

Supporting Information

Cheap metal catalyzed ring expansion/cross-coupling cascade: A new route to functionalized medium-sized and macrolactones

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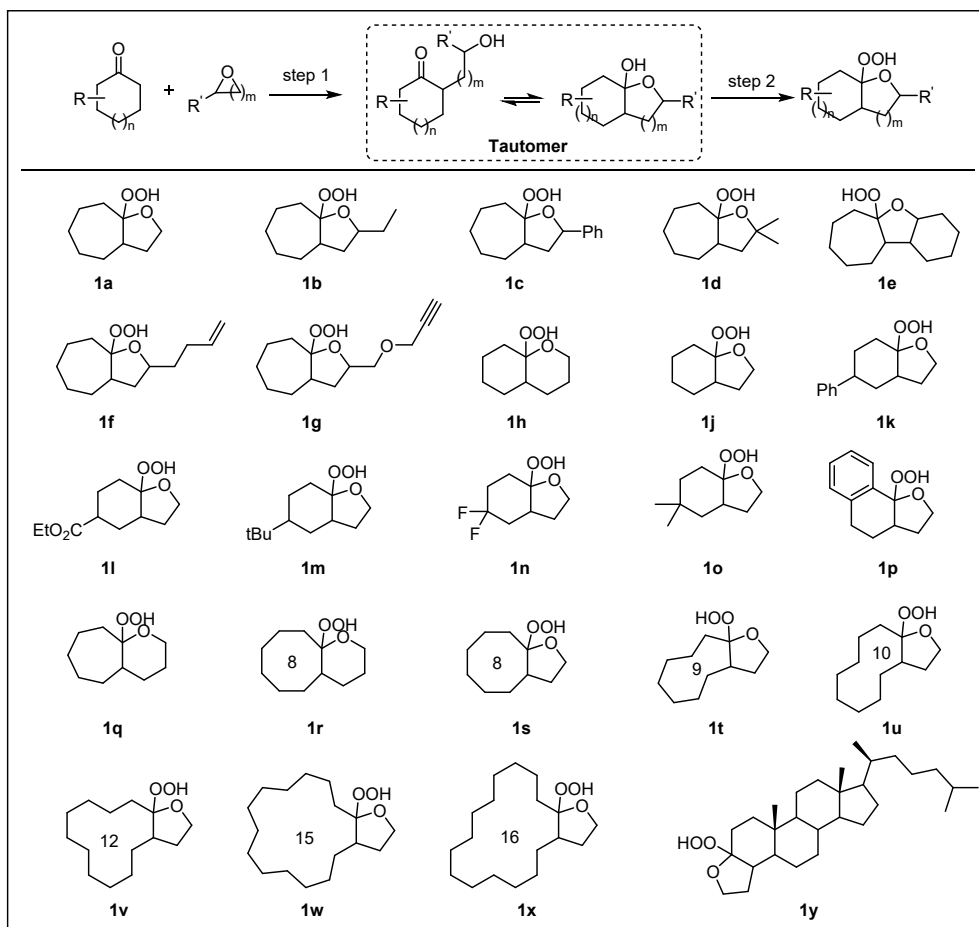
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1. General Information

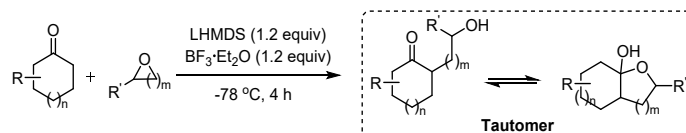
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere, reagents and solvents were obtained from commercial suppliers and were used without further purification. The concentration of HX (aq) are HCl (36%), HBr (40%) and HI (55%-58%). Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60F-254. Column chromatography purifications were carried out using 200-300 mesh silica gel. Melting points were measured using open glass capillaries in a SGW® X-4A apparatus. ^1H and ^{13}C NMR spectra were recorded on a JNM-ECZ400S/L1 400 MHz spectrometer at ambient temperature. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were recorded on a Bruker V 70 and only major peaks were reported in cm^{-1} . HRMS were obtained on a WATERS I-Class VION IMS Q-ToF with an ESI source. Compounds were visualized by exposure to UV-light or by dipping the plates in KMnO_4 stain followed by heating.

2. Starting Materials

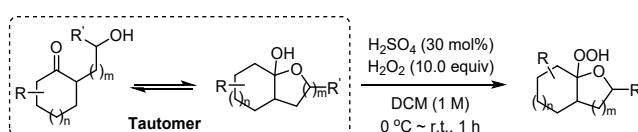


Followed General Procedure for the Synthesis of Hemiketal Hydroperoxides.

2.1 General Procedure for the Synthesis of Hemiketal Hydroperoxides^{1,3}

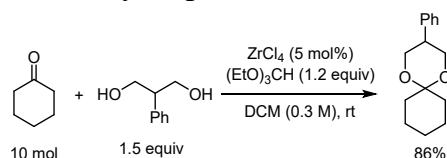


To a stirred solution of LHMDS (1.0 M in THF, 1.2 equiv.) in THF at -78°C was added cyclic ketone (10 mmol, 1.0 equiv.) over 5 min. After 1 h, epoxide (3.0 M in THF, 2.0 equiv.) was added to the reaction solution. After 1 h, the $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.2 equiv.) was added very slowly. The reaction mixture was stirred for 2 h at -78°C and the reaction was quenched by the addition of saturated aqueous NH_4Cl solution at -78°C . Layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layer were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to obtain the tautomer of α -hydroxyalkylketones and lactols.

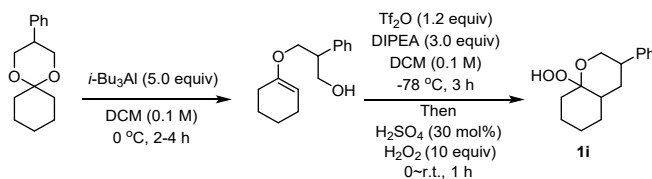


Based on the amount of the tautomer of α -hydroxyalkylketones and lactols: To a reaction flask was added a solution of H_2O_2 (30% wt in H_2O , 10.0 equiv.), and conc. H_2SO_4 (30 mol%). Then a solution of the tautomer of α -hydroxyalkylketones and lactols in DCM (1.0 M) at 0 °C was added. The reaction mixture was stirred for 1 h at room temperature. The aqueous layer was extracted with DCM, the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1~10:1) to obtain the hemiketal hydroperoxides.

2.2 Synthesis of the Hemiketal Hydroperoxide **1i**^{2,3}



To a solution of cyclic ketones (10 mmol) and 2-phenyl-1,3-propanediol (1.5 equiv.), was added $(\text{EtO})_3\text{CH}$ (1.0 M) in dry DCM (0.3 M) and ZrCl_4 (5 mol%). Then, the resulting solution was stirred at room temperature. After completion of the reaction, it was quenched with a cold aqueous solution of NaOH (10%) and the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to obtain the 3-phenyl-1,5-dioxaspiro[5.5]undecane (2.0 g, 86%).



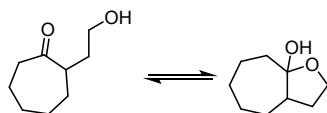
To a cold (0 °C) solution of 3-Phenyl-1,5-dioxaspiro[5.5]undecane (8.6 mmol) in DCM (0.1 M) was added $i\text{-Bu}_3\text{Al}$ (5.0 equiv., 1.0 M in dry toluene). The reaction mixture was stirred at 0 °C for 2-4 h, then, poured into cold 1 N NaOH (aq). The aqueous layer was extracted with DCM, the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~4:1) to obtain the hydroxy vinyl ether (1.5 g, 76%)

The hydroxy vinyl ether (6.5 mmol) was diluted in DCM (0.1 M) and N,N -diisopropylethylamine (1.0 M). After cooling to -78 °C, trifluoromethanesulfonic anhydride (1.2 equiv.) was slowly added dropwise to this solution. The reaction mixture was stirred at the same temperature for 3 h. After the reaction completed, the reaction mixture was diluted with DCM and brine, the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Then the residue was diluted with DCM in 0 °C, and was added a solution of H_2O_2 (30% wt in H_2O , 10.0 equiv.), and conc. H_2SO_4 (30 mol%). The reaction mixture was stirred vigorously for 1 h at room temperature. The aqueous layer was extracted with DCM, the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to obtain the hemiketal hydroperoxides **1i** (0.5 g, 31%); (20%, three steps)

2.3 Notes for Starting Materials

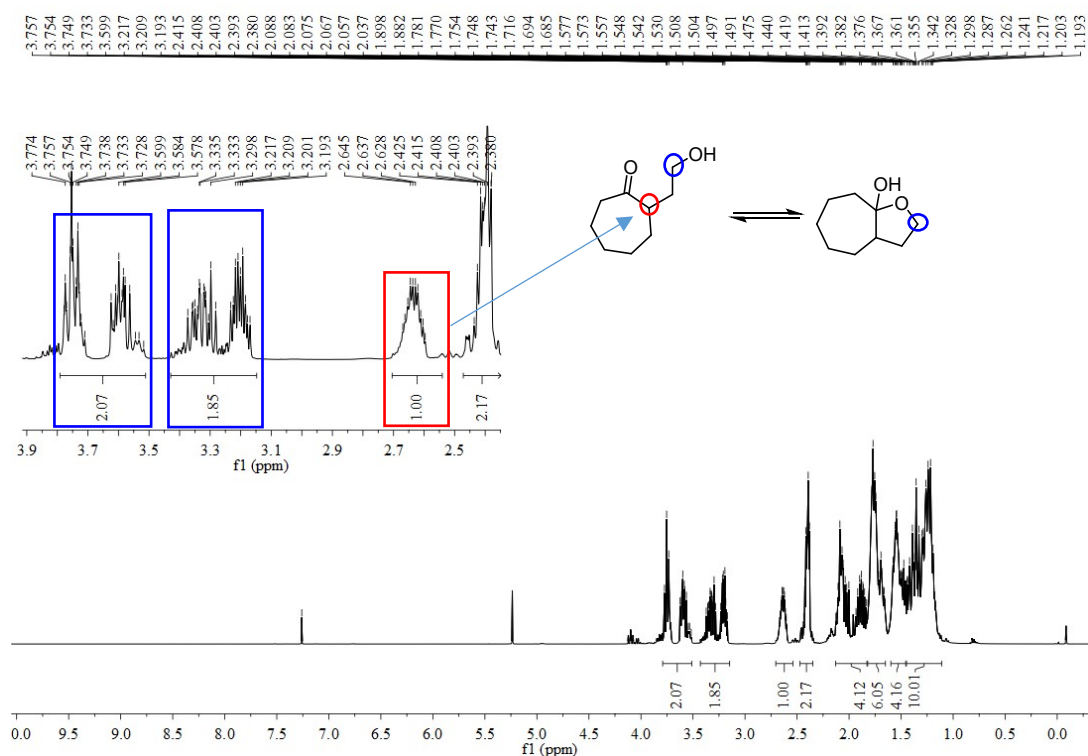
1. These α -hydroxyalkyl ketones readily tautomerize to the lactols in solution, and the ratio of the two tautomers could be affected easily under acid or basic conditions, concentration, solvent, temperature, and others. This property was also described in these articles: *Tetrahedron*, 1969, **25**, 3157; *Tetrahedron*, 1987, **43**, 3371; *Angew. Chem., Int. Ed.*, 2021, **60**, 5370.

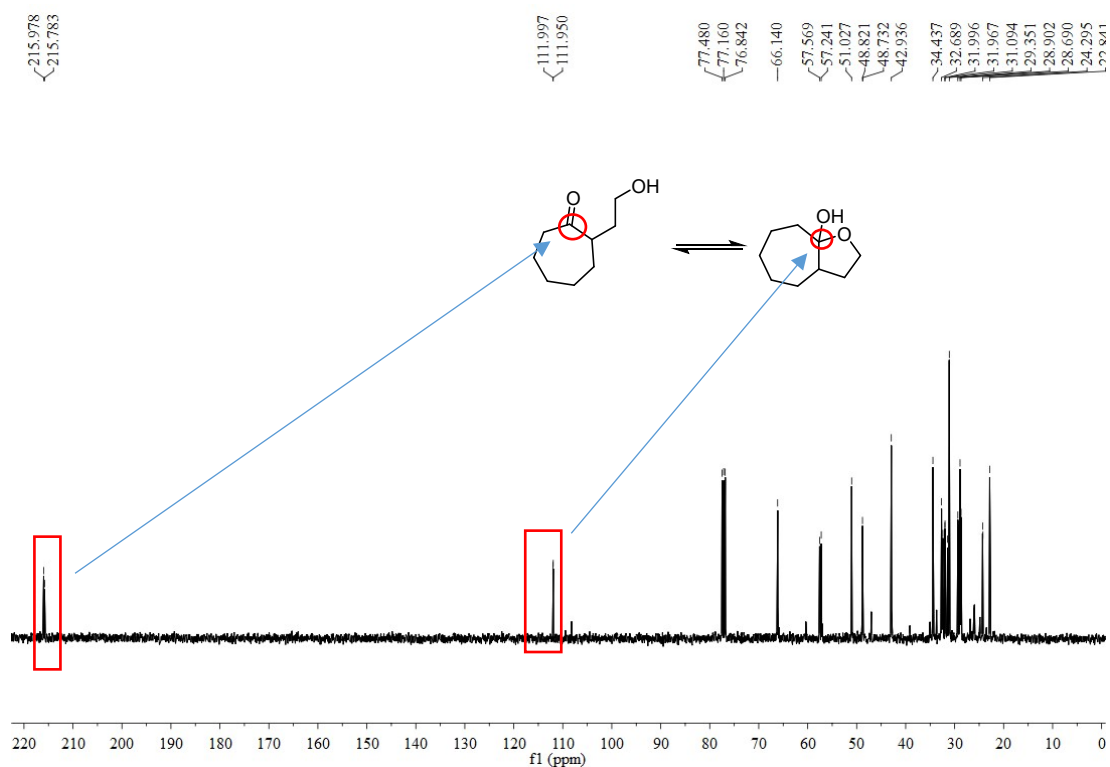
For an example NMR data of automer of α -hydroxyalkylketone and lactol. The ^1H NMR spectra showed that the ratio were 2.1:1.9, by comparing the signal areas of protons connected hydroxyl group and protons ether of lactol. Both the ketone carbonyl carbon (216.0, 215.8 ppm) and the tetrasubstituted carbon of lactol (111.99, 111.95 ppm) could be observed in the ^{13}C NMR spectrum.



^1H NMR (400 MHz, CDCl_3) δ 3.79 – 3.51 (m, 2H), 3.43 – 3.15 (m, 1.85H), 2.70 – 2.54 (m, 1H), 2.47 – 2.35 (m, 2H), 2.13 – 1.83 (m, 4H), 1.82 – 1.65 (m, 6H), 1.60 – 1.46 (m, 4H), 1.45 – 1.11 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.0, 215.8, 112.0, 112.0, 66.1, 57.6, 57.2, 51.0, 48.8, 48.7, 42.9, 34.4, 32.7, 32.5, 32.4, 32.0, 32.0, 31.5, 31.1, 29.4, 29.2, 28.9, 28.7, 24.3, 24.2, 22.8.

^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of tautomer of α -hydroxyalkylketones and lactols.





Consider the hemiketal peroxides **1** derived from the mixture of α -hydroxyalkyl ketones and the lactols are pure and stable. Thus, the hemiketal peroxides **1** characterization and ¹H NMR, ¹³C NMR spectral data and IR, HRMS data for these compounds were given.

2. All hemiketal hydroperoxides were heated and concentrated by vacuo at below 30 °C and were stored under -20 °C. We have never experienced a safety problem with these materials.

3. Hydroperoxides are bicyclic fused compounds with an inseparable mixture of *cis-trans* isomers, we have tried our utmost to get cleaner ¹H NMR and ¹³C NMR spectra of hydroperoxides.

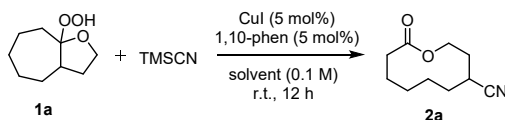
3. Optimization of Reaction Conditions

3.1 General Procedure for Ring Expansion/Functionalization of Hydroperoxide **1a**

A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added catalyst and ligand. Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) and nucleophiles (0.3 mmol, 1.5 equiv.) in solvent (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for specified time. After the reaction completed, the reaction mixture was concentrated in vacuo and then purified by column chromatography on silica gel to give the target products.

3.2 Optimization of Reaction 1a with TMSCN^a

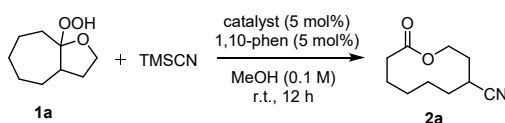
Screening of Solvents



Entry	Solvent	Yield (%)
1	NMP	78
2	DMF	78
3	MeCN	87
4	MeOH	98(95)^b
5	THF	88
6	DCE	85
7	toluene	14
8	1,4-dioxane	25
9	MTBE	trace

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%), and solvent (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yield was given in parenthesis.

Screening of Catalysts

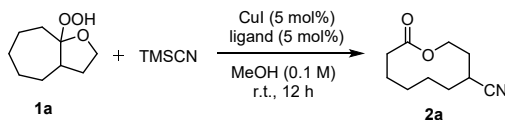


^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), catalyst (0.01 mmol, 5 mol%),

Entry	Catalyst (5 mol%)	Yield (%)
1	CuI	98
2	CuOTf	40
3	Cu(OAc) ₂	12
4	Fe(OTf) ₂	N.R.

1,10-phen (0.01 mmol, 5 mol%), and MeOH (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard.

Screening of Ligands

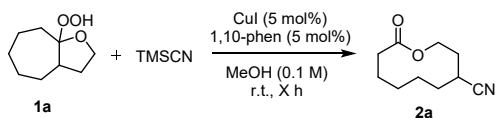


^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), ligand

Entry	Ligand (5 mol%)	Yield (%)
1	1,10-phen	98
2	2,2'-bpy	70
3	-	40

(0.01 mmol, 5 mol%), and MeOH (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard.

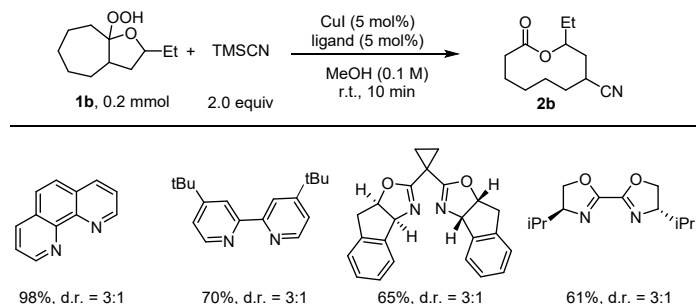
Screening of Time



Entry	Time (X h)	Yield (%)
1	12	98
2	6	95
3	1	96
4	0.5	97
5	15 min	97(94) ^b
6	10 min	98(95)^b
7	5 min	92(88) ^b

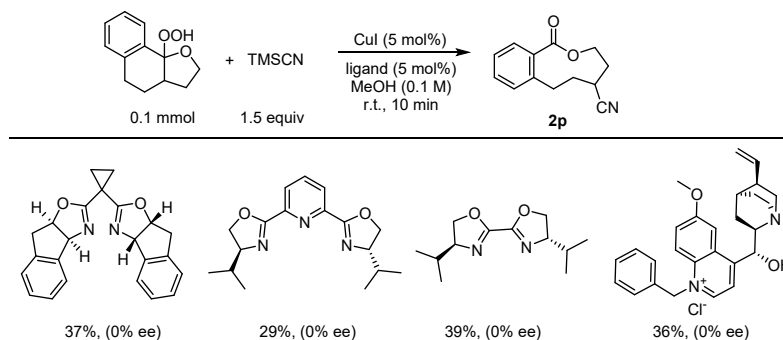
^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%), and MeOH (2.0 mL) at 25 °C for X h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yields were given in parenthesis.

Screening of Ligands



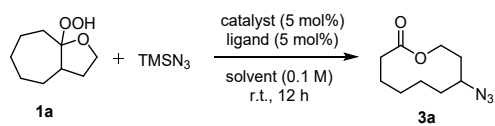
^aReaction conditions: **1b** (0.2 mmol, 1.0 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), ligand (0.01 mmol, 5 mol%), and MeOH (2.0 mL) at 25 °C for 10 min under N₂. Isolated yields

Screening of Chiral Ligands



^aReaction conditions: **1p** (0.1 mmol, 1.0 equiv.), TMSCN (0.15 mmol, 1.5 equiv.), CuI (0.005 mmol, 5 mol%), ligand (0.005 mmol, 5 mol%), and MeOH (1.0 mL) at 25 °C for 10 min under N₂. Isolated yields. The ee values were determined by HPLC analysis.

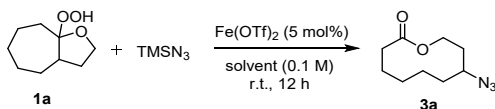
3.3 Optimization of Reaction 1a with TMSN₃^a



Entry	Catalyst (5 mol%)	Solvent	Ligand	Yield (%)
1	CuI	MeOH	1,10-phen	10
2	CuI	NMP	1,10-phen	18
3	CuI	DMF	1,10-phen	14
4	CuI	THF	1,10-phen	27
5	Fe(OTf)₂	MeOH	1,10-phen	74
6	Fe(OTf) ₂	MeOH	-	70

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSN₃ (0.3 mmol, 1.5 equiv.), catalyst (0.01 mmol, 5 mol%), ligand (0.01 mmol, 5 mol%), and solvent (2.0 mL) at 25 °C for 12 h under N₂. Isolated yields.

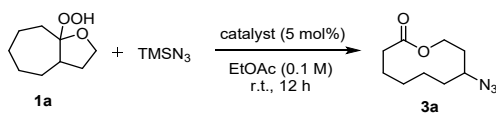
Screening of Solvents



Entry	Solvent	Yield (%)
1	DMF	14
2	MeCN	70
3	DCE	12
4	THF	67
5	toluene	trace
6	acetone	trace
7	MTBE	73
8	MeOH	70
9	<i>i</i> -PrOH	75
10	DME	80(70) ^b
11	EtOAc	89(84)^b

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSN₃ (0.3 mmol, 1.5 equiv.), Fe(OTf)₂ (0.01 mmol, 5 mol%), and solvent (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yields were given in parenthesis.

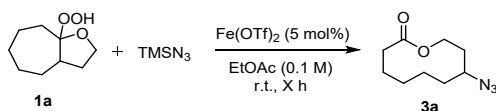
Screening of Catalysts



Entry	Catalyst (5 mol%)	Yield (%)
1	Fe(OTf)₂	89
2	Fe(OTf) ₃	73
3	Fe(OTs) ₃	50
4	FeBr ₂	49
5	Fe(OAc) ₂	41
6	FeCl ₂	42
7	CuI	trace
8	CuOTf	trace

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSN₃ (0.3 mmol, 1.5 equiv.), catalyst (0.01 mmol, 5 mol%), and EtOAc (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard.

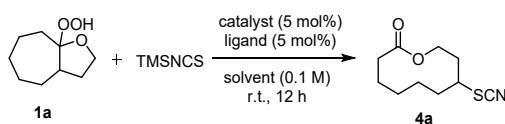
Screening of Time



Entry	Time (X h)	Yield (%)
1	1	88
6	10 min	87(82)^b
7	5 min	82(78) ^b

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSN₃ (0.3 mmol, 1.5 equiv.), Fe(OTf)₂ (0.01 mmol, 5 mol%), and EtOAc (2.0 mL) at 25 °C for X h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yields were given in parenthesis.

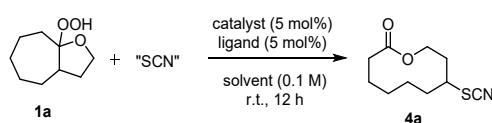
3.4 Optimization of Reaction 1a with NH₄SCN^a



Entry	Catalyst (5 mol%)	Solvent	Ligand	Yield (%)
1	CuI	MeOH	1,10-phen	trace
2	CuI	NMP	1,10-phen	trace

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSNCS (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%), and solvent (2.0 mL) at 25 °C for 12 h under N₂. Isolated yields.

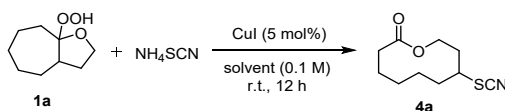
Screening of “SCN” Source



Entry	Catalyst	“SCN” Source	Solvent	Ligand	Yield (%)
1	CuI	TMSNCS	NMP	1,10-phen	trace
2	CuI	NH ₄ SCN	NMP	1,10-phen	67
3	CuI	NH ₄ SCN	NMP	-	60

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), thiocyanation source (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), ligand (0.01 mmol, 5 mol%), and NMP (2.0 mL) at 25 °C for 12 h under N₂. Isolated yields.

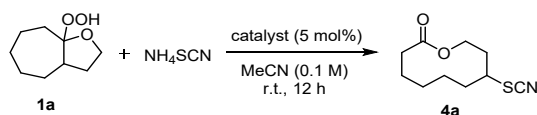
Screening of Solvents



Entry	Solvent	Yield (%)
1	DMF	66
2	NMP	60
3	DMA	39
4	DMSO	36
5	DCE	52
6	THF	trace
7	MeOH	trace
8	MeCN	82

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), NH₄SCN (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5 mol%), and solvent (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard.

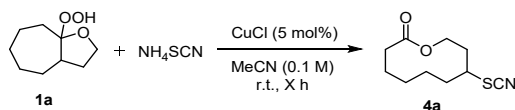
Screening of Catalysts



Entry	Catalyst (5 mol%)	Yield (%)
1	CuI	82
2	CuOTf	82
3	Cu(OAc) ₂	92
4	Cu(CH ₃ CN) ₄ PF ₆	96
5	CuCl	99(94)^b
6	CuSCN	87

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), NH₄SCN (0.3 mmol, 1.5 equiv.), catalyst (0.01 mmol, 5 mol%), and MeCN (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yield was given in parenthesis.

Screening of Time

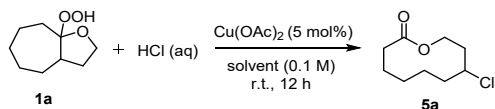


Entry	Time (X h)	Yield (%)
1	3	97
2	1	98(93)^b
3	10 min	82(73) ^b

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), NH₄SCN (0.3 mmol, 1.5 equiv.), CuCl (0.01 mmol, 5 mol%), and MeCN (2.0 mL) at 25 °C for X h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yields were given in parenthesis.

3.5 Optimization of Reaction 1a with HCl (aq)^a

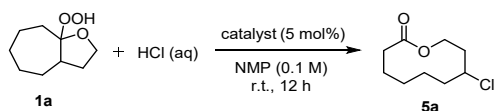
Screening of Solvents



Entry	Solvent	Yield (%)
1	DMF	68
2	NMP	76
3	MeCN	46
4	THF	9
5	toluene	trace

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), HCl (aq) (0.4 mmol, 2.0 equiv.), Cu(OAc)₂ (0.01 mmol, 5 mol%), and solvent (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard.

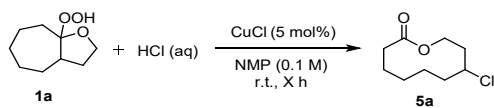
Screening of Catalysts



Entry	Catalyst (5 mol%)	Yield (%)
1	CuI	90
2	CuOTf	86
3	Cu(OAc) ₂	76
4	Cu(CH ₃ CN) ₄ PF ₆	90
5	CuCl	92(88)^b
6	CuSCN	88
7	CuTC	81
8	CuCl ₂	87

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), HCl (aq) (0.4 mmol, 2.0 equiv.), catalyst (0.01 mmol, 5 mol%), and NMP (2.0 mL) at 25 °C for 12 h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yield was given in parenthesis.

Screening of Time

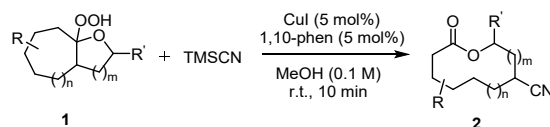


Entry	Time (X h)	Yield (%)
1	1	90(87) ^b
2	10 min	92(88)^b
3	5 min	88(83) ^b

^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), HCl (aq) (0.4 mmol, 2.0 equiv.), CuCl (0.01 mmol, 5 mol%), and NMP (2.0 mL) at 25 °C for X h under N₂. Yields were determined by GC-FID analysis of the crude reaction mixture with dodecane as the internal standard. ^bIsolated yields were given in parenthesis.

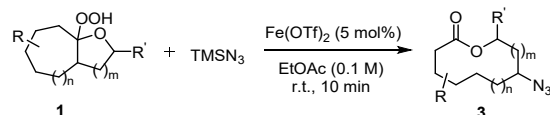
4. Representative Procedure for Schemes 2 and 3

4.1 Representative Procedure for the Reaction of **1** with TMSCN



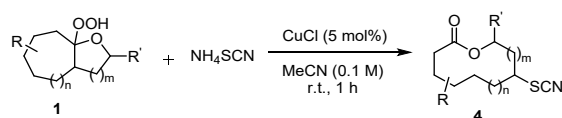
To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxides **1** (0.2 mmol, 1.0 equiv.), and TMSCN (0.3 mmol, 1.5 equiv.) in MeOH (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at 25 °C for 10 min. After the reaction completed, the reaction mixture was concentrated and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target products **2**.

4.2 Representative Procedure for the Reaction of **1** with TMSN₃



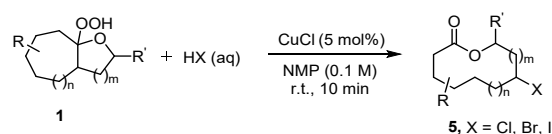
To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added Fe(OTf)₂ (0.01 mmol, 5 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxides **1** (0.2 mmol, 1.0 equiv.), and TMSN₃ (0.3 mmol, 1.5 equiv.) in EtOAc (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 10 min. After the reaction completed, the reaction mixture was concentrated and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1) to give the target products **3**.

4.3 Representative Procedure for the Reaction of **1** with NH₄SCN



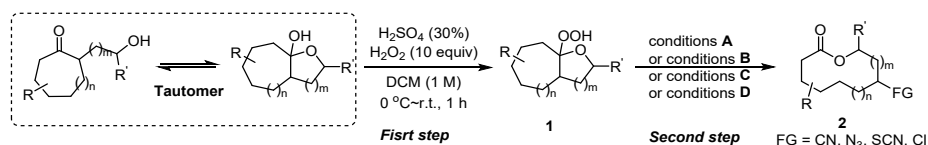
To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added NH₄SCN (0.3 mmol, 1.5 equiv.), CuCl (0.01 mmol, 5 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxides **1** (0.2 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 1 h. After the reaction completed, the reaction mixture was concentrated and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target products **4**.

4.4 Representative Procedure for the Reaction of **1** with HX (aq)



To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuCl (0.01 mmol, 5 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxides **1** (0.2 mmol, 1.0 equiv.), and HCl (aq) or HBr (aq) or HI (aq) (0.4 mmol, 2.0 equiv.) in NMP (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 10 min. After the reaction completed, the reaction mixture was diluted with EtOAc (5.0 mL) and H₂O (5.0 mL). The organic layer was separated and the water layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with saturated brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1) to give the target products **5**.

4.5 Representative Telescoped Procedure for Ring Expansion/Functionalization of α -Hydroxyalkylketones with Nucleophiles



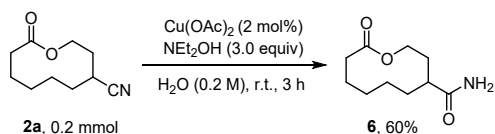
First step:

To a 10 mL reaction tube equipped with a magnetic stirrer was added a solution of H₂O₂ (30% wt in H₂O, 10.0 equiv.), and conc. H₂SO₄ (30 mol%). Then a solution of the tautomer of α -hydroxyalkylketones and lactols (0.2 mmol, 1.0 equiv.) in DCM (1.0 M) at 0 °C was added. Then, the reaction mixture was stirred for 1 h from 0 °C to 25 °C. After the reaction completed, it was diluted with DCM (5.0 mL) and H₂O (5.0 mL). The organic layer was separated and the water layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with saturated brine, dried over Na₂SO₄ and concentrated in vacuo. The crude products of **1** were used in the next step without further purification.

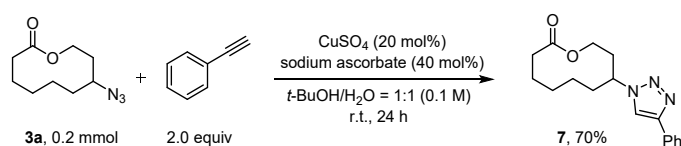
Second step:

Followed the above-mentioned representative procedure for ring-expansion/cyanation or azidation or thiocyanation or halogenation of **1**. The total yields based on the mixture of α -hydroxyalkyl ketones and lactols were given in Scheme 2 and 3.

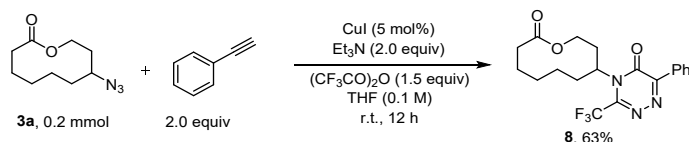
5. Procedures for Diverse Derivatizations of **2a**, **3a** and **4a**⁴⁻⁷



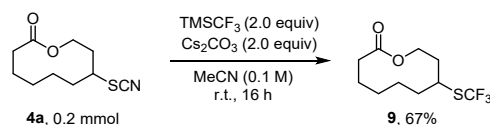
To a 10 mL reaction tube equipped with a magnetic stirrer was added **2a** (0.2 mmol, 1.0 equiv.), Cu(OAc)₂ (0.04 mmol, 2 mol%), NEt₂OH (0.6 mmol, 3.0 equiv.) in H₂O (1 mL). The reaction mixture was stirred at 25°C for 3 h. After the reaction completed, the reaction mixture was diluted with EtOAc (5.0 mL) and H₂O (5.0 mL). The organic layer was separated and the water layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with saturated brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate) to give the target product **6** in 60% yield.



To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added **3a** (0.2 mmol, 1.0 equiv.), CuSO₄ (0.04 mmol, 20 mol%) and sodium ascorbate (0.08 mmol, 40 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of phenylacetylene (0.4 mmol, 2.0 equiv.) in *t*-BuOH/H₂O (1:1, 2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 24 h. After the reaction completed, the reaction mixture was diluted with EtOAc (5.0 mL) and H₂O (5.0 mL). The organic layer was separated and the water layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with saturated brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the target product **7** in 70% yield.

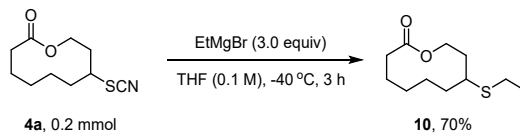


To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added **3a** (0.2 mmol, 1.0 equiv.), CuI (0.01 mmol, 5 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of phenylacetylene (0.4 mmol, 2.0 equiv.), Et₃N (0.4 mmol, 2.0 equiv.) and (CF₃CO)₂O (0.3 mmol, 1.5 equiv.) in dry THF (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 12 h. After the reaction completed, the reaction mixture was concentrated in vacuo and was further purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the target product **8** in 63% yield.



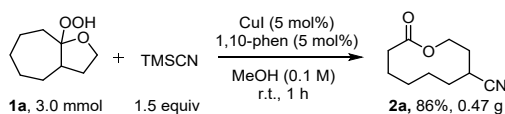
To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added **4a** (0.2 mmol, 1.0 equiv.), Cs₂CO₃ (0.4 mmol, 2.0 equiv.). Then, the tube was evacuated and backfilled with nitrogen for

three times. Subsequently, MeCN (2.0 mL) was added by syringe under nitrogen atmosphere. Then, TMSCF₃ (0.4 mmol, 2.0 equiv.) was added slowly by microsyringe at 0 °C. The tube was then sealed and the mixture was stirred at 25 °C for 16 h. After the reaction completed, the reaction mixture was concentrated in vacuo and was further purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1) to give the target product **9** in 67% yield.

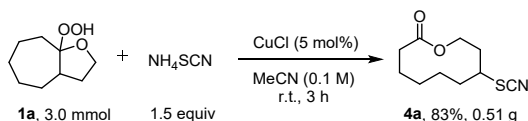


To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added **4a** (0.2 mmol, 1.0 equiv.), and backfilled with nitrogen for three times. Subsequently, dry THF (2.0 mL) was added by syringe under nitrogen atmosphere. Then, EtMgBr (1M THF) (0.6 mmol, 3.0 equiv.) was added slowly at -40 °C. The tube was then sealed and the mixture was stirred at -40 °C for 3 h. After the reaction completed, the reaction mixture was concentrated in vacuo, and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give the target product **10** in 70% yield.

6. Scale-up Synthesis



To a 100 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuI (0.15 mmol, 5 mol%), 1,10-phen (0.15 mmol, 5 mol%). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **1a** (3 mmol, 1.0 equiv.), and TMSCN (4.5 mmol, 1.5 equiv.) in MeOH (30 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 1 h. After the reaction completed, the reaction mixture was concentrated in vacuo, and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target products **2a** (470 mg, 86%).

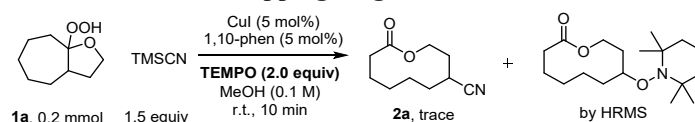


To a 100 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuCl (0.15 mmol, 5 mol%), NH₄SCN (4.5 mmol, 1.5 equiv.). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **1a** (3 mmol, 1.0 equiv.) in MeCN (30 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 3 h. After the reaction completed, the reaction mixture was concentrated in vacuo, and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target products **4a** (513 mg, 83%).

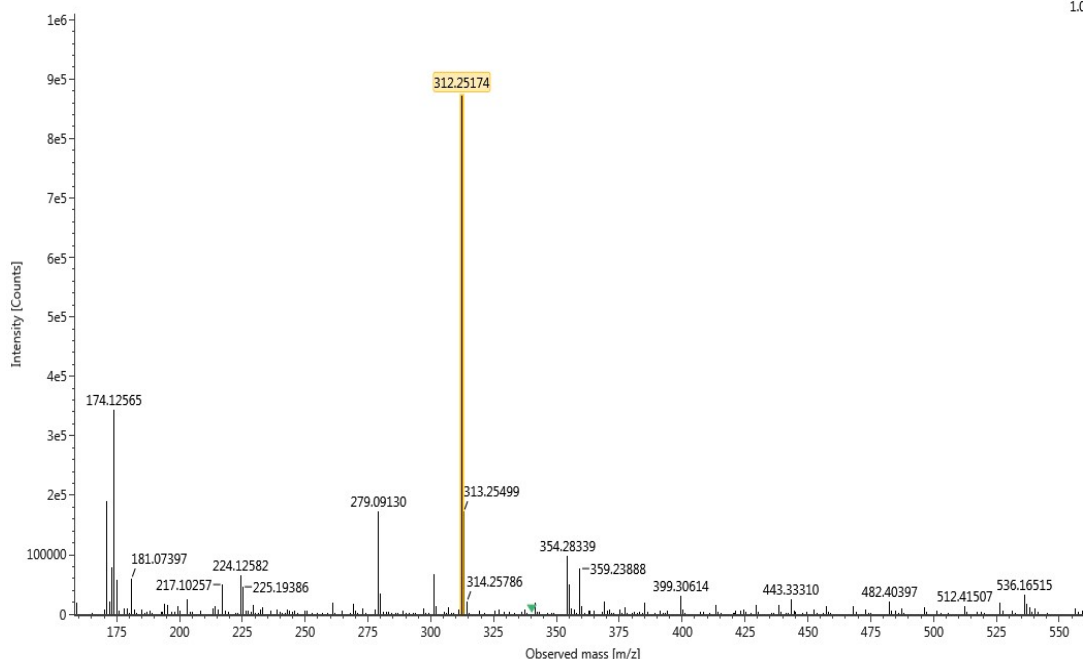
7. Investigation of the Reaction Mechanism

7.1 Radical Trapping Experiments

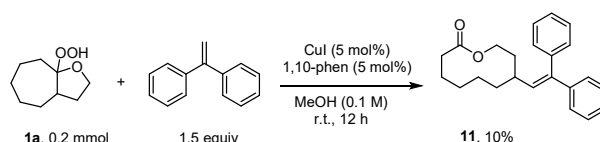
(1) Using TEMPO as the radical trapping reagent



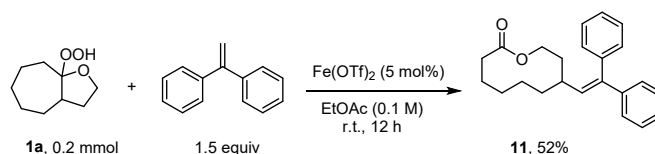
To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%), and TEMPO (0.4 mmol, 2.0 equiv.). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **1a** (0.2 mmol, 1.0 equiv.), and TMSCN (0.3 mmol, 1.5 equiv.) in MeOH (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 10 min. After the reaction completed, it was found that the reaction was totally inhibited and the TEMPO-adduct could be detected by LC-MS (HRMS (ESI) calcd for C₁₈H₃₄NO₃ [M+H]⁺ 312.2533, found 312.2517. These results indicate that a radical intermediate might be involved in this transformation.



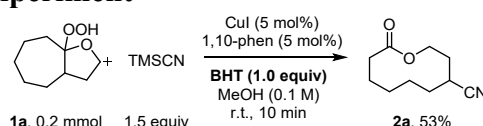
(2) Using 1,1-diphenylethylene as the radical trapping reagent



To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%), and 1,1-diphenylethylene (1.5 equiv.). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) in MeOH (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 12 h. After the reaction completed, the reaction mixture was concentrated in vacuo, and then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the alkenylated product **11** in 10% yield. This result proved that the reaction probably proceeded *via* a radical pathway. Notably, when the reaction was conducted under the Fe(OTf)₂ catalysis in EtOAc, a 52% yield of **11** could be obtained.



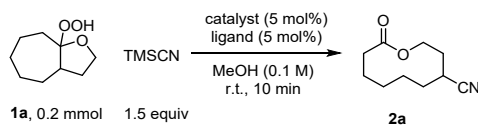
7.2 Radical Inhibiting Experiment



To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added CuI (0.01 mmol, 5 mol%), 1,10-phen (0.01 mmol, 5 mol%), and BHT (0.2 mmol, 1.0 equiv.). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **1a** (0.2 mmol, 1.0 equiv.), and TMSCN (0.3 mmol, 1.5 equiv.) in MeOH (2.0 mL) was added by syringe under

nitrogen atmosphere. The tube was then sealed and the mixture was stirred at 25 °C for 10 min. After the reaction completed, the reaction mixture was concentrated in vacuo, and then purified by column chromatography on silica gel. In this case, the yield of **2a** was reduced to 53%. This result indicates that the reaction might proceed via a radical pathway.

7.3 Ligand Effect Experiments



^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), catalyst (0.01 mmol, 5 mol%),

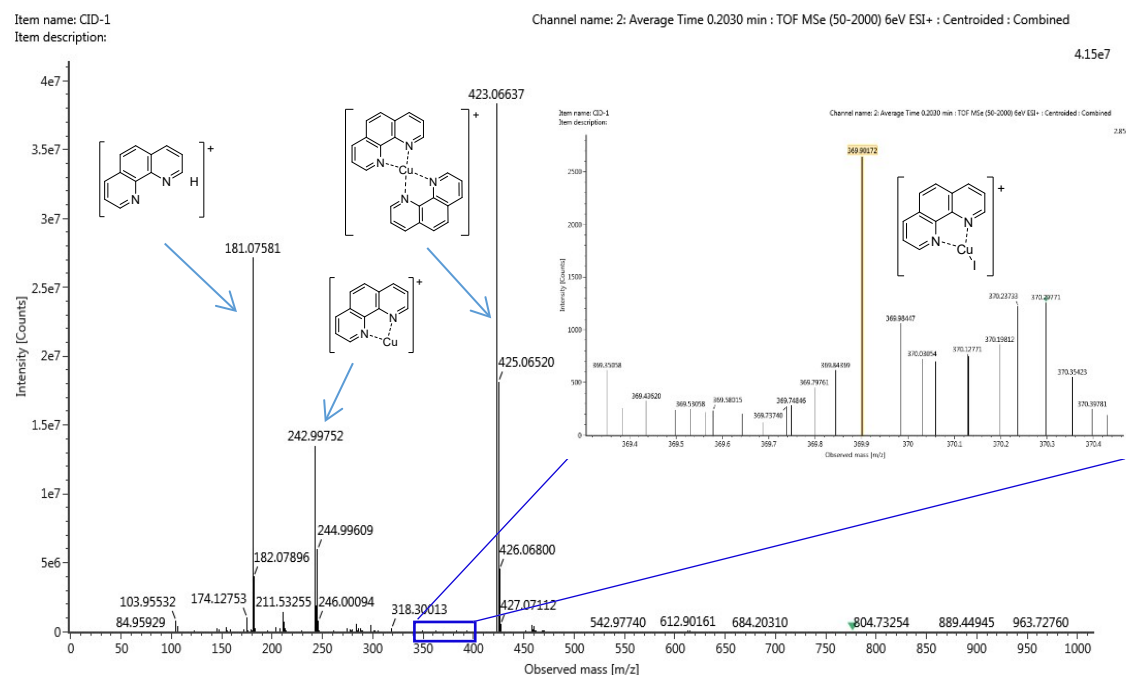
Entry	Catalyst + Ligand (5 mol%)	Yield (%)
1	CuI+1,10-phen	95
2	CuI+2,2'-bpy	70
3	CuI	40
4	CuI·(1,10-phen) complex	77

ligand (0.01 mmol, 5 mol%), and MeOH (2.0 mL) at 25 °C for 10 min under N₂. Isolated yields.

8. Mass Spectrometry Experiments

The experiments were performed with an I-Class VION IMS Q-ToF instrument with an electrospray ion source, it was purchased from the Waters company. The instrument equipped a quadrupole mass filter after ion source for the selection of target ions. In the collision induced dissociation (CID) process, the mass-selected ions enter an argon filled linear ion trap (argon pressure: 8×10^{-3} mbar) after accelerated by electric field. After collision, the ions enter a reflection time-of-flight (TOF) region for determination. For a given ion of interest, its type is defined via mass-to-charge ratio and collision induced dissociation. Collision induced dissociation was also employed to analyze structural fragments.

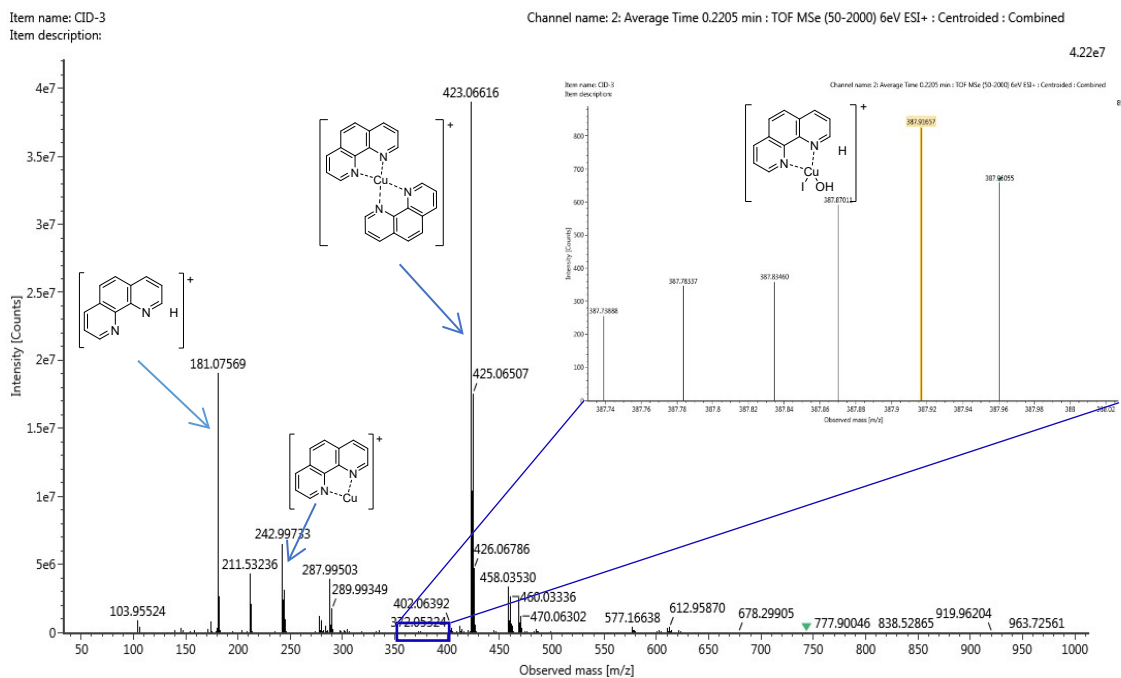
Procedure 1. CuI (0.01 mmol) and 1,10-phen (0.015 mmol) were dissolved in MeOH (1.0 mL), and the mixture was stirred at room temperature for 30 minutes. After 30 minutes, 10.0 μ L reaction mixture was picked up with pipette and dissolved into 1.0 mL MeCN. Next, this dilution was transferred into an injection syringe, and injected into the high-resolution electrospray mass spectrometry (I-Class VION IMS Q-ToF) by injection pump. Finally, the MS data were collected and analyzed.



The mass spectra of **procedure 1**

The mass spectra of procedure 1. We successfully detected moderate intensity of the intermediate **[Cu(1,10-phen)I]⁺** HRMS (ESI) calcd for $C_{12}H_8CuIN_2$ [M]⁺ 369.9028, found 369.9017.

Procedure 2: CuI (0.01 mmol) and 1,10-phen (0.015 mmol) were dissolved in MeOH (1.0 mL), and the mixture was stirred at room temperature for 30 minutes. Then hemiketal hydroperoxide **1a** (0.1 mmol) was added to the mixture. After 30 minutes, 10.0 μ L reaction mixture was picked up with pipette and dissolved into 1.0 mL MeCN. Next, this dilution was transferred into an injection syringe, and injected into the high-resolution electrospray mass spectrometry (I-Class VION IMS Q-ToF) by injection pump. Finally, the MS data were collected and analyzed.



The mass spectra of **procedure 2**

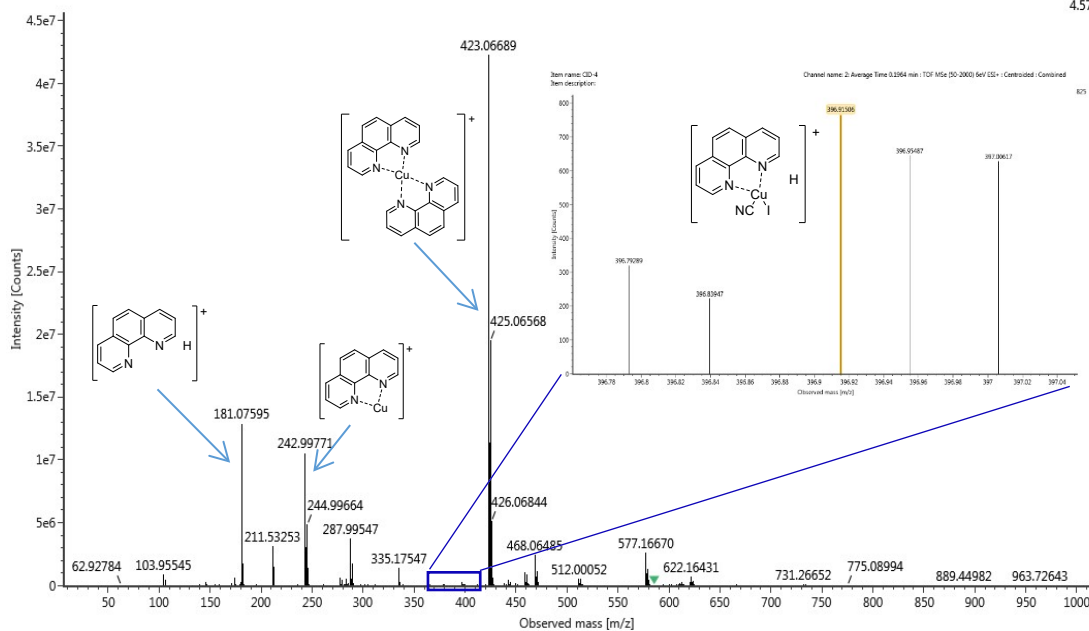
The mass spectra of procedure 2. We successfully detected moderate intensity of the intermediate **[Cu(1,10-phen)(OH)I]H⁺** HRMS (ESI) calcd for C₁₂H₁₀CuIN₂O [M+H]⁺ 387.9128, found 387.9165.

Procedure 3: CuI (0.01 mmol) and 1,10-phen (0.015 mmol) were dissolved in MeOH (1.0 mL), and the mixture was stirred at room temperature for 30 minutes. Then hemiketal hydroperoxide **1a** (0.1 mmol) was added to the mixture, and the reaction mixture was stirred at room temperature for 30 minutes. Finally, TMSCN (0.1 mmol) was added to the mixture. After 30 minutes, 10.0 μ L reaction mixture was picked up with pipette and dissolved into 1.0 mL MeCN. Next, this dilution was transferred into an injection syringe, and injected into the high-resolution electrospray mass spectrometry (I-Class VION IMS Q-ToF) by injection pump. At last, the MS data were collected and analyzed.

Item name: CID-4
Item description:

Channel name: 2: Average Time 0.1964 min : TOF MSe (50-2000) 6eV ESI+ : Centroided : Combined

4.57e7



The mass spectra of procedure 3

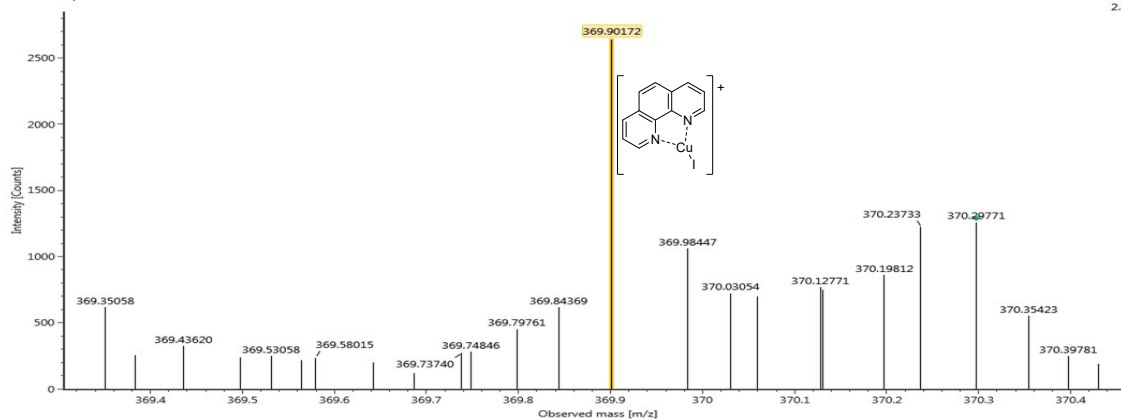
The mass spectra of procedure 3. We successfully detected moderate intensity of the intermediate $[\text{Cu}(\text{1,10-phen})(\text{CN})]\text{I}^+\text{H}^+$ HRMS (ESI) calcd for $\text{C}_{13}\text{H}_9\text{CuIN}_3$ $[\text{M}+\text{H}]^+$ 396.9132, found 396.9150.

Related CID data:

Item name: CID-1
Item description:

Channel name: 2: Average Time 0.2030 min : TOF MSe (50-2000) 6eV ESI+ : Centroided : Combined

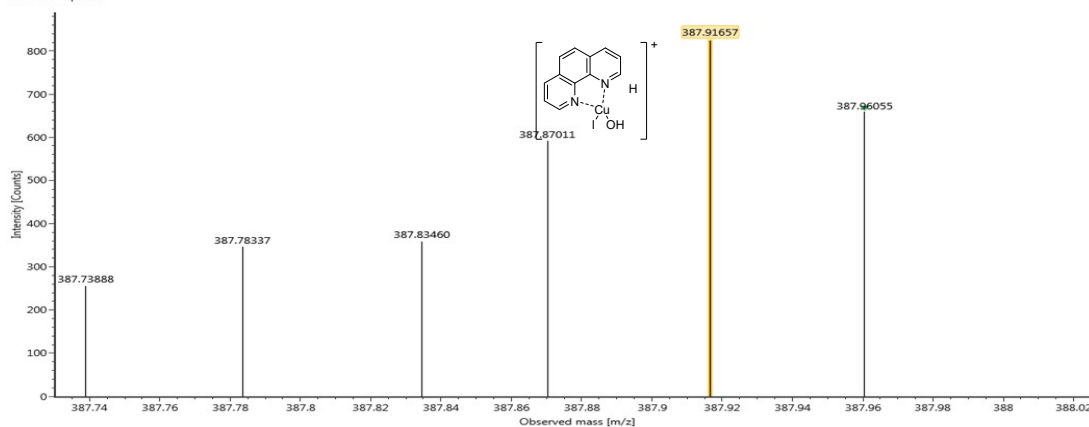
2.85e3

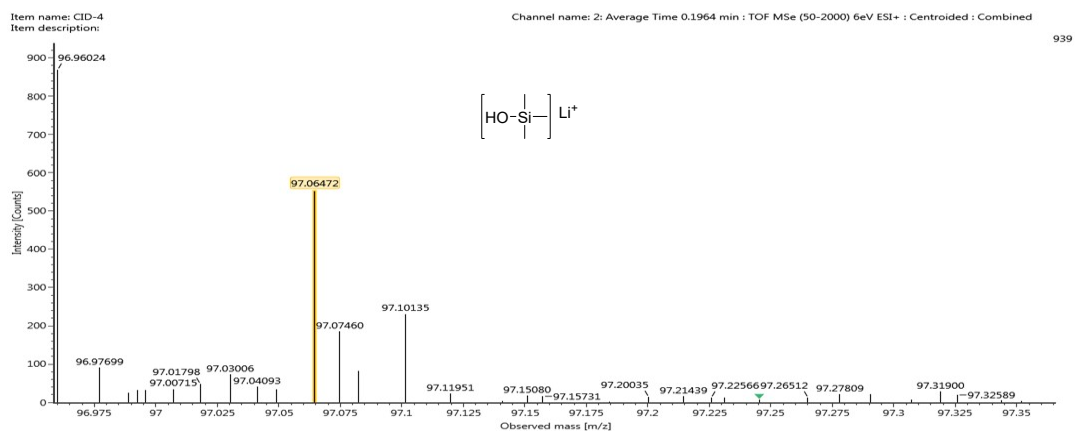
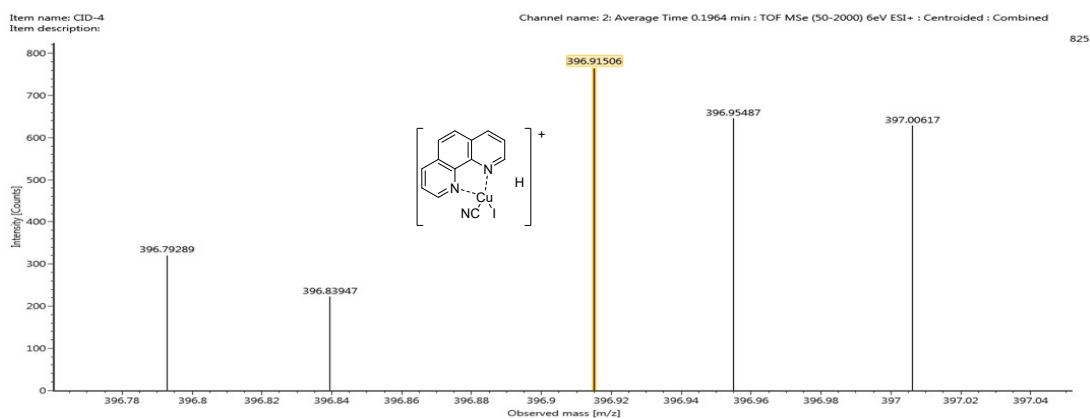


Item name: CID-3
Item description:

Channel name: 2: Average Time 0.2205 min : TOF MSe (50-2000) 6eV ESI+ : Centroided : Combined

890





9. Computational Details

All calculations were carried out with the Gaussian 16 Rev. A.03.⁸ Molecular geometry optimizations and frequency calculations were performed by the B3LYP⁹ functional with D3(BJ) dispersion correction¹⁰, which have been proven to be particularly effective in calculating transition metal complexes. Frequency calculations were conducted to determine the stationary points (no imaginary frequencies) and transition state structures (only one imaginary frequency). A mixed basis set of SDD¹¹ was used for Cu and I, the 6-31G(d)¹² was used for all other atoms. The single point energies were calculated at the B3LYP-D3(BJ)/def2-TZVP¹³ level with SMD¹⁴ solvation model (methanol as solvent). All the transition states were confirmed by using the IRC (intrinsic reaction coordinate)¹⁵ calculation. Molecular structure visualizations were generated by using CYL view 1.0¹⁶.

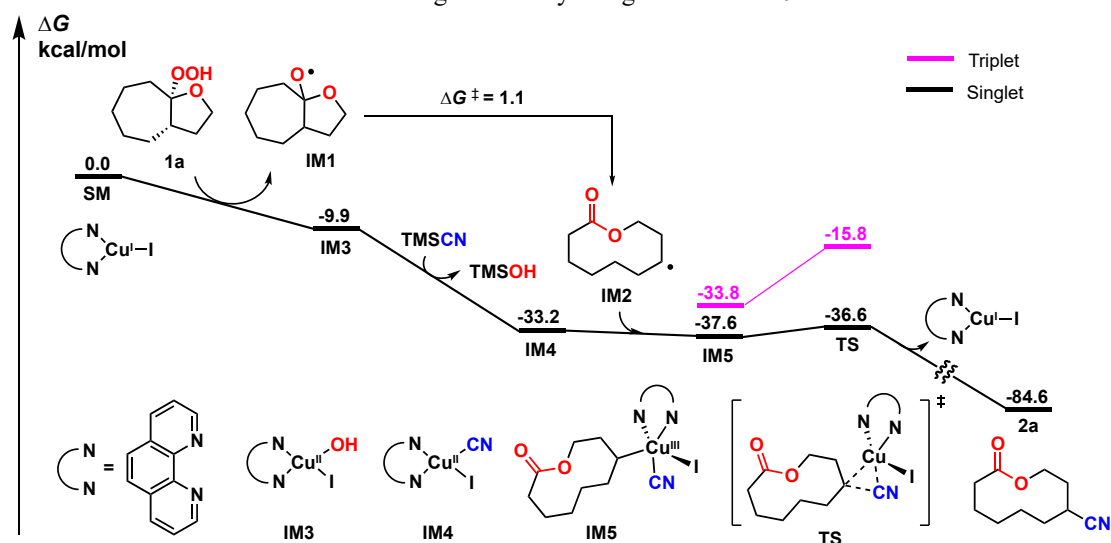


Figure S1: Computed Energy Profile for the Cu-Catalyzed Ring Expansion/Cyanation Reaction in Singlet and Triplet State. Energies are in kcal/mol.

The Cartesian Coordinates of Calculated Structures.**SM**

C	-1.54475400	6.49144200	0.32439700
C	-2.12634900	7.77202900	0.40994200
C	-3.49004100	7.87869400	0.60257300
C	-4.27265700	6.70714900	0.70982500
C	-3.59440400	5.46843500	0.61081800
C	-4.33767300	4.23526000	0.71254900
C	-4.31293700	1.92174400	0.70324700
C	-5.70489500	1.86531700	0.89946600
C	-6.41820900	3.04346700	1.00310500
C	-5.73877700	4.27806900	0.91039500
C	-6.39584400	5.55084000	1.00642200
C	-5.69357700	6.71528000	0.91035000
H	-6.20101900	7.67288800	0.98446000
H	-7.47128300	5.56609200	1.15821300
H	-7.49396200	3.03391500	1.15485600
H	-6.19675300	0.90102800	0.96640600
H	-3.71950200	1.01719600	0.61733600
H	-3.96966900	8.85112000	0.67286000
H	-1.50003300	8.65349700	0.32398500
H	-0.47672100	6.36144600	0.17333500
Cu	-1.63050200	3.30706700	0.32758500
I	0.63649800	2.39776600	0.00451300
N	-3.64683400	3.06920400	0.61215500
N	-2.25722000	5.37781700	0.42187000

1a

C	-0.45115700	1.81782800	1.45542500
C	-1.47420600	0.71422400	1.78277900
C	-2.14917300	0.08889200	0.54620300
C	-1.36427800	-1.03086500	-0.17327100
C	0.15954000	-0.92479400	-0.09100100
C	0.75588100	0.46807600	-0.39763100
C	0.87897600	1.36794600	0.83308600
C	0.94437500	-1.86308100	-1.01740000
C	2.30804600	-1.17561700	-1.06068100
H	-0.21226500	2.36452900	2.37664400
H	-0.93031300	2.54008700	0.78370900
H	-1.01313100	-0.06260800	2.40987800
H	-2.25620900	1.17079100	2.40235500
H	-3.12513700	-0.31668100	0.83963200
H	-2.35274800	0.89465000	-0.16685300
H	-1.64174900	-2.00398000	0.25273800

H	-1.66310600	-1.05379300	-1.22617200
H	0.46564600	-1.15393200	0.93833900
H	1.47171000	0.80732800	1.56594400
H	1.47002000	2.24487700	0.54855900
H	1.00544700	-2.88751900	-0.63695600
H	0.48588000	-1.88343800	-2.00960500
H	2.86706500	-1.34684800	-1.98590600
H	2.93851600	-1.48588700	-0.21524900
H	0.87859700	0.66271900	-2.87599600
O	2.04516800	0.23362600	-0.96034400
O	0.01040100	1.25452100	-1.32360300
O	-0.05179700	0.55894800	-2.59462500

2a

C	4.67450900	0.87270900	-1.45414600
C	3.45879700	0.11343600	-2.02105700
H	3.39525900	0.27230400	-3.10398200
H	2.54349200	0.54648000	-1.60020900
C	3.52663000	-1.40257300	-1.74344900
H	4.06306200	-1.58573200	-0.80755000
H	4.14394700	-1.87100700	-2.51997600
C	2.17350900	-2.12459500	-1.70571300
C	1.30136000	-1.74417500	-0.47982200
C	1.97466800	-2.08493500	0.88565300
H	1.39335600	-2.84042900	1.42364700
H	2.96316300	-2.51618700	0.71128000
C	2.11830100	-0.86379200	1.78943900
H	1.14279700	-0.48917400	2.10817900
O	2.70758800	0.24629100	1.07665200
C	4.05793400	0.24331600	0.93329700
O	4.78596000	-0.57750400	1.44855900
C	4.49448500	1.35602000	0.00629300
H	3.74552300	2.15274000	0.03555600
H	5.44368300	1.75068600	0.38013200
H	2.72796900	-1.09659900	2.66527700
H	1.12518500	-0.66310400	-0.51550200
C	-0.01359900	-2.38527400	-0.58733500
N	-1.04836000	-2.90543200	-0.67116600
H	2.33666500	-3.20882600	-1.68685000
H	1.60679600	-1.90856700	-2.61945900
H	5.56540900	0.23562400	-1.51352500
H	4.88417800	1.76078000	-2.06064800

IM1

C	-0.48075400	1.84916900	1.43538100
C	-1.50541000	0.75249500	1.77482500
C	-2.14531300	0.08678700	0.54250600
C	-1.34709400	-1.06341000	-0.10423800
C	0.17515300	-0.94027500	-0.06829200
C	0.79914000	0.48231800	-0.38521700
C	0.86536800	1.38024700	0.88376100
C	0.92989700	-1.81226000	-1.07596200
C	2.32441900	-1.18012300	-1.09379100
H	-0.27156800	2.43138000	2.34262400
H	-0.93940200	2.54326100	0.72099900
H	-1.05189000	-0.00330200	2.43282900
H	-2.30390700	1.22032000	2.36386100
H	-3.13280800	-0.30484200	0.81554700
H	-2.31689100	0.86363200	-0.20980200
H	-1.59717900	-2.00805300	0.39728600
H	-1.67526900	-1.17374400	-1.14448100
H	0.53804300	-1.17033000	0.94106400
H	1.41693900	0.80007600	1.63226300
H	1.48809200	2.24326700	0.62611500
H	0.94832200	-2.86820200	-0.78750100
H	0.45138400	-1.73397900	-2.05852800
H	2.81279800	-1.25498200	-2.07146100
H	2.98264800	-1.64546800	-0.34628600
O	2.15081500	0.20056700	-0.76114900
O	0.08462000	1.06991400	-1.34985200

IM2

C	-0.31628500	1.79888300	1.46131400
C	-1.39975700	0.71687400	1.60311800
C	-1.87979900	0.06784100	0.28170000
C	-1.49787700	-1.43145500	0.13523500
C	-0.04229500	-1.74449900	0.25342900
C	0.87292800	1.38849500	-0.74489700
C	0.98069600	1.33276500	0.77536900
C	0.89089600	-1.89138400	-0.90315000
C	1.97595200	-0.80594000	-1.02150500
H	-0.06392100	2.16671400	2.46315100
H	-0.70616100	2.65183100	0.89645300
H	-1.03341600	-0.06431700	2.28321800
H	-2.25404000	1.17536500	2.11549600
H	-2.97291100	0.13058200	0.21500700
H	-1.50049900	0.62695100	-0.57854200
H	-2.04773400	-1.98823400	0.90852200

H	-1.87330100	-1.78438200	-0.83499100
H	0.38401100	-1.84928700	1.24966700
H	1.27475900	0.35171600	1.14896900
H	1.79224000	2.02817700	1.02945900
H	1.42857100	-2.85229900	-0.83350600
H	0.33608100	-1.90648000	-1.84909900
H	2.71088600	-1.09983500	-1.77603700
H	2.50671700	-0.66208400	-0.07515500
O	1.44137100	0.42719800	-1.51669700
O	0.33740900	2.31613700	-1.30798300

IM3

C	-1.54661200	6.31846300	0.25104800
C	-2.06299800	7.62098300	0.39124200
C	-3.41021100	7.79712300	0.63708600
C	-4.24879200	6.66530900	0.74396200
C	-3.63949600	5.39940300	0.58865000
C	-4.44114700	4.21215700	0.68705200
C	-4.47451400	1.89781100	0.60724900
C	-5.86252100	1.88441900	0.85332000
C	-6.53691800	3.08048200	1.01746800
C	-5.82871500	4.30136500	0.93689300
C	-6.41930900	5.60045200	1.09002900
C	-5.66122700	6.73153900	0.99735100
H	-6.11776700	7.71002500	1.11475700
H	-7.48624500	5.66735000	1.28202800
H	-7.60659600	3.09383200	1.20800100
H	-6.38534200	0.93596600	0.91104800
H	-3.87253500	1.00451300	0.46716300
H	-3.83285200	8.79180100	0.74914300
H	-1.39175100	8.46819800	0.30354600
H	-0.49465300	6.13309100	0.05731900
Cu	-1.73567200	3.20196300	0.16884100
I	0.82402800	3.63062200	-0.26710200
O	-1.69572600	1.36900200	0.09202800
H	-0.78201600	1.09321300	-0.08000800
N	-3.80056000	3.03578600	0.52968500

IM4

C	-1.39775400	1.42710800	-0.15932400
N	-1.49474000	0.28498300	-0.38497600
C	-1.51768600	6.34955500	0.23408900
C	-2.06672100	7.64326600	0.30706600
C	-3.41902800	7.79497200	0.53962700

C	-4.23078700	6.64894300	0.69240800
C	-3.59306800	5.39086300	0.59443000
C	-4.36907500	4.18951700	0.72630700
C	-4.37693700	1.87297500	0.70682400
C	-5.76640400	1.84766400	0.93994400
C	-6.45639700	3.03776500	1.06519800
C	-5.76166800	4.26406000	0.95516900
C	-6.38016300	5.55475500	1.05802200
C	-5.64549600	6.69724000	0.93193400
H	-6.12247400	7.66985500	1.00834300
H	-7.45012700	5.60458500	1.23707200
H	-7.52813500	3.04404500	1.24323500
H	-6.27501900	0.89287700	1.01443400
H	-3.78886500	0.96846000	0.58086200
H	-3.86712900	8.78244600	0.60614700
H	-1.41624800	8.50201000	0.18404700
H	-0.45645200	6.18359800	0.07991100
Cu	-1.61516600	3.26886500	0.30256700
N	-3.70795100	3.01494500	0.61194800
N	-2.25883600	5.25547900	0.37329500
I	0.90189300	3.75218800	0.84179100

IM5

C	0.64000100	1.16612400	-1.52672300
C	0.59398900	-0.17952300	-2.27938500
H	0.57824000	0.02060400	-3.35715200
H	-0.36603000	-0.66290400	-2.06367900
C	1.76994300	-1.14193500	-1.96840800
H	2.28910800	-0.81643800	-1.06236400
H	2.51320100	-1.07031200	-2.77163700
C	1.36707800	-2.62984400	-1.81978600
C	0.53071400	-2.81216000	-0.56694400
C	1.30846300	-2.77908000	0.74496000
H	1.50528400	-3.78450000	1.12885800
H	2.29329400	-2.34120900	0.54215800
C	0.62778100	-1.94304500	1.83768200
H	-0.17213000	-2.48862400	2.33584600
O	-0.04168600	-0.79408500	1.26132900
C	0.75661700	0.21127100	0.82456100
O	1.92875600	0.31103500	1.11706800
C	0.01680300	1.14426400	-0.11141600
H	-1.03678400	0.85313700	-0.16457900
H	0.07298800	2.15309900	0.31362800
H	1.35460200	-1.60532100	2.57929600

H	-0.26647800	-2.07592400	-0.55588800
C	0.61298500	-5.32536400	-0.94592600
N	1.58076300	-5.95260100	-1.12448400
C	-2.50757400	-3.26527400	1.62569100
C	-3.33712900	-2.36818700	2.31687600
C	-3.90507100	-1.31304200	1.62909300
C	-3.67987900	-1.18421300	0.24260700
C	-2.84678300	-2.14819500	-0.37553900
C	-2.64575600	-2.11034900	-1.80377400
C	-1.72667500	-3.10094200	-3.66956900
C	-2.28015900	-2.12010900	-4.51663100
C	-3.03662700	-1.10593700	-3.96204300
C	-3.25144100	-1.08054000	-2.56641400
C	-4.04497600	-0.08640600	-1.90272100
C	-4.25603300	-0.14060300	-0.55696800
H	-4.87531900	0.60350700	-0.06476200
H	-4.49124100	0.70395000	-2.49938000
H	-3.47674500	-0.33269500	-4.58557000
H	-2.10707100	-2.17241400	-5.58610300
H	-1.12984700	-3.91710400	-4.06732700
H	-4.53618200	-0.59053300	2.13861900
H	-3.51045000	-2.50986200	3.37772400
H	-2.04536500	-4.11037200	2.12478400
H	2.25785200	-3.26157000	-1.77527500
H	0.80643400	-2.93771300	-2.70688800
H	1.67603200	1.51586500	-1.44923500
H	0.09315300	1.92350900	-2.10087300
Cu	-0.88882700	-4.30334900	-0.64536500
N	-2.24651600	-3.13722600	0.32950500
N	-1.89652600	-3.08795100	-2.35705400
I	-2.58453800	-6.31025800	-0.67183000

TS

C	0.06730800	1.26577000	-0.53124700
C	0.08693700	0.14845900	-1.59602000
H	0.12603100	0.59423300	-2.57467500
H	0.75339100	-0.53086300	-1.40388300
C	1.42035700	-0.64081100	-1.68938300
H	2.03379600	-0.43753400	-0.80665100
H	1.99997800	-0.26498300	-2.54096800
C	1.25911800	-2.17129000	-1.85785600
C	0.66699800	-2.75338100	-0.59072700
C	1.59735100	-2.87627300	0.61002200
H	2.03400000	-3.87419800	0.69295200

H	2.43332700	-2.18358400	0.46053300
C	0.90225000	-2.51819900	1.92609900
H	0.22589000	-3.31063000	2.25250900
O	0.03602700	-1.36804100	1.74528800
C	0.63886700	-0.18206500	1.48287300
O	1.82043400	0.02322300	1.65807300
C	0.33599300	0.81649600	0.89287200
H	1.34170500	0.38575400	0.88608300
H	0.34521700	1.69586100	1.54730800
H	1.62942400	-2.30885800	2.71347900
H	0.20519200	-2.16700000	-0.31934100
C	0.71424400	-4.86850300	-1.25809500
N	1.60984500	-5.40621700	-1.78305700
C	-2.67579800	-2.73141400	1.29586400
C	-3.60530900	-1.76011800	1.70485100
C	-4.22489200	-0.97939800	0.74906600
C	-3.93619000	-1.18955800	-0.61722500
C	-2.99414400	-2.19820400	-0.93613200
C	-2.69490800	-2.48034700	-2.31960600
C	-1.52999000	-3.77082300	-3.83747900
C	-2.09913000	-3.07880700	-4.92554200
C	-2.99264200	-2.05511500	-4.67511100
C	-3.32250900	-1.72563900	-3.34135600
C	-4.24804400	-0.68990800	-2.98281300
C	-4.54573900	-0.43729000	-1.67675800
H	-5.25694100	0.34019900	-1.41331500
H	-4.71740000	-0.11562100	-3.77640000
H	-3.44943500	-1.50163100	-5.49094800
H	-1.83104100	-3.35550400	-5.93949400
H	-0.81655400	-4.57754500	-3.98421600
H	-4.94065200	-0.21280400	1.03265800
H	-3.81499700	-1.63340100	2.76098500
H	-2.17660900	-3.37281100	2.01283600
H	2.22319100	-2.63780000	-2.07781400
H	0.60357900	-2.37315700	-2.70988700
H	1.04983500	1.74933700	-0.48212600
H	-0.64959100	2.03920000	-0.83110900
Cu	-0.88629200	-4.21399800	-0.64195500
N	-2.36458600	-2.92768900	0.02097800
N	-1.82185400	-3.47646500	-2.58013800
I	-2.08928100	-6.35267600	0.22007600

TMSCN

Si	-0.99502900	0.56596300	-0.05984900
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C	-0.37154700	1.44820500	1.46788000
N	0.01607700	1.99684800	2.41786100
C	-0.32933600	1.50763900	-1.54351000
H	-0.66264000	1.03652700	-2.47591100
H	-0.68073500	2.54490400	-1.54558500
H	0.76573300	1.52217400	-1.54585700
C	-2.87225800	0.60838600	0.01371600
H	-3.30033700	0.10359800	-0.86055300
H	-3.24593900	0.10362900	0.91092400
H	-3.24592600	1.63777400	0.02511900
C	-0.32911700	-1.18965700	0.01395900
H	-0.68086700	-1.71029600	0.91095700
H	-0.66190500	-1.76145600	-0.86051100
H	0.76595100	-1.19878500	0.02589600

TMSI

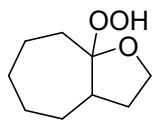
Si	-0.99919900	0.56017700	-0.06995300
C	-0.33497300	1.49972400	-1.55516000
H	-0.67323200	1.02244500	-2.48415700
H	-0.68733400	2.53614500	-1.55616800
H	0.75963500	1.51217600	-1.55692300
C	-2.87618700	0.60109500	0.00115100
H	-3.29704000	0.09392700	-0.87686700
H	-3.24814500	0.09559600	0.89805800
H	-3.24826400	1.63054700	0.01145900
C	-0.33462900	-1.19565300	0.00138400
H	-0.68840000	-1.71533500	0.89754300
H	-0.67114600	-1.76114000	-0.87738000
H	0.75996000	-1.20301900	0.01324200
I	-0.16046700	1.74716800	1.98534600

TMSOH

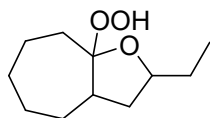
Si	-0.98112200	0.60353400	-0.01548400
C	-0.35791800	1.50289300	-1.55097800
H	-0.71595500	1.00952700	-2.46322900
H	-0.70308900	2.54360300	-1.58733300
H	0.73748700	1.51292900	-1.58455400
C	-2.86656200	0.61582400	-0.01467100
H	-3.25953900	0.11059100	-0.90580200
H	-3.26373400	0.09760300	0.86558500
H	-3.27183300	1.63528000	-0.01364000
C	-0.33132500	-1.15461100	0.03061900
H	-0.68163300	-1.67887500	0.92660700
H	-0.66572900	-1.72370600	-0.84496100

H	0.76414600	-1.16779100	0.04223600
O	-0.38044600	1.32209100	1.38033500
H	-0.62584500	2.24755600	1.51435000

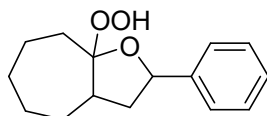
10. Characterization of Hemiketal Hydroperoxides 1



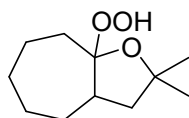
8a-Hydroperoxyoctahydro-2H-cyclohepta[b]furan (1a) White solid (1.0 g, 58%, two steps). Melting point (°C): 46-47. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.59 (br, 1H), 3.95 – 3.90 (m, 1H), 3.84 – 3.77 (m, 1H), 2.41 – 2.36 (m, 1H), 2.15 – 1.99 (m, 2H), 1.75 – 1.71 (m, 3H), 1.63 – 1.47 (m, 4H), 1.42 – 1.33 (m, 1H), 1.29 – 1.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 117.9, 66.9, 47.5, 34.4, 32.3, 31.7, 31.2, 28.3, 23.2. IR (neat): ν_{max} (cm^{-1}) 2938, 1734, 1267, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{16}\text{O}_3\text{Li}$ $[\text{M}+\text{Li}]^+$ 179.1254, found 179.1262.



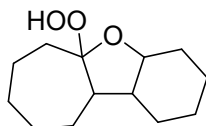
2-Ethyl-8a-hydroperoxyoctahydro-2H-cyclohepta[b]furan (1b) Colorless oil (1.3 g, 65%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 7:1). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (br, 0.6H), 4.15 – 3.91 (m, 1H), 2.48 – 2.33 (m, 1H), 2.20 – 2.15 (m, 1H), 2.10 – 1.99 (m, 1H), 1.78 – 1.61 (m, 6H), 1.53 – 1.46 (m, 2H), 1.39 – 1.24 (m, 3H), 1.19 – 1.14 (m, 1H), 0.94 – 0.90 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) major isomer δ 117.6, 79.4, 47.8, 39.7, 32.5, 31.9, 31.3, 28.2, 27.5, 23.3, 10.1; minor isomer δ 118.5, 82.1, 47.5, 39.1, 32.7, 32.1, 31.1, 29.8, 29.3, 23.3, 10.6. IR (neat): ν_{max} (cm^{-1}) 2895, 1268, 755. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3\text{K}$ $[\text{M}+\text{K}]^+$ 239.1044, found 239.1046.



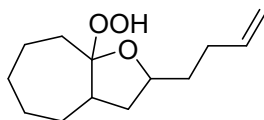
8a-Hydroperoxy-2-phenyloctahydro-2H-cyclohepta[b]furan (1c) Colorless oil (0.7 g, 28%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.62 (br, 0.7H), 7.31 – 7.20 (m, 5H), 4.18 – 4.10 (m, 1H), 3.98 – 3.93 (m, 1H), 2.98 – 2.91 (m, 1H), 2.48 – 2.42 (dd, J = 14.0, 7.6 Hz, 1H), 2.13 – 2.07 (m, 1H), 1.75 – 1.56 (m, 6H), 1.44 – 1.19 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.0, 128.8, 128.1, 127.2, 118.1, 73.0, 56.2, 32.0, 31.4, 30.6, 27.9, 23.3. IR (neat): ν_{max} (cm^{-1}) 2967, 1756, 1421, 1267, 755, 689. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$ 266.1751, found 266.1735.



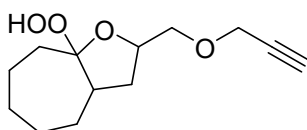
8a-Hydroperoxy-2,2-dimethyloctahydro-2H-cyclohepta[b]furan (1d) Colorless oil (0.4 g, 20%, two steps). $R_f = 0.3$ (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (br, 1H), 2.37 – 2.32 (m, 1H), 2.29 – 2.21 (m, 1H), 2.10 (dd, $J = 12.4, 8.8$ Hz, 1H), 1.80 – 1.71 (m, 3H), 1.67 – 1.42 (m, 6H), 1.36 (s, 3H), 1.29 (s, 3H), 1.27 – 1.26 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 118.4, 82.3, 48.1, 46.7, 32.8, 32.7, 31.3, 29.8, 28.6, 28.3, 23.3. IR (neat): ν_{max} (cm^{-1}) 2894, 1730, 1266, 753. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$ 218.1751, found 218.1762.



5a-Hydroperoxydodecahydro-1H-cyclohepta[b]benzofuran (1e) White solid (1.03 g, 46%, two steps). Melting point ($^{\circ}\text{C}$): 92-93. $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.63 (s, 0.2H), 8.47 (s, 0.7H), 3.49 – 3.40 (m, 1H), 2.55 – 2.29 (m, 1H), 2.14 – 1.95 (m, 2H), 1.89 – 1.57 (m, 10H), 1.41 – 1.31 (m, 2H), 1.29 – 1.08 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) major isomer δ 118.3, 82.1, 50.2, 48.2, 33.7, 32.3, 31.2, 30.6, 25.8, 25.7, 24.9, 24.2, 23.5. minor isomer δ 117.5, 81.0, 52.9, 52.5, 35.1, 31.6, 30.7, 30.0, 27.9, 27.2, 26.0, 25.1, 24.3. IR (neat): ν_{max} (cm^{-1}) 2978, 2298, 1268, 755. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{26}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$ 244.1907, found 244.1921.

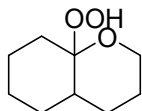


2-(But-3-en-1-yl)-8a-hydroperoxyoctahydro-2H-cyclohepta[b]furan (1f) Colorless oil (0.8 g, 35%, two steps). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 0.14H), 7.75 (s, 0.85H), 5.89 – 5.78 (m, 1H), 5.06 – 4.94 (m, 2H), 4.24 – 4.17 (m, 0.88H), 4.04 – 3.97 (m, 0.13H), 2.46 – 2.33 (m, 1H), 2.22 – 1.98 (m, 4H), 1.85 – 1.67 (m, 4H), 1.65 – 1.51 (m, 5H), 1.47 – 1.24 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 118.6, 115.0, 80.1, 47.5, 39.5, 36.1, 32.6, 32.2, 31.2, 30.7, 29.2, 23.2. IR (neat): ν_{max} (cm^{-1}) 2922, 2098, 1722, 1640, 1448, 1006, 910, 639. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{K}$ $[\text{M}+\text{K}]^+$ 265.1200, found 265.1191.

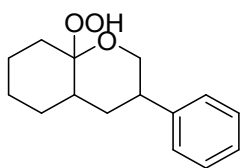


8a-Hydroperoxy-2-((prop-2-yn-1-yloxy)methyl)octahydro-2H-cyclohepta[b]furan (1g) Colorless oil (0.7 g, 29%, two steps). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3)

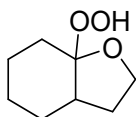
δ 8.59 (s, 1H), 4.46 – 4.40 (m, 1H), 4.28 – 4.18 (m, 2H), 3.68 – 3.59 (m, 2H), 2.67 (t, J = 2.4 Hz, 1H), 2.44 (t, J = 6.4 Hz, 1H), 2.27 – 2.15 (m, 2H), 1.84 – 1.74 (m, 2H), 1.68 – 1.52 (m, 5H), 1.46 – 1.26 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 118.1, 79.6, 76.67, 74.9, 71.8, 58.7, 47.3, 36.5, 32.5, 31.8, 31.2, 28.2, 23.2. IR (neat): ν_{max} (cm^{-1}) 2937, 2176, 1722, 1407, 1260, 669. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{24}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$ 258.1700, found 258.1714.



8a-Hydroperoxyoctahydro-2H-chromene (1h) Colorless oil (0.73 g, 42%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 6:1). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (br, 0.6H), 3.94 – 3.87 (m, 1H), 3.74 – 3.70 (m, 1H), 2.27 – 2.20 (m, 1H), 1.76 – 1.68 (m, 2H), 1.65 – 1.56 (m, 4H), 1.53 – 1.47 (m, 1H), 1.39 – 1.33 (m, 3H), 1.27 – 1.19 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) major isomer δ 103.9, 61.8, 43.7, 32.3, 29.5, 26.3, 25.9, 24.9, 22.8; minor isomer δ 104.3, 62.2, 35.6, 33.3, 28.3, 25.1, 24.2, 22.9, 20.3. IR (neat): ν_{max} (cm^{-1}) 2928, 1268, 1078, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{16}\text{O}_3\text{Li}$ $[\text{M}+\text{Li}]^+$ 179.1254, found 179.1244.

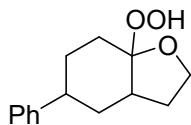


8a-Hydroperoxy-3-phenyloctahydro-2H-chromene (1i) Colorless oil (0.5 g, 20%, two steps) R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (br, 0.6H), 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 3.93 – 3.77 (m, 2H), 2.20 – 2.98 (m, 1H), 2.38 – 2.35 (m, 1H), 1.90 – 1.77 (m, 3H), 1.71 – 1.60 (m, 3H), 1.55 – 1.46 (m, 2H), 1.37 – 1.26 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 128.7, 127.5, 126.9, 103.3, 66.8, 43.6, 43.4, 32.1, 31.7, 29.4, 25.9, 22.9. IR (neat): ν_{max} (cm^{-1}) 2893, 1271, 755, 701. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$ 249.1485, found 249.1499.

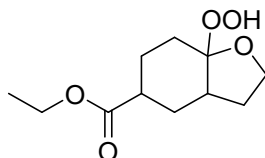


7a-Hydroperoxyoctahydrobenzofuran (1j) Colorless oil (0.79 g, 50%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (br, 0.5H), 4.08 – 3.99 (m, 2H), 2.36 – 2.19 (m, 2H), 2.03 – 1.97 (m, 1H), 1.73 – 1.50 (m, 5H), 1.32 – 1.03 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3)

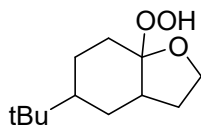
δ 113.1, 66.9, 40.2, 30.7, 29.69, 29.65, 24.0, 22.4. IR (neat): $\nu_{\max}$ (cm⁻¹) 2987, 2360, 1268, 755. HRMS (ESI) calcd for C₈H₁₈NO₃ [M+NH₄]⁺ 176.1281, found 176.1269.



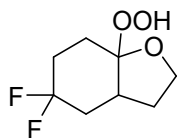
7a-Hydroperoxy-5-phenyloctahydrobenzofuran (1k) White solid (0.93 g, 40%, two steps). Melting point (°C): 79-80. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ¹H NMR (400 MHz, CDCl₃) δ 8.38 (br, 0.5H), 7.33 – 7.28 (m, 2H), 7.23 – 7.20 (m, 3H), 4.20 – 4.10 (m, 2H), 2.63 – 2.57 (m, 2H), 2.37 – 2.35 (m, 1H), 2.28 – 2.22 (m, 1H), 1.94 – 1.86 (m, 3H), 1.68 – 1.57 (m, 2H), 1.39 – 1.29 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 146.1, 128.6, 126.8, 126.4, 112.6, 67.1, 42.3, 40.9, 38.0, 30.7, 30.2, 29.9. IR (neat): $\nu_{\max}$ (cm⁻¹) 2893, 2378, 1267, 755. HRMS (ESI) calcd for C₁₄H₁₉O₃ [M+H]⁺ 235.1329, found 235.1334.



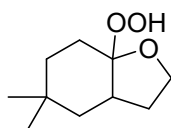
Ethyl 7a-hydroperoxyoctahydrobenzofuran-5-carboxylate (1l) Colorless oil (0.85 g, 37%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (br, 0.4H), 4.15 – 3.99 (m, 4H), 2.61 – 2.45 (m, 1H), 2.34 – 2.04 (m, 3H), 2.02 – 1.79 (m, 2H), 1.76 – 1.35 (m, 3H), 1.32 – 1.19 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 175.3, 112.2, 66.9, 60.6, 41.4, 39.9, 31.9, 30.6, 29.0, 25.4, 14.3. IR (neat): $\nu_{\max}$ (cm⁻¹) 2923, 1725, 1267, 755. HRMS (ESI) calcd for C₁₁H₁₈O₅Na [M+Na]⁺ 253.1046, found 253.1028.



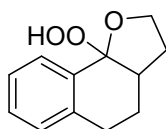
5-(tert-butyl)-7a-Hydroperoxyoctahydrobenzofuran (1m) White solid (1.1 g, 51%, two steps). Melting point (°C): 50-51. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (br, 0.3H), 4.09 – 3.99 (m, 2H), 2.43 – 2.40 (m, 1H), 2.32 – 2.23 (m, 1H), 2.04 – 1.98 (m, 1H), 1.74 – 1.63 (m, 3H), 1.55 – 1.50 (m, 1H), 1.08 – 0.99 (m, 2H), 0.83 – 0.81 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 113.1, 67.0, 46.0, 41.2, 32.3, 31.3, 31.1, 30.1, 27.6, 23.5. IR (neat): $\nu_{\max}$ (cm⁻¹) 2921, 1268, 755. HRMS (ESI) calcd for C₁₂H₂₂O₃Na [M+Na]⁺ 237.1461, found 237.1461.



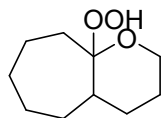
5,5-Difluoro-7a-hydroperoxyoctahydrobenzofuran (1n) White solid (1.1 g, 57%, two steps). Melting point (°C): 64-65. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.44 (br, 1H), 4.14 – 4.06 (m, 2H), 2.46 – 2.27 (m, 3H), 2.20 – 1.98 (m, 3H), 1.95 – 1.78 (m, 1H), 1.67 – 1.50 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 122.8 (t, J = 239 Hz), 111.5, 67.1, 38.3 (d, J = 9 Hz), 35.9 (t, J = 24 Hz), 30.1, 30.0 (t, J = 25 Hz), 26.1 (d, J = 8 Hz). IR (neat): ν_{max} (cm^{-1}) 2918, 1369, 1267, 755. HRMS (ESI) calcd for $\text{C}_8\text{H}_{12}\text{F}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 217.0647, found 217.0645.



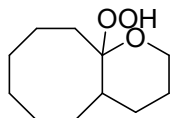
7a-Hydroperoxy-5,5-dimethyloctahydrobenzofuran (1o) Colorless oil (0.56 g, 30%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.73 – 7.39 (br, 0.4H), 4.08 – 3.98 (m, 2H), 2.33 – 2.23 (m, 2H), 2.19 – 2.12 (m, 1H), 1.90 – 1.82 (m, 1H), 1.51 – 1.46 (m, 1H), 1.40 – 1.23 (m, 3H), 0.99 (d, J = 12.8 Hz, 1H), 0.91 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 113.0, 66.7, 42.7, 37.6, 35.1, 31.9, 30.6, 30.1, 26.3, 23.3. IR (neat): ν_{max} (cm^{-1}) 2923, 1268, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 209.1148, found 209.1163.



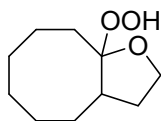
9b-Hydroperoxy-2,3,3a,4,5,9b-hexahydronaphtho[1,2-b]furan (1p) White solid (0.37 g, 18%, two steps). Melting point (°C): 70-71. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.0 Hz, 1H), 7.47 (td, J = 7.6, 1.2 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 3.87 – 3.84 (m, 2H), 3.10 – 2.96 (m, 2H), 2.73 – 2.66 (m, 1H), 2.40 (br, 1H), 2.27 – 2.15 (m, 2H), 2.02 – 1.92 (m, 1H), 1.79 – 1.72 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 133.5, 132.3, 128.7, 127.6, 126.7, 100.0, 61.3, 46.0, 33.3, 29.7, 28.9. IR (neat): ν_{max} (cm^{-1}) 2923, 1268, 755. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 229.0835, found 229.0829.



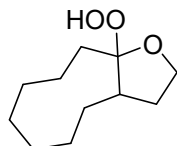
9a-Hydroperoxydecahydrocyclohepta[b]pyran (1q) White solid (0.56 g, 30%, two steps). Melting point (°C): 43–44. $R_f = 0.3$ (petroleum ether/ethyl acetate = 7:1). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (br, 0.6H), 3.79 – 3.69 (m, 2H), 2.47 – 2.42 (m, 0.5H), 2.26 – 2.20 (m, 0.5H), 1.88 – 1.57 (m, 8H), 1.50 – 1.27 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 108.5, 106.5, 69.8, 64.8, 61.8, 61.4, 45.0, 38.7, 36.5, 34.0, 31.4, 31.0, 30.8, 29.8, 27.72, 27.65, 26.8, 26.6, 26.4, 25.9, 21.5, 21.1, 20.7. IR (neat): ν_{max} (cm^{-1}) 2897, 2278, 1268, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 209.1148, found 209.1161.



10a-Hydroperoxydecahydro-2H-cycloocta[b]pyran (1r) Colorless oil (0.5 g, 25%, two steps). $R_f = 0.3$ (petroleum ether/ethyl acetate = 15:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (s, 0.25H), 7.69 (s, 0.7H), 3.84 – 3.68 (m, 2H), 2.05 – 1.88 (m, 3H), 1.82 – 1.38 (m, 13H), 1.27 – 1.08 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) major isomer δ 106.8, 61.4, 38.7, 34.2, 30.8, 29.3, 28.1, 26.6, 26.3, 24.7, 21.4; minor isomer δ 107.7, 61.9, 35.4, 31.5, 29.8, 29.2, 27.6, 26.3, 25.7, 21.5, 20.10. IR (neat): ν_{max} (cm^{-1}) 2931, 2332, 1722, 1421, 1223, 710. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 223.1304, found 223.1305.

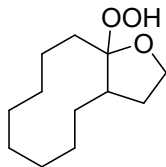


9a-Hydroperoxydecahydrocycloocta[b]furan (1s) Colorless oil (1.1 g, 59%, two steps). $R_f = 0.3$ (petroleum ether/ethyl acetate = 6:1). ^1H NMR (400 MHz, CDCl_3) δ 8.66 (br, 0.7H), 3.85 – 3.72 (m, 2H), 2.23 – 2.18 (m, 2H), 1.96 – 1.86 (m, 1H), 1.72 – 1.60 (m, 5H), 1.54 – 1.39 (m, 6H), 1.34 – 1.30 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) major isomer δ 116.8, 65.2, 45.0, 36.3, 31.6, 30.6, 28.4, 25.3 (overlapped), 24.3. minor isomer δ 113.2, 65.8, 45.3, 36.25, 35.3, 33.7, 29.7, 28.1, 25.5, 22.7. IR (neat): ν_{max} (cm^{-1}) 2987, 2321, 1268, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 209.1148, found 209.1152.

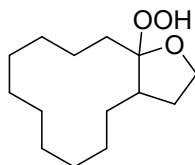


10a-Hydroperoxydecahydro-2H-cyclonona[b]furan (1t) Colorless oil (0.8 g, 40%, two steps). $R_f = 0.3$ (petroleum ether/ethyl acetate = 15:1). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 11.2$ Hz, 0.14H), 8.07 (d, $J = 7.2$ Hz, 0.86H), 3.99 – 3.75 (m, 2H), 2.48 – 2.26 (m, 2H), 2.15 – 2.02 (m, 1H), 1.91 – 1.68 (m, 5H), 1.61 – 1.44 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) minor isomer δ 117.7, 65.6, 45.0, 35.8, 30.7,

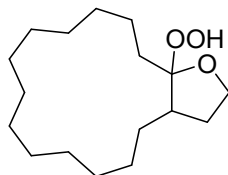
28.1, 27.7, 25.7, 25.4, 25.1, 21.8 (overlapped); major isomer δ 114.0, 66.1, 45.4, 34.7, 33.2, 29.4, 29.2, 29.1, 26.1, 25.9, 21.8 (overlapped). IR (neat): $\nu_{\max}$ (cm⁻¹) 2922, 2101, 1721, 1422, 1166, 821. HRMS (ESI) calcd for C₁₁H₂₀O₃ [M]⁺ 200.1407, found 200.1399.



11a-Hydroperoxydodecahydrocycloodeca[b]furan (1u) Colorless oil (0.7 g, 20%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.80 (s, 0.3H), 10.75 (s, 0.7H), 3.91 – 3.85 (m, 0.7H), 3.78 – 3.65 (m, 1.3H), 2.40 – 2.32 (m, 0.6H), 2.16 – 1.95 (m, 1.5H), 1.89 – 1.70 (m, 3H), 1.65 – 1.24 (m, 14H). ¹³C NMR (100 MHz, DMSO-*d*₆) major isomer δ 113.2, 65.8, 41.4, 33.12, 30.7, 27.7, 26.3, 24.3, 23.9, 23.6, 23.3, 19.5; minor isomer δ 116.0, 64.9, 42.5, 33.06, 29.2, 28.5, 27.0, 25.8, 25.7, 23.7, 23.5, 21.7. IR (neat): $\nu_{\max}$ (cm⁻¹) 2922, 2101, 1721, 1422, 1166, 821. HRMS (ESI) calcd for C₁₂H₂₂O₃Li [M+Li]⁺ 221.1723, found 221.1726.

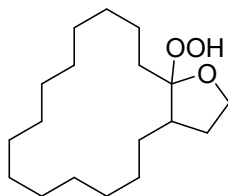


13a-Hydroperoxytetradecahydrocycloodeca[b]furan (1v) White solid (1.25 g, 52%, two steps). Melting point (°C): 92-93. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ¹H NMR (400 MHz, CDCl₃) δ 8.47 (br, 0.7H), 4.11 (td, J = 8.8, 2.0 Hz, 1H), 3.89 – 3.83 (m, 1H), 2.33 – 2.21 (m, 1H), 2.10 – 2.00 (m, 2H), 1.87 – 1.69 (m, 2H), 1.65 – 1.59 (m, 1H), 1.49 – 1.27 (m, 17H). ¹³C NMR (100 MHz, CDCl₃) δ 115.0, 68.3, 40.0, 30.6, 27.5, 26.2, 26.0, 25.0, 24.2, 22.3, 22.2, 22.0, 21.7, 19.5. IR (neat): $\nu_{\max}$ (cm⁻¹) 2987, 1268, 755. HRMS (ESI) calcd for C₁₄H₂₆O₃Na [M+Na]⁺ 265.1774, found 265.1788.

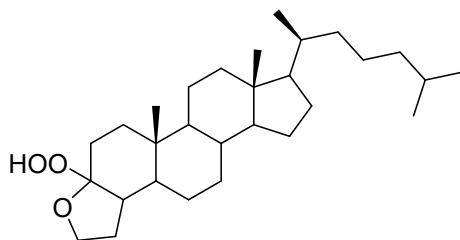


16a-Hydroperoxyhexadecahydro-2H-cyclopentadeca[b]furan (1w) Colorless oil (0.28 g, 10%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ¹H NMR (400 MHz, CDCl₃) δ 8.67 (br, 0.6H), 4.10 – 3.78 (m, 2H), 2.16 – 1.99 (m, 2H), 1.90 – 1.69 (m, 2H), 1.45 – 1.27 (m, 25). ¹³C NMR (100 MHz,

CDCl₃) δ 117.1, 114.2, 67.6, 66.7, 44.6, 42.7, 33.6, 31.8, 30.7, 29.6, 27.8, 27.7, 27.3, 26.79, 26.75, 26.71, 26.67, 26.6, 26.5, 26.4, 26.33, 26.30, 26.23, 26.15, 26.0, 25.3, 25.1, 22.6, 22.4. IR (neat): $\nu_{\max}$ (cm⁻¹) 2921, 1752, 1267, 755. HRMS (ESI) calcd for C₁₇H₃₃O₃ [M+H]⁺ 285.2424, found 285.2415.

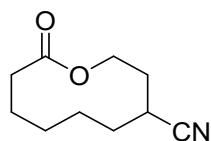


17a-Hydroperoxyoctadecahydrocyclohexadeca[b]furan (1x) Colorless oil (1.2 g, 40%, two steps). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (br, 0.3H), 4.11 – 3.82 (m, 2H), 2.21 – 1.97 (m, 2H), 1.90 – 1.75 (m, 2H), 1.68 – 1.61 (m, 1H), 1.43 – 1.21 (m, 26H). ¹³C NMR (100 MHz, CDCl₃) 117.1, 114.3, 67.7, 66.8, 44.2, 42.9, 32.7, 31.2, 30.3, 29.7, 28.5, 27.8, 27.7, 27.5, 27.4, 27.3, 27.2, 27.0, 26.9, 26.8, 26.6, 26.54, 26.47, 26.4, 26.3, 26.11, 26.06, 25.8, 23.3, 22.7. IR (neat): $\nu_{\max}$ (cm⁻¹) 2924, 1250, 1268, 755. HRMS (ESI) calcd for C₁₈H₃₅O₃ [M+H]⁺ 299.2581, found 299.2573.

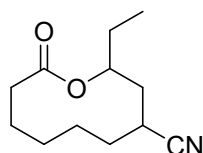


(5aR,7aR)-3a-Hydroperoxy-5a,7a-dimethyl-8-((S)-6-methylheptan-2-yl)octadecahydro-2H-cyclopenta[7,8]phenanthro[2,1-b]furan (1y) White solid (2.0 g, 45%, two steps). Melting point (°C): 150-151. R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (br, 0.7H), 4.17 – 3.94 (m, 2H), 2.35 – 2.26 (m, 1H), 2.18 – 2.04 (m, 2H), 2.01 – 1.94 (m, 1H), 1.85 – 1.72 (m, 2H), 1.67 – 1.60 (m, 2H), 1.57 – 1.44 (m, 4H), 1.35 – 1.19 (m, 9H), 1.16 – 1.05 (m, 6H), 1.03 – 0.94 (m, 3H), 0.90 – 0.85 (m, 11H), 0.80 (s, 3H), 0.64 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 113.2, 66.8, 56.5, 56.3, 53.5, 42.6, 42.3, 42.0, 40.1, 39.6, 37.4, 36.2, 36.0, 35.9, 35.4, 33.4, 31.9, 30.8, 28.3, 28.1, 24.3, 23.9, 22.9, 22.7, 21.3, 18.8, 12.1, 11.3. IR (neat): $\nu_{\max}$ (cm⁻¹) 2926, 2298, 1268, 755. HRMS (ESI) calcd for C₂₉H₅₁O₃ [M+H]⁺ 447.3833, found 447.3813.

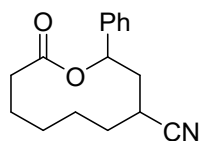
11. Characterization of Functionalized Lactones 2-5



10-Oxooxecane-4-carbonitrile (2a) Colorless oil (34.4 mg, 95%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.42 – 4.34 (m, 2H), 2.85 – 2.79 (m, 1H), 2.45 – 2.27 (m, 2H), 2.23 – 2.15 (m, 1H), 2.03 – 1.81 (m, 4H), 1.79 – 1.71 (m, 1H), 1.58 – 1.48 (m, 2H), 1.37 – 1.28 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 122.1, 62.4, 34.6, 28.4, 27.2, 26.9, 26.4, 20.7, 20.3. IR (neat): ν_{max} (cm^{-1}) 2932, 2398, 1725, 1267, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 182.1175, found 182.1157.

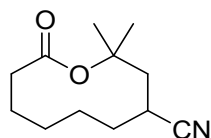


2-Ethyl-10-oxooxecane-4-carbonitrile (2b) Colorless oil (41.0 mg, 98%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). d.r. = 3:1, ^1H NMR (400 MHz, CDCl_3) δ 4.88 – 4.82 (m, 1H), 3.02 – 2.96 (m, 0.22H), 2.57 – 2.44 (m, 1.85H), 2.36 – 2.15 (m, 2H), 2.00 – 1.89 (m, 3H), 1.87 – 1.34 (m, 7H), 1.25 – 1.15 (m, 1H), 0.95 – 0.91 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.8, 123.1, 75.6, 34.79, 32.9, 28.4, 27.24, 27.15, 26.1, 23.0, 20.5, 9.9; minor isomer δ 173.4, 122.1, 74.1, 34.75, 29.8, 26.5, 26.4, 25.23, 25.19, 20.8, 20.3, 10.1. IR (neat): ν_{max} (cm^{-1}) 2927, 2093, 1727, 1265, 755. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{NH}_4]^+$ 227.1754, found 227.1761.

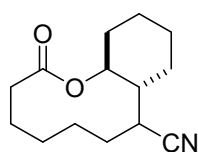


10-Oxo-2-phenyloxecane-4-carbonitrile (2c) Colorless oil (50.6 mg, 98%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 8:1). d.r. = 1.8:1 ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.23 (m, 5H), 4.58 (dd, $J = 11.8, 3.4$ Hz, 0.51H), 4.14 – 4.12 (m, 0.24H), 4.07 (t, $J = 11.6$ Hz, 0.61H), 3.96 – 3.91 (m, 0.29H), 3.57 (td, $J = 11.6, 3.2$ Hz, 0.53H), 3.14 (td, $J = 11.6, 3.6$ Hz, 0.5H), 3.00 – 2.93 (m, 0.27H), 2.58 (dd, $J = 4.4, 2.4$ Hz, 0.23H), 2.54 (dd, $J = 4.0, 2.4$ Hz, 0.33H), 2.49 – 2.43 (m, 0.29H), 2.37 – 2.28 (m, 1.19H), 2.13 – 1.98 (m, 1H), 1.89 – 1.46 (m, 5.6H), 1.46 – 1.14 (m, 2.68H), 0.94 – 0.86 (m, 0.29H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.2 (overlapped), 137.6, 129.2, 127.9, 127.2,

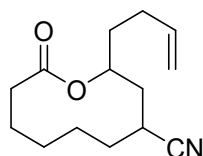
121.0, 67.1, 56.3, 42.5, 36.6, 34.5, 26.8, 26.5, 20.4. minor isomer δ 173.2 (overlapped), 139.1, 128.7, 128.3, 128.1, 118.0, 72.9, 53.9, 31.9, 31.3, 30.6, 28.0, 23.2, 20.5. IR (neat): $\nu_{\max}$ (cm⁻¹) 2928, 2201, 1728, 1248, 754, 699. HRMS (ESI) calcd for C₁₆H₂₀NO₂ [M+H]⁺ 258.1489, found 258.1472.



2,2-Dimethyl-10-oxooxocane-4-carbonitrile (2d) Colorless oil (39.8 mg, 95%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 2.97 – 2.91 (m, 1H), 2.69 (dd, J = 15.2, 10.0 Hz, 1H), 2.36 (ddd, J = 15.2, 8.0, 2.8 Hz, 1H), 2.17 (ddd, J = 15.2, 10.8, 2.8 Hz, 1H), 2.00 – 1.84 (m, 3H), 1.78 – 1.71 (m, 1H), 1.70 – 1.56 (m, 3H), 1.65 (s, 3H), 1.54 – 1.44 (m, 1H), 1.41 – 1.30 (m, 1H), 1.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 122.4, 81.6, 36.3, 34.1, 28.4, 26.8, 26.6, 26.3, 25.6, 21.1, 19.9. IR (neat): $\nu_{\max}$ (cm⁻¹) 2931, 2203, 1727, 1267, 755. HRMS (ESI) calcd for C₁₂H₂₀NO₂ [M+H]⁺ 210.1488, found 210.1470.

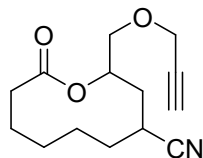


2-Oxododecahydro-2H-benzo[b]oxecine-8-carbonitrile (2e) Colorless oil (43.2 mg, 92%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). d.r. > 20:1, ¹H NMR (400 MHz, CDCl₃) δ 4.49 (td, J = 10.3, 4.8 Hz, 1H), 2.49 (ddd, J = 15.7, 5.9, 3.3 Hz, 1H), 2.33 – 2.18 (m, 3H), 2.10 – 1.96 (m, 2H), 1.93 – 1.79 (m, 3H), 1.78 – 1.70 (m, 3H), 1.66 – 1.53 (m, 2H), 1.38 – 1.27 (m, 3H), 1.26 – 1.17 (m, 2H), 1.15 – 1.03 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 122.3, 77.7, 44.5, 36.3, 35.1, 32.6, 31.6, 29.8, 26.0, 25.3, 25.1, 24.4, 20.3. IR (neat): $\nu_{\max}$ (cm⁻¹) 2931, 2210, 1724, 1249, 755. HRMS (ESI) calcd for C₁₄H₂₂NO₂ [M+H]⁺ 236.1645, found 236.1628.

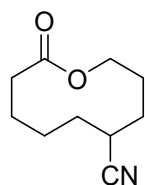


2-(But-3-en-1-yl)-10-oxooxocane-4-carbonitrile (2f) Colorless oil (26.1 mg, 56%). R_f = 0.3 (petroleum ether/ethyl acetate = 15:1). d.r. = 3:1, ¹H NMR (400 MHz, CDCl₃) δ 5.83 – 5.73 (m, 1H), 5.06 – 4.93 (m, 3H), 2.59 – 2.46 (m, 2H), 2.26 – 2.19 (m, 2H), 2.13 – 2.08 (m, 2H), 2.0 – 1.87 (m, 4H), 1.80 – 1.71 (m, 2H), 1.68 – 1.56 (m, 3H), 1.45 – 1.36 (m, 1H), 1.26 – 1.15 (m, 1H). ¹³C NMR (100 MHz, CDCl₃,

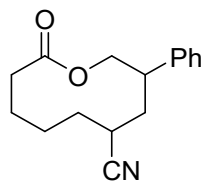
single isomer) δ 173.8, 137.2, 123.0, 115.6, 73.8, 34.9, 33.3, 33.0, 29.7, 28.4, 27.1, 26.2, 23.0, 20.6. IR (neat): $\nu_{\max}$ (cm^{-1}) 3076, 2237, 1726, 1640, 1455, 1251, 842. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{22}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 236.1645, found 236.1651.



10-Oxo-2-((prop-2-yn-1-yloxy)methyl)oxecane-4-carbonitrile (2g) Colorless oil (30.0 mg, 60%). R_f = 0.3 (petroleum ether/ethyl acetate = 12:1). d.r. = 3:1, ^1H NMR (400 MHz, CDCl_3) δ 5.15 – 5.10 (m, 0.24H), 5.05 – 5.00 (m, 0.75H), 4.19 (t, J = 2.4 Hz, 2H), 3.74 – 3.65 (m, 2H), 3.14 – 3.08 (m, 0.23H), 2.56 – 2.45 (m, 2.84H), 2.33 – 2.20 (m, 2H), 2.15 – 1.90 (m, 3H), 1.82 – 1.55 (m, 4H), 1.51 – 1.36 (m, 1H), 1.25 – 1.11 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.8, 122.7, 79.1, 75.2, 72.6, 70.3, 58.6, 34.8 (overlapped), 31.6, 28.6, 27.6, 26.2, 23.3, 20.6; minor isomer δ 173.3, 121.9, 79.0, 75.4, 70.9, 69.8, 58.7, 34.8 (overlapped), 29.4, 26.7, 26.6, 26.1, 21.0, 20.9. IR (neat): $\nu_{\max}$ (cm^{-1}) 3272, 2958, 2239, 1723, 1455, 1092. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 250.1437, found 250.1433.

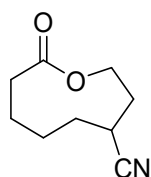


10-Oxo-5-carbonitrile (2h) Colorless oil (29.0 mg, 80%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.75 – 4.70 (m, 1H), 3.89 – 3.83 (m, 1H), 3.11 – 3.04 (m, 1H), 2.59 – 2.53 (m, 1H), 2.23 – 2.16 (m, 1H), 2.13 – 1.89 (m, 3H), 1.83 – 1.75 (m, 2H), 1.69 – 1.56 (m, 4H), 1.54 – 1.46 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 123.4, 65.3, 34.5, 29.7, 26.7, 26.5, 25.5, 23.1, 20.2. IR (neat): $\nu_{\max}$ (cm^{-1}) 2893, 2298, 1726, 1267, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 204.0995, found 204.1011.

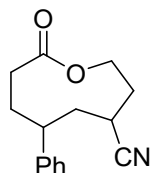


10-Oxo-3-phenyloxecane-5-carbonitrile (2i) Colorless oil (47.2 mg, 92%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). d.r. = 1.4:1, ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.31 (m, 2H), 7.29 – 7.22

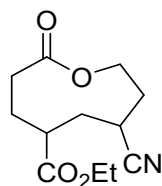
(m, 2H), 7.20 – (m, 1H), 4.77 – 4.73 (m, 0.2H), 4.52 – 4.39 (m, 0.7H), 4.19 – 4.06 (m, 0.7H), 3.93 (t, J = 11.2Hz, 0.2H), 3.81 – 3.73 (m, 0.1H), 3.46 – 3.37 (m, 0.45H), 3.24 – 3.16 (m, 0.64H), 3.01 – 2.96 (m, 0.64H), 2.79 (t, J = 13.2Hz, 0.1H), 2.65 – 2.22 (m, 3H), 2.08 – 1.51 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.3, 140.6, 129.1, 127.6, 127.4, 123.3, 68.99, 44.7, 37.6, 34.7, 31.3, 27.6, 24.4, 20.4; minor isomer δ 172.8, 139.6, 129.0, 127.6, 127.5, 123.1, 68.96, 43.7, 38.3, 36.7, 34.4, 26.2, 25.8, 20.1. IR (neat): ν_{max} (cm^{-1}) 2923, 2237, 1734, 1289, 755. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 258.1489, found 258.1470.



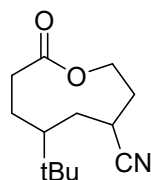
9-Oxooxonane-4-carbonitrile (2j) Colorless oil (29.7 mg, 89%). R_f = 0.3 (petroleum ether/ethyl acetate = 7:1). ^1H NMR (400 MHz, CDCl_3) δ 4.45 – 4.39 (m, 1H), 4.32 – 4.27 (m, 1H), 2.79 – 2.73 (m, 1H), 2.38 – 2.26 (m, 2H), 2.20 – 2.05 (m, 2H), 1.89 – 1.78 (m, 2H), 1.77 – 1.62 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.3, 122.3, 61.6, 34.2, 31.3, 30.5, 26.7, 24.4, 22.1. IR (neat): ν_{max} (cm^{-1}) 2931, 2250, 1726, 1261, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{17}\text{N}_2\text{O}_2$ $[\text{M}+\text{NH}_4]^+$ 185.1285, found 185.1272.



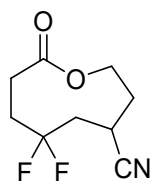
9-Oxo-6-phenyloxonane-4-carbonitrile (2k) Colorless oil (38.8 mg, 80%) R_f = 0.3 (petroleum ether/ethyl acetate = 7:1). d.r. = 1.1:1. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 2H), 7.16 – 7.13 (m, 1H), 4.87 – 4.81 (m, 0.5H), 4.65 – 4.59 (m, 0.43H), 4.30 – 4.24 (m, 0.44H), 4.20 – 4.15 (m, 0.51H), 3.12 – 3.06 (m, 0.43H), 2.93 – 2.86 (m, 1H), 2.78 – 2.71 (m, 0.52H), 2.50 – 2.40 (m, 2.4H), 2.22 – 1.91 (m, 5.4H). ^{13}C NMR (100 MHz, CDCl_3 , both diastereoisomers) 174.2, 173.8, 147.1, 146.1, 129.0, 128.9, 127.2, 127.04, 127.69, 126.8, 122.4, 121.5, 61.6, 61.4, 40.8, 40.7, 40.1, 38.5, 34.4, 32.9, 32.0, 31.3, 29.6, 26.1, 25.4. IR (neat): ν_{max} (cm^{-1}) 2936, 2231, 1732, 1453, 1249, 755, 701. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 244.1332, found 244.1322.



Ethyl 7-cyano-2-oxooxonane-5-carboxylate (2l) Colorless oil (35.9 mg, 75%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 5:1). d.r. = 1.5:1 ^1H NMR (400 MHz, CDCl_3) δ 4.77 – 3.96 (m, 4H), 2.95 – 2.79 (m, 1H), 2.62 – 2.04 (m, 6H), 1.93– 1.48 (m, 3H), 1.30 – 1.25 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3 , both diastereoisomers) δ 175.3, 174.7, 174.3, 173.5, 173.1, 122.0, 121.2, 111.1, 111.0, 66.7, 61.53, 61.49, 61.4, 61.3, 60.5, 41.7, 41.4, 40.4, 40.24, 40.19, 40.1, 33.8, 33.6, 33.3, 32.6, 32.3, 32.0, 31.0, 30.6, 29.8, 29.7, 29.6, 27.9, 27.3, 27.0, 25.53, 25.49, 25.3, 14.3, 14.2. IR (neat): ν_{max} (cm^{-1}) 2935, 2309, 1730, 1453, 1267, 755. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 240.1230, found 240.1219.

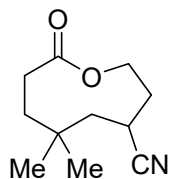


6-(tert-butyl)-9-Oxooxonane-4-carbonitrile (2m) Colorless oil (28.1 mg, 63%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). d.r. = 1:1, ^1H NMR (400 MHz, CDCl_3) δ 4.67 – 4.61 (m, 0.5H), 4.53 – 4.57 (m, 0.5H), 4.29 – 4.23 (m, 0.5H), 4.16 – 4.10 (m, 0.5H), 2.85 – 2.79 (m, 0.5H), 2.59 – 2.53 (m, 0.5H), 2.50 – 2.43 (m, 1H), 2.29 – 1.83 (m, 5H), 1.50 – 1.25 (m, 3H), 0.91 (s, 4.5H), 0.89 (s, 4.5H). ^{13}C NMR (100 MHz, CDCl_3 , both diastereoisomers) δ 175.0, 173.5, 122.9, 122.8, 61.9, 61.7, 47.8, 43.6, 37.1, 36.4, 35.9, 34.6, 34.5, 31.9, 31.0, 30.3, 28.8, 27.7, 27.3, 27.1, 24.9. IR (neat): ν_{max} (cm^{-1}) 2954, 2260, 1738, 1460, 1267, 755. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Li}$ $[\text{M}+\text{Li}]^+$ 230.1727, found 230.1736.

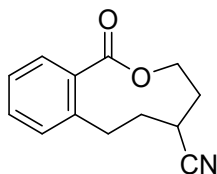


6,6-Difluoro-9-oxooxonane-4-carbonitrile (2n) Colorless oil (30.3 mg, 75%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.72 – 4.66 (m, 1H), 4.20 (dt, $J = 11.2, 8.0$ Hz, 1H), 2.83 – 2.77 (m, 1H), 2.65 – 2.42 (m, 4H), 2.38 – 2.29 (m, 1H), 2.25 – 2.19 (m, 2H), 2.09 (ddt, $J = 34.0, 16.0, 3.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 123.9 (t, $J = 241$ Hz), 121.4, 60.1, 39.6 (dd, $J = 27.0, 4.0$ Hz), 32.42 (t, $J = 28.0$ Hz), 31.1, 30.0 (d, $J = 40.0$ Hz), 20.9 (d, $J = 40.0$ Hz). IR (neat):

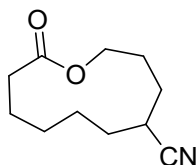
$\nu_{\max}$ (cm^{-1}) 2931, 2367, 1765, 1267, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{12}\text{F}_2\text{NO}_2$ $[\text{M}+\text{H}]^+$ 204.0831, found 204.0823.



6,6-Dimethyl-9-oxooxonane-4-carbonitrile (2o) Colorless oil (36.0 mg, 92%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.75 – 4.69 (m, 1H), 4.07 – 4.00 (m, 1H), 2.65 – 2.60 (m, 1H), 2.44 (ddd, J = 15.2, 5.2, 3.6 Hz, 1H), 2.34 – 2.30 (m, 1H), 2.18 – 2.10 (m, 2H), 2.09 – 1.99 (m, 1H), 1.71 (ddd, J = 16.8, 7.2, 0.8 Hz, 1H), 1.53 (d, J = 16.0 Hz, 1H), 1.41 – 1.35 (m, 1H), 1.04 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 124.0, 59.4, 43.4, 35.2, 34.8, 31.4, 31.1, 28.8, 28.3, 21.0. IR (neat): $\nu_{\max}$ (cm^{-1}) 2897, 2321, 1732, 1267, 754. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{NH}_4]^+$ 213.1598, found 213.1593.

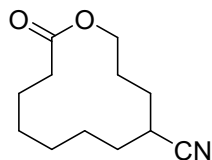


1-Oxo-1,3,4,5,6,7-Hexahydrobenzo[c]oxonine-5-carbonitrile (2p) Colorless oil (35.6 mg, 83%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, J = 7.6, 1.6 Hz, 1H), 7.41 (td, J = 7.6, 1.6 Hz, 1H), 7.32 (td, J = 7.6, 1.2 Hz, 1H), 7.22 (dd, J = 7.6, 0.8 Hz, 1H), 4.79 – 4.74 (m, 1H), 4.56 – 4.50 (m, 1H), 3.40 (dt, J = 14.8, 5.6 Hz, 1H), 3.04 – 2.91 (m, 2H), 2.28 – 2.20 (m, 3H), 1.79 – 1.75 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 143.7, 132.3, 131.1, 130.8, 130.5, 127.1, 121.1, 63.3, 33.3, 32.4, 30.7, 29.0. IR (neat): $\nu_{\max}$ (cm^{-1}) 2789, 2319, 1729, 1265, 749. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{Li}$ $[\text{M}+\text{Li}]^+$ 222.1101, found 222.1087.

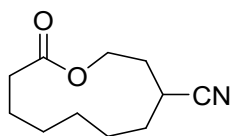


11-Oxooxacycloundecane-5-carbonitrile (2q) Colorless oil (31.2 mg, 80%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.24 – 4.15 (m, 2H), 2.68 – 2.60 (m, 1H), 2.45 – 2.39 (m, 1H), 2.32 – 2.25 (m, 1H), 1.99 – 1.84 (m, 4H), 1.81 – 1.53 (m, 6H), 1.45 – 1.27 (m, 2H). ^{13}C

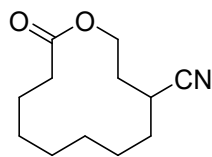
NMR (100 MHz, CDCl₃) δ 173.7, 122.8, 64.0, 35.1, 28.3, 27.4, 26.1, 25.8, 24.0, 22.9, 21.0. IR (neat): $\nu_{\max}$ (cm⁻¹) 2920, 2250, 1768, 1267, 755. HRMS (ESI) calcd for C₁₁H₁₇NO₂K [M+K]⁺ 234.0891, found 234.0906.



12-Oxooxacyclododecane-5-carbonitrile (2r) Colorless oil (18 mg, 43%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 4.55 – 4.50 (m, 1H), 3.98 – 3.92 (m, 1H), 2.92 – 2.85 (m, 1H), 2.45 – 2.33 (m, 2H), 1.99 – 1.90 (m, 1H), 1.88 – 1.57 (m, 8H), 1.54 – 1.47 (m, 1H), 1.42 – 1.32 (m, 3H), 1.30 – 1.24 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 122.9, 64.2, 33.7, 28.6, 27.2, 26.6, 24.7, 24.2, 23.5, 23.3, 22.6. IR (neat): $\nu_{\max}$ (cm⁻¹) 2936, 2237, 1730, 1456, 1239, 784. HRMS (ESI) calcd for C₁₂H₁₉NO₂Na [M+Na]⁺ 232.1308, found 232.1305.

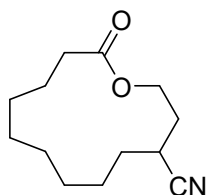


11-Oxooxacycloundecane-4-carbonitrile (2s) Colorless oil (35.5 mg, 91%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 4.31 – 4.17 (m, 2H), 2.80 – 2.74 (m, 1H), 2.42 – 2.26 (m, 2H), 2.23 – 2.15 (m, 1H), 2.13 – 2.04 (m, 1H), 1.79 – 1.57 (m, 4H), 1.52 (m, 2H), 1.46 – 1.32 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 122.6, 61.7, 35.1, 28.5, 27.9, 27.5, 24.94, 24.85, 21.5, 20.6. IR (neat): $\nu_{\max}$ (cm⁻¹) 2942, 2245, 1768, 1267, 755. HRMS (ESI) calcd for C₁₁H₂₁N₂O₂ [M+NH₄]⁺ 213.1598, found 213.1590.

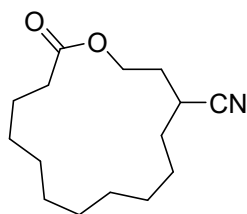


12-Oxooxacyclododecane-4-carbonitrile (2t) Colorless oil (25.0 mg, 60%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 4.60 – 4.54 (m, 1H), 4.10 – 4.04 (m, 1H), 2.88 – 2.81 (m, 1H), 2.50 – 2.44 (m, 1H), 2.34 – 2.27 (m, 1H), 2.07 – 1.93 (m, 2H), 1.85 – 1.71 (m, 3H), 1.66 – 1.60 (m, 1H), 1.57 – 1.41 (m, 2H), 1.41 – 1.28 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 122.5, 61.2, 34.1, 29.4, 28.4, 26.6, 24.7, 24.0, 23.7, 23.4, 21.8. IR (neat): $\nu_{\max}$ (cm⁻¹) 2935, 2239, 1731, 1455, 1234, 750. HRMS (ESI) calcd for C₁₂H₁₉NO₂Na [M+Na]⁺ 232.1308, found

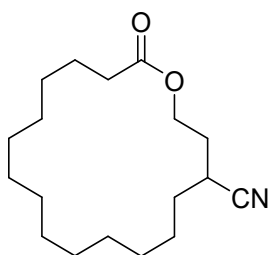
232.1305.



13-oxoxacyclotridecane-4-carbonitrile (2u) Colorless oil (18 mg, 40%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3). δ 4.33 – 4.20 (m, 2H), 2.74 – 2.67 (m, 1H), 2.46 – 2.40 (m, 1H), 2.35 – 2.28 (m, 1H), 2.12 – 1.91 (m, 2H), 1.76 – 1.64 (m, 4H), 1.60 – 1.50 (m, 1H), 1.48 – 1.29 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 122.4, 61.7, 34.5, 31.1, 30.2, 26.8, 26.7, 26.4, 25.2, 24.9, 24.4, 23.7. IR (neat): ν_{max} (cm^{-1}) 2921, 2224, 1733, 1466, 1221, 765. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 246.1464, found 246.1460.



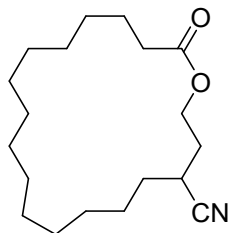
15-Oxoxacyclopentadecane-4-carbonitrile (2v) Colorless oil (47.7 mg, 95%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3). δ 4.33 – 4.28 (m, 1H), 4.18 – 4.12 (m, 1H), 2.73 (q, $J = 7.2$ Hz, 1H), 2.41 – 2.29 (m, 2H), 2.08 – 1.99 (m, 1H), 1.96 – 1.88 (m, 1H), 1.69 – 1.60 (m, 5H), 1.598 – 1.51 (m, 1H), 1.41 – 1.22 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 121.9, 61.1, 33.8, 31.7, 29.4, 27.9, 26.9, 26.60, 26.57, 26.5, 25.5, 25.1, 24.8, 24.7. IR (neat): ν_{max} (cm^{-1}) 2857, 2230, 1733, 1165, 755. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 274.1777, found 274.1756.



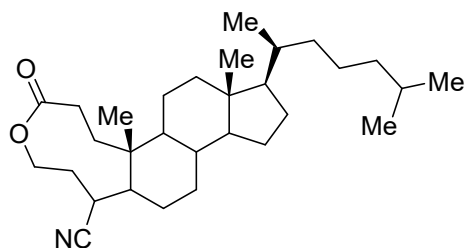
18-Oxoxacyclooctadecane-4-carbonitrile (2w) Colorless oil (49.1 mg, 84%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3). δ 4.37 – 4.32 (m, 1H), 4.18 – 4.12 (m, 1H), 2.78 – 2.70 (m, 1H), 2.32 (t, $J = 7.2$ Hz, 2H), 1.95 – 1.90 (m, 2H), 1.72 – 1.47 (m, 6H), 1.38 – 1.24 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 121.6, 61.0, 34.6, 31.5, 31.2, 28.3, 28.0, 27.7, 27.2, 27.0,

26.92, 26.91, 26.7, 26.6, 26.1, 25.8, 24.8. IR (neat): $\nu_{\max}$ (cm⁻¹) 2925, 2260, 1734, 1453, 1265, 755.

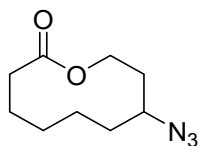
HRMS (ESI) calcd for C₁₈H₃₂NO₂ [M+H]⁺ 294.2428, found 294.2411.



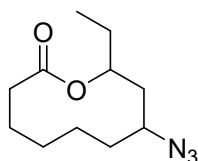
19-Oxooxacyclononadecane-4-carbonitrile (2x) Colorless oil (46.0 mg, 75%). R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃). 4.35 – 4.30 (m, 1H), 4.20 – 4.14 (m, 1H), 2.73 – 2.66 (m, 1H), 2.33 (t, J = 7.2 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.70 – 1.48 (m, 7H), 1.35 – 1.27 (m, 19H). ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 121.7, 61.2, 34.5, 31.6, 28.5, 28.2, 28.0, 27.7, 27.6, 27.5, 27.34, 27.29, 26.9, 26.5, 24.8. IR (neat): $\nu_{\max}$ (cm⁻¹) 2924, 2210, 1734, 1451, 1266, 1159, 755. HRMS (ESI) calcd for C₁₉H₃₄NO₂ [M+H]⁺ 308.2584, found 308.2581.



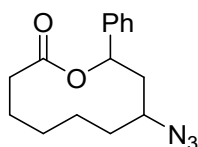
(7aR,9aR,10R)-7a,9a-Dimethyl-10-((S)-6-methylheptan-2-yl)-5-oxooctadecahydro-1H cyclopenta[5,6] naphtho[1,2-e]oxonine-1-carbonitrile (2y) Colorless oil (59.1 mg, 65%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃). δ 4.85 – 4.79 (m, 1H), 3.96 – 3.89 (m, 1H), 2.84 – 2.79 (m, 1H), 2.31 – 1.97 (m, 8H), 1.86 – 1.76 (m, 2H), 1.71 – 1.65 (m, 1H), 1.57 – 1.39 (m, 4H), 1.36 – 1.28 (m, 4H), 1.25 – 1.23 (m, 2H), 1.14 – 0.93 (m, 10H), 0.88 (d, J = 6.8 Hz, 3H), 0.85 (dd, J = 4.4, 2.0 Hz, 6H), 0.81 (s, 3H), 0.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 123.2, 59.1, 56.7, 56.0, 47.9, 42.5, 41.3, 40.8, 39.9, 39.60, 39.55, 39.2, 36.2, 35.9, 35.5, 31.8, 31.1, 29.5, 28.4, 28.1, 24.2, 23.8, 22.9, 22.7, 21.8, 19.2, 18.7, 15.6, 12.3. IR (neat): $\nu_{\max}$ (cm⁻¹) 2936, 2198, 1737, 1459, 1268, 754. HRMS (ESI) calcd for C₃₀H₄₉NO₂Na [M+Na]⁺ 478.3656, found 478.3659.



8-Azido-10-oxo-10,12-dihydrocyclohexa[1,1-b]oxep-2-one (3a) Colorless oil (32.3 mg, 82%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3). δ 4.36 – 4.28 (m, 2H), 3.74 – 3.69 (m, 1H), 2.44 – 2.37 (ddd, $J = 16.4, 8.0, 2.8$ Hz, 1H), 2.29 (ddd, $J = 16.4, 10.0, 2.8$ Hz, 1H), 2.13 – 2.05 (m, 1H), 1.94 – 1.70 (m, 5H), 1.59 – 1.45 (m, 2H), 1.40 – 1.31 (m, 1H), 1.24 – 1.13 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 61.2, 60.1, 34.7, 29.0, 28.4, 27.2, 20.4, 20.0. IR (neat): ν_{max} (cm^{-1}) 2930, 2092, 1726, 1454, 1262, 1060, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{15}\text{N}_3\text{O}_2\text{Li}$ $[\text{M}+\text{Li}]^+$ 204.1319, found 204.1335.

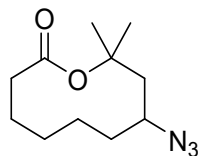


8-Azido-10-ethoxy-10,12-dihydrocyclohexa[1,1-b]oxep-2-one (3b) Colorless oil (41.0 mg, 91%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). d.r. = 3:1 ^1H NMR (400 MHz, CDCl_3). δ 4.87 – 4.79 (m, 1H), 3.88 – 3.82 (m, 0.2H), 3.46 – 3.41 (m, 0.8H), 2.51 – 2.43 (m, 1H), 2.24 – 2.12 (m, 1H), 2.06 – 1.93 (m, 2H), 1.91 – 1.79 (m, 2H), 1.77 – 1.62 (m, 3H), 1.61 – 1.52 (m, 3H), 1.46 – 1.37 (m, 1H), 1.17 – 1.07 (m, 1H), 0.95 – 0.89 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.1, 73.7, 59.4, 34.6, 33.9, 29.3, 26.7, 25.6, 21.1, 19.6, 8.9; minor isomer δ 172.7, 72.6, 56.7, 33.8, 30.5, 27.4, 25.9, 24.6, 19.9, 17.9, 9.3. IR (neat): ν_{max} (cm^{-1}) 2934, 2093, 1723, 1456, 1249, 737. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{20}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 226.1550, found 226.1568.

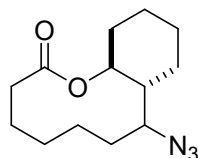


8-Azido-10-phenyl-10,12-dihydrocyclohexa[1,1-b]oxep-2-one (3c) Colorless oil (44.9 mg, 82%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). d.r. = 4:1 ^1H NMR (400 MHz, CDCl_3). δ 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 4.68 (dd, $J = 8.4, 2.8$ Hz, 0.2H), 4.52 (dd, $J = 8.4, 3.6$ Hz, 0.8H), 4.67 (d, $J = 11.2$ Hz, 0.2H), 4.00 (d, $J = 12$ Hz, 0.6H), 3.98 – 3.93 (m, 1H), 3.75 – 3.70 (m, 0.2H), 3.56 (dt, $J = 11.2, 2.8$ Hz, 0.2H), 3.40 (td, $J = 11.6, 3.6$ Hz, 0.8H), 2.61 – 2.52 (m, 1H), 2.32 – 2.02 (m, 3H), 1.95 – 1.75 (m, 1H), 1.73 – 1.53 (m, 4H), 1.40 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.3, 138.5, 129.0, 128.1, 127.8, 65.9, 65.8, 44.7, 34.5, 28.7, 27.2, 20.4, 19.1; minor isomer δ

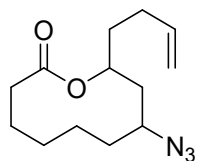
173.5, 138.9, 128.6, 128.4, 127.4, 63.3, 63.0, 42.1, 34.6, 29.3, 27.3, 20.7, 20.2. IR (neat): $\nu_{\max}$ (cm⁻¹) 2893, 2098, 1728, 1262, 733. HRMS (ESI) calcd for C₁₅H₁₉N₃O₂Li [M+Li]⁺ 280.1631, found 280.1625.



8-Azido-10,10-dimethyloxecan-2-one (3d) Colorless oil (33.8 mg, 75%). R_f = 0.3 (petroleum ether/ethyl acetate = 30:1). ¹H NMR (400 MHz, CDCl₃) δ 3.86–3.80 (m, 1H), 2.55 (dd, J = 15.2, 10.0 Hz, 1H), 2.37 (ddd, J = 15.2, 7.2, 2.8 Hz, 1H), 2.17–2.10 (m, 1H), 1.96–1.84 (m, 2H), 1.78–1.71 (m, 2H), 1.67–1.58 (m, 5H), 1.53–1.41 (m, 2H), 1.37 (s, 3H), 1.32–1.28 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 81.3, 58.9, 36.4, 36.2, 28.8, 27.6, 27.2, 27.1, 21.1, 18.7. IR (neat): $\nu_{\max}$ (cm⁻¹) 2897, 2099, 1725, 1262, 733. HRMS (ESI) calcd for C₁₁H₂₀N₃O₂ [M+H]⁺ 226.1550, found 226.1561.

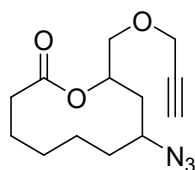


8-Azidododecahydro-2H-benzo[b]oxecin-2-one (3e) Colorless oil (46.8 mg, 93%). R_f = 0.3 (petroleum ether/ethyl acetate = 30:1). d.r. > 20:1. ¹H NMR (400 MHz, CDCl₃) δ 4.51 (td, J = 10.4, 4.4 Hz, 1H), 2.96–2.92 (m, 1H), 2.48 (ddd, J = 15.6, 6.4, 3.2 Hz, 1H), 2.27– (m, 2H), 2.09–1.92 (m, 3H), 1.78–1.67 (m, 4H), 1.66–1.58 (m, 3H), 1.46–1.38 (m, 1H), 1.35–1.27 (m, 2H), 1.23–1.113 (m, 2H), 1.02–0.92 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 75.9, 67.4, 46.7, 35.1, 32.7, 31.3, 30.3, 26.7, 25.1, 24.6, 23.7, 20.6. IR (neat): $\nu_{\max}$ (cm⁻¹) 2934, 2095, 1723, 1258, 734. HRMS (ESI) calcd for C₁₃H₂₁N₃O₂K [M+K]⁺ 290.1265, found 290.1254.

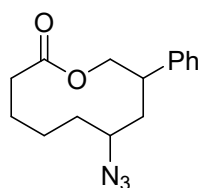


8-Azido-10-(but-3-en-1-yl)oxecan-2-one (3f) Colorless oil (31.0 mg, 62%). R_f = 0.3 (petroleum ether/ethyl acetate = 30:1). d.r. = 3.3:1. ¹H NMR (400 MHz, CDCl₃) δ 5.84–5.74 (m, 1H), 5.05–4.90 (m, 3H), 3.89–3.84 (m, 0.22H), 3.50–3.45 (m, 0.75H), 2.51–2.43 (m, 1H), 2.25–1.96 (m, 5H), 1.91–1.78 (m, 3H), 1.74–1.54 (m, 5H), 1.46–1.40 (m, 1H), 1.17–1.10 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, two diastereoisomers) major isomer δ 174.1, 137.6, 115.3, 73.1, 60.4, 35.6, 35.0, 33.8, 30.3, 29.9, 26.7, 22.1, 20.8; minor isomer δ 173.7, 137.3, 115.6, 71.8, 57.9, 34.9, 31.9, 31.7, 30.1, 28.6, 27.0, 21.0.

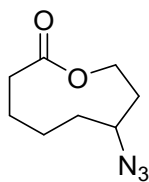
19.0. IR (neat): $\nu_{\max}$ (cm⁻¹) 3074, 2095, 1727, 1642, 1455, 1249, 913. HRMS (ESI) calcd for C₁₃H₂₂N₃O₂ [M+H]⁺ 252.1706, found 252.1693.



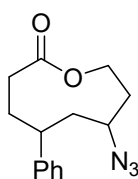
8-Azido-10-((prop-2-yn-1-yloxy)methyl)oxecan-2-one (3g) Colorless oil (31.6 mg, 60%). R_f = 0.3 (petroleum ether/ethyl acetate = 30:1). d.r. = 3:1, ¹H NMR (400 MHz, CDCl₃) δ 5.13 – 5.08 (m, 0.24H), 5.05 – 5.00 (m, 0.76H), 4.19 (t, J = 2.0 Hz, 2H), 3.94 – 3.88 (m, 0.22H), 3.77 – 3.65 (m, 2H), 3.50 – 3.44 (m, 0.76H), 2.56 – 2.48 (m, 1H), 2.47 – 2.44 (m, 1H), 2.27 – 2.09 (m, 2H), 2.07 – 1.83 (m, 3H), 1.66 – 1.53 (m, 4H), 1.50 – 1.41 (m, 1H), 1.15 – 1.03 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, two diastereoisomers) major isomer δ 174.0, 79.3, 75.1, 72.0, 70.9, 60.3, 58.6, 34.9, 33.2, 30.3, 26.8, 22.1, 20.6; minor isomer δ 173.7, 79.2, 75.2, 70.4, 70.2, 58.6, 58.2, 34.8, 30.7, 28.7, 27.0, 21.2, 19.5. IR (neat): $\nu_{\max}$ (cm⁻¹) 3289, 2937, 2093, 1724, 1453, 1240, 1093, 637. HRMS (ESI) calcd for C₁₃H₁₉N₃O₃Na [M+Na]⁺ 288.1318, found 288.1317.



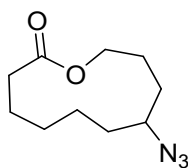
7-Azido-9-phenyloxecan-2-one (3h) Colorless oil (34.3 mg, 63%). R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). d.r. = 2.5:1. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 4.74 (ddd, J = 11.2, 3.6, 1.6 Hz, 0.3H), 4.48 (t, J = 11.6 Hz, 0.8H), 4.07 (dd, J = 11.2, 4.4 Hz, 1H), 3.92 (t, J = 11.6 Hz, 0.3H), 3.78 – 3.73 (m, 0.74H), 3.36 (tt, J = 12, 4.0 Hz, 0.3H), 3.28 – 3.20 (m, 0.75H), 2.64 – 2.56 (m, 1H), 2.34 – 2.24 (m, 1.4H), 2.17 – 2.04 (m, 0.4H), 2.03 – 2.0 (m, 1H), 1.97 – 1.65 (m, 4H), 1.59 – 1.42 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, two diastereoisomers) major isomer δ 173.5, 141.3, 128.92, 127.6 (overlapped), 127.4, 68.93, 60.5, 44.2, 40.3, 34.8, 33.0, 23.9, 20.9; minor isomer δ 173.1, 140.3, 128.86, 127.6 (overlapped), 127.3, 68.87, 58.0, 39.3, 39.1, 34.5, 28.0, 25.2, 20.7. IR (neat): $\nu_{\max}$ (cm⁻¹) 2944, 2090, 1729, 1243, 807, 697. HRMS (ESI) calcd for C₁₅H₁₉N₃O₂Li [M+Li]⁺ 280.1632, found 280.1618.



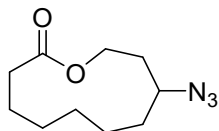
7-Azido-2-oxononan-2-one (3i) Colorless oil (22.6 mg, 62%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3). δ 4.37 – 4.28 (m, 2H), 3.64 – 3.59 (m, 1H), 2.35 – 2.25 (m, 2H), 2.07 – 1.93 (m, 2H), 1.80 – 1.59 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 61.5, 59.4, 34.2, 32.8, 32.4, 24.7, 20.8. IR (neat): ν_{max} (cm^{-1}) 2943, 2091, 1728, 1254, 754. HRMS (ESI) calcd for $\text{C}_8\text{H}_{13}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 206.0900, found 206.0909.



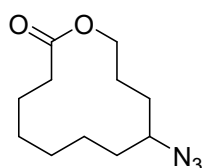
7-Azido-5-phenyloxonan-2-one (3j) Colorless oil (31.0 mg, 60%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). d.r. = 1:1, ^1H NMR (400 MHz, CDCl_3). δ 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 4.87 – 4.81 (m, 0.5H), 4.63 (td, $J = 12.0, 2.4$ Hz, 0.5H), 4.18 (dt, $J = 11.6, 3.6$ Hz, 0.6H), 4.06 – 4.01 (m, 0.5H), 3.78 – 3.71 (m, 0.5H), 3.67 – 3.61 (m, 0.5H), 3.08 – 3.02 (m, 0.5H), 2.95 – 2.90 (m, 0.5H), 2.50 – 2.35 (m, 2.5H), 2.24 – 1.89 (m, 5H), 1.84 – 1.78 (m, 0.5H). ^{13}C NMR (100 MHz, CDCl_3 , both diastereoisomers) δ 174.6, 174.1, 148.2, 147.2, 128.2, 128.8, 127.2, 127.1, 126.7, 126.4, 62.0, 61.0, 58.7, 57.8, 41.3, 40.7, 40.3, 39.1, 34.4, 33.4, 33.0, 32.8, 32.1. IR (neat): ν_{max} (cm^{-1}) 2936, 2078, 1768, 1265, 760, 701. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2$ $[\text{M}+\text{NH}_4]^+$ 277.1659, found 277.1656.



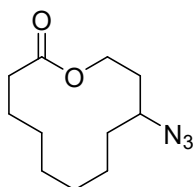
8-Azido-2-oxacycloundecan-2-one (3k) Colorless oil (29.1 mg, 69%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.25 – 4.14 (m, 2H), 3.52 – 3.46 (m, 1H), 2.46 – 2.40 (m, 1H), 2.30 – 2.25 (m, 1H), 1.94 – 1.61 (m, 8H), 1.49 – 1.32 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 64.4, 60.1, 35.2, 29.4, 27.6, 26.5, 23.1, 22.1, 21.0. IR (neat): ν_{max} (cm^{-1}) 2894, 2489, 2289, 1754, 1267, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 234.1213, found 234.1196.



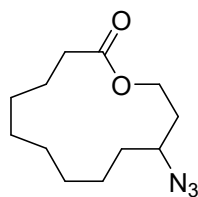
9-Azidooxacycloundecan-2-one (3l) Colorless oil (29.5 mg, 70%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 4.26 – 4.15 (m, 2H), 3.69 – 3.63 (m, 1H), 2.39 – 2.27 (m, 2H), 2.09 – 2.02 (m, 1H), 1.99 – 1.91 (m, 1H), 1.75 – 1.65 (m, 1H), 1.64 – 1.56 (m, 3H), 1.51 – 1.44 (m, 3H), 1.41 – 1.33 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 61.0, 60.0, 35.4, 30.4, 29.5, 25.7, 24.6, 21.3, 19.7. IR (neat): ν_{max} (cm^{-1}) 2898, 2154, 1733, 1267, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{21}\text{N}_4\text{O}_2$ $[\text{M}+\text{NH}_4]^+$ 229.1659, found 229.1654.



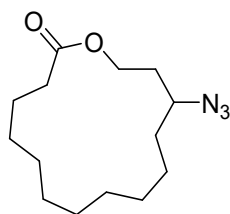
9-Azidooxacyclododecan-2-one (3m) Colorless oil (16.2 mg, 36%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.53 – 4.89 (m, 1H), 3.98 – 3.92 (m, 1H), 3.67 – 3.61 (m, 1H), 2.45 – 2.32 (m, 2H), 1.85 – 1.52 (m, 8H), 1.48 – 1.31 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 64.3, 59.3, 34.0, 30.3, 28.5, 24.6, 24.5, 24.0, 23.5, 21.9. IR (neat): ν_{max} (cm^{-1}) 2906, 2162, 1743, 1254, 763. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 248.1369, found 248.1362.



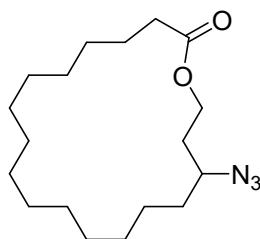
10-Azidooxacyclododecan-2-one (3n) Colorless oil (24.4 mg, 54%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.54 – 4.90 (m, 1H), 4.08 – 4.03 (m, 1H), 3.67 – 3.61 (m, 1H), 2.48 – 2.42 (m, 1H), 2.34 – 2.27 (m, 1H), 1.94 – 1.86 (m, 1H), 1.82 – 1.72 (m, 3H), 1.67 – 1.59 (m, 2H), 1.50 – 1.28 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 60.9, 58.9, 34.1, 31.5, 30.5, 24.6, 24.3, 24.2, 23.5, 21.2. IR (neat): ν_{max} (cm^{-1}) 2936, 2094, 1455, 1232, 1143, 825. HRMS (ESI) calcd $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 248.1369, found 248.1369.



11-azidooxacyclotridecan-2-one (3o) Colorless oil (24.5 mg, 51%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.26 – 4.24 (m, 2H), 3.50 – 3.44 (m, 1H), 2.45 – 2.27 (m, 2H), 1.95 – 1.87 (m, 1H), 1.82 – 1.75 (m, 1H), 1.69 – 1.60 (m, 4H), 1.57 – 1.48 (m, 1H), 1.44 – 1.30 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 61.5, 58.7, 34.5, 33.1, 32.3, 26.7, 26.2, 25.5, 25.4, 24.5, 22.6. IR (neat): ν_{max} (cm^{-1}) 2912, 2160, 1753, 12561, 755. HRMS (ESI) calcd $\text{C}_{12}\text{H}_{22}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 240.1706, foun 240.1699.

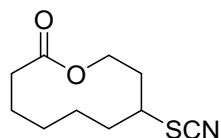


13-Azidooxacyclopentadecan-2-one (3p) Colorless oil (36.1 mg, 68%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 4.27 (ddd, $J = 11.6, 6.0, 3.6$ Hz, 1H), 4.17 (ddd, $J = 16.0, 8.0, 3.6$ Hz, 1H), 3.50 – 3.43 (m, 1H), 2.38 – 2.34 (m, 2H), 1.91 – 1.78 (m, 2H), 1.71 – 1.62 (m, 3H), 1.61 – 1.52 (m, 3H), 1.48 – 1.41 (m, 2H), 1.38 – 1.27 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.1, 61.0, 58.3, 34.1, 33.8, 32.0, 27.9, 26.7, 26.62, 26.60, 26.1, 25.6, 24.9, 23.9. IR (neat): ν_{max} (cm^{-1}) 2929, 2092, 1730, 1244, 756. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{25}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 290.1839, found 290.1850.

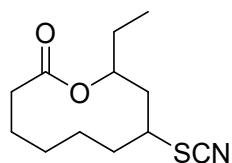


17-Azidooxacyclononadecan-2-one (3q) Colorless oil (44 mg, 68%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 100:1). ^1H NMR (400 MHz, CDCl_3) δ 4.28 – 4.14 (m, 2H), 3.47 – 3.40 (m, 1H), 2.32 (t, $J = 7.2$ Hz, 2H), 1.91 – 1.83 (m, 1H), 1.77 – 1.69 (m, 1H), 1.65 – 1.51 (m, 4H), 1.46 – 1.41 (m, 2H), 1.35 – 1.26 (m, 20H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 60.9, 59.4, 34.5, 34.0, 33.5, 28.49, 28.46, 28.1, 27.9, 27.7, 27.61, 27.57 (overlapped), 27.4, 27.0, 25.4, 24.9. IR (neat): ν_{max} (cm^{-1}) 2924, 2095, 1734,

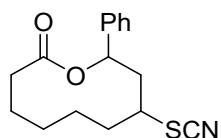
1450, 1241, 796. HRMS (ESI) calcd for $C_{18}H_{33}N_3O_2Li$ $[M+Li]^+$ 330.2727, found 330.2732.



8-Thiocyanatooxecan-2-one (4a) Colorless oil (39.5 mg, 93%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.45 (ddd, $J = 12.0, 7.6, 2.4$ Hz, 1H), 4.34 (ddd, $J = 12.0, 7.6, 2.4$ Hz, 1H), 3.71 – 3.65 (m, 1H), 2.44 – 2.28 (m, 3H), 2.17 – 2.08 (m, 1H), 2.04 – 1.90 (m, 2H), 1.89 – 1.73 (m, 2H), 1.61 – 1.46 (m, 2H), 1.42 – 1.30 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 111.9, 61.6, 48.4, 34.6, 30.2, 29.4, 26.9, 20.8, 20.4. IR (neat): ν_{max} (cm^{-1}) 2929, 2092, 1726, 1454, 1264, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 214.0896, found 214.0883.

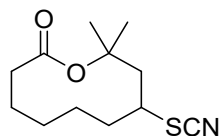


10-Ethyl-8-thiocyanatooxecan-2-one (4b) Colorless oil (41.0 mg, 85%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 5:1). d.r. = 3.5:1. ^1H NMR (400 MHz, CDCl_3) δ 4.91 – 4.85 (m, 1H), 3.88 – 3.83 (m, 0.2H), 3.24 (ddd, $J = 13.6, 6.4, 3.2$ Hz, 0.8H), 2.48 (ddd, $J = 15.2, 6.0, 3.2$ Hz, 1H), 2.42 – 2.32 (m, 0.2H), 2.28 – 2.17 (m, 2H), 2.14 – 1.99 (m, 1.8H), 1.97 – 1.87 (m, 1H), 1.78 – 1.54 (m, 6H), 1.41 – 1.33 (m, 0.8H), 1.27 – 1.20 (m, 0.8H), 1.15 – 1.06 (m, 0.2H), 0.97 – 0.89 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 174.0, 112.0, 75.3, 47.0, 39.3, 34.9, 32.3, 28.2, 25.9, 23.6, 20.7, 9.6; minor isomer δ 173.5, 119.2, 74.1, 46.2, 36.7, 34.7, 29.3, 26.6, 25.2, 20.9, 19.3, 10.3. IR (neat): ν_{max} (cm^{-1}) 2938, 2109, 1726, 1456, 1265, 755. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 264.1029, found 264.1013.

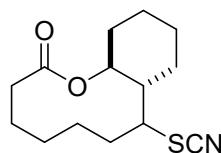


10-Phenyl-8-thiocyanatooxecan-2-one (4c) Colorless oil (40.6 mg, 70%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1). d.r. = 1:1 ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.29 (m, 3H), 7.25 – 7.23 (m, 2H), 4.54 (dd, $J = 12.0, 3.6$ Hz, 1H), 4.13 (dt, $J = 11.2, 3.6$ Hz, 1H), 3.95 (t, $J = 12.0$ Hz, 1H), 3.56 (td, $J = 11.6, 3.6$ Hz, 1H), 2.56 (ddd, $J = 16.8, 6.4, 2.0$ Hz, 1H), 2.32 – 2.22 (m, 2H), 2.10 – 2.00 (m, 1H), 1.96 – 1.87 (m, 1H), 1.75 – 1.62 (m, 3H), 1.60 – 1.52 (m, 1H), 1.41 – 1.31 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , single isomer) δ 173.3, 137.8, 129.2, 128.2, 128.0, 65.5, 62.6, 45.9, 34.5, 30.3, 26.9, 20.5, 19.2.

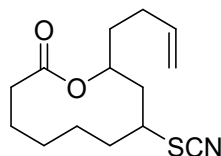
IR (neat): $\nu_{\max}$ (cm⁻¹) 2943, 2082, 1729, 1453, 1265, 755, 701. HRMS (ESI) calcd for C₁₆H₂₀NO₂S [M+H]⁺ 290.1209, found 290.1193.



10,10-Dimethyl-8-thiocyanatooxecan-2-one (4d) Colorless oil (33.7 mg, 70%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 3.90 – 3.84 (m, 1H), 2.84 (dd, J = 15.2, 11.6 Hz, 1H), 2.44 (ddd, J = 14.8, 6.8, 2.8 Hz, 1H), 2.25 – 2.18 (m, 1H), 2.14 – 2.04 (m, 1H), 2.01 – 1.90 (m, 1H), 1.86 – 1.76 (m, 2H), 1.70 – 1.44 (m, 4H), 1.66 (s, 3H), 1.37 (s, 3H), 1.31 – 1.21 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 112.2, 81.7, 47.5, 37.5, 36.3, 28.8, 28.2, 26.8, 26.5, 21.2, 18.8. IR (neat): $\nu_{\max}$ (cm⁻¹) 2924, 2109, 1733, 1452, 1267, 755. HRMS (ESI) calcd for C₁₂H₂₃N₂O₂S [M+NH₄]⁺ 259.1474, found 259.1473.

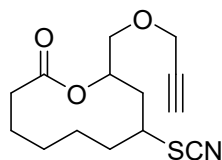


8-Thiocyanatododecahydro-2H-benzo[b]oxecin-2-one (4e) Colorless oil (43.0 mg, 81%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). d.r. = 13:1. ¹H NMR (400 MHz, CDCl₃) δ 4.51 – 4.45 (m, 1H), 3.35 – 3.30 (m, 1H), 2.50 – 2.44 (m, 1H), 2.25 – 2.20 (m, 2H), 2.11 – 2.04 (m, 2H), 1.94 – 1.84 (m, 2H), 1.77 – 1.72 (m, 3H), 1.66 – 1.58 (m, 3H), 1.34 – 1.20 (m, 5H), 1.09 – 1.02 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, single isomer) δ 173.8, 129.9, 75.5, 63.0, 47.1, 35.1, 33.5, 32.5, 30.6, 26.3, 24.9, 24.4, 23.3, 20.8. IR (neat): $\nu_{\max}$ (cm⁻¹) 2935, 2095, 1727, 1266, 755. HRMS (ESI) calcd for C₁₄H₂₁NO₂SNa [M+Na]⁺ 290.1185, found 290.1178.

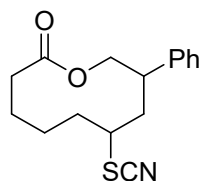


10-(But-3-en-1-yl)-8-thiocyanatooxecan-2-one (4f) Colorless oil (32.0 mg, 60%). R_f = 0.3 (petroleum ether/ethyl acetate = 15:1). d.r. = 3.5:1. ¹H NMR (400 MHz, CDCl₃) δ 5.83 – 5.73 (m, 1H), 5.07 – 4.95 (m, 3H), 3.90 – 3.85 (m, 0.22H), 3.29 – 3.23 (m, 0.77H), 2.53 – 2.37 (m, 1H), 2.30 – 2.00 (m, 6H), 1.96 – 1.57 (m, 8H), 1.43 – 1.29 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, two diastereoisomers) major isomer δ 174.0, 137.3, 115.5, 112.0, 73.8, 47.0, 39.6, 35.0, 34.4, 32.3, 29.5, 26.0, 23.6, 20.8; minor isomer δ

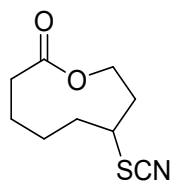
173.4, 136.9, 115.9, 119.9, 72.2, 46.3, 34.8, 32.6, 31.2, 29.9, 29.4, 26.6, 21.0, 19.3. IR (neat): $\nu_{\max}$ (cm^{-1}) 2930, 2151, 1726, 1641, 1452, 1246, 916. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 290.1185, found 290.1181.



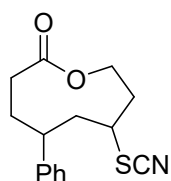
10-((Prop-2-yn-1-yloxy)methyl)-8-thiocyanatooxecan-2-one (4g) Colorless oil (37.4 mg, 67%). R_f = 0.3 (petroleum ether/ethyl acetate = 15:1). d.r. = 3.8:1. ^1H NMR (400 MHz, CDCl_3) δ 5.17 – 5.12 (m, 0.21H), 5.05 – 5.00 (m, 0.79H), 4.22 – 4.13 (m, 2H), 3.97 – 3.91 (m, 0.2H), 3.75 – 3.61 (m, 2H), 3.29 – 3.23 (m, 0.78H), 2.56 – 2.47 (m, 1H), 2.46 (t, J = 2.4 Hz, 1H), 2.40 – 2.20 (m, 3H), 2.15 – 1.91 (m, 2H), 1.97 – 1.54 (m, 4H), 1.52 – 1.35 (m, 1H), 1.22 – 1.09 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.9, 111.8, 79.1, 75.3, 72.5 (overlapped), 70.7, 58.6, 47.0, 36.9, 34.9, 32.3, 26.2, 23.8, 20.6; minor isomer δ 173.2, 111.9, 79.0, 75.4, 72.5 (overlapped), 69.7, 58.7, 46.6, 34.8, 31.4, 29.7, 26.6, 21.1, 19.8. IR (neat): $\nu_{\max}$ (cm^{-1}) 2925, 2123, 1726, 1458, 1237, 1089, 710. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$ 304.0977, found 304.0975.



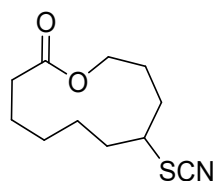
9-Phenyl-7-thiocyanatooxecan-2-one (4h) Colorless oil (40.6 mg, 70%). R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). d.r. = 1.5:1. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 4.79 (ddd, J = 11.2, 3.6, 1.6 Hz, 0.4H), 4.58 (t, J = 11.6 Hz, 0.6H), 4.15 – 4.05 (m, 0.7H), 3.95 (t, J = 11.6 Hz, 0.3H), 3.93 – 3.86 (m, 0.4H), 3.64 – 3.58 (m, 0.6H), 3.49 – 3.41 (m, 0.4H), 3.30 (ddd, J = 16.4, 8.4, 4.4 Hz, 0.6H), 2.69 – 2.57 (m, 1H), 2.51 (ddd, J = 14.0, 12.4, 4.4 Hz, 0.4H), 2.37 – 2.28 (m, 1H), 2.26 – 2.17 (m, 1.6H), 2.04 – 1.85 (m, 3H), 1.82 – 1.76 (m, 1H), 1.65 – 1.58 (m, 1H), 1.56 – 1.45 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.1, 140.5, 129.03, 127.6 (overlapped), 127.4 (overlapped), 112.0, 68.8, 48.0, 45.0, 42.7, 40.0, 34.8, 24.3, 20.5; minor isomer δ 172.7, 139.4, 128.96, 127.6 (overlapped), 127.4 (overlapped), 111.4, 68.9, 46.0, 42.5, 34.7, 34.4, 28.4, 25.1, 20.2. IR (neat): $\nu_{\max}$ (cm^{-1}) 2853, 2367, 1764, 1478, 1267, 755. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 290.1209, found 290.1189.



7-Thiocyanatooxonan-2-one (4i) Colorless oil (34.8 mg, 87%). R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 4.44 – 4.33 (m, 2H), 3.55 – 3.49 (m, 1H), 2.40 – 2.16 (m, 4H), 1.90 – 1.76 (m, 3H), 1.75 – 1.66 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.5, 111.8, 61.6, 46.2, 34.3, 34.1, 33.7, 24.3, 22.0. IR (neat): ν_{max} (cm^{-1}) 2949, 2208, 1733, 1457, 1266, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{13}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 222.0559, found 222.0543.

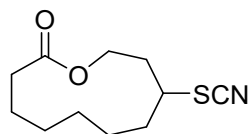


5-Phenyl-7-thiocyanatooxonan-2-one (4j) Colorless oil (38.5 mg, 70%). R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). d.r. = 1.4:1. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.16 – 7.14 (m, 1H), 4.95 – 4.89 (m, 0.4H), 4.63 (td, J = 11.6, 2.8 Hz, 0.6H), 4.30 (ddd, J = 11.6, 4.0, 2.8 Hz, 0.6H), 4.13 (ddd, J = 12.0, 4.8, 3.6 Hz, 0.4H), 3.63 – 3.55 (m, 1H), 3.05 – 2.99 (m, 1H), 2.71 – 2.63 (m, 0.4H), 2.51 – 2.39 (m, 2.6H), 2.24 – 1.89 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 174.5, 146.9, 129.0, 127.3 (overlapped), 127.0, 111.7 (overlapped), 62.3, 44.9, 42.8, 40.3, 35.0, 34.5, 33.0; minor isomer δ 174.0, 146.1, 129.1, 127.3 (overlapped), 126.9, 111.7 (overlapped), 60.5, 45.5, 41.6, 41.1, 33.1, 33.0 (overlapped), 32.4. IR (neat): ν_{max} (cm^{-1}) 2947, 2150, 1734, 1453, 1267, 755, 702. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 298.0872, found 298.0856.

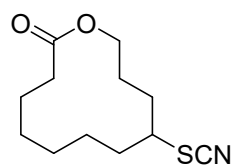


8-Thiocyanatooxacycloundecan-2-one (4k) Colorless oil (28.2 mg, 62%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 4.27 – 4.15 (m, 2H), 3.40 – 3.36 (m, 1H), 2.47 – 2.41 (m, 1H), 2.31 – 2.24 (m, 1H), 2.12 – 1.94 (m, 4H), 1.86 – 1.55 (m, 6H), 1.44 – 1.35 (m, 1H), 1.29 – 1.21 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 111.8, 64.2, 48.1, 35.1, 32.2, 28.6, 25.7, 24.3, 23.2, 21.3. IR (neat): ν_{max} (cm^{-1}) 2867, 2358, 1729, 1438, 1267, 755. HRMS (ESI) calcd for

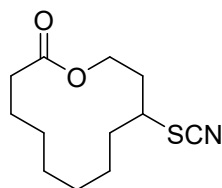
$C_{11}H_{17}NO_2SLi$ $[M+Li]^+$ 234.1135, found 234.1126.



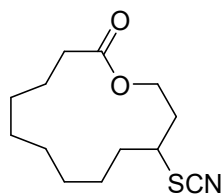
9-Thiocyanatooxacycloundecan-2-one (4l) Colorless oil (31.8 mg, 70%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, $CDCl_3$) δ 4.30 – 4.23 (m, 2H), 3.57 – 3.51 (m, 1H), 2.43 – 2.18 (m, 4H), 1.79 – 1.71 (m, 3H), 1.66 – 1.59 (m, 1H), 1.56 – 1.50 (m, 2H), 1.48 – 1.44 (m, 1H), 1.41 – 1.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 111.9, 61.4, 47.2, 34.9, 32.1, 31.1, 24.92, 24.89, 21.5, 21.1. IR (neat): ν_{max} (cm^{-1}) 2896, 2208, 1735, 1267, 755. HRMS (ESI) calcd for $C_{11}H_{21}N_2O_2S$ $[M+NH_4]^+$ 245.1318, found 245.1319.



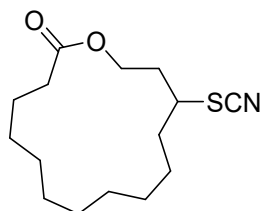
9-Thiocyanatooxacyclododecan-2-one (4m) Colorless oil (20.0 mg, 41%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1). 1H NMR (400 MHz, $CDCl_3$) δ 4.63 – 4.58 (m, 1H), 3.95 – 3.89 (m, 1H), 3.54 – 3.48 (m, 1H), 2.46 – 2.32 (m, 2H), 2.05 (q, $J = 6.4$ Hz, 2H), 1.97 – 1.76 (m, 4H), 1.72 – 1.59 (m, 3H), 1.54 – 1.44 (m, 1H), 1.43 – 1.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 111.7, 64.4, 47.3, 33.6, 33.3, 29.7, 25.2, 24.4, 23.6, 23.2, 22.8. IR (neat): ν_{max} (cm^{-1}) 2911, 2213, 1745, 1278, 765. HRMS (ESI) calcd for $C_{12}H_{19}NO_2SNa$ $[M+Na]^+$ 264.1028, found 264.1026.



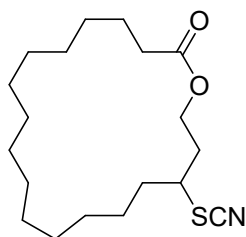
10-Thiocyanatooxacyclododecan-2-one (4n) Colorless oil (31.7 mg, 66%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 15:1). 1H NMR (400 MHz, $CDCl_3$) 4.65 – 4.60 (m, 1H), 4.06 – 4.00 (m, 1H), 3.46 – 3.40 (m, 1H), 2.50 – 2.44 (m, 1H), 2.32 – 2.45 (m, 1H), 2.22 – 2.14 (m, 1H), 2.09 – 1.92 (m, 2H), 1.83 – 1.71 (m, 2H), 1.65 – 1.51 (m, 2H), 1.48 – 1.29 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 111.4, 60.9, 45.9, 34.4, 33.2, 32.5, 25.0, 24.4, 23.7, 23.2, 22.3. IR (neat): ν_{max} (cm^{-1}) 2932, 2150, 1729, 1452, 1231, 1038, 799. HRMS (ESI) calcd for $C_{12}H_{19}NO_2SNa$ $[M+Na]^+$ 264.1028, found 264.1025.



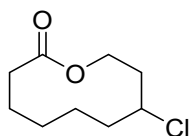
11-Thiocyanatooxacyclotridecan-2-one (4o) Colorless oil (30.7 mg, 60%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 4.41 – 4.34 (m, 1H), 4.23 – 4.22 (m, 1H), 3.16 – 3.09 (m, 1H), 2.47 – 2.40 (m, 1H), 2.32 – 2.25 (m, 1H), 2.21 – 2.03 (m, 2H), 1.95 – 1.76 (m, 2H), 1.68 – 1.54 (m, 3H), 1.42 – 1.29 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 111.1, 61.2, 45.9, 34.9, 34.5, 33.8, 26.6, 26.2, 25.1, 24.8, 24.4, 23.5. IR (neat): ν_{max} (cm^{-1}). 2907, 2213, 1745, 1287, 762. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 278.1185, found 278.1182.



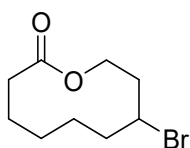
13-Thiocyanatooxacyclopentadecan-2-one (4p) Colorless oil (26.0 mg, 46%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 4.30 – 4.27 (m, 2H), 3.18 – 3.11 (m, 1H), 2.42 – 2.29 (m, 2H), 2.16 – 2.12 (m, 2H), 1.94 – 1.82 (m, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 1.61 (m, 3H), 1.58 – 1.48 (m, 1H), 1.36 – 1.25 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 110.7, 61.1, 46.3, 35.5, 33.8, 32.4, 27.8, 26.7, 26.6, 26.4, 25.6, 25.3, 24.7, 24.6. IR (neat): ν_{max} (cm^{-1}) 2928, 2130, 1732, 1452, 1267, 755. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 306.1498, found 306.1479.



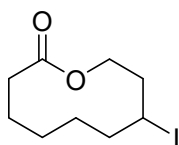
17-Thiocyanatooxacyclononadecan-2-one (4q) Colorless oil (51.6 mg, 76%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 4.33 – 4.22 (m, 2H), 3.17 – 3.10 (m, 1H), 2.32 (t, $J = 7.2$ Hz, 2H), 2.19 – 2.00 (m, 2H), 1.83 – 1.78 (m, 2H), 1.64 – 1.60 (m, 2H), 1.53 – 1.46 (m, 2H), 1.35 – 1.27 (m, 20H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 110.8, 60.9, 47.4, 34.9, 34.8, 34.4, 28.4, 28.3, 28.0, 27.9, 27.7, 27.43, 27.37 (overlapped), 27.3, 26.9, 26.3, 24.8. IR (neat): ν_{max} (cm^{-1}) 2924, 2201, 1733, 1450, 1267, 755. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{34}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 340.2305, found 340.2302.



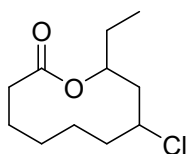
8-Chlorooxecan-2-one (5a) Colorless oil (33.6 mg, 88%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.48 – 4.42 (m, 1H), 4.37 – 4.35 (m, 1H), 4.27 – 4.21 (m, 1H), 2.47 – 2.37 (m, 2H), 2.29 (ddd, $J = 16.4, 10.0, 2.4$ Hz, 1H), 2.13 – 1.91 (m, 4H), 1.78 – 1.69 (m, 1H), 1.55 – 1.50 (m, 2H), 1.42 – 1.33 (m, 1H), 1.29 – 1.21 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 61.1, 60.1, 34.6, 33.9, 32.1, 27.1, 20.6, 20.4. IR (neat): ν_{max} (cm^{-1}) 2931, 1725, 1454, 1266, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{15}\text{ClO}_2\text{K}$ $[\text{M}+\text{K}]^+$ 229.0392, found 229.0388.



8-Bromooxecan-2-one (5a-2) Colorless oil (26.6 mg, 57%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.47 – 4.34 (m, 3H), 2.48 – 2.39 (m, 2H), 2.33 – 2.26 (m, 1H), 2.21 – 2.07 (m, 3H), 1.95 – 1.87 (m, 1H), 1.75 – 1.73 (m, 1H), 1.56 – 1.48 (m, 2H), 1.42 – 1.31 (m, 1H), 1.27 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 62.3, 53.2, 34.8, 34.7, 32.7, 27.1, 21.4, 20.5. IR (neat): ν_{max} (cm^{-1}) 2923, 1726, 1455, 1267, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{15}\text{BrO}_2\text{K}$ $[\text{M}+\text{K}]^+$ 272.9887, found 272.9891.

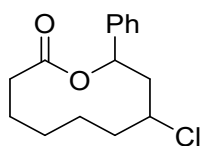


8-Iodooxecan-2-one (5a-3) Colorless oil (25.0 mg, 44%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.54 – 4.48 (m, 1H), 4.39 – 4.34 (m, 2H), 2.44 – 2.25 (m, 5H), 2.19 – 2.11 (m, 1H), 1.94 – 1.85 (m, 1H), 1.78 – 1.73 (m, 1H), 1.59 – 1.44 (m, 2H), 1.39 – 1.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 64.2, 36.8, 34.7, 34.5, 32.4, 27.0, 22.7, 20.6. IR (neat): ν_{max} (cm^{-1}) 2930, 1727, 1453, 1267, 755. HRMS (ESI) calcd for $\text{C}_9\text{H}_{16}\text{IO}_2$ $[\text{M}+\text{H}]^+$ 283.0189, found 283.0177.

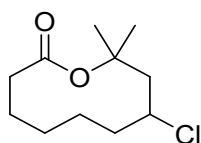


8-Chloro-10-ethyloxecan-2-one (5b) Colorless oil (36.3 mg, 83%). $R_f = 0.3$ (petroleum ether/ethyl

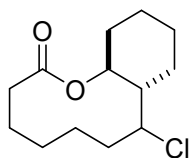
acetate = 40:1). d.r. = 2.7:1. ^1H NMR (400 MHz, CDCl_3) δ 4.87 – 4.76 (m, 1H), 4.44 – 4.38 (m, 0.3H), 4.04 – 3.98 (m, 0.7H), 2.51 – 2.40 (m, 1.4H), 2.28 – 2.20 (m, 2H), 2.18 – 2.12 (m, 0.7H), 2.09 – 1.91 (m, 2.3H), 1.83 – 1.56 (m, 6H), 1.45 – 1.38 (m, 0.8H), 1.29 – 1.21 (m, 1H), 0.96 – 0.89 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 174.6, 75.2, 59.6, 40.6, 35.0, 34.9, 28.1, 26.5, 22.0, 21.4, 9.9; minor isomer δ 173.8, 74.2, 58.6, 36.0, 34.9 (overlapped), 32.5, 26.9, 25.4, 21.1, 19.2, 10.4. IR (neat): ν_{max} (cm^{-1}) 2933, 1725, 1455, 1263, 755. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{19}\text{ClO}_2$ $[\text{M}]^+$ 218.1068, found 218.1060.



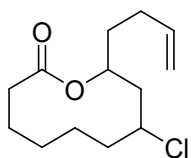
8-Chloro-10-phenyloxecan-2-one (5c) Colorless oil (46.4 mg, 87%). R_f = 0.3 (petroleum ether/ethyl acetate = 40:1). d.r. = 1:1. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 7.20 – 7.18 (m, 1H), 4.78 (d, J = 10.0 Hz, 0.5H), 4.66 (t, J = 11.2 Hz, 0.5H), 4.59 (dd, J = 11.6, 3.2 Hz, 0.5H), 4.53 (dt, J = 11.2, 3.2 Hz, 0.5H), 4.21 (ddd, J = 12.0, 4.8, 2.4 Hz, 0.5H), 3.90 (t, J = 12.0 Hz, 0.5H), 3.78 (dt, J = 11.2, 2.4 Hz, 0.5H), 3.60 (td, J = 11.6, 3.6 Hz, 0.5H), 2.63 – 2.56 (m, 1H), 2.52 – 2.38 (m, 1H), 2.28 (ddd, J = 16.4, 12.4, 2.0 Hz, 1H), 2.15 – 1.93 (m, 2H), 1.85 – 1.54 (m, 4H), 1.38 – 1.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , both diastereoisomers) δ 173.5, 173.2, 139.1, 139.0, 128.8, 128.4, 128.3, 127.9, 127.6, 127.3, 66.7, 66.4, 65.7, 63.1, 47.5, 34.7, 34.6, 34.5, 32.4, 27.3, 27.0, 21.8, 20.7, 20.2, 19.1. IR (neat): ν_{max} (cm^{-1}) 2946, 2156, 1729, 1453, 1263, 755, 695. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{20}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 267.1146, found 267.1135.



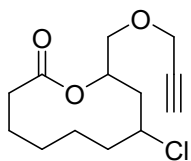
8-Chloro-10,10-dimethyloxecan-2-one (5d) Colorless oil (30.0 mg, 69%). R_f = 0.3 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.45 – 4.39 (m, 1H), 2.94 (dd, J = 15.2, 11.2 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.16 – 2.04 (m, 2H), 1.99 – 1.77 (m, 3H), 1.67 – 1.56 (m, 3H), 1.63 (s, 3H), 1.51 – 1.41 (m, 1H), 1.32 (s, 3H), 1.30 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 62.7, 42.7, 34.9, 30.4, 29.0, 27.3, 25.0, 21.4, 20.6, 14.9. IR (neat): ν_{max} (cm^{-1}) 2925, 1725, 1457, 1266, 755. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{23}\text{ClNO}_2$ $[\text{M}+\text{NH}_4]^+$ 236.1411, found 236.1415.



8-Chlorododecahydro-2H-benzo[b]oxecin-2-one (5e) Colorless oil (39.8 mg, 82%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1). d.r. = 20:1, ^1H NMR (400 MHz, CDCl_3) δ 4.55 – 4.49 (m, 1H), 3.71 – 3.66 (m, 1H), 2.49 – 2.40 (m, 2H), 2.30 – 2.23 (m, 1H), 2.12 – 2.04 (m, 2H), 1.94 – 1.90 (m, 2H), 1.80 – 1.73 (m, 3H), 1.67 – 1.60 (m, 3H), 1.42 – 1.28 (m, 5H), 1.01 – 0.91 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , single isomer) δ 173.4, 75.1, 66.9, 47.3, 34.6, 34.2, 31.9, 30.7, 25.7, 24.3, 23.8, 21.8, 20.8. IR (neat): ν_{max} (cm^{-1}) 2929, 1725, 1453, 1265, 755. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{25}\text{ClNO}_2$ $[\text{M}+\text{NH}_4]^+$ 262.1568, found 262.1577.



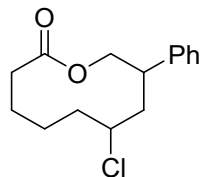
10-(but-3-en-1-yl)-8-chlorooxecan-2-one (5f) Colorless oil (38.8 mg, 80%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1). d.r. = 3.3:1, ^1H NMR (400 MHz, CDCl_3) δ 5.84 – 5.73 (m, 1H), 5.04 – 4.86 (m, 3H), 4.44 – 4.38 (m, 0.22H), 4.05 – 3.99 (m, 0.73H), 2.50 – 2.40 (m, 1H), 2.30 – 1.91 (m, 7H), 1.88 – 1.69 (m, 3H), 1.68 – 1.49 (m, 3H), 1.48 – 1.34 (m, 1H), 1.29 – 1.20 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 174.4, 137.6, 115.3, 73.6, 59.5, 40.4, 35.0, 34.8, 34.1, 29.8, 26.5, 21.9, 21.3; minor isomer δ 173.6, 137.3, 115.6, 72.3, 58.5, 36.3, 34.8, 32.5, 31.4, 30.0, 26.9, 21.0, 19.1. IR (neat): ν_{max} (cm^{-1}) 3938, 1727, 1642, 1433, 1212, 860. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{21}\text{ClO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 267.1122, found 267.1120.



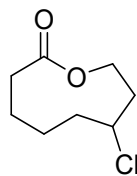
8-Chloro-10-((prop-2-yn-1-yloxy)methyl)oxecan-2-one (5g) Colorless oil (39.0 mg, 76%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1). d.r. = 3.:1, ^1H NMR (400 MHz, CDCl_3) δ 5.15 – 5.10 (m, 0.24H), 5.01 – 4.96 (m, 0.75), 4.47 – 4.41 (m, 0.24H), 4.20 – 4.17 (m, 2H), 4.05 – 3.99 (m, 0.77H), 3.78 – 3.65 (m, 2H), 2.52 – 2.35 (m, 3H), 2.28 – 2.17 (m, 2H), 2.11 – 1.94 (m, 2H), 1.88 – 1.76 (m, 1H), 1.68 – 1.53 (m, 3H), 1.47 – 1.41 (m, 1H), 1.24 – 1.13 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 174.2, 79.3, 75.1, 72.5, 71.0, 59.2, 58.6, 37.8, 34.9 (overlapped), 34.8, 26.7, 22.0, 21.1;

minor isomer δ 173.6, 79.2, 75.2, 70.9, 70.1, 58.8, 58.6, 36.8, 34.9 (overlapped), 32.7, 26.9, 21.2, 19.7.

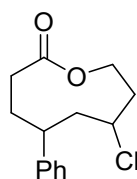
IR (neat): $\nu_{\max}$ (cm^{-1}) 3294, 2091, 1721, 1445, 1205, 875. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{ClO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 281.0914, found 281.0916.



7-Chloro-9-phenyloxecan-2-one (5h) Colorless oil (32.6 mg, 61%). R_f = 0.3 (petroleum ether/ethyl acetate = 40:1). d.r. = 4.5:1, ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.20 (m, 1H), 4.75 – 4.67 (m, 0.3H), 4.46 (t, J = 11.6 Hz, 0.8H), 4.34 (ddd, J = 10.8, 6.0, 4.4 Hz, 0.8H), 4.09 (dd, J = 11.2, 4.0 Hz, 0.8H), 3.91 (t, J = 11.6 Hz, 0.1H), 3.46 – 3.24 (m, 1H), 2.64 – 2.44 (m, 1H), 2.36 – 2.06 (m, 3H), 2.19 – 2.05 (m, 0.4H), 1.97 – 1.65 (m, 5H), 1.59 – 1.43 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , two diastereoisomers) major isomer δ 173.6, 141.2, 129.0, 127.5, 127.36, 68.8, 60.1, 44.7, 44.3 (overlapped), 37.3, 34.9, 23.7, 20.9; minor isomer δ 173.1, 140.2, 128.9, 127.7, 127.41, 69.0, 58.1, 44.3 (overlapped), 40.3, 34.6, 32.5, 25.0, 20.6. IR (neat): $\nu_{\max}$ (cm^{-1}) 2341, 1728, 1263, 737, 700. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{20}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 267.1146, found 267.1134.

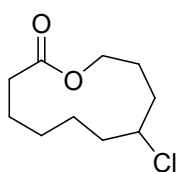


7-Chlorooxonan-2-one (5i) Colorless oil (25.0 mg, 71%). R_f = 0.3 (petroleum ether/ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.39 (ddd, J = 11.6, 6.8, 3.2 Hz, 1H), 4.31 (ddd, J = 11.6, 8.0, 2.4 Hz, 1H), 4.19 – 4.13 (m, 1H), 2.39 – 2.30 (m, 1H), 2.31 (t, J = 6.8 Hz, 2H), 2.27 – 2.18 (m, 1H), 1.93 – 1.87 (m, 2H), 1.79 – 1.56 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 61.6, 58.9, 36.8, 36.3, 33.9, 24.5, 21.0. IR (neat): $\nu_{\max}$ (cm^{-1}) 2251, 1733, 1455, 1265, 755. HRMS (ESI) calcd for $\text{C}_8\text{H}_{13}\text{ClO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 199.0496, found 199.0480.

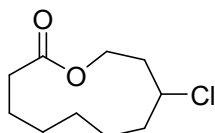


7-Chloro-5-phenyloxonan-2-one (5j) Colorless oil (34.1 mg, 68%). R_f = 0.3 (petroleum ether/ethyl

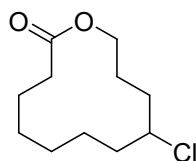
acetate = 40:1). d.r. = 1:1, ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.14 (m, 1H), 5.03 – 4.97 (m, 0.5H), 4.62 (td, J = 11.6, 2.4 Hz, 0.5H), 4.27 – 4.22 (m, 0.5H), 4.18 (dt, J = 11.6, 3.6 Hz, 0.5H), 4.15 – 4.05 (m, 1H), 3.11 – 3.06 (m, 0.5H), 2.92 – 2.87 (m, 0.5H), 2.76 – 2.67 (m, 0.5H), 2.54 – 2.39 (m, 2.5H), 2.37 – 2.20 (m, 2H), 2.18 – 2.03 (m, 2H), 1.96 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , both diastereoisomers) δ 174.5, 174.1, 148.7, 147.1, 128.9, 128.7, 127.3, 127.0, 126.7, 126.3, 62.3, 60.8, 57.5, 57.1, 45.5, 45.5, 41.0, 39.7, 37.8, 35.9, 34.4, 33.9, 33.5, 32.8. IR (neat): ν_{max} (cm^{-1}) 2949, 1736, 1453, 1238, 1147, 756, 700. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 253.0989, found 253.0969.



8-Chlorooxacycloundecan-2-one (5k) Colorless oil (23.3 mg, 57%). R_f = 0.3 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.27 – 4.07 (m, 3H), 2.48 – 2.41 (m, 1H), 2.31 – 2.23 (m, 1H), 2.13 – 1.97 (m, 4H), 1.77 – 1.56 (m, 6H), 1.37 – 1.30 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 64.4, 60.7, 35.3, 34.3, 32.0, 26.1, 23.9, 22.7, 21.1. IR (neat): ν_{max} (cm^{-1}) 2924, 2389, 1727, 1267, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{21}\text{ClNO}_2$ $[\text{M}+\text{NH}_4]^+$ 222.1255, found 222.1270.

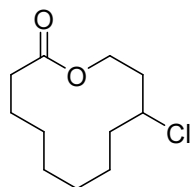


9-Chlorooxacycloundecan-2-one (5l) Colorless oil (23.6 mg, 58%). R_f = 0.3 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.35 (ddd, J = 11.6, 8.0, 1.6 Hz, 1H), 4.24 – 4.14 (m, 2H), 2.41 – 2.34 (m, 1H), 2.34 (t, J = 6.0 Hz, 2H), 2.24 – 2.16 (m, 1H), 1.84 – 1.43 (m, 7H), 1.42 – 1.32 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 60.9, 60.2, 35.5, 34.2, 34.0, 26.0, 24.2, 21.3, 20.2. IR (neat): ν_{max} (cm^{-1}) 2920, 1756, 1267, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{18}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 205.0990, found 205.1009.

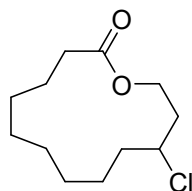


9-Chlorooxacyclododecan-2-one (5m) Colorless oil (15.4 mg, 35%). R_f = 0.3 (petroleum ether/ethyl

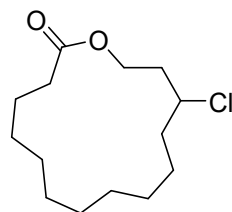
acetate = 60:1). ^1H NMR (400 MHz, CDCl_3) δ 4.57 – 4.52 (m, 1H), 4.29 – 4.23 (m, 1H), 3.96 – 3.90 (m, 1H), 2.46 – 2.32 (m, 2H), 2.09 – 1.99 (m, 2H), 1.97 – 1.74 (m, 4H), 1.67 – 1.56 (m, 3H), 1.50 – 1.28 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 64.3, 60.0, 35.2, 33.9, 33.2, 25.0, 24.6, 23.7, 23.6, 22.5. IR (neat): ν_{max} (cm^{-1}) 2913, 1745, 1259, 745. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{23}\text{ClNO}_2$ $[\text{M}+\text{NH}_4]^+$ 236.1411, found 236.1421.



10-Chlorooxacyclododecan-2-one (5n) Colorless oil (26.2 mg, 60%). R_f = 0.3 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.64 – 4.59 (m, 1H), 4.25 – 4.19 (m, 1H), 4.14 – 4.08 (m, 1H), 2.49 – 2.43 (m, 1H), 2.34 – 2.27 (m, 1H), 2.19 – 2.13 (m, 1H), 2.08 – 1.93 (m, 2H), 1.87 – 1.73 (m, 2H), 1.66 – 1.60 (m, 1H), 1.52 – 1.29 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.7, 60.9, 58.9, 35.7, 35.6, 34.2, 24.7, 24.4, 24.2, 23.6, 21.9. IR (neat): ν_{max} (cm^{-1}) 2032, 1727, 1455, 1256, 983, 801. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{19}\text{ClO}_2\text{K}$ $[\text{M}+\text{K}]^+$ 257.0705, found 257.0703.

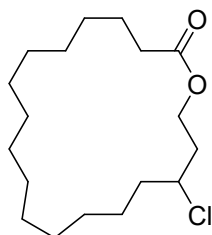


11-Chlorooxacyclotridecan-2-one (5o) Colorless oil (22.8 mg, 49%). R_f = 0.3 (petroleum ether/ethyl acetate = 60:1). ^1H NMR (400 MHz, CDCl_3) δ 4.35 – 4.28 (m, 2H), 4.08 – 4.01 (m, 1H), 2.45 – 2.38 (m, 1H), 2.33 – 2.26 (m, 1H), 2.23 – 2.15 (m, 1H), 2.07 – 1.99 (m, 1H), 1.93 – 1.74 (m, 2H), 1.70 – 1.64 (m, 2H), 1.60 – 1.54 (m, 1H), 1.42 – 1.29 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 61.5, 58.6, 37.5, 36.8, 34.7, 26.8, 26.4, 25.3, 25.1, 24.6, 23.3. IR (neat): ν_{max} (cm^{-1}) 2913, 1745, 1269, 758. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{21}\text{ClO}_2$ $[\text{M}]^+$ 232.1224, found 232.1216.



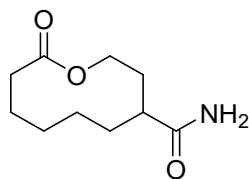
13-Chlorooxacyclopentadecan-2-one (5p) Colorless oil (37.5 mg, 72%). R_f = 0.3 (petroleum ether/ethyl

acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 4.36 – 4.22 (m, 2H), 4.05 (ddd, J = 12.8, 9.6, 4.8 Hz, 1H), 2.41 – 2.30 (m, 2H), 2.17 – 2.09 (m, 1H), 2.05 – 1.97 (m, 1H), 1.84 (ddd, J = 14.4, 8.8, 4.8 Hz, 1H), 1.74 (dt, J = 10.4, 4.8 Hz, 1H), 1.70 – 1.61 (m, 3H), 1.51 – 1.41 (m, 2H), 1.38 – 1.24 (m, 11H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 61.3, 58.8, 38.1, 35.9, 34.0, 28.0, 26.8, 26.6, 25.61, 25.62, 25.4, 24.9, 24.3. IR (neat): ν_{max} (cm^{-1}) 2927, 1733, 1263, 755. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{25}\text{ClNO}_2\text{K}$ $[\text{M}+\text{K}]^+$ 299.1175, found 299.1181.

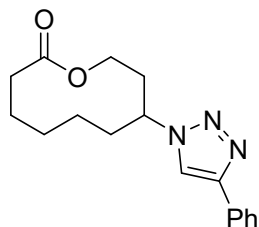


17-Chlorooxacyclononadecan-2-one (5q) Colorless oil (43.6 mg, 69%). R_f = 0.3 (petroleum ether/ethyl acetate = 100:1). ^1H NMR (400 MHz, CDCl_3) δ 4.33 – 4.21 (m, 2H), 4.07 – 3.99 (m, 1H), 2.33 – 2.29 (m, 2H), 2.15 – 2.08 (m, 1H), 1.99 – 1.90 (m, 1H), 1.79 – 1.74 (m, 2H), 1.66 – 1.63 (m, 2H), 1.50 – 1.44 (m, 2H), 1.35 – 1.27 (m, 20H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 61.2, 59.7, 38.1, 37.6, 34.6, 28.5, 28.1, 27.9, 27.7, 27.60, 27.55, 27.4, 27.0, 25.9, 24.9. IR (neat): ν_{max} (cm^{-1}) 2924, 1733, 1451, 1267, 1111, 755. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{34}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 317.2242, found 317.2226.

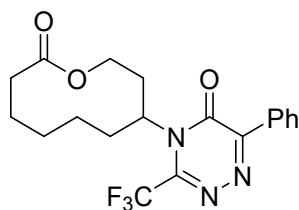
12. Characterization of Products 6-11



10-Oxooxecane-4-carboxamide (6) Colorless oil (23.9 mg, 60%). R_f = 0.3 (ethyl acetate). ^1H NMR (400 MHz, CDCl_3) δ 5.65 – 5.68 (br, 2H), 4.45 – 4.34 (m, 2H), 2.46 – 2.39 (m, 2H), 2.31 – 2.24 (m, 1H), 2.10 – 1.98 (m, 2H), 1.95 – 1.84 (m, 2H), 1.78 – 1.69 (m, 2H), 1.59 – 1.45 (m, 2H), 1.44 – 1.33 (m, 1H), 1.30 – 1.21 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 178.3, 173.8, 63.5, 43.2, 34.9, 27.8, 27.1, 26.8, 22.0, 20.7. IR (neat): ν_{max} (cm^{-1}) 2932, 1729, 1453, 1266, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{NH}_4]^+$ 217.1547, found 217.1548.

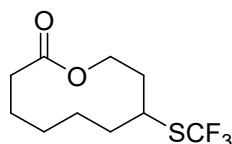


8-(4-Phenyl-1H-1,2,3-triazol-1-yl)oxecan-2-one (7) White solid (41.9 mg, 70%). Melting point ($^{\circ}\text{C}$): 140-141. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.80 (m, 3H), 7.41 (t, J = 7.2 Hz, 2H), 7.32 (tt, J = 7.6, 1.2 Hz, 1H), 4.89 – 4.83 (m, 1H), 4.42 (t, J = 4.8 Hz, 2H), 2.50 – 2.44 (m, 1H), 2.40 – 2.28 (m, 4H), 2.08 – 1.91 (m, 2H), 1.86 – 1.78 (m, 1H), 1.63 – 1.52 (m, 3H), 1.36 – 1.25 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 147.5, 130.7, 128.9, 128.2, 125.7, 118.2, 61.6, 59.6, 34.7, 30.3, 29.8, 27.0, 20.60, 20.55. IR (neat): ν_{max} (cm^{-1}) 2920, 1726, 1432, 1267, 755. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{25}\text{N}_4\text{O}_2$ $[\text{M}+\text{NH}_4]^+$ 317.1972, found 317.1952.

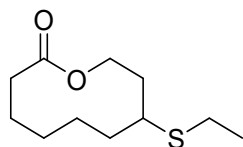


4-(10-Oxooxecan-4-yl)-6-phenyl-3-(trifluoromethyl)-1,2,4-triazin-5(4H)-one (8) Colorless oil (49.7 mg, 63%). R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.27 – 8.25 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 4.36 – 4.33 (m, 2H), 4.24 (t, J = 8.4 Hz, 1H), 3.10 – 3.00

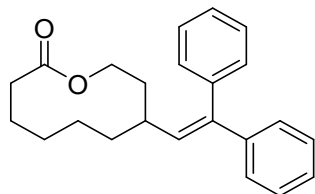
(m, 1H), 2.67 – 2.59 (m, 1H), 2.54 (dt, $J = 15.2, 4.0$ Hz, 1H), 2.32 – 2.24 (m, 1H), 1.94 – 1.89 (m, 2H), 1.73 – 1.67 (m, 2H), 1.62 – 1.54 (m, 2H), 1.50 – 1.42 (m, 1H), 1.30 – 1.24 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 159.8, 151.8, 142.4 (d, $J = 33.7$ Hz), 132.0, 131.5, 129.7, 128.5, 118.2 (q, $J = 275.7$ Hz), 62.4, 60.9, 34.8, 31.8, 31.2, 25.6, 25.0, 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.96. IR (neat): ν_{max} (cm^{-1}) 2934, 2345, 1767, 1267, 755. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{24}\text{F}_3\text{N}_4\text{O}_3$ $[\text{M}+\text{NH}_4]^+$ 413.1795, found 413.1785.



8-((Trifluoromethyl)thio)oxecan-2-one (9) Colorless oil (34.4 mg, 67%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.44 – 4.32 (m, 2H), 3.58 – 3.52 (m, 1H), 2.43 – 2.24 (m, 3H), 2.08 – 1.91 (m, 2H), 1.88 – 1.72 (m, 3H), 1.58 – 1.47 (m, 2H), 1.36 – 1.28 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 132.6 (q, $J = 304.6$ Hz), 62.1, 43.8, 34.7, 30.5, 29.8, 27.0, 20.8, 20.5. ^{19}F NMR (376 MHz, CDCl_3) δ -39.56. IR (neat): ν_{max} (cm^{-1}) 2926, 1731, 1454, 1267, 1109, 755. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{15}\text{F}_3\text{O}_2\text{SLi}$ $[\text{M}+\text{Li}]^+$ 263.0899, found 263.0878.



8-(Ethylthio)oxecan-2-one (10) Colorless oil (30.3 mg, 70%). $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, CDCl_3) δ 4.45 – 4.39 (m, 1H), 4.35 – 4.30 (m, 1H), 2.98 – 2.92 (m, 1H), 2.51 (q, $J = 7.2$ Hz, 2H), 2.39 (ddd, $J = 16.4, 8.0, 3.2$ Hz, 1H), 2.27 (ddd, $J = 16.0, 10.4, 2.8$ Hz, 1H), 2.19 – 2.12 (m, 1H), 1.88 – 1.68 (m, 5H), 1.53 – 1.46 (m, 2H), 1.34 – 1.26 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.1, 81.7, 59.3, 40.8, 36.4, 31.2, 28.9, 27.0, 26.6, 21.3, 18.4. IR (neat): ν_{max} (cm^{-1}) 2932, 1728, 1453, 1265, 755. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2\text{SLi}$ $[\text{M}+\text{Li}]^+$ 223.1339, found 223.1323.



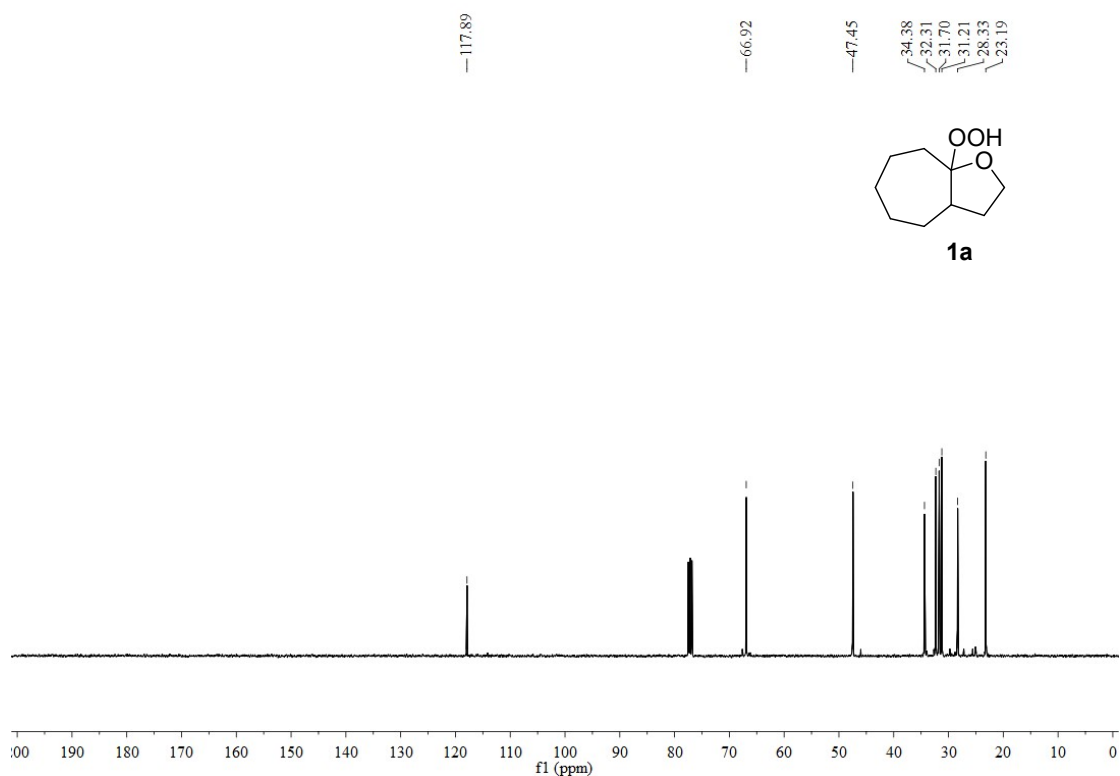
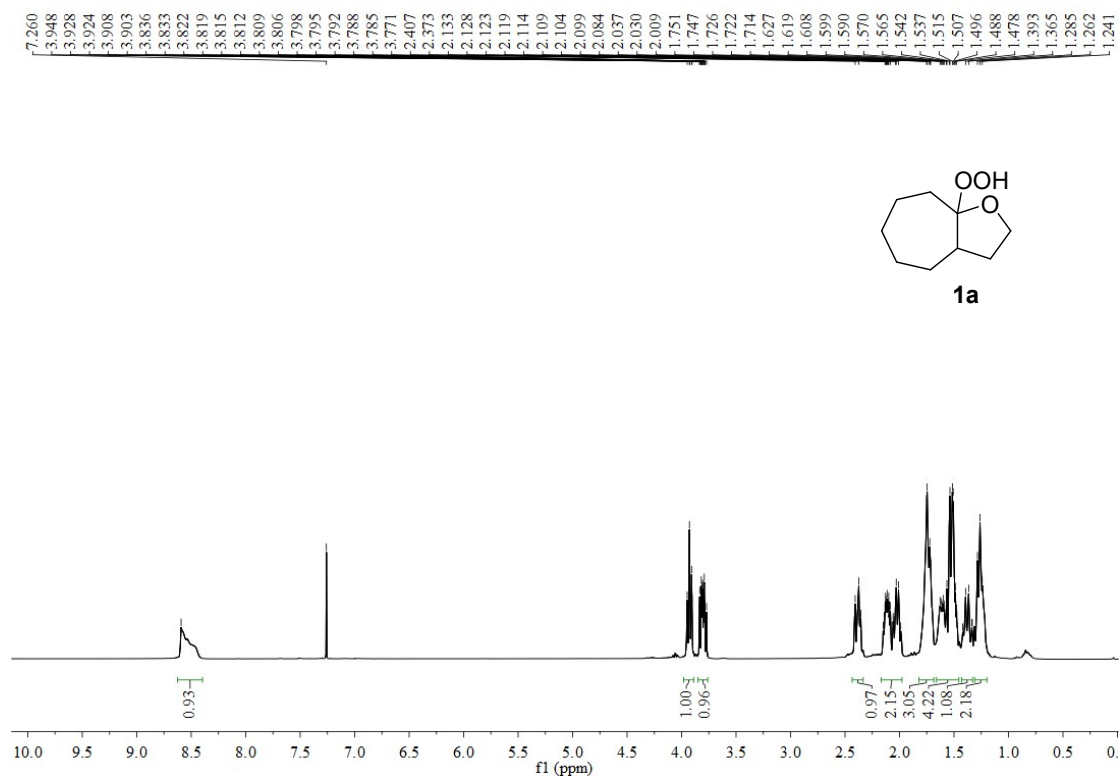
8-(2,2-Diphenylvinyl)oxecan-2-one (11) Colorless oil (6.7 mg, 10%). R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.28 (m, 4H), 7.25 – 7.19 (m, 4H), 7.17 – 7.15 (m, 2H), 6.12 (d, J = 10.4 Hz, 1H), 4.44 – 4.39 (m, 1H), 4.21 – 4.15 (m, 1H), 2.55 – 2.48 (m, 1H), 2.40 – 2.31 (m, 2H), 1.90 – 1.73 (m, 4H), 1.67 – 1.42 (m, 4H), 1.34 – 1.27 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 142.6, 140.3, 140.2, 133.5, 129.7, 128.4, 128.2, 127.2, 127.1, 63.6, 36.9, 35.0, 30.5, 29.8, 27.5, 20.8, 20.7. IR (neat): ν_{max} (cm^{-1}) 2946, 1727, 1701, 1450, 1235, 1029, 764, 699. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$ 335.2006, found 335.1991.

13. References

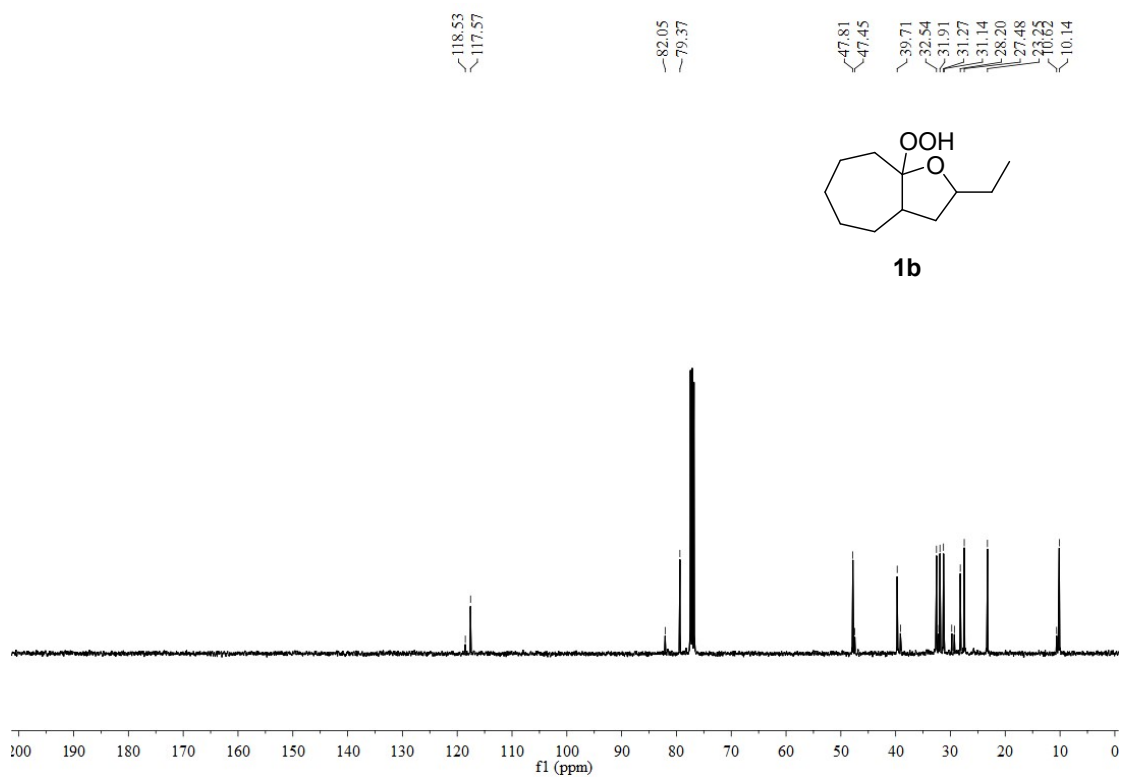
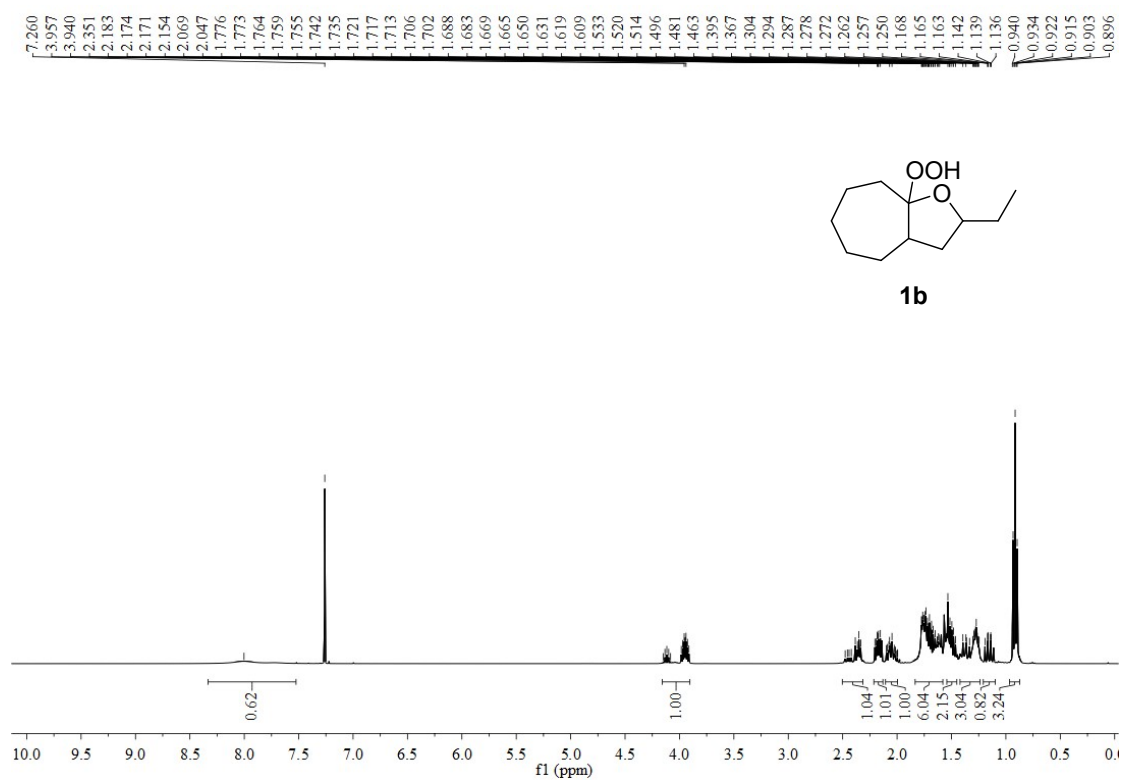
1. (a) G. H. Posner, J. P. Maxwell and M. Kahraman, *J. Org. Chem.*, 2003, **68**, 3049; (b) J. Du, X. Yang, X. Wang, Q. An, X. He, H. Pan and Z. Zuo, *Angew. Chem., Int. Ed.*, 2021, **60**, 5370.
2. N. Hanaki, K. Ishihara, M. Kaino, Y. Naruse and H. Yamamoto, *Tetrahedron*, 1996, **52**, 7297.
3. S. Liu, M. Bai, P.-F. Xu, Q.-X. Sun, X.-H. Duan and L.-N. Guo, *Chem. Commun.*, 2021, **57**, 8652.
4. P. Marce, J. Lynch, A. J. Blacker and J. M. J. Williams, *Chem. Commun.*, 2016, **52**, 1436.
5. Y.-L. Su, L. Tram, D. Wherritt, H. Arman, W. P. Griffith and M. P. Doyle, *ACS Catal.*, 2020, **10**, 13682.
6. W. Wu, J. Wang, Y. Wang, Y. Huang, Y. Tan and Z. Weng, *Angew. Chem., Int. Ed.*, 2017, **56**, 10476.
7. K. Zhang, T. Liang, Y. Wang, C. He, Y. Hu, X.-H. Duan and L. Liu, *Org. Chem. Front.*, 2022, **9**, 966.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G.E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Jr. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16, Revision A.03*; Gaussian, Inc.: Wallingford, CT, 2016.
9. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) K. Raghavachari, *Theor. Chem. Acc.*, 2000, **103**, 361; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (d) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785.
10. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
11. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta.*, 1990, **77**, 123.
12. (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (b) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
13. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
14. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem., B* 2009, **113**, 6378.
15. (a) K. Fukui, *J. Phys. Chem.* 1970, **74**, 4161; (b) K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363.
16. CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (<http://www.cylview.org>).

14. ^1H NMR and ^{13}C NMR Spectra of Hemiketal Hydroperoxides 1

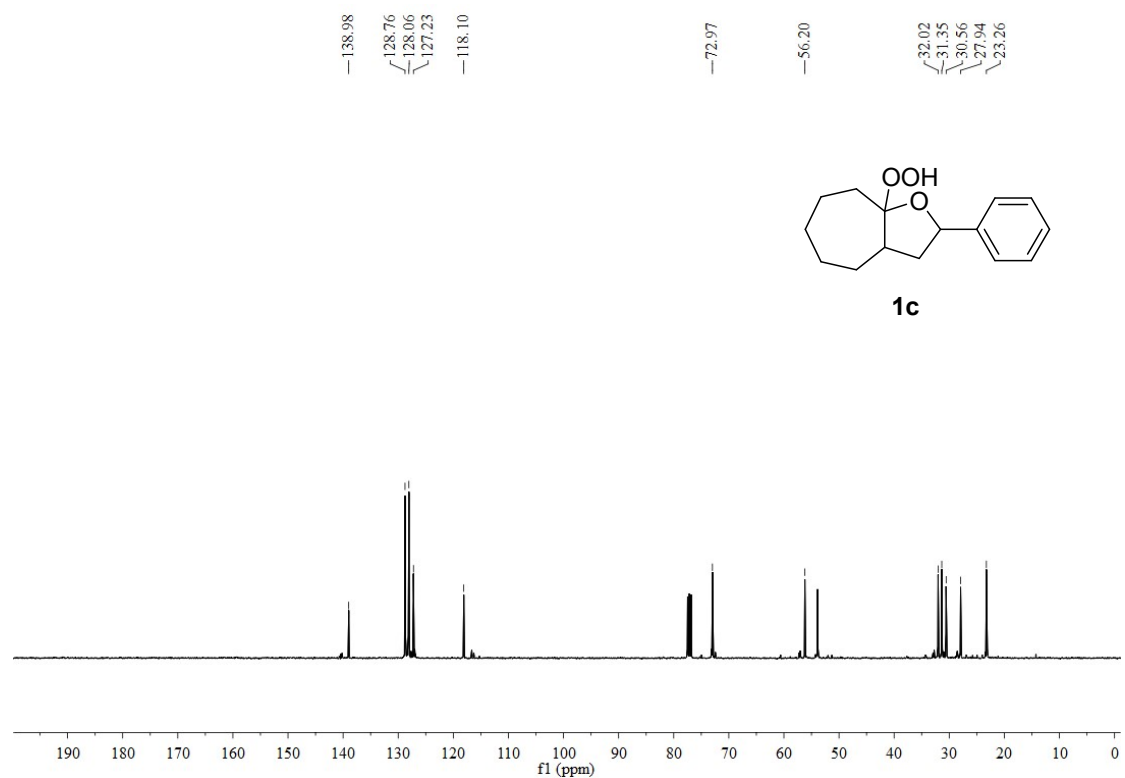
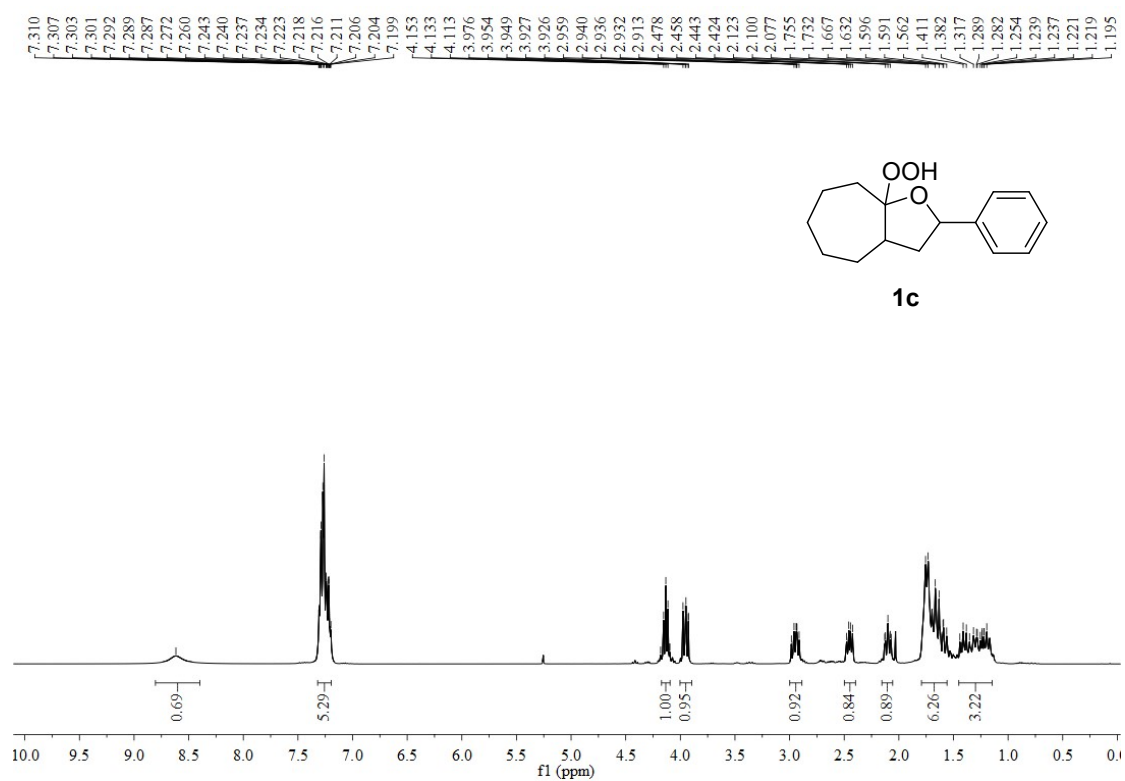
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **1a**



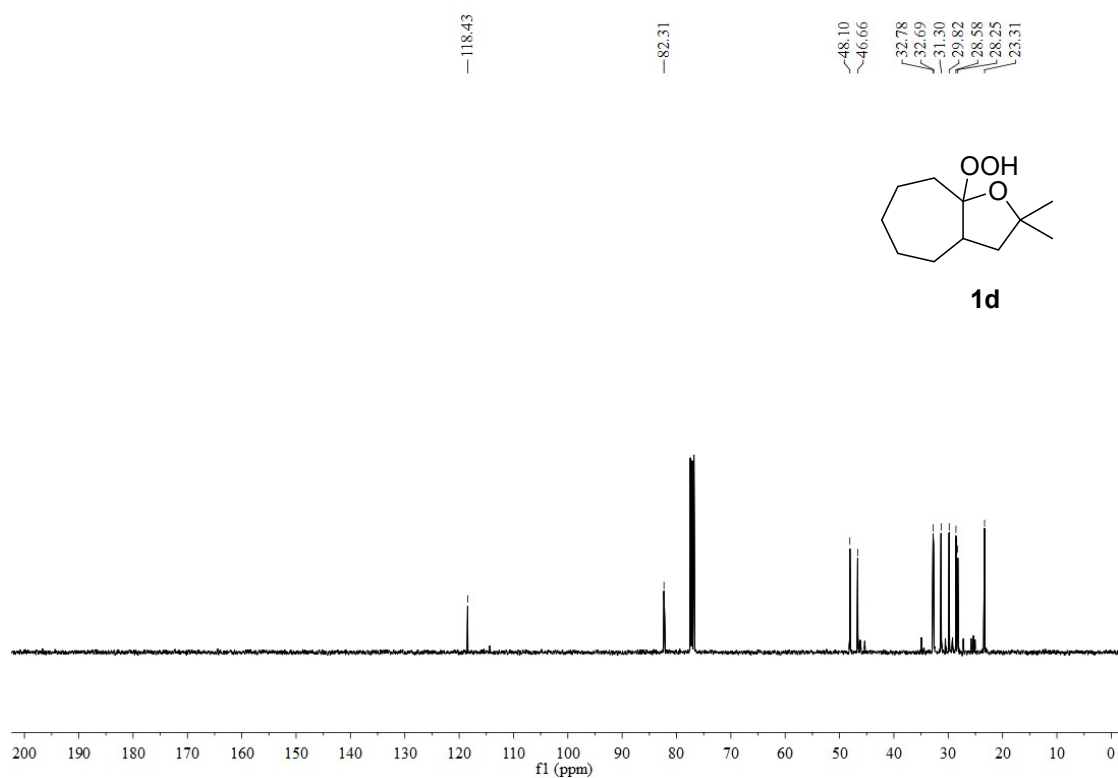
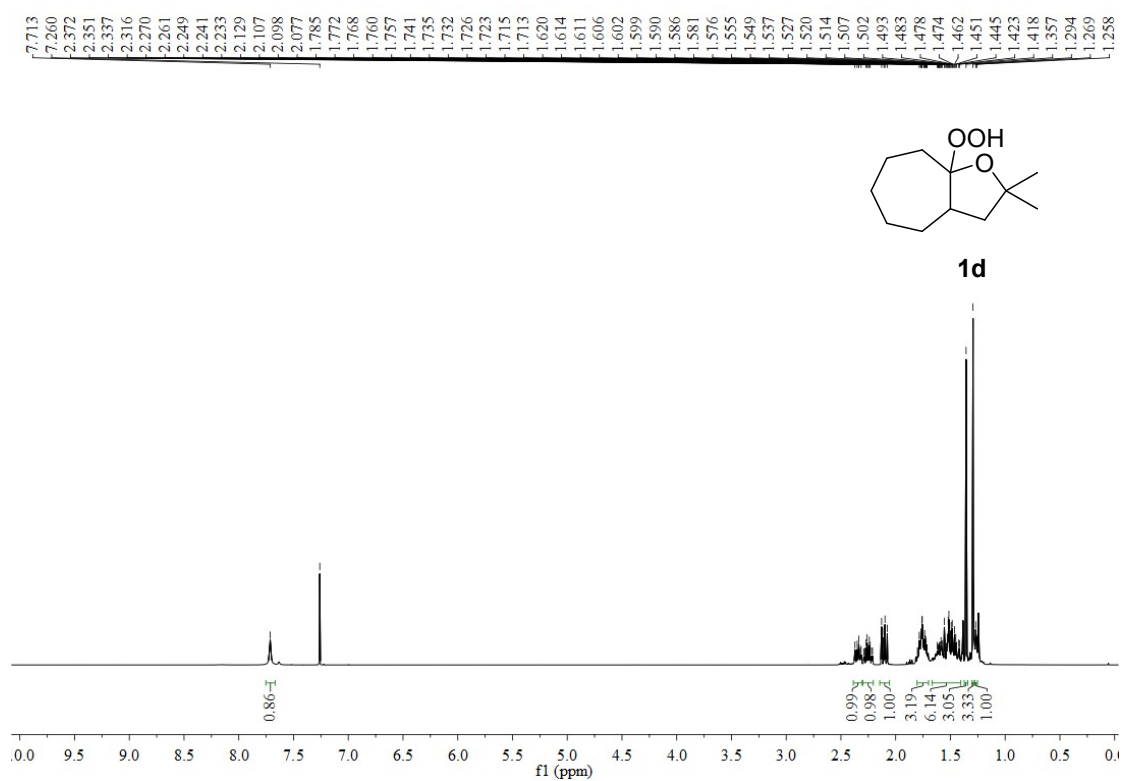
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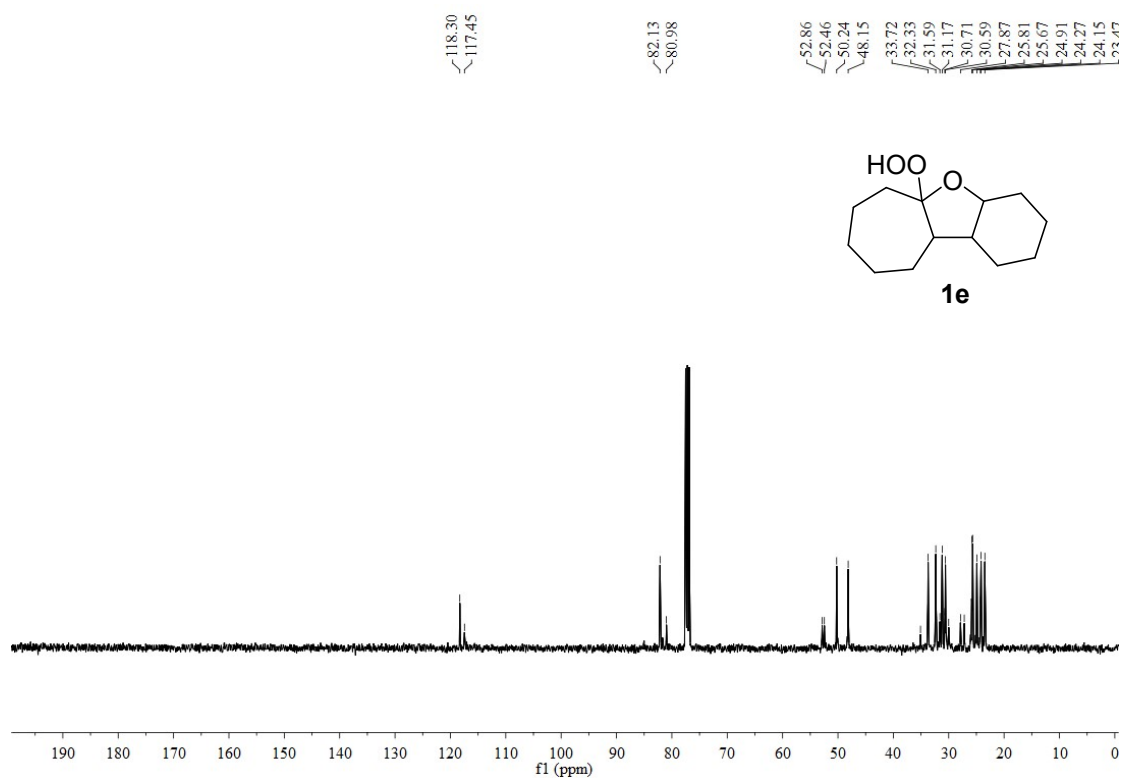
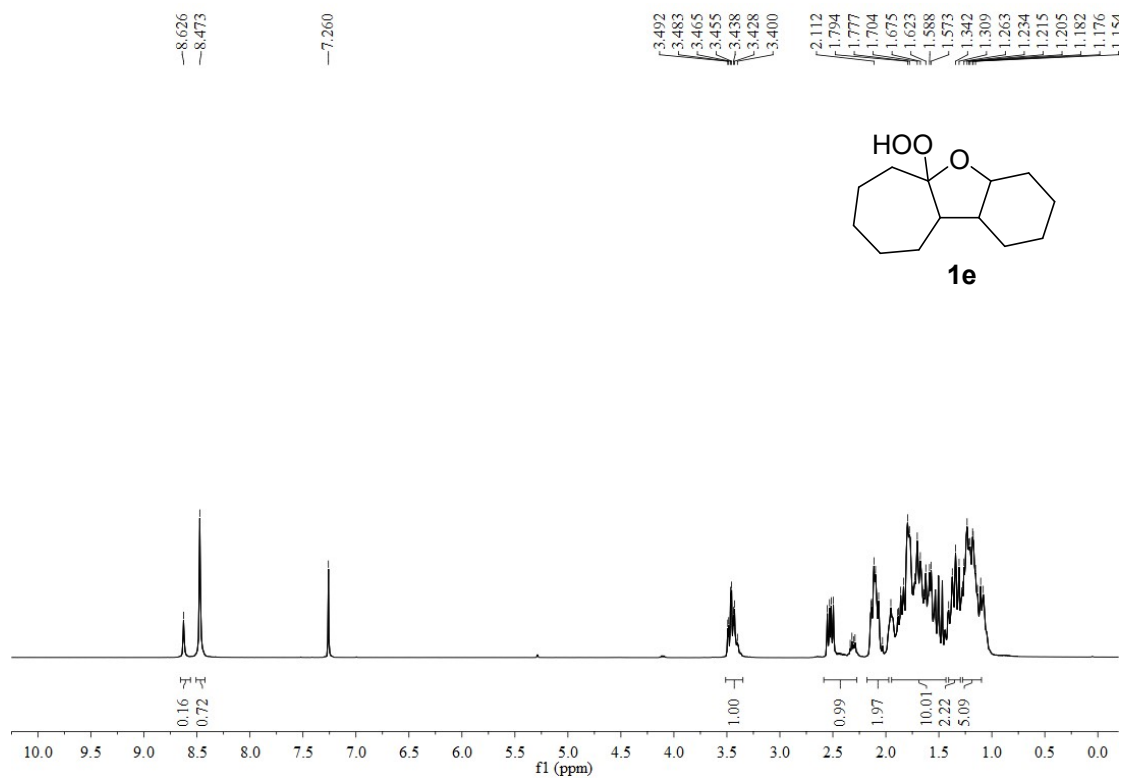
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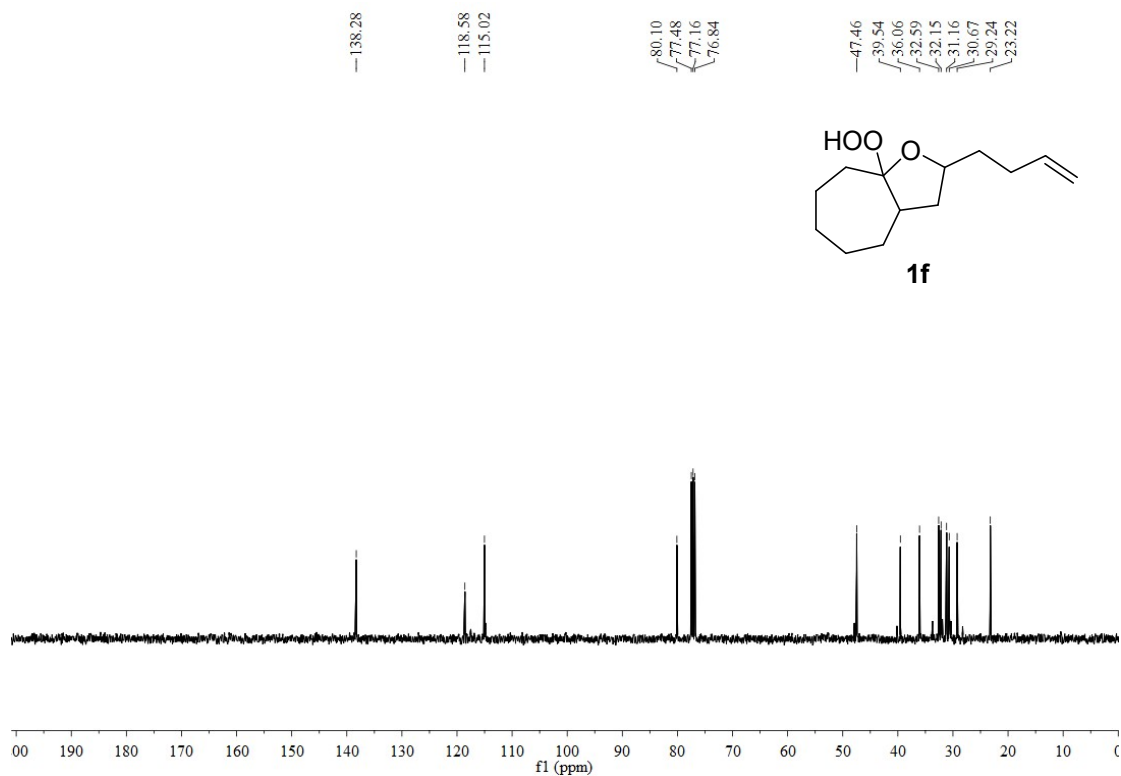
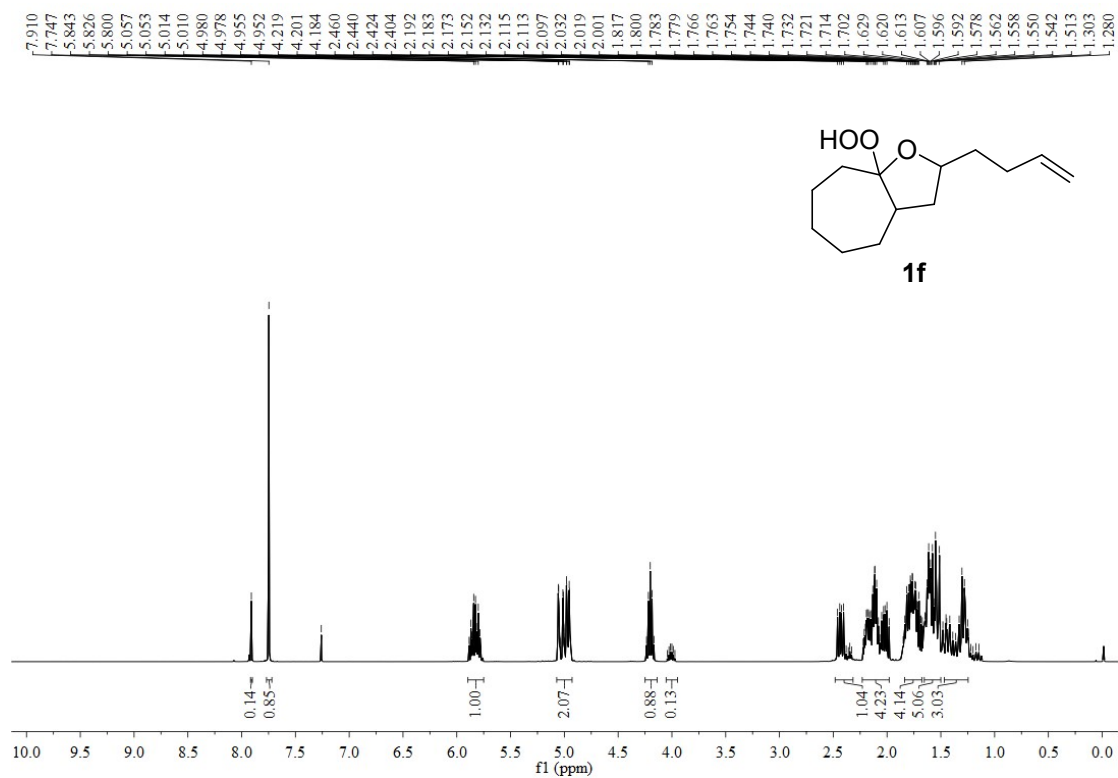
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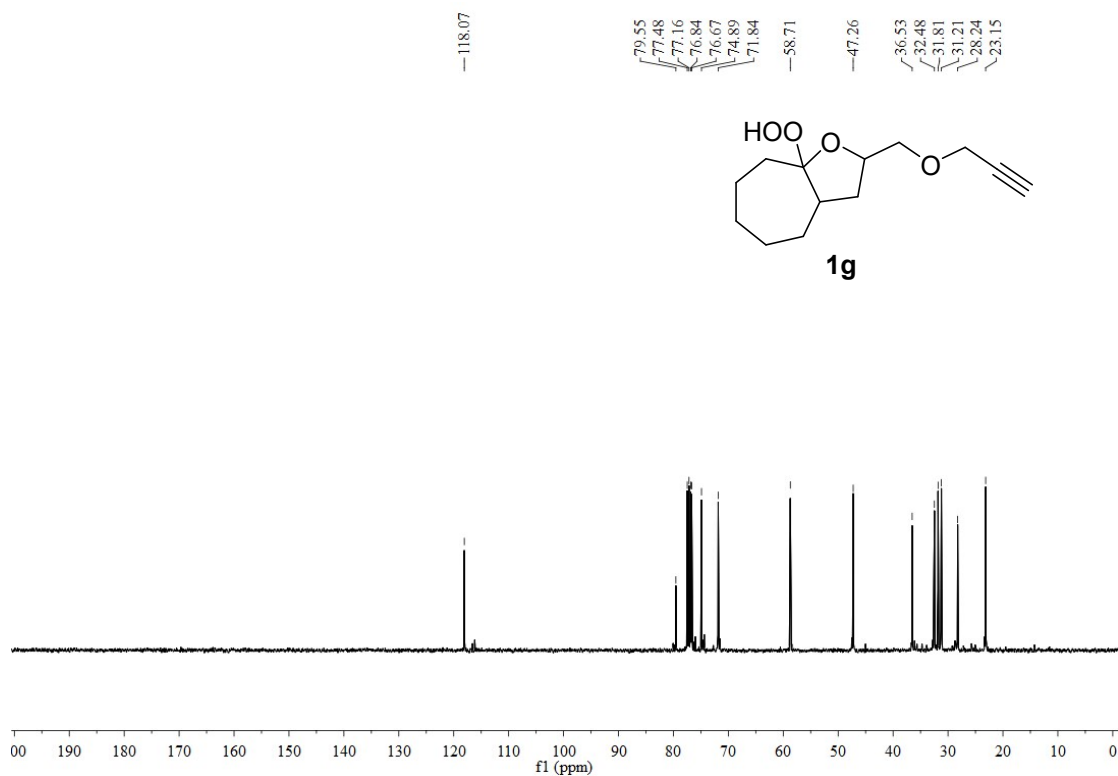
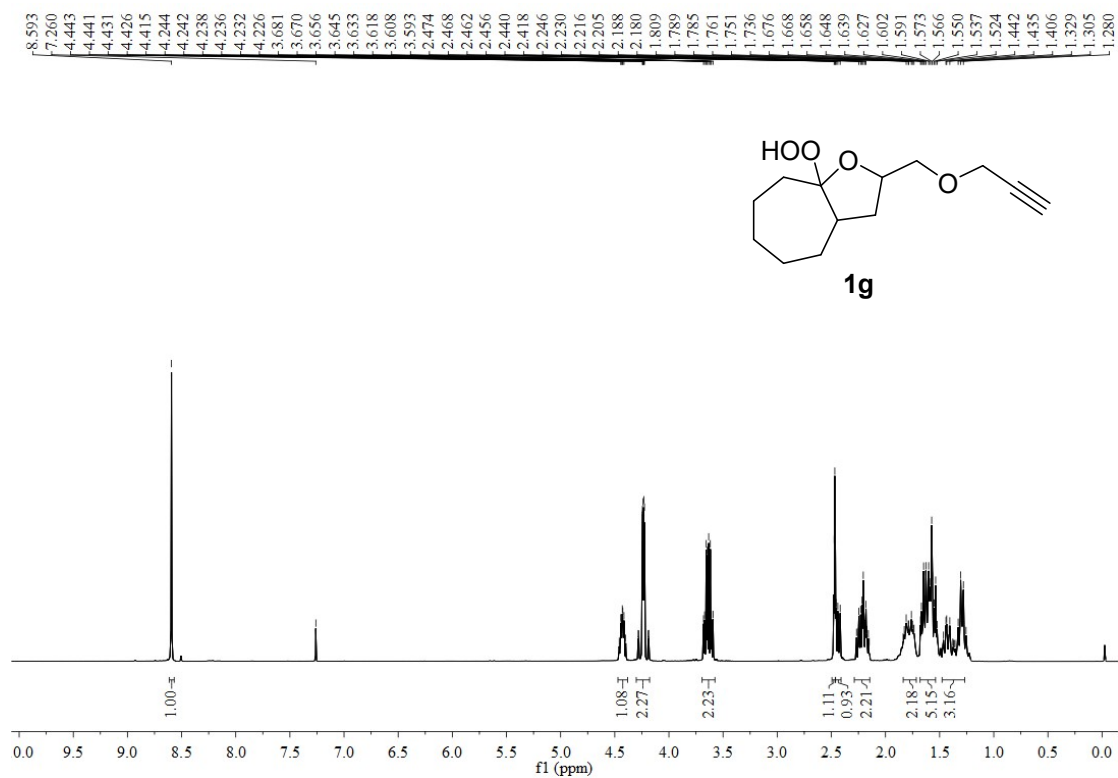
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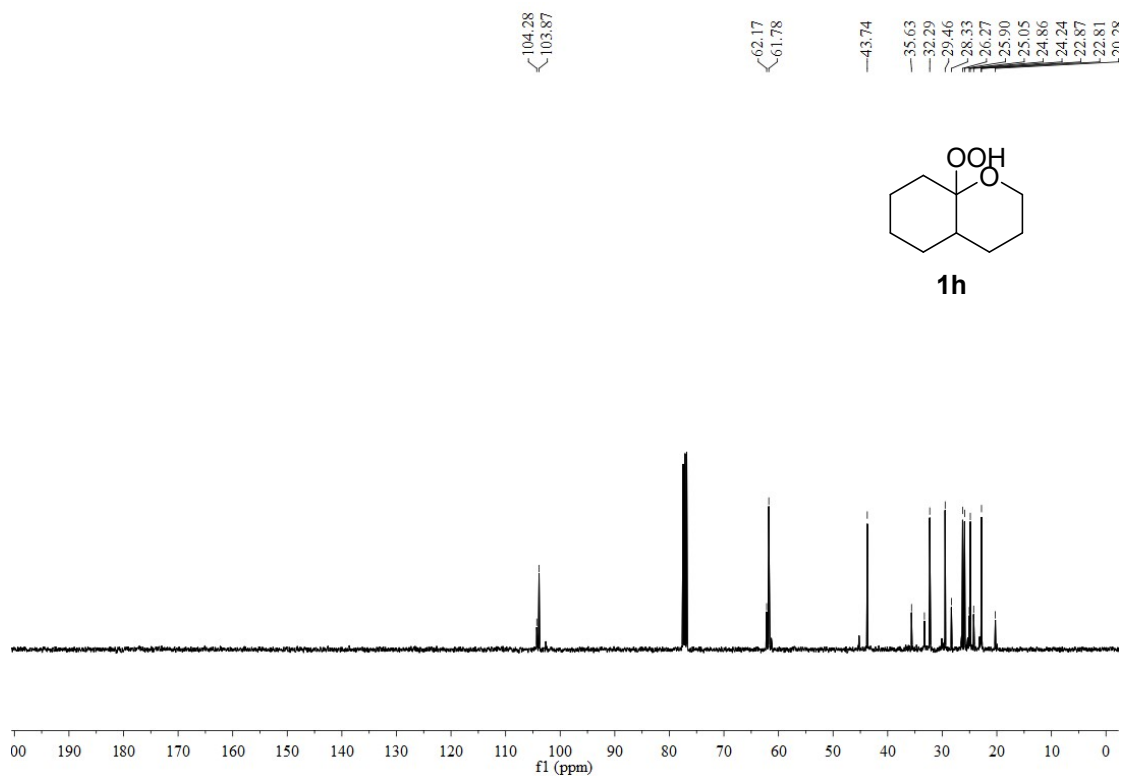
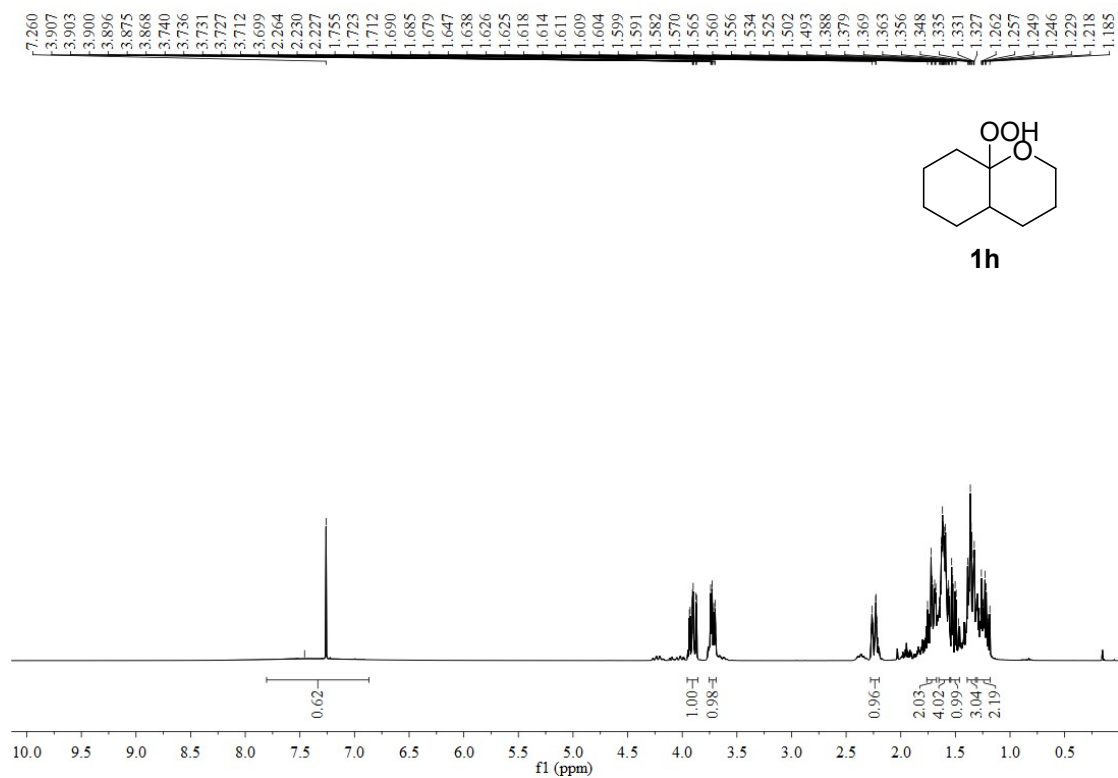
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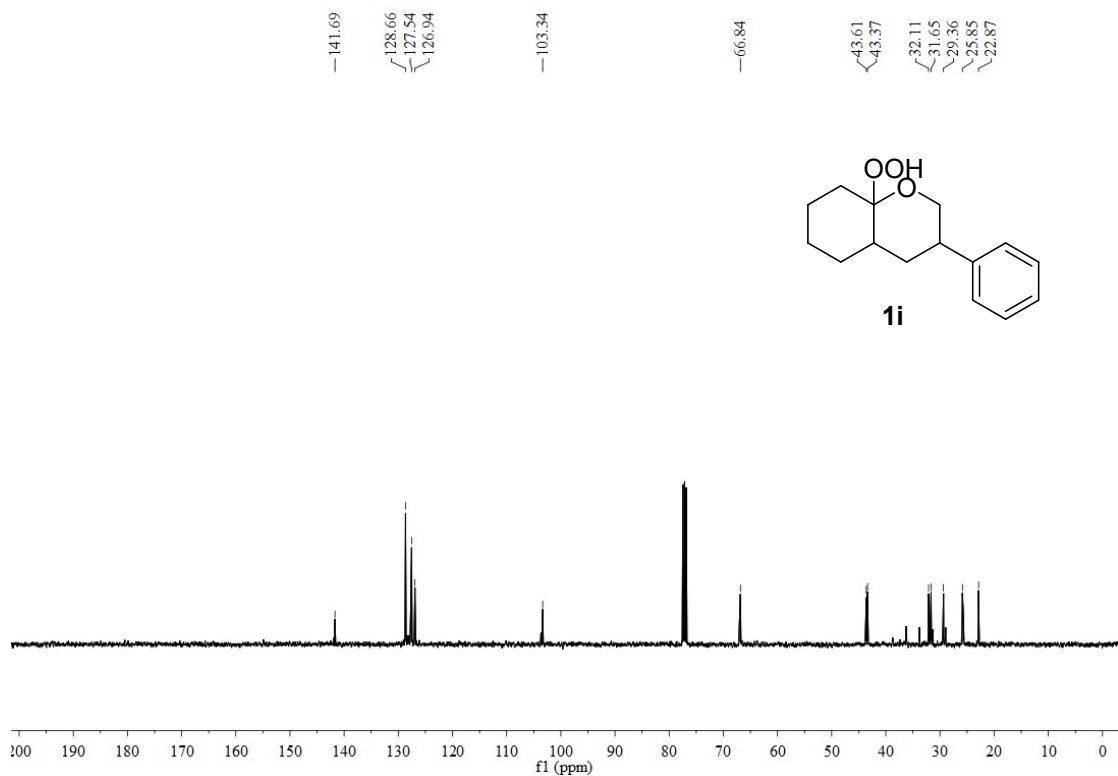
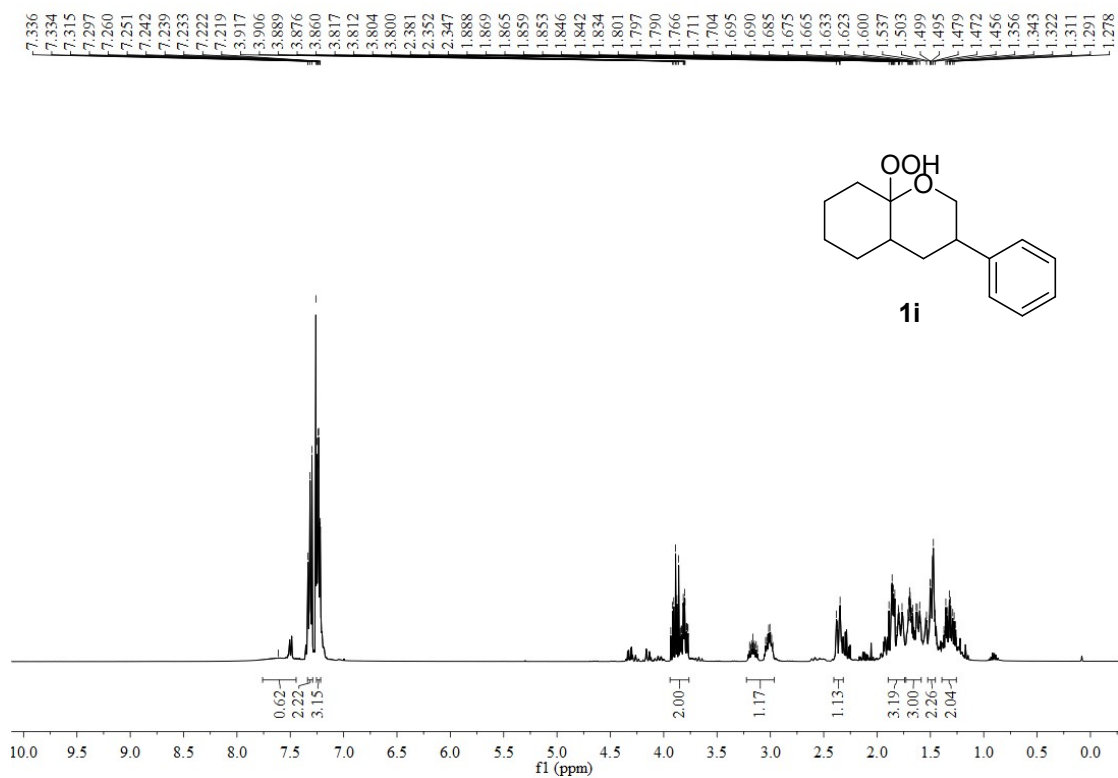
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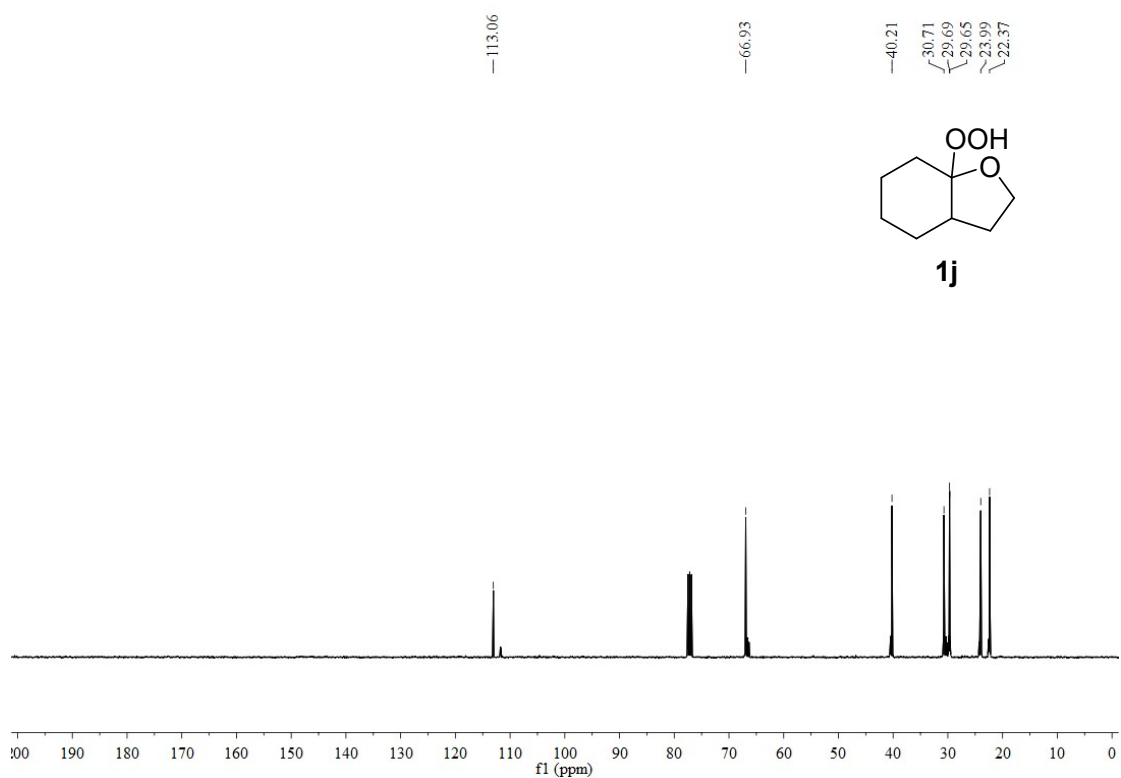
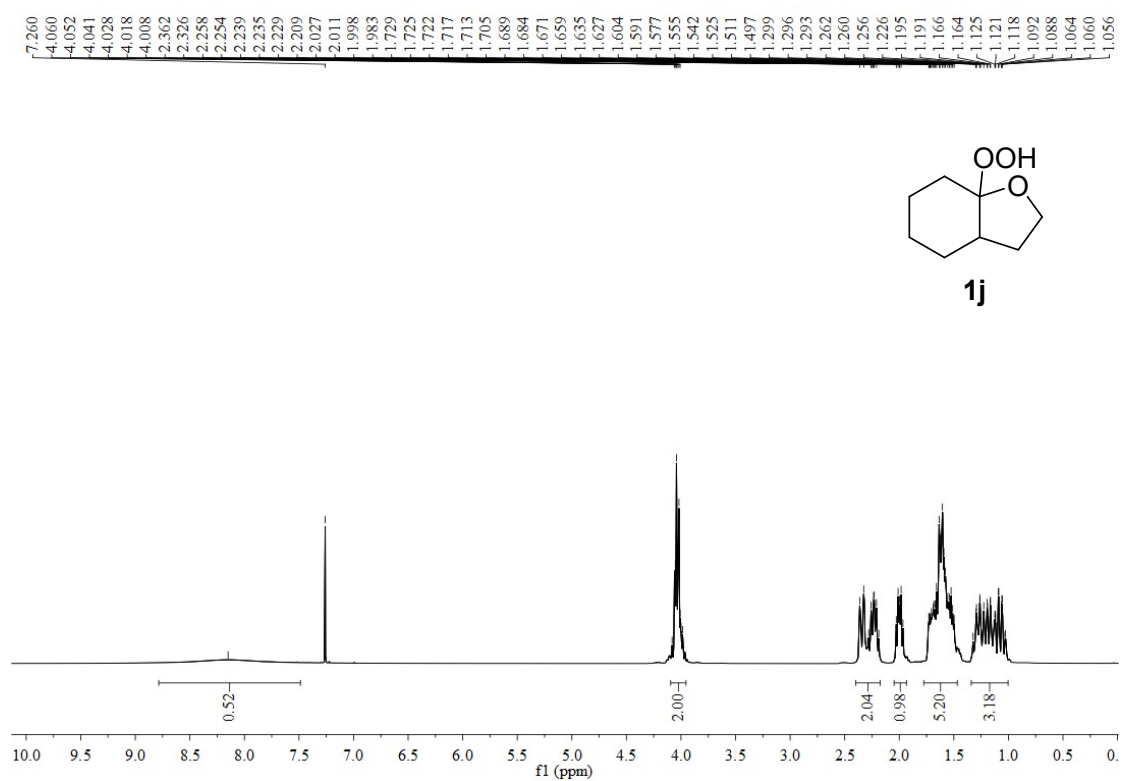
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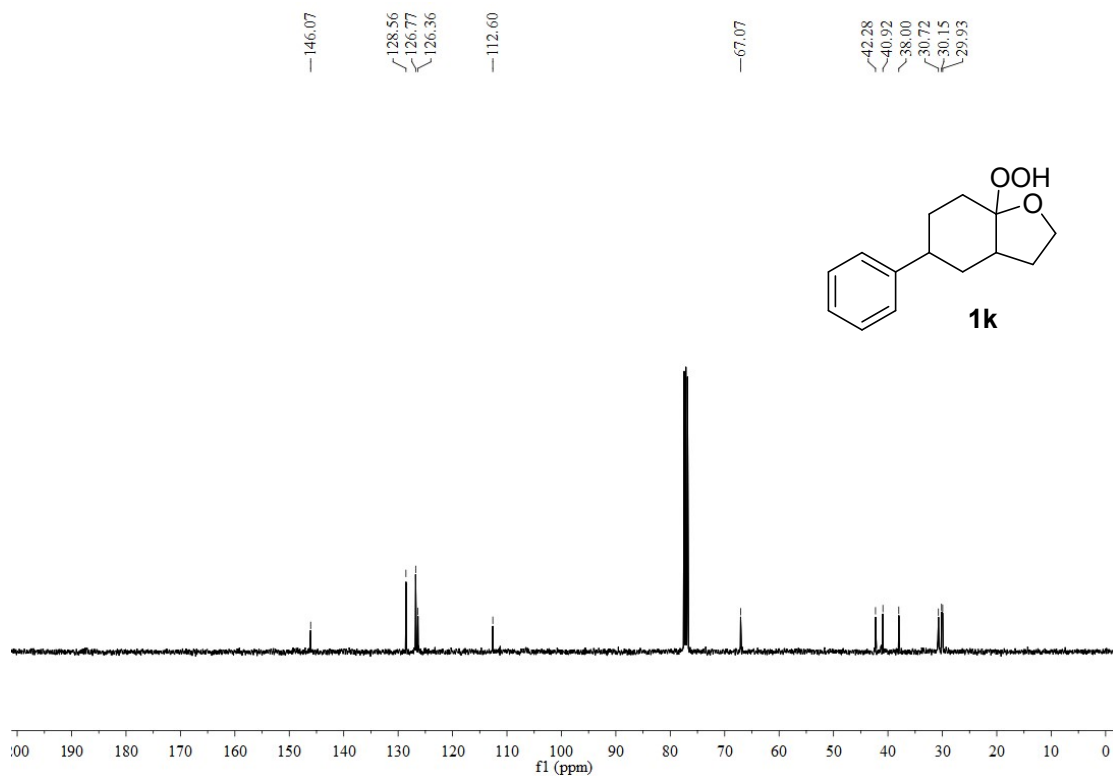
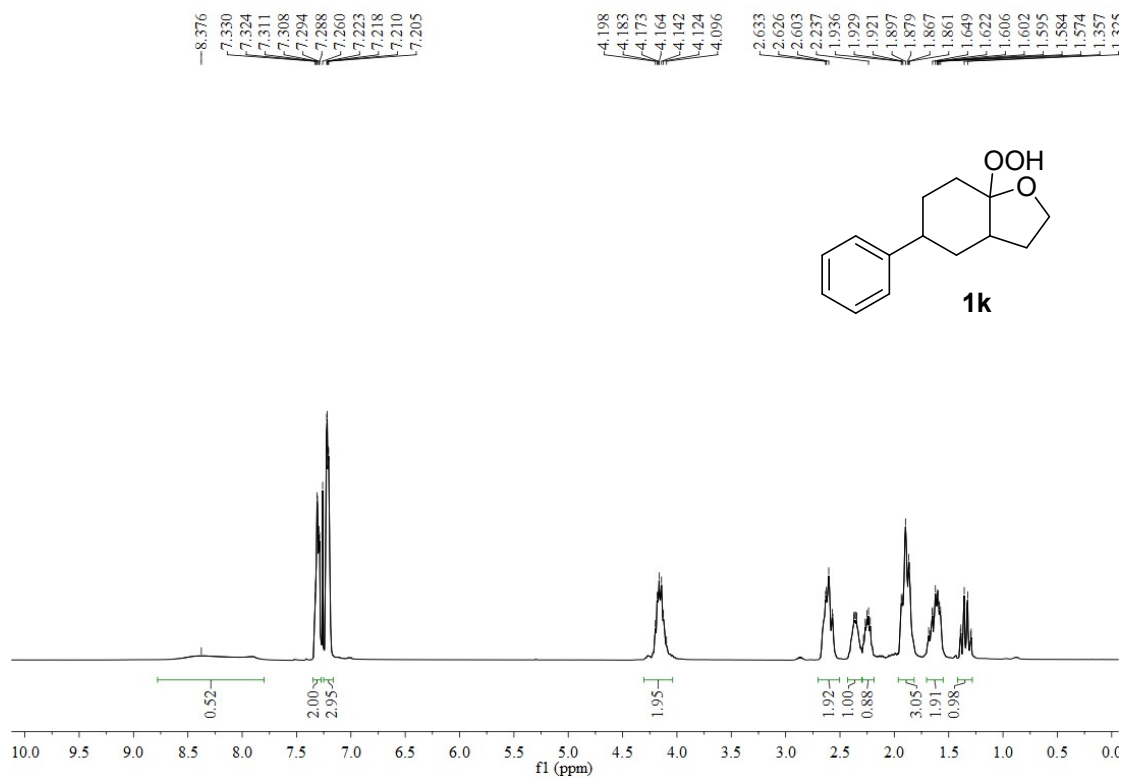
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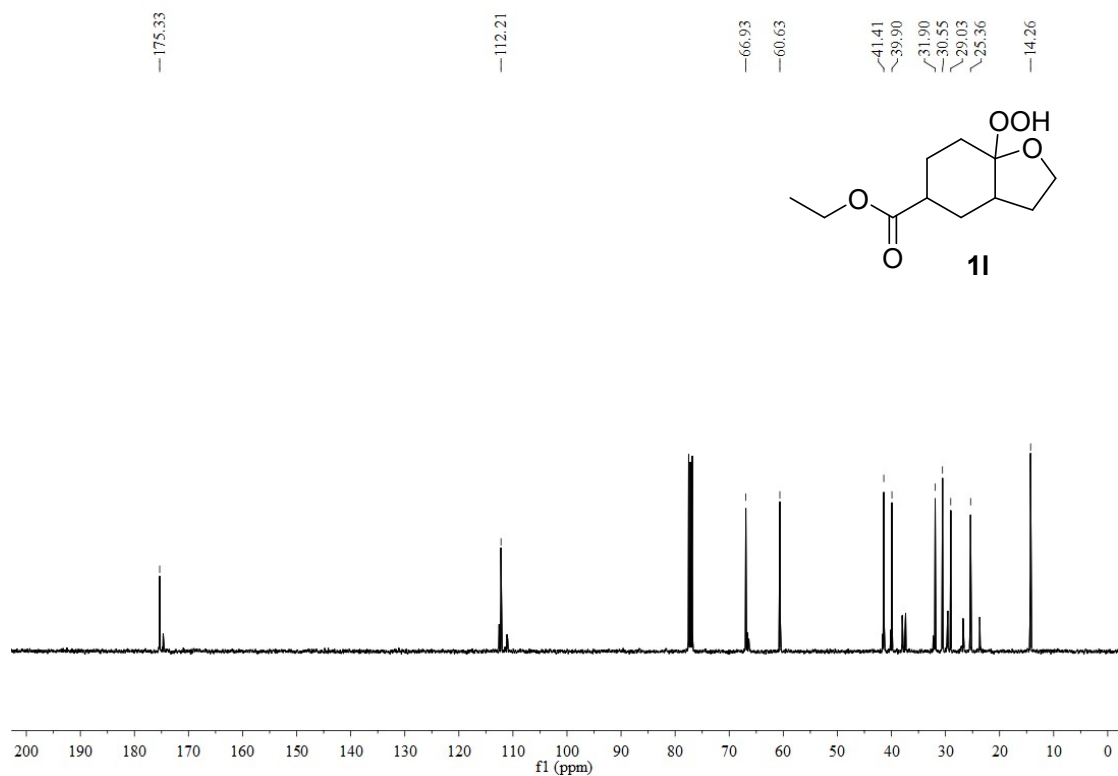
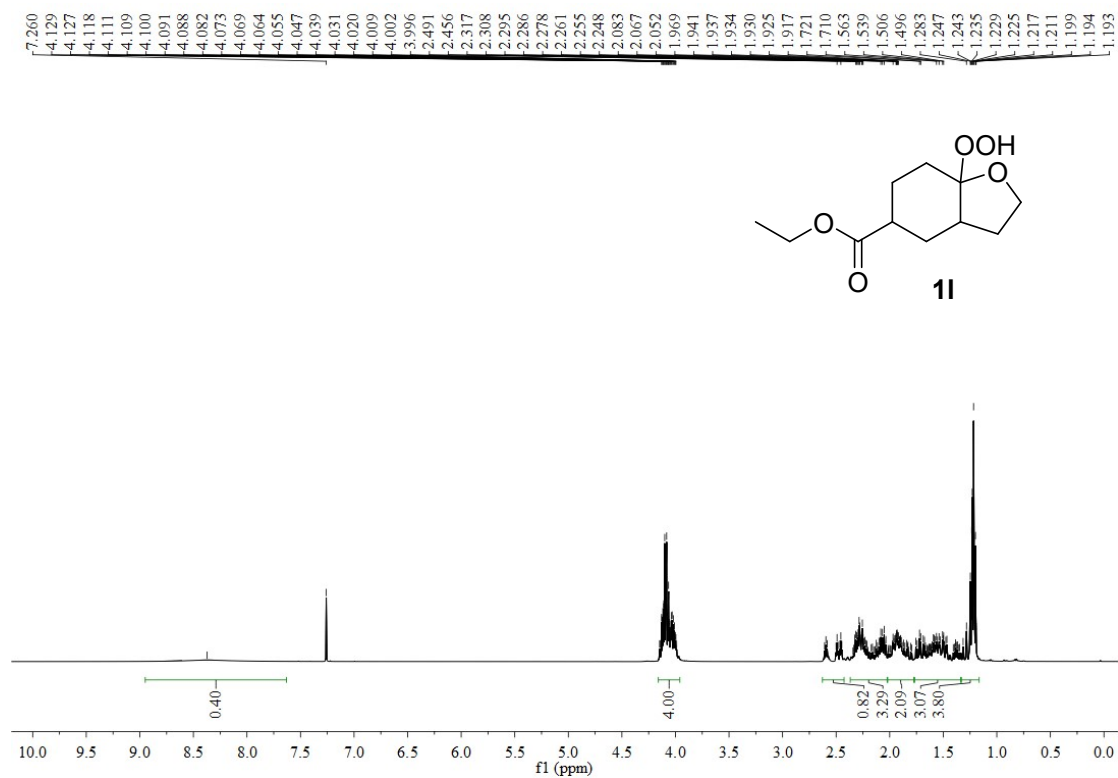
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1j**



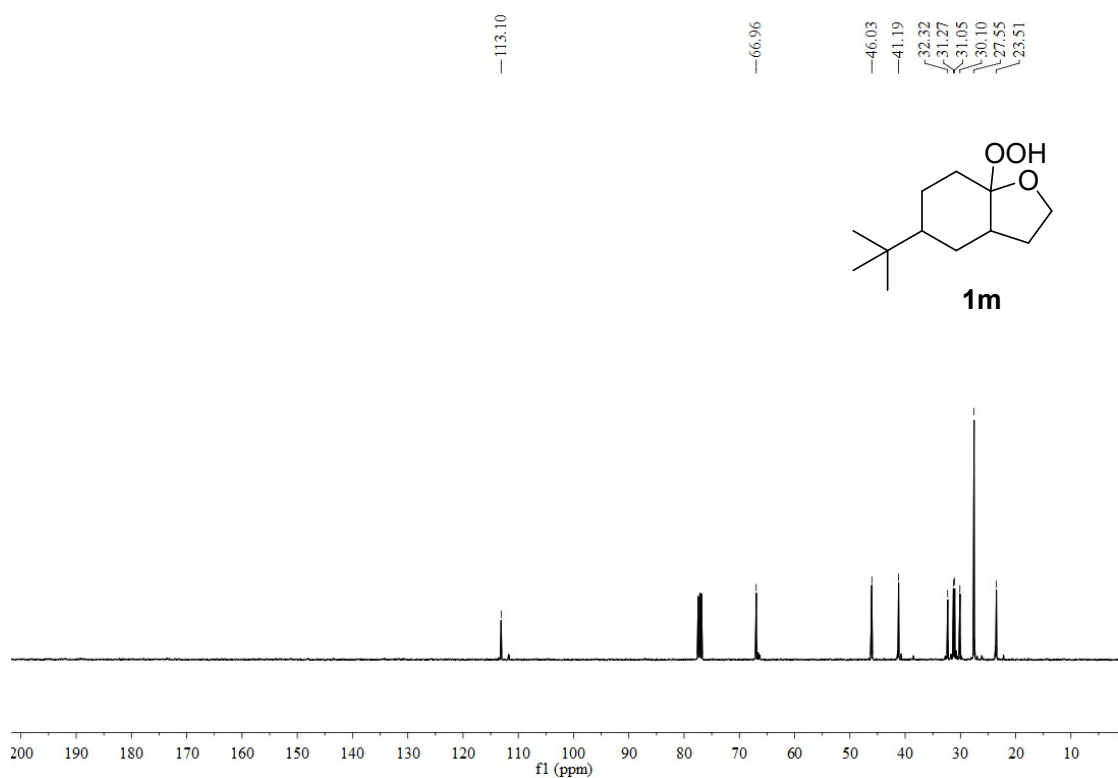
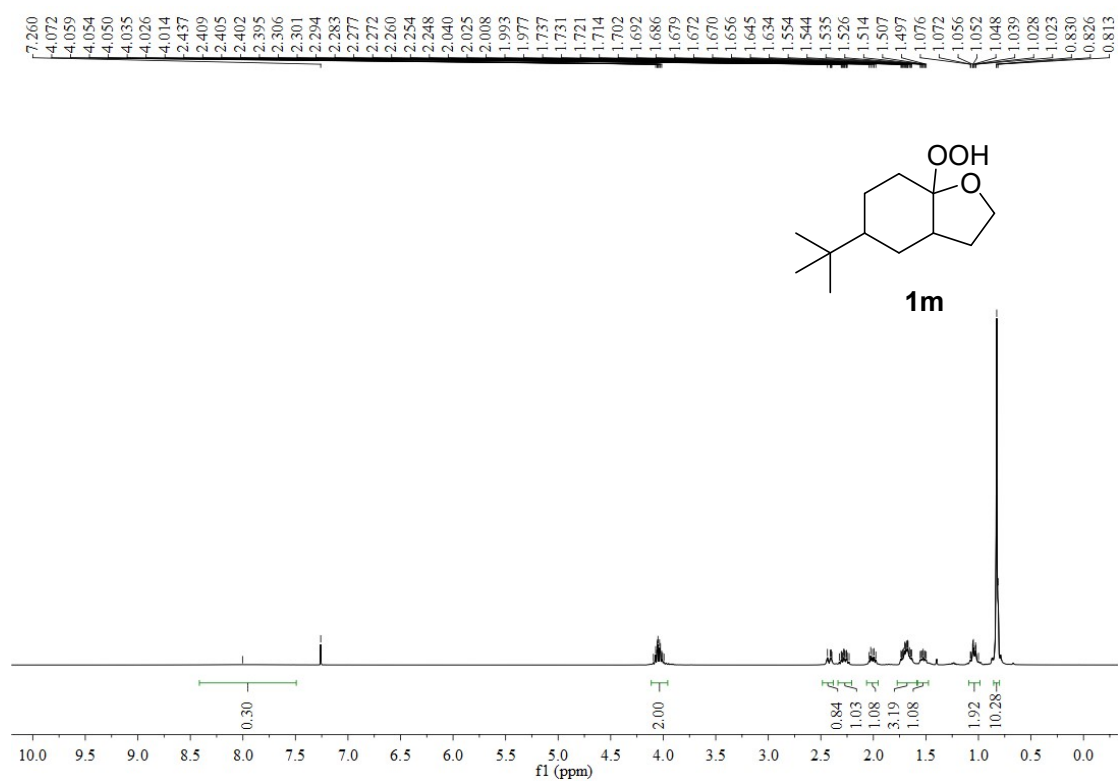
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1k**



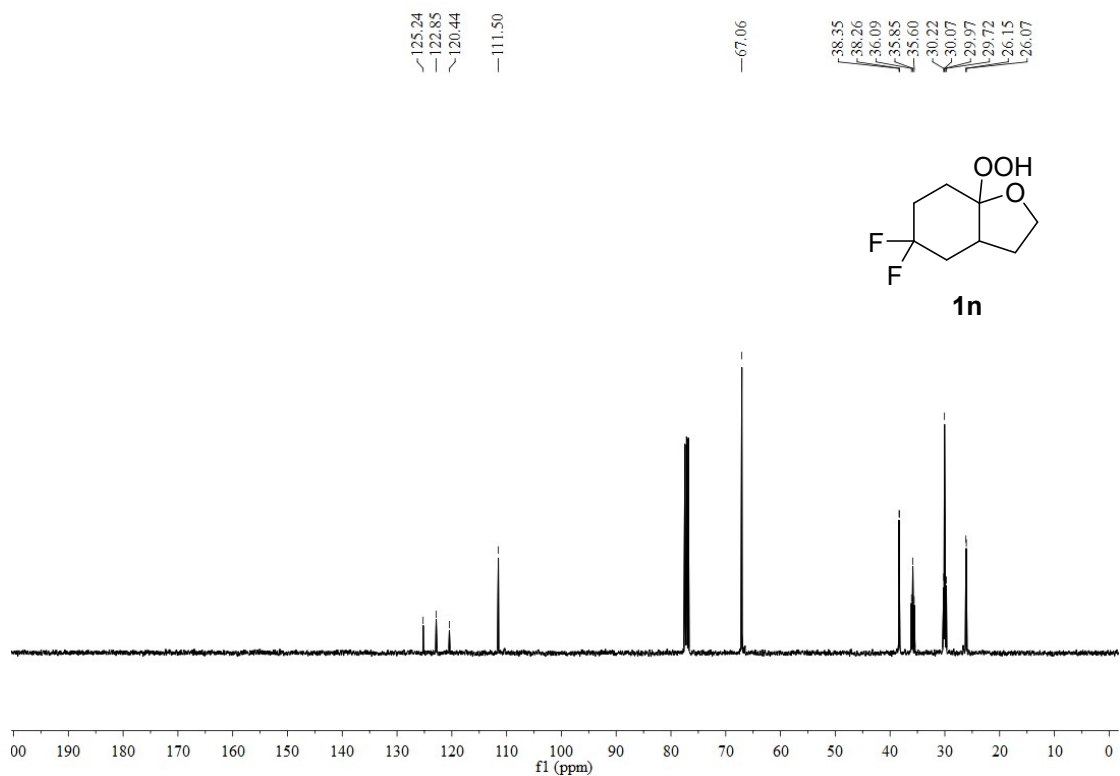
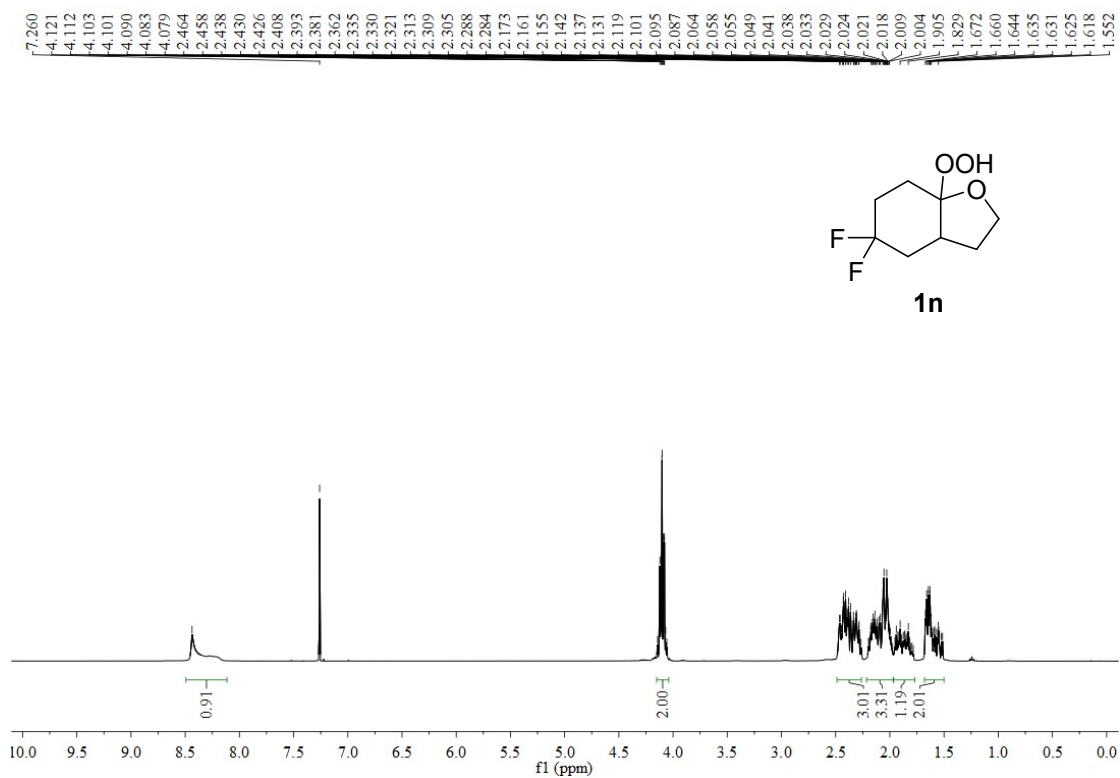
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **11**



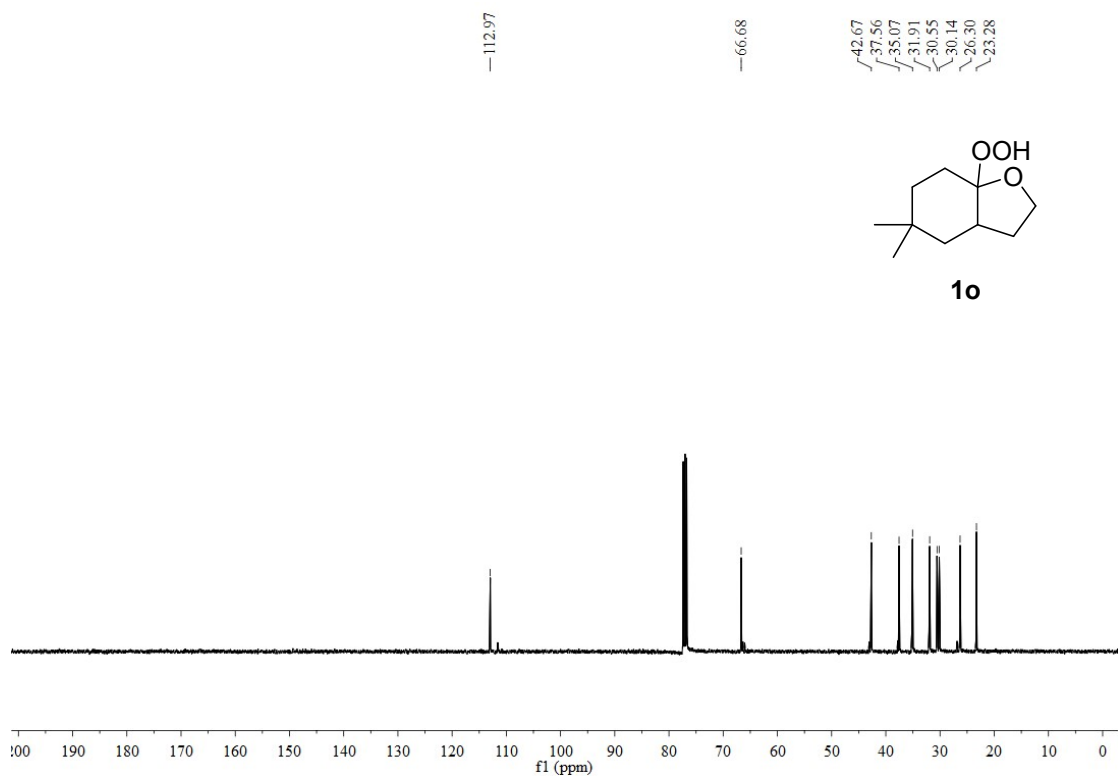
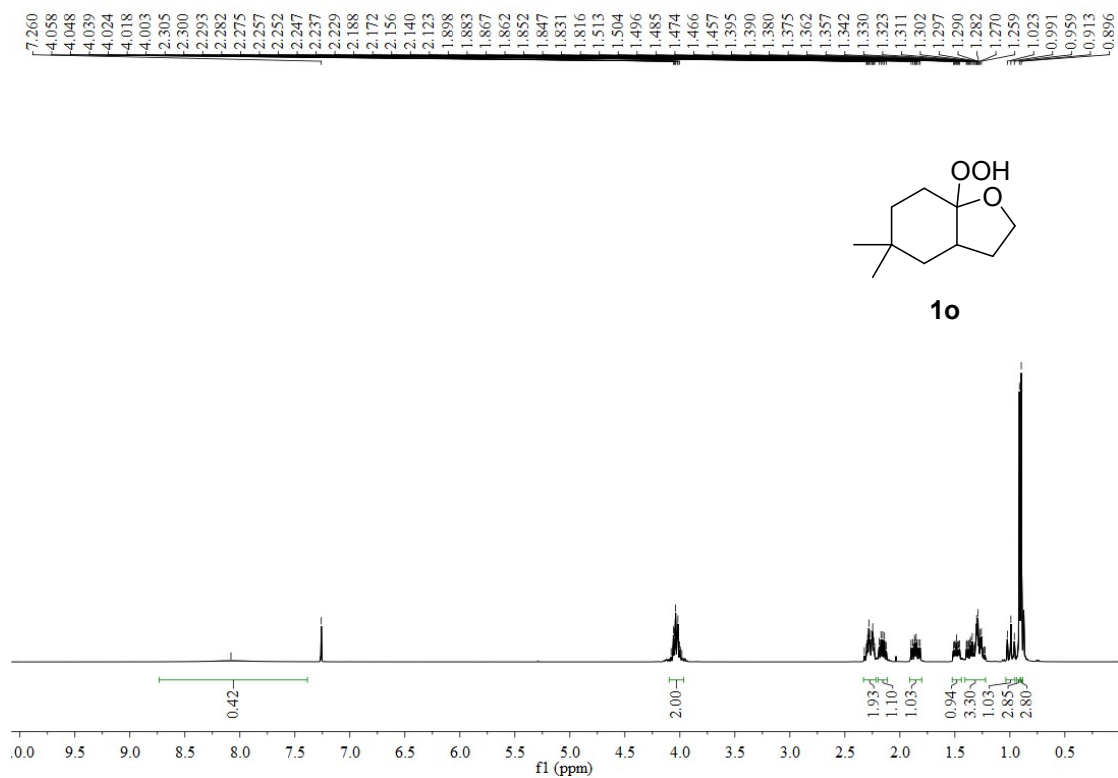
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1m**



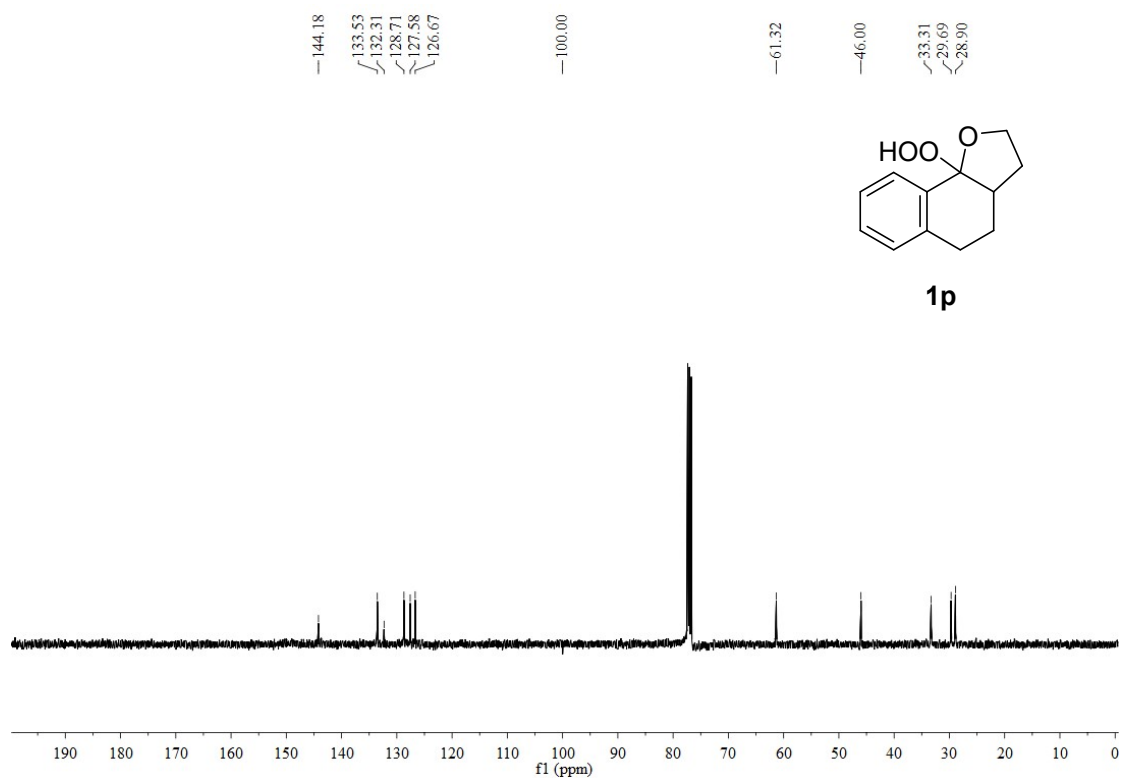
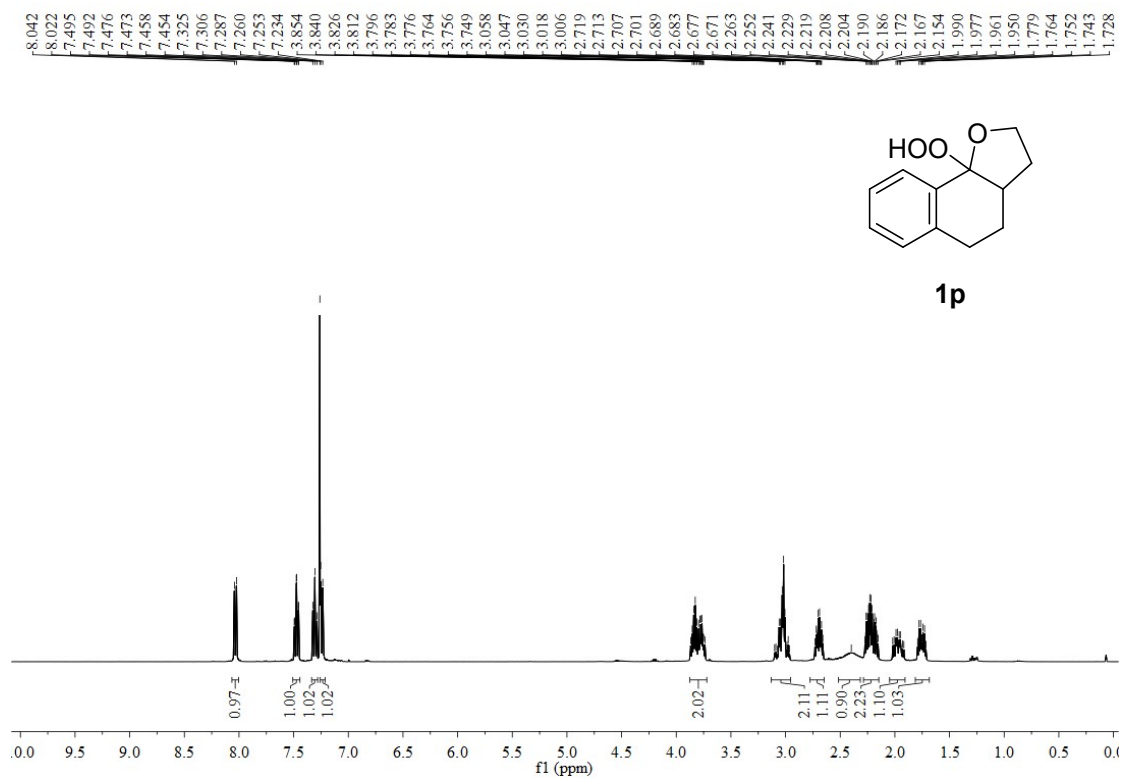
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1n**



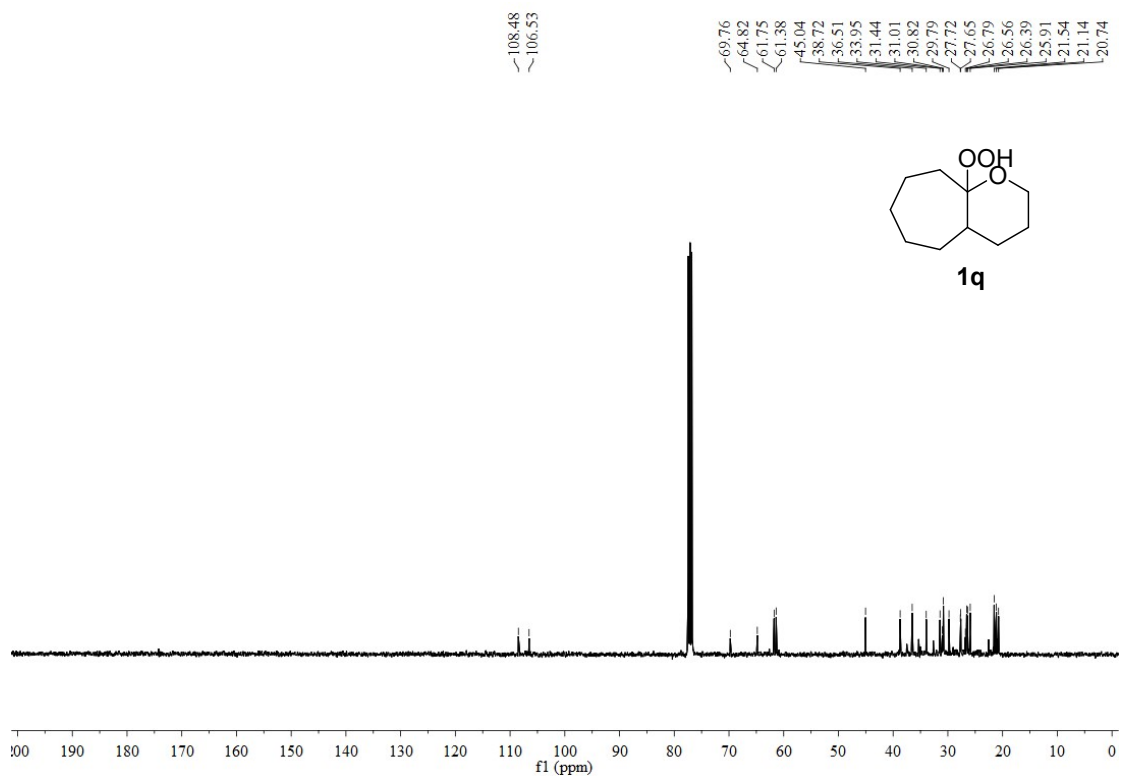
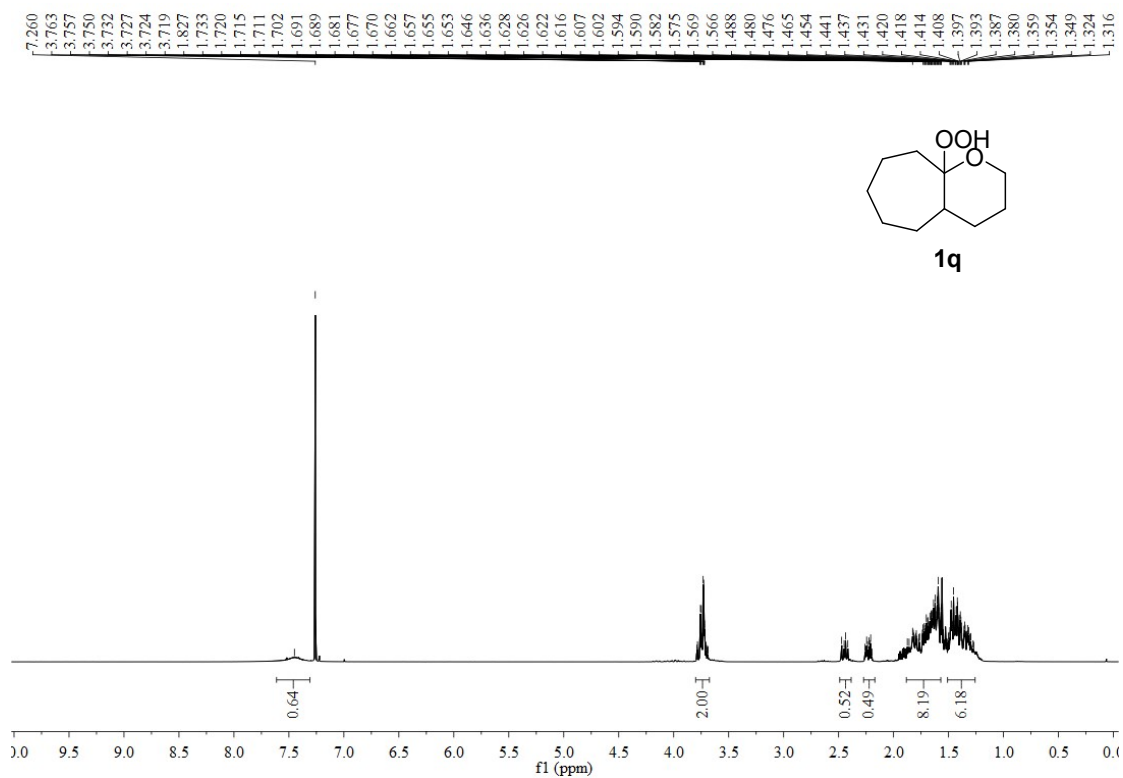
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1o**



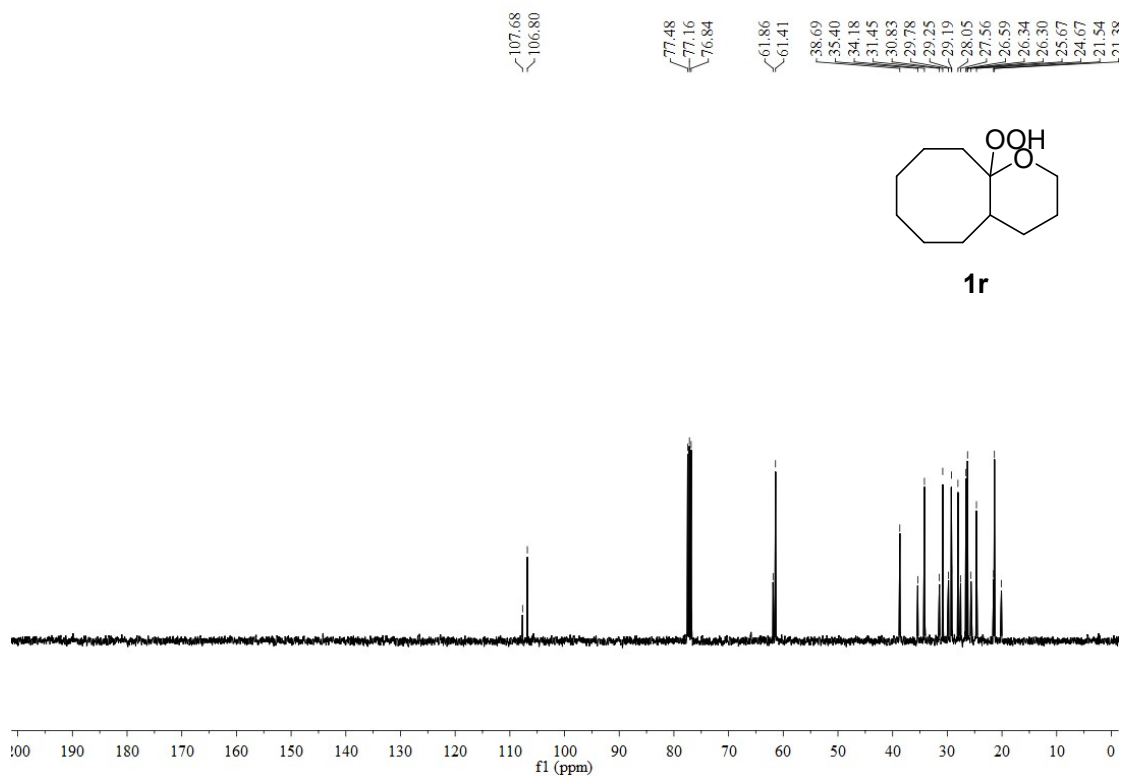
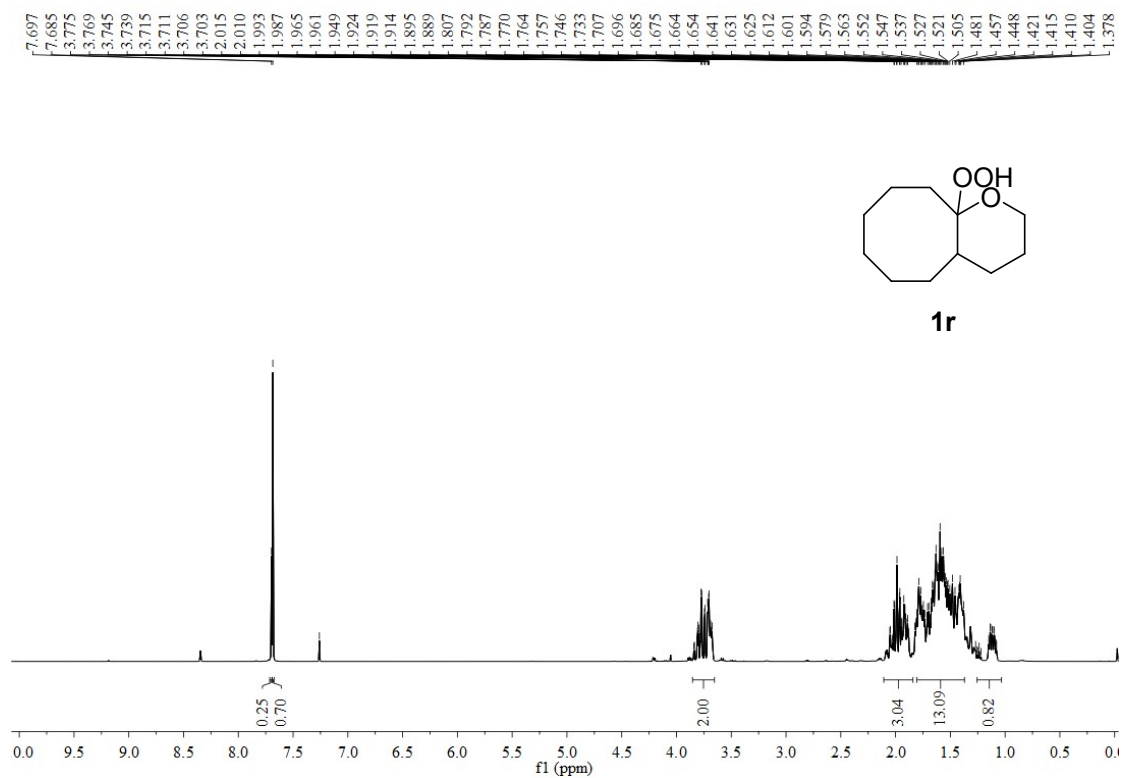
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1p**



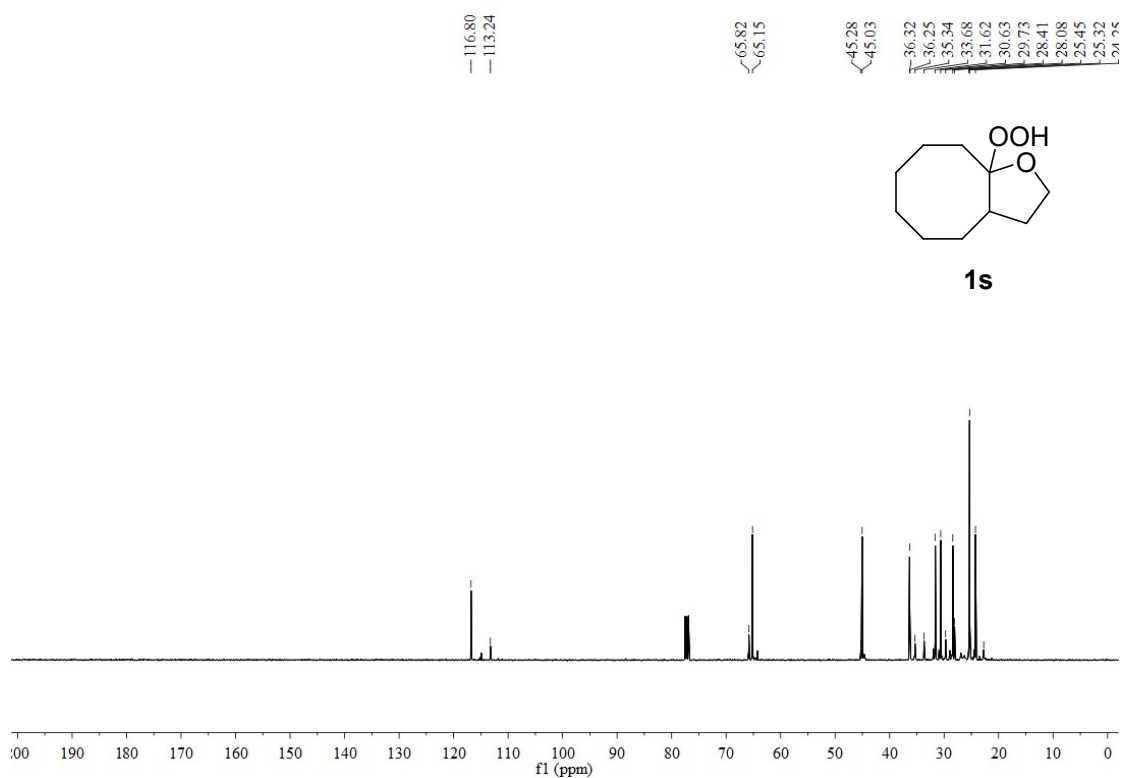
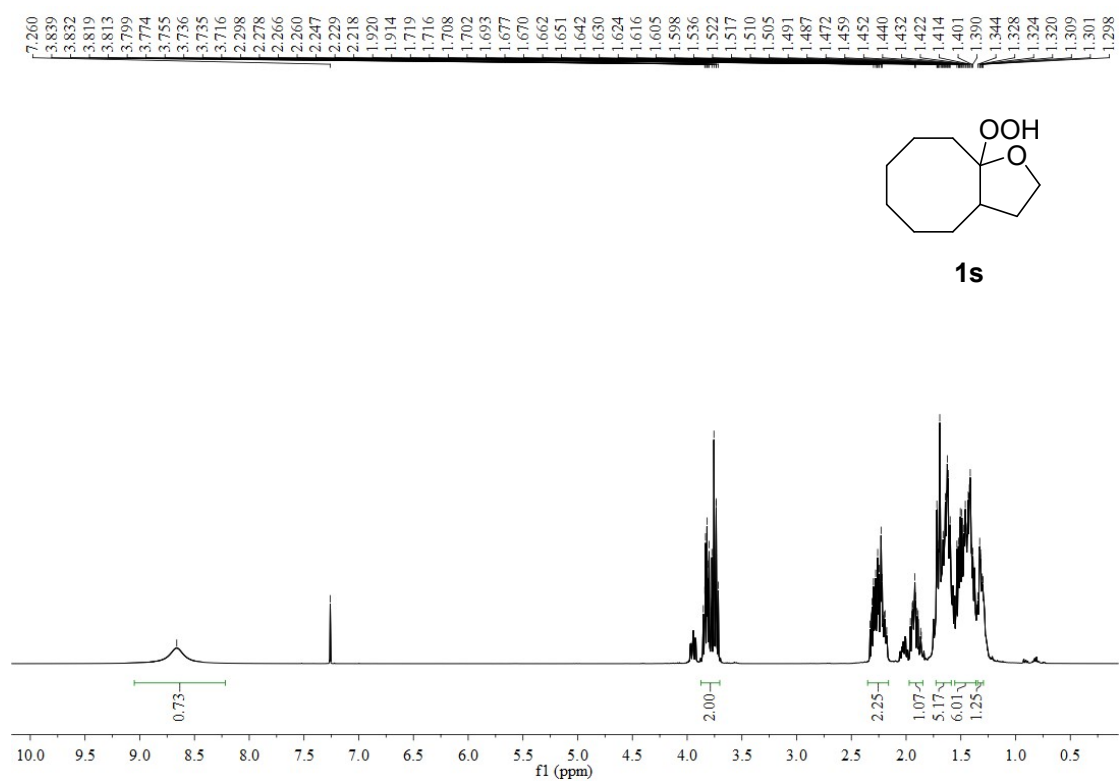
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1q**



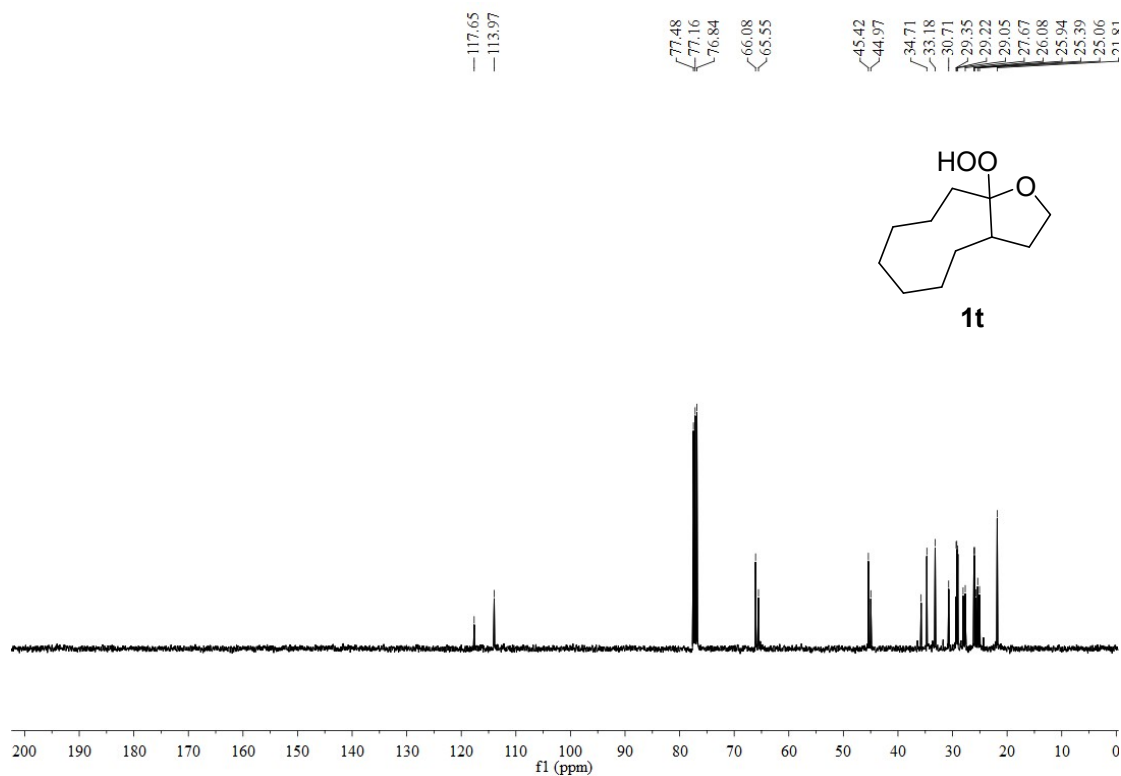
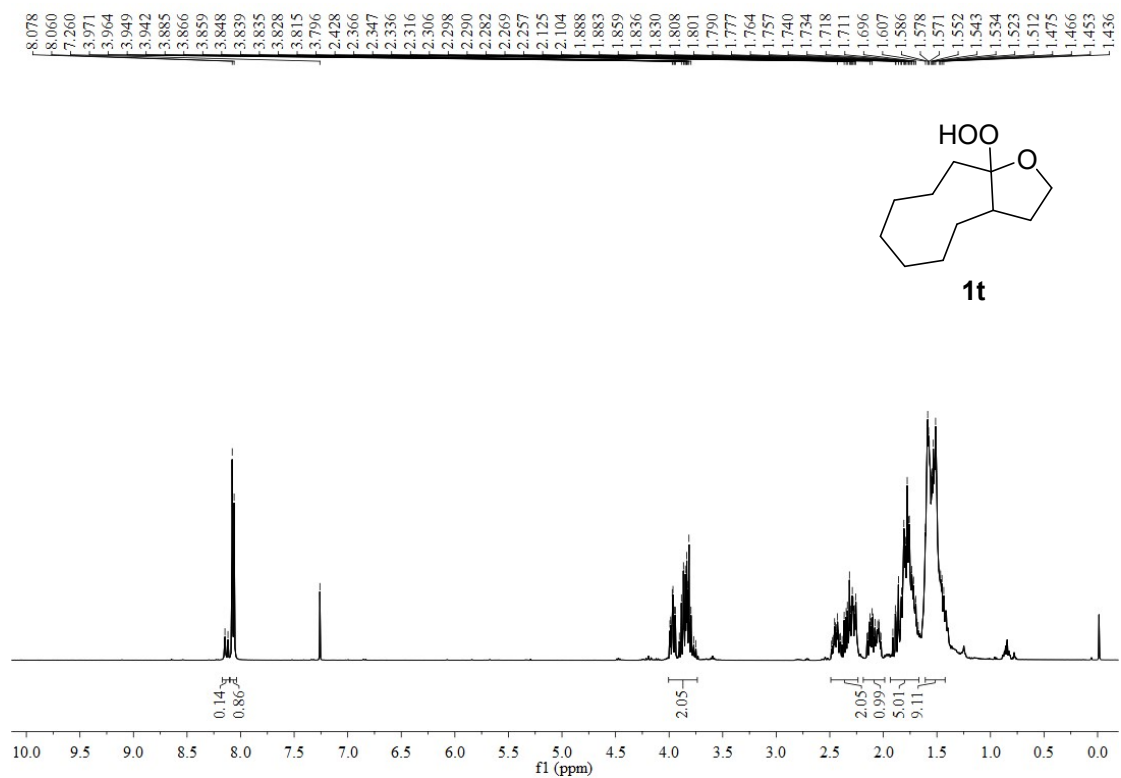
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1r**



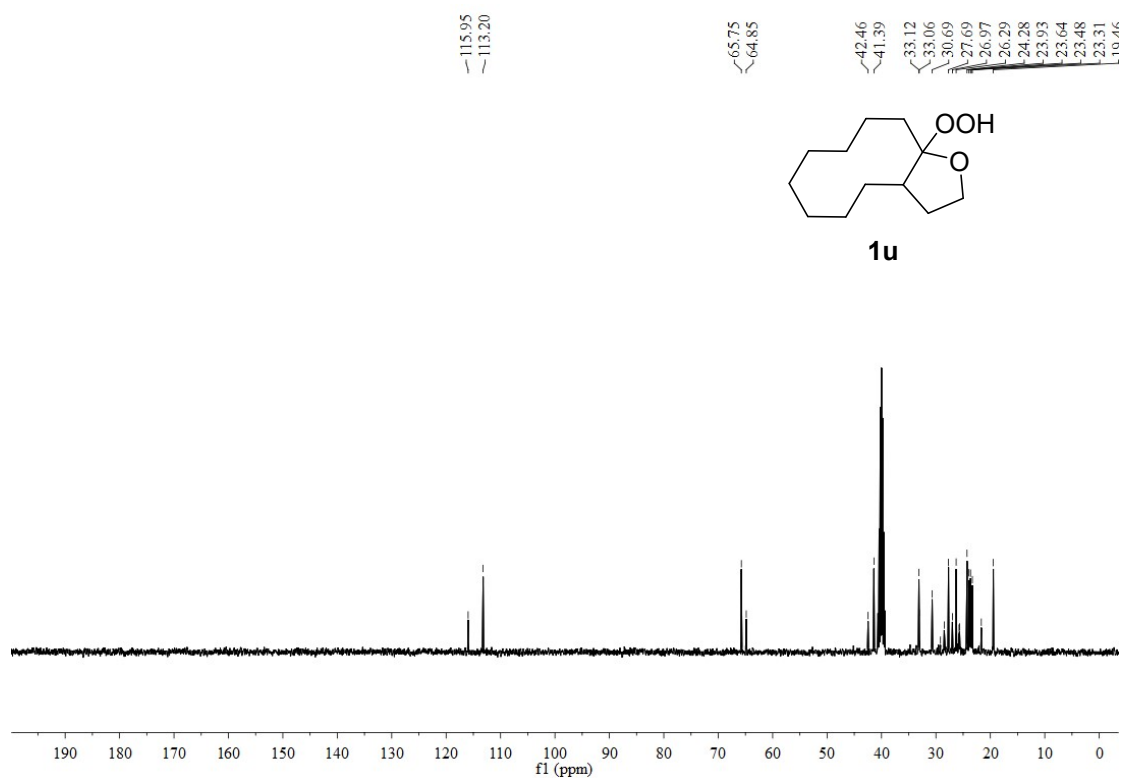
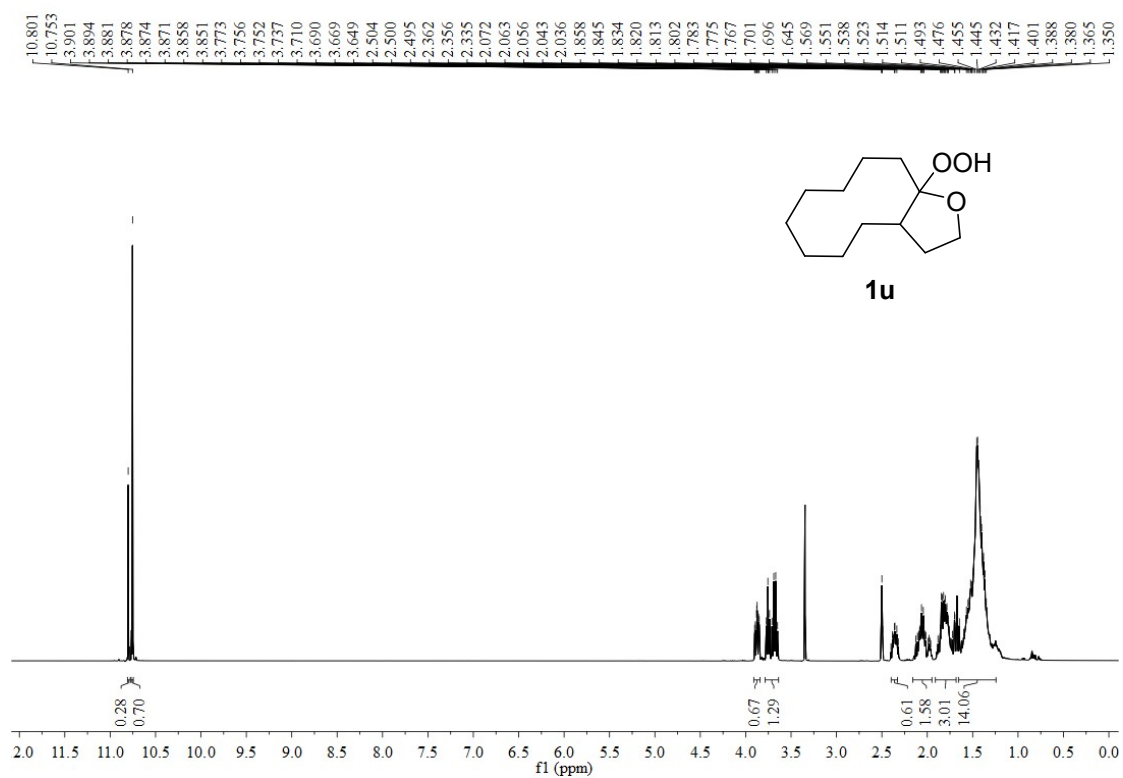
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1s**



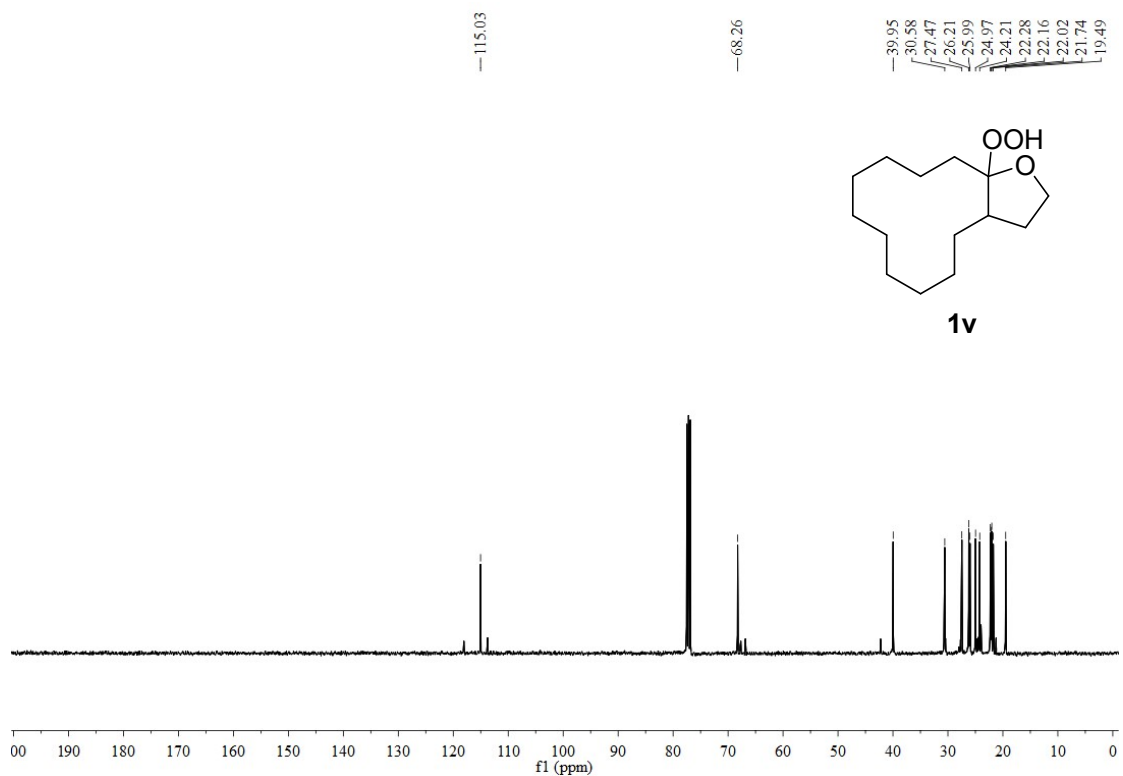
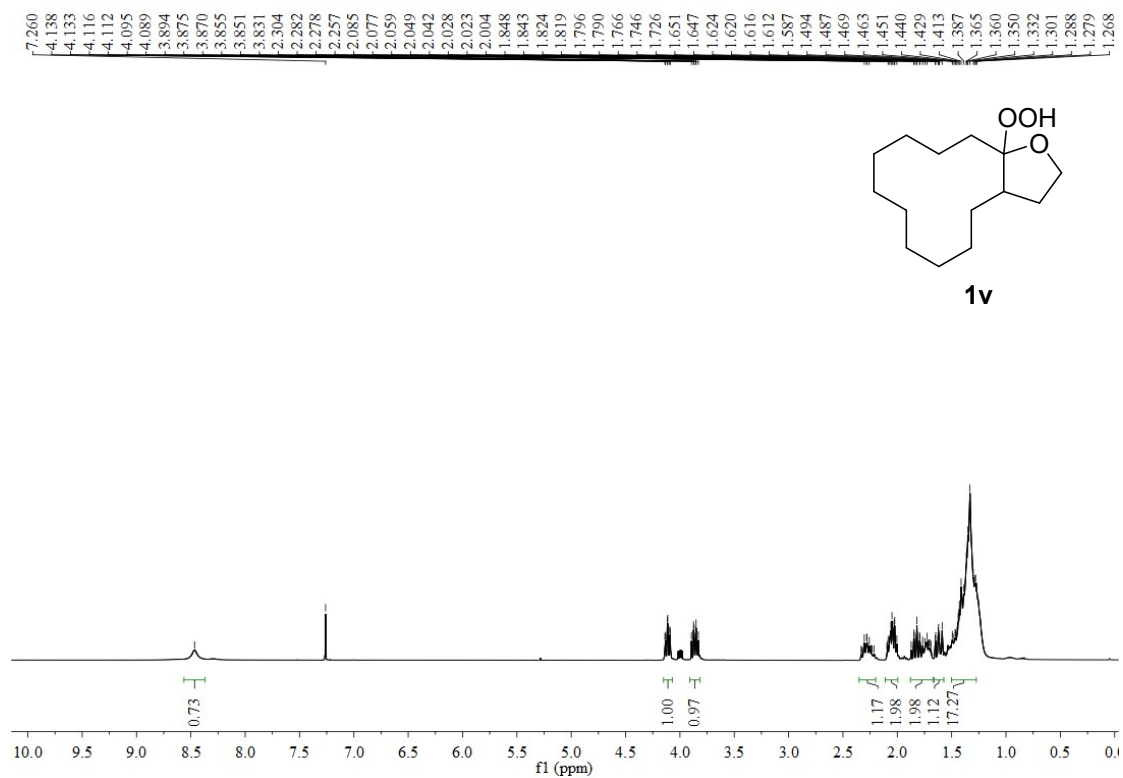
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1t**



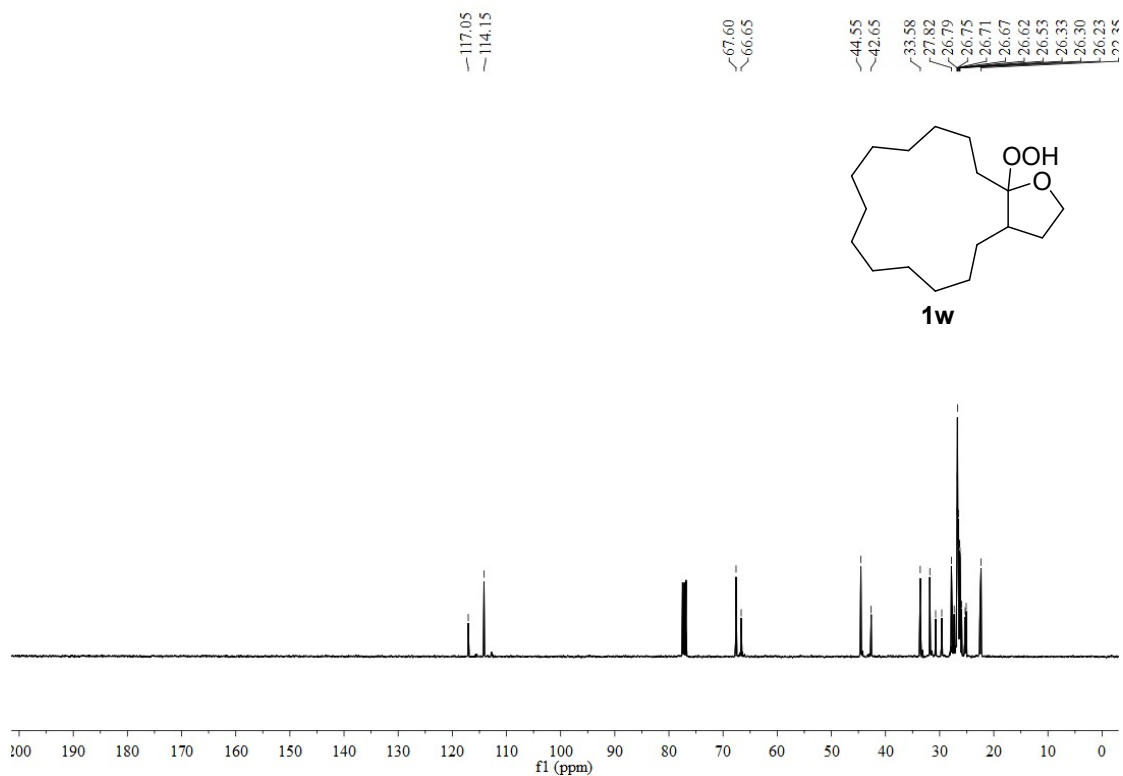
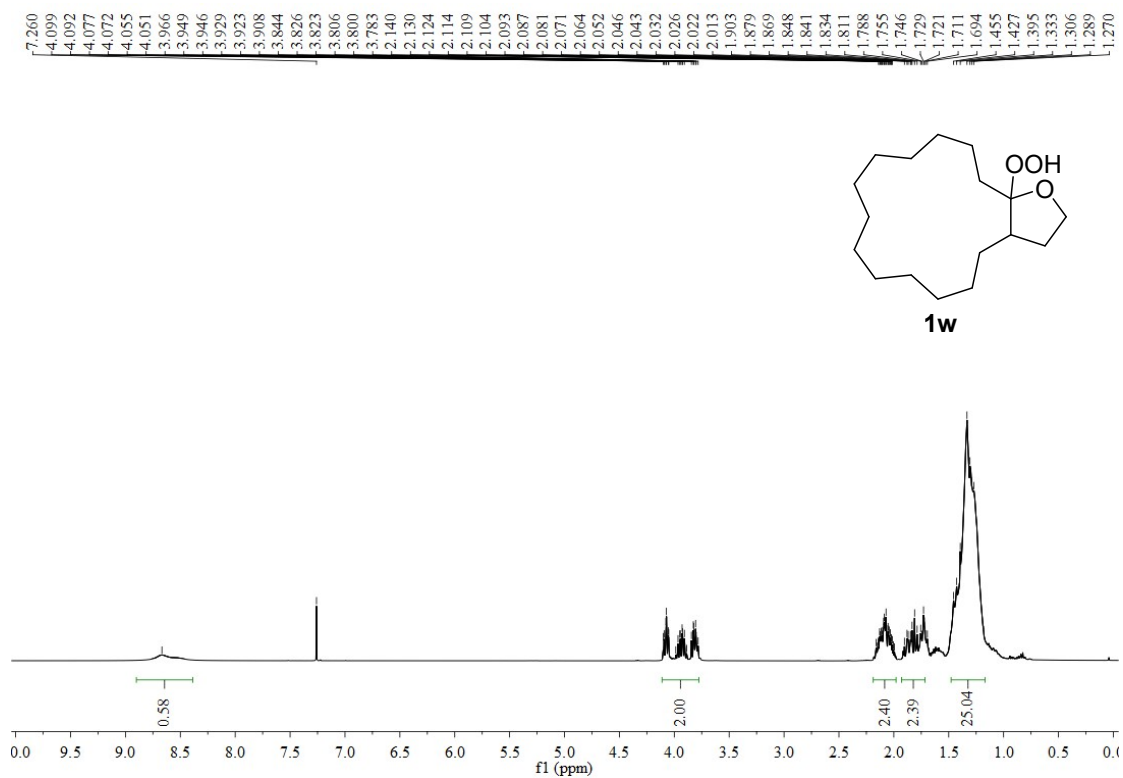
¹H NMR (400 MHz, DMSO-*d*₆) and ¹³C NMR (100 MHz, DMSO-*d*₆) spectra of product **1u**



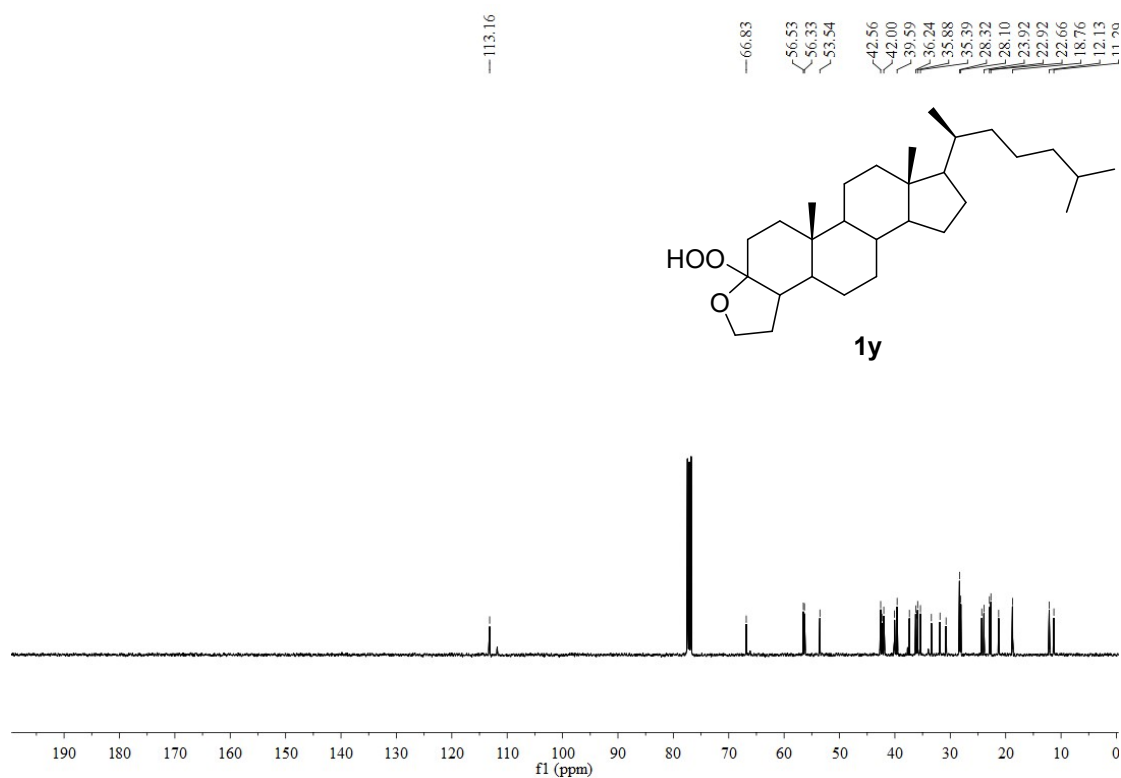
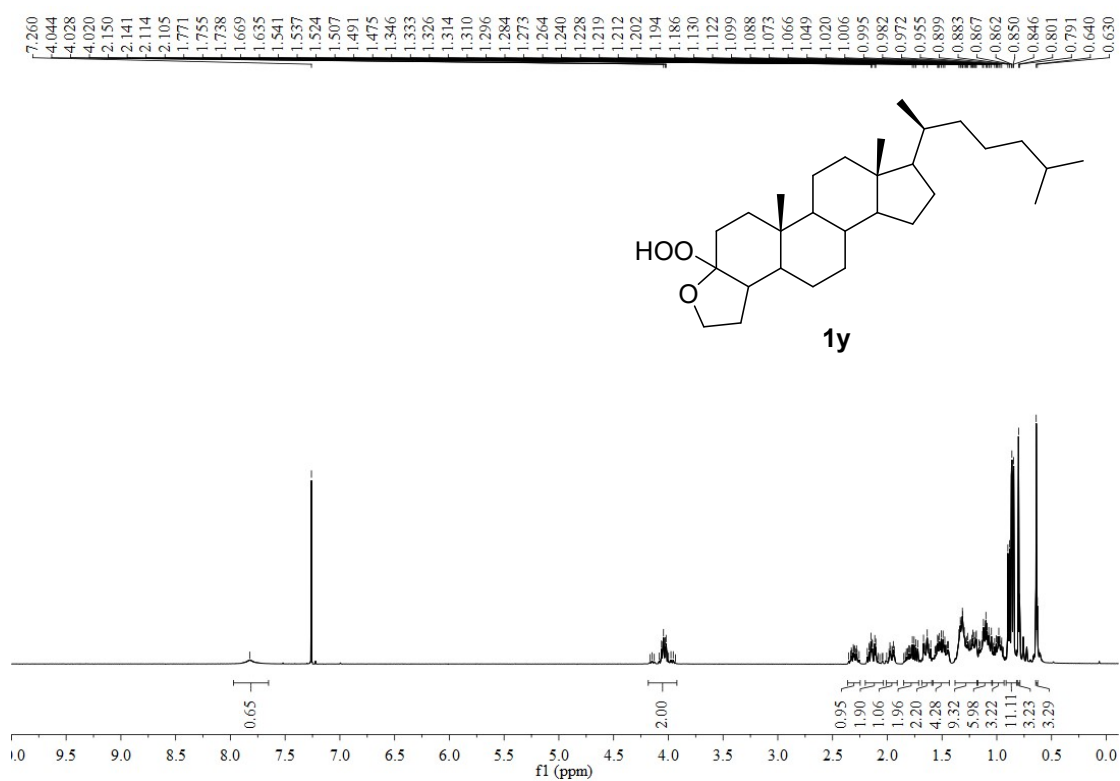
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1v**



¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1w**

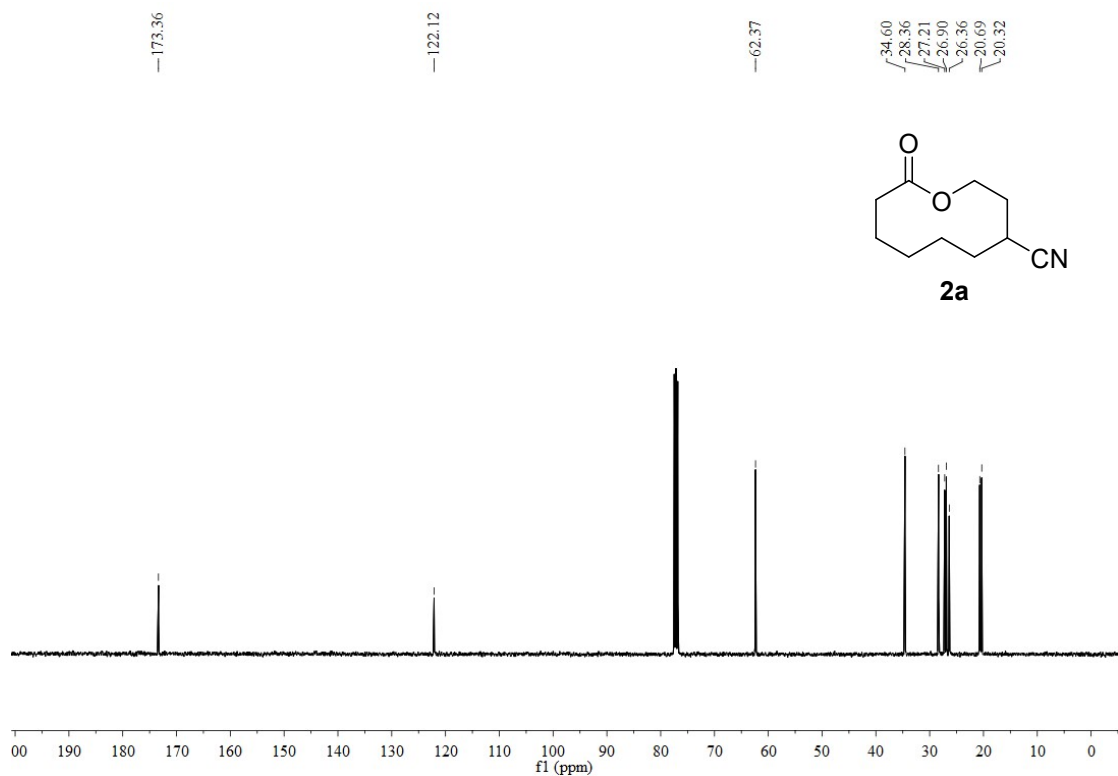
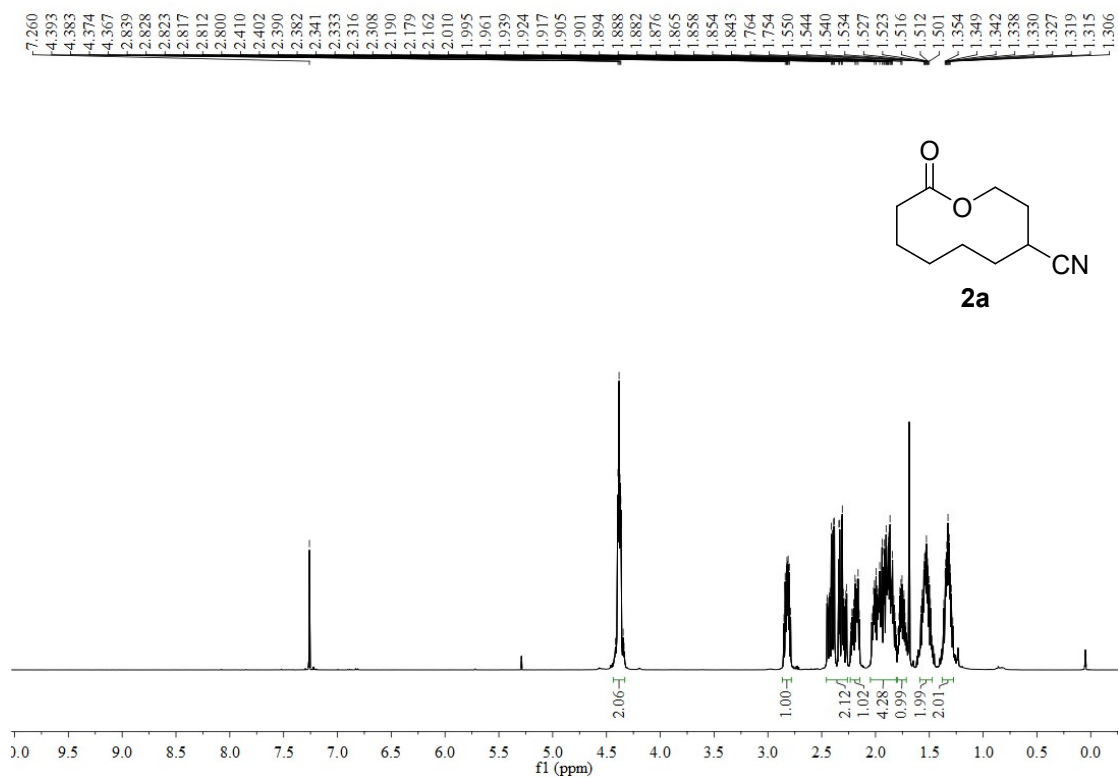


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **1x**

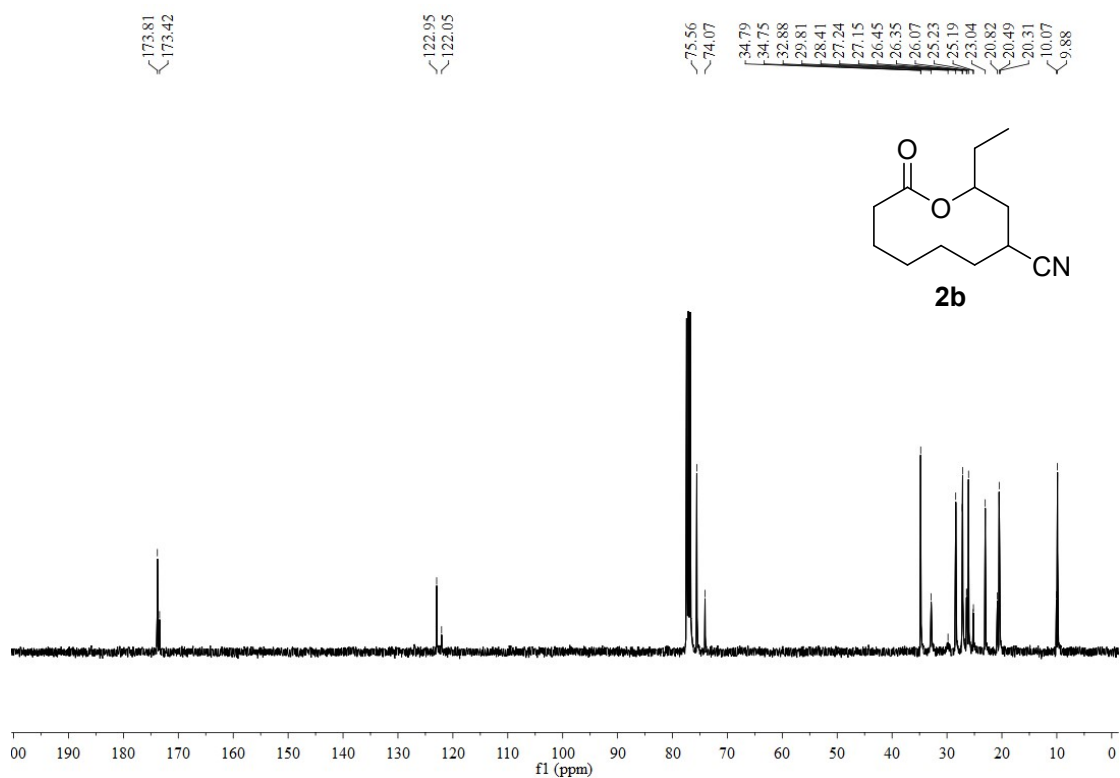
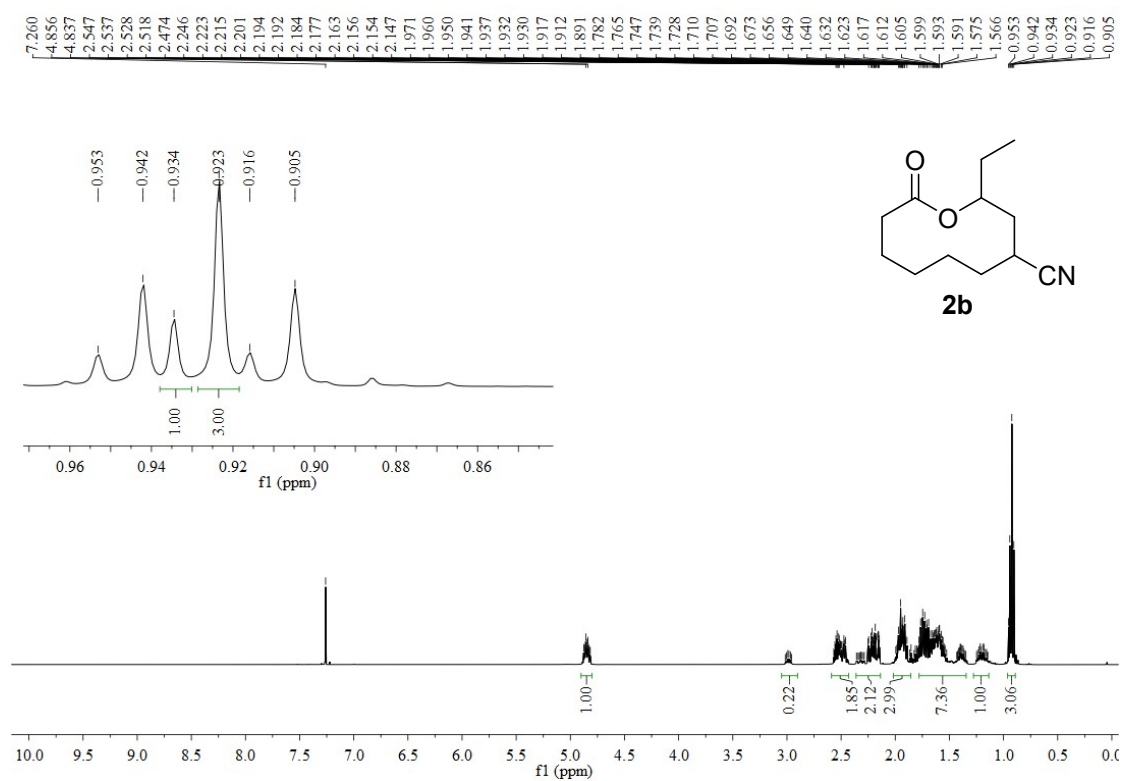


15. ¹H NMR and ¹³C NMR Spectra of Products 2-5

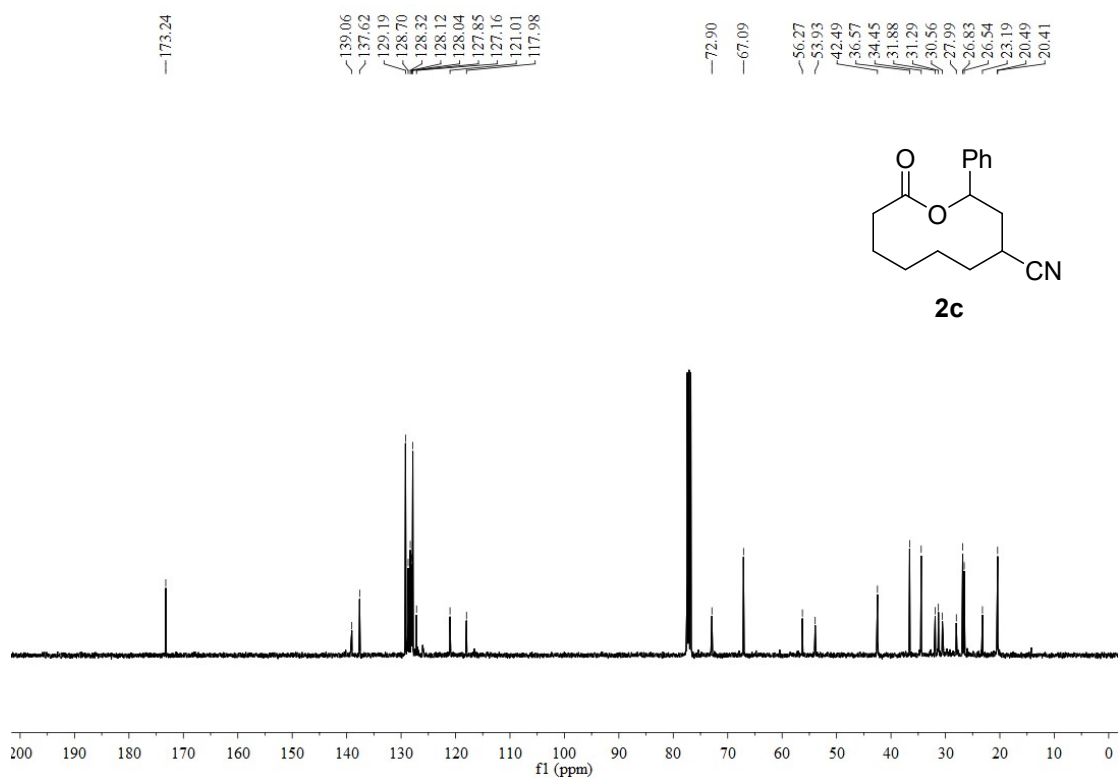
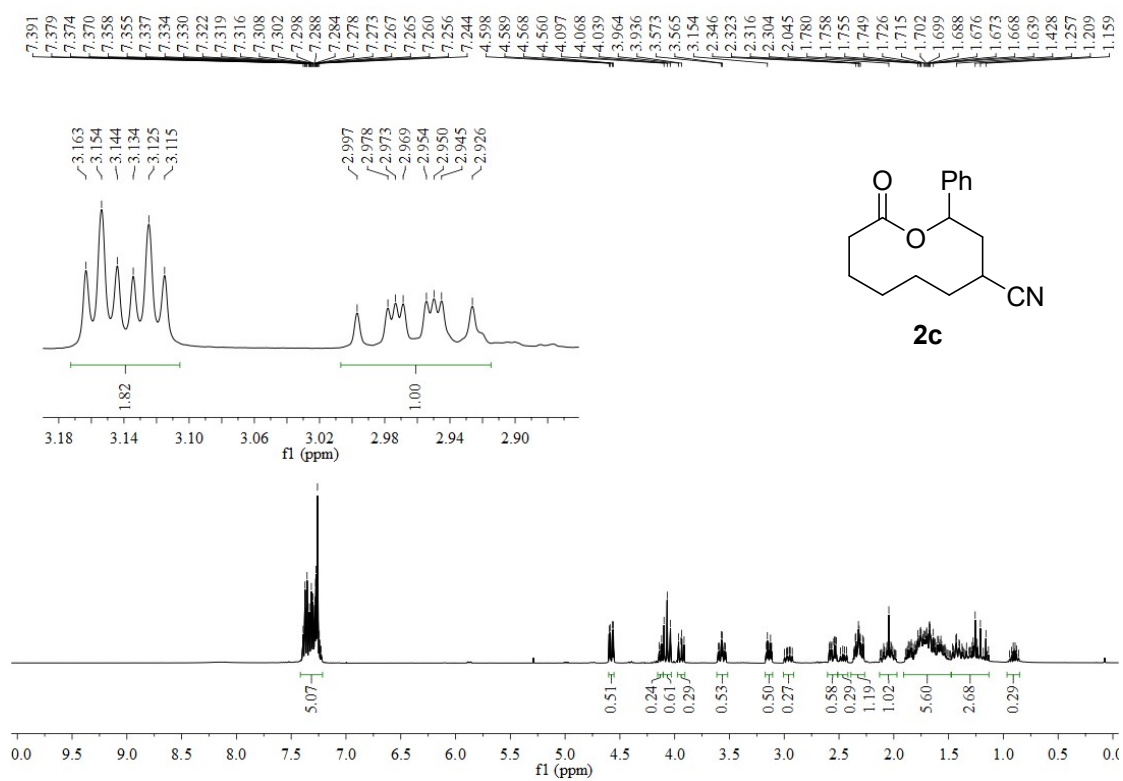
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2a**



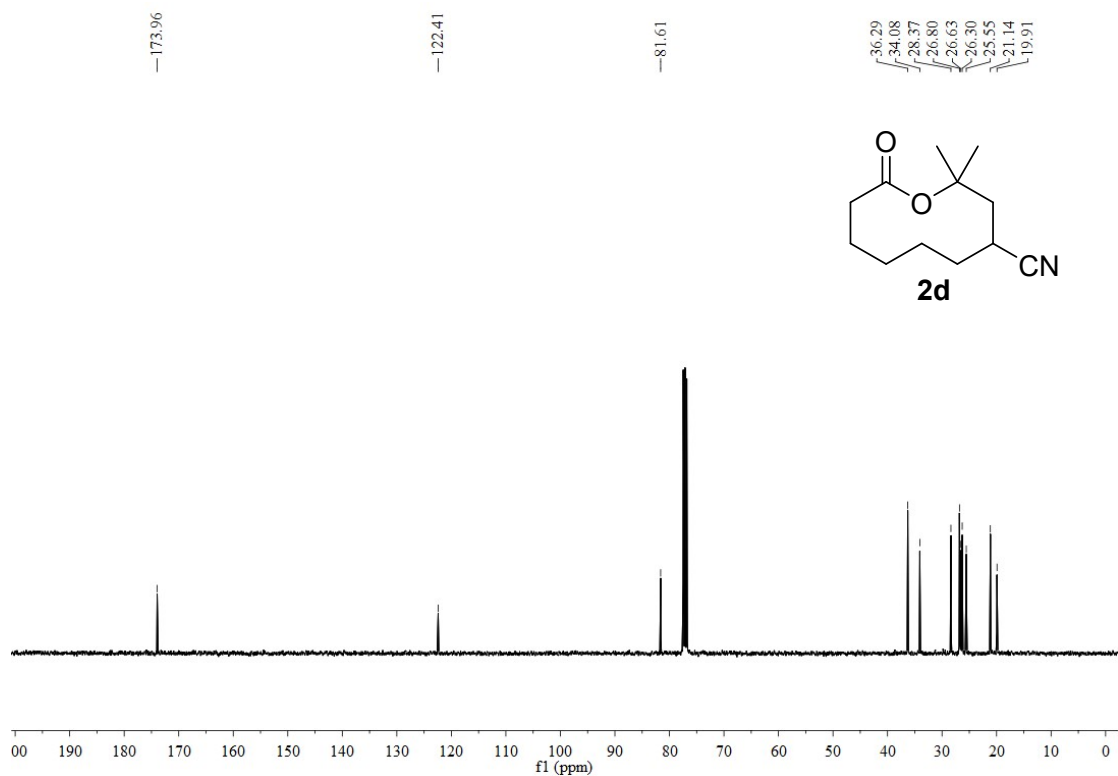
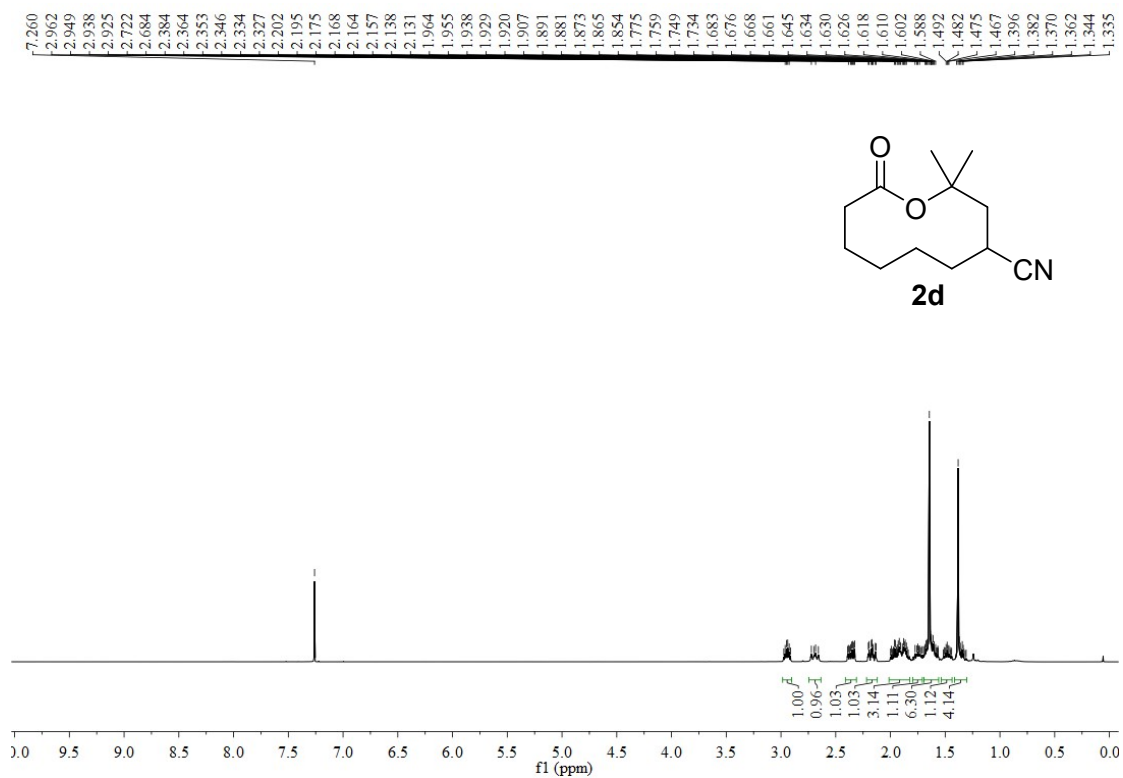
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2b**



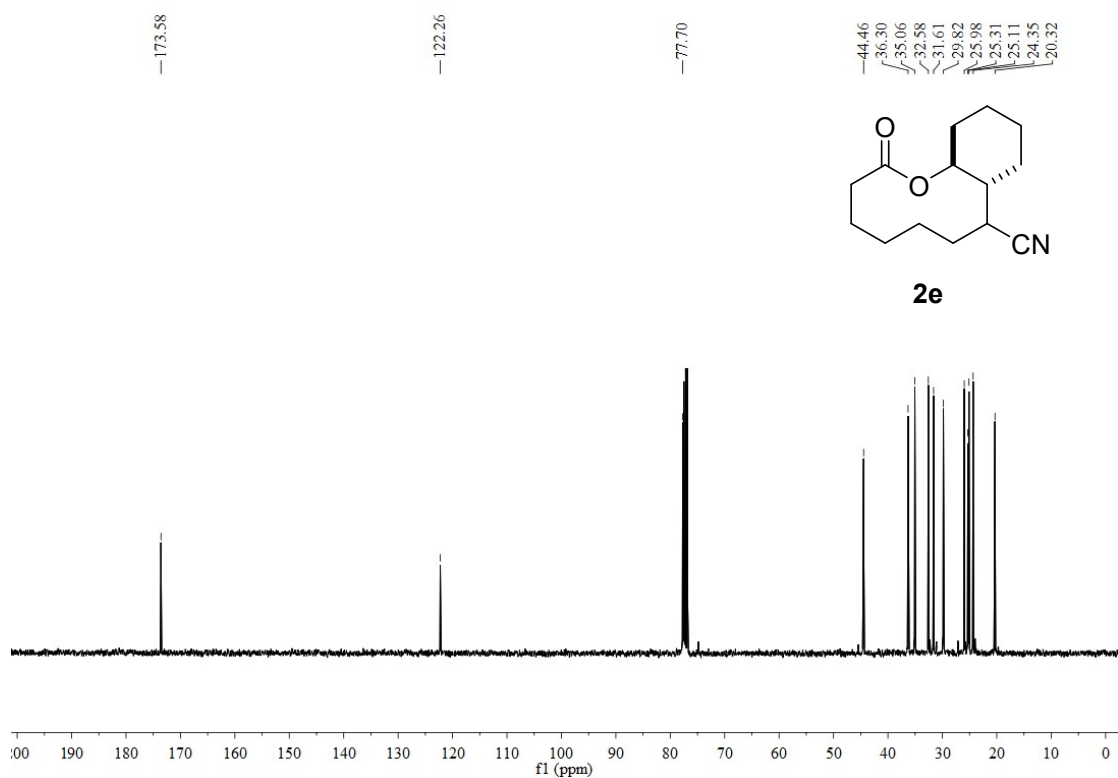
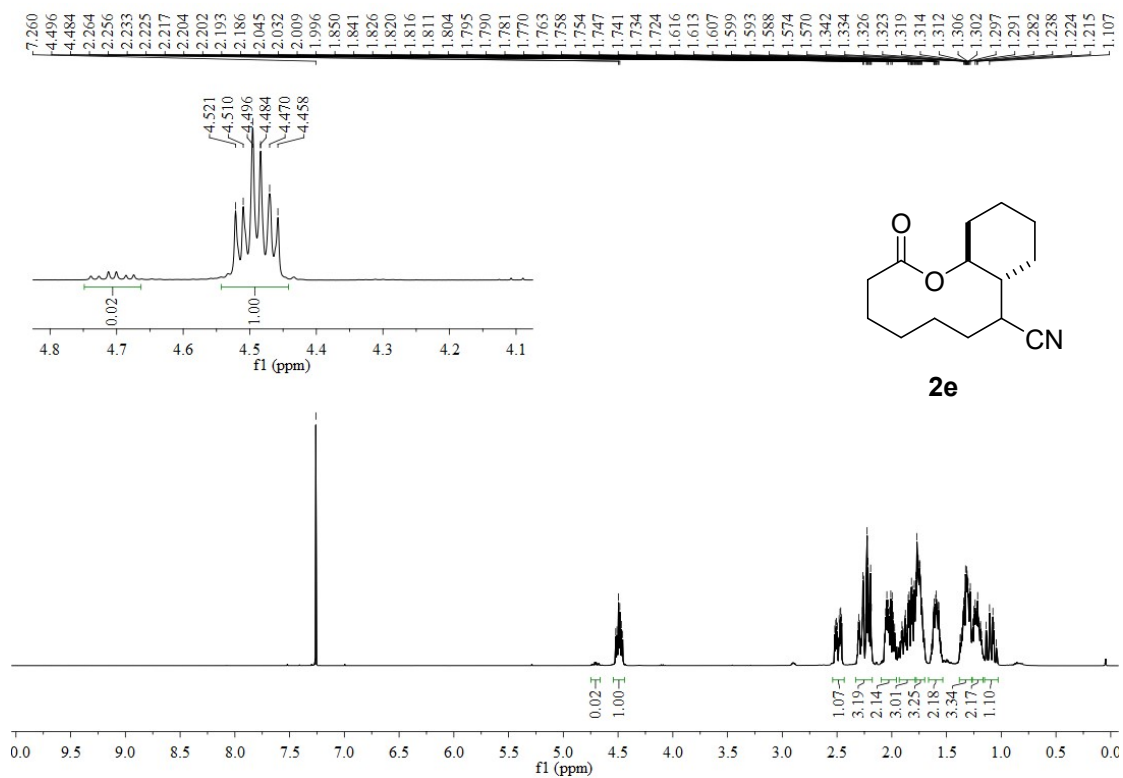
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2c**



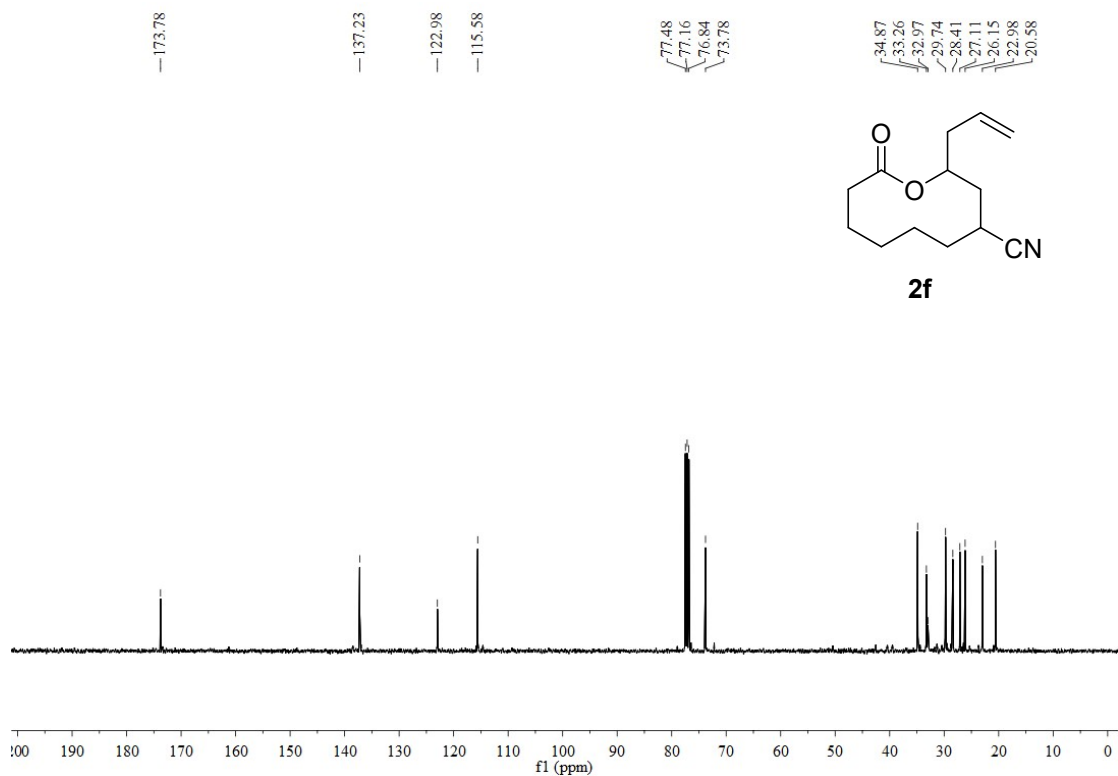
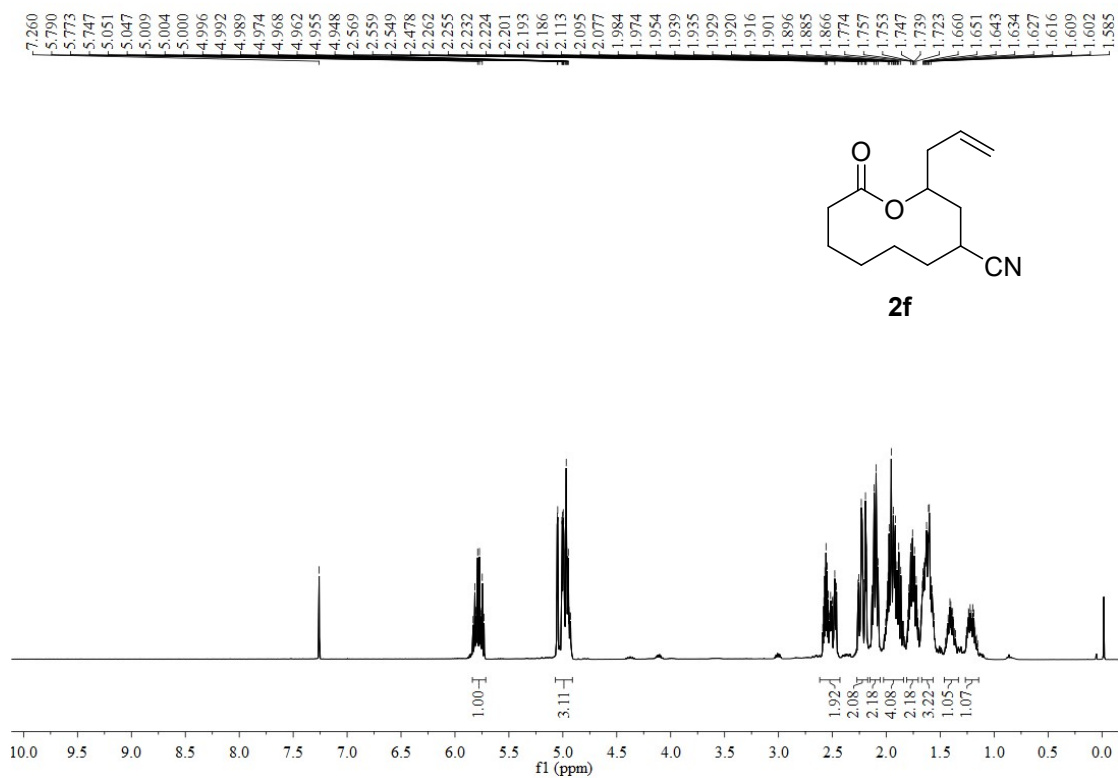
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2d**



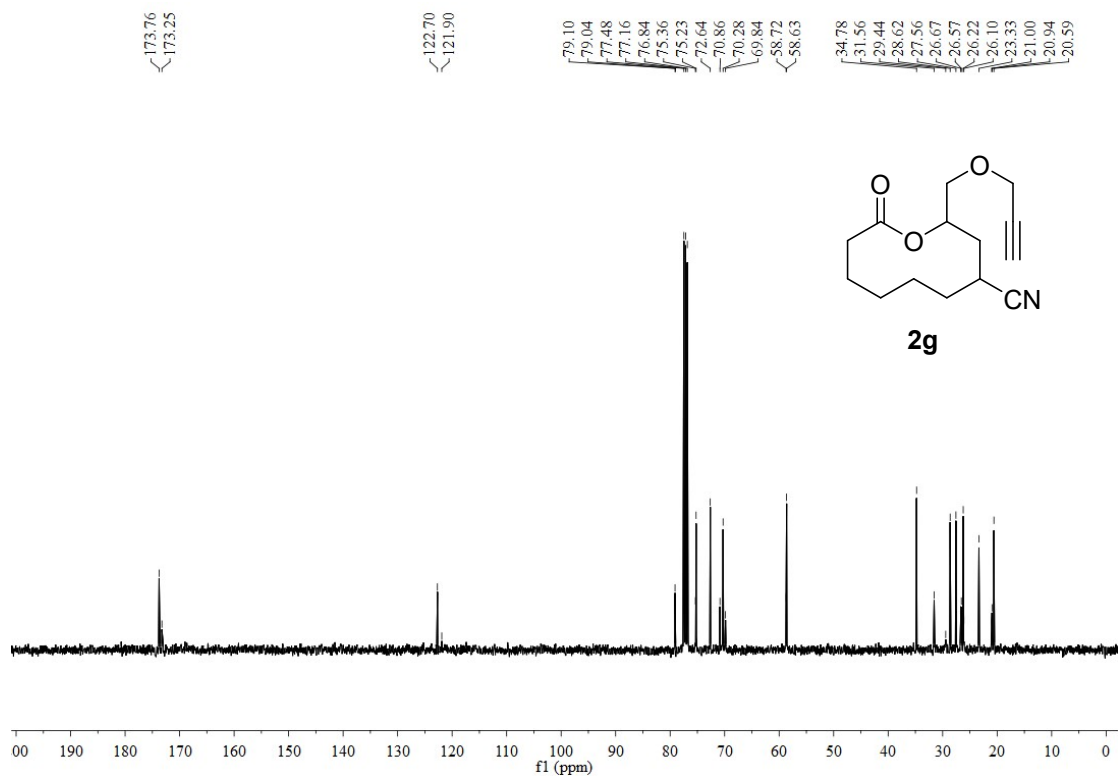
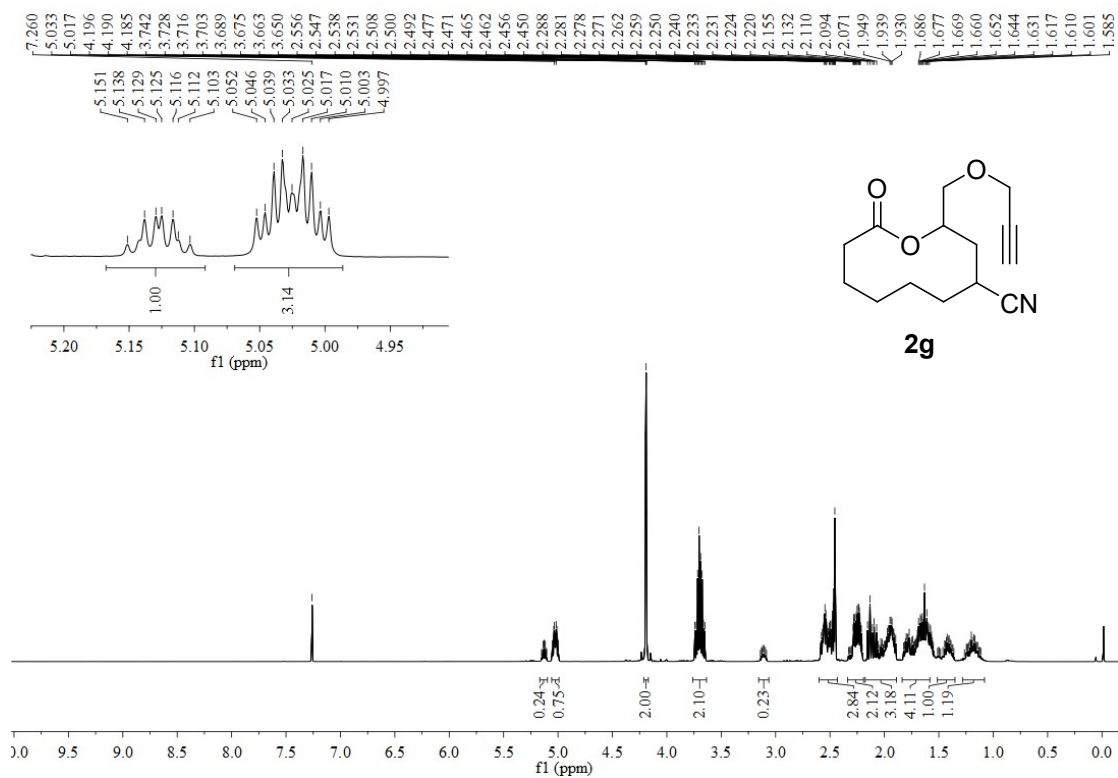
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2e**



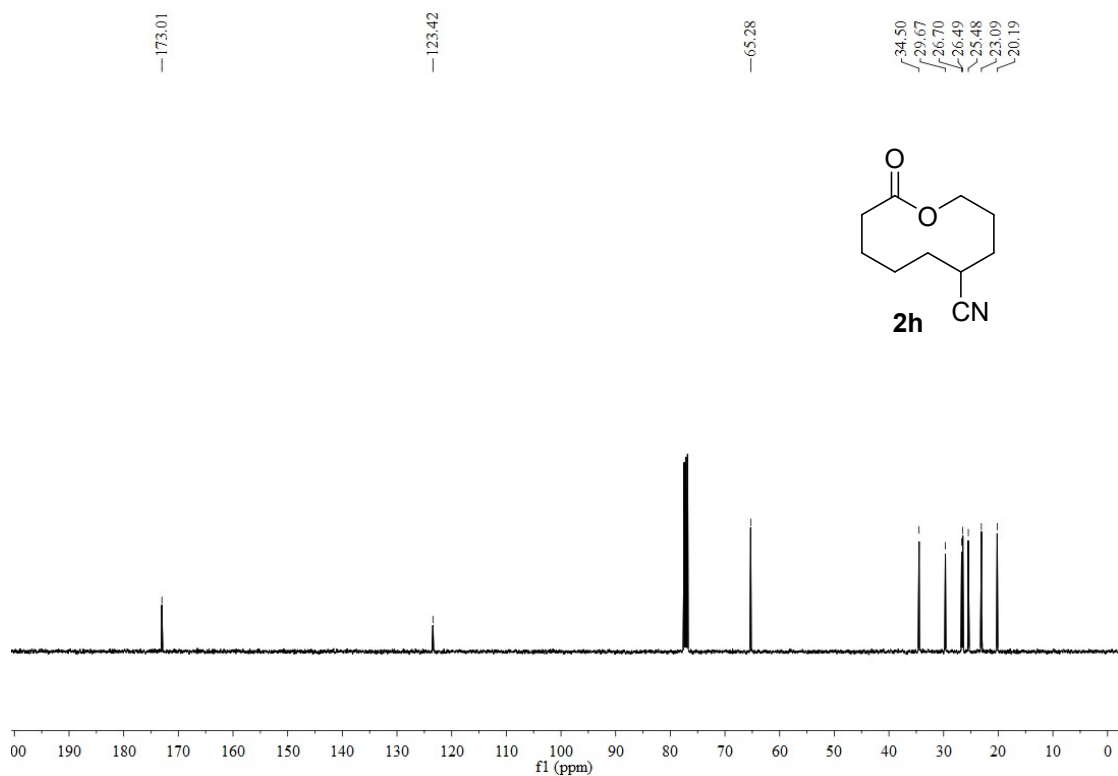
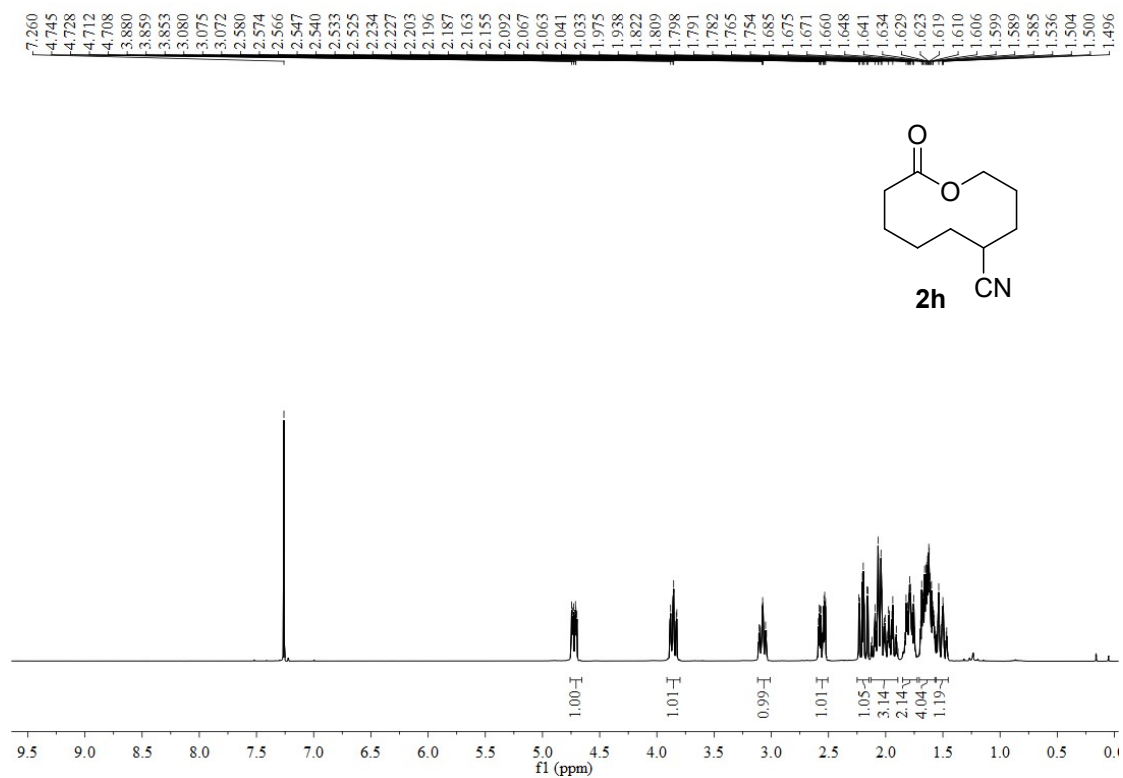
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product 2f



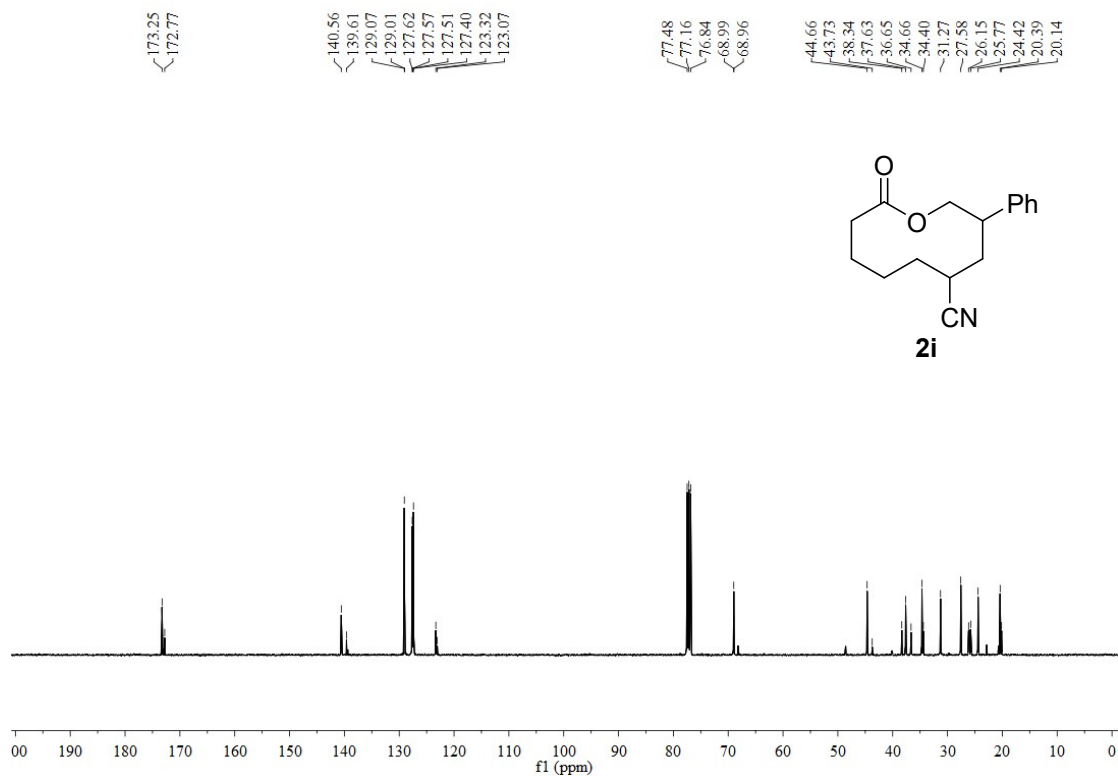
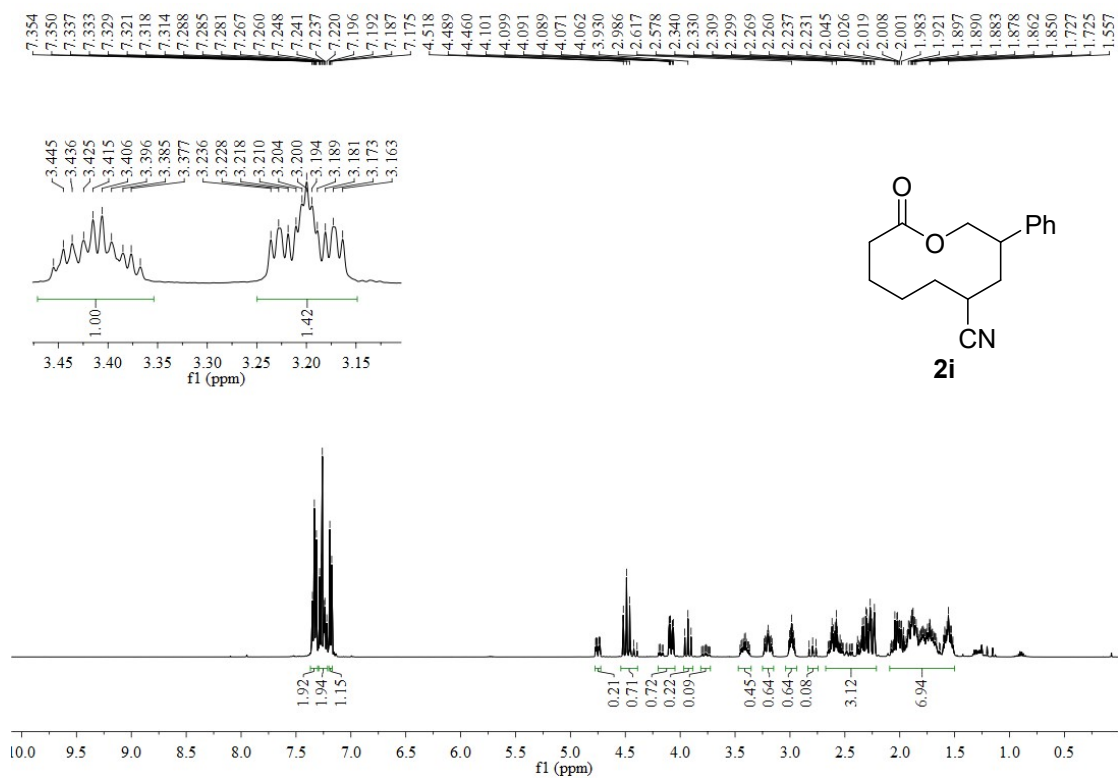
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2g**



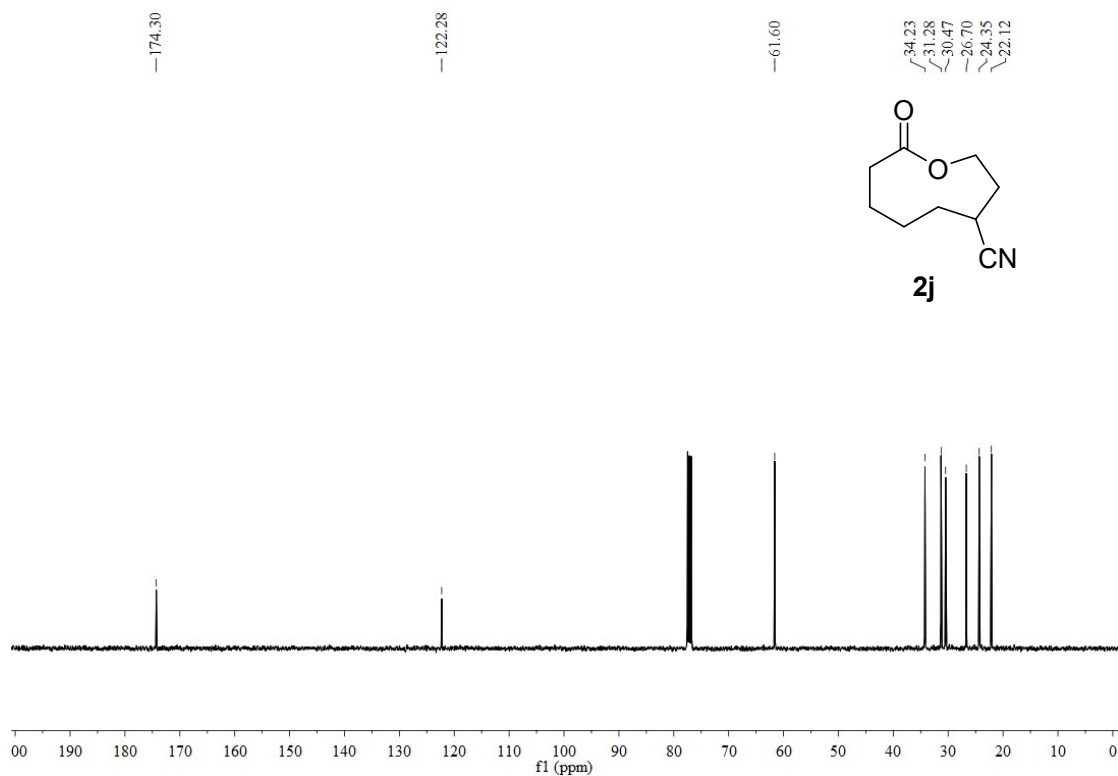
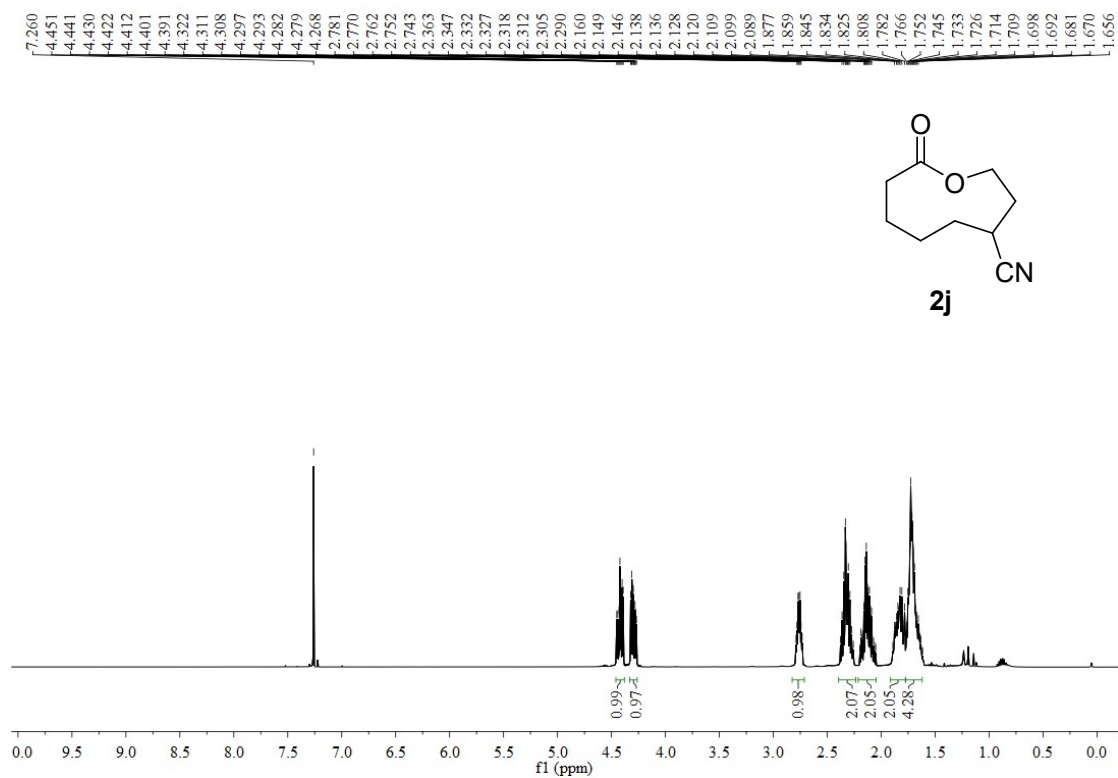
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2h**



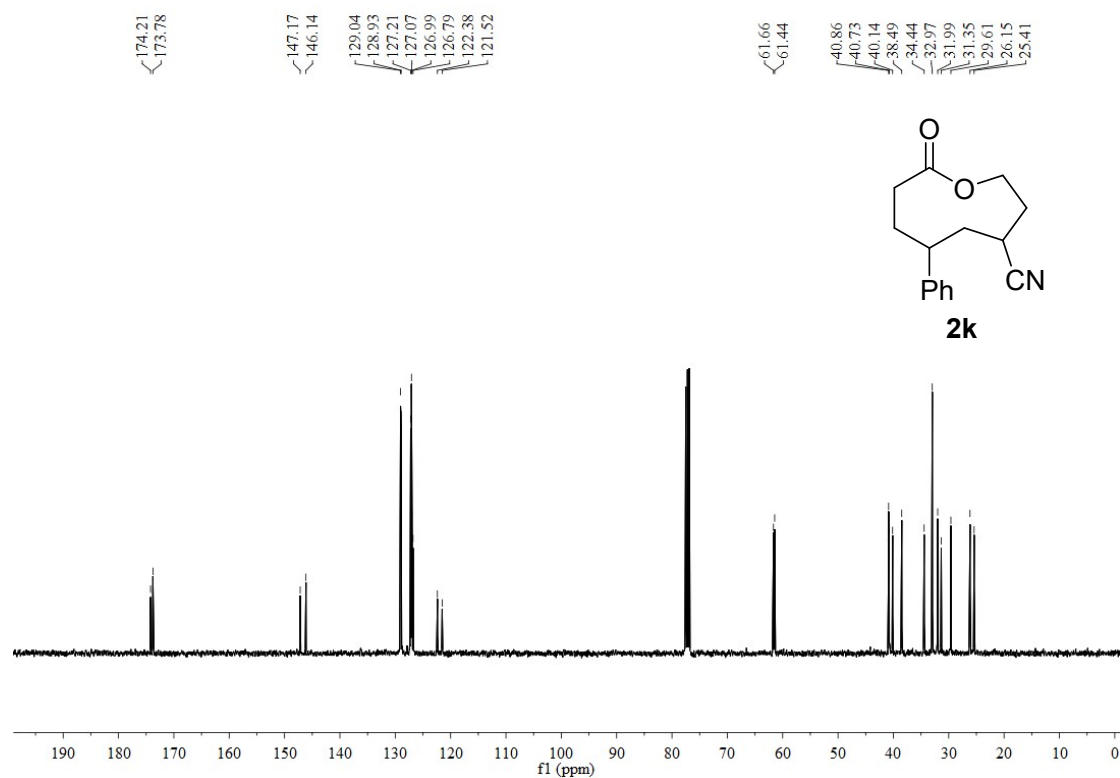
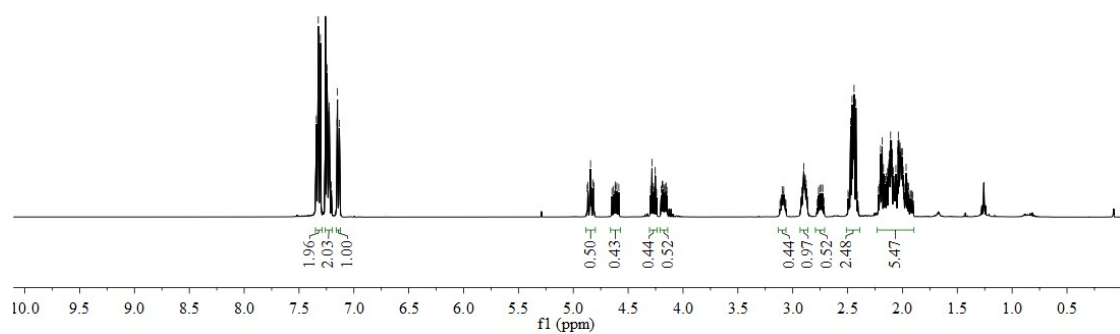
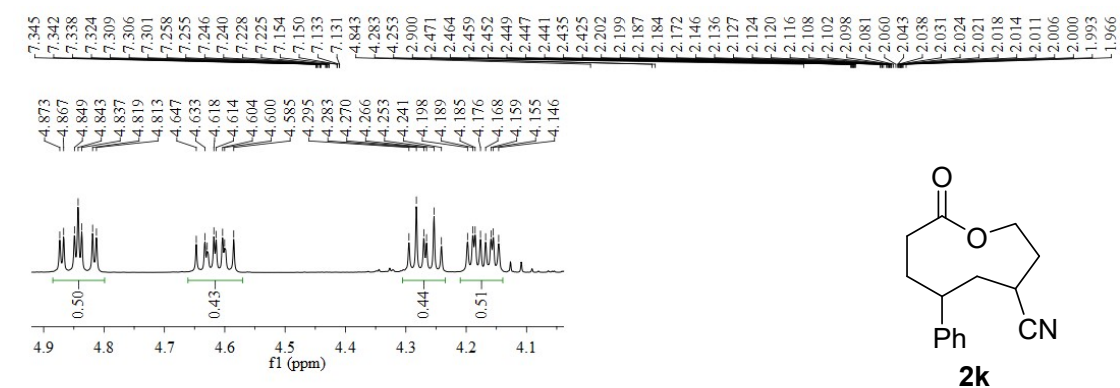
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2i**



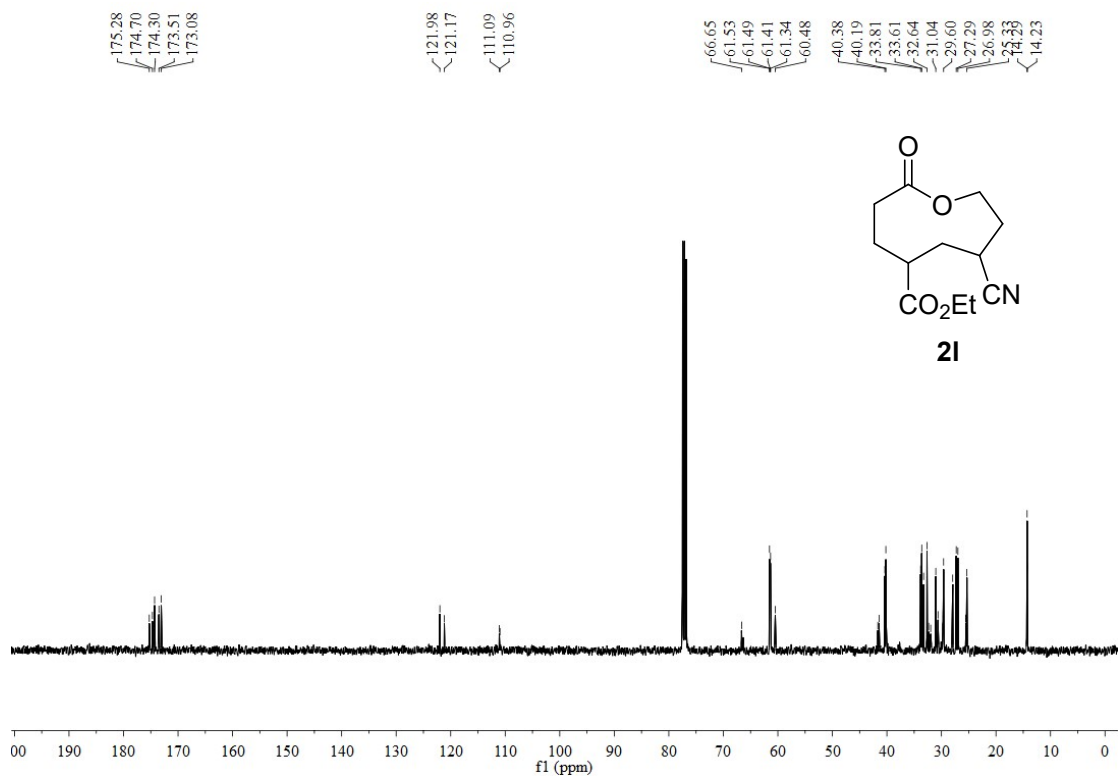
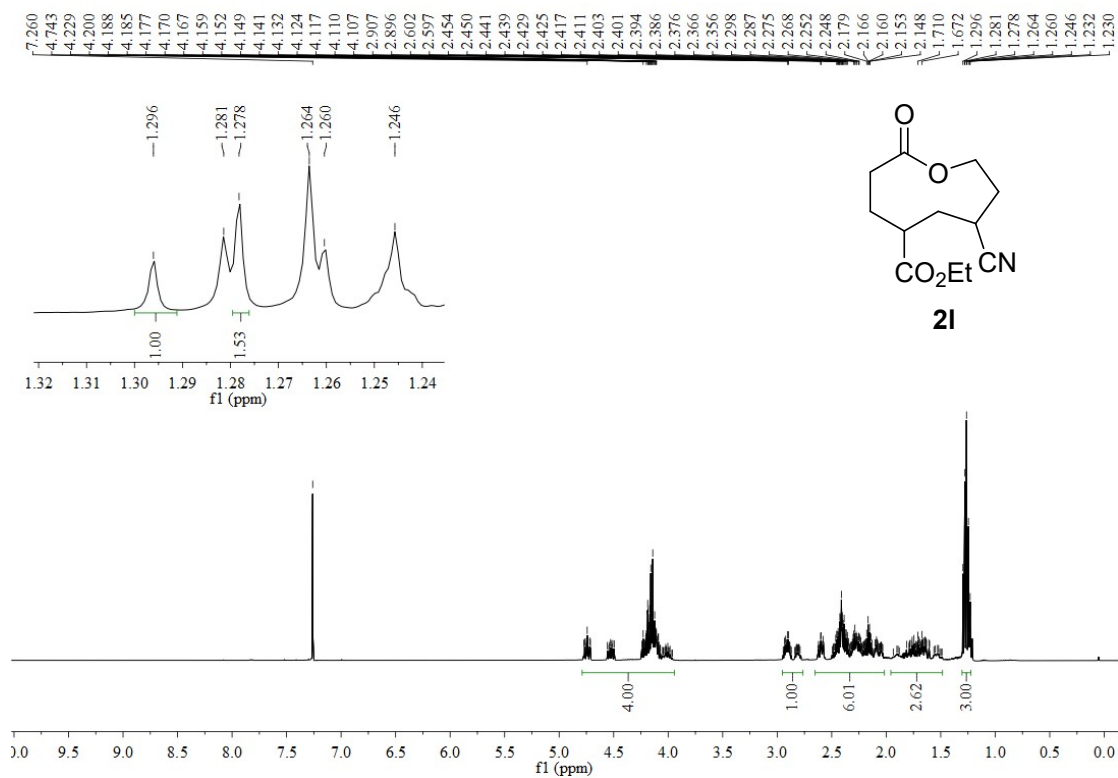
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2j**



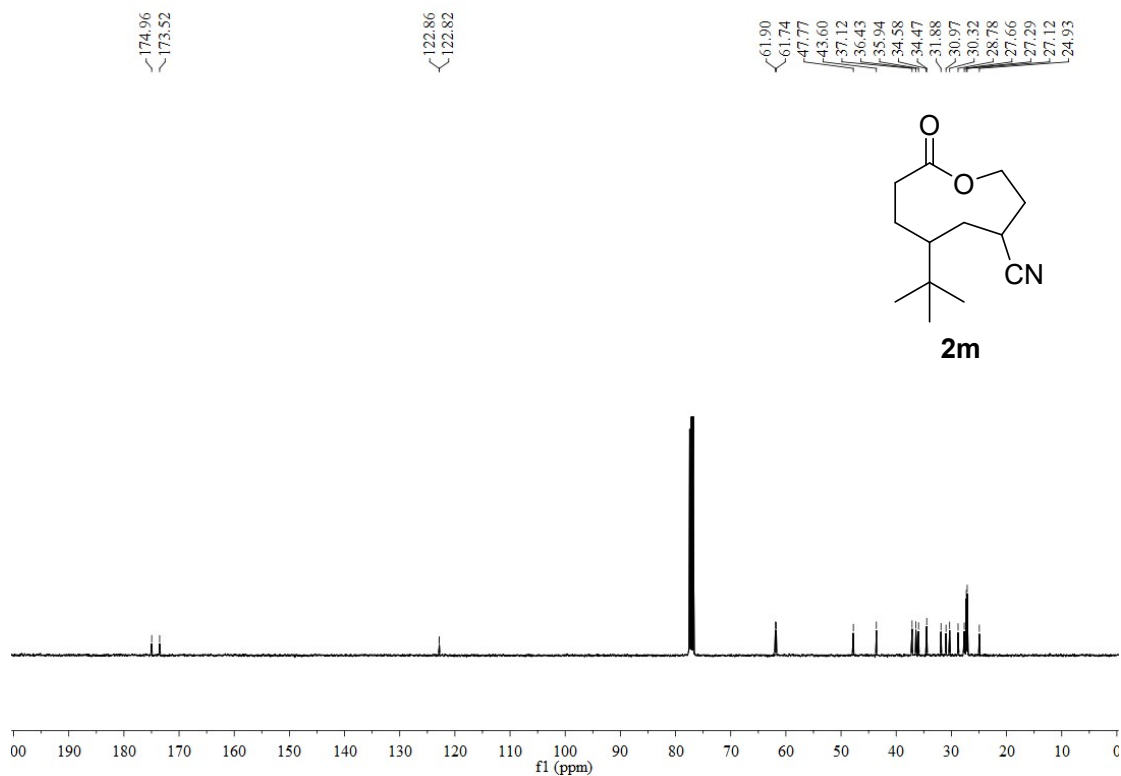
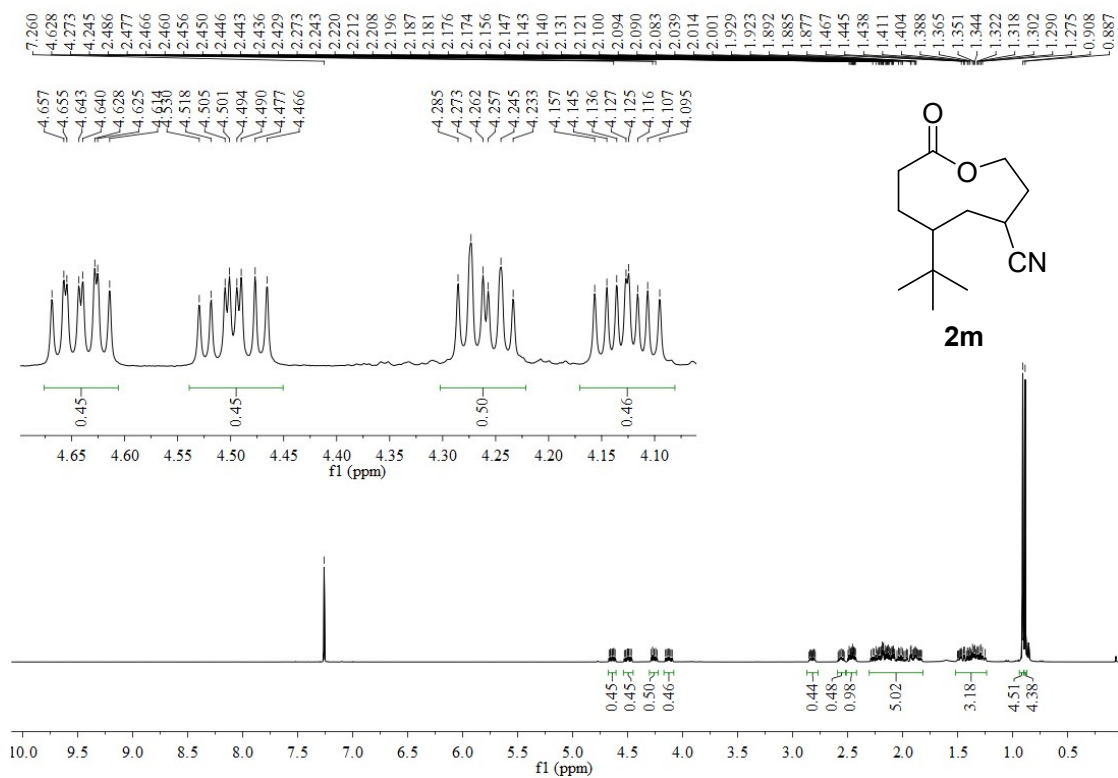
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2k**

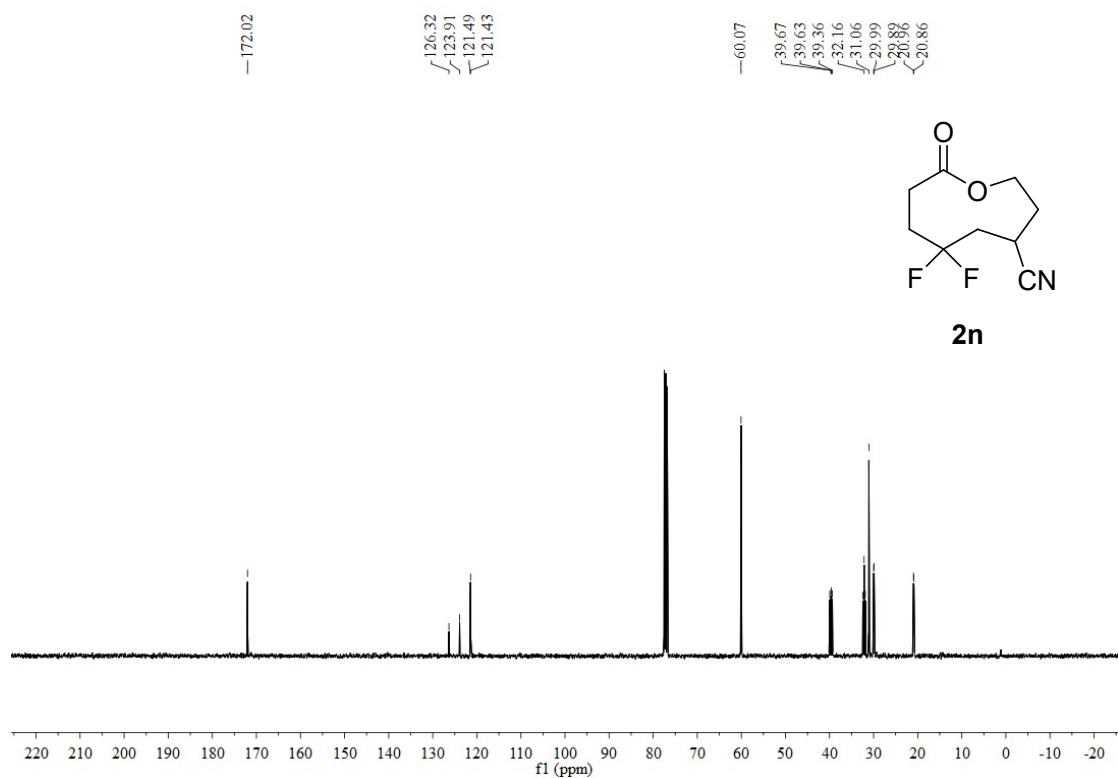
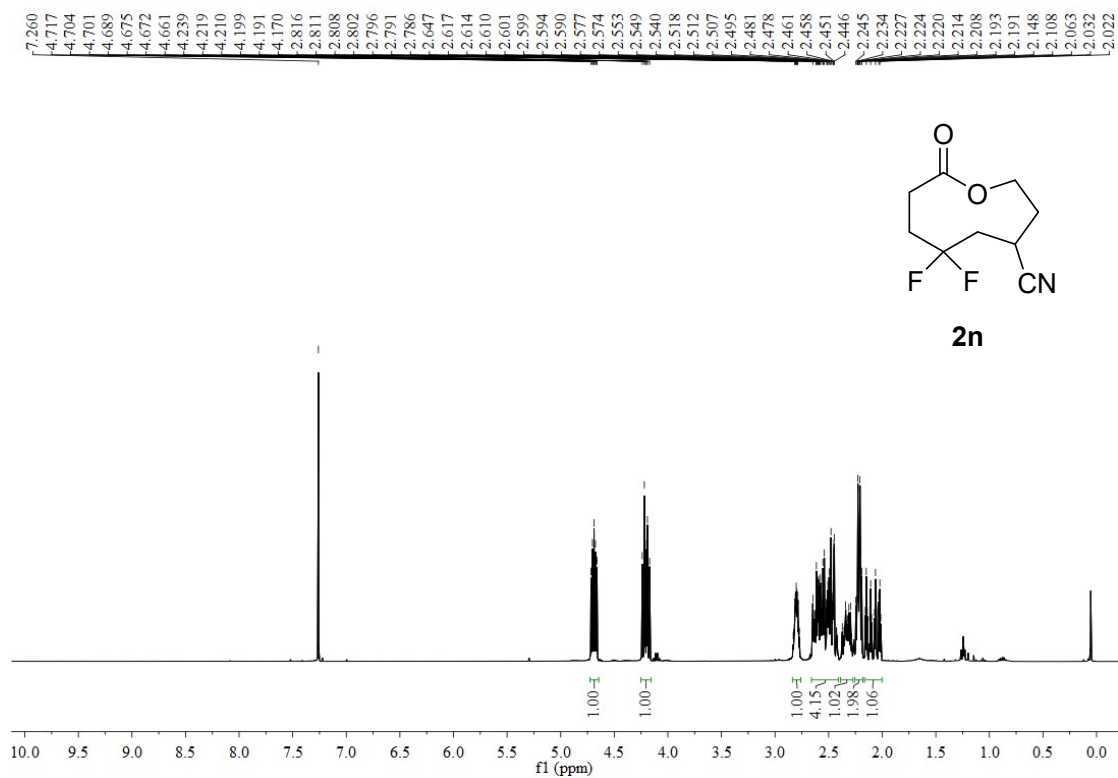


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2i**

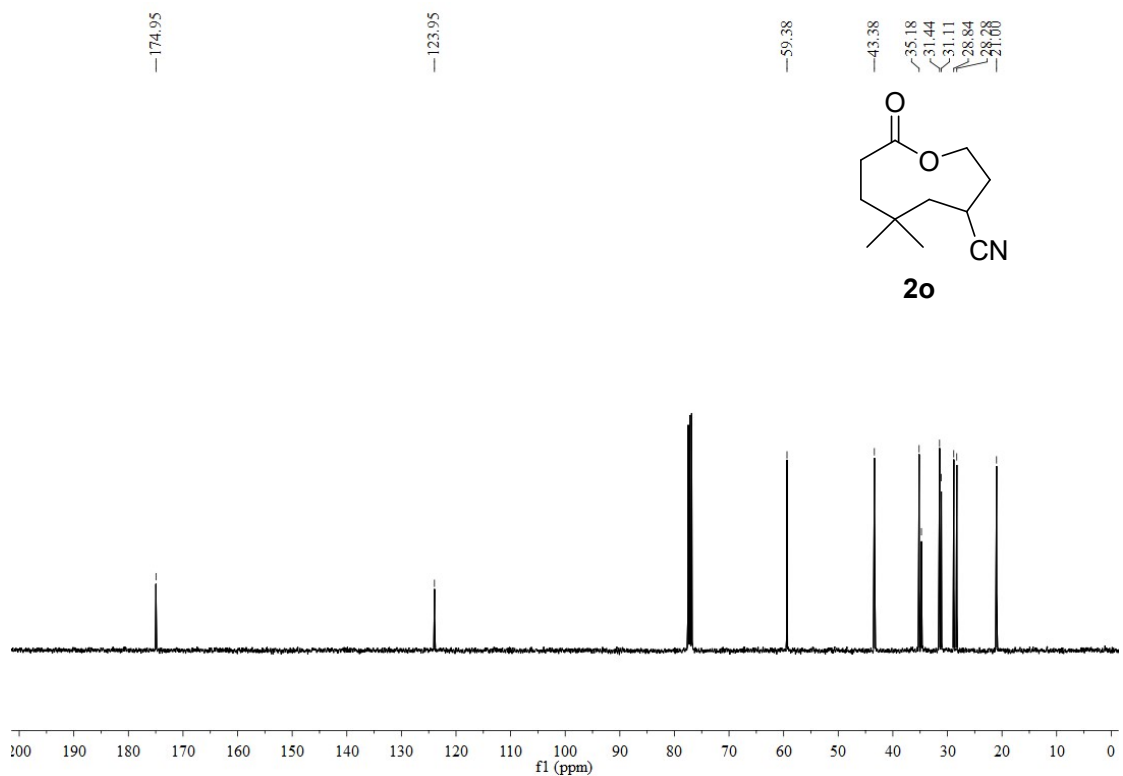
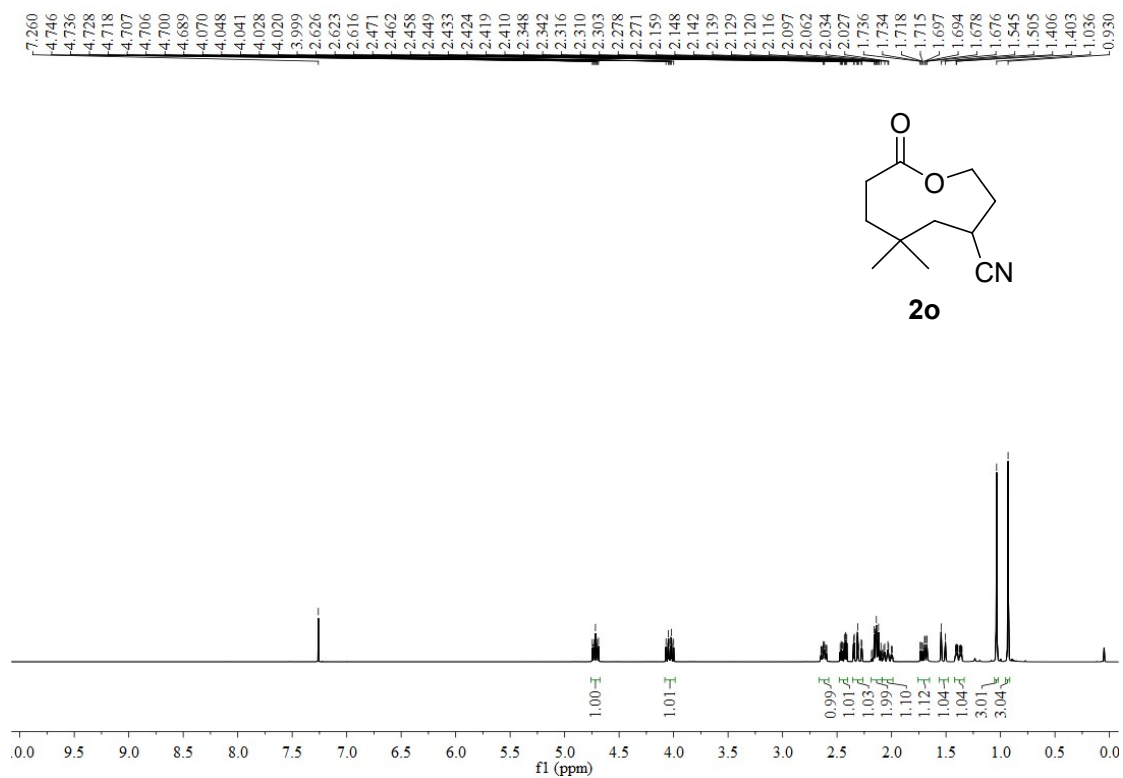


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2m**

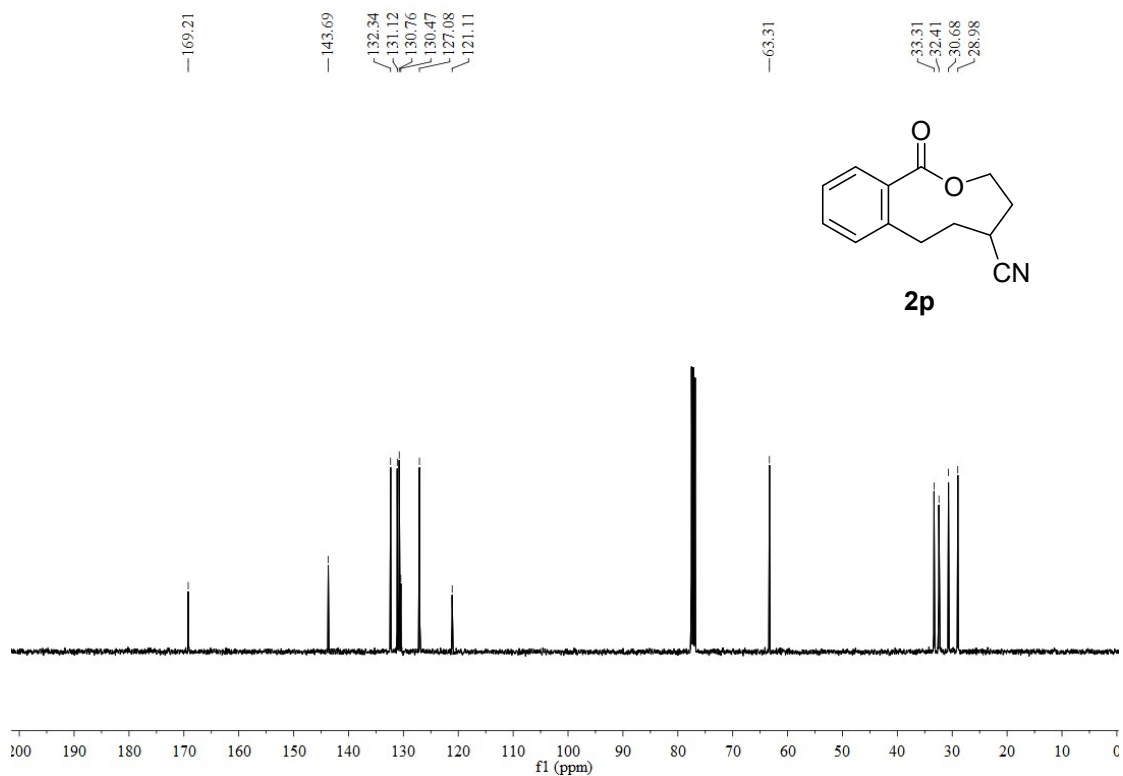
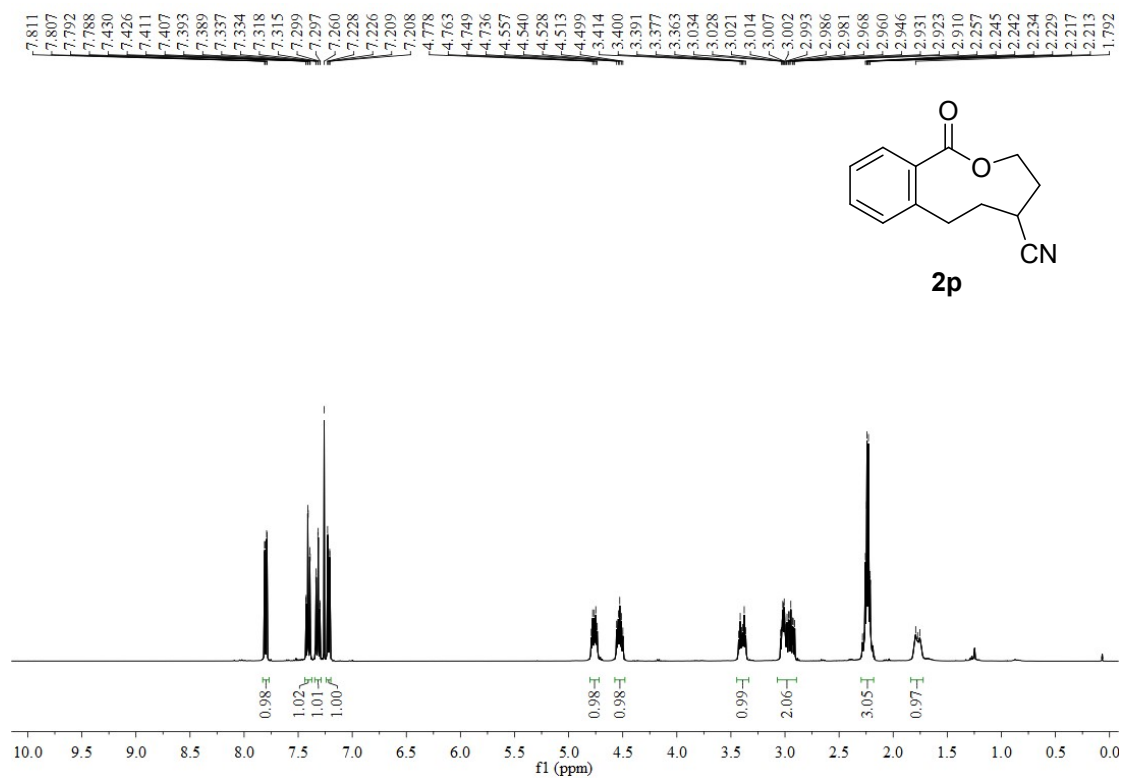
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2n**



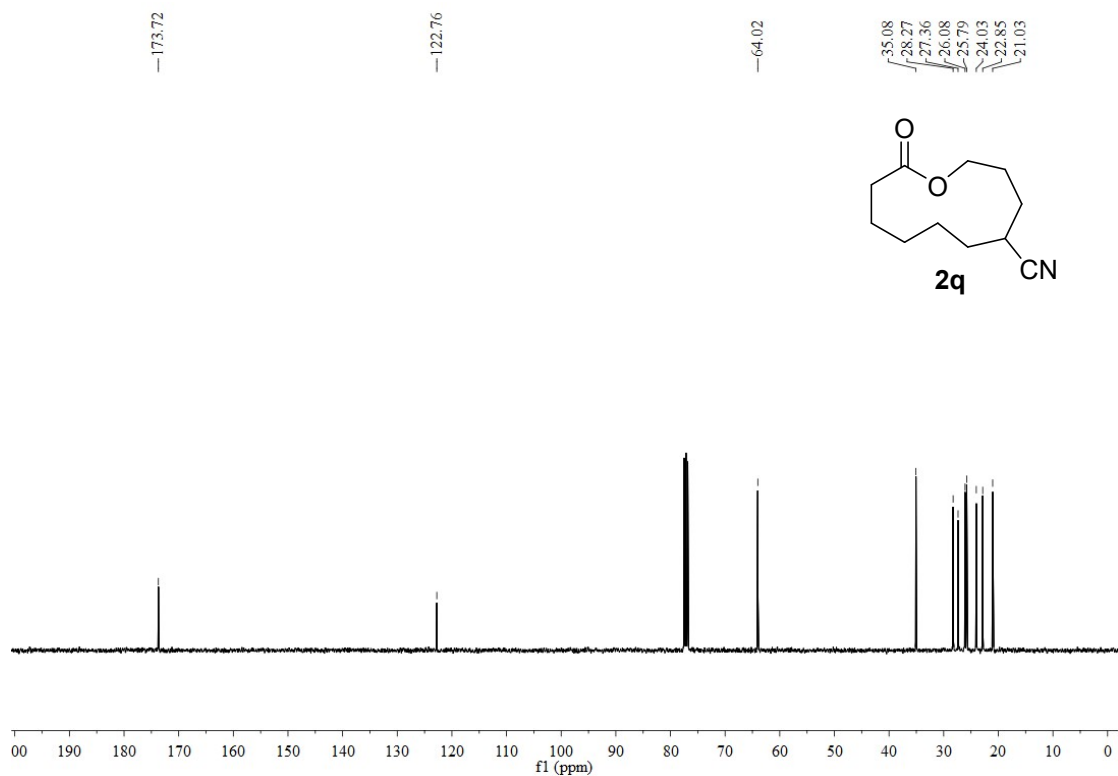
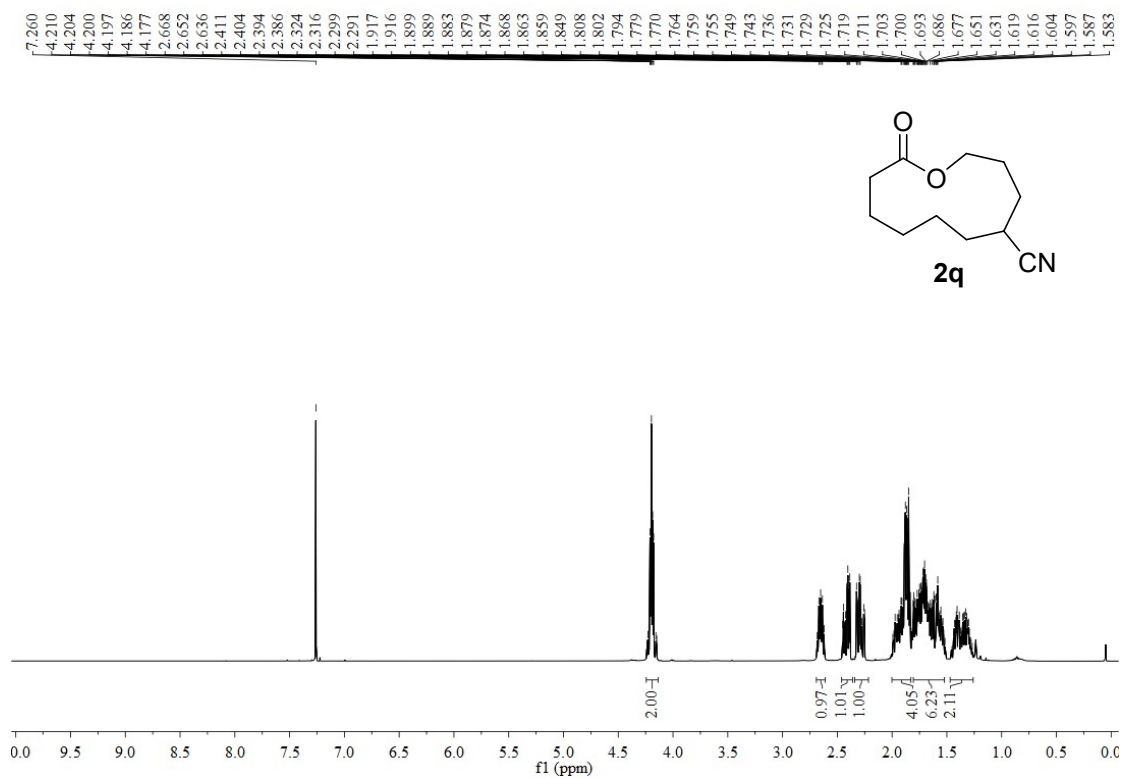
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2o**



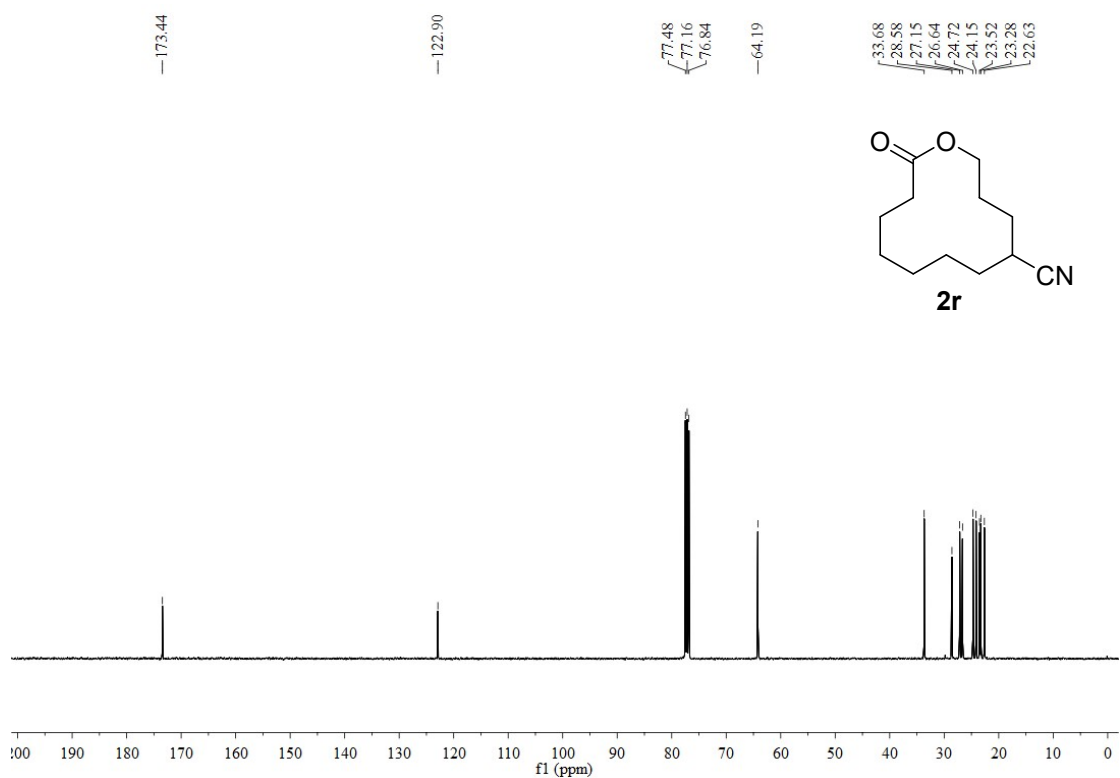
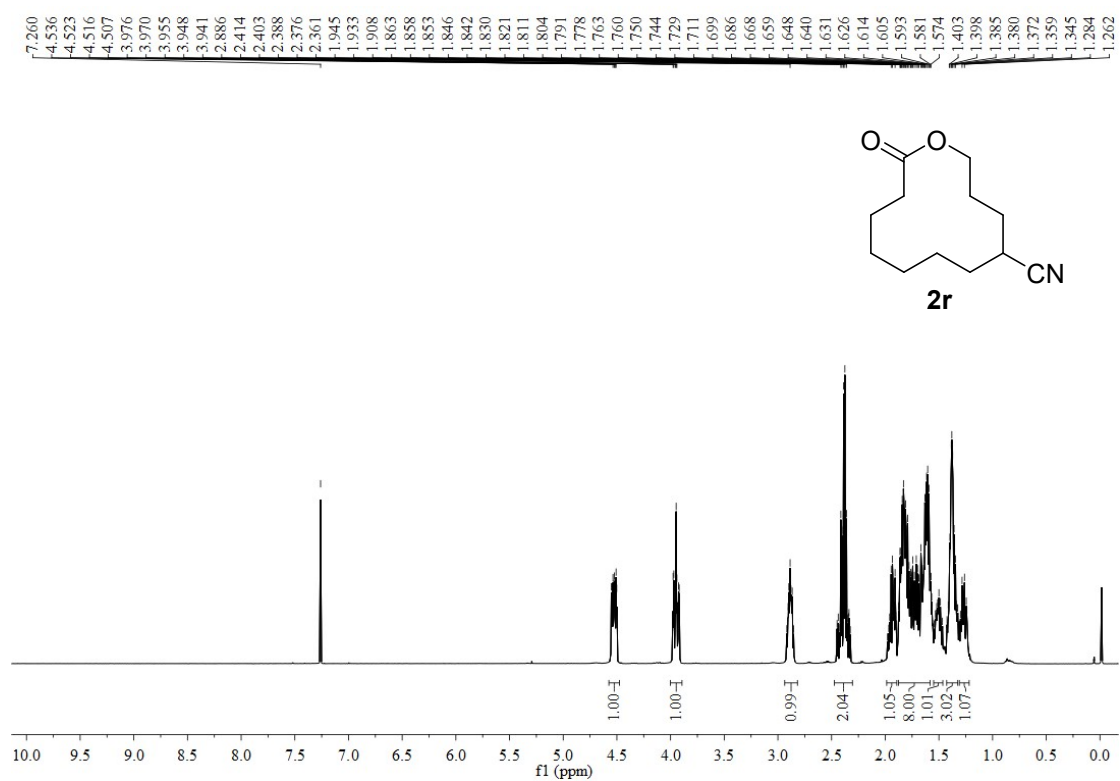
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2p**



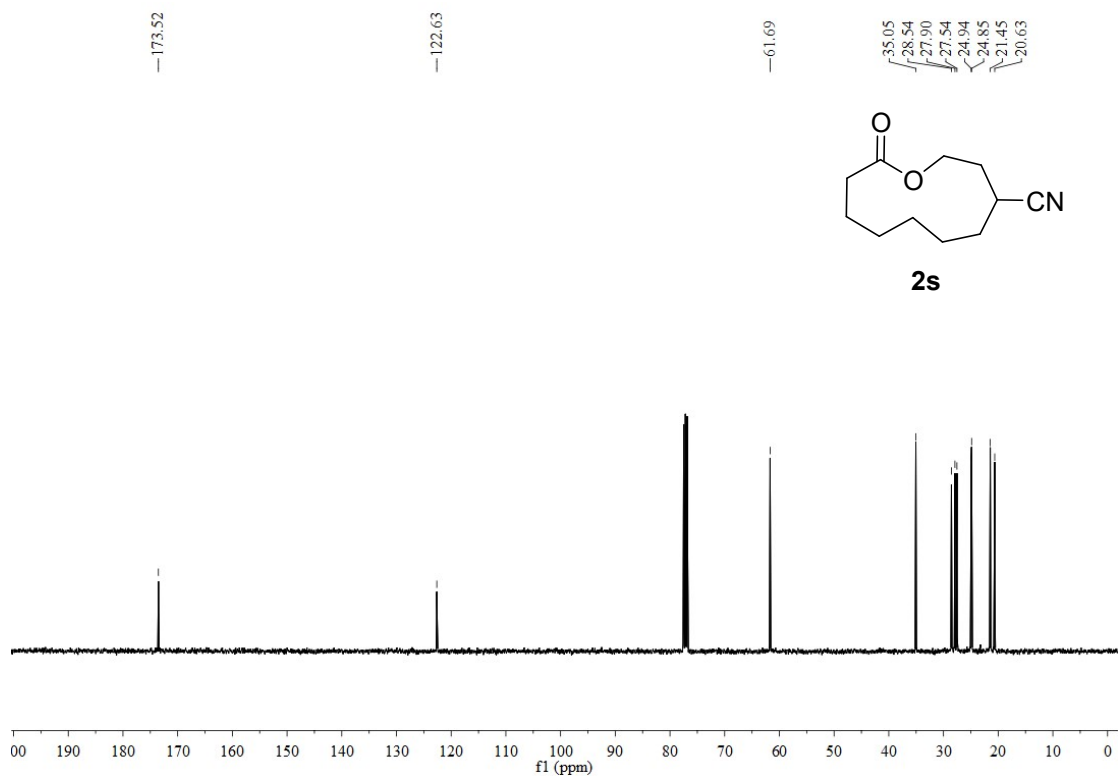
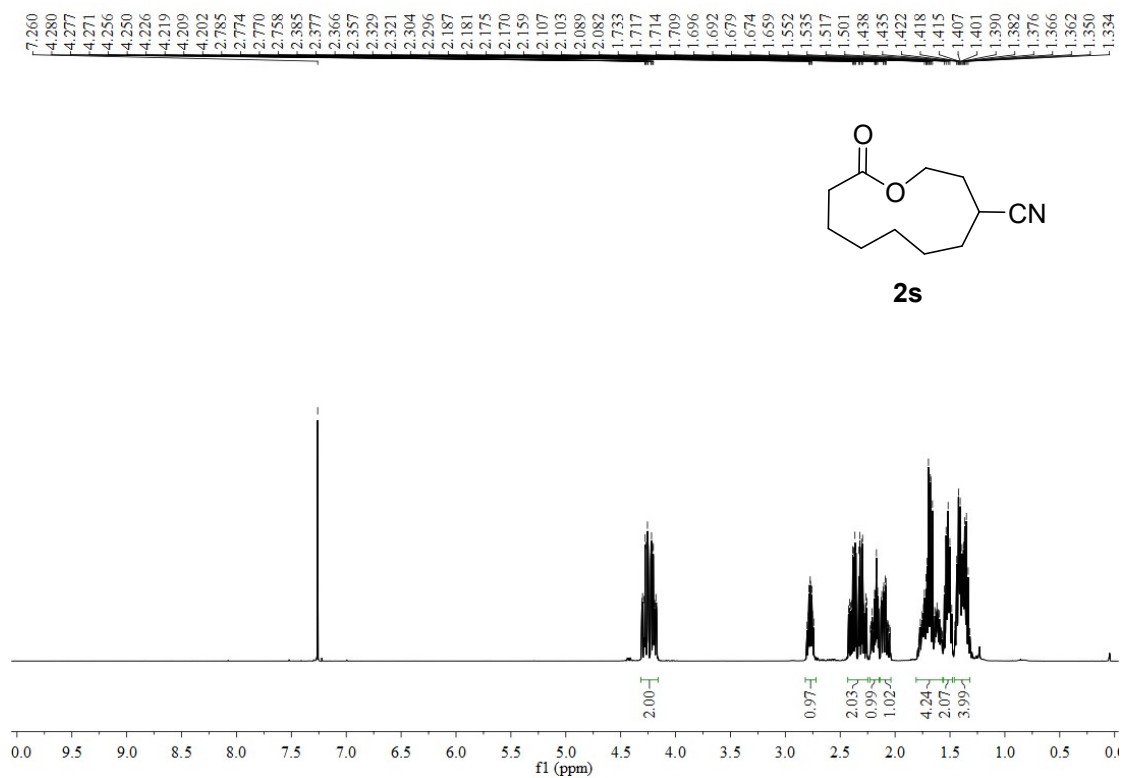
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2q**



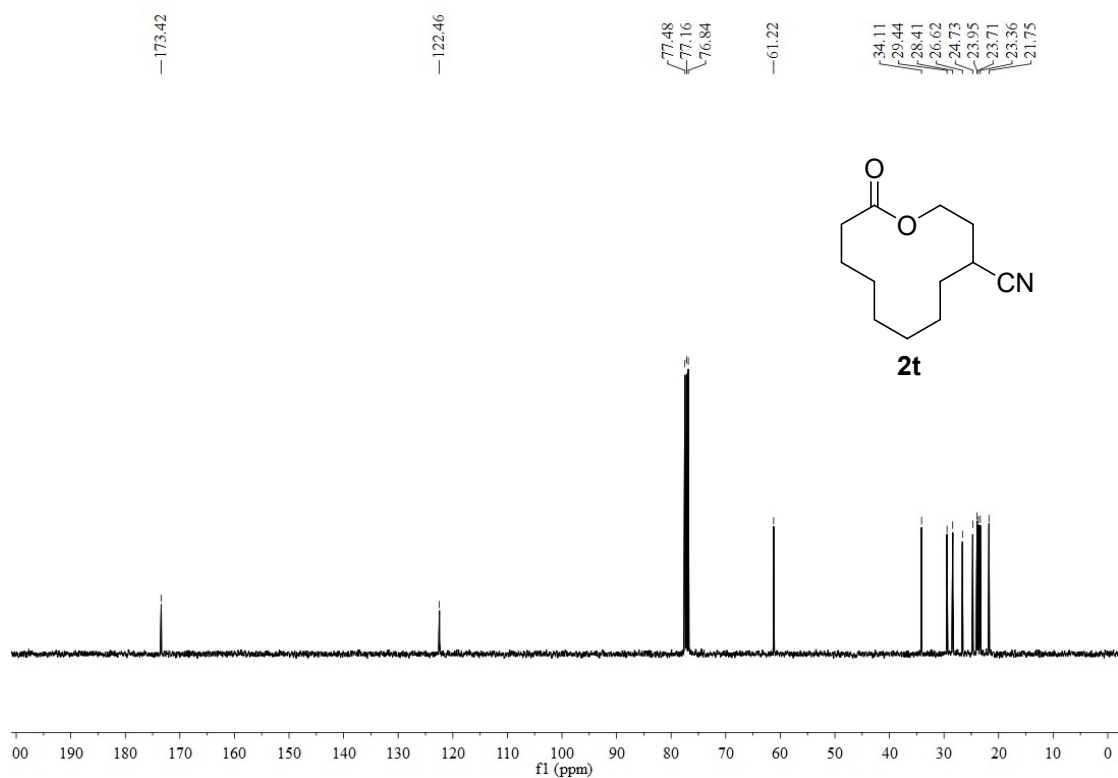
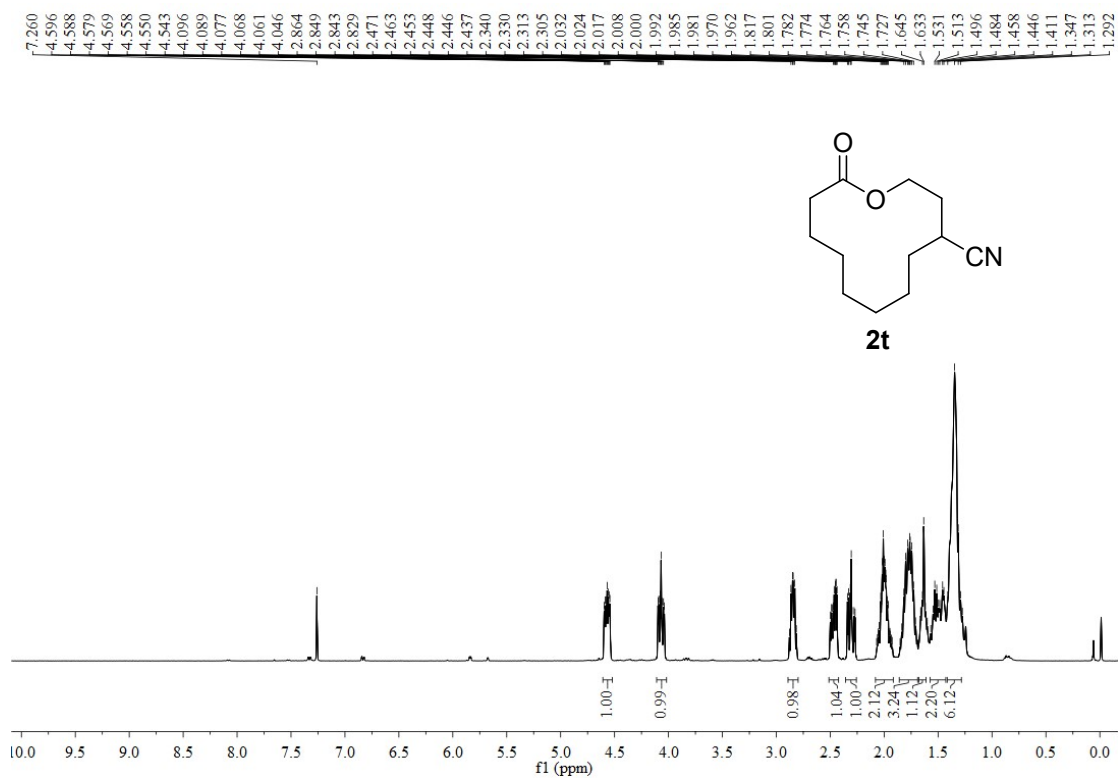
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2r**



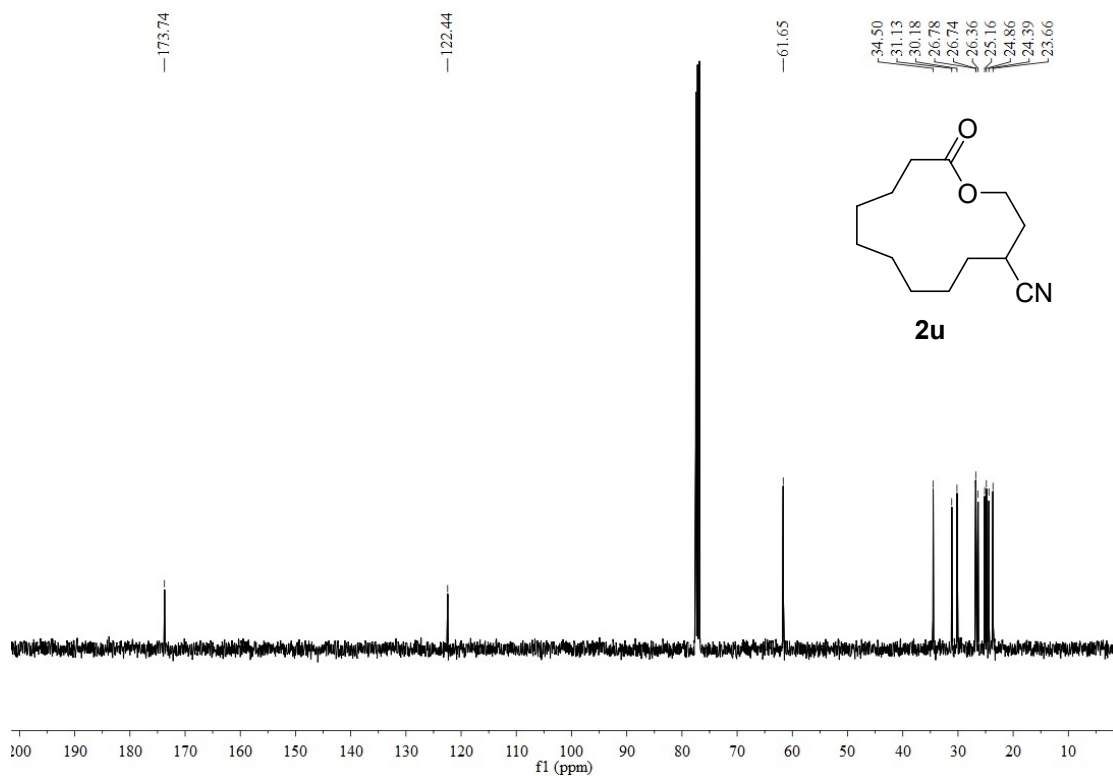
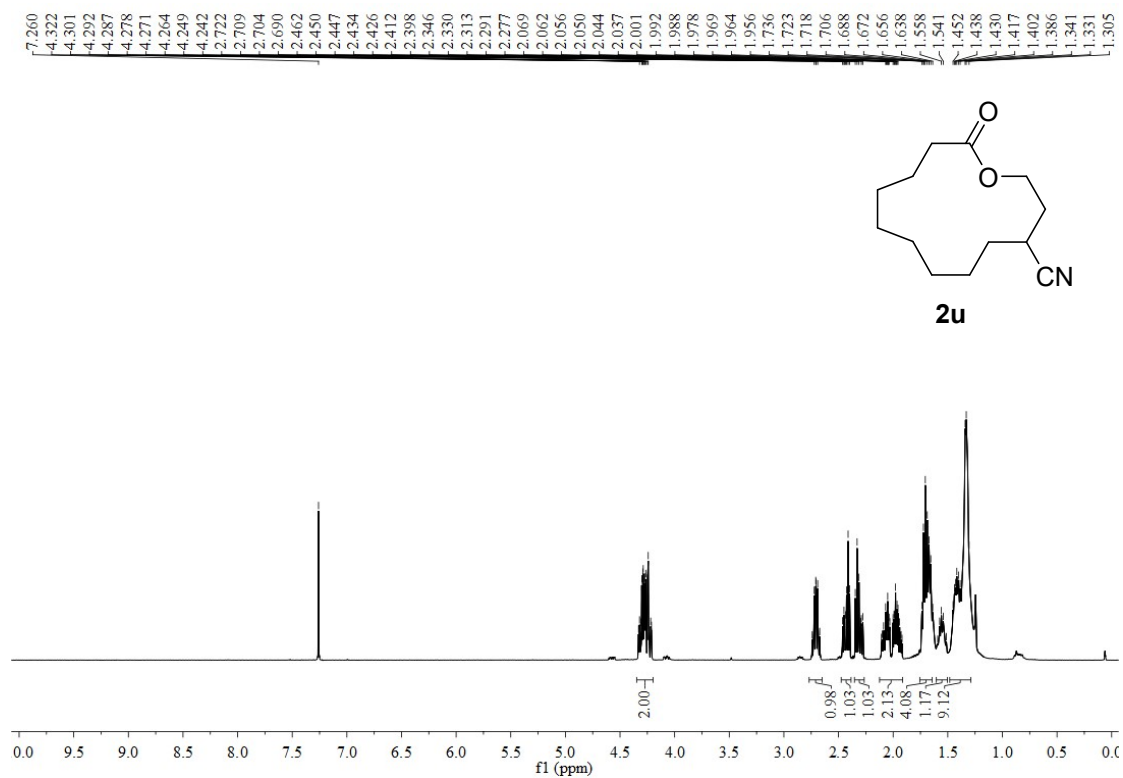
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2s**



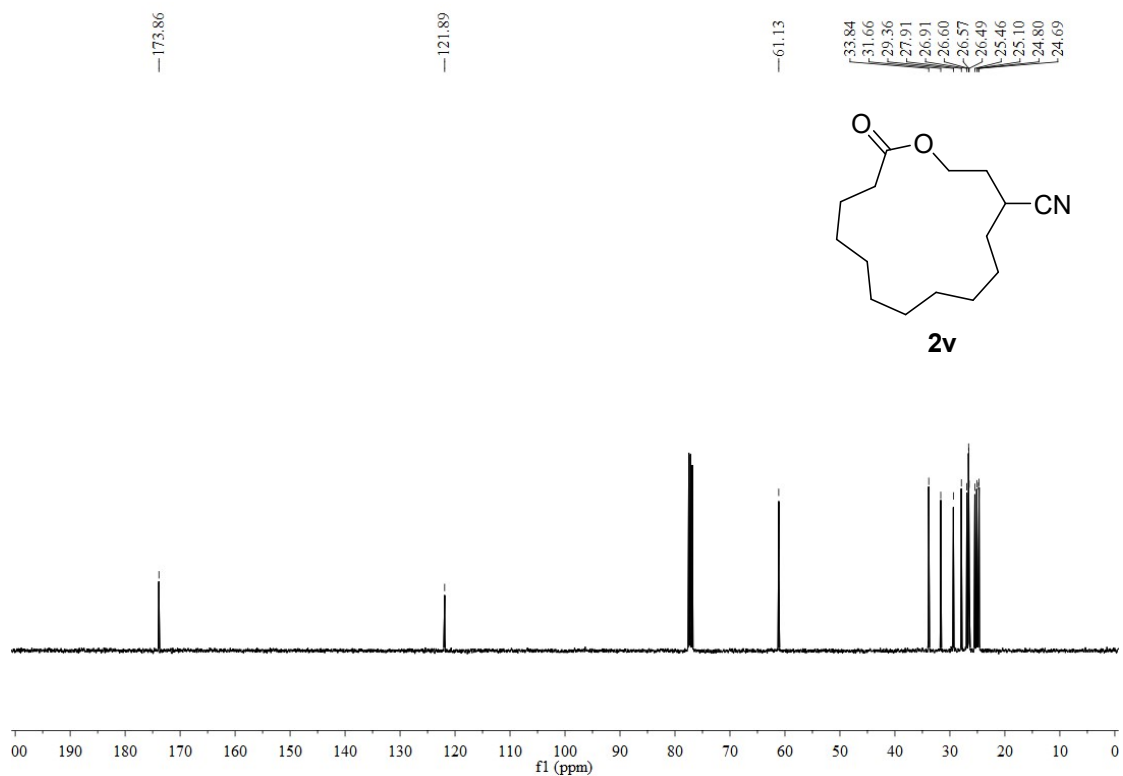
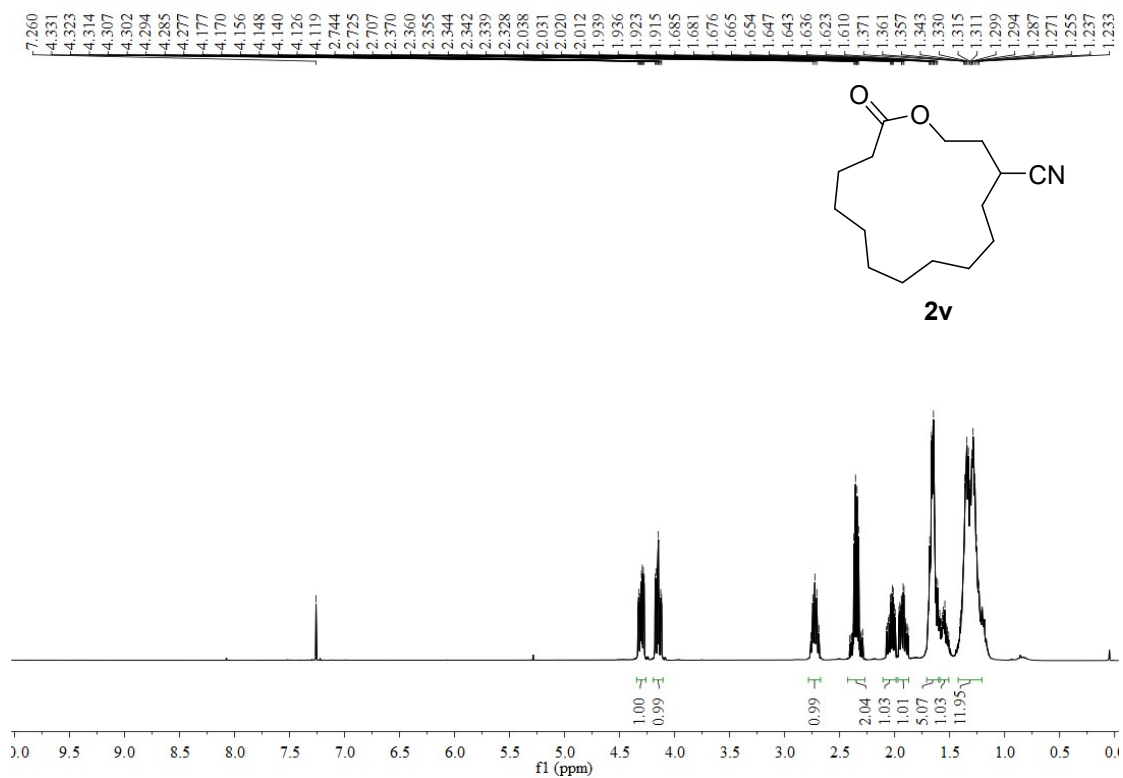
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2t**



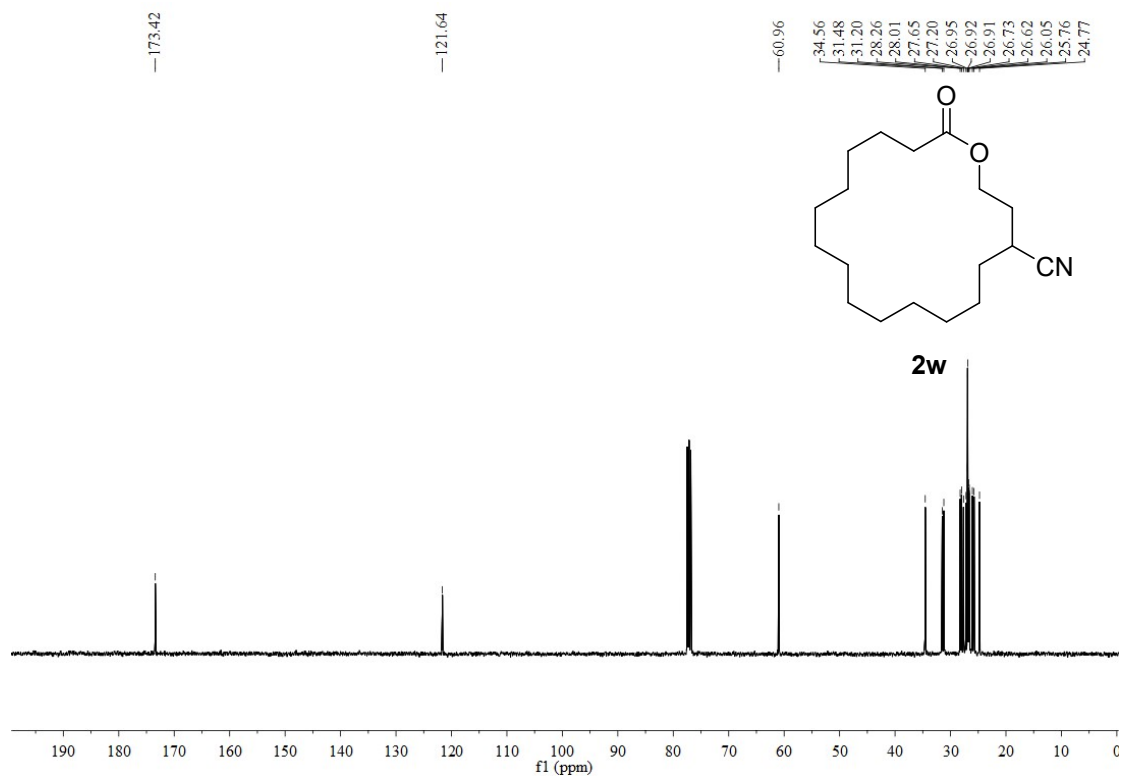
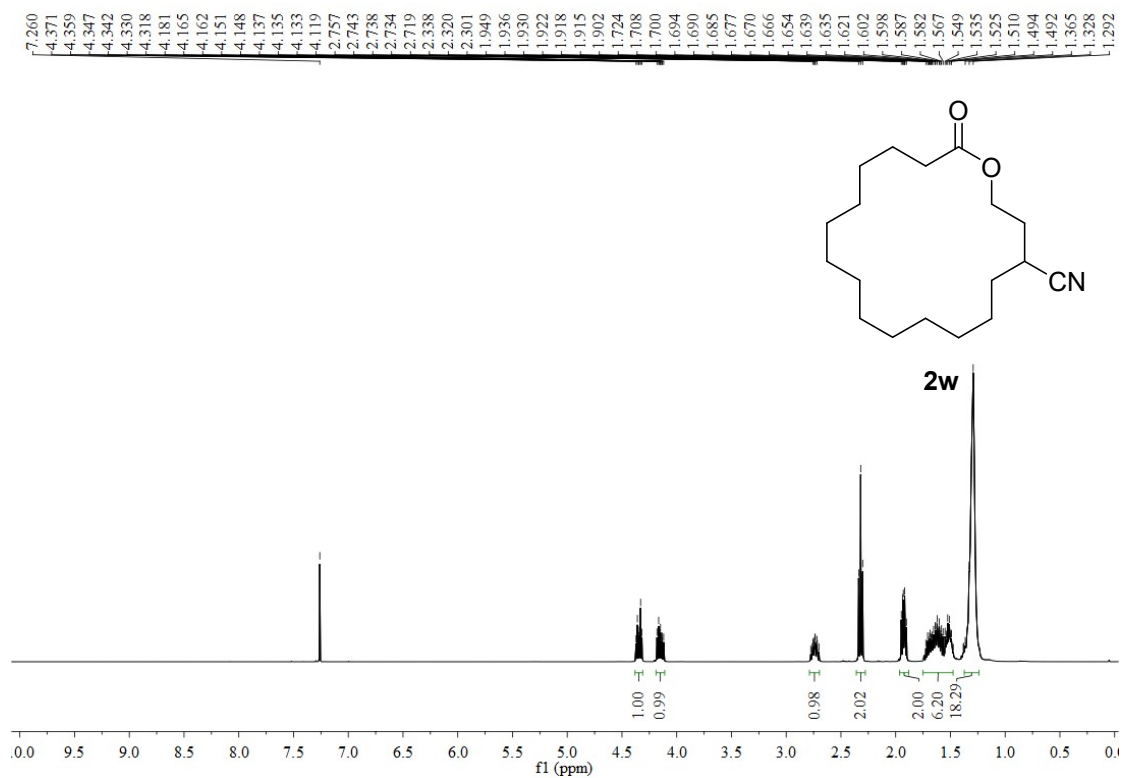
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2u**



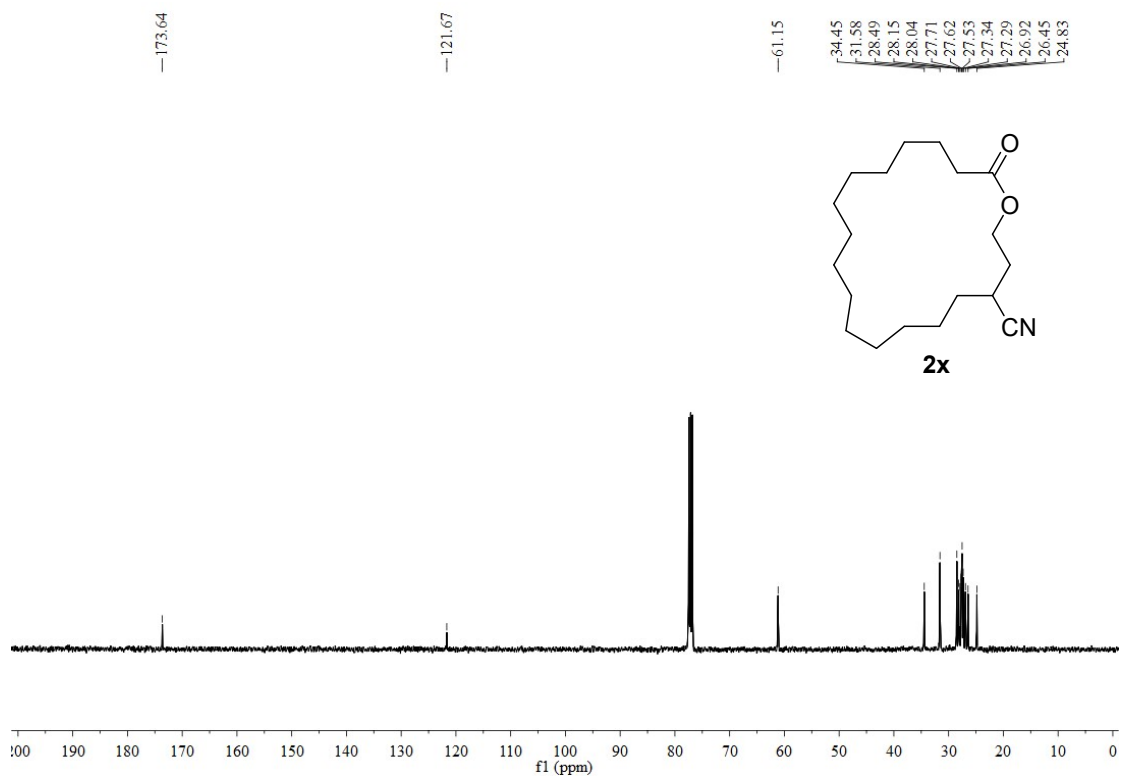
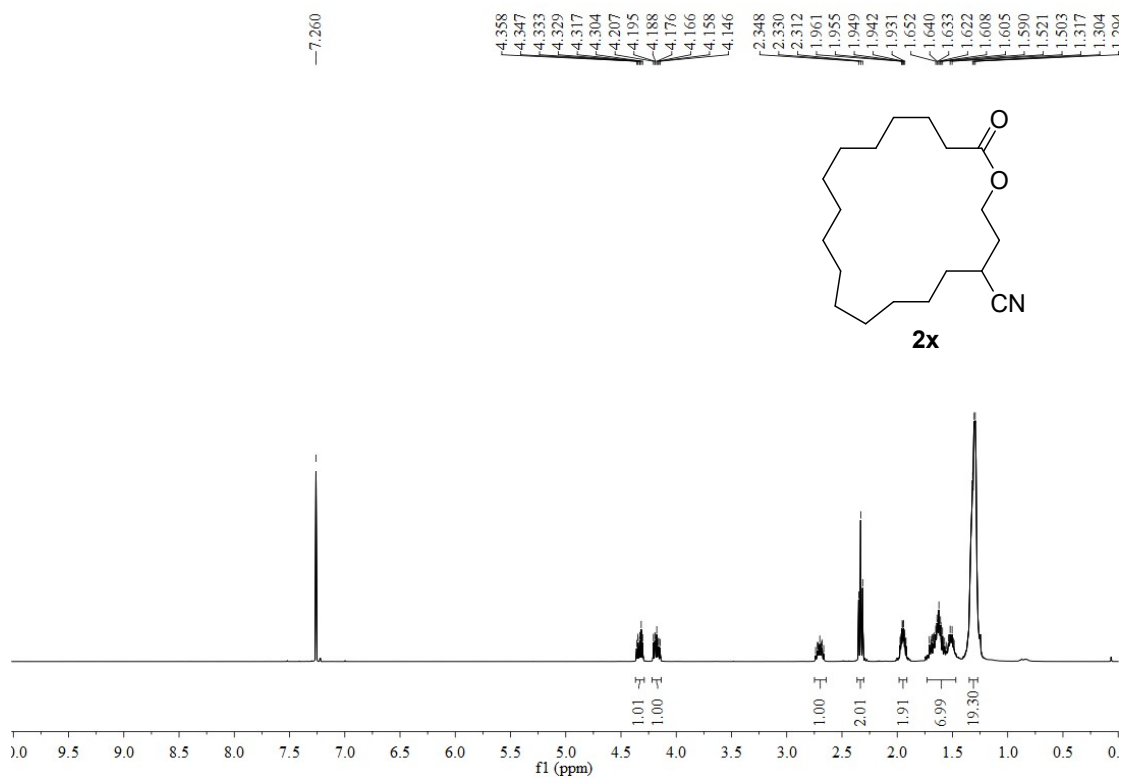
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2v**



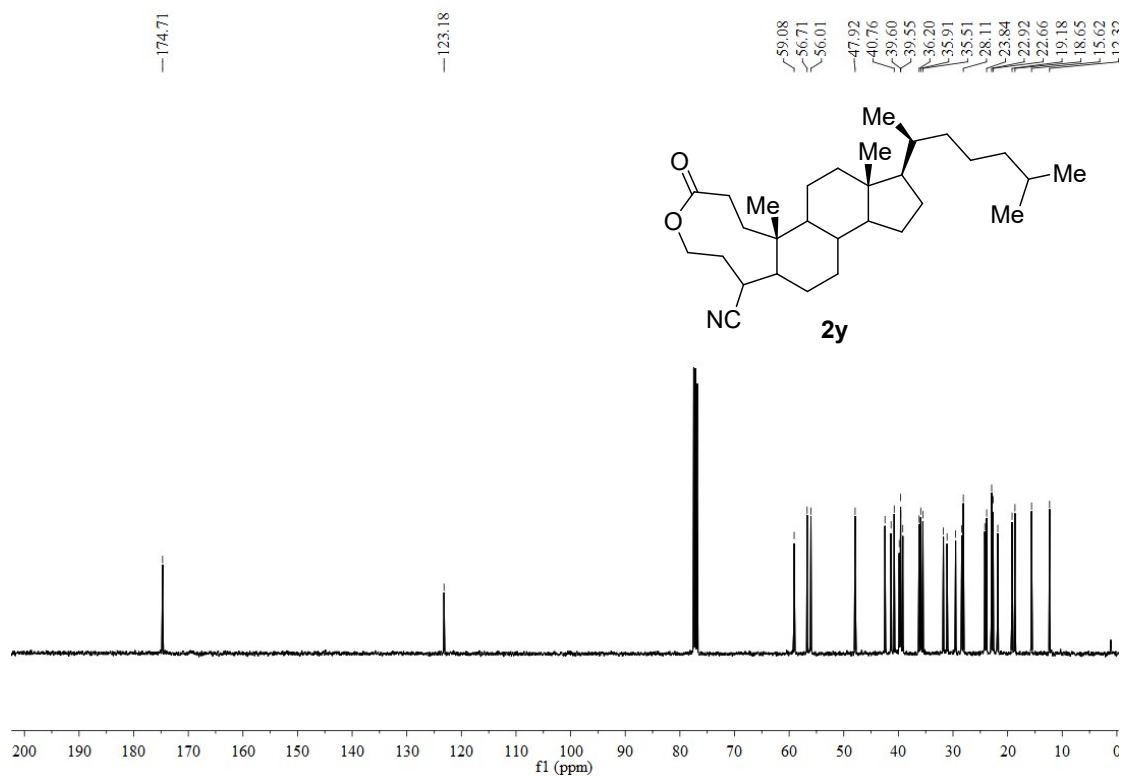
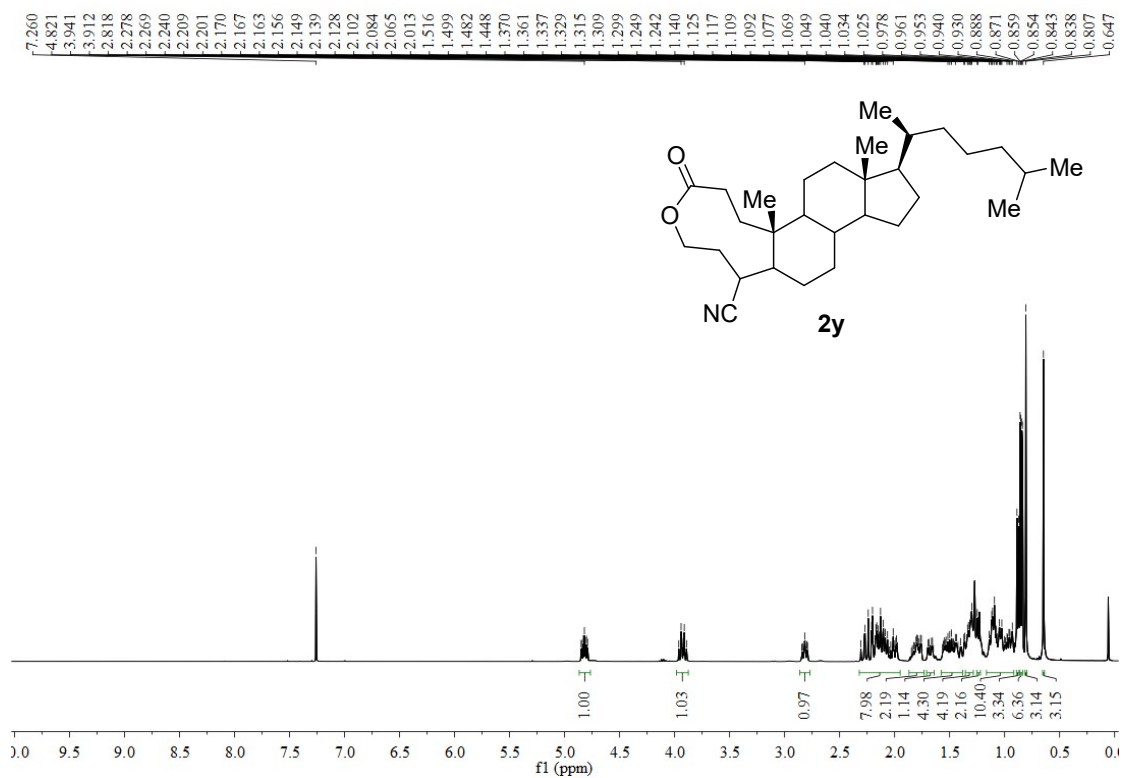
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2w**



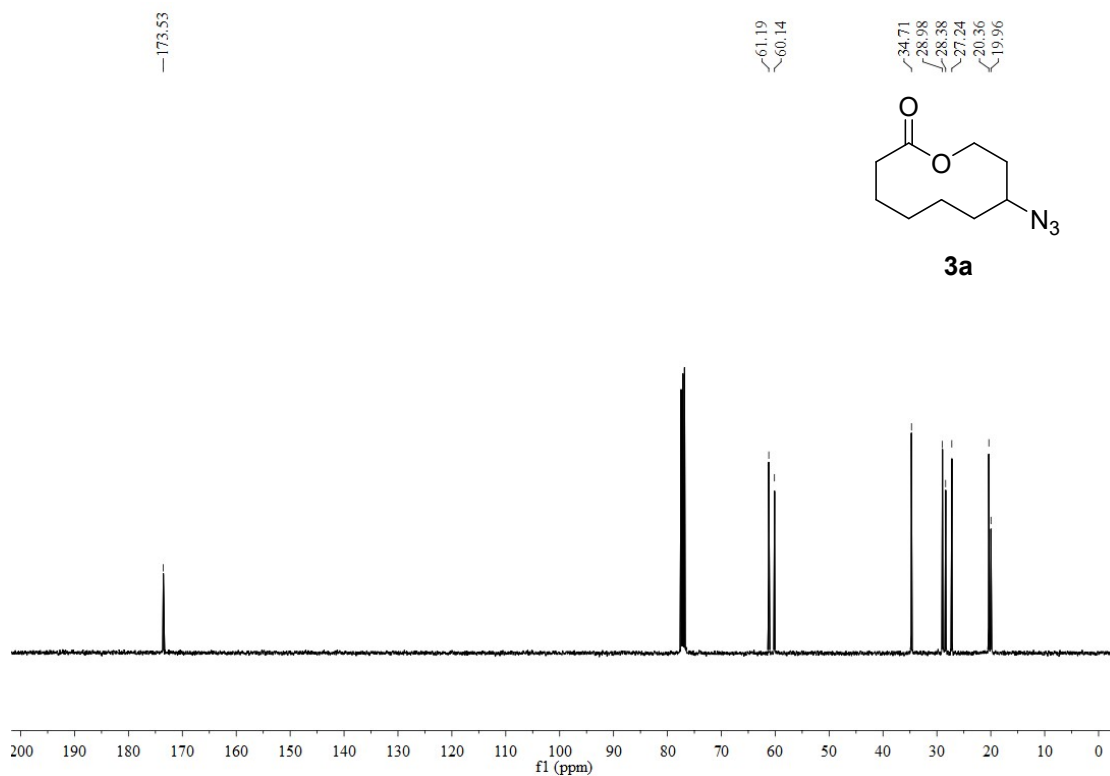
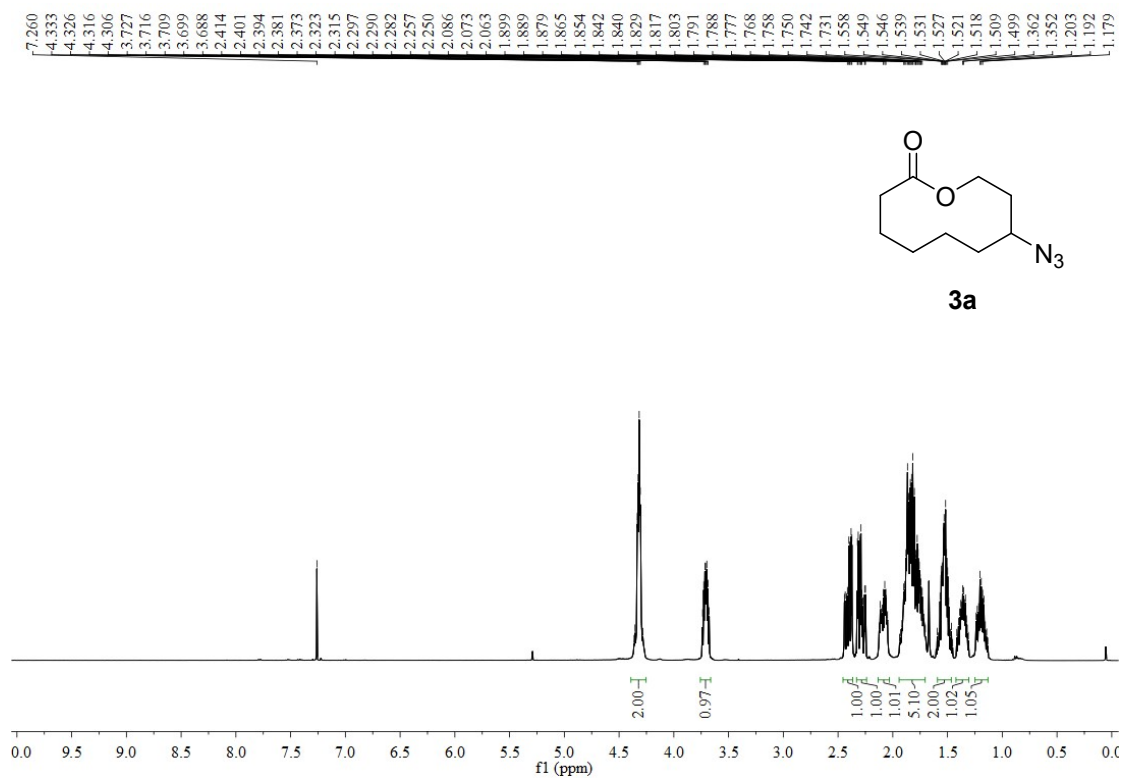
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2x**



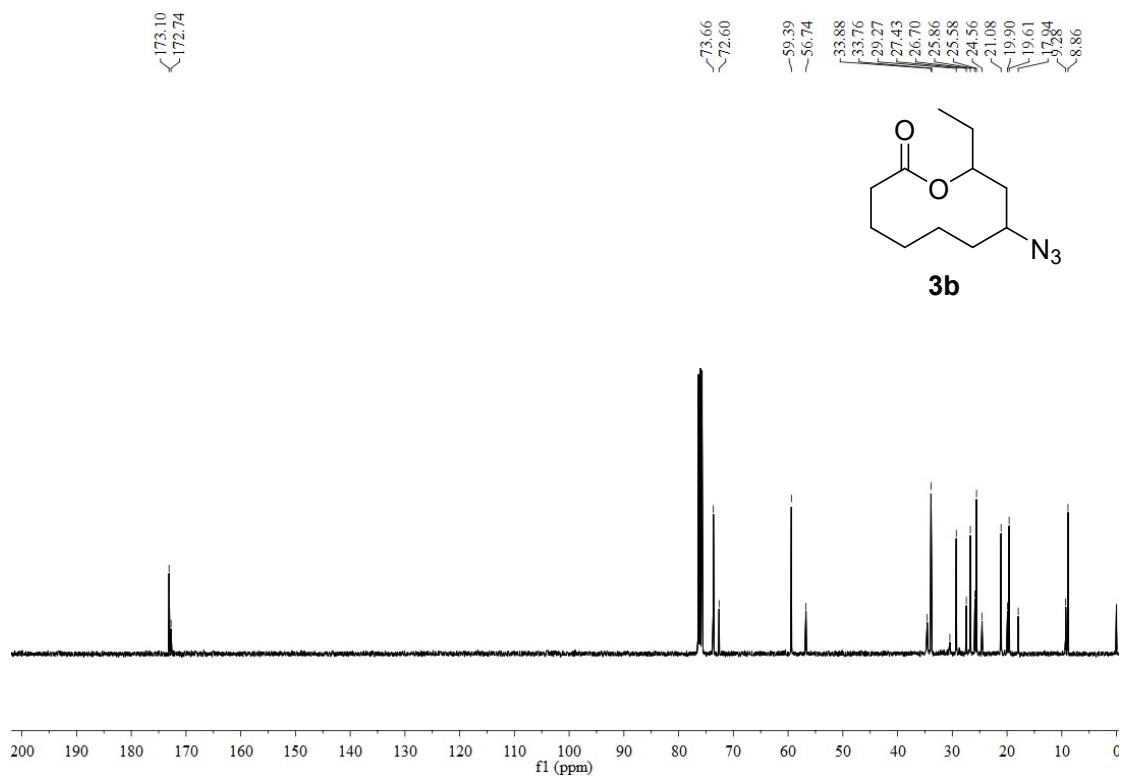
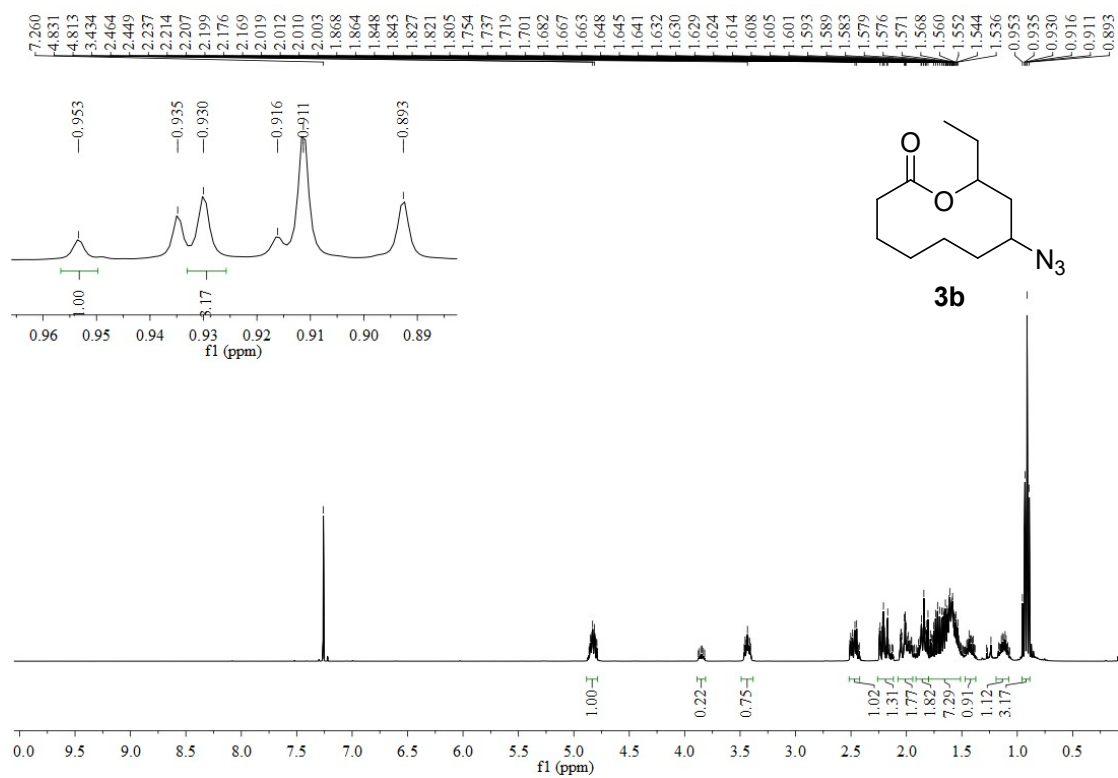
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **2y**



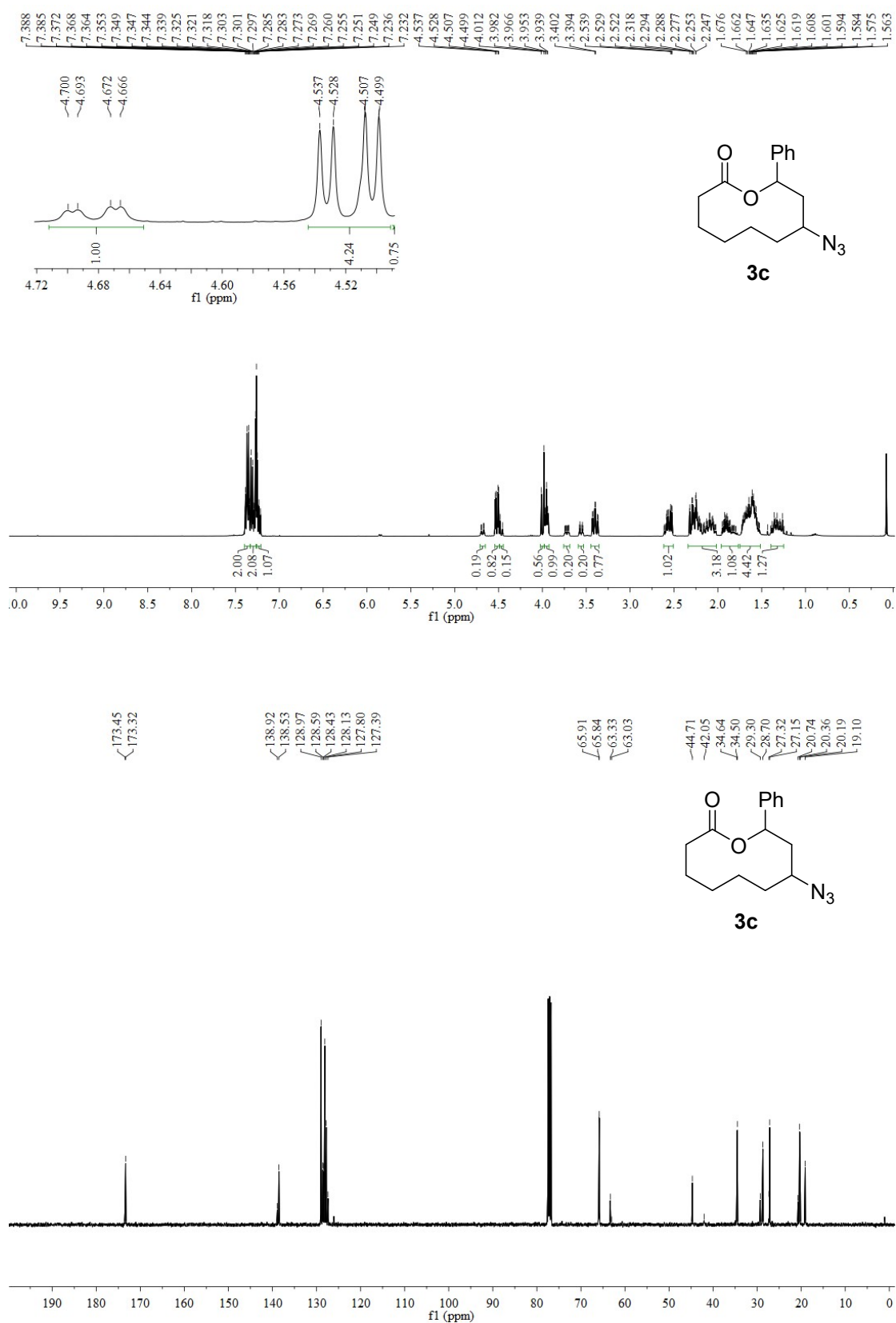
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3a**



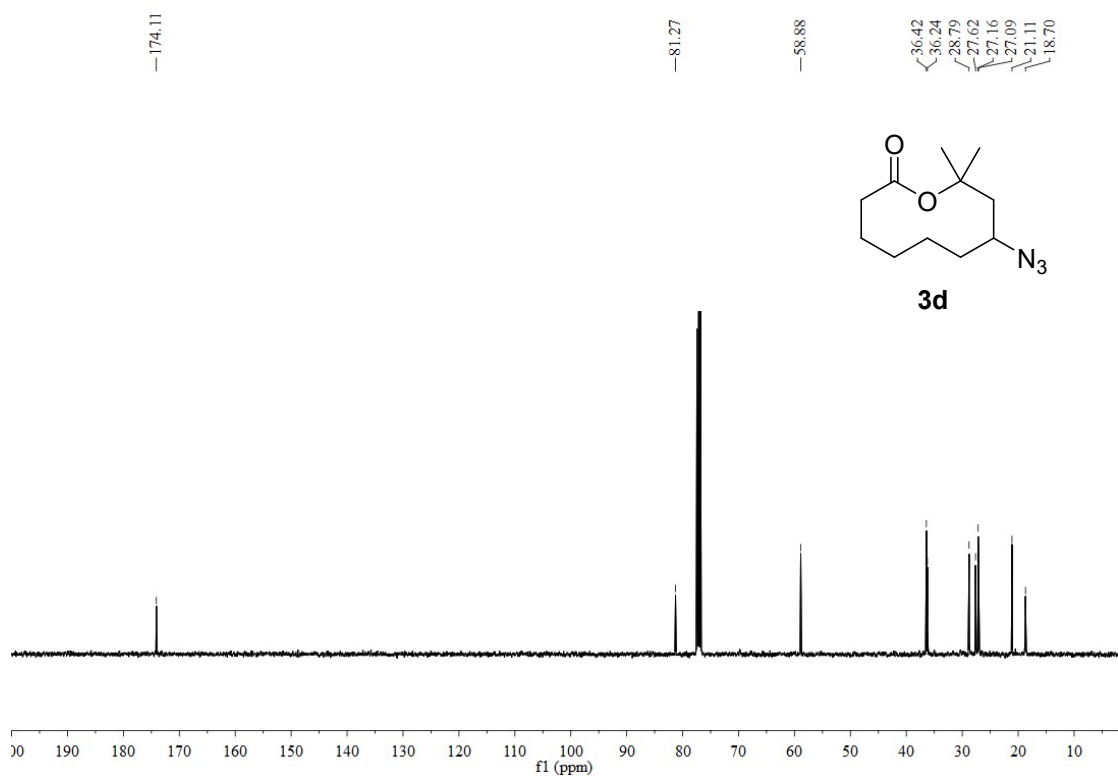
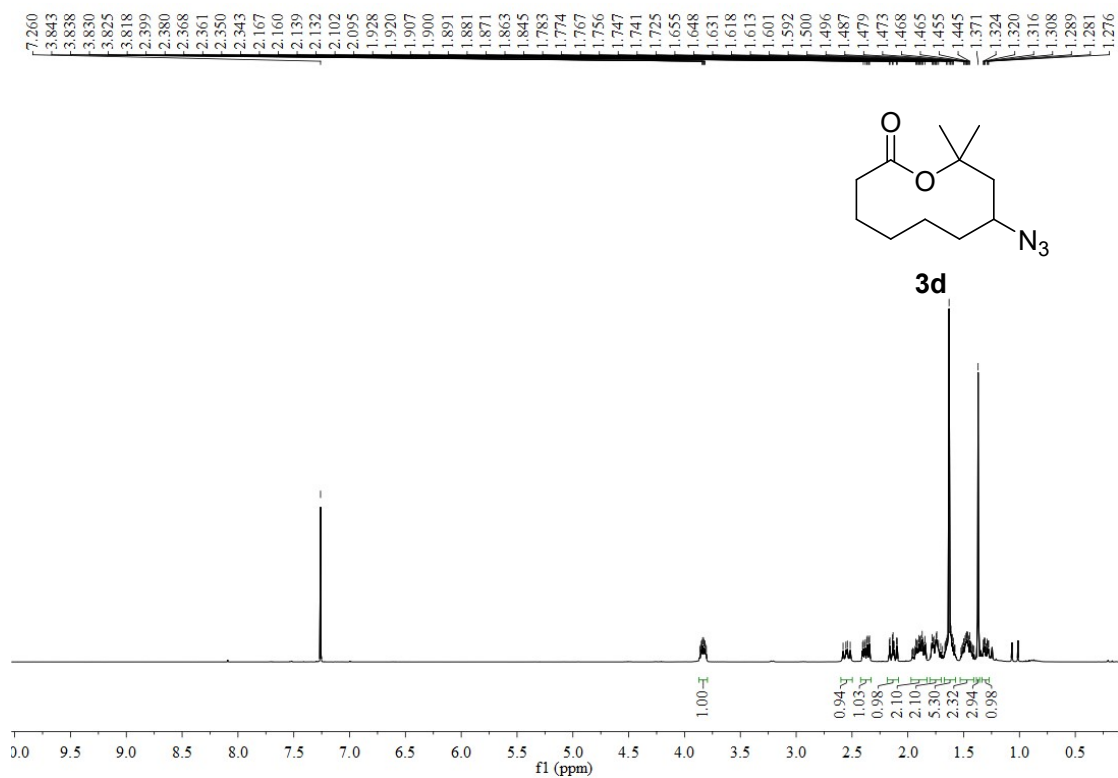
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3b**



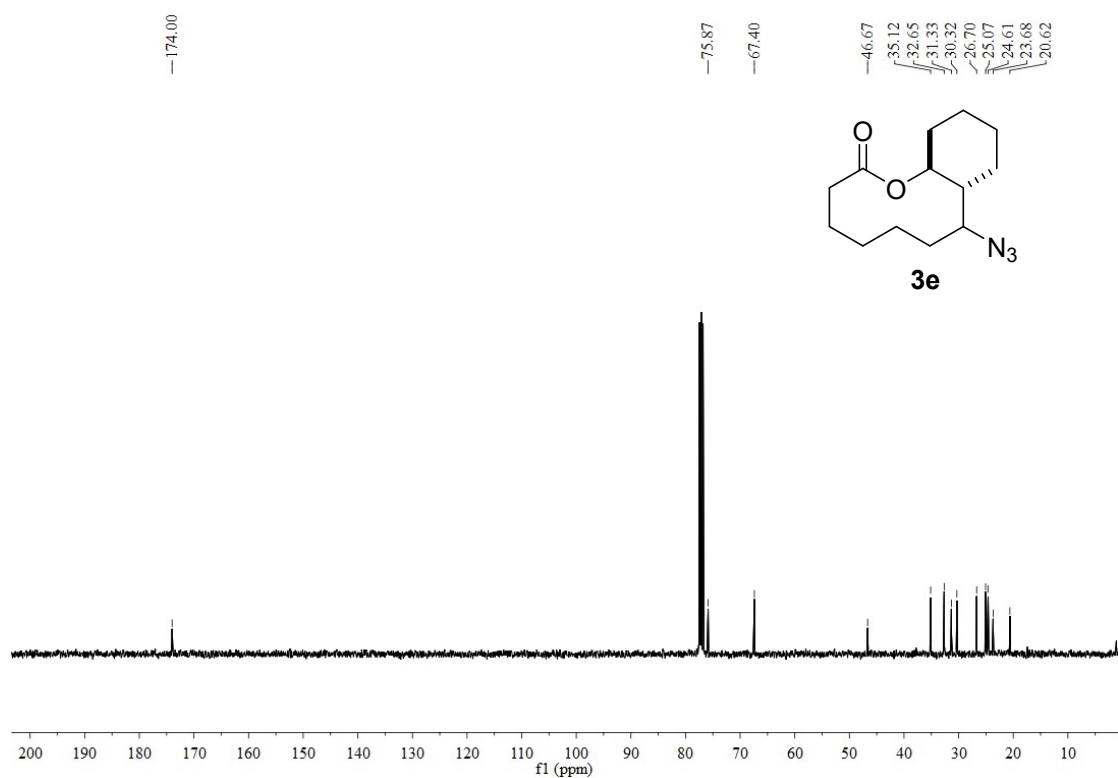
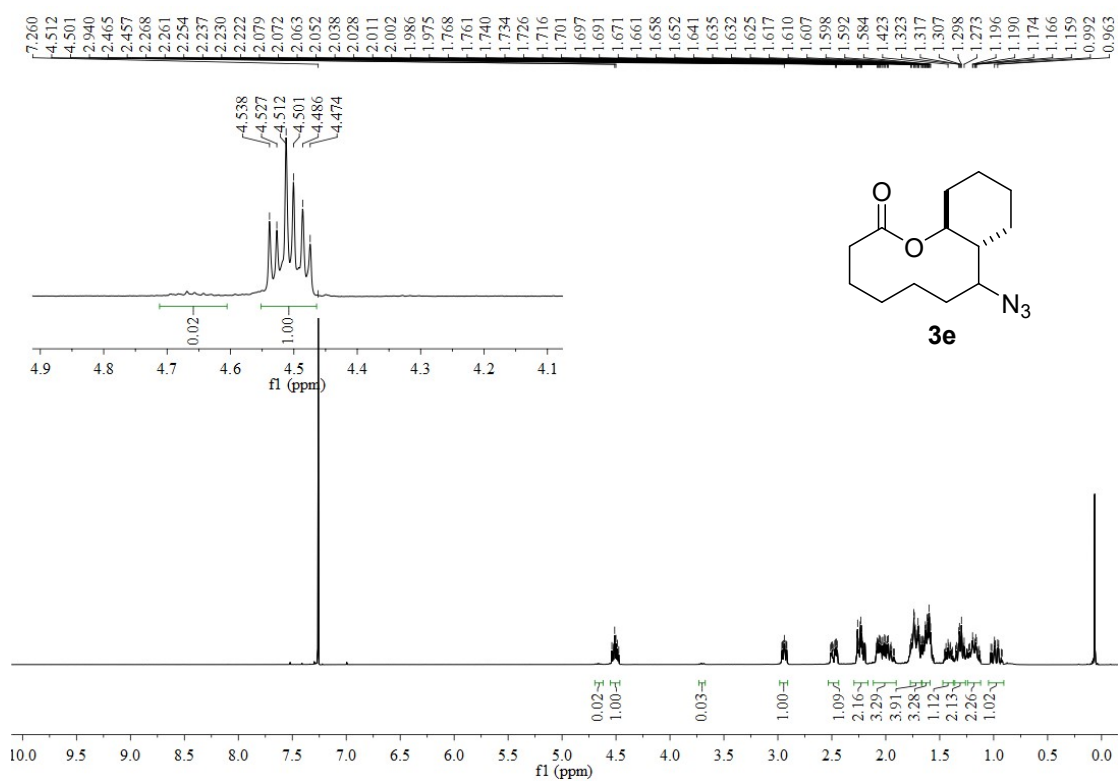
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3c**



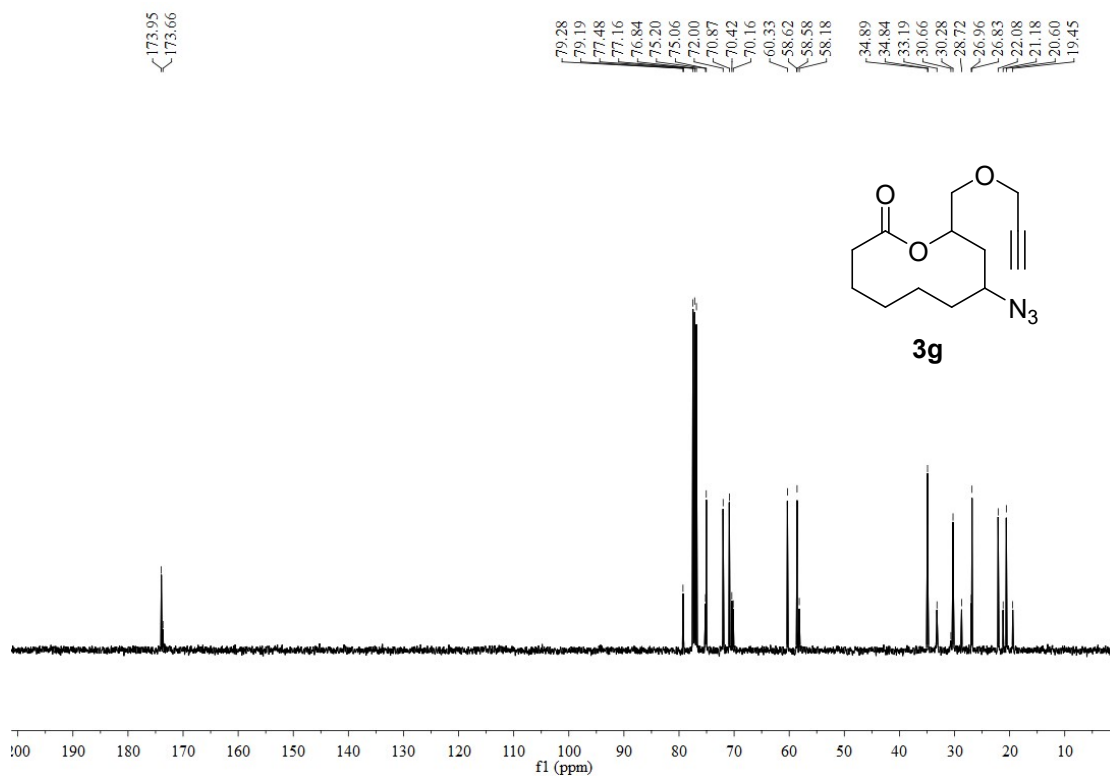
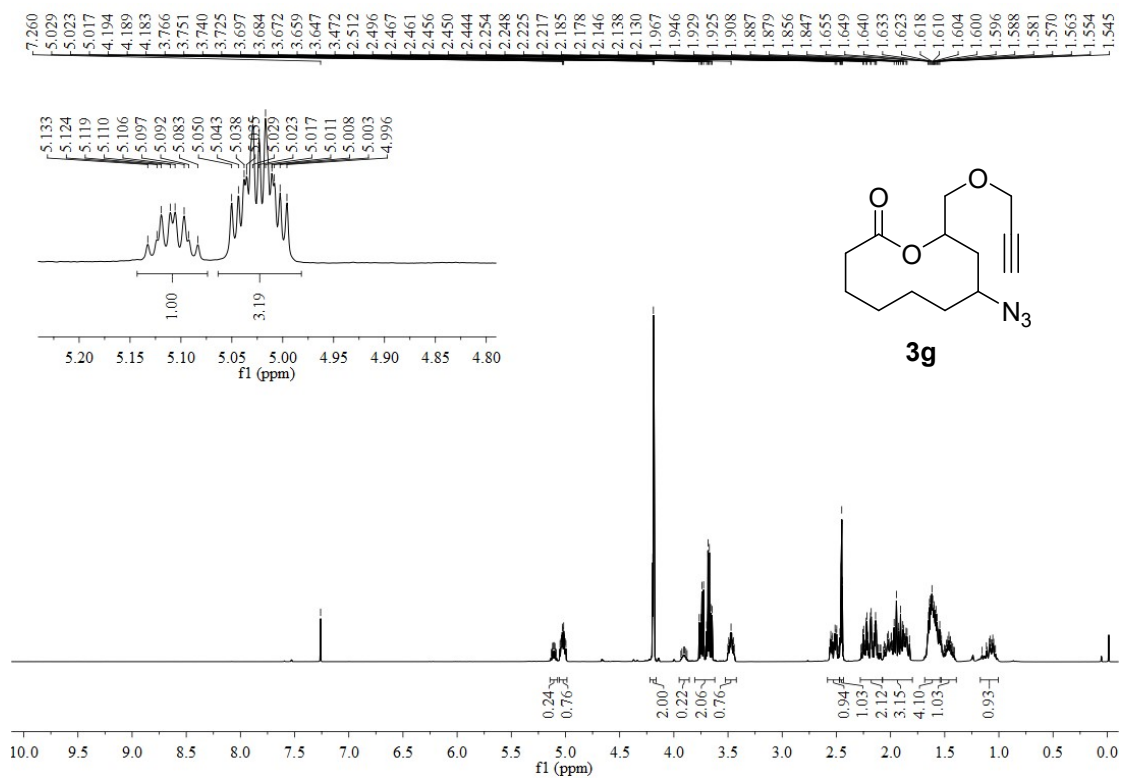
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product 3d



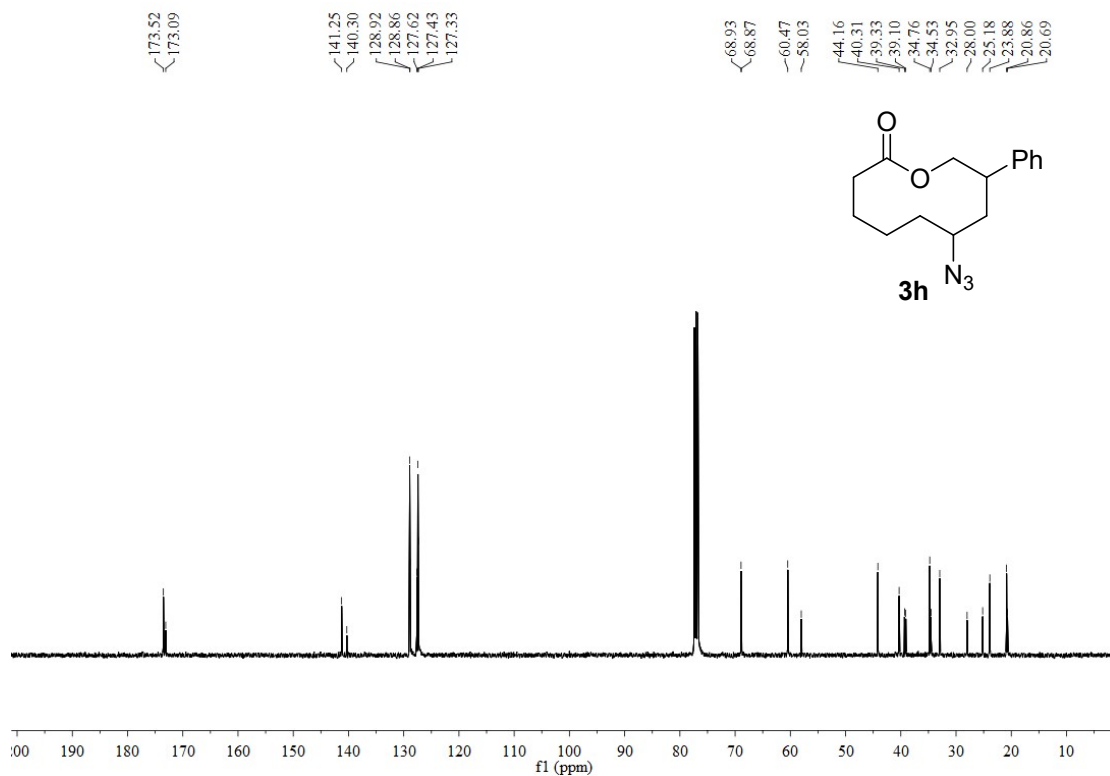
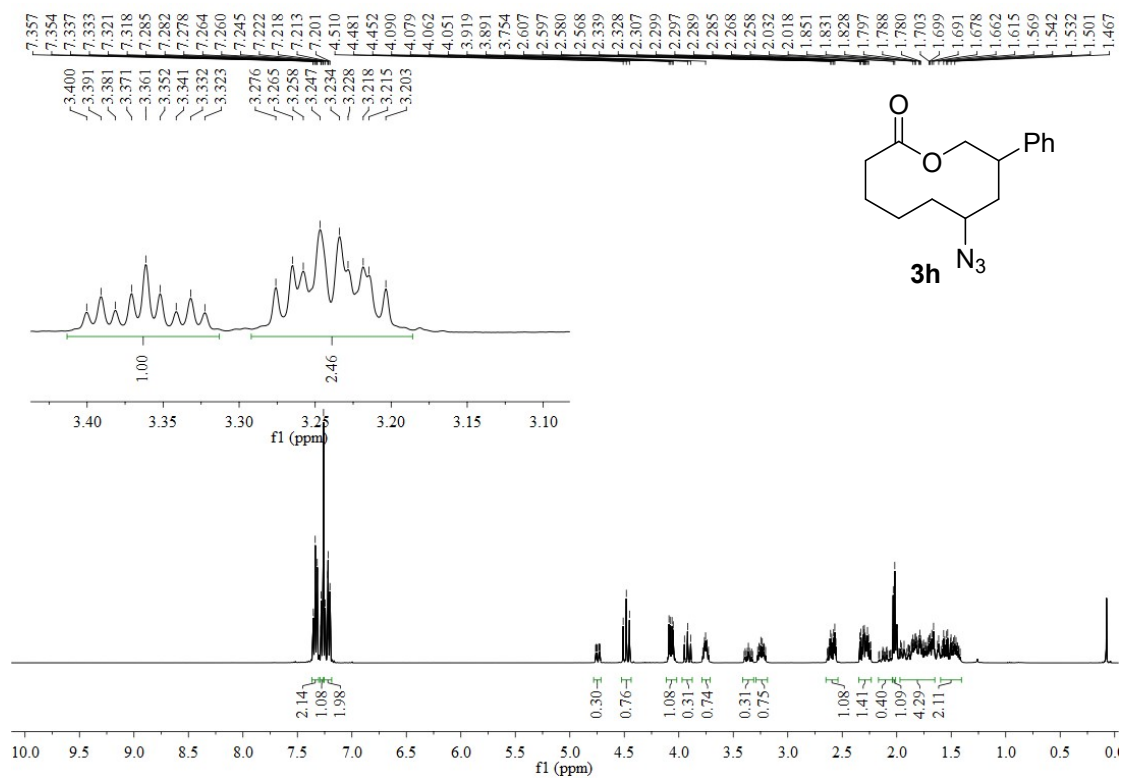
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3e**

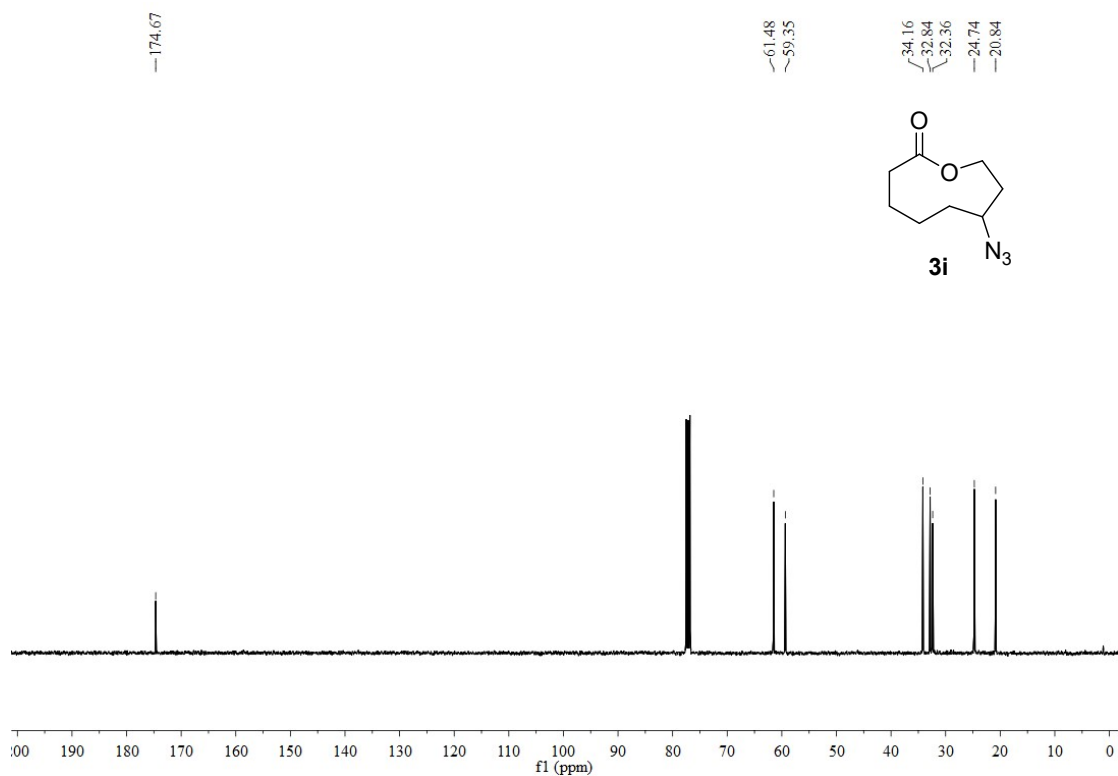
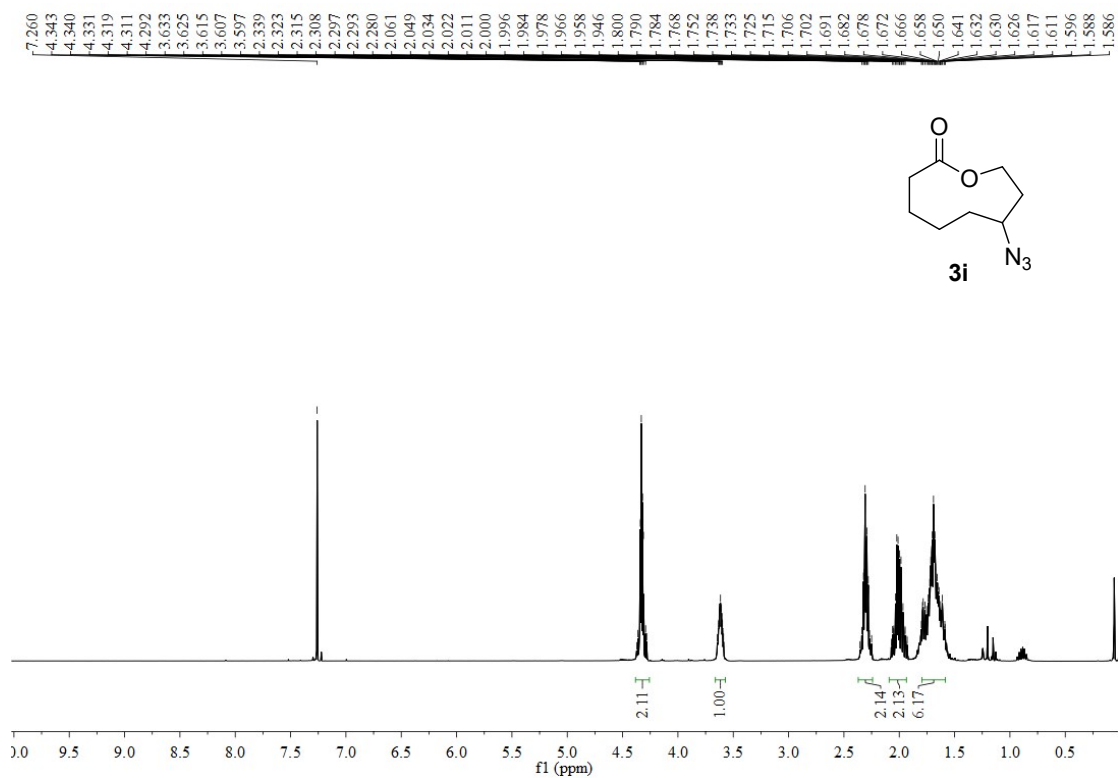


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3f**

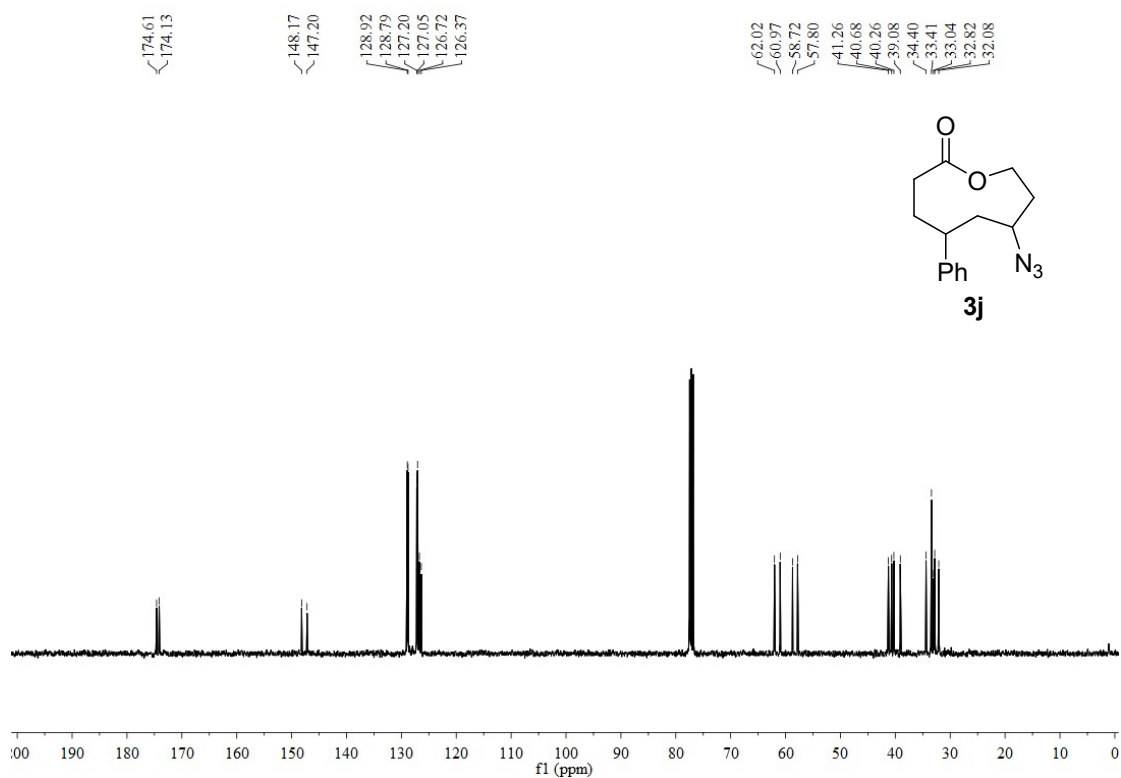
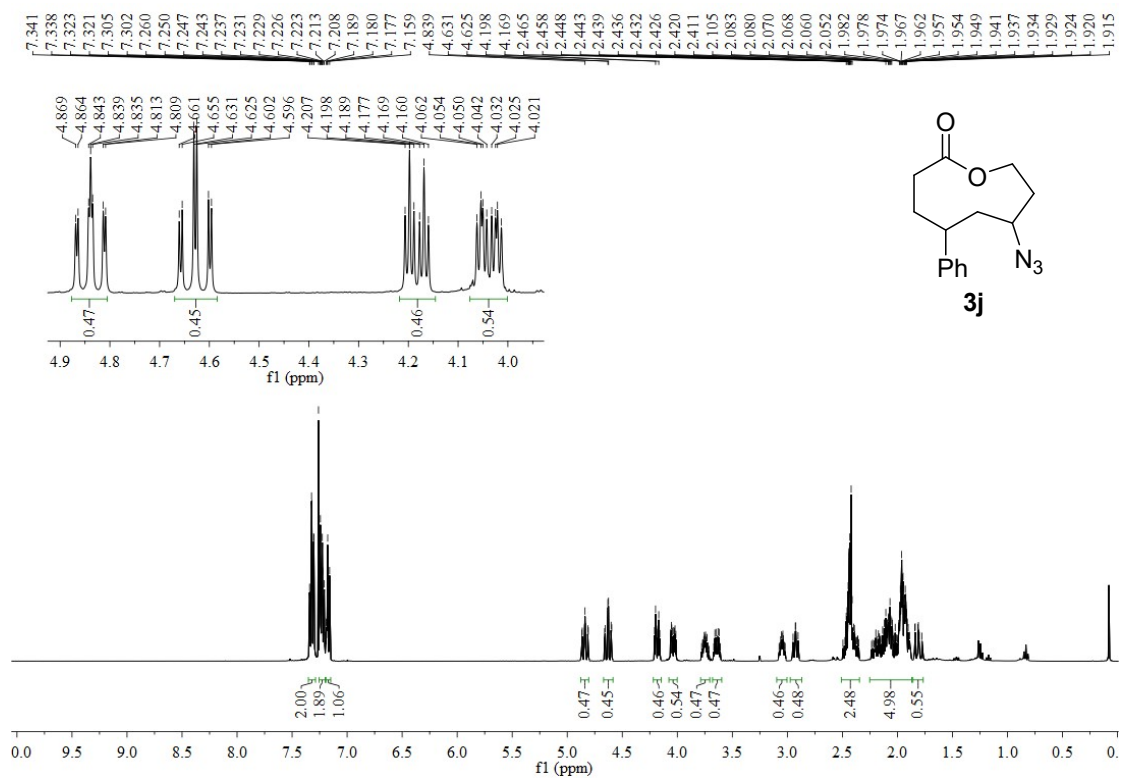


^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3h**

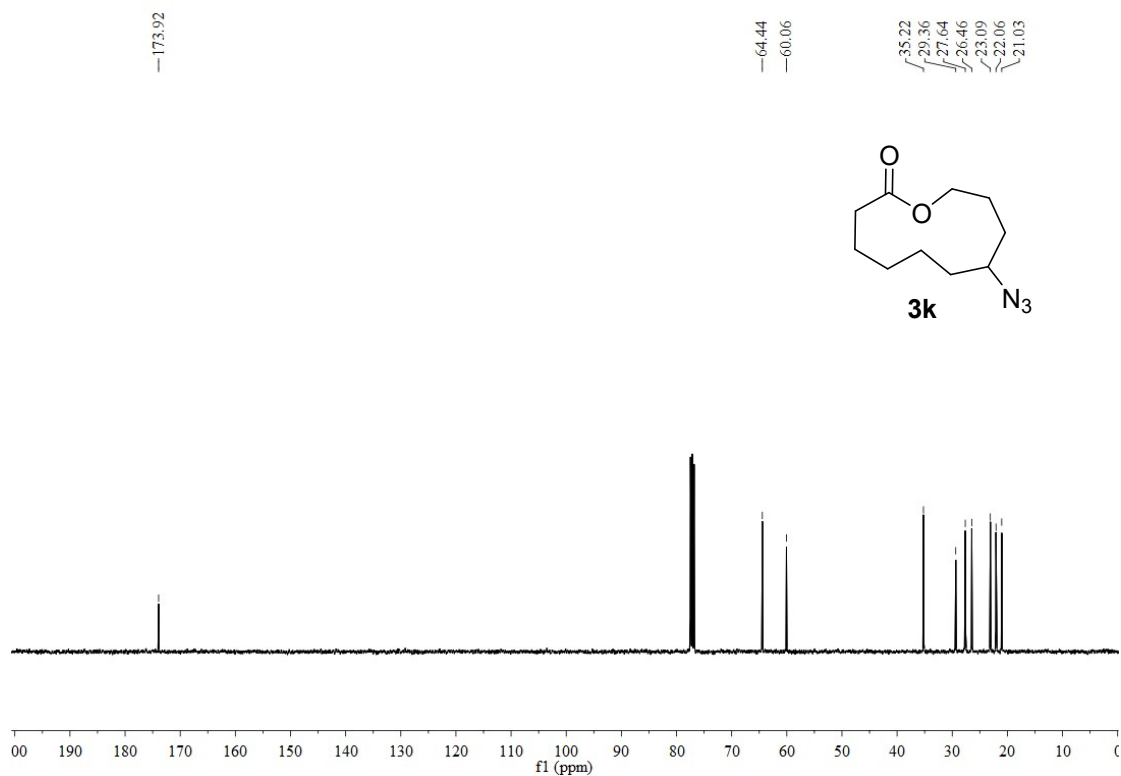
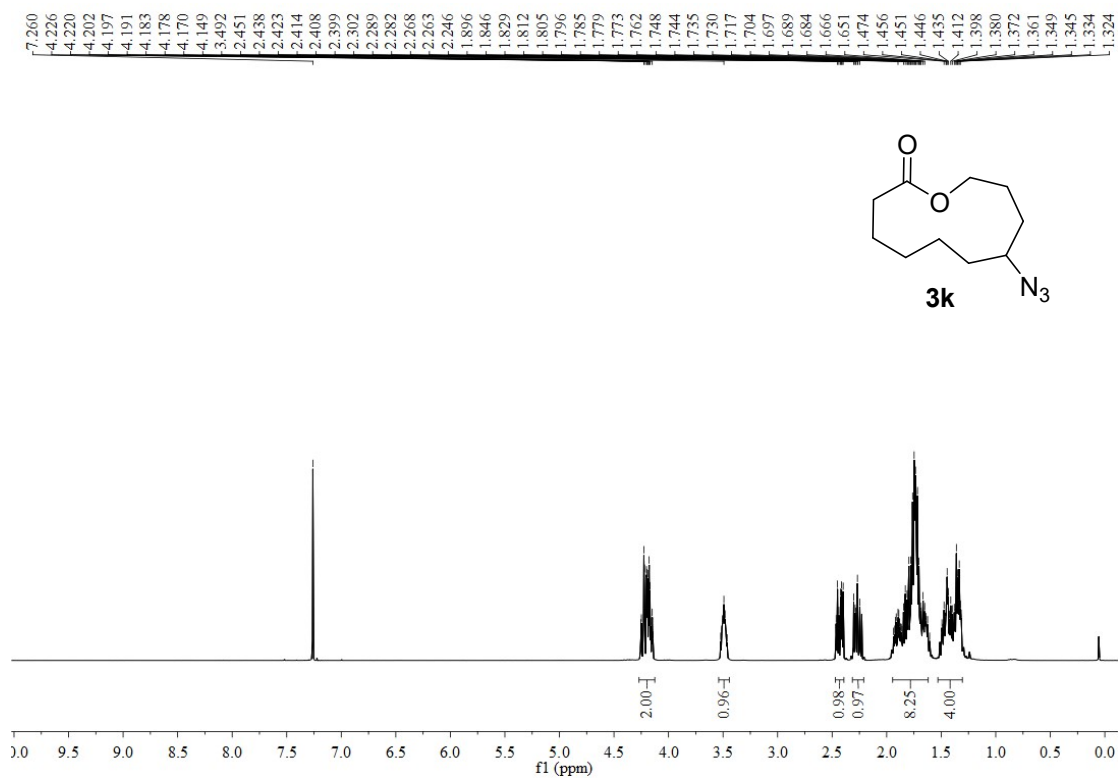
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3i**



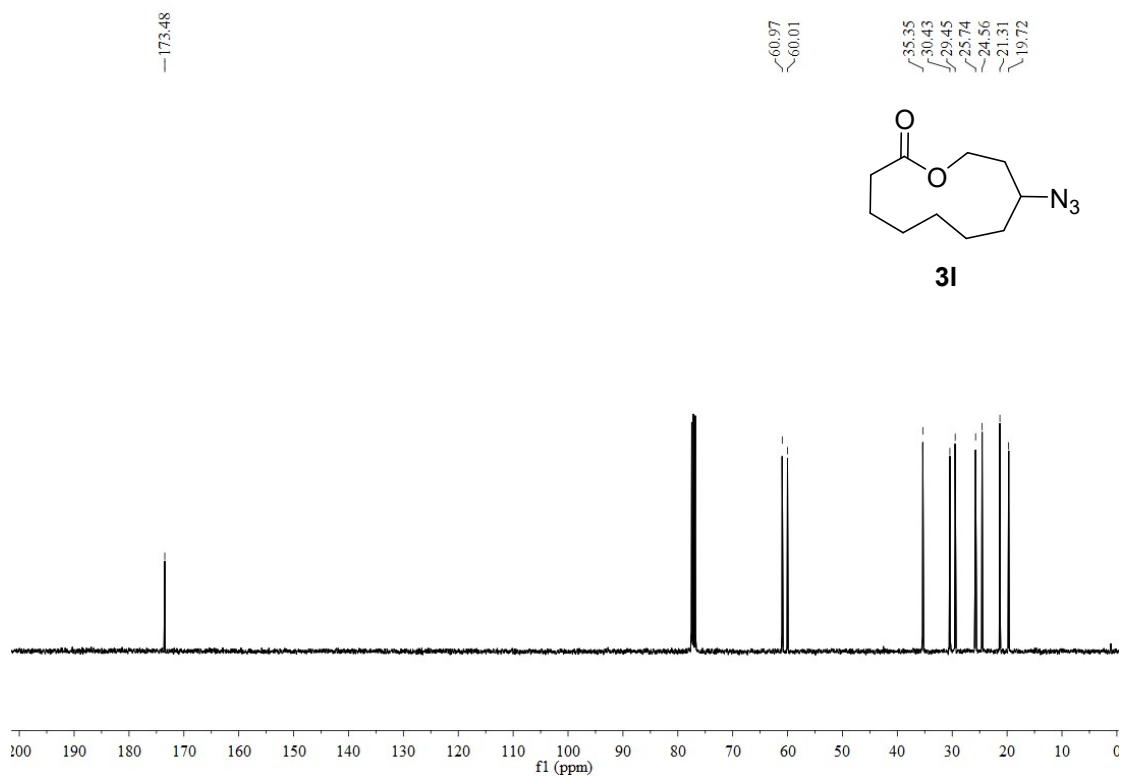
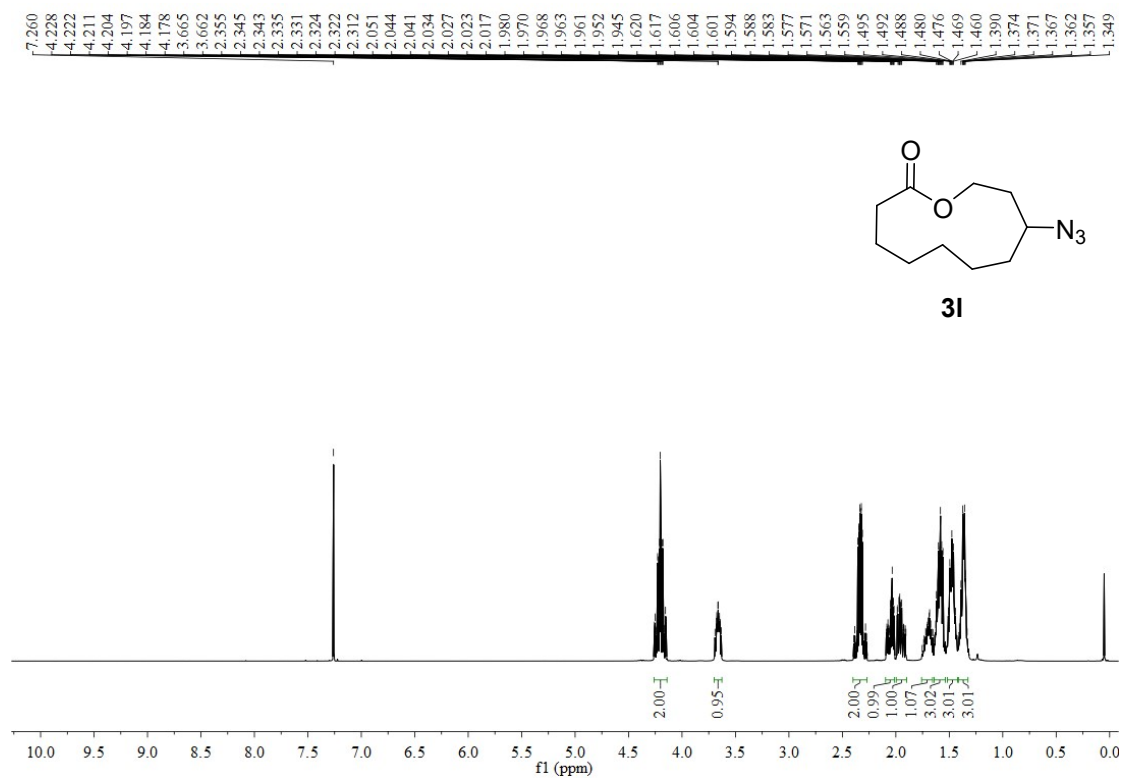
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3j**



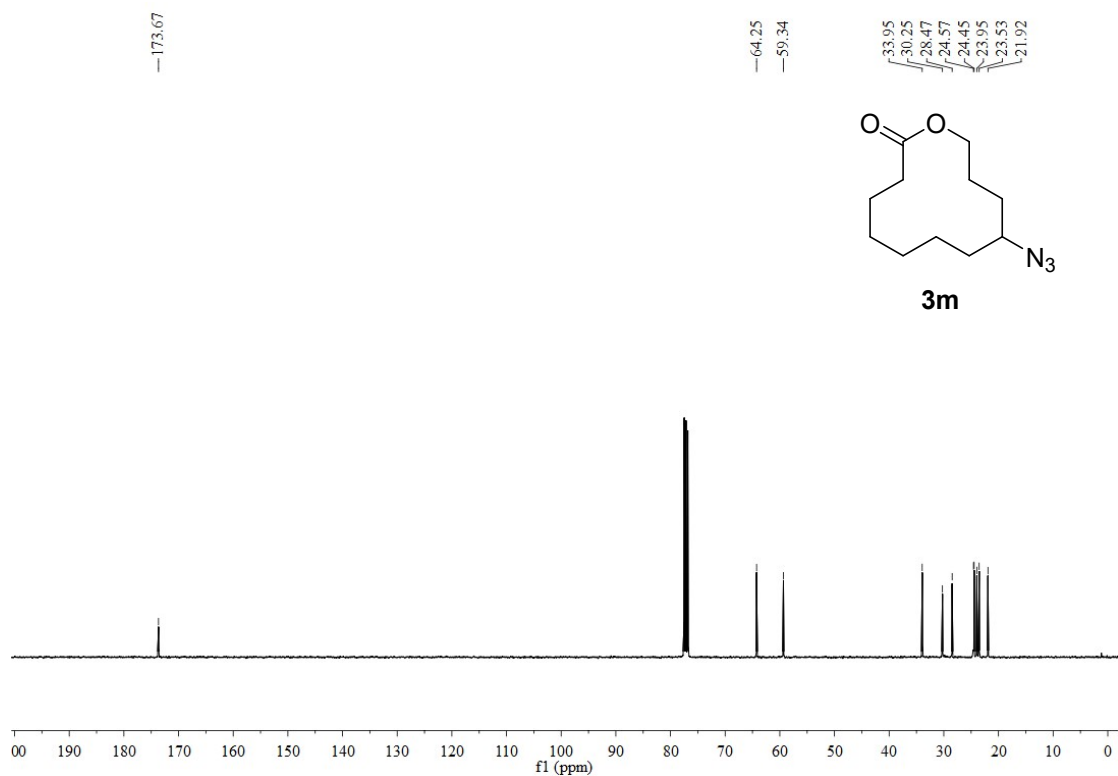
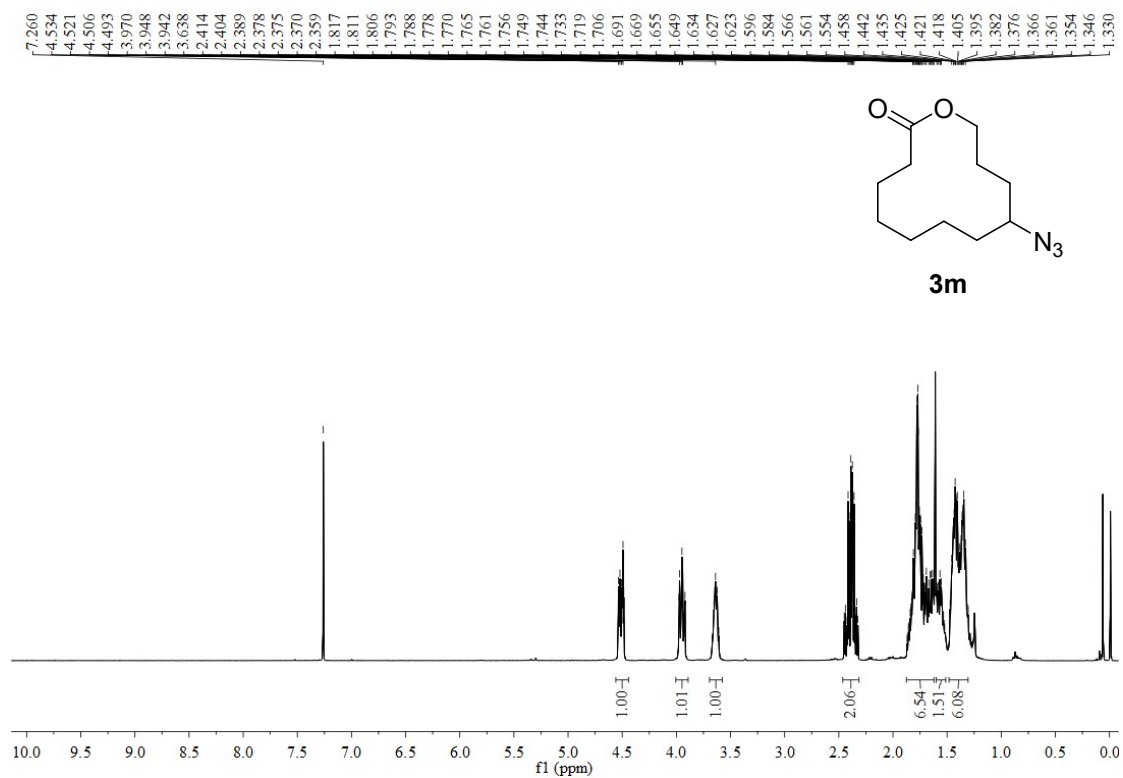
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3k**



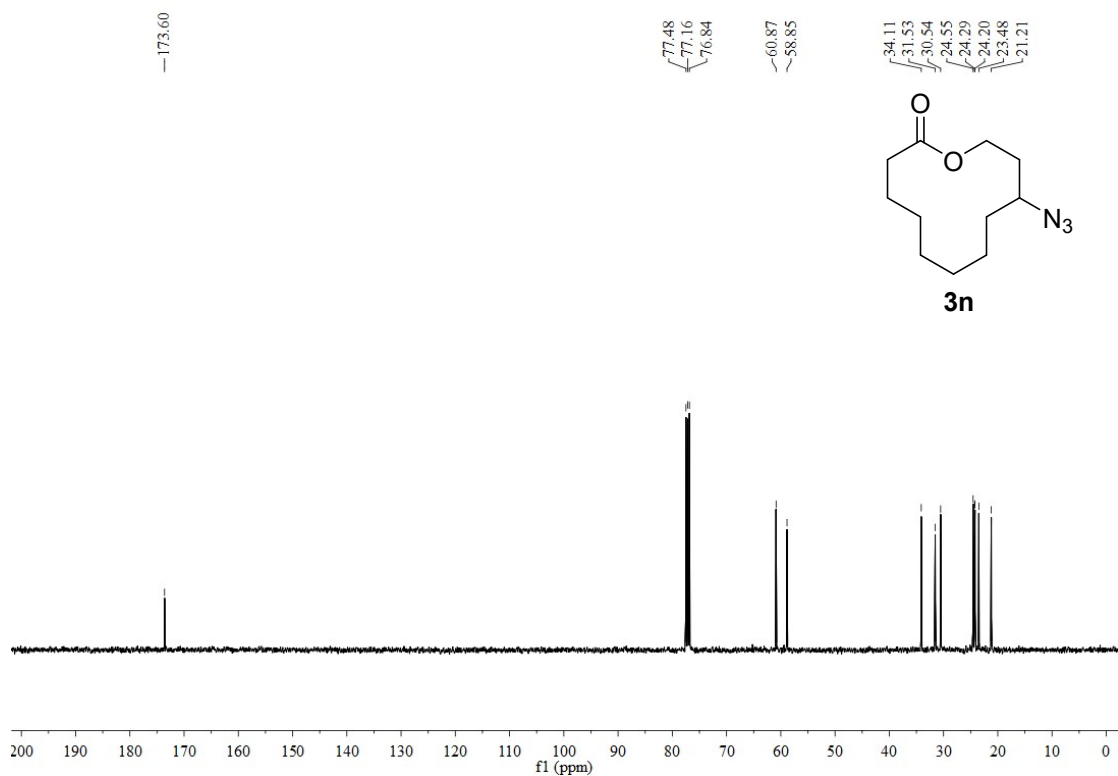
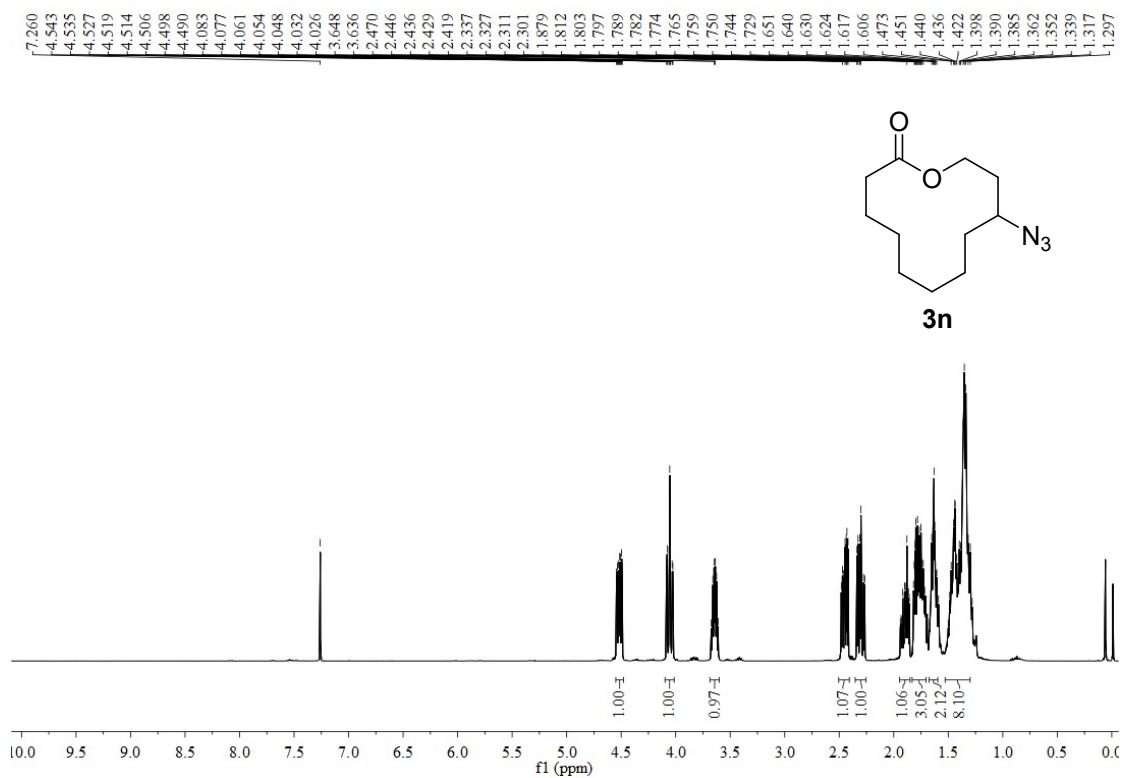
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3l**



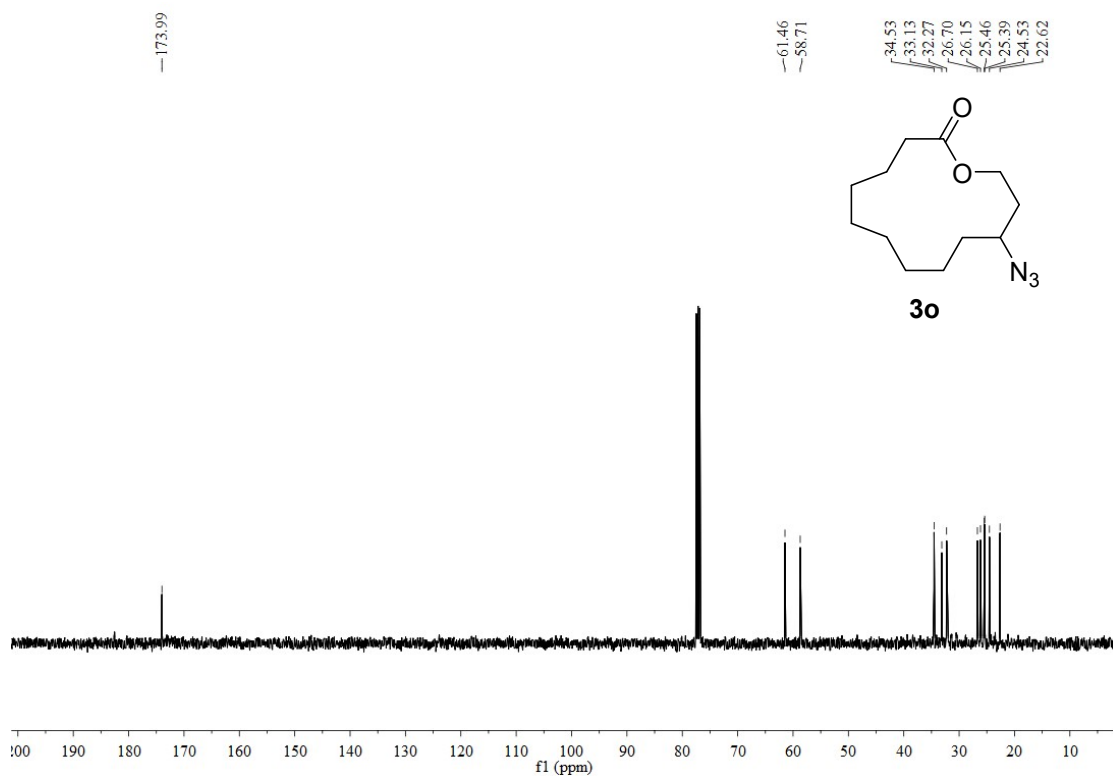
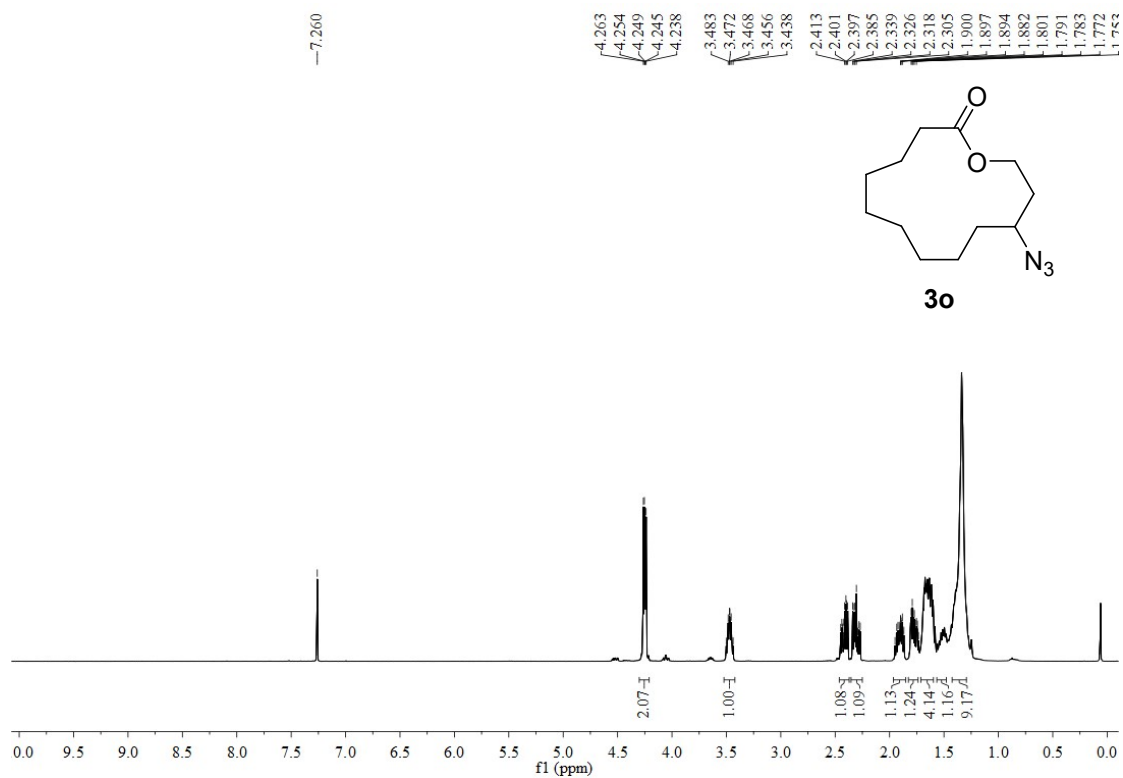
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3m**



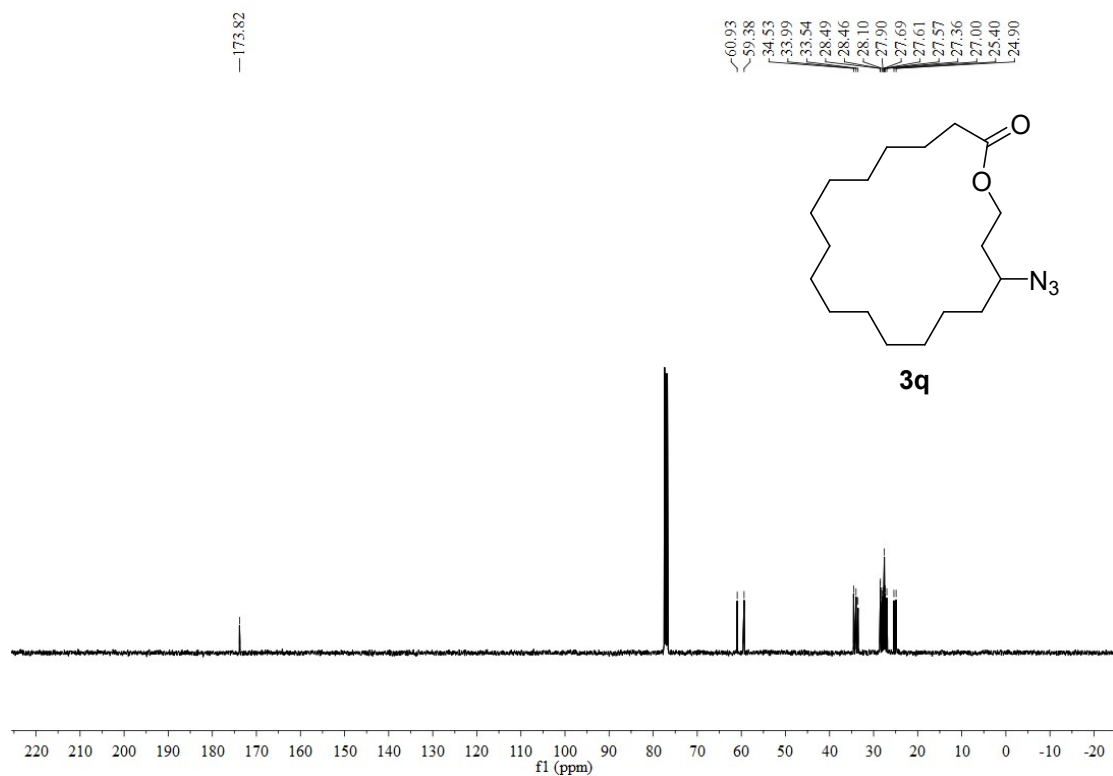
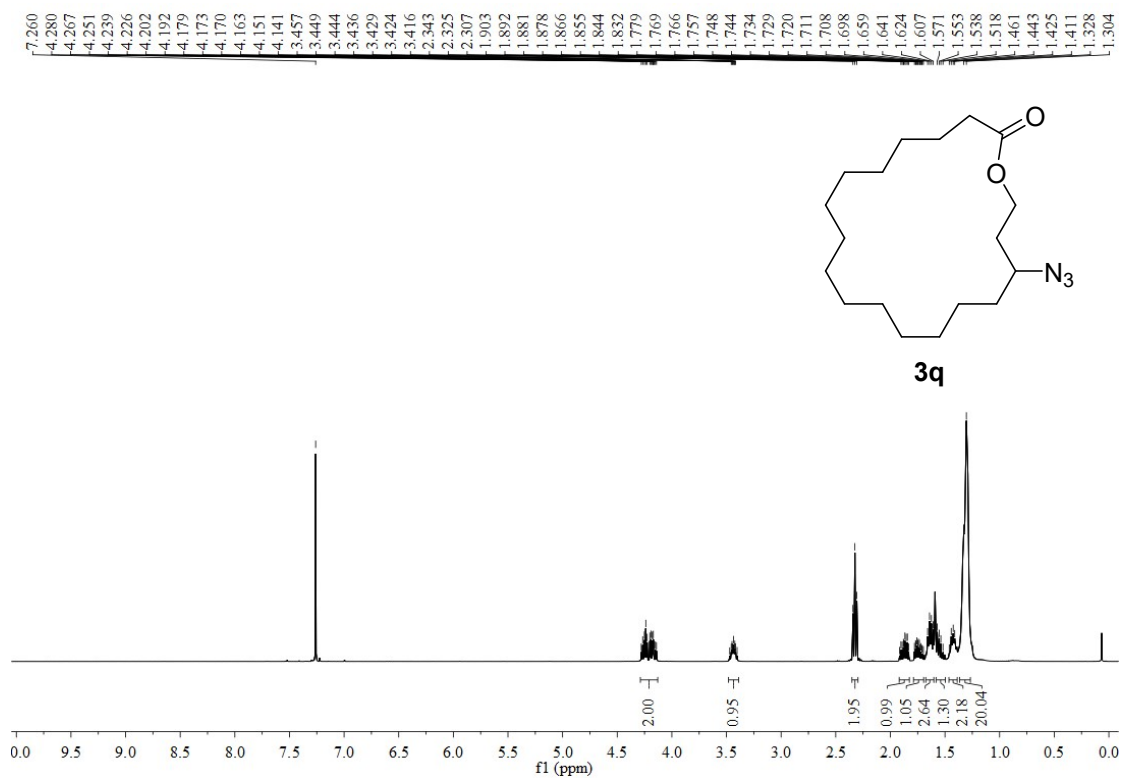
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3n**



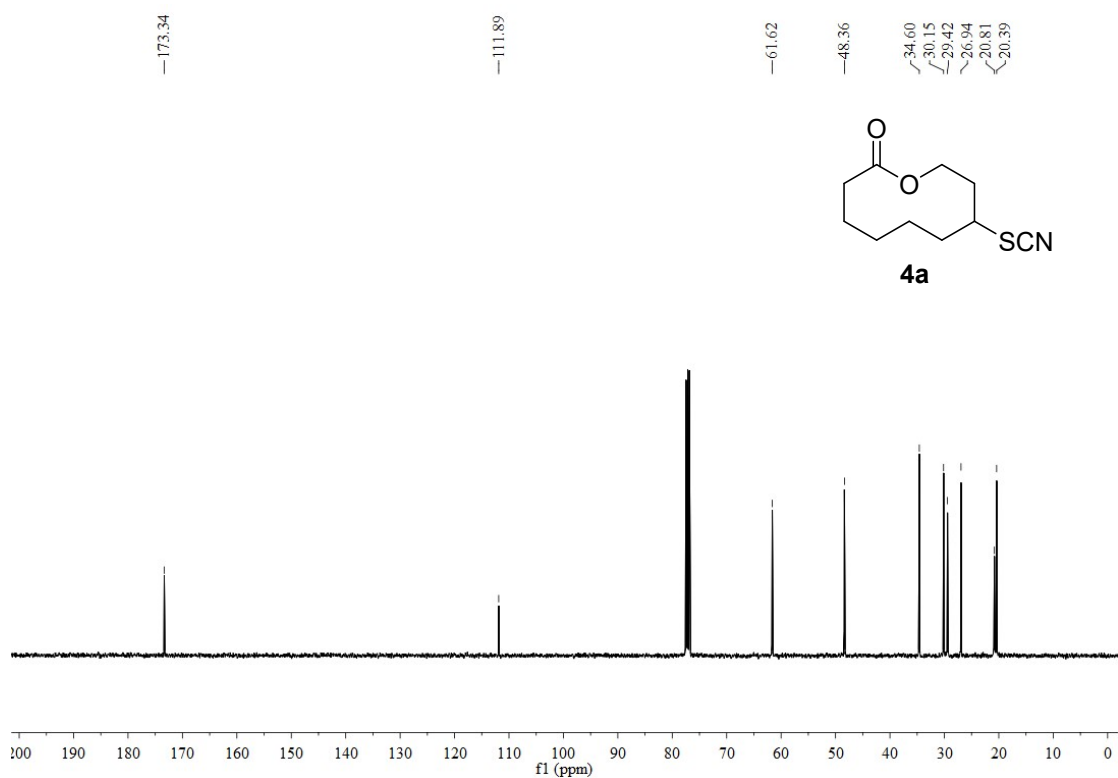
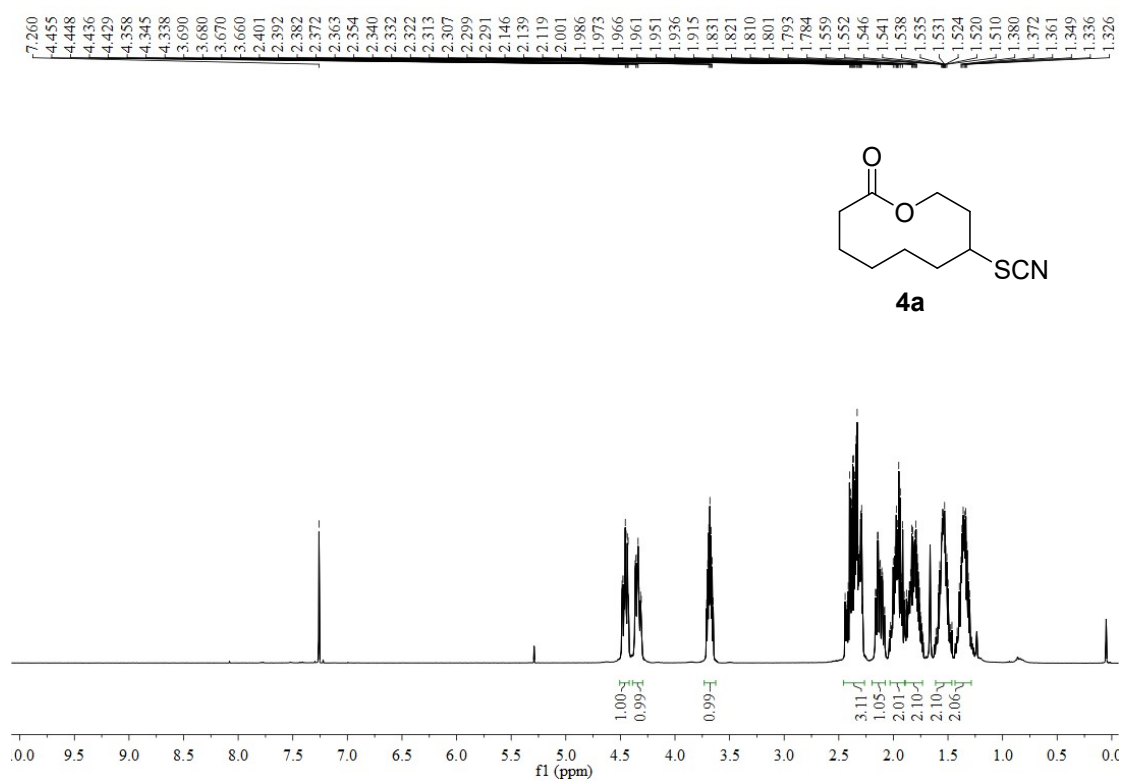
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3o**

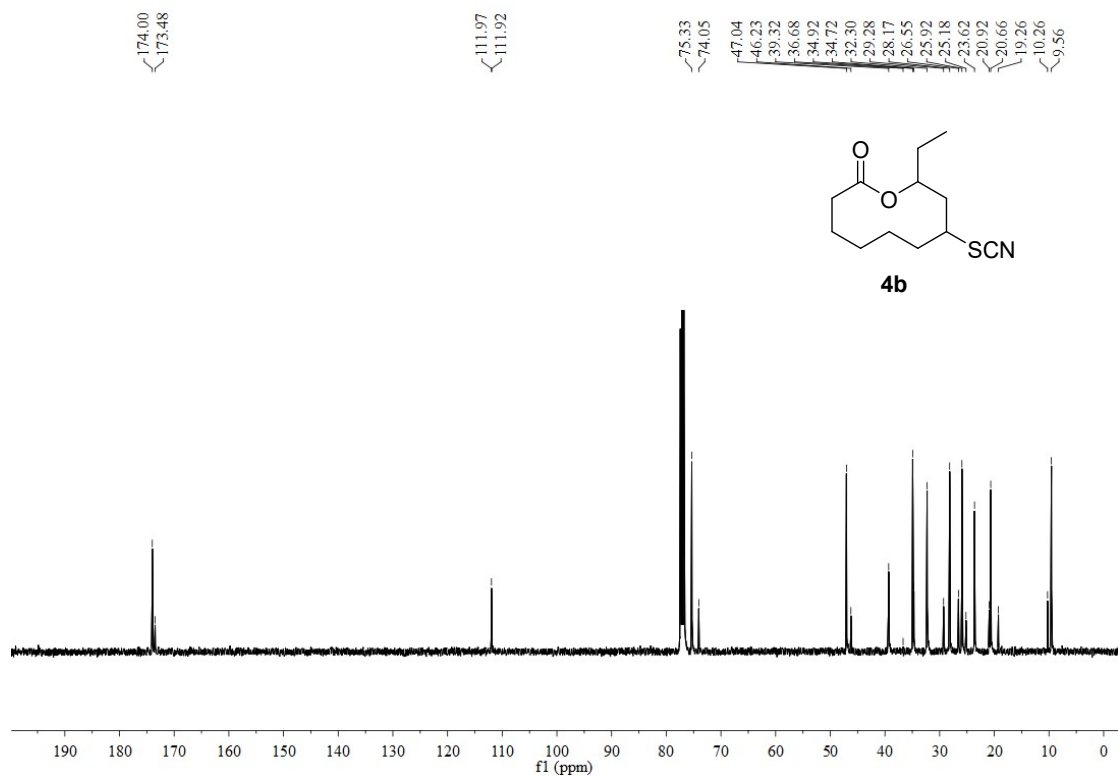
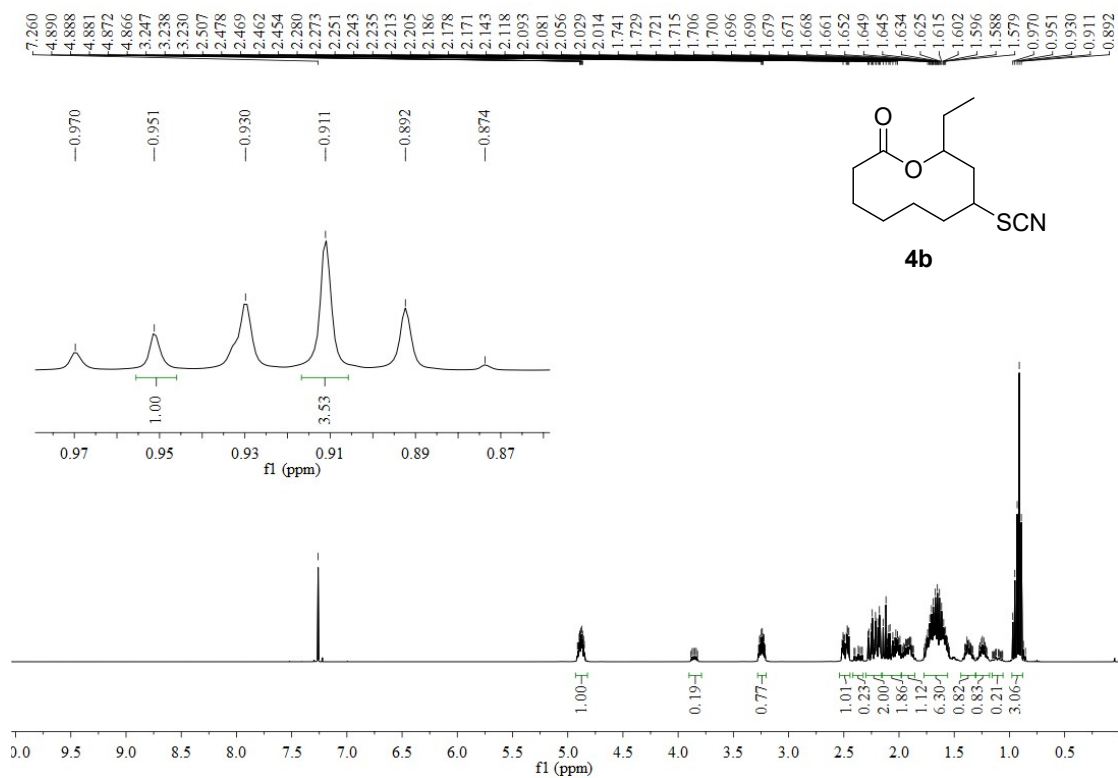


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3p**

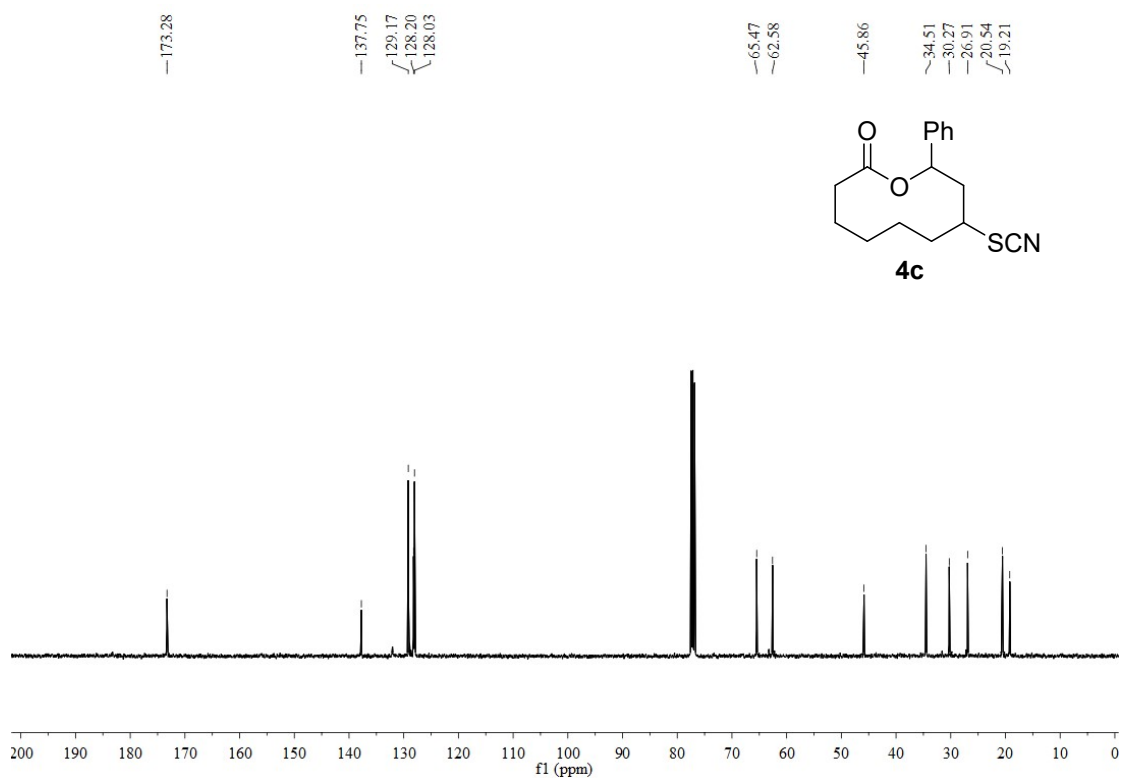
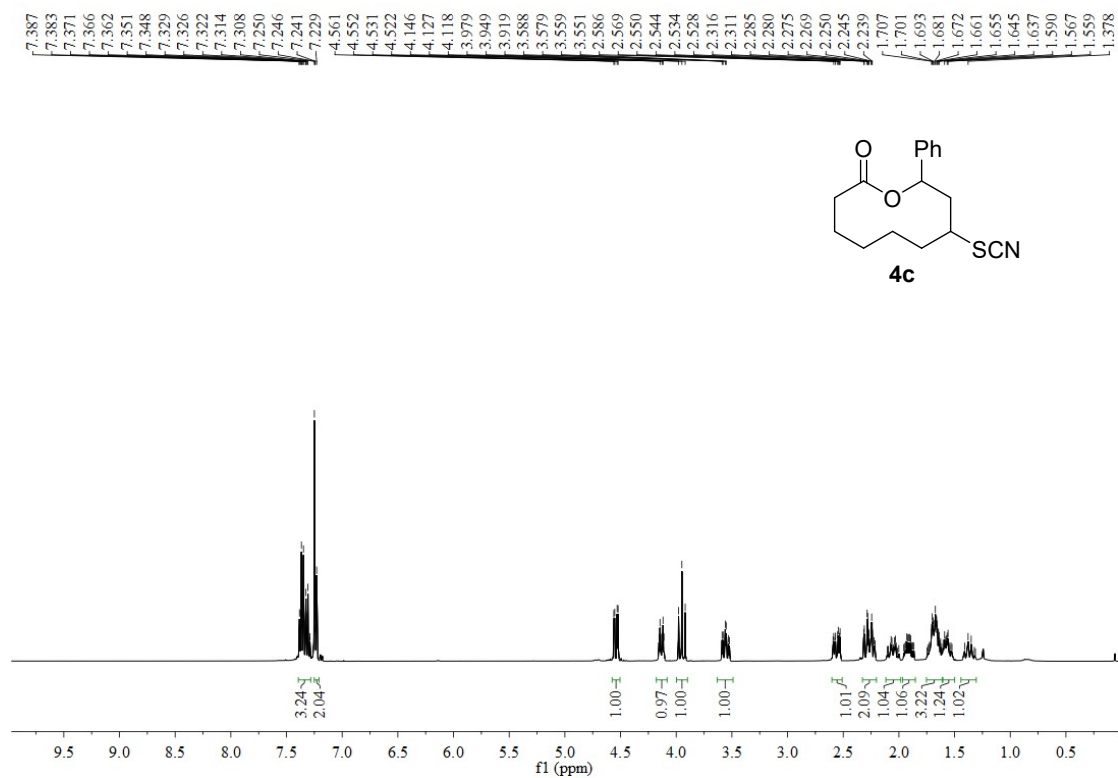


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4a**

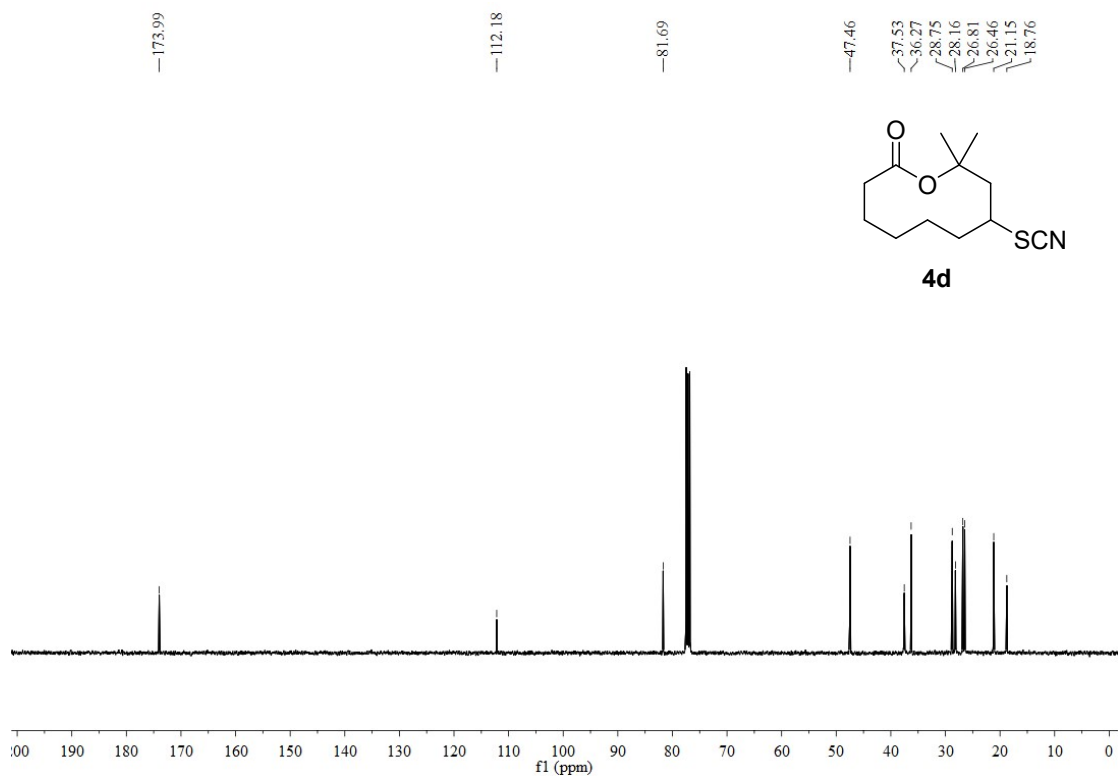
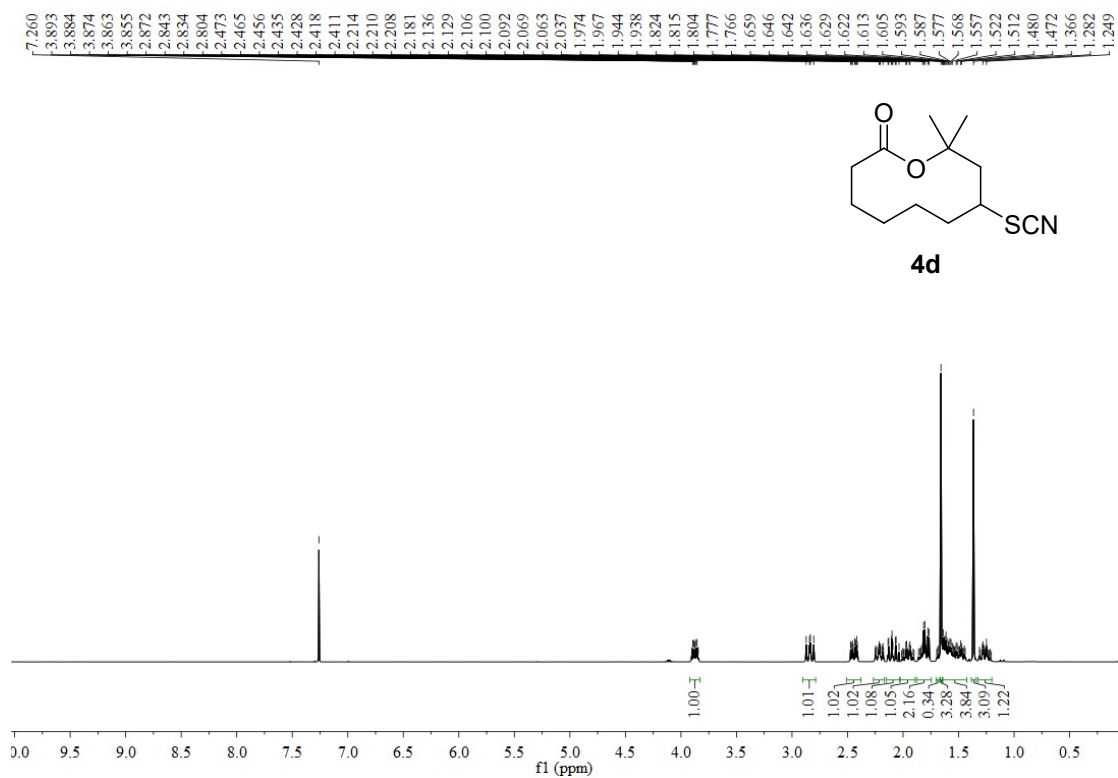
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4b**



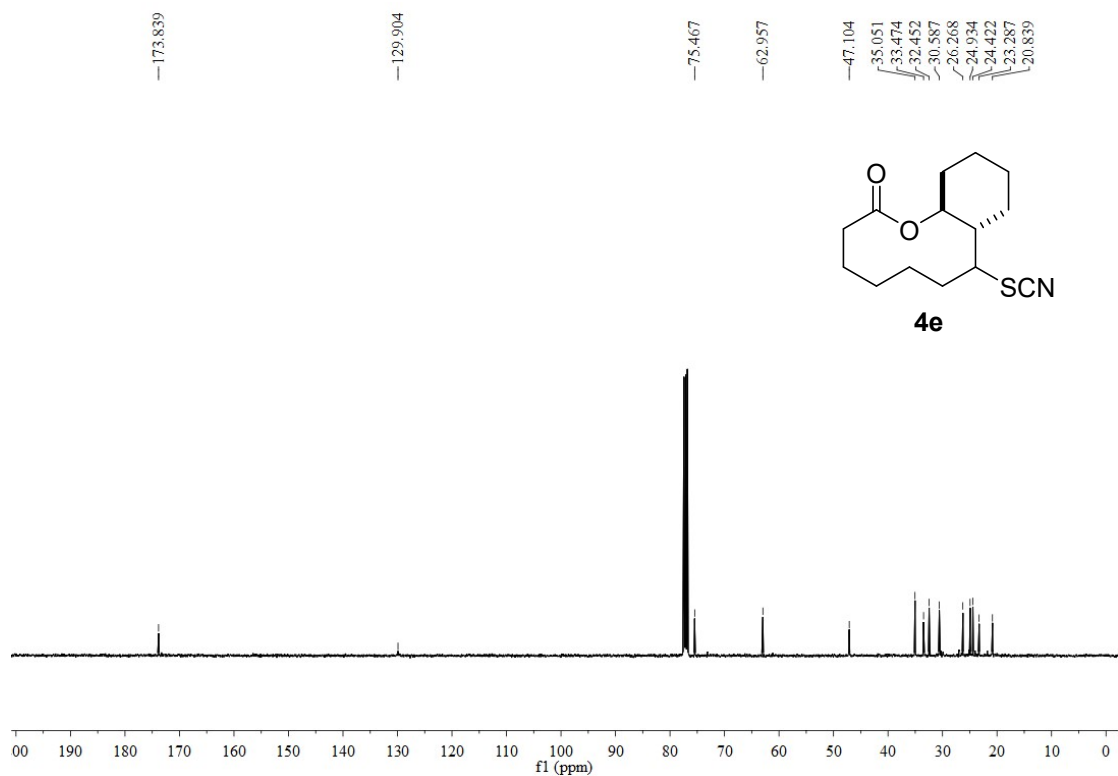
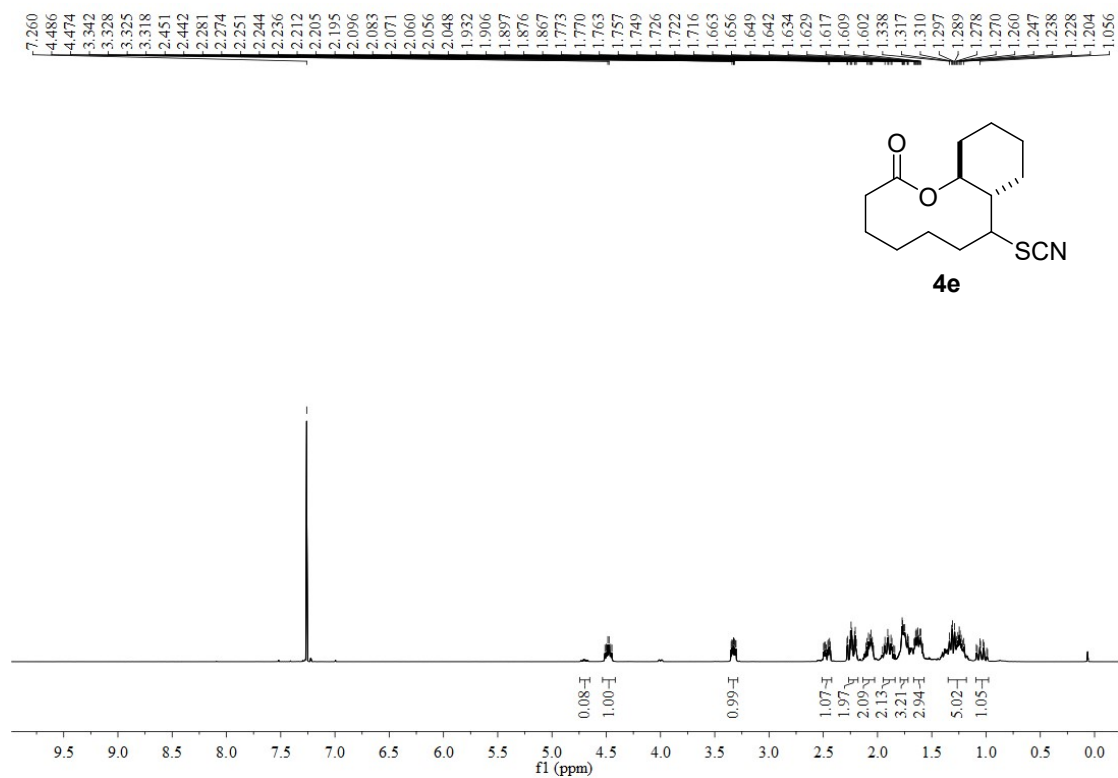
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4c**



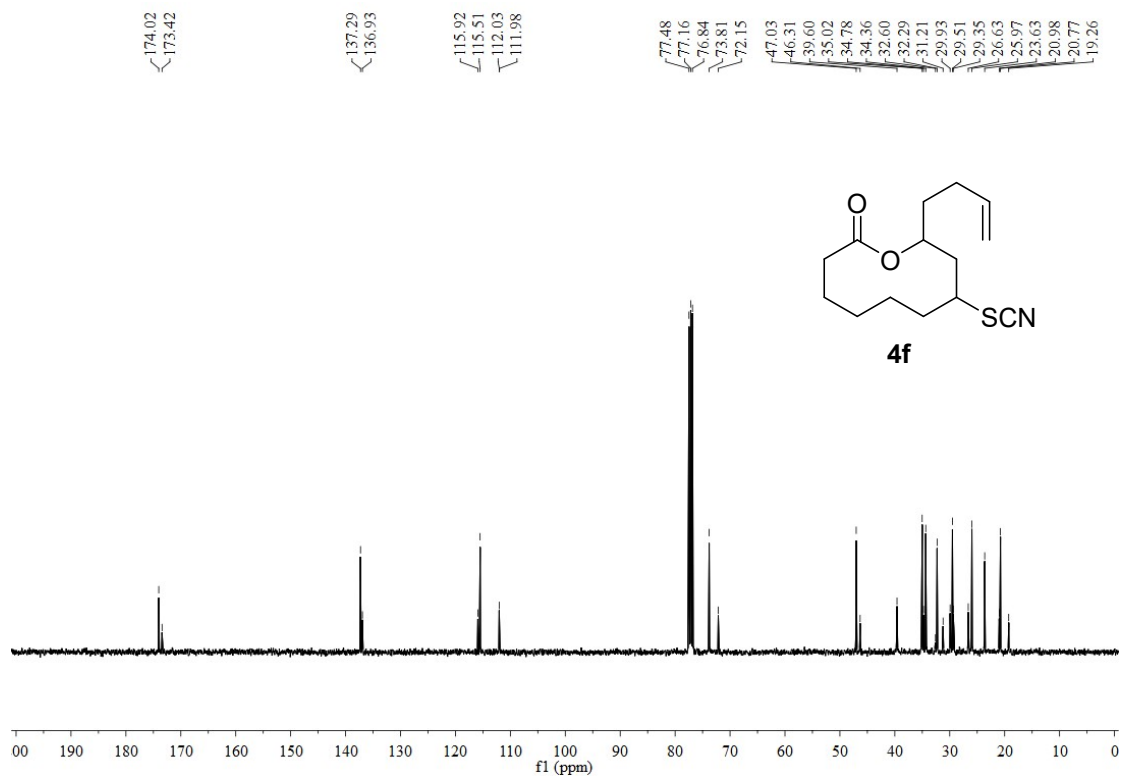
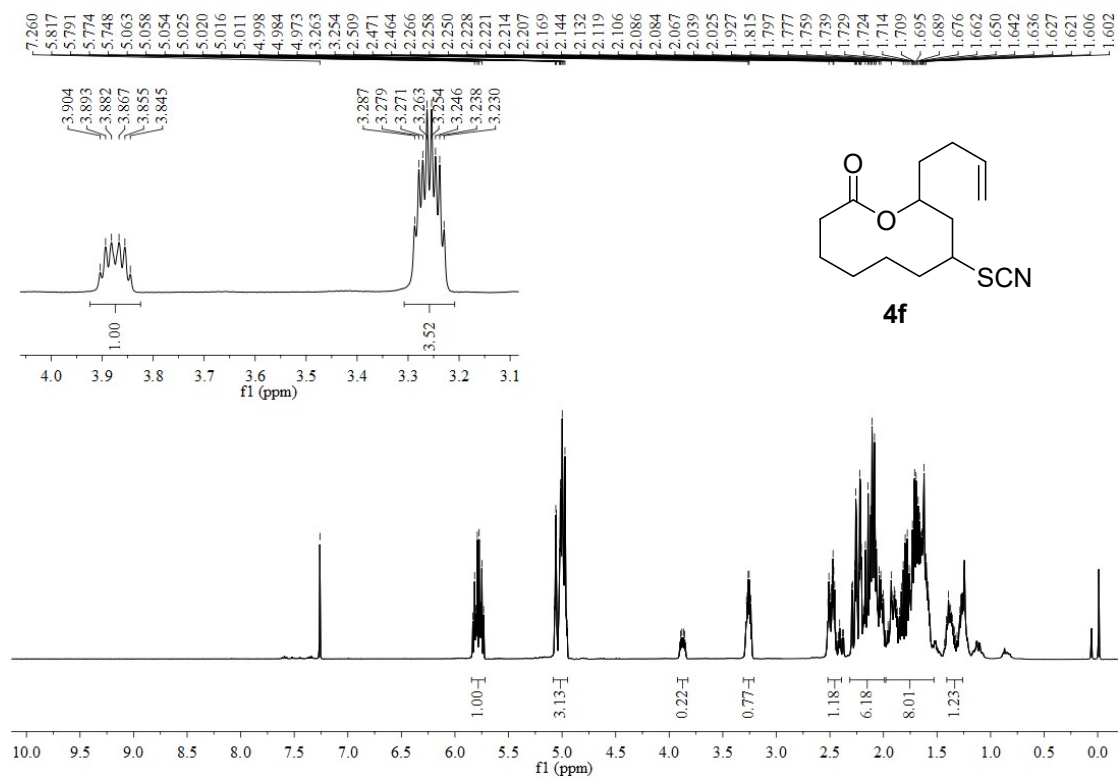
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4d**



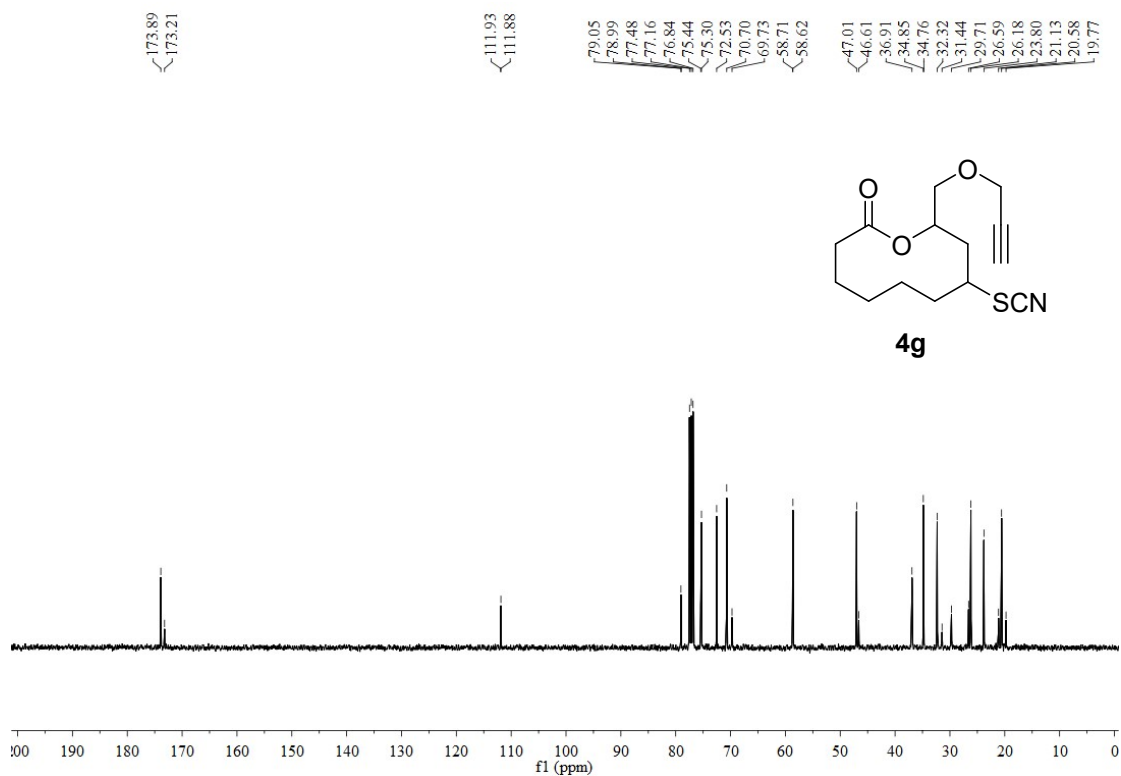
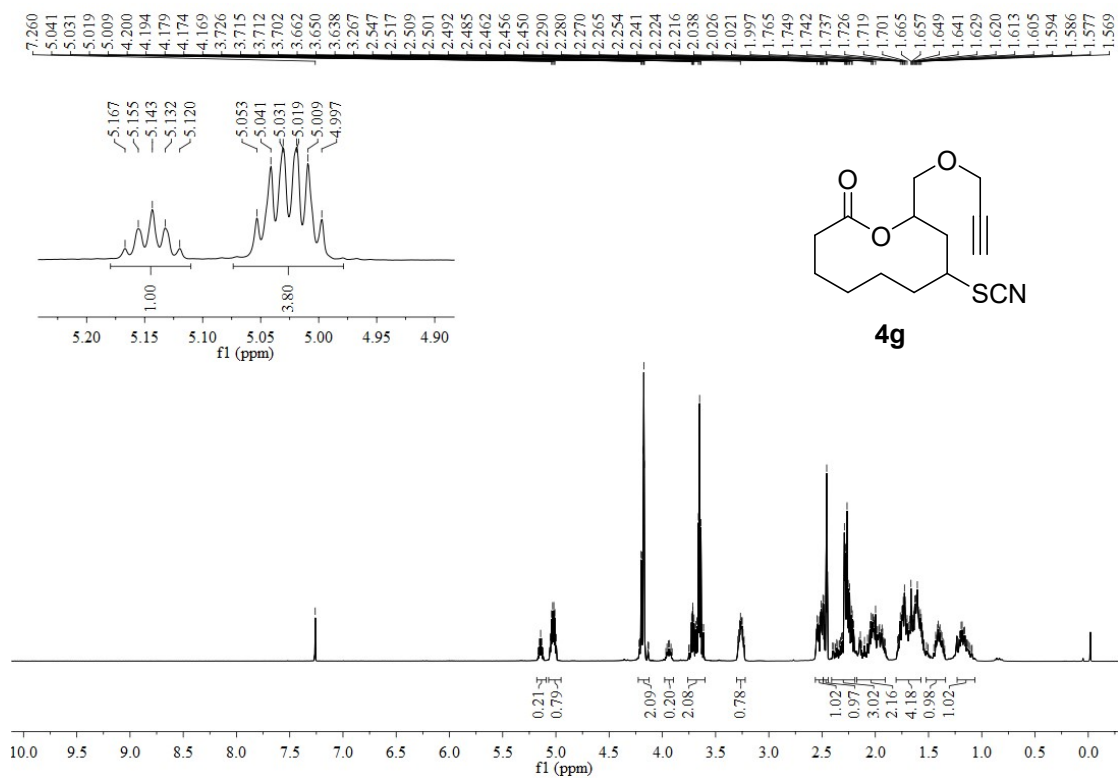
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4e**



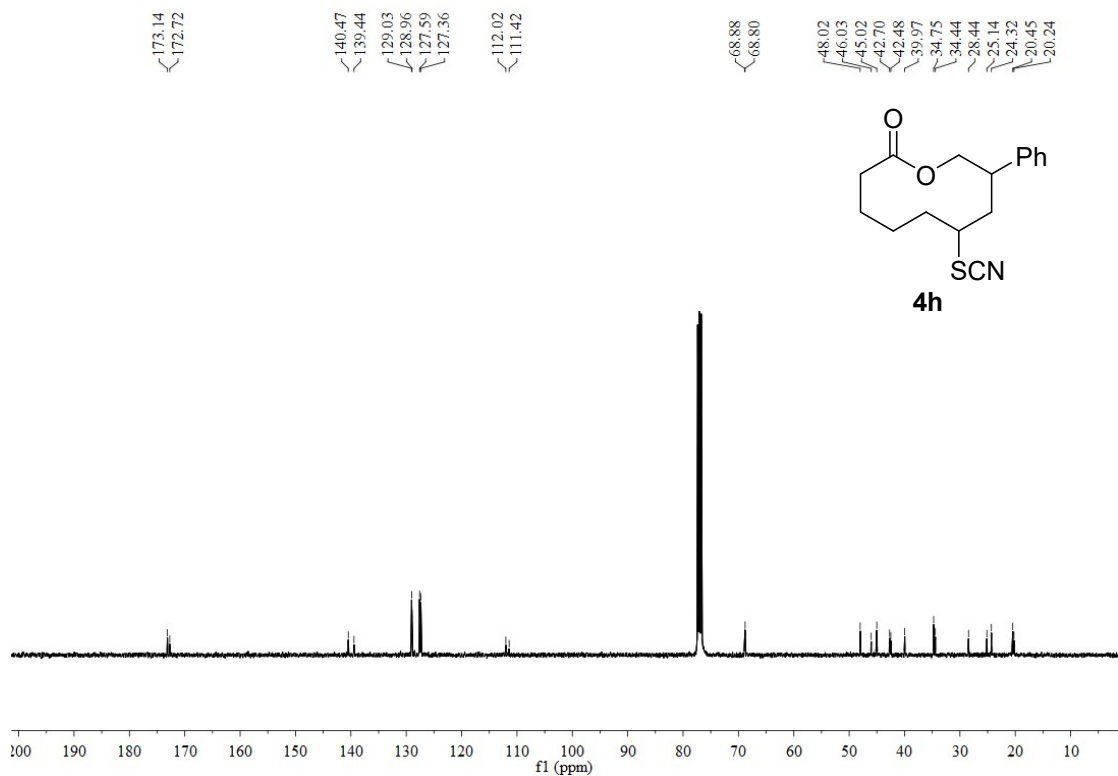
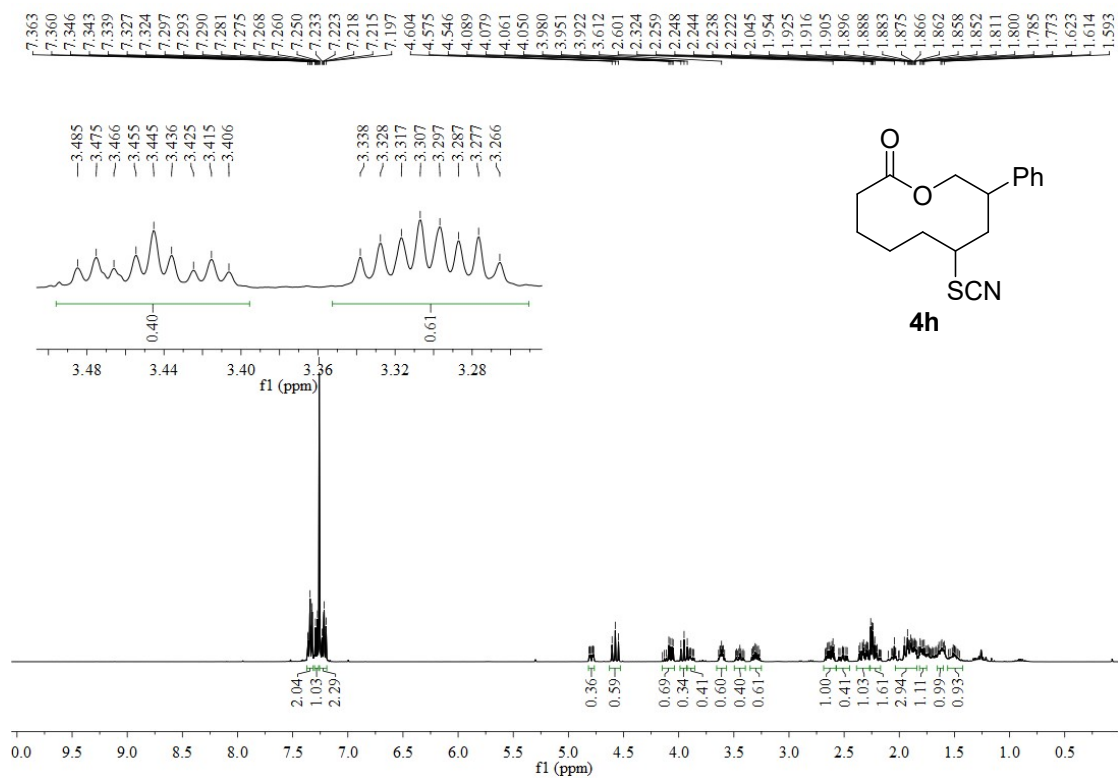
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4f**



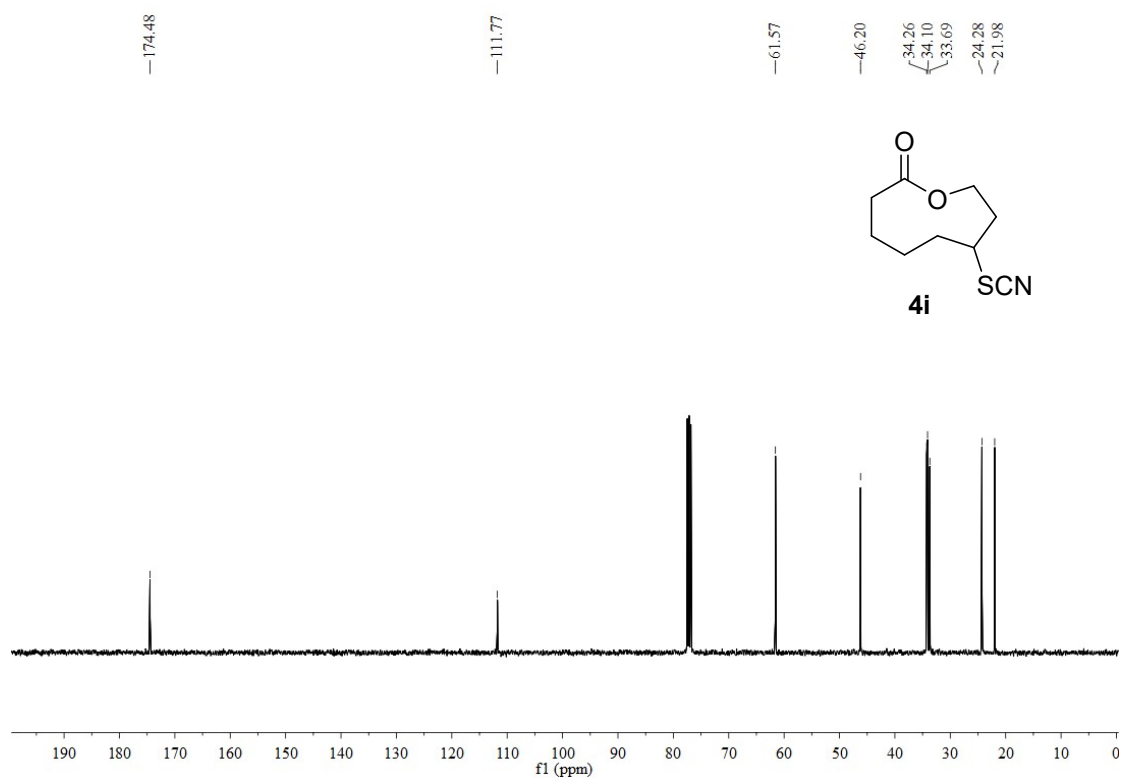
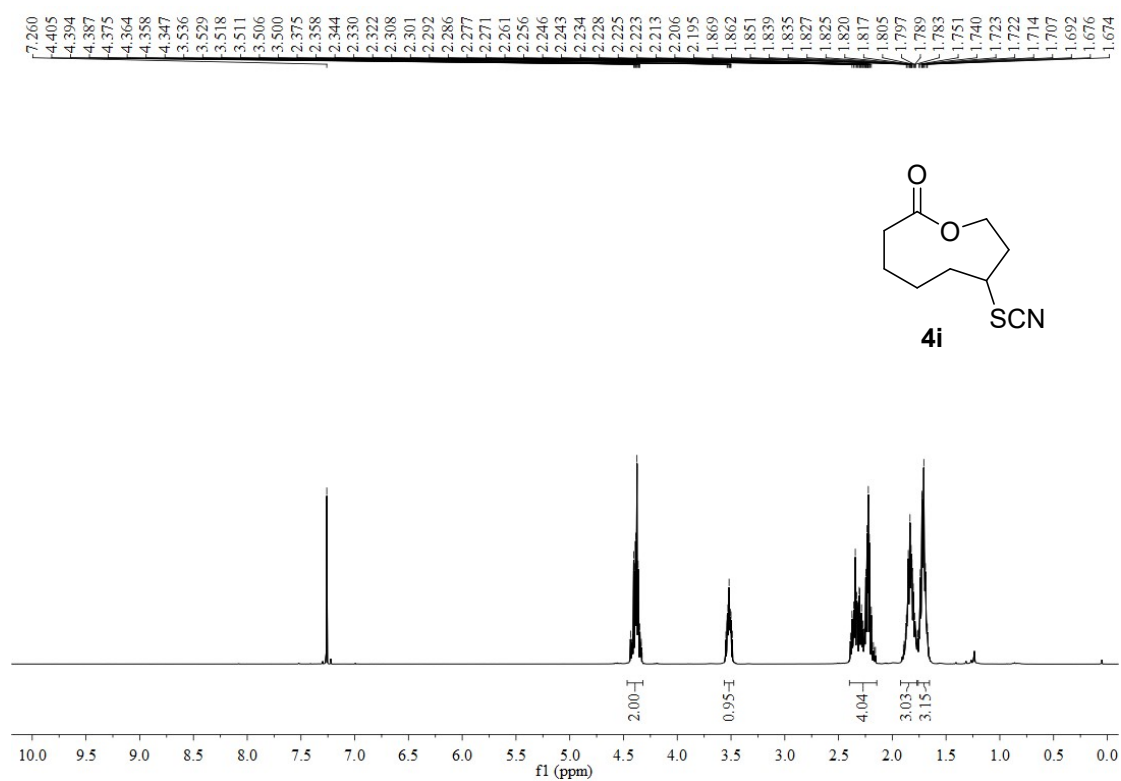
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4g**



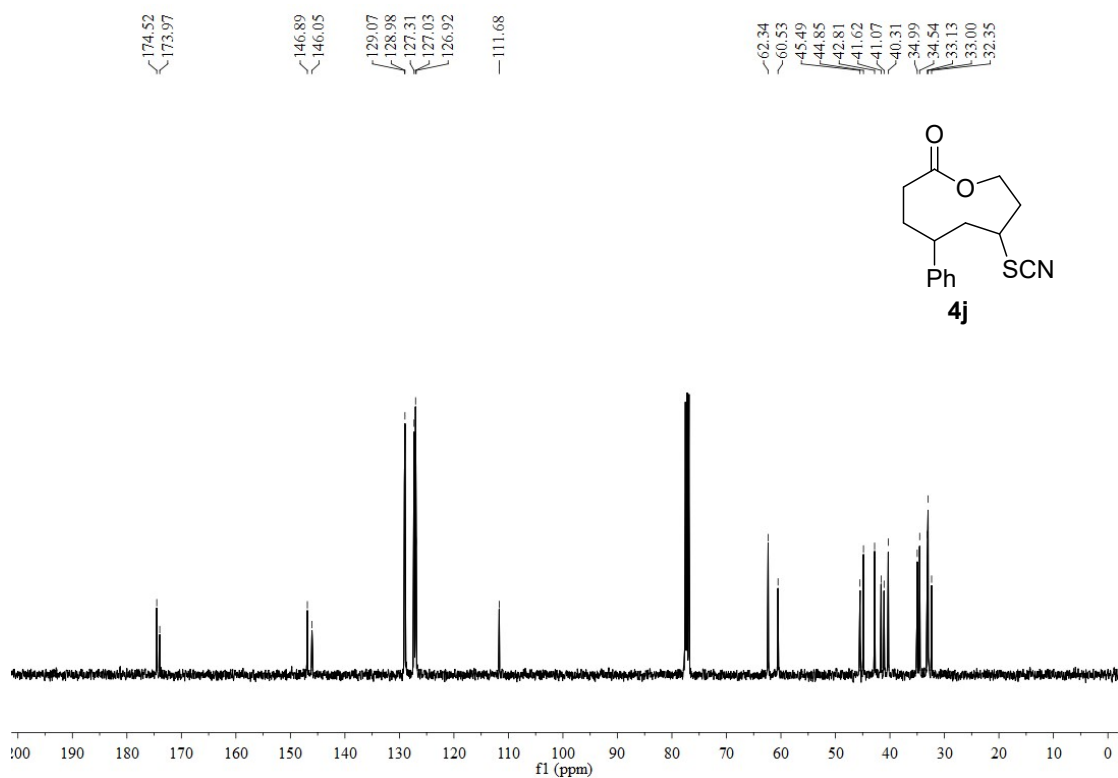
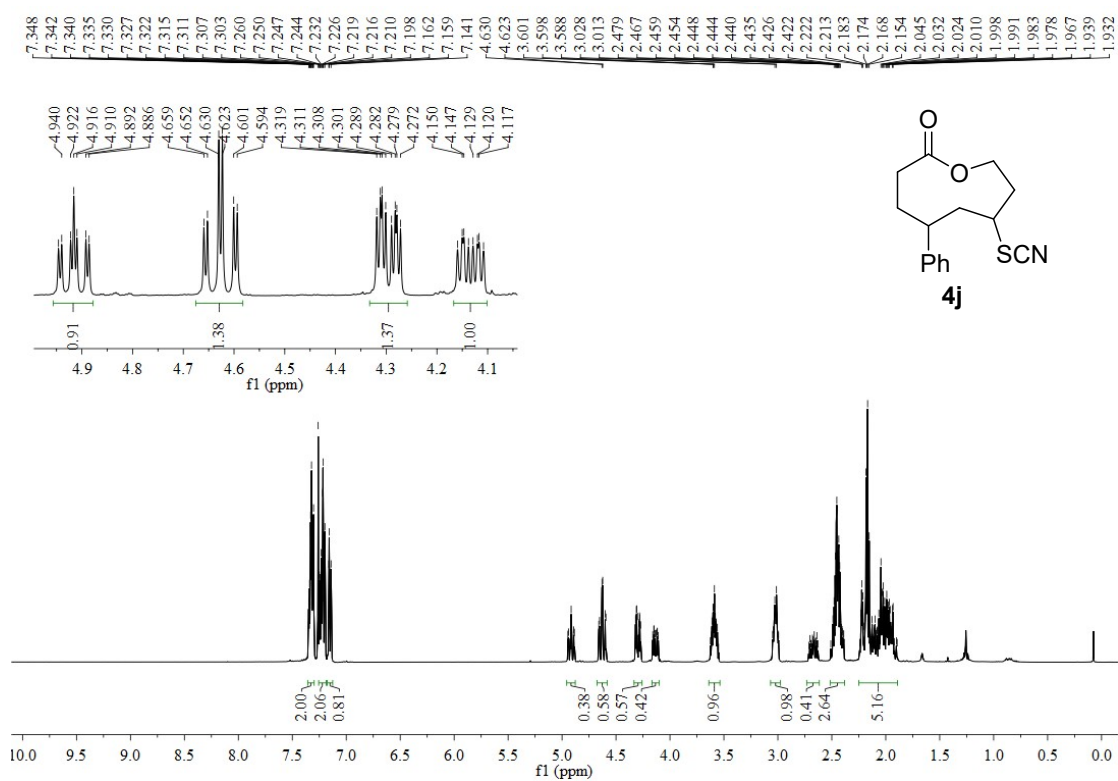
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4h**



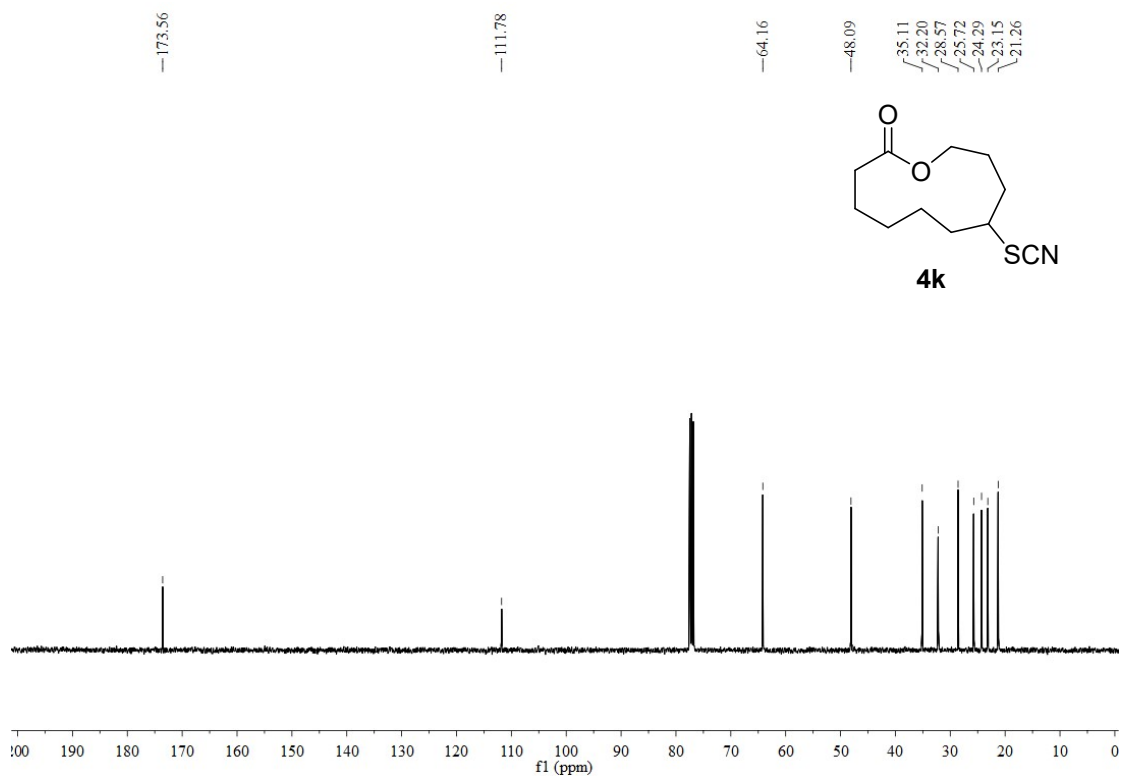
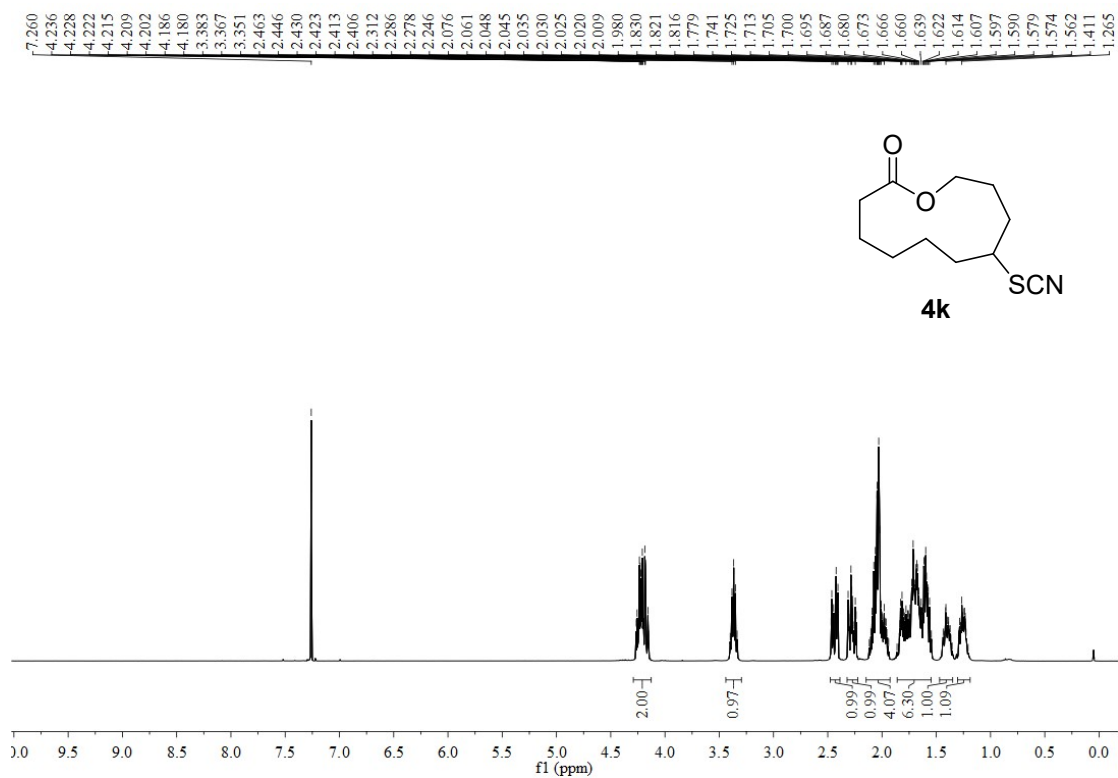
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4i**



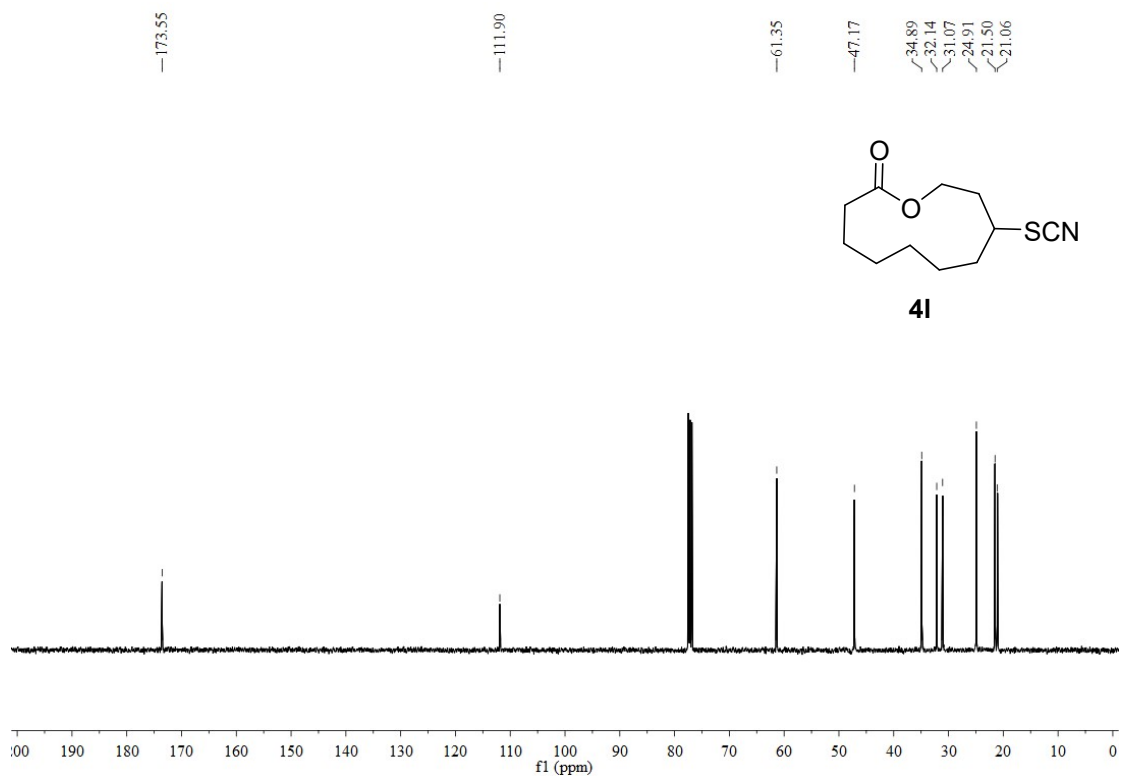
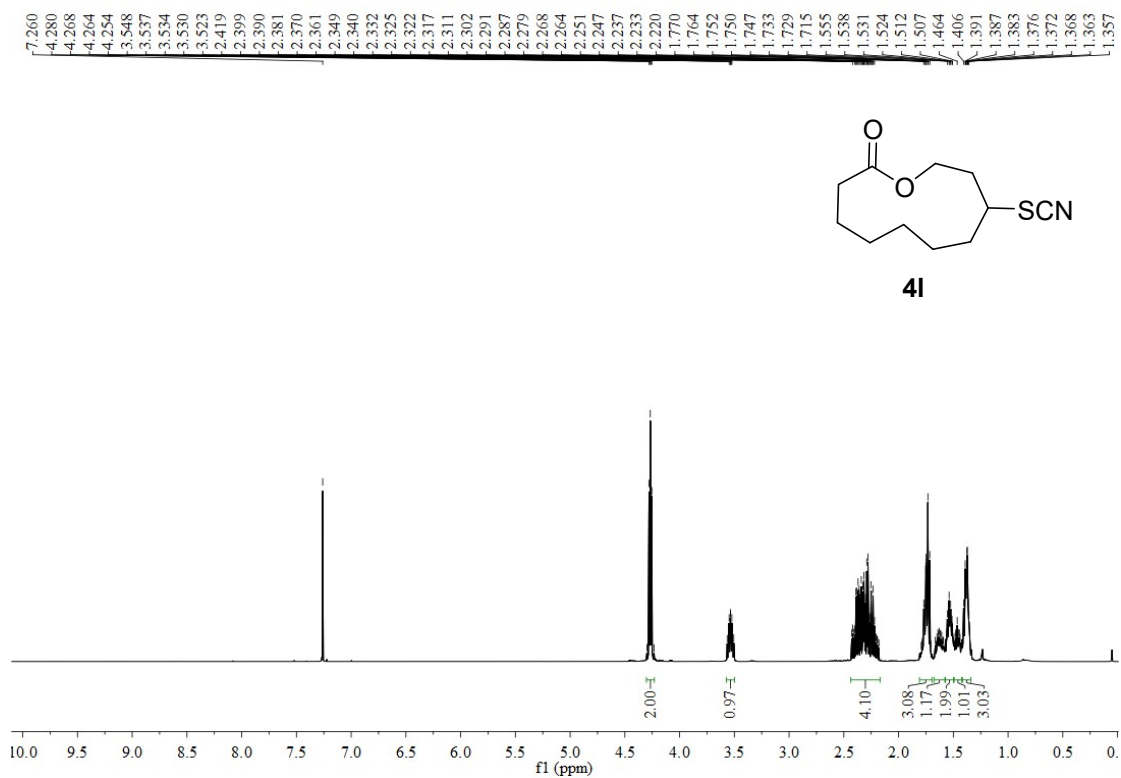
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4j**



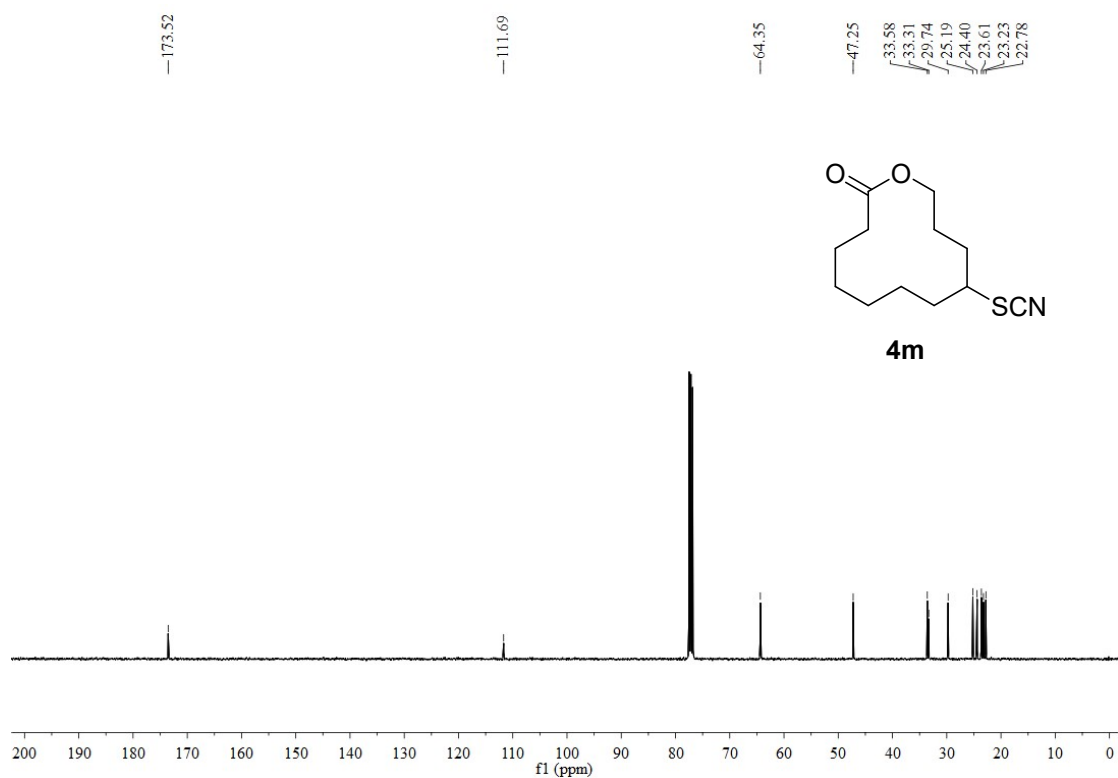
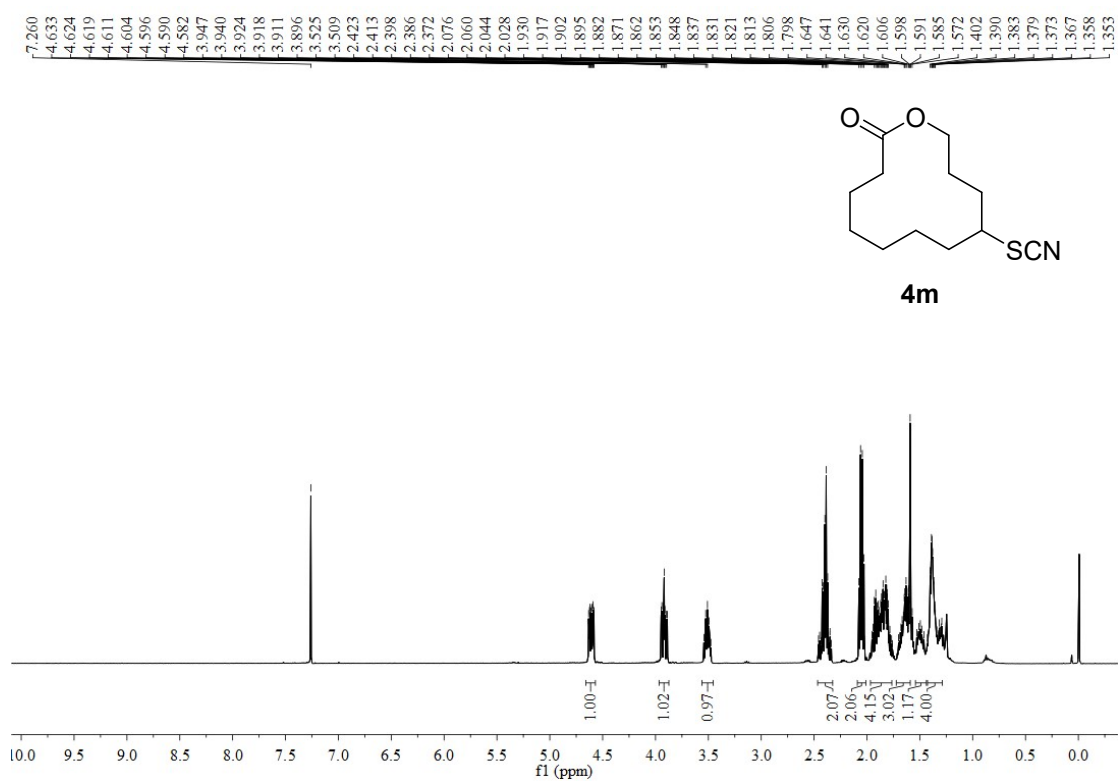
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4k**



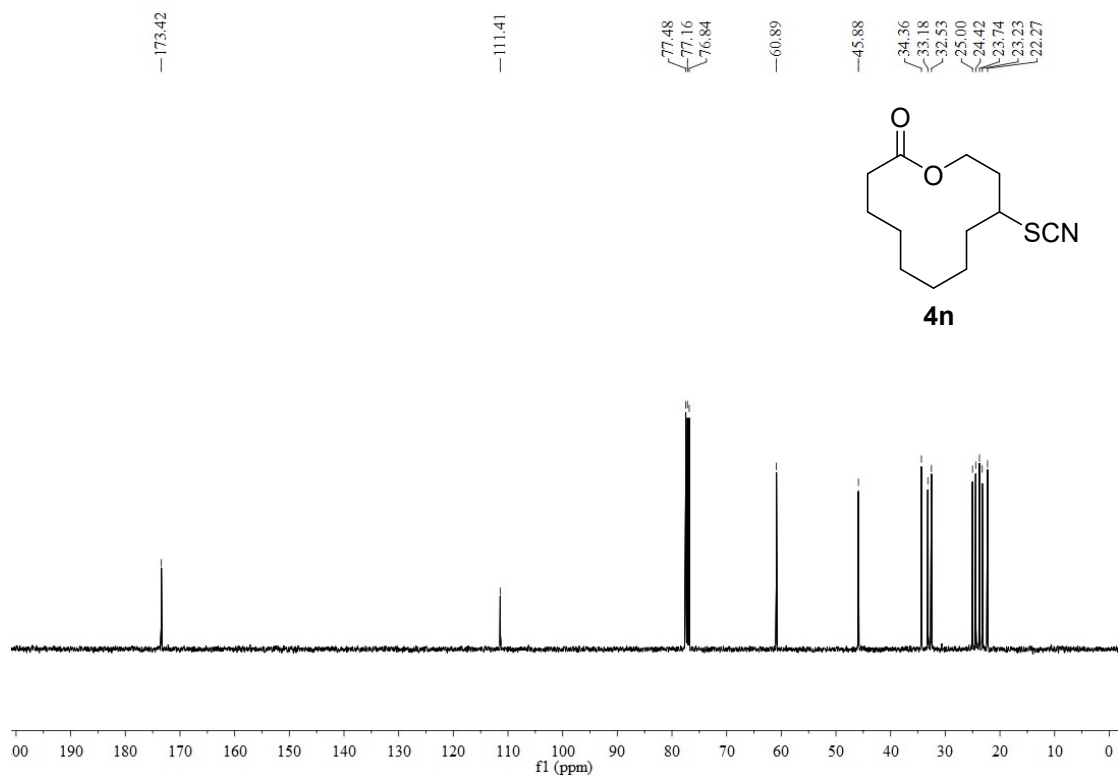
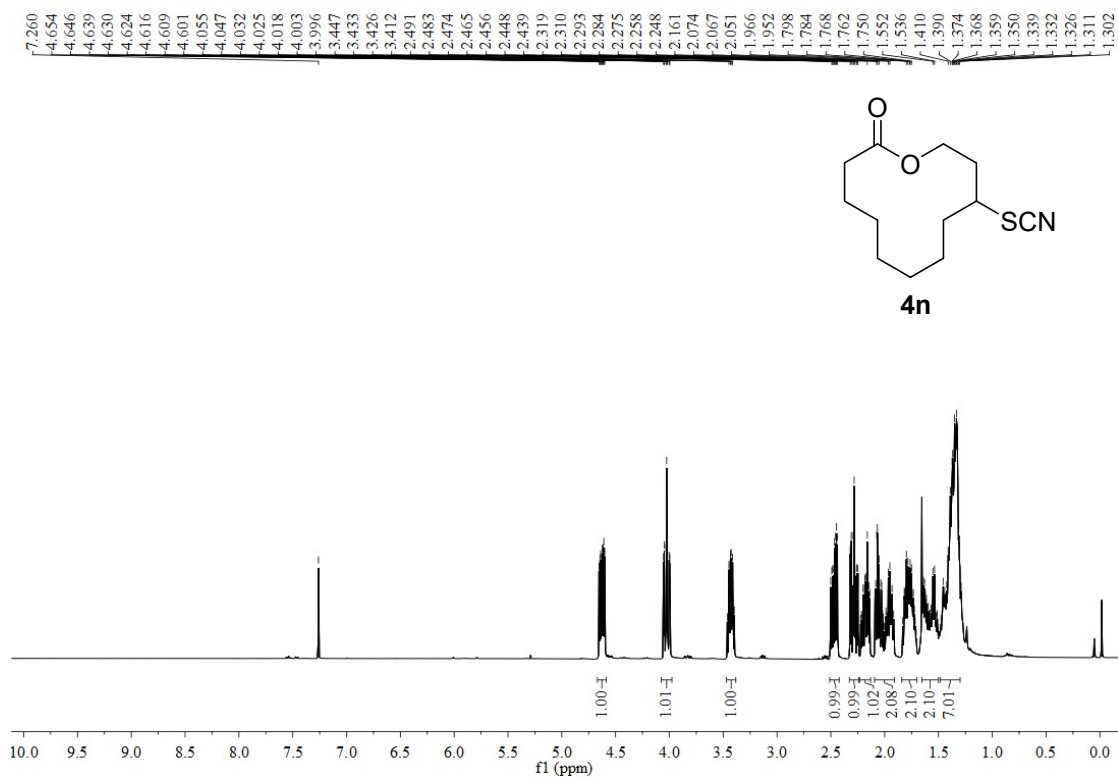
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4l**



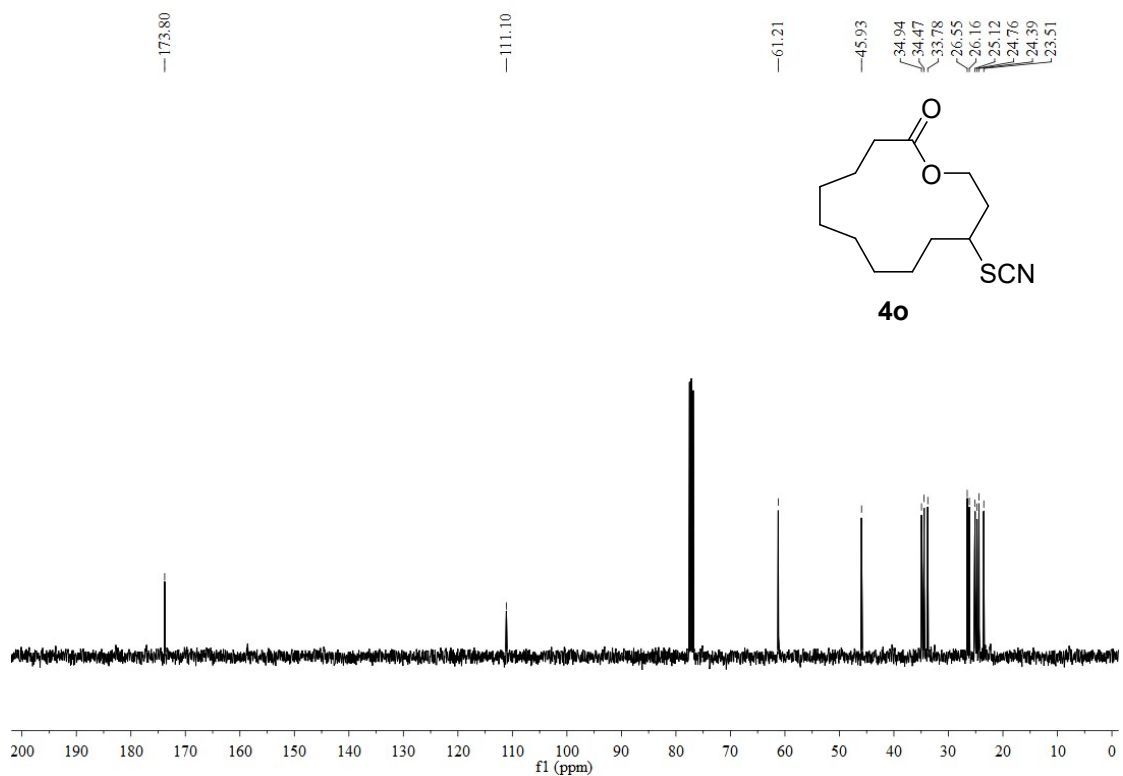
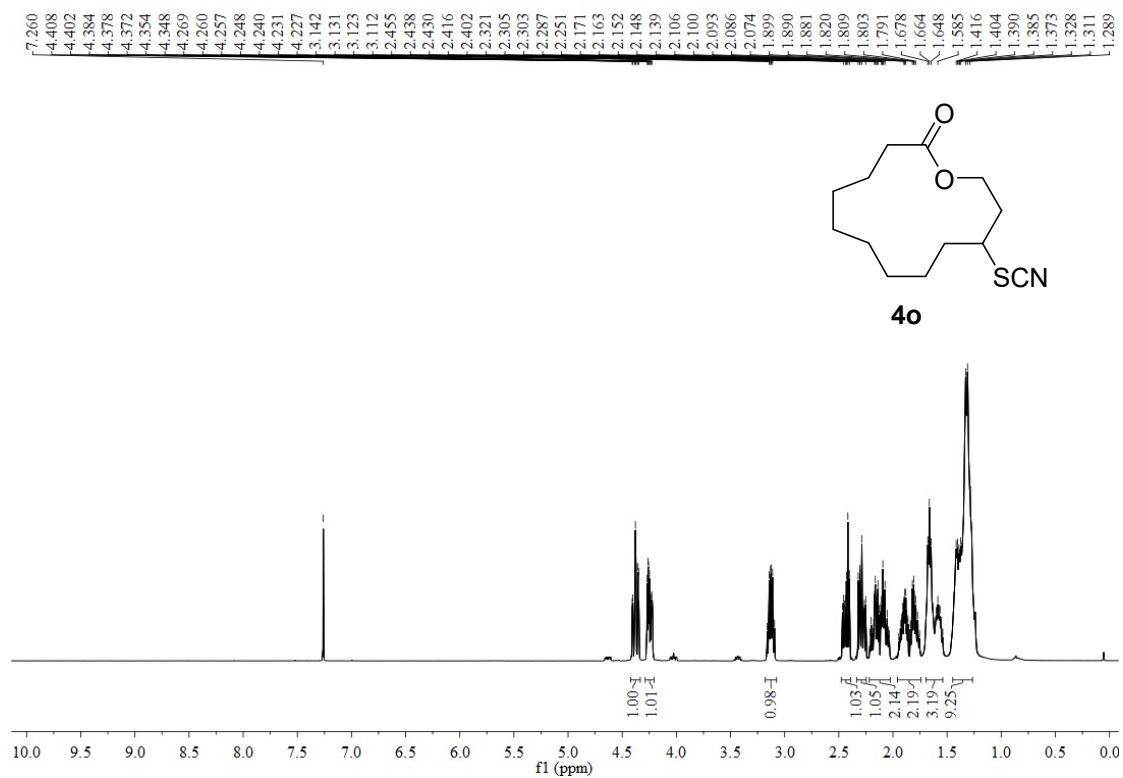
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4m**



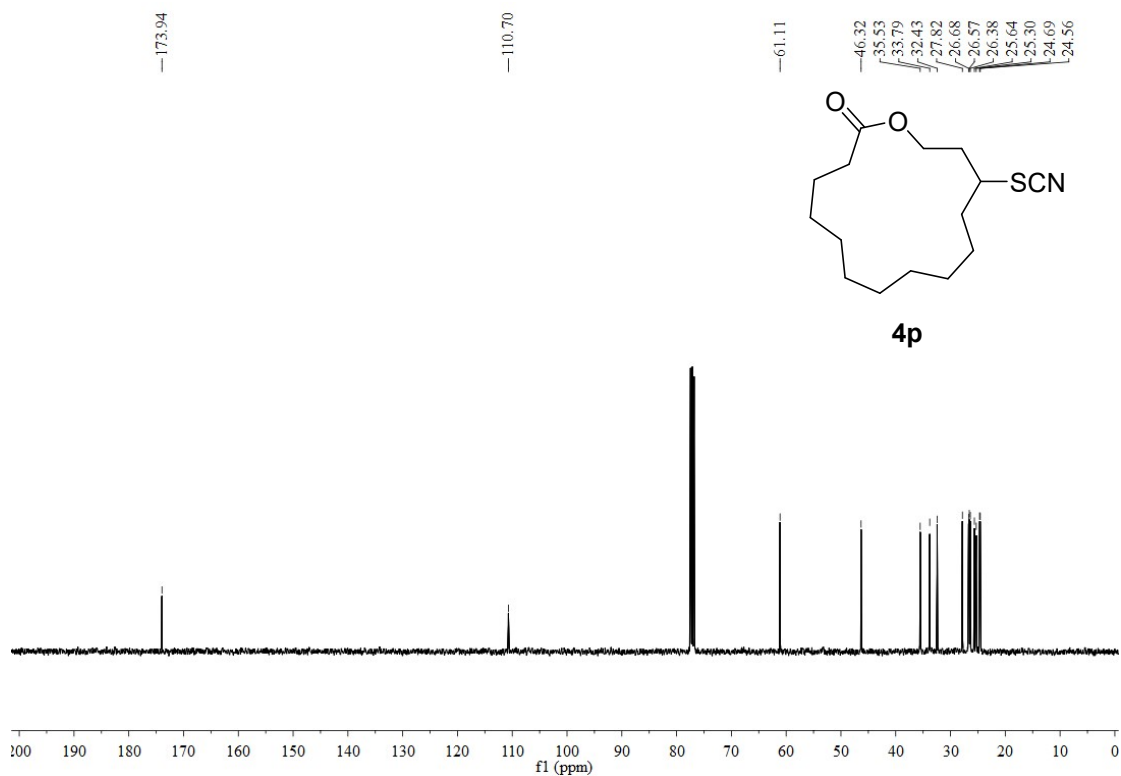
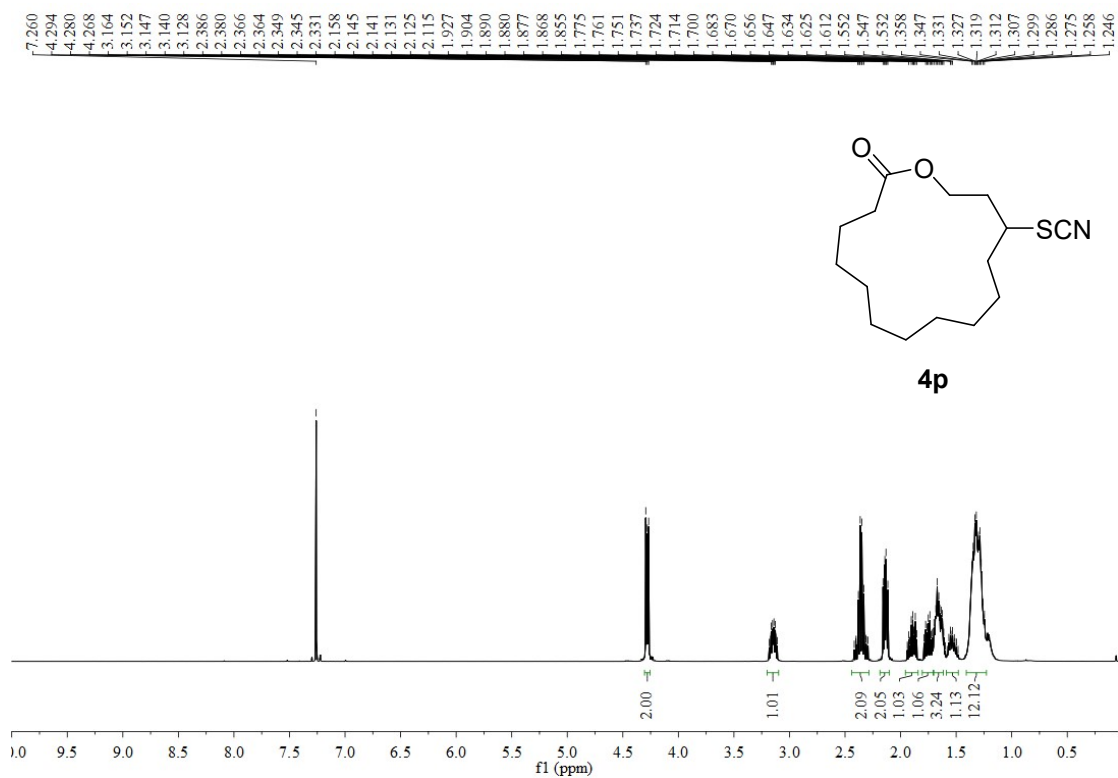
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product 4n



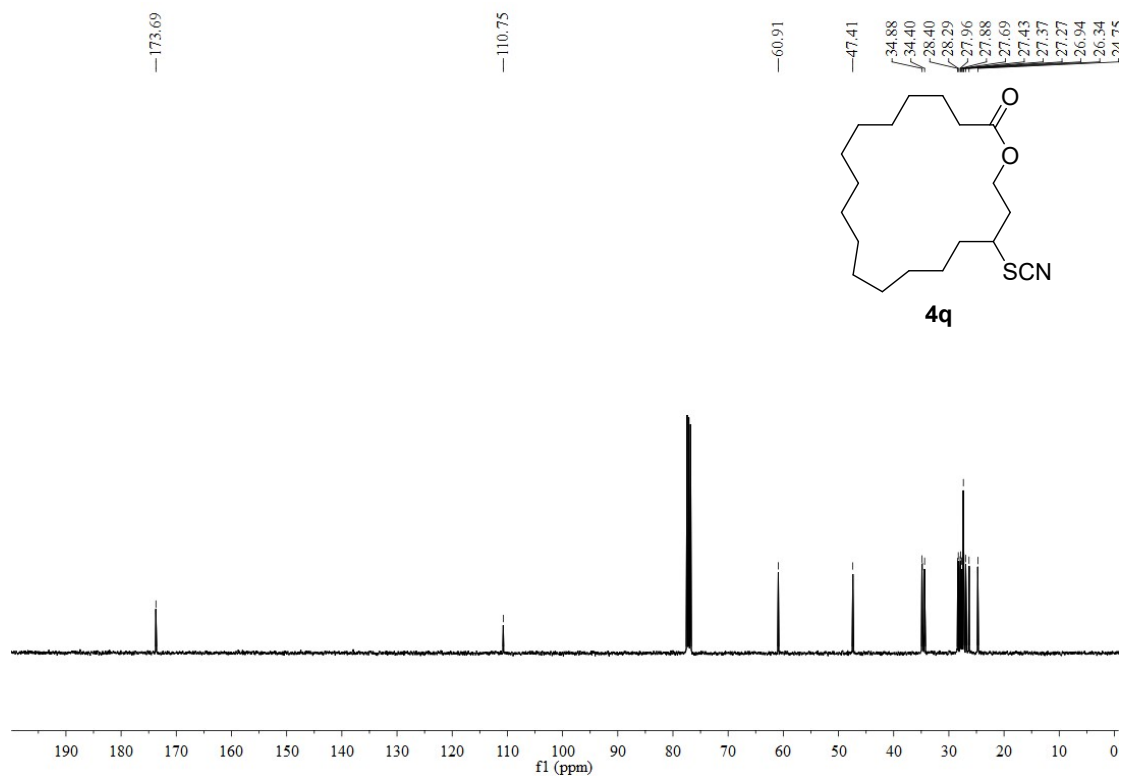
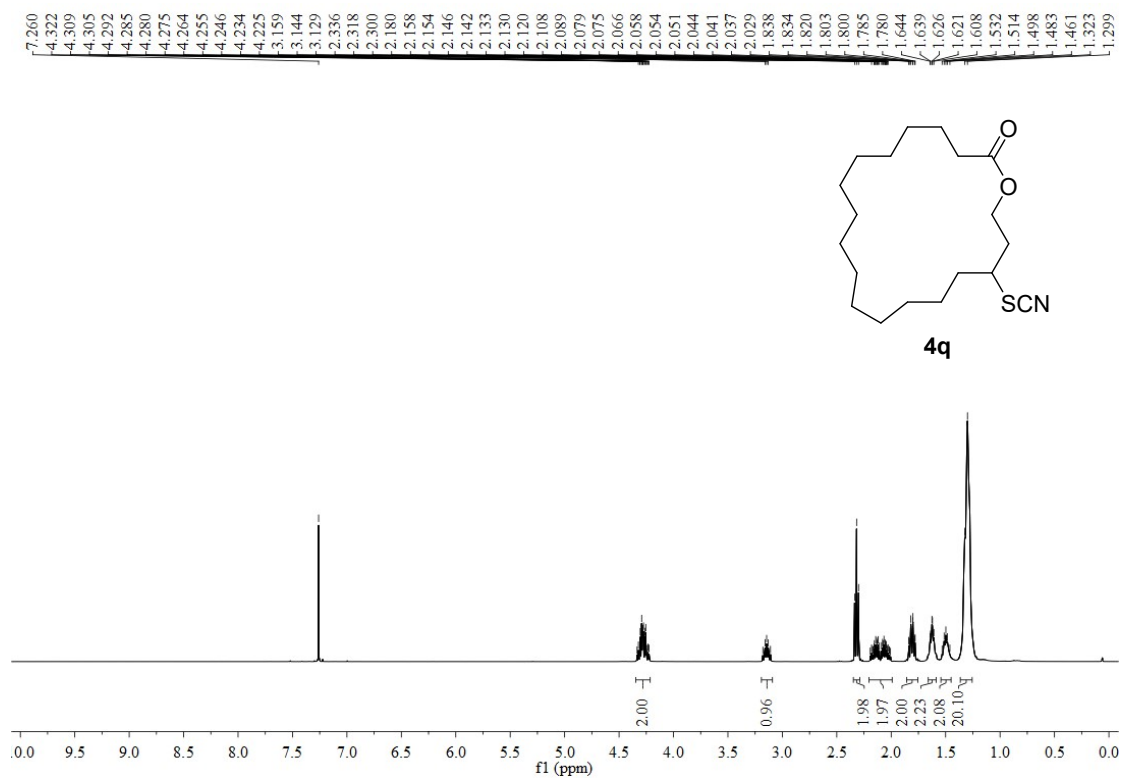
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4o**



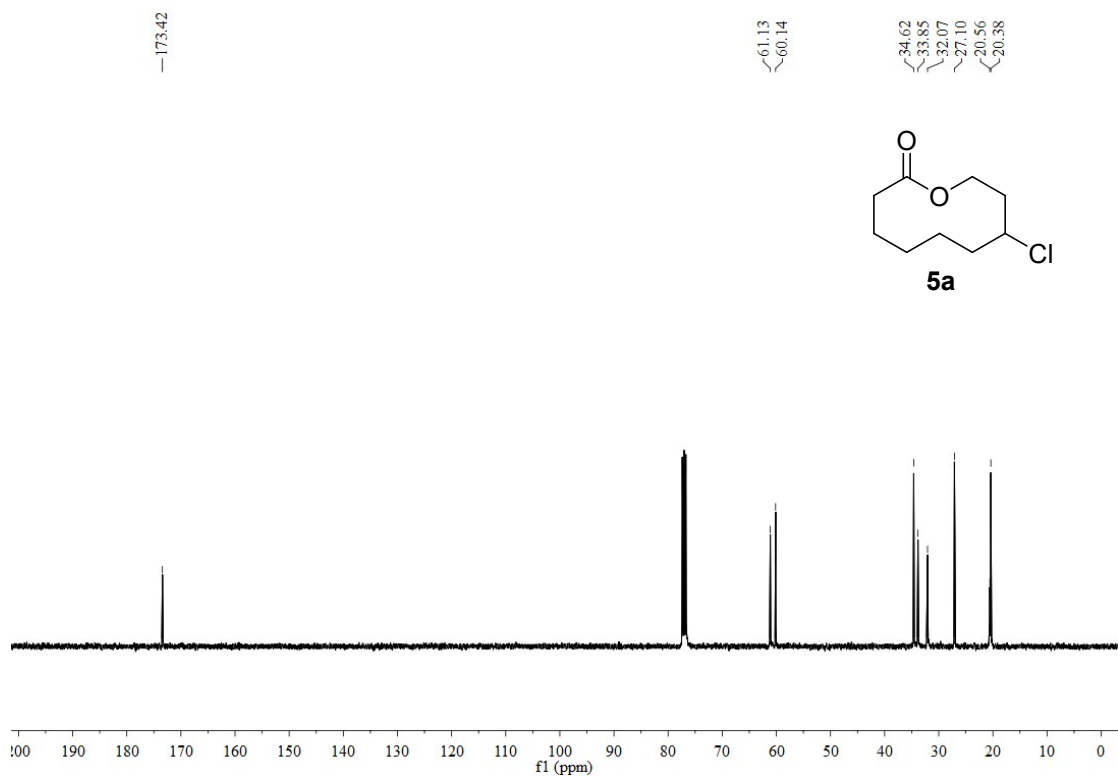
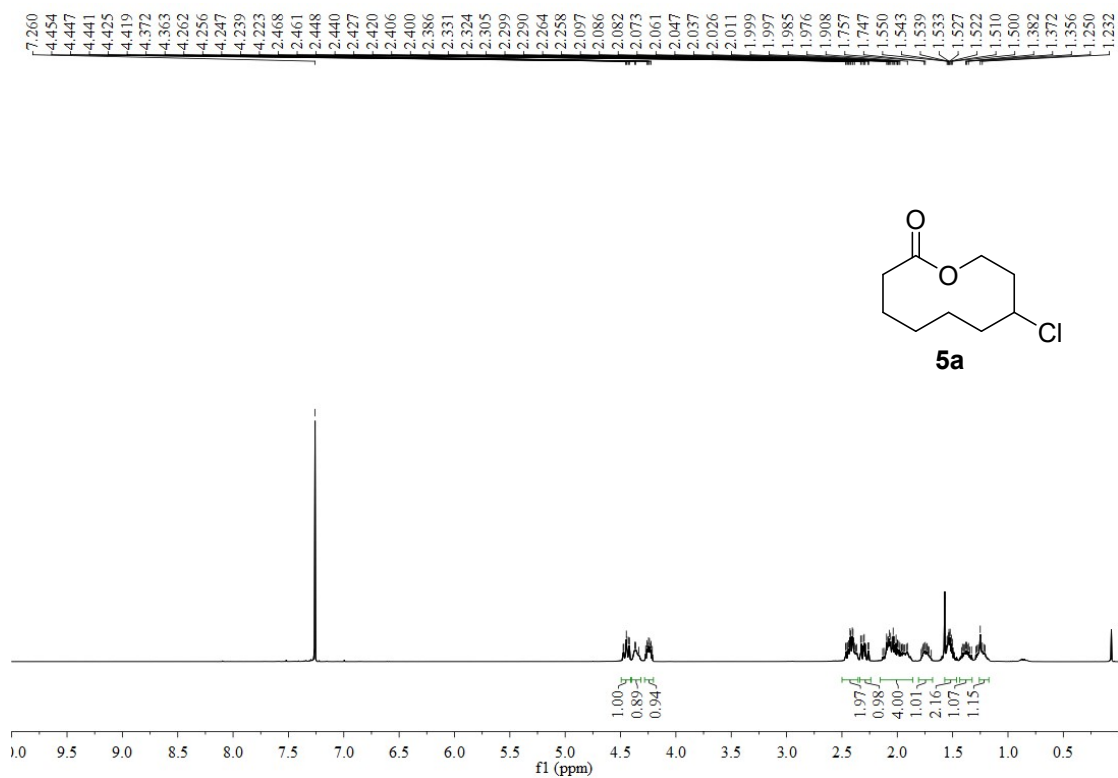
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4p**



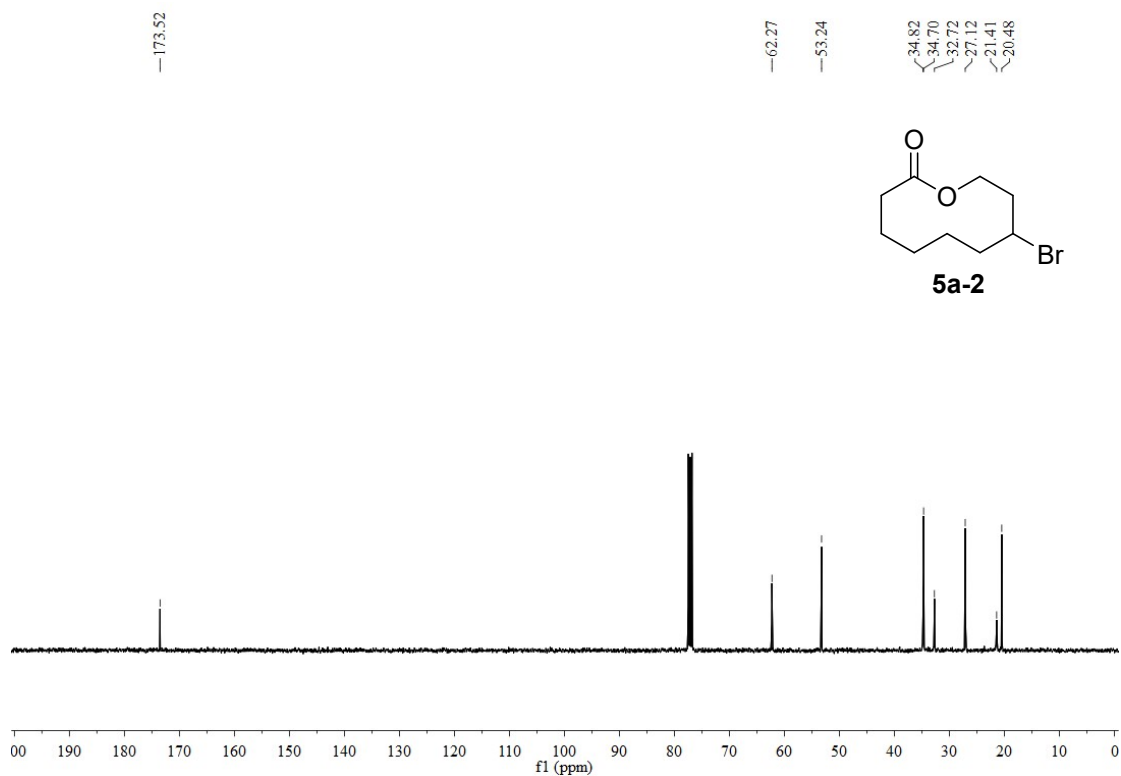
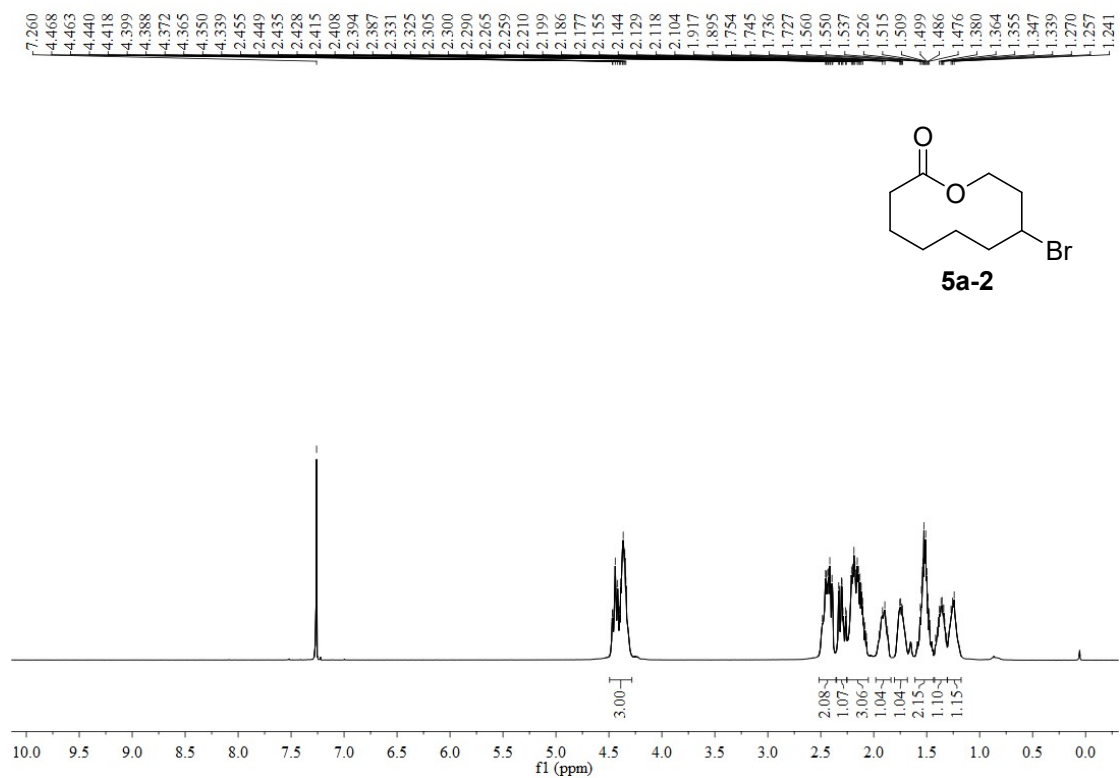
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **4q**



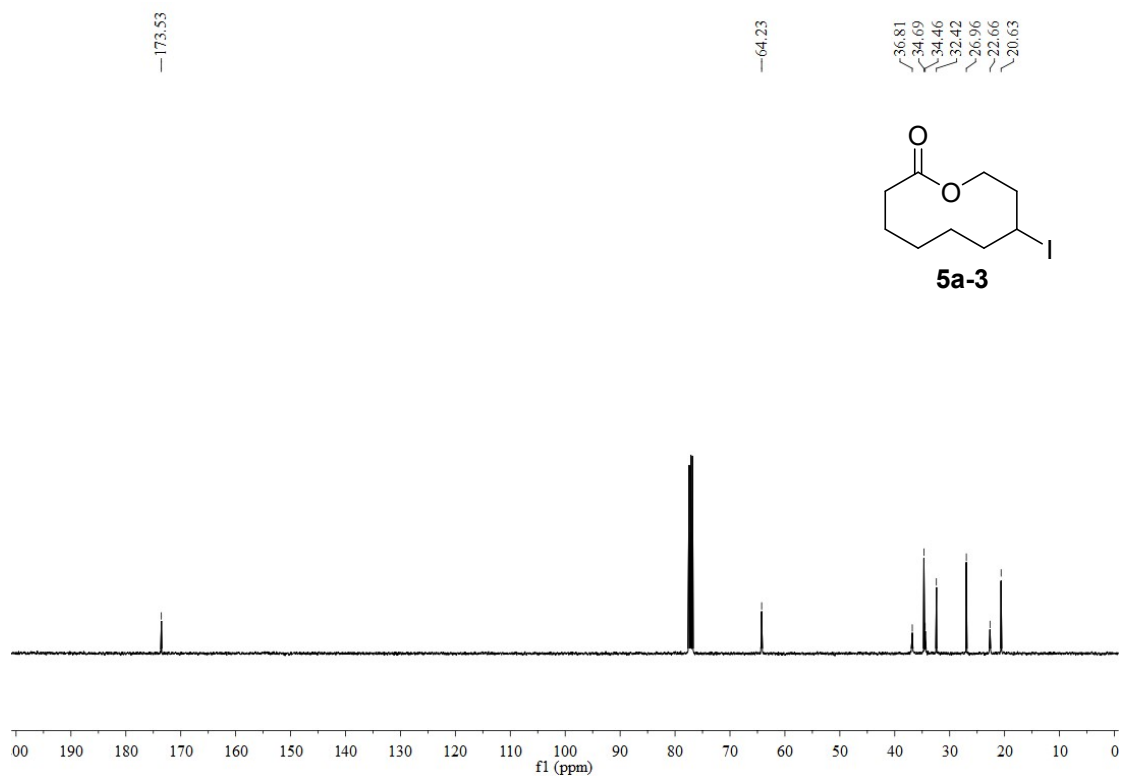
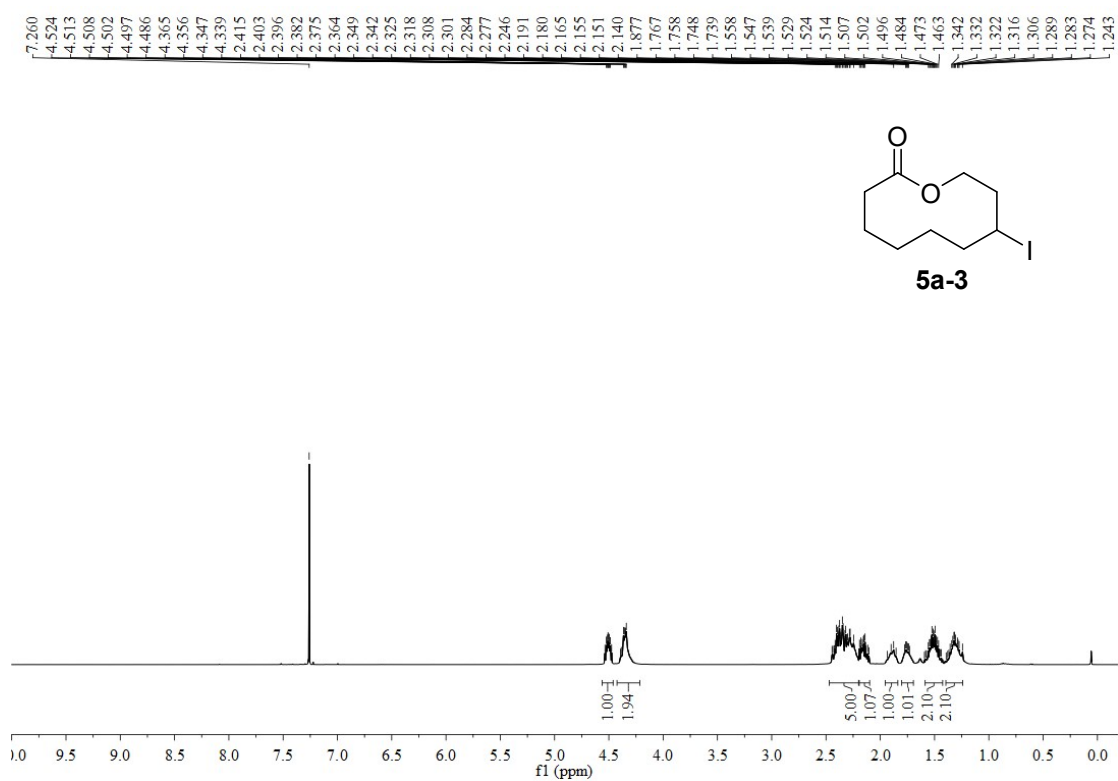
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5a**



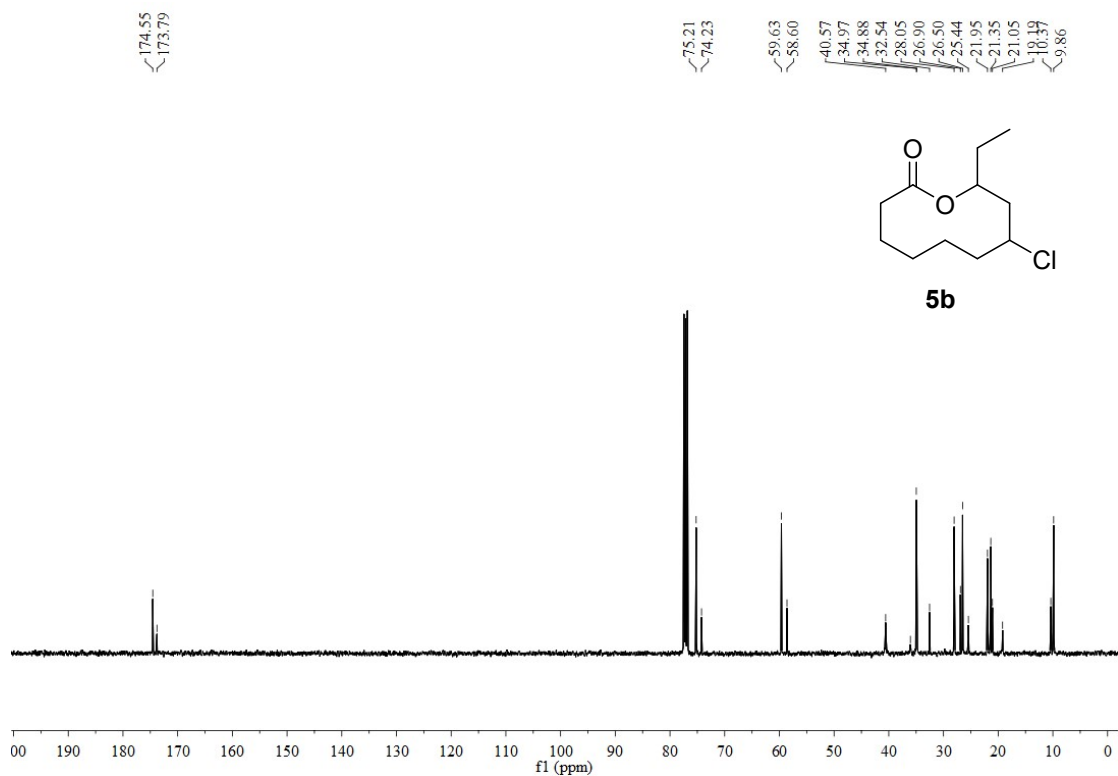
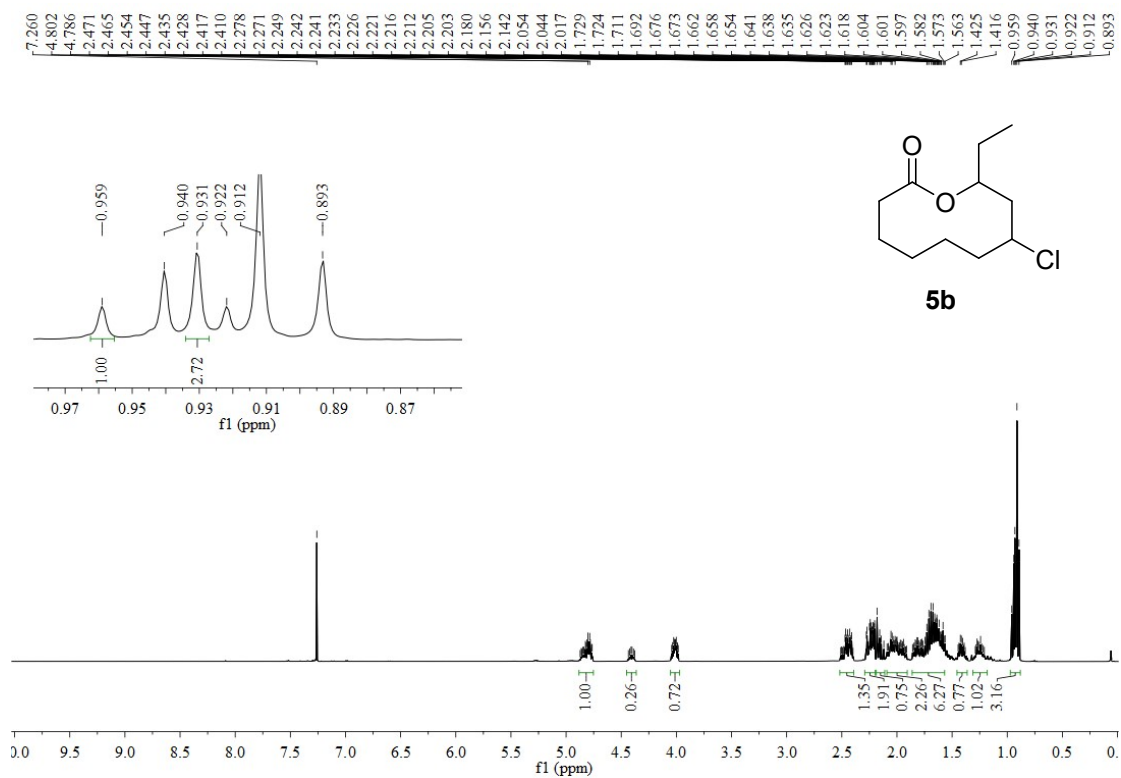
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5a-2**



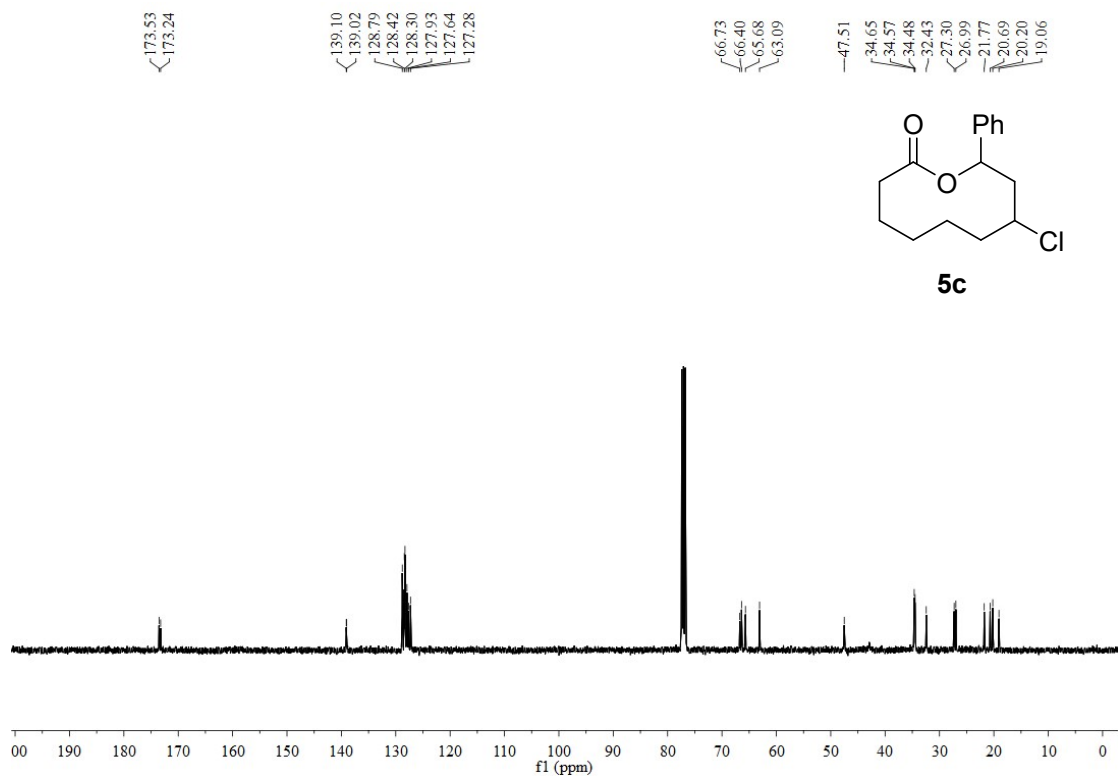
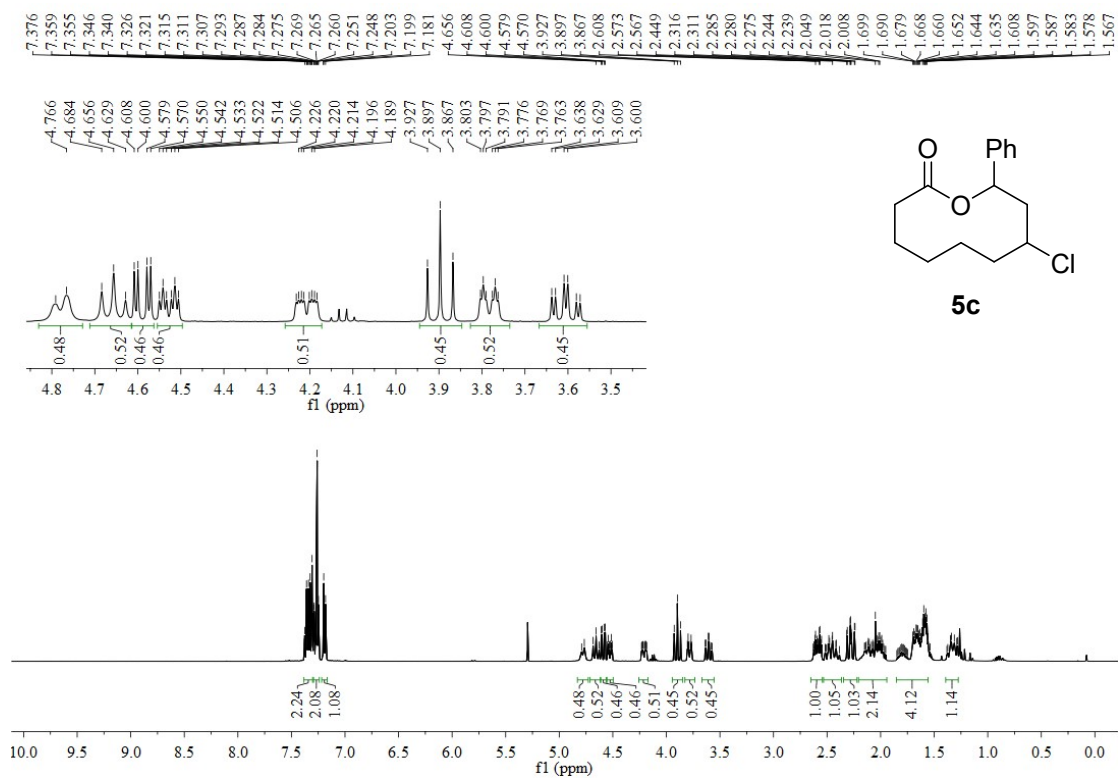
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5a-3**



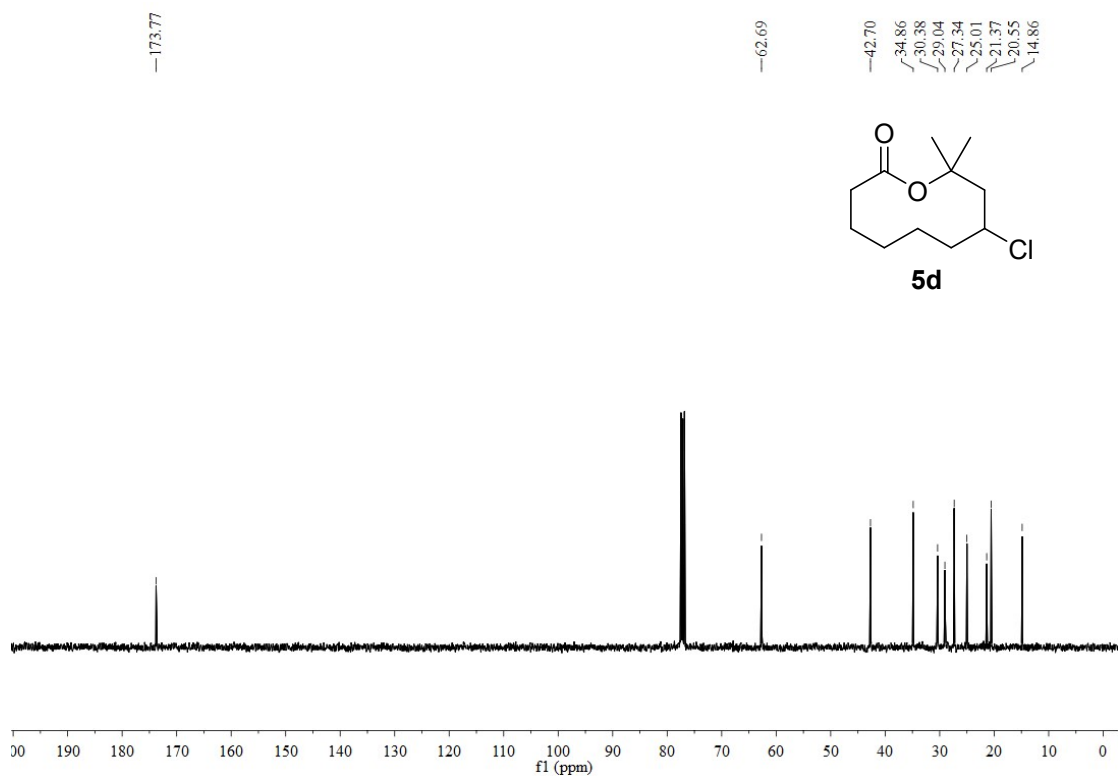
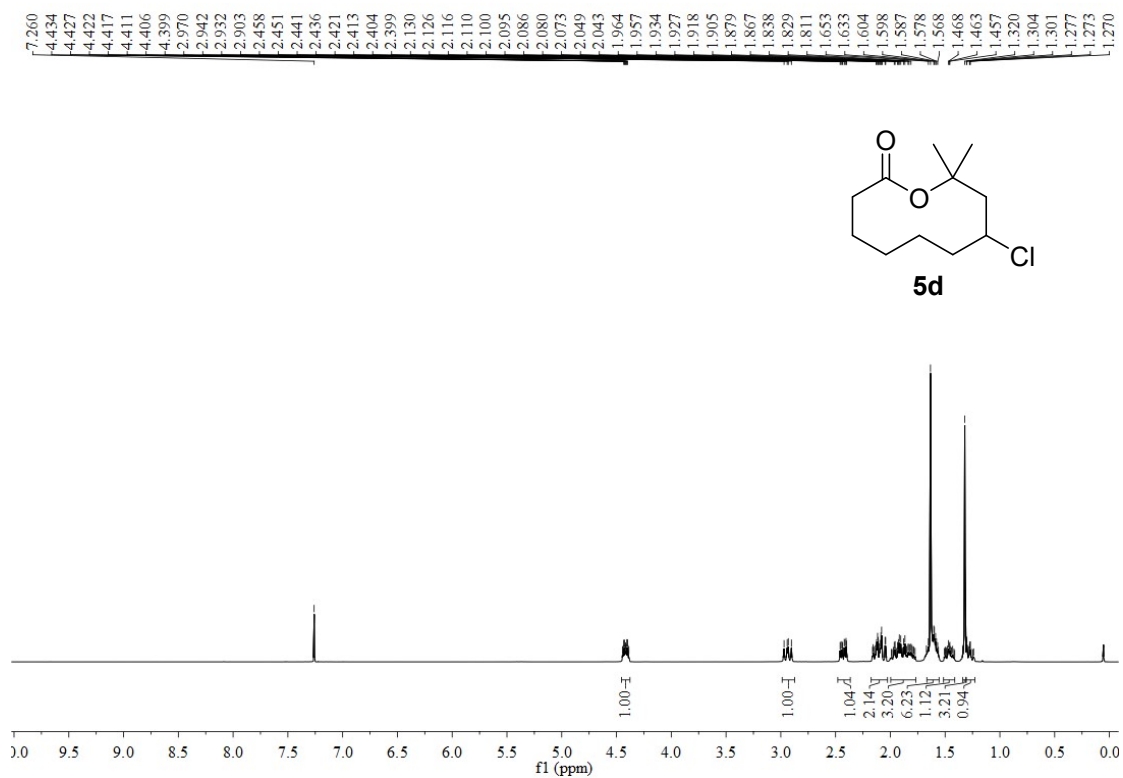
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **5b**



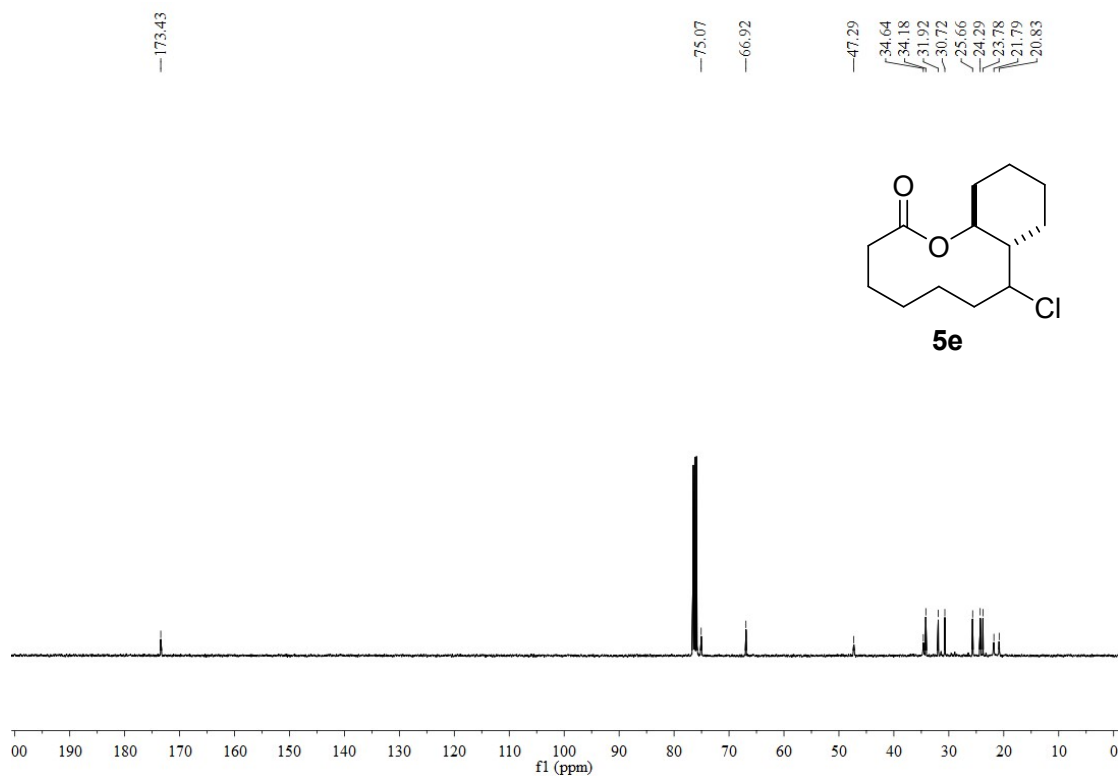
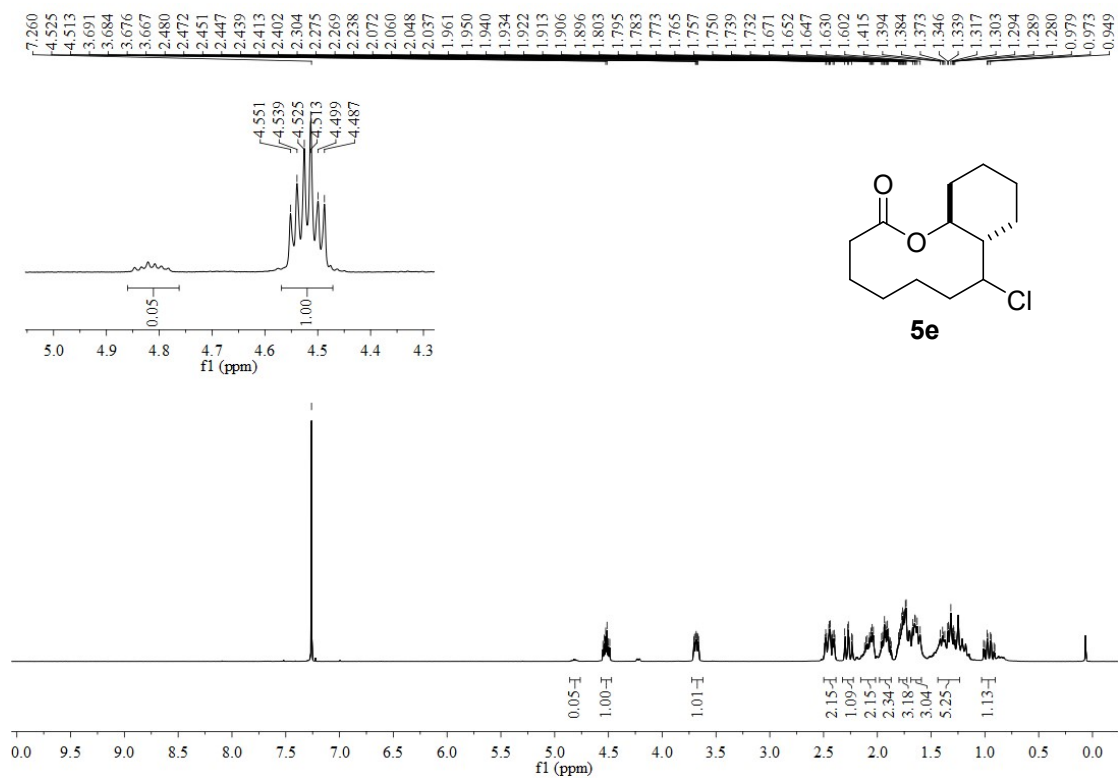
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5c**



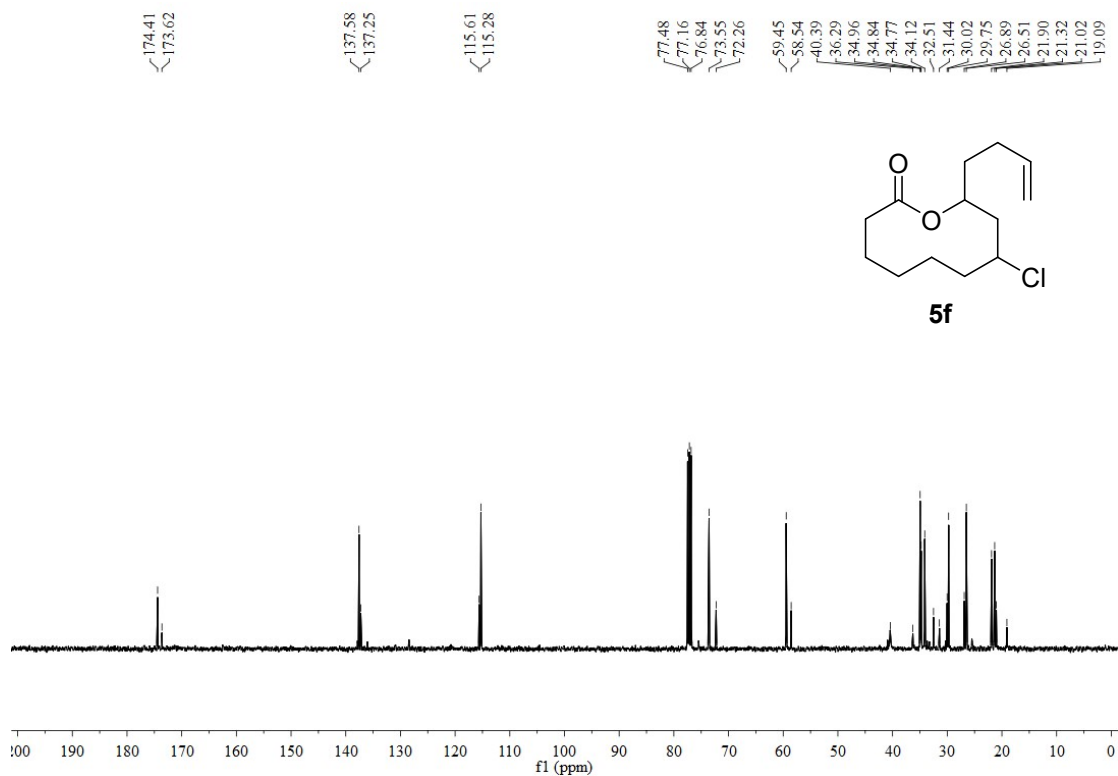
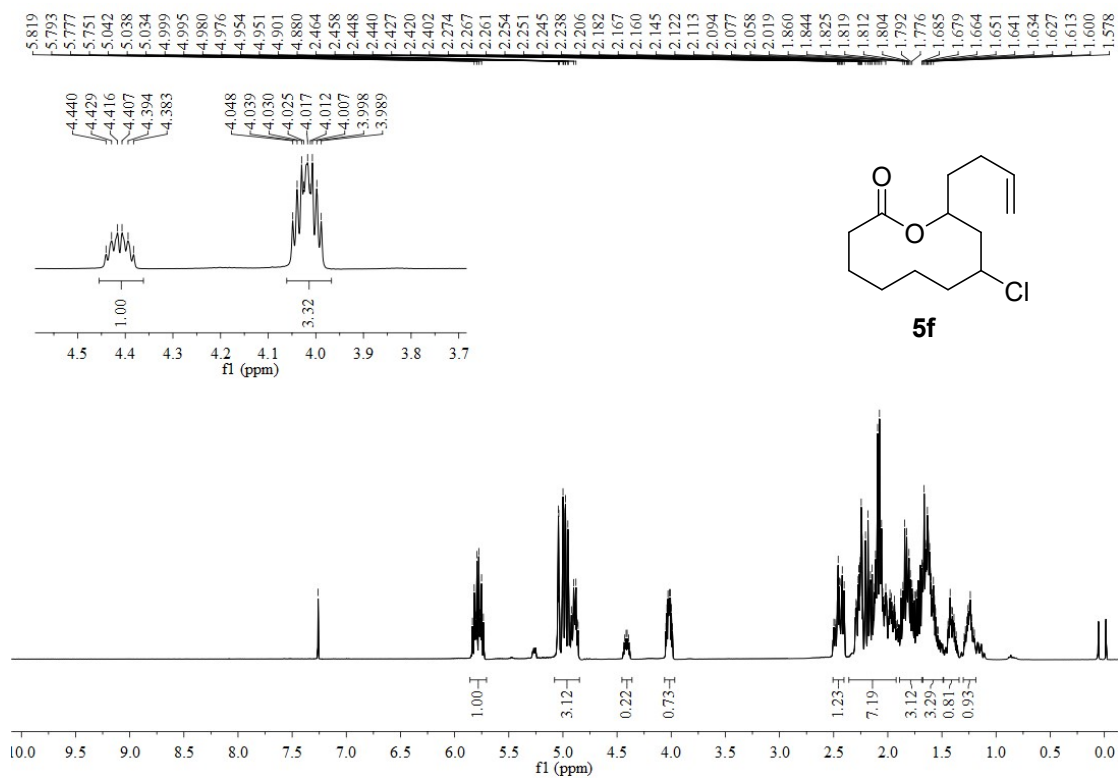
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5d**



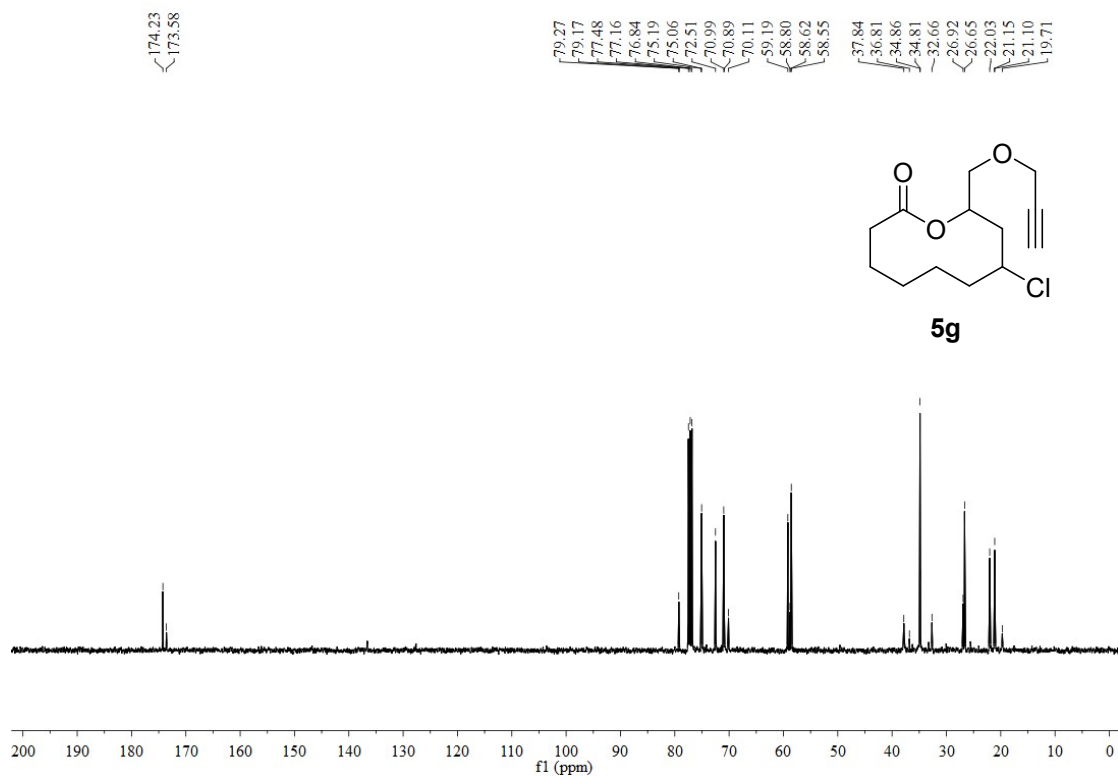
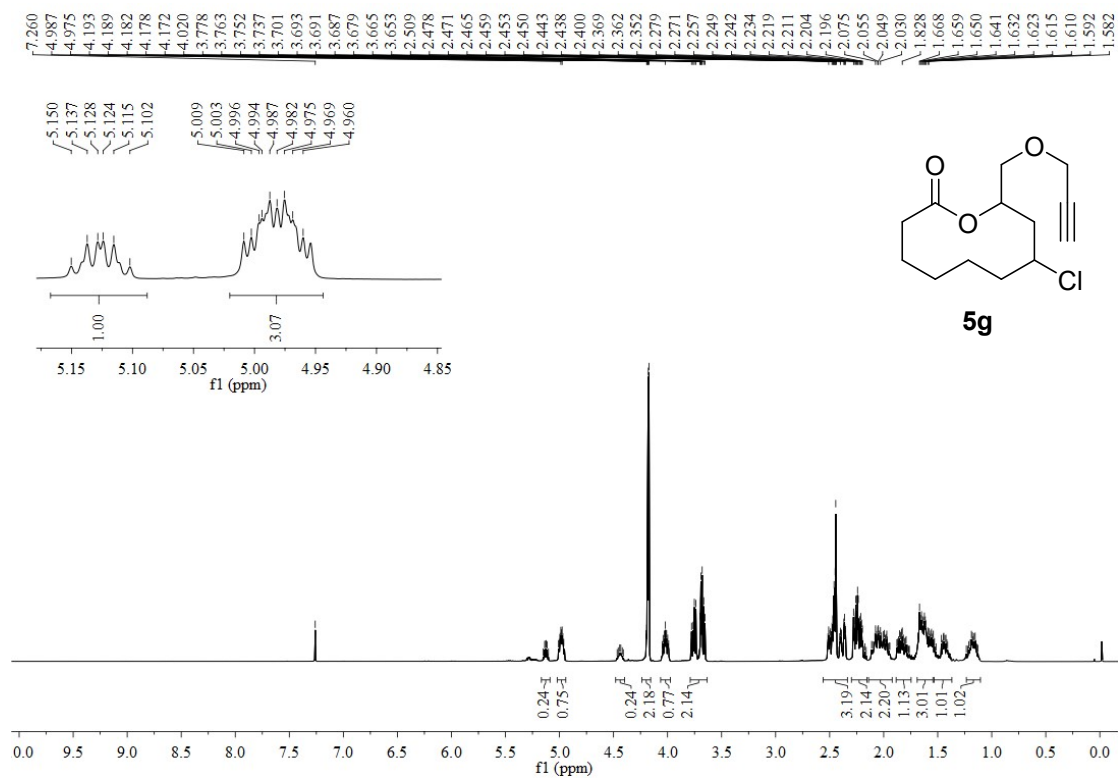
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5e**



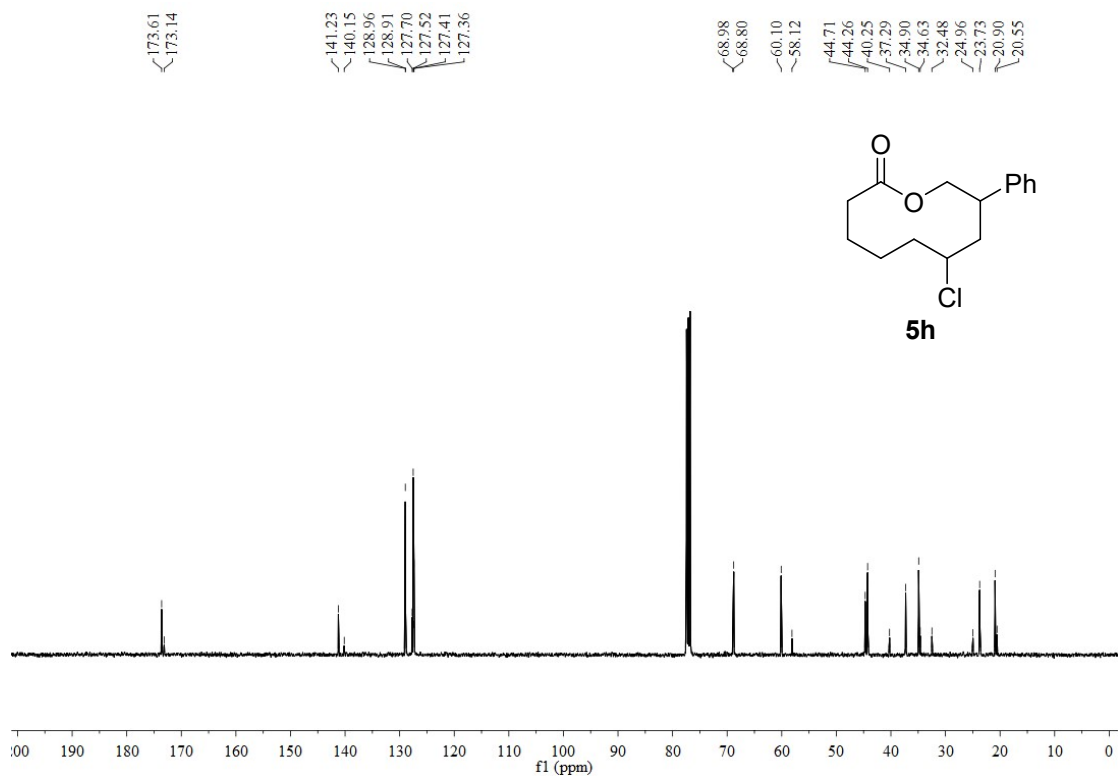
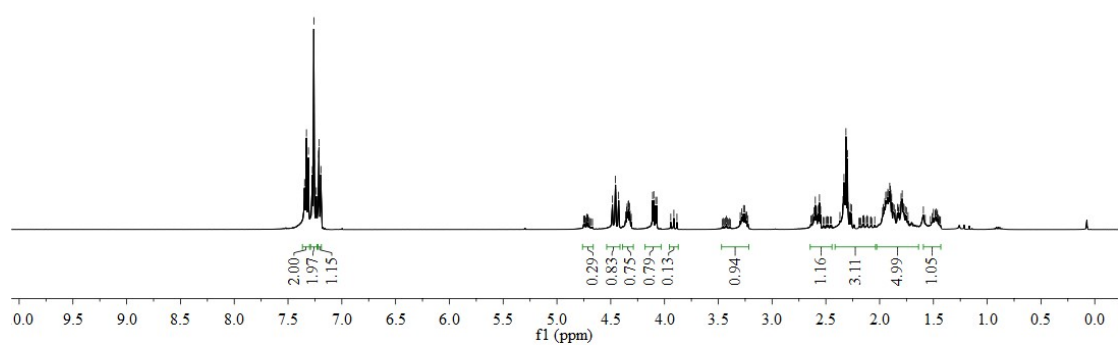
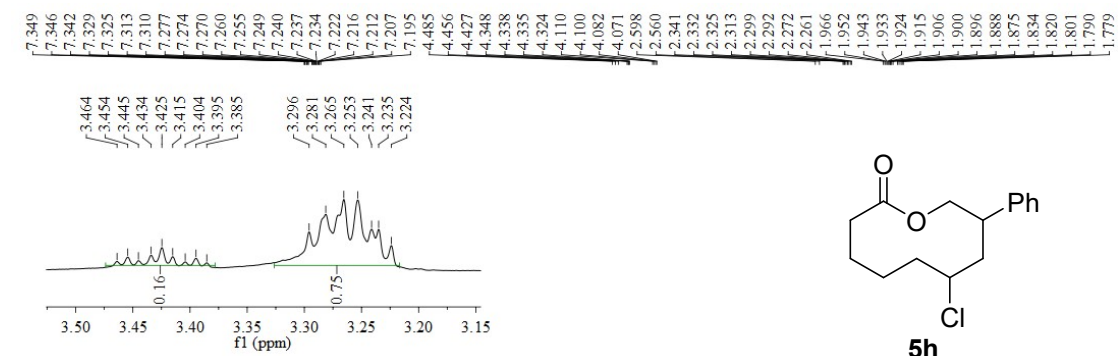
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5f**



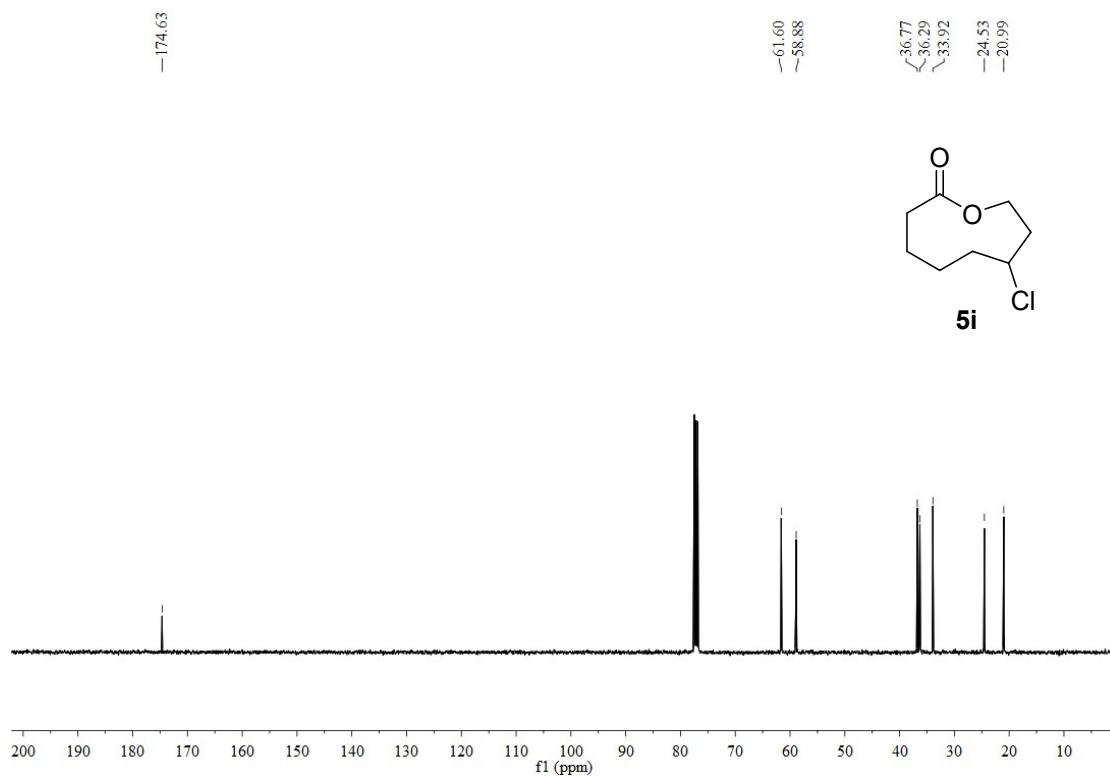
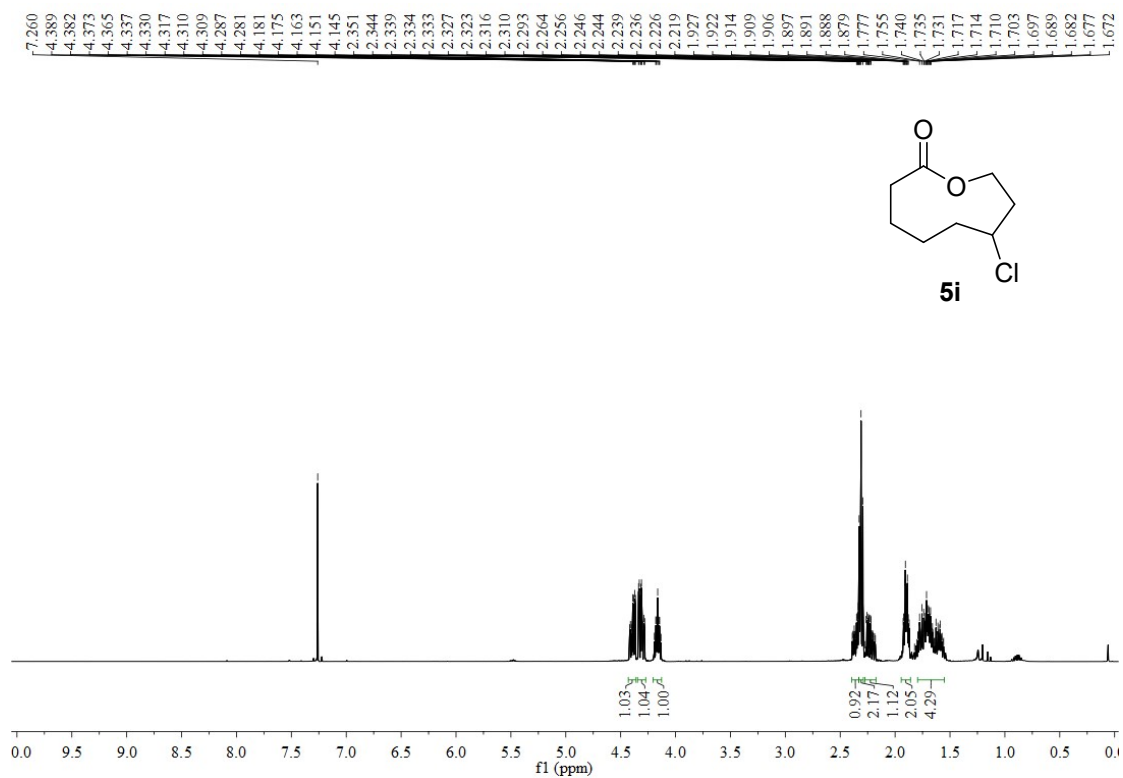
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5g**



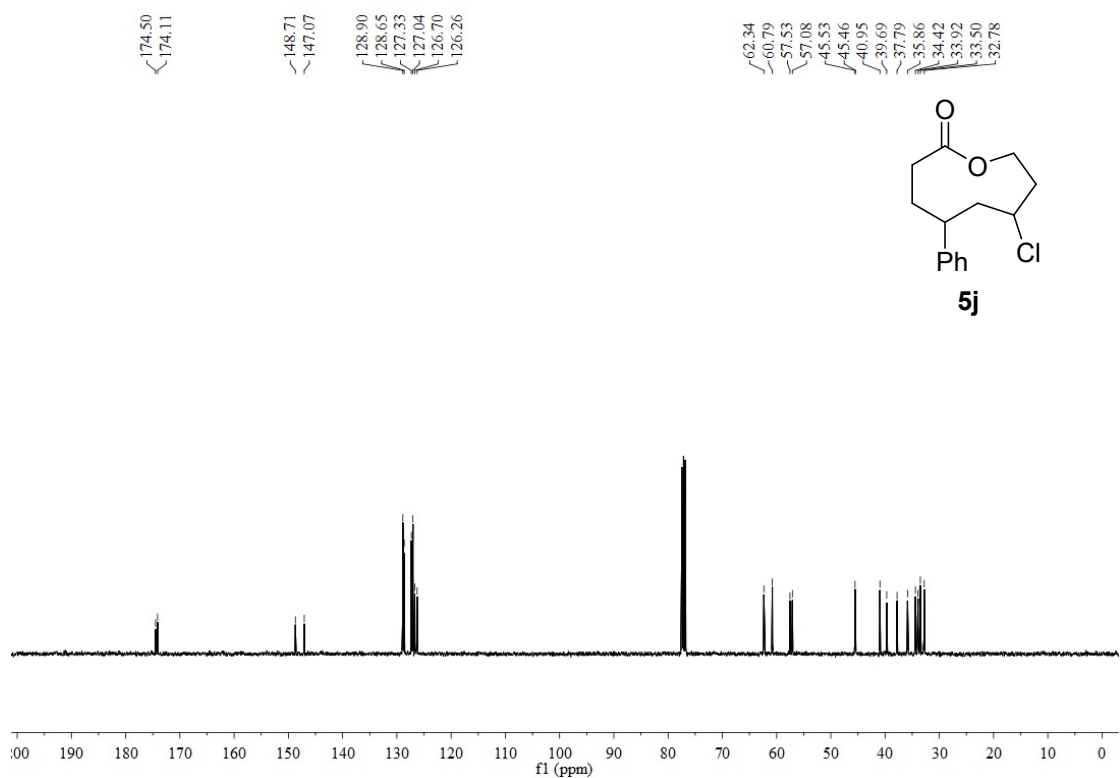
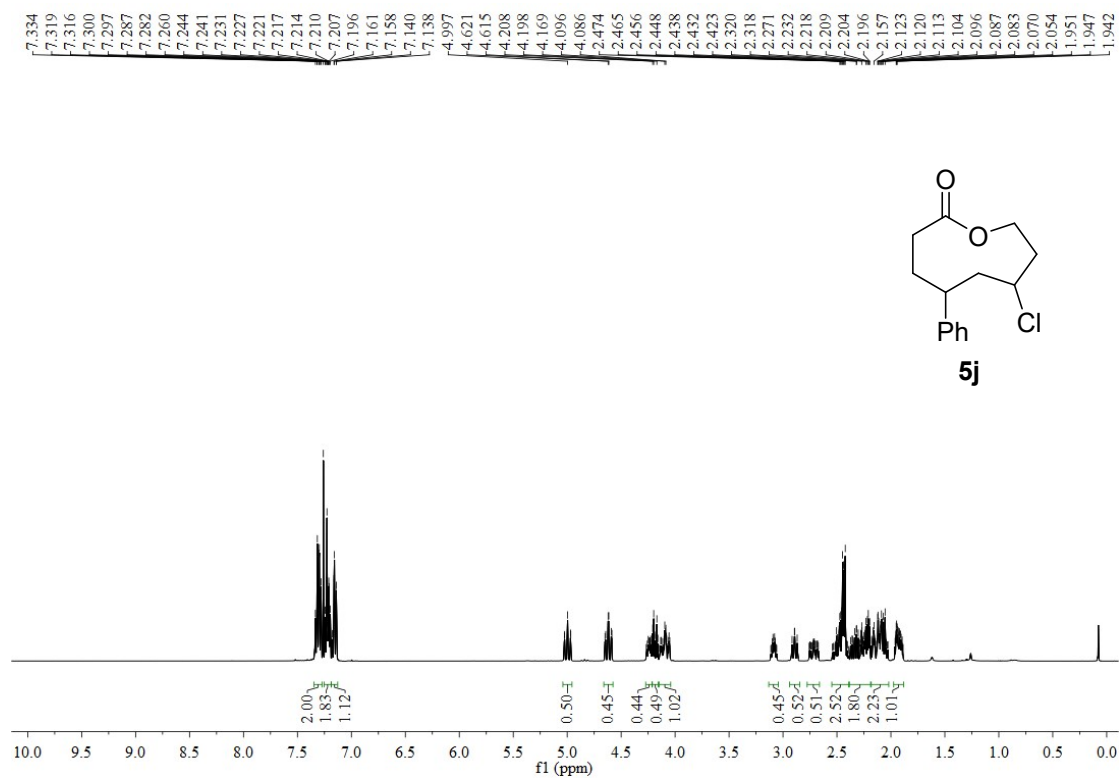
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5h**



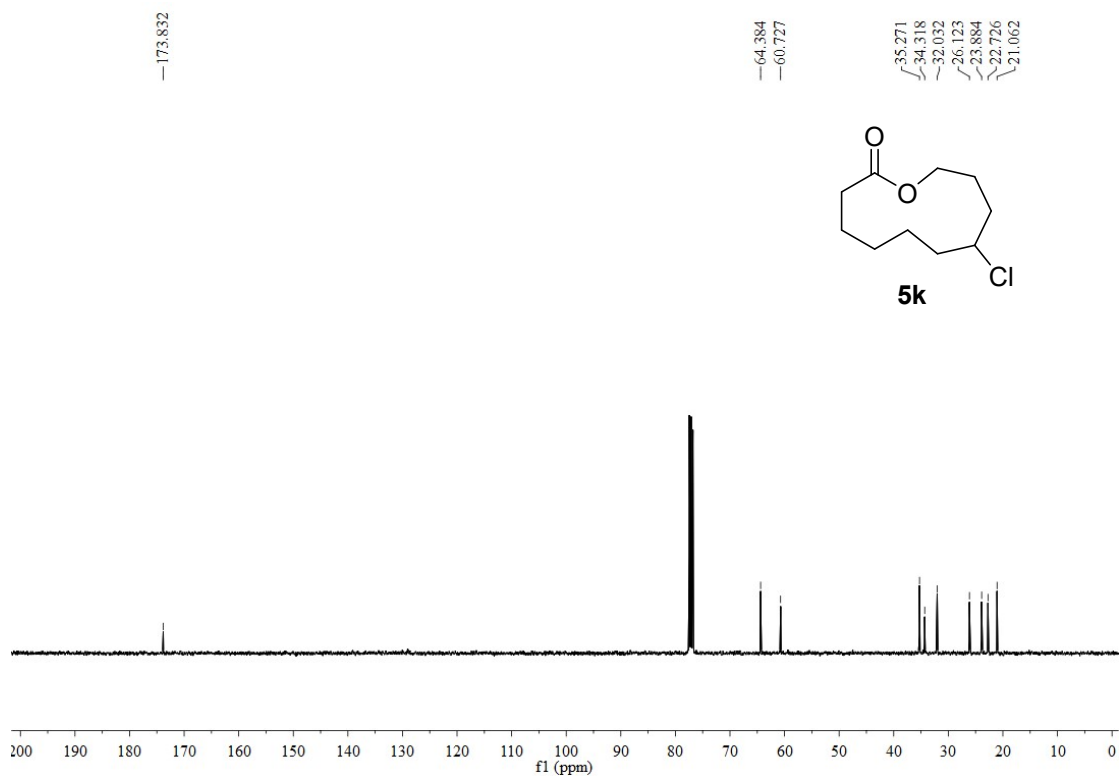
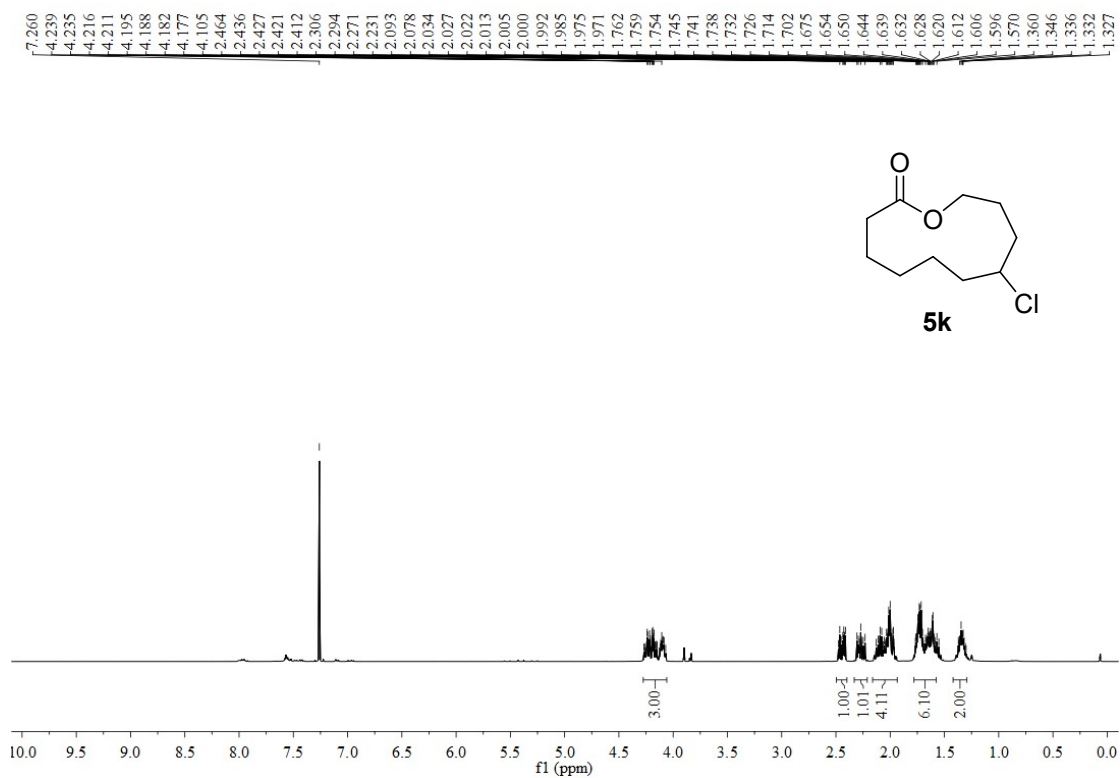
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5i**



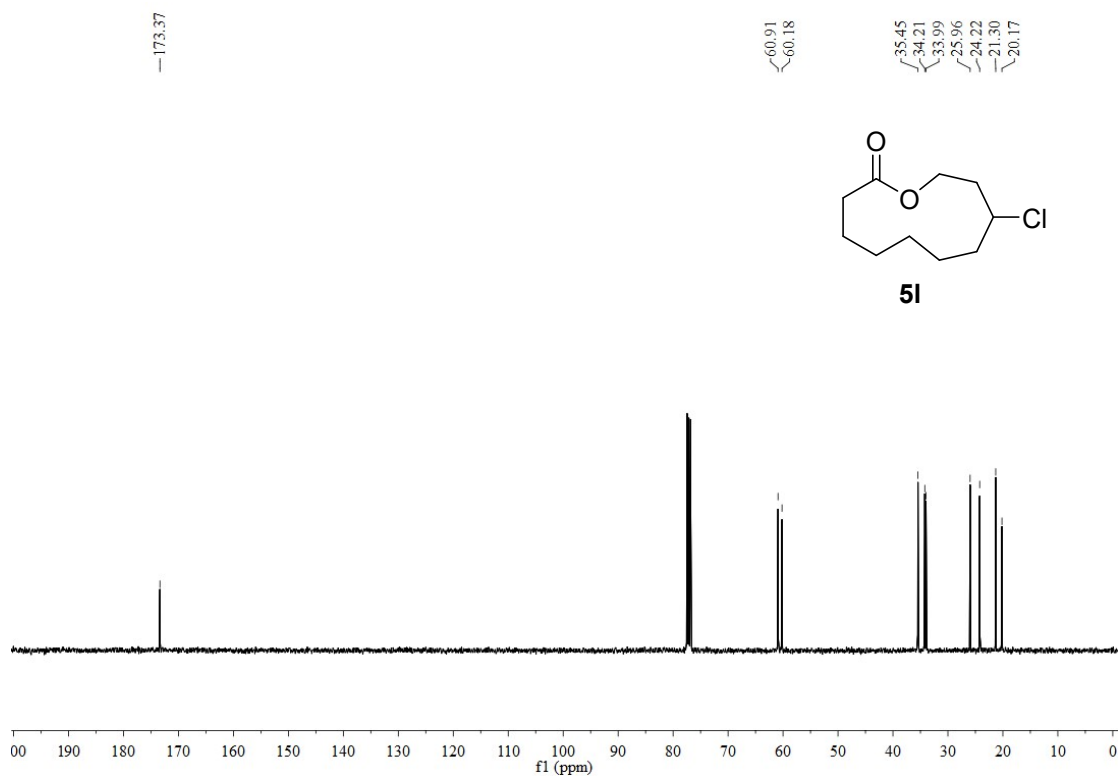
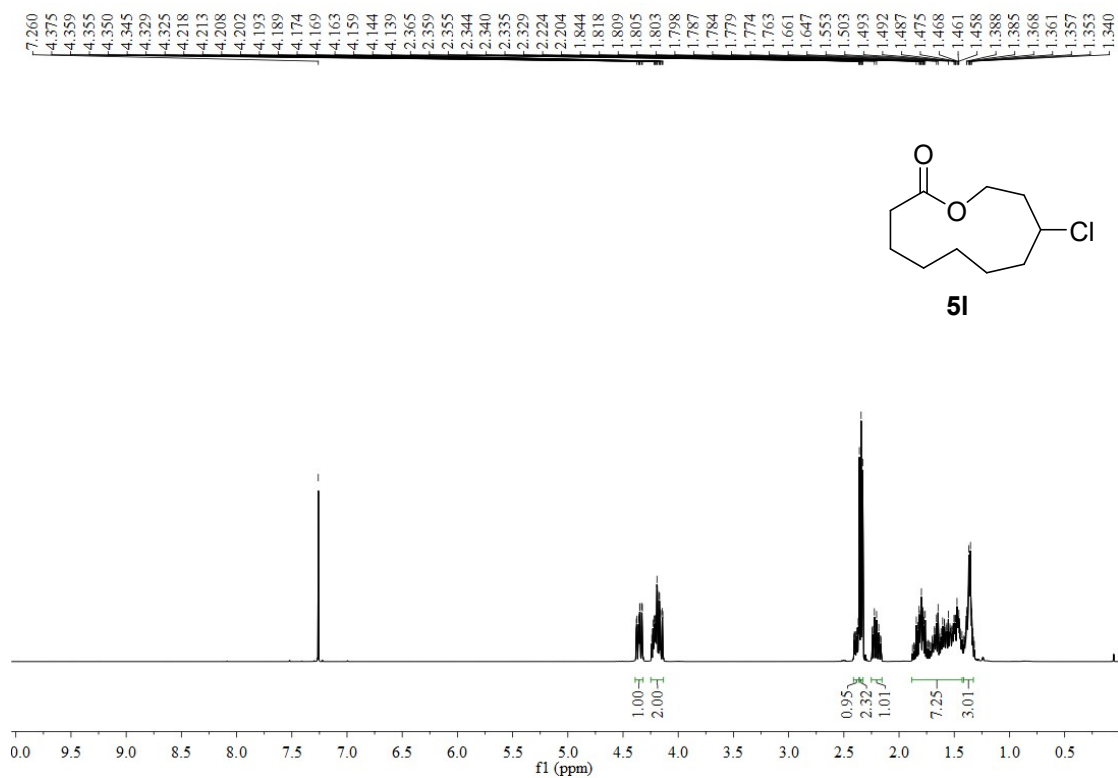
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5j**



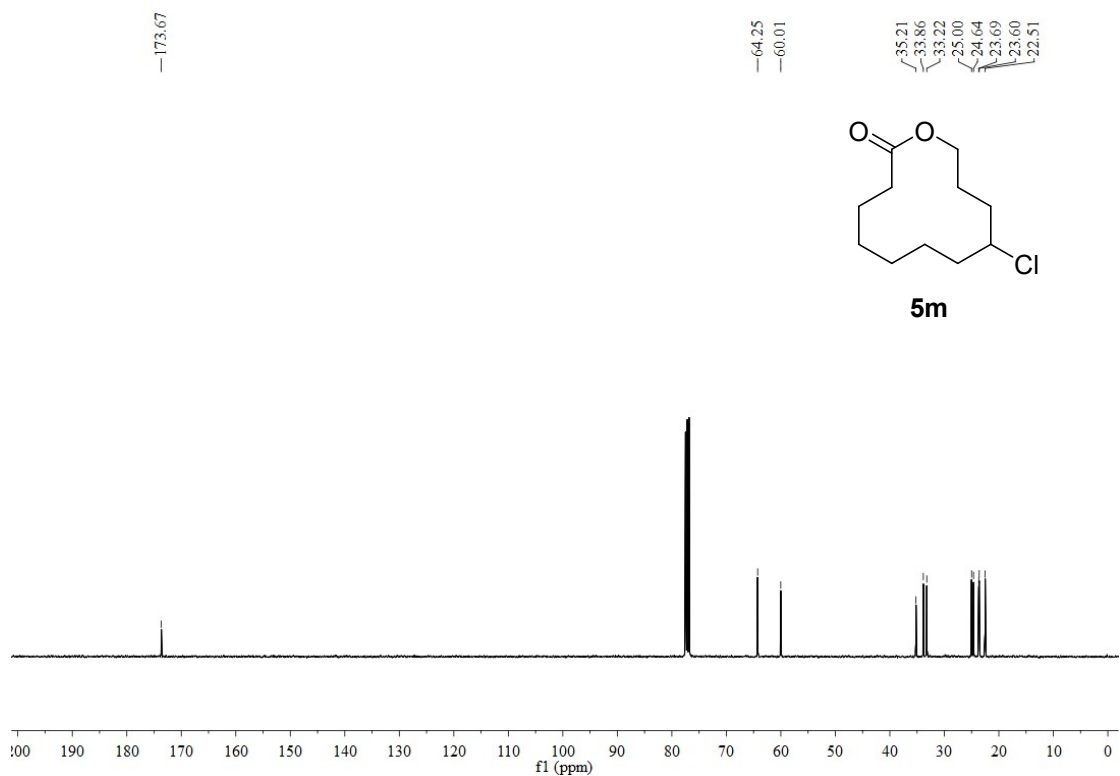
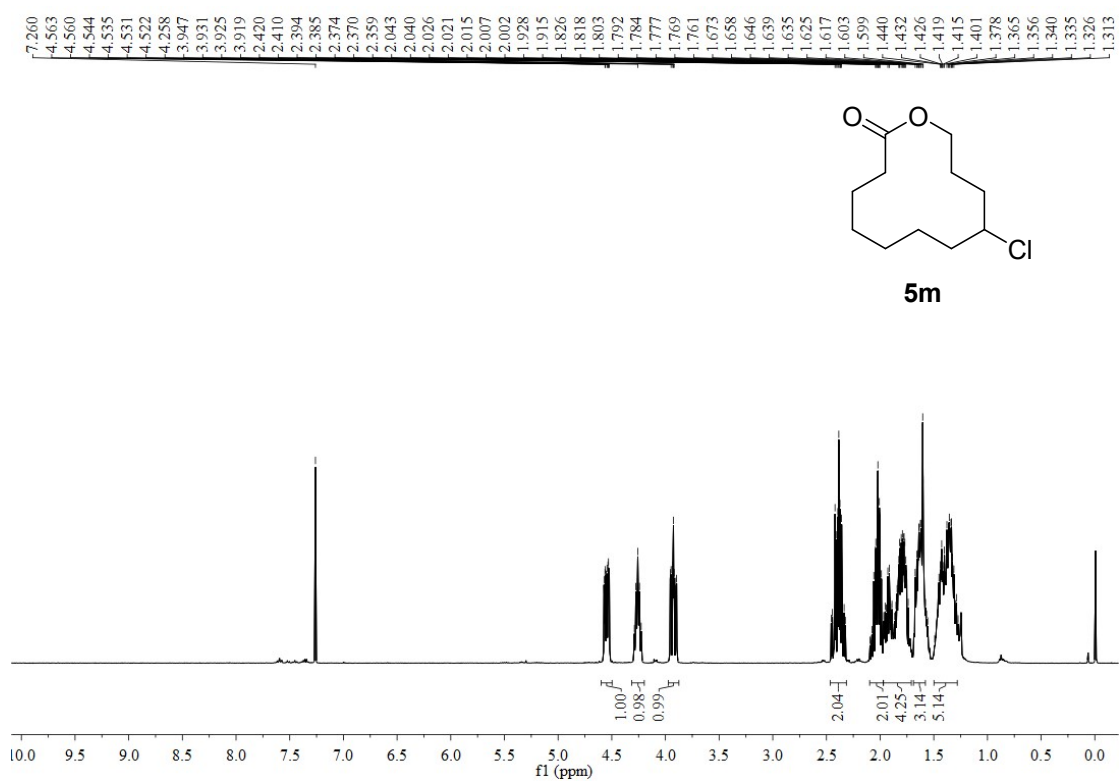
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5k**



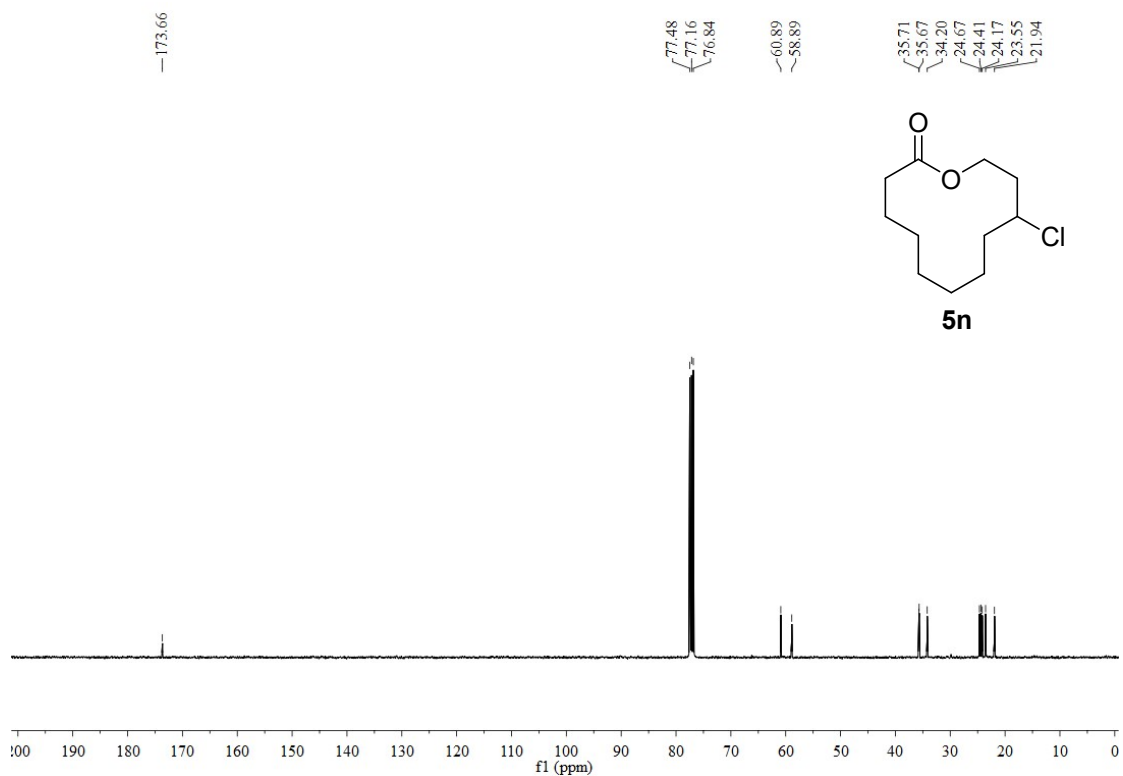
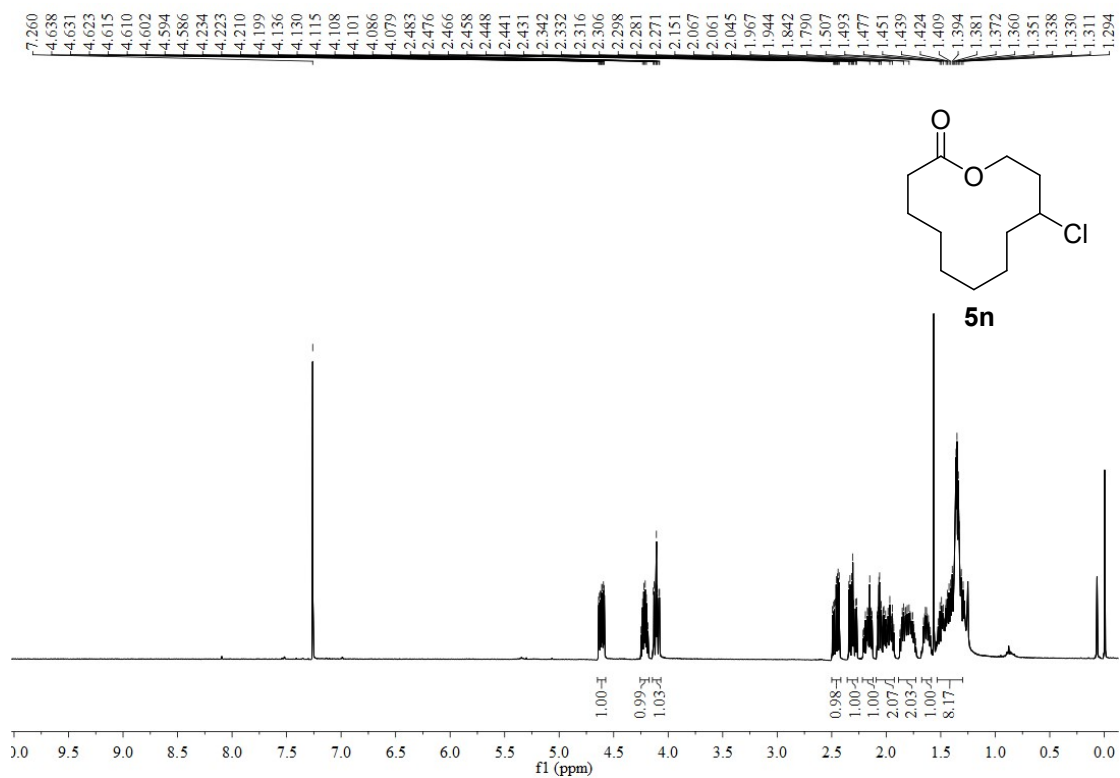
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5l**



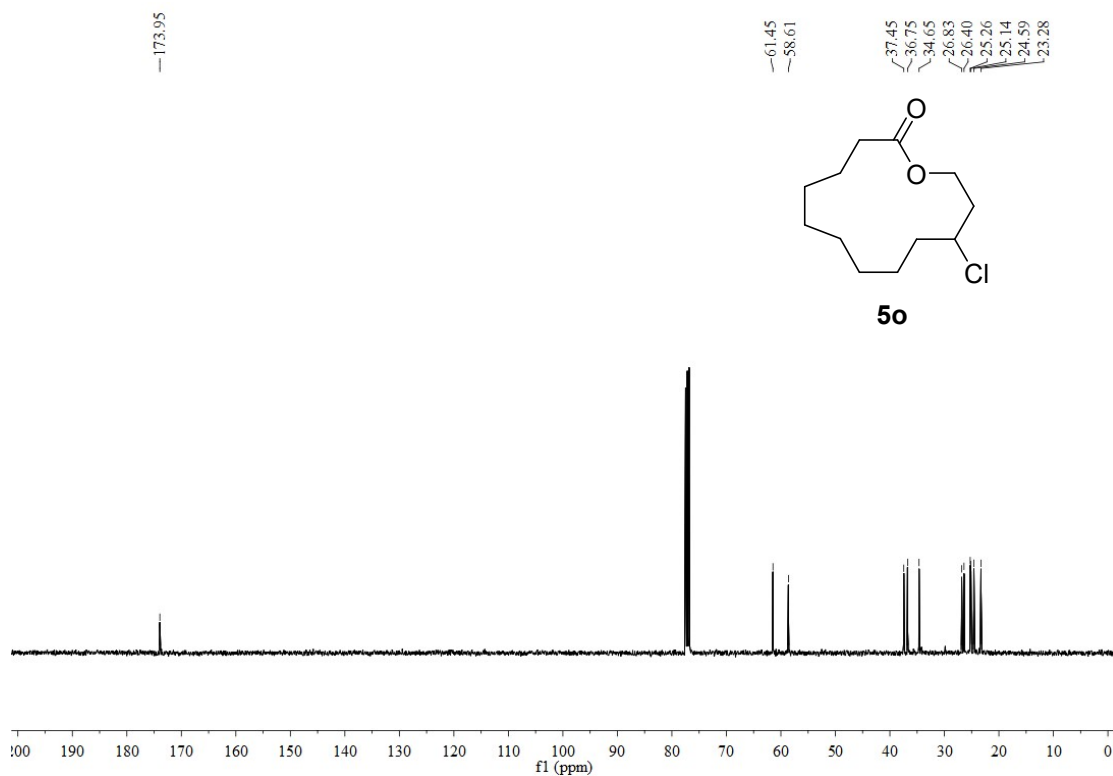
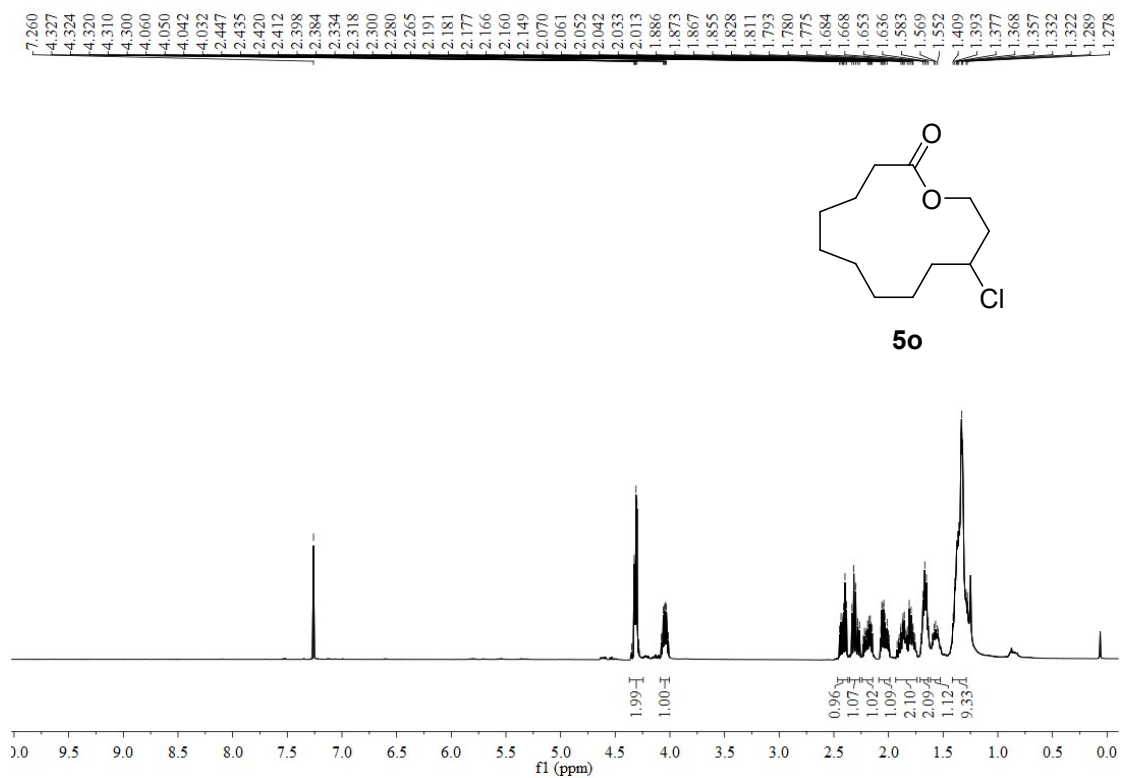
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5m**



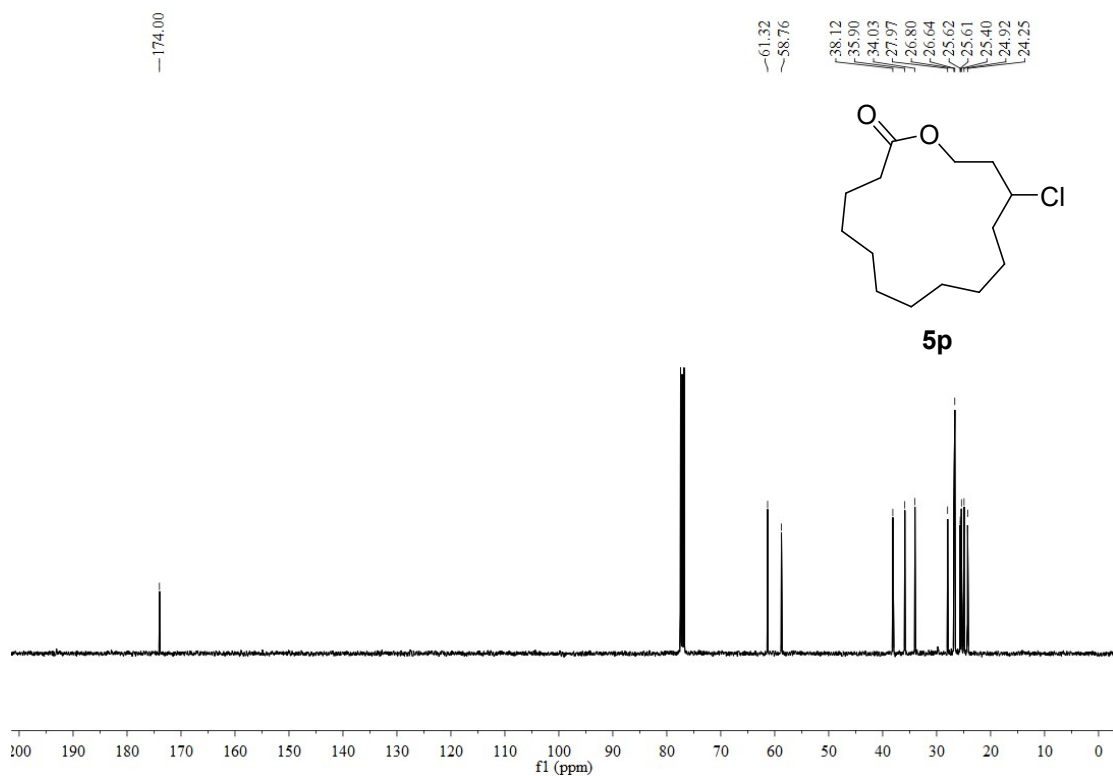
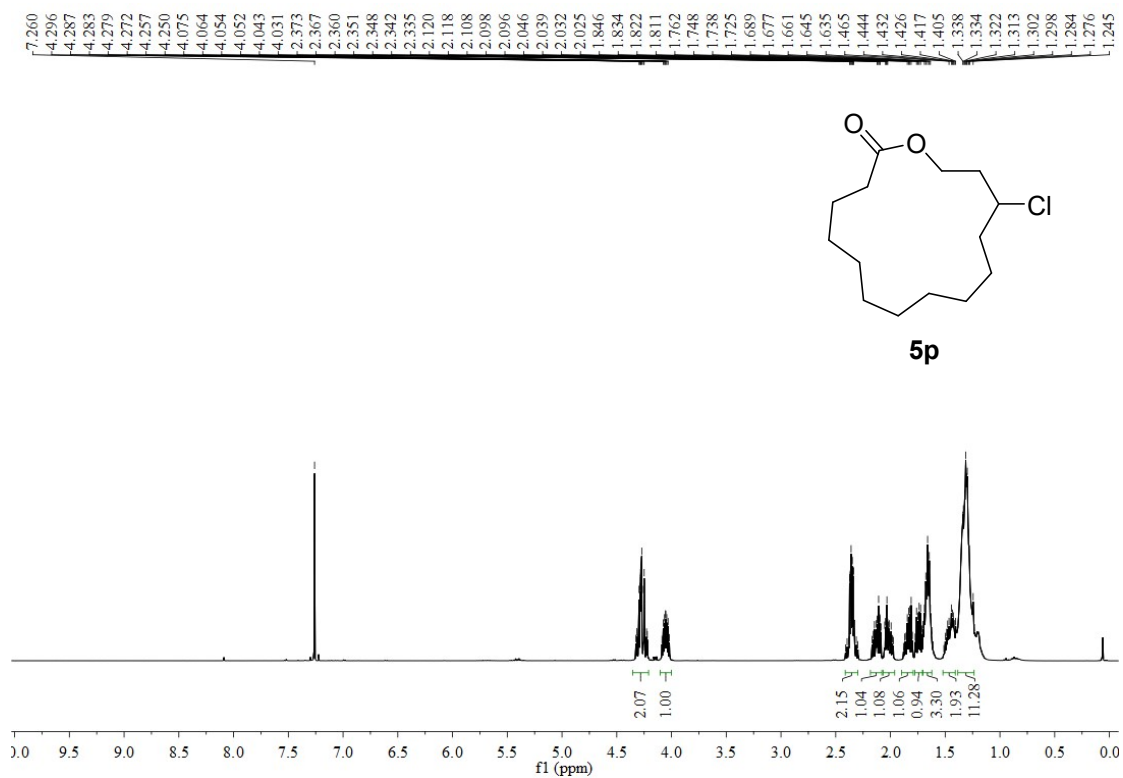
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5n**



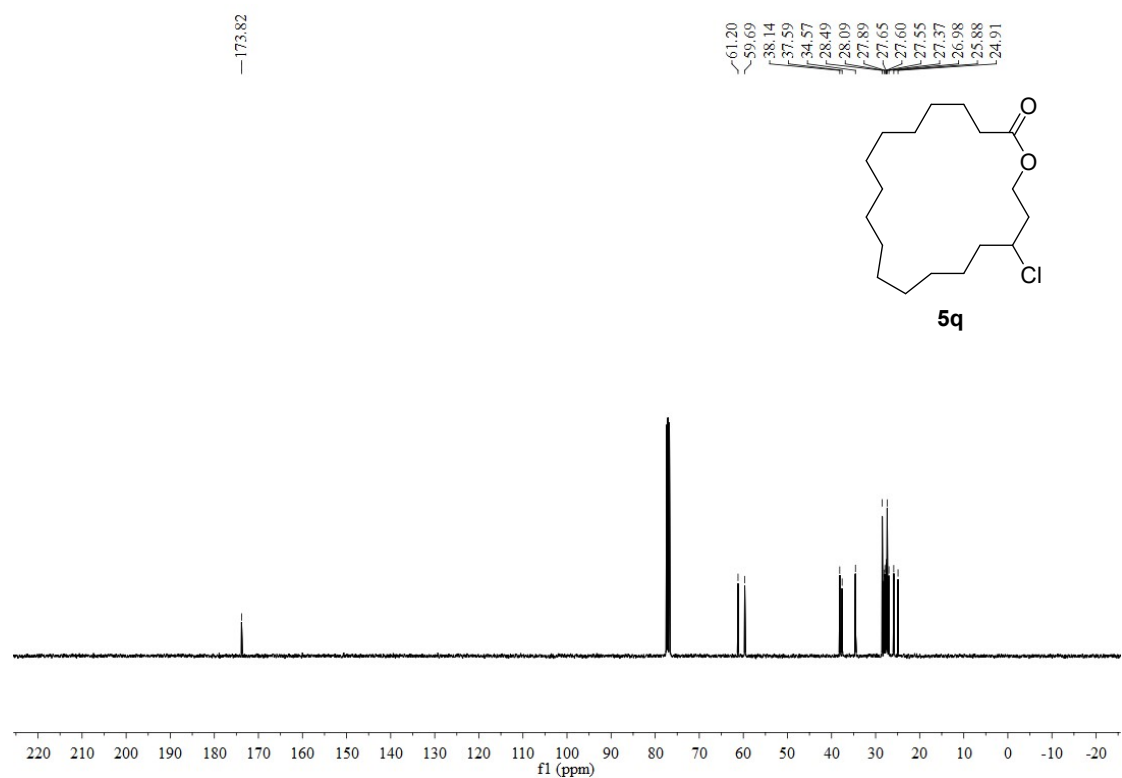
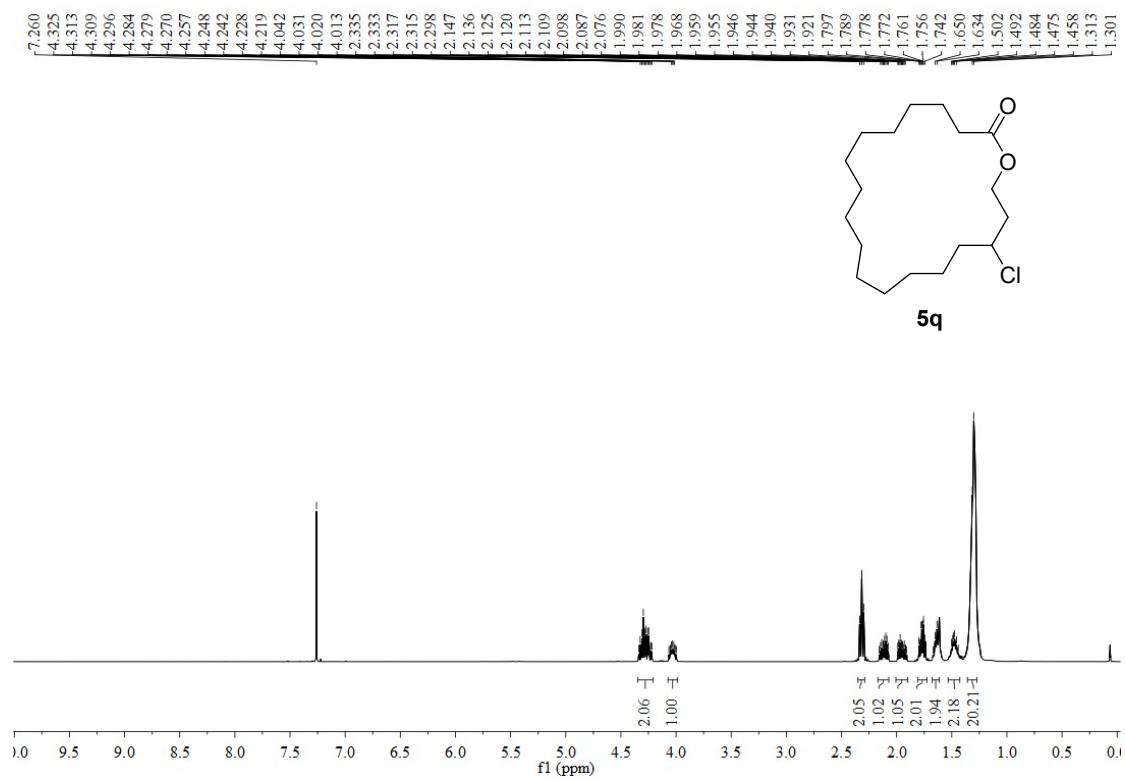
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5o**



¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5p**

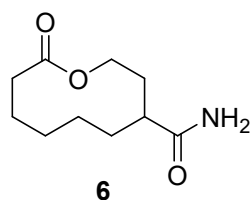
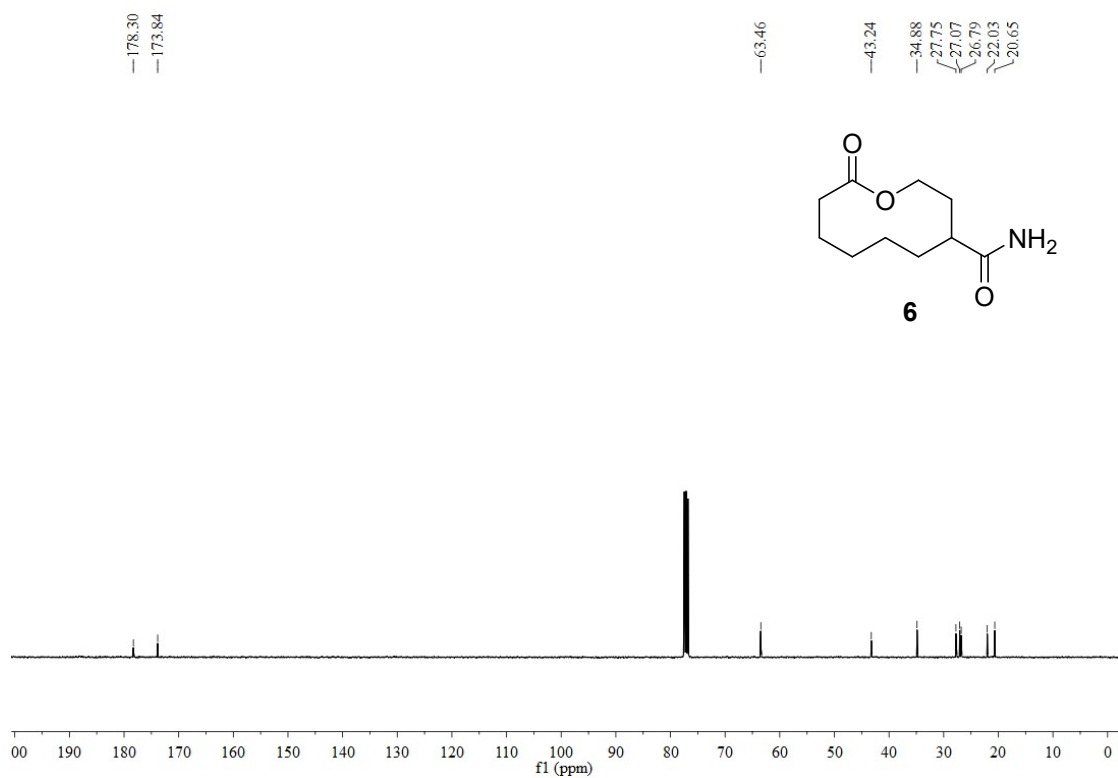
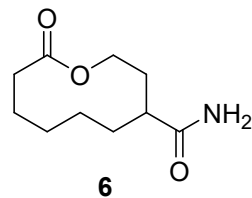
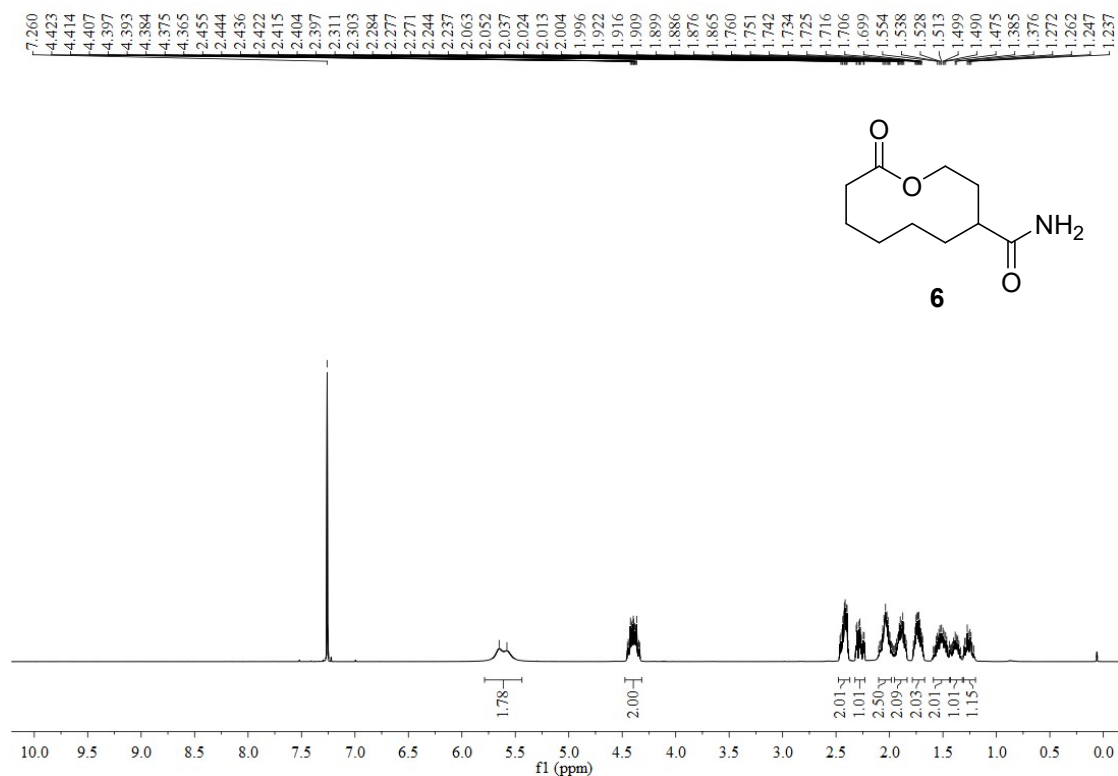


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **5q**

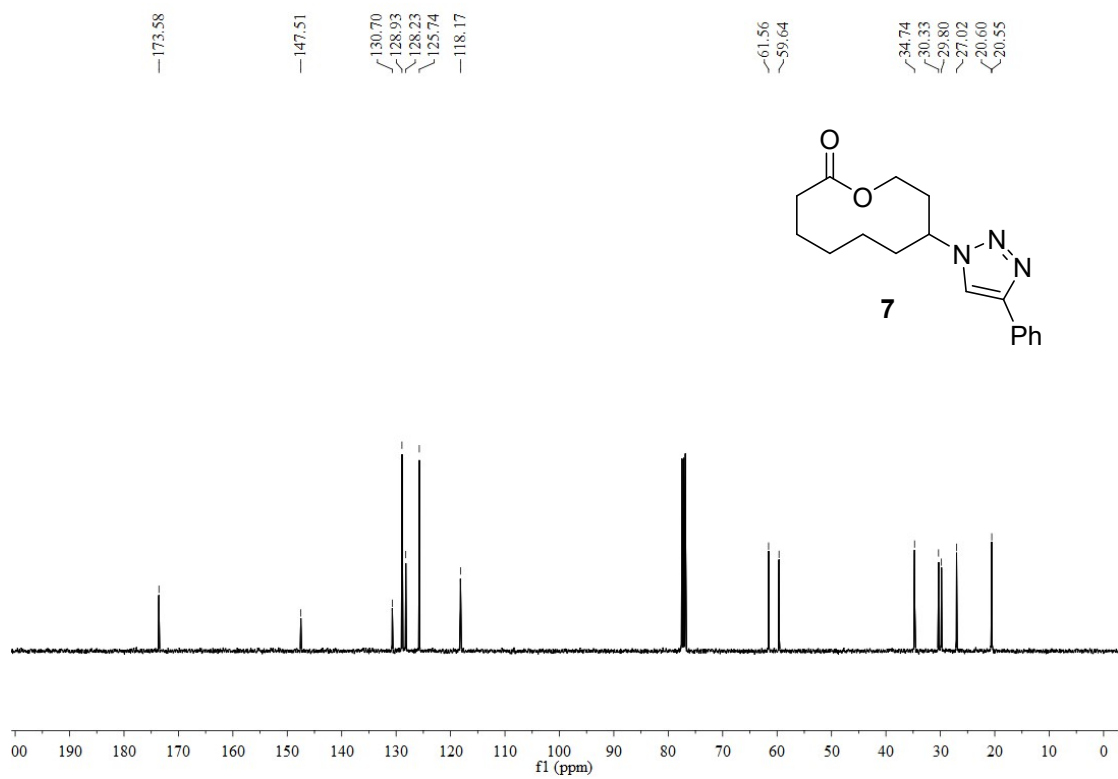
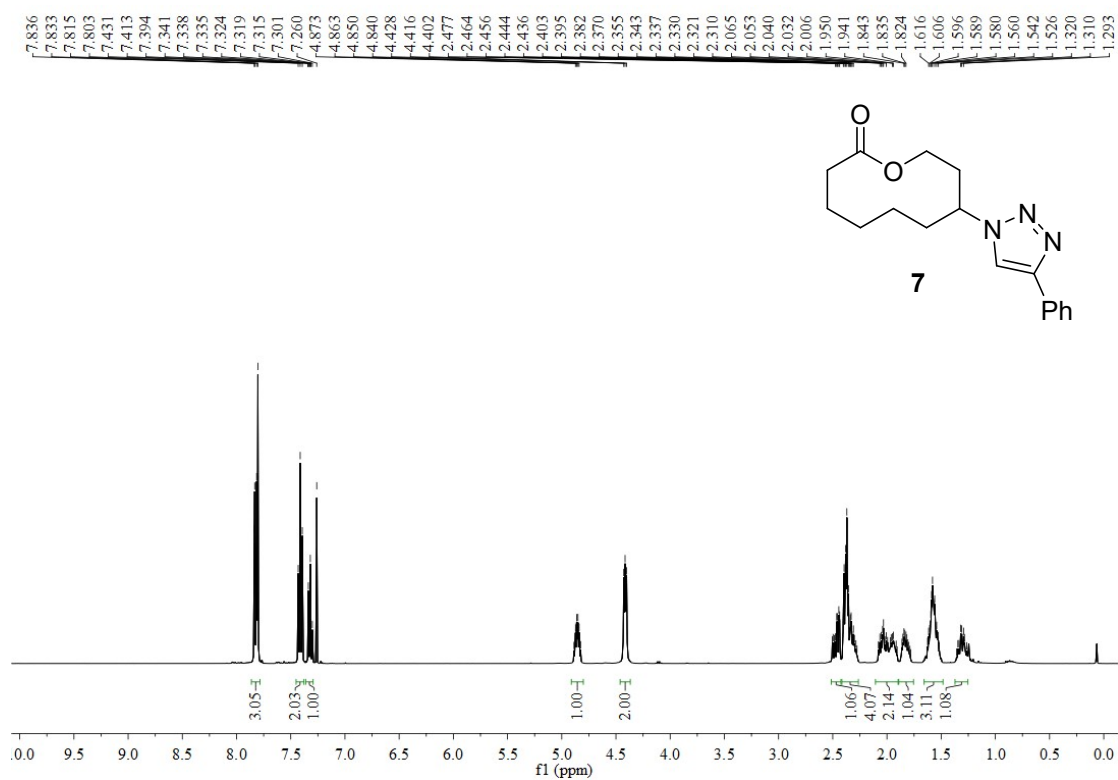


16. ^1H NMR and ^{13}C NMR Spectra of Products 6-11

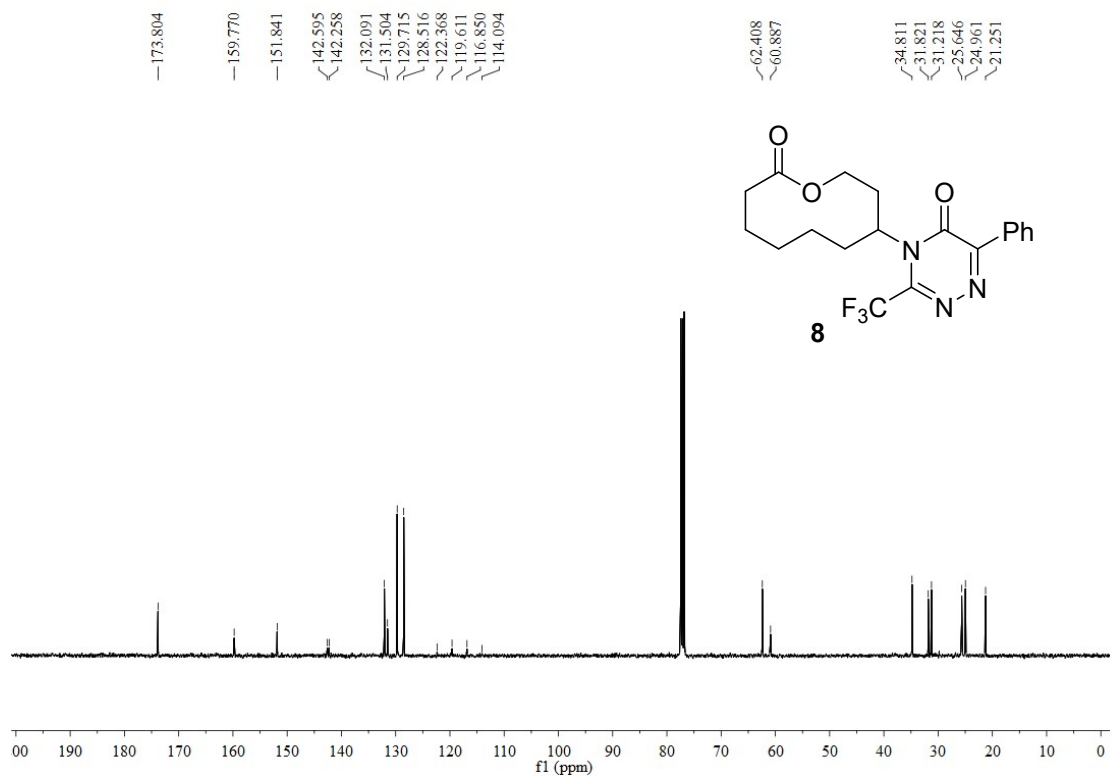
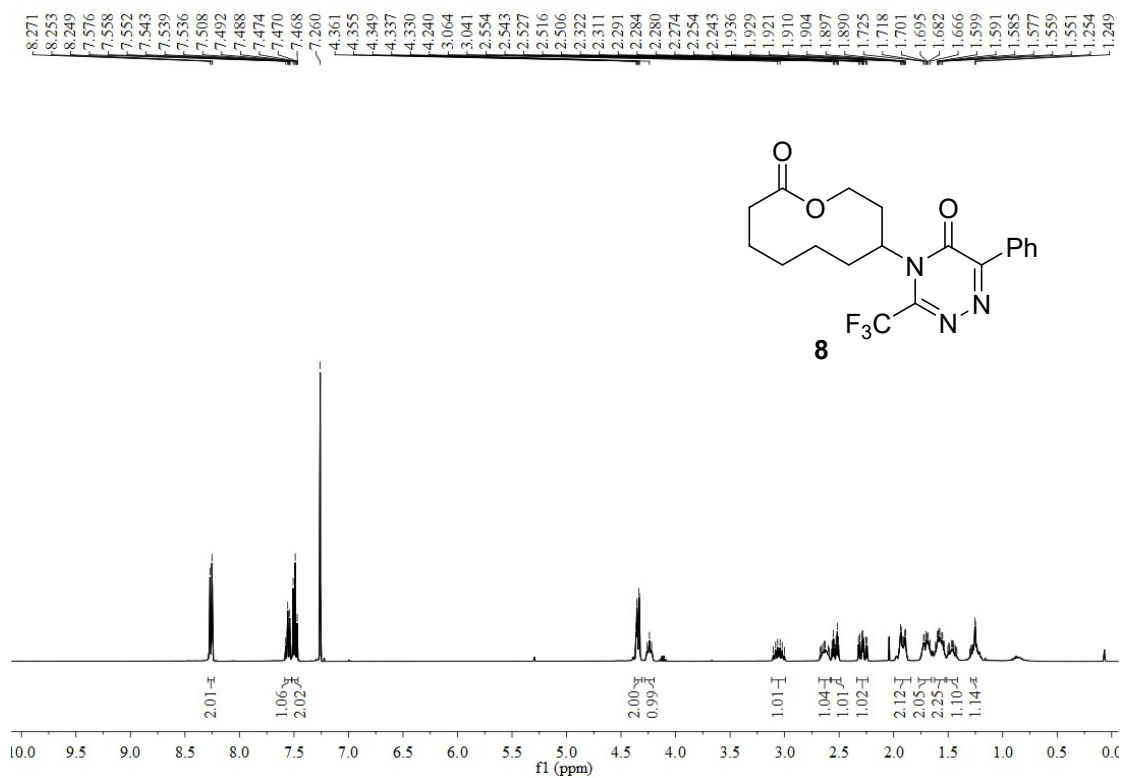
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **6**



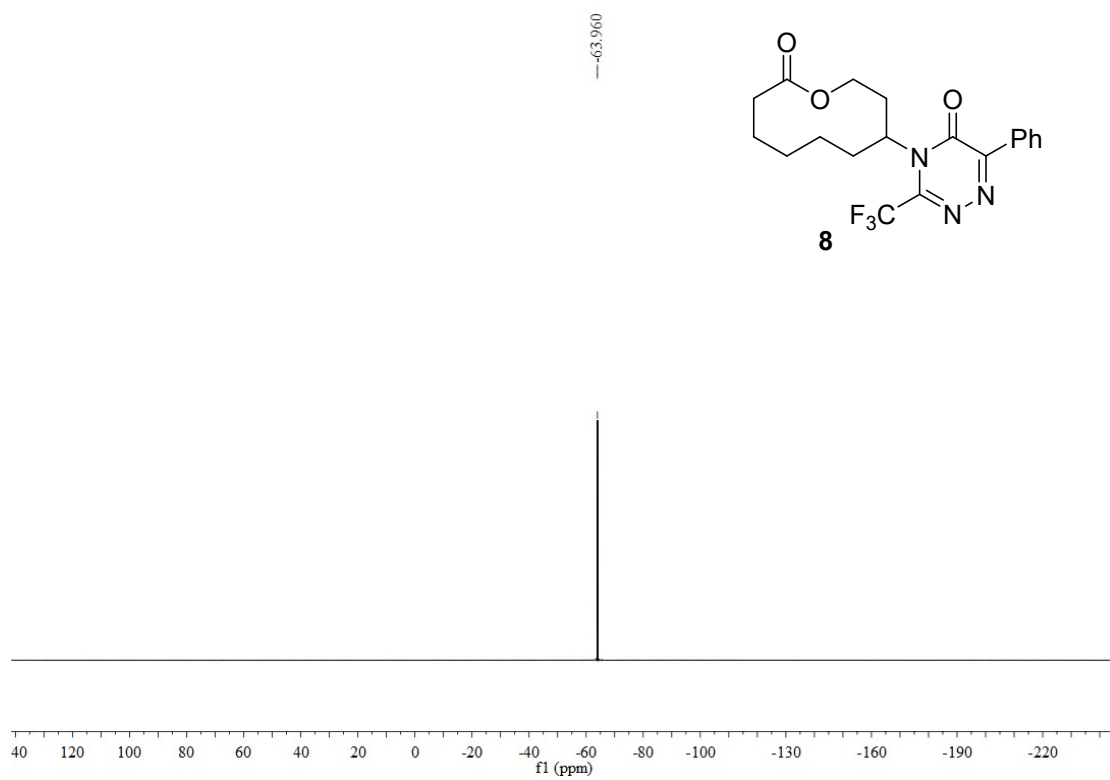
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **7**



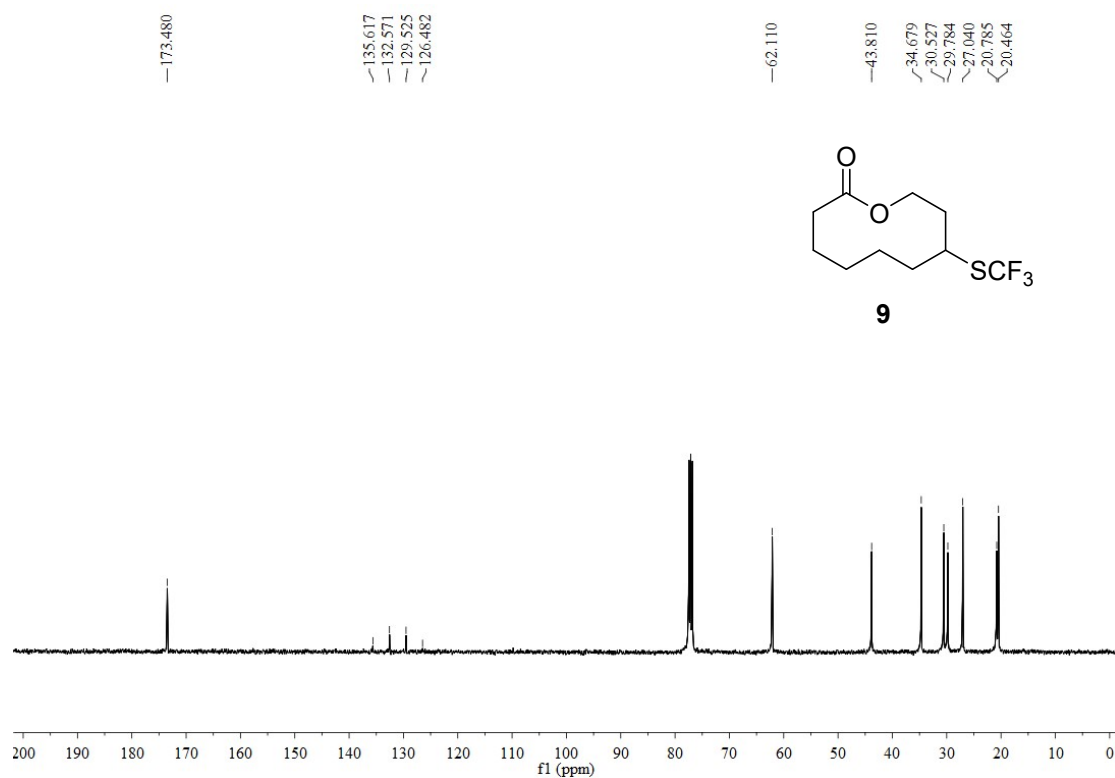
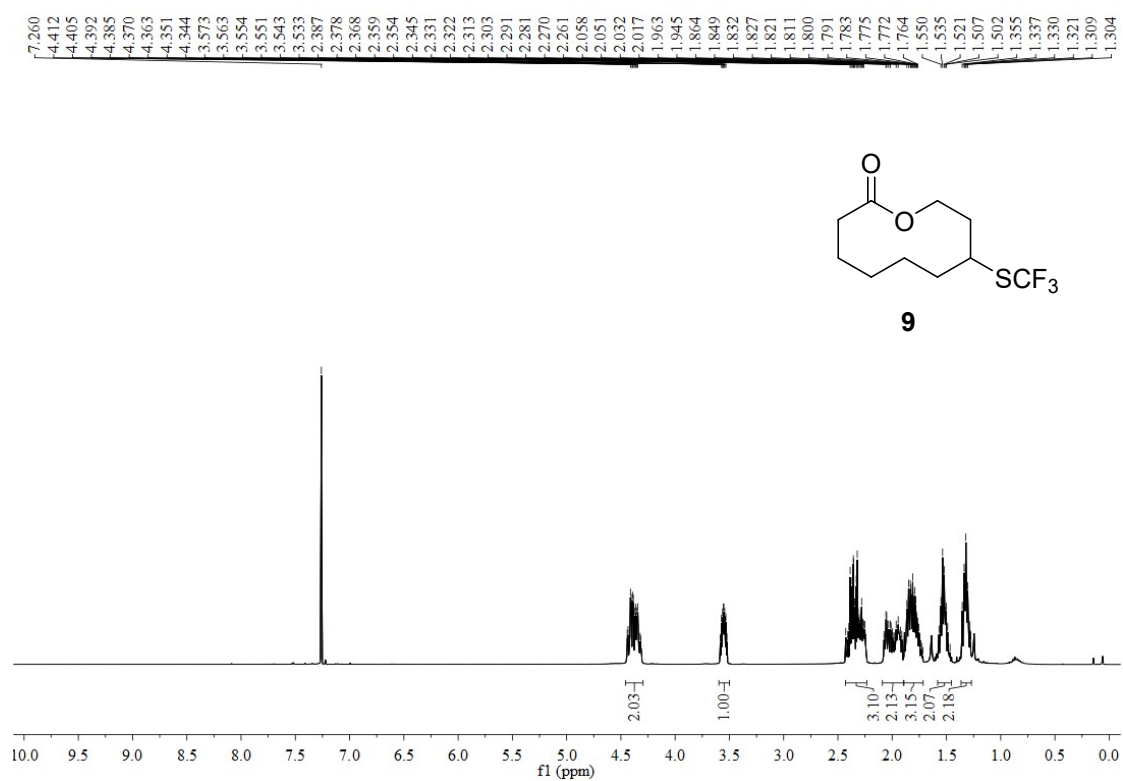
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **8**



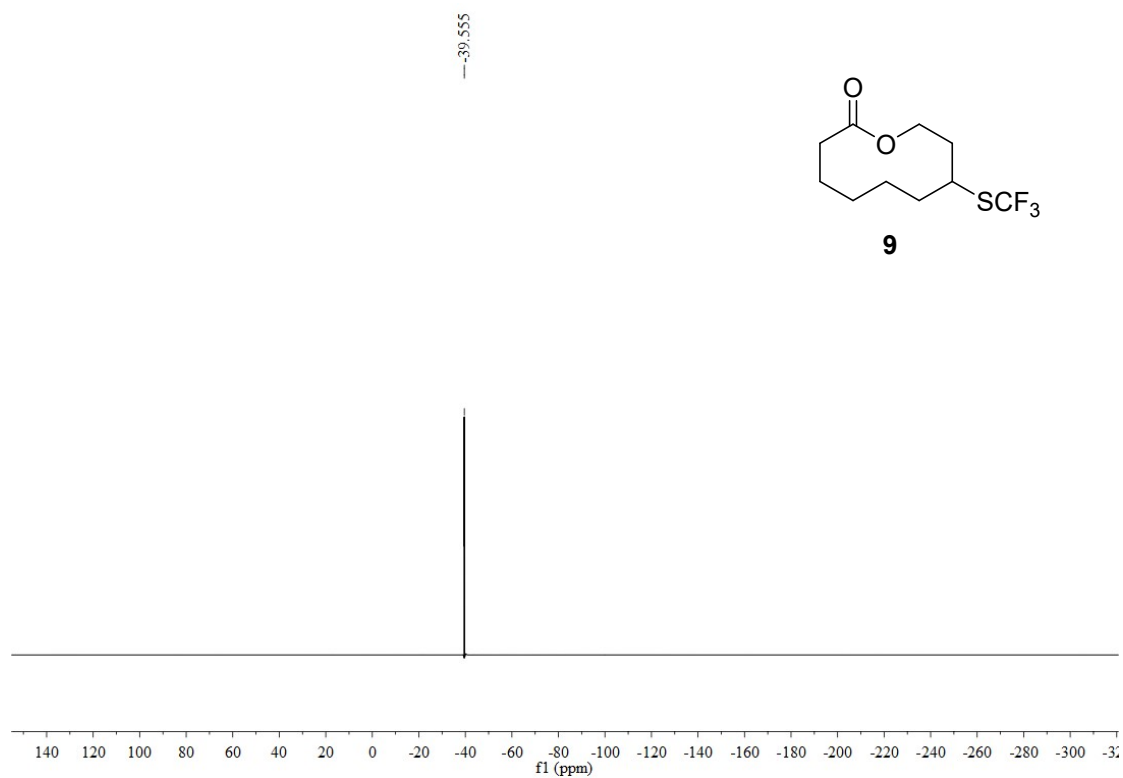
¹⁹F NMR (376 MHz, CDCl₃) spectra of product 8



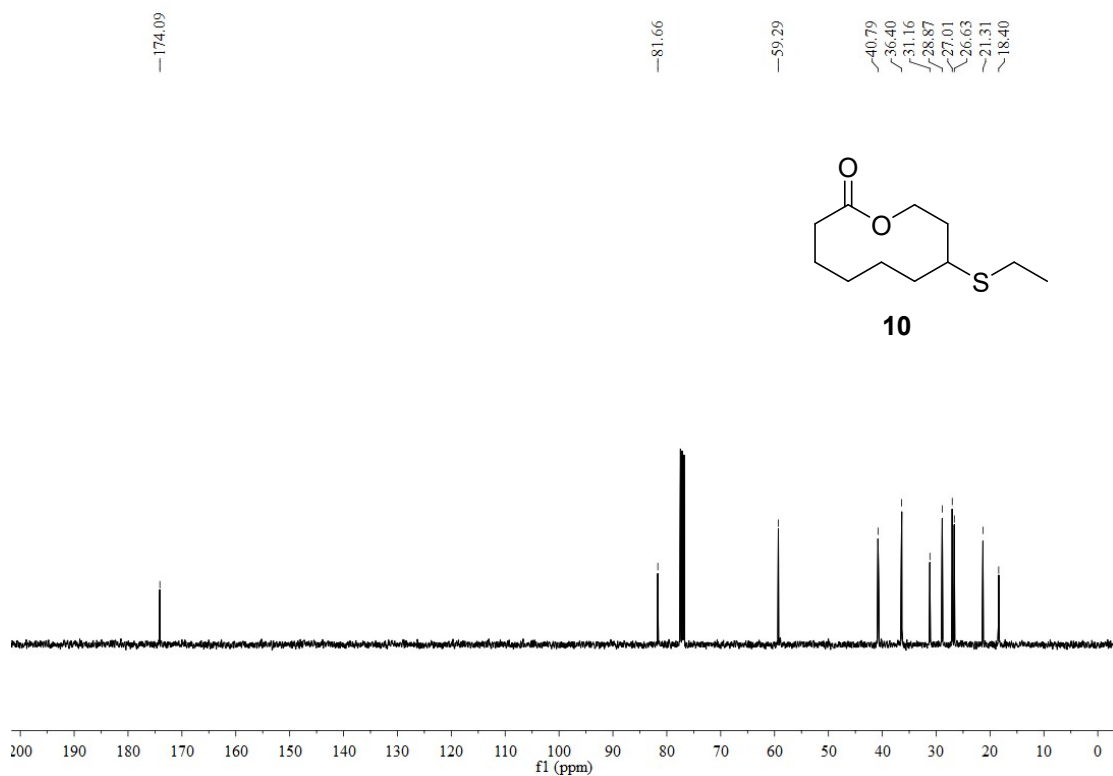
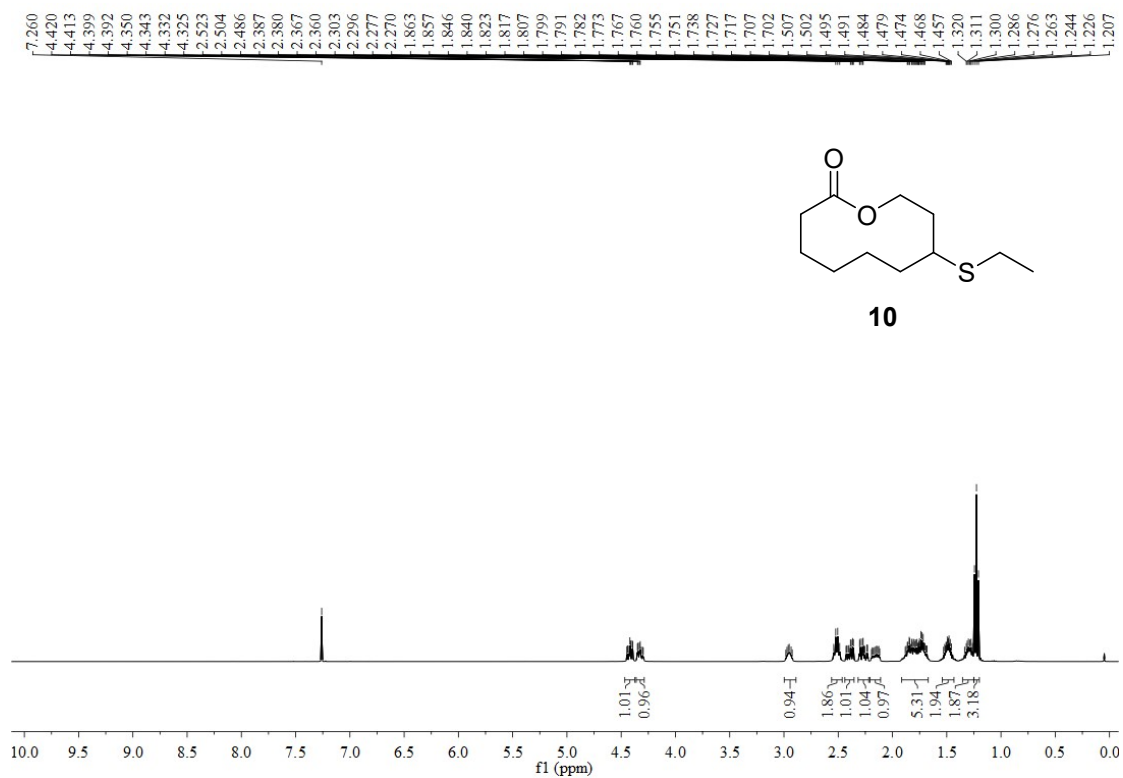
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **9**



¹⁹F NMR (376 MHz, CDCl₃) spectra of product **9**



¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **10**



¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **11**

