Supporting Information

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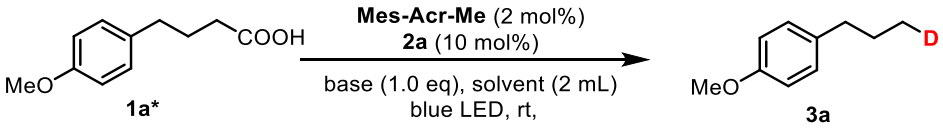
1. General Information.

All the reactions were conducted in oven-dried Schlenk tubes or recirculation reactor under argon atmosphere. All solvents and chemicals were obtained from commercial suppliers and used without further purification. Anhydrous Dichloromethane (DCM) was purified from DCM (≥99.9%, HPLC) by Solvent Purification System. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR ^{11}B NMR spectra were recorded on a 400 or 500 MHz spectrometer in $CDCl_3$ (δH = 7.26 ppm, δC = 77.00 ppm as standard). Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). MS (EI) analyses were performed on a GC-MS (Agilent 7890B-5977B GC/MSD) with an EI mode. High-resolution mass spectra were obtained by ESI on a TOF mass analyzer. The 45 W blue LEDs light was purchased from Kessil (A360WE) and the peristaltic pump was purchased from Chuangrui (YZ1515x).

2. Optimization of the reaction conditions.

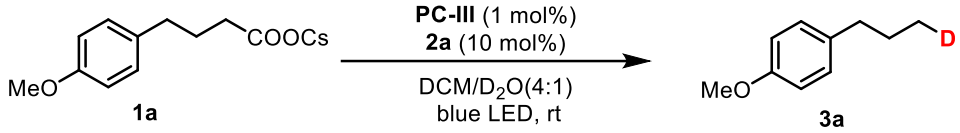
Table S1. Direct decarboxylative deuteration of 4-(4-Methoxyphenyl)butyric acid.



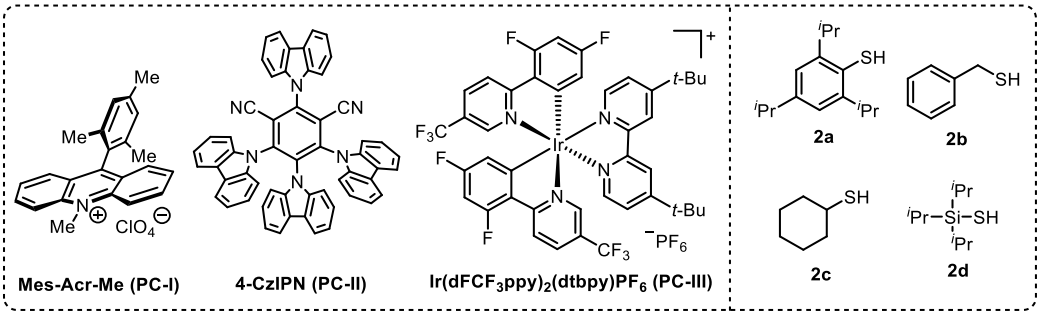
Entry	Base	Solvent	Yield[b]	D-inc.[c]
2	collidine	DCM/D_2O(4:1)	32%	95%
3	Cs_2CO_3(1eq)	DCM/D_2O(4:1)	16%	-
4	CsOH(2 eq)	DCM/D_2O(4:1)	57%	60%
5	Pr_2NEt	DCM/D_2O(4:1)	10%	-
6	KOBu	DCM/D_2O(4:1)	6%	-
7	2.6-lutidine	DCM/D_2O (4:1)	48%	95%
8	2.6-lutidine	CF_3CH_2OH/D_2O(4:1)	n.d	-
9	2.6-lutidine	DCM/$DCCl_3$(4:1)	19%	-
10	2.6-lutidine	DCE/D_2O(4:1)	36%	94%
11	2.6-lutidine	CH_3CN/D_2O(4:1)	nd	-
12	2.6-lutidine	pentane/D_2O(4:1)	nd	-

Reaction conditions: **1a*** (0.2 mmol), **PC** (2 mol%), thiol (10 mol%), DCM/D_2O (4:1, v/v; 2 mL), base (1 eq), blue LEDs, 18 h. [b] Measured by GC using acetophenone as internal standard due to the high volatility. [c] Deuterium incorporation was determined by HRMS-ESI. DCM = Dichloromethane, DCE = 1,2-Dichloroethane, N.D.= not detected.

Table S2. Decarboxylative deuteration of cesium 4-(4-methoxyphenyl)butanoate.

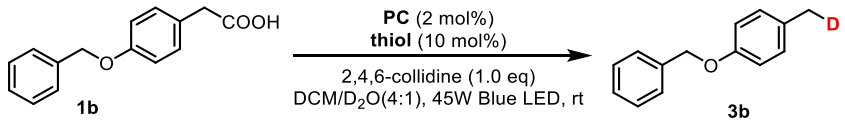


Entry	Variation of standard conditions	Yield[b]	D-inc.[c]
1	None	75%	96%
2	From sodium 4-(4-methoxyphenyl)butanoate	75%	77%
3	From potassium 4-(4-methoxyphenyl)butanoate	75%	83%
2	**PC-I** instead of **PC-III**	4%	-
3	**PC-II** instead of **PC-III**	3%	-
4	**2b** instead of **2a**	trace	-
5	**2c** instead of **2a**	23%	96%
6	**2c** instead of **2a**	14%	96%
6	CD_3OD instead of D_2O	12%	92%
7	THF instead of DCM	trace	-
8	CH_3CN instead of DCM	N.D.	-
9	DMF instead of DCM	Trace	-
10	Acetone instead of DCM	Trace	-
11	DMSO instead of DCM	N.D.	-



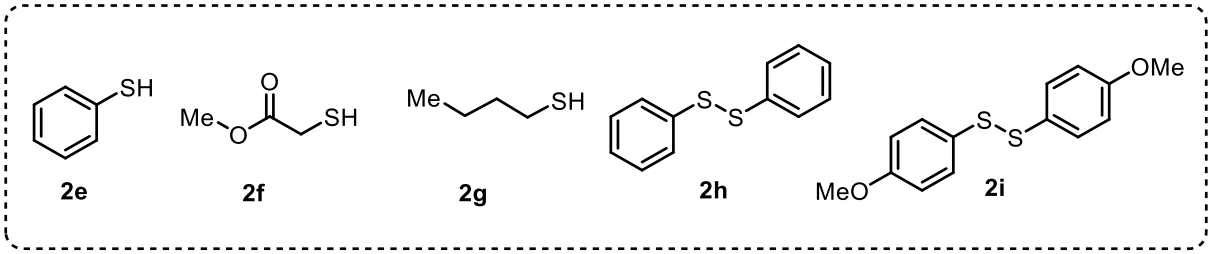
Reaction conditions: **1a** (0.2 mmol), **PC** (1 mol%), thiol (10 mol%), DCM/D_2O (4:1, v/v; 2 mL), blue LEDs, 18 h. [b] Measured by GC using acetophenone as internal standard due to the high volatility. [c] Deuterium incorporation was determined by HRMS-ESI. DCM = Dichloromethane, THF = Tetrahydrofuran, DMF = Dimethylformamide, DMSO = Dimethyl sulfoxide, N.D. = not detected. **2a** was synthesized according to Ref. 1

Table S3. Screening of photocatalysts and thilos for 2-(4-(benzyloxy)phenyl)acetic acid.



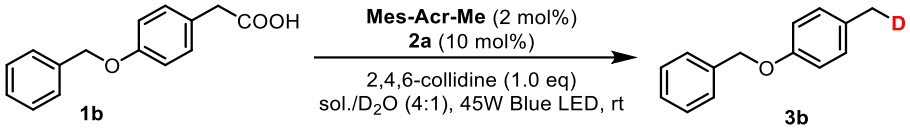
Entry	PC	HAT cat.	Yield	D-inc.
1	**PC-I**	**2a**	97%	95%
2	**PC-II**	**2a**	20%	95%
3	**PC-III**	**2a**	74%	95%
4	**PC-I**	**2b**	33%	95%
5	**PC-I**	**2c**	11%	94%

6	**PC-I**	**2d**	10%	94%
7	**PC-I**	**2e**	93%	95%
8	**PC-I**	**2f**	25%	95%
9	**PC-I**	**2g**	9%	94%
10	**PC-I**	**2h**	95%	94%
11	**PC-I**	**2i**	90%	94%



Reaction conditions: **1b** (0.2 mmol), **PC** (2 mol%), **2a** (10 mol%), 2,4,6-collidine (1.0 equiv), DCM/D_2O (4:1, v/v; 2 mL), blue LEDs, ambient temperature, 10 h. Yield of the isolated product was shown and the deuterium incorporation was determined by ^1H NMR analysis.

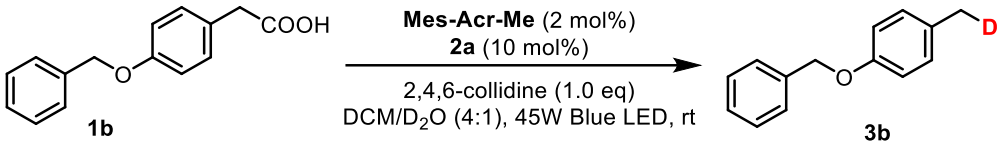
Table S4. Screening of solvents for 2-(4-(benzyloxy)phenyl)acetic acid.



Entry	Solvent	Yield	D-inc.
1	DCM	97%	95%
2	THF	trace	-
3	DMA	trace	-
4	DMSO	trace	-
5	Et_2O	trace	-
6	DCE	75%	93%
7	pentane	31%	93%
8	CH_3CN	78%	90%
9	Acetone	41%	86%
10	DCM/D_2O(1:1)	92%	95%
11	DCM/D_2O(19:1)	99%	82%
12	DCM/D_2O(99:1)	99%	60%

Reaction conditions: **1b** (0.2 mmol), **PC** (2 mol%), **2a** (10 mol%), 2,4,6-collidine (1.0 equiv), DCM/D_2O (4:1, v/v; 2 mL), blue LEDs, ambient temperature, 10 h. Yield of the isolated product was shown and the deuterium incorporation was determined by ^1H NMR analysis. DCM = Dichloromethane, THF = Tetrahydrofuran, DMA = Dimethylaniline, DMSO = Dimethyl sulfoxide, DCE = 1,2-Dichloroethane, N.D.= not detected.

Table S5. Decarboxylative deuteration in scale-up reaction.



Entry	Scale	Injection pump	Rate	Solvent	Time	Yield[b]	D-inc.[c]
1	0.4 mmol	syringe pump	2 mL/h	10 mL	7 h	56%	37%
2	0.4 mmol	syringe pump	4 mL/h	10 mL	7 h	47%	33%
3	0.4 mmol	syringe pump	8 mL/h	10 mL	7 h	66%	37%
4	0.4 mmol	peristaltic pump	10 mL/min	10 mL	7 h	65%	92%
5	0.4 mmol	peristaltic pump	30 mL/min	10 mL	7 h	65%	95%
6	5.0 mmol	peristaltic pump	30 mL/min	25 mL	8 h	87%	95%
7[d]	50 mmol	peristaltic pump	80 mL/min	100 mL	16 h	92%(86%)	95%

Reaction conditions: **1b** (1.0 equiv), **PC** (2 mol%), **2a** (10 mol%), 2,4,6-collidine (1.0 equiv), DCM/D_2O (4:1, v/v), blue LEDs. [b] Measured by GC using acetophenone as internal standard. The isolated yield was given in the parentheses. [c] Deuterium incorporation was determined by ^1H NMR analysis. [d] Conducted by using **PC** (1 mol%), **2a** (5 mol%). DCM = Dichloromethane.

3. General procedure for 0.2 mmol scale reaction.

3.1 Setup of 0.2 mmol scale reaction.

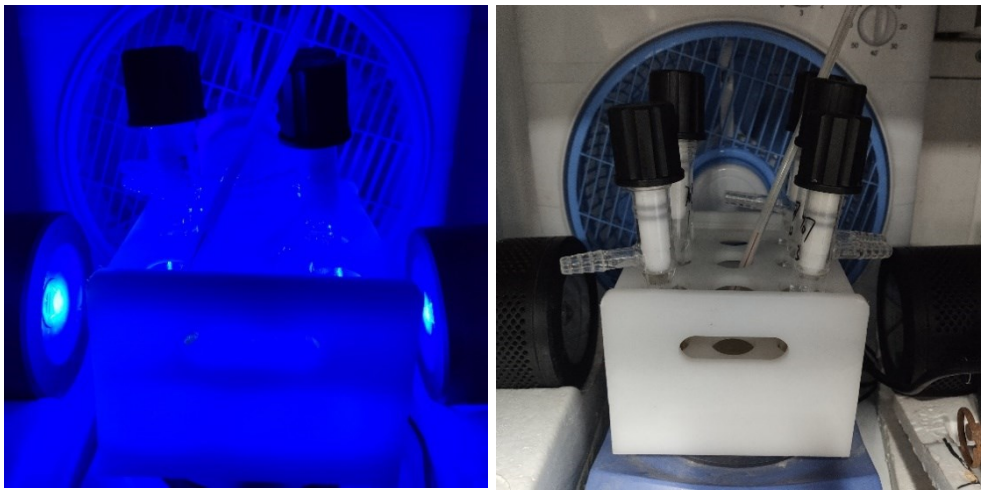
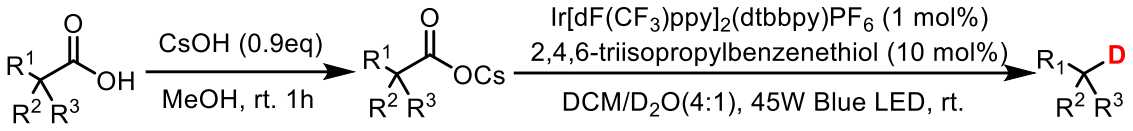


Figure S1 Setup of 0.2 mmol scale reaction

The reaction was stirred and irradiated using 45 W blue LED lamps (6 cm away, with cooling fan to keep the reaction at room temperature).

3.2 Procedure for decarboxylative deuteration of cesium carboxylate (GP1).



(R^1=alkyl)

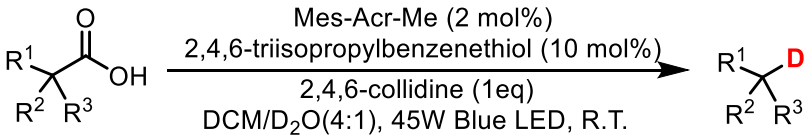
(1) Synthesis of cesium carboxylate.[2]

A 100 mL round-bottom flask equipped with a stirring bar was charged with carboxylic acid (10 mmol, 1.0 equiv.), Cesium hydroxide monohydrate (9 mmol, 0.9 equiv.), MeOH (40 mL). The mixture was stirred for 1 hour at room temperature. The solvent and water (by-product) were removed under reduced pressure at 60℃. The obtained solid was washed with ethyl acetate, filtered and dried in a vacuum drying box (50℃, 5h) to get the anhydrous white solid.

(2) Decarboxylative deuteration of cesium carboxylate

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, carboxylic acid (1 equiv., 0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol%). The flask was evacuated and backfilled with Ar for 3 times. 1.6 mL DCM, 0.4 mL D_2O and 2,4,6-triisopropylbenzenethiol (10 mol%) was added with syringe under Ar. The tube was then sealed and was stirred under the irradiation of two 45 W blue LEDs at room temperature for 10-18 h. After the reaction was finished, the reaction mixture was extracted by ethyl acetate, dried by anhydrous Na_2SO_4, filtered and collected the organic layer. The organic solvent was removed under the reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product.

3.3 Procedure for decarboxylative deuteration of carboxylic acid(GP2).



(R^1=aryl or NR^4R^5 or OR^6)

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, carboxylic acid (1 equiv., 0.2 mmol), 9-Mesityl-10-methyl acridinium perchlorate (Mes-Acr-Me) (2 mol%). The flask was evacuated and backfilled with Ar for 3 times. 1.6 mL DCM, 0.4 mL D_2O, 2,4,6-triisopropylbenzenethiol (10 mol%) and 2,4,6-collidine (1.0 eq) were added successively with syringe under Ar. The tube was then sealed and was stirred under the irradiation of two 45 W blue LEDs at room temperature for 10-18 h. After the reaction was finished, the reaction mixture was extracted by ethyl acetate, dried by anhydrous Na_2SO_4, filtered and collected the organic layer. The organic solvent

was removed under the reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product.

4. General procedure for scale-up reaction.

4.1 Recirculation reactor.

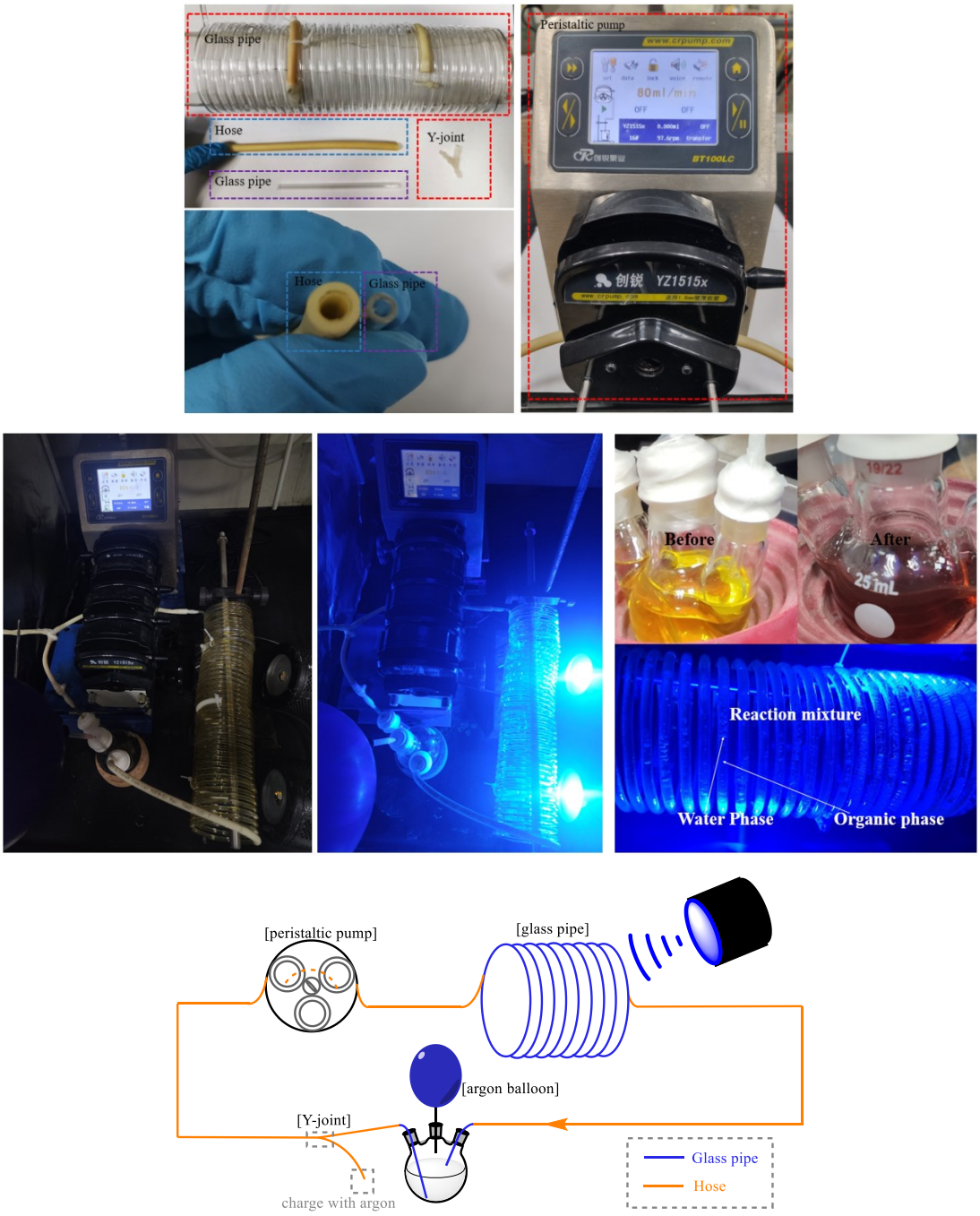


Figure S2 Recirculation reactor setup

The recirculation reactor was equipped with a peristaltic pump (Chuangrui YZ1515x with maximum peristaltic rate of 82 mL/h), a three necked bottle, glass pipe (inner diameter = 2.4 nm, outer diameter = 4.0 nm), hose with teflon material on the inner wall (Norprene®Chemical 16# : inner

diameter = 3.2 nm, outer diameter = 6.4 nm) and 45W blue LEDs(two 45W blue LEDs for 5.0 mmol scale reaction and four 45W blue LEDs for 50.0 mmol scale reaction).

4.2 Procedure for 5.0 mmol scale reaction (GP3).

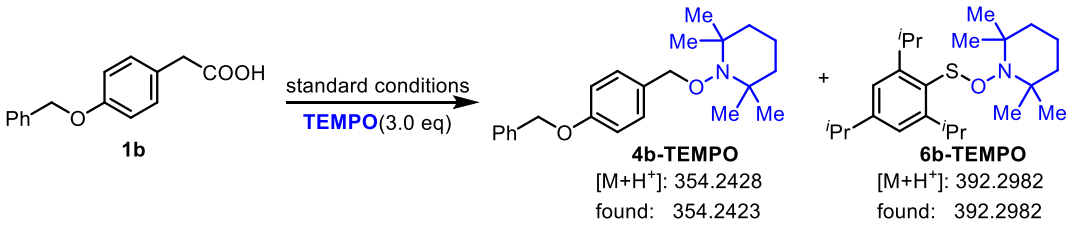
An oven-dried three-necked round bottom flask (25 mL) was equipped with carboxylic acid (5.0 mmol), and Mes-Acr-Me (2 mol%). The equipment was evacuated and backfilled with Ar for 3 times, the equipment was protected with a argon balloon. Then, 20 mL DCM and 5 mL D_2O, 2,4,6-triisopropylbenzenethiol (10 mol%), 2,4,6-collidine (1.0 eq) was injected with syringe. Next, the reaction mixture was recirculating under the irradiation of two 45 W blue LEDs with a fan at room temperature at the peristalsis rate of 30 mL/min for 8-16 h. After the reaction was finished, the reaction mixture was extracted by ethyl acetate, dried by anhydrous Na_2SO_4, filtered and collected the organic layer. The organic solvent was removed under the reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product.

4.3 Procedure for 50 mmol scale reaction (GP4).

An oven-dried three-necked round bottom flask (100 mL) was equipped with carboxylic acid (50.0 mmol) and Mes-Acr-Me (1 mol%). The equipment was evacuated and backfilled with Ar for 3 times, the equipment was protected with a argon balloon. Then, 80 mL DCM and 20.9 mL D_2O (22.0 eq), 2,4,6-triisopropylbenzenethiol (5 mol%), 2,4,6-collidine (1.0 eq) was injected with syringe. Next, the reaction mixture was recirculating under the irradiation of four 45 W blue LEDs with a fan at room temperature at the peristalsis rate of 80 mL/min for 16 h. After the reaction was finished, the reaction mixture was extracted by ethyl acetate, dried by anhydrous Na_2SO_4, filtered and collected the organic layer. The organic solvent was removed under the reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product.

5. Mechanistic investigations.

5.1 TEMPO trap experiment



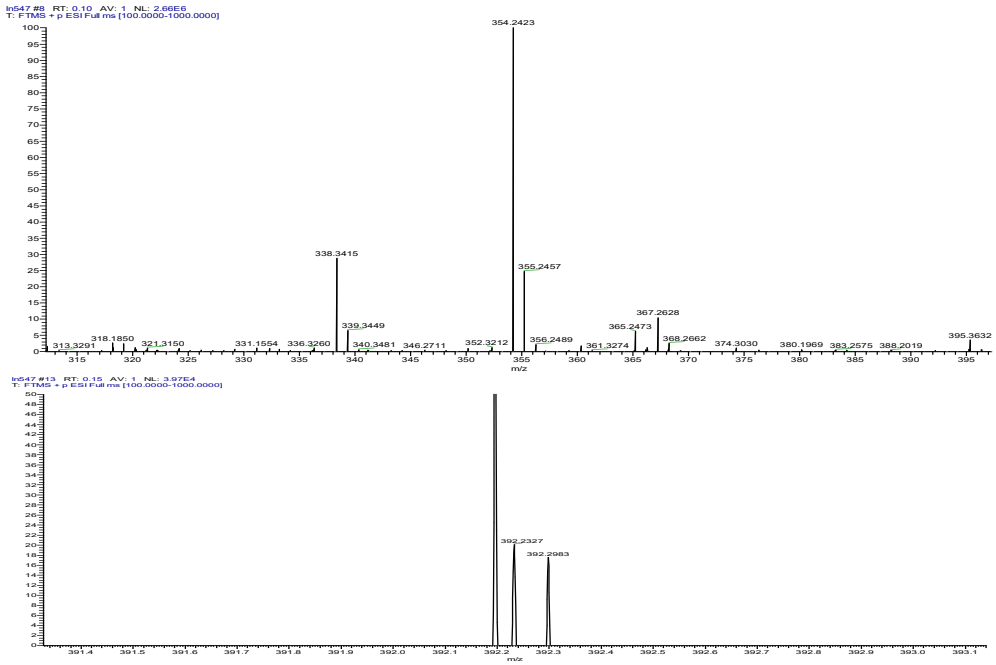


Figure S3. TEMPO trap experiment.

The reaction was completely inhibited by TEMPO, the production of **4b-TEMPO** (HRMS-ESI: m/z Calculated for $C_{23}H_{32}NO_2^+$ [M+H$^+$]: 354.2428, found 354.2423) and **6b-TEMPO** (HRMS-ESI: m/z Calculated for $C_{24}H_{42}NOS^+$ [M+H$^+$]: 392.2982, found 392.2982) proved the existence of benzyl radical and thiyl radical intermediates.

5.2 Quantum yield.

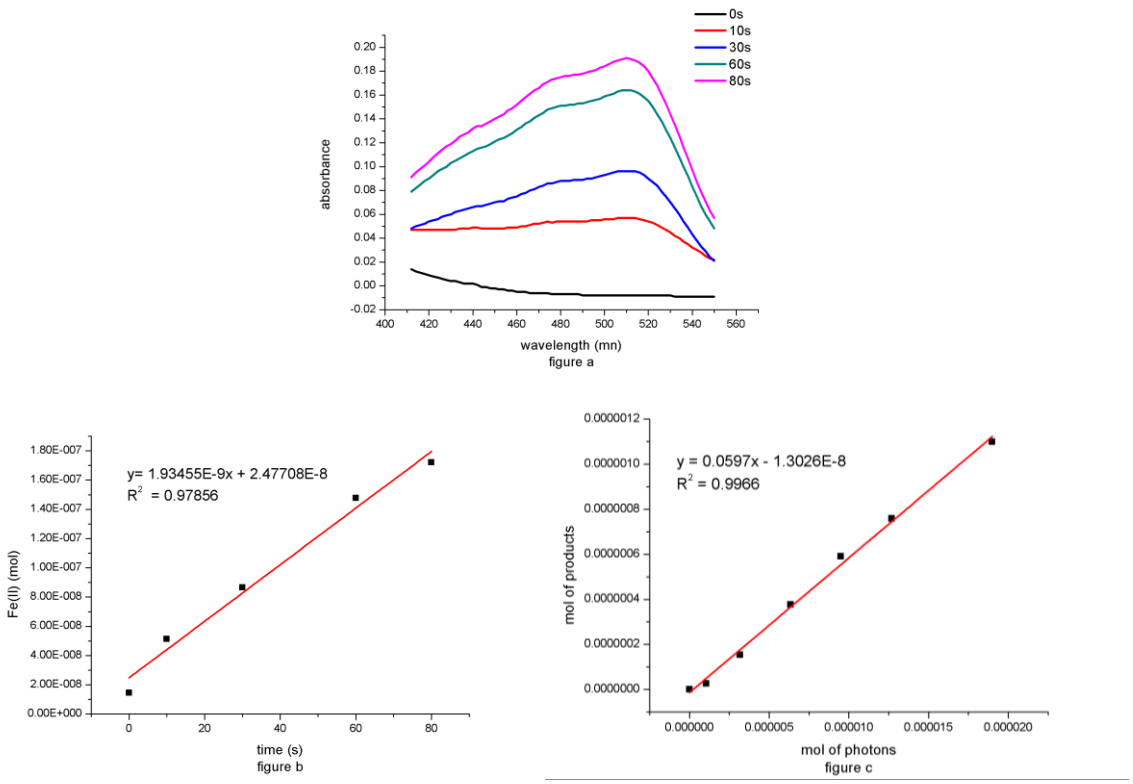


Figure S4. The UV-Vis spectrum and data of quantum yield

The quantum yield (Φ) was determined by the known ferrioxalate actinometry method. A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in *Handbook of Photochemistry*. The actinometry solutions (1.0 mL) were irradiated with two 45 W blue LEDs for specified time intervals (0 s, 10 s, 30 s, 60 s, 80 s). The UV-Vis spectra is shown in figure a. Based on the data, we got the graph between the number of moles of products (y axis) and time (x axis). Then, the irradiated light intensity was estimated to 1.76 x 10^{-9} einstein S^{-1} by using $K_3[Fe(C_2O_4)_3$ as an actinometer. For a clean tube, according to the **GP2**, the 0.2 mmol scale model reaction（1b）solution was irradiated with two 45 W blue LEDs for specified time intervals (0 min, 30 min, 60 min, 90 min, 120 min and 180 min). The moles of products formed were determined by GC yield with biphenyl as internal standard. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from the light intensity. The slope gives the quantum yield (Φ) of the photoreaction, 0.0579 (6.0%).

5.3 Cyclic voltammetry (CV).

Cyclic Voltammetry were collected using CHI660E from Shanghai Chenhua Instruments Limited (SCHI). Sample (0.001 M) and tetrabutylammonium hexafluorophosphate (0.1 M) in anhydrous MeCN were used for tests. Measurements were run using glassy carbon working electrode, platinum wire counter electrode, and 0.01 M $AgNO_3$ silver-silver chloride reference electrode in a scan rate of 0.1 V/s. In addition, ferrocene was used as conversion constant calibration to SCE.

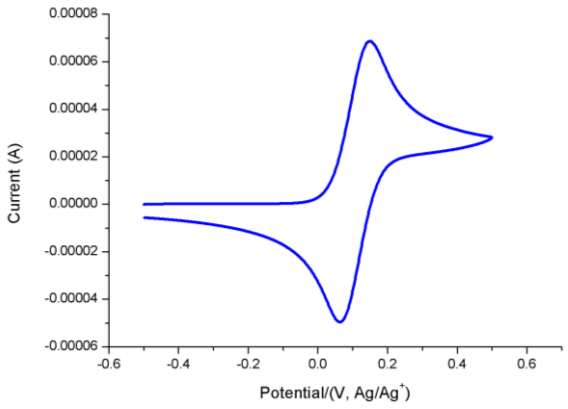


Figure S5. The CV data of ferrocene

$E_{1/2}[Fc^+/Fc]$ = +0.1065 V vs $Ag/AgNO_3$ (0.01 M) in acetonitrile.

$E_{1/2}[Fc^+/Fc]$ = +0.380 V vs SCE in acetonitrile. (reference value)

The conversion constant between the reference electrode and SCE is + 0.2735 V.

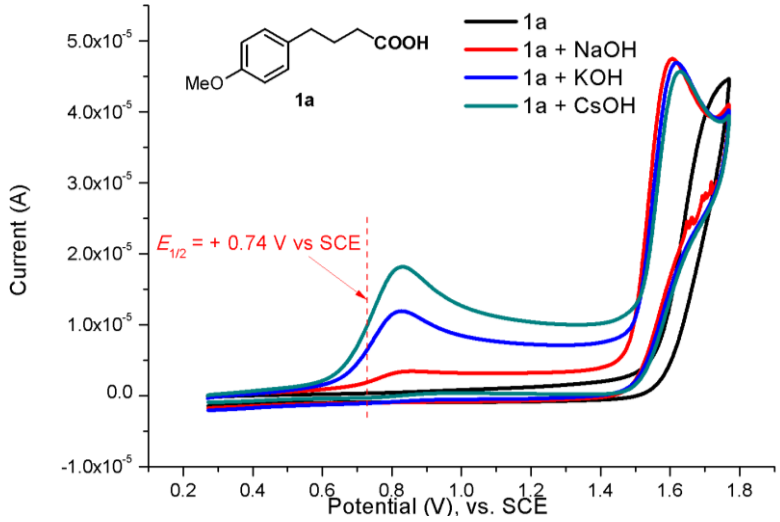


Figure S6. The CV data of diffferent carboxylate

With the addition of 10 equiv of different inorganic bases to **1a**, there occurs a significant peak (especially CsOH was added) at 0.74 V vs SCE (the oxidation potential of carboxylate).

6. Light-dependent evidence.

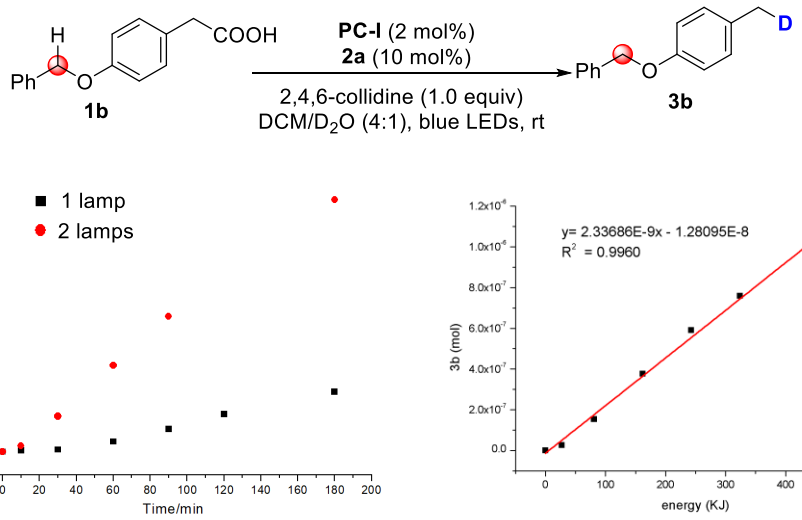
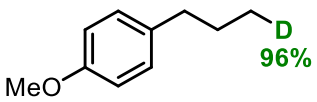


Figure S7. Comparison of initial rate under 2 blue LED lamps and 1 blue LED lamp.

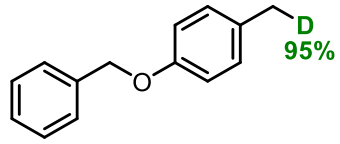
The initial reaction rate of this decarboxylative deuteration was heavily light-dependent since a dramatically decreased rate was observed when only one LED lamp was used rather than two lamps. And it is found that the energy efficiency is 2.3^10^{-6} mol/KJ for the decarboxylative deuteration of **1b** under the irridation of the 45W blue LEDs.

7. Characterization of products.



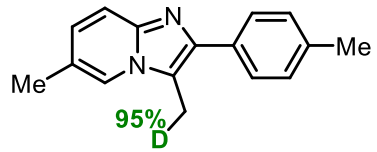
1-methoxy-4-(propyl-3-d)benzene **(3a)**

Following **GP1** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3a** (15.7 mg) was obtained in 52% yield as a colorless oil (75% GC yield due to the high volatility) with 96% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.56 – 2.49 (m, 2H), 1.60 (p, *J* = 7.5 Hz, 2H), 0.91 (tt, *J* = 7.4, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.6, 134.8, 129.3, 113.6, 55.3, 37.1, 24.7, 13.5 (t, *J* = 19.1 Hz, C-D). IR (ATR): ν = 3363, 2922, 2852, 2349, 1660, 1634, 1109, 803 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{10}H_{14}DO^{+}$ [M+H^{+}]: 152.1180, found 152.1181.



*1-(benzyloxy)-4-(methyl-d)benzene***(3b)**

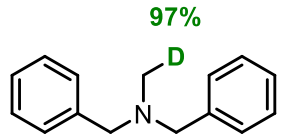
Following **GP2** with reaction time of 10 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =100:1), compound **3b** (38.6 mg) was obtained in 97% yield as a white powder (mp: 210-214 °C) with 95% D-incorporation (determined by ^{1}H NMR). Large-scale reaction was conducted following **GP4** with reaction time of 16 h, obtained **3b** (8.6 g) in 86% isolated yield (92% GC yield) with 95% D- incorporation. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.9 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.07 (s, 2H), 2.31 (t, *J* = 1.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.7, 137.3, 130.2, 129.9, 128.6, 127.9, 127.5, 114.8, 70.1, 20.2 (t, *J* = 19.2 Hz, C-D). IR (ATR): ν = 3032, 2918, 1610, 1580, 1508, 1234, 1009, 726, 503 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{14}H_{13}DNaO^{+}$ [M+Na^{+}]: 222.1000, found 222.0995.



*6-methyl-3-(methyl-d)-2-(p-tolyl)imidazo[1,2-a]pyridine***(3c)**

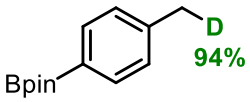
Following **GP2** (CH_3CN as solvent due to **1c** is insoluble in DCM) with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =1:2), compound **3c** (36.2 mg) was obtained in 76% yield as a yellow powder (mp: 107-111 °C) with 95% D-inc. (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.67 (d, *J* = 3.7 Hz, 2H), 7.54 (d, *J* = 9.1 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.02 (dd, *J* = 9.1, 1.6 Hz, 1H), 2.58 (t, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 142.3, 136.9, 132.1, 129.2, 128.1, 126.5, 121.5, 120.6, 116.7, 115.3, 21.3, 18.4, 9.5 (t, *J* = 19.7 Hz, C-D). IR (ATR):

ν = 2919, 2858, 1501, 1389, 1338, 822, 794, 508 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{16}H_{16}DN_2^+$ [M+H$^+$]: 238.1449, found 238.1445.



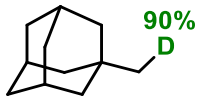
N,N-dibenzylmethanamine-d (**3d**)

Following **GP2** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3d** (32.4 mg) was obtained in 76% yield as a light yellow oil with 97% D-incorporation (determined by HRMS). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 8H), 7.27 – 7.20 (m, 2H), 3.52 (s, 4H), 2.15 (t, J = 1.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 139.2, 128.9, 128.2, 126.9, 61.8, 41.9 (t, J = 20.3 Hz). IR (ATR): ν = 3062, 3027, 2925, 2792, 1494, 1453, 1367, 1059, 734, 679 cm^{-1}. HRMS (ESI): Calculated for $C_{15}H_{17}DN^+$ [M+H$^+$]: 213.1497, found 213.1495.



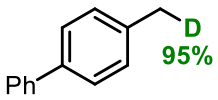
4,4,5,5-tetramethyl-2-(4-(methyl-d)phenyl)-1,3,2-dioxaborolane **(3e)**

Following **GP2** with reaction time of 20 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3e** (21.8 mg) was obtained in 50% yield as a light yellow oil with 94% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.36 (t, *J* = 2.1 Hz, 2H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.3, 134.8, 128.5, 121.7, 83.6, 24.8, 21.5 (t, *J* = 19.2 Hz). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.3. IR (ATR): ν = 2977, 2927, 1613, 1356, 1182, 1142, 858, 670, 436 cm^{-1}. HRMS (ESI): Calculated for $C_{13}H_{19}DBO_2^+$ [M+H$^+$]: 220.1614, found 220.1607



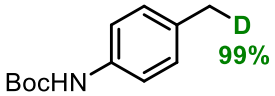
*(3r,5r,7r)-1-(methyl-d)adamantane***(3f)**

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: *n*-pentan), compound **3f** (17.9 mg) was obtained in 59% yield as a white powder (mp: 104-107 ℃) with 90% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.96 – 1.87 (m, 3H), 1.72 – 1.56 (m, 6H), 1.45 (d, *J* = 2.8 Hz, 6H), 0.74 (t, *J* = 1.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 44.6, 36.9, 31.1 (t, *J* = 18.9 Hz, C-D), 28.9. IR (ATR): ν = 3355, 3186, 2920, 2850, 1659, 1632, 1470, 763, 749 cm^{-1}. MS (EI): m/z: 151.1, 135.1.



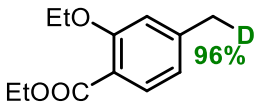
*4-(methyl-d)-1,1'-biphenyl***(3g)**

Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether), compound **3g** (28.6 mg) was obtained in 85% yield as a white solid(mp: 70-73 ℃) with 95% D-incorporation (determined by ^{1}H-NMR). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (dt, *J* = 8.1, 1.9 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.36 (td, *J* = 7.2, 1.5 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.45 – 2.39 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.1, 138.3, 136.9, 129.5, 128.7, 127.0, 126.9, 20.8 (t, *J* = 19.4 Hz). IR (ATR): ν = 3056, 3030, 2921, 1487, 1007, 817, 751, 696, 473 cm^{-1}. MS (EI): m/z: 169.1, 153.1.



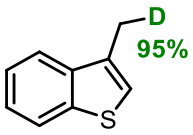
*tert-butyl (4-(methyl-d)phenyl)carbamate***(3h)**

Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =3:1), compound **3h** (30.1 mg) was obtained in 72% yield as a white solid(mp: 82-85 ℃) with 99% D-incorporation (determined by ESI-HRMS and ^{1}H-NMR). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.46 (s, 1H), 2.32 – 2.25 (m, 2H), 1.52 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.9, 135.7, 132.4, 129.4, 118.2, 28.3, 20.4 (t, *J* = 19.3 Hz). IR (ATR): ν = 3329, 2978, 2927, 1698, 1522, 1156, 1028, 1018, 549 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{12}H_{16}DNO_2Na^+$ [M+Na$^+$]: 231.1214, found 231.1207



*ethyl 2-ethoxy-4-(methyl-d)benzoate***(3i)**

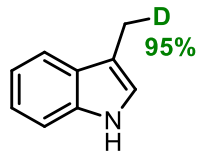
Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3i** (32.5 mg) was obtained in 78% yield as a colorless oil with 96% D-incorporation (determined by ESI-HRM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.42 – 2.23 (m, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.4, 158.6, 144.1, 131.6, 120.8, 117.7, 114.0, 64.4, 60.5, 21.6 (t, *J* = 19.4 Hz), 14.7, 14.3. IR (ATR): ν = 2980, 2931, 1726, 1698, 1237, 1076, 1041, 772, 704 cm^{-1}.HRMS (ESI): m/z Calculated for $C_{12}H_{16}DO_3^+$ [M+H$^+$]: 210.1235, found 210.1237.



*3-(methyl-d)benzo[b]thiophene***(3j)**

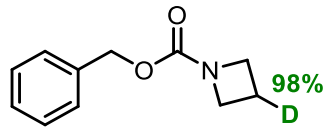
Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3j** (20.5 mg) was obtained in 69% yield as a

colorless oil with 95% D-incorporation (determined by ^{1}H-NMR). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.39 (dddd, *J* = 23.8, 8.4, 7.2, 1.2 Hz, 2H), 7.09 (s, 1H), 2.49 – 2.42 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.2, 139.6, 132.1, 124.0, 123.8, 122.7, 121.7, 121.4, 13.7 (t, *J* = 19.5 Hz). IR (ATR): ν = 3062, 2918, 1082, 1019, 1426, 832, 765, 703, 416 cm^{-1}. HRMS (ESI): m/z Calcd for $C_9H_8DS^+$ [M+H$^+$]: 150.0482, found 150.0478.



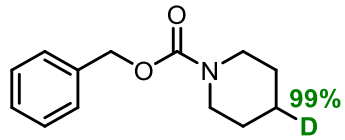
*3-(methyl-d)-1H-indole***(3k)**

Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =5:1), compound **3k** (21.7 mg) was obtained in 82% yield as a yellow solid(mp: 80-85 ℃) with 95% D-incorporation (determined by ^{1}H NMR) 95% D-incorporation (determined by ^{1}H-NMR). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.91 (m, 1H), 2.37 – 2.34 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.2, 128.2, 121.8, 121.5, 119.1, 118.8, 111.6, 110.9, 9.4 (d, *J* = 19.4 Hz). IR (ATR): ν = 3416, 2921, 1456, 1265, 1086, 1070, 737, 423 cm^{-1}. HRMS (ESI): m/z Calcd for $C_9H_9DN^+$ [M+H$^+$]: 133.0871, found 133.0868.



*benzyl azetidine-1-carboxylate-3-d***(3l)**

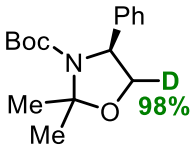
Following **GP1** with reaction time of 16 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =10:1), compound **3l** (13.4 mg) was obtained in 35% yield as a colorless oil with 98% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.27 (m, 5H), 5.09 (s, 2H), 4.02 (d, *J* = 7.7 Hz, 4H), 2.21 (pt, *J* = 7.5, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.3, 136.8, 128.4, 127.9, 127.9, 66.4, 15.4 (t, *J* = 21.3 Hz, C-D). IR (ATR): ν = 2955, 2888, 1699, 1408, 1351, 1116, 976, 767, 751, 603 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{11}H_{13}DNO_2^+$ [M+H$^+$]: 193.1082, found 193.1082.



*benzyl piperidine-1-carboxylate-4-d***(3m)**

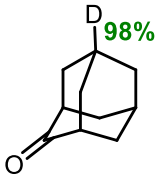
Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =10:1), compound **3m** (30.2 mg) was obtained in 68% yield as a light yellow oil with 99% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.35 – 7.27 (m, 1H), 5.13 (s, 2H), 3.44 (t, *J* = 5.5 Hz, 4H), 1.61 – 1.47 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.3, 137.0, 128.4, 127.9, 127.8, 66.9, 44.9, 25.6, 24.0 (t, *J* = 19.3 Hz, C-D). IR (ATR): ν = 2927, 2852, 1692, 1424, 1222, 1127, 1021, 733 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{13}H_{17}DNO_2^+$ [M+H$^+$]: 221.1395, found 221.1389.



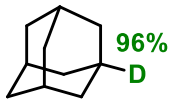
*tert-butyl (4S)-2,2-dimethyl-4-phenyloxazolidine-3-carboxylate-5-d***(3n)**

Following **GP1** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =10:1), compound **3n** (30.5 mg) was obtained in 55% yield as a white powder(mp: 82-85 ℃) with 98% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 5H), 4.86 (d, *J* = 67.0 Hz, 1H), 3.84 (s, 1H), 1.78 (s, 3H), 1.61 (s, 3H), 1.46 (s, 3H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 142.3, 128.2, 127.1, 126.3, 94.5, 70.5 (t, *J* = 21.8 Hz, C-D), 61.2, 28.1, 25.9, 23.9. IR (ATR): ν = 2977, 2934, 1693, 1375, 1363, 1087, 1061, 851, 698, 657 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{16}H_{22}DNNaO_3^+$ [M+Na$^+$]: 301.1633, found 301.1627.



*(1R,3S,5r,7s)-adamantan-2-one-5-d***(3o)**

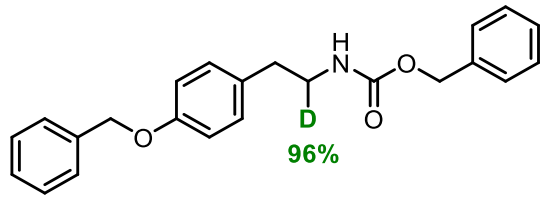
Following **GP1** with reaction time of 16 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3o** (27.2 mg) was obtained in 90% yield as a white powder(mp: 110-116 ℃) with 92% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.58 – 2.46 (m, 2H), 2.08 – 2.03 (m, 4H), 2.01 – 1.97 (m, 4H), 1.96 – 1.94 (m, 1H), 1.91 – 1.89 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 218.5, 46.9, 39.2, 391, 36.1, 27.4, 27.0 (t, *J* = 20.3 Hz, C-D). IR (ATR): ν = 2918, 2853, 1719, 1703, 145, 1057, 465 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{10}H_{14}DO^+$ [M+H$^+$]: 152.1180, found 152.1180.



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

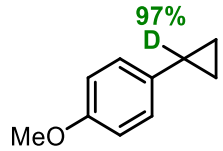
Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: *n*-pentane), compound **3p** (8.5 mg) was obtained in 31% yield (98% GC yield) as a white powder (mp: 93-102 ℃) with 96% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.90 – 1.85 (m, 3H), 1.76 – 1.73 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ

37.8, 37.6, 28.3, 27.8 (t, J = 20.0 Hz, C-D). IR (ATR): ν = 3361, 2899, 2847, 1659, 1632, 1264, 734, 704 cm^{-1}. MS (EI): m/z: 137.1, 122.1, 94.1, 80.1, 67.1.



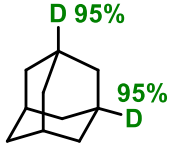
*benzyl (2-(4-(benzyloxy)phenyl)ethyl-1-d)carbamate***(3q)**

Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3q** (42.9 mg) was obtained in 60% yield as a white powder (mp: 183-190 ℃) with 96% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.36 (m, 5H), 7.39 – 7.29 (m, 5H), 7.10 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 5.11 (s, 2H), 5.05 (s, 2H), 4.79 (s, 1H), 3.42 (q, J = 6.9 Hz, 1H), 2.76 (d, J = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.5, 156.3, 137.0, 136.5, 130.9, 129.7, 128.5, 128.5, 128.0, 127.9, 127.4, 115.0, 70.0, 66.6, 42.0 (t, J = 21.0 Hz), 35.0. IR (ATR): ν = 3324, 3061, 3036, 2922, 2863, 1680, 1535, 1511, 1244, 696, 577 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{23}H_{23}DNO_3^+$ [M+H^+]: 363.1813, found 363.1811.



*1-(cyclopropyl-1-d)-4-methoxybenzene***(3r)**

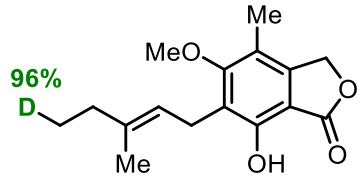
Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =100:1), compound **3r** (16.3 mg) was obtained in 55% yield as a light yellow powder with 97% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 – 7.01 (m, 2H), 6.83 – 6.80 (m, 2H), 3.78 (s, 3H), 0.90 – 0.87 (m, 2H), 0.63 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 135.8, 126.8, 113.8, 55.3, 14.3 (d, J = 24.4 Hz, C-D), 8.4. IR (ATR): ν = 3002, 2926, 2834, 1514, 1244, 1035, 822, 538 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{10}H_{12}DO^+$ [M+H^+]: 150.1024, found 150.1024.



(1r,3r,5s,7s)-adamantane-1,3-d_2**(3s)**

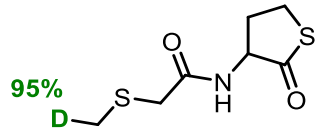
Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: *n*-pentane), compound **3s** (5.5 mg) was obtained in 20% yield (37% GC yield) as a white powder (mp: 95-99 ℃) with 95% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.87 (p, J = 3.1 Hz, 2H), 1.74 (d, J = 3.4 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-

d) δ 37.8, 37.6, 37.5, 28.3, 27.8 (t, *J* = 19.9 Hz, C-D). IR (ATR): ν = 3361, 3186, 2921, 2851, 1658, 1632, 1468, 749 cm^{-1}. MS (EI): m/z: 138.1, 123.1, 94.1, 80.1, 68.1.



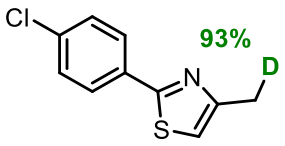
*(E)-7-hydroxy-5-methoxy-4-methyl-6-(3-methylpent-2-en-1-yl-5-d)isobenzofuran-1(3H)-one***(3t)**

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =5:1), compound **3t** (27.1 mg) was obtained in 49% yield as a white powder(mp: 77-79 ℃) with 96% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 5.19 (s, 2H), 5.18 – 5.13 (m, 1H), 3.77 (s, 3H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.14 (s, 3H), 1.97 (t, *J* = 7.4 Hz, 2H), 1.78 (s, 3H), 0.94 (tt, *J* = 7.5, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 163.7, 153.7, 143.9, 137.7, 122.6, 120.4, 116.7, 106.3, 70.0, 61.0, 32.3, 22.6, 16.1, 12.3 (t, *J* = 19.2 Hz, C-D), 11.6. IR (ATR): ν = 3425, 2932, 2852, 1729, 1622, 1191, 1166, 1133, 1074, 542 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{16}H_{20}DO_4^+$ [M+H^+]: 278.1497, found 278.1490.



*2-((methyl-d)thio)-N-(2-oxotetrahydrothiophen-3-yl)acetamide***(3u)**

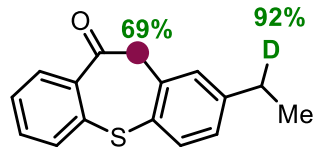
Following **GP2** with reaction time of 20 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =1:1), compound **3u** (37.8 mg) was obtained in 92% yield as a white powder (mp: 152-156 ℃) with 95% D-incorporation (determined by HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.58 (dt, *J* = 13.0, 7.0 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.29 – 3.24 (m, 1H), 3.22 (s, 2H), 2.86 – 2.79 (m, 1H), 2.34 – 2.09 (m, 2H), 2.00 (qd, *J* = 12.4, 7.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.8, 169.1, 59.3, 37.8, 31.4, 27.4, 15.9 (t, *J* = 21.3 Hz). IR (ATR): ν = 3293, 3055, 2932, 2862, 1697, 1649, 1514, 731 cm^{-1}. HRMS (ESI): m/z Calculated for $C_7H_{11}DNO_2S_2^+$ [M+H^+]: 207.0367, found 207.0367.



*2-(4-chlorophenyl)-4-(methyl-d)thiazole***(3v)**

Following **GP2**, the yield was less than 30%. To improve the conversion rate, we increased the catalyst equivalent and reaction time (**PC-I** 5mmol%, **2a** 20 mmol%, 24 h). After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3v** (32.6 mg) was obtained in 77% yield as a white powder (mp: 145-149 ℃) with 93% D-incorporation (determined by

^{1}H-NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 2H), 7.40 – 7.38 (m, 2H), 6.88 (s, 1H), 2.56 – 2.37 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 154.0, 135.7, 132.3, 129.1, 127.6, 113.7, 17.0 (t, *J* = 19.5 Hz). HRMS (ESI): m/z Calculated for $C_{10}H_8DClNS^+$ [M+H$^+$]: 211.0202, found 211.0206.



*2-(ethyl-1-d)dibenzo[b,f]thiepin-10(11H)-one***(3w)**

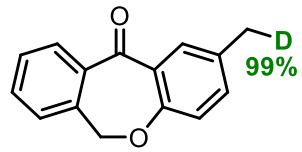
Following **GP2** with reaction time of 20 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3w** (50.2 mg) was obtained in 98% yield as a light yellow oil with 92% D-incorporation (determined by ^{1}H-NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.41 (td, *J* = 7.5, 1.6 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.03 (dd, *J* = 7.9, 2.0 Hz, 1H), 4.34 (s, 1H), 2.68 – 2.56 (m, 1H), 1.21 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.7, 146.6, 140.6, 137.5, 136.1, 132.3, 131.4, 131.3, 131.1, 130.7, 128.9, 126.7, 126.6, 51.0 (C-H), 50.7 (t, *J* = 20.1 Hz, C-D), 28.5 (C-H), 28.1 (t, *J* = 19.3 Hz, C-D), 15.3. IR (ATR): ν = 2963, 2928, 1667, 1457, 1428, 1273, 751, 512, 491 cm^{-1}.

HRMS (ESI): m/z Calculated for $C_{16}H_{11}D_3OS^+$ [M+H$^+$]: 258.1026, found 258.1021 (Relative: 73.74)

HRMS (ESI): m/z Calculated for $C_{16}H_{12}D_2OS^+$ [M+H$^+$]: 257.0964, found 257.0958 (Relative: 100.00)

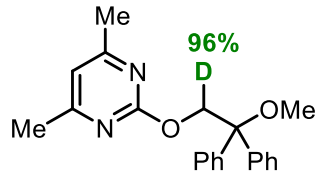
HRMS (ESI): m/z Calculated for $C_{16}H_{13}DOS^+$ [M+H$^+$]: 256.0901, found 256.0896 (Relative: 32.97)

HRMS (ESI): m/z Calculated for $C_{16}H_{14}OS^+$ [M+H$^+$]: 255.0838, found 255.0834 (Relative: 3.46)



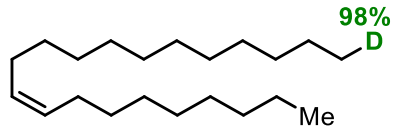
*2-(methyl-d)dibenzo[b,e]oxepin-11(6H)-one***(3x)**

Following **GP2** with reaction time of 18 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3x** (29.7 mg) was obtained in 66% yield as light yellow needle-like crystals(mp: 93-95 ℃), 99% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (td, *J* = 7.4, 1.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 2H), 2.45 (t, *J* = 2.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 143.0, 141.8, 139.0, 136.5, 127.5, 126.6, 126.2, 125.7, 124.9, 119.5, 119.5, 36.7, 21.3 (t, *J* = 19.3 Hz). IR (ATR): ν = 3021, 2917, 1454, 1264, 953, 759, 417 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{15}H_{12}DO_2^+$ [M+H$^+$]: 226.0973, found 226.0969.



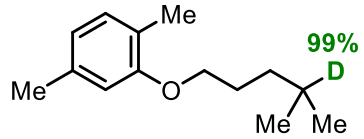
*2-(2-methoxy-2,2-diphenylethoxy-1-d)-4,6-dimethylpyrimidine***(3y)**

Following **GP2** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =1:1), compound **3y** (51.8 mg) was obtained in 77% yield as light yellow plate-like crystals(mp: 102-106 ℃) with 96% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 7.2, 1.5 Hz, 4H), 7.33 – 7.27 (m, 4H), 7.26 – 7.20 (m, 2H), 6.60 (s, 1H), 5.08 (s, 1H), 3.31 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 164.7, 142.8, 127.9, 127.7, 127.1, 114.0, 81.7, 69.2 (t, *J* = 22.4 Hz, C-D), 52.0, 23.7. IR (ATR): ν = 3026, 2935, 2827, 1590, 1557, 1545, 1096, 1075, 754, 732, 697 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{21}H_{22}DN_2O_2^+$ [M+H$^+$]: 336.1817, found 336.1808.



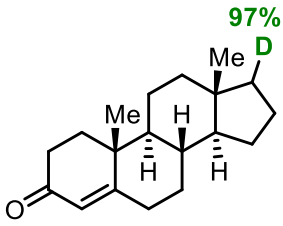
*(Z)-henicos-9-ene-21-d***(3z)**

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether), compound **3z** (58.1 mg) was obtained in 98% yield as a colorless oil with 98% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.40 – 5.30 (m, 2H), 2.05 – 1.97 (m, 4H), 1.34 – 1.25 (m, 30H), 0.92 – 0.83 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 130.4, 129.9, 32.6, 31.9, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.2, 27.2, 22.7, 22.6, 14.1, 13.8 (t, *J* = 19.0 Hz, C-D). MS (EI): m/z: 295.3, 168.2, 139.1, 111.1, 83.1, 55.1.



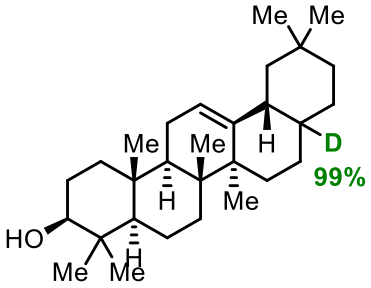
*1,4-dimethyl-2-((4-methylpentyl-4-d)oxy)benzene***(3aa)**

Following **GP1** with reaction time of 16 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =100:1), compound **3aa** (38.3 mg) was obtained in 92% yield as a light yellow oil with 99% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 1.85 – 1.77 (m, 2H), 1.40 – 1.35 (m, 2H), 0.94 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 136.4, 130.2, 123.6, 120.5, 112.0, 68.2, 35.2, 27.3 (t, *J* = 19.0 Hz, C-D), 27.3, 22.5, 21.4, 15.8. IR (ATR): ν = 2921, 2852, 1464, 749, 721 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{14}H_{22}DO^+$ [M+H$^+$]: 208.1806, found 208.1806.



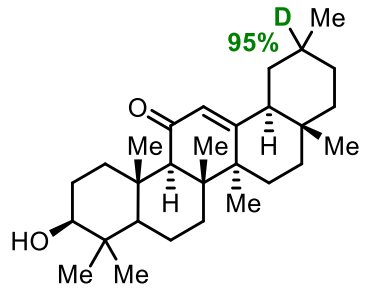
*(8S,9S,10R,13S,14S)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one-17-d***(3bb)**

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3bb** (50.5 mg) was obtained in 92% yield as white needled crystals(mp: 125-127 ℃) with 97% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.70 (s, 1H), 2.44 – 2.21 (m, 4H), 2.04 – 1.97 (m, 1H), 1.88 – 1.81 (m, 1H), 1.77 – 1.38 (m, 9H), 1.22 – 1.01 (m, 6H), 0.97 – 0.85 (m, 2H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.5, 171.5, 123.7, 54.0, 53.9, 40.5, 39.7 (t, *J* = 19.2 Hz, C-D), 38.6, 38.4, 35.9, 35.7, 34.0, 33.0, 32.3, 25.4, 21.0, 20.3, 17.3, 17.3. IR (ATR): ν = 2934, 2847, 1673, 1448,1376, 1268, 1229, 864, 734 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{19}H_{28}DO^{+}$ [M+H^{+}]: 274.2276, found 274.2268.



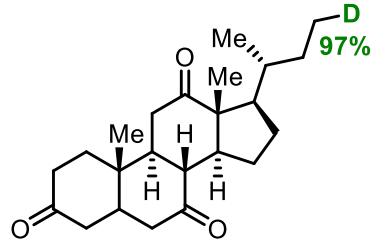
*(3R,8R,9S,10S,13R,14S,17R)-17-((R)-butan-2-yl-4-d)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol***(3cc)**

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =5:1), compound **3cc** (67.0 mg) was obtained in 81% yield as white needled crystals(mp: 156-158 ℃) with 99% D-incorporation (determined by ESI-HRMS and ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.19 (t, *J* = 3.7 Hz, 1H), 3.22 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.34 (dd, *J* = 13.8, 4.4 Hz, 1H), 1.87 (dd, *J* = 8.9, 3.6 Hz, 2H), 1.81 – 1.49 (m, 10H), 1.45 – 1.17 (m, 7H), 1.11 (s, 3H), 1.00 (s, 6H), 0.93 (s, 3H), 0.89 (s, 3H), 0.87 (s, 6H), 0.79 (s, 3H), 0.75 (dd, *J* = 11.3, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.9, 121.1, 79.0, 55.2, 47.7, 45.0, 42.5, 40.8, 39.1, 38.8, 38.5, 37.1, 35.2(t, *J* = 18.9 Hz, C-D), 33.7, 33.6, 33.1, 31.2, 31.1, 28.1, 27.9, 27.2, 25.1, 23.8, 23.3, 22.2, 18.4, 17.5, 15.6, 15.3. IR (ATR): ν = 2944, 2924, 2859, 1462, 1360, 1044, 1029, 995, 741 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{29}H_{46}D^{+}$ [M-H$_2$O+H^{+}]: 396.3735, found 396.3731.



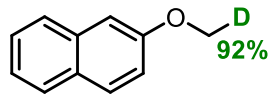
*(4aR,6aS,6bR,10S,12aS,12bR,14bS)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2H)-one-2-d***(3dd)**

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =5:1), compound **3cc** (82.7 mg) was obtained in 97% yield as a white powder(mp: 173-178 ℃) with 95% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.57 (s, 1H), 3.19 (dd, *J* = 11.0, 5.3 Hz, 1H), 2.76 (dd, *J* = 13.5, 2.6 Hz, 1H), 2.31 (s, 1H), 2.13 – 1.35 (m, 15H), 1.34 (s, 3H), 1.30 – 1.13 (m, 3H), 1.11 (s, 6H), 0.97 (s, 3H), 0.95 (d, *J* = 2.4 Hz, 1H), 0.85 (s, 3H), 0.80 (s, 3H), 0.78 (s, 3H), 0.67 (dd, *J* = 11.8, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.3, 170.3, 127.9, 78.6, 61.7, 54.9, 51.6, 45.6, 43.3, 41.3, 40.8, 39.0, 37.0, 34.2, 32.7 (t, *J* = 19.1 Hz, C-D), 32.6, 32.3, 30.4, 28.7, 28.1, 27.2, 26.6, 23.3, 22.2, 18.6, 17.4, 16.7, 16.3, 15.5. IR (ATR): ν = 3423, 2923, 2862, 1654, 1454, 1358, 1037, 733 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{29}H_{46}DO_2^+$ [M+H$^+$]: 428.3633, found 428.3625.



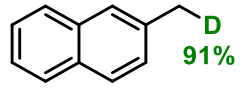
(8R,9S,10S,13R,14S,17R)-17-((R)-butan-2-yl-4-d)-10,13-dimethyldodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (**3ee**).

Following **GP1** with reaction time of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =3:1), compound **3ee** (53.0 mg) was obtained in 74% yield as a white powder(mp: 183-185 ℃) with 97% D-incorporation (determined by ESI-HRMS and ^{1}H NMR).^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.97 – 2.80 (m, 3H), 2.37 – 1.80 (m, 12H), 1.67 – 1.55 (m, 1H), 1.54 – 1.42 (m, 1H), 1.40 (s, 3H), 1.35 – 1.09 (m, 5H), 1.08 (s, 3H), 0.90 – 0.80 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 212.0, 209.0, 208.8, 56.9, 51.8, 49.0, 46.8, 46.8, 45.6, 45.5, 45.0, 42.8, 38.7, 37.4, 36.5, 36.0, 35.3, 27.7, 25.2, 21.9, 18.4, 11.9, 10.5 (t, *J* = 19.0 Hz, C-D). IR (ATR): ν = 2961, 2930, 2899, 2869, 1719, 1700, 1386, 1296, 1275 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{23}H_{34}DO_3^+$ [M+H$^+$]: 360.2643, found 360.2643.



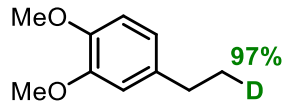
*2-(methoxy-d)naphthalene***(3ff)**

Following **GP3** with peristaltic period of 10 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3ff** (0.4140 g) was obtained in 52% yield as light yellow plate-like crystals(mp: 70-73 ℃) with 92% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 11.4, 8.6 Hz, 3H), 7.48 – 7.43 (m, 1H), 7.38 – 7.33 (m, 1H), 7.19 – 7.13 (m, 2H), 3.92 (t, *J* = 1.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.6, 134.6, 129.4, 129.0, 127.6, 126.7, 126.4, 123.6, 118.7, 105.7, 55.0 (t, *J* = 21.9 Hz, C-D). IR (ATR): ν = 2923, 2852, 1629, 1258, 1179, 837, 742, 479 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{11}H_{10}DO^+$ [M+H$^+$]: 160.0867, found 160.0866.



*2-(methyl-d)naphthalene***(3gg)**

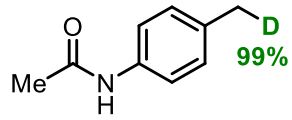
Following **GP3** with peristaltic period of 13 h. After purified by column chromatography on silica gel (eluent: petroleum ether), compound **3gg** (0.4941 g) was obtained in 69% yield as a white powder(mp: 45-47 ℃) with 91% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 (dd, *J* = 8.5, 4.3 Hz, 2H), 7.64 (s, 1H), 7.50 – 7.39 (m, 2H), 7.34 (dd, *J* = 8.3, 1.8 Hz, 1H), 2.52 (t, *J* = 3.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.4, 133.7, 131.7, 128.1, 127.7, 127.6, 127.2, 126.8, 125.8, 124.9, 21.4 (t, *J* = 19.3 Hz, C-D). IR (ATR): ν = 3052, 2918, 1507, 1272, 961, 808, 476 cm^{-1}. MS (EI): m/z: 143.1, 116.0.



*4-(ethyl-2-d)-1,2-dimethoxybenzene***(3hh)**

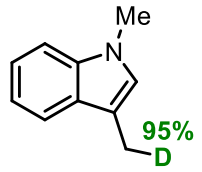
Large-scale reaction procedure: An oven-dried three-necked round bottom flask (25 mL) was equipped with cesium carboxylate (2.0 mmol), and Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.5 mol%). The flask was evacuated and backfilled with Ar for 3 times and the tube was sealed with rubber plug and equipped with an argon balloon. Then, 8 mL DCM and 2 mL D_2O, 2,4,6-triisopropylbenzenethiol (5 mol%), 18-crown-6 (1eq, solved in 1mL DCM) was added with syringe under Ar. Next, the reaction mixture was irradiated under two 45 W blue LEDs with a fan at room temperature at the peristalsis speed of 80 mL/min for 9 h. After the reaction was finished, the reaction mixture was extracted by ethyl acetate, dried by anhydrous Na_2SO_4, filtered and collected the organic layer. The organic solvent was removed under the reduced pressure. The residue was purified by column chromatography on silica gel(eluent: petroleum ether/EtOAc =10:1), compound **3hh** (0.1611 g) was obtained in 48% yield (71% GC yield) as a yellow oil with 97% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400

MHz, Chloroform-*d*) δ 6.81 – 6.79 (m, 1H), 6.75 – 6.73 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.22 (tt, *J* = 7.5, 5.7, 2.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.8, 147.0, 136.9, 119.4, 111.3, 111.2, 56.0, 55.7, 28.3, 15.5 (d, *J* = 19.3 Hz, C-D). HRMS (ESI): m/z Calculated for $C_{10}H_{14}DO_2^+$ [M+H$^+$]: 168.1129, found 168.1127.



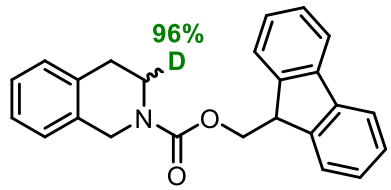
*N-(4-(methyl-d)phenyl)acetamide***(3ii)**

Following **GP3** with peristaltic period of 14 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =3:1), compound **3ii** (0.5033 g) was obtained in 67% yield as white needle-like crystals(mp: 135-139 ℃) with 99% D-incorporation (determined by ESI-HRMS).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.29 (t, *J* = 1.8 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 135.3, 133.8, 129.4, 120.0, 24.5, 20.5 (t, *J* = 19.3 Hz, C-D). HRMS (ESI): m/z Calculated for $C_9H_{11}DNO^+$ [M+H$^+$]: 151.0976, found 151.0977.



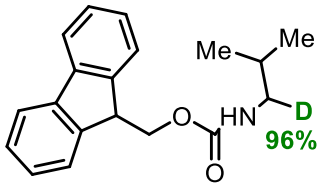
*1-methyl-3-(methyl-d)-1H-indole***(3jj)**

Following **GP3** with peristaltic period of 16 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =10:1), compound **3jj** (0.4388 g) was obtained in 60% yield as a light yellow powder(mp: 93-98 ℃) with 95% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 9.1 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.06 (m, 1H), 6.79 (s, 1H), 3.70 (s, 3H), 2.33 – 2.28 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.0, 128.6, 126.5, 121.4, 118.9, 118.5, 110.0, 109.0, 32.4, 9.3 (t, *J* = 19.3 Hz, C-D). IR (ATR): ν = 3356, 2919, 2850, 1658, 1632, 1468, 1261, 1094, 1019, 800 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{10}H_{11}DN^+$ [M+H$^+$]: 147.1027, found 147.1024.



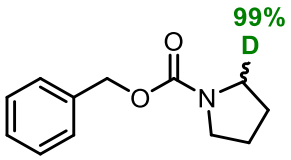
*(9H-fluoren-9-yl)methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate-3-d***(3kk)**

Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =10:1), compound **3kk** (1.5406 g) was obtained in 86% yield as a light yellow oil with 96% D-incorporation (determined by ESI-HRMS).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (q, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.39 – 7.32 (m, 2H), 7.28 – 7.09 (m, 4H), 4.66 (d, *J* = 25.0 Hz, 2H), 4.53 (d, *J* = 6.8 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 1H), 3.80 – 3.63 (m, 1H), 2.86 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.3, 143.9, 141.2, 134.5, 133.3, 128.8, 127.6, 126.9, 126.4, 126.3, 126.1, 124.9, 119.9, 67.3, 47.3, 45.6, 41.1 (t, *J* = 20.1 Hz, C-D), 287. IR (ATR): ν = 3064, 2896, 2841, 1694, 1448, 1421, 1097, 735 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{24}H_{21}DNO_2^+$ [M+H$^+$]: 357.1708, found 357.1704.



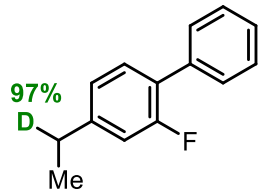
*(9H-fluoren-9-yl)methyl (2-methylpropyl-1-d)carbamate***(3ll)**

Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =5:1), compound **3ll** (1.2804 g) was obtained in 86% yield as a white powder(mp: 76-79 °C) with 96% D-incorporation (determined by ESI-HRMS).. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.59 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.31 (td, *J* = 7.5, 1.2 Hz, 2H), 4.79 (d, *J* = 6.0 Hz, 1H), 4.41 (d, *J* = 6.9 Hz, 2H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.08 – 2.92 (m, 1H), 1.76 (h, *J* = 6.7 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 144.0, 141.3, 127.6, 127.0, 125.0, 112.0, 66.5, 48.2 (t, *J* = 20.9 Hz, C-D), 47.3, 28.7, 19.9. IR (ATR): ν = 3331, 2956, 2868, 1689, 1533, 1250, 1152, 986, 738, 621, 424 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{19}H_{21}DNO_2^+$ [M+H$^+$]: 297.1708, found 297.1700.



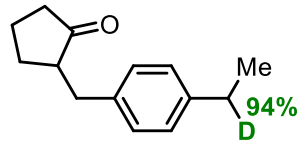
*benzyl pyrrolidine-1-carboxylate-2-d***(3mm)**

Following **GP3** with peristaltic period of 12 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =10:1), compound **3mm** (0.4551 g) was obtained in 44% yield as a light yellow oil with 99% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 10.1 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 5.14 (s, 2H), 3.44 – 3.34 (m, 3H), 1.88 – 1.82 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 137.1, 128.4, 127.8, 127.8, 66.5, 46.2, 45.4 (t, *J* = 22.3 Hz, C-D), 25.7, 24.9. IR (ATR): ν = 2950, 2876, 1695, 1447, 1412, 1356, 1098, 734, 537 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{12}H_{15}DNO_2^+$ [M+H$^+$]: 207.1238, found 207.1236.



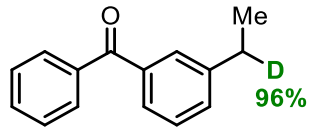
*4-(ethyl-1-d)-2-fluoro-1,1'-biphenyl***(3nn)**

Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether), compound **3nn** (0.6939 g) was obtained in 69% yield as a colorless oil with 97% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 2H), 7.45 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.07 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.02 (dd, *J* = 11.8, 1.7 Hz, 1H), 2.68 (qt, *J* = 7.6, 2.3 Hz, 1H), 1.29 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6 (d, *J* = 247.5 Hz), 145.8 (d, *J* = 7.5 Hz), 135.9, 130.4 (d, *J* = 4.0 Hz), 128.9 (d, *J* = 3.0 Hz), 128.4, 127.4, 126.2 (d, *J* = 13.6 Hz), 123.9 (d, *J* = 3.2 Hz), 115.3 (d, *J* = 22.6 Hz), 28.0 (td, *J* = 19.3, 1.0 Hz, C-D), 15.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.80. IR (ATR): ν = 3032, 2965, 2931, 1560, 1515, 1129, 765, 696, 575, 451 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{14}H_{13}DF^{+}$ [M+H^{+}]: 202.1137, found 202.1133.



*2-(4-(ethyl-1-d)benzyl)cyclopentan-1-one***(3oo)**

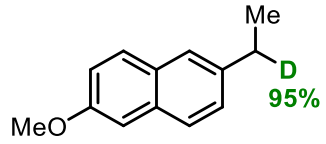
Following **GP3** with peristaltic period of 12 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3oo** (0.6963 g) was obtained in 69% yield as a light yellow oil with 94% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.12 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.60 (qt, *J* = 7.6, 2.2 Hz, 1H), 2.51 (dd, *J* = 13.8, 9.5 Hz, 1H), 2.40 – 2.27 (m, 2H), 2.14 – 2.04 (m, 2H), 1.99 – 1.91 (m, 1H), 1.77 – 1.68 (m, 1H), 1.61 – 1.51 (m, 1H), 1.22 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.3, 142.0, 137.1, 128.8, 127.8, 51.1, 38.2, 35.1, 29.1, 28.0 (t, *J* = 19.2 Hz, C-D), 20.5, 15.5. IR (ATR): ν = 2962, 2930, 2874, 1726, 1513, 1152, 845, 577 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{14}H_{18}DO^{+}$ [M+H^{+}]: 204.1493, found 204.1491.



*(3-(ethyl-1-d)phenyl)(phenyl)methanone***(3pp)**

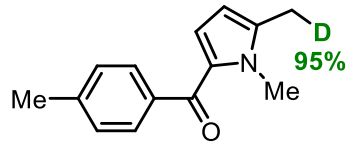
Following **GP3** with peristaltic period of 12 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3pp** (0.7728 g) was obtained in 73% yield as a colorless oil with 96% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-

d) δ 7.86 – 7.77 (m, 2H), 7.66 (s, 1H), 7.58 (ddd, *J* = 7.7, 4.7, 3.1 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.40 (dt, *J* = 15.0, 7.6 Hz, 2H), 2.70 (qt, *J* = 7.6, 2.3 Hz, 1H), 1.26 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.0, 144.4, 137.8, 137.7, 132.3, 132.0, 130.0, 129.3, 128.2, 128.1, 127.6, 28.4 (t, *J* = 19.3 Hz, C-D), 15.4. IR (ATR): ν = 3058, 2964, 2930, 1656, 1597, 1580, 1316, 719 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{15}H_{14}DO^+$ [M+H$^+$]: 212.1180, found 212.1186.



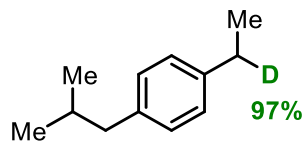
*2-(ethyl-1-d)-6-methoxynaphthalene***(3qq)**

Following **GP3** with peristaltic period of 10 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =100:1), compound **3qq** (0.6340 g) was obtained in 68% yield as a white powder(mp: 72-75 ℃) with 95% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.65 (m, 2H), 7.57 (s, 1H), 7.33 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.17 – 7.10 (m, 2H), 3.92 (s, 3H), 2.78 (qt, *J* = 7.4, 2.2 Hz, 1H), 1.32 (dt, *J* = 7.6, 1.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 139.4, 132.9, 129.2, 128.9, 127.5, 126.7, 125.4, 118.6, 105.7, 55.3, 28.5 (t, *J* = 19.3 Hz, C-D), 15.5. IR (ATR): ν = 3007, 2959, 1632, 1602, 1195, 1028, 851, 815, 482 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{13}H_{14}DO^+$ [M+H$^+$]: 188.1180, found 188.1178.



*(1-methyl-5-(methyl-d)-1H-pyrrol-2-yl)(p-tolyl)methanone***(3rr)**

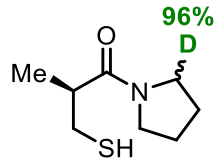
Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =20:1), compound **3rr** (0.7397 g) was obtained in 69% yield as a white powder(mp: 65-71 ℃) with 95% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 4.0 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 3.92 (s, 3H), 2.42 (s, 3H), 2.31 – 2.25 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.4, 141.5, 139.2, 137.7, 130.6, 129.3, 128.6, 122.7, 108.1, 32.9, 21.5, 12.4 (t, *J* = 19.5 Hz, C-D). IR (ATR): ν = 2920, 2851, 1604, 1478, 1451, 1366, 1162, 749 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{14}H_{15}DNO^+$ [M+H$^+$]: 215.1289, found 215.1282.



*1-(ethyl-1-d)-4-isobutylbenzene***(3ss)**

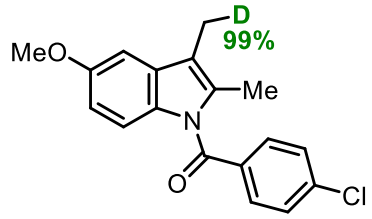
Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether), compound **3ss** (0.4420 g) was obtained in 54% yield as a colorless oil

with 97% D-incorporation (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.69 – 2.57 (m, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.86 (hept, *J* = 8.0 Hz, 1H), 1.24 (d, *J* = 7.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.4, 138.8, 129.0, 127.5, 45.1, 30.3, 28.4(C-H), 28.1 (t, *J* = 19.2 Hz, C-D), 22.4, 15.5. IR (ATR): ν = 3363, 2920, 2349, 1260, 794, 670, 665 cm^{-1}. MS (EI): m/z: 163.1, 120.1, 105.1, 92.1, 78.0.



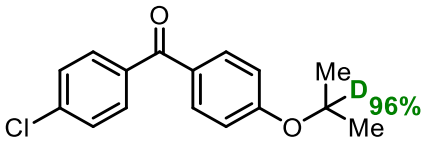
*(2S)-3-mercapto-2-methyl-1-(pyrrolidin-1-yl-2-d)propan-1-one***(3tt)**

Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =5:1), compound **3tt** (0.6539 g) was obtained in 75% yield as a colorless oil with 96% D-incorporation (determined by ESI-HRMS). It's notable that we didn't detected the H/D exchange signal of S-H in product in ^{1}H NMR and HRMS (ESI) although. We envisioned that the produced RS-D was exchanged back to RS-H during work-up. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.62 – 3.51 (m, 1H), 3.49 – 3.38 (m, 2H), 2.91 (ddd, *J* = 13.2, 8.8, 7.9 Hz, 1H), 2.73 (dqdd, *J* = 8.2, 6.7, 5.3, 1.3 Hz, 1H), 2.43 (ddd, *J* = 13.2, 9.5, 5.3 Hz, 1H), 1.98 – 1.92 (m, 2H), 1.88 – 1.83 (m, 2H), 1.53 (dd, *J* = 9.5, 7.9 Hz, 1H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 45.7, 45.4 (t, *J* = 21.9 Hz, C-D), 42.4, 28.0, 25.9, 24.2, 17.1. IR (ATR): ν = 2968, 2929, 2873, 1625, 1429, 1369, 1321, 512 cm^{-1}. HRMS (ESI): m/z Calculated for $C_8H_{15}DNOS^+$ [M+H$^+$]: 175.1010, found 175.1006.



*(4-chlorophenyl)(5-methoxy-2-methyl-3-(methyl-d)-1H-indol-1-yl)methanone***(3uu)**

Following **GP3** with peristaltic period of 15 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3uu** (1.1030 g) was obtained in 71% yield as a yellow oil with 99% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.92 – 6.88 (m, 2H), 6.66 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.85 (s, 3H), 2.31 (s, 3H), 2.20 – 2.16 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 155.9, 138.9, 134.4, 133.8, 132.0, 131.0, 130.9, 129.0, 115.4, 114.9, 111.1, 101.3, 55.7, 13.3, 8.5 (t, *J* = 19.3 Hz, C-D). IR (ATR): ν = 2925, 2832, 1673, 1474, 1454, 1211, 752, 480 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{18}H_{16}DClNO_2^+$ [M+H$^+$]: 315.1005, found 315.0999.

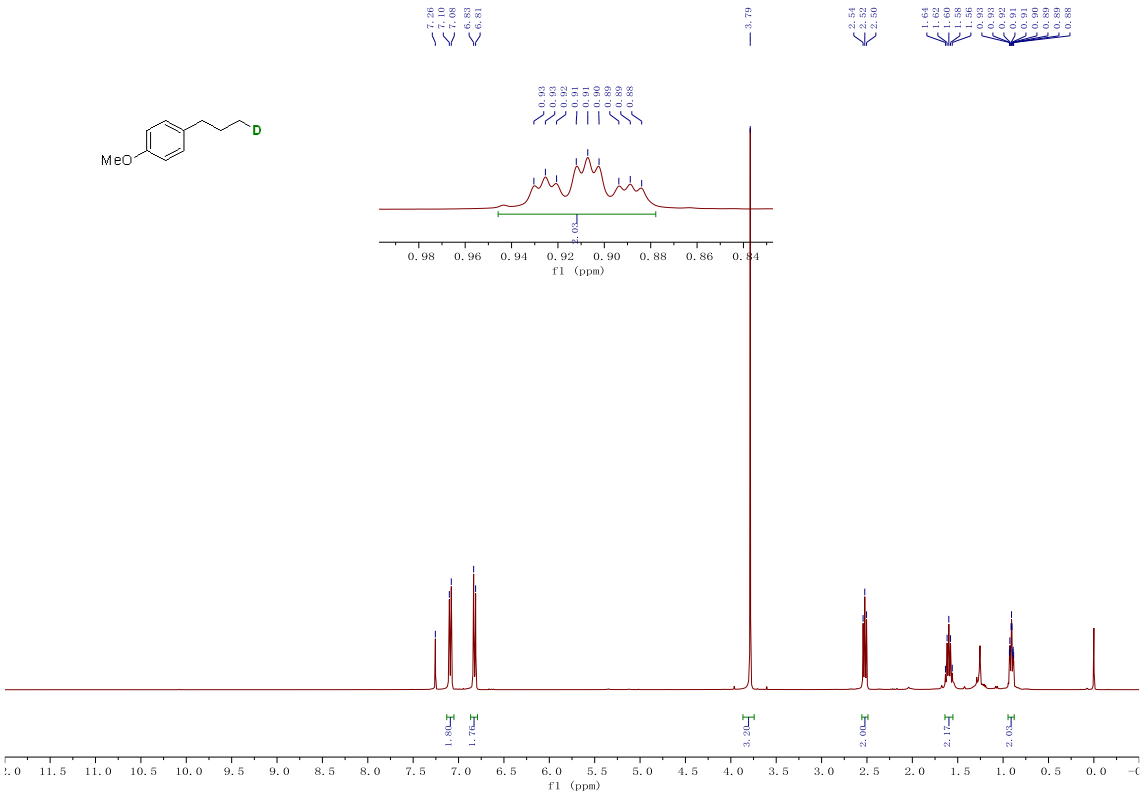


*(4-chlorophenyl)(4-((propan-2-yl-2-d)oxy)phenyl)methanone***(3vv)**

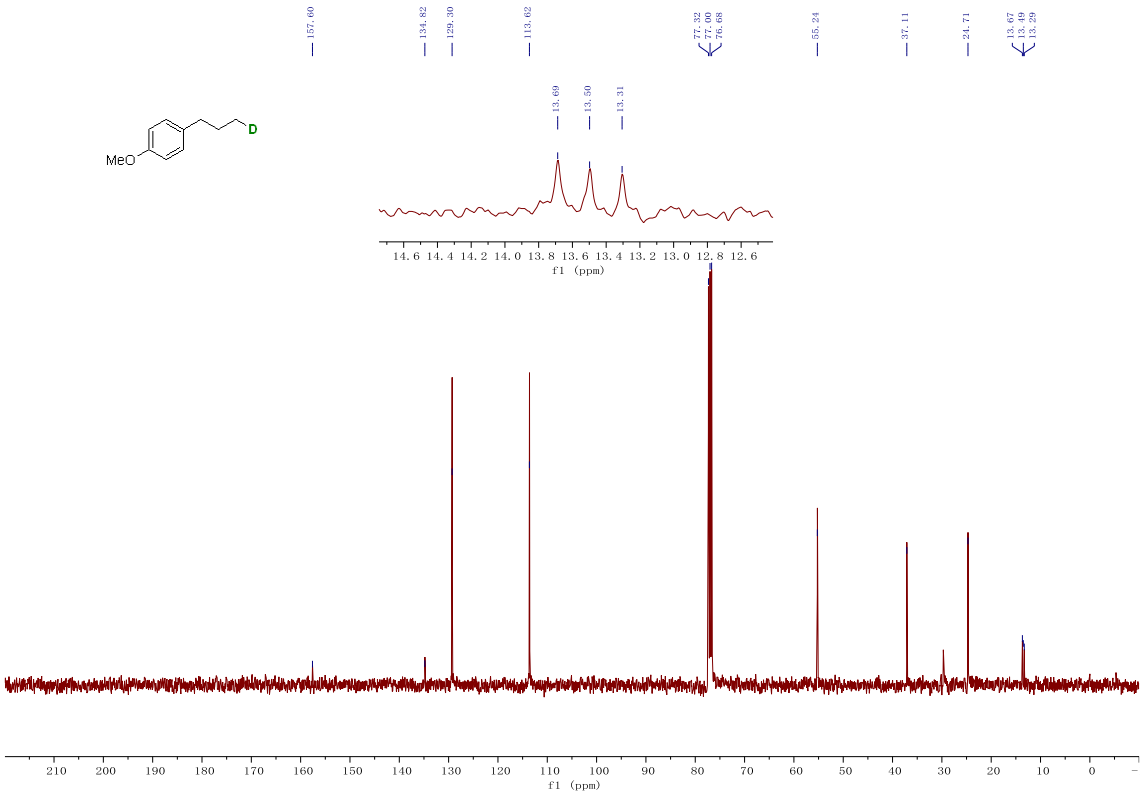
Following **GP4** with peristaltic period of 16 h. After purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc =50:1), compound **3vv** (13.0 g) was obtained in 94% yield as light yellow plate-like crystals (mp: 90-93 ℃) with 96% D-incorporation (determined by ESI-HRMS). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.67 (hept, *J* = 6.3 Hz, 0.08H), 1.38 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.2, 161.9, 138.2, 136.6, 132.5, 131.1, 129.3, 128.5, 115.0, 69.8 (t, *J* = 17.5 Hz, C-D), 21.8. IR (ATR): ν = 2982, 2931, 1595, 1583, 1501, 1168, 820, 654 cm^{-1}. HRMS (ESI): m/z Calculated for $C_{16}H_{15}DClO_2^+$ [M+H$^+$]: 276.0896, found 276.0890.

NMR spectra

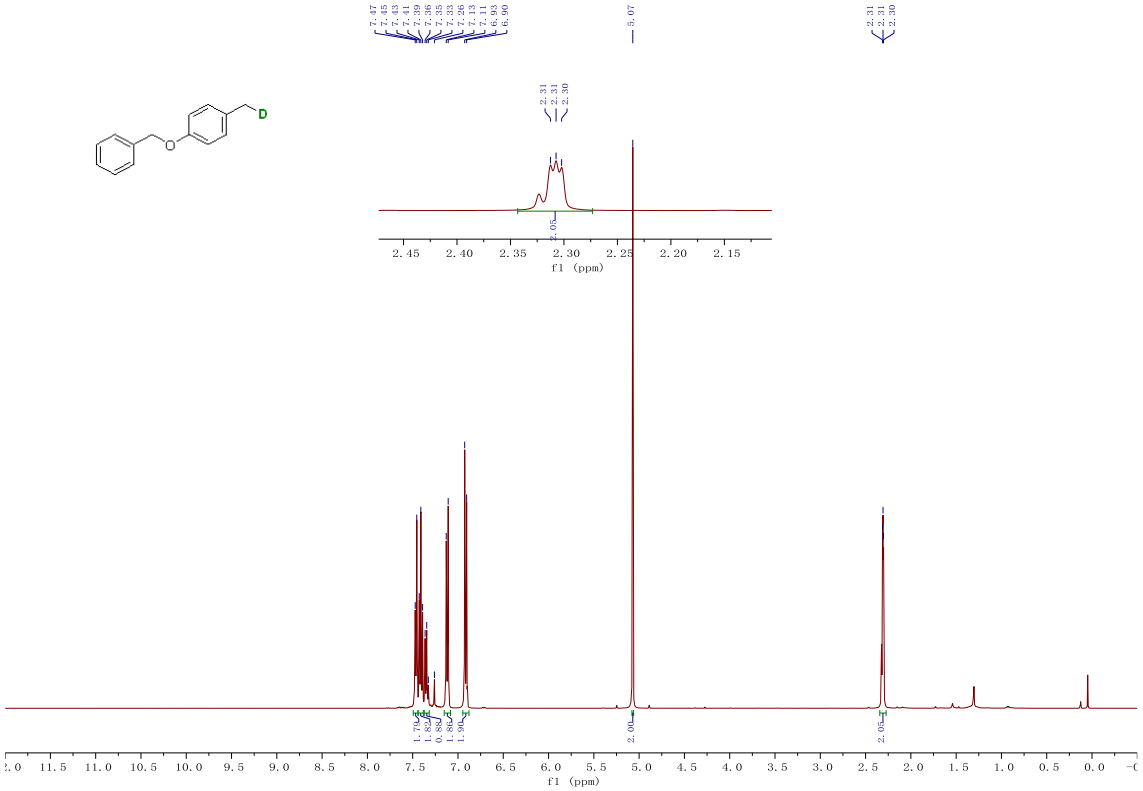
^{1}H NMR spectrum for compound **3a**



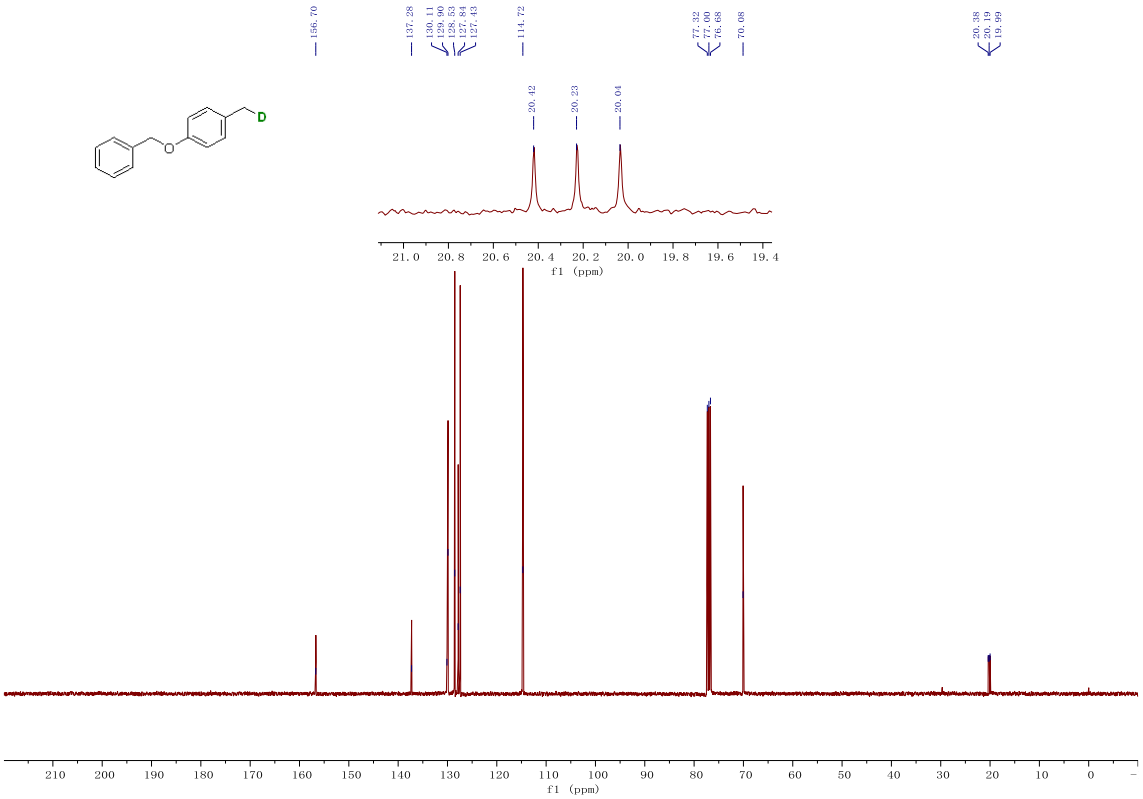
^{13}C NMR spectrum for compound **3a**



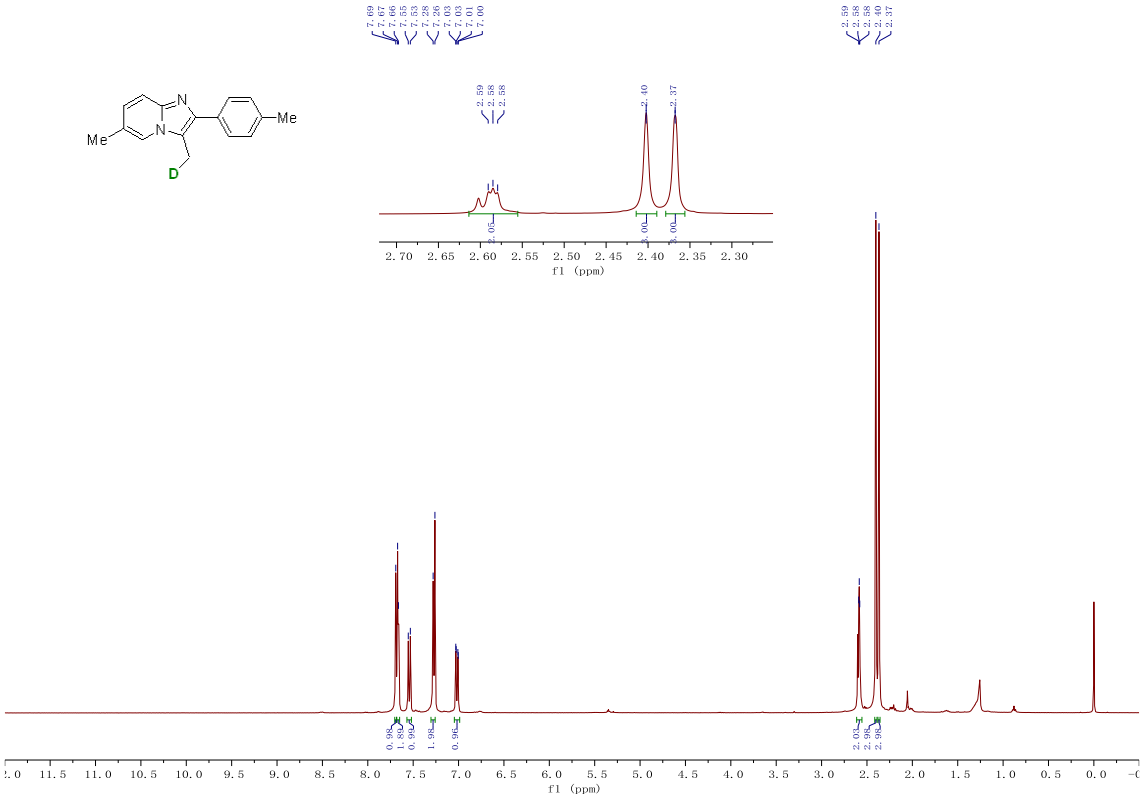
^{1}H NMR spectrum for compound **3b**



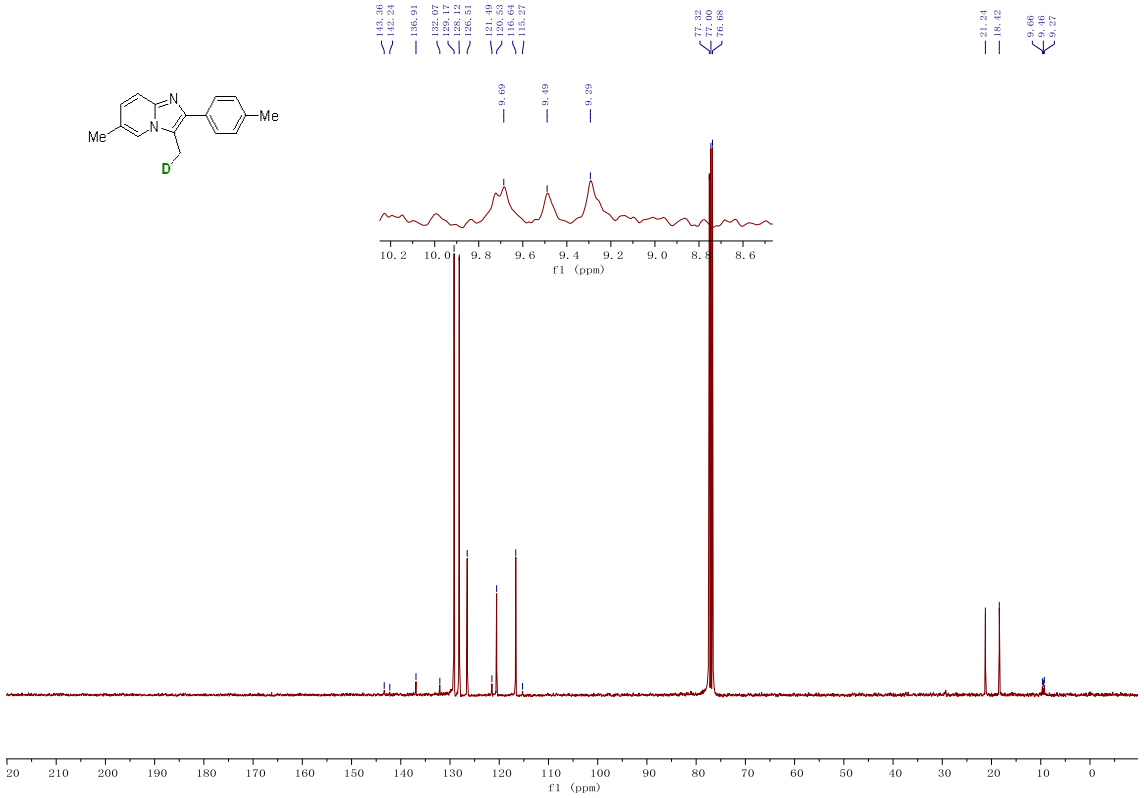
^{13}C NMR spectrum for compound **3b**



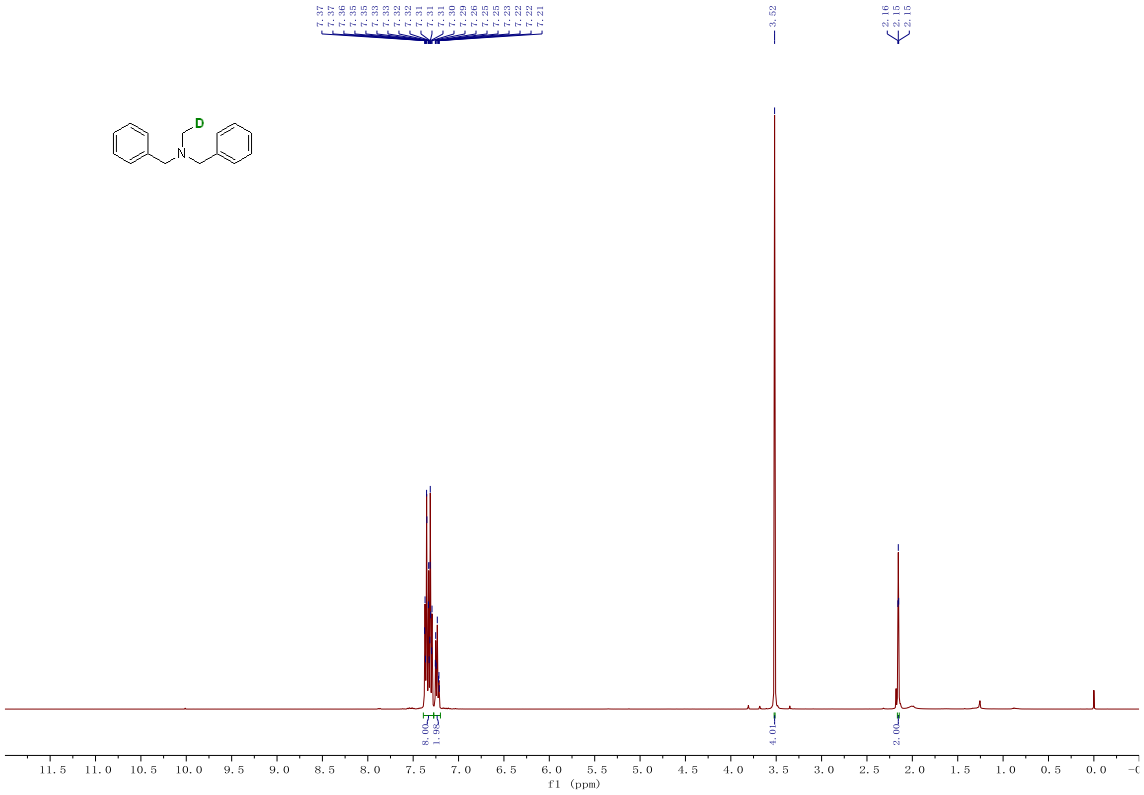
^{1}H NMR spectrum for compound **3c**



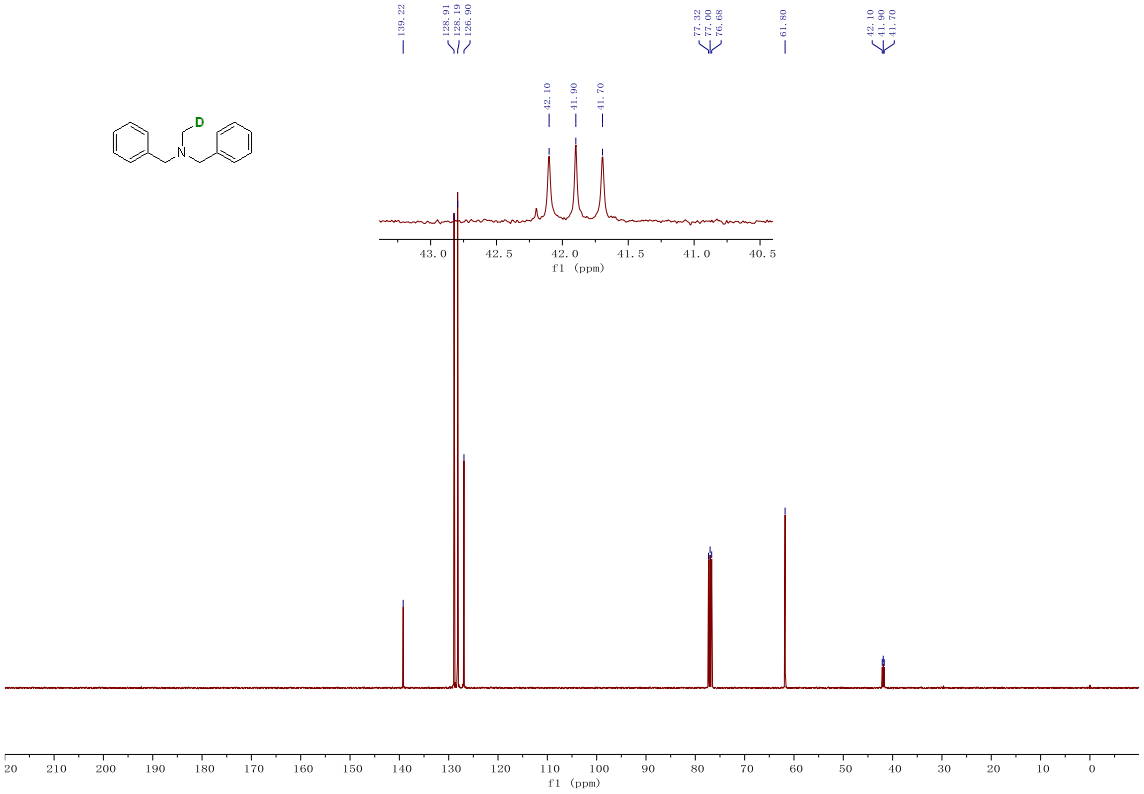
^{13}C NMR spectrum for compound **3c**



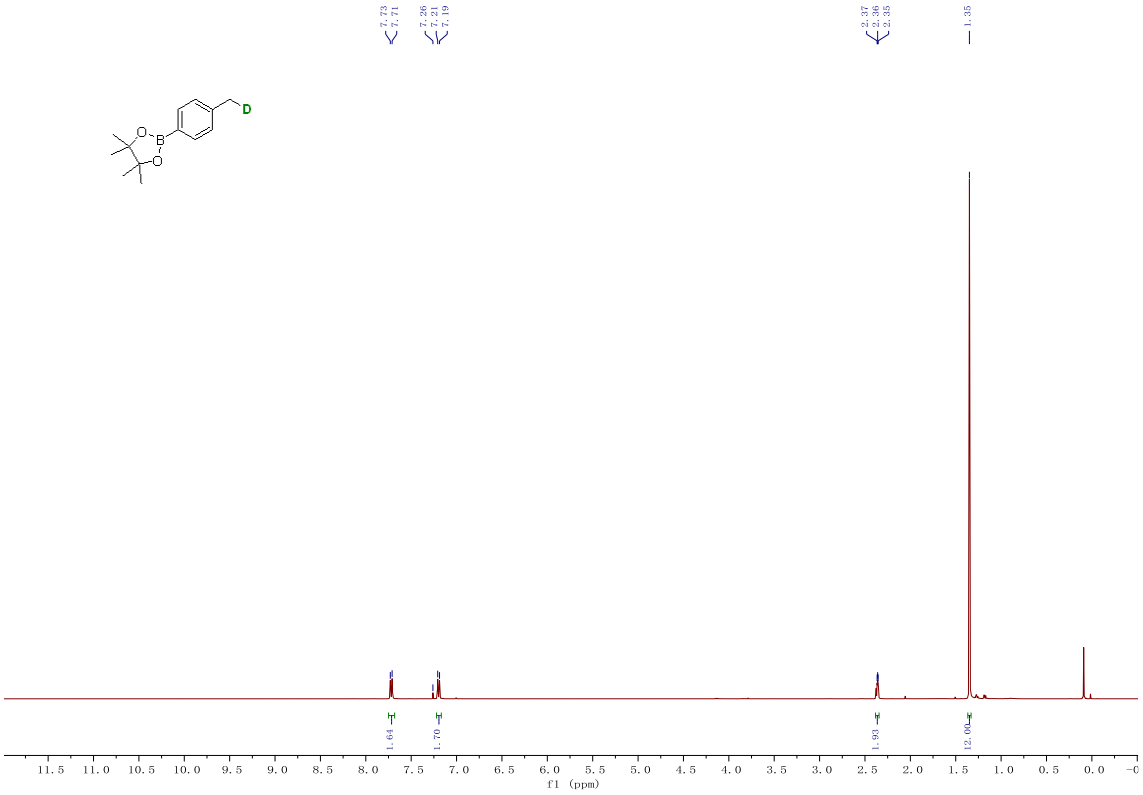
^{1}H NMR spectrum for compound **3d**



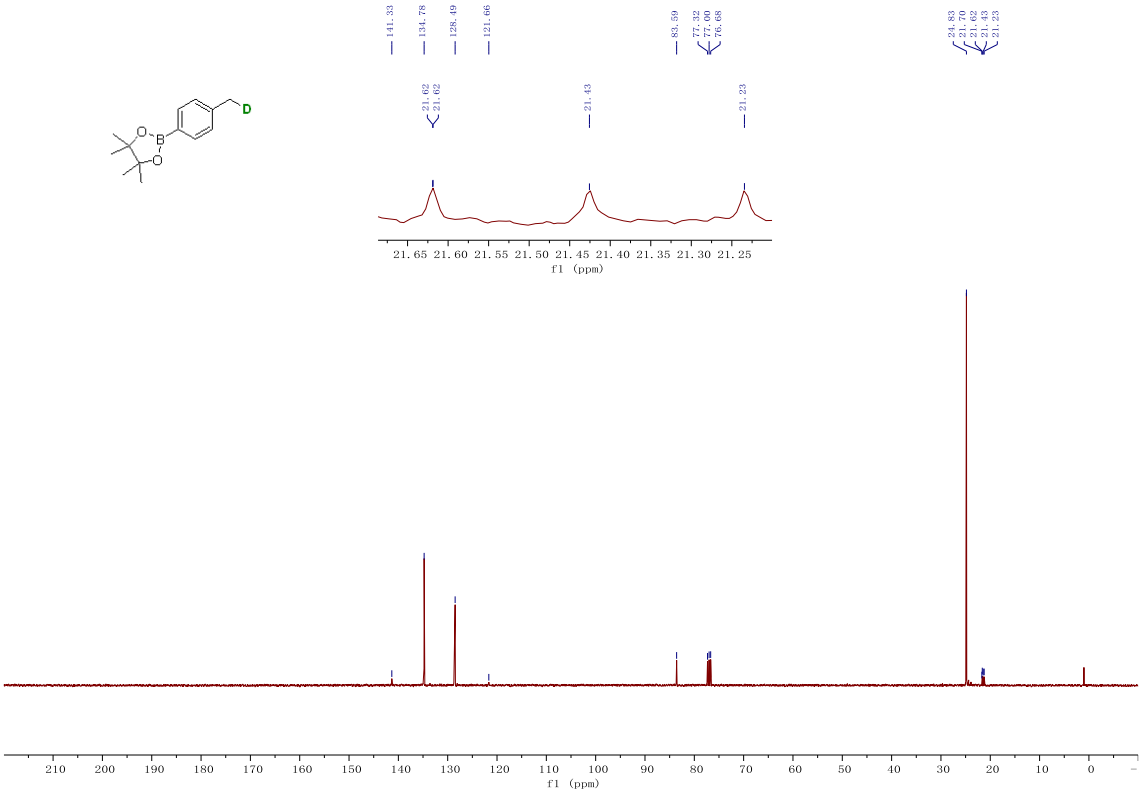
^{13}C NMR spectrum for compound **3d**



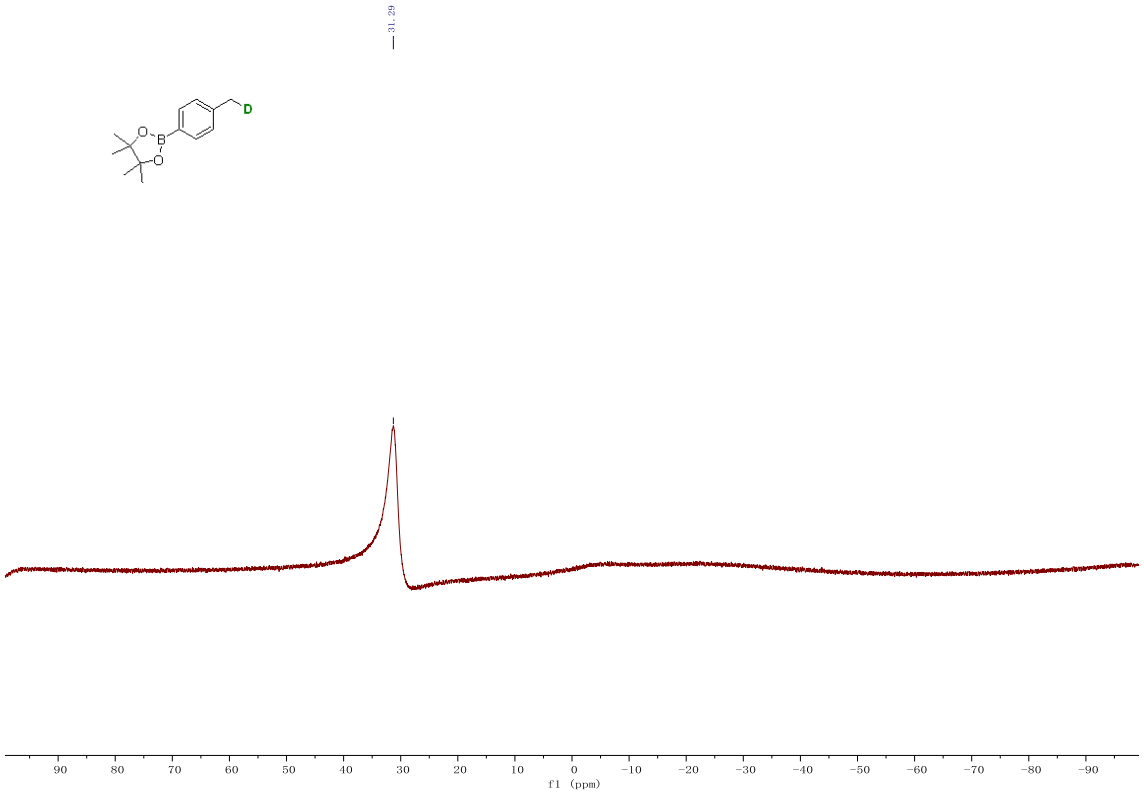
^{1}H NMR spectrum for compound **3e**



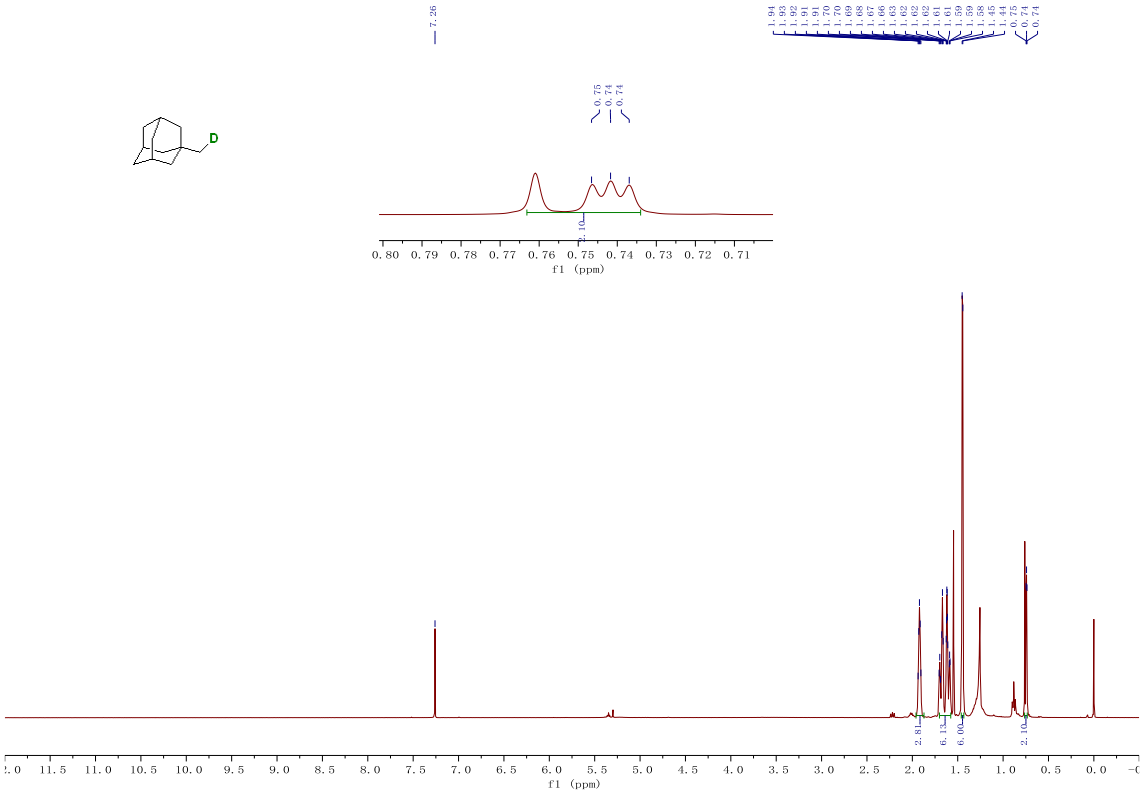
^{13}C NMR spectrum for compound **3e**



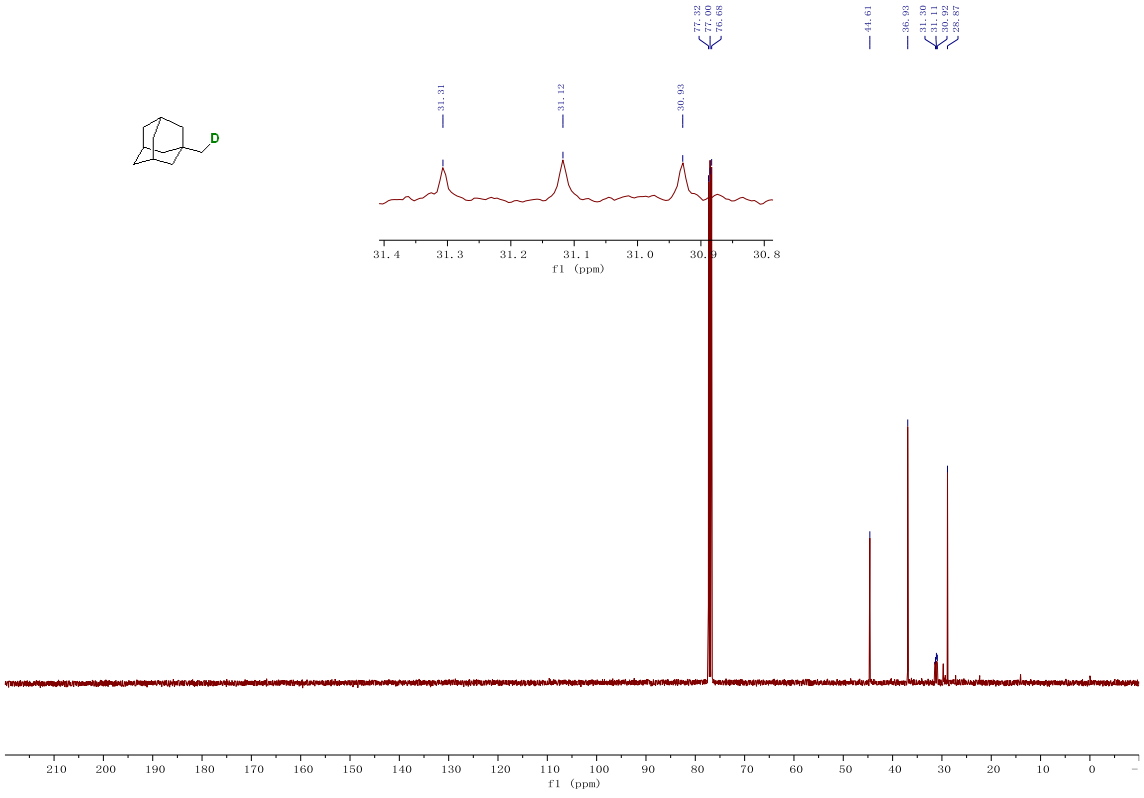
^{11}B NMR spectrum for compound **3e**



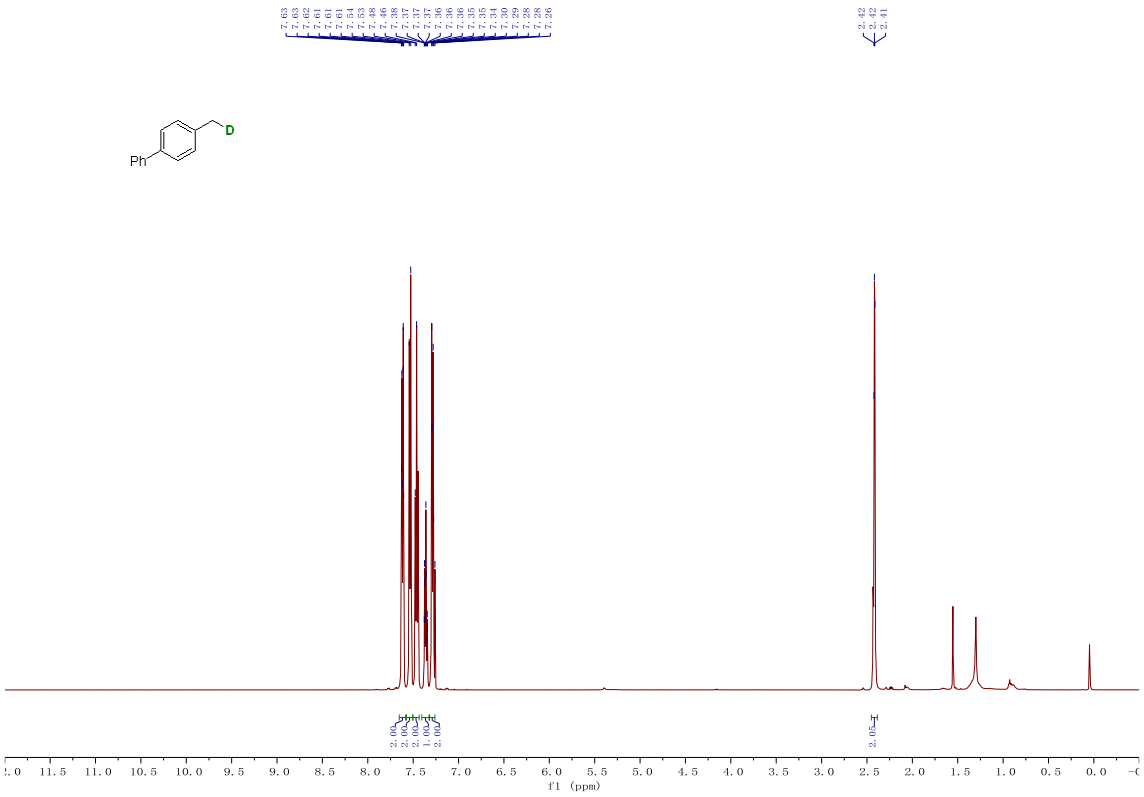
^{1}H NMR spectrum for compound **3f**



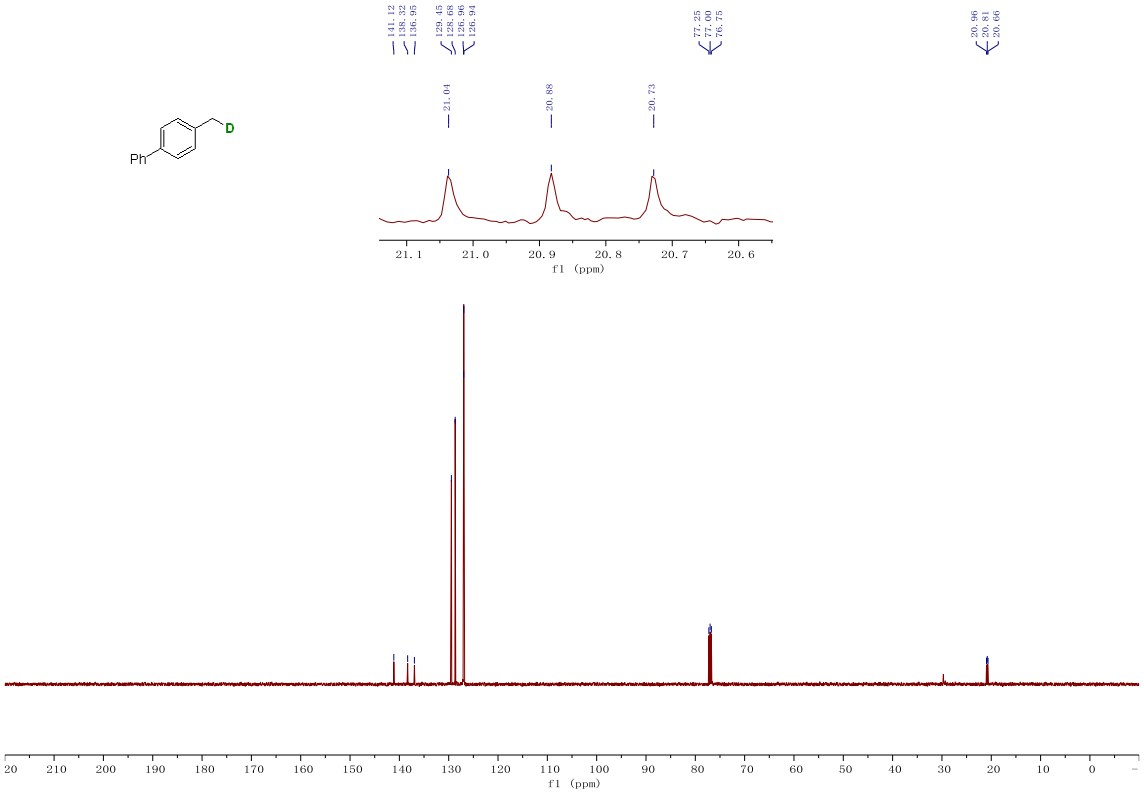
^{13}C NMR spectrum for compound **3f**



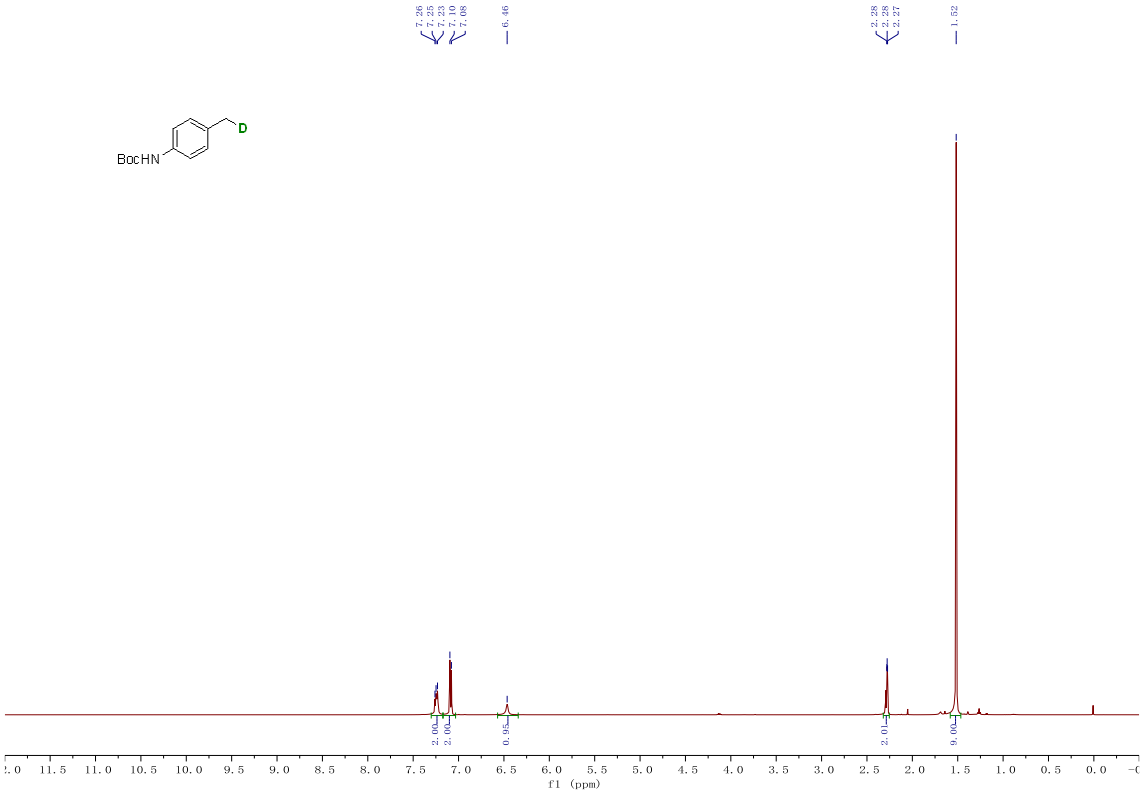
^{1}H NMR spectrum for compound **3g**



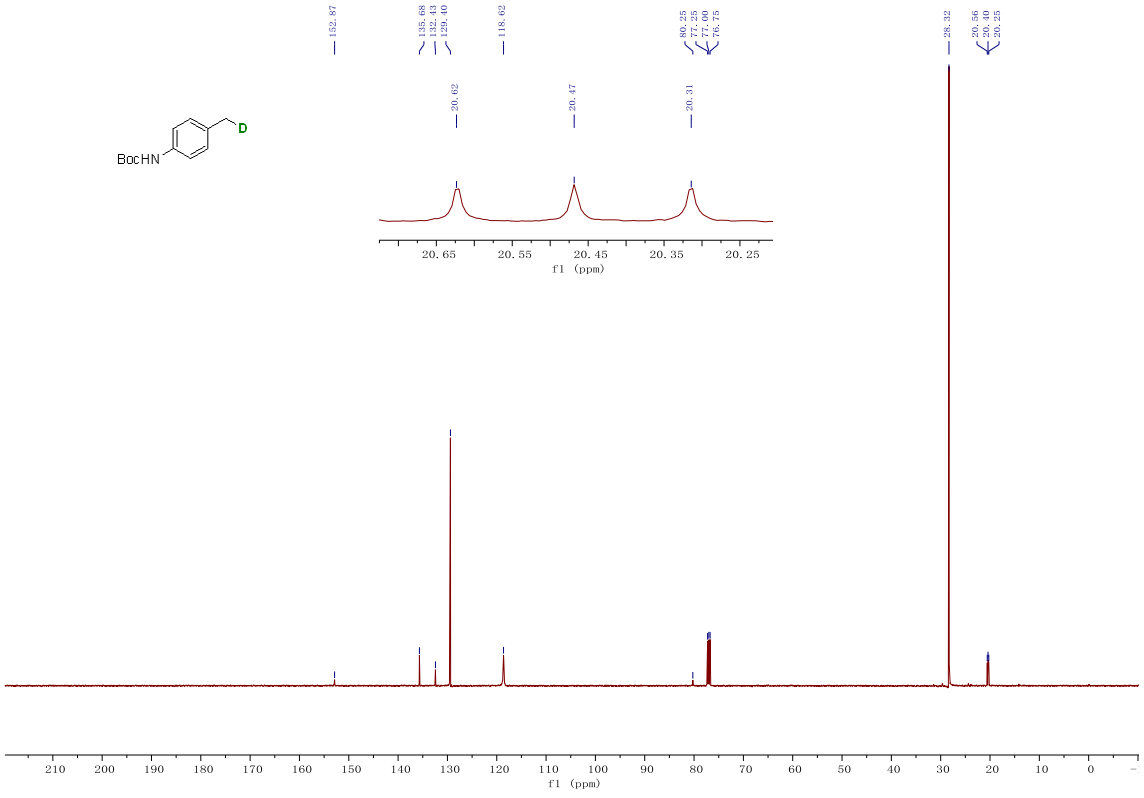
^{13}C NMR spectrum for compound **3g**



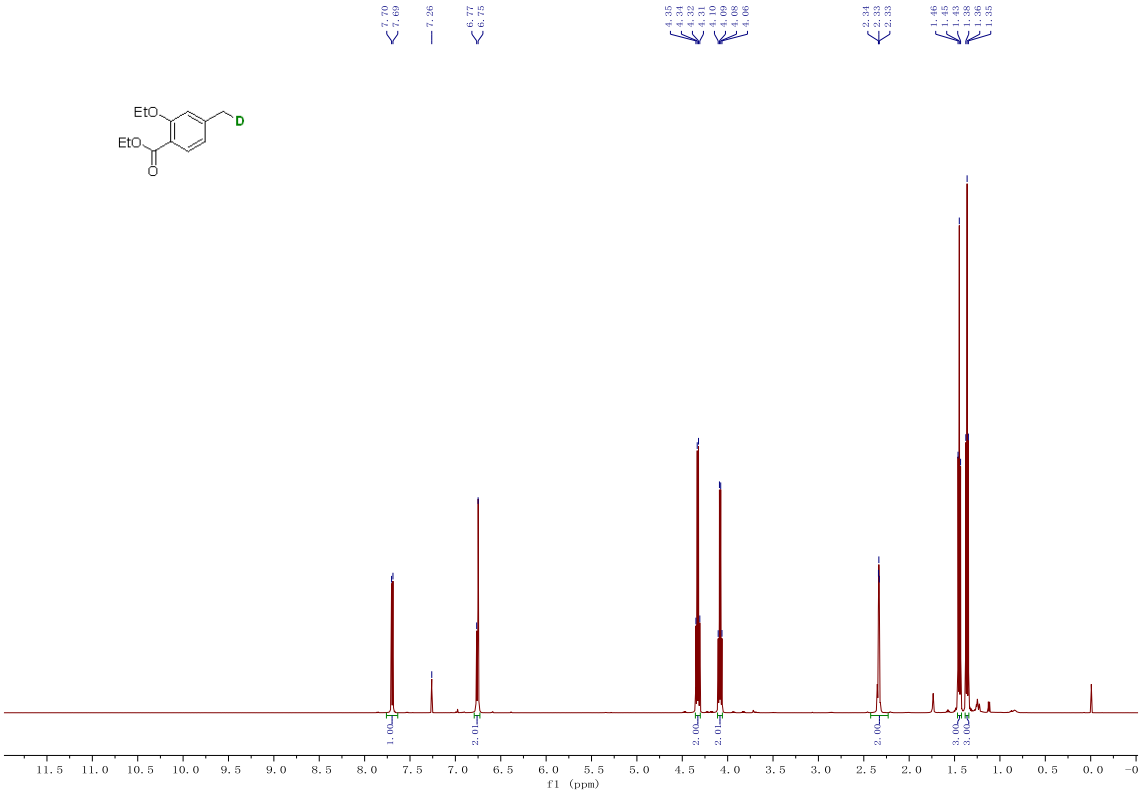
^{1}H NMR spectrum for compound **3h**



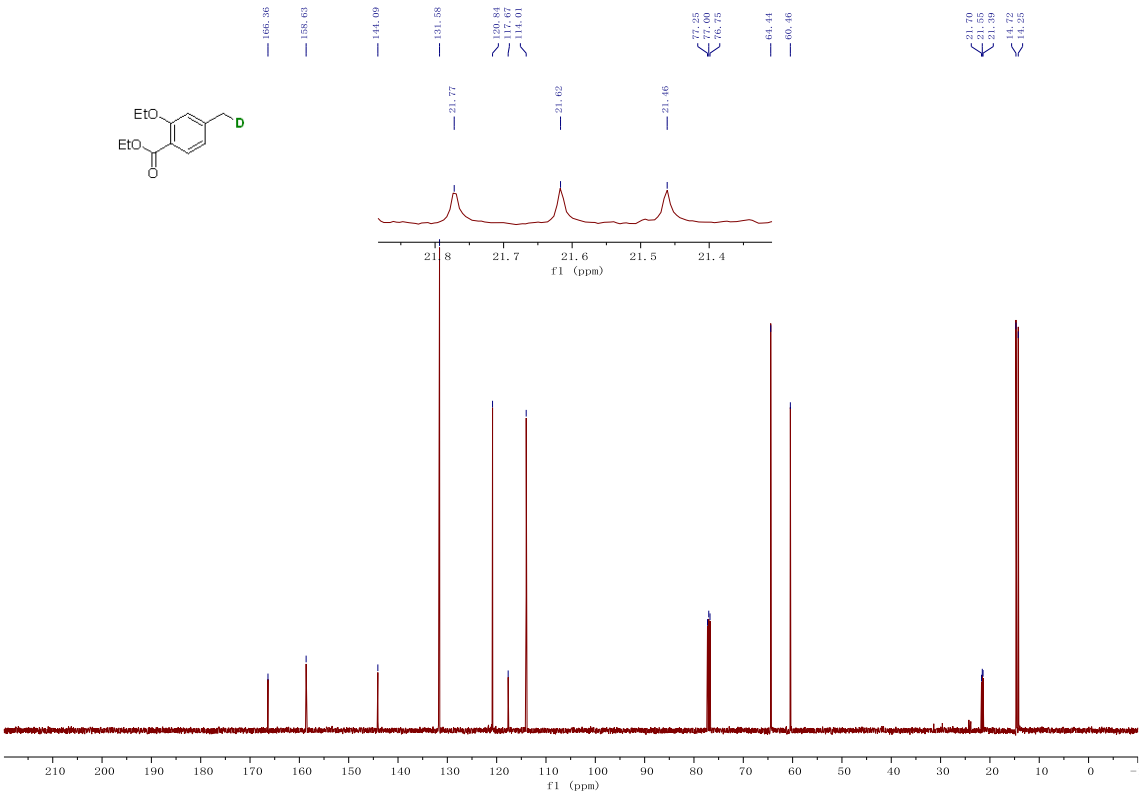
^{13}C NMR spectrum for compound **3h**



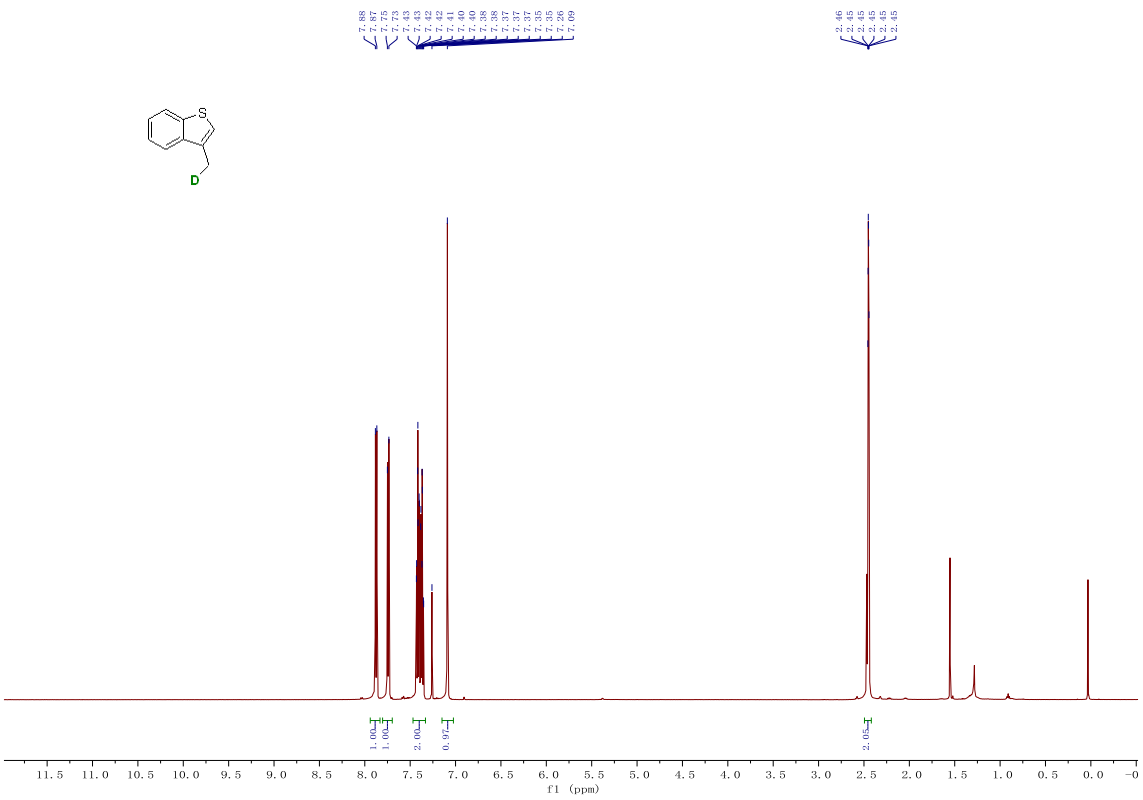
^{1}H NMR spectrum for compound **3i**



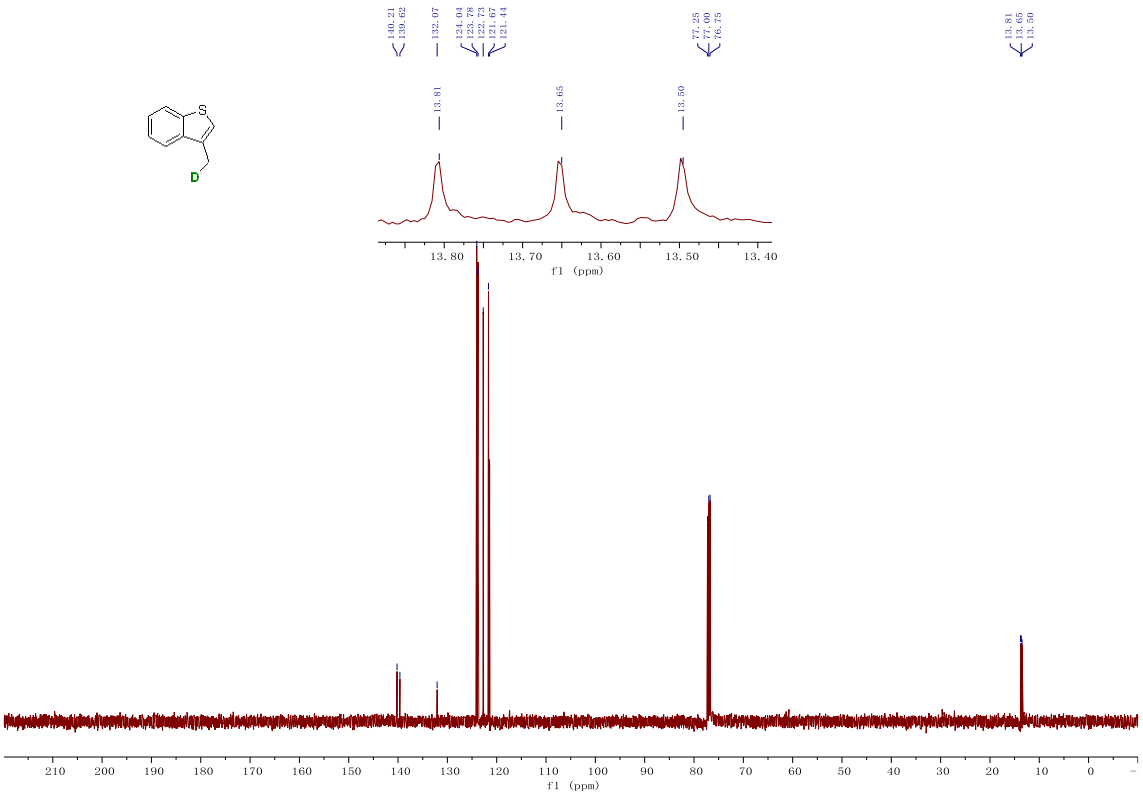
^{13}C NMR spectrum for compound **3i**



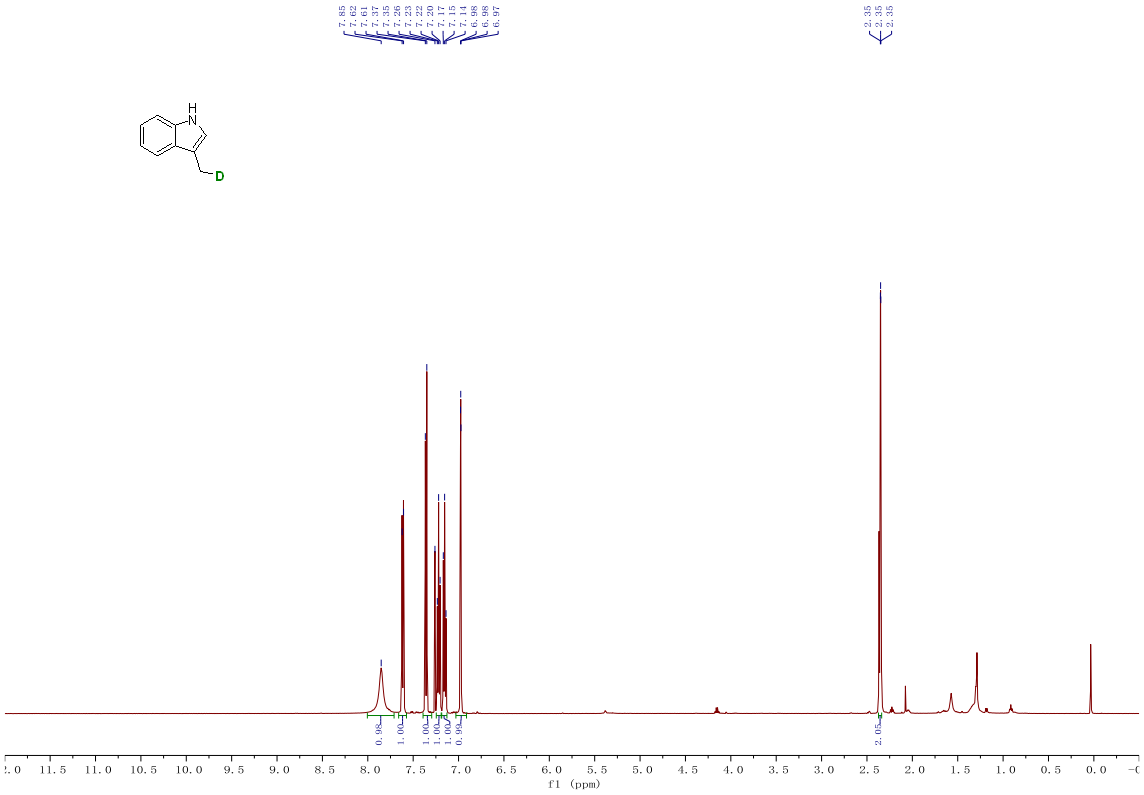
^{1}H NMR spectrum for compound **3j**



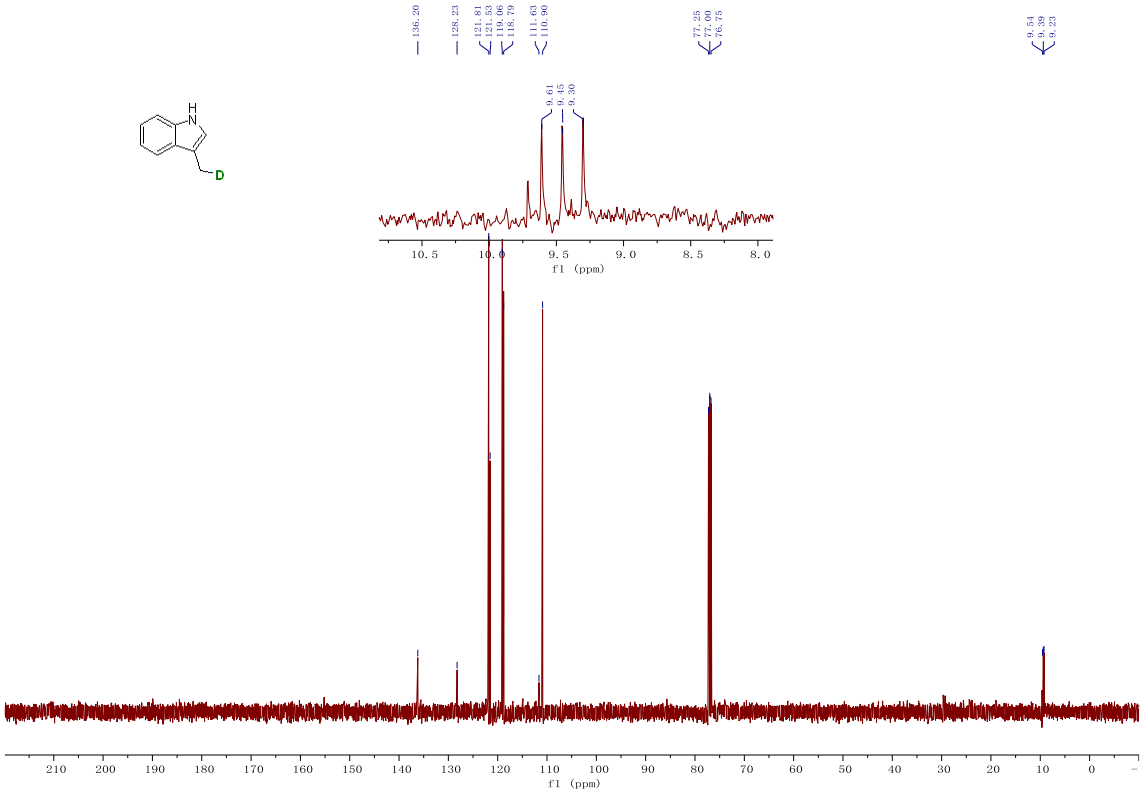
^{13}C NMR spectrum for compound **3j**



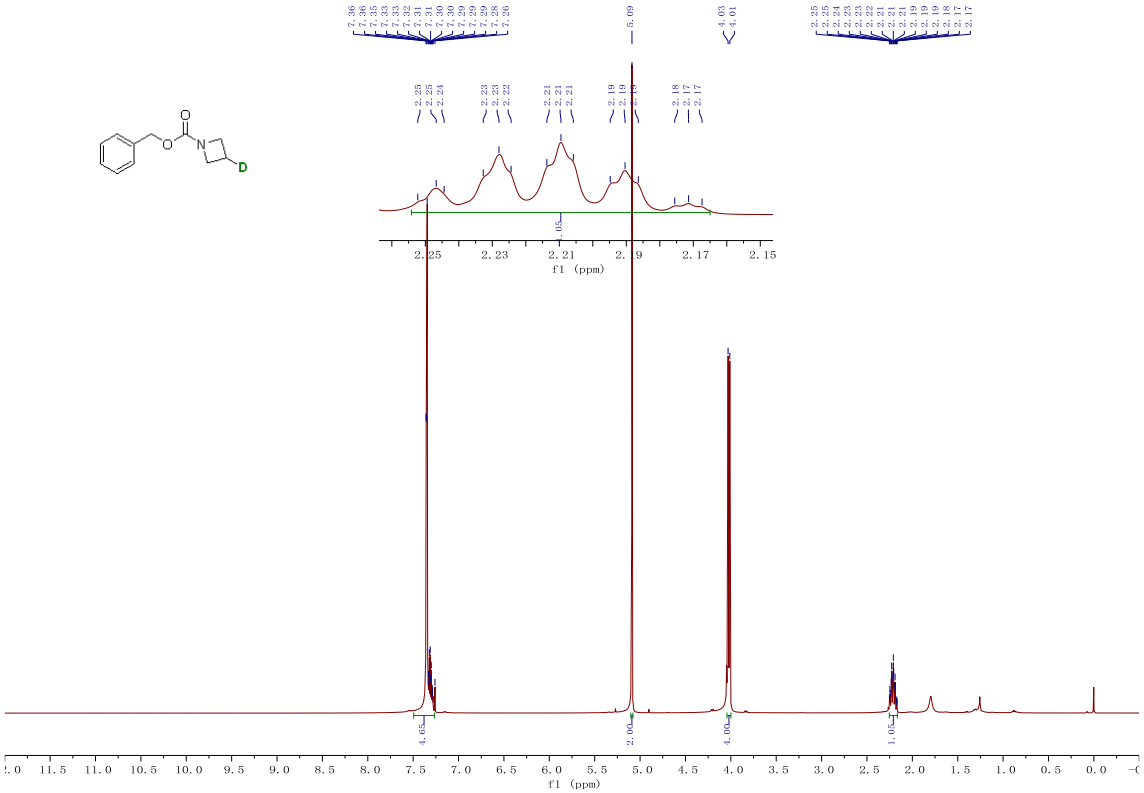
^{1}H NMR spectrum for compound **3k**



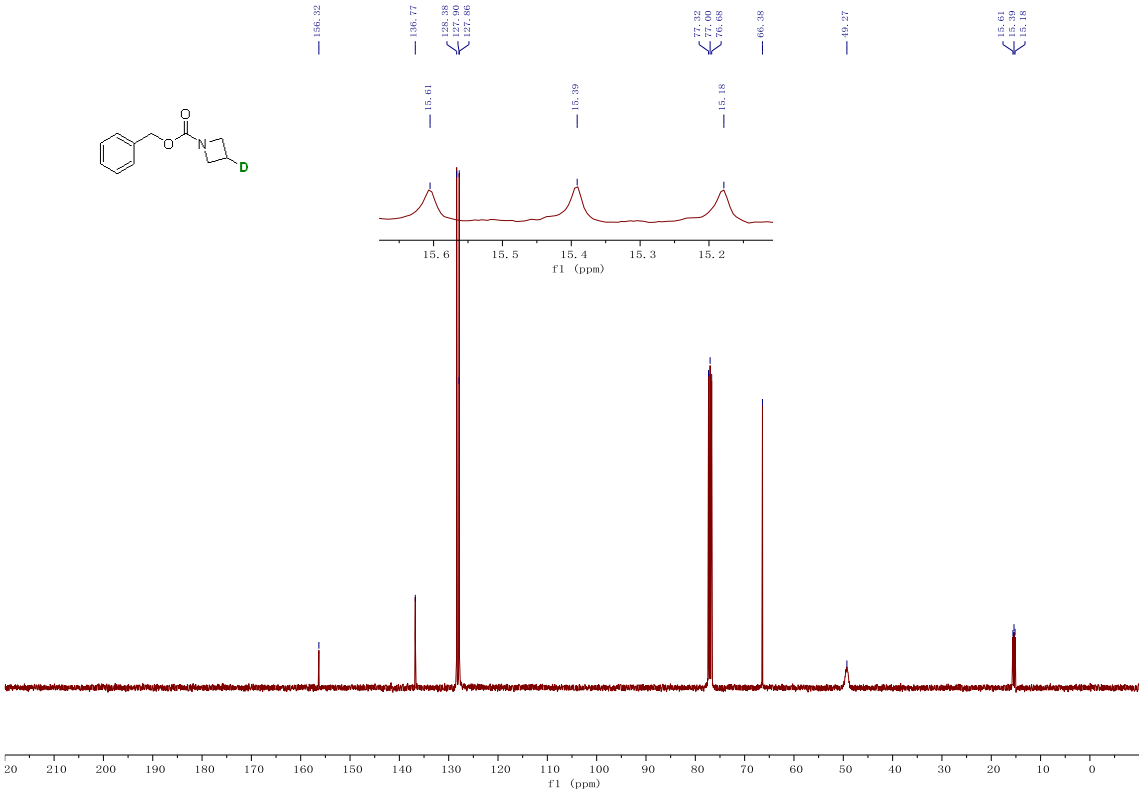
^{13}C NMR spectrum for compound **3k**



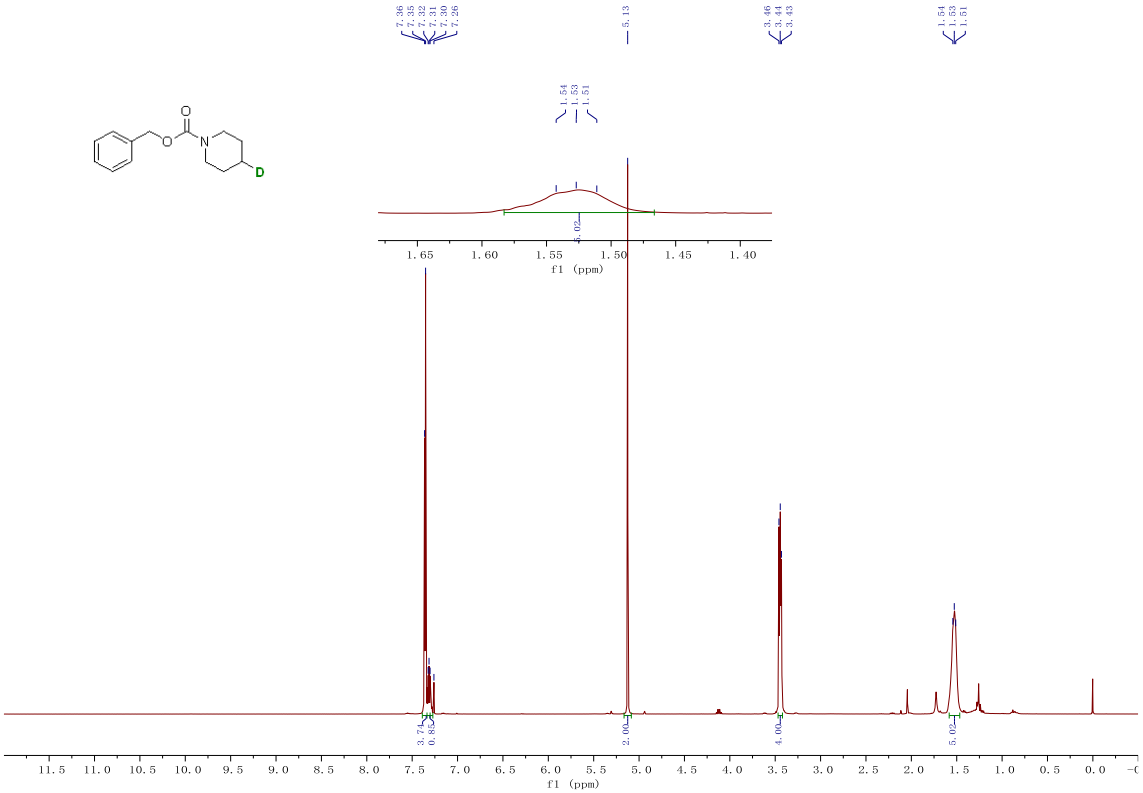
^{1}H NMR spectrum for compound **3l**



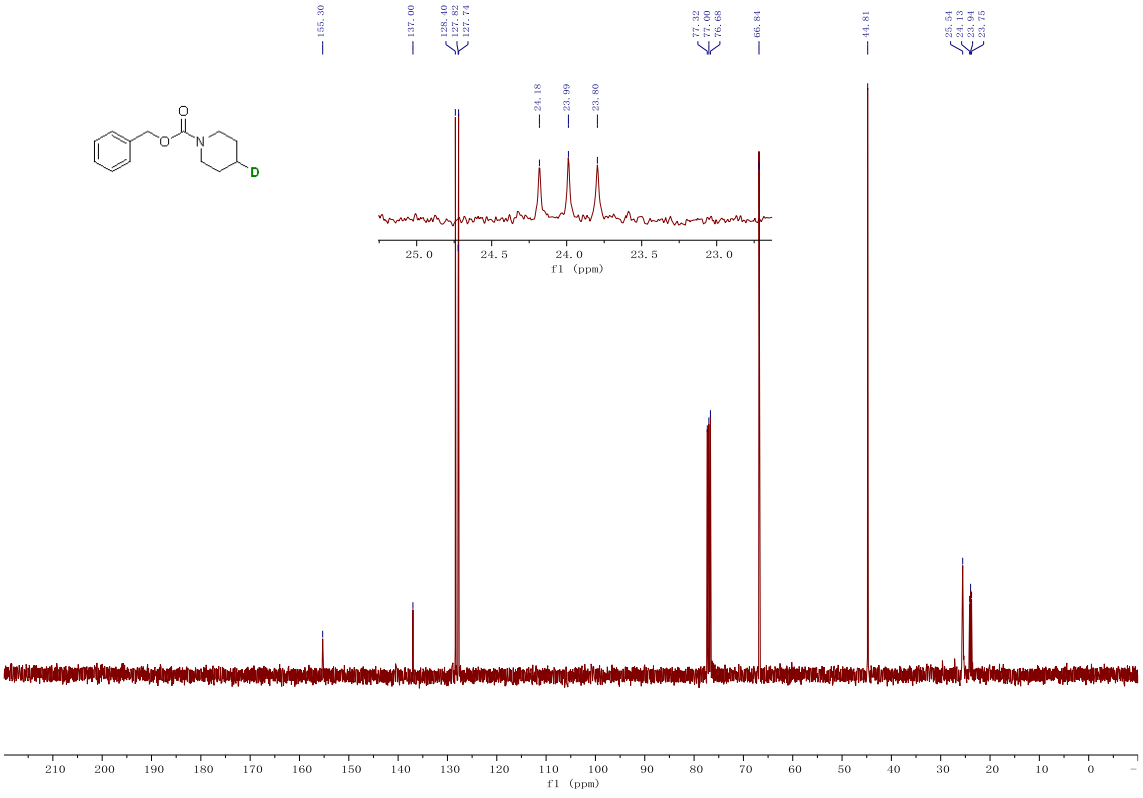
^{13}C NMR spectrum for compound **3l**



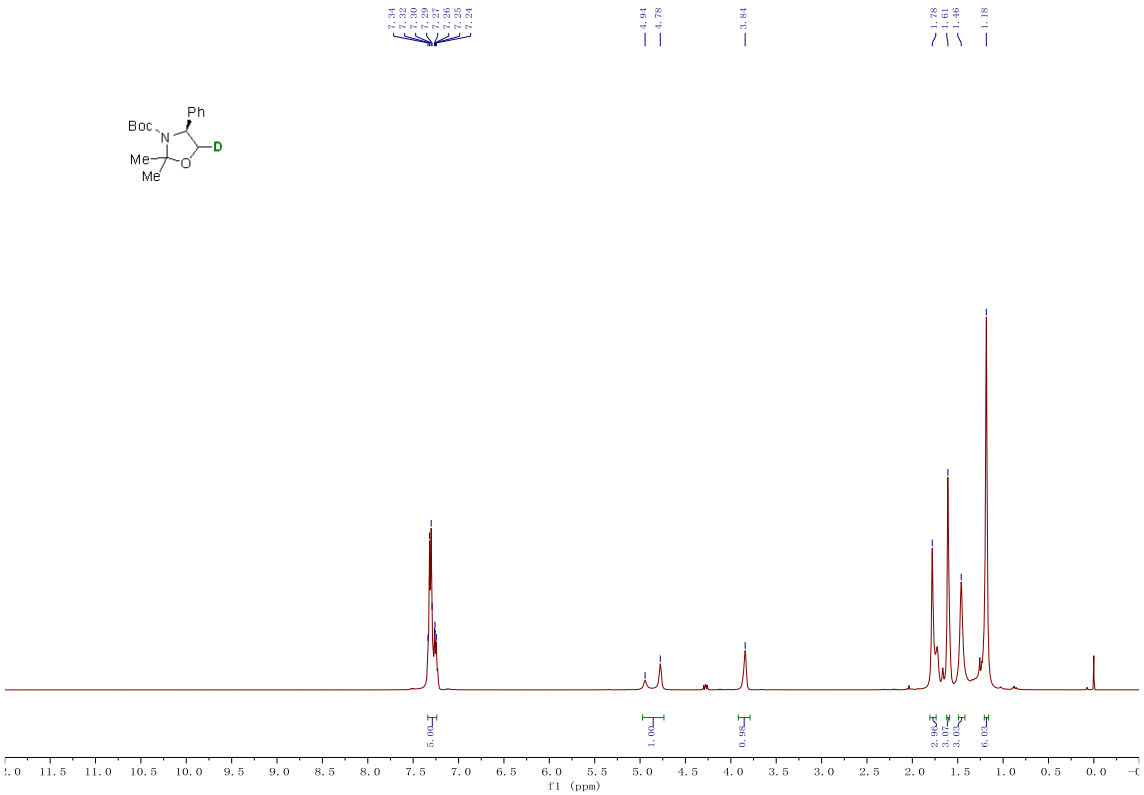
^{1}H NMR spectrum for compound **3m**



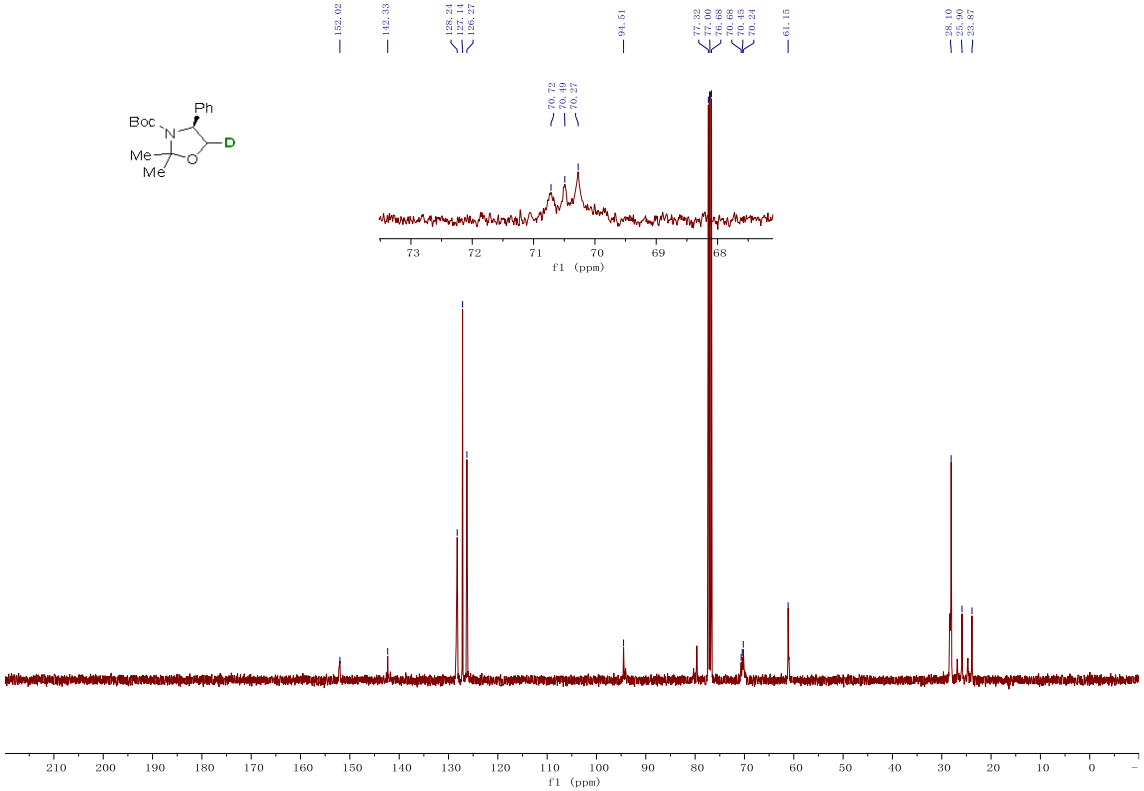
^{13}C NMR spectrum for compound **3m**



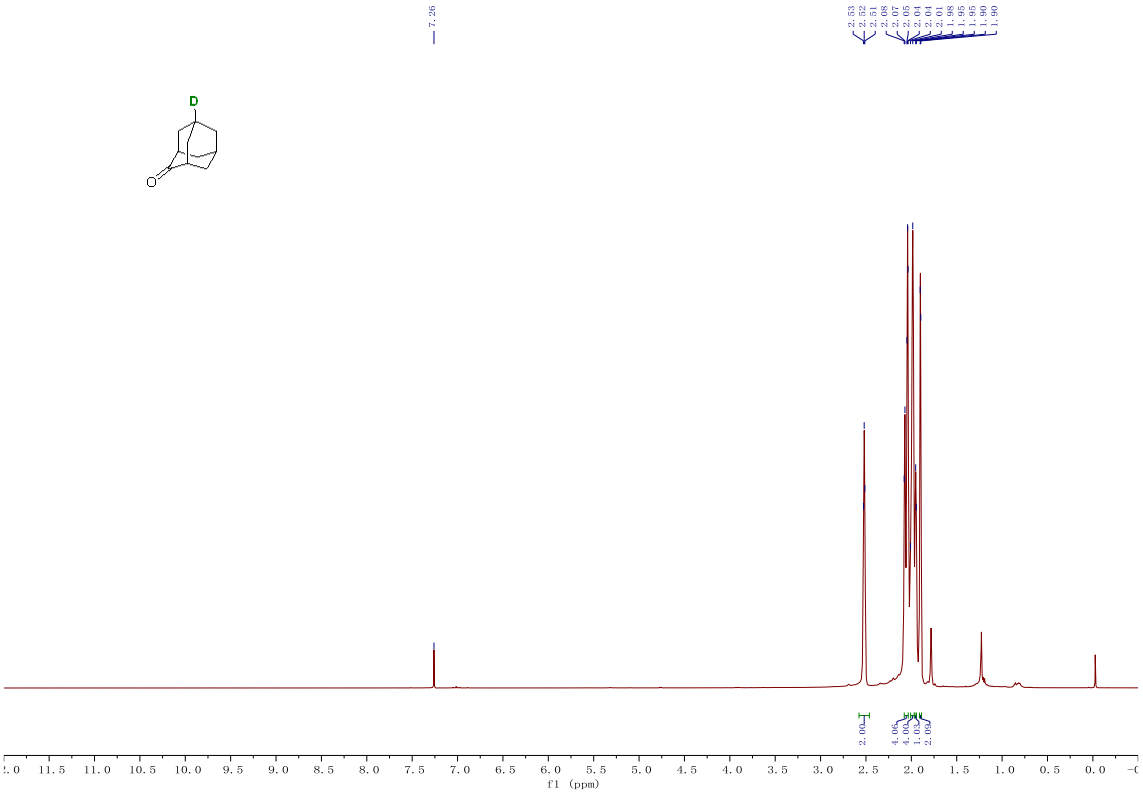
^{1}H NMR spectrum for compound **3n**



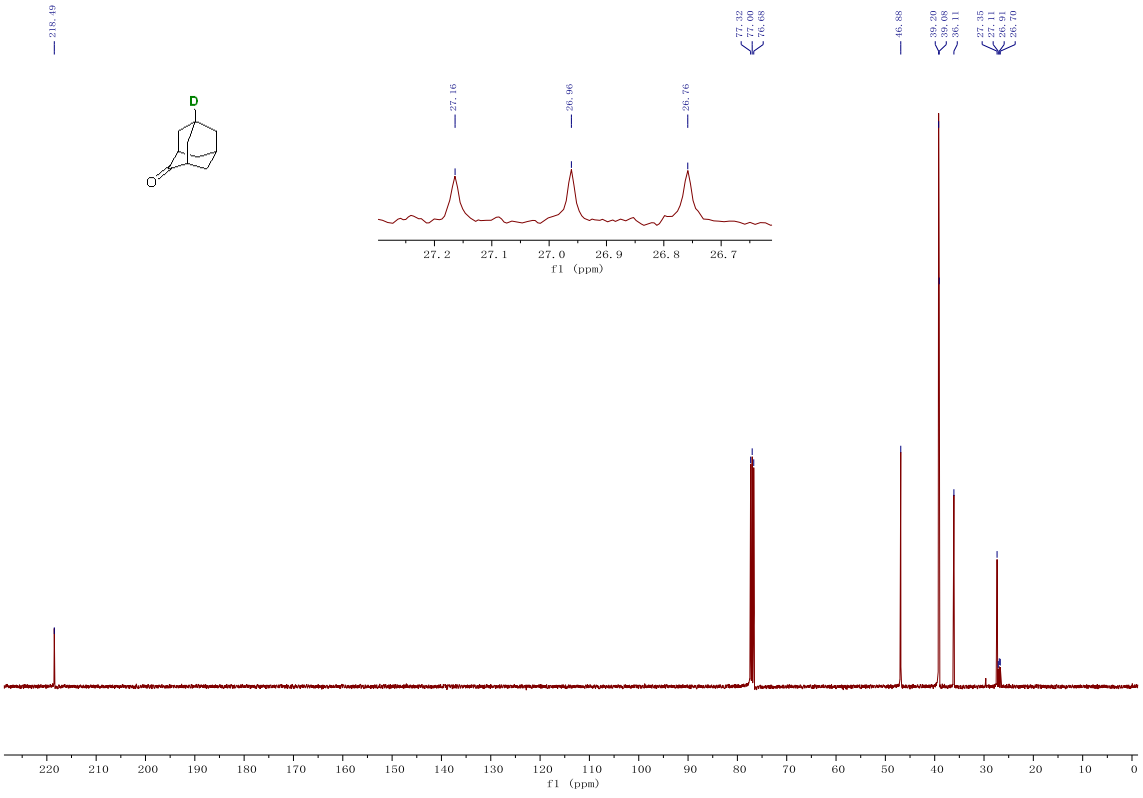
^{13}C NMR spectrum for compound **3n**



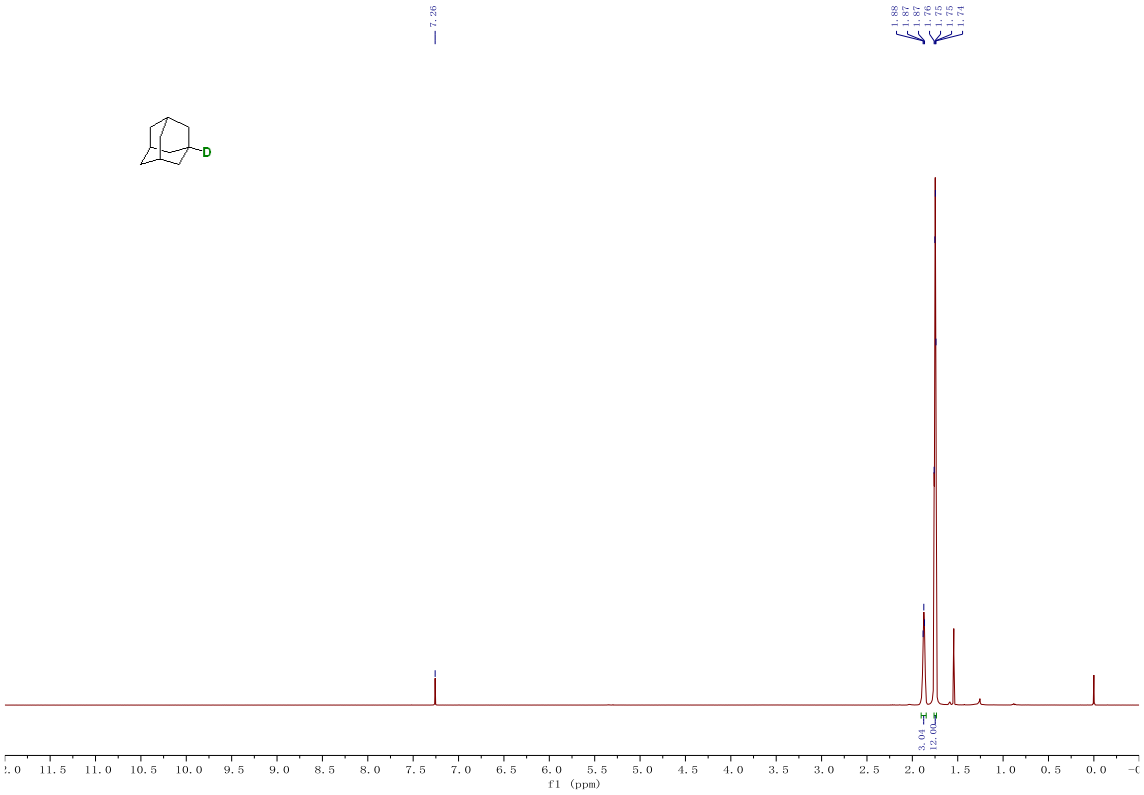
^{1}H NMR spectrum for compound **3o**



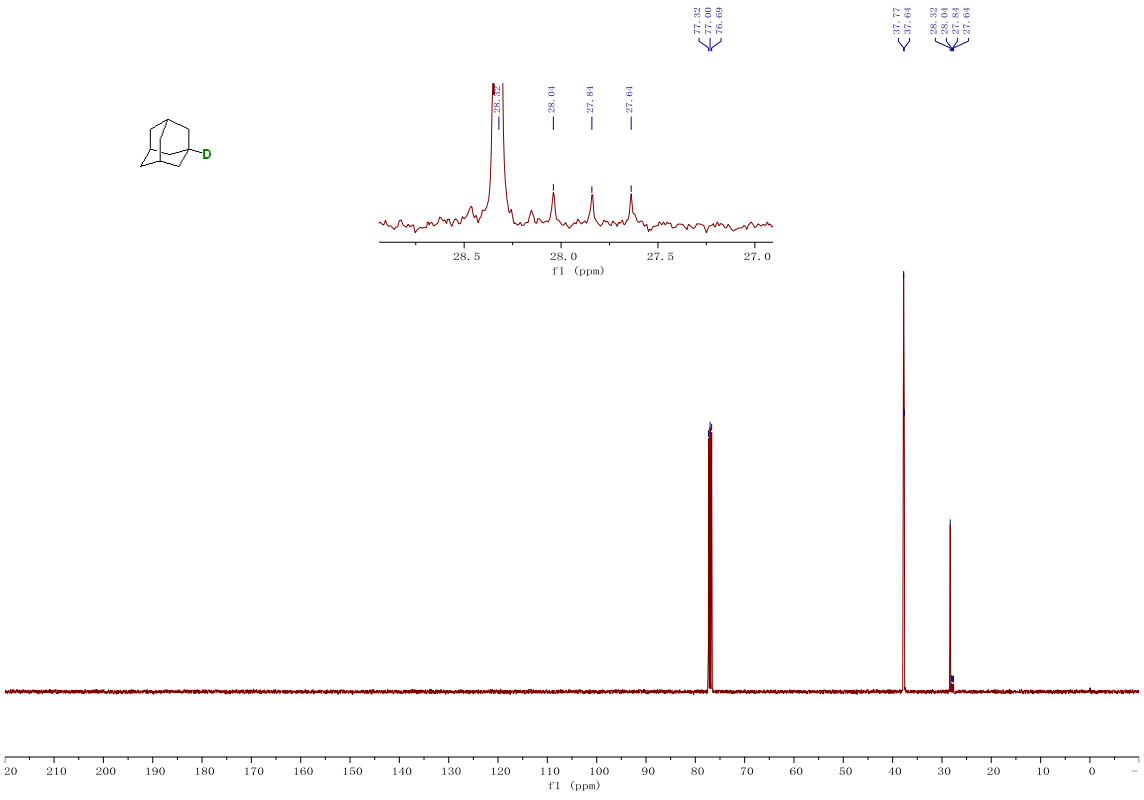
^{13}C NMR spectrum for compound **3o**



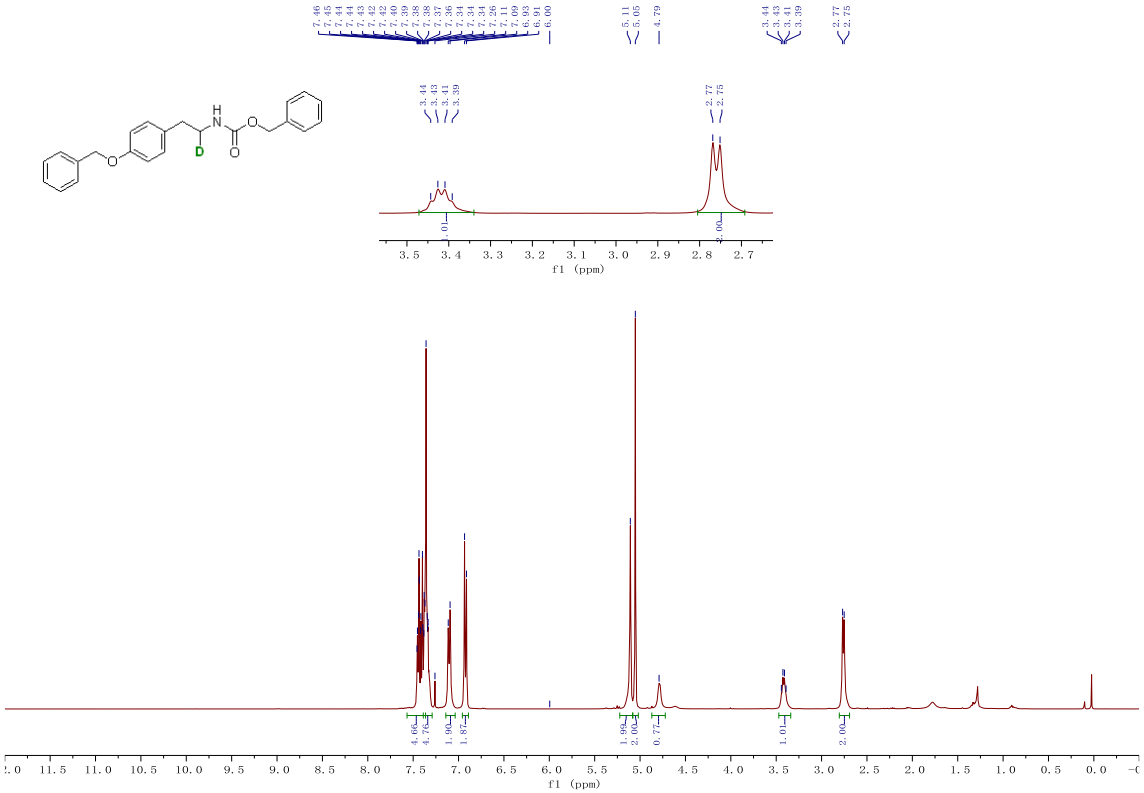
^{1}H NMR spectrum for compound **3p**



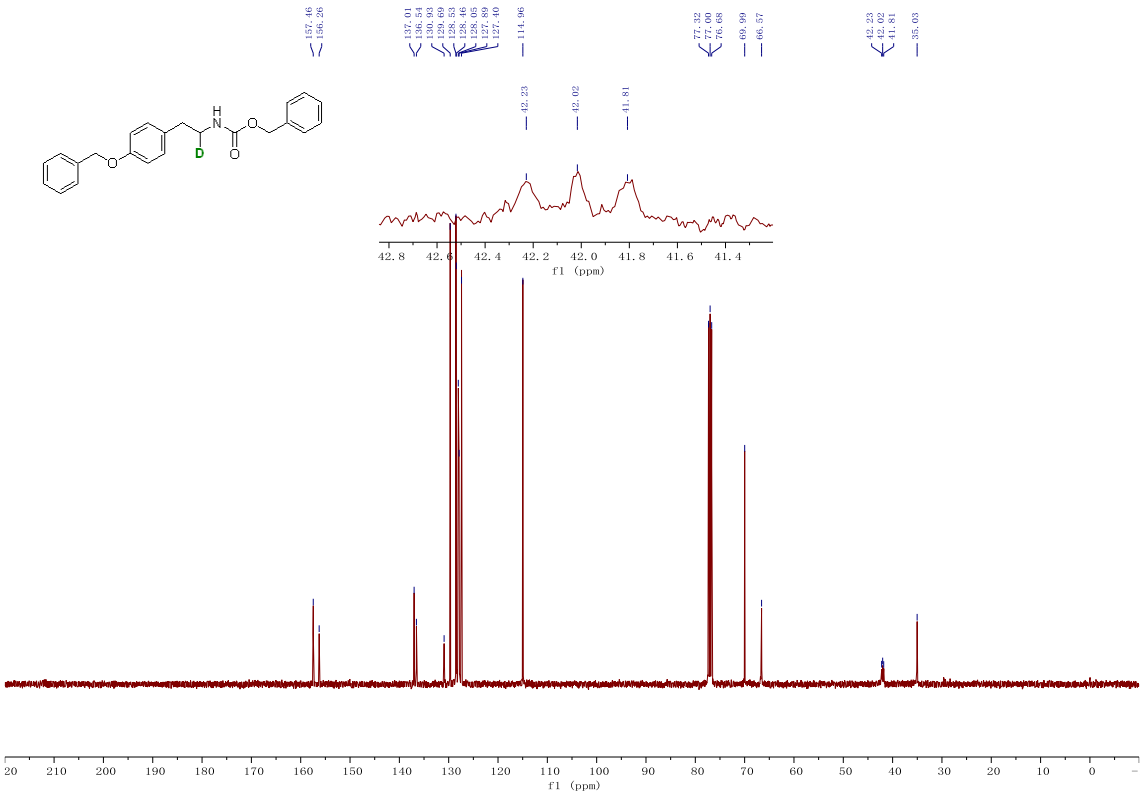
^{13}C NMR spectrum for compound **3p**



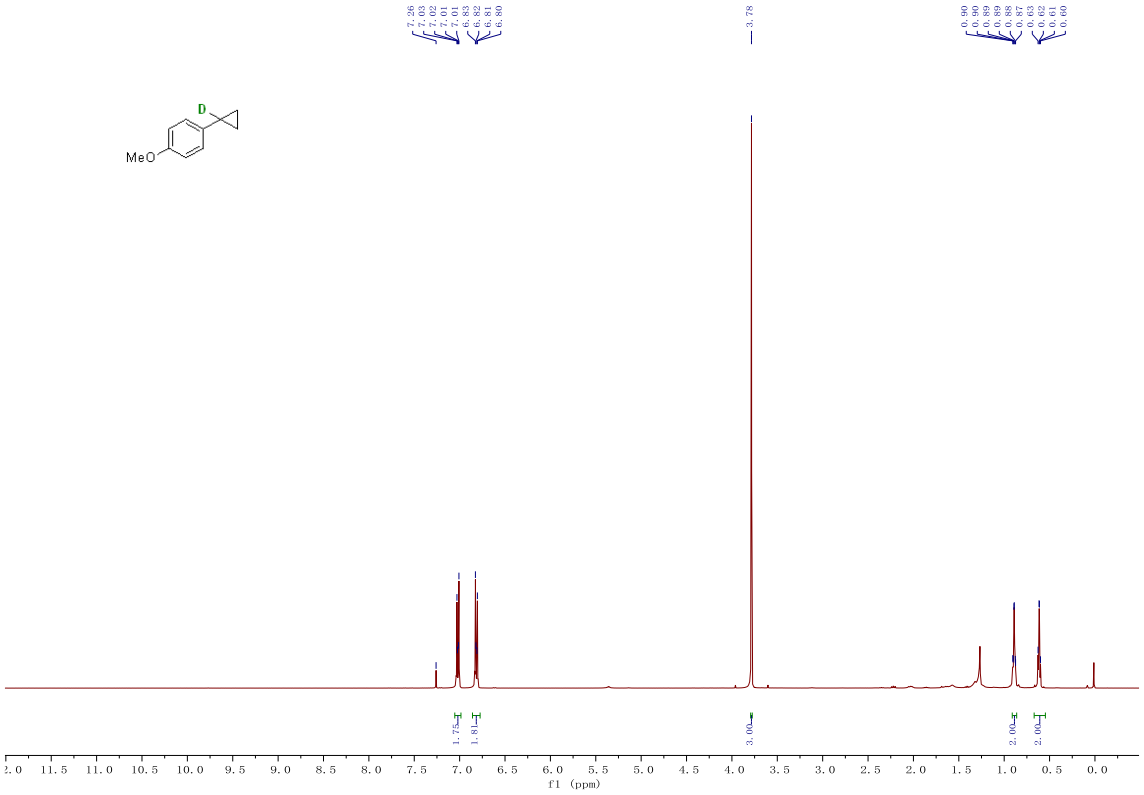
^{1}H NMR spectrum for compound **3q**



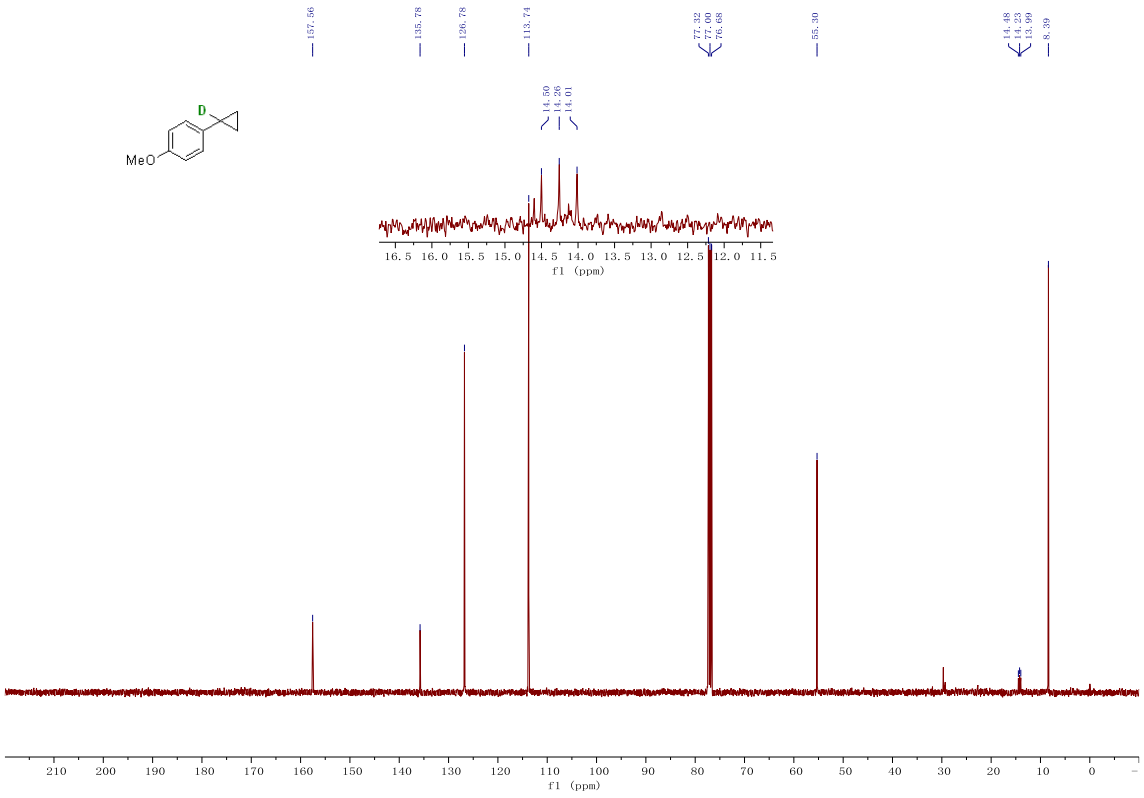
^{13}C NMR spectrum for compound **3q**



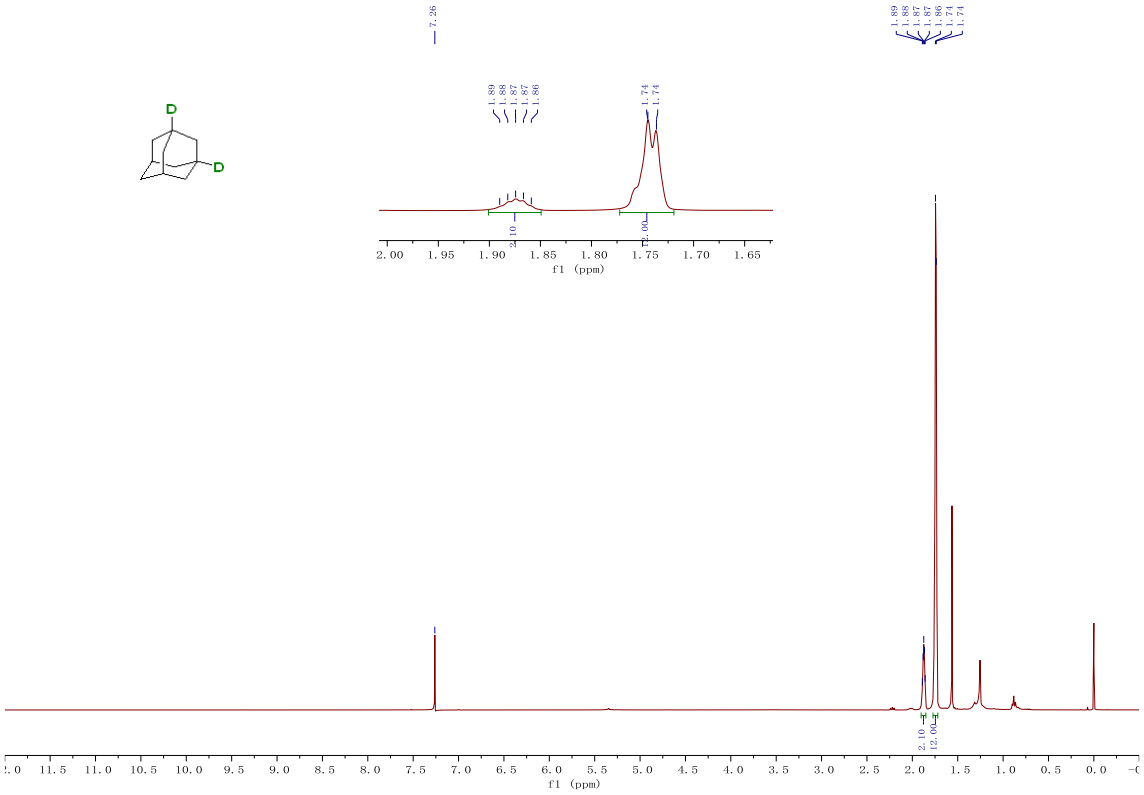
^{1}H NMR spectrum for compound **3r**



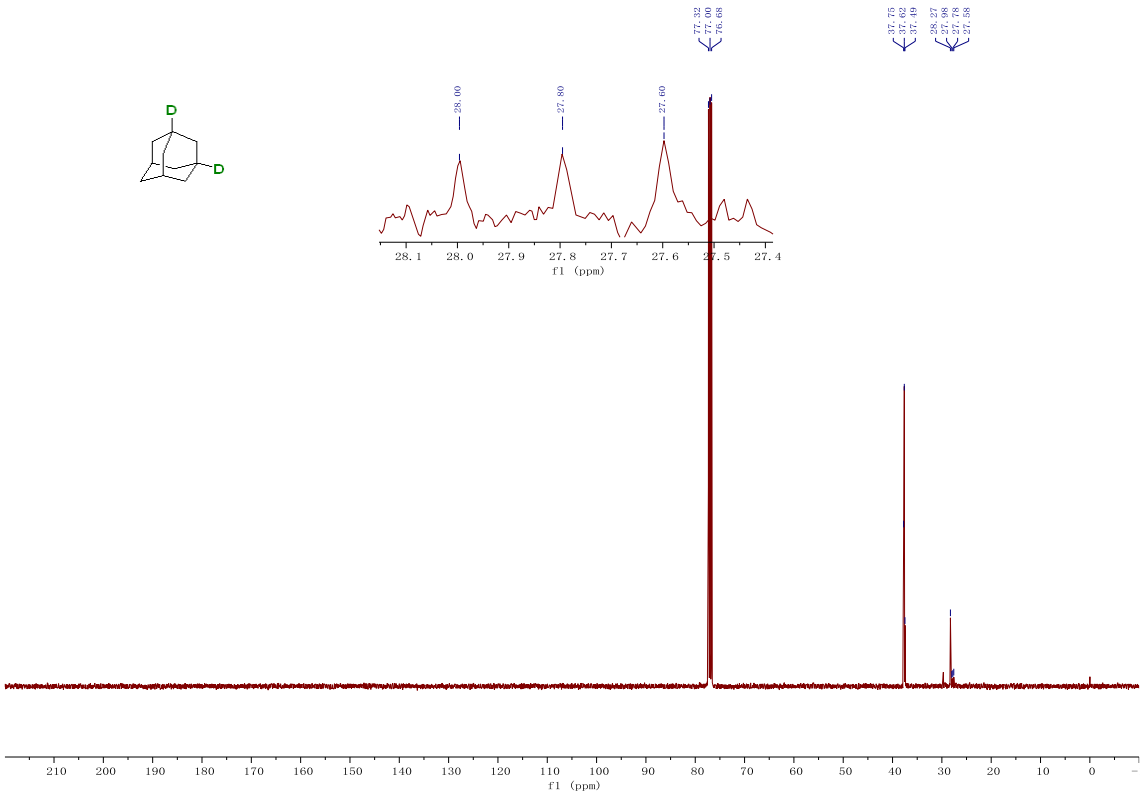
^{13}C NMR spectrum for compound **3r**



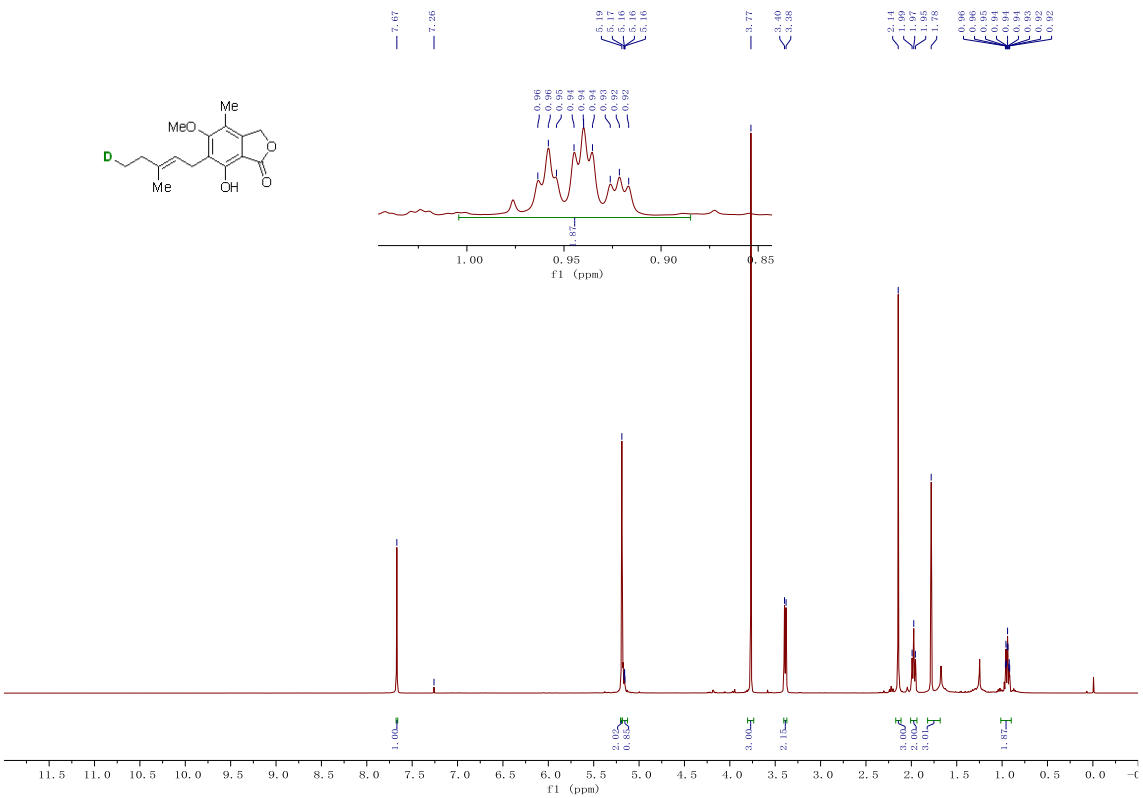
^{1}H NMR spectrum for compound **3s**



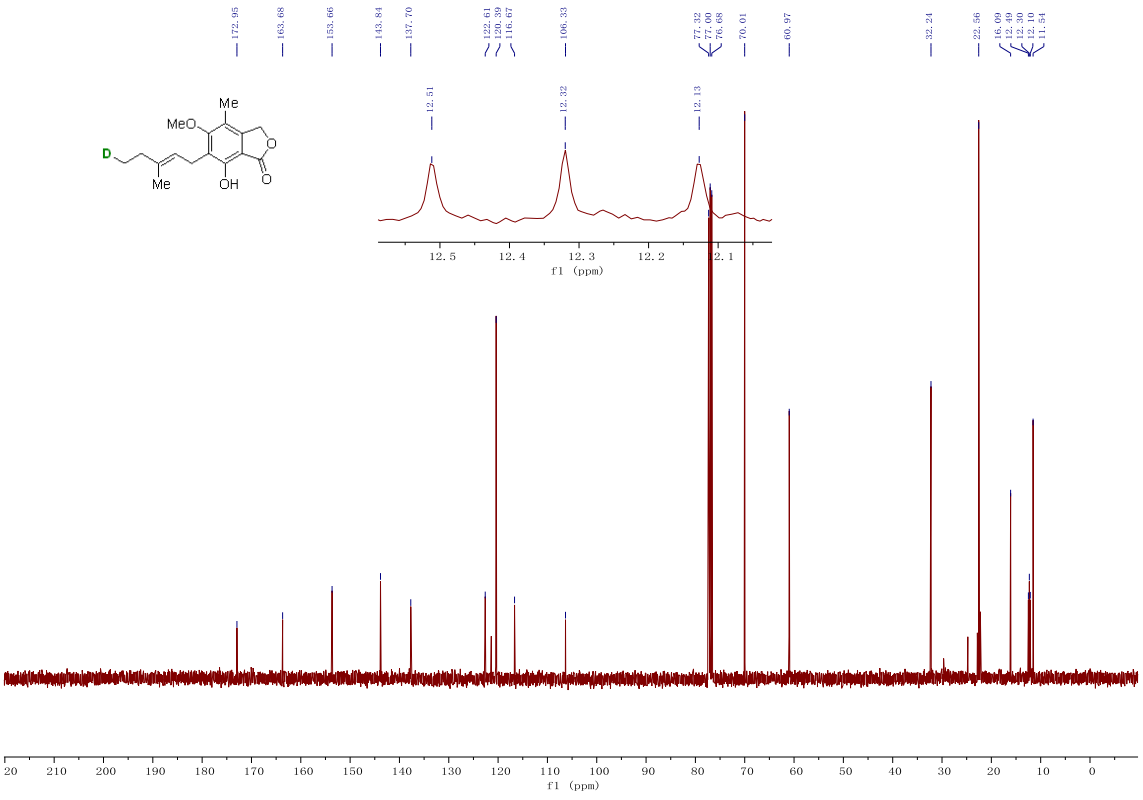
^{13}C NMR spectrum for compound **3s**



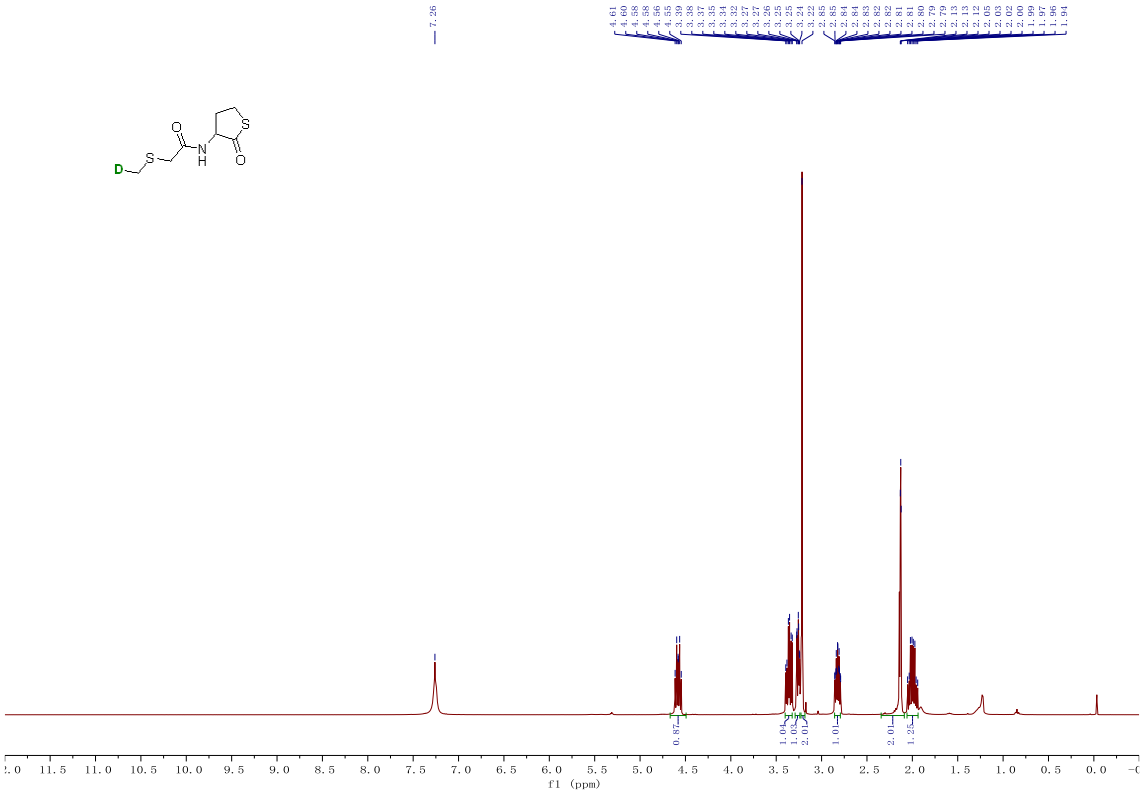
^{1}H NMR spectrum for compound **3t**



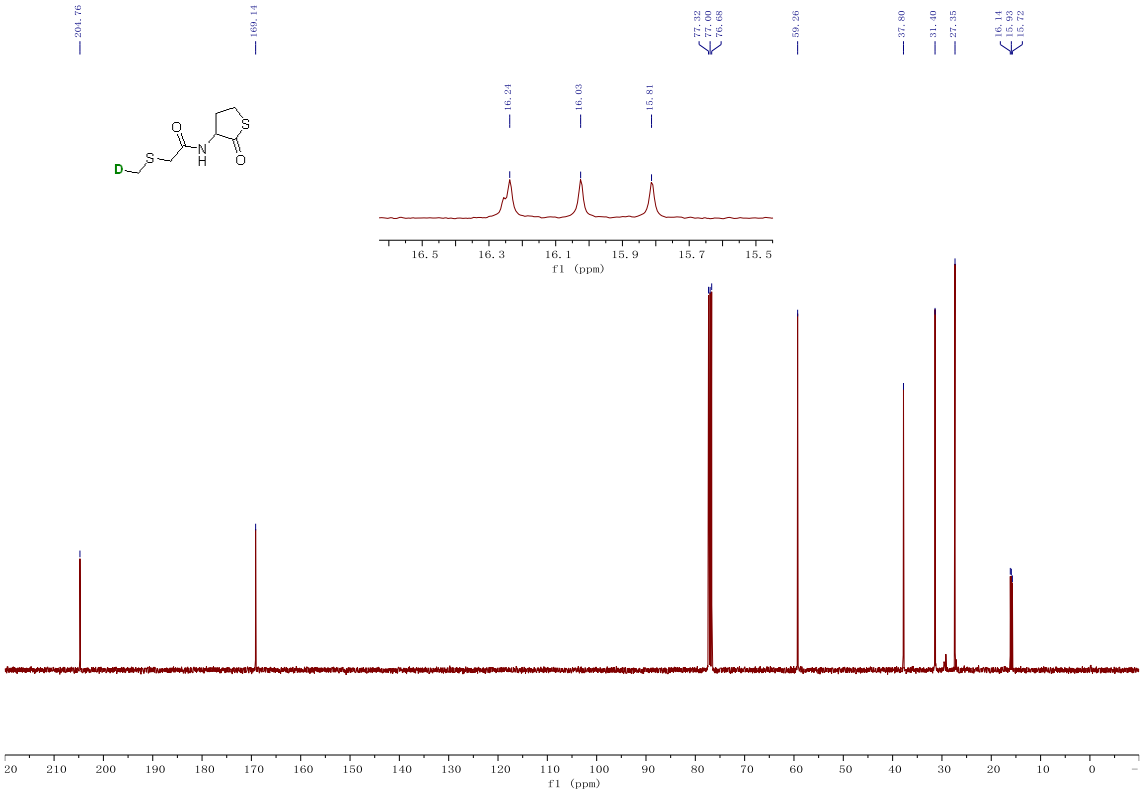
^{13}C NMR spectrum for compound **3t**



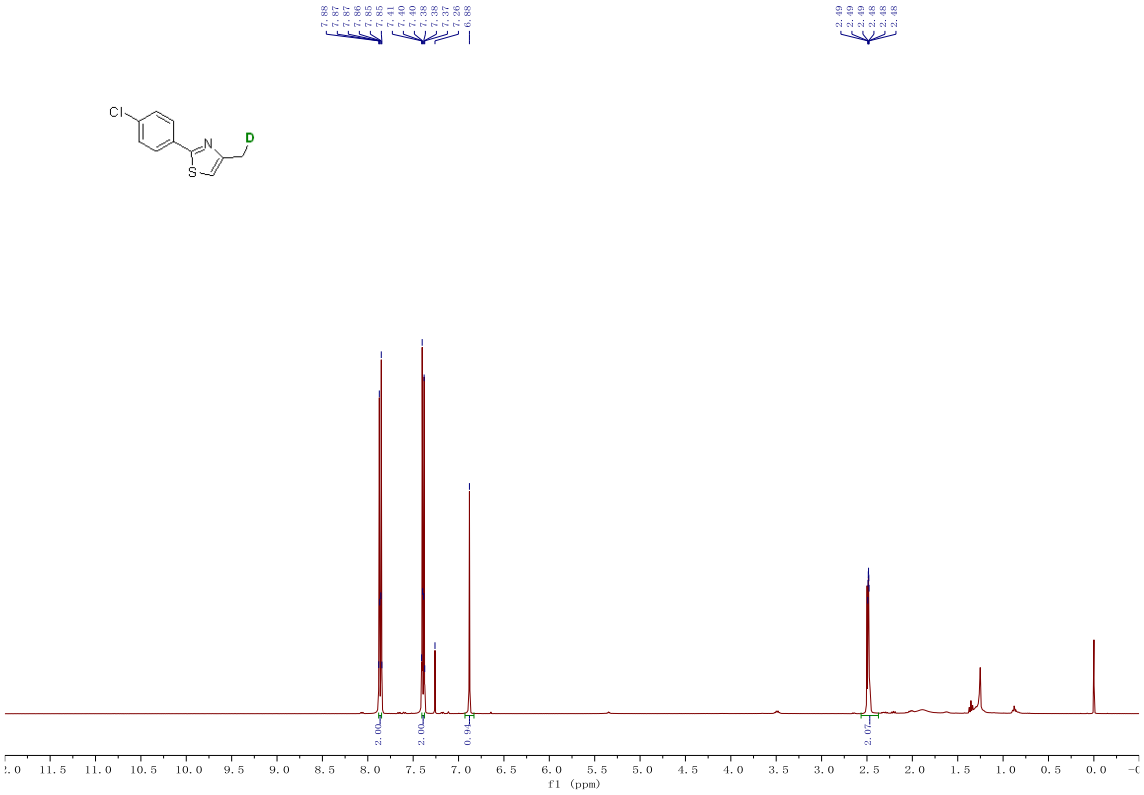
^{1}H NMR spectrum for compound **3u**



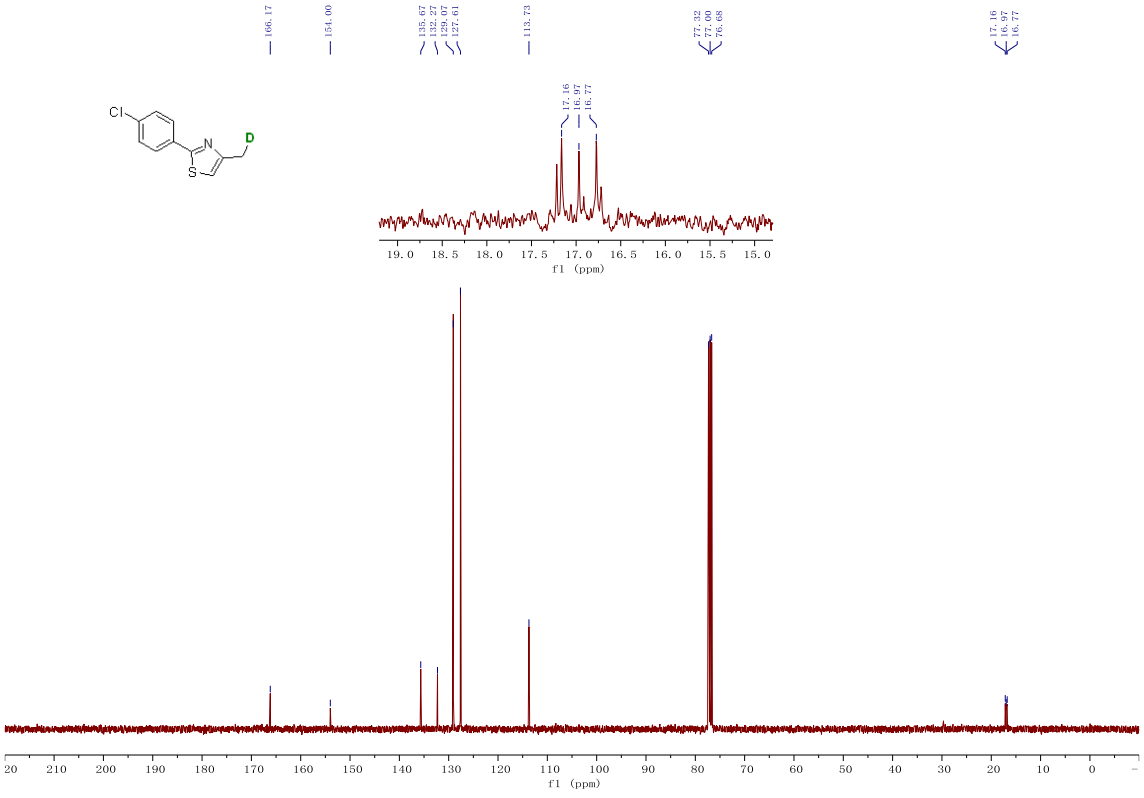
^{13}C NMR spectrum for compound **3u**



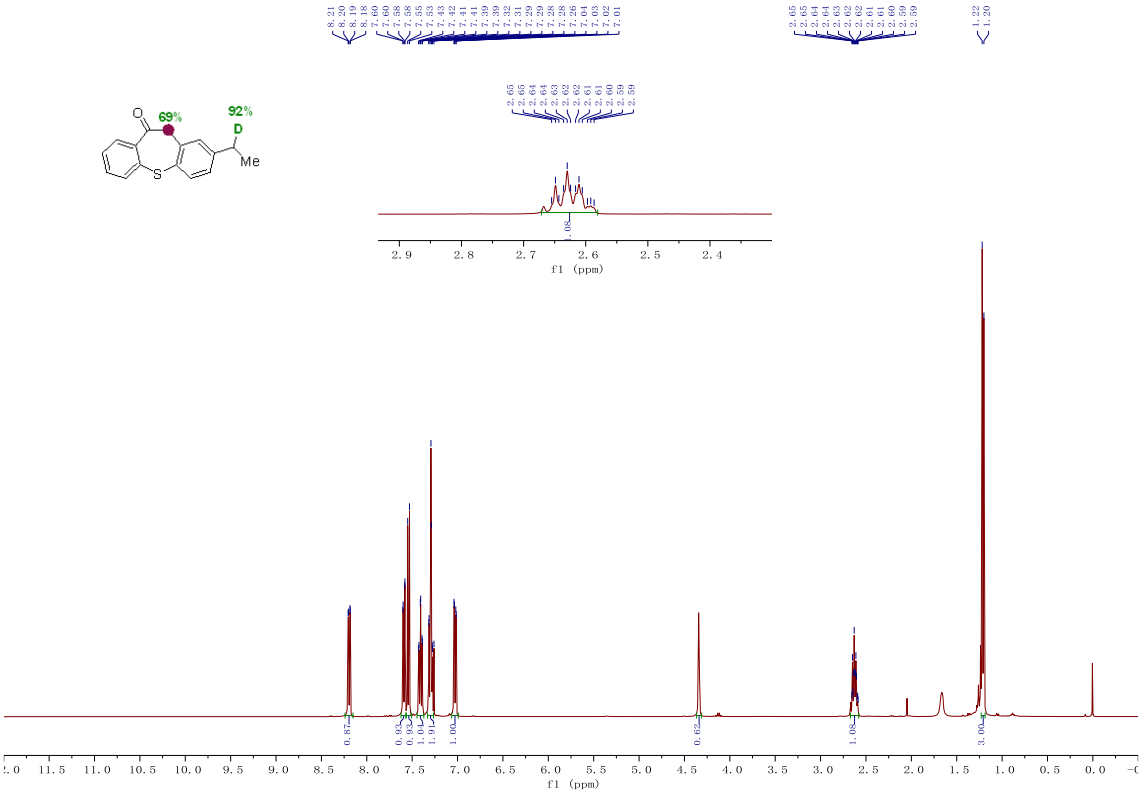
^{1}H NMR spectrum for compound **3v**



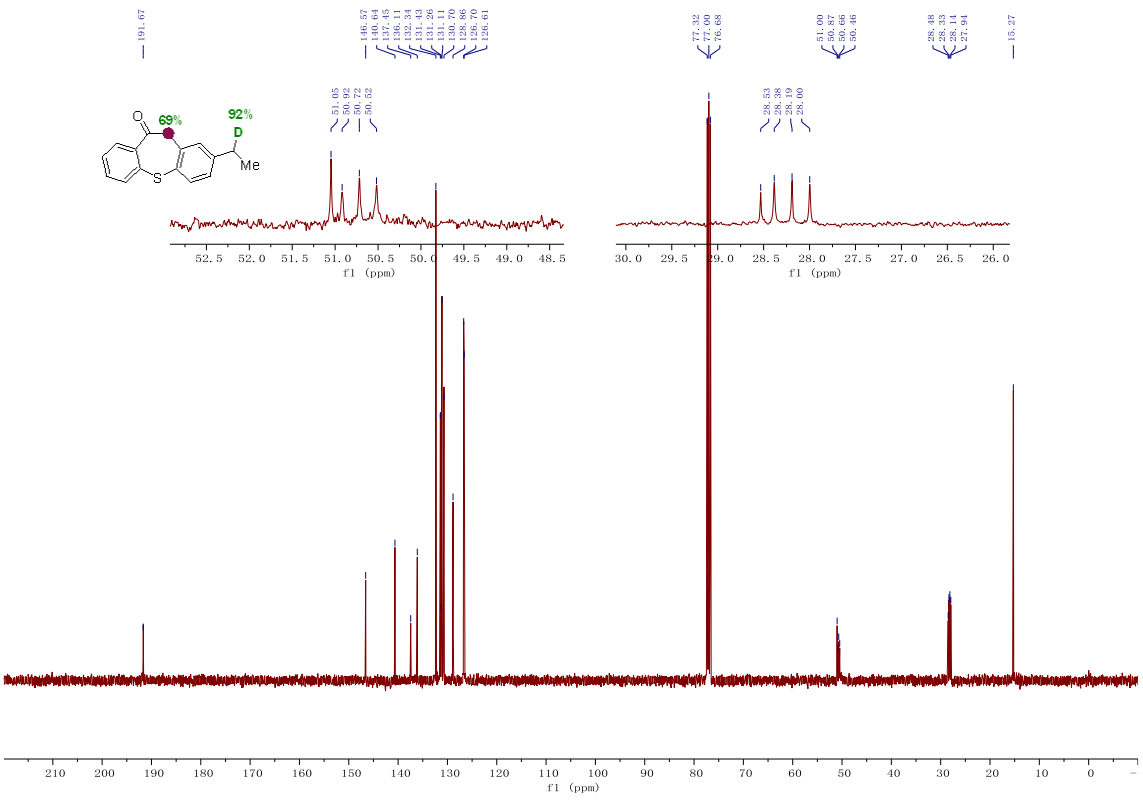
^{13}C NMR spectrum for compound **3v**



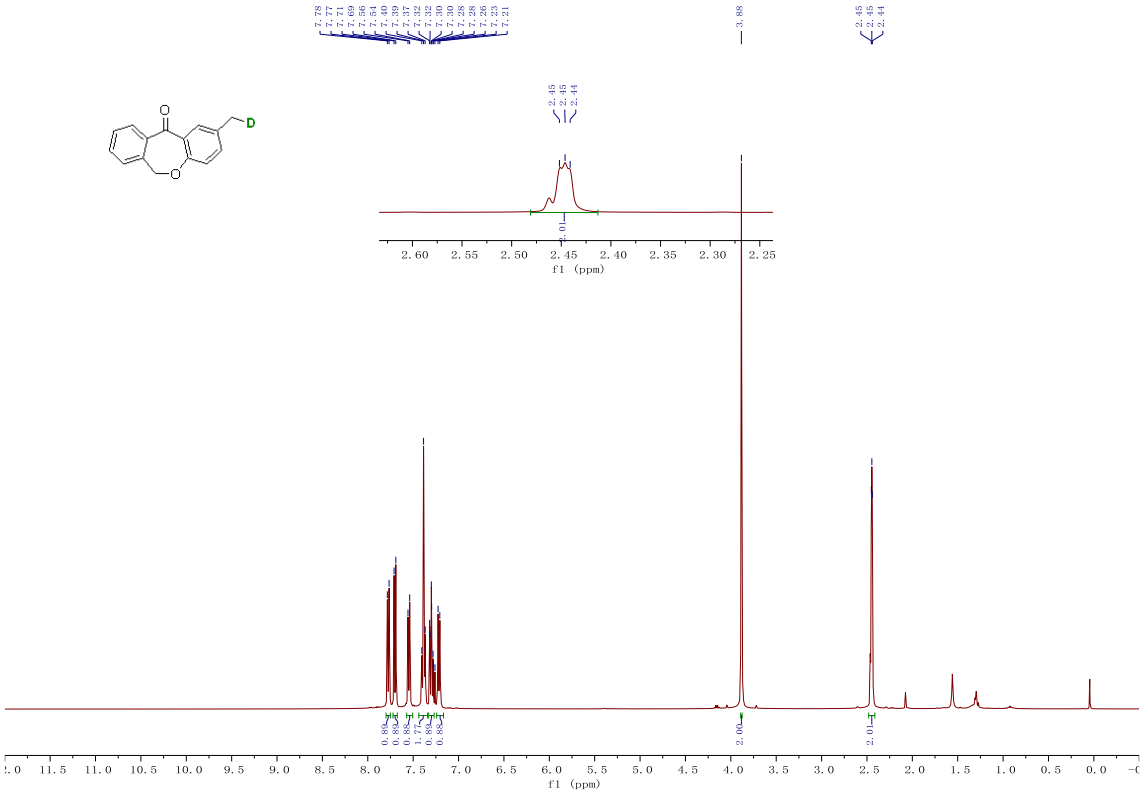
^{1}H NMR spectrum for compound **3w**



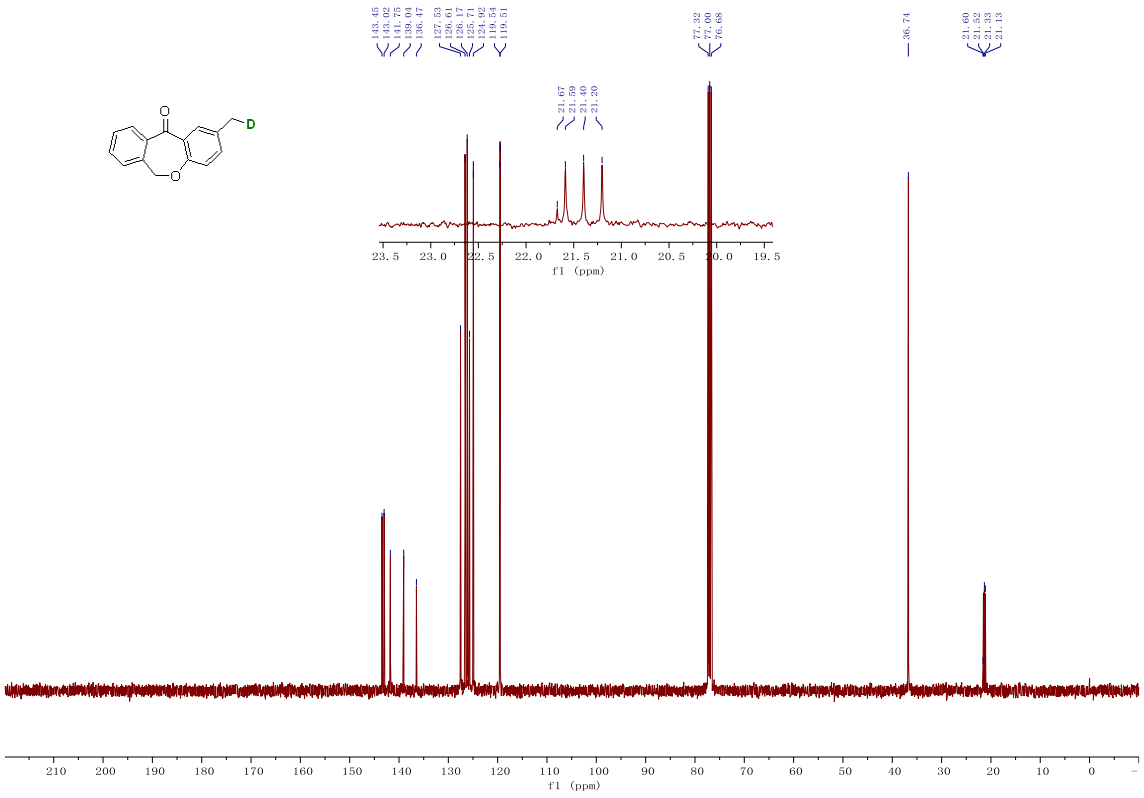
^{13}C NMR spectrum for compound **3w**



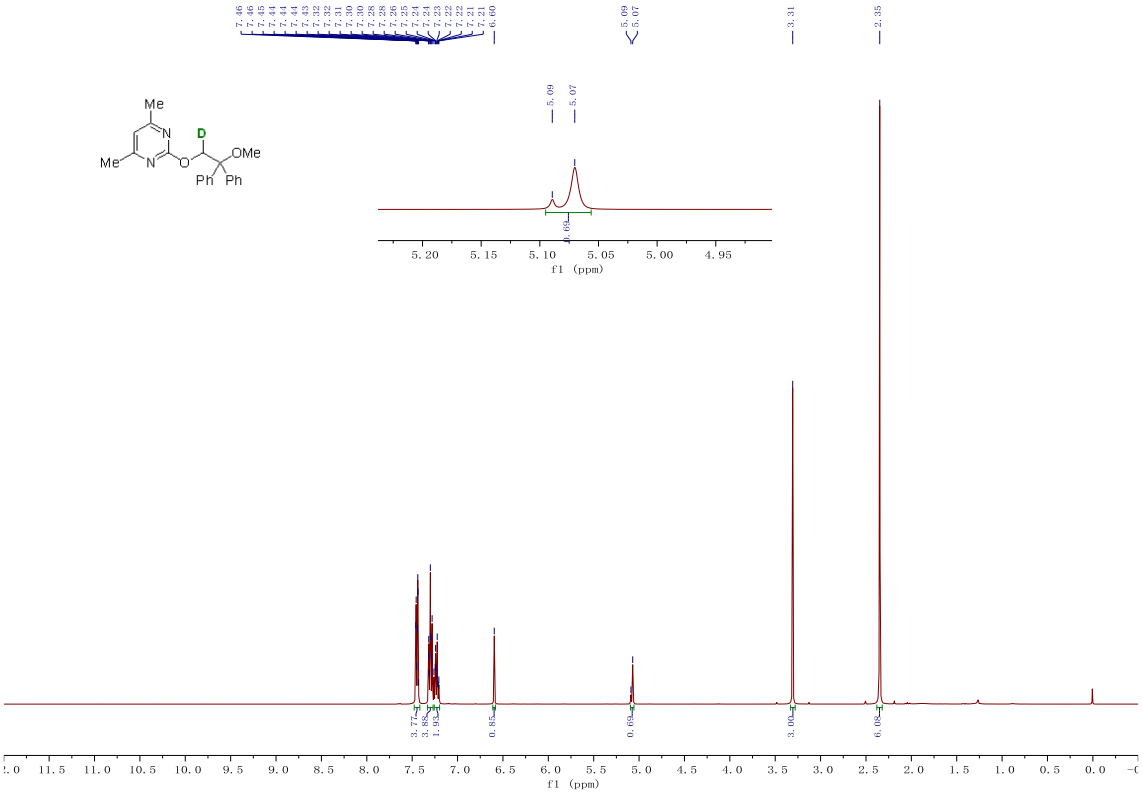
^{1}H NMR spectrum for compound **3x**



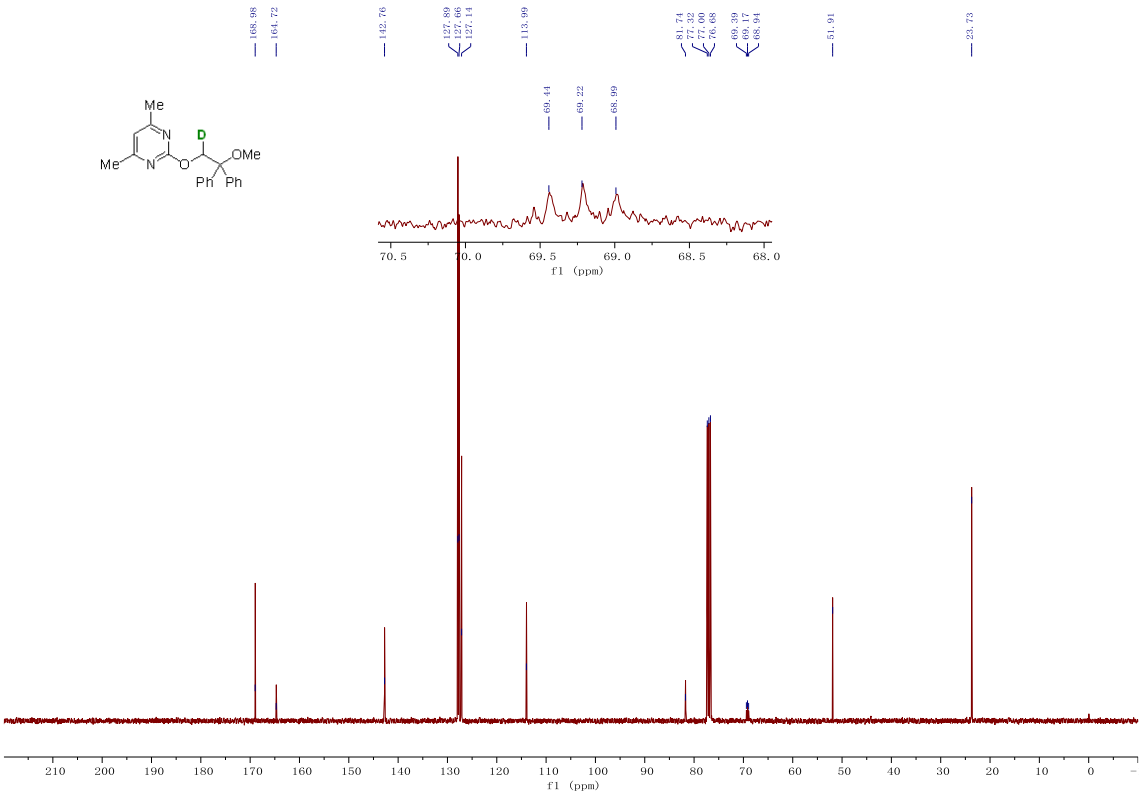
^{13}C NMR spectrum for compound **3x**



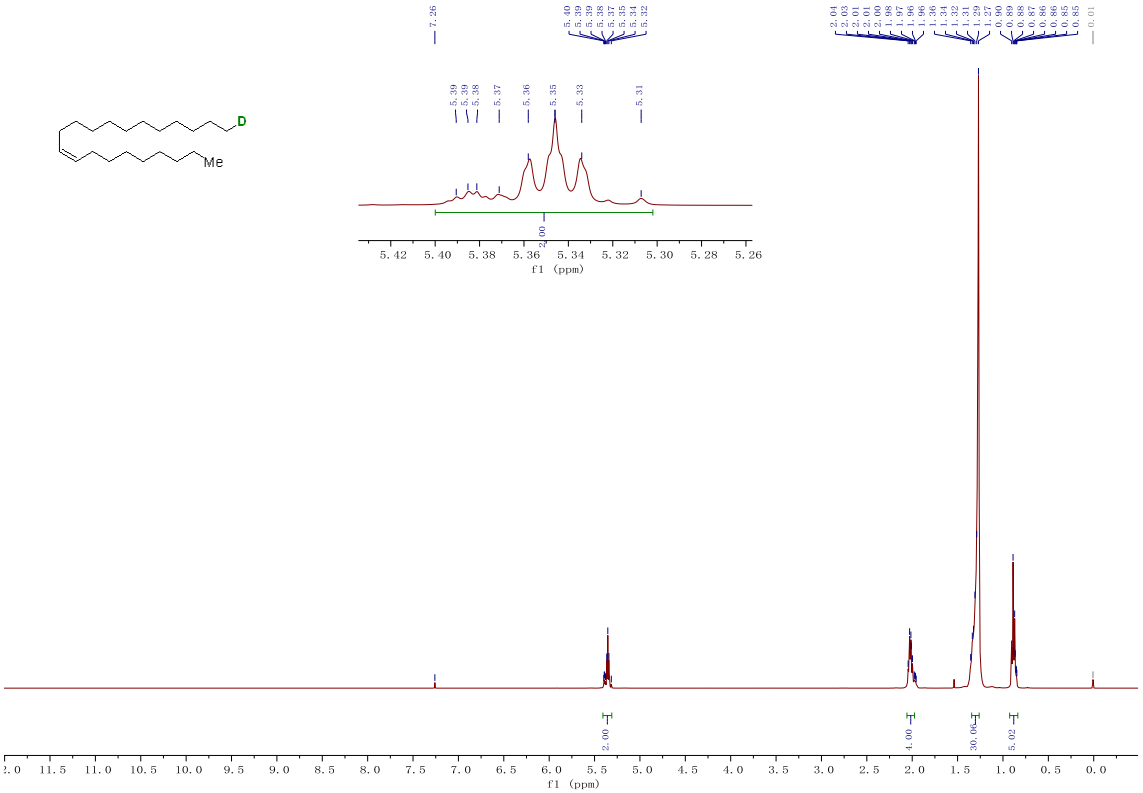
^{1}H NMR spectrum for compound **3y**



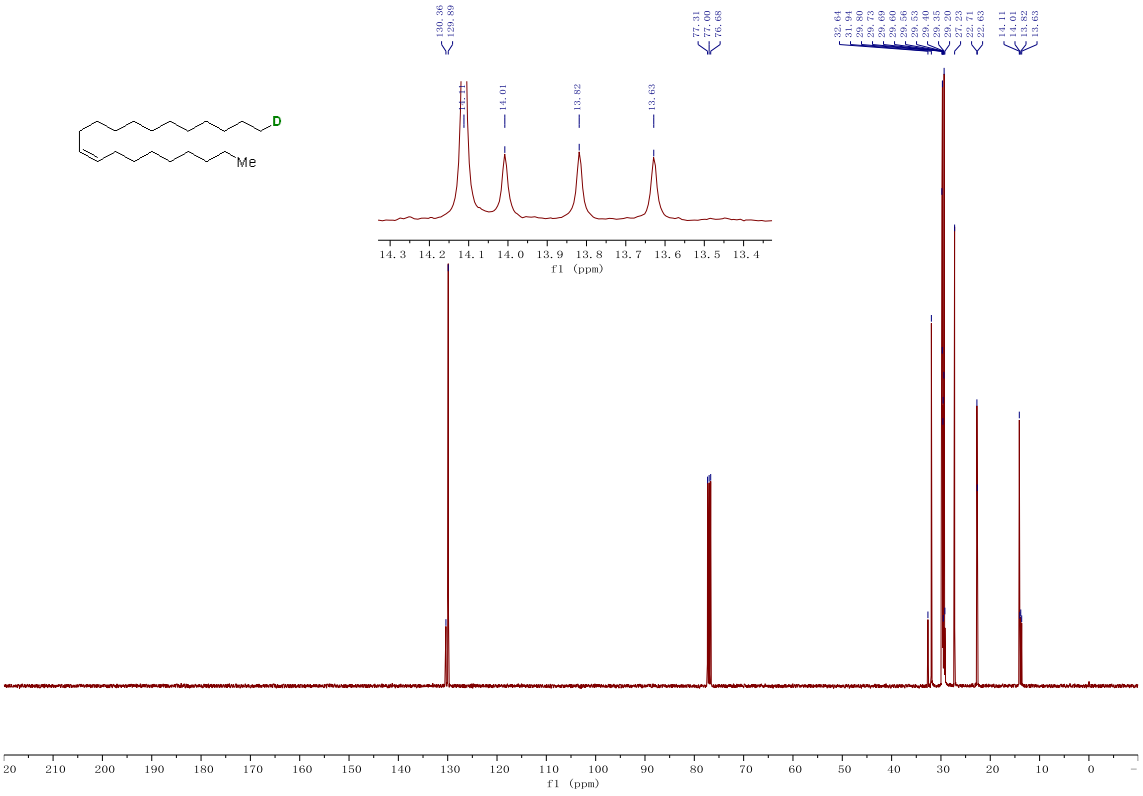
^{13}C NMR spectrum for compound **3y**



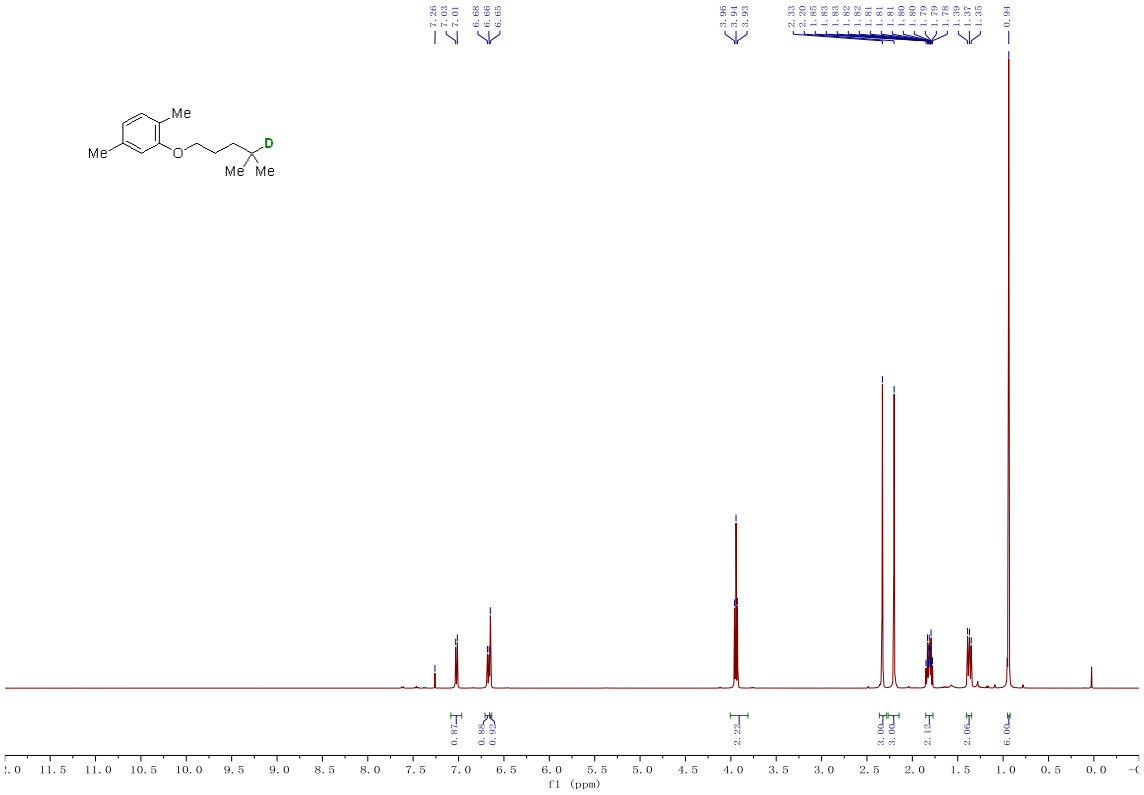
^{1}H NMR spectrum for compound **3z**



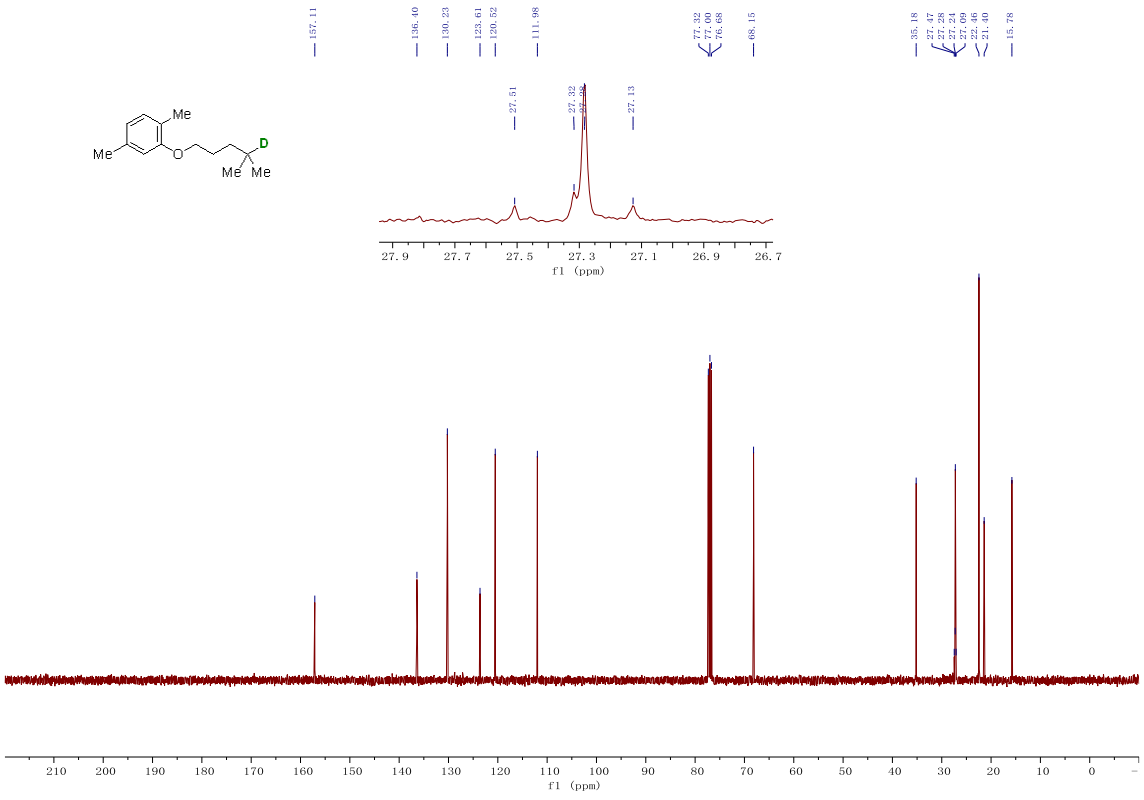
^{13}C NMR spectrum for compound **3z**



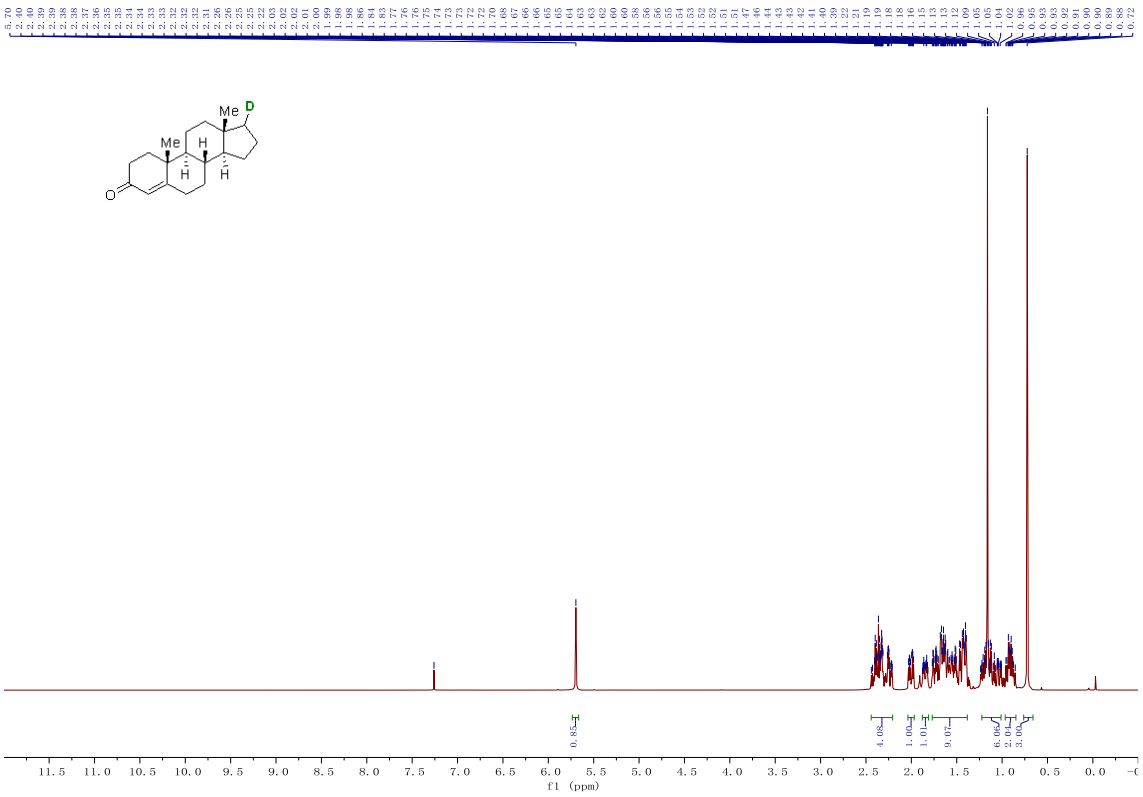
^{1}H NMR spectrum for compound **3aa**



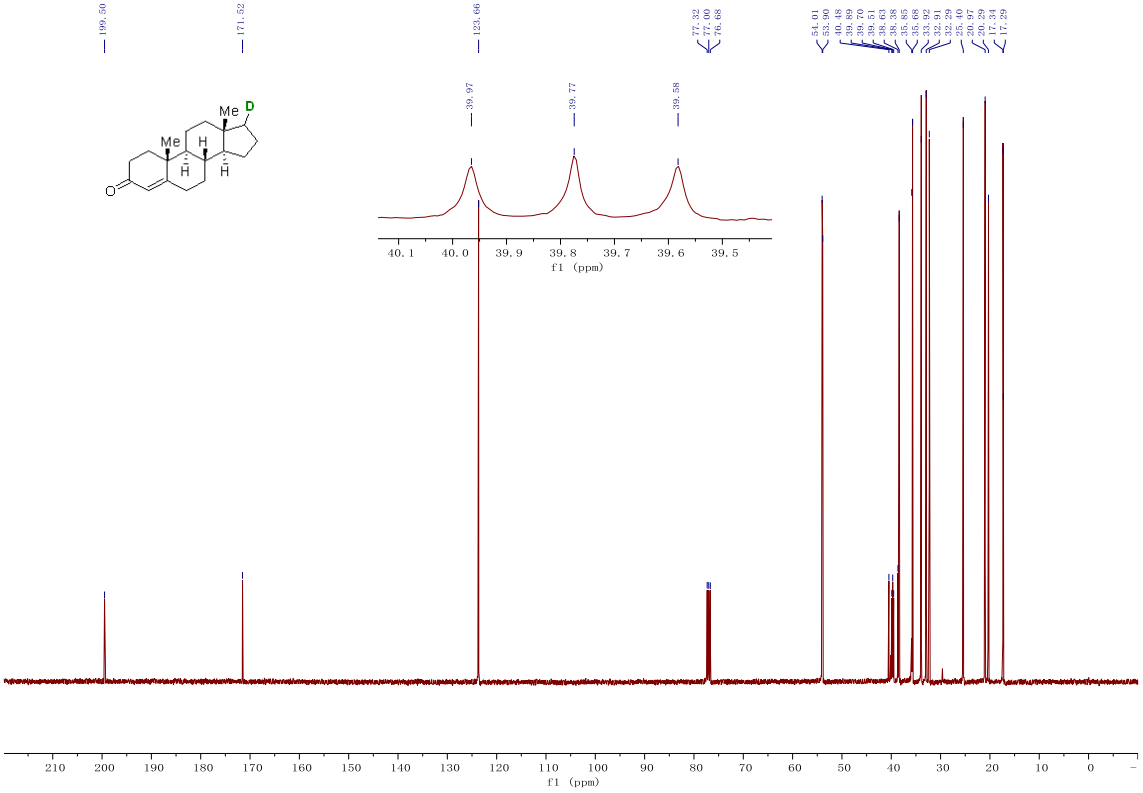
^{13}C NMR spectrum for compound **3aa**



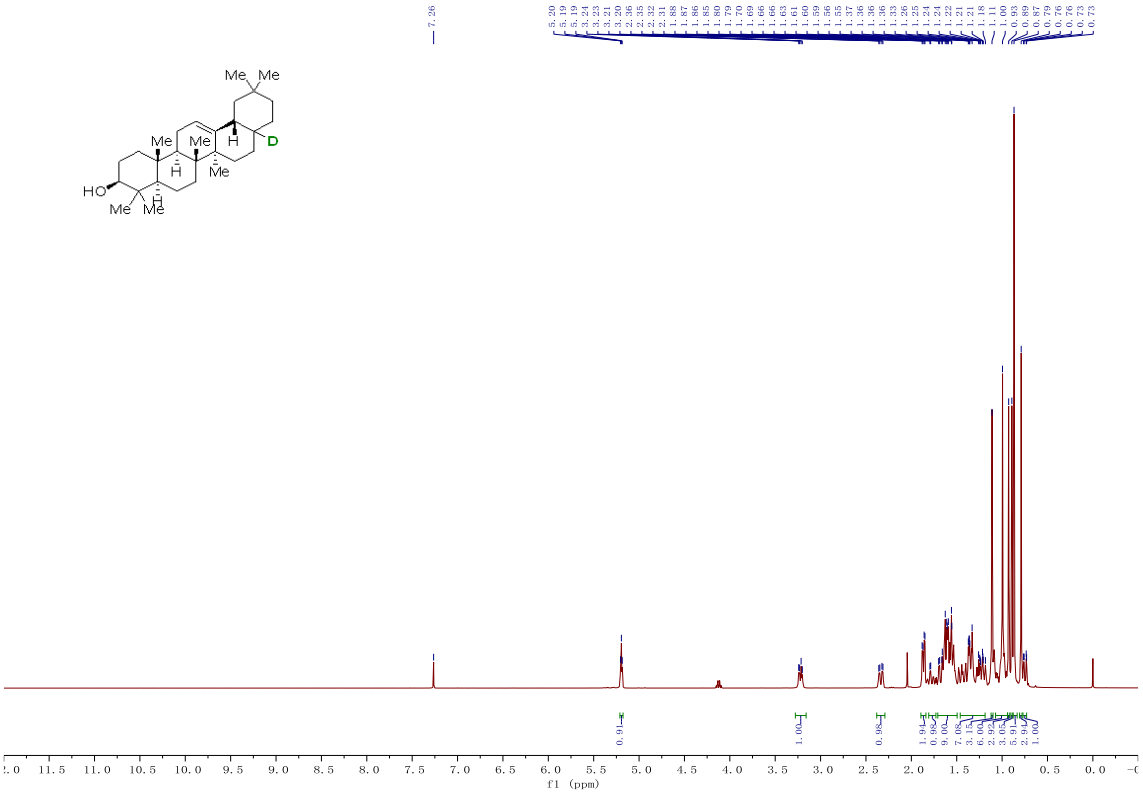
^{1}H NMR spectrum for compound **3bb**



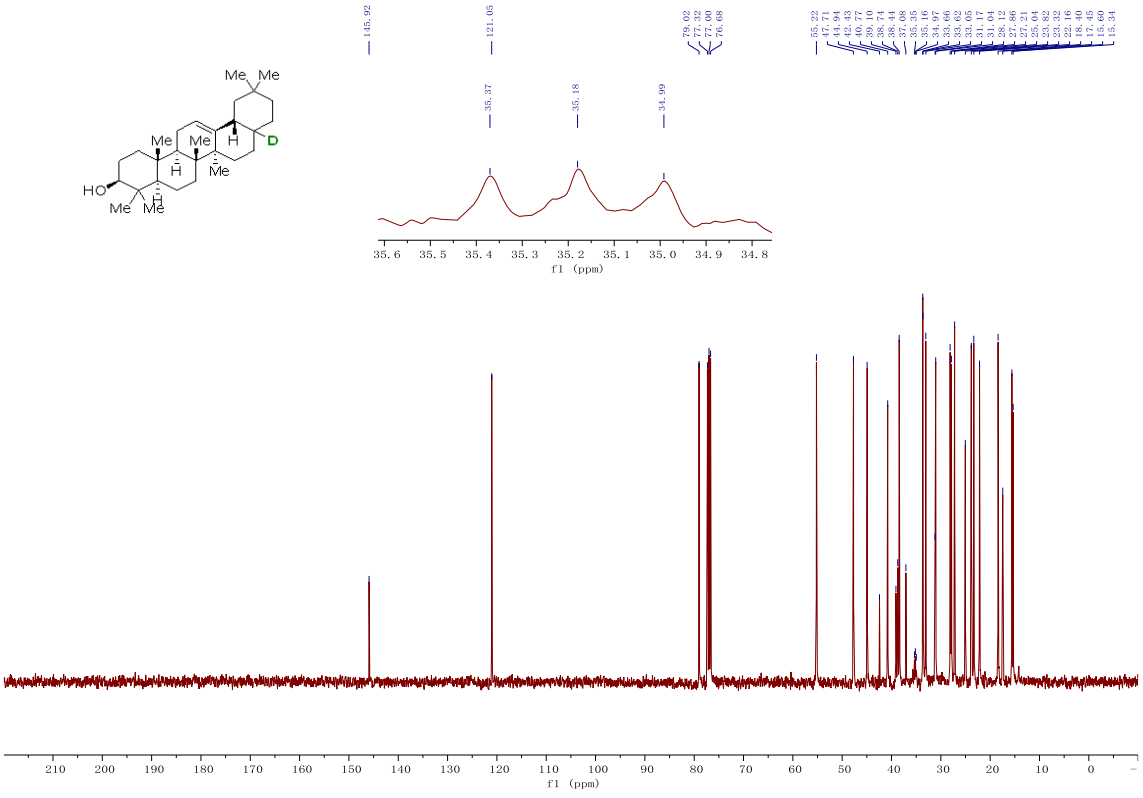
^{13}C NMR spectrum for compound **3bb**



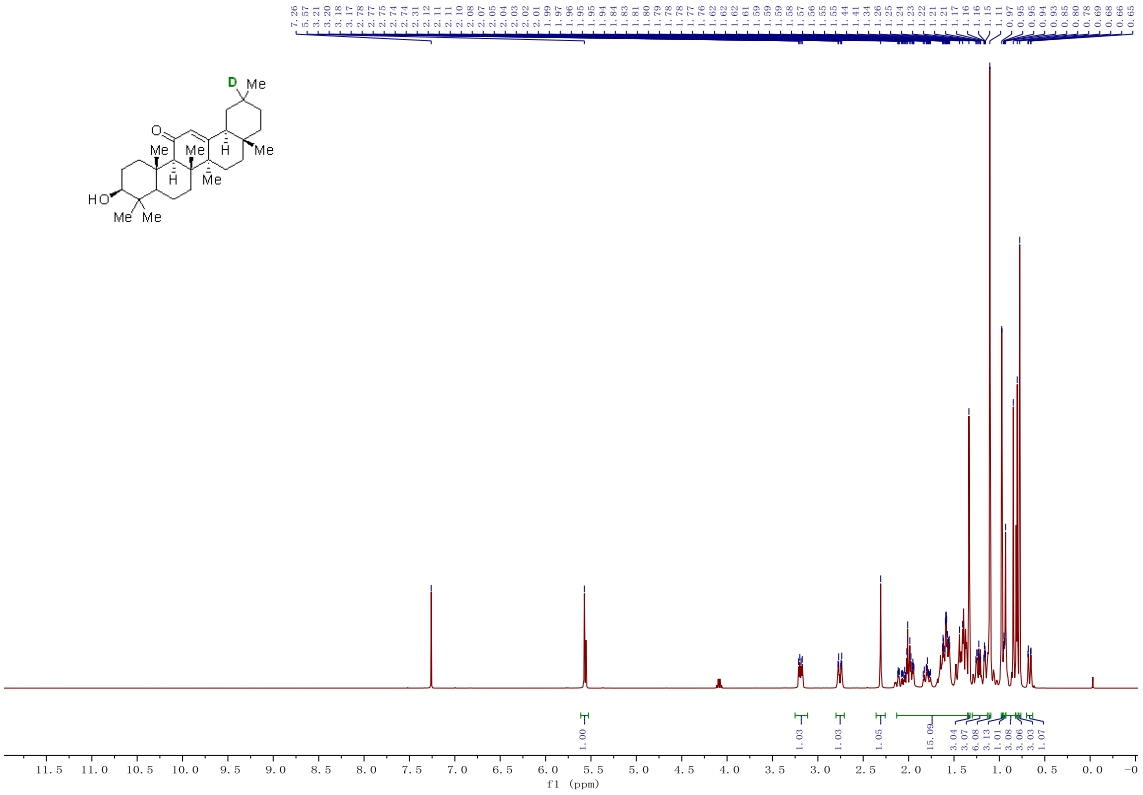
^{1}H NMR spectrum for compound **3cc**



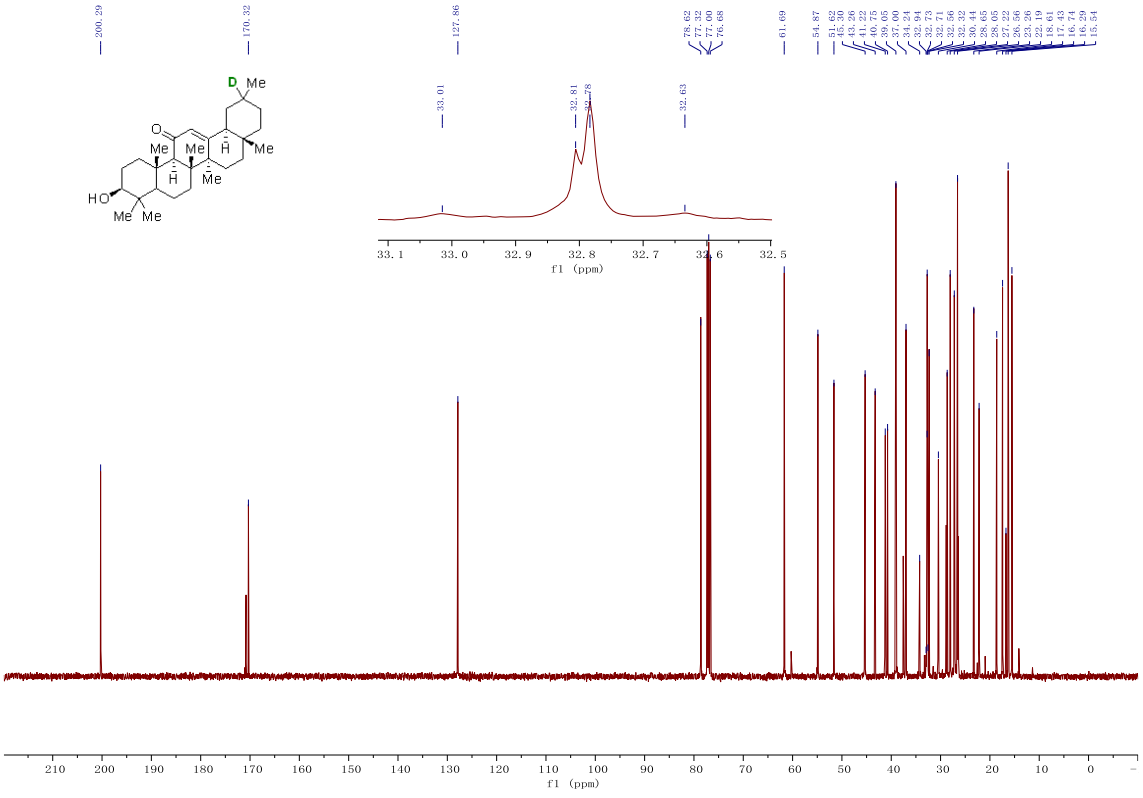
^{13}C NMR spectrum for compound **3cc**



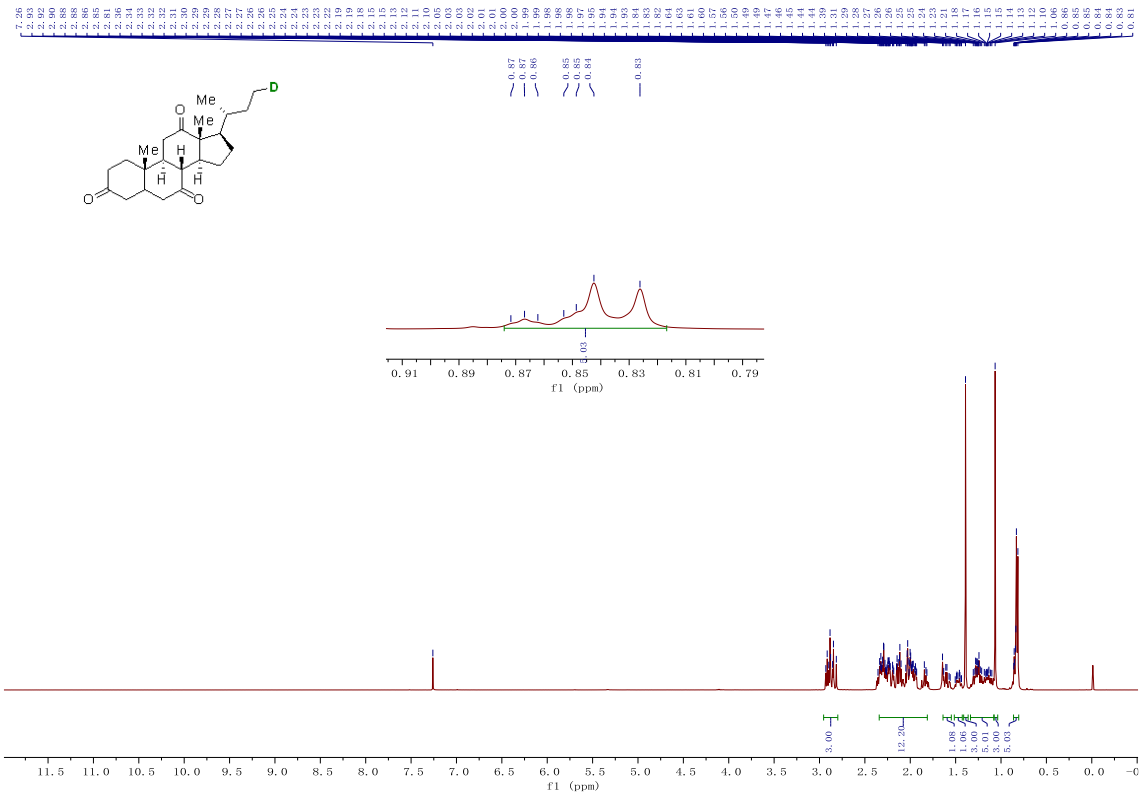
^{1}H NMR spectrum for compound **3dd**



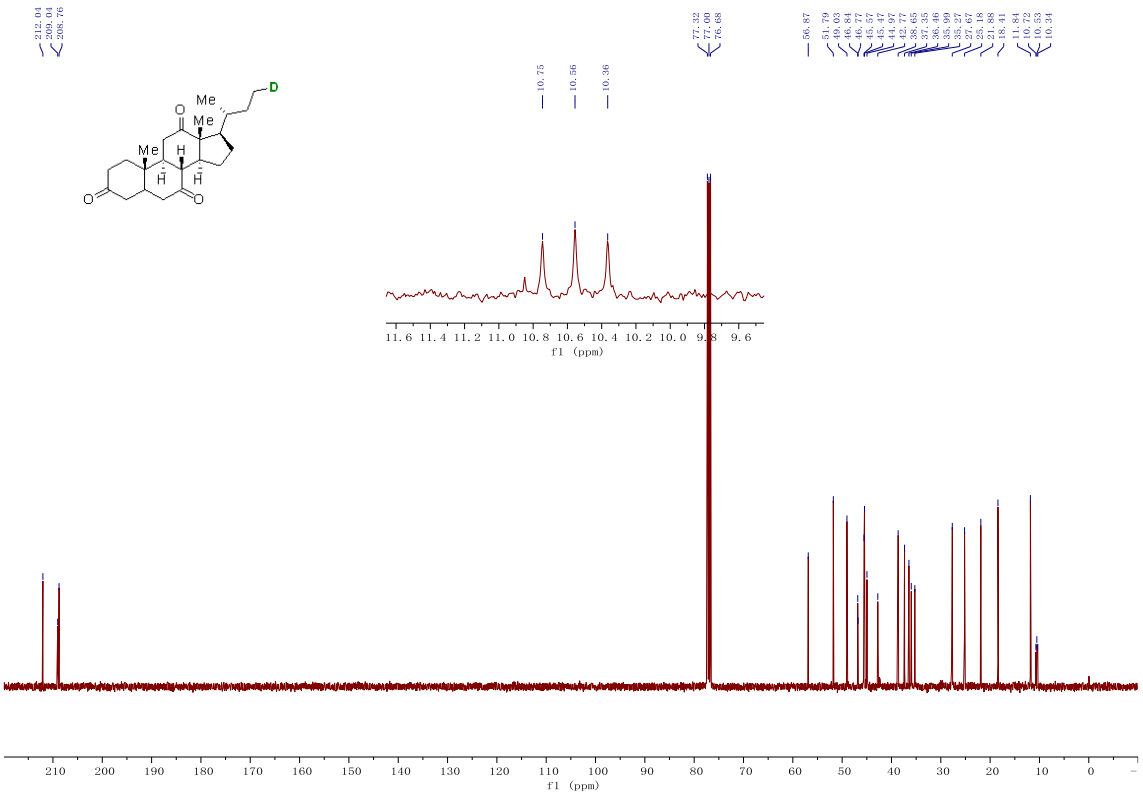
^{13}C NMR spectrum for compound **3dd**



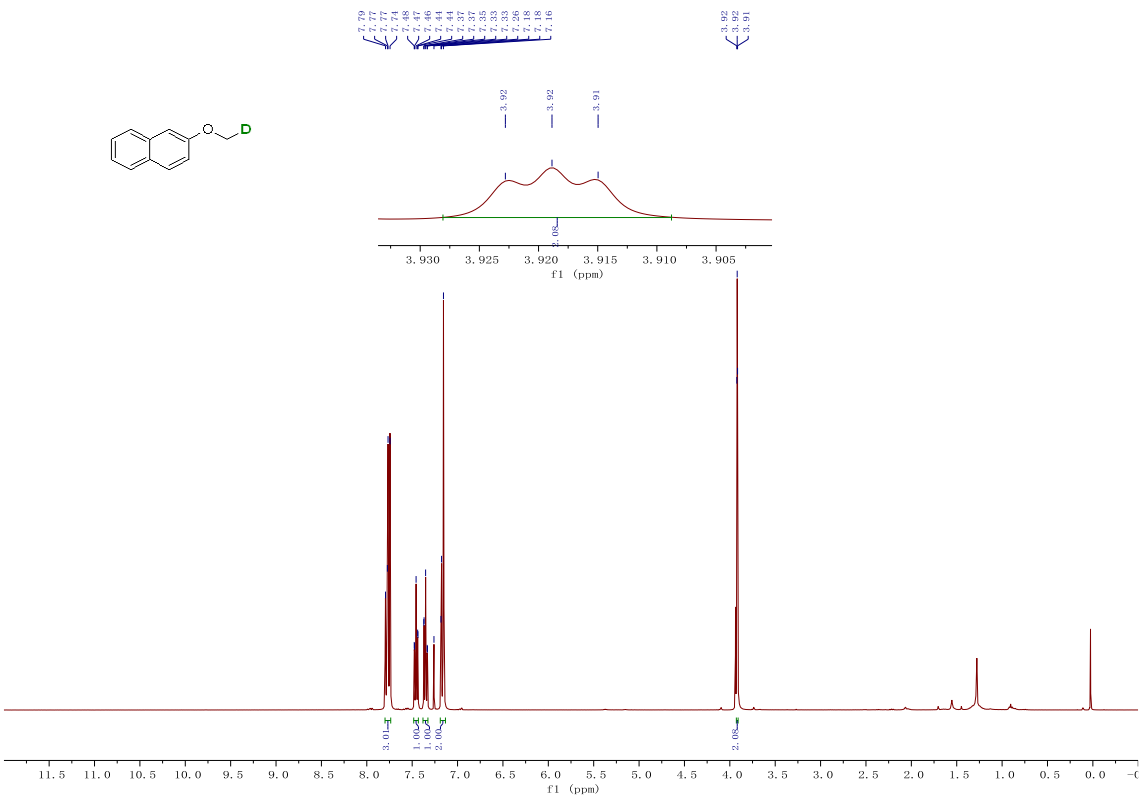
^{1}H NMR spectrum for compound **3ee**



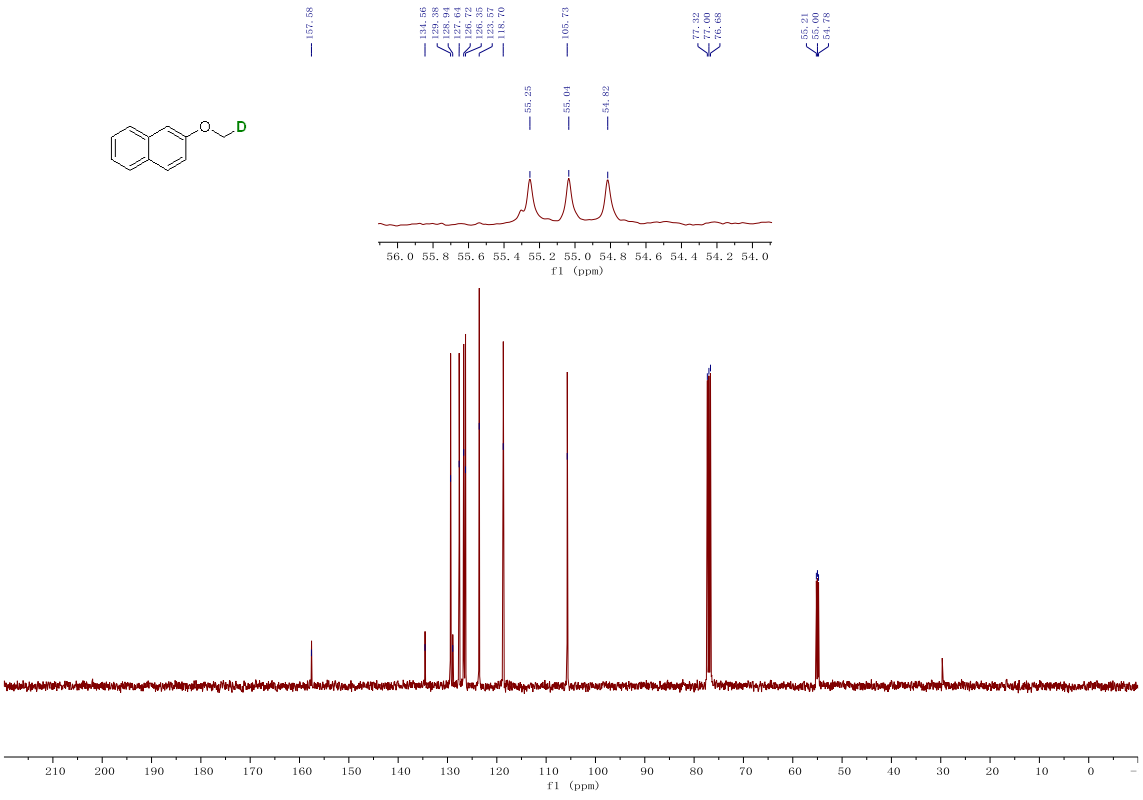
^{13}C NMR spectrum for compound **3ee**



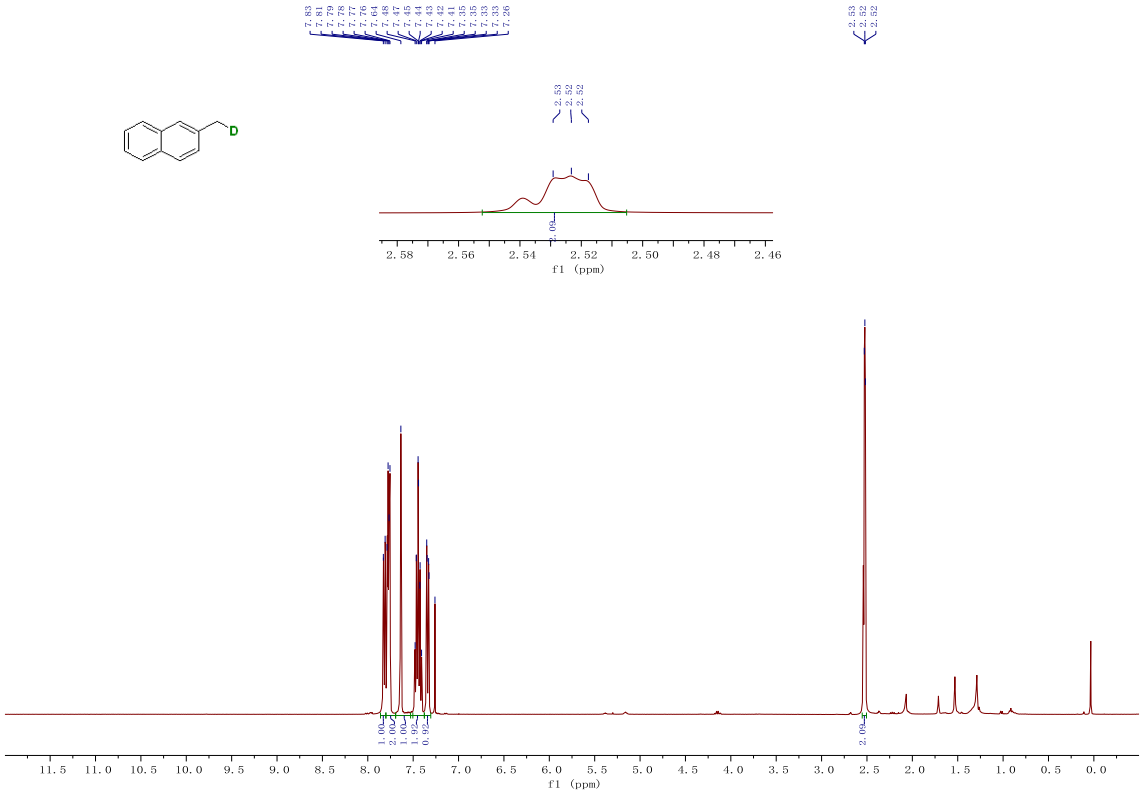
^{1}H NMR spectrum for compound **3ff**



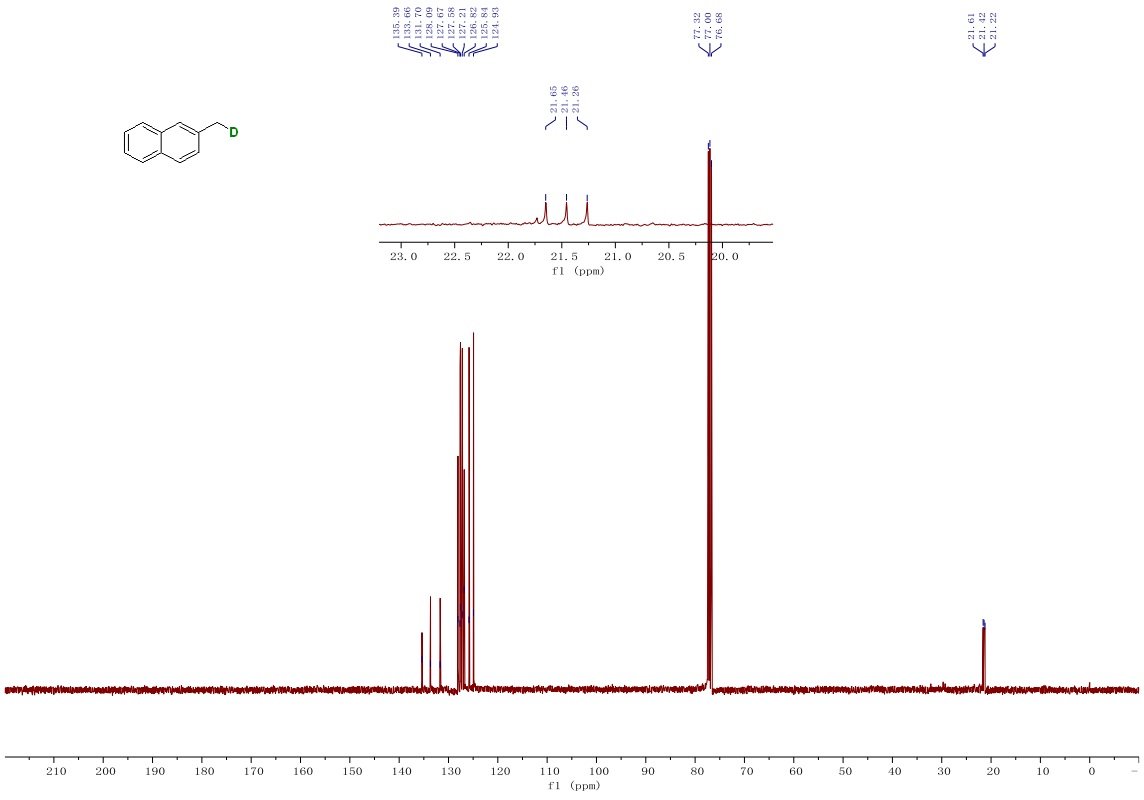
^{13}C NMR spectrum for compound **3ff**



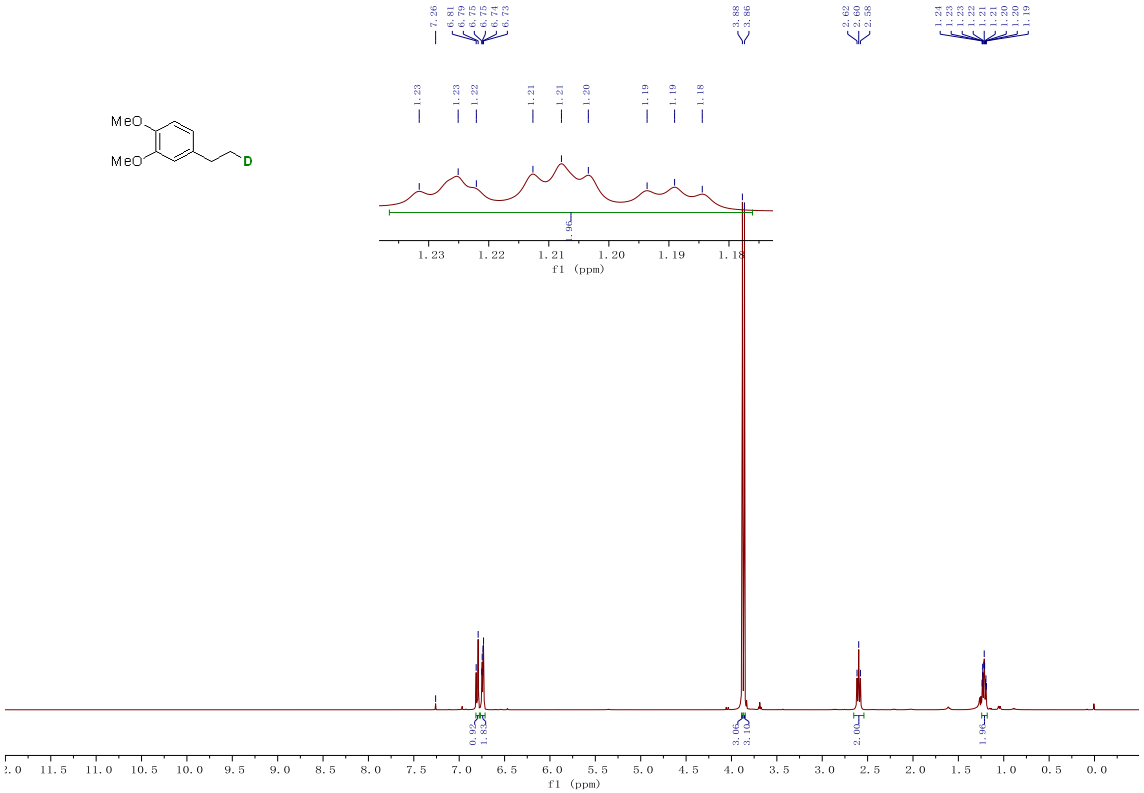
^{1}H NMR spectrum for compound **3gg**



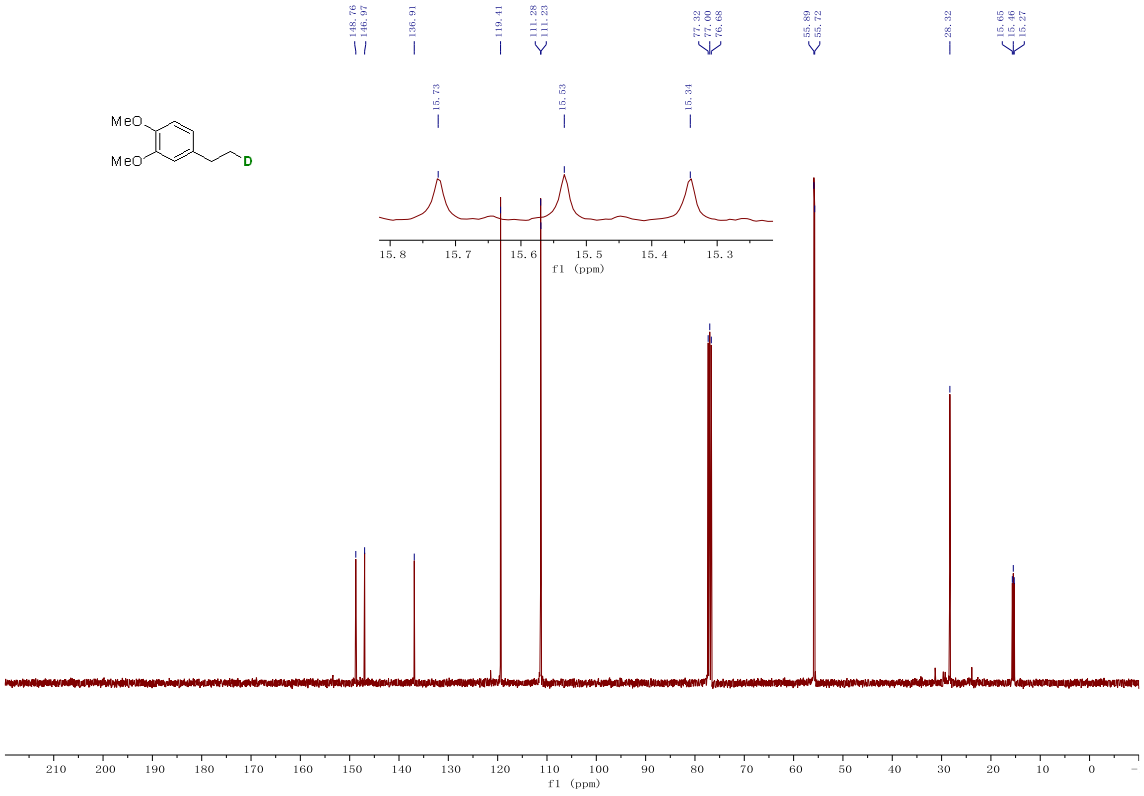
^{13}C NMR spectrum for compound **3gg**



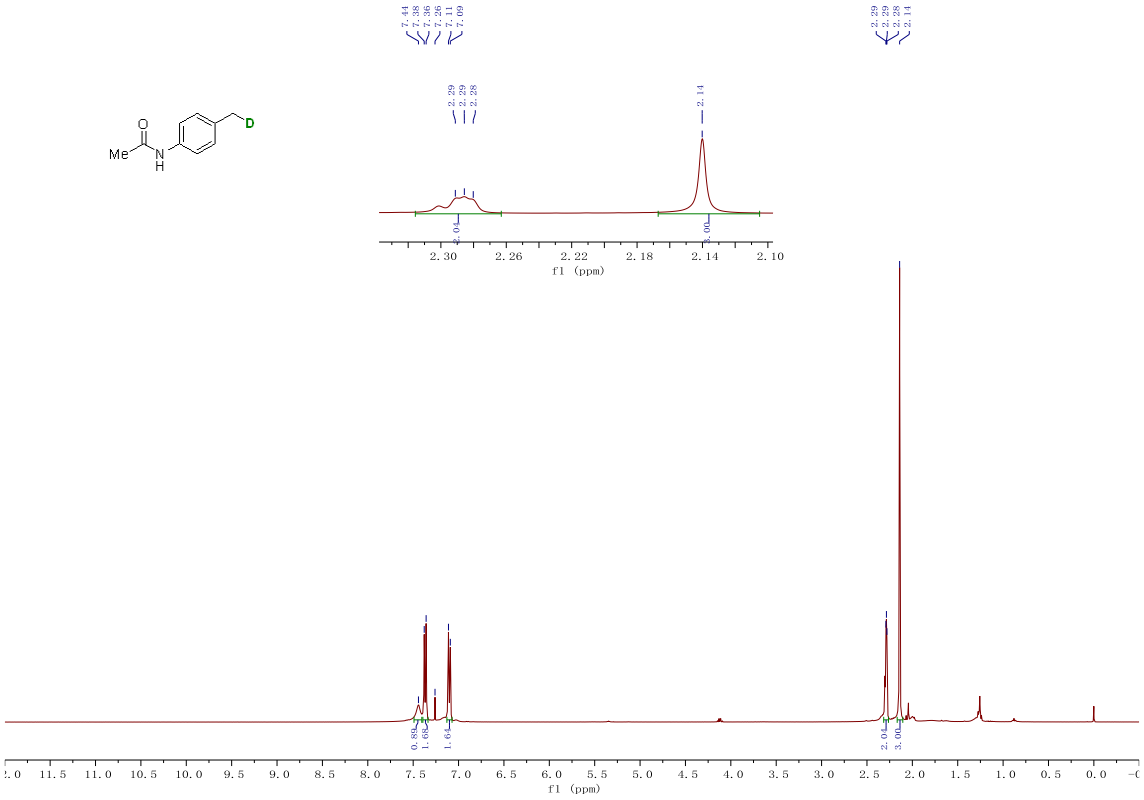
^{1}H NMR spectrum for compound **3hh**



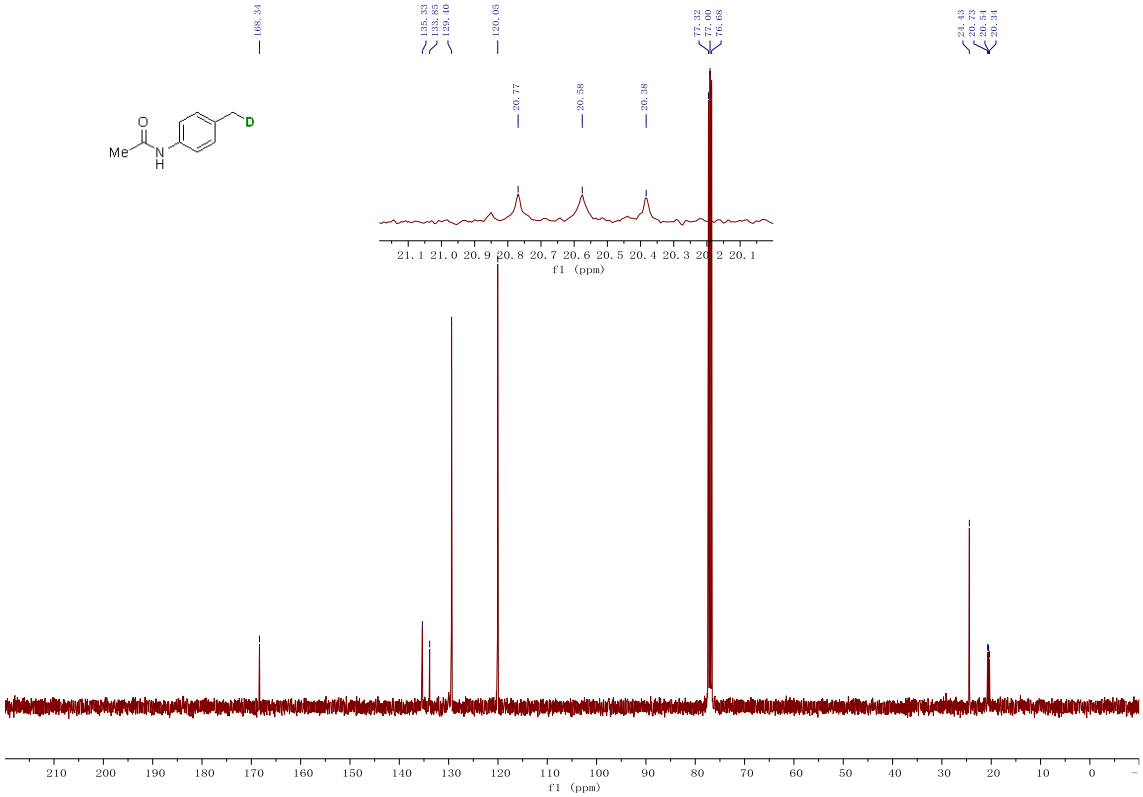
^{13}C NMR spectrum for compound **3hh**



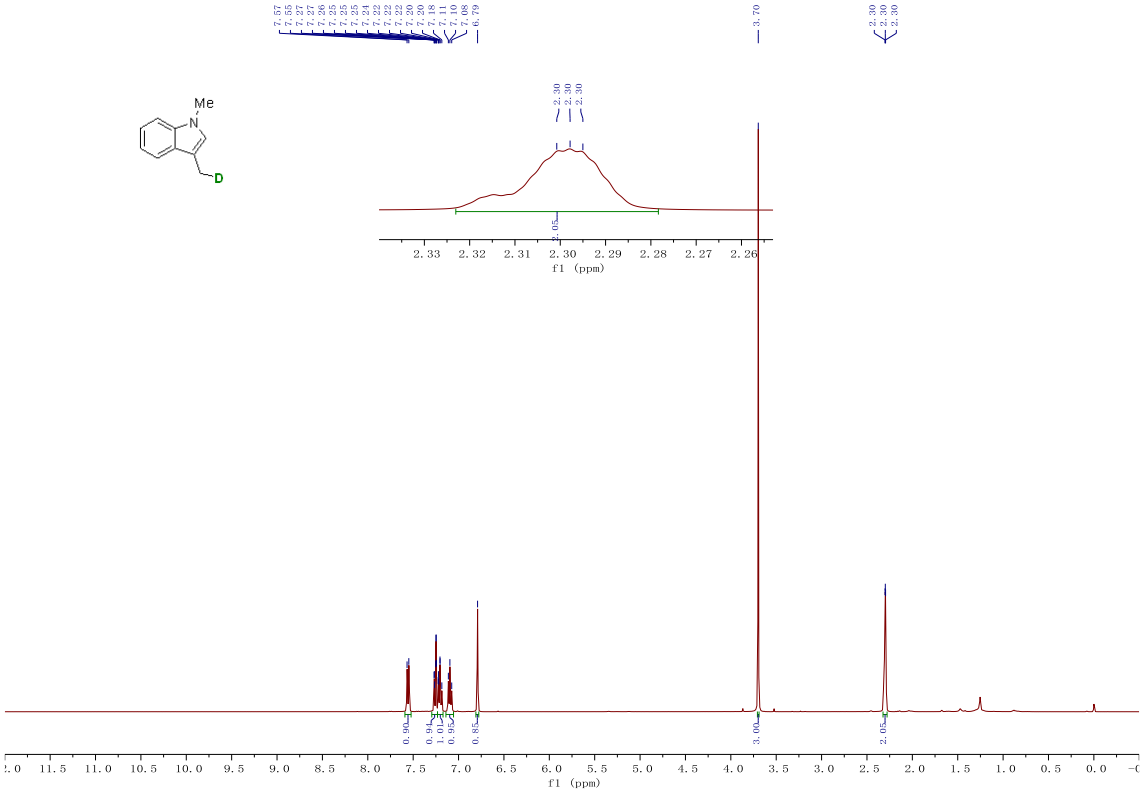
^{1}H NMR spectrum for compound **3ii**



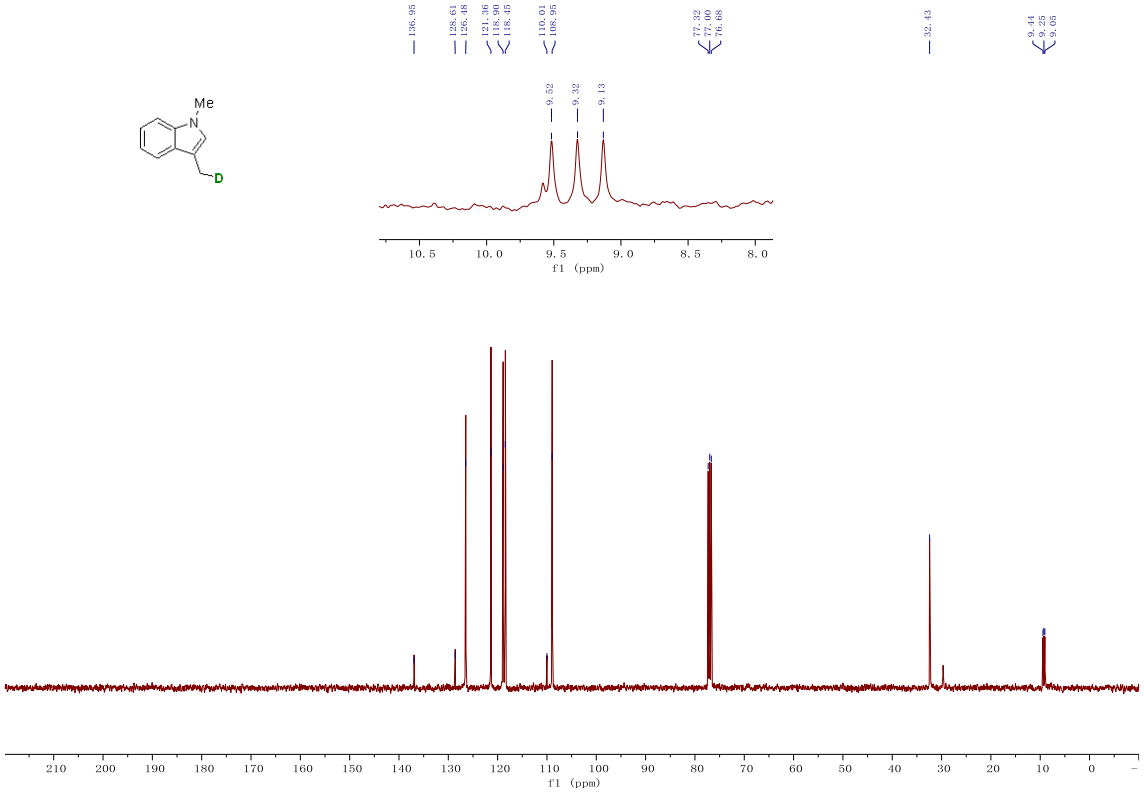
^{13}C NMR spectrum for compound **3ii**



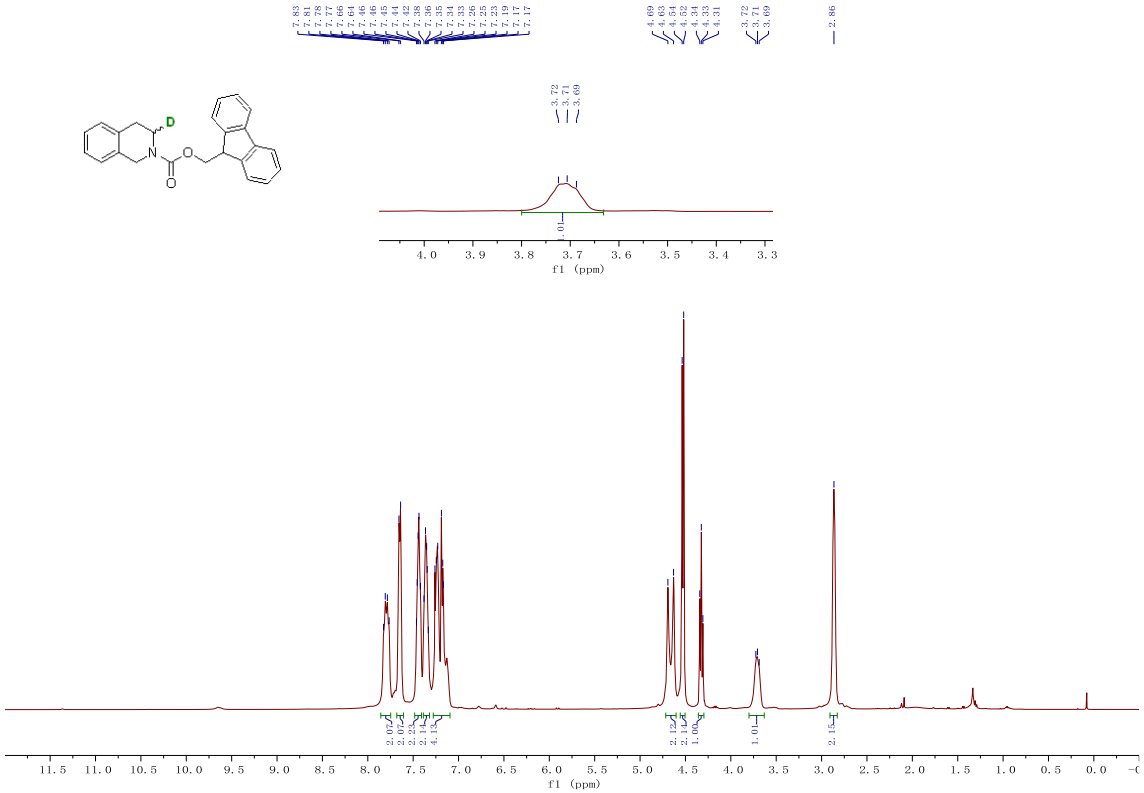
^{1}H NMR spectrum for compound **3jj**



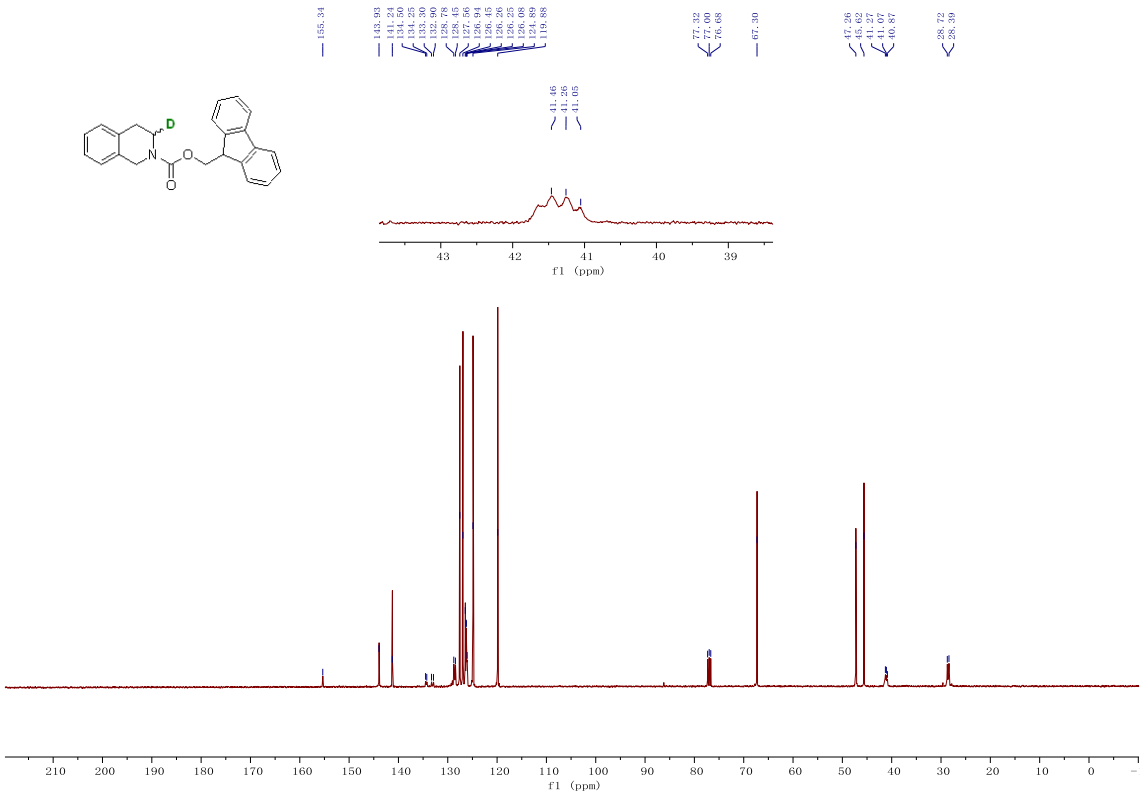
^{13}C NMR spectrum for compound **3jj**



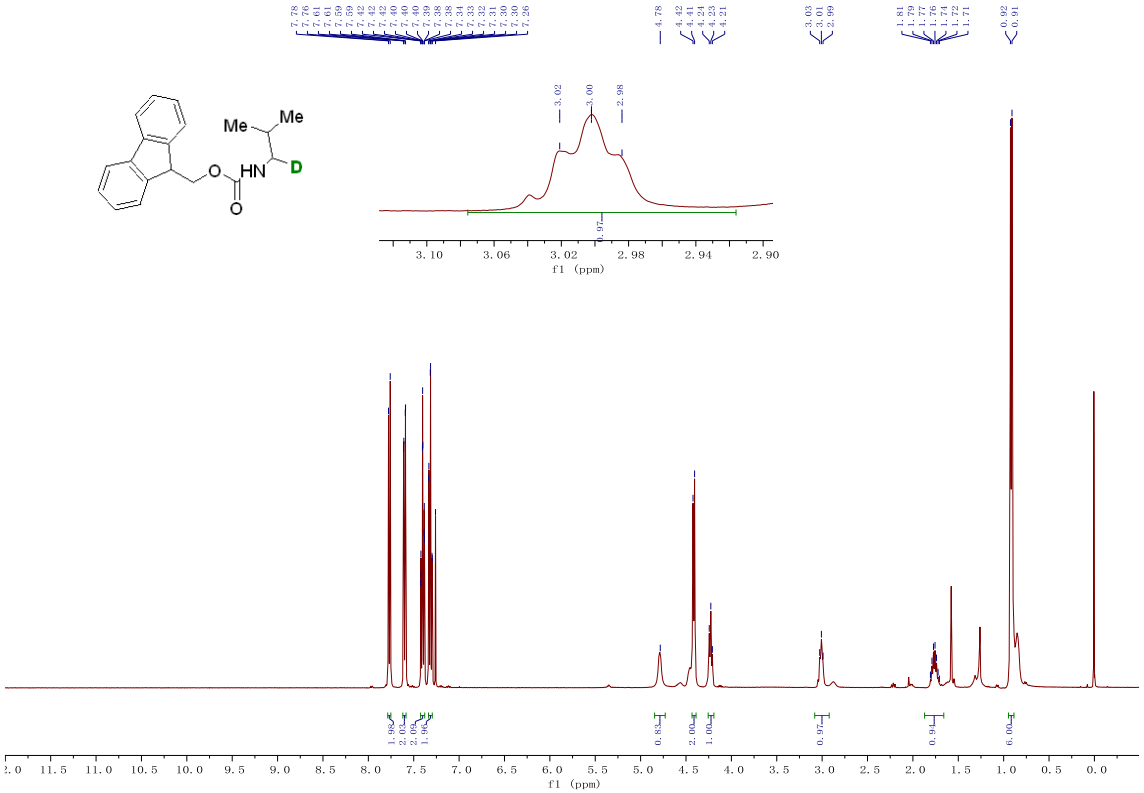
^{1}H NMR spectrum for compound **3kk**



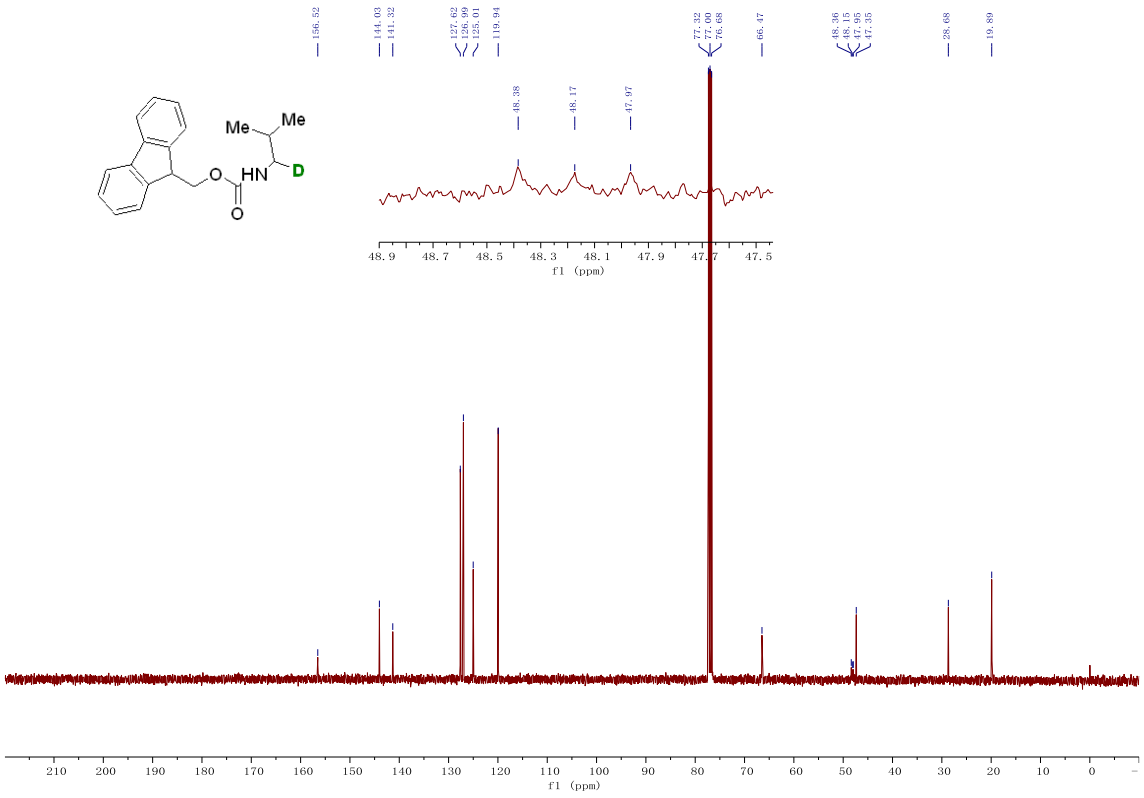
^{13}C NMR spectrum for compound **3kk**



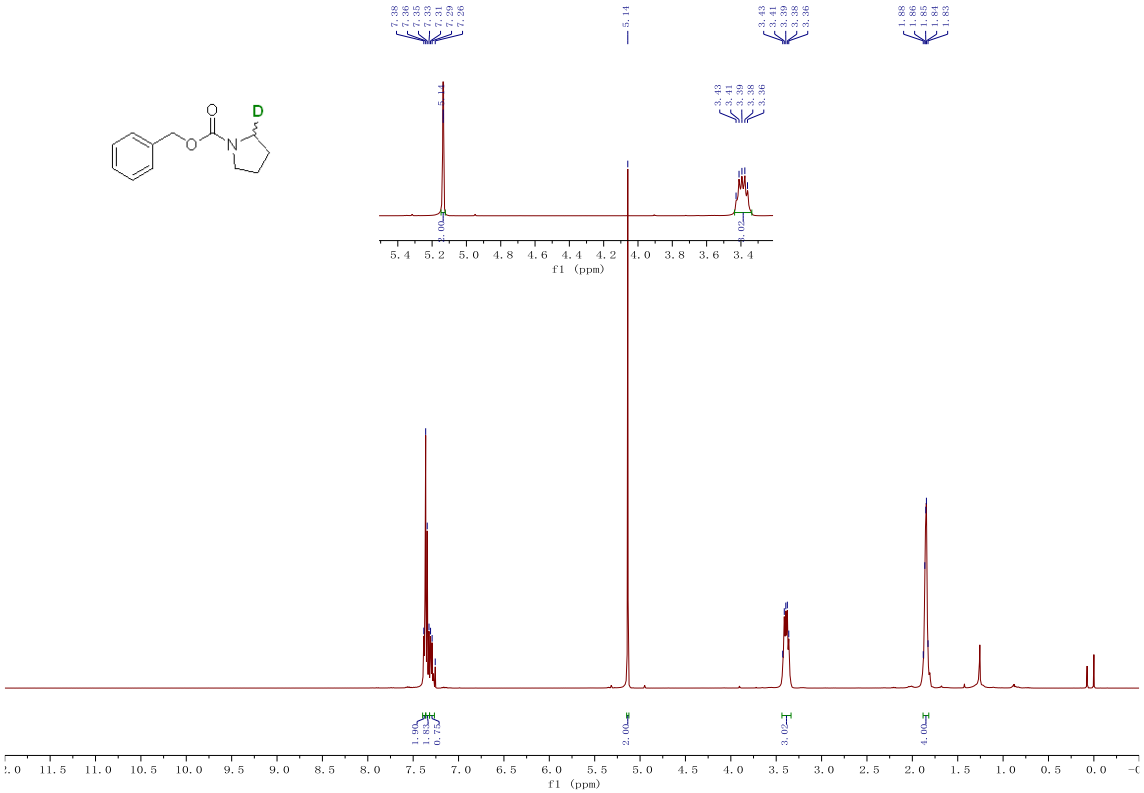
^{1}H NMR spectrum for compound **3ll**



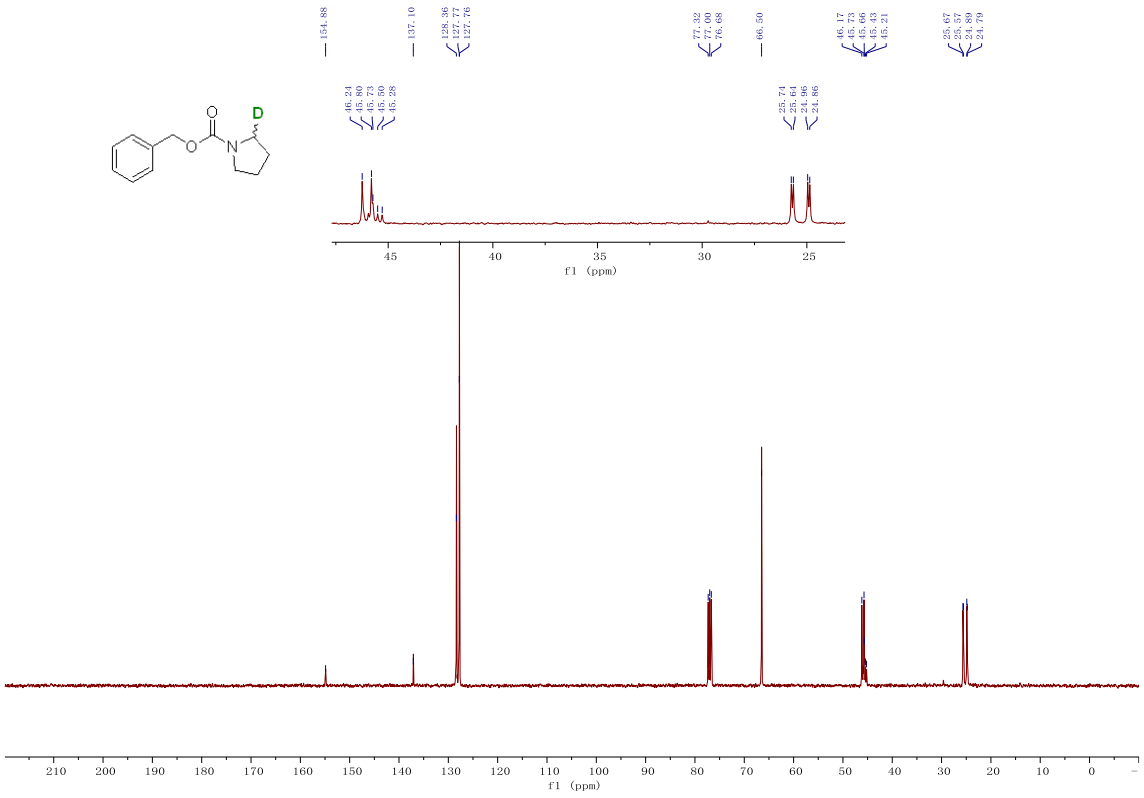
^{13}C NMR spectrum for compound **3ll**



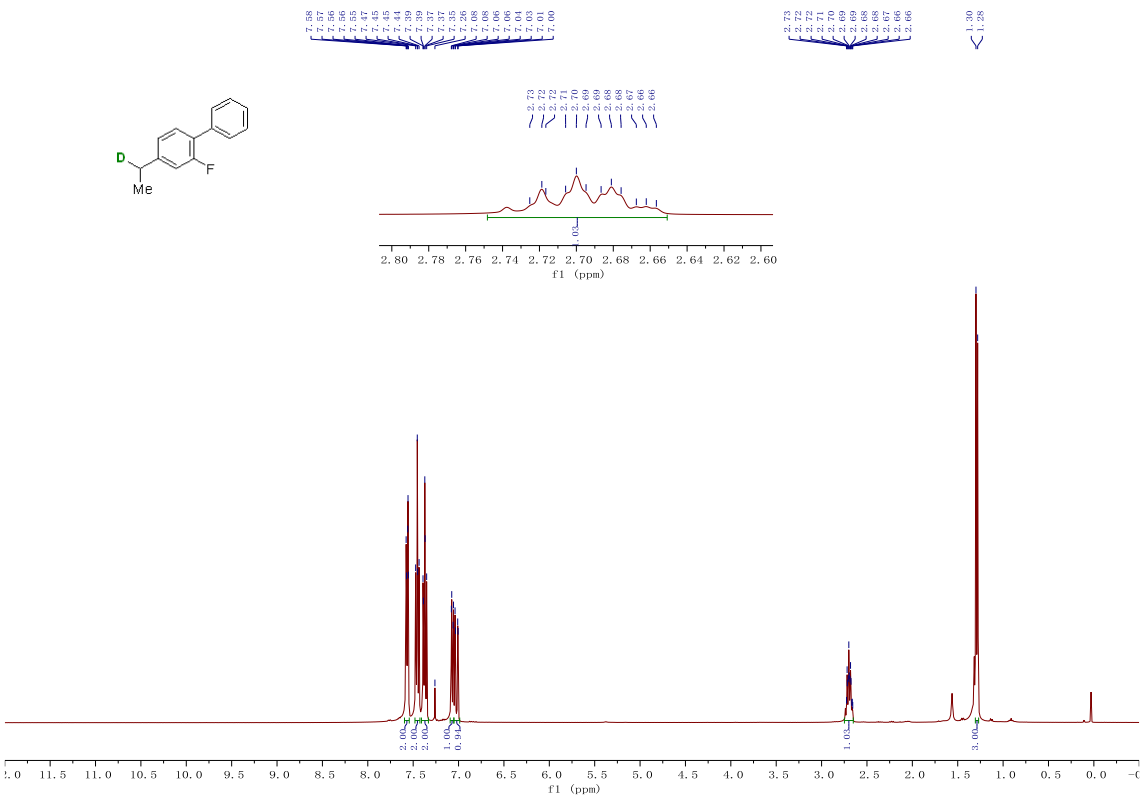
^{1}H NMR spectrum for compound **3mm**



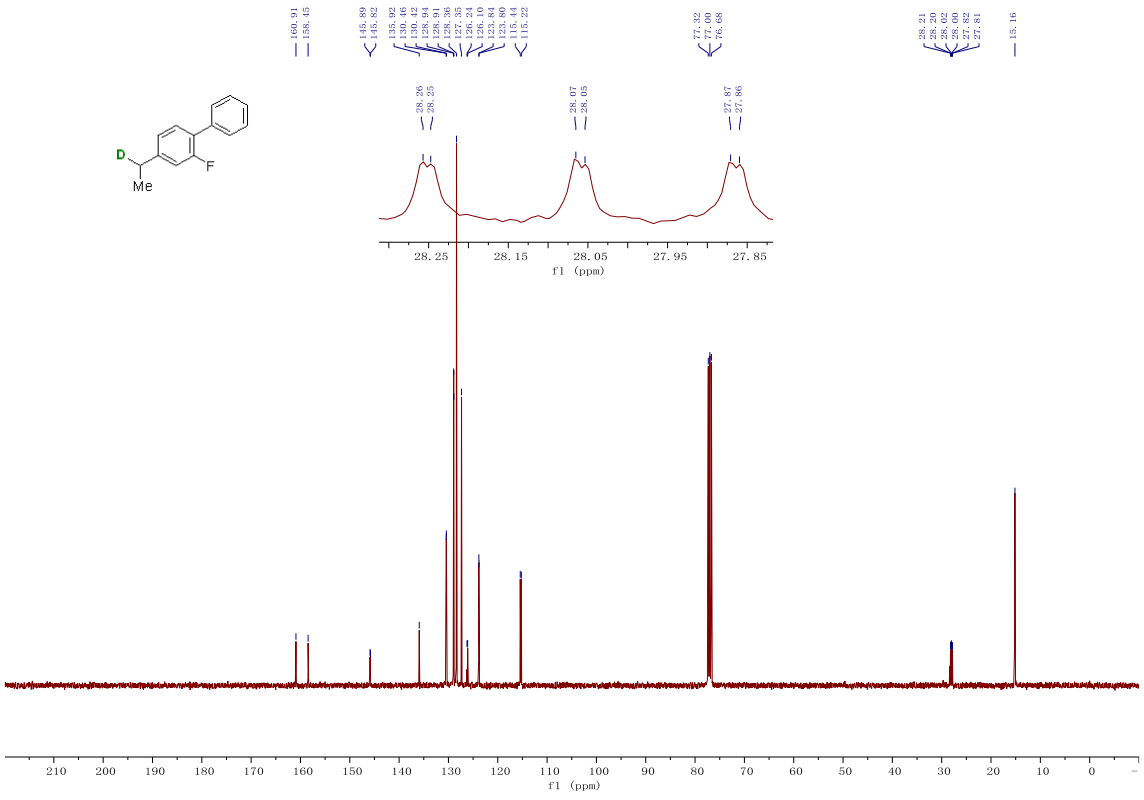
^{13}C NMR spectrum for compound **3mm**



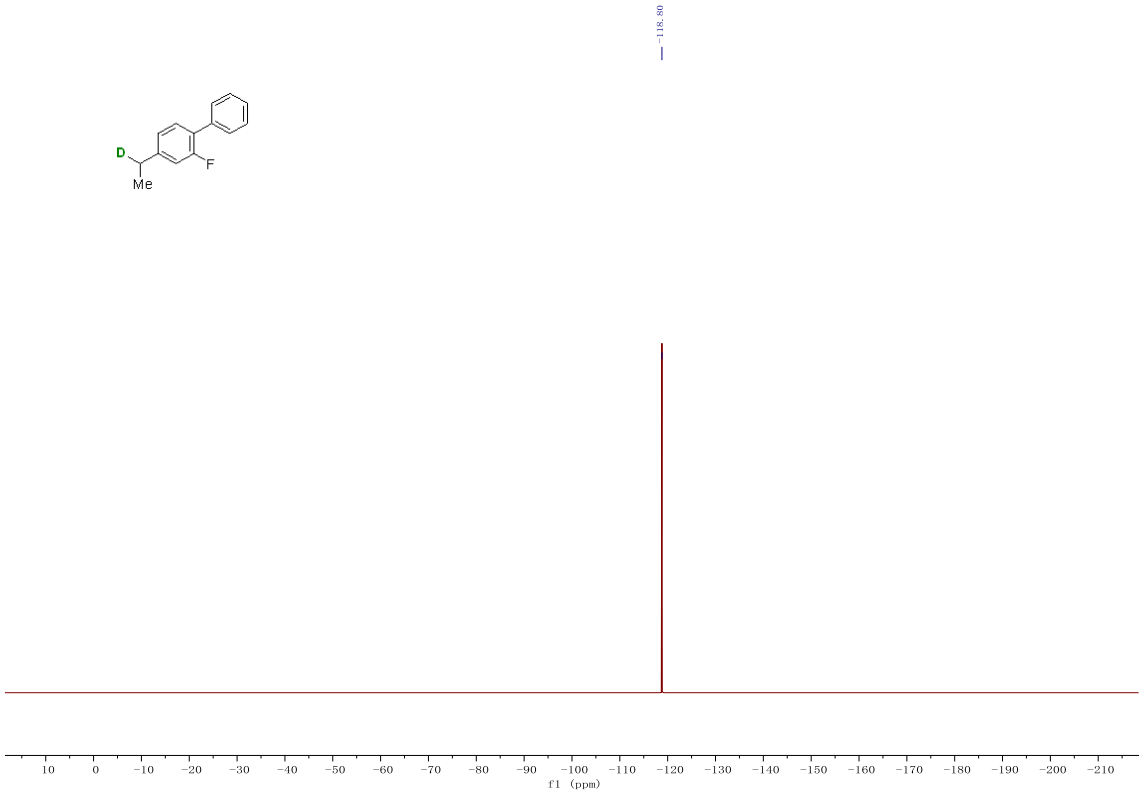
^{1}H NMR spectrum for compound **3nn**



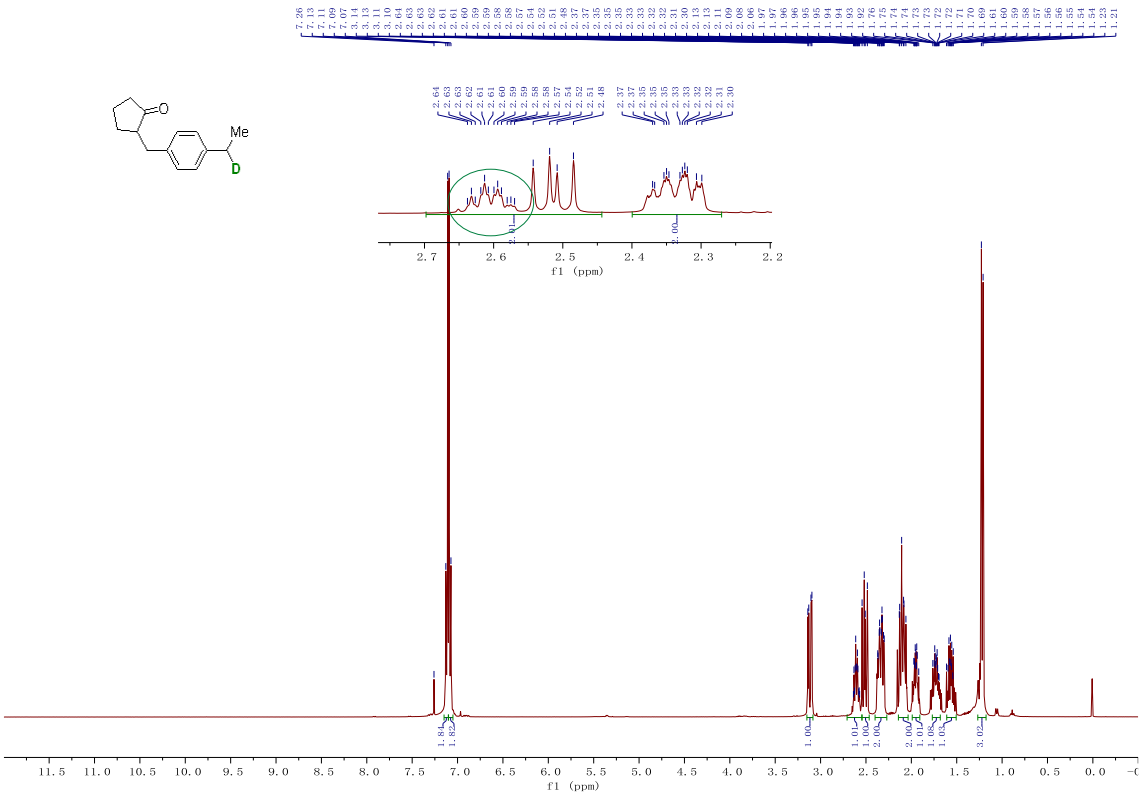
^{13}C NMR spectrum for compound **3nn**



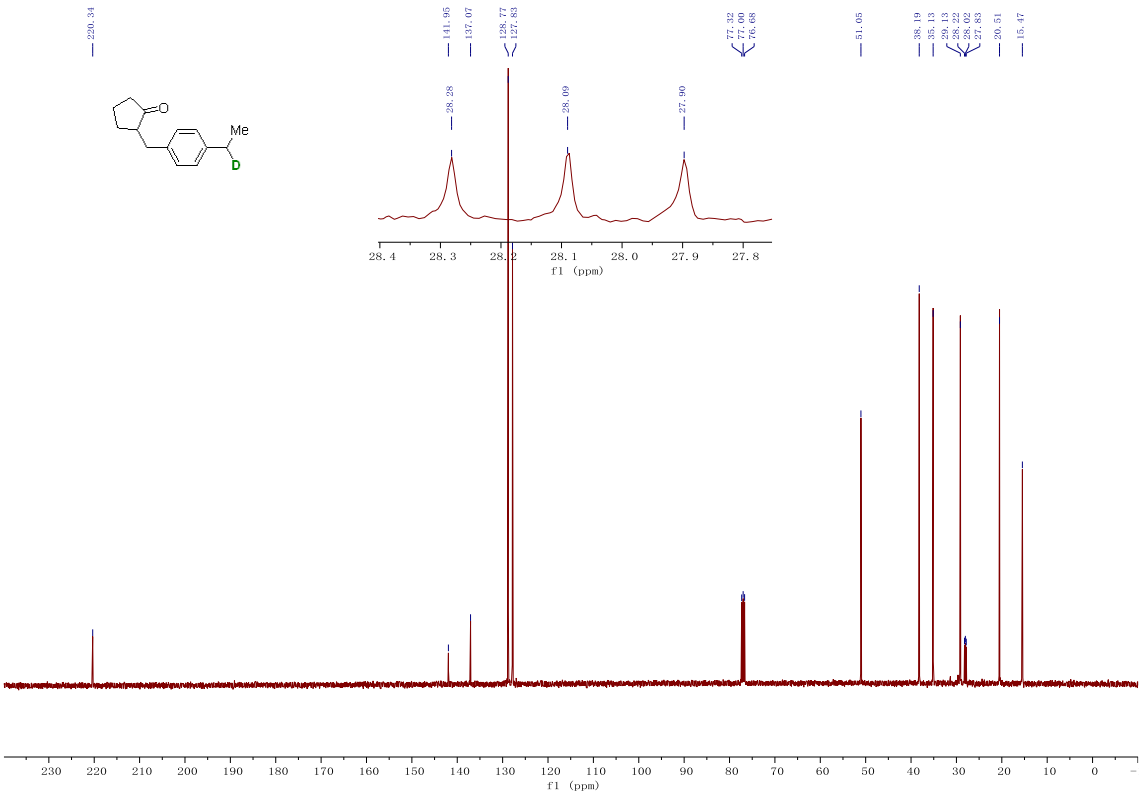
^{19}F NMR spectrum for compound **3nn**



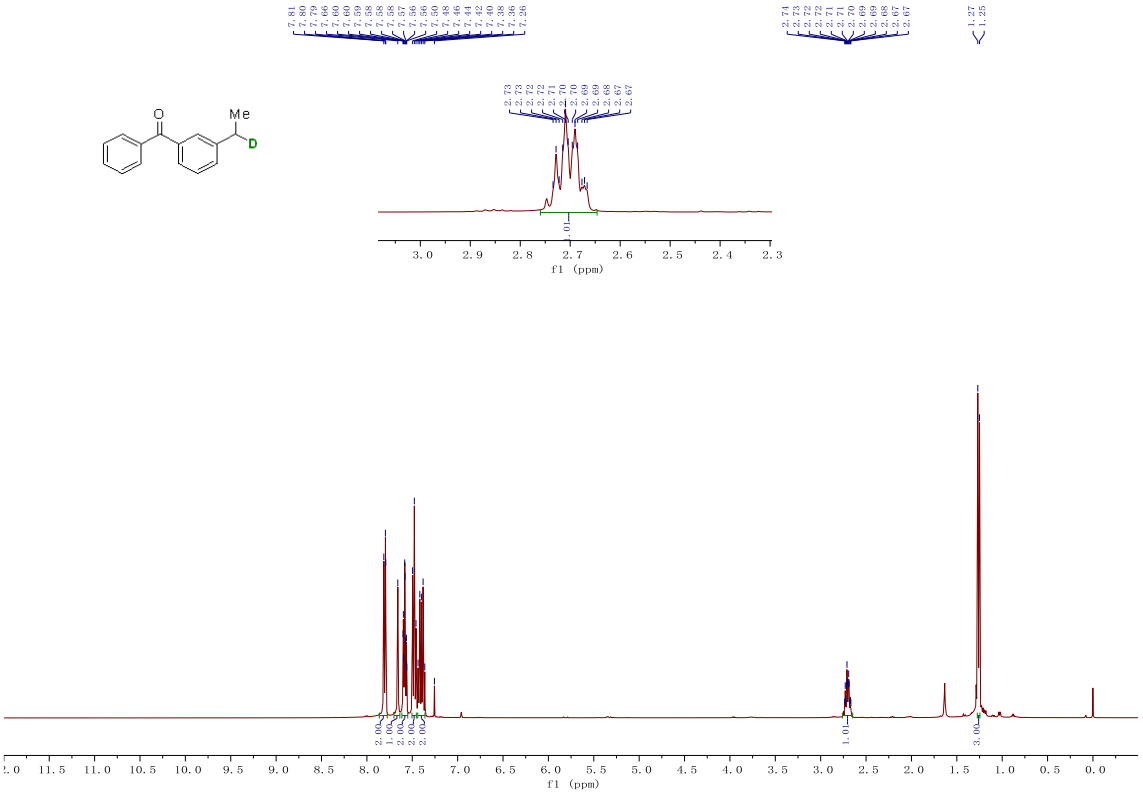
^{1}H NMR spectrum for compound **3oo**



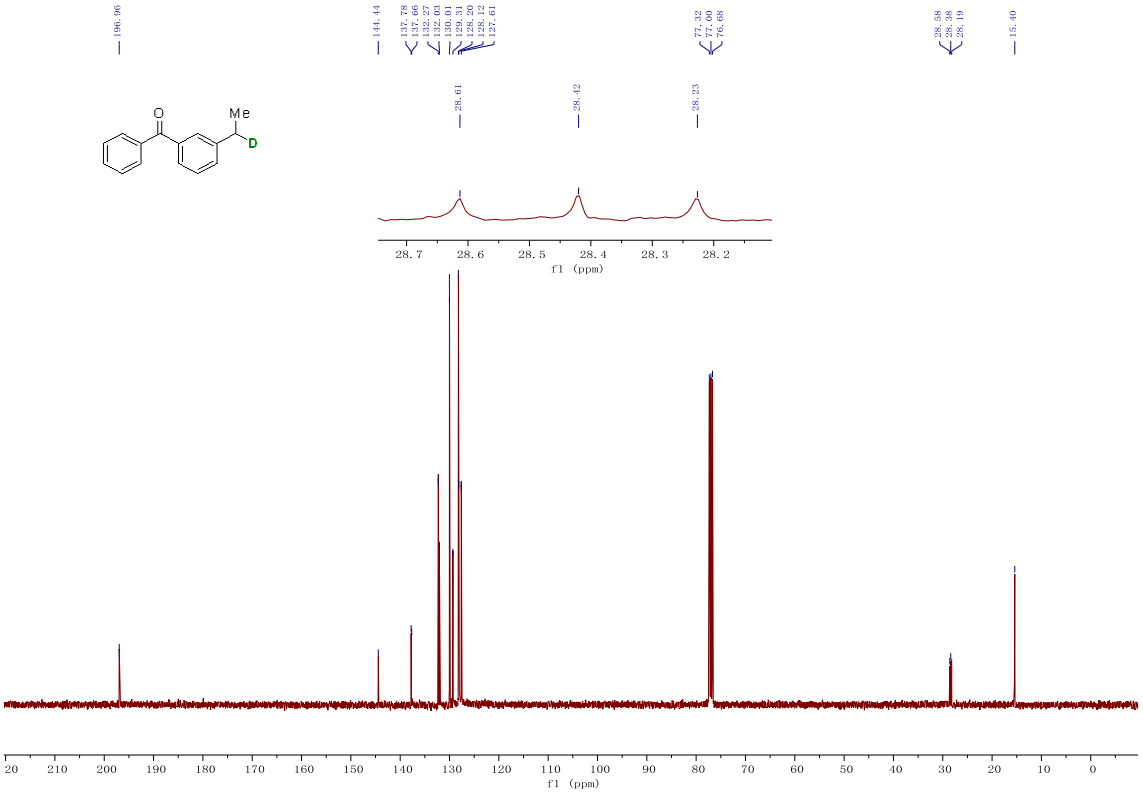
^{13}C NMR spectrum for compound **3oo**



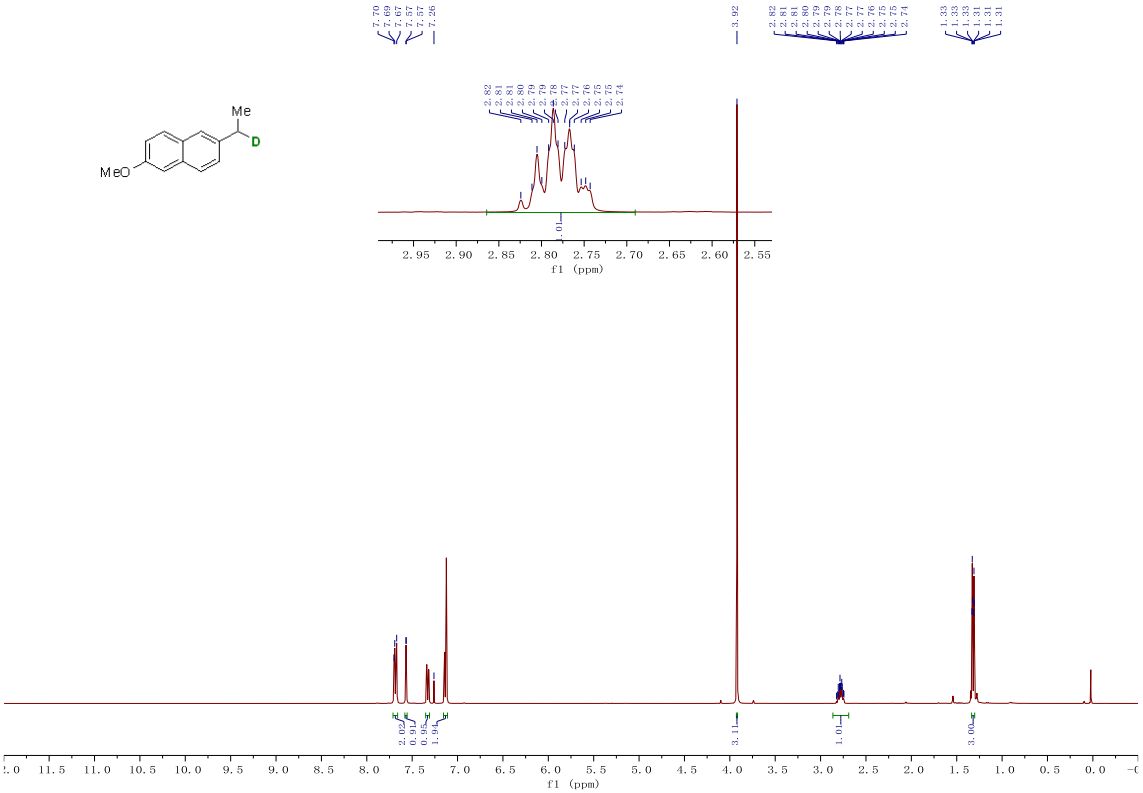
^{1}H NMR spectrum for compound **3pp**



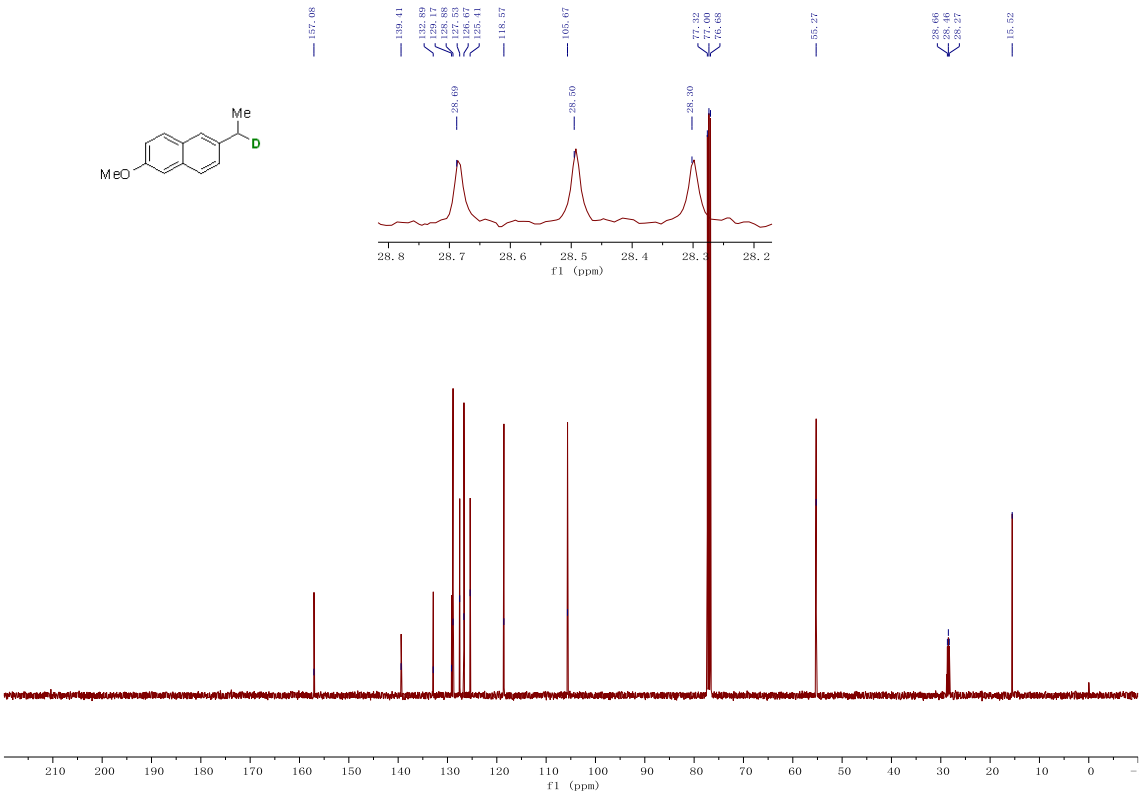
^{13}C NMR spectrum for compound **3pp**



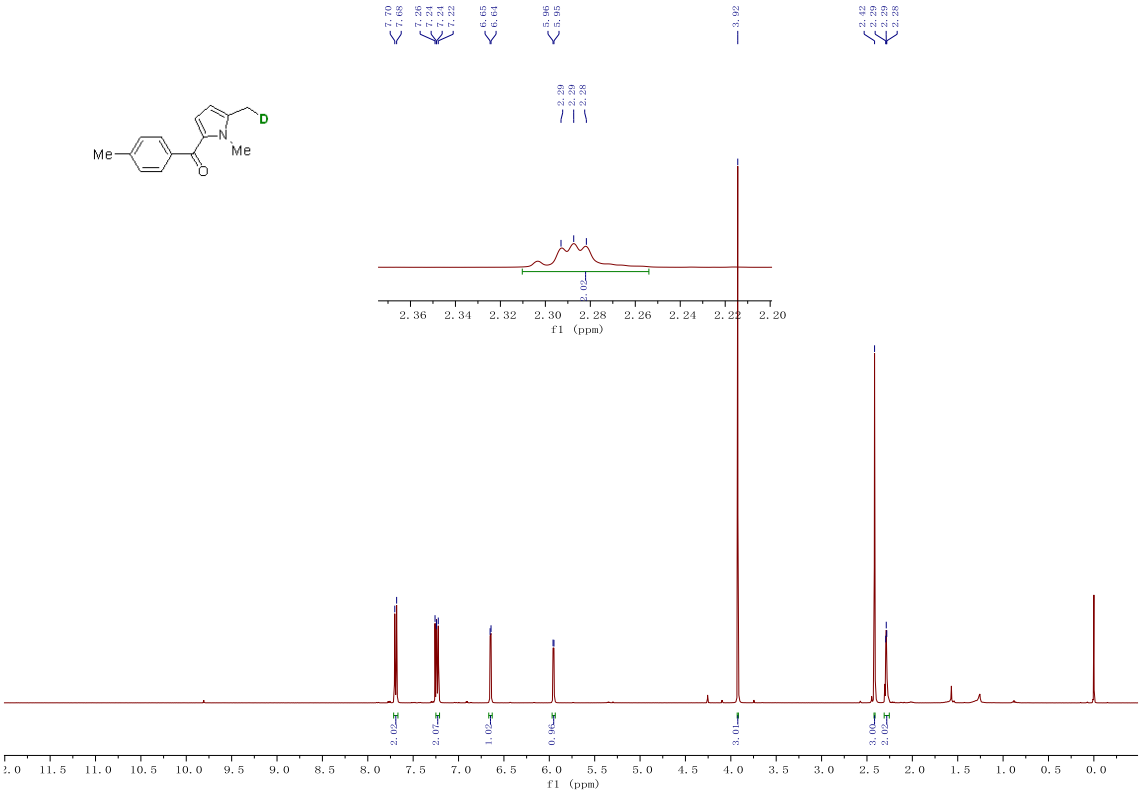
^{1}H NMR spectrum for compound **3qq**



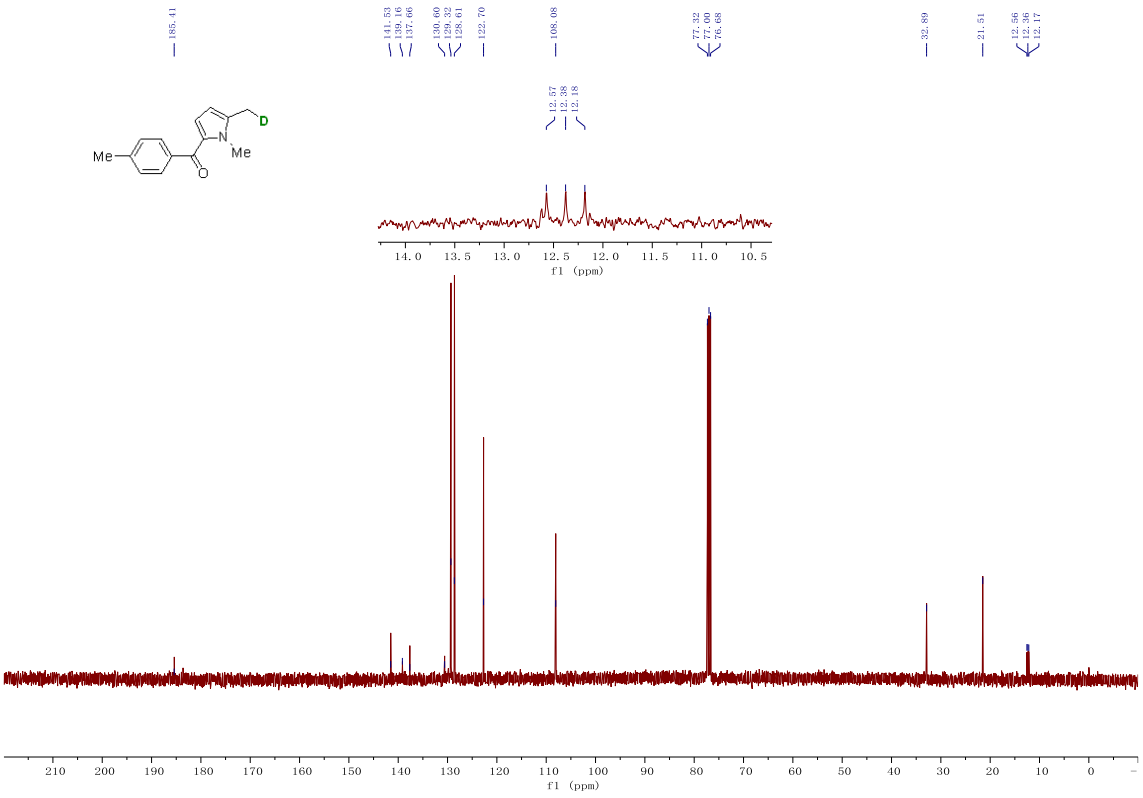
^{13}C NMR spectrum for compound **3qq**



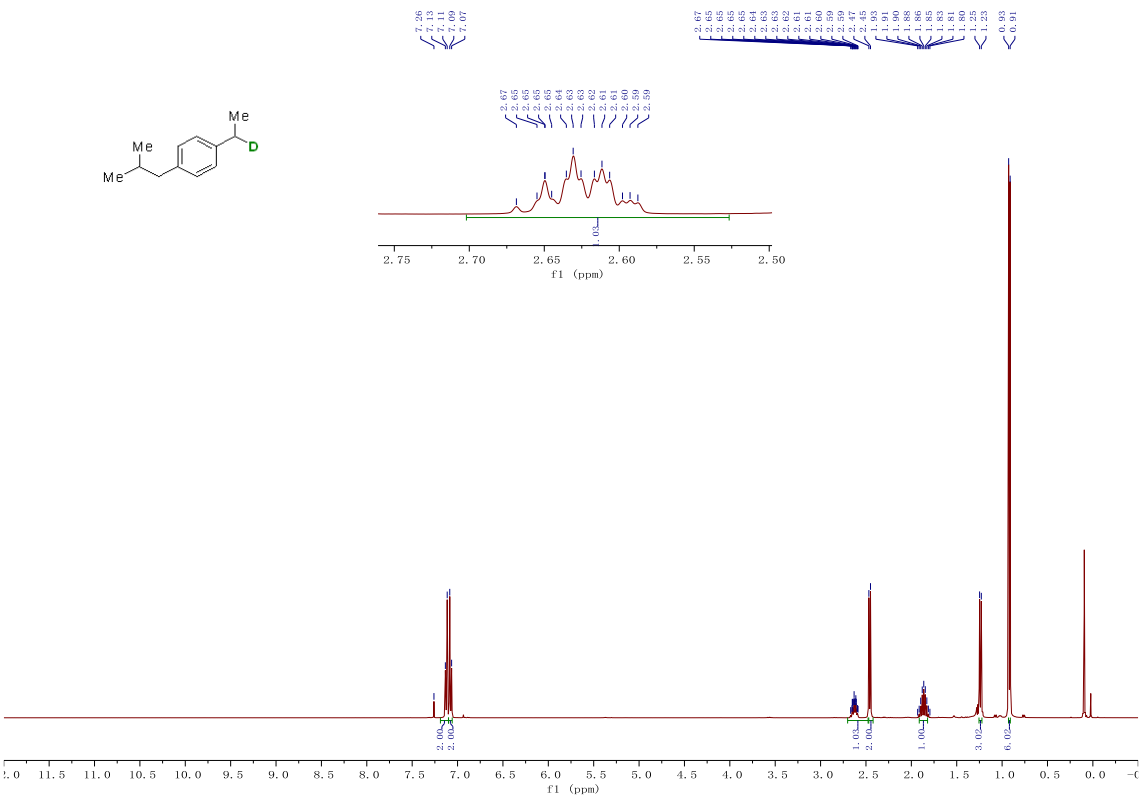
^{1}H NMR spectrum for compound **3rr**



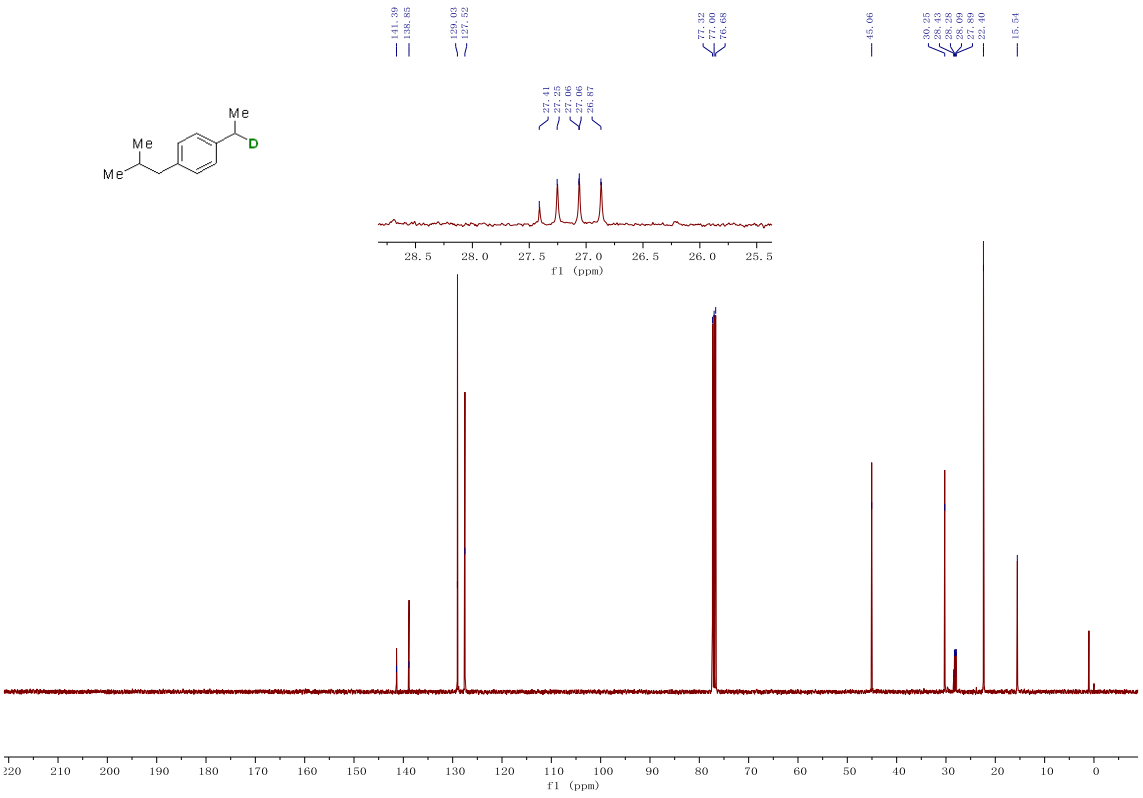
^{13}C NMR spectrum for compound **3rr**



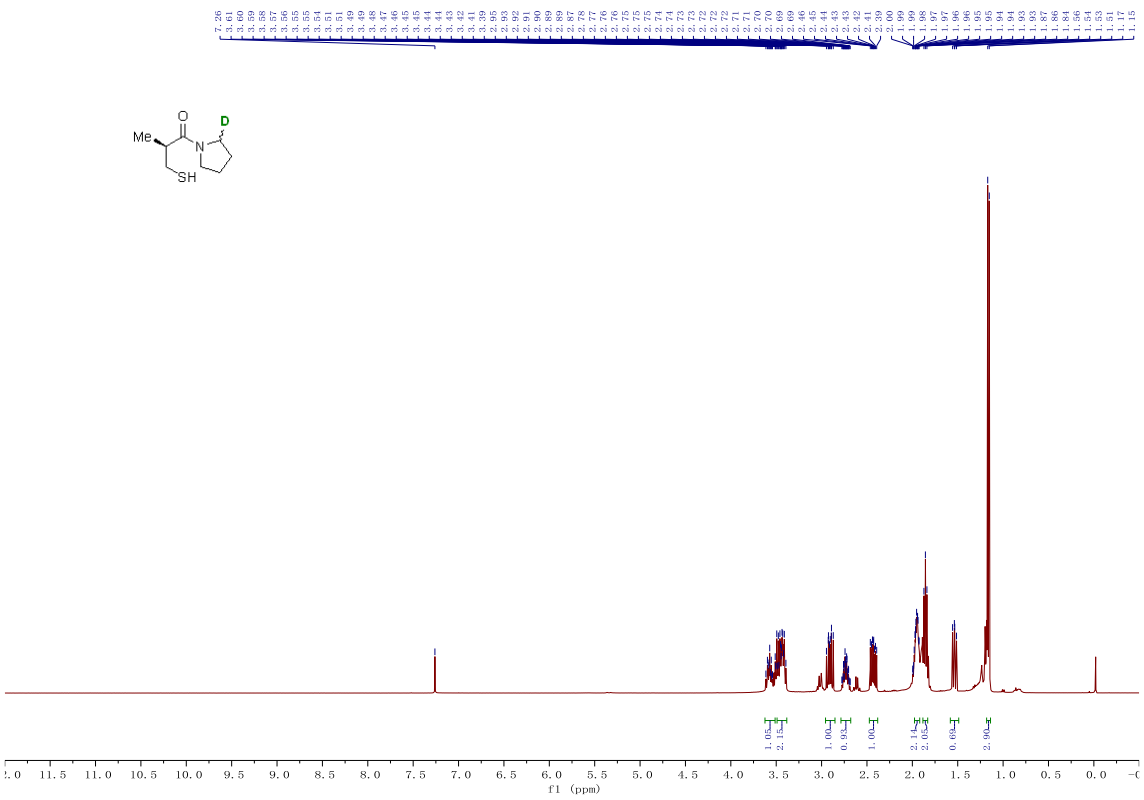
^{1}H NMR spectrum for compound **3ss**



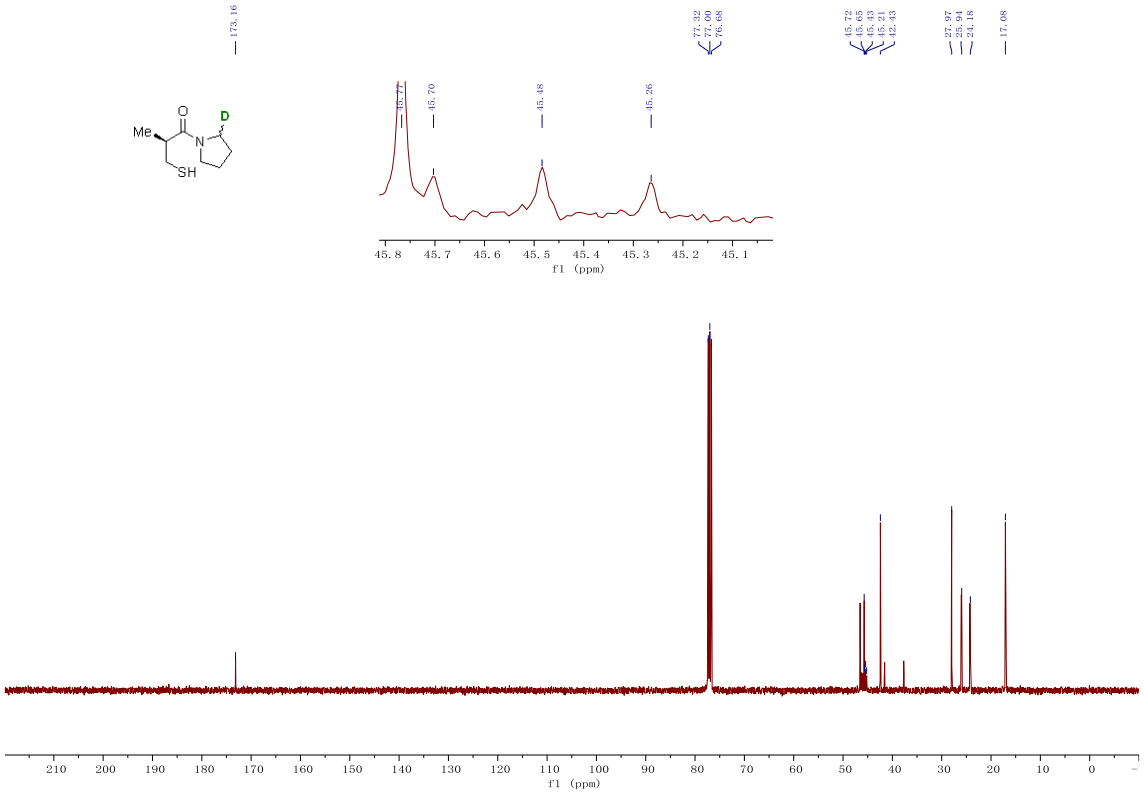
^{13}C NMR spectrum for compound **3ss**



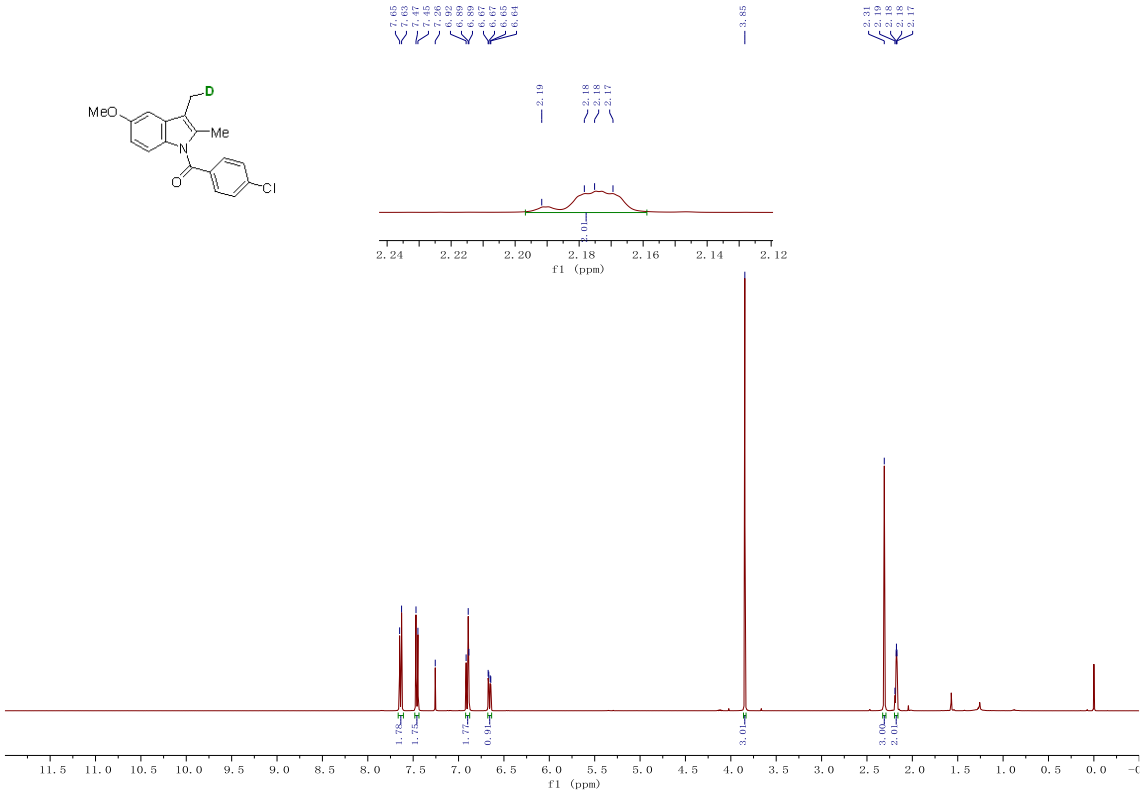
^{1}H NMR spectrum for compound **3tt**



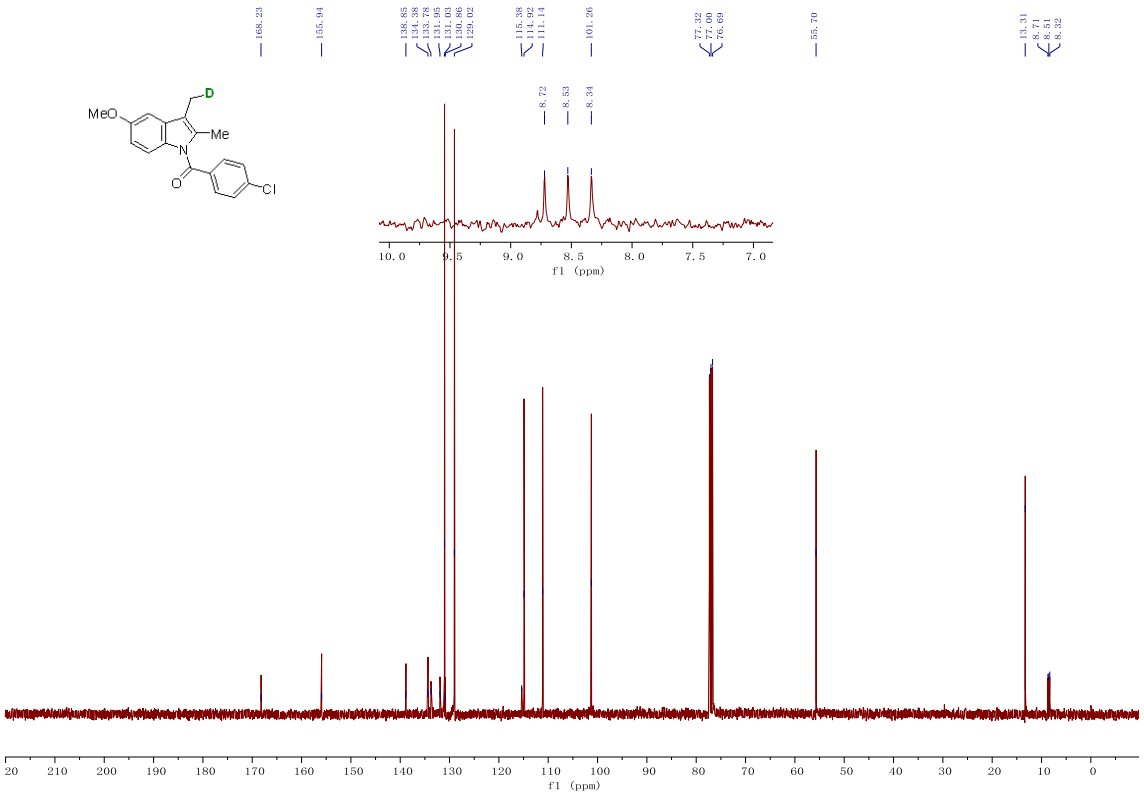
^{13}C NMR spectrum for compound **3tt**



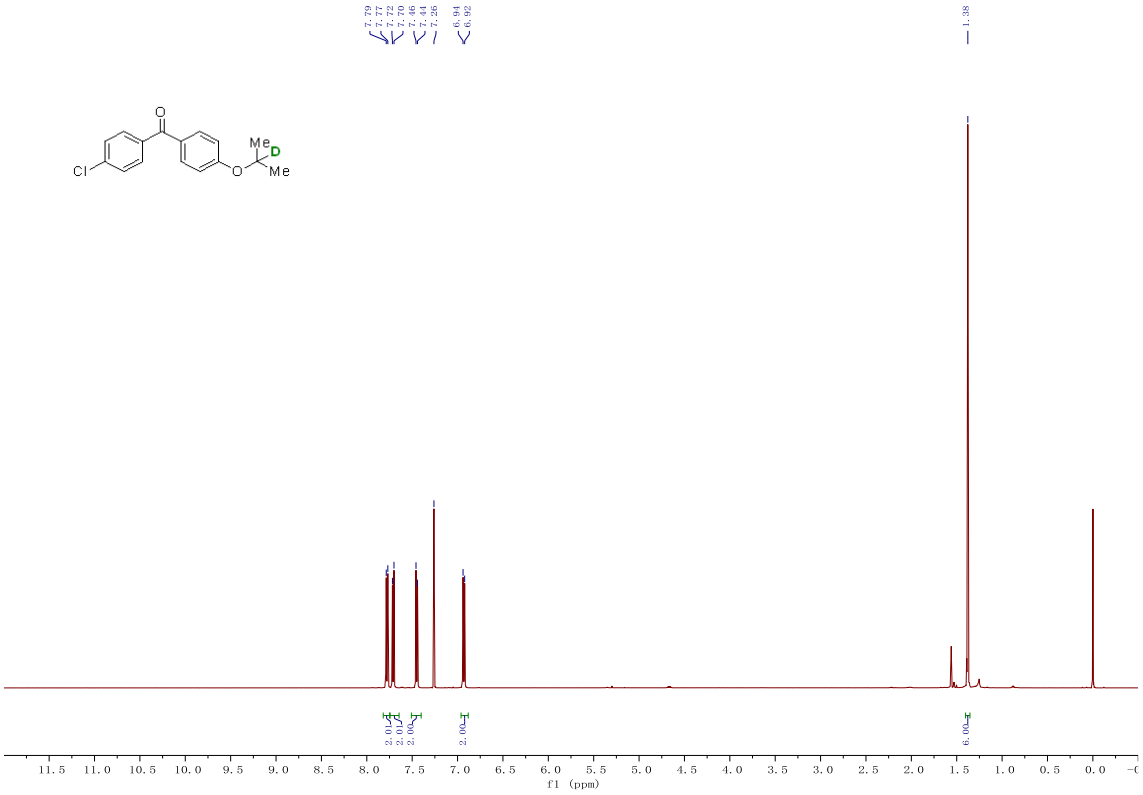
^{1}H NMR spectrum for compound **3uu**



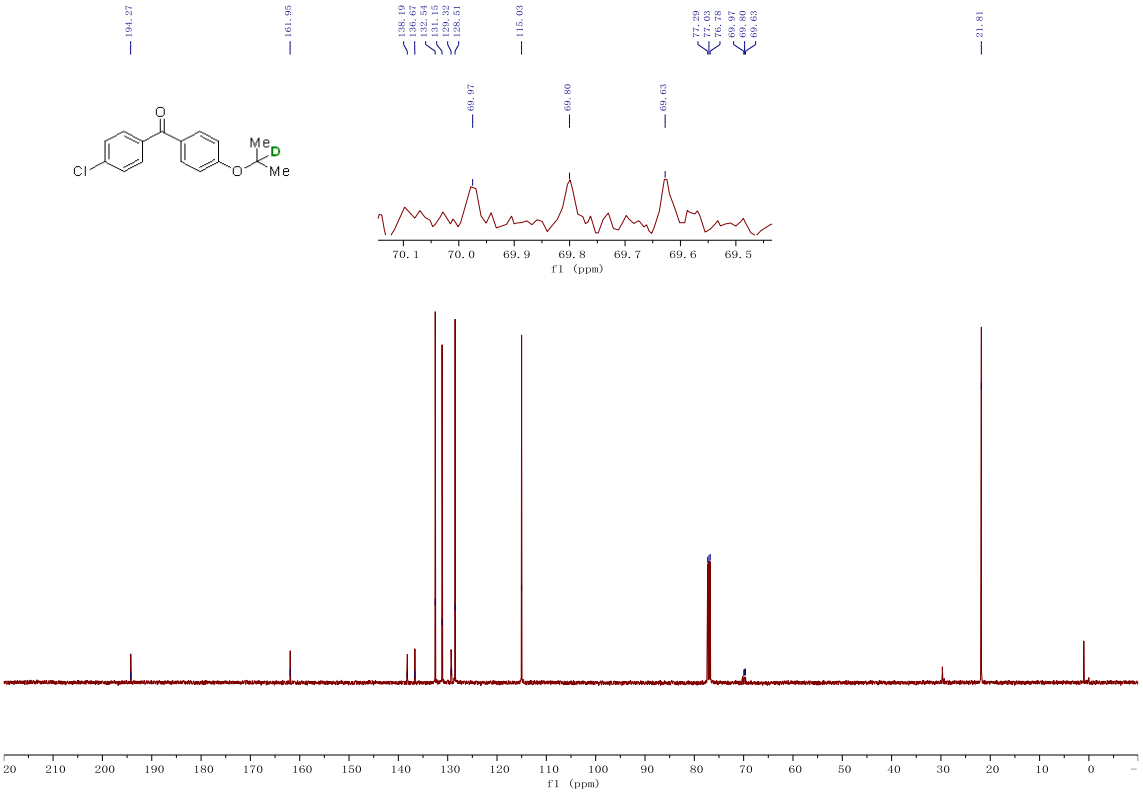
^{13}C NMR spectrum for compound **3uu**



^{1}H NMR spectrum for compound **3vv**



^{13}C NMR spectrum for compound **3vv**



Supplementary References

1 Zhu, Q.; Graff, D. E.; Knowles, R. R. Intermolecular Anti-Markovnikov Hydroamination of Unactivated Alkenes with Sulfonamides Enabled by Proton-Coupled Electron Transfer. *J. Am. Chem. Soc.* **2018**, *140*, 741-747.

2 Sun, Y.; Zhang, W.; Wang, B.; Xu, X.; Chou, J.; Shimoni, O.; Ung, A. T.; Jin, D. A supramolecular self-assembly strategy for upconversion nanoparticle bioconjugation. *Chem. Commu.* **2018**, *54*, 3851-3854.