Supplementary Information

Superacid-Catalysed α-Deuteration of Ketones with D_2O

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1. General Information

1.1 Reagents and materials.

All chemicals were purchased from commercial suppliers and used directly as received. Deuterated solvents were purchased from Konoscince and directly used. Unless otherwise noted, reagents were commercially available and used without further purification. All reactions were conducted under indicated atmosphere by using standard Schlenk techniques. All glassware and vials were oven-dried prior to use. All work-up and purification procedures were carried out with reagent-grade solvents.

1.2 Analytical methods.

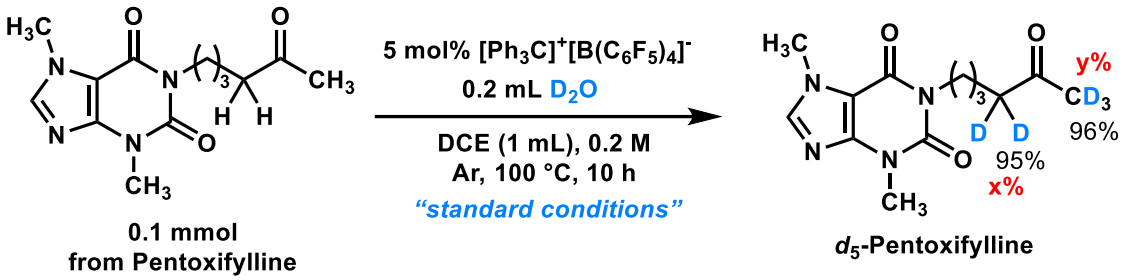
Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm Yantai silica plates (GF-254). The developed chromatography was analyzed by UV lamp (254 nm and 365 nm). Flash chromatography was performed on 200-300 mesh Yantai silica gel with the indicated eluents. Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR and spectra were recorded respectively at 500 MHz or 400 MHz and 126 MHz or 101 MHz in indicated deuterated solvents ($CDCl_3$, or DMSO-d_6). Fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 376 MHz, and the chemical shifts were accurate to one decimal place or two decimal places to help distinguish overlapping peaks. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals ($CDCl_3$: δ H 7.26 and δ C 77.16 ppm; DMSO-d_6: δ H 2.50 and δ C 39.50 ppm). The signals of water were observed at about 1.58 ppm in $CDCl_3$ and 3.33 ppm in DMSO-d_6, respectively. Coupling constants (J) were reported in Hertz (Hz). Splitting patterns were designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets, etc. High resolution mass spectrometry (HRMS) data were obtained on a Q-Tof MS/MS system (Agilent 1290-6546) using electrospray ionization (ESI) in positive mode.

2. General Procedure

General procedure for the deuteration: To a well-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.01 mmol, 10 mol%) and substrates (0.1 mmol, 1.0 equiv.) were added. Then, the tube was evacuated and backfilled with argon for three times before 0.2 mL deuterated water and 1.0 mL solvent were charged via syringe. Subsequently, the tube was sealed with screw cap. The resulting solution was heated in an oil bath at 100 °C and stirred vigorously for 10 hours. Once the reaction was complete, the mixture was diluted with ethyl acetate (2 mL), extracted with ethyl acetate (3*5 mL), combined organic solvent, washed with saturated sodium chloride solution, dried with anhydrous sodium sulfate, filtered by a sand core funnel. The filtrate was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography or flash column chromatography eluted with hexane/ethyl acetate to obtain the products.

3. Optimization of the Reaction Conditions

Table S1. Screening the optical reaction conditions



Entry	Change from the "standard conditions"	x (%[a])	y (%[a])	Yield(%[b])
1	none	95	96	93(89[d])
2	without $[Ph_3C]^+[B(C_6F_5)_4]^-$	n.d.	n.d.	99
3	$[Ph_3C]^+[BF_4]^-$ instead of $[Ph_3C]^+[B(C_6F_5)_4]^-$	n.d.	n.d.	90
4	$K^+[B(C_6F_5)_4]^-$ instead of $[Ph_3C]^+[B(C_6F_5)_4]^-$	40	34	86
5	DCM instead of DCE	91	96	86
6	90 ºC instead of 100 ºC	90	93	94
7	8 h instead of 10 h	89	93	86
8	oxygen instead of argon	50	50	82

[a]Reaction conditions: Pentoxifylline (0.1 mmol, 27.8 mg), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (5 mol%, 0.005 mmol), D_2O (55 equiv., 0.2 mL), DCE (1 mL), 100 °C, Argon, 10 hours. [b]Yield of deuteration was based on hydrogen highlighted in red. [c]All yields are NMR yields by using CH_3NO_2 as an internal standard. [d]Isolated yields. n.d.: no deuteration.

4. Gram-scale Reactions

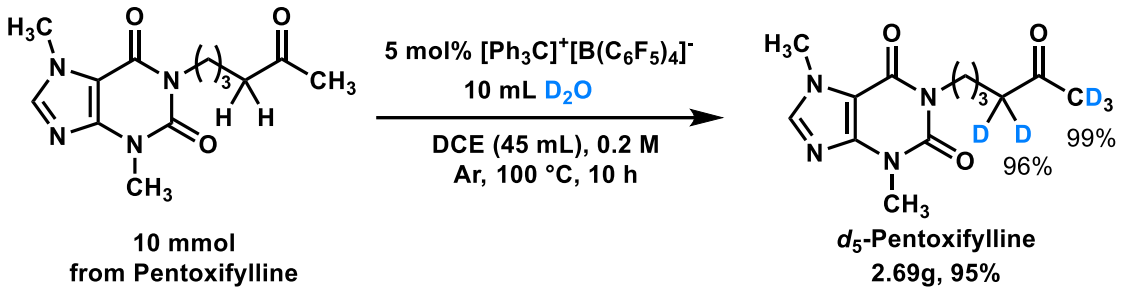


Figure S1. Gram-scale synthesis of ***d*$_5$-Pentoxifylline**

10 mmol-scale synthesis of *d*$_5$-Pentoxifylline (1): To a well-dried round bottom flask (250 mL) equipped with a magnetic stir bar, $[Ph_3C]^+[B(C_6F_5)_4]^-$ (461 mg, 0.5 mmol, 0.05 equiv.) and Pentoxifylline (2.78 g, 10 mmol, 1.0 equiv.) were added. Then, the flask was sealed, evacuated and backfilled with Ar for three times before 10 mL deuterated water and 45 mL DCE were charged via syringe. The resulting yellow solution was heated in an oil bath at 100 °C and stirred vigorously for 10 hours. When the reaction was complete, the mixture was diluted with DCE (20 mL), extracted with DCE (3*20 mL), combined organic solvent, washed with saturated sodium chloride solution, dried with anhydrous sodium sulfate, filtered by a funnel. The filtrate was concentrated under reduced pressure and the residue was stirred with the mixture of PE/EA (100:1) for 12 hours and filtered to obtain the desired compound *d*$_5$-Pentoxifylline (2.69 g, 95%) as a white solid. TLC: Rf = 0.35 (silica gel, PE/EA, 5:1).

5. Preliminary Mechanistic Studies

5.1 Reverse D/H exchange.

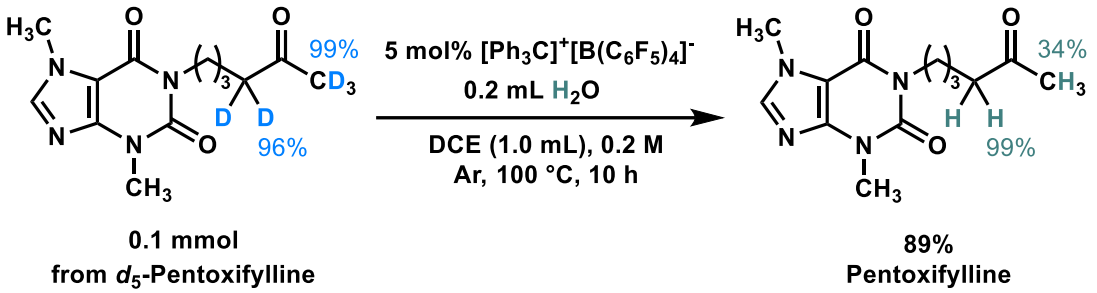


Figure S2. Reverse D/H exchange using ***d*$_5$-Pentoxifylline**

Reverse D/H exchange using ***d*$_5$-Pentoxifylline**: To a well-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, $[Ph_3C]^+[B(C_6F_5)_4]^-$ (4.6mg, 0.005 mmol, 5 mol%) and *d*$_5$-Pentoxifylline (28.3mg, 0.1 mmol, 1.0 equiv.) were added. Then, the tube was evacuated and backfilled with argon for three times before 0.2 mL water and 1.0 mL DCE were charged via syringe. Subsequently, the tube was sealed with screw cap. The resulting solution was heated in an oil bath at 100 °C and stirred vigorously for 10 hours. Once the reaction was complete, the mixture was diluted with ethyl acetate (2 mL), extracted with ethyl acetate (3*5 mL), combined organic solvent, washed with saturated sodium chloride solution, dried with anhydrous sodium sulfate, filtered by a sand core funnel. The filtrate was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography or flash column chromatography eluted with hexane/ethyl acetate to obtain the products.

5.2 Deuteration with 1 equiv. Brønsted acids vs. 10 mol% Ion pair.

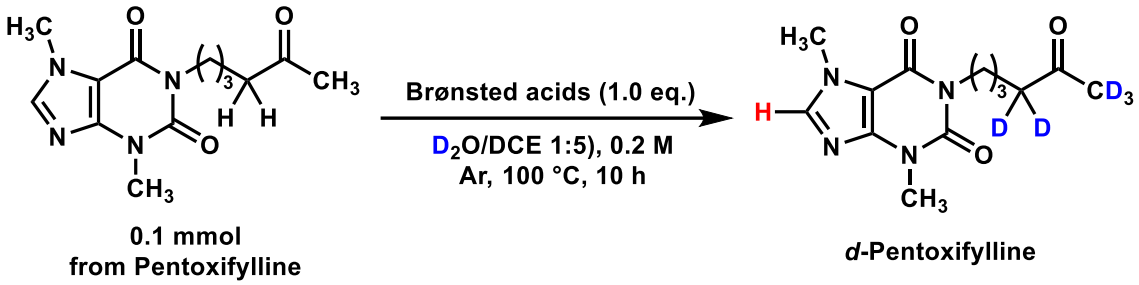


Figure S3. Deuteration with 1 equiv. Brønsted acids vs. 10 mol% Ion pair.

Reactions were performed with on a scale of 0.1 mmol Pentoxifylline in presence of 1.0 eq. Brønsted acids in 0.2 mL D_2O (55 equiv.) and 1.0 mL DCE under Ar atmosphere at 100 °C for 10 h. Yield of deuteration was based on hydrogen highlighted in red. All of yields were isolated yields.

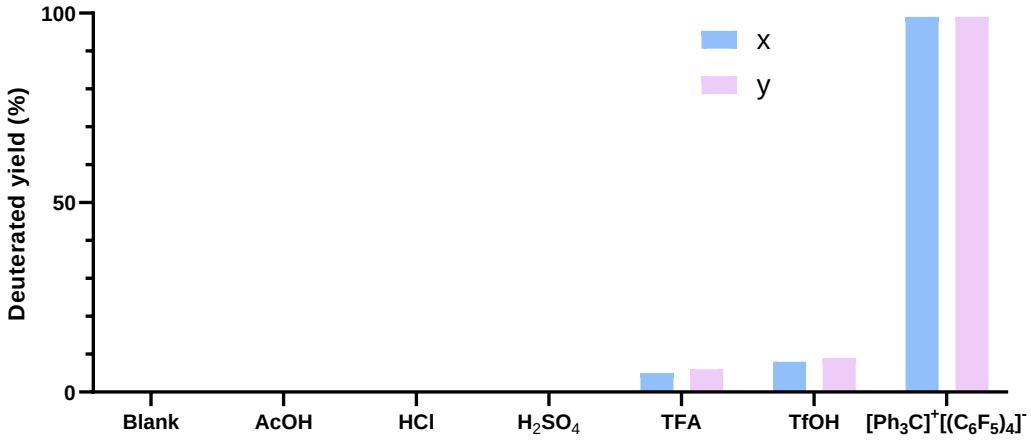


Figure S4. H/D exchange using 1.0 eq. Brønsted acids vs. 5 mol% $[Ph_3C]^+[B(C_6F_5)_4]^-$

5.3 Deuteration with 1.0 or 0.1 equiv. K_2CO_3 as catalyst.

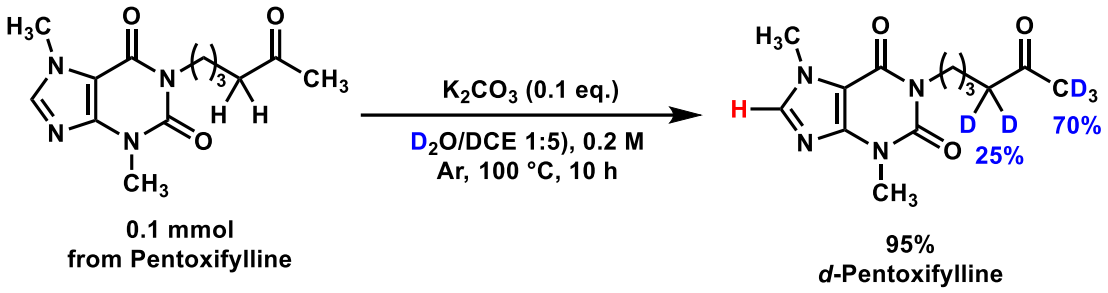


Figure S5. Deuteration with 0.1 equiv. K_2CO_3

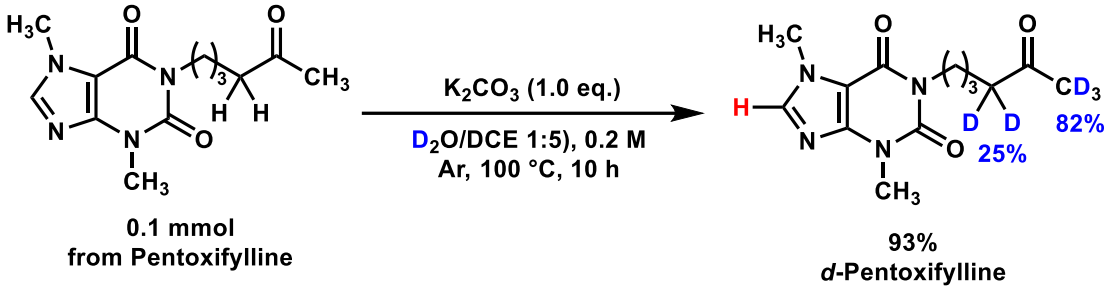
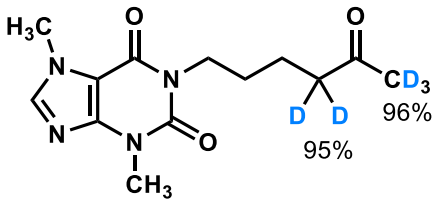


Figure S6. Deuteration with 1.0 equiv. K_2CO_3

Reactions were performed with on a scale of 0.1 mmol Pentoxifylline in presence of 1.0 eq. or 0.1eq. K_2CO_3 in 0.2 mL D_2O (55 equiv.) and 1.0 mL DCE under Ar atmosphere at 100 °C for 10 h. Yield of deuteration was based on hydrogen highlighted in red. All of yields were isolated yields.

6. Characterization Data of Products

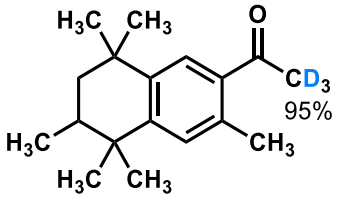
3,7-dimethyl-1-(5-oxohexyl-4,4,6,6,6-d_5)-3,7-dihydro-1H-purine-2,6-dione (2)



TLC: R*f* = 0.30 (silica gel, PE/EA, 2:1), (25mg, 89% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 3.95 (d, *J* = 7.6 Hz, 5H), 3.52 (d, *J* = 0.7 Hz, 3H), 2.06 (p, *J* = 2.1 Hz, 0.10H), 1.99 (s, 0.12H), 1.68 – 1.57 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.17, 155.31, 151.51, 148.80, 141.54, 107.69, 40.86, 33.67, 29.75, 27.44, 20.89, 14.28, 5.95.

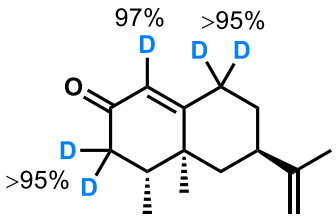
1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-one-2,2,2-d_3 (3)



TLC: R*f* = 0.35 (silica gel, PE/EA, 2:1), (25.3mg, 97% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.22 (s, 1H), 2.56 (dt, *J* = 3.7, 1.8 Hz, 0.15H), 2.54 (s, 3H), 1.91 (dqd, *J* = 13.4, 6.8, 2.6 Hz, 1H), 1.72 – 1.61 (m, 1H), 1.43 (dd, *J* = 13.5, 2.7 Hz, 1H), 1.35 (s, 6H), 1.30 (s, 3H), 1.10 (s, 3H), 1.02 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.42, 150.17, 142.21, 135.34, 135.04, 130.62, 128.22, 55.46, 43.44, 37.90, 34.43, 34.03, 32.45, 31.96, 28.33, 24.70, 21.57, 16.79.

(4*R*,4a*S*,6*R*)-4,4a-dimethyl-6-(prop-1-en-2-yl)-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one-1,3,3,8,8-d_5 (4)



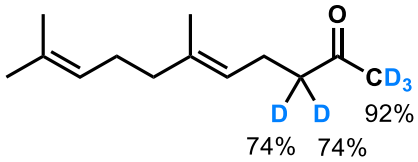
TLC: R*f* = 0.50 (silica gel, PE/EA, 2:1), (18.5mg, 83% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 0.03H), 4.76 – 4.68 (m, 2H), 2.38 – 2.22 (m, 1H), 2.22 – 2.19 (m, 0.05H), 2.01 – 1.84 (m, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.38 – 1.28 (m, 1H), 1.11 (d, *J* = 6.0 Hz, 4H), 0.96 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.99, 169.63, 148.24, 127.03, 108.36, 43.02, 39.40, 38.34, 30.71, 30.53, 21.77, 19.94, 15.96, 13.98, 13.25.

HRMS (ESI-TOF) Calcd for $C_{15}H_{19}D_3O$: $[M+Na]^+$ 246.1876 Found: m/z 246.1874.

(*E*)-6,10-dimethylundeca-5,9-dien-2-one-1,1,1,3,3-*d*$_5$ (5)



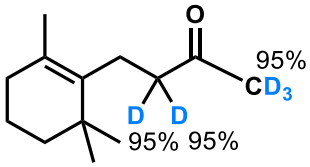
TLC: R*f* = 0.30 (silica gel, PE/EA, 10:1), (12.9mg, 65% yield), transparent liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (t, *J* = 7.4 Hz, 2H), 2.43 (tdd, *J* = 7.4, 5.1, 2.5 Hz, 0.52H), 2.25 (q, *J* = 5.6, 4.9 Hz, 2H), 2.19 – 2.12 (m, 0.26H), 2.09 – 1.89 (m, 4H), 1.75 – 1.53 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.59 (d, *J* = 11.5 Hz), 130.85, 130.59, 123.30 (d, *J* = 2.4 Hz), 121.63, 38.77, 30.99, 25.73, 25.62, 24.85 (d, *J* = 2.9 Hz), 22.50, 16.81 (d, *J* = 4.1 Hz), 15.11.

HRMS (ESI-TOF) Calcd for $C_{13}H_{17}D_5O$: $[M+K]^+$ 238.1616. Found: m/z 238.1630.

4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-one-1,1,1,3,3-*d*$_5$ (6)



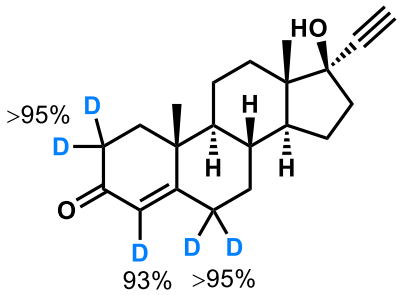
TLC: R*f* = 0.34 (silica gel, PE/EA,10:1), (18.7mg, 94% yield), light liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.47 (ddt, *J* = 9.6, 6.6, 2.5 Hz, 0.10H), 2.24 (s, 2H), 2.11 (p, *J* = 2.3 Hz, 0.15H), 1.90 (t, *J* = 6.4 Hz, 2H), 1.61 – 1.52 (m, 5H), 1.44 – 1.38 (m, 2H), 0.98 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.49, 135.91, 127.81, 89.65, 77.30, 77.05, 76.79, 43.82, 39.72, 35.03, 32.73, 29.09, 28.43, 22.15, 19.73, 19.45.

HRMS (ESI-TOF) Calcd for $C_{13}H_{17}D_5O$: $[M+H]^+$ 200.2057. Found: m/z 200.2058.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-ethynyl-17-hydroxy-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[*a*]phenanthren-3-one-2,2,4,6,6-d_5 (7)



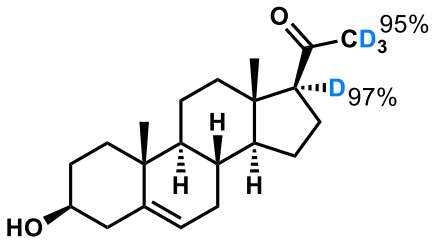
TLC: R*f* = 0.25 (silica gel, EA), (25.6mg, 81% yield), white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (s, 0.07H), 2.58 (s, 1H), 2.30 (ddd, *J* = 13.8, 9.7, 5.5 Hz, 1H), 2.15 – 1.95 (m, 2H), 1.93 (s, 1H), 1.84 (dd, *J* = 12.8, 3.5 Hz, 1H), 1.80 – 1.63 (m, 5H), 1.57 – 1.30 (m, 4H), 1.20 (s, 3H), 1.13 – 0.95 (m, 2H), 0.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.74, 171.07, 87.21, 83.20, 81.20, 79.68, 74.22, 53.40, 49.87, 46.67, 38.85, 38.54, 36.17, 35.53, 32.42, 31.29, 23.06, 20.72, 17.44, 12.71, 1.37.

HRMS (ESI-TOF) Calcd for $C_{21}H_{23}D_5O_2$: $[M+Na]^+$ 340.2295. Found: m/z 340.2294.

1-((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl-17-d)ethan-1-one-2,2,2-d_3 (8)



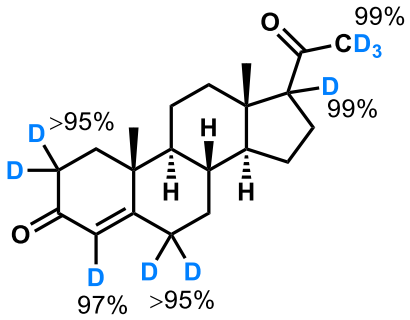
TLC: R*f* = 0.23 (silica gel, EA), (20.8mg, 65% yield), white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (dt, *J* = 5.0, 2.0 Hz, 1H), 3.52 (tt, *J* = 11.2, 4.6 Hz, 1H), 2.52 (t, *J* = 8.9 Hz, 0.03H), 2.34 – 2.13 (m, 3H), 2.08 (t, *J* = 2.2 Hz, 0.14H), 2.06 – 1.94 (m, 2H), 1.94 – 1.81 (m, 2H), 1.76 – 1.37 (m, 9H), 1.29 – 1.04 (m, 3H), 0.99 (d, *J* = 7.1 Hz, 4H), 0.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.92, 140.76, 121.44, 77.30, 77.05, 76.79, 71.72, 56.92, 50.55, 49.98, 49.48, 45.43, 43.98, 42.25, 38.79, 37.26, 36.53, 35.08, 32.02, 31.85, 31.78, 31.61, 24.52, 22.67, 21.09, 19.42, 13.26.

HRMS (ESI-TOF) Calcd for $C_{21}H_{28}D_4O_2$: $[M+K]^+$ 359.2285. Found: m/z 359.2285.

(8*S*,9*S*,10*R*,13*S*,14*S*)-17-(acetyl-d_3)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one-2,2,4,6,6,17-d_6 (9)



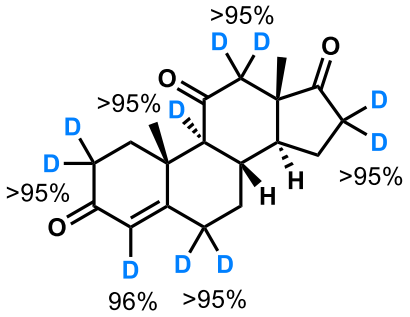
TLC: R*f* = 0.20 (silica ge, EA), (31mg, 96% yield), yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (t, *J* = 9.0 Hz, 0.03H), 2.44 – 2.10 (m, 1H), 2.10 – 1.93 (m, 2H), 1.82 (dd, *J* = 12.8, 3.7 Hz, 1H), 1.77 – 1.37 (m, 7H), 1.33 – 1.18 (m, 2H), 1.16 (s, 3H), 1.11 – 0.90 (m, 2H), 0.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz,) δ 209.76, 199.78, 171.05, 56.10, 53.72, 53.13, 49.81, 45.48, 43.97, 38.67, 35.79, 35.58 (d, *J* = 4.5 Hz), 34.96, 31.78, 25.92, 24.28, 22.74, 21.08, 20.73, 17.43, 13.43.

HRMS (ESI-TOF) Calcd for $C_{21}H_{21}D_9O_2$: $[M+H]^+$ 324.2884. Found: m/z 324.2881.

(8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-6,7,8,9,10,12,13,14,15,16-decahydro-1*H*-cyclopenta[*a*]phenanthrene-3,11,17(2*H*)-trione-2,2,4,6,6,16,16-d_7 (10)



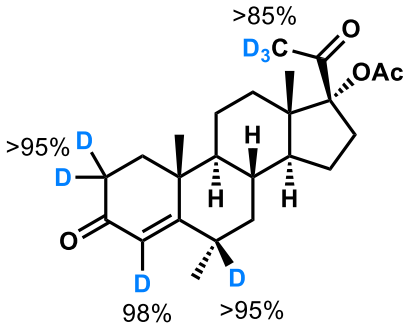
TLC: R*f* = 0.23 (silica gel, EA), (28.5mg, 94% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 0.02H), 2.71 (dd, *J* = 13.6, 1.1 Hz, 1H), 2.44 (d, *J* = 1.7 Hz, 1H), 2.30 (dd, *J* = 12.9, 0.9 Hz, 0.32H), 2.17 – 1.96 (m, 3H), 1.87 (ddd, *J* = 12.2, 10.9, 5.8 Hz, 1H), 1.74 – 1.55 (m, 2H), 1.40 (s, 3H), 1.27 (t, *J* = 12.4 Hz, 1H), 0.85 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.10, 207.85, 199.76, 189.72, 167.92, 114.08, 100.56, 63.39, 50.50, 50.45, 49.86, 38.19, 36.25, 34.55, 30.78, 21.44, 17.34, 14.67, 8.59.

HRMS (ESI-TOF) Calcd for $C_{19}H_{17}D_7O_3$: $[M+H]^+$ 308.2238. Found: m/z 308.2237.

(6*S*,8*R*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-(acetyl-d_3)-6,10,13-trimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl-2,2,4,6-d_4 acetate (11)



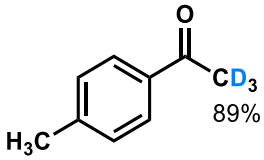
TLC: R*f* = 0.19 (silica gel, EA), (36.6mg, 93% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (s, 0.02H), 2.90 (ddd, *J* = 17.2, 11.5, 5.9 Hz, 1H), 2.51 – 2.29 (m, 0.04H), 2.08 (s, 3H), 2.02 (s, 0.45H), 2.00 – 1.89 (m, 2H), 1.82 (dd, *J* = 12.8, 2.6 Hz, 1H), 1.79 – 1.61 (m, 6H), 1.58 – 1.49 (m, 1H), 1.49 – 1.18 (m, 2H), 1.16 (s, 3H), 1.04 (s, 3H), 1.02 – 0.95 (m, 1H), 0.91 – 0.78 (m, 1H), 0.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.35, 200.06, 174.06, 170.86, 96.77, 53.41, 52.78, 51.60, 51.01, 46.84, 40.84, 38.88, 37.71, 35.82, 35.49, 33.78, 33.41, 31.10, 30.38, 23.87, 21.35, 20.87, 18.34, 14.50.

HRMS (ESI-TOF) Calcd for $C_{24}H_{27}D_7O_4$: $[M+H]^+$ 394.2969. Found: m/z 394.2968.

1-(*p*-tolyl)ethan-1-one-2,2,2-d_3 (12)

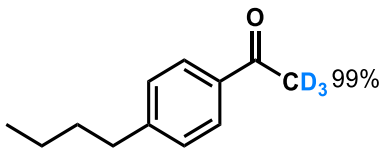


TLC: R*f* = 0.44 (silica gel, PE/EA, 10:1), (12.7mg, 93% yield), yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 2.78 – 2.51 (m, 0.33H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.96, 143.87, 134.73, 129.23, 128.42, 28.25, 21.63.

1-(4-butylphenyl)ethan-1-one-2,2,2-d_3 (13)



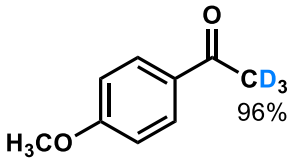
TLC: R*f* = 0.30(silica gel, PE/EA, 10:1), (12.5mg, 70% yield), yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.21 (m, 2H), 2.77 – 2.64 (m, 2H), 2.59 (s,0.01H), 1.74 – 1.55 (m, 2H), 1.36 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.12, 148.86, 134.89, 128.64, 128.48, 35.71, 33.29, 25.87, 22.35, 13.94.

HRMS (ESI-TOF) Calcd for $C_{12}H_{13}D_3O$: $[M+H]^+$ 180.1462. Found: m/z 180.1463.

1-(4-methoxyphenyl-3,5-*d*$_2$)ethan-1-one-2,2,2-*d*$_3$ (14)

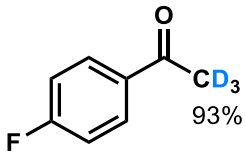


TLC: R*f* = 0.40 (silica gel, PE/EA, 2:1), (14.1mg, 91% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 6.98 – 6.90 (m, 2H), 3.87 (s, 3H), 2.53 (p, *J* = 2.2 Hz, 0.13H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.05, 164.24, 130.69, 130.46, 113.79, 55.57, 32.06.

1-(4-fluorophenyl)ethan-1-one-2,2,2-*d*$_3$ (15)



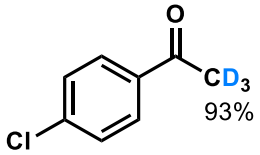
TLC: R*f* = 0.46 (silica gel, PE/EA, 2:1), (13.4mg, 95% yield), yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 7.80 (m, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 2.58 (p, *J* = 2.2 Hz, 0.21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.45, 165.77 (d, *J* = 254.6 Hz), 133.60 (d, *J* = 3.0 Hz), 130.92 (d, *J* = 9.4 Hz), 115.65 (d, *J* = 21.9 Hz), 22.35.

^{19}F NMR (377 MHz, $CDCl_3$) δ -105.29, -105.31, -105.32, -105.33, -105.34, -105.35, -105.37, -105.39.

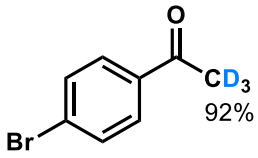
1-(4-chlorophenyl)ethan-1-one-2,2,2-*d*$_3$ (16)



TLC: R*f* = 0.45 (silica gel, PE/EA, 2:1), (15.2mg, 97% yield), yellow solid.

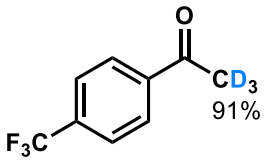
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.48 – 7.42 (m, 2H), 2.57 (dq, *J* = 4.5, 2.1 Hz, 0.21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.52, 139.56, 136.40, 129.70, 128.21, 28.25.

1-(4-bromophenyl)ethan-1-one-2,2,2-*d*$_3$ (17)



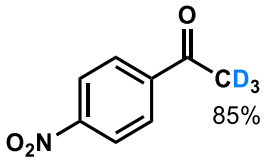
TLC: R*f* = 0.41 (silica gel, PE/EA, 2:1), (19mg, 94% yield), yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.65 – 7.59 (m, 2H), 2.62 – 2.54 (m, 0.24H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.56, 137.07, 131.89, 129.32, 127.48, 26.48.

1-(4-(trifluoromethyl)phenyl)ethan-1-one-2,2,2-*d*$_3$ (18)



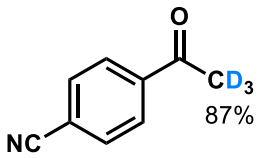
TLC: R*f* = 0.39 (silica gel, PE/EA, 2:1), (17.4mg, 91% yield), yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dp, *J* = 7.6, 0.8 Hz, 2H), 7.75 – 7.68 (m, 2H), 2.64 – 2.57 (m, 0.27H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.21, 139.74, 134.50 (q, *J* = 32.7 Hz), 128.69, 125.75 (q, *J* = 3.9 Hz), 123.67 (q, *J* = 271.5 Hz), 27.39.
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.80.

1-(4-nitrophenyl)ethan-1-one-2,2,2-*d*$_3$ (19)



TLC: R*f* = 0.44 (silica gel, PE/EA, 2:1), (15.6mg, 93% yield), yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.29 (m, 2H), 8.16 – 8.09 (m, 2H), 2.71 – 2.64 (m, 0.45H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.40, 150.36, 143.41, 130.43, 124.52, 27.59.

4-(acetyl-*d*$_3$)benzonitrile (20)

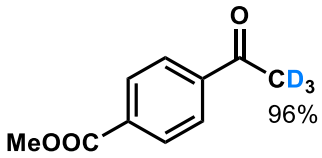


TLC: R*f* = 0.39 (silica gel, PE/EA, 2:1), 13mg, 89% yield), yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.68 (m, 1H), 2.63 (dp, *J* = 6.7, 2.2 Hz, 0.39H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.63, 139.91, 132.51, 128.68, 117.91, 116.41, 26.48.

methyl 4-(acetyl-*d*$_3$)benzoate (21)

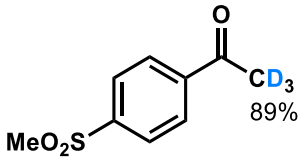


TLC: R*f* = 0.33 (silica gel, PE/EA, 2:1), (16.7mg, 92% yield), white wolid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 3.97 (d, *J* = 0.9 Hz, 3H), 2.63 (t, *J* = 2.4 Hz, 0.12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.87, 166.65, 140.23, 135.00, 129.82, 128.18, 53.34, 27.15.

1-(4-(methylsulfonyl)phenyl)ethan-1-one-2,2,2-*d*$_3$ (22)

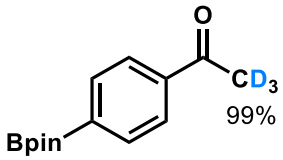


TLC: R*f* = 0.34 (silica gel, PE/EA, 2:1), (18.9mg, 94% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 8.07 – 7.99 (m, 2H), 3.06 (d, *J* = 0.5 Hz, 3H), 2.66 – 2.58 (m, 0.34H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.21, 144.27, 140.99, 129.22, 127.89, 44.39, 26.50.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one-2,2,2-*d*$_3$ (23)



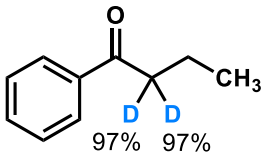
TLC: R*f* = 0.31 (silica gel, PE/EA, 10:1), 18.6mg, 87% yield), white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (q, *J* = 8.0 Hz, 4H), 2.61 (dp, *J* = 4.5, 3.2, 2.2 Hz, 0.06H), 1.38 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.83, 138.99, 134.91, 129.26, 127.79, 127.26, 84.21, 37.33, 24.88.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.18.

1-phenylbutan-1-one-2,2-*d*$_2$ (24)

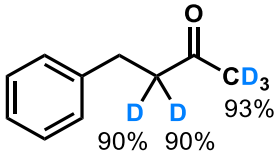


TLC: R*f* = 0.40 (silica gel, PE/EA, 10:1), (14mg, 95% yield), yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 2.94 (t, *J* = 7.4, 2.6 Hz, 0.06H), 1.78 (q, *J* = 7.4 Hz, 2H), 1.03 (td, *J* = 7.4, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.56, 137.10, 132.86, 128.54, 128.04, 77.35, 77.04, 76.72, 39.82, 17.71, 13.85.

4-phenylbutan-2-one-1,1,1,3,3-*d*$_5$ (25)

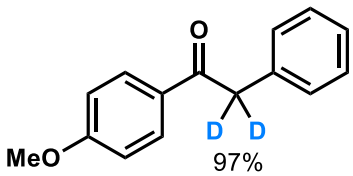


TLC: R*f* = 0.35 (silica gel, PE/EA, 10:1), (14mg, 89% yield), yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 2H), 7.16 (td, *J* = 7.4, 1.2 Hz, 3H), 2.85 (s, 2H), 2.75 – 2.66 (m, 0.2 H), 2.11 – 2.04 (m, 0.21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.99, 141.03, 128.56, 128.34, 126.17, 44.87, 37.49, 29.66.

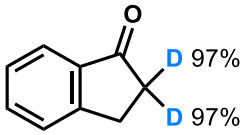
1-(4-methoxyphenyl)-2-phenylethan-1-one-2,2-*d*$_2$ (26)



TLC: R*f* = 0.25(silica gel, PE/EA, 10:1), (21mg, 92% yield), yellow liquid.

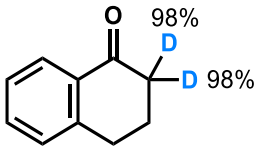
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.84 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 6.96 – 6.90 (m, 2H), 4.21 (t, *J* = 2.2 Hz, 0.06H), 3.85 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.39, 163.54, 134.92, 131.00, 129.61, 129.37, 128.68, 126.82, 113.82, 55.51, 44.83.
HRMS (ESI-TOF) Calcd for $C_{15}H_{12}D_2O_2$: $[M+H]^+$ 229.1192. Found: m/z 229.1192.

2,3-dihydro-1*H*-inden-1-one-2,2-*d*$_2$ (27)



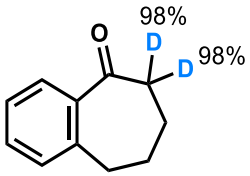
TLC: R*f* = 0.39 (silica gel, PE/EA, 10:1), (7.5mg, 55% yield), yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 3.15 (s, 2H), 2.75 – 2.65 (m, 0.05H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.33, 155.29, 137.13, 134.66, 127.32, 126.75, 123.76, 89.66, 25.66.
HRMS (ESI-TOF) Calcd for $C_9H_6D_2O$: $[M+K]^+$ 173.0333. Found: m/z 173.0323.

3,4-dihydronaphthalen-1(2H)-one-2,2-*d*$_2$ (28)



TLC: R*f* = 0.30 (silica gel, PE/EA, 10:1), (10.3mg, 70% yield), yellow liquid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.64 (ddt, *J* = 9.0, 5.7, 2.5 Hz, 0.04H), 2.13 (t, *J* = 6.1 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.63, 144.56, 133.45, 132.62, 128.81, 127.17, 126.66, 38.51, 29.67, 23.12.
HRMS (ESI-TOF) Calcd for $C_{11}H_{10}O_2$: $[M+H]^+$ 149.0930. Found: m/z 149.0930.

6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one-6,6-*d*$_2$ (29)



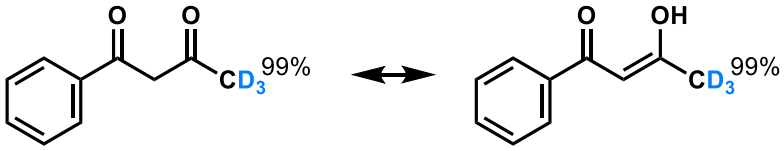
TLC: R*f* = 0.29 (silica gel, PE/EA, 10:1), (15mg, 95% yield), yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 2.97 – 2.90 (m, 2H), 2.72 (ddt, *J* = 9.8, 5.0, 2.1 Hz, 0.04H), 1.89 (pd, *J* = 6.5, 1.0 Hz, 2H), 1.80 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.31, 141.45, 138.82, 132.21, 129.74, 128.58, 126.65, 40.23, 32.57, 25.22, 20.82.

HRMS (ESI-TOF) Calcd for $C_{11}H_{10}D_2O$: $[M+H]^+$ 163.1087. Found: m/z 163.1093.

(*Z*)-3-hydroxy-1-phenylbut-2-en-1-one-4,4,4-*d*$_3$ (30)



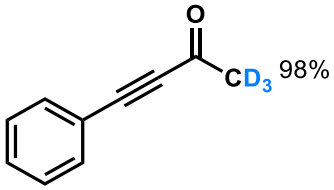
TLC: R*f* = 0.30 (silica gel, PE/EA, 10:1), (10mg, 60% yield), white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 6.19 (s, 1H), 2.21 (s, 0.02H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.71, 183.55, 134.91, 132.34, 128.65, 127.04, 96.75, 25.47.

HRMS (ESI-TOF) Calcd for $C_{10}H_7D_3O_2$: $[M+H]^+$ 166.0942. Found: m/z 166.0941.

4-phenylbut-3-yn-2-one-1,1,1-*d*$_3$ (31)



TLC: R*f* = 0.35 (silica gel, PE/EA, 10:1), (10mg, 66% yield), yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.55 – 7.43 (m, 1H), 7.39 (td, *J* = 7.5, 1.6 Hz, 2H), 2.44 (s, 0.06H).

^{13}C NMR (126 MHz, $CDCl_3$)δ 184.89, 133.10, 130.79, 128.67, 119.90, 90.41, 88.30, 32.05.

HRMS (ESI-TOF) Calcd for $C_{10}H_5D_3O$: $[M+H]^+$ 148.0836. Found: m/z 146.0830.

7. NMR Spectra of Products

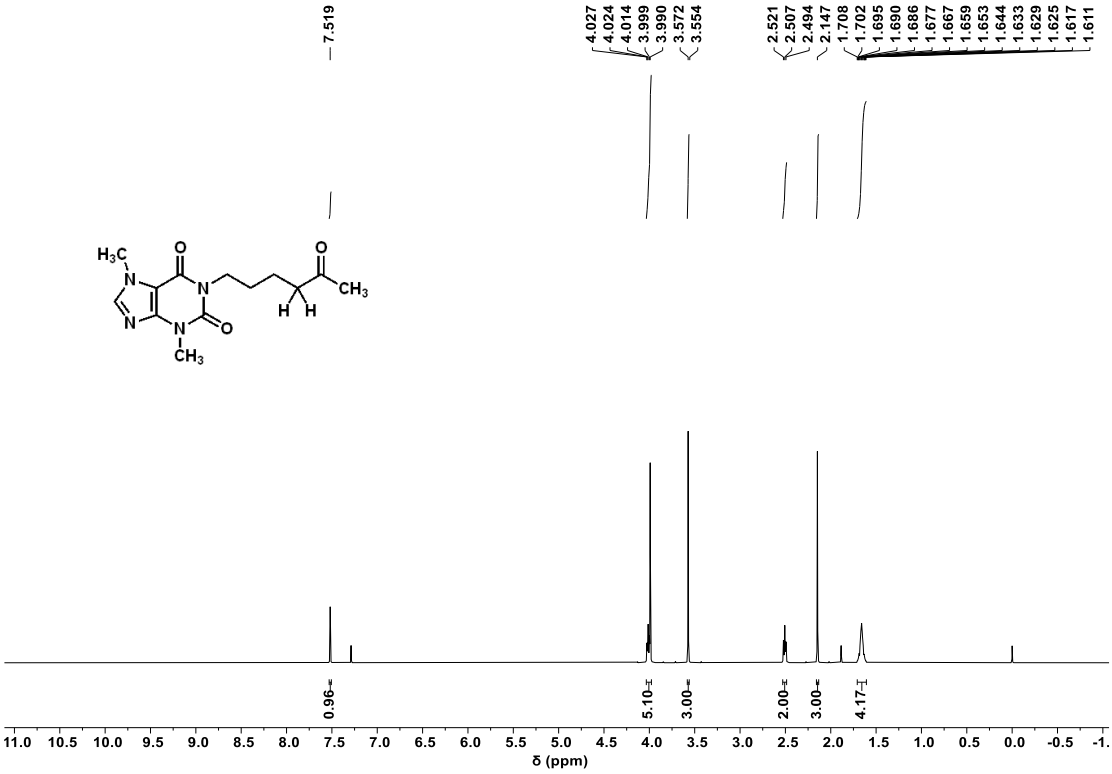


Figure S7. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **1**

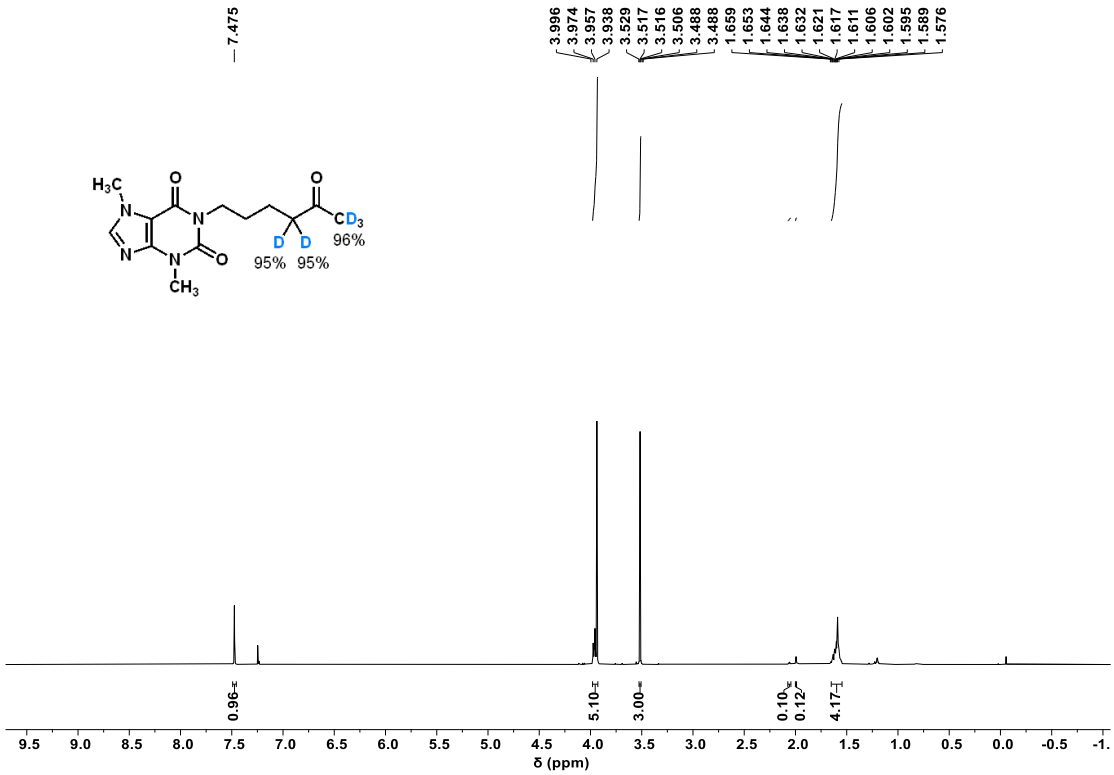


Figure S8. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **2**

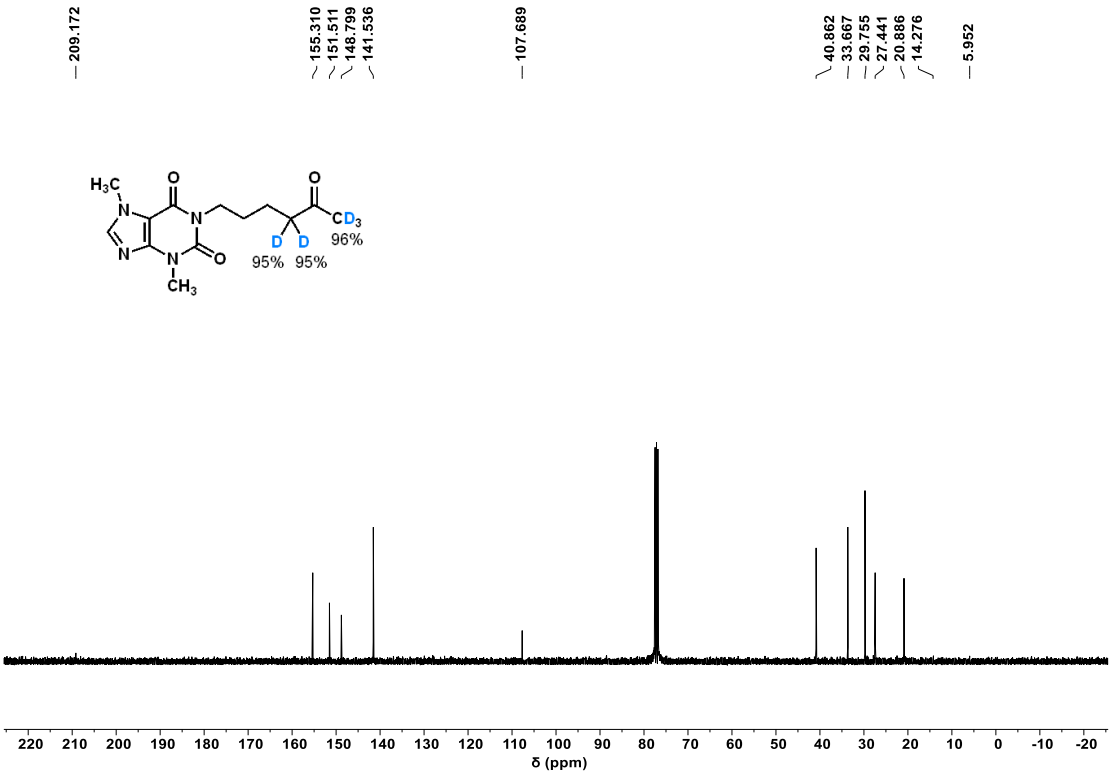


Figure S9. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **2**

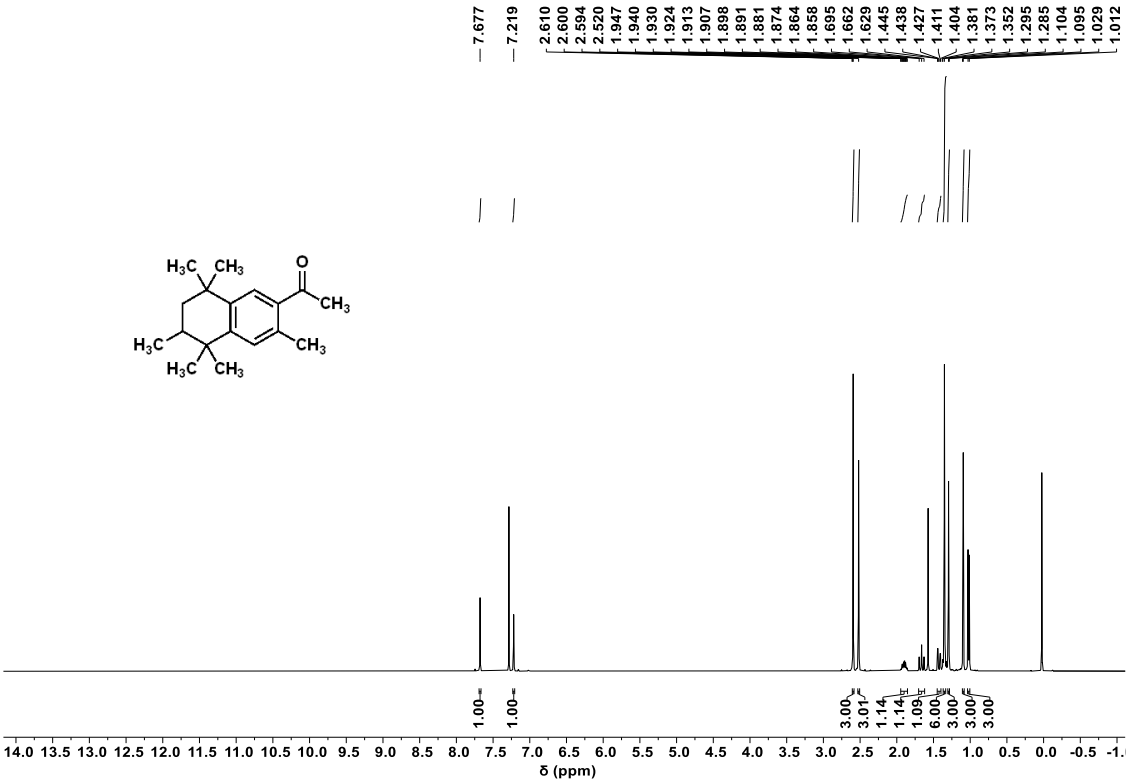


Figure S10. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S3**

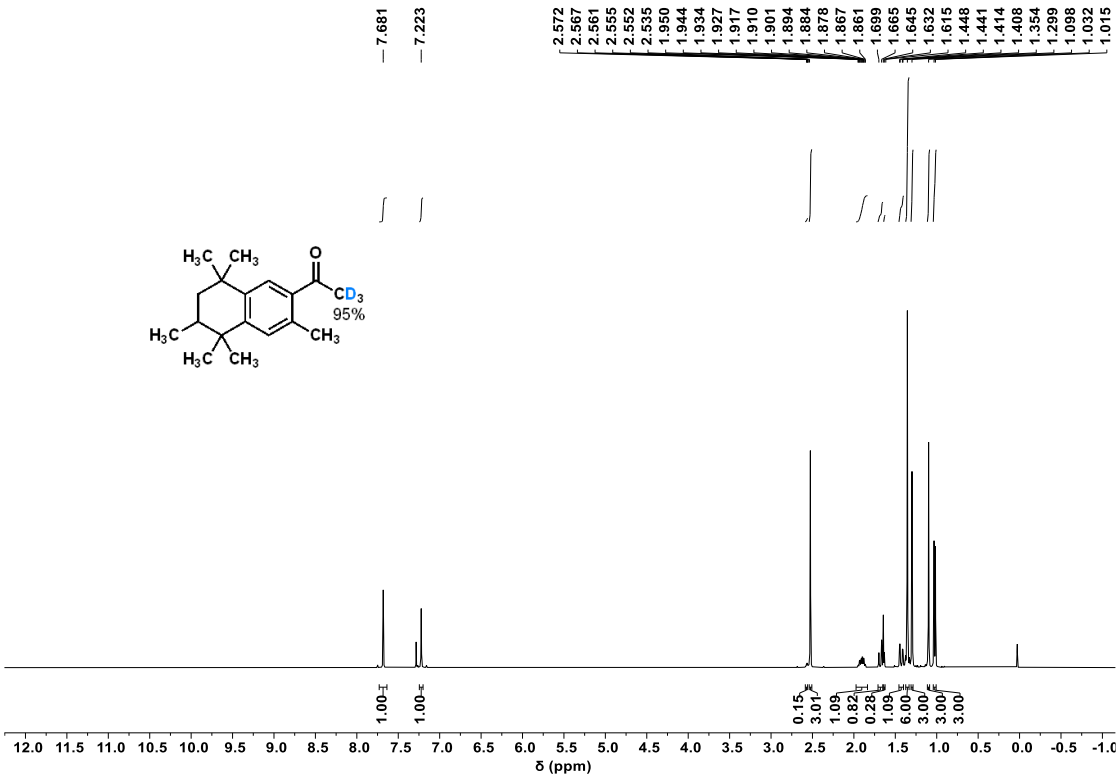


Figure S11. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **3**

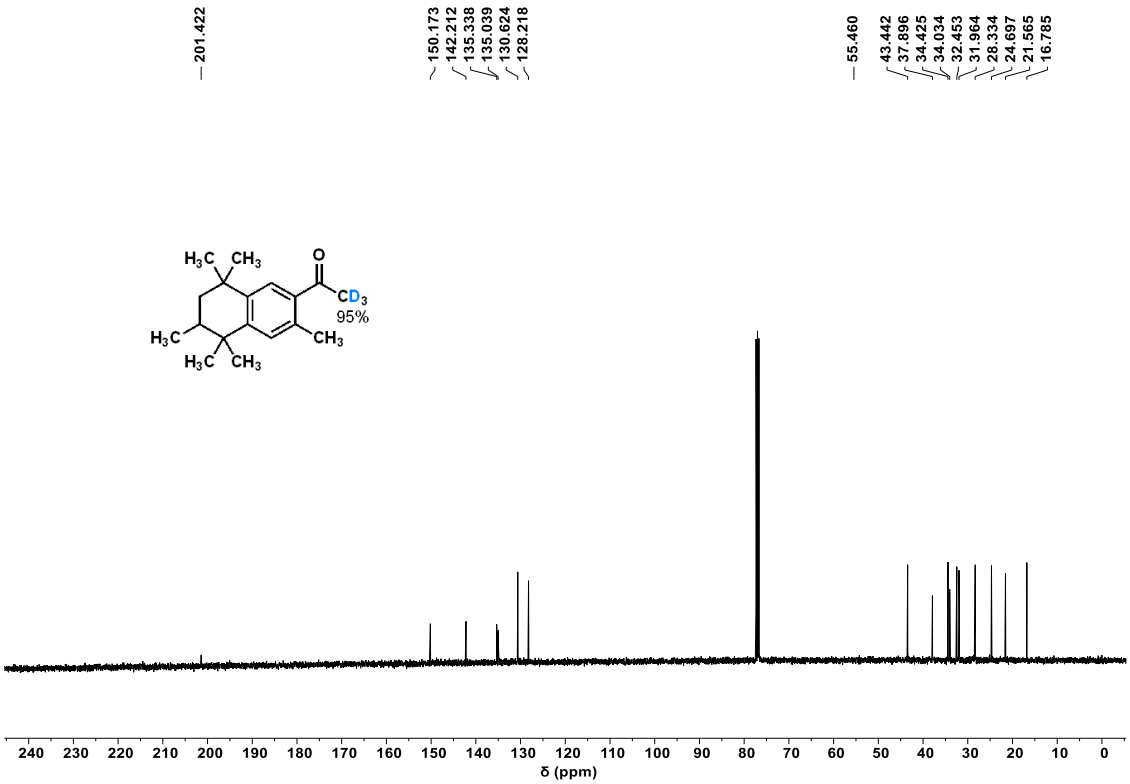


Figure S12. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **3**

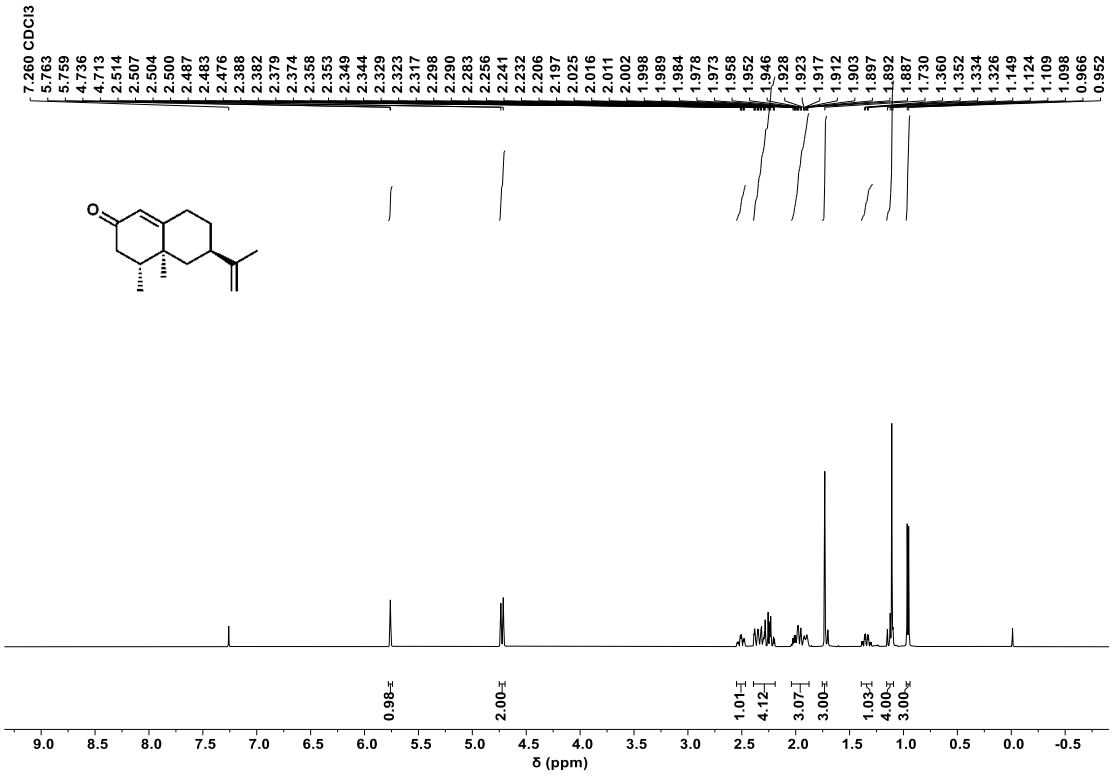


Figure S13. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S4**

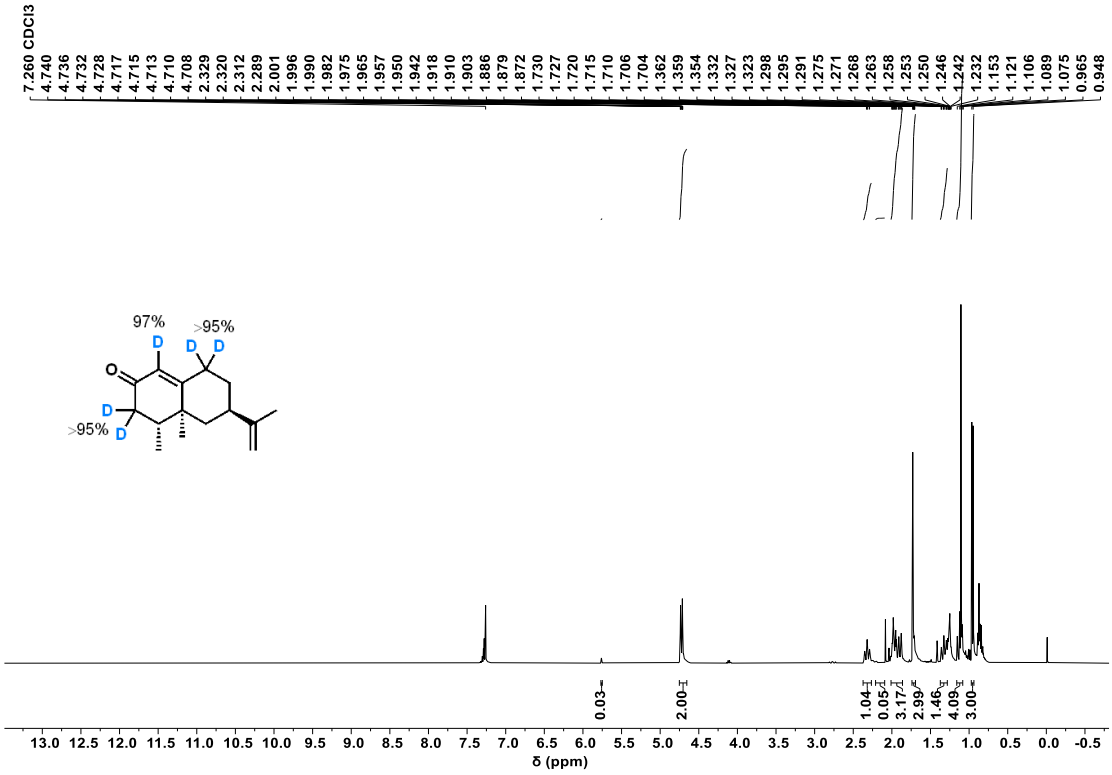


Figure S14. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **4**

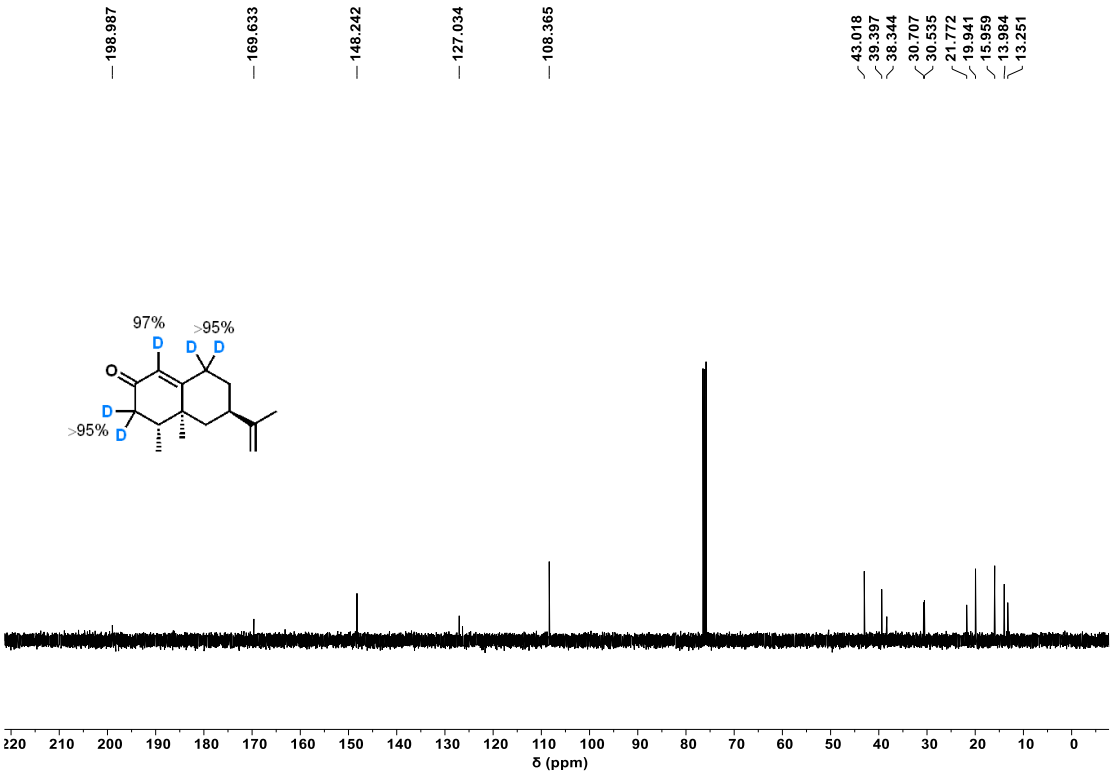


Figure S15. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **4**

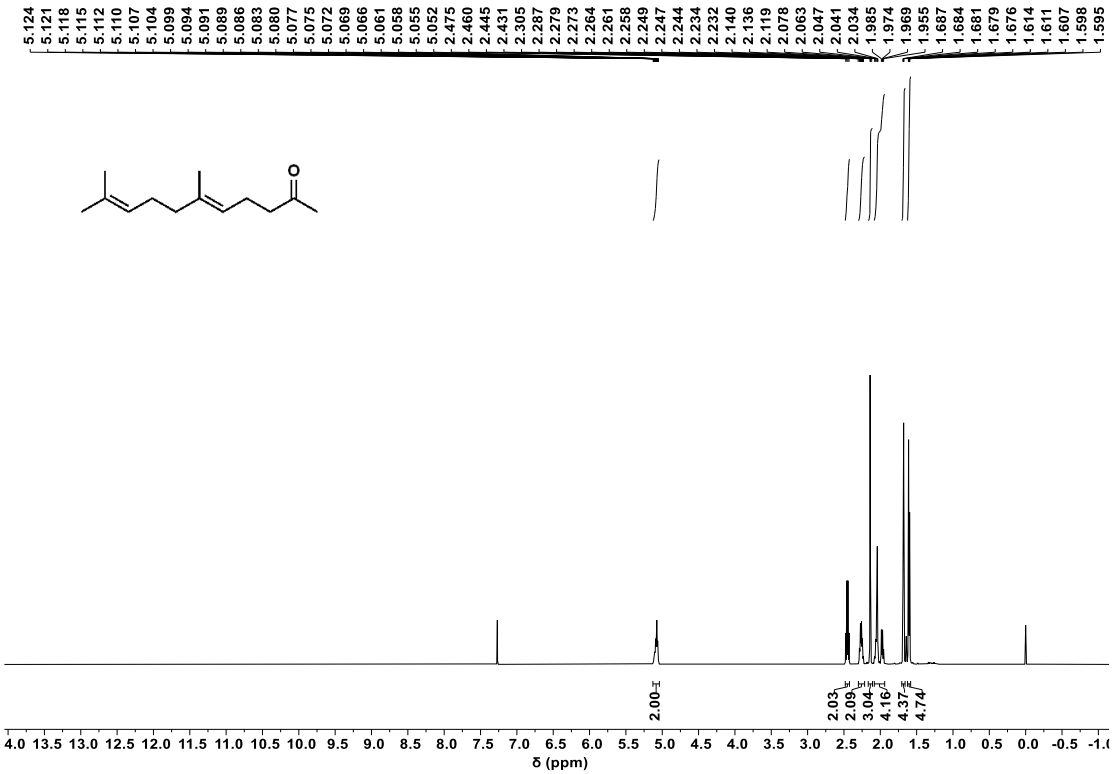


Figure S16. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S5**

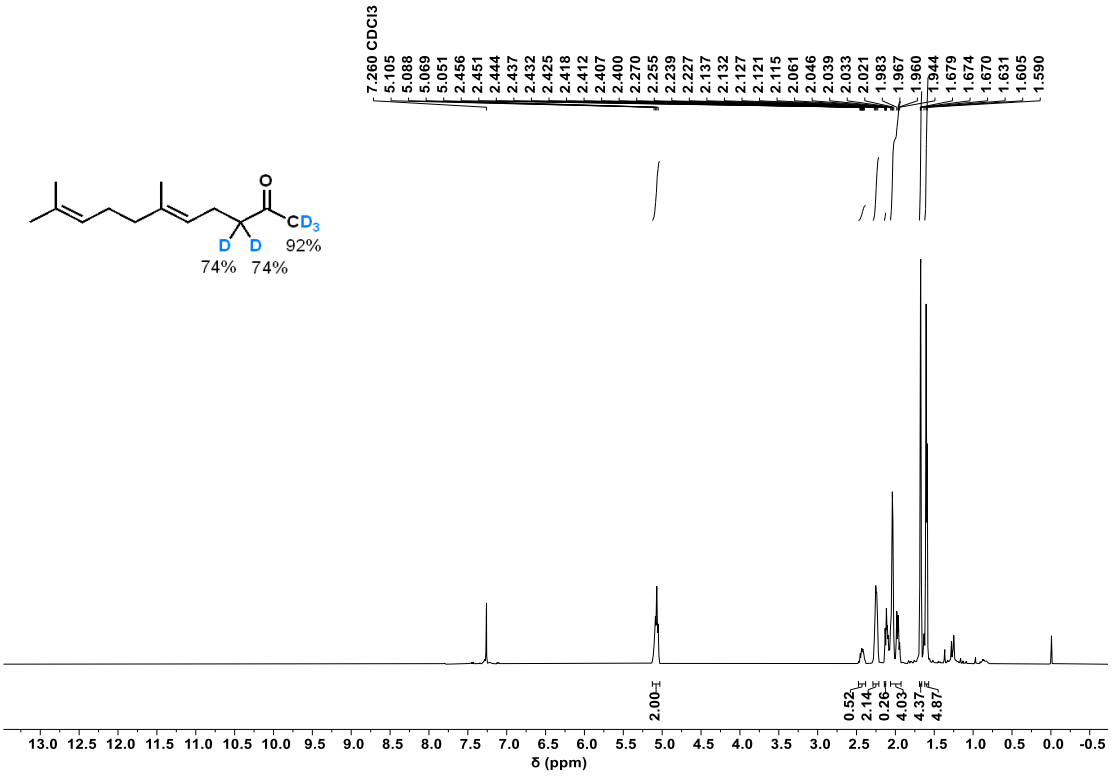


Figure S17. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **5**

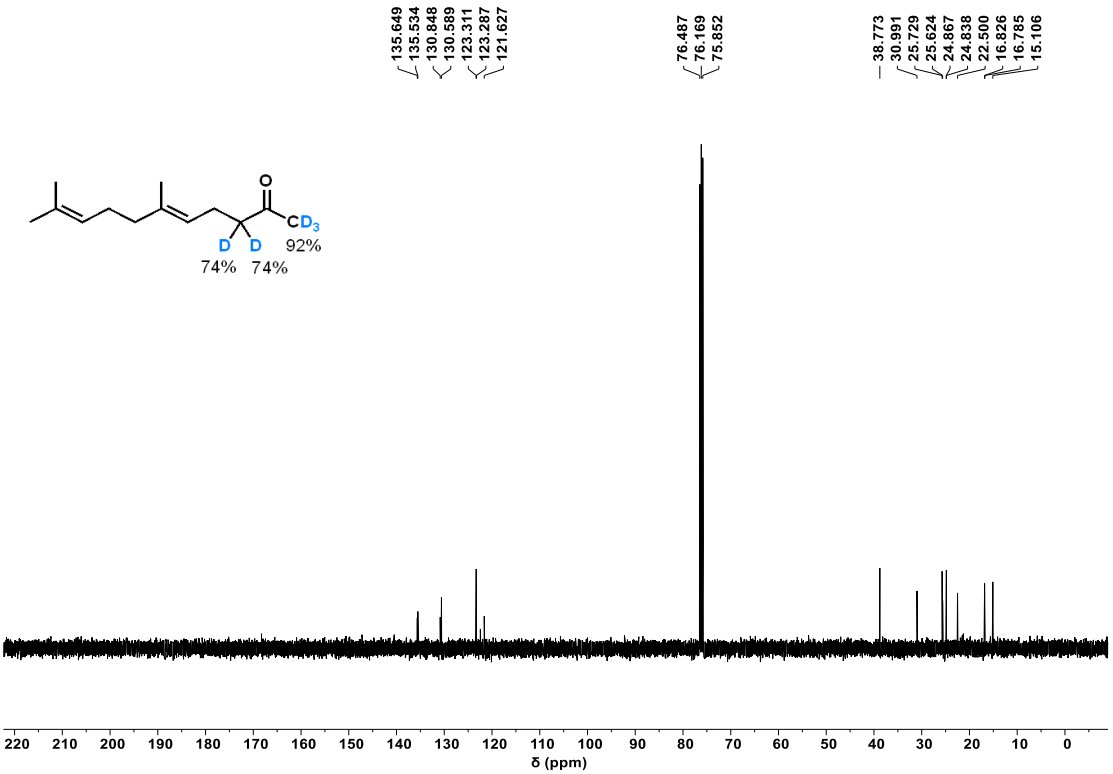


Figure S18. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **5**

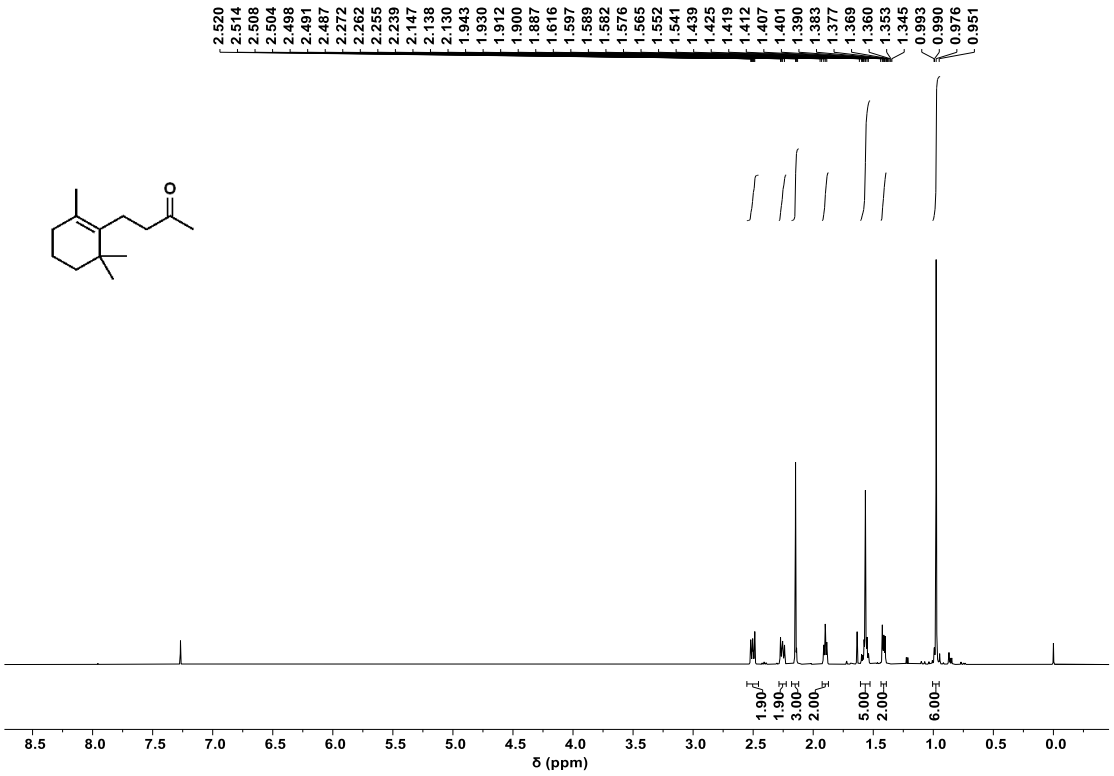


Figure S19. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S6**

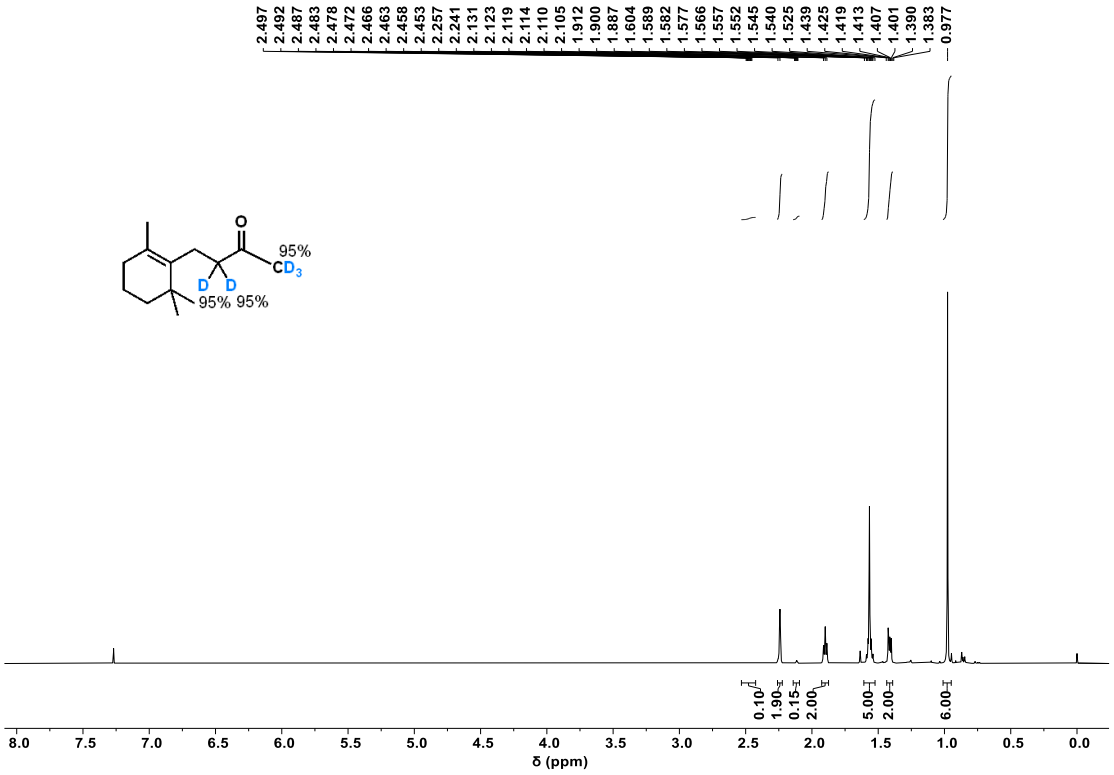


Figure S20. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **6**

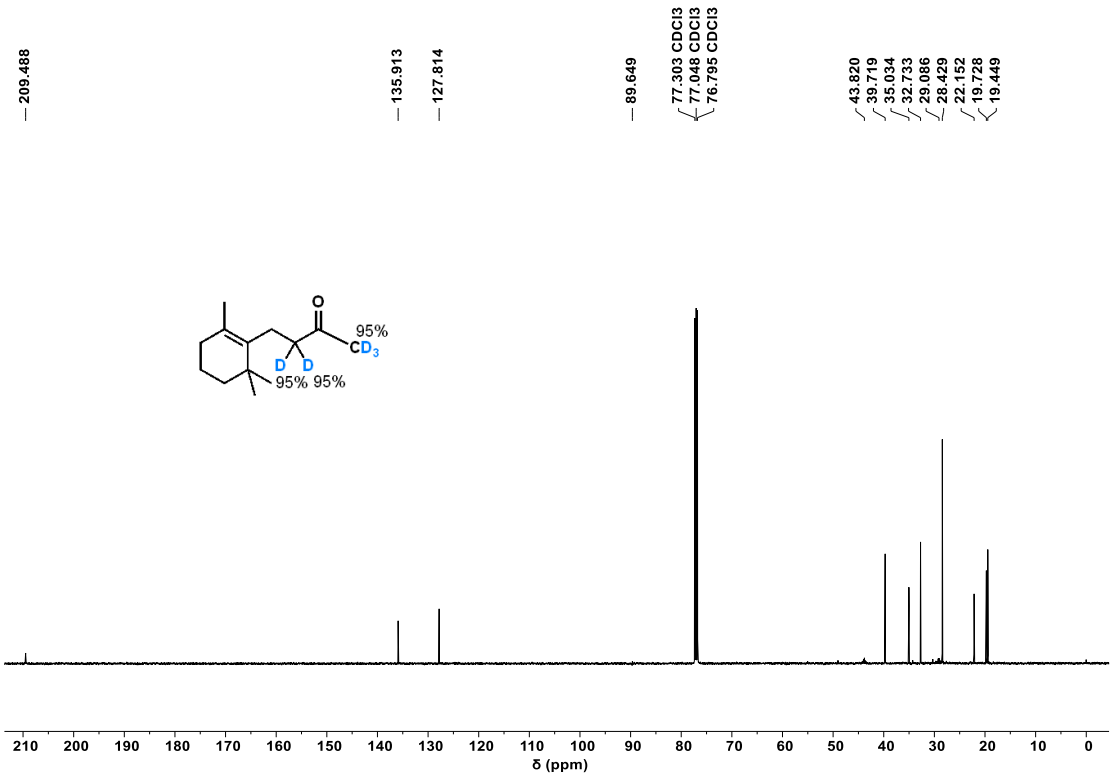


Figure S21. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **6**

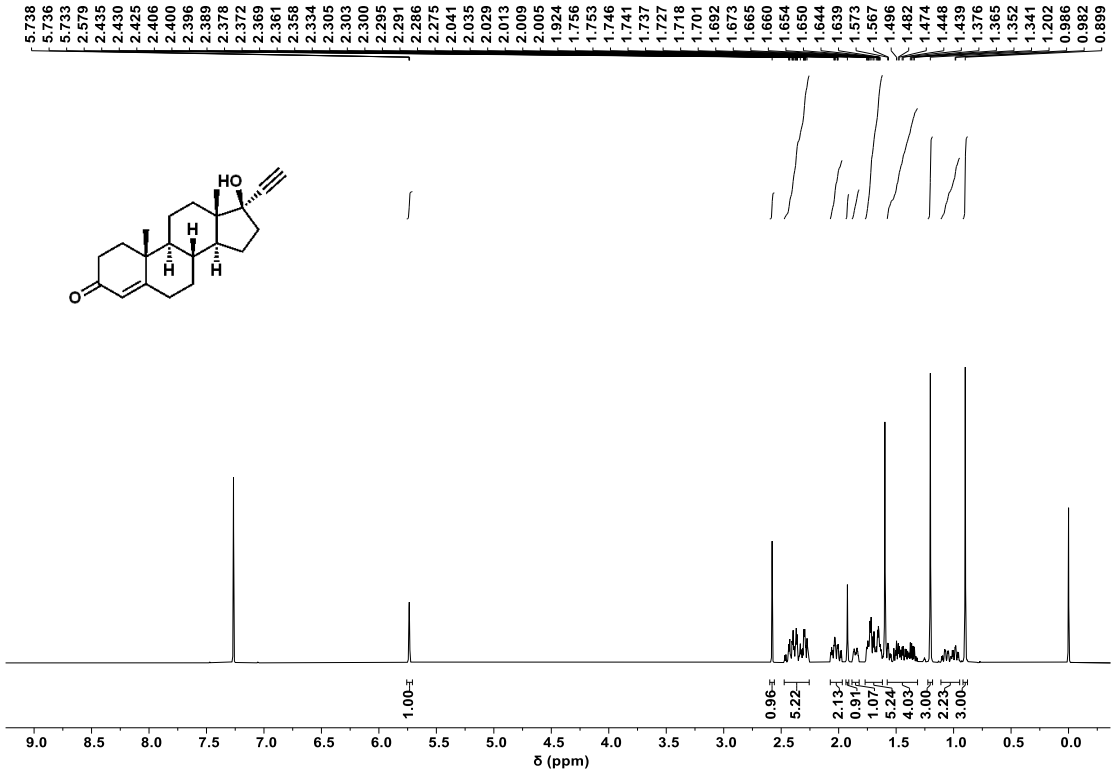


Figure S22. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S7**

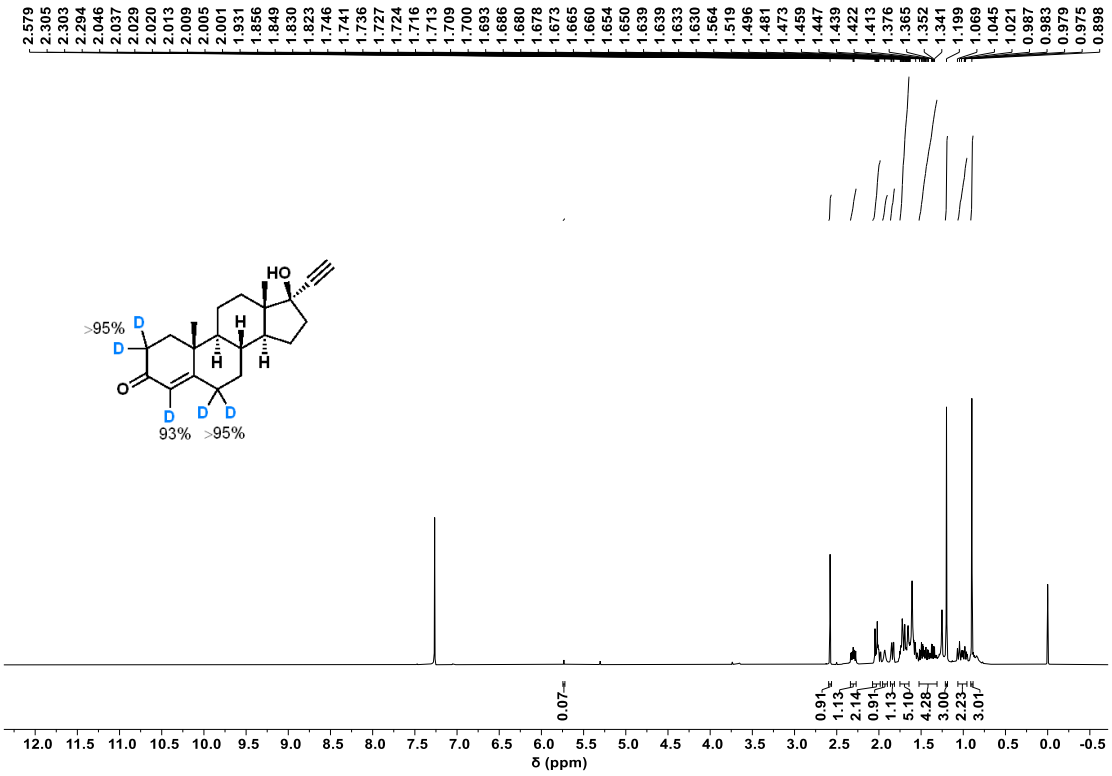


Figure S23. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **7**

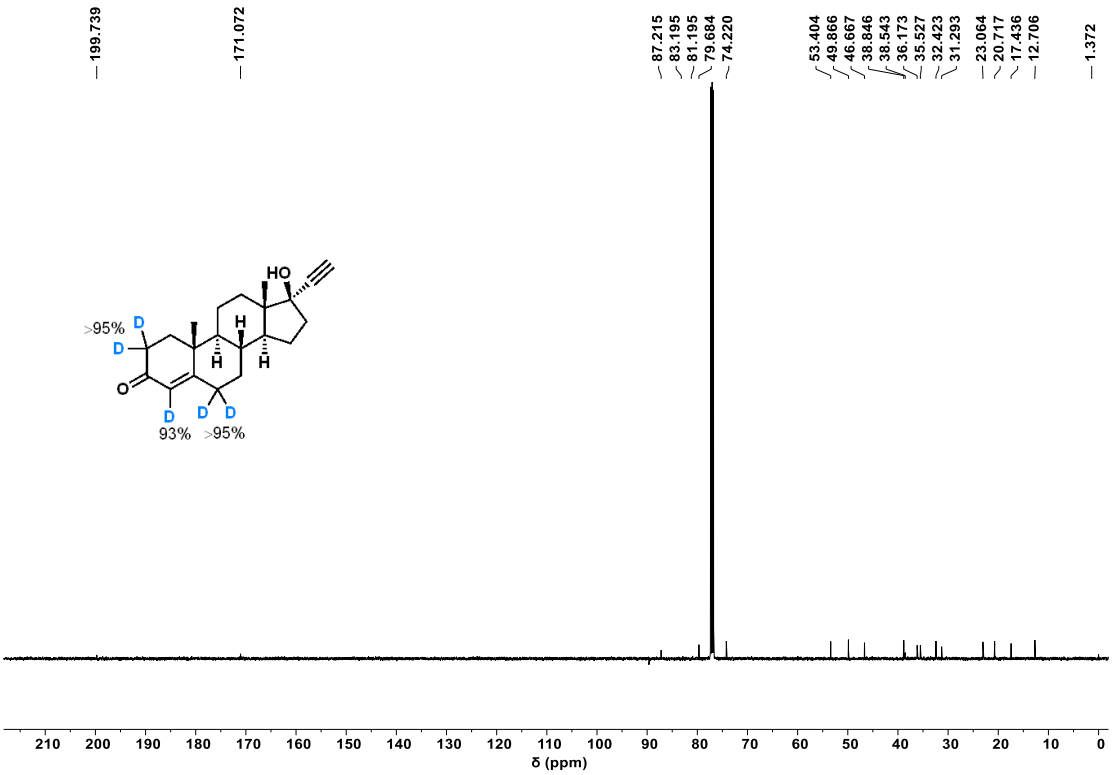


Figure S24. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **7**

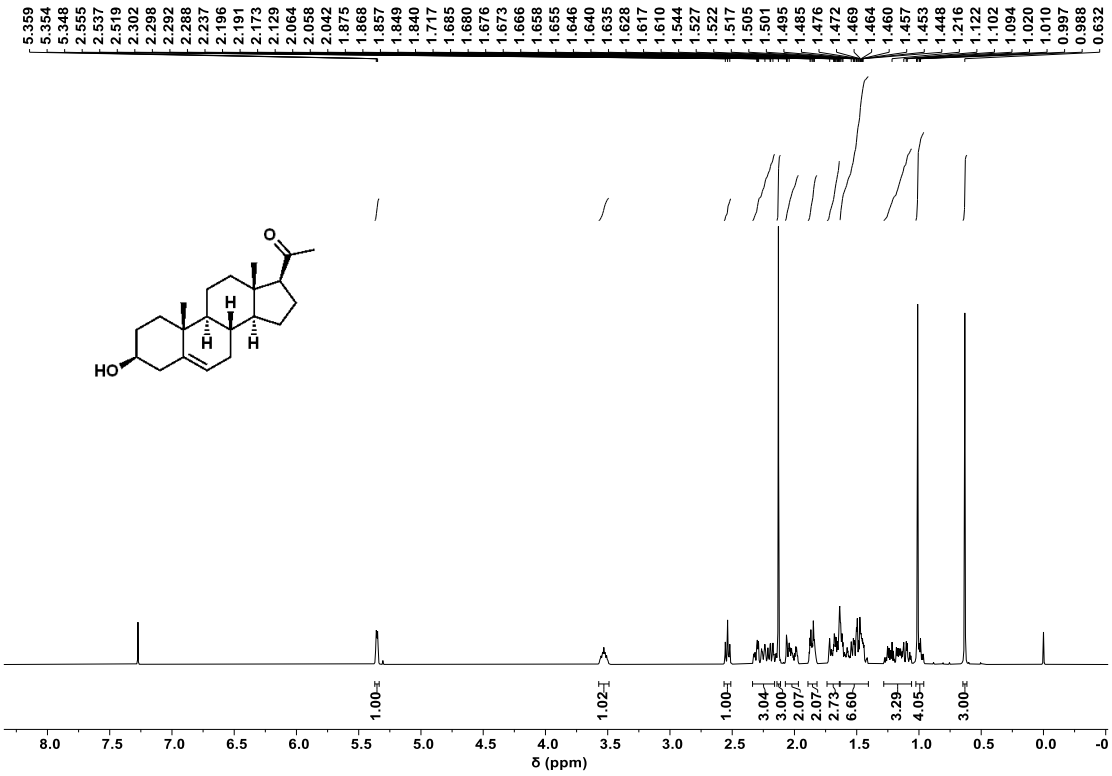


Figure S25. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S8**

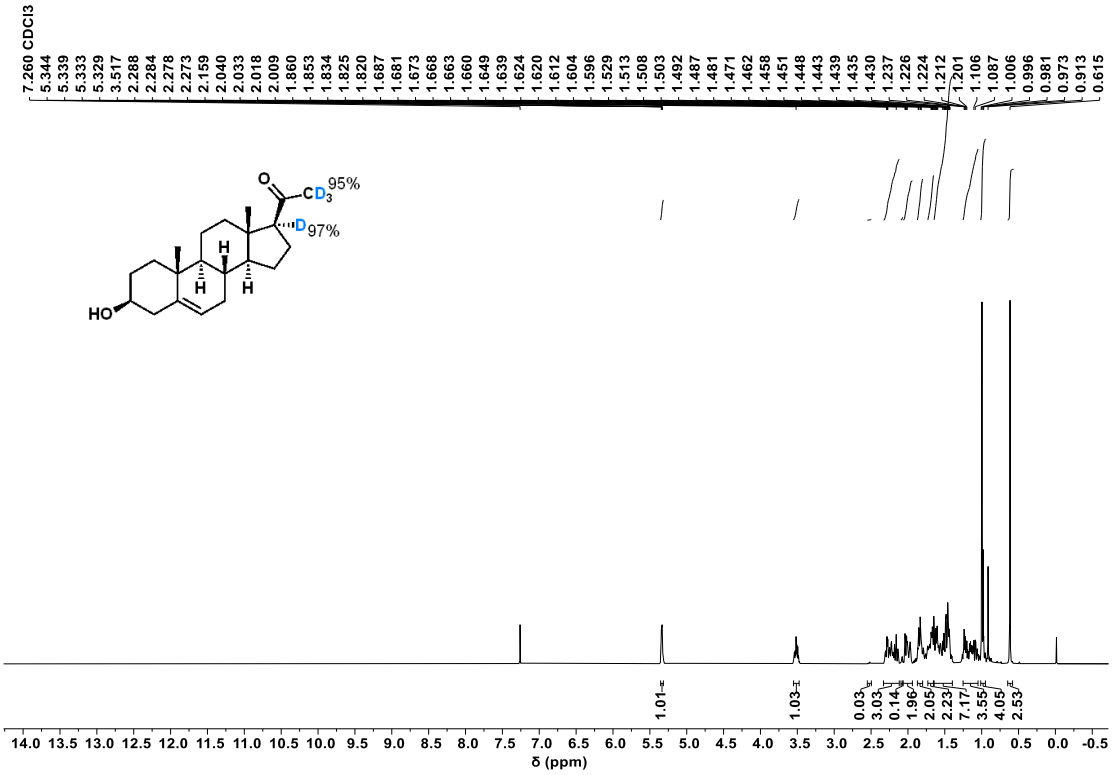


Figure S26. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **8**

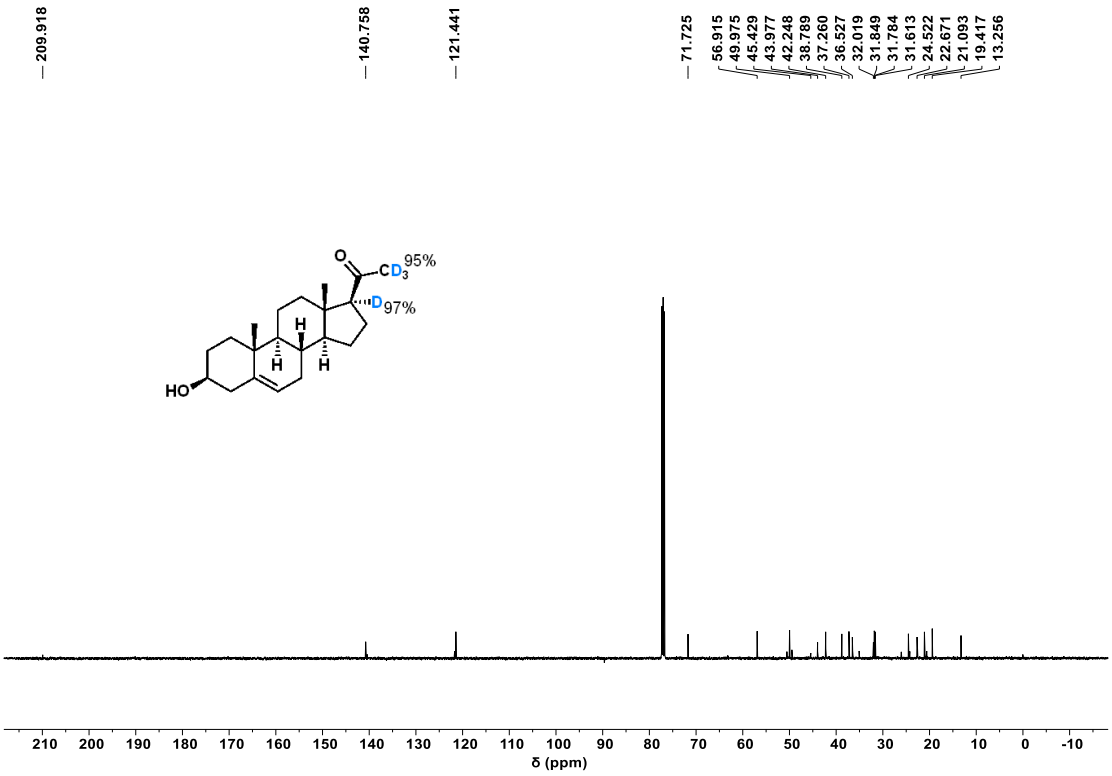


Figure S27. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **8**

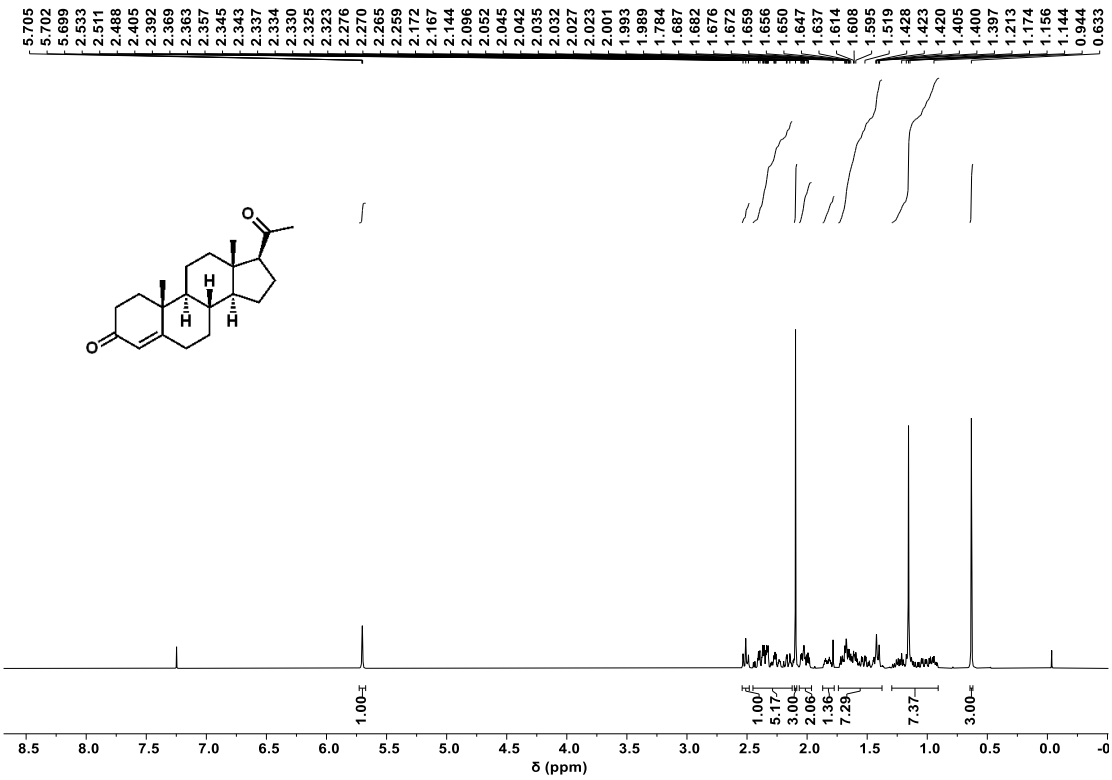


Figure S28. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S9**

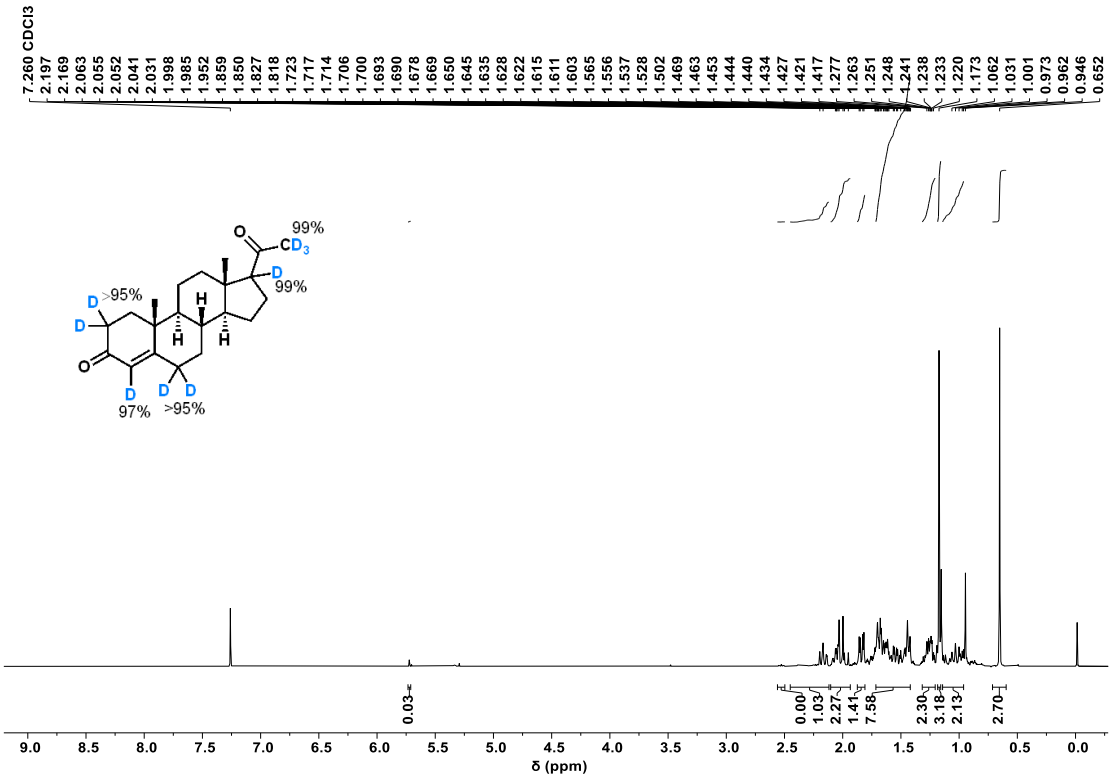


Figure S29. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **9**

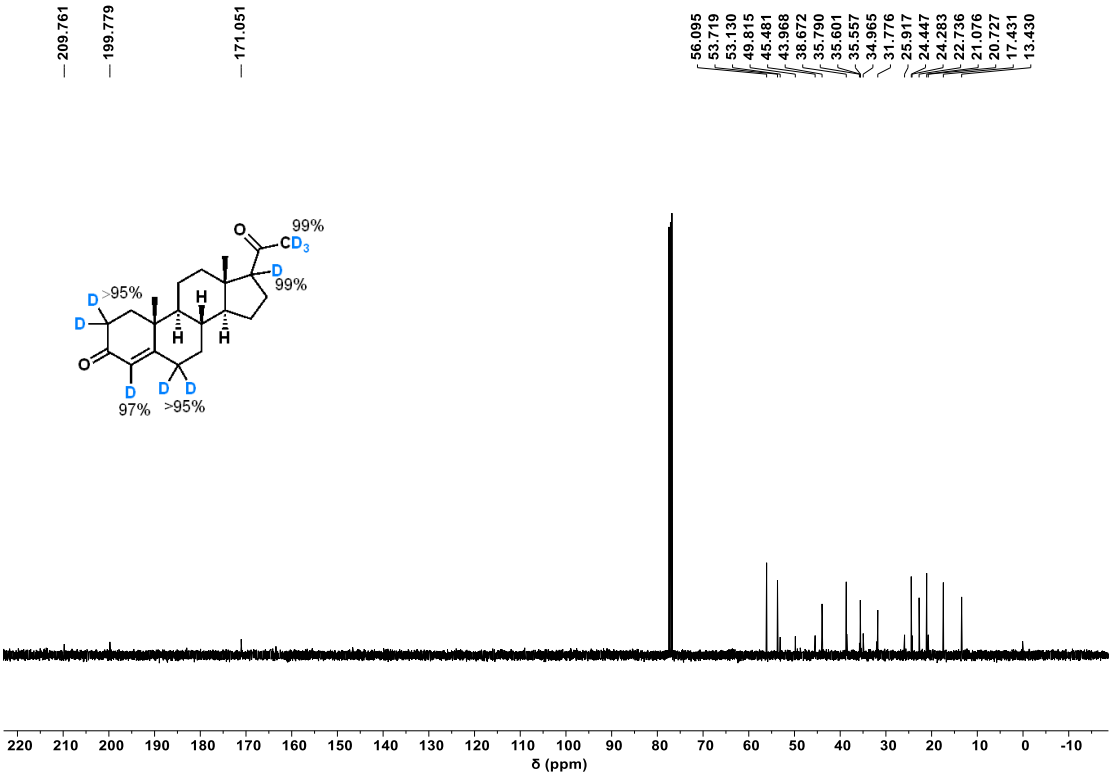


Figure S30. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **9**

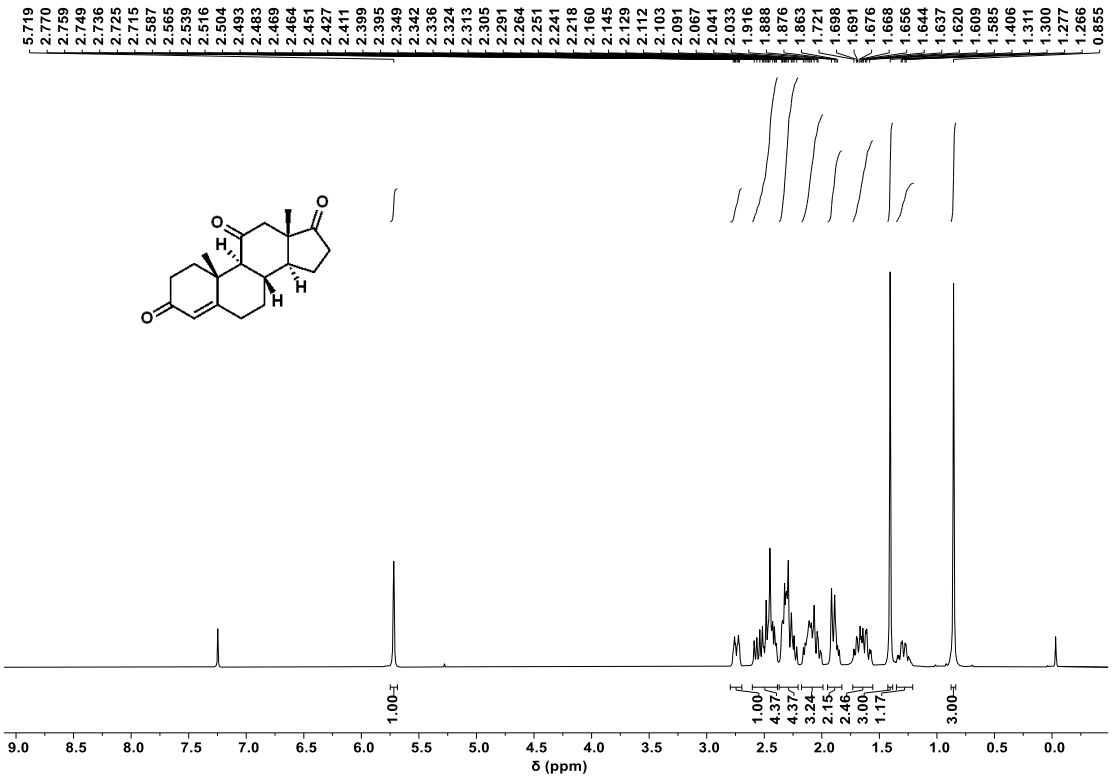


Figure S31. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S10**

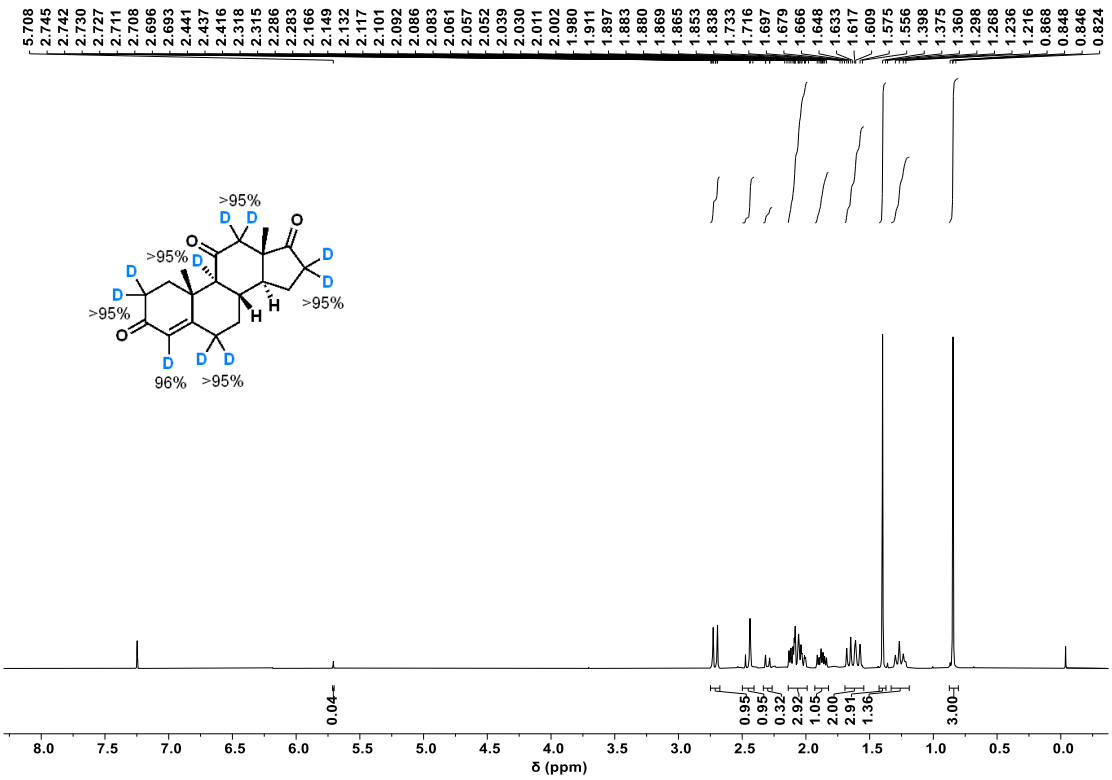


Figure S32. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **10**

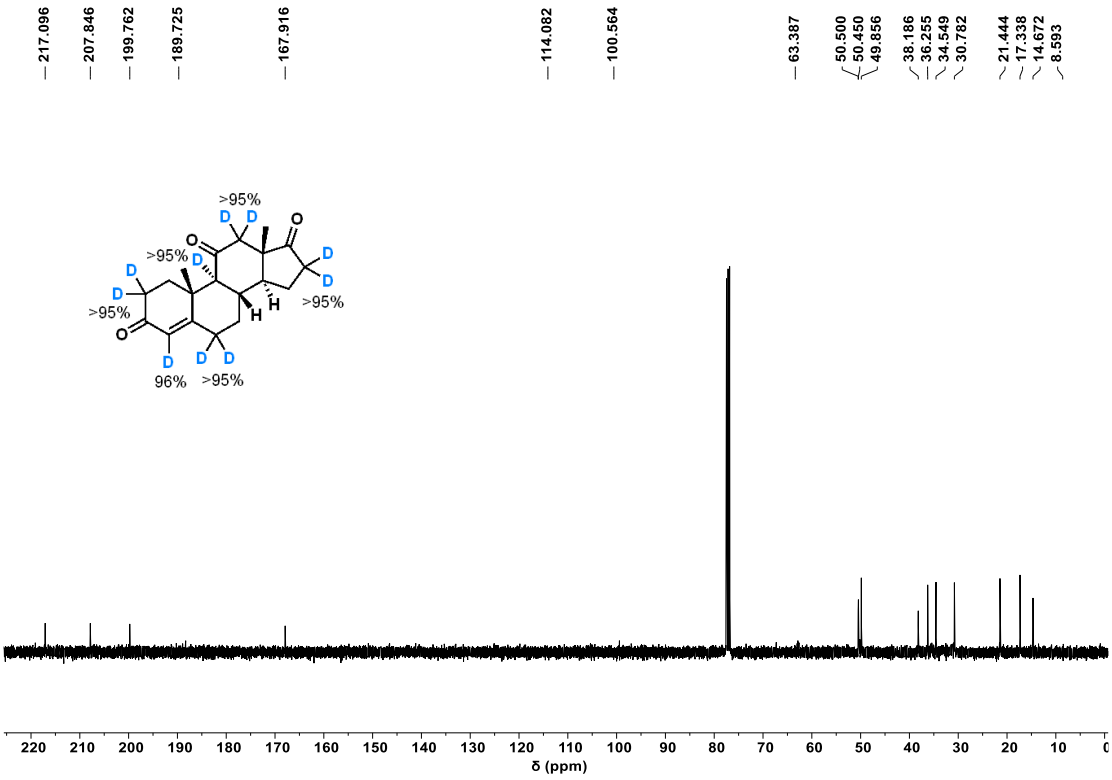


Figure S33. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **10**

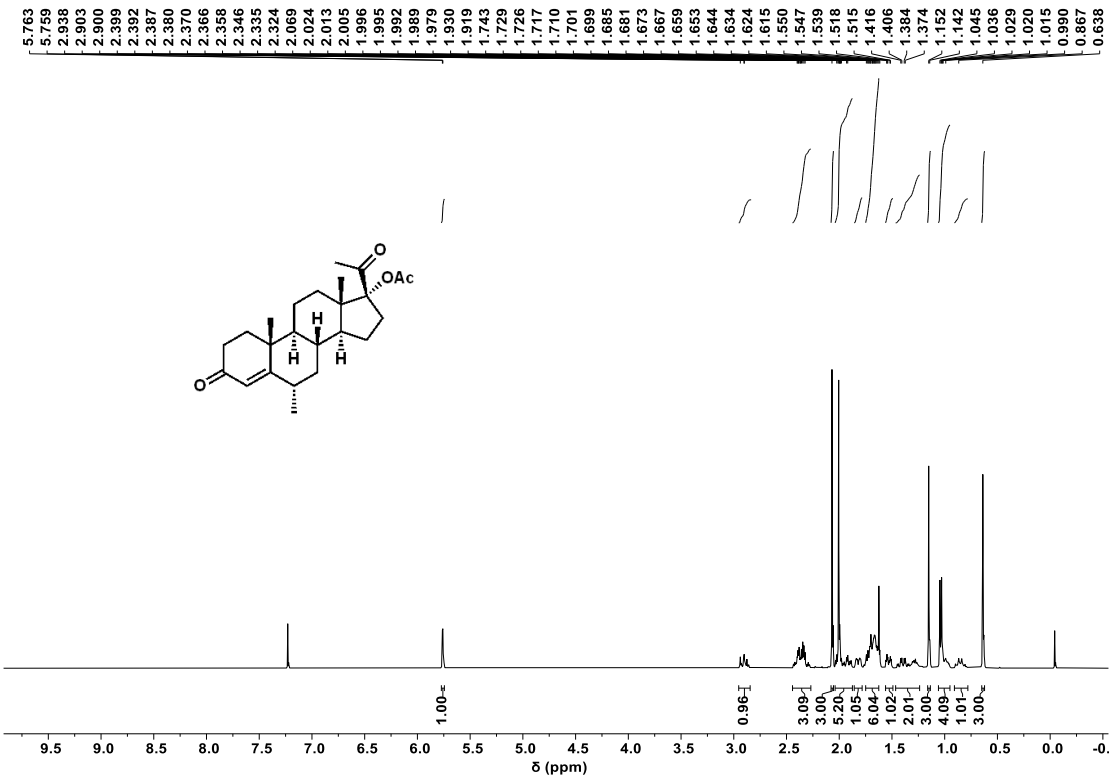


Figure S34. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S11**

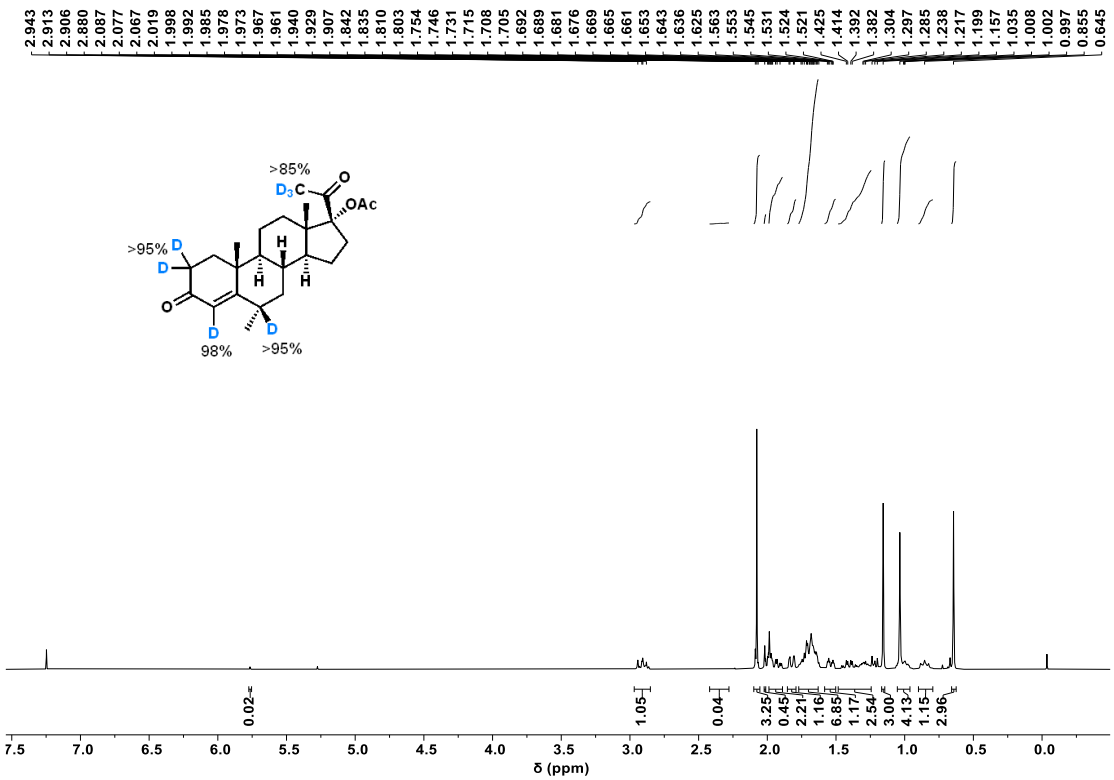


Figure S35. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **11**

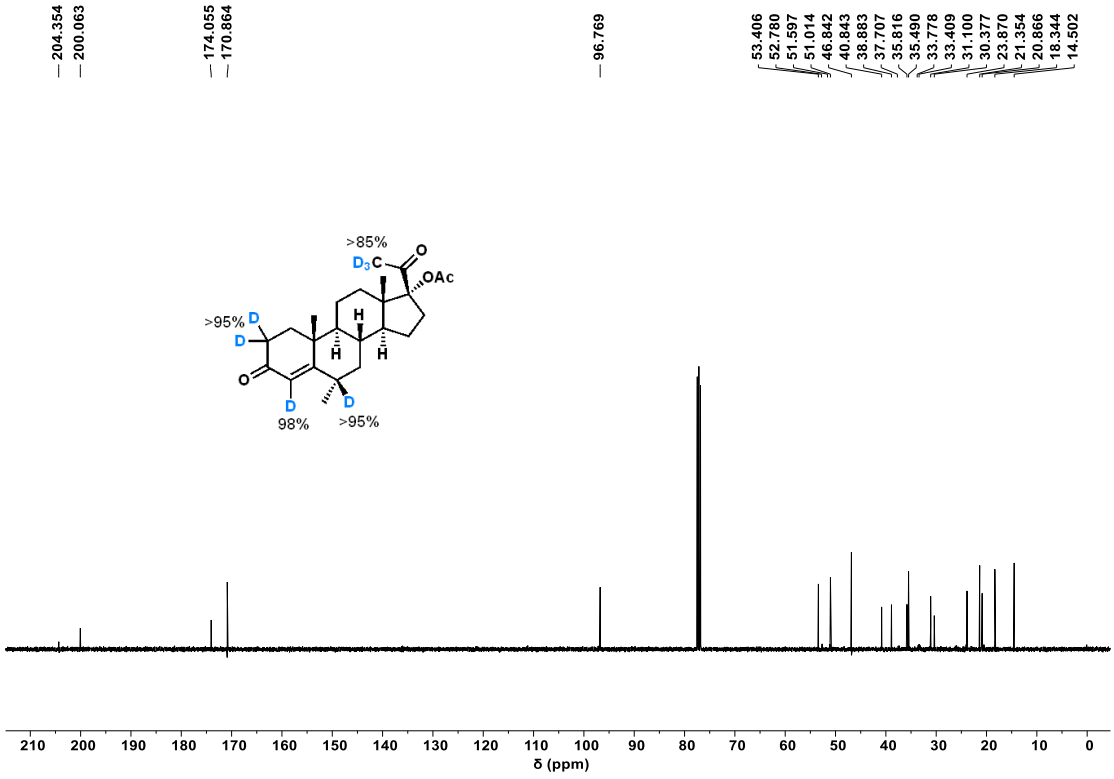


Figure S36. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **11**

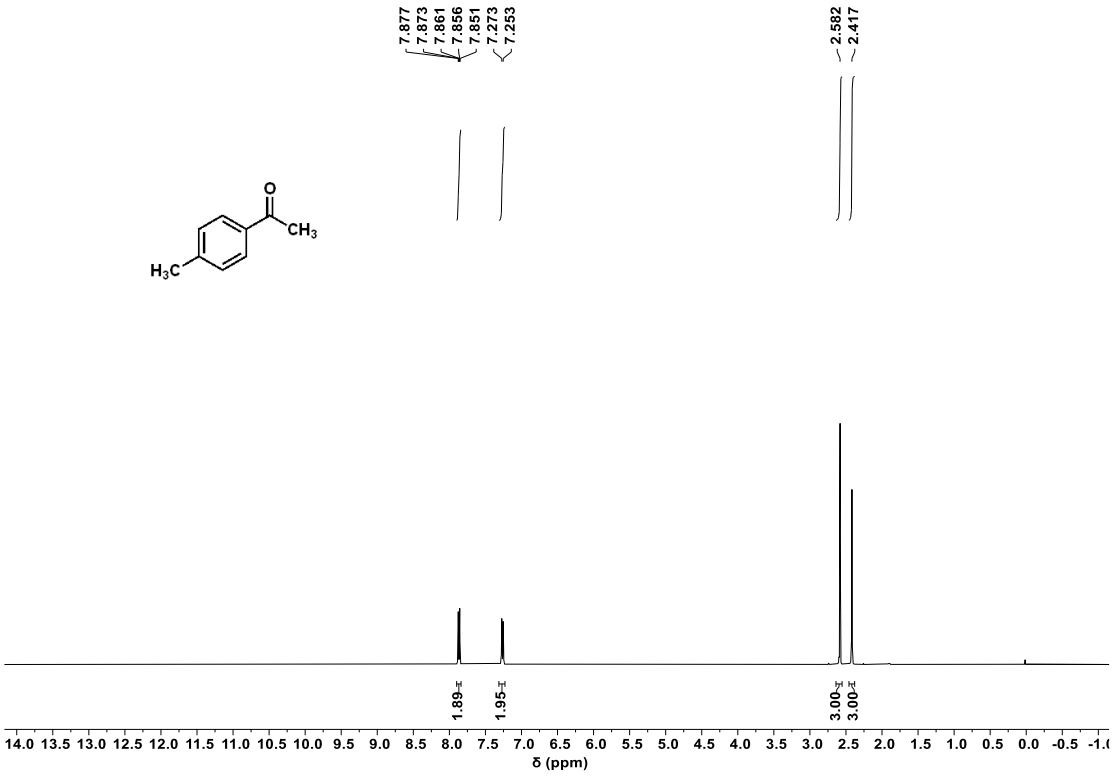


Figure S37. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S12**

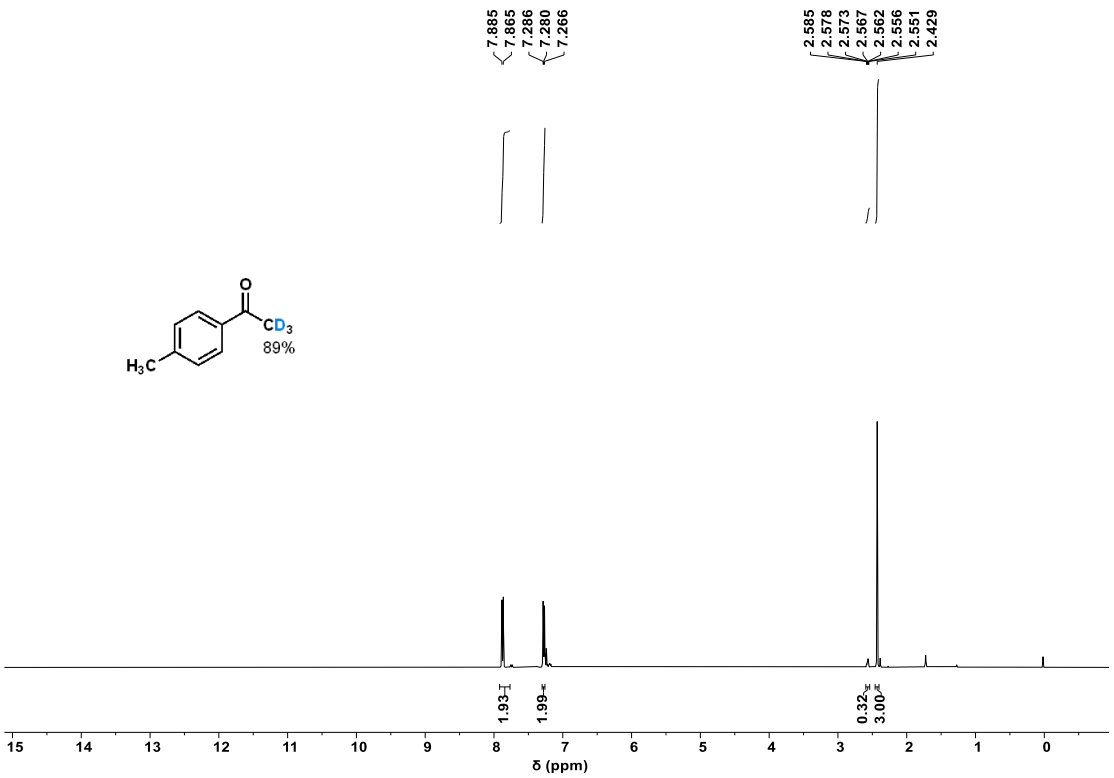


Figure S38. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$)of **12**

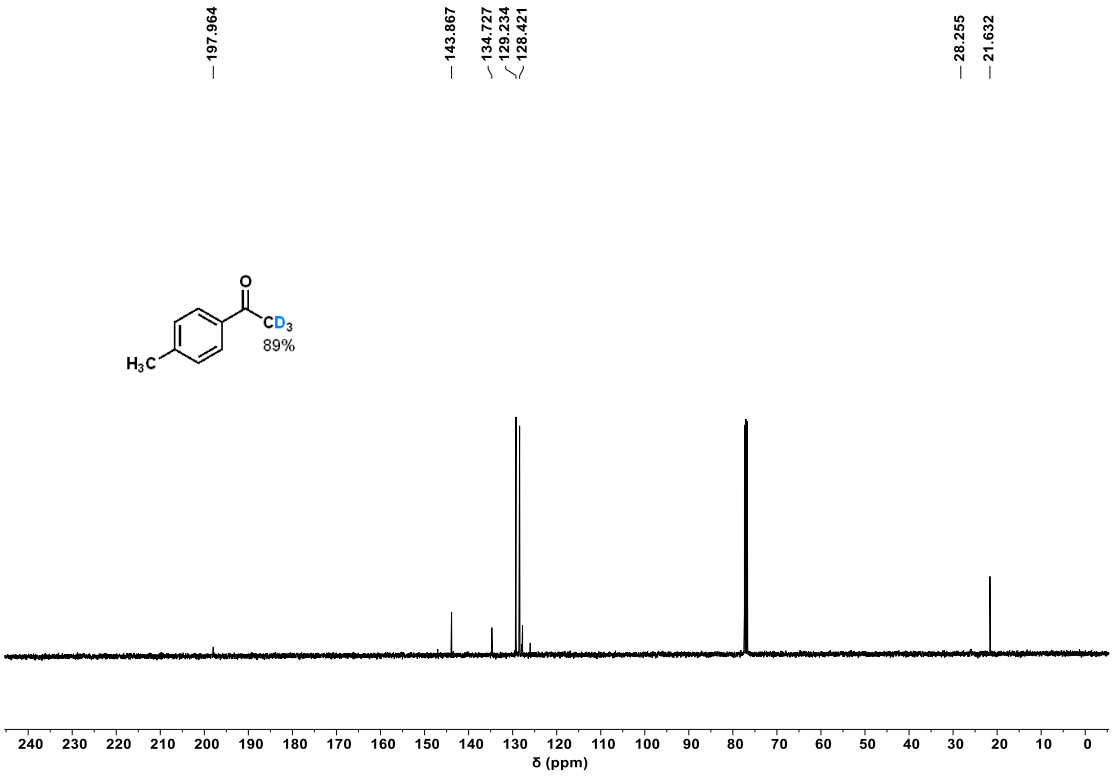


Figure S39. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **12**

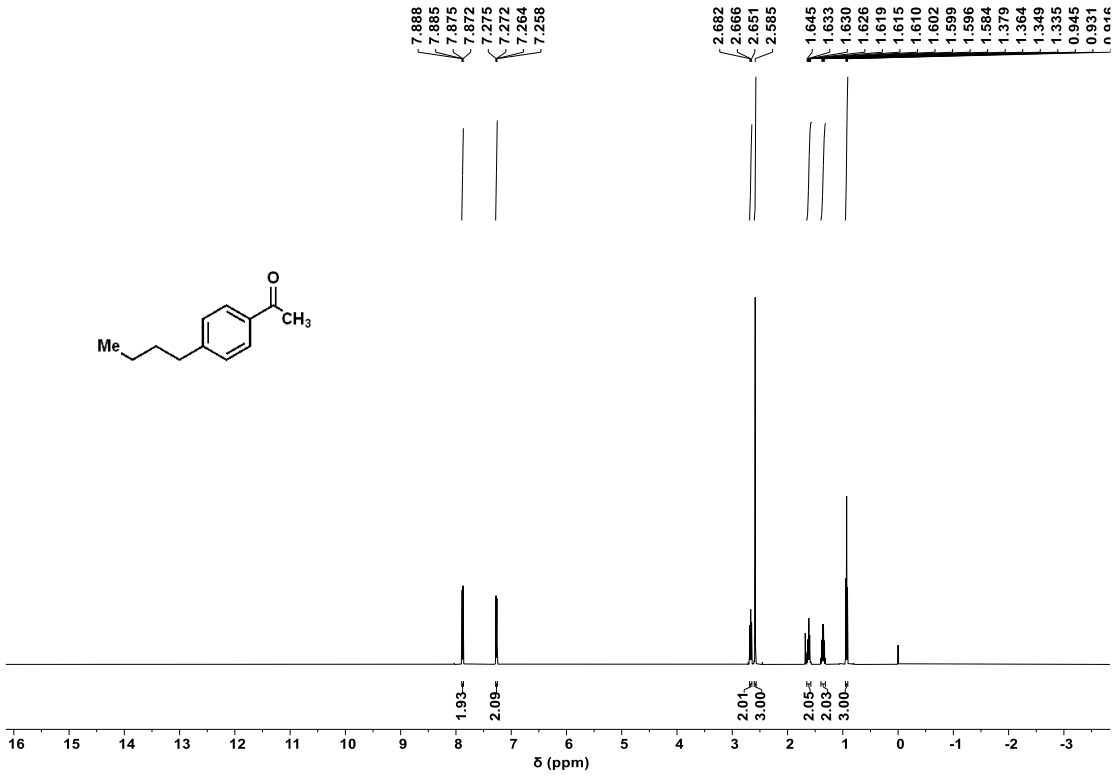


Figure S40. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S13**

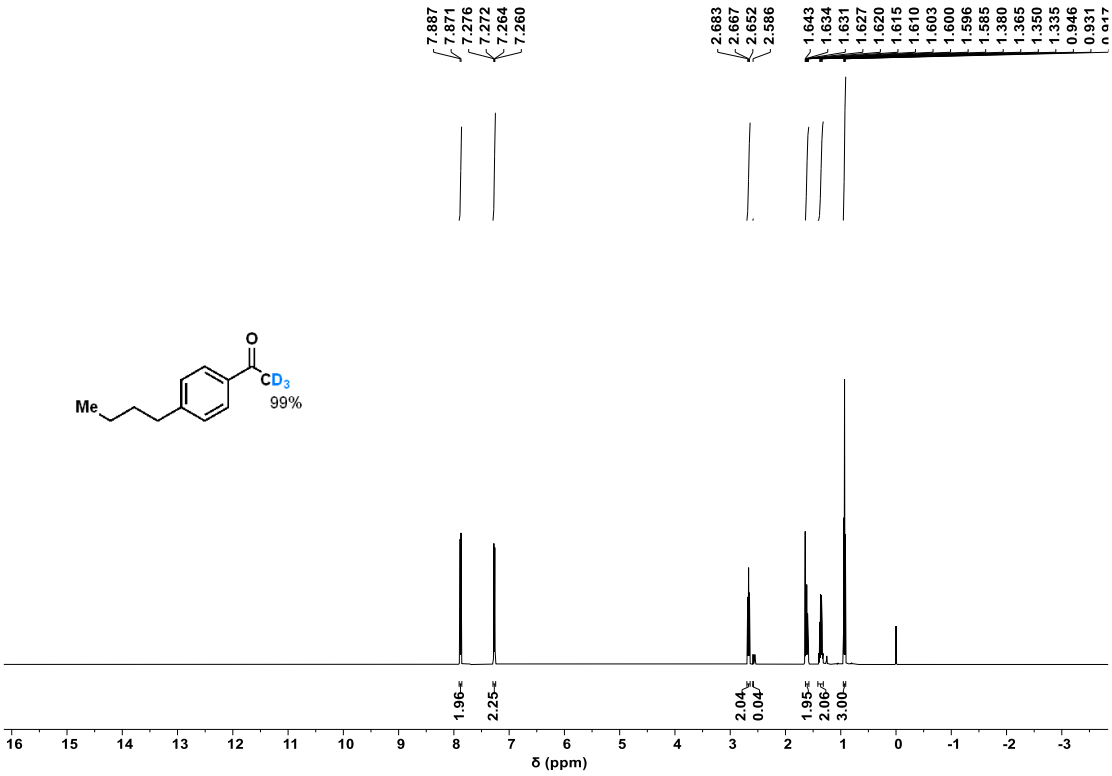


Figure S41. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **13**

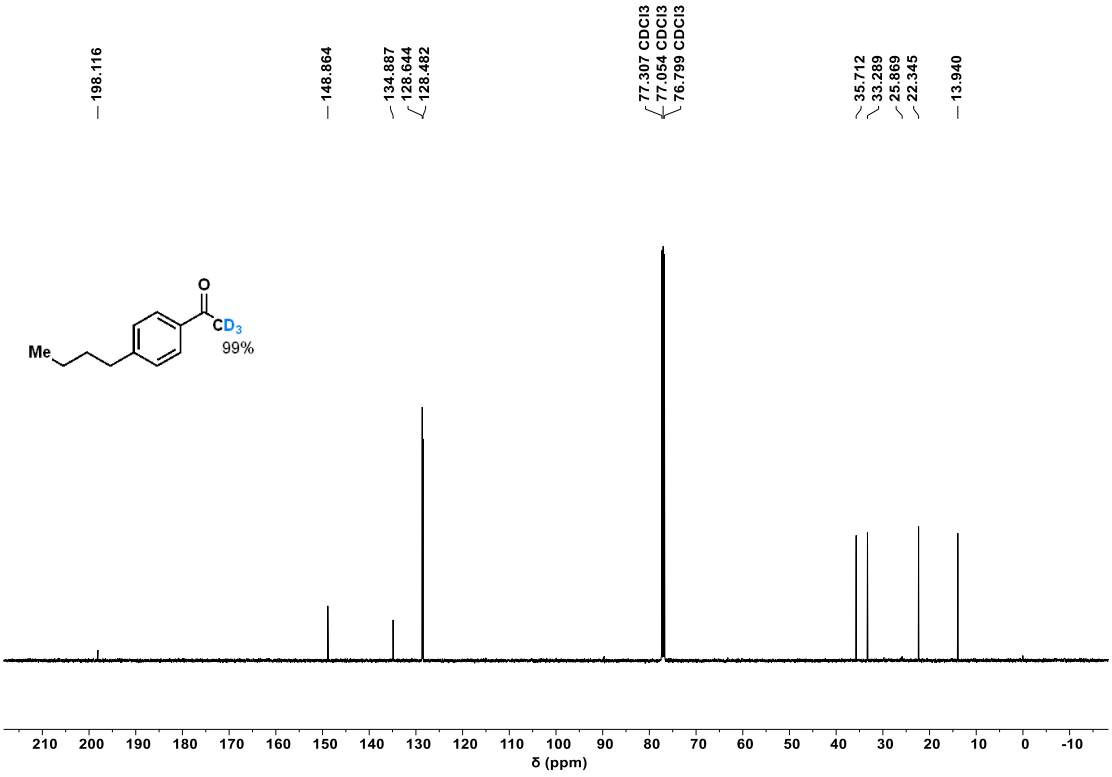


Figure S42. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **13**

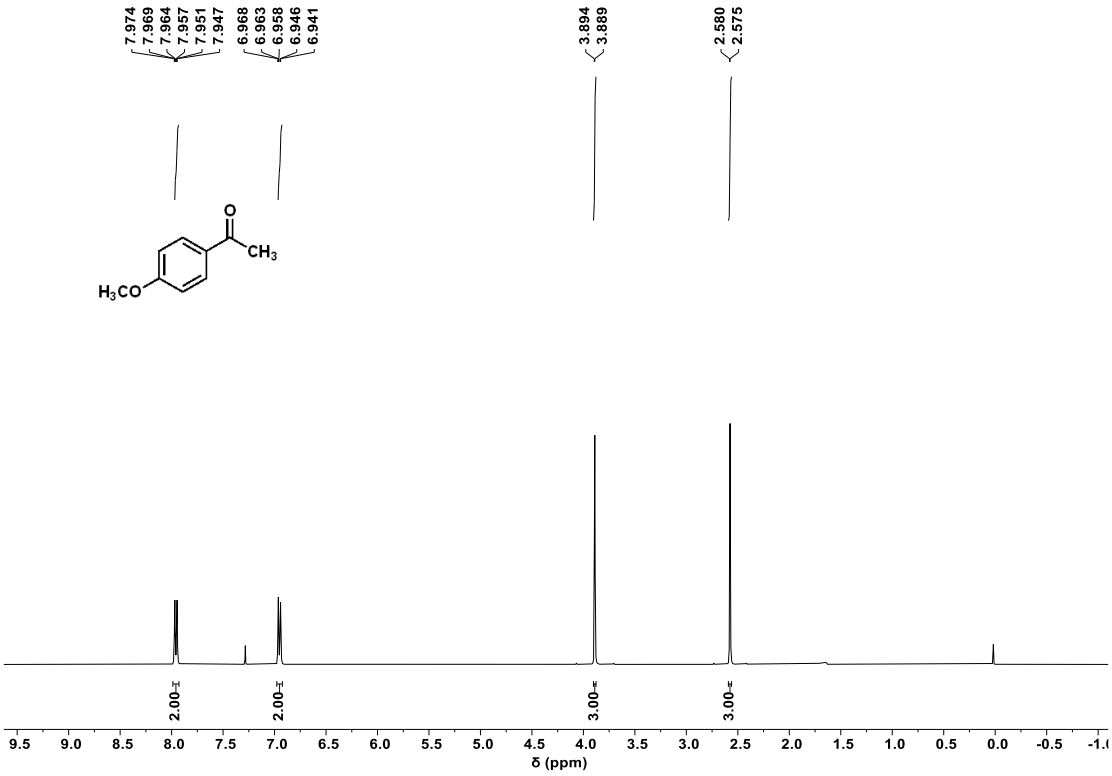


Figure S43. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S14**

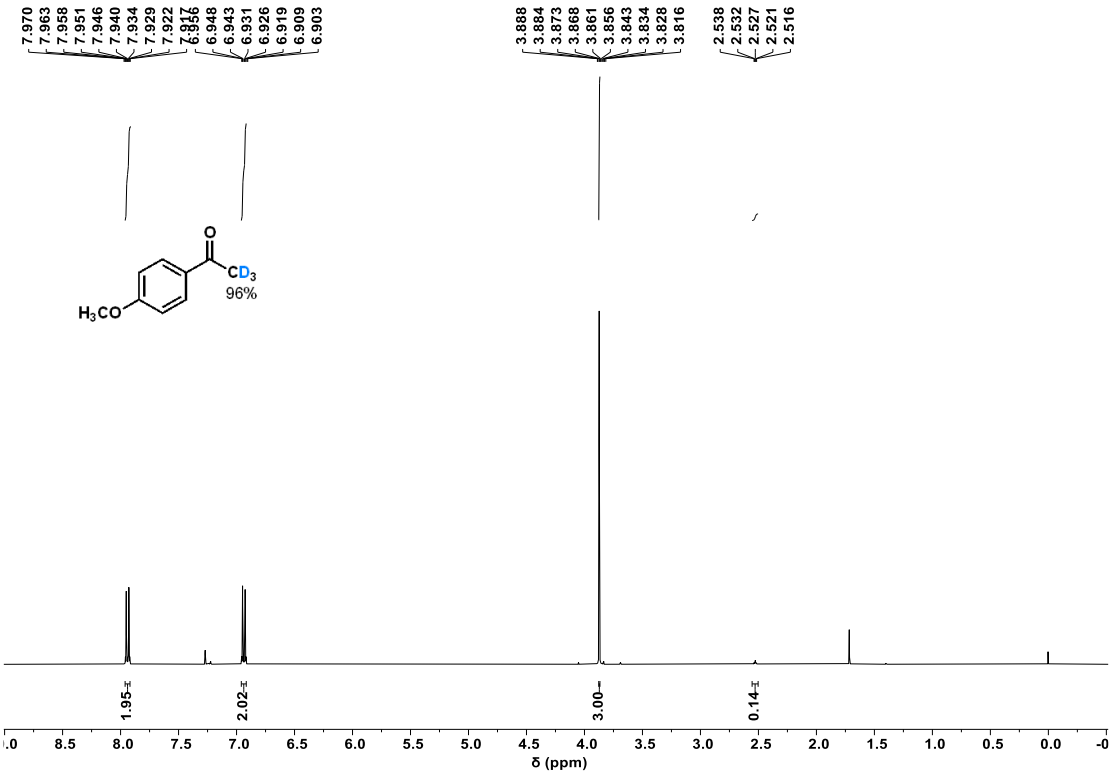


Figure S44. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **14**

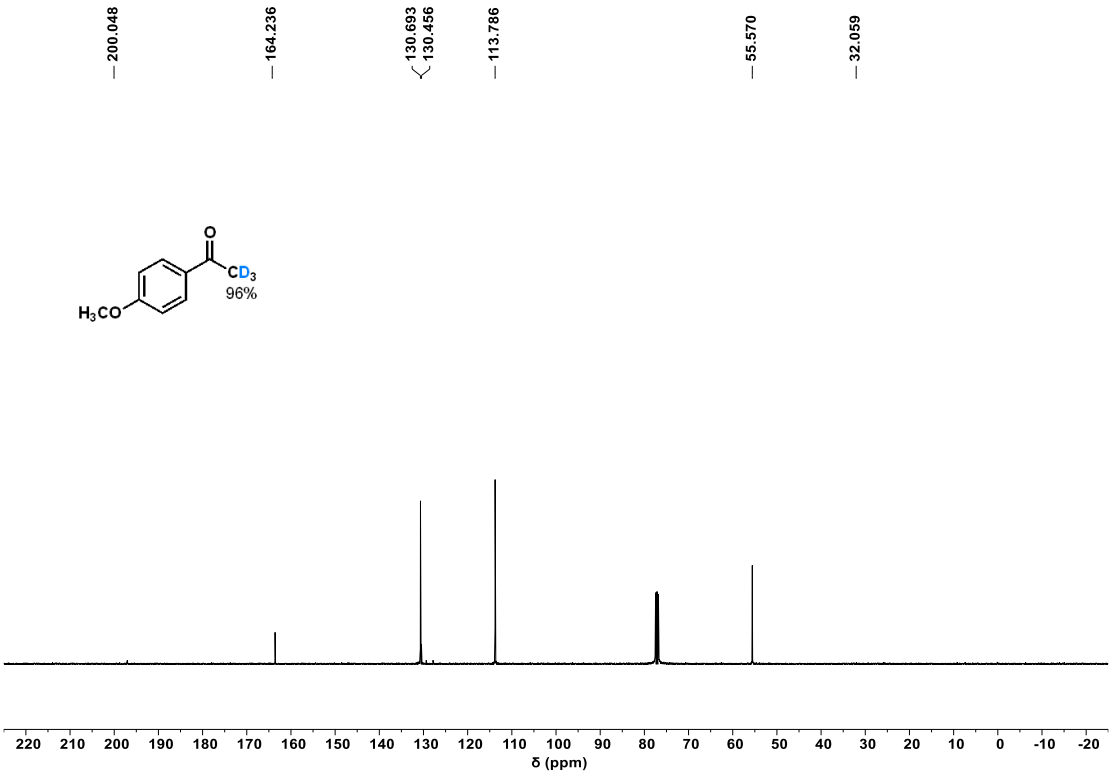


Figure S45. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **14**

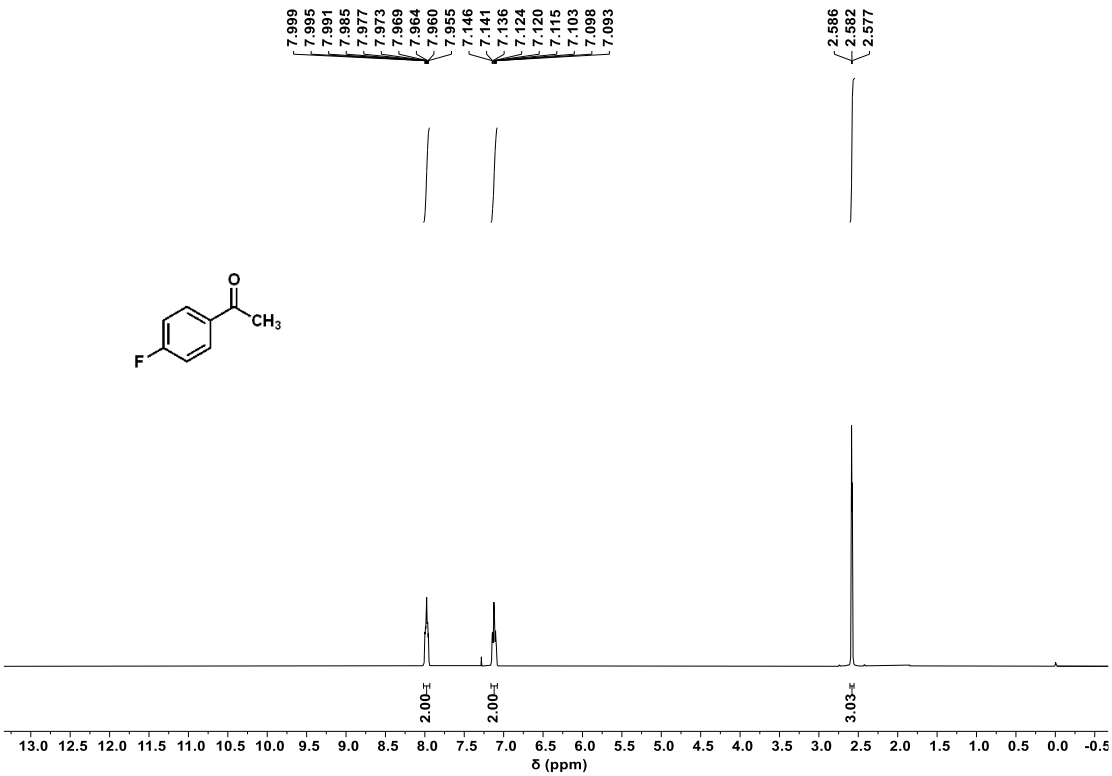


Figure S46. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S15**

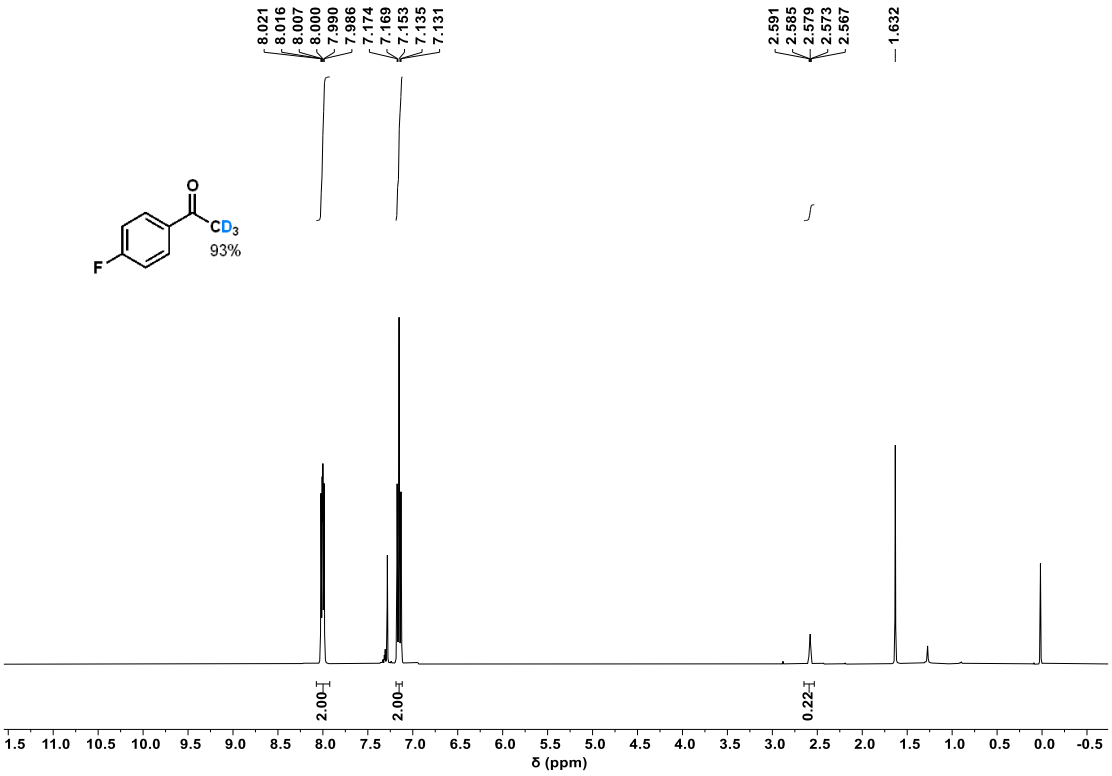


Figure S47. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$)of **15**

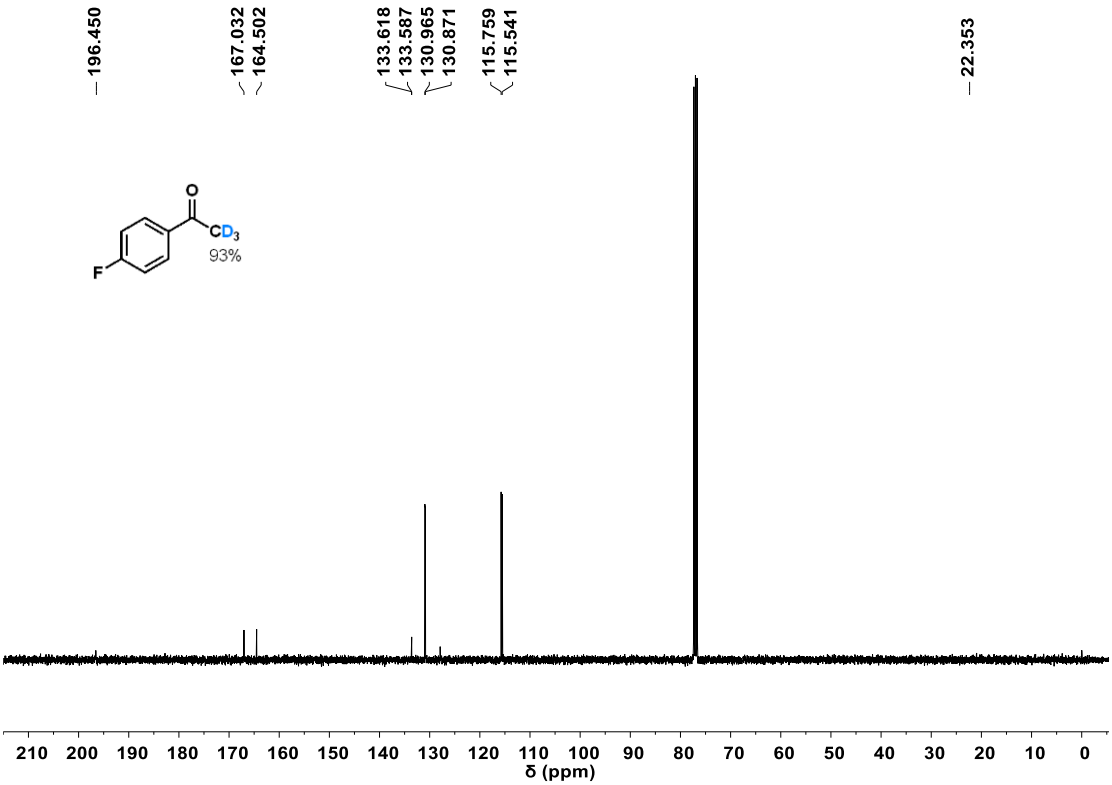


Figure S48. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **15**

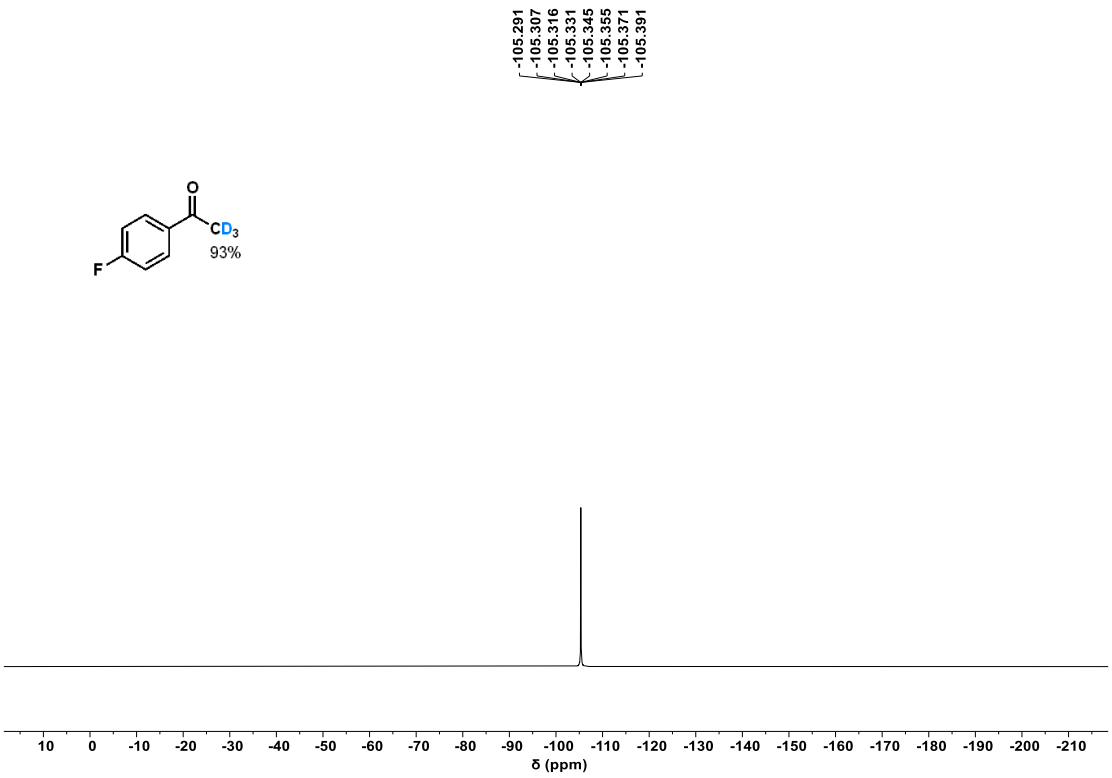


Figure S49. ^{19}F-NMR spectrum (376 MHz, $CDCl_3$) of **15**

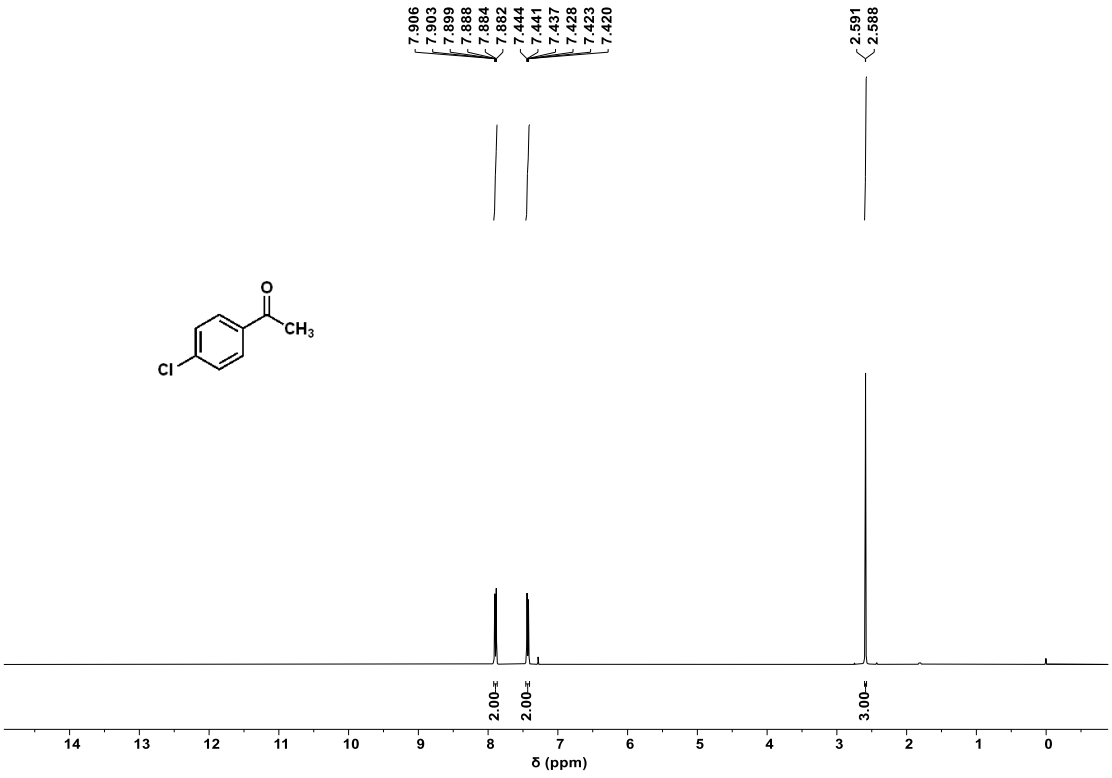


Figure S50. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S16**

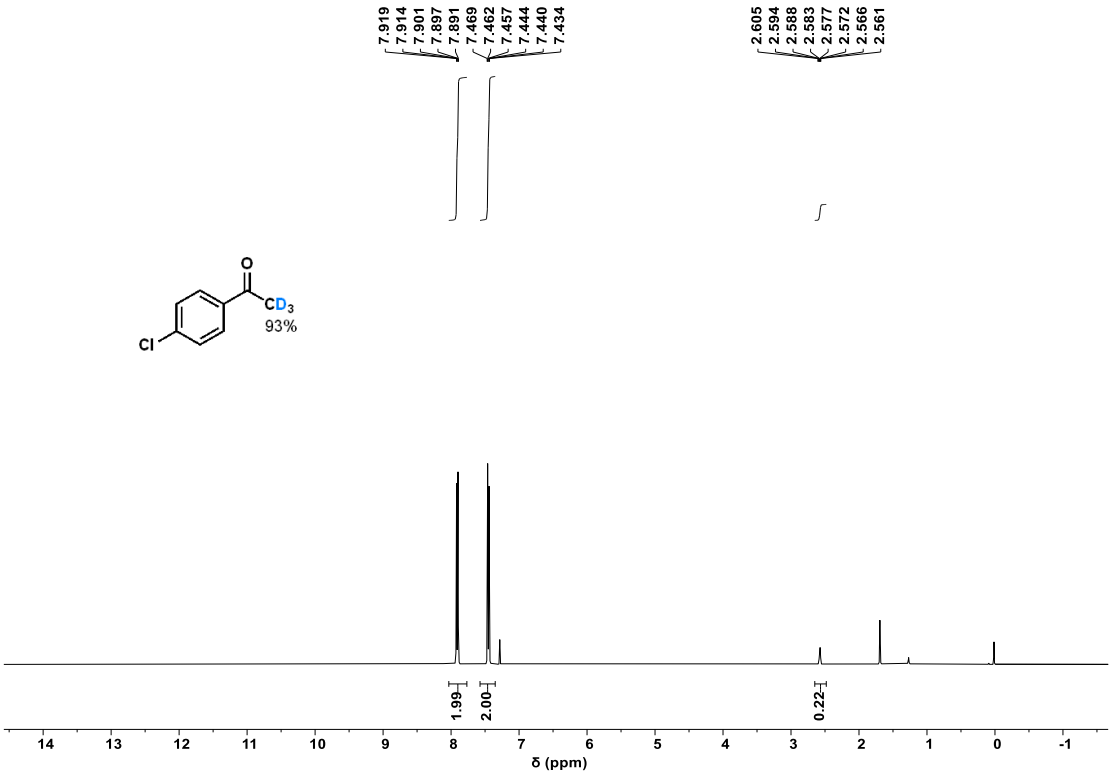


Figure S51. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **16**

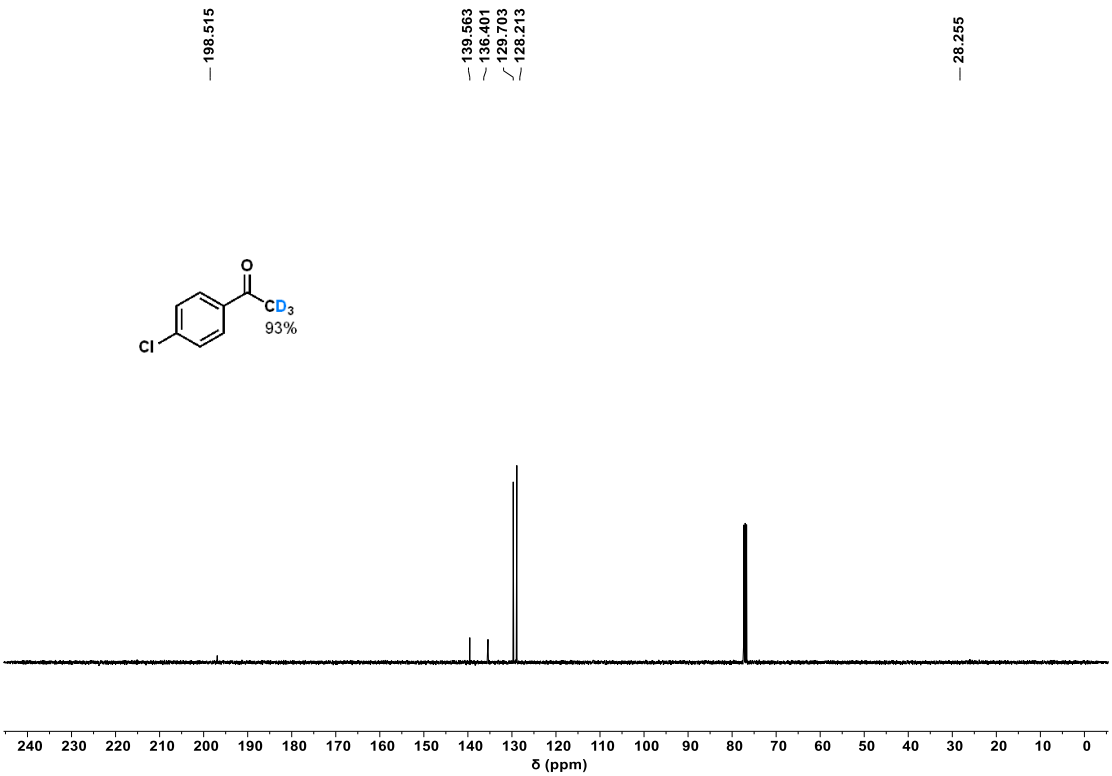


Figure S52. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **16**

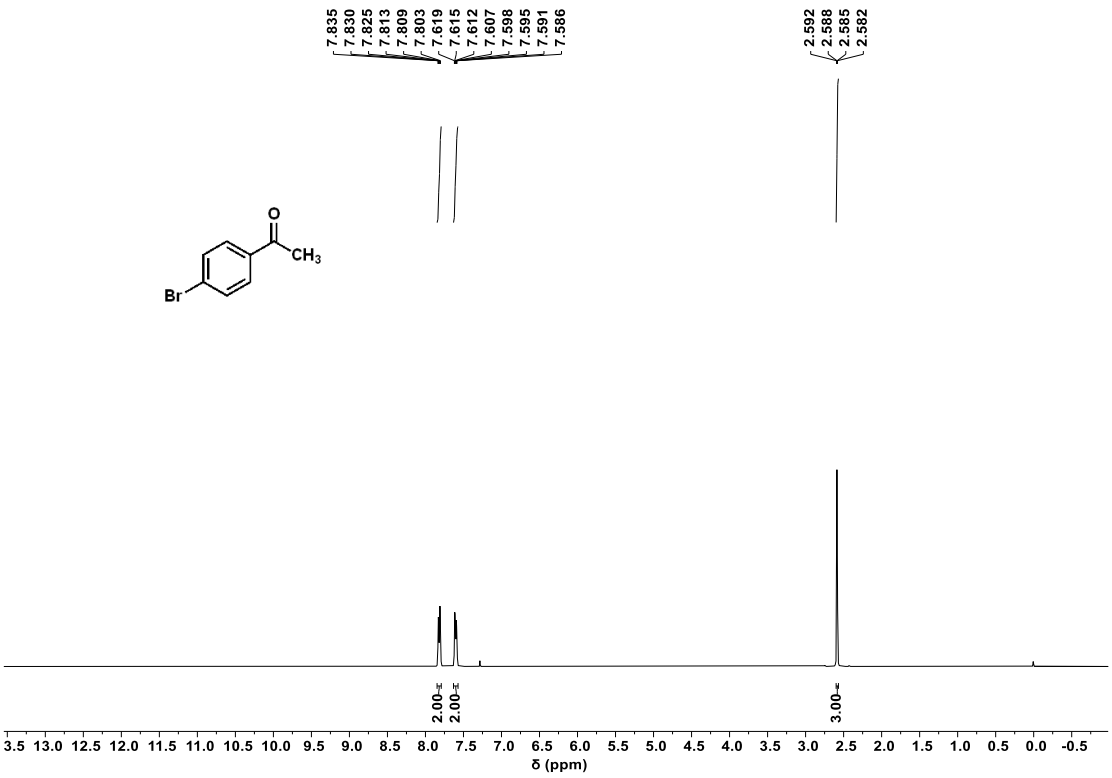


Figure S53. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S17**

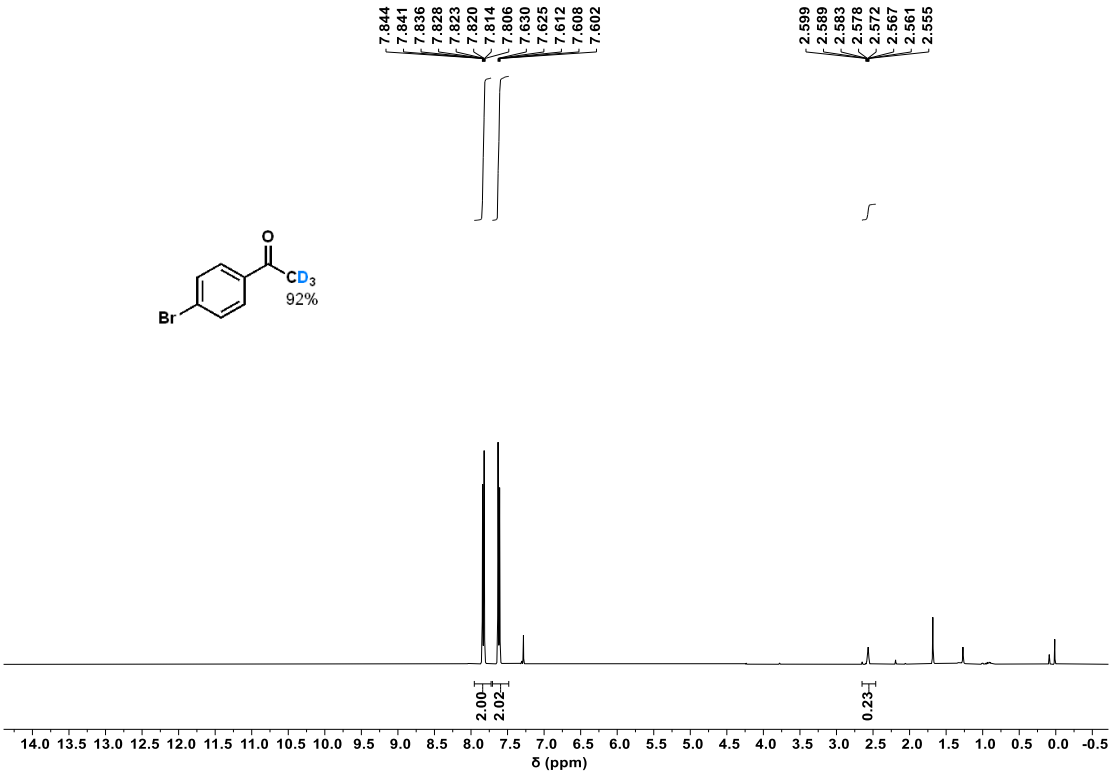


Figure S54. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **17**

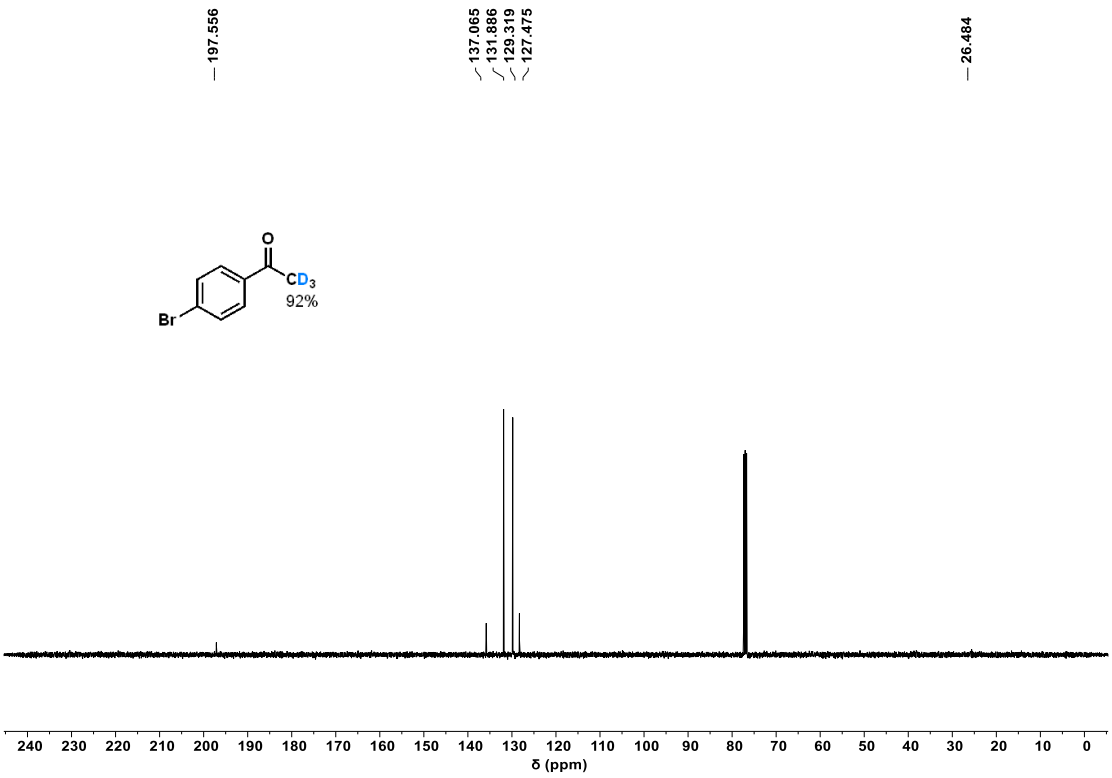


Figure S55. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **17**

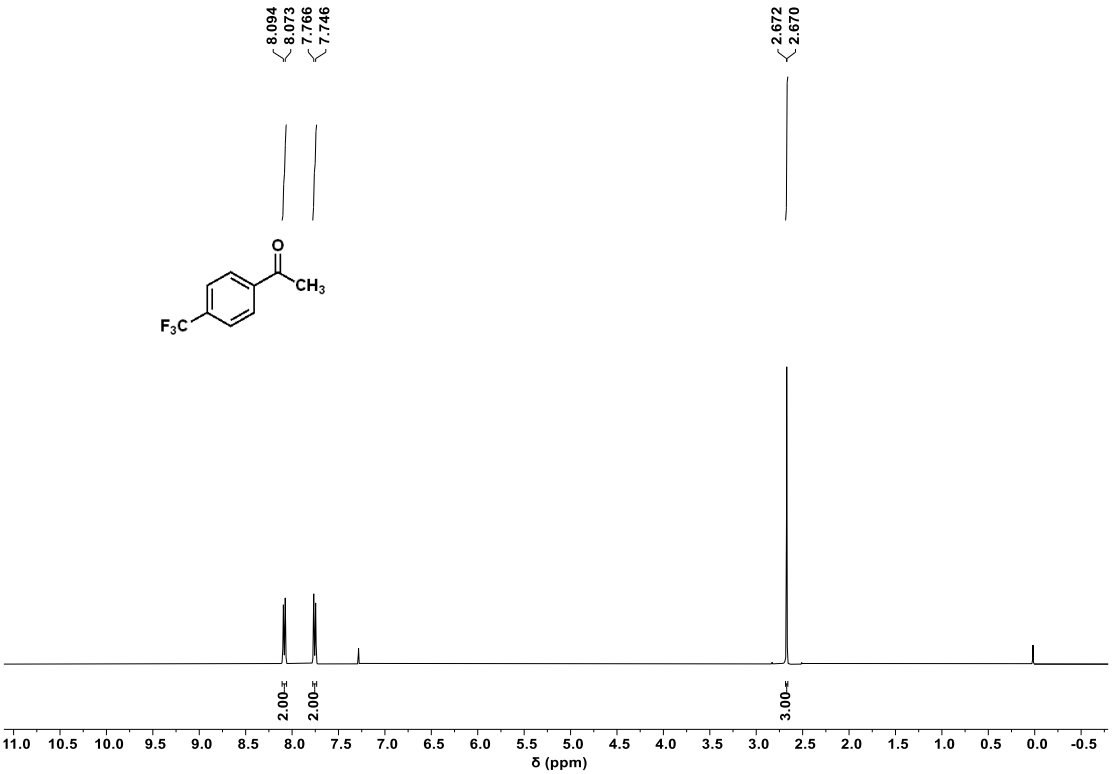


Figure S56. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S18**

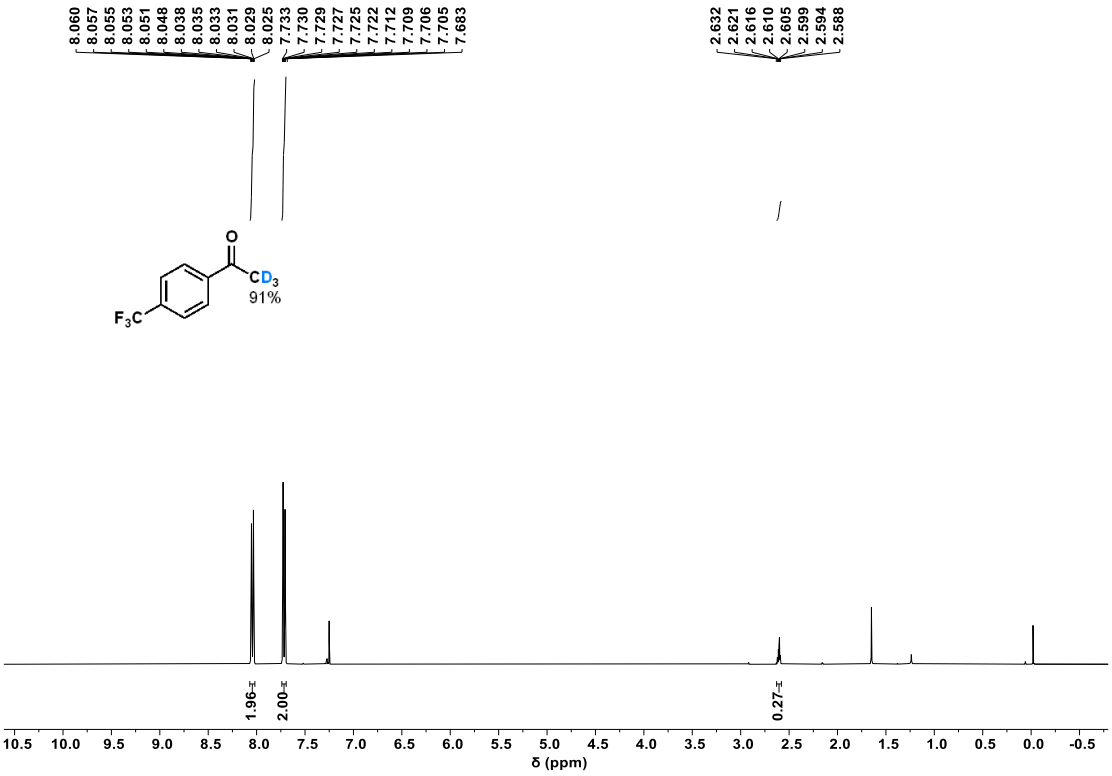


Figure S57. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **18**

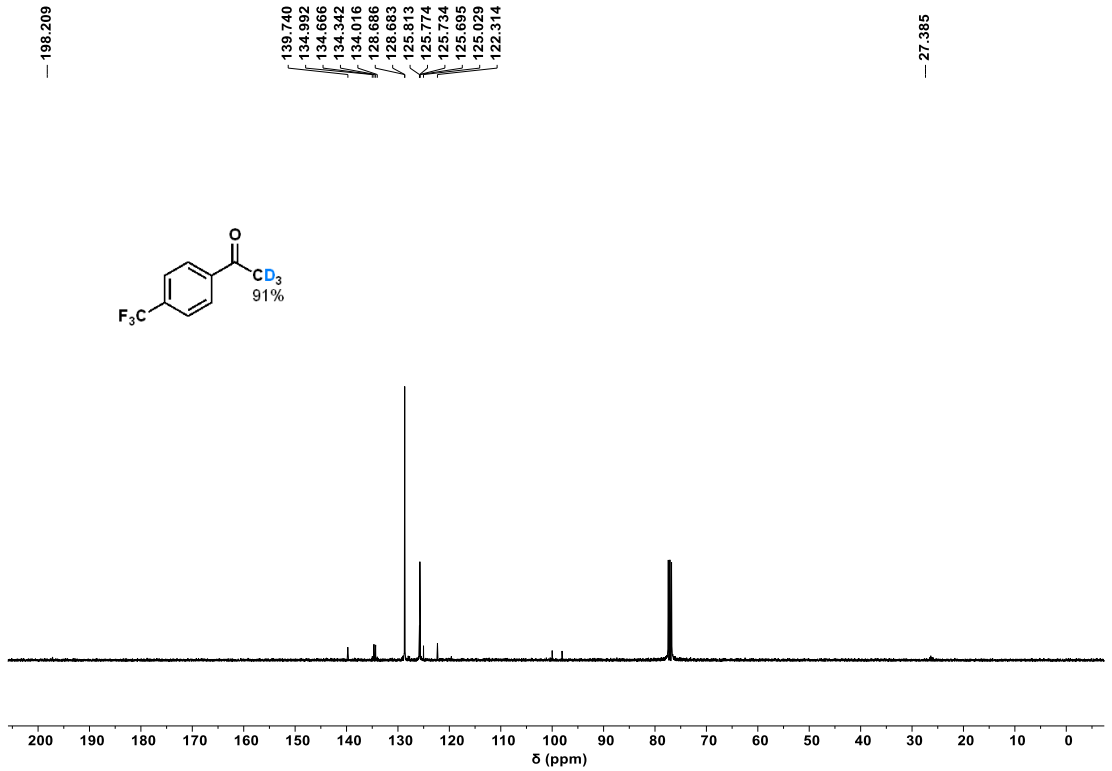


Figure S58. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **18**

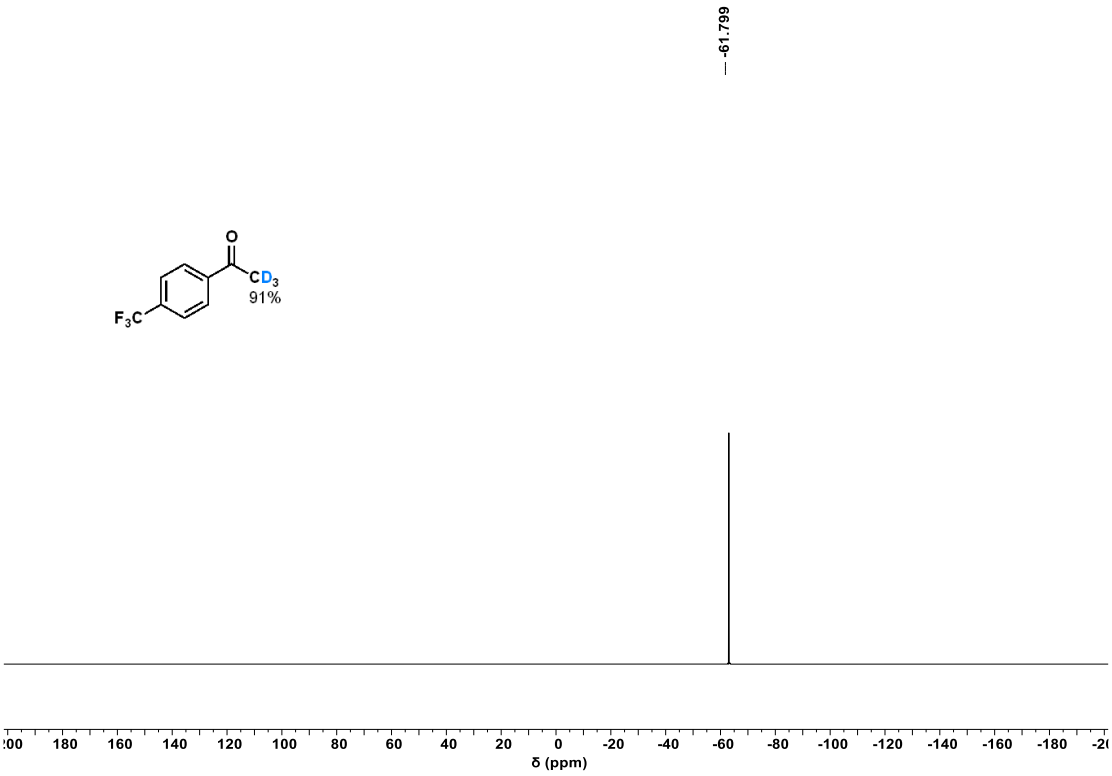


Figure S59. ^{19}F-NMR spectrum (376 MHz, $CDCl_3$) of **18**

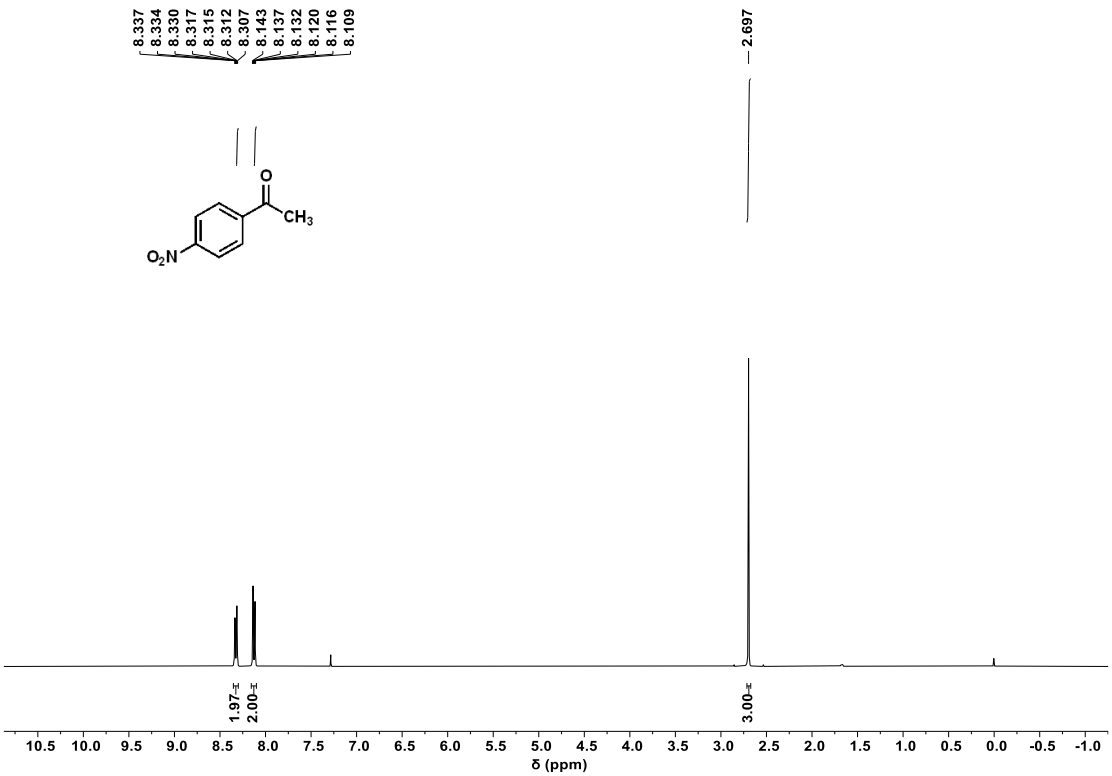


Figure S60. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S19**

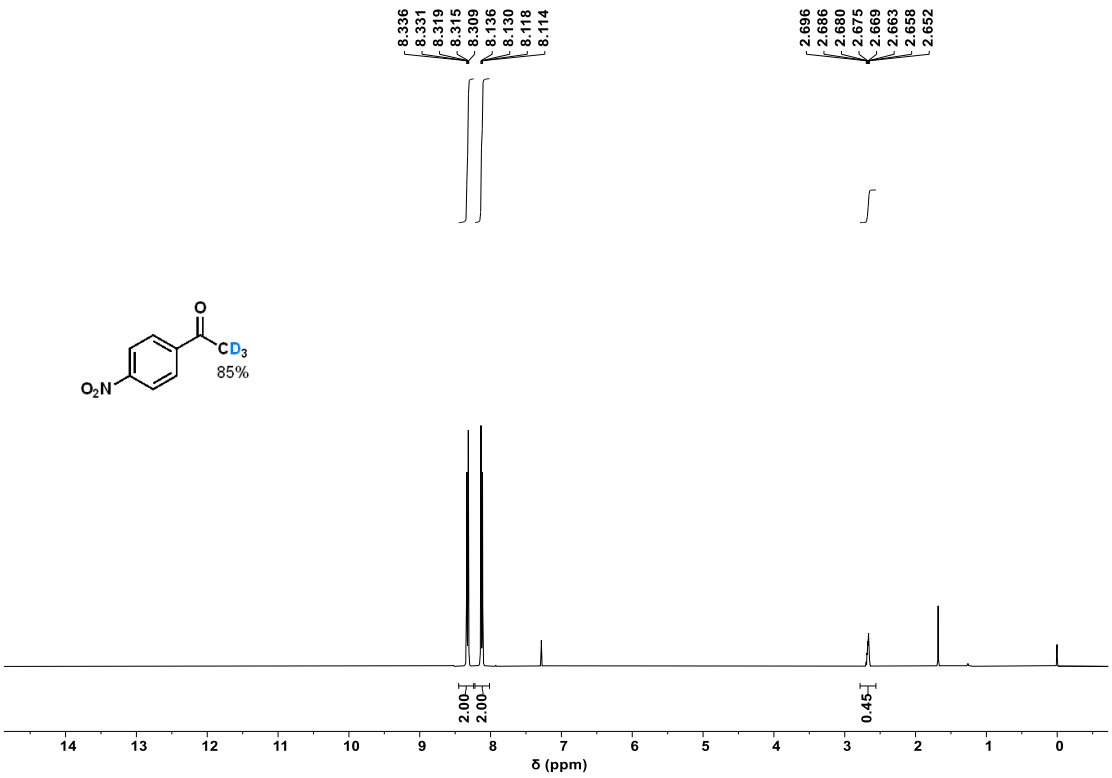


Figure S61. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **19**

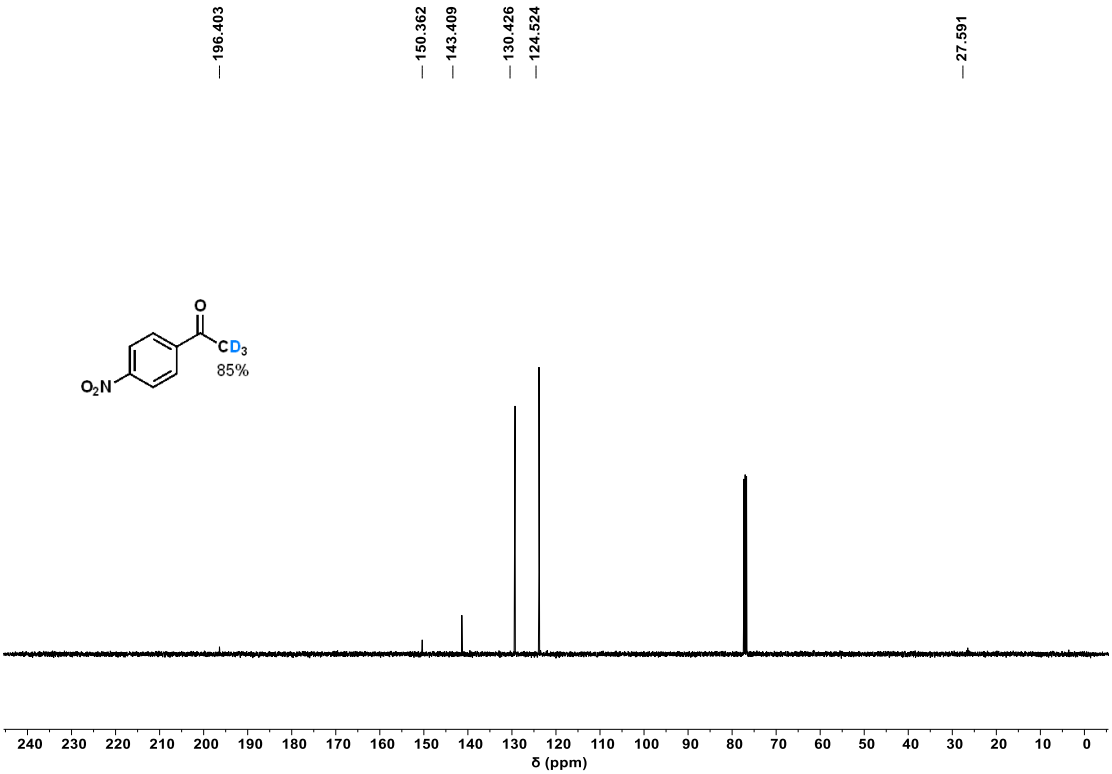


Figure S62. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **19**

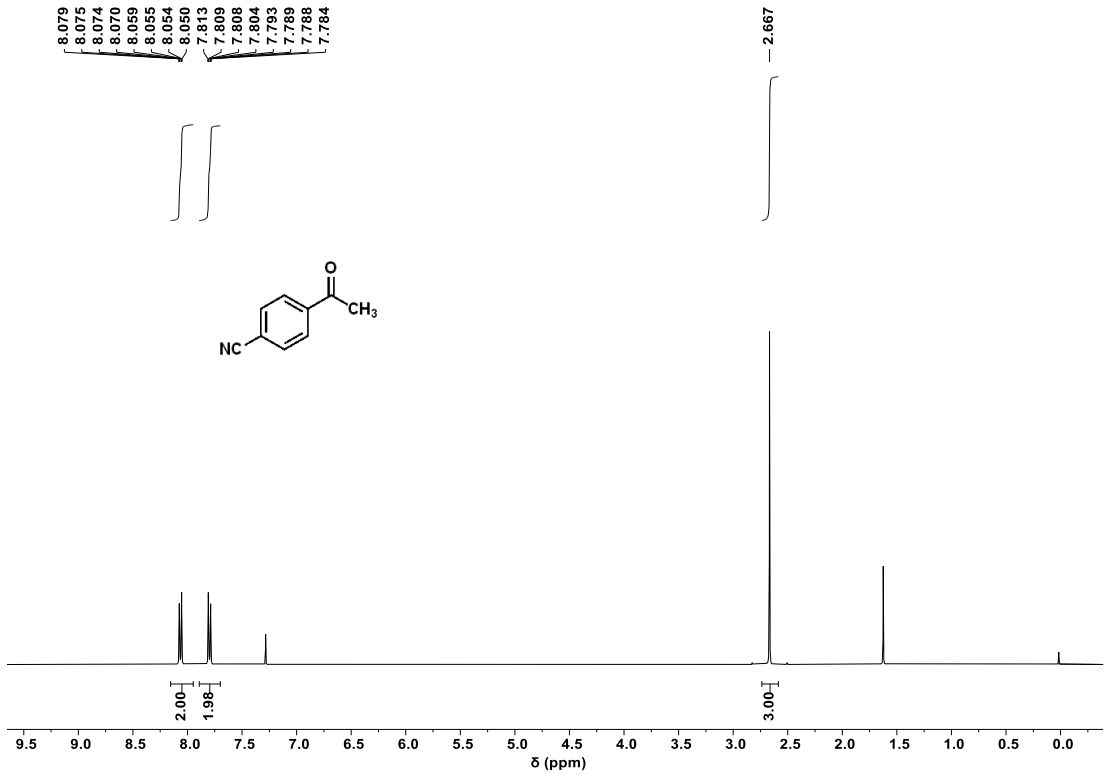


Figure S63. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$)of **S20**

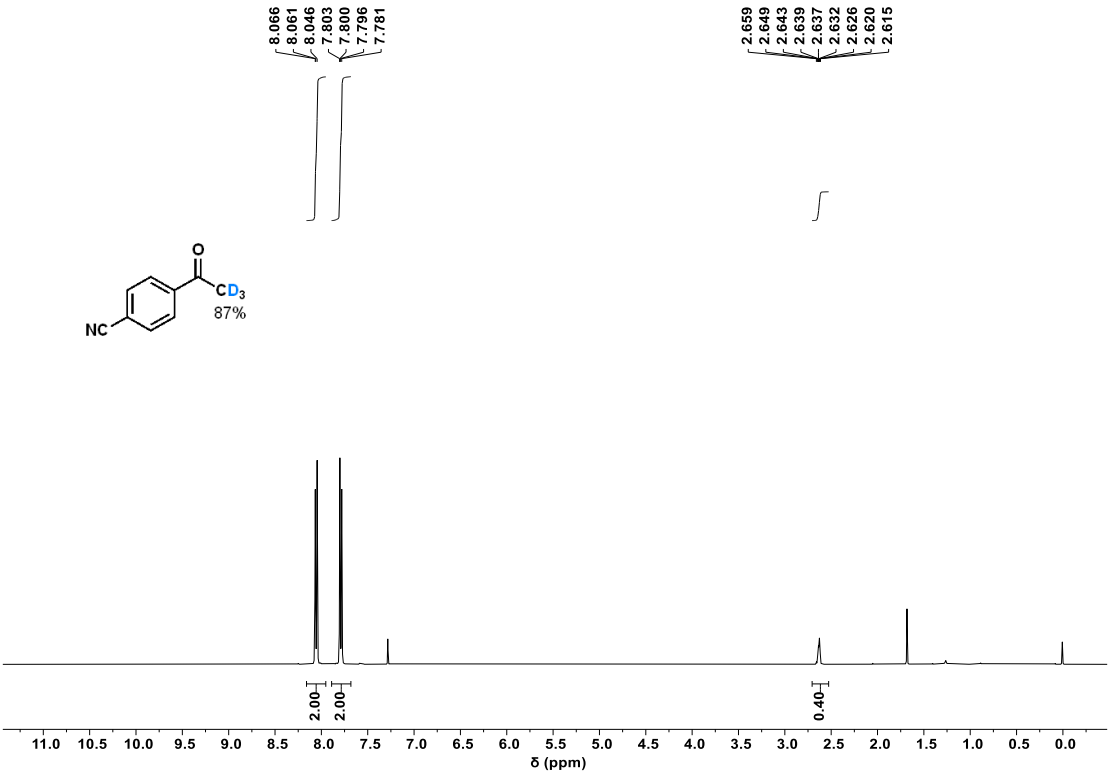


Figure S64. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **20**

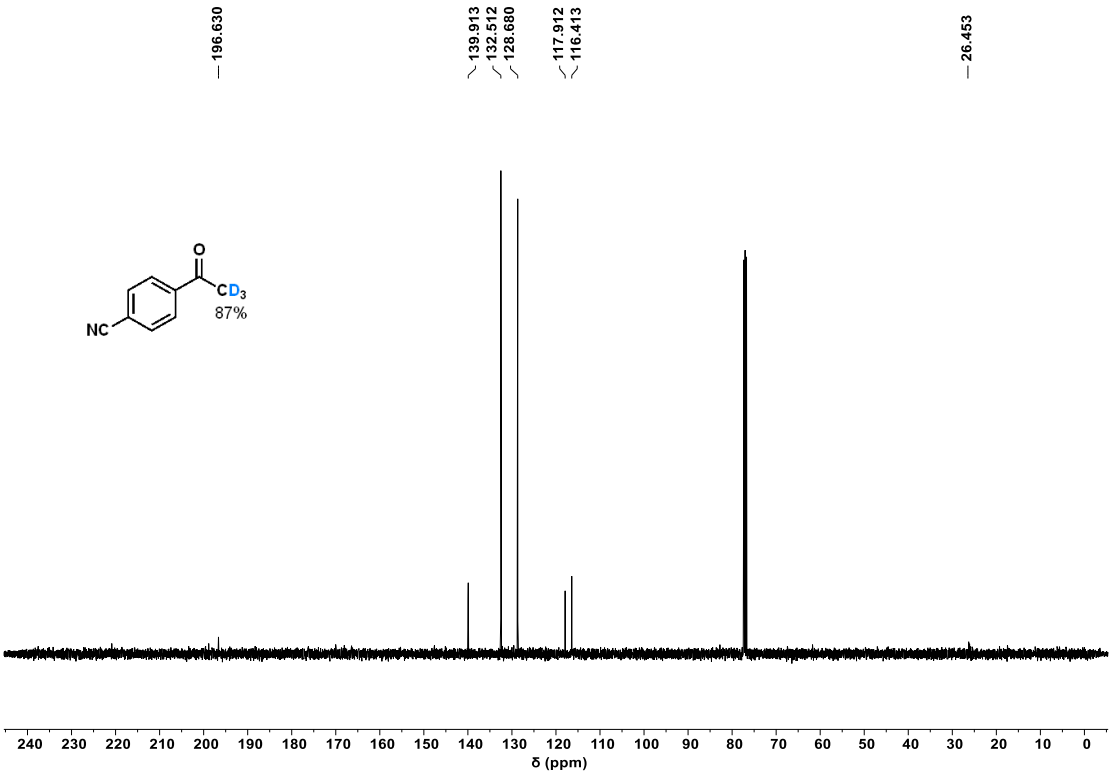


Figure S65. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **20**

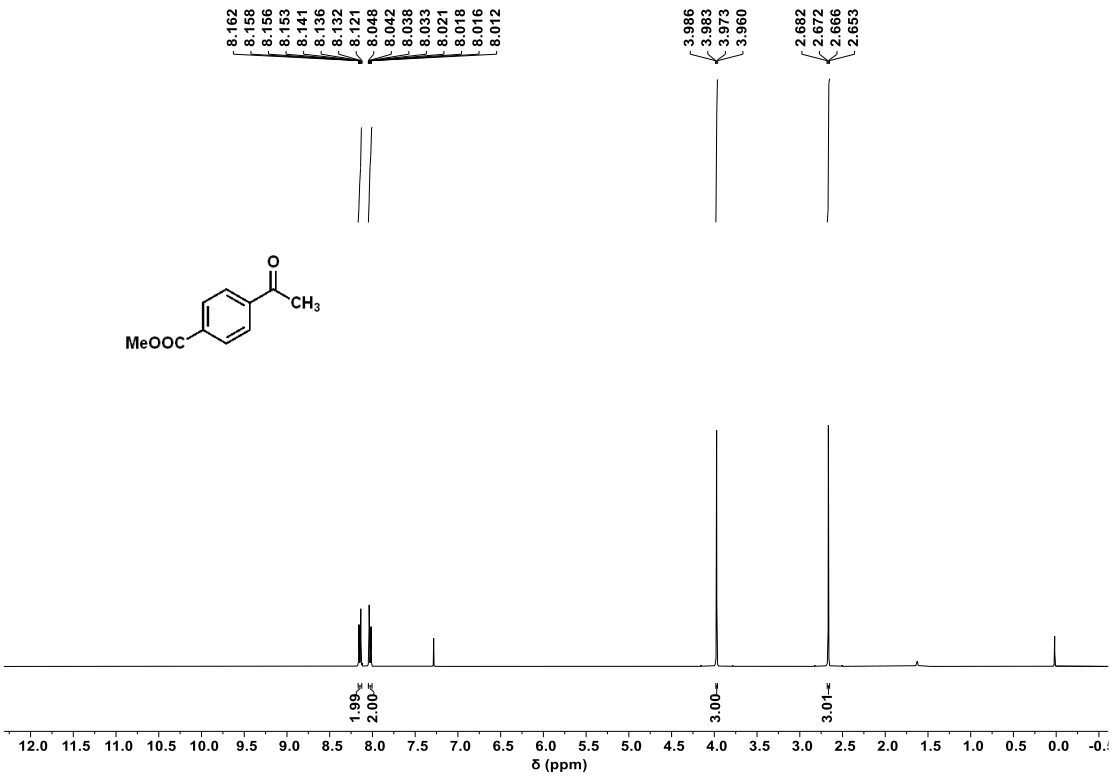


Figure S66. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S21**

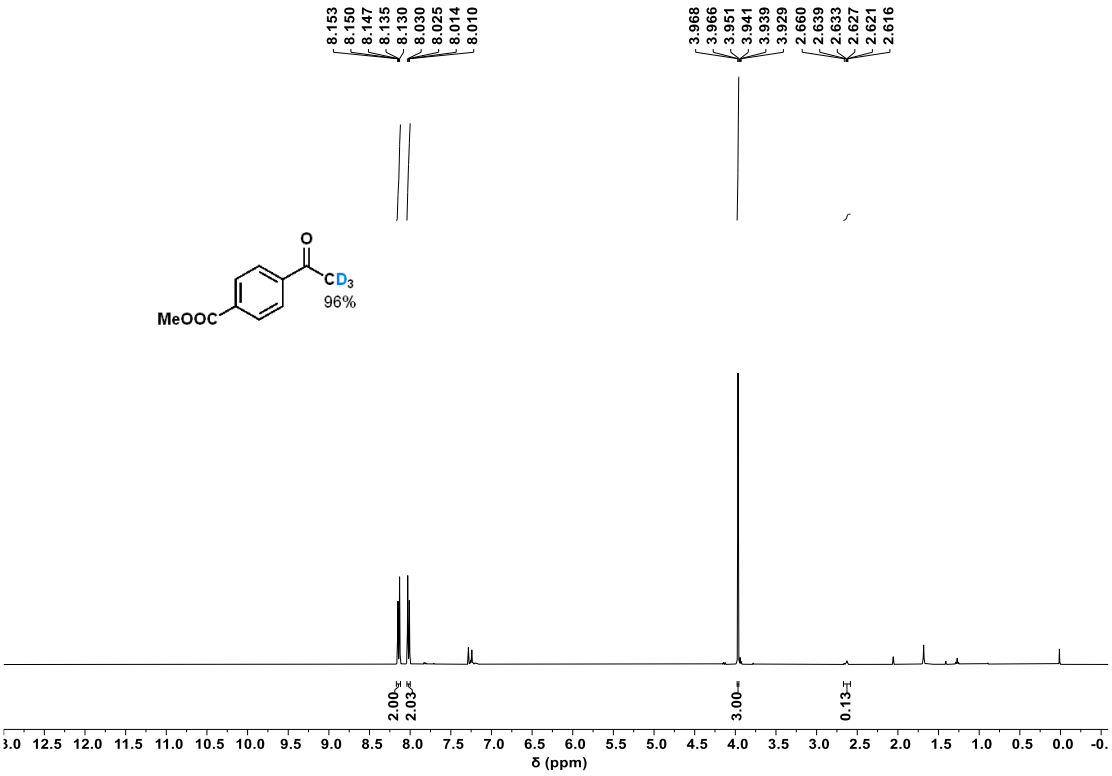


Figure S67. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **21**

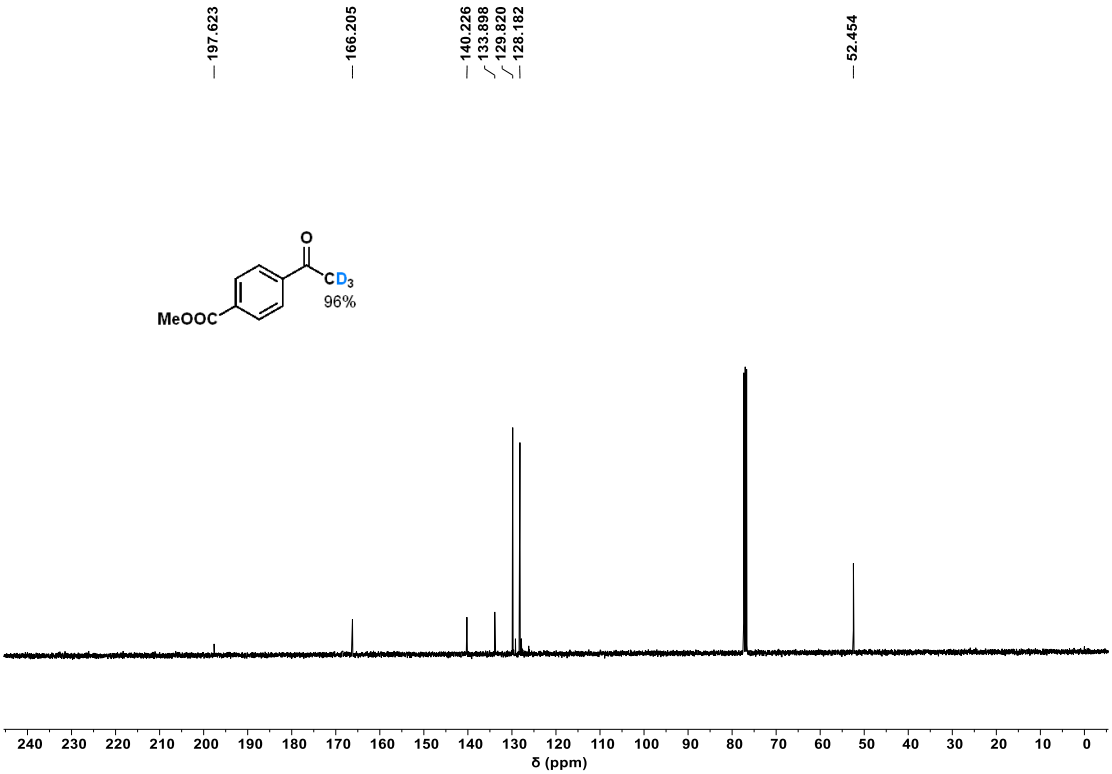


Figure S68. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **21**

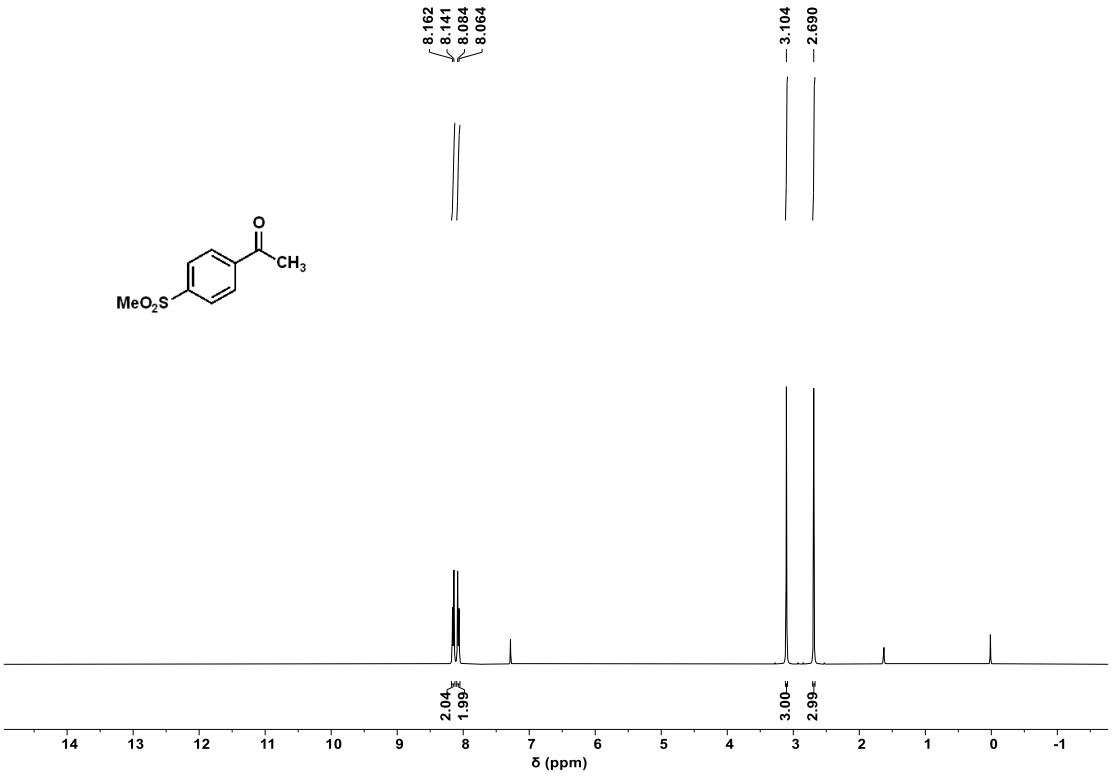


Figure S69. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S22**

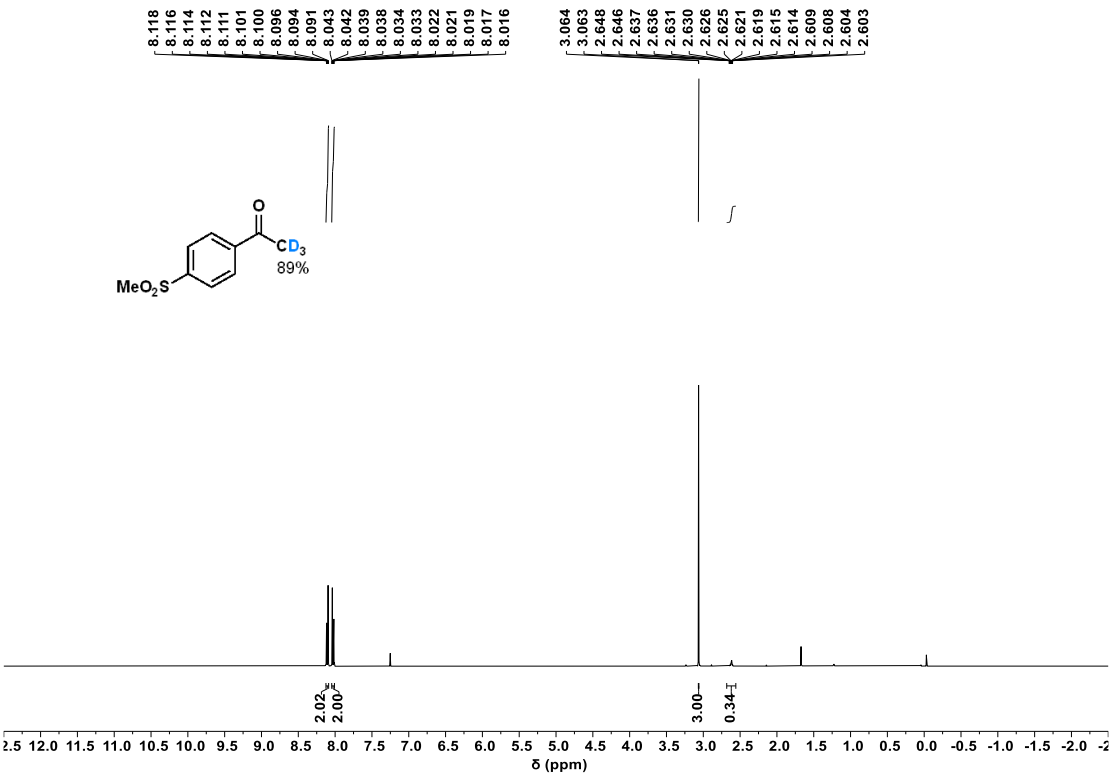


Figure S70. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **22**

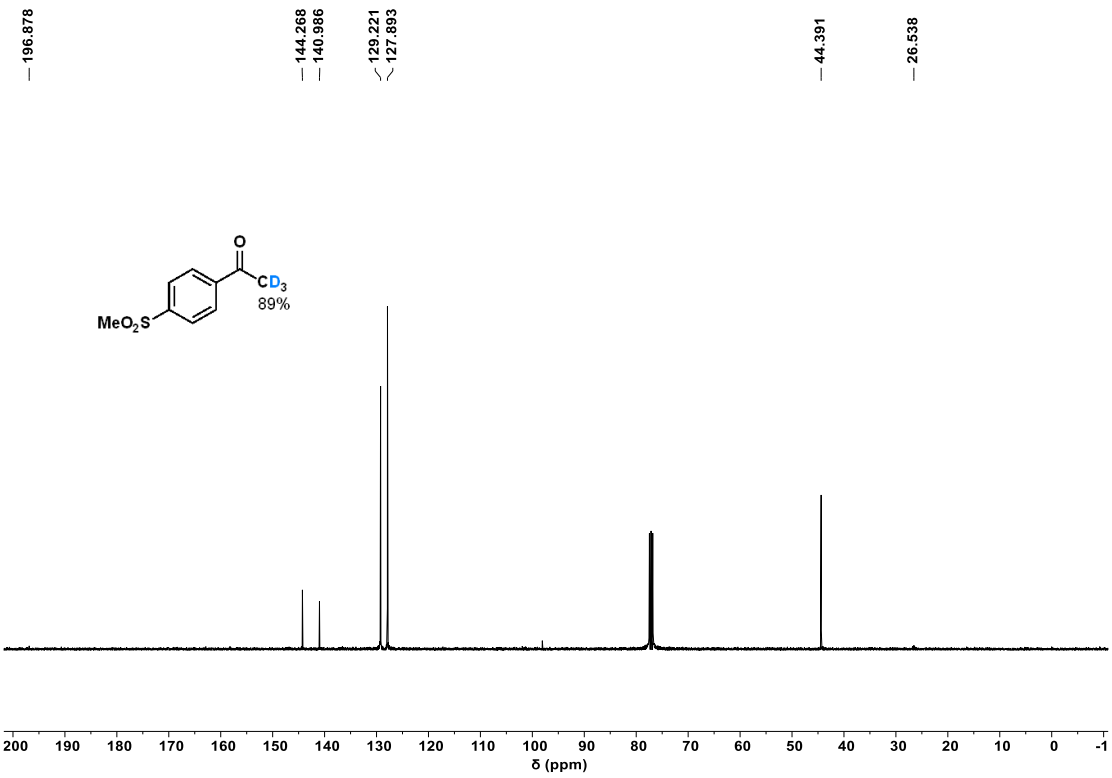


Figure S71. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **22**

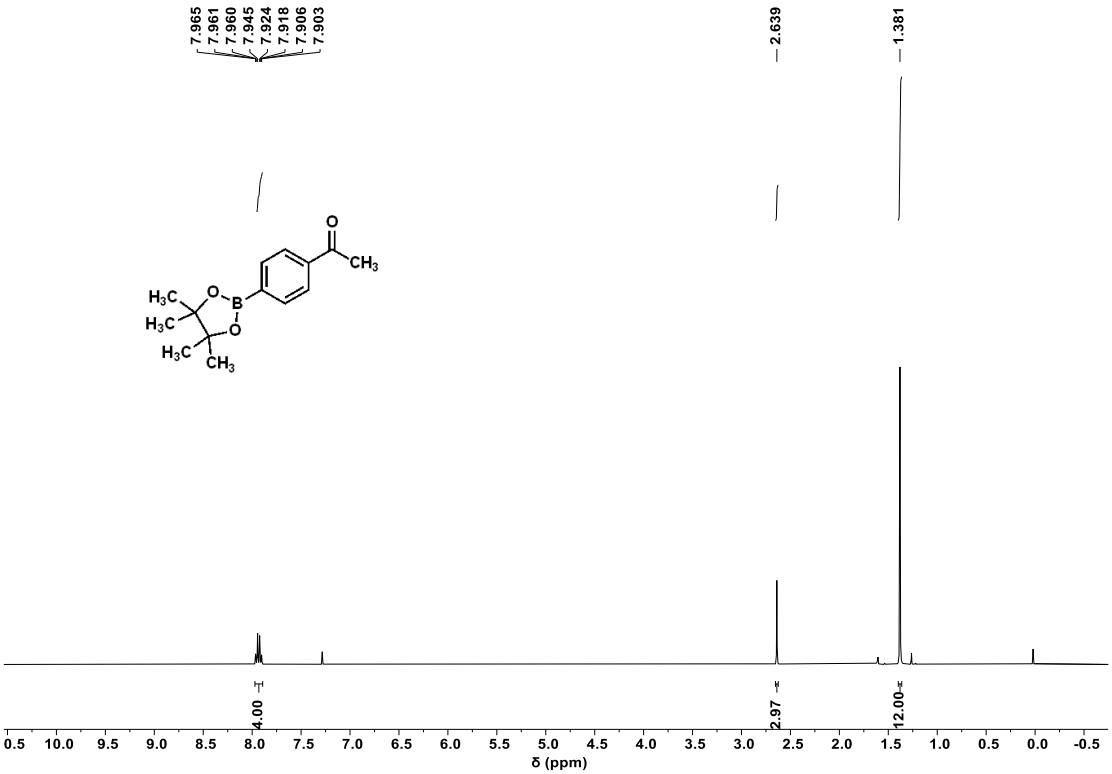


Figure S72. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S23**

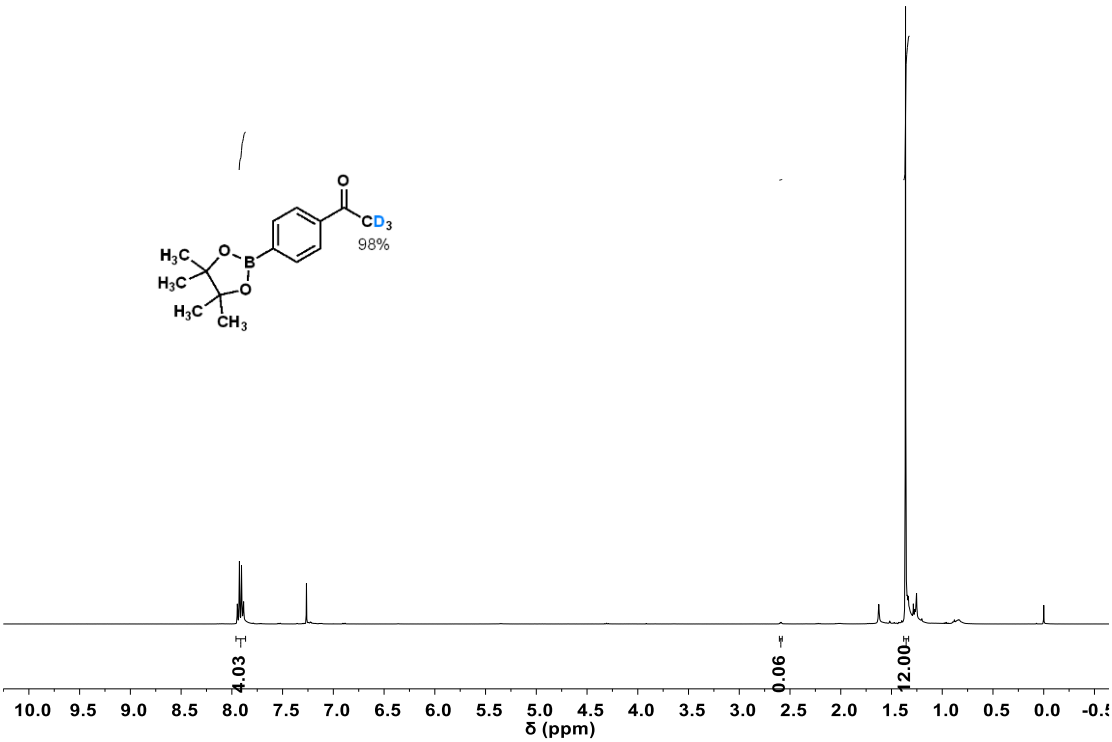


Figure S73. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **23**

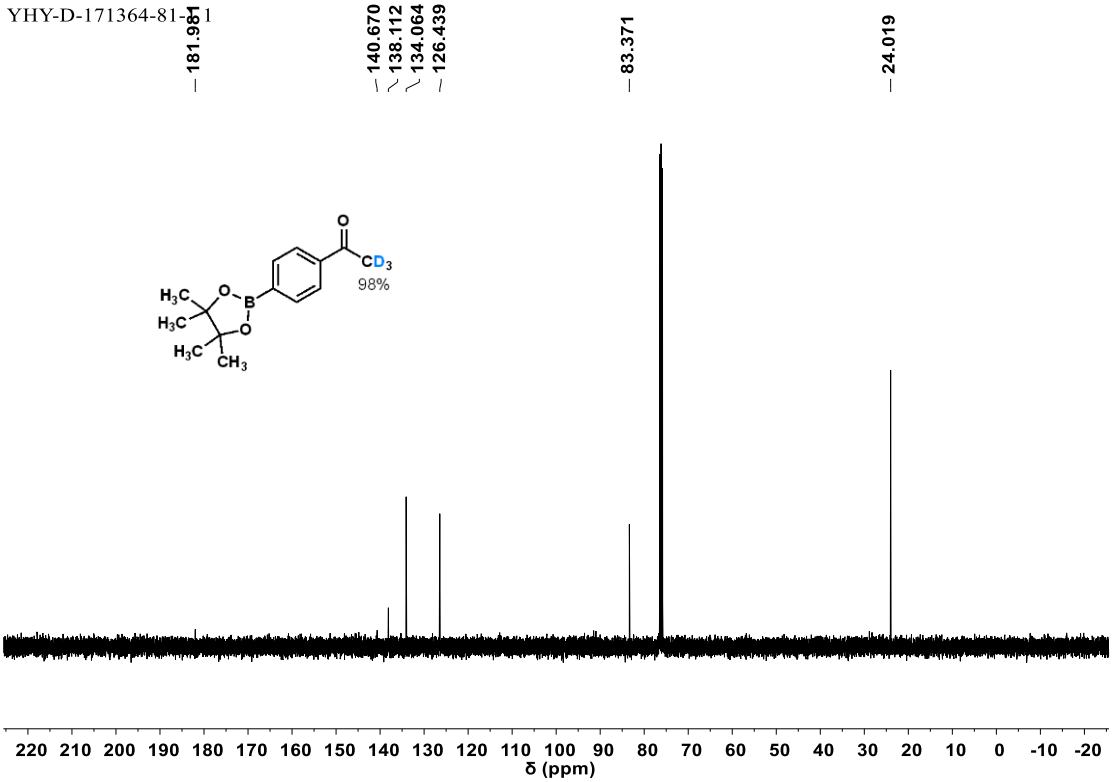


Figure S74. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **23**

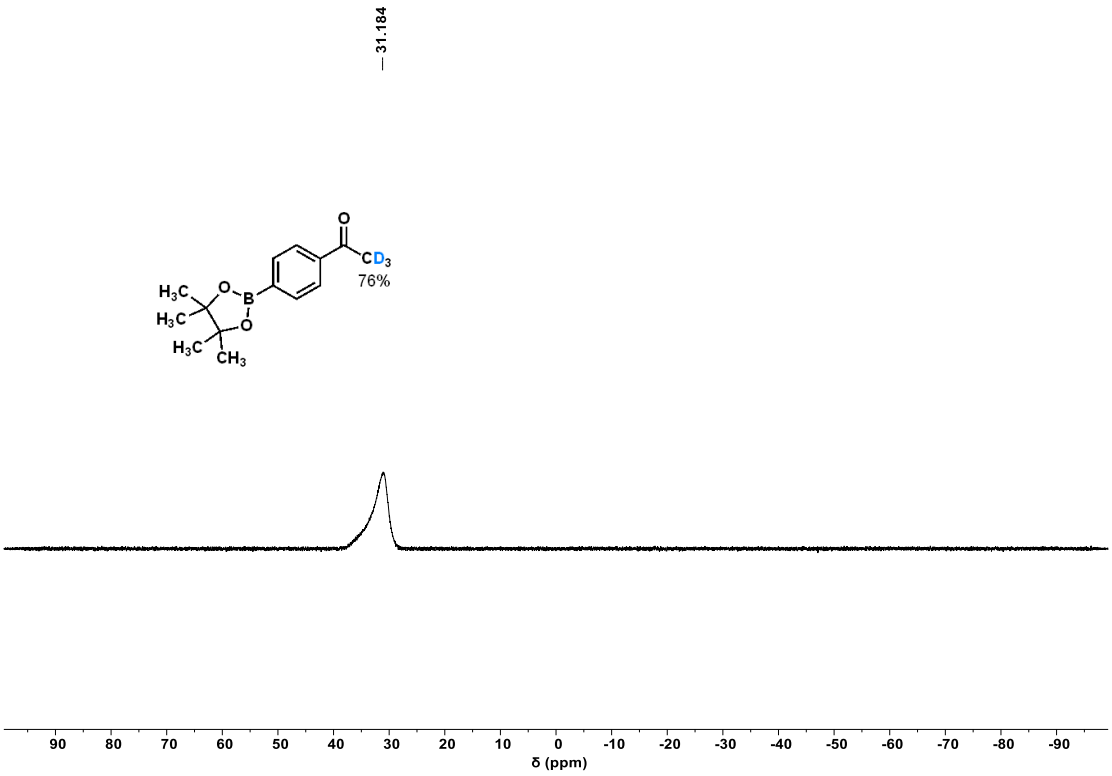


Figure S75. ^{11}B-NMR spectrum (128 MHz, $CDCl_3$) of **23**

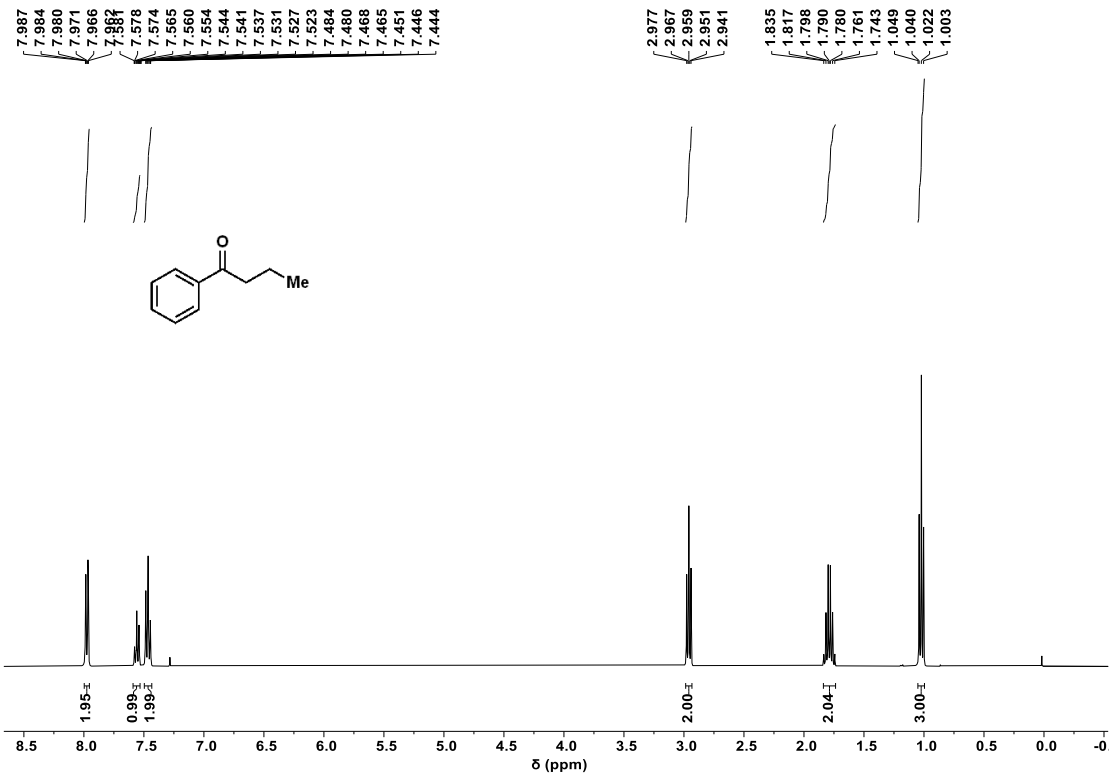


Figure S76. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S24**

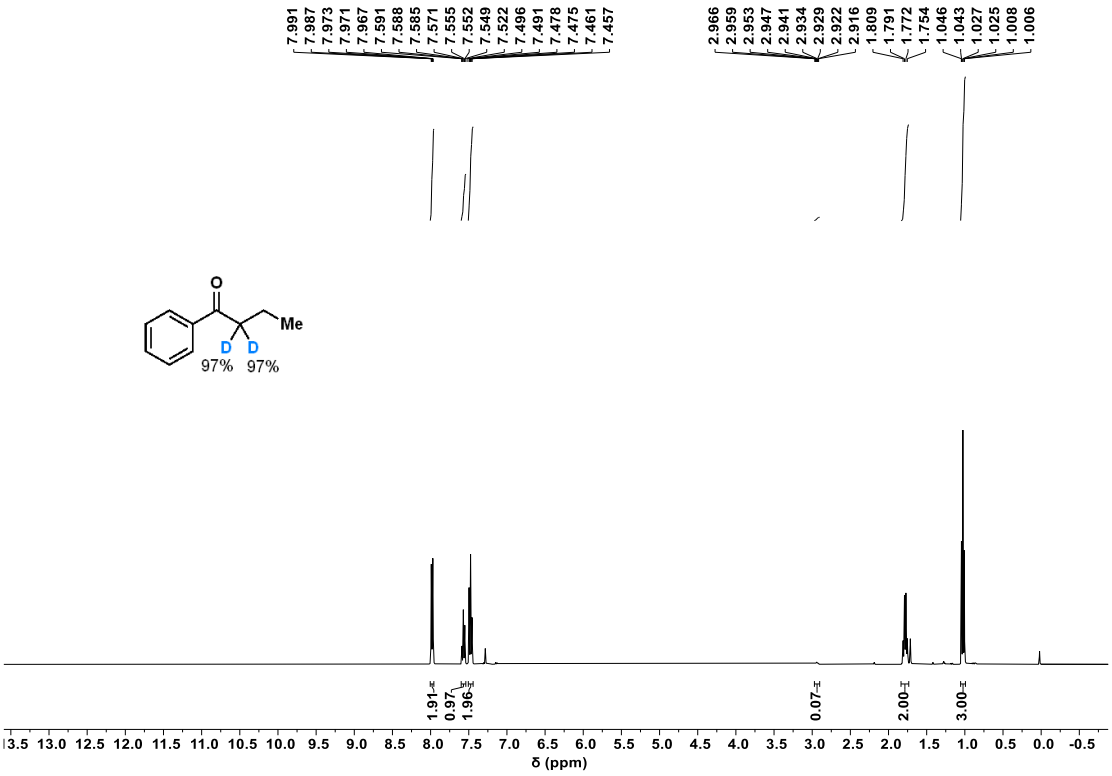
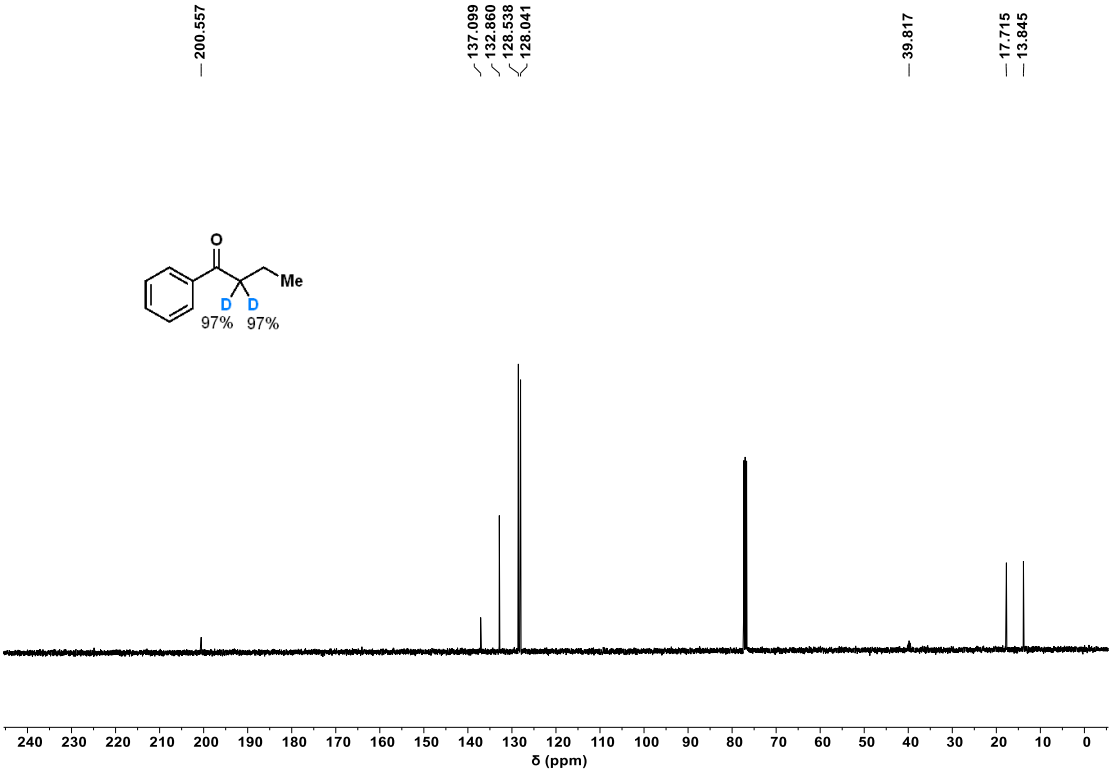


Figure S77. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **24**



F**igure S78.** ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **24**

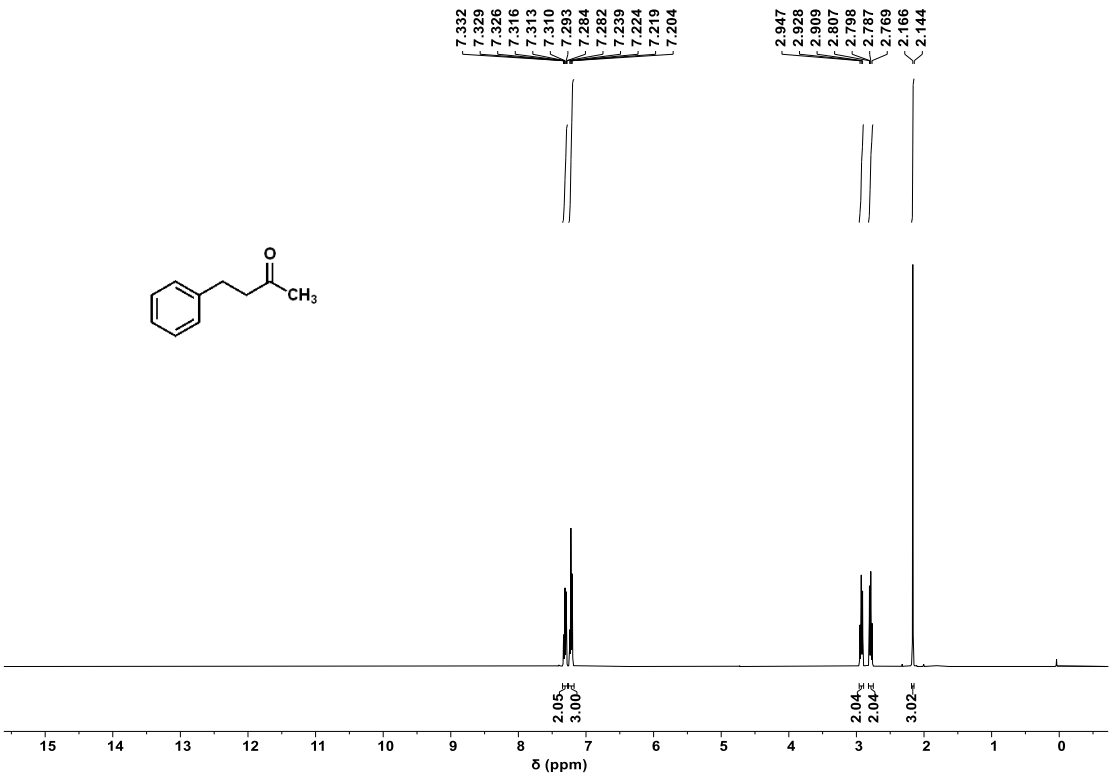


Figure S79. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **S25**

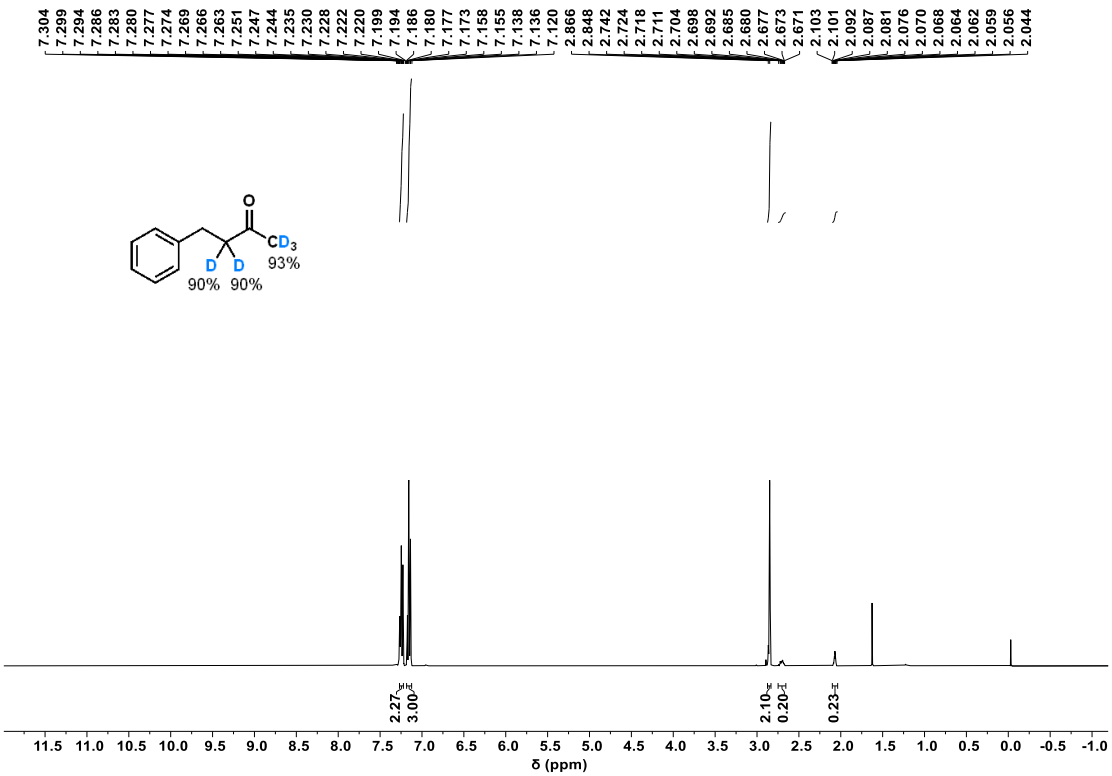


Figure S80. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **25**

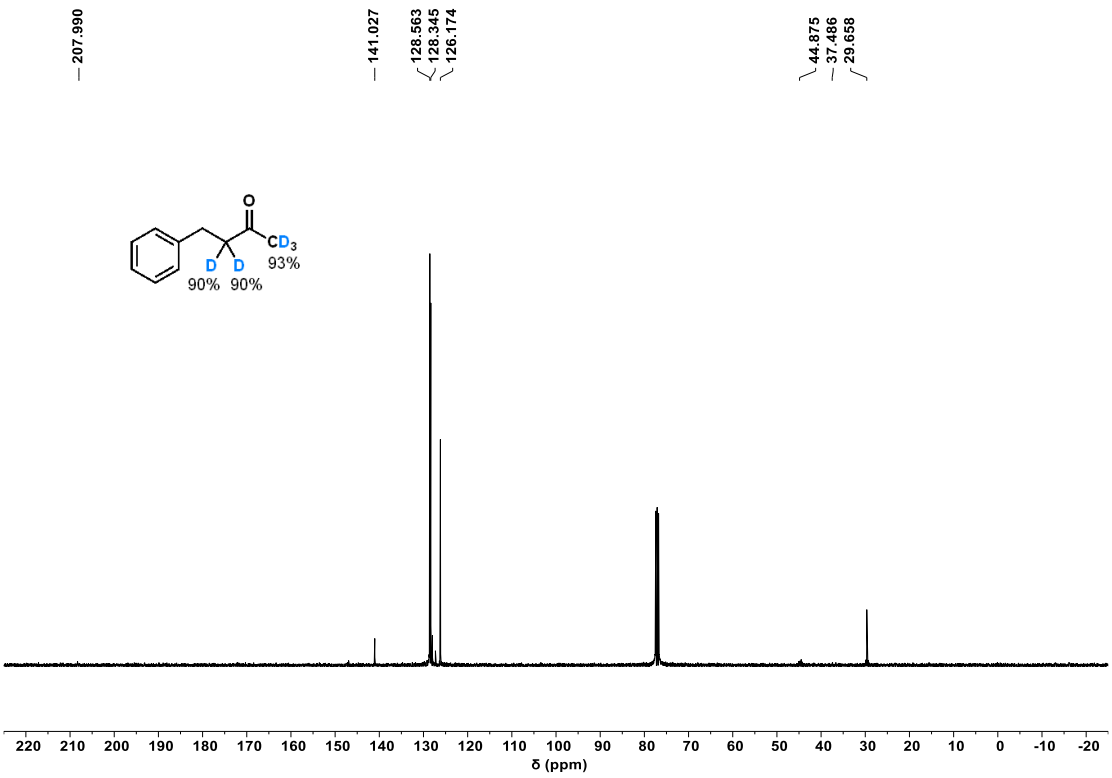


Figure S81. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **25**

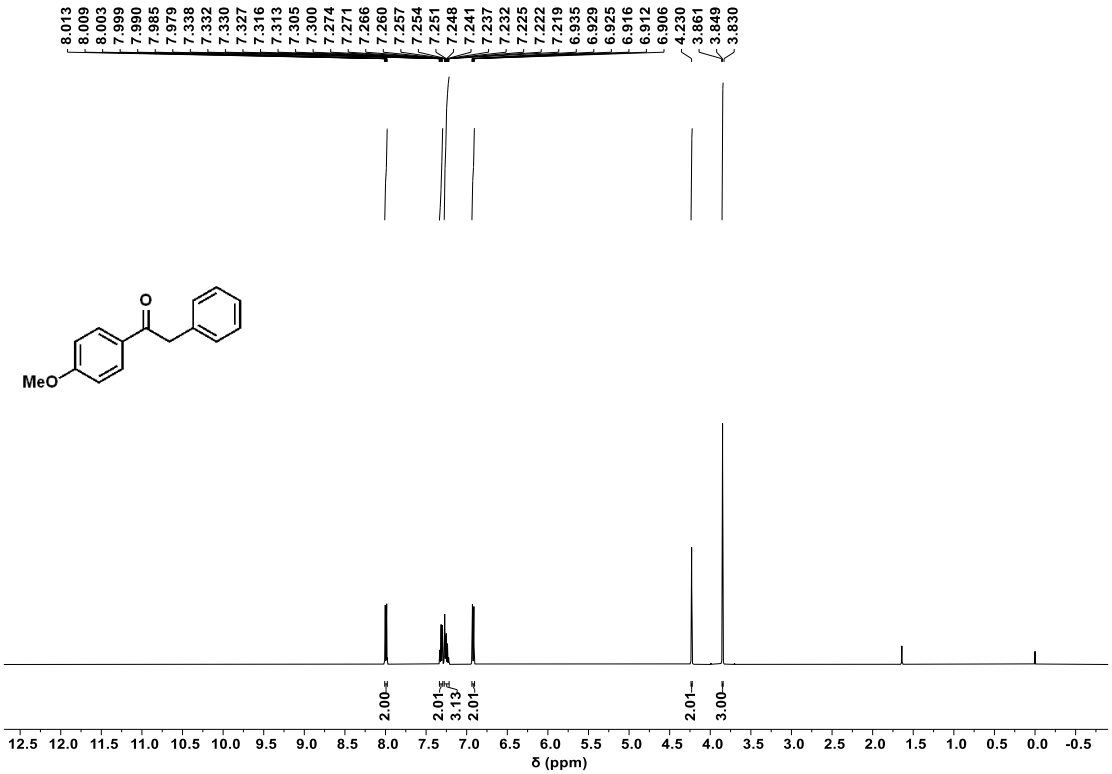


Figure S82. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S26**

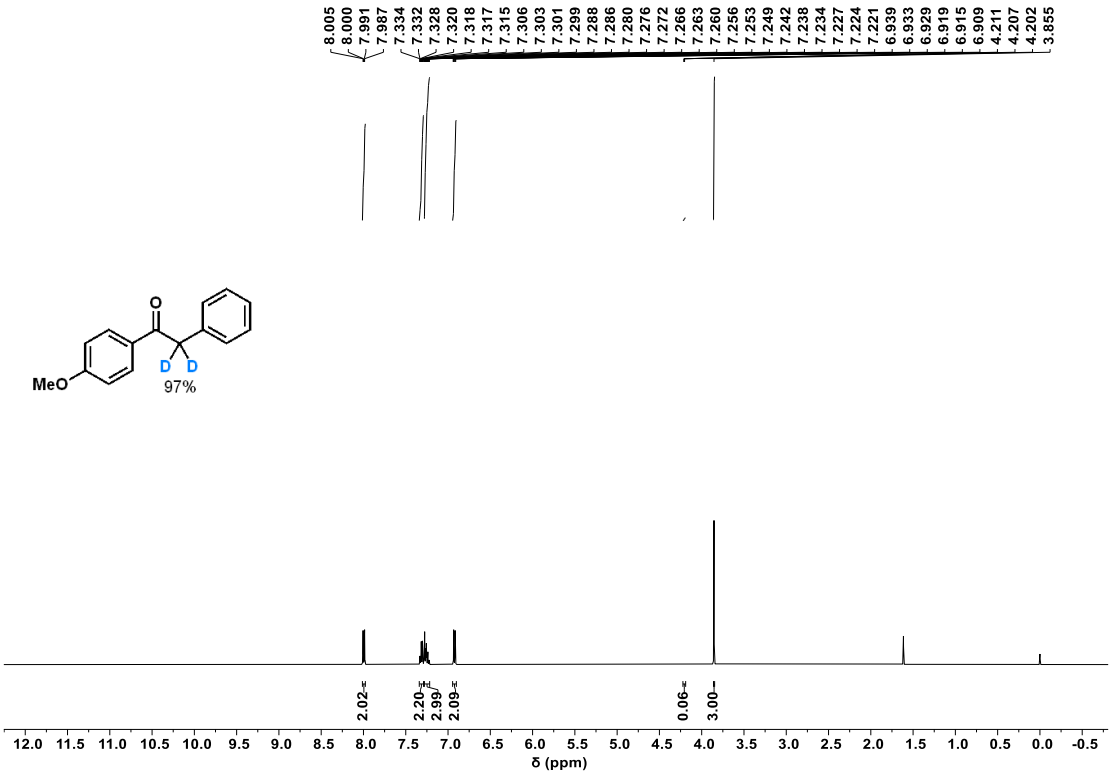


Figure S83. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **26**

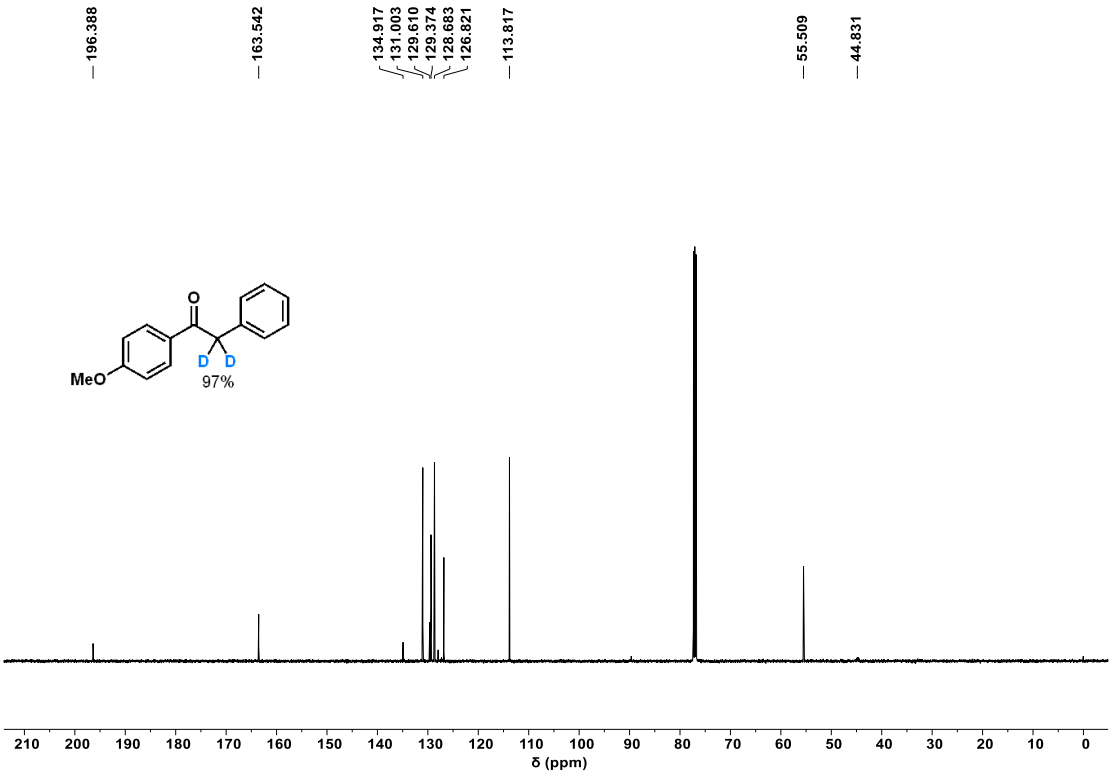


Figure S84. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **26**

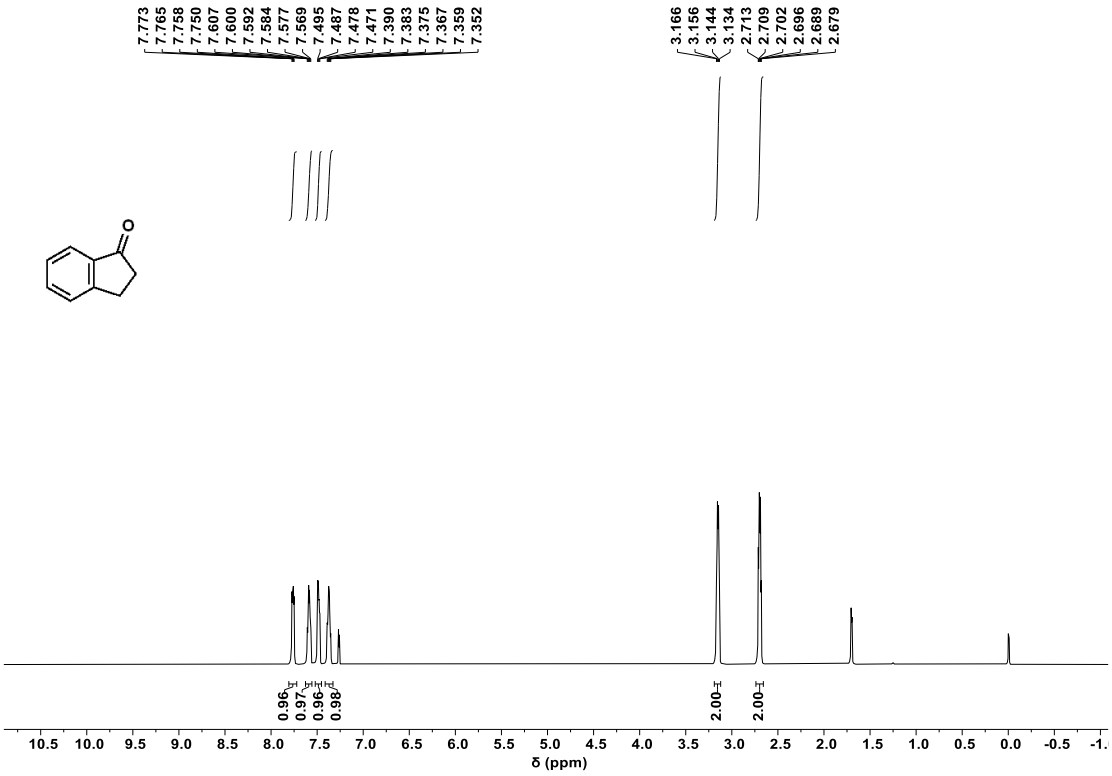


Figure S85. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S27**

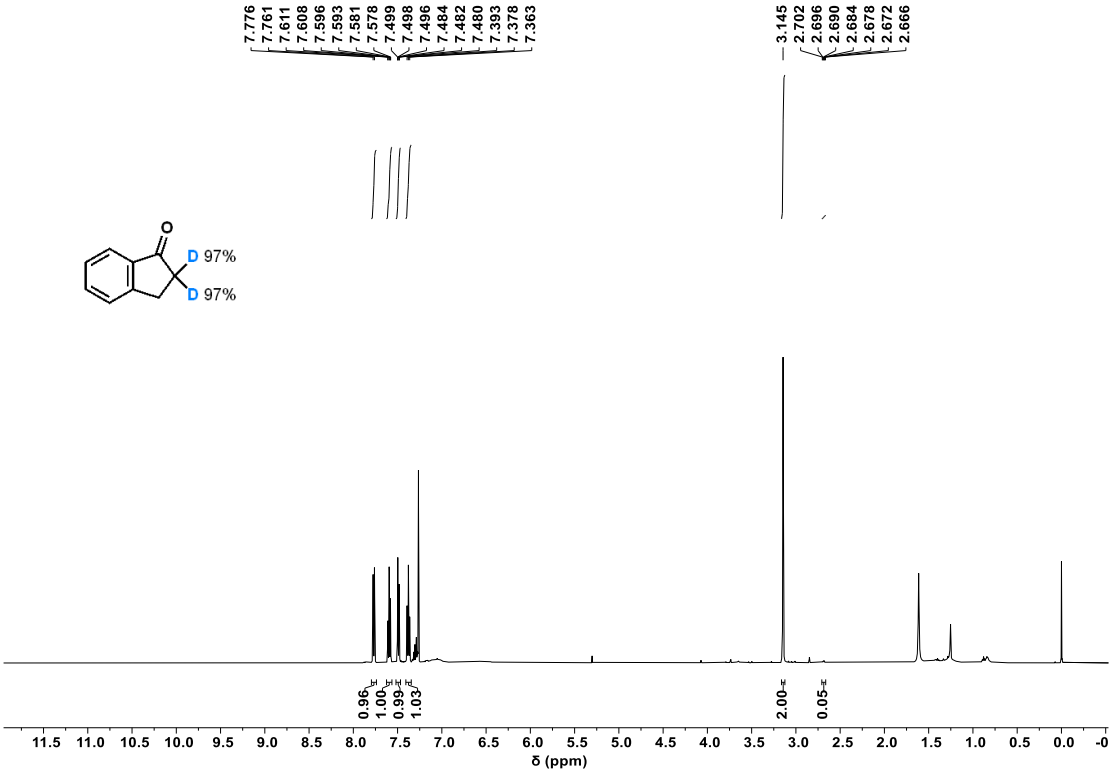


Figure S86. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **27**

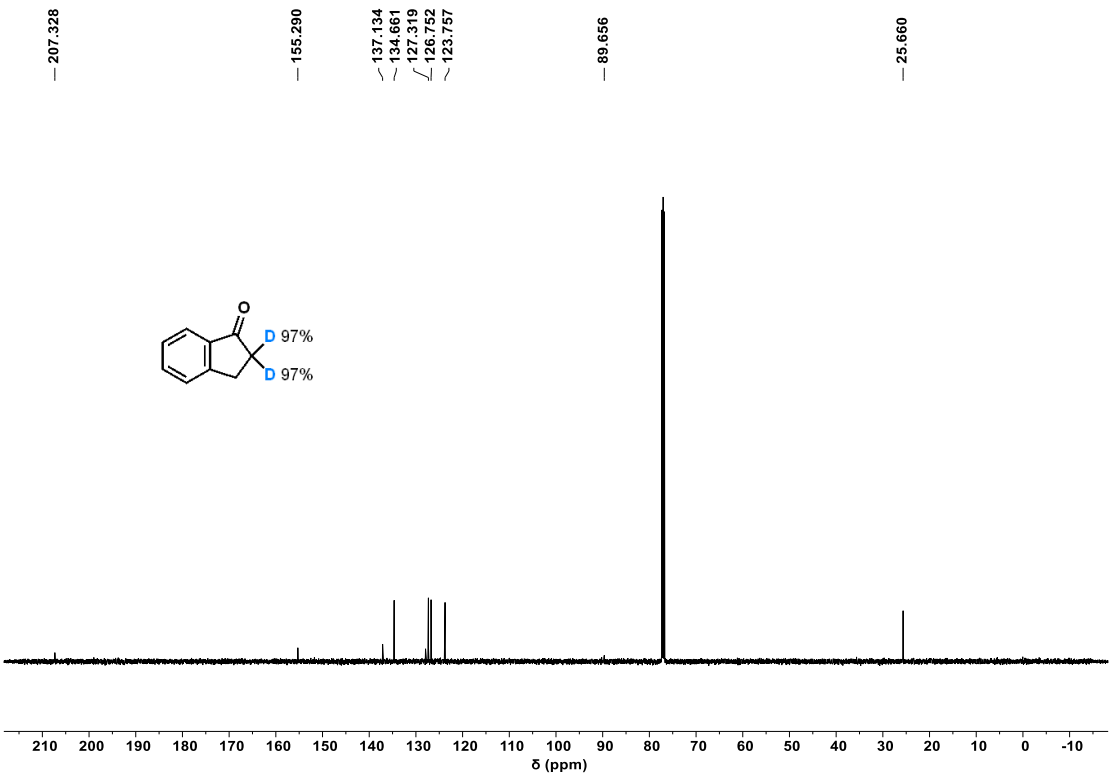


Figure S87. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **27**

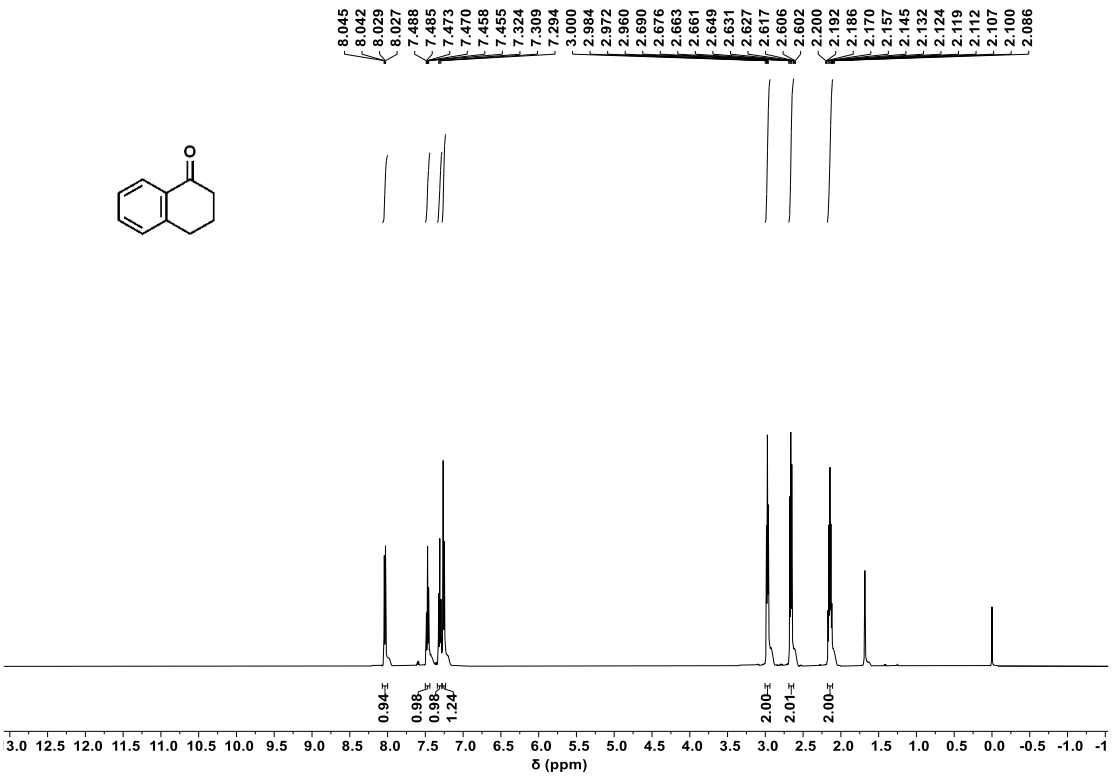


Figure S88. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S28**

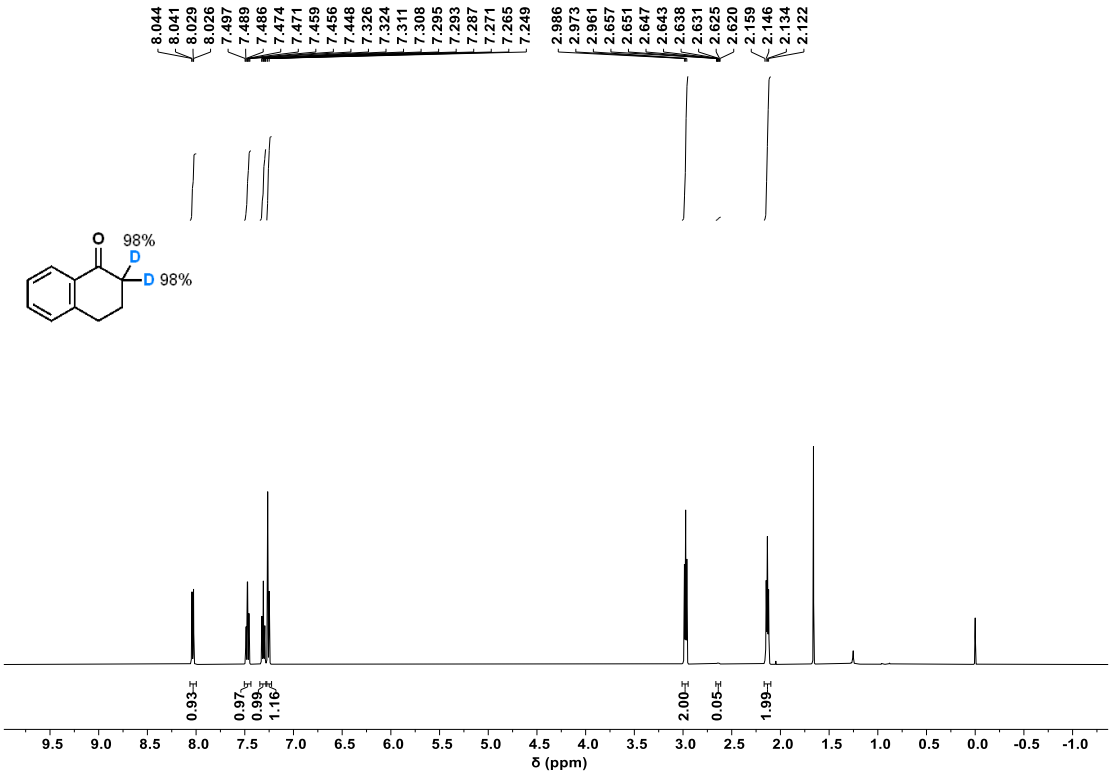


Figure S89. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **28**

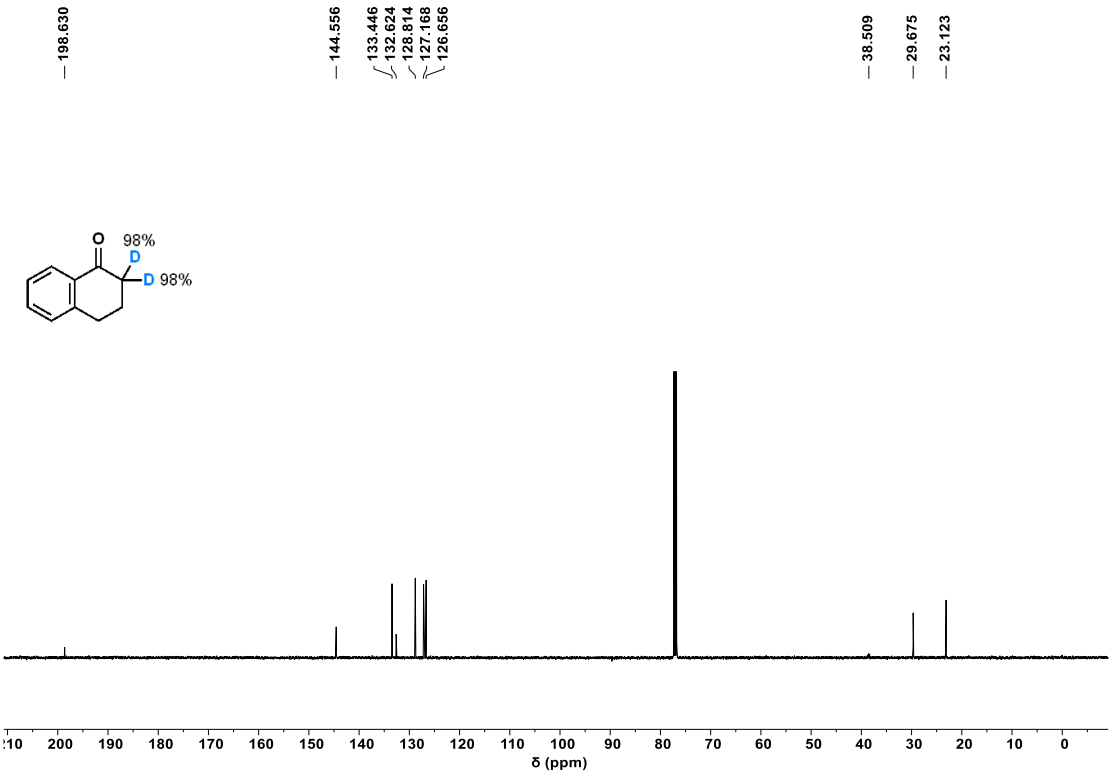


Figure S90. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **28**

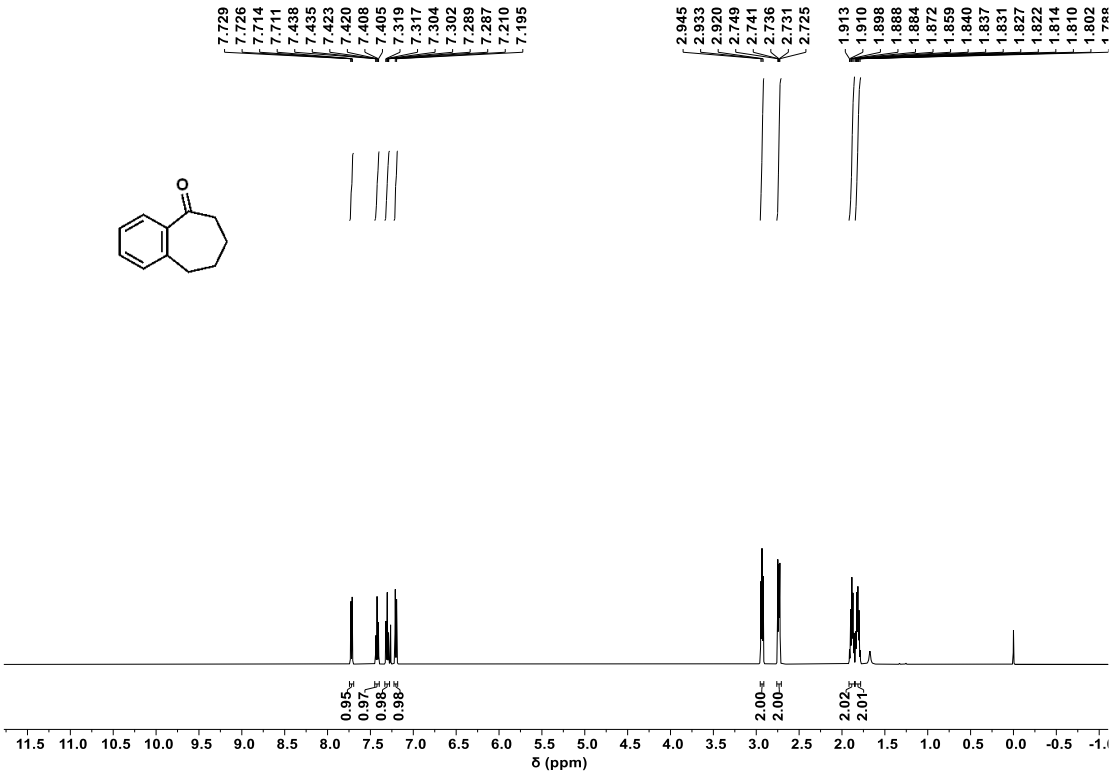


Figure S91. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S29**

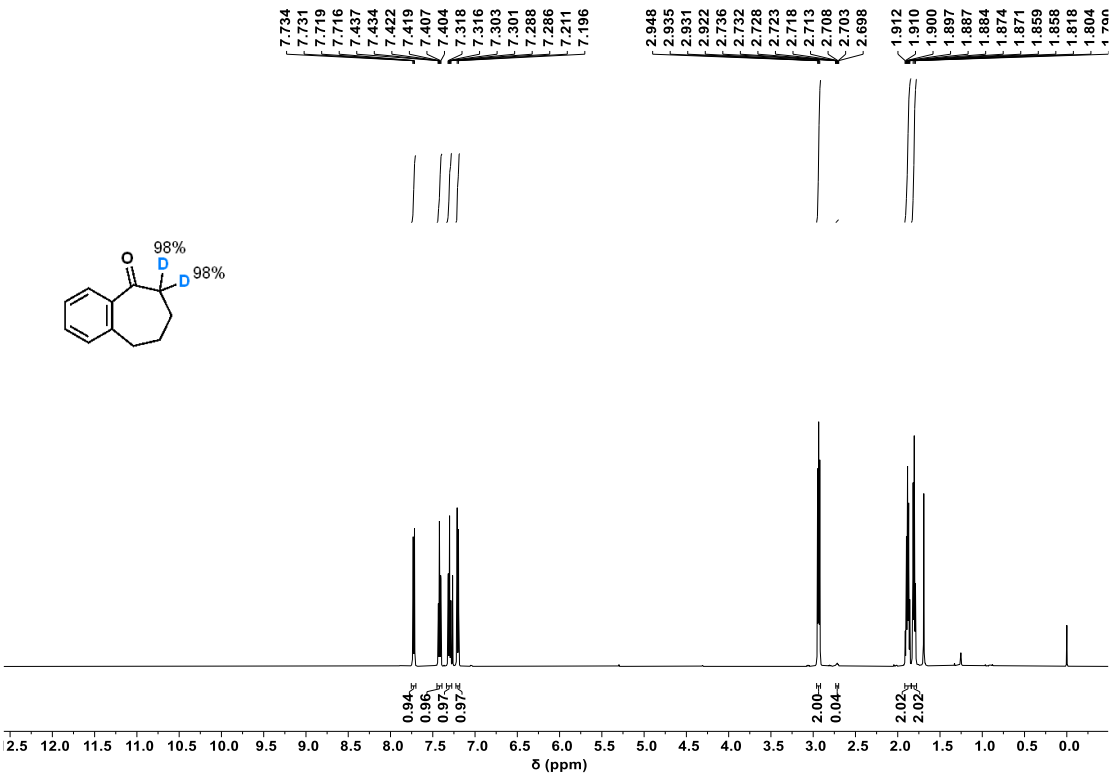


Figure S92. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **29**

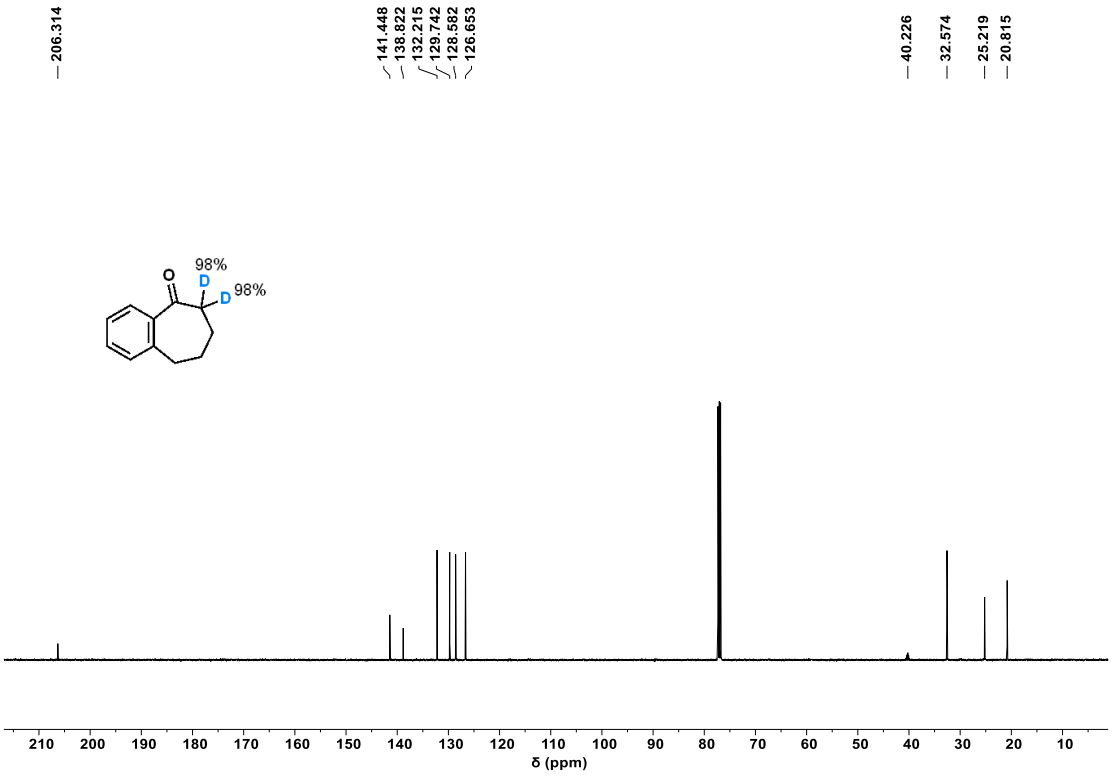


Figure S93. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **29**

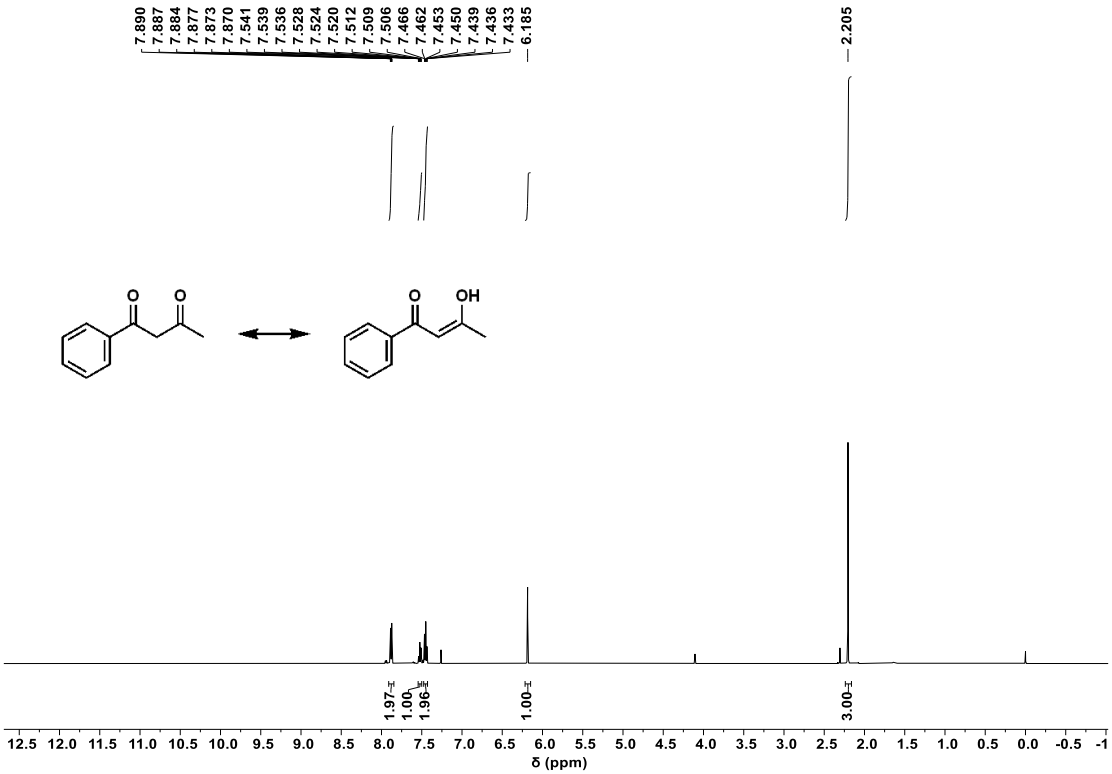


Figure S94. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S30**

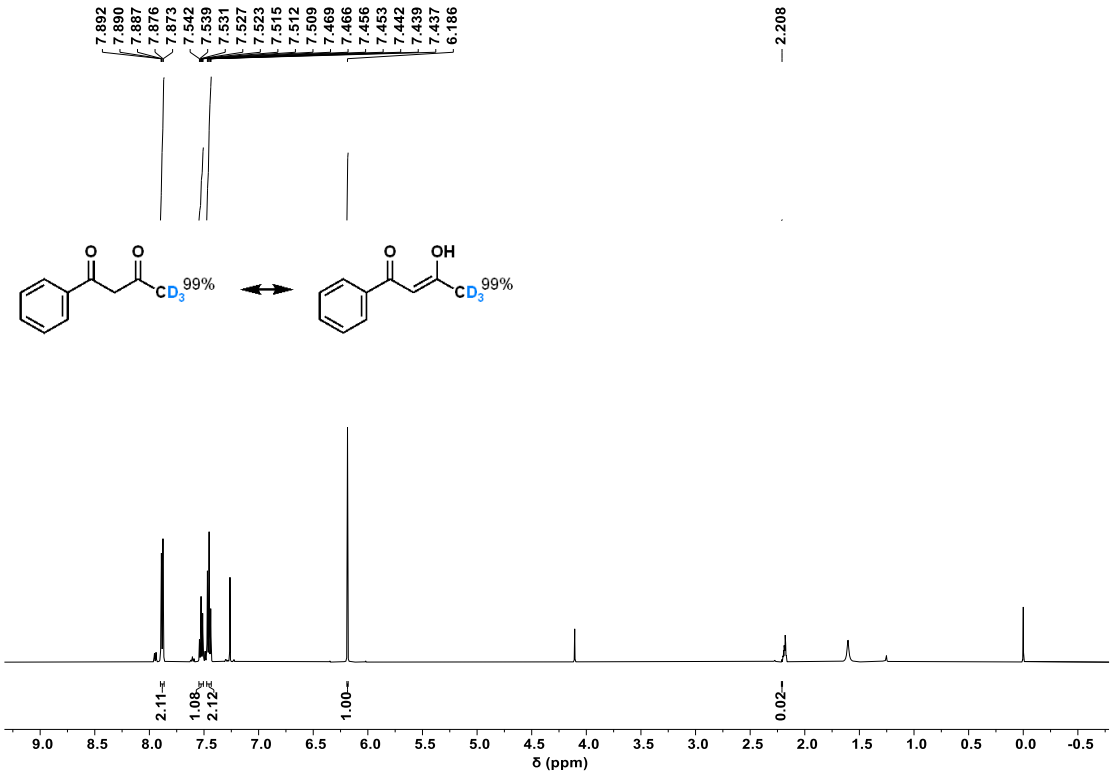


Figure S95. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **30**

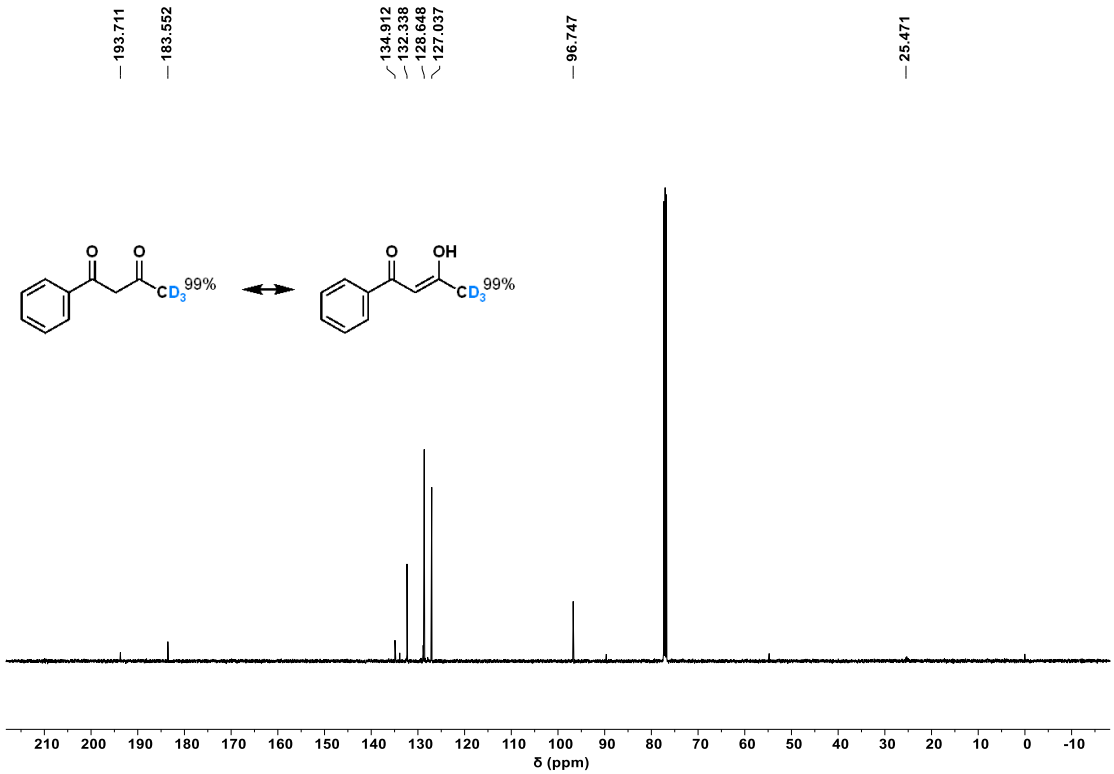


Figure S96. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **30**

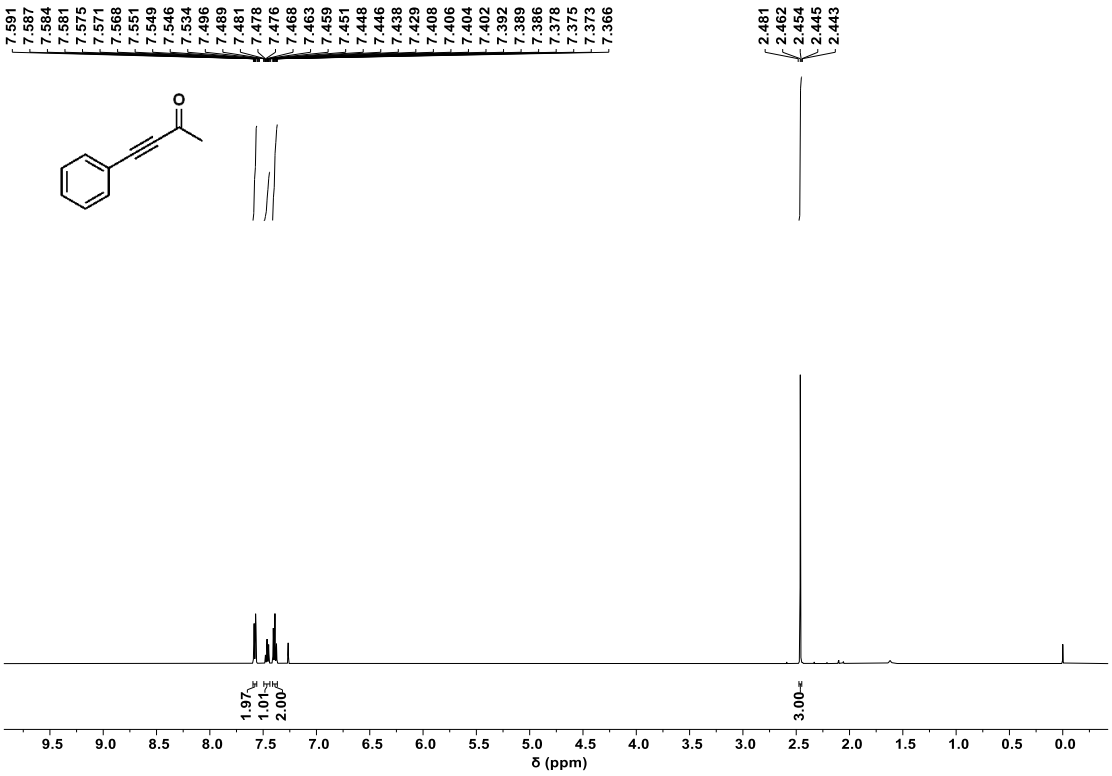


Figure S97. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **S31**

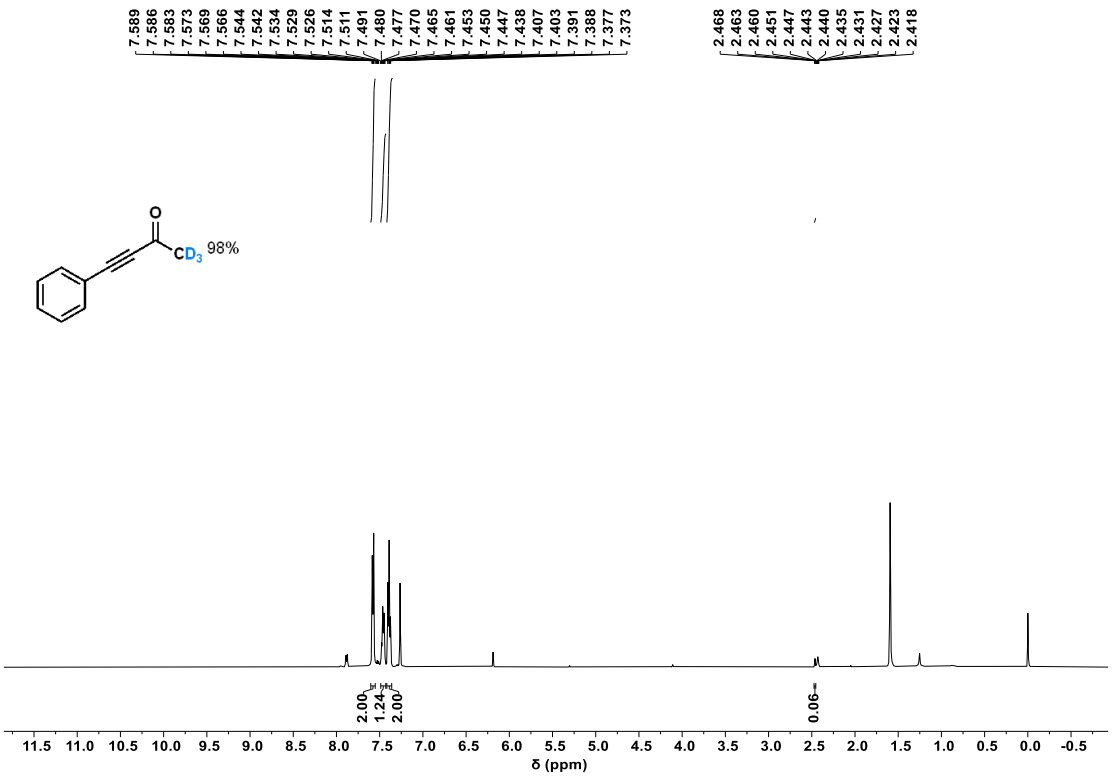


Figure S98. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **31**

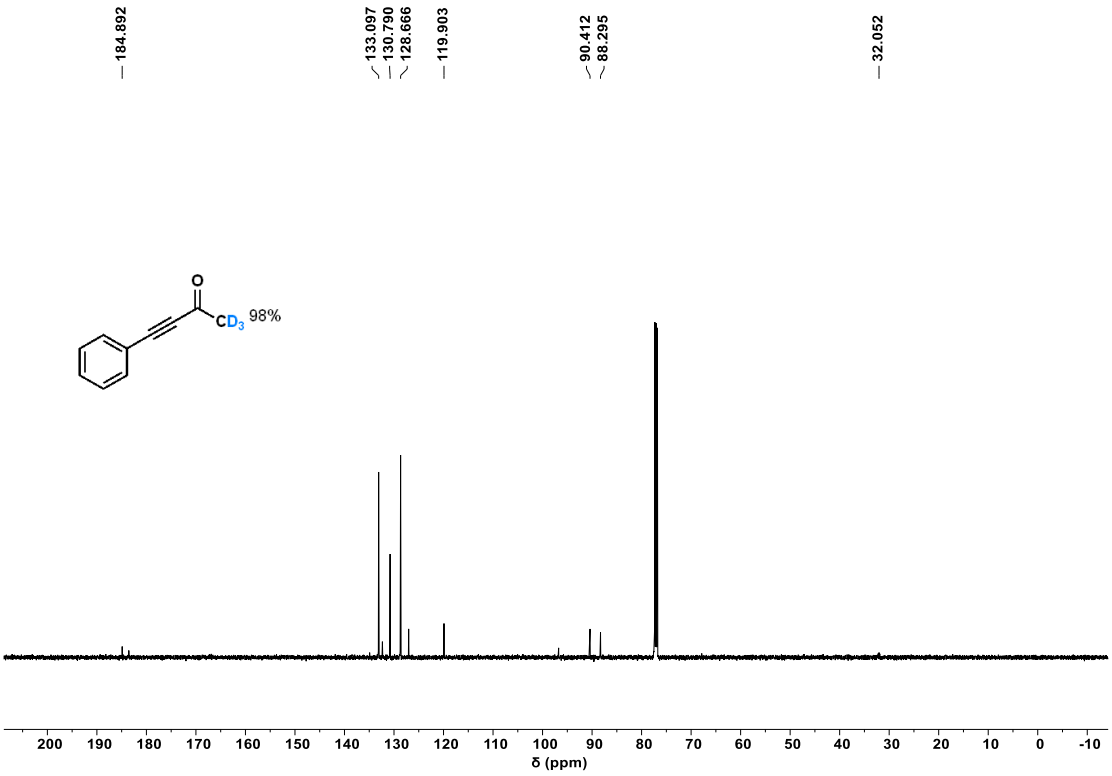


Figure S99. ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **31**