Supporting Information

Magnesium/Methanol-d1: A Practical Reductive Deuteration System for the Deuterium Labeling of α, β-unsaturated Esters, Nitriles and Amides

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1. General remarks

^{1}H NMR and ^{13}C NMR spectra were recorded on AVANCE AV400 spectrometer. The NMR chemical shifts were referenced to TMS as an internal standard. NMR Spectra recorded in $CDCl_3$ were referenced to residual $CHCl_3$ at 7.26 ppm for ^{1}H or 77.0 ppm for ^{13}C. The peak patterns are indicated as follows: s, singlet; d, doublet; bs, broad singlet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. All coupling constants *J* were quoted in Hertz (Hz). Data were reported as follows: chemical shift, multiplicity, coupling constant and integration. High-resolution mass spectrometry (HRMS) was measured using Q-TOF LC–MS and the ESI-FTICR (Electron spray ionization–Fourier transform ion cyclotron resonance) technique. Reactions were monitored by thin-layer chromatography (TLC) on 0.25mm silica gel glass plates coated with 60 F254. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether (60-90°C)/ethyl acetate as eluent. **Deuterium rate was abbreviated as D% in the following text. α-D% means the deuterium rate of alpha position of ester group. β-D% means the deuterium rate of beta position of ester group. δ-D% means the deuterium rate of delta position of ester group. ζ-D% means the deuterium rate of zeta position of ester group.** Mg turnings were washed by 5% HCl then dried by air blower before added into the reaction. Unless otherwise noted, all commercially available reagents were used as received without further purification.

Formula for calculating deuterium rate:

$$\frac{D_1\%(\text{Product deuterization rate})}{D_2\%(\text{MeOD deuterization rate})}\times 100\%$$

1a-1c, **1p** and **1ah-1aj** were bought from commercial sources. **1d-1o, 1q**, **1s-1z**, **1aa-1ag** and **1ak-1am** were prepared by known methods [1-26]. Analytical data matched literature values.

2. Experimental Procedures

(i) General preparation of 2a-2d, 2h, 2k, 2m-2r, 2t-2x, 4a

To a solution of the compounds (**1a-1d, 1h, 1k, 1m-1r, 1t-1x**, **1aa-1ai**, **1ak-1am**, **3a**, 1 eq) in 2 mL MeOD and 2 mL MeCN at room temperature was added I_2 (3 eq) into the solution. The mixture was stirred for 5 min, and then Mg turnings (10 eq) were added into the mixture. The resulting mixture was stirred under water bath (15-20 ℃) for 2 min, and then stirred at room temperature for 30 min. Ethyl acetate (10 mL) was added into the reaction and the mixture was filtrated under reduced pressure using a sand core funnel with a layer of diatomaceous earth. The filtrate was washed with saturated $Na_2S_2O_3$ aqueous for two times. The organic layer was dried by $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography, to give products (**2a-2d, 2j-2k, 2m-2r, 2t-2x**, **2aa-2ai**, **4a**). Yield: 37-91%.

(ii) General preparation of 2i, 2j, 2l, 2s, 2y, 4b-4d

To a solution of the compounds (**1i, 1j, 1l, 1s, 1y, 3b-3d**, 1 eq) in 2 mL MeOD and 2 mL MeCN at room temperature was added I_2 (3 eq) into the solution. The mixture was stirred for 5 min, and then Mg turnings (10 eq) were added into the mixture. The resulting mixture was stirred under water bath (15-20 ℃) for 2 min, and then stirred at room temperature for 30 min. Ethyl acetate (10 mL) was added into the reaction and the mixture was filtrated under reduced pressure using sand core funnel covered with a layer of diatomaceous earth. The filtrate was washed by saturated $Na_2S_2O_3$ aqueous for two times. The organic layer was dried by $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography, to give products (**2i, 2j, 2l, 2s, 2y, 4b-4d**). Yield: 60-94%.

(iii) Preparation of 2e-2g, 2aj, 2z

Preparation of 2e and 2g

To a solution of 161 mg **1e** or **1j** (0.82 mmol, 1 eq) in 2 mL MeOD, 1 mL MeCN and 1 mL toluene was added 30.4 mg TBAI (0.082 mmol, 0.1 eq) and 1.04 g I_2 (4.1 mmol, 5 eq). The mixture was stirred for 5 min, and then 299 mg Mg turnings (12.3 mmol, 15 eq) were added into the mixture. The resulting mixture was stirred under water bath (15-20 ℃) for 2 min, and then stirred at room temperature for 30 min. Ethyl acetate (10

mL) was added into the reaction and the mixture was filtrated under reduced pressure using sand core funnel with a layer of diatomaceous earth. The filtrate was washed by saturated $Na_2S_2O_3$ aqueous for two times. The organic layer was dried by $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography and was eluted with petrol ether: ethyl acetate = 75:1 (v/v), to give the products 43.2 mg **2e** as light-yellow liquid and 103.7 mg **2j** as colorless liquid. Yield: 26% (**2e**); Yield: 63% (**2j**).

Preparation of 2f

To a solution of 161 mg **1f** (0.82 mmol, 1 eq) in 2 mL MeOD, 1 mL MeCN and 1 mL toluene was added 30.4 mg TBAI (0.082 mmol, 0.1 eq) and 1.04 g I_2 (4.1 mmol, 5 eq) The mixture was stirred for 5 min, then 299 mg Mg turnings (12.3 mmol, 15 eq) were added into the mixture. The resulting mixture was stirred under water bath (15-20 ℃) for 2 min, then stirred at room temperature for 30 min. Ethyl acetate (10 mL) was added into the reaction and the mixture was filtrated under reduced pressure using sand core funnel with a layer of diatomaceous earth. The filtrate was washed by saturated $Na_2S_2O_3$ aqueous for two times. The organic layer was dried by $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography and was eluted with petrol ether: ethyl acetate = 50:1 (v/v), to give the product 144.1 mg **2f** as colorless liquid. Yield: 88%.

Preparation of 2aj

To a solution of 128 mg **1aj** (0.80 mmol, 1 eq) in 2 mL MeOD and 2 mL MeCN was added 1.22 g I_2 (4.8 mmol, 6 eq) The mixture was stirred for 5 min, then 292 mg Mg turnings (12.0 mmol, 15 eq) were added into the mixture. The resulting mixture was stirred under water bath (15-20 ℃) for 2 min, then stirred at room temperature for 30 min. Ethyl acetate (10 mL) was added into the reaction and the mixture was filtrated under reduced pressure using sand core funnel with a layer of diatomaceous earth. The filtrate was washed by saturated $Na_2S_2O_3$ aqueous for two times. The organic layer was dried by $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography and was eluted with petrol ether: ethyl acetate = 50:1 (v/v), to give the product 124.1 mg **2aj** as colorless liquid. Yield: 92%.

Preparation of 2z

To a solution of 167.5 mg **2y** (0.753 mmol, 1 eq) in 5 mL THF was added 10 mL 3 mol/L KOH aqueous. The reaction mixture was stirred at 65 ℃ overnight. The solution was concentrated under reduced pressure, and then 35% HCl aqueous was added into the residue until pH = 1. The aqueous was extracted by 10 mL ethyl acetate for three times. The organic layer was dried by $MgSO_4$, filtered, and evaporated under reduced pressure, to give 145.8 mg **2z** as colorless sticky liquid. The liquid converted to white solid after cooled down. Yield: 93%.

3. The characterization of the products

methyl 3-phenylpropanoate-2,3-*d*$_2$ (2a): 115.6 mg as colorless liquid; α-D%: 97%; β-D%:98%; Yield: 91%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.24-7.20 (m, 3H), 3.68 (s, 3H), 2.93 (d, J = 8.0 Hz, 1H), 2.61 (d, J = 8.0 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.4, 140.5, 128.5, 128.3, 126.3, 51.6, 35.6, 35.4, 35.2, 30.8, 30.6, 30.4; HRMS (ESI) m/z calcd for $C_{10}H_{10}D_2O_2Na^+$ $[M+Na]^+$: 189.0855, found 189.0860.

methyl 3-(p-tolyl)prpranoate-2,3-*d*$_2$ (2b): 82.4 mg as colorless liquid; α-D%: 97%; β-D%: 99%; Yield: 90%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.12-7.07 (m, 4H), 3.67 (s, 3H), 2.89 (d, J = 8.0 Hz, 1H), 2.61 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.5, 137.4, 135.7, 129.2, 128.1, 51.6, 35.7, 35.5, 35.3, 30.3, 30.1, 29.9, 21.0; HRMS (ESI) m/z calcd for $C_{11}H_{12}D_2O_2Na^+$ $[M+Na]^+$: 203.1012, found 203.1017.

methyl 3-(4-methoxyphenyl)propanoate-2,3-*d*$_2$ (2c [26]): 89.2 mg as colorless liquid; α-D%: 94%; β-D%: 97%; Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 3.66 (s, 3H), 2.87 (d, J = 8.0 Hz, 1H), 2.58 (d, J = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 158.0, 132.5, 129.2, 113.9, 55.2, 51.6, 35.8, 35.6, 35.4, 29.9, 29.7, 29.5; HRMS (ESI) m/z calcd for $C_{11}H_{12}D_2O_3Na^+$ $[M+Na]^+$: 219.0961, found 219.0969.

methyl 3-(4-(methylthio)phenyl)propanoate-2,3-*d*$_2$ (2d): 117.1 mg as colorless liquid; α-D%: 98%; β-D%: 99%; Yield: 77%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21-7.18 (m, 2H), 7.14-7.11 (m, 2H), 3.66 (s, 3H), 2.89 (d, J = 6.8 Hz, 1H), 2.59 (d, J

= 6.4 Hz, 1H), 2.46 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.2, 137.4, 135.9, 128.8, 127.1, 51.6, 35.4, 35.2, 35.0, 30.1, 30.0, 29.8, 16.1. HRMS (ESI) m/z calcd for $C_{11}H_{12}D_2SO_2Na^+$ $[M+Na]^+$: 235.0732, found 235.0730.

methyl 3-(2-chlorophenyl)propanoate-2,3-*d*$_2$ (2e): 43.2 mg as light yellow liquid; α-D%: 96%; β-D%: 97%; Yield: 26%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.34 (dd, J = 7.2, 2.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.21-7.13 (m, 2H), 3.68 (s, 3H), 3.04 (d, J = 7.6 Hz, 1H), 2.63 (d, J = 7.2 Hz, 1H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 173.1, 138.0, 134.0, 130.4, 129.6, 127.9, 126.9, 51.6, 33.6, 33.4, 33.2, 28.8, 28.6, 28.4; HRMS (ESI) m/z calcd for $C_{10}H_{10}D_2ClO_2^+$: $[M+H]^+$: 201.0646, found 201.0644.

methyl 3-(3-chlorophenyl)propanoate-2,3-*d*$_2$ (2f): 144.1 mg as colorless liquid; α-D%: 95%; β-D%: 97%; Yield: 88%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.24-7.16 (m, 3H), 7.09-7.06 (m, 1H), 3.67 (s, 3H), 2.90 (d, J = 7.6 Hz, 1H), 2.59 (d, J = 8.4 Hz, 1H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 173.0, 142.4, 134.2, 129.7, 128.4, 126.5, 51.6, 35.1, 34.9, 34.7, 30.3, 30.1, 29.9; HRMS (ESI) m/z calcd for $C_{10}H_9D_2ClO_2Na^+$: $[M+Na]^+$: 223.0465, found 223.0462.

methyl 3-(4-chlorophenyl)propanoate-2,3-*d*$_2$ (2g): 103.7 mg as colorless liquid; α-D%: 96%; β-D%: 97%; Yield: 63%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.25 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 3.67 (s, 3H), 2.90 (d, J = 7.6 Hz, 1H), 2.59 (d, J = 8.0 Hz, 1H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 173.0, 138.9, 132.1, 129.7, 128.6, 51.7, 35.3, 35.1, 34.9, 30.1, 29.9, 29.7; HRMS (ESI) m/z calcd for $C_{10}H_{10}D_2ClO_2^+$: $[M+H]^+$: 201.0646, found 201.0655.

methyl 3-(3-cyanophenyl)propanoate-2,3-*d*$_2$ (2h): 109.3 mg as colorless sticky liquid; α-D%: 97%; β-D%: 98%; Yield: 79%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.47-7.44 (m, 1H), 7.42-7.38 (m, 1H), 3.68 (s, 3H), 2.97 (d, J = 7.6 Hz, 1H), 2.62 (d, J = 8.4 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.6, 141.8, 132.9, 131.9, 130.1, 129.3, 118.8, 112.5, 51.7, 34.8, 34.6, 34.4, 30.1, 29.9, 29.7; HRMS (ESI) m/z calcd for $C_{11}H_{10}ND_2O_2^+$ $[M+H]^+$: 192.0988, found 192.0990.

methyl 3-(naphthalen-2-yl)propanoate-2,3-*d*$_2$ (2i): 111.3 mg as white powder; α-D%: 98%; β-D%: 96%; Yield: 90%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 3H), 7.65 (s, 1H), 7.49-7.42 (m, 2H), 7.35 (d, J = 10.0 Hz, 1H), 3.69 (s, 3H), 3.11 (d,

J = 7.6 Hz, 1H), 2.72 (d, *J* = 6.8 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.3, 137.9, 133.6, 132.1, 128.1, 127.6, 127.5, 126.9, 126.4, 126.0, 125.4, 51.6, 35.4, 35.2, 35.0, 30.9, 30.7, 30.5; HRMS (ESI) m/z calcd for $C_{10}H_{10}D_2O_3Na^+$ $[M+Na]^+$: 205.0804, found 205.0813.

methyl 3-(6-methoxynaphthalen-2-yl)propanoate-2,3-*d*$_2$ (2j): 165.2 mg as white solid; α-D%: 99%; β-D%: 97%; Yield: 88%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 2H), 7.57(s, 1H), 7.31-7.29 (m, 1H), 7.15-7.11 (m, 2H), 3.91 (s, 3H), 3.68 (s, 3H), 3.06 (d, *J* = 8.0 Hz, 1H), 2.68 (d, *J* = 9.2 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.4, 157.3, 135.6, 133.2, 129.0, 129.0, 127.4, 127.0, 126.3, 118.8, 105.6, 55.3, 51.6, 35.6, 35.4, 35.2, 30.7, 30.5, 30.3; HRMS (ESI) m/z calcd for $C_{15}H_{14}D_2O_3Na^+$ $[M+Na]^+$: 269.1117, found 269.1124.

methyl 2-phenylpropanoate-2,3-*d*$_2$ (2k): 161.0 mg as colorless liquid; α-D%: >95%; β-D%: 98%; Yield: 88%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 5H), 3.66 (s, 3H), 1.48 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 175.0, 140.5, 128.6, 127.4, 127.1, 52.0, 45.2, 45.0, 18.4, 18.2, 18.0; HRMS (ESI) m/z calcd for $C_{10}H_{10}D_2O_2Na^+$ $[M+Na]^+$: 189.0855, found 189.0854.

methyl 2-(1,2,3,4-tetrahydronaphthalen-1-yl-1-*d*)acetate-2-*d* (2l): 79.7 mg as colorless liquid. α-D%: 98%; β-D%: 96%; Yield: 68%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17-7.06 (m, 4H), 3.72 (s, 3H), 2.84-2.75 (m, 2H), 2.70 (s, 0.66H), 2.53 (s, 0.36H), 1.94-1.88 (m, 1H), 1.86-1.74 (m, 2H),1.72-1.67 (m, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.3, 139.1, 137.1, 129.3, 128.2, 126.0, 125.8, 51.6, 41.6, 41.4, 41.2, 34.2, 34.0, 33.8, 29.5, 27.9, 27.9, 19.4; HRMS (ESI) m/z calcd for $C_{13}H_{14}D_2O_2Na^+$ $[M+Na]^+$: 229.1168, found 229.1180.

methyl 3-phenylbutanoate-2,3-*d*$_2$ (2m [4]): 87.3 mg as colorless liquid; α-D%: 99%; β-D%: 97%; Yield: 87%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.24-7.19 (m, 3H), 3.63 (s, 1.75H), 3.62 (s, 1.25H), 2.61 (s, 0.6H), 2.54 (s, 0.4H), 1.29 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.9, 145.6, 128.5, 126.7, 126.4, 51.5, 42.5, 42.3, 42.1, 36.1, 35.9, 35.7, 21.6, 21.6; HRMS (ESI) m/z calcd for $C_{11}H_{12}D_2O_3Na^+$ $[M+Na]^+$: 203.1012, found 203.1016.

methyl 2-methyl-3-phenylpropanoate-2,3-*d*$_2$ (2n): 130.8 mg as colorless liquid;

α-D%: 69%; β-D%: 98%; Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 3H), 7.23-7.15 (m, 3H), 3.64(s, 1.4H), 3.64(s, 1.6H), 3.01(s, 0.5H), 2.65(s, 0.52H), 2.13 (d, J = 1.6 Hz, 0.31H), 1.15(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 139.3, 128.9, 128.3, 126.3, 52.0, 51.5, 41.3, 41.1, 40.9, 40.7, 39.5, 39.4, 39.3, 39.2, 39.1, 39.0, 16.6, 14.0; HRMS (ESI) m/z calcd for $C_{11}H_{12}D_2O_2Na^+$ $[M+Na]^+$: 203.1012, found 203.1010.

methyl 2,3-dimethyl-3-phenylpropanoate-2,3-*d*$_2$ & ethyl 2,3-dimethyl-3-phenyl propanoate-2,3-*d*$_2$ (2o & 2o' [27]): 74.3 mg as light yellow liquid; **2o** : **2o'** = 6:11 (n/n); α-D%: 79%; β-D%: 98%; Yield (**2o**): 31%; Yield (**2o'**): 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, J = 7.6, 2.0 Hz, 2H), 7.21-7.15 (m, 3H), 4.21-4.15 (m, 1.1H), 3.72 (s, 0.64H), 3.71 (s, 0.26H), 3.47 (s, 0.21H), 1.28 (td, J = 7.2, 2.4 Hz, 2.2H), 1.24 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 176.4, 144.4, 144.3, 128.5, 128.4, 128.2, 127.5, 127.3, 126.5, 126.4, 126.3, 60.2, 51.5, 51.3, 46.8, 42.9, 20.5, 17.3, 16.1, 16.1, 14.3, 13.9.. HRMS (ESI) m/z calcd for $C_{12}H_{14}D_2O_2Na^+$ $[M+Na]^+$: 217.1168, found 217.1171. HRMS (ESI) m/z calcd for $C_{13}H_{16}D_2O_2Na^+$ $[M+Na]^+$: 231.1325, found 231.1329.

methyl 3-(2-hydroxyphenyl)propanoate-2,3-*d*$_2$ (2p): 78.8 mg as light yellow liquid. α-D%: 99%; β-D%: 94%; Yield: 37%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.14-7.07 (m, 2H), 6.89-6.85 (m, 2H), 3.69 (s, 3H), 2.89 (d, J = 6.4 Hz, 1H), 2.70 (d, J = 8.4 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 176.0, 154.3, 130.5, 128.0, 127.2, 120.9, 117.2, 52.2, 34.8, 34.6, 34.4, 24.4, 24.2, 24.0; HRMS (ESI) m/z calcd for $C_{10}H_{10}D_2O_3Na^+$ $[M+Na]^+$: 205.0804, found 205.0813.

methyl 3-cyclohexylpropanoate-2,3-*d*$_2$ (2q): 96.4 mg as light yellow liquid; α-D%: 99%; β-D%: 94%; Yield: 81%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.29 (d, J = 7.6 Hz, 1H), 1.71-1.62 (m, 5H), 1.50 (d, J = 8.0 Hz, 1H), 1.28-1.14 (m, 6H) ; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 175.7, 51.4, 37.1, 32.9, 32.1, 31.9, 31.7, 31.5, 31.4, 31.3, 31.1, 26.5, 26.2; HRMS (ESI) m/z calcd for $C_{10}H_{16}D_2O_2Na^+$ $[M+H]^+$: 173.1505, found 173.1517.

dimethyl succinate-2,3-*d*$_2$ (2r [27]): 73.2 mg as colorless liquid; D%: 99%, Yield: 57%; Yield: 57%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.59 (d, J = 1.6 Hz, 1H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.7, 51.8, 28.8, 28.5, 28.3; HRMS (ESI) m/z calcd for $C_6H_8D_2O_4Na^+$ $[M+Na]^+$: 171.0597, found 171.0600.

methyl 2-(cycloheptyl-1-*d*)acetate-2-*d* & methyl 2-(cyclohept-1-en-1-yl)acetate-2-*d* (2s & 2s'): 124.2 mg as colorless liquid**;** was cannot be separated mixture of methyl 2-(cycloheptyl-1-*d*)acetate-2-*d* (**2s**) and methyl 2-(cyclohept-1-en-1-yl)acetate-2-*d* (**2s'**), **2s**:**2s'** = 7:2 (n/n); Yield: 47% (**2s**); Yield: 13% (**2s'**); α-D% (**2s**): 97%; β-D% (**2s**): 98%; D% (**2s'**): 98%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 5.69 (t, J = 6.0 Hz, 0.24H), 3.68 (s, 0.67H), 3.66 (s, 2.33H), 2.99 (s, 0.23H), 2.22-2.16 (m, 1.25H), 2.13-2.09 (m, 0.49H), 1.74-1.52 (m, 5H), 1.58-1.43 (m, 4H), 1.26-1.18 (m, 2H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 173.8, 137.4, 130.8, 51.6, 51.3, 45.2, 45.0, 44.8, 42.4, 42.3, 42.2, 42.1, 42.0, 41.9, 36.4, 36.1, 35.7, 34.5, 34.4, 34.3, 34.3, 32.8, 32.3, 28.4, 28.2, 26.9, 26.4, 26.2, 26.1; HRMS (ESI) m/z calcd for $C_{10}H_{17}D_2O_2^+$ $[M+H]^+$: 173.1505, found 173.1512; HRMS (ESI) m/z calcd for $C_{10}H_{16}DO_2^+$ $[M+H]^+$: 170.1286, found 170.1286.

methyl 4-phenylbutanoate-2,3-d_2 & methyl 4-phenylbut-3-enoate-2,2-d_2 (2t & 2t'):

101.8 mg as colorless liquid; was cannot be separated mixture of methyl 4-phenylbutanoate-2,3-d_2 (**2t**) and methyl 4-phenylbut-3-enoate-2-*d* (**2t'**), **2t**:**2t'** = 4:3 (n/n); Yield: 48% (**2t**); Yield: 36% (**2t'**); α-D% (**2t**): 93%; β-D% (**2t**): 93%; D% (**2t'**) : 95%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.39-7.36 (m, 1H), 7.34-7.27 (m, 2H), 7.24-7.16 (m, 2H), 6.52-6.48 (m, 0.45H), 6.31-6.27 (m, 0.45H), 3.72 (s, 1.3H), 3.67 (s, 1.7H), 2.65 (d, J = 7.6 Hz, 1.2H), 2.31 (d, J = 9.2 Hz, 0.6H), 1.97-1.91 (m, 0.6H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 174.0, 141.4, 136.8, 133.5, 128.5, 128.5, 128.4, 127.6, 126.3, 121.5, 51.9, 51.5, 35.0, 33.2, 33.0, 32.8, 26.2, 26.0, 25.8; HRMS (ESI) m/z calcd for $C_{11}H_{12}D_2O_2Na^+$ $[M+Na]^+$: 203.1012, found 203.1015; HRMS (ESI) m/z calcd for $C_{11}H_{11}D_2O_2^+$ $[M+H]^+$: 179.1036, found 179.1037.

methyl 3-(thiophen-2-yl)propanoate-2,3-d_2 (2u): 116.2 mg as colorless liquid; α-D%: 117%; β-D%: 95%; The deuterium rate of thiophen-5-position was 17%; Yield: 75%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.13 (d, J = 5.2 Hz, 1H), 6.92 (dd, J = 2.8, 8.4Hz, 1H), 6.82 (d, J = 3.6 Hz, 1H), 3.69 (s, 3H), 3.15 (d, J = 7.4 Hz, 1H), 2.67 (d, J = 6.0

Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.8, 142.9, 126.8, 126.7, 124.6, 123.5, 51.7, 35.8, 35.6, 35.4, 25.0, 24.8, 24.6; HRMS (ESI) m/z calcd for $C_8H_8D_2O_2SNa^+$ $[M+Na]^+$: 195.0419, found 195.0417.

methyl 3-(quinolin-2-yl-4-*d*)propanoate2,3-*d*$_2$ (2v): 106.0 mg as light yellow liquid; α-D%: 104%; β-D%: 85%; The deuterium rate of quinolin-4-position was 59%; Yield: 52%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 0.41H), 8.03 (d, J = 8.4 Hz, 1H), 7.81-7.76 (m, 1H), 7.70-7.66 (m, 1H), 7.51-7.47 (m, 1H), 7.33 (dd, J = 8.4, 4.0 Hz, 1H), 3.69 (s, 3H), 3.29 (d, J = 7.2 Hz, 1H), 2.92 (d, J = 8.0 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.6, 160.4, 129.4, 128.8, 127.51, 127.46, 126.9, 126.8, 125.9, 121.5, 121.4, 51.6, 33.2, 33.0, 32.8, 32.8, 32.6, 32.4; HRMS (ESI) m/z calcd for $C_{13}H_{11}D_3O_2N^+$ $[M+H]^+$: 219.1207, found 219.1214; HRMS (ESI) m/z calcd for $C_{13}H_{12}D_2O_2N^+$ $[M+H]^+$: 218.1145, found 218.1154; HRMS (ESI) m/z calcd for $C_{13}H_{10}D_3O_2NNa^+$ $[M+Na]^+$: 241.1027, found 241.1034; HRMS (ESI) m/z calcd for $C_{13}H_{11}D_2O_2NNa^+$ $[M+Na]^+$: 240.0964, found 240.0972.

methyl 3-(1-methyl-1H-pyrrol-2-yl-3,4,5-*d*$_3$)propanoate-2,3-*d*$_2$ (2w): 91.2 mg as brown liquid; α-D%: 98%; β-D%: 99%; The deuterium rate of pyrrol-3,4,5-position was 44%; Yield: 61%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 6.56 (s, 0.56H), 6.07-6.05 (m, 0.56H), 5.88 (d, J = 2.4 Hz, 1H), 3.70 (s, 3H), 3.55 (s, 3H), 2.86 (d, J = 7.6 Hz, 1H), 2.64 (d, J = 8.4 Hz, 1H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 173.3, 131.3, 121.5, 121.4, 106.6, 106.5, 106.5, 106.4, 105.4, 105.3, 51.7, 33.5, 33.4, 33.0, 32.8, 32.6, 21.4, 21.2, 21.0; HRMS (ESI) m/z calcd for $C_9H_{11}D_2O_2NNa^+$ $[M+Na]^+$: 192.0964, found 192.0961; HRMS (ESI) m/z calcd for $C_9H_{10}D_3O_2NNa^+$ $[M+Na]^+$: 193.1027, found 193.1023; HRMS (ESI) m/z calcd for $C_9H_9D_4O_2NNa^+$ $[M+Na]^+$: 194.1090, found 194.1083; HRMS (ESI) m/z calcd for $C_9H_8D_5O_2NNa^+$ $[M+Na]^+$: 195.1152, found 195.1138.

methyl 3-(furan-2-yl-5-*d*)propanoate-2,3-*d*$_2$ (2x): 108.8 mg as light yellow liquid; α-D%: 99%; β-D%: 96%; The deuterium rate of furan-5-position was 12%; Yield: 64%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.30 (d, J = 1.2 Hz, 0.88H), 6.27 (dd, J = 3.2, 2.0 Hz, 1H), 6.02 (d, J = 3.2 Hz, 1H), 3.69 (s, 3H), 2.95 (d, J = 7.6 Hz, 1H), 2.63 (d, J = 8.0 Hz, 1H); ^{13}C-NMR (101MHz, $CDCl_3$) δ 173.0, 154.1, 141.2, 110.2, 105.3, 51.7,

32.3, 32.1, 31.9, 23.2, 23.1, 22.9; HRMS (ESI) m/z calcd for $C_8H_8D_2O_2Na^+$ $[M+Na]^+$: 179.0648, found 179.0644; HRMS (ESI) m/z calcd for $C_8H_7D_3O_2Na^+$ $[M+Na]^+$: 180.0710, found 180.0682.

methyl 2-(4-isobutylphenyl)propanoate-2,3-*d*$_2$ (2y): 195.5 mg as colorless liquid; α-D%: 98%; β-D%:97%; Yield: 84%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.20 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.66 (s, 3H), 2.45 (d, J = 7.2 Hz, 2H), 1.85 (qt, J = 13.6, 6.8 Hz, 1H), 1.47 (s, 2H), 0.91 (s, 3H), 0.90 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 175.2, 140.6, 137.7, 129.3, 127.1, 51.9, 45.0, 44.8, 44.6, 30.2, 22.4, 18.4, 18.2, 18.0. HRMS (ESI) m/z calcd for $C_{14}H_{18}D_2O_2Na^+$ $[M+Na]^+$: 245.1481, found 245.1485.

2-(4-isobutylphenyl)propanoic-2,3-*d*$_2$ acid (2z [28]**)**: 145.8 mg as white solid; α-D%: 98%; β-D%:97%; Yield: 93%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.45 (d, J = 7.2 Hz, 2H), 1.84 (qt, J = 13.6, 6.8 Hz, 1H), 1.48 (s, 2H), 0.91 (s, 3H), 0.89 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 180.8, 140.8, 136.9, 129.4, 127.2, 45.0, 44.7, 44.5, 44.3, 30.1, 22.4, 17.9, 17.7, 17.5. HRMS (ESI) m/z calcd for $C_{13}H_{16}D_2O_2Na^+$ $[M+Na]^+$: 231.1325, found 231.1322.

3-phenyl-1-(piperidin-1-yl)propan-1-one-2,3-*d*$_2$ (2aa [29]**):** 127.9 mg as colorless and sticky liquid; α-D%: 98%; β-D%: 97%; Yield: 81%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.18 (m, 3H), 3.56 (t, J = 5.6Hz, 2H), 3.33 (t, J = 5.6Hz, 2H), 2.94 (d, J = 8.0 Hz, 1H), 2.59 (d, J = 7.2 Hz, 1H), 1.6 (q, J = 6.0 Hz, 2H), 1.55-1.44 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.4, 141.4, 128.42, 128.39, 126.1, 46.6, 42.7, 34.9, 34.7, 34.5, 31.4, 31.2, 31.0, 26.3, 25.5, 24.5; HRMS (ESI) m/z calcd for $C_{14}H_{17}D_2ONNa^+$ $[M+Na]^+$: 242.1484, found 242.1495; HRMS (ESI) m/z calcd for $C_{14}H_{18}D_2ON^+$ $[M+H]^+$: 220.1665, found 220.1673.

1-morpholino-3-phenylpropan-1-one-2,3-*d*$_2$ (2ab [29]**):** 136.5 mg as colorless and sticky liquid; α-D%: 96%; β-D%: 98%; Yield: 85%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.24-7.17 (m, 3H), 3.62 (s, 4H), 3.50 (t, J = 4.8 Hz, 2H), 3.35 (t, J = 4.8 Hz, 2H), 2.96 (d, J = 6.6 Hz, 1H), 2.59 (d, J = 7.2 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.9, 141.0, 128.5, 128.4, 126.3, 66.8, 66.4, 45.9, 41.9, 34.6, 34.4, 34.2, 31.2, 31.1, 30.9; HRMS (ESI) m/z calcd for $C_{13}H_{15}D_2O_2NNa^+$ $[M+Na]^+$: 244.1277,

found 244.1276.

N-methyl-N,3-diphenylpropanamide-2,3-*d*$_2$ (2ac): 187.2 mg as colorless and sticky liquid; α-D%: 96%; β-D%: 98%; Yield: 83%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.24-7.21 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H), 7.07-7.01 (m, 4H), 3.25 (s, 3H), 2.89 (d, J = 7.6 Hz, 1H), 2.35 (d, J = 8.0 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.2, 144.0, 141.2, 129.7, 128.4, 128.3, 127.7, 127.3, 126.0, 37.3, 35.8, 35.6, 35.4, 31.5, 31.3, 31.1; HRMS (ESI) m/z calcd for $C_{16}H_{15}D_2ONNa^+$ $[M+Na]^+$: 264.1328, found 264.1335; HRMS (ESI) m/z calcd for $C_{16}H_{16}D_2ON^+$ $[M+H]^+$: 242.1508, found 242.1510.

N,N-diphenylpropanamide-2,3-*d*$_2$ (2ad): 102.2 mg as white solid; α-D%: 97%; β-D%: 98%; Yield: 76%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.38-7.35 (m, 4H), 7.26-7.23 (m, 6H), 2.25 (t, J = 8.4 Hz,1H) , 1.11 (d, J = 5.2 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 174.0, 142.9, 129.3-126.0 (m), 28.6, 28.4, 28.2, 9.5, 9.3, 9.1; HRMS (ESI) m/z calcd for $C_{15}H_{14}D_2ON^+$ $[M+H]^+$: 228.1352, found 228.1356; HRMS (ESI) m/z calcd for $C_{15}H_{13}D_2ONNa^+$ $[M+Na]^+$: 250.1171, found 250.1176.

N-methyl-N-phenylbutanamide-2,3-*d*$_2$ (2ae): 167.8 mg as colorless and sticky liquid; α-D%: 96%; β-D%: 98%; Yield: 86%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.34-7.30 (m, 1H), 7.16 (d, J = 7.6 Hz, 2H), 3.25 (s, 3H), 2.01 (d, J = 6.8 Hz, 1H), 1.59-1.54 (m, 1H), 0.80 (d, J = 7.6 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.1, 144.3, 129.7, 127.6, 127.3, 37.2, 35.7, 35.5, 35.3, 18.7, 18.5, 18.3, 13.7; HRMS (ESI) m/z calcd for $C_{11}H_{13}D_2ONNa^+$ $[M+Na]^+$: 202.1171, found 202.1168; HRMS (ESI) m/z calcd for $C_{11}H_{14}D_2ON^+$ $[M+H]^+$: 180.1352, found 180.1349.

N,2-dimethyl-N-phenylpropanamide-2,3-*d*$_2$ (2af): 241.6 mg as white solid; α-D%: 97%; β-D%: 95%; Yield: 84%;^{1}H-NMR (400MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.20-7.17 (m, 2H), 3.25 (s, 3H), 1.01 (s, 3H), 1.00 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 177.4, 144.3, 129.7, 127.7, 127.3, 37.4, 30.7, 30.5, 30.3, 19.5, 19.4, 19.2, 19.1; HRMS (ESI) m/z calcd for $C_{11}H_{13}D_2ONNa^+$ $[M+Na]^+$: 202.1171, found 202.1170; HRMS (ESI) m/z calcd for $C_{11}H_{14}D_2ON^+$ $[M+H]^+$: 180.1352, found 180.1356.

N,2-dimethyl-N-(p-tolyl)propanamide-2,3-*d*$_2$ (2ag): 263.3 mg as light yellow and

sticky liquid; α-D%: 98%; β-D%: 96%; Yield: 87%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.20 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 3.21 (s, 3H), 2.37 (s, 3H), 1.01 (s, 3H), 0.99 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 177.6, 141.7, 137.6, 130.3, 127.0, 37.4, 30.4, 21.0, 19.5, 19.4, 19.2, 19.0; HRMS (ESI) m/z calcd for $C_{12}H_{16}D_2ON^+$ $[M+H]^+$: 194.1508, found 194.1505; HRMS (ESI) m/z calcd for $C_{12}H_{15}D_2ONNa^+$ $[M+Na]^+$: 216.1328, found 216.1323.

1-benzylpyrrolidine-2,5-dione-3,4-*d*$_2$ (2ah): 73.2 mg as light yellow solid; D%: 144%, Yield: 57%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.33-7.25 (m, 3H), 4.66 (s,2H), 2.68 (s, 1.12H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 177.4, 51.8, 28.8, 28.5, 28.3; HRMS (ESI) m/z calcd for $C_{11}H_9D_2O_2NNa^+$ $[M+Na]^+$: 214.0808, found 214.0809; HRMS (ESI) m/z calcd for $C_{11}H_8D_3O_2NNa^+$ $[M+Na]^+$: 215.0870, found 215.0858; HRMS (ESI) m/z calcd for $C_{11}H_7D_4O_2NNa^+$ $[M+Na]^+$: 216.0933, found 216.0923.

3-phenylpropanenitrile-2,3-*d*$_2$ (2ai [30]): 134.1 mg as colorless liquid; α-D%: 98%; β-D%: 94%, Yield: 85%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.30-7.22 (m, 3H), 2.94 (d, J = 5.2 Hz, 1H), 2.62 (d, J = 5.6 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 138.0, 128.8, 128.2, 127.2, 119.1, 31.3, 31.1, 30.9, 19.2, 19.0, 18.8; HRMS (ESI) m/z calcd for $C_9H_8D_2N^+$ $[M+H]^+$: 134.0933, found 134.0932

methyl 3-phenylpropanoate-2,2,3,3-*d*$_4$ (2aj [30]): 124.1 mg as colorless liquid; α-D%: 97%; β-D%:99%; Yield: 92%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.23-7.19 (m, 3H), 3.67 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.4, 140.4, 128.5, 128.2, 126.3, 51.4, 35.2, 35.0 34.7, 30.3, 30.1, 29.9; HRMS (ESI) m/z calcd for $C_{10}H_8D_4O_2Na^+$ $[M+Na]^+$: 191.0981, found 191.0988.

methyl 5-phenylpent-3-enoate-2,5-*d*$_2$ (4a): 101.3 mg as colorless liquid, was cannot be separated mixture of *E*-esters and *Z*-esters; α-D%: 193%; δ-D%: 99%; Yield: 82%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.32-7.28 (m 2H), 7.23-7.18 (m, 3H), 5.75 (dd, J = 6.4 Hz, 0.33H), 5.73 (d, J = 6.4 Hz, 0.66H), 5.65 (s, 0.6H), 5.61 (s, 0.3H), 3.69 (s, 3H), 3.37 (d, J = 7.6 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.3, 140.0, 133.2, 128.5, 128.4, 127.1, 126.1, 126.0, 122.9, 53.4, 51.7, 38.7, 38.5, 38.3, 37.3, 37.1, 36.9; HRMS (ESI) m/z calcd for $C_{12}H_{11}D_3O_2Na^+$ $[M+Na]^+$: 216.1074, found 216.1079.

methyl 3,5-diphenylpent-3-enoate-2,5-*d*$_2$ & methyl 3,5-diphenylpent-4-enoate-2,3-*d*$_2$ (4b, 4b'): 108.1 mg as light yellow liquid, was cannot be separated mixture of 1,4-reduction product, 1,2-reduction product; The ratio of 1,4-reduction product (**4b**): 1,2-reduction product (**4b'**) was 7:1 (n/n); Yield (**4b**): 63%; Yield (**4b'**): 9%; α-D% (**4b**): 105%; δ-D% (**4b**): 99%; α-D% (**4b'**): 160%; β-D% (**4b'**): >95%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.42-7.40 (m, 0.24H), 7.37-7.33 (m, 2H), 7.31-7.24 (m, 5H), 7.21-7.14 (m, 2.72H), 6.42-6.36 (m, 0.07H), 6.13 (d, J = 7.6 Hz, 0.12H), 5.80 (d, J = 7.6 Hz, 0.84H), 3.66 (s, 0.4H), 3.61 (s, 2.8H), 3.39 (s, 0.8H), 3.34 (d, J = 7.6 Hz, 0.83H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.9, 140.6, 139.5, 134.6, 130.8, 130.2, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.5, 127.3, 127.2, 126.3, 126.2, 126.0, 126.0, 52.0, 51.7, 44.3, 44.1, 43.9, 35.1, 34.9, 34.7; HRMS (ESI) m/z calcd for $C_{18}H_{16}D_2O_2Na^+$ $[M+Na]^+$: 291.1325, found 291.1335.

methyl 3-(phenanthren-9(10H)-ylidene-10-*d*)propanoate-2-*d* & methyl 3-(phenanthren-9-yl)propanoate-2,3-*d*$_2$ (4c &4c'): 242.8 mg as colorless sticky liquid, was cannot be separated mixture of 1,4-reduction product and 1,2-reduction product; The ratio of 1,4-reduction product (**4c**): 1,2-reduction product (**4c'**) was 1:2 (n/n); Yield (**4c**): 31%; Yield (**4c'**): 63%; α-D% (**4c**): 195%; δ-D% (**4c**): 113%; α-D% (**4c'**): 111%; β-D% (**4c'**): 99%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.78-8.72 (m, 0.67H), 8.66 (d, J = 7.2 Hz, 0.67H), 8.13-8.05 (m, 0.67H), 7.88-7.76 (m, 1.5H), 7.70 -7.64 (m, 1.5H), 7.64-7.55 (m, 2H), 7.40-7.23 (m, 2H), 6.01 (s, 0.33H), 3.72 (s, 3H), 3.67(s, 0.29H), 3.46 (d, J = 8.0 Hz, 1H), 2.82 (d, J = 9.6 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.5, 172.1, 136.9, 136.3, 135.0, 134.5, 133.5, 133.4, 131.7, 130.8, 130.7, 129.8, 128.4, 128.2, 128.0, 127.9, 127.6, 127.1, 126.8, 126.7, 126.3, 126.3, 125.2, 124.0, 123.7, 123.4, 122.4, 117.2, 51.9, 51.7, 34.4, 34.2, 34.0, 32.1, 31.9, 31.7, 28.3, 28.1, 27.9; HRMS (ESI) m/z calcd for $C_{18}H_{14}D_2O_2Na^+$ $[M+Na]^+$: 289.1168, found 289.1160; HRMS (ESI) m/z calcd for $C_{18}H_{13}D_3O_2Na^+$ $[M+Na]^+$: 290.1231, found 290.1260.

methyl trideca-3,6-dienoate-2,5-*d*$_2$, methyl trideca-4,6-dienoate-2,3-*d*$_2$ & methyl trideca-3,5-dienoate-2,7-*d*$_2$ (4d, 4d'&4d"): 93.8 mg as light yellow liquid, was cannot be separated mixture of 1,6-, 1,4- and 1,2-reduction product; The ratio of **4d**,

4d' and **4d''** was 10:1:4 (n/n/n); Yield (**4d**): 55%; Yield (**4d'**): 5%; Yield (**4d''**): 22%; α-D% (**4d**): 195%; δ-D% (**4d**): 91%; α-D% (**4d'**): 97%; β-D% (**4d'**): 98%; α-D% (**4d''**): 195%; ζ-D% (**4d''**): 97%; ^{1}H-NMR (400MHz, $CDCl_3$) δ 6.10-5.94 (m, 1H), 5.67-5.58 (m, 1H), 5.55-5.50 (m, 1H), 5.47-5.35 (m, 1H), 3.69 (s, 0.2H), 3.68 (s, 2H), 3.67 (s, 0.8H), 2.72-2.68 (m, 0.4H), 2.38-2.35 (m, 0.5H), 2.05-1.96 (m, 1.75H), 1.36-1.25 (m, 9H) ,0.87 (t, J = 7.6 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.5,172.5, 135.0, 134.2, 133.7, 133.3, 131.9 131.6, 129.8, 129.4, 129.3, 127.4, 122.1, 122.0, 121.9, 51.8, 51.7, 51.5, 37.5, 37.3, 37.1, 35.3, 35.1, 34.9, 33.7, 33.5, 33.3, 32.6, 32.5, 32.3, 32.2, 32.0, 31.8, 31.7, 29.4, 29.3, 29.1, 29.1, 28.9, 28.8, 27.6, 27.4, 27.2, 27.1, 22.6, 14.1; HRMS (ESI) m/z calcd for $C_{14}H_{22}D_2O_2Na^+$ $[M+Na]^+$: 249.1794, found 249.1787.

4. References

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2,3-Dideuterioesters Promoted by Samarium Diiodide. *J. Org. Chem.* **2003,** *68* (4), 1585-1588.

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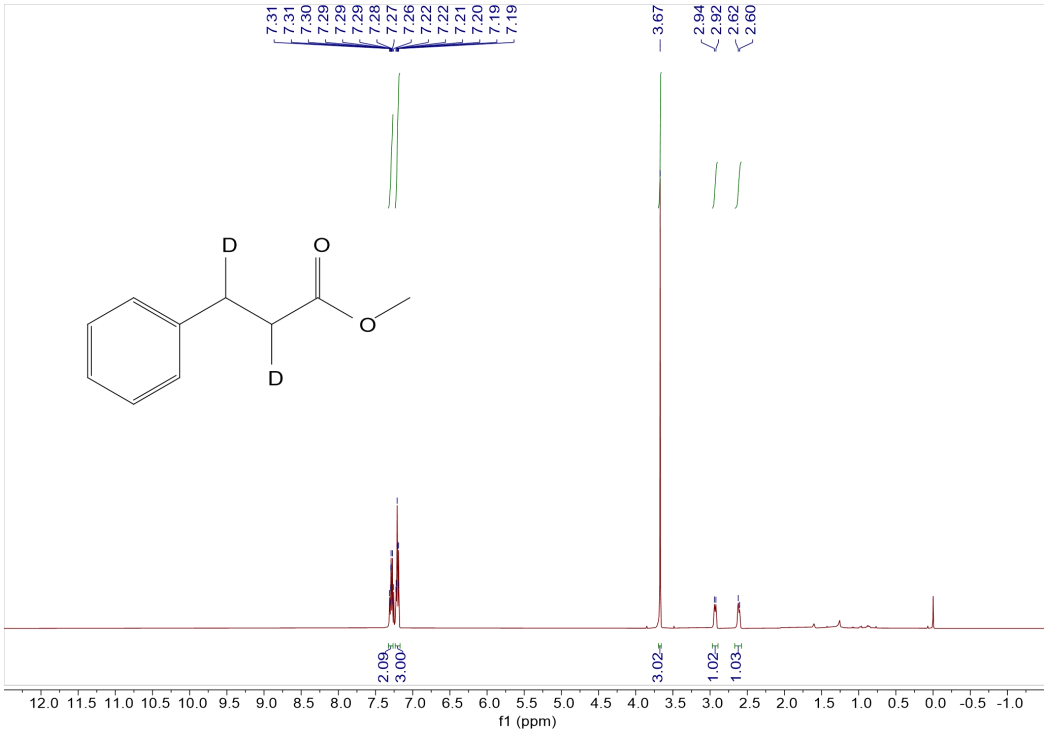
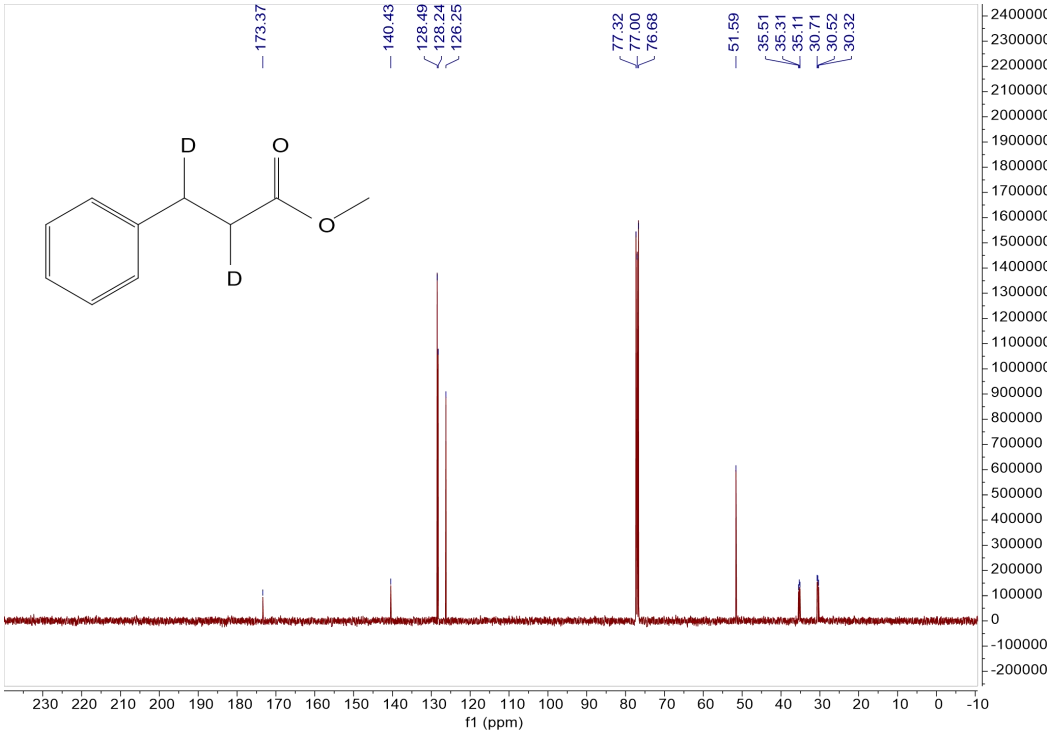
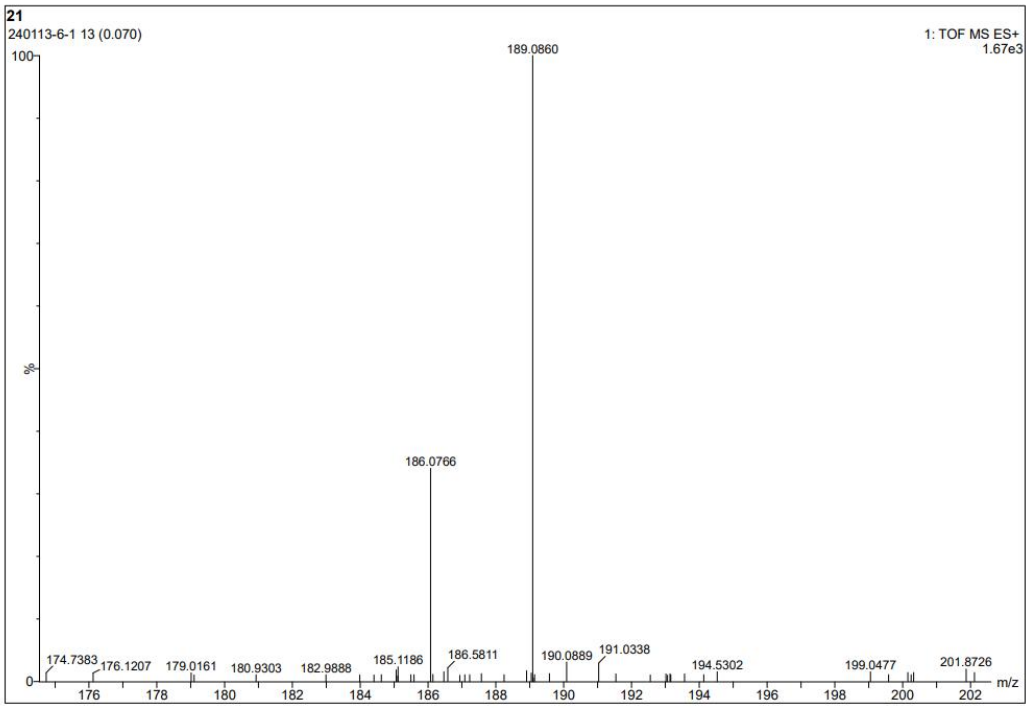
5. NMR and HRMS Spectra

methyl 3-phenylpropanoate-2,3-d_2 (2a)







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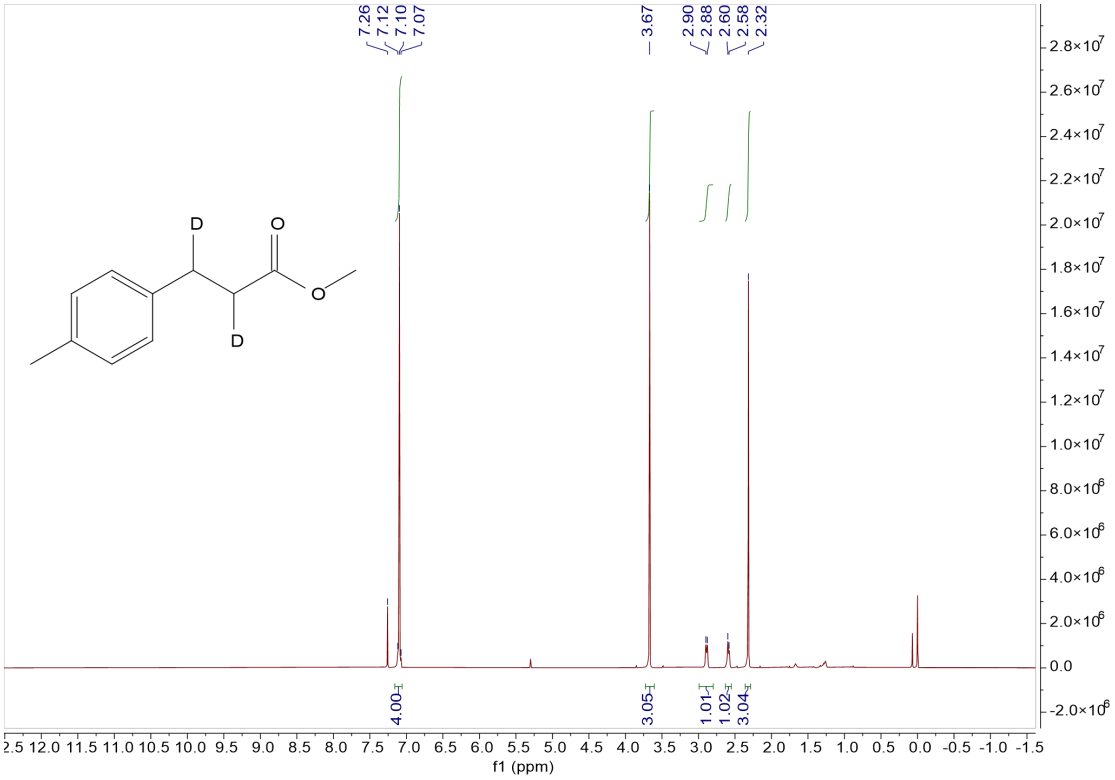
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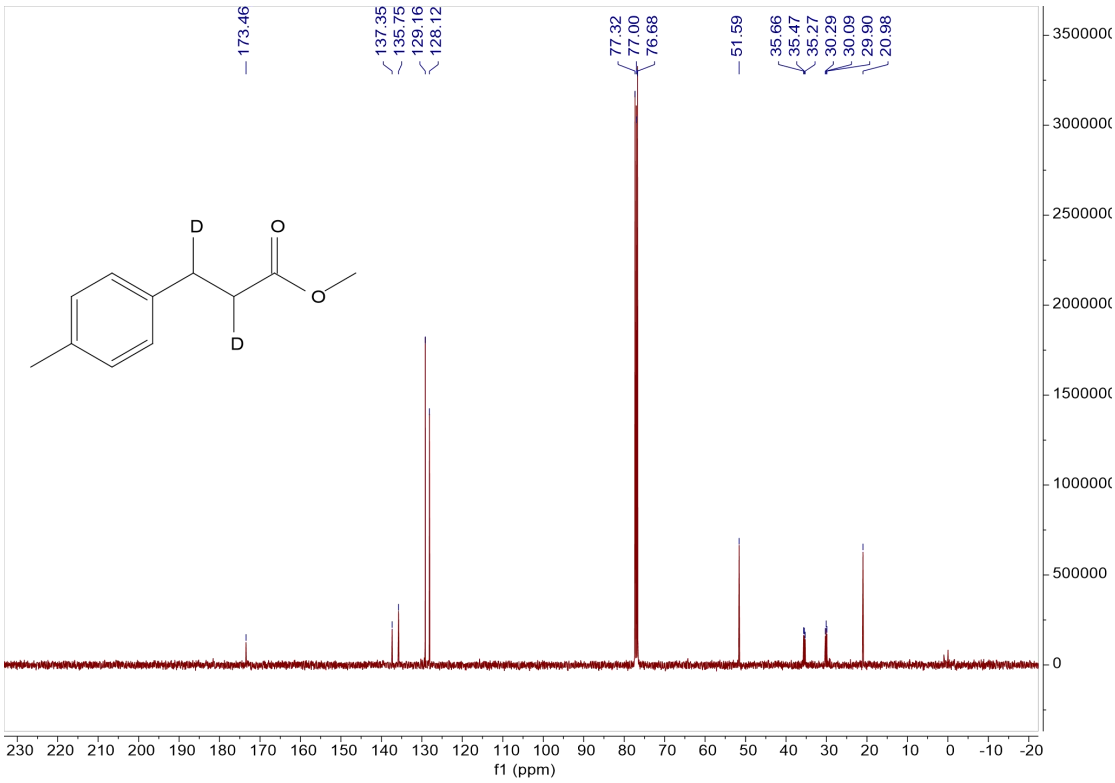
1.01
1.02
3.04
f1 (ppm)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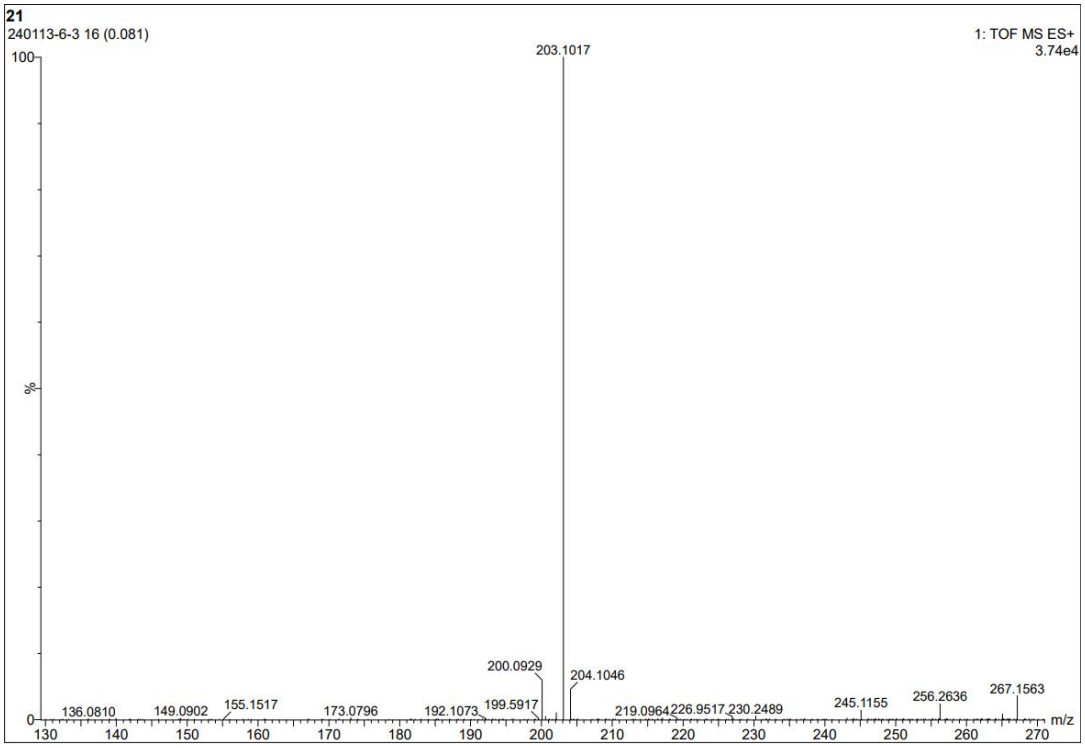
O
D
f1 (ppm)



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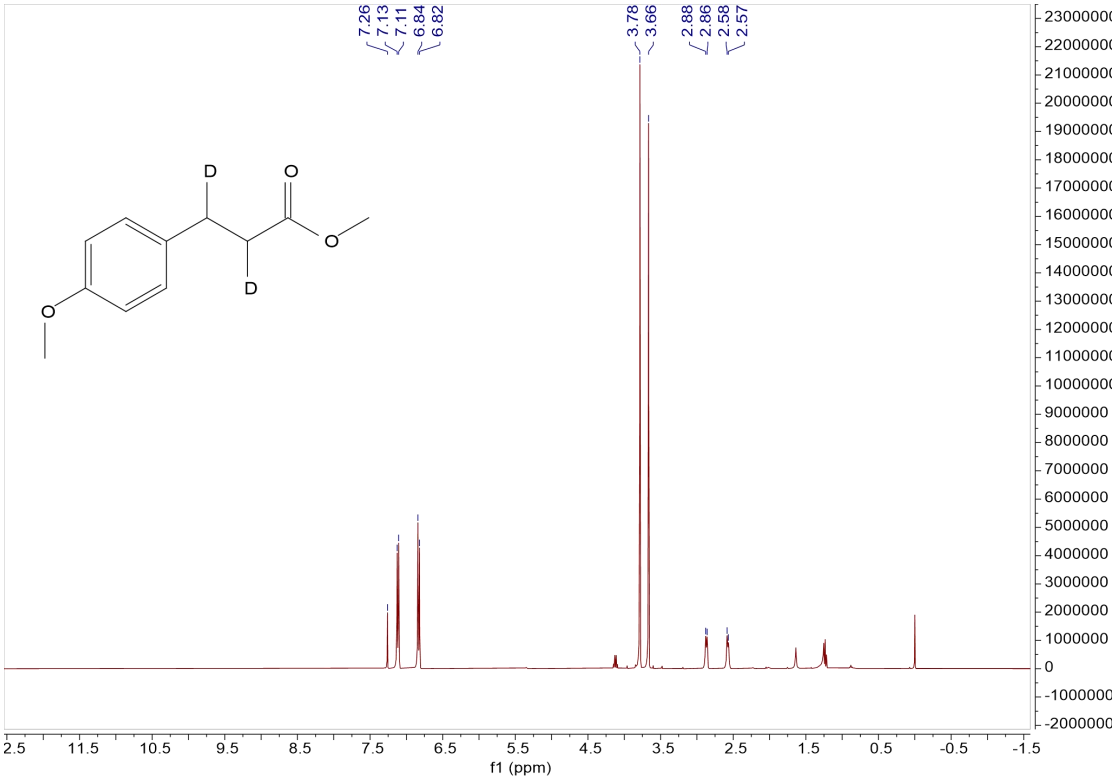

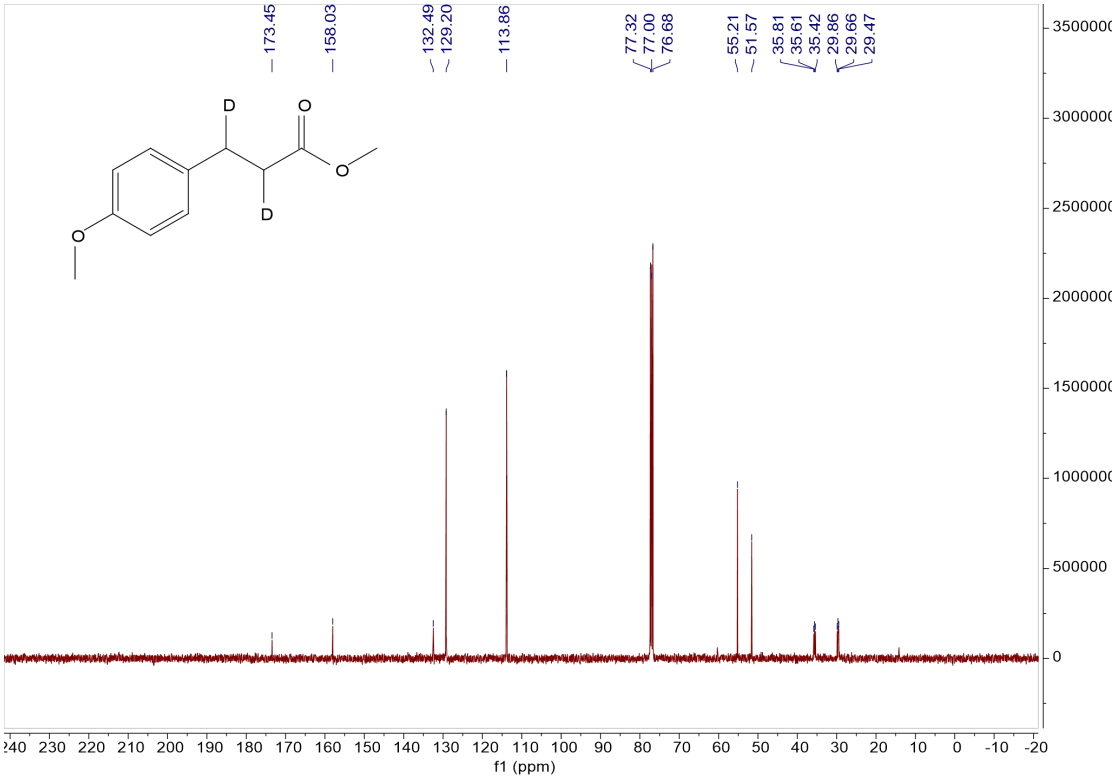

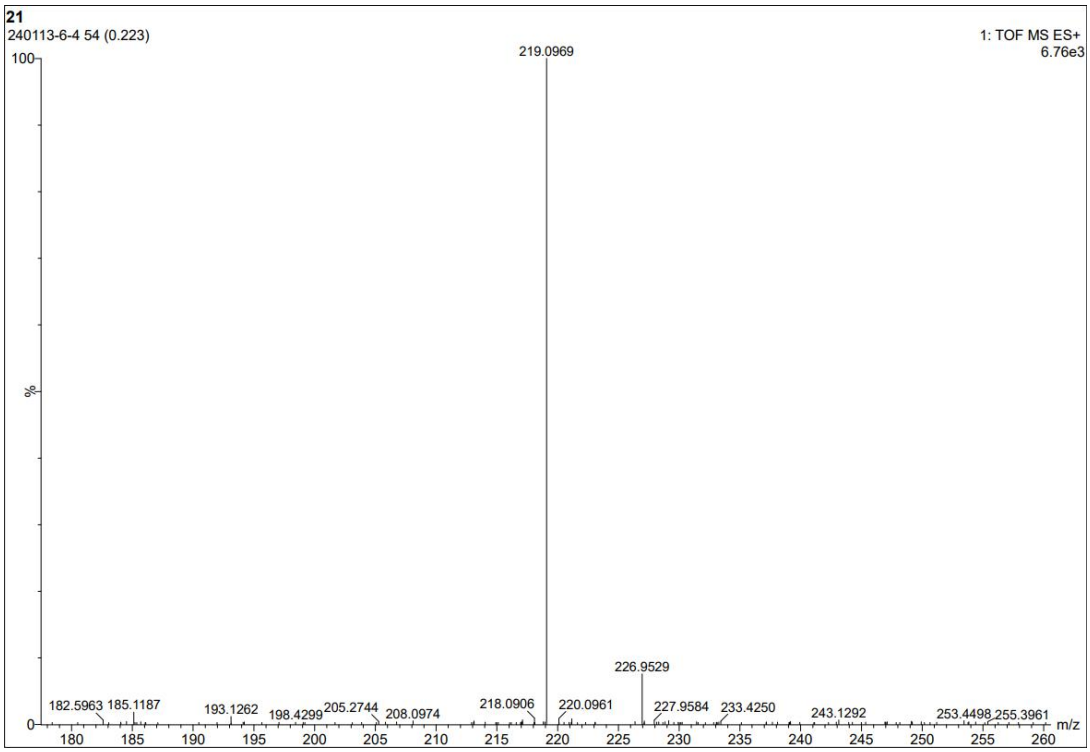

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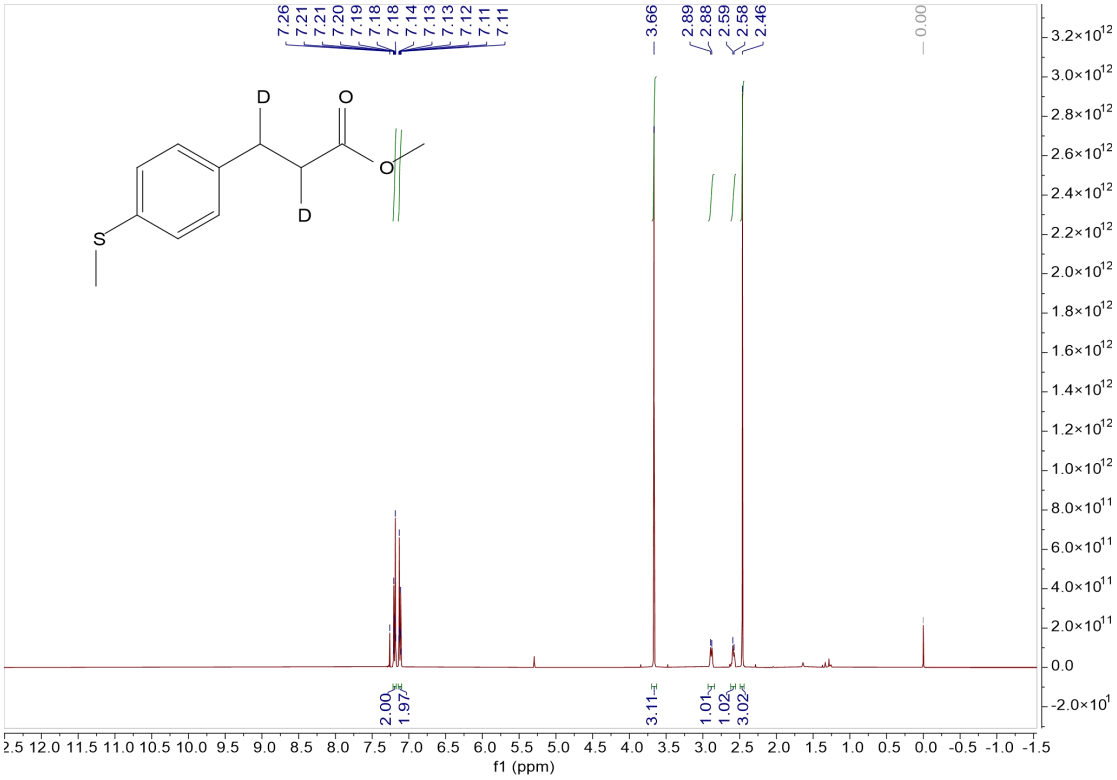
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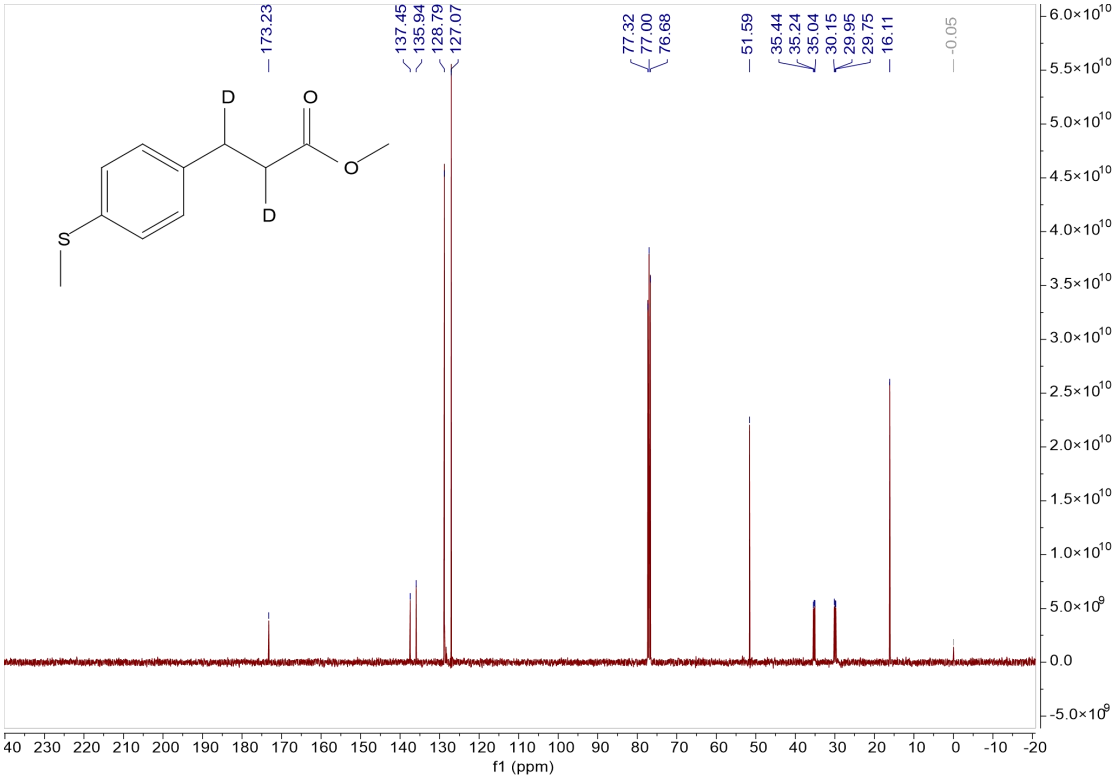
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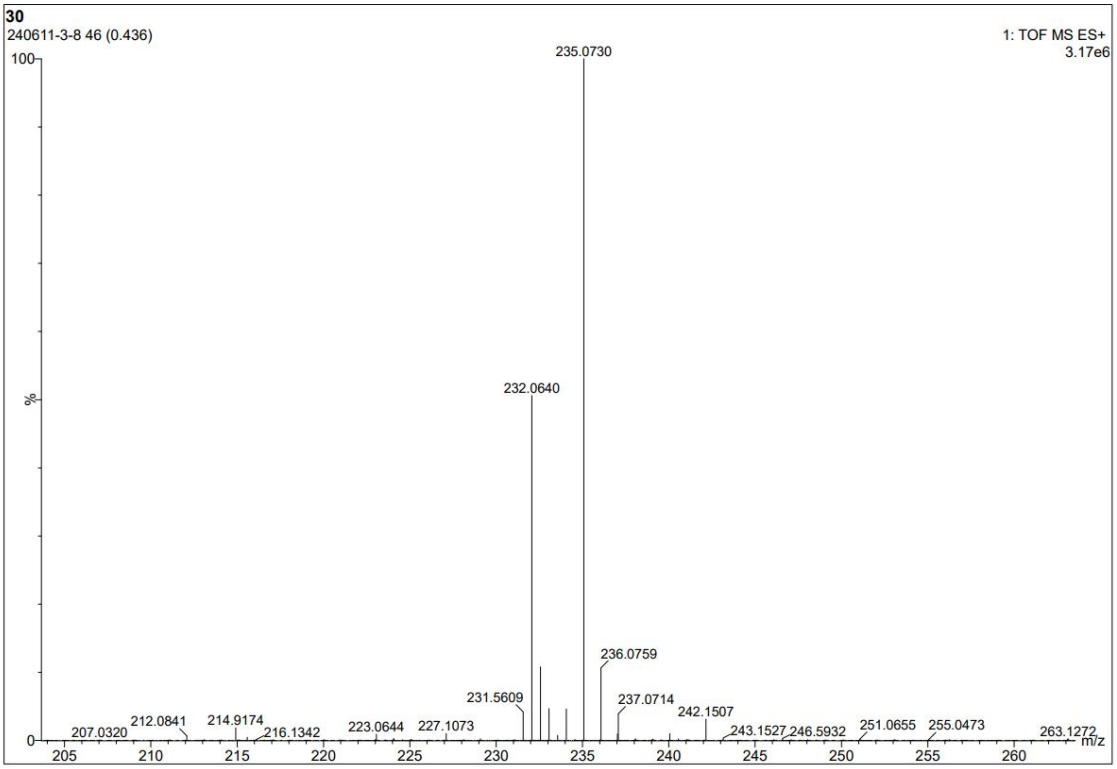
D
O
O
D
S
f1 (ppm)



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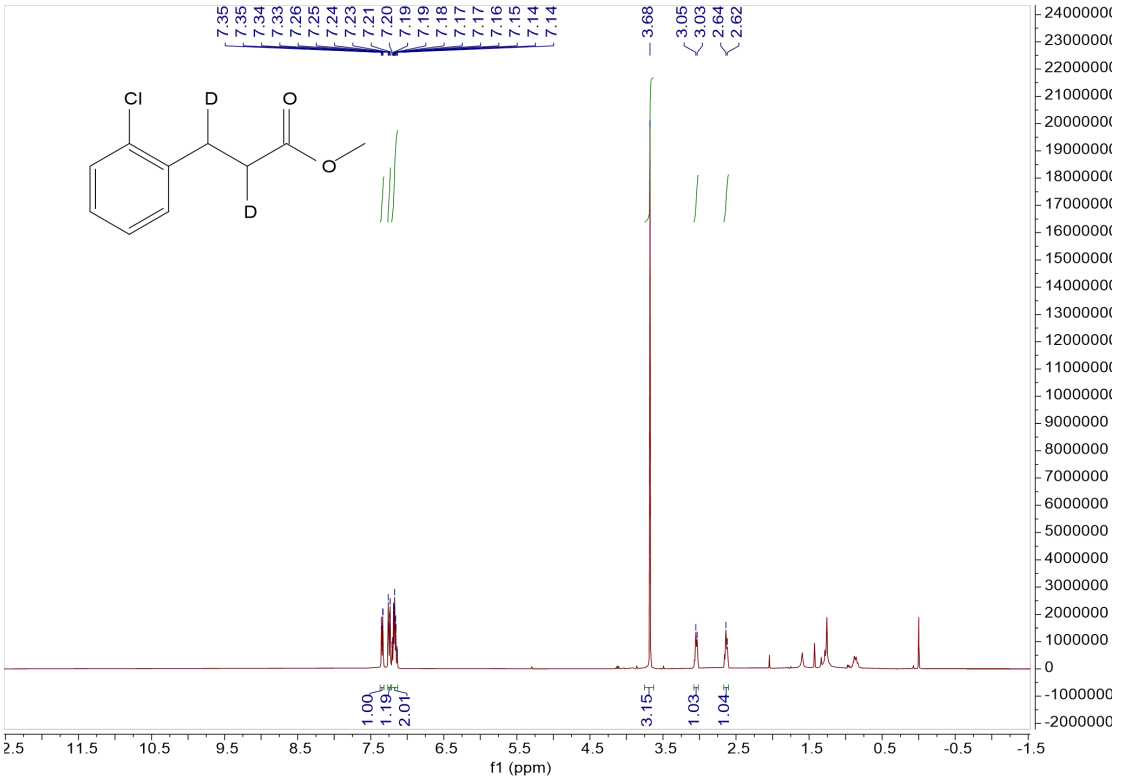
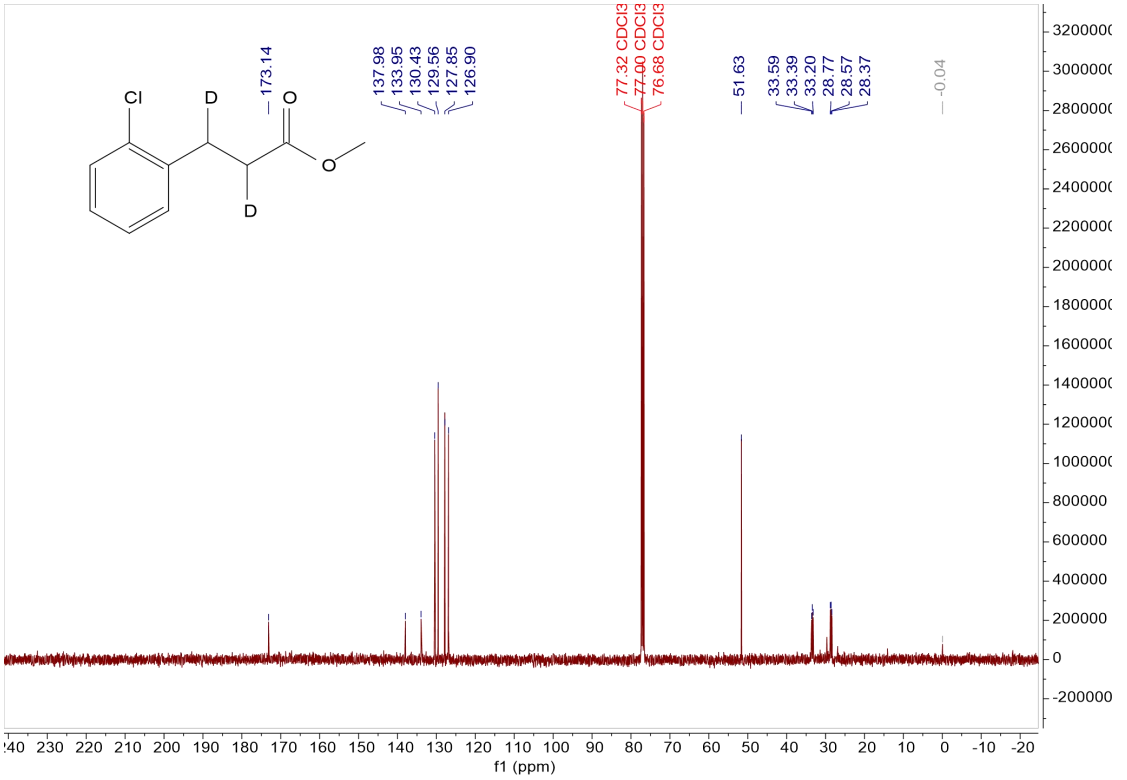
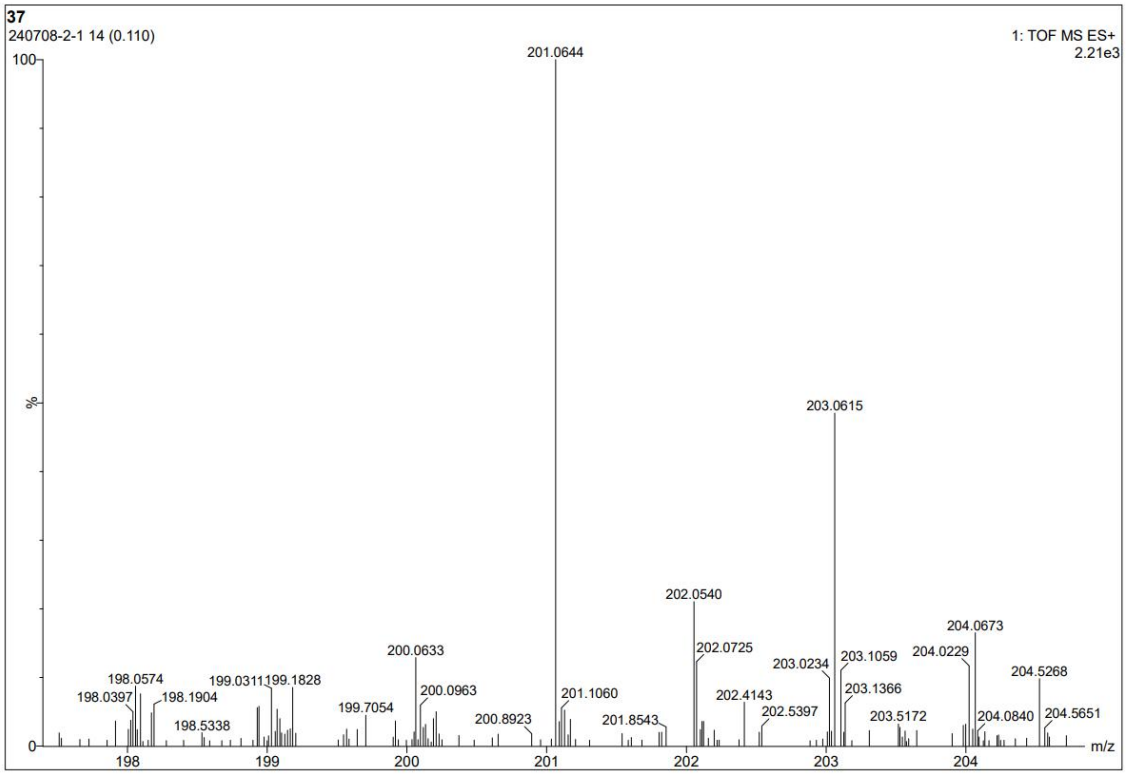
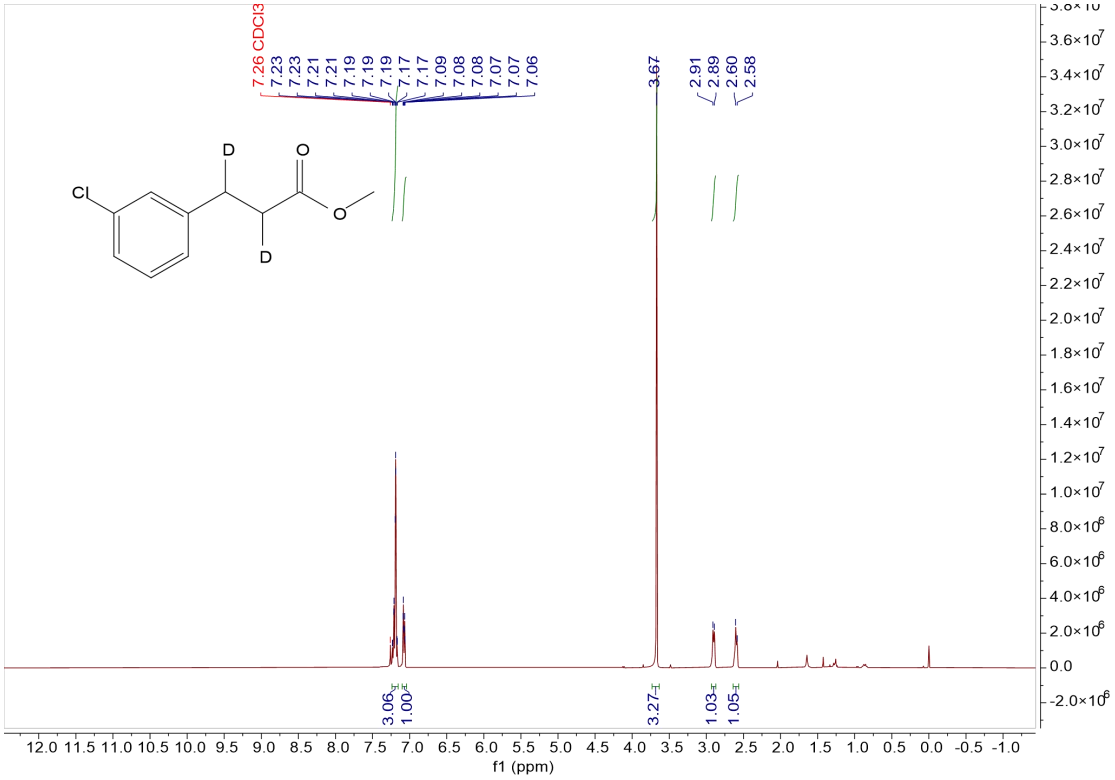






methyl 3-(3-chlorophenyl)propanoate-2,3-d_2 (2f)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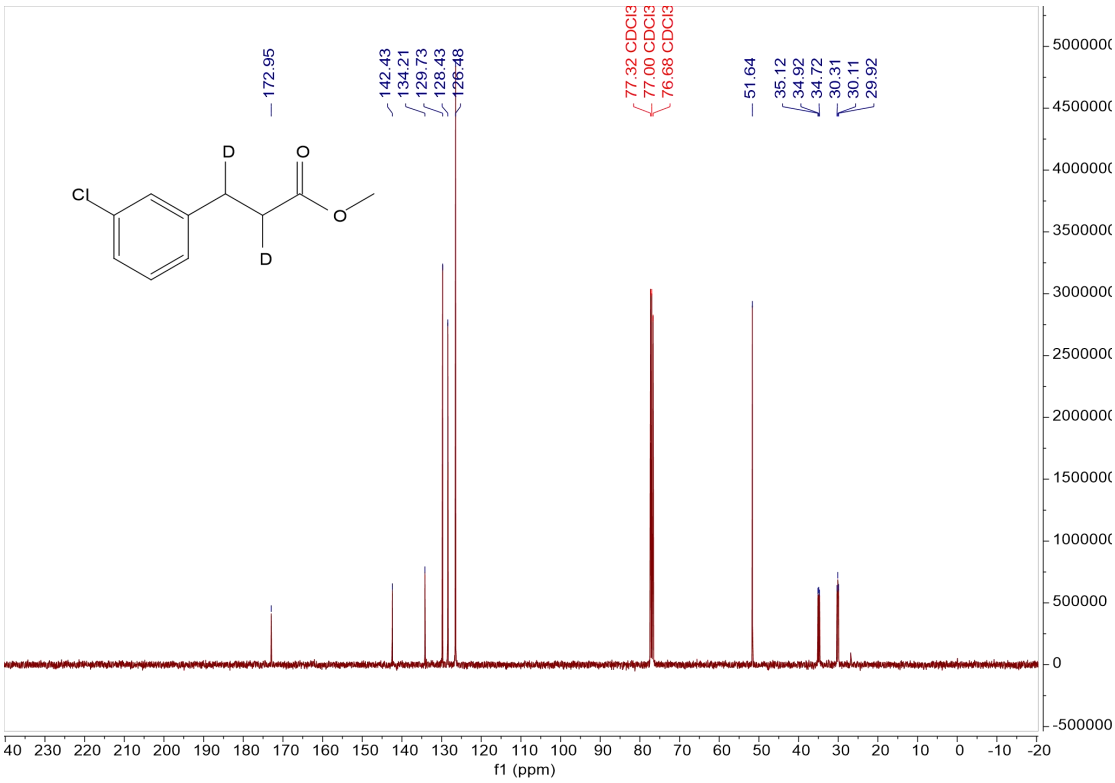
f1 (ppm)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30.31
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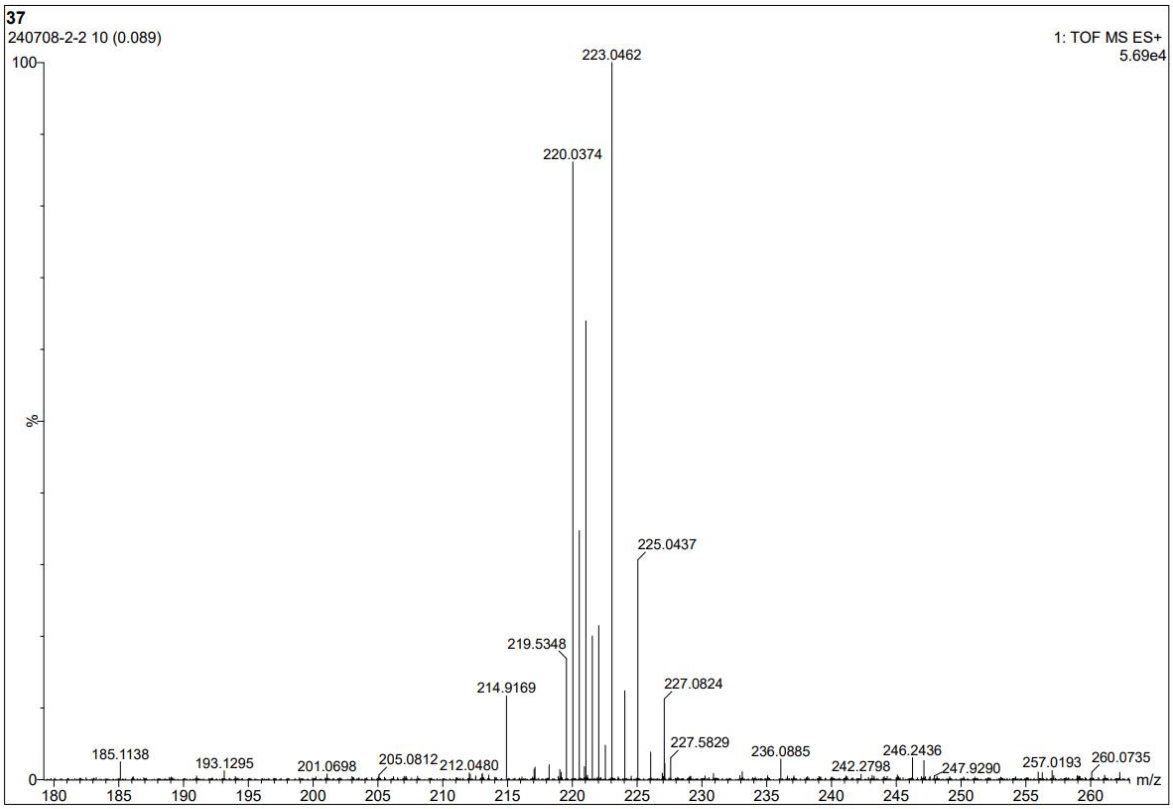
29.92
Cl
D
O
O
D
f1 (ppm)



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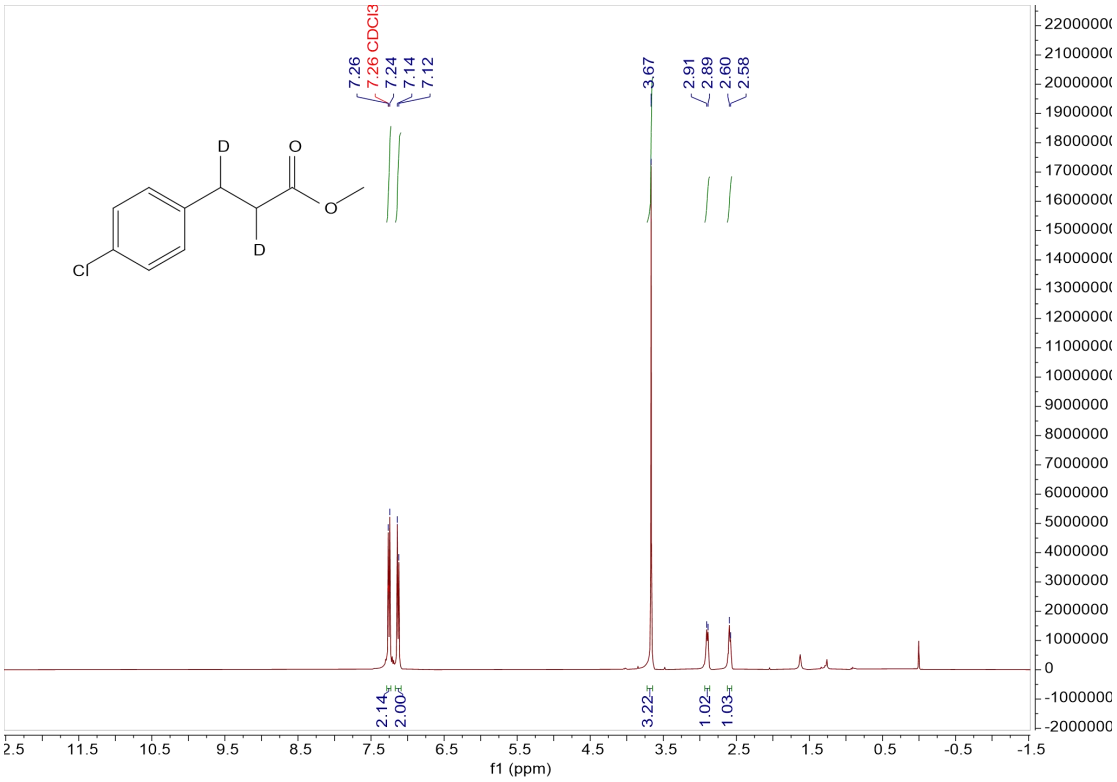

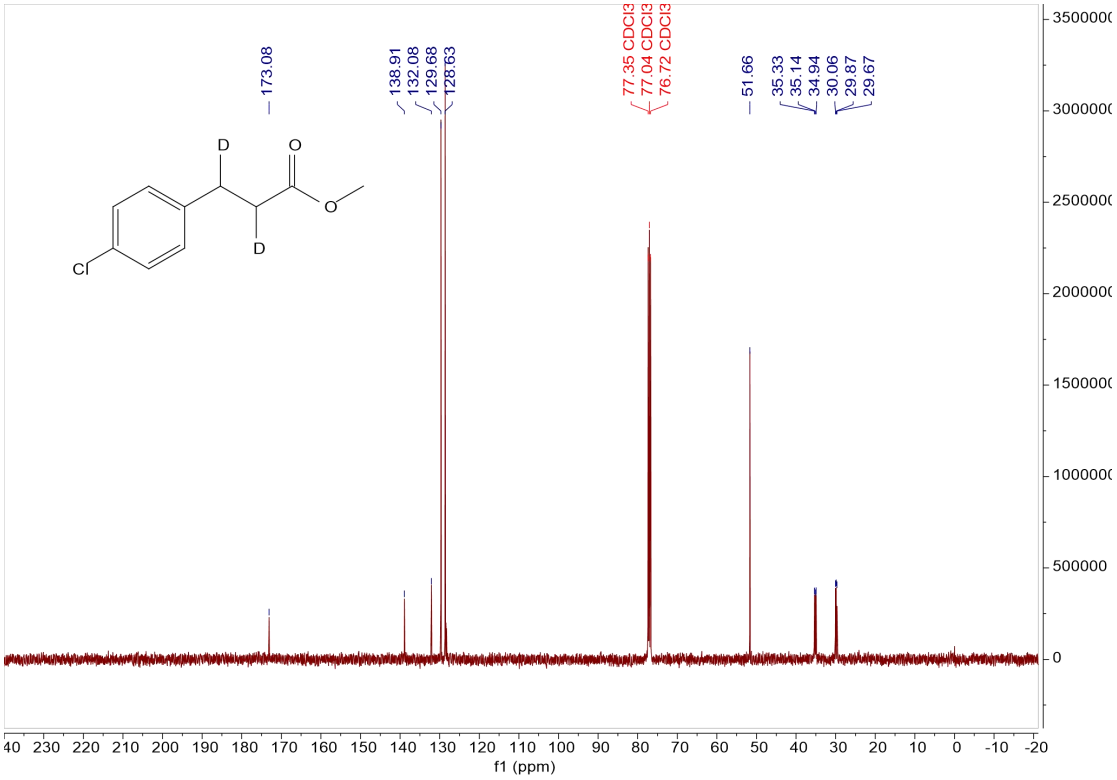

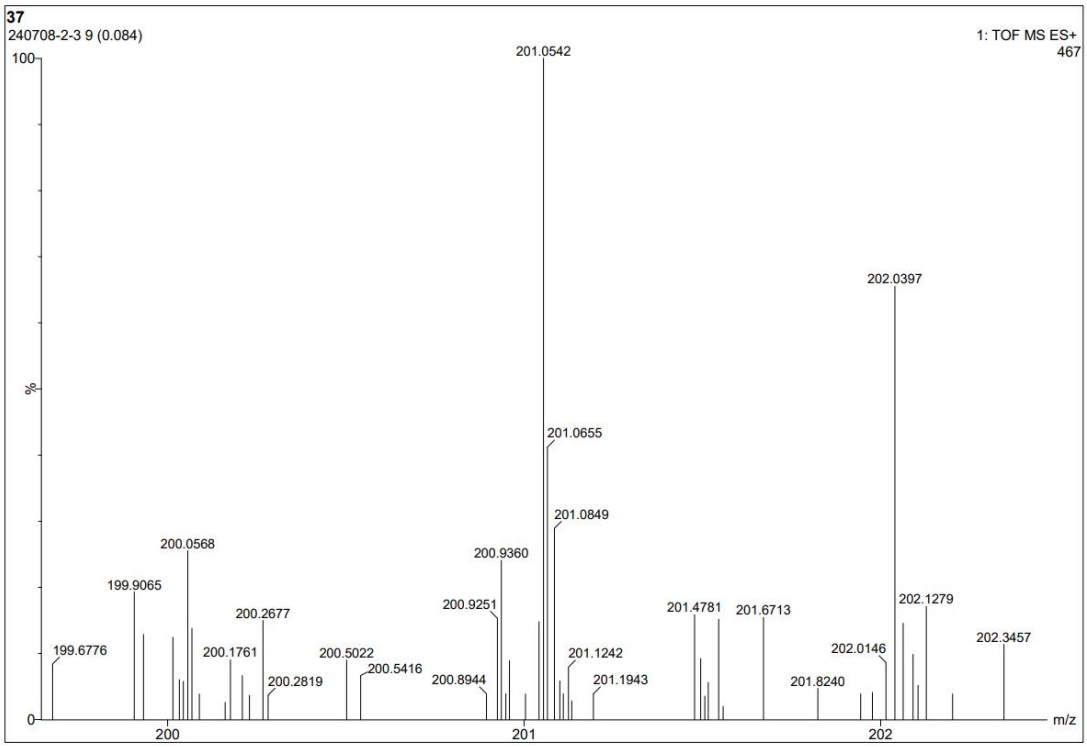

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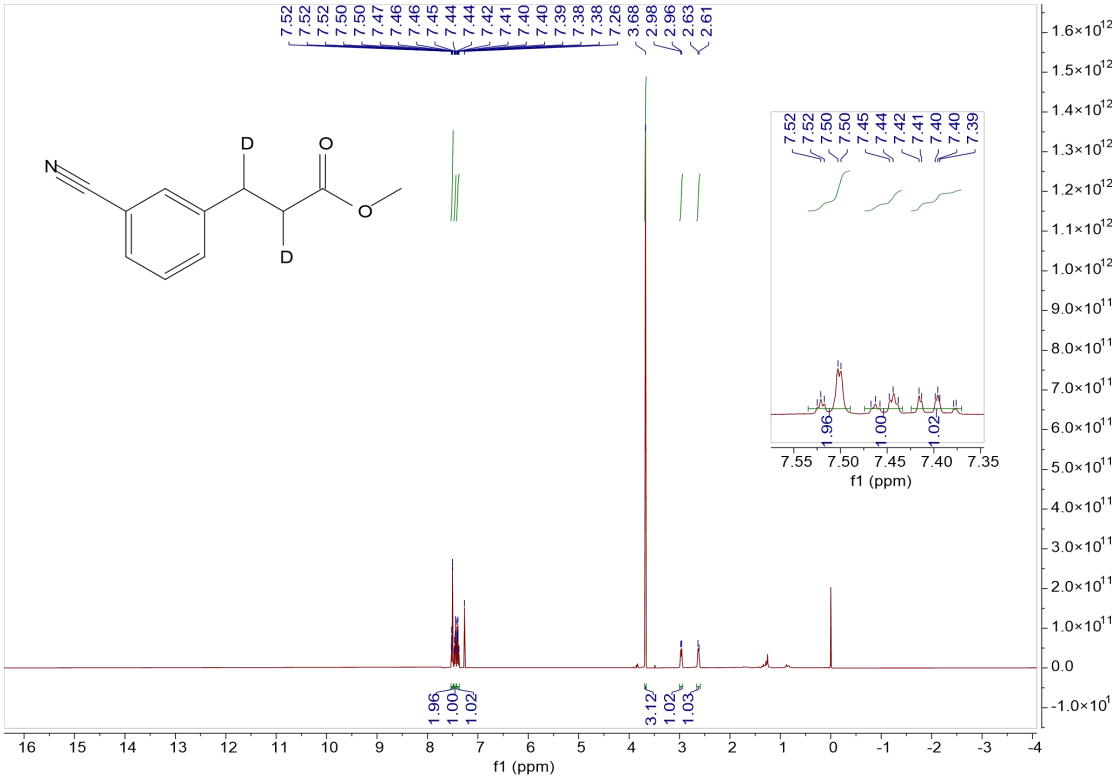
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7.40
7.39
7.38
7.38
7.26
3.68
2.98
2.96
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D
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O
D
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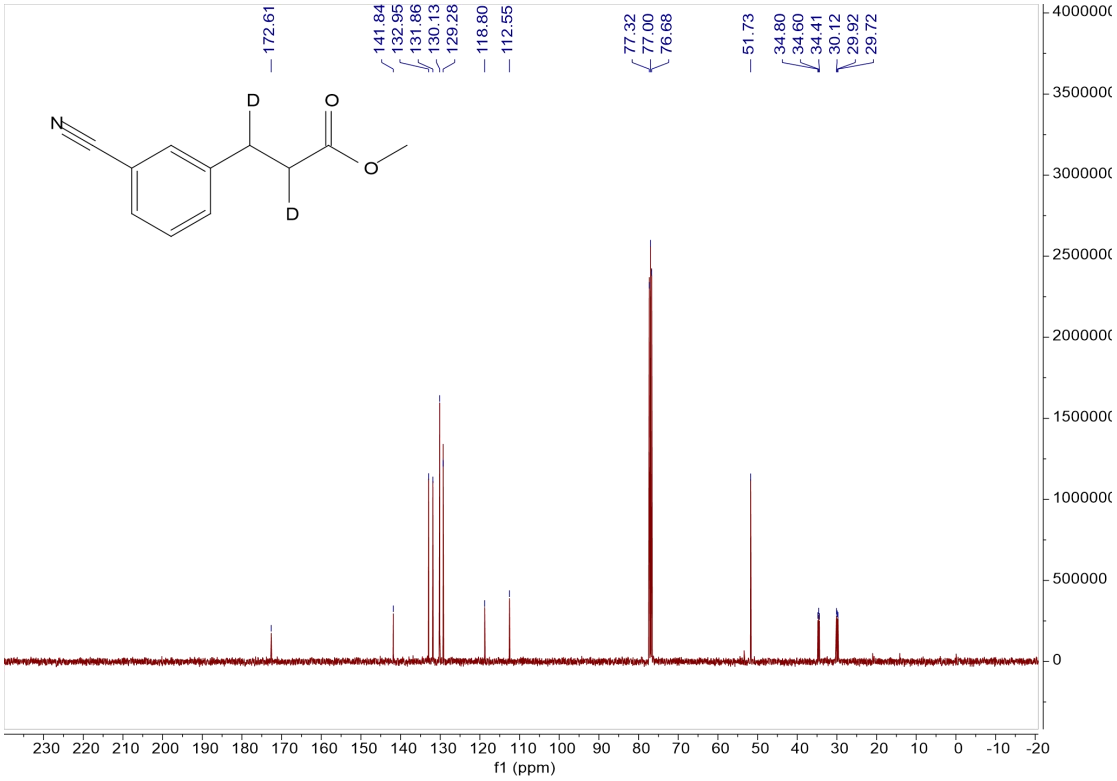
1.02
3.12
1.02
1.03
f1 (ppm)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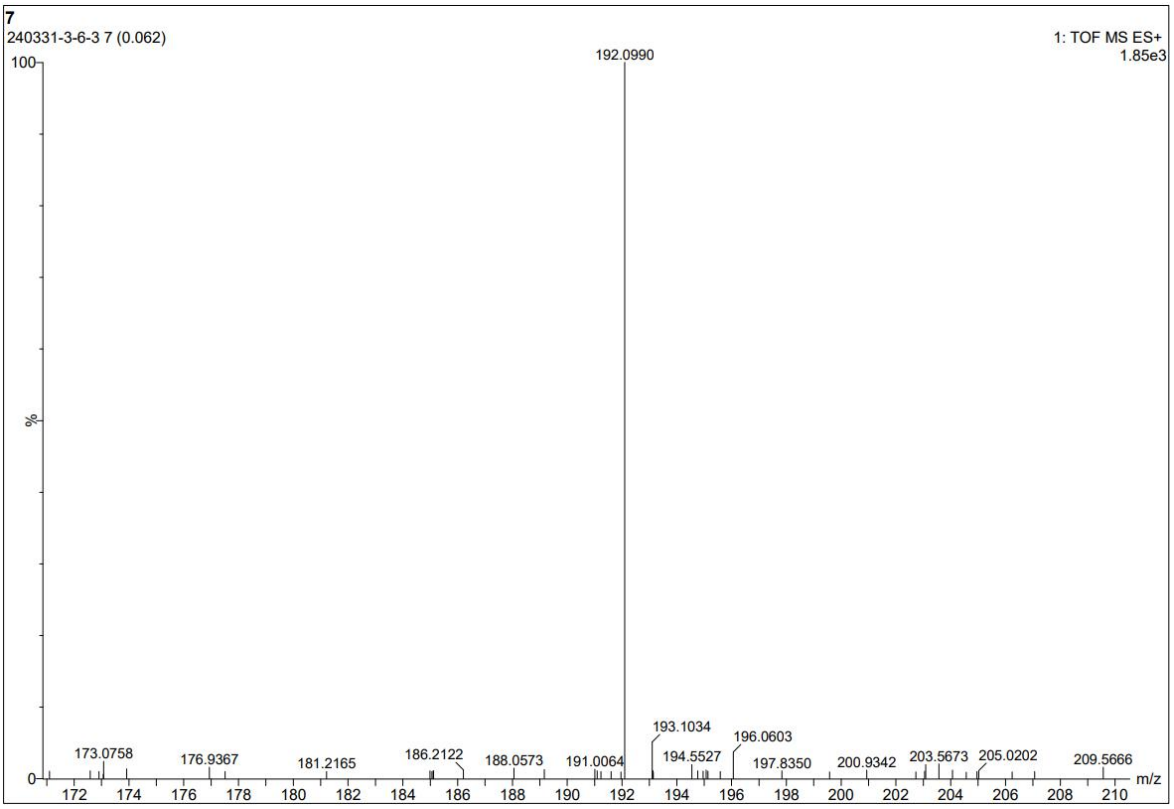
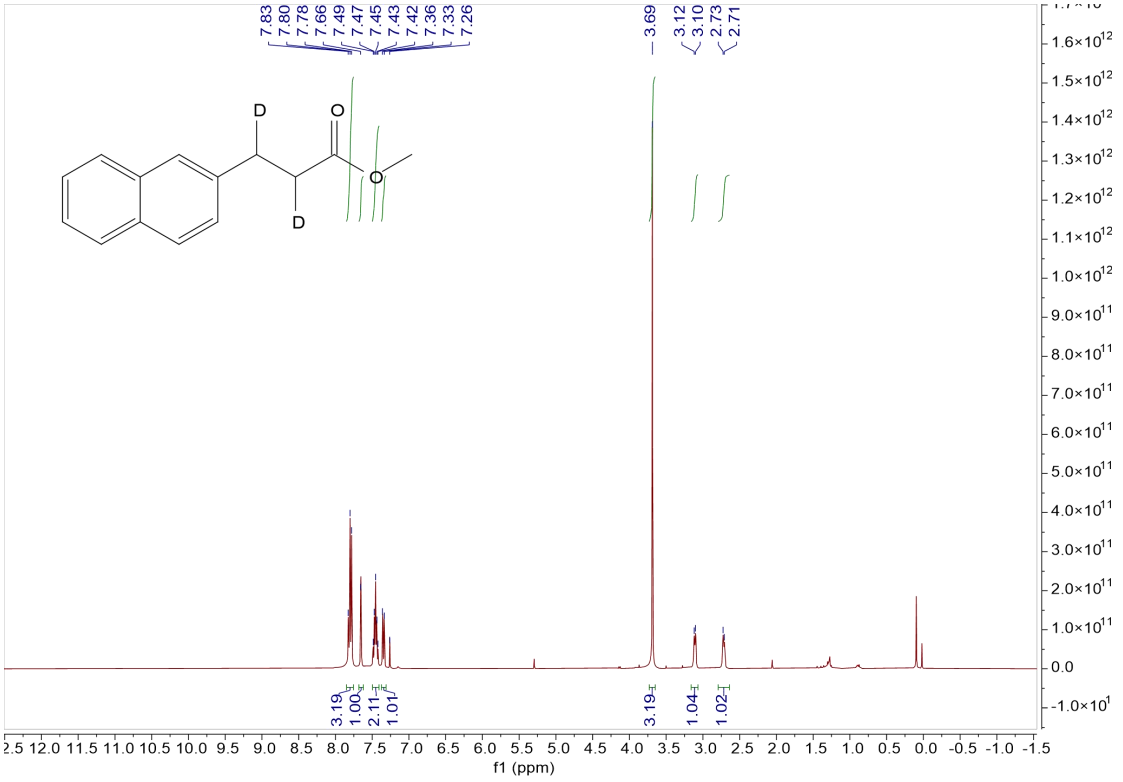
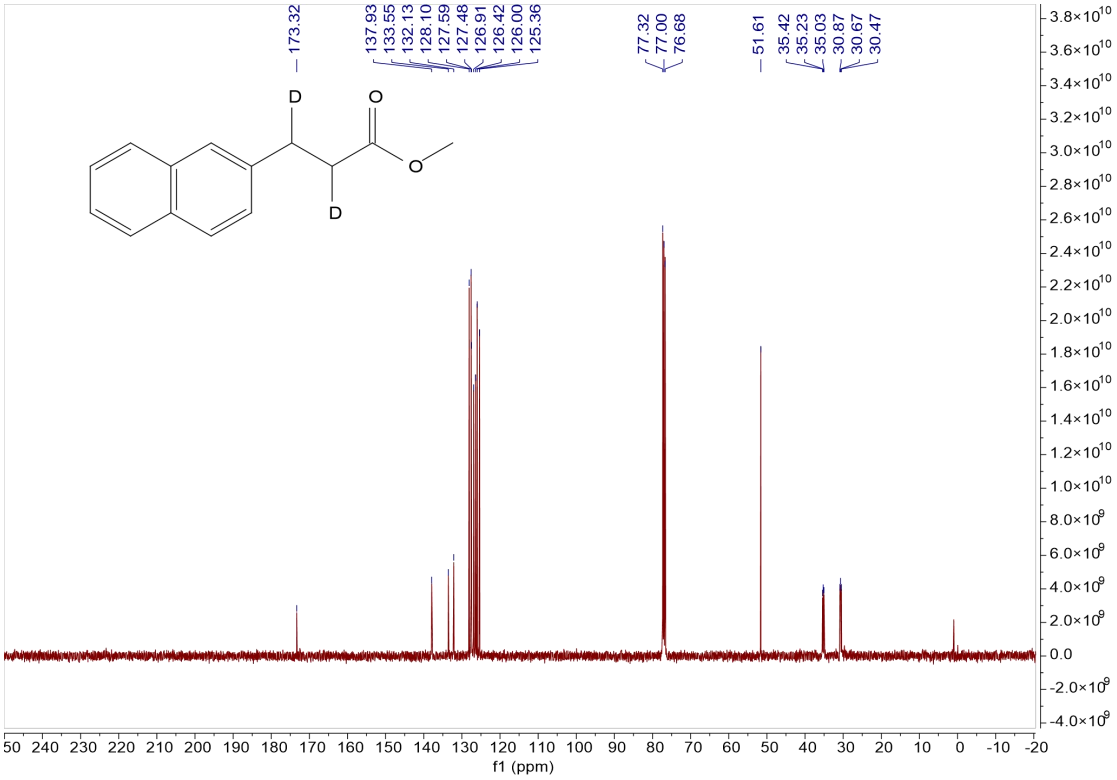
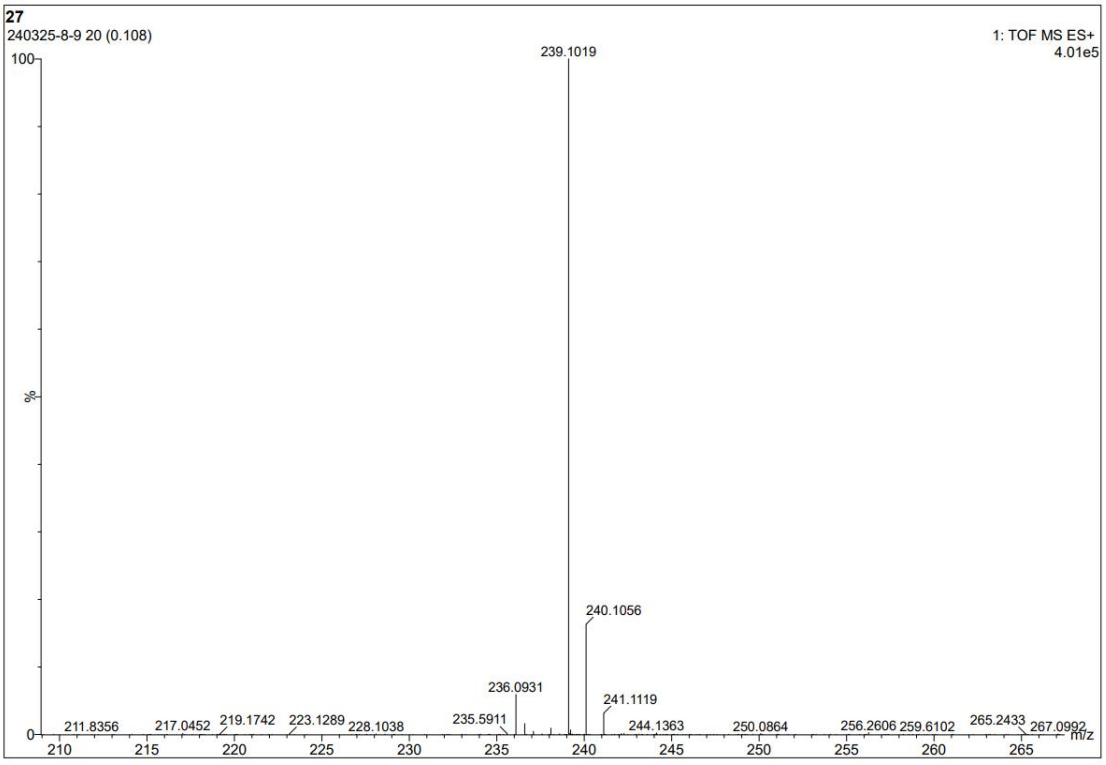
N
D
O
O
D
f1 (ppm)



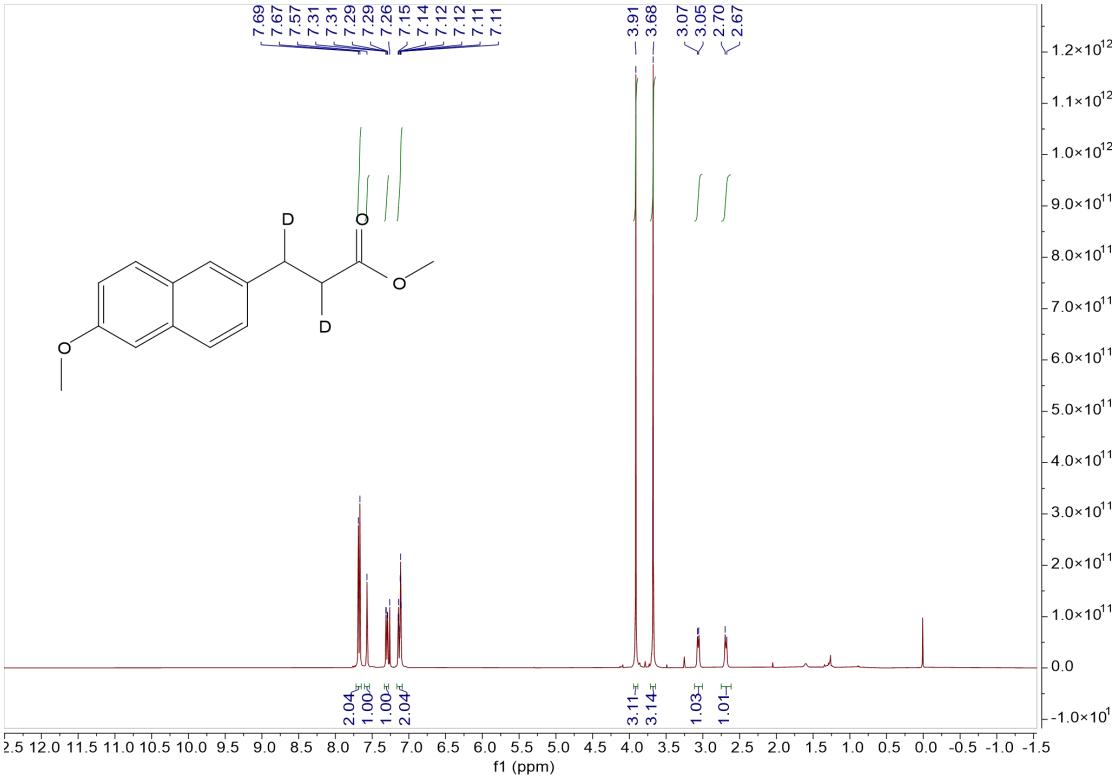
methyl 3-(naphthalen-2-yl)propanoate-2,3-*d*$_2$ (2i)

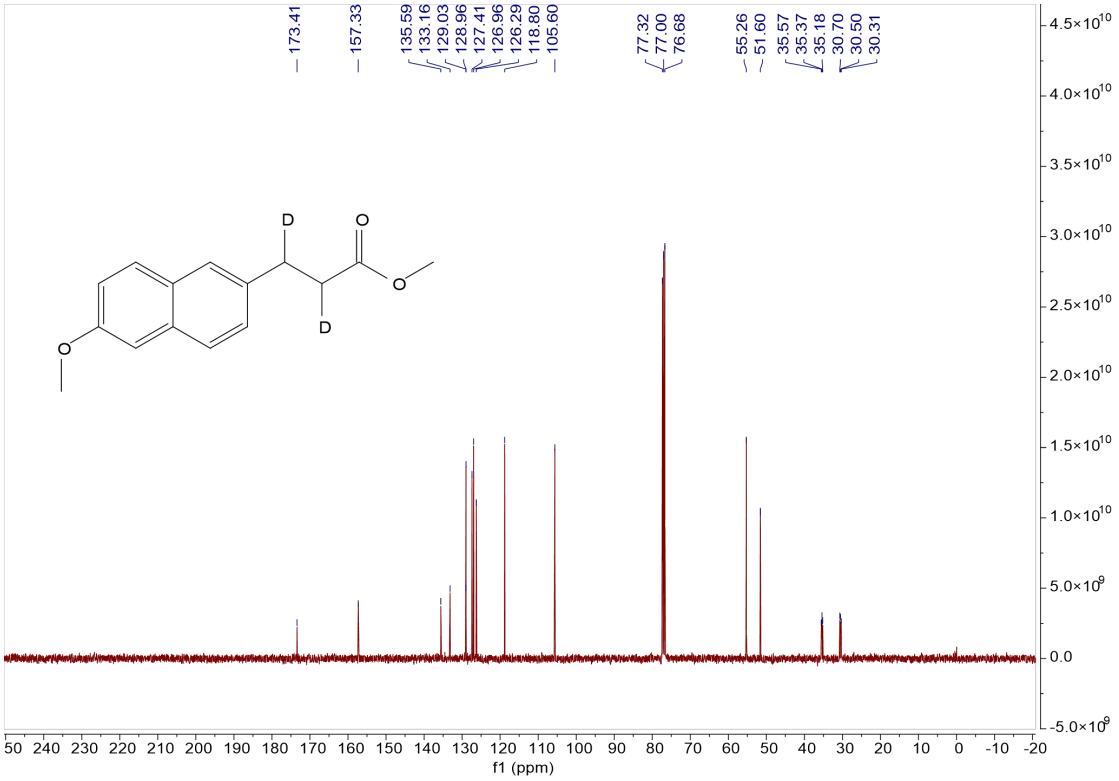


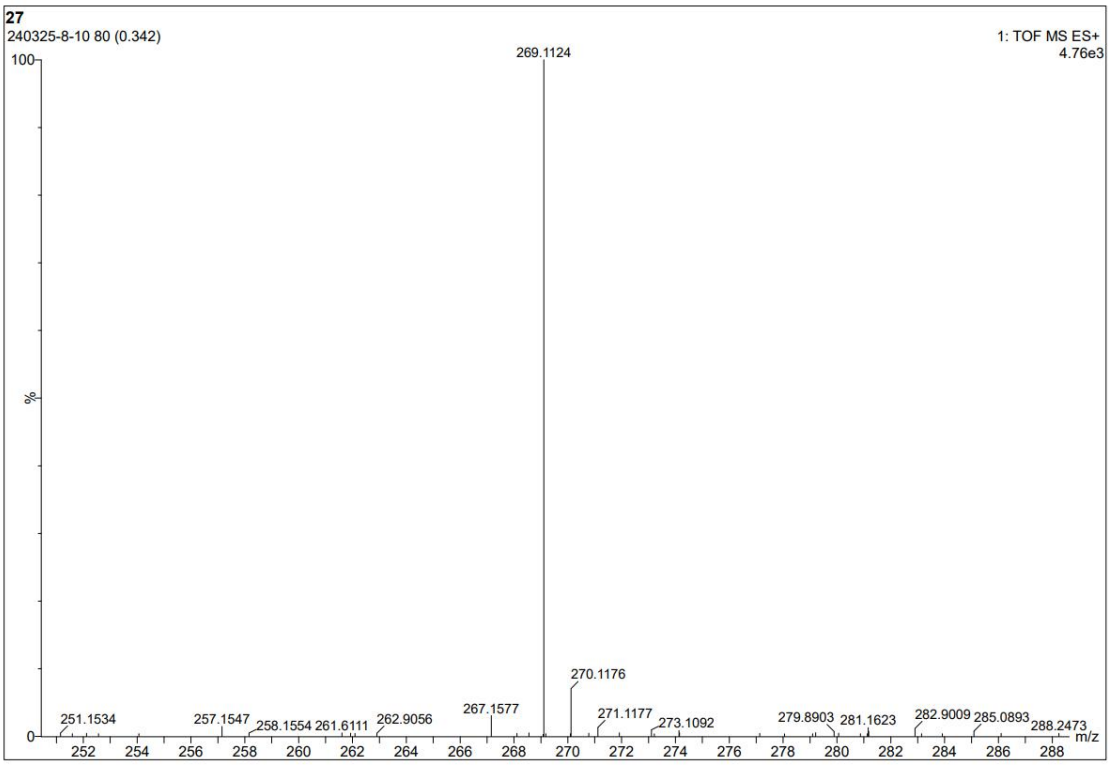




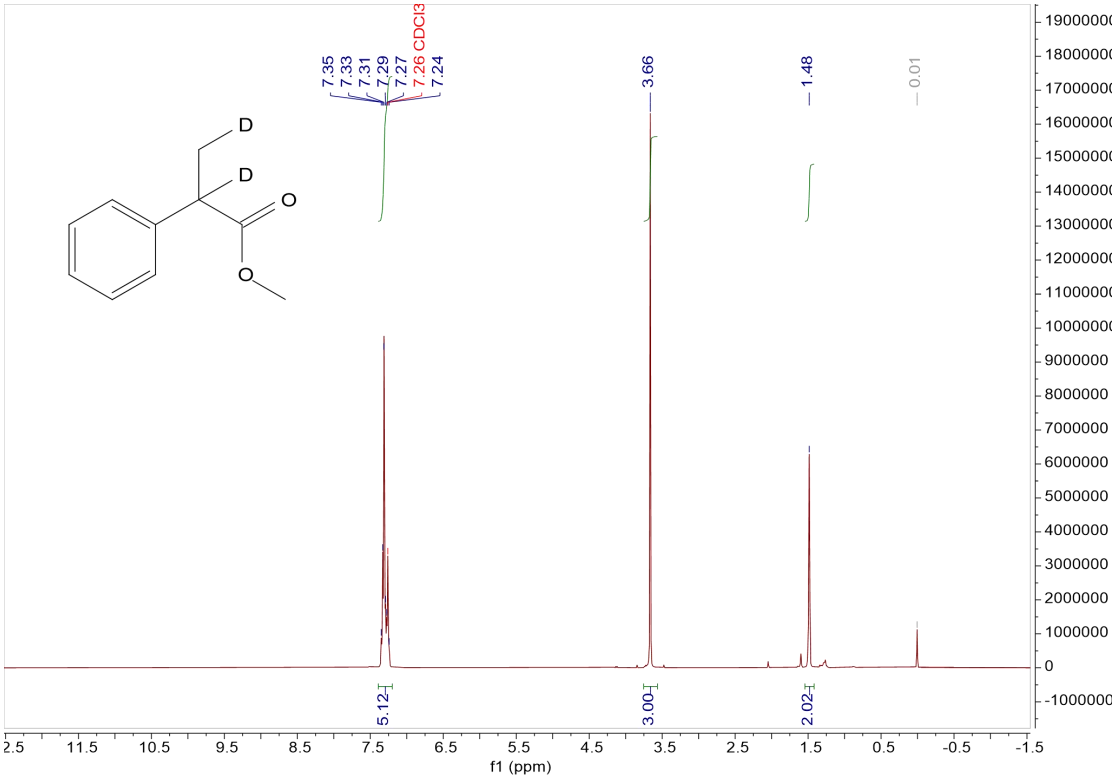
methyl 3-(6-methoxynaphthalen-2-yl)propanoate-2,3-d_2 (2j)

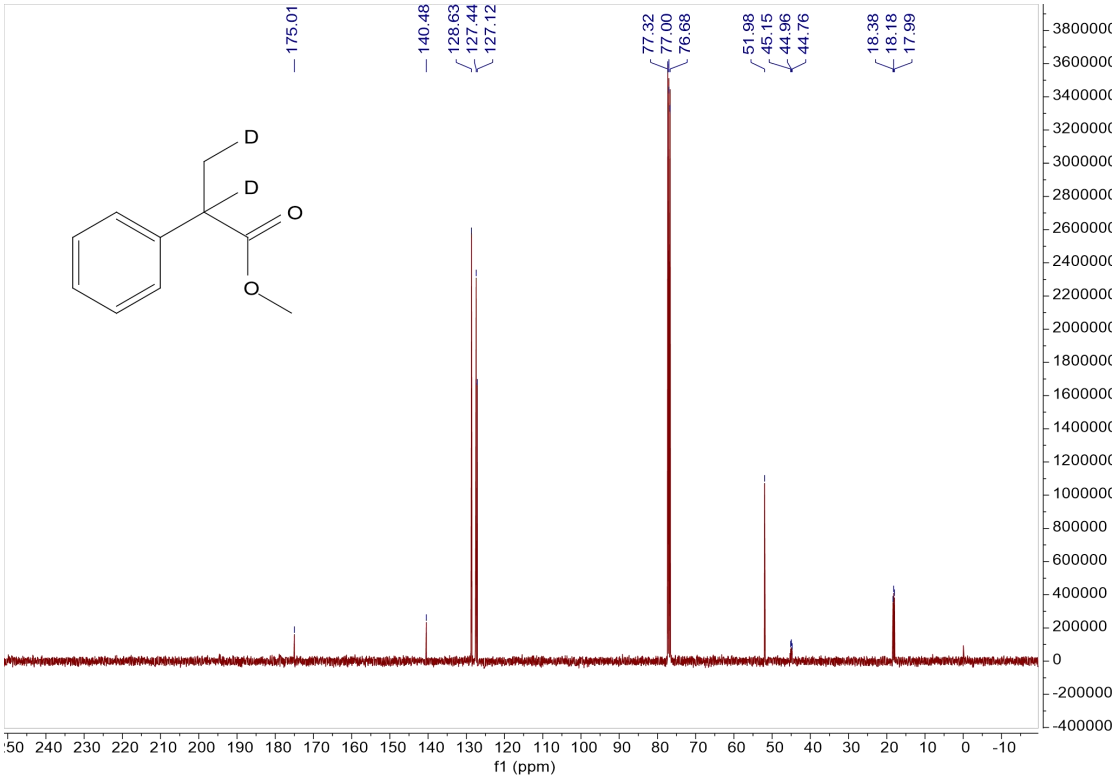

7.69
7.67
7.57
7.31
7.31
7.29
7.29
7.26
7.15
7.14
7.12
7.12
7.11
7.11
3.91
3.68
3.07
3.05
2.70
2.67
D
O
O
D
O
2.04
1.00
1.00
2.04
3.11
3.14
1.03
1.01
f1 (ppm)

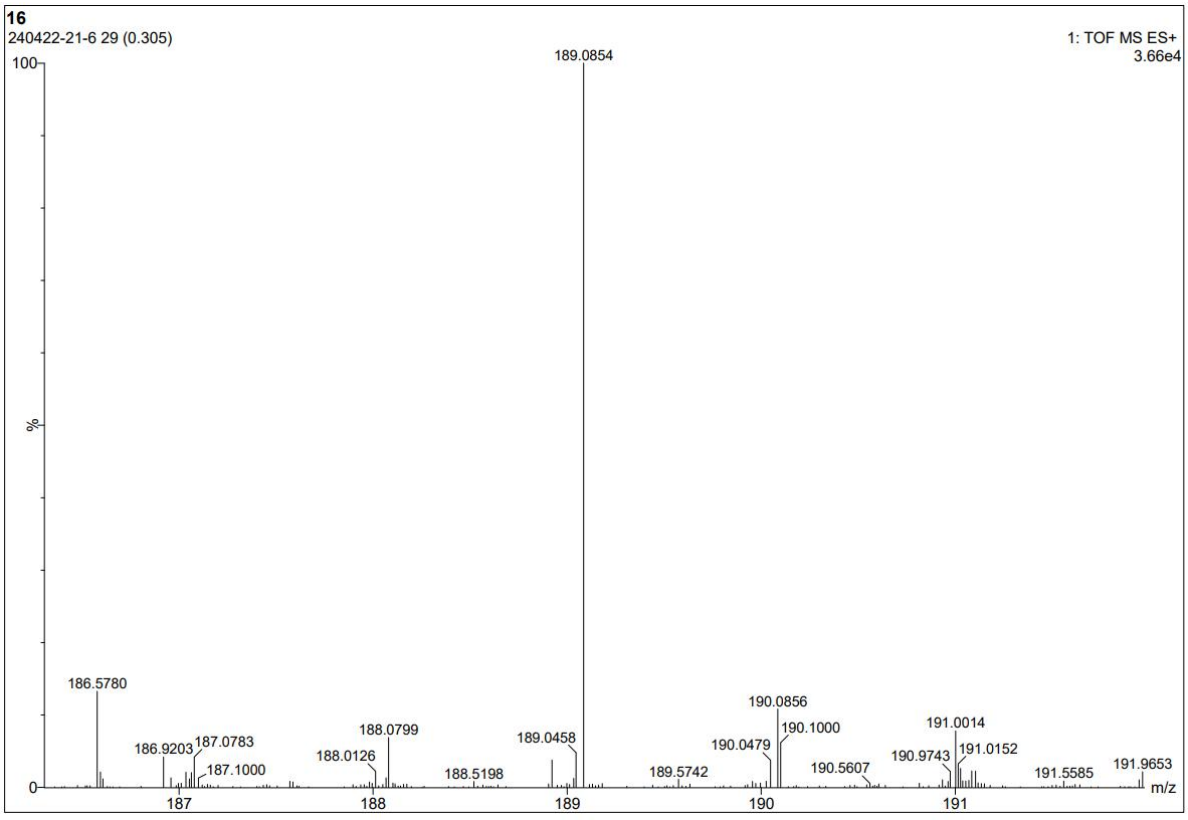

173.41
157.33
135.59
133.16
129.03
128.96
127.41
126.96
126.29
118.80
105.60
77.32
77.00
76.68
55.26
51.60
35.57
35.37
35.18
30.70
30.50
30.31
D
O
O
D
O
f1 (ppm)



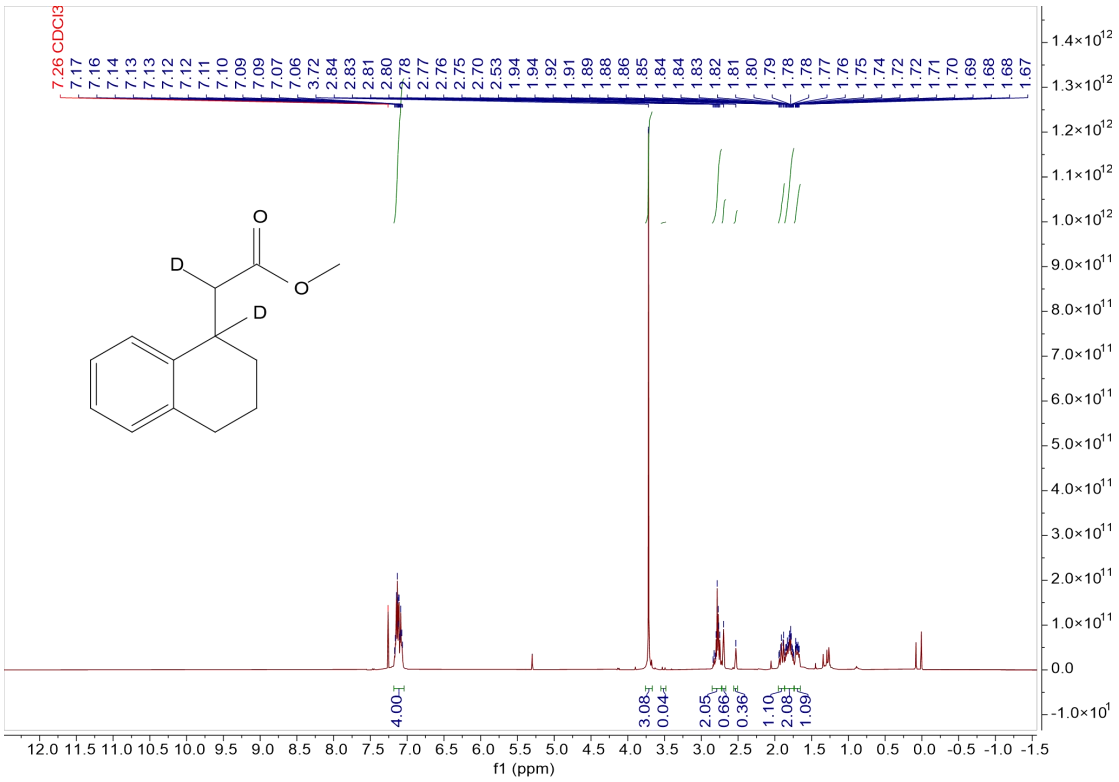
methyl 2-phenylpropanoate-2,3-d_2 (2k)

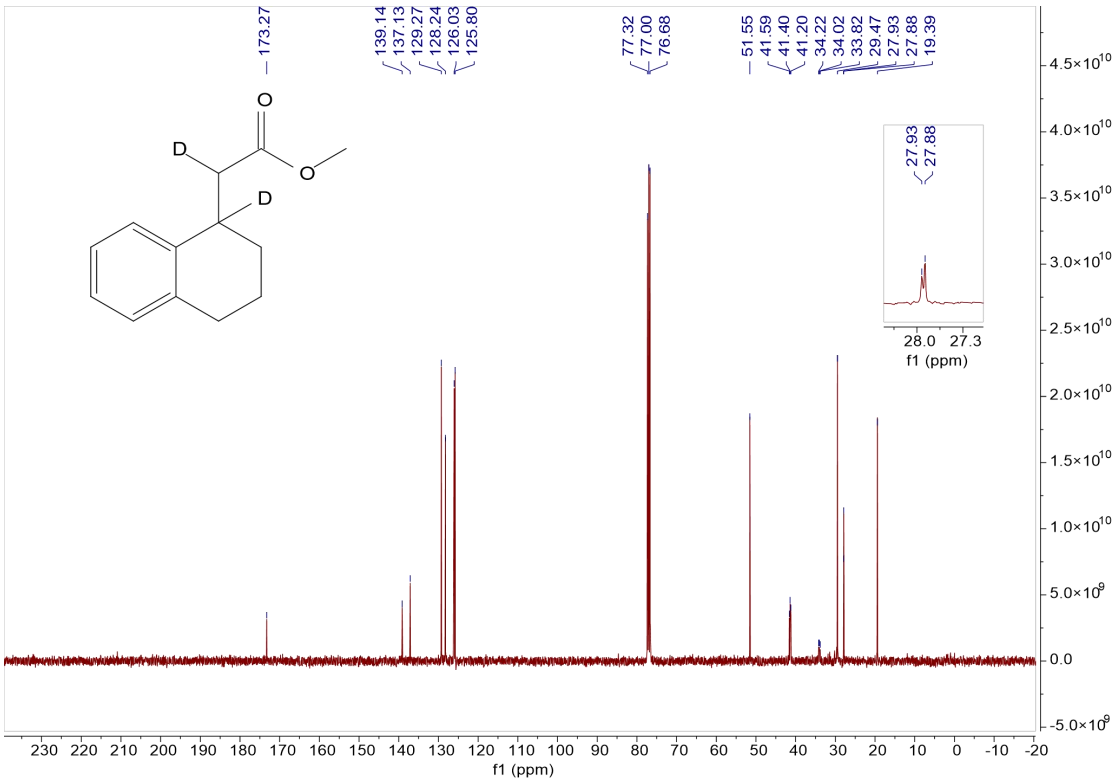


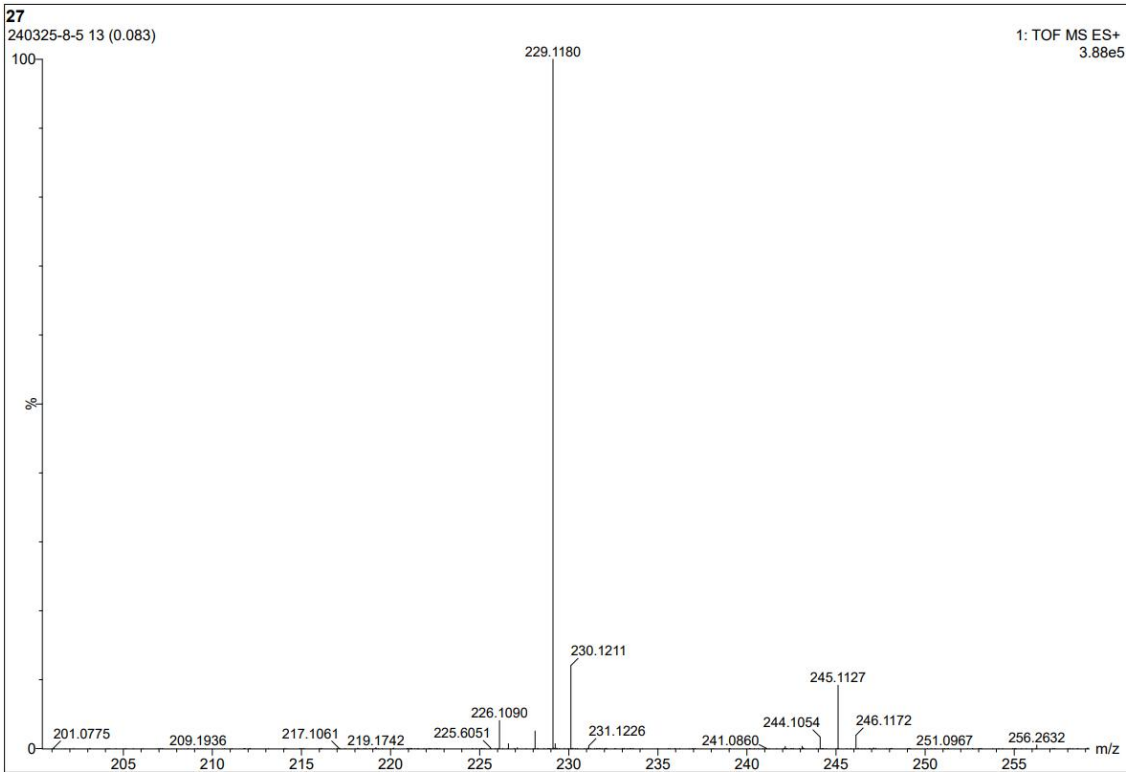




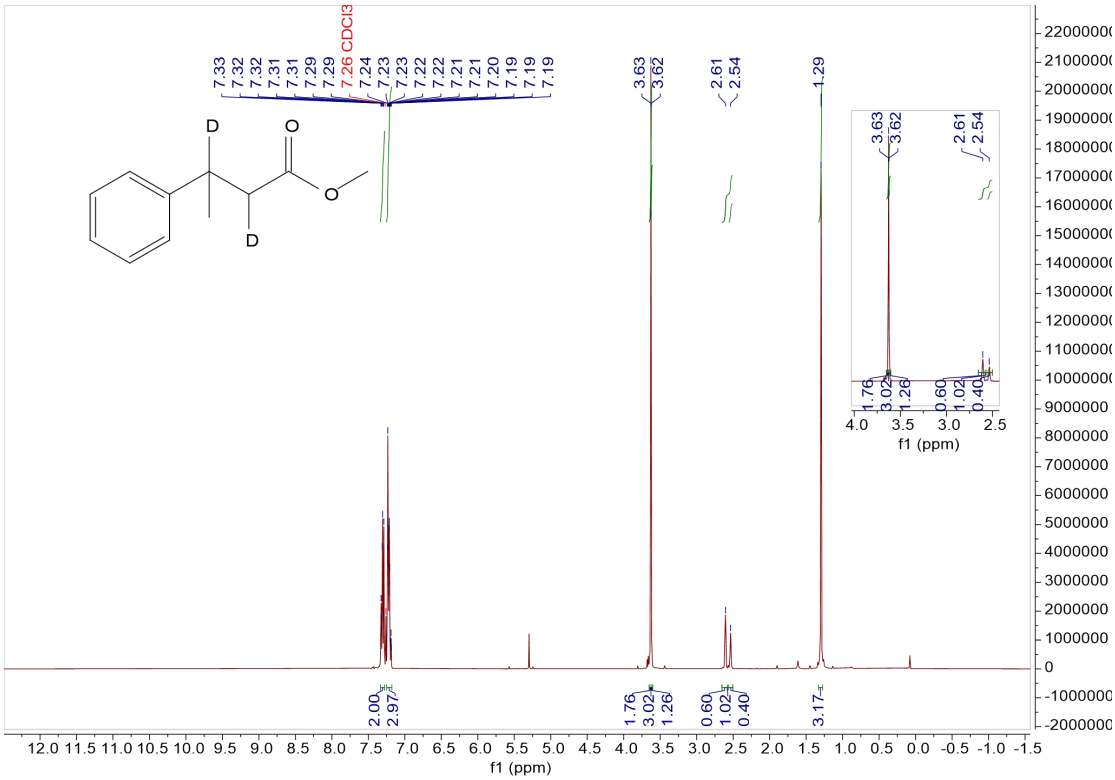
methyl 2-(1,2,3,4-tetrahydronaphthalen-1-yl-1-*d*)acetate-2-*d* (2l)

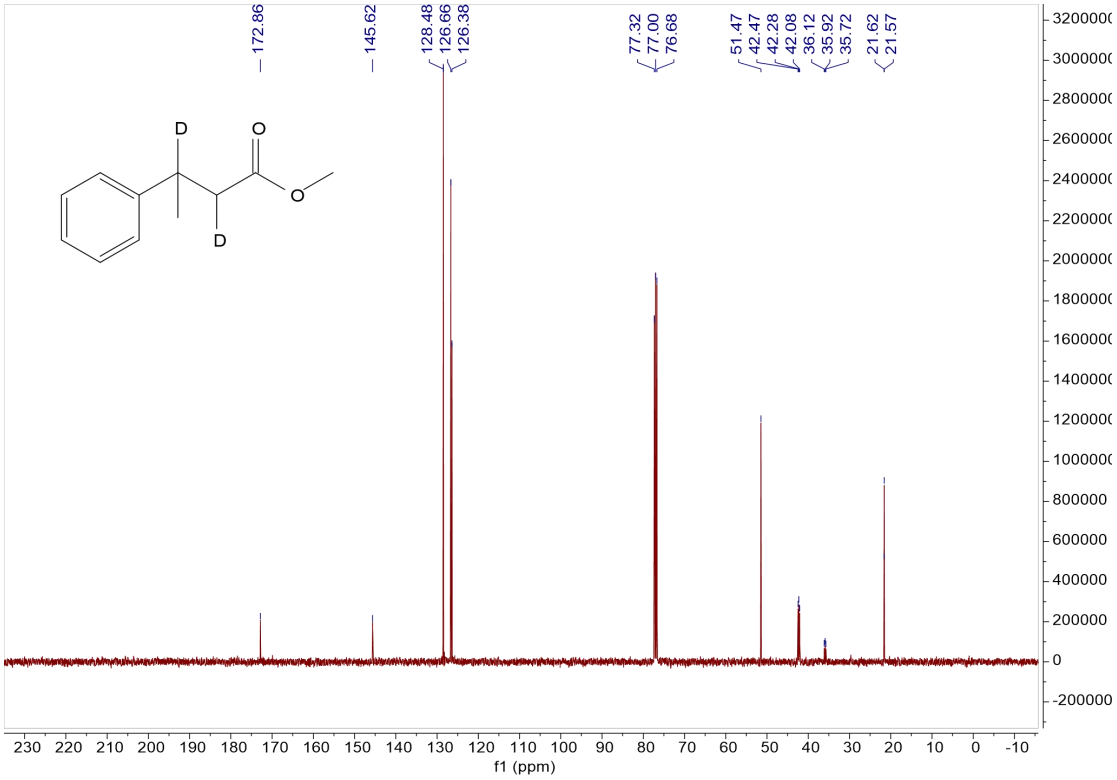

7.26 CDCl3
7.17 7.16 7.14 7.13 7.13 7.12 7.12 7.11 7.10 7.09 7.09 7.07 7.06 3.72 2.84 2.83 2.81 2.80 2.78 2.77 2.76 2.75 2.70 2.53 1.94 1.94 1.92 1.91 1.89 1.88 1.86 1.85 1.84 1.84 1.83 1.82 1.81 1.80 1.79 1.78 1.78 1.77 1.76 1.75 1.74 1.72 1.72 1.71 1.70 1.69 1.68 1.68 1.67
O
D
O
D
4.00
3.08
0.04
2.05
0.66
0.36
1.10
2.08
1.09
f1 (ppm)

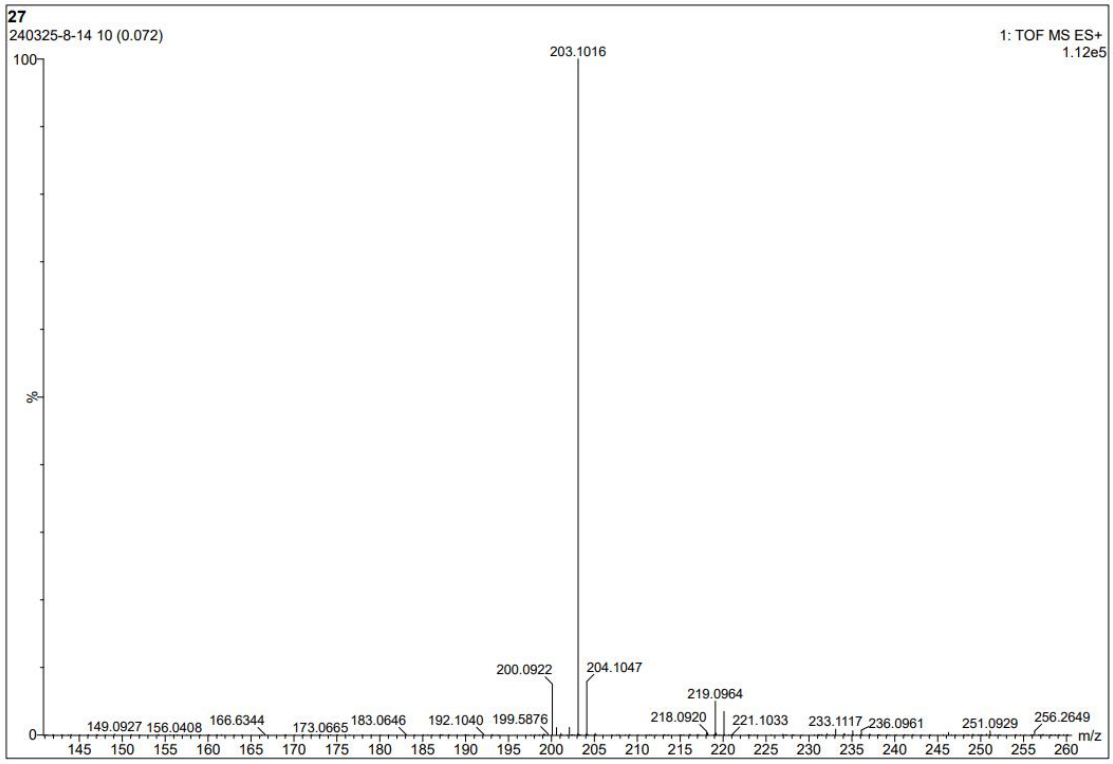

173.27
139.14 137.13 129.27 128.24 126.03 125.80
77.32 77.00 76.68
51.55 41.59 41.40 41.20 34.22 34.02 33.82 29.47 27.93 27.88 19.39
O
D
O
D
27.93
27.88
28.0 27.3
f1 (ppm)
f1 (ppm)



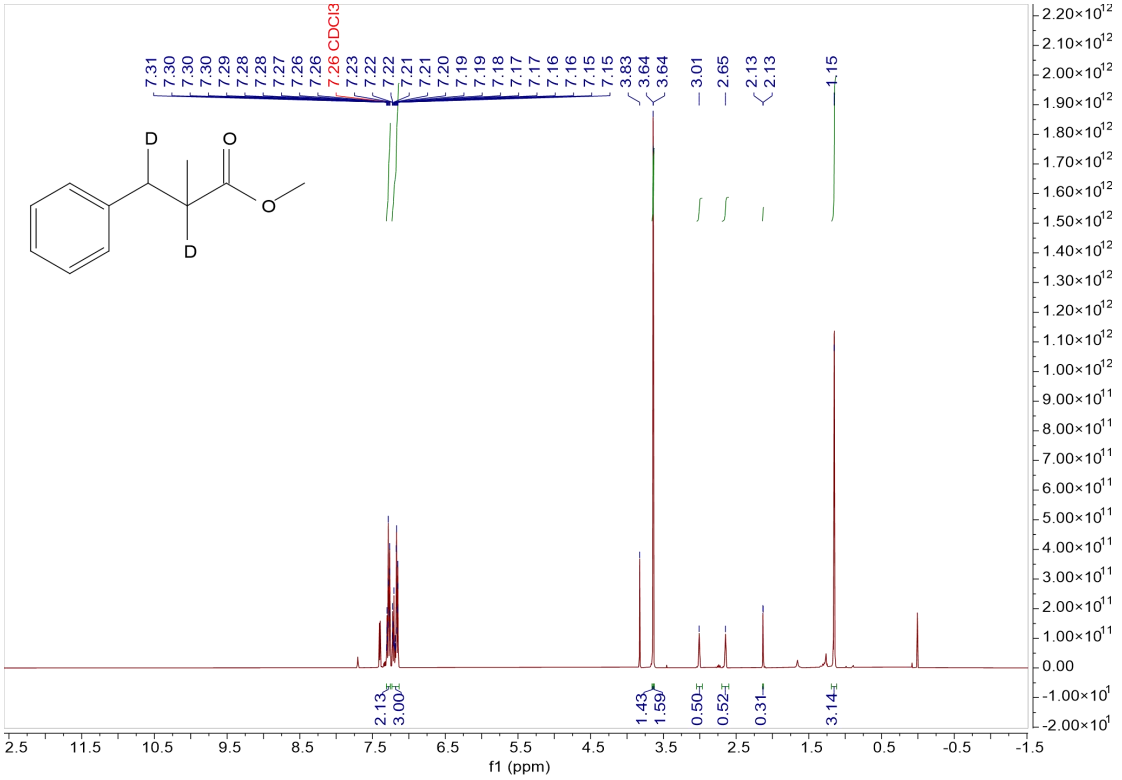
methyl 3-phenylbutanoate-2,3-d_2 (2m)

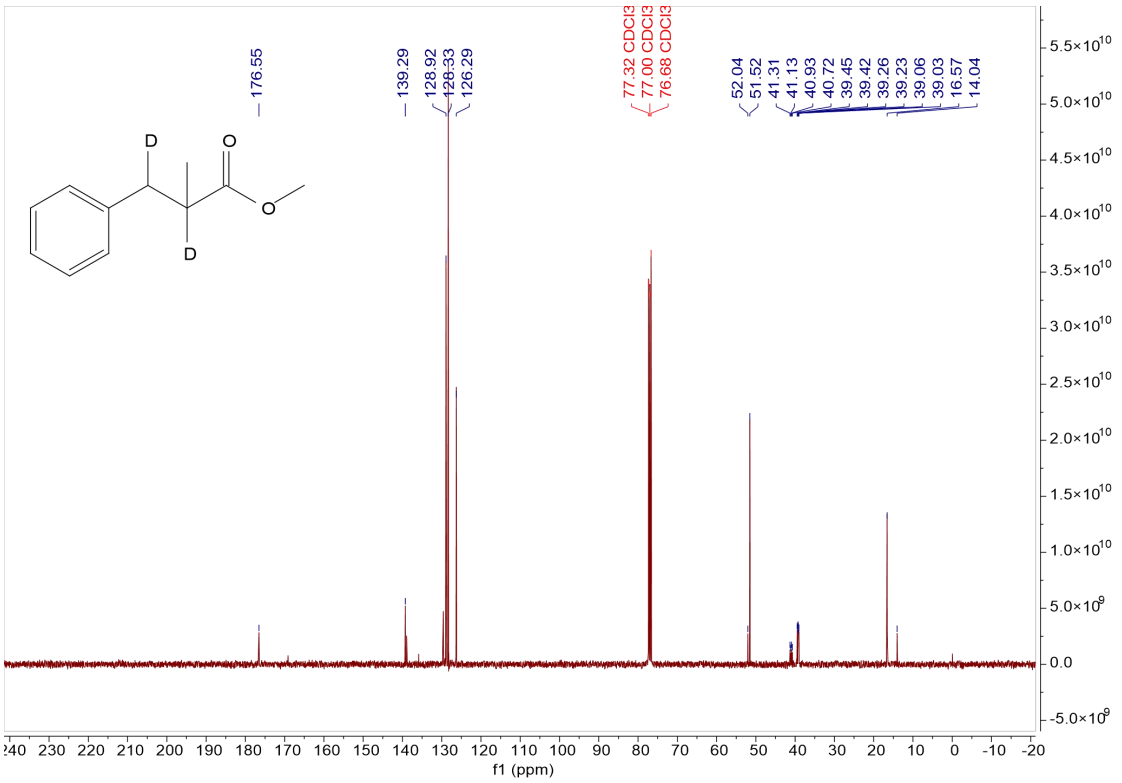


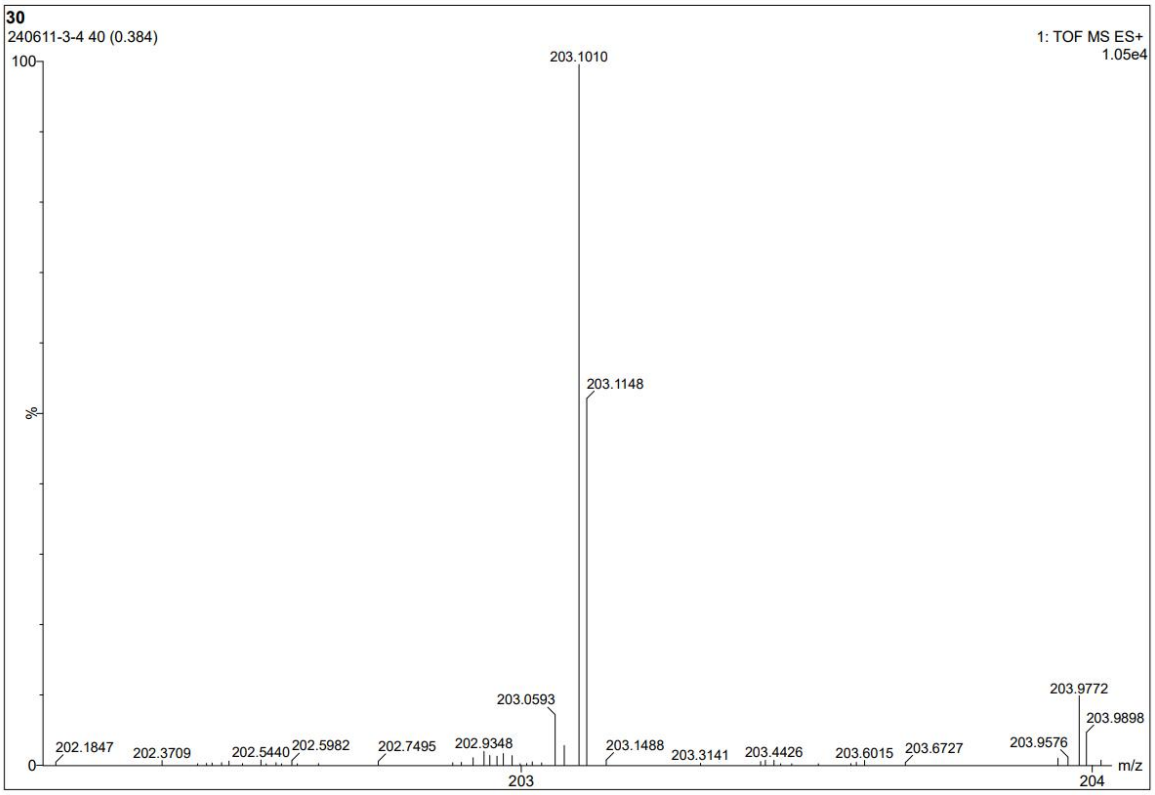




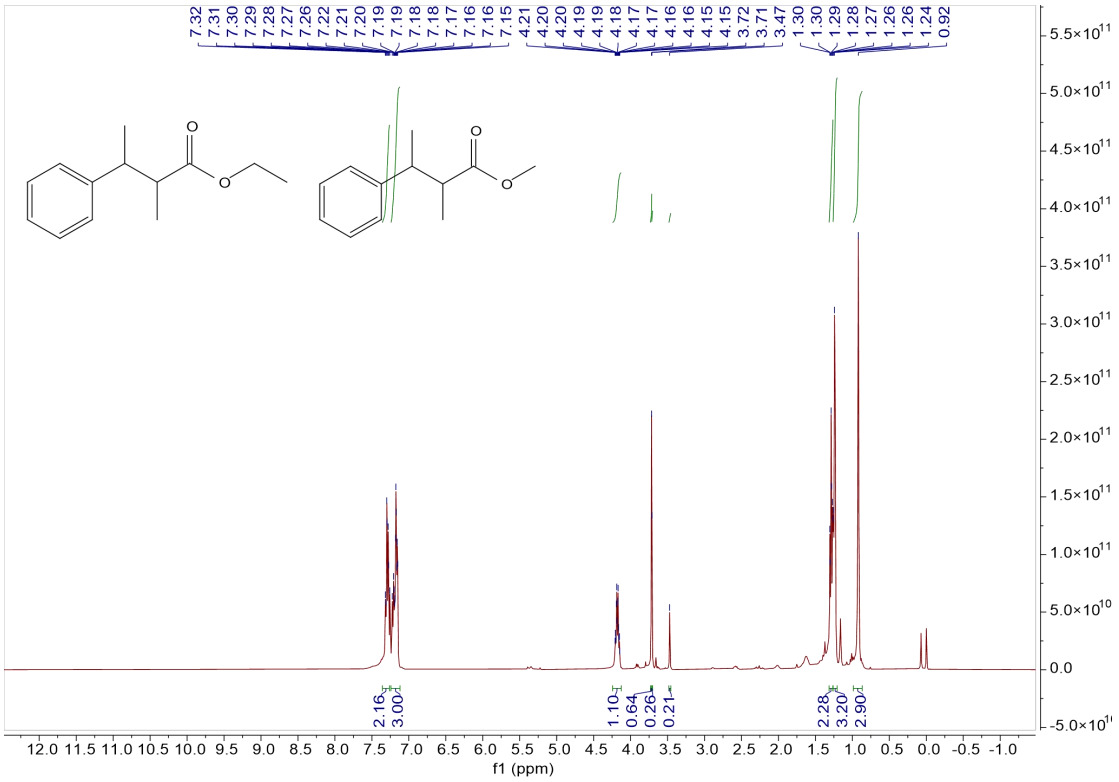
methyl 2-methyl-3-phenylpropanoate-2,3-d_2 (2n)

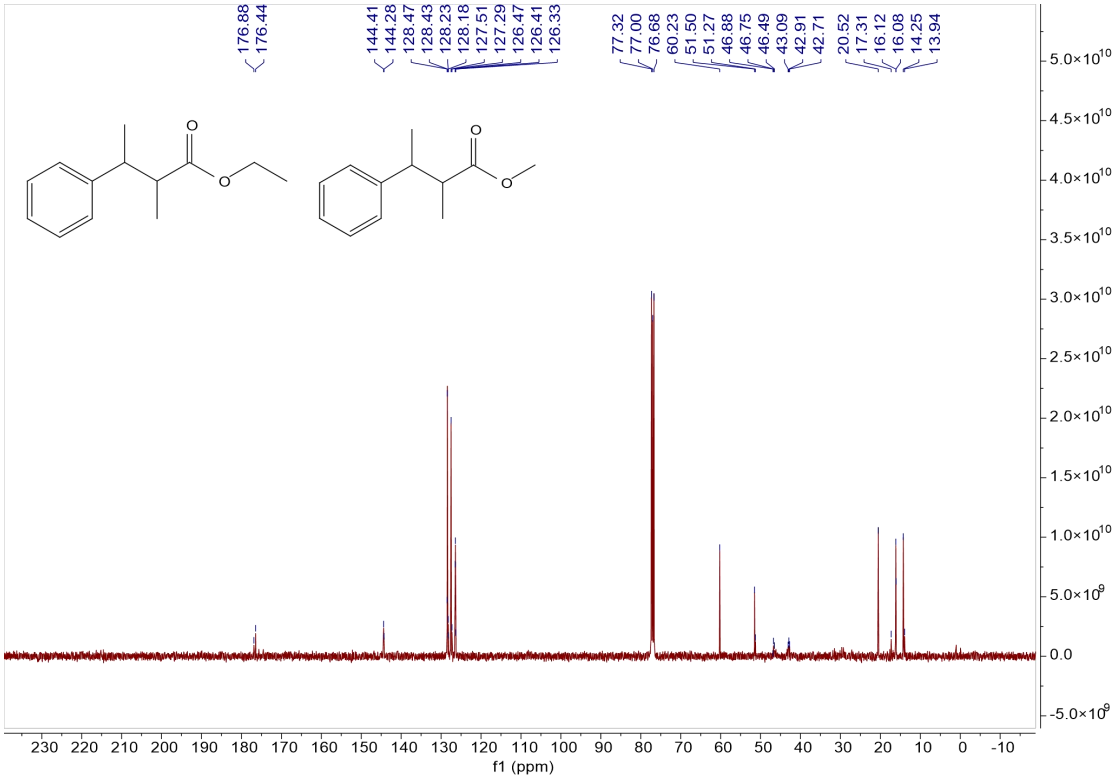

7.31
7.30
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.26 CDCl3
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
3.83
3.64
3.64
3.01
2.65
2.13
2.13
1.15
D
O
O
D
2.13
3.00
1.43
1.59
0.50
0.52
0.31
3.14
f1 (ppm)


176.55
139.29
128.92
128.33
126.29
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
52.04
51.52
41.31
41.13
40.93
40.72
39.45
39.42
39.26
39.23
39.06
39.03
16.57
14.04
D
O
O
D
f1 (ppm)

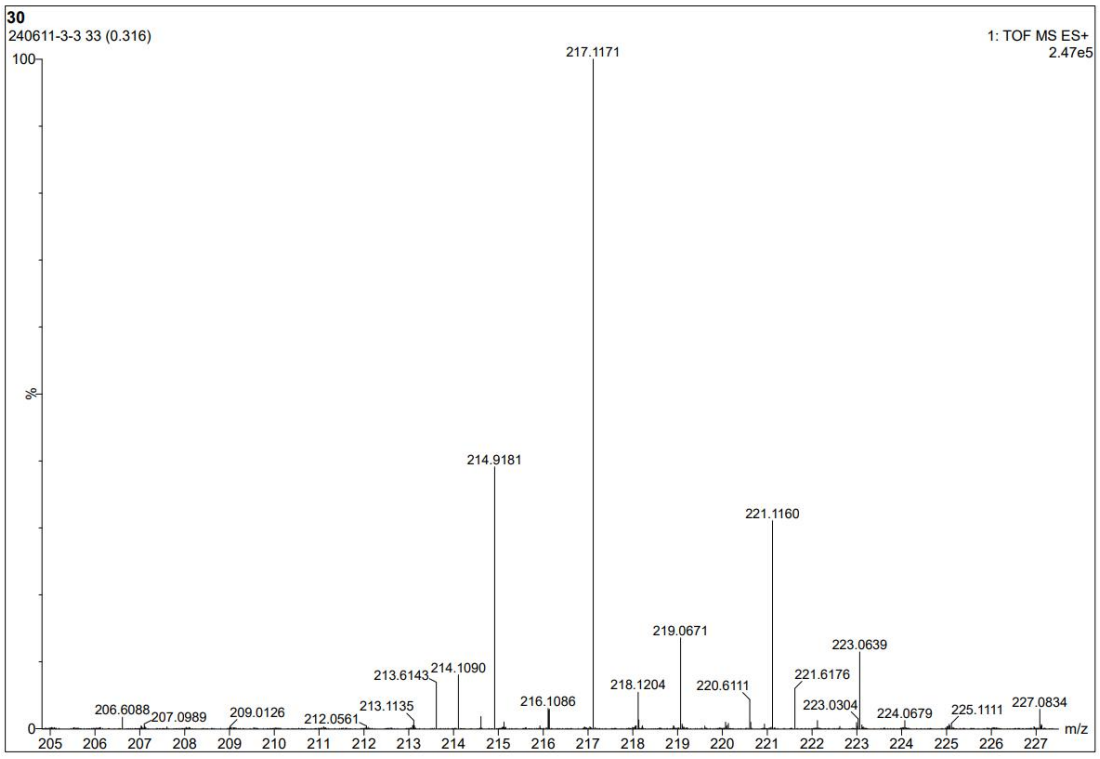


methyl 2,3-dimethyl-3-phenylpropanoate-2,3-d_2 & ethyl 2,3-dimethyl-3-phenyl propanoate-2,3-d_2 (2o & 2o'):

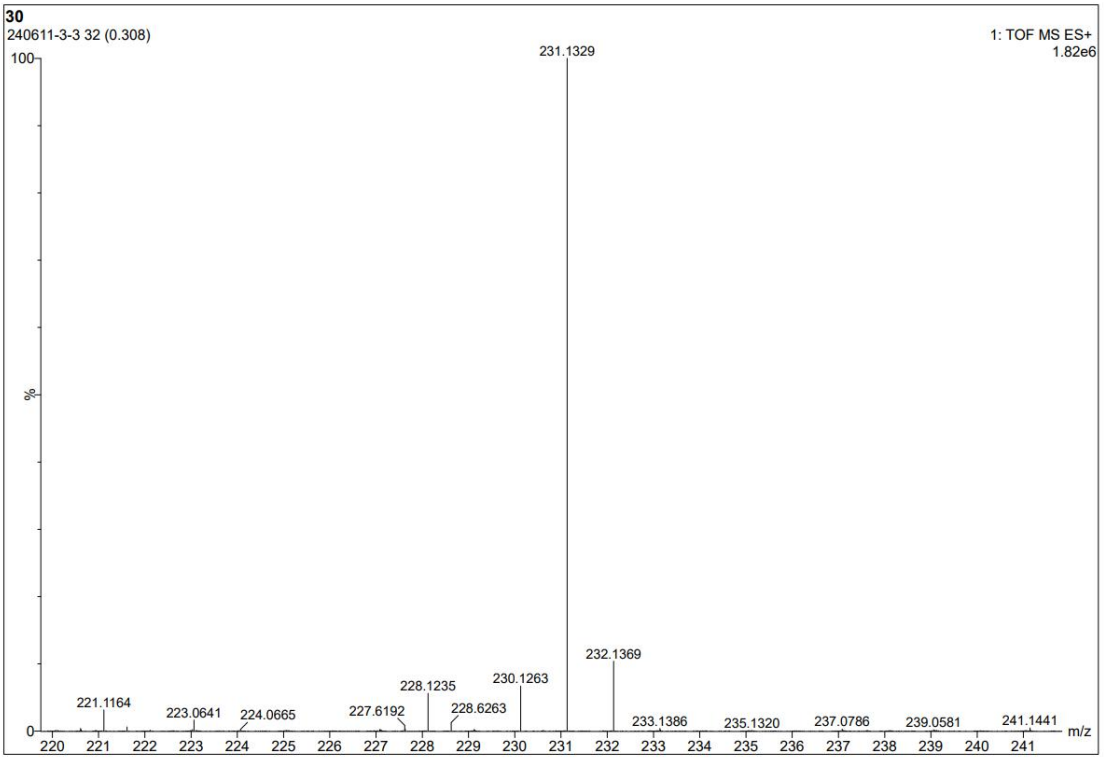




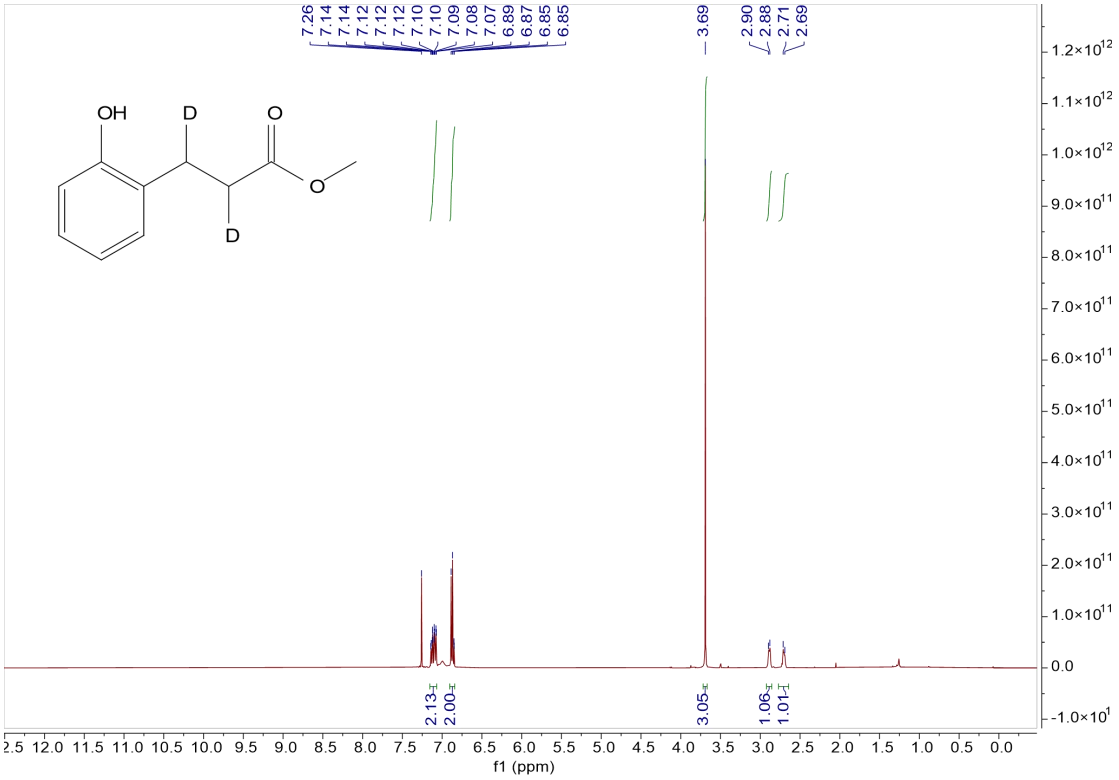
HRMS of methyl 2,3-dimethyl-3-phenyl propanoate-2,3-d_2 (2o)

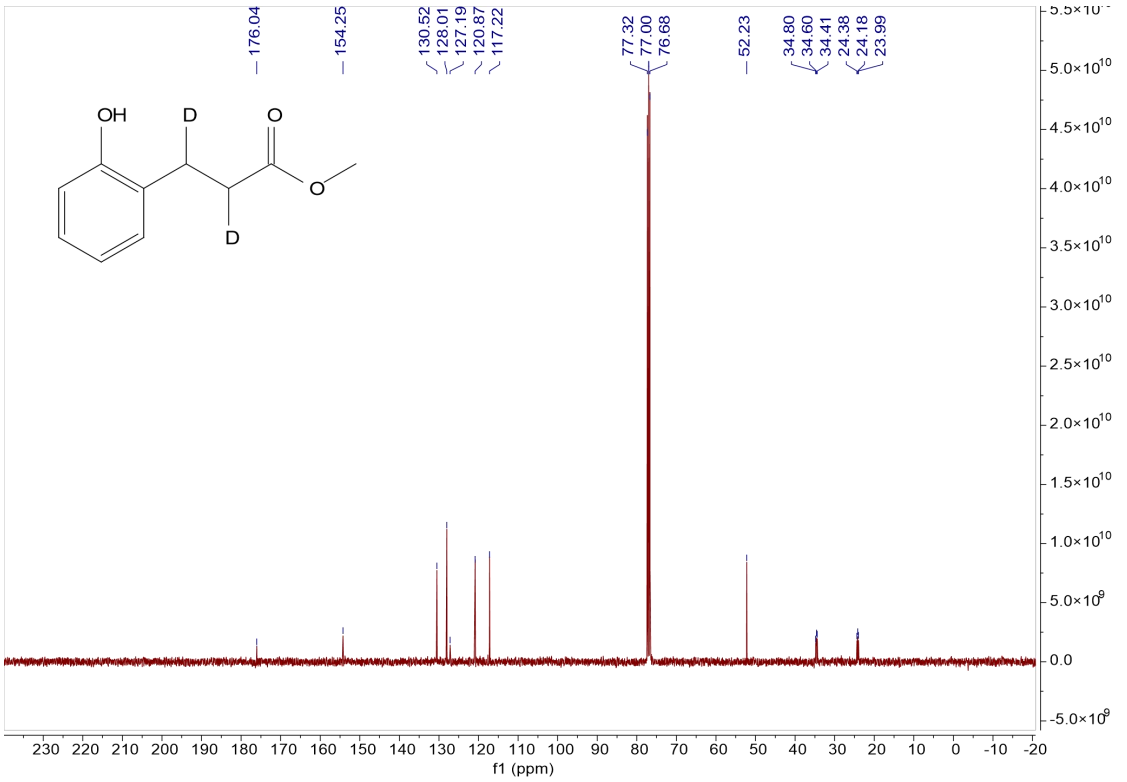


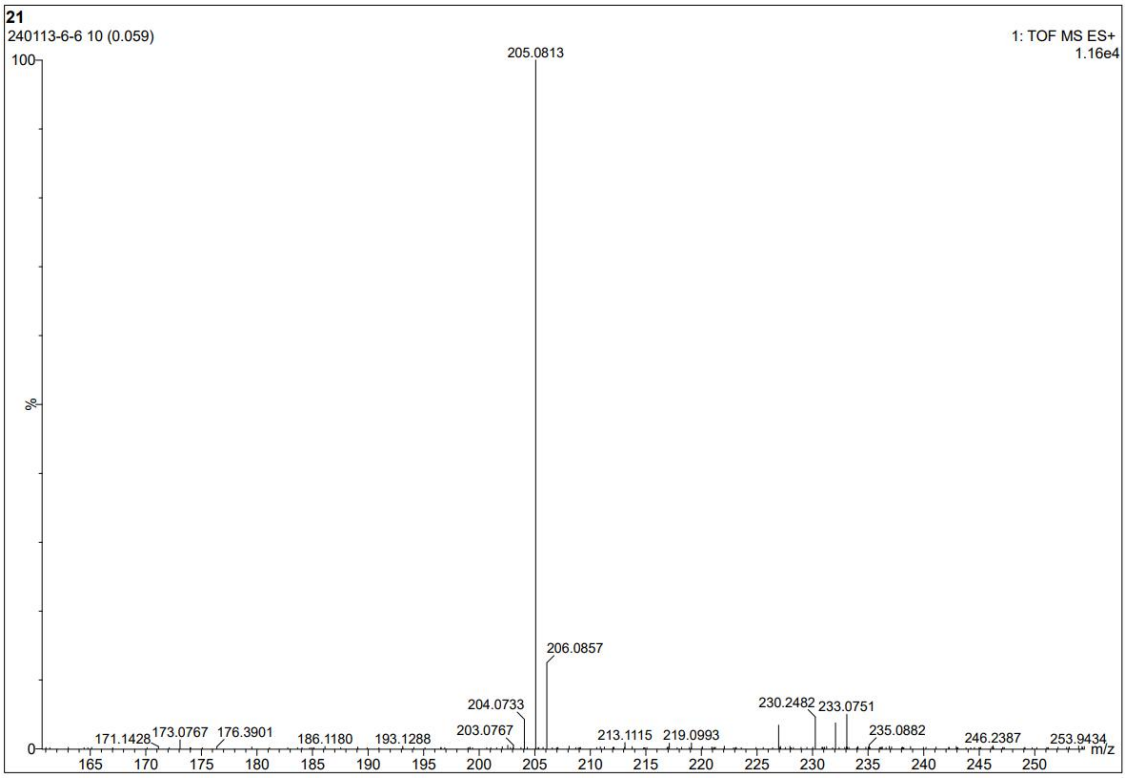
HRMS of ethyl 2,3-dimethyl-3-phenyl propanoate-2,3-d_2 (2o')



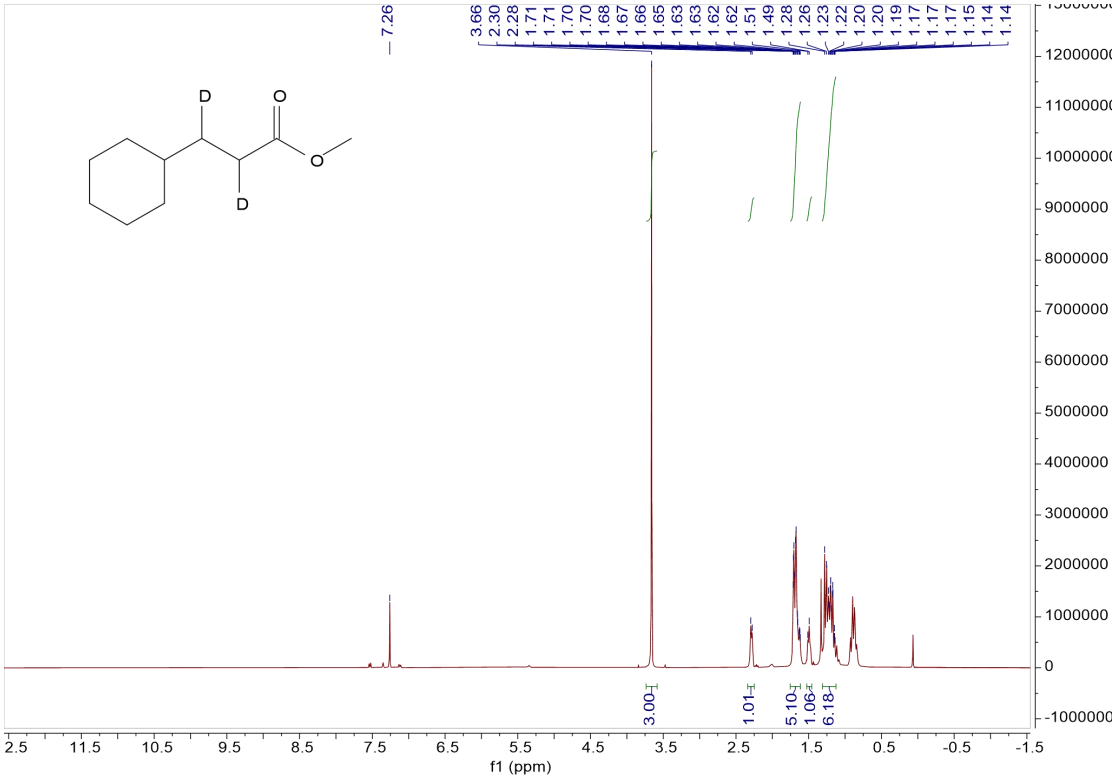
methyl 3-(2-hydroxyphenyl)propanoate-2,3-d_2 (2p)

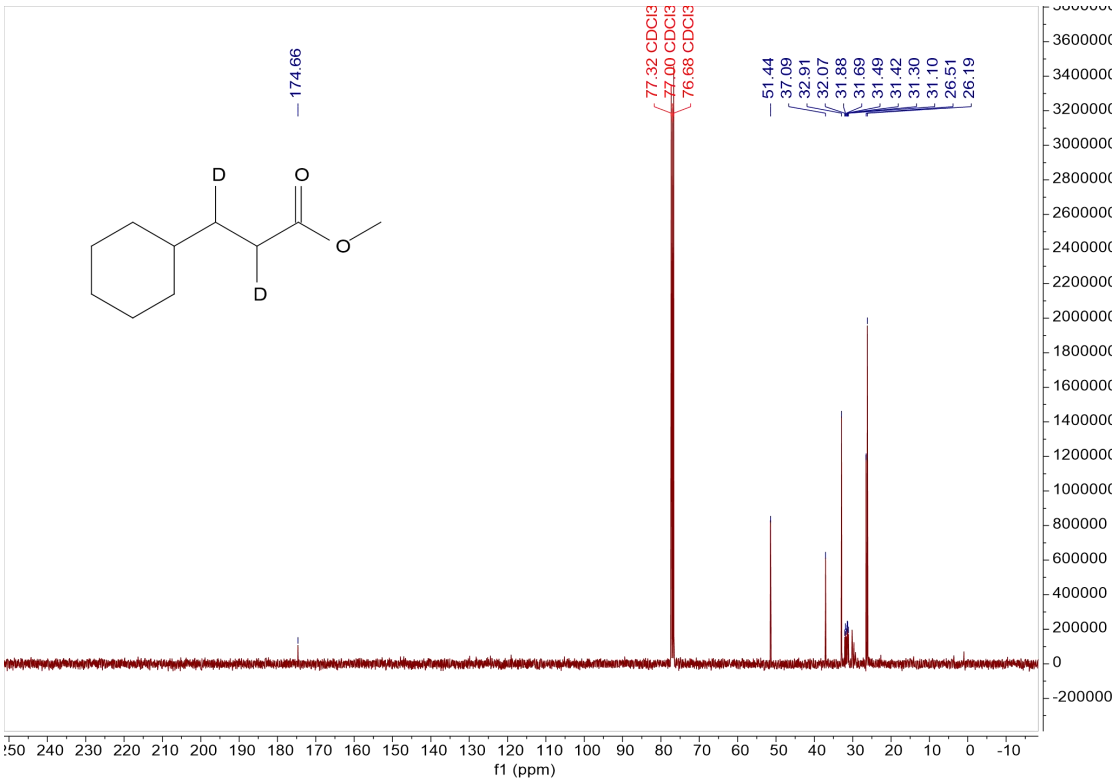


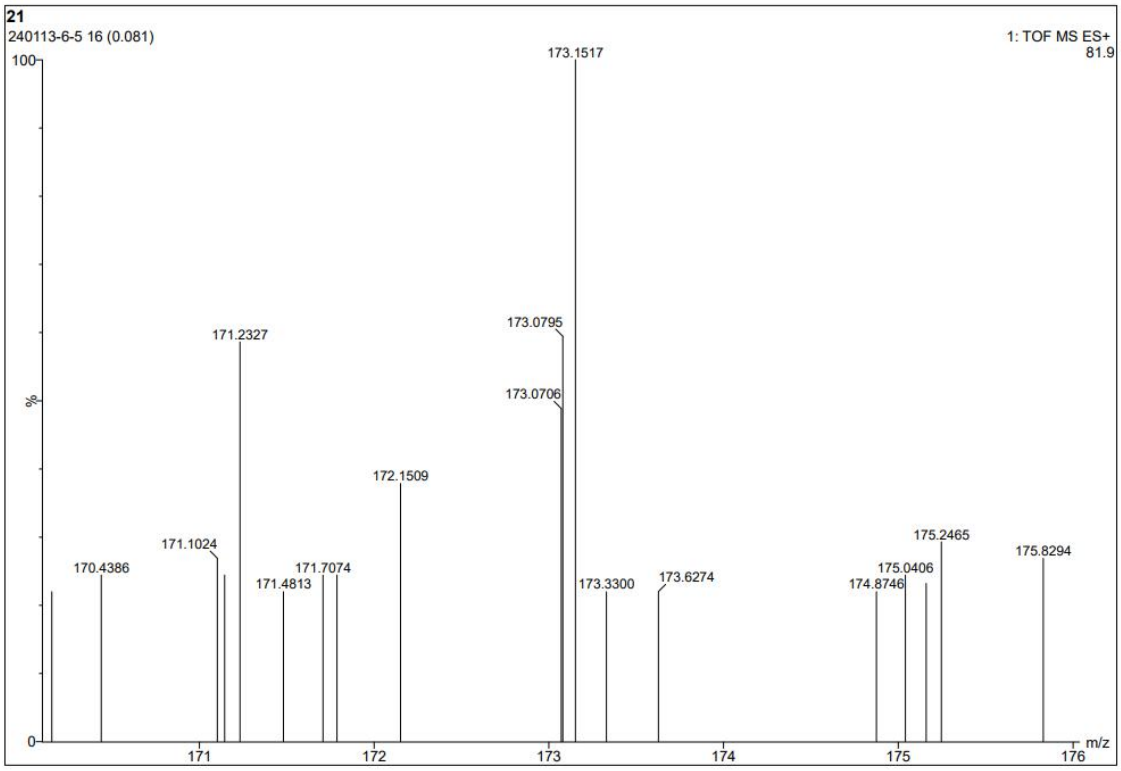




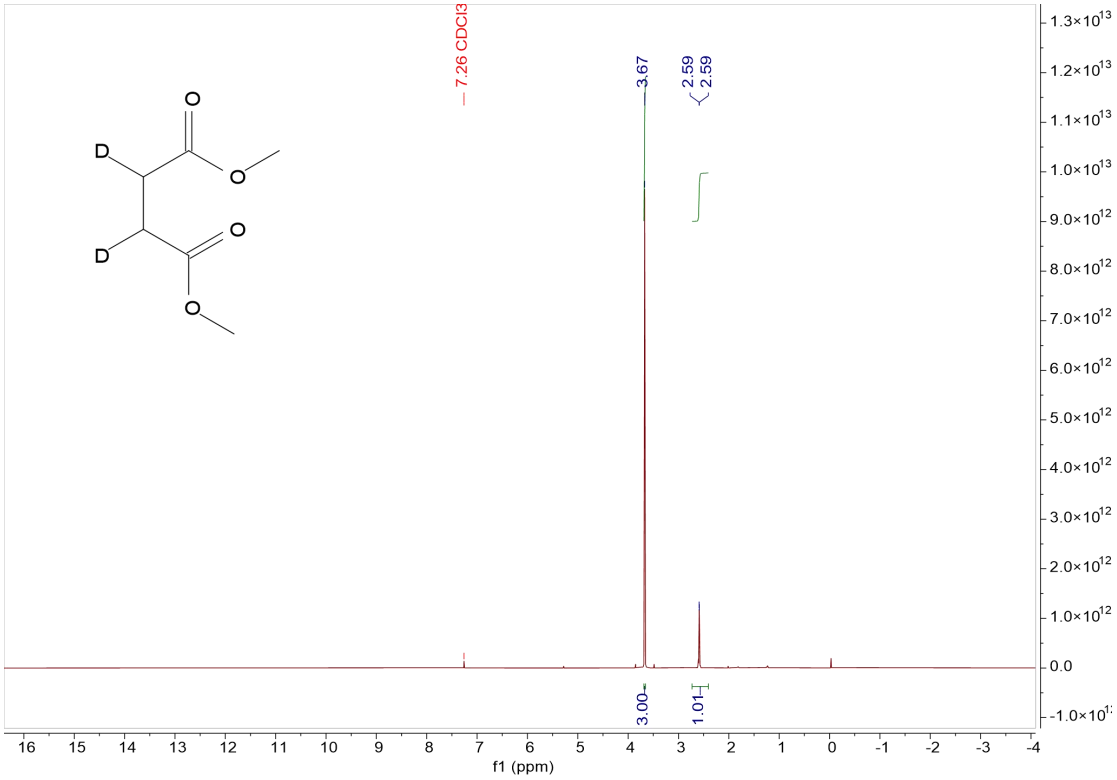
methyl 3-cyclohexylpropanoate-2,3-d_2 (2q):

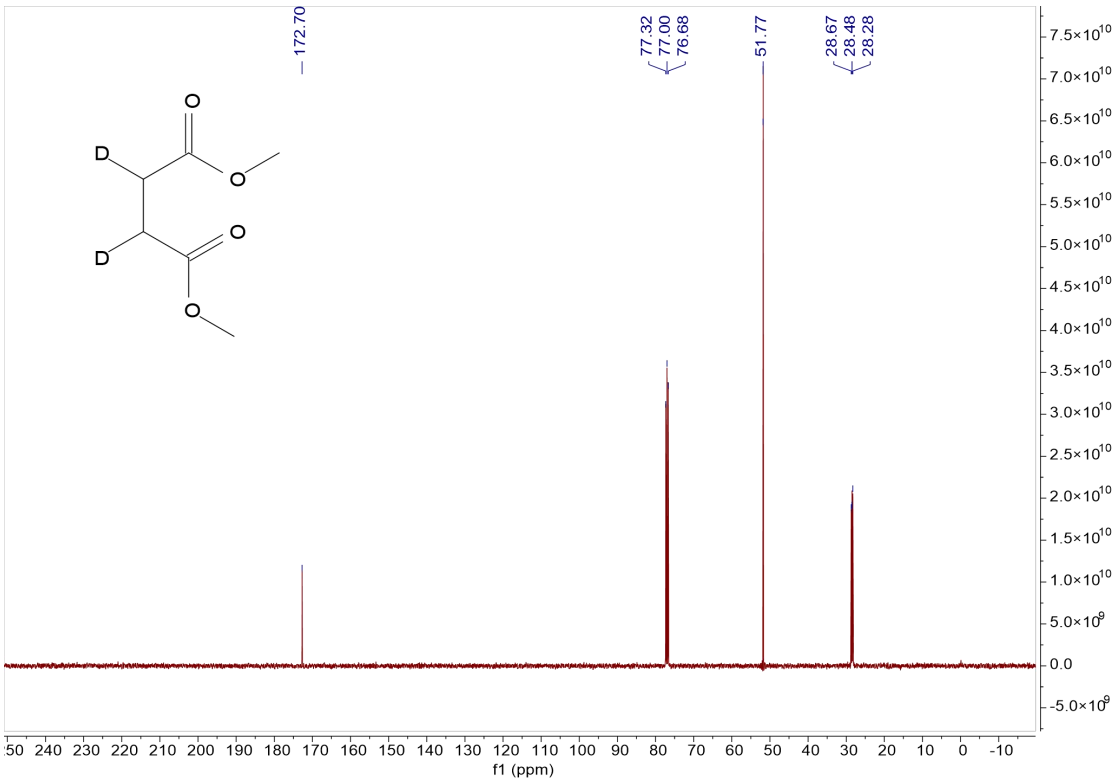

7.26
3.66
2.30
2.28
1.71
1.71
1.70
1.70
1.68
1.67
1.66
1.65
1.63
1.63
1.62
1.62
1.51
1.49
1.28
1.26
1.23
1.22
1.20
1.20
1.19
1.17
1.17
1.17
1.15
1.14
1.14
D
O
O
D
3.00
1.01
5.10
1.06
6.18
f1 (ppm)

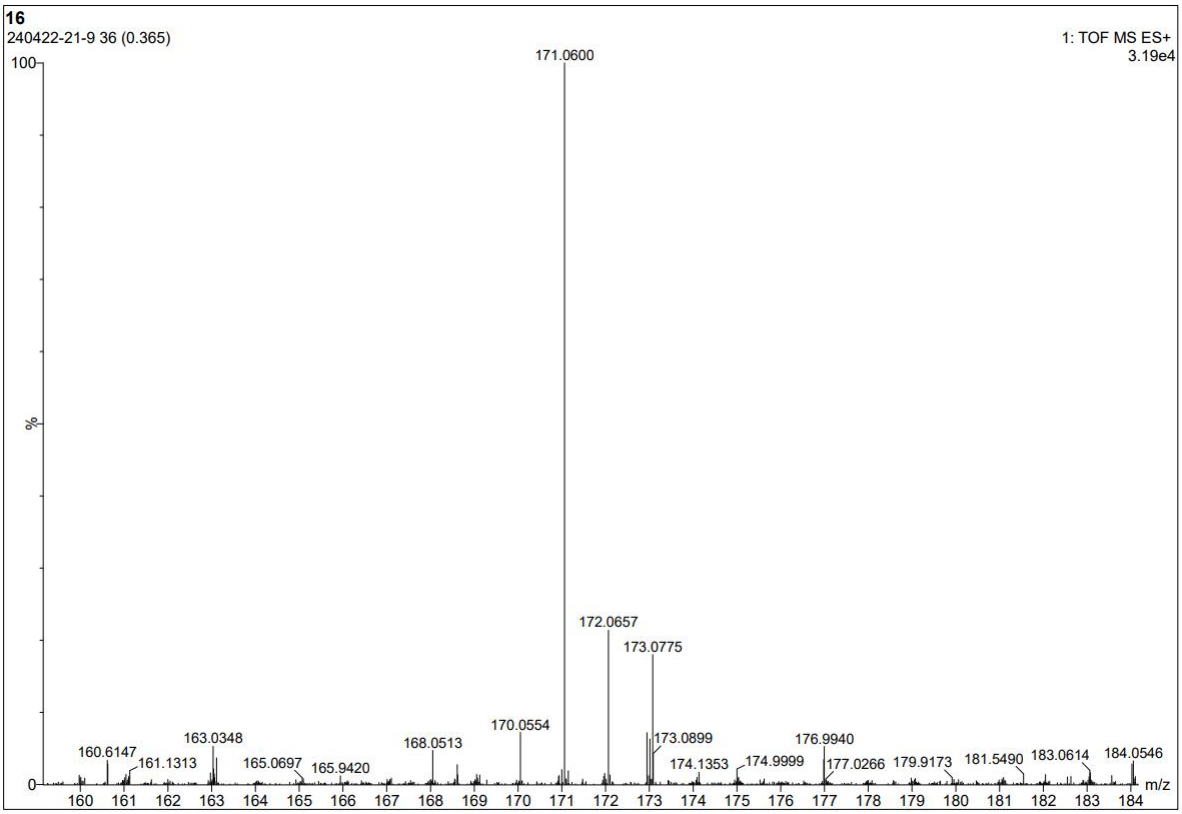

174.66
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.44
37.09
32.91
32.07
31.88
31.69
31.49
31.42
31.30
31.10
26.51
26.19
D
O
O
D
f1 (ppm)



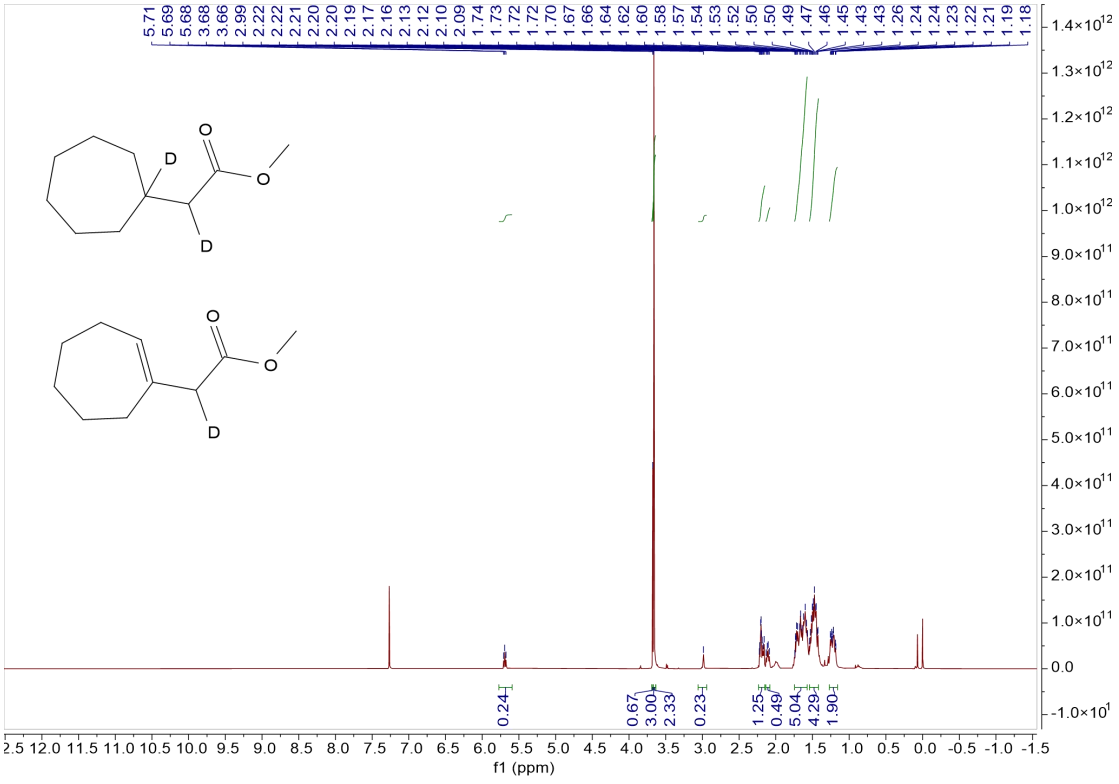
dimethyl succinate-2,3-d_2 (2r)

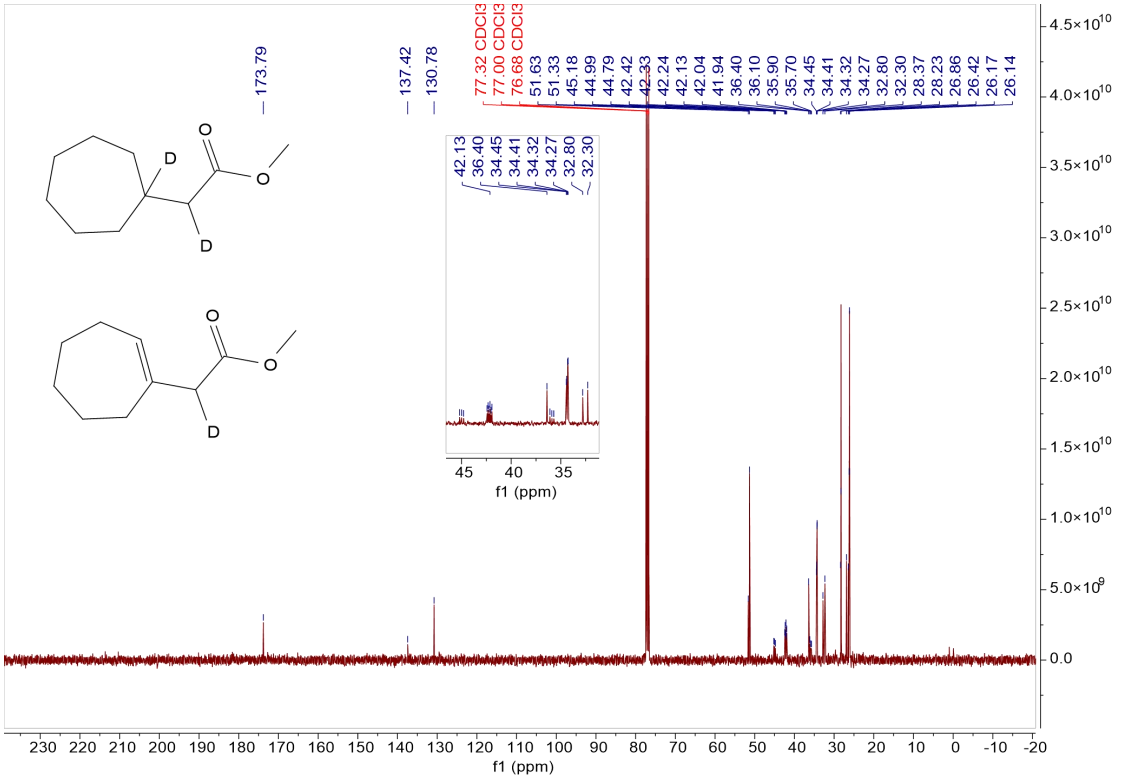

7.26 CDCl3
3.67
2.59
2.59
D
D
O
O
O
O
3.00
1.01
f1 (ppm)


172.70
77.32
77.00
76.68
51.77
28.67
28.48
28.28
D
D
O
O
O
O
f1 (ppm)

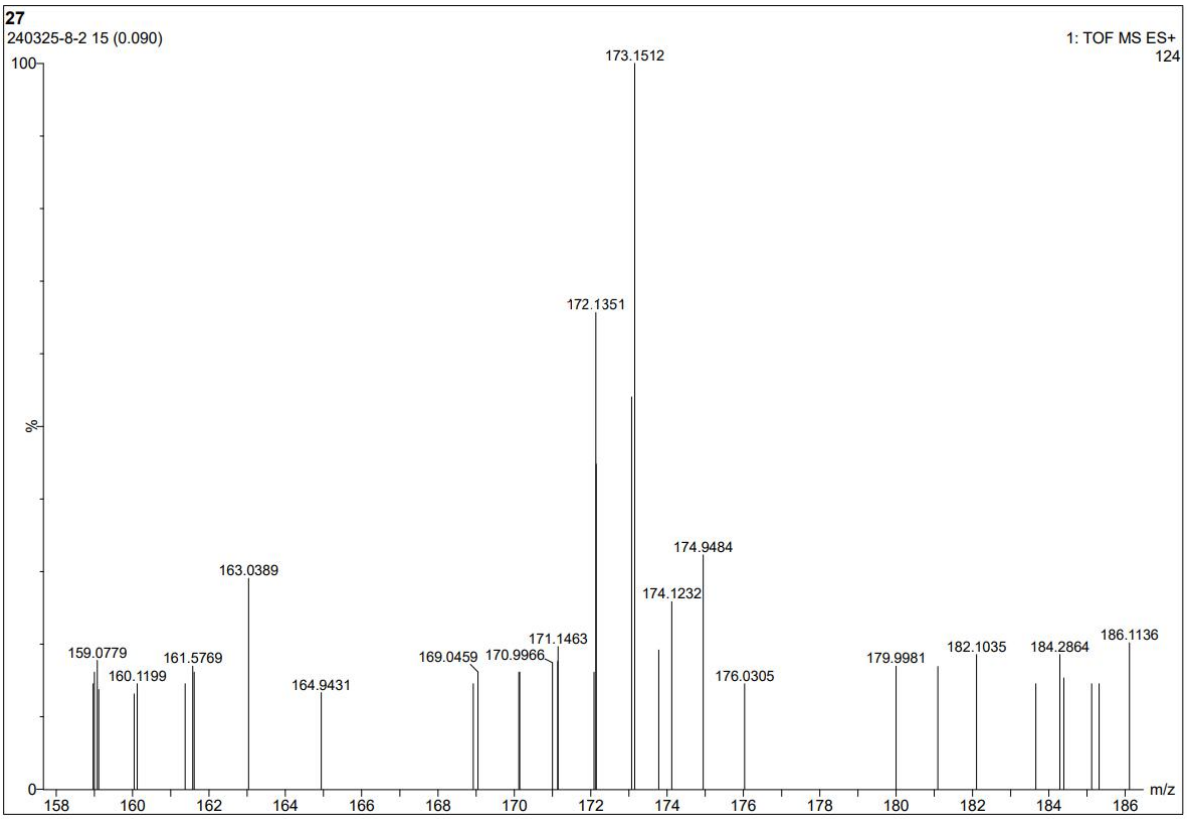


methyl 2-(cycloheptyl-1-*d*)acetate-2-*d* & methyl 2-(cyclohept-1-en-1-yl)acetate-2-*d* (2s & 2s'):

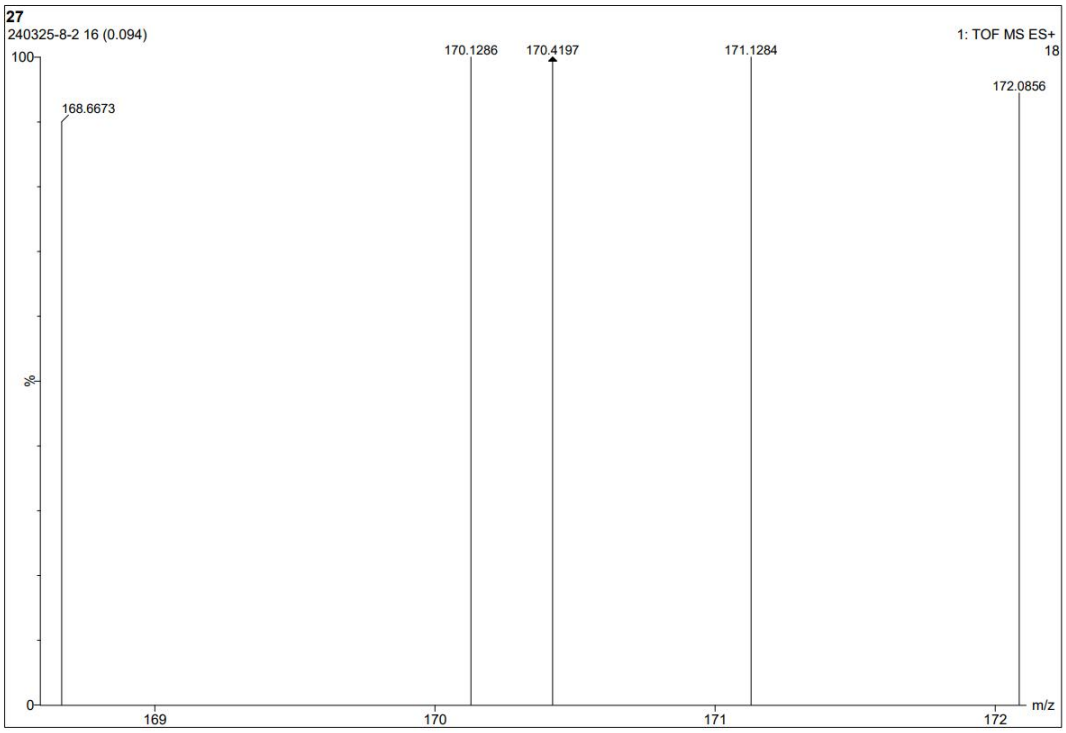




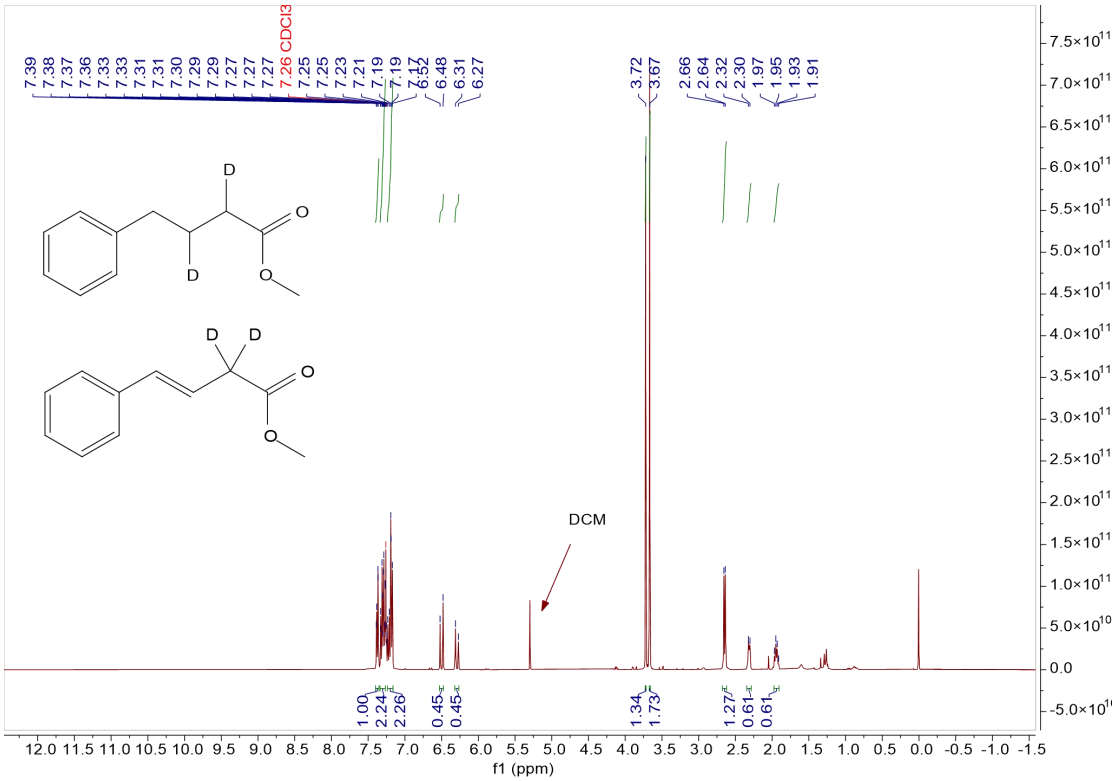
HRMS of methyl 2-(cycloheptyl-1-*d*)acetate-2-*d* (2s)

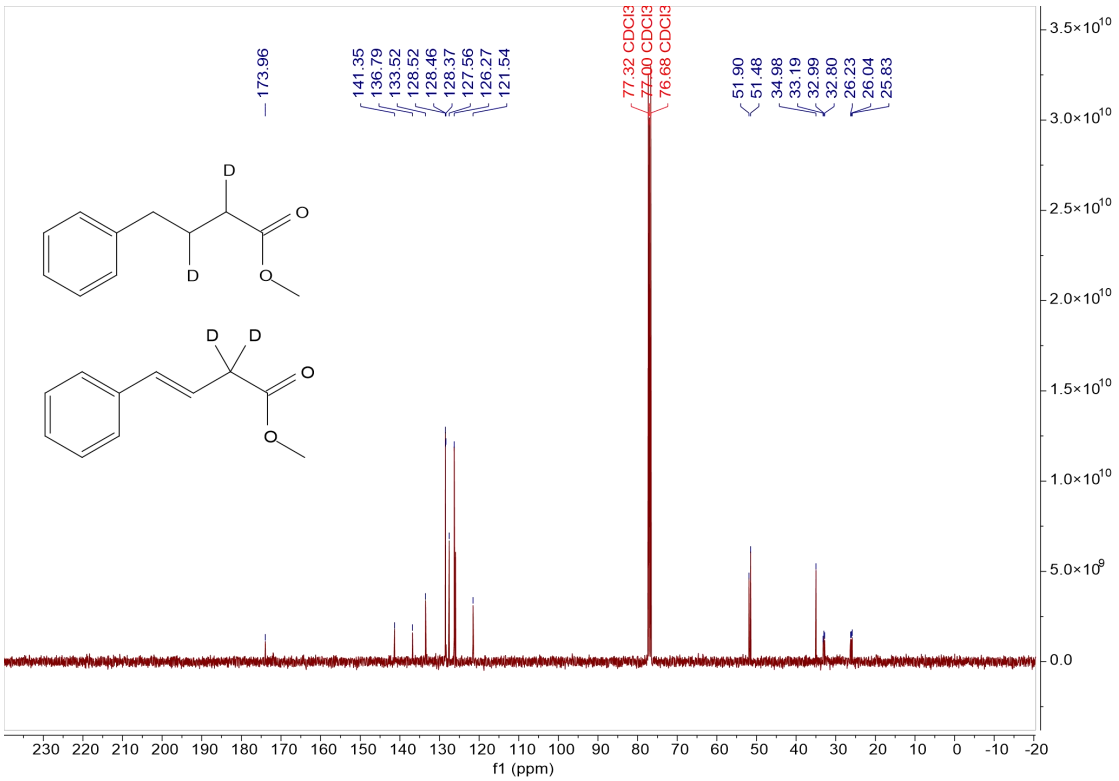


HRMS of methyl 2-(cyclohept-1-en-1-yl)acetate-2-*d* (2s')

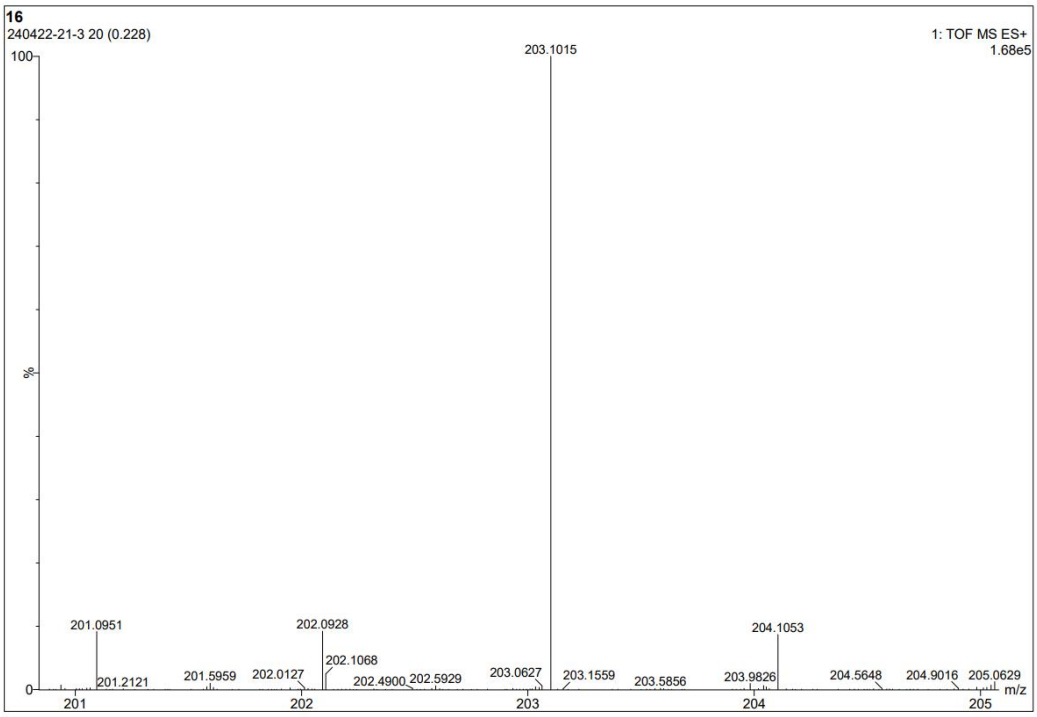


methyl 4-phenylbutanoate-2,3-*d*$_2$ & methyl 4-phenylbut-3-enoate-2,2-*d*$_2$ (2t & 2t'):

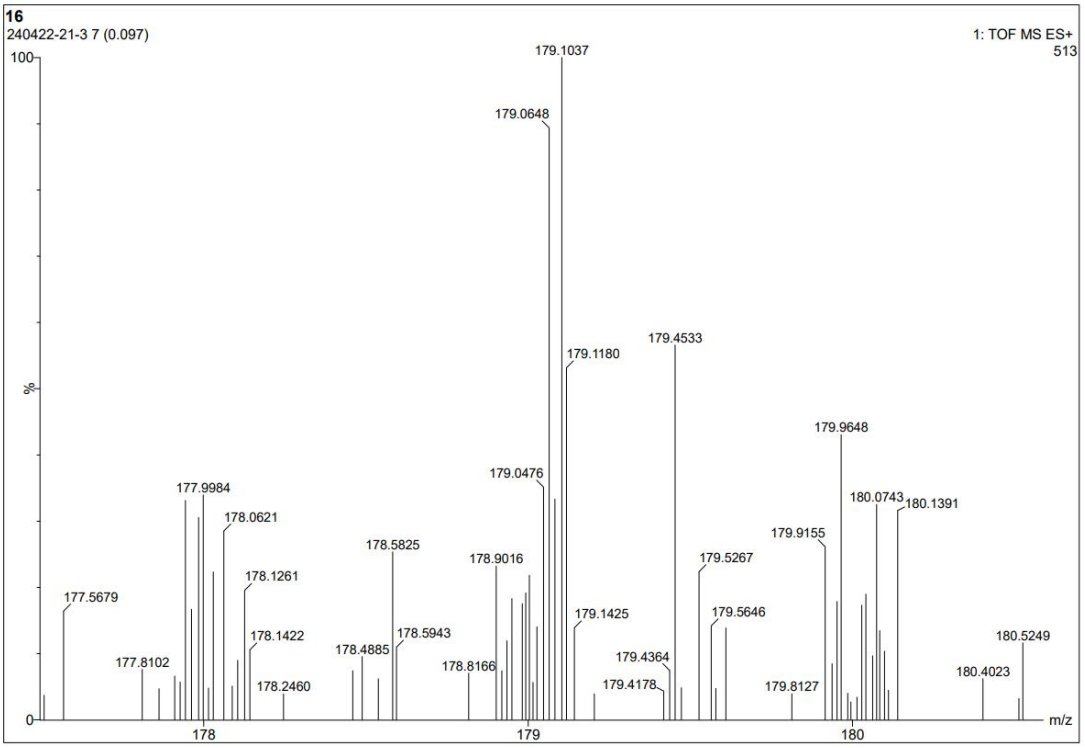




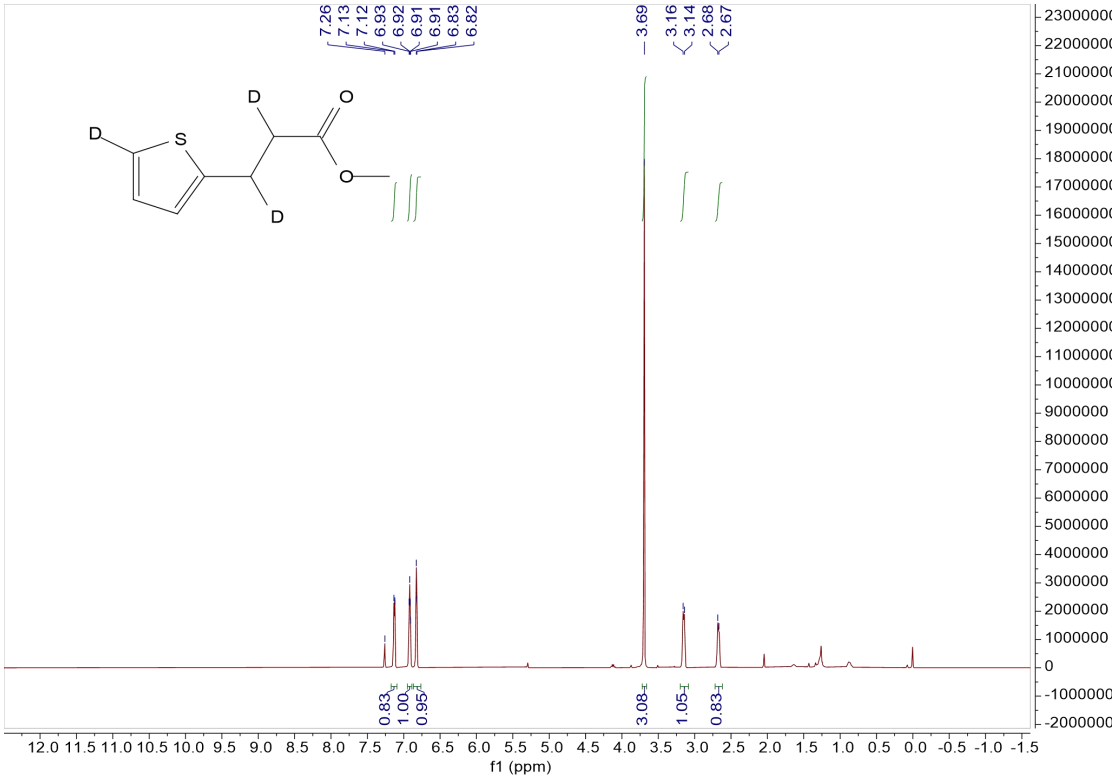
HRMS of methyl 4-phenylbutanoate-2,3-d_2 (2t)

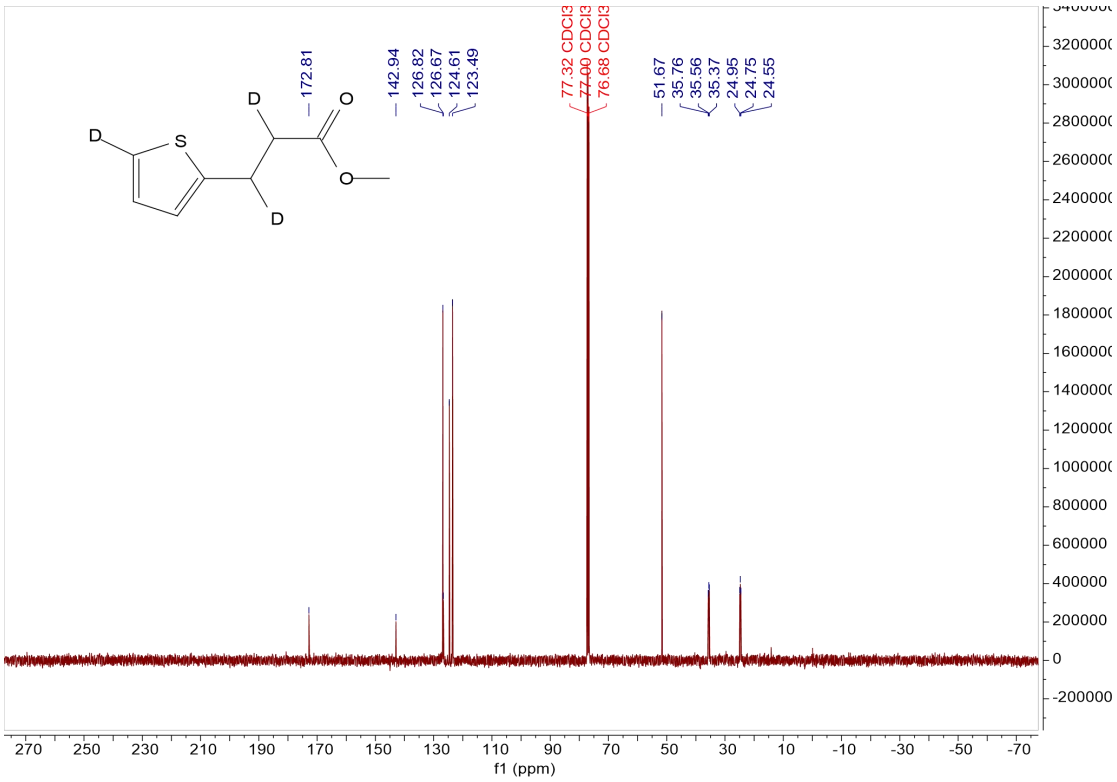


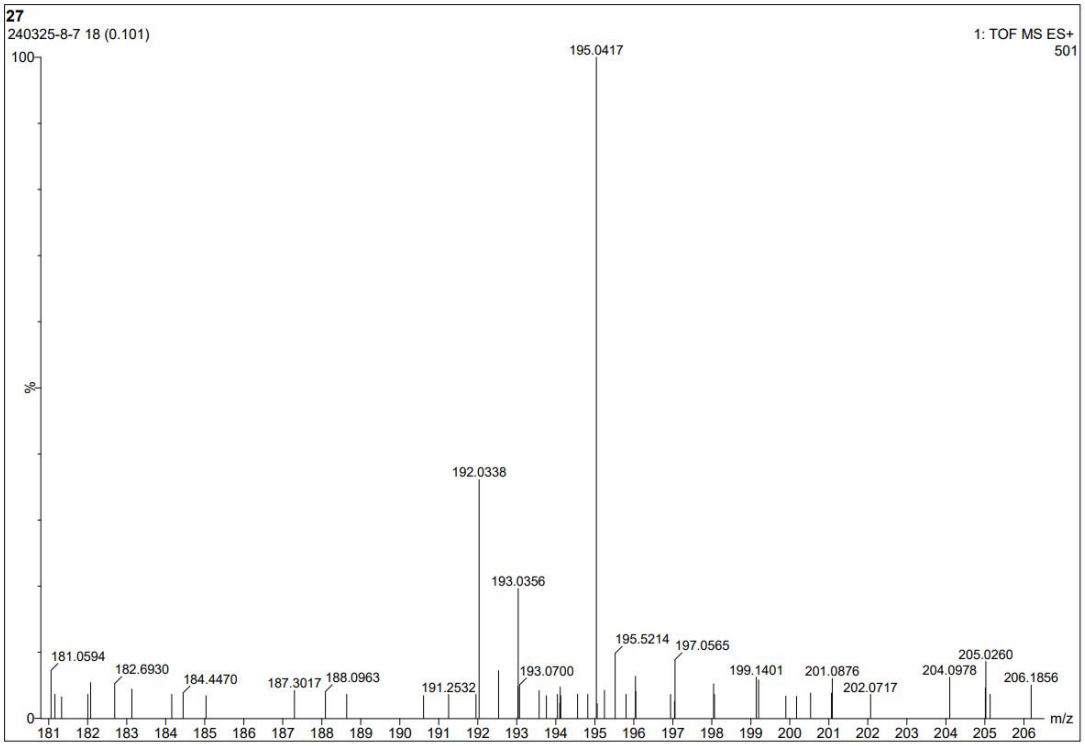
HRMS of methyl 4-phenylbut-3-enoate-2,2-d_2 (2t')



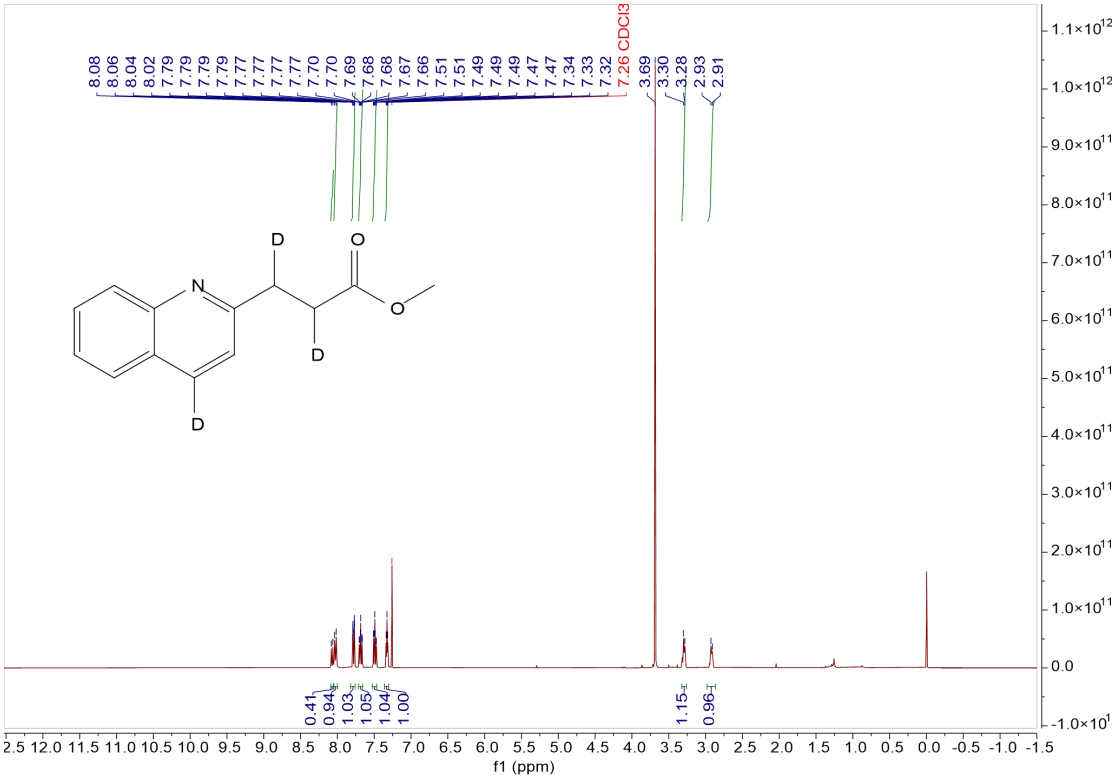
methyl 3-(thiophen-2-yl-5-*d*)propanoate-2,3-d_2 (2u):

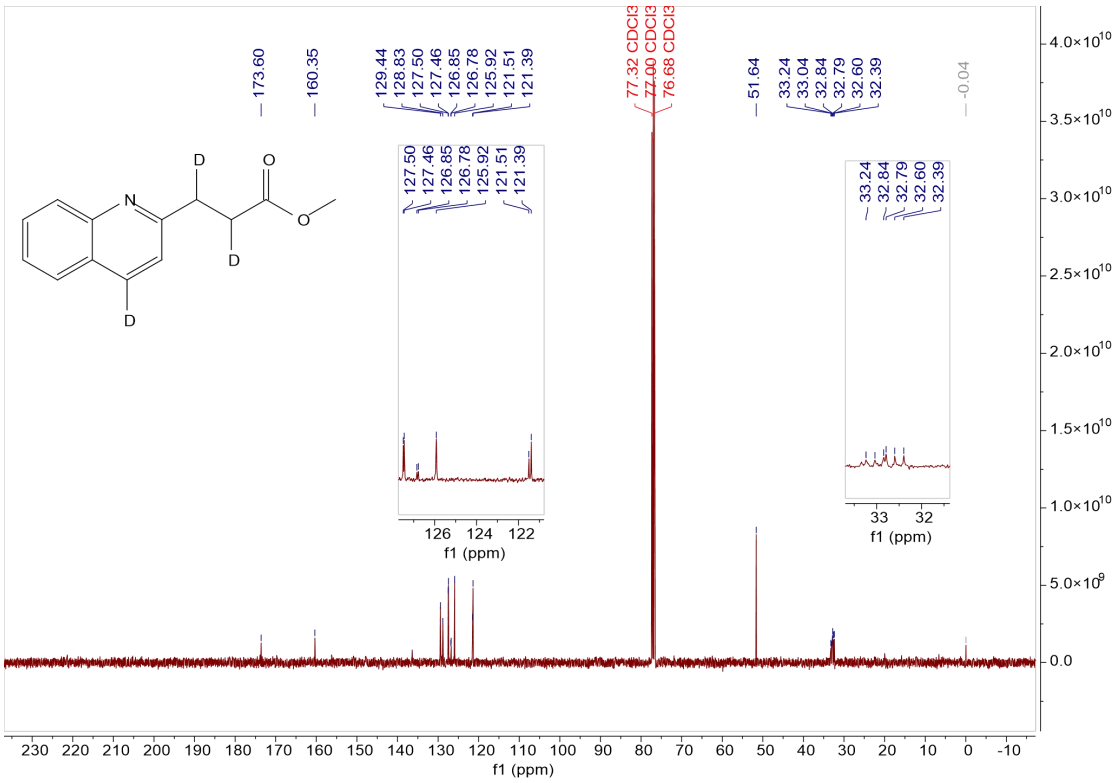


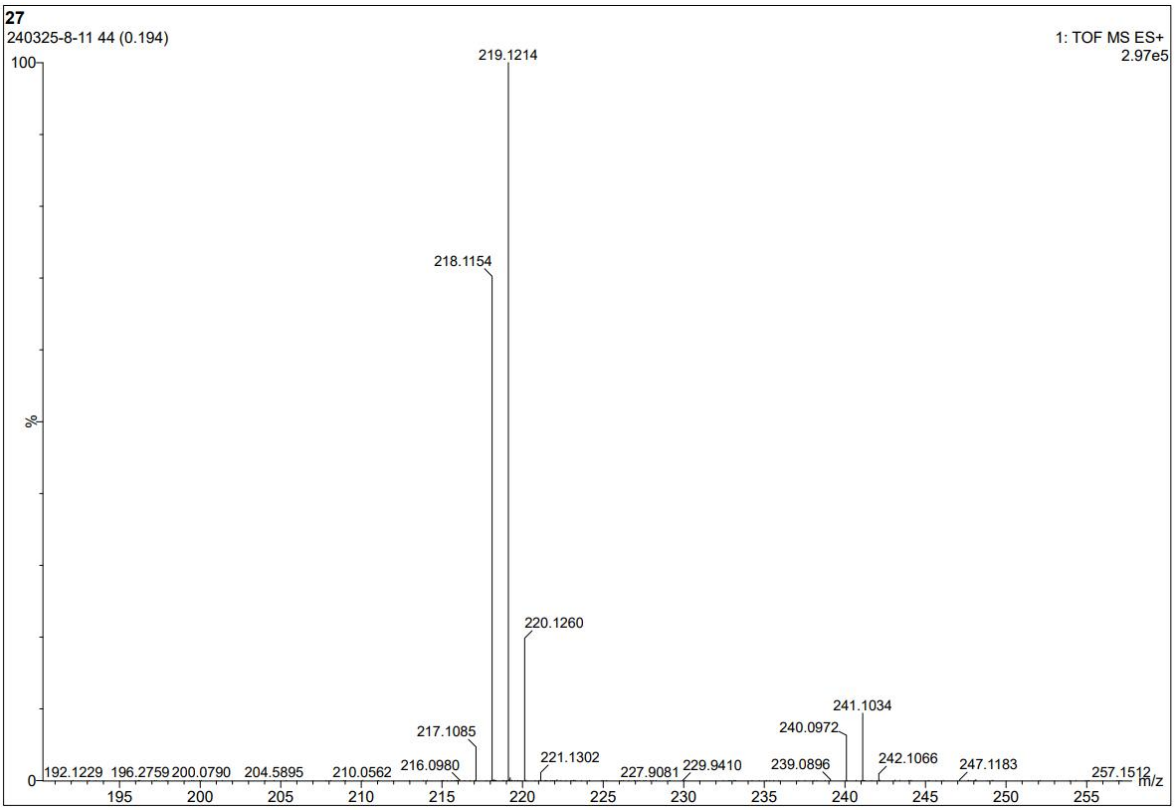




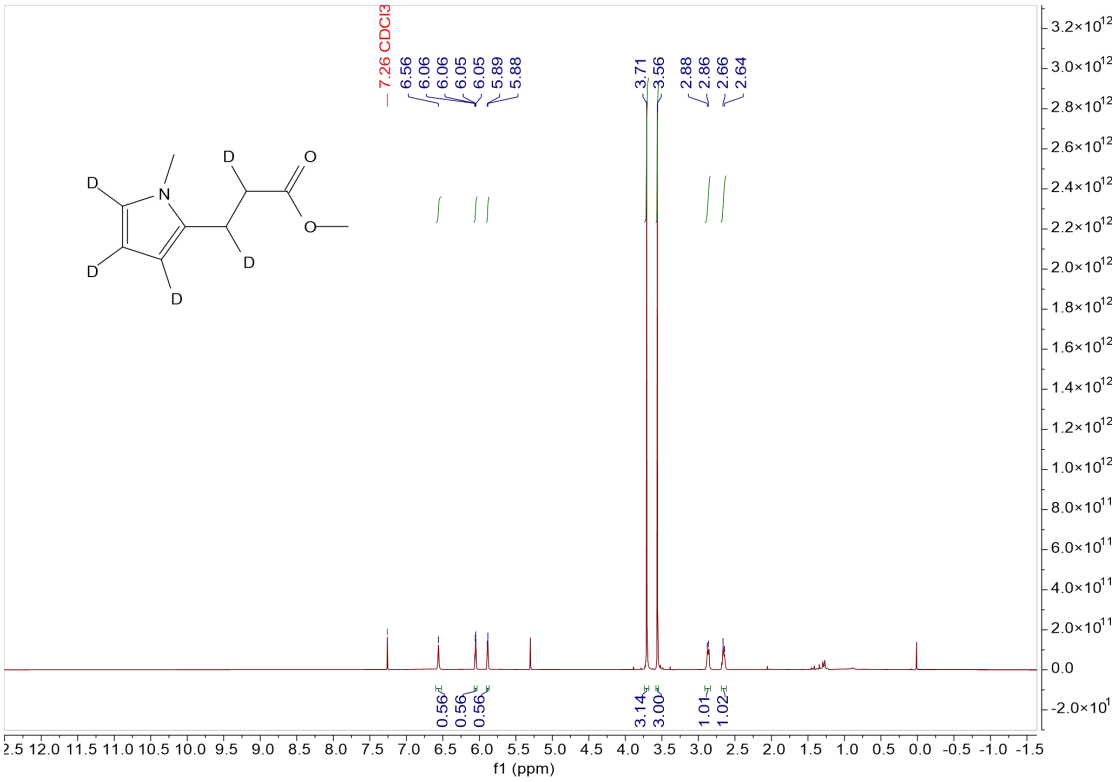
methyl 3-(quinolin-2-yl-4-*d*)propanoate2,3-d_2 (2v):

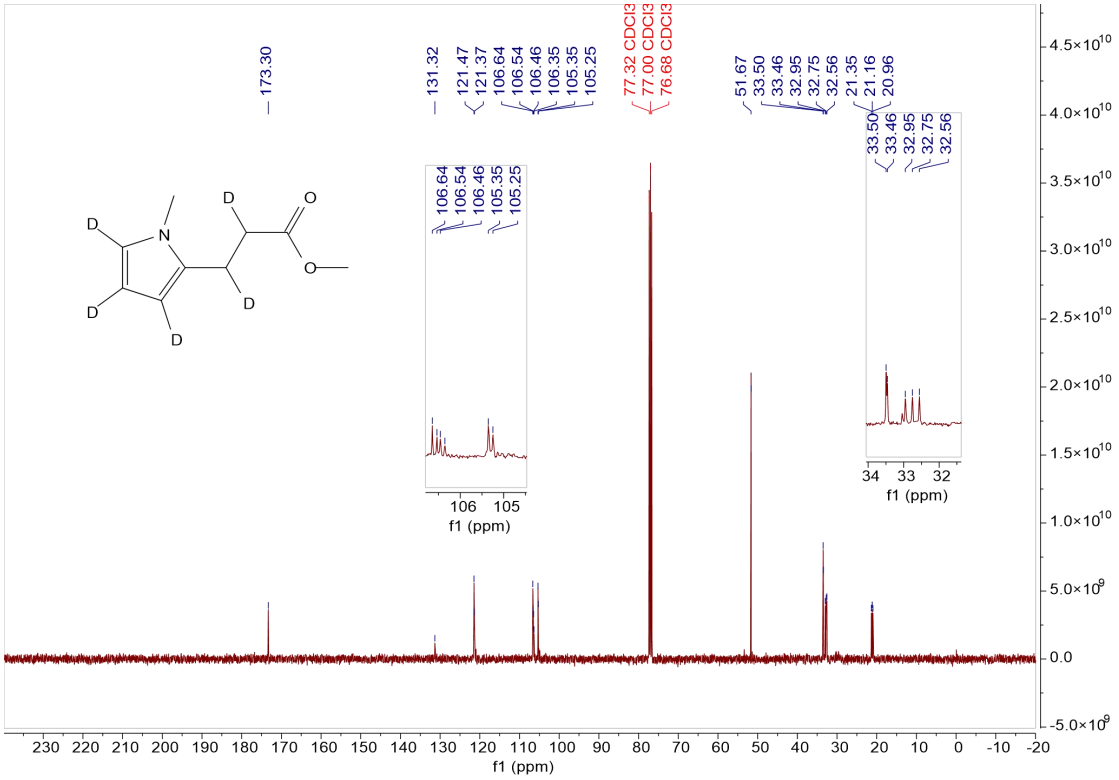

8.08 8.06 8.04 8.02 7.79 7.79 7.79 7.77 7.77 7.77 7.77 7.70 7.70 7.69 7.68 7.68 7.67 7.66 7.51 7.51 7.49 7.49 7.49 7.47 7.47 7.34 7.33 7.32 7.26 CDCl3 3.69 3.30 3.28 2.93 2.91
D O N O D D
0.41 0.94 1.03 1.05 1.04 1.00 1.15 0.96
f1 (ppm)

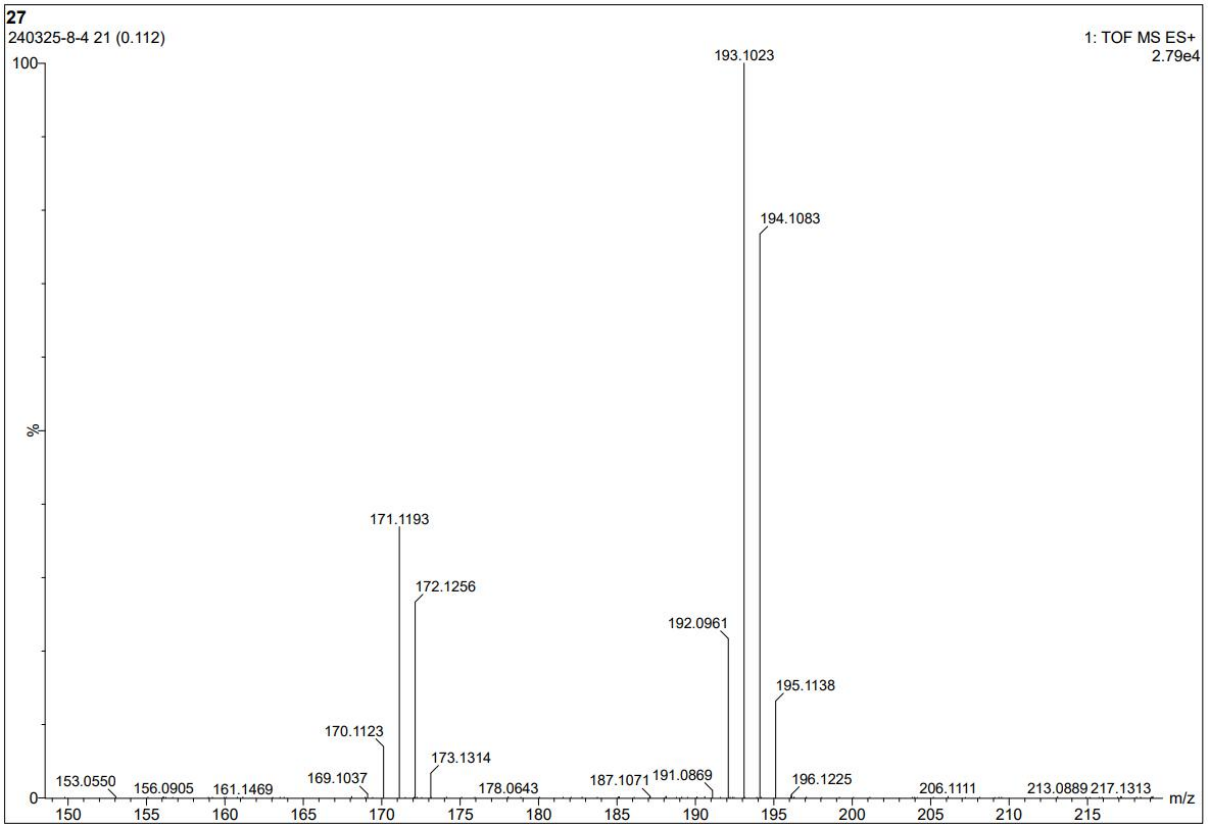

173.60 160.35 129.44 128.83 127.50 127.46 126.85 126.78 125.92 121.51 121.39 77.32 CDCl3 77.00 CDCl3 76.68 CDCl3 51.64 33.24 33.04 32.84 32.79 32.60 32.39 -0.04
D O N O D D
127.50 127.46 126.85 126.78 125.92 121.51 121.39
33.24 32.84 32.79 32.60 32.39
f1 (ppm)



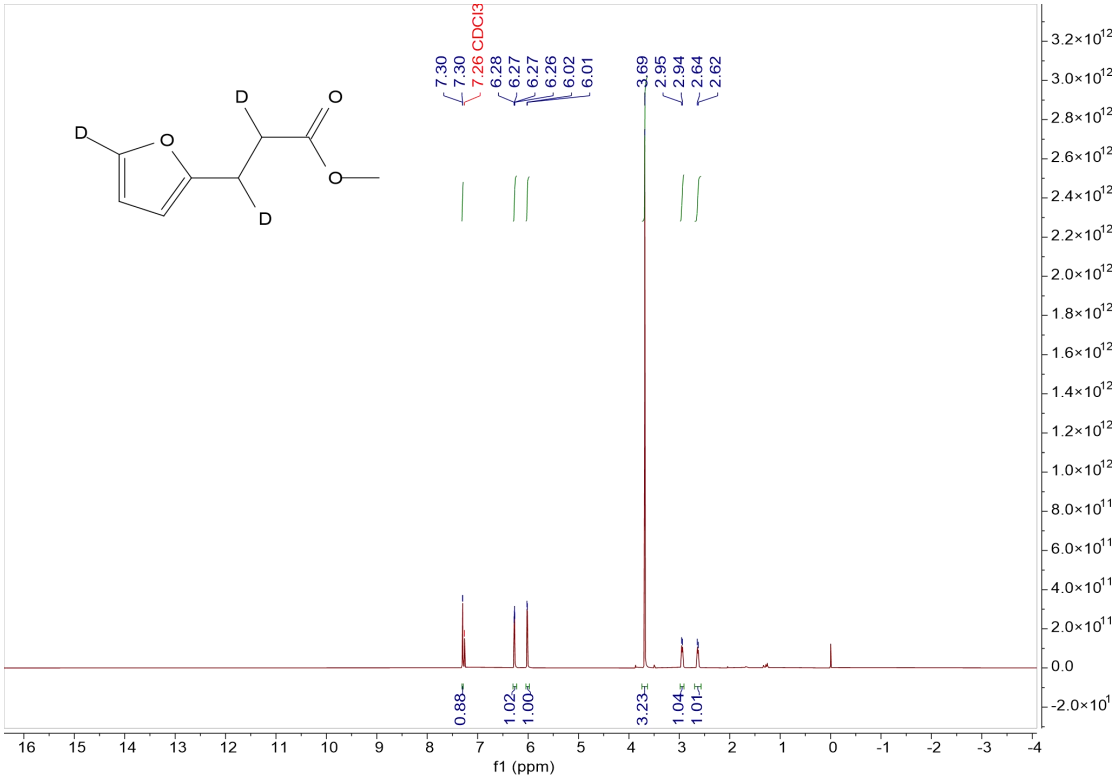
methyl 3-(1-methyl-1H-pyrrol-2-yl-3,4,5-d_3)propanoate-2,3-d_2 (2w):

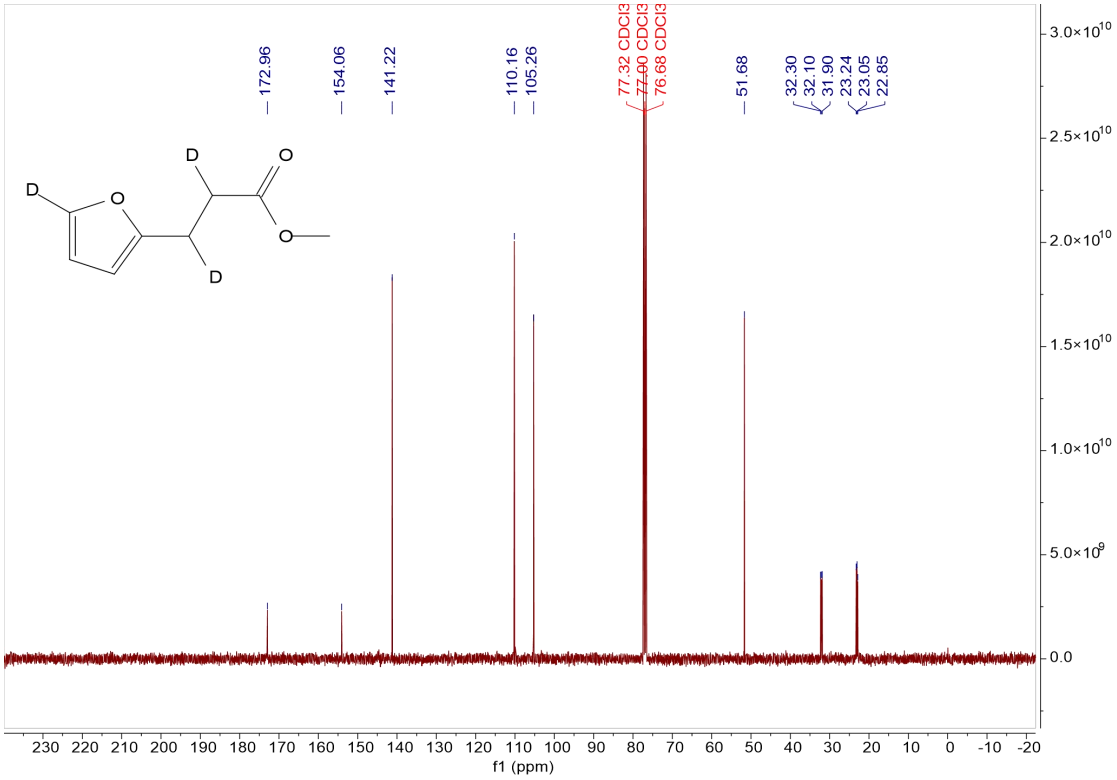


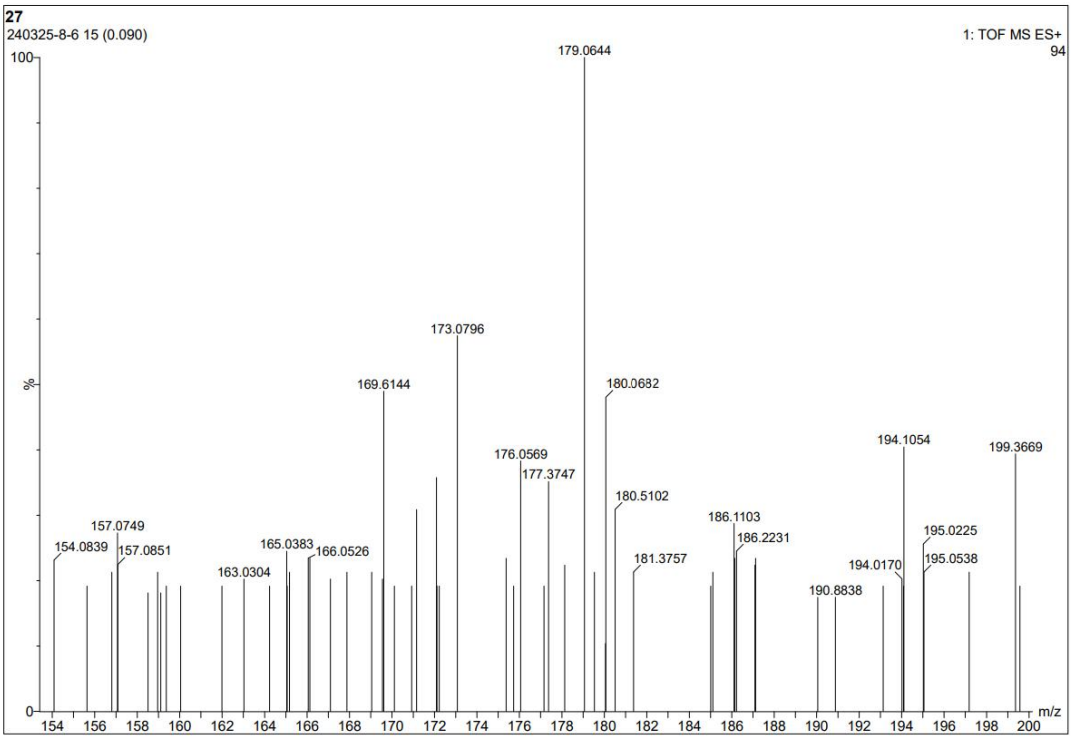




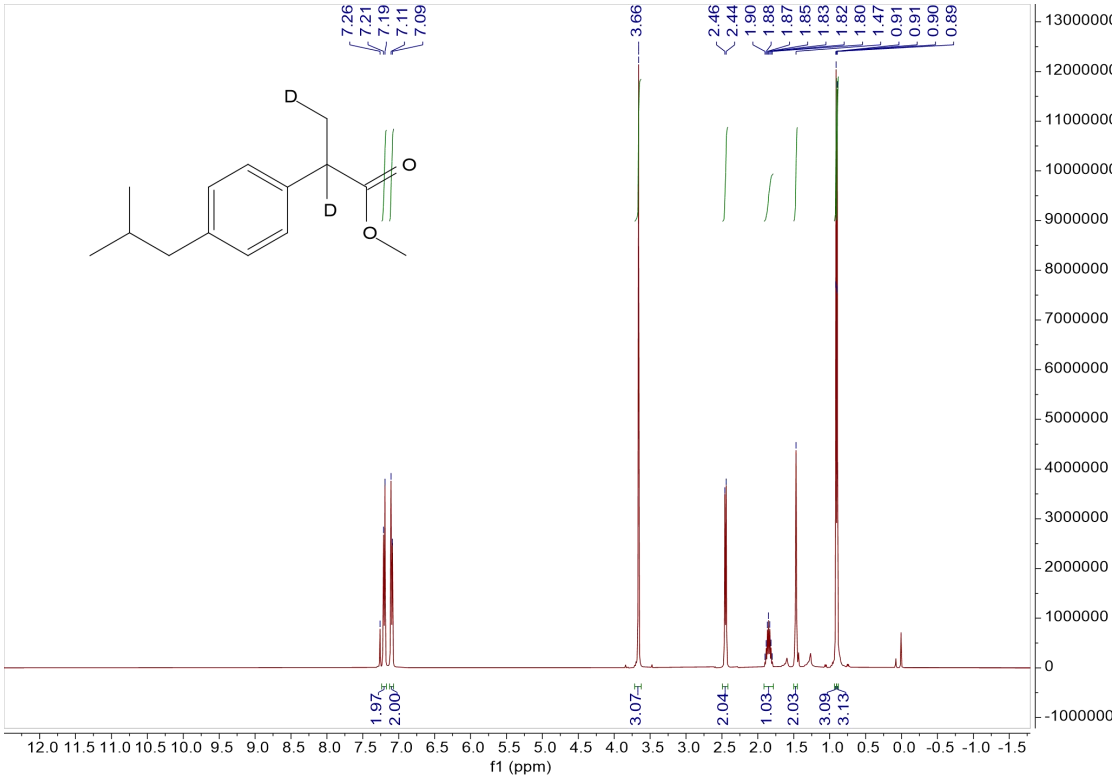
methyl 3-(furan-2-yl-5-*d*)propanoate-2,3-d_2 (2x):

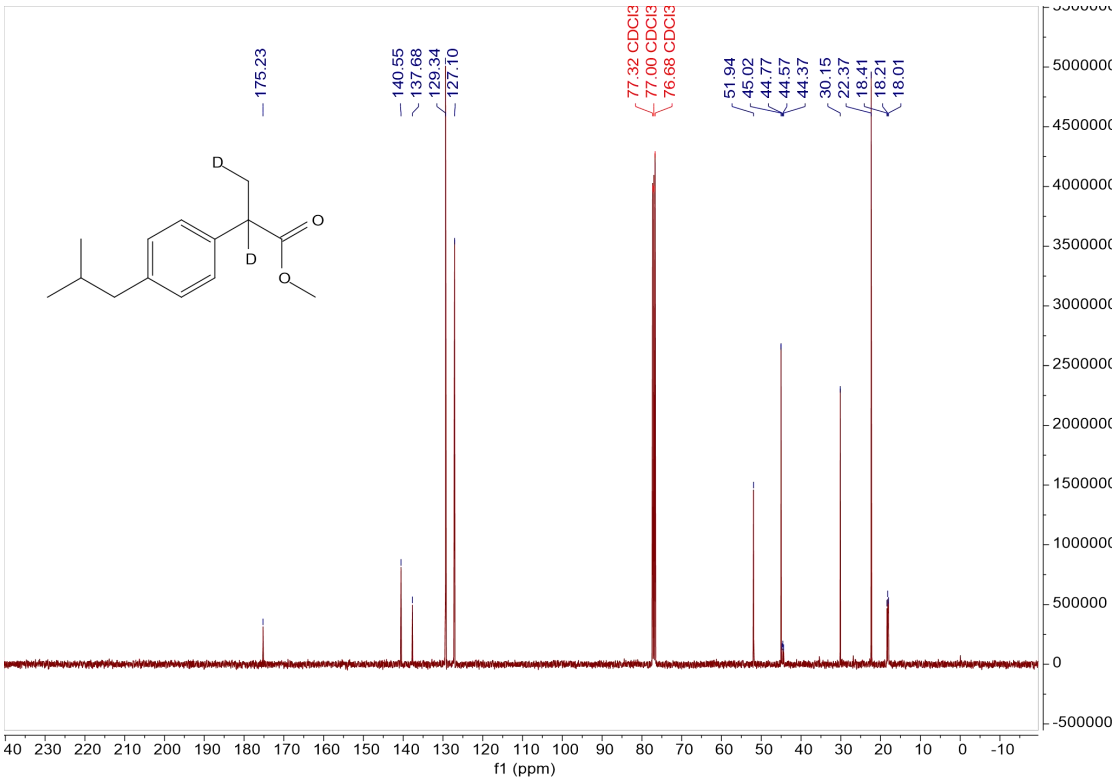

7.30
7.30
7.26 CDCl3
6.28
6.27
6.27
6.26
6.02
6.01
3.69
2.95
2.94
2.64
2.62
0.88
1.02
1.00
3.23
1.04
1.01
f1 (ppm)

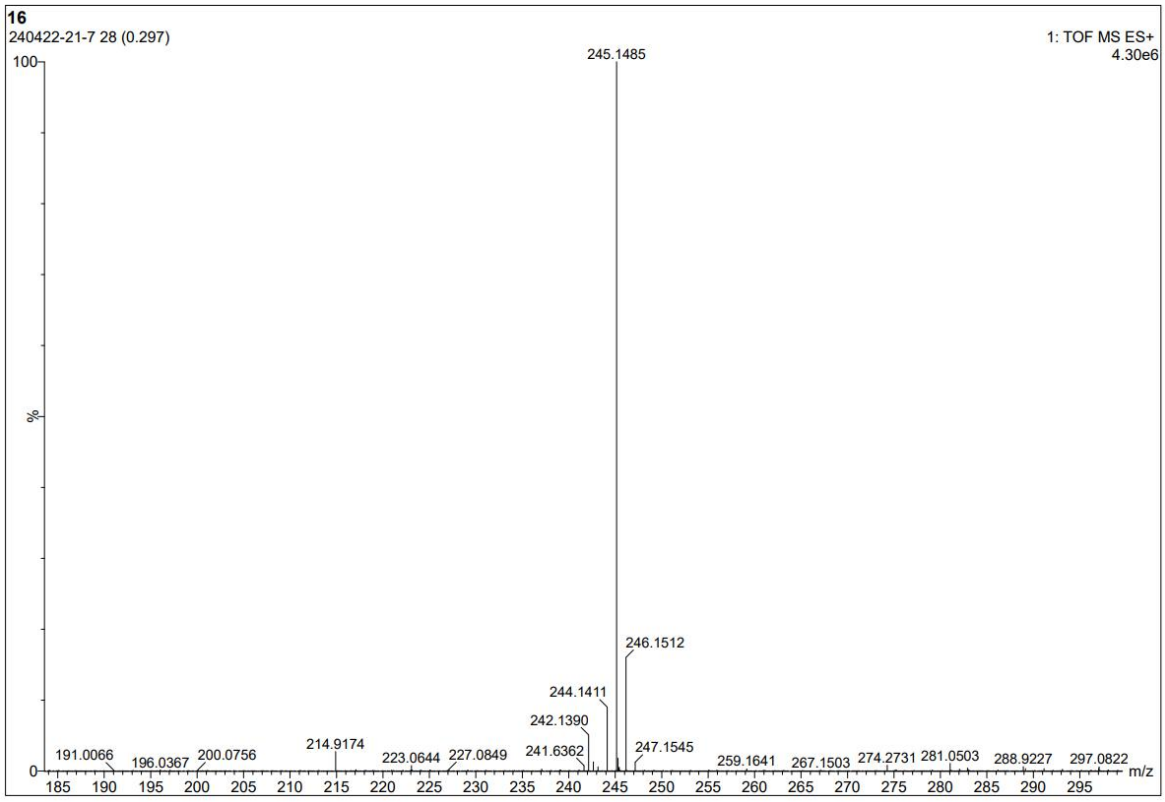

172.96
154.06
141.22
110.16
105.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.68
32.30
32.10
31.90
23.24
23.05
22.85
f1 (ppm)



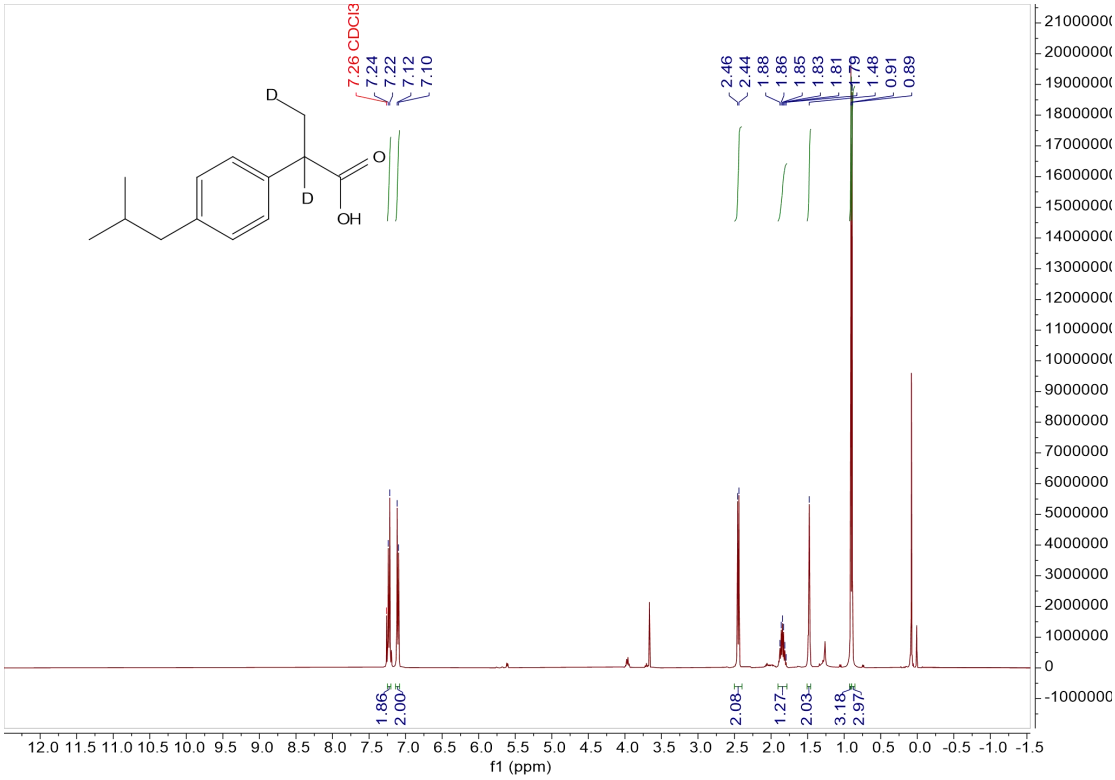
methyl 2-(4-isobutylphenyl)propanoate-2,3-d_2 (2y):

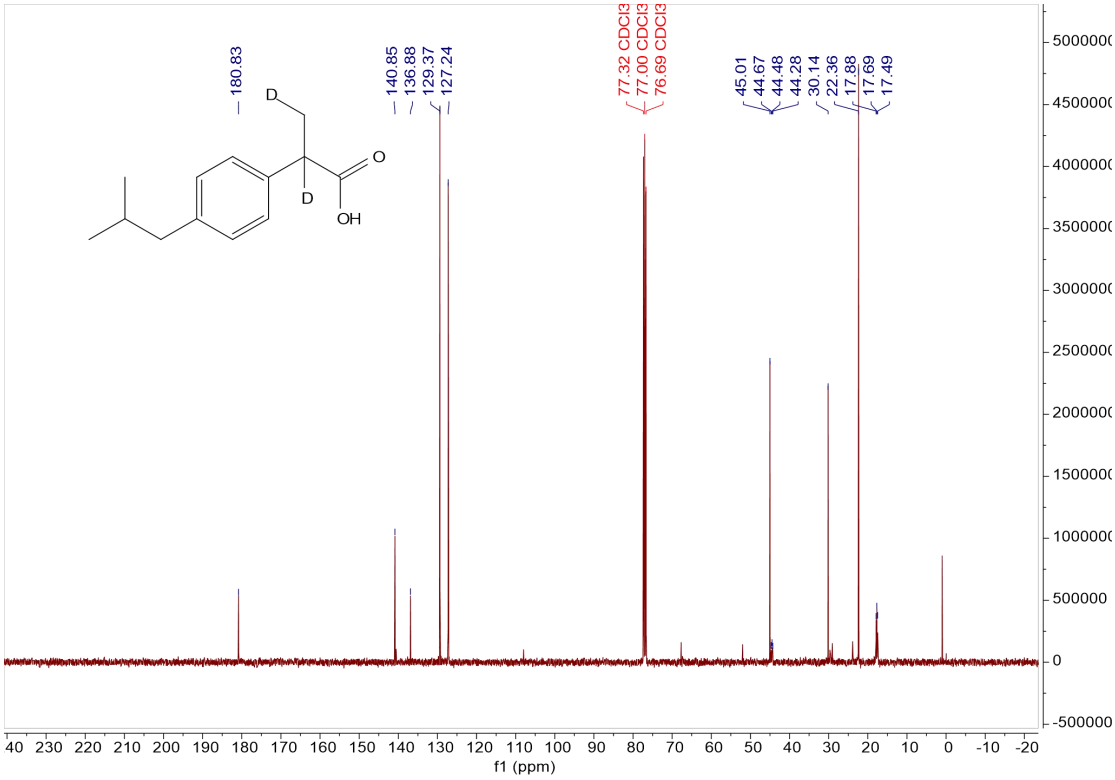


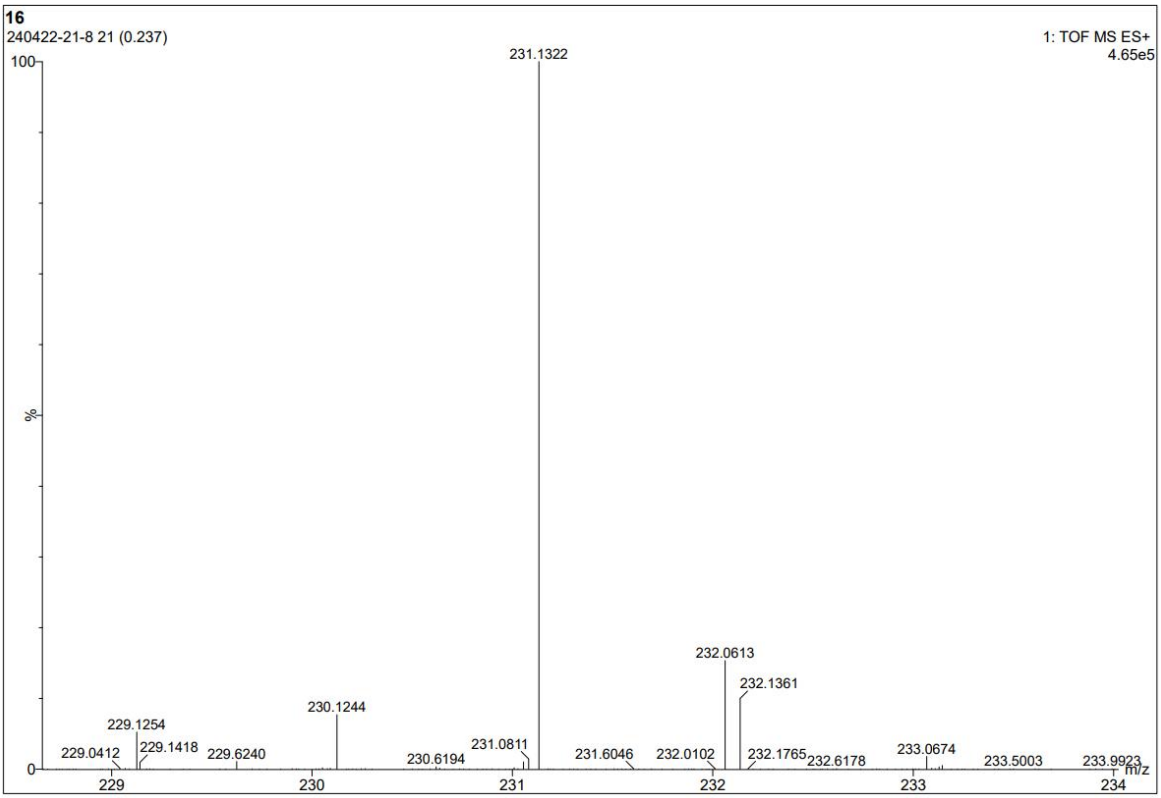




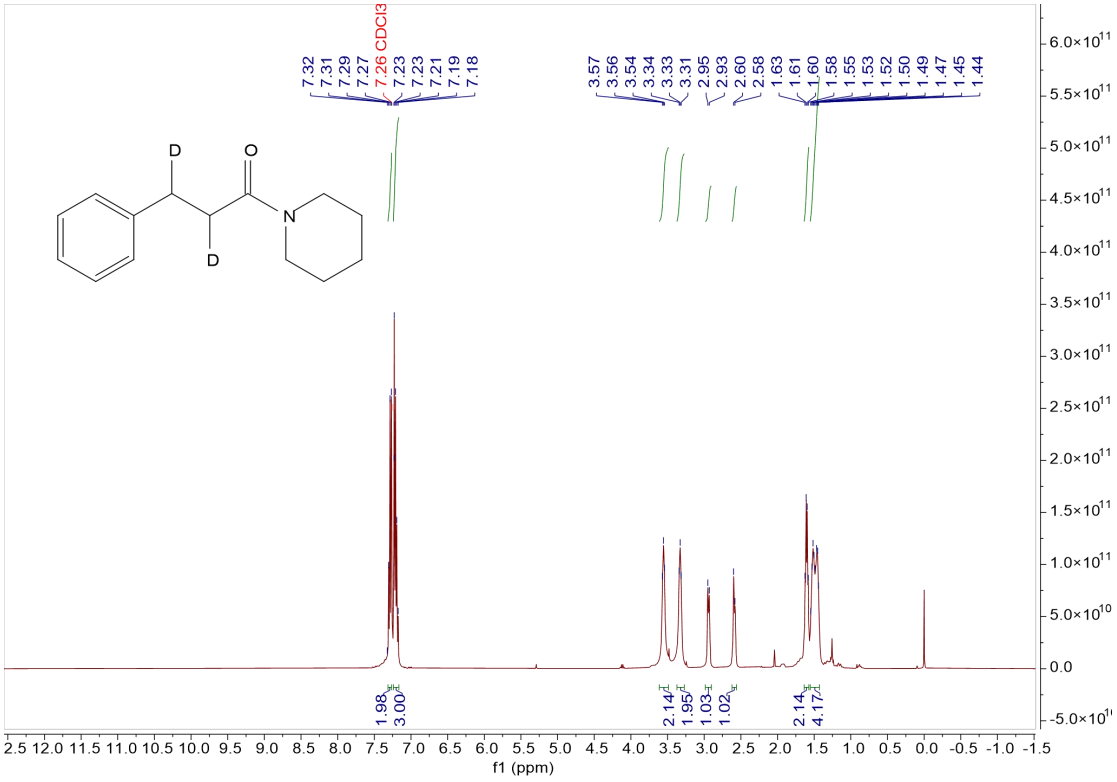
2-(4-isobutylphenyl)propanoic-2,3-d_2 acid (2z)

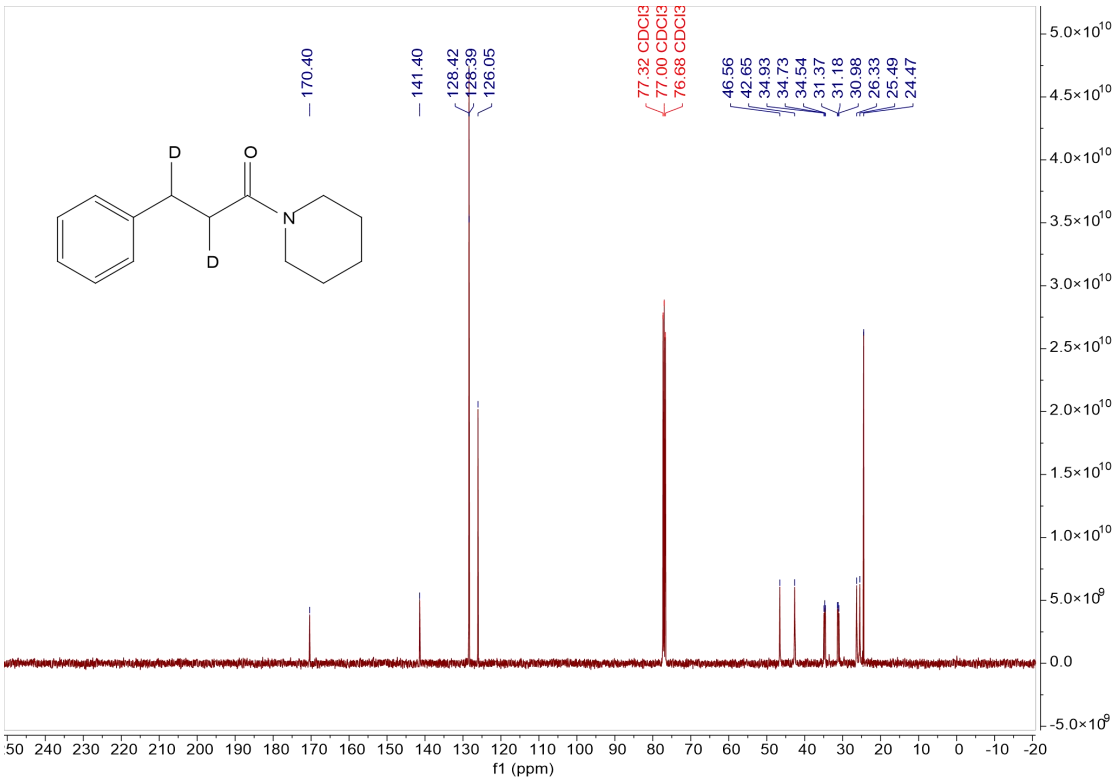

7.26 CDCl3
7.24
7.22
7.12
7.10
2.46
2.44
1.88
1.86
1.85
1.83
1.81
1.79
1.48
0.91
0.89
D
O
D
OH
1.86
2.00
2.08
1.27
2.03
3.18
2.97
f1 (ppm)

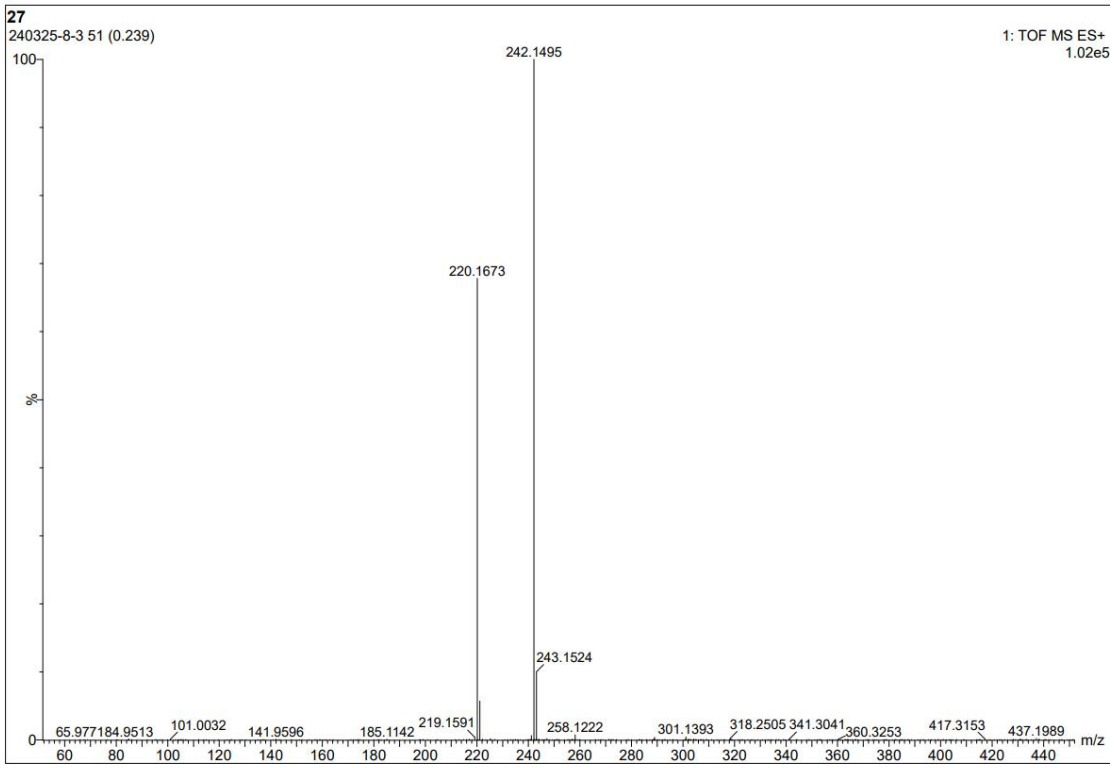

180.83
140.85
136.88
129.37
127.24
77.32 CDCl3
77.00 CDCl3
76.69 CDCl3
45.01
44.67
44.48
44.28
30.14
22.36
17.88
17.69
17.49
D
O
D
OH
f1 (ppm)



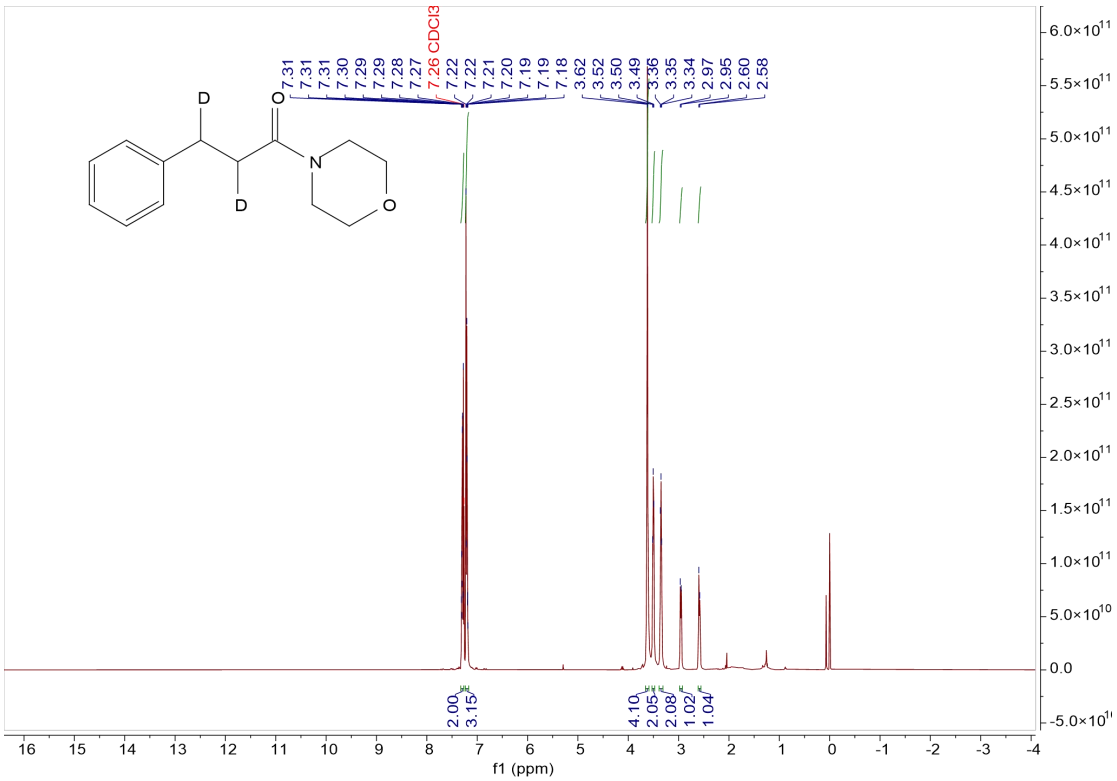
3-phenyl-1-(piperidin-1-yl)propan-1-one-2,3-d_2 (2aa):

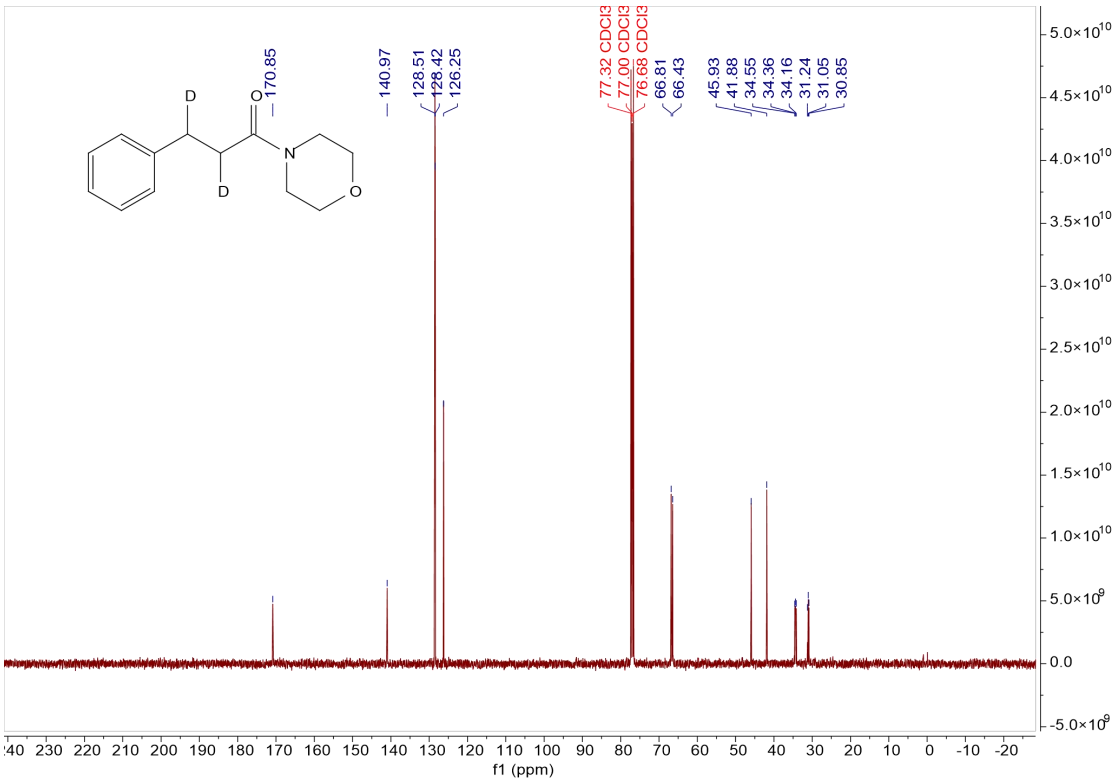


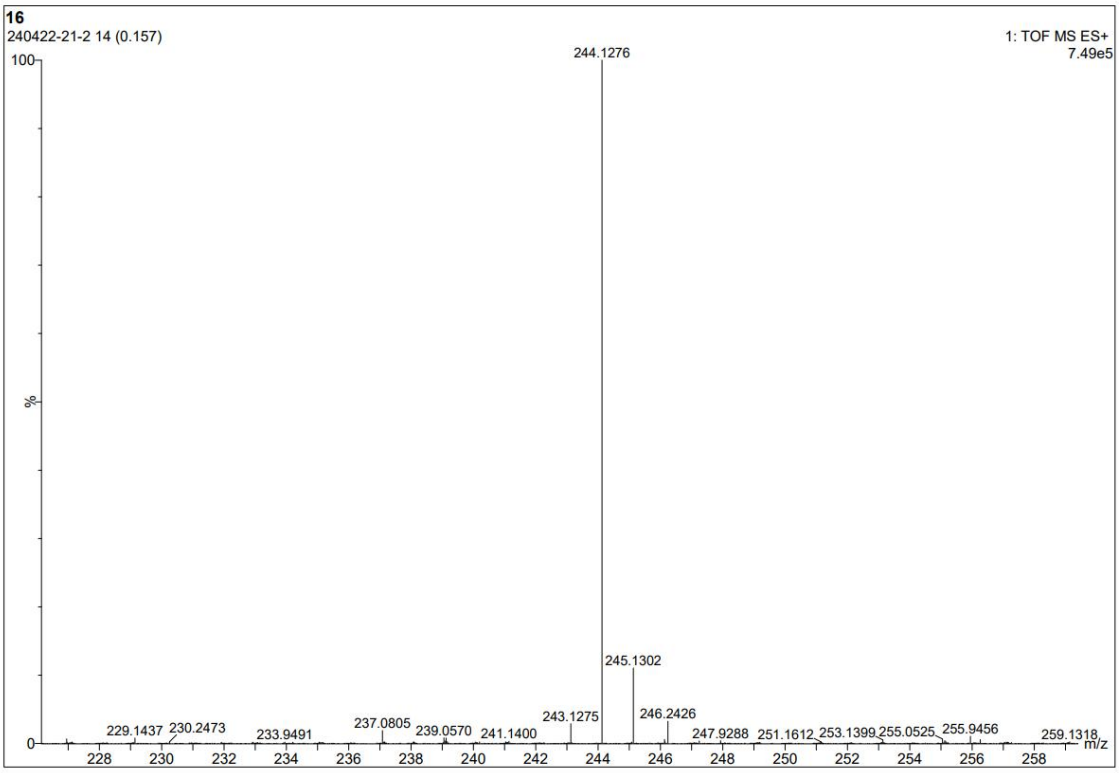




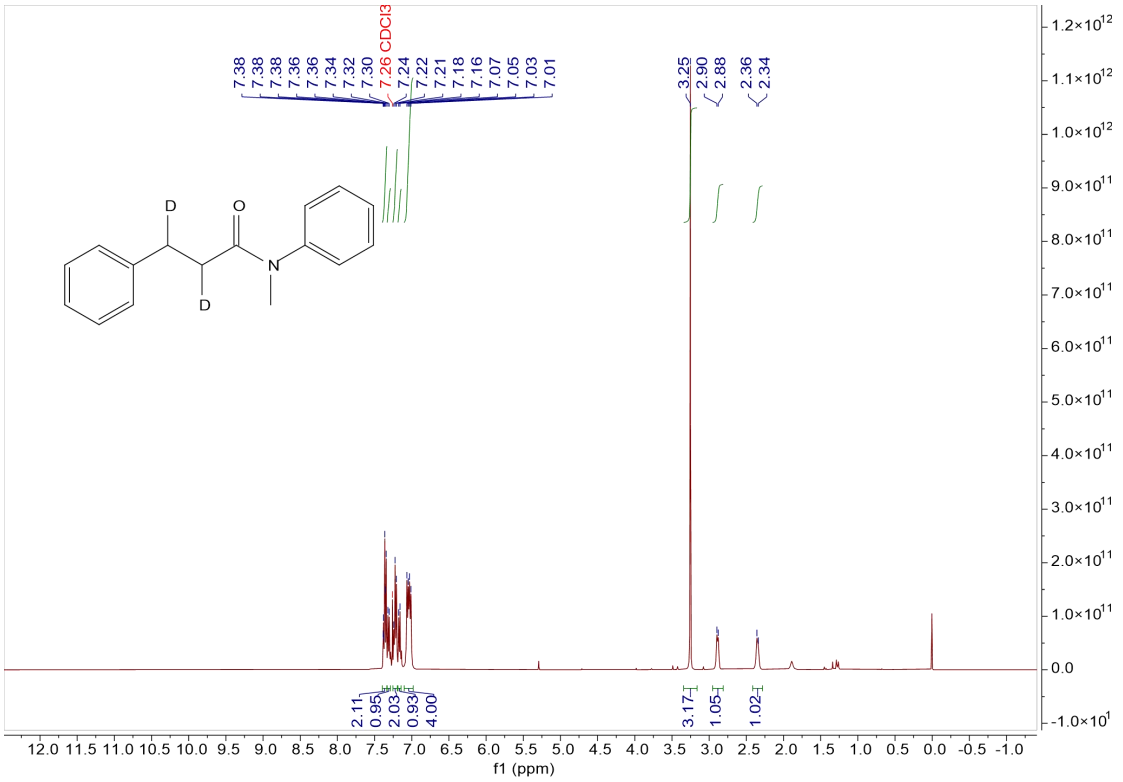
1-morpholino-3-phenylpropan-1-one-2,3-d_2 (2ab):

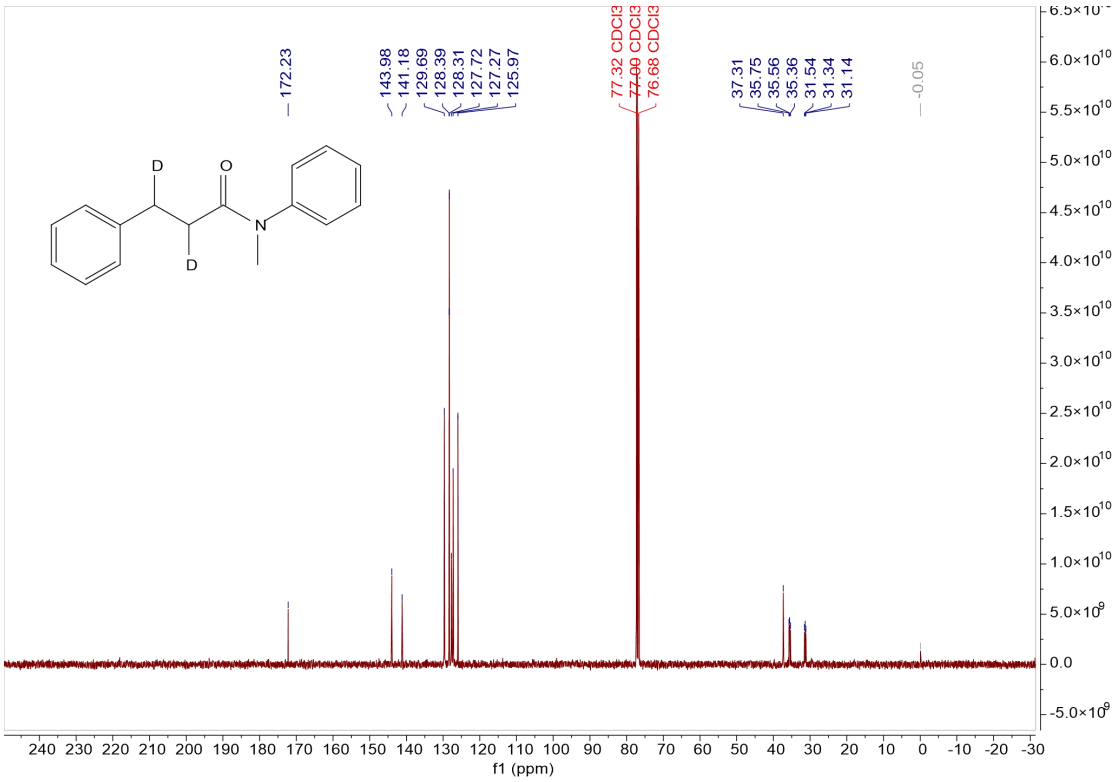

7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.26 CDCl3
7.22
7.22
7.21
7.20
7.19
7.19
7.18
3.62
3.52
3.50
3.49
3.36
3.35
3.34
2.97
2.95
2.60
2.58
D
O
N
O
D
2.00
3.15
4.10
2.05
2.08
1.02
1.04
f1 (ppm)

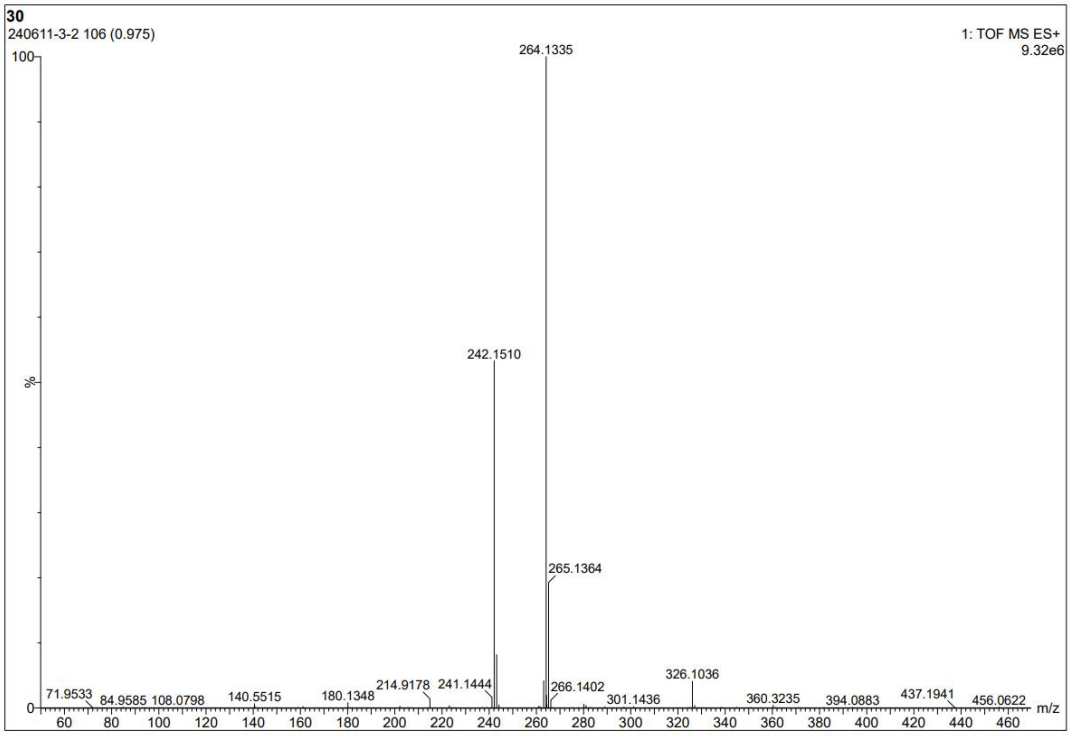

170.85
140.97
128.51
128.42
126.25
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.81
66.43
45.93
41.88
34.55
34.36
34.16
31.24
31.05
30.85
D
O
N
O
D
f1 (ppm)



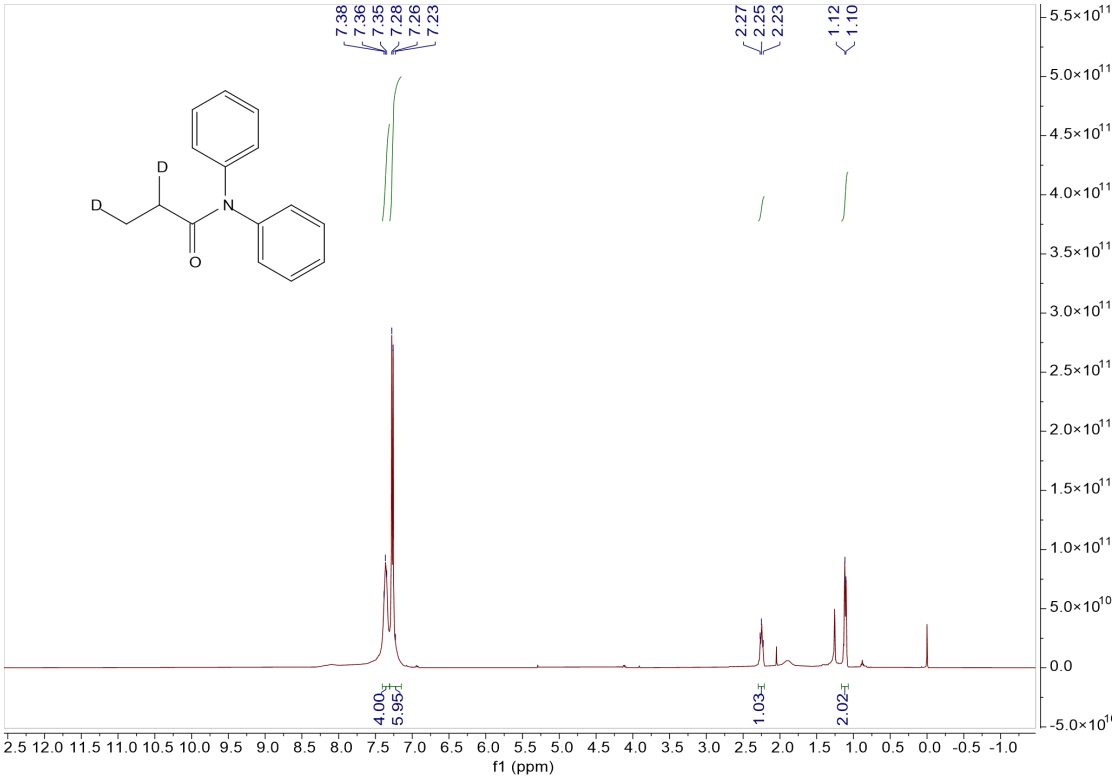
N-methyl-N,3-diphenylpropanamide-2,3-d_2 (2ac):

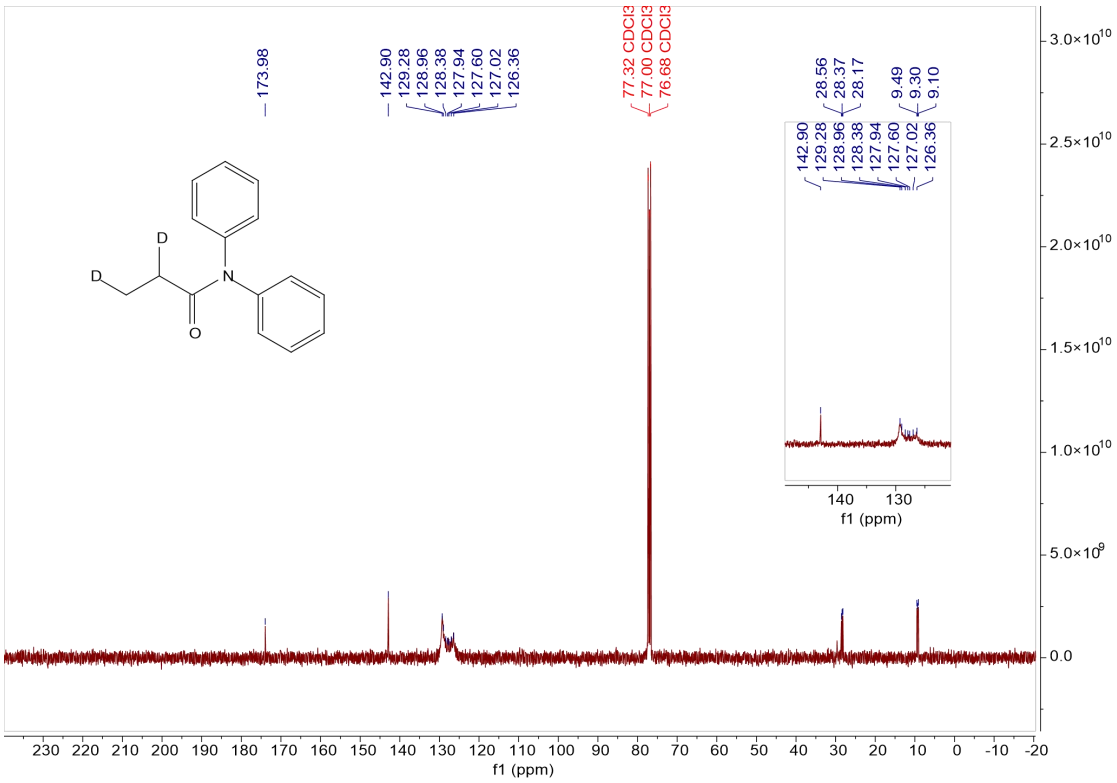


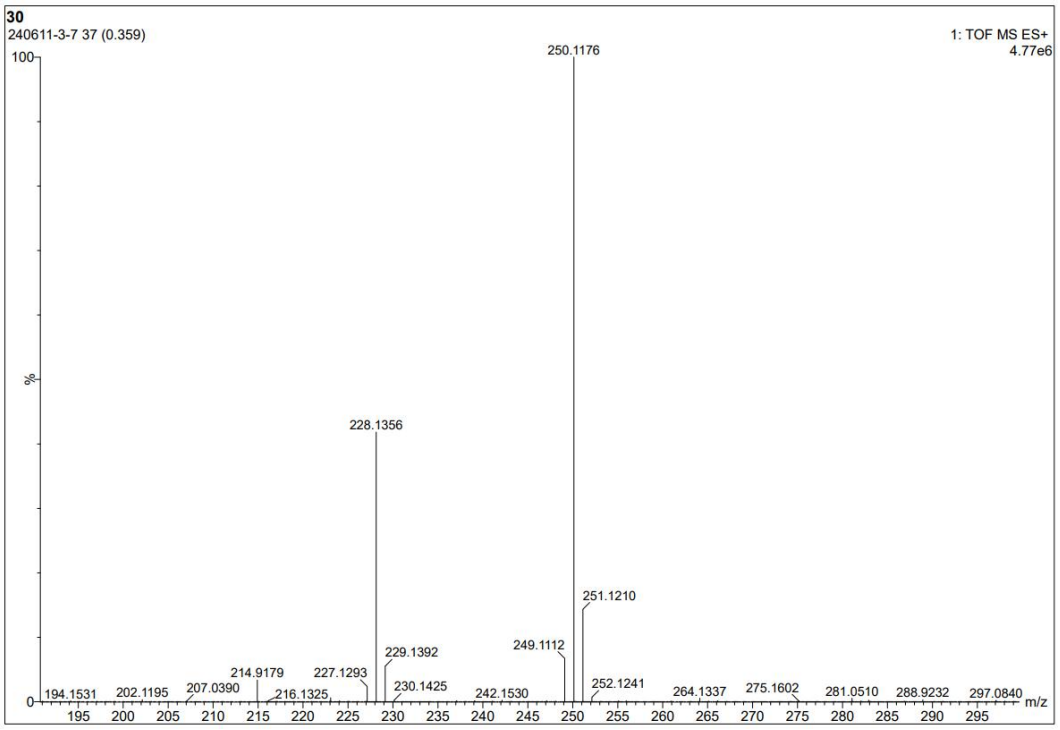




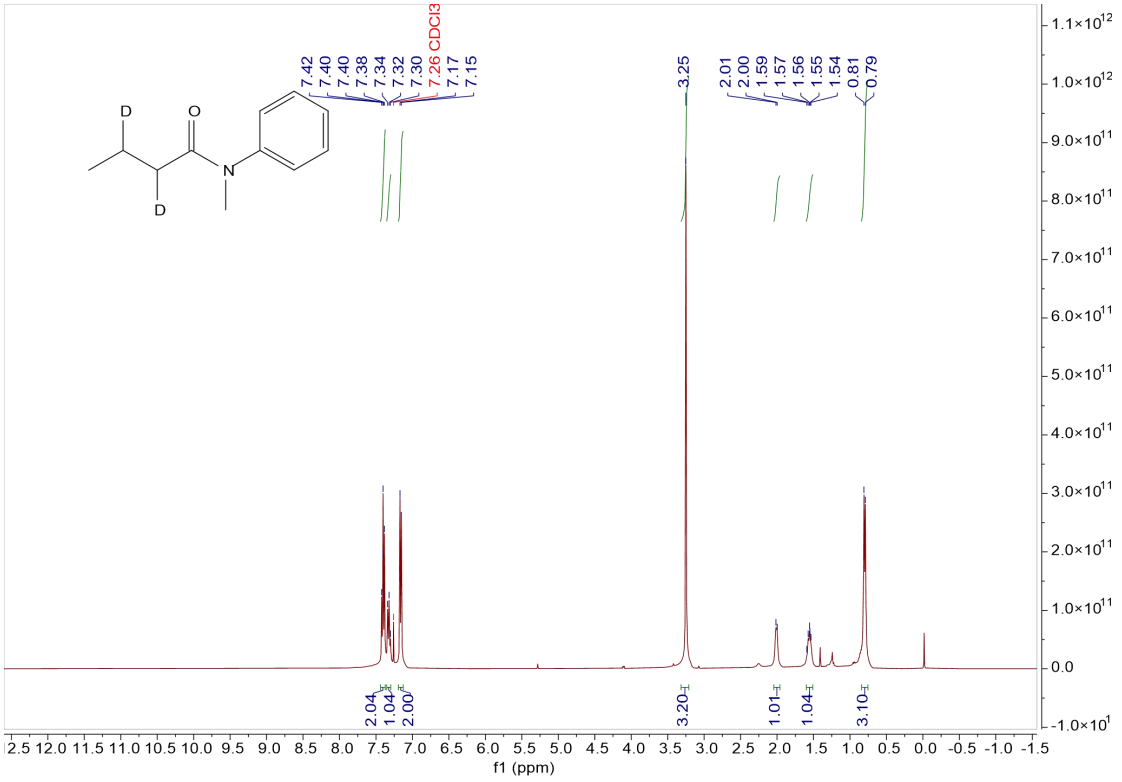
N,N-diphenylpropanamide-2,3-d_2 (2ad):

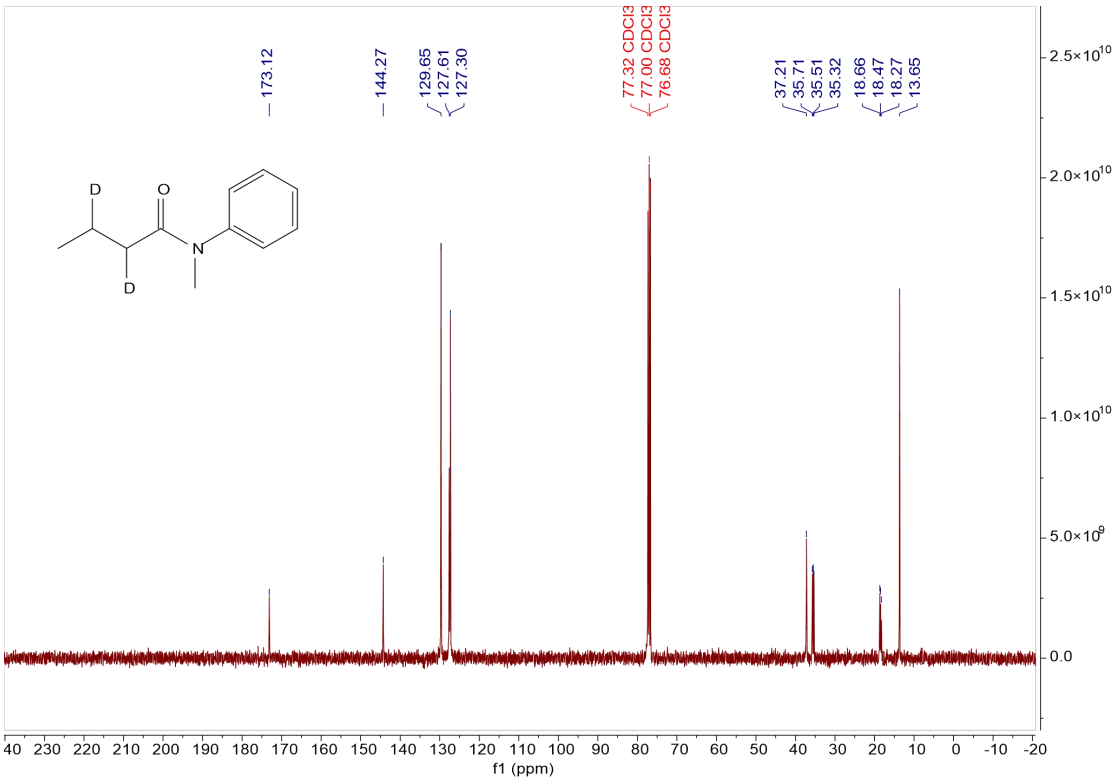

7.38
7.36
7.35
7.28
7.26
7.23
2.27
2.25
2.23
1.12
1.10
D
D
N
O
4.00
5.95
1.03
2.02
f1 (ppm)

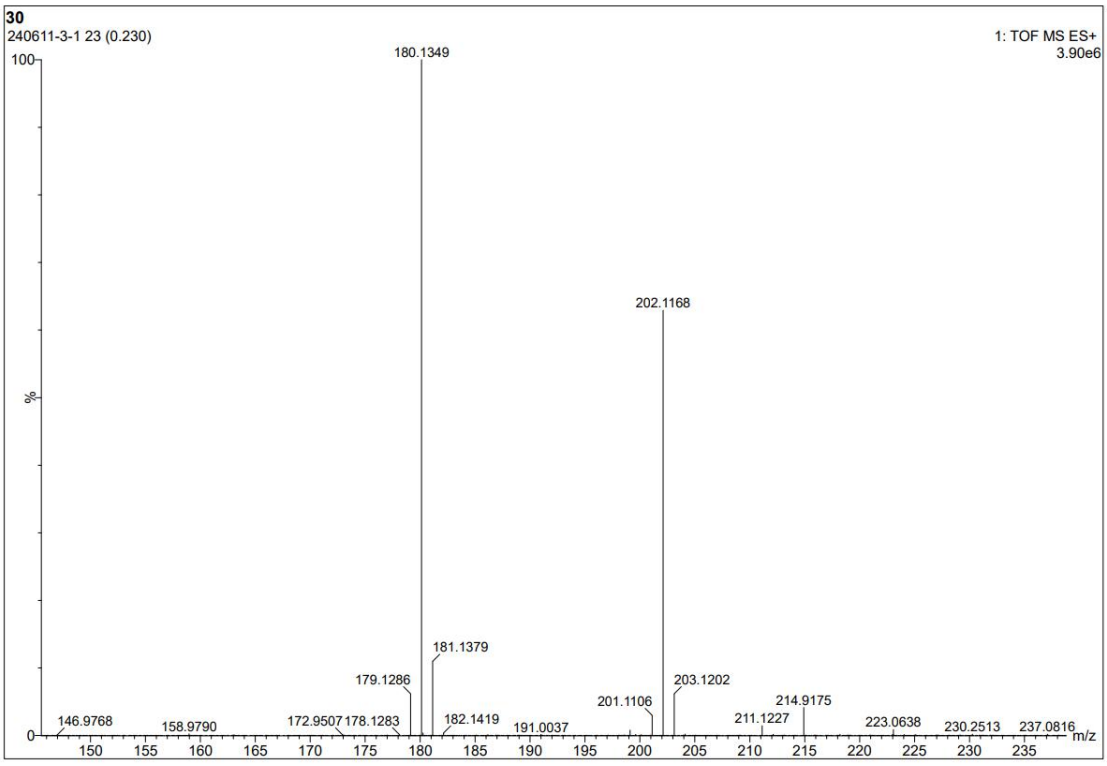

173.98
142.90
129.28
128.96
128.38
127.94
127.60
127.02
126.36
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
28.56
28.37
28.17
9.49
9.30
9.10
D
D
N
O
f1 (ppm)



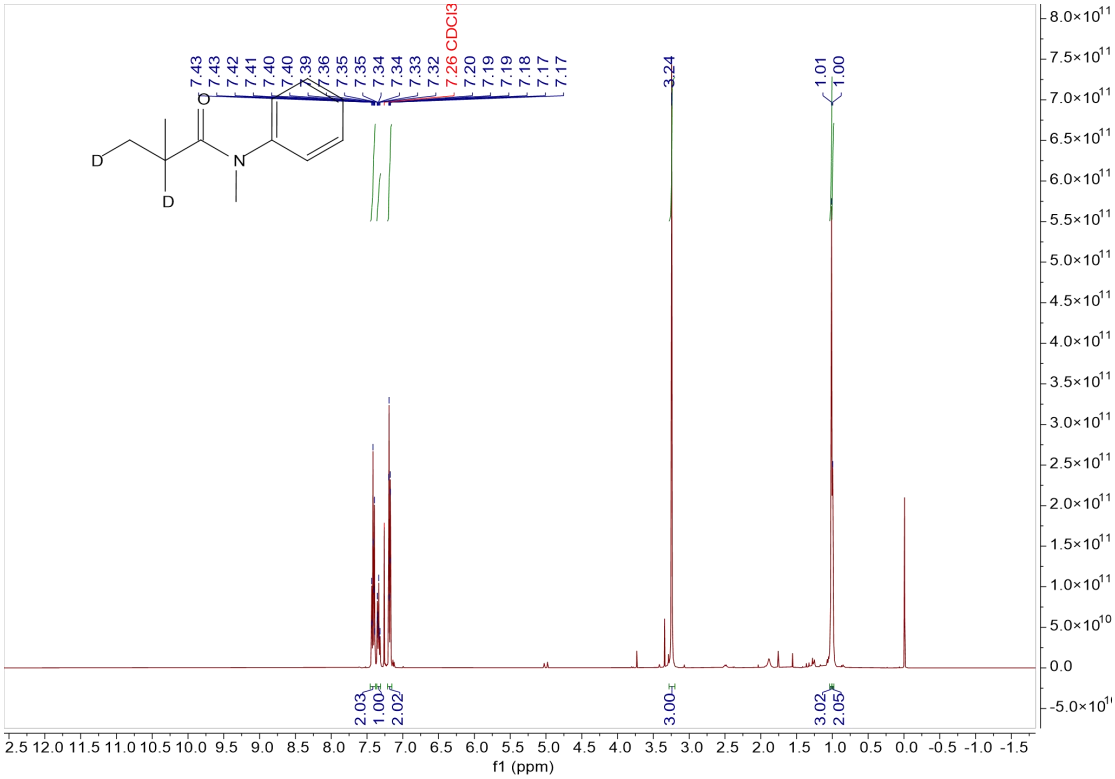
N-methyl-N-phenylbutanamide-2,3-d_2 (2ae):

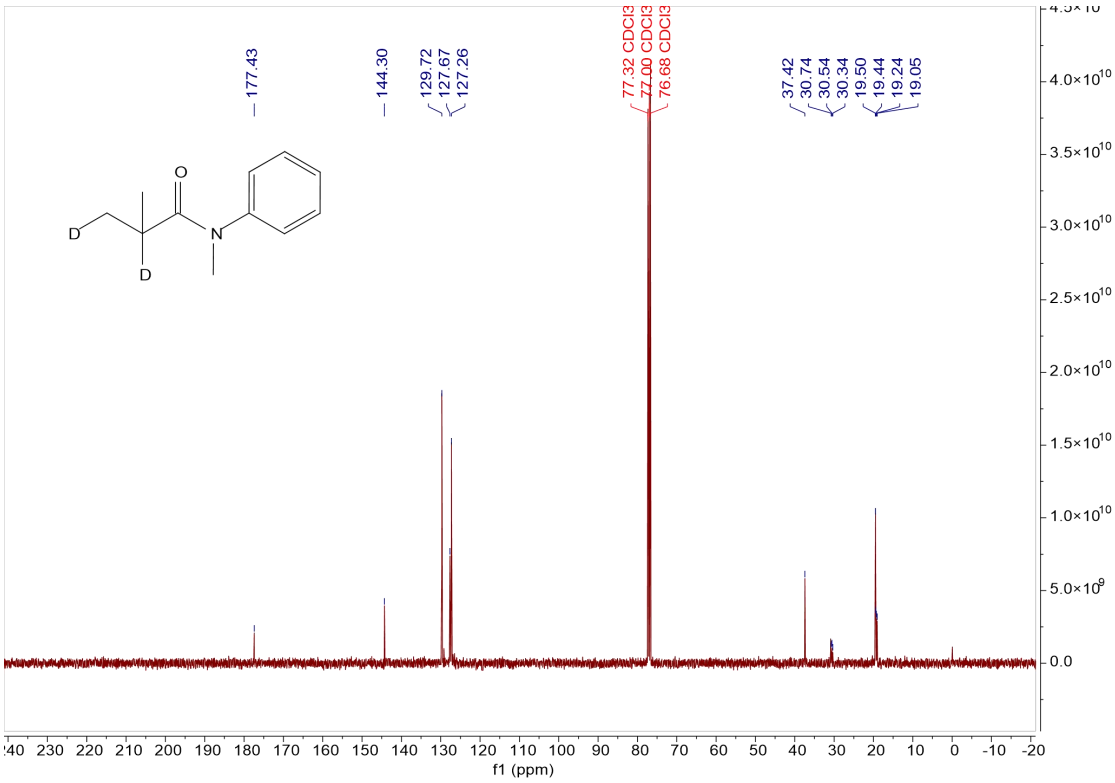


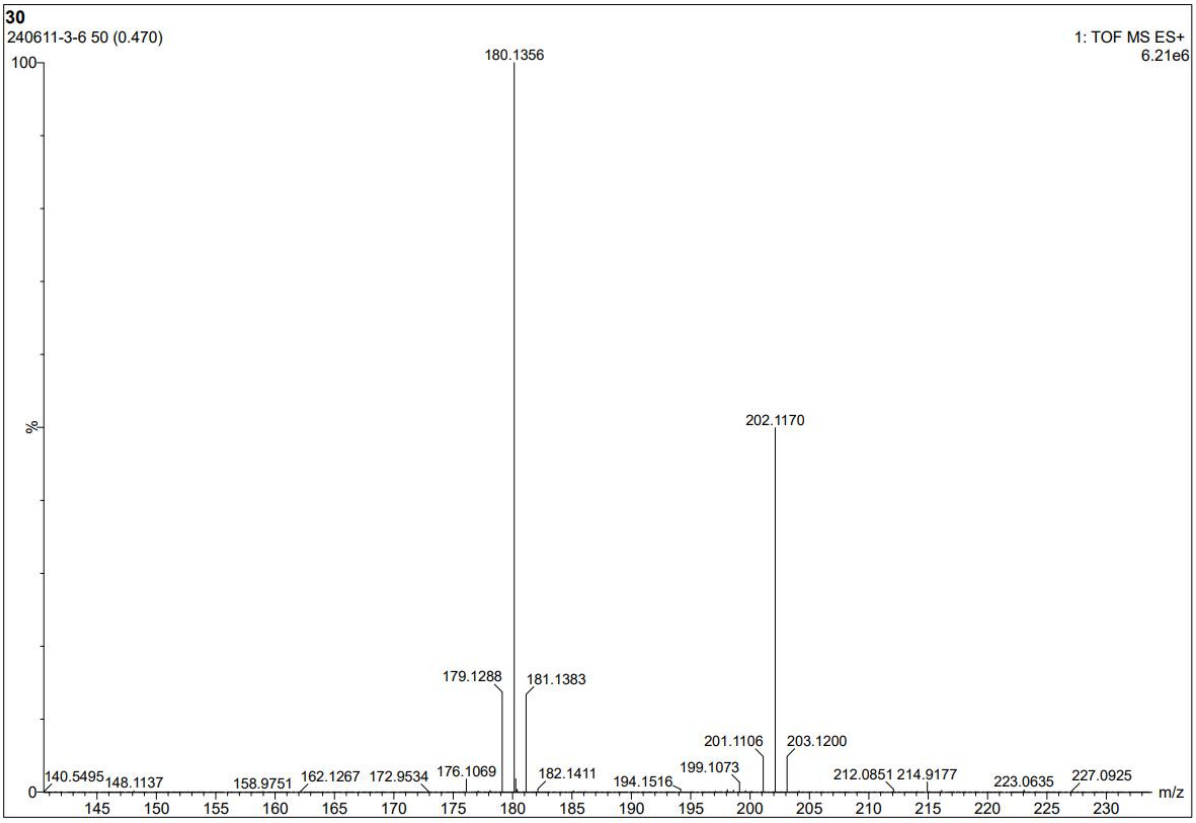




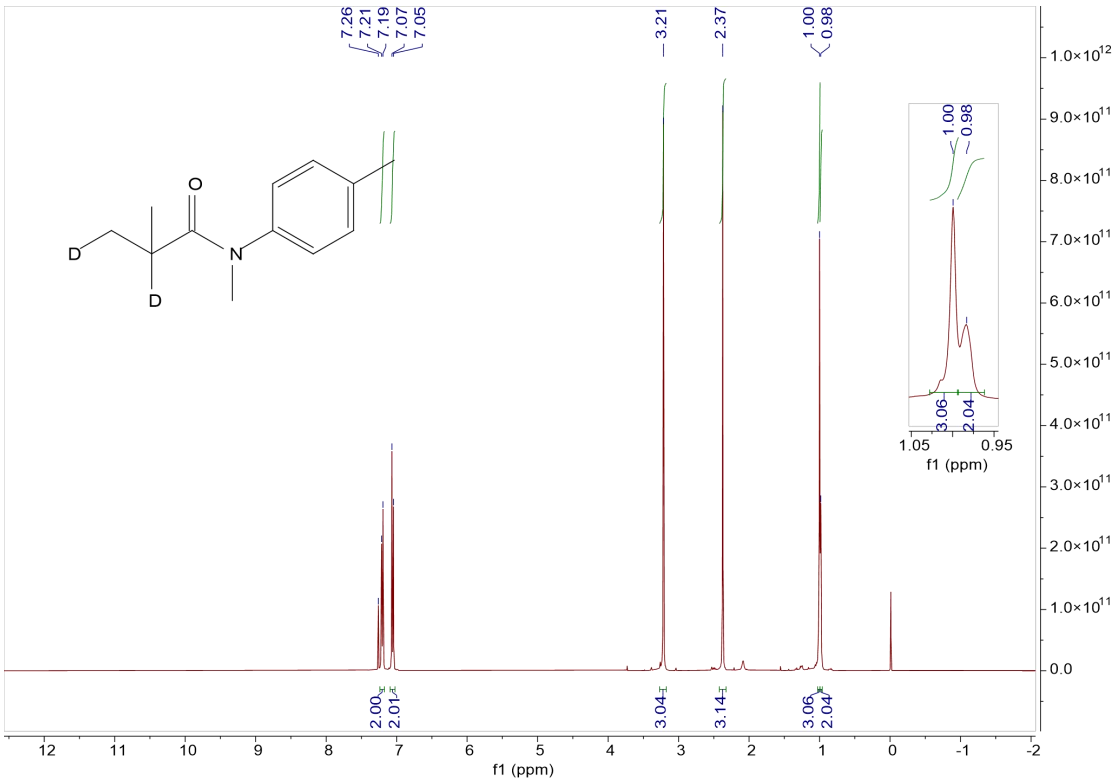
N,2-dimethyl-N-phenylpropanamide-2,3-d_2 (2af):

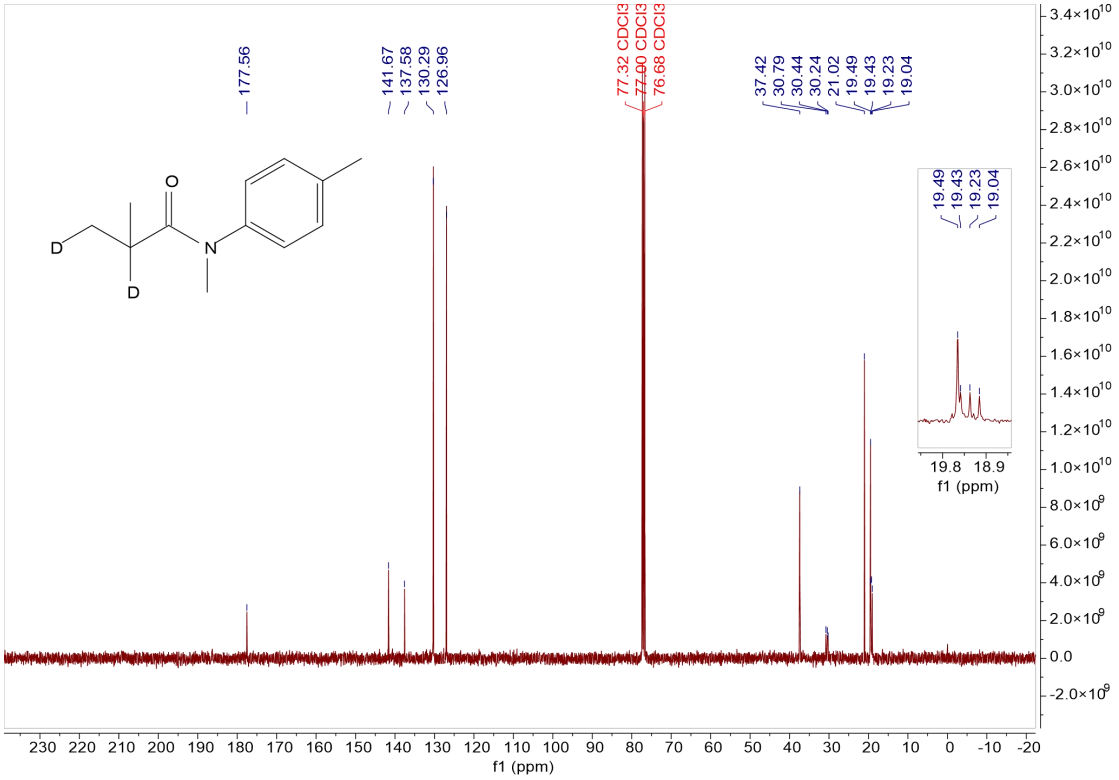

7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.26 CDCl3
7.20
7.19
7.19
7.18
7.17
7.17
3.24
1.01
1.00
O
N
D
D
2.03
1.00
2.02
3.00
3.02
2.05
f1 (ppm)

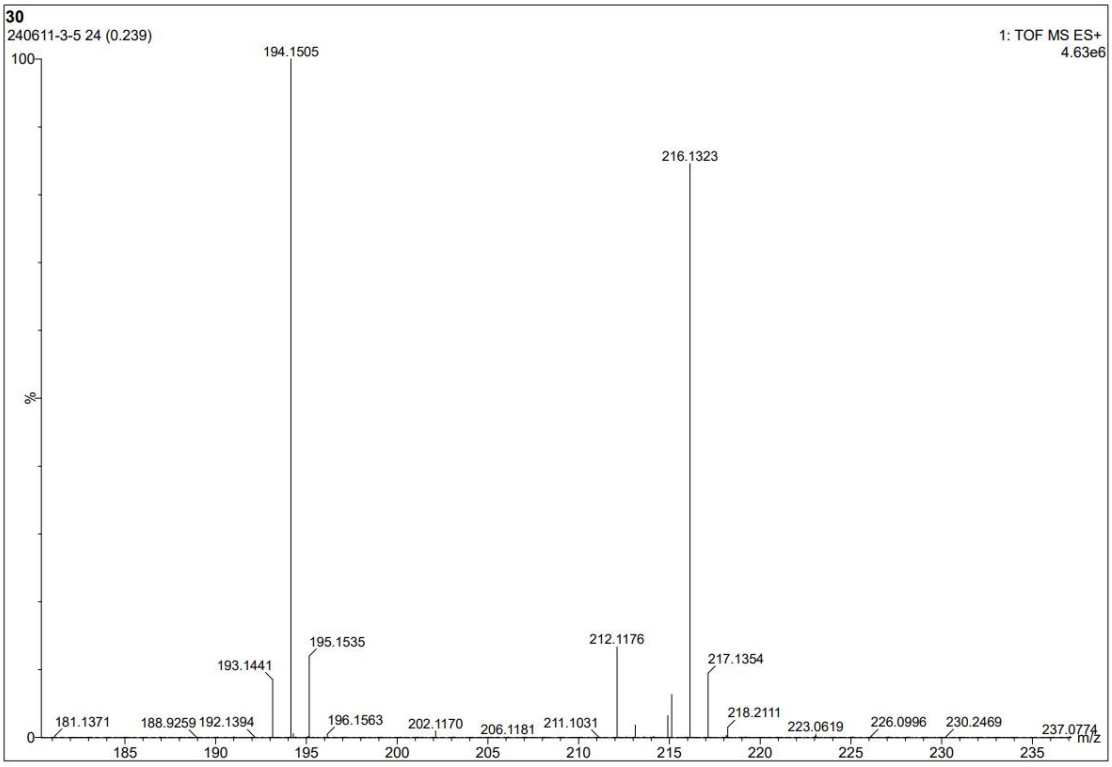

177.43
144.30
129.72
127.67
127.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
37.42
30.74
30.54
30.34
19.50
19.44
19.24
19.05
O
N
D
D
f1 (ppm)



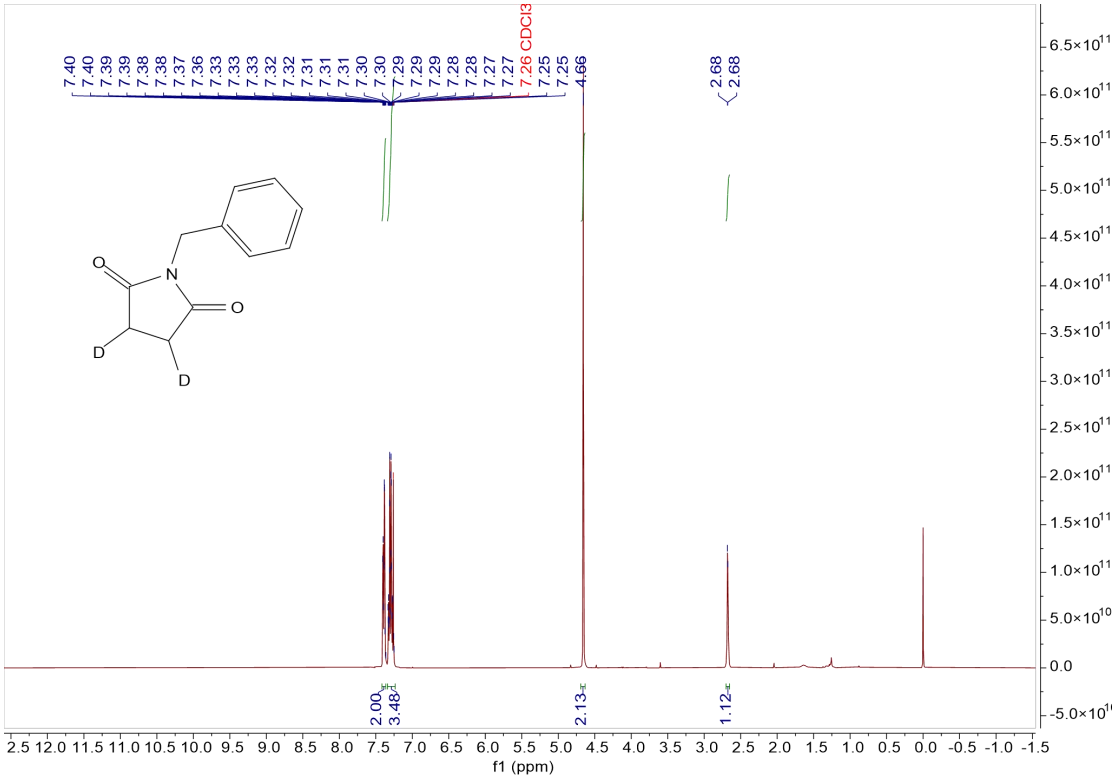
N,2-dimethyl-N-(p-tolyl)propanamide-2,3-d_2 (2ag):

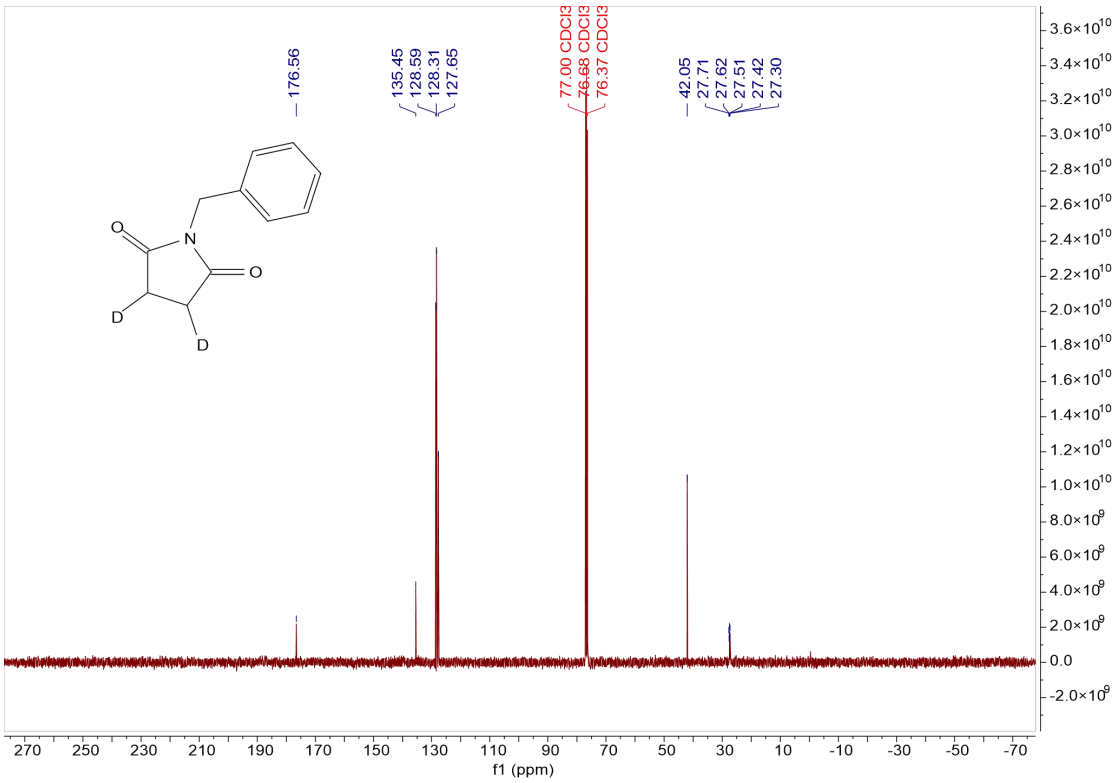


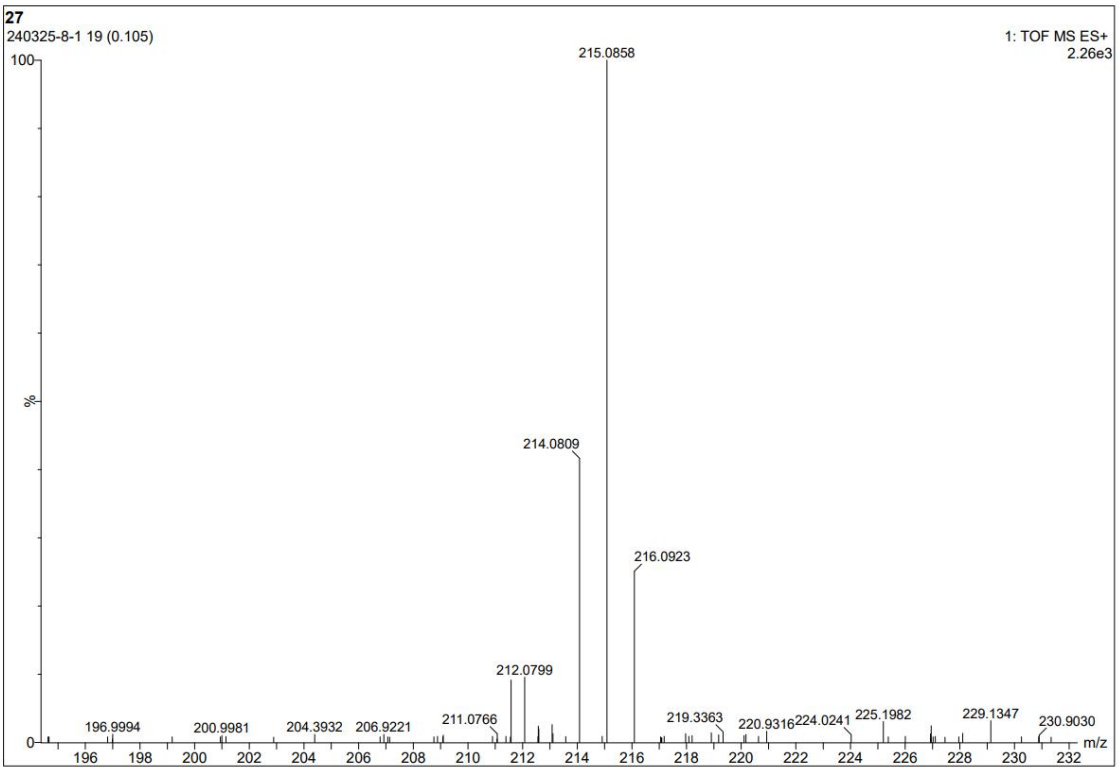




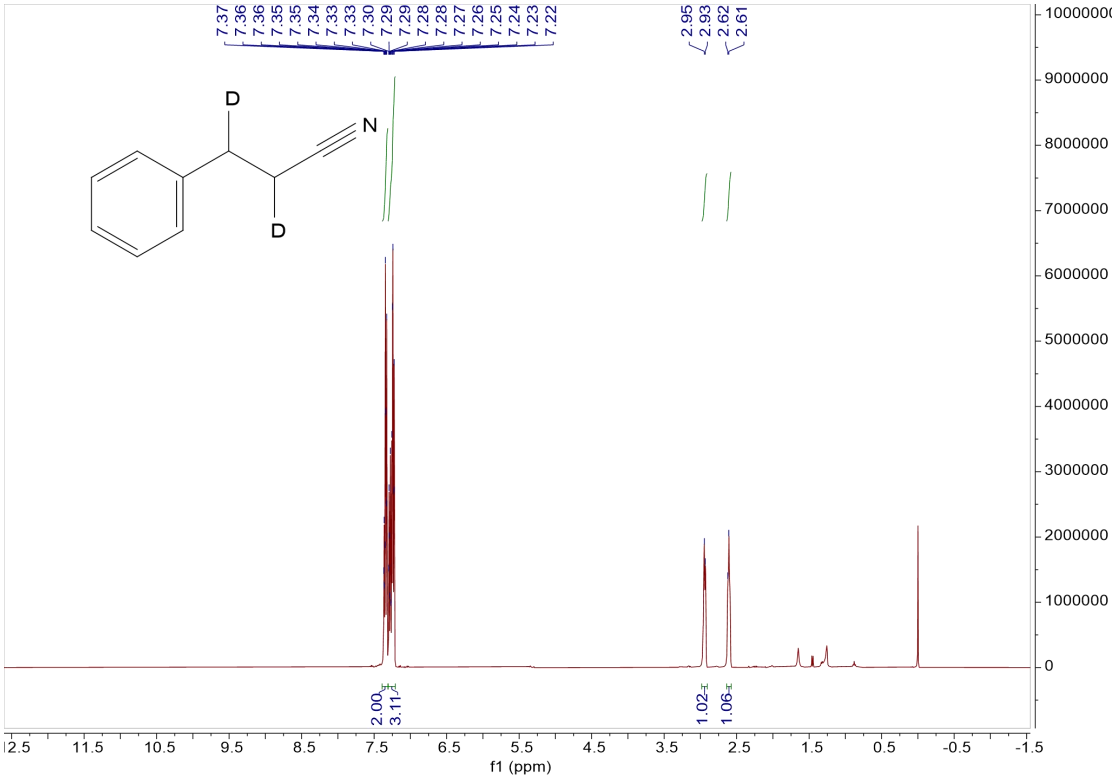
1-benzylpyrrolidine-2,5-dione-3,4-*d*$_2$ (2ah):

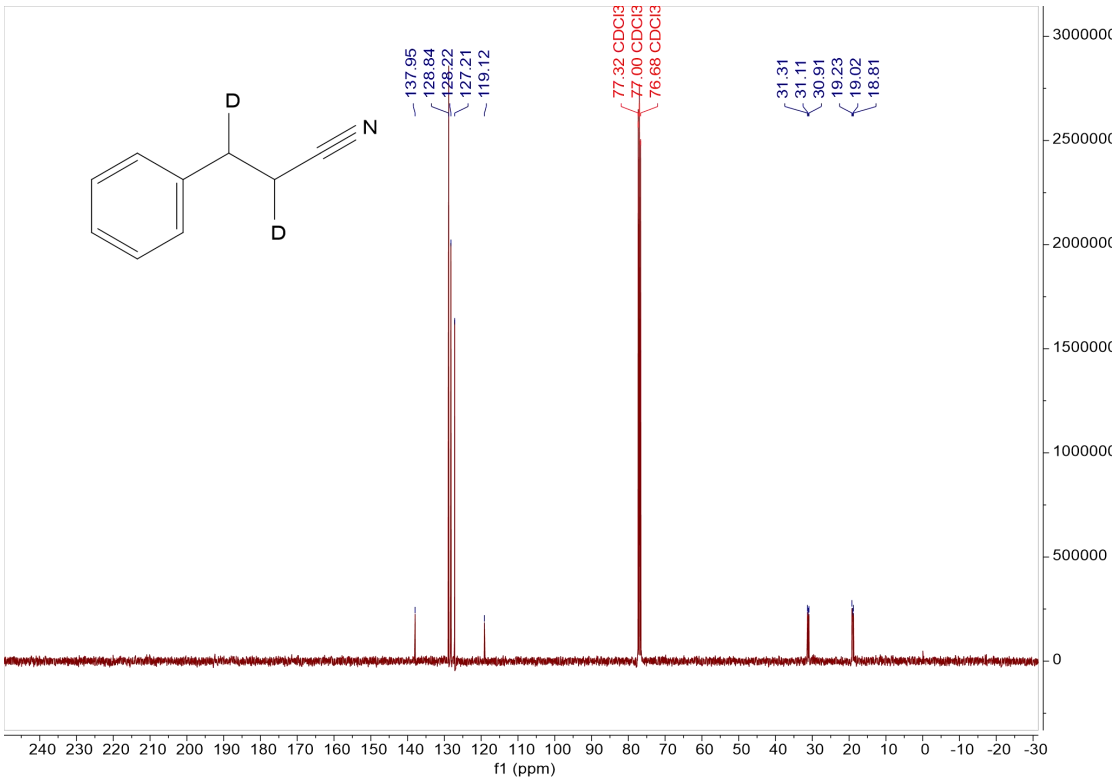

7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26 CDCl3
7.25
7.25
4.66
2.68
2.68
O
N
O
D
D
2.00
3.48
2.13
1.12
f1 (ppm)

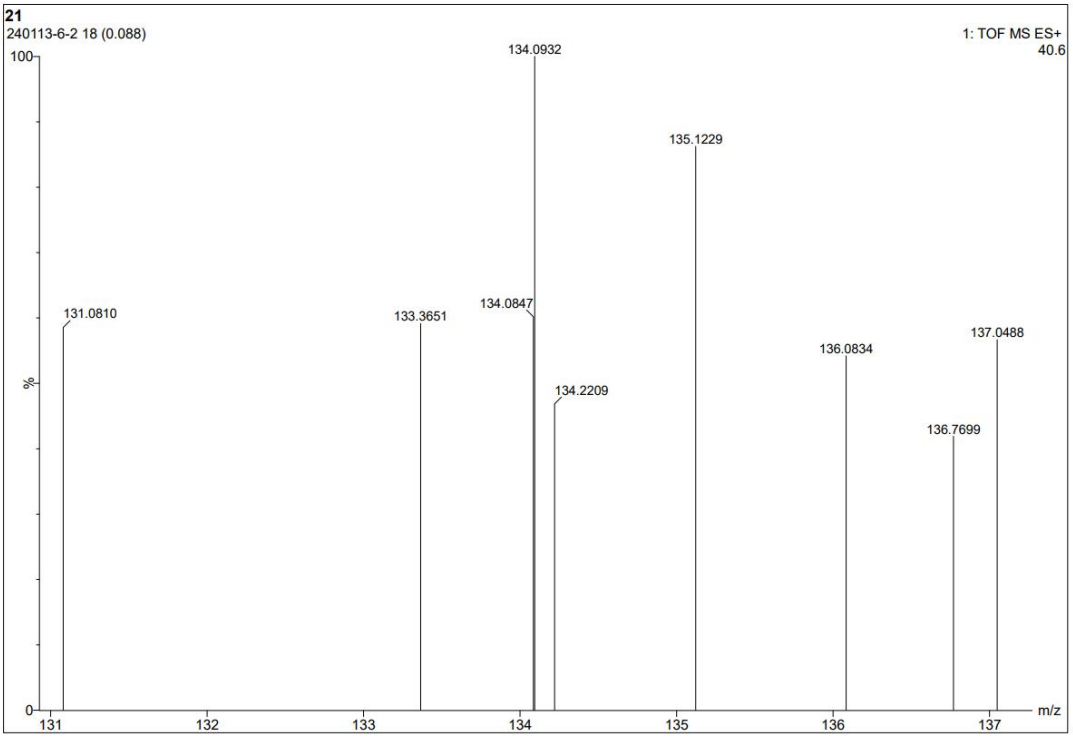

176.56
135.45
128.59
128.31
127.65
77.00 CDCl3
76.68 CDCl3
76.37 CDCl3
42.05
27.71
27.62
27.51
27.42
27.30
O
N
O
D
D
f1 (ppm)



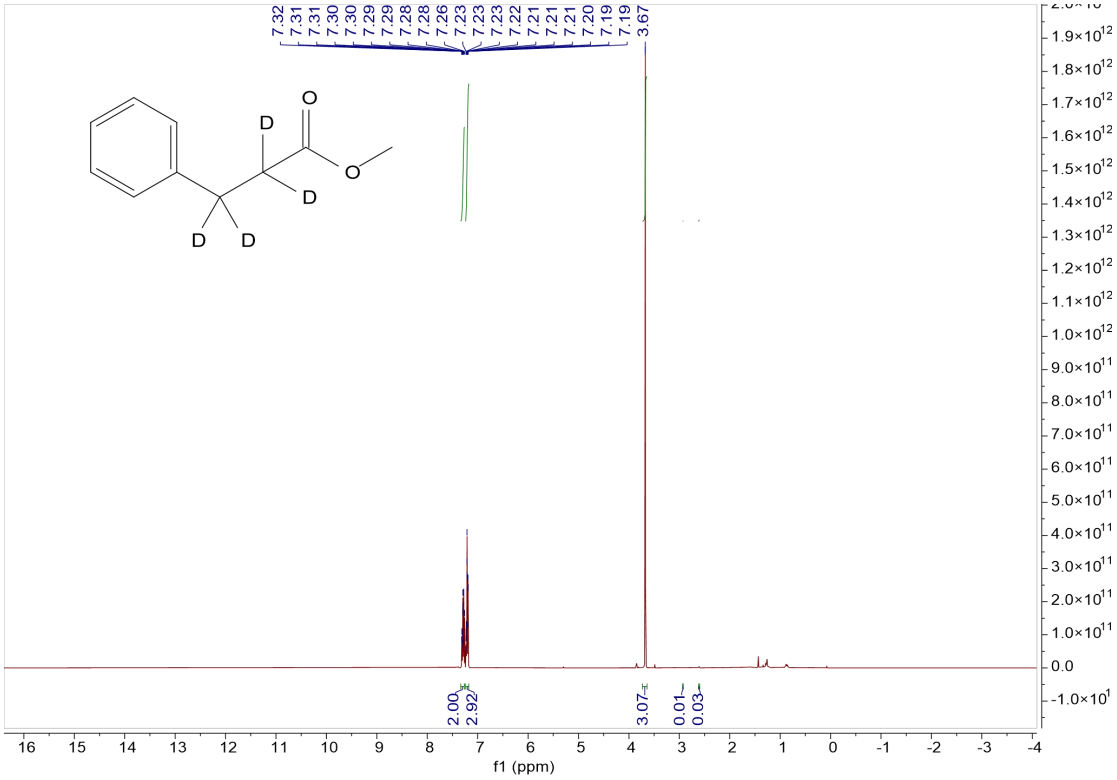
3-phenylpropanenitrile-2,3-d_2 (2ai):

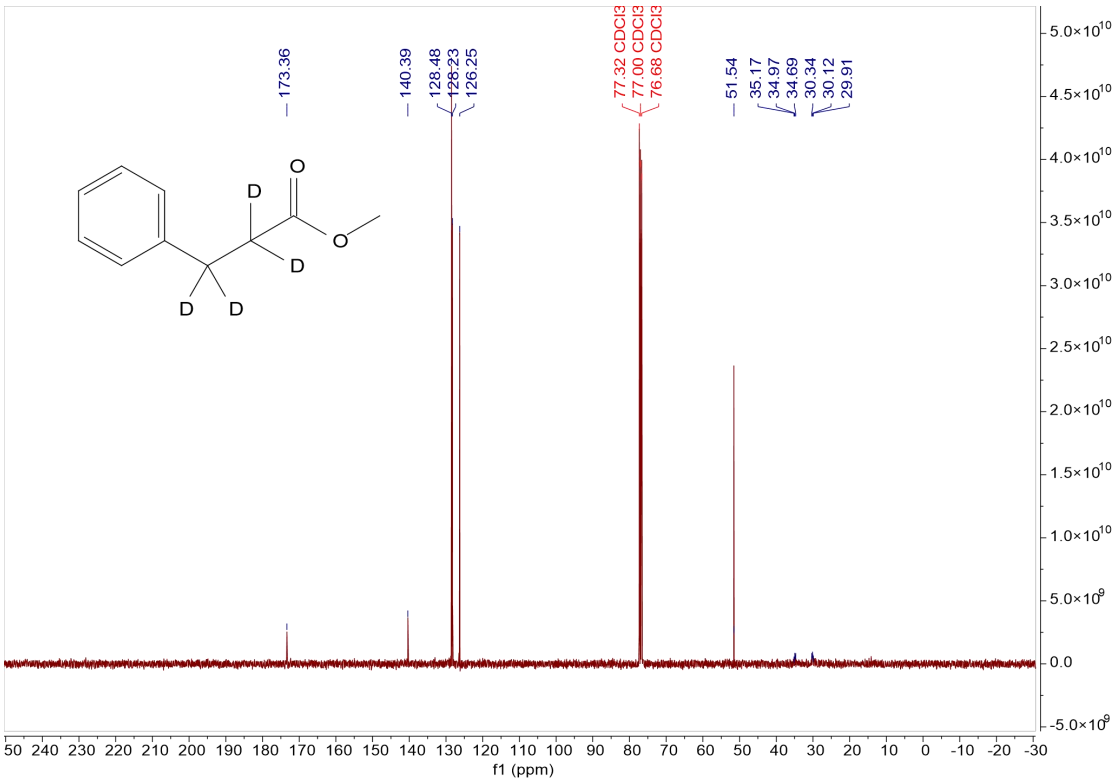


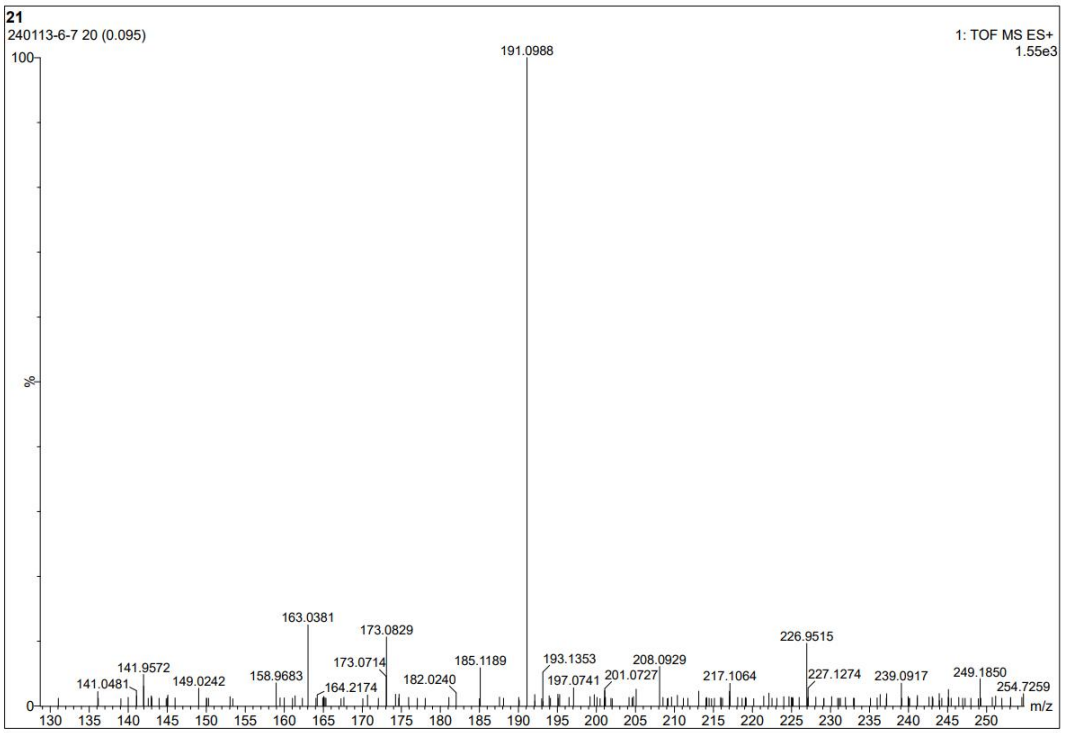




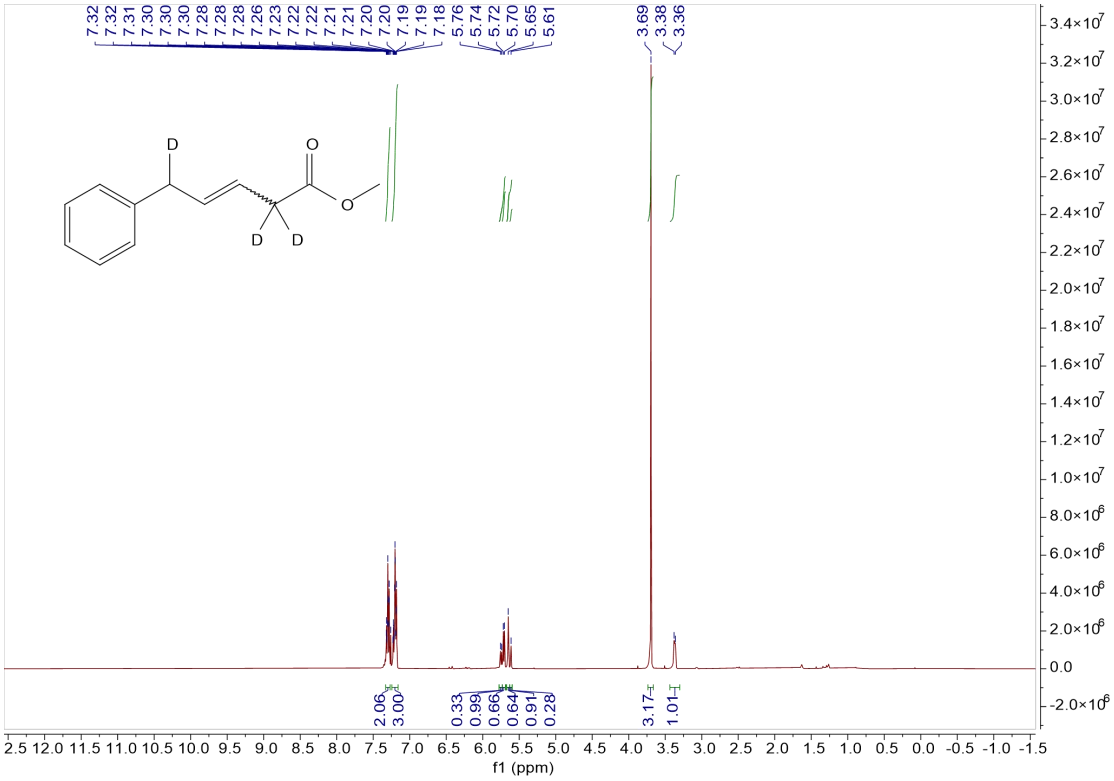
methyl 3-phenylpropanoate-2,2,3,3-*d*$_4$ (2aj):

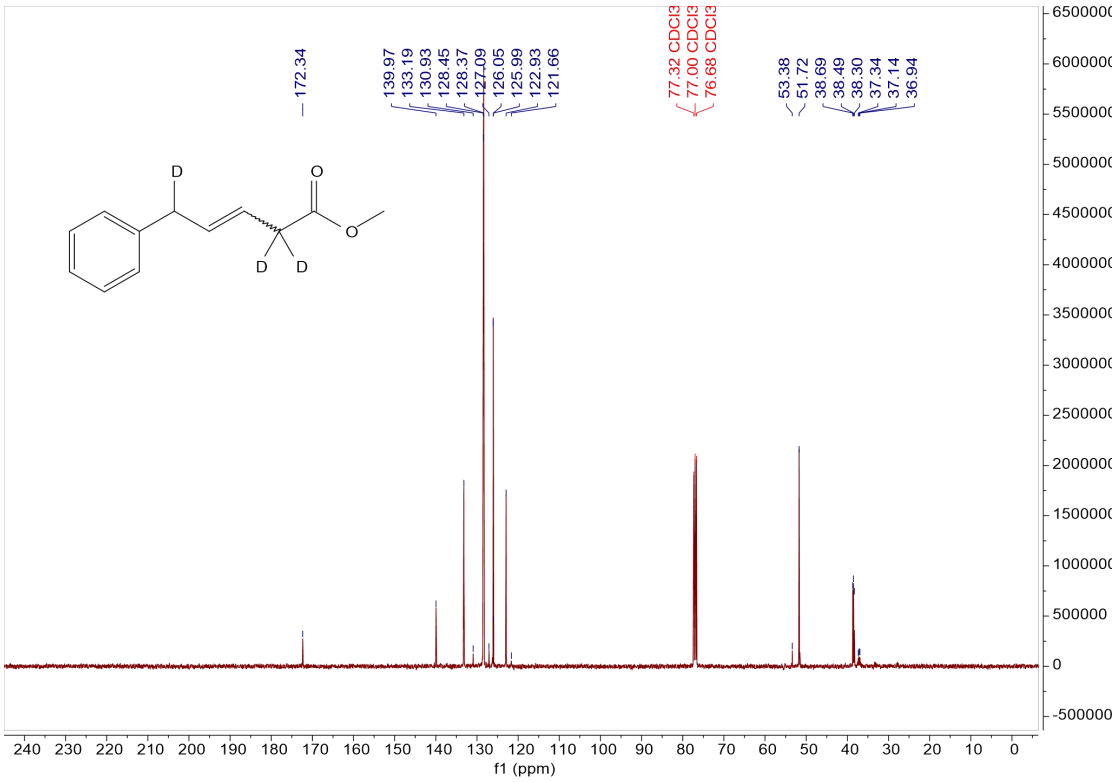

7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.19
3.67
O
D
O
D
D
D
2.00
2.92
3.07
0.01
0.03
f1 (ppm)

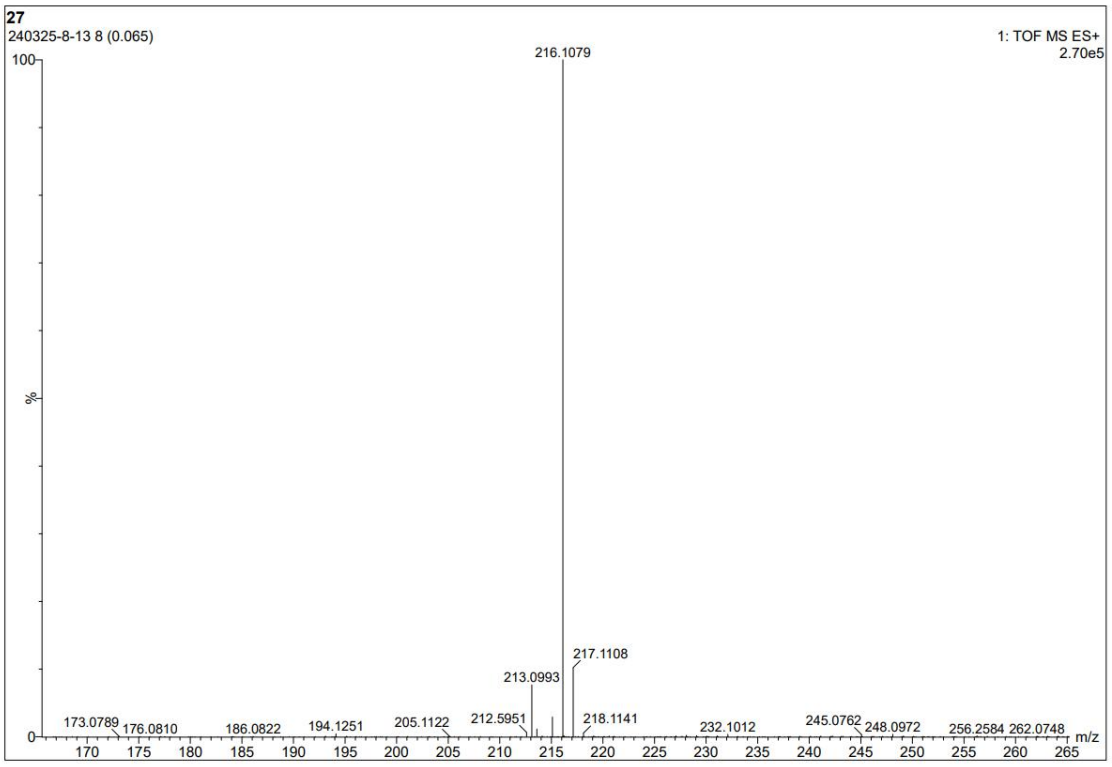

173.36
140.39
128.48
128.23
126.25
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.54
35.17
34.97
34.69
30.34
30.12
29.91
O
D
O
D
D
D
f1 (ppm)



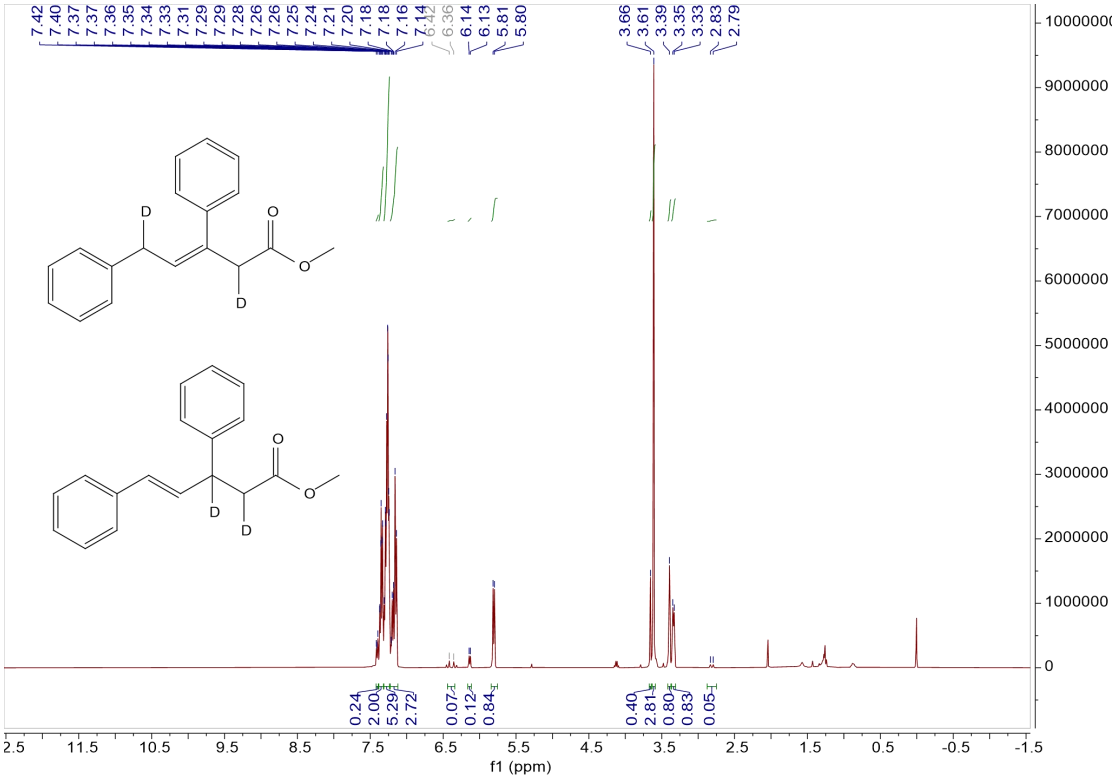
methyl 5-phenylpent-3-enoate-2,2,5-d_3 (4a):

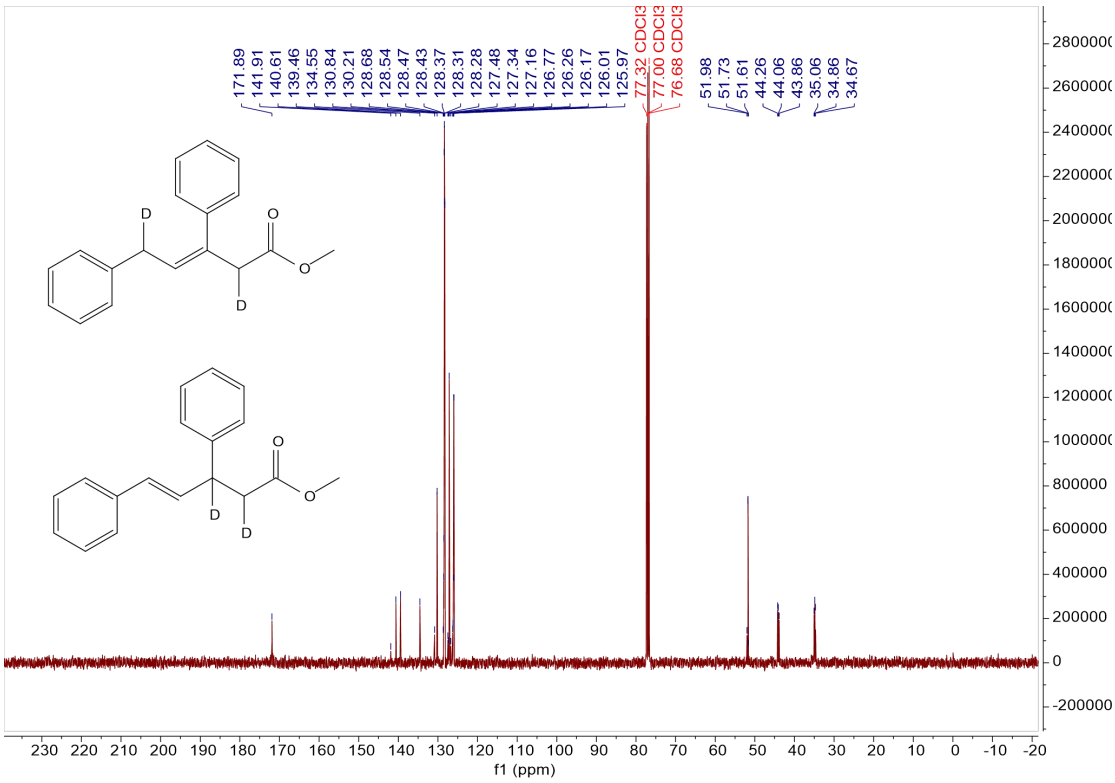


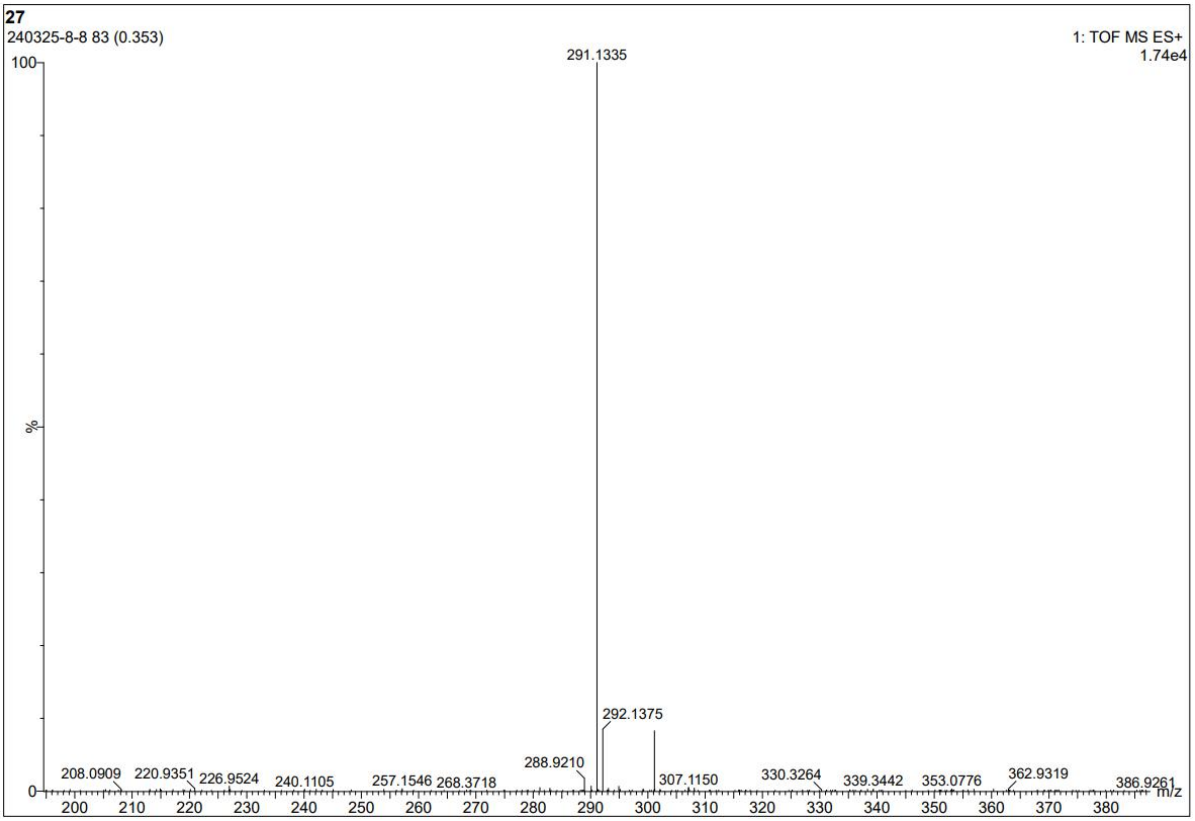




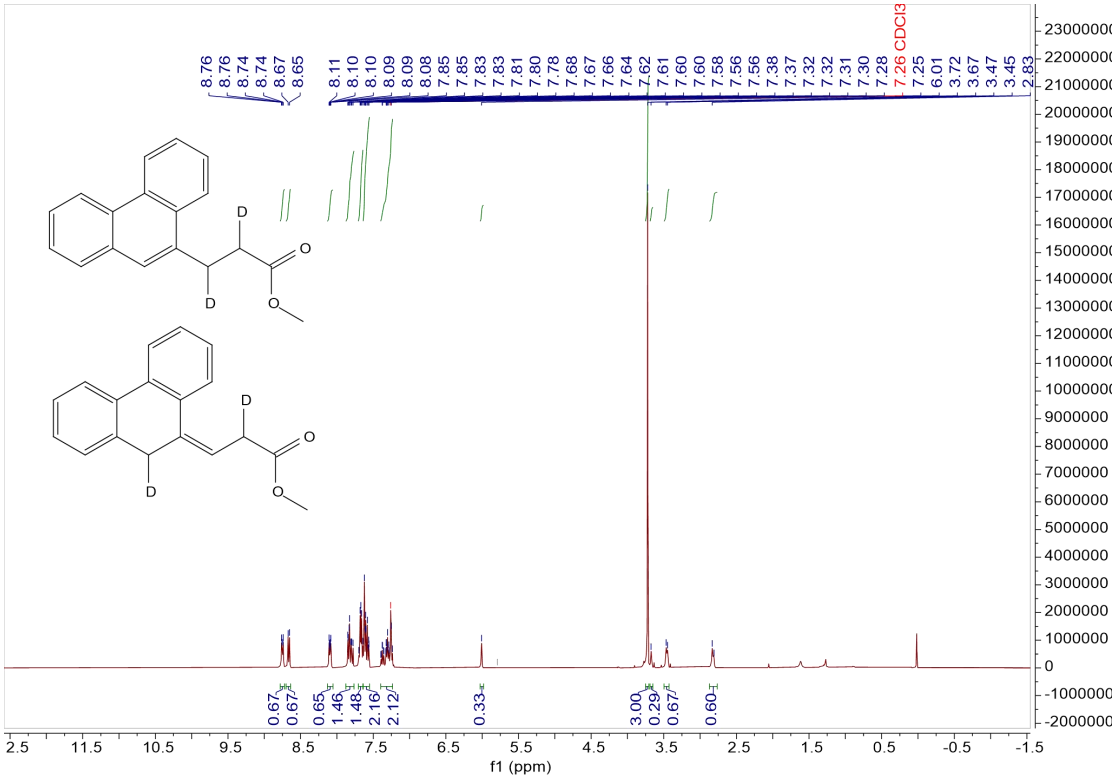
methyl 3,5-diphenylpent-3-enoate-2,5-d_2 & methyl 3,5-diphenylpent-4-enoate-2,3-d_2 (4b & 4b'):

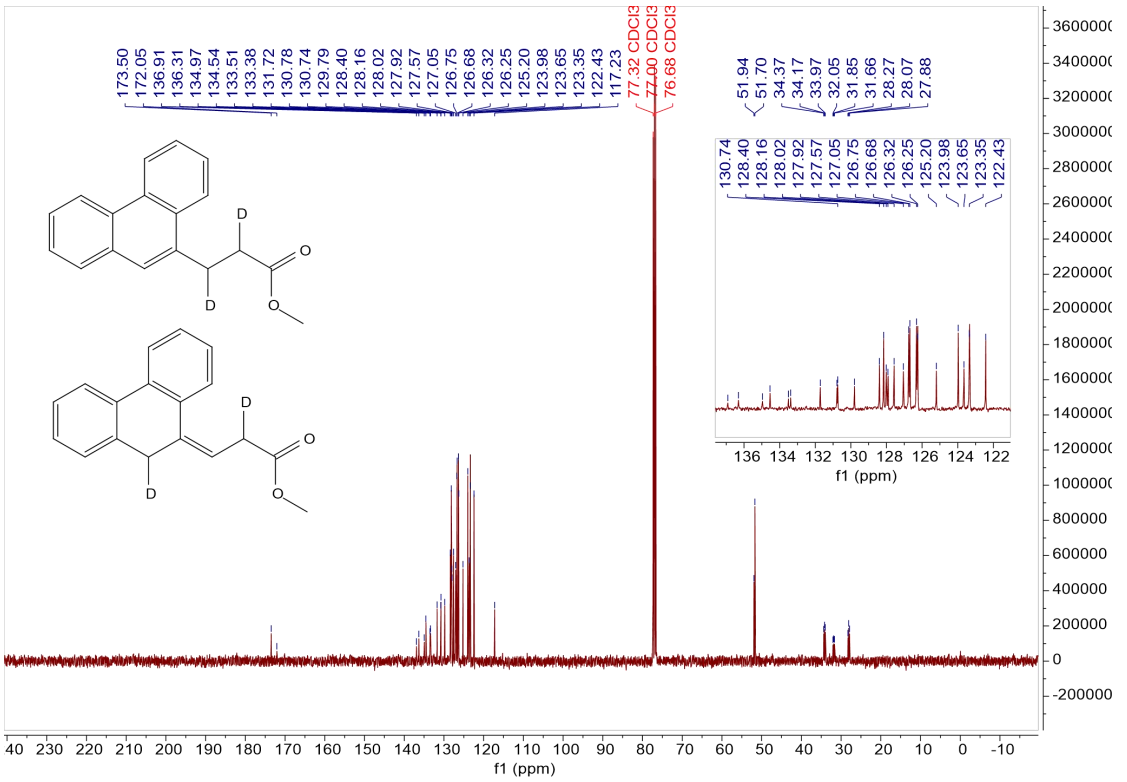

7.42
7.40
7.37
7.37
7.36
7.35
7.34
7.33
7.31
7.29
7.29
7.28
7.26
7.26
7.25
7.24
7.21
7.20
7.18
7.18
7.16
7.14
6.42
6.36
6.14
6.13
5.81
5.80
3.66
3.61
3.39
3.35
3.33
2.83
2.79
D
O
O
D
O
O
D
D
0.24
2.00
5.29
2.72
0.07
0.12
0.84
0.40
2.81
0.80
0.83
0.05
f1 (ppm)

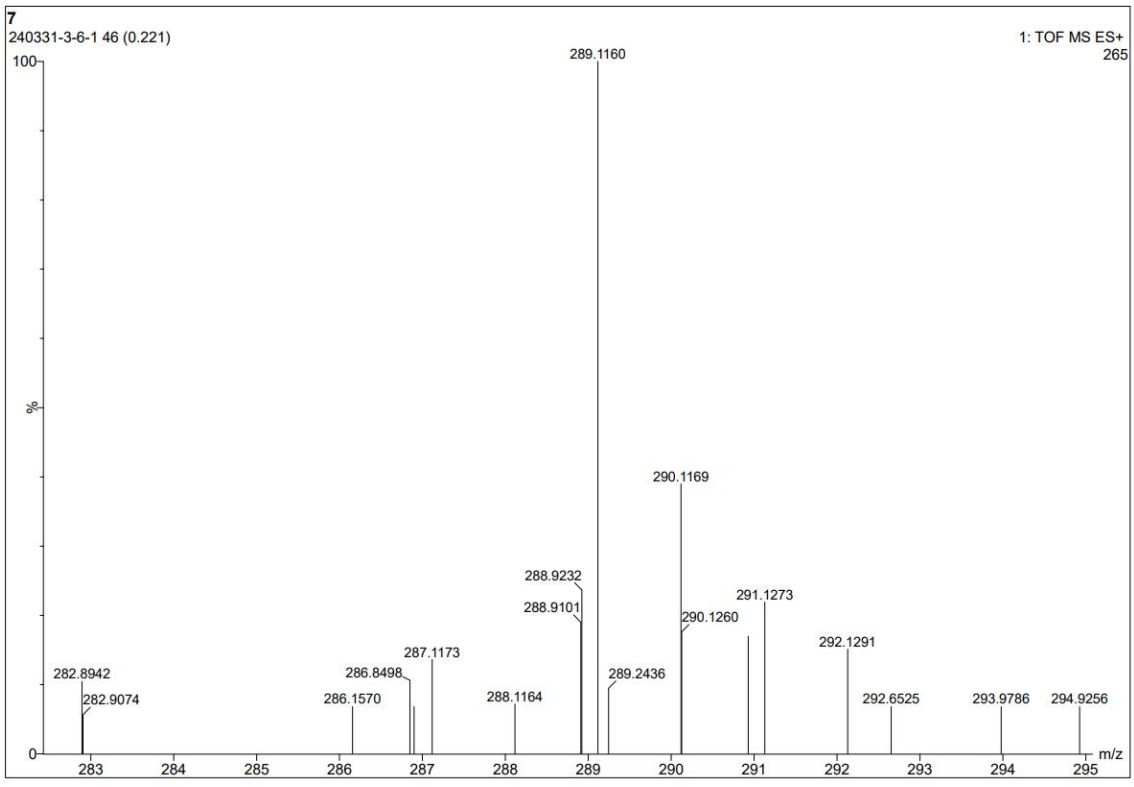

171.89
141.91
140.61
139.46
134.55
130.84
130.21
128.68
128.54
128.47
128.43
128.37
128.31
128.28
127.48
127.34
127.16
126.77
126.26
126.17
126.01
125.97
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.98
51.73
51.61
44.26
44.06
43.86
35.06
34.86
34.67
D
O
O
D
O
O
D
D
f1 (ppm)



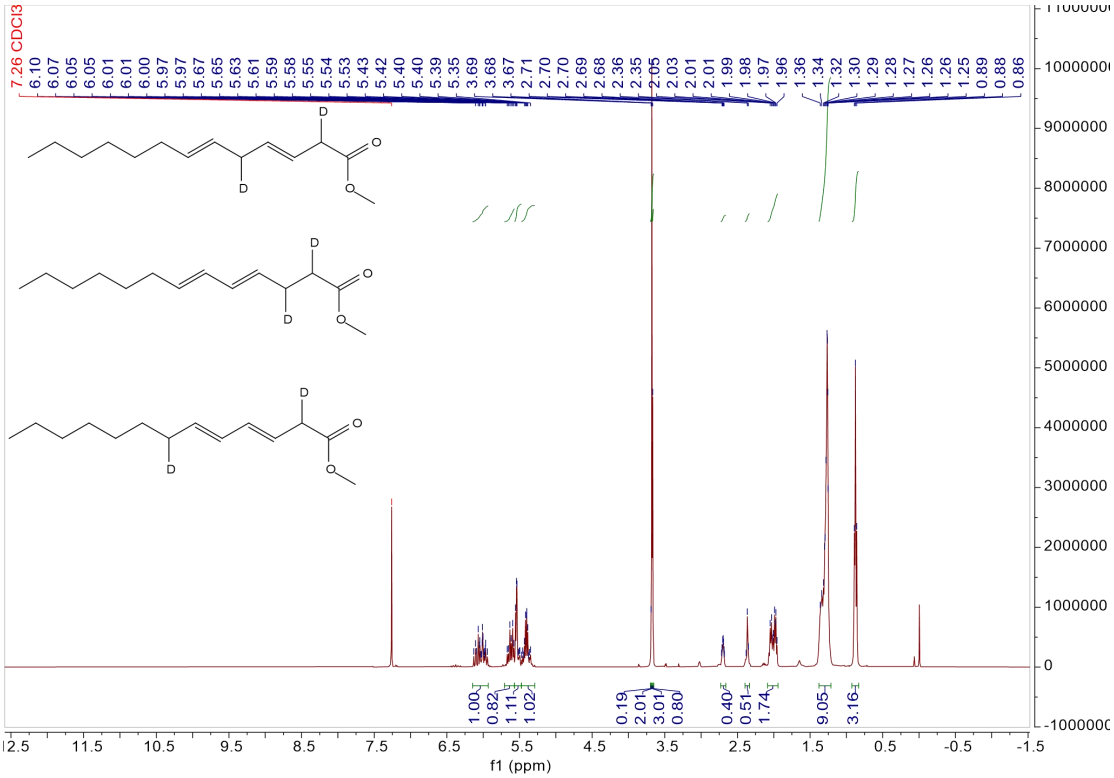
methyl 3-(phenanthren-9-yl)propanoate-2,3-d_2 & methyl 3-(phenanthren-9(10H)-ylidene-10-*d*)propanoate-2-*d* (4c &4c'):

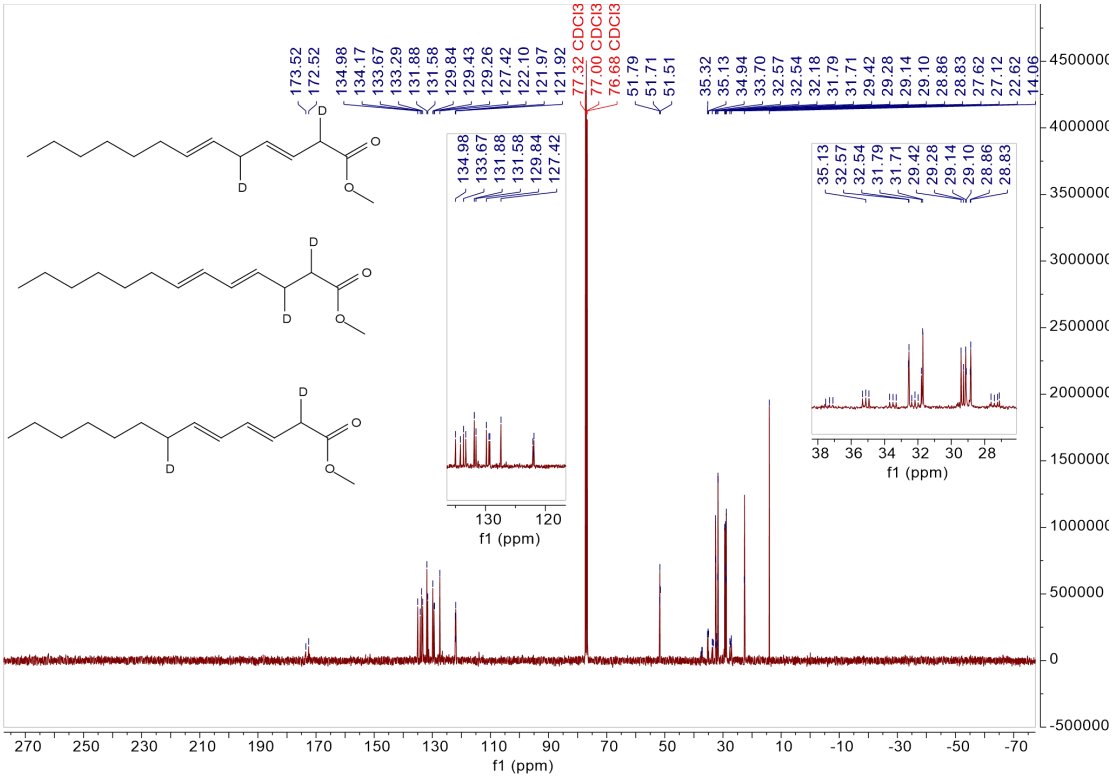


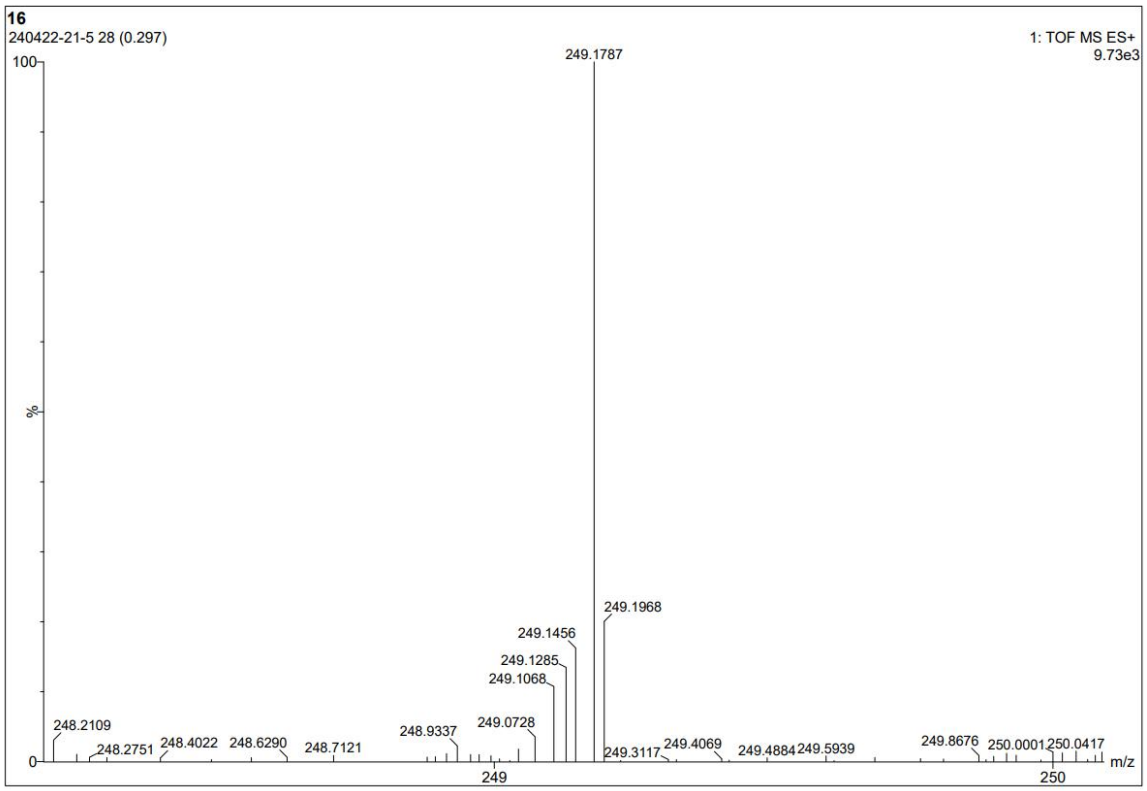




methyl trideca-3,6-dienoate-2,5-d_2, methyl trideca-4,6-dienoate-2,3-d_2 & methyl trideca-3,5-dienoate-2,7-d_2 (4d, 4d'&4d"):

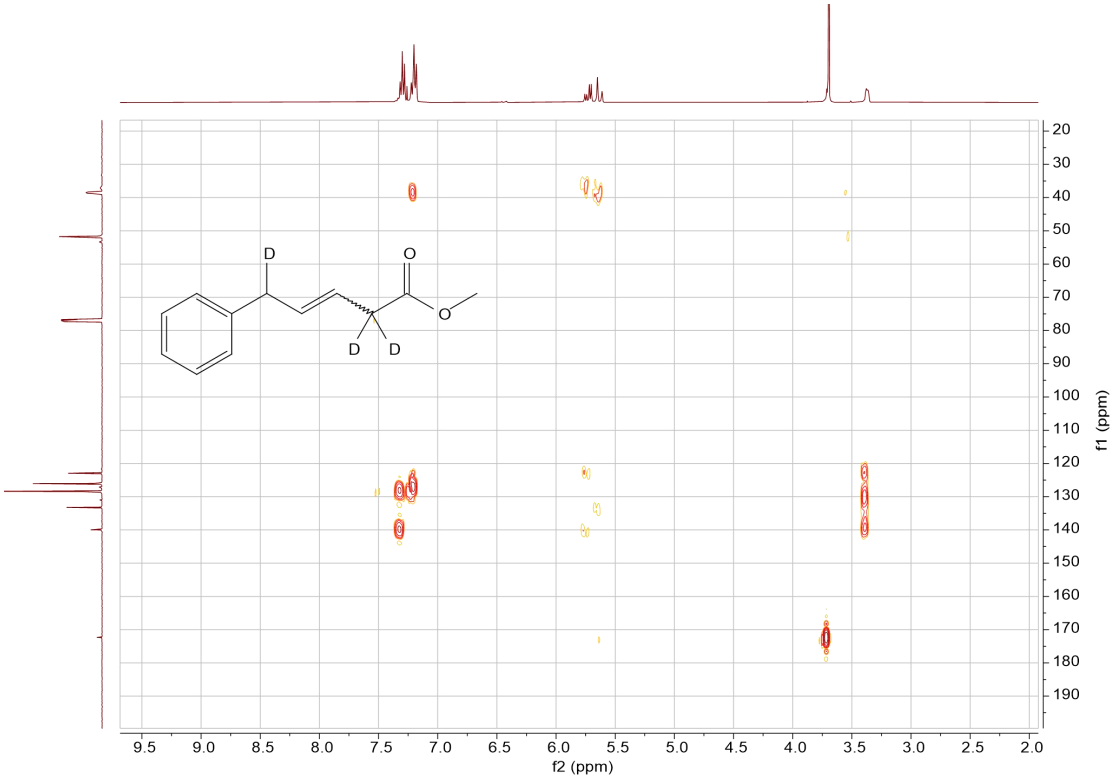

7.26 CDCl3
f1 (ppm)


77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
f1 (ppm)

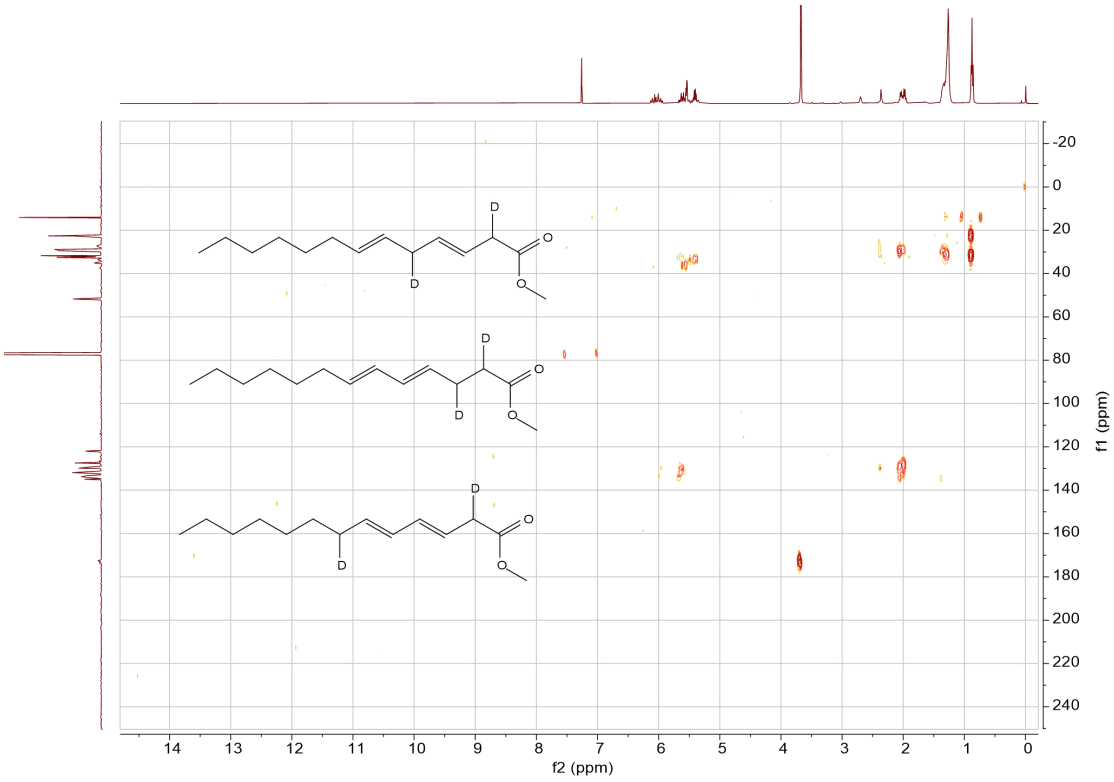


6. HMBC (4a, 4d, 4d', 4d'')

HMBC (4a)



HMBC (4d, 4d', 4d'')


D
D
O
O
D
D
O
O
D
D
O
O
-20
0
20
40
60
80
100
120
140
160
180
200
220
240
f1 (ppm)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f2 (ppm)