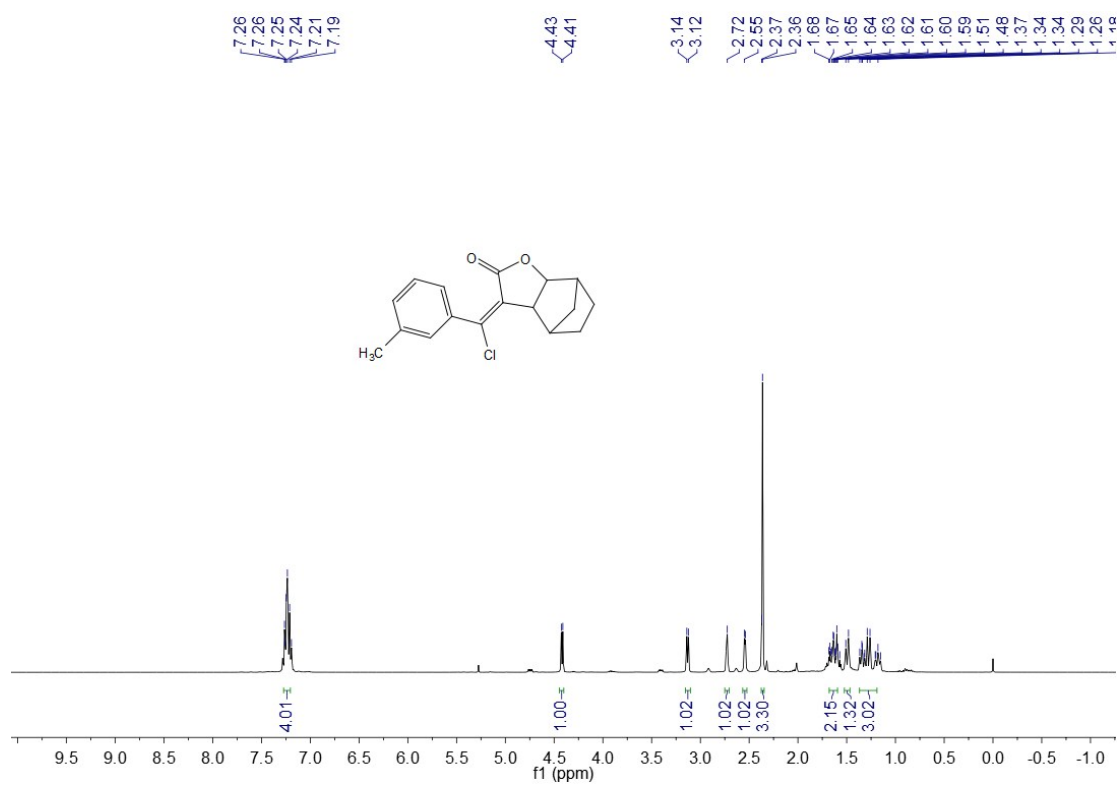
¹H NMR of Compound 3b



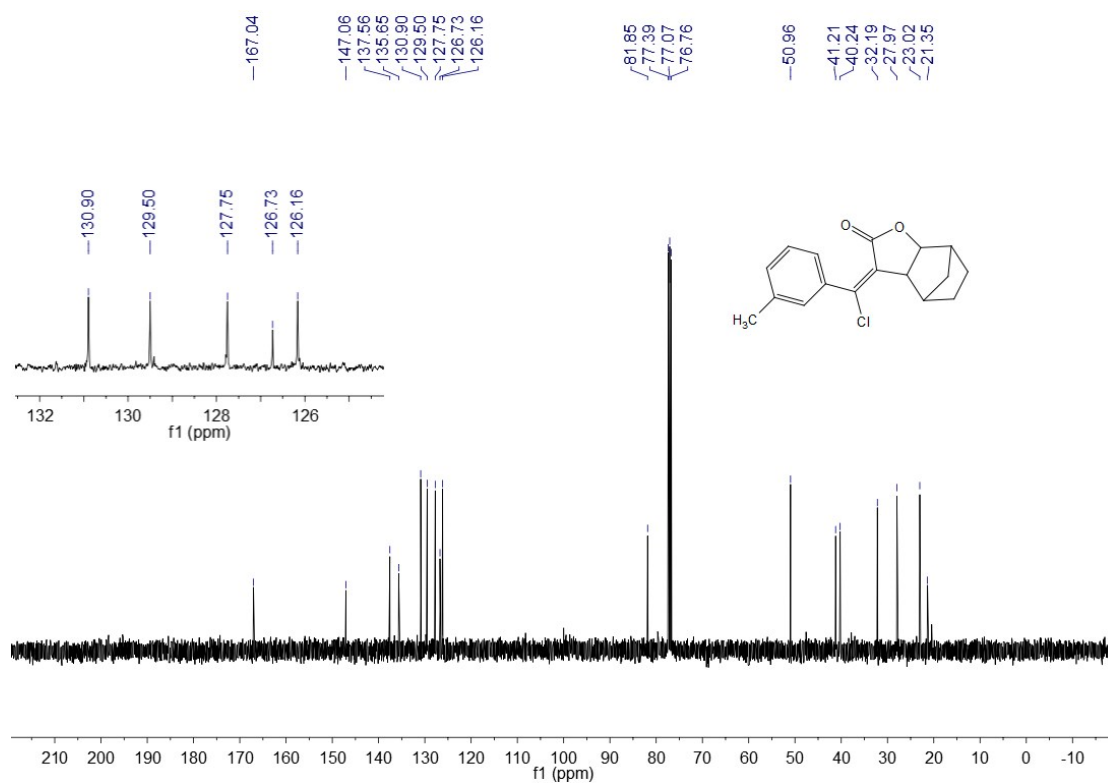
¹³C NMR of Compound 3b



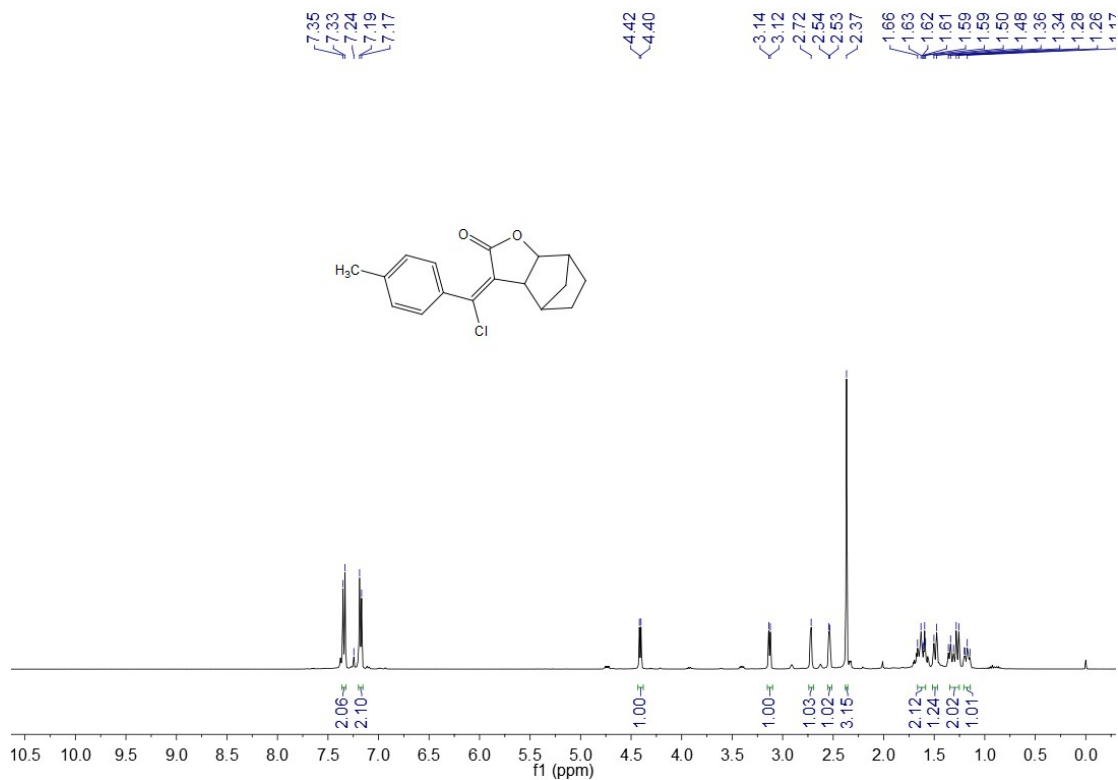
¹H NMR of Compound 3c



¹³C NMR of Compound **3c**



¹H NMR of Compound **3d**



Chemical structure of 2-(4-methylphenyl)-2-chloro-2H-chromene is shown above the spectrum.

Chemical structure of 2-(4-methylphenyl)-2-chloro-2H-chromene is shown above the spectrum.

Peak list (ppm):

- 167.15
- 147.20
- 140.42
- 132.78
- 129.08
- 128.56
- 126.36
- 81.82
- 77.41
- 77.10
- 76.78
- 51.08
- 41.22
- 40.28
- 32.19
- 27.97
- 23.03
- 21.51

Chemical structure of compound 10: CC1=CC=C(C(=C1)C(=C2C3C4C5C6C7C8C9C10C11C12C13C14C15C16C17C18C19C20C21C22C23C24C25C26C27C28C29C30C31C32C33C34C35C36C37C38C39C40C41C42C43C44C45C46C47C48C49C50C51C52C53C54C55C56C57C58C59C60C61C62C63C64C65C66C67C68C69C70C71C72C73C74C75C76C77C78C79C80C81C82C83C84C85C86C87C88C89C90C91C92C93C94C95C96C97C98C99C100C101C102C103C104C105C106C107C108C109C110C111C112C113C114C115C116C117C118C119C120C121C122C123C124C125C126C127C128C129C130C131C132C133C134C135C136C137C138C139C140C141C142C143C144C145C146C147C148C149C150C151C152C153C154C155C156C157C158C159C160C161C162C163C164C165C166C167C168C169C170C171C172C173C174C175C176C177C178C179C180C181C182C183C184C185C186C187C188C189C190C191C192C193C194C195C196C197C198C199C200C201C202C203C204C205C206C207C208C209C210C211C212C213C214C215C216C217C218C219C220C221C222C223C224C225C226C227C228C229C230C231C232C233C234C235C236C237C238C239C240C241C242C243C244C245C246C247C248C249C250C251C252C253C254C255C256C257C258C259C260C261C262C263C264C265C266C267C268C269C270C271C272C273C274C275C276C277C278C279C280C281C282C283C284C285C286C287C288C289C290C291C292C293C294C295C296C297C298C299C300C301C302C303C304C305C306C307C308C309C310C311C312C313C314C315C316C317C318C319C320C321C322C323C324C325C326C327C328C329C330C331C332C333C334C335C336C337C338C339C340C341C342C343C344C345C346C347C348C349C350C351C352C353C354C355C356C357C358C359C360C361C362C363C364C365C366C367C368C369C370C371C372C373C374C375C376C377C378C379C380C381C382C383C384C385C386C387C388C389C390C391C392C393C394C395C396C397C398C399C400C401C402C403C404C405C406C407C408C409C410C411C412C413C414C415C416C417C418C419C420C421C422C423C424C425C426C427C428C429C430C431C432C433C434C435C436C437C438C439C440C441C442C443C444C445C446C447C448C449C450C451C452C453C454C455C456C457C458C459C460C461C462C463C464C465C466C467C468C469C470C471C472C473C474C475C476C477C478C479C480C481C482C483C484C485C486C487C488C489C490C491C492C493C494C495C496C497C498C499C500C501C502C503C504C505C506C507C508C509C510C511C512C513C514C515C516C517C518C519C520C521C522C523C524C525C526C527C528C529C530C531C532C533C534C535C536C537C538C539C540C541C542C543C544C545C546C547C548C549C550C551C552C553C554C555C556C557C558C559C560C561C562C563C564C565C566C567C568C569C570C571C572C573C574C575C576C577C578C579C580C581C582C583C584C585C586C587C588C589C590C591C592C593C594C595C596C597C598C599C600C601C602C603C604C605C606C607C608C609C610C611C612C613C614C615C616C617C618C619C620C621C622C623C624C625C626C627C628C629C630C631C632C633C634C635C636C637C638C639C640C641C642C643C644C645C646C647C648C649C650C651C652C653C654C655C656C657C658C659C660C661C662C663C664C665C666C667C668C669C670C671C672C673C674C675C676C677C678C679C680C681C682C683C684C685C686C687C688C689C690C691C692C693C694C695C696C697C698C699C700C701C702C703C704C705C706C707C708C709C710C711C712C713C714C715C716C717C718C719C720C721C722C723C724C725C726C727C728C729C730C731C732C733C734C735C736C737C738C739C740C741C742C743C744C745C746C747C748C749C750C751C752C753C754C755C756C757C758C759C760C761C762C763C764C765C766C767C768C769C770C771C772C773C774C775C776C777C778C779C780C781C782C783C784C785C786C787C788C789C790C791C792C793C794C795C796C797C798C799C800C801C802C803C804C805C806C807C808C809C810C811C812C813C814C815C816C817C818C819C820C821C822C823C824C825C826C827C828C829C830C831C832C833C834C835C836C837C838C839C840C841C842C843C844C845C846C847C848C849C850C851C852C853C854C855C856C857C858C859C860C861C862C863C864C865C866C867C868C869C870C871C872C873C874C875C876C877C878C879C880C881C882C883C884C885C886C887C888C889C890C891C892C893C894C895C896C897C898C899C900C901C902C903C904C905C906C907C908C909C910C911C912C913C914C915C916C917C918C919C920C921C922C923C924C925C926C927C928C929C930C931C932C933C934C935C936C937C938C939C940C941C942C943C944C945C946C947C948C949C950C951C952C953C954C955C956C957C958C959C960C961C962C963C964C965C966C967C968C969C970C971C972C973C974C975C976C977C978C979C980C981C982C983C984C985C986C987C988C989C990C991C992C993C994C995C996C997C998C999C1000)C1=C2C(=C(C=C2)C(=C3C4C5C6C7C8C9C10C11C12C13C14C15C16C1

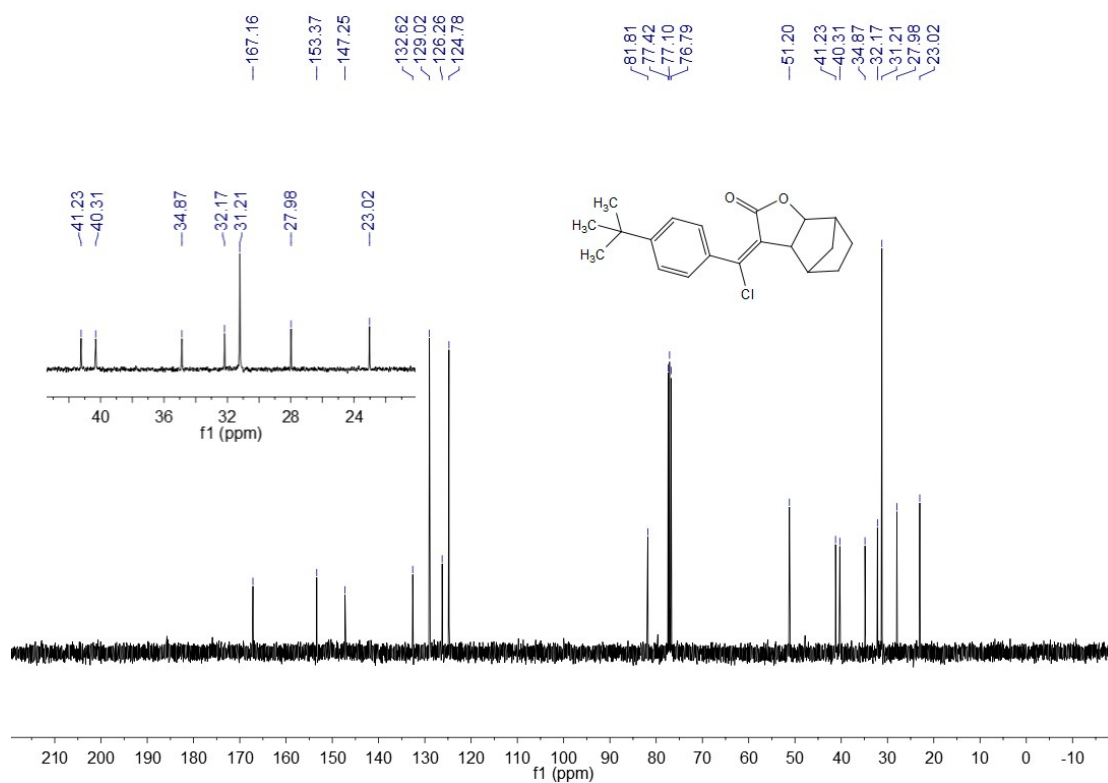
Chemical structure of 2-(4-(chloromethyl)phenyl)-2-chloro-1,3-dioxolane-5-carboxylic acid derivative (labeled 10) is shown above the corresponding ¹³C NMR spectrum. The spectrum displays peaks in the aromatic region (126.32–147.25 ppm), a carbonyl region (167.16 ppm), and an aliphatic region (15.10–41.82 ppm). The x-axis represents the chemical shift in ppm, ranging from -10 to 210.

Chemical structure of 10: ClC1=CC=C(C=C1)C(=C2C(=O)OC3CC2C3)C(=O)O

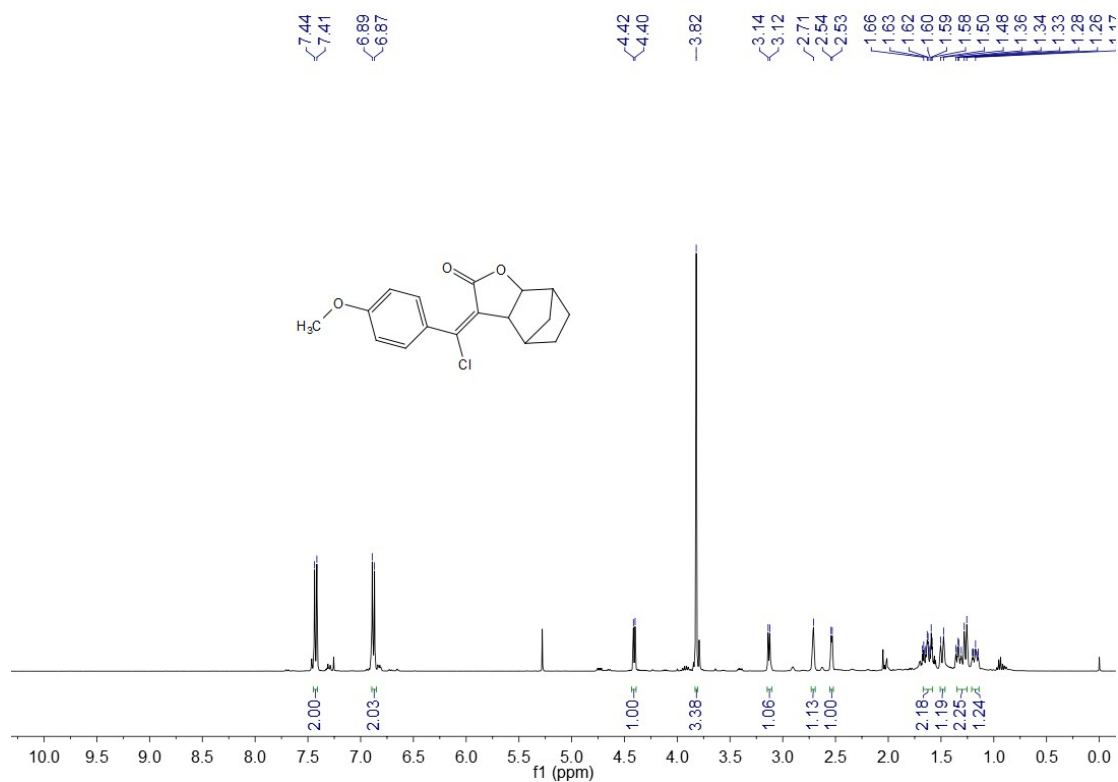
¹³C NMR peaks (ppm): 167.16, 147.25, 146.55, 132.95, 129.20, 127.38, 127.34, 126.32, 81.82, 77.45, 77.13, 76.81, 51.12, 41.23, 40.30, 32.19, 28.78, 27.97, 23.03, 15.10.

[illegible]

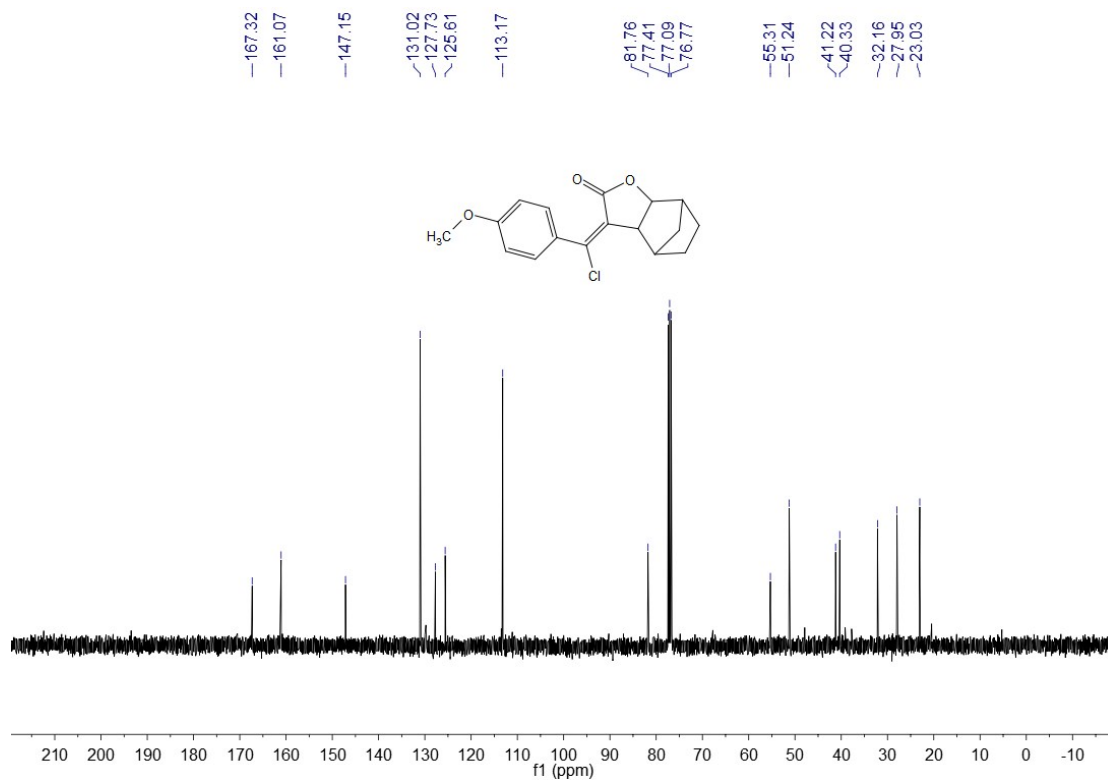
¹³C NMR of Compound **3f**



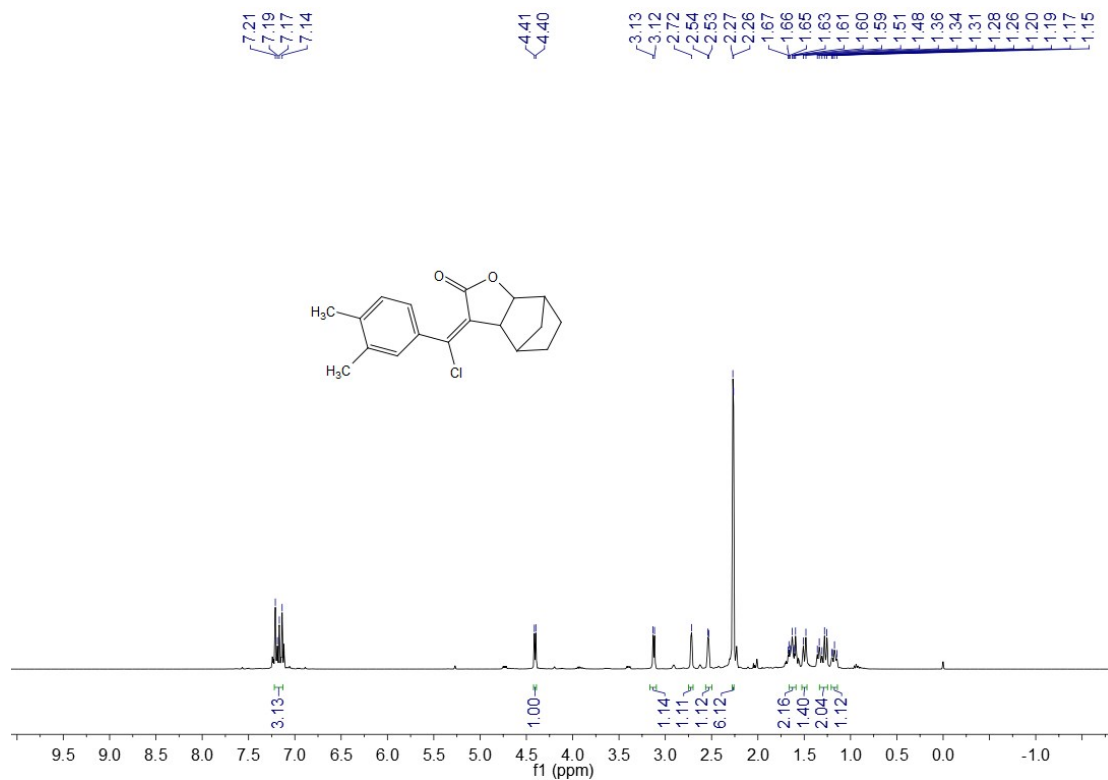
¹H NMR of Compound **3g**



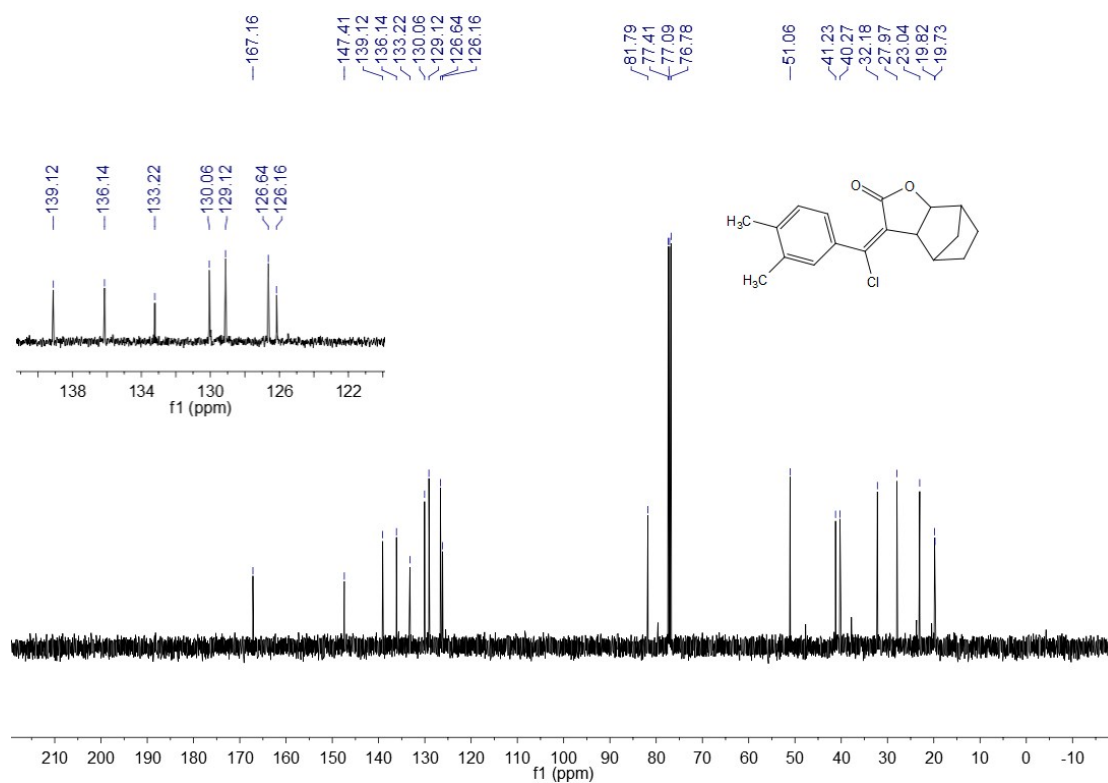
¹³C NMR of Compound **3g**



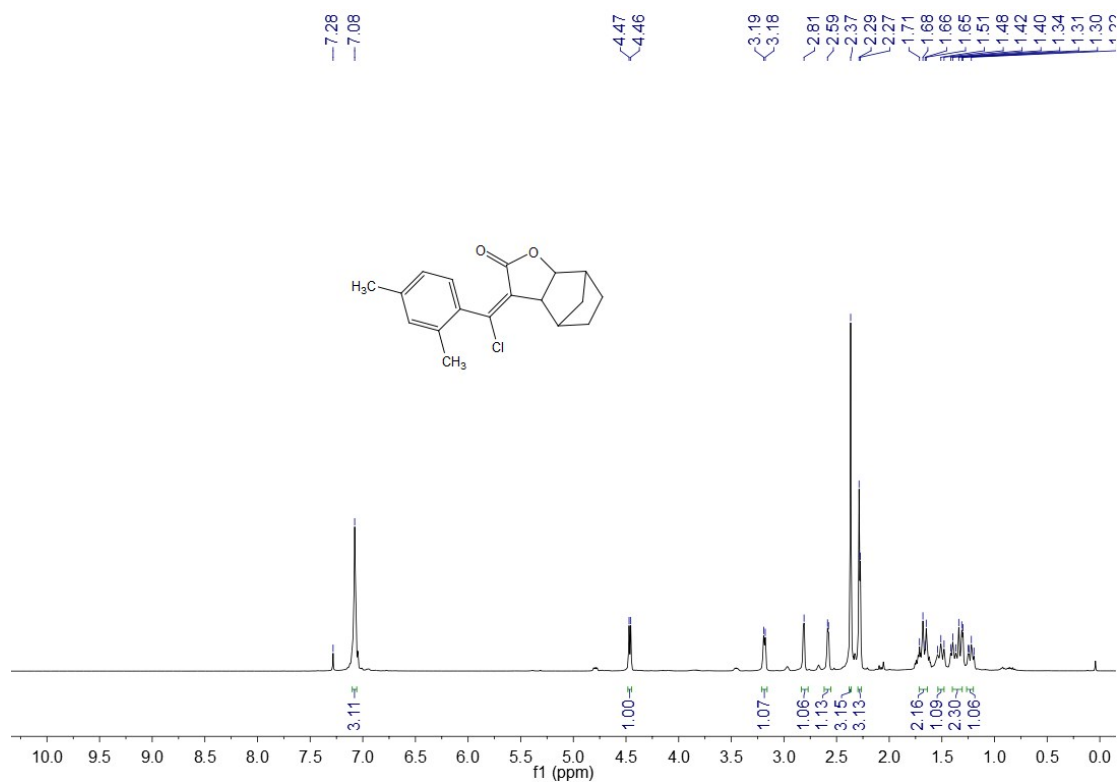
¹H NMR of Compound **3h**



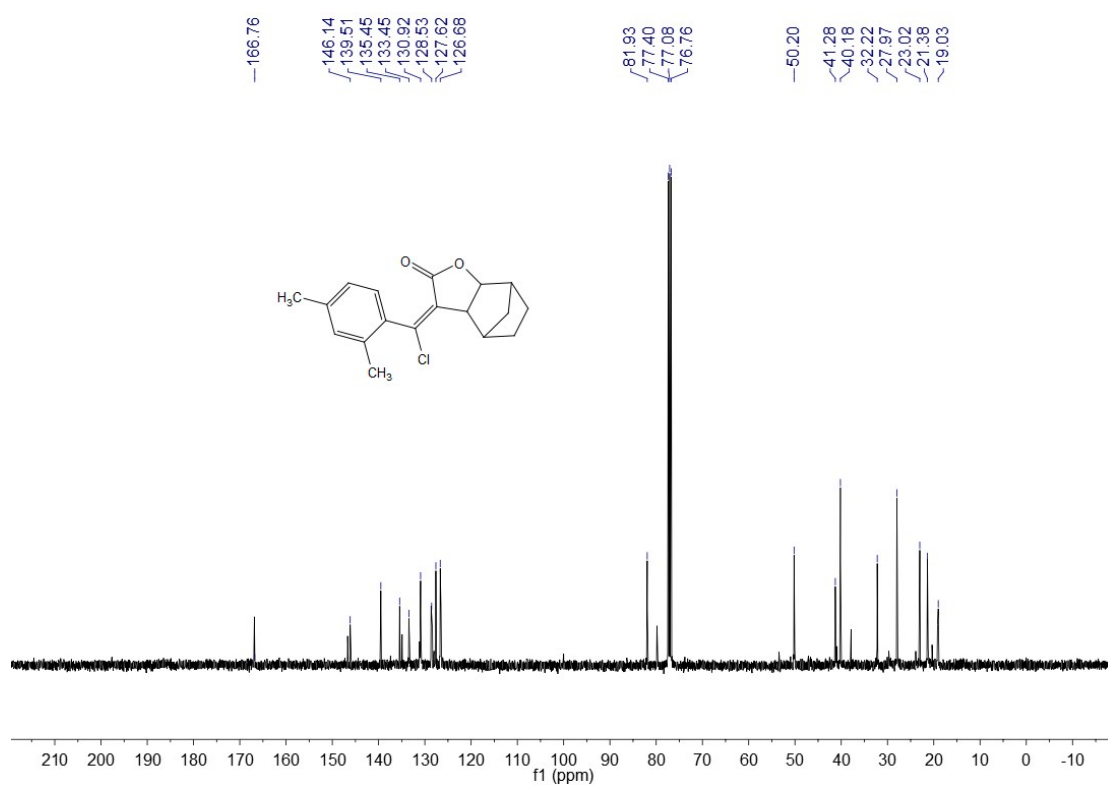
¹³C NMR of Compound **3h**



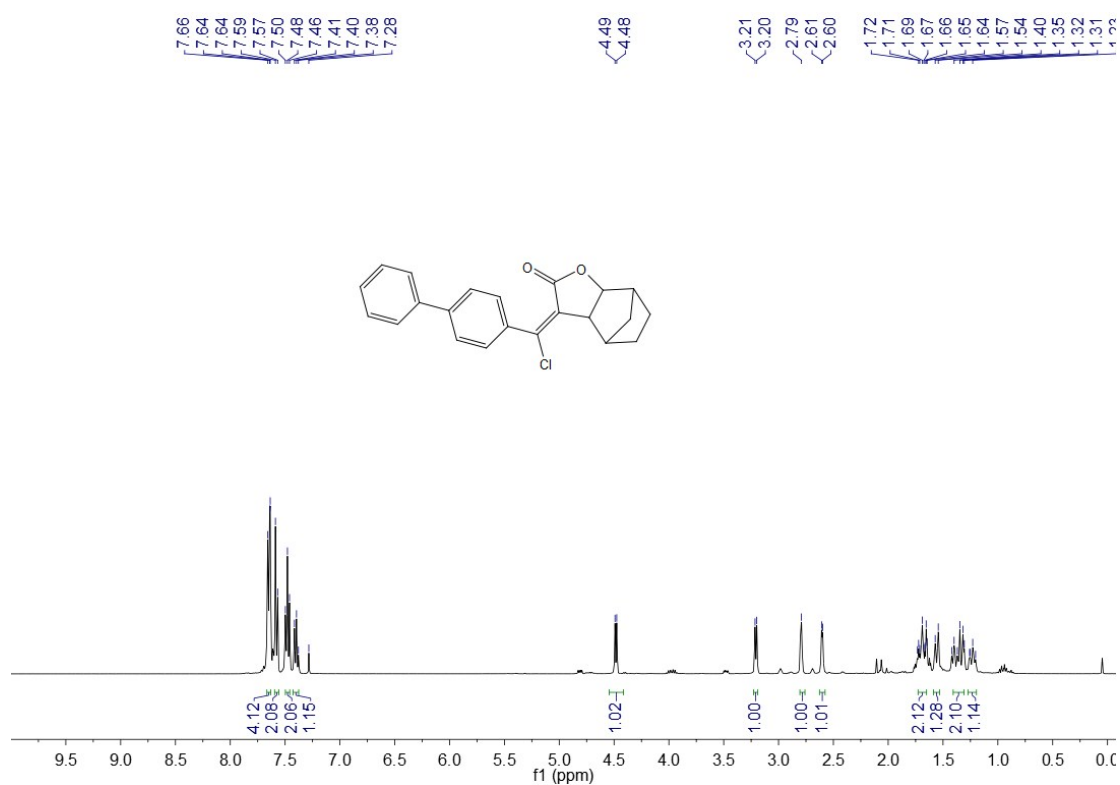
¹H NMR of Compound **3i**



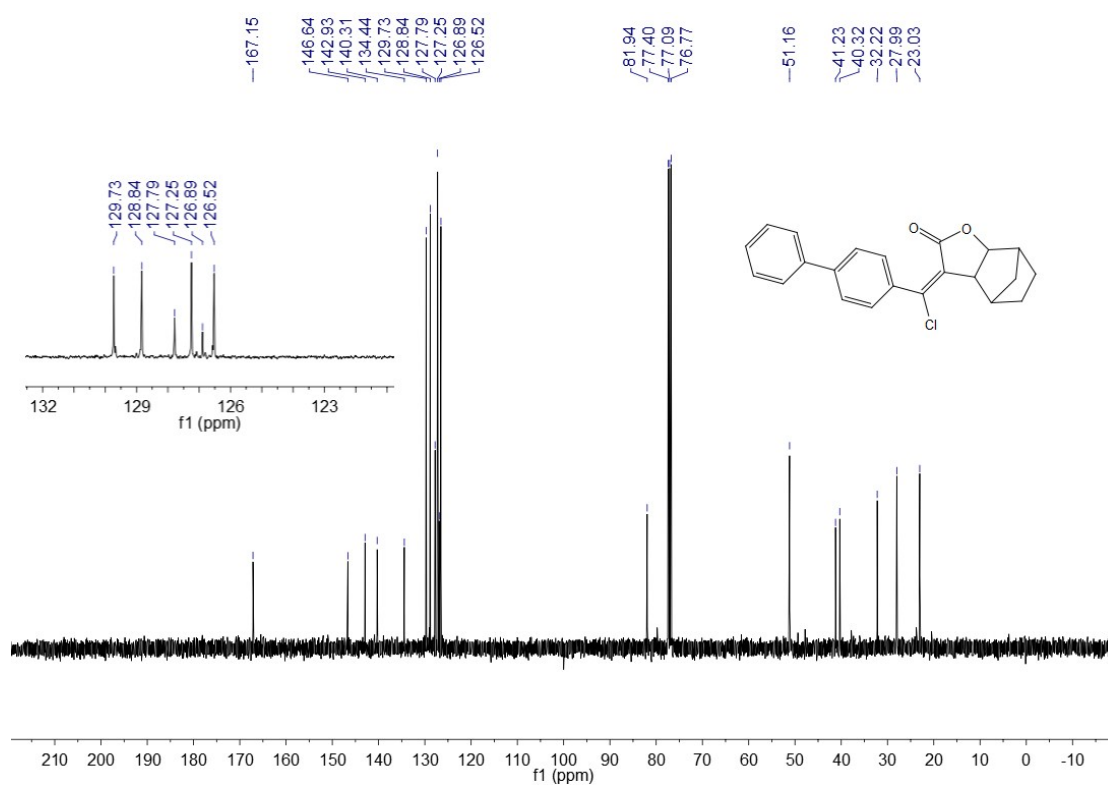
¹³C NMR of Compound **3i**



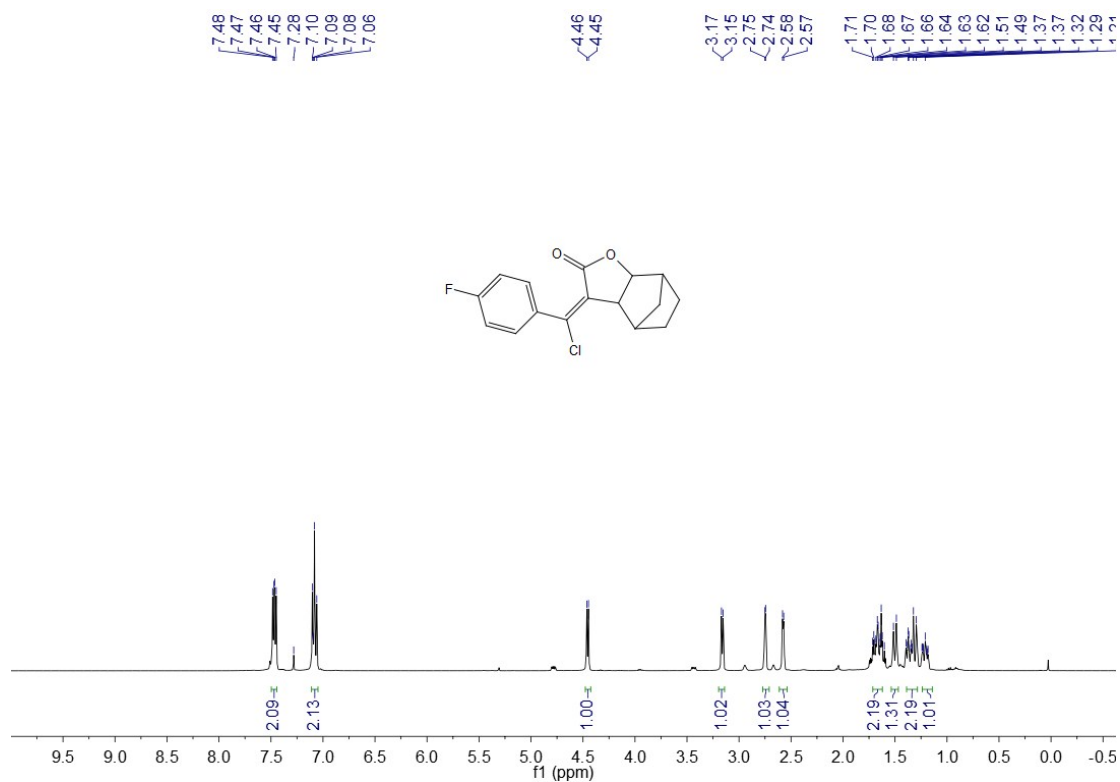
¹H NMR of Compound **3j**



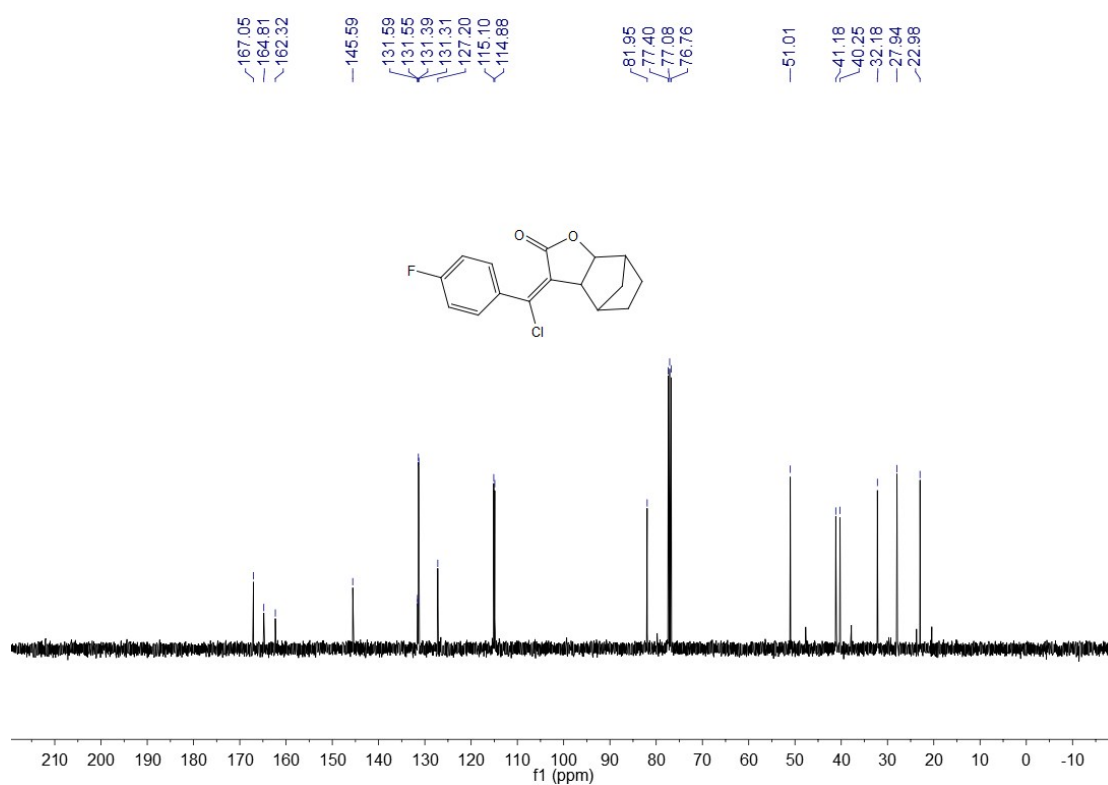
¹³C NMR of Compound **3j**



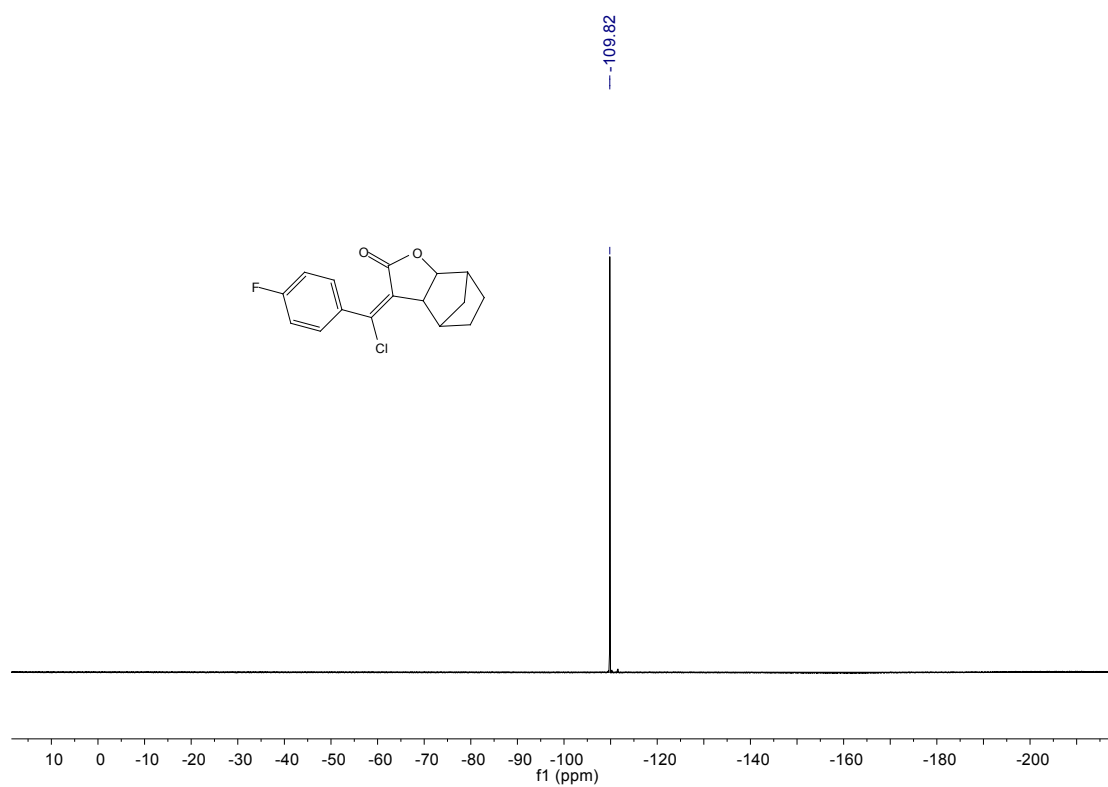
¹H NMR of Compound **3k**



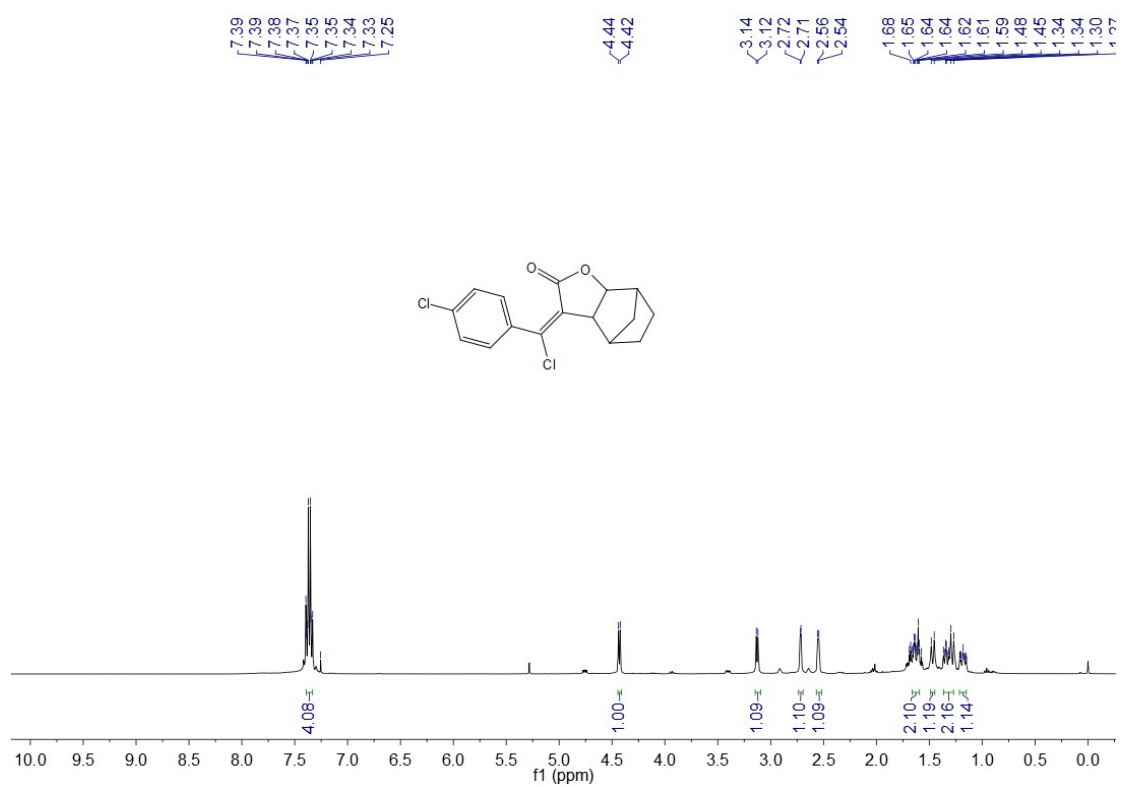
¹³C NMR of Compound **3k**



¹⁹F NMR of Compound **3k**



¹H NMR of Compound **3l**

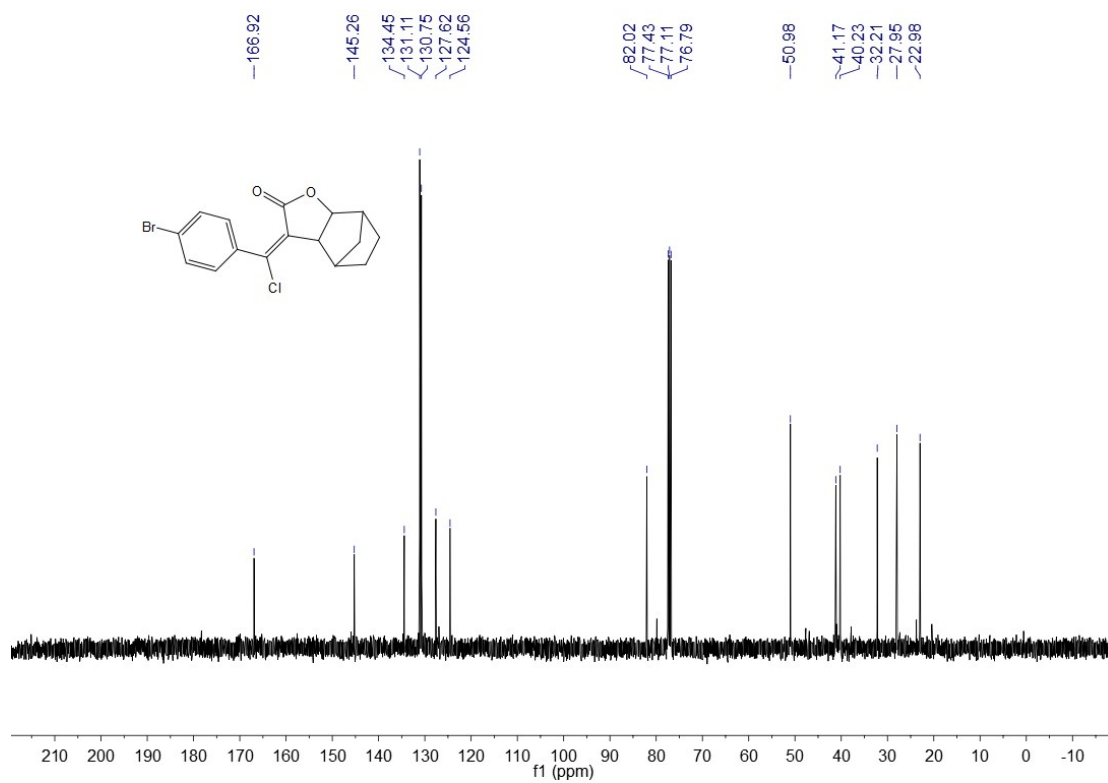


Chemical structure of compound 10 is shown. The ¹³C NMR spectrum (CDCl₃) shows peaks at the following chemical shifts (ppm): 166.95, 145.27, 136.17, 133.95, 130.55, 128.16, 127.57, 82.01, 77.41, 77.09, 76.77, 50.99, 41.17, 40.24, 32.21, 27.95, and 22.97.

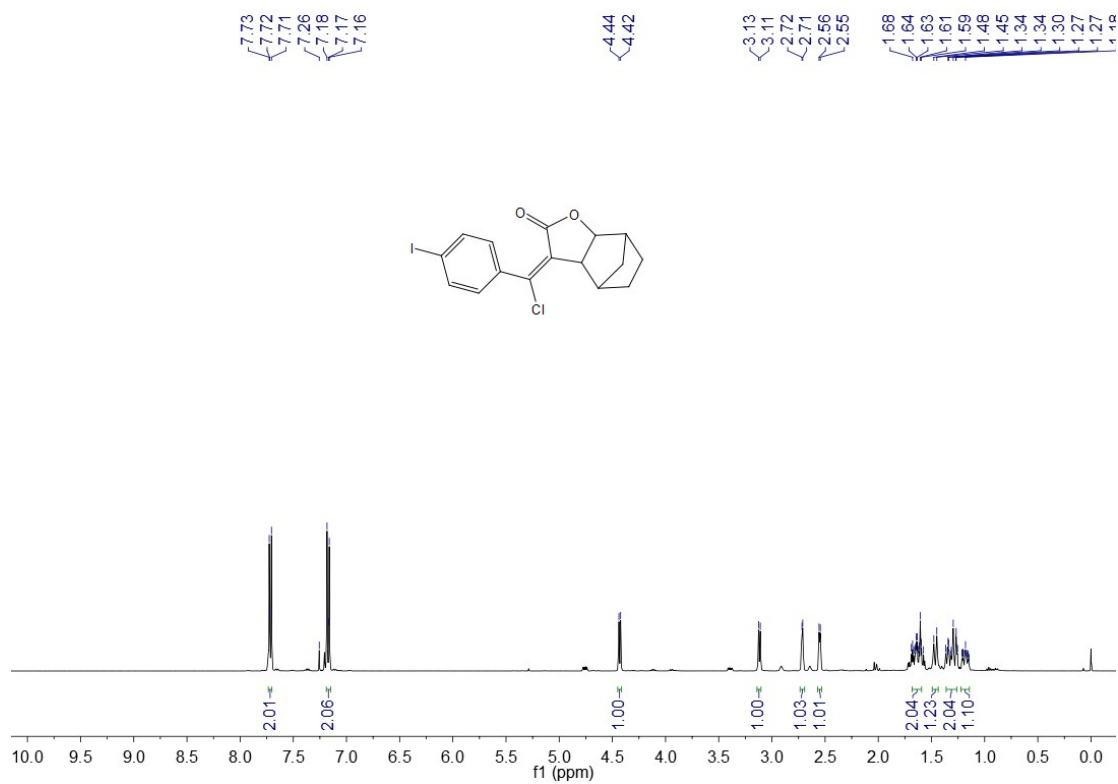
Chemical structure of compound 10 is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with integration values provided below the peaks.

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.51 | 2.18 |
| 7.49 | 2.14 |
| 7.32 | |
| 7.30 | |
| 7.25 | |
| 4.43 | 1.00 |
| 4.42 | |
| 3.13 | 1.00 |
| 3.11 | |
| 2.71 | 1.02 |
| 2.55 | 1.00 |
| 2.54 | |
| 1.67 | 2.05 |
| 1.64 | |
| 1.63 | 1.13 |
| 1.61 | |
| 1.60 | 2.12 |
| 1.59 | |
| 1.48 | 1.11 |
| 1.45 | |
| 1.36 | |
| 1.34 | |
| 1.31 | |
| 1.29 | |
| 1.26 | |
| 1.15 | |

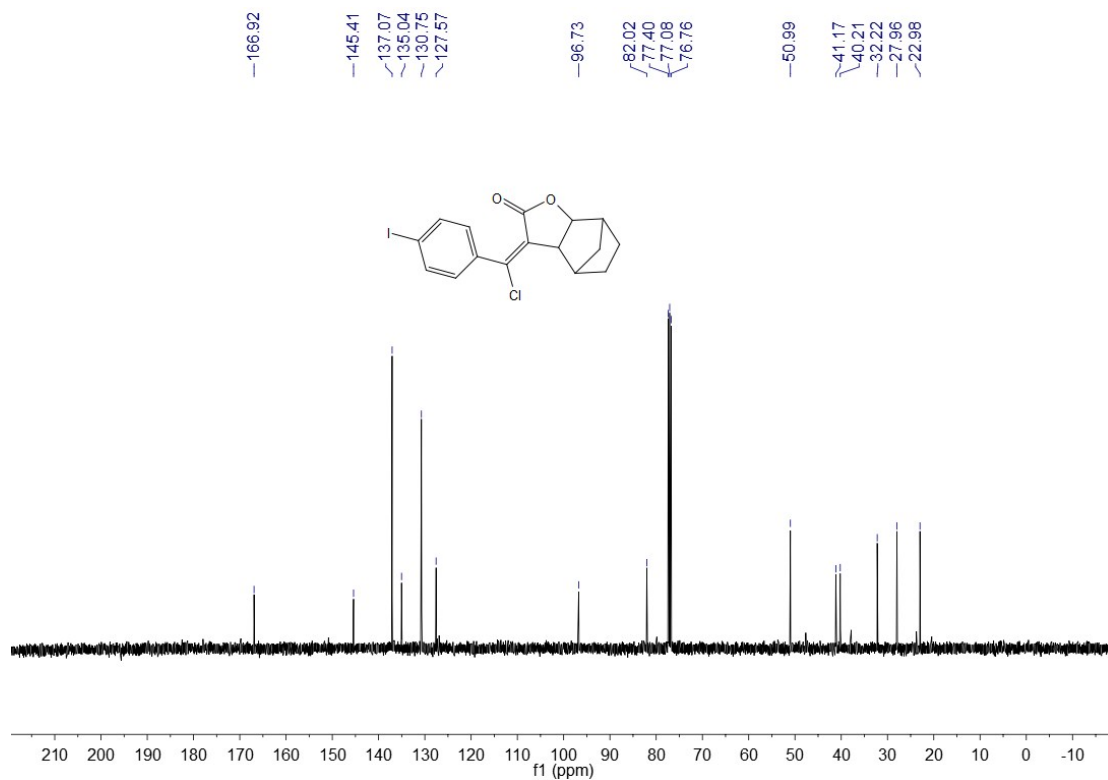
¹³C NMR of Compound **3m**



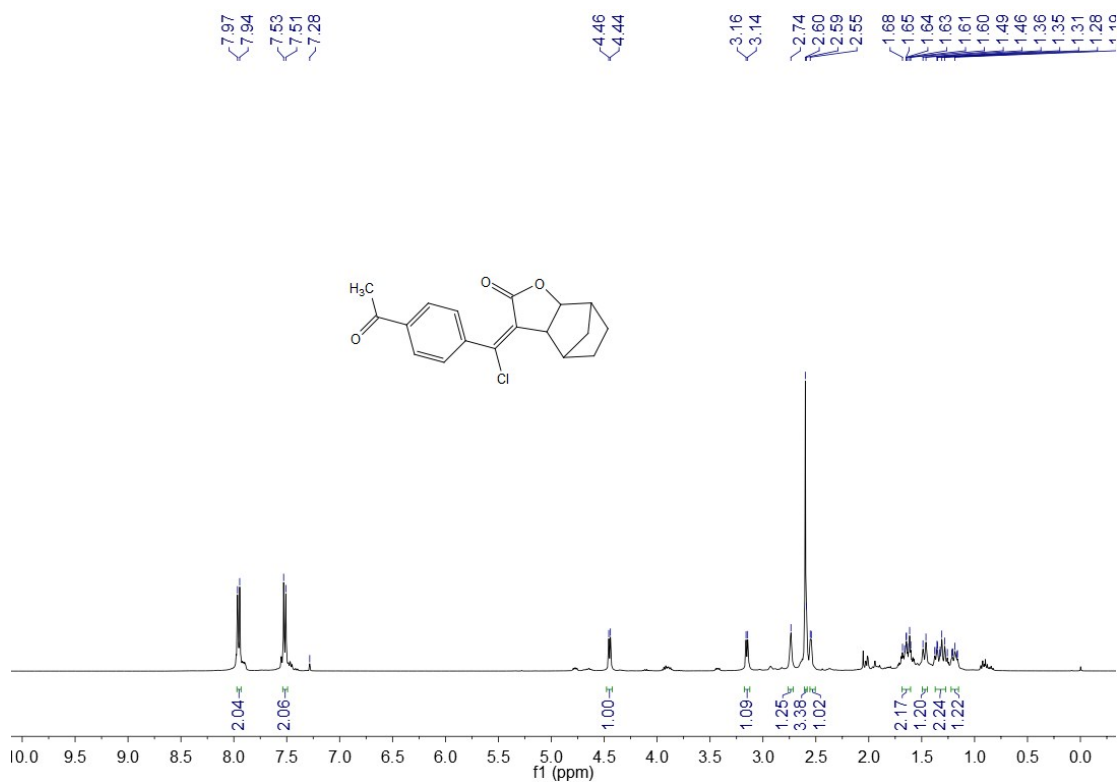
¹H NMR of Compound **3n**



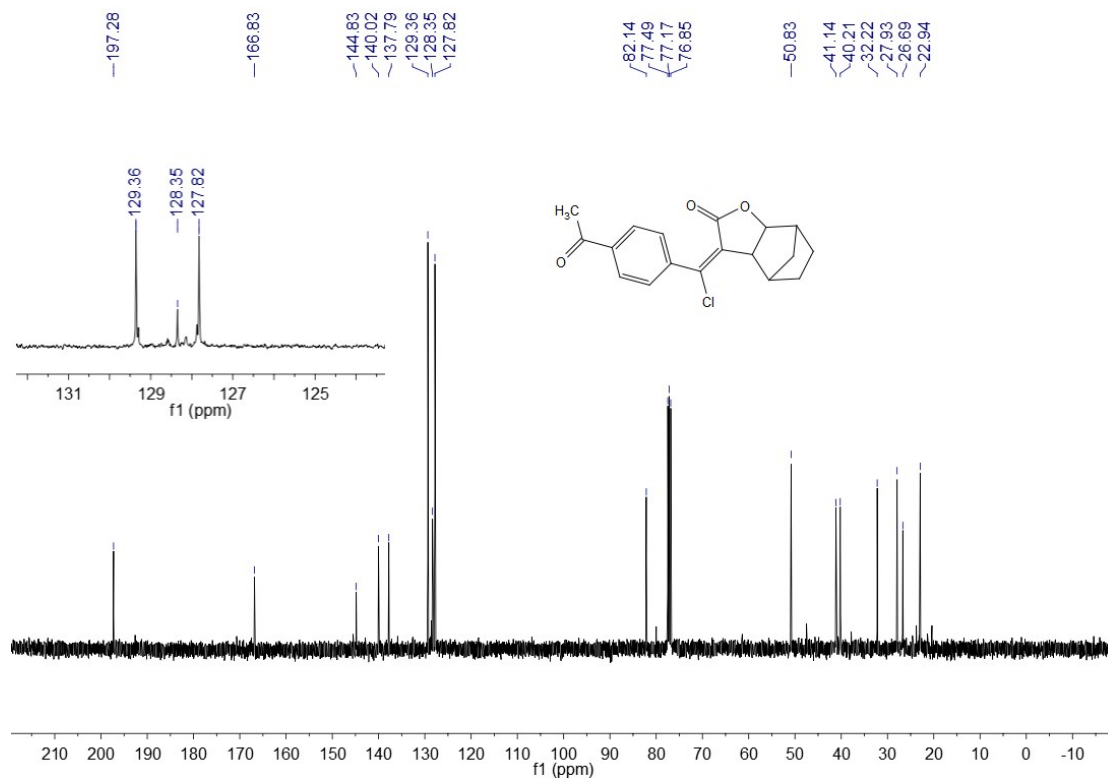
¹³C NMR of Compound **3n**



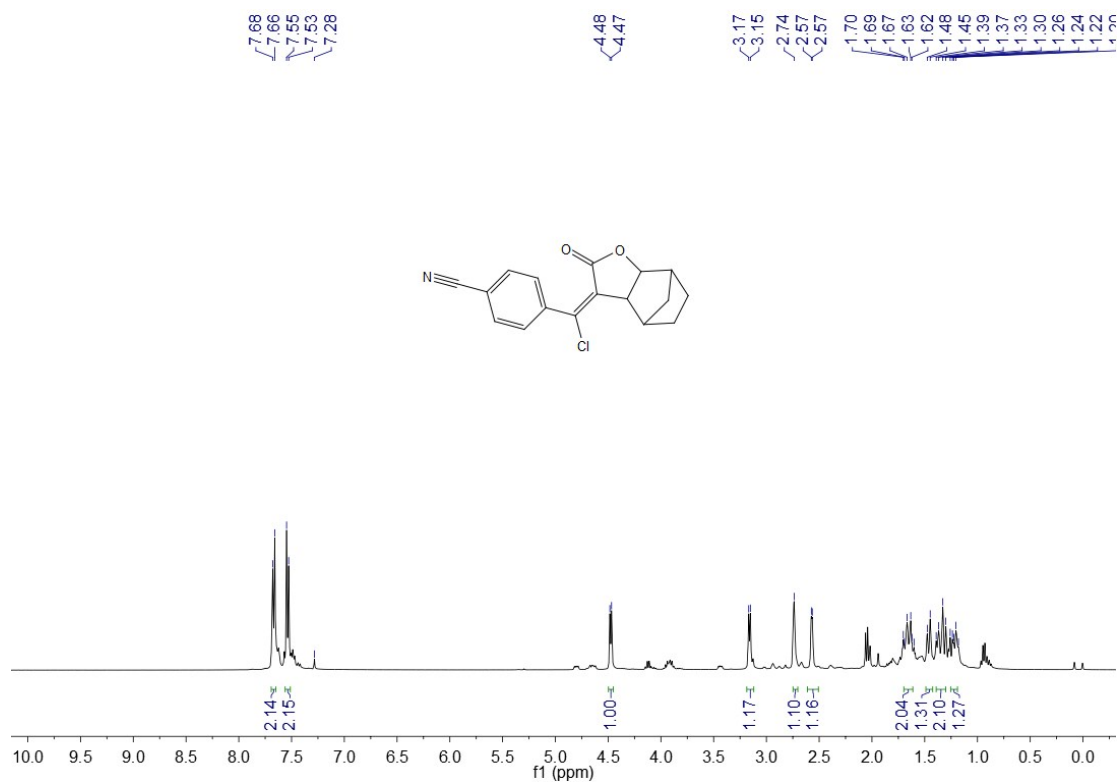
¹H NMR of Compound **3o**



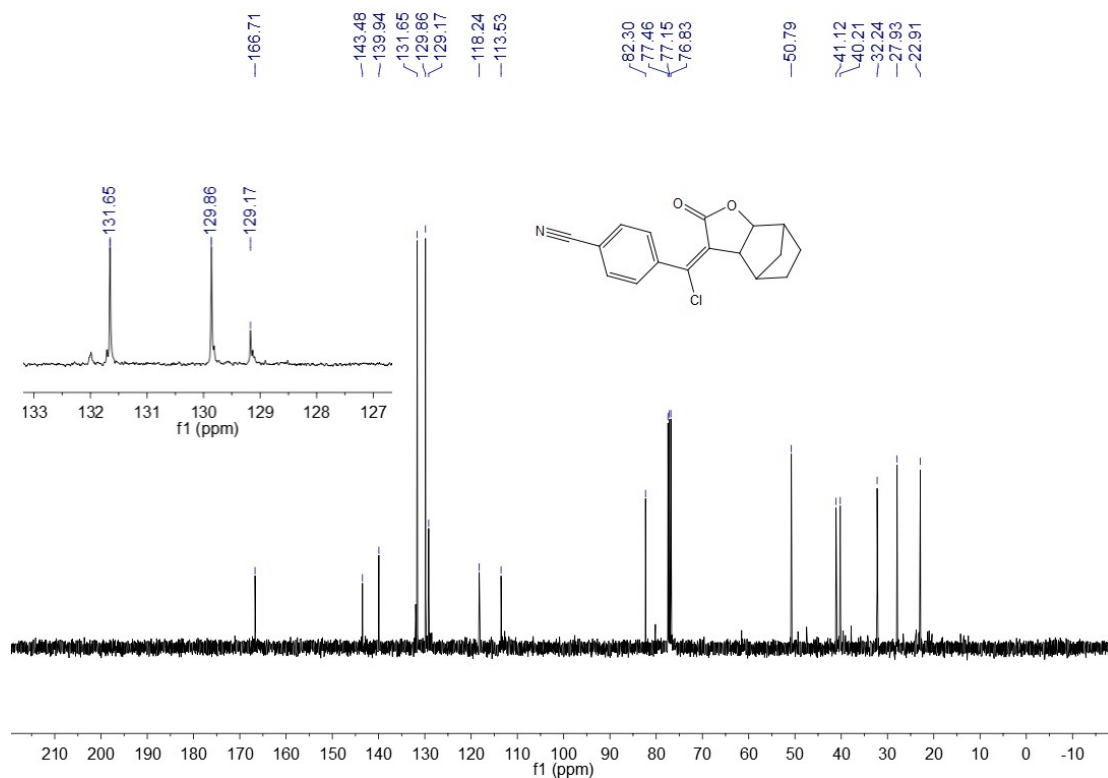
¹³C NMR of Compound **3o**



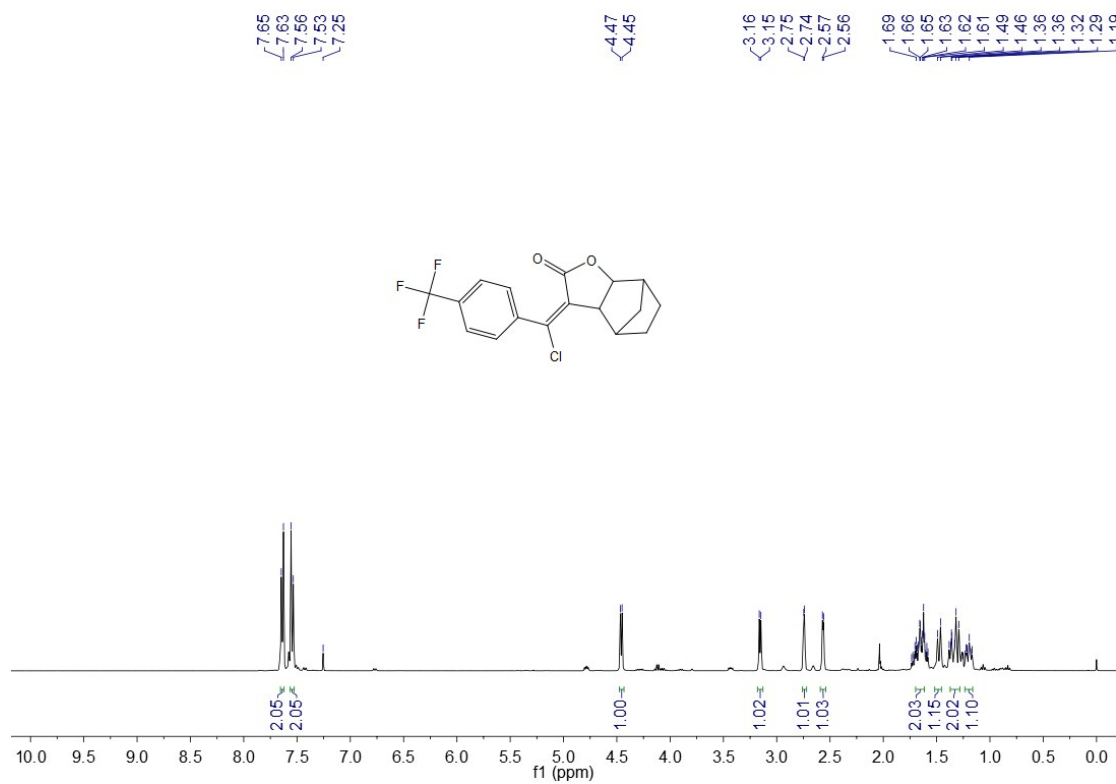
¹H NMR of Compound **3p**



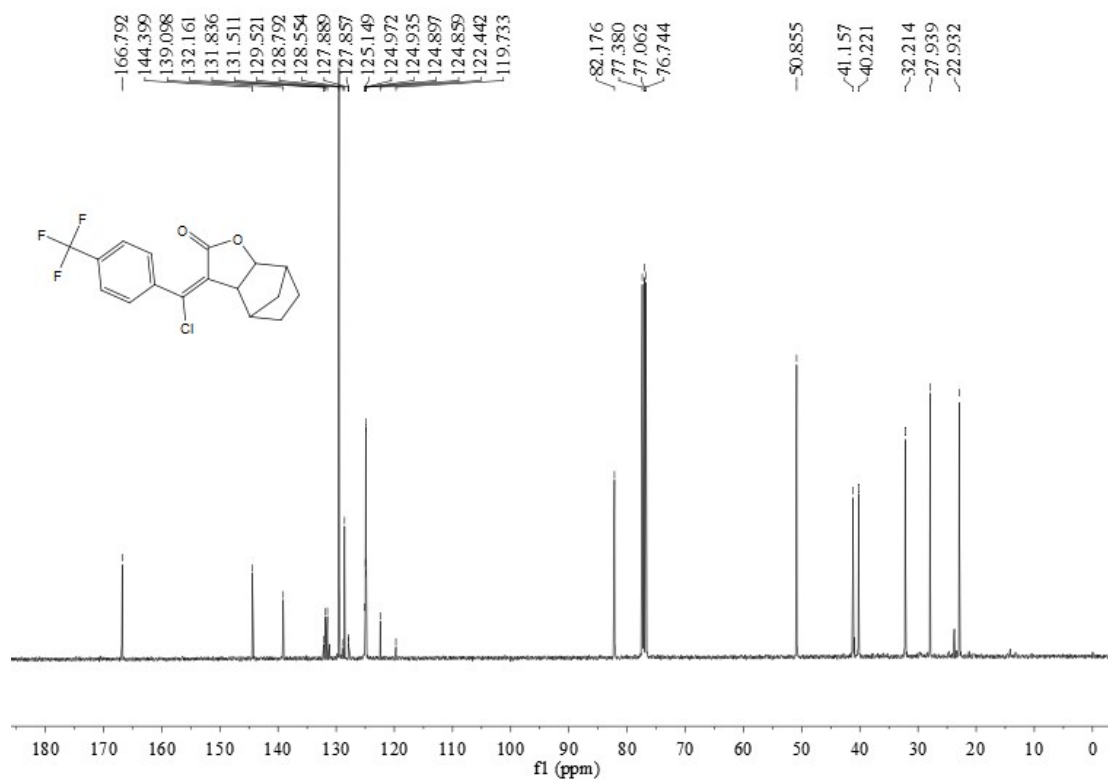
¹³C NMR of Compound **3p**



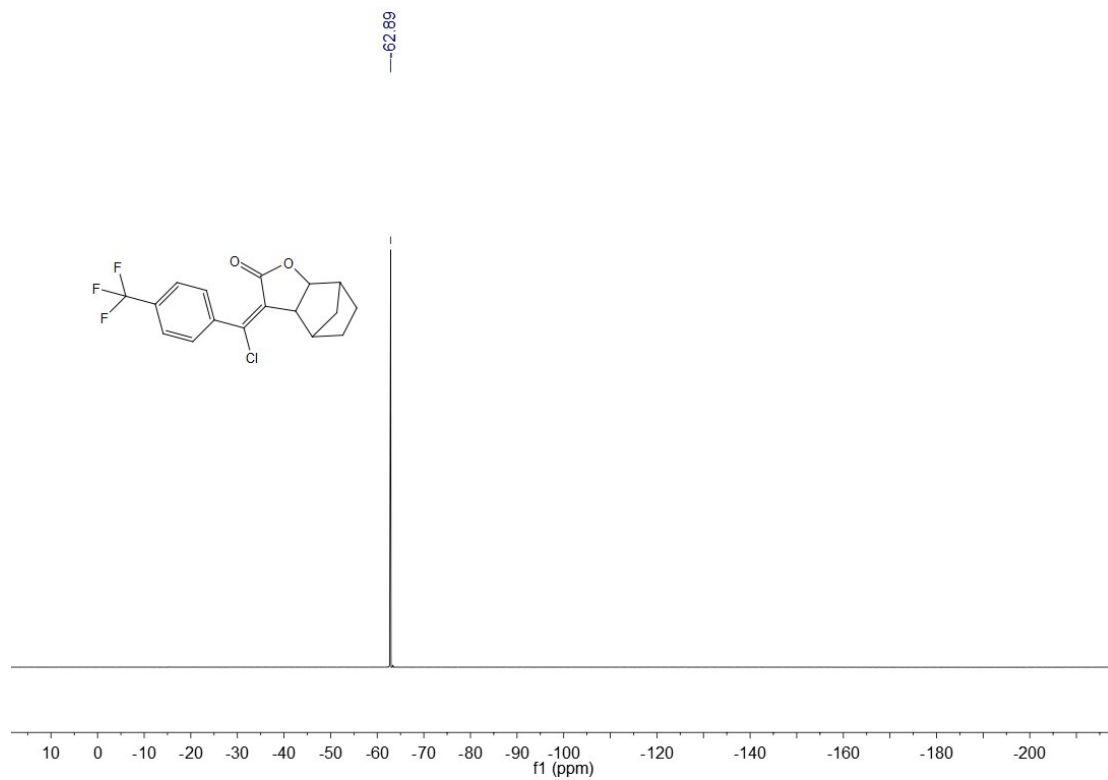
¹H NMR of Compound **3q**



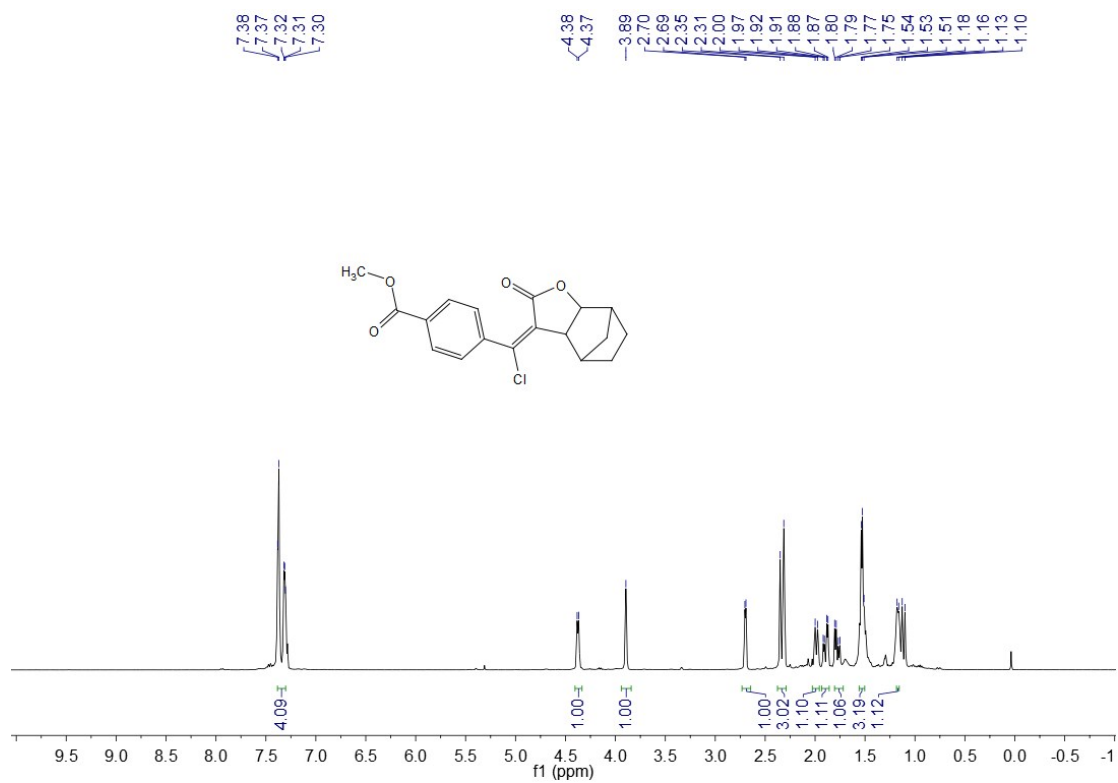
¹³C NMR of Compound **3q**



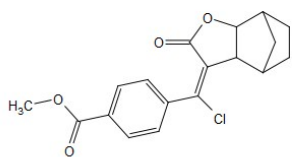
¹⁹F NMR of Compound **3q**



¹H NMR of Compound **3r**



¹³C NMR of Compound **3r**

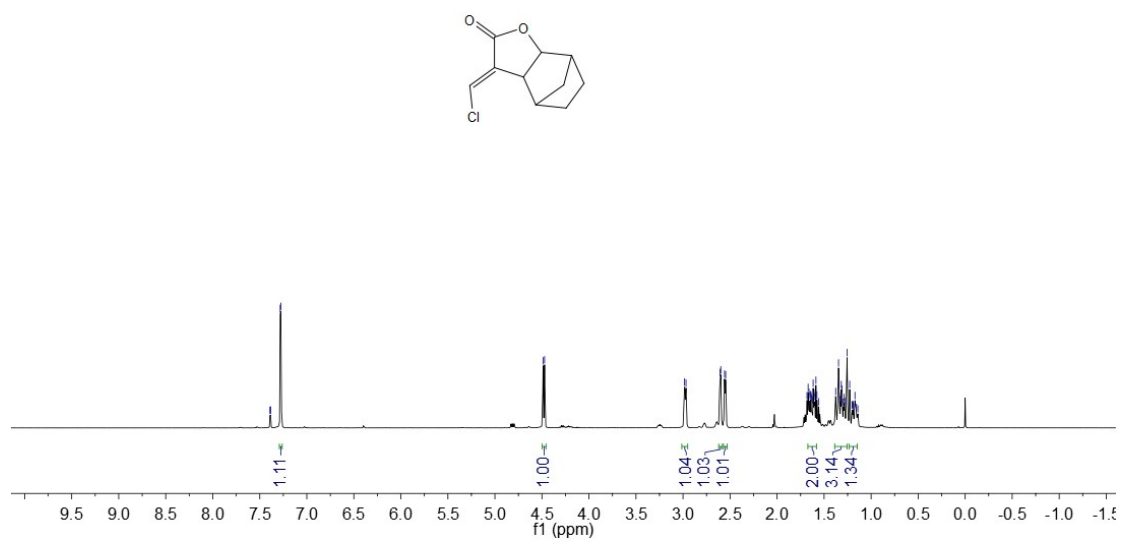


7.39
7.38
7.28
7.28

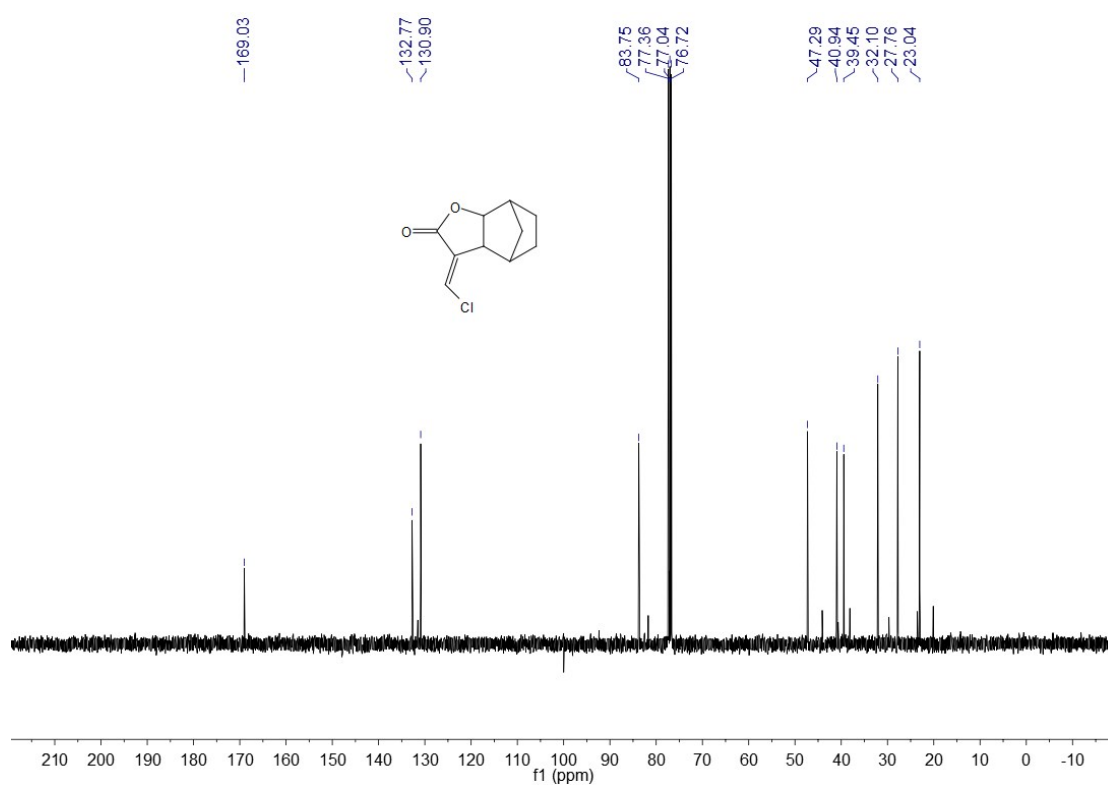
4.49
4.47

2.98
2.97
2.61
2.60
2.56
2.55

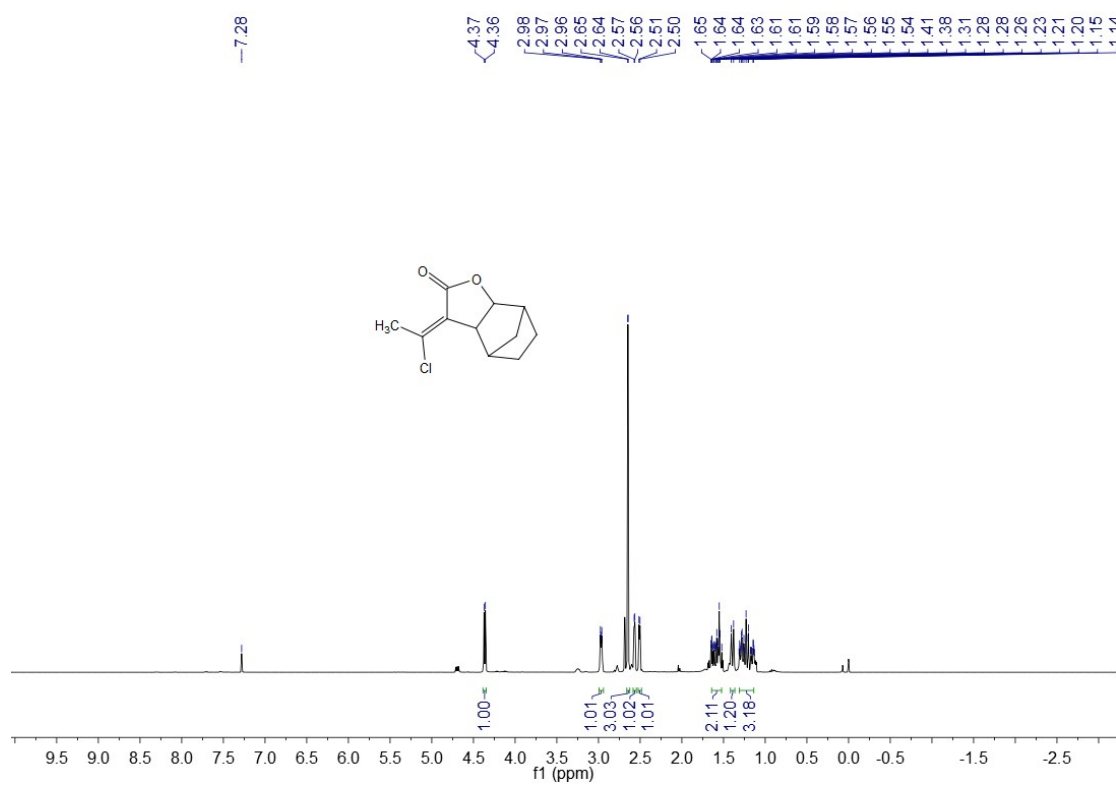
1.68
1.67
1.66
1.65
1.64
1.64
1.62
1.61
1.59
1.58
1.38
1.35
1.34
1.34
1.31
1.31
1.26
1.23
1.17



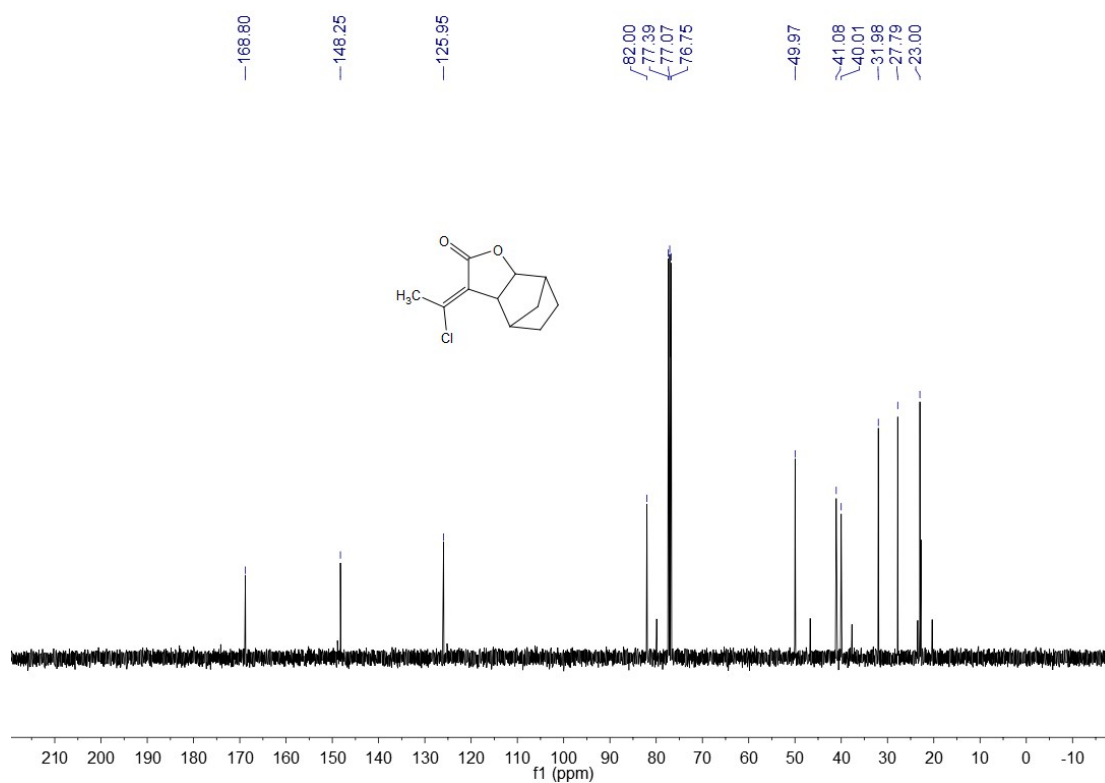
¹³C NMR of Compound **3s**



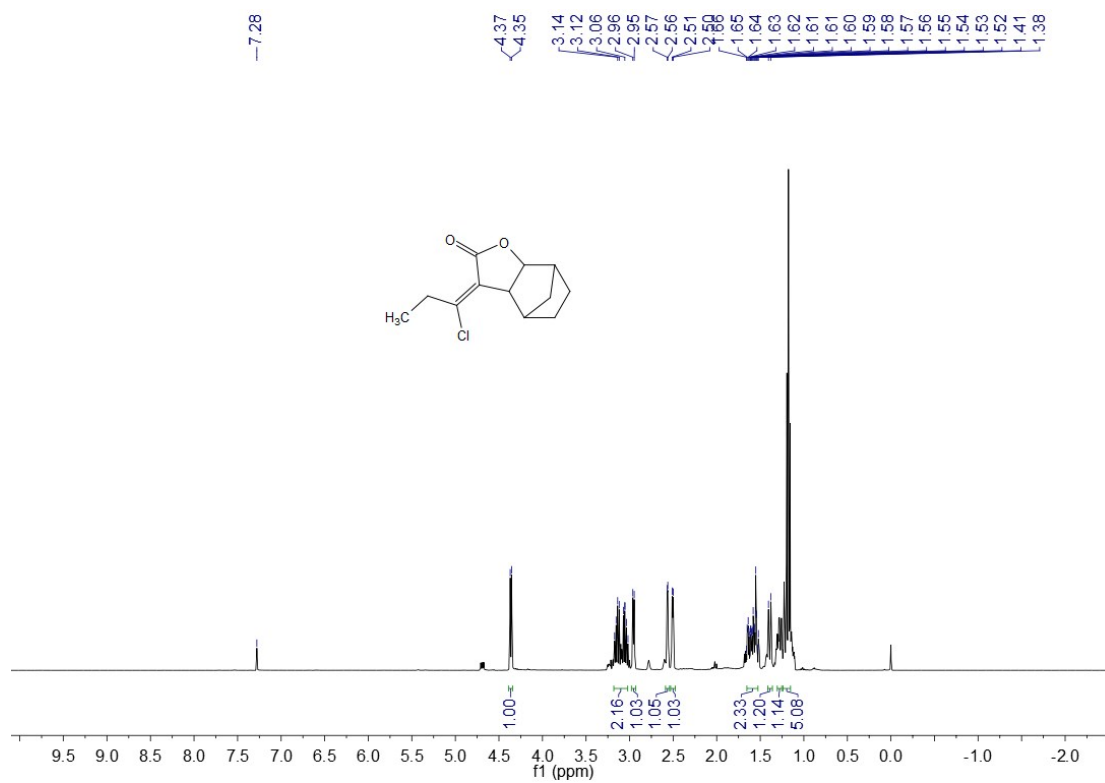
¹H NMR of Compound **3t**



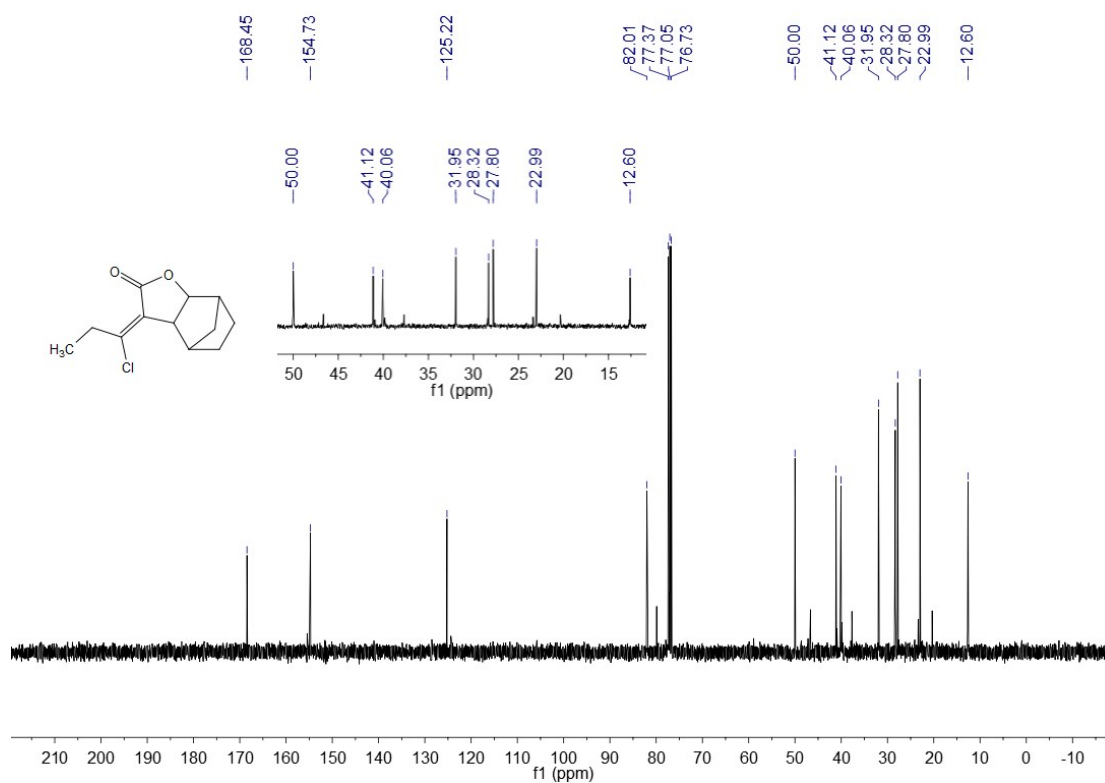
¹³C NMR of Compound **3t**



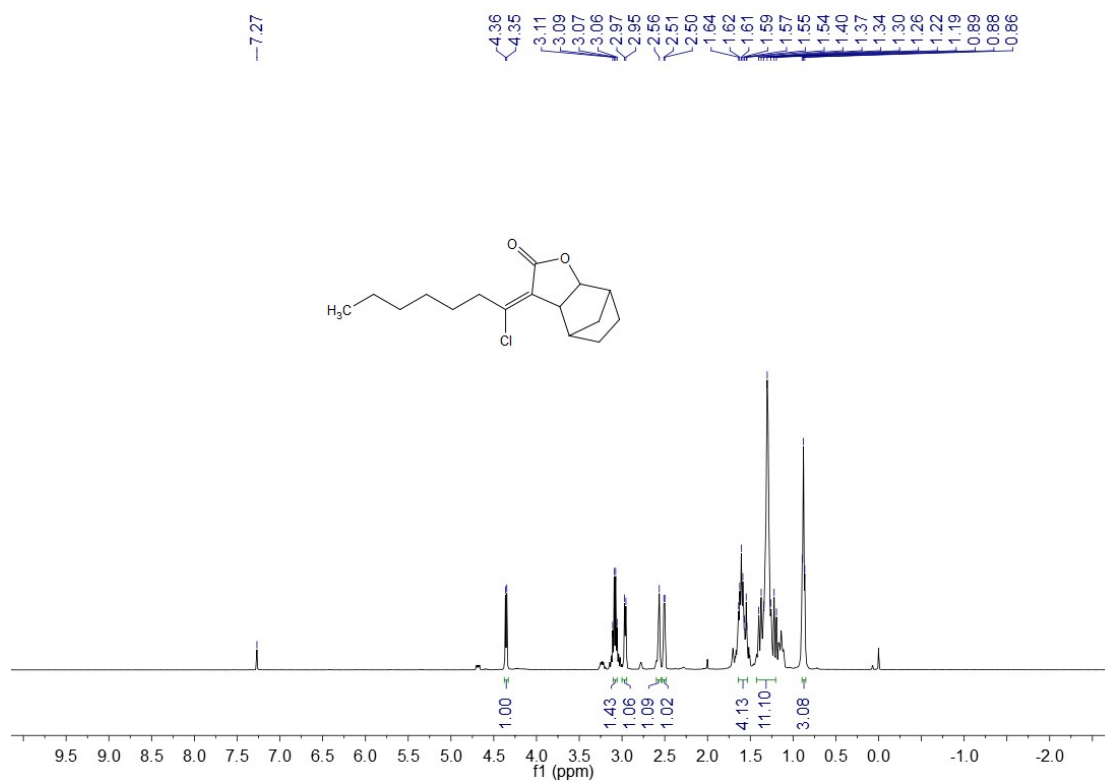
¹H NMR of Compound **3u**



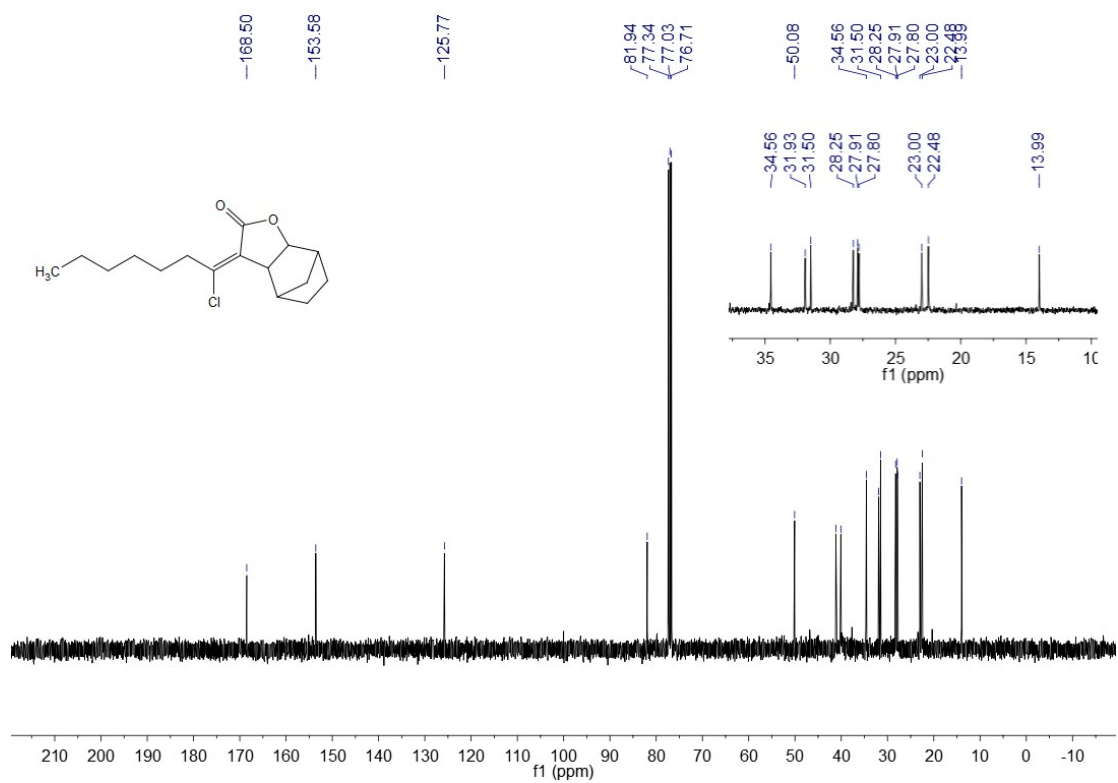
¹³C NMR of Compound **3u**



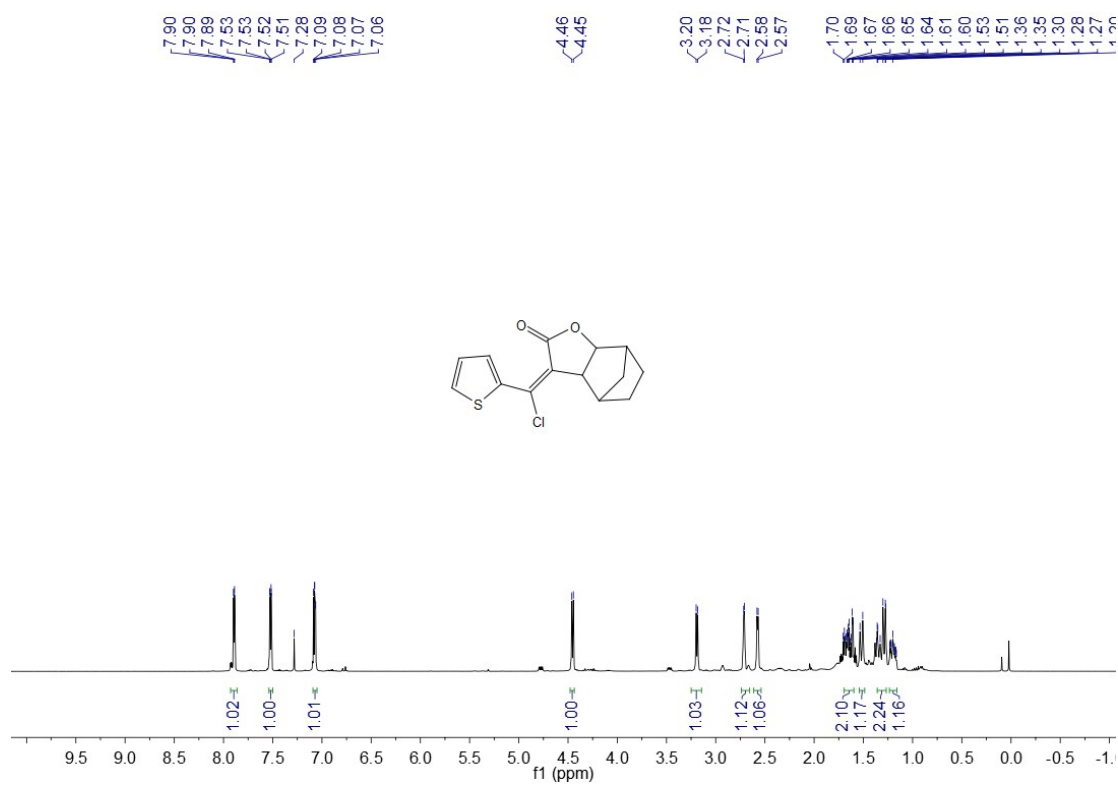
¹H NMR of Compound **3v**



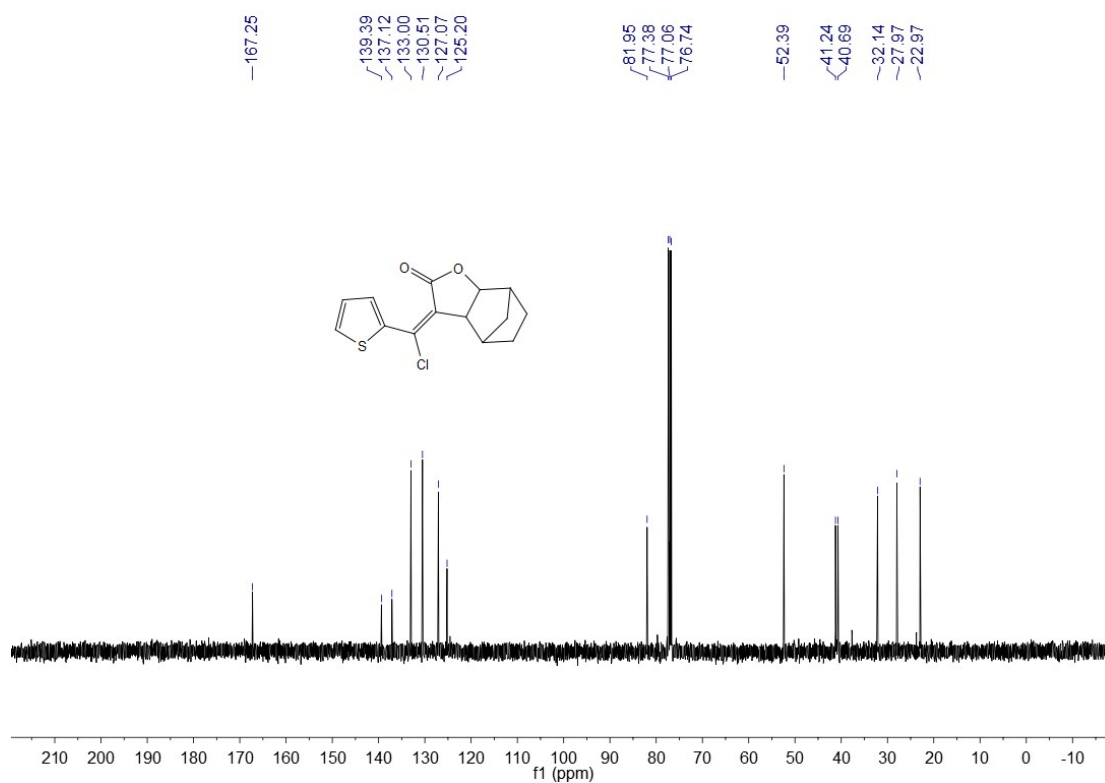
¹³C NMR of Compound **3v**



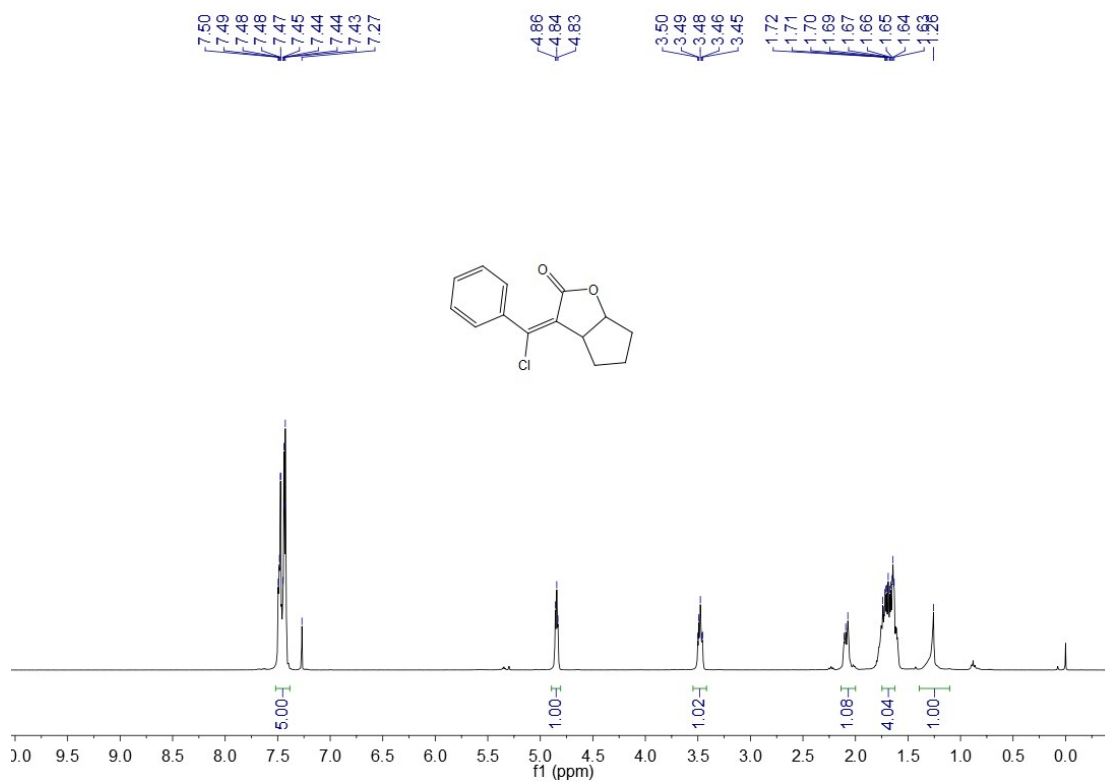
¹H NMR of Compound **3w**



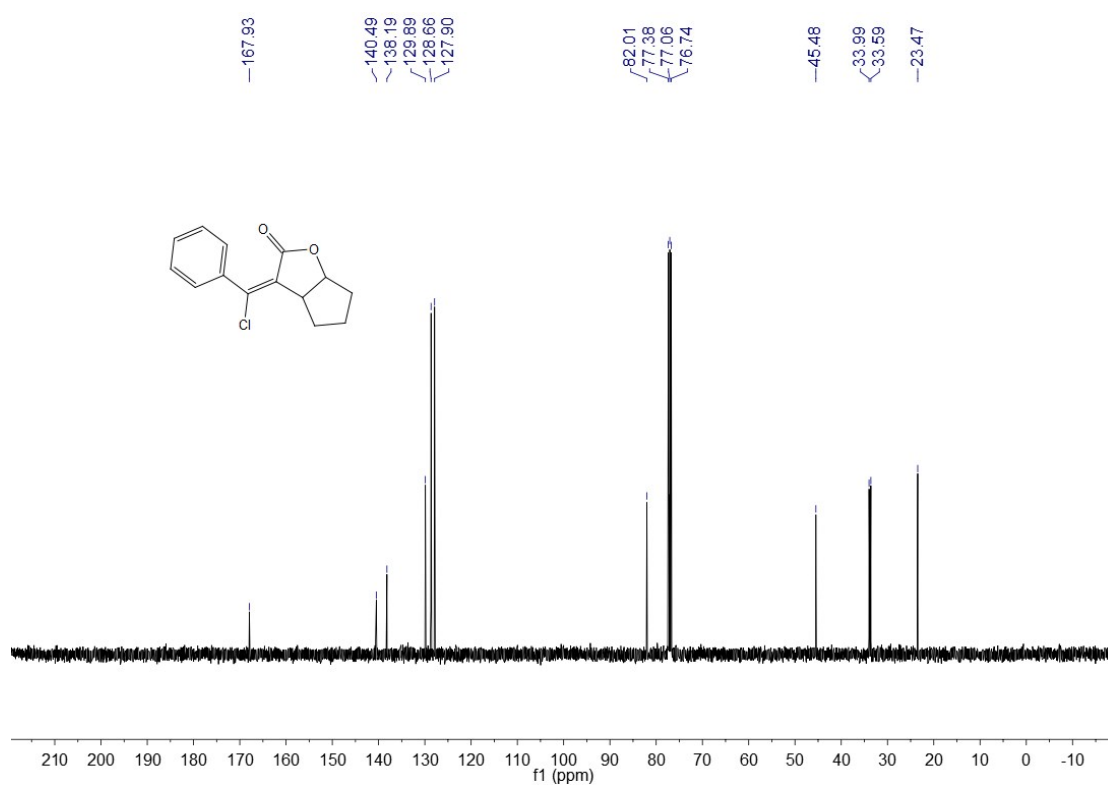
¹³C NMR of Compound **3w**



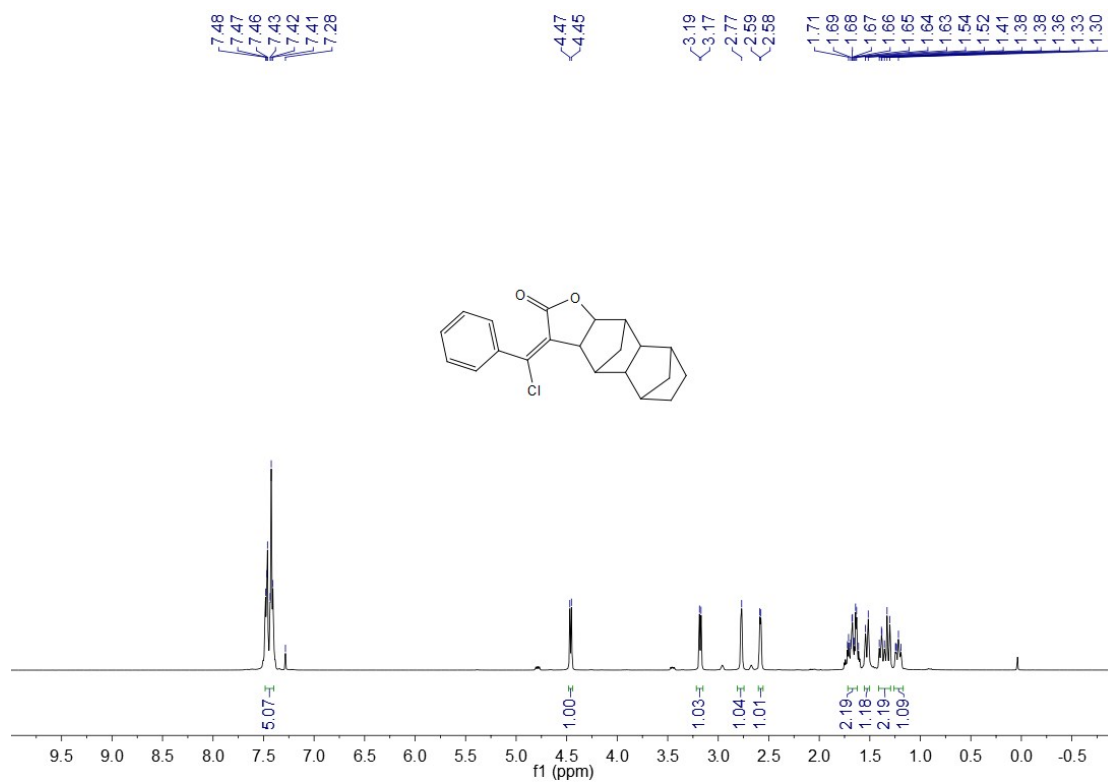
¹H NMR of Compound **3x**



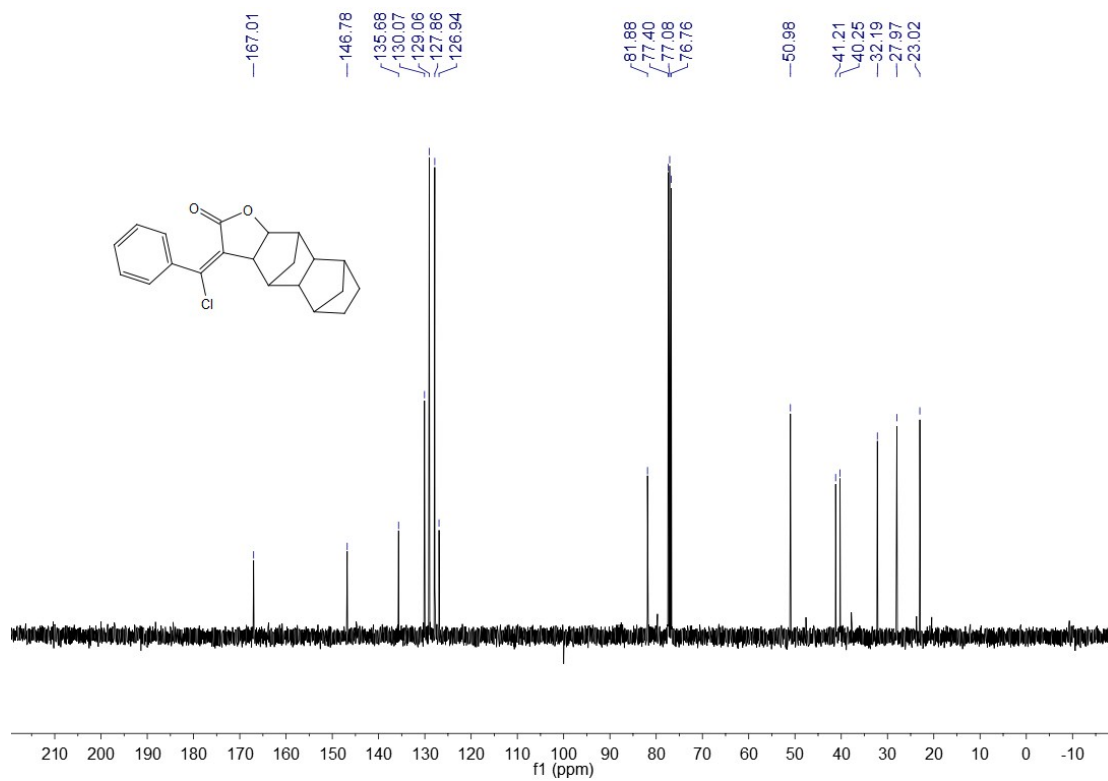
¹³C NMR of Compound **3x**



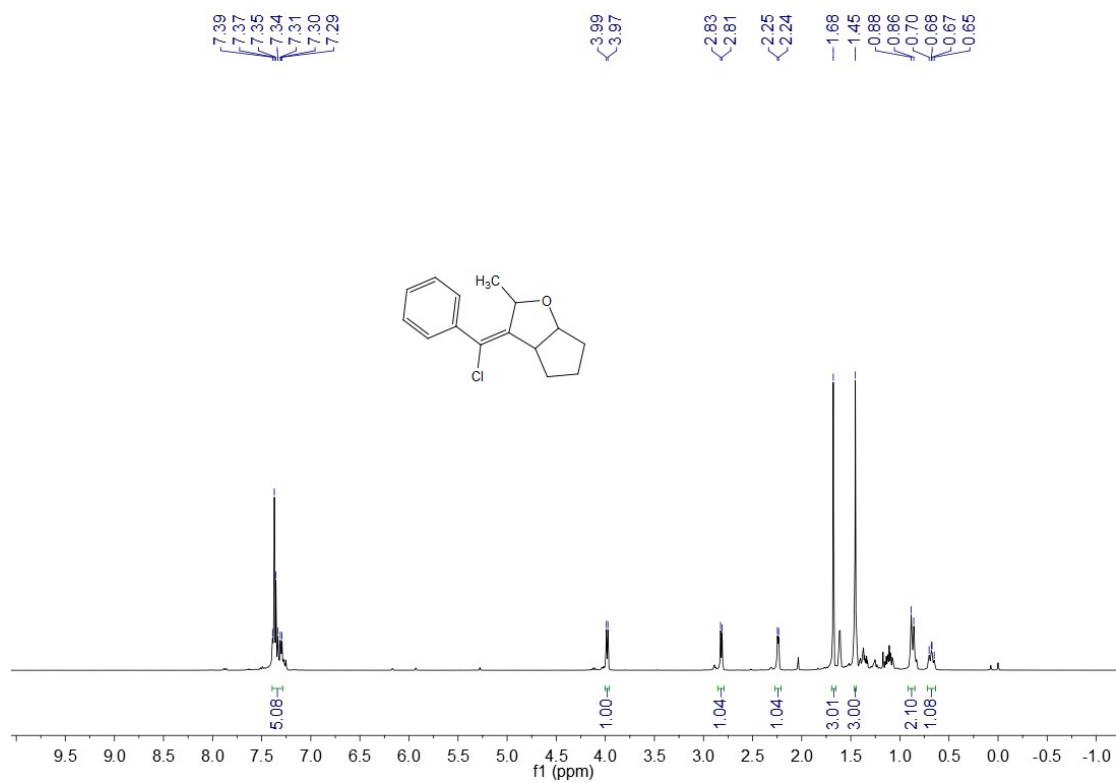
¹H NMR of Compound **3y**



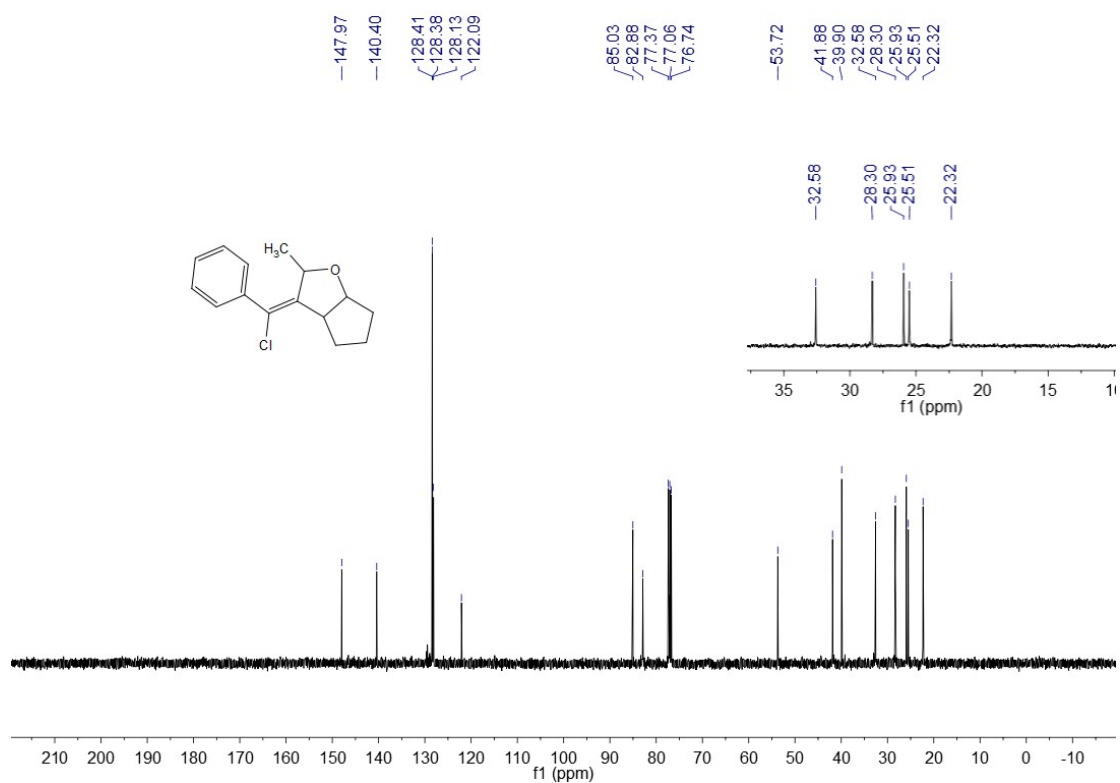
¹³C NMR of Compound **3y**



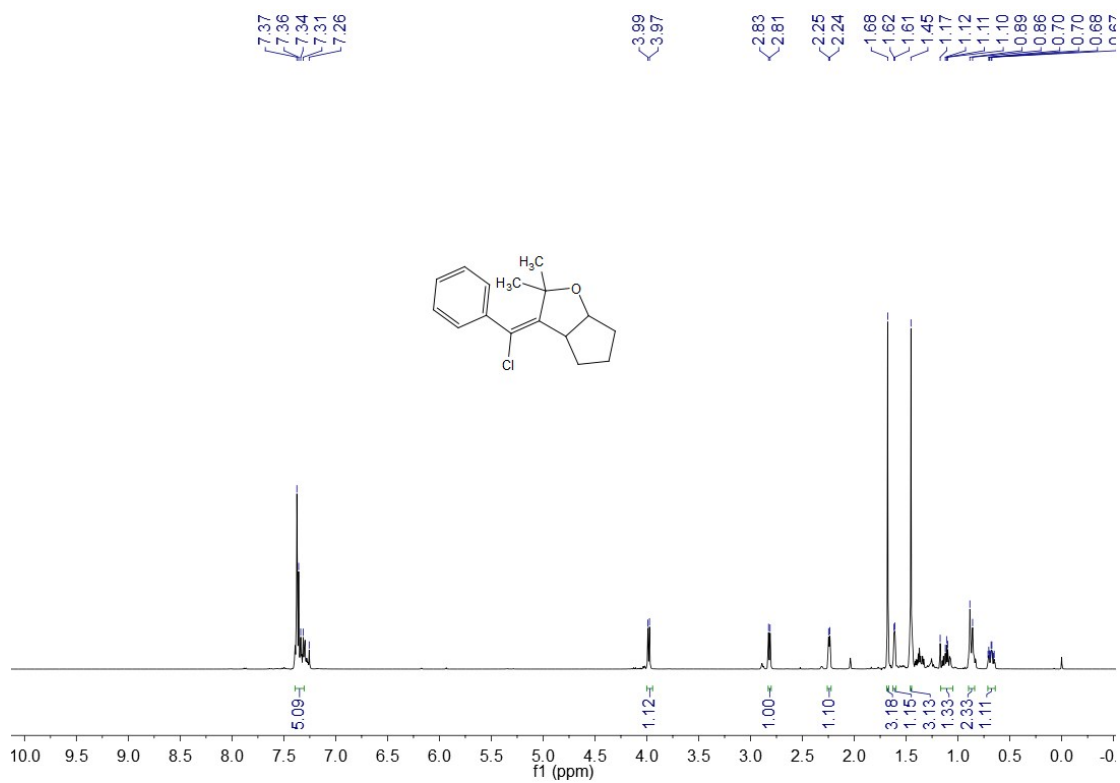
¹H NMR of Compound **5a**



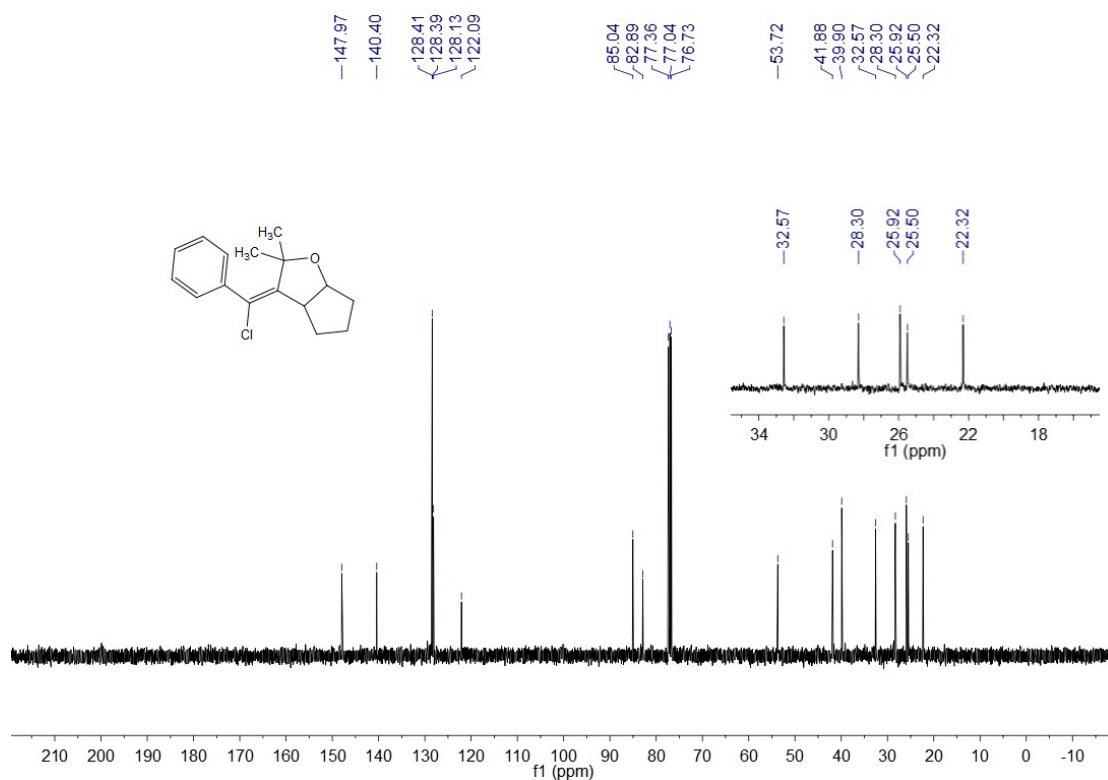
¹³C NMR of Compound **5a**



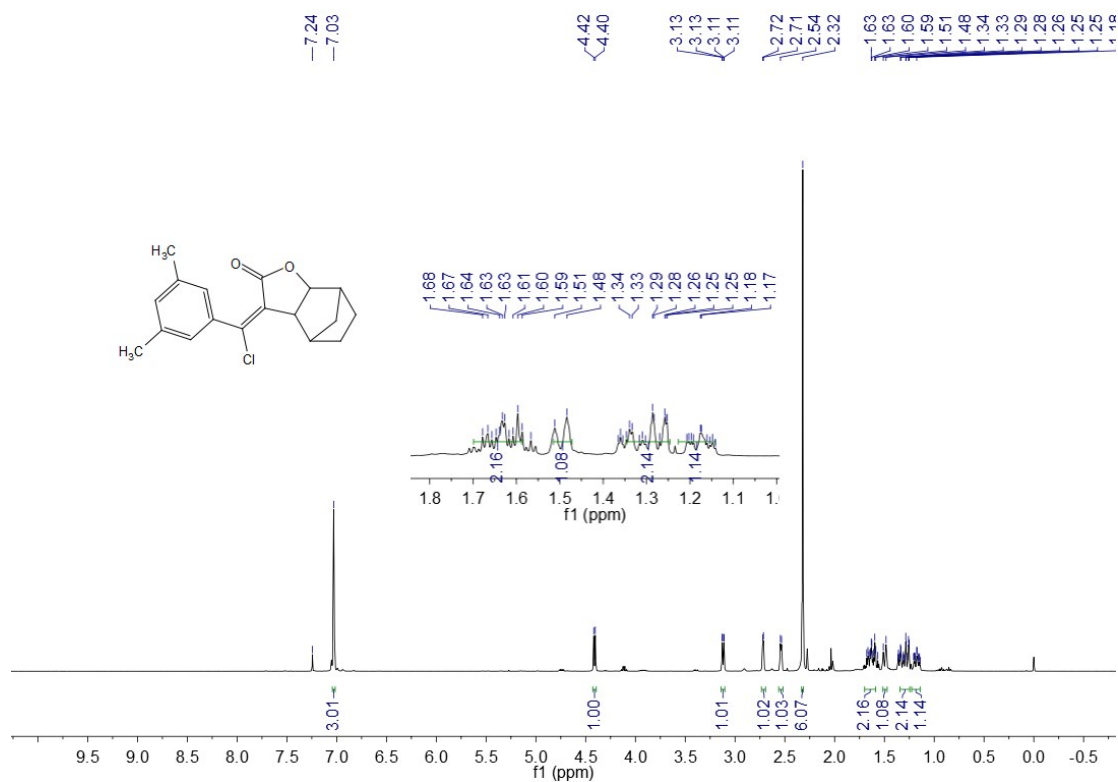
¹H NMR of Compound **5b**



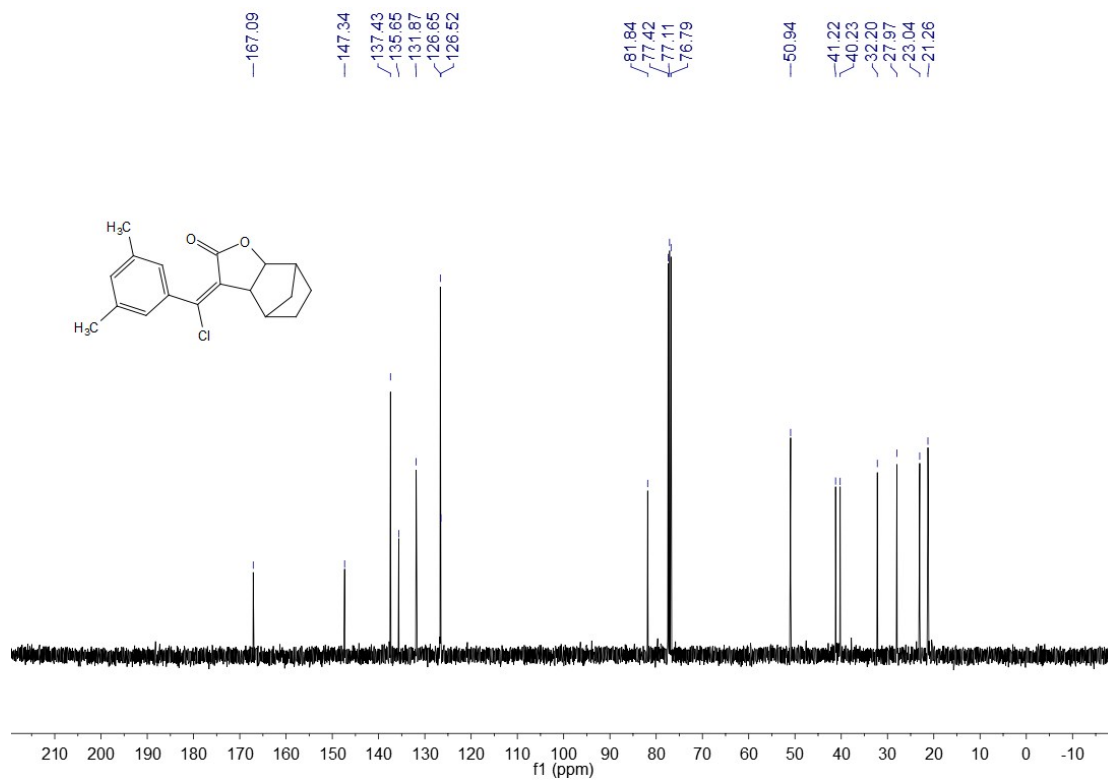
¹³C NMR of Compound **5b**



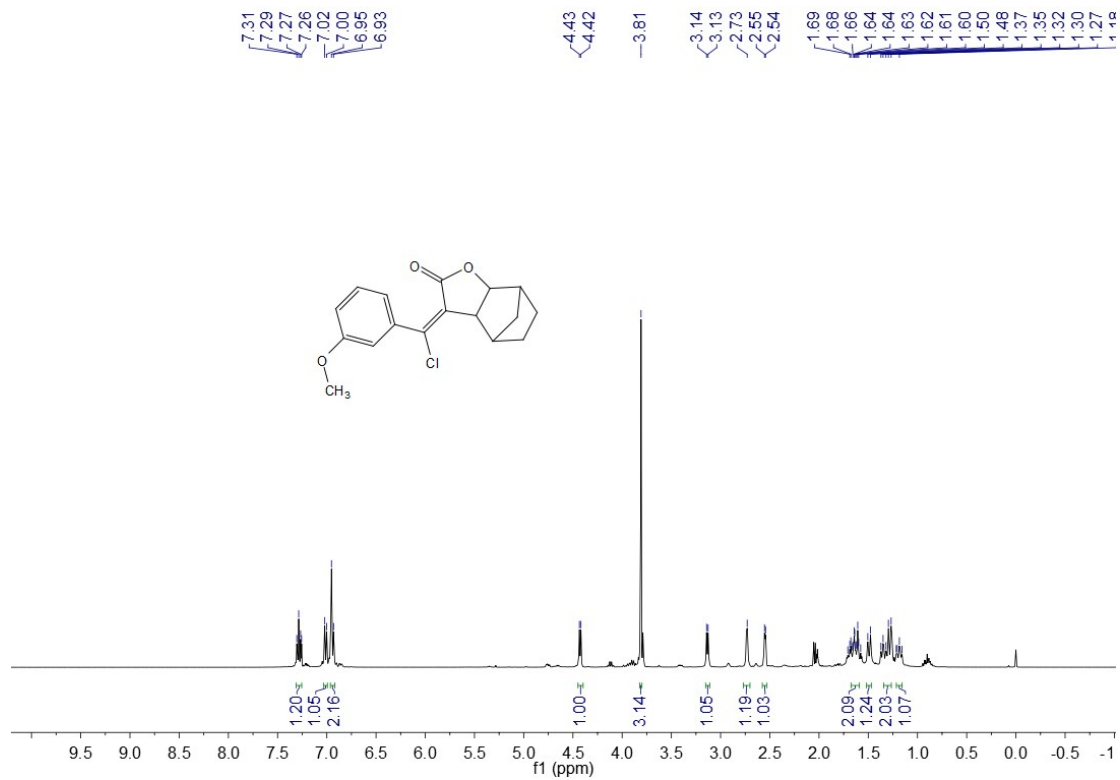
¹H NMR of Compound 7a



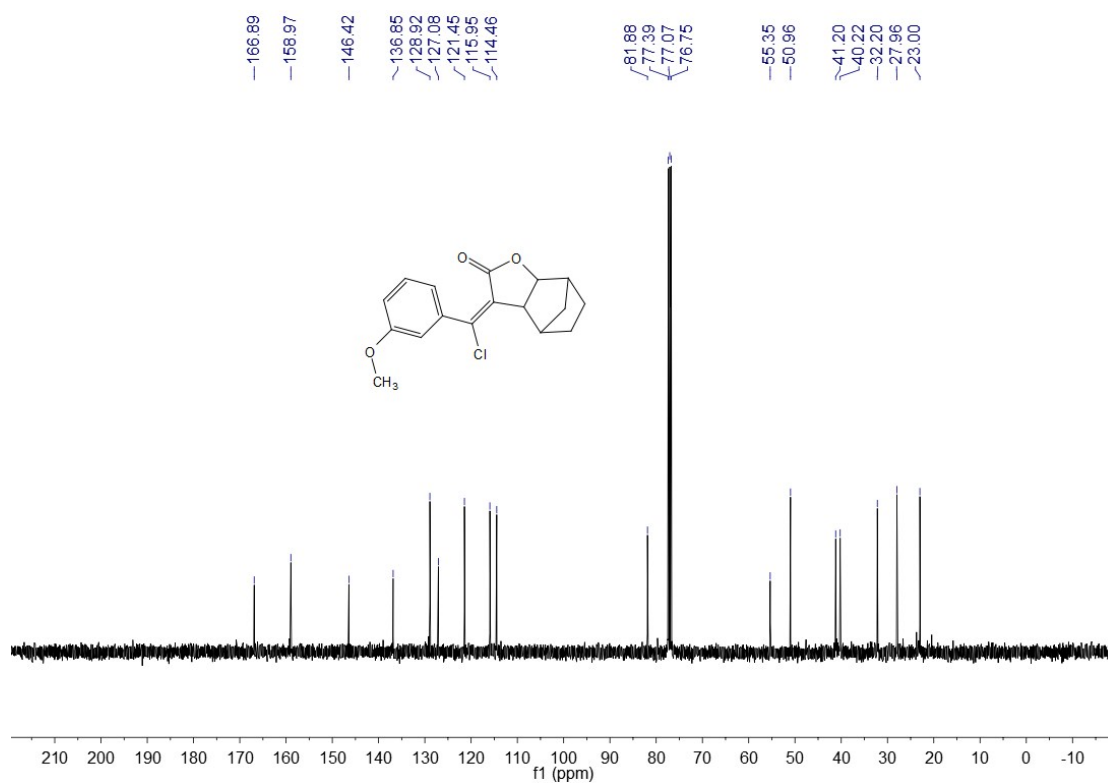
¹³C NMR of Compound **7a**



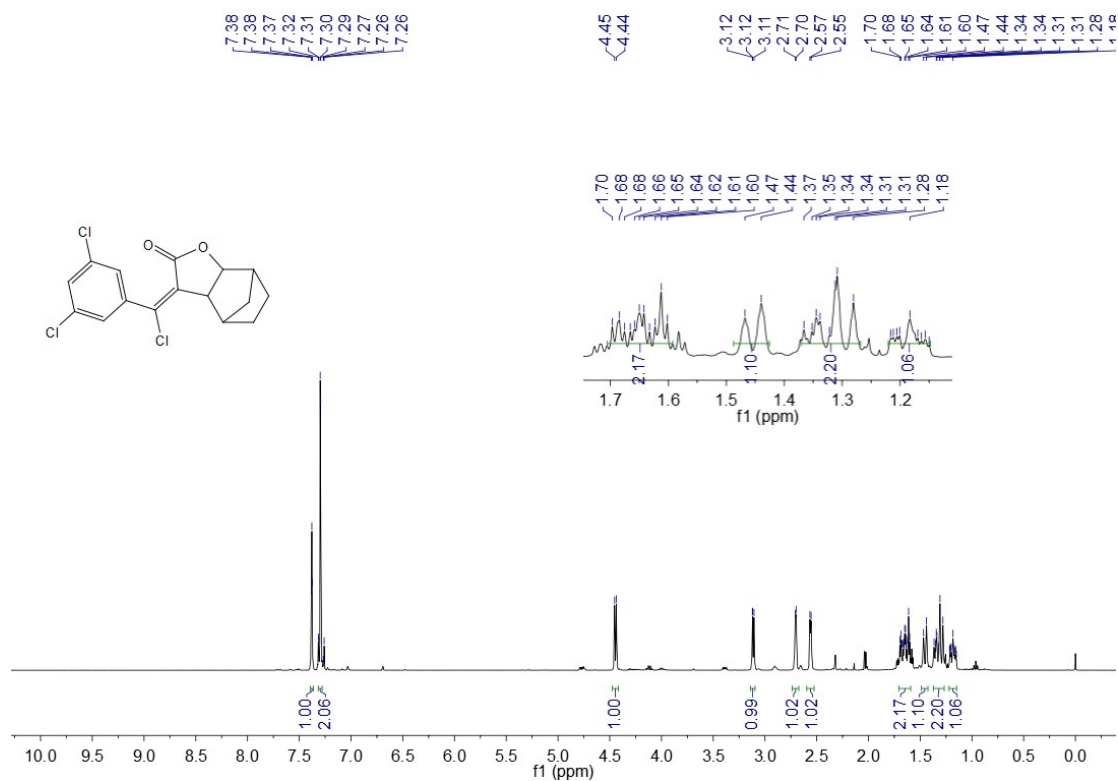
¹H NMR of Compound **7b**



¹³C NMR of Compound **7b**



¹H NMR of Compound **7c**



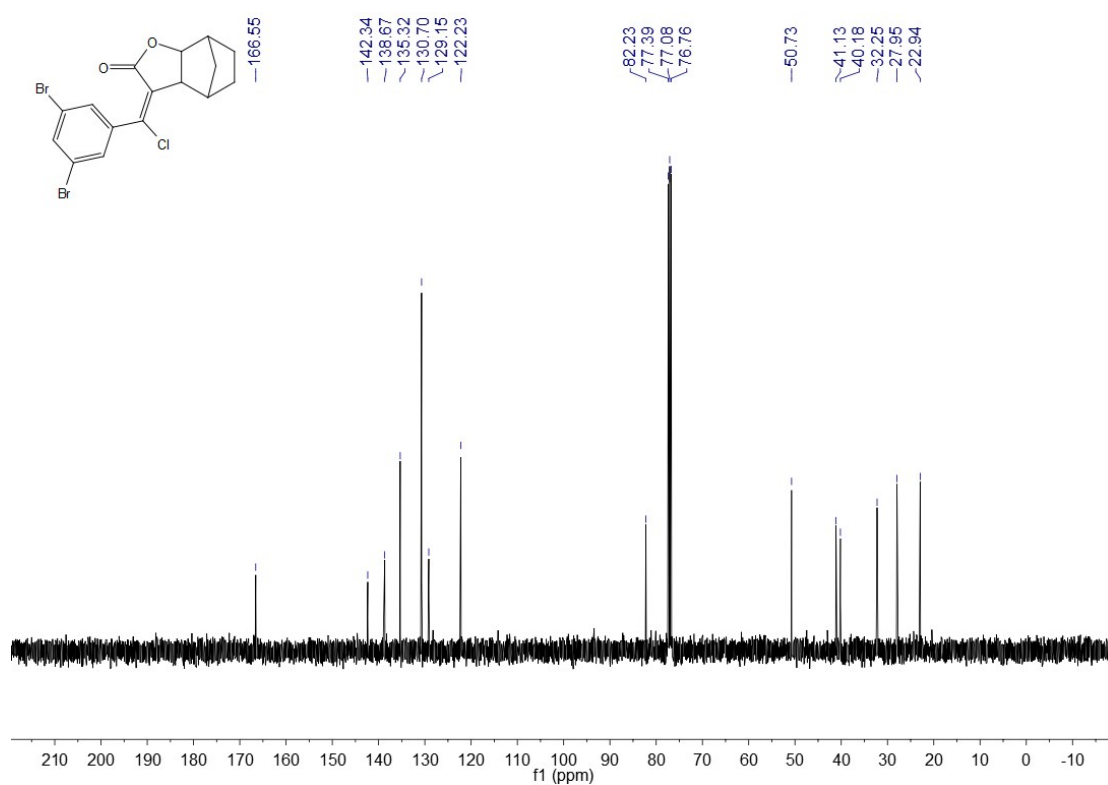
Chemical structure of 2-(2,4-dichlorophenyl)-2-oxobicyclo[2.2.1]hept-5-ene-5-carboxylic acid is shown. The ¹³C NMR spectrum (CDCl₃) displays peaks at the following chemical shifts (ppm): 166.59, 142.61, 138.22, 134.49, 129.90, 129.13, 127.51, 82.24, 80.42, 77.42, 77.11, 76.79, 50.73, 41.13, 40.17, 32.25, 27.95, and 22.93.

Chemical structure: ClC1=C(C2=CC(=CC=C2C3=CC(=CC=C3)Br)Br)C4=CC5C(C1)CC6C(C5)CC4C6

¹H NMR spectrum (CDCl₃) showing peaks from -1.0 to 10.0 ppm. The spectrum is characterized by aromatic signals between 7.5 and 7.7 ppm, a methine signal at 4.45 ppm, and a complex aliphatic region between 1.1 and 2.0 ppm. Integration values are provided below the peaks.

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.68 | 1.02 |
| 7.50 | 2.14 |
| 4.45 | 1.00 |
| 1.68 | 1.00 |
| 1.65 | 1.02 |
| 1.64 | 1.03 |
| 1.63 | 2.14 |
| 1.61 | 1.10 |
| 1.60 | 2.10 |
| 1.59 | 1.08 |
| 1.58 | |
| 1.47 | |
| 1.44 | |
| 1.37 | |
| 1.35 | |
| 1.31 | |
| 1.28 | |
| 1.26 | |
| 1.21 | |
| 1.19 | |
| 1.16 | |

¹³C NMR of Compound 7d



Chemical structure: O=C1C2(C1)CC3(C2)C(C3)COC4=CC=CC=C4

¹³C NMR spectrum (ppm):

- 179.24
- 139.24
- 128.67
- 128.11
- 126.40
- 84.39
- 77.45
- 77.13
- 76.81
- 44.87
- 41.78
- 40.93
- 36.07
- 32.34
- 31.84
- 28.70
- 22.75

ClC1=C(C23C4C1CC5C2C(C4)CC5)C(=O)O3C=Cc1ccc(cc1)/C=C/c2ccccc2

7.52, 7.50, 7.50, 7.47, 7.44, 7.38, 7.36, 7.34, 7.28, 7.27, 7.24, 7.18, 7.14, 7.11, 4.44, 4.42, 3.16, 3.14, 2.73, 2.56, 2.55, 1.68, 1.64, 1.63, 1.62, 1.61, 1.60, 1.52, 1.49, 1.37, 1.35, 1.32, 1.30, 1.27, 1.26, 1.23, 1.21, 1.20, 1.18, 1.69, 1.68, 1.64, 1.63, 1.62, 1.61, 1.60, 1.52, 1.49, 1.37, 1.35, 1.32, 1.30, 1.27, 1.26, 1.23, 1.21, 1.20, 1.18

4.07, 2.00, 2.14, 1.22, 2.01, 1.00, 1.03, 1.03, 1.00, 2.84, 1.03, 3.06

f1 (ppm)

