Supporting Information

Photocatalytic deuterocarboxylation of alkynes with oxalate

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Table of Contents

1. General information

^{1}H NMR (400 MHz) spectra, ^{13}C NMR (100 MHz) spectra, and ^{19}F NMR (376 MHz) spectra were recorded on a JEOL ECZ400 (400 MHz) spectrometers in $CDCl_3$, CD_3OD or DMSO-d_6. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, sep = septet, m = multiplet, br = broad. Flash column chromatography was performed using Nuo Tai silica gel (Size: 200-300) with distilled solvents. High Resolution mass spectra were obtained from the Xuzhou Medical University Mass Spectral facility: Agilent G6550A Q-TOF (ESI).

All reactions were set up on the bench top and conducted under carbon dioxide or nitrogen atmosphere while subject to irradiation from blue LEDs (Xuzhou Aijia Electronic Technology Co., Ltd, AC220V, 45 W, λmax = 450 nm). The material of the irradiation vessel is borosilicate glass. The distance from the light source to the irradiation vessel is 2 cm. Reagents, solvents, and photocatalysts were purchased from various vendors and used as received, unless stated otherwise. Thin-layer chromatography (TLC) was performed on 0.2-0.3 mm SiliCycle silica gel F-254 plates.

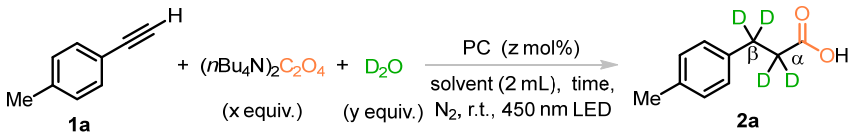
2. Optimization of the reaction conditions

General procedure A:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (3.0 equiv or 4.0 equiv or 6.0 equiv), 4DPAIPN (3.2 mg, 0.004 mmol, 2 mol%). The tube was filled with nitrogen. Then D_2O (15.0 equiv or 30.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at the distance of 3-4 cm and stirred at room temperature for 8-57 hours. After completion of the reaction, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by

silica gel flash chromatography (petroleum ether/ EtOAc 10/1 ~ 2/1) to give the pure desired product.

Table S1A. Screening table of the alkyne with oxalate.



Entry	PC (mol%)	Oxalate (equiv.)	D_2O (equiv.)	Solvent (anhydrous)	Time (h)	Yield (%)[a]	D content (%) of **2a** α	D content (%) of **2a** β
1	Tris(2-phenylpyridine)iridium(III) (1)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	68	80	75
2	$Ir[df(CF_3)ppy]_2(dtbby)PF_6$ (1)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	65	86	69
3	4CzIPN (1)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	0		
4	4DPAIPN (1)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	80	90	95
5	EosinB (1)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	0		
6	-	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	0		
7	4DPAIPN (0.5)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	81	87	93
8	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (5)	28	DMF	12	89	85	93
9	4DPAIPN (2)	$(NH_4)_2C_2O_4$ (5)	28	DMF	12	0		
10	4DPAIPN (2)	$Na_2C_2O_4$ (5)	28	DMF	12	0		
11	4DPAIPN (2)	$H_2C_2O_4$ (5)	28	DMF	12	0		
12	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (2)	28	DMF	12	50	89	95
13	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	28	DMF	12	91	88	94
14	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	5	DMF	12	21	65	76
15	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	8	DMF	12	91	75	86
16	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	10	DMF	12	99	82	89
17	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	DMF	12	91	86	94
18	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	20	DMF	12	94	85	92
19	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	30	DMF	12	92	88	94
20	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	DMSO	12	85	82	78
21	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	DMA	12	96	85	89
22	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	THF	12	83	83	89
23	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	DMF	4	72	86	93
24	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	DMF	8	91(85)[b]	89	94
25	4DPAIPN (2)	$(n\mathrm{Bu_4N})_2C_2O_4$ (3)	15	DMF	8	0[c]	89	94

[a]Yields were determined by ^{1}HNMR using 1, 2-dichloroethane as an internal standard. [b]Isolated yield. [c] In dark.

Large scale reaction procedure:

An oven-dried Schlenk tube (100 mL) containing a stirring bar was charged with the substrate (0.44 mL, 4 mmol, 1.0 equiv), $(n\mathrm{Bu_4N})_2C_2O_4$ (6.88 g, 12 mmol, 3.0 equiv), 4DPAFIPN (63.8 mg, 0.08 mmol, 2 mol%). The tube was filled with nitrogen gas. Then D_2O (1.09 mL, 60 mmol, 15.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at the distance of 3-4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (60 mL) and extracted with

EtOAc (3 x 60 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ EtOAc 5/1) to give the pure desired product.

Figure S1. Standard setup for large scale reaction.

3. Synthesis of substrates

The scope of various alkynes and dienes.

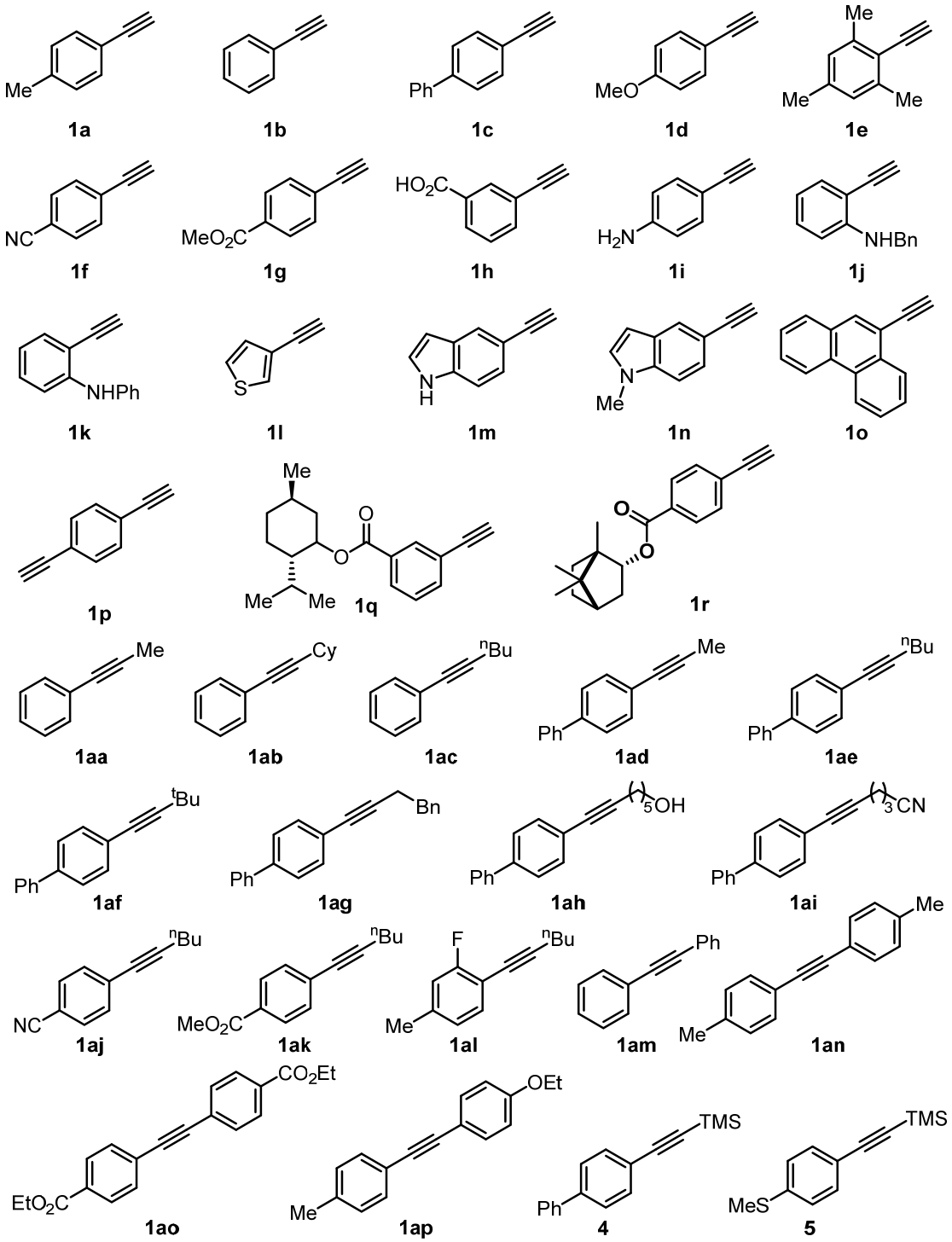
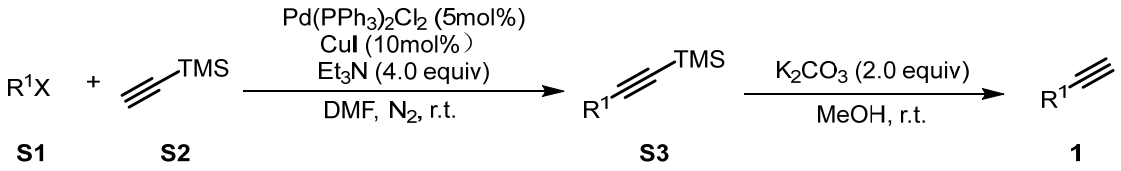


Figure S2. The scope of various alkynes.

Substrates **1a, 1b, 1c, 1d, 1f, 1g, 1h, 1i, 1o, 1p, 1aa, 1ac, 1ad, 1am, 1ao, and 1ap** were purchased from commercial sources.

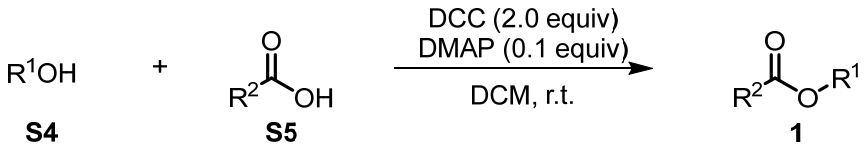
General procedure A: substrates **1e, 1j-1n** were synthesized following the reported procedures in the literature. [1]



To a 50 mL round-bottom flask was added aryl halides **S1** (5.0 mmol), $Pd(PPh_3)Cl_2$ (351.0 mg, 0.25 mmol, 0.05 equiv) and CuI (190.5 mg, 0.5 mmol, 0.1 equiv), then add DMF (20 mL), triethylamine (2.1 mL, 15.0 mmol, 4.0 equiv) and trimethylsilylacetylene **S2** (0.9 mL, 6.5 mmol, 1.3 equiv) was added under nitrogen atmosphere. The resulting solution was stirred at room temperature for 12 hours, extracted with DCM (40 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give corresponding intermediates **S3**.

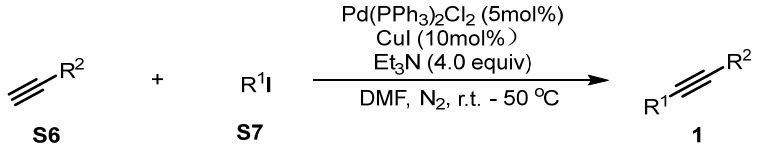
To a 50 mL round-bottom flask was added the solution of corresponding intermediates **S3** (2.0 mmol) in MeOH or MeOH/THF (1:1) (15 mL). The mixture was stirred at room temperature and K_2CO_3 (552.8 mg, 4.0 mmol, 2.0 equiv) was added. The resulting solution was stirred at room temperature for 8-24 hours, solvent was removed under reduced pressure and extracted with EtOAc (20 mL x3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give product **1e**, **1j-1n.**

General procedure B: substrates **1q and 1r** were synthesized following the reported procedures in the literature. [2]



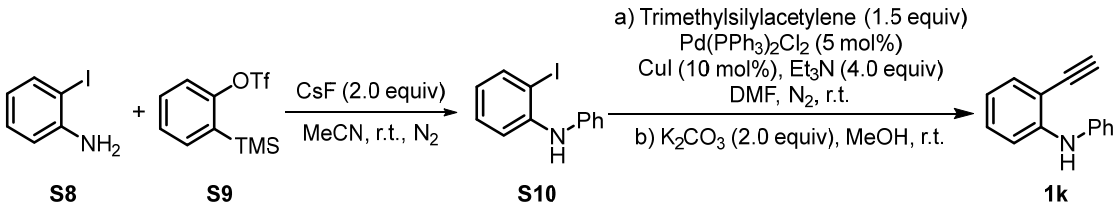
To a 50 mL round-bottom flask was added substituted alcohol **S4** (3.0 mmol), alkyne acid **S5** (3.6 mmol, 1.2 equiv), DCC (1.24 g, 6.0 mmol, 2.0 equiv) and DMAP (36.7 mg, 0.3 mmol, 0.1 equiv) then add dry DCM (15 mL). The resulting solution was stirred at room temperature for 9 hours, extracted with DCM (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give product **1q**, **1r**.

General procedure C: substrates **1ab, 1ae-1an** were synthesized following the reported procedures in the literature. [1]



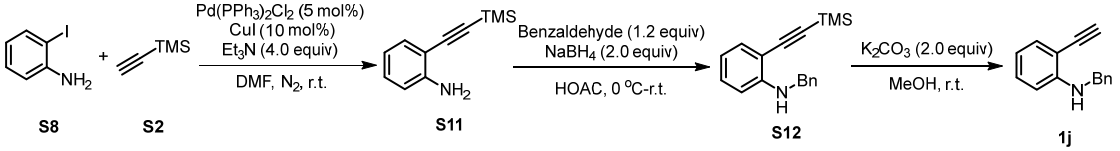
To a 50 mL round-bottom flask was added aryl alkynes **S6** (3.0 mmol), aryl iodide **S7** (3.6 mmol, 1.2 equiv), $Pd(PPh_3)Cl_2$ (105.3 mg, 0.15 mmol, 0.05 equiv) and CuI (57.1 mg, 0.3 mmol, 0.1 equiv), then add DMF (15 mL) , triethylamine (1.7 mL, 12.0 mmol, 4.0 equiv) under nitrogen atmosphere. The resulting solution was stirred at room temperature for 12 hours, extracted with DCM (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give product **1ab, 1ae-1an**.

General procedure D: substrates **1k** were synthesized following the reported procedures in the literature. [3]



To an oven-dried 50 mL round-bottom flask was added 2-iodoaniline **S8** (10.0 mmol) in dry MeCN (25 mL) under nitrogen atmosphere, CsF (3.03 g, 20.0 mmol, 2.0 equiv), stirred at room temperature for 1 hour, then add 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (2.7 mL, 11.2 mmol, 1.12 equiv). The resulting solution was stirred at room temperature for 24 hours, extracted with EtOAc (40 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give corresponding intermediates **S10,** then through general procedure A to give product **1k**.

General Procedure E: substrates **1j** were synthesized following the reported procedures in the literature. [4]



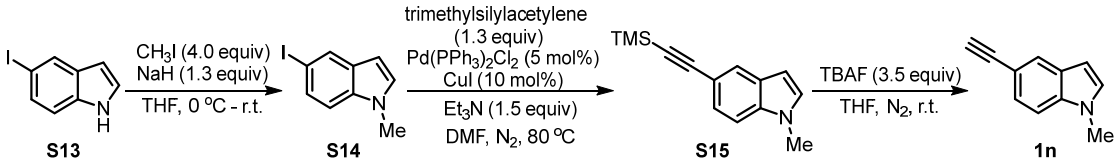
To a 50 mL round-bottom flask was added 2-iodoaniline **S8** (10.0 mmol), $Pd(PPh_3)Cl_2$ (351.0 mg, 0.5 mmol, 0.05 equiv) and CuI (190.5 mg, 1 mmol, 0.1 equiv), then add trimethylsilylacetylene **S2** (1.8 mL, 13 mmol, 1.3 equiv), dry DMF (25 mL), triethylamine (5.6 mL, 40.0 mmol, 4.0 equiv) under nitrogen atmosphere. The resulting solution was stirred at room temperature for 24 hours, then extracted with DCM (40 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether and EtOAc (100:1-10:1, v/v) as the eluent to give corresponding intermediates **S11**.

To a 50 mL round-bottom flask was added the solution of corresponding intermediates **S11** (5.0 mmol), benzaldehyde (0.6 mL, 6.0 mmol, 1.2 equiv) in HOAc

(15 mL). The mixture was stirred at 0 ℃ and $NaBH_4$ (0.38 g, 6.0 mmol, 2.0 equiv) was added. The resulting solution was stirred at room temperature for 3 hours, followed by the addition of NaOH (1M, 10 mL) to quench excess acetic acid, extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give corresponding intermediates **S12.**

To a 50 mL round-bottom flask was added the solution of corresponding intermediates **S12** (5.0 mmol) in MeOH (15 mL). The mixture was stirred at room temperature, and K_2CO_3 (1.4 g, 10.0 mmol, 2.0 equiv) was added. The resulting solution was stirred at room temperature for 12 hours and solvent was removed under reduced pressure and extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (100:1-50:1, v/v) as the eluent to give corresponding compounds **1j.**

General procedure F: substrates **1n** were synthesized following the reported procedures in the literature. [5]



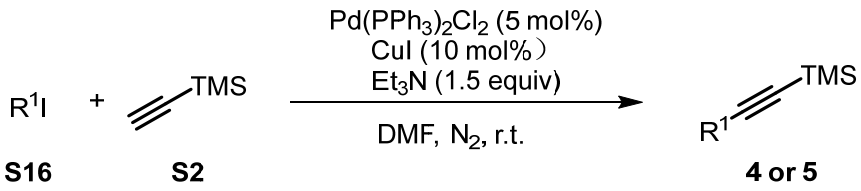
To an oven-dried 50 mL round-bottom flask was added NaH (0.24 g, 6.5 mmol, 1.3 equiv, 60% dispersion in mineral oil,) under nitrogen atmosphere, then dropwise add 5-iodo-1*H*-indole **S13** (1.2 g, 5.0 mmol, 1.0 equiv) in THF (10 mL) at 0 ℃. The mixture was stirred at 0 ℃ for 10 min, iodomethane (1.3 mL, 20.0 mmol, 4.0 equiv) was added. After 4 h, the reaction mixture was cooled to 0 ℃, quenched with water (10 mL), extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was

purified by flash chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (50:1-10:1, v/v) as the eluent to give corresponding intermediates **S14**.

To a 50 mL round-bottom flask was added 5-iodo-1-methyl-1*H*-indole **S15** (5.0 mmol), $Pd(PPh_3)Cl_2$ (351.0 mg, 0.25 mmol, 0.05 equiv) and CuI (190.5 mg, 0.5 mmol, 0.1 equiv), then add DMF (20 mL) , triethylamine (2.1 mL, 15.0 mmol, 4.0 equiv) under nitrogen atmosphere. The mixture was stirred at room temperature and trimethylsilylacetylene **S2** (0.9 mL, 6.5 mmol, 1.3 equiv) was added slowly under nitrogen atmosphere. The resulting solution was stirred at 80 ℃ for 24 hours, extracted with DCM (40 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (10:1-5:1, v/v) as the eluent to give corresponding intermediates **S15**.

To a 25 mL round-bottom flask was added 1-methyl-5-((trimethylsilyl)ethynyl)-1*H*-indole **S15** (2.2 mmol) dissolved in THF (7 mL), then add TBAF (3.5 mL, 3.5 mmol, 3.6 equiv). The mixture was stirred at room temperature for 20 hours. The reaction extracted with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether or petroleum ether and EtOAc (50:1, v/v) as the eluent to give product **1n**.

General procedure G: substrates **4 and 5** were synthesized following the reported procedures in the literature. [1]

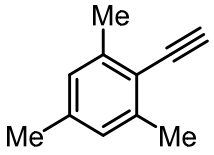


To a 50 mL round-bottom flask was added aryl iodide **S16** (5.0 mmol), $Pd(PPh_3)Cl_2$ (175.5 mg, 0.25 mmol, 0.05 equiv) and CuI (95.2 mg, 0.5 mmol, 0.1 equiv), then add trimethylsilylacetylene **S2** (0.91 mL, 6.5 mmol, 1.3 equiv), dry DMF (15 mL) , triethylamine (1 mL, 7.5 mmol, 4.0 equiv) under nitrogen atmosphere. The resulting

solution was stirred at room temperature for 24 hours, then extracted with DCM (40 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether and EtOAc (100:1-10:1, v/v) as the eluent to give product **4, 5**.

General procedure H: Synthesis of tetrabutylammonium oxalate

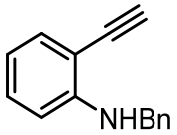
To a 50 mL round-bottom flask was added oxalic acid (10 mmol) and tetrabutylammonium hydroxide hydrate (1:1 molar ratio). The mixture was stirred at room temperature for 5 hours before remove the solvent under reduced pressure to give the desired product as white solid in quantitative yield.



2-ethynyl-1,3,5-trimethylbenzene (1e): Prepared according to general procedure A from 2-iodo-1,3,5-trimethylbenzene and trimethylsilylacetylene. The spectra matched with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H), 3.64 (s, 1H), 2.60 (s, 6H), 2.46 (s, 3H).

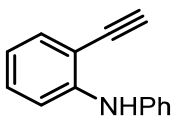
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 138.2, 127.7, 119.1, 84.7, 81.5, 21.4, 21.0.



***N*-benzyl-2-ethynylaniline (1j):** Prepared according to general procedure E from 2-iodoaniline and trimethylsilylacetylene. The spectra matched with reported literature.[4]

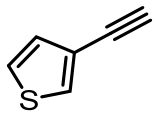
1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, J = 2.4 Hz, 5H), 7.490 – 7.454 (m, 1H), 7.36 (t, J = 7.2 Hz, 1H), 6.83 (t, J = 6.4 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 5.29 (s, 1H), 4.60 (s, 2H), 3.59 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 139.0, 132.8, 130.5, 128.8, 127.3, 127.2, 116.5, 110.0, 106.3, 83.2, 80.9, 47.7.

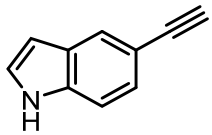


2-ethynyl-*N*-phenylaniline (1k): Prepared according to general procedure D from 2-

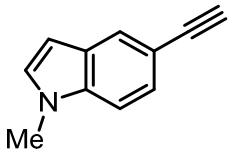
iodoaniline and trimethylsilylacetylene. The spectra matched with reported literature.[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 1H), 7.36 – 7.29 (m, 2H), 7.23 – 7.16 (m, 4H), 7.06 – 7.01 (m, 1H), 6.80 – 6.76 (m, 1H), 6.46 (brs, 1H), 3.46 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.9, 131.6, 128.4, 127.9, 121.2, 118.9, 117.5, 111.8, 107.4, 82.3, 79.1.



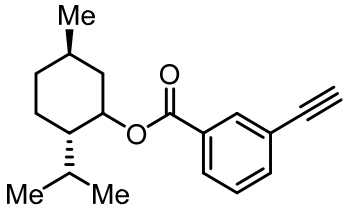
3-ethynylthiophene (1l): Prepared according to general procedure A from 3-bromothiophene and trimethylsilylacetylene. The spectra matched with reported literature.[7]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 3.6, 1.2 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.15 (dd, J = 5.2, 1.2 Hz, 1H), 3.04 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 130.2, 130.1, 125.4, 121.5, 78.9, 77.0.



5-ethynyl-1*H*-indole (1m): Prepared according to general procedure A from 5-iodo-1*H*-indole and trimethylsilylacetylene. The spectra matched with reported literature.[8]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (brs, 1H), 7.83 (s, 1H), 7.33 (s, 2H), 7.23 (d, J = 3.2 Hz, 1H), 6.55 (s, 1H), 2.99 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 127.7, 126.0, 125.3(9), 125.3(6), 113.1, 111.3, 102.9, 85.5, 74.9.



5-ethynyl-1-methyl-1*H*-indole (1n): Prepared according to general procedure F from 5-iodo-1-methyl-1*H*-indole, iodomethane and trimethylsilylacetylene. The spectra matched with reported literature.[9]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.35 (dd, J = 8.4, 1.6 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.07 (d, J = 3.2 Hz, 1H), 6.47 (d, J = 2.8 Hz, 1H), 3.79 (s, 3H), 3.00 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 130.0, 128.3, 125.6, 112.7, 109.4, 100.4, 85.6, 74.7, 33.1.

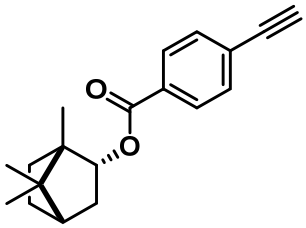


(2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-ethynylbenzoate (1q): Prepared according to general procedure B from (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexan-1-ol and 3-ethynylbenzoic acid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 4.94 (t, J = 10.6 Hz, 1H), 3.13 (s, 1H), 2.11 (d, J = 12.0 Hz, 1H), 1.96 – 1.91 (m, 1H), 1.73 (d, J = 12.0 Hz, 2H), 1.56 (s, 2H), 1.18 – 1.06 (m, 2H), 0.94 – 0.91 (m, 7H), 0.79 (d, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 136.1, 133.2, 131.2, 129.9, 128.5, 122.6, 82.8, 78.2, 75.2, 47.3, 41.0, 34.4, 31.5, 26.5, 23.6, 22.1, 20.9, 16.5.

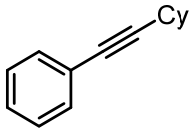
HRMS (ESI-TOF): m/z Calcd. For $C_{19}H_{24}O_2Na$: $(M+Na)^+$ 307.1669. Found: 307.1679.



(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-ethynylbenzoate (1r): Prepared according to general procedure B from *L*(-)-borneol and 4-ethynyl-benzoic acid. The spectra matched with reported literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.43 –7.39 (m, 1H), 5.01 – 4.89 (t, J = 10.4 Hz, 1H), 3.13 (s, 1H), 2.11 (d, J = 12.0 Hz, 1H), 1.96 – 1.92 (m, 1H), 1.73 (d, J = 12.0 Hz, 2H), 1.19 – 1.04 (m, 2H), 0.94 – 0.90 (m, 6H), 0.79 (d, J = 4.8 Hz, 3H).

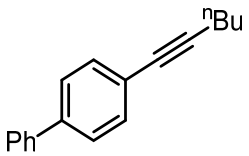
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 132.1, 130.9, 129.5, 126.7, 83.0, 80.9, 80.1, 49.2, 48.0, 45.0, 37.0, 28.2, 27.5, 19.8, 19.0, 13.7.



(cyclohexylethynyl)benzene (1ab): Prepared according to general procedure C from cyclohexylacetylene and iodobenzene. The spectra matched with reported literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.32 (m, 2H), 7.24 – 7.16 (m, 3H), 2.59 – 2.52 (m, 1H), 1.88 – 1.81 (m, 2H), 1.76 – 1.68 (m, 2H), 1.57 – 1.43 (m, 3H), 1.36 – 1.23 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.3, 127.8, 127.1, 124.0, 94.0, 80.5, 32.5, 29.4, 25.7, 24.6.

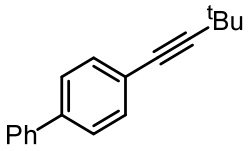


4-(hex-1-yn-1-yl)-1,1'-biphenyl (1ae): Prepared according to general procedure C

from 1-hexyne and 4-iodobiphenyl. The spectra matched with reported literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.37 (t, J = 7.2 Hz, 2H), 7.30 – 7.26 (m, 1H), 2.44 (t, J = 7.2 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.55 – 1.45 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H).

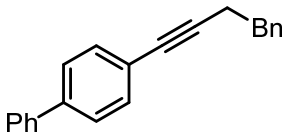
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.2, 132.0, 128.9, 127.5, 127.0, 126.9, 123.2, 91.2, 80.6, 30.9, 22.1, 19.3, 13.8.



4-(3,3-dimethylbut-1-yn-1-yl)-1,1'-biphenyl (1af): Prepared according to general procedure C from 3,3-dimethyl-1-butyne and 4-iodobiphenyl. The spectra matched with reported literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.2 Hz, 2H), 7.44 (m, 4H), 7.40 – 7.32 (m, 2H), 7.30 – 7.24 (m, 1H), 1.32 (s, 9H).

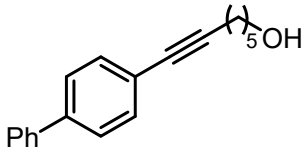
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.2, 132.1, 128.9, 127.5, 127.0, 126.9, 123.2, 99.3, 79.1, 31.2, 28.1.



4-(4-phenylbut-1-yn-1-yl)-1,1'-biphenyl (1ag): Prepared according to general procedure C from 4-phenyl-1-butyne and 4-iodobiphenyl. The spectra matched with reported literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 2H), 7.46 – 7.38 (m, 4H), 7.33 (t, J = 8.0 Hz, 2H), 7.22 (m, 6H), 2.86 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.4, 140.3, 132.0, 128.8, 128.6, 128.4, 127.5, 127.0, 126.9, 126.4, 122.9, 90.4, 81.4, 35.2, 21.8.

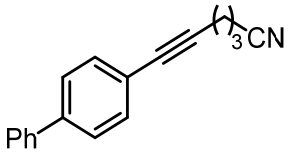


7-([1,1'-biphenyl]-4-yl)hept-6-yn-1-ol (1ah): Prepared according to general procedure C from 5-hexyn-1-ol and 4-iodobiphenyl.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.34 (t, J = 7.2 Hz, 1H), 3.69 (t, J = 6.4 Hz, 2H), 2.46 (t, J = 6.8 Hz, 2H), 1.69 – 1.61 (m, 4H), 1.60 – 1.52 (m, 2H), 1.26 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 140.2, 132.0, 128.8, 127.4, 126.9, 126.8, 122.9, 90.9, 80.7, 62.5, 32.1, 28.5, 25.1, 19.4.

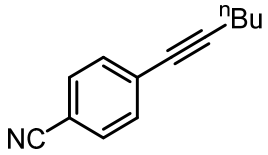
HRMS (ESI-TOF): m/z Calcd. For $C_{19}H_{21}O$: $(M+H)^+$ 265.1587. Found: 265.1583.



6-([1,1'-biphenyl]-4-yl)hex-5-ynenitrile (1ai): Prepared according to general procedure C from 6-heptynenitrile and 4-iodobiphenyl. The spectra matched with reported literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 4H), 7.50 – 7.41 (m, 4H), 7.39 – 7.32 (m, 1H), 2.63 (t, J = 6.4 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 1.99 (p, J = 6.4 Hz, 2H).

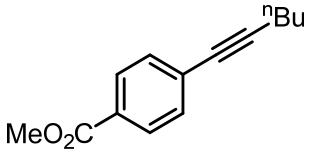
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.3, 132.0, 128.9, 127.6, 127.0, 122.2, 119.3, 87.7, 82.2, 24.6, 18.6, 16.2.



4-(hex-1-yn-1-yl)benzonitrile (1aj): Prepared according to general procedure C from 1-hexyne and 4-iodobenzonitrile. The spectra matched with reported literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.48 – 7.40 (m, 2H), 2.43 (t, J = 6.8 Hz, 2H), 1. 63 – 1.55 (m, 2H), 1.52 – 1.42 (m, 2H), 0.95 (t, J = 7.2, 3H).

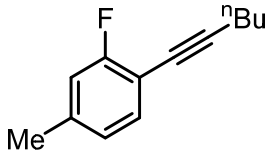
^{13}C NMR (100 MHz, $CDCl_3$) δ131.9, 131.8, 129.0, 118.4, 110.7, 95.5, 79.3, 30.4, 21.9, 19.0, 13.4.



methyl 4-(hex-1-yn-1-yl)benzoate (1ak): Prepared according to general procedure C from 1-hexyne and Methyl 4-iodobenzoate. The spectra matched with reported literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.44 – 7.37 (m, 2H), 3.90 (s, 3H), 2.41 – 2.34 (m, 2H), 1.61 – 1.35 (m, 4H), 0.95 (t, J = 7.2, 3H).

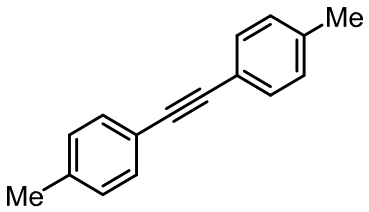
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 131.1, 129.1, 128.7, 128.6, 93.4, 80.0, 51.5, 30.5, 21.8, 18.9, 13.3.



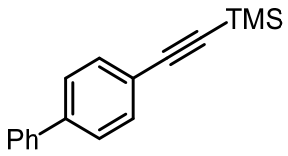
2-fluoro-1-(hex-1-yn-1-yl)-4-methylbenzene (1al): Prepared according to general procedure C from 1-hexyne and 3-fluoro-4-iodotoluene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 9.2 Hz, 2H), 2.44 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.64 – 1.56 (m, 2H), 1.51 – 1.46 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H).

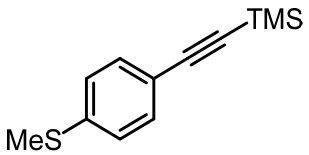
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J_{FC} = 248.5 Hz), 140.0 (d, J_{FC} = 7.7 Hz), 133.1 (d, J_{FC} = 2.3 Hz), 124.6 (d, J_{FC} = 3.3 Hz), 115.9 (d, J_{FC} = 20.9 Hz), 109.5 (d, J_{FC} = 15.8 Hz), 94.9 (d, J_{FC} = 3.3 Hz), 74.0, 30.8, 22.0, 21.2, 19.3, 13.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5.
HRMS (ESI-TOF): m/z Calcd. For $C_{13}H_{14}F$: $(M-H)^+$ 189.1085. Found: 189.1078.



1,2-di-*p*-tolylethyne (1an): Prepared according to general procedure C from 4-ethynyltoluene and 4-iodotoluene. The spectra matched with reported literature.[16]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 4H), 7.17 – 7.11 (d, J = 8.0 Hz, 4H), 2.36 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 131.5, 129.2, 120.5, 89.0, 21.6.



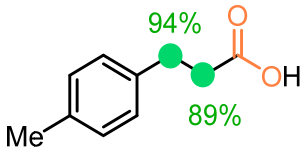
([1,1'-biphenyl]-4-ylethynyl)trimethylsilane (4): Prepared according to general procedure G from 4-iodobiphenyl and trimethylsilylacetylene. The spectra matched with reported literature.[17]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 2H), 7.54 (s, 4H), 7.44 (t, J = 7.2 Hz, 2H), 7.36 (d, J = 6.8 Hz, 1H), 0.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.3, 132.5, 128.9, 127.7, 127.1, 127.0, 122.1, 105.2, 94.9, 0.16.



trimethyl((4-(methylthio)phenyl)ethynyl)silane (5): Prepared according to general procedure G from 4-iodothioanisole and trimethylsilylacetylene. The spectra matched with reported literature.[18]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 2.48 (s, 3H), 0.24 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 132.3, 125.7, 119.5, 105.0, 94.3, 15.4, 0.12.

4. Derivatives

All reactions were conducted according to the general procedure with 0.2 mmol alkynes unless otherwise stated.

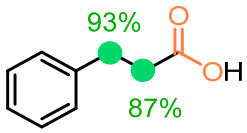


3-(*p*-tolyl)propanoic-2,2,3,3-d_4 acid (2a): Prepared according to general procedure using 1-ethynyl-4-methylbenzene (24.7 μL, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (28.6 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 2.89 – 2.91 (m, 0.12H, **1.88D**), 2.63 – 2.65 (m, 0.23H, **1.77D**), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 137.1, 136.0, 129.4, 128.3, 35.6 – 35.1 (m, CD_2), 30.1 – 29.3 (m, CD_2), 21.2.

HRMS (ESI-TOF) *m/z*: $[M\text{-}H]^-$ calcd for $C_{10}H_7D_4O_2^-$: 167.1016; found: 167.1023.

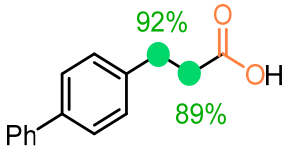


3-phenylpropanoic-2,2,3,3-d_4 acid (2b): Prepared according to general procedure using ethynylbenzene (21.9 μL, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (24.8 mg, 80% yield).

^{1}H NMR (400 MHz, CD_3OD) δ 7.28 – 7.13 (m, 5H). 2.8 – 2.87 (m, 0.14H, **1.86D**), 2.57 – 2.55 (m, 0.26H, **1.74D**).

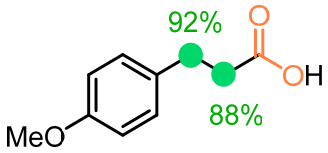
^{13}C NMR (100 MHz, CD_3OD) δ 176.8, 142.1, 129.5, 129.3, 127.2, 36.5 – 36.1 (m, CD_2), 31.5 – 30.7 (m, CD_2).

HRMS (ESI-TOF) *m/z*: $[M\text{-}H]^-$ calcd for $C_9H_5D_4O_2^-$: 153.0859; found: 153.0856.

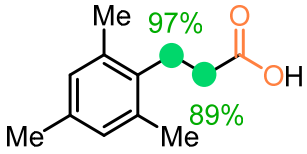


3-([1,1'-biphenyl]-4-yl)propanoic-2,2,3,3-d_4 acid (2c): Prepared according to general procedure using 4-ethynyl-1,1'-biphenyl (35.6 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (40.6 mg, 88% yield).

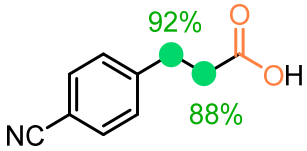
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.36 – 7.25 (m, 3H). 2.99 – 2.94 (m, 0.17H, **1.83D**), 2.71 – 2.69 (m, 0.22H, **1.78D**).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 141.0, 139.5, 139.3, 128.9, 128.8, 127.4, 127.3, 127.2, 35.7 – 34.7 (m, CD_2), 30.2 – 29.5 (m, CD_2).
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{15}H_9D_4O_2^-$: 229.1172; found: 229.1173.



3-(4-methoxyphenyl)propanoic-2,2,3,3-d_4 acid (2d): Prepared according to general procedure using 1-ethynyl-4-methoxybenzene (25.9 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as brown solid (27.4 mg, 74% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.89 – 2.87 (m, 0.17H, **1.83D**), 2.63 – 2.62 (m, 0.25H, **1.75D**).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 158.3, 132.3, 129.4, 114.1, 55.4, 35.9 – 35.4 (m, CD_2), 29.8 – 29.1 (m, CD_2).
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{10}H_7D_4O_3^-$: 183.0965; found: 183.0974.

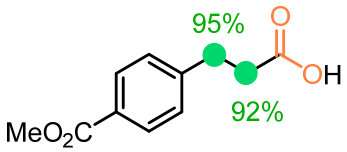


3-mesitylpropanoic-2,2,3,3-d_4 acid (2e): Prepared according to general procedure using 2-ethynyl-1,3,5-trimethylbenzene (28.8 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as brown solid (22.3 mg, 57% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 2.95 – 2.93 (m, 0.07H, **1.93D**), 2.48 – 2.46 (m, 0.22H, **1.78D**), 2.30 (s, 6H), 2.25 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 136.2, 135.9, 133.7, 129.2, 33.3 – 32.5 (m, CD_2), 24.2 – 23.5 (m, CD_2), 21.0, 19.7.
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{12}H_{11}D_4O_2^-$: 195.1329; found: 195.1337.

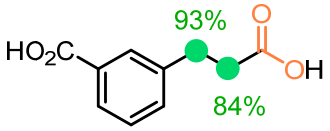


3-(4-cyanophenyl)propanoic-2,2,3,3-d_4 acid (2f): Prepared according to general procedure using 4-ethynylbenzonitrile (25.4 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as

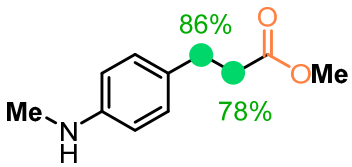
yellow solid (18.5 mg, 52% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 3.00 – 2.99 (m, 0.16H, **1.84D**), 2.70 – 2.68 (m, 0.24H, **1.76D**).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 145.7, 132.5, 129.3, 119.0, 110.5, 34.6 – 34.1 (m, CD_2), 30.1 – 29.6 (m, CD_2).
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{10}H_4D_4NO_2^-$: 178.0812; found: 178.0807.



3-(4-(methoxycarbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2g): Prepared according to general procedure using methyl 4-ethynylbenzoate (32.0 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2C_2O_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (32.2 mg, 76% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 2.87 – 2.89 (m, 0.10H, **1.90D**), 2.70 – 2.68 (m, 0.19H, **1.81D**).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 167.2, 145.6, 130.1, 128.5, 128.5, 52.2, 35.0 – 34.43 (m, CD_2), 29.9 – 29.3 (m, CD_2).
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{11}H_7D_4O_4^-$: 211.0914; found: 211.0914.



3-(2-carboxyethyl-1,1,2,2-d_4)benzoic acid (2h): Prepared according to general procedure using 3-ethynylbenzoic acid (29.2 mg, 0.2 mmol, 1.0 equiv), D_2O (109.0 μL, 6.0 mmol, 30.0 equiv) and $(n\text{Bu}_4\text{N})_2C_2O_4$ (343.8 mg, 0.6 mmol, 3.0 equiv) at 50 °C. After 34 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/2 as the eluent) and obtained as white solid (25.5 mg, 64% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.90 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H). 2.96 – 2.95 (m, 0.14H, **1.86D**), 2.62 – 2.60 (m, 0.32H, **1.68D**).
^{13}C NMR (100 MHz, CD_3OD) δ 176.5, 169.9, 142.6, 134.1, 132.1, 130.6, 129.6, 128.7, 36.2 – 35.8 (m, CD_2), 31.5 – 30.8 (m, CD_2).
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{10}H_5D_4O_4^-$: 197.0757; found: 197.0755.

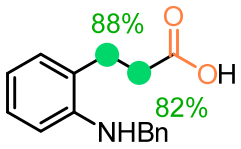


methyl 3-(4-(methylamino)phenyl)propanoate-2,2,3,3-d_4 (2i): Prepared according to

general procedure using 4-ethynylaniline (23.4 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours add MeI (2 mmol, 0.12 mL, 10.0 equiv), then the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as red solid (17.3 mg, 44% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.61 (brs, 1H), 3.77 (s, 3H), 3.66 (s, 3H). 2.89 – 2.88 (m, 0.28H, **1.72D**), 2.59 – 2.57 (m, 0.44H, **1.56D**).

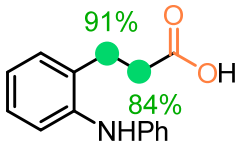
^{13}C NMR (100 MHz, CDCl$_3$) δ 173.5, 154.2, 136.2, 129.0, 119.1, 52.5, 51.8, 35.7 – 35.3 (m, CD$_2$), 30.2 – 29.3 (m, CD$_2$).



3-(2-(benzylamino)phenyl)propanoic-2,2,3,3-d_4 acid (2j): Prepared according to general procedure using *N*-benzyl-2-ethynylaniline (41.5 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (42.7 mg, 82% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 7.16 (dd, J = 7.6, 1.6 Hz, 1H), 7.10 (td, J = 7.6, 1.6 Hz, 1H), 6.96 (td, J = 7.2, 1.2 Hz, 1H), 6.89 – 6.84 (m, 1H), 5.18 (s, 2H), 2.97 – 2.95 (m, 0.25H, **1.75D**), 2.59 – 2.57 (m, 0.36H, **1.64D**).

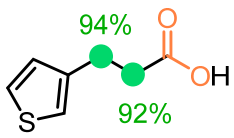
^{13}C NMR (100 MHz, CDCl$_3$) δ 170.7, 140.0, 137.1, 128.8, 128.0, 127.6, 127.2, 126.5, 126.4, 123.0, 115.7, 46.3, 31.7 – 31.3 (m, CD$_2$), 25.5 – 24.4 (m, CD$_2$).



3-(2-(phenylamino)phenyl)propanoic-2,2,3,3-d_4 acid (2k): Prepared according to general procedure using 2-ethynyl-*N*-phenylaniline (38.7 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (32.4 mg, 66% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 (t, J = 7.2 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.25 – 7.18 (m, 3H), 7.07 – 6.95 (m, 2H), 6.35 (dd, J = 8.0, 1.2 Hz, 1H), 2.97 – 2.95 (m, 0.19H, **1.81D**), 2.82 – 2.80 (m, 0.32H, **1.68D**).

^{13}C NMR (100 MHz, CDCl$_3$) δ 170.4, 141.8, 138.6, 130.0, 129.1, 128.3, 127.9, 127.3, 125.7, 123.1, 117.1, 32.1 – 31.2 (m, CD$_2$), 25.8 – 24.7 (m, CD$_2$).

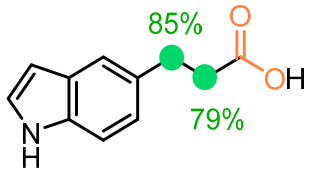


3-(thiophen-3-yl)propanoic-2,2,3,3-d_4 acid (2l): Prepared according to general procedure using 3-ethynylthiophene (22.0 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (4.5 mg, 14% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.00 (dd, J = 3.6, 1.6 Hz, 1H), 6.96 (dd, J = 3.6, 1.6 Hz, 1H), 2.97 – 2.95 (m, 0.13H, **1.87D**), 2.82 – 2.80 (m, 0.17H, **1.83D**).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 140.5, 128.0, 125.9, 120.9, 29.9 – 28.7 (m, CD_2), 24.8 – 24.3 (m, CD_2).

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_7H_3D_4O_2S^-$: 159.0423; found: 159.0430.

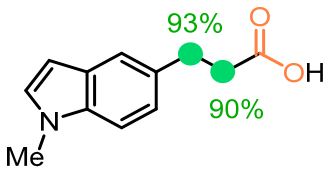


3-(1*H*-indol-5-yl)propanoic-2,2,3,3-d_4 acid (2m): Prepared according to general procedure using 5-ethynyl-1*H*-indole (28.2 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (13.9 mg, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (brs, 1H), 7.47 (d, J = 1.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 2.4 Hz, 1H), 7.05 (dd, J = 8.0, 1.6 Hz, 1H), 6.50 (m, 1H). 3.04 – 3.02 (m, 0.30H, **1.70D**), 2.71 – 2.69 (m, 0.42, **1.58D**).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 134.7, 131.6, 128.3, 124.6, 122.8, 120.0, 111.2, 102.5, 36.4 – 35.4 (m, CD_2), 30.9 – 29.9 (m, CD_2).

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{11}H_6D_4NO_2^-$: 192.0968; found: 192.0962.

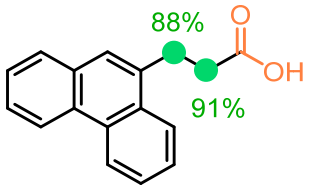


3-(1-methyl-1*H*-indol-5-yl)propanoic-2,2,3,3-d_4 acid (2n): Prepared according to general procedure using 5-ethynyl-1-methyl-1*H*-indole (31.0 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (36.5 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.25 (dd, J = 8.0, 2.0 Hz, 1H), 7.07 (d, J = 8.8 Hz, 1H), 7.02 (s, 1H), 6.42 (s, 1H), 3.76 (s, 3H), 3.04 – 3.02 (m, 0.15H, **1.85D**), 2.70 – 2.69 (m, 0.21, **1.79D**).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 135.7, 131.0, 129.2, 128.8, 122.3, 120.1, 109.4, 100.7, 36.6 – 35.4 (m, CD_2), 33.0, 30.3 – 29.7 (m, CD_2).

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{12}H_8D_4NO_2^-$: 206.1125; found: 206.1119.

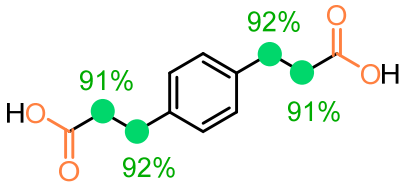


3-(phenanthren-9-yl)propanoic-2,2,3,3-*d*$_4$ acid (2o): Prepared according to general procedure using 9-ethynylphenanthrene (40.5 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (39.9 mg, 78% yield).

^{1}H NMR (400 MHz, CD$_3$OD) δ 8.82 – 8.76 (m, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.16 – 8.09 (m, 1H), 7.84 (dd, J = 7.6, 1.6 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.62 – 7.53 (m, 2H), 3.04 – 3.02 (m, 0.24H, **1.76D**), 2.78 – 2.76 (m, 0.18H, **1.82D**).

^{13}C NMR (100 MHz, CD$_3$OD) δ 176.9, 136.0, 133.2, 132.1(0), 132.0(8), 131.1, 129.2, 127.8, 127.7, 127.4, 127.3, 127.2, 125.1, 124.4, 123.5, 35.4 – 34.6 (m, CD$_2$), 29.2 – 28.5 (m, CD$_2$).

HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for C$_{17}$H$_9$D$_4$O$_2^-$: 253.1172; found: 253.1165.

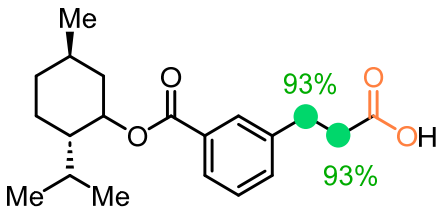


3,3'-(1,4-phenylene)bis(propanoic-2,2,3,3-*d*$_4$ acid) (2p): Prepared according to general procedure using 1,4-diethynylbenzene (25.2 mg, 0.2 mmol, 1.0 equiv), (nBu$_4$N)$_2$C$_2$O$_4$ (687.6 mg, 1.2 mmol, 6.0 equiv) and D$_2$O (109.2 μL, 6.0 mmol, 30.0 equiv). After 57 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/2 as the eluent) and obtained as white solid (9.8 mg, 21% yield).

^{1}H NMR (400 MHz, CD$_3$OD) δ 7.13 (s, 4H). 3.04 – 3.02 (m, 0.31H, **1.69D**), 2.78 – 2.76 (m, 0.38H, **1.62D**).

^{13}C NMR (100 MHz, CD$_3$OD) δ 176.8, 139.9, 129.4, 36.4 – 35.9 (m, CD$_2$), 31.4 – 30.5 (m, CD$_2$).

HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for C$_{12}$H$_5$D$_8$O$_4^-$: 229.1321; found: 229.1315.



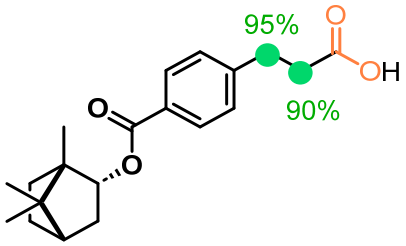
3-(3-((((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)propanoic-2,2,3,3-*d*$_4$ acid (2q): Prepared according to general procedure using (2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-ethynylbenzoate (49.6 mg, 0.2 mmol, 1.0 equiv) and

(nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (40.7 mg, 60% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.89 (m, 2H), 7.43 – 7.34 (m, 2H), 4.94 (td, J = 10.8, 4.4 Hz, 1H), 3.00 – 2.99 (m, 0.14H, **1.86D**), 2.71 – 2.69 (m, 0.14H, **1.86D**), 2.16 – 2.08 (m, 1H), 1.95 (pd, J = 6.8, 2.4 Hz, 1H), 1.73 (dt, J = 14.4, 3.2 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.19 – 1.06 (m, 2H), 0.93 (dd, J = 6.4, 3.2 Hz, 7H), 0.79 (d, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 178.6, 166.2, 140.4, 132.9, 131.3, 129.5, 128.7, 127.8, 75.0, 47.4, 41.1, 35.1 – 34.8 (m, CD$_2$), 34.5, 31.6, 30.0 – 29.6 (m, CD$_2$), 26.6, 23.7, 22.2, 20.9, 16.6.

HRMS (ESI-TOF) *m/z:* [M-H]$^-$ calcd for $C_{20}H_{23}D_4O_4^-$: 335.2166; found: 335.2165.

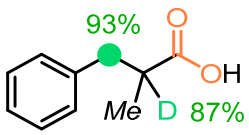


3-(4-((((1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2r): Prepared according to general procedure using (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-ethynylbenzoate (56.5 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv). After 13 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (54.7 mg, 82% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.10 (m, 1H), 3.00 – 2.99 (m, 0.10H, **1.90D**), 2.71 – 2.69 (m, 0.20H, **1.80D**), 2.52 – 2.41 (m, 1H), 2.13 (m, 1H), 1.81 (m, 1H), 1.73 (t, J = 4.4 Hz, 1H), 1.45 – 1.36 (m, 1H), 1.34 – 1.24 (m, 1H), 1.11 (dd, J = 14.0, 3.6 Hz, 1H), 0.97 (s, 3H), 0.91 (d, J = 3.6 Hz, 6H).

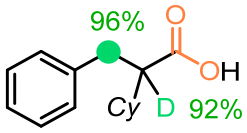
^{13}C NMR (100 MHz, CDCl$_3$) δ 178.1, 166.9, 145.4, 130.0, 129.3, 128.5, 80.6, 49.2, 48.0, 45.1, 37.1, 34.7 – 34.2 (m, CD$_2$), 30.3 – 29.4 (m, CD$_2$), 28.2, 27.5, 19.9, 19.1, 13.8.

HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for $C_{20}H_{21}D_4O_4^-$: 333.2009; found: 333.2008.

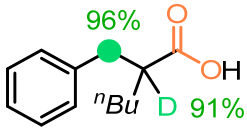


2-methyl-3-phenylpropanoic-2,3,3-d_3 acid (3a): Prepared according to general procedure using prop-1-yn-1-ylbenzene (24.7 μL, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 24 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as brown liquid (11.9 mg, 36% yield).

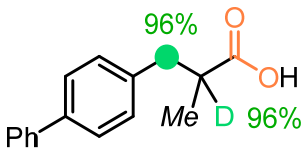
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 3.05 (s, 0.07H, **0.93D**), 2.78 – 2.73 (q, J = 6.8 Hz, 0.13H, **0.87D**), 2.65 (s, 0.07H, **0.93D**), 1.17 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 137.9, 127.9, 127.4, 125.4, 40.0 – 39.3 (m, CD), 37.9 – 37.4 (m, CD_2), 15.3.
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{10}H_8D_3O_2^-$: 166.0953; found: 166.0953.



2-cyclohexyl-3-phenylpropanoic-2,3,3-d_3 acid (3b): Prepared according to general procedure using (cyclohexylethynyl)benzene (36.9 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2C_2O_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as brown liquid (26.9 mg, 57% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.21 – 7.11 (m, 3H), 2.85 (s, 0.04H, **0.96D**), 2.81 (s, 0.05H, **0.95D**), 2.47 (d, J = 7.2 Hz, 0.08H, **0.92D**), 1.88 – 1.58 (m, 6H), 1.17 – 1.04 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 181.8, 139.2, 129.0, 128.5, 126.5, 53.7 – 52.7 (m, CD), 40.2, 34.8 – 34.1 (m, CD_2), 30.8, 30.7, 26.4.
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{15}H_{16}D_3O_2^-$: 234.1579; found: 234.1569.



2-(phenylmethyl-d_2)hexanoic-2-*d* acid (3c): Prepared according to general procedure using hex-1-yn-1-ylbenzene (35.2 μL, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2C_2O_4$ (458.4 mg, 0.8 mmol, 4.0 equiv) at r.t. for 24 hours and then at 50 °C for 6 hours. The product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as yellow liquid (26.8 mg, 64% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.13 (m, 3H), 2.95 (s, 0.04H, **0.96D**), 2.74 (s, 0.04H, **0.96D**), 2.68 – 2.63 (m, 0.9H, **0.91D**), 1.63 (dd, J = 13.6, 4.4 Hz, 1H), 1.58 – 1.47 (m, 1H), 1.40 – 1.22 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 139.2, 129.0, 128.5, 126.5, 47.4 – 46.7 (m, CD), 38.1 – 37.1 (m, CD_2), 31.5, 29.5, 22.7, 14.0.
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{13}H_{14}D_3O_2^-$: 208.1422; found: 208.1422.



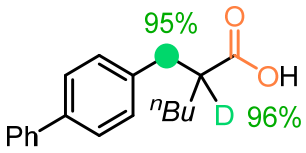
3-([1,1'-biphenyl]-4-yl)-2-methylpropanoic-2,3,3-d_3 acid (3d): Prepared according to general procedure using 4-(prop-1-yn-1-yl)-1,1'-biphenyl (38.5 mg, 0.2 mmol, 1.0

equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as brown solid (46.9 mg, 96% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.54 (m, 2H), 7.54 – 7.50 (m, 2H), 7.44 – 7.39 (m, 2H), 7.35 – 7.29 (m, 1H), 7.28 – 7.22 (m, 2H), 3.09 (s, 0.04H, **0.96D**), 2.79 (q, J = 7.2 Hz, 0.04H, **0.96D**), 2.70 (s, 0.05H, **0.95D**), 1.20 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 182.8, 141.0, 139.5, 138.2, 129.6, 128.9, 127.3, 127.1, 41.2 – 40.6 (m, CD), 38.7 – 37.9 (m, CD$_2$), 16.5.

HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for $C_{16}H_{12}D_3O_2^-$: 242.1266; found: 242.1267.

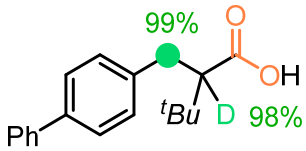


2-([1,1'-biphenyl]-4-ylmethyl-*d*$_2$)hexanoic-2-*d* acid (3e): Prepared according to general procedure using 4-(hex-1-yn-1-yl)-1,1'-biphenyl (46.9 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as white solid (55.3 mg, 97% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.54 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.25 (d, J = 8.4 Hz, 2H), 2.99 (s, 0.05H, **0.95D**), 2.77 (s, 0.05H, **0.95D**), 2.70 (q, J = 5.2 Hz, 0.04H, **0.96D**), 1.70 – 1.64 (m, 1H), 1.58 – 1.51 (m, 1H), 1.38 – 1.24 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 182.2, 141.0, 139.4, 138.3, 129.4, 128.9, 127.3, 127.1, 47.4 – 46.4 (m, CD), 37.9 – 36.3 (m, CD$_2$), 31.5, 29.5, 22.7, 14.0.

HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for $C_{19}H_{18}D_3O_2^-$: 284.1735; found: 284.1731.

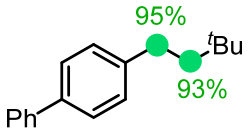


2-([1,1'-biphenyl]-4-ylmethyl-*d*$_2$)-3,3-dimethylbutanoic-2-*d* acid (3f): Prepared according to general procedure using 4-(3,3-dimethylbut-1-yn-1-yl)-1,1'-biphenyl (46.9 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as pale yellow solid (27.0 mg, 47% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, J = 7.6 Hz, 2H), 7.46 (dd, J = 8.2, 2.0 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.34 – 7.27 (m, 1H), 7.26 – 7.19 (m, 2H), 2.89 (s, 0.01H, **0.99D**), 2.85 (s, 0.01D, **0.99D**), 2.48 (s, 0.02H, **0.98D**), 1.08 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 180.7, 141.0, 139.2, 139.1, 129.2, 128.3, 127.3, 127.2, 127.1, 58.2 – 57.8 (m, CD), 33.1, 29.5 (m, CD$_2$), 27.9.

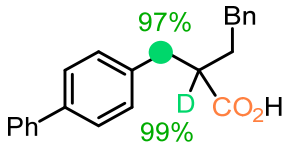
HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for $C_{19}H_{18}D_3O_2^-$: 284.1735; found: 284.1748.



4-(3,3-dimethylbutyl-1,1,2,2-*d*$_4$)-1,1'-biphenyl (3f'): The product was purified by flash column chromatography (petroleum as the eluent) and obtained as colourless liquid (18.6 mg, 38% yield)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 – 7.56 (m, 2H), 7.53 – 7.49 (m, 2H), 7.45 – 7.39 (m, 2H), 7.35 – 7.29 (m, 1H), 7.26 (d, J = 8.0 Hz, 2H), 2.58 (s, 0.05H, **0.95D**), 1.50 (s, 0.07H, **0.93D**), 1.02 (s, 3H), 0.97 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 142.9, 142.8, 141.3, 138.7, 128.8, 127.2, 127.1(5), 127.0(9), 46.2 – 45.5 (m, CD_2), 31.4 – 30.2 (m, CD), 30.6, 29.5.

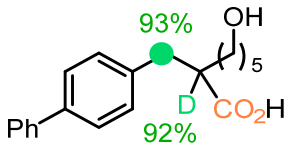


2-([1,1'-biphenyl]-4-ylmethyl-*d*$_2$)-4-phenylbutanoic-2-*d* acid (3g): Prepared according to general procedure using 4-(4-phenylbut-1-yn-1-yl)-1,1'-biphenyl (56.5 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 24 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as white solid (43.7 mg, 66% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.52 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.27 – 7.12 (m, 7H), 3.04 (s, 0.02H, **0.98D**), 2.97 (d, 0.01H, **0.99D**), 2.81 (s, 0.03H, **1.97D**), 2.77 – 2.70 (m, 1H), 2.67 – 2.59 (m, 1H), 2.06 – 1.98 (m, 1H), 1.89 – 1.81 (m, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 182.1, 141.3, 140.9, 139.5, 137.8, 129.4, 128.9, 128.6, 128.5, 127.2(9), 127.2(7), 127.1, 126.2, 46.7 – 46.1 (m, CD), 37.5 – 36.6 (m, CD_2), 33.5, 33.2.

HRMS (ESI-TOF) *m/z*: [M-H]$^-$ calcd for $C_{23}H_{18}D_3O_2^-$: 332.1735; found: 332.1750.

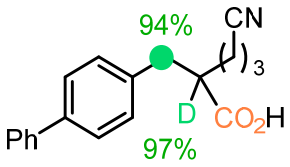


2-([1,1'-biphenyl]-4-ylmethyl-*d*$_2$)-7-hydroxyheptanoic-2-*d* acid (3h): Prepared according to general procedure using 7-([1,1'-biphenyl]-4-yl)hept-6-yn-1-ol (52.9 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 – 1/2 as the eluent) and obtained as pale yellow solid (48.6 mg, 77% yield).

^{1}H NMR (400 MHz, CD$_3$OD) δ 7.58 – 7.54 (m, 2H), 7.50 (dd, J = 8.0, 1.6 Hz, 2H), 7.39 (td, J = 7.2, 2.0 Hz, 2H), 7.29 (dd, J = 7.2, 2.0 Hz, 1H), 7.25 (dd, J = 8.0, 2.0 Hz, 2H), 3.51 (t, J = 6.8 Hz, 2H), 2.90 (s, 0.07H, **0.93D**), 2.74 (s, 0.07H, **0.93D**), 2.65 – 2.62 (m, 0.08H, **0.92D**), 1.70 – 1.59 (m, 1H), 1.57 – 1.44 (m, 3H), 1.43 – 1.26 (m, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 176.4, 140.0, 138.9, 138.0, 129.4, 128.9, 127.2, 126.5, 60.6, 46.7 -45.5(m, CD_2), 37.2 - 35.9(CD), 32.4, 31.7, 26.7, 25.5.

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{20}H_{20}D_3O_3^-$: 314.1841; found: 314.1851.

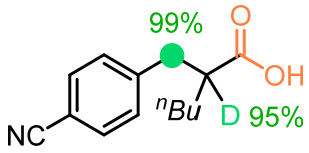


2-([1,1'-biphenyl]-4-ylmethyl-d_2)-5-cyanopentanoic-2-*d* acid (3i): Prepared according to general procedure using 6-([1,1'-biphenyl]-4-yl)hex-5-ynenitrile (49.1 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as white solid (22.0 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.33 – 7.26 (m, 3H), 2.96 (s, 0.06H, **0.94D**), 2.80 (s, 0.06H, **0.94D**), 2.71 – 2.68 (m, 0.03H, **0.97D**), 2.44 (td, J = 6.8, 1.6 Hz, 2H), 1.80 – 1.60 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 142.2, 140.6, 139.6, 130.5, 129.8, 128.2, 128.0, 127.8, 120.9, 48.0 – 47.1(m, CD), 38.6 – 38.0 (m, CD_2), 31.9, 24.5, 17.3.

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{19}H_{15}D_3NO_2^-$: 295.1531; found: 295.1545.

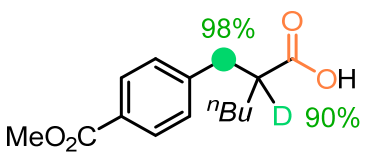


2-((4-cyanophenyl)methyl-d_2)hexanoic-2-*d* acid (3j): Prepared according to general procedure using 4-(hex-1-yn-1-yl)benzonitrile (36.7 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as yellow solid (26.3 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 2.98 (s, 0.01H, **0.99D**), 2.80 (s, 0.01H, **0.99D**), 2.68 – 2.65 (m, 0.05H, **0.95D**), 1.69 – 1.63 (m, 1H), 1.59 – 1.46 (m, 1H), 1.36 – 1.26 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 144.8, 132.4, 129.8, 119.0, 110.6, 46.8 – 46.2 (m, CD), 37.7 – 37.1 (m, CD_2), 31.6, 29.3, 22.6, 14.0.

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{14}H_{13}D_3NO_2^-$: 233.1375; found: 233.1374.



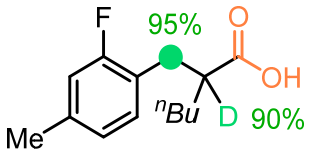
2-((4-(methoxycarbonyl)phenyl)methyl-d_2)hexanoic-2-*d* acid (3k): Prepared according to general procedure using methyl 4-(hex-1-yn-1-yl)benzoate (43.3 mg, 0.2 mmol, 1.0 equiv) and (nBu$_4$N)$_2$C$_2$O$_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours,

the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as brown solid (35.0 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 2.99 (s, 0.02H, **0.98D**), 2.79 (s, 0.02H, **0.98D**), 2.69 – 2.65 (m,0.10H, **0.90D**), 1.70 – 1.60 (m, 1H), 1.55 – 1.47 (m, 1H), 1.35 – 1.27 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 167.2, 144.7, 129.9, 129.1, 128.5, 52.2, 47.0 – 46.4 (m, CD), 37.5 – 37.1 (m, CD_2), 31.5, 29.4, 22.6, 14.0.

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{15}H_{16}D_3O_4^-$: 266.1477; found: 266.1470.



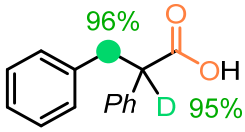
2-((2-fluoro-4-methylphenyl)methyl-d_2)hexanoic-2-d acid (3l): Prepared according to general procedure using 2-fluoro-1-(hex-1-yn-1-yl)-4-methylbenzene (38.1 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as colourless liquid (33.8 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, J = 8.0 Hz, 1H), 6.87 – 6.80 (m, 2H), 2.86 (s, 0.05H, **0.95D**), 2.80 (s, 0.05H, **0.95D**), 2.67 (dd, J = 8.8, 5.6 Hz, 0.10H, **0.90D**), 2.31 (s, 3H), 1.64 (dt, J = 9.6, 4.4 Hz, 1H), 1.56 – 1.46 (m, 1H), 1.30 (qd, J = 7.2, 6.8, 3.6 Hz, 4H), 0.88 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 161.2 (d, J = 243.6 Hz), 138.7 (d, J = 7.9 Hz), 130.9 (d, J = 5.1 Hz), 124.8 (d, J = 2.4 Hz), 122.8 (d, J = 15.8 Hz), 116.0 (d, J = 21.6 Hz), 46.0 – 45.4 (m, CD), 31.6, 31.0 – 30.2 (m, CD_2), 29.4, 22.7, 21.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.2.

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{14}H_{15}D_3FO_2^-$: 240.1485; found: 240.1472.

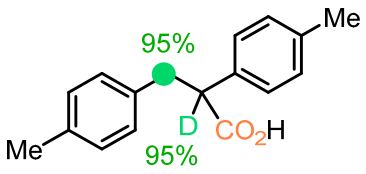


2,3-diphenylpropanoic-2,3,3-d_3 acid (3m): Prepared according to general procedure using 1,2-diphenylethyne (35.6 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (458.4 mg, 0.8 mmol, 4.0 equiv) at r.t. for 24 hours and then at 50 °C for 6 hours. T he product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as yellow solid (28.2 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.30 (m, 4H), 7.28 – 7.16 (m, 4H), 7.11 – 7.07 (m, 2H), 3.85 – 3.83 (m, 0.05H, **0.95D**), 3.39 – 3.37 (m, 0.03H, **0.97D**), 3.02 – 3.00 (m, 0.05H, **0.95D**).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 138.7, 138.0, 129.0, 128.8, 128.5, 128.2, 127.8, 126.6, 53.7 – 52.7 (m, CD), 38.8 – 38.1(m, CD_2).

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{15}H_{10}D_3O_2^-$: 228.1109; found: 228.1104.

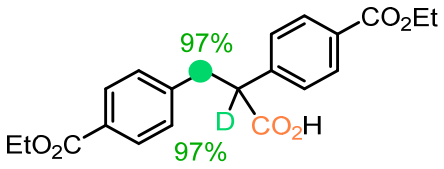


2,3-di-*p*-tolylpropanoic-2,3,3-d_3 acid (3n): Prepared according to general procedure using 1,2-di-*p*-tolylethyne (36.5 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as tawny solid (29.7 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.04-6.96 (m, 4H), 3.77 (s, 0.05H, **0.95D**), 3.31 (s, 0.05H, **0.95D**), 2.94 (s, 0.05H, **0.95D**), 2.31 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 137.4, 136.0, 135.7, 135.1, 129.5, 129.2, 128.9, 128.1, 53.10 – 52.5 (m, CD), 38.7 – 37.75 (m, CD_2), 21.2(2), 21.1(7).

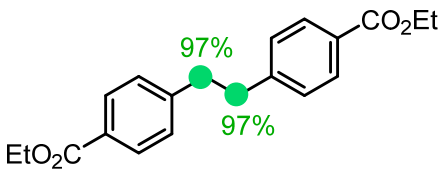
HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{17}H_{14}D_3O_2^-$: 256.1422; found: 256.1408.



2,3-bis(4-(ethoxycarbonyl)phenyl)propanoic-2,3,3-d_3 acid (3o): Prepared according to general procedure using diethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (64.5 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 8 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/10 - 1/5 as the eluent) and obtained as pale yellow solid (24.2 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.22 (s, 0.03H, **0.97D**), 2.77 (s, 0.03H, **0.97D**), 2.62 (s, 0.03H, **0.97D**), 1.41 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H).

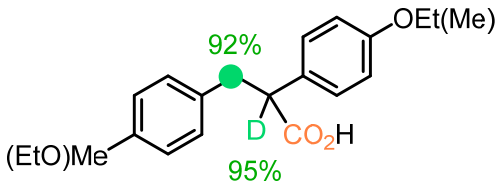
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.5, 147.6, 145.0, 130.1, 129.5, 129.4, 128.8, 128.5, 128.4, 61.2, 61.0, 54.1 – 52.9 (m, CD), 40.8 – 39.9 (m, CD_2), 14.5, 14.4.



diethyl 4,4'-(ethane-1,2-diyl-d_4)dibenzoate (3o'): The product was purified by flash column chromatography (petroleum as the eluent) and obtained as yellow solid (21.3 mg, 32% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 4H), 7.18 (d, J = 7.2 Hz, 4H), 4.36 (q, J = 6.0 Hz, 4H),2.96 (s, 0.14H, **3.86D**), 1.39 (t, J = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 146.4, 129.8, 128.6, 128.5, 61.0, 37.3 – 36.3 (m, CD_2), 14.5.



2-(4-ethoxyphenyl)-3-(*p*-tolyl)propanoic-2,3,3-d_3 acid and 3-(4-ethoxyphenyl)-2-(*p*-tolyl)propanoic-2,3,3-d_3 acid (3p + 3p', 1:1.3): Prepared according to general procedure. using 1-ethoxy-4-(*p*-tolylethynyl)benzene (47.3 mg, 0.2 mmol, 1.0 equiv) and $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (458.4 mg, 0.8 mmol, 4.0 equiv). After 36 hours, the product was purified by flash column chromatography (EtOAc/petroleum 1/5 as the eluent) and obtained as white solid (45.3 mg, 79% yield).

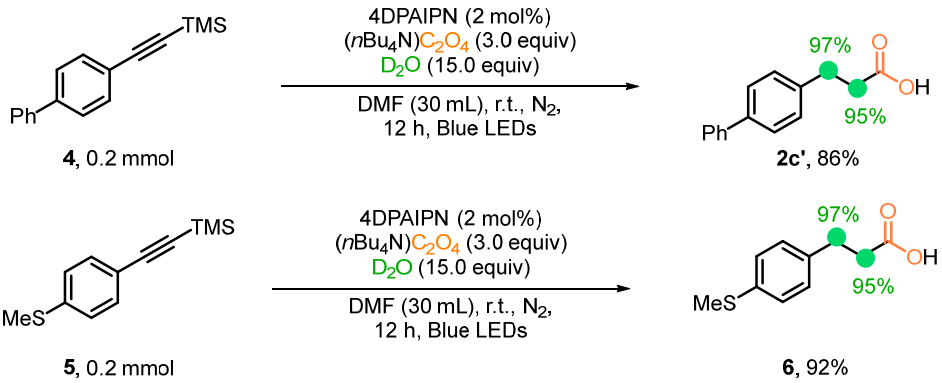
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J = 8.4, 6.8 Hz, 2H), 7.10 (d, J = 8.0 Hz, 1H), 7.03 – 6.96 (m, 3H), 6.81 (d, J = 8.8 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 3.97 (dq, J = 12.0, 7.2 Hz, 2H), 3.74 (s, 0.05H, **0.95D**), 3.28 (d, J = 3.2 Hz, 0.08H, **0.92D**), 2.92 (d, J = 6.0 Hz, 0.08H, **0.92D**), 2.31 (s, 1.28H), 2.27 (s, 1.66H), 1.42 – 1.34 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 179.9, 158.5, 157.6, 137.4, 136.0, 135.7, 135.1, 130.8, 130.0, 129.5, 129.2(2), 129.1(7), 128.9, 128.1, 114.7, 114.5, 63.5, 63.4, 53.5 – 51.7 (m, CD), 38.6 – 37.3 (m, CD_2), 21.2, 21.1, 14.9(8), 14.9(5).

HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{18}H_{16}D_3O_3^-$: 286.1528; found: 256.1525.

5. The application of the reaction

5.1 TMS-protected alkynes



To An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol, 3.0 equiv), 4DPAIPN (3.2 mg, 0.004 mmol, 2 mol%). The tube was filled with inert gas. Then D_2O (15.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at a distance of 3-4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ EtOAc 10/1 ~ 5/1) to give the pure desired product **2c'** (white solid, 39.6 mg, 86%) or **6** (pale yellow solid, 36.9 mg, 92%).

3-([1,1'-biphenyl]-4-yl)propanoic-2,2,3,3-*d*$_4$ acid (2c')

^{1}H NMR (400 MHz, CDCl_3) δ 7.55 (dd, J = 18.0, 7.6 Hz, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.35 -7.27 (m, 3H), 2.98 (m, 0.06H, **1.94D**), 2.70 (m, 0.10H, **1.90D**).

^{13}C NMR (100 MHz, CDCl_3) δ 179.3, 141.0, 139.5, 139.3, 128.9, 128.8, 127.4, 127.3, 127.2, 35.3 – 34.5 (m, CD_2), 30.1 – 29.0 (m, CD_2).

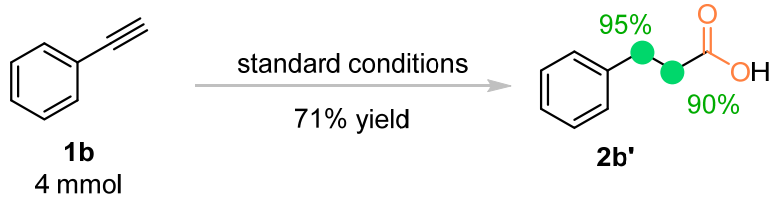
3-(4-(methylthio)phenyl)propanoic-2,2,3,3-*d*$_4$ acid (6)

^{1}H NMR (400 MHz, CDCl_3) δ 7.20 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 6.0 Hz, 2H), 2.89 (m, 0.06H, **1.94D**), 2.63 (m, 0.11H, **1.89D**), 2.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 179.3, 137.2, 136.3, 128.9, 127.2, 35.4 – 34.2 (m, CD_2), 30.0 – 28.9 (m, CD_2), 16.3.

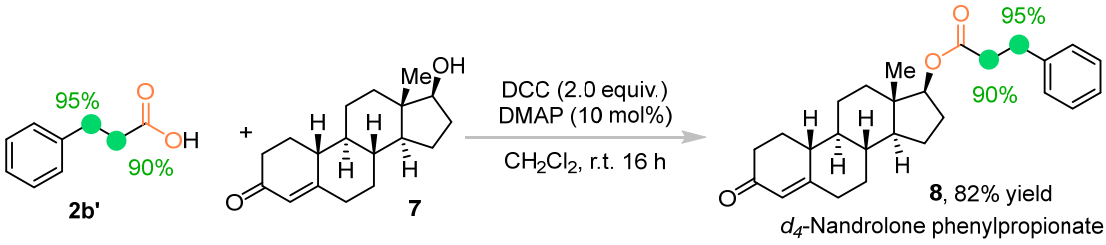
HRMS (ESI-TOF): m/z $[\text{M-H}]^-$ calcd for $\text{C}_{10}\text{H}_7\text{D}_4\text{O}_2\text{S}^-$: 199.0736; found: 199.0732.

5.2 Synthesis of the deuterated analogue of nandrolone phenylpropionate



An oven-dried Schlenk tube (100 mL) containing a stirring bar was charged with the substrate (0.44 mL, 4 mmol, 1.0 equiv), (nBu$_4$N)$_2$C$_2$O$_4$ (6.88 g, 12 mmol, 3.0 equiv), 4DPAFIPN (63.8 mg, 0.08 mmol, 2 mol%). The tube was filled with nitrogen gas. Then D_2O (1.09 mL, 60 mmol, 15.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at the distance of 3-4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (3 x 60 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ EtOAc 5/1) to give the pure desired product **2b'**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.94 (s, 0.11H, **1.89D**), 2.70 -2.63 (m, 0.21H, **1.79D**).



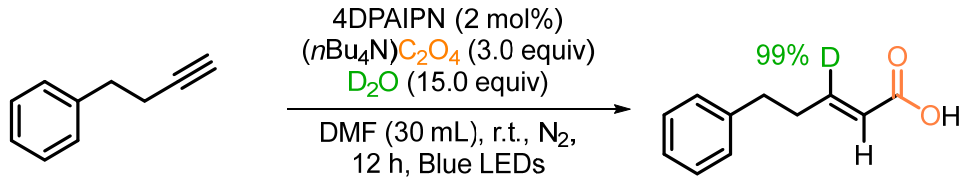
An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), DCC (2.0 equiv, 0.4 mmol, 82.5 mg), DMAP (0.1 equiv, 0.02 mmol, 2.44 mg). Then DCM (2 mL) was added. Finally, the Schlenk tube was stirred at room temperature for 16 hours. After completion of the reaction, the reaction mixture was extracted with DCM (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ EtOAc 10/1 ~ 5/1) to give the pure desired product **8** (white solid, 67.6 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 6.0 Hz, 2H), 7.20 (d, J = 7.2 Hz, 3H), 5.82 (s, 1H), 4.69 – 4.53 (t, J = 7.2 Hz, 1H), 2.92 (s, 0.09H, **1.91D**), 2.62 – 2.60 (m, 0.21H, **1.79D**), 2.44 (m, 2H), 2.29 – 2.05 (m, 5H), 1.82 (d, J = 11.2 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.48 – 1.04 (m, 8H), 0.89 – 0.85 (m, 1H), 0.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 173.1, 166.5, 140.5, 128.6, 128.4, 126.3, 124.8, 82.6, 49.6, 49.4, 42.8, 42.6, 40.3, 36.6, 36.0, 35.5, 30.7, 27.5, 26.7, 26.1, 23.4, 12.1. 35.3 – 34.5 (m, CD_2), 30.1 – 29.0 (m, CD_2).

6. Control experiments

6.1 Unactivated alkynes



9, 0.2 mmol

10, 8%

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), $(n\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$ (343.8 mg, 0.6 mmol,3.0 equiv), 4DPAIPN (3.2 mg, 0.004 mmol, 2 mol%). The tube was filled with inert gas. Then D_2O (15.0 equiv or 30.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at a distance of 3-4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ EtOAc 10/1 ~ 5/1) to give the pure desired product **10** (white solid, 2.8 mg, 8%).

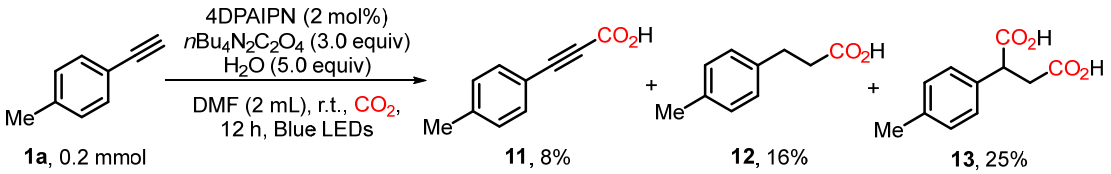
5-phenylpent-2-enoic-3-*d* acid (10)

^{1}H NMR (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.21 (d, J = 7.4 Hz, 3H), 6.38 (t, J = 7.6 Hz, 1H), 3.01 (q, J = 7.6 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H).

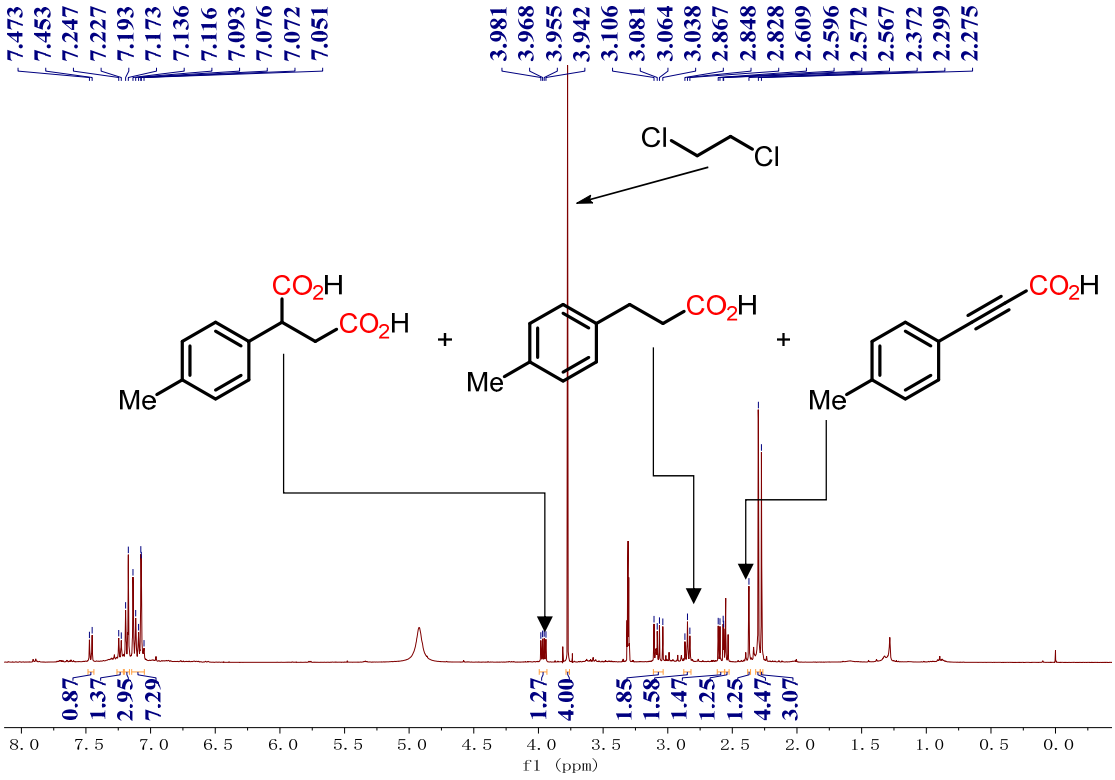
^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 152.0, 141.1, 128.6, 128.5, 126.3, 119.6 -119.4 (m, CD), 35.1, 30.7.

HRMS (ESI-TOF): m/z $[\text{M-H}]^-$ calcd for $\text{C}_{11}\text{H}_{10}\text{DO}_2^-$: 176.0827; found: 176.0835.

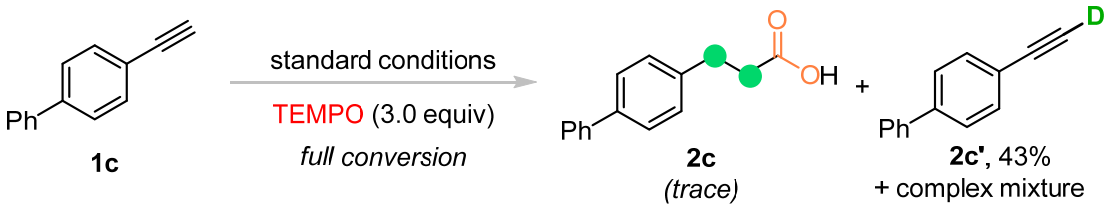
6.2 Under CO_2 atmosphere with H_2O



An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), $(n\mathrm{Bu_4N})_2C_2O_4$ (343.8 mg, 0.6 mmol,3.0 equiv), 4DPAIPN (3.2 mg, 0.004 mmol, 2 mol%). The tube was filled with inert gas. Then H_2O (5.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at a distance of 3-4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was determined by ^{1}H NMR using 1, 2-dichloroethane as an internal standard. And compounds **11, 12, 13** could be dected.



6.3 TEMPO trapping experiment

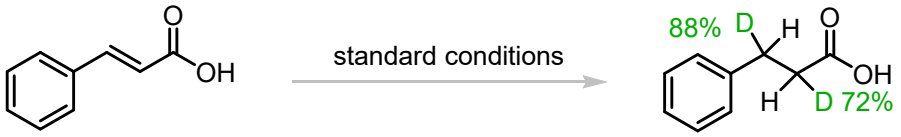


An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), $(n\mathrm{Bu_4N})_2C_2O_4$ (343.8 mg, 0.6 mmol, 3.0 equiv), 4DPAIPN (3.2 mg, 0.004 mmol, 2 mol%), TEMPO (0.6 mmol, 3.0 equiv). The tube was filled with inert gas. Then H_2O (5.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at a distance of 3-4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether), product **2c'** (15.4 mg, 43% yield).

4-(ethynyl-d)-1,1'-biphenyl (2c')

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 6H), 7.47 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H).

6.4 Cinnamic acid under standard reaction conditions



14 **15**, 28%

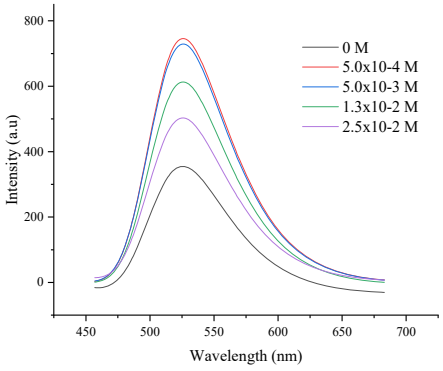
An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with substrate **14** (0.2 mmol), (nBu$_4$N)$_2$C$_2$O$_4$ (343.8 mg, 0.6 mmol, 3.0 equiv), and 4DPAIPN (3.2 mg, 0.004 mmol, 2 mol%). The tube was filled with inert gas. Then D_2O (15.0 equiv) and anhydrous DMF (2 mL) were added. Finally, the Schlenk tube was placed under the 45 W blue LED (wavelength: 450 nm) at the distance of 3 - 4 cm and stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ EtOAc 10/1 ~ 5/1) to give the pure desired product **15** (white solid, 8.4 mg, 28%).

3-phenylpropanoic-2,3-d_2 acid (15)

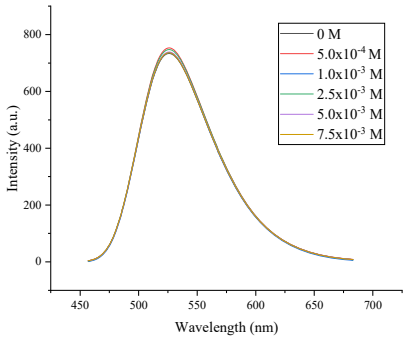
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 2.98 – 2.90 (m, 1.12H, **0.88D**), 2.71 – 2.63 (m, 1.28H, **0.72D**).

6.5 Stern-Volmer fluorescence quenching analysis

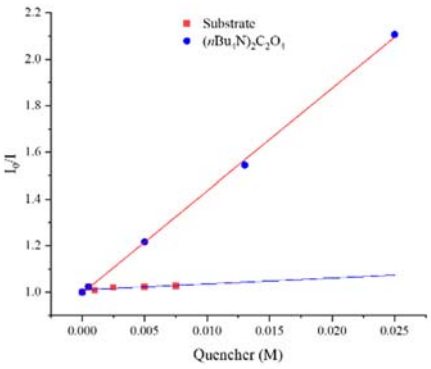
Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 5×10^{-5} M 4DPAIPN in degassed anhydrous DMF at room temperature. The solution was irradiated at 440 nm and the fluorescence was measured from 440 nm to 750 nm. Data was collected on an Agilent Technologices F-4600 spectrofluorometer at 25 °C. Parameters: data interval = 1 nm, scan rate = 645 nm/min, Averaging time = 0.1 sec. The samples were measured in Jingke ES quartz cuvettes (chamber volume = 2.5 mL, H × W × D = 56 nm × 12.5 nm × 12.5 nm).



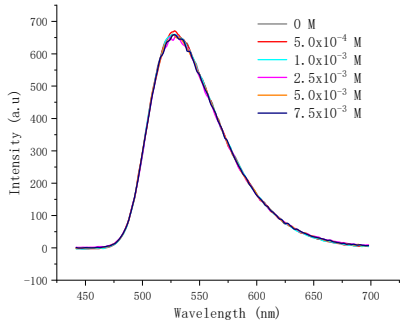
$(n\mathrm{Bu_4N})_2\mathrm{C_2O_4}$



1a



Stern-Volmer Quenching



cinnamic acid

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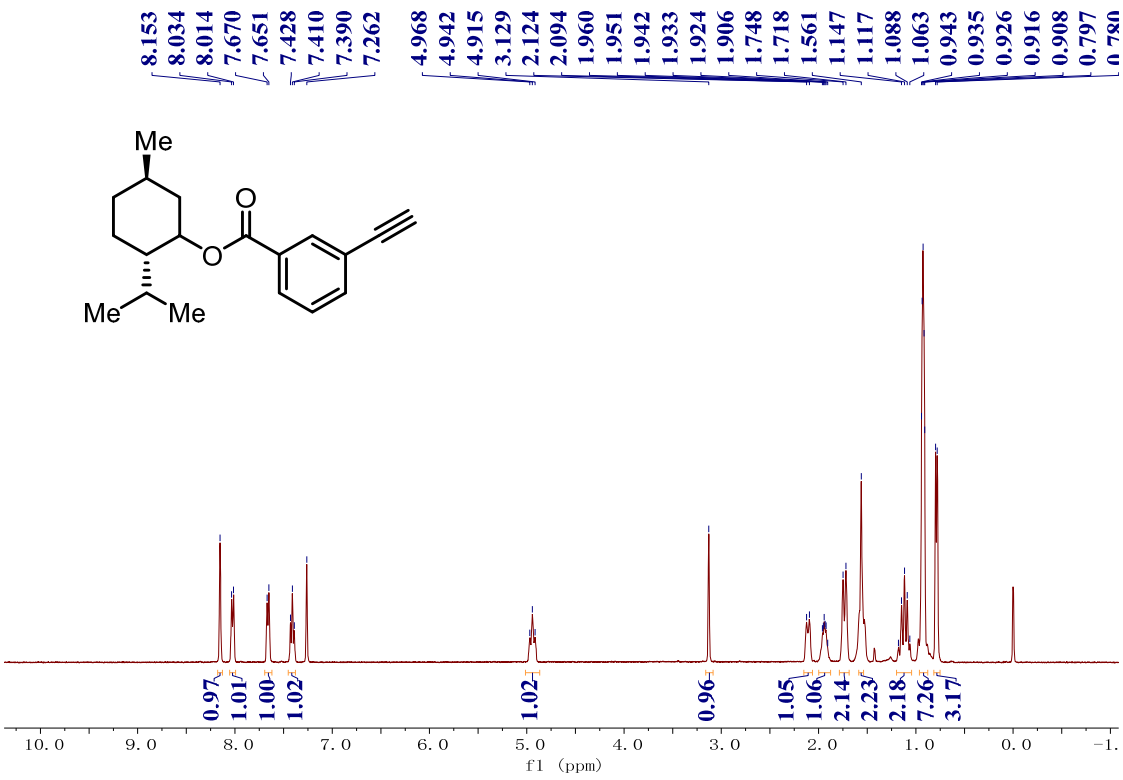
8. NMR spectra

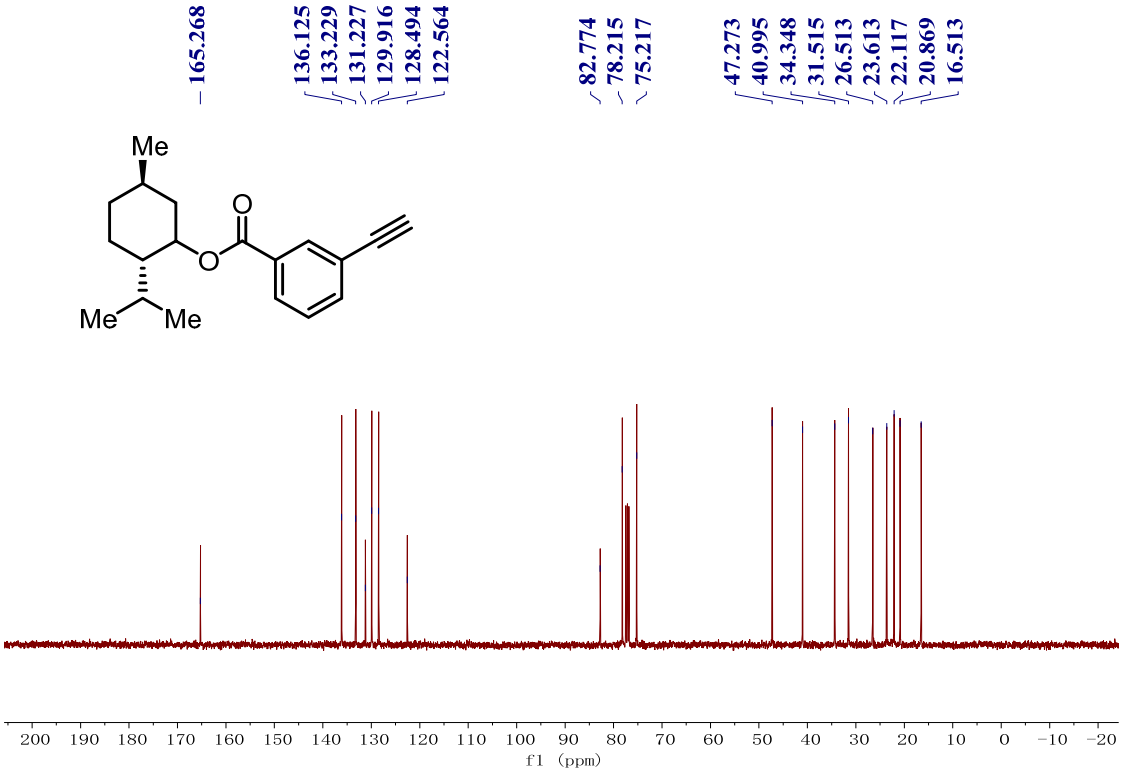
(2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-ethynylbenzoate (1n)

^{1}H NMR (400 MHz, $CDCl_3$)



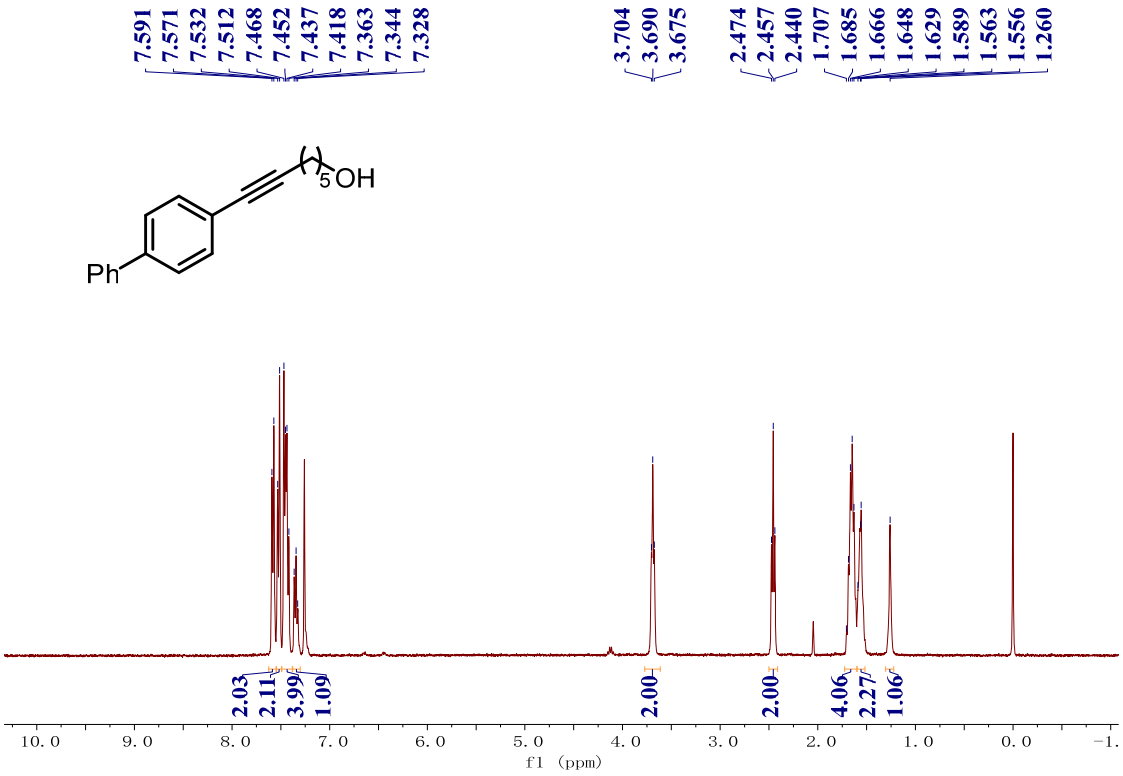
(2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-ethynylbenzoate (1n)

^{13}C NMR (100 MHz, $CDCl_3$)



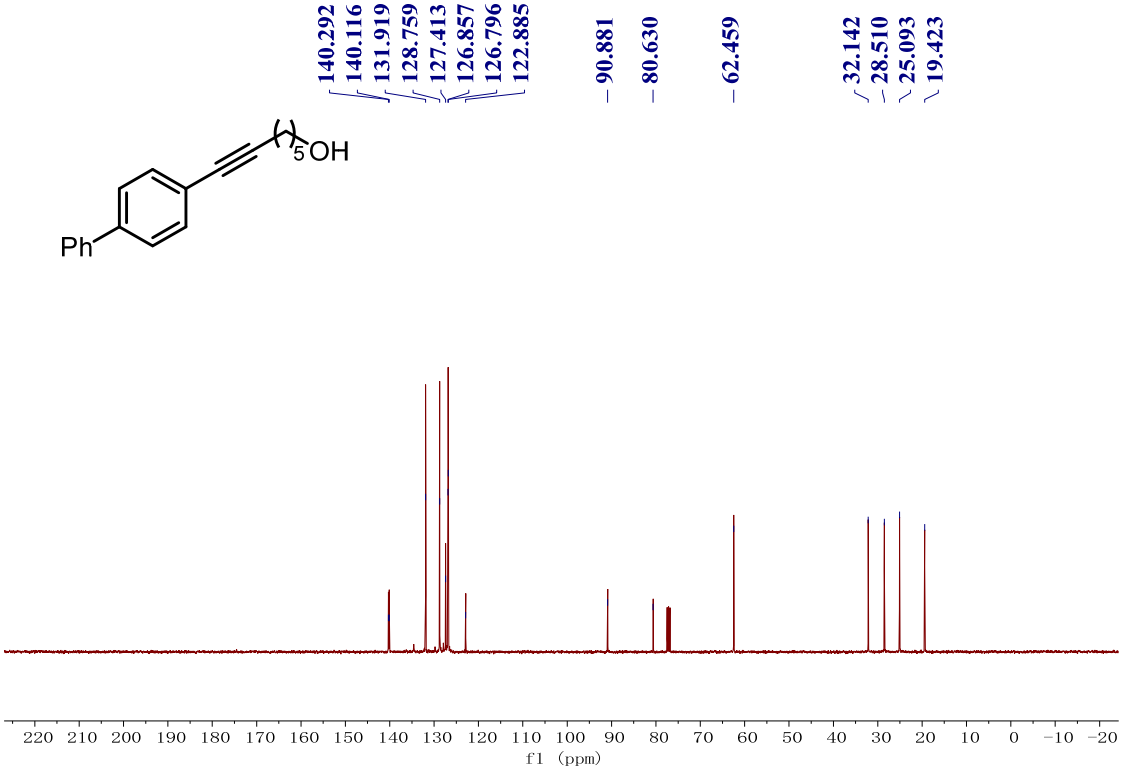
7-([1,1'-biphenyl]-4-yl)hept-6-yn-1-ol (1ah)

^{1}H NMR (400 MHz, $CDCl_3$)



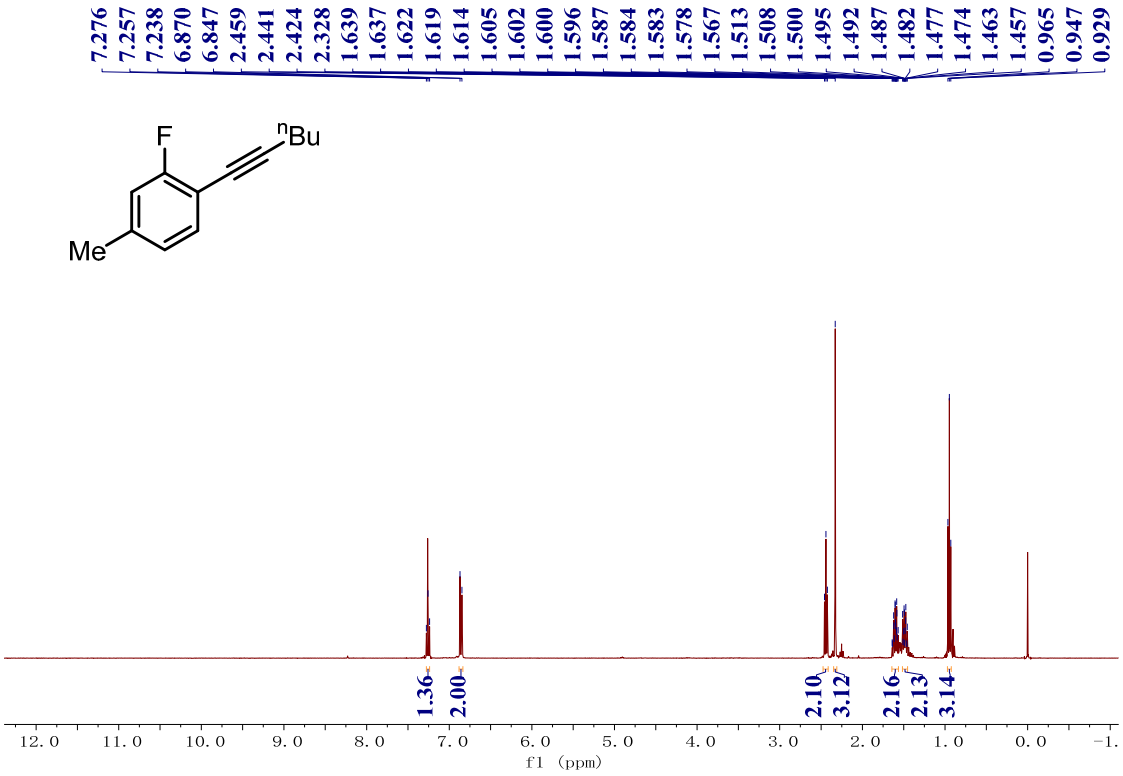
7-([1,1'-biphenyl]-4-yl)hept-6-yn-1-ol (1ah)

^{13}C NMR (100 MHz, $CDCl_3$)



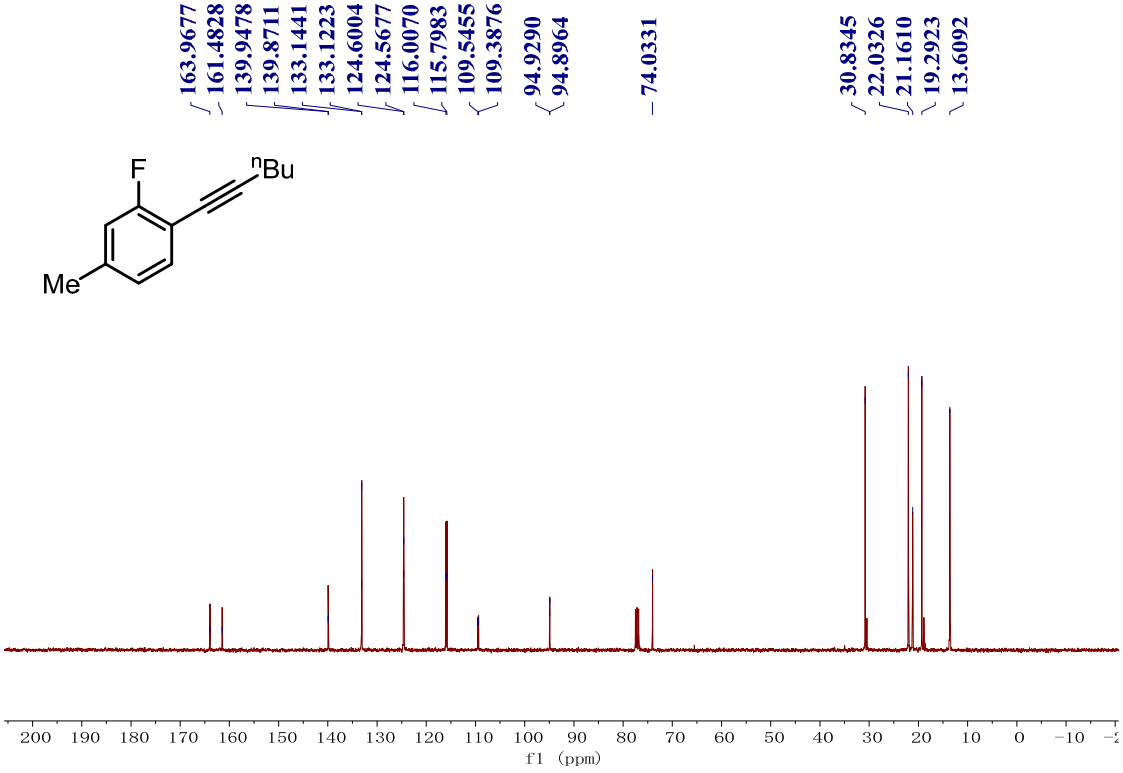
2-fluoro-1-(hex-1-yn-1-yl)-4-methylbenzene (1al)

^{1}H NMR (400 MHz, $CDCl_3$)



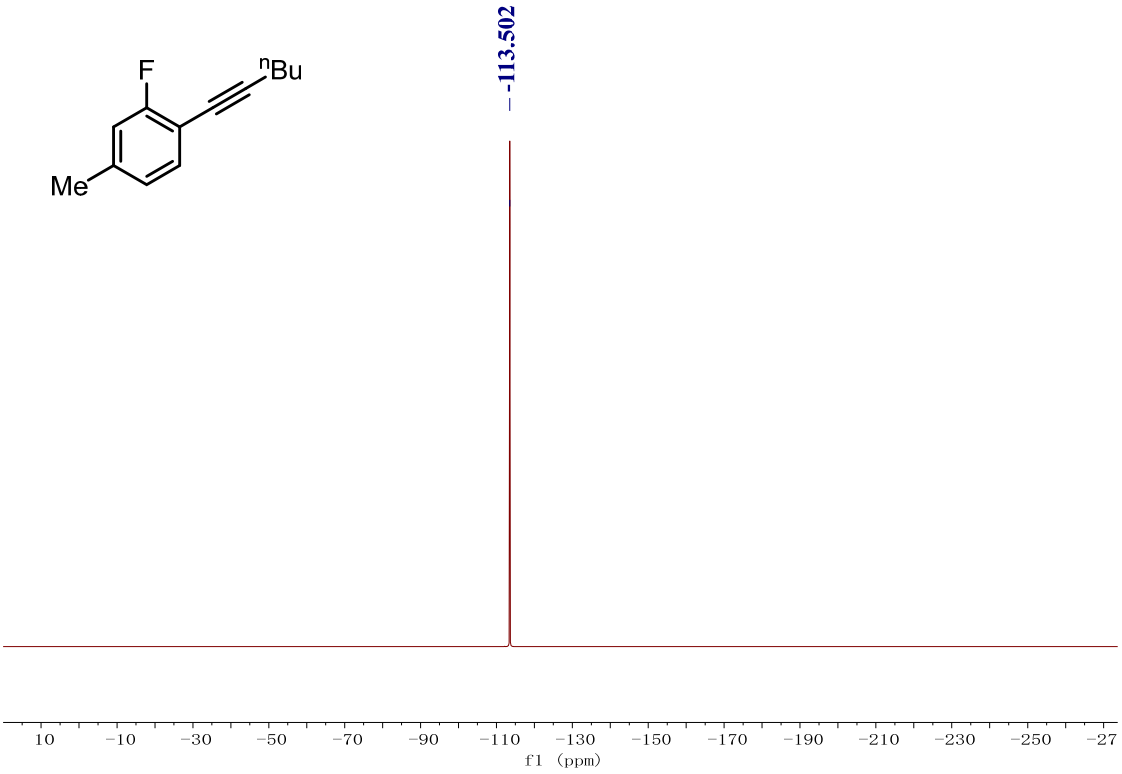
2-fluoro-1-(hex-1-yn-1-yl)-4-methylbenzene (1al)

^{13}C NMR (100 MHz, $CDCl_3$)



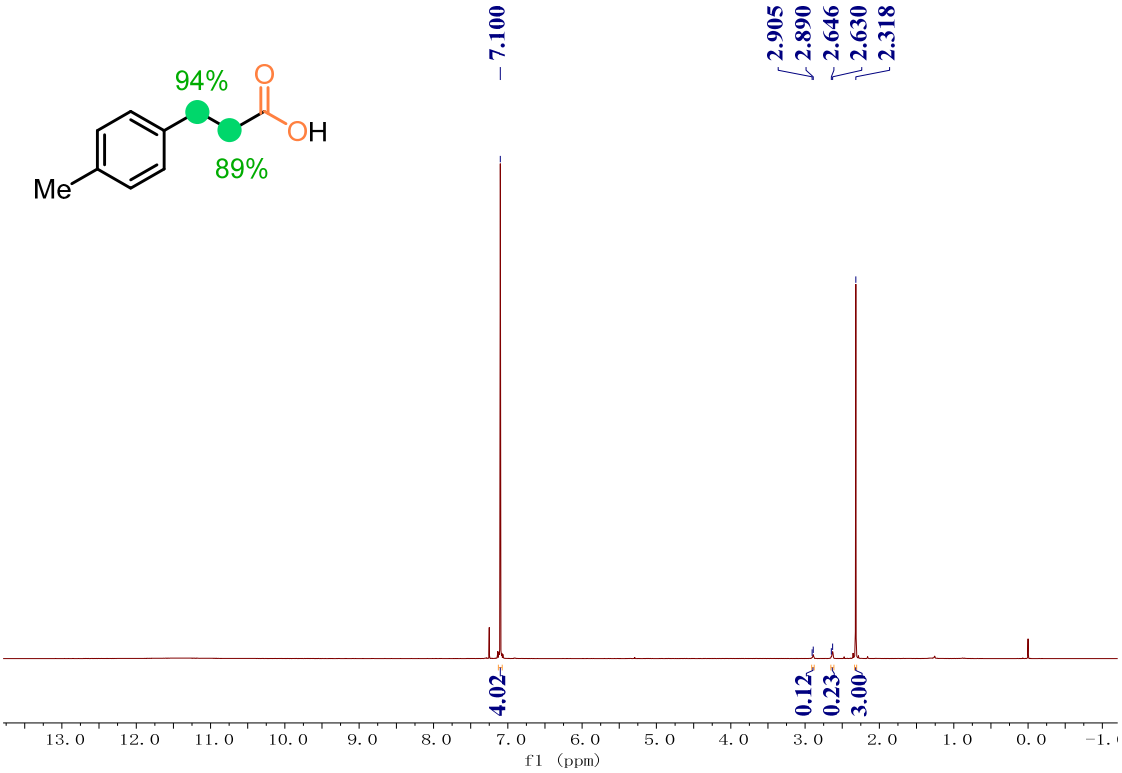
2-fluoro-1-(hex-1-yn-1-yl)-4-methylbenzene (1al)

^{19}F NMR (376 MHz, $CDCl_3$)



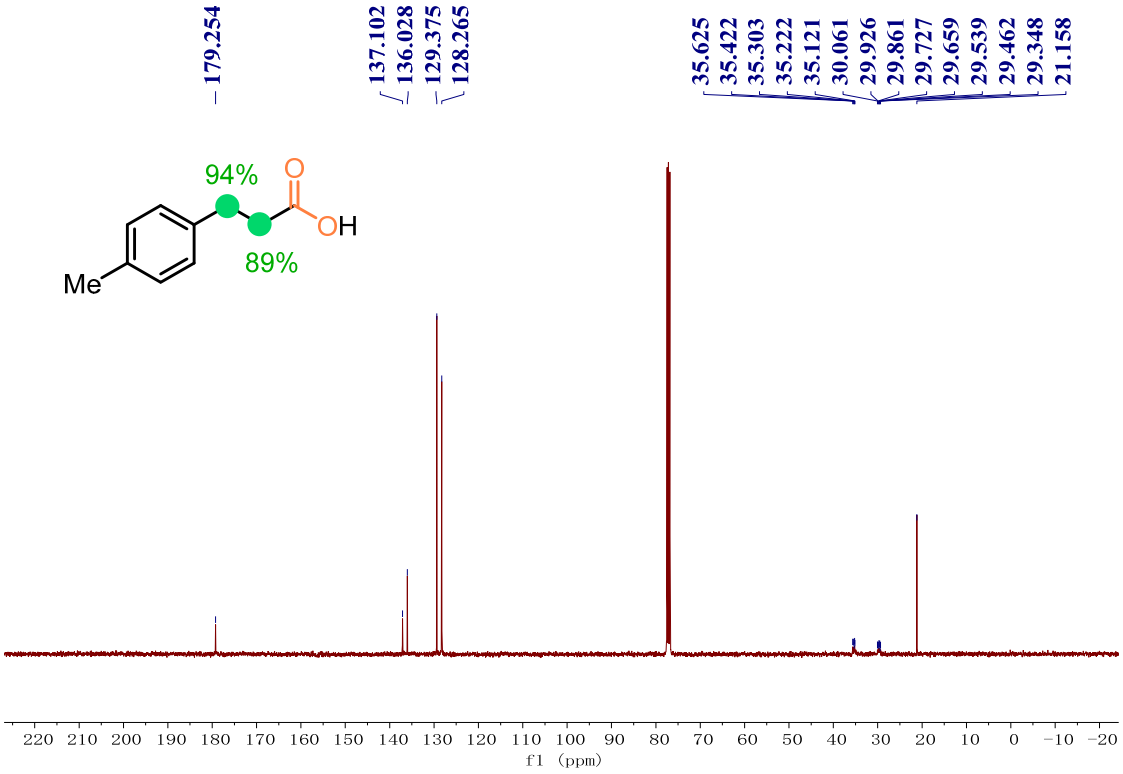
3-(*p*-tolyl)propanoic-2,2,3,3-d_4 acid (2a)

^{1}H NMR (400 MHz, $CDCl_3$)



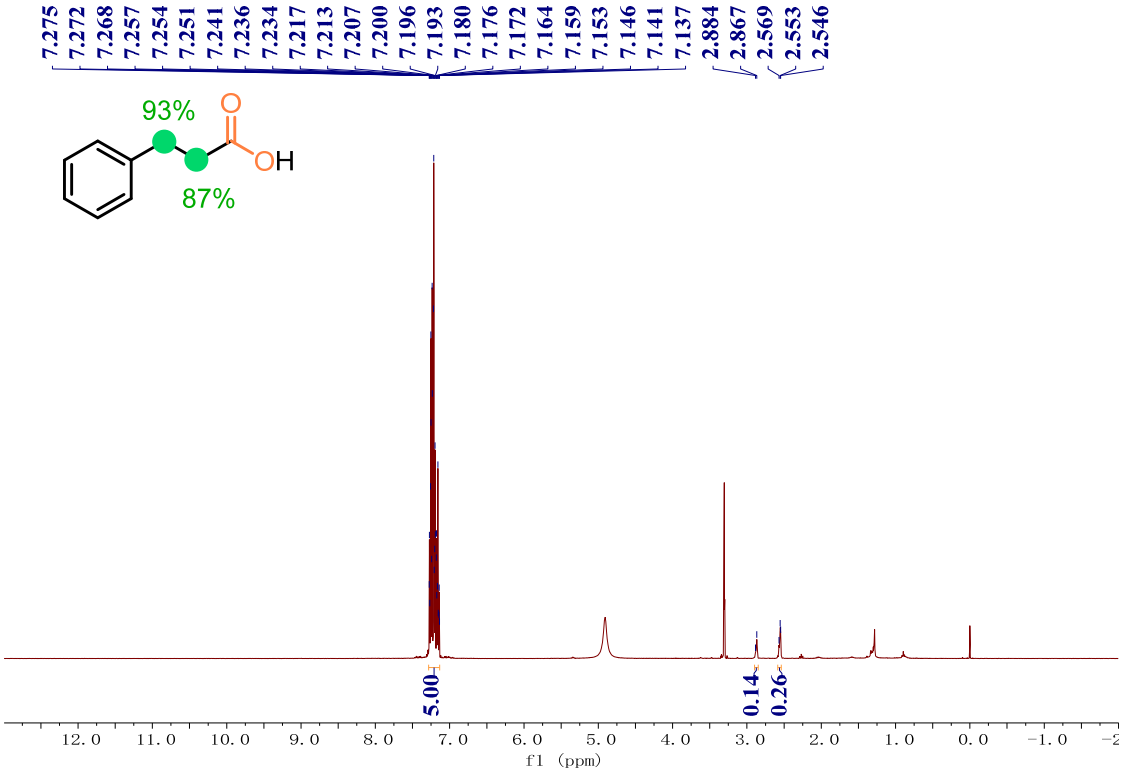
3-(*p*-tolyl)propanoic-2,2,3,3-d_4 acid (2a)

^{13}C NMR (100 MHz, $CDCl_3$)



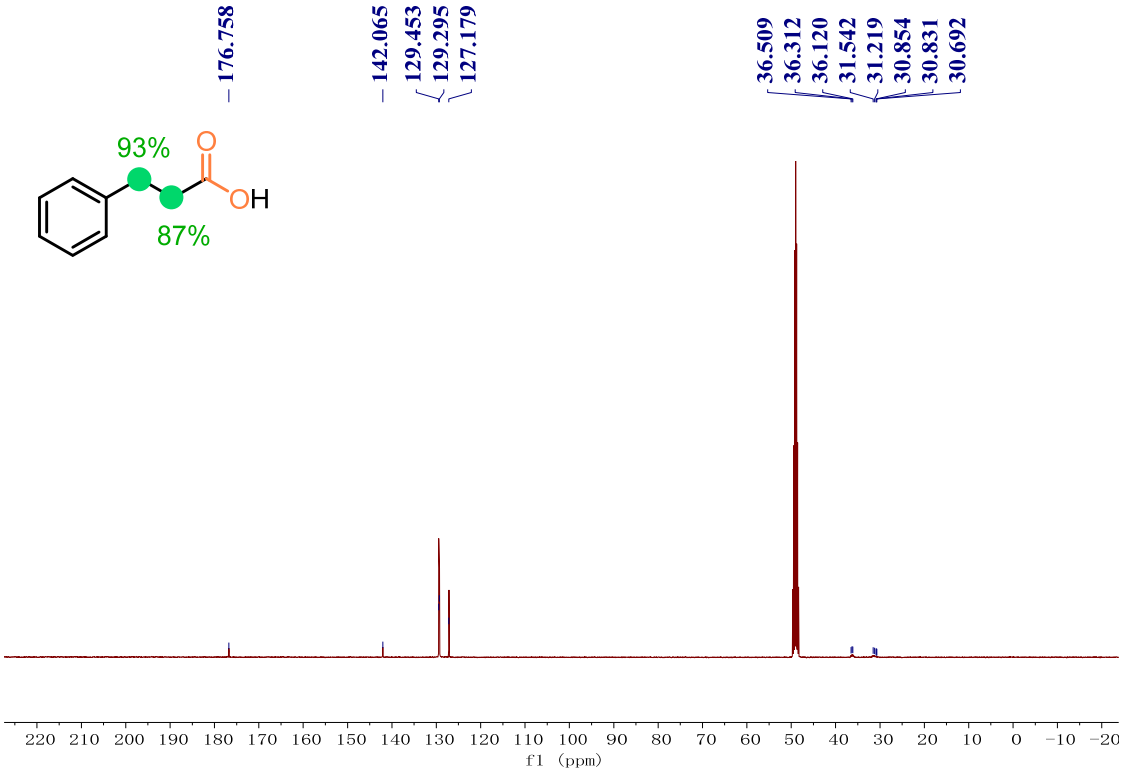
3-phenylpropanoic-2,2,3,3-d_4 acid (2b)

^{1}H NMR (400 MHz, CD_3OD)



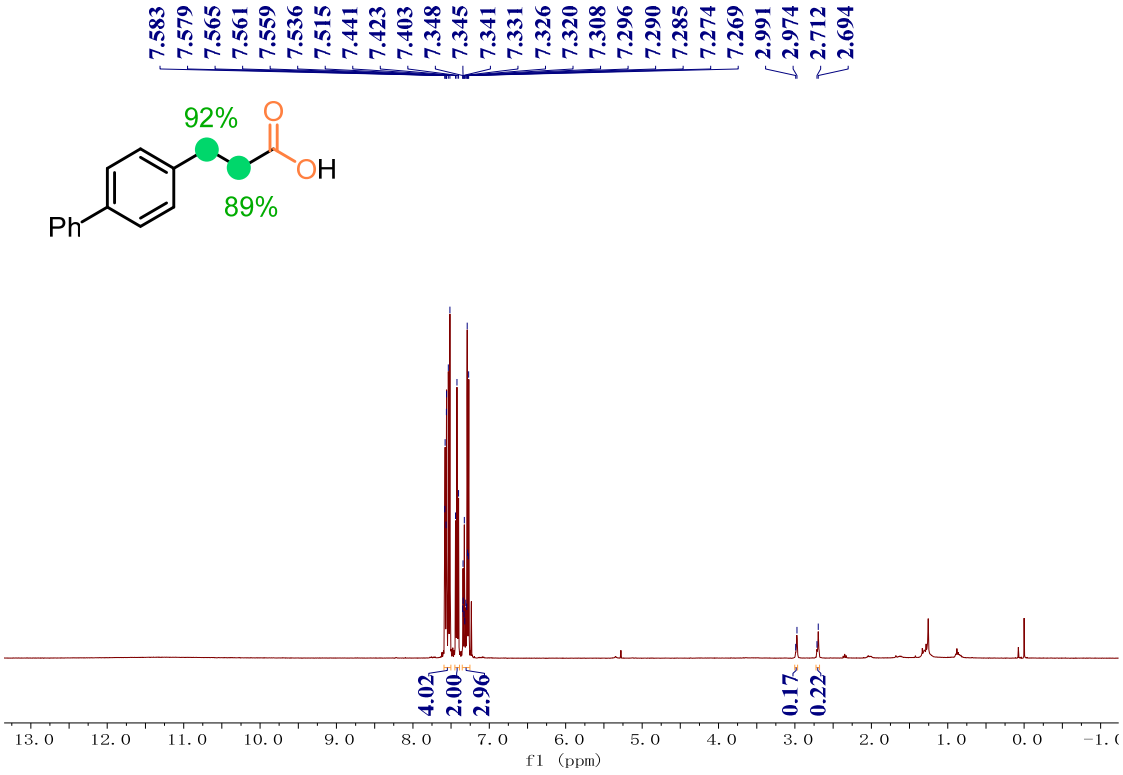
3-phenylpropanoic-2,2,3,3-d_4 acid (2b)

^{13}C NMR (100 MHz, CD_3OD)



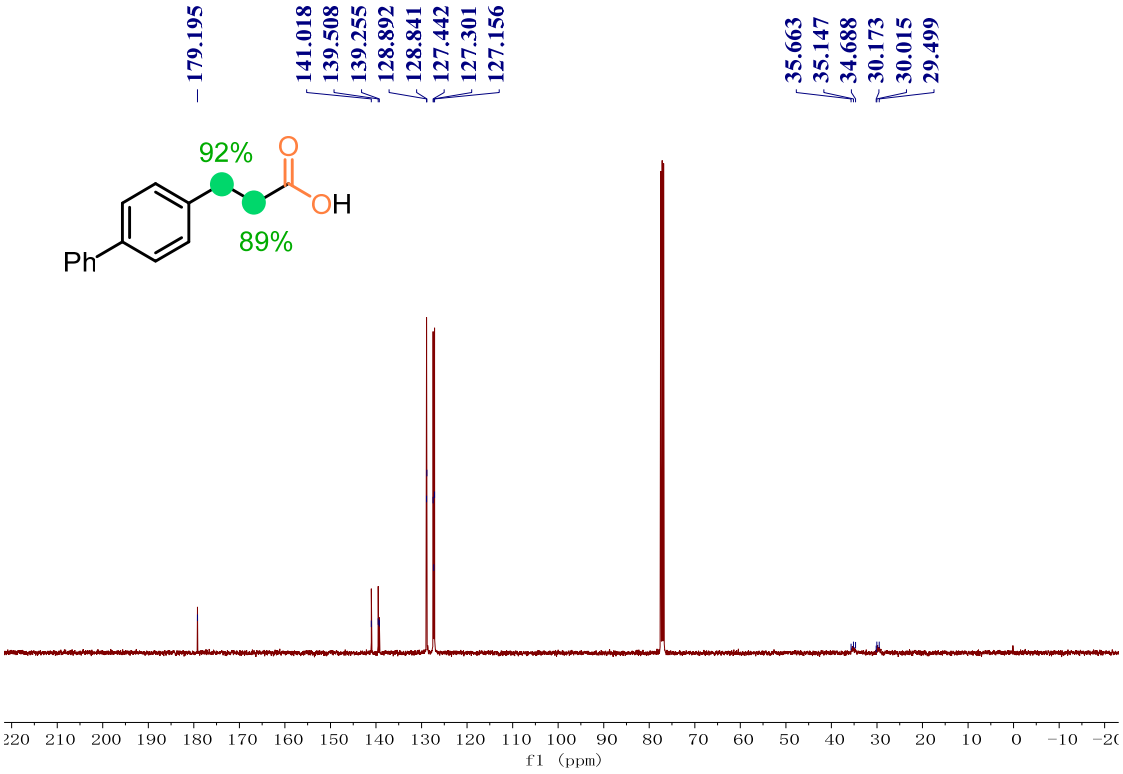
3-([1,1'-biphenyl]-4-yl)propanoic-2,2,3,3-d_4 acid (2c)

^{1}H NMR (400 MHz, $CDCl_3$)



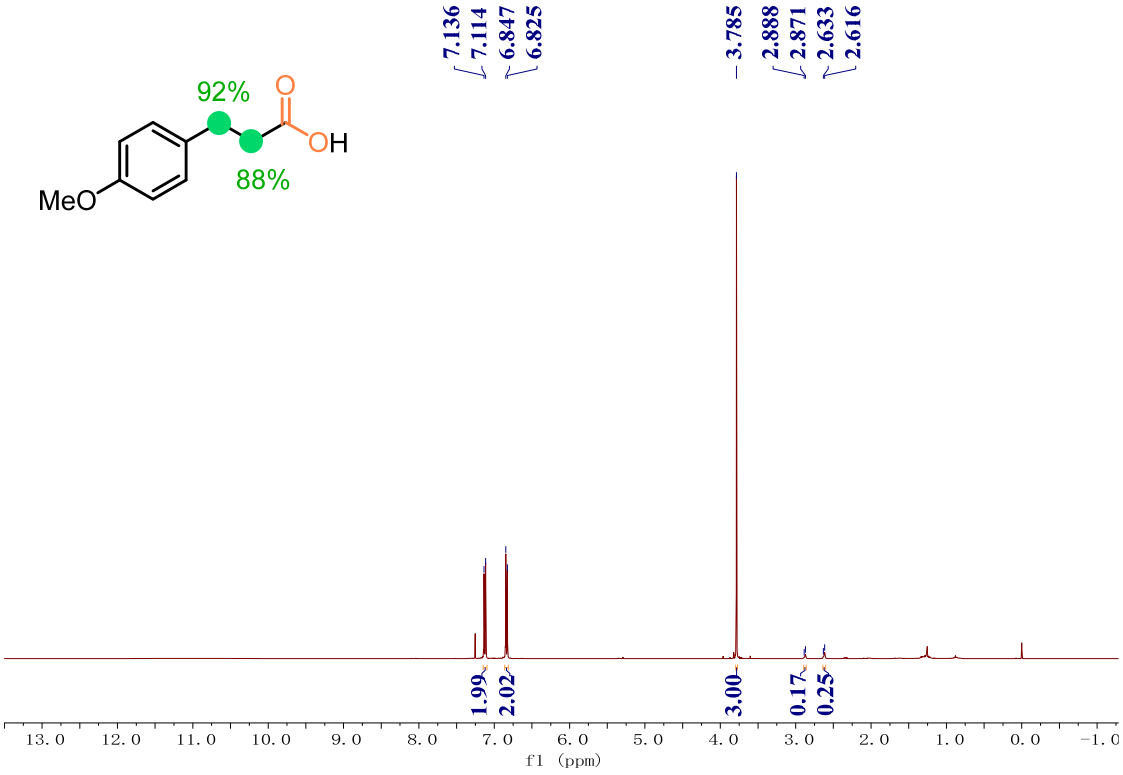
3-([1,1'-biphenyl]-4-yl)propanoic-2,2,3,3-d_4 acid (2c)

^{13}C NMR (100 MHz, $CDCl_3$)



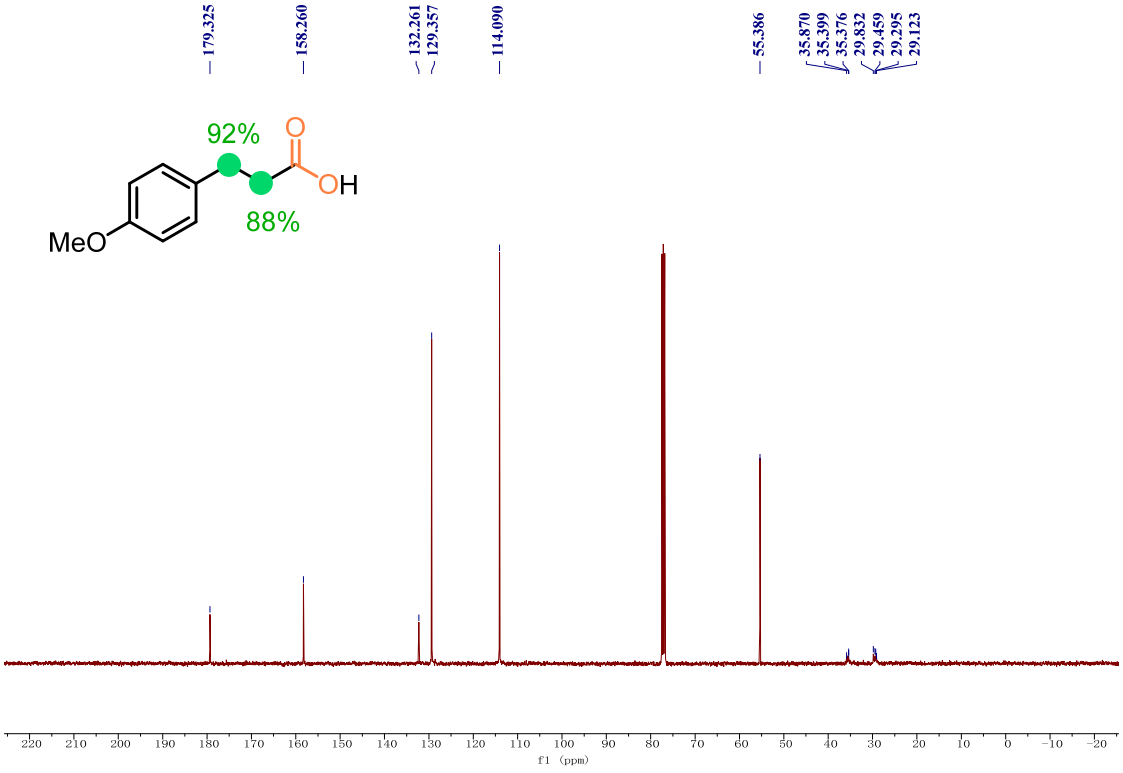
3-(4-methoxyphenyl)propanoic-2,2,3,3-d_4 acid (2d)

^{1}H NMR (400 MHz, $CDCl_3$)



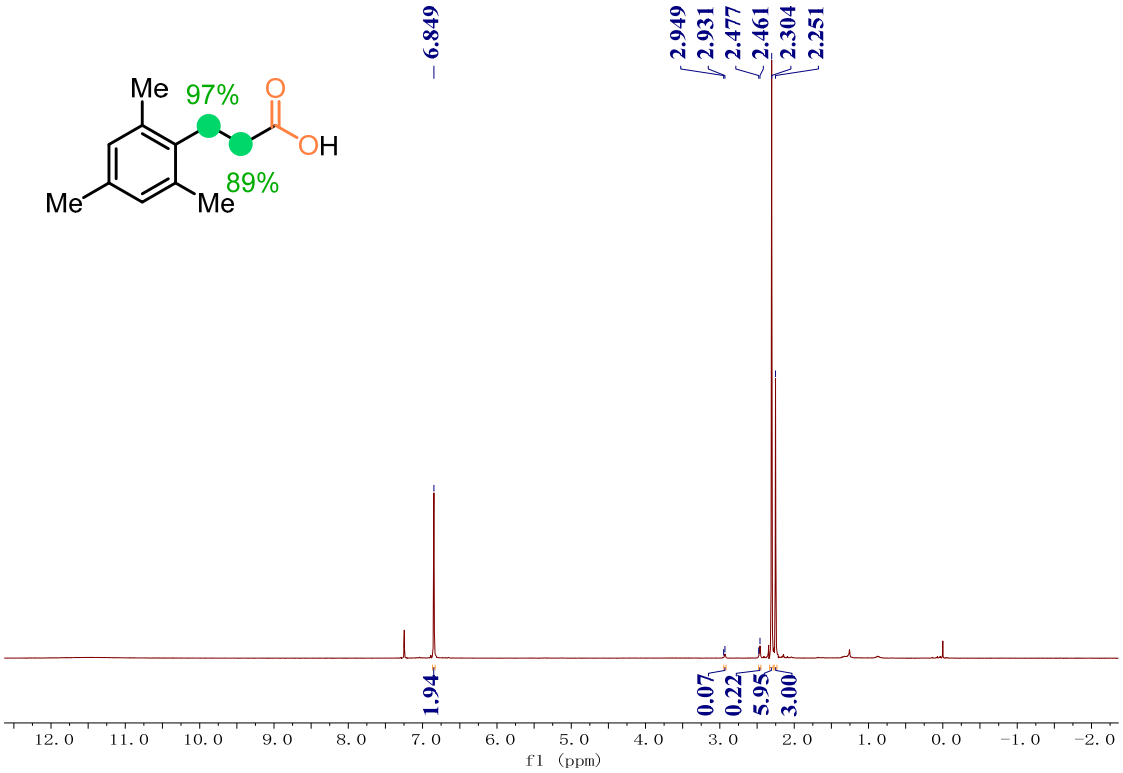
3-(4-methoxyphenyl)propanoic-2,2,3,3-*d*$_4$ acid (2d)

^{13}C NMR (100 MHz, CDCl$_3$)



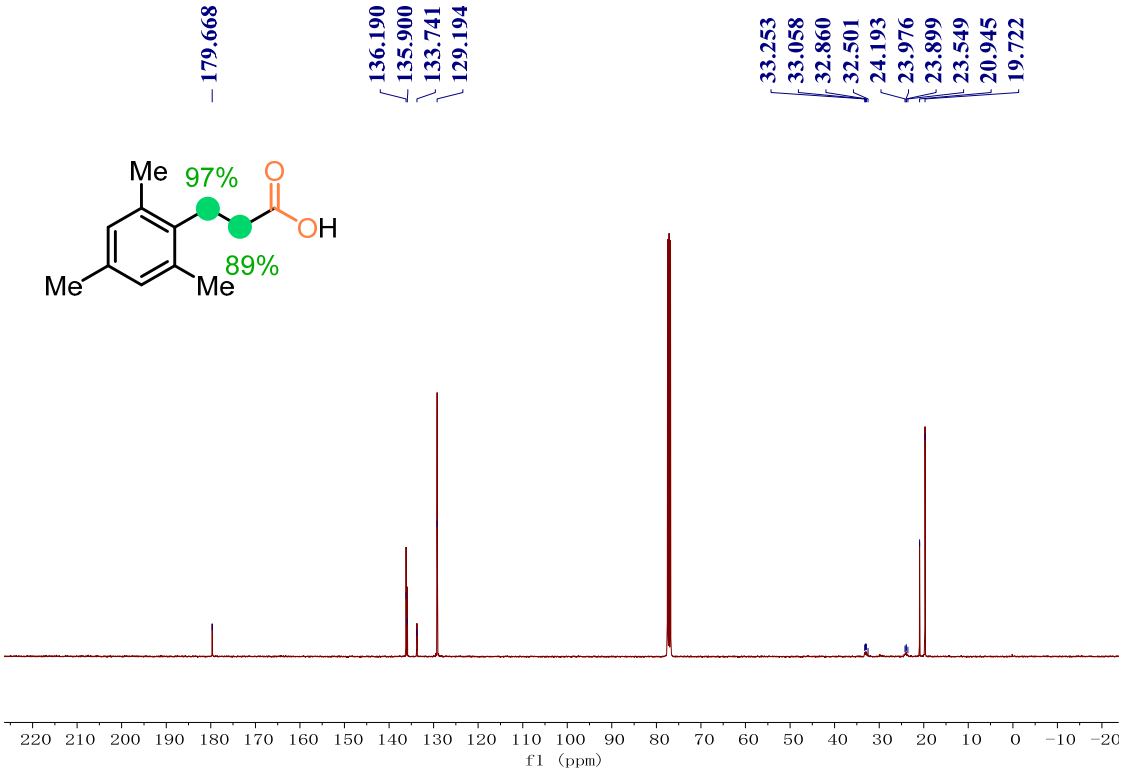
3-mesitylpropanoic-2,2,3,3-*d*$_4$ acid (2e)

^{1}H NMR (400 MHz, CDCl$_3$)



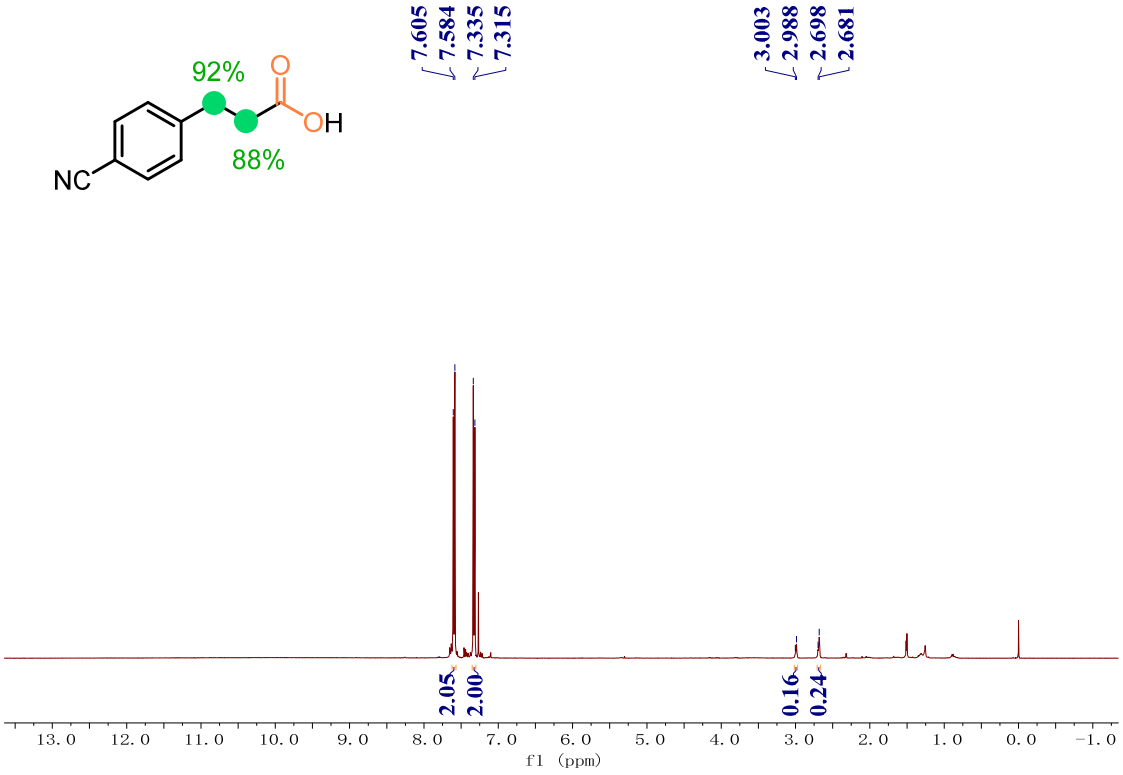
3-mesitylpropanoic-2,2,3,3-d_4 acid (2e)

^{13}C NMR (100 MHz, $CDCl_3$)



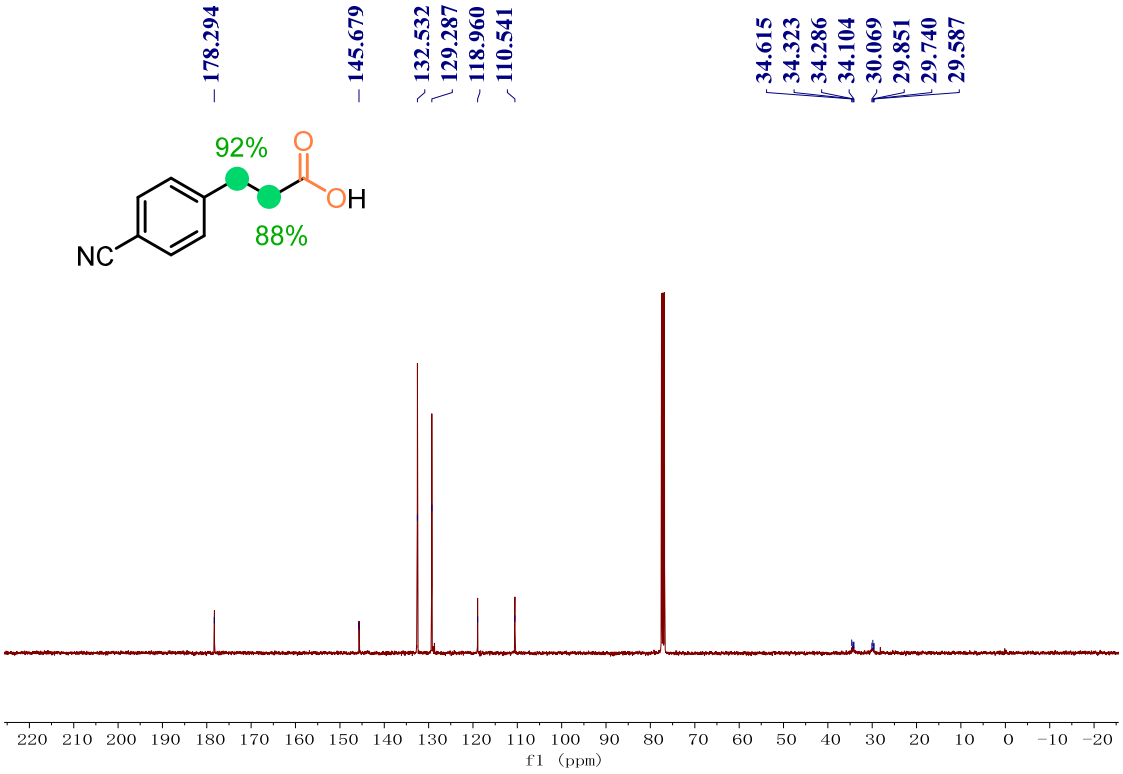
3-(4-cyanophenyl)propanoic-2,2,3,3-d_4 acid (2f)

^{1}H NMR (400 MHz, $CDCl_3$)



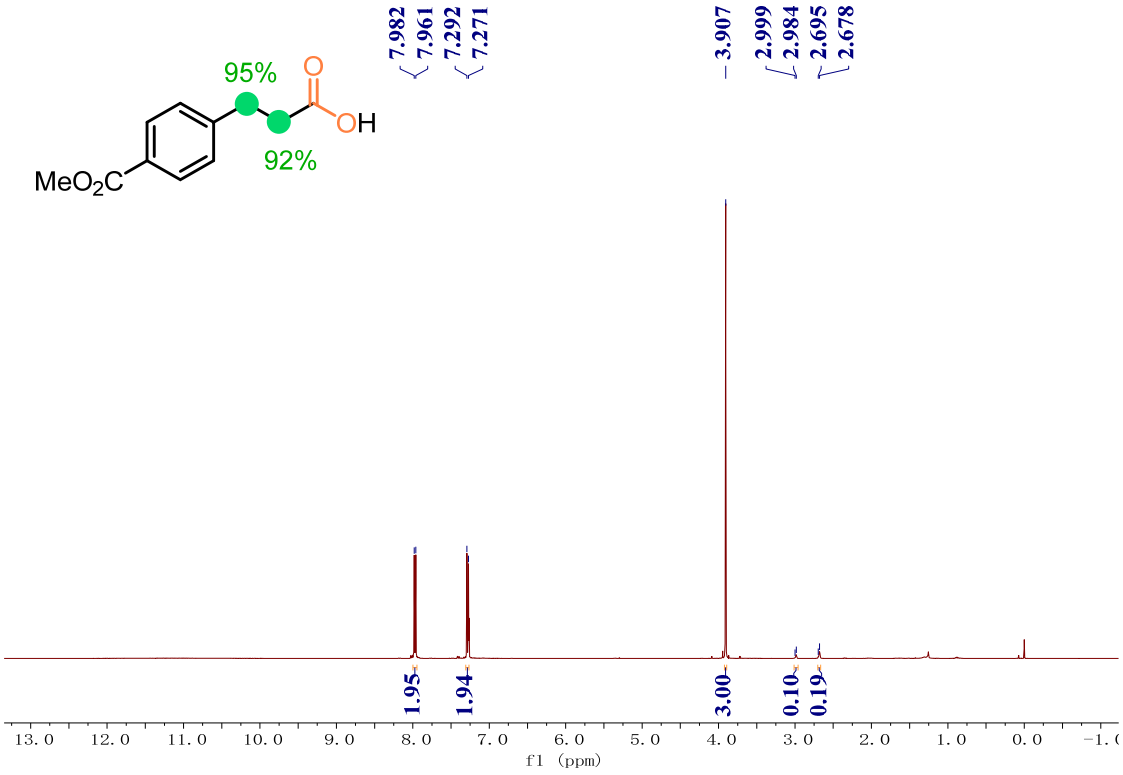
3-(4-cyanophenyl)propanoic-2,2,3,3-d_4 acid (2f)

^{13}C NMR (100 MHz, $CDCl_3$)



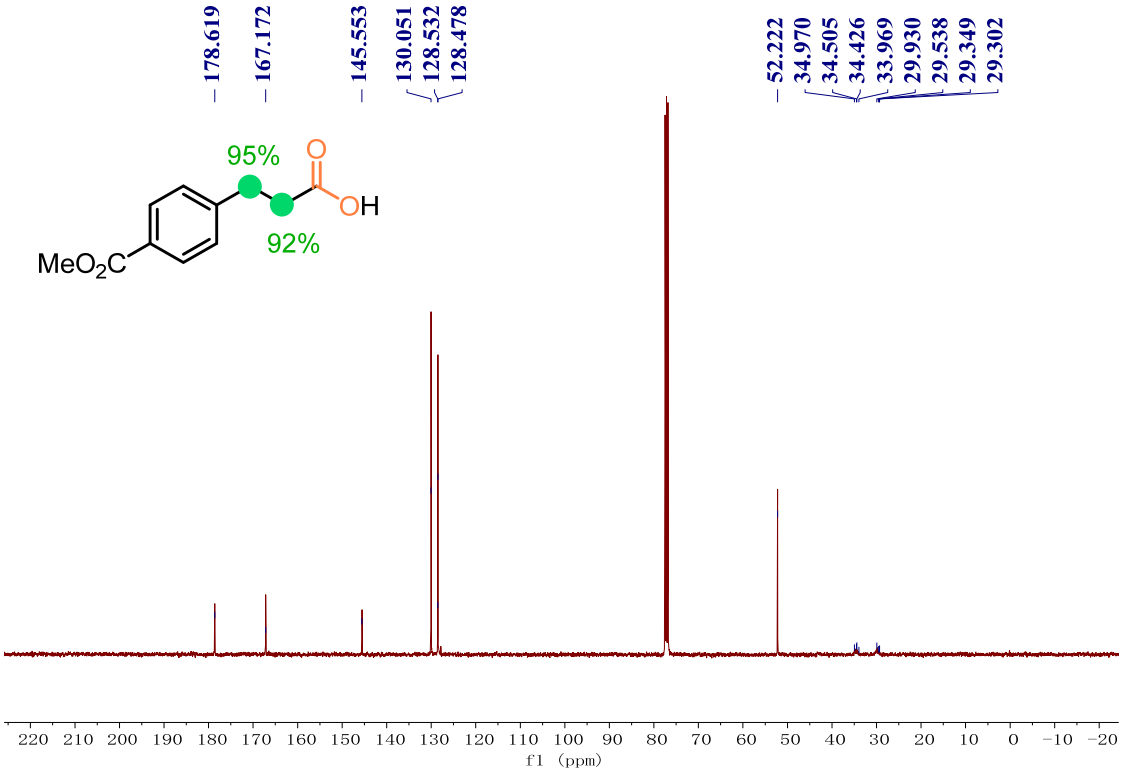
3-(4-(methoxycarbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2g)

^{1}H NMR (400 MHz, $CDCl_3$)



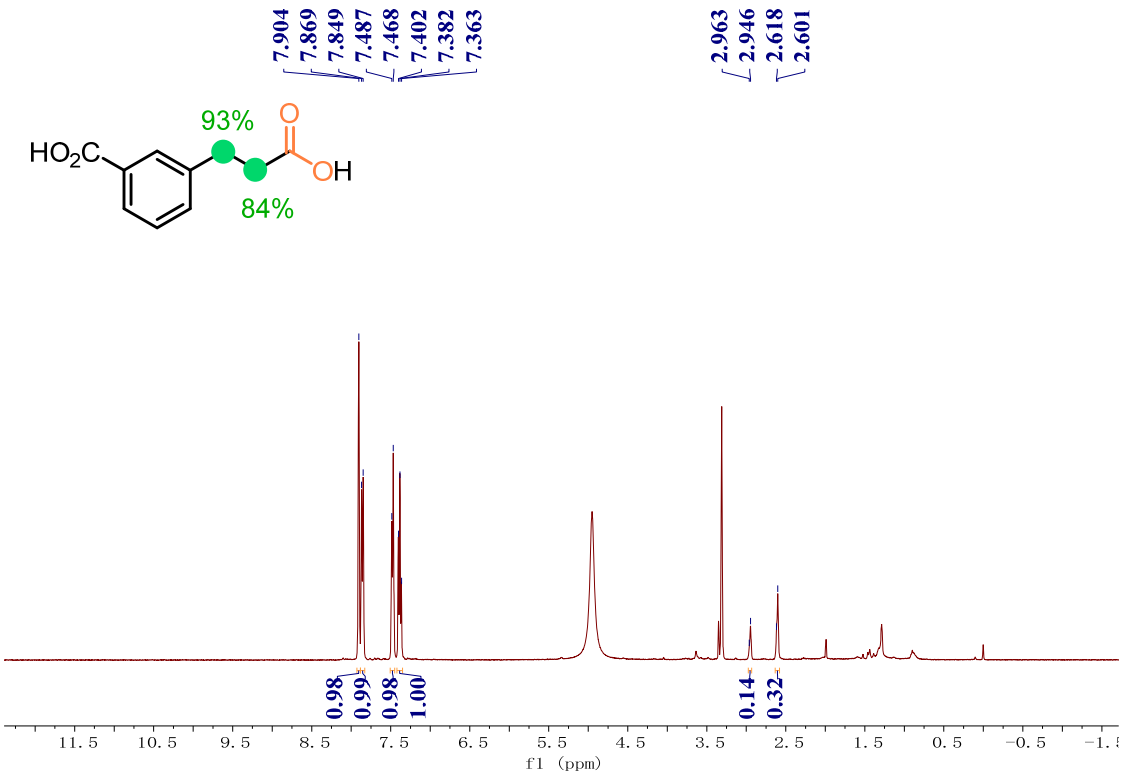
3-(4-(methoxycarbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2g)

^{13}C NMR (100 MHz, $CDCl_3$)



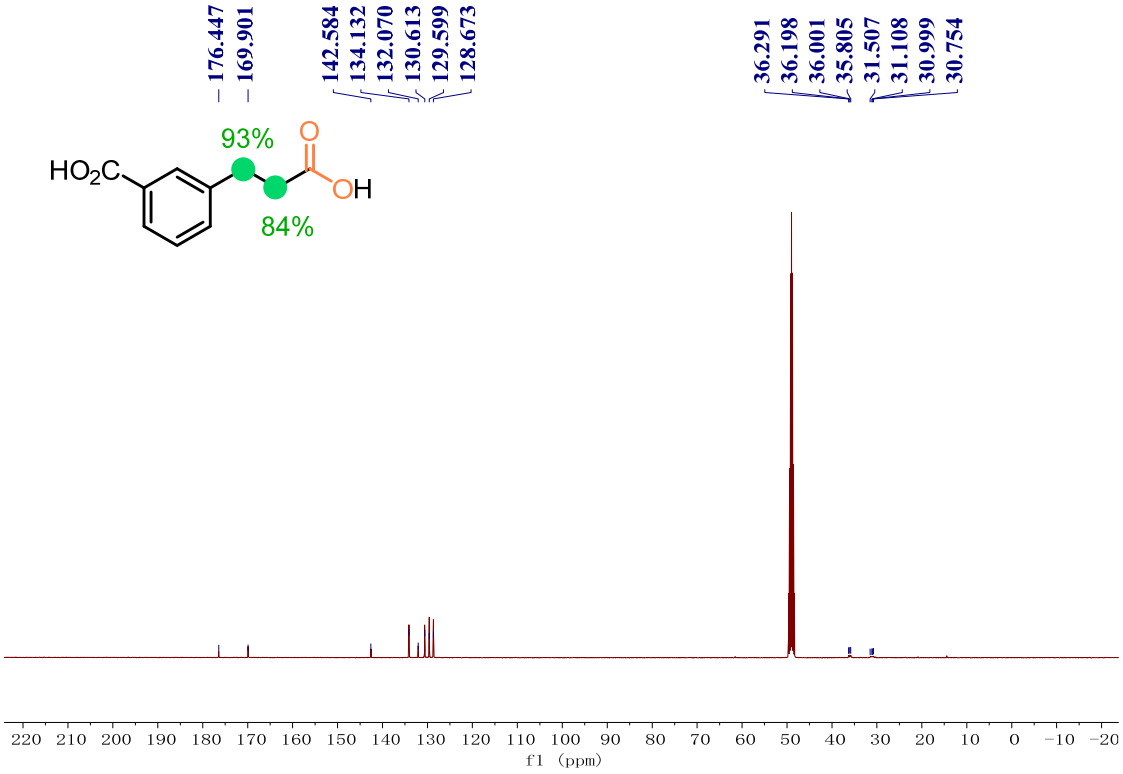
3-(2-carboxyethyl-1,1,2,2-d_4)benzoic acid (2h)

^{1}H NMR (400 MHz, CD_3OD)



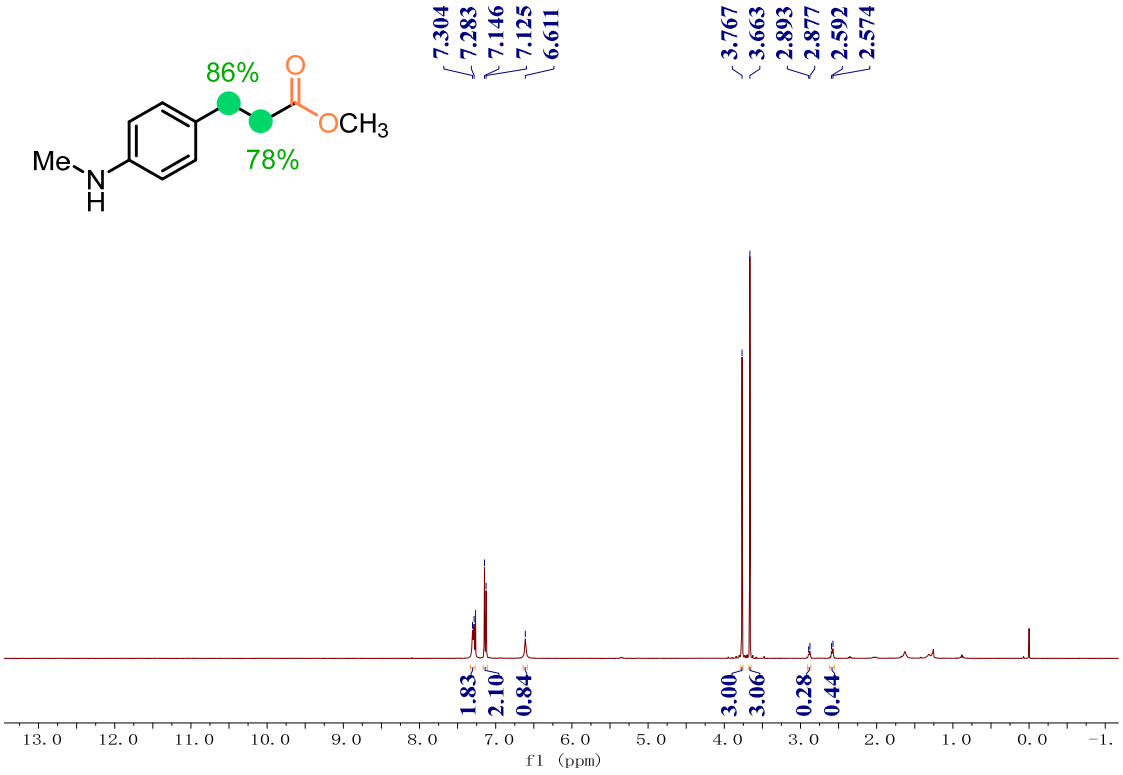
3-(2-carboxyethyl-1,1,2,2-*d*$_4$)benzoic acid (2h)

^{13}C NMR (100 MHz, CD_3OD)



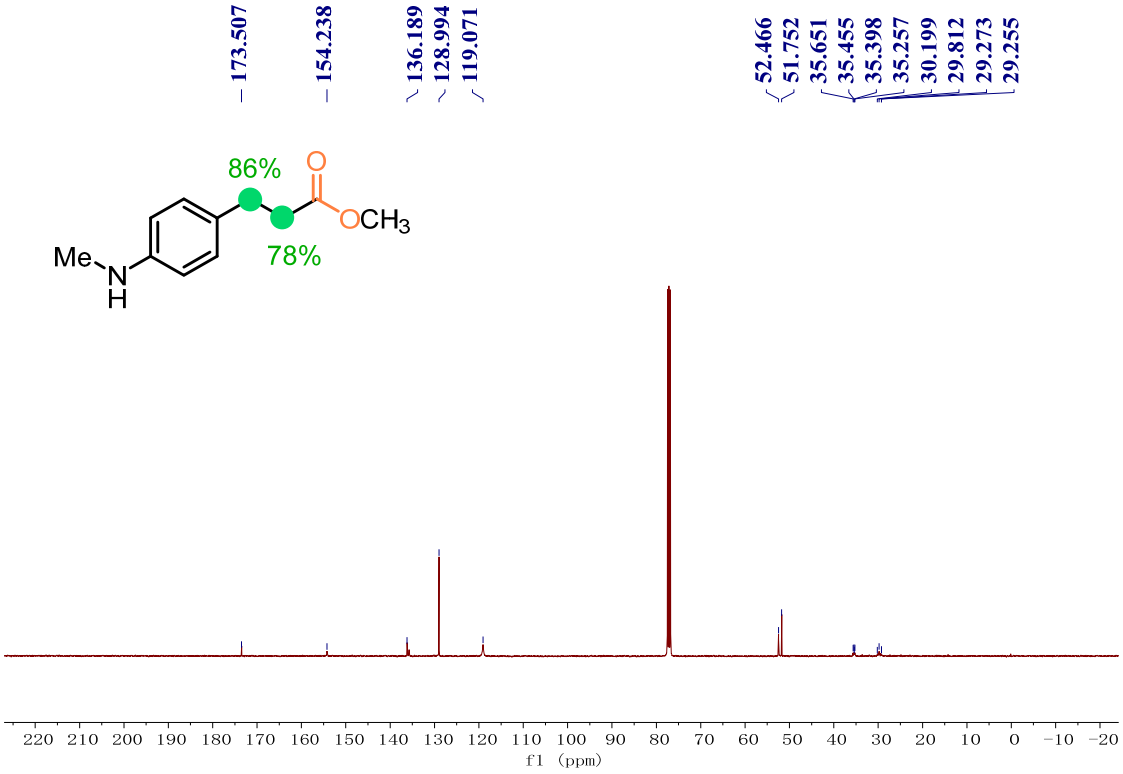
methyl 3-(4-(methylamino)phenyl)propanoate-2,2,3,3-*d*$_4$ (2i)

^{1}H NMR (400 MHz, $CDCl_3$)



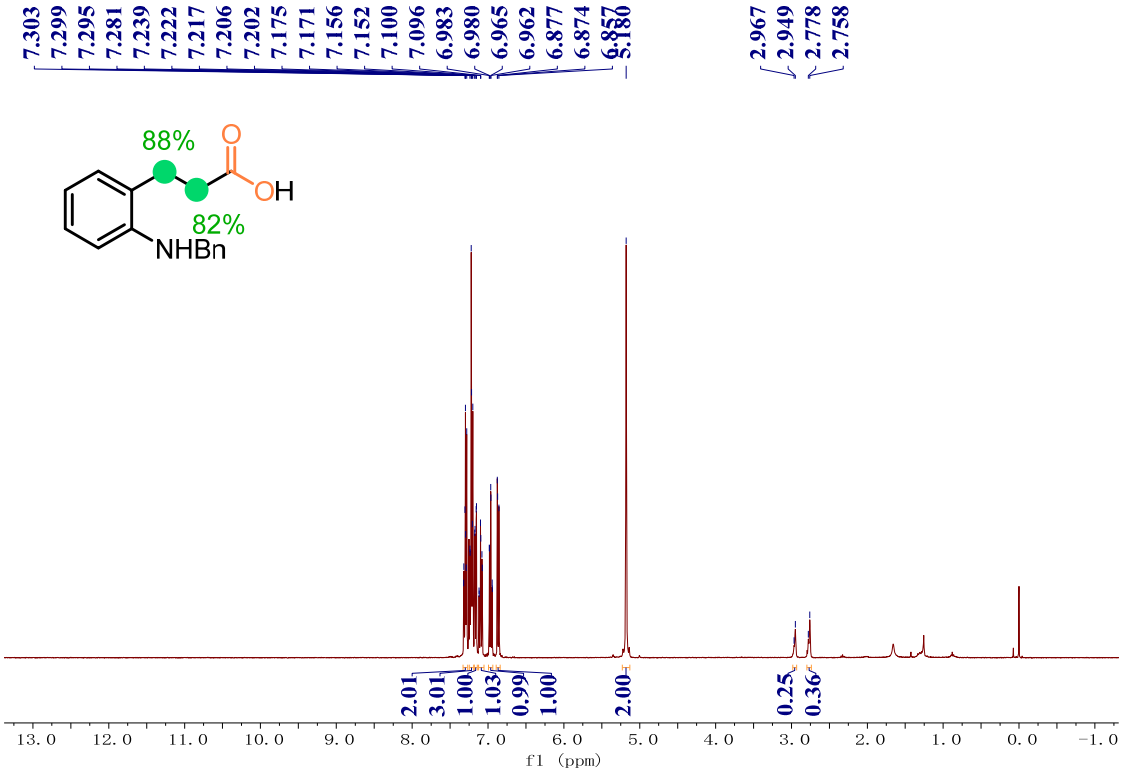
methyl 3-(4-(methylamino)phenyl)propanoate-2,2,3,3-d_4 (2i)

^{13}C NMR (100 MHz, $CDCl_3$)



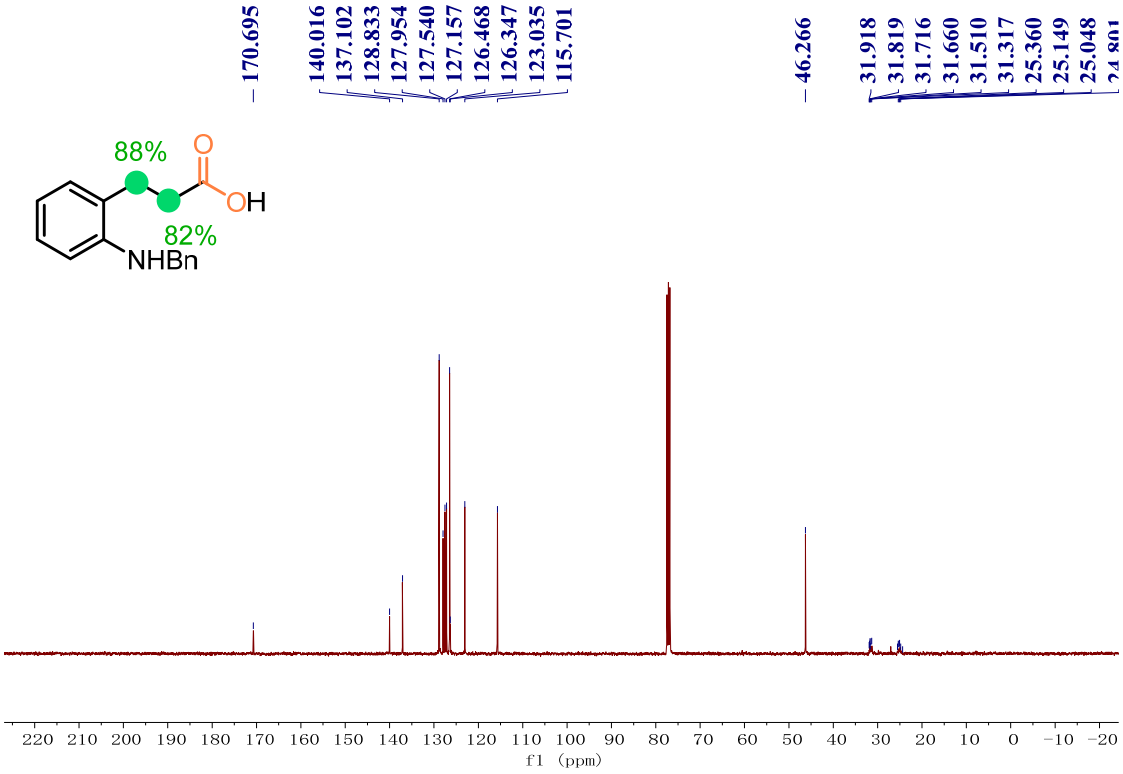
3-(2-(benzylamino)phenyl)propanoic-2,2,3,3-d_4 acid (2j)

^{1}H NMR (400 MHz, $CDCl_3$)



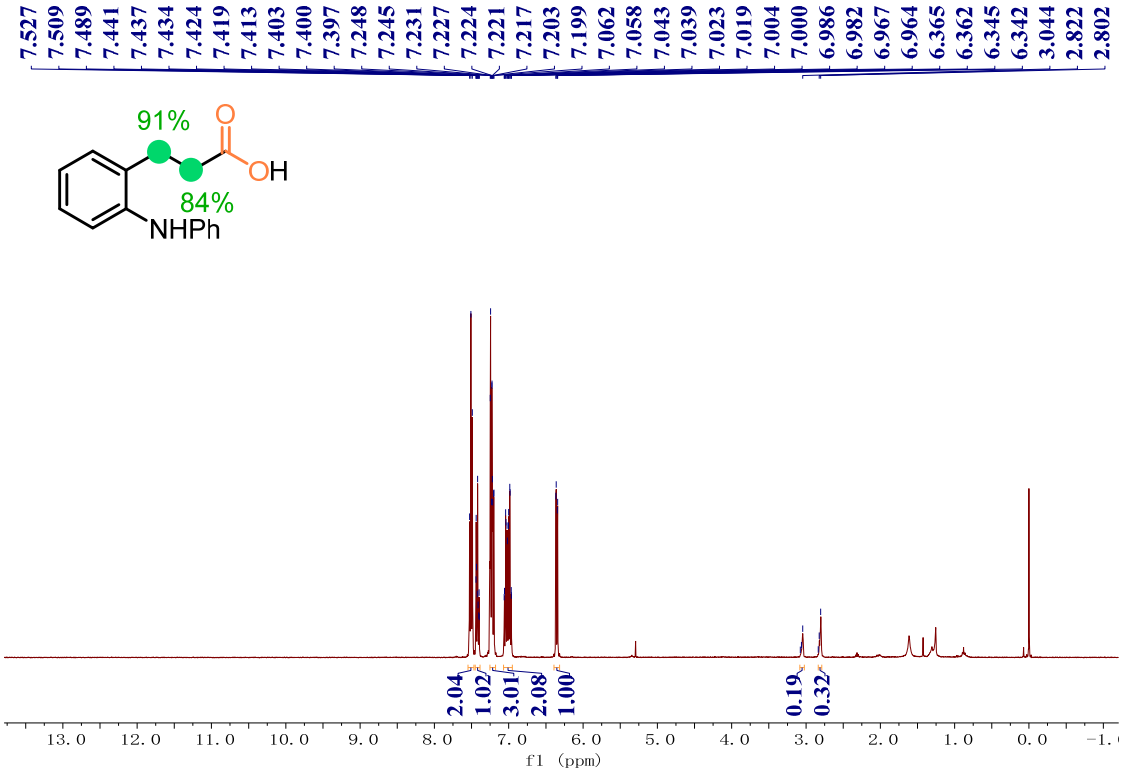
3-(2-(benzylamino)phenyl)propanoic-2,2,3,3-d_4 acid (2j)

^{13}C NMR (100 MHz, $CDCl_3$)



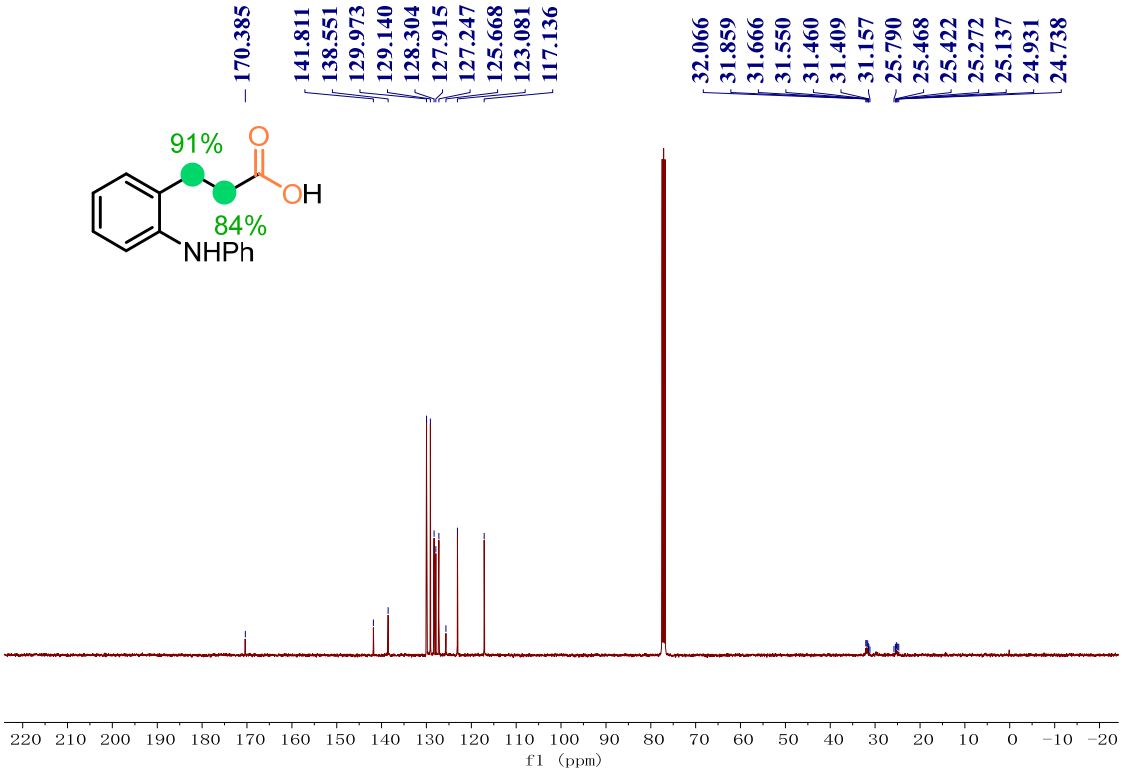
3-(2-(phenylamino)phenyl)propanoic-2,2,3,3-d_4 acid (2k)

^{1}H NMR (400 MHz, $CDCl_3$)



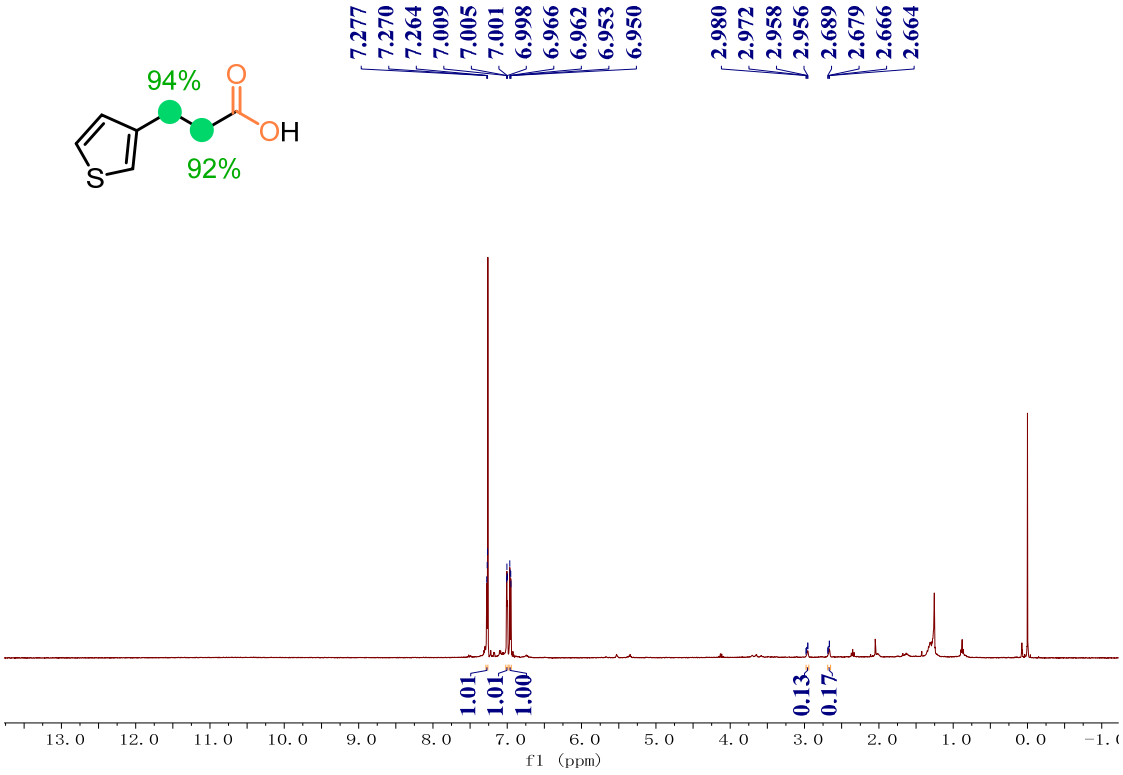
3-(2-(phenylamino)phenyl)propanoic-2,2,3,3-d_4 acid (2k)

^{13}C NMR (100 MHz, $CDCl_3$)



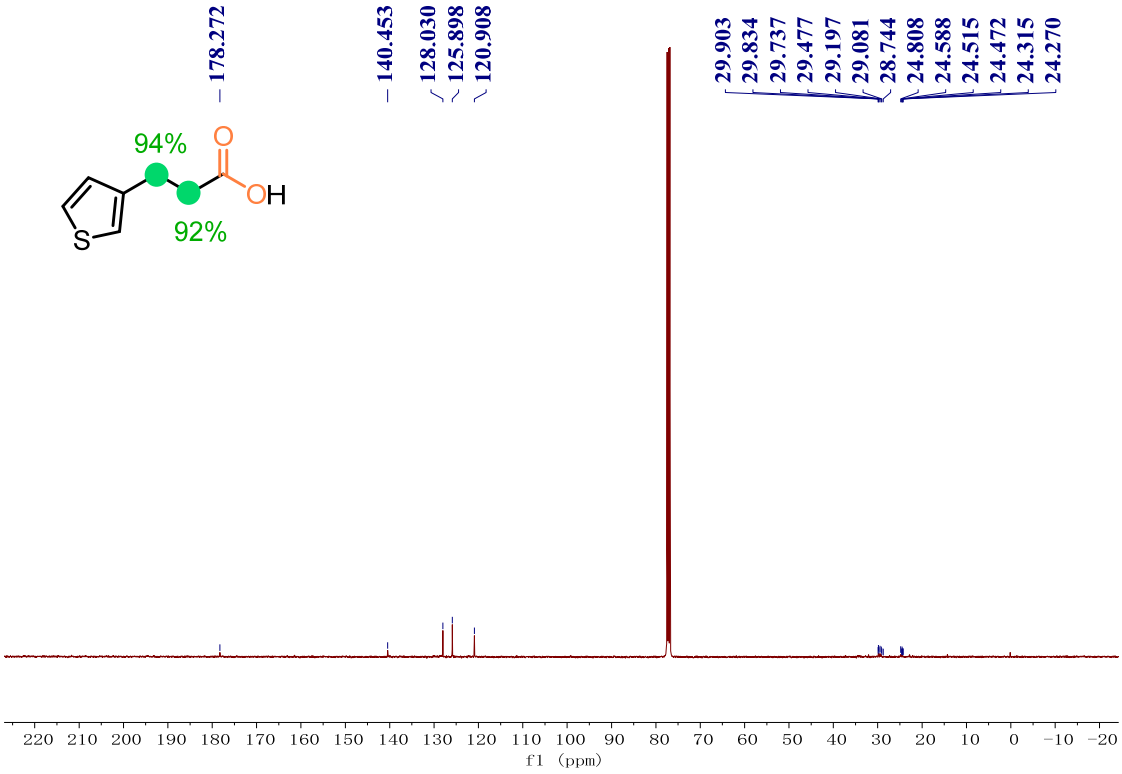
3-(thiophen-3-yl)propanoic-2,2,3,3-d_4 acid (2l)

^{1}H NMR (400 MHz, $CDCl_3$)



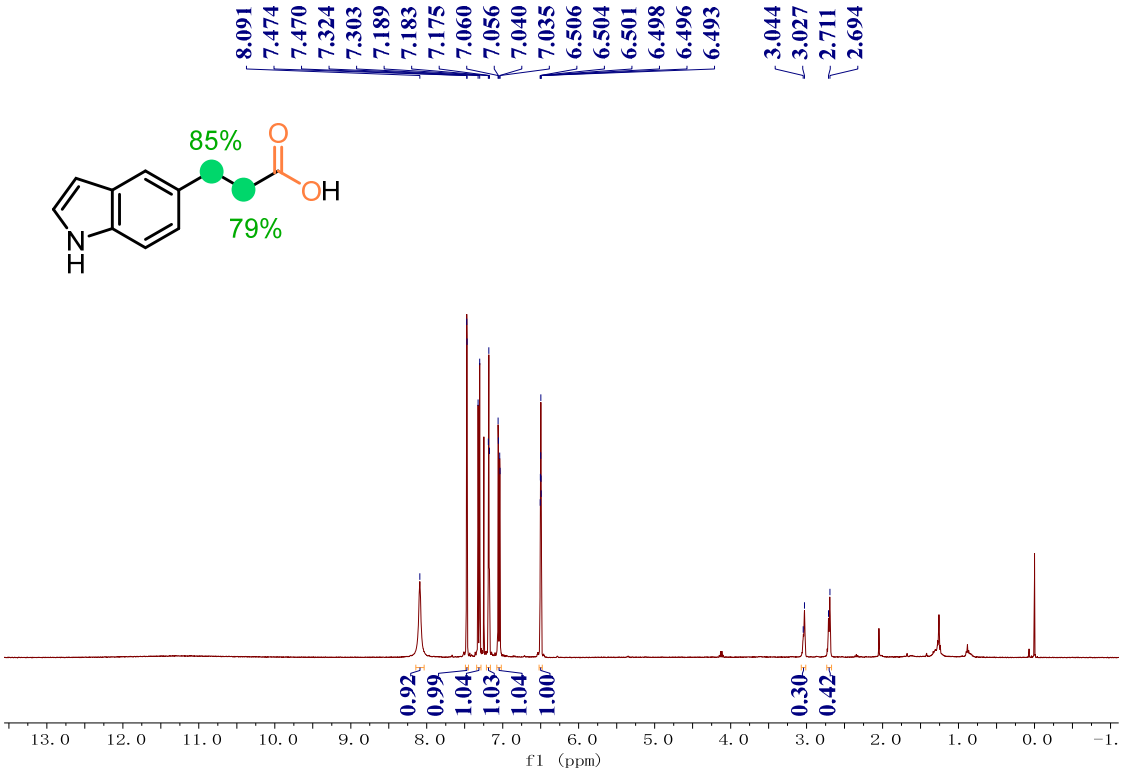
3-(thiophen-3-yl)propanoic-2,2,3,3-d_4 acid (2l)

^{13}C NMR (100 MHz, $CDCl_3$)



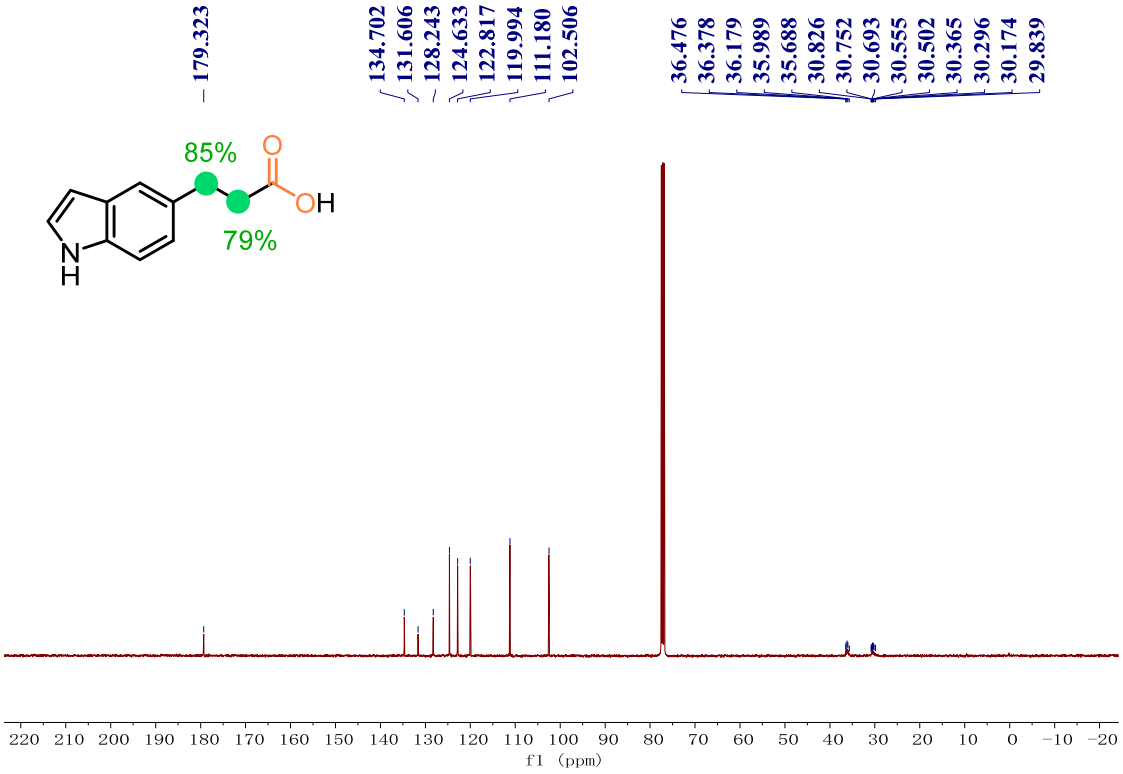
3-(1*H*-indol-5-yl)propanoic-2,2,3,3-d_4 acid (2m)

^{1}H NMR (400 MHz, $CDCl_3$)



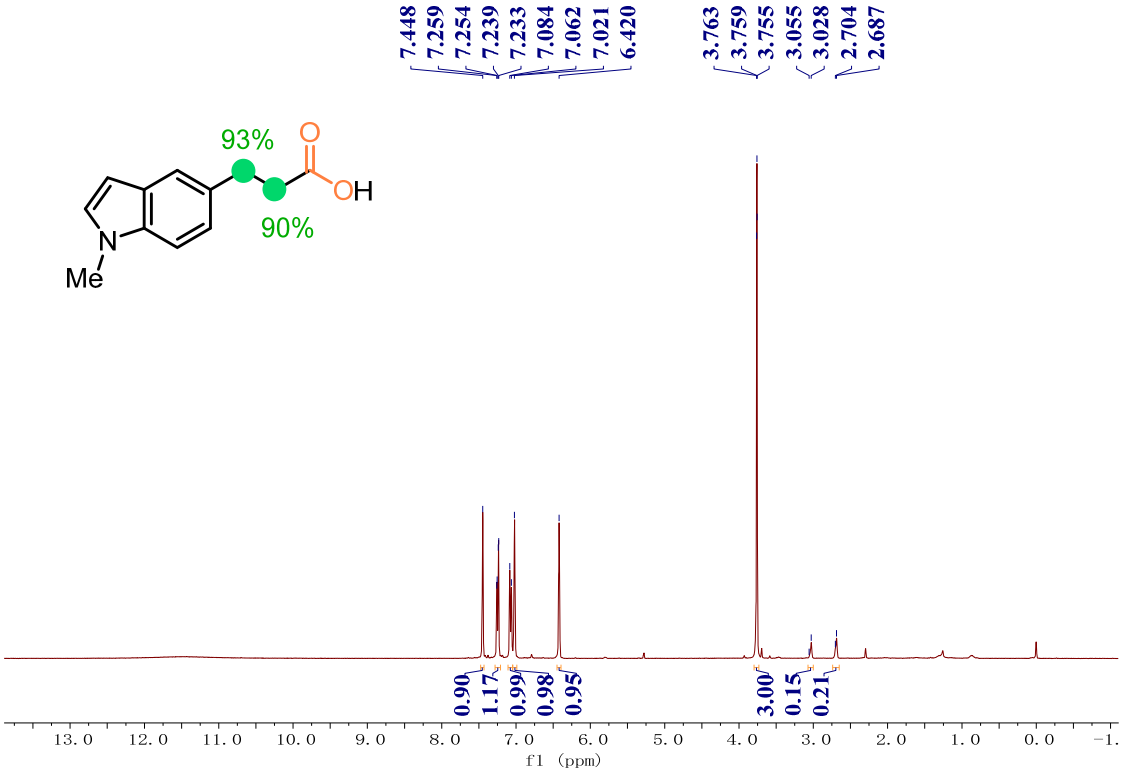
3-(1*H*-indol-5-yl)propanoic-2,2,3,3-d_4 acid (2m)

^{13}C NMR (100 MHz, $CDCl_3$)



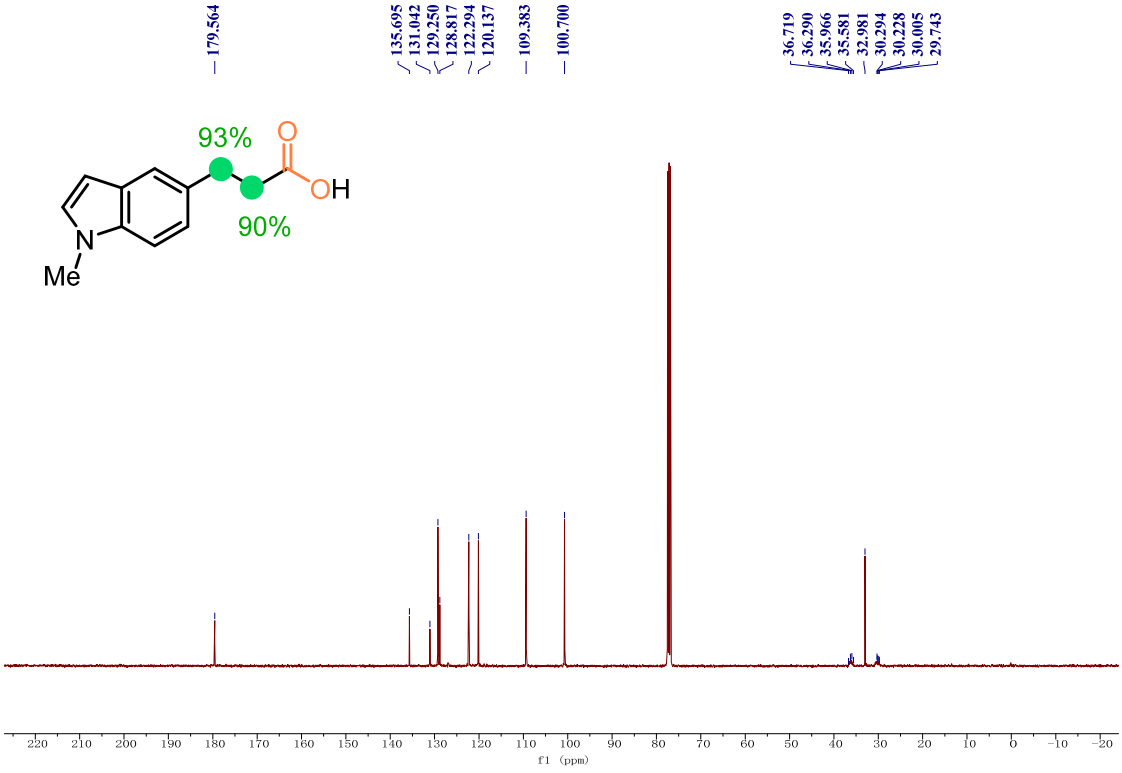
3-(1-methyl-1*H*-indol-5-yl)propanoic-2,2,3,3-d_4 acid (2n)

^{1}H NMR (400 MHz, $CDCl_3$)



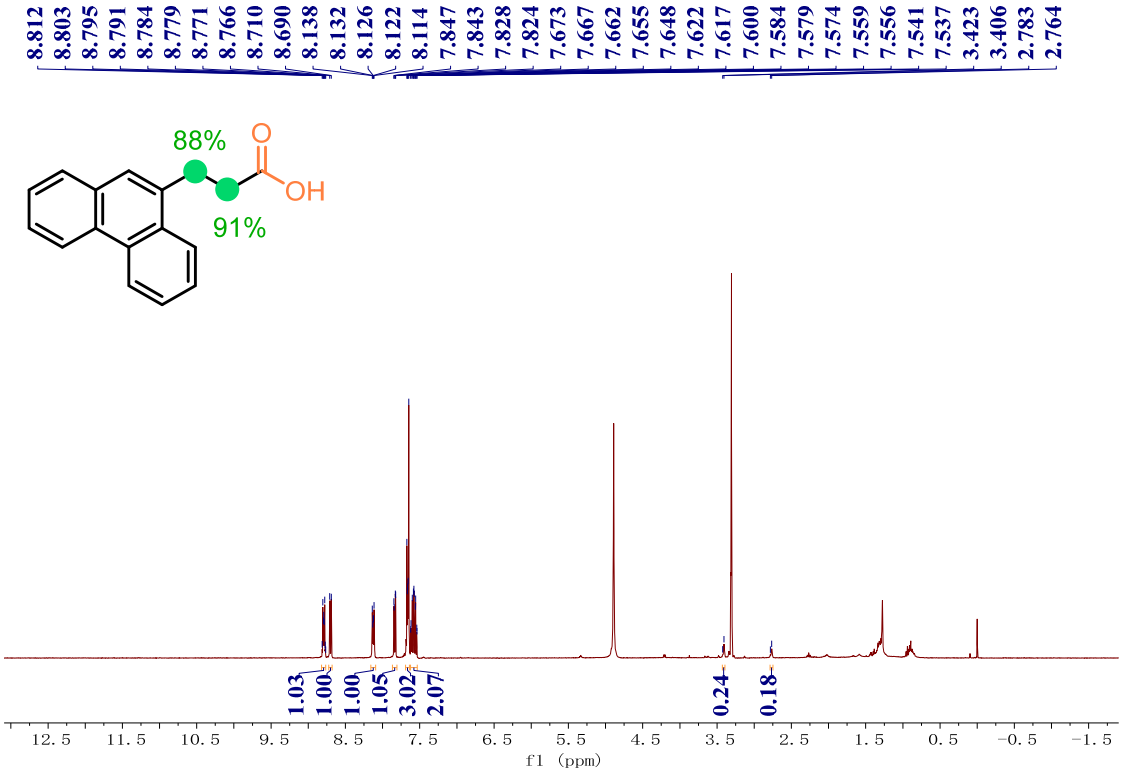
3-(1-methyl-1*H*-indol-5-yl)propanoic-2,2,3,3-d_4 acid (2n)

^{13}C NMR (100 MHz, $CDCl_3$)



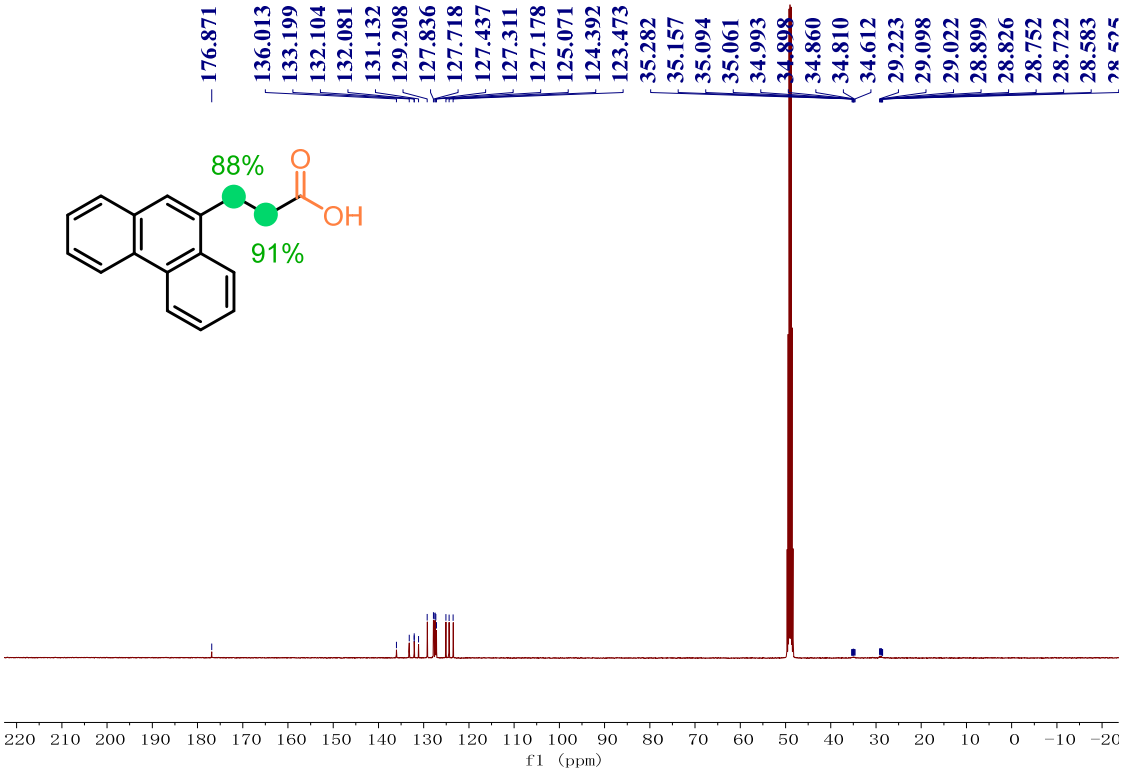
3-(phenanthren-9-yl)propanoic-2,2,3,3-d_4 acid (2o)

^{1}H NMR (400 MHz, CD_3OD)



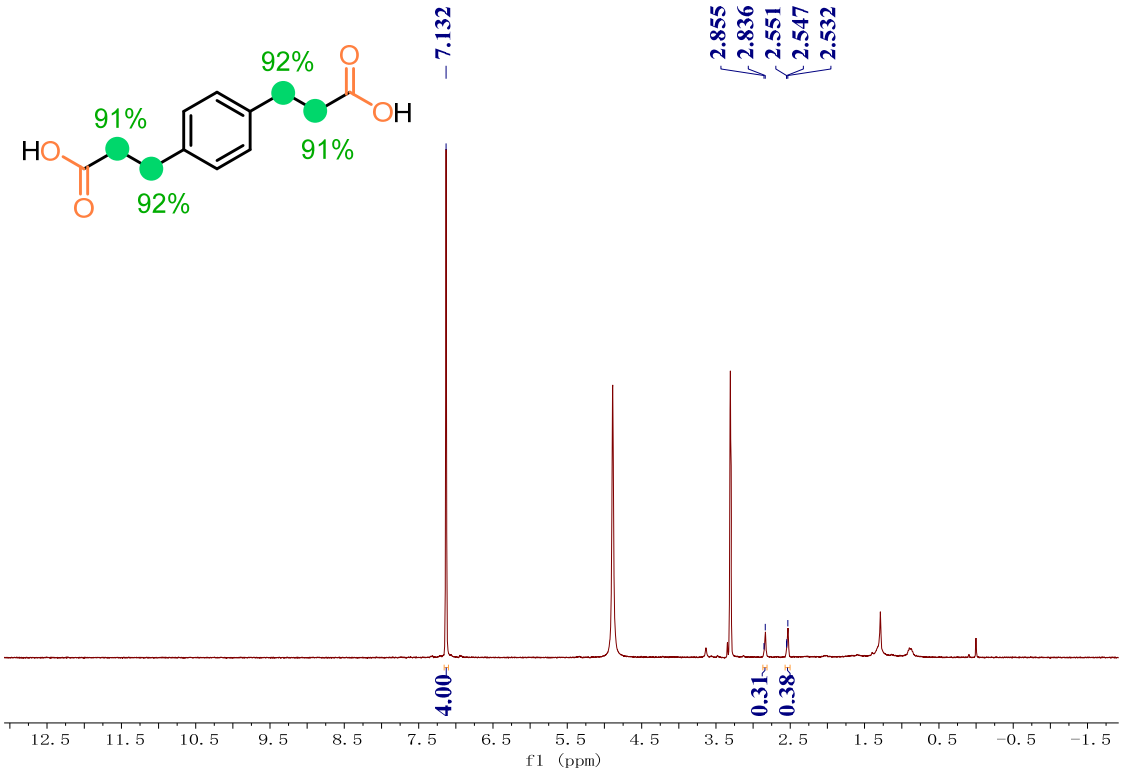
3-(phenanthren-9-yl)propanoic-2,2,3,3-d_4 acid (2o)

^{13}C NMR (100 MHz, CD_3OD)



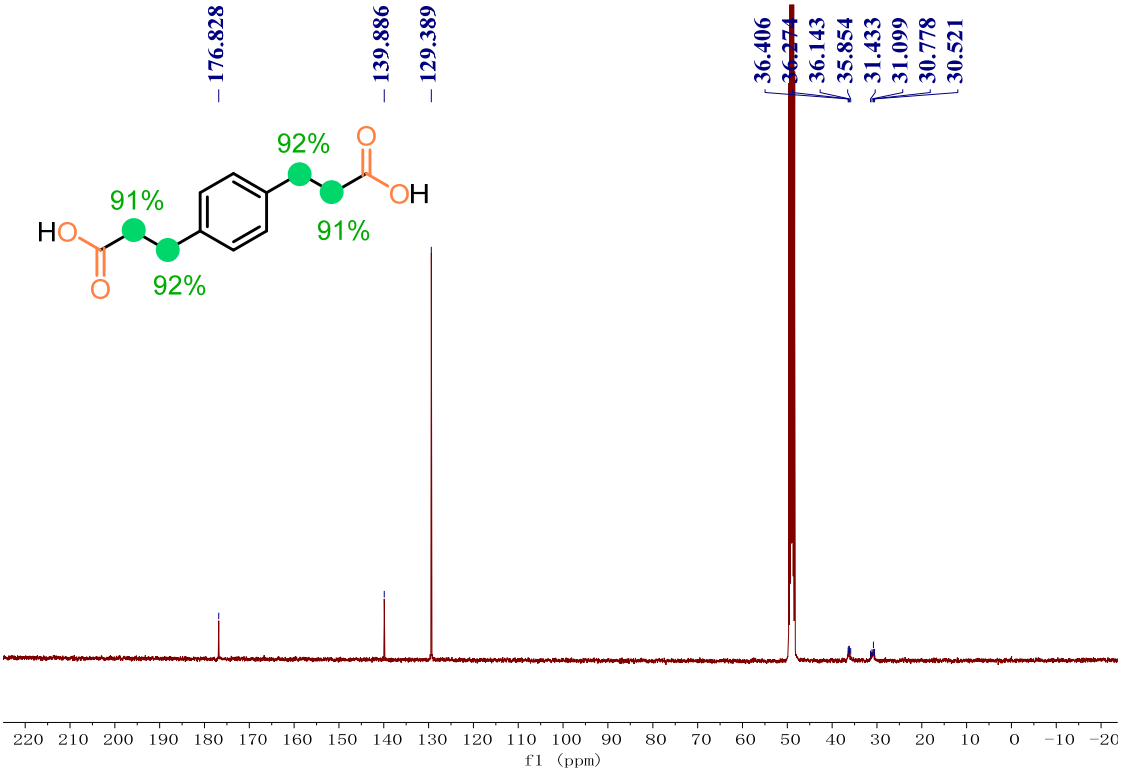
3,3'-(1,4-phenylene)bis(propanoic-2,2,3,3-d_4 acid) (2p)

^{1}H NMR (400 MHz, CD_3OD)



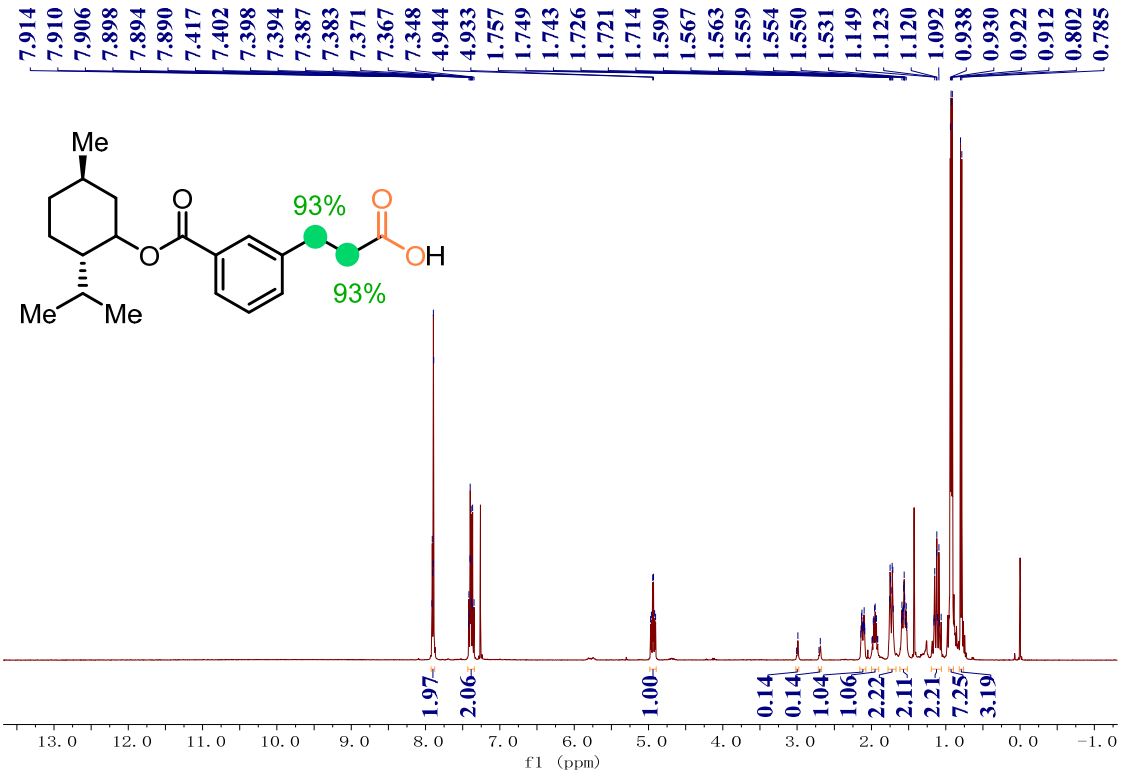
3,3'-(1,4-phenylene)bis(propanoic-2,2,3,3-d_4 acid) (2p)

^{13}C NMR (100 MHz, CD_3OD)



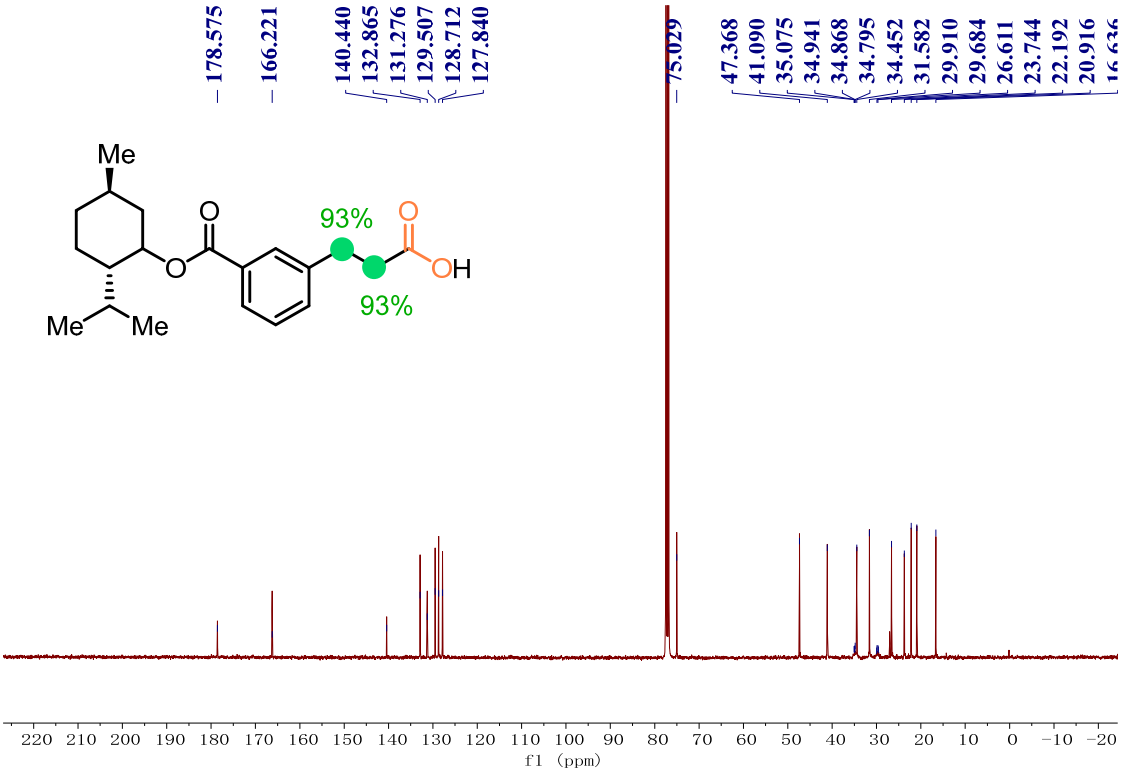
3-(3-((((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2q)

^{1}H NMR (400 MHz, $CDCl_3$)



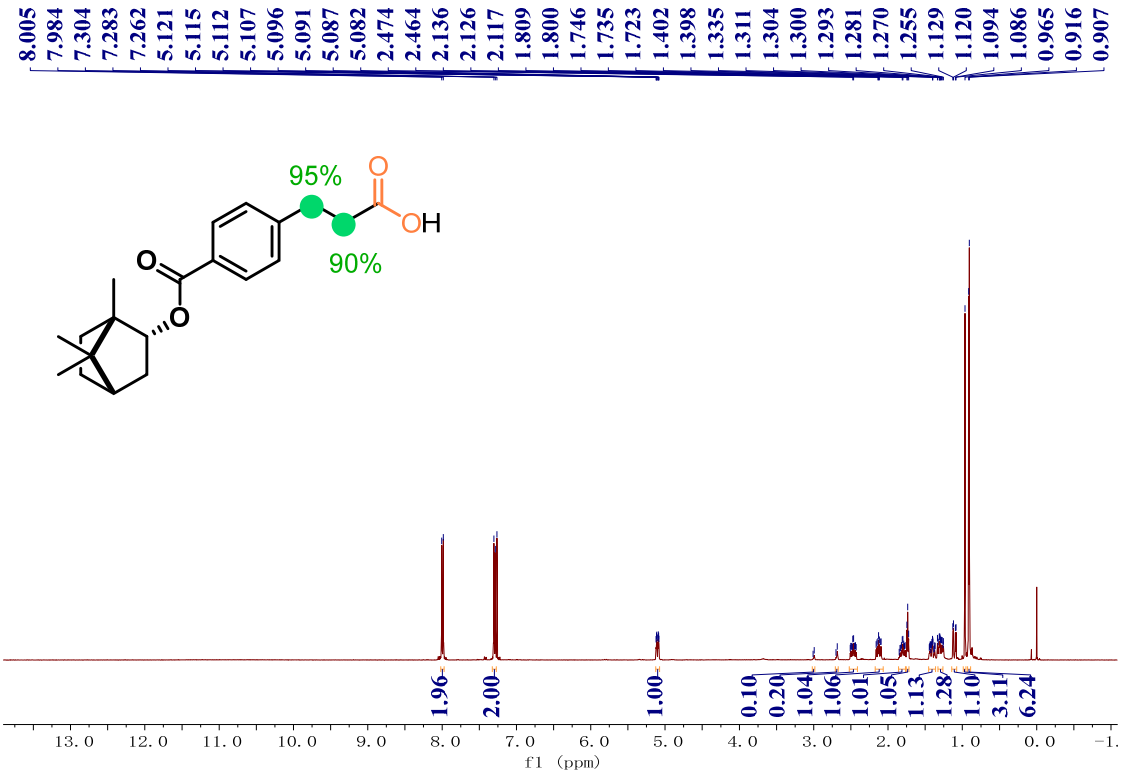
3-(3-((((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2q)

^{13}C NMR (100 MHz, $CDCl_3$)



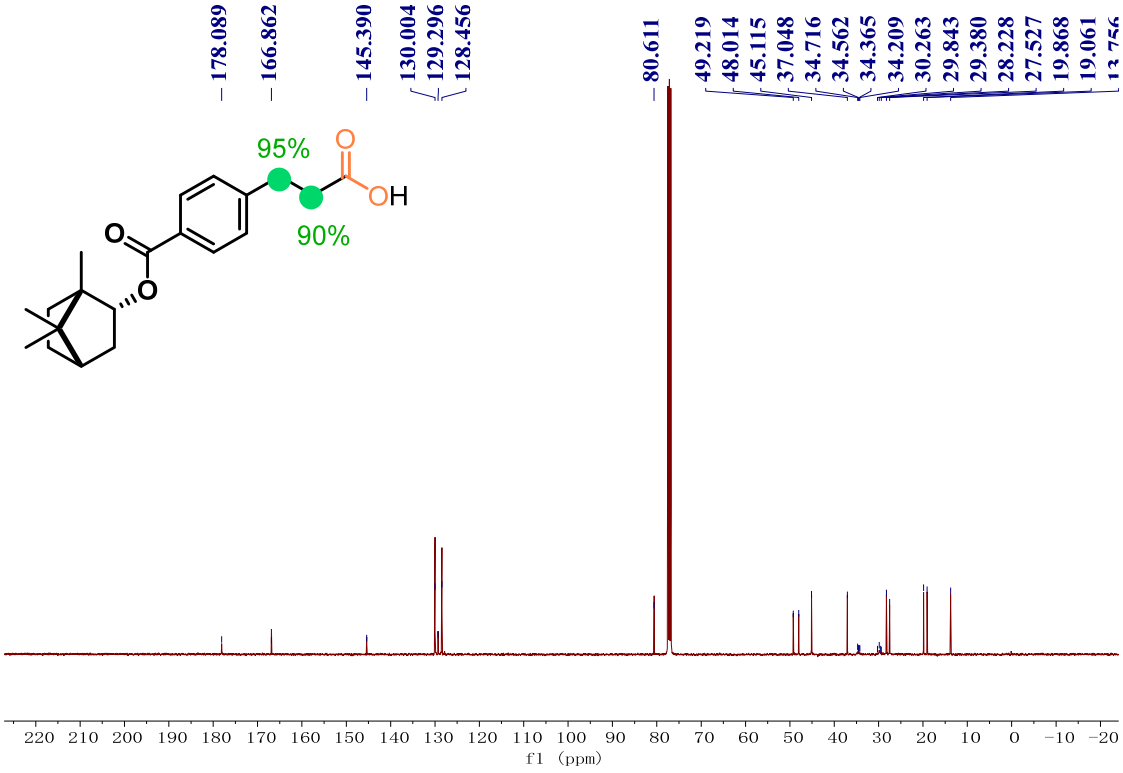
3-(4-((((1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2r)

^{1}H NMR (400 MHz, $CDCl_3$)



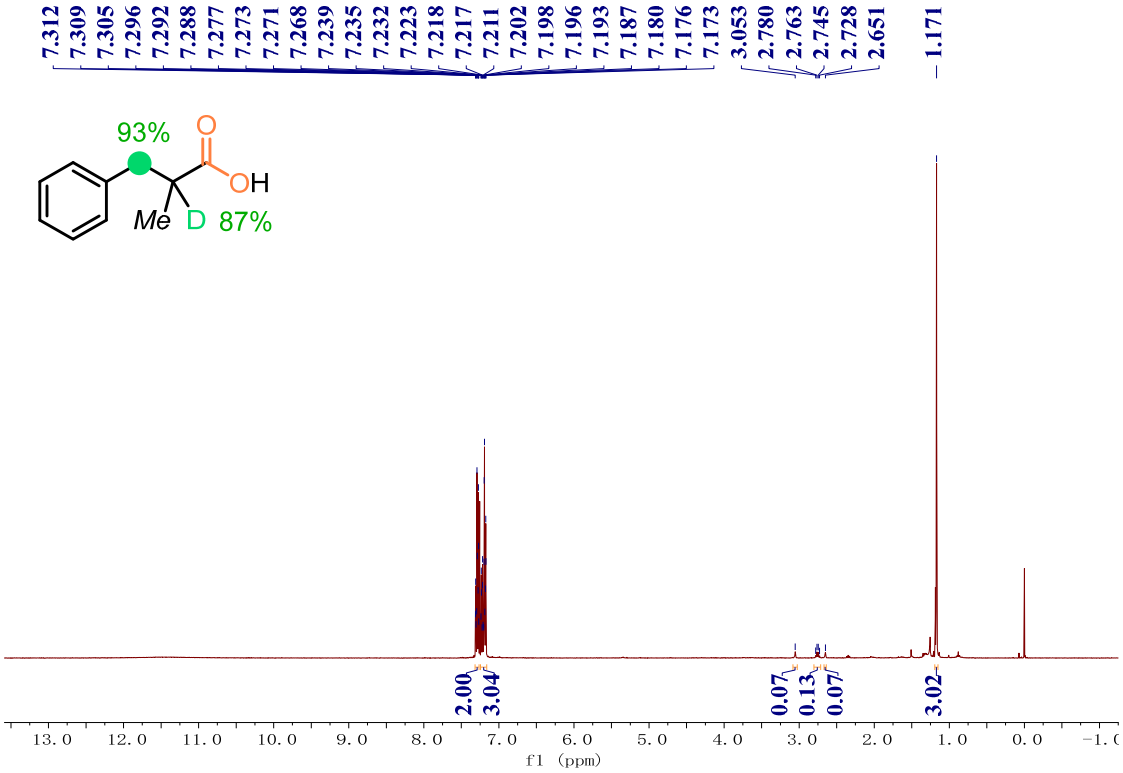
3-(4-((((1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)propanoic-2,2,3,3-d_4 acid (2r)

^{13}C NMR (100 MHz, $CDCl_3$)



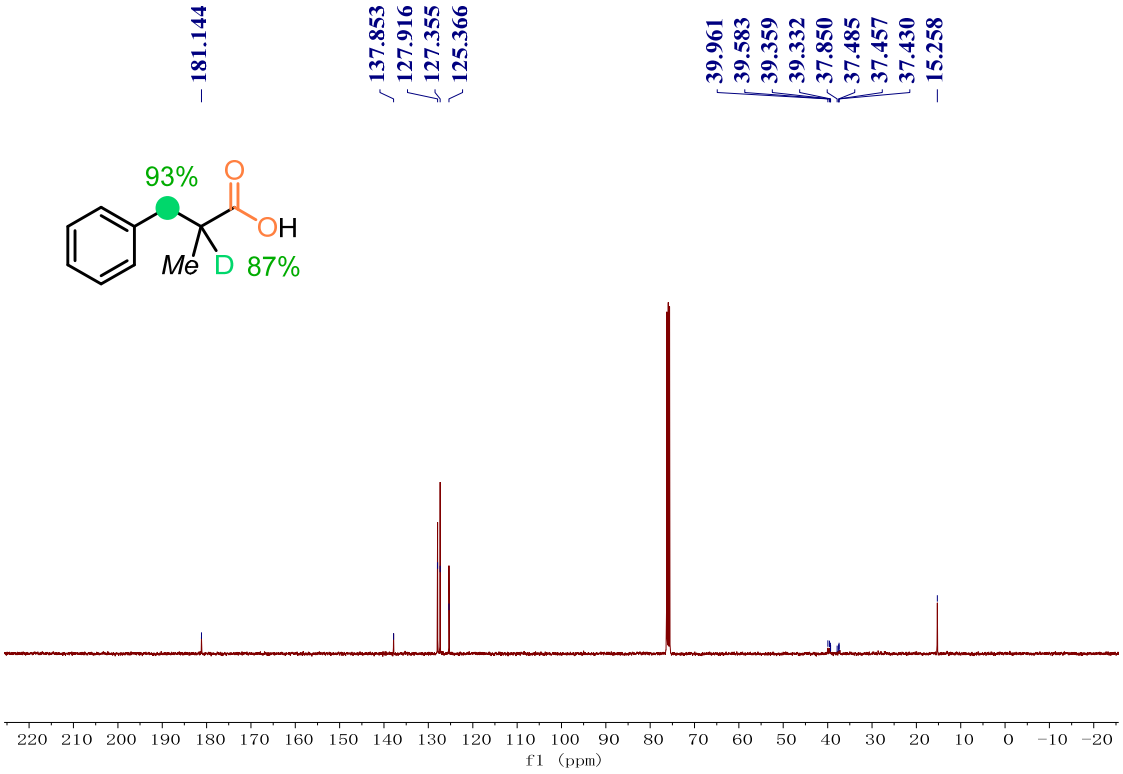
2-methyl-3-phenylpropanoic-2,3,3-d_3 acid (3a)

^{1}H NMR (400 MHz, $CDCl_3$)



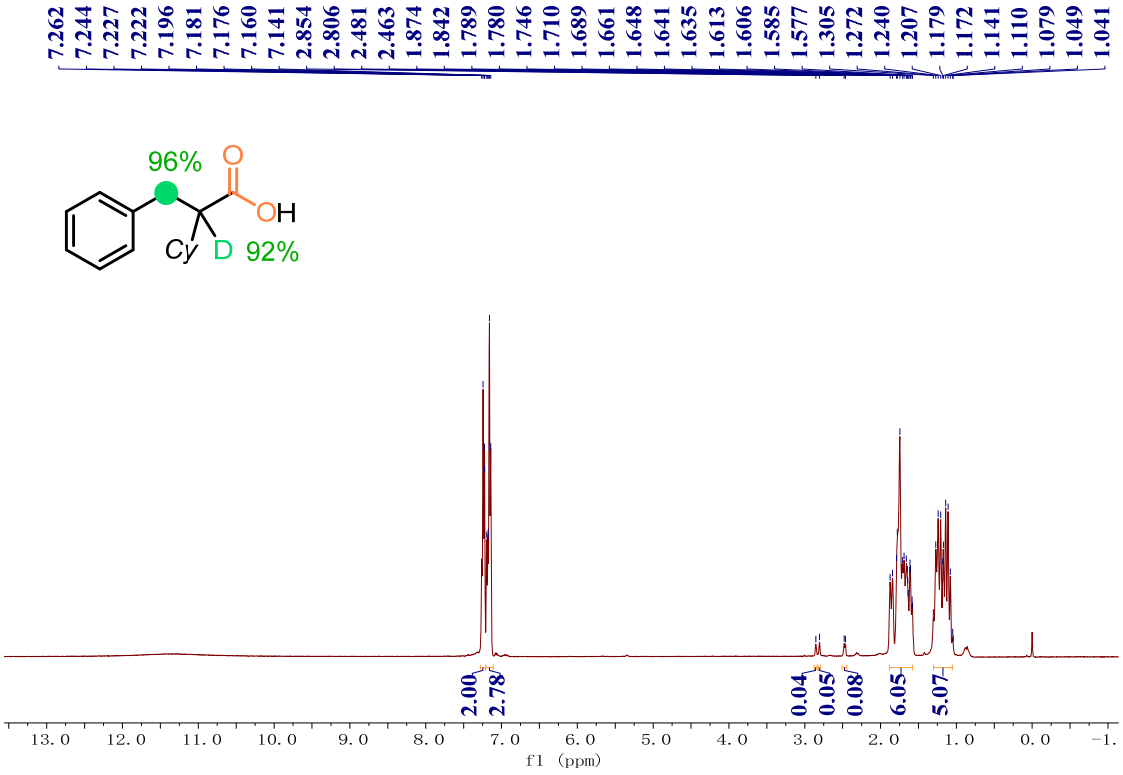
2-methyl-3-phenylpropanoic-2,3,3-d_3 acid (3a)

^{13}C NMR (100 MHz, $CDCl_3$)



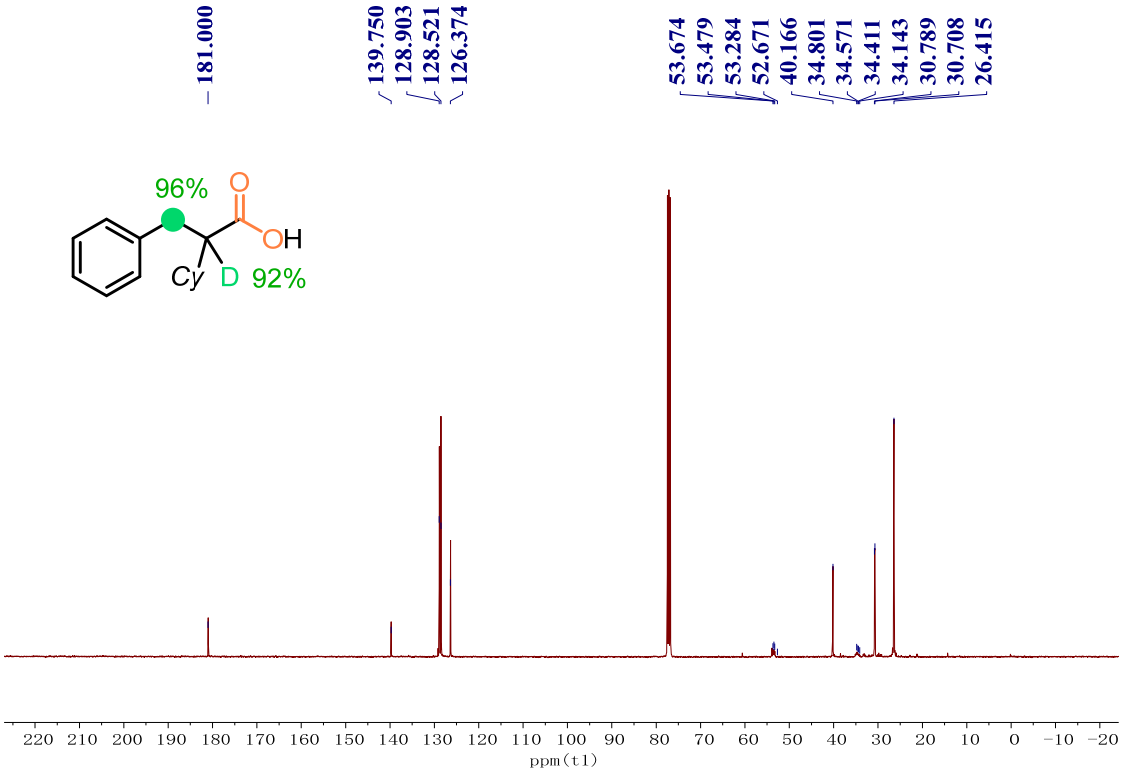
2-cyclohexyl-3-phenylpropanoic-2,3,3-d_3 acid (3b)

^{1}H NMR (400 MHz, $CDCl_3$)



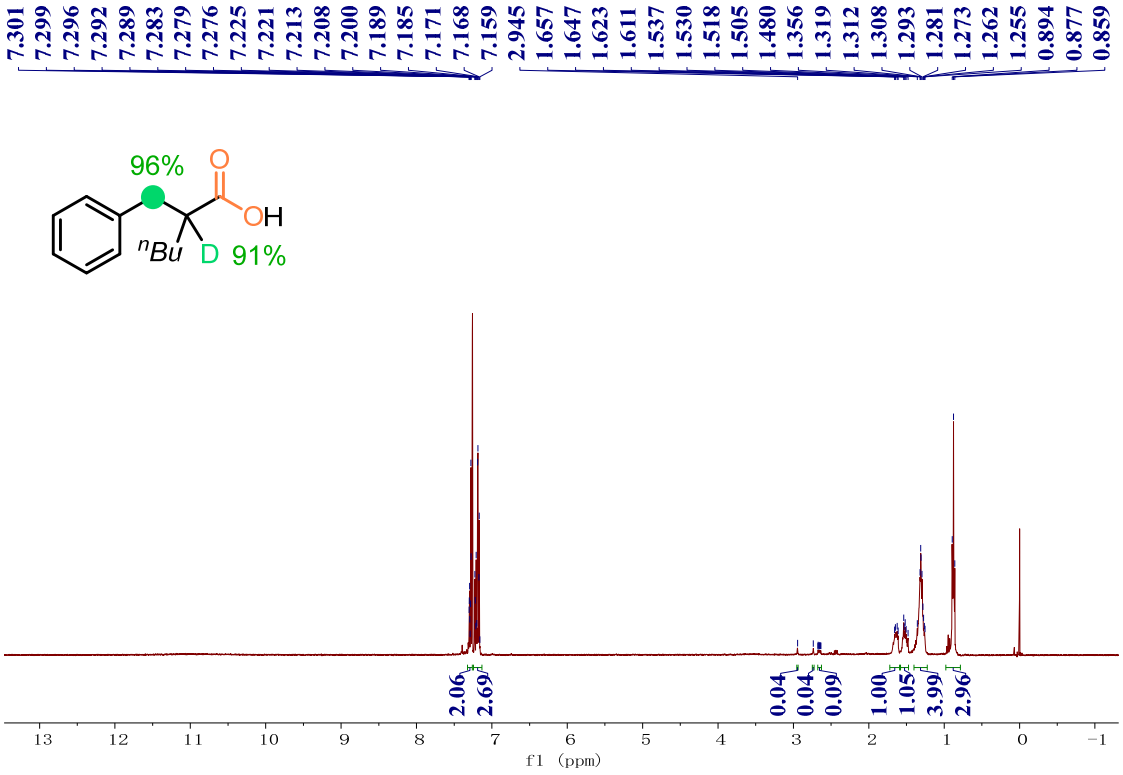
2-cyclohexyl-3-phenylpropanoic-2,3,3-d_3 (3b)

^{13}C NMR (100 MHz, $CDCl_3$)



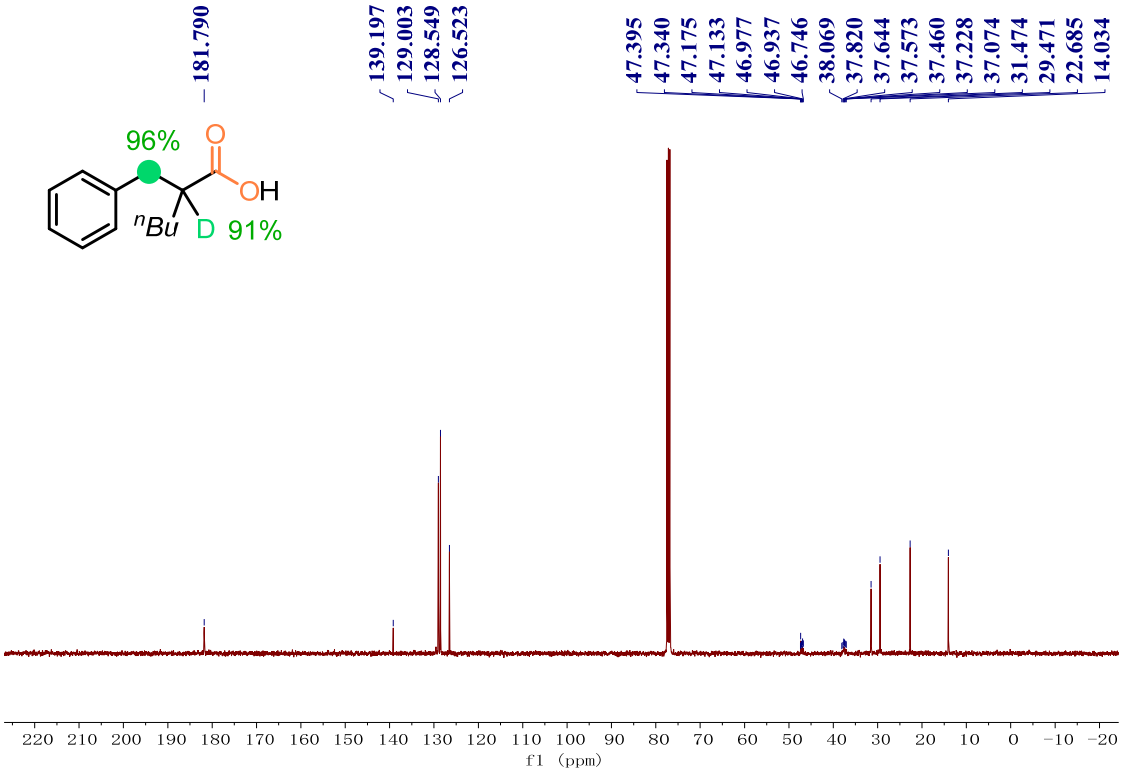
2-(phenylmethyl-d_2)hexanoic-2-*d* acid (3c)

^{1}H NMR (400 MHz, $CDCl_3$)



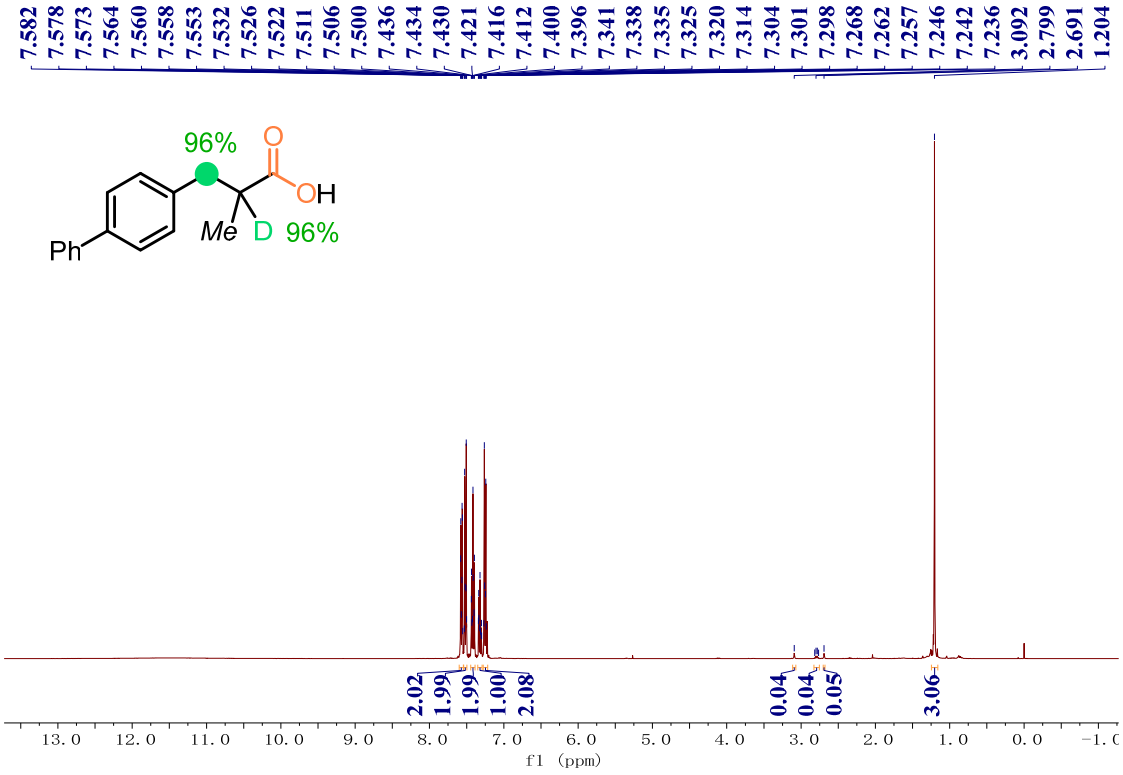
2-(phenylmethyl-d_2)hexanoic-2-*d* acid (3c)

^{13}C NMR (100 MHz, $CDCl_3$)



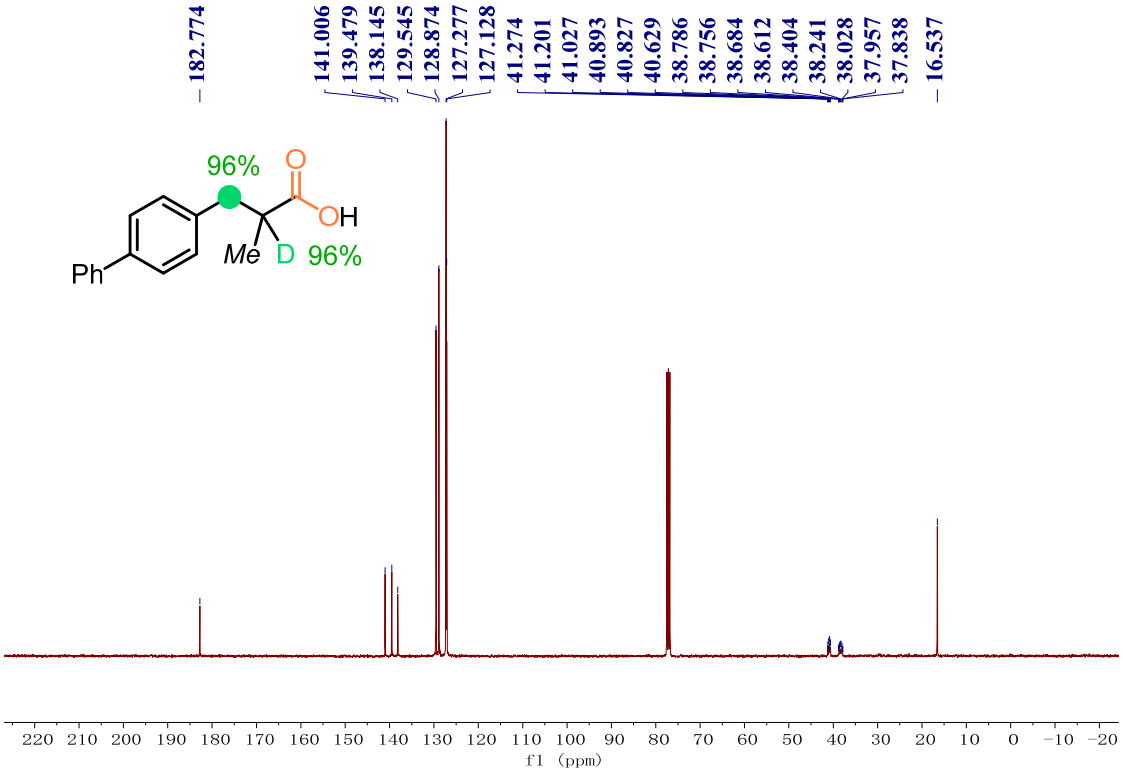
3-([1,1'-biphenyl]-4-yl)-2-methylpropanoic-2,3,3-d_3 acid (3d)

^{1}H NMR (400 MHz, $CDCl_3$)



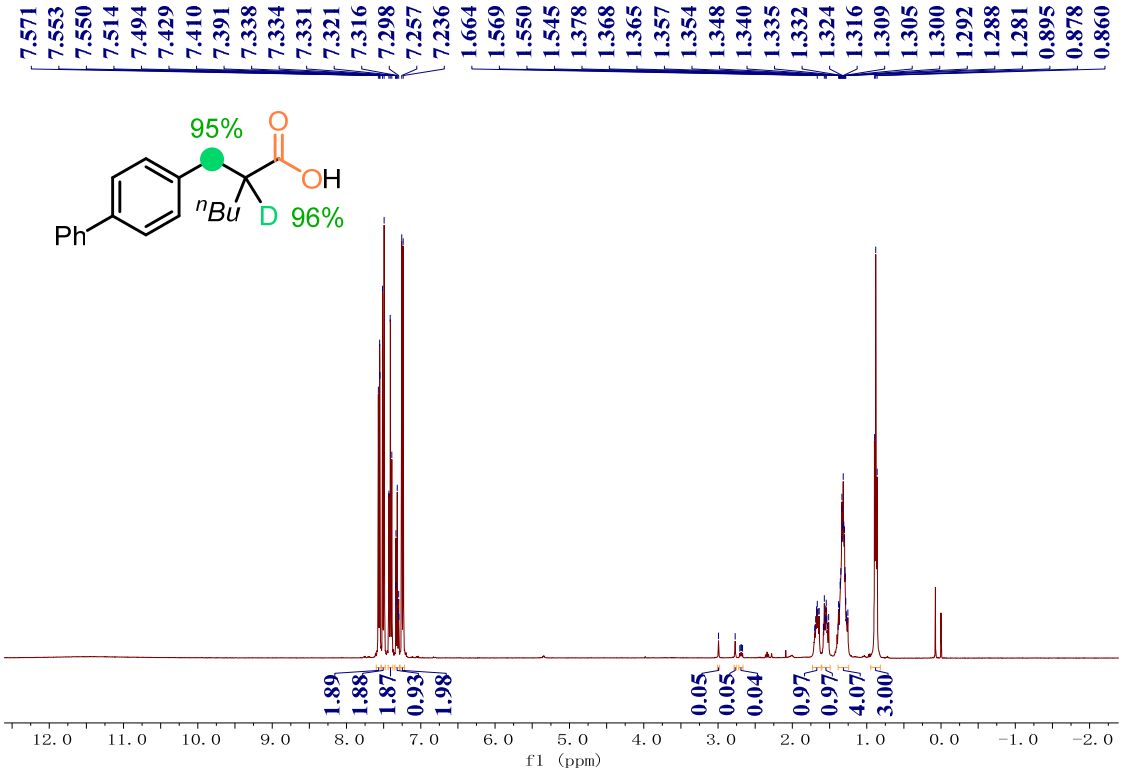
3-([1,1'-biphenyl]-4-yl)-2-methylpropanoic-2,3,3-d_3 acid (3d)

^{13}C NMR (100 MHz, $CDCl_3$)



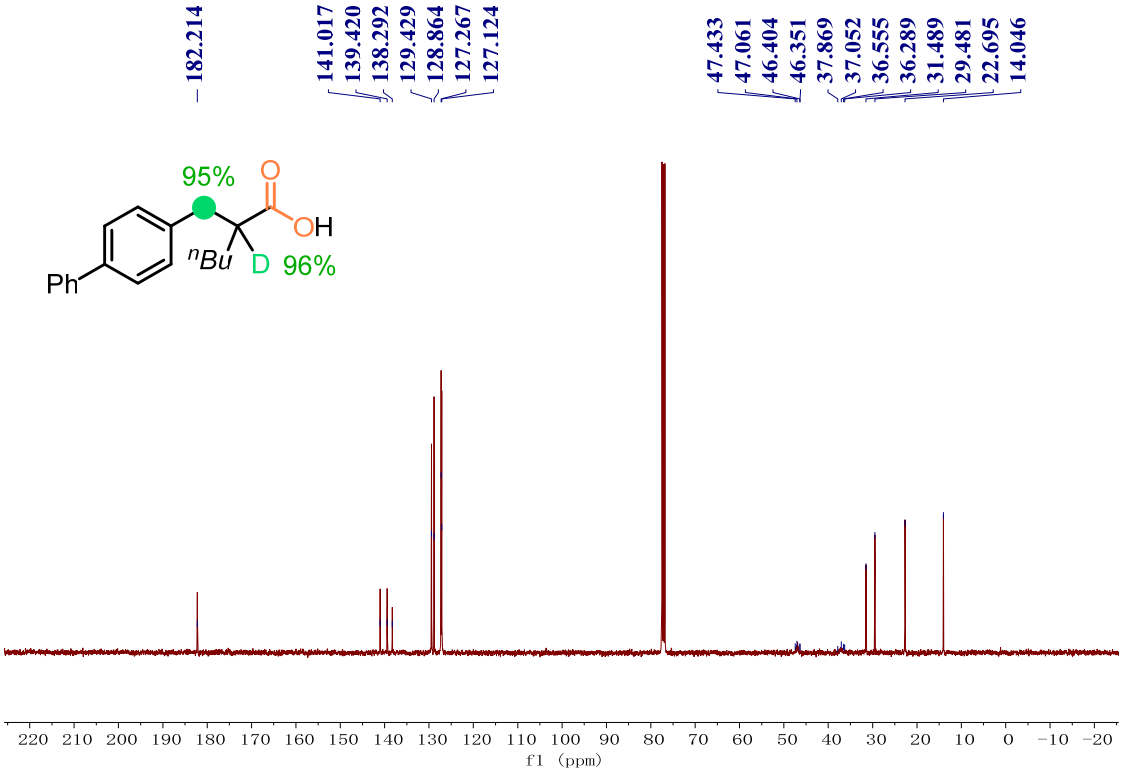
2-([1,1'-biphenyl]-4-ylmethyl-d_2)hexanoic-2-d acid (3e)

^{1}H NMR (400 MHz, $CDCl_3$)



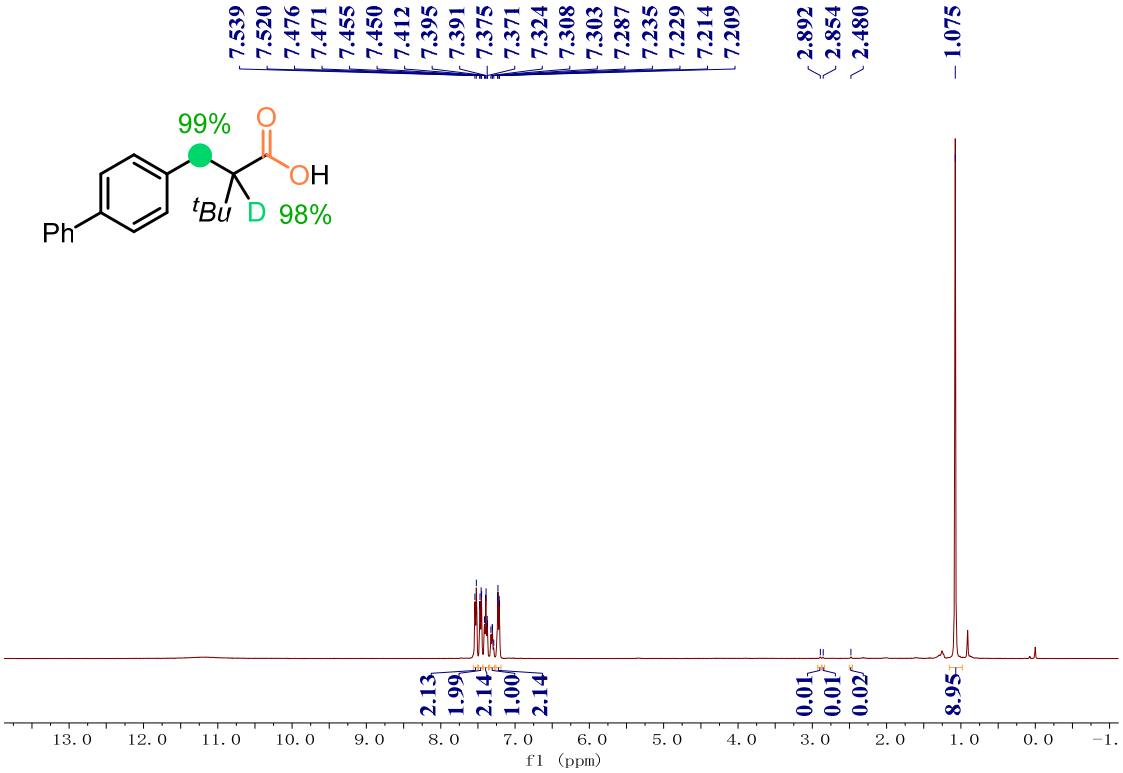
2-([1,1'-biphenyl]-4-ylmethyl-d_2)hexanoic-2-*d* acid (3e)

^{13}C NMR (100 MHz, $CDCl_3$)



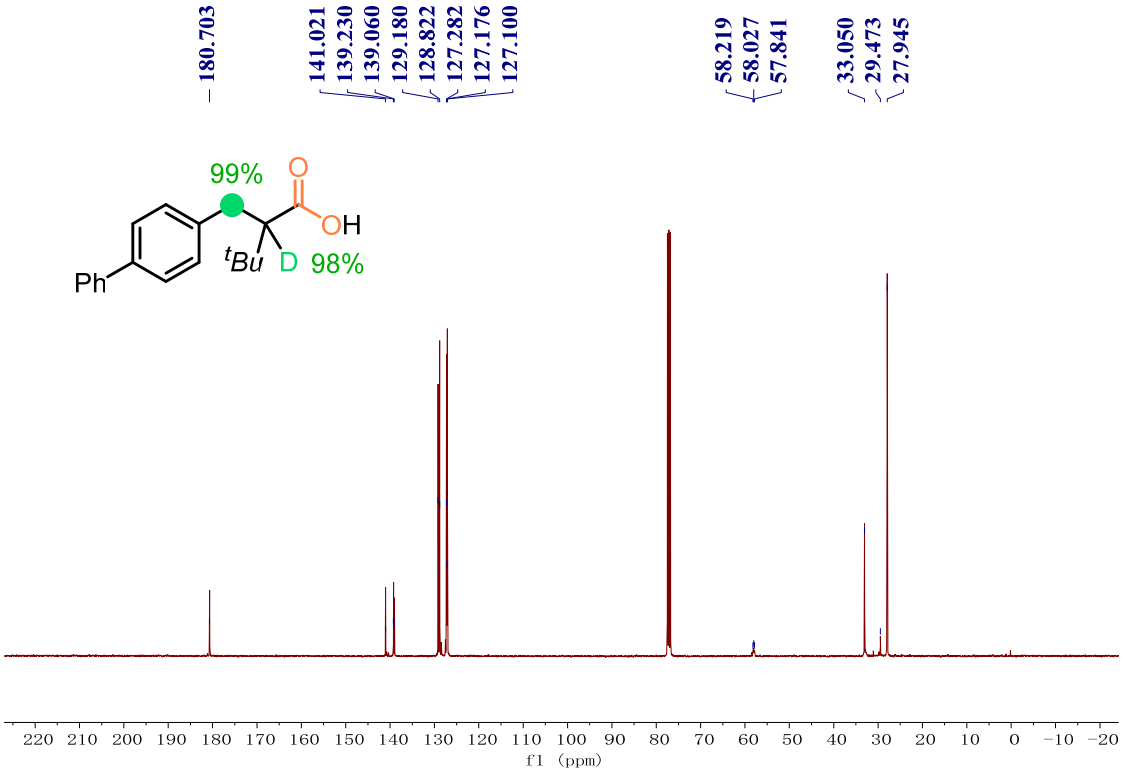
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-3,3-dimethylbutanoic-2-*d* acid (3f)

^{1}H NMR (400 MHz, $CDCl_3$)



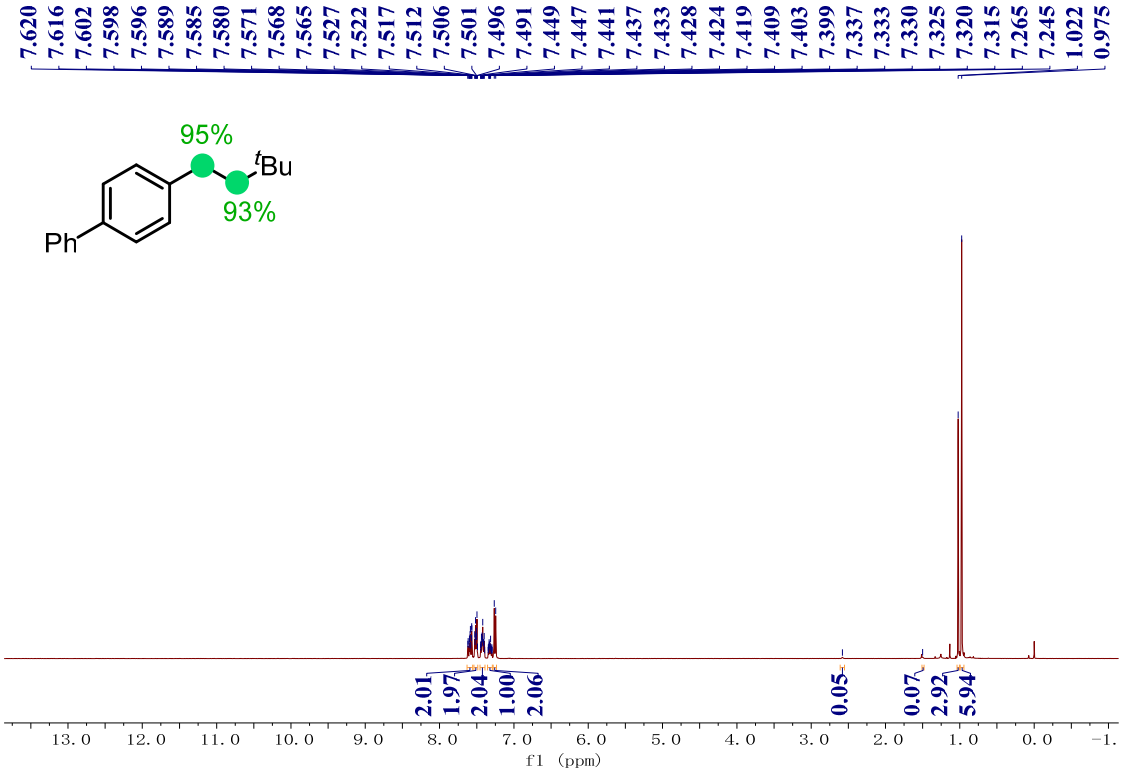
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-3,3-dimethylbutanoic-2-*d* acid (3f)

^{13}C NMR (100 MHz, $CDCl_3$)



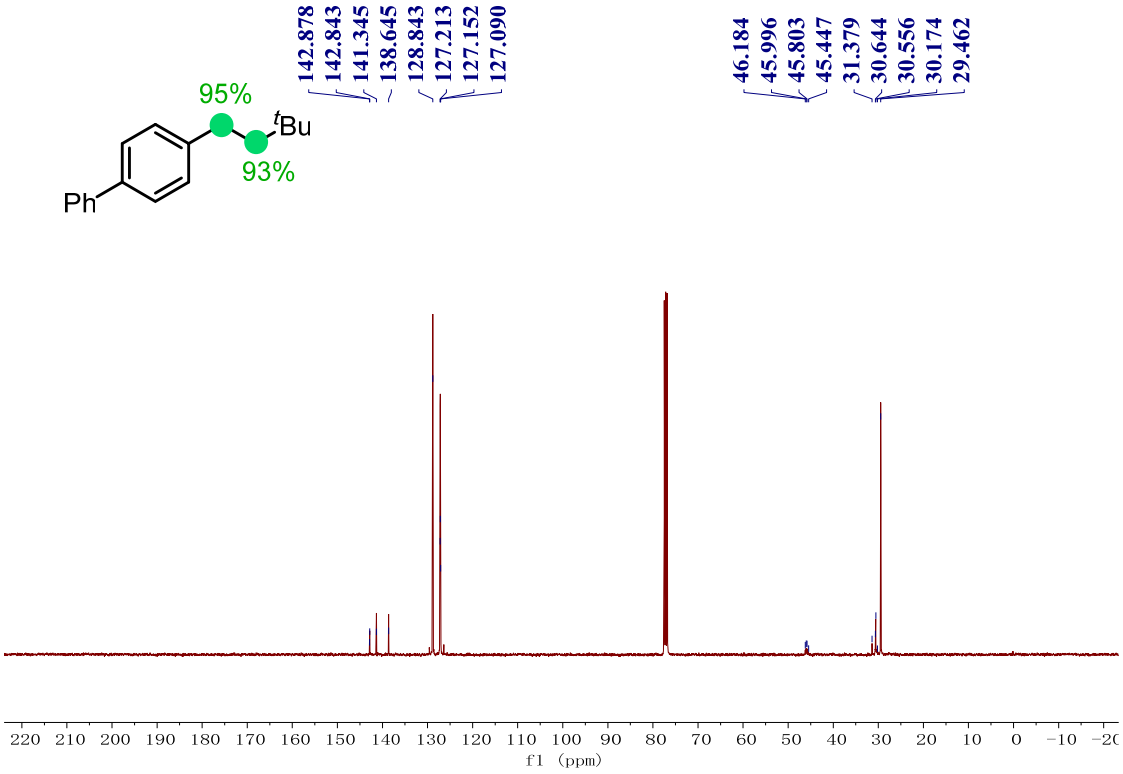
4-(3,3-dimethylbutyl-1,1,2,2-d_4)-1,1'-biphenyl (3f')

^{1}H NMR (400 MHz, $CDCl_3$)



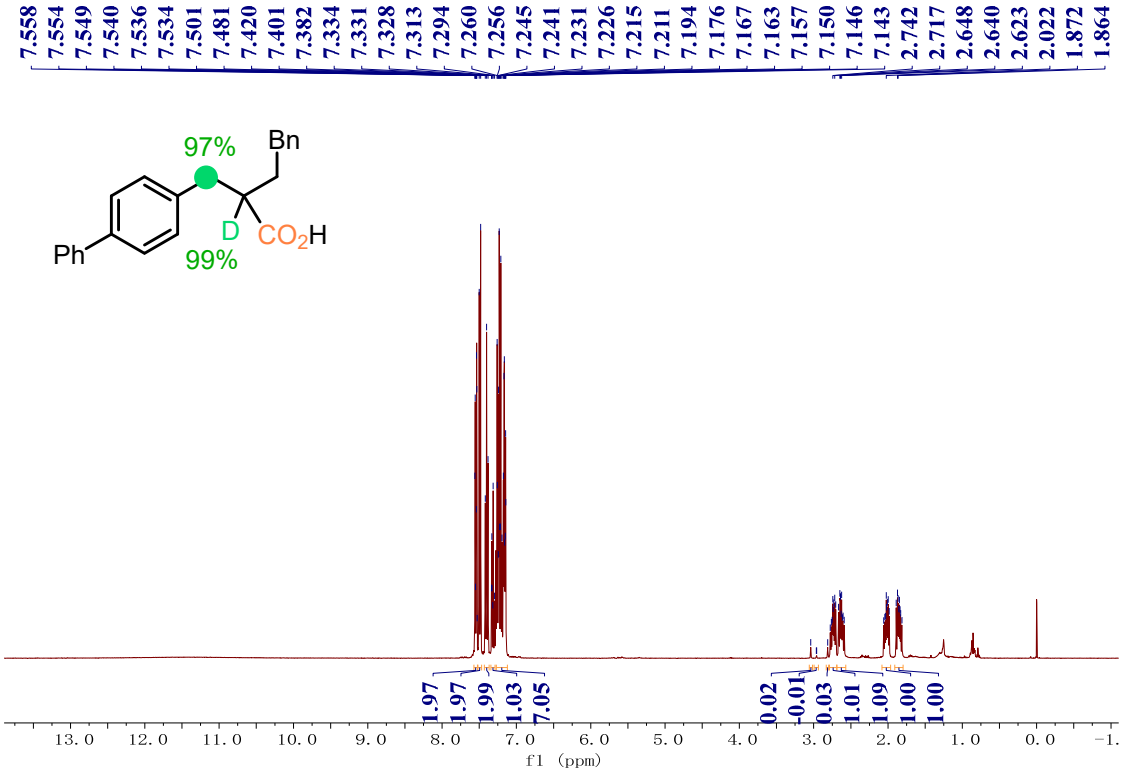
4-(3,3-dimethylbutyl-1,1,2,2-d_4)-1,1'-biphenyl (3f')

^{13}C NMR (100 MHz, $CDCl_3$)



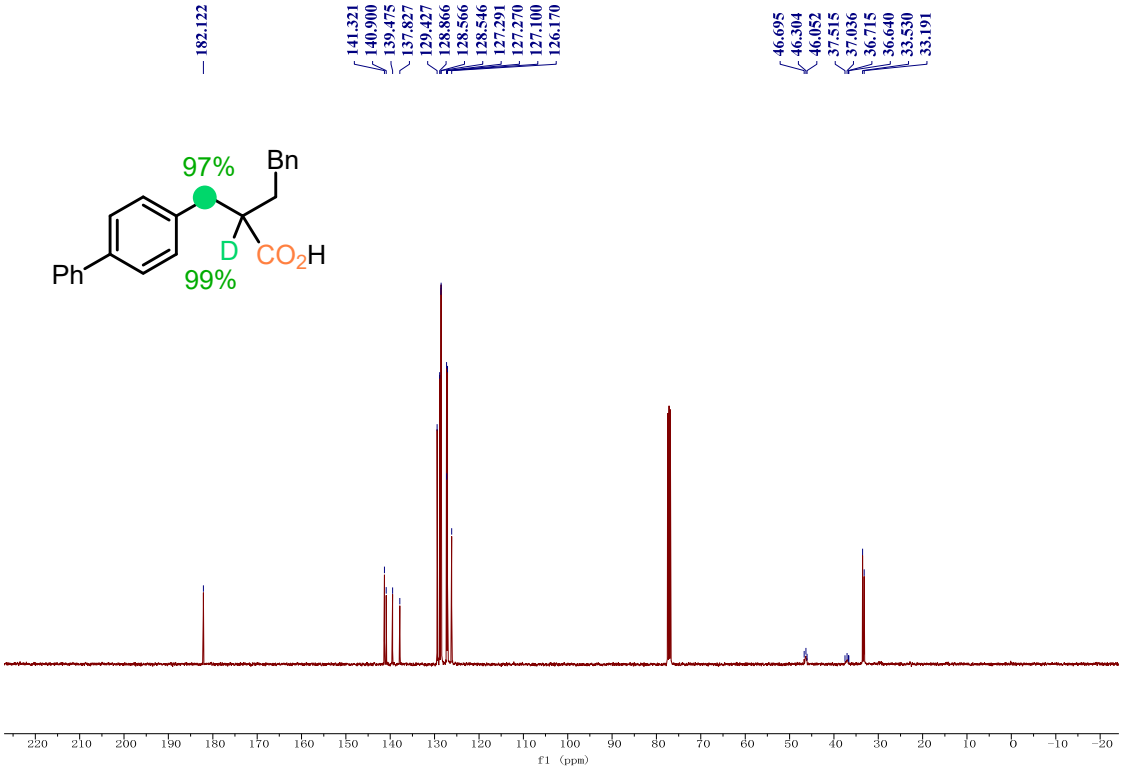
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-4-phenylbutanoic-2-*d* acid (3g)

^{1}H NMR (400 MHz, $CDCl_3$)



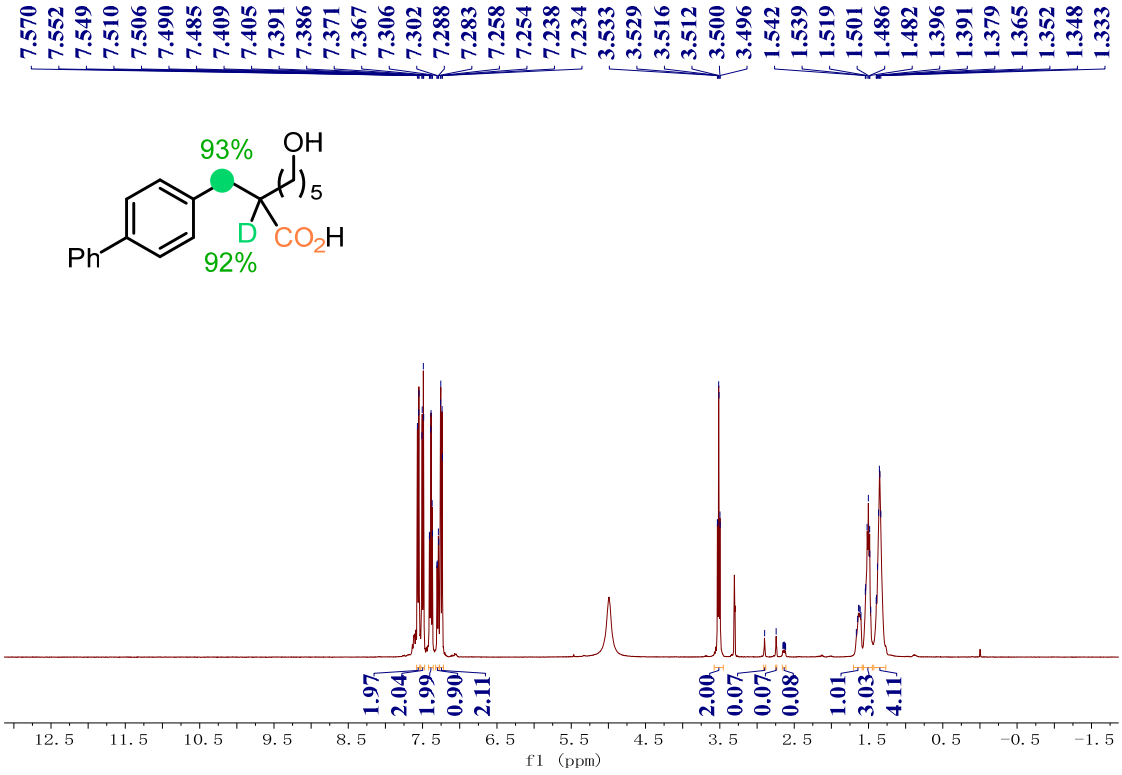
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-4-phenylbutanoic-2-*d* acid (3g)

^{13}C NMR (100 MHz, $CDCl_3$)



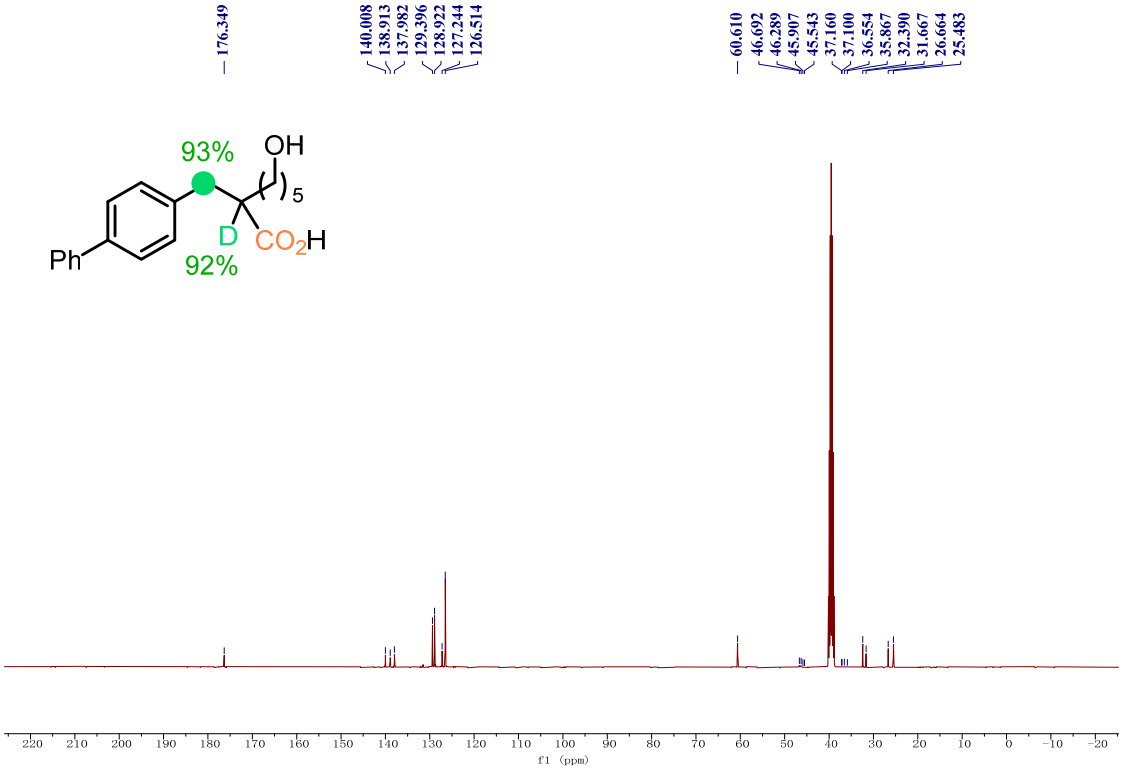
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-7-hydroxyheptanoic-2-*d* acid (3h)

^{1}H NMR (400 MHz, CD_3OD)



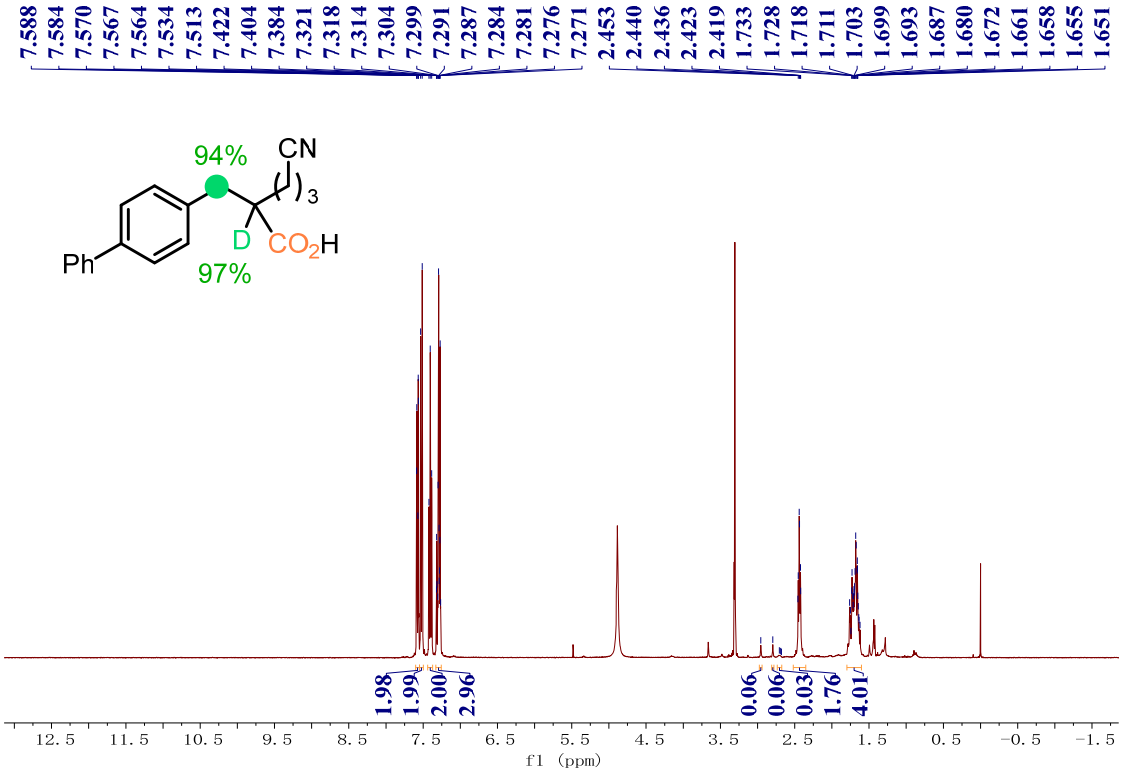
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-7-hydroxyheptanoic-2-*d* acid (3h)

^{13}C NMR (100 MHz, DMSO-d_6)



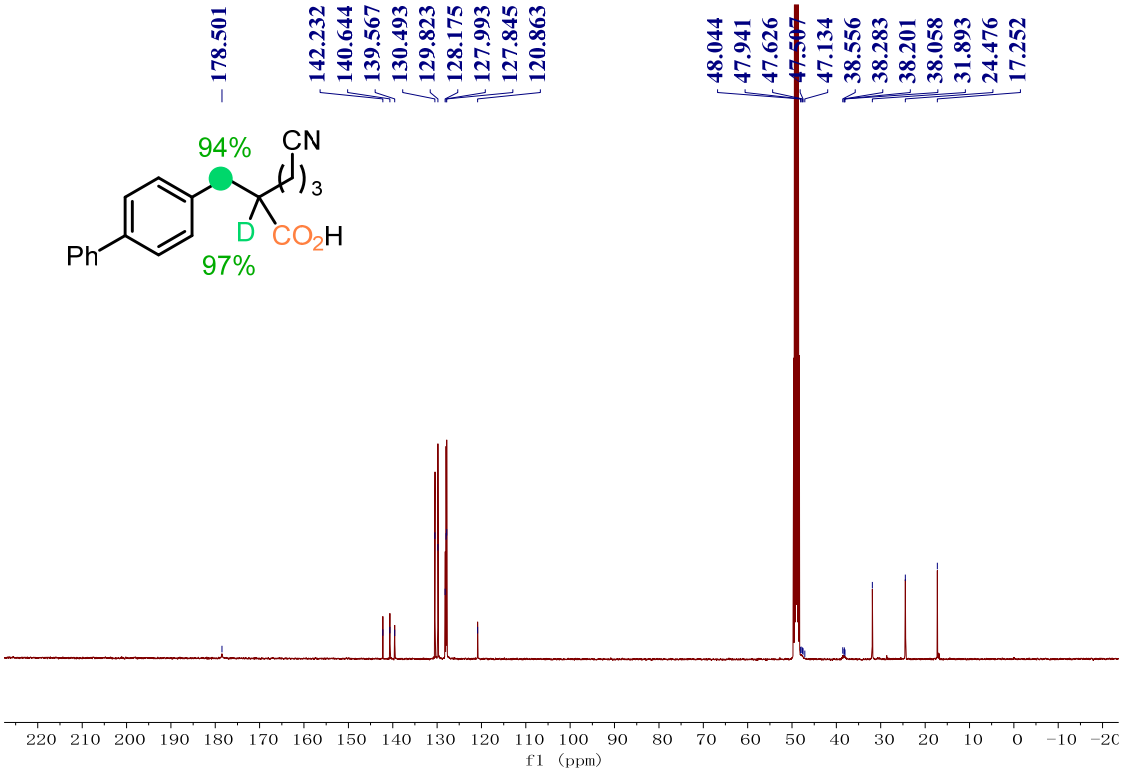
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-5-cyanopentanoic-2-*d* acid (3i)

^{1}H NMR (400 MHz, CD_3OD)



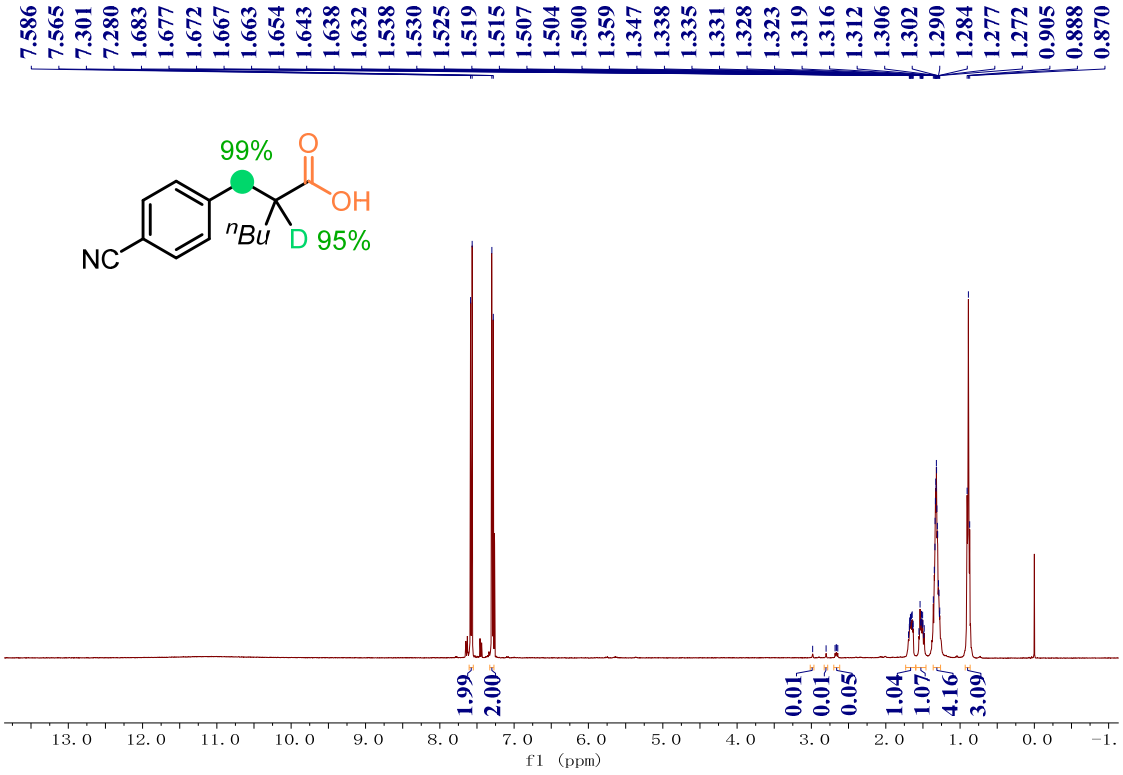
2-([1,1'-biphenyl]-4-ylmethyl-d_2)-5-cyanopentanoic-2-*d* acid (3i)

^{13}C NMR (100 MHz, CD_3OD)



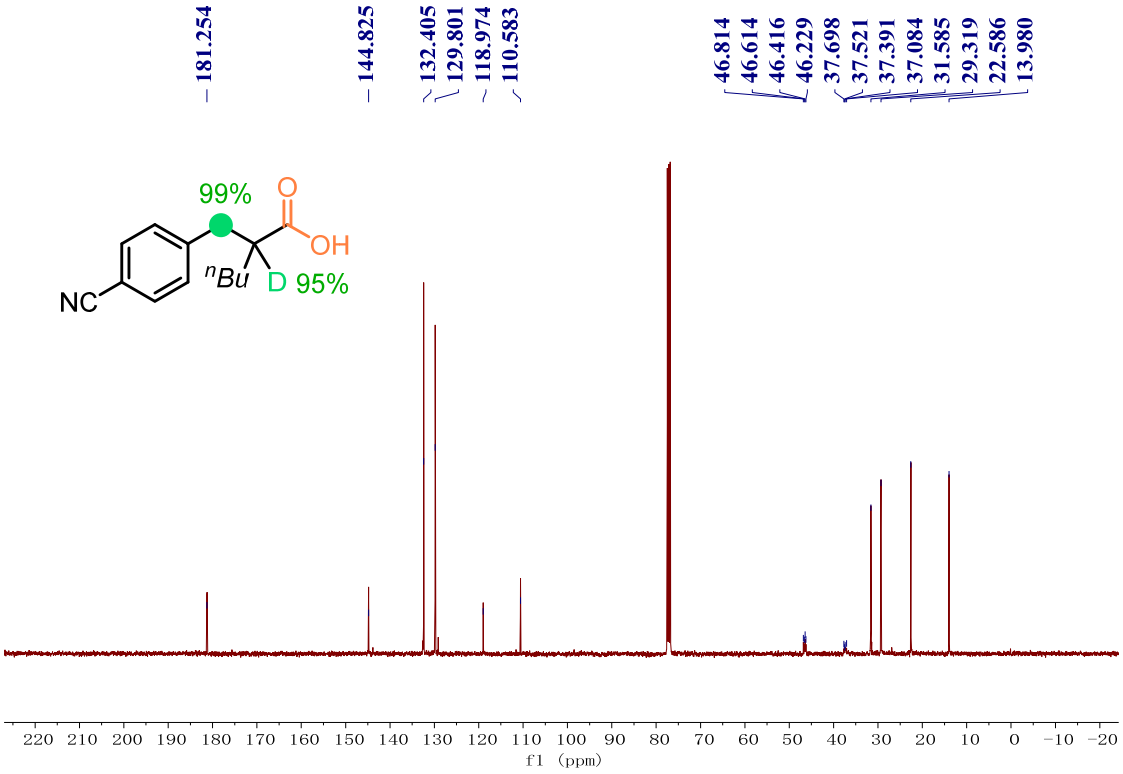
2-((4-cyanophenyl)methyl-d_2)hexanoic-2-*d* acid (3j)

^{1}H NMR (400 MHz, $CDCl_3$)



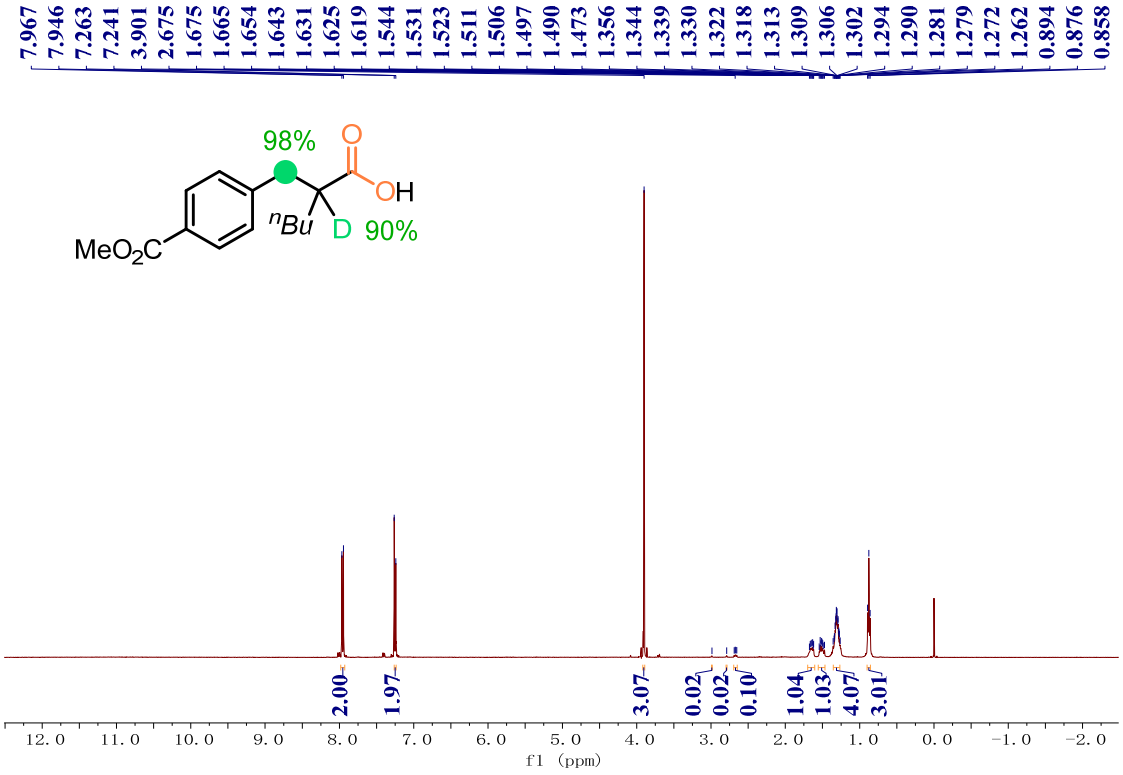
2-((4-cyanophenyl)methyl-d_2)hexanoic-2-*d* acid (3j)

^{13}C NMR (100 MHz, $CDCl_3$)



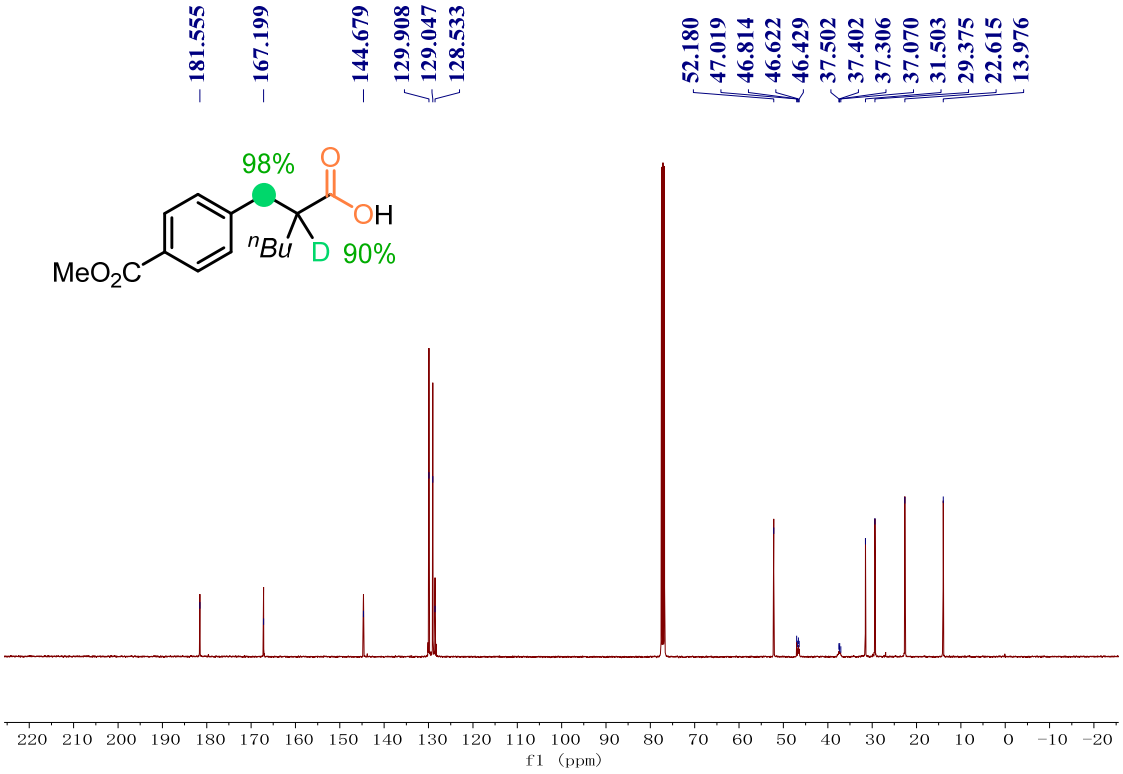
2-((4-(methoxycarbonyl)phenyl)methyl-d_2)hexanoic-2-*d* acid (3k)

^{1}H NMR (400 MHz, $CDCl_3$)



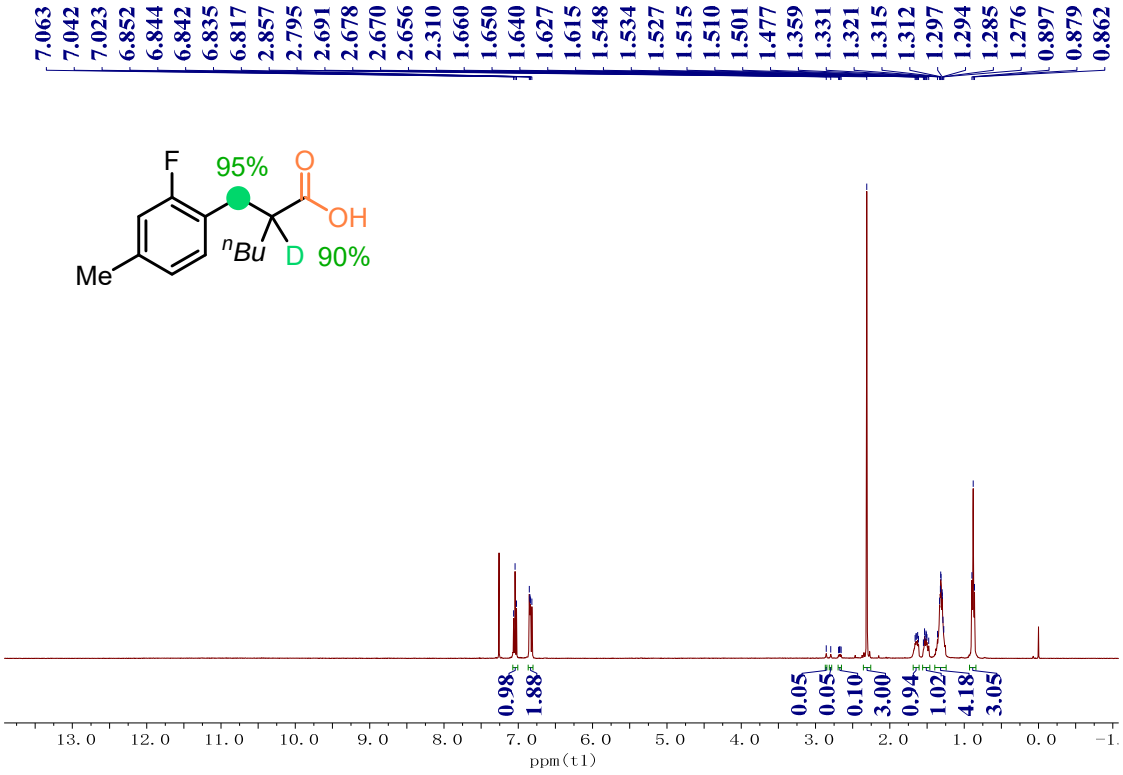
2-((4-(methoxycarbonyl)phenyl)methyl-d_2)hexanoic-2-*d* acid (3k)

^{13}C NMR (100 MHz, $CDCl_3$)



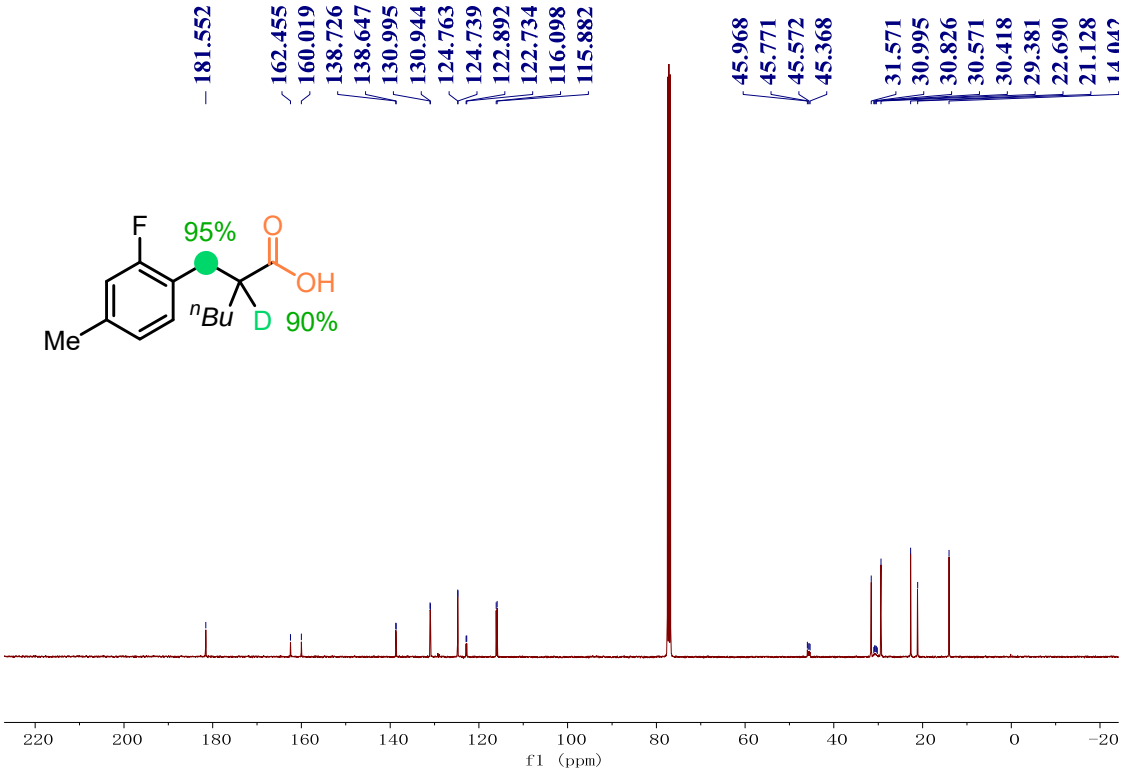
2-((2-fluoro-4-methylphenyl)methyl-d_2)hexanoic-2-*d* acid (3l)

^{1}H NMR (400 MHz, $CDCl_3$)



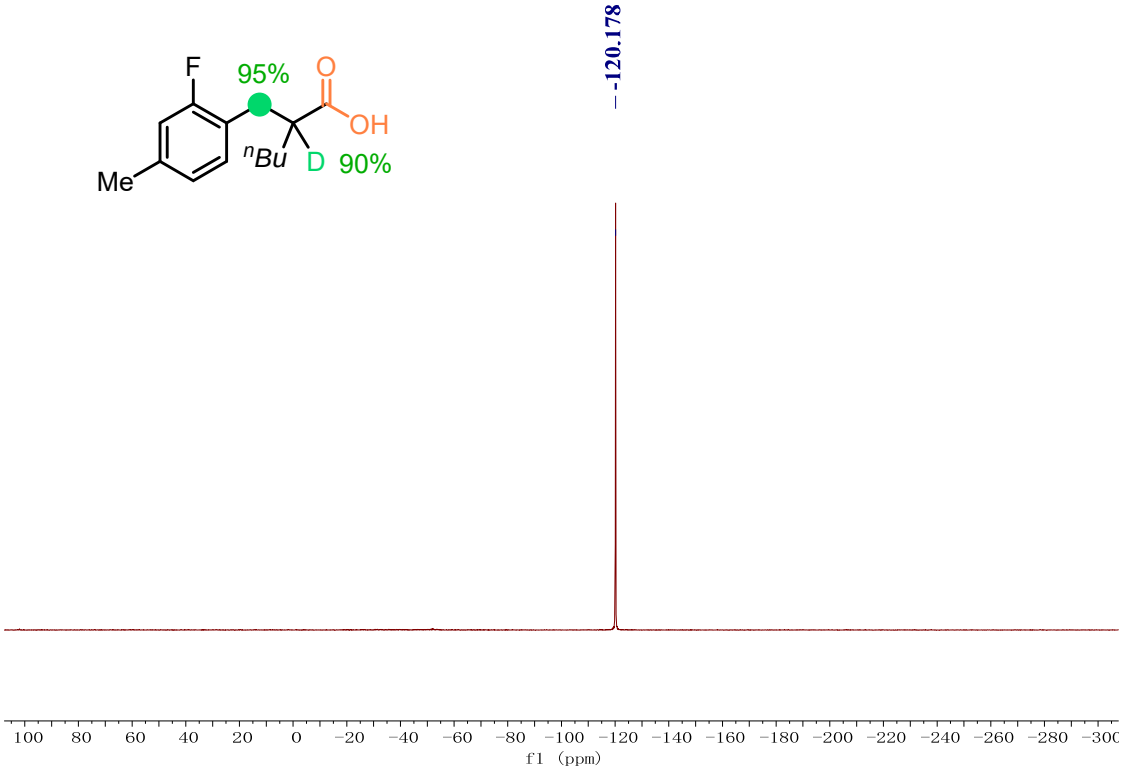
2-((2-fluoro-4-methylphenyl)methyl-d_2)hexanoic-2-*d* acid (3l)

^{13}C NMR (100 MHz, $CDCl_3$)



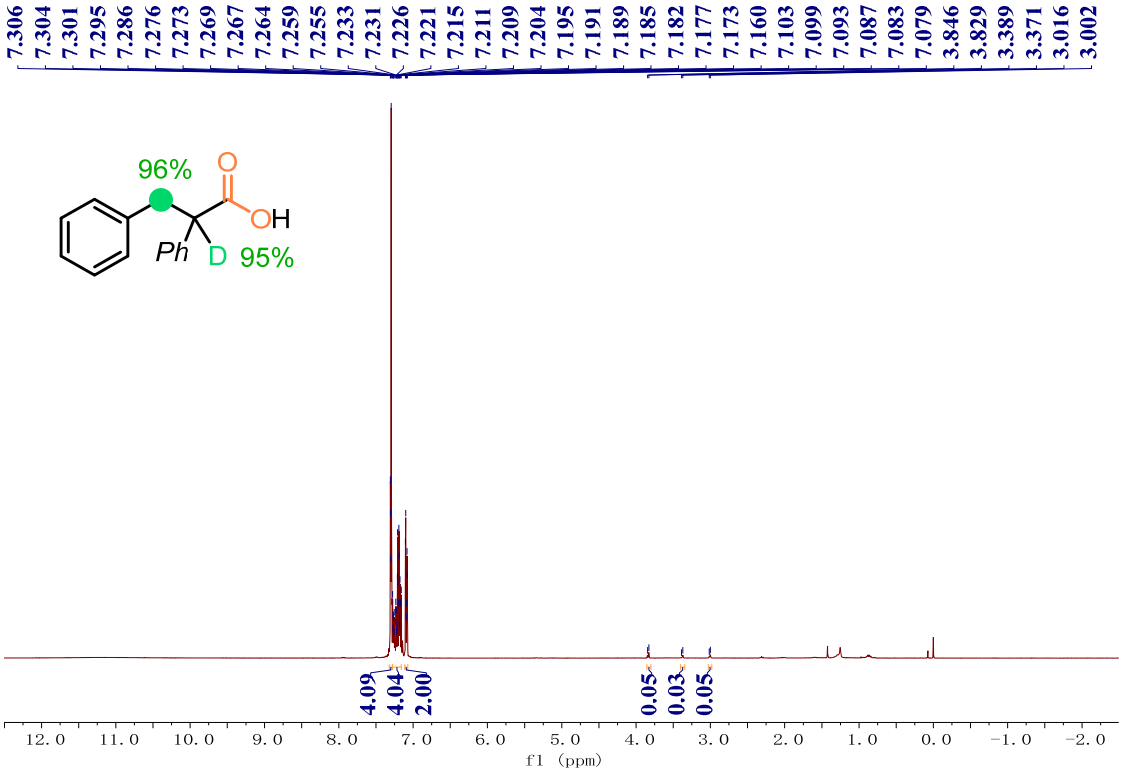
2-((2-fluoro-4-methylphenyl)methyl-d_2)hexanoic-2-*d* acid (3l)

^{19}F NMR (376 MHz, $CDCl_3$)



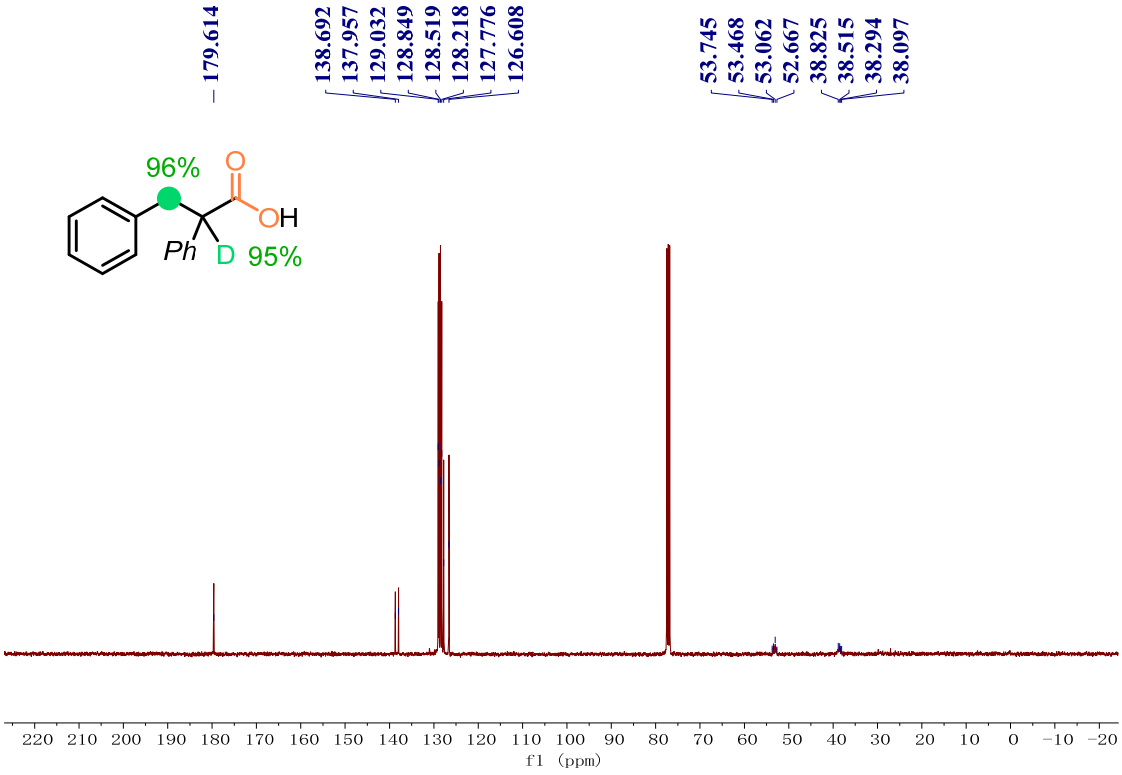
2,3-diphenylpropanoic-2,3,3-d_3 acid (3m)

^{1}H NMR (400 MHz, $CDCl_3$)



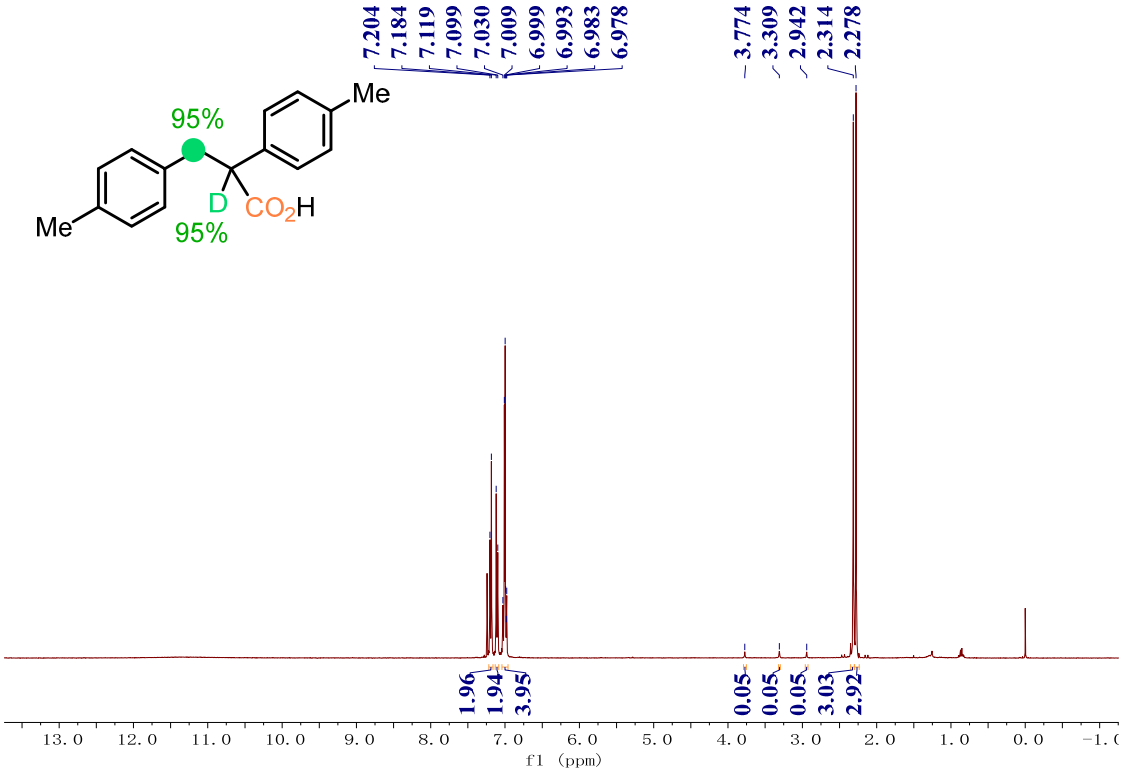
2,3-diphenylpropanoic-2,3,3-d_3 acid (3m)

^{13}C NMR (100 MHz, $CDCl_3$)



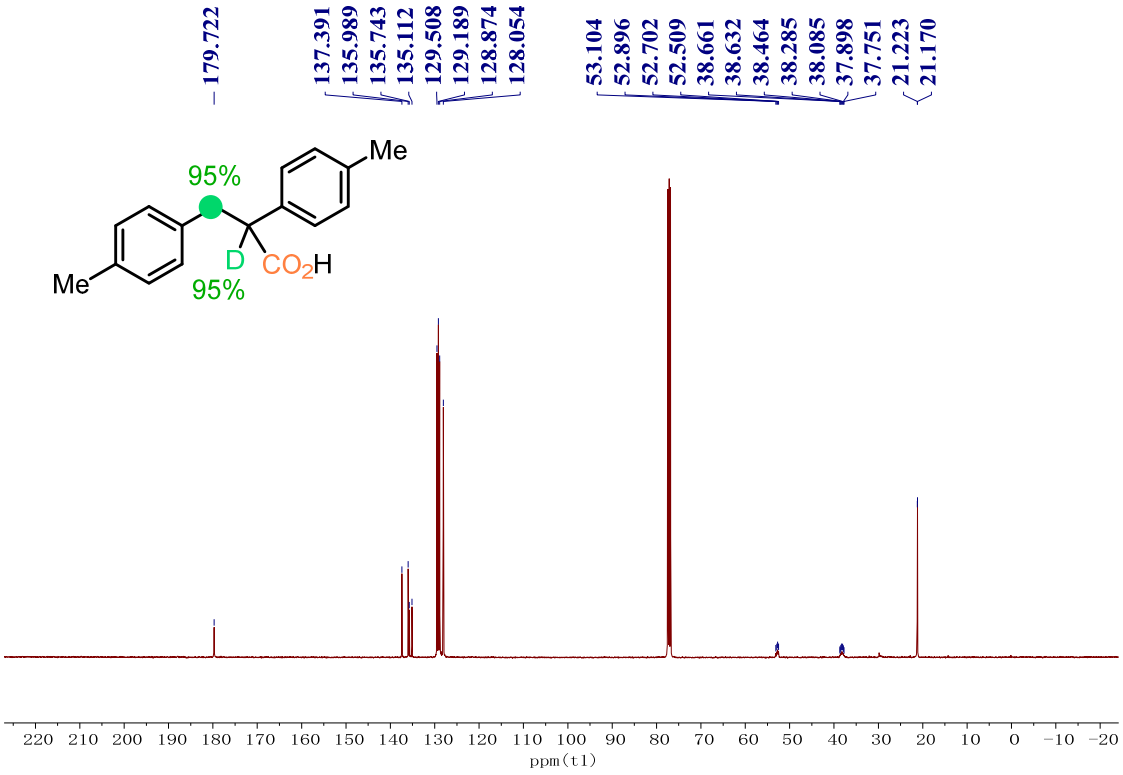
2,3-di-*p*-tolylpropanoic-2,3,3-d_3 acid (3n)

^{1}H NMR (400 MHz, $CDCl_3$)



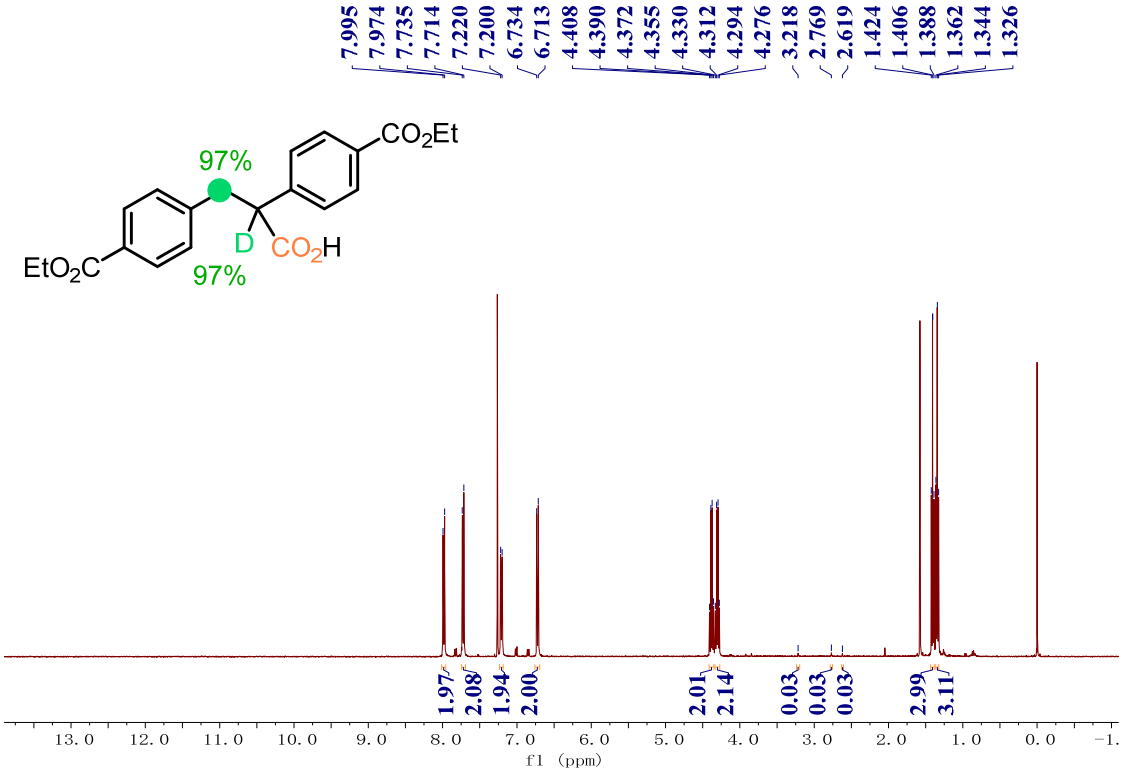
2,3-di-*p*-tolylpropanoic-2,3,3-d_3 acid (3n)

^{13}C NMR (100 MHz, $CDCl_3$)



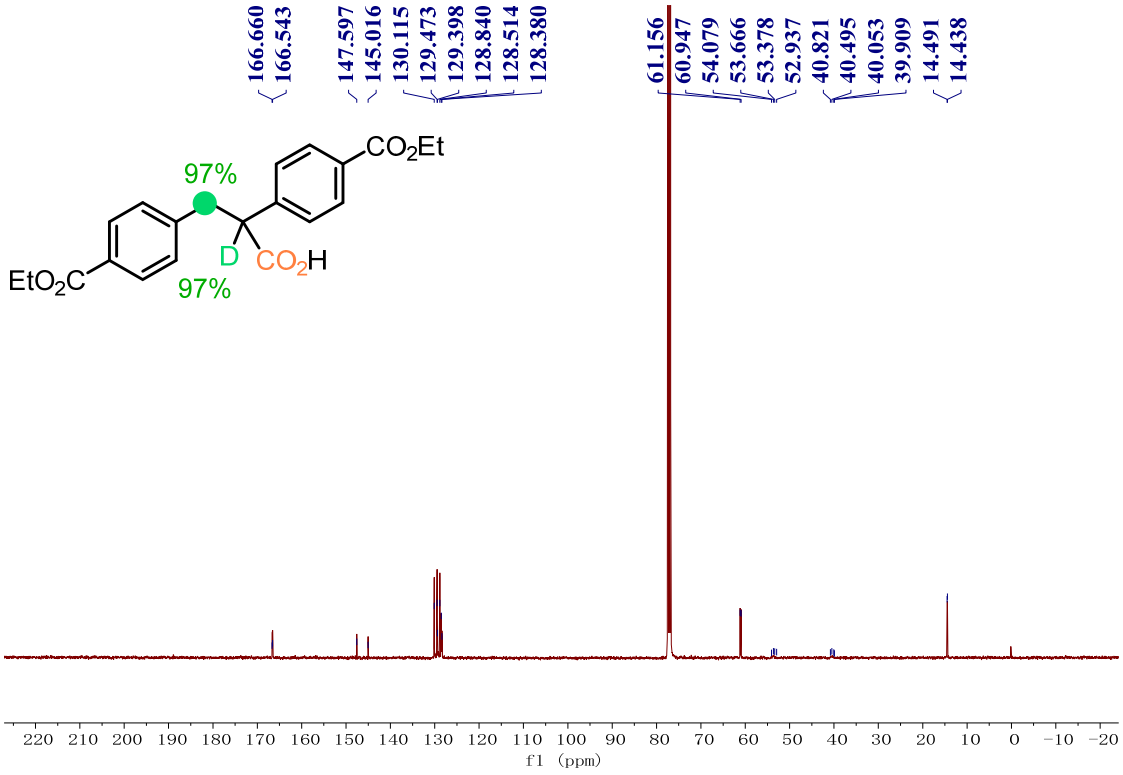
2,3-bis(4-(ethoxycarbonyl)phenyl)propanoic-2,3,3-*d*$_3$ acid (3o)

^{1}H NMR (400 MHz, $CDCl_3$)



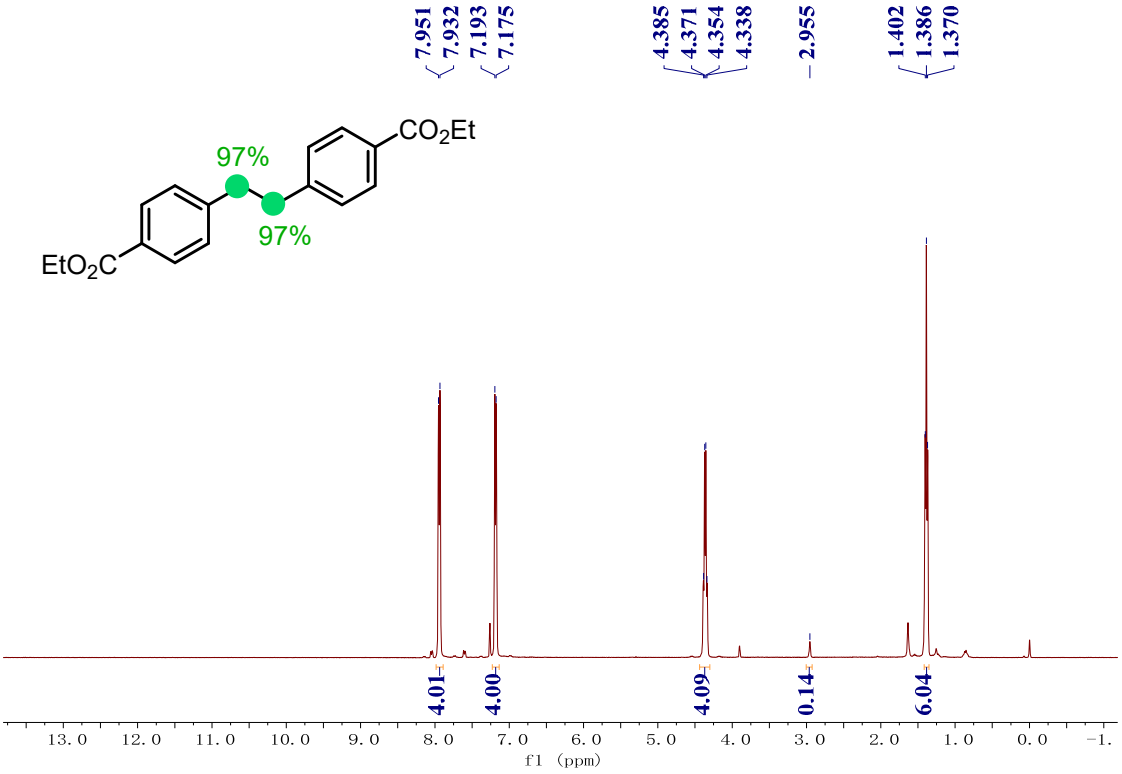
2,3-bis(4-(ethoxycarbonyl)phenyl)propanoic-2,3,3-*d*$_3$ acid (3o)

^{13}C NMR (100 MHz, $CDCl_3$)



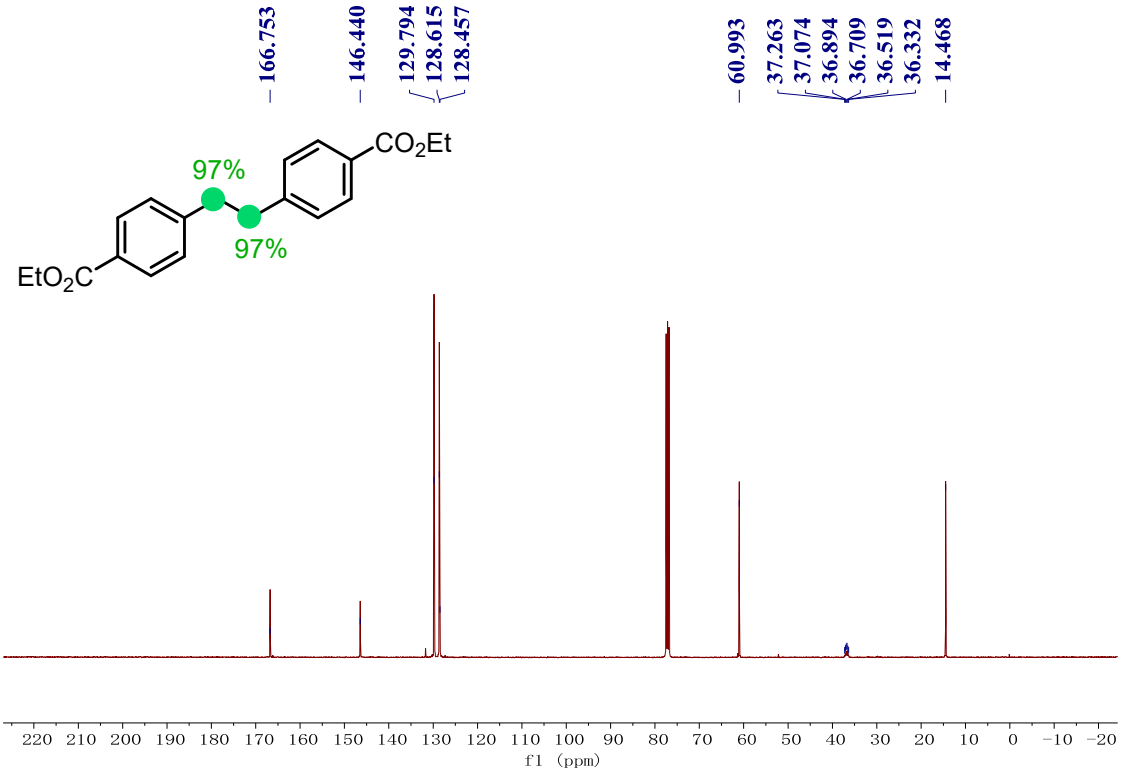
diethyl 4,4'-(ethane-1,2-diyl-*d*$_4$)dibenzoate (3o')

^{1}H NMR (400 MHz, $CDCl_3$)



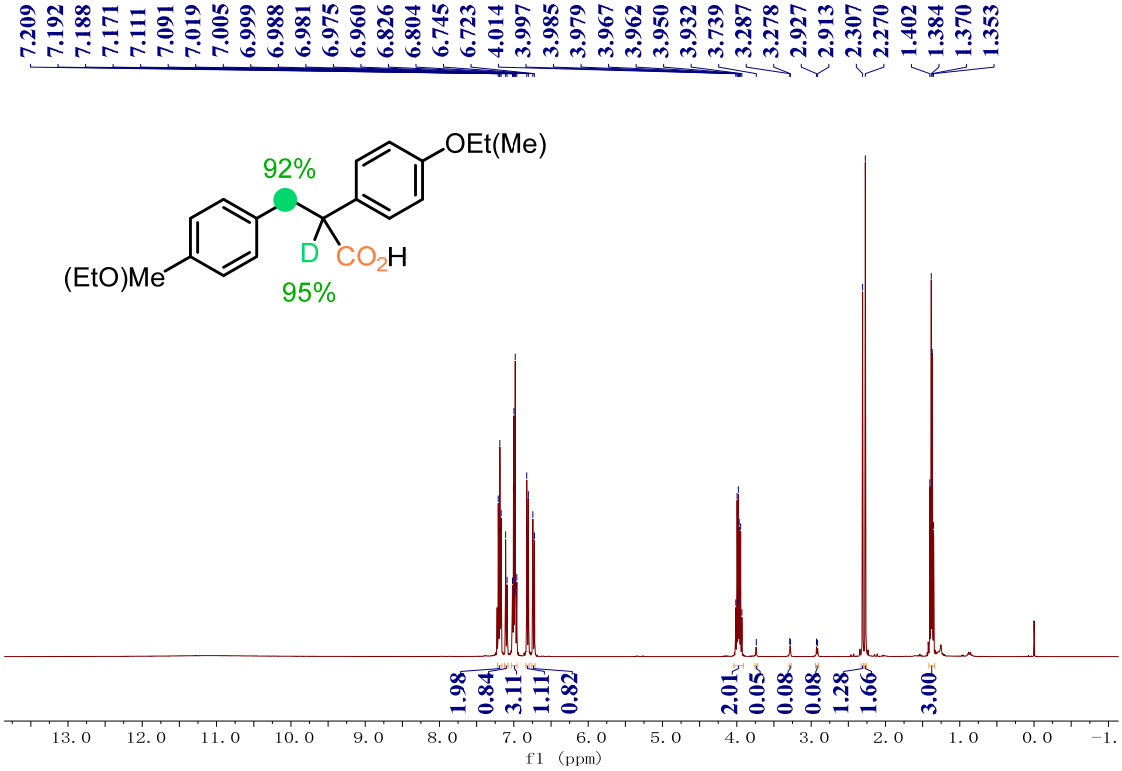
diethyl 4,4'-(ethane-1,2-diyl-*d*$_4$)dibenzoate (3o')

^{13}C NMR (100 MHz, $CDCl_3$)



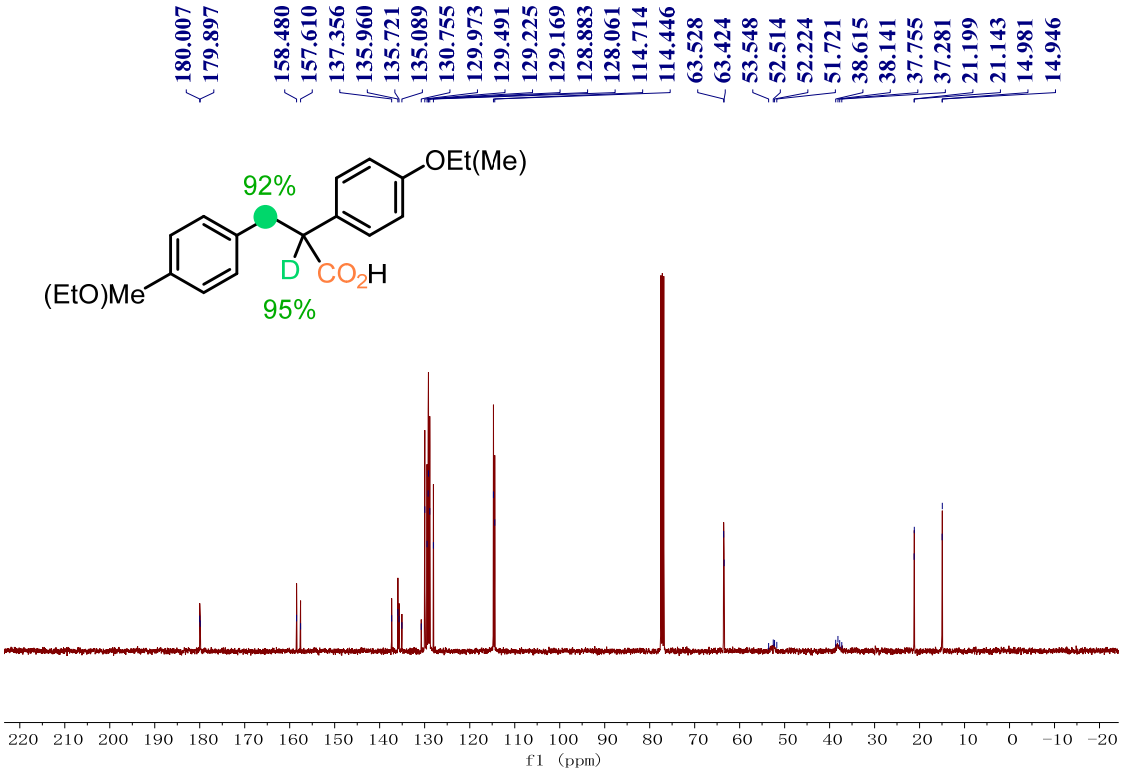
2-(4-ethoxyphenyl)-3-(*p*-tolyl)propanoic-2,3,3-d_3 acid and 3-(4-ethoxyphenyl)-2-(*p*-tolyl)propanoic-2,3,3-d_3 acid (3p + 3p', 1:1.3)

^{1}H NMR (400 MHz, $CDCl_3$)



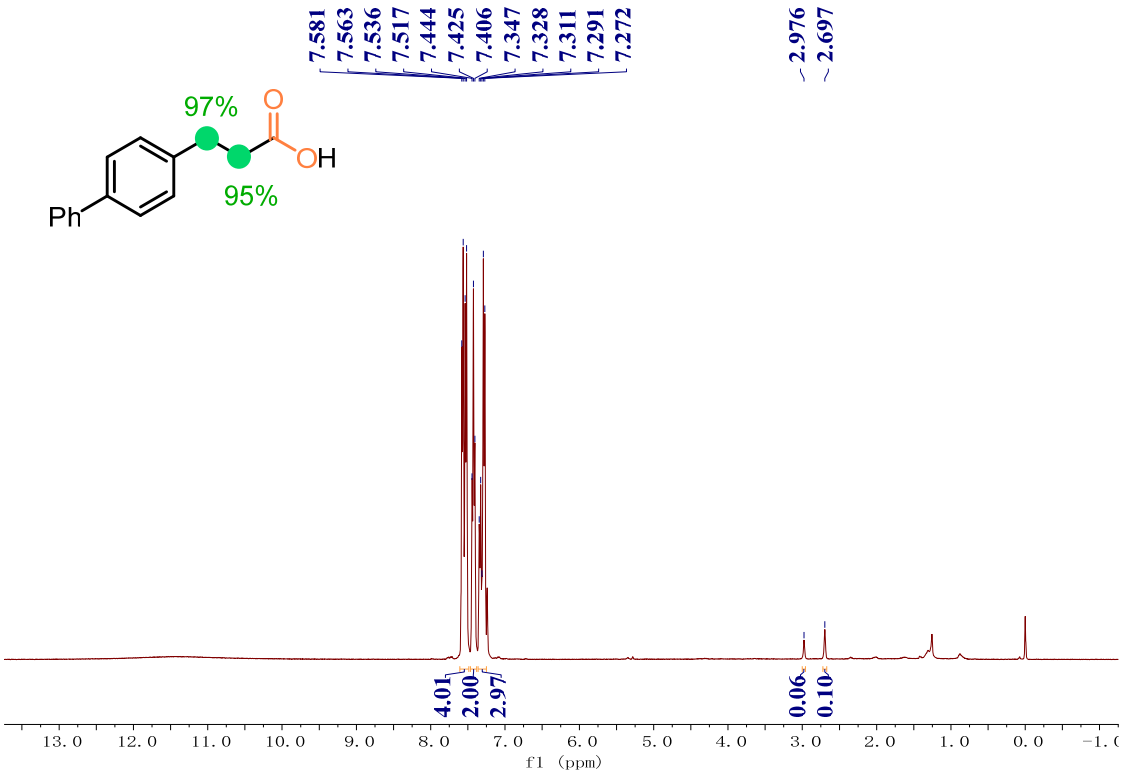
2-(4-ethoxyphenyl)-3-(*p*-tolyl)propanoic-2,3,3-d_3 acid and 3-(4-ethoxyphenyl)-2-(*p*-tolyl)propanoic-2,3,3-d_3 acid (3p + 3p', 1:1.3)

^{13}C NMR (100 MHz, $CDCl_3$)



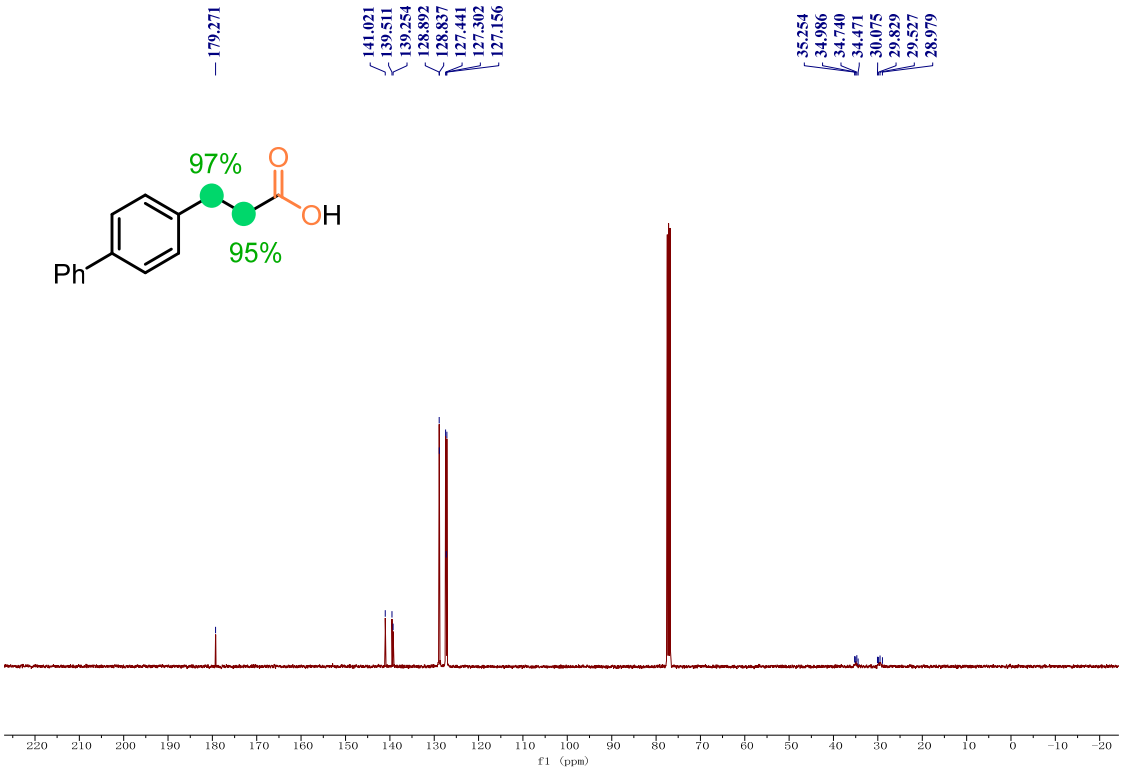
3-([1,1'-biphenyl]-4-yl)propanoic-2,2,3,3-*d*$_4$ acid (2c')

^{1}H NMR (400 MHz, $CDCl_3$)



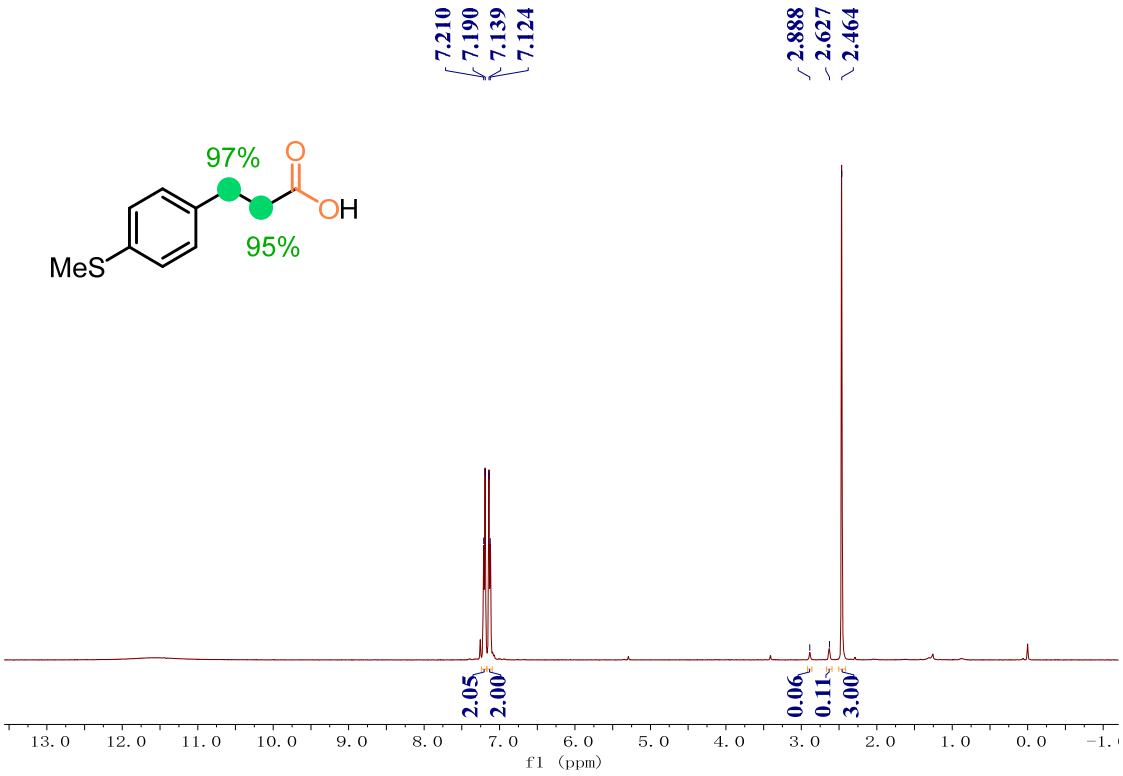
3-([1,1'-biphenyl]-4-yl)propanoic-2,2,3,3-*d*$_4$ acid (2c')

^{13}C NMR (100 MHz, $CDCl_3$)



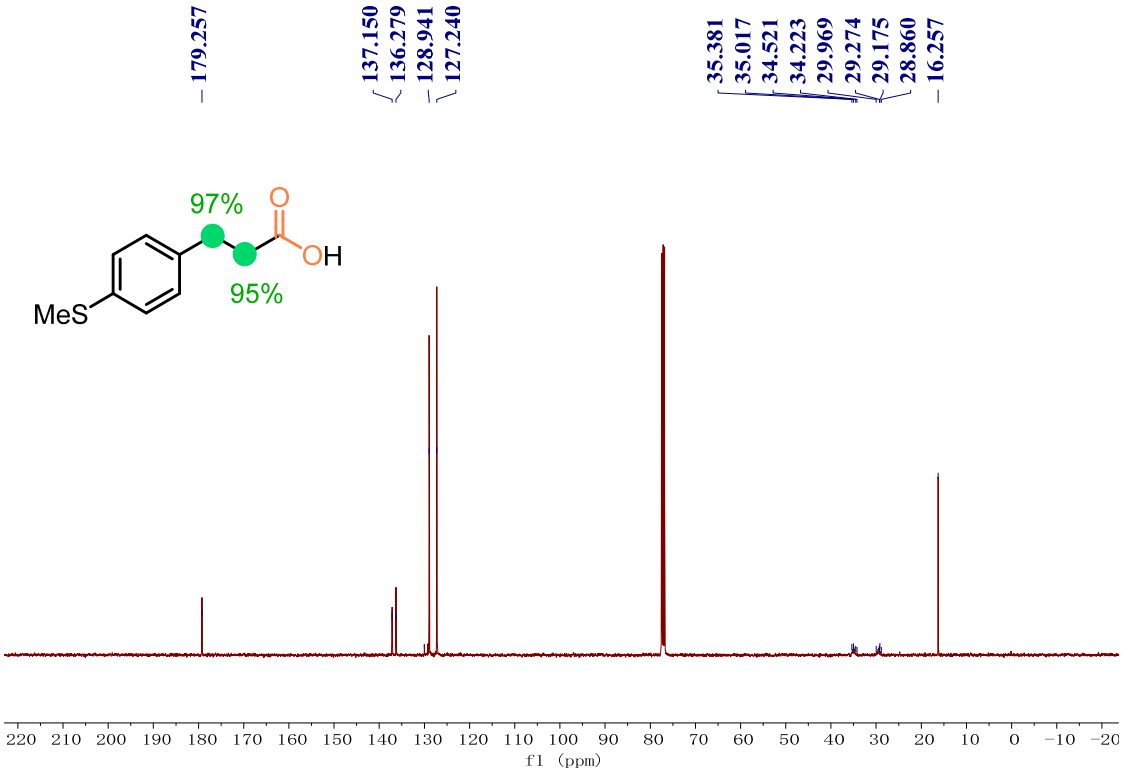
3-(4-(methylthio)phenyl)propanoic-2,2,3,3-d_4 acid (6)

^{1}H NMR (400 MHz, $CDCl_3$)



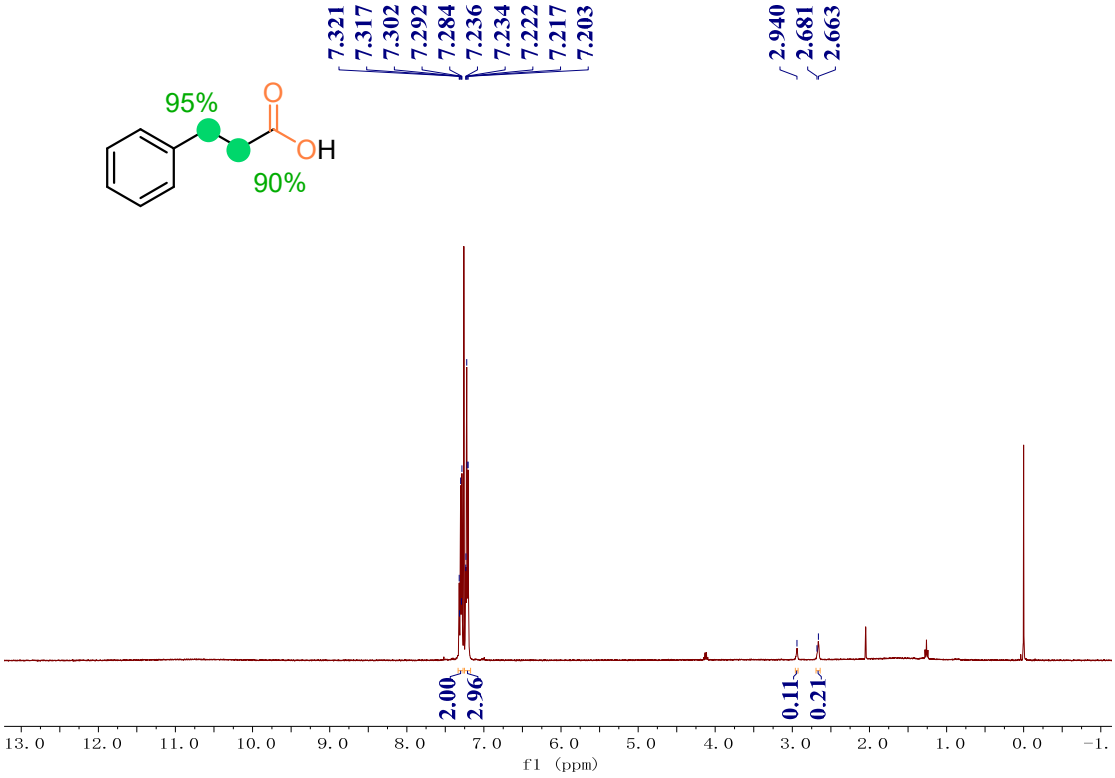
3-(4-(methylthio)phenyl)propanoic-2,2,3,3-d_4 acid (6)

^{13}C NMR (100 MHz, $CDCl_3$)



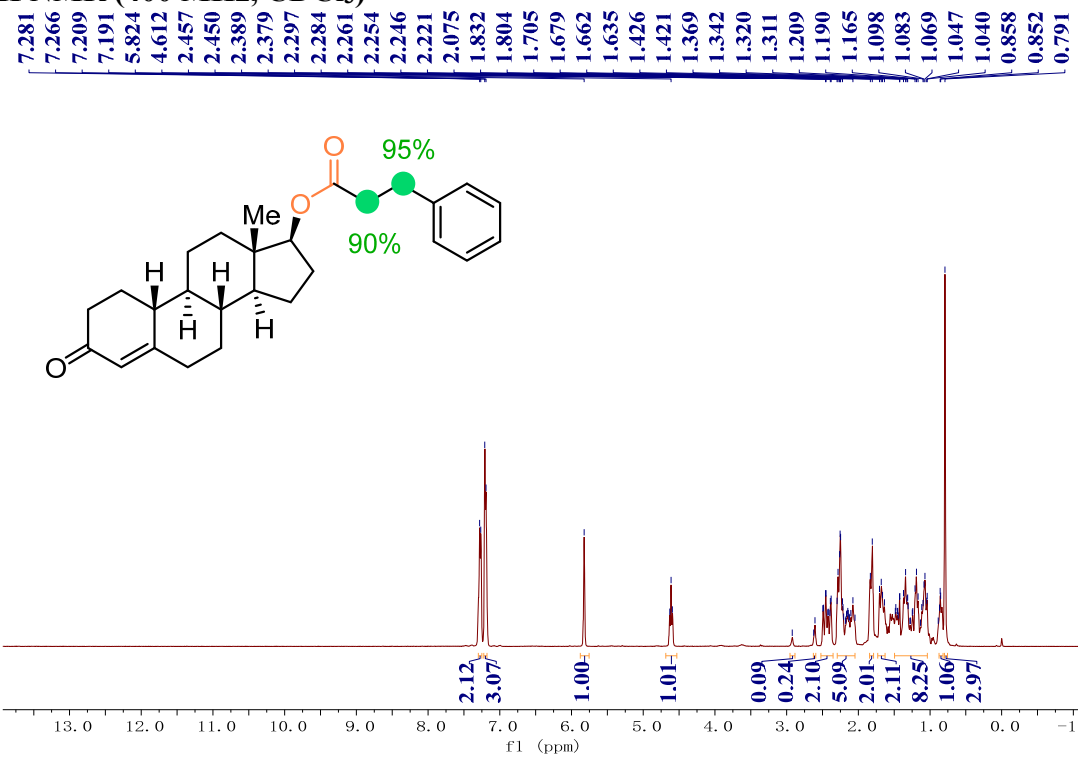
3-phenylpropanoic-2,2,3,3-d_4 acid (2b')

^{1}H NMR (400 MHz, CD_3OD)



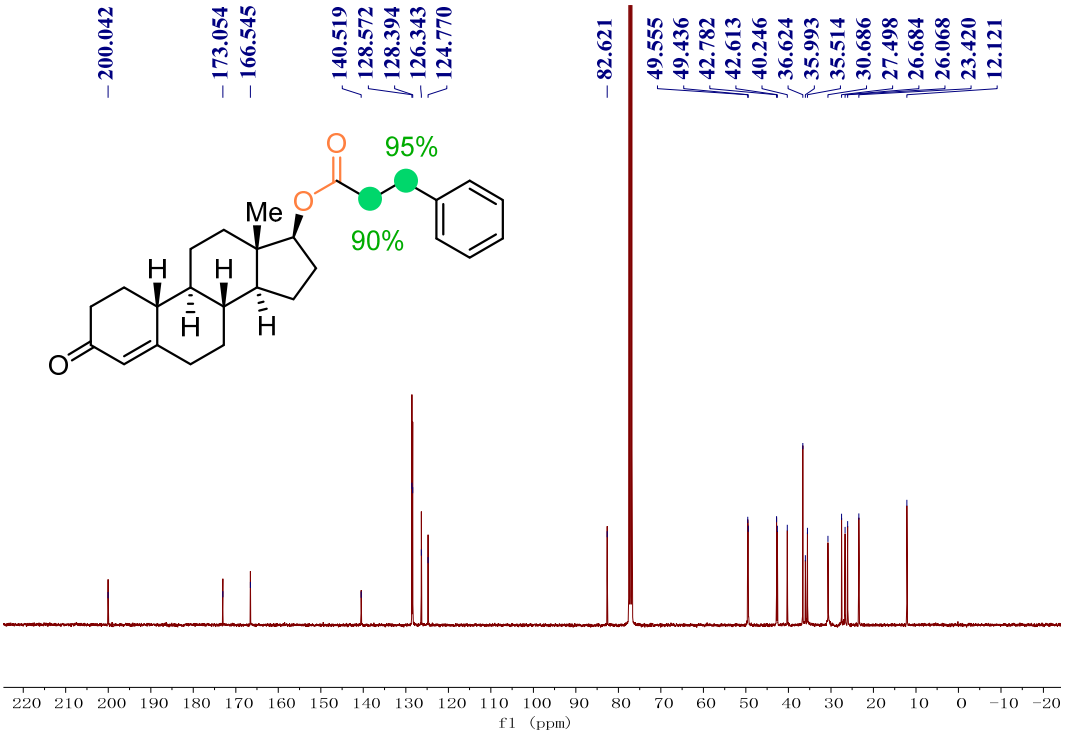
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-13,17-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 3-phenylpropanoate-2,2,3,3-d_4 (8)

^{1}H NMR (400 MHz, $CDCl_3$)



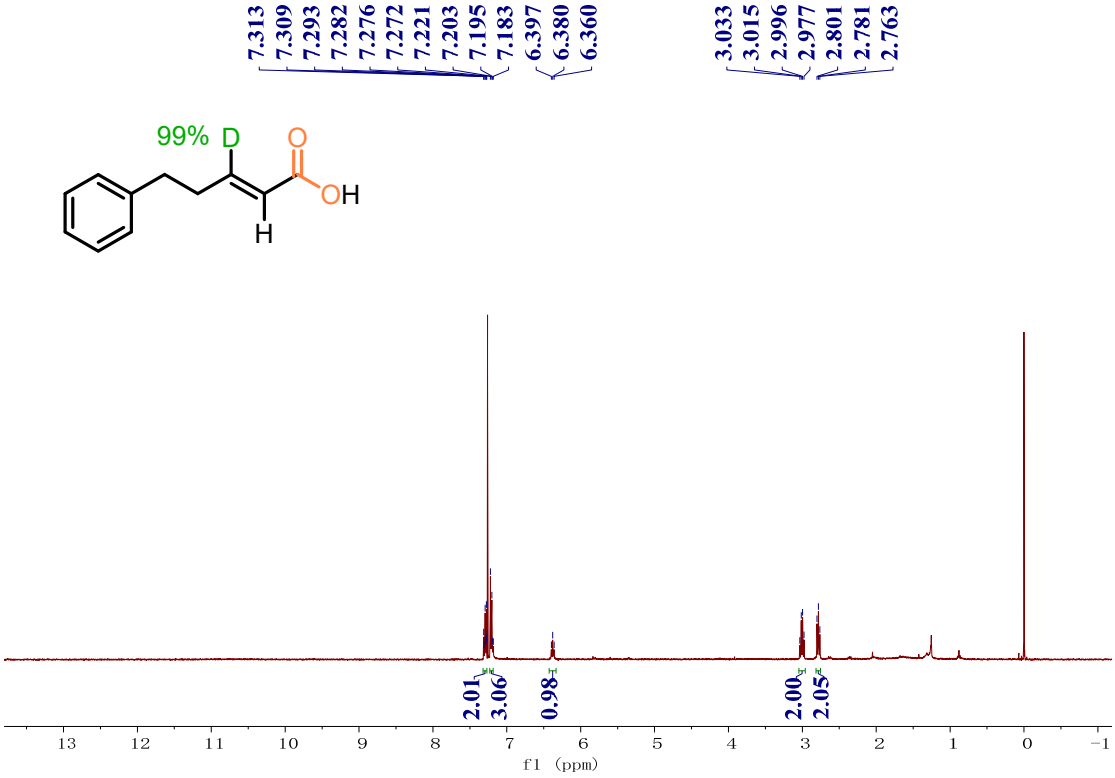
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-13,17-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 3-phenylpropanoate-2,2,3,3-d_4 (8)

^{13}C NMR (100 MHz, $CDCl_3$)



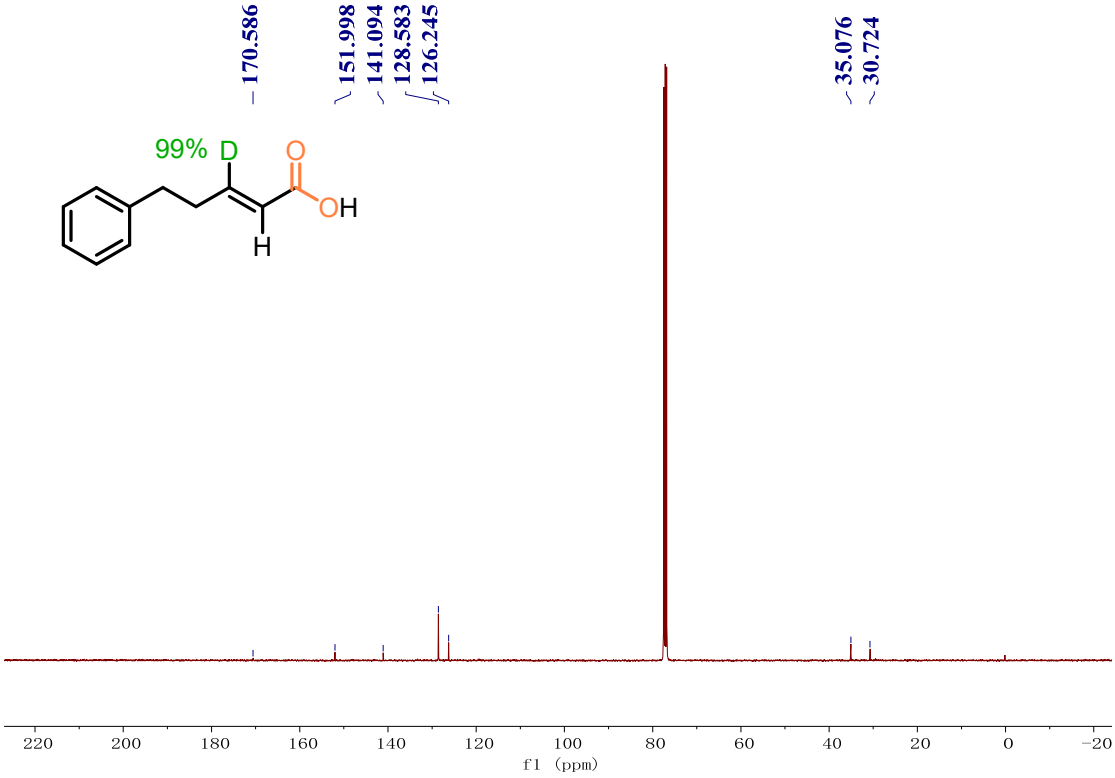
5-phenylpent-2-enoic-3-*d* acid (10)

^{1}H NMR (400 MHz, $CDCl_3$)



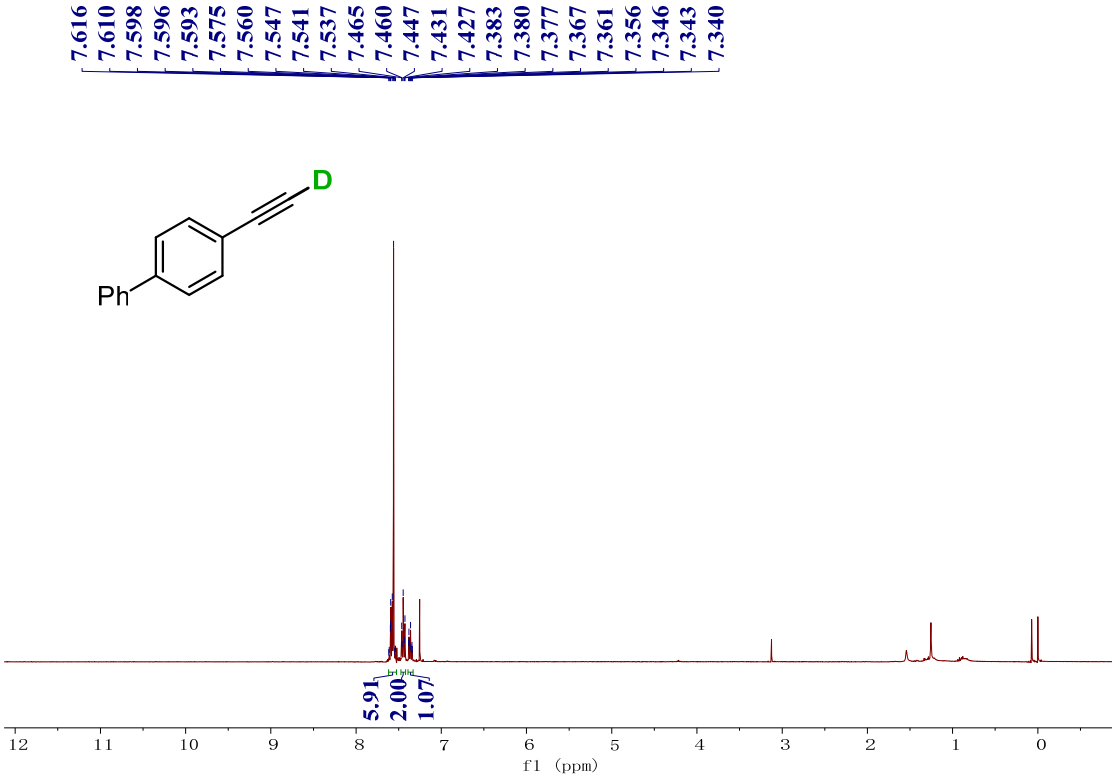
5-phenylpent-2-enoic-3-*d* acid (10)

^{13}C NMR (100 MHz, $CDCl_3$)



4-(ethynyl-*d*)-1,1'-biphenyl (1c')

^{1}H NMR (400 MHz, $CDCl_3$)



3-phenylpropanoic-2,3-d_2 acid (15)

^{1}H NMR (400 MHz, $CDCl_3$)