Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

A mild, general, metal-free method for site-specific deuteration induced by visible light

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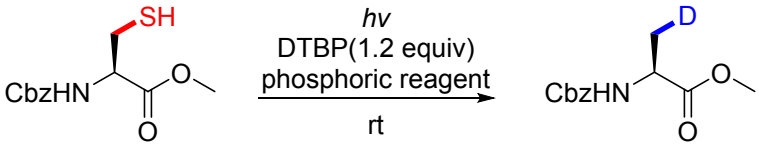
1. General Remarks on Materials and Methods

All commercial reagents were used without further purification. All glassware was oven dried at 120 °C for more than 1 hour before used. DCM was dried and preserved with 4Å molecular sieves under nitrogen. Unless otherwise noted, all solvents in reagent grade or analytical grade were used as received. Organic solutions were concentrated under reduced pressure on an IKA rotary evaporator using a water bath. Chromatographic purification of products was accomplished using force-flow chromatography on silica gel (200-300 mesh) according to the method of Still[1]. Thin-layer chromatography (TLC) was performed on 250 μm silica gel plates. TLC visualization was performed by fluorescence quenching or iodine stain. All small molecular compounds were characterized by ^{1}H NMR, ^{13}C NMR and MS. ^{1}H NMR spectra were recorded on an Agilent NMR Systems 400 MHz Spectrometer (^{1}H NMR at 400 MHz) and are internally referenced to residual protic $CDCl_3$ (δ 7.26 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and assignment. ^{13}C NMR spectra were recorded on an Agilent NMR Systems 400 MHz Spectrometer (^{13}C NMR at 101 MHz) and data are reported in terms of chemical shift relative to $CDCl_3$ (77.16 ppm). ^{2}H NMR spectra were recorded on a Bruker ADVANCE 600 MHz and reported as chemical shifts relative to $CDCl_3$ (7.26 ppm) or D_2O (4.79 ppm). EPR spectra were obtained on a Bruker EMX-8. UV-visible absorption spectrum were executed on SHIMADZU UV-2450 spectrophotometer. MS: electrospray ionization mass (ESI-MS) was performed on Agilent 6210 Series TOF MS. GC-MS analyses were performed on a GC-MS with an EI mode. LC-MS spectra were acquired by Acquity^{TM} UPLC/Xevo-G2-XS-QTOF-MS using C18 column (150mm×2.1mm, 1.7μm). HPLC: analytical revered-phase HPLC was performed on Agilent (1200 series HPLC system) instrument employing an analytical C18 column (250 × 4.6 mm, 5 μm). Mobile phases of HPLC are as followed: solvent A: 0.1% TFA (v/v) in acetonitrile; Solvent B: 0.1% TFA (v/v) in water. The peptides substrates were synthesized by the SPPS procedure and provided by GL Biochem. The 36 W household CFL bulbs were directly purchased from supermarket.

2. Optimization of reaction conditions

Supplementary Figure S1. Optimization of reaction conditions for the deuteration of **1a**[a].

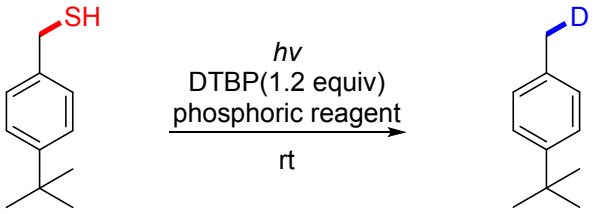


1a **2a**

entry	phosphoric reagent	solvent	Yield (%)[b]	D-incorp. (%)[c]
1	2.0 eq PPh_3	DCM/D_2O(V:V=2:1)	91	95
2	2.0 eq Ph_2POEt	DCM/D_2O(V:V=2:1)	96	96
3	2.0 eq $P(OEt)_3$	DCM/D_2O (V:V=2:1)	N.D.	—
4	2.0 eq Ph_2POEt	CD_3OD	93	64
5	2.0 eq Ph_2POEt	D_6-DMSO	95	N.D.
6	2.0 eq Ph_2POEt	$CDCl_3$	91	N.D.
7	—	DCM/D_2O(V:V=2:1)	N.D.	—
8[d]	2.0 eq Ph_2POEt	DCM/D_2O(V:V=2:1)	N.D.	—
9[e]	2.0 eq Ph_2POEt	DCM/D_2O(V:V=2:1)	N.D.	—

[a]Standard conditions: **1a** (0.75 mmol), DTBP (0.90 mmol), phosphoric reagent (0.90 mmol), solvent (6 ml), 36 W household CFL bulb irradiation on two sides, 10 h. [b]Yield of the isolated product. [c]Deuterium incorporation was determined by ^1H NMR spectroscopy. [d]Without DTBP. [e]Without visible light. N.D. = not detected. DCM = dichloromethane. DTBP = di-*tert*-butyl peroxide.

Supplementary Figure S2. Optimization of reaction conditions for the deuteration of **1g**[a].



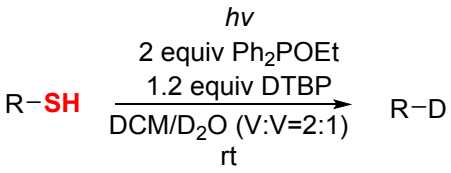
1g **2g**

entry	phosphoric reagent	solvent	Yield (%)[b]	D-incorp. (%)[c]
1	2.0 eq $P(OEt)_3$ (sensitive to water)	DCM/D_2O (V:V=2:1)	N.D.	—
2	2.0 eq Ph_2POEt	DCM/D_2O (V:V=2:1)	89	90
3	2.0 eq PPh_3	DCM/D_2O (V:V=2:1)	26	91
4	2.0 eq Ph_2POEt	CD_3OD	91	58

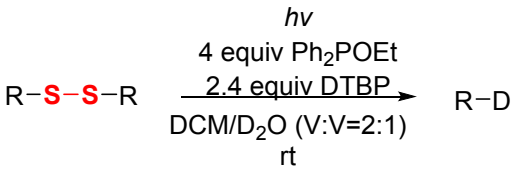
[a]Standard conditions: **1g** (0.75 mmol), DTBP (0.90 mmol), phosphoric reagent (0.90 mmol), solvent (6 ml), 36 W household bulb irradiation on two sides, 10 h. [b]Yield of the isolated product. [c]Deuterium incorporation was determined by ^1H NMR spectroscopy. N.D. = not detected. DCM=dichloromethane. DTBP=di-*tert*-butyl peroxide.

3. Desulfurization-deuteration reactions of thiol/disulfide-containing compounds

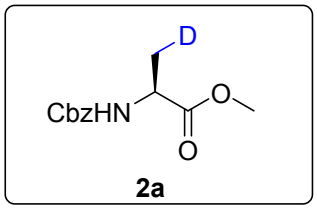
General procedure for desulfurization-deuteration reactions



To a 25 ml round-bottom flask equipped with a stir bar was added the substrate (0.75 mmol, 1.0 equiv) and Ph_2POEt (0.3454 g, 1.5 mmol, 2.0 equiv). Solvent (DCM/D_2O, 6ml, V:V = 2:1) was added followed by the addition of DTBP (0.1316 g, 0.9 mmol, 1.2 equiv). The flask was capped and the reaction was stirred and irradiated using two 36 W household CFL bulbs (6 cm away, to keep the reaction at room temperature) at room temperature for 10 hours. When the reaction was complete, the reaction mixture was extracted with ethyl acetate (3×20 ml). The combined organic layer was dried with sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate mixture as the eluent.



To a 25 ml round-bottom flask equipped with a stir bar was added the substrate (0.375 mmol, 1.0 equiv.) and Ph_2POEt (0.3454 g, 1.5 mmol, 4.0 equiv.). Solvent (DCM/D_2O, 6ml, V:V = 2:1) was added followed by the addition of DTBP (0.1316 g, 0.9 mmol,2.4 equiv.). The flask was capped and the reaction was stirred and irradiated using two 36 W household CFL bulb (6 cm away, to keep the reaction at room temperature) at room temperature for 10 hours. When the reaction was complete, the reaction mixture was extracted with ethyl acetate (3×20 ml). The combined organic layer was dried with sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate mixture as the eluent.

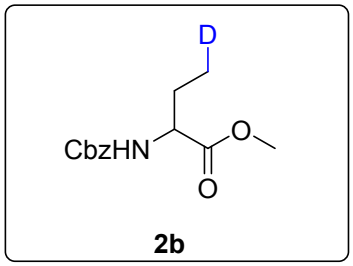


2a

Methyl ((benzyloxy)carbonyl)-L-alaninate-3-*d*

The reaction was carried out according to the general procedure on 0.75 mmol scale. When the reaction was complete, the reaction mixture was extracted with ethyl acetate (3×20 ml). The combined organic layers were dried with sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (5:1) to afford **2a** (171.5 mg, 96% yield) as colorless oil. D-incorporation ratio was based on ^1H NMR:

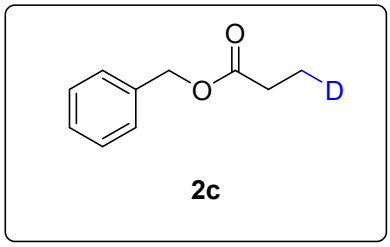
96%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.07 (m, 5H), 5.38 (d, *J* = 4.9 Hz, 1H), 5.10 (s, 2H), 4.38 (dt, *J* = 6.7, 4.9 Hz, 1H), 3.73 (s, 3H), 1.38 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ173.44, 155.58, 136.25, 128.50, 128.14, 128.08, 66.90, 52.41, 49.52, 18.38 (t, *J* = 20.8 Hz). ^{2}H NMR (92 MHz, $CDCl_3$) δ 1.42 (s, 1D). HRMS (ESI) calcd for $C_{12}H_{14}DNO_4$ [M + Na]$^+$ m/z = 261.0956, found: 261.0953.



2b

Methyl 2-(((benzyloxy)carbonyl)amino)butanoate-4-*d*

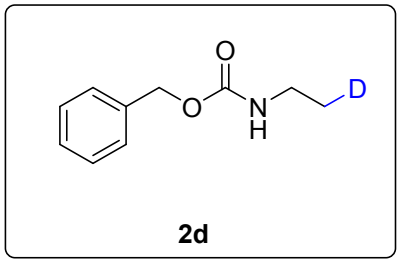
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (5:1) to afford **2b** (183.5 mg, 97% yield) as colorless oil. D-incorporation ratio was based on ^{1}H NMR: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.17 (m, 5H), 5.41 (d, *J* = 7.4 Hz, 1H), 5.10 (s, 2H), 4.34 (m, 1H), 3.72 (s, 3H), 1.89 – 1.76 (m, 1H), 1.73 – 1.60 (m, 1H), 0.89 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.88, 155.88, 136.28, 128.49, 128.12, 128.07, 66.91, 54.94, 52.25, 25.70, 9.21 (t, *J* = 19.5 Hz). ^{2}H NMR (92 MHz, $CDCl_3$) δ 0.94 (s, 1D). HRMS (ESI) calcd for $C_{13}H_{16}DNO_4$ [M + Na]$^+$ m/z = 275.1113, found: 275.1108.



2c

Benzyl propanoate-3-*d*

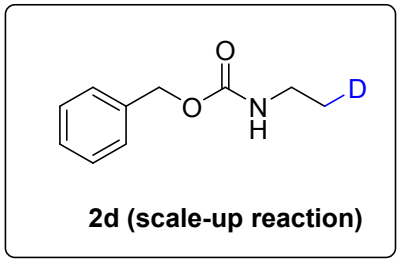
The reaction was carried out according to the general procedure on 0.75 mmol scale. As the compound is volatile, the 92% yield was based on ^{1}H NMR. D-incorporation ratio was calculated by ^{1}H NMR and mass spectrometry: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 5.10 (s, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 2H). GC-MS (EI): m/z = 165.15.



2d

Benzyl (ethyl-2-*d*)carbamate

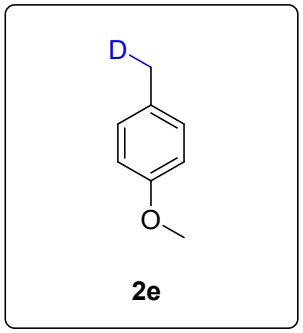
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (8:1) to afford **2d** (125.7 mg, 93% yield) as colorless liquid. D-incorporation ratio was based on ^{1}H NMR: 98%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.26 (m, 5H), 5.09 (s, 2H), 4.81 (br s, 1H), 3.22 (dt, *J* = 6.4 Hz, *J* = 6.2 Hz, 2H), 1.11 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.28, 136.67, 128.48, 128.03, 66.50, 35.84, 14.94 (t, *J* = 19.8 Hz). HRMS (ESI) calcd for $C_{10}H_{12}DNO_2$ [M + Na] $^+$ m/z = 203.0901, found: 203.0904.



2d (scale-up reaction)

Benzyl (ethyl-2-*d*)carbamate

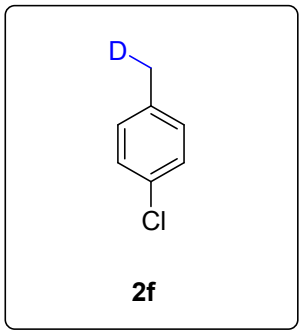
The reaction was carried out according to the general procedure on 7.5 mmol scale (1.5846g substrate). The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (8:1) to afford **2d** (1.1769 g, 87% yield) as colorless liquid. D-incorporation ratio was based on ^{1}H NMR: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.17 (m, 5H), 5.08 (s, 2H), 4.71 (brs, 1H), 3.21 (dt, *J* = 6.4 Hz, *J* = 6.2 Hz, 2H), 1.10 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.24, 136.65, 128.45, 128.00, 66.51, 35.83, 15.10, 14.90, 14.72 (t, *J* = 19.8 Hz). HRMS (ESI) calcd for $C_{10}H_{12}DNO_2$ [M + Na] $^+$ m/z = 203.0901, found: 203.0904.



2e

1-methoxy-4-(methyl-*d*) benzene

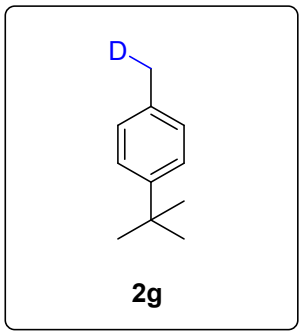
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with 100% petroleum ether to afford **2e** (74.8 mg, 81% yield) as colorless liquid. D-incorporation ratio was based on ^{1}H NMR: 93%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 3.79 (s, 3H), 2.28 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.44, 129.85, 129.77, 113.67, 55.24, 20.15 (t, *J* = 19.8 Hz). GC-MS (EI): m/z = 123.08.



2f

1-chloro-4-(methyl-*d*) benzene

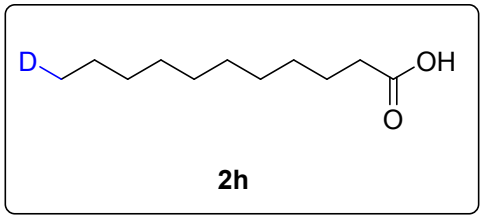
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with 100% petroleum ether to afford **2f** (87.1 mg, 91% yield) as colorless liquid. D-incorporation ratio was based on ^{1}H NMR: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.23, 136.20, 131.07, 130.38, 128.27, 20.58 (t, *J* = 19.6 Hz). ^{2}H NMR (92 MHz, $CDCl_3$) δ 2.34 (t, 1D). GC-MS (EI): m/z = 127.03.



2g

1-(tert-butyl)-4-(methyl-*d*) benzene

The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with 100% petroleum ether to afford **2g** (99.6 mg, 89% yield) as colorless liquid. D-incorporation ratio was based on ^{1}H NMR: 90%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 2.37 – 2.28 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.17, 134.84, 128.79, 125.19, 34.35, 31.48, 20.62 (t, *J* = 19.3 Hz).GC-MS (EI): m/z = 149.14.

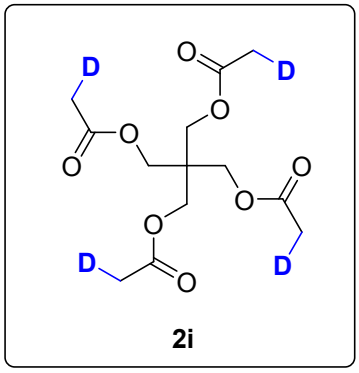


2h

Undecanoic-11-d acid

The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (1:5). As the compound is volatile, the pure product was difficult to be obtained. As such NMR spectra is

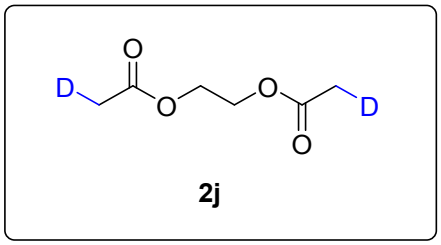
not clean and the crude NMR spectra was acquired. The 85% yield was based on ^{1}H NMR. D-incorporation ratio was calculated by ^{1}H NMR and mass spectrometry: 91%. The crude ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.49 (m, 2H), 1.25 – 1.14 (m, 14H), 0.78 (t, *J* = 7.2 Hz, 2H). GC-MS (EI): m/z = 187.17.



2i

2, 2-bis ((acetoxy-2-d) methyl) propane-1, 3-diyl bis (acetate-2, 2'-d_2)

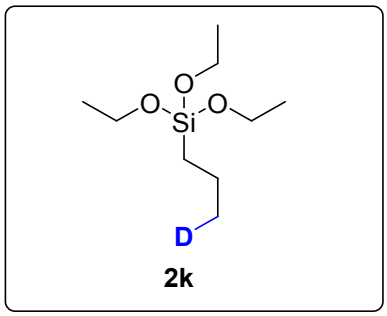
The reaction was carried out according to the general procedure using 0.75 mmol of the substrate, Ph_2POEt (0.6908 g, 1.5 mmol, 8.0 equiv.) and DTBP (0.2632g, 4.8 equiv.). The product was purified by column chromatography on silica with petroleum ether/ethyl acetate (1:1) to afford **5i** (217.4 mg, 94% yield) as white solid. D-incorporation ratio was based on ^{1}H NMR: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (s, 1H), 2.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.51, 62.25, 41.62, 20.49 (t, *J*= 19.8 Hz). ^{2}H NMR (92 MHz, $CDCl_3$) δ 2.07 (s, 4D). HRMS (ESI) calcd for $C_{13}H_{16}DO_8$ $[M + Na]^+$ m/z = 331.1301, found: 331.1297.



2j

Ethane-1, 2-diyl bis (acetate-2, 2'-d2)

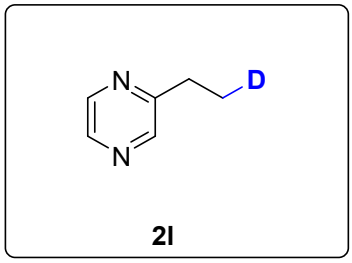
The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 90% based on ^{1}H NMR. D-incorporation ratio was based on ^{1}H NMR: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (s, 2H), 2.00 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.66, 62.16, 20.60 (t, *J* = 20.0 Hz). HRMS (ESI) calcd for $C_6H_8D_2O_4$ $[M + H]^+$ m/z = 149.0777, found: 149.0959.



2k

Triethoxy(propyl-3-d)silane

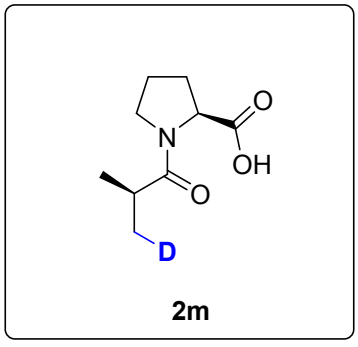
The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 95% based on ^{1}H NMR. D-incorporation ratio was calculated by ^{1}H NMR: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.0 Hz, 6H), 1.50 – 1.40 (m, 2H), 1.20 (t, *J* = 7.0 Hz, 9H), 0.94 (t, *J* = 7.3 Hz, 2H), 0.63 (t, *J* = 8.2 Hz, 2H). GC-MS (EI): m/z = 207.04.



2l

2-(ethyl-2-d) pyrazine

The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 73% based on ^{1}H NMR. D-incorporation ratio was based on ^{1}H NMR: 95%. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.46 (dd, *J* = 8.5, 2.7 Hz, 2H), 8.36 (d, *J* = 2.4 Hz, 1H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.11 (t, *J* = 7.4 Hz, 2H). GC-MS (EI): m/z = 109.08.

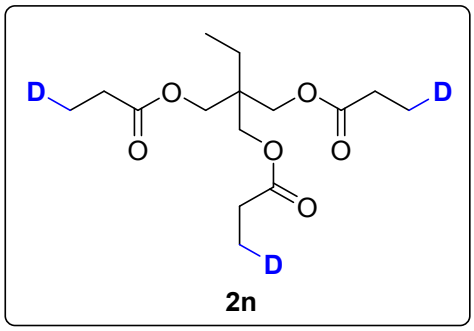


2m

((R)-2-methylpropanoyl-3-d)-L-proline

The reaction was carried out according to the general procedure on 0.75 mmol scale. When the reaction is complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography (CH_3CN/H_2O, 20% –90%) to afford **2m** (126.5 mg, 91% yield) as white solid. D-incorporation ratio was based on ^{1}H NMR: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 – 4.27 (m, 1H), 3.66 – 3.38 (m, 2H), 2.69 – 2.39 (m, 1H), 2.23 – 1.67 (m, 4H), 1.24 – 0.71 (m, 5H). ^{13}C

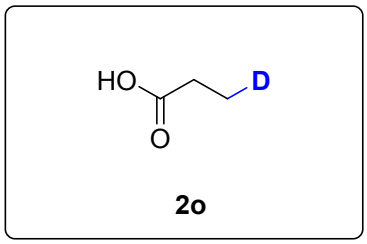
NMR (101 MHz, $CDCl_3$) δ 177.22, 175.94, 60.26, 47.20, 32.20, 28.49, 24.81, 18.65, 18.37 (t, *J* = 19.8). ^2H NMR (92 MHz, $CDCl_3$) δ 1.08 (s, 1D). HRMS (ESI) calcd for $C_9H_{14}DNO_3$ $[M + H]^+$ m/z =187.1187, found: 187.1175.



2n

2-ethyl-2-(((propanoyl-3-d)oxy)methyl)propane-1,3-diyl bis(propanoate-3-d)

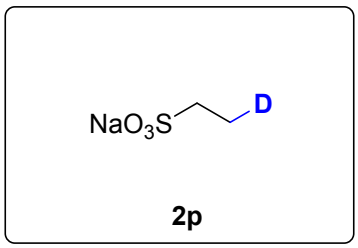
The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 92% based on ^1H NMR. D-incorporation ratio was calculated by ^1H NMR: 98%. ^1H NMR (400 MHz, $CDCl_3$) δ 4.02 (s, 6H), 2.27 (t, *J* = 7.4 Hz, 6H), 1.46 (q, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 6H), 0.85 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.94, 63.71, 40.75, 27.38, 23.10, 8.84 (t, *J* = 19.7 Hz), 7.41. HRMS (ESI) calcd for $C_{15}H_{23}D_3O_6$ $[M + H]^+$ m/z =306.1990, found:306.1986.



2o

Propanoic-3-d acid

The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 95% based on ^1H NMR. D-incorporation ratio was based on ^1H NMR: 95%. ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (t, *J* = 7.0 Hz, 2H), 1.05 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.33, 27.47, 8.91 (t, *J* = 19.8 Hz). GC-MS (EI): m/z = 75.04.

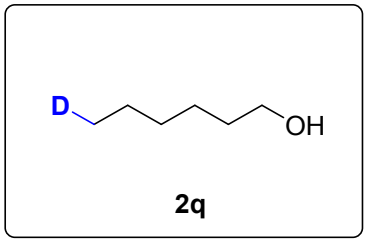


2p

Sodium ethane-1-sulfonate-2-d

The reaction was carried out according to the general procedure on 0.75 mmol scale in CD_3OD/D_2O (4ml/2ml) in order to dissolve all compounds. When the reaction is complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography (CH_3CN/H_2O, 10% –80%) to afford **2p** (74.7 mg, 75% yield) as white solid. D-incorporation ratio

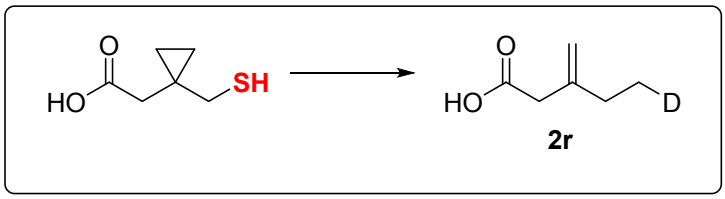
was based on ^{1}H NMR: 96%. ^{1}H NMR (400 MHz, D_2O) δ 2.80 (t, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, D_2O) δ 45.32, 8.14 (t, *J* = 20.0 Hz). ^{2}H NMR (92 MHz, D_2O) δ 1.27 (s, 1D). HRMS (ESI) calcd for $C_2H_4DNaO_3S$ [M + Na] $^+$ m/z =155.9812, found: 155.9923.



2q

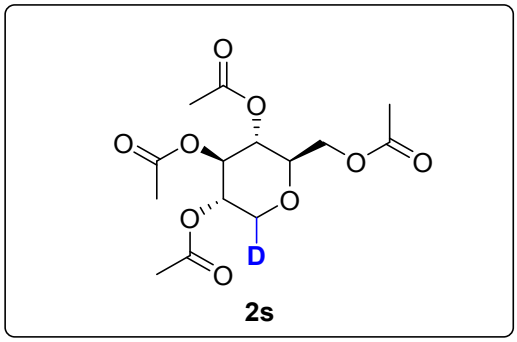
Hexan-6-d-1-ol

The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 92% based on ^{1}H NMR. D-incorporation ratio was based on ^{1}H NMR: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (t, *J* = 6.7 Hz, 2H), 3.11 (brs, 1H), 1.57 – 1.43 (m, 2H), 1.43 – 1.06 (m, 6H), 0.83 (t, *J* = 7.1 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 62.43, 32.68, 31.61, 25.47, 22.50, 13.76 (t, *J* = 19.2 Hz). GC-MS (EI) [M-H_2O]: m/z = 85.09.



2r

The reaction was carried out according to the general procedure on 0.75 mmol scale. When the reaction is complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography (CH_3CN/H_2O, 20% –90%) to afford **2r** (83.7 mg, 97% yield) as colorless liquid. D-incorporation ratio was based on ^{1}H NMR: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (d, *J* = 12.2 Hz, 2H), 3.07 (s, 2H), 2.11 (t, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.03, 143.39, 112.91, 41.84, 28.56, 11.60 (t, *J* = 19.5 Hz). ^{2}H NMR (92 MHz, $CDCl_3$) δ 1.07 (s, 1D). HRMS (ESI) calcd for $C_6H_9DO_2$ [M + H] + m/z =116.0816, found: 116.0814.

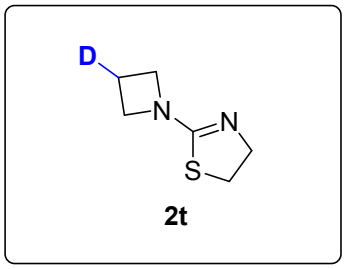


2s

(2R, 3R, 4R, 5S)-2-(acetoxymethyl) tetrahydro-2H-pyran-3, 4, 5-triyl-6-d triacetate

The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (3:1) to afford **2s** (239.8 mg, 96% yield) as colorless oil. D-incorporation ratio was calculated by ^{1}H NMR:

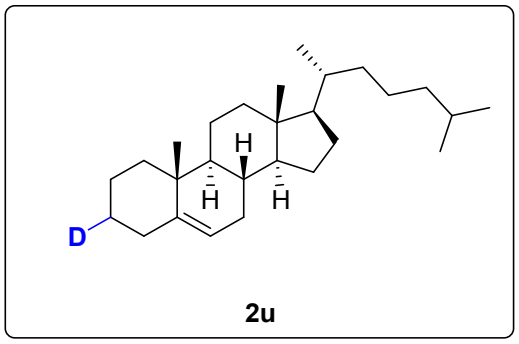
96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (t, *J* = 9.5 Hz, 1H), 4.99 – 4.85 (m, 2H), 4.19 – 3.98 (m, 3H), 3.52 (ddd, *J* = 10.0, 4.8, 2.2 Hz, 1H), 2.00 (s, 3H), 1.94 (s, 6H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.51, 170.18, 169.63, 169.39, 76.29, 73.60, 68.80, 68.34, 66.34 (t, *J* = 21.6 Hz), 62.11, 20.59, 20.56, 20.54, 20.47. ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.24 (s, 1D). HRMS (ESI) calcd for $C_{14}H_{19}DO_9$ $[M + H]^+$ m/z =334.1243, found: 334.1230.



2t

2-(azetidin-1-yl-3-d)-4, 5-dihydrothiazole

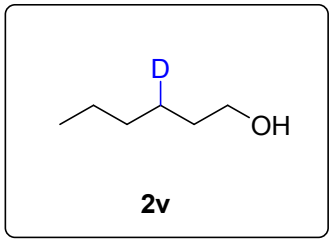
The reaction was carried out according to the general procedure on 0.75 mmol scale. When the reaction is complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography (CH_3CN/H_2O, 20% –90%) to afford **2t** (100.8 mg, 94% yield) as colorless liquid. D-incorporation ratio was calculated by ^{1}H NMR: 94%. ^{1}H NMR (400 MHz, D_2O) δ 4.15 (t, *J* = 7.3 Hz, 4H), 3.80 (t, *J* = 7.5 Hz, 2H), 3.45 (t, *J* = 7.4 Hz, 2H), 2.42 – 2.22 (m, 1H). ^{13}C NMR (101 MHz, D_2O) δ 170.14, 54.32, 53.72, 49.25, 32.07, 15.78 (t, *J* = 21.6 Hz). ^{2}H NMR (92 MHz, D_2O) δ 2.67 (s, 1D). HRMS (ESI) calcd for $C_6H_9DN_2S$ $[M + H]^+$ m/z =144.0700, found: 144.0699.



2u

(8S, 9S, 10R, 13R, 14S, 17R)-10, 13-dimethyl-17-((R)-6-methylheptan-2-yl)-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17-tetradecahydro-1H-cyclopenta[a]phenanthrene-3-d

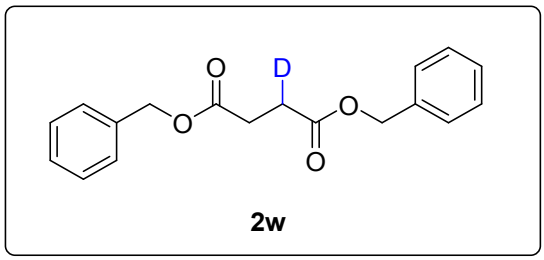
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with 100% petroleum ether to afford **2u** (270.2 mg, 97% yield) as white solid. D-incorporation ratio was assessed by mass spectrometry: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 – 5.20 (m, 1H), 2.45 – 0.33 (m, 44H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.67, 118.93, 56.87, 56.18, 50.60, 42.29, 39.87, 39.51, 37.51, 36.19, 35.78, 32.78, 31.87, 31.84, 29.67, 28.22, 27.98, 27.62 (t, *J* = 18.9 Hz), 24.26, 23.82, 22.77, 22.52, 22.45, 20.76, 19.42, 18.70, 11.84. ^{2}H NMR (92 MHz, $CDCl_3$) δ 1.20 (s, 1D). GC-MS (EI): m/z = 371.36.



2v

Hexan-3-d-1-ol

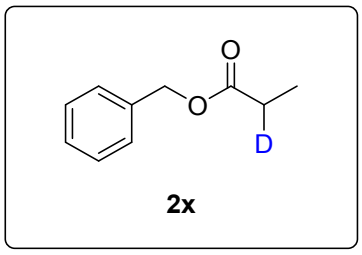
The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 90% based on ^{1}H NMR. D-incorporation ratio was based on ^{1}H NMR: 94%. ^{1}H NMR (400 MHz, cdcl$_3$) δ 3.54 (t, *J* = 6.7 Hz, 2H), 2.84 (brs, 1H), 1.49 (dd, *J* = 13.6, 6.8 Hz, 2H), 1.39 – 1.09 (m, 5H), 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 62.57, 32.63, 31.55, 25.08 (t, *J* = 19.2 Hz), 22.59, 14.08. ^{2}H NMR (92 MHz, CDCl$_3$) δ 1.27 (s, 1D). GC-MS (EI)[M-H$_2$O]: m/z = 85.09.



2w

Dibenzyl succinate-2-*d*

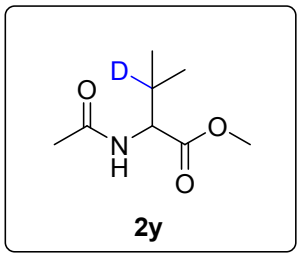
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (8:1) to afford **2w** (215.5 mg, 96% yield) as white solid. D-incorporation ratio was based on ^{1}H NMR: 97%.^{11}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.22 (m, 10H), 5.12 (s, 4H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.03, 135.72, 128.55, 128.26, 128.22, 66.56, 29.10. ^{2}H NMR (92 MHz, CDCl$_3$) δ 2.72 (s, 1D). HRMS (ESI) calcd for $C_{18}H_{17}DO_4$ [M + Na]$^+$ m/z = 322.1160, found: 322.1158.



2x

Benzyl propanoate-2-*d*

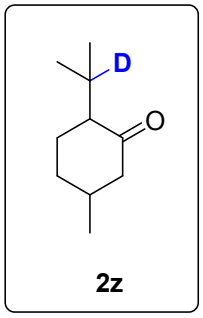
The reaction was carried out according to the general procedure on 0.75 mmol scale. The pure product was difficult to be obtained. As such NMR spectra is not clean and the crude NMR spectra was acquired. The 95% yield was calculated based on ^{1}H NMR. D-incorporation ratio was calculated by ^{1}H NMR: 99%.^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 5H), 5.09 (s, 2H), 2.33 (q, *J* = 7.5 Hz, 1H), 1.10 (d, *J* = 7.5 Hz, 3H). GC-MS (EI): m/z = 165.15.



2y

Methyl acetylvalinate-3-*d*

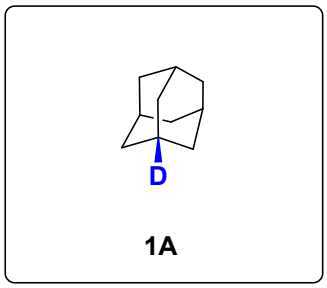
The reaction was carried out according to the general procedure on 0.75 mmol scale. The crude ^{1}H NMR was obtained. The 89% yield was calculated based on ^{1}H NMR. D-incorporation was calculated by ^{1}H NMR: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (d, *J* = 8.8 Hz), 4.54 (d, *J* = 8.8 Hz, 1H), 3.71 (s, 3H), 2.03 (s, 3H), 0.91 (s, 3H), 0.88 (s, 3H). HRMS (ESI) calcd for $C_8H_{15}NO_3$ [M + Na] $^+$ m/z = 197.1007, found: 197.1012.



2z

5-methyl-2-(propan-2-yl-2-*d*)cyclohexan-1-one

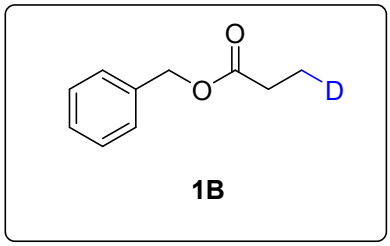
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (20:1) to afford **2z** (110.6 mg, 95% yield) as colorless liquid. D-incorporation was calculated by ^{1}H NMR: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (m, 1H), 2.11 – 1.78 (m, 5H), 1.42 – 1.22 (m, 2H), 0.97 (d, *J* = 6.3 Hz, 3H), 0.86 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.41, 55.72, 50.83, 35.43, 33.88, 27.76, 25.40 (t, *J* = 19.6 Hz), 22.27, 21.08, 18.53. GC-MS (EI): m/z = 155.14.



1A

(3r,5r,7r)-adamantane-1-d

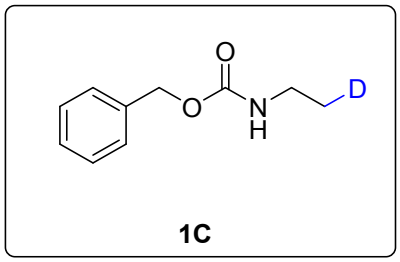
The reaction was carried out according to the general procedure on 0.75 mmol scale. The residue was purified by column chromatography on silica with 100% petroleum ether to afford **1A** (92.6 mg, 90% yield) as white solid. D-incorporation ratio was calculated by ^{1}H NMR: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 1.75 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.73, 37.60, 28.30, 27.81 (t, *J* = 20.2 Hz). GC-MS (EI): m/z = 137.14.



1B

Benzyl propanoate-3-*d*

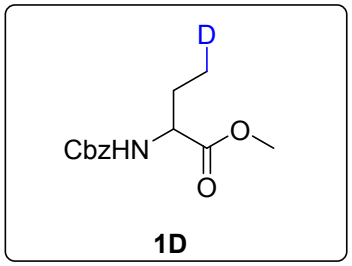
The reaction was carried out according to the general procedure on 0.375 mmol scale. The pure product was difficult to be obtained. As such NMR spectra is not clean and the crude NMR spectra was acquired. The 81% yield was calculated based on ^{1}H NMR. D-incorporation was calculated by ^{1}H NMR: 95%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 5H), 5.03 (s, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.04 (t, *J* = 7.5 Hz, 2H). GC-MS (EI): m/z = 165.15.



1C

Benzyl (ethyl-2-*d*)carbamate

The reaction was carried out according to the general procedure on 0.375 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (8:1) to afford **1C** (113.5 mg, 84% yield) as colorless liquid. D-incorporation was calculated by ^{1}H NMR: 99%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 5H), 5.09 (s, 2H), 4.71 (br s, 1H), 3.23 (dt, *J* = 6.4 Hz, *J* = 6.2 Hz, 2H), 1.12 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.28, 136.67, 128.47, 128.03, 66.50, 35.84, 14.9 (t, *J* = 19.8 Hz). HRMS (ESI) calcd for $C_{10}H_{12}DNO_2$ $[M + Na]^+$ m/z = 203.0901, found: 203.0904.

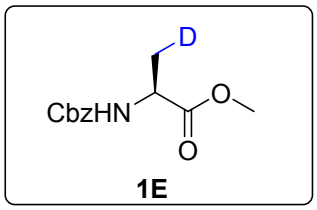


1D

Methyl 2-(((benzyloxy)carbonyl)amino)butanoate-4-*d*

The reaction was carried out according to the general procedure on 0.375 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (5:1) to afford **1D** (157.0 mg, 83% yield) as colorless oil. D-incorporation was calculated by ^{1}H NMR: 98%.^{1}H NMR (400 MHz, $CDCl_3$) δ7.56 – 7.21 (m, 5H), 5.36 (d, *J* = 7.4 Hz, 1H), 5.10 (s, 2H), 4.46 – 4.23 (m, 1H), 3.73 (s, 3H), 1.93 – 1.82 (m, 1H), 1.74 – 1.64 (m, 1H), 0.90 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.87, 155.85, 136.26, 128.50, 128.14, 128.07, 66.93, 54.92, 52.27,

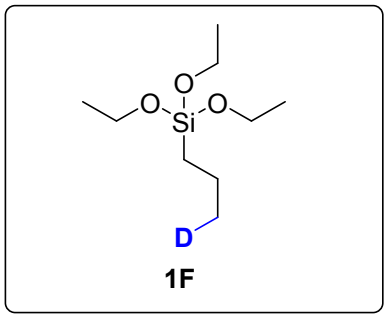
25.72, 9.19 (t, *J* = 19.5 Hz). HRMS (ESI) calcd for $C_{13}H_{16}DNO_4$ [M + Na]$^+$ m/z = 275.1113, found: 275.1108.



1E

Methyl ((benzyloxy)carbonyl)-L-alaninate-3-*d*

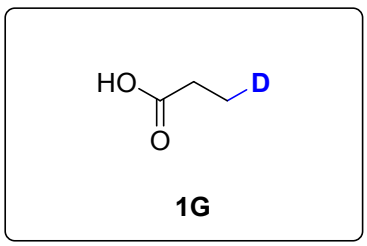
The reaction was carried out according to the general procedure on 0.375 mmol scale. The residue was purified by column chromatography on silica with petroleum ether/ethyl acetate (5:1) to afford **1E** (141.2 mg, 79% yield) as colorless oil. D-incorporation was calculated by ^{1}H NMR: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.19 (m, 5H), 5.37 (d, *J* = 4.9 Hz, 1H), 5.10 (s, 2H), 4.38 (dt, *J* = 6.7, 4.9 Hz, 1H), 3.74 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.44, 155.58, 136.25, 128.50, 128.14, 128.08, 66.90, 52.41, 49.53, 18.37 (t, *J* = 20.8 Hz). HRMS (ESI) calcd for $C_{12}H_{14}DNO_4$ [M + Na]$^+$ m/z = 261.0956, found: 261.0953.



1F

Triethoxy(propyl-3-d)silane

The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 90% based on ^{1}H NMR. D-incorporation ratio was calculated by ^{1}H NMR: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.0 Hz, 6H), 1.53 – 1.38 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.94 (t, *J* = 7.3 Hz, 2H), 0.64 (t, *J* = 8.2 Hz, 2H). GC-MS (EI): m/z = 207.04.



1G

Propanoic-3-d acid

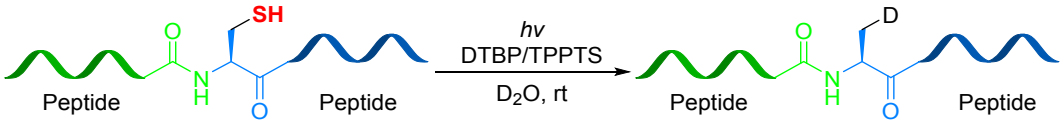
The reaction was carried out according to the general procedure on 0.75 mmol scale. This compound was obtained as a crude product due to its volatility. The yield was 92% based on ^{1}H NMR. D-incorporation ratio was calculated by ^{1}H NMR: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (t, *J*

= 7.0 Hz, 2H), 1.06 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.63, 27.46, 8.84 (t, *J* = 19.8). GC-MS (EI): m/z = 75.04.

4. Desulfurization-deuteration reactions of peptides

General procedure for desulfurization-deuteration of peptides

The reaction was operated in D_2O. The reaction conditions were consistent to the general procedure of desulfurization of cysteinyl peptides. The optimal condition for deuteration of peptides is as follows.

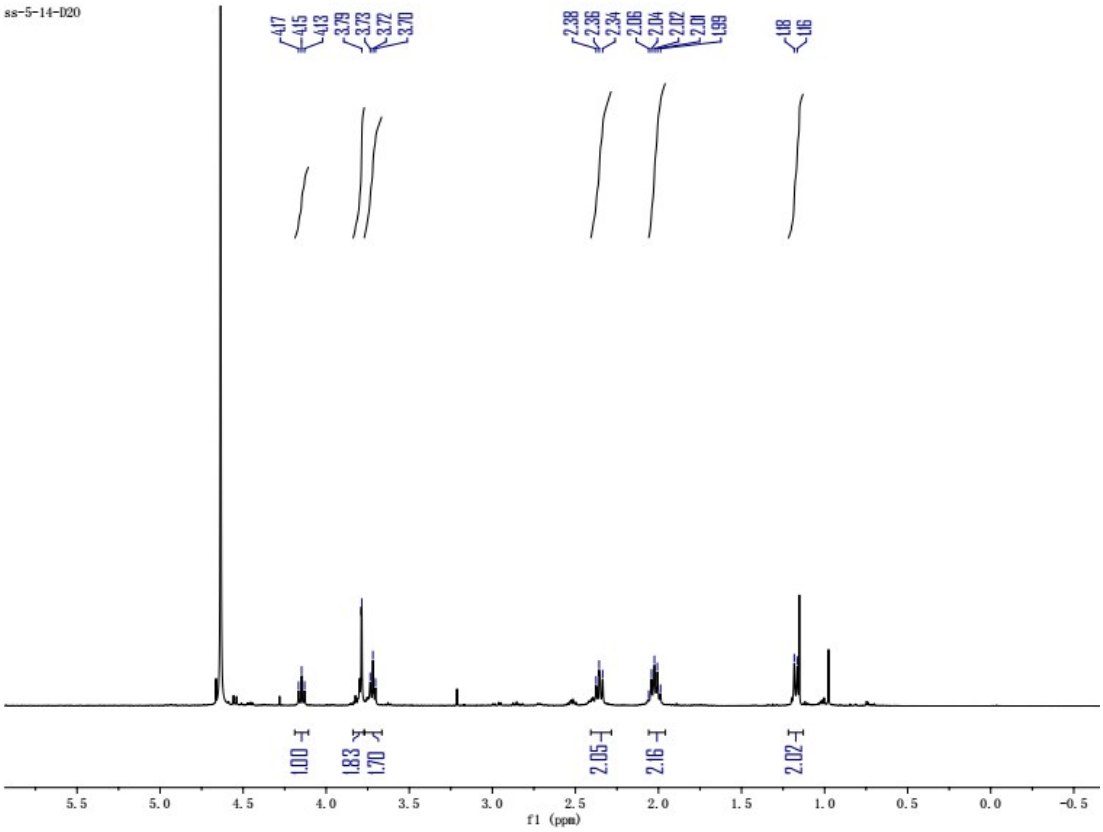


To a solution of cysteinyl peptide (1 mM, 1.0 equiv.) in D_2O (2 ml), TPPTS (34.1 mg, 30mM, 30.0 equiv.), DTBP (8.8 mg, 30mM, 30.0 equiv.) and *t*-BuSH (5.4 mg, 30mM, 30.0 equiv.) were added. The mixture was stirred and irradiated employing two 36 W household CFL bulb at room temperature for 6 hours. When the reaction is complete, it was analyzed by LC-MS.

Peptide **1H** (GSH) to peptide **2H**

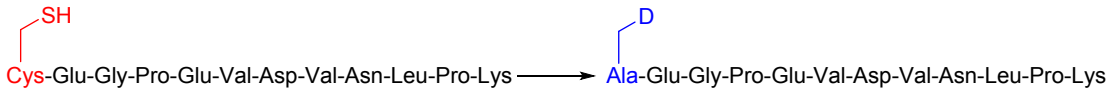
1H **2H**

To a solution of GSH (0.6 mg, 1 mM) in D_2O (2 ml), TPPTS (34.1mg, 30 mM, 30.0 equiv.) and DTBP (8.8 mg, 30mM, 30.0 equiv.) were added. The resulting clear solution was stirred and irradiated with two 36 W household CFL bulb at room temperature for 10 hours. When the reaction is complete, **2H** was characterized by ^{1}H NMR and ESI-MS spectrometry. ^{1}H NMR (400 MHz, D_2O) δ 4.15 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 2H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 7.2, 2H), 2.02 (dt, *J* = 7.2, 6.3 Hz, 2H), 1.17 (d, *J* = 7.2 Hz, 2H).ESI-MS calcd for **2H** $C_{10}H_{16}DN_3O_6$ [M+Na]+m/z = 299.1072, found:299.1023. Conversion (>95%) and D-incoporation (98%) were based on ^{1}H NMR and mass spectrometry respectively.



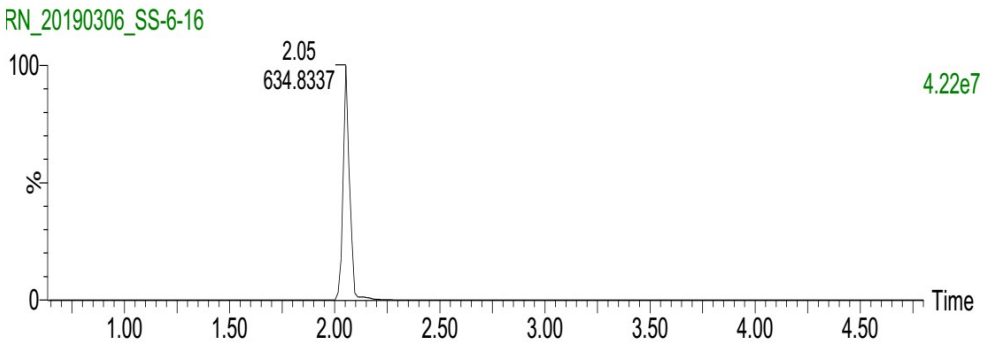
Supplementary Figure S3. ^{1}H NMR spectrum of desulfurization product of **2H.**

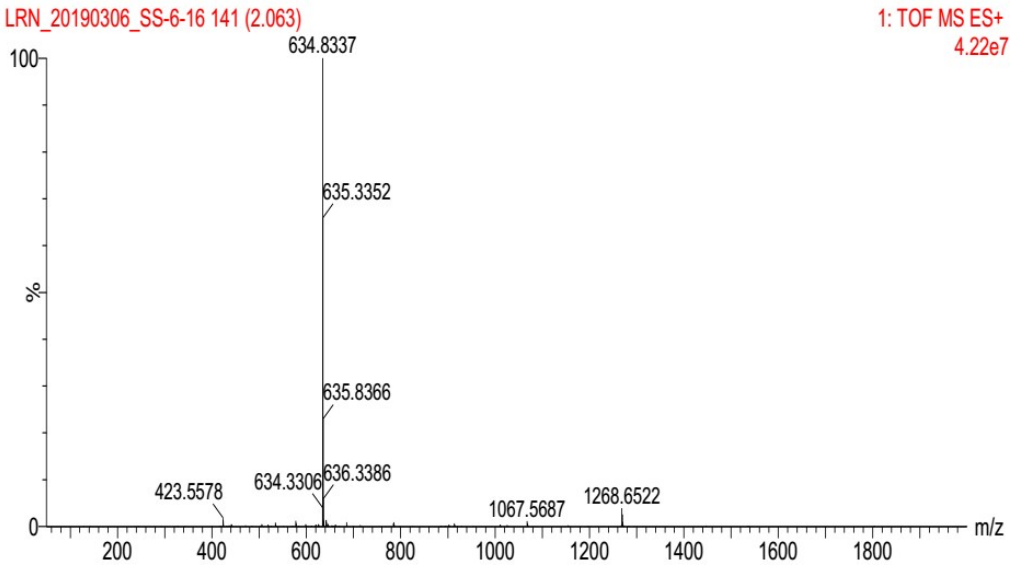
Peptide **1I** to peptide **2I**



3d **6d**

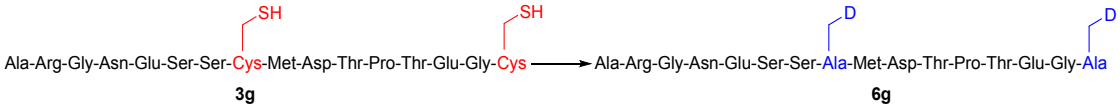
2.6 mg of peptide **2I** was subjected to the standard desulfurization conditions as illustrated in the general procedure. The reaction was monitored by LC-MS. The conversion of the desulfurized product was analyzed by LC-MS. D-incorporation ratio was assessed by mass spectrometry: 99%. The desulfurized product was characterized by mass spectrometry.



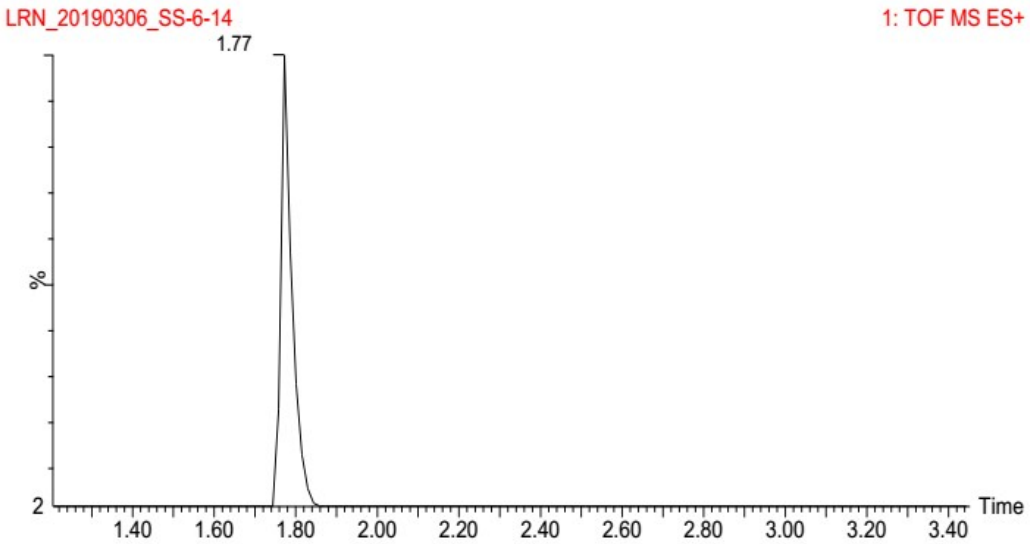


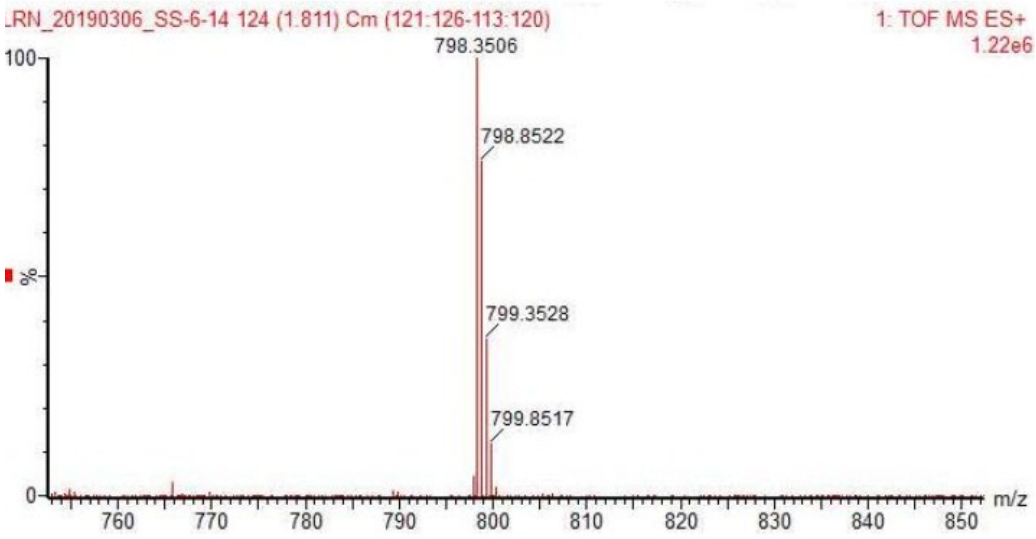
Supplementary Figure S4. Corresponding LC-MS analysis of peptide **2I** (10—65% solvent A in solvent B over 15 min at a flow rate of 0.6 mL/min). ESI-MS calcd for $C_{55}H_{89}DN_{14}O_{20}$ $[M+H]^{+}m/z$ = 1268.6591, $[M+2H]^{2+}m/z$ = 634.8332, found: 1268.6522, 634.8337.

Peptide **1J** to peptide **2J**



3.3 mg of peptide **2J** was subjected to the standard desulfurization conditions as illustrated in the general procedure. The reaction was monitored by LC-MS. The conversion of the desulfurized product was analyzed by LC-MS. D-incorporation ratio was assessed by mass spectrometry: 97%. The desulfurized product was characterized by mass spectrometry.

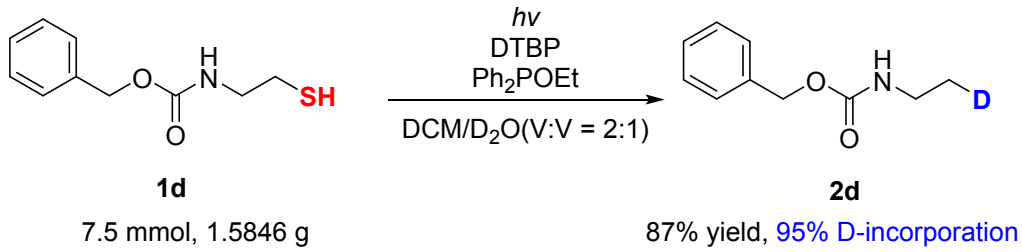




Supplementary Figure S5. Corresponding LC-MS analysis of peptide **2J** (10—65% solvent A in solvent B over 15 min at a flow rate of 0.6 mL/min). ESI-MS calcd for $C_{61}H_{98}D_2N_{20}O_{28}S$ $[M+2H]^{2+}$m/z = 798.3504, found: 798.3506.

5. Scale-up reaction

In order to test the applicability of this novel desulfurization method, gram scale reactions were carried out based on substrate **1d.** It was found that the reaction proceeded smoothly and the corresponding products were obtained with 87% yield and 95% D-incorporation.



1d

7.5 mmol, 1.5846 g

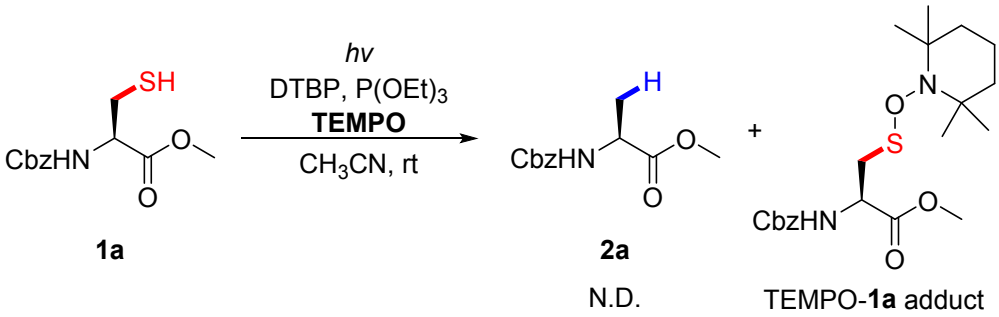
2d

87% yield, 95% D-incorporation

Supplementary Figure S6. Reactions executed on large scale.

6. Mechanistic studies

To elucidate the reaction mechanism, the radical-inhibitor experiments was performed by addition of 2 equivalent radical-trapping reagent 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) to the reaction of **1a**. Eventually, the reaction was completely inhibited. TEMPO-**1a** adduct was observed in the LC-MS while there was no **2a**, thus suggesting a radical process.



Supplementary Figure S7. Radical trapping experiment.

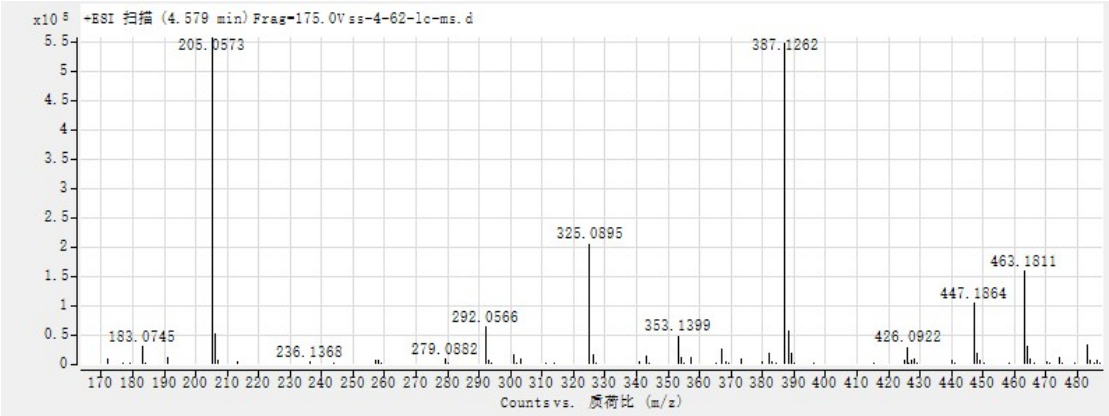
The radical trapping experiment was conducted as follows.

To a 25 ml round-bottom flask equipped with a stir bar were added **1a** (0.75 mmol, 1.0 equiv.) and $P(OEt)_3$ (1.5 mmol, 2.0 equiv.). Solvent CH_3CN was added (6 ml) followed by the addition of DTBP (1.2 equiv.). TEMPO (2.0 eq) was introduced into the solution. The flask was capped and the reaction was stirred and irradiated using two 36 W household CFL bulb (6 cm away, to keep the reaction at room temperature) at room temperature for 6 hours. After 6 hours, the reaction was monitor by LC-MS. Substrate **1a** and TEMPO-**1a**-adduct can be detected in mass spectrometry. However, the product **2a** was not detected.

TEMPO-**1a**-adduct: ESI-MS calcd for $C_{21}H_{32}N_2O_5S$ $[M+Na]^+$m/z = 447.1924, $[M+K]^+$m/z =463.1664, found: 447.1864, 463.1811.

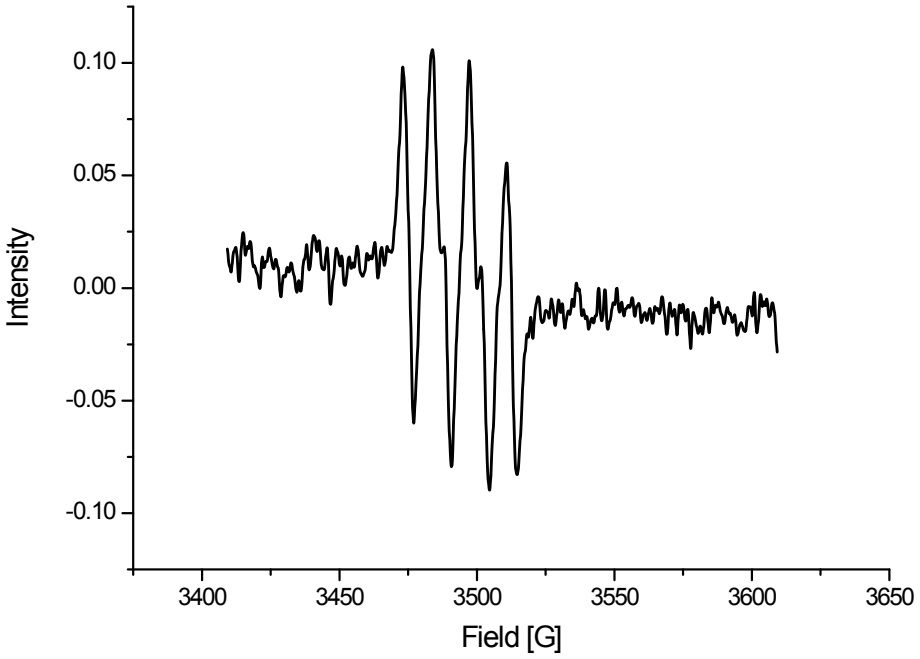
1a: ESI-MS calcd for $C_{12}H_{15}NO_4S$ $[M+Na]^+$m/z = 292.0614, found: 292.0566.

$PO(OEt)_3$: ESI-MS calcd for $C_6H_{15}O_4P$ $[M + Na]^+$m/z = 205.0600, $[2M + Na]^+$m/z = 387.1308, found: 205.0573, 387.1262.



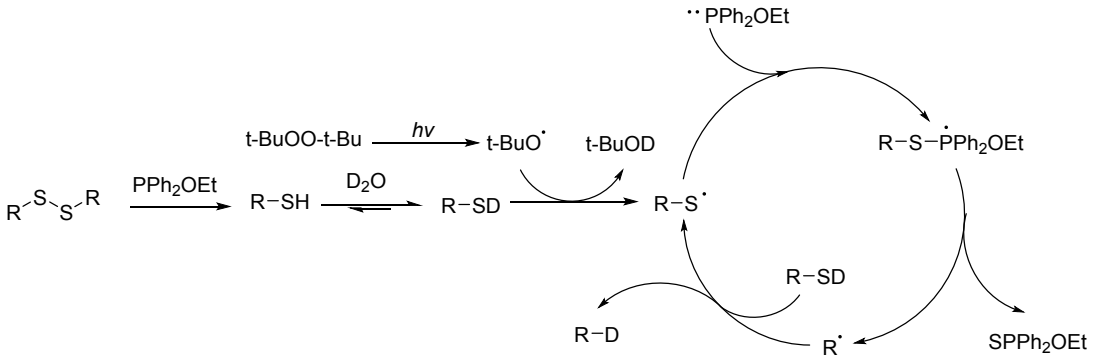
Supplementary Figure S8. The ESI-MS spectra of radical trapping experiment.

In order to further confirm the proposed mechanism, EPR experiment of the reaction system was performed using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as an EPR spin trap. The experiment revealed that DMPO-radical adduct was produced during the initial reaction time at room temperature. The EPR spectra is shown in **Fig. S9**.

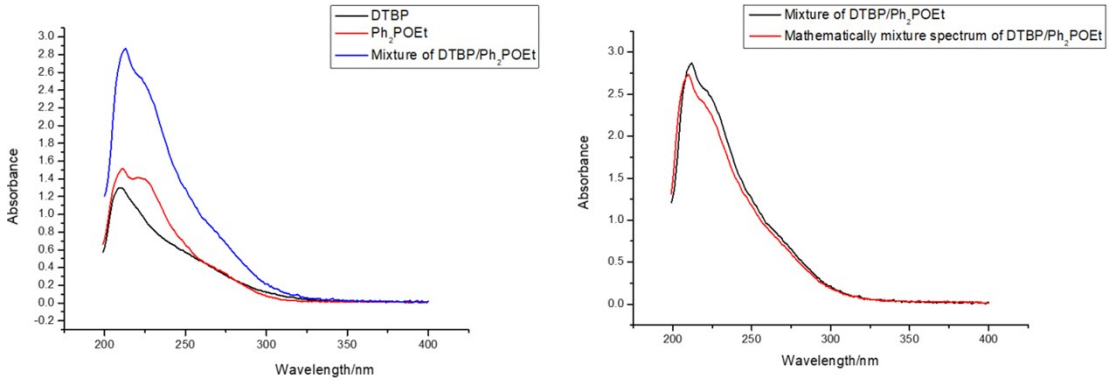


Supplementary Figure S9. EPR spectra of the reaction system. Reaction condition: *c* (**1a**) = 0.1 mol/L, *c* (phosphoric reagent) = 0.15 mol/L, *c* (DTBP) = 0.15 mol/L, *c* (DMPO) = 0.3 mol/L, room temprerature, 10 min after the reaction started.

Based on the above results, a plausible radical mechanism was proposed in **Fig. S10**.



Supplementary Figure S10 | Plausible reaction mechanism of the desulfurization-deuteration reaction



Supplementary Figure S11. UV-Vis Titration Analysis of DTBP, Ph_2POEt, and the mixture of Ph_2POEt and DTBP. The experiments were executed on SHIMADZU UV—2450 spectrophotometer. Concentration of Ph_2POEt and DTBP were 0.1 mmol/L and 0.1 mol/L.

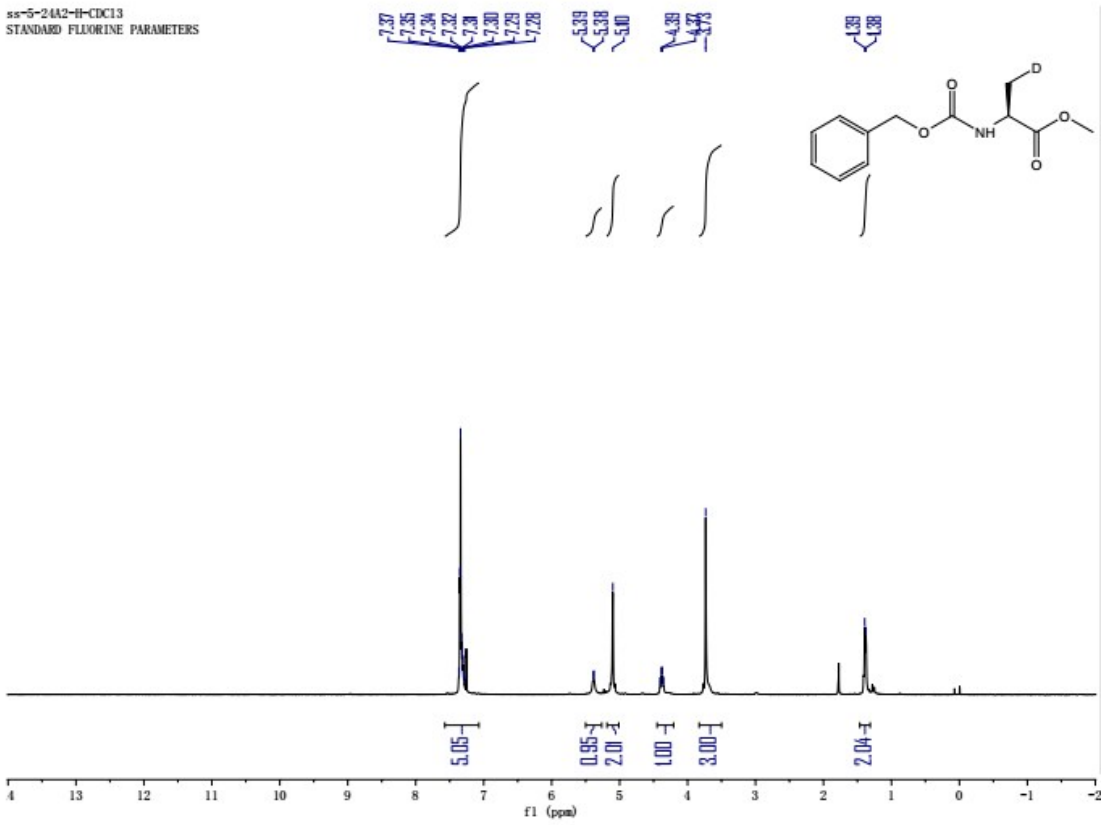
The measured spectrum of the 1:1 mixture of DTBP and Ph_2POEt shifted a little to the visible light region compared with the spectrum add-up of DTBP and Ph_2POEt. Therefore, Ph_2POEt might interact with DTBP and help cleave the O-O bond in the peroxide under visible light irradiation.

7. References

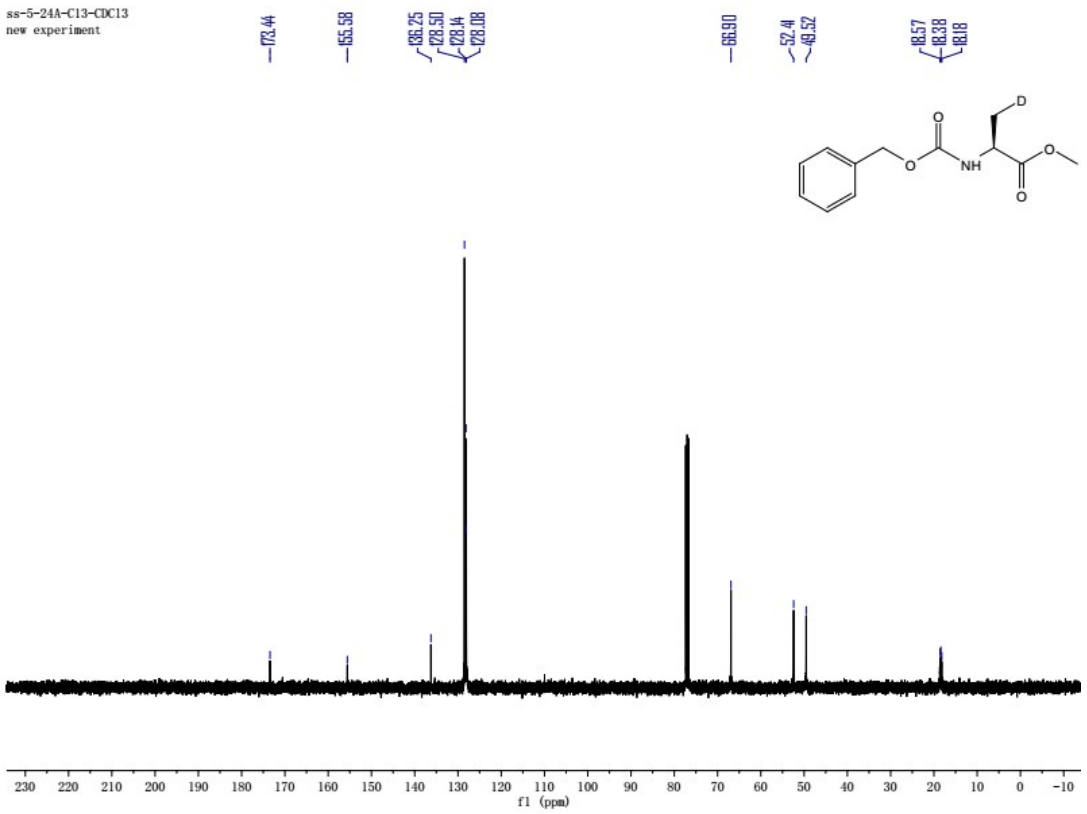
1. Still, W.C., Kahn, M., and Mitra, A. (1978). Rapid chromatographic technique for preparative separations with moderate resolution. The Journal of Organic Chemistry *43*, 2923-2925.

8. Spectral data

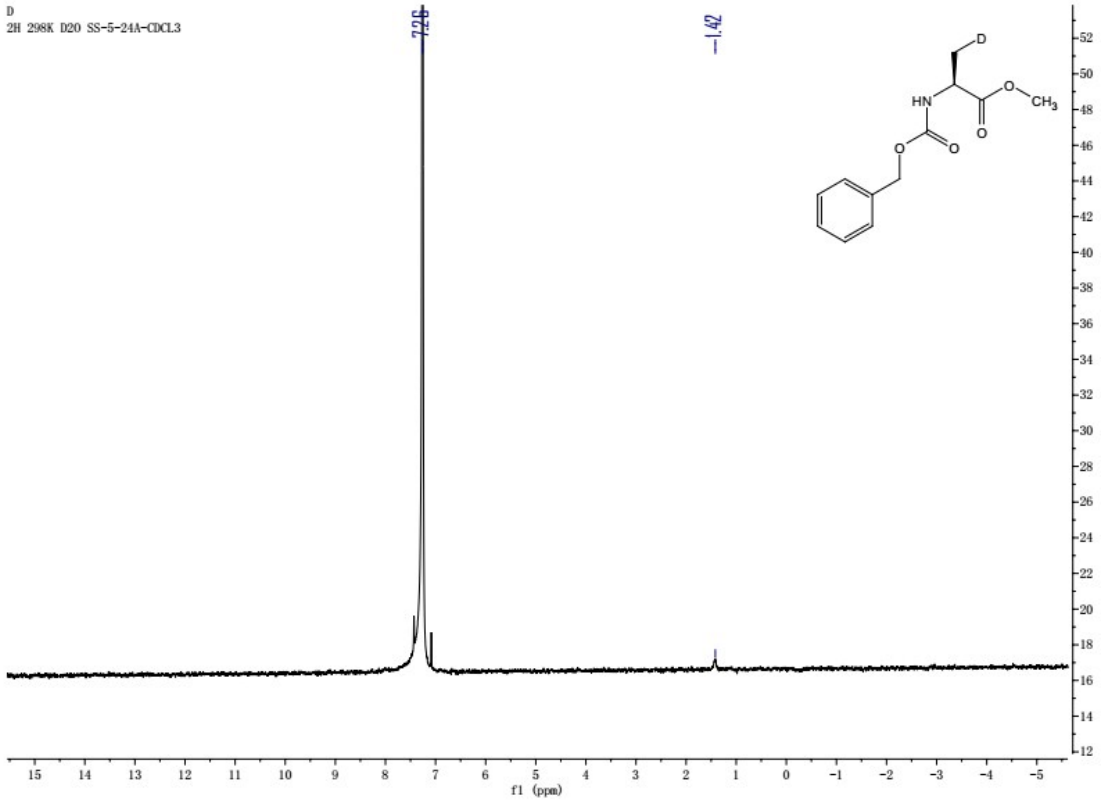
^{1}H NMR of **2a** in $CDCl_3$



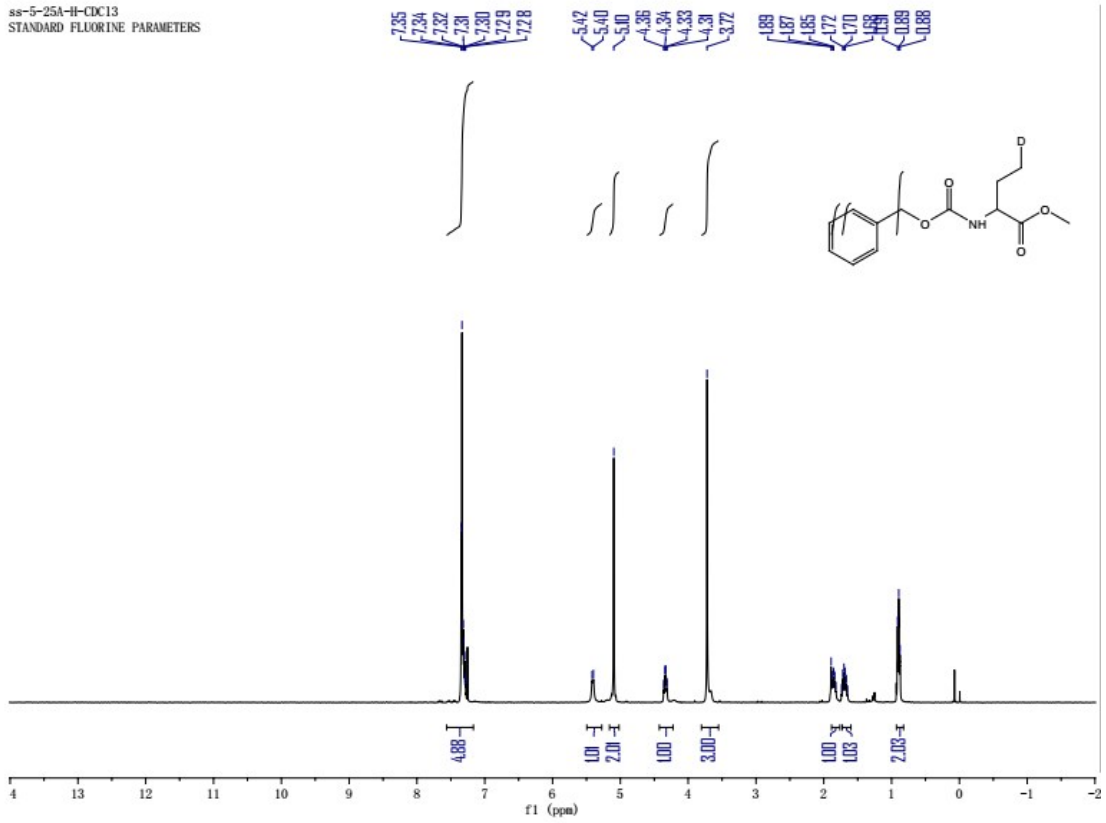
^{13}C NMR of **2a** in $CDCl_3$



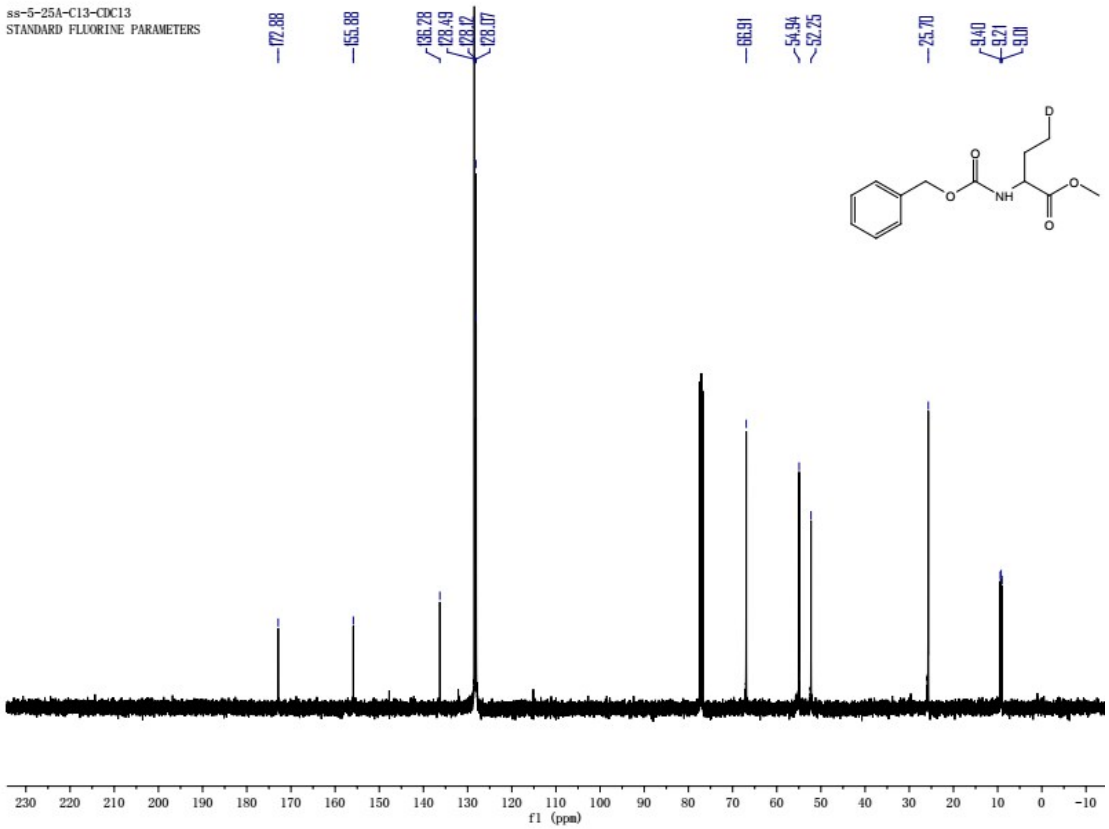
^{2}H NMR of **2a** in $CDCl_3$



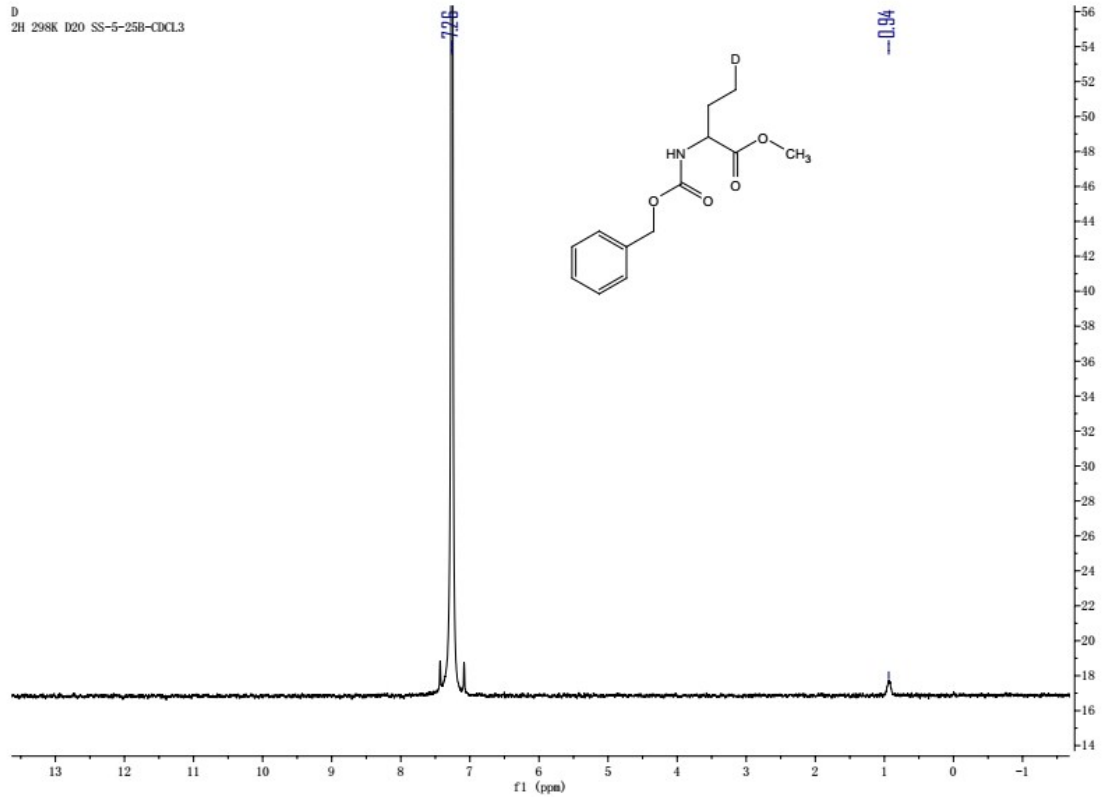
^{1}H NMR of **2b** in $CDCl_3$



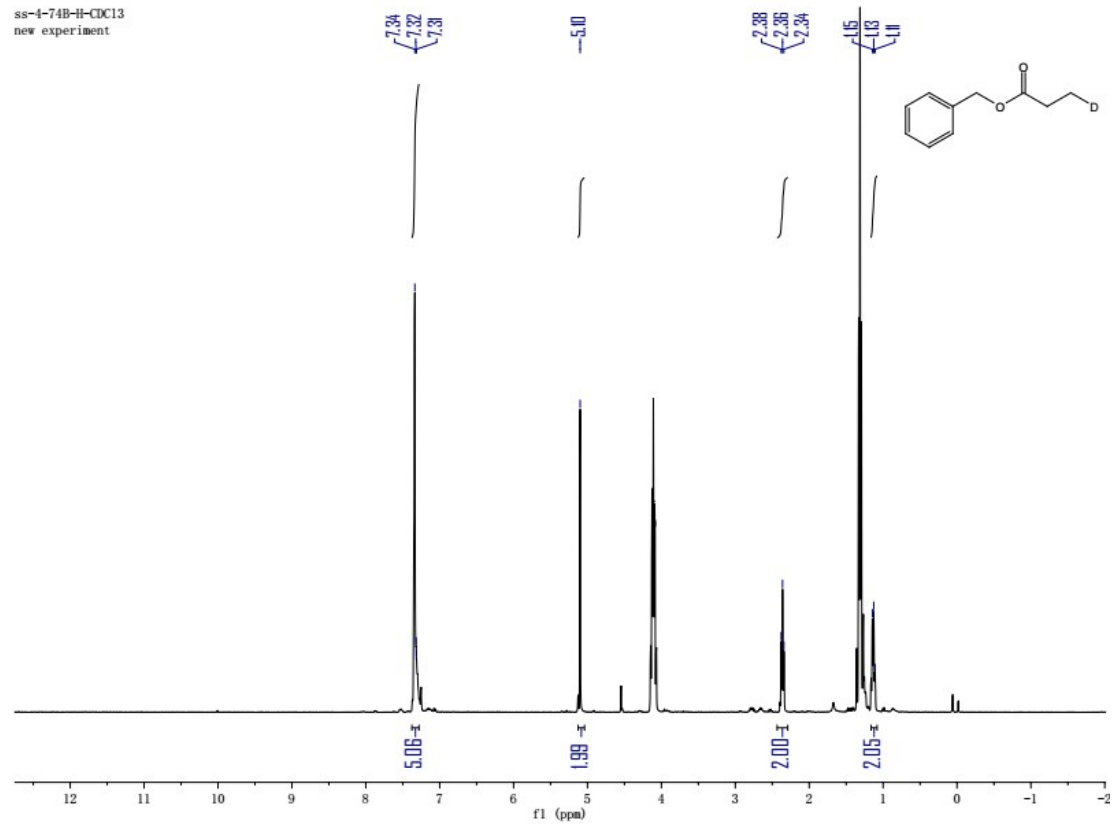
^{13}C NMR of **2b** in $CDCl_3$



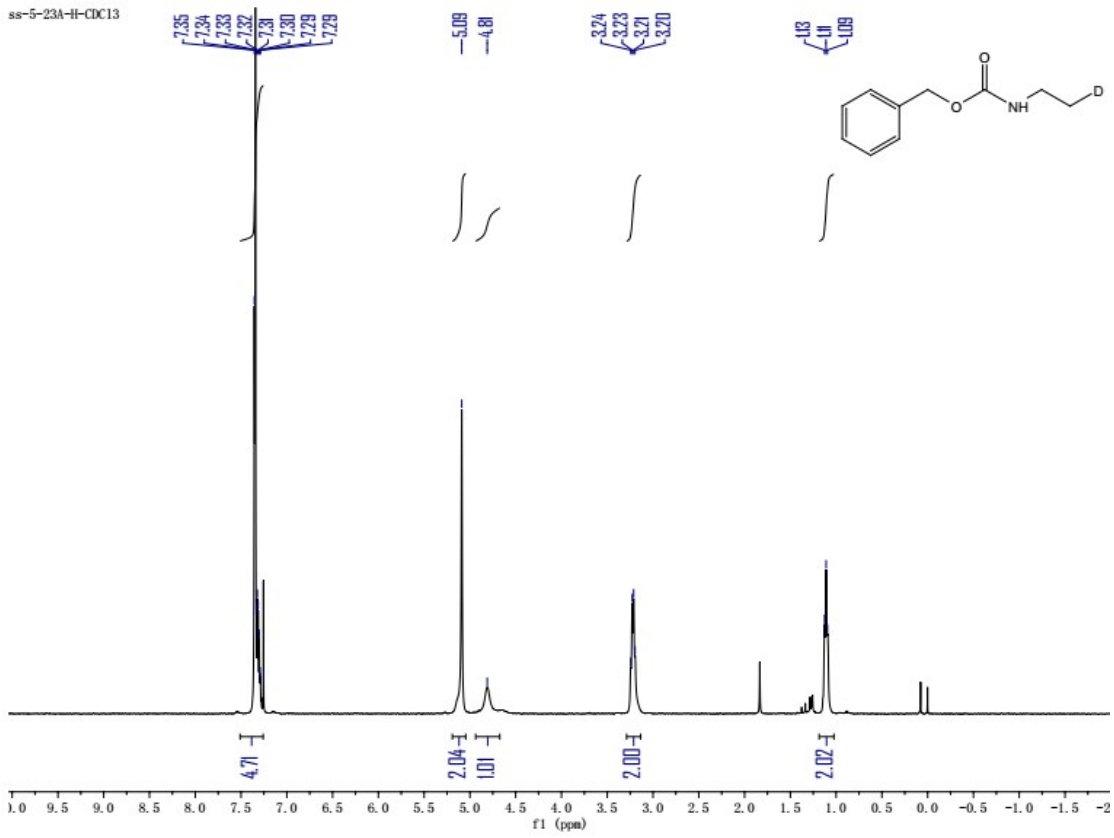
^{2}H NMR of **2b** in $CDCl_3$



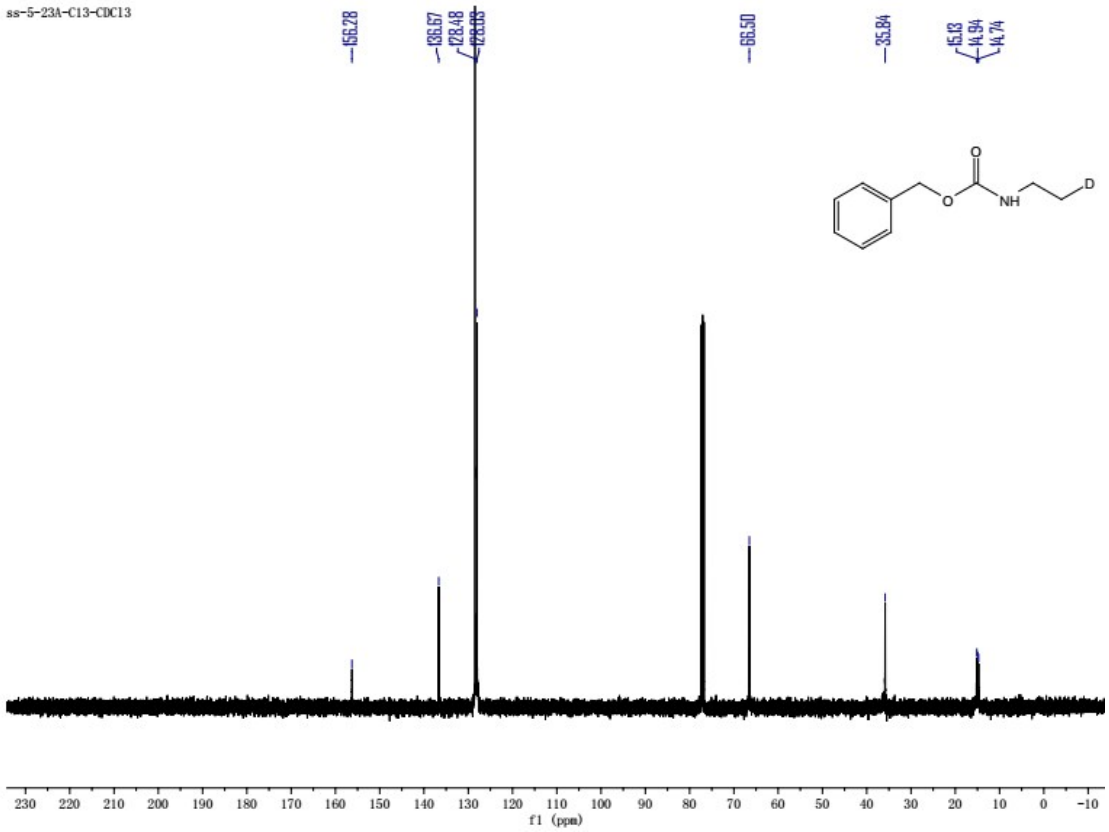
The crude ^{1}H NMR of **2c** in $CDCl_3$



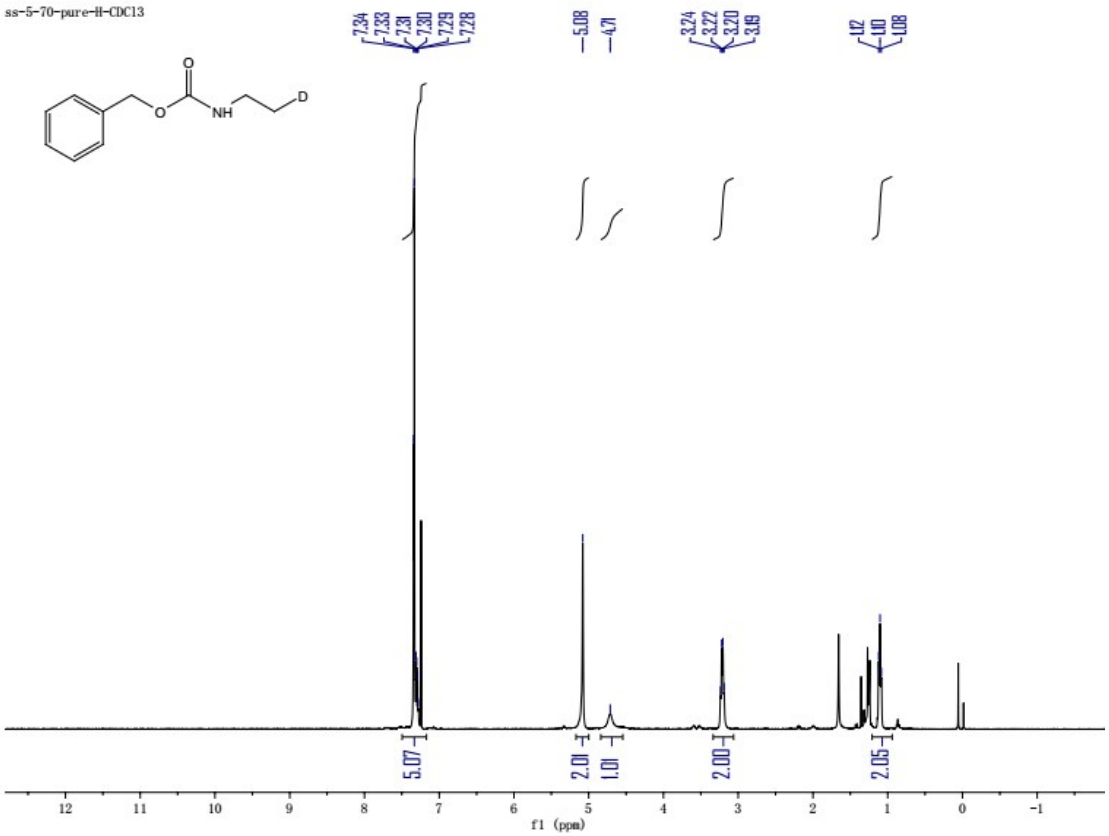
^{1}H NMR of **2d** in $CDCl_3$



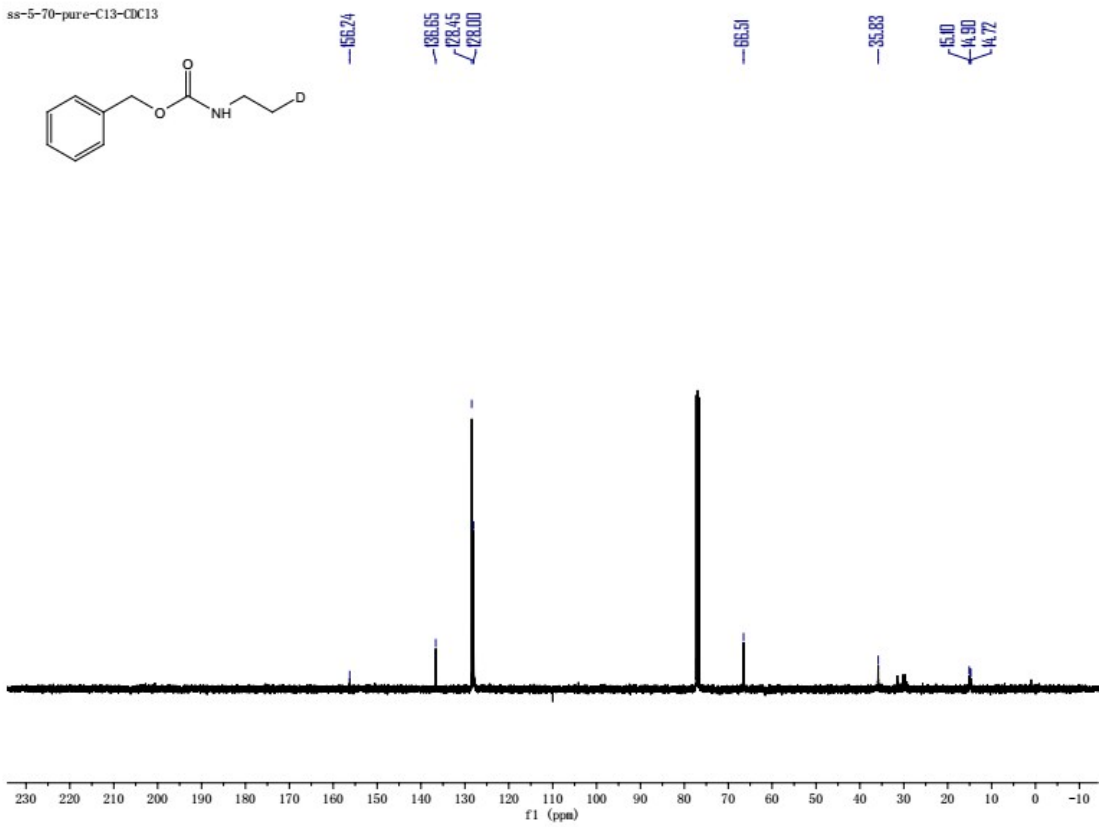
^{13}C NMR of **2d** in $CDCl_3$



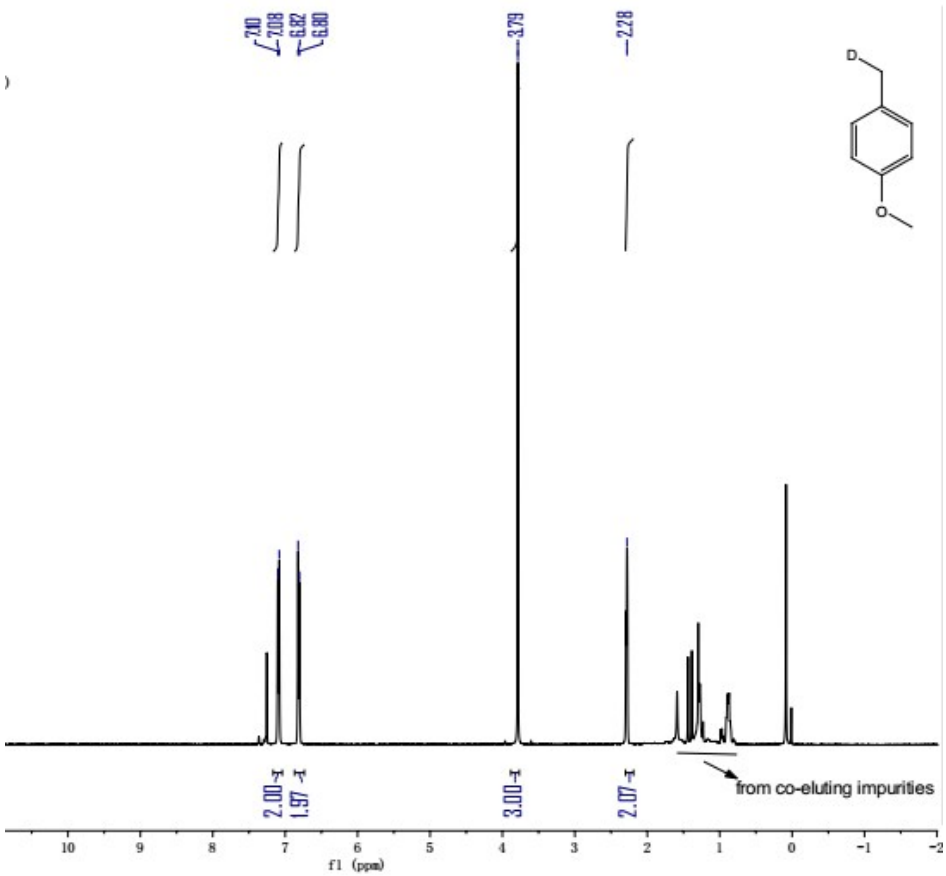
^{1}H NMR of **2d** in $CDCl_3$ (scale-up reaction)



^{13}C NMR of **2d** in $CDCl_3$ (scale-up reaction)



^{1}H NMR of **2e** in $CDCl_3$



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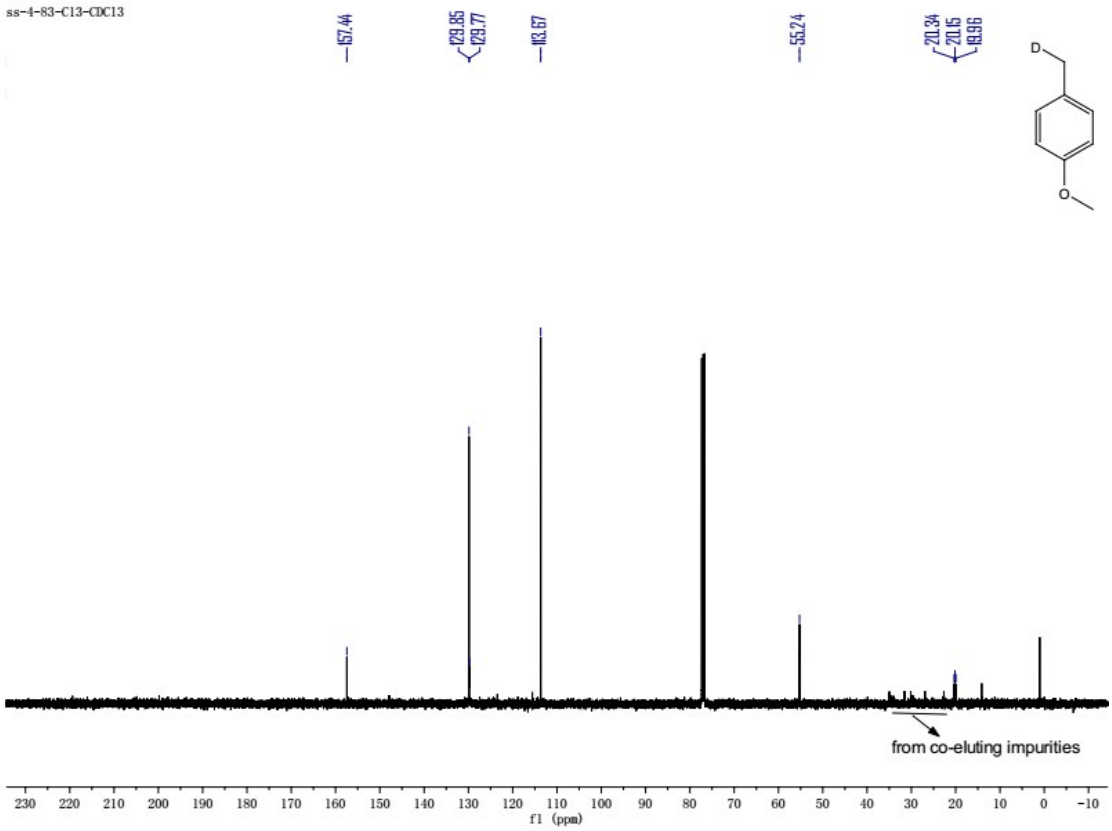
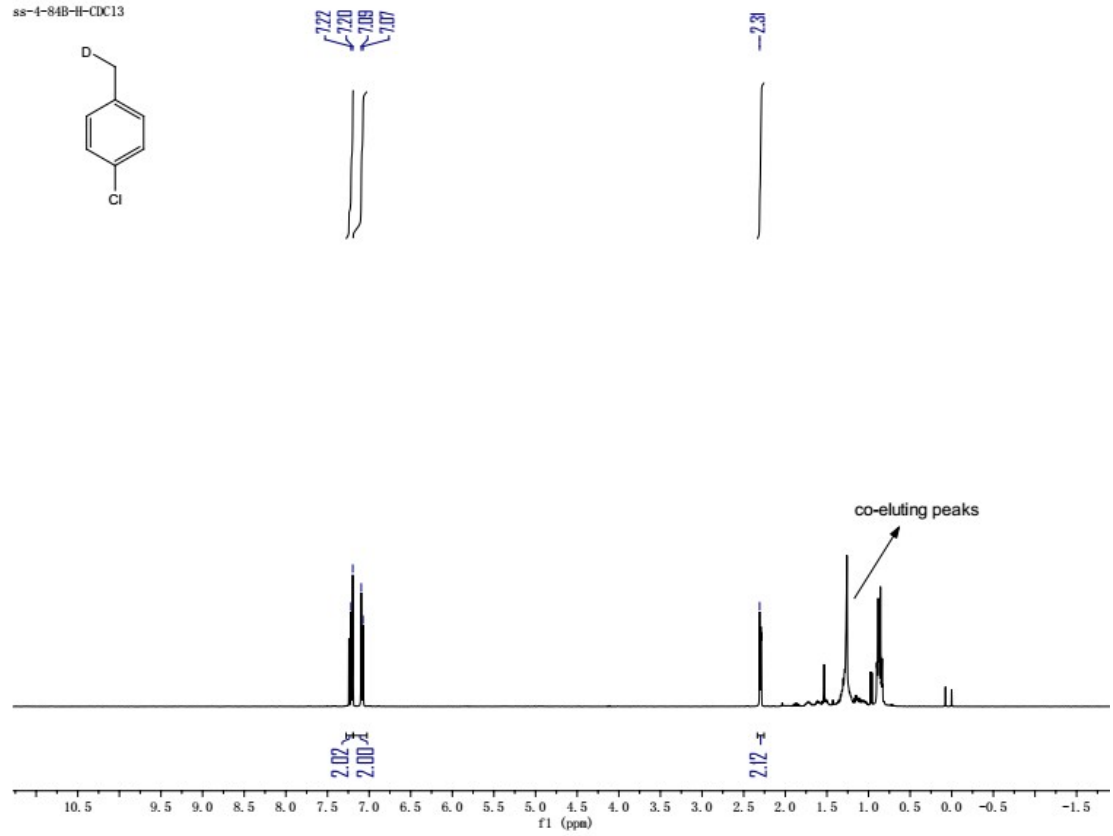


^{1}H NMR of **2f** in $CDCl_3$



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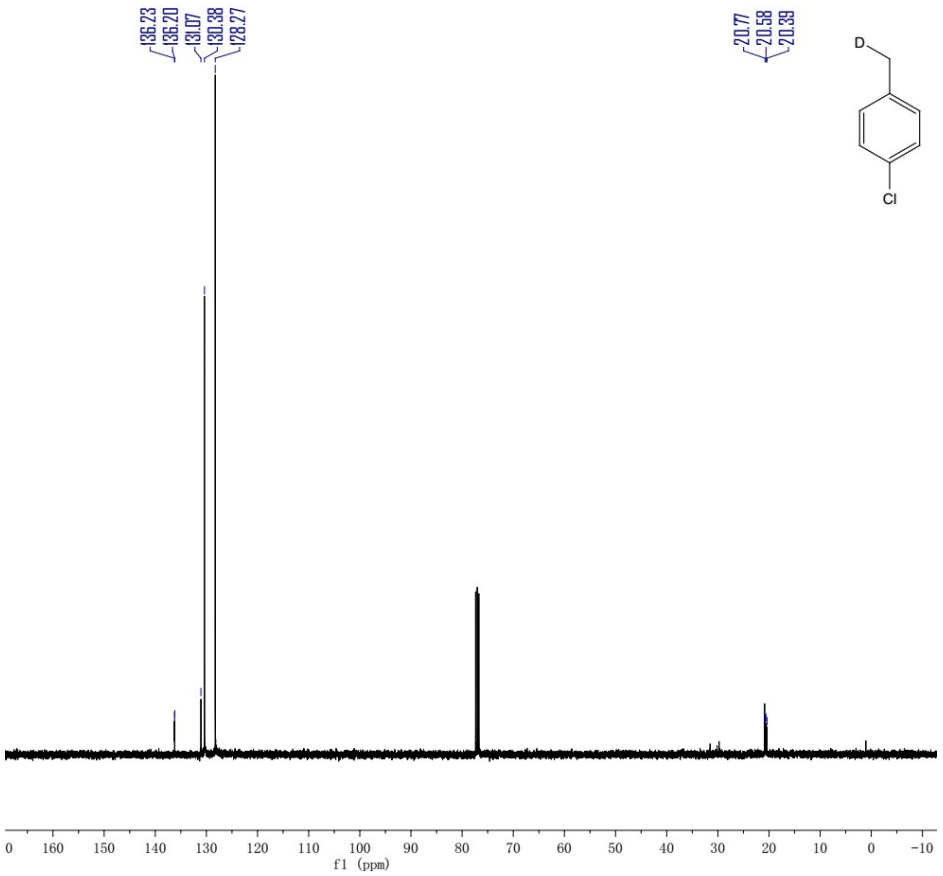
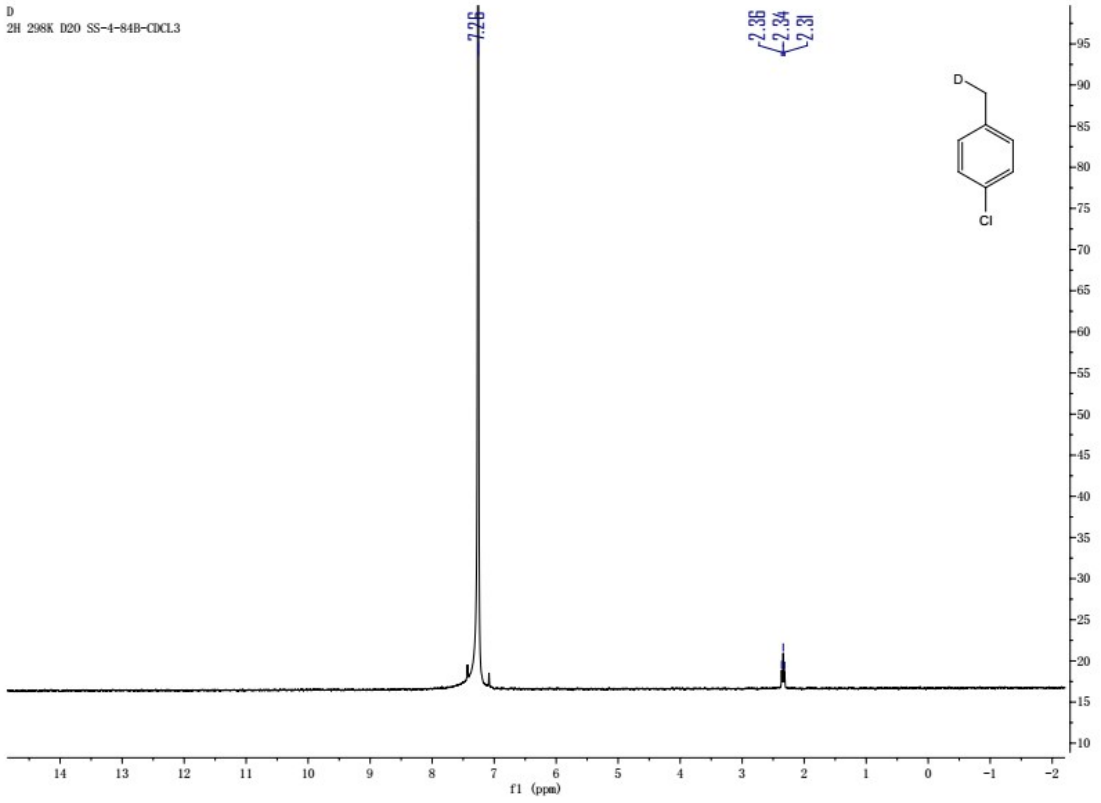
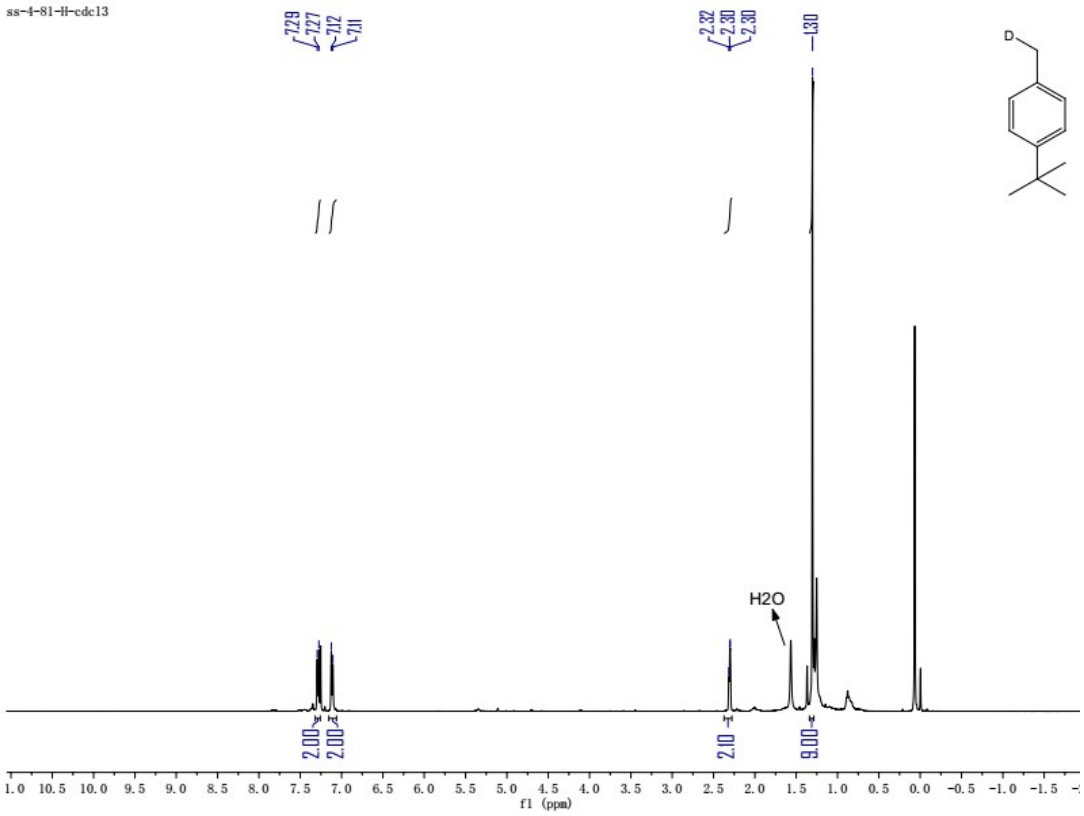


^{2}H NMR of **2f** in $CDCl_3$



^{1}H NMR of **2g** in $CDCl_3$



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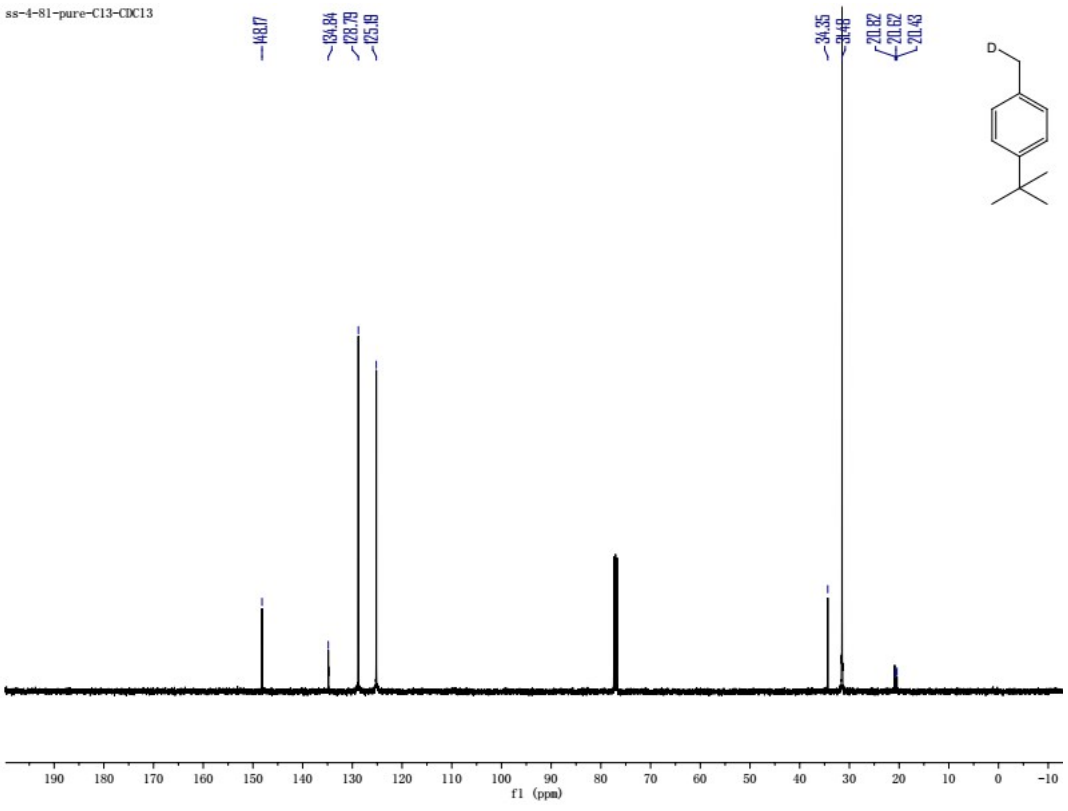
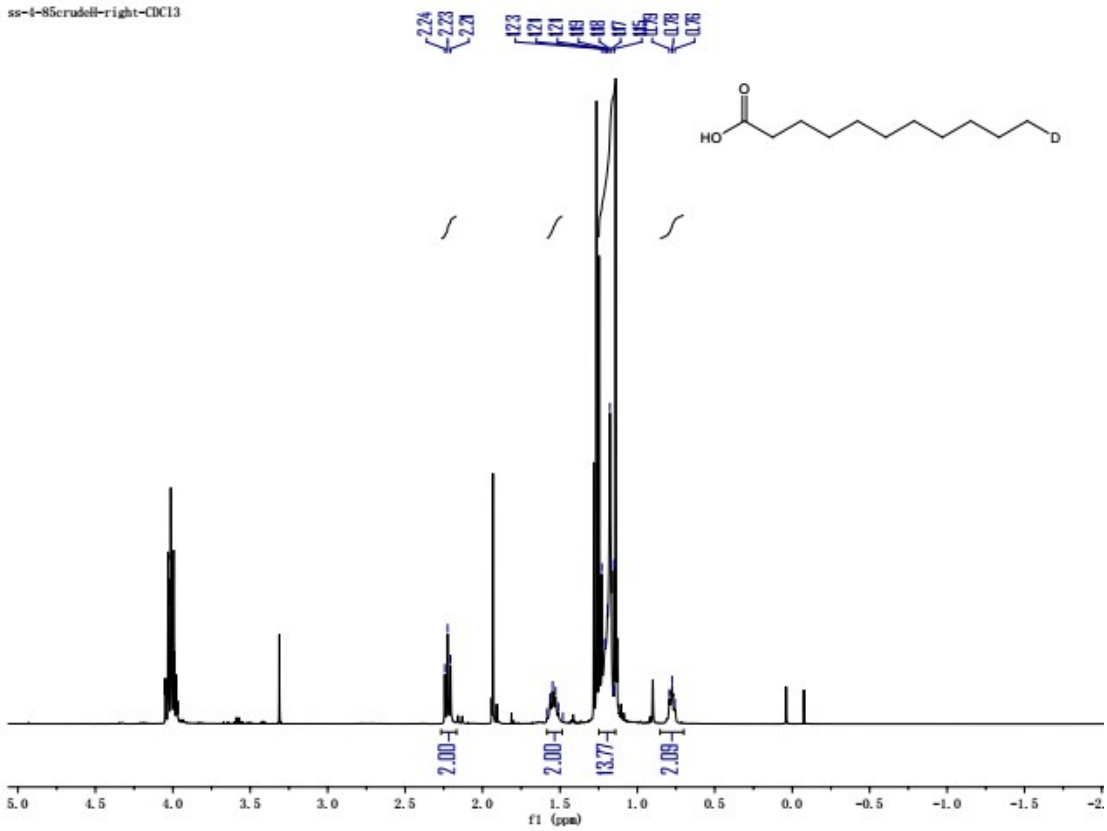
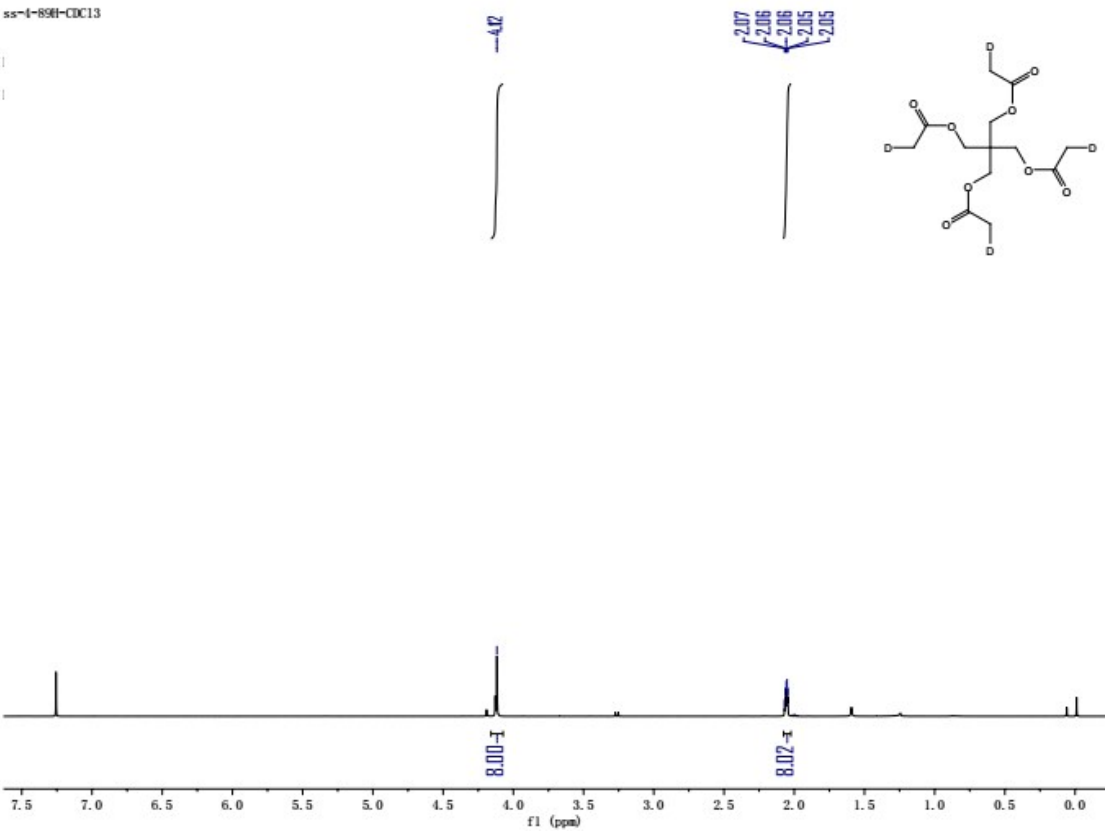


The crude ^{1}H NMR of **2h** in $CDCl_3$



^{1}H NMR of **2i** in $CDCl_3$



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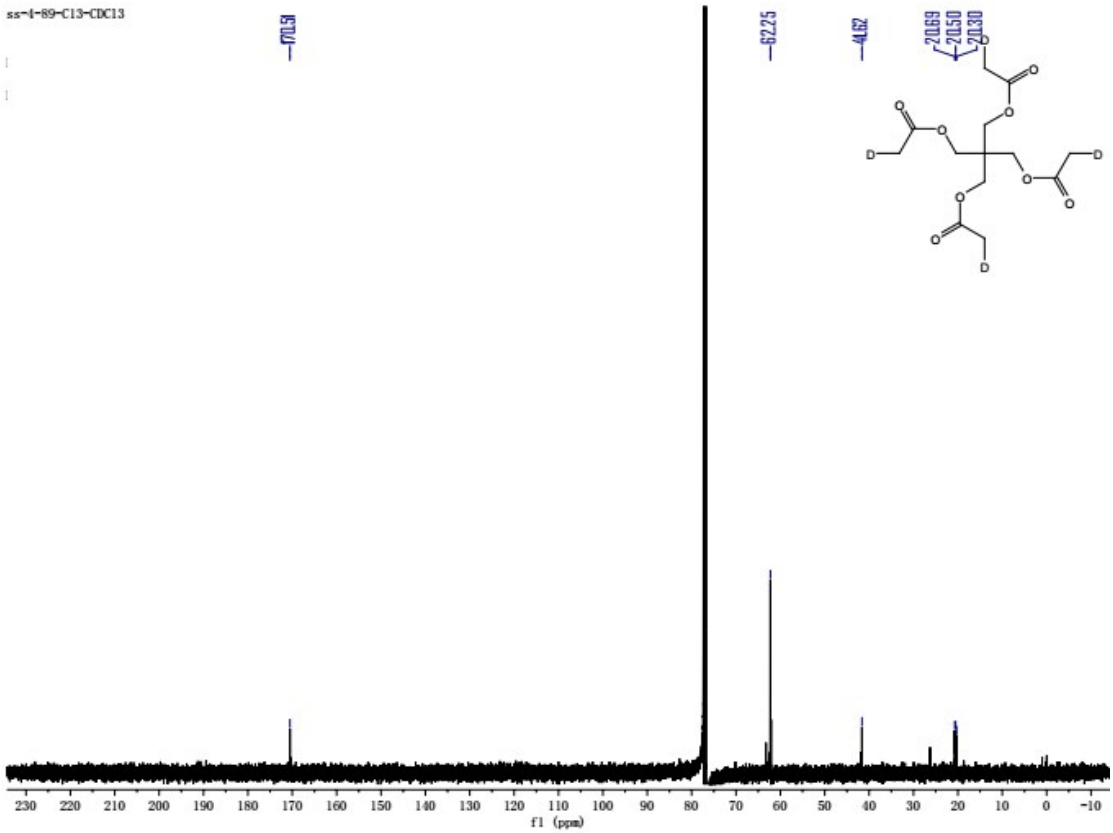

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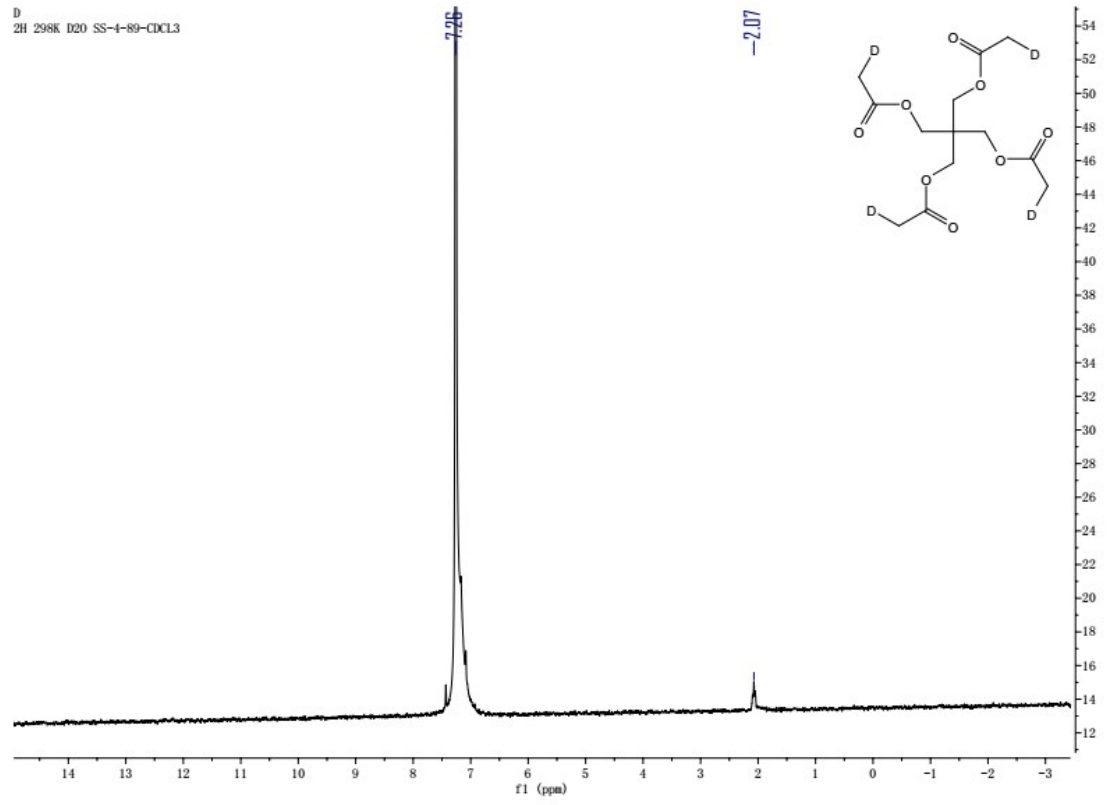

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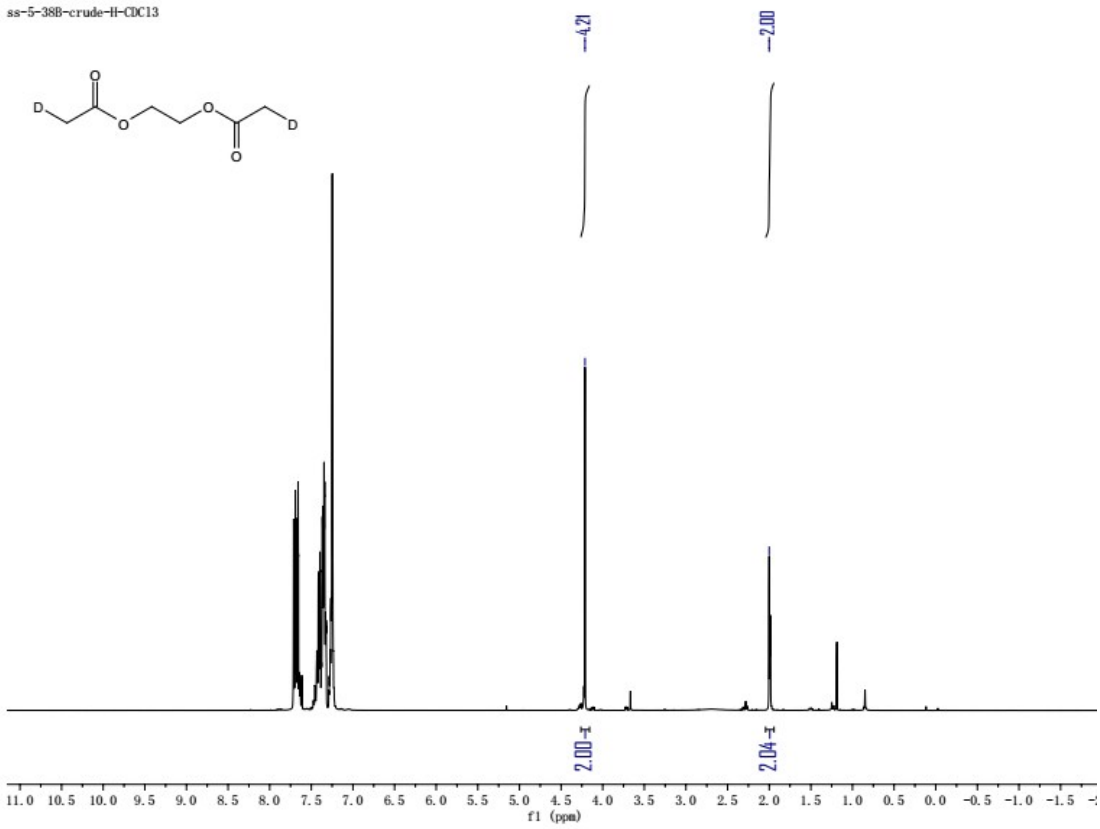

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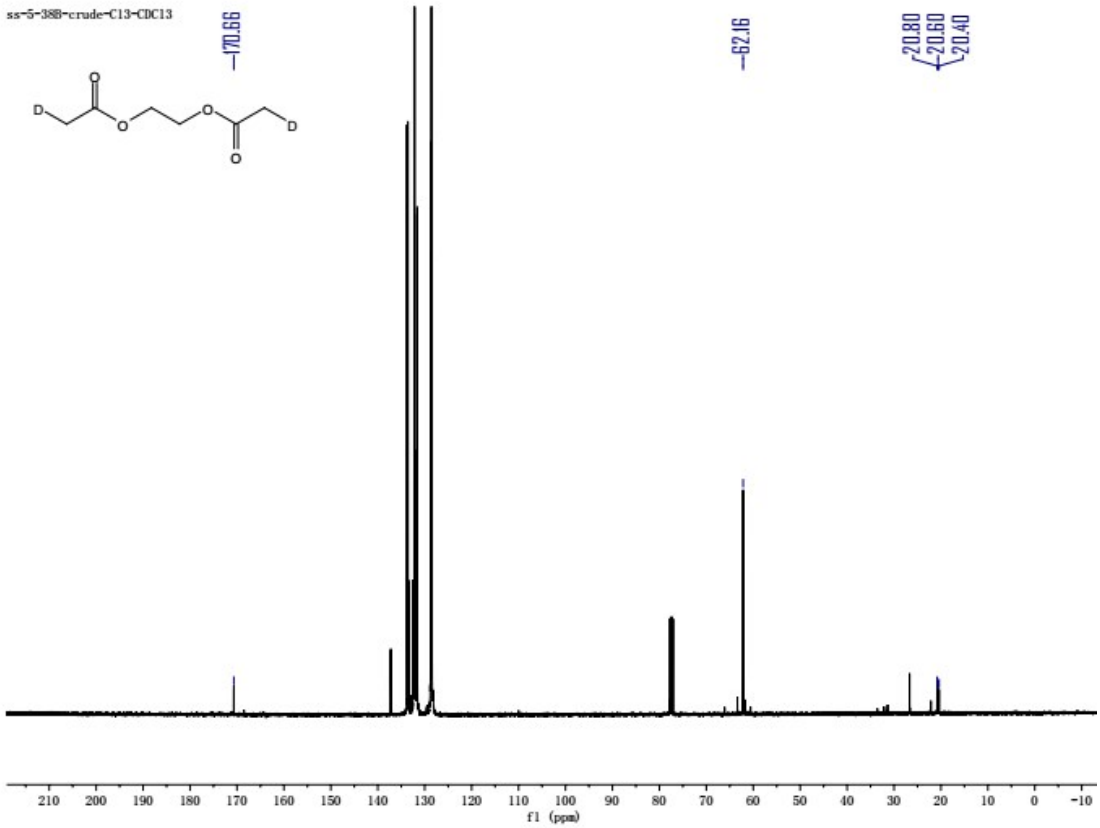

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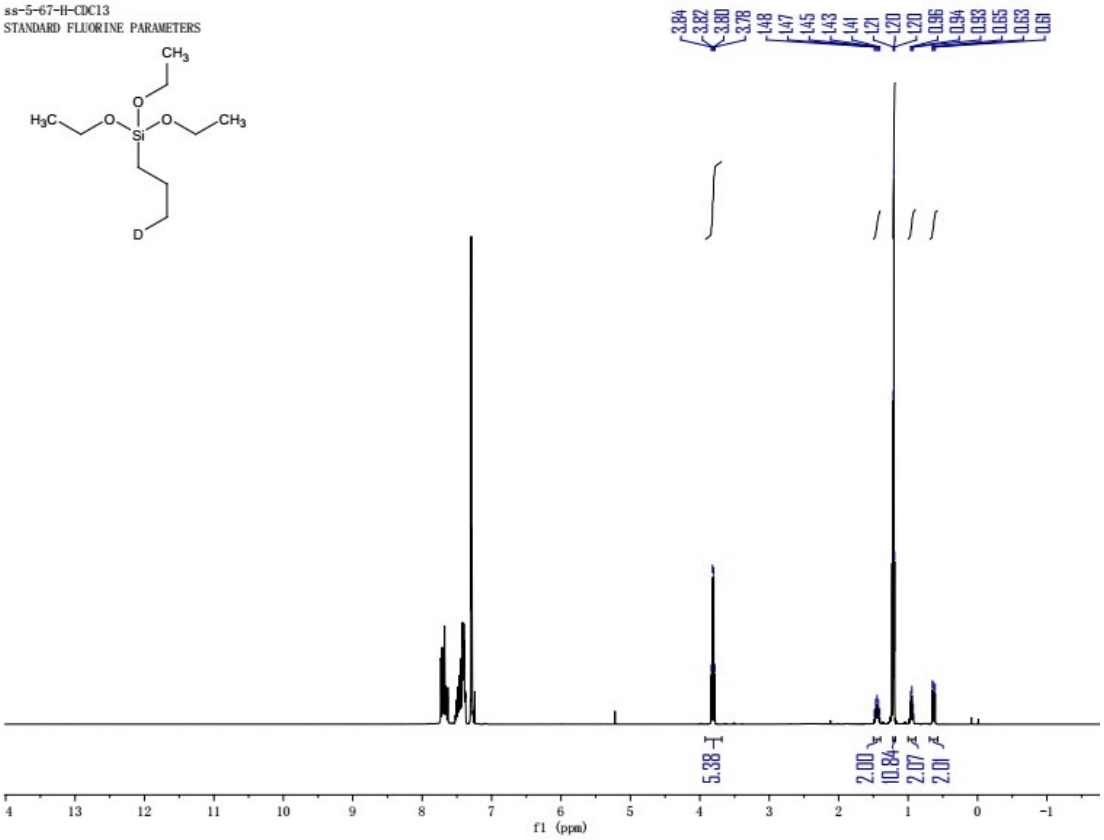
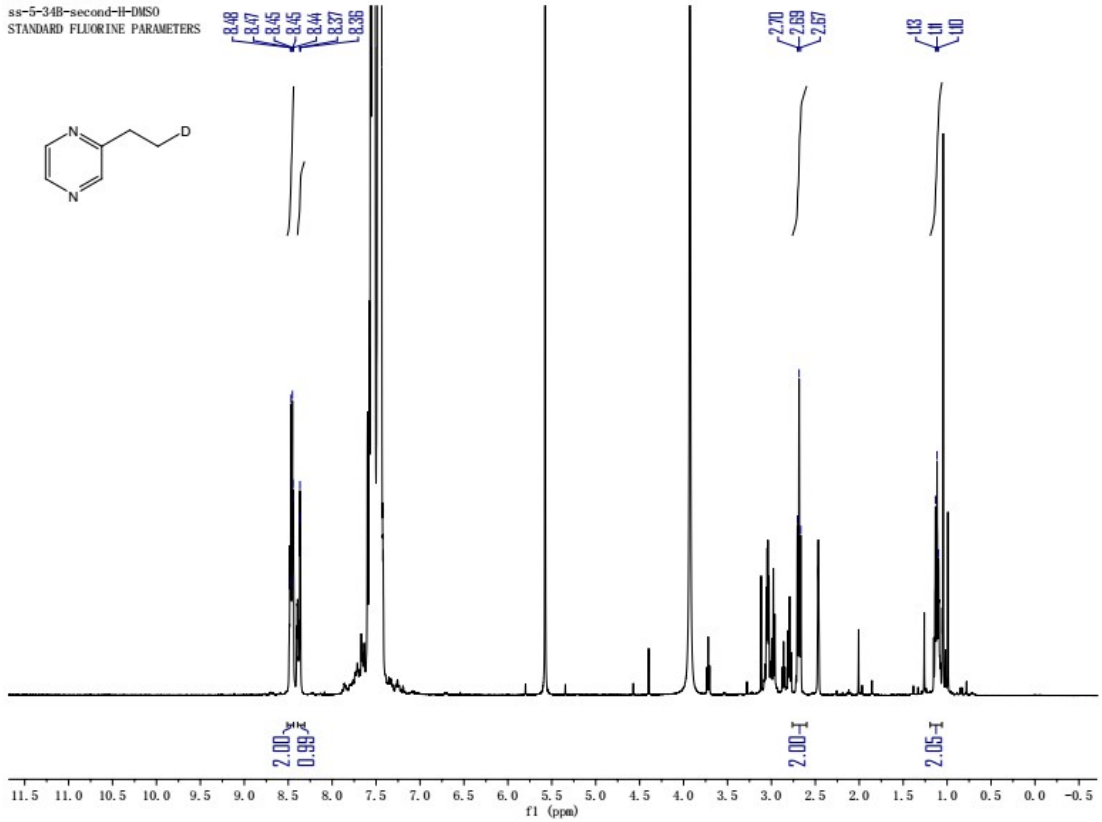
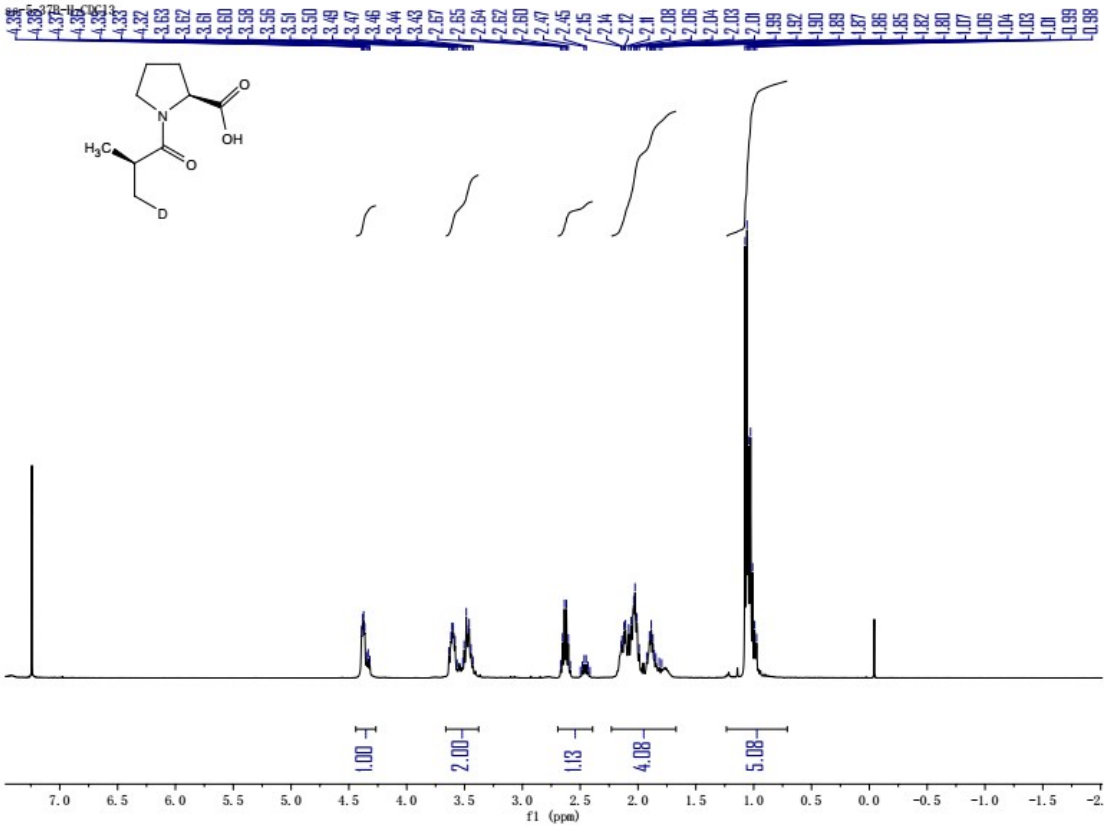


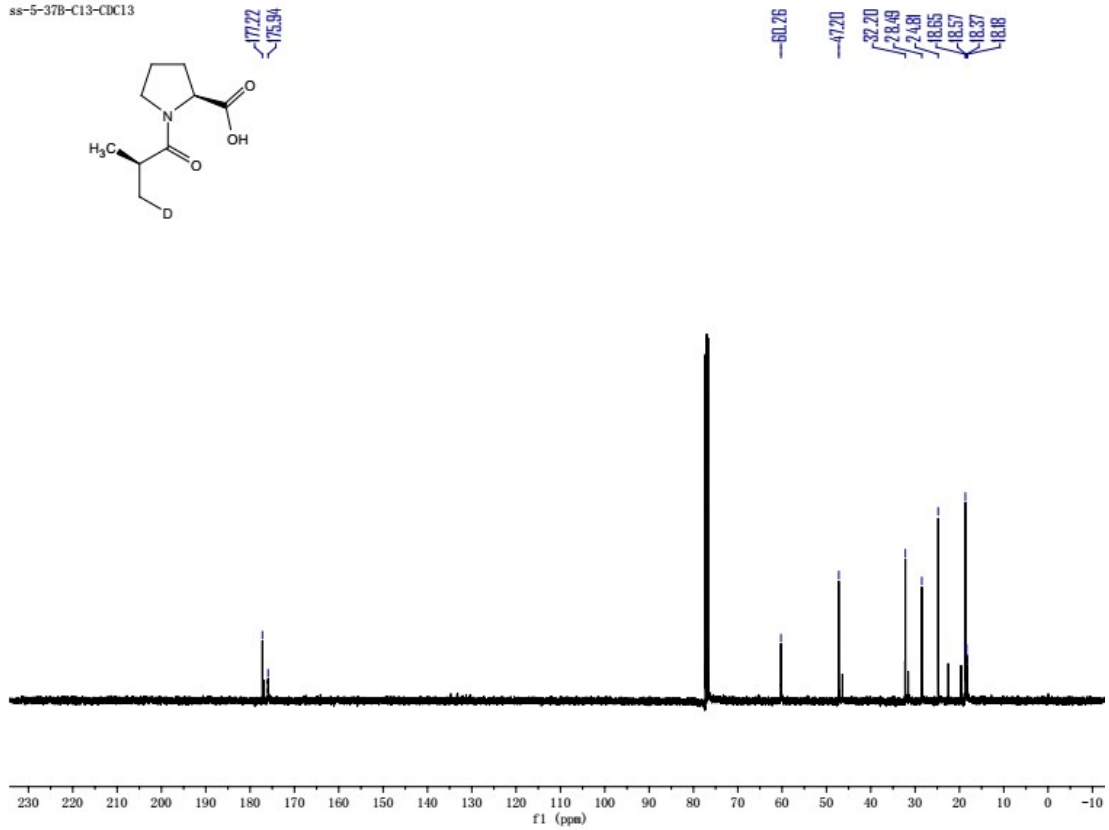
The crude ^{1}H NMR of **2l** in $CDCl_3$



^{1}H NMR of **2m** in $CDCl_3$



^{13}C NMR of **2m** in $CDCl_3$



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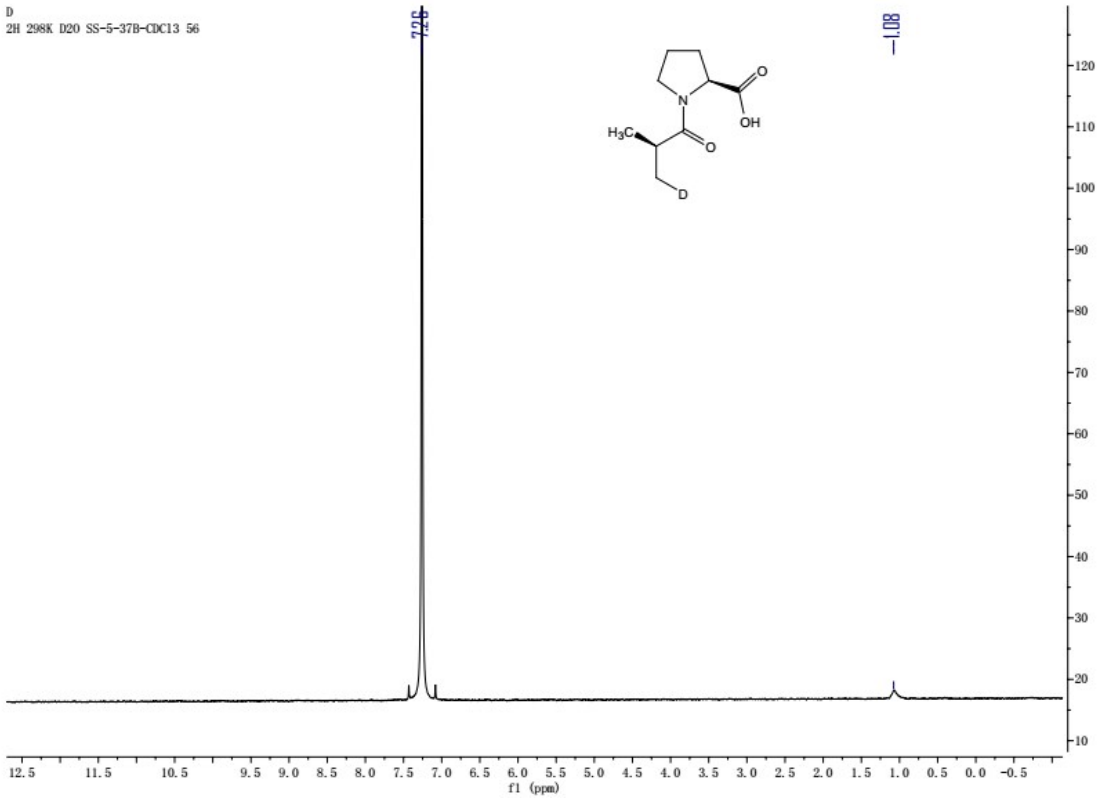

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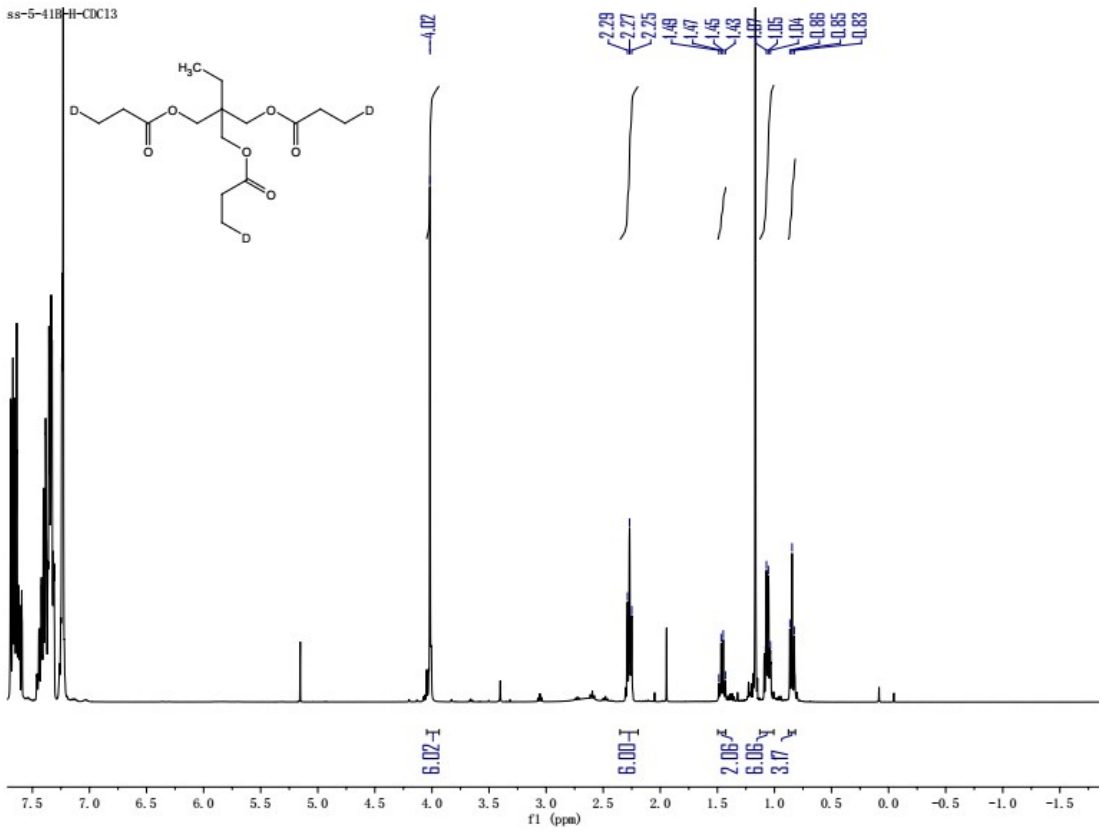
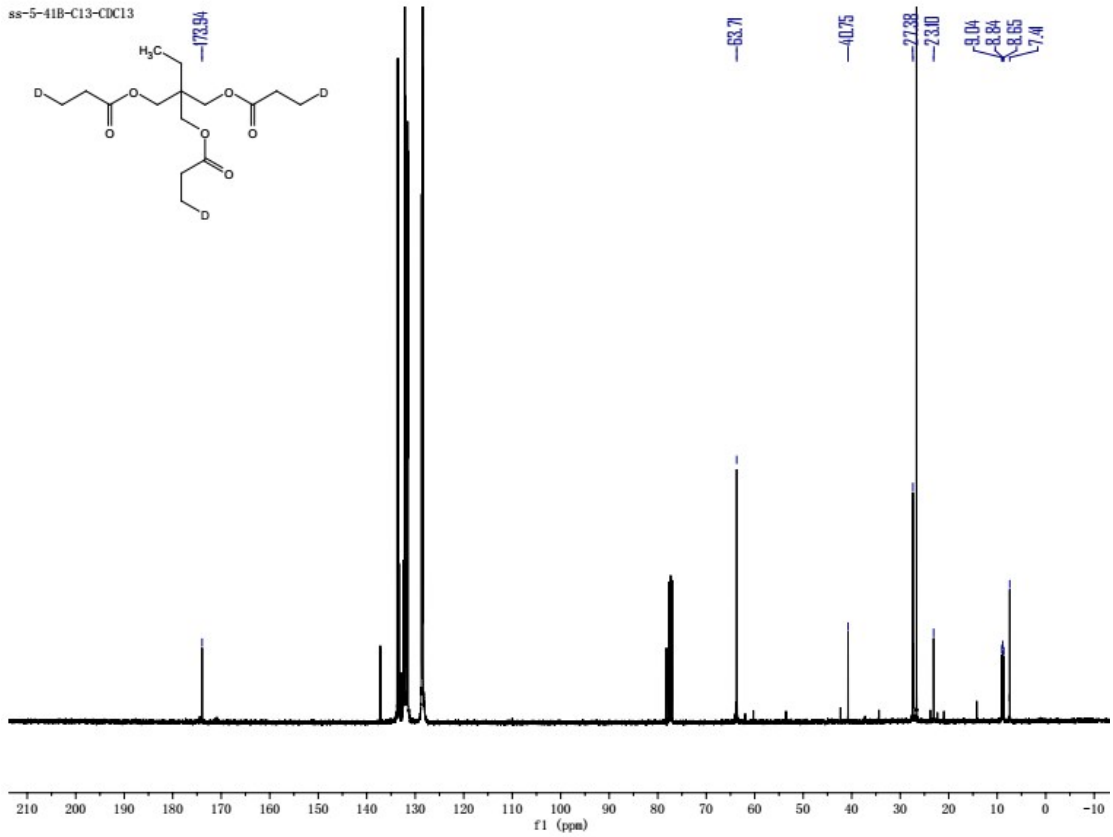
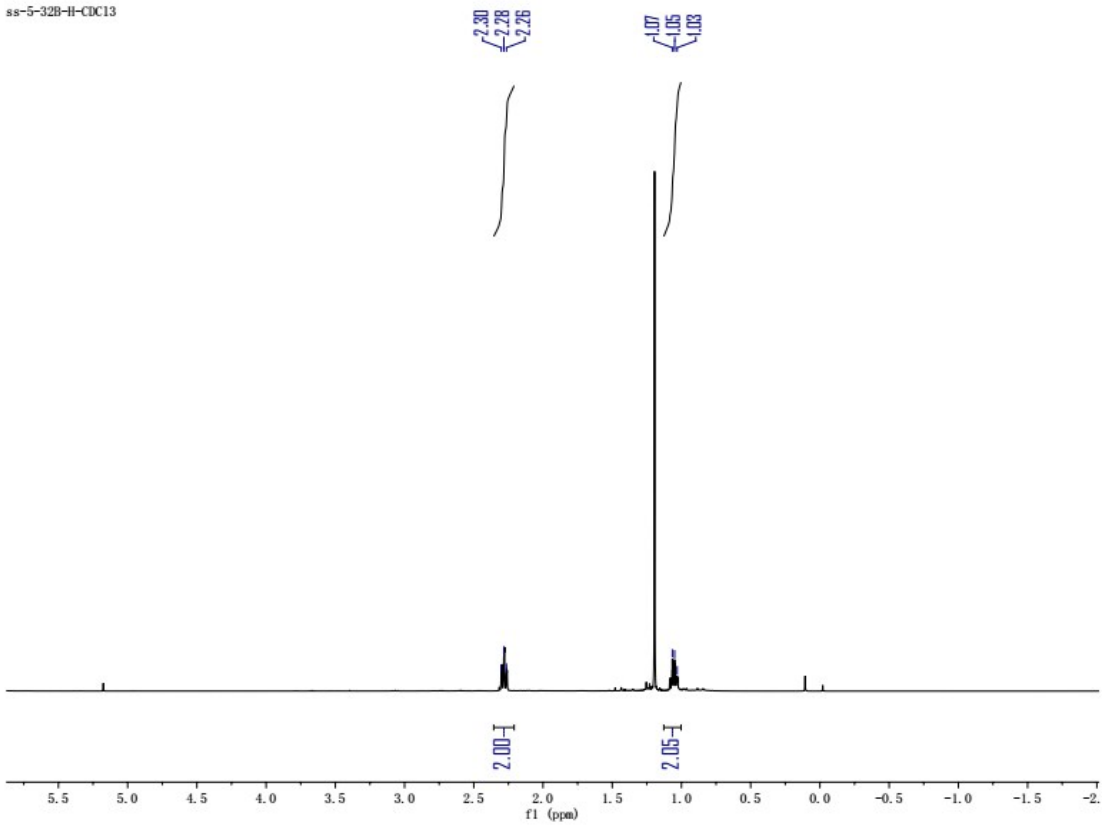


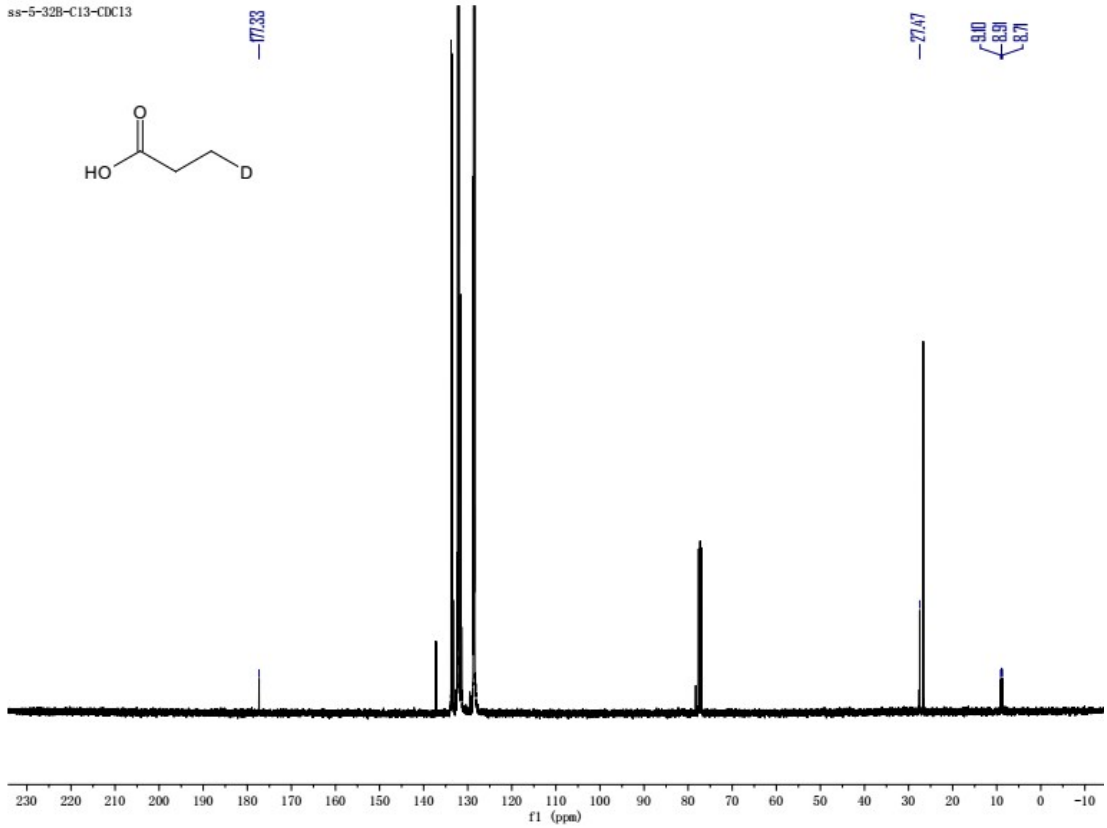
The crude ^{13}C NMR of **2n** in $CDCl_3$



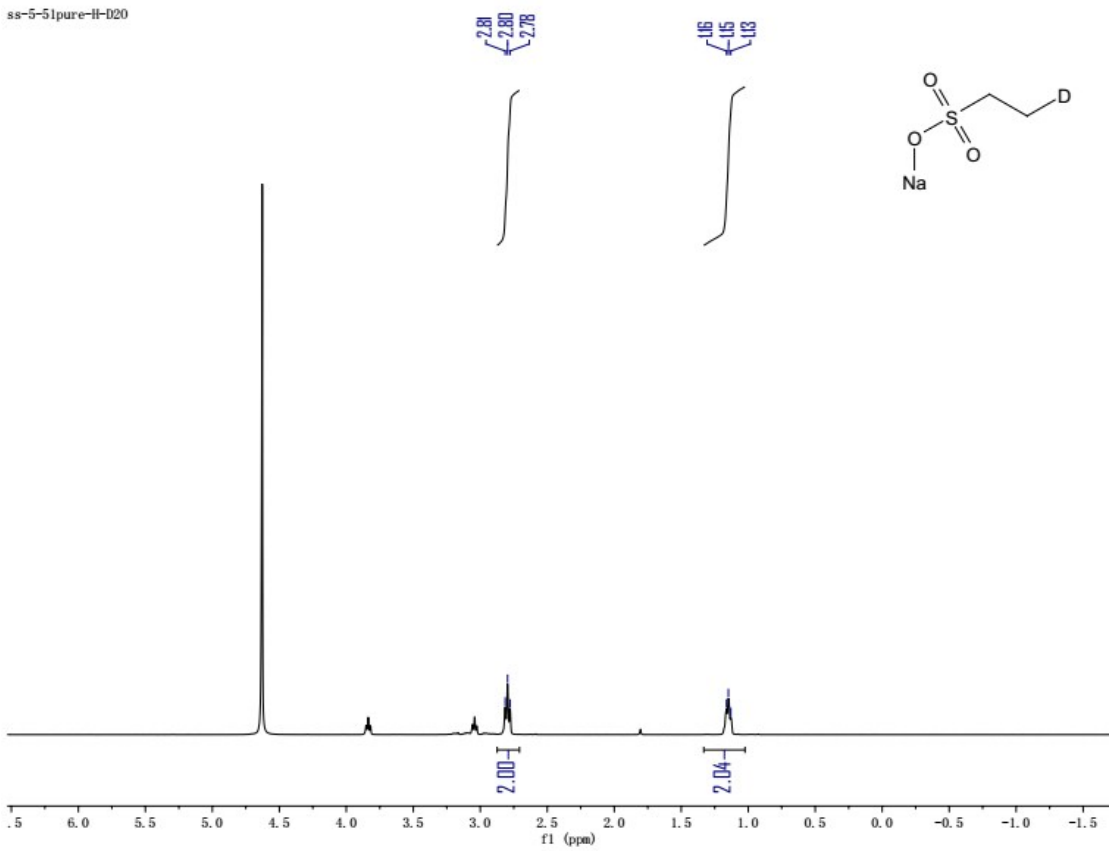
The crude ^{1}H NMR of **2o** in $CDCl_3$



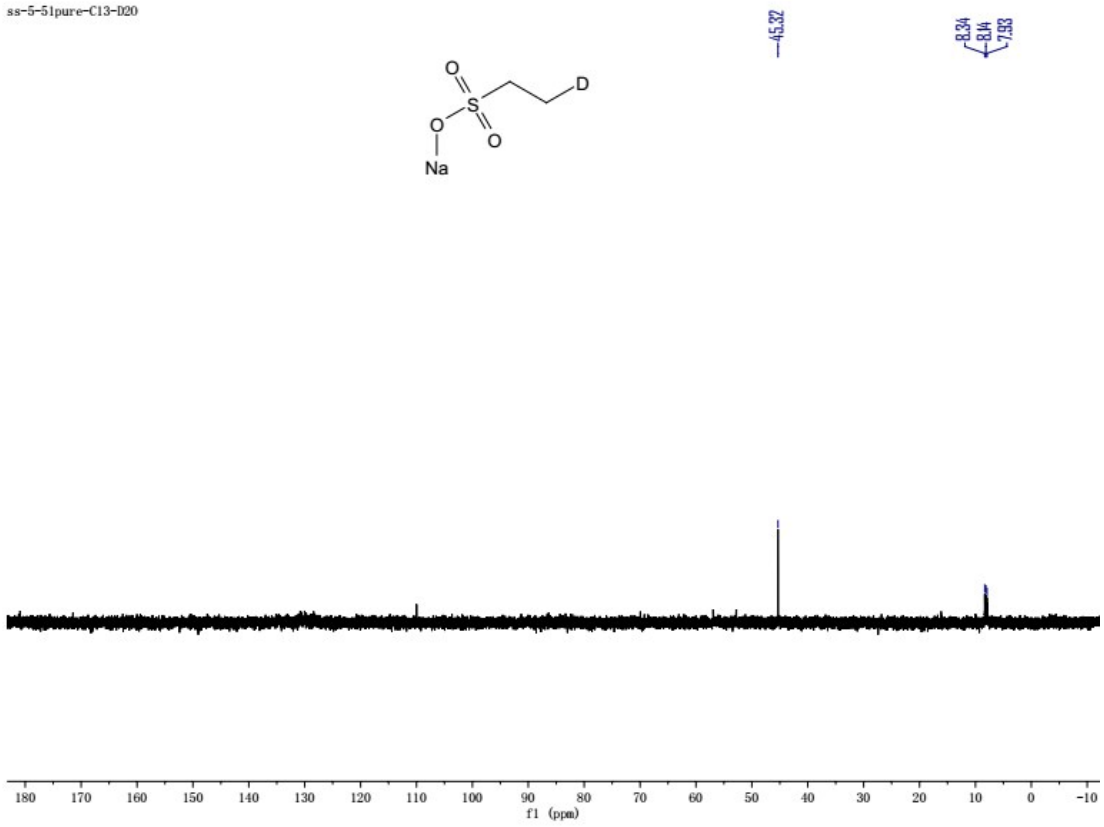
The crude ^{13}C NMR of **2o** in $CDCl_3$



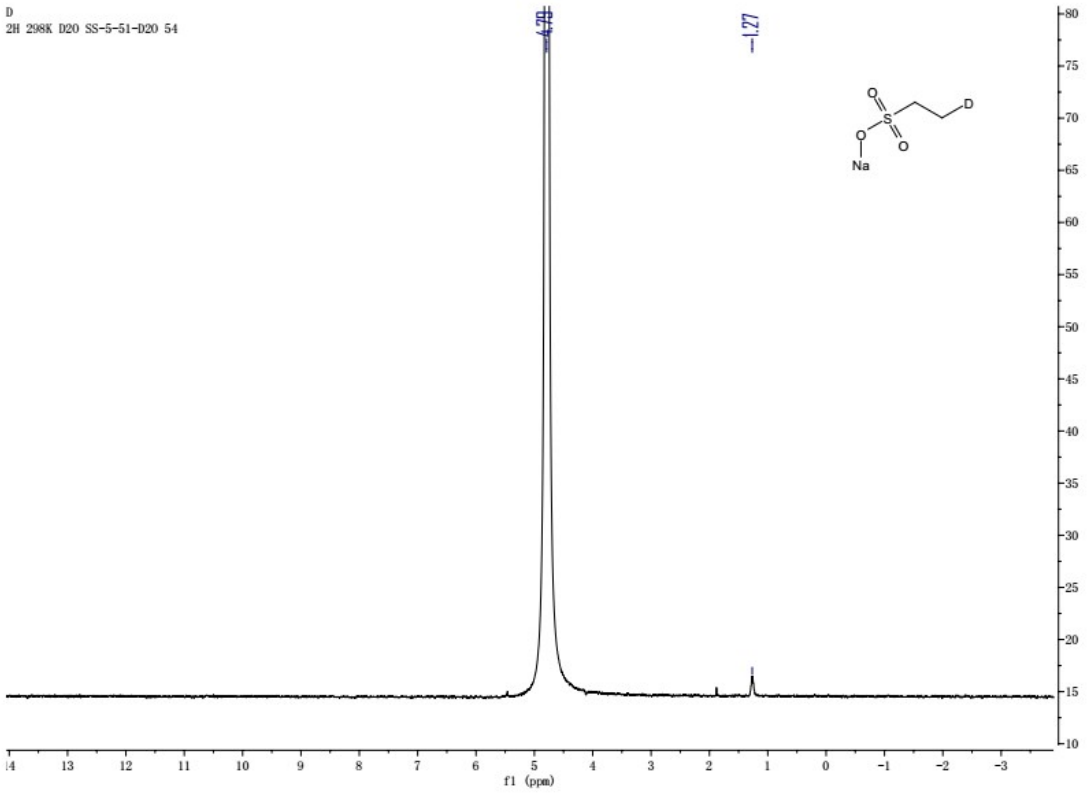
^{1}H NMR of **2p** in D_2O



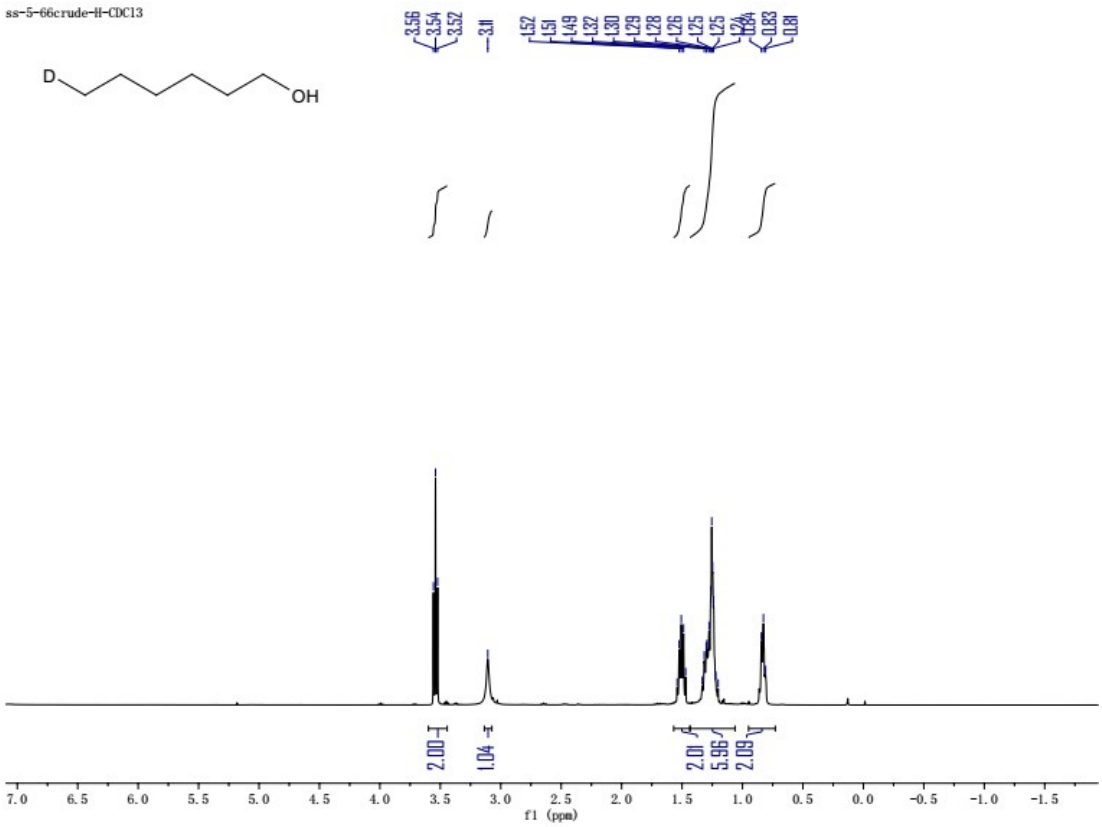
^{13}C NMR of **2p** in D_2O



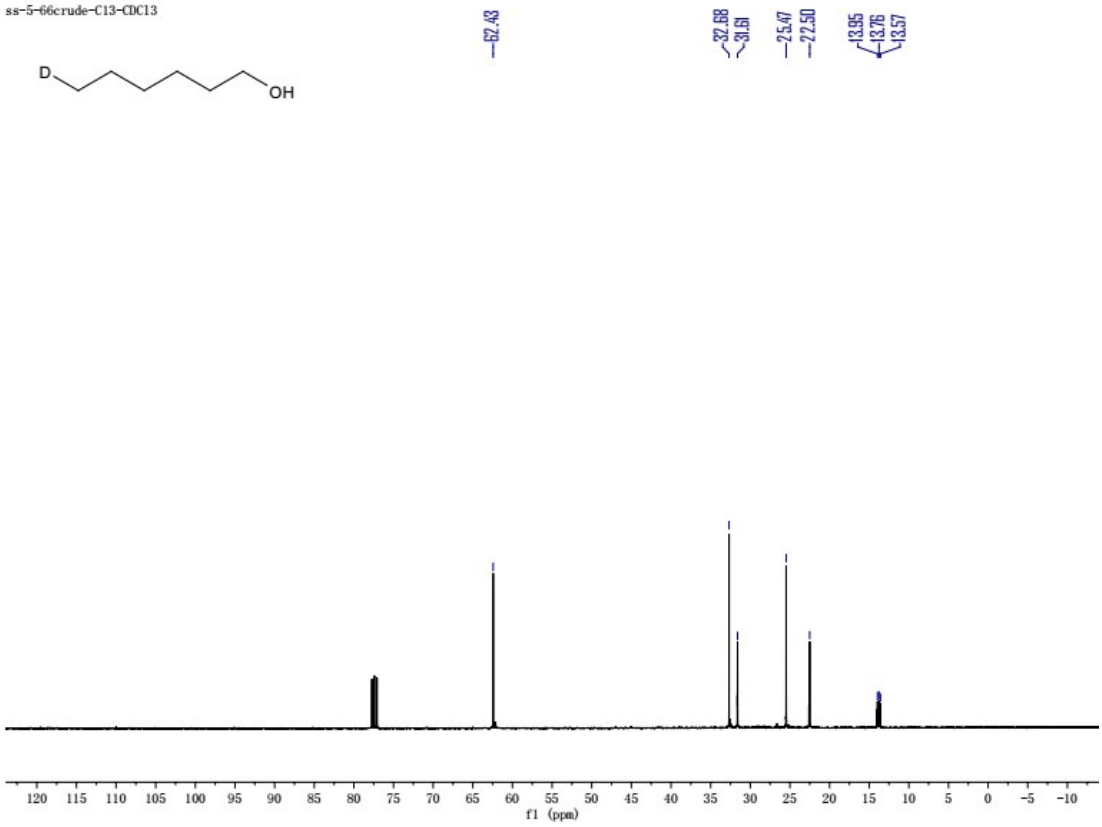
^{2}H NMR of **2p** in D_2O



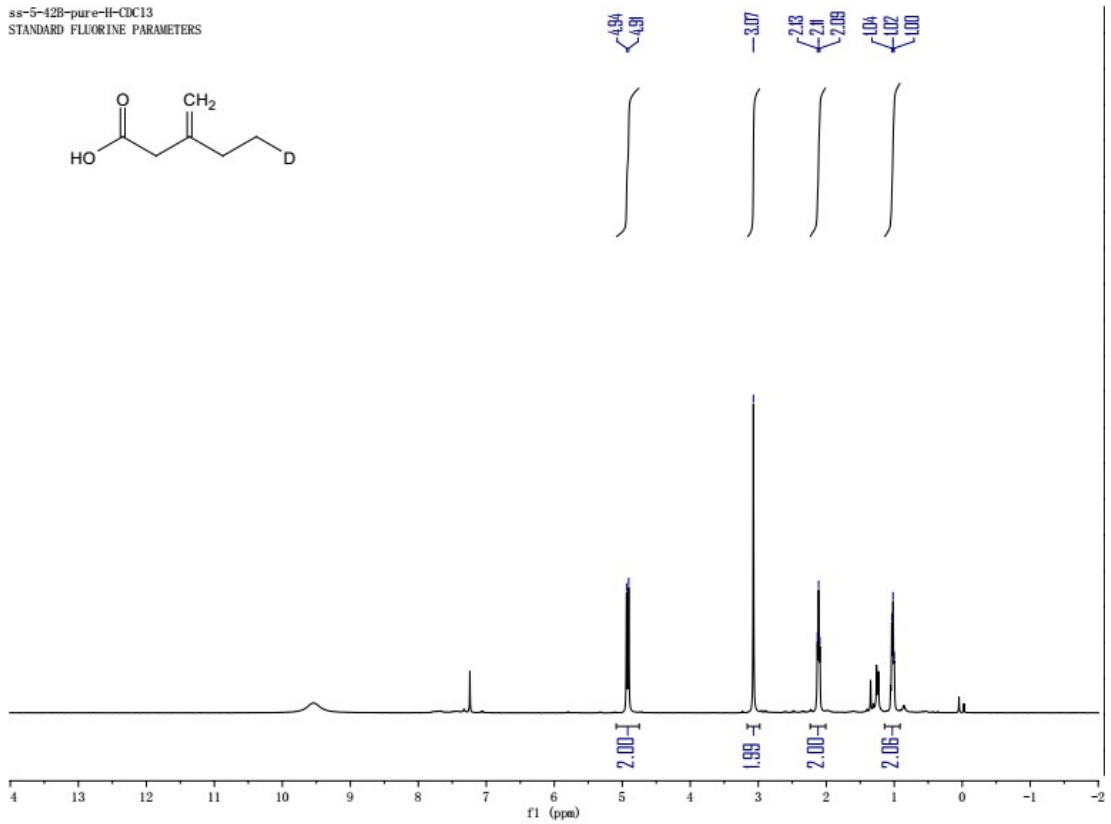
The crude ^{1}H NMR of **2q** in $CDCl_3$



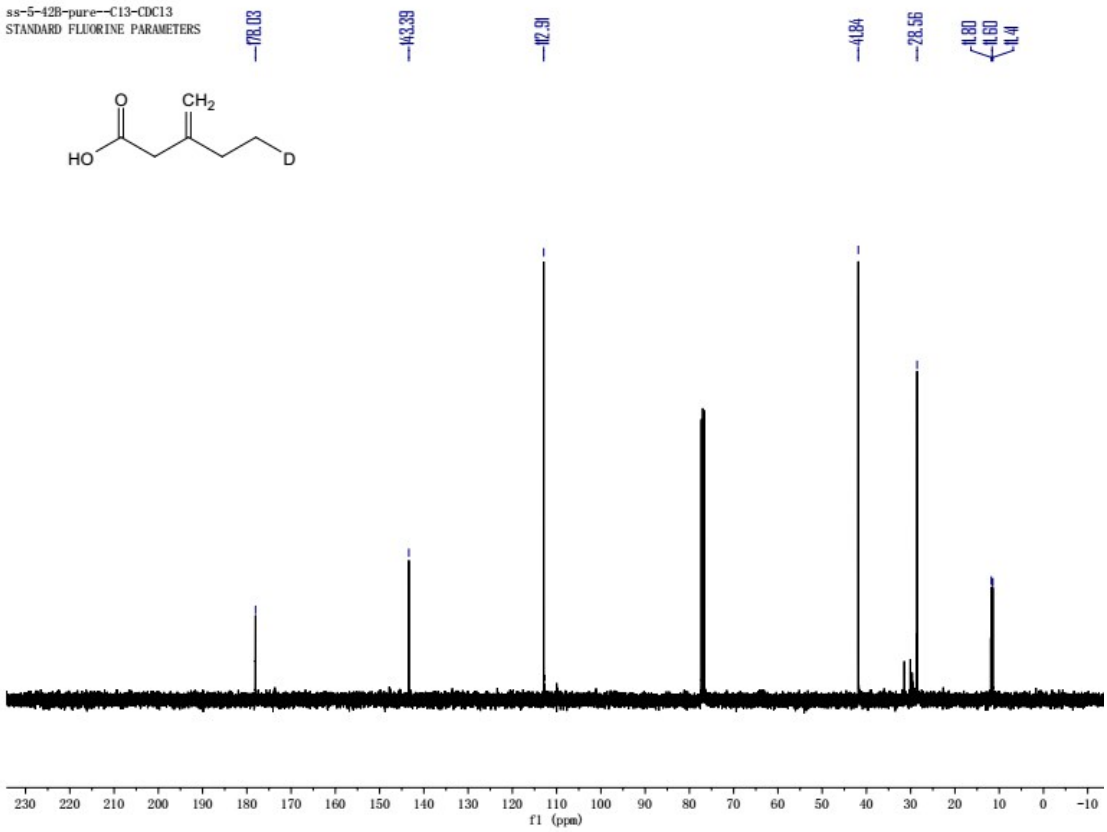
The crude ^{13}C NMR of **2q** in $CDCl_3$



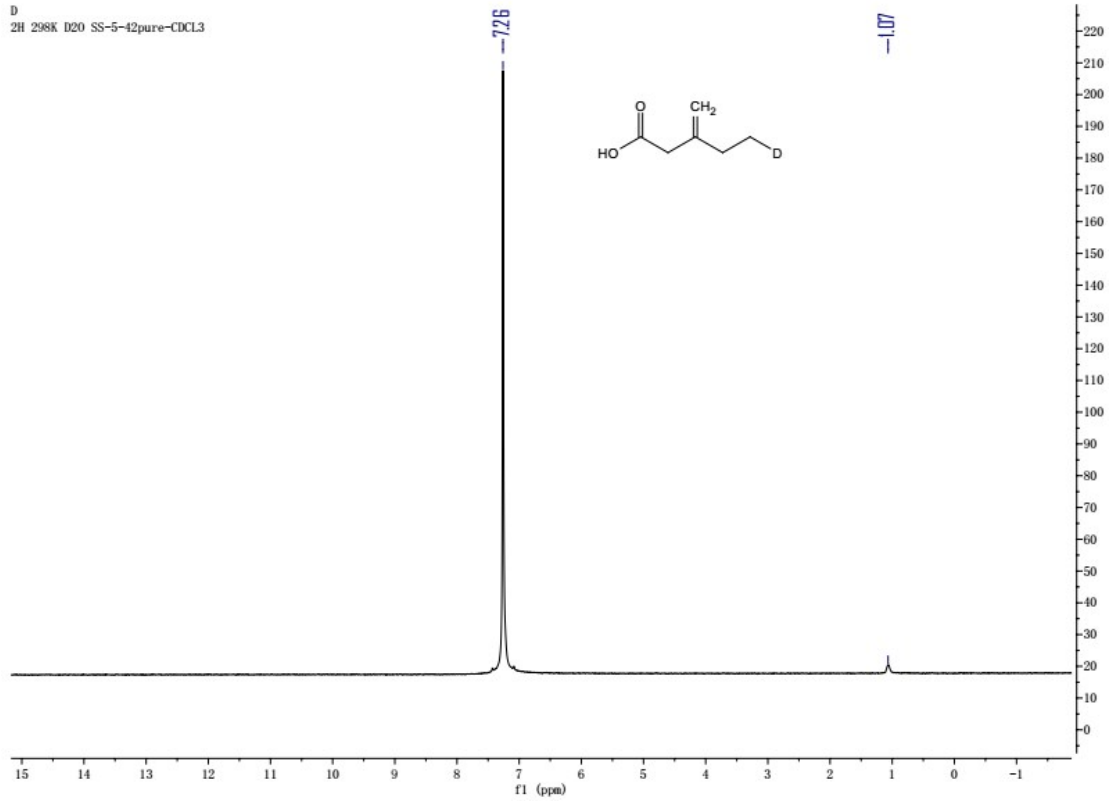
^{1}H NMR of **2r** in $CDCl_3$



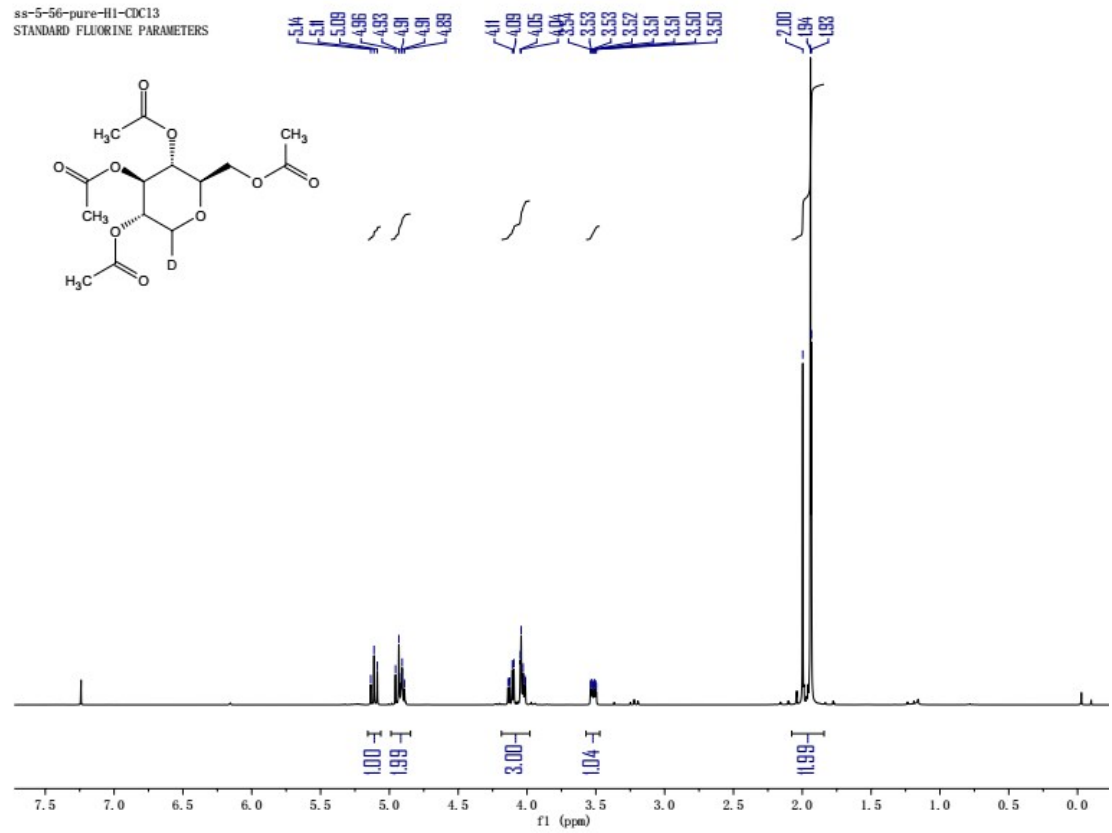
^{13}C NMR of **2r** in $CDCl_3$



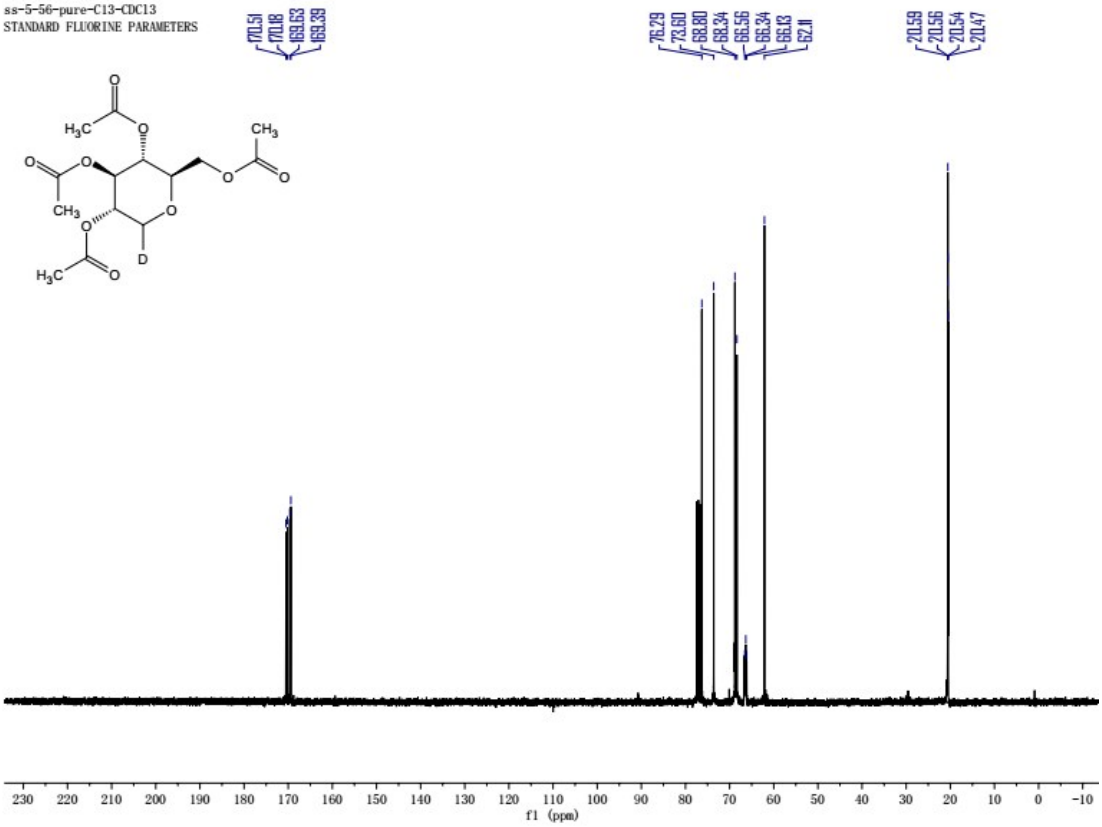
^{2}H NMR of **2r** in $CDCl_3$



^{1}H NMR of **2s** in $CDCl_3$



^{13}C NMR of **2s** in $CDCl_3$



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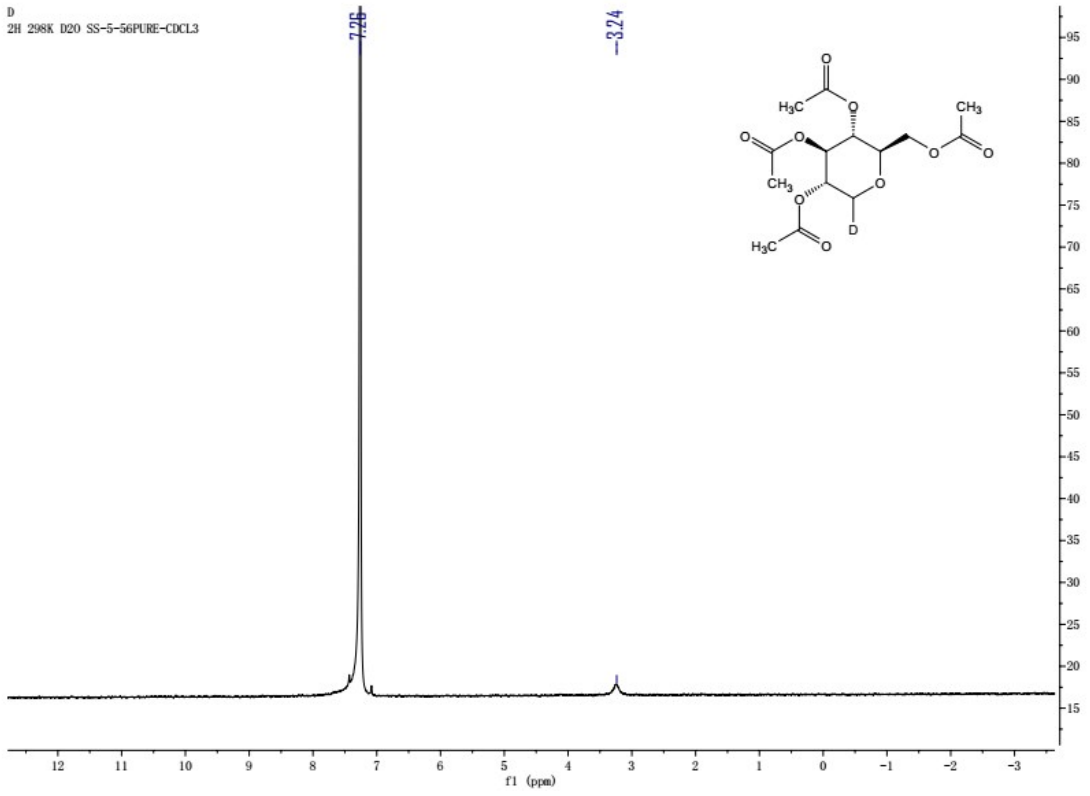
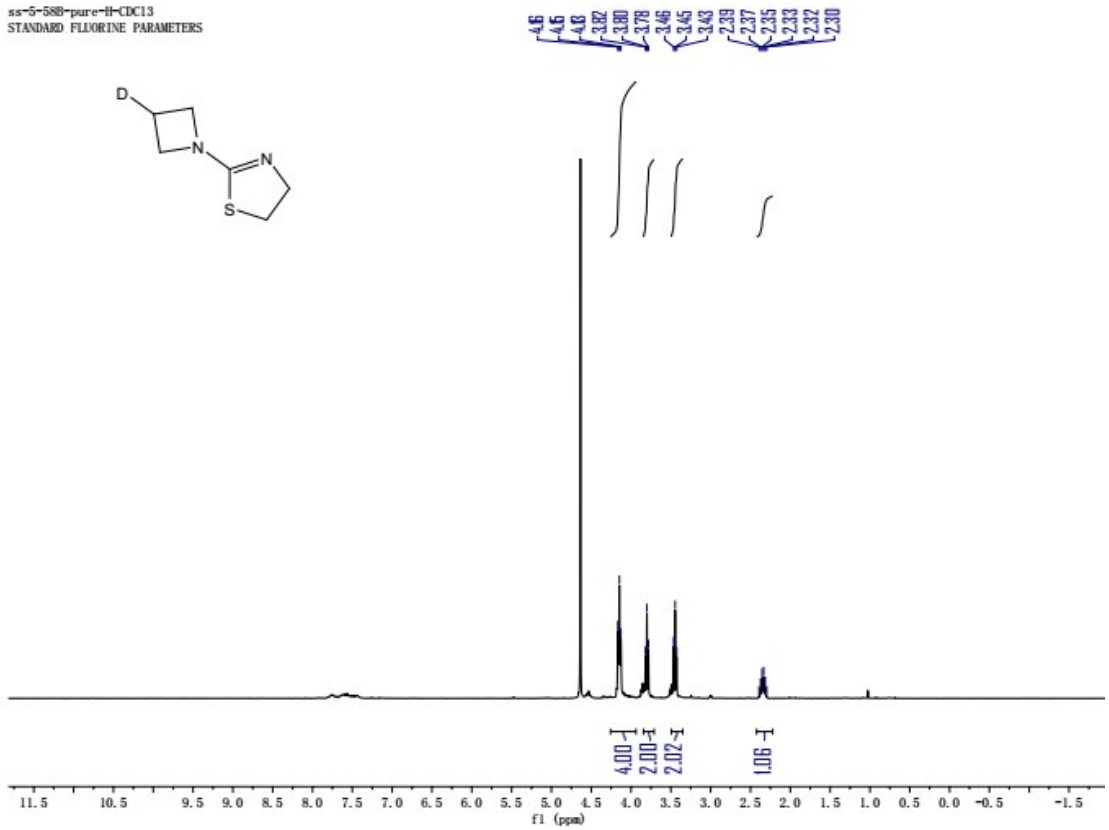
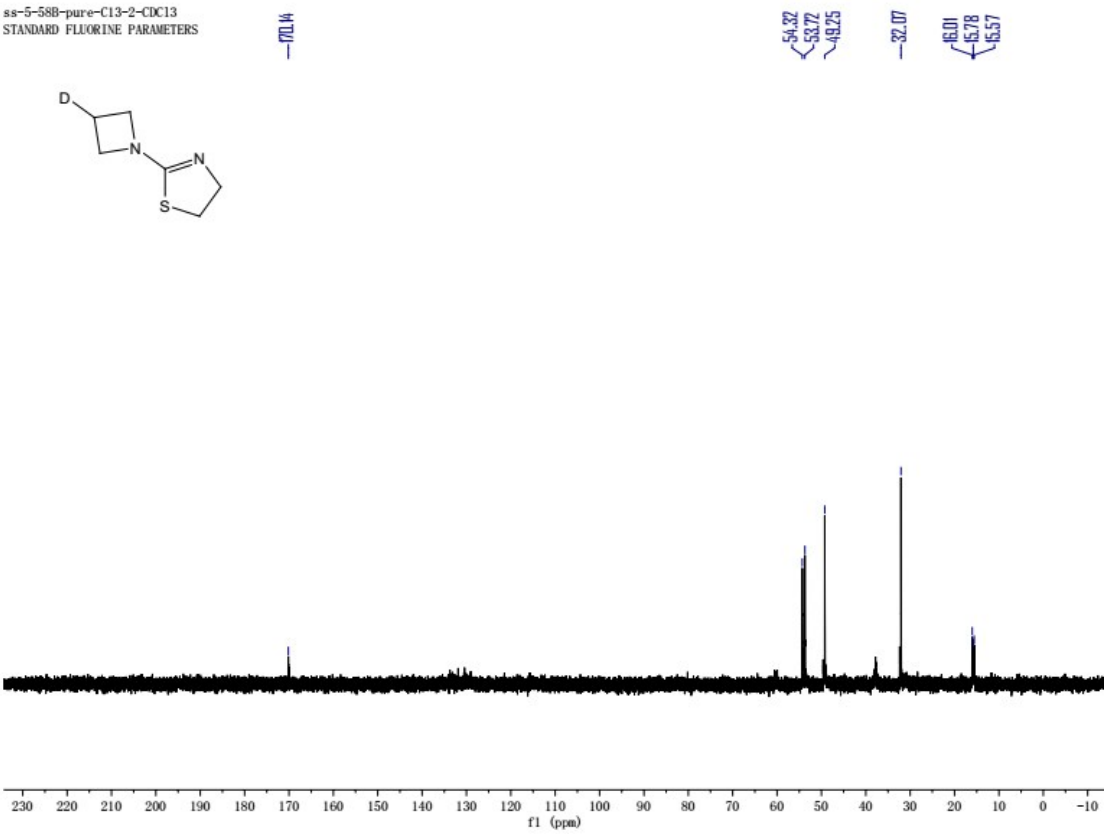


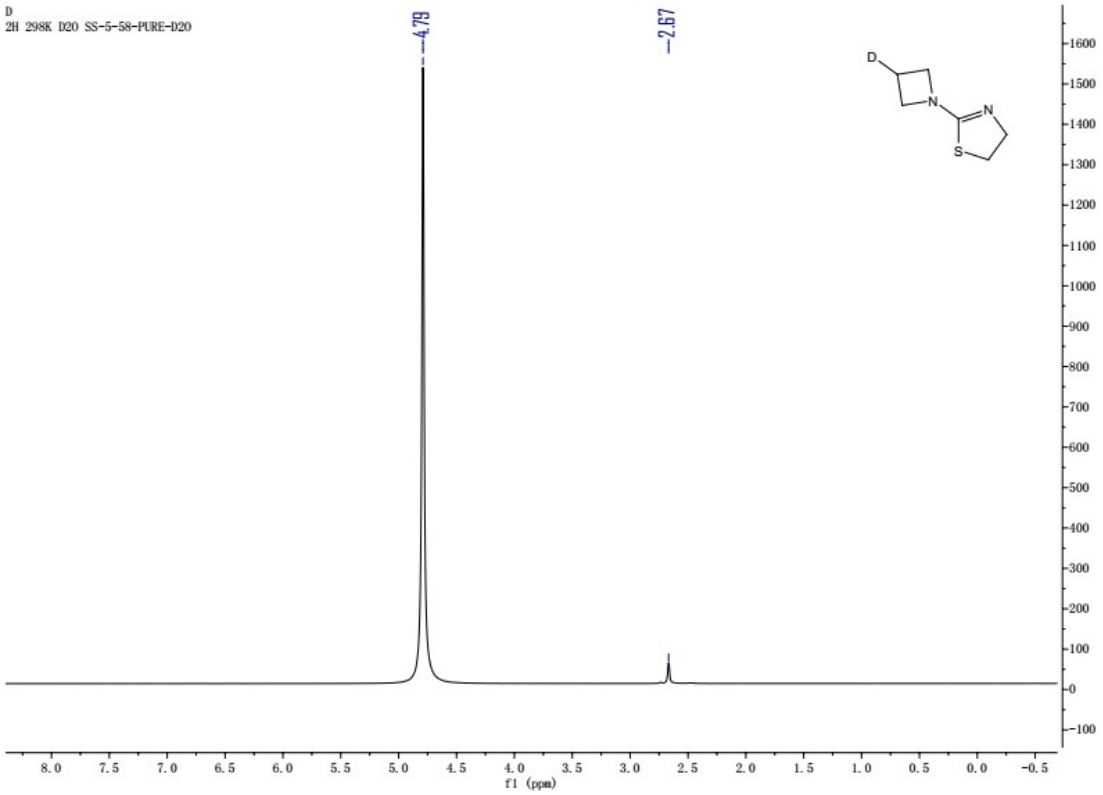
^{1}H NMR of **2t** in D_2O



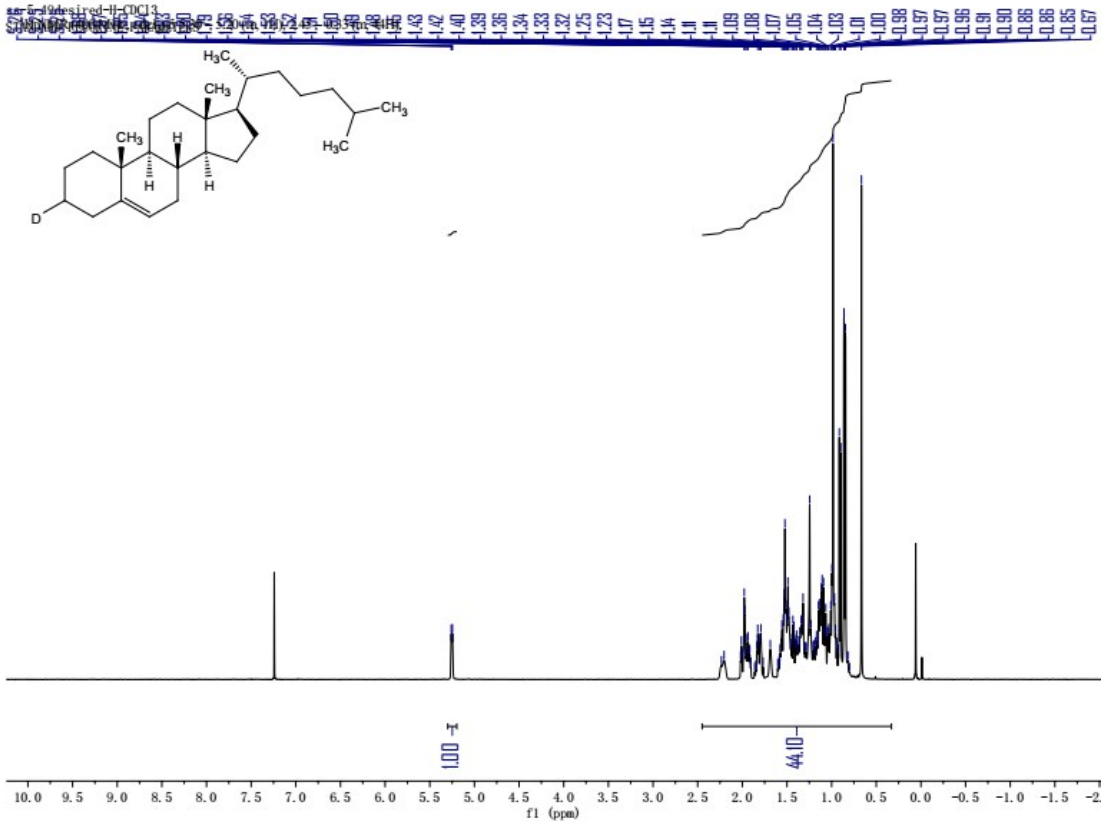
^{13}C NMR of **2t** in D_2O



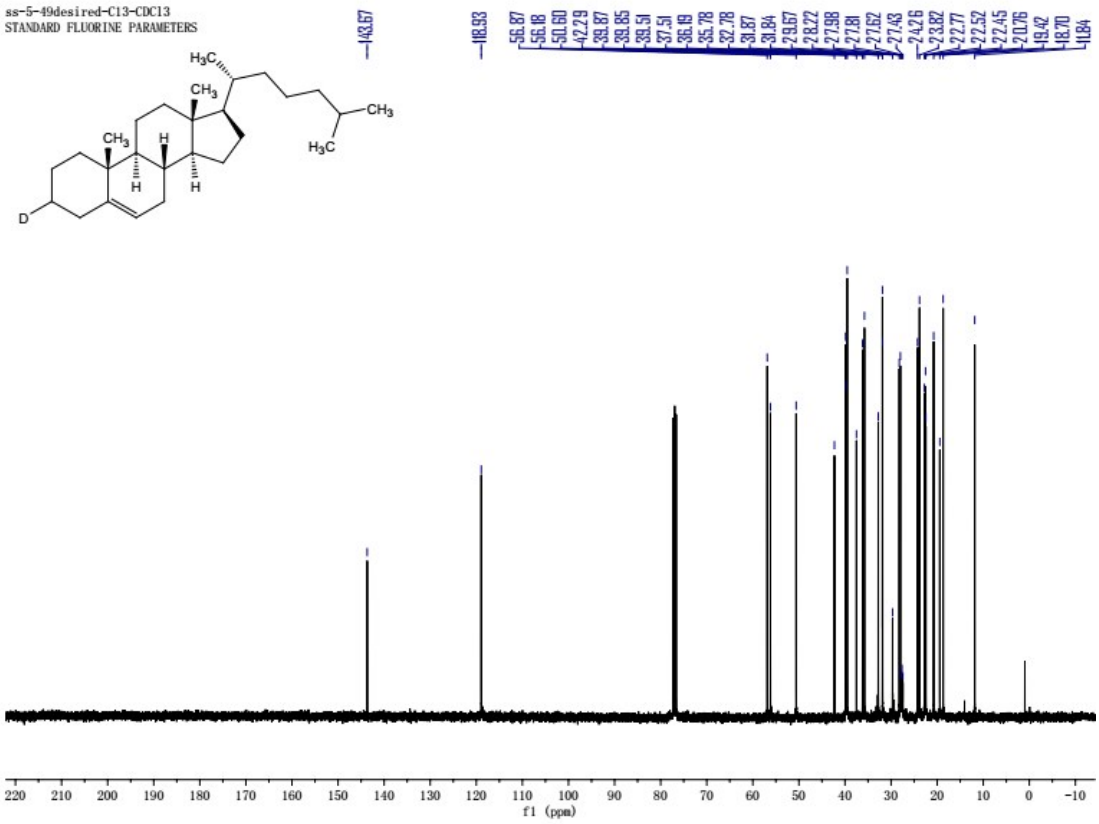
^{2}H NMR of **2t** in D_2O



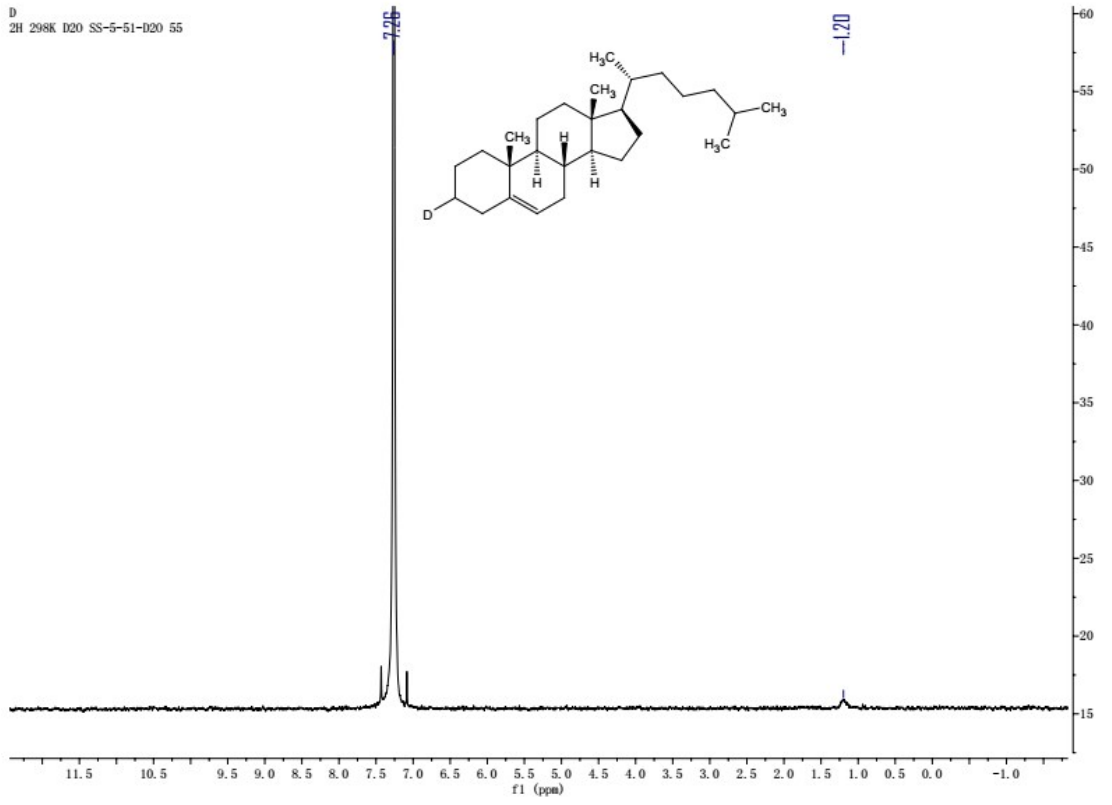
^{1}H NMR of **2u** in $CDCl_3$



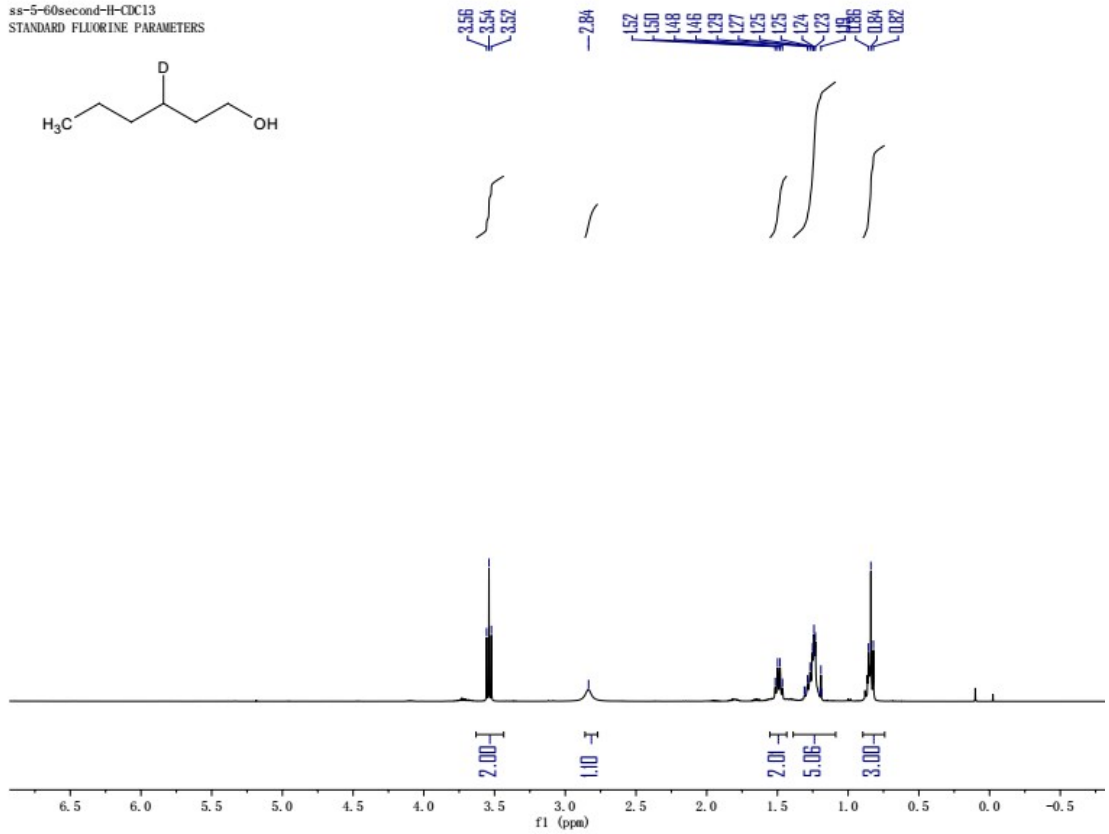
^{13}C NMR of **2u** in $CDCl_3$



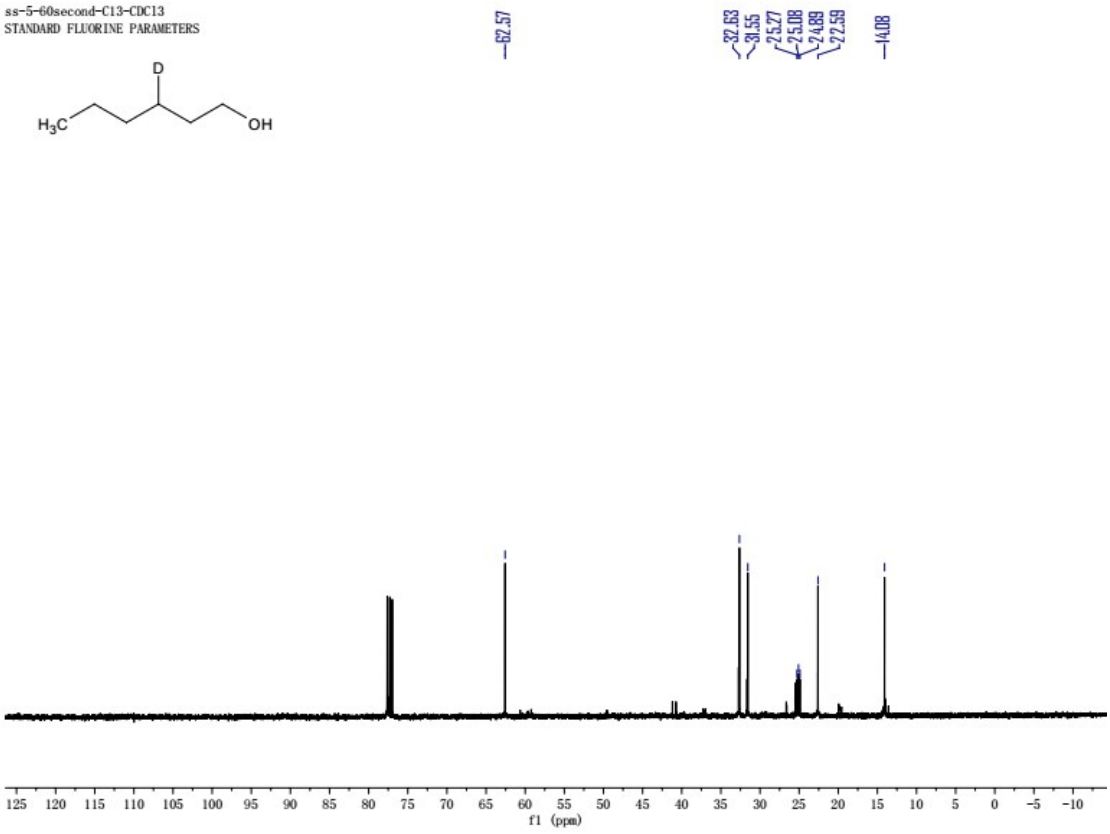
^{2}H NMR of **2u** in $CDCl_3$



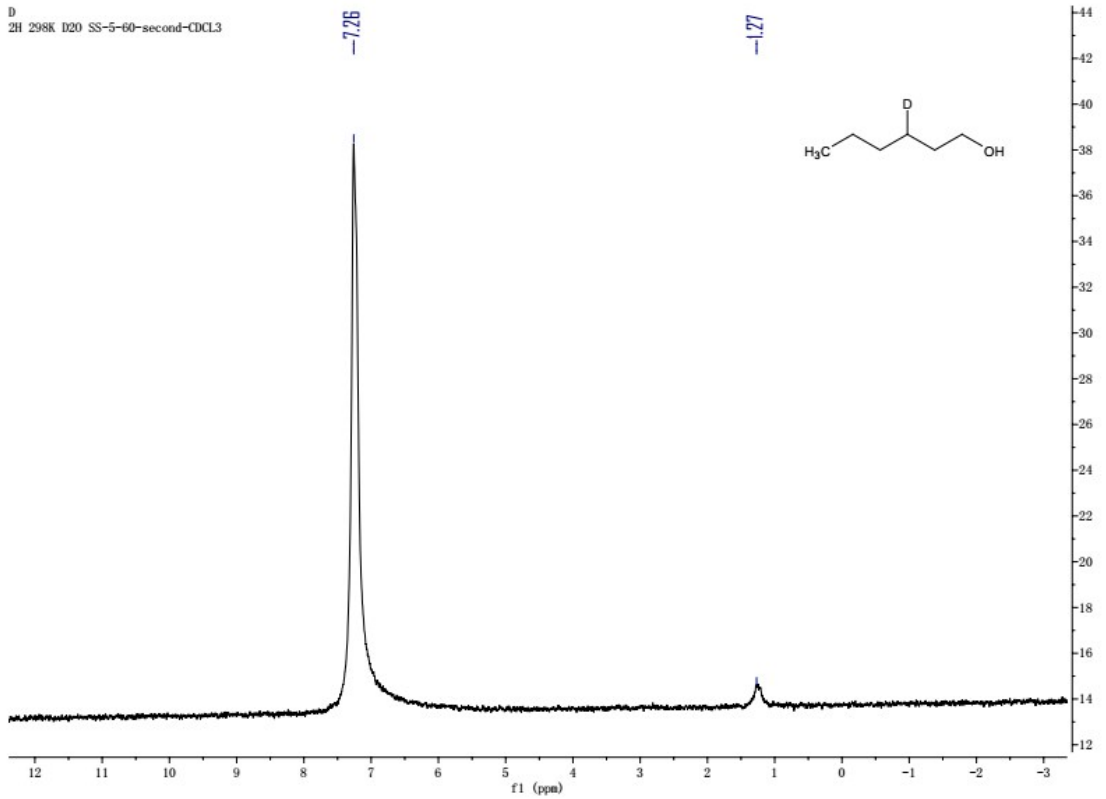
^{1}H NMR of **2v** in $CDCl_3$



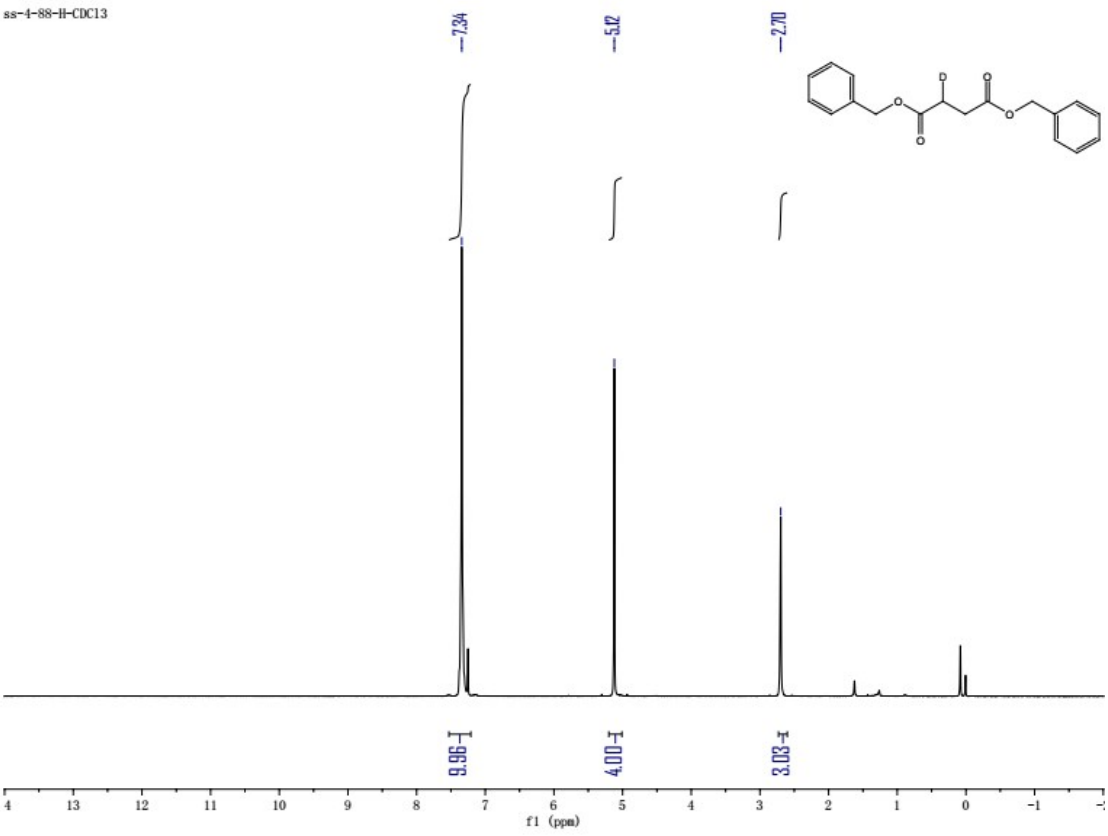
^{13}C NMR of **2v** in $CDCl_3$



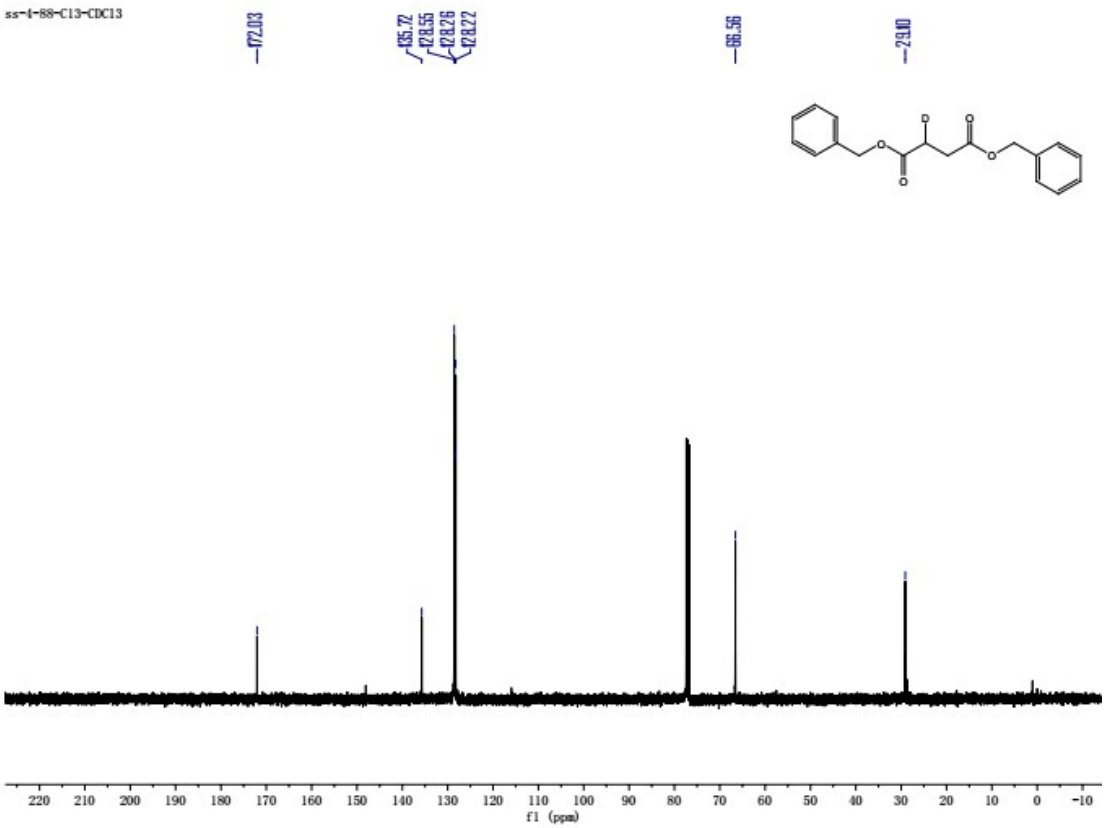
^{2}H NMR of **2v** in $CDCl_3$



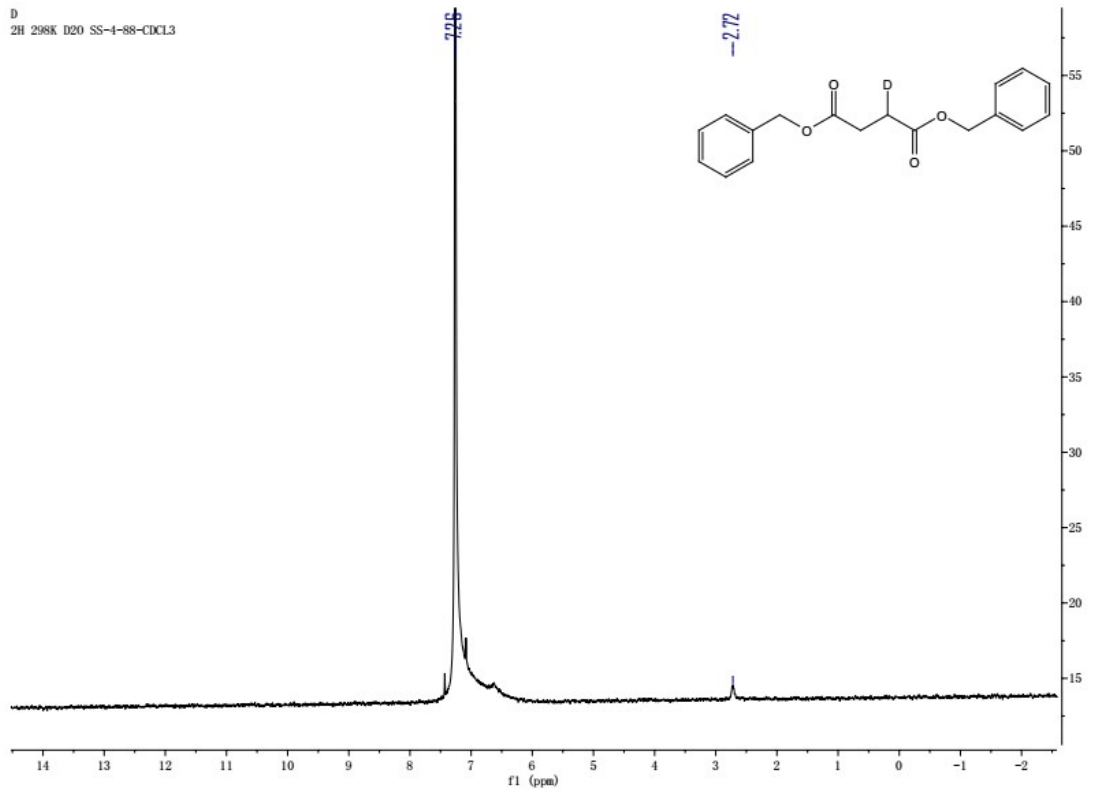
^{1}H NMR of **2w** in $CDCl_3$



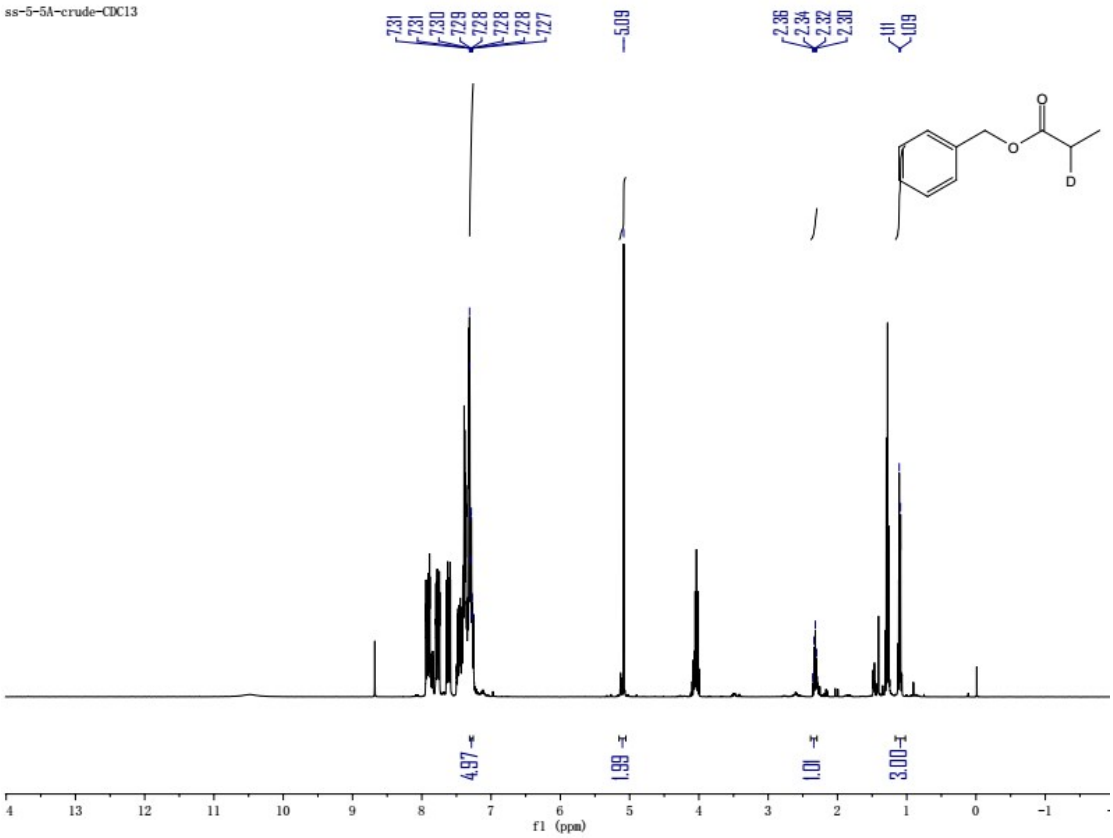
^{13}C NMR of **2w** in $CDCl_3$



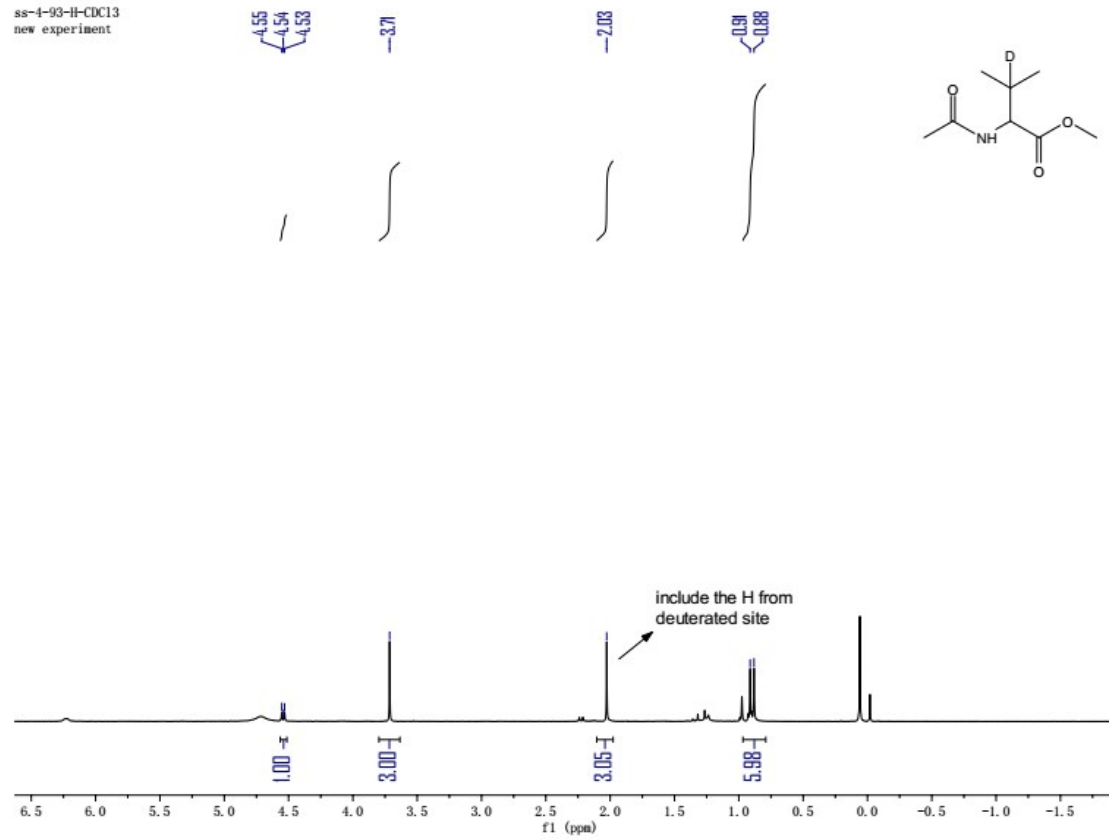
^{2}H NMR of **2w** in $CDCl_3$



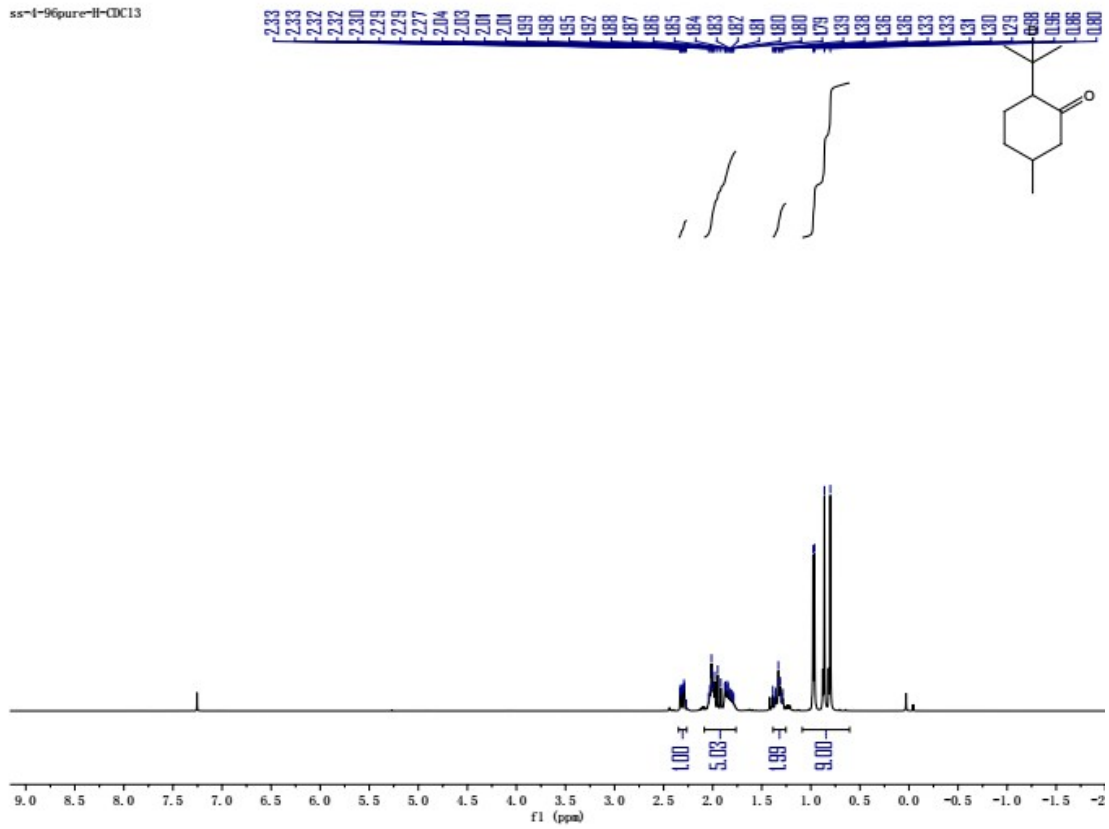
The crude ^{1}H NMR of **2x** in $CDCl_3$



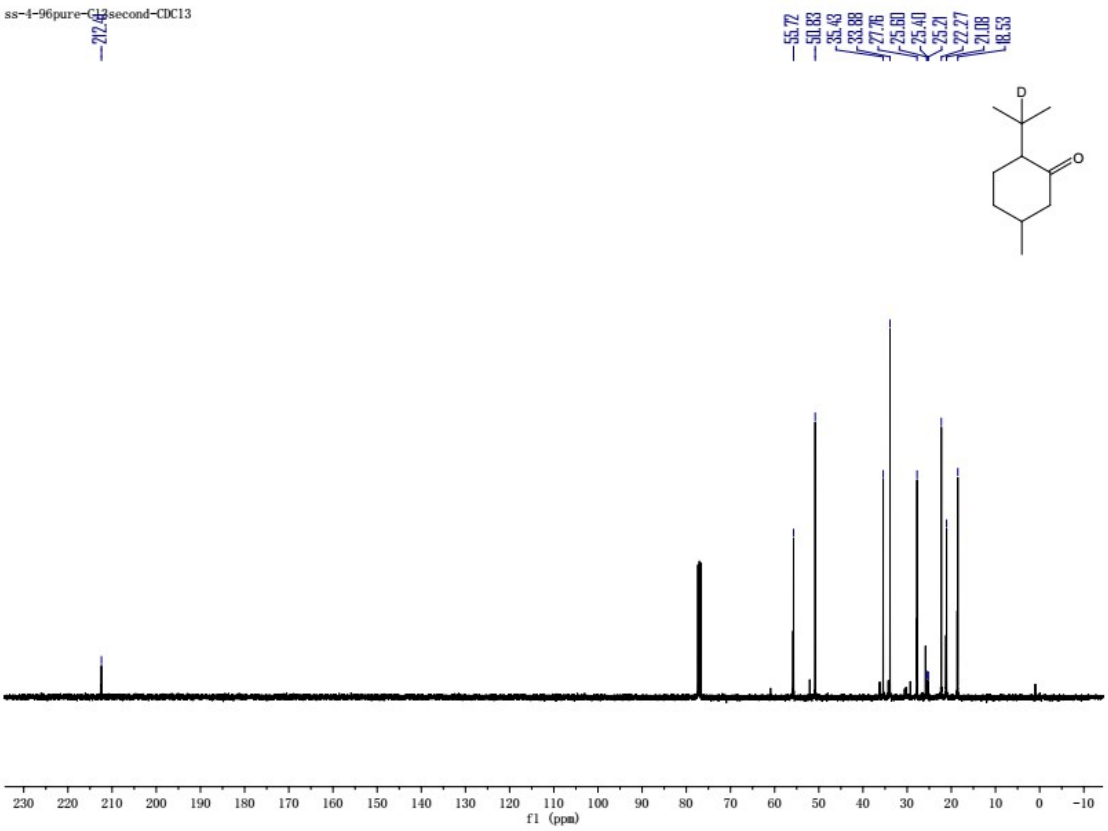
The crude ^{1}H NMR of **2y** in $CDCl_3$



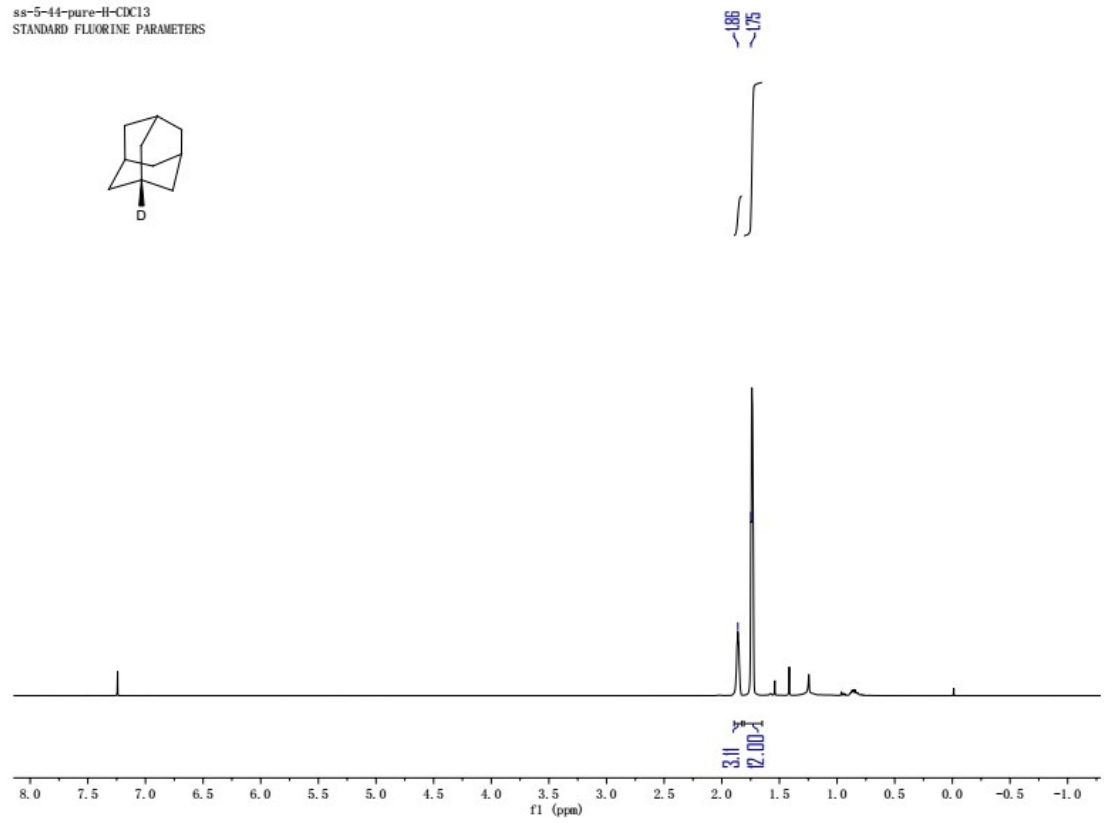
^{1}H NMR of **2z** in $CDCl_3$



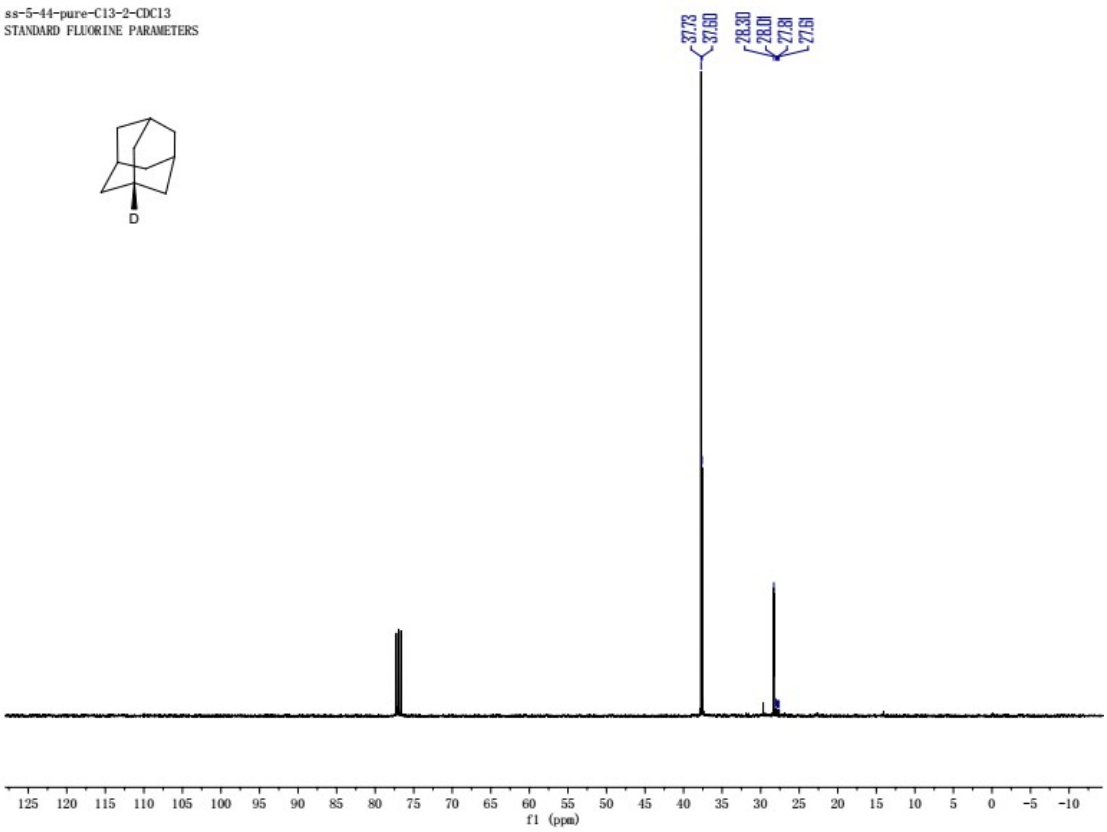
^{13}C NMR of **2z** in $CDCl_3$



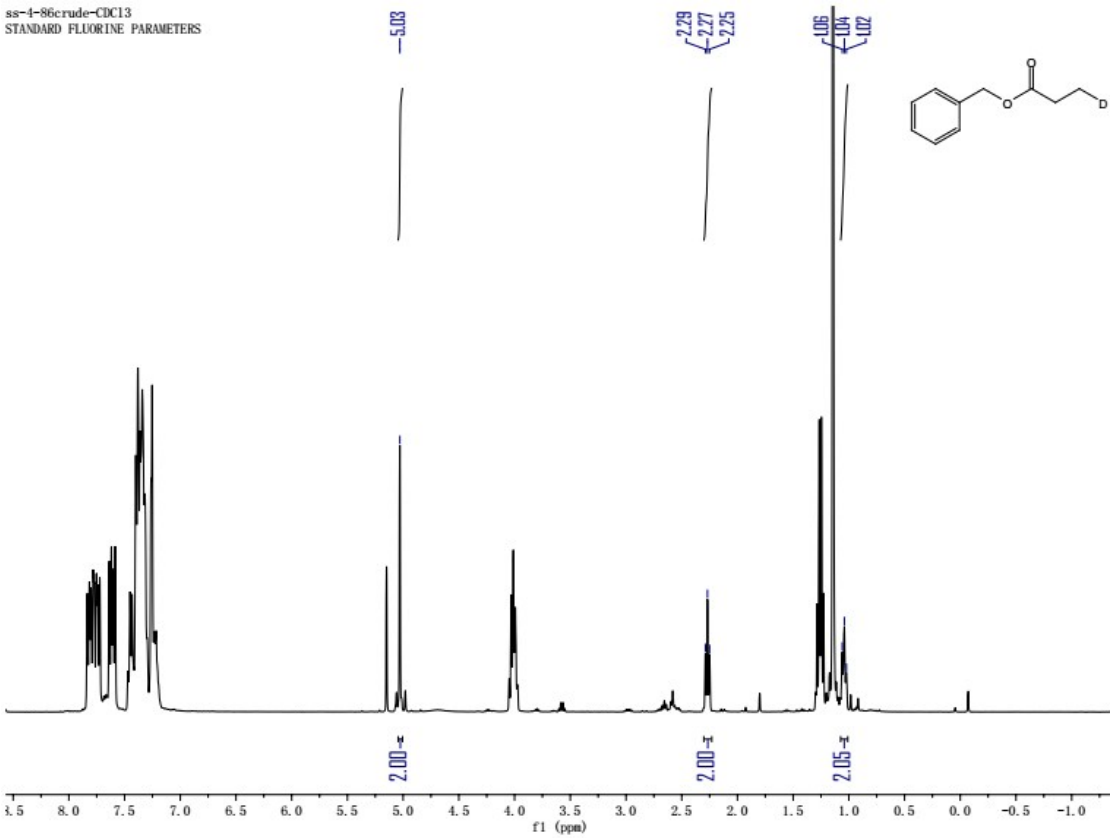
^{1}H NMR of **2A** in $CDCl_3$



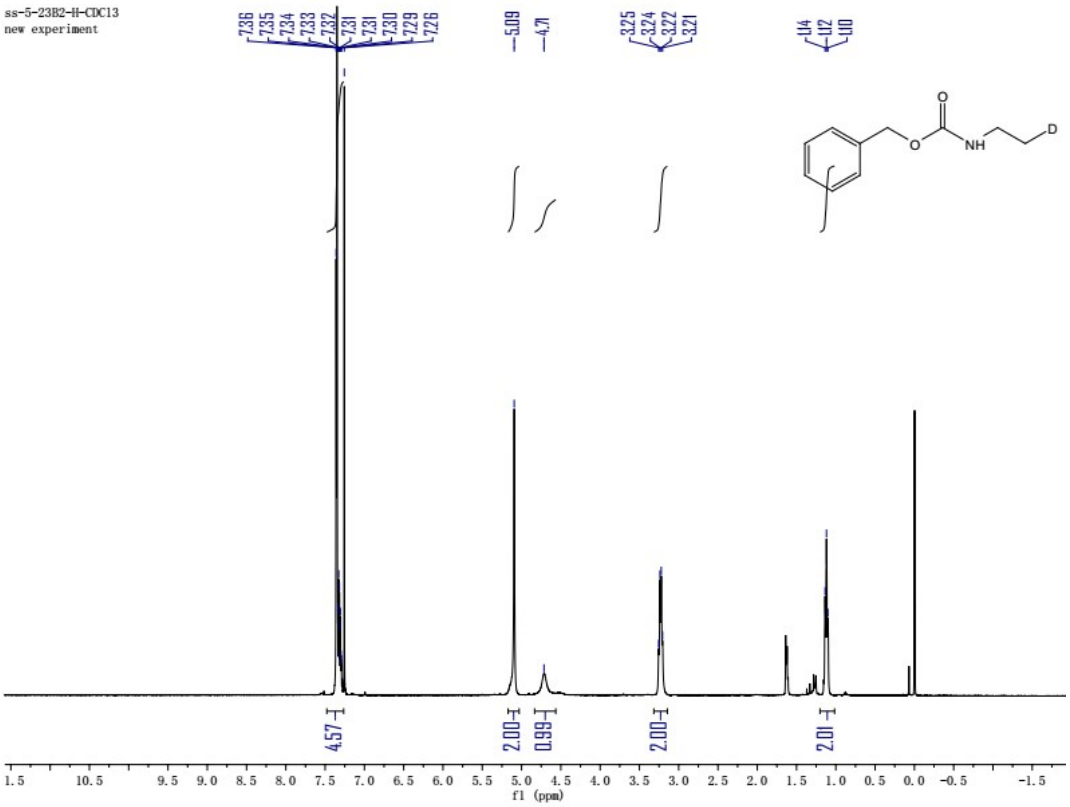
^{13}C NMR of **2A** in $CDCl_3$



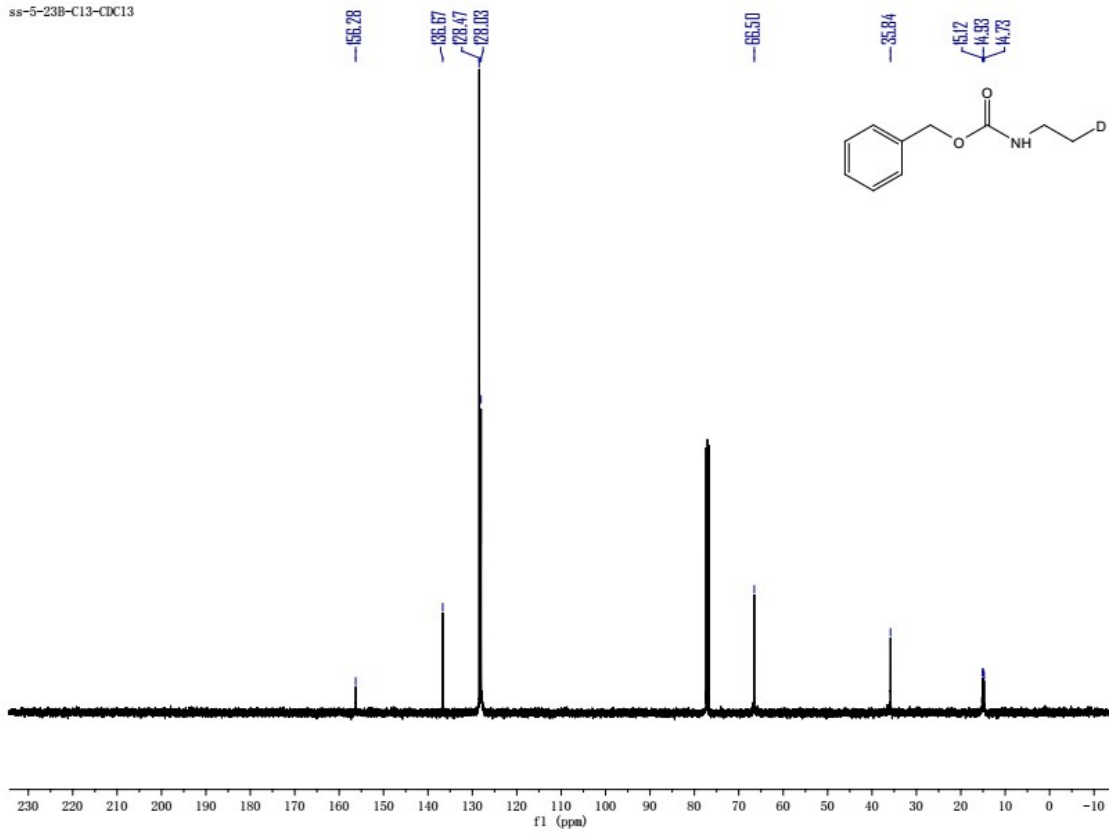
The crude ^{1}H NMR of **2B** in $CDCl_3$



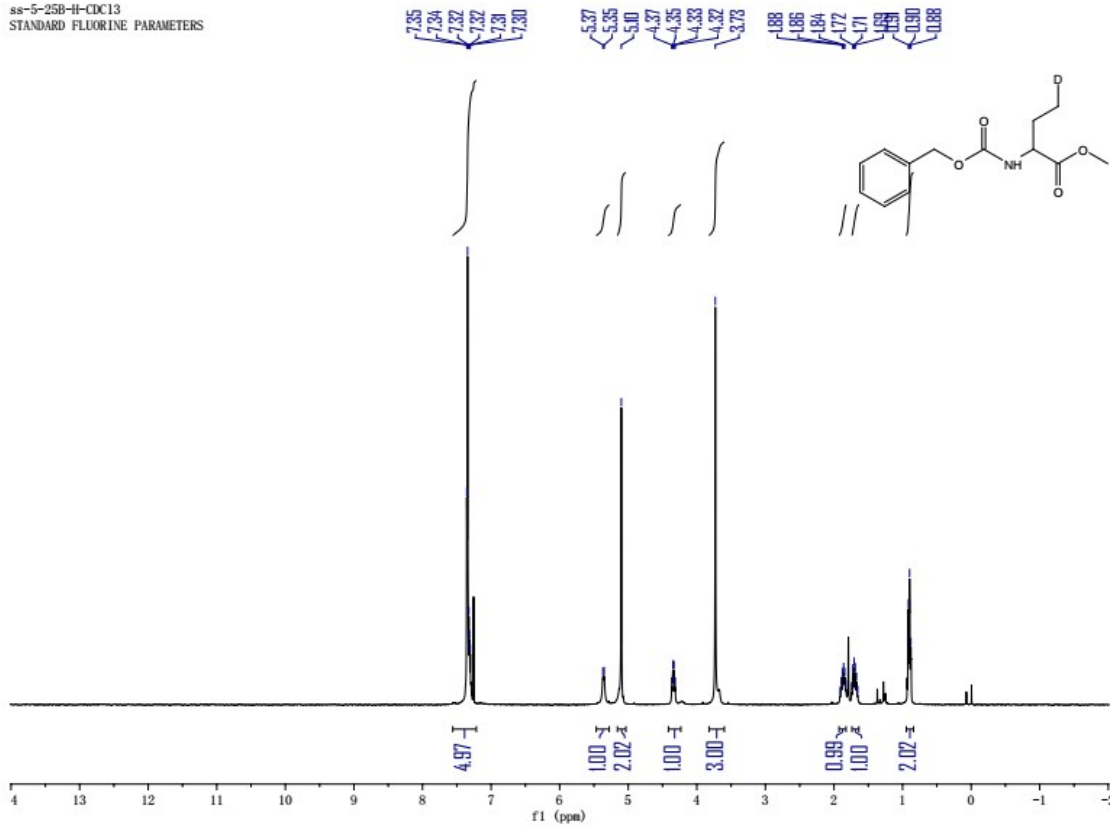
^{1}H NMR of **2C** in $CDCl_3$



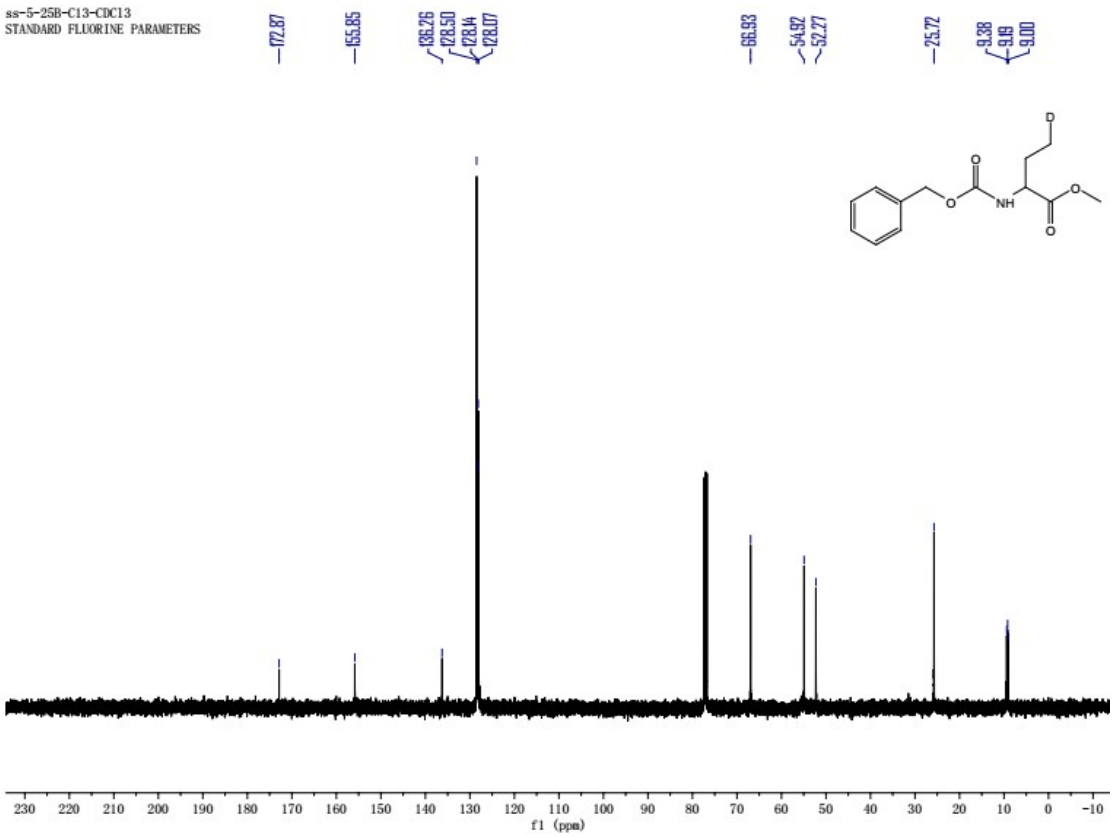
^{13}C NMR of **2C** in $CDCl_3$



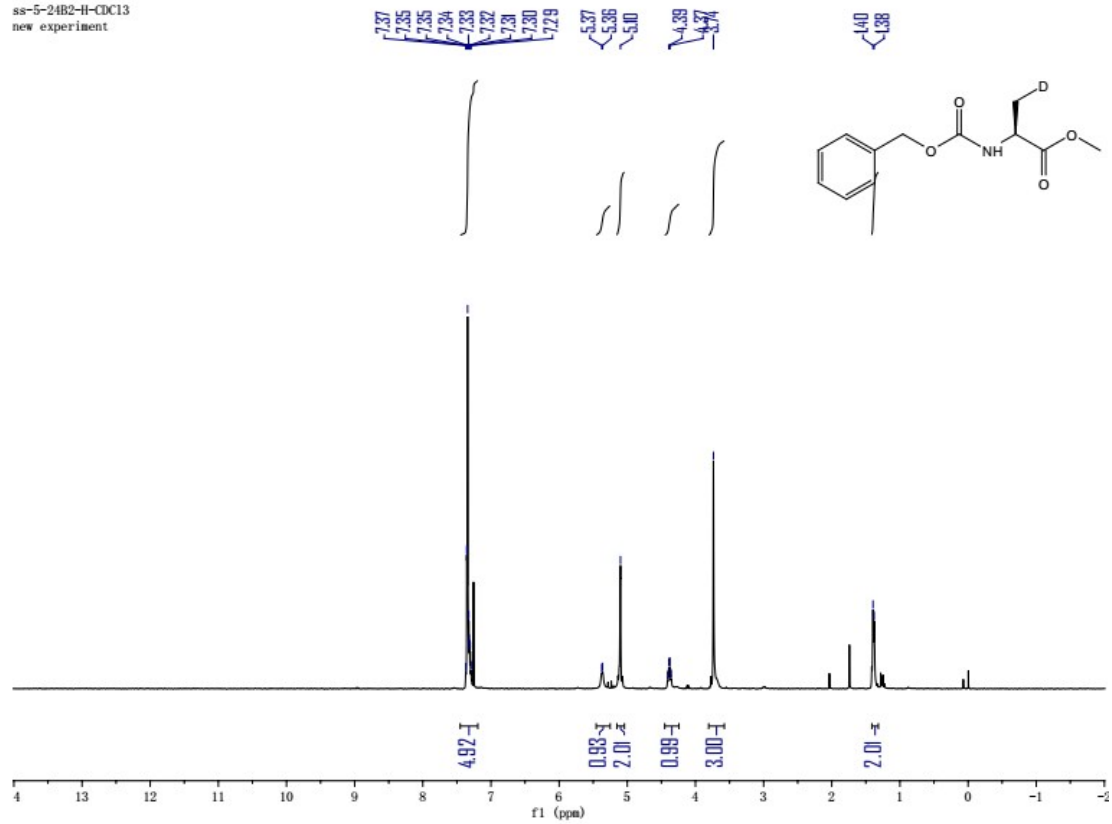
^{1}H NMR of **2D** in $CDCl_3$



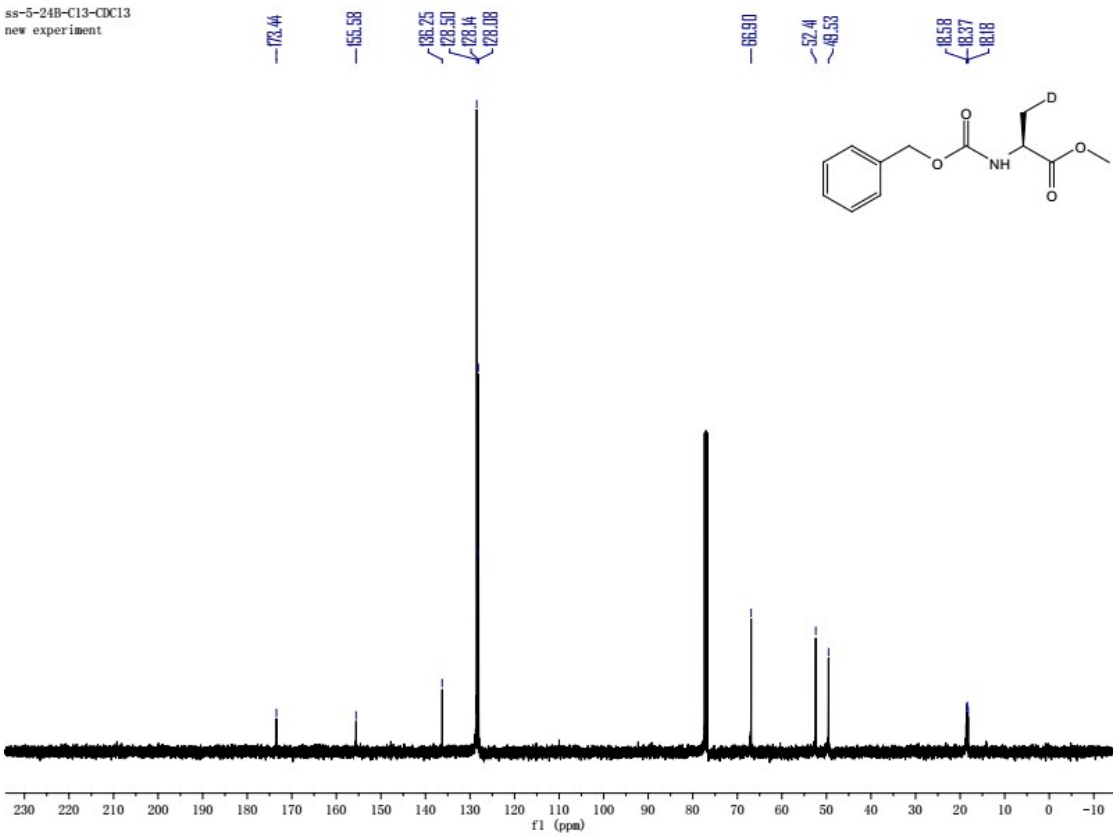
^{13}C NMR of **2D** in $CDCl_3$



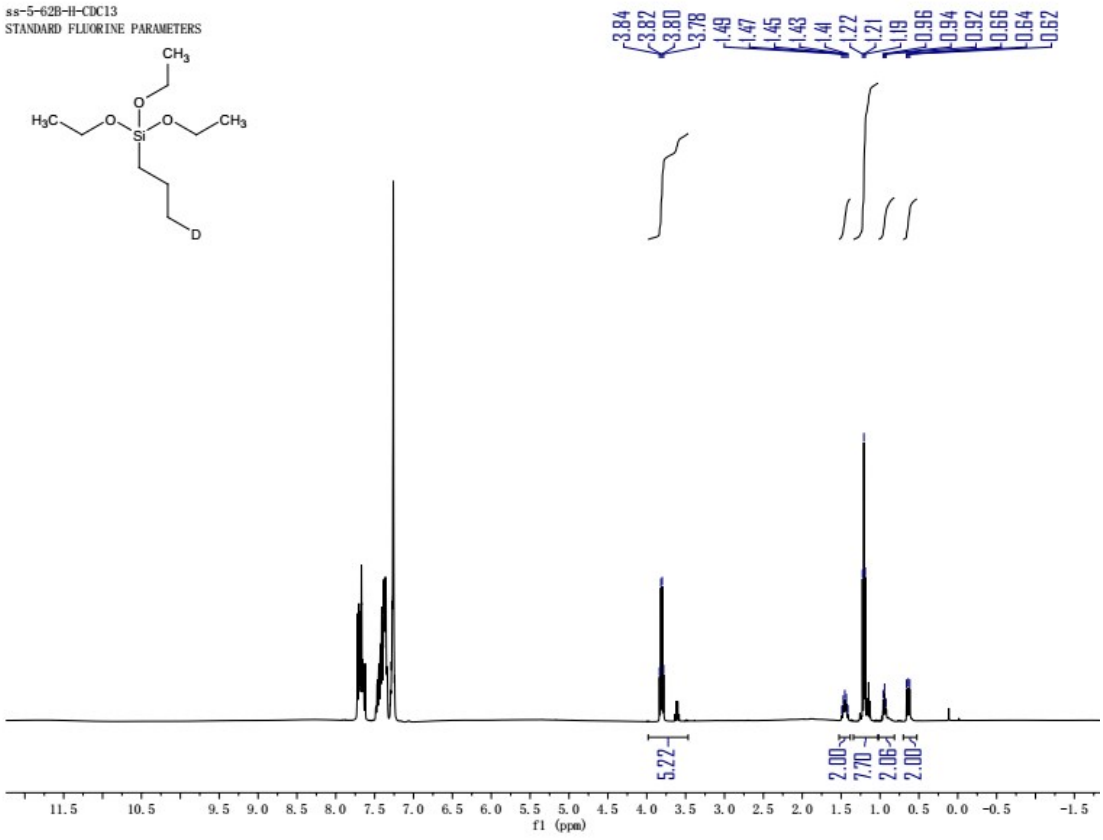
^{1}H NMR of **2E** in $CDCl_3$



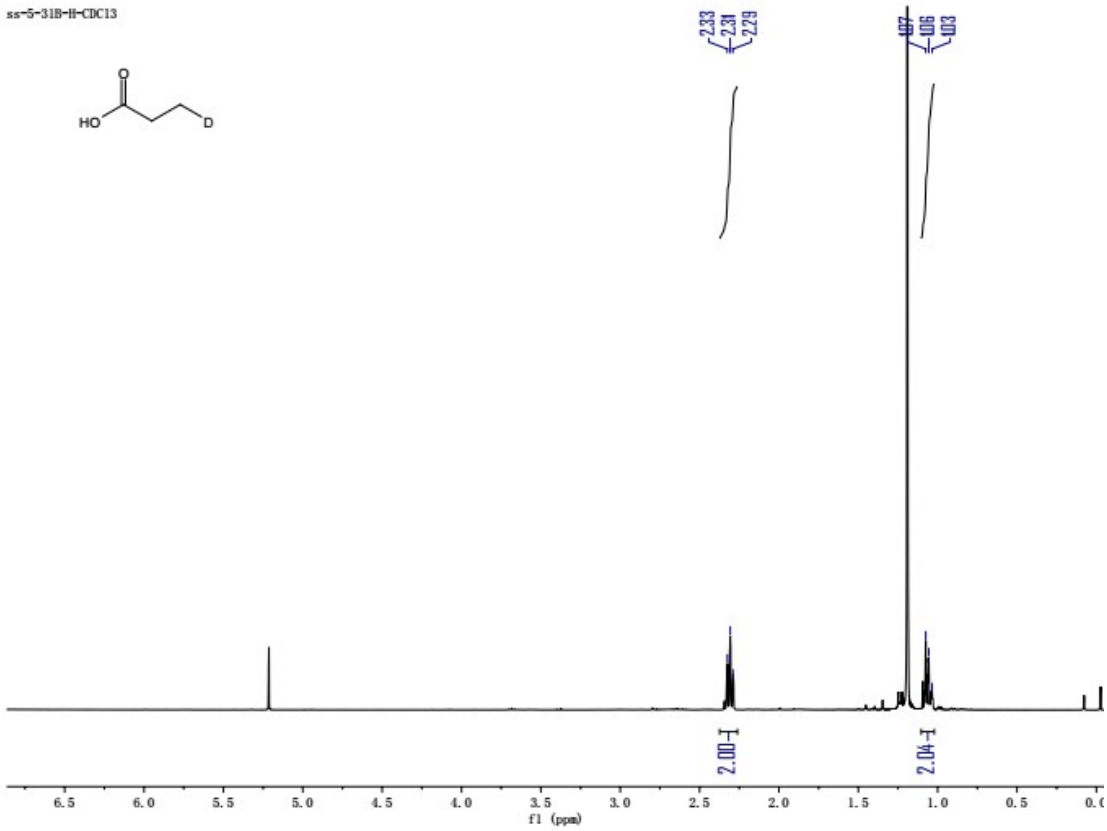
^{13}C NMR of **2E** in $CDCl_3$



The crude ^{1}H NMR of **2F** in $CDCl_3$



The crude ^{1}H NMR of **2G** in $CDCl_3$



The crude ^{13}C NMR of **2G** in $CDCl_3$