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Cascade Alkylation and Deuteration with Aryl Iodide via Pd/Noborene Catalysis: An Efficient Method for the Synthesis of Congested Deuterium-Labeled Arenes

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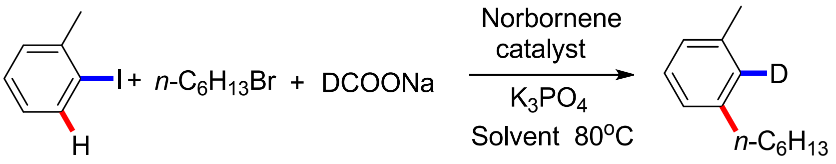
Supporting Information

General: NMR spectra were recorded at 23ºC on a Varian 400 MHz NMR spectrometer, operating at 499.7 MHz for proton, in $CDCl_3$ unless otherwise noted. Chemical shifts were determined relative to residual $CHCl_3$ (7.26 ppm) for proton, and to the $CDCl_3$ “triplet” at 77.23 ppm for carbon. All yields reported refer to isolated yields unless otherwise indicated. GC-MS experiments were carried out using an Agilent 6890 series GC and a 5973 Mass Selective Detector System. All the solvents were degassed by purging with dry nitrogen for 2h before use. All the reagents were purchased from commercial sources and used as received.

Experimental Section:

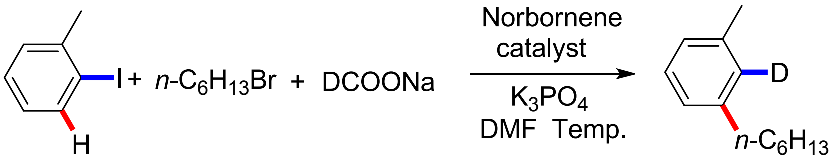
Table S1: Optimization of the catalysts:



Entry	"Pd" catalyst	Solvent	Yield[a]	D incorporation[a]
1	$Pd(OAc)_2$+$(furan)_3P$	DMF	12	>98
2	**$Pd(OAc)_2$+Ph_3P**	DMF	**39**	>98
3	**$Pd(OAc)_2$+$(4\text{-}OMePh)_3P$**	DMF	**39**	>98
4	$Pd(OAc)_2$+$(4\text{-}MePh)_3P$	DMF	35	>98
5	$Pd(OAc)_2$+$(2\text{-}MePh)_3P$	DMF	26	>98
6	$Pd(OAc)_2$+PCY3	DMF	19	>98
7	$Pd(OAc)_2$+S-Phos	DMF	15	>98
8	$Pd_2(dba)_3$+Ph_3P	DMF	34	>98
9	$Pd_2(dba)_3$+S-Phos	DMF	11	>98
10	$Pd(OAc)_2$+Ph_3P	DMSO	31	>98

[a] Determined by GC/MS.

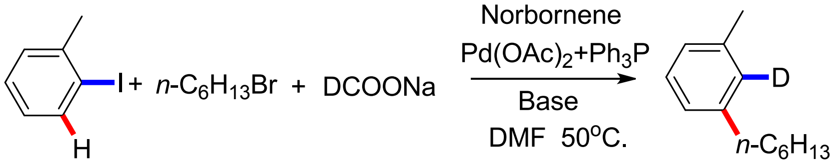
Table S2: Optimization of temperature:



Entry	"Pd" catalyst	Temp.	Yield[a]	D incorporation[a]
1	$Pd(OAc)_2$+Ph_3P	40	47	>98
2	$Pd(OAc)_2$+Ph_3P	50	74	>98
3	$Pd(OAc)_2$+Ph_3P	60	45	>98
4	$Pd(OAc)_2$+Ph_3P	70	37	>98
5	$Pd(OAc)_2$+Ph_3P	80	39	>98
6	$Pd(OAc)_2$+Ph_3P	100	34	>98
7	$Pd(OAc)_2$+$(4\text{-}OMePh)_3P$	50	44	>98
8	$Pd_2(dba)_3$+Ph_3P	50	58	>98

[a] Determined by GC/MS.

Table S3: Optimization of base:



Entry	Base (ratio)	Yield[a]	D incorporation[a]
1	Cs_2CO_3	25	>98
2	K_2CO_3	25	>98
3	KOAc	46	>98
4	Na_2CO_3	20	>98
5	KOH	34	>98
6	NaOH	0	>98
7	CsOAc	39	>98
8	K_3PO_4+KOAc (3:2)	89	>98
9	K_3PO_4+KOAc (4:1)	56	>98
10	K_3PO_4+KOAc (4:2)	57	>98
11	K_3PO_4+KOAc (5:1)	56	>98
12	K_3PO_4+KOAc (5:2)	88	>98
13	K_3PO_4+KOAc (6:2)	94	>98
14	K_3PO_4+KOAc (6:3)	94	>98
14	K_3PO_4+KOAc (6:6)	69	>98

[a]Determined by GC/MS.

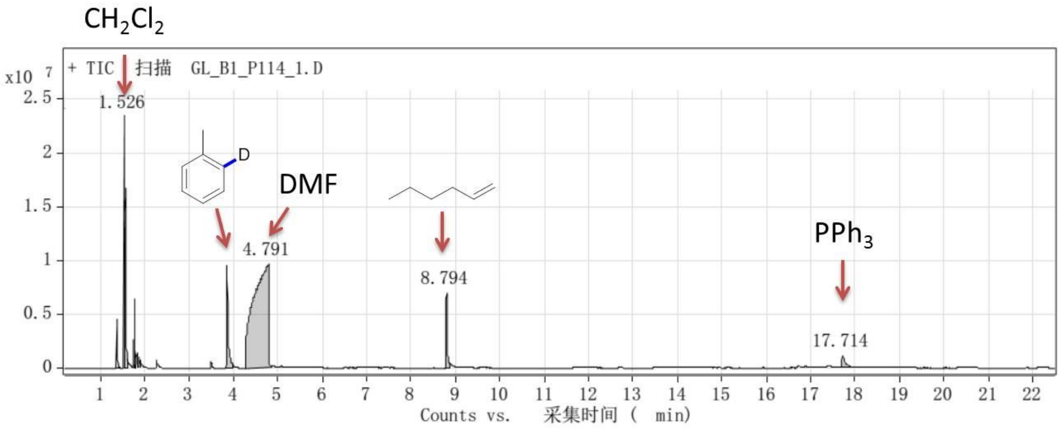
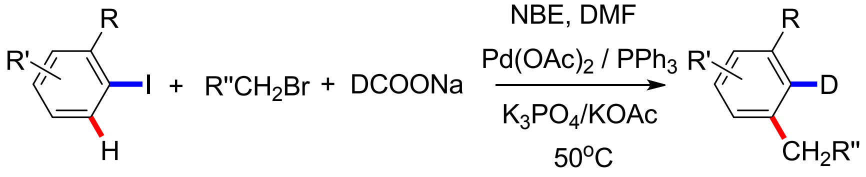
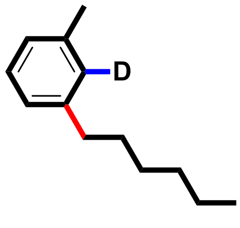


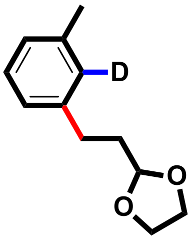
Figure S1: **GC-MS profile of the reaction with $NaBD_4$ as deuterium source (entry 2, table 1). The compound 1-hexene is probably formed by elimination of hydrogen bromide from 1-bromohexane. The sample for GC-MS analysis was prepared with CH_2Cl_2 as solvent. Fully conversion of 2-iodotoluene to 2-d-toluene indicated that $NaBD_4$ should have higher reactivity to aryl iodide over norbornene.**



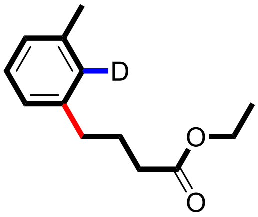
General procedure for the synthesis of deuterated arene 3 with DCOONa as deuterium source: In a argon glovebox, to an 10 mL vial containing Pd(OAc)$_2$ (44 mg, 0.2 mmol), PPh$_3$ (52 mg, 0.2 mmol), norbornene (188 mg, 2 mmol), K$_3$PO$_4$ (2544 mg, 12 mmol), KOAc (490 mg, 5 mmol), DCOONa (276 mg, 4 mmol) and aryl iodide **1** (526 mg, 2 mmol) in DMF (10ml) was added alkylbromides **2** (6 mmol). Then the sealed vial was brought out of the glovebox and put into an oil bath with pre-set to 50°C. The reaction mixture was stirred vigorously until the GC-MS showed the reaction was completed. The reaction was quenched by water. Then, the mixture was extracted with dichloromethane (3 x 25 mL). The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. After removal of solvents under vacuum, the crude product was purified via column chromatography (silica gel) using the appropriate binary solvent system (vol/vol).



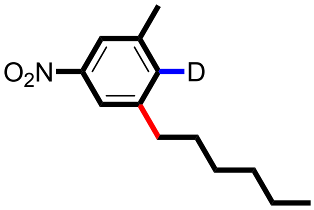
3a: Purified via column chromatography (hexane : CH$_2$Cl$_2$ = 50 : 1), Yield: 58% with hexyl bromide as starting material; 62% with hexyl iodide as starting material, colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.21 (t, *J* = 6.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.98 (s, 3H), 1.67 ~ 1.63 (m, 2H), 1.43 ~ 1.28 (s, 6H), 0.94 (t, *J* = 9.0 Hz, 3H).^{13}C NMR (125 MHz, CDCl$_3$): δ 142.8, 137.5, 128.1, 126.2, 125.4, 35.9, 31.7, 31.5, 29.0, 22.6, 21.3, 14.0. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{19}D^+$ ([M]$^+$) 177.1628; Found 177.1634.



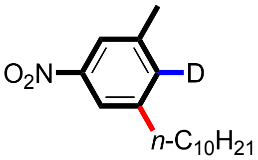
3b: Purified via column chromatography (hexane : CH$_2$Cl$_2$ = 5 : 1), Yield: 74% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18 (t, *J* = 7.5 Hz, 1H), 7.01 (dd, *J* = 7.4, 3.0 Hz, 2H), 4.91 (t, *J* = 4.7 Hz, 1H), 3.94 (m, 4H), 2.73 (dd, *J* = 9.5, 6.9 Hz, 2H), 2.33 (s, 3H), 1.99 (m, 2H).^{13}C NMR (125 MHz, CDCl$_3$): δ 141.88, 138.24, 128.68, 127.01, 125.78, 104.34, 77.00, 65.35, 35.95, 30.43, 21.70. HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{15}NaDO_2^+$ ([M+Na]$^+$) 216.1116; Found 216.1111.



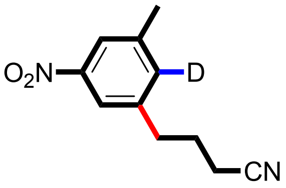
3c: Purified via column chromatography (hexane : CH_2Cl_2 = 4 : 1), Yield: 65% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.32 (m, 5H), 1.96 (dd, *J* = 15.0, 7.6 Hz, 3H), 1.26 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 141.1, 137.6, 127.9, 126.5, 125.3, 60.0, 34.9, 33.5, 26.4, 21.1, 14.1. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{17}NaDO_2^+$ ([M+Na]$^+$) 230.1269; Found 230.1267.



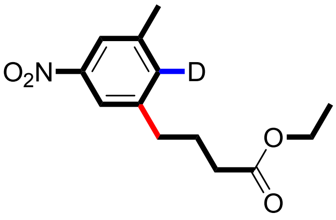
3d: Purified via column chromatography (hexane : CH_2Cl_2 = 4 : 1), Yield: 75% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (s, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.53 ~ 1.69 (m, 2H), 1.22 ~ 1.36 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.6, 144.6, 139.5, 135.1, 121.4, 120.6, 35.7, 31.8, 31.2, 29.0, 22.7, 21.3, 14.2. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{18}NKDO_2^+$ ([M+K]$^+$) 261.1114; Found 216.1110.



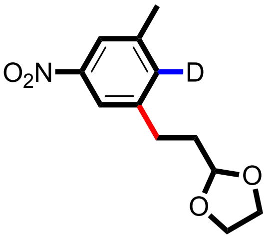
3e: Purified via column chromatography (hexane : CH_2Cl_2 = 6 : 1), Yield: 71% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (s, 1H), 2.66 (t, *J* = 4.5, 2H), 2.42 (s, 3H), 1.68 ~ 1.59 (m, 2H), 1.36 ~ 1.20 (m, 14H), 0.88 (t, *J* = 4.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.2, 144.4, 139.6, 121.5, 120.6, 35.7, 32.0, 31.3, 29.7, 29.7, 29.6, 29.5, 29.3, 22.8, 21.3, 14.2. HRMS (ESI) *m*/*z*: calcd for $C_{17}H_{26}NDO_2^+$ ([M]$^+$) 278.2105; Found 278.2100.



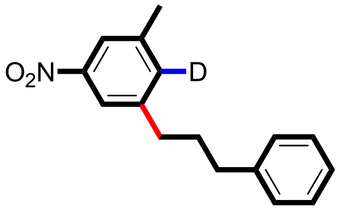
3f: Purified via column chromatography (hexane : CH_2Cl_2 = 2 : 1), Yield: 81% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 13.5 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.37 (t, *J* = 7.2 Hz, 2H), 2.07 ~ 1.97 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.0, 139.8, 129.7, 122.0, 120.3, 118.6, 61.7, 33.7, 29.5, 29.1, 26.4, 20.9, 16.3. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{12}N_2DO_2^+$ ([M+H]$^+$) 206.1037; Found: 206.1034.



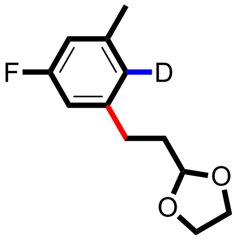
3g: Purified via column chromatography (hexane : CH_2Cl_2 = 3 : 1), Yield: 73% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 4.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.66 ~ 2.74 (m, 2H), 2.41 (s, 3H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.90 ~ 2.03 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ 172.8, 148.3, 142.9, 139.4, 138.2, 135.0, 121.5, 120.3, 60.2, 34.4, 33.2, 25.9, 20.9, 14.0. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{16}NNaDO_4^+$ ([M+Na]$^+$) 275.2796; Found 275.2796.



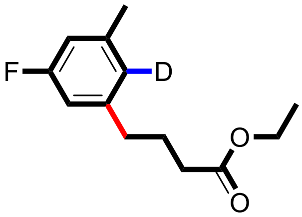
3h: Purified via column chromatography (hexane : CH_2Cl_2 = 3 : 1), Yield: 69% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.2 Hz, 1H), 4.90 (t, *J* = 4.5 Hz, 1H), 4.01 ~ 3.85 (m, 2H), 2.81 (dd, *J* = 9.3, 7.0 Hz, 1H), 2.42 (s, 2H), 2.03 ~ 1.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.4, 143.3, 139.5, 121.5, 120.5, 103.3, 65.2, 34.9, 29.5, 27.0, 21.1. HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{14}ND^+$ ([M]$^+$) 238.1064; Found 238.1061.



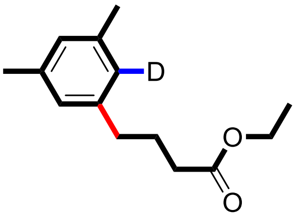
3i: Purified via column chromatography (hexane : CH_2Cl_2 = 3 : 1), Yield: 71% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.36 ~ 7.21(m, 5H), 2.73 (dd, J_1 = 8.7 Hz, J_2 = 16.5 Hz, 4H), 2.46 (s, 3H), 1.98 ~ 2.08 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 148.4, 143.8, 141.4, 139.4, 135.2, 129.9, 128.6, 126.0, 121.6, 120.1, 35.3, 34.8, 32.5, 29.5, 29.3, 27.4, 21.1. HRMS (ESI) m/z: calcd for $C_{16}H_{16}NDO_2^+$ ($[M]^+$) 256.1322; Found 256.1327.



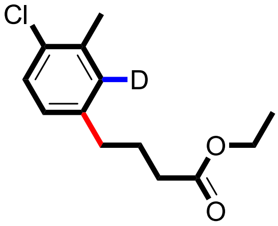
3j: Purified via column chromatography (hexane : CH_2Cl_2 = 5 : 1), Yield: 71% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 6.70 (dd, J = 9.7, 2.6 Hz, 2H), 4.89 (t, J = 4.6 Hz, 1H), 3.83 ~ 4.04 (m, 4H), 2.70 (dd, J = 9.4, 6.9 Hz, 2H), 2.31 (s, 3H), 1.90 ~ 2.02 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.3, 161.4, 142.9, 139.5, 112.7, 111.5, 102.9, 64.4, 34.4, 29.1, 20.6. HRMS (ESI) m/z: calcd for $C_{12}H_{14}FNaDO_2^+$ ($[M+Na]^+$): 234.1013. Found: 234.1011.



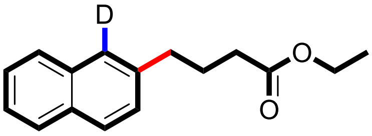
3k: Purified via column chromatography (hexane : CH_2Cl_2 = 5 : 1), Yield: 70% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 6.69 (m, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.37 ~ 2.34 (m, 5H), 1.86 ~ 1.96 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 164.4, 161.1, 143.4, 143.3, 139.9, 113.4, 113.2, 112.2, 111.9, 77.0, 60.1, 34.6, 33.4, 29.5, 26.1, 14.0. HRMS (ESI) m/z: calcd for $C_{13}H_{17}FDO_2^+$ ($[M+H]^+$) 226.1359; Found 226.1354.



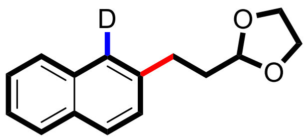
3l: Purified via column chromatography (hexane : CH_2Cl_2 = 4 : 1), Yield: 80% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 6.66 (d, *J* = 9.4 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.51 (t, *J* = 8.4 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 2.22 (s, 6H), 1.91 ~ 1.81 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 140.8, 137.5, 127.5, 125.8, 59.8, 34.8, 33.6, 26.4, 20.9, 13.9. HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{15}KDO_2^+$ ($[M+K]^+$) 260.1162; Found 260.1163.



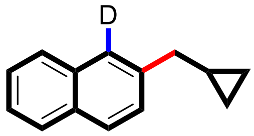
3m: Purified via column chromatography (hexane : CH_2Cl_2 = 5 : 1), Yield: 78% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, *J* = 4.8 Hz, 1H), 6.93 (d, *J* = 4.8 Hz, 1H), 4.13 (dd, J_1 = 4.2 Hz, J_2 = 8.4 Hz, 2H), 2.59 (t, *J* = 8.4 Hz, 2H), 2.34 (s, 3H), 2.30 (t, *J* = 4.5 Hz, 2H), 1.95 ~ 1.89 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.8, 139.4, 135.1, 128.4, 126.7, 59.8, 33.9, 32.9, 29.2, 26.0, 19.4, 13.8. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{16}DO_2Cl^+$ ($[M]^+$) 241.0980; Found 241.0988.



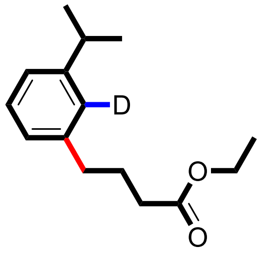
3n: Purified via column chromatography (hexane : CH_2Cl_2 = 4 : 1), Yield: 73% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (t, *J* = 8.3 Hz, 1H), 7.48 ~ 7.40 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.10 ~ 2.06 (m, 2H), 1.29 ~ 1.29 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ 173.0, 138.4, 133.1, 131.6, 127.5, 127.1, 126.9, 126.8, 125.3, 124.7, 59.8, 34.7, 33.2, 25.9, 13.8. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{18}DO_2^+$ ($[M+H]^+$) 244.3335; Found 244.3334.



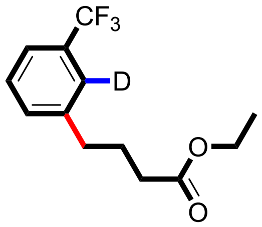
3o: Purified via column chromatography (hexane : CH_2Cl_2 = 4 : 1), Yield: 72% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 ~ 7.77 (m, 3H), 7.48 ~ 7.35 (m, 3H), 4.95 (t, J = 4.5 Hz, 1H), 4.02 ~ 3.89 (m, 4H), 2.93 (t, J = 8.1 Hz, 2H), 2.12 ~ 2.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.4, 134.0, 132.4, 128.3, 128.0, 127.7, 127.6, 126.3, 125.5, 104.2, 77.0, 65.4, 35.8, 30.6, 25.2. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{21}NaDO_2^+$ ([M+Na]$^+$) 225.1114; Found 225.1111.



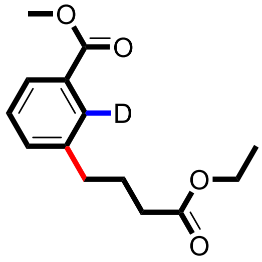
3p: Purified via column chromatography (hexane : CH_2Cl_2 = 53 : 1), Yield: 69% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (dd, J_1 = 8.0 Hz, J_2 = 16.8 Hz, 3H), 7.47 (dt, J_1 = 7.4 Hz, J_2 = 16.2 Hz, 3H), 2.76 (d, J = 6.9 Hz, 2H), 1.08 ~1.16 (m, 1H), 0.59 ~ 0.63 (m, 2H), 0.31 (q, J = 4.9 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$): δ 139.8, 133.8, 132.3, 128.1, 127.9, 127.8, 127.6, 126.2, 126.0, 125.9, 125.2, 40.6, 12.0, 4.9. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{13}NaD$([M+Na]$^+$): 206.1056. Found: 206.1057.



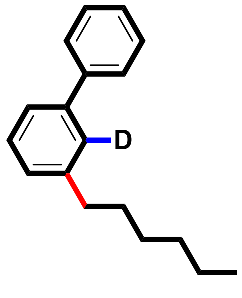
3q: Purified via column chromatography (hexane : CH_2Cl_2 = 4 : 1), Yield: 77% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (t, J = 3.9 Hz, 1H), 7.06 (d, J = 4.5 Hz, 1H), 7.00 (d, J = 1.8 Hz, 1H), 4.13 (q, J = 4.2 Hz, 2H), 2.90 ~ 2.84 (m, 1H), 2.64 (t, J = 4.8 Hz, 2H), 2.33 (t, J = 4.5 Hz, 2H), 1.99 ~ 1.90 (m, 2H), 1.29 ~ 1.24 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 149.2, 141.3, 128.4, 126.0, 124.1, 60.4, 35.3, 33.9, 29.7, 26.6, 23.9, 14.5. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{21}KDO_2^+$ ([M+K]$^+$) 274.1310; Found 274.1314.



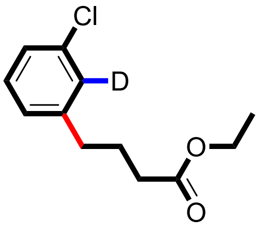
3r: Purified via column chromatography (hexane : CH_2Cl_2 = 5 : 1), Yield: 73% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 ~ 7.35 (m, 3H), 4.13 (dd, J_1 = 4.2 Hz, J_2 = 8.4 Hz, 2H), 2.71 (t, J = 8.4 Hz, 2H), 2.32 (t, J = 4.5 Hz, 2H), 2.01 ~ 1.92 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 142.2, 131.8, 128.7, 122.8, 60.3, 34.8, 33.5, 29.6, 27.2, 26.2, 25.4, 22.6, 14.1. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{14}F_3NaDO_2^+$ ($[M+Na]^+$) 284.0974; Found 284.0977.



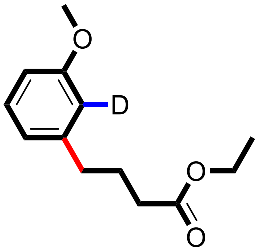
3s: Purified via column chromatography (hexane : CH_2Cl_2 = 5 : 1), Yield: 75 % Transparent liquid. ^{1}H NMR: δ 7.84 (dd, J_1 = 2.2 Hz, J_2 = 6.6 Hz, 1H), 7.29 ~ 7.36 (m, 2H), 4.10 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 2.65 ~ 2.70 (m, 2H), 2.29 (t, J = 7.4 Hz, 2H), 1.87 ~ 1.99 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H).^{13}C NMR: δ 173.3, 167.2, 141.8, 133.2, 130.3, 129.4, 128.5, 127.4, 60.4, 52.1, 34.9, 33.7, 26.5, 14.3. HRMS (ESI) *m*/*z*: calcd. for $C_{14}H_{17}NaDO_4^+$ ($[M+Na]^+$) 274.1163. Found 274.1166.



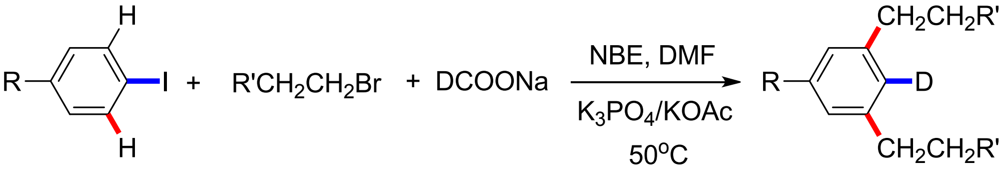
3t: Purified via column chromatography (hexane : CH_2Cl_2 = 80 : 1), Yield: 69% Transparent liquid. ^{1}H NMR: δ 7.26 ~ 7.48 (m, 8H), 2.61 ~ 2.66 (m, 2H), 1.52 (dd, J_1 = 7.4 Hz, J_2 = 14.8 Hz, 2H), 1.20 ~ 1.84 (m, 6H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR: δ 144.5, 143.4, 142.0, 141.8, 140.3, 129.9, 129.1, 127.9, 127.8, 127.2, 126.6, 125.4, 33.0, 31.5, 31.2, 29.0, 22.4, 14.0. HRMS (ESI) *m*/*z*: calcd. for $C_{18}H2_1NaD^+$ ($[M+Na]^+$) 262.3706. Found 262.3701.



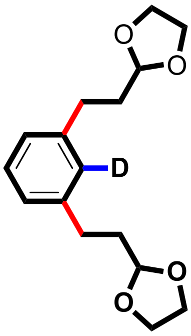
3u: Purified via column chromatography (hexane : CH_2Cl_2 = 6 : 1), Yield: 41% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 ~ 7.15 (m, 2H), 7.06 (d, J = 7.2 Hz, 1H), 4.13 (q, J = 4.2 Hz, 1H), 2.63 (t, J = 4.8 Hz, 2H), 2.31 (t, J = 4.5 Hz, 1H), 1.99 ~ 1.90 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 159.1, 142.3, 128.8, 120.4, 110.8, 59.7, 54.6, 34.5, 33.2, 29.3, 25.9, 13.7. HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{14}ClKDO_2^+$ ($[M+K]^+$) 266.0453; Found 266.0455.



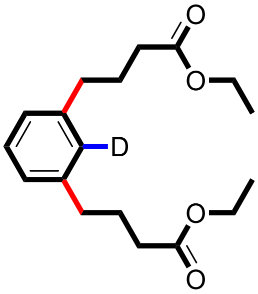
3v: Purified via column chromatography (hexane : CH_2Cl_2 = 2 : 1), Yield: 25% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (t, J = 7.8 Hz, 1H), 6.76 (t, J = 8.7 Hz, 2H), 4.17 (q, J = 4.2 Hz, 2H), 3.84 (s, 3H), 2.67 (t, J = 4.8 Hz, 2H), 2.36 (t, J = 4.5 Hz, 2H), 1.99 ~ 1.90 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 159.9, 143.2, 129.8, 121.5, 111.8, 60.9, 55.6, 35.6, 34.1, 29.9, 26.5, 14.7. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{17}KDO_3^+$ ($[M+K]^+$) 262.0965; Found 262.0960.



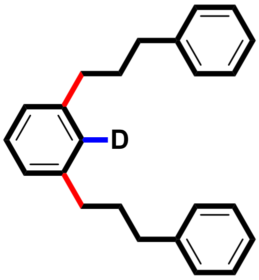
General procedure for the synthesis of deuterated arene 7 with DCOONa as deuterium source: In a argon glovebox, to an 10 mL vial containing $Pd(OAc)_2$ (44 mg, 0.2 mmol), PPh_3 (52 mg, 0.2 mmol), norbornene (188 mg, 2 mmol), K_3PO_4 (2.54 g, 12 mmol), KOAc (490 mg, 5 mmol), DCOONa (276 mg, 4 mmol) and aryl iodide **1** (526 mg, 2 mmol) in DMF (10ml) was added alkylbromides **2** (12 mmol). Then the sealed vial was brought out of the glovebox and put into an oil bath with pre-set to 50°C. The reaction mixture was stirred vigorously until the GC-MS showed the reaction was completed. The reaction was quenched by water. Then, the mixture was extracted with dichloromethane (3 x 25 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of solvents under vacuum, the crude product was purified via column chromatography (silica gel) using the appropriate binary solvent system (vol/vol).



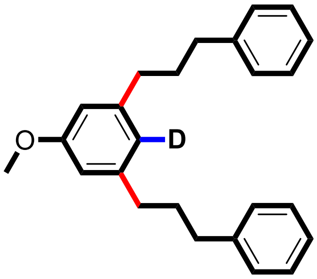
7a: Purified via column chromatography (hexane : CH_2Cl_2 = 1 : 1), Yield: 73% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.17 (d, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 2H), 4.89 (t, *J* = 4.8 Hz, 2H), 3.84 ~ 4.02 (m, 8H), 2.73 (t, *J* = 8.1 Hz, 4H), 1.91 ~ 2.01 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.4, 129.7, 128.2, 125.7, 103.7, 64.7, 35.7, 35.3, 31.7, 29.8, 29.6, 29.5, 29.4, 29.1, 27.0, 25.3, 22.5, 13.9. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{21}KDO_4^+$ ($[M+K]^+$) 318.1215; Found 318.1212.



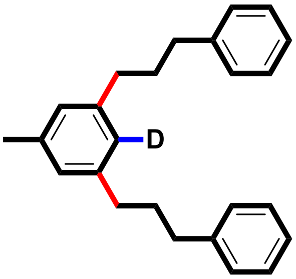
7b: Purified via column chromatography (hexane : CH_2Cl_2 = 1 : 1), Yield: 76% colorless liquid. The level of deuterium incorporation was determined as >98%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 4.05 (q, *J* = 4.2 Hz, 4H), 2.62 (t, *J* = 4.5 Hz, 4H), 2.32 (t, *J* = 4.5 Hz, 4H), 1.99 ~ 1.89 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 141.4, 128.8, 128.7, 126.2, 60.3, 35.2, 33.8, 29.9, 26.6, 14.4. HRMS (ESI) *m*/*z*: calcd for $C_{18}H_{26}DO_2^+$ ($[M+H]^+$) 308.1971; Found 308.1972.



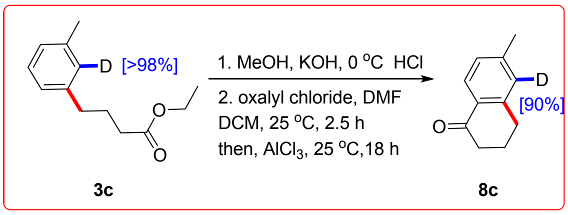
7c: Purified via column chromatography (hexane : CH_2Cl_2 = 3 : 1), Yield: 63% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 ~ 7.29 (m, 4H), 7.24 ~ 7.18 (m, 7H), 7.04 (d, J = 7.5 Hz, 2H), 2.67 (dd, J_1 = 7.2 Hz, J_2 = 15.0 Hz 8H), 2.04 ~ 1.94 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 144.0, 142.7, 128.8, 126.1, 111.8, 55.5, 35.8, 33.2, 29.8, 27.7, 25.9. HRMS (ESI) *m*/*z*: calcd for $C_{24}H_{25}D^+$ ($[M]^+$) 315.2088; Found 315.2097.



7d: Purified via column chromatography (hexane : CH_2Cl_2 = 3 : 1), Yield: 61% colorless liquid. The level of deuterium incorporation was determined as >98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 ~ 7.30 (m, 5H), 7.26 ~ 7.22 (m, 5H), 6.62 (s, 2H), 3.85 (s, 3H), 2.6d (dt, J_1 = 4.5 Hz, J_2 = 15.0 Hz, 8H), 2.04 ~ 1.98 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 143.8, 142.6, 128.8, 128.7, 126.1, 111.8, 55.5, 35.9, 33.2, 30.1, 29.7, 27.6. HRMS (ESI) *m*/*z*: calcd for $C_{25}H_{28}DO^+$ ($[M+H]^+$) 346.2284; Found 346.2281.

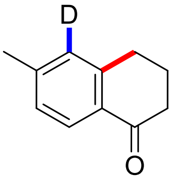


7e: Purified via column chromatography (hexane : CH_2Cl_2 = 3 : 1), Yield: 69% colorless liquid. The level of deuterium incorporation was determined as >98%.^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 ~ 7.18 (m, 10H), 6.86 (s, 2H), 2.65 (dt, J_1 = 4.8 Hz, J_2 = 15.0 Hz, 8H), 2.33 (s, 3H), 2.04 ~ 1.93 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.8, 141.7, 137.2, 128.0, 127.8, 126.2, 125.2, 35.1, 34.9, 32.5, 20.9. HRMS (ESI) *m*/*z*: calcd for $C_{25}H_{27}D^+$ ($[M]^+$) 329.2254; Found 329.2251.



Scheme S1 Synthesis of deuterium-labeled naphthalenone

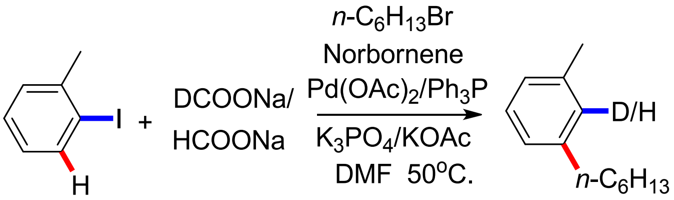
Procedure for the synthesis of deuterium-labeled 1-naphthalenone: Potassium hydroxide pellets (112 mg, 2 mmol) were added to a solution of 2-deuterated ethyl-3-methylphenylbutyrate **3c** (414 mg, 2 mmol) in methanol (10 mL) and the mixture stirred at 0 °C for 8 hours. Then, methanol was removed by evaporation under vacuum. The white salt was washed with copious amounts of ethyl acetate to remove any remaining starting material. The salt was then dissolved in water (25 mL), and solution was acidified with 4 M HCl to pH 2. The aqueous solution was extracted with chloroform (25 mL × 3), and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the crude product was obtained by evaporation of the solvent under vacuum and directly dissolved in the mixture of anhydrous DMF (1 drops) and DCM (3 mL). Then, oxalyl chloride (252 mg, 2 mmol) was added dropwise at 0 ºC. The solution was first stirred at 0 ºC for 1 hour, then at room temperature for 1.5 hours. The mixture was cooled to 0 ºC again, and aluminium chloride (239 mg, 1.8 mmol) was added. The reaction was then warmed to room temperature and stirred for 18 hours, and quenched at 0 ºC with 1N aqueous HCl (1 mL). The reaction mixture was diluted with EtOAc (100 mL) and washed with brine (50 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After removal of solvents under vacuum, the crude product was purified via column chromatography (silica gel) using the appropriate binary solvent system (vol/vol).



Purification by flash column chromatography (hexanes : EtOAc = 9 : 1) , yield: 84 % light yellow liquid. The level of deuterium incorporation was determined as 90%. ^{1}H NMR: δ 7.93 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.05 (s, 1H), 2.91 (t, J = 6.1 Hz, 2H), 2.62 (m, 2H), 2.37 (s, 3H), 2.11 (m, 2H). ^{13}C NMR: δ 197.9, 144.3, 143.9, 130.2, 129.0, 127.5, 127.1, 39.0, 29.5, 23.2, 21.4. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{11}NaDO^+$ ([M+Na]$^+$): 184.0849. Found: 184.0842.

Procedure for the synthesis of deuterated arene 3 in the presence of TEMPO as radical inhibitor: In a argon glovebox, to an 10 mL vial containing $Pd(OAc)_2$ (44 mg, 0.2 mmol), PPh_3 (52 mg, 0.2 mmol), norbornene (188 mg, 2 mmol), K_3PO_4 (2544 mg, 12 mmol), KOAc (490 mg, 5 mmol), DCOONa (276 mg, 4 mmol), TEMPO (302 mg, 2 mmol) and aryl iodide **1** (526 mg, 2 mmol) in DMF (10ml) was added alkylbromides **2** (6 mmol). Then the sealed vial was brought out of the glovebox and put into an oil bath with pre-set to 50°C. The reaction mixture was stirred vigorously for 12 hours. The analysis showed the GC-MS yield of the desired product is 88%, which is comparable to the reaction without TEMPO as additive. This result suggested that the mechanism involving free radical should be ruled out.

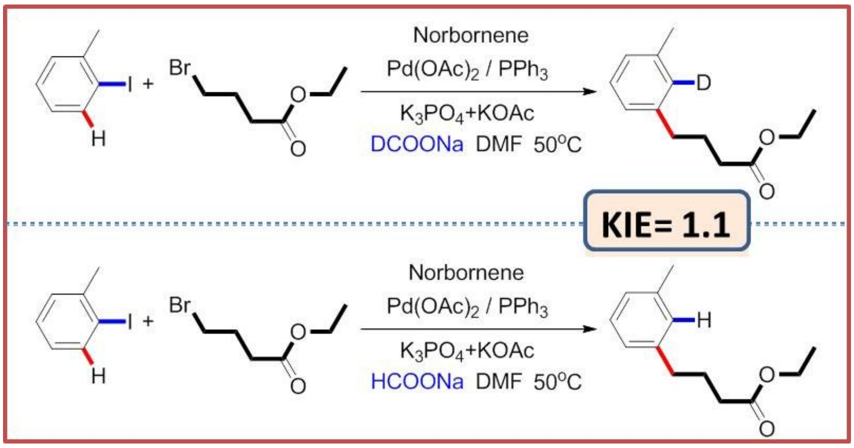
Table S4: Experiment for kinetic isotope effect:



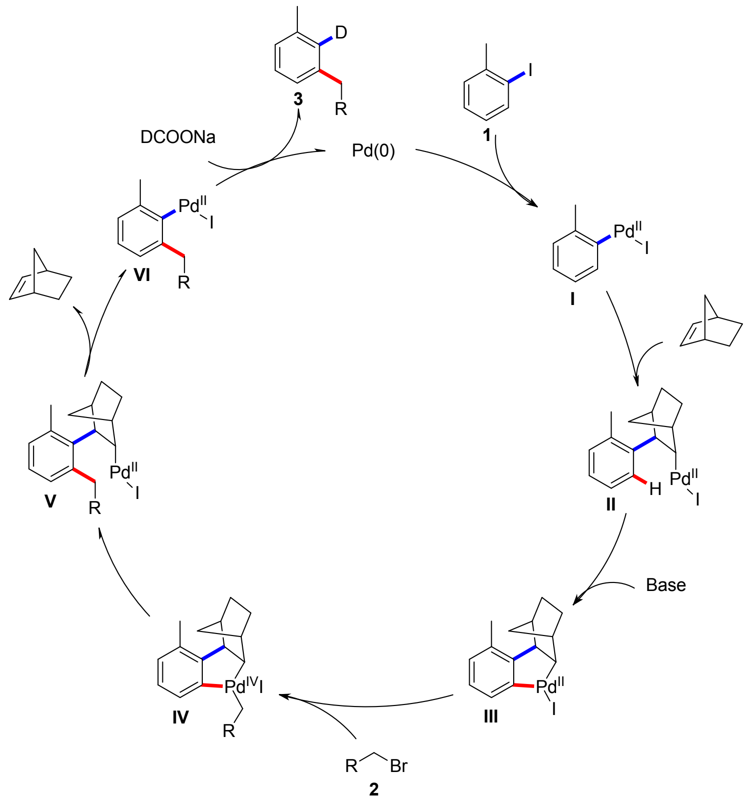
Entry	DCOONa/HCOONa (ratio)	D incorporation[a]
1	100/0	>98%
2	75/25	64%
3	50/50	46%
4	25/75	20%
5	0/100	0%

[a] Determined by GC/MS.

Reactions to incorporate deuterium/hydrogen were carried out following the general procedure for the synthesis of arene **3**, using DCOONa/HCOONa with different ratio as reductive reagents. After 16 hours, a small aliquot of the organic phase of the reaction mixture was sampled and analyzed by GC-MS to determine the deuterium incorporation. According to the deuterium incorporation obtained from the mixture of DCOONa/HCOONa with 50/50 ratio, the kinetic isotope effect of this reaction can be calculated as 1.1.

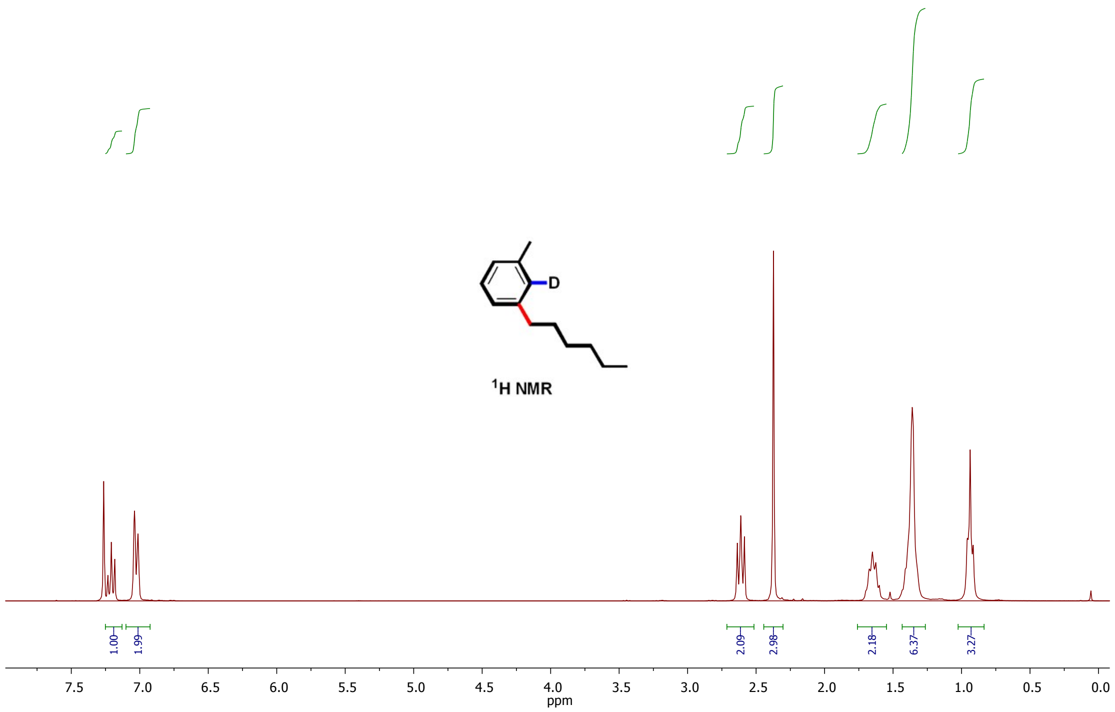


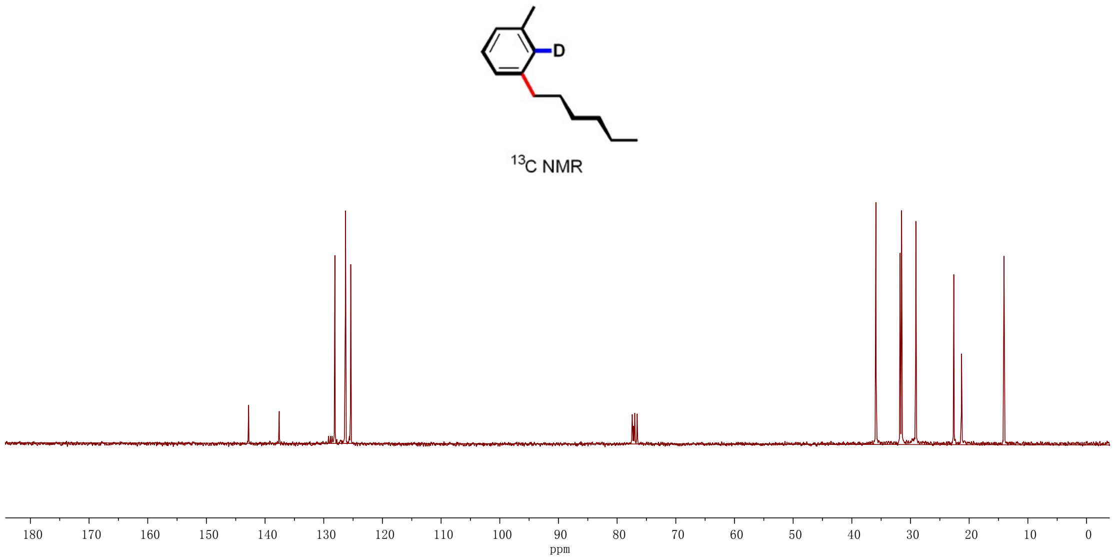
Scheme S2: Experiment for kinetic isotope effect

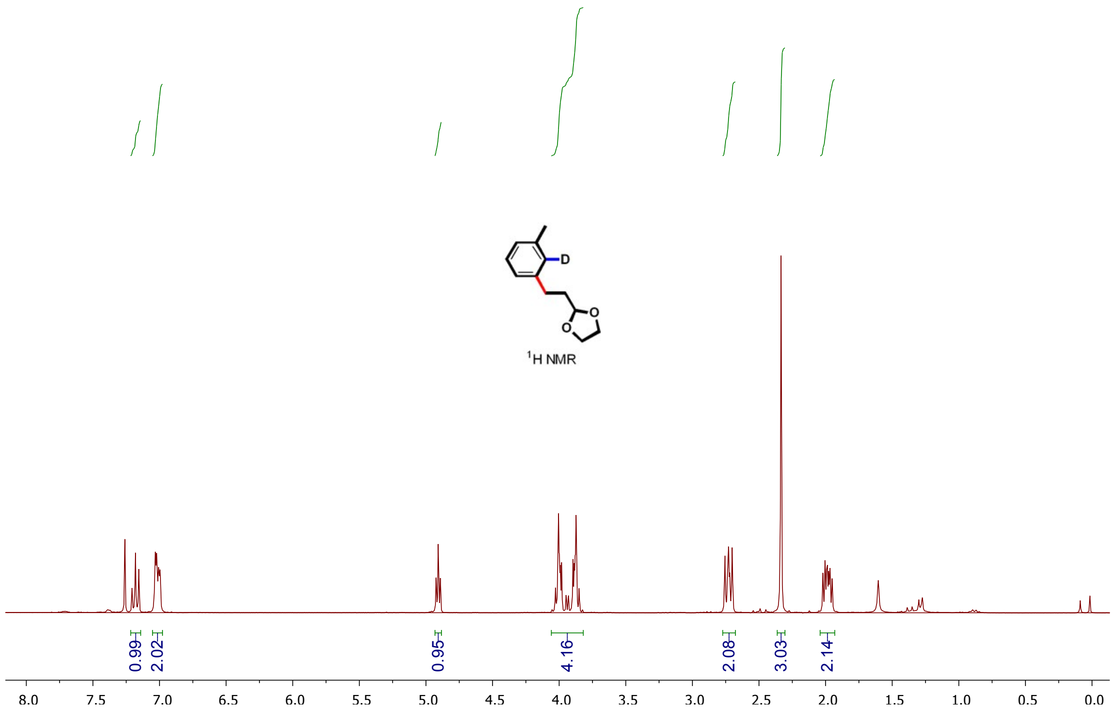


Scheme S3 Proposed mechanism for palladium catalyzed cascade alkylation and deuteration

NMR spectrum:






D
O
O
^{1}H NMR
0.99
2.02
0.95
4.16
2.08
3.03
2.14
8.0
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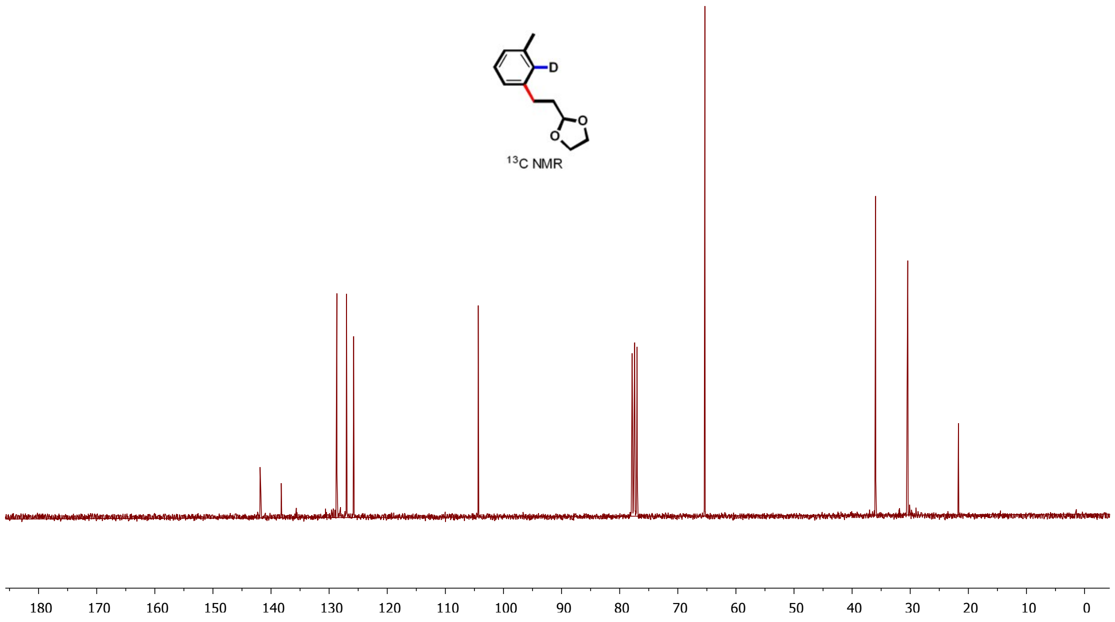
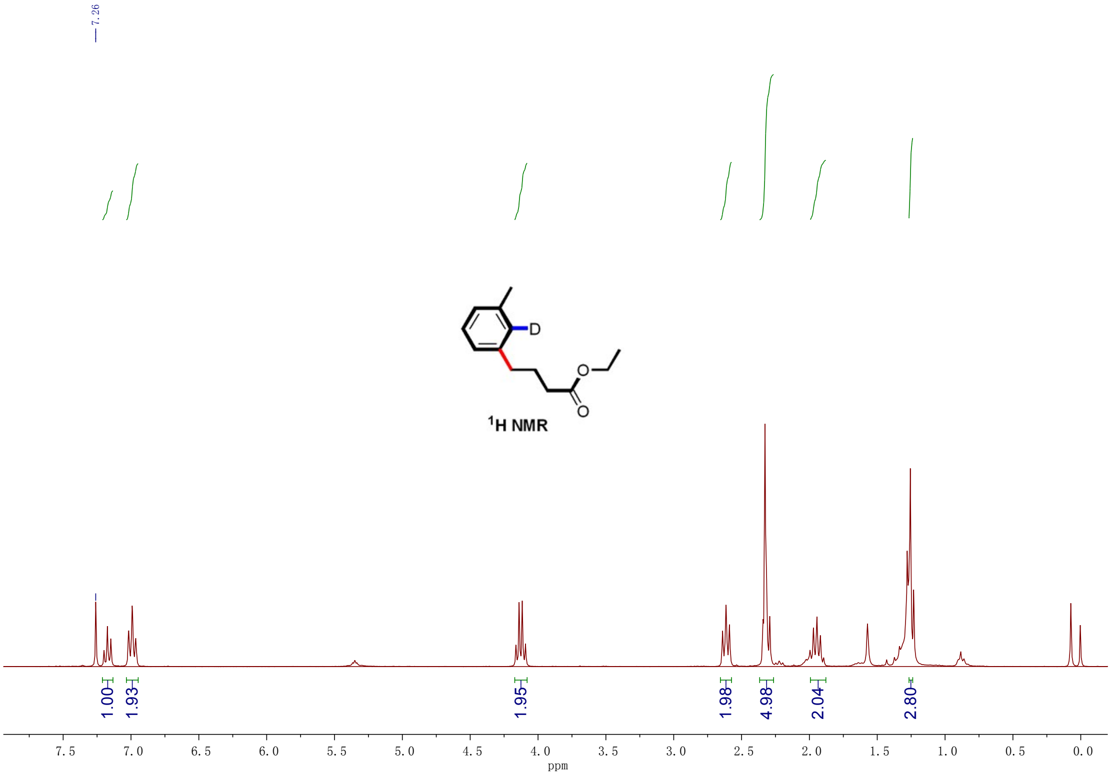
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


D
O
O
^{13}C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.26
D
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O
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1.95
1.98
4.98
2.04
2.80
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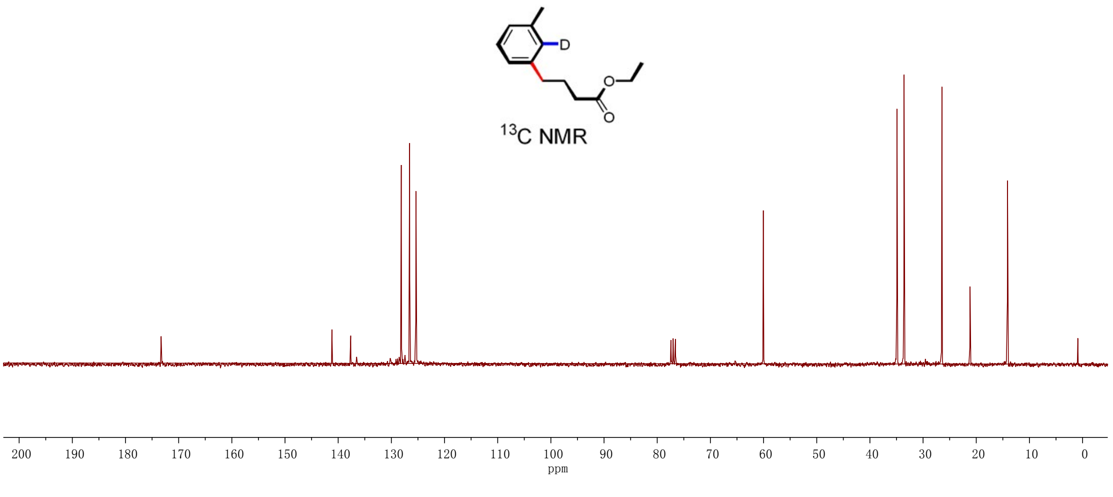
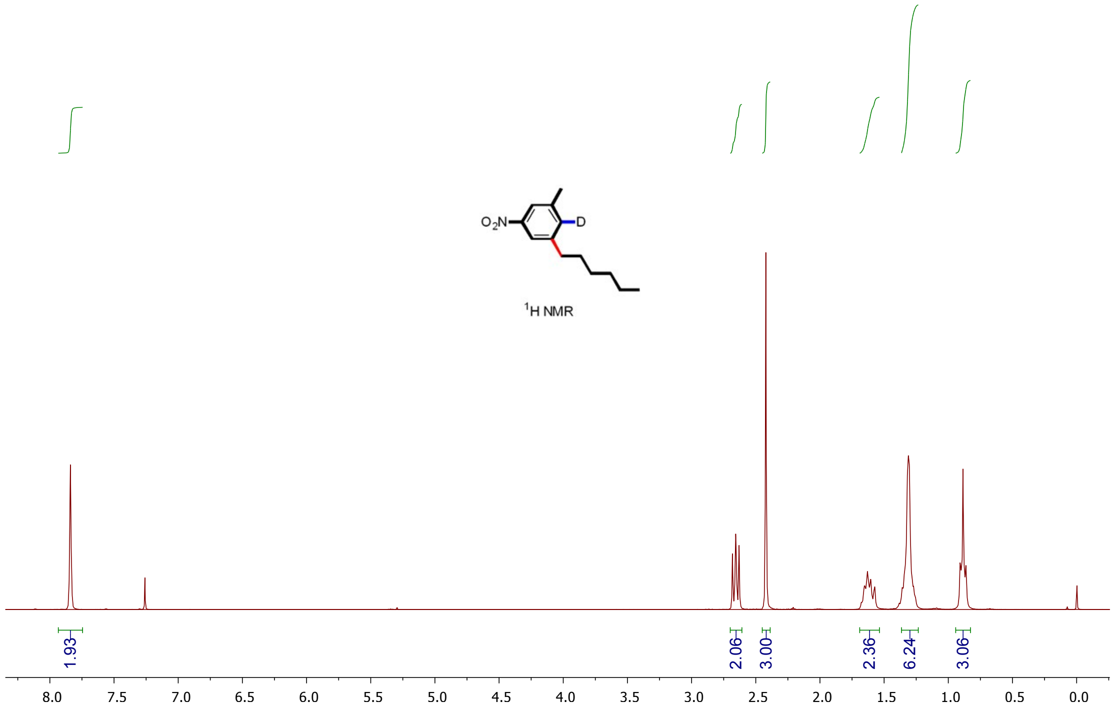
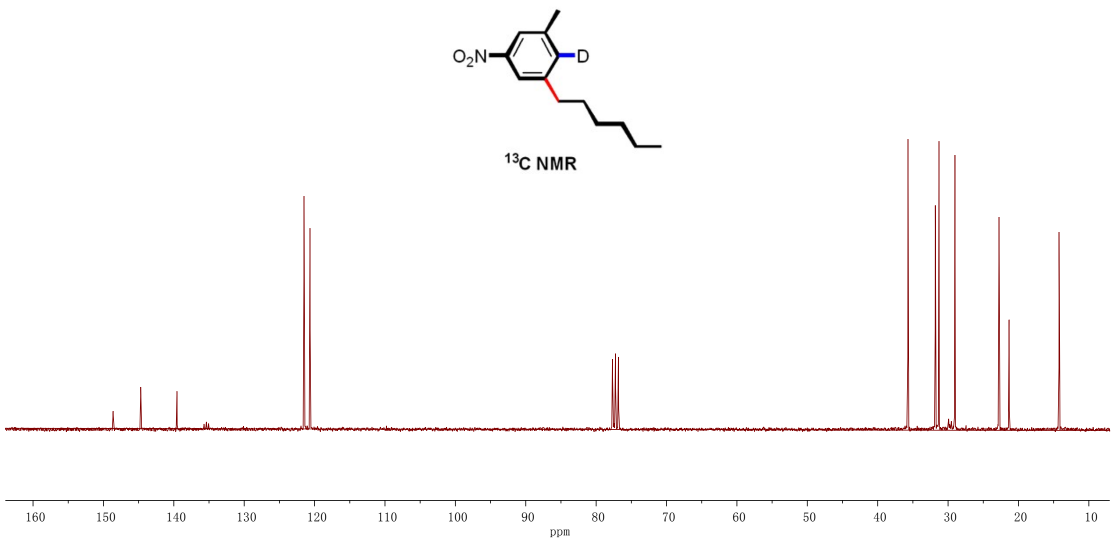
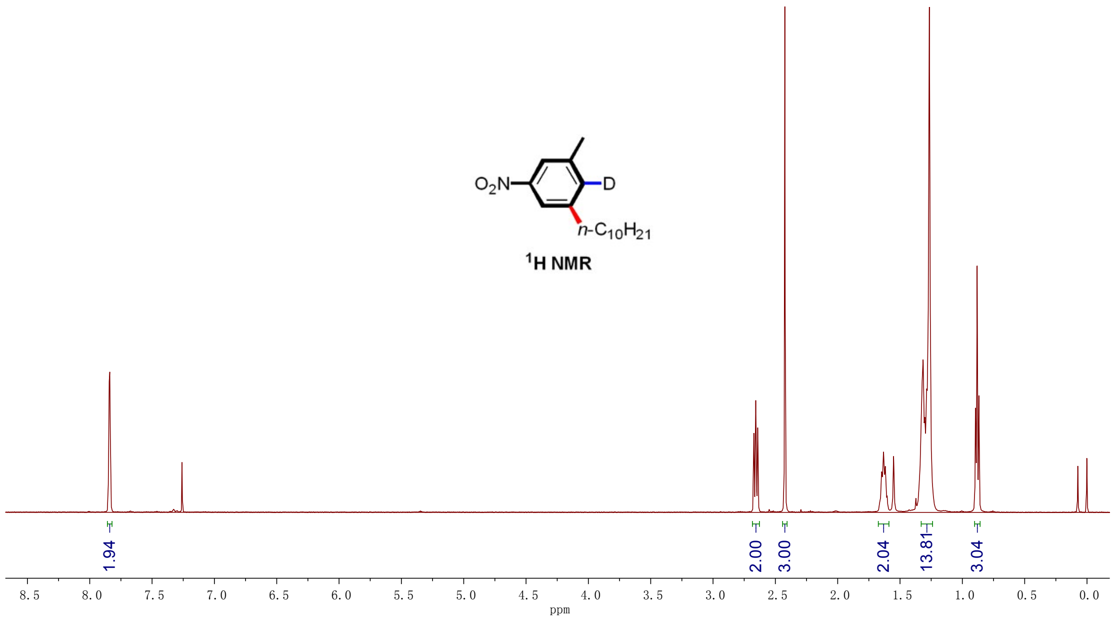
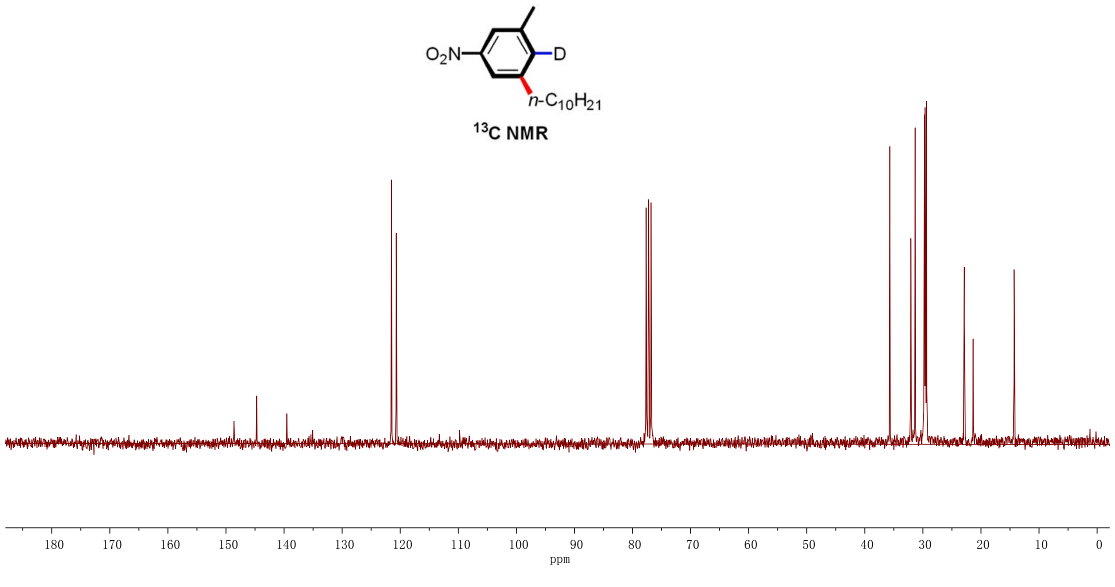
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

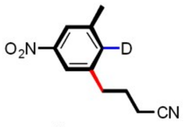

D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O$_2$N
D
^{1}H NMR
1.93
2.06
3.00
2.36
6.24
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

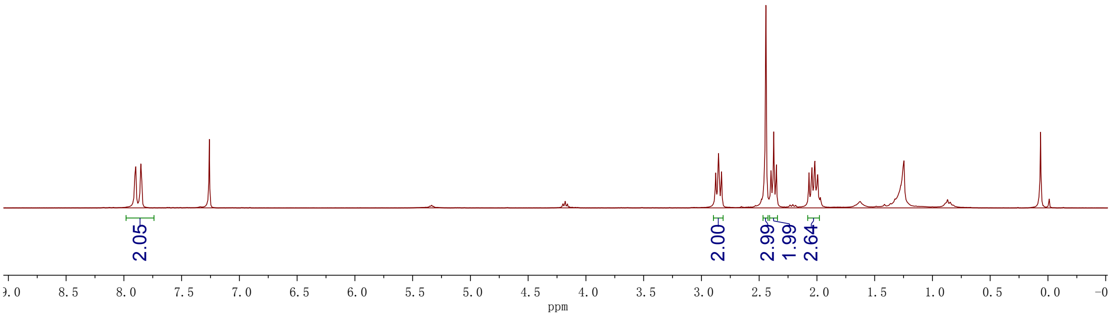

O$_2$N
D
^{13}C NMR
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

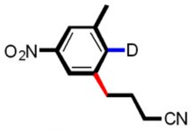

O2N
D
n-C10H21
1H NMR
1.94
2.00
3.00
2.04
13.81
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O2N
D
n-C10H21
13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

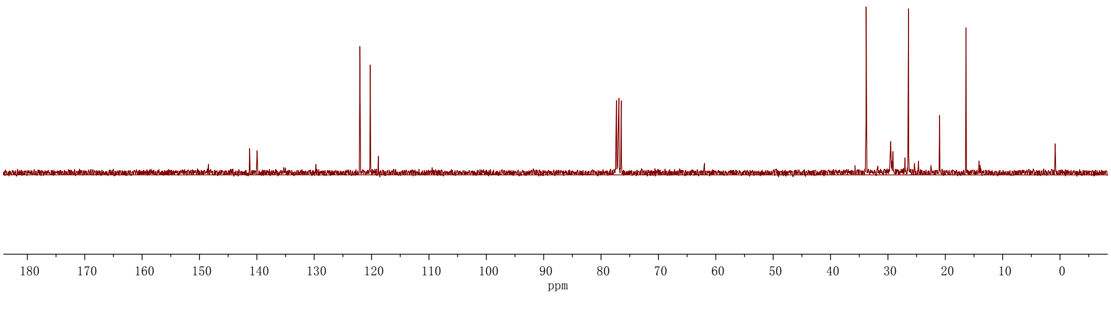


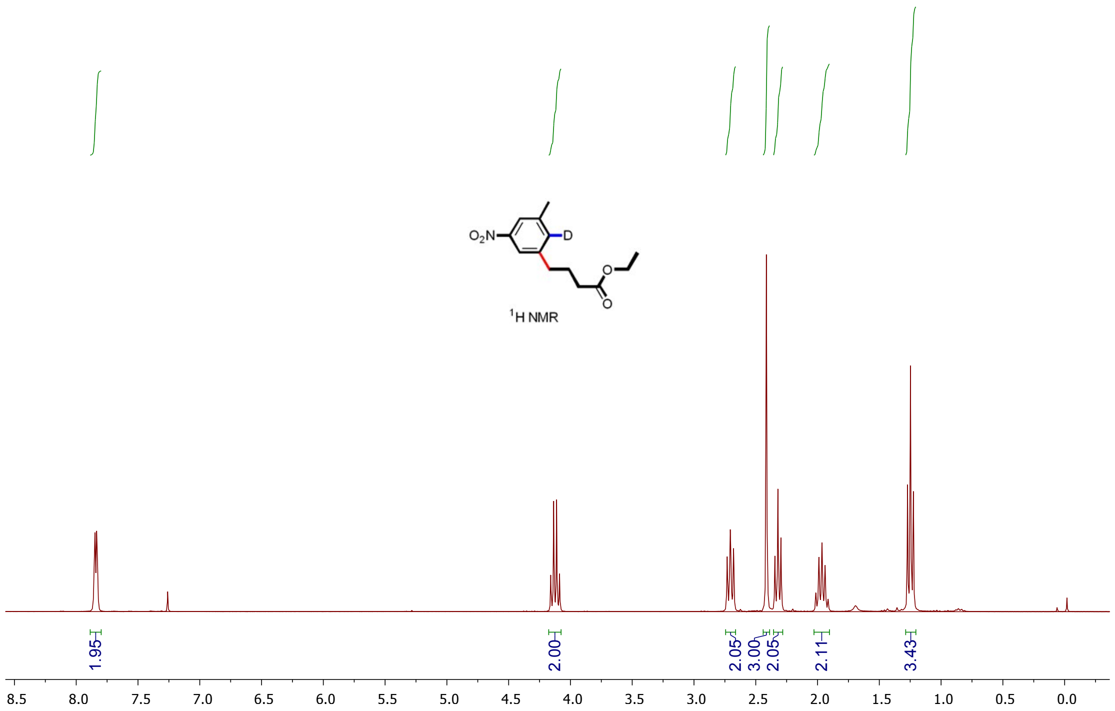
^{1}H NMR

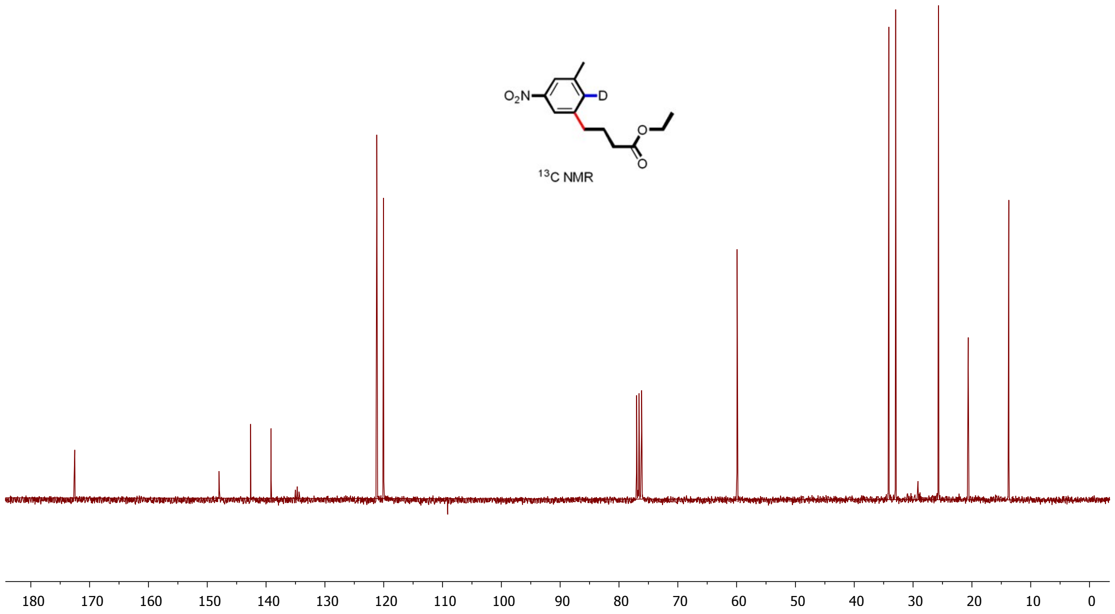


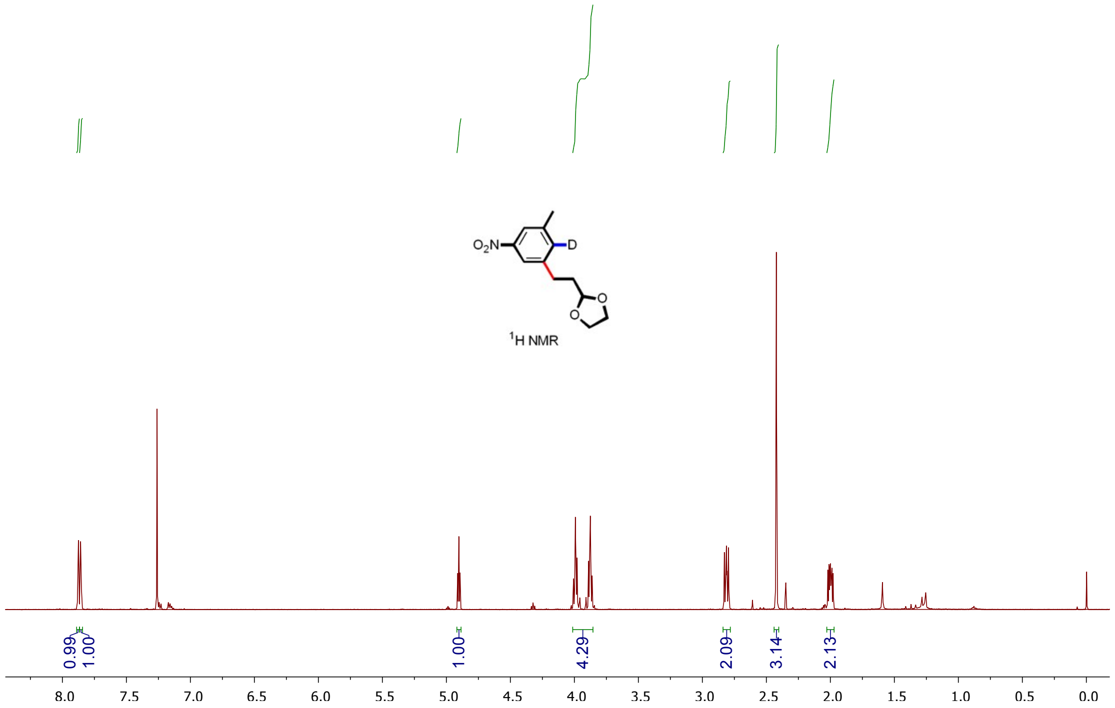


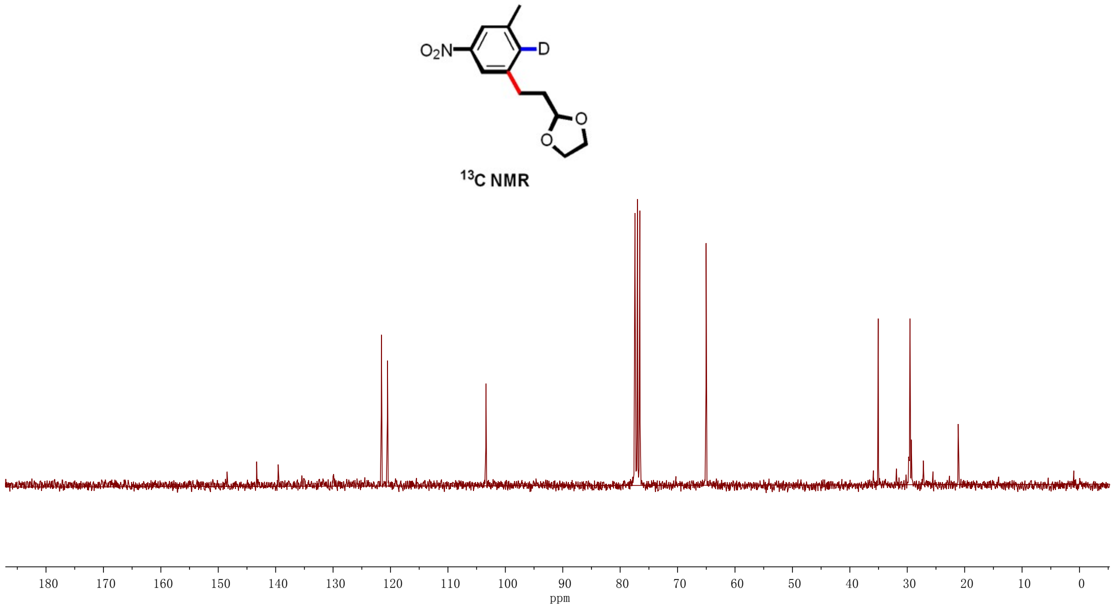
^{13}C NMR

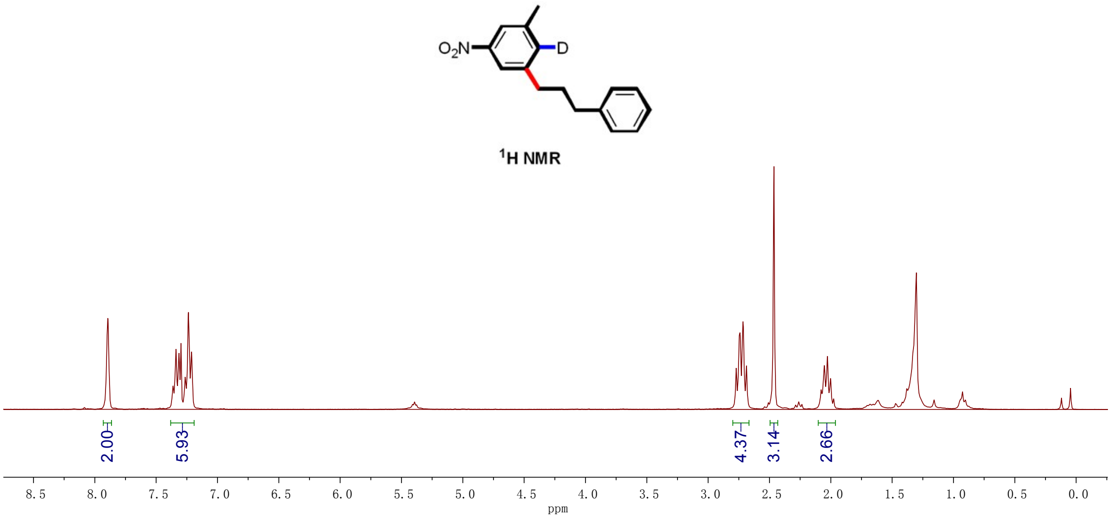


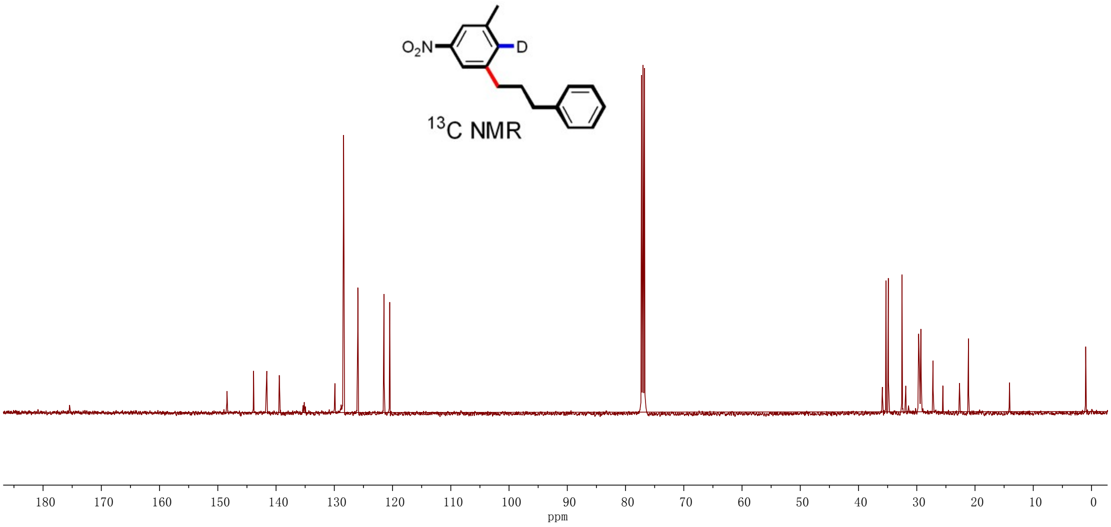

O2N
D
O
O
1H NMR
1.95
2.00
2.05
3.00
2.05
2.11
3.43
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

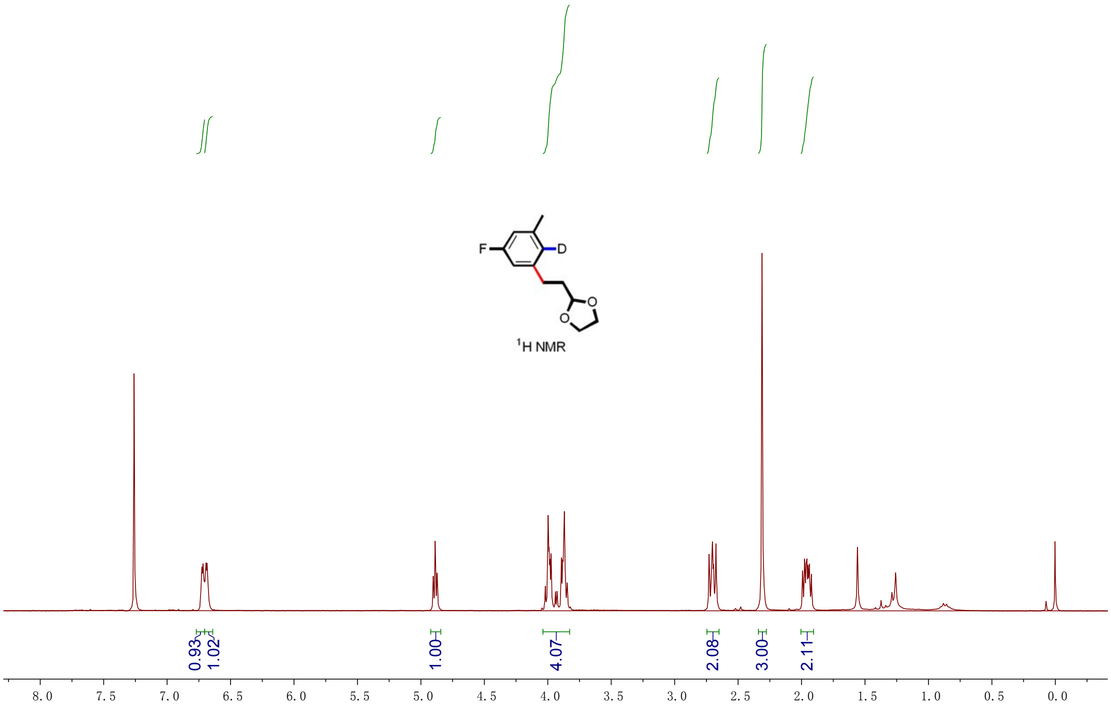

O2N
D
O
O
13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

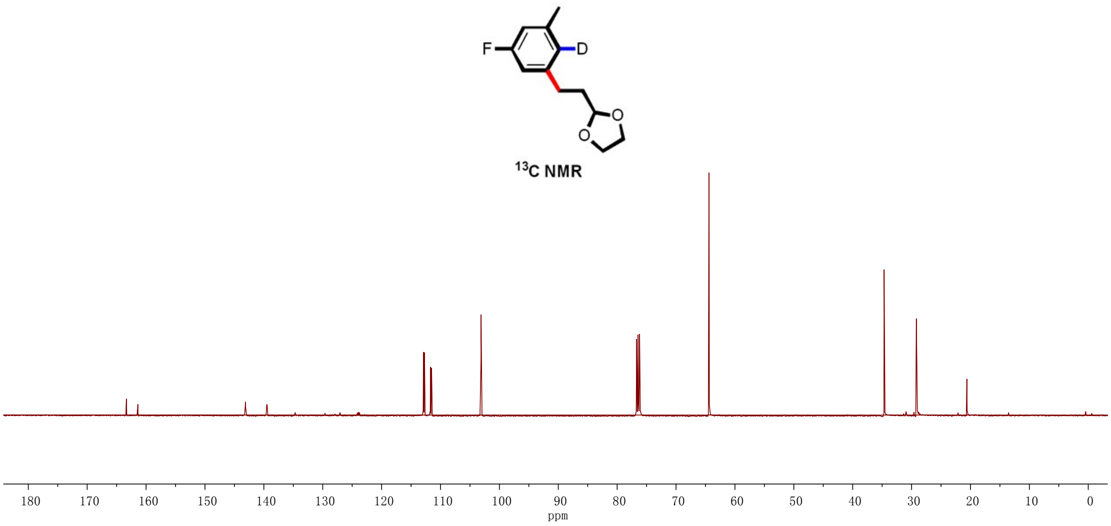

O2N
D
O
O
1H NMR
0.99
1.00
1.00
4.29
2.09
3.14
2.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

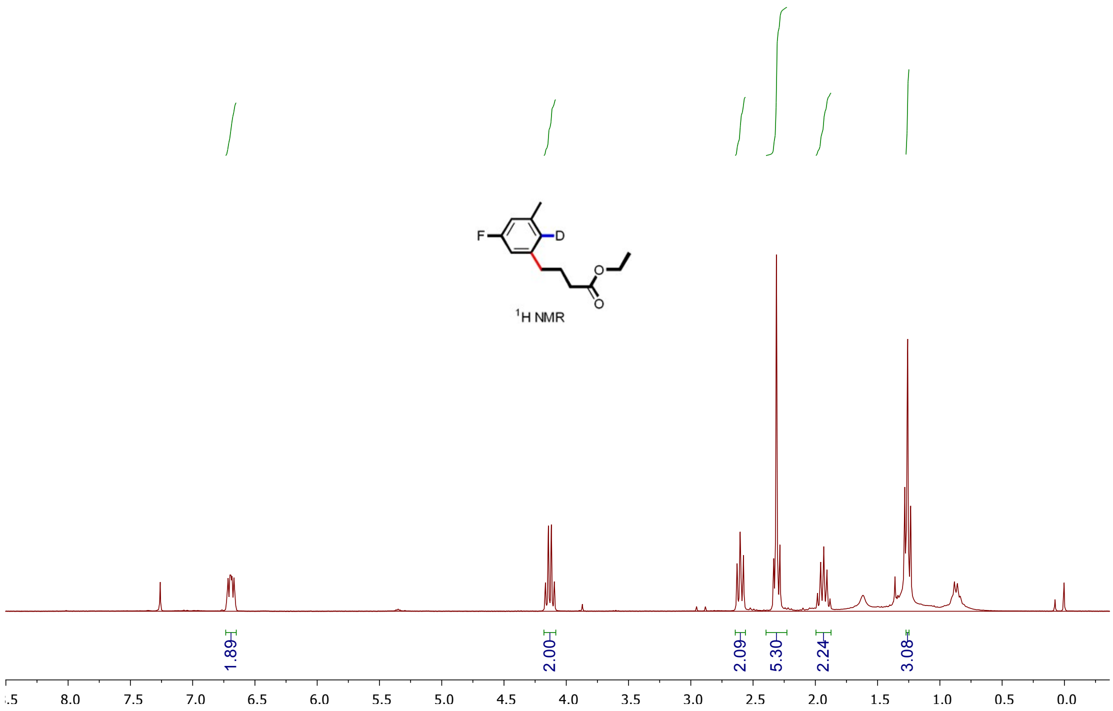

O2N
D
O
O
13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

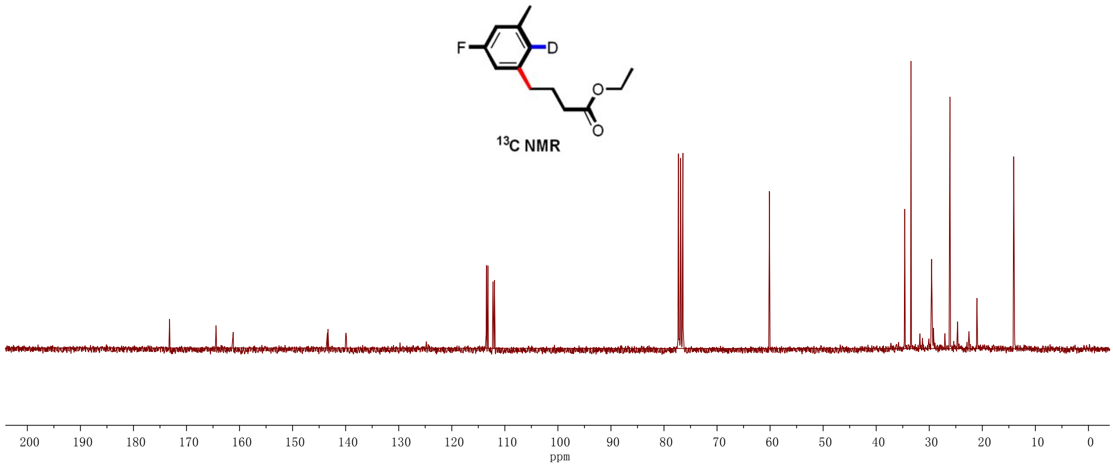

O$_2$N
D
^{1}H NMR
2.00
5.93
4.37
3.14
2.66
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

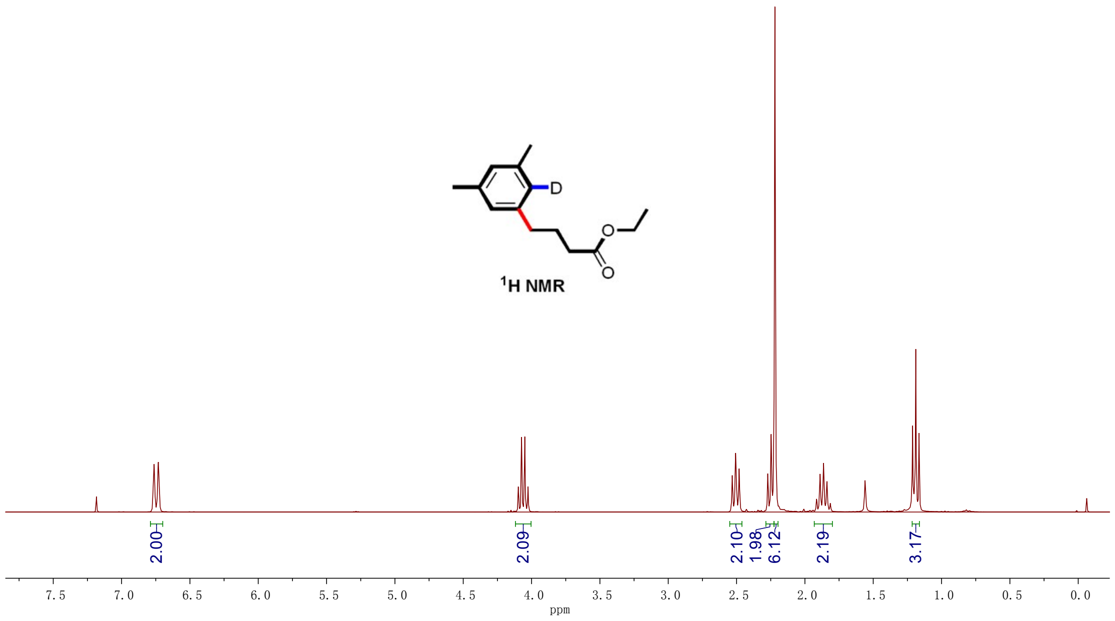

O$_2$N
D
^{13}C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

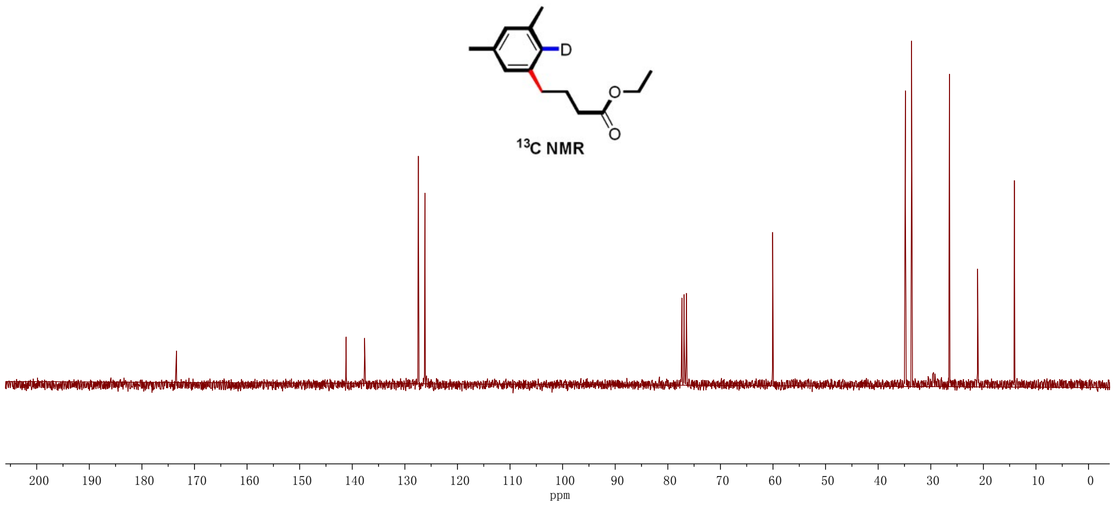

F
D
O
O
^{1}H NMR
0.93
1.02
1.00
4.07
2.08
3.00
2.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

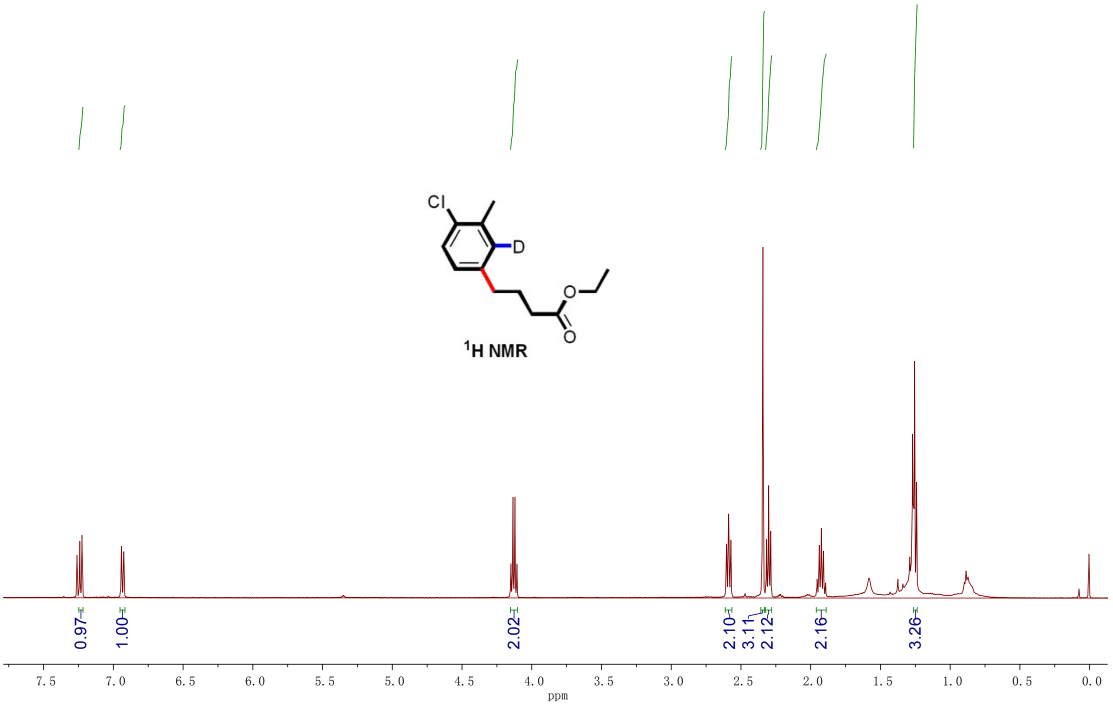

F
D
O
O
^{13}C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

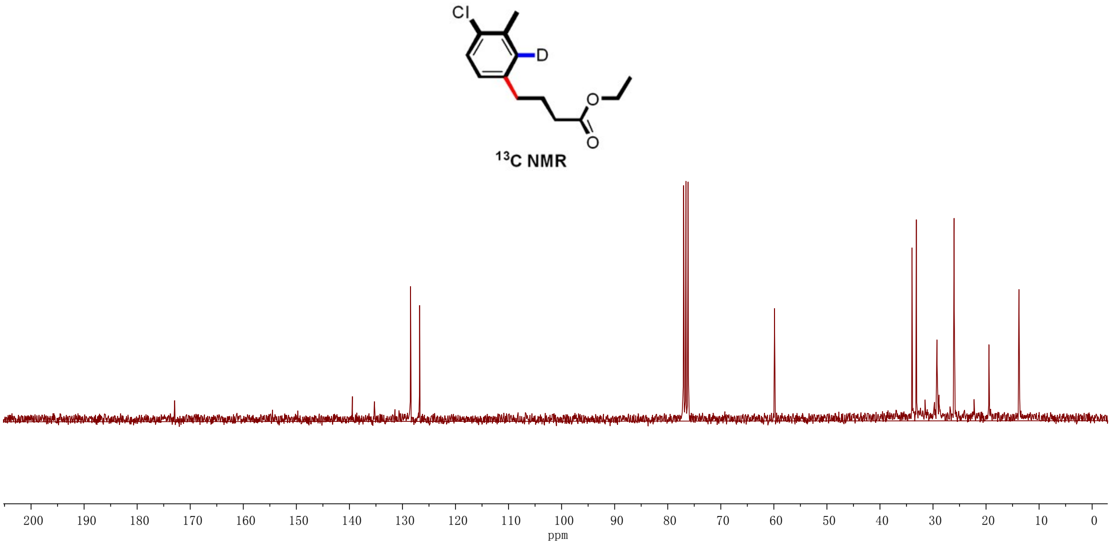

F
D
O
O
^{1}H NMR
1.89
2.00
2.09
5.30
2.24
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

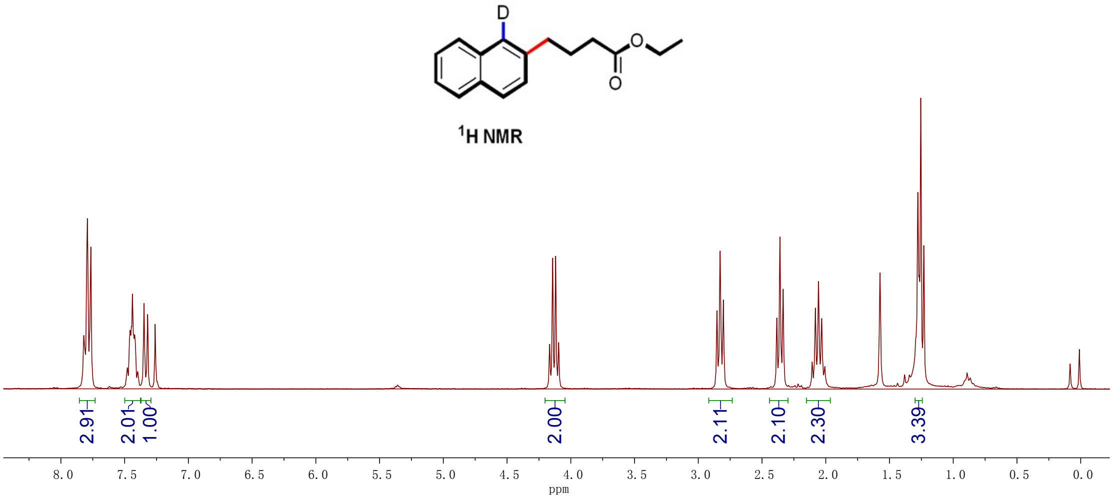

F
D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

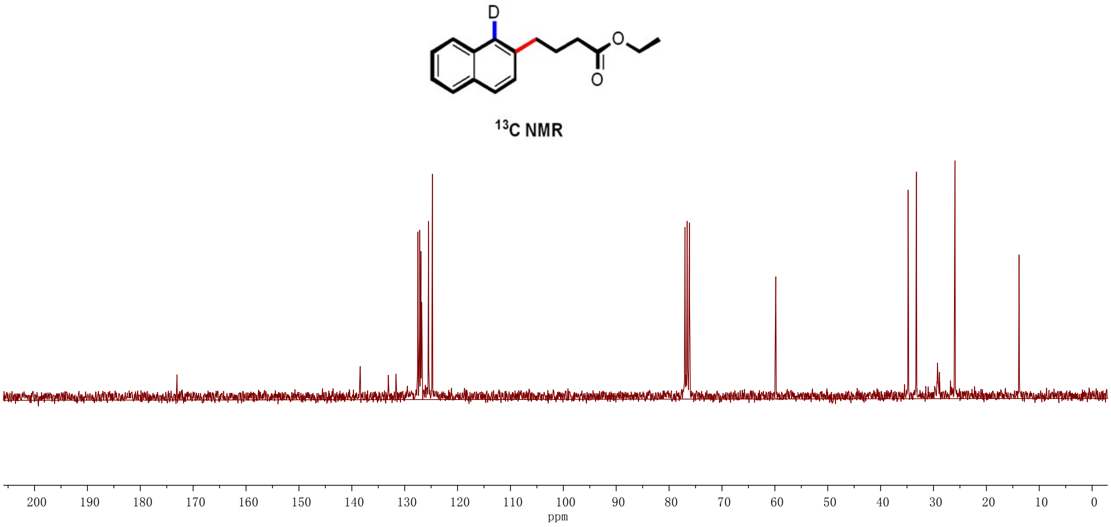

D
O
O
^{1}H NMR
2.00
2.09
2.10
1.98
6.12
2.19
3.17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

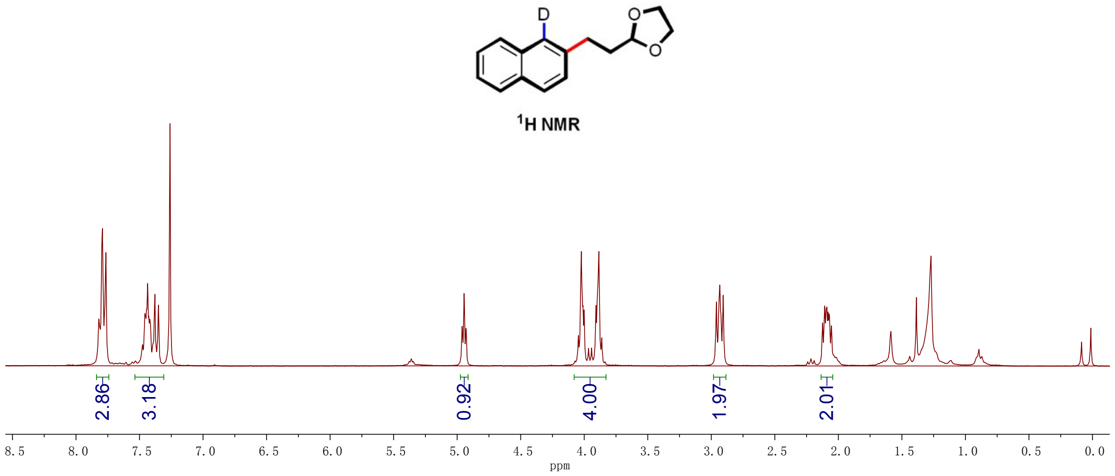

D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

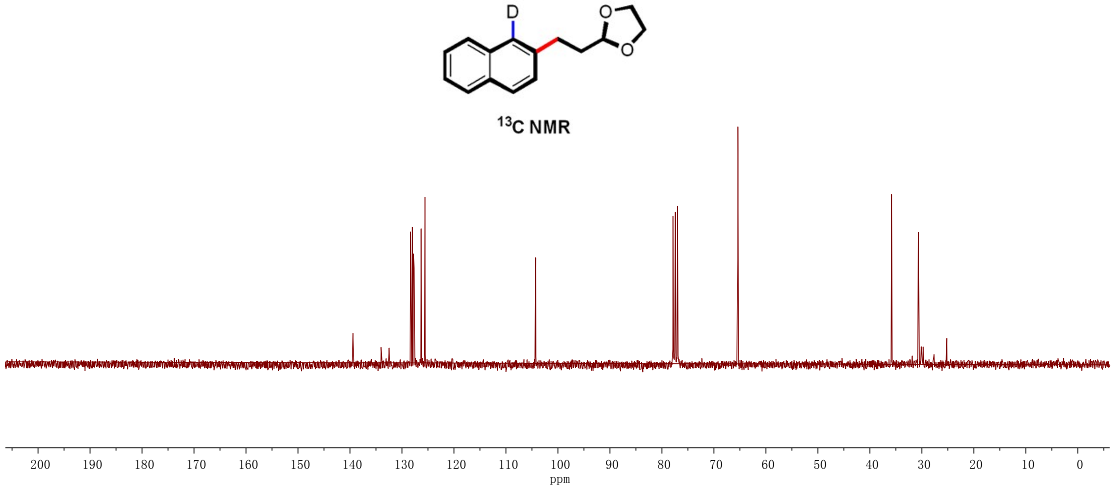

Cl
D
O
O
¹H NMR
0.97
1.00
2.02
2.10
3.11
2.12
2.16
3.26
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

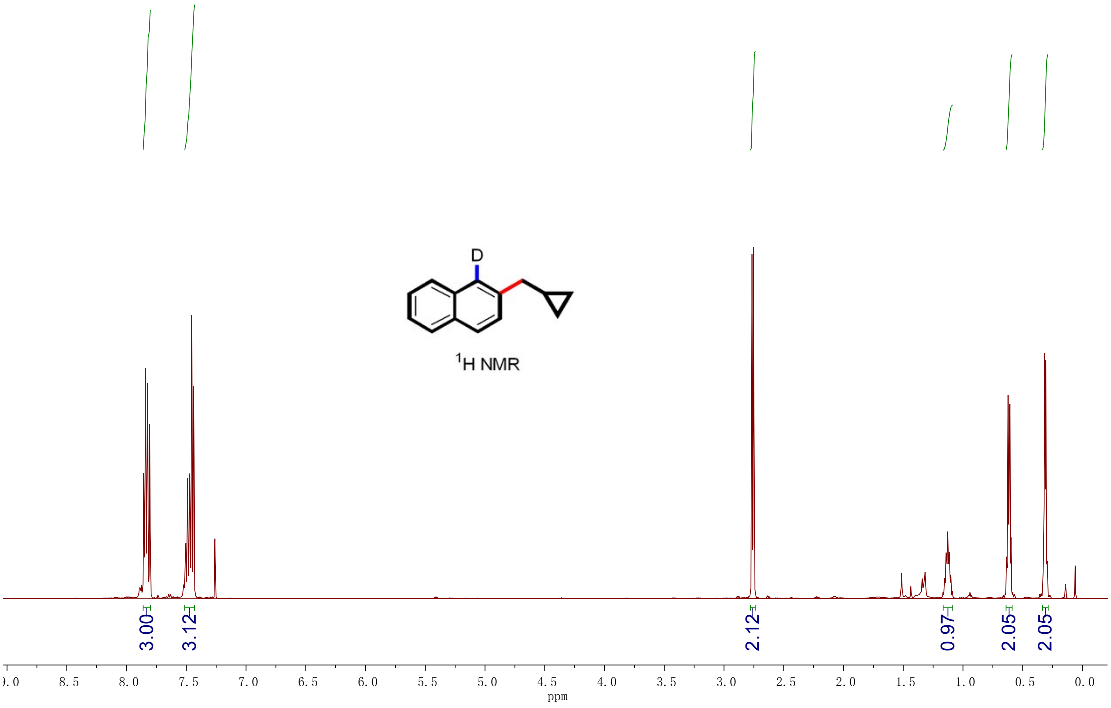

Cl
D
O
O
¹³C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

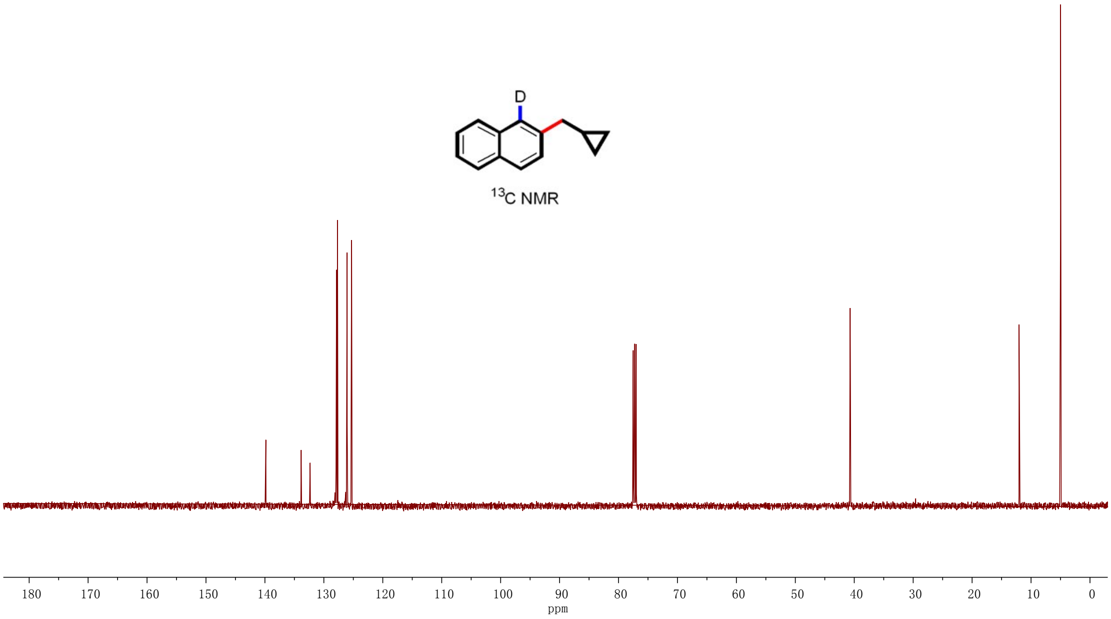

D
O
O
^{1}H NMR
2.91
2.01
1.00
2.00
2.11
2.10
2.30
3.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

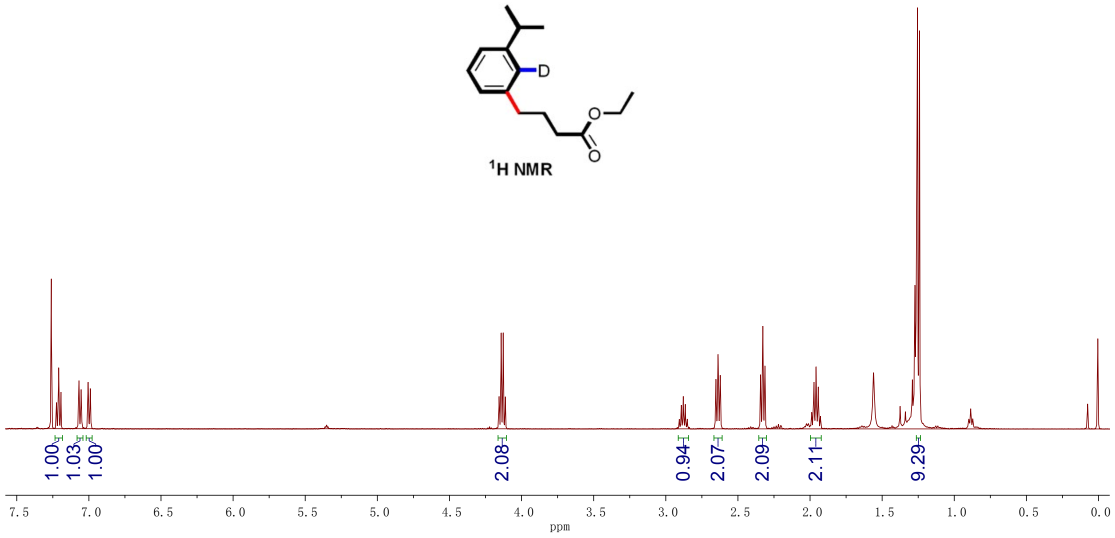

D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

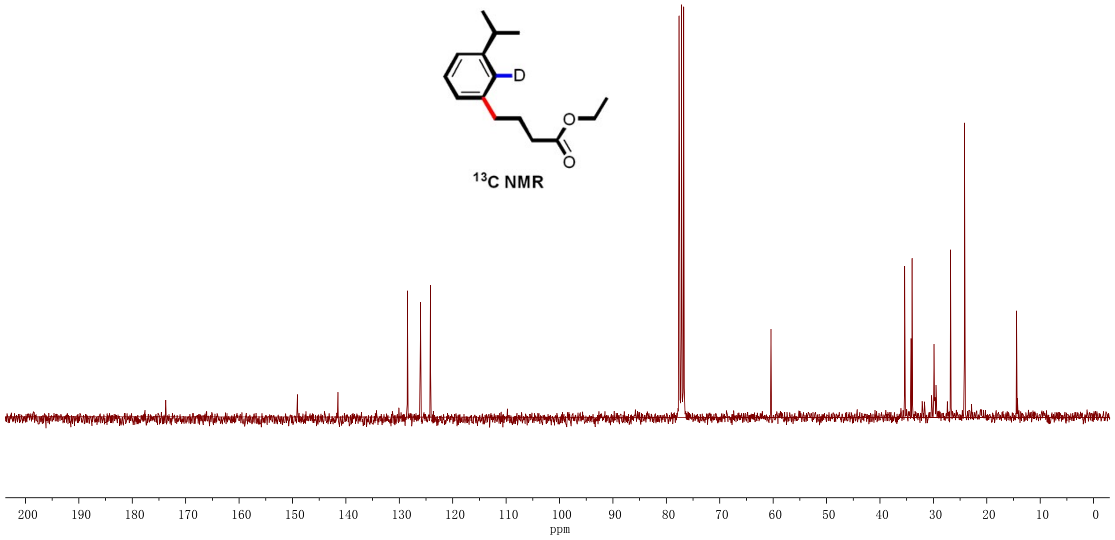

D
O
O
^{1}H NMR
2.86
3.18
0.92
4.00
1.97
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

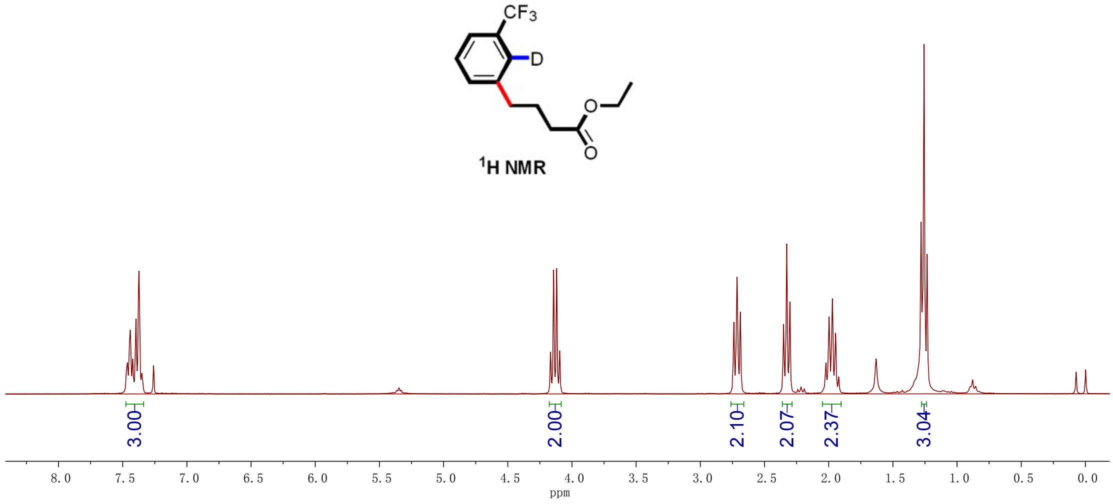

D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

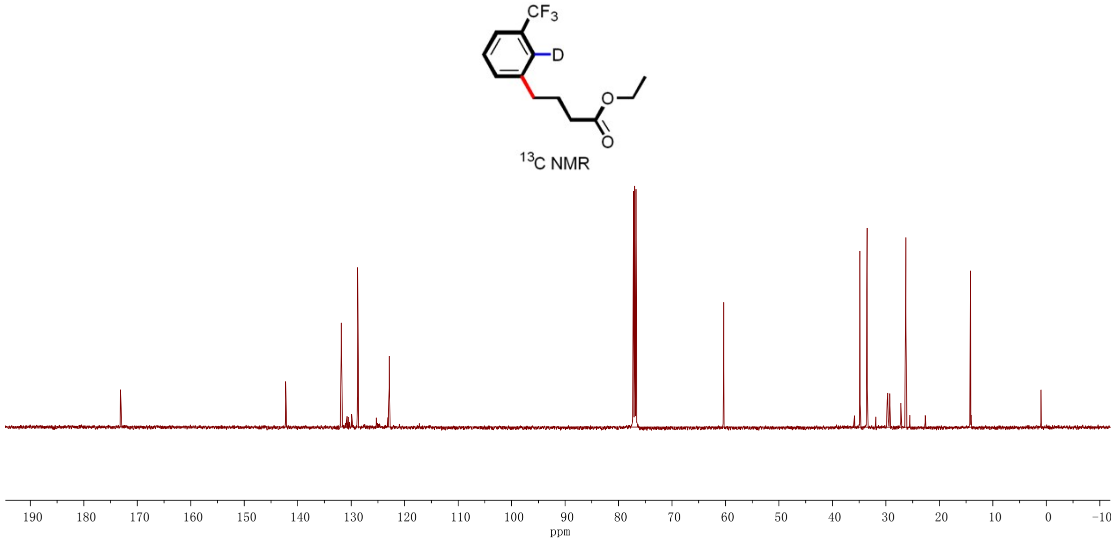

D
^{1}H NMR
3.00
3.12
2.12
0.97
2.05
2.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

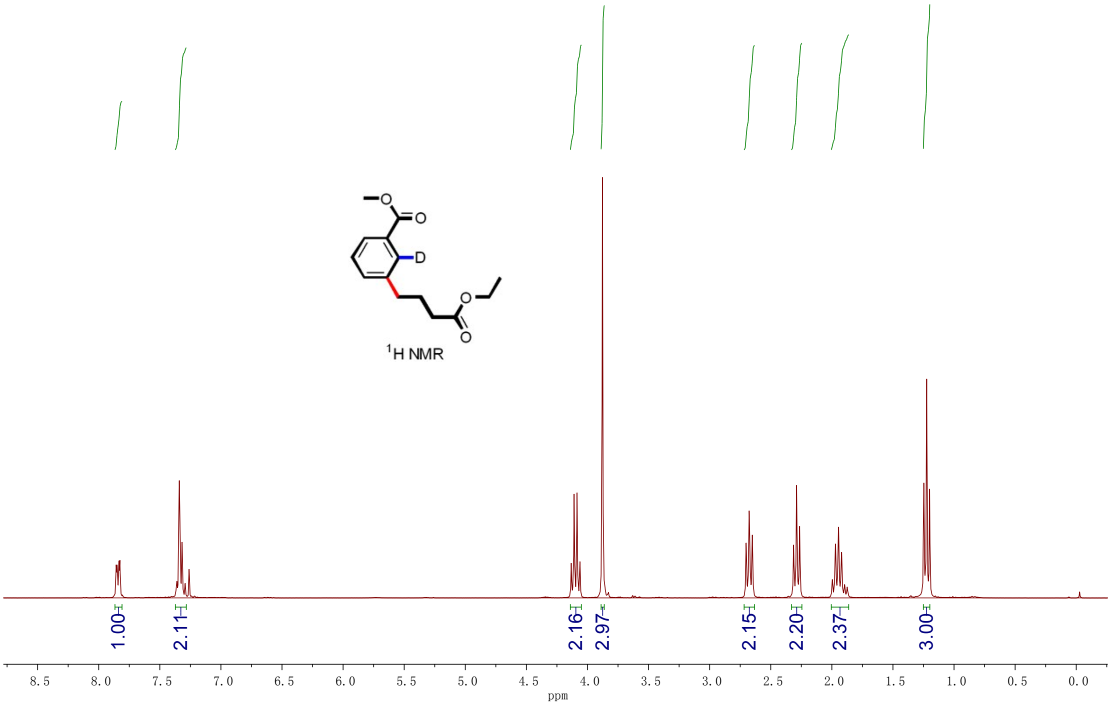

D
^{13}C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


D
O
O
^{1}H NMR
1.00
1.03
1.00
2.08
0.94
2.07
2.09
2.11
9.29
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

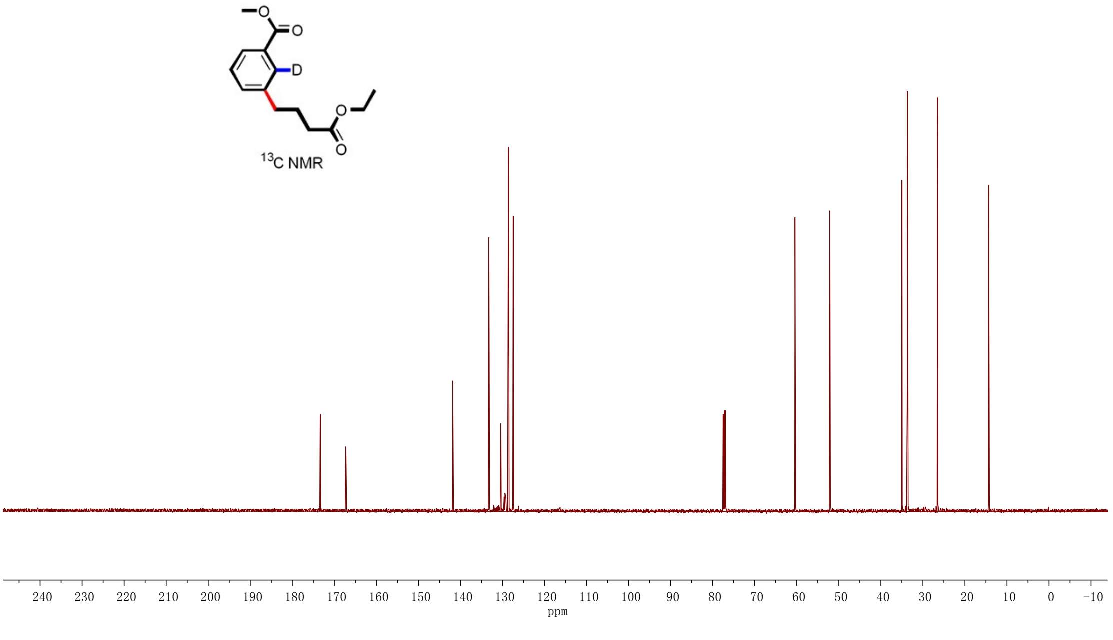

D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CF$_3$
D
O
O
^{1}H NMR
3.00
2.00
2.10
2.07
2.37
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

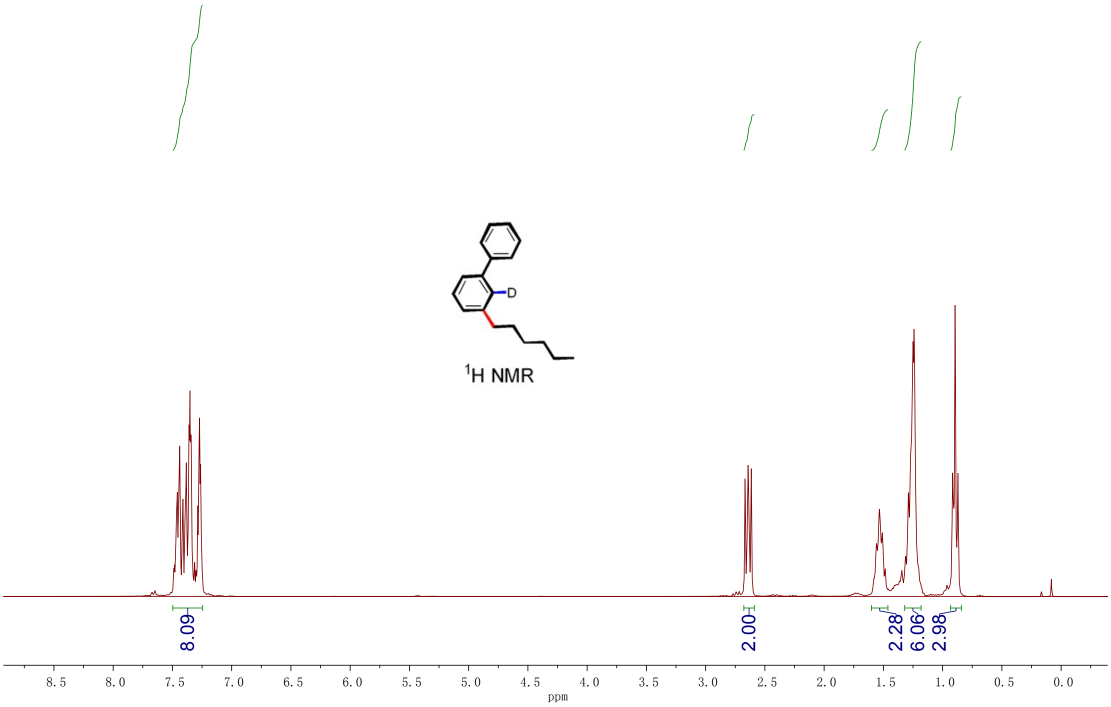

CF$_3$
D
O
O
^{13}C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm

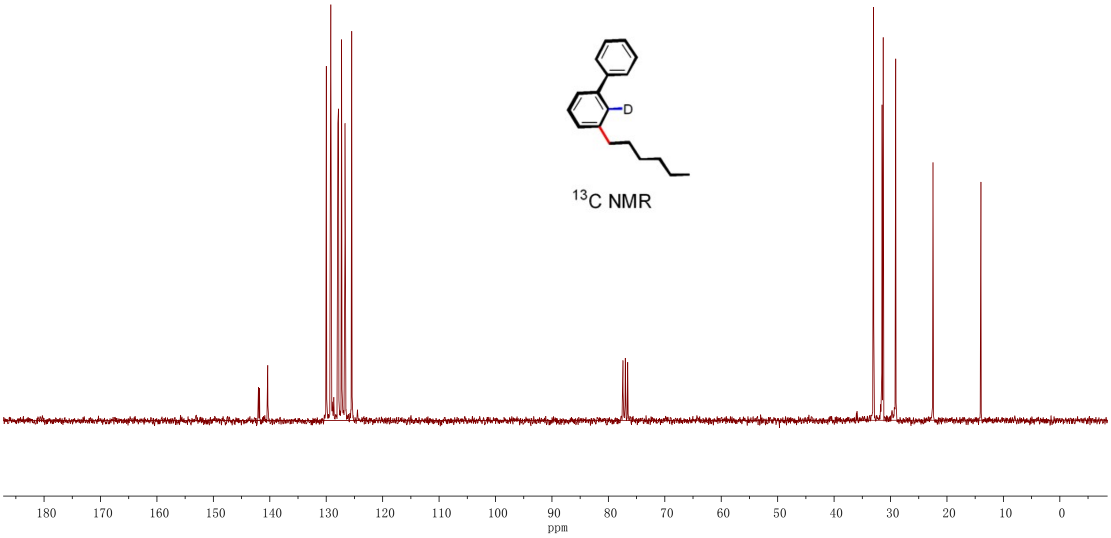


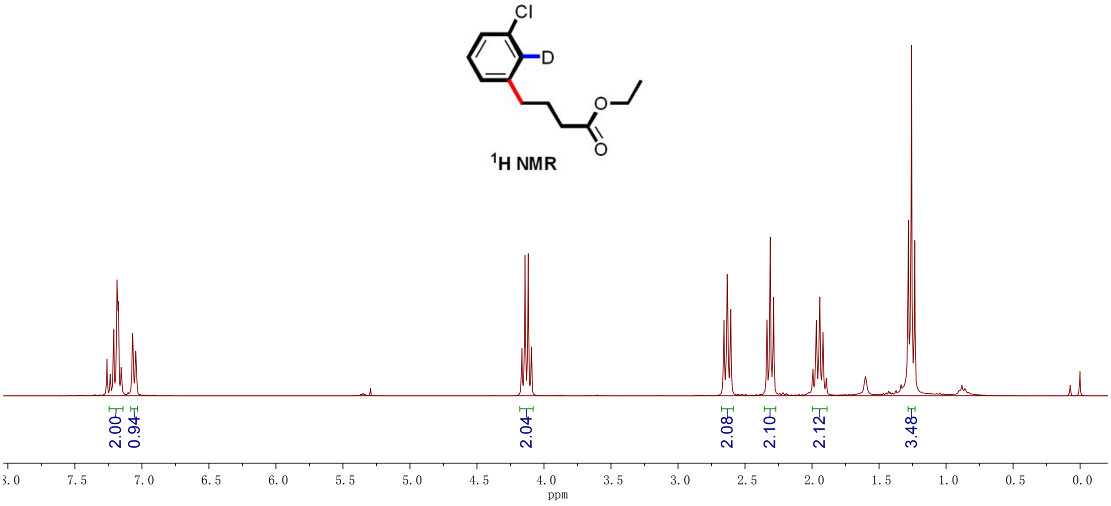
D
O
O
O
O
1H NMR
1.00
2.11
2.16
2.97
2.15
2.20
2.37
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

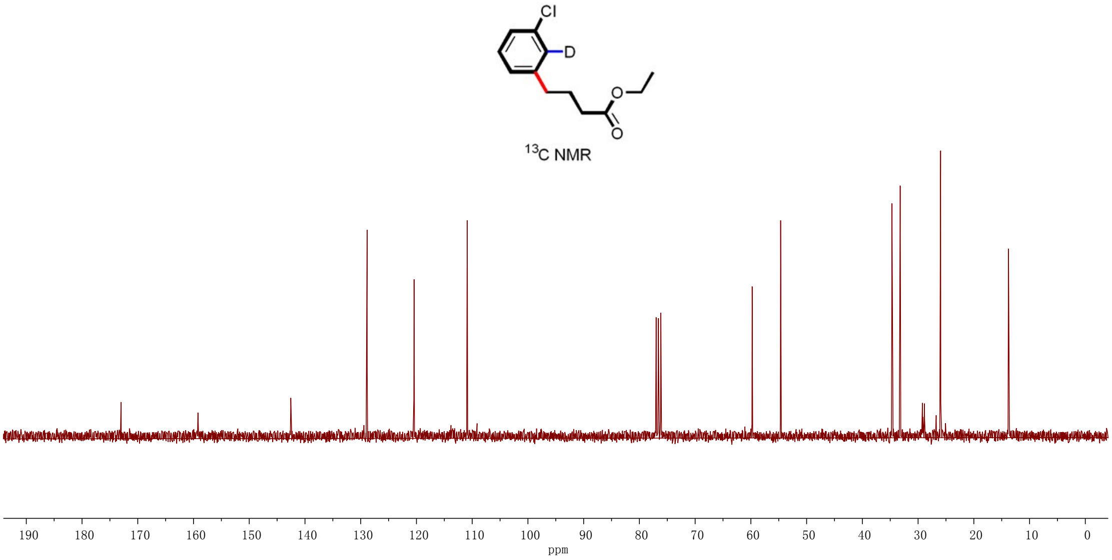


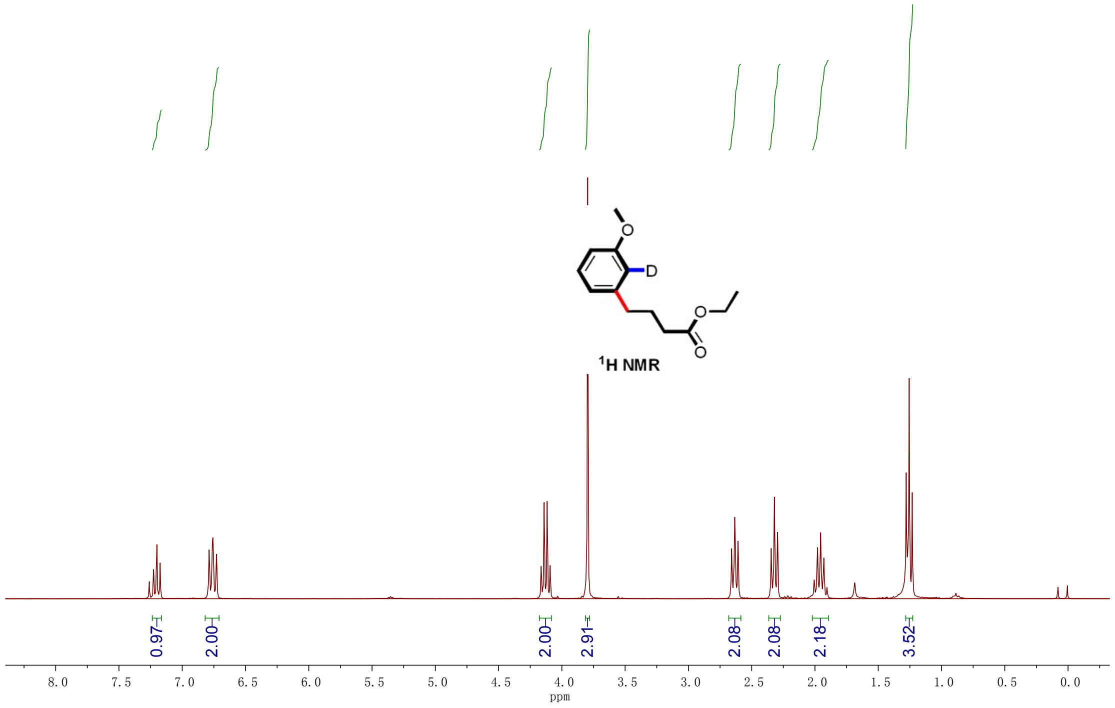
D
O
O
O
O
13C NMR
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm

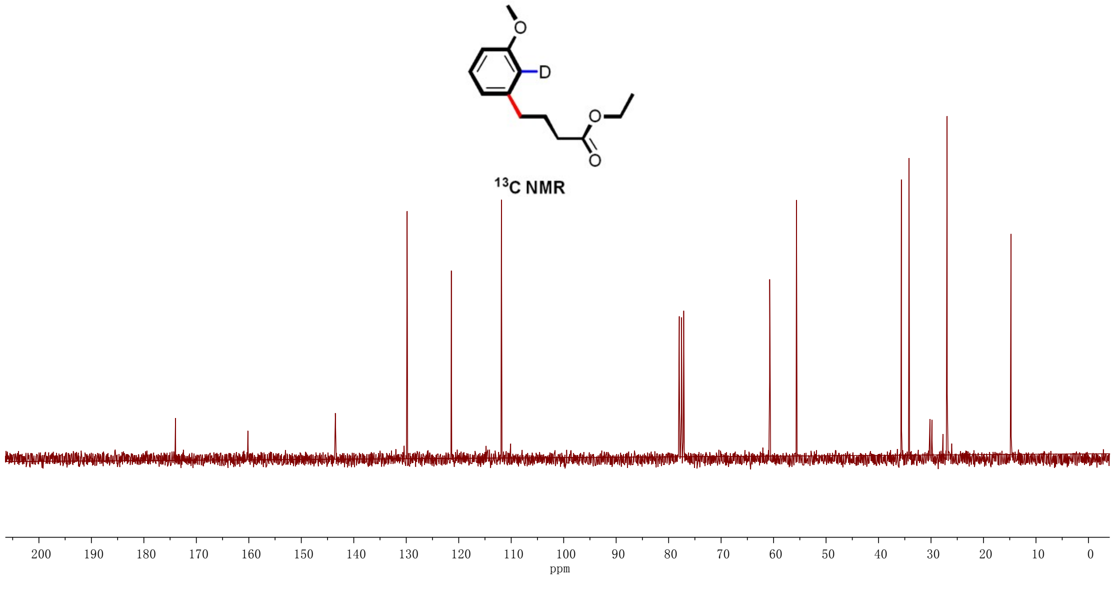

D
^{1}H NMR
8.09
2.00
2.28
6.06
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

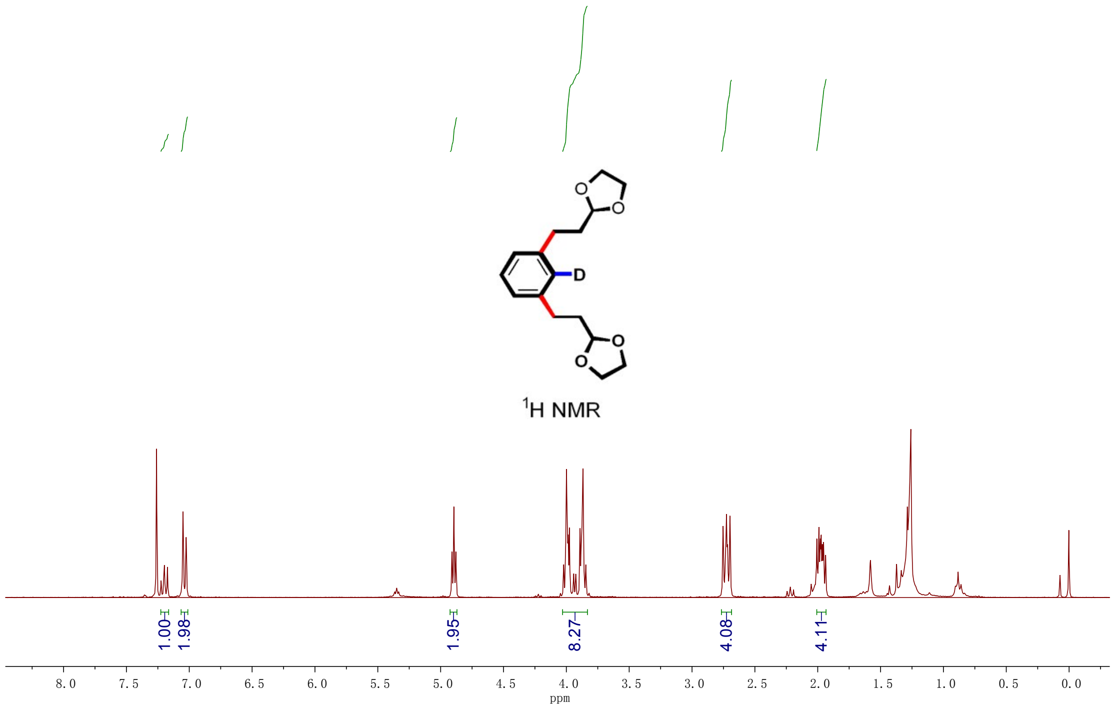

D
^{13}C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Cl
D
O
O
1H NMR
2.00
0.94
2.04
2.08
2.10
2.12
3.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Cl
D
O
O
13C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


D
O
O
O
¹H NMR
0.97
2.00
2.00
2.91
2.08
2.08
2.18
3.52
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


D
O
O
O
¹³C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
O
D
O
O
^{1}H NMR
1.00
1.98
1.95
8.27
4.08
4.11
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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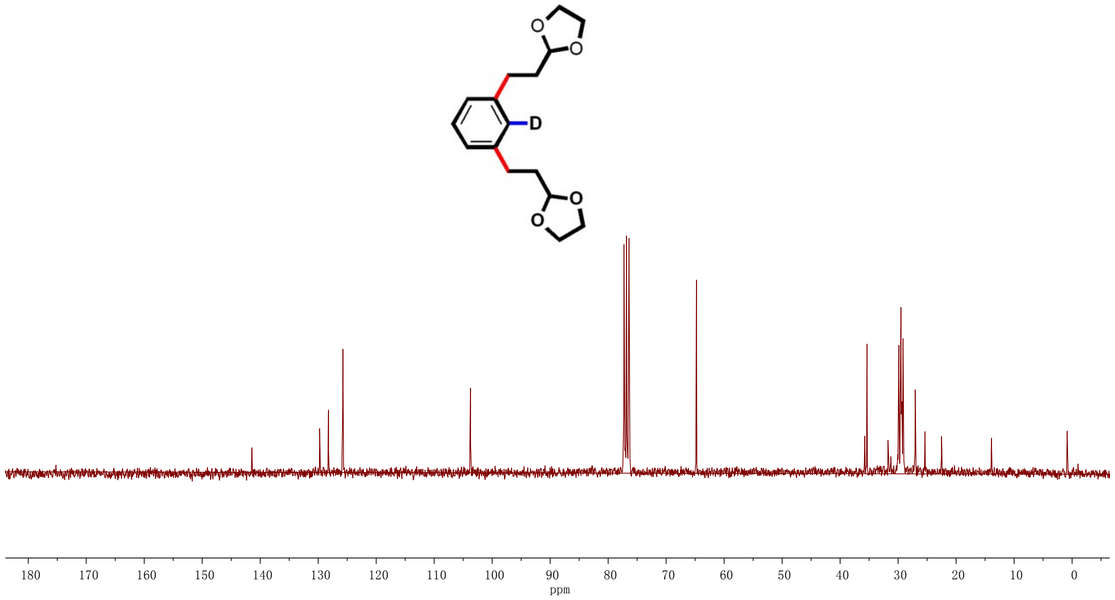
O
O
D
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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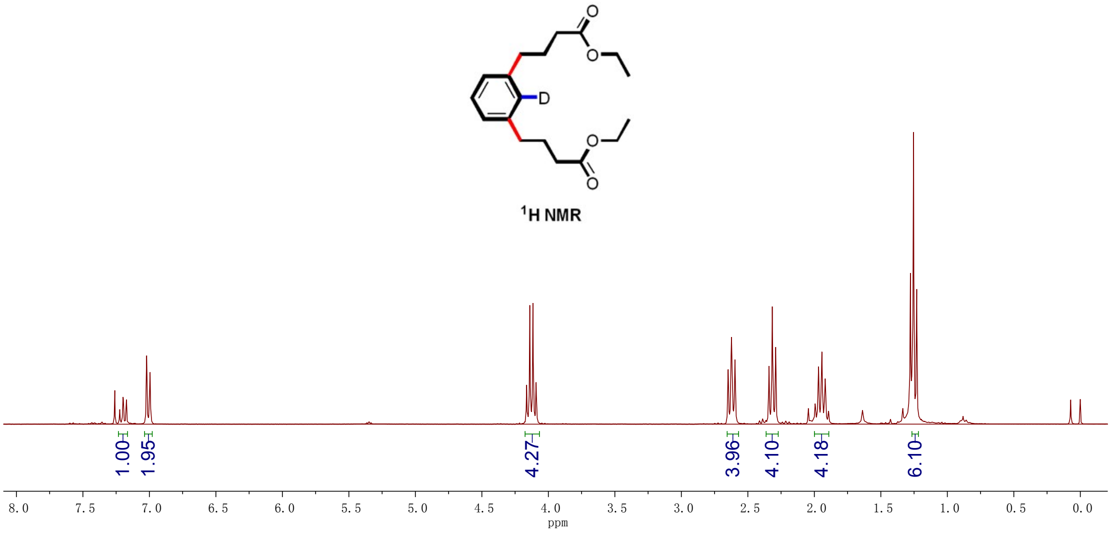
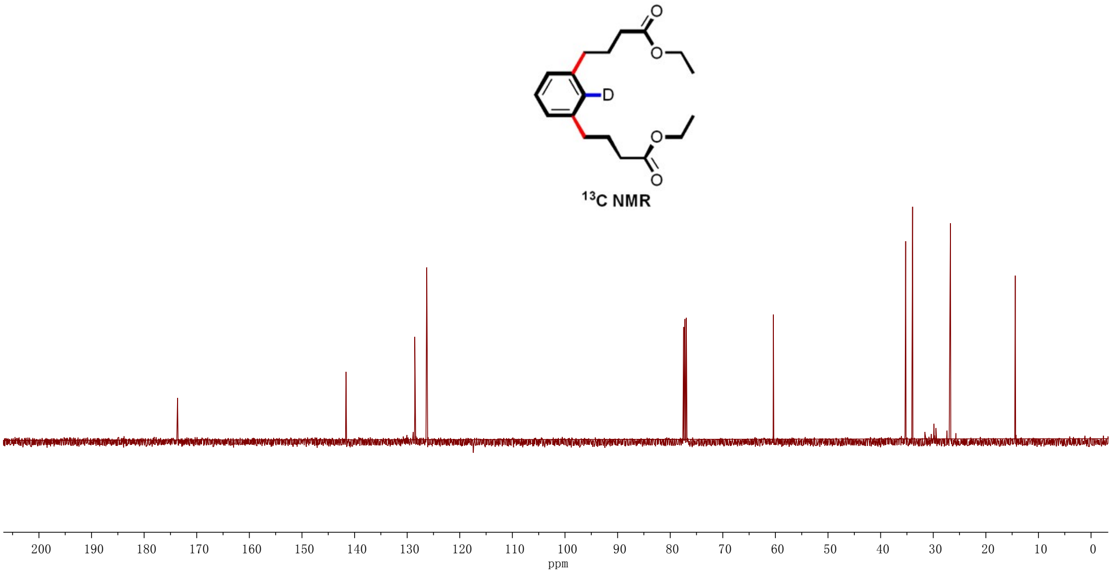
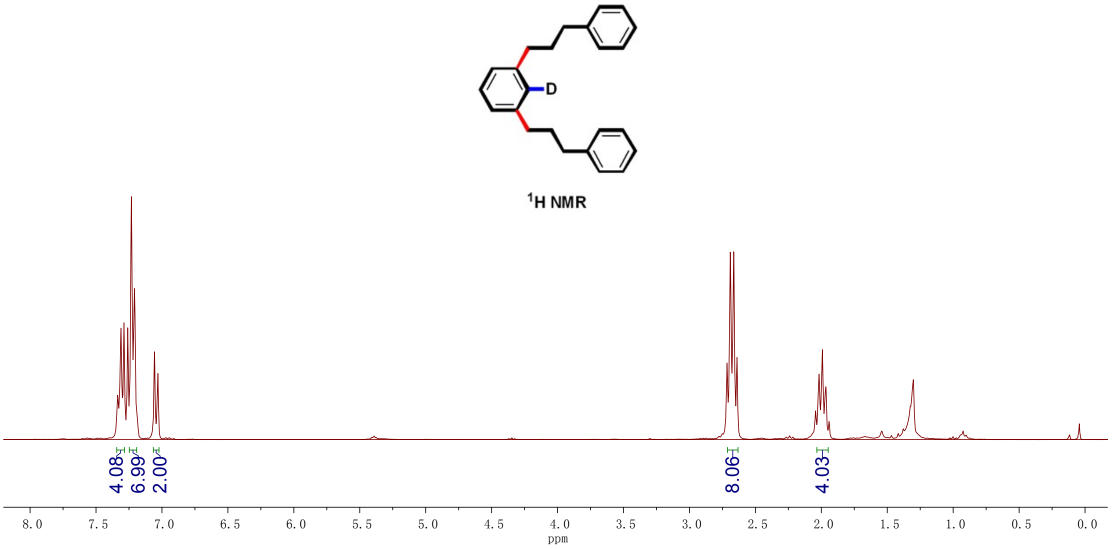
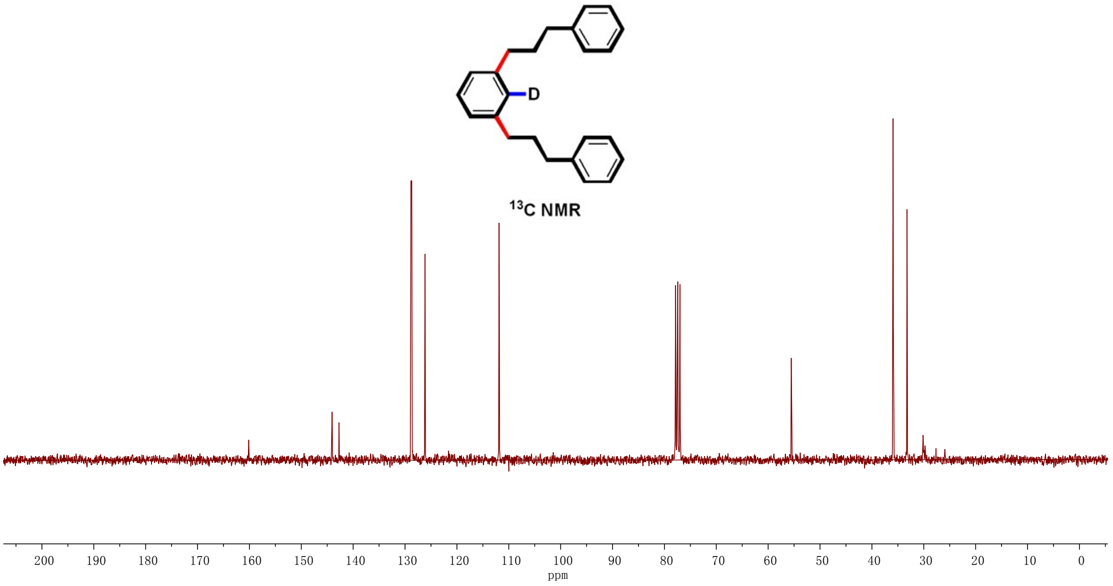
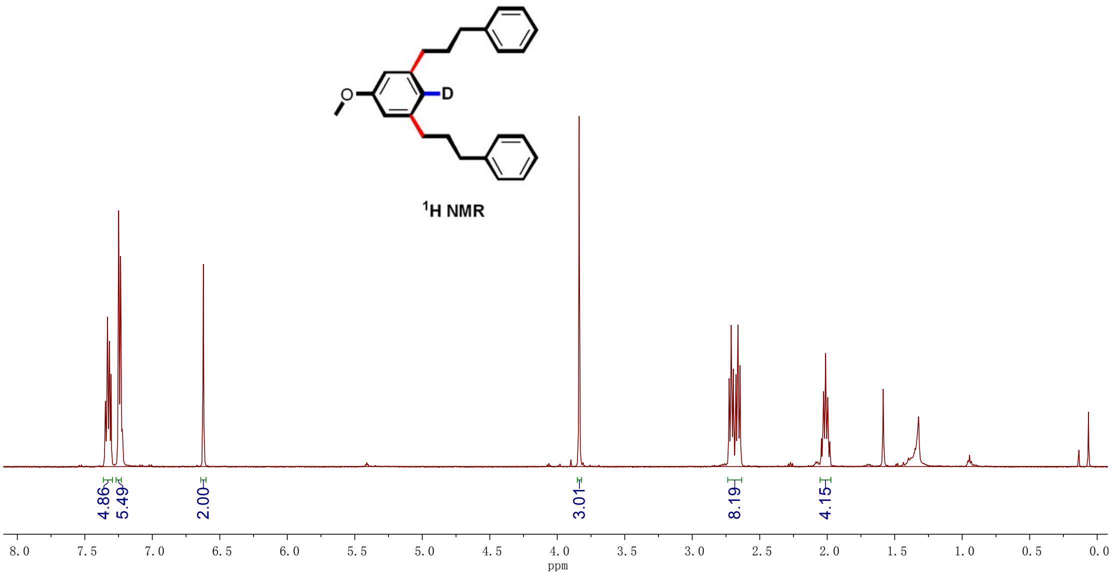
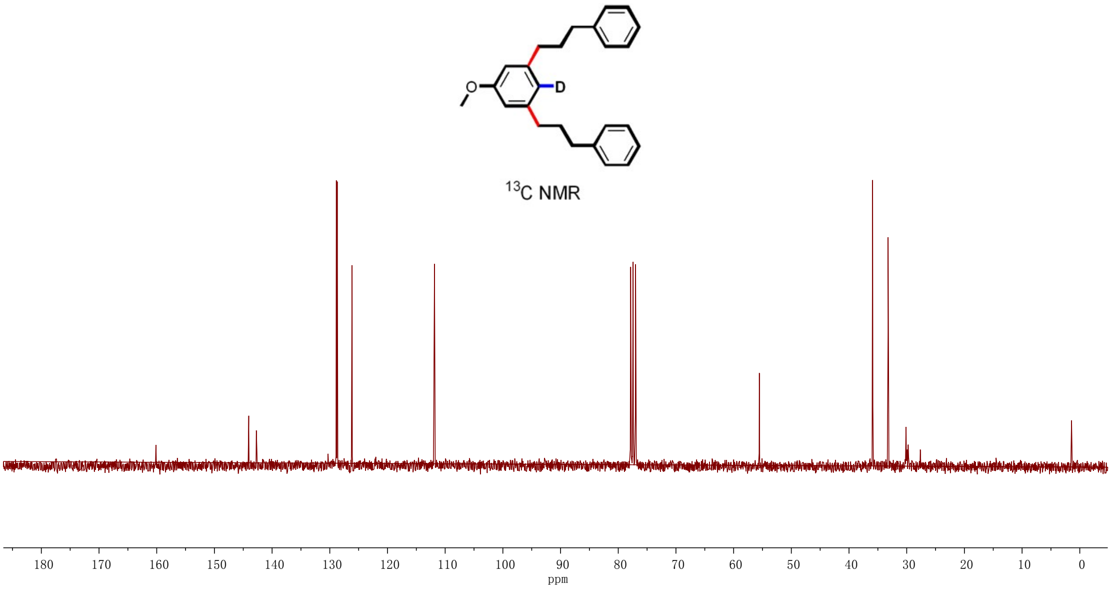

O
O
D
O
O
^{1}H NMR
1.00
1.95
4.27
3.96
4.10
4.18
6.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

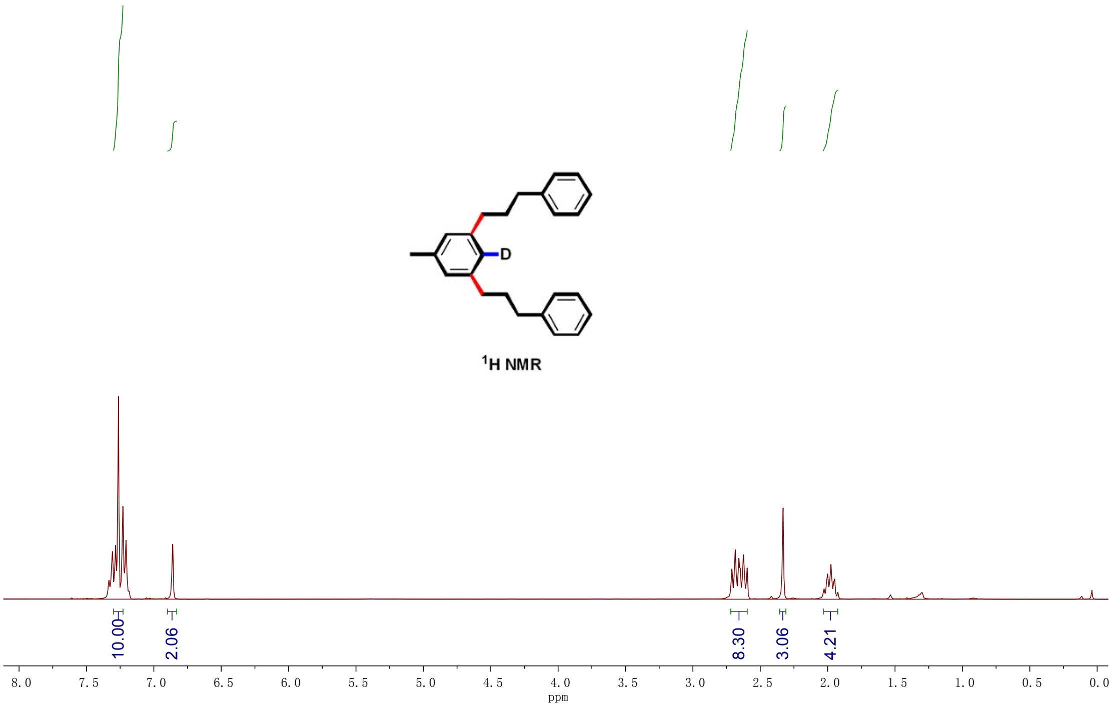

O
O
D
O
O
^{13}C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

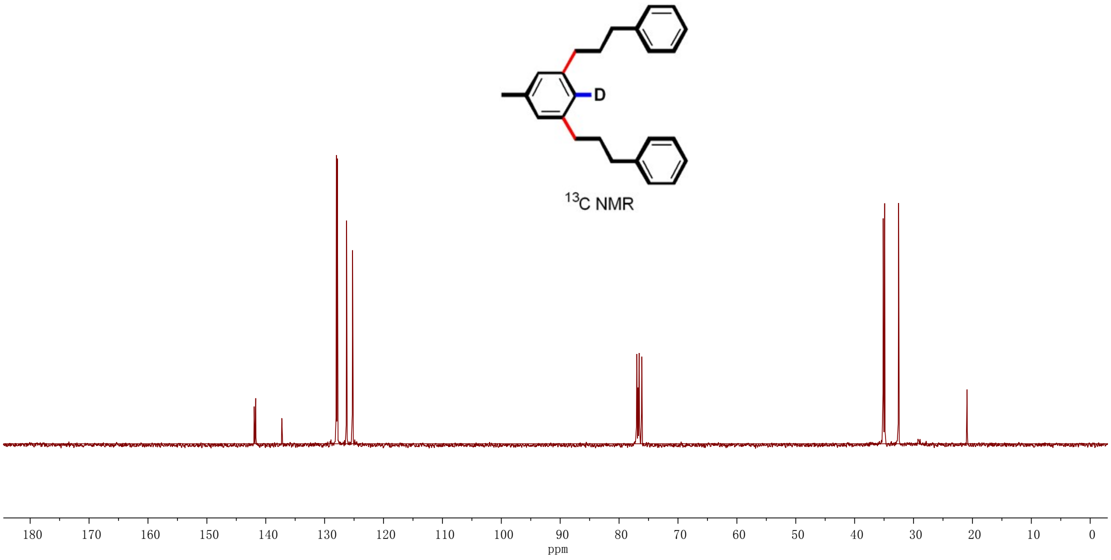

D
¹H NMR
4.08
6.99
2.00
8.06
4.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

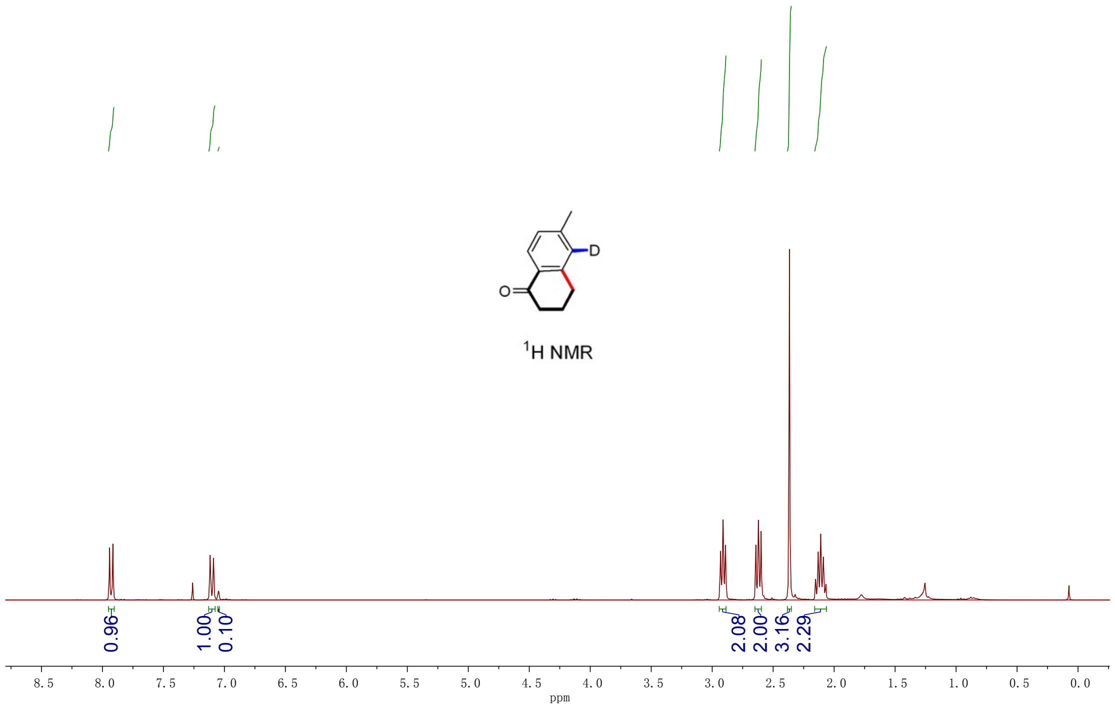

D
¹³C NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

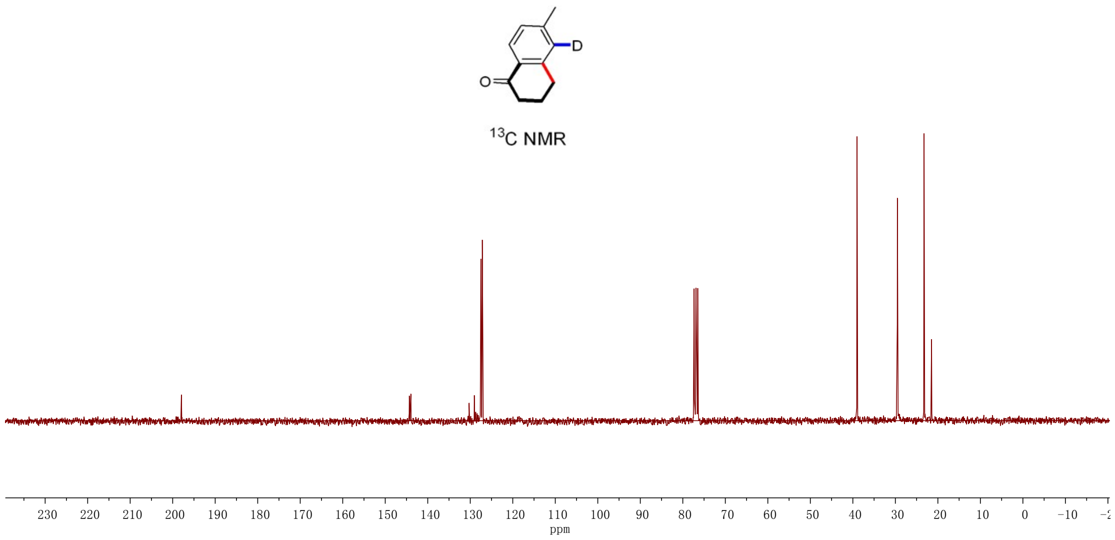

O
D
1H NMR
4.86
5.49
2.00
3.01
8.19
4.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
D
13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


D
^{1}H NMR
10.00
2.06
8.30
3.06
4.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


D
^{13}C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


D
O
^{1}H NMR
0.96
1.00
0.10
2.08
2.00
3.16
2.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


D
O
^{13}C NMR
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm