Supplementary Information

For

Photocatalytic organosulfur reagent-promoted selective mono-(deutero)hydrodechlorination

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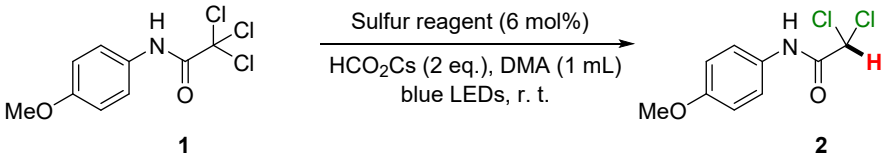
1. General Information

All of reactions were performed under an ambient temperature, magnetically stirred, and monitored by thin-layer chromatography (TLC) using Qingdao Puke Separation Materials Co., Ltd TLC plates pre-coated with 250 um thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. All of the manipulations were carried out using oven-dried glassware, including standard Schlenk techniques. All of the reagents were purchased from Alfa, Energy-Chemical or Sigma-Aldrich and used without further purification. Solvents were purified according to the method of Grubbs.[1] ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AV-400 (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, ^{19}F NMR at 376 MHz) spectrometers using tetramethylsilane (TMS) as internal standard. ^{1}H and ^{19}F multiplicities are indicated as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br). Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). High resolution massspectra (HRMS) were collected on Bruker Esquire LC mass spectrometer using electrospray ionization. Flash column chromatography was carried out on silica gel (particle size 300-400 mesh) and eluted with petroleum/ethyl acetate.

2. Optimization of reaction conditions.

2.1 Hydrodechlorination optimization.

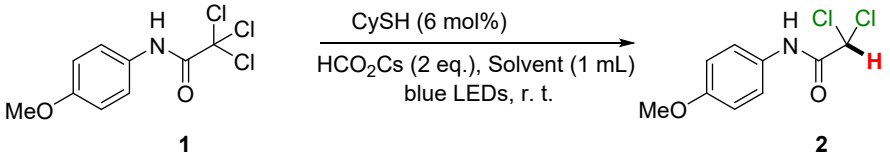
Table S1. Sulfur reagent Screening.[a,b]



Entry	Sulfur reagent	Base	Solvent	Conversion(%)	Y(%)[b]
1	CySH	HCO_2Cs	DMA	100	70
2	4-Methoxythiophenol	HCO_2Cs	DMA	72	19
3	BnSH	HCO_2Cs	DMA	79	66
4	4-SH-Py	HCO_2Cs	DMA	66	3
5	^{n}BuSH	HCO_2Cs	DMA	89	43

[a]Reaction conditions: Sulfur reagent (6 mol%), **1a** (0.1 mmol, 1.0 equiv), HCO_2Cs (2 equiv.), DMA (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs. [b]isolated yields are shown.

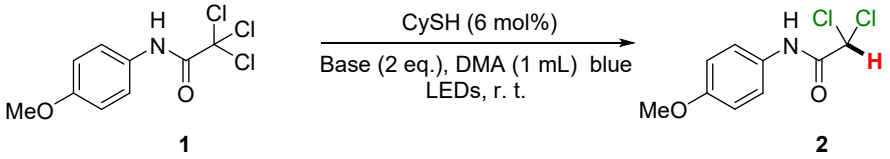
Table S2.Solvent Screening.[a,b]



Entry	Sulfur reagent	Base	Solvent	Y(%)[b]
1	CySH	HCO_2Cs	DMSO	45
2	CySH	HCO_2Cs	DMF	41
3	CySH	HCO_2Cs	DMA	70
4	CySH	HCO_2Cs	CH_3CN	10
5	CySH	HCO_2Cs	CH_3OH	0
6	CySH	HCO_2Cs	EA	0
7	CySH	HCO_2Cs	1,4-Dioxane	0
8	CySH	HCO_2Cs	CF_3CH_2OH	0
9	CySH	HCO_2Cs	THF	0
10	CySH	HCO_2Cs	DCM	0
11	CySH	HCO_2Cs	DCE	0

[a]Reaction conditions: CySH (6 mol%), **1a** (0.1 mmol, 1.0 equiv), HCO_2Cs (2 equiv.), Solvent (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs. [b]isolated yields are shown.

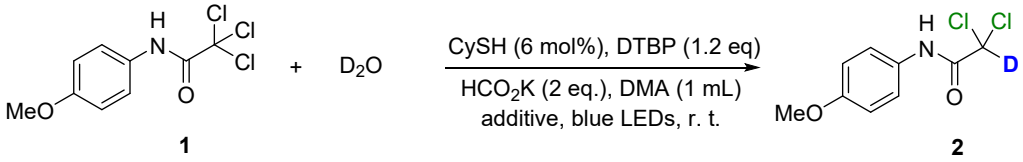
Table S3. Base Screening.[a,b]



Entry	Sulfur reagent	Base	Solvent	Y(%)[b]
1	CySH	HCO_2Cs	DMA	70
2	CySH	HCO_2Na	DMA	74
3	CySH	HCO_2K	DMA	93
4	CySH	HCO_2NH_4	DMA	84

[a]Reaction conditions: Sulfur reagent (6 mol%), **1a** (0.1 mmol, 1.0 equiv), HCO_2Cs (2 equiv.), DMA (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs. [b]isolated yields are shown.

2.2 Deuterodechlorination optimization.

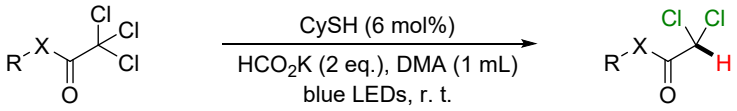


Entry	Sulfur reagent	Base	Additive		Solvent	Y(%)[b]	Deuterated incorporation(%)
1	CySH	HCO_2K	1,3-Bis(diphenylphosphino)propane	DTBP	DMA	80	86
2	CySH	HCO_2K	Ph_3P	DTBP	DMA	80	80
3	CySH	HCO_2K	Ph_2POEt	DTBP	DMA	77	64
4	CySH	HCO_2K	PCy_3	DTBP	DMA	67	95
5	CySH	HCO_2K	$ClPPh_2$	DTBP	DMA	0	0
6	CySH	HCO_2K	$P(OMe)_3$	DTBP	DMA	43	25
7	CySH	HCO_2K	PCy_3	/	DMA	58	72
8	CySH	HCO_2K	/	DTBP	DMA	67	72
9	CySH	/	PCy_3	DTBP	DMA	36	85
10	/	HCO_2K	PCy_3	DTBP	DMA	19	87
11	CySH	HCO_2K	/	/	DMA	89	65

[a]Reaction conditions: CySH (6 mol%), **1a** (0.1 mmol, 1.0 equiv), HCO_2K (2 equiv.), DMA (1 mL), room temperature, N_2 atmosphere, 12*2 W blue LEDs. [b]isolated yields are shown.

3. General Procedure for (deutero)hydrodechlorination Reactions

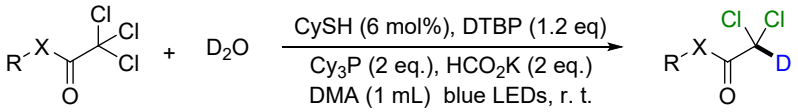
General procedure for hydrodechlorination A:



1 **2**, **3**

In a 10 mL Schlenk tube with a stirring bar**,** **1** (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired products. The reaction set-up with blue LEDs (2*12 W, Manufacturer: ouying, Model: 5317 (blue), WLP: 459.1 nm, Φ: 436.9 lm, Tc: 25000 K) as the light source. The irradiation vessel was in the middle of the two spotlights, approximate 7 cm to the light source.

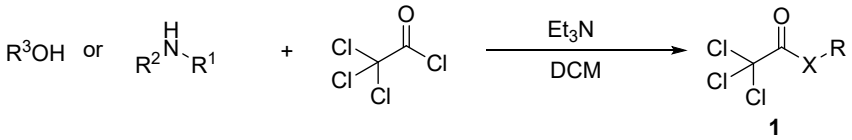
General procedure for deuterodechlorination B:



1 **3**

In a 10 mL Schlenk tube with a stirring bar**,** **1** (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol)， Cy_3P (0.2 mmol), DTBP (1.2 eq.) were dissolved in DMA (1.0 mL), and then D_2O (50 eq.) was added to the reaction mixture. The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired products. The reaction set-up with blue LEDs (2*12 W, Manufacturer: ouying, Model: 5317 (blue), WLP: 459.1 nm, Φ: 436.9 lm, Tc: 25000 K) as the light source. The irradiation vessel was in the middle of the two spotlights, approximate 7 cm to the light source.

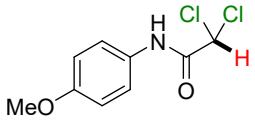
4. General procedure for the synthesis of substrates.



1

Amine or alcohol (1.0 equiv.), Et_3N (2 equiv.) were dissolved in DCM (0.2 M). And Trichloroacetyl chloride (1.1 equiv.) was added in dropwise at 0 °C. After addition, the reaction mixture was stirred at room temperature for 12 hours[1]. After the material was completed consumed, 10 mL saturated NH_4Cl was added in the reaction mixture, and extracted with DCM (20 mL*3), the combine solvents was washed with brine (30 mL), dried over $MgSO_4$. The solvent was concentrated and purification by chromatography on silica gel to afford the desired substrates.

5. Product Characterization



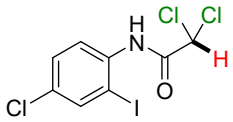
2a

The reaction was performed according to the general procedure A using **1a** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2a** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2a** in 93% yield, colorless oil, 21.7 mg.

^{1}H NMR (400 MHz,$CDCl_3$): δ_H 8.08 (s, 1H), 7.48-7.43 (m, 2H), 6.93 -6.87 (m, 2H), 6.04 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.8, 157.6, 129.3, 122.2, 114.5, 67.0, 55.6.

HRMS (ESI): calcd for $C_9H_{10}Cl_2NO_2^+$, $(M+H)^+$, 234.0083, found, 234.0079.



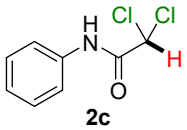
2b

The reaction was conducted according to the general procedure A using **1b** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2b** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2b** in 50% yield, colorless oil, 18.2 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.60 (s, 1H), 8.13 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 2.3 Hz, 1H), 7.38 (dd, J = 8.9, 2.4 Hz, 1H), 6.06 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.1, 138.4, 135.8, 131.5, 129.7, 122.3, 90.2, 67.0.

HRMS (ESI): calcd for $C_8H_6Cl_3INO^+$, $(M+H)^+$, 363.8554, found, 363.8560.



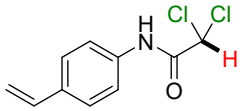
2c

The reaction was conducted according to the general procedure A using **1c** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2c** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2c** in 76% yield, colorless oil, 15.5 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.16 (s, 1H), 7.58- 7.53 (m, 2H), 7.42 -7.35 (m, 2H), 7.24 -7.18 (m, 1H), 6.05 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$):δ_C 161.9, 136.4, 129.4, 125.9, 120.4, 67.0.

HRMS (ESI): calcd for $C_8H_8Cl_2NO^+$, $(M+H)^+$, 203.9977, found, 203.9976.

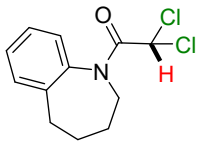


2d

The reaction was conducted according to the general procedure A using **1c** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2d** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2c** in 82% yield, colorless oil, 18.9 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.17 (s, 1H), 7.54 -7.50 (m, 2H), 7.44- 7.39 (m, 2H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 6.05 (s, 1H), 5.72 (dd, J = 17.6, 0.8 Hz, 1H), 5.25 (dd, J = 10.9, 0.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$):δ_C 161.8, 135.97, 135.8, 135.3, 127.1, 120.3, 114.1, 66.98.

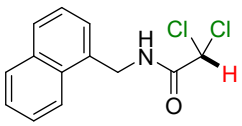
HRMS (ESI): calcd for $C_{10}H_{10}Cl_2NO^+$, $(M+H)^+$, 230.0134, found, 230.0128.



2e

The reaction was conducted according to the general procedure A using **1e** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2e** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2e** in 74% yield, colorless oil, 19.1 mg.

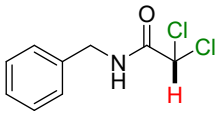
^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.33-7.28 (m, 3H), 7.22 -7.17 (m, 1H), 6.00 (s, 1H), 4.68 (dtd, J = 13.3, 3.6, 1.3 Hz, 1H), 2.87 (ddd, J = 14.5, 12.4, 2.1 Hz, 1H), 2.78-2.71 (m, 2H), 2.06-1.94 (m, 2H), 1.87-1.80 (m, 1H), 1.47-1.36 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$):δ_C 162.9, 141.2, 141.17, 131.0, 129.4, 127.99, 126.7, 63.8, 48.8, 34.4, 28.6, 26.4.
HRMS (ESI): calcd for $C_{12}H_{14}Cl_2NO^+$, $(M+H)^+$, 258.0447, found, 258.0456.



2f

The reaction was conducted according to the general procedure A using **1f** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2e** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2f** in 43% yield with the conversion of 69%, colorless oil, 11.6 mg (24.3 mg with the recovery of starting material, 91% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97-7.89 (m, 2H), 7.86 (dd, J = 6.8, 2.7 Hz, 1H), 7.60-7.52 (m, 2H), 7.49-7.43 (m, 2H), 6.75 (s, 1H), 5.98 (s, 1H), 4.96 (d, J = 5.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.9, 134.1, 132.0, 131.4, 129.3, 129.1, 127.1, 126.97, 126.4, 125.5, 123.2, 66.5, 42.7.
HRMS (ESI): calcd for $C_{13}H_{12}Cl_2NO^+$, $(M+H)^+$, 268.0290, found,268.0285.



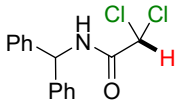
2g

The reaction was conducted according to the general procedure A using **1g** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2g** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2g** in 51% yield with the conversion of 85%, colorless oil, 11.1 mg (15.4 mg with the recovery of starting material, 71%brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41-7.28 (m, 5H), 6.77 (s, 1H), 5.98 (s, 1H), 4.52 (d, J = 5.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.2, 136.8, 129.1, 128.2, 127.9, 66.5, 44.4.

HRMS (ESI): calcd for $C_9H_{10}Cl_2NO^+$, $(M+H)^+$, 218.0134, found,218.0139.



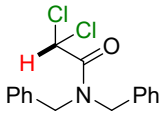
2h

The reaction was conducted according to the general procedure A using **1h** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2h** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2h** in 62% yield, colorless oil, 18.2 mg.

^{1}H NMR (400 MHz, $CDCl_3$):δ_H 7.39-7.31 (m, 6H), 7.26 -7.23 (m, 4H), 7.04 (d, J = 8.0 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H), 5.96 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.4, 140.3, 129.1, 128.1, 127.5, 66.6, 57.8.

HRMS (ESI): calcd for $C_{15}H_{14}Cl_2NO^+$, $(M+H)^+$, 294.0447, found, 294.0450.



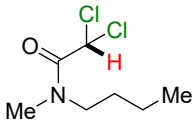
2i

The reaction was conducted according to the general procedure A using **1i** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2i** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2i** in 48% yield with the conversion of 77%, colorless oil, 14.9 mg (25.2 mg with the recovery of starting material, 82% brsm).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42- 7.30 (m, 6H), 7.22 -7.16 (m, 4H), 6.28 (s, 1H), 4.62 (d, J = 4.5 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 135.95, 135.2, 129.3, 128.97, 128.3, 128.0, 126.7, 65.4, 50.4, 49.4.

HRMS (ESI): calcd for $C_{16}H_{16}Cl_2NO^+$, $(M+H)^+$, 308.0603, found, 308.0610.



2j

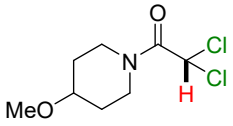
The reaction was conducted according to the general procedure A using **1j** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2j** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2j** in 43% yield , colorless oil, 8.5 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.25 (s, 0.4H), 6.23 (s, 0.55H), 3.41 (dd, J = 15.4, 8.1 Hz, 2H), 3.17 (s, 1.75H), 2.99 (s, 1.25H), 1.68-1.60 (m, 1H), 1.59-1.51 (m, 1H), 1.34 (tt, J = 14.6, 7.3 Hz, 2H), 0.95 (dt, J = 14.5, 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, major): major δ_C 163.2, 65.6, 49.2, 35.6, 28.8, 19.9, 13.8.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 163.5, 64.8, 50.1, 34.6, 30.4, 19.9, 13.8.

HRMS (ESI): calcd for $C_7H_{14}Cl_2NO^+$, $(M+H)^+$, 198.0447, found, 198.0456.



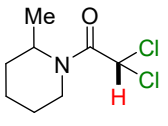
2k

The reaction was conducted according to the general procedure A using **1k** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2k** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2k** in 64% yield, colorless oil, 14.5 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.21 (s, 1H), 3.89-3.81 (m, 1H), 3.79-3.69 (m, 1H), 3.52 (dtt, J = 20.7, 6.9, 3.6 Hz, 3H), 3.36 (s, 3H), 1.96-1.80 (m, 2H), 1.78-1.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.1, 74.5, 65.97, 55.99, 43.4, 40.5, 30.7, 29.95.

HRMS (ESI): calcd for $C_8H_{14}Cl_2NO_2^+$, $(M+H)^+$, 226.0396, found, 226.0395.



2l

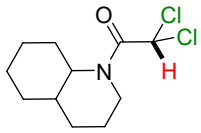
The reaction was conducted according to the general procedure A using **1l** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2l** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2l** in 18% yield, colorless oil, 3.8 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H δ 6.19 (s, 0.41H), 6.17 (s, 0.53H), 3.35 (dd, J = 15.3, 7.8 Hz, 2H), 3.11 (s, 1.77H), 2.93 (s, 1.24H), 1.64-1.54 (m, 1H), 1.53 -1.45 (m, 1H), 1.35-1.21 (m, 2H), 0.89 (dt, J = 11.1, 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) Major: δ_C 163.3, 65.7, 49.4, 35.7, 34.8, 28.9, 19.97, 13.95.

^{13}C NMR (101 MHz, $CDCl_3$) Minor: δ_C 163.6, 64.95, 50.3, 35.7, 30.6, 20.0, 19.97, 13.9.

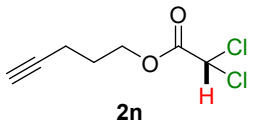
HRMS (ESI): calcd for $C_8H_{13}Cl_2NNaO^+$, $(M+Na)^+$, 232.0266, found, 232.0269.



2m

The reaction was conducted according to the general procedure A using **1m** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2m** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2m** in 43% yield with the conversion of 77%, colorless oil, 10.8 mg (18.2 mg with the recovery of starting material, 73% brsm).

^{1}H NMR (400 MHz, $CDCl_3$):δ_H 6.16 (s, 1H), 3.84 (d, J = 14.8 Hz, 1H), 3.31 (tt, J = 10.8, 5.4 Hz, 2H), 2.16-2.08 (m, 1H), 1.99-1.88 (m, 1H), 1.78-1.69 (m, 4H), 1.66-1.53 (m, 2H), 1.42 (qt, J = 12.3, 3.3 Hz, 1H), 1.30 (tt, J = 12.9, 3.8 Hz, 2H), 1.20-1.13 (m, 1H), 1.10-1.01 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.1, 66.2, 62.6, 39.97, 37.9, 32.9, 30.1, 26.2, 25.8, 25.4, 22.7.
HRMS (ESI): calcd for $C_{11}H_{18}Cl_2NO^+$, $(M+H)^+$, 250.0760, found, 250.0761.

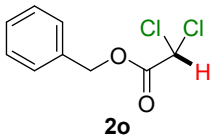


2n

The reaction was conducted according to the general procedure A using **1n** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2n** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2n** in 22% yield, colorless oil, 4.3 mg.

^{1}H NMR (400 MHz,$CDCl_3$): δ_H 5.95 (s, 1H), 4.39 (t, J = 6.3 Hz, 2H), 2.33 (td, J = 6.9, 2.7 Hz, 2H), 2.00-1.97 (m, 1H), 1.96 -1.90 (m, 2H).
^{13}C NMR (101 MHz,$CDCl_3$): δ_C 164.6, 82.5, 69.6, 66.1, 64.4, 27.3, 15.1.

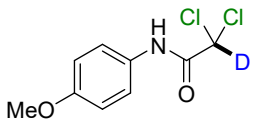
HRMS (ESI): calcd for $C_7H_9Cl_2O_2^+$, $(M+H)^+$, 194.9974, found, 194.9971.



2o

The reaction was conducted according to the general procedure A using **1o** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **2o** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **2o** in 63% yield, colorless oil, 13.8 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 -7.35 (m, 5H), 5.98 (s, 1H), 5.29 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.5, 134.4, 129.1, 128.9, 128.6, 69.2, 64.4.
HRMS (ESI): calcd for $C_9H_9Cl_2O_2^+$, $(M+H)^+$, 218.9974, found, 218.9968.

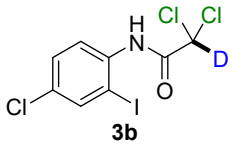


3a

The reaction was conducted according to the general procedure B using **1a** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3a** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3a** in 67% yield (95% **D**), colorless oil, 15.7 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.13 (s, 1H), 7.47-7.44 (m, 2H), 6.91-6.88 (m, 2H), 6.05 (s, 0.05H), 3.80 (s, 3H).

HRMS (ESI): calcd for $C_9H_9DCl_2NO_2^+$, $(M+H)^+$, 235.0146, found, 235.0155.

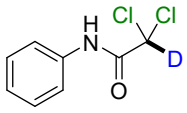


3b

The reaction was conducted according to the general procedure B using **1b** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3b** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3b** in 42% yield (74% **D**), colorless oil, 15.3 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.59 (s, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 2.3 Hz, 1H), 7.38 (dd, J = 8.9, 2.4 Hz, 1H), 6.06 (s, 0.26H).

HRMS (ESI): calcd for $C_8H_6DCl_3NO^+$, $(M+H)^+$, 364.8617, found, 364.8610.

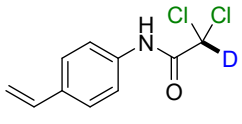


3c

The reaction was conducted according to the general procedure B using **1c** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3c** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3c** in 47% yield (89% D), colorless oil, 9.6 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.04 (s, 1H), 7.49 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 5.97 (s, 0.11H).

HRMS (ESI): calcd for $C_8H_7DCl_2NO^+$, $(M+H)^+$, 205.0040, found, 205.0037.

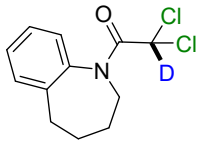


3d

The reaction was conducted according to the general procedure B using **1d** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product

3b was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3d** in 44% yield (92% **D**), colorless oil, 10.1 mg.

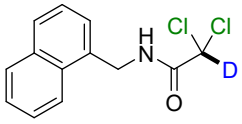
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.15 (s, 1H), 7.54-7.50 (m, 2H), 7.44-7.40 (m, 2H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (dd, J = 17.6, 0.8 Hz, 1H), 6.05 (s, 0.08H), 5.25 (dd, J = 10.9, 0.9 Hz, 1H).
HRMS (ESI): calcd for $C_{10}H_9DCl_2NO^+$, $(M+H)^+$, 231.0197, found, 231.0200.



3e

The reaction was conducted according to the general procedure B using **1e** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3e** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3e** in 33% yield (92% **D**), colorless oil, 8.5 mg.

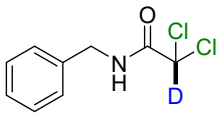
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.33-7.27 (m, 3H), 7.21-7.18 (m, 1H), 6.00 (s, 0.08H), 4.68 (dtd, J = 13.3, 3.5, 1.3 Hz, 1H), 2.86 (ddd, J = 14.5, 12.5, 2.1 Hz, 1H), 2.78-2.70 (m, 2H), 2.01 (ddt, J = 15.0, 9.4, 3.2 Hz, 2H), 1.87-1.81 (m, 1H), 1.46- 1.36 (m, 1H).
HRMS (ESI): calcd for $C_{12}H_{13}DCl_2NO^+$, $(M+H)^+$, 259.0510, found, 259.0517.



3f

The reaction was conducted according to the general procedure B using **1f** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3e** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3f** in 55% yield (91% **D**), colorless oil, 14.8 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96-7.84 (m, 3H), 7.60 - 7.52 (m, 2H), 7.48-7.43 (m, 2H), 6.76 (s, 1H), 6.00 (s, 0.09H), 4.95 (d, J = 5.5 Hz, 2H).
HRMS (ESI): calcd for $C_{13}H_{11}DCl_2NO^+$, $(M+H)^+$, 269.0353, found, 269.0351.

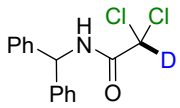


3g

The reaction was conducted according to the general procedure B using **1g** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3e** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3g** in 56% yield (77% **D**), colorless oil, 12.3 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39-7.27 (m, 5H), 6.84 (s, 1H), 6.00 (s, 0.23H), 4.51 (d, J = 5.8 Hz, 2H).

HRMS (ESI): calcd for $C_9H_9DCl_2NO^+$, $(M+H)^+$, 219.0197, found, 219.0190.

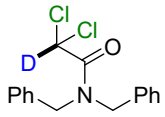


3h

The reaction was conducted according to the general procedure B using **1h** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3h** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3h** in 24% yield (70% D), colorless oil, 7.1 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41-7.29 (m, 6H), 7.27- 7.20 (m, 4H), 7.00 (s, 1H), 6.19 (d, J = 8.0 Hz, 1H), 6.00 (s, 0.3H).

HRMS (ESI): calcd for $C_{15}H_{13}DCl_2NO^+$, $(M+H)^+$, 295.0510, found, 295.0516.

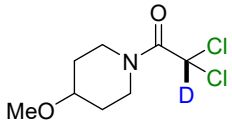


3i

The reaction was conducted according to the general procedure B using **1i** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3e** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3i** in 92% yield (90% **D**), colorless oil, 28.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42-7.30 (m, 6H), 7.22-7.16 (m, 4H), 6.28 (s, 0.10H), 4.62 (d, J = 4.6 Hz, 4H).

HRMS (ESI): calcd for $C_{16}H_{15}DCl_2NO^+$, $(M+H)^+$, 309.0666, found, 309.0670.

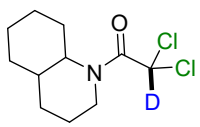


3j

The reaction was conducted according to the general procedure B using **1k** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3j** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3j** in 35% yield (91% **D**), colorless oil, 7.9 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.21 (s, 0.09H), 3.83 (ddd, J = 13.8, 8.1, 3.6 Hz, 1H), 3.74 (ddd, J = 12.5, 8.2, 3.7 Hz, 1H), 3.51 (dtq, J = 20.4, 6.9, 3.6 Hz, 3H), 3.35 (s, 3H), 1.93-1.81 (m, 2H), 1.69 (dddd, J = 20.9, 13.5, 6.7, 3.5 Hz, 2H).

HRMS (ESI): calcd for $C_8H_{13}DCl_2NO_2^+$, $(M+H)^+$, 227.0459, found, 227.0461.

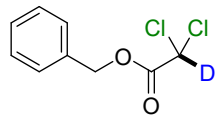


3k

The reaction was conducted according to the general procedure B using **1m** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3k** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3k** in 22% yield (84% **D**), colorless oil, 5.5 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.16 (s, 0.16H), 3.87 (s, 1H), 3.33 (td, J = 14.1, 11.0, 3.6 Hz, 2H), 2.19-2.10 (m, 1H), 1.99-1.90 (m, 1H), 1.78-1.72 (m, 3H), 1.68-1.54 (m, 3H), 1.43 (dt, J = 12.8, 3.4 Hz, 1H), 1.28 (ddd, J = 14.2, 7.0, 2.5 Hz, 2H), 1.19-1.06 (m, 2H).

HRMS (ESI): calcd for $C_{11}H_{17}DCl_2NO^+$, $(M+H)^+$, 251.0823, found, 251.0832.



3l

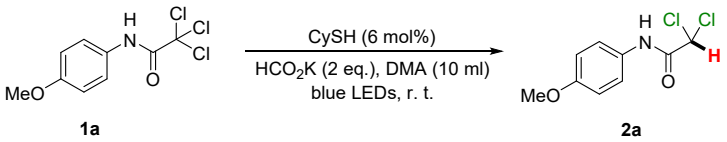
The reaction was conducted according to the general procedure B using **1o** with DMA as the solvent. The reaction stopped until the starting material was completely consumed, the corresponding product **3l** was purified by flash column chromatography with PE/EA (30:1-10:1) to provide **3l** in 24% yield (87% **D**), colorless oil, 5.3 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (d, J = 2.9 Hz, 5H), 6.00 (s, 0.17H), 5.29 (s, 2H).

HRMS (ESI): calcd for $C_9H_8DCl_2NO_2^+$, $(M+H)^+$, 220.0037, found, 220.0029.

6. Synthetic applications.

a) Gram Scale-up Reaction

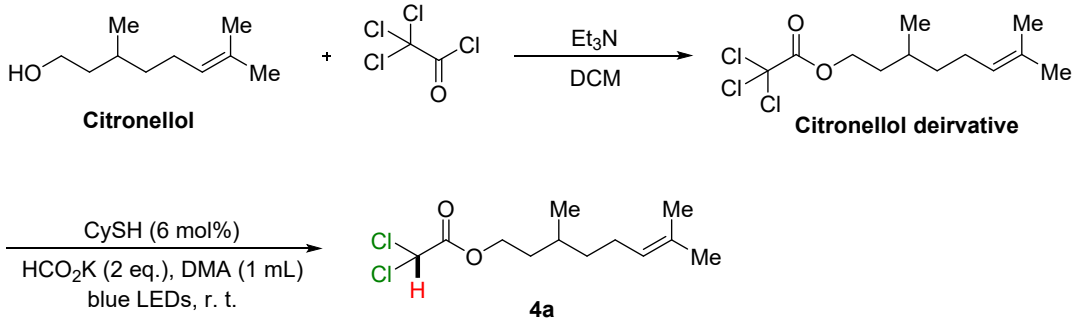


In a sealed tube**, 1a** (2.0 mmol), CySH (6.0 mol %), HCO_2K (4.0 mmol) were dissolved in DMA (10.0 mL). The open flask was caped and degassed with nitrogen for three times at -78 °C. Subsequently, the reaction mixture was irradiated with 12 W*2 blue LEDs at rt until the **1a** was completely consumed (monitored by TLC). The reaction solvent was distill under vacuum after the reaction finished, Finally, the residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate to afford the corresponding product **2a** in 86% yield.

b) Late-stage alkylation of complex molecules

Synthesis of 4a:

Synthesis of Citronellol derivative: Citronellol (468 mg, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the citronellol derivative.



Characterization data of Citronellol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.08 (t, J = 7.1 Hz, 1H), 4.46-4.33 (m, 2H), 2.12-1.92 (m, 2H), 1.81 (qd, J = 7.0, 4.6 Hz, 1H), 1.68 (s, 3H), 1.63-1.51 (m, 5H), 1.37 (ddd, J = 14.5, 8.1, 4.2 Hz, 1H), 1.26-1.18 (m, 1H), 0.95 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.2, 131.7, 124.4, 90.1, 68.2, 36.9, 35.1, 29.4, 25.9, 25.5, 19.5, 17.8.

Synthesis of 4a: In a 10 mL Schlenk tube with a stirring bar, citronellol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column

chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4a** in 52% yield.

Characterization data of 4a:

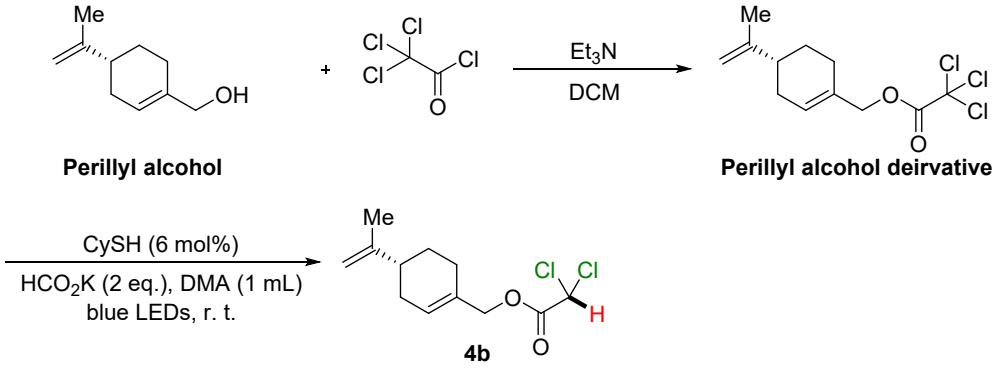
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.93 (s, 1H), 5.08 (ddq, J = 8.6, 5.7, 1.5 Hz, 1H), 4.36-4.27 (m, 2H), 2.07-1.91 (m, 2H), 1.76 (dtd, J = 13.4, 7.2, 4.8 Hz, 1H), 1.68 (q, J = 1.4 Hz, 3H), 1.60 (d, J = 1.3 Hz, 3H), 1.57-1.48 (m, 2H), 1.36 (dddd, J = 13.4, 9.3, 6.6, 5.2 Hz, 1H), 1.25-1.17 (m, 1H), 0.93 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.6, 131.6, 124.4, 66.2, 64.4, 36.9, 35.1, 29.2, 25.7, 25.3, 19.3, 17.7.

HRMS (ESI): calcd for $C_{12}H_{21}Cl_2O_2^+$, $(M+H)^+$, 267.0913, found, 267.0907.

Synthesis of 4b:

Synthesis of Perillyl alcohol derivative: Perillyl alcohol (456 mg, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Perillyl alcohol derivative.



Characterization data of Perillyl alcohol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.90 (s, 1H), 4.74 (t, J = 11.2 Hz, 4H), 2.17 (ddd, J = 13.7, 10.7, 4.0 Hz, 4H), 2.05-1.94 (m, 1H), 1.92-1.79 (m, 1H), 1.76-1.64 (m, 3H), 1.60-1.42 (m, 1H).

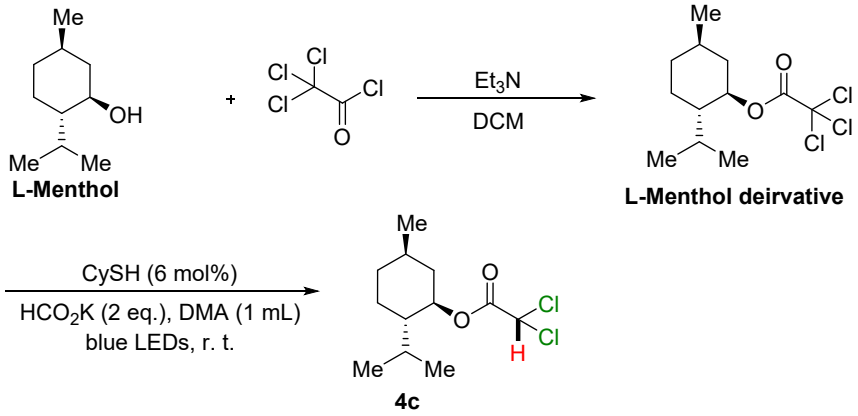
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.97, 149.3, 131.1, 128.4, 109.1, 90.2, 73.3, 40.7, 30.6, 27.3, 26.2, 20.9.

Synthesis of 4b: In a 10 mL Schlenk tube with a stirring bar, Perillyl alcohol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4b** in 36% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.95 (s, 1H), 5.85 (dt, J = 3.6, 1.7 Hz, 1H), 4.75-4.71 (m, 2H), 4.67-4.64 (m, 2H), 2.24-2.15 (m, 2H), 2.11 (dd, J = 7.1, 3.0 Hz, 2H), 2.00 (dddd, J = 14.2, 7.3, 3.3, 1.7 Hz, 1H), 1.86 (dtt, J = 12.7, 4.2, 2.2 Hz, 1H), 1.74 (t, J = 1.1 Hz, 3H), 1.54-1.46 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.5, 149.3, 131.3, 127.8, 108.96, 71.4, 64.4, 40.6, 30.5, 27.2, 26.2, 20.8.
HRMS (ESI): calcd for $C_{12}H_{17}Cl_2O_2^+$, $(M+H)^+$, 263.0600, found, 263.0607.

Synthesis of 4c:

Synthesis of L-Menthol derivative: L-Menthol (468 mg, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the L-Menthol derivative.



Characterization data of L-Menthol derivative:

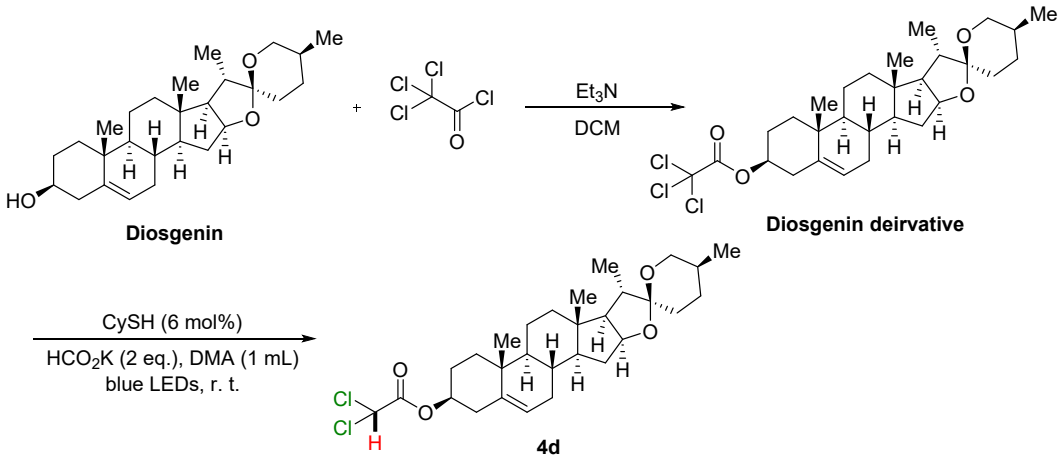
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.74 (td, J = 11.0, 4.4 Hz, 1H), 2.02 (ddd, J = 9.6, 7.6, 4.9 Hz, 1H), 1.91 (dtd, J = 13.9, 7.0, 2.8 Hz, 1H), 1.67 (tdd, J = 9.0, 6.1, 3.1 Hz, 2H), 1.48 (qdd, J = 12.9, 6.4, 3.1 Hz, 2H), 1.13 -0.96 (m, 2H), 0.93-0.79 (m, 7H), 0.73 (d, J = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.6, 90.5, 80.7, 47.1, 39.9, 34.1, 31.6, 26.3, 23.4, 22.1, 20.8, 16.3.

Synthesis of 4c: In a 10 mL Schlenk tube with a stirring bar, L-Menthol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4c** in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.91 (s, 1H), 4.77 (dt, J = 10.9, 5.5 Hz, 1H), 2.04 (t, J = 6.1 Hz, 1H), 1.93 (d, J = 2.8 Hz, 1H), 1.75-1.66 (m, 2H), 1.56-1.46 (m, 2H), 1.13-1.03 (m, 2H), 0.94-0.92 (m, 3H), 0.92-0.89 (m, 3H), 0.88 (d, J = 3.7 Hz, 1H), 0.77 (d, J = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.3, 78.4, 64.9, 47.1, 40.2, 34.2, 31.6, 26.3, 23.5, 22.1, 20.8, 16.3.
HRMS (ESI): calcd for $C_{12}H_{21}Cl_2O_2^+$, $(M+H)^+$, 267.0913, found, 267.0917.

Synthesis of 4d:

Synthesis of Diosgenin derivative: Diosgenin (1.2 g, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Diosgenin derivative.



Characterization data of Diosgenin derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.36 (d, J = 5.1 Hz, 1H), 4.77-4.62 (m, 1H), 4.35 (dd, J = 14.9, 7.5 Hz, 1H), 3.48-3.36 (m, 1H), 3.31 (t, J = 10.9 Hz, 1H), 2.46-2.34 (m, 2H), 2.03-1.86 (m, 4H), 1.79 (dd, J = 13.7, 6.9 Hz, 1H), 1.74-1.65 (m, 3H), 1.59-1.50 (m, 4H), 1.48-1.30 (m, 4H), 1.24 -1.13 (m, 6H), 1.12-1.06 (m, 2H), 1.00 (s, 3H), 0.91 (d, J = 6.9 Hz, 3H), 0.72 (d, J = 5.0 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.4, 138.7, 123.4, 109.3, 90.2, 80.8, 79.7, 66.9, 62.1, 56.4, 49.9, 41.6, 40.3, 39.7, 37.3, 36.7, 36.7, 32.1, 31.8, 31.4, 31.4, 30.3, 28.8, 27.1, 20.9, 19.3, 17.2, 16.3, 14.5.

Synthesis of 4d: In a 10 mL Schlenk tube with a stirring bar, L-Menthol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 ^{o}C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4d** in 25% yield.

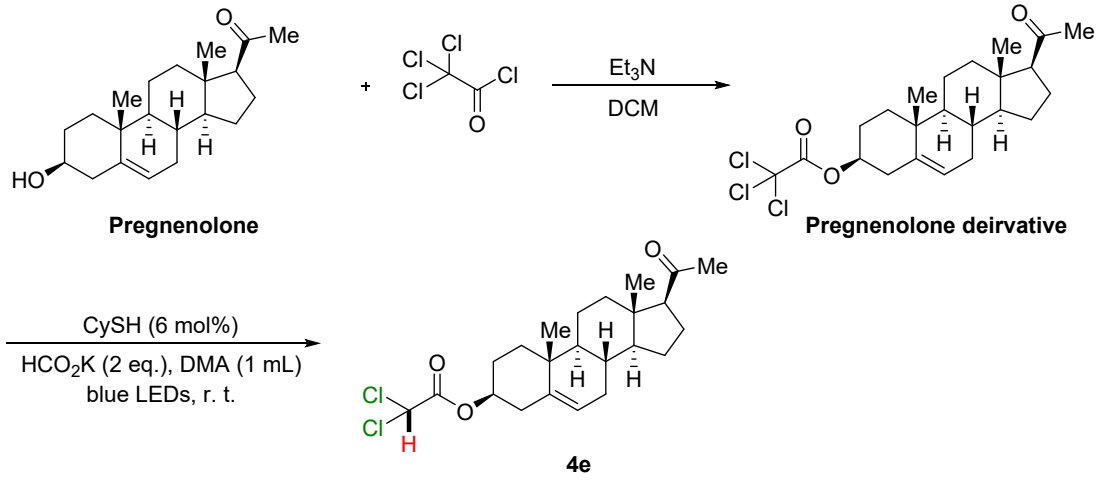
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.90 (s, 1H), 5.41 (d, J = 4.8 Hz, 1H), 4.71 (tdd, J = 11.8, 7.3, 4.4 Hz, 1H), 4.41 (dd, J = 14.9, 7.5 Hz, 1H), 3.51-3.43 (m, 1H), 3.37 (t, J = 10.9 Hz, 1H), 2.40 (d, J = 7.7 Hz, 2H), 2.05-1.96 (m, 2H), 1.95-1.83 (m, 3H), 1.81-1.69 (m, 3H), 1.67 (d, J = 4.7 Hz, 1H), 1.63-1.56 (m, 4H), 1.55-1.38 (m, 4H), 1.32-1.24 (m, 2H), 1.21-1.17 (m, 1H), 1.12 (dd, J = 12.2, 3.8 Hz, 2H), 1.05 (s, 3H), 0.97 (d, J = 6.9 Hz, 3H), 0.78 (t, J = 3.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.1, 139.0, 123.3, 109.4, 80.9, 77.7, 66.99, 64.7, 62.2, 56.5, 50.0, 41.8, 40.4, 39.8, 37.6, 36.9, 36.8, 32.2, 31.97, 31.5, 31.5, 30.4, 28.9, 27.4, 20.97, 19.5, 17.3, 16.4, 14.7.

HRMS (ESI): calcd for $C_{29}H_{43}Cl_2O_4^+$, $(M+H)^+$, 525.2533, found, 525.2531.

Synthesis of 4e:

Synthesis of Pregnenolone derivative: Pregnenolone (0.948 g, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Pregnenolone derivative.



Characterization data of Pregnenolone derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.42 (d, J = 5.1 Hz, 1H), 4.80-4.68 (m, 1H), 2.53 (t, J = 8.9 Hz, 1H), 2.49-2.37 (m, 2H), 2.19 (dd, J = 11.0, 9.4 Hz, 1H), 2.14-2.09 (m, 3H), 1.98 (dddd, J = 20.3, 13.4, 7.9, 3.2 Hz, 4H), 1.82-1.72 (m, 1H), 1.70-1.57 (m, 4H), 1.57-1.43 (m, 3H), 1.26-1.10 (m, 3H), 1.04 (s, 3H), 1.01 (dd, J = 11.1, 4.5 Hz, 1H), 0.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 209.5, 161.5, 138.8, 123.5, 90.3, 79.7, 63.7, 56.9, 49.9, 44.1, 38.9, 37.4, 36.9, 36.7, 31.9, 31.7, 27.2, 24.6, 22.95, 21.2, 19.4, 13.3.

Synthesis of 4e: In a 10 mL Schlenk tube with a stirring bar, L-Menthol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4e** in 38% yield.

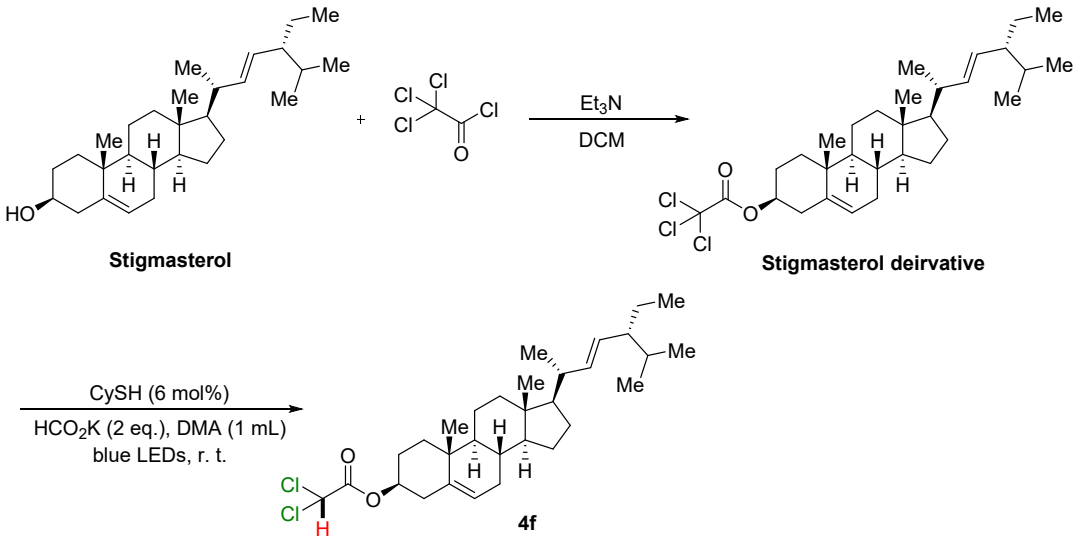
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.90 (s, 1H), 5.40 (dq, J = 5.1, 1.6 Hz, 1H), 4.76-4.67 (m, 1H), 2.53 (t, J = 8.9 Hz, 1H), 2.42-2.38 (m, 2H), 2.21-2.15 (m, 1H), 2.12 (s, 3H), 2.07-1.99 (m, 2H), 1.95-1.87 (m, 2H), 1.74-1.57 (m, 6H), 1.50 (d, J = 4.2 Hz, 1H), 1.44 (t, J = 1.9 Hz, 1H), 1.28-1.10 (m, 4H), 1.03 (s, 3H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 209.5, 163.98, 138.9, 123.1, 77.5, 64.6, 63.7, 56.8, 49.8, 43.96, 38.8, 37.5, 36.8, 36.6, 31.8, 31.8, 31.6, 27.2, 24.5, 22.8, 21.1, 19.3, 13.2.

HRMS (ESI): calcd for $C_{23}H_{33}Cl_2O_3^+$, $(M+H)^+$, 427.1801, found, 427.1810.

Synthesis of 4f:

Synthesis of Stigmasterol derivative: Stigmasterol (1.248 g, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Stigmasterol derivative.



Characterization data of Stigmasterol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.36 (d, J = 5.1 Hz, 1H), 5.09 (dd, J = 15.2, 8.6 Hz, 1H), 4.95 (dd, J = 15.2, 8.7 Hz, 1H), 4.69 (tt, J = 10.9, 5.4 Hz, 1H), 2.54-2.30 (m, 2H), 2.06-1.79 (m, 5H), 1.75-1.57 (m, 2H), 1.52-1.40 (m, 6H), 1.19 (s, 6H), 1.14-1.05 (m, 4H), 0.98 (s, 3H), 0.96 (d, J = 6.7 Hz, 3H), 0.80-0.71 (m, 9H), 0.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.5, 138.8, 138.4, 129.5, 123.8, 90.4, 79.9, 56.9, 56.1, 51.4, 50.1, 42.4, 40.7, 39.7, 37.5, 36.9, 36.7, 32.0, 31.97, 29.9, 29.1, 27.3, 25.6, 24.5, 21.4, 21.3, 21.2, 19.5, 19.1, 12.4, 12.2.

Synthesis of 4f: In a 10 mL Schlenk tube with a stirring bar, Stigmasterol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4f** in 51% yield.

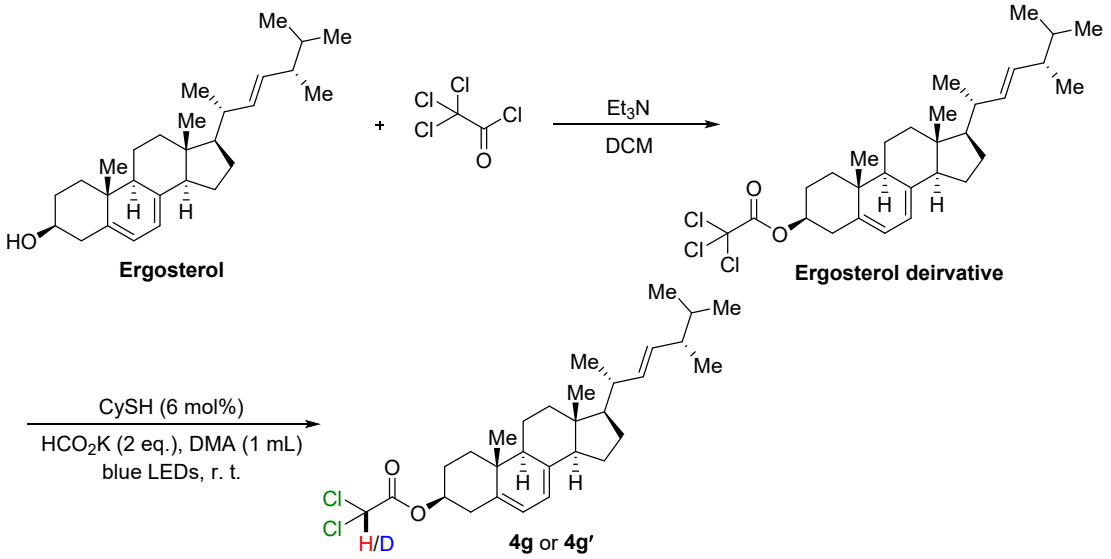
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.91 (s, 1H), 5.41 (d, J = 4.9 Hz, 1H), 5.16 (dd, J = 15.2, 8.6 Hz, 1H), 5.02 (dd, J = 15.2, 8.7 Hz, 1H), 4.79-4.65 (m, 1H), 2.41 (dd, J = 8.0, 4.3 Hz, 2H), 1.96 (dddd, J = 17.8, 13.7, 6.8, 3.4 Hz, 5H), 1.70 (ddd, J = 8.2, 6.7, 3.7 Hz, 2H), 1.59-1.52 (m, 3H), 1.52-1.41 (m, 5H), 1.34-1.24 (m, 2H), 1.16 (ddd, J = 12.4, 11.2, 4.0 Hz, 4H), 1.08-0.98 (m, 8H), 0.87-0.82 (m, 4H), 0.80 (d, J = 7.0 Hz, 5H), 0.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.1, 138.98, 138.4, 129.5, 123.6, 77.8, 64.7, 56.9, 56.1, 51.4, 50.2, 42.4, 40.6, 39.8, 37.7, 36.95, 36.7, 32.0, 31.98, 29.0, 27.4, 25.6, 24.5, 21.4, 21.2, 21.18, 19.4, 19.1, 12.4, 12.2.

HRMS (ESI): calcd for $C_{31}H_{49}Cl_2O_2^+$, $(M+H)^+$, 523.3104, found, 523.3100.

Synthesis of 4g:

Synthesis of Ergosterol derivative: Ergosterol (1.2 g, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Ergosterol derivative.



Characterization data of Ergosterol derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.62 (dd, J = 5.6, 2.1 Hz, 1H), 5.40 (dt, J = 5.3, 2.4 Hz, 1H), 5.30 – 5.11 (m, 2H), 4.93 -4.77 (m, 1H), 2.71-2.41 (m, 2H), 2.12 -1.93 (m, 5H), 1.86 (dd, J = 12.9, 6.7 Hz, 1H), 1.80-1.58 (m, 5H), 1.52-1.40 (m, 2H), 1.35 (dd, J = 11.7, 4.4 Hz, 2H), 1.31-1.23 (m, 4H), 1.04 (d, J = 6.6 Hz, 3H), 0.99 (s, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.83 (t, J = 6.4 Hz, 6H), 0.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.5, 142.1, 137.3, 135.7, 132.2, 121.1, 116.4, 90.4, 78.8, 55.9, 54.7, 46.1, 42.98, 40.6, 39.1, 37.8, 37.2, 36.0, 33.2, 29.9, 28.4, 27.6, 23.1, 21.3, 21.2, 20.1, 19.8, 17.8, 16.3, 12.2.

Synthesis of 4g: In a 10 mL Schlenk tube with a stirring bar, Ergosterol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4f** in 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.84 (d, J = 2.7 Hz, 1H), 5.53 (dd, J = 5.6, 2.2 Hz, 1H), 5.33 (dd, J = 5.4, 2.6 Hz, 1H), 5.21-5.05 (m, 2H), 4.76 (tt, J = 11.4, 4.7 Hz, 1H), 2.50 (ddd, J = 14.3, 5.0, 2.2 Hz,

1H), 2.39 (t, J = 12.3 Hz, 1H), 2.03-1.95 (m, 2H), 1.95-1.89 (m, 2H), 1.86-1.74 (m, 3H), 1.71-1.67 (m, 1H), 1.61-1.50 (m, 3H), 1.40 (dd, J = 12.9, 6.6 Hz, 1H), 1.36-1.25 (m, 3H), 1.24-1.17 (m, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.90 (s, 3H), 0.85 (d, J = 6.8 Hz, 3H), 0.76 (t, J = 6.4 Hz, 6H), 0.56 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.1, 142.0, 137.6, 135.7, 132.2, 120.97, 116.4, 76.7, 64.7, 55.9, 54.7, 46.2, 42.99, 40.6, 39.2, 37.9, 37.2, 36.2, 33.3, 28.4, 27.8, 23.1, 21.3, 21.2, 20.1, 19.8, 17.8, 16.3, 12.2.

HRMS (ESI): calcd for $C_{30}H_{45}Cl_2O_2^+$, $(M+H)^+$, 507.2791, found, 507.2796.

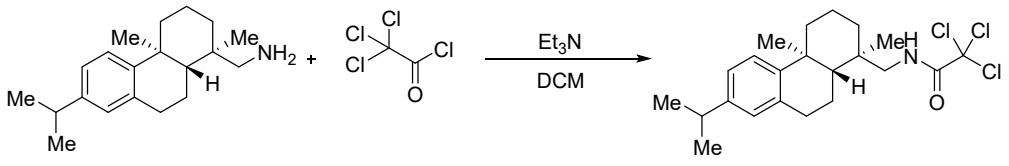
Synthesis of 4g´: In a 10 mL Schlenk tube with a stirring bar**,** Ergosterol derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) ，Cy_3P (0.2 mmol), DTBP (1.2 eq.) ，D_2O (50 eq.) were dissolved in DMA (1.0 mL), and then D_2O (50 eq.) was added to the reaction mixture. The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired products.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.92 (s, 0.25H), 5.60 (dd, J = 5.5, 2.1 Hz, 1H), 5.44-5.35 (m, 1H), 5.27-5.14 (m, 2H), 4.83 (ddd, J = 16.1, 11.4, 4.6 Hz, 1H), 2.58 (ddd, J = 14.3, 5.0, 2.1 Hz, 1H), 2.46 (t, J = 12.8 Hz, 1H), 2.10-1.97 (m, 4H), 1.96-1.84 (m, 3H), 1.80-1.65 (m, 4H), 1.62 (dd, J = 9.6, 4.6 Hz, 1H), 1.53-1.42 (m, 2H), 1.40-1.33 (m, 2H), 1.31-1.24 (m, 3H), 1.03 (t, J = 6.6 Hz, 3H), 0.96 (d, J = 10.1 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.83 (t, J = 6.4 Hz, 6H), 0.61 (d, J = 19.7 Hz, 3H).

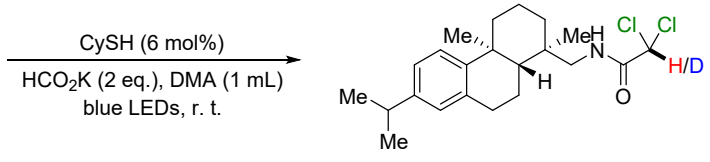
HRMS (ESI): calcd for $C_{30}H_{44}DCl_2O_2^+$, $(M+H)^+$, 508.2854, found, 508.2853.

Synthesis of 4h:

Synthesis of Dehydroabietylamine derivative: Desloratadine (921 mg, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Dehydroabietylamine derivative.



Dehydroabietylamine **Dehydroabietylamine deirvative**



4h

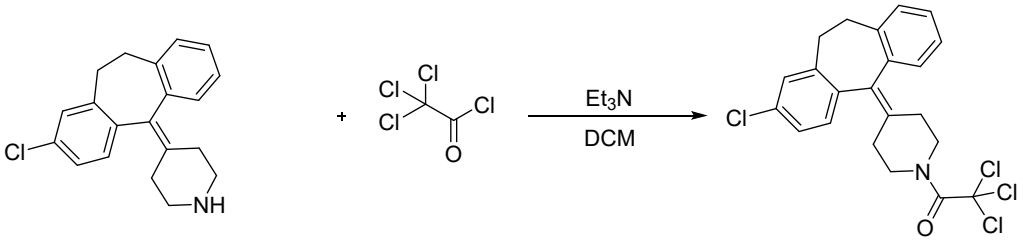
Characterization data of Dehydroabietylamine derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.18 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.90 (s, 1H), 6.74 (s, 1H), 3.45-3.21 (m, 2H), 3.01-2.75 (m, 3H), 2.33 (d, *J* = 12.8 Hz, 1H), 1.96-1.66 (m, 4H), 1.54 (d, *J* = 12.8 Hz, 1H), 1.49-1.28 (m, 3H), 1.24 (d, *J* = 6.8 Hz, 9H), 1.01 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.2, 146.8, 145.8, 134.6, 127.0, 124.4, 124.1, 93.1, 52.2, 46.4, 38.4, 38.0, 37.7, 36.4, 33.5, 30.4, 25.5, 24.1, 24.1, 19.3, 18.6, 18.5.

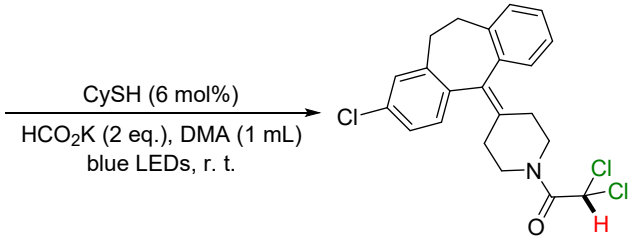
Synthesis of 4h: In a 10 mL Schlenk tube with a stirring bar, Dehydroabietylamine derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4h** in 85% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.19 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.91 (s, 1H), 6.61 (s, 1H), 5.94 (s, 1H), 3.36-3.19 (m, 2H), 3.01-2.78 (m, 3H), 2.33 (d, *J* = 12.8 Hz, 1H), 1.96-1.67 (m, 4H), 1.40 (dddd, *J* = 21.7, 18.1, 17.3, 8.5 Hz, 4H), 1.25 (dd, *J* = 8.4, 4.7 Hz, 9H), 1.00 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.4, 146.9, 145.8, 134.6, 127.0, 124.3, 124.0, 66.8, 50.9, 46.1, 38.4, 37.9, 37.7, 36.3, 33.5, 30.4, 25.5, 24.1, 24.1, 19.2, 18.7, 18.6.
HRMS (ESI): calcd for $C_{22}H_{32}Cl_2NO_2^+$, $(M+H)^+$, 396.1855, found, 396.1859.

Synthesis of 4h´: In a 10 mL Schlenk tube with a stirring bar**,** Dehydroabietylamine derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) ，Cy_3P (0.2 mmol), DTBP (1.2 eq.) ，D_2O (50 eq.) were dissolved in DMA (1.0 mL), and then D_2O (50 eq.) was added to the reaction mixture. The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired products.
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.18 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.57 (s, 1H), 5.93 (s, 0.27H), 3.26 (dd, *J* = 6.6, 3.0 Hz, 2H), 3.01-2.79 (m, 3H), 2.39-2.26 (m, 1H), 1.94-1.84 (m, 1H), 1.82-1.67 (m, 3H), 1.55-1.48 (m, 1H), 1.46-1.36 (m, 2H), 1.31 (dd, *J* = 13.1, 4.5 Hz, 1H), 1.25 (dd, *J* = 8.3, 4.8 Hz, 9H), 0.99 (s, 3H).
HRMS (ESI): calcd for $C_{22}H_{31}DCl_2NO^+$, $(M+H)^+$, 397.1918, found, 397.1912.

Synthesis of 4i:
Synthesis of Desloratadine derivative: Desloratadine (921 mg, 3.0 mmol), Et_3N (606 mg, 6.0 mmol) were dissolved in DCM (20 mL) at 0-5 °C, trichloroacetyl chloride (598.3 mg, 3.3 mmol) was added with dropwise. Subsequently, the reaction mixture was removed to room temperature, and stirring overnight at the same temperature. When the starting material was completely consumed, saturated NH_4Cl (20 ml) was added, extracted with DCM (20 ml*3), the combined phase was washed with brine, dried over $MgSO_4$, concentrated and purified by chromatography on silica gel to give the Desloratadine derivative.



Desloratadine **Desloratadine deirvative**



4i

Characterization data of Desloratadine derivative:

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.41 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.30-7.00 (m, 5H), 4.15 (s, 2H), 3.57 (s, 1H), 3.43-3.28 (m, 3H), 2.94-2.77 (m, 2H), 2.68 (s, 1H), 2.48 (dd, J = 28.8, 11.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.4, 146.7, 139.7, 138.1, 137.5, 136.0, 135.1, 133.6, 133.4, 130.5, 129.2, 126.5, 122.7, 93.3, 31.7, 31.7, 30.6, 30.4, 29.8.

Synthesis of 4i: In a 10 mL Schlenk tube with a stirring bar, Desloratadine derivative (0.1 mmol), CySH (6.0% mmol), HCO_2K (0.2 mmol) were dissolved in DMA (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction system was placed to 12 W*2 blue LEDs at room temperature. The reaction time determined to be completed by the TLC analysis. After the reaction finished, the reaction solvent was distill under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA) to afford the desired product **4i** in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.41 (d, J = 4.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.19-7.09 (m, 4H), 6.21 (d, J = 1.5 Hz, 1H), 4.06-3.85 (m, 2H), 3.46 (ddd, J = 13.1, 8.4, 3.9 Hz, 1H), 3.32 (dddd, J = 22.6, 13.4, 9.9, 5.2 Hz, 3H), 2.84 (ddt, J = 13.3, 8.7, 5.8 Hz, 2H), 2.72-2.35 (m, 4H), 1.25 (t, J = 7.1 Hz, 1H).

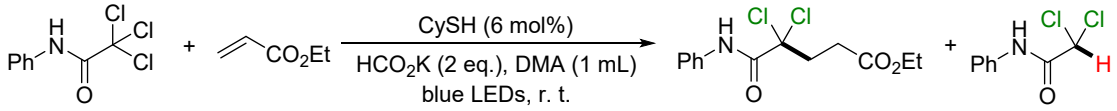
^{13}C NMR (101 MHz, $CDCl_3$)，major：δ_C 162.1, 156.5, 146.6, 139.6, 137.9, 137.5, 137.3, 135.97, 135.0, 133.5, 133.3, 130.4, 129.1, 126.4, 122.5, 65.9, 47.0, 44.5, 31.6, 30.7, 30.2.

^{13}C NMR (101 MHz, $CDCl_3$)，minor：162.0, 156.3, 146.6, 139.5, 137.96, 137.5, 137.3, 136.1, 135.0, 133.4, 133.3, 130.4, 129.0, 126.3, 122.5, 65.9, 47.0, 44.4, 31.6, 30.5, 29.97

7. Mechanistic Studies

a) Radical trapping experiment

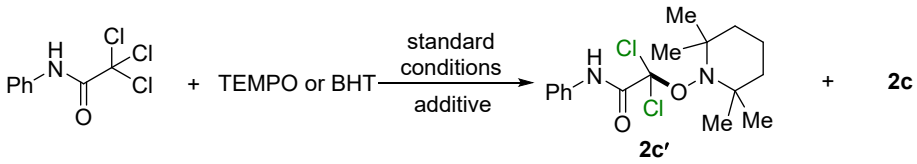
The control experiment were conducted: In a dried sealed tube, **1c** (0.1 mmol), **CySH** (6.0% mmol), HCO_2K (2.0 eq.) were dissolved in DMA (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. Subsequently, the reaction system was moved to 12 W*2 blue leds until completely consumed (monitored by TLC) and quenched with 4 mL saturated NH_4Cl. The mixture was extracted with DCM (5 mL*3). The combined solvent were dried over $MgSO_4$ and filtered. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether and ethyl acetate to afford the hydrodechlorination product **2c** in 72% yield, while there was no radical addition product **5** was provided.



1c **5**, 0% **2c**

b) Radical inhibition experiment

In a dried sealed tube, **1c** (0.1 mmol), **CySH** (6.0% mmol), HCO_2K(0.2 mmol), , TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (0.2 mmol) were dissolved in DMA (1.0 mL). The flask was caped and degassed oxygen with N_2 for three times at -78 °C. And then, the reaction flask was exposed to 12 W*2 blue LEDs at room temperature. The starting material could not completely consumed even elongation the reaction time. Subsequently, quenched with 4 mL saturated NH_4Cl. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether and ethyl acetate to afford the hydrodechlorination product **2c** in 35% yield with the conversion of 60%, which indicate the novel transformation was radical intermediate involved through a single-electron transfer.

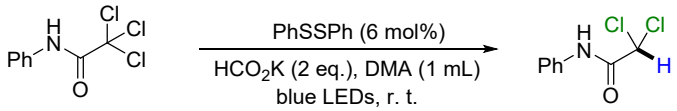


2c′

1c	additive (2 equiv.)	yield of **2c′**	yield of **2c**
	--	--	76%
	Tempo	0%	35% (60% conversion)

c) Determination the intermediate of the catalyst

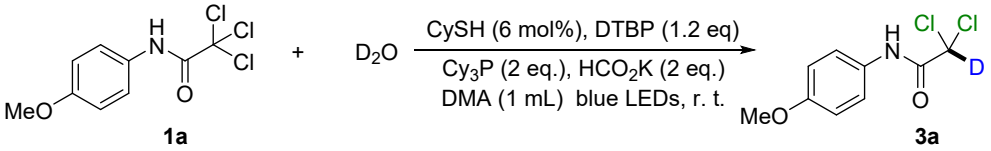
In a dried sealed tube, **1c** (0.1 mmol), PhSSPh (6.0% mmol), HCO_2K (2.0 eq.) were dissolved in DMA (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. Subsequently, the reaction system was moved to 12 W*2 blue leds until completely consumed (monitored by TLC) and quenched with 4 mL saturated NH_4Cl. The mixture was extracted with DCM (5 mL*3). The combined solvent were dried over $MgSO_4$ and filtered. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether and ethyl acetate to afford the hydrodechlorination product **2c** in 66% yield, which indicate the reaction cycle maybe proceeded with PhSSPh as the intermediate of catalyst.



1c **2c**, 66%

d) Deuterium experiment to confirm the origination of the deuterium atom

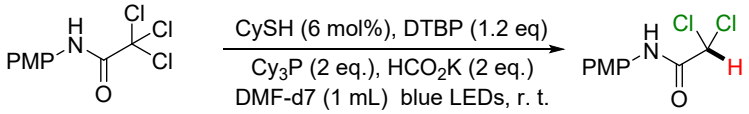
In a dried sealed tube, **1a** (0.1 mmol), CySH (6.0% mmol), HCO_2K (2.0 eq.), DTBP (1.2 eq.), Cy_3P (2 eq.) and D_2O (50 eq.) were dissolved in DMA (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. Subsequently, the reaction system was moved to 12 W*2 blue leds until completely consumed (monitored by TLC) and quenched with 4 mL saturated NH_4Cl. The mixture was extracted with DCM (5 mL*3). The combined solvent were dried over $MgSO_4$ and filtered. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether and ethyl acetate to afford the hydrodechlorination product **3a** in 67% yield (95% D), which indicate the Deuterium atom maybe originate from D_2O.



1a **3a**

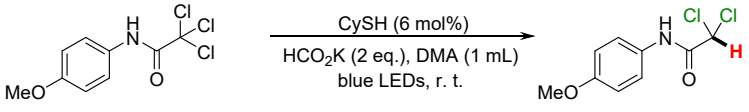
e) Deuterium labeling experiment to rule out the deuterium atom from DMF-d7

In a dried sealed tube, **1c** (0.1 mmol), CySH (6.0% mmol), HCO_2K (2.0 eq.), DTBP (1.2 eq.), Cy_3P (2 eq.) were dissolved in DMF-d_7 (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. Subsequently, the reaction system was moved to 12 W*2 blue leds until completely consumed (monitored by TLC) and quenched with 4 mL saturated NH_4Cl. The mixture was extracted with DCM (5 mL*3). The combined solvent were dried over $MgSO_4$ and filtered. The filtrate was concentrated and purification by chromatography on silica gel with a eluent of petroleum ether and ethyl acetate to afford the hydrodechlorination product **3c** in 58% yield (0%D), which indicate the Deuterium atom maybe originate from D_2O.



1a **3a**

f) UV-Vis Absorption Spectroscopic Measurements



1a **2a**

The UV/Vis absorption spectra were recorded with the same concentration used in the reaction in 1 cm path quartz cuvettes by using a Thermo Nanodrop 2000 UV/Vis-spectrometer, respectively. The corrresponding charge-transfer bands in UV/vis absorption spectra were obtained were shown in Fig S1.

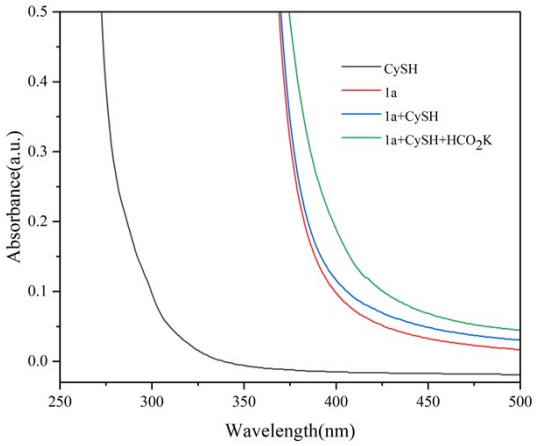


Figure S1. Optical absorption spectra of catalyst, substrate, and reaction mixture.

g) Stern-Volmer Quenching Study

To evaluate the role of CySH anion in this process, we conducted Stern-Volmer fluorescence quenching experiments (Fig S2, Fig S3). The samples were prepared mixing the CySH anion (2.5×10^{-3} M, freshly prepared in situ by the deprotonation of CySH with Cs_2CO_3) with the required amount of **1a** in a total volume of **1** mL of dry DMA in a 10 × 10 mm light path quartz fluorescence cuvette under an argon atmosphere. The excitation wavelength was fixed at 420 nm, the emission light was acquired from 395 nm to 500 nm.

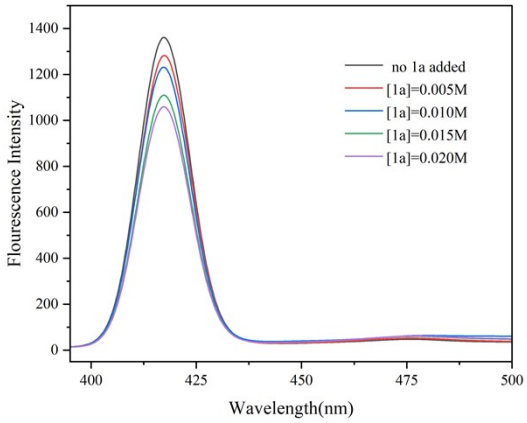


Figure S2. Quenching of the CySH anion emission (2.5×10^{-3} M in DMA) in the presence of increasing amounts of **1a** .

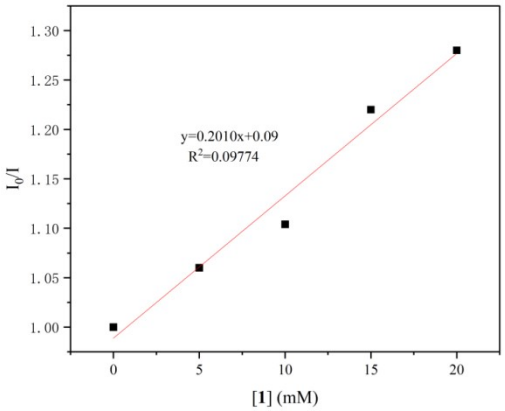


Figure S3. Stern-Volmer quenching plot of substrate **1a**.

h) Electrochemical Measurements

Tetrabutylammonium hexafluorophosphate (1161 mg, 3.0 mmol) was added to a 0.01 M solution of the CySH anion catalyst (generated in situ by the deprotonation of the CySH catalyst with 1.2 equiv. KO^{t}Bu) in 30 mL of dry DMA and the solution was vigorously bubbled with argon for 5 minutes prior to the measurement. The oxidation/reduction potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.

2,2,2-trichloro-N-(4-methoxyphenyl)acetamide

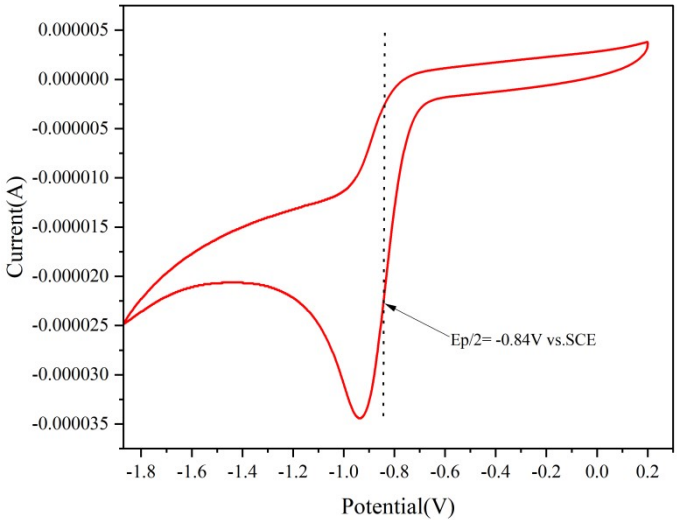


Figure S4. The cyclic voltammogram of the 2,2,2-trichloro-N-(4-methoxyphenyl)acetamide vs SCE in DMA at 0.1V/s.

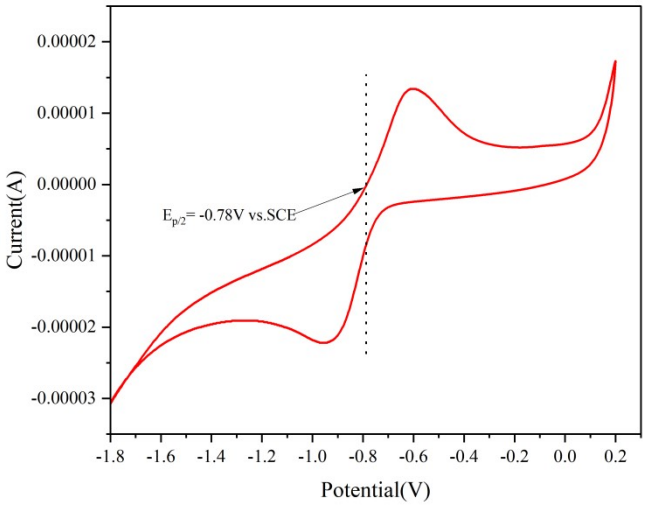


Figure S5. The cyclic voltammogram of the CySH anions vs SCE in DMA at 0.1V/s.

With this data in hand, we calculated the redox potential of the excited S1 anion employing the following equation[2]：

$$E_{p/2}(\mathbf{S^{\bullet}/\ S^{-*}}) = E_{p/2}(\mathbf{S^{\bullet}\ /\ S^{-}}) - E_{0\text{-}0}(\mathbf{S^{-*}/\ S^{-}})$$

$E_{p/2}(\mathbf{S^{\bullet}/\ S^{-}})$= -0.78 V vs.SCE ,In the absence of vibrational structures, $E_{0\text{-}0}$ can be roughly estimated from the absorption spectrum[3]. This corresponds to 385 nm, which translates into an $E_{0\text{-}0}$ $(\mathbf{S^{-*}/\ S^{-}})$ of 3.22 eV for the CySH anion.

$E_{p/2}(S^{\bullet}/S^{-*}) = E_{p/2}(S^{\bullet}/S^{-}) - E_{0\text{-}0}(S^{-*}/S^{-}) = -0.78-3.22 = -4.00$ V vs.SCE

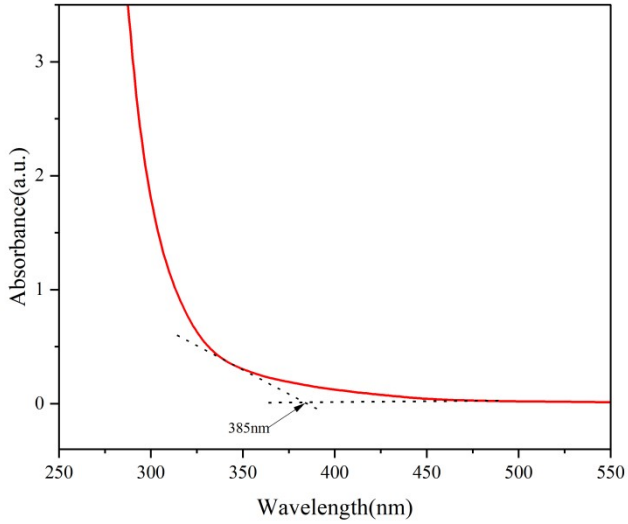
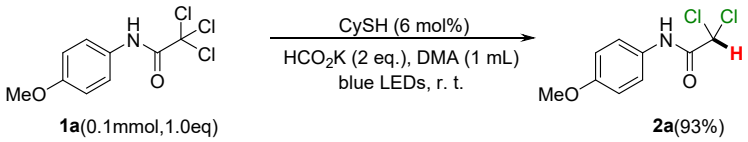


Figure S6. UV/vis absorption spectra of CySH anions.

i) Mass Metrics.



1a(0.1mmol,1.0eq) **2a**(93%)

Component		Amount'volume	Mol. wt./ ρ	Weight
Reactants	**1a**	0.1mmol	268.52	0.0268g
Catalyst	CySH	0.06mmol	116.22	0.0069g
Base	HCO_2K	0.2mmol	84.11	0.0168g
Solvent	DMA	1mL	0.937g/mL	0.937g
Product	**2a**	0.093mmol	234.07	0.0217g

Isolated Yield of 2a = 93%

E-factor $= \dfrac{\text{Mass of waste}}{\text{Mass of the product}}$

$= \dfrac{\text{Mass of all the reaction components - Mass of the product}}{\text{Mass of the product}}$

$= \dfrac{0.0268 + 0.0069 + 0.0168 - 0.0217}{0.0217}$ **=1.33g waste /g product**

Mass Intensity= $\dfrac{\text{Total mass of all the reagents}}{\text{Mass of the product}}$ **=E-factor** + 1=**2.33g waste /g product**

Atom Economy= $100\% \times \frac{\text{Molecular weight of the product}}{\text{Molecular weight of all the stoichiometric reactants}}$

$= 100\% \times \frac{\text{MWP}}{\text{MWA}} = 100\% \times \frac{234.07}{268.52} =$ **87.17%**

Atom Utilization= $\frac{\text{Mass of the product}}{\text{Total mass of all the substances produced}} = 100\% \times \frac{\text{mP}}{\text{mA}} = 100\% \times \frac{0.0217}{0.0234} =$ **92.73%**

Atom Effciency= Isolated Yield of product × **Atom Economy=** 93% × 87.17% **=81.06%**

Relative Mass Efficiency= $100\% \times \frac{\text{mass of the product}}{\text{Total mass of all the stoichiometric reagents}}$

$= 100\% \times \frac{0.0217}{0.0268} =$ **80.97%**

Carbon Efficiency= $100\% \times \frac{\text{Mass of the element in the product}}{\text{Total mass of the element in the stoichiometric reagents}}$

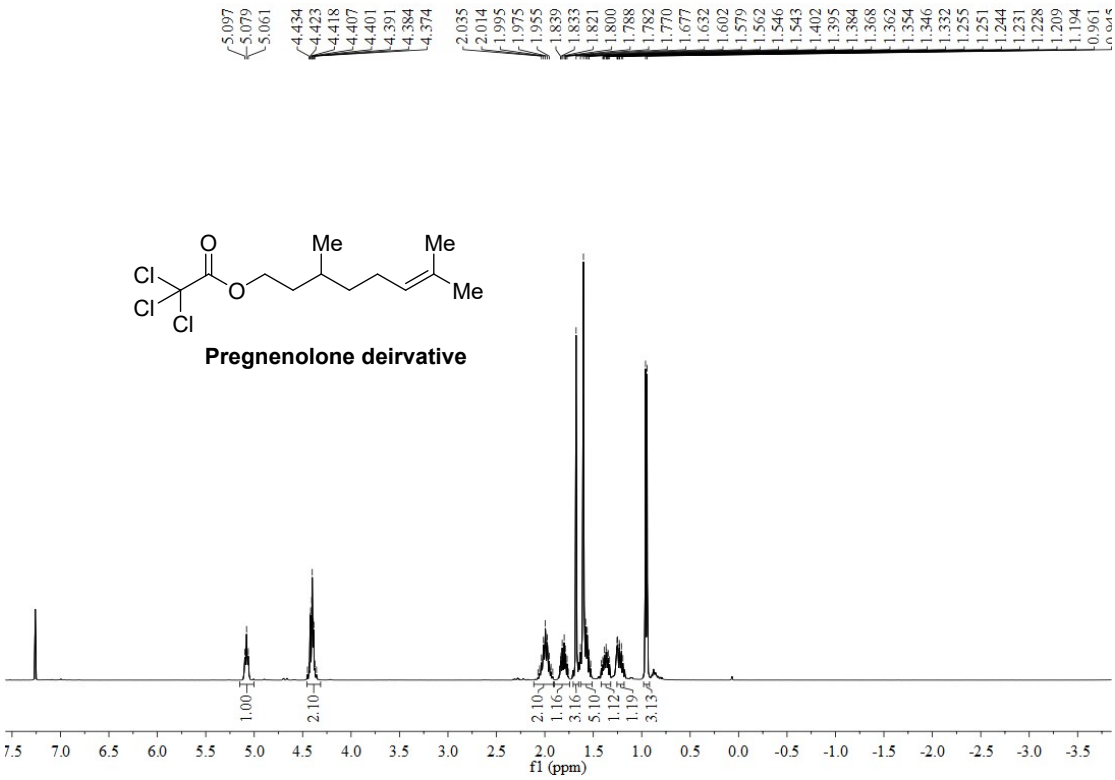
$= 100\% \times \frac{\text{nP XP}}{\text{nAXA}} = 100\% \times \frac{0.093 \times 9}{0.1 \times 9} =$ **93%**

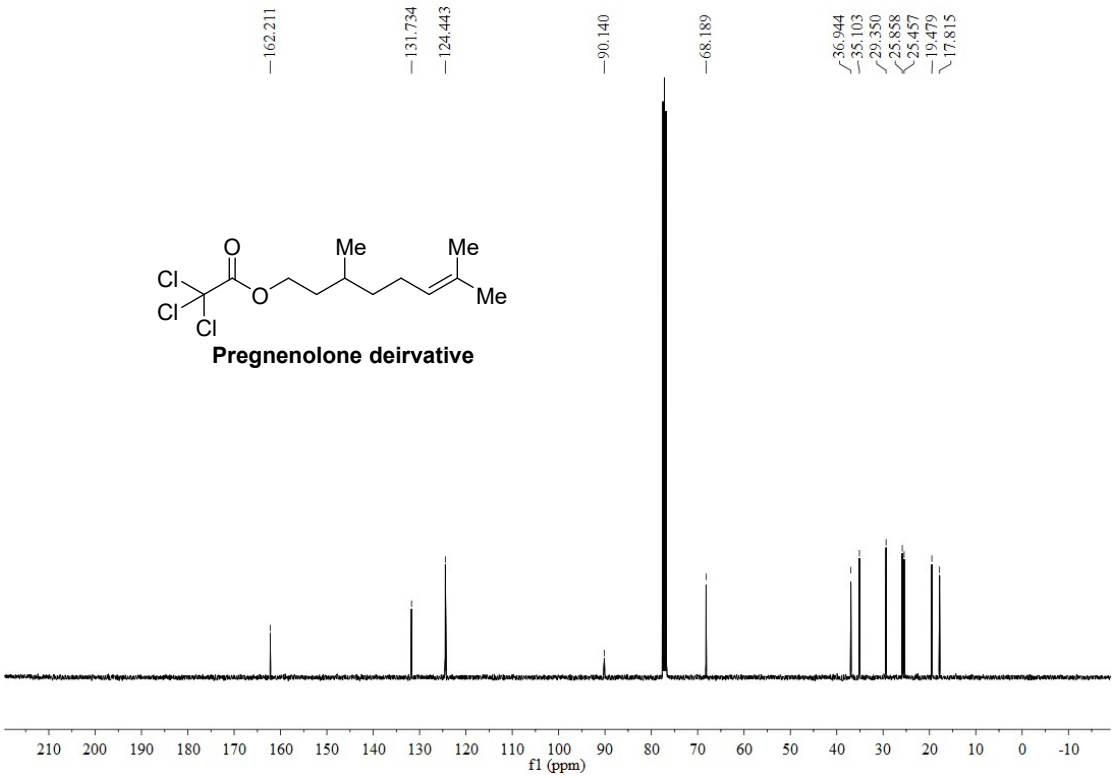
8. Reference

1. T. Imanishi, Y. Fujiwara, Y. Sawama, Y. Monguchi, H. Sajiki, *Adv. Syn & Catal.* **2012**, *354*, 771-776.
2.. Silvi, M.; Arceo, E.; Jurberg, I. D.; Cassani, C.; Melchiorre, P., *J. Am. Chem. Soc.* **2015**, *137*, 6120−6123.
3. Buzzetti, L.; Crisenza, G. E. M.; Melchiorre, P., *Angew. Chem., Int. Ed.,* **2019**, *58* ,3730 – 3747.

9. Spectra for Substrates and Products Product Characterization

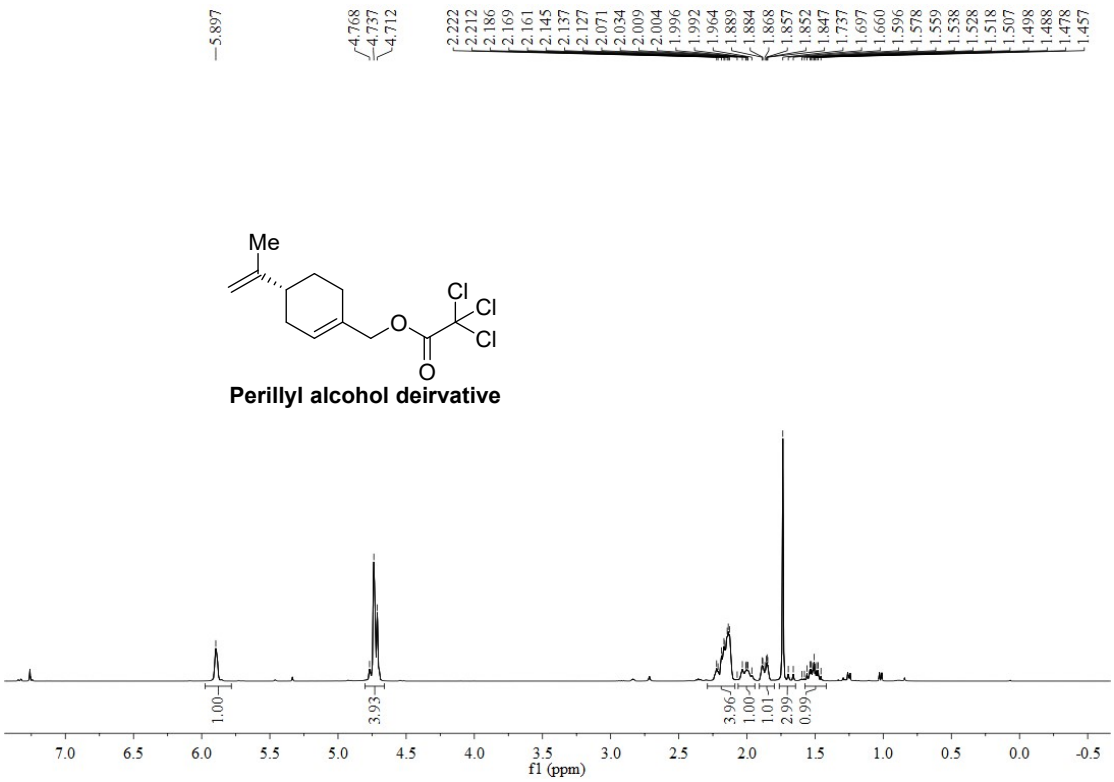
Pregnenolone deirvative, $^{1}H+^{13}C$



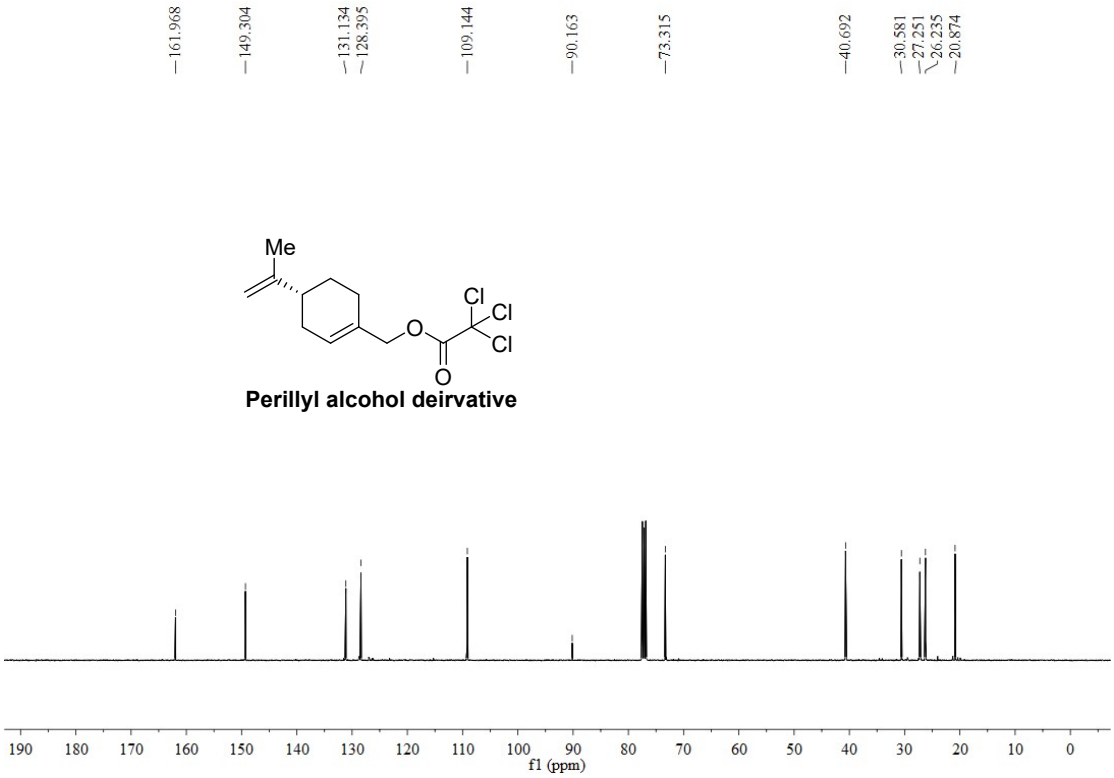


Pregnenolone deirvative

Perillyl alcohol deirvative, $^{1}H+^{13}C$

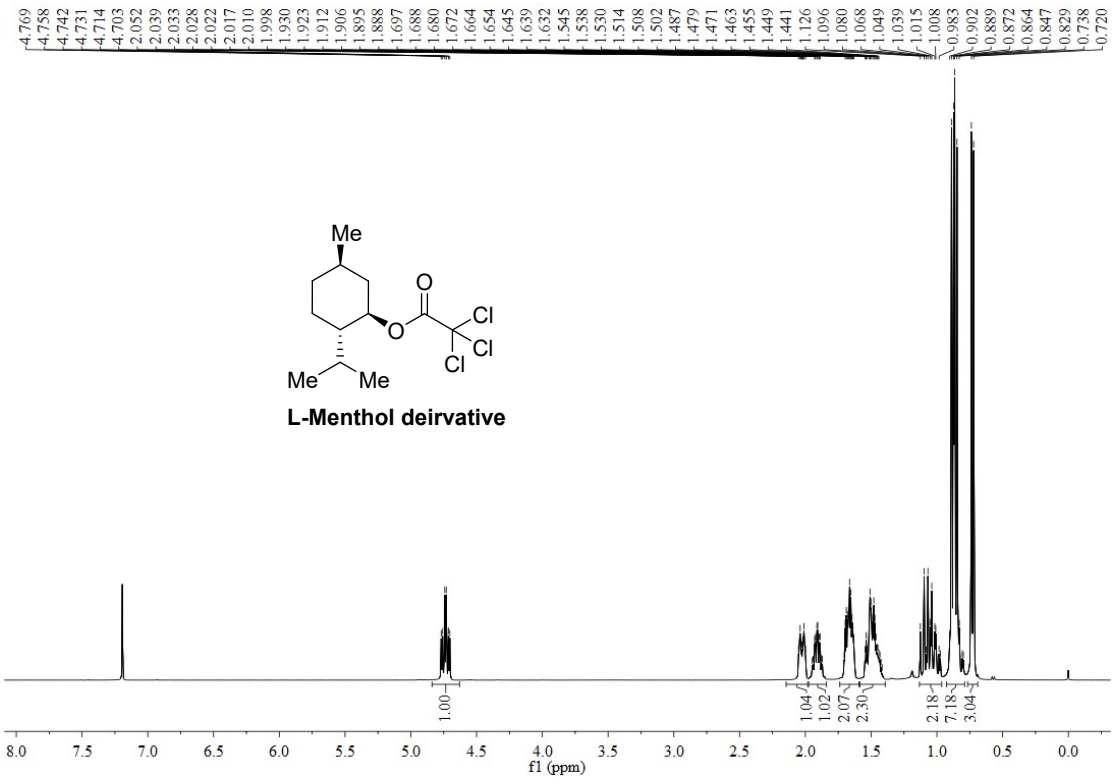


Perillyl alcohol deirvative

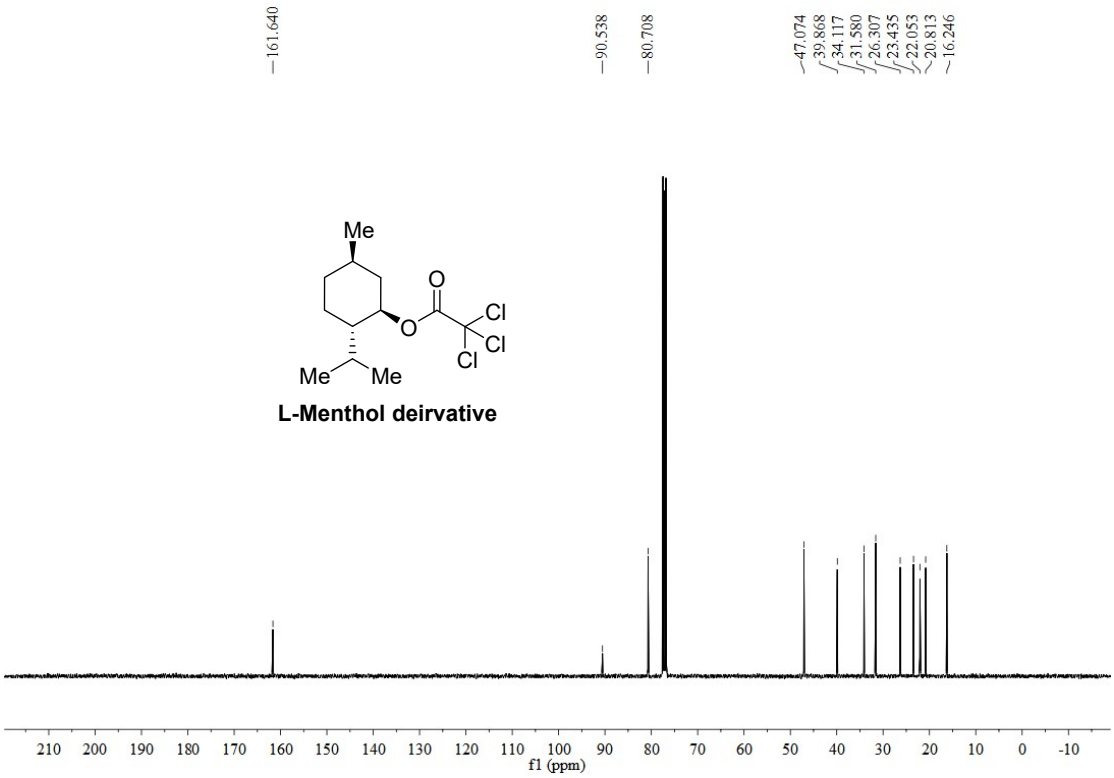


Perillyl alcohol deirvative

L-Menthol deirvative, $^{1}H+^{13}C$

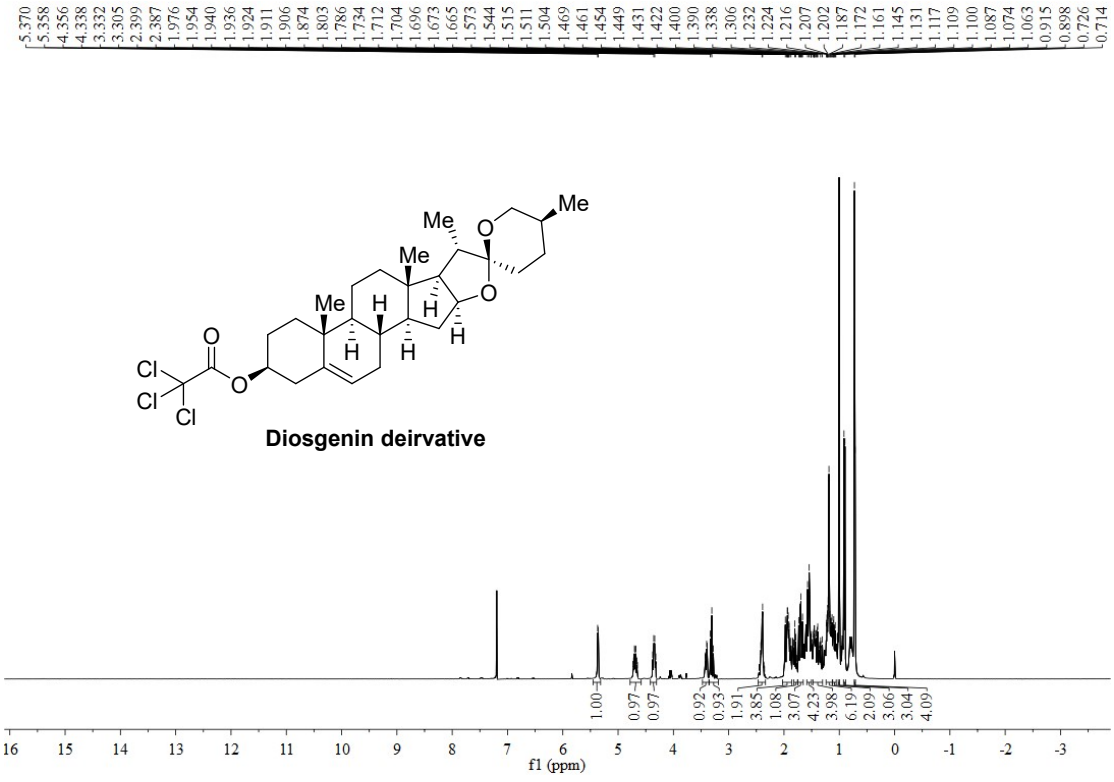


L-Menthol deirvative

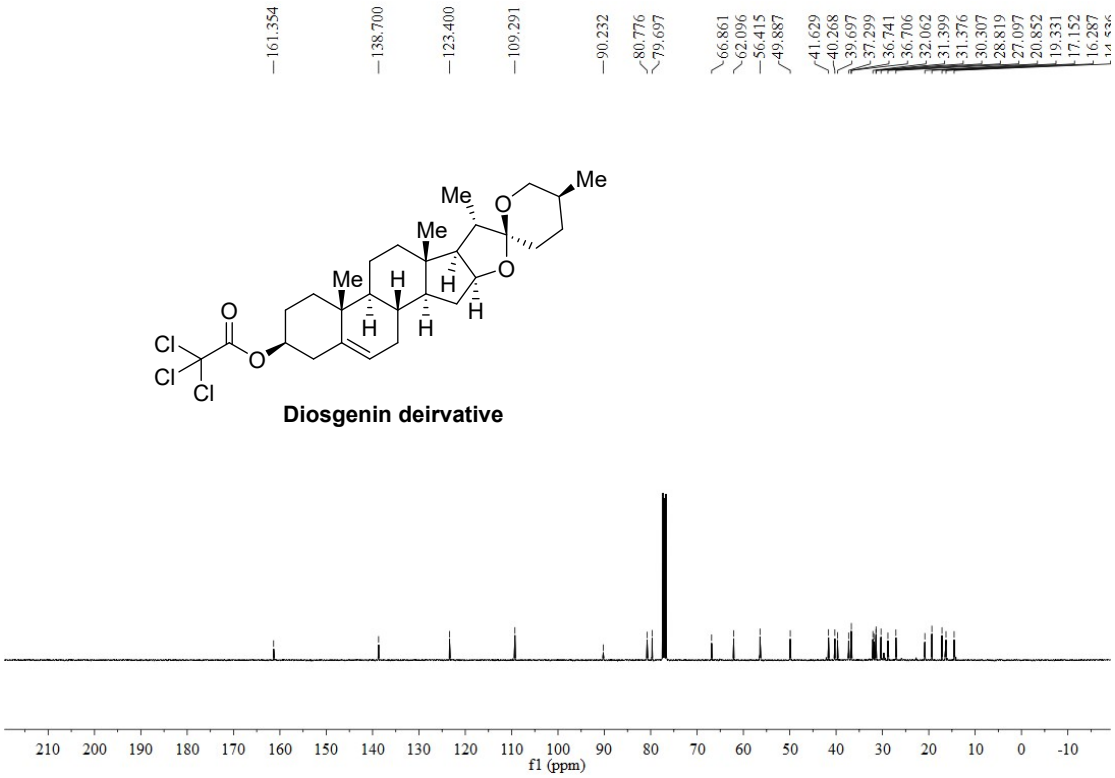


L-Menthol deirvative

Diosgenin deirvative, $^{1}H+^{13}C$

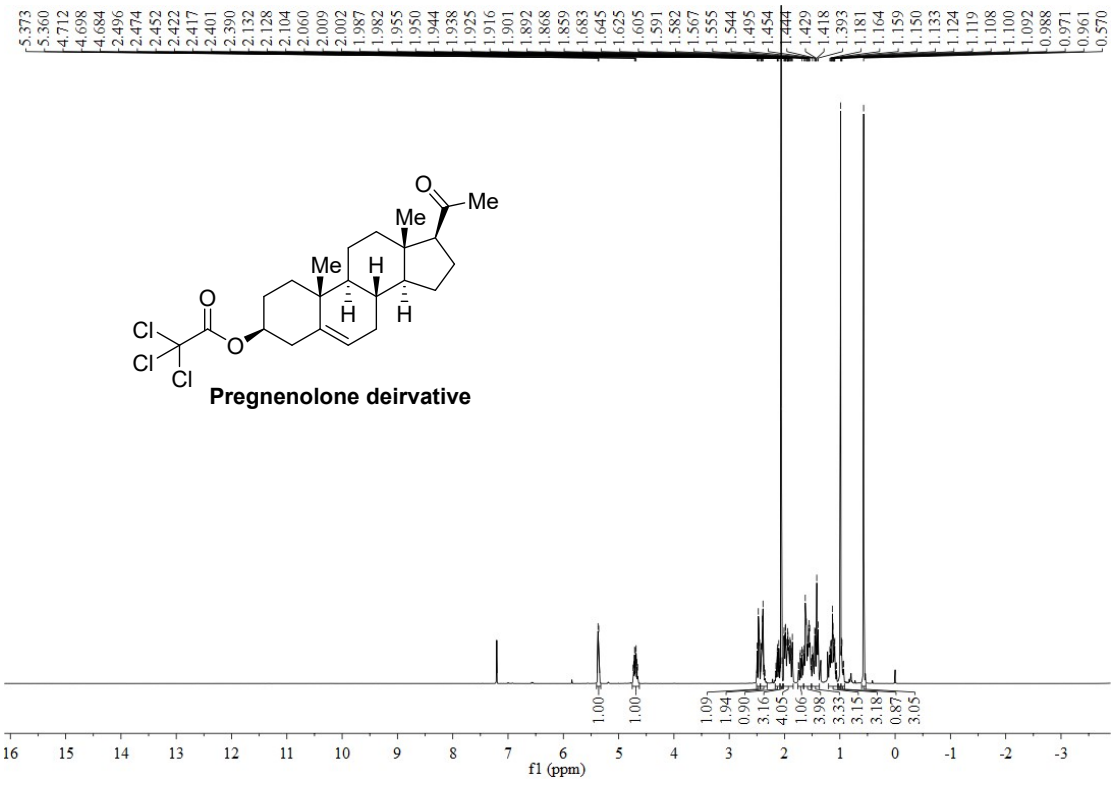


Diosgenin deirvative

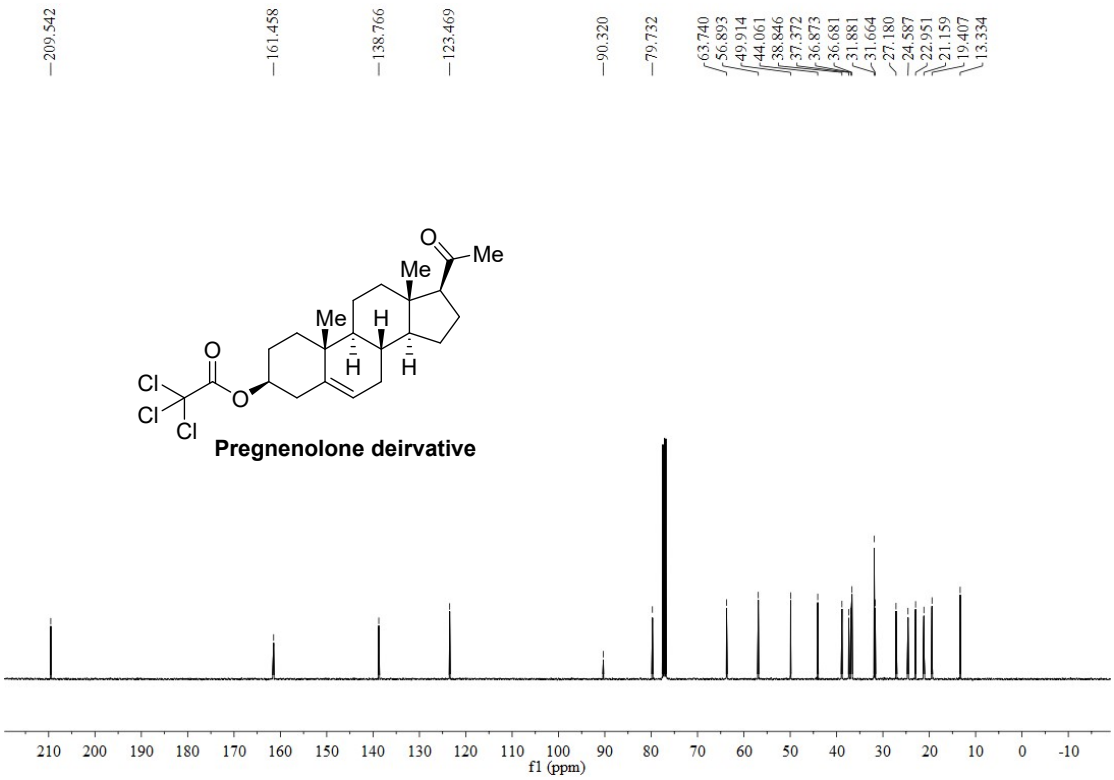


Diosgenin deirvative

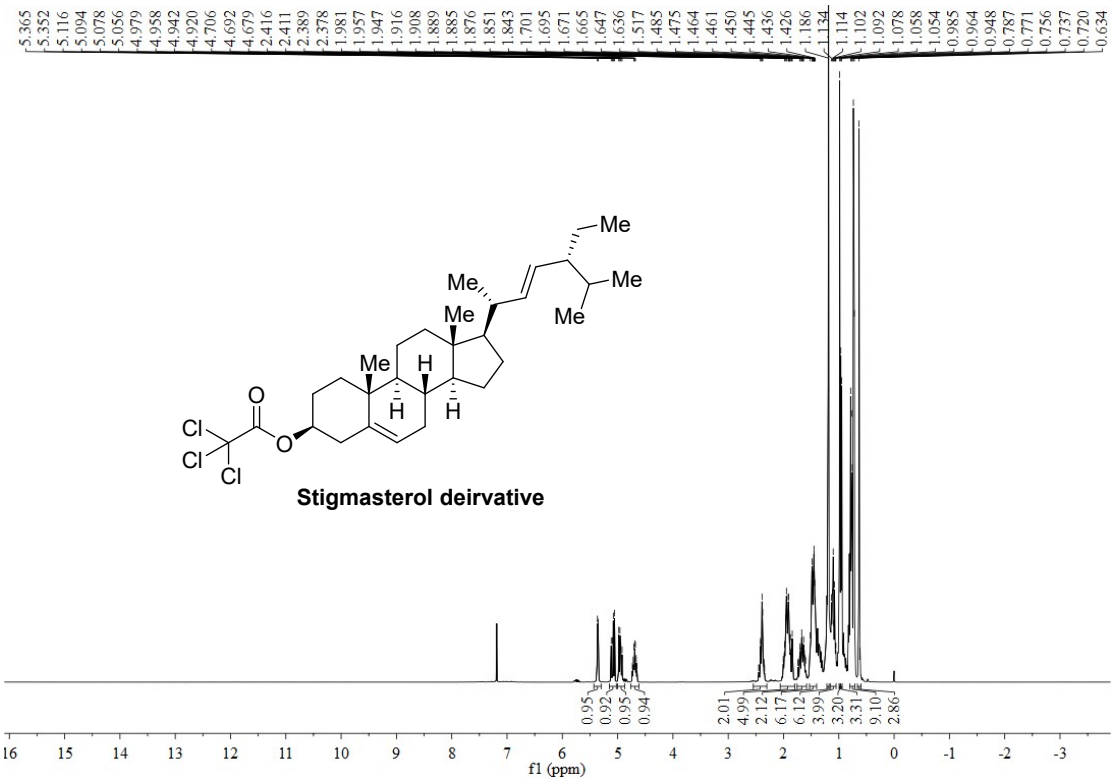
Pregnenolone deirvative, $^{1}H+^{13}C$

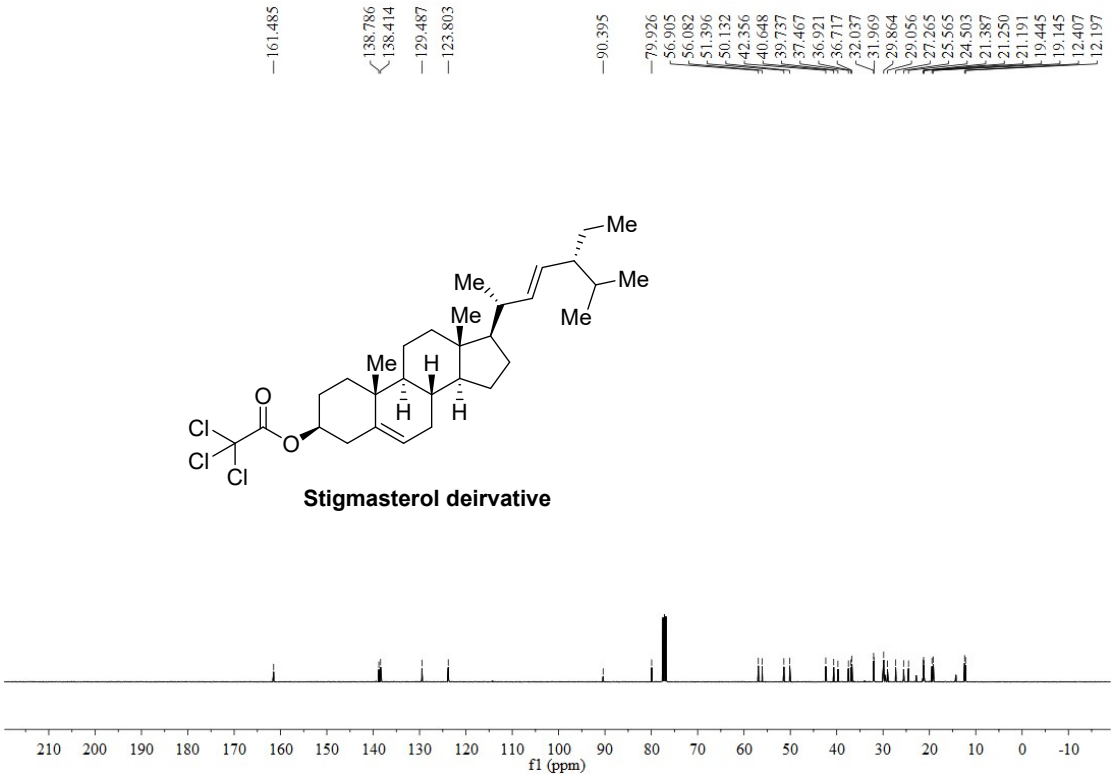


Pregnenolone deirvative

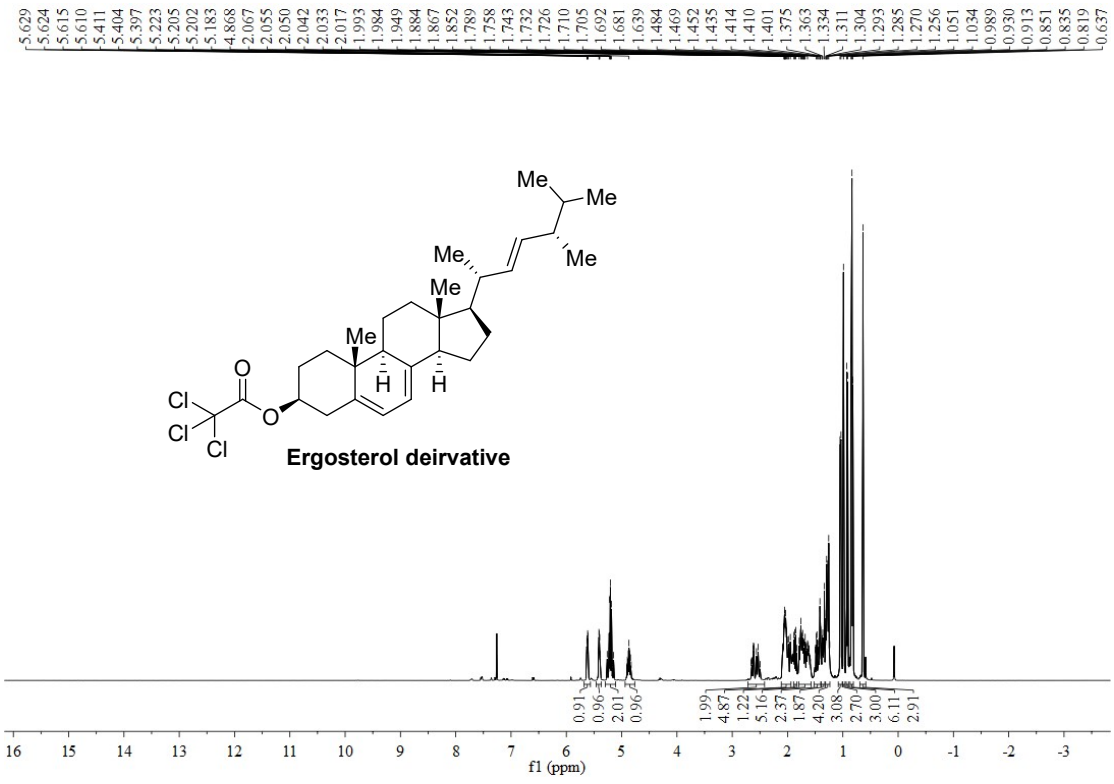


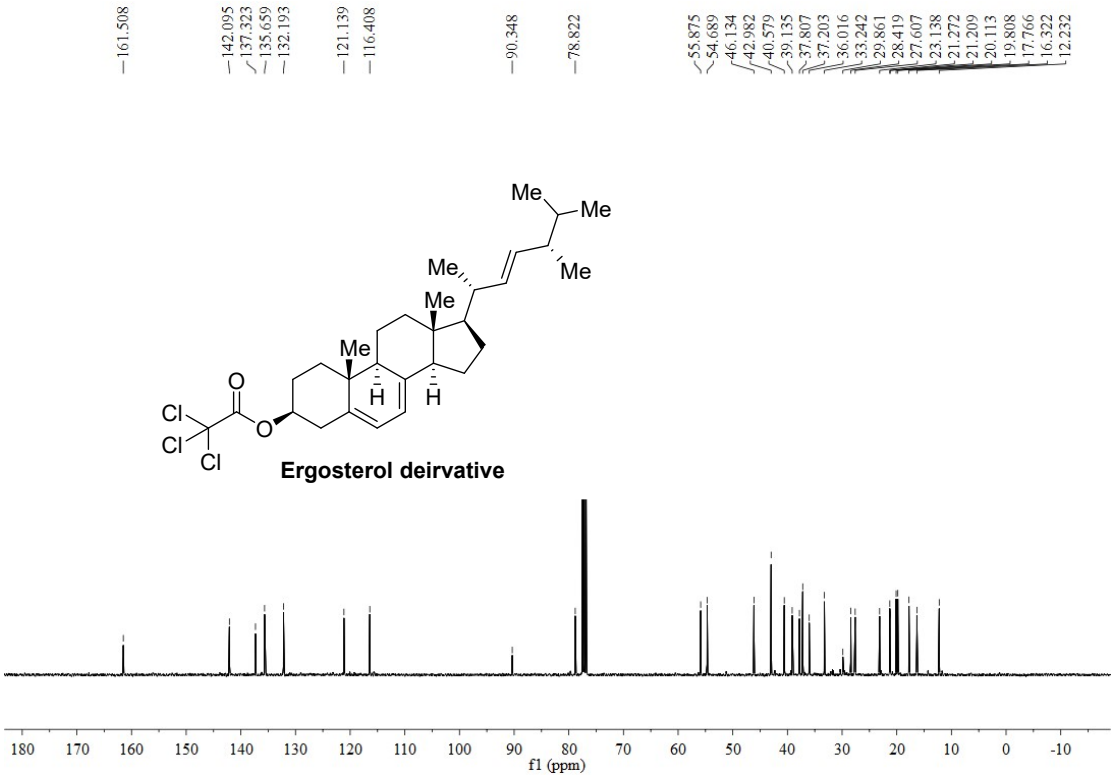
Stigmasterol deirvative, $^{1}H+^{13}C$



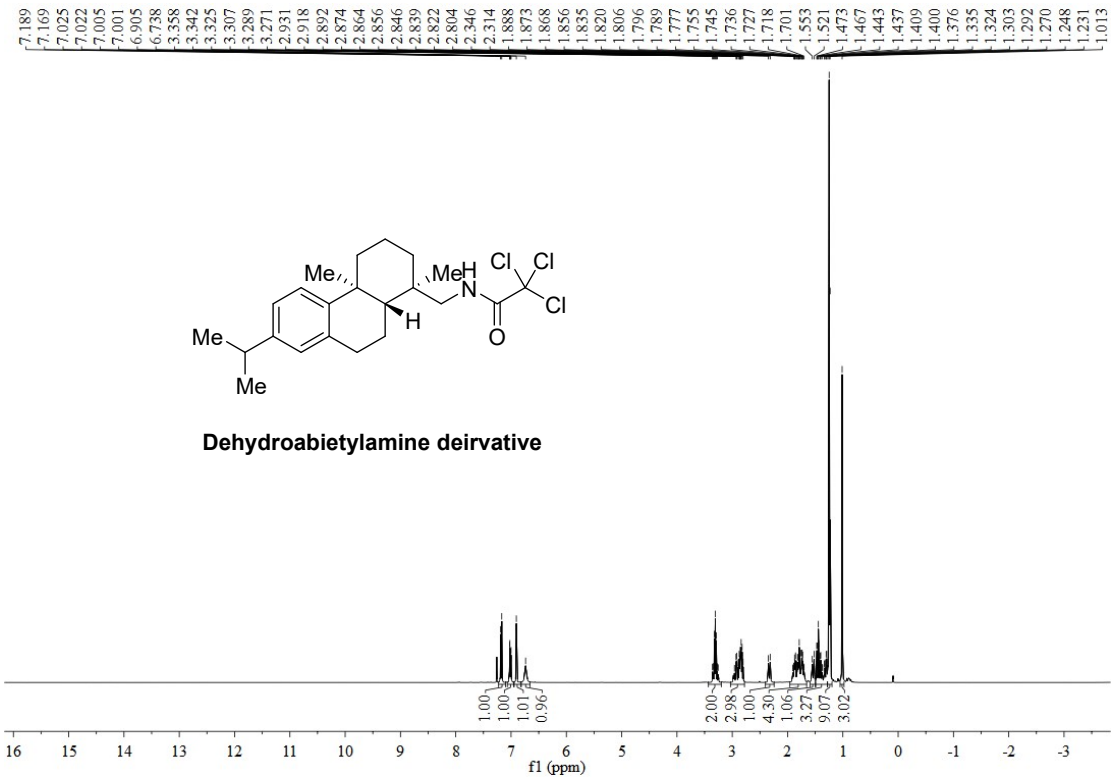


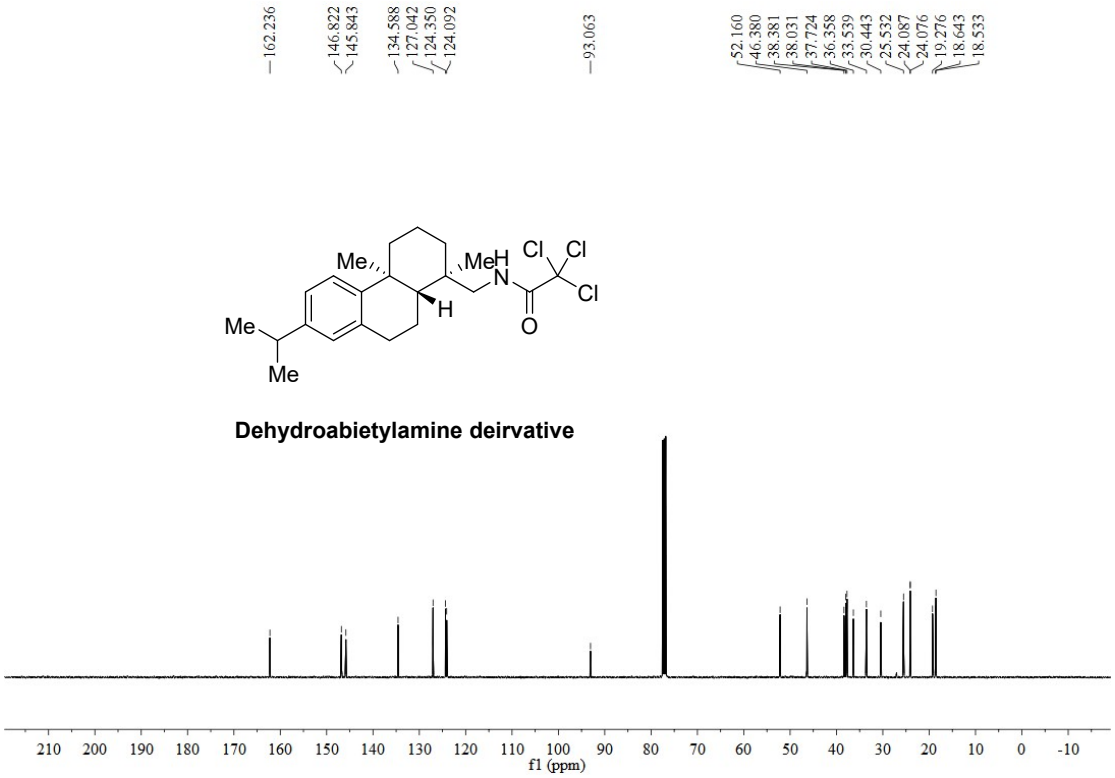
Ergosterol deirvative, $^{1}H+^{13}C$





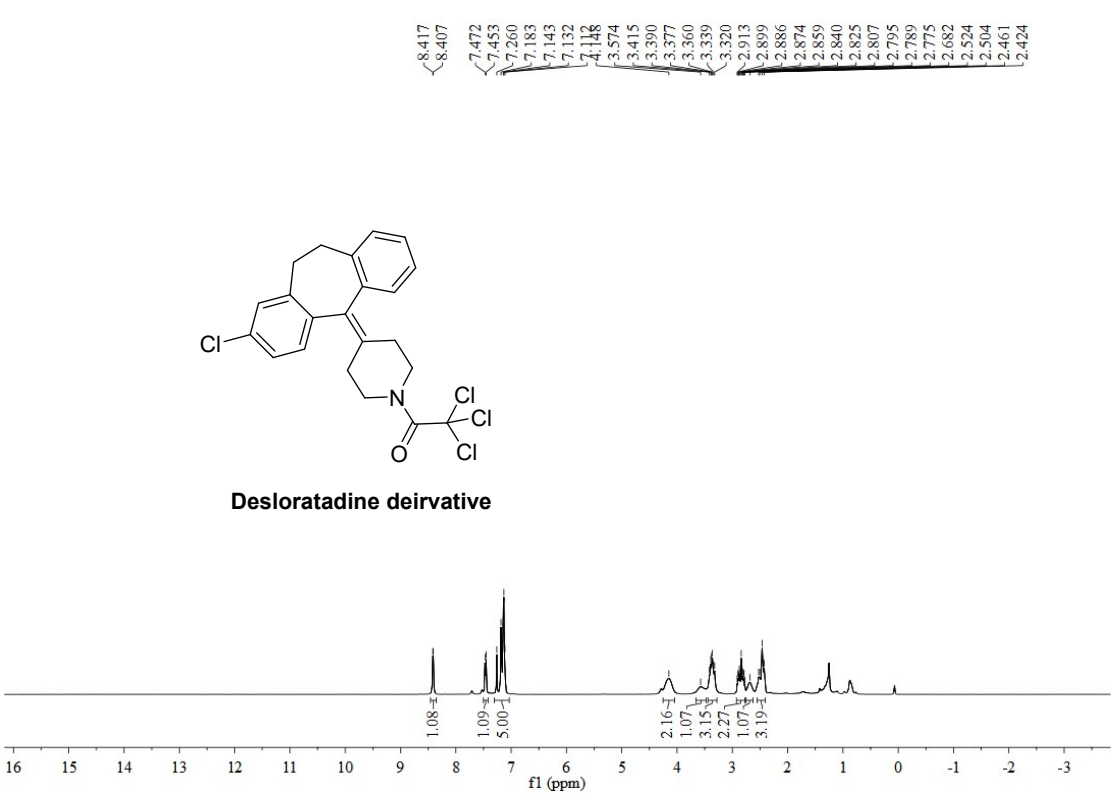
Dehydroabietylamine deirvative, $^{1}H+^{13}C$



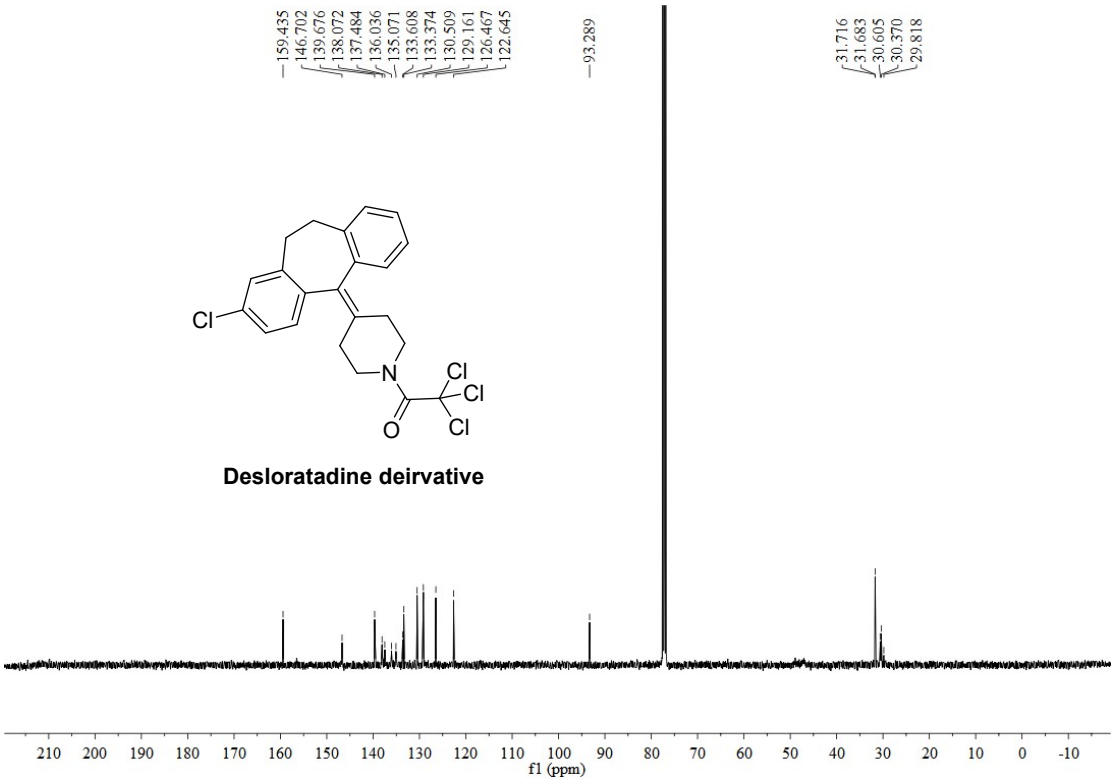


Dehydroabietylamine deirvative

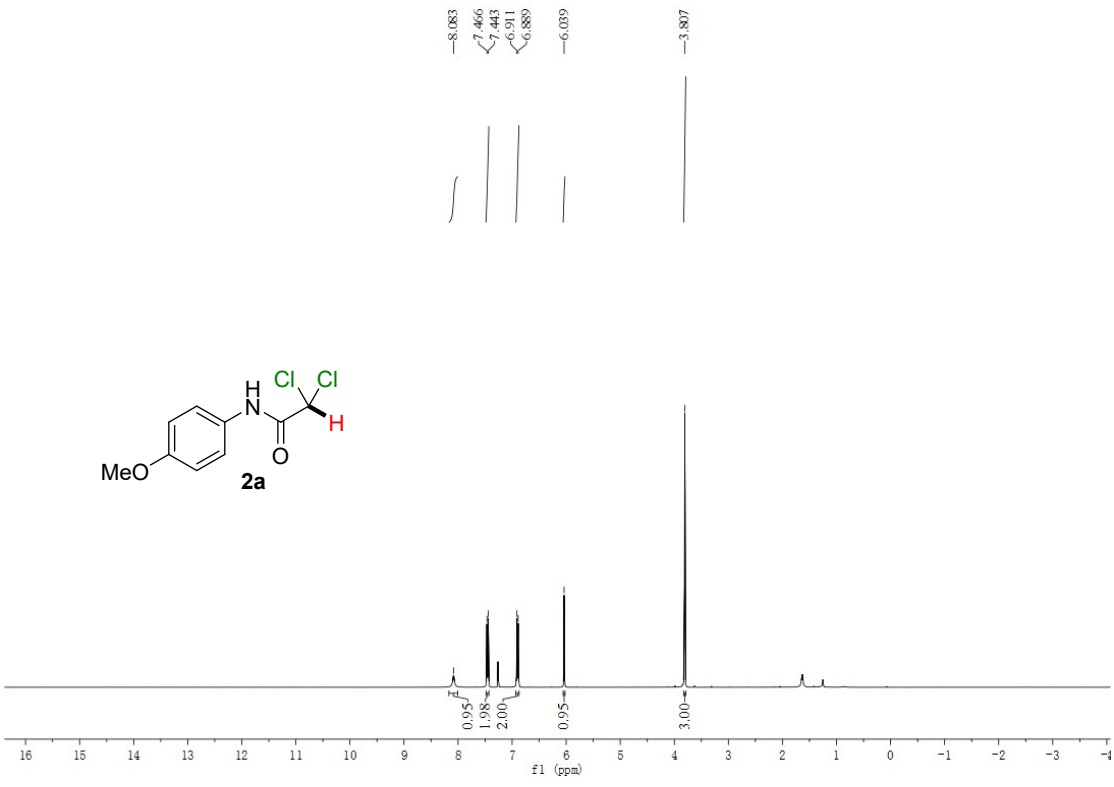
Desloratadine deirvative, $^{1}H+^{13}C$

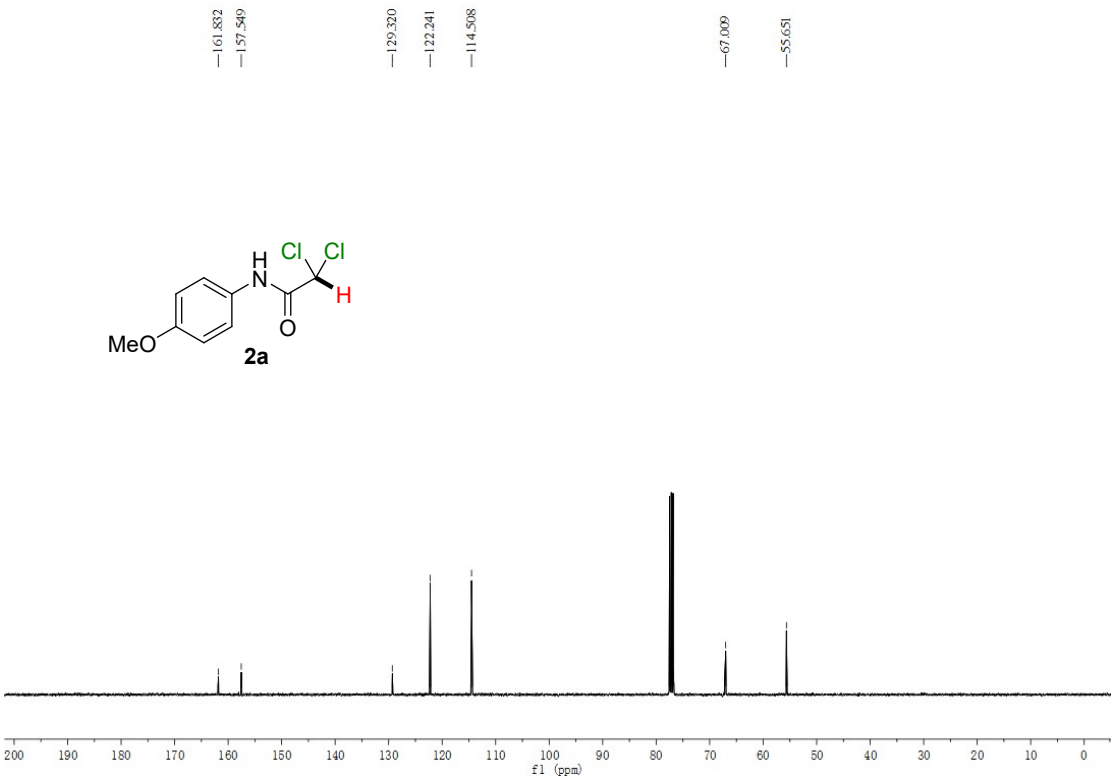


Desloratadine deirvative

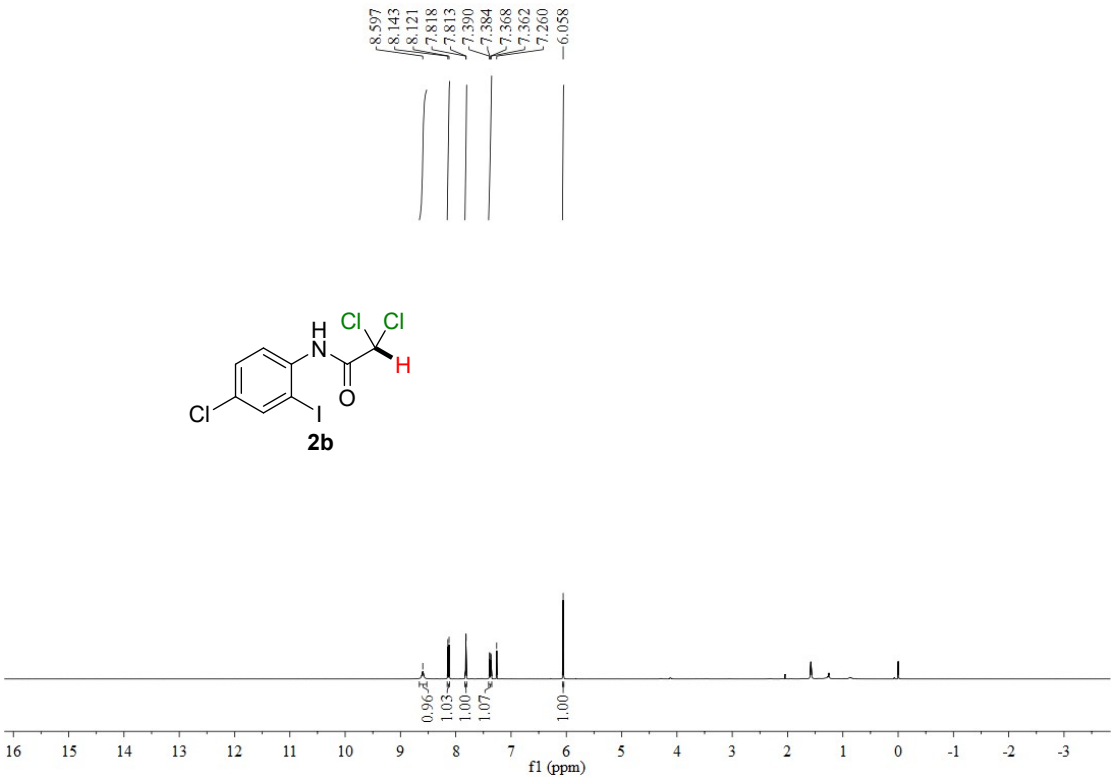

159.435
146.702
139.676
138.072
137.484
136.036
135.071
133.608
133.374
130.509
129.161
126.467
122.645
93.289
31.716
31.683
30.605
30.370
29.818
Cl
N
Cl
Cl
Cl
O
Desloratadine deirvative
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

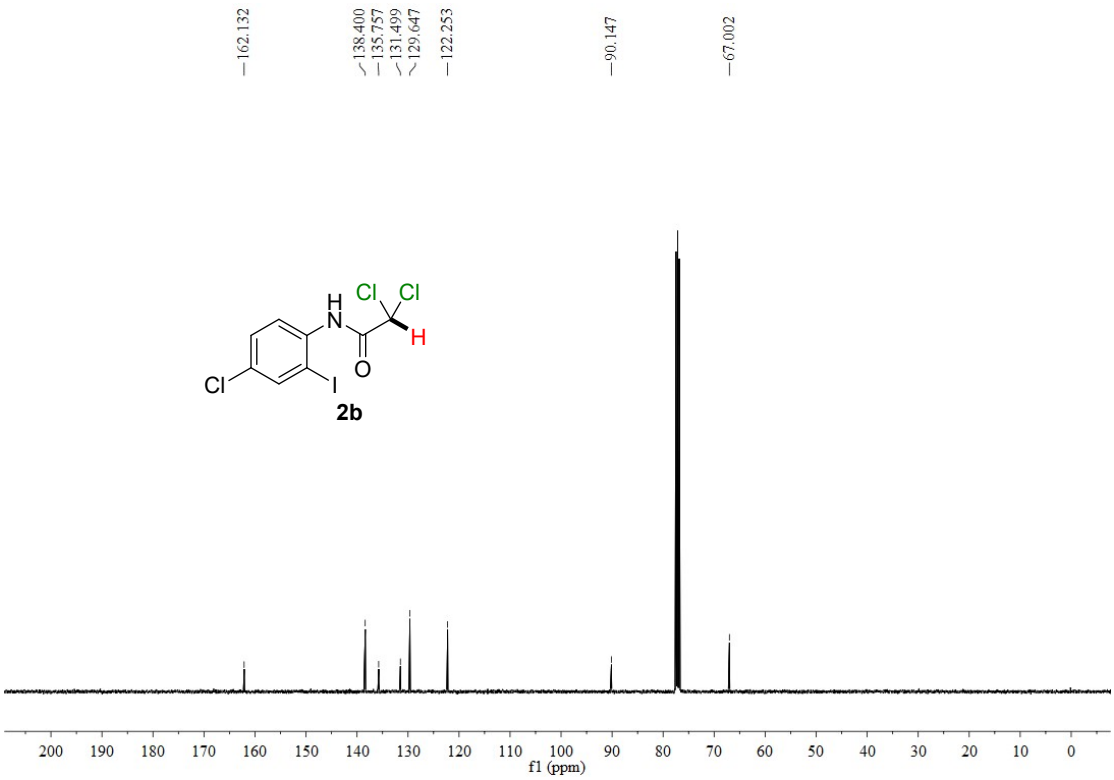
2a, $^{1}H+^{13}C$


8.083
7.466
7.443
6.911
6.889
6.039
3.807
H
N
Cl
Cl
H
O
MeO
2a
0.95
1.98
2.00
0.95
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

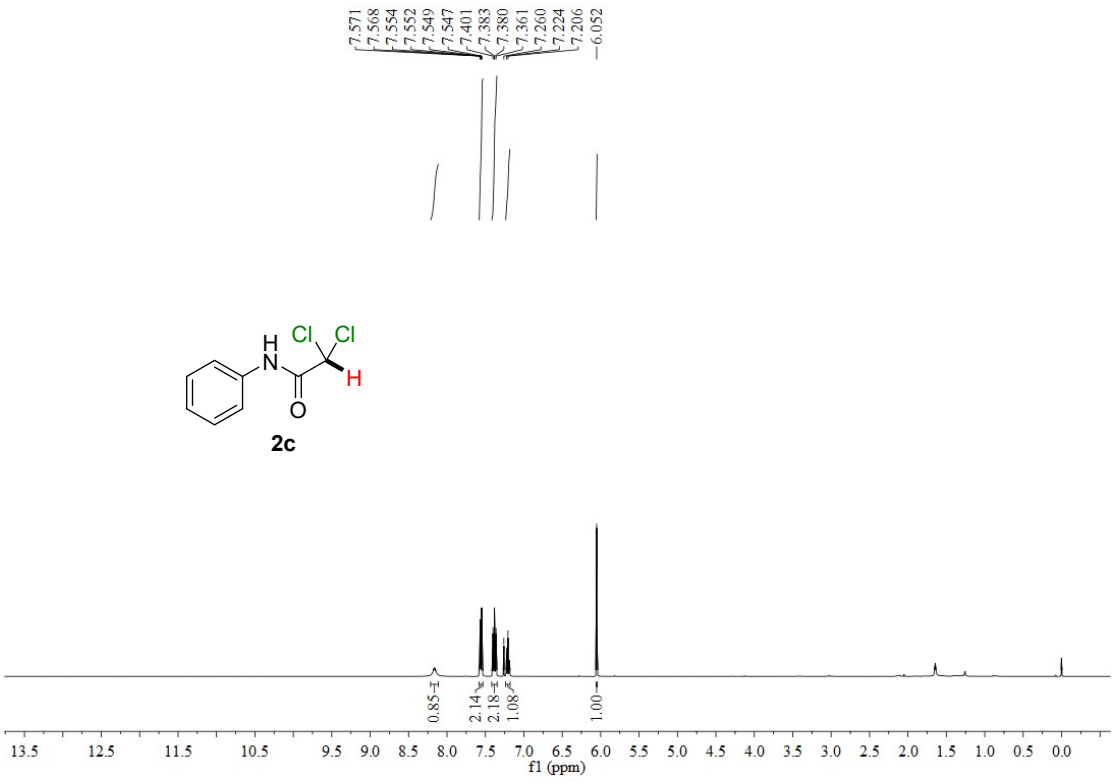

161.832
157.549
129.320
122.241
114.508
67.009
55.651
Cl
Cl
H
N
H
O
MeO
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

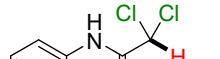
2b, $^{1}H+^{13}C$

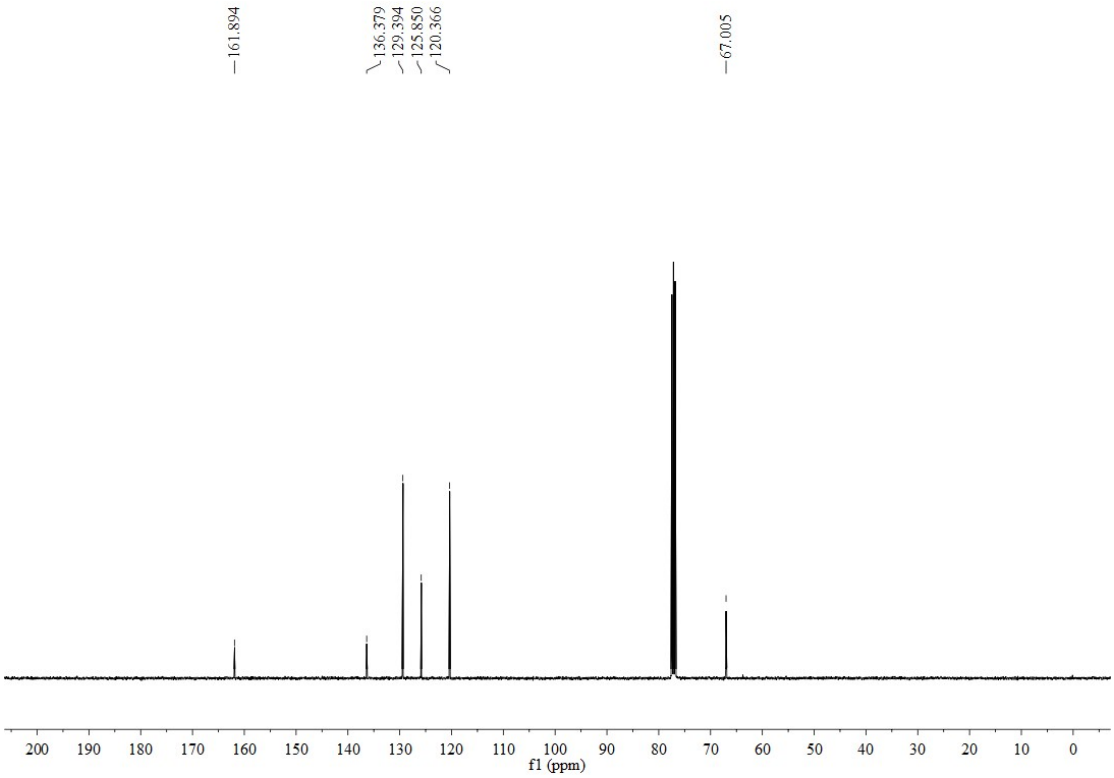

8.597
8.143
8.121
7.818
7.813
7.390
7.384
7.368
7.362
7.260
6.058
Cl
Cl
H
N
H
O
Cl
I
2b
0.96
1.03
1.00
1.07
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


162.132
138.400
135.757
131.499
129.647
122.253
90.147
67.002
Cl
Cl
H
N
O
Cl
I
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

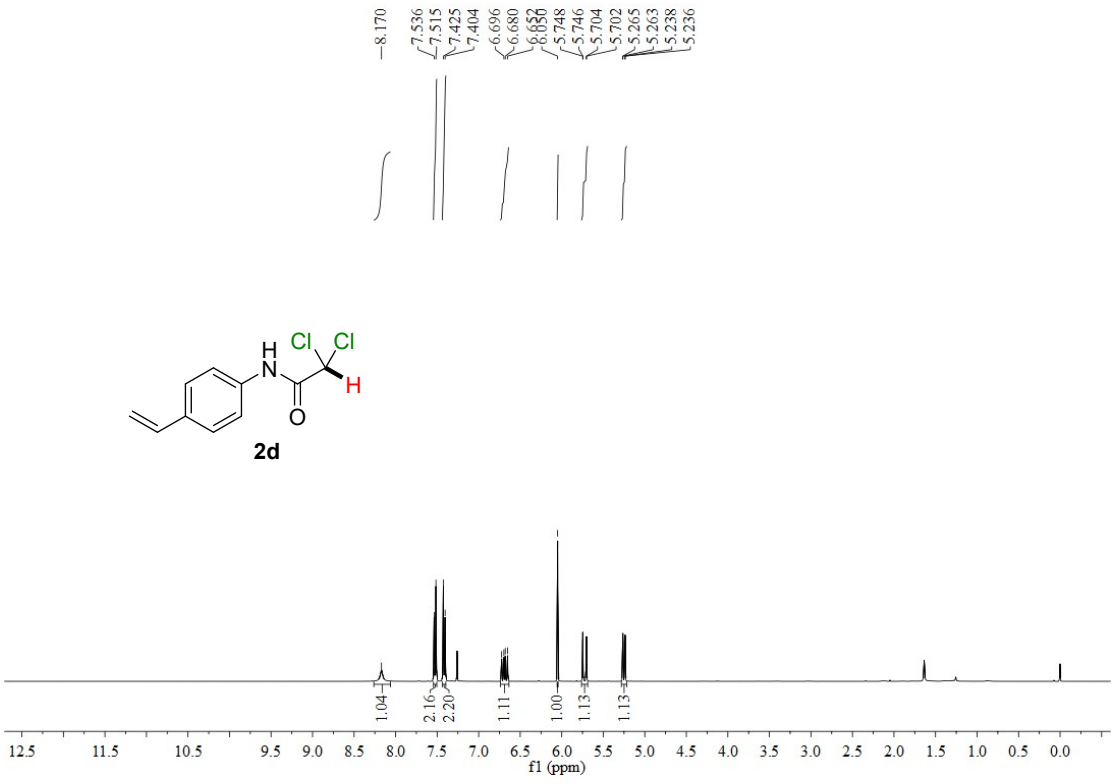
2c, $^{1}H+^{13}C$

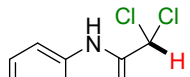

7.571
7.568
7.554
7.552
7.549
7.547
7.401
7.383
7.380
7.361
7.260
7.224
7.206
6.052
Cl
Cl
H
N
O
2c
0.85
2.14
2.18
1.08
1.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

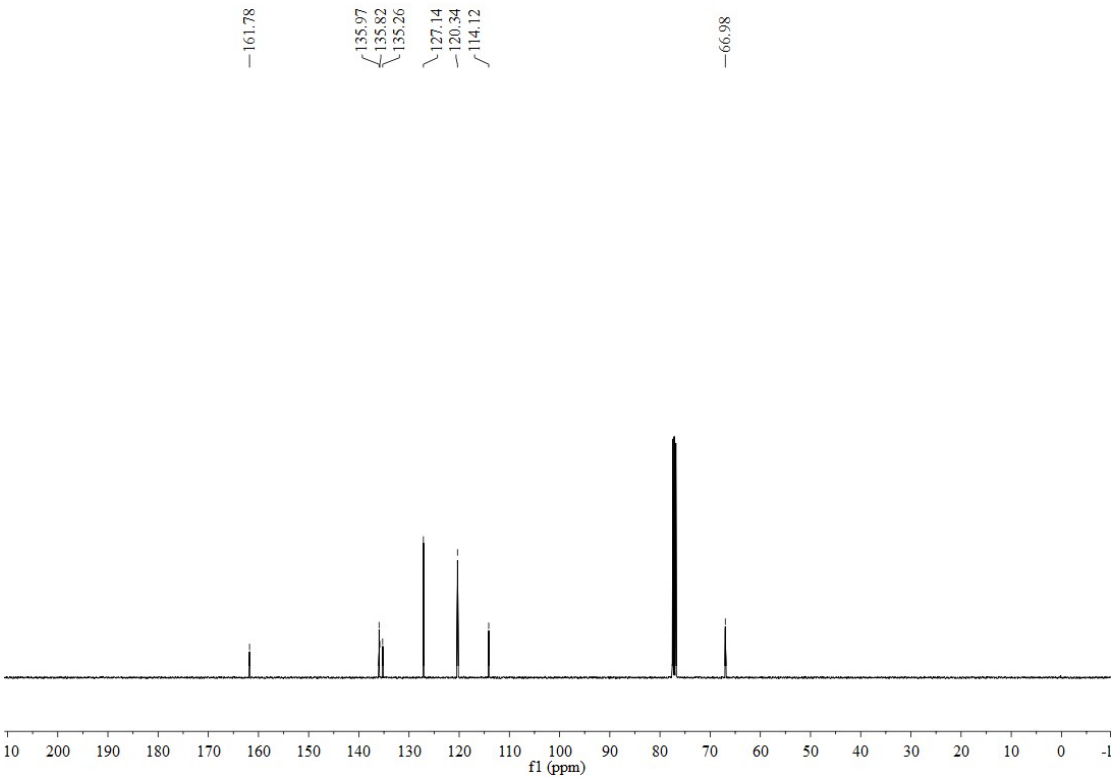

Cl
Cl
H
N


161.894
136.379
129.394
125.850
120.366
67.005
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

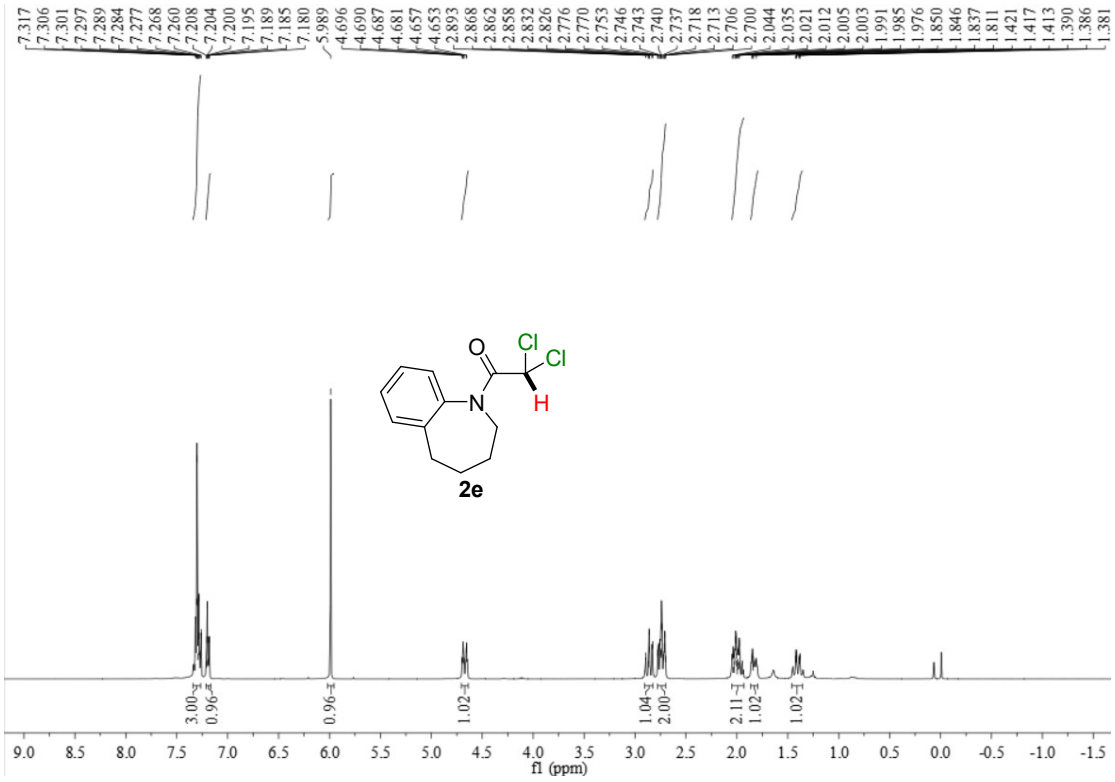
2d, $^{1}H+^{13}C$

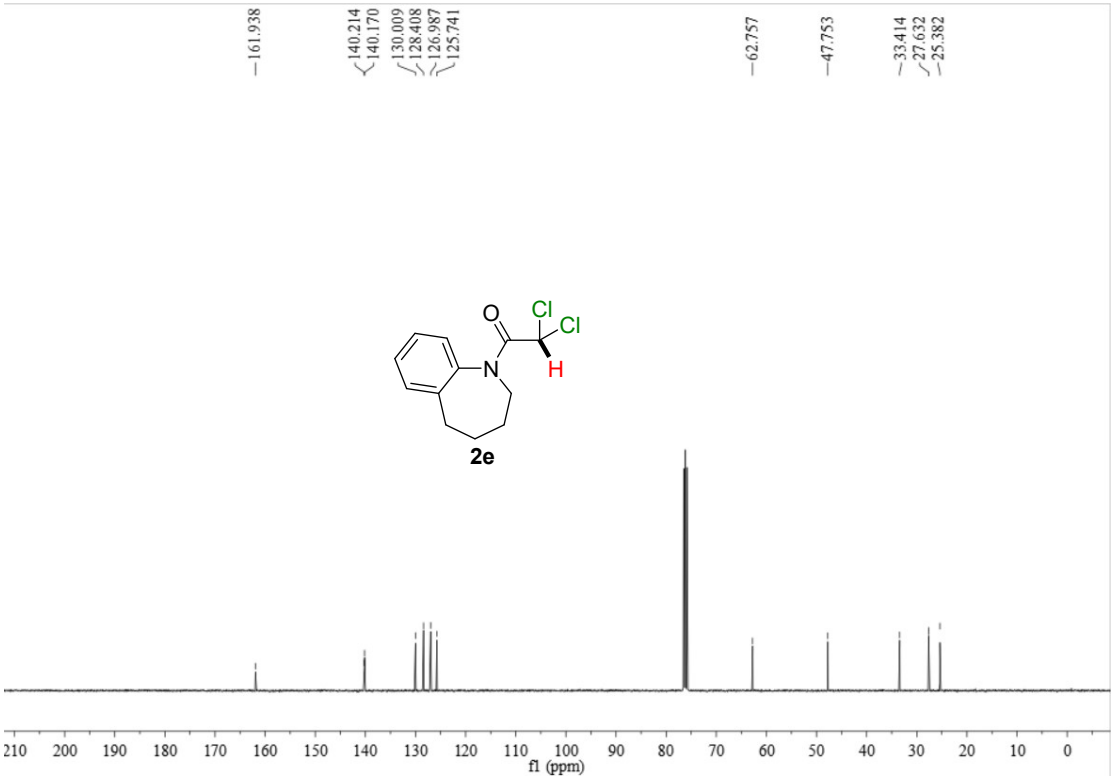

8.170
7.536
7.515
7.425
7.404
6.696
6.680
5.748
5.746
5.704
5.702
5.265
5.263
5.238
5.236
Cl
Cl
H
N
H
O
2d
1.04
2.16
2.20
1.11
1.00
1.13
1.13
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
Cl
H
N
H

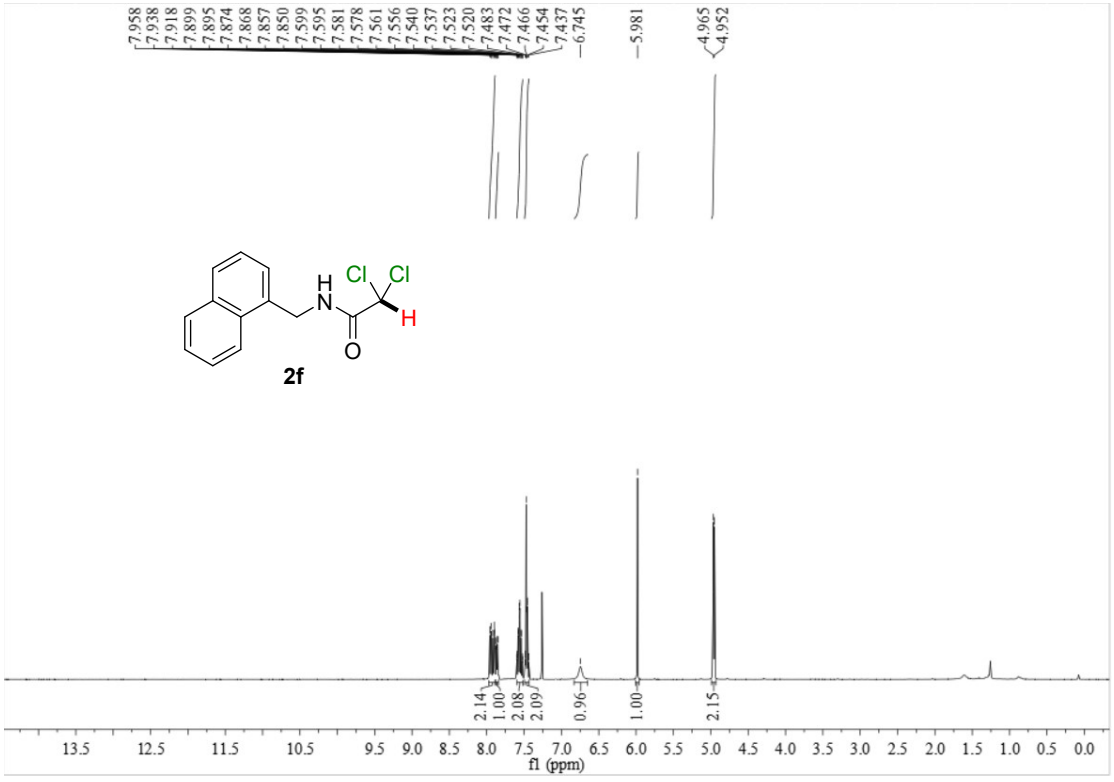

161.78
135.97
135.82
135.26
127.14
120.34
114.12
66.98
f1 (ppm)

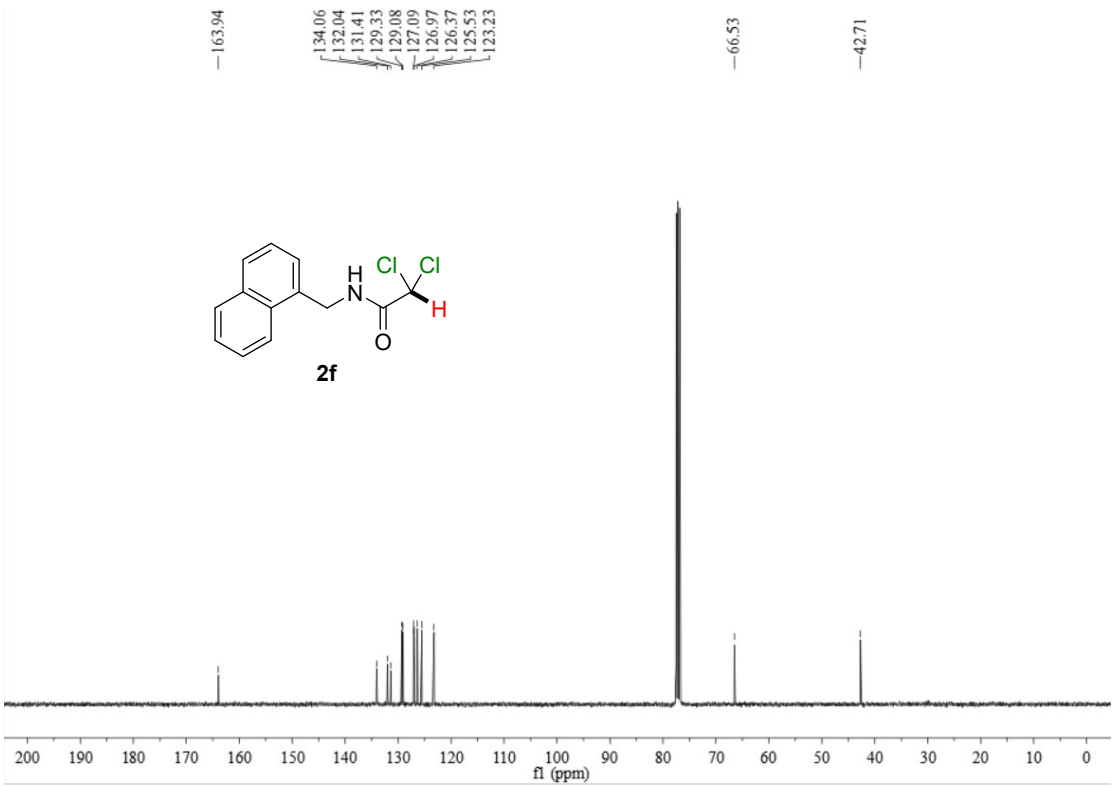
2e, $^{1}H+^{13}C$


7.317
7.306
7.301
7.297
7.289
7.284
7.277
7.268
7.260
7.208
7.204
7.200
7.195
7.189
7.185
7.180
5.989
4.696
4.690
4.687
4.681
4.657
4.653
2.893
2.868
2.862
2.858
2.832
2.826
2.776
2.770
2.753
2.746
2.743
2.740
2.737
2.718
2.713
2.706
2.700
2.044
2.035
2.021
2.012
2.005
2.003
1.991
1.985
1.976
1.850
1.846
1.837
1.811
1.421
1.417
1.413
1.390
1.386
1.381
O
Cl
Cl
H
N
2e
3.00
0.96
0.96
1.02
1.04
2.00
2.11
1.02
1.02
f1 (ppm)

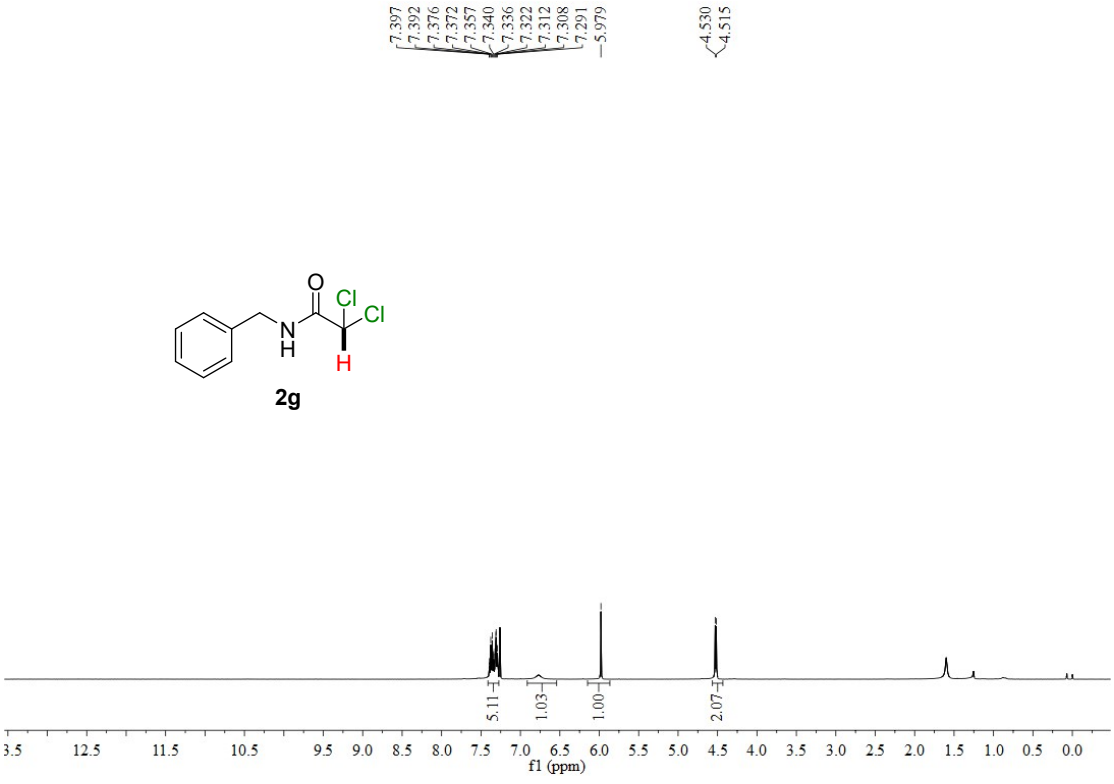

161.938
140.214
140.170
130.009
128.408
126.987
125.741
62.757
47.753
33.414
27.632
25.382
O
Cl
Cl
N
H
2e
f1 (ppm)

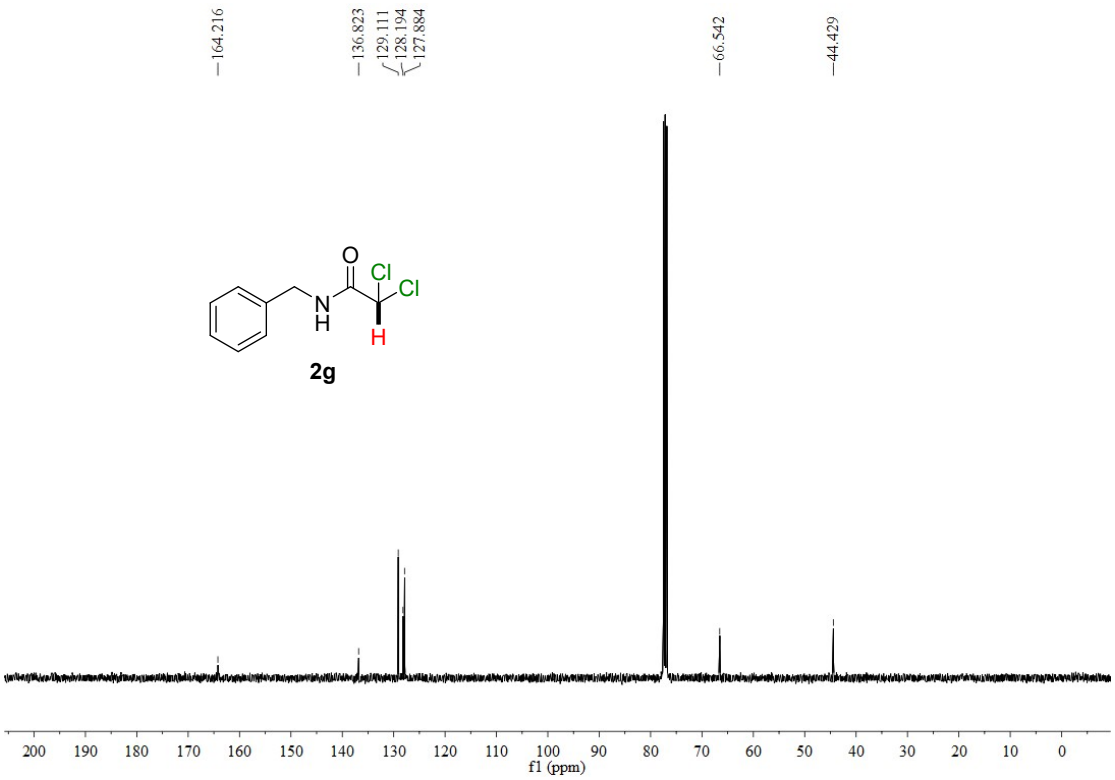
2f, $^{1}H+^{13}C$


7.958
7.938
7.918
7.899
7.895
7.874
7.868
7.857
7.850
7.599
7.595
7.581
7.578
7.561
7.556
7.540
7.537
7.523
7.520
7.483
7.472
7.466
7.454
7.437
6.745
5.981
4.965
4.952
H
N
Cl
Cl
H
O
2f
2.14
1.00
2.08
2.09
0.96
1.00
2.15
f1 (ppm)

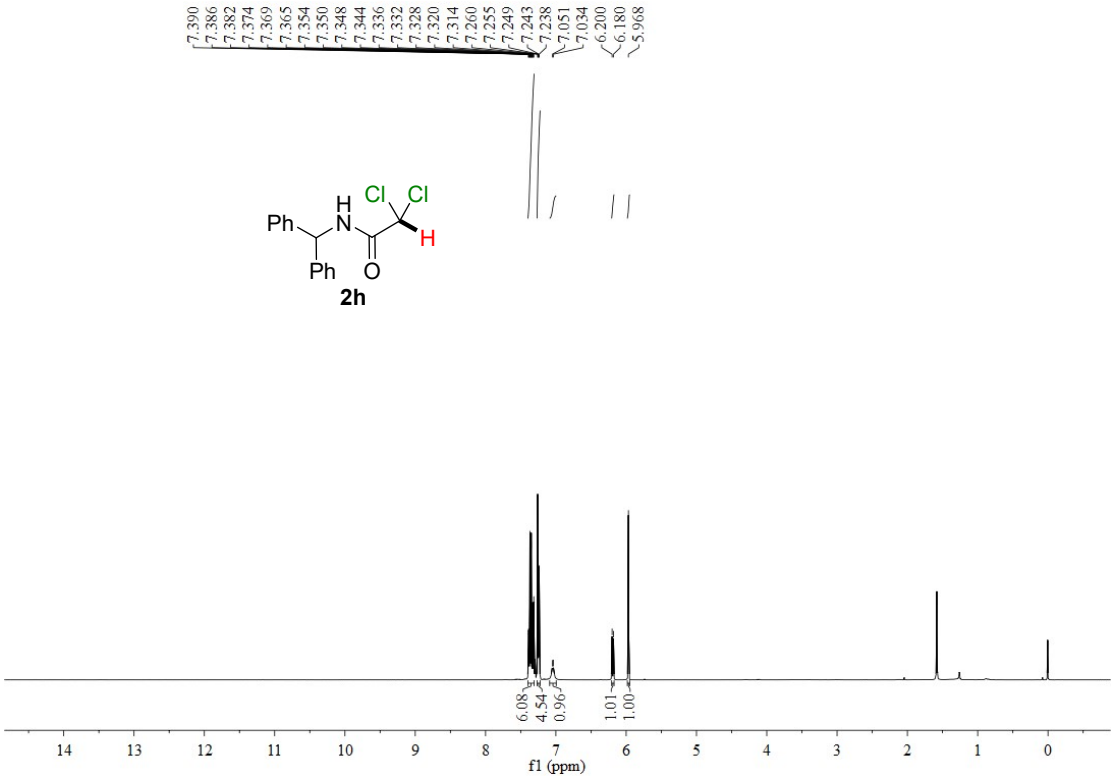

163.94
134.06
132.04
131.41
129.33
129.08
127.09
126.97
126.37
125.53
123.23
66.53
42.71
Cl
Cl
H
N
H
O
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

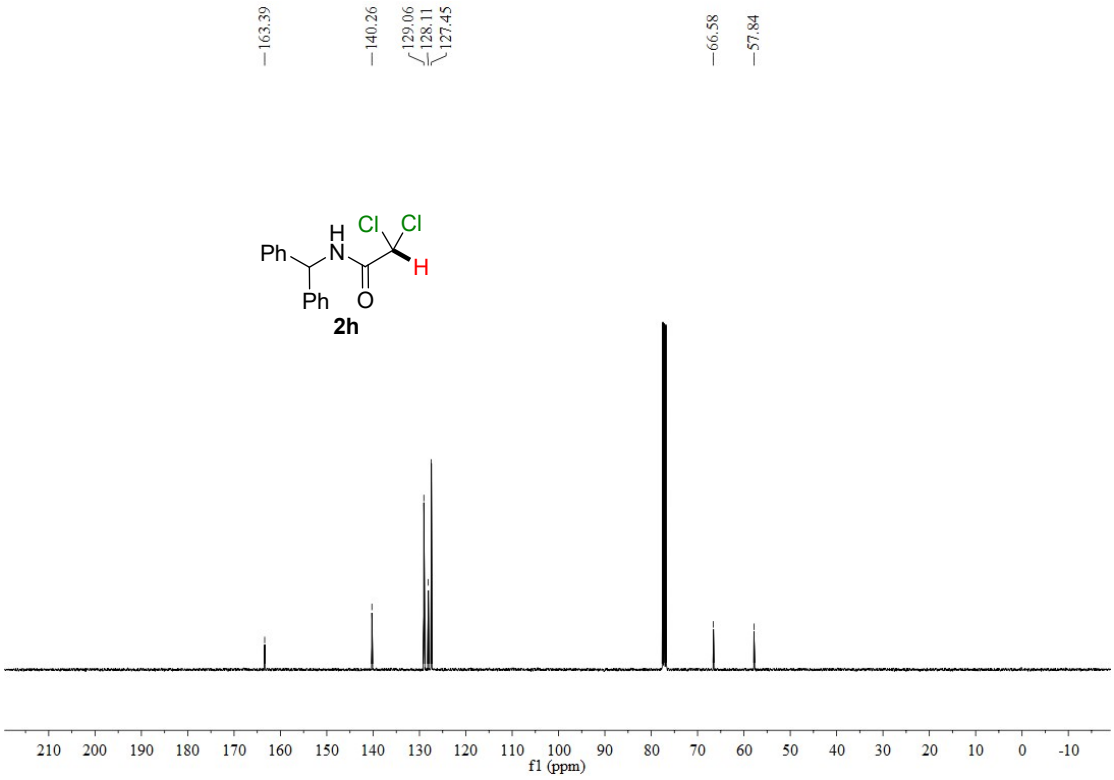
2g, $^{1}H+^{13}C$


7.397
7.392
7.376
7.372
7.357
7.340
7.336
7.322
7.312
7.308
7.291
5.979
4.530
4.515
O
Cl
Cl
N
H
H
2g
5.11
1.03
1.00
2.07
3.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

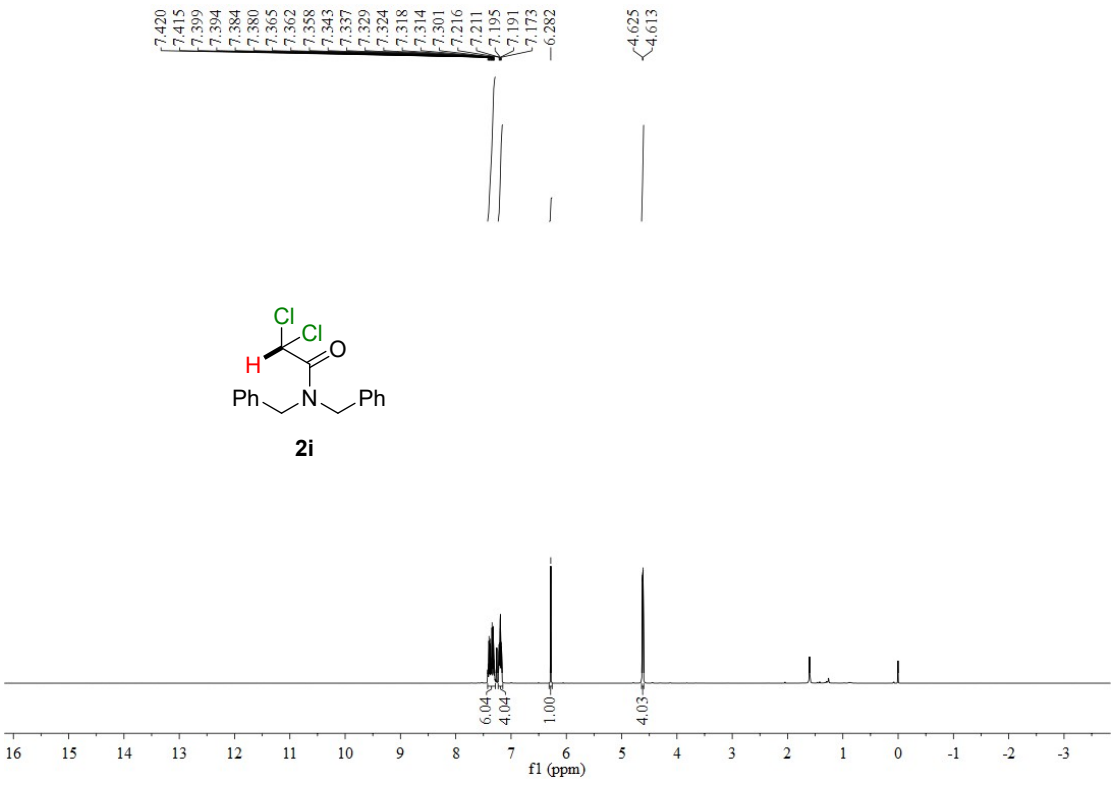

164.216
136.823
129.111
128.194
127.884
66.542
44.429
O
Cl
Cl
N
H
H
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

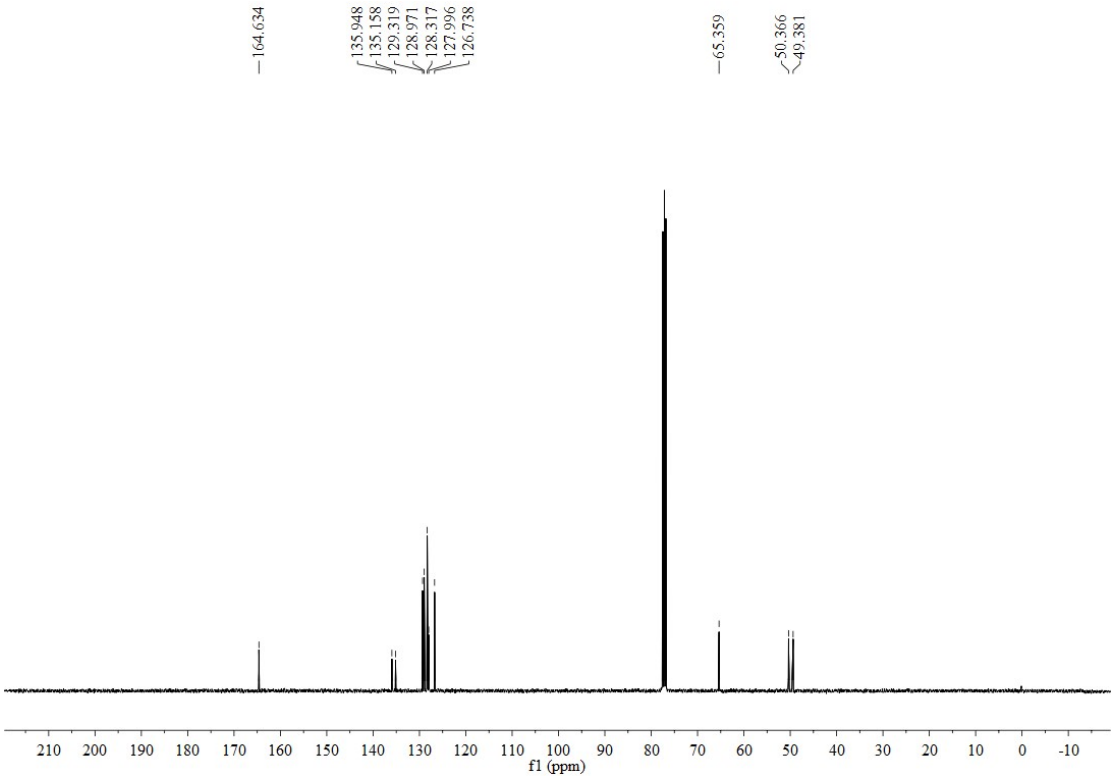
2h, $^{1}H+^{13}C$


7.390
7.386
7.382
7.374
7.369
7.365
7.354
7.350
7.348
7.344
7.336
7.332
7.328
7.320
7.314
7.260
7.255
7.249
7.243
7.238
7.051
7.034
6.200
6.180
5.968
Cl
Cl
H
N
Ph
Ph
O
2h
6.08
4.54
0.96
1.01
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

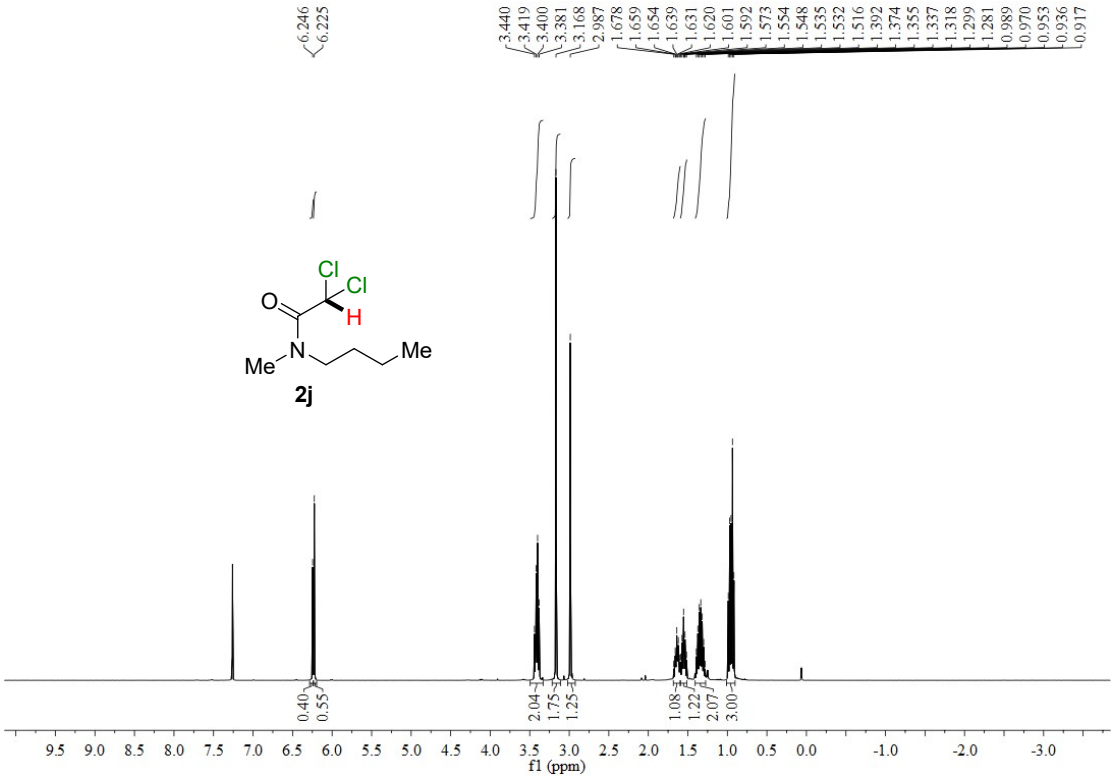

163.39
140.26
129.06
128.11
127.45
66.58
57.84
Ph
H
N
Cl
Cl
H
Ph
O
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

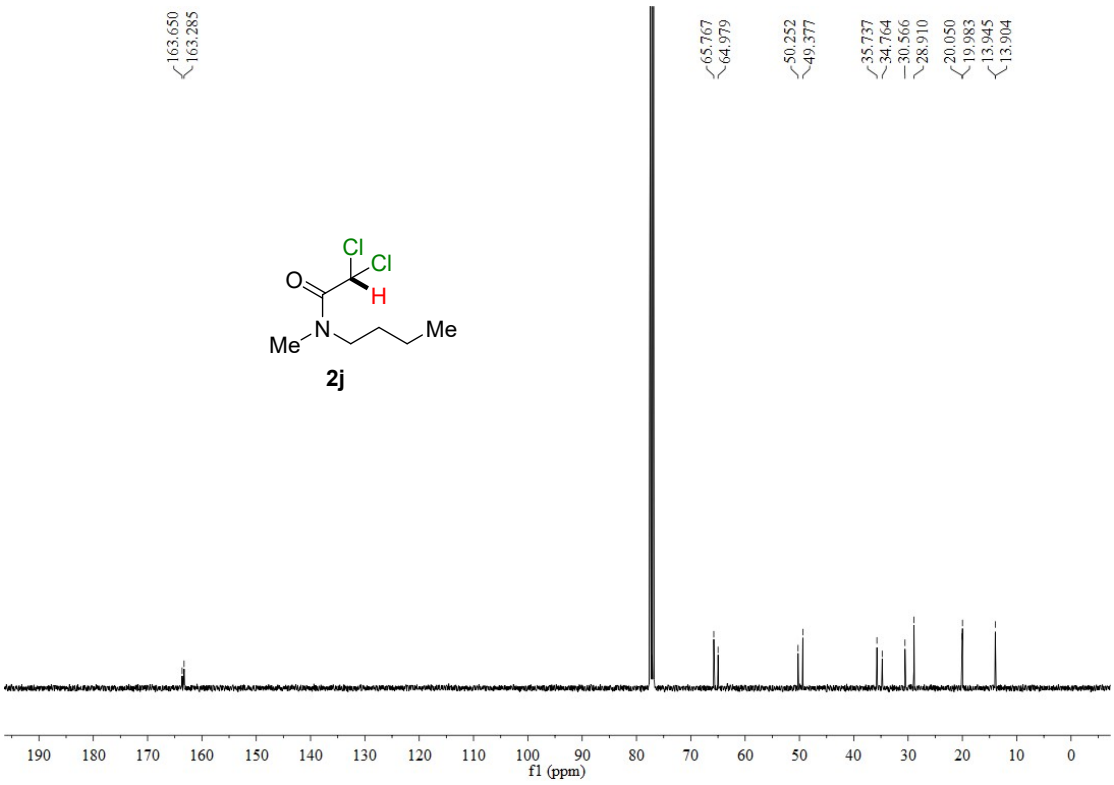
2i, $^{1}H+^{13}C$


7.420
7.415
7.399
7.394
7.384
7.380
7.365
7.362
7.358
7.343
7.337
7.329
7.324
7.318
7.314
7.301
7.216
7.211
7.195
7.191
7.173
6.282
4.625
4.613
Cl
Cl
H
O
Ph
N
Ph
2i
6.04
4.04
1.00
4.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

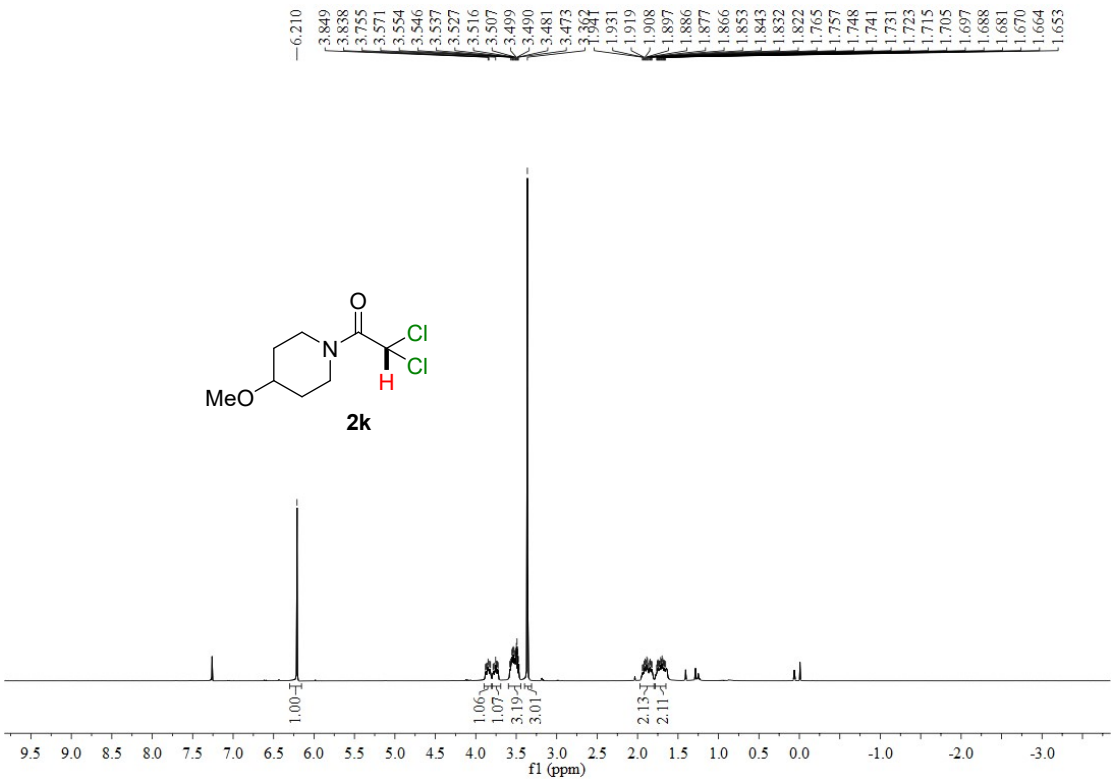

164.634
135.948
135.158
129.319
128.971
128.317
127.996
126.738
65.359
50.366
49.381
f1 (ppm)

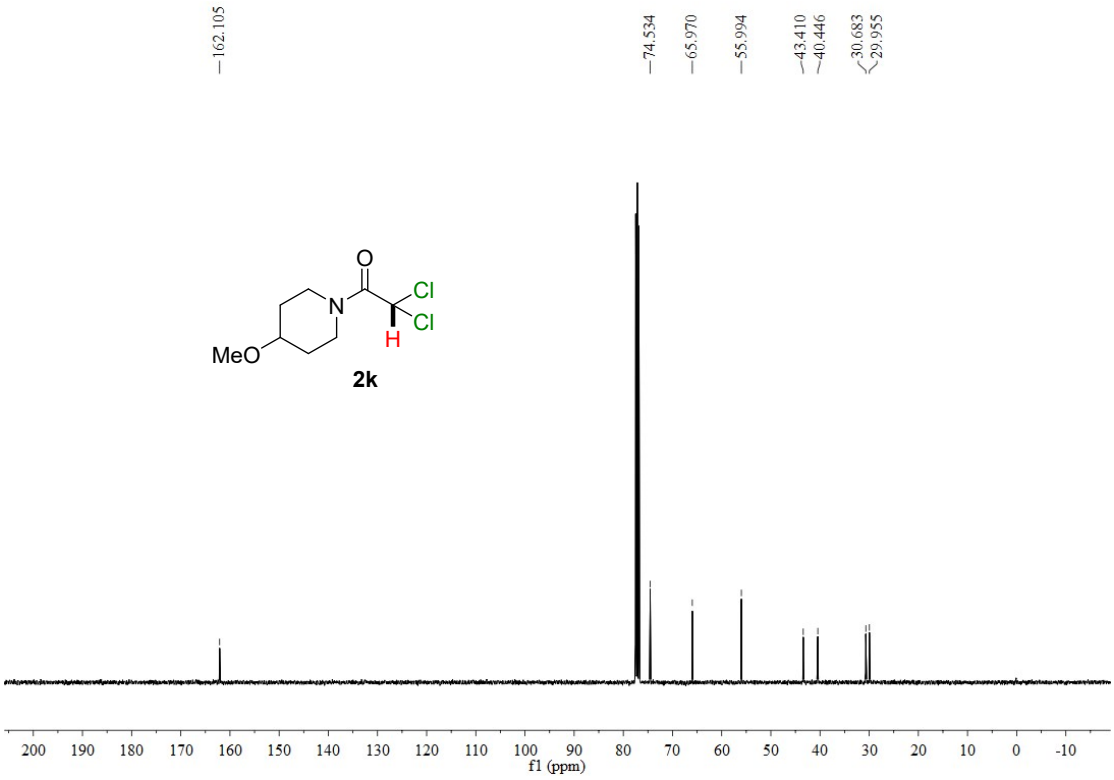
2j, $^{1}H+^{13}C$


6.246
6.225
3.440
3.419
3.400
3.381
3.168
2.987
1.678
1.659
1.654
1.639
1.631
1.620
1.601
1.592
1.573
1.554
1.548
1.535
1.532
1.516
1.392
1.374
1.355
1.337
1.318
1.299
1.281
0.989
0.970
0.953
0.936
0.917
Cl
Cl
O
H
N
Me
Me
2j
0.40
0.55
2.04
1.75
1.25
1.08
1.22
2.07
3.00
f1 (ppm)

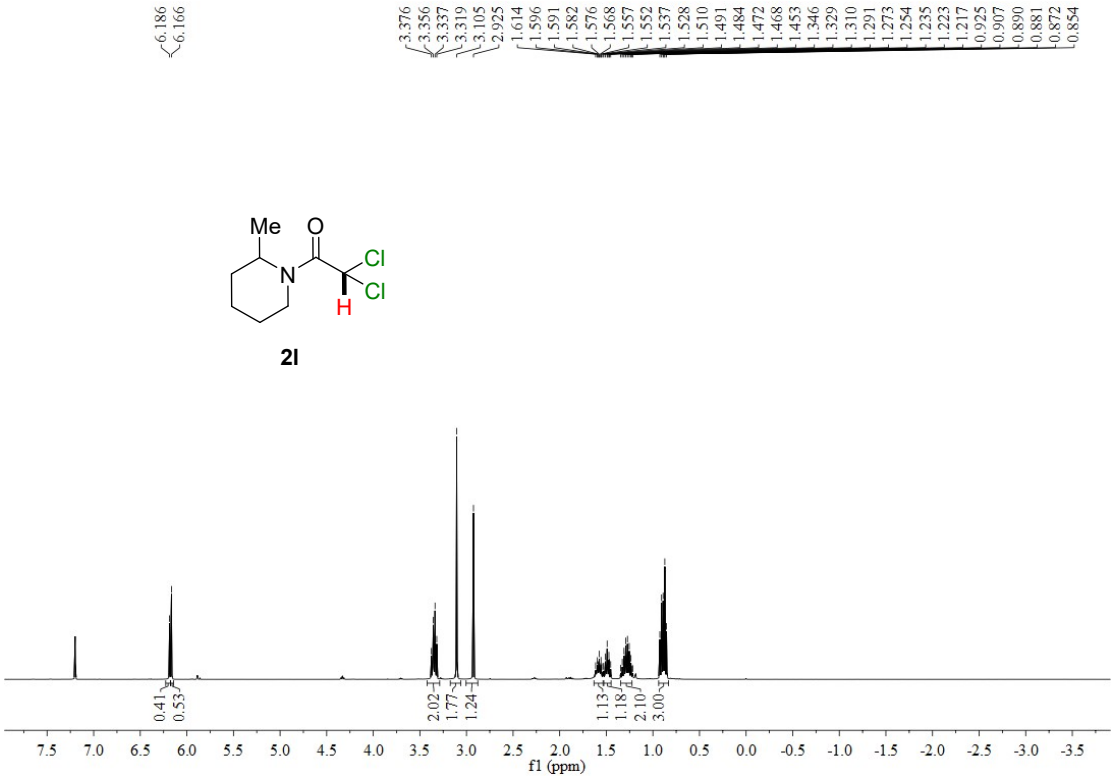

163.650
163.285
65.767
64.979
50.252
49.377
35.737
34.764
30.566
28.910
20.050
19.983
13.945
13.904
Cl
Cl
O
H
N
Me
Me
2j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

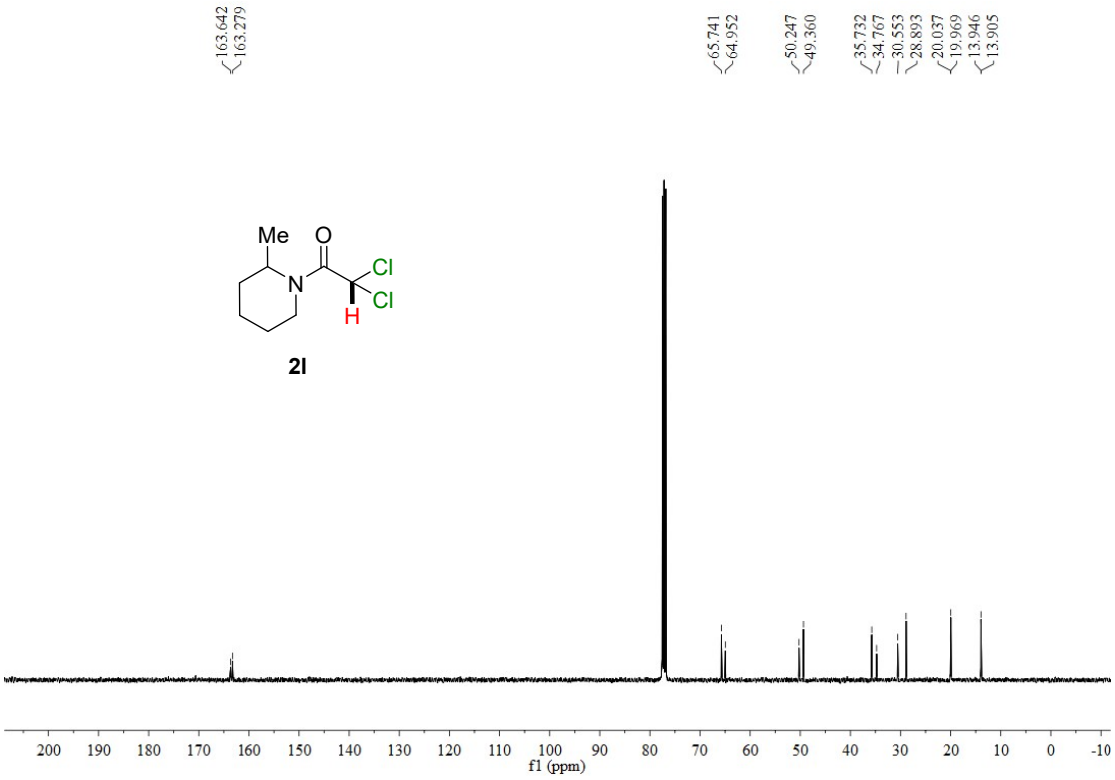
2k, $^{1}H+^{13}C$


6.210
3.849
3.838
3.755
3.571
3.554
3.546
3.537
3.527
3.516
3.507
3.499
3.490
3.481
3.473
1.931
1.919
1.908
1.897
1.886
1.877
1.866
1.853
1.843
1.832
1.822
1.765
1.757
1.748
1.741
1.731
1.723
1.715
1.705
1.697
1.688
1.681
1.670
1.664
1.653
O
N
Cl
Cl
H
MeO
2k
1.00
1.06
1.07
3.19
3.01
2.13
2.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0 -3.0
f1 (ppm)

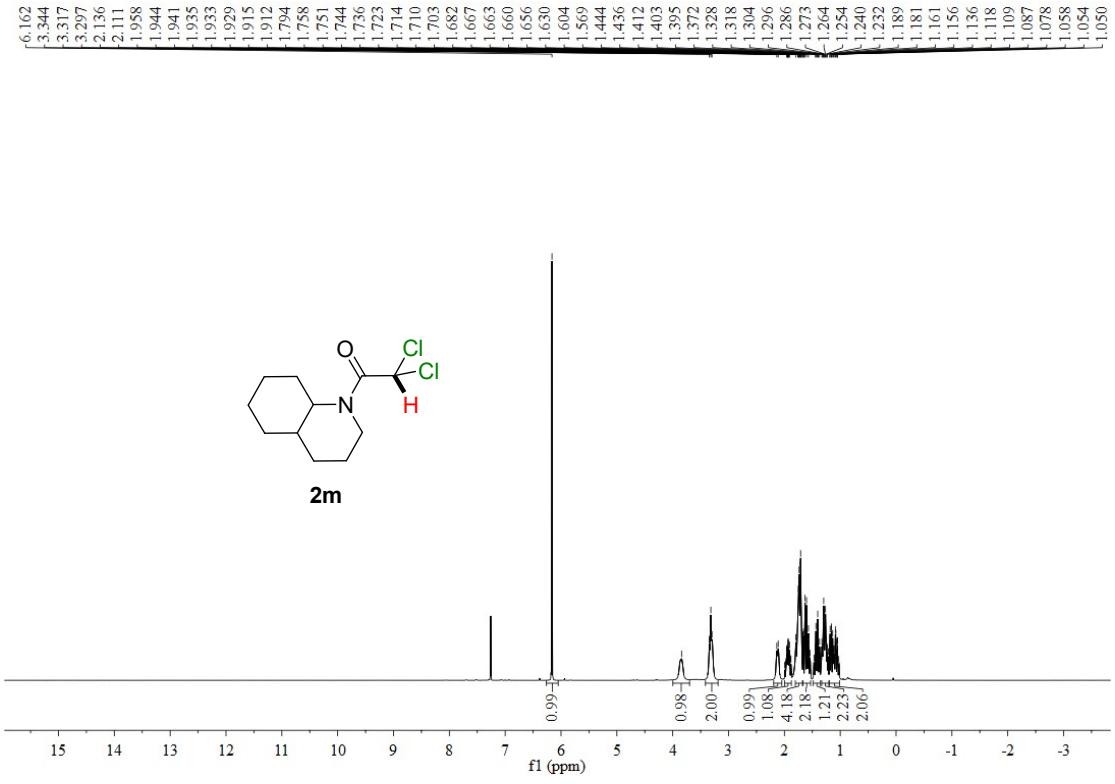

162.105
74.534
65.970
55.994
43.410
40.446
30.683
29.955
O
N
Cl
Cl
H
MeO
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

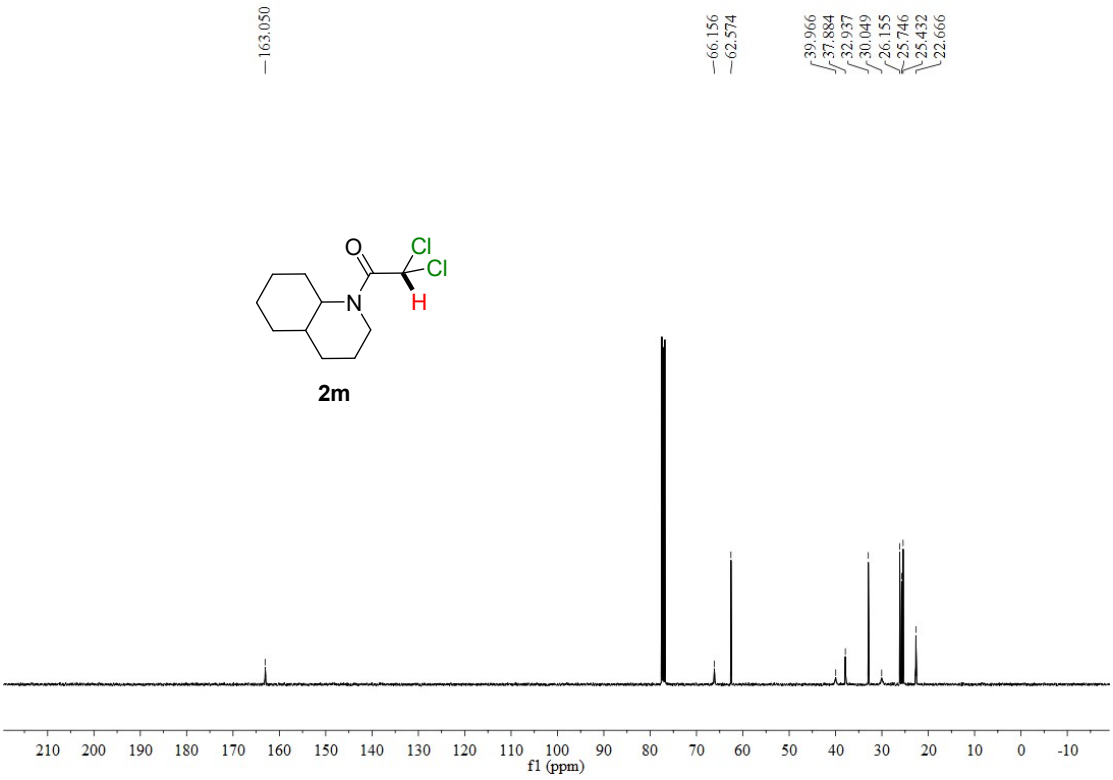
2l, $^{1}H+^{13}C$


6.186
6.166
3.376
3.356
3.337
3.319
3.105
2.925
1.614
1.596
1.591
1.582
1.576
1.568
1.557
1.552
1.537
1.528
1.510
1.491
1.484
1.472
1.468
1.453
1.346
1.329
1.310
1.291
1.273
1.254
1.235
1.223
1.217
0.925
0.907
0.890
0.881
0.872
0.854
Me
O
N
Cl
Cl
H
2l
0.41
0.53
2.02
1.77
1.24
1.13
1.18
2.10
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5
f1 (ppm)

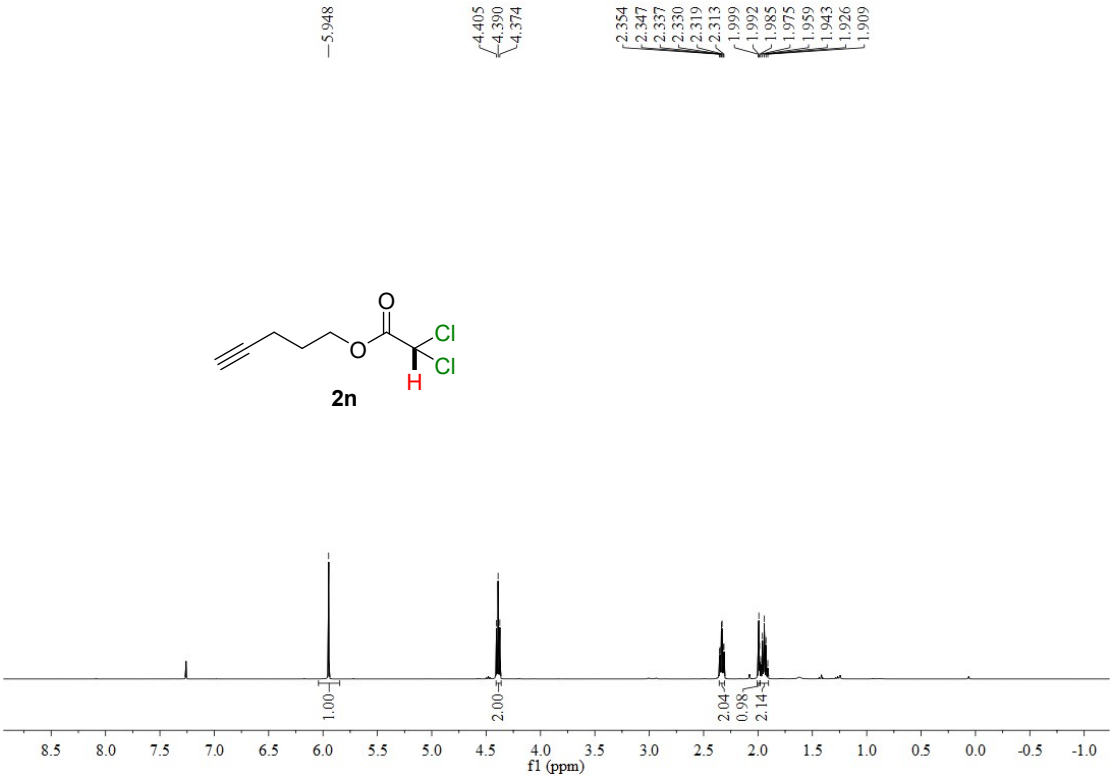

163.642
163.279
65.741
64.952
50.247
49.360
35.732
34.767
30.553
28.893
20.037
19.969
13.946
13.905
Me
O
N
Cl
Cl
H
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

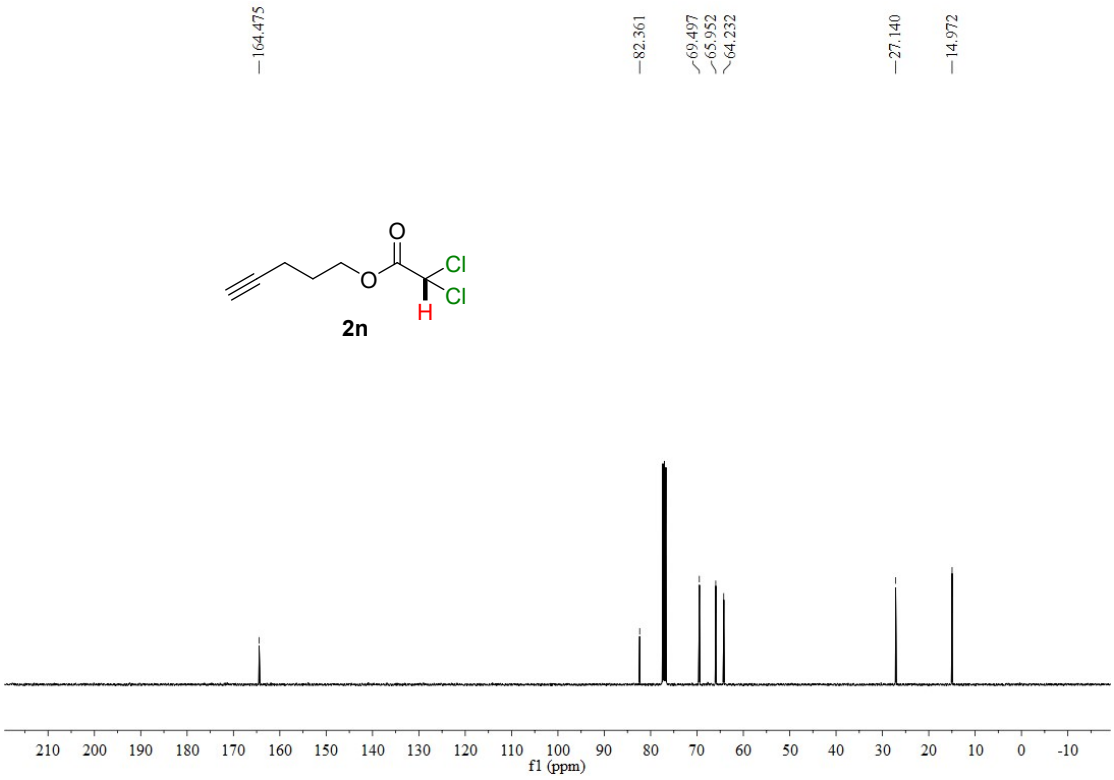
2m, $^{1}H+^{13}C$


6.162
3.344
3.317
3.297
2.136
2.111
1.958
1.944
1.941
1.935
1.933
1.929
1.915
1.912
1.794
1.758
1.751
1.744
1.736
1.723
1.714
1.710
1.703
1.682
1.667
1.663
1.660
1.656
1.630
1.604
1.569
1.444
1.436
1.412
1.403
1.395
1.372
1.328
1.318
1.304
1.296
1.286
1.273
1.264
1.254
1.240
1.232
1.189
1.181
1.161
1.156
1.136
1.118
1.109
1.087
1.078
1.058
1.054
1.050
O
Cl
Cl
N
H
2m
0.99
0.98
2.00
0.99
1.08
4.18
2.18
1.21
2.23
2.06
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

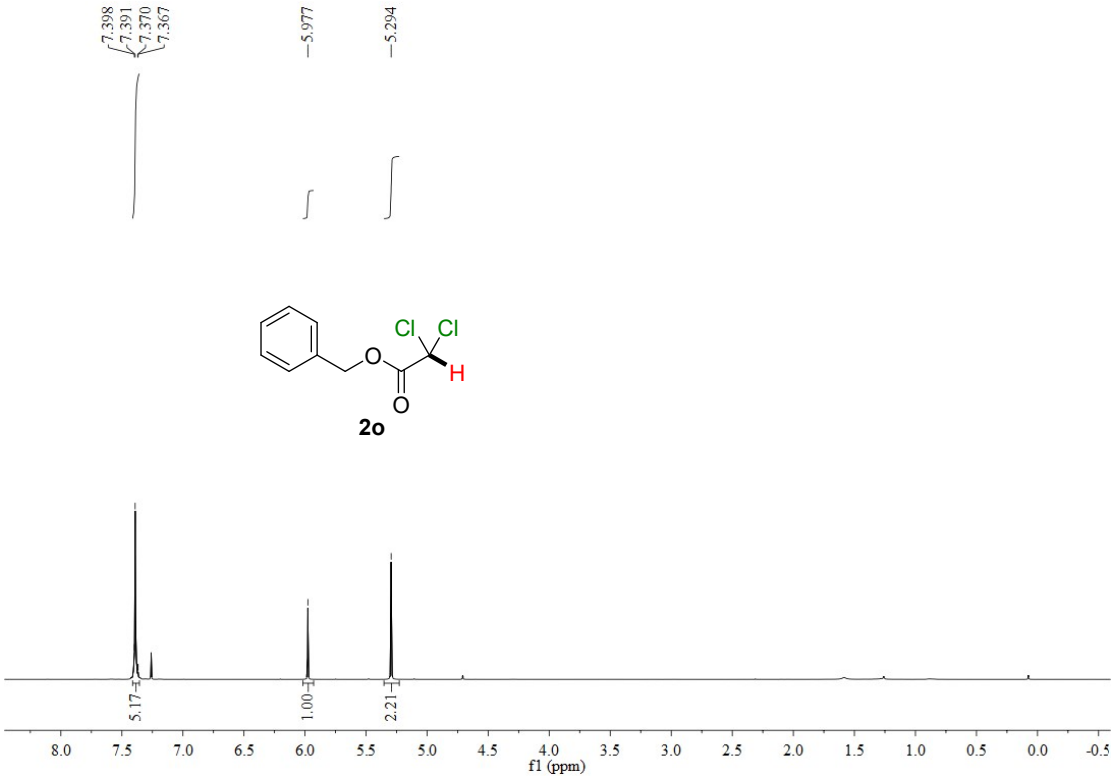

163.050
66.156
62.574
39.966
37.884
32.937
30.049
26.155
25.746
25.432
22.666
O
Cl
Cl
N
H
2m
f1 (ppm)

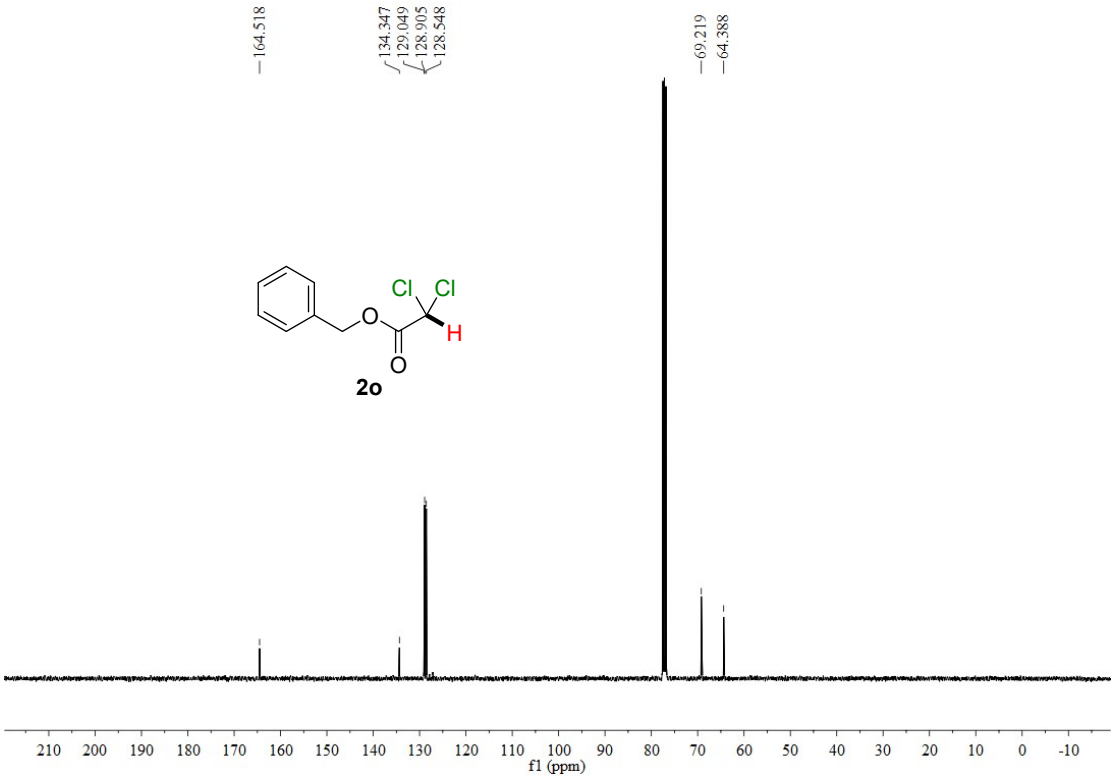
2n, $^{1}H+^{13}C$


5.948
4.405
4.390
4.374
2.354
2.347
2.337
2.330
2.319
2.313
1.999
1.992
1.985
1.975
1.959
1.943
1.926
1.909
O
O
Cl
Cl
H
2n
1.00
2.00
2.04
0.98
2.14
f1 (ppm)

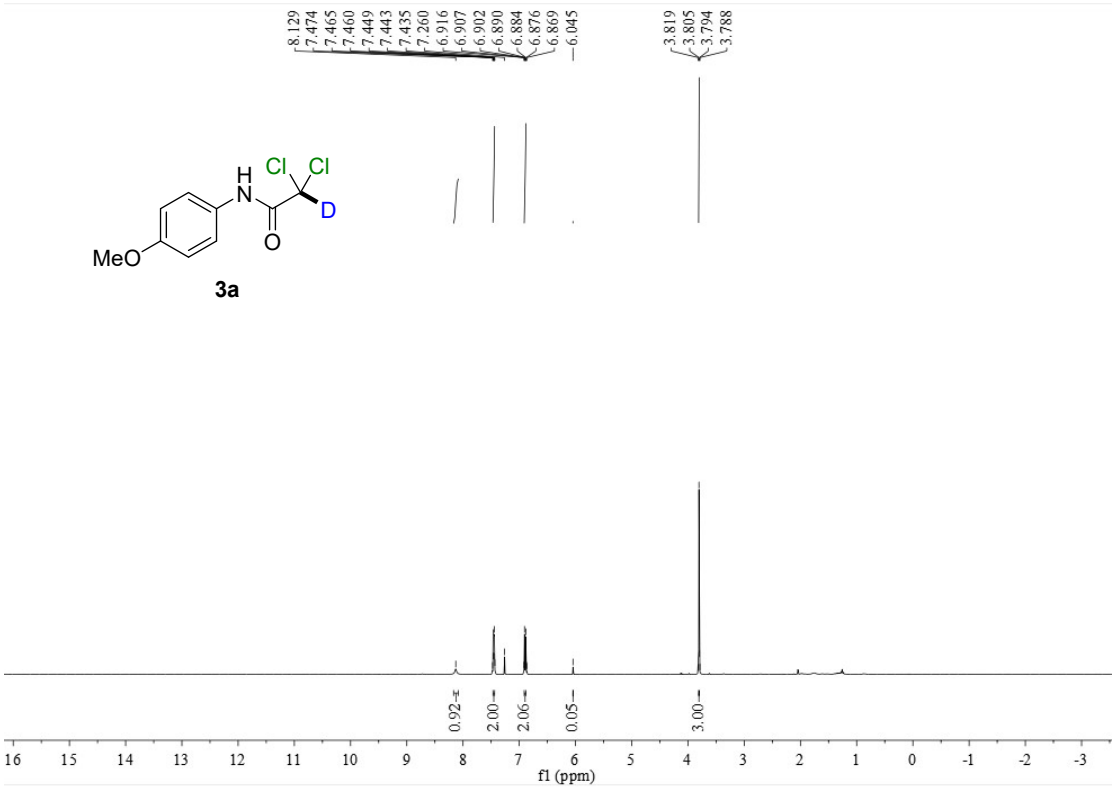

164.475
82.361
69.497
65.952
64.232
27.140
14.972
O
O
Cl
Cl
H
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2o, $^{1}H+^{13}C$

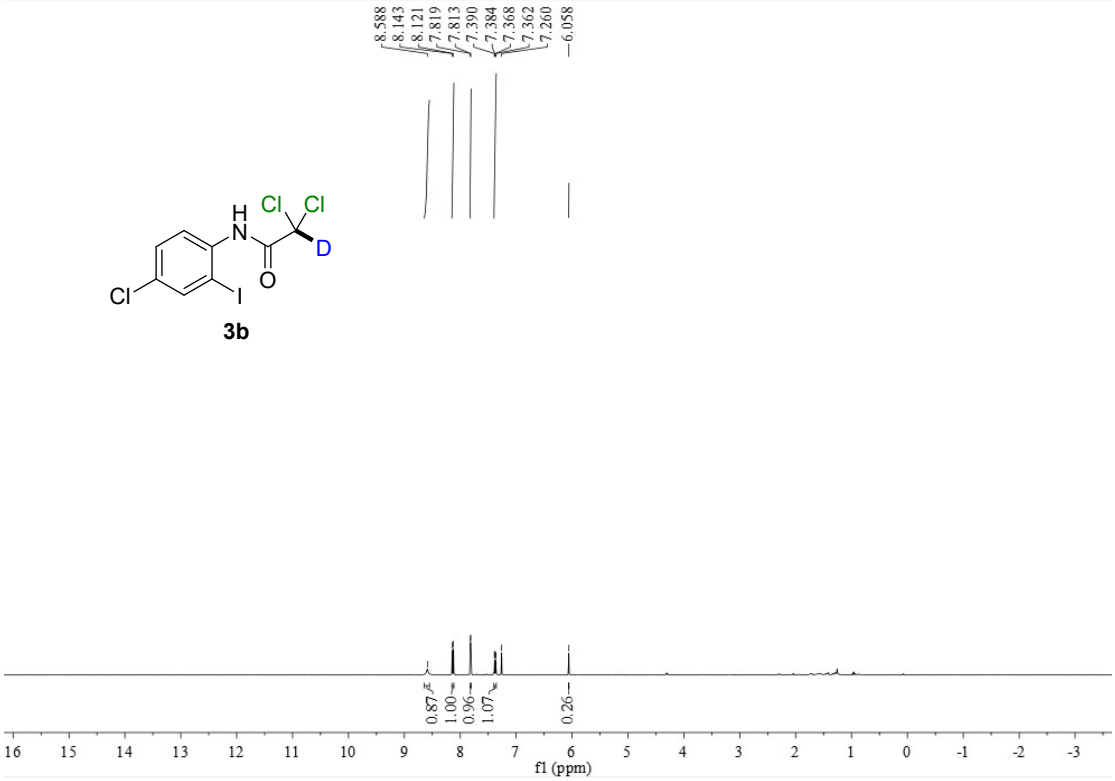

7.398
7.391
7.370
7.367
5.977
5.294
Cl
Cl
O
H
O
2o
5.17
1.00
2.21
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.518
134.347
129.049
128.905
128.548
69.219
64.388
Cl
Cl
O
H
O
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3a, $^{1}H+^{13}C$

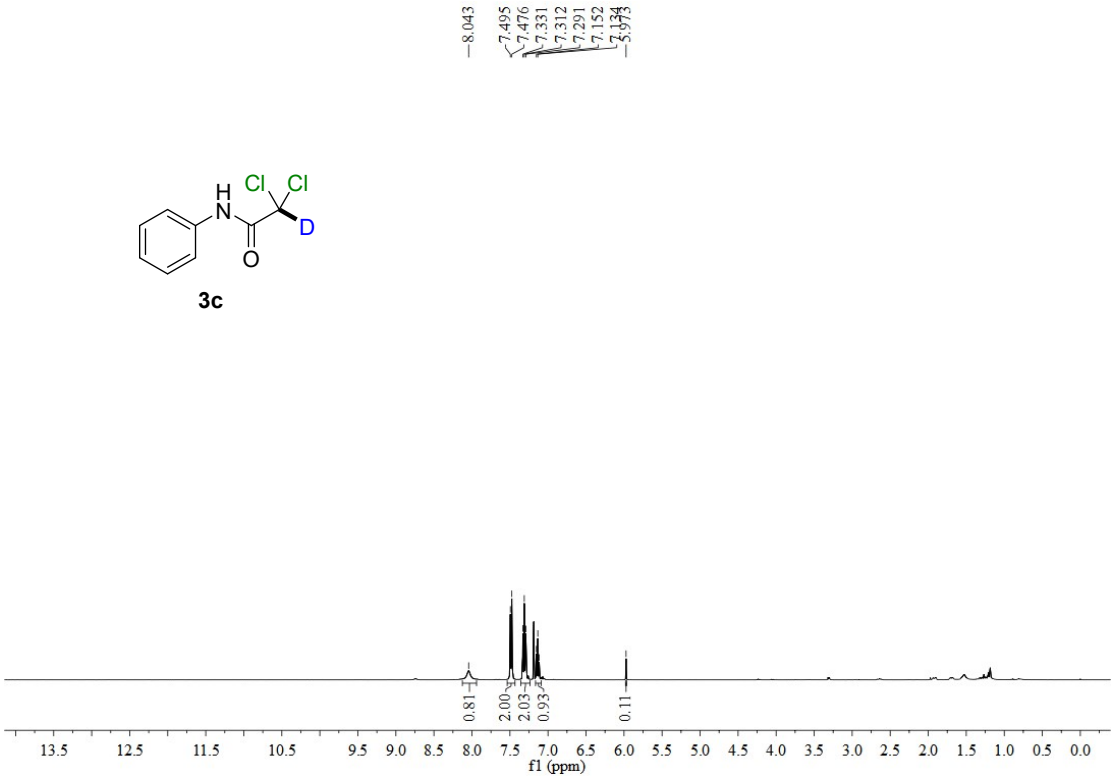

8.129
7.474
7.465
7.460
7.449
7.443
7.435
7.260
6.916
6.907
6.902
6.890
6.884
6.876
6.869
6.045
3.819
3.805
3.794
3.788
H
N
Cl
Cl
D
O
MeO
3a
0.92
2.00
2.06
0.05
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

3b, $^{1}H+^{13}C$



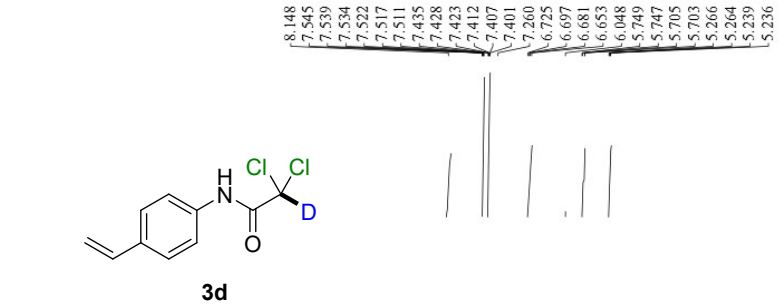
3b

3c, $^{1}H+^{13}C$

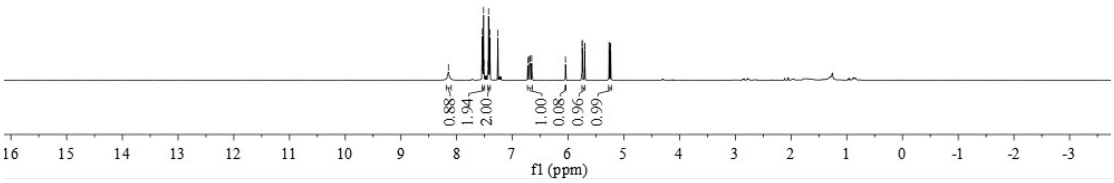


3c

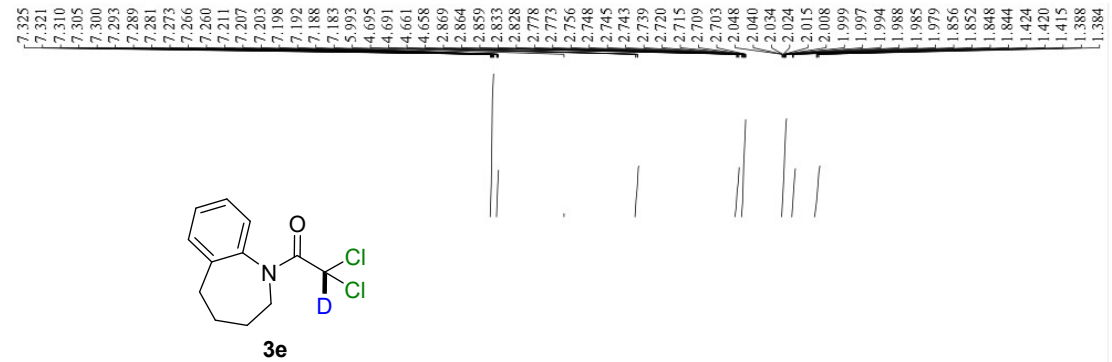
3d, $^{1}H+^{13}C$



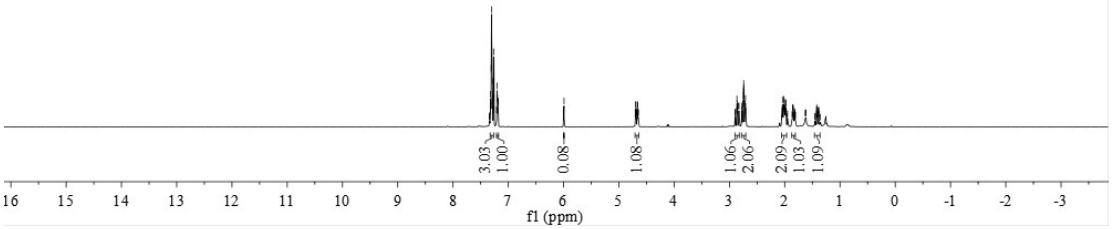
3d



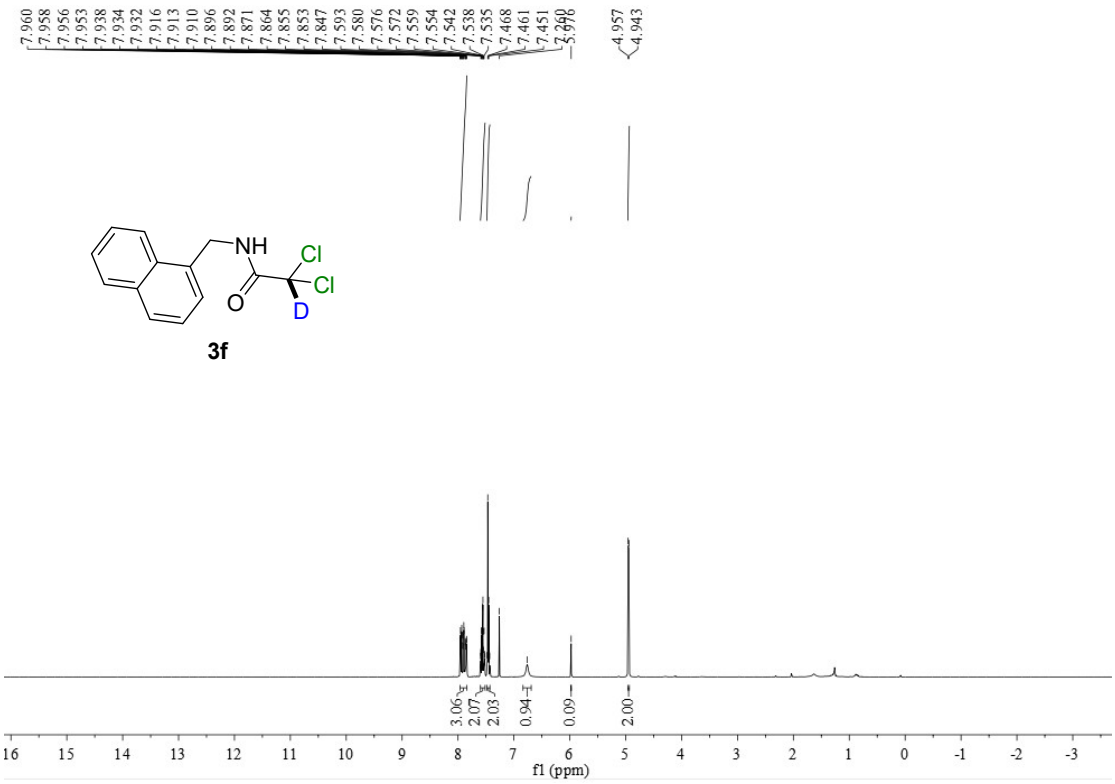
3e, $^{1}H+^{13}C$



3e

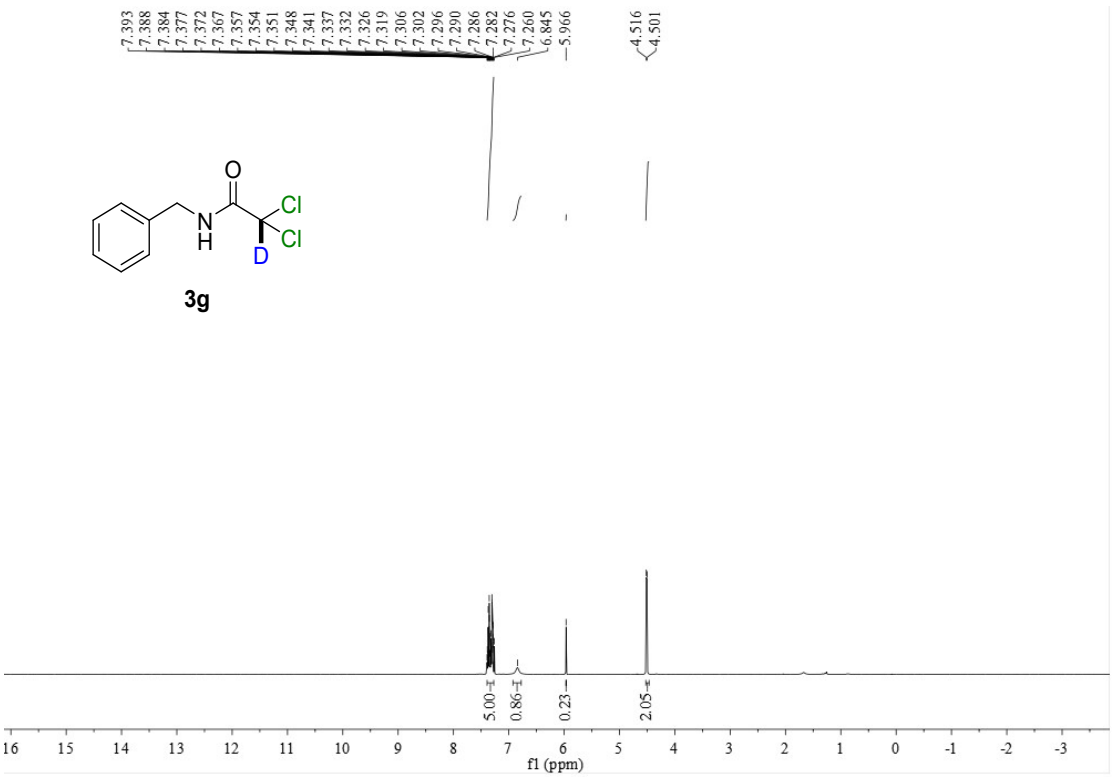


3f, $^{1}H+^{13}C$



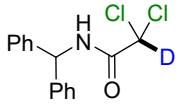
3f

3g, $^{1}H+^{13}C$

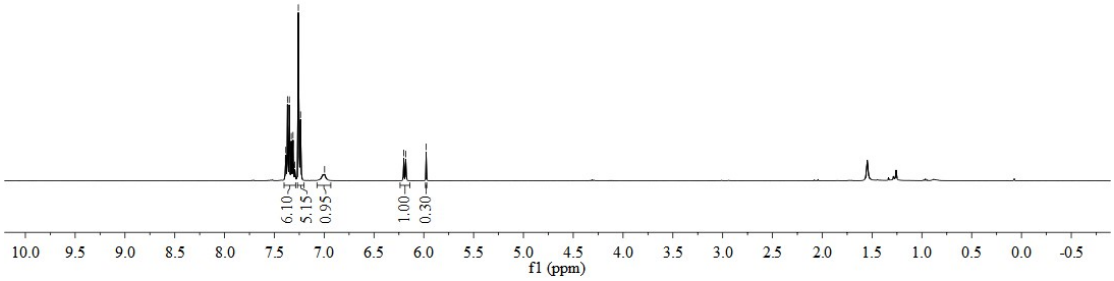


3g

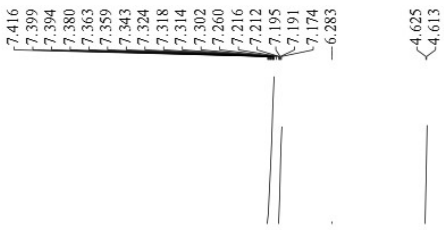
3h, $^{1}H+^{13}C$

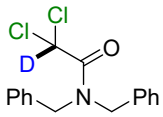


3h

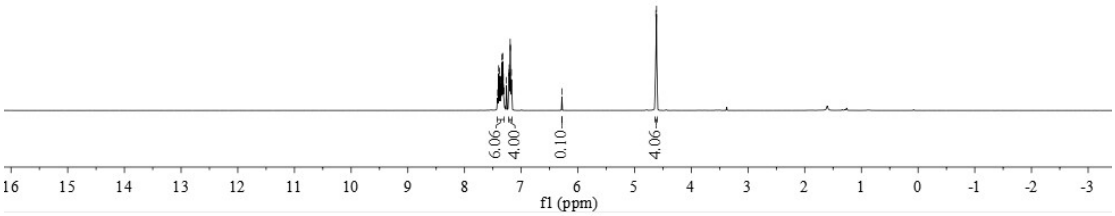


3i, $^{1}H+^{13}C$

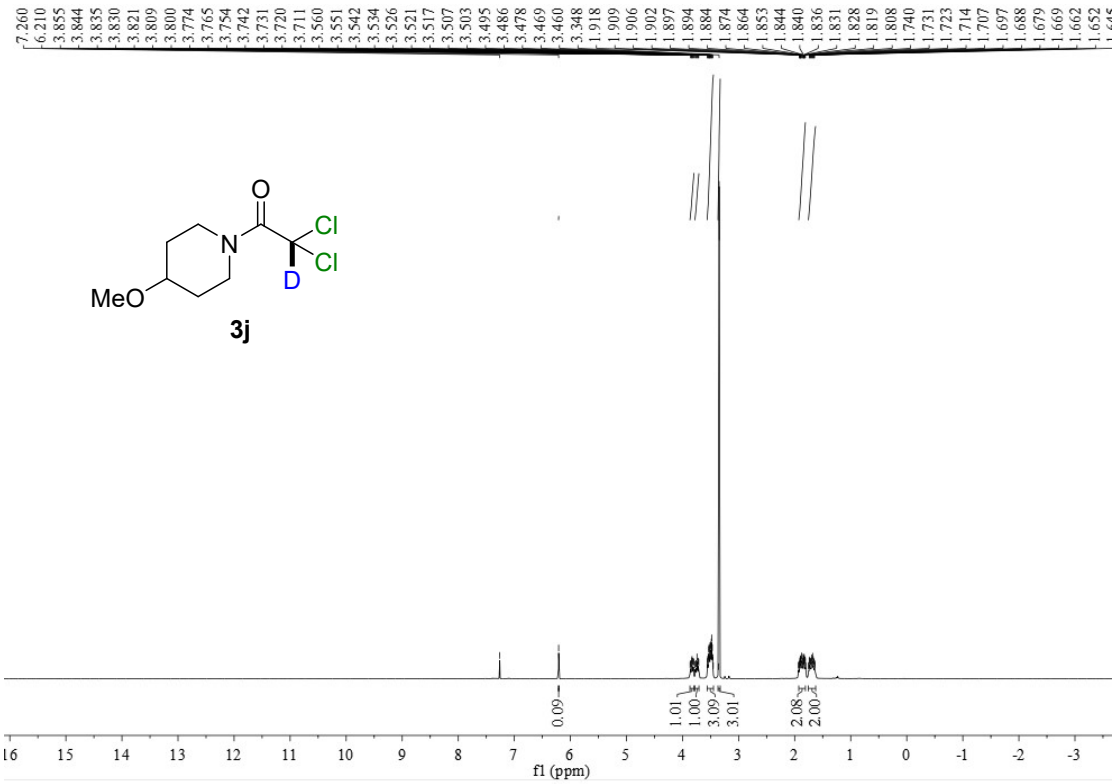




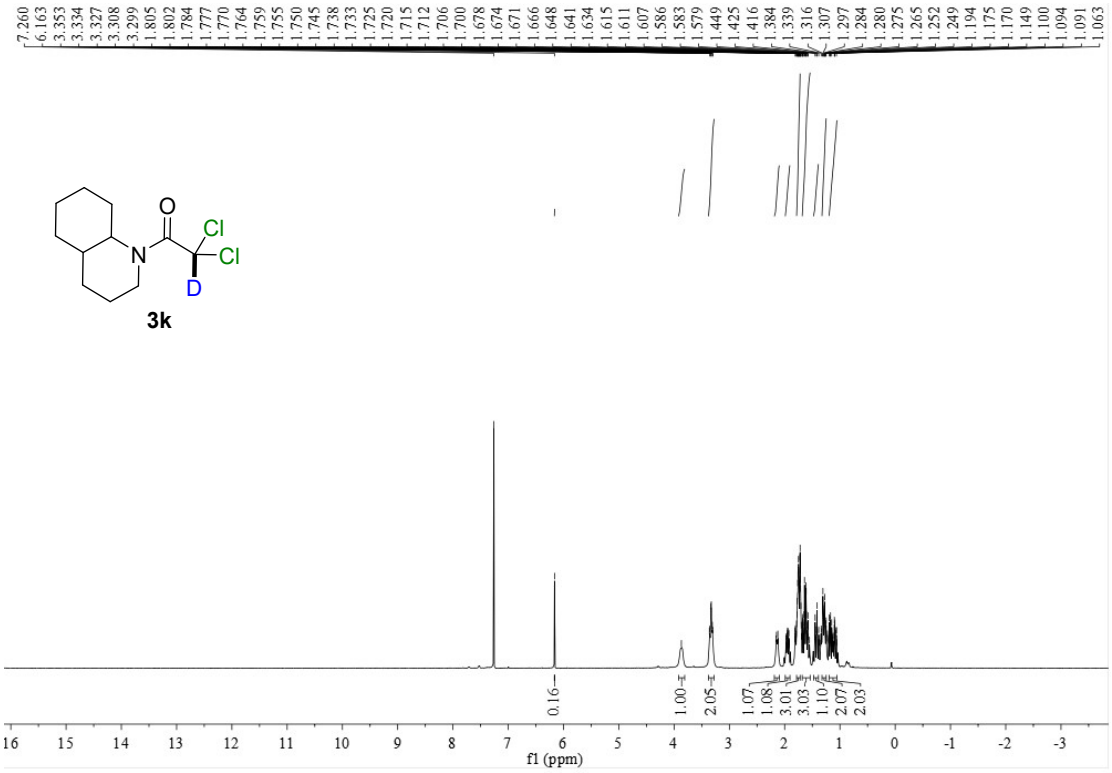
3i



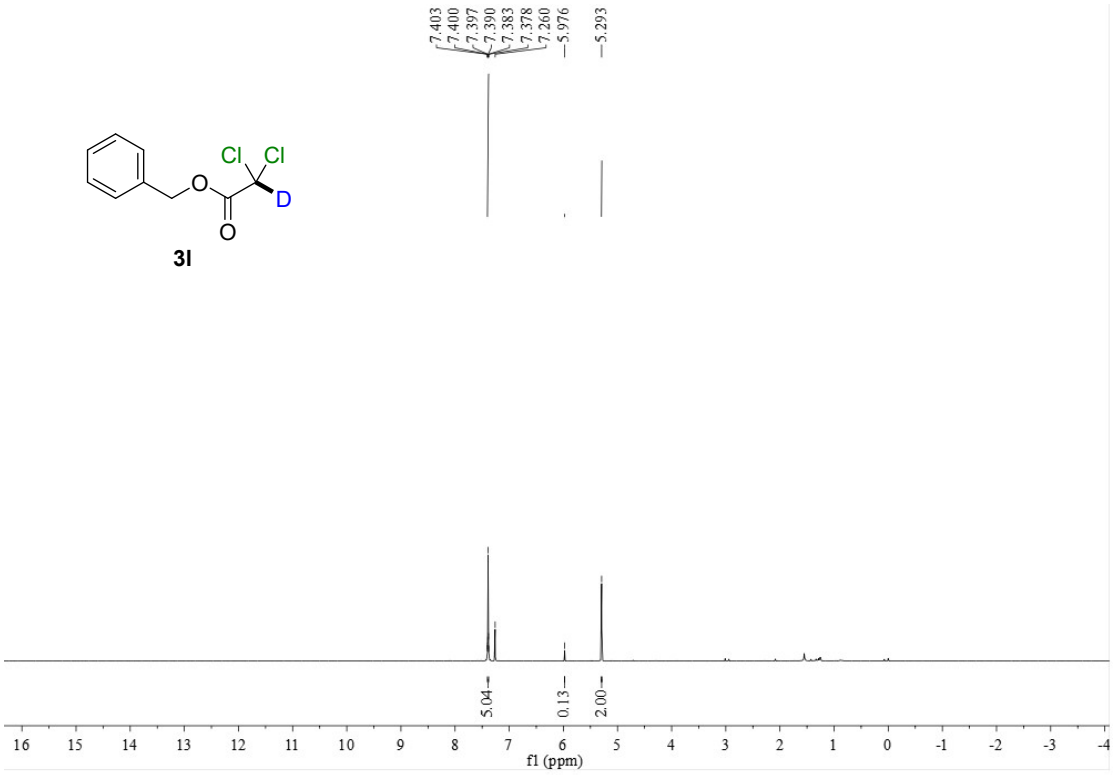
3j, $^{1}H+^{13}C$



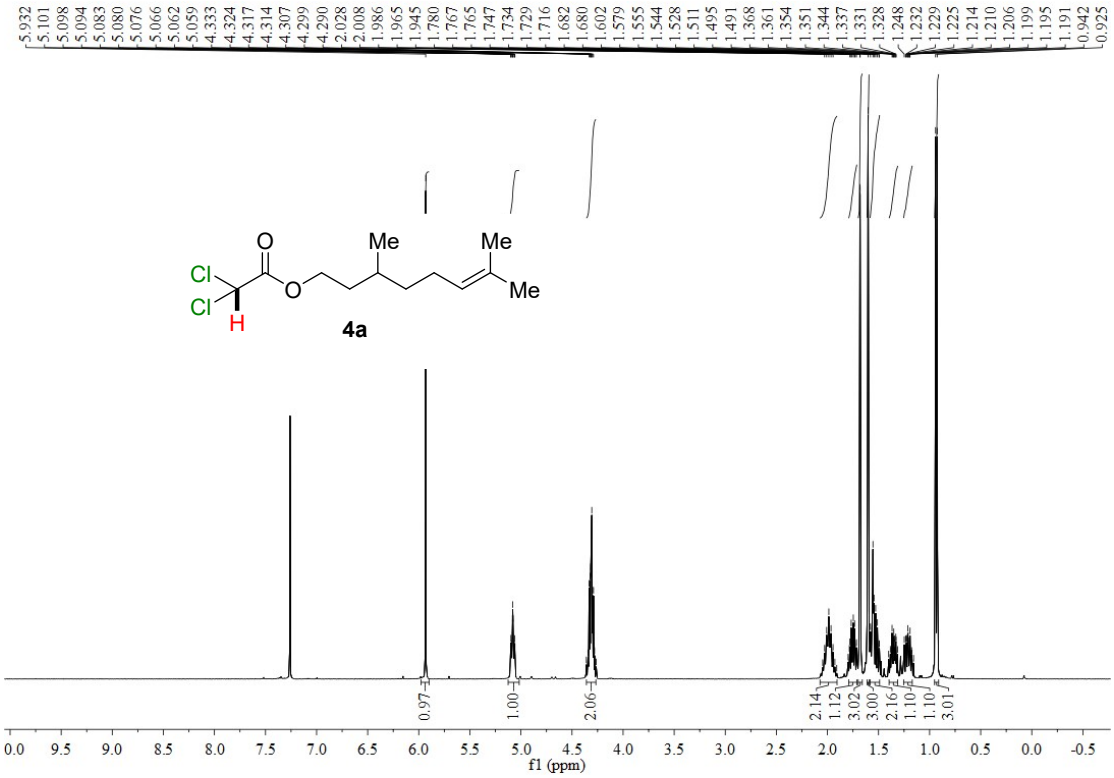
3k, $^{1}H+^{13}C$

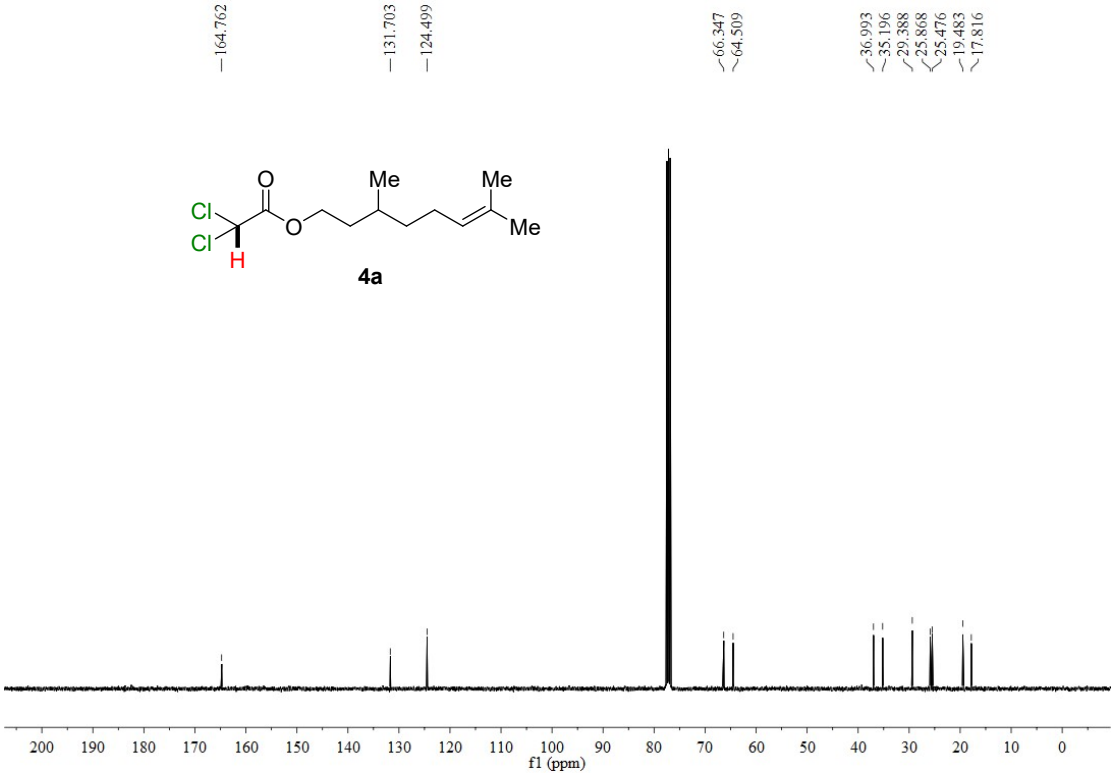


3l, $^{1}H+^{13}C$

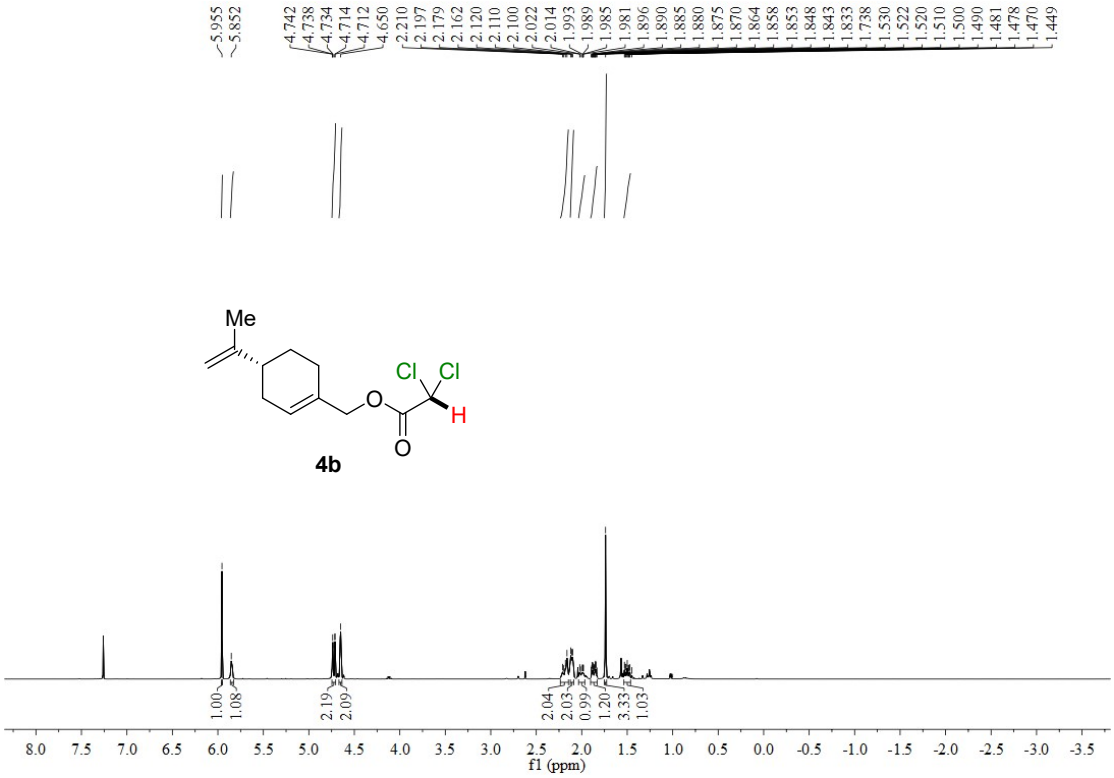

7.403
7.400
7.397
7.390
7.383
7.378
7.260
5.976
5.293
Cl
Cl
D
O
O
3l
5.04
0.13
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

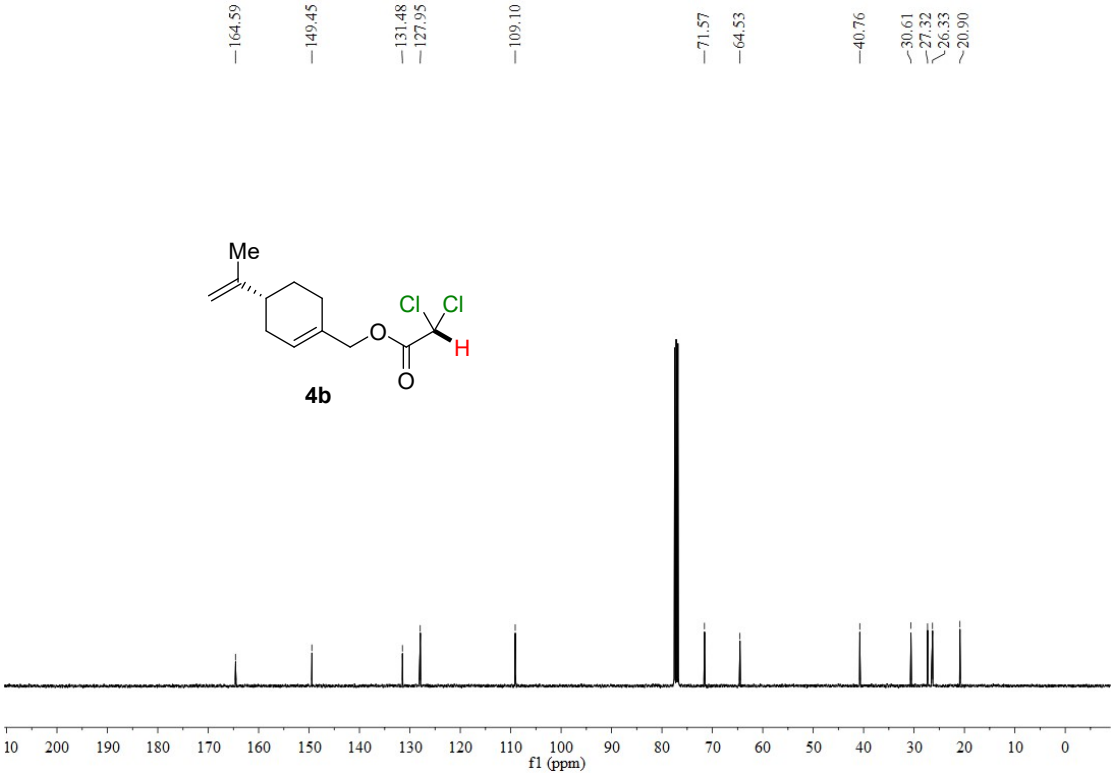
4a, $^{1}H+^{13}C$


5.932
5.101
5.098
5.094
5.083
5.080
5.076
5.066
5.062
5.059
4.333
4.324
4.317
4.314
4.307
4.299
4.290
2.028
2.008
1.986
1.965
1.945
1.780
1.767
1.765
1.747
1.734
1.729
1.716
1.682
1.680
1.602
1.579
1.555
1.544
1.528
1.511
1.495
1.491
1.368
1.361
1.354
1.351
1.344
1.337
1.331
1.328
1.248
1.232
1.229
1.225
1.214
1.210
1.206
1.199
1.195
1.191
0.942
0.925
O
Me
Me
Cl
Cl
O
Me
H
4a
0.97
1.00
2.06
2.14
1.12
3.02
3.00
2.16
1.10
1.10
3.01
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

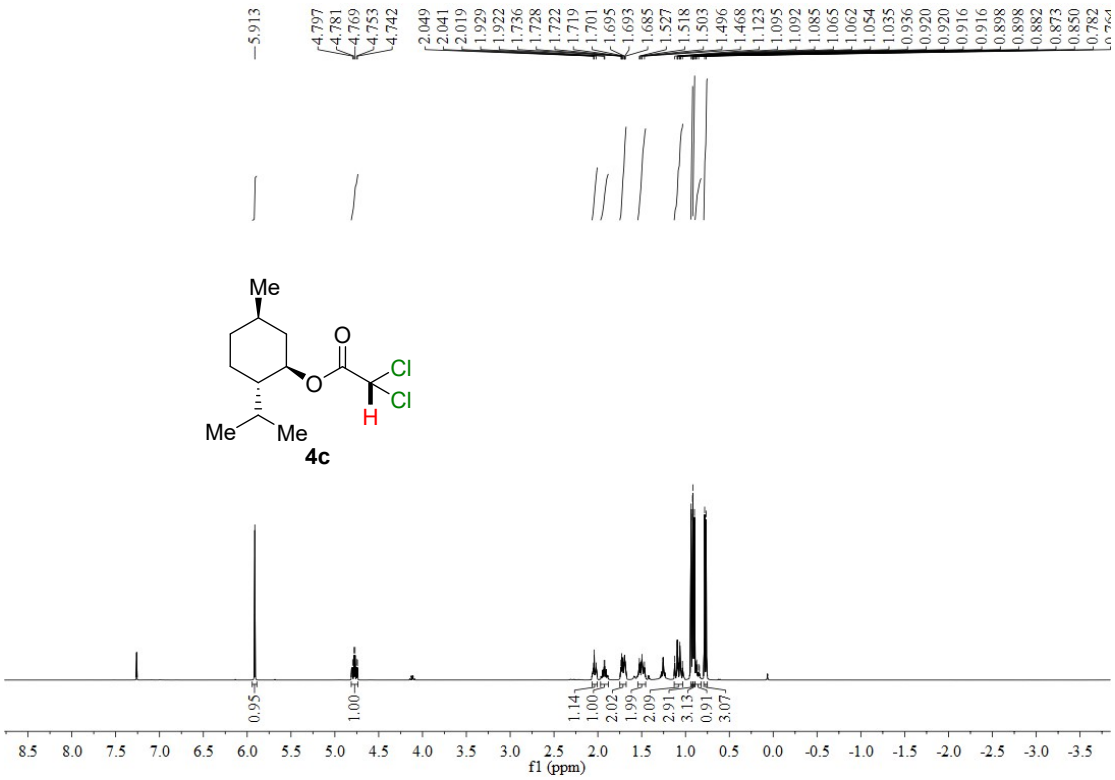

164.762
131.703
124.499
66.347
64.509
36.993
35.196
29.388
25.868
25.476
19.483
17.816
O
Me
Me
Cl
Cl
O
Me
H
4a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

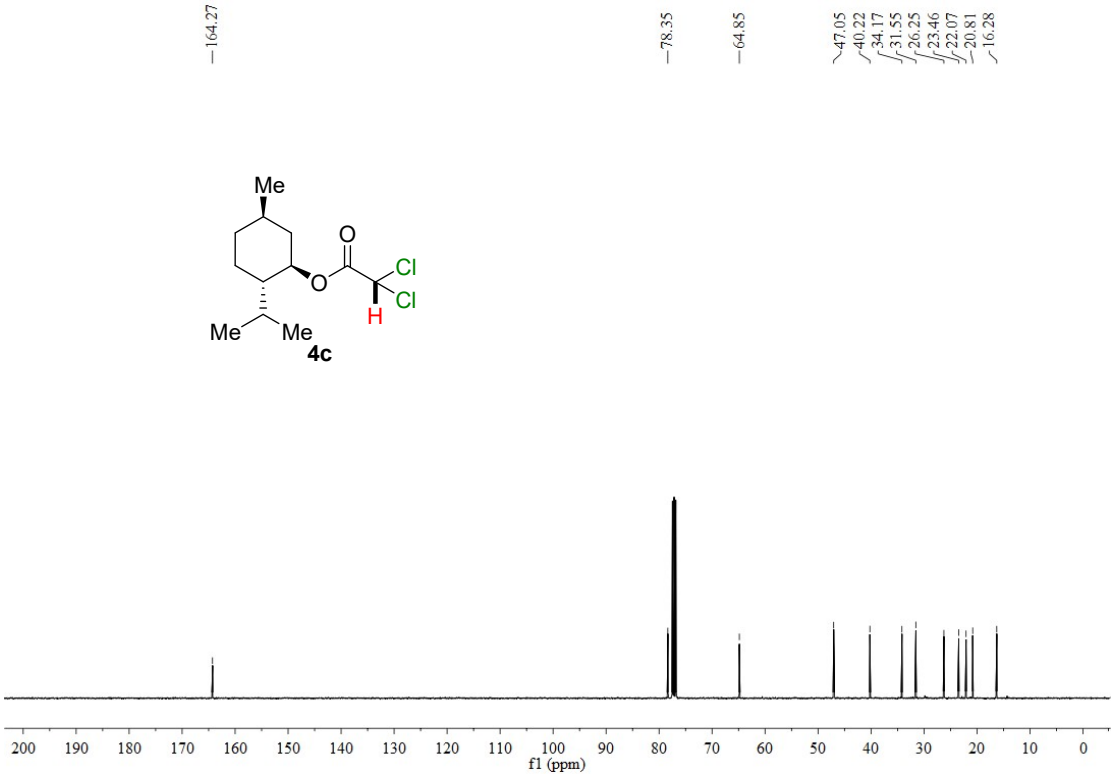
4b, $^{1}H+^{13}C$


5.955
5.852
4.742
4.738
4.734
4.714
4.712
4.650
2.210
2.197
2.179
2.162
2.120
2.110
2.100
2.022
2.014
1.993
1.989
1.985
1.981
1.896
1.890
1.885
1.880
1.875
1.870
1.864
1.858
1.853
1.848
1.843
1.833
1.738
1.530
1.522
1.520
1.510
1.500
1.490
1.481
1.478
1.470
1.449
Me
Cl
Cl
O
H
O
4b
1.00
1.08
2.19
2.09
2.04
2.03
0.99
1.20
3.33
1.03
f1 (ppm)

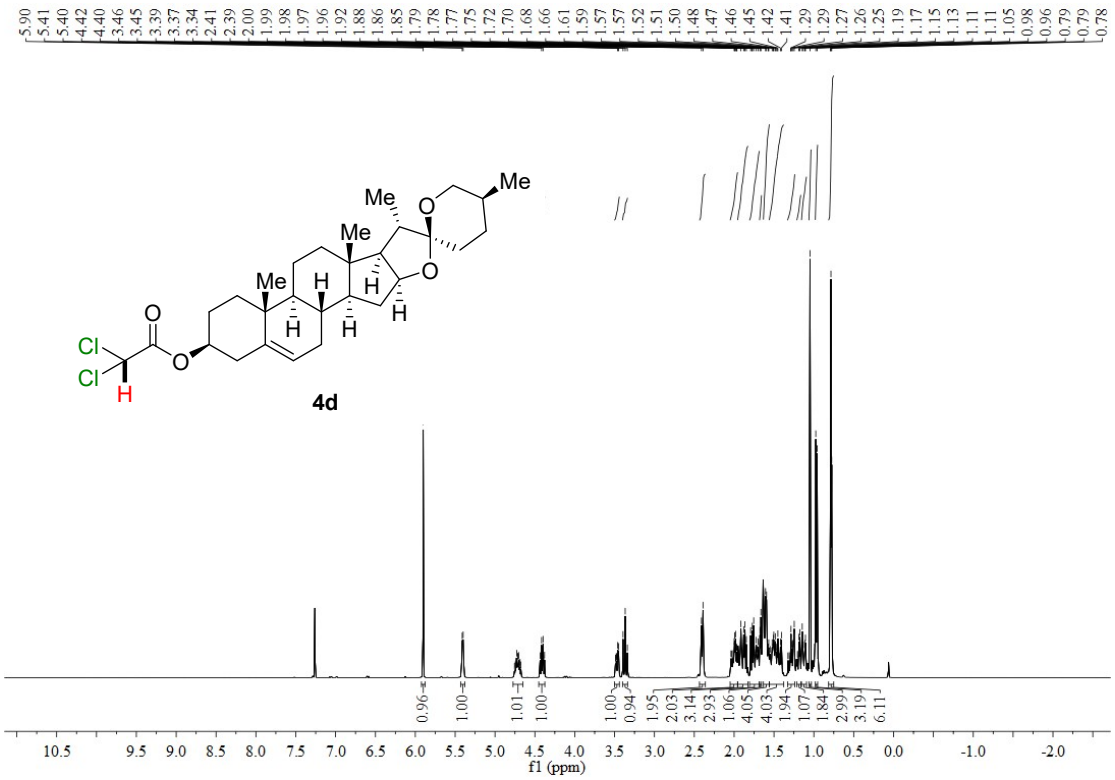

164.59
149.45
131.48
127.95
109.10
71.57
64.53
40.76
30.61
27.32
26.33
20.90
Me
Cl
Cl
O
H
O
4b
f1 (ppm)

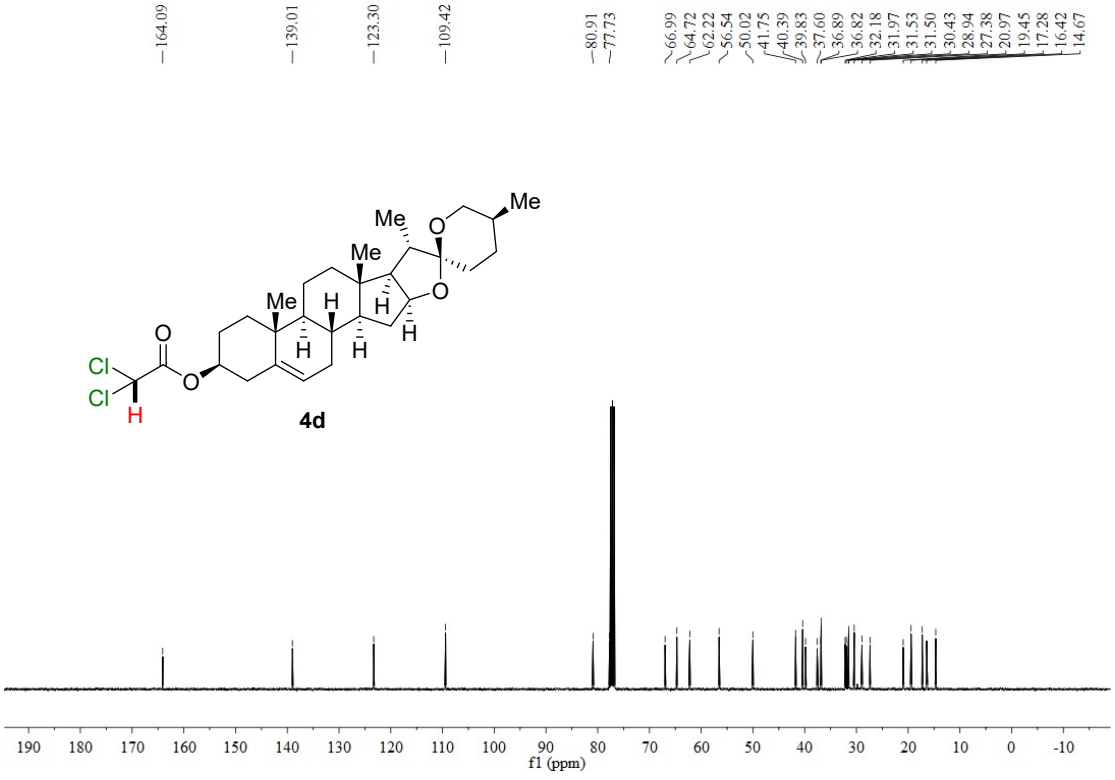
4c, $^{1}H+^{13}C$


5.913
4.797
4.781
4.769
4.753
4.742
2.049
2.041
2.019
1.929
1.922
1.736
1.728
1.722
1.719
1.701
1.695
1.693
1.685
1.527
1.518
1.503
1.496
1.468
1.123
1.095
1.092
1.085
1.065
1.062
1.054
1.035
0.936
0.920
0.920
0.916
0.916
0.898
0.898
0.882
0.873
0.850
0.782
Me
O
Cl
Cl
H
Me
Me
4c
0.95
1.00
1.14
1.00
2.02
1.99
2.09
2.91
3.13
0.91
3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5
f1 (ppm)

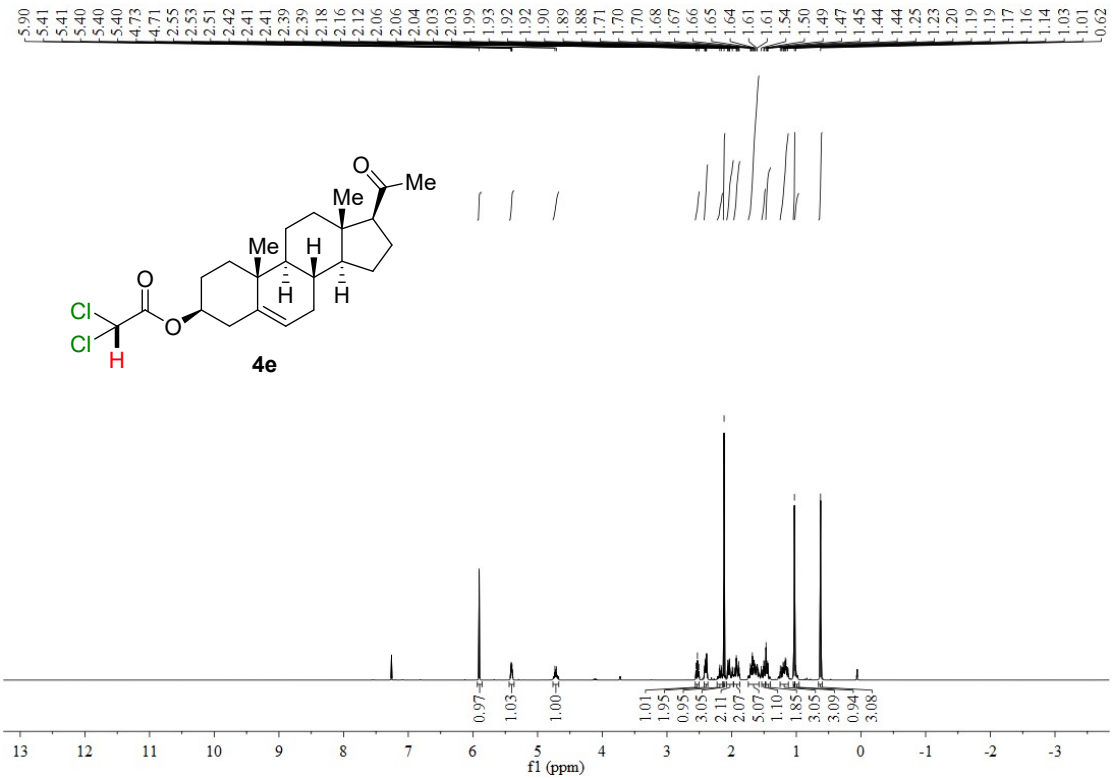

164.27
78.35
64.85
47.05
40.22
34.17
31.55
26.25
23.46
22.07
20.81
16.28
Me
O
Cl
Cl
H
Me
Me
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

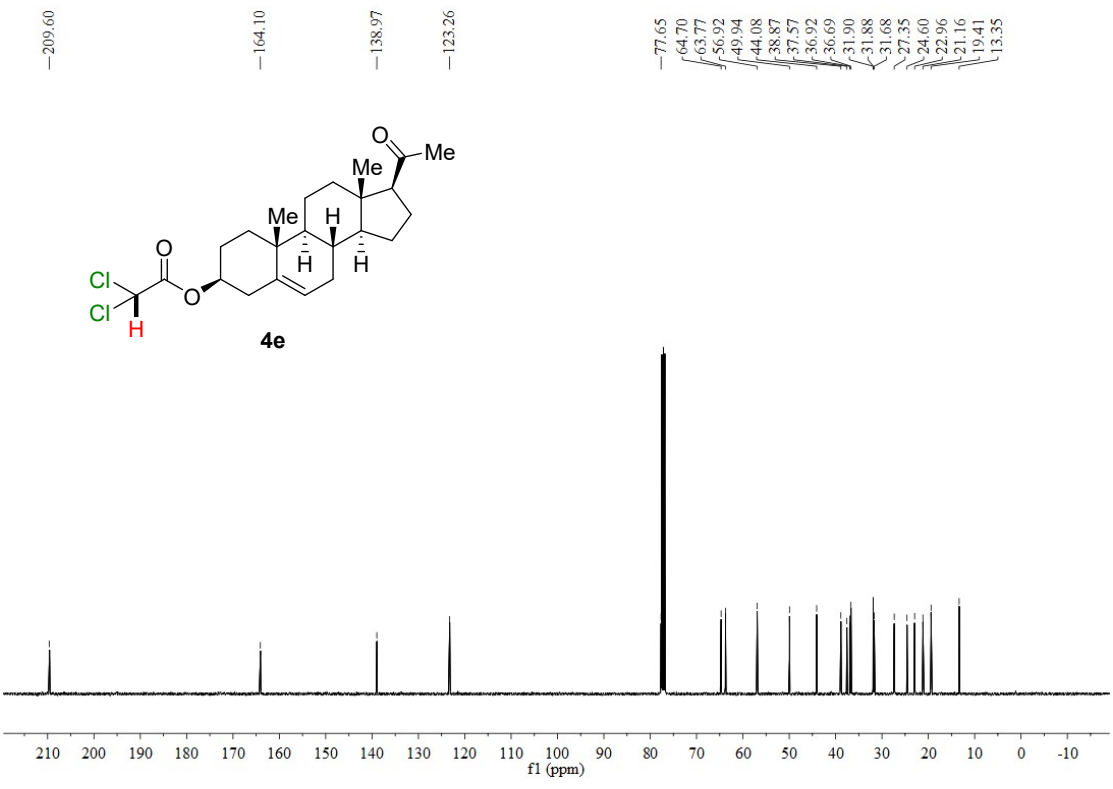
4d, $^{1}H+^{13}C$



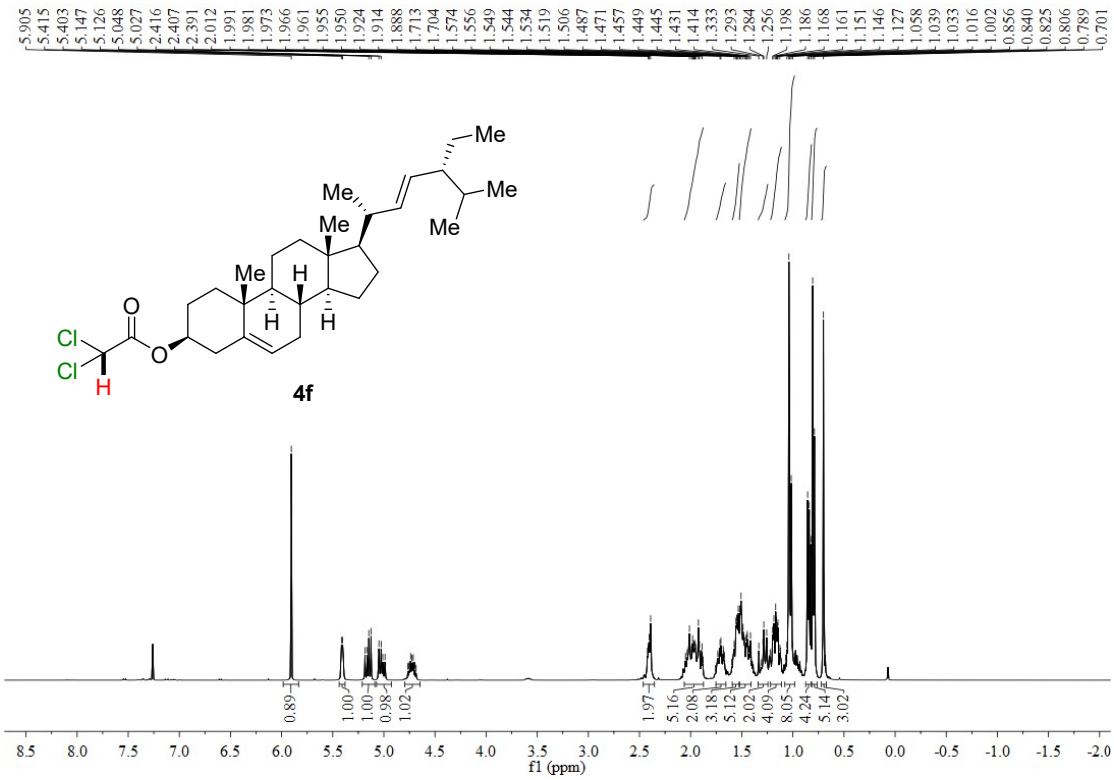


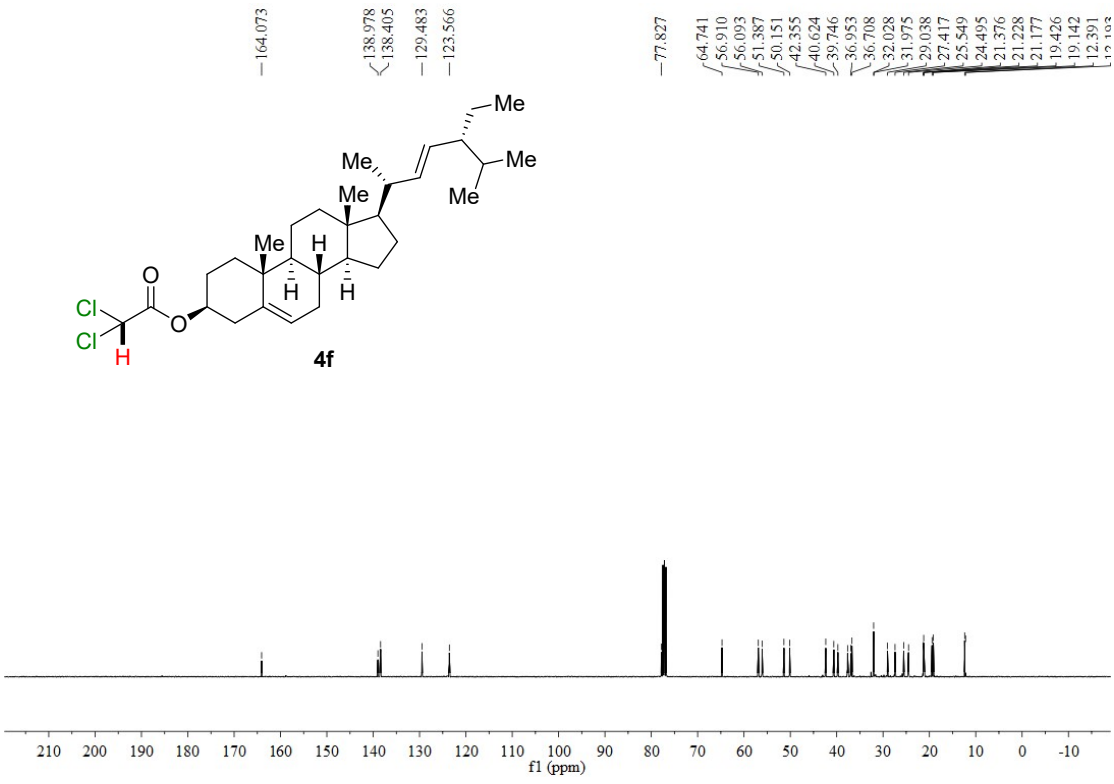
4e, $^{1}H+^{13}C$



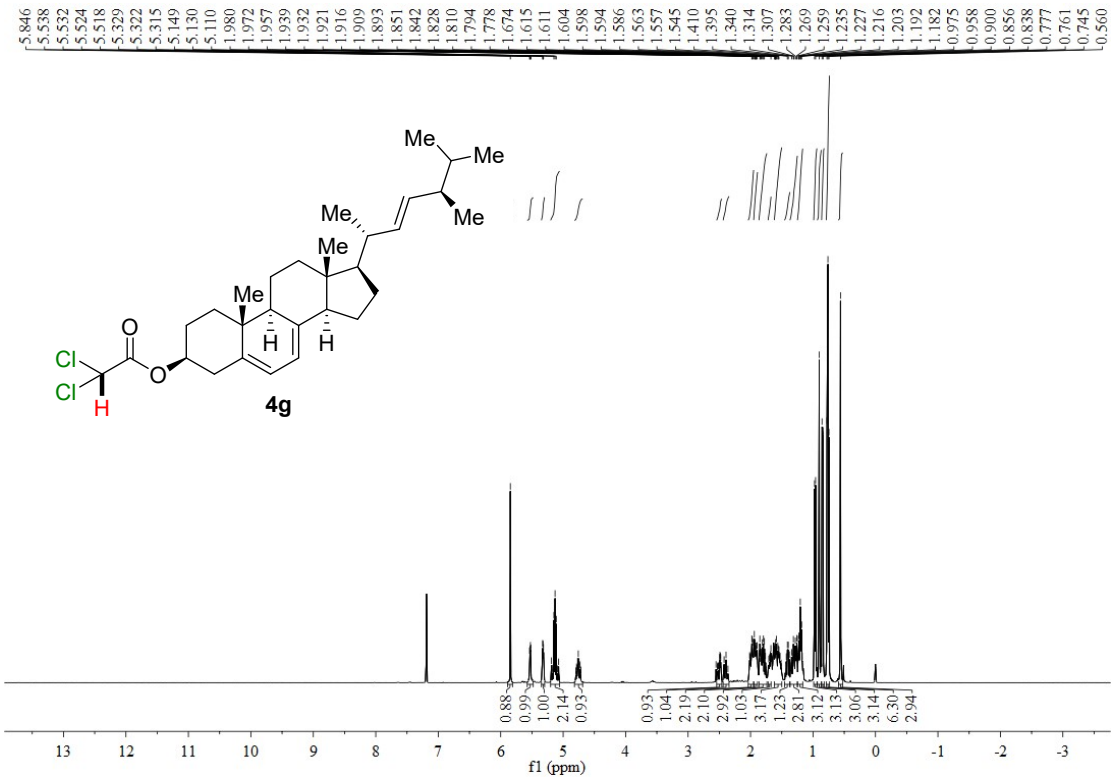


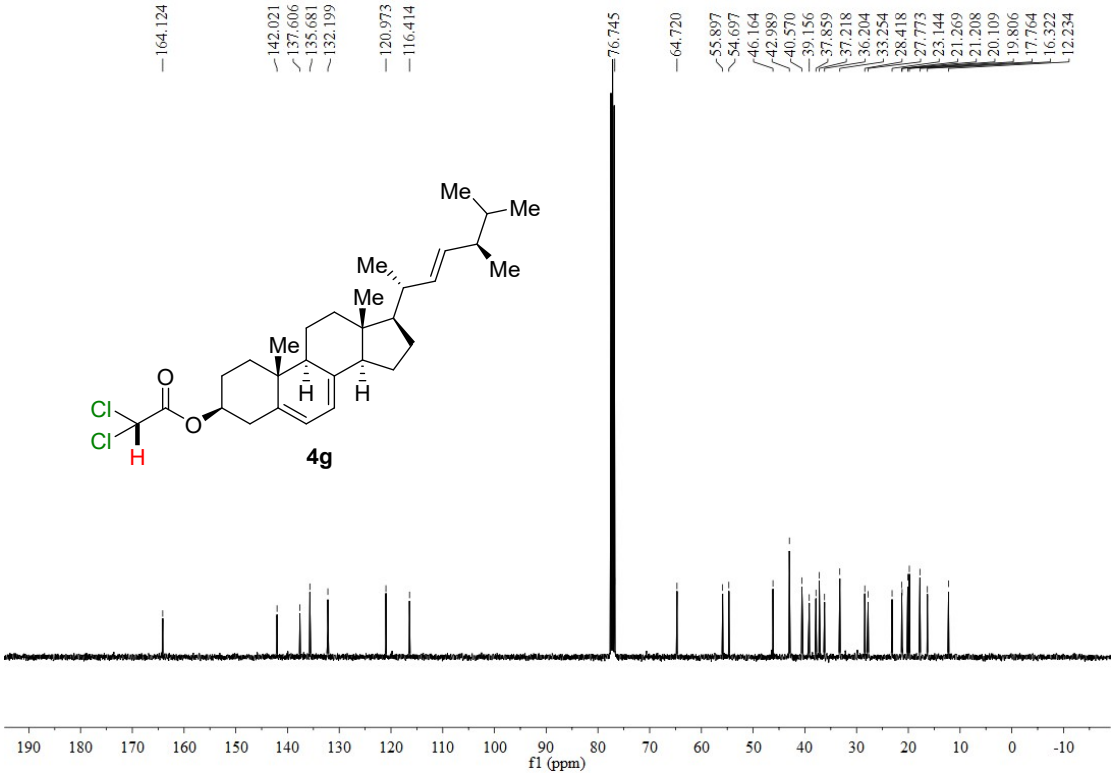
4f, $^{1}H+^{13}C$



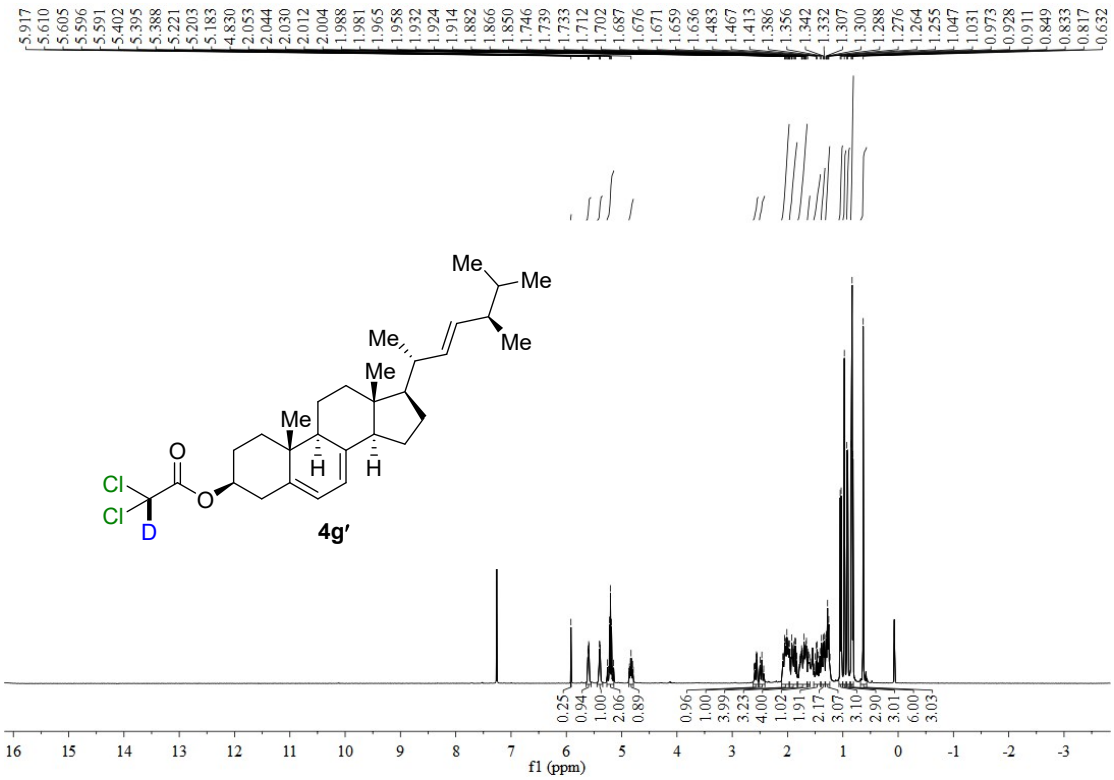


4g, $^{1}H+^{13}C$

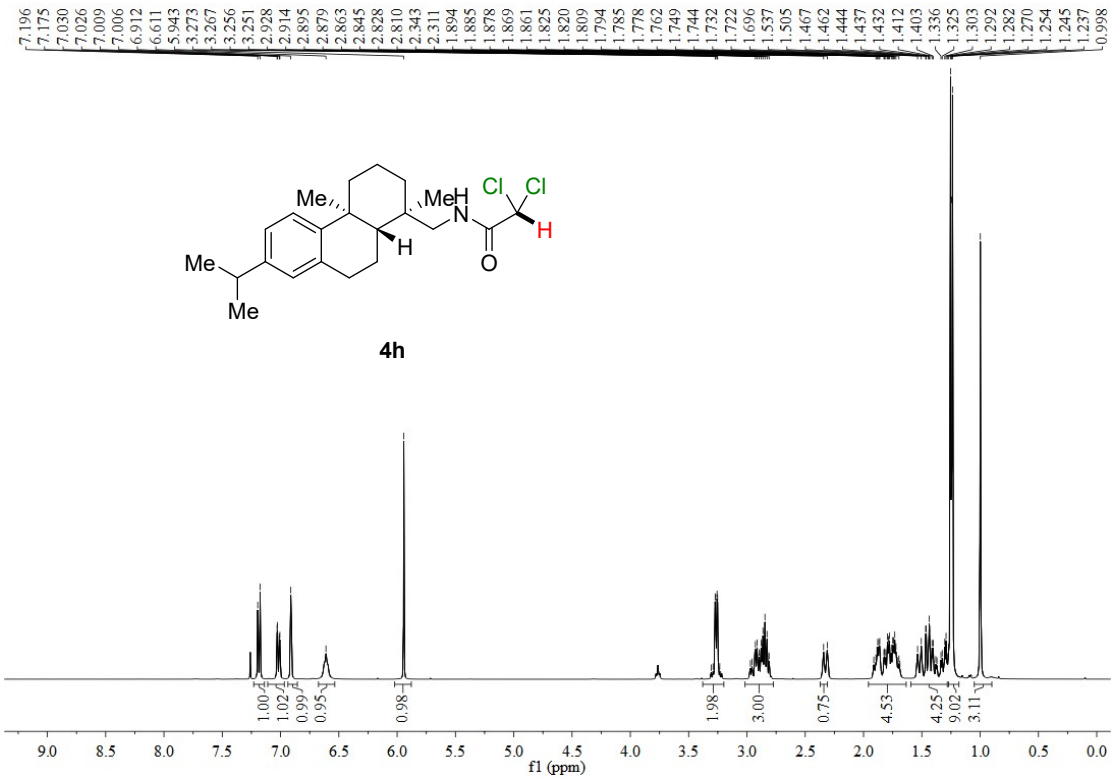

5.846
5.538
5.532
5.524
5.518
5.329
5.322
5.315
5.149
5.130
5.110
1.980
1.972
1.957
1.939
1.932
1.921
1.916
1.909
1.893
1.851
1.842
1.828
1.810
1.794
1.778
1.674
1.615
1.611
1.604
1.598
1.594
1.586
1.563
1.557
1.545
1.410
1.395
1.340
1.314
1.307
1.283
1.269
1.259
1.235
1.227
1.216
1.203
1.192
1.182
0.975
0.958
0.900
0.856
0.838
0.777
0.761
0.745
0.560
Me
Me
Me
Me
Me
Me
O
O
Cl
Cl
H
H
H
4g
0.88
0.99
1.00
2.14
0.93
0.93
1.04
2.19
2.10
2.92
1.03
3.17
1.23
2.81
3.12
3.13
3.06
3.14
6.30
2.94
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


164.124
142.021
137.606
135.681
132.199
120.973
116.414
76.745
64.720
55.897
54.697
46.164
42.989
40.570
39.156
37.859
37.218
36.204
33.254
28.418
27.773
23.144
21.269
21.208
20.109
19.806
17.764
16.322
12.234
Me
Me
Me
Me
Me
Me
O
O
Cl
Cl
H
H
H
4g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

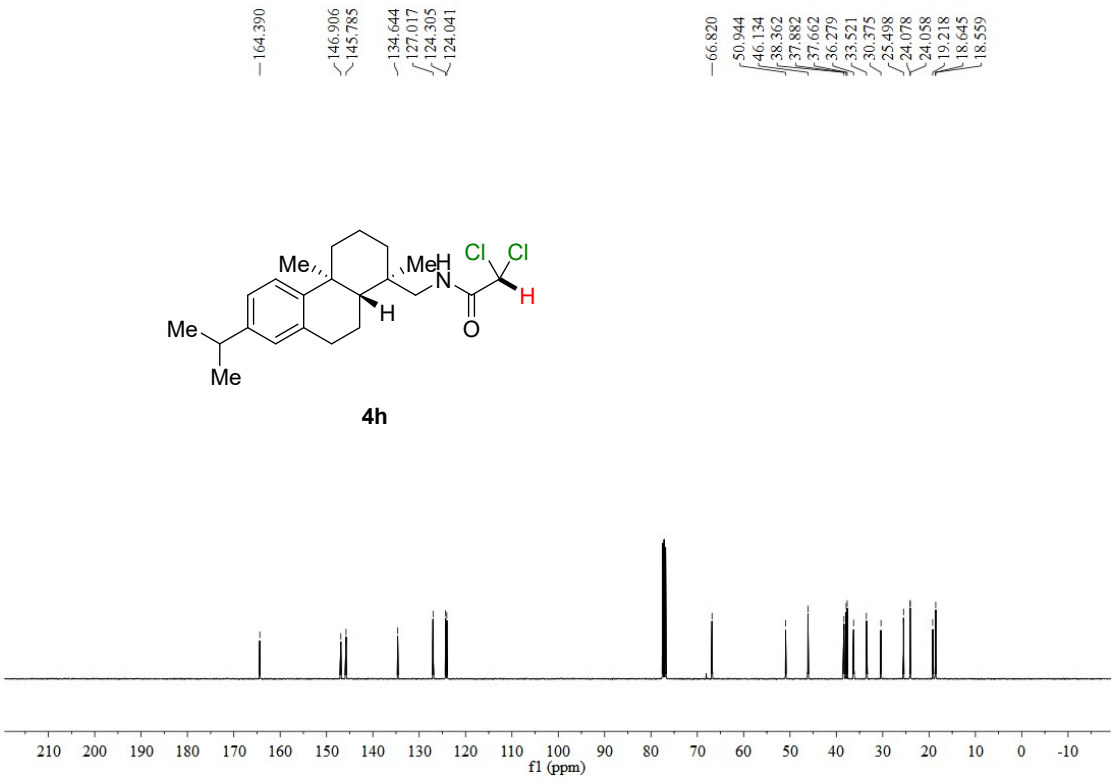
4g′, ^{1}H


5.917
5.610
5.605
5.596
5.591
5.402
5.395
5.388
5.221
5.203
5.183
4.830
2.053
2.044
2.030
2.012
2.004
1.988
1.981
1.965
1.958
1.932
1.924
1.914
1.882
1.866
1.850
1.746
1.739
1.733
1.712
1.702
1.687
1.676
1.671
1.659
1.636
1.483
1.467
1.413
1.386
1.356
1.342
1.332
1.307
1.300
1.288
1.276
1.264
1.255
1.047
1.031
0.973
0.928
0.911
0.849
0.833
0.817
0.632
Me
Me
Me
Me
Me
H
H
O
O
Cl
Cl
D
4g′
0.25
0.94
1.00
2.06
0.89
0.96
1.00
3.99
3.23
4.00
1.02
1.91
2.17
3.07
3.10
2.90
3.01
6.00
3.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

4h, $^{1}H+^{13}C$

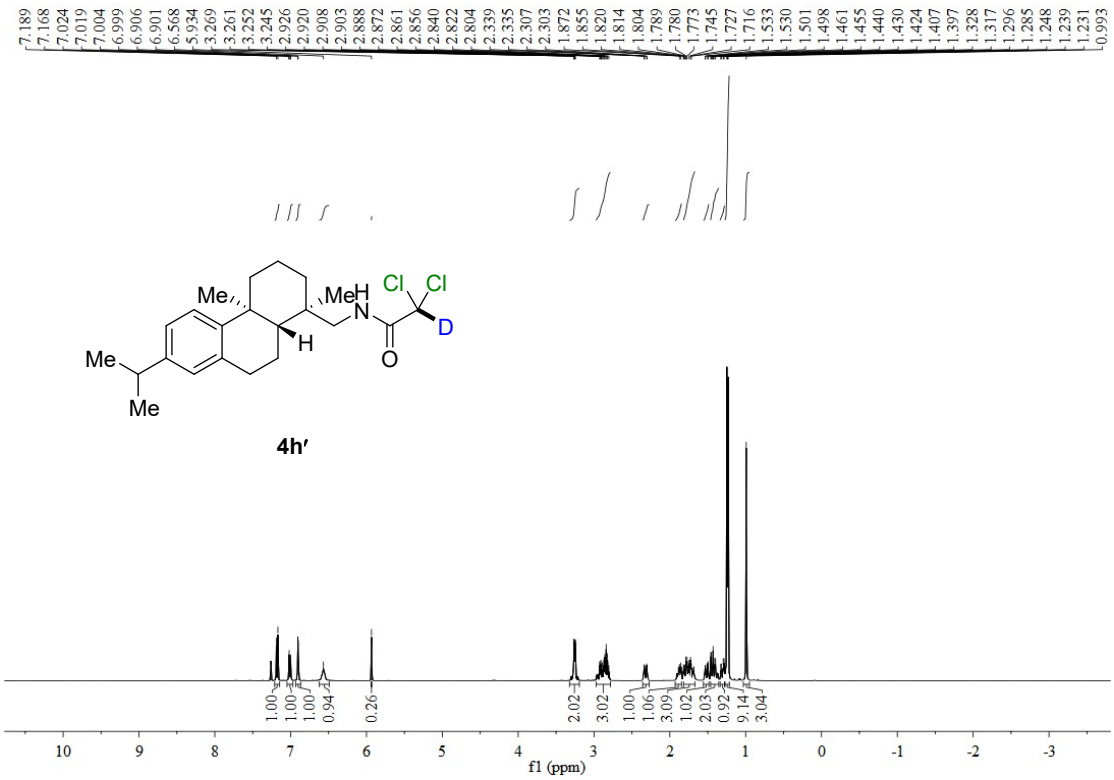


4h

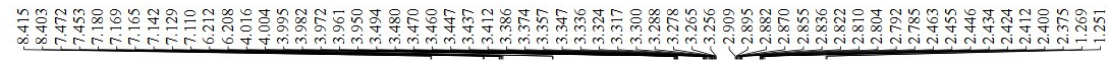


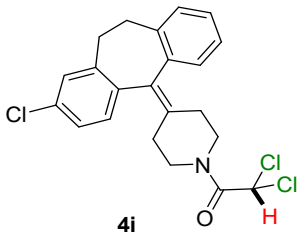
4h

4h´, ^{1}H

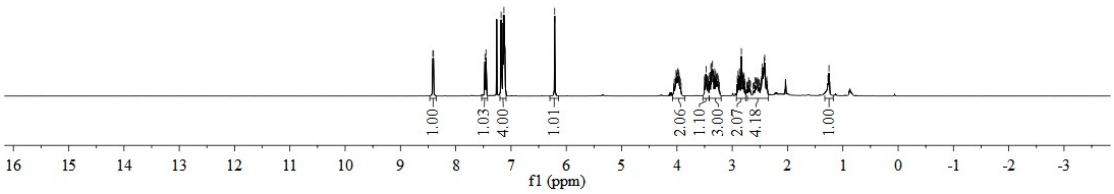

7.189
7.168
7.024
7.019
7.004
6.999
6.906
6.901
6.568
5.934
3.269
3.261
3.252
3.245
2.926
2.920
2.908
2.903
2.888
2.872
2.861
2.856
2.840
2.822
2.804
2.339
2.335
2.307
2.303
1.872
1.855
1.820
1.814
1.804
1.789
1.780
1.773
1.745
1.727
1.716
1.533
1.530
1.501
1.498
1.461
1.455
1.440
1.430
1.424
1.407
1.397
1.328
1.317
1.296
1.285
1.248
1.239
1.231
0.993
Me
Me
H
N
Cl
Cl
D
O
Me
Me
H
4h′
1.00
1.00
1.00
0.94
0.26
2.02
3.02
1.00
1.06
3.09
1.02
2.03
0.92
9.14
3.04
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

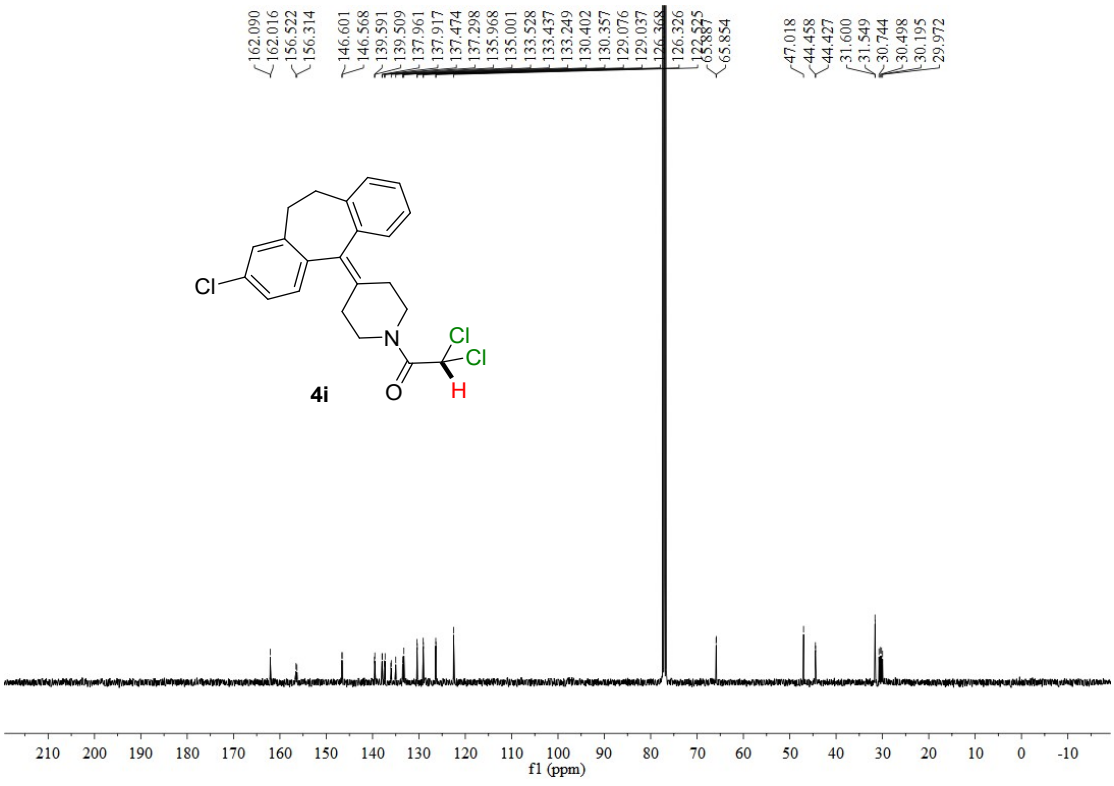
4i, $^{1}H+^{13}C$





4i





4i