

SUPPORTING INFORMATION

Programmable Iodization/Deuterolysis Sequences of Phosponium

Ylide to Access Deuterated Benzyl Iodides and Aromatic Aldehydes

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1. General Information

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. The CH_3Li used herein was a solution in diethoxymethane (1.6 M) with safe seal, which was purchased from Adamas-Beta, China. Flash chromatography was carried out on silica gel (200 – 300 mesh, Petroleum Ether/EtOAc solvent systems). ^1H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s, single; d, doublet; t, triplet; m, multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{31}P NMR data were collected at 162 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT – IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES^+ Mass spectrometer and acetonitrile was used to dissolve the sample. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

2. General Procedures

2.1 Procedure A: preparation of phosphonium salts 1 from benzyl halide

PPh_3 (1.05 equiv., 1.76 g, 5.25 mmol) was added to a solution of benzyl halide (1.0 equiv., 5.00 mmol) in toluene (5 mL). The well-mixed reaction mixture was placed in an oil bath at 110 °C (pre-heated) for 12 h. The mixture was filtered, and the obtained precipitate was washed by diethyl ether and dried *in vacuo* to give the corresponding phosphonium salts.

2.2 Procedure B: preparation of deuterated benzyl iodine 2

CH_3Li (0.53 mL, 1.05 equiv., 0.84 mmol) was added to a suspension of phosphonium salts (1.0 equiv., 0.80 mmol) in dry THF (5 mL) under argon atmosphere at 0 °C. The mixture was stirred at 0 °C for 15 min. Then, a solution of I_2 (213 mg, 1.05 equiv., 0.84 mmol) in dry THF (1 mL) was added and stirred from 0 °C to room temperature

for additional 8 h. Thereafter, a solution of NaOH (128 mg, 4.0 equiv., 3.20 mmol) in D₂O (60 equiv.) was added (pre-mixed for 1 h). The reaction mixture was cooled to 0 °C again and stirred from 0 °C to room temperature for another 18 h. Then H₂O (10 mL) was added and the obtained solution was extracted by DCM (20 mL x 3), then dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 100:0 to 99:1) to afford the desired deuterated benzyl iodine **2**.

2.3 Procedure C: preparation of deuterated aldehyde 3

CH₃Li (0.53 mL, 1.05 equiv., 0.84 mmol) was added to a suspension of phosphonium salts (1.0 equiv., 0.80 mmol) in dry THF (5 mL) under argon atmosphere at 0 °C. The mixture was stirred at 0 °C for 15 min. Then, a solution of I₂ (213 mg, 1.05 equiv., 0.84 mmol) in dry THF (1 mL) was added and stirred from 0 °C to room temperature for additional 8 h. Thereafter, a solution of NaOAc (262 mg, 4.0 equiv., 3.20 mmol) in D₂O (60 equiv.) was added. The reaction mixture was cooled to 0 °C again and stirred from 0 °C to room temperature for another 18 h. Then the reaction was quenched by a solution of sodium sulfite, extracted by DCM (20 mL x 3), and dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure in ice bath conditions and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 100:0 to 99:1) to afford the desired deuterated aldehyde **3**.

2.4 Procedure D: preparation of deuterated drug analogues 5

K₂CO₃ (3.0 equiv.) was added to the mixture of deuterated benzyl iodine (1.0 equiv.) and the corresponding secondary amine **4** (1.05 equiv.) in CH₃CN (4 mL) under argon atmosphere. The reaction mixture was stirred at 45 °C for 18 h, then added 10 mL H₂O, extracted by DCM (15 mL x 3), and finally dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 95:5 to 90:10) to afford the desired deuterated drug analogues **5**.

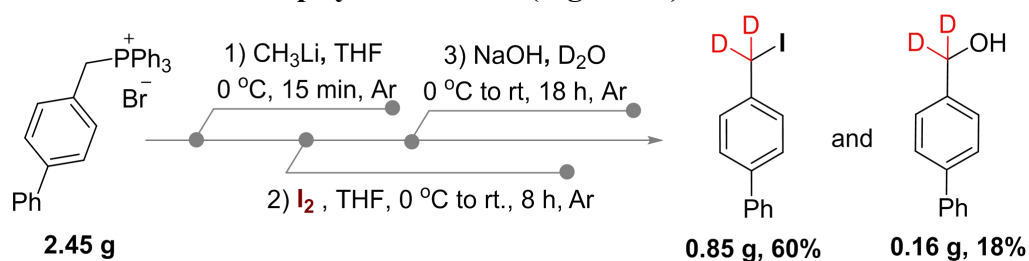
2.5 Procedure E: preparation of product 6

NaBH₄ (15 mg, 2.0 equiv., 0.30 mmol) was added to the suspension of **3t** (1.0 equiv., 0.15 mmol) in dry MeOH (3 mL). The reaction mixture was stirred at room temperature for 0.5 h, then quenched by NH₄Cl aqueous solution, extracted by DCM (10 mL x 3), and finally dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EtOAc-PE/EtOAc = 95:5 to 90:10) to afford the desired product **6**.

2.6 Procedure F: preparation of product 7

Ethyl 2-(triphenyl-15-phosphanylidene) acetate (58 mg, 1.10 equiv., 0.17 mmol) was added to the suspension of 2-naphthaldehyde-*α-d* (1.0 equiv., 0.15 mmol) in dry DCM (2 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 100:0 to 99:1) to afford the desired product.

2.7 Procedure G: scale-up synthesis of 2a (Figure S1)



CH₃Li (3.20 mL, 1.06 equiv., 5.12 mmol) was added to a suspension of phosphonium salt **1a** (2.45 g, 1.0 equiv., 4.80 mmol) in dry THF (30 mL) in a 100 mL round bottomed flask under argon atmosphere at 0 °C. The mixture was stirred at 0 °C for 0.5 h. Then, a solution of I₂ (1.32 g, 1.08 equiv., 5.20 mmol) in dry THF (5 mL) was added and stirred from 0 °C to room temperature for additional 12 h. Thereafter, a solution of NaOH (0.77 g, 4.0 equiv., 19.20 mmol) in D₂O (42 equiv., 4 mL) was added. The reaction mixture was stirred for another 24 h from 0 °C to room temperature, then 50 mL H₂O was added, extracted by DCM (100 mL x 3), and finally dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure,

and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 100:0 to 99:1) to afford the desired product **2a** (0.85 g, 60%) and [1,1'-biphenyl]-4-ylmethan-*d*₂-ol (PE/EtOAc-PE/EtOAc = 95:5 to 90:10) as byproduct (0.16 g, 18%).

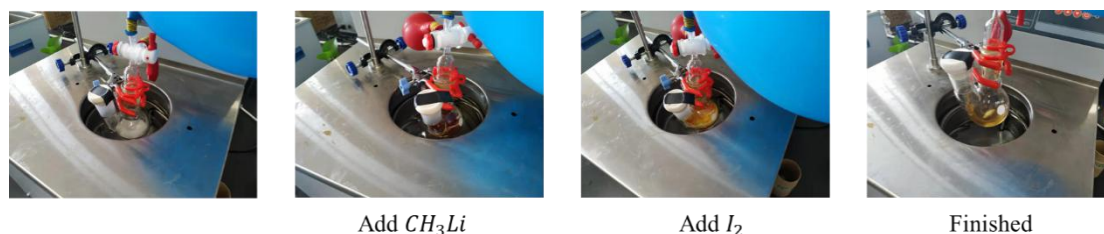
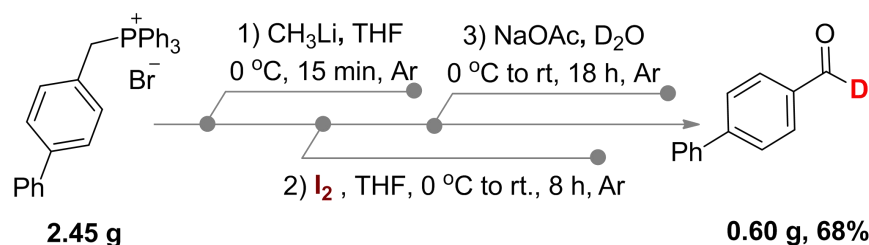


Figure S1: Scale-up synthesis of **2a** (photographed by Xian-Chen He)

2.8 Procedure H: scale-up synthesis of **3a** (Figure S2)



CH_3Li (3.15 mL, 1.05 equiv., 5.04 mmol) was added to a suspension of phosphonium salt **1a** (2.45 g, 1.0 equiv., 4.80 mmol) in dry THF (30 mL) in a 100 mL round bottomed flask under argon atmosphere at 0 °C. The mixture was stirred at 0 °C for 0.5 h. Then, a solution of I_2 (1.28 g, 1.05 equiv., 5.04 mmol) in dry THF (5 mL) was added and stirred from 0 °C to room temperature for additional 12 h. Thereafter, a solution of NaOAc (1.57 g, 4.0 equiv., 19.20 mmol) in D_2O (42 equiv., 4 mL) was added. The reaction mixture was stirred for another 24 h from 0 °C to room temperature, then quenched by sodium sulfite solution until the organic phase turned yellow, extracted by DCM (100 mL x 3), and finally dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 100:0 to 99:1) to afford the desired product **3a** (0.60 g, 68%).

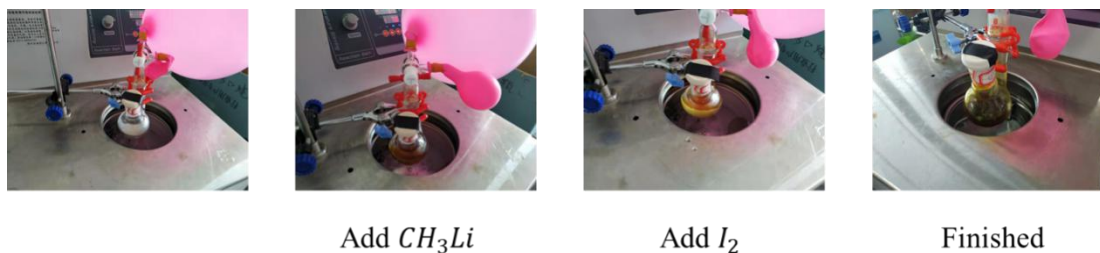
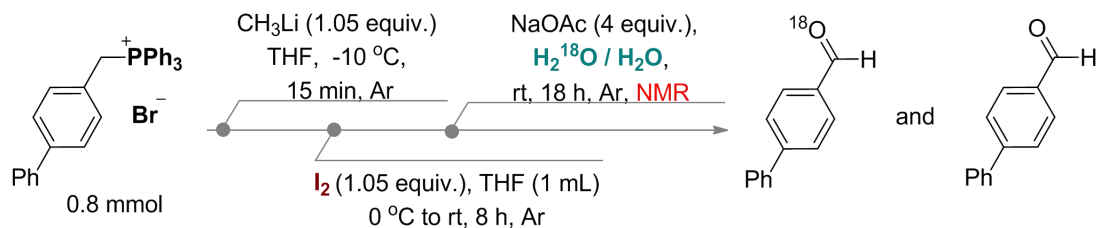


Figure S2: Scale-up synthesis of **3a** (photographed by Xian-Chen He)

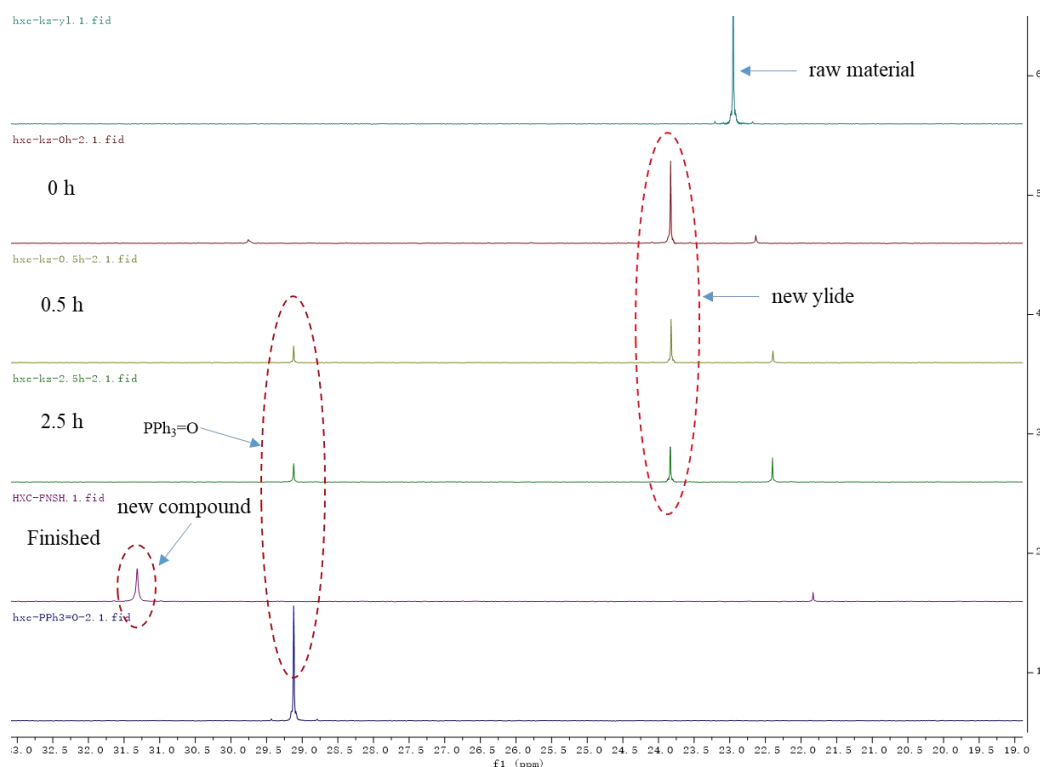
2.9 Procedure I: one-pot procedure for the synthesis of drug analogues

PPh₃ (110 mg, 1.05 equiv., 0.42 mmol) was added to a suspension of benzyl bromide (1.0 equiv., 0.40 mmol) in dry THF (4 mL) in a 15 mL Schleck flask with sidearm under argon atmosphere at 60 °C overnight. Next, CH₃Li (0.28 mL, 1.1 equiv., 0.44 mmol) was added to the mixture at 0 °C in 15 min. Then, a solution of I₂ (107 mg, 1.05 equiv., 0.42 mmol) in dry THF (0.5 mL) was added and stirred from 0 °C to room temperature for additional 12 h. Thereafter, a solution of NaOH (48 mg, 3.0 equiv., 1.20 mmol) in D₂O (42 equiv., 0.5 mL) was added (pre-mixed for 1 h). The reaction mixture was stirred for another 8 h from 0 °C to room temperature, then the corresponding secondary amine (1.05 equiv.) in THF (0.5 mL) was added and the reaction mixture was stirred for 12 h. Then 10 mL H₂O was added, the obtained solution was extracted by DCM (15 mL x 3), then dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE-PE/EtOAc = 95:5 to 90:10) to afford the desired product.

3. Mechanistic studies.



We monitored the reaction mixture of the model reaction by ^{31}P NMR and ESI-MS after adding $\text{H}_2^{18}\text{O}/\text{H}_2\text{O}$ (1/1, v/v). The results showed that new ylide was formed after the addition of iodine. As the reaction progressed, Ph_3PO was detected during the hydrolysis process. But Ph_3PO would disappear at the end of the reaction with generating a new P-containing compound.



ESI-MS analysis of the crude reaction mixture was performed (Figure S3). Two peaks corresponding to the product **3a** (HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{10}\text{NaO}^+$ 205.0624; Found 205.0624) and ^{18}O -labelled **3a** (HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{10}\text{Na}^{18}\text{O}^+$ 207.0666; Found 207.0676) were detected. According to the results,

it can be concluded that the oxygen atom on the aldehyde group of the product comes from water.

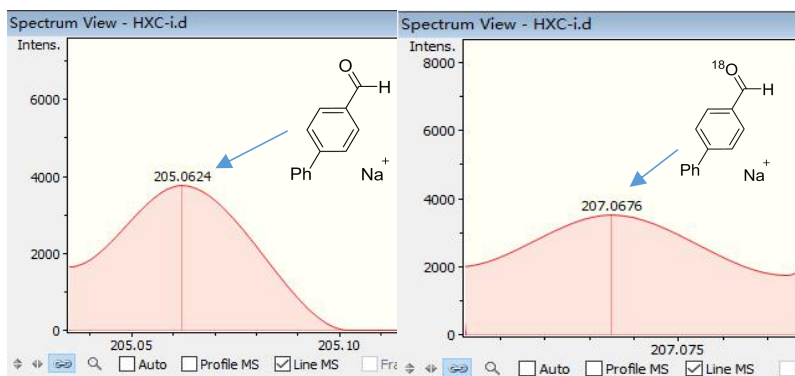
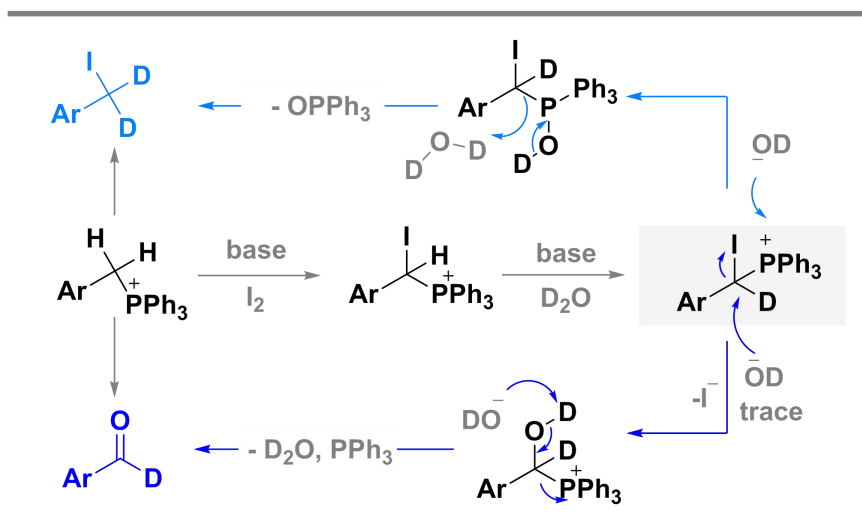
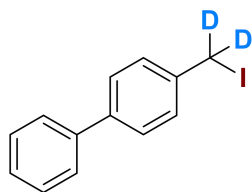


Figure S3: ESI-MS result of the Non-¹⁸O-labelled and ¹⁸O-labelled **3a**

Proposed mechanism



4. Characterization data of Deuterated Benzyl iodine 2



2a: yellow solid (183 mg, yield 77%) by following the general procedure **B** from ([1,1'-biphenyl]-4-ylmethyl)triphenylphosphonium bromide (408 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 97%;

R_f = 0.6 (Petroleum ether/EtOAc, 99/1);

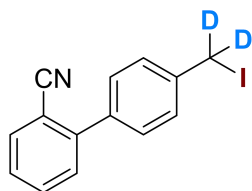
m.p. 101 – 103 °C;

IR (neat) ν 3027, 2269, 1793, 1483, 1117, 895, 754, 687 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.58 – 7.54 (m, 2H), 7.52 – 7.48 (m, 2H), 7.46 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 4.54 – 4.53 (m, 0.07H, $\text{CH}_2\text{I} + \text{CD}_2\text{I}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 140.8, 140.4, 138.2, 129.1, 128.8, 127.53, 127.47, 127.0, 5.7 – 5.2 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M}-\text{I}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{D}_2^+$ 169.0981; Found 169.0981.



2b: white solid (147 mg, yield 57%) by following the general procedure **B** from ((2'-cyano-[1,1'-biphenyl]-4-yl)methyl)triphenylphosphonium bromide (426 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 93%;

R_f = 0.5 (Petroleum ether/EtOAc, 90/10);

m.p. 91 – 93 °C;

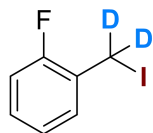
IR (neat) ν 2923, 2219, 1913, 1593, 1401, 1111, 902, 756 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.76 (dd, J = 7.8, 1.4 Hz, 1H), 7.64 (td, J = 7.7, 1.4 Hz, 1H), 7.52 – 7.51 (m, 1H), 7.50 (s, 4H), 7.45 (td, J = 7.6, 1.2 Hz, 1H), 4.51 – 4.50 (m,

0.15H, $\underline{CH_2I+CDHI}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.7, 139.8, 137.6, 133.8, 132.9, 130.0, 129.24, 129.16, 127.8, 118.6, 111.2, 4.9 – 4.4 (m, $\underline{CD_nH_{2-n}}$);

HRMS (ESI) m/z : $[\text{M-I}]^+$ Calcd for $\text{C}_{14}\text{H}_8\text{D}_2\text{N}^+$ 194.0933; Found 194.0932.



2c: light yellow oil (118 mg, yield 62%) by following the general procedure **B** from (2-fluorobenzyl)triphenylphosphonium chloride (323 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 96%;

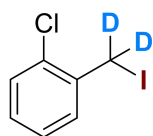
R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 2917, 2849, 1583, 1492, 1454, 1236, 899, 753 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.33 (td, J = 7.6, 1.8 Hz, 1H), 7.23 (tdd, J = 7.4, 5.2, 1.8 Hz, 1H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 6.99 (ddd, J = 9.7, 8.2, 1.2 Hz, 1H), 4.42 – 4.40 (m, 0.09H, $\underline{CH_2I+CDHI}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 160.4 (d, $^1J_{\text{C-F}}$ = 249.8 Hz), 130.8 (d, $^3J_{\text{C-F}}$ = 3.1 Hz), 129.9 (d, $^3J_{\text{C-F}}$ = 8.3 Hz), 126.6 (d, $^2J_{\text{C-F}}$ = 14.6 Hz), 124.5 (d, $^4J_{\text{C-F}}$ = 3.7 Hz), 115.9 (d, $^2J_{\text{C-F}}$ = 21.0 Hz), -3.4 – -4.0 (m, $\underline{CD_nH_{2-n}}$);

HRMS (ESI) m/z : $[\text{M-I}]^+$ Calcd for $\text{C}_7\text{H}_4\text{D}_2\text{F}^+$ 111.0574; Found 111.0563.



2d: light yellow oil (163 mg, yield 80%) by following the general procedure **B** from (2-chlorobenzyl)triphenylphosphonium bromide (373 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 91%;

R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

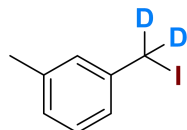
IR (neat) ν 2916, 1593, 1419, 1411, 1217, 1047, 846, 751 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.38 – 7.36 (m, 1H), 7.33 – 7.28 (m, 1H), 7.20 – 7.14 (m, 2H), 4.49 – 4.48 (m, 0.18H, $\underline{CH_2I+CDHI}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 134.3, 131.4, 128.2, 127.8, 127.0, 125.0, 0.5 –

-0.5 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M-I}+\text{OH}^-+\text{Na}]^+$ Calcd for $\text{C}_7\text{H}_5\text{D}_2\text{ClNaO}^+$ 167.0203; Found 167.0215.



2e: Light yellow oil (128 mg, yield 68%) by following the general procedure **B** from (3-methylbenzyl)triphenylphosphonium bromide (357 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 95%;

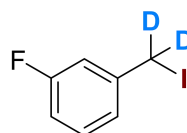
R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 1998, 1746, 1530, 1343, 1206, 937, 773 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.20 – 7.12 (m, 3H), 7.02 (s, 1H), 4.38 (s, 0.10H, $\text{CH}_2\text{I}+\text{CDHI}$), 2.30 (s, 3H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 139.2, 138.5, 129.5, 128.81, 128.79, 125.9, 21.4, 6.4 – 5.5 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M-I}+\text{OH}^-+\text{K}]^+$ Calcd for $\text{C}_8\text{H}_8\text{D}_2\text{KO}^+$ 163.0489; Found 163.0467.



2f: light yellow oil (125 mg, yield 66%) by following the general procedure **B** from (3-fluorobenzyl)triphenylphosphonium chloride (325 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 95%;

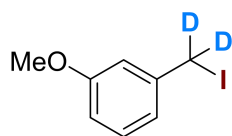
R_f = 0.6 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 2251, 1684, 1439, 1265, 1151, 858, 779, 684 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.24 (td, J = 8.0, 5.8 Hz, 1H), 7.13 (dt, J = 7.6, 1.3 Hz, 1H), 7.06 (dt, J = 9.5, 2.1 Hz, 1H), 6.92 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H), 4.39 – 4.38 (m, 0.10H, $\text{CH}_2\text{I}+\text{CDHI}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 162.7 (d, $^1J_{\text{C-F}}$ = 246.9 Hz), 141.5 (d, $^3J_{\text{C-F}}$ = 7.5 Hz), 130.4 (d, $^3J_{\text{C-F}}$ = 8.3 Hz), 124.4 (d, $^4J_{\text{C-F}}$ = 2.7 Hz), 115.7 (d, $^2J_{\text{C-F}}$ = 22.0 Hz), 115.0 (d, $^2J_{\text{C-F}}$ = 21.1 Hz), 4.3 – 3.2 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[M-I]^+$ Calcd for $C_7H_4D_2F^+$ 111.0574; Found 111.0568.



2g: light yellow oil (164 mg, yield 82%) by following the general procedure **B** (3-methoxybenzyl)triphenylphosphonium chloride (335 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 95%;

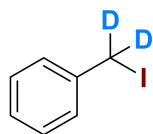
R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 2932, 2357, 1597, 1485, 1263, 1036, 773, 687 cm^{-1} ;

1H NMR ($CDCl_3$, 400 MHz) δ 7.09 (t, J = 7.9 Hz, 1H), 6.87 – 6.84 (m, 1H), 6.82 – 6.79 (m, 1H), 6.69 – 6.67 (m, 1H), 4.31 – 4.30 (m, 0.11H, $CH_2I+CDHI$), 3.68 (s, 3H);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 159.7, 140.6, 129.9, 121.1, 114.2, 113.7, 55.3, 6.0 – 5.2 (m, CD_nH_{2-n});

HRMS (ESI) m/z : $[M-I]^+$ Calcd for $C_8H_7D_2O^+$ 123.0773; Found 123.0773.



2h: light yellow oil (75 mg, yield 43%) by following the general procedure **B** from benzyltriphenylphosphonium bromide (346 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 96%;

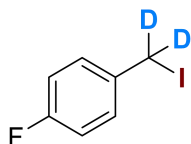
R_f = 0.6 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 2917, 2850, 1529, 1455, 1376, 1145, 723 cm^{-1} ;

1H NMR ($CDCl_3$, 400 MHz) δ 7.42 (d, J = 7.2 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.26 (m, 1H), 4.50 – 4.49 (m, 0.09H, $CH_2I+CDHI$);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 139.2, 128.8, 128.7, 127.9, 5.8 – 5.2 (m, CD_nH_{2-n});

HRMS (ESI) m/z : $[M-I+OH+Na]^+$ Calcd for $C_7H_6D_2NaO^+$ 133.0593; Found 133.0591.



2i: light yellow oil (125 mg, yield 66%) by following the general procedure **B** from (4-fluorobenzyl)triphenylphosphonium chloride (325 mg, 0.80 mmol, 1 equiv.);

*d*₂-Deuteration: 96%;

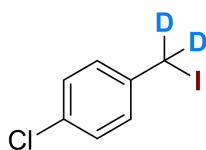
*R*_f = 0.6 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 2921, 2851, 1603, 1508, 1230, 816, 543 cm⁻¹;

¹H NMR (CDCl₃, 400 MHz) δ 7.37– 7.30 (m, 2H), 6.99– 6.94 (m, 2H), 4.42 – 4.40 (m, 0.09H, CH₂I+CDHI);

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 162.1 (d, ¹*J*_{C-F} = 247.7 Hz), 135.11 (d, ⁴*J*_{C-F} = 3.6 Hz), 130.46 (d, ³*J*_{C-F} = 8.2 Hz), 115.80 (d, ²*J*_{C-F} = 21.7 Hz), 6.25 – 1.62 (m);

HRMS (ESI) *m/z*: [M-I]⁺ Calcd for C₇H₄D₂F⁺ 111.0574; Found 111.0551.



2j: white solid (175mg, yield 86%) by following the general procedure **B** from (4-chlorobenzyl)triphenylphosphonium bromide (374 mg, 0.80 mmol, 1 equiv.);

*d*₂-Deuteration: 97%;

m.p. 55 – 57 °C;

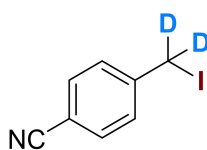
*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 2916, 2274, 1905, 1592, 1490, 1224, 1087, 818 cm⁻¹;

¹H NMR (CDCl₃, 400 MHz) δ 7.29 – 7.22 (m, 4H), 4.38 – 4.37 (m, 0.06H, CH₂I+CDHI).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 137.8, 133.6, 130.1, 129.1, 4.8 – 3.9 (m, CD_nH_{2-n});

HRMS (ESI) *m/z*: [M-I]⁺ Calcd for C₇H₄D₂Cl⁺ 127.0278; Found 127.0278.



2k: white solid (120 mg, yield 62%) by following the general procedure **B** from (4-cyanobenzyl)triphenylphosphonium bromide (366 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 94%;

m.p. 99 – 101 °C;

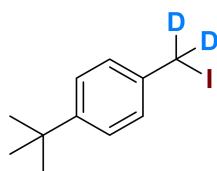
R_f = 0.3 (Petroleum ether/EtOAc, 95/5);

IR (neat) ν 2917, 2222, 1932, 1605, 1503, 833, 812, 736 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.61 – 7.56 (m, 2H), 7.49 – 7.44 (m, 2H), 4.44 – 4.43 (m, 0.12H, $\text{CH}_2\text{I}+\text{CDHI}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 144.6, 132.6, 129.4, 118.5, 111.6, 3.1 – 2.5 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M}-\text{I}+\text{OH}+\text{H}]^+$ Calcd for $\text{C}_8\text{H}_6\text{D}_2\text{NO}^+$ 136.0726; Found 136.0725.



2l: light yellow oil (188 mg, yield 85%) by following the general procedure **B** from (4-(*tert*-butyl)benzyl)triphenylphosphonium bromide (391 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 95%;

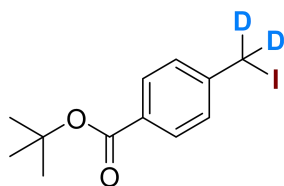
R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

IR (neat) ν 3049, 2958, 2066, 1599, 1505, 1191, 799, 473 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.30 (s, 4H), 4.44 – 4.43 (m, 0.11H, $\text{CH}_2\text{I}+\text{CDHI}$), 1.30 (s, 9H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 151.0, 136.1, 128.5, 125.8, 34.7, 31.3, 6.2 – 5.6 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M}-\text{I}]^+$ Calcd for $\text{C}_{11}\text{H}_{13}\text{D}_2^+$ 149.1294; Found 149.1291.



2m: light yellow oil (156 mg, yield 61%) by following the general procedure **B** from

(4-(*tert*-butoxycarbonyl)benzyl)triphenylphosphonium bromide (426 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 91%;

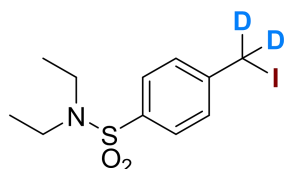
R_f = 0.4 (Petroleum ether/EtOAc, 90/10);

IR (neat) ν 2813, 2533, 1670, 1420, 1280, 1016, 849, 695 cm^{-1} ;

^1H NMR(CDCl_3 , 400 MHz) δ 7.83 – 7.79 (m, 2H), 7.31 – 7.28 (m, 2H), 4.34 – 4.33 (m, 0.18H, $\text{CH}_2\text{I} + \text{CDHI}$), 1.49 (s, 9H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 165.2, 143.7, 131.5, 130.0, 128.6, 81.1, 28.2, 4.3 – 3.8 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M}-\text{I}]^+$ Calcd for $\text{C}_{12}\text{H}_{13}\text{D}_2\text{O}_2^+$ 193.1192; Found 193.1169.



2n: white solid (241 mg, yield 85%) by following the general procedure **B** from (4-(*N,N*-diethylsulfamoyl)benzyl)triphenylphosphonium bromide (454 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 96%;

m.p. 71 – 73 $^{\circ}\text{C}$;

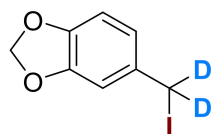
R_f = 0.3 (Petroleum ether/EtOAc, 90/10);

IR (neat) ν 2972, 2928, 1932, 1464, 1326, 1145, 1087, 941 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.71 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 4.46 – 4.45 (m, 0.09H, $\text{CH}_2\text{I} + \text{CDHI}$), 3.23 (q, J = 7.1 Hz, 4H), 1.12 (t, J = 7.2 Hz, 6H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 143.8, 139.5, 129.4, 127.4, 42.2, 14.3, 3.8 – 2.9 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M}-\text{I}]^+$ Calcd for $\text{C}_{11}\text{H}_{14}\text{D}_2\text{NO}_2\text{S}^+$ 228.1022; Found 228.1025.



2o: light yellow oil (106 mg, yield 50%) by following the general procedure **B**

from(benzo[*a*][1,3]dioxol-5-ylmethyl)triphenylphosphonium bromide (381 mg, 0.80 mmol, 1 equiv.);

*d*₂-Deuteration: 95%;

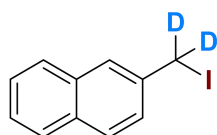
*R*_f = 0.3 (Petroleum ether/EtOAc, 90/10);

IR (neat) ν 2192, 1980, 1529, 1343, 1206, 1148, 937 cm⁻¹;

¹H NMR (CDCl₃, 400 MHz) δ 6.86 – 6.83 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.92 (s, 2H), 4.42 – 4.40 (m, 0.10H, CH₂I+CDH₁);

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 147.9, 147.4, 132.9, 122.2, 109.3, 108.4, 101.4, 7.2 – 6.3 (m, CD_nH_{2-n});

HRMS (ESI) *m/z*: [M-I]⁺ Calcd for C₈H₅D₂O₂⁺ 137.0566; Found 137.0557.



2p: white solid (197 mg, yield 91%) by following the general procedure **B** from (naphthalen-2-ylmethyl)triphenylphosphonium bromide (386 mg, 0.80 mmol, 1 equiv.);

*d*₂-Deuteration: 96%;

*R*_f = 0.6 (Petroleum ether/EtOAc, 99/1);

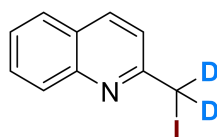
m.p. 71 – 73 °C;

IR (neat) ν 2174, 1980, 1734, 1528, 1344, 1145, 918 cm⁻¹;

¹H NMR(CDCl₃, 400 MHz) δ 7.82 – 7.73 (m, 4H), 7.49 – 7.40 (m, 3H), 4.65 – 4.63 (m, 0.08H, CH₂I+CDH₁);

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 136.5, 133.3, 132.8, 128.8, 127.83, 127.77, 127.1, 126.9, 126.5, 126.4, 6.6 – 6.1 (m, CD_nH_{2-n});

HRMS (ESI) *m/z*: [M-I+OH+Na]⁺ Calcd for C₁₁H₈D₂NaO⁺ 183.0749; Found 183.0772.



2q: green-yellowish solid (95 mg, yield 44%) by following the general procedure **B**

from triphenyl(quinolin-2-ylmethyl)phosphonium chloride (455 mg, 0.80 mmol, 1 equiv.);

d_2 -Deuteration: 95%;

m.p. 69 – 71 °C;

R_f = 0.3 (Petroleum ether/EtOAc, 95/5);

IR (neat) ν 2922, 2359, 1694, 1502, 1426, 1117, 912, 822 cm^{-1} ;

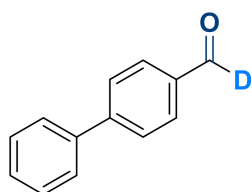
^1H NMR (CDCl_3 , 400 MHz) δ 8.06 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.69 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.53 – 7.46 (m, 2H), 4.66 – 4.64 (m, 0.11H, $\text{CH}_2\text{I} + \text{CDHI}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 158.3, 147.6, 137.2, 129.9, 129.1, 127.5, 127.1, 126.9, 121.1, 7.3 – 6.4 (m, $\text{CD}_n\text{H}_{2-n}$);

HRMS (ESI) m/z : $[\text{M-I}]^+$ Calcd for $\text{C}_{10}\text{H}_6\text{D}_2\text{N}^+$ 144.0777; Found 144.0779.

5. Characterization data of Deuterated Aldehyde 3

The data for all the known compounds is in agreement with literature values.^[1-8]

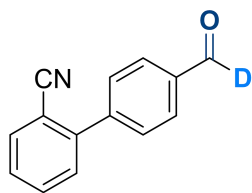


3a: light yellow oil (110 mg, yield 75%) by following the general procedure C from ([1,1'-biphenyl]-4-ylmethyl)triphenylphosphonium bromide (408 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 96%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 10.05 (s, 0.04H, CHO), 7.98 – 7.92 (m, 2H), 7.77 – 7.72 (m, 2H), 7.66 – 7.61 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H).



3b: white solid (95 mg, yield 57%) by following the general procedure C from ((2'-cyano-[1,1'-biphenyl]-4-yl)methyl)triphenylphosphonium bromide (427 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 95%;

*R*_f = 0.2 (Petroleum ether/EtOAc, 99/1);

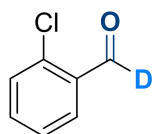
m.p. 145 – 146 °C;

IR (neat) ν 2220, 1670, 1476, 1226, 814, 696, 451 cm⁻¹;

¹H NMR (CDCl₃, 400 MHz) δ 10.10 (s, 0.05H, CHO), 8.02 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.49 (m, 2H);

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 192.0 – 190.9 (m, CDO), 144.0, 143.9, 136.2, 133.9, 133.0, 130.02, 130.00, 129.6, 128.5, 118.2, 111.3;

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₈DNNaO⁺ 231.0639; Found 231.0638.

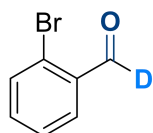


3c: colorless oil (43 mg, yield 38%) by following the general procedure **C** from (2-chlorobenzyl)triphenylphosphonium bromide (373 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 95%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 10.40 (s, 0.05H, CHO), 7.84 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.45 (ddd, *J* = 8.2, 7.2, 1.8 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H).

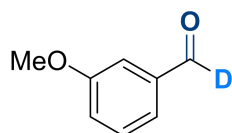


3d: light yellow oil (37 mg, yield 25%) by following the general procedure **C** from (2-bromobenzyl)triphenylphosphonium bromide (410 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 94%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 10.37 (s, 0.06H, CHO), 7.96 – 7.90 (m, 1H), 7.68 – 7.63 (m, 1H), 7.49 – 7.40 (m, 2H).

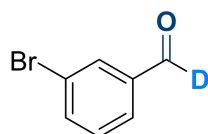


3e: Light yellow oil (52 mg, yield 47%) by following the general procedure **C** from (3-methoxybenzyl)triphenylphosphonium chloride (335 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 95%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 9.98 (s, 0.05H, CHO), 7.49 – 7.44 (m, 2H), 7.41 – 7.38 (m, 1H), 7.20 – 7.17 (m, 1H), 3.87 (s, 3H).

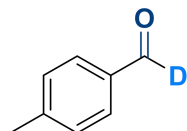


3f: light yellow oil (61 mg, yield 41%) by following the general procedure **C** from (3-bromobenzyl)triphenylphosphonium bromide (335 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 96%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 9.96 (s, 0.04H, CHO), 8.02 (t, *J* = 1.8 Hz, 1H), 7.82 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.76 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H).

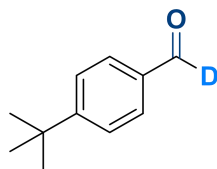


3g: light yellow oil (53 mg, yield 55%) by following the general procedure **C** from (4-methylbenzyl)triphenylphosphonium chloride (322mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 97%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 9.86 (s, 0.03H, CHO), 7.68 (d, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 2.34 (s, 3H).

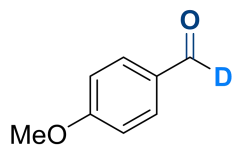


3h: light yellow-green oil (82 mg, yield 63%) by following the general procedure **C** from (4-(*tert*-butyl)benzyl)triphenylphosphonium bromide (391 mg, 0.80 mmol, 1 equiv.);

*d*₁-deuteration: 96%;

*R*_f = 0.25 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 9.89 (s, 0.04H, CHO), 7.73 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.46 (dd, *J* = 8.3, 1.6 Hz, 2H), 1.27 (s, 9H).

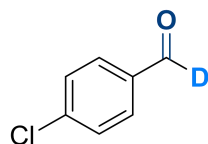


3i: light yellow oil (72 mg, yield 65%) by following the general procedure **C** from (4-methoxybenzyl)triphenylphosphonium chloride (335 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 94%;

R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 9.79 (s, 0.06H, CHO), 7.78 – 7.72 (m, 2H), 6.94 – 6.88 (m, 2H), 3.80 (s, 3H).

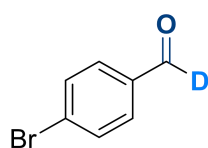


3j: white solid (58 mg, yield 57%) by following the general procedure **C** from (4-chlorobenzyl)triphenylphosphonium bromide (374 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 96%;

R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 9.90 (s, 0.04H, CHO), 7.74 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H).

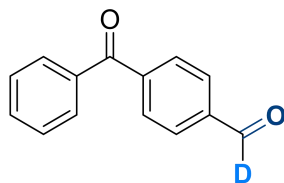


3k: white solid (71 mg, yield 48%) by following the general procedure **C** from (4-bromobenzyl)triphenylphosphonium bromide (410 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 96%;

R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 9.98 (s, 0.04H, CHO), 7.78 – 7.73 (m, 2H), 7.71 – 7.67 (m, 2H).



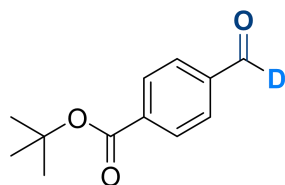
3l: light yellow oil (70 mg, yield 41%) by following the general procedure **C** from (4-benzoylbenzyl)triphenylphosphonium chloride (394 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 95%;

R_f = 0.2 (Petroleum ether/EtOAc, 99/1);

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 10.13 (s, 0.05H, CHO), 8.03 – 7.98 (m, 2H), 7.95 –

7.90 (m, 2H), 7.83 – 7.79 (m, 2H), 7.66 – 7.61 (m, 1H), 7.51 (t, $J = 8.4$ Hz, 2H).



3m: light yellow oil (98 mg, yield 59%) by following the general procedure **C** from (4-(*tert*-butoxycarbonyl)benzyl)triphenylphosphonium bromide (454mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 98%;

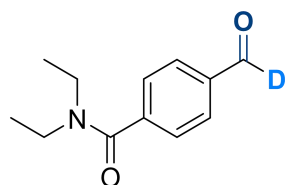
$R_f = 0.3$ (Petroleum ether/EtOAc, 90/10);

IR (neat) ν 2981, 2126, 1704, 1367, 1102, 897, 663 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 10.09 (s, 0.02H, CHO), 8.14 (d, $J = 8.4$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H), 1.62 (s, 9H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 192.0 – 190.9 (m, CDO), 164.6, 138.8, 137.1, 130.0, 129.4, 82.0, 28.1;

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{13}\text{DNaO}_3^+$ 230.0898; Found 230.0898.



3n: yellow oil (69 mg, yield 42%) by following the general procedure **C** from (4-(diethylcarbamoyl)benzyl)triphenylphosphonium chloride (390 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 93%;

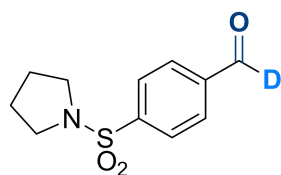
$R_f = 0.3$ (Petroleum ether/EtOAc, 80/20);

IR (neat) ν 2972, 2111, 1678, 1428, 1221, 1093, 799, 563 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 10.05 (s, 0.07H, CHO), 7.93 (d, $J = 7.9$ Hz, 2H), 7.53 (d, $J = 8.1$ Hz, 2H), 3.57 (q, $J = 7.2$ Hz, 2H), 3.23 (q, $J = 7.2$ Hz, 2H), 1.27 (t, $J = 7.9$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 191.5 – 190.9 (m, CDO), 169.9, 143.0, 136.5, 129.9, 126.9, 43.2, 39.4, 14.2, 12.9;

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{12}H_{14}DNNaO_2^+$ 229.1058; Found 229.1060.



3o: white solid (55 mg, yield 35%) by following the general procedure **C** from triphenyl(4-(pyrrolidin-1-ylsulfonyl)benzyl)phosphonium bromide (452 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 94%;

R_f = 0.3 (Petroleum ether/EtOAc, 70/30);

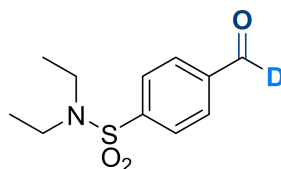
m.p. 106 – 108 °C;

IR (neat) ν 2874, 2127, 1679, 1334, 1156, 805, 685, 578 cm^{-1} ;

1H NMR ($CDCl_3$, 400 MHz) δ 10.12 (s, 0.06H, $\underline{C}HO$), 8.06 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H), 3.32 – 3.26 (m, 4H), 1.83 – 1.76 (m, 4H);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 191.1 – 190.3 (m, $\underline{C}DO$), 142.3, 138.7, 130.1, 128.0, 48.0, 25.3;

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{11}H_{12}DNNaO_3S^+$ 263.0571; Found 263.0571.



3p: white solid (62 mg, yield 34%) by following the general procedure **C** from (4-(*N,N*-diethylsulfonyl)benzyl)triphenylphosphonium bromide (454 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 92%;

R_f = 0.3 (Petroleum ether/EtOAc, 70/30);

m.p. 77 – 79 °C;

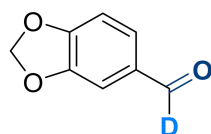
IR (neat) ν 2942, 2114, 1692, 1334, 1085, 798, 552 cm^{-1} ;

1H NMR ($CDCl_3$, 400 MHz) δ 10.02 (s, 0.08H, $\underline{C}HO$), 7.94 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 3.21 (q, J = 7.1 Hz, 4H), 1.06 (t, J = 7.2 Hz, 6H);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 190.0 – 189.3 (m, $\underline{C}DO$), 144.7, 137.5, 129.2,

126.5, 41.1, 13.1;

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{11}H_{14}DNNaO_3S^+$ 265.0728; Found 265.0728.

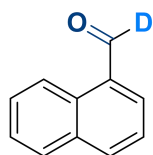


3q: light yellow oil (87 mg, yield 73%) by following the general procedure **C** from (benzo[*d*][1,3]dioxol-5-ylmethyl)triphenylphosphonium bromide (381 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 91%;

R_f = 0.3 (Petroleum ether/EtOAc, 90/10);

¹H NMR (CDCl₃, 400 MHz) δ 9.70 (s, 0.09H, CHO), 7.30 (dd, J = 8.0, 1.7 Hz, 1H), 7.21 (d, J = 1.8 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 5.97 (s, 2H).

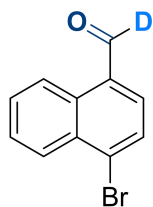


3r: light yellow oil (93 mg, yield 74%) by following the general procedure **C** from (naphthalen-1-ylmethyl)triphenylphosphonium bromide (386 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 97%;

R_f = 0.3 (Petroleum ether/EtOAc, 99/1);

¹H NMR (CDCl₃, 400 MHz) δ 10.21 (s, 0.03H, CHO), 9.13 – 9.07 (m, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 7.0 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.51 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H).



3s: white solid (137 mg, yield 73%) by following the general procedure **C** from ((4-bromonaphthalen-1-yl)methyl)triphenylphosphonium bromide (450 mg, 0.80 mmol, 1 equiv.);

*d*₁-Deuteration: 97%;

$R_f = 0.3$ (Petroleum ether/EtOAc, 95/5);

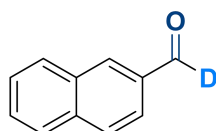
m.p. 89 – 91 °C;

IR (neat) ν 2919, 2827, 1679, 1506, 1240, 1134, 1027, 759 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 10.21 (s, 0.03H, CHO), 9.15 – 9.09 (m, 1H), 8.19 (dd, $J = 8.3, 1.5$ Hz, 1H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.60 – 7.51 (m, 2H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 192.6 – 191.9 (m, CDO), 135.9, 132.1, 131.4, 131.3, 130.9 – 130.7 (m), 129.7, 129.3, 128.2, 127.7, 125.1;

HRMS (ESI) m/z : $[\text{M}+\text{K}]^+$ Calcd for $\text{C}_{11}\text{H}_6\text{DBrKO}^+$ 273.9375; Found 273.9367.

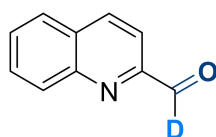


3t: white solid (78 mg, yield 62%) by following the general procedure **C** from (naphthalen-2-ylmethyl)triphenylphosphonium bromide (387 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 96%;

$R_f = 0.3$ (Petroleum ether/EtOAc, 99/1);

^1H NMR (CDCl_3 , 400 MHz) δ 10.16 (s, 0.04H, CHO), 8.34 (s, 1H), 8.04 – 7.87 (m, 4H), 7.64 (t, $J = 7.1$ Hz, 1H), 7.58 (t, $J = 7.2$ Hz, 1H).



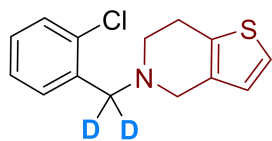
3u: white solid (35 mg, yield 28%) by following the general procedure **C** from triphenyl(quinolin-2-ylmethyl)phosphonium chloride (455 mg, 0.80 mmol, 1 equiv.);

d_1 -Deuteration: 94%;

$R_f = 0.3$ (Petroleum ether/EtOAc, 95/5);

^1H NMR (CDCl_3 , 400 MHz) δ 10.24 (s, 0.06H, CHO), 8.32 (d, $J = 8.4$ Hz, 1H), 8.26 (d, $J = 8.5$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.2$ Hz, 1H), 7.83 (t, $J = 7.2$ Hz, 1H), 7.69 (t, $J = 7.5$ Hz, 1H).

6. Characterization data of Deuterated Drug molecule 5



5a: light yellow oil (146 mg, yield 92%) by following the general procedure **D** from **2d** (145 mg, 0.57 mmol, 1 equiv.) and 4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine (83 mg, 0.60 mmol, 1.05 equiv.);

d_2 -Deuteration: 91%;

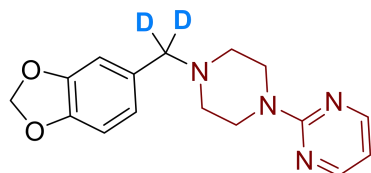
R_f = 0.4 (Petroleum ether/EtOAc, 90/10);

IR (neat) ν 2917, 1650, 1436, 1242, 1025, 748, 697 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.52 (dd, J = 7.6, 1.9 Hz, 1H), 7.33 (dd, J = 7.7, 1.5 Hz, 1H), 7.20 (td, J = 7.5, 1.6 Hz, 1H), 7.15 (td, J = 7.6, 1.9 Hz, 1H), 7.02 (d, J = 5.2 Hz, 1H), 6.67 (d, J = 5.1 Hz, 1H), 3.79 – 3.77 (m, **0.18H**, $\text{CH}_2\text{N}+\text{CDHN}$), 3.60 (s, 2H), 2.86 – 2.80 (m, 4H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 136.2, 134.4, 134.0, 133.5, 130.7, 129.5, 128.3, 126.8, 125.4, 122.7, 58.6 – 57.6 (m, $\text{CD}_n\text{H}_{2-n}$), 53.2, 50.8, 25.7;

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{12}\text{D}_2\text{ClNNaS}^+$ 288.0553; Found 288.0557.



5b: brown-orange solid (101 mg, yield 88%) by following the general procedure **D** from **2o** (101 mg, 0.38 mmol, 1 equiv.) and 2-(piperazin-1-yl)pyrimidine (66 mg, 0.40 mmol, 1.05 equiv.);

d_2 -Deuteration: 96%;

R_f = 0.5 (Petroleum ether/EtOAc, 50/50);

m.p. 96 – 98 $^\circ\text{C}$;

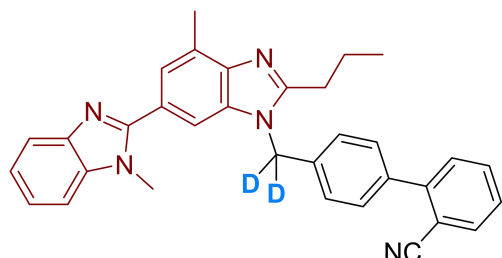
IR (neat) ν 2923, 2056, 1578, 1480, 1248, 1037, 886, 638 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 8.28 (d, J = 4.7 Hz, 2H), 6.88 (s, 1H), 6.75 (s, 2H), 6.44 (t, J = 4.7 Hz, 1H), 5.93 (s, 2H), 3.86 – 3.77 (m, 4H), 3.44 – 3.40 (m, **0.09H**,

$\underline{CH_2N+CDHN}$, 2.52 – 2.42 (m, 4H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 161.7, 157.7, 147.7, 146.7, 131.7, 122.2, 109.7, 109.5, 107.9, 100.9, 62.7 – 61.7 (m, $\underline{CD_nH_{2-n}}$), 52.8, 43.7;

HRMS (ESI) m/z : $[\text{M}+\text{K}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{D}_2\text{KN}_4\text{O}_2^+$ 339.1187; Found 339.1189.



5c: white solid (92 mg, yield 41%) by following the general procedure **D** from **2b** (146 mg, 0.46 mmol, 1 equiv.) and 7'-dimethyl-2'-propyl-1H, 3'H-2,5'-bibenzo[*d*]imidazole (146 mg, 0.48 mmol, 1.05 equiv.);

d_2 -Deuteration: 95%;

R_f = 0.3 (dichloromethane/methanol, 95/5);

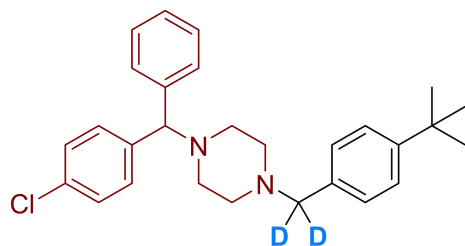
m.p. 195 – 197 °C;

IR (neat) ν 2921, 2223, 1595, 1282, 863, 763, 562 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.83 – 7.77 (m, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.52 – 7.37 (m, 6H), 7.34 – 7.23 (m, 3H), 7.16 (d, J = 7.9 Hz, 2H), 5.42 (s, 0.11H, $\underline{CH_2N+CDHN}$), 3.72 (s, 3H), 2.92 (t, J = 7.9 Hz, 2H), 2.77 (s, 3H), 1.87 (m, J = 7.5 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 156.4, 154.6, 144.5, 143.2, 142.9, 137.9, 136.7, 136.4, 134.9, 133.7, 132.9, 130.0, 129.6, 129.4, 127.8, 126.5, 124.0, 123.9, 122.5, 122.3, 119.5, 118.5, 111.1, 109.6, 108.8, 47.0 – 46.1 (m, $\underline{CD_nH_{2-n}}$), 31.8, 29.8, 21.9, 16.9, 14.1;

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{27}\text{D}_2\text{N}_5\text{Na}^+$ 520.2441; Found 520.2449.



5d: light yellow oil (250 mg, yield 89%) brown-orange solid (101 mg, yield 88%) by

following the general procedure **D** from **2I** (178 mg, 0.65 mmol, 1 equiv.) and 1-((4-chlorophenyl)(phenyl)methyl)piperazine (194 mg, 0.68 mmol, 1.05 equiv.);

d_2 -Deuteration: 95%;

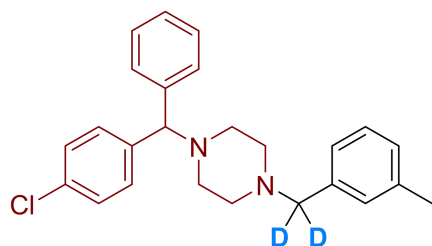
R_f = 0.2 (Petroleum ether/EtOAc, 90/10);

IR (neat) ν 2960, 2803, 1738, 1487, 1139, 906, 731, 543 cm^{-1} ;

^1H NMR(CDCl_3 , 400 MHz) δ 7.34 – 7.27 (m, 6H), 7.23 – 7.15 (m, 6H), 7.11 (t, J = 7.3 Hz, 1H), 4.18 (s, 1H), 3.45 – 3.42 (m, 0.11H, $\text{CH}_2\text{N}+\text{CDHN}$), 2.44 – 2.37 (m, 8H), 1.27 (s, 9H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 145.0, 142.3, 141.6, 135.0, 132.6, 129.4, 129.2, 128.8, 128.7, 128.1, 127.3, 125.2, 75.6, 62.9 – 61.7 (m, $\text{CD}_n\text{H}_{2-n}$), 53.4, 52.0, 34.6, 31.6;

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{31}\text{D}_2\text{ClN}_2\text{Na}^+$ 457.2350; Found 457.2319.



5e: light yellow oil (161 mg, yield 90%) by following the general procedure **D** from **2e** (108 mg, 0.46 mmol, 1 equiv.) and 1-((4-chlorophenyl)(phenyl)methyl)piperazine (138 mg, 0.48 mmol, 1.05 equiv.);

d_2 -Deuteration: 95%;

R_f = 0.2 (Petroleum ether/EtOAc, 90/10);

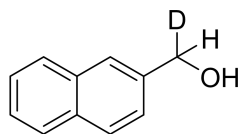
IR (neat) ν 3024, 2803, 2042, 1679, 1486, 1139, 756 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz) δ 7.33 – 7.30 (m, 4H), 7.23 – 7.17 (m, 4H), 7.15 – 7.11 (m, 2H), 7.10 – 7.04 (m, 2H), 7.01 (d, J = 7.4 Hz, 1H), 4.18 (s, 1H), 3.43 – 3.42 (m, 0.10H, $\text{CH}_2\text{N}+\text{CDHN}$), 2.45 – 2.39 (m, 8H), 2.29 (s, 3H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 142.3, 141.5, 137.9, 137.8, 132.6, 130.1, 129.3, 128.7, 128.6, 128.2, 128.0, 127.9, 127.2, 126.5, 75.6, 63.0 – 62.9 (m, $\text{CD}_n\text{H}_{2-n}$), 53.4, 51.9, 21.5;

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{26}\text{D}_2\text{ClN}_2^+$ 393.2061; Found 393.2077.

7. Characterization data of other Deuterated product

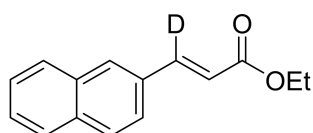


6: white solid (21 mg, yield 88%) by following the general procedure **E** from **3r** (24 mg, 0.15 mmol, 1 equiv.);

*d*₁-Deuteration: 93%;

*R*_f = 0.3 (Petroleum ether/EtOAc, 85/15);

¹H NMR (CDCl₃, 400 MHz) δ 7.84 – 7.78 (m, 3H), 7.76 (s, 1H), 7.50 – 7.41 (m, 3H), 4.81 – 4.79 (m, **1.07H**, CDH₂OH+CH₂OH), 1.95 (s, 1H).



7: white solid (30 mg, yield: 88%) by following the general procedure **F** from **3r** (24 mg, 0.15 mmol, 1 equiv.);

*d*₁-Deuteration: 95%;

*R*_f = 0.6 (Petroleum ether/EtOAc, 95/5);

m.p. 72 – 74 °C;

IR (neat) ν 2980, 2251, 1693, 1614, 1365, 1155, 824, 479 cm⁻¹;

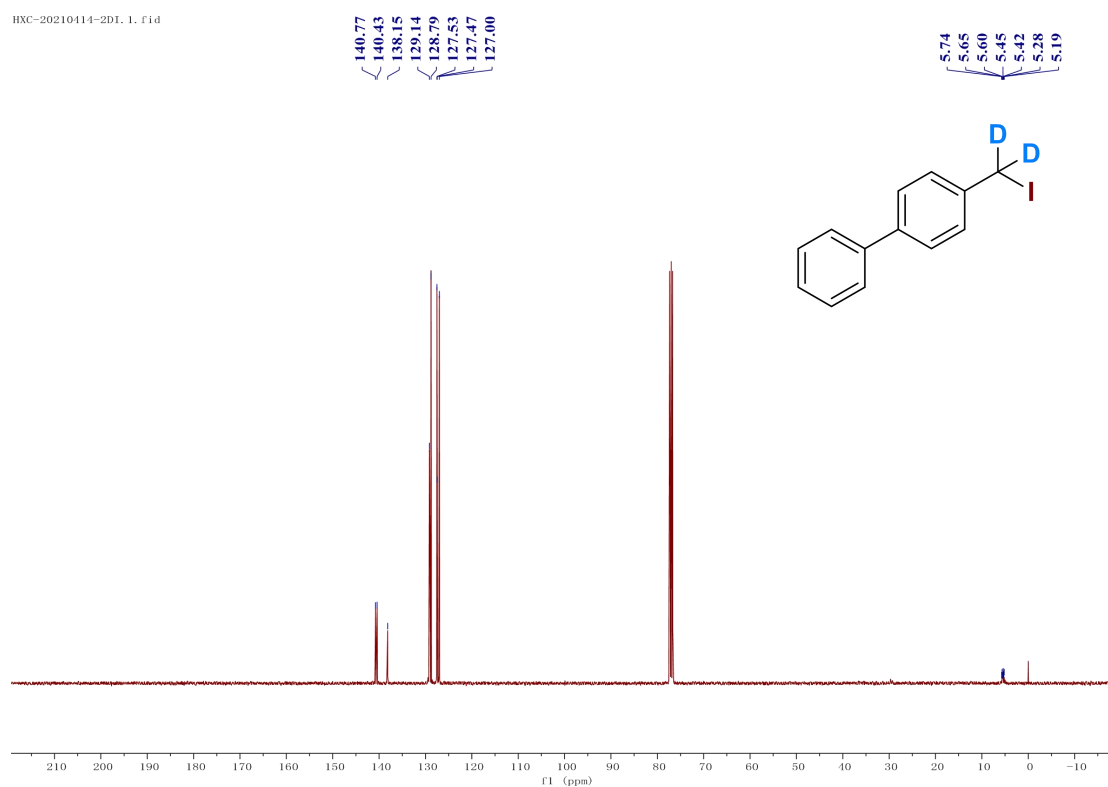
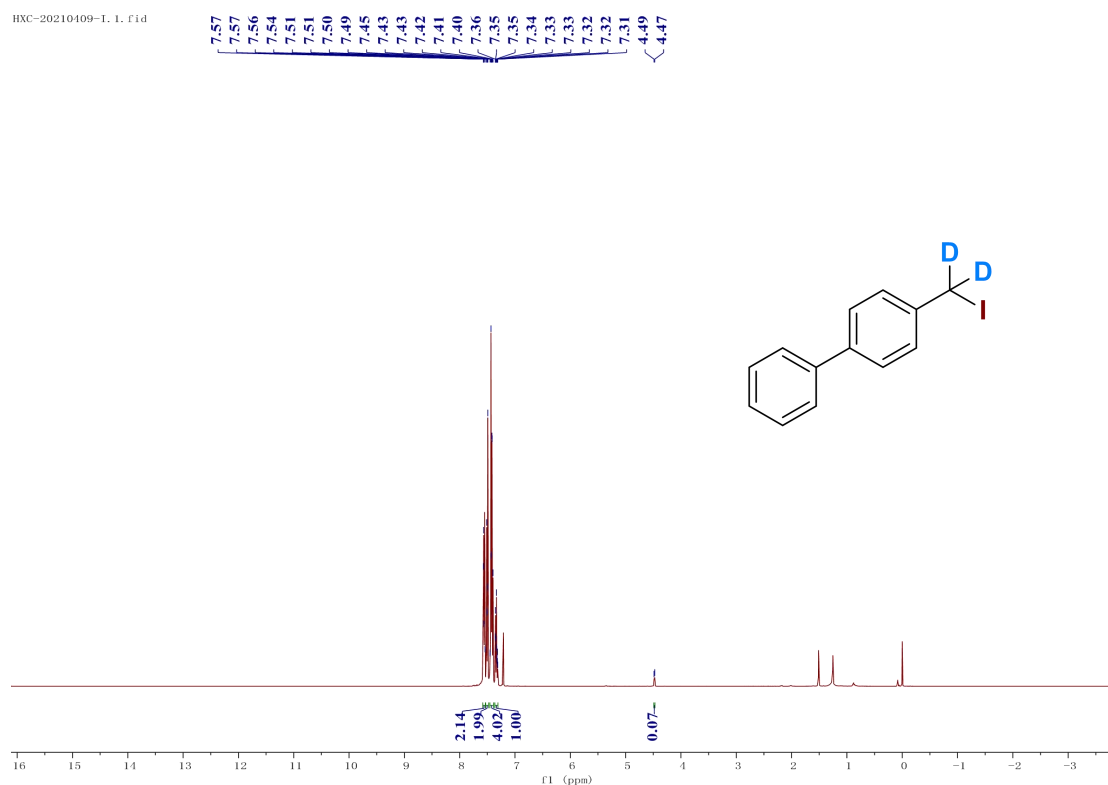
¹H NMR (CDCl₃, 400 MHz) δ 7.91 (s, 1H), 7.86 – 7.80 (m, 3H), 7.64 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.52 – 7.46 (m, 2H), 6.54 (d, *J* = 15.8 Hz, 0.08H, ArCHCHCO₂Et), 6.53 (m, 0.92H, ArCDCHCO₂Et), 5.27 (s, **0.08H**, ArCHCHCO₂Et), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H);

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 167.1, 144.6 – 144.1 (m, ArCD_nH_{1-n}), 134.2, 133.3, 132.0, 129.8, 128.7, 128.6, 127.8, 127.2, 126.7, 123.5, 118.4, 60.5, 14.4;

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₅H₁₃DNaO₂⁺ 250.0949; Found 250.0951.

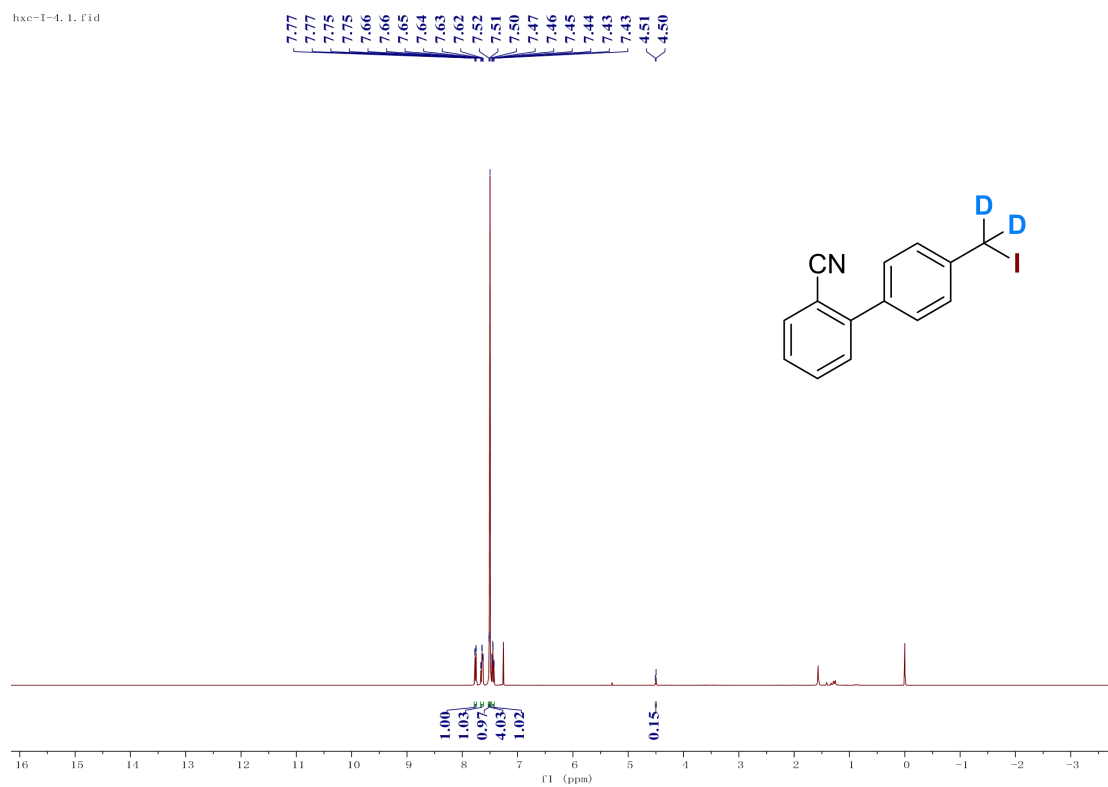
8. Copies of NMR spectra

Substrate **2a**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

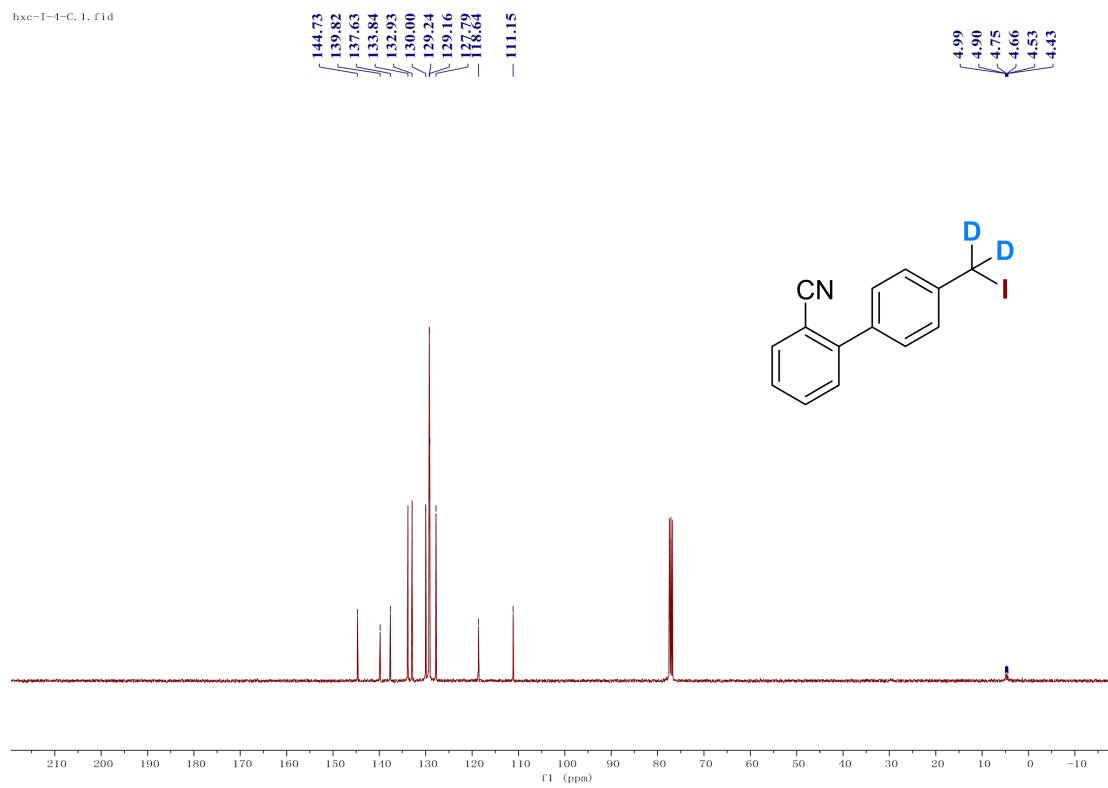


Substrate **2b**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

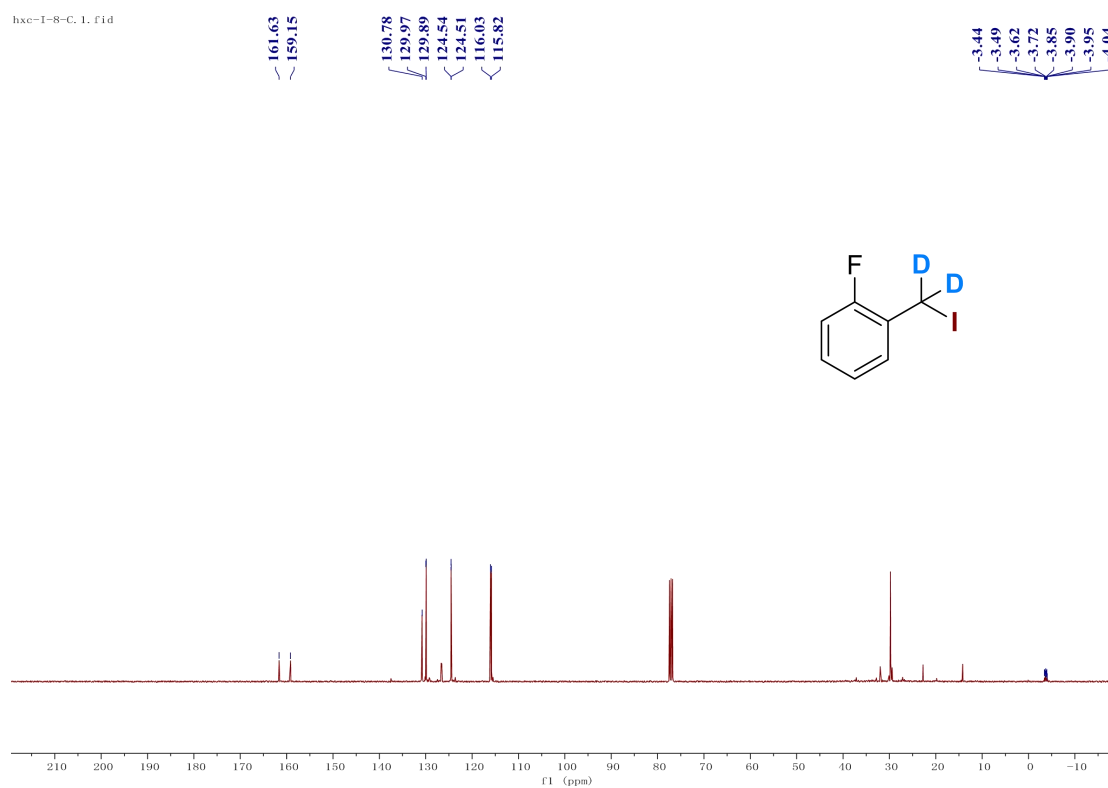
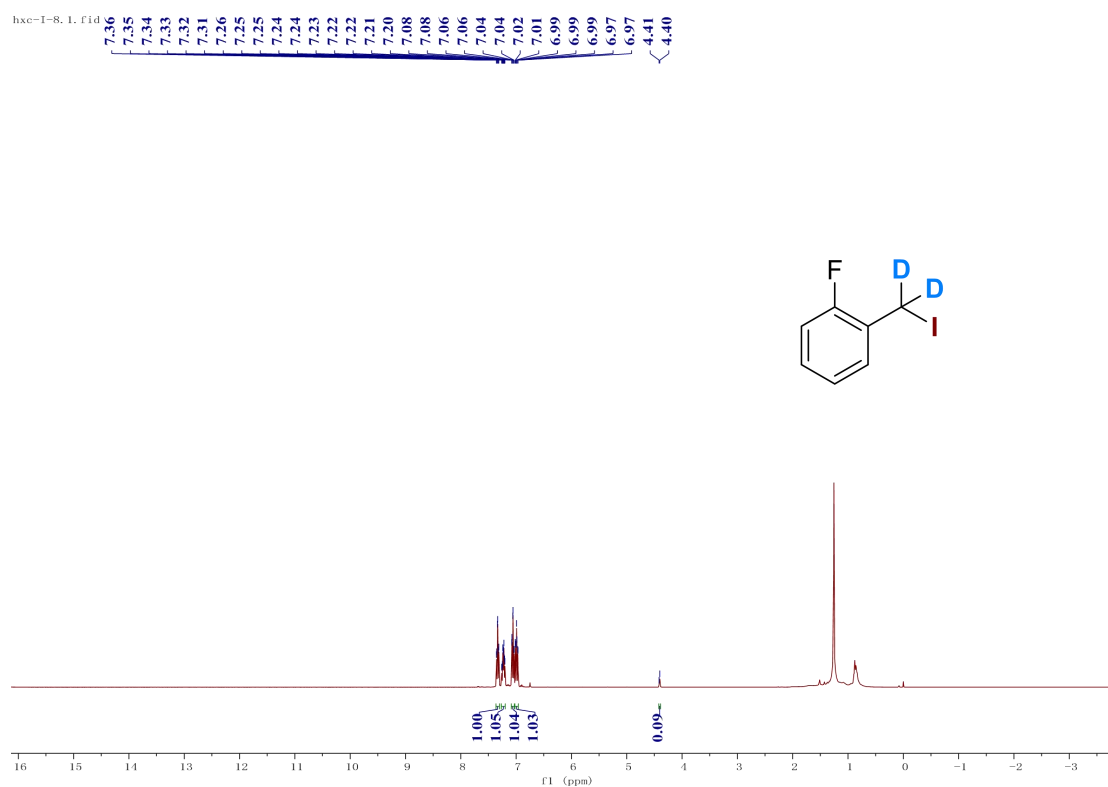
hxc-1-4-1.fid



hxc-1-4-C-1.fid

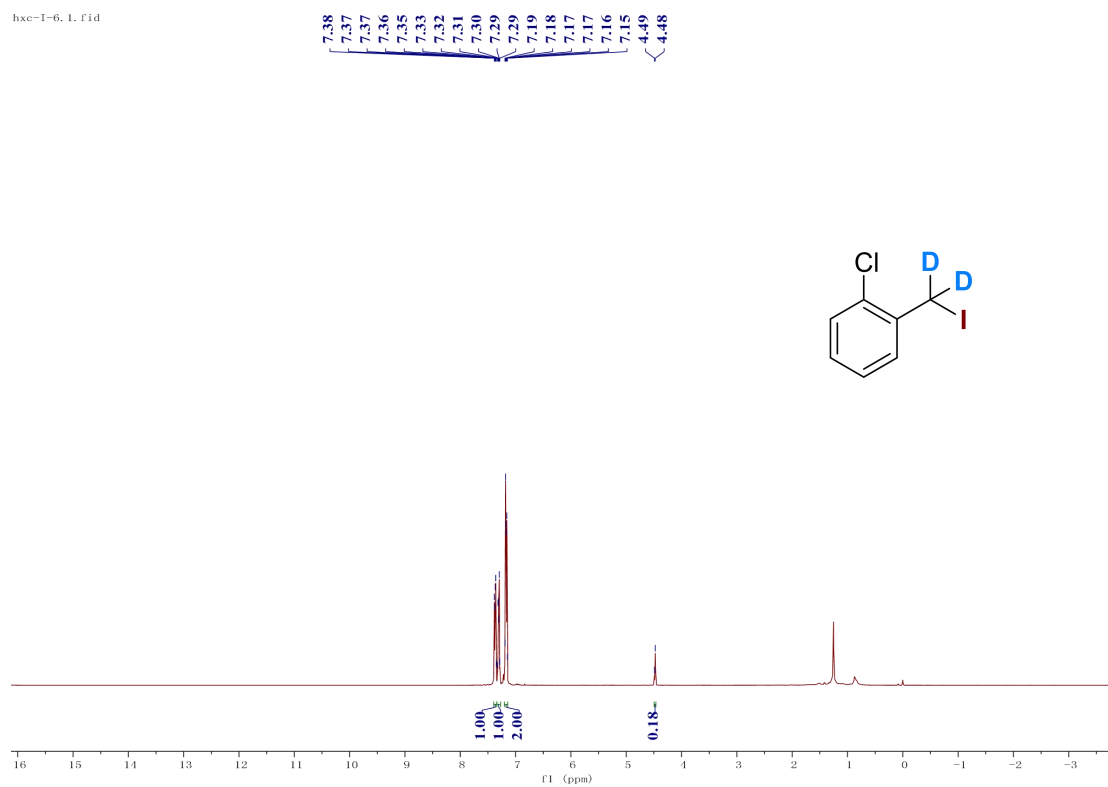


Substrate **2c**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

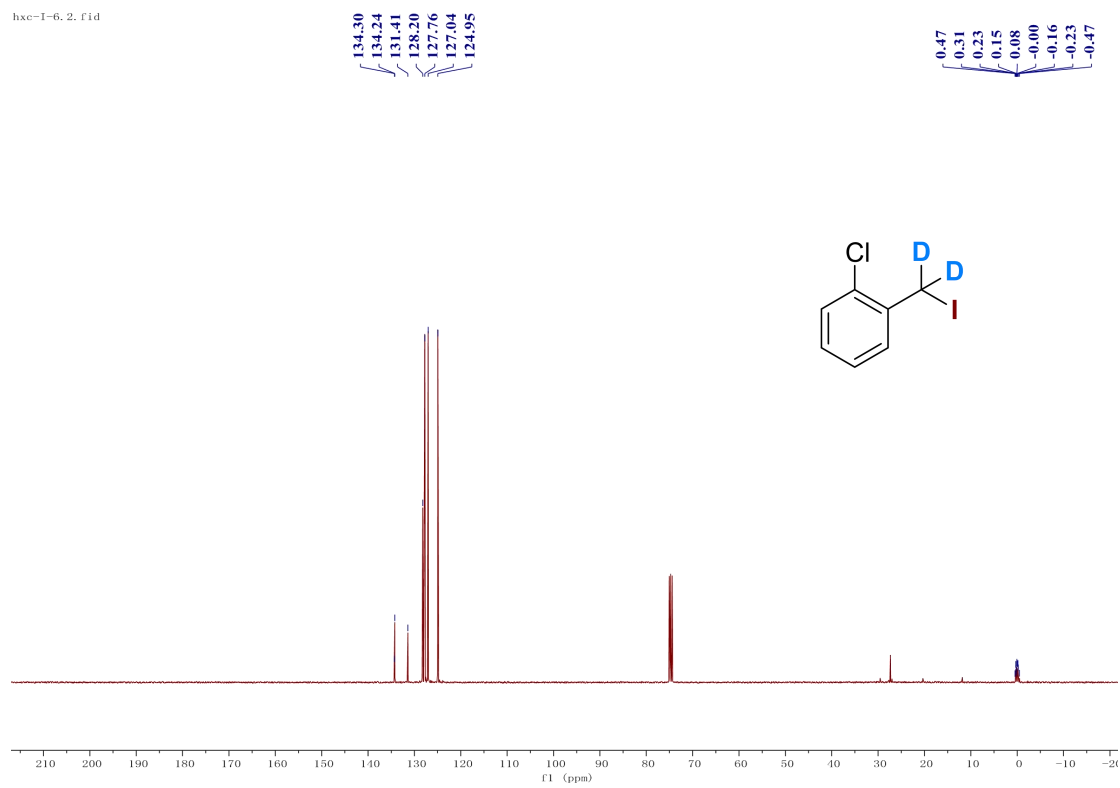


Substrate **2d**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-1-6. 1. fid

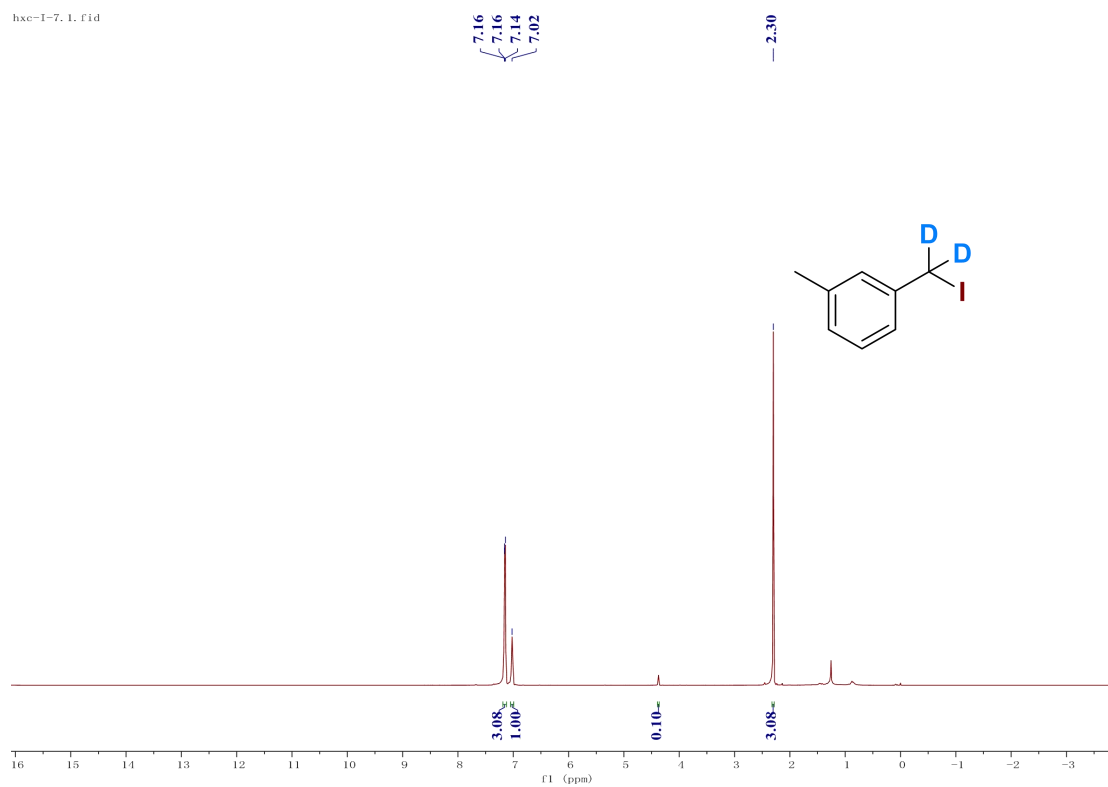


hxc-1-6. 2. fid

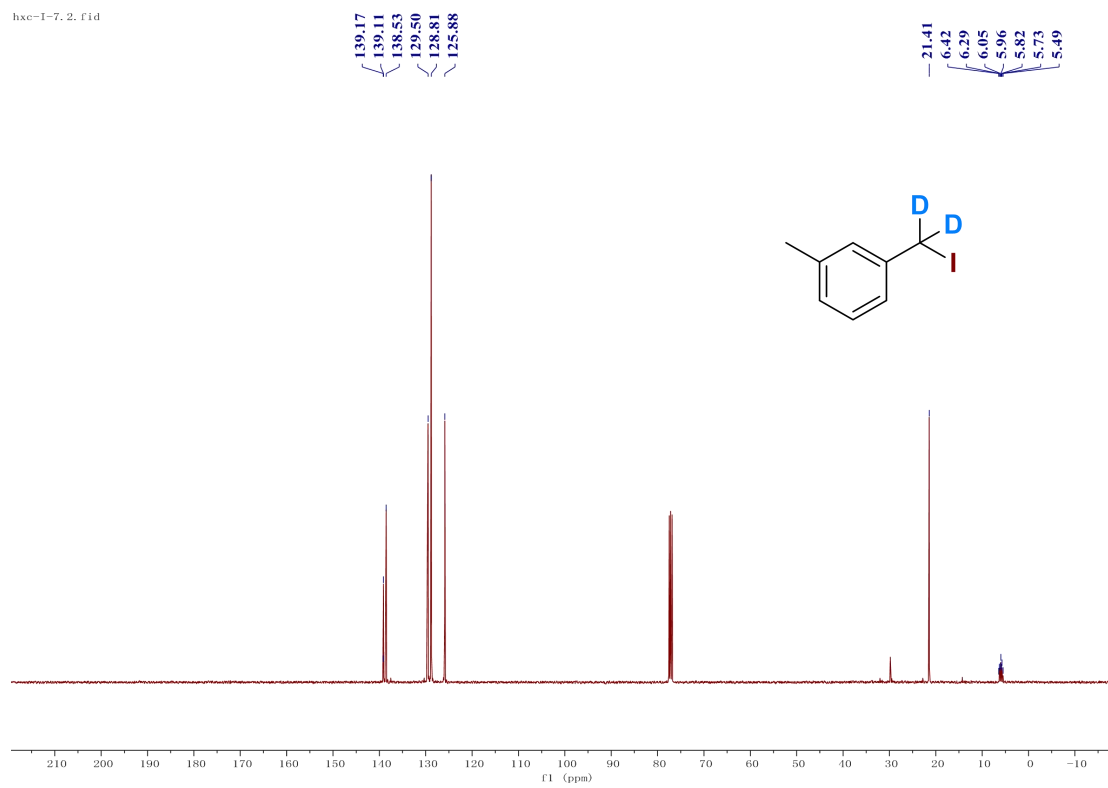


Substrate **2e**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

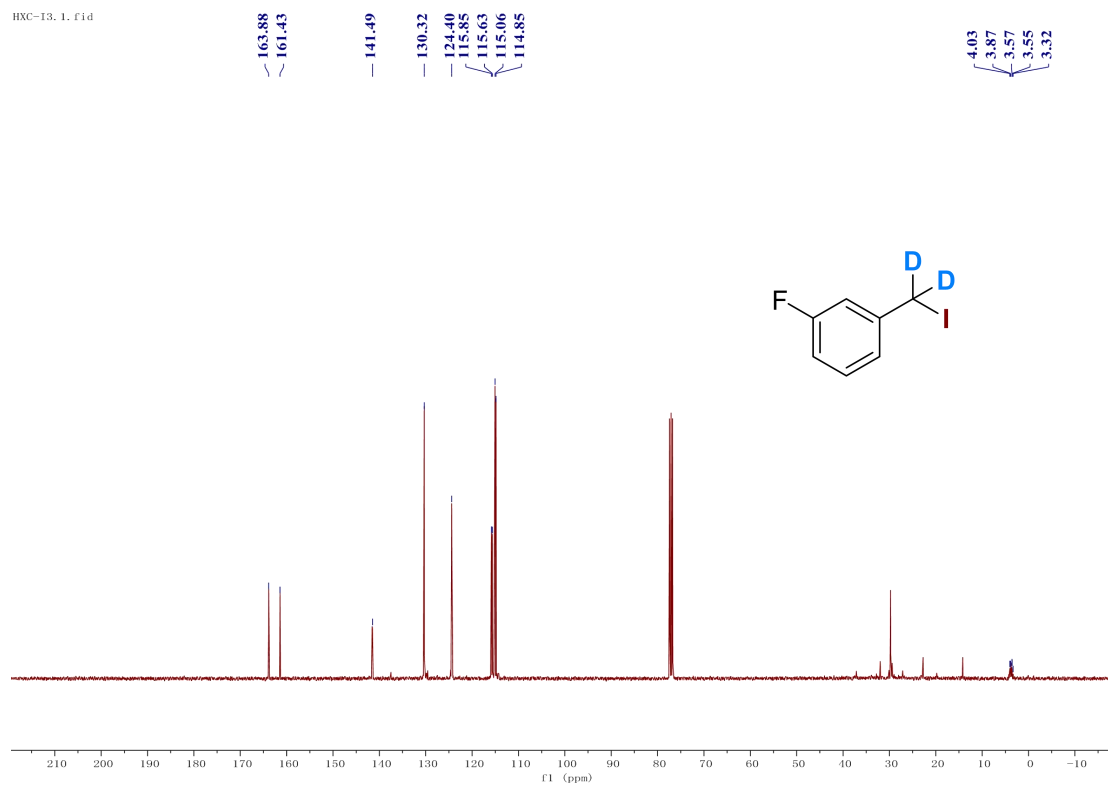
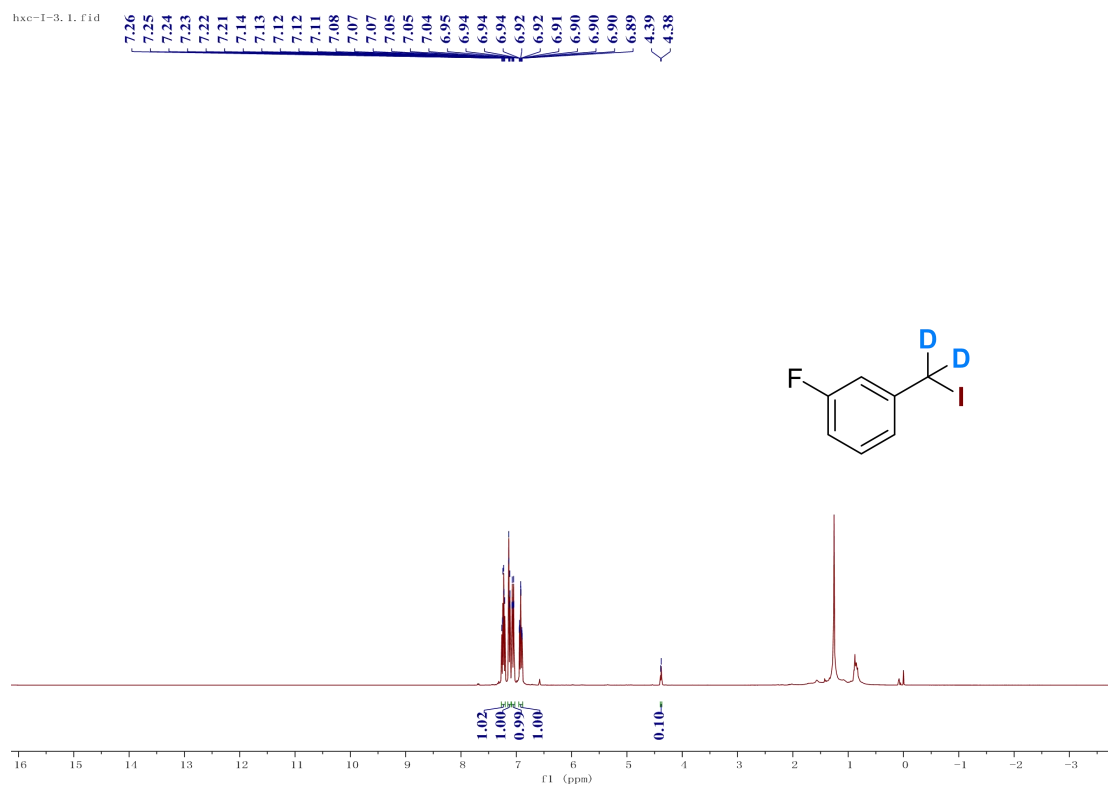
hxc-1-7. 1. f1d



hxc-1-7. 2. f1d

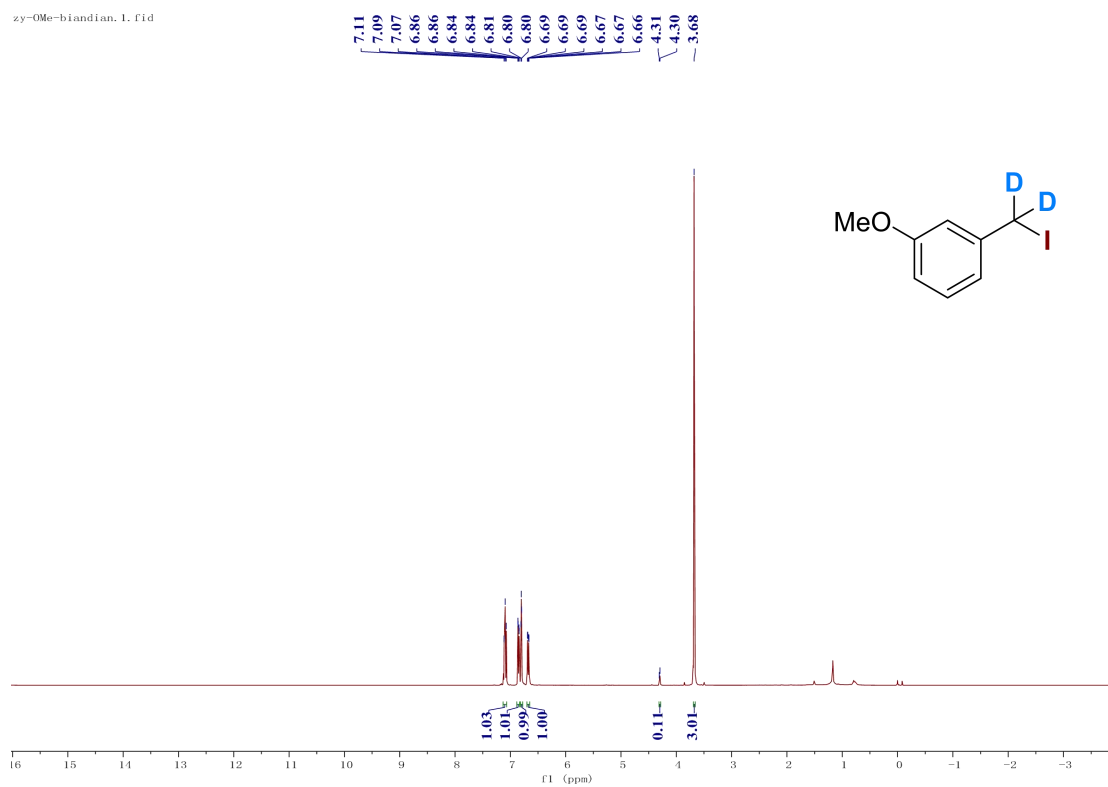


Substrate **2f**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

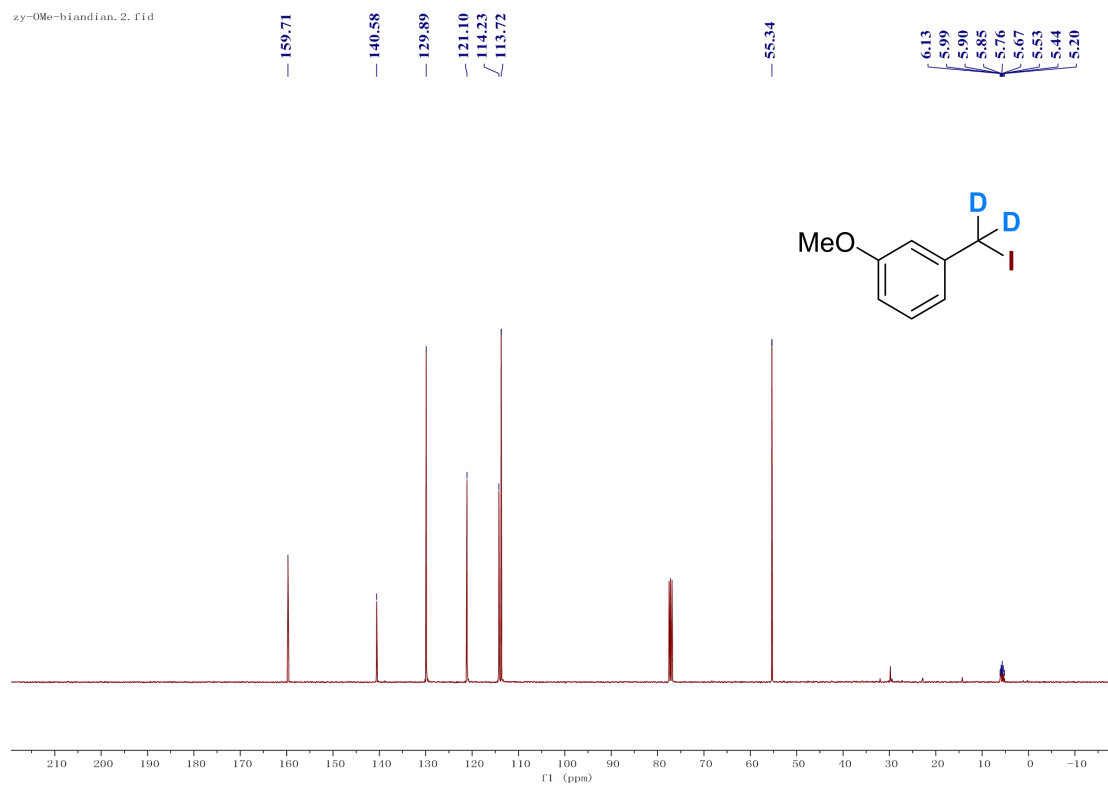


Substrate **2g**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

zy-OMe-biandian. 1. F1d

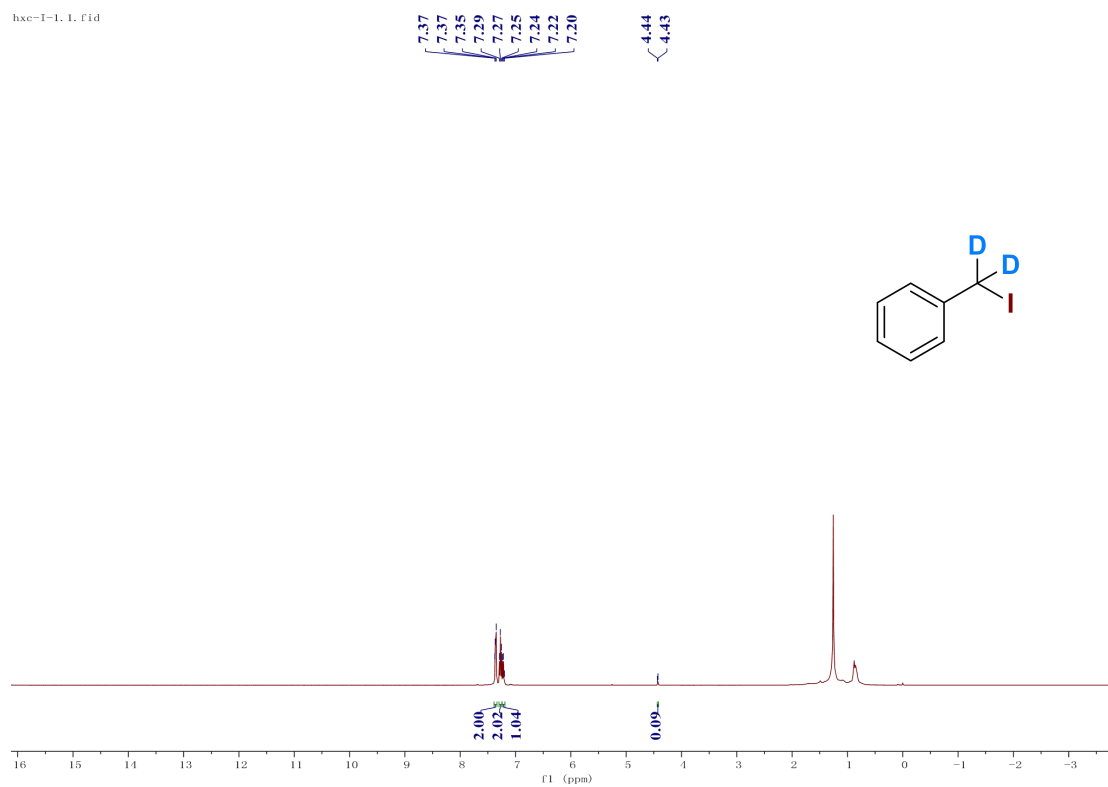


zy-OMe-biandian. 2. F1d

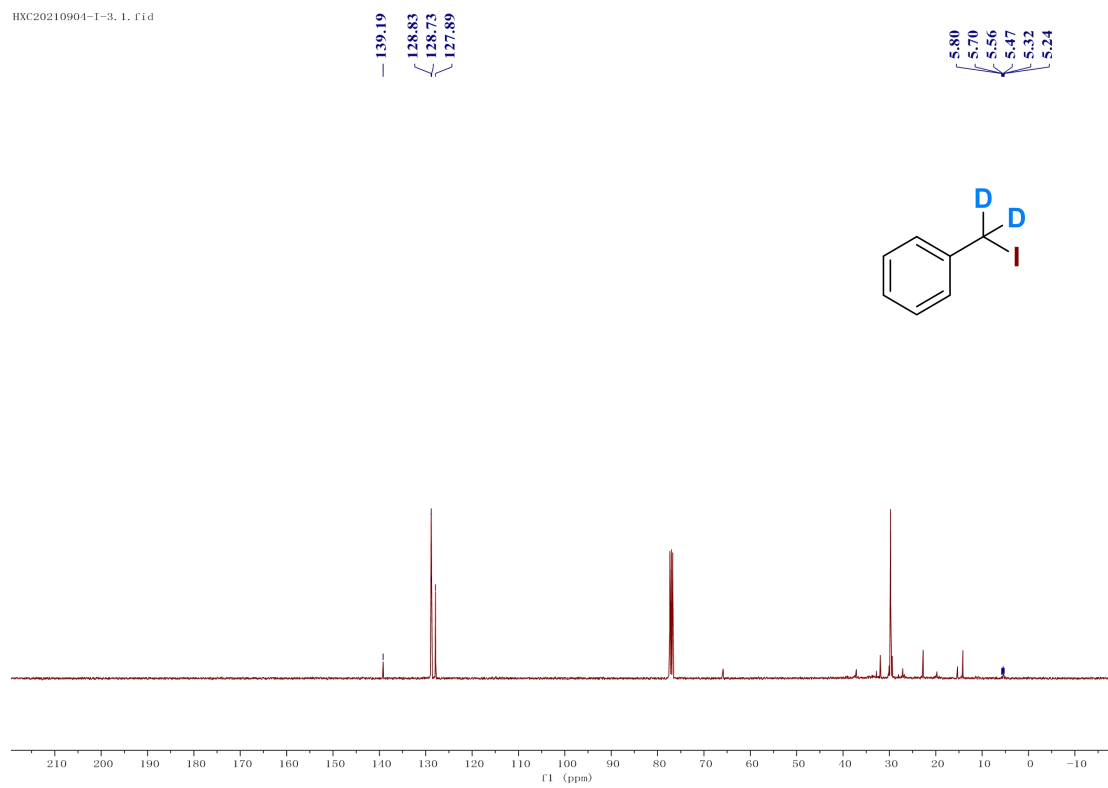


Substrate **2h**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-1-1. 1. f1d

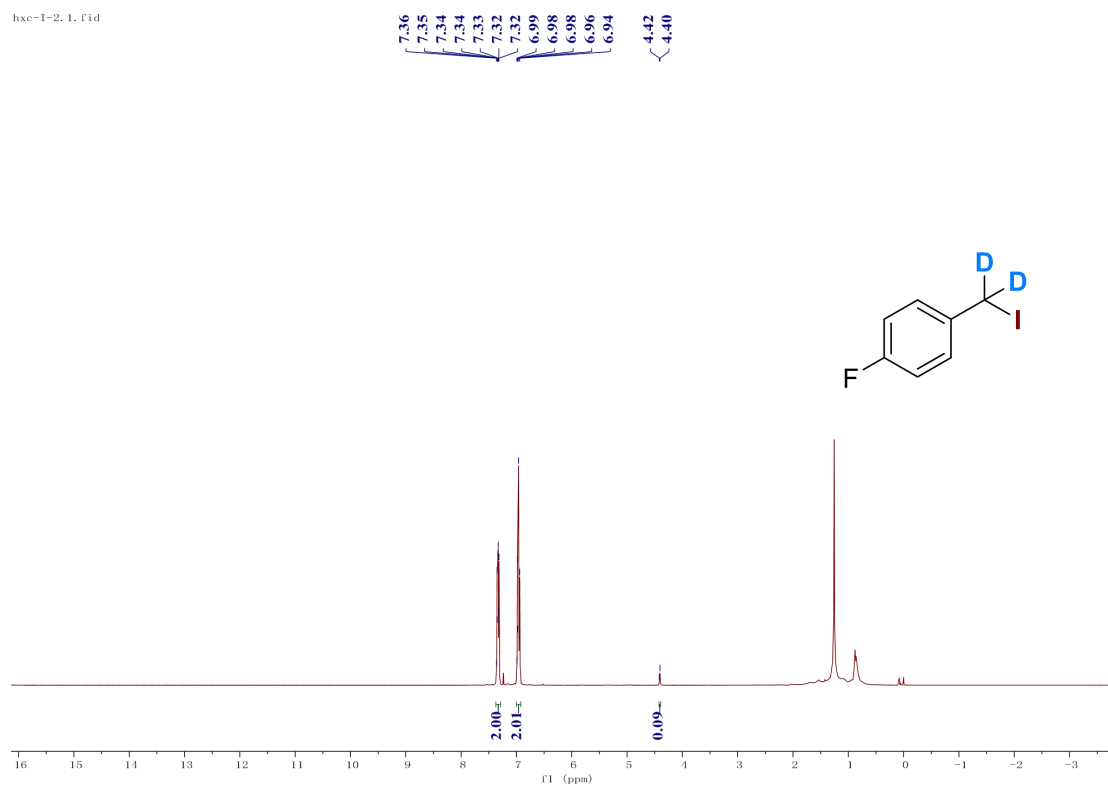


HXC20210904-1-3. 1. f1d

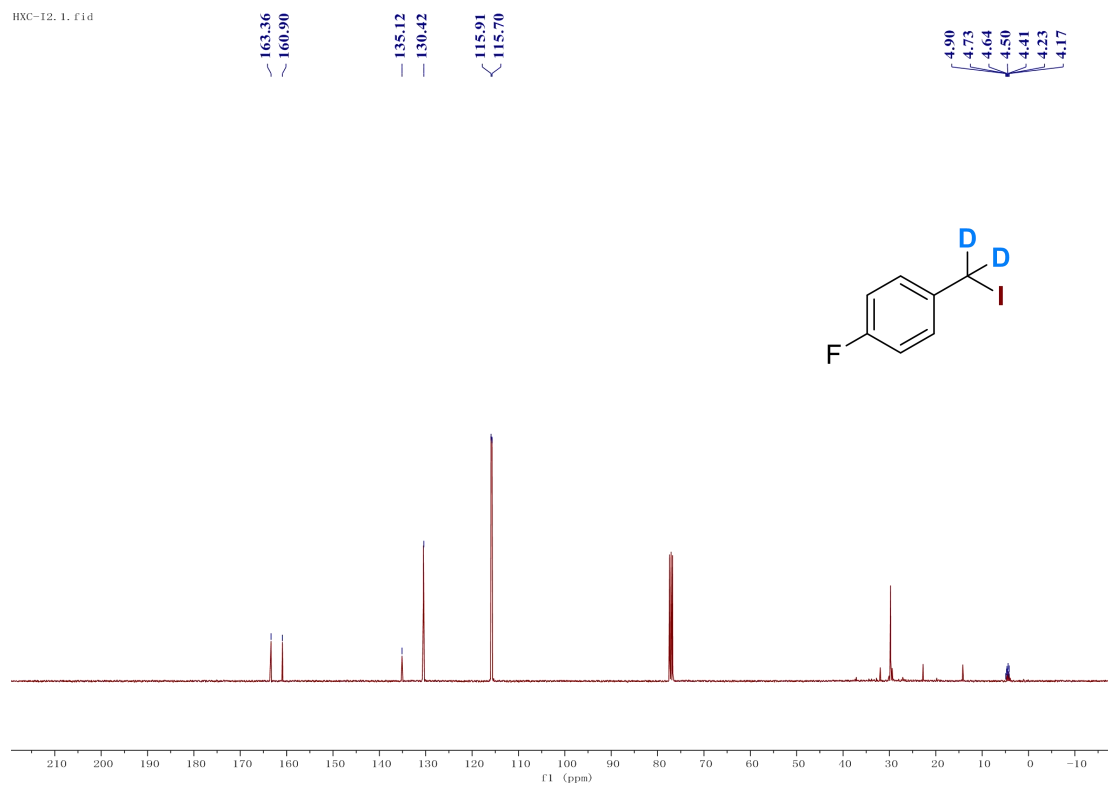


Substrate **2i**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-1-2_1.fid

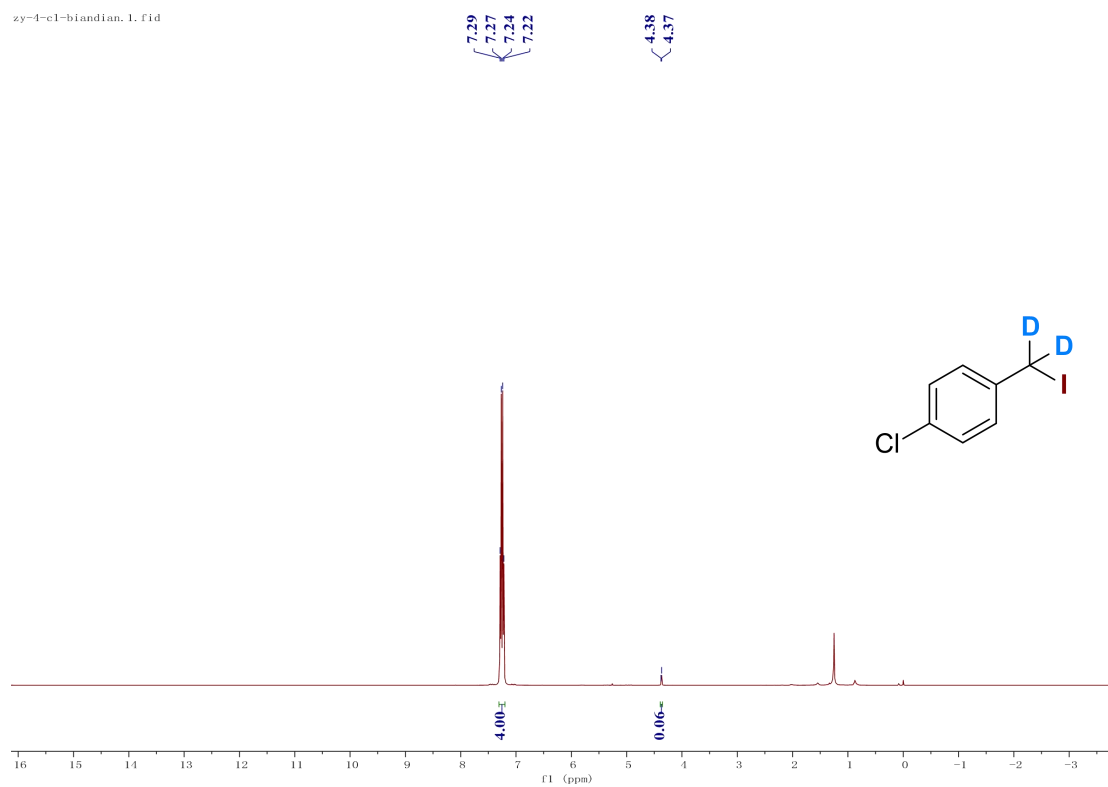


HXC-12_1.fid

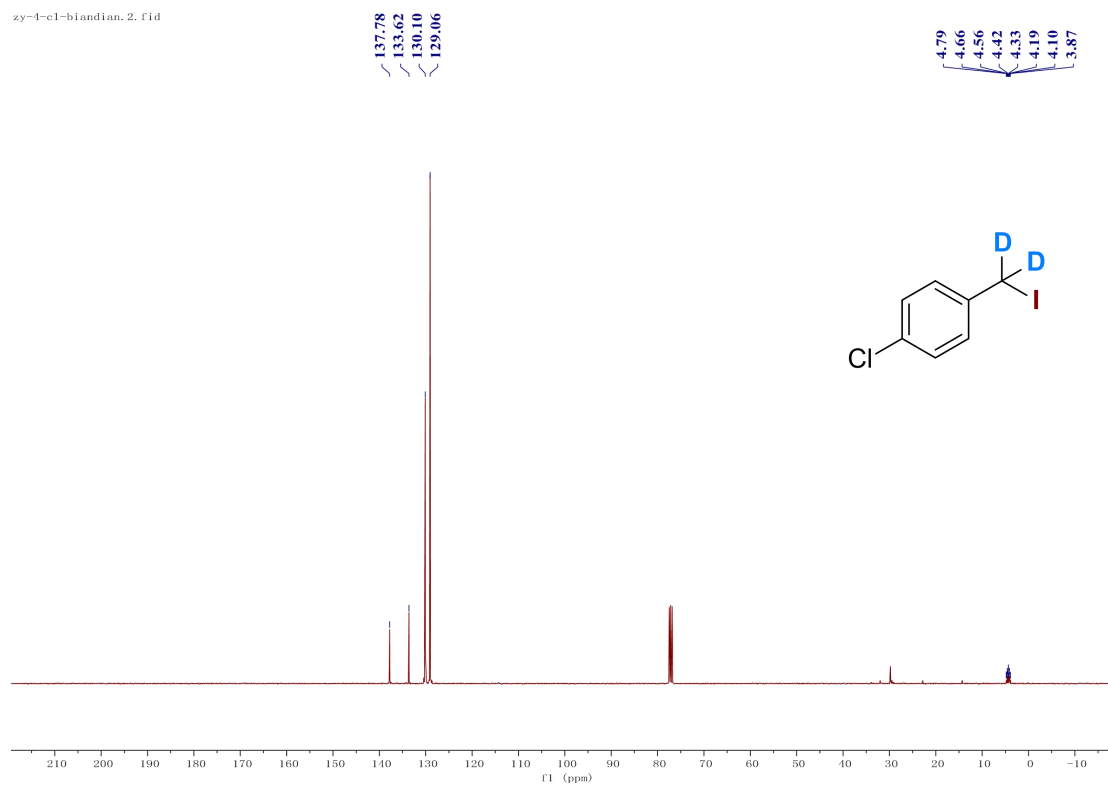


Substrate **2j**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

zy-4-cl-biandian. 1.fid

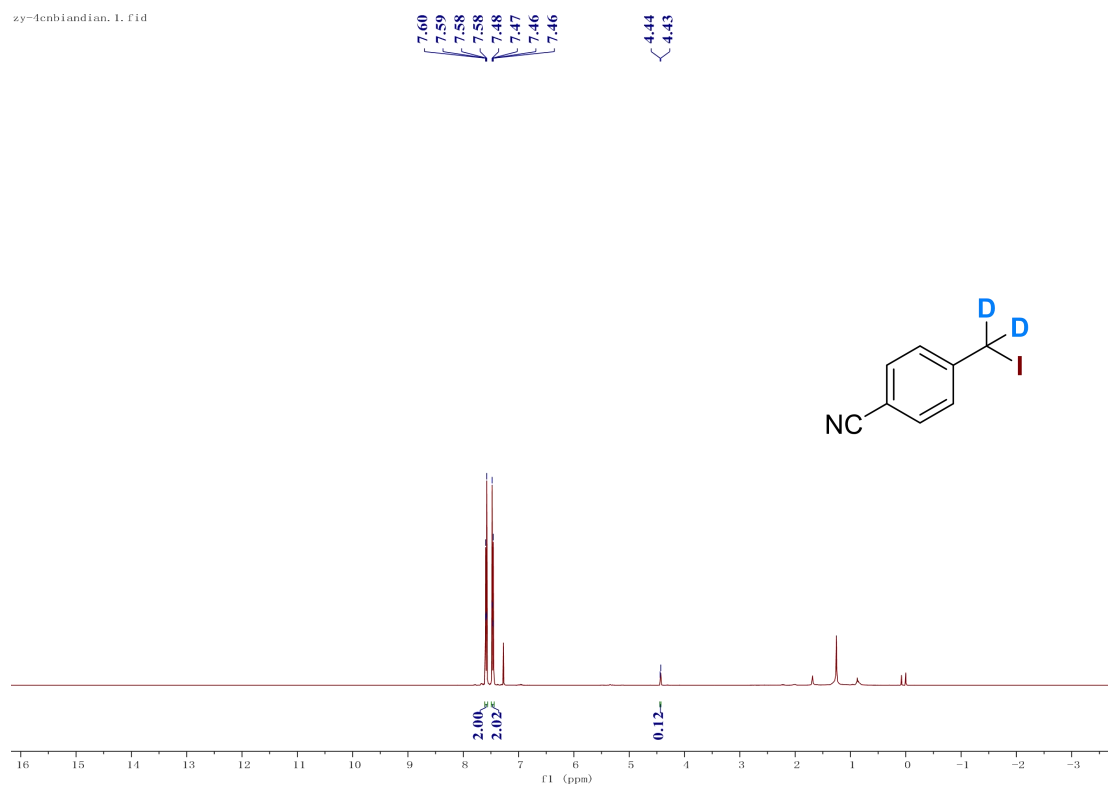


zy-4-cl-biandian. 2.fid

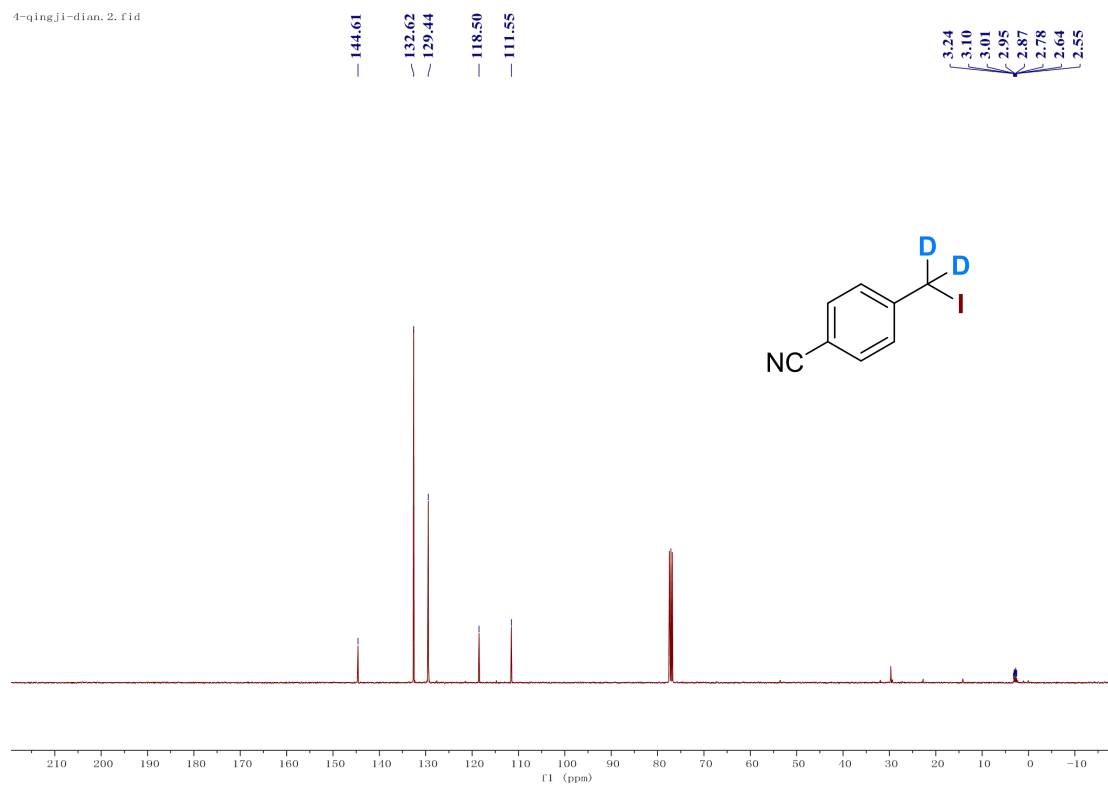


Substrate **2k**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

zy-4enbiandian. 1. f1d

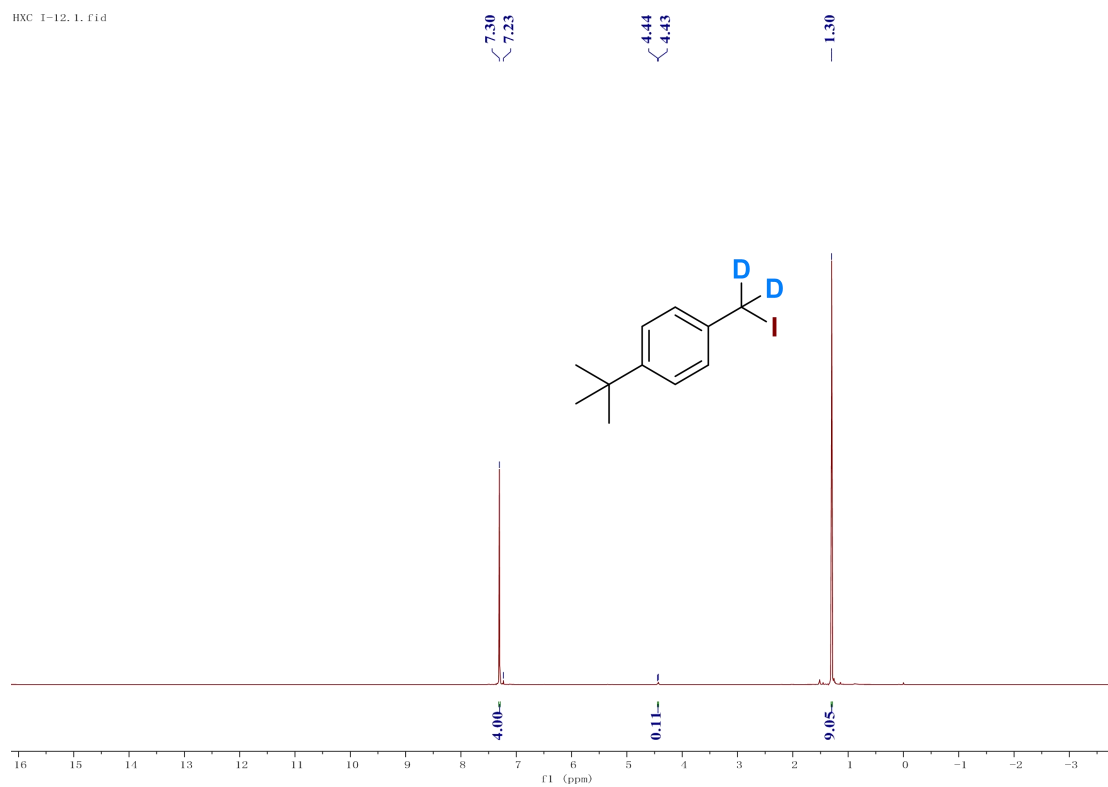


4-qingji-dian. 2. f1d

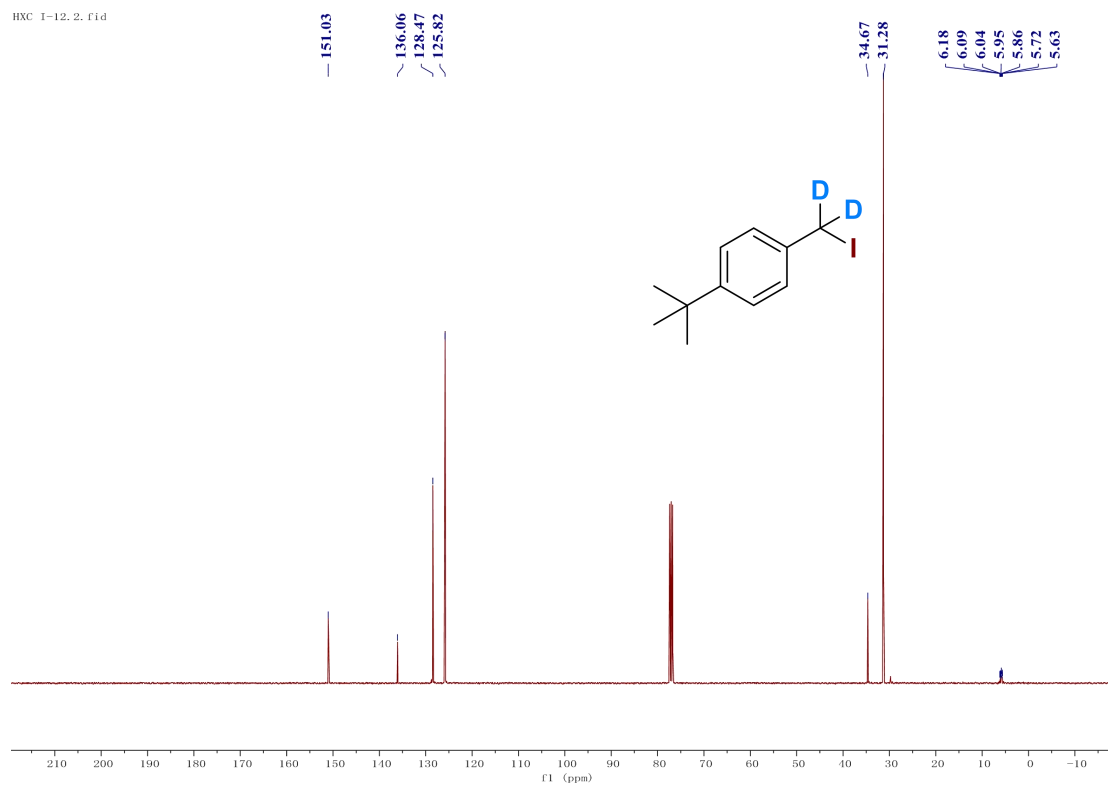


Substrate **2I**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

HXC 1-12.1.fid

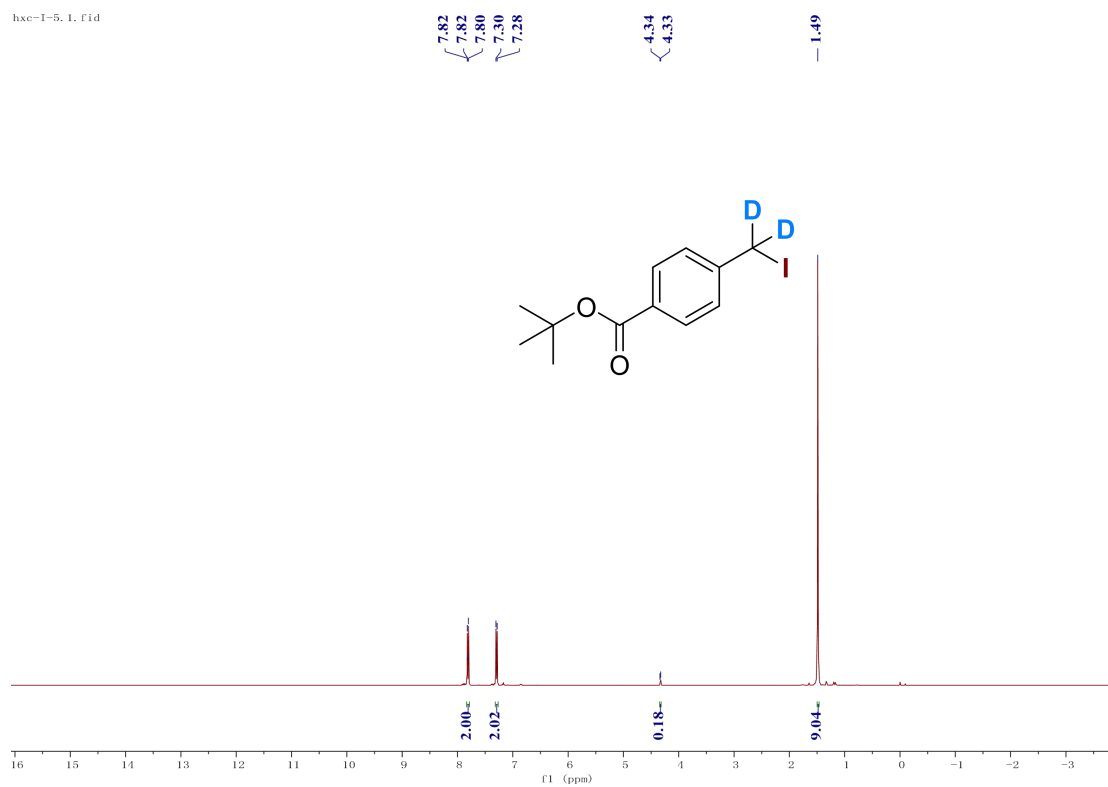


HXC 1-12.2.fid

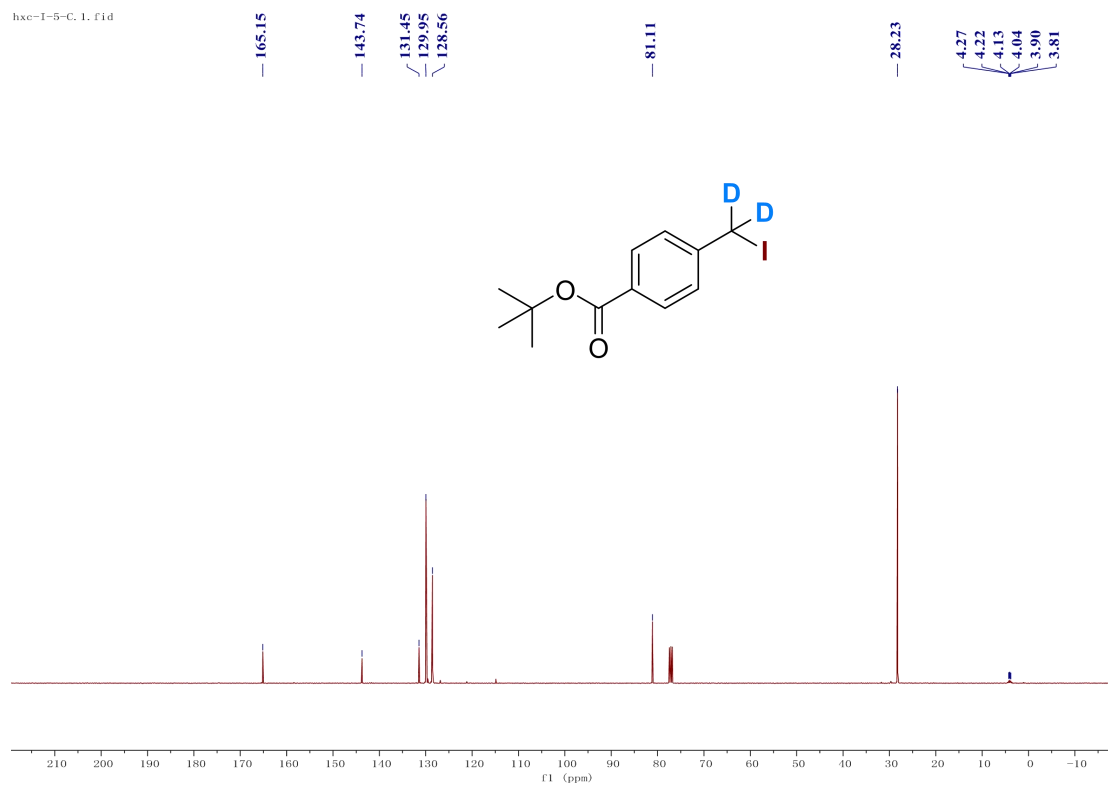


Substrate **2m**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-1-5. 1. f1d

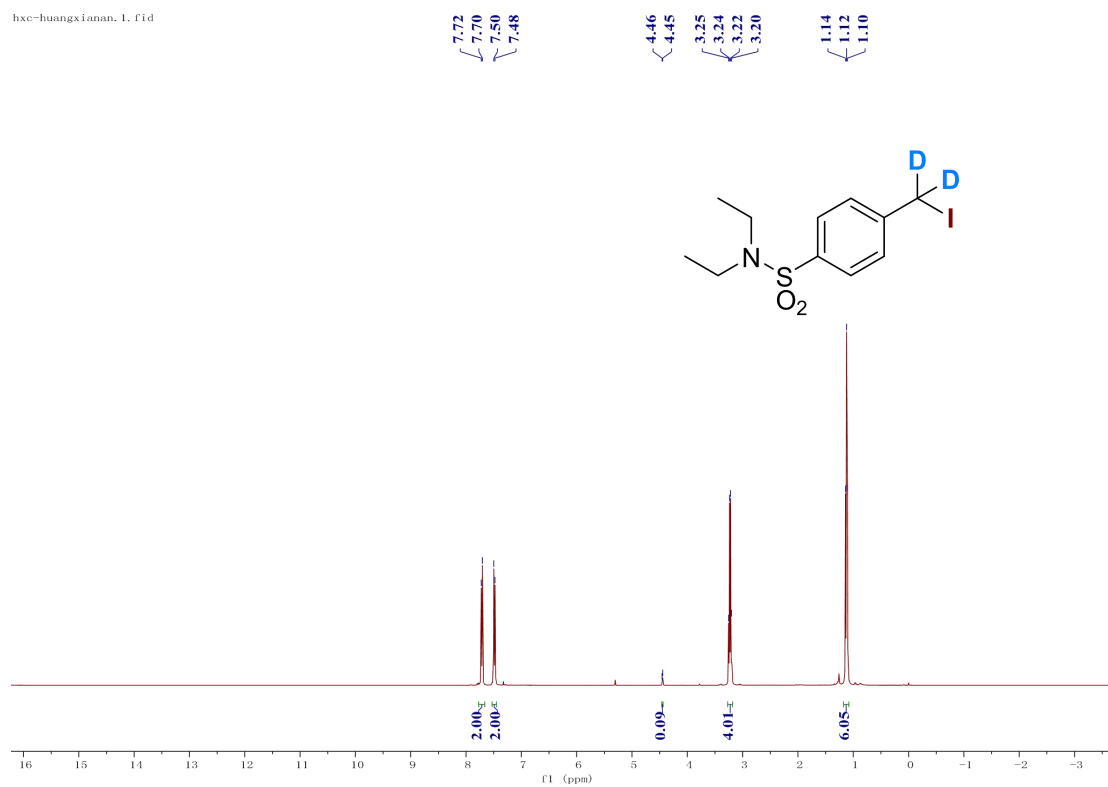


hxc-1-5-C. 1. f1d

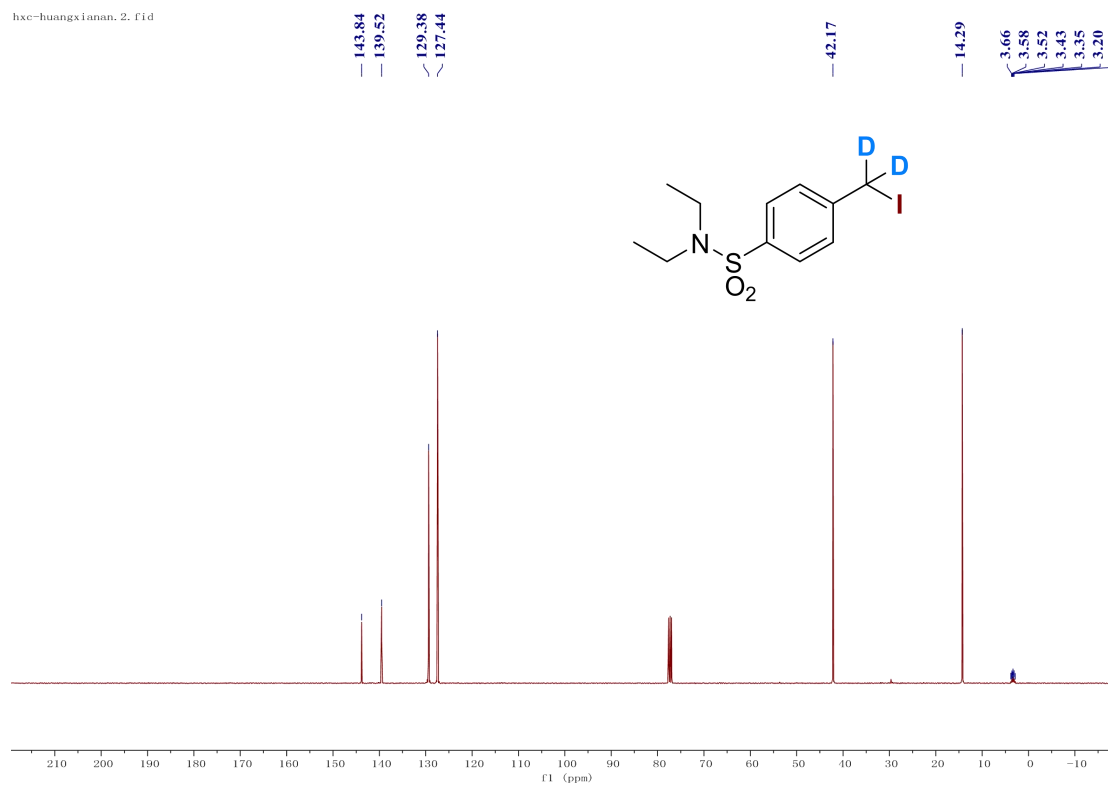


Substrate **2n**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-huangxianan. 1. F1d

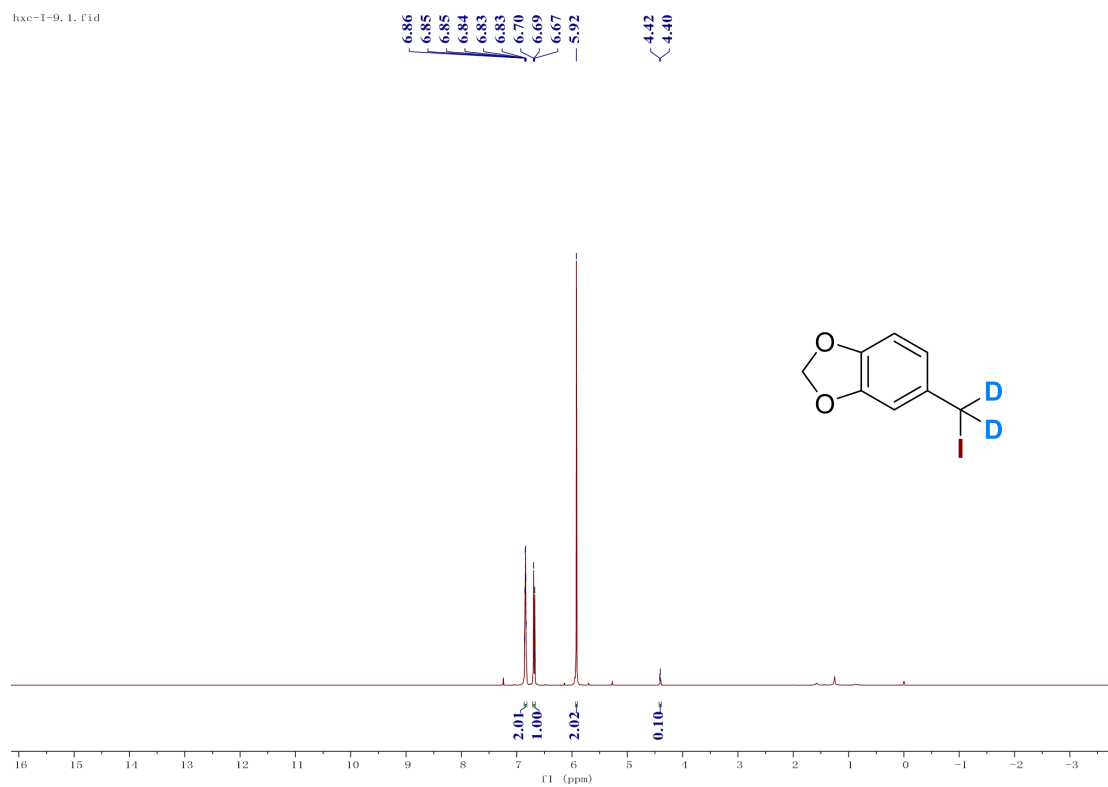


hxc-huangxianan. 2. F1d

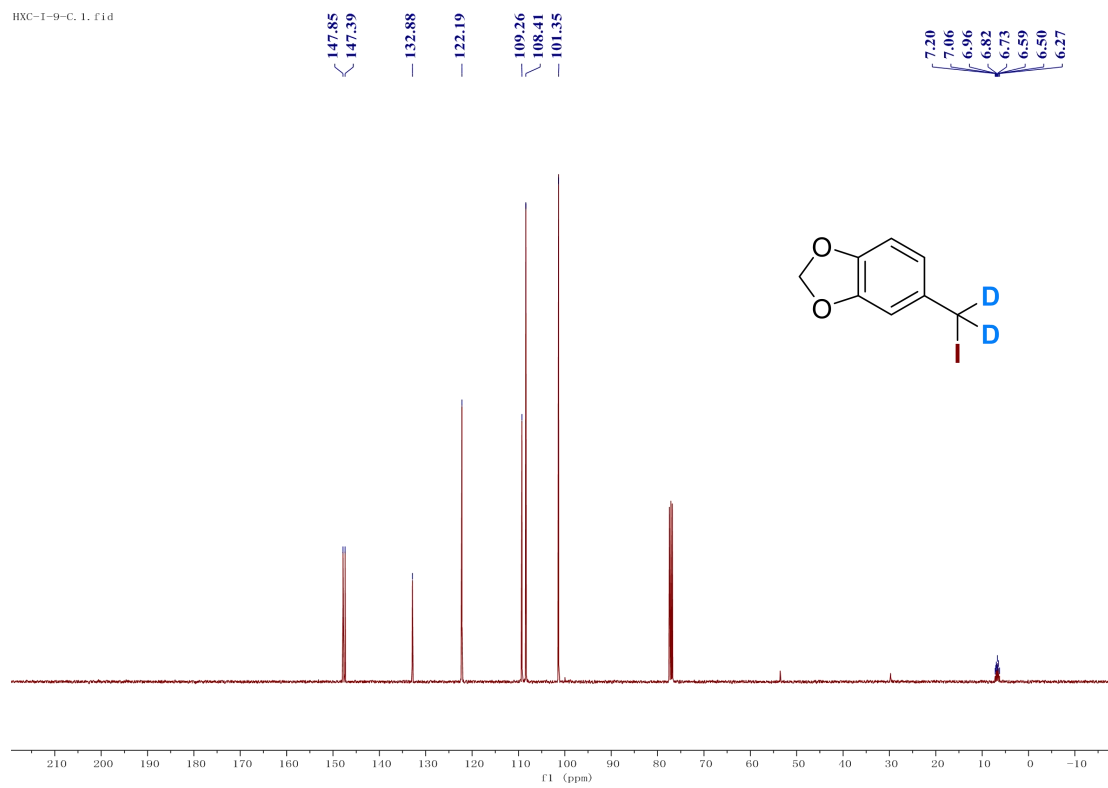


Substrate **2o**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-1-9-1.fid

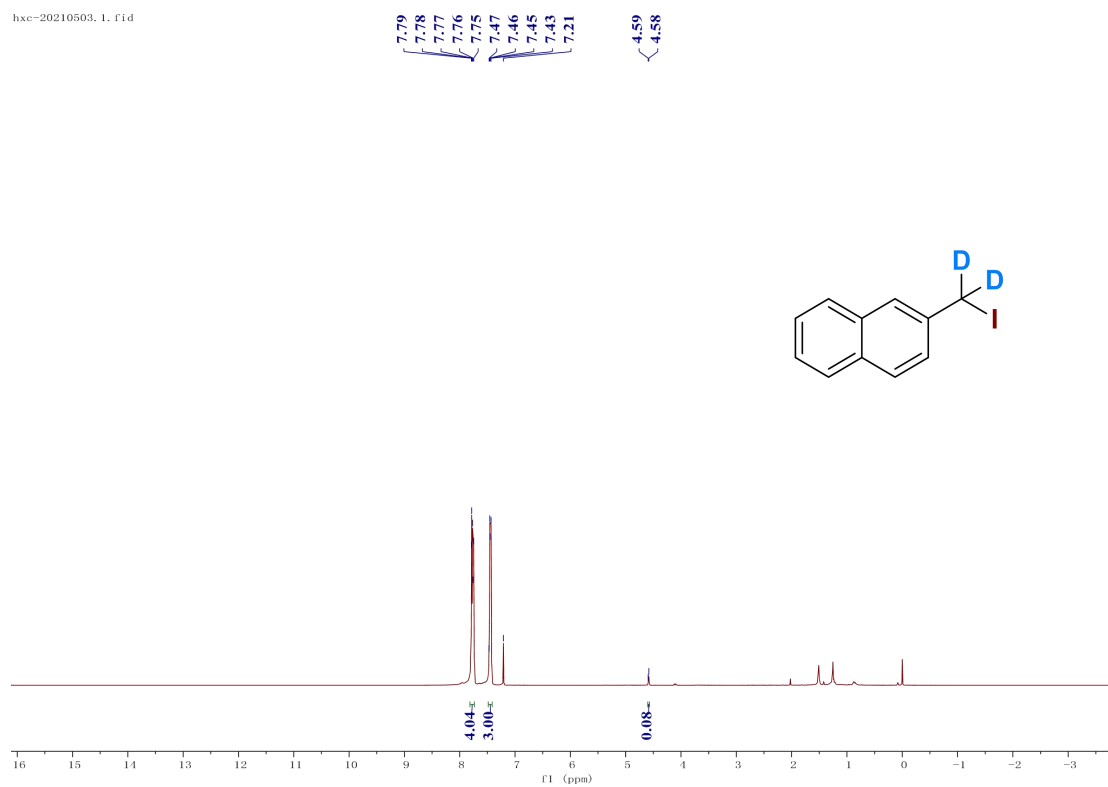


HXC-1-9-C-1.fid

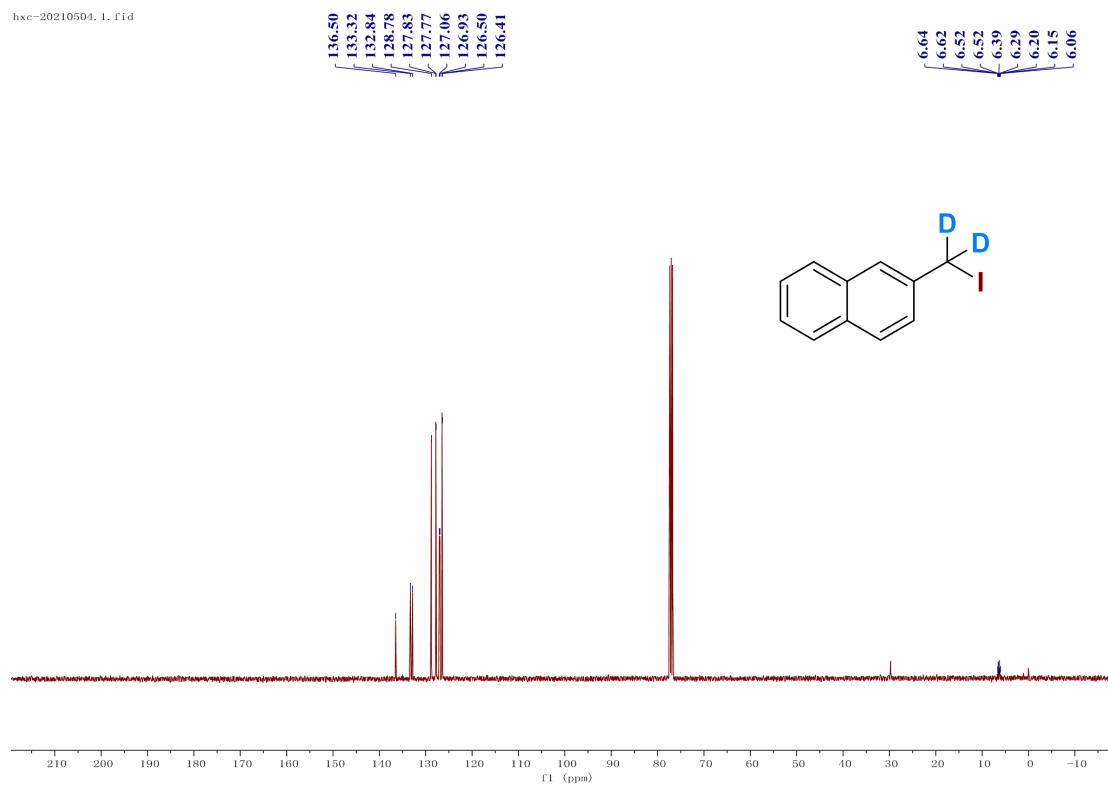


Substrate **2p**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-20210503_1.fid

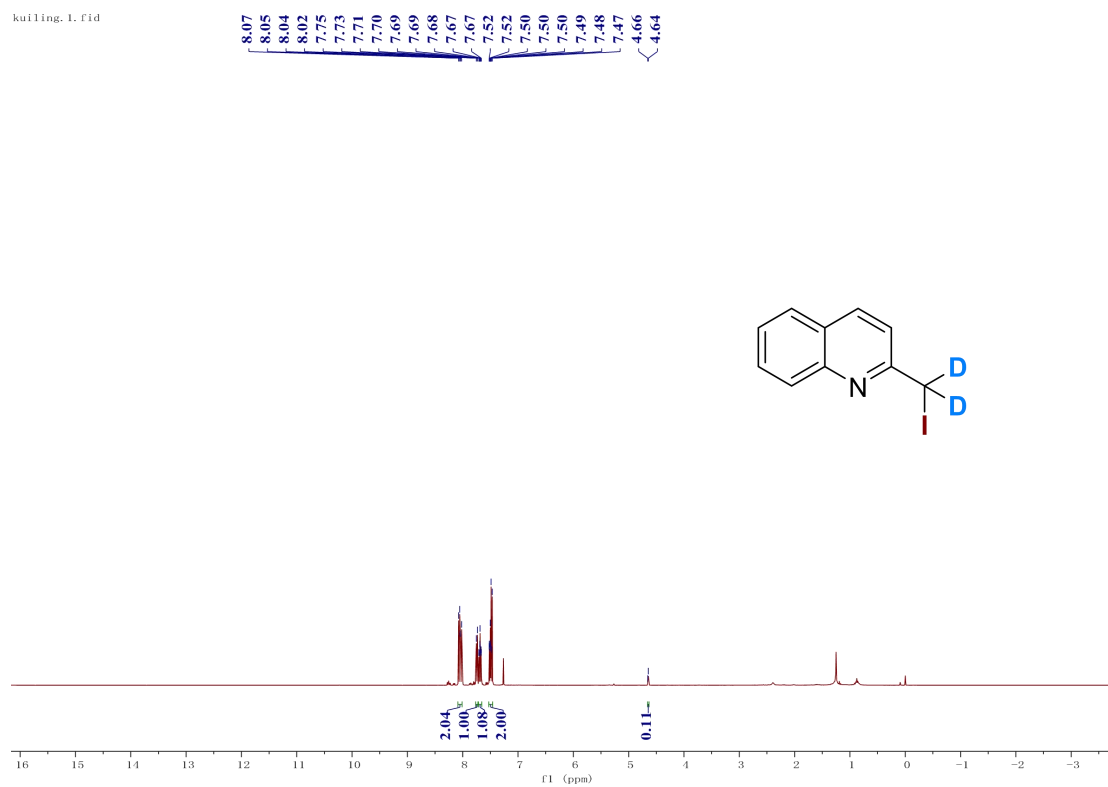


hxc-20210504_1.fid

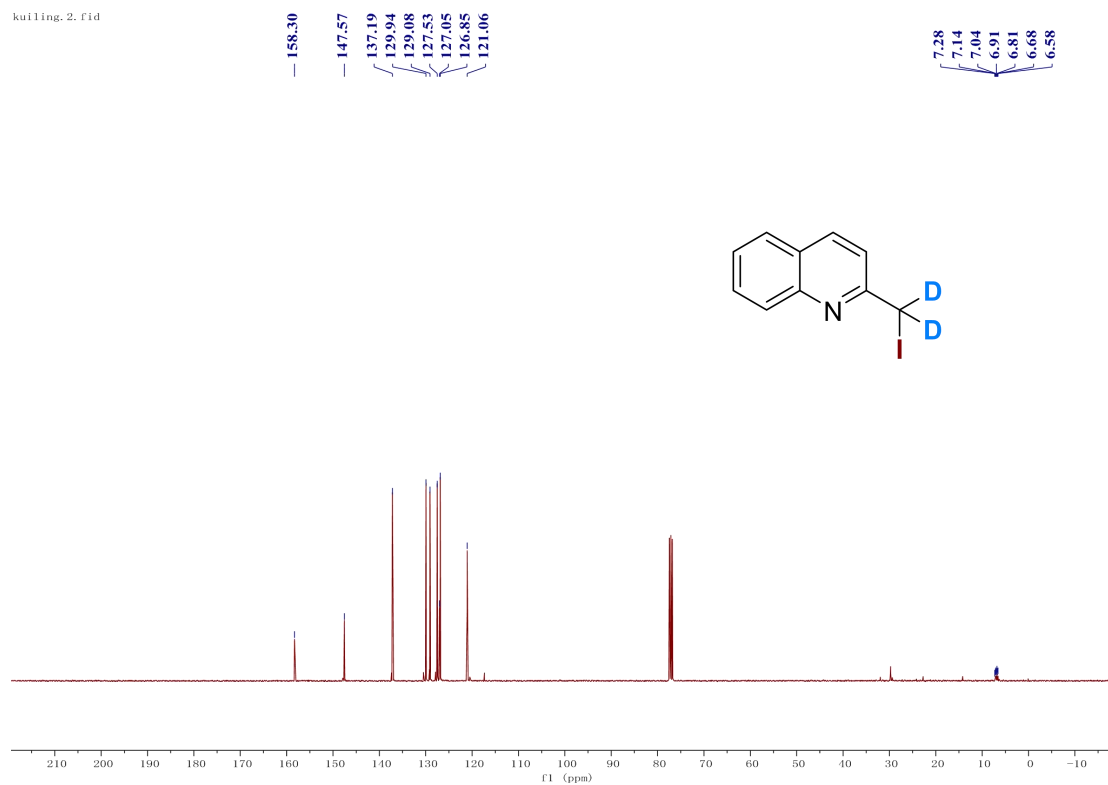


Substrate **2q**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

kuiling.1.fid

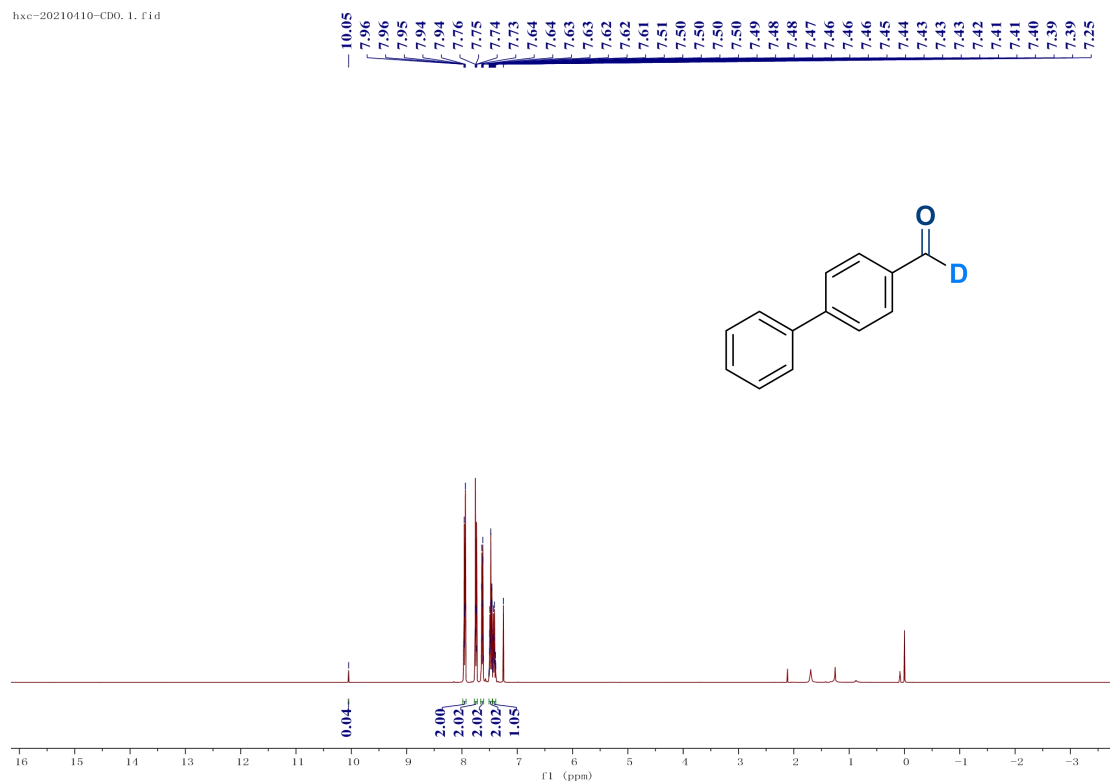


kuiling.2.fid



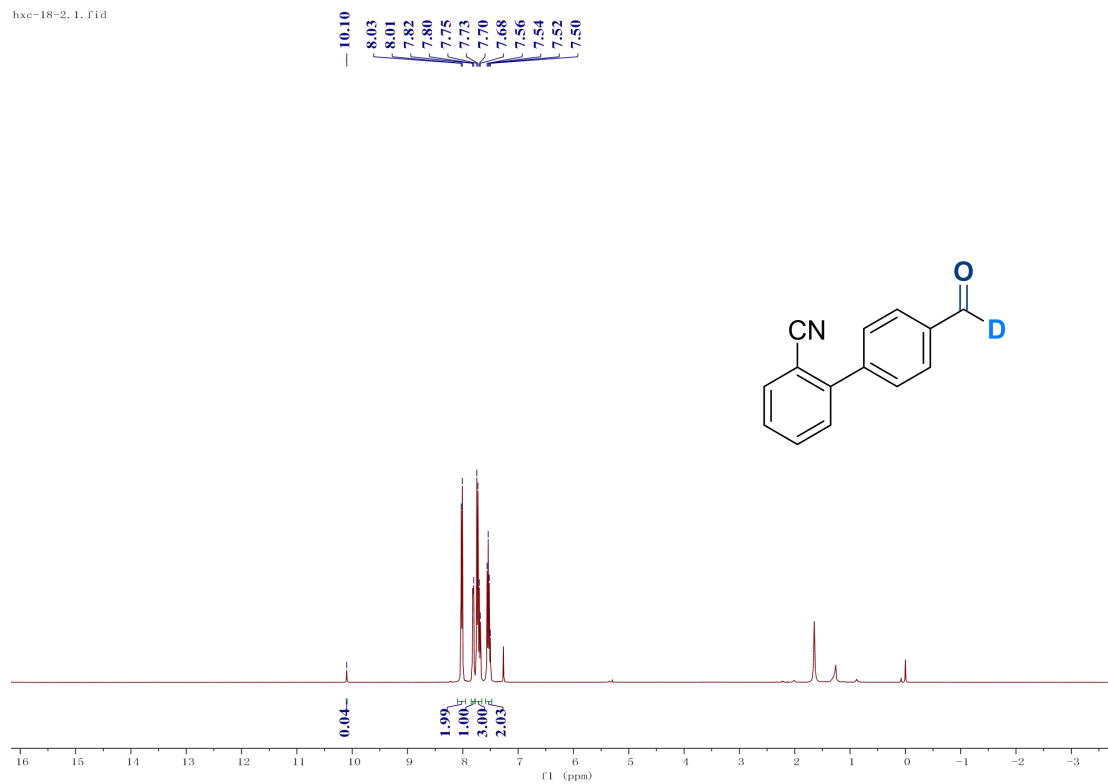
Substrate **3a**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-20210410-CD0. 1. F1d



Substrate **3b**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

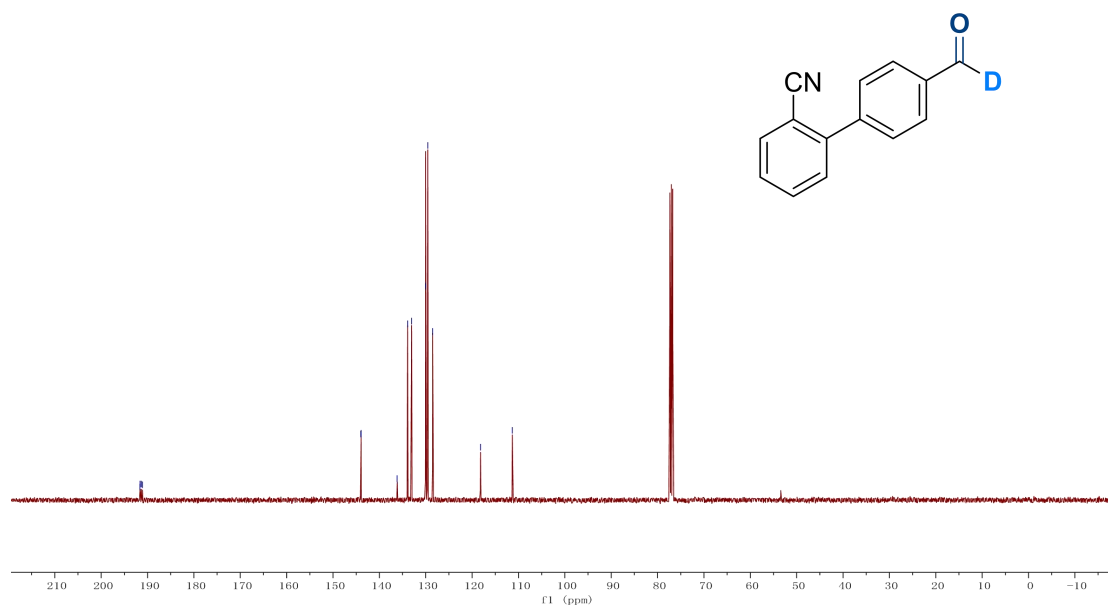
hxc-18-2.1.fid



hxc-20210817-1

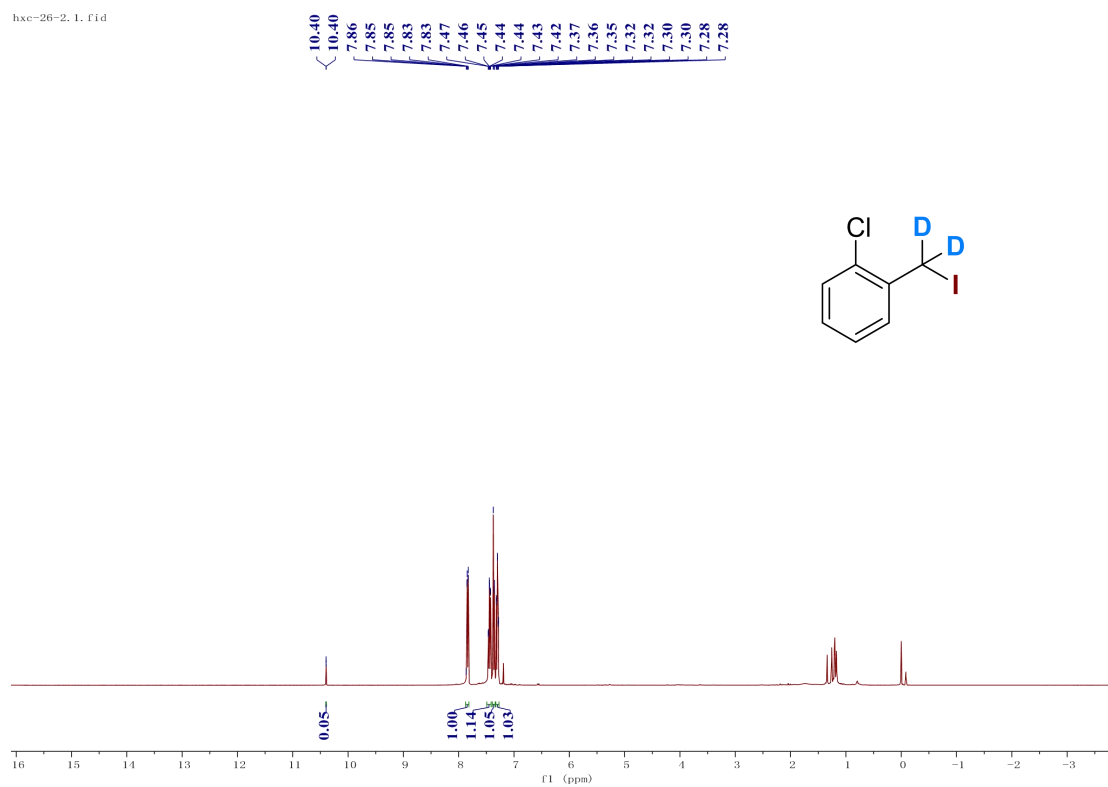
191.65
191.61
191.33
191.08

144.01
143.94
136.19
133.92
133.04
133.04
130.00
129.55
128.52
118.19
111.33



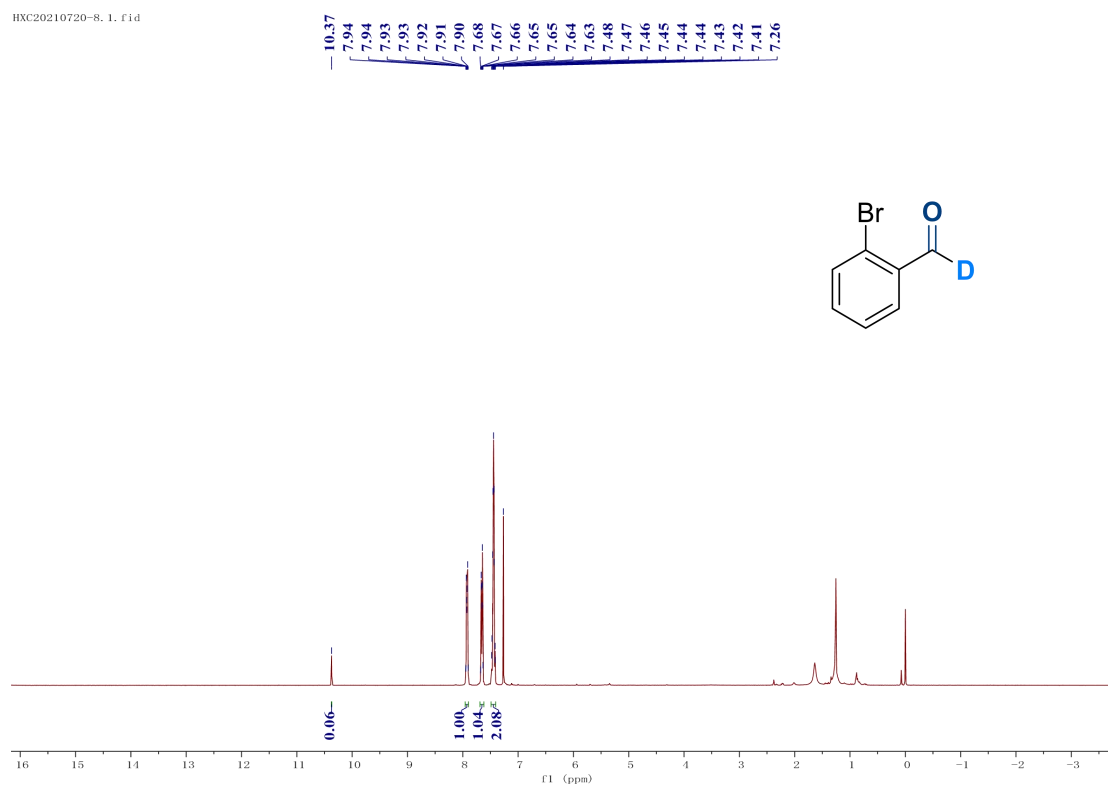
Substrate **3c**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-26-2.1.fid



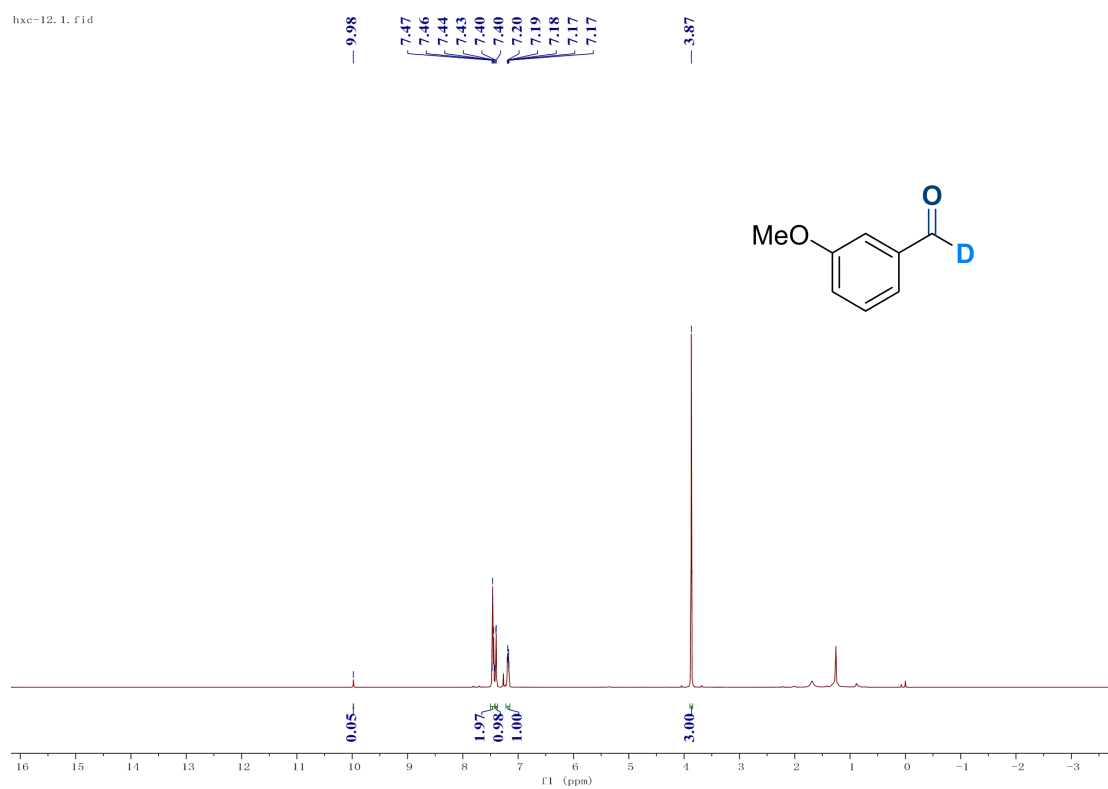
Substrate **3d**: ^1H NMR (CDCl_3 , 400 MHz)

HXC20210720-8_1.fid



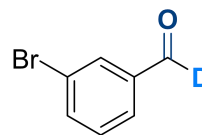
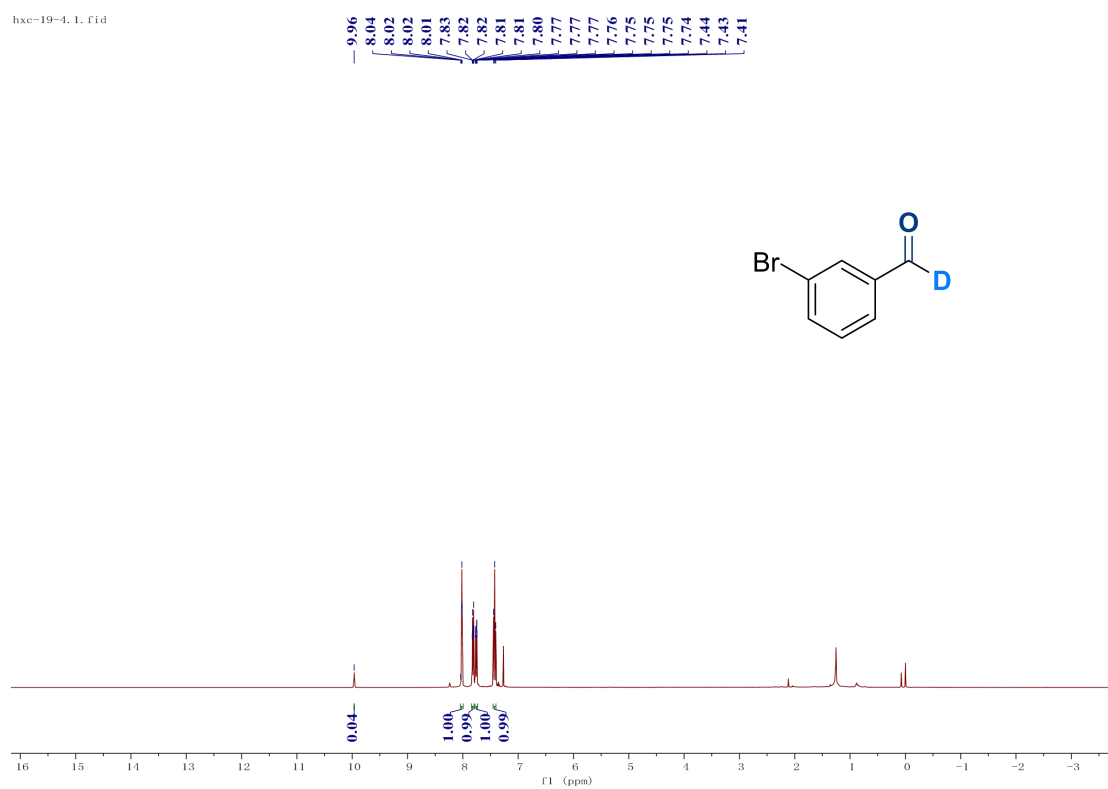
Substrate **3e**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-12.1.fid



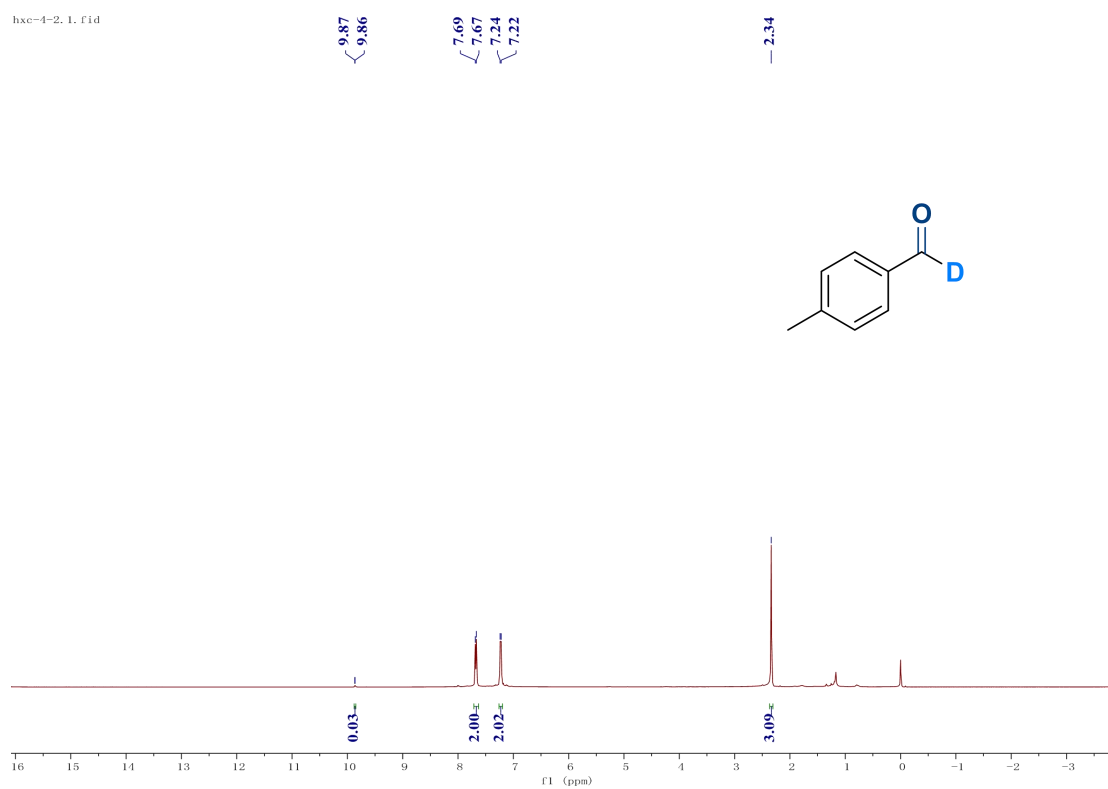
Substrate **3f**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-19-4.1. f1d



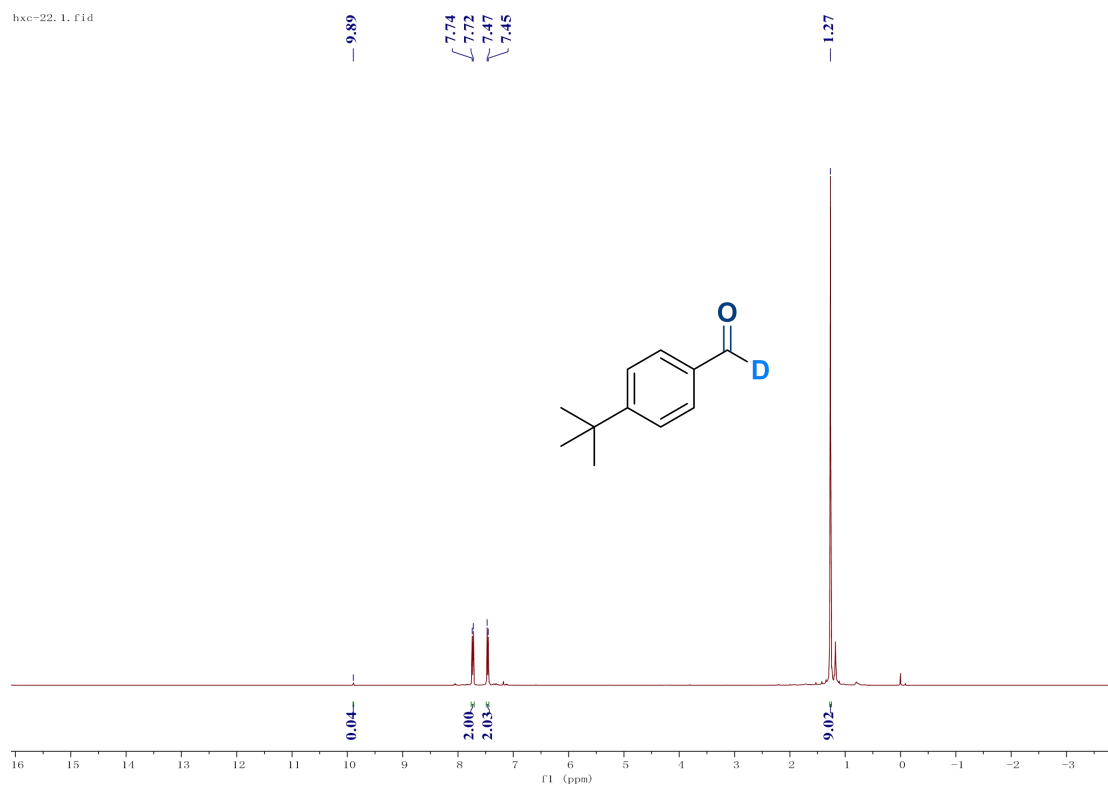
Substrate **3g**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-4-2. 1. f1d



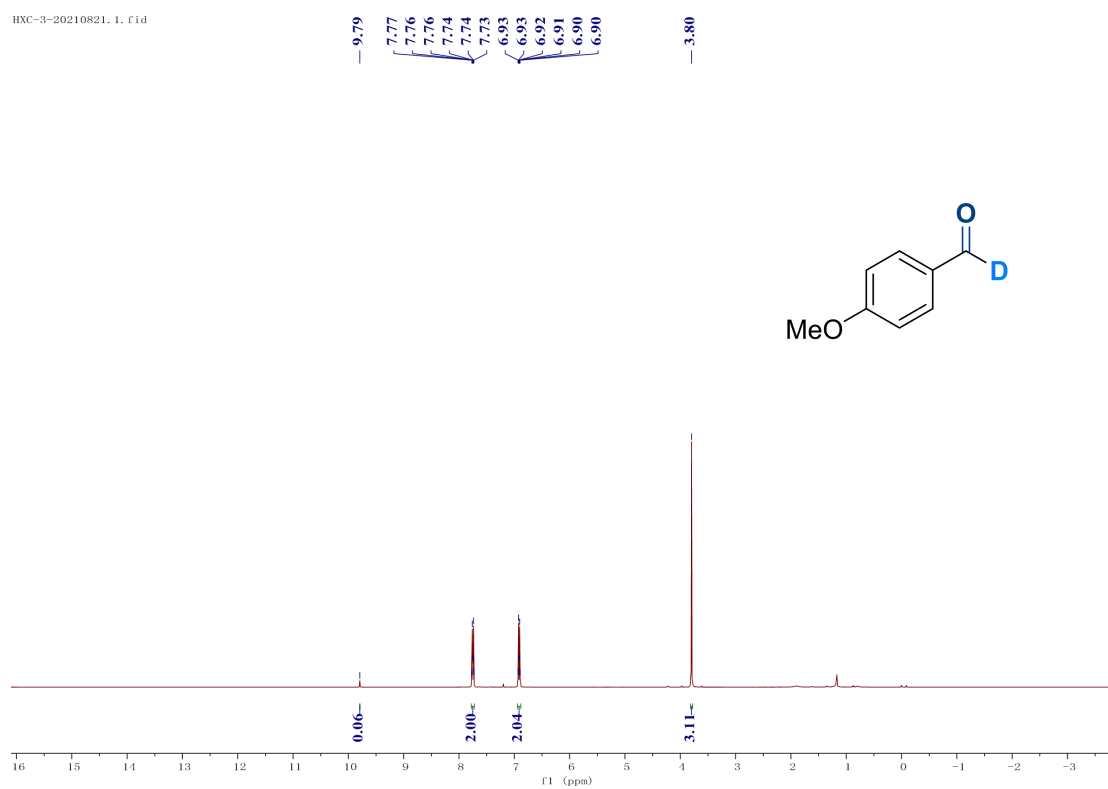
Substrate **3h**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-22.1.fid



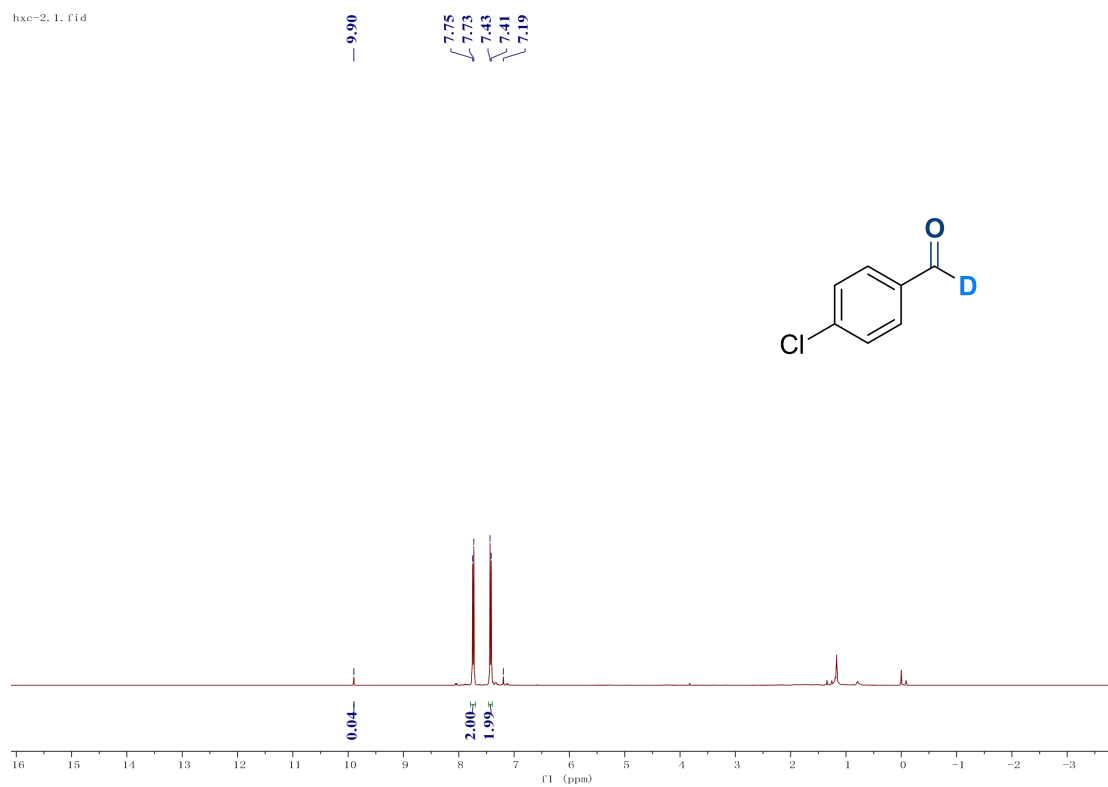
Substrate **3i**: ^1H NMR (CDCl_3 , 400 MHz)

HXC-3-20210821_1.fid



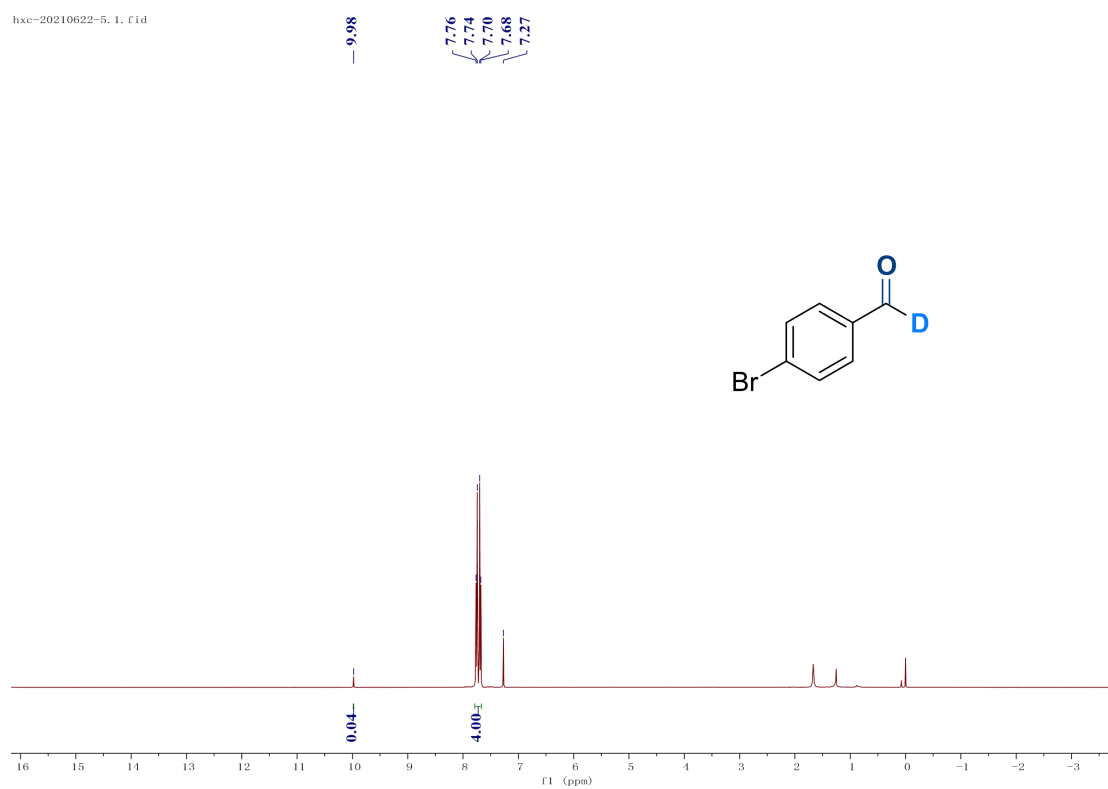
Substrate **3j**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-2, 1, fid



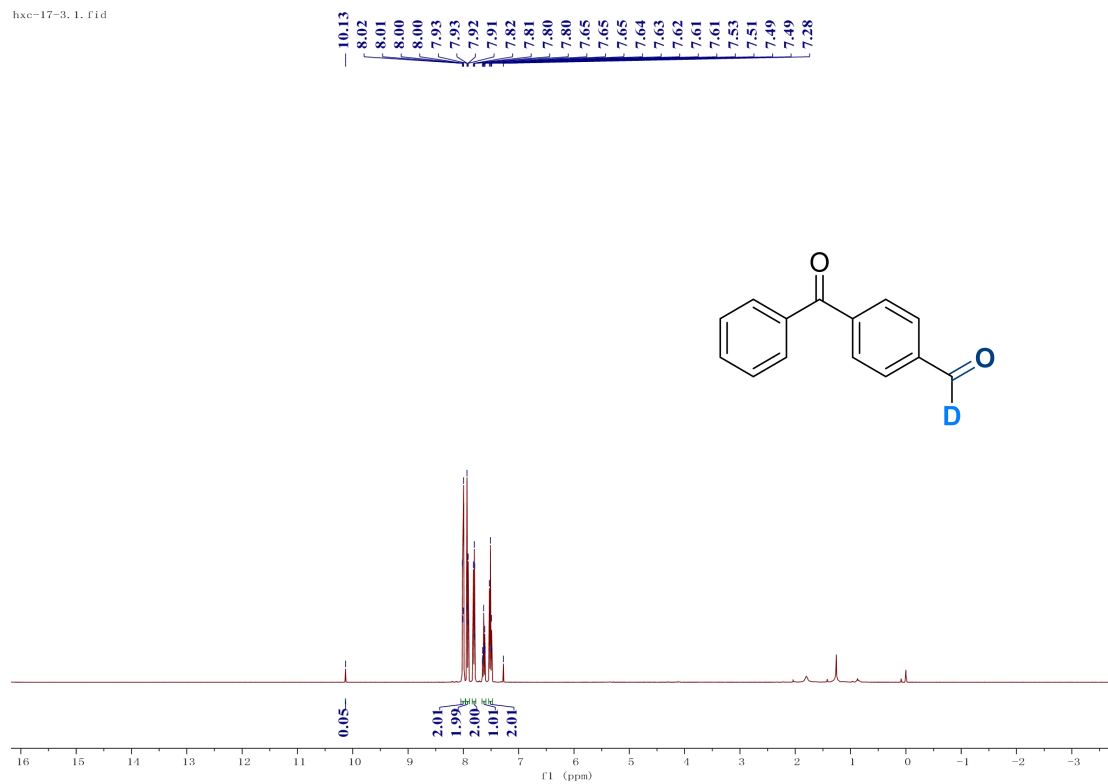
Substrate **3k**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-20210622-5, 1, f1d



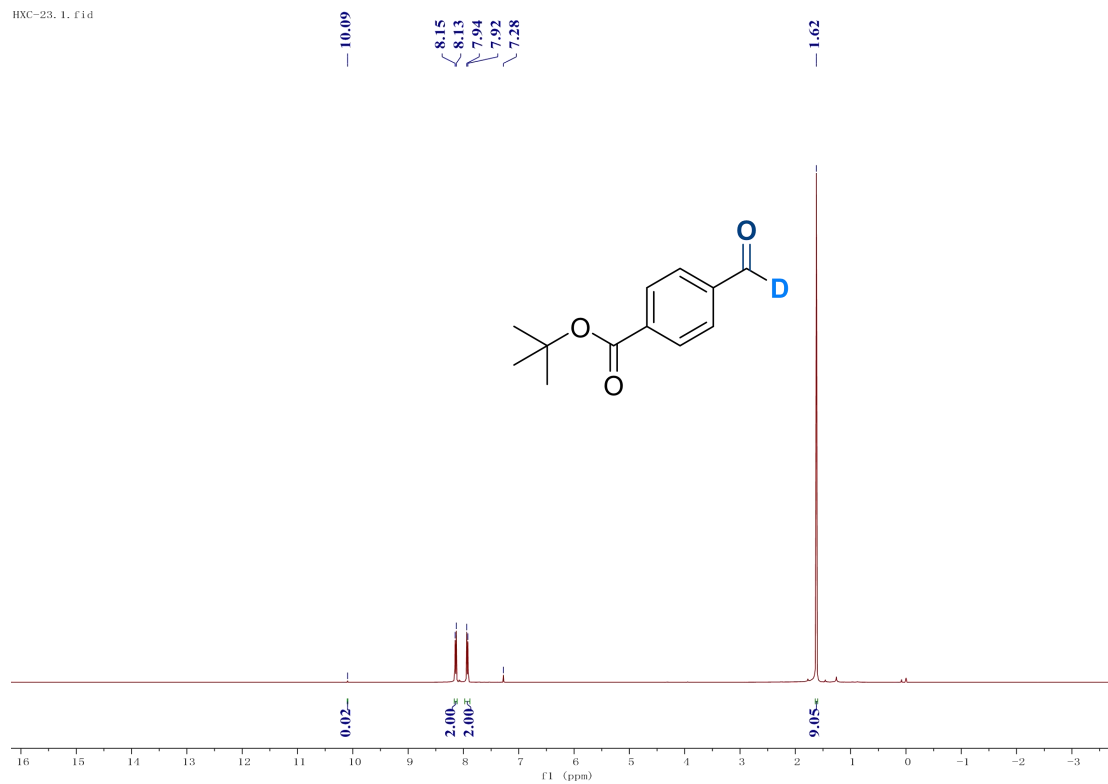
Substrate **3I**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-17-3.1.fid

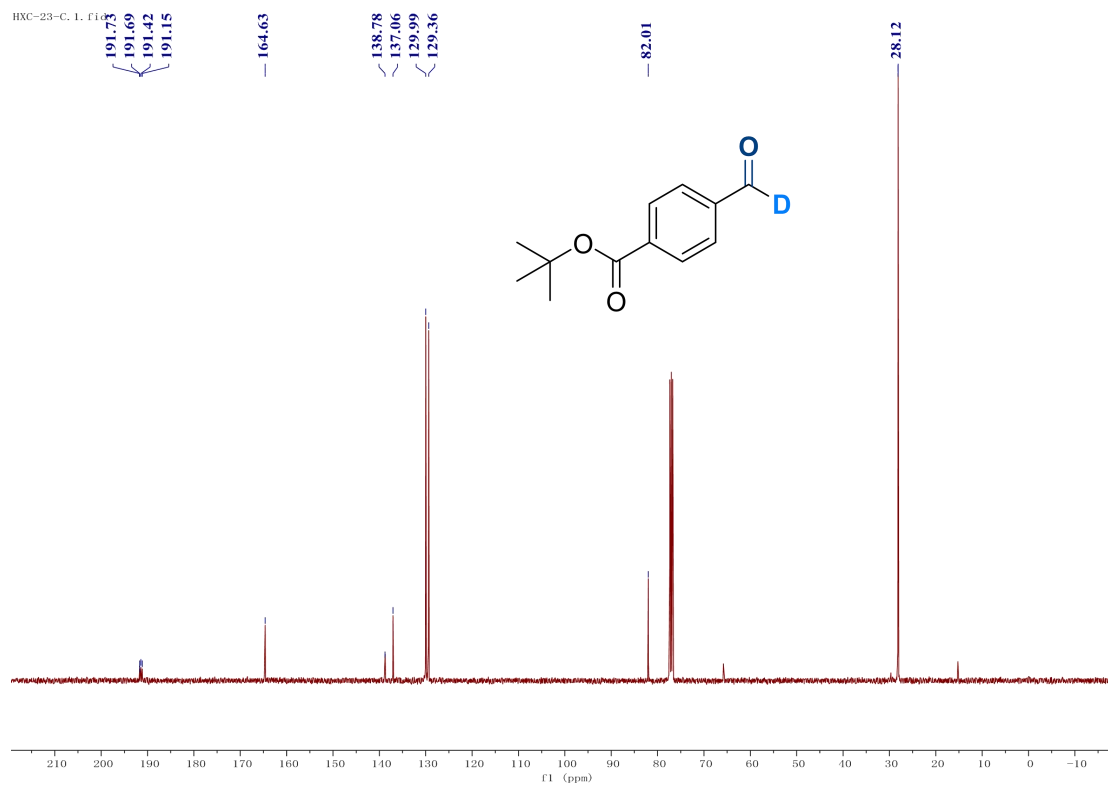


Substrate **3m**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

HXC-23-1.f1d

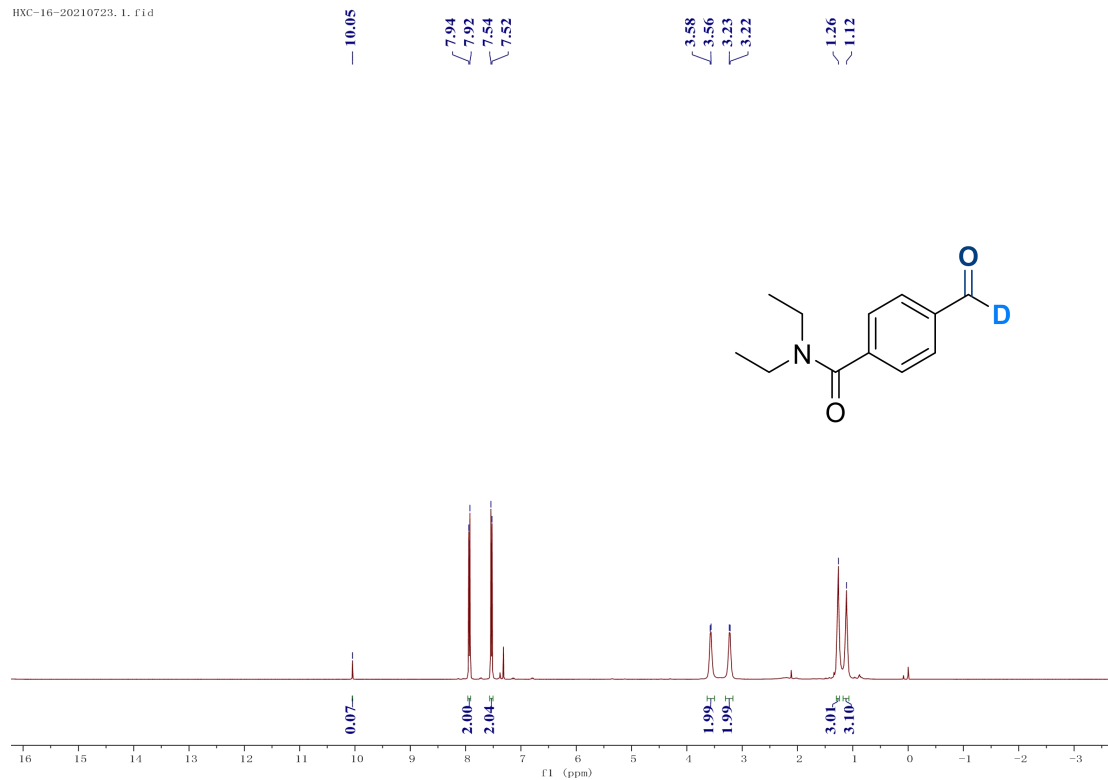


HXC-23-C-1.f1d

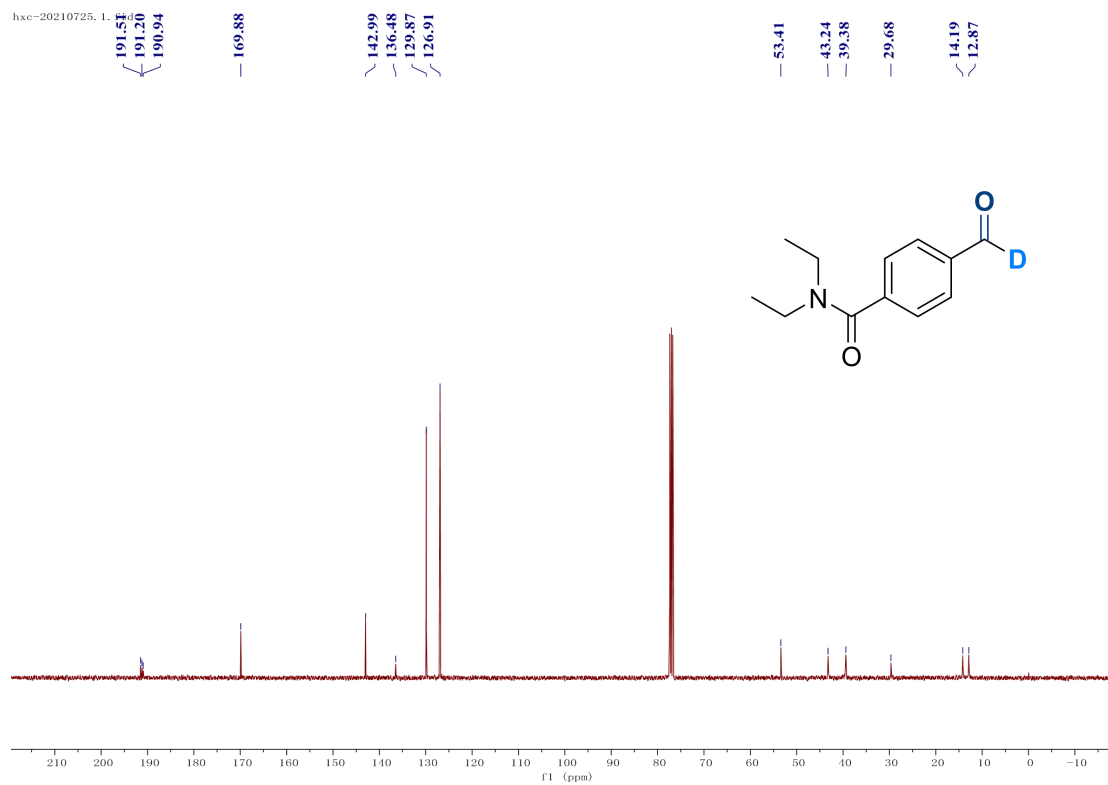


Substrate **3n**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

HXC-16-20210723. 1. F1d

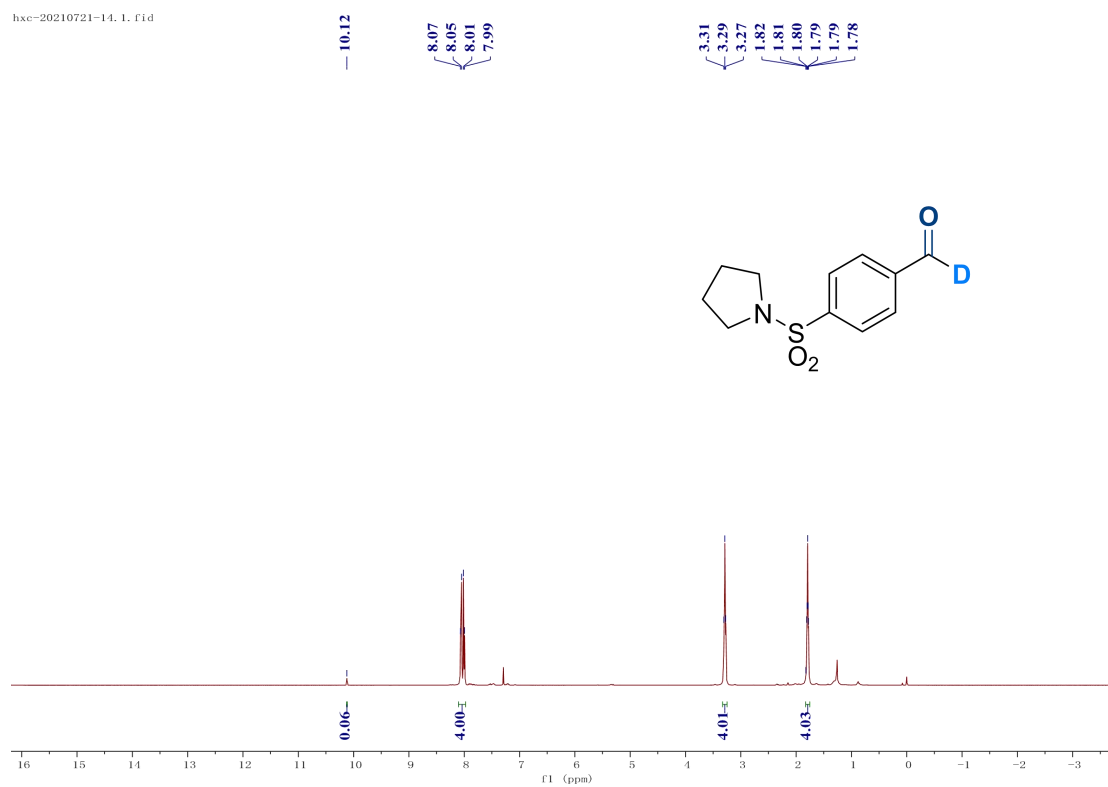


hxc-20210725. 1. F1d

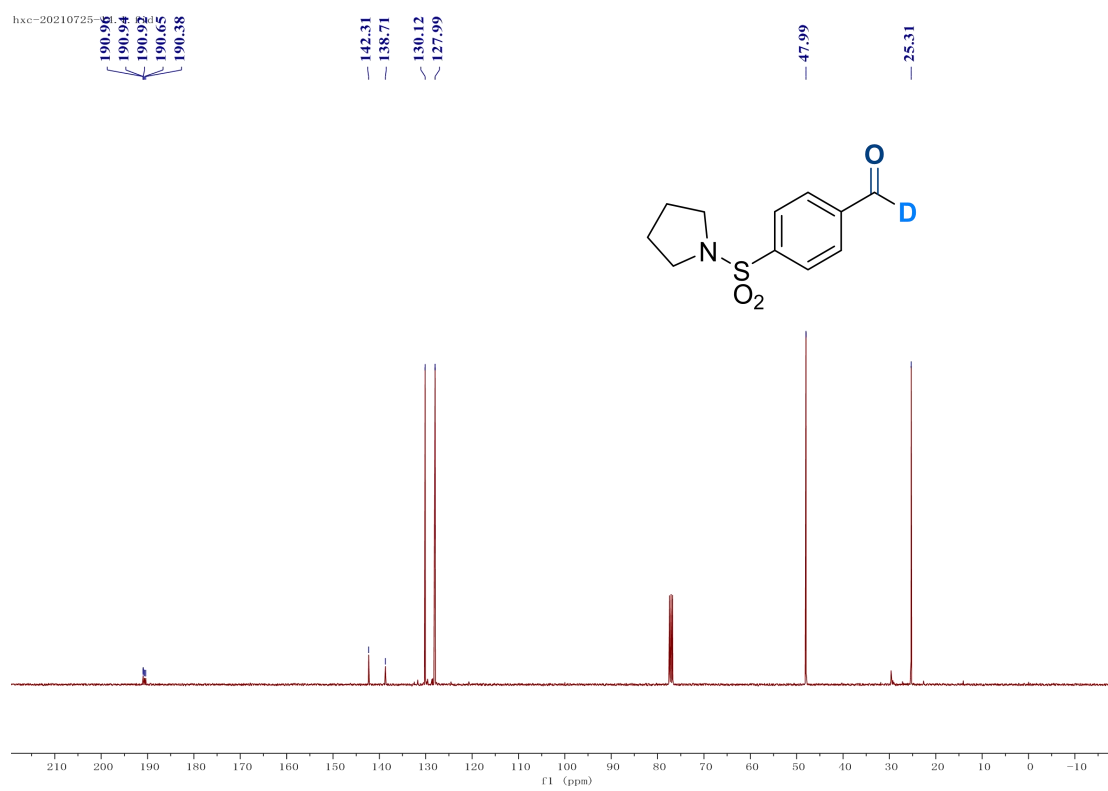


Substrate **3o**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-20210721-14.1.fid

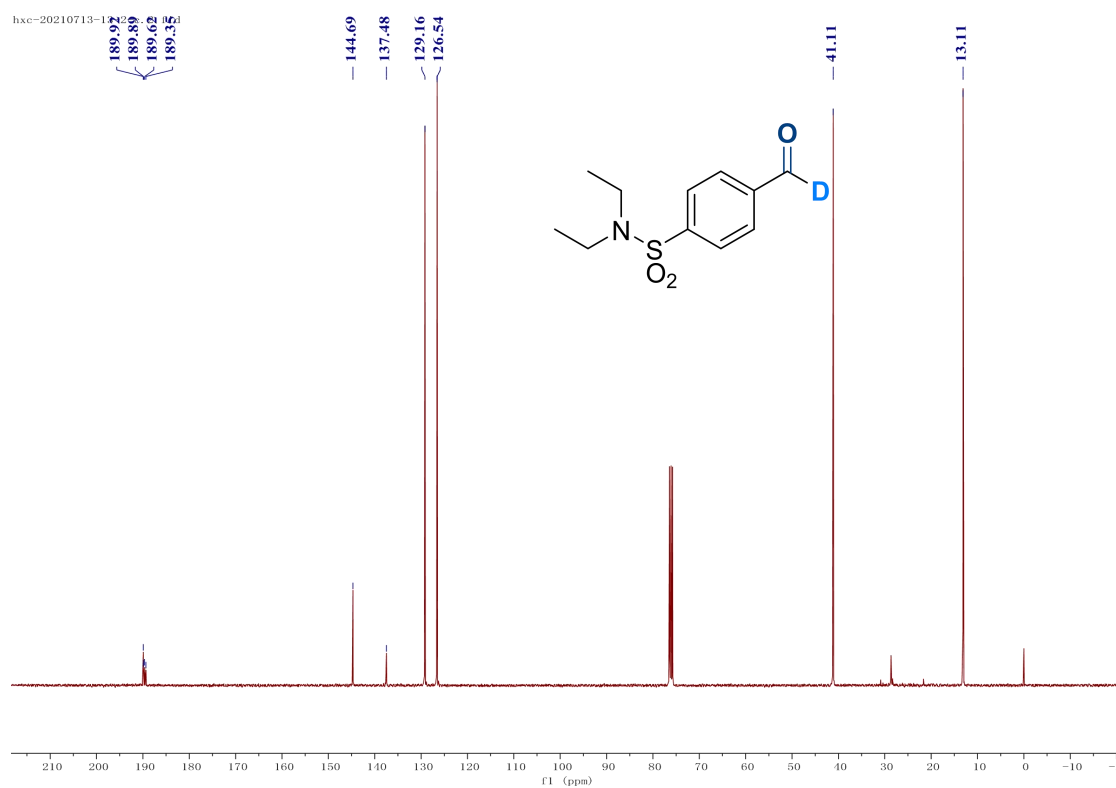
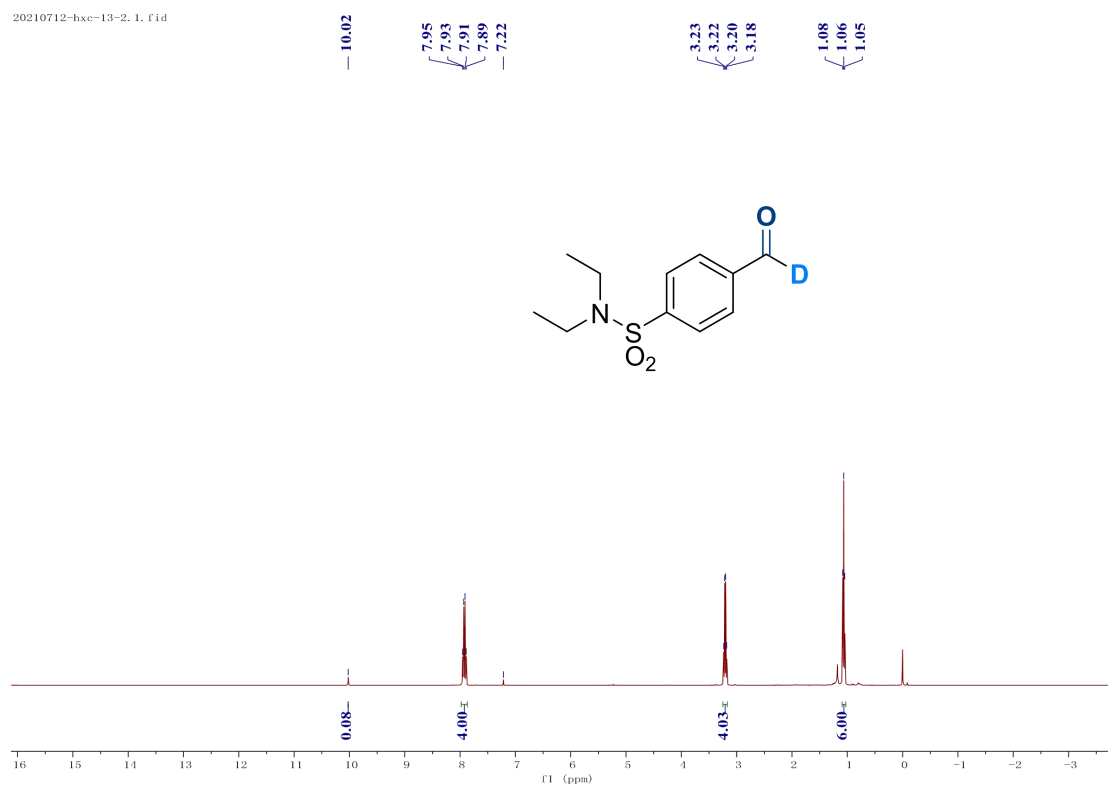


hxc-20210725-



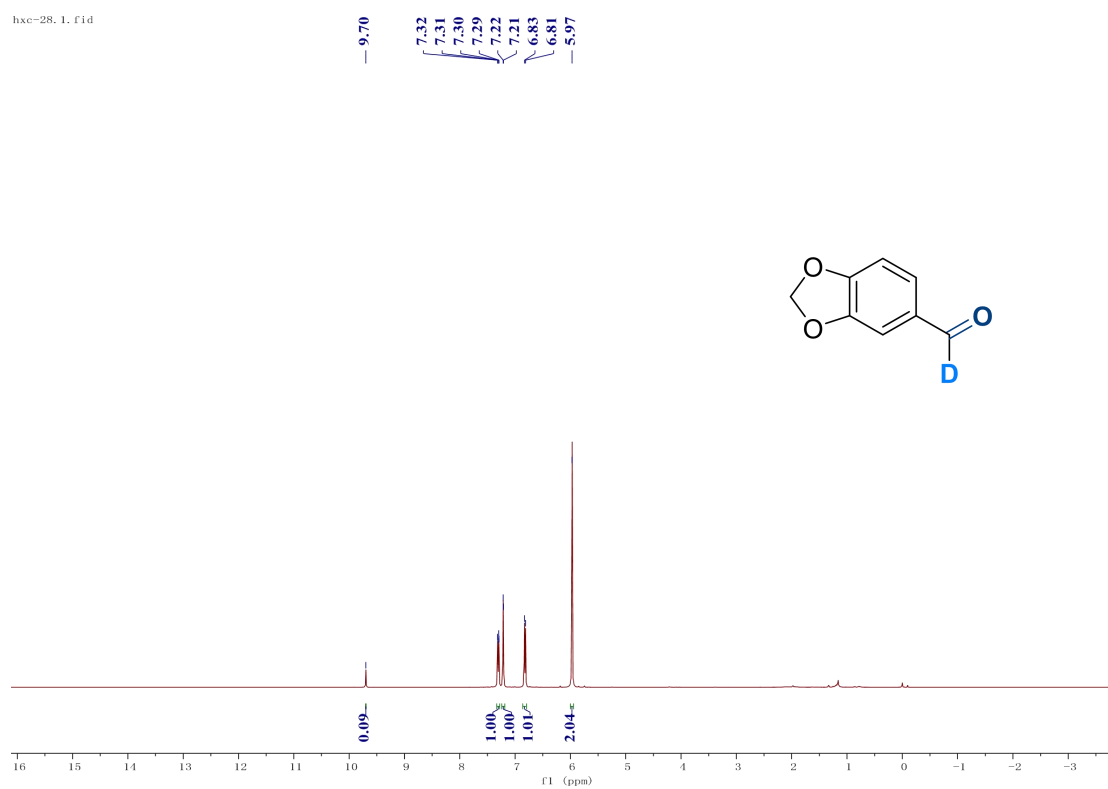
Substrate **3p**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

20210712-hxe-13-2, 1, F1.d



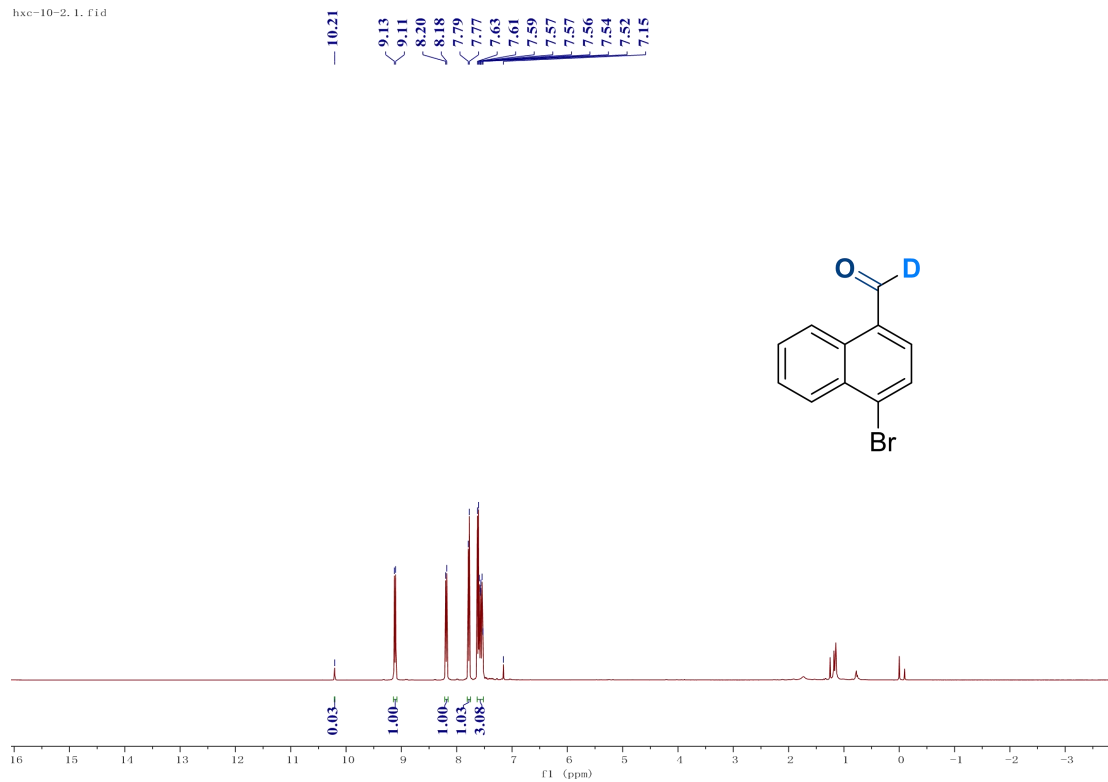
Substrate **3q**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-28.1.fid

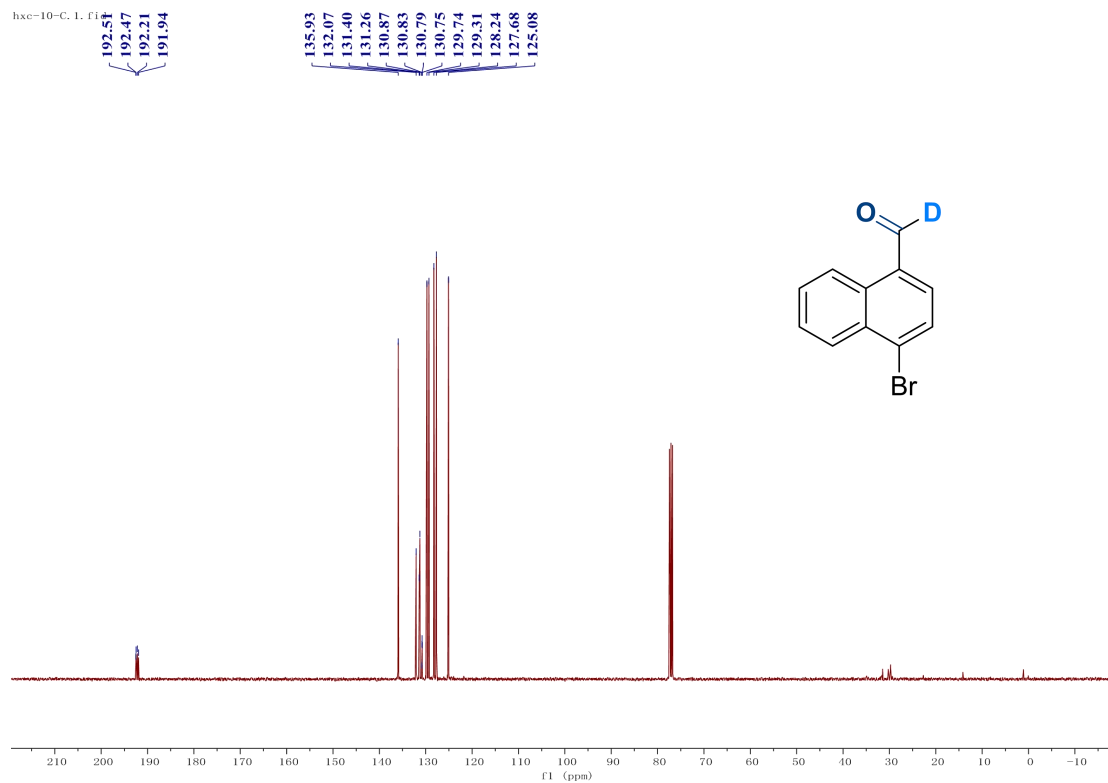


Substrate **3s**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-10-2.1.f1d

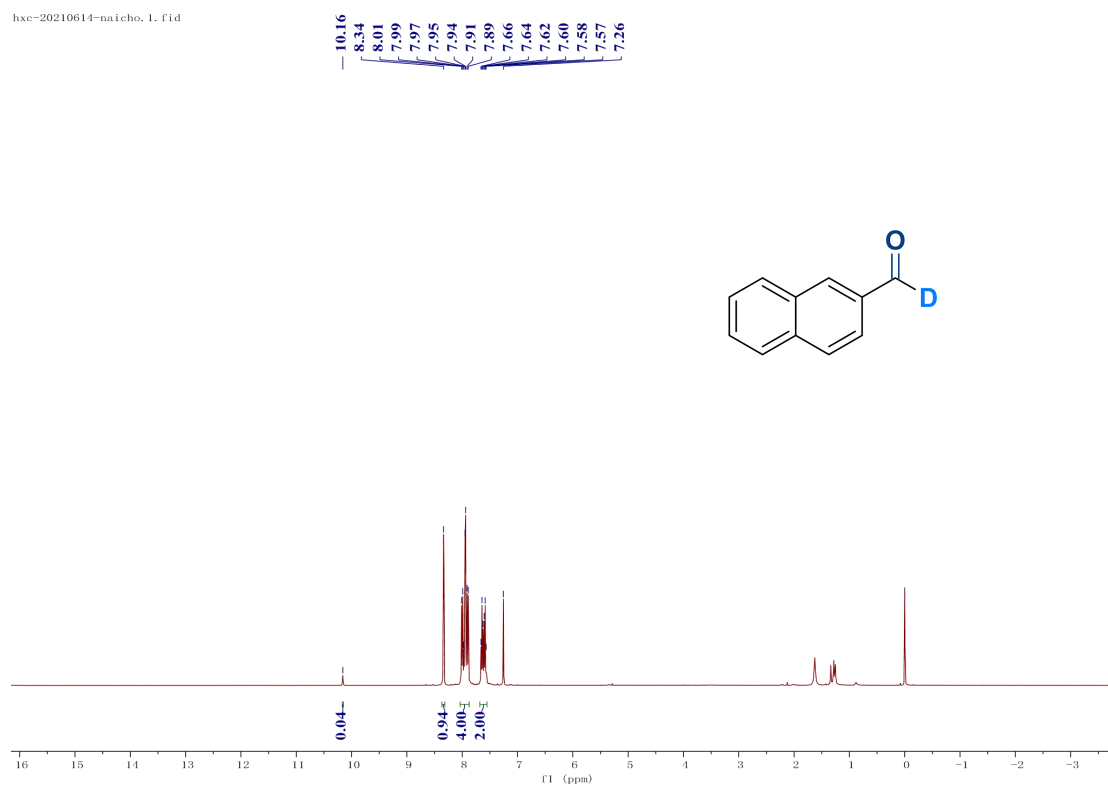


hxc-10-C.1.f1d



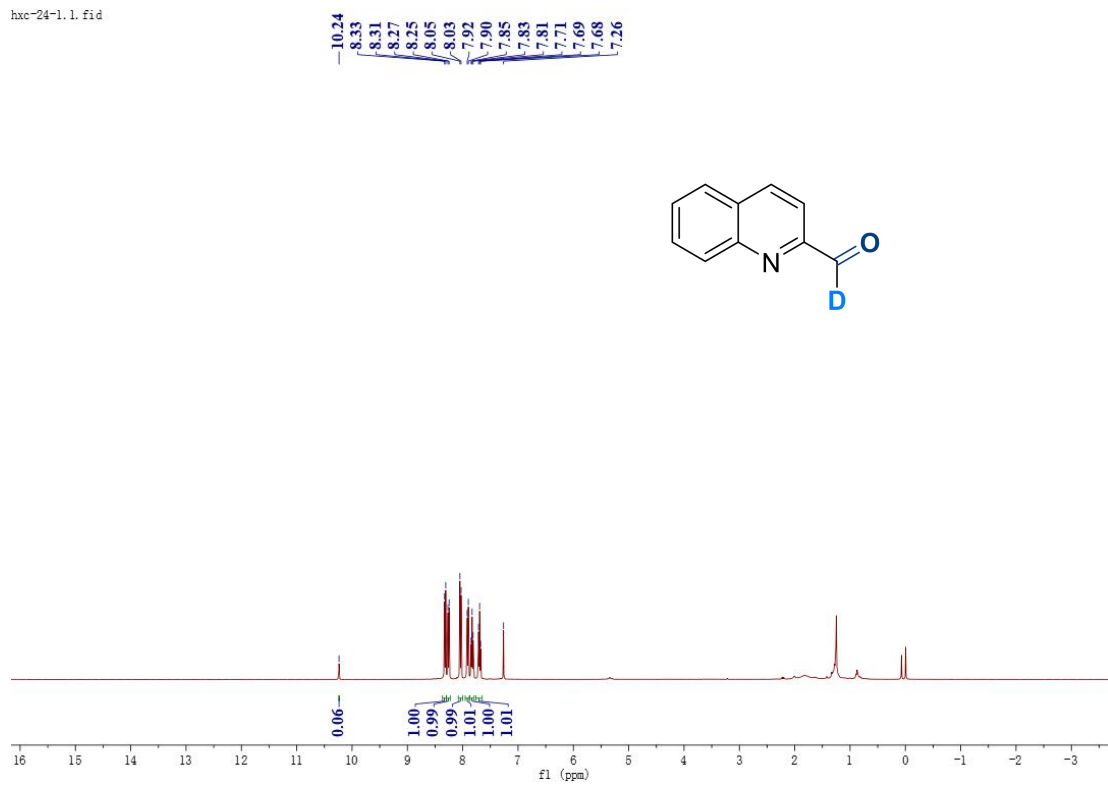
Substrate **3t**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-20210614-naicho_1.fid



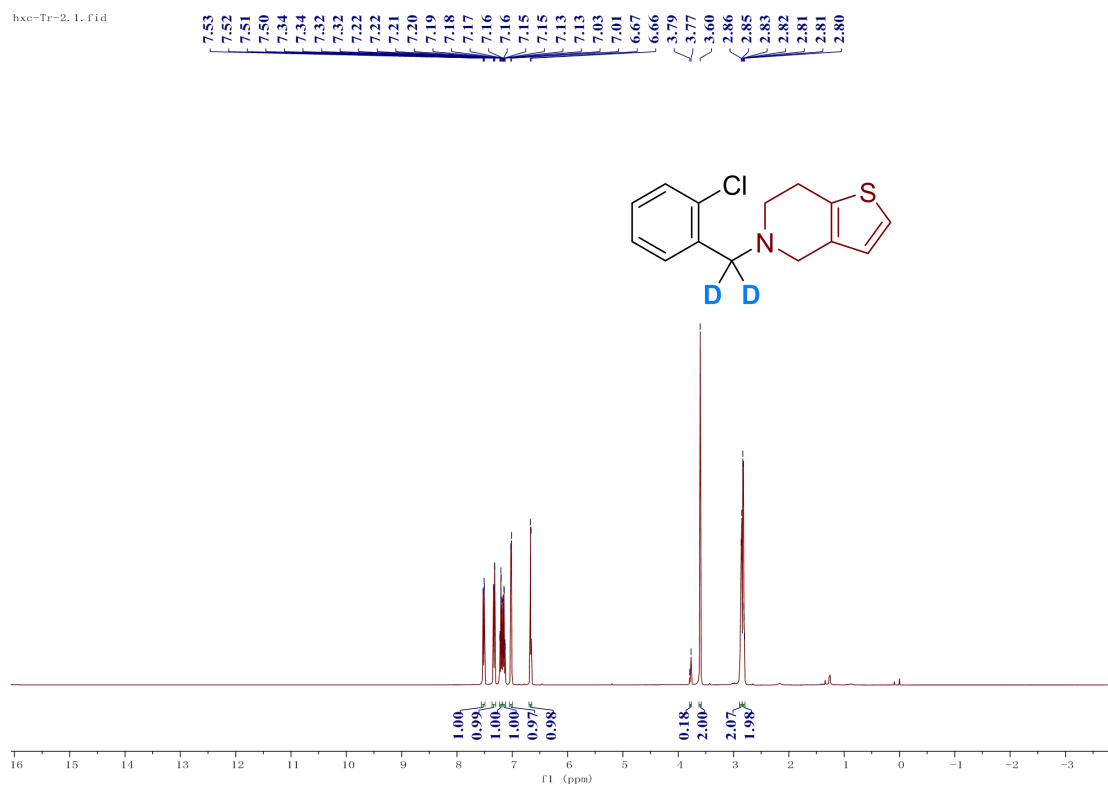
Substrate **3u**: ^1H NMR (CDCl_3 , 400 MHz)

hxc-24-1.1.fid

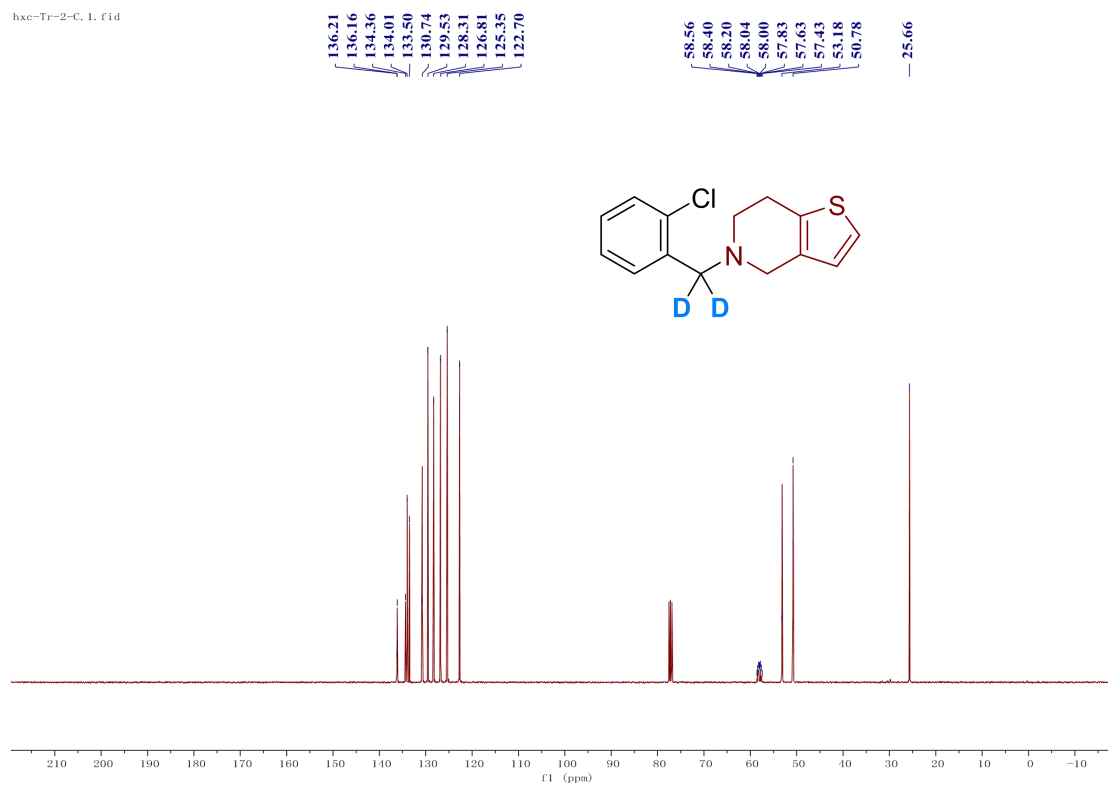


Substrate **5a**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-Tr-2.1. F1d

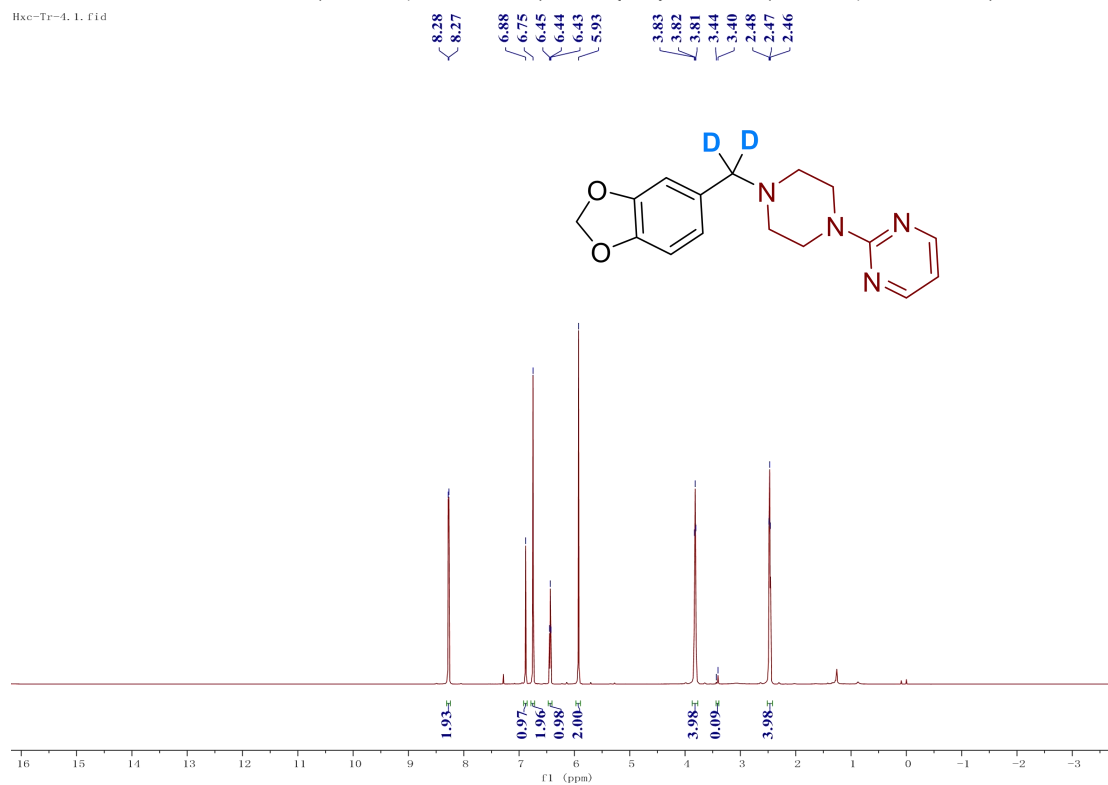


hxc-Tr-2-C. 1. F1d

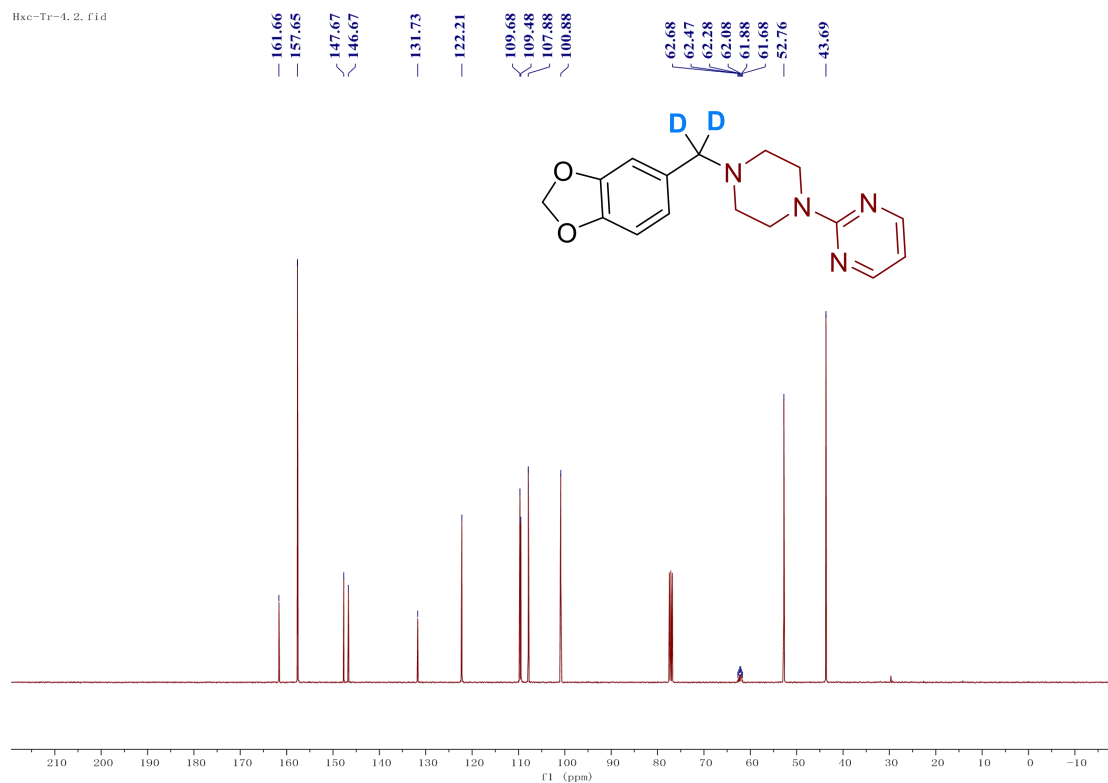


Substrate **5b**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

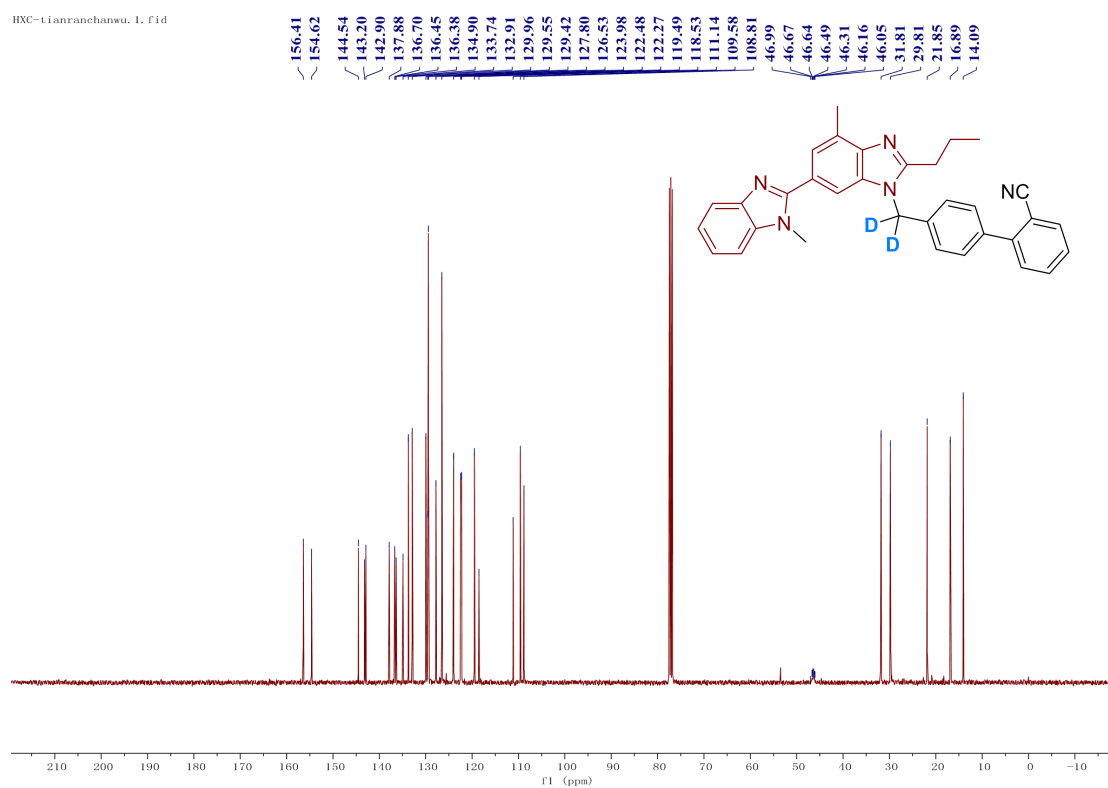
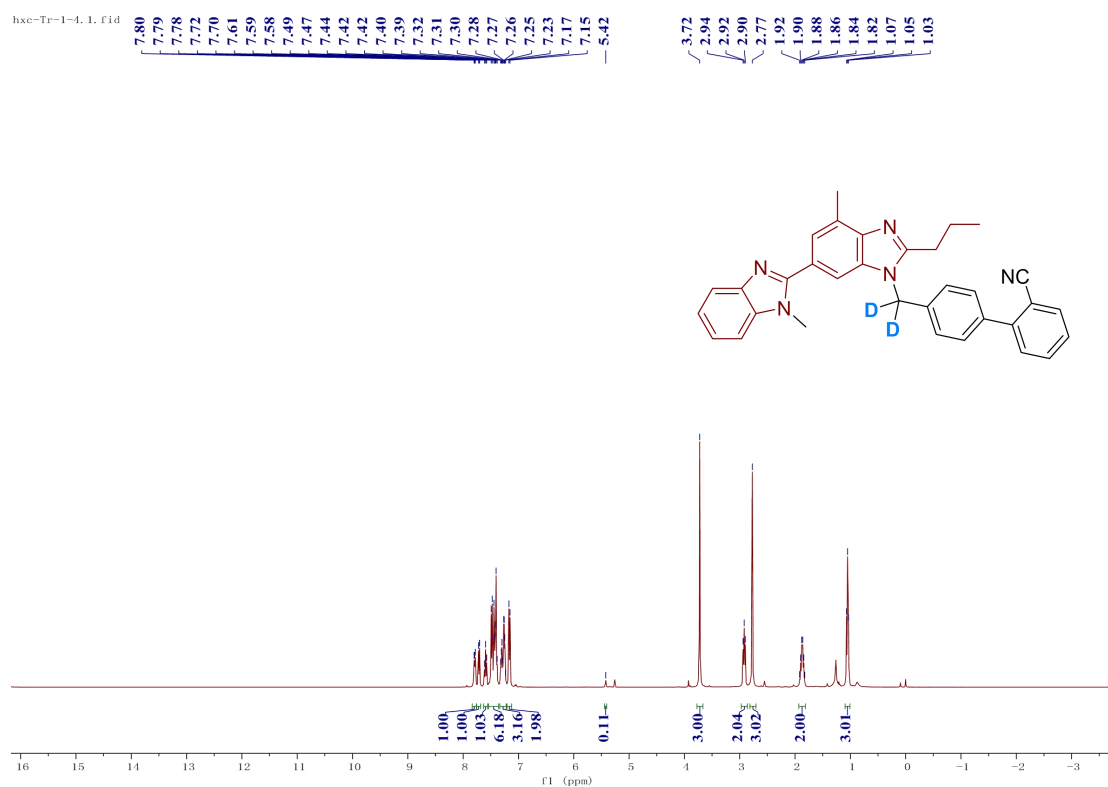
Hxc-Tr-4.1.f1d



Hxc-Tr-4.2.f1d

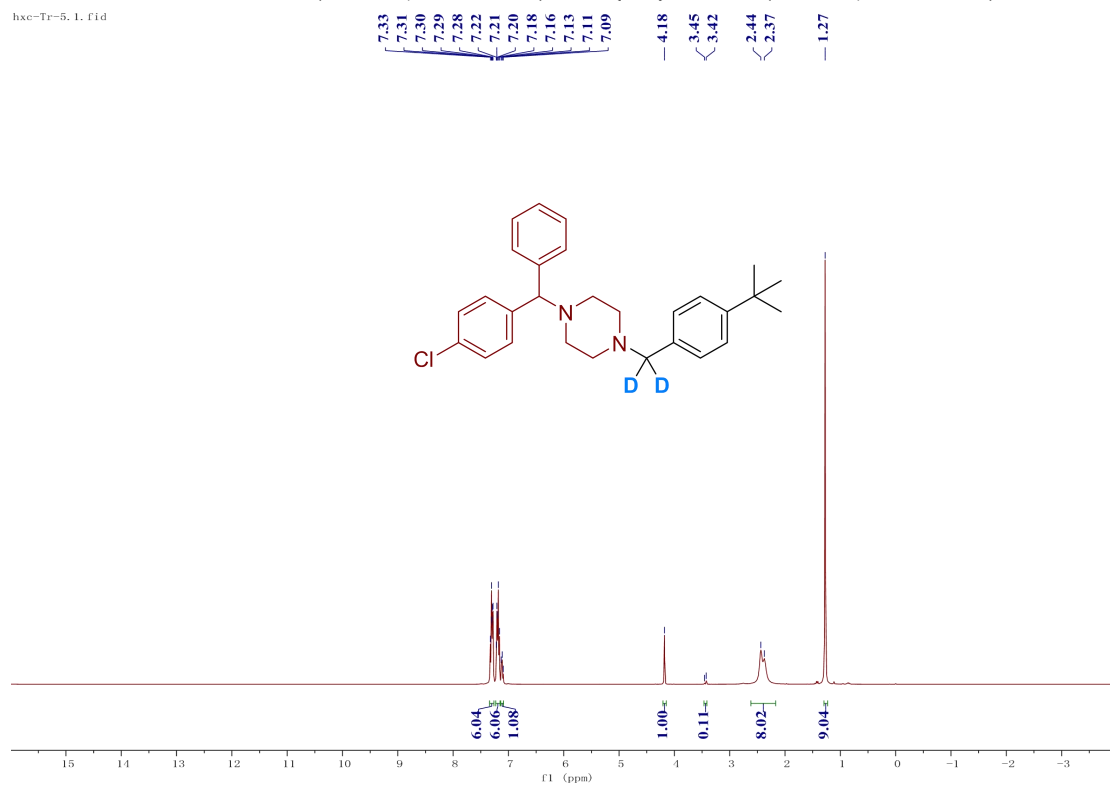


Substrate **5c**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

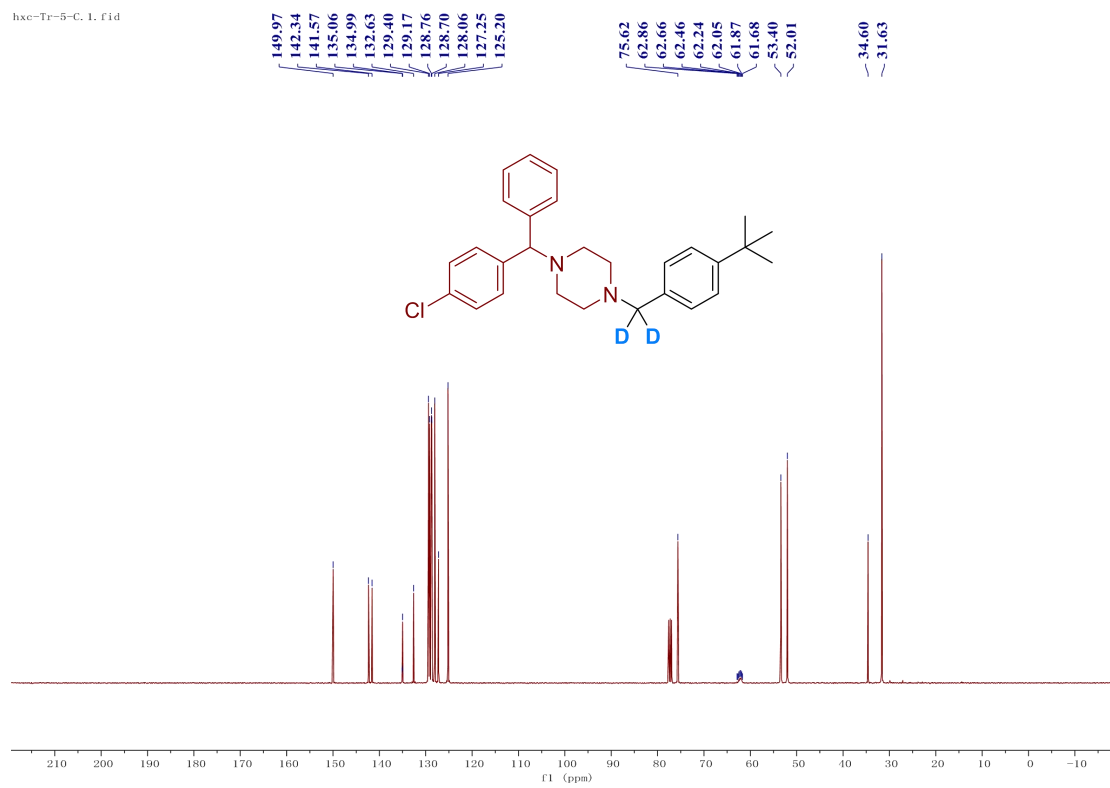


Substrate **5d**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-Tr-5. 1. f1d

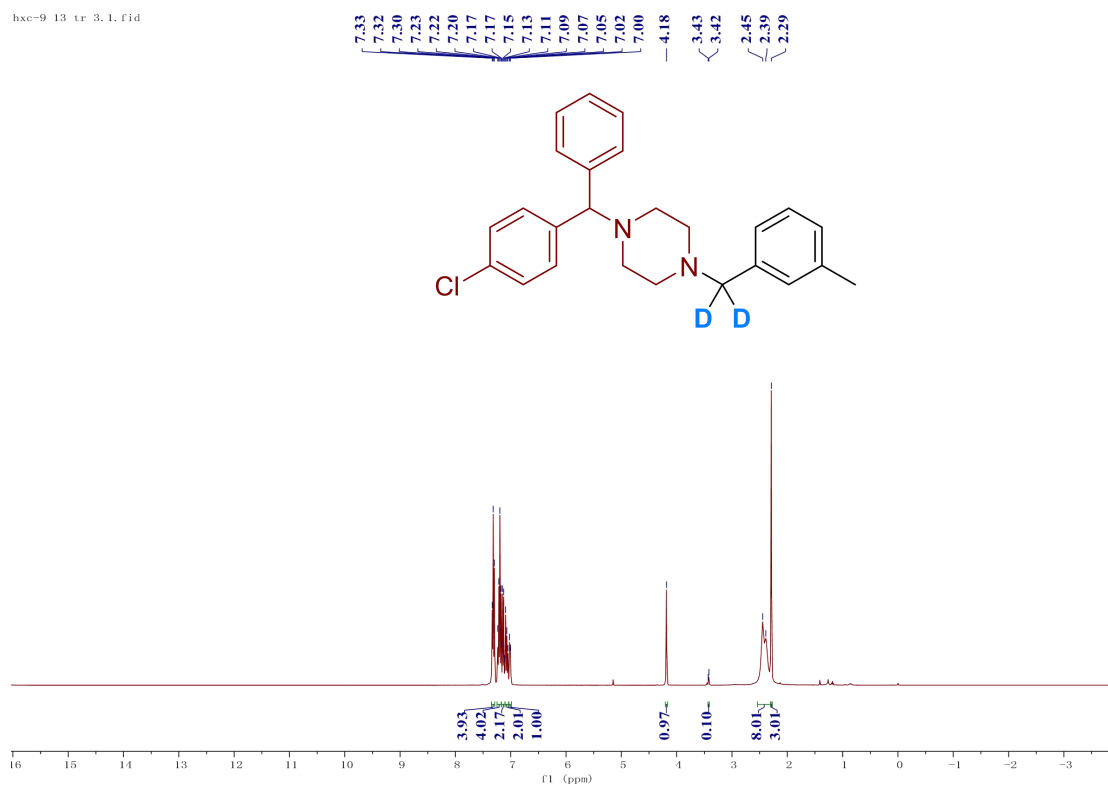


hxc-Tr-5-C. 1. f1d

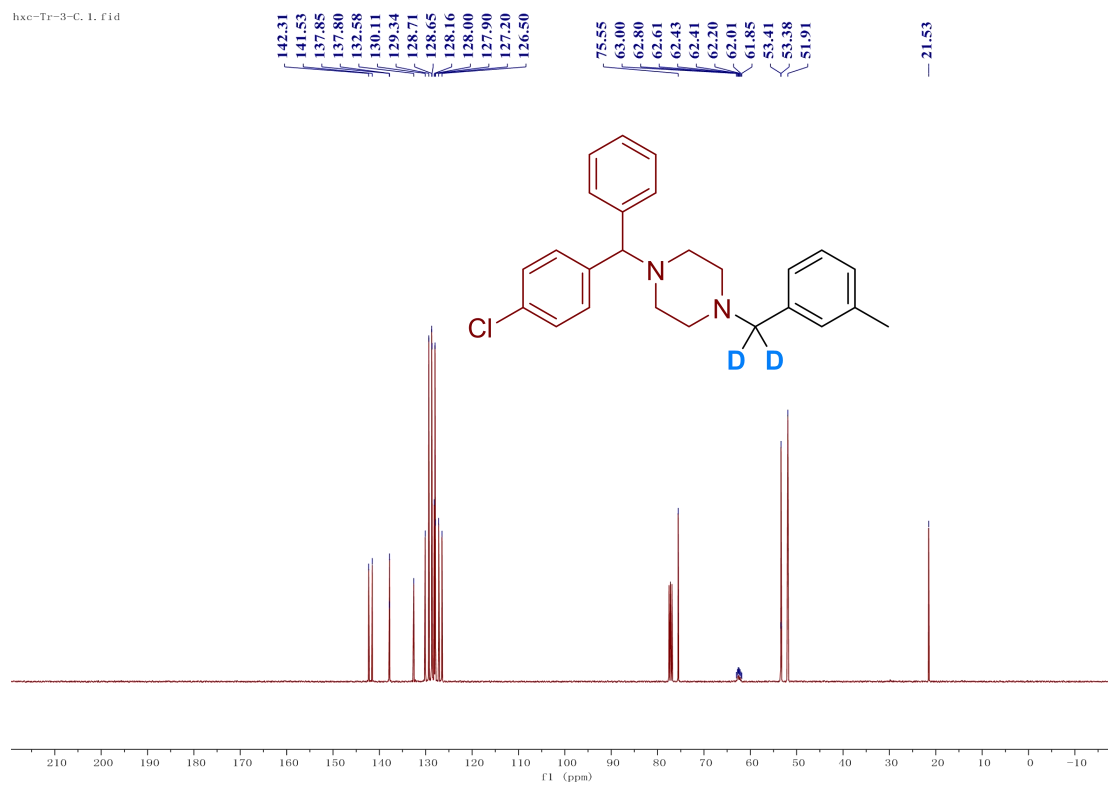


Substrate **5e**: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-9 13 tr 3.1.fid



hxc-Tr-3-C. 1.fid

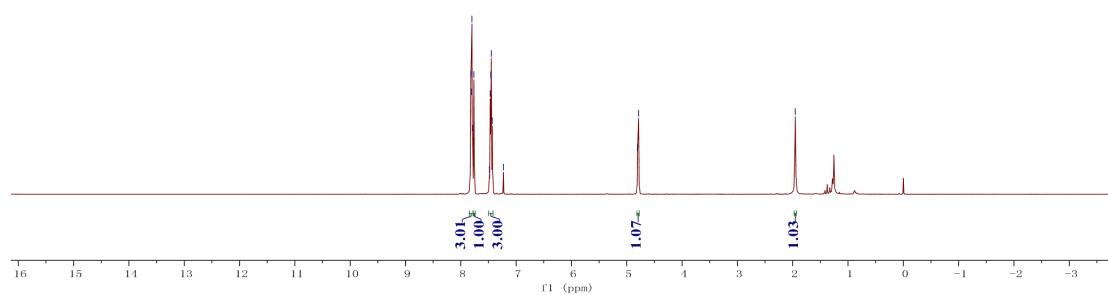
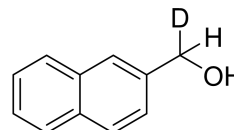


Substrate 6: ^1H NMR (CDCl_3 , 400 MHz)

hxc-nai-1DOH.1.fid

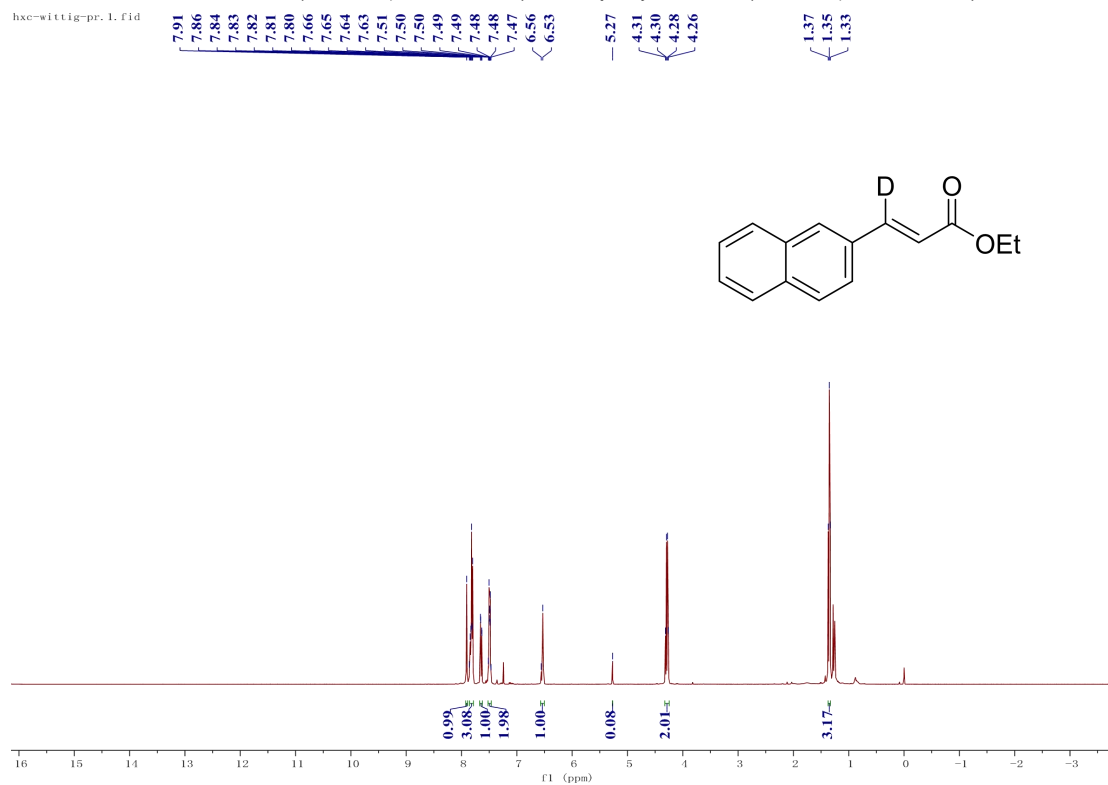
7.82
7.81
7.80
7.79
7.76
7.48
7.47
7.46
7.45
7.43
7.23
4.81
4.79

1.95

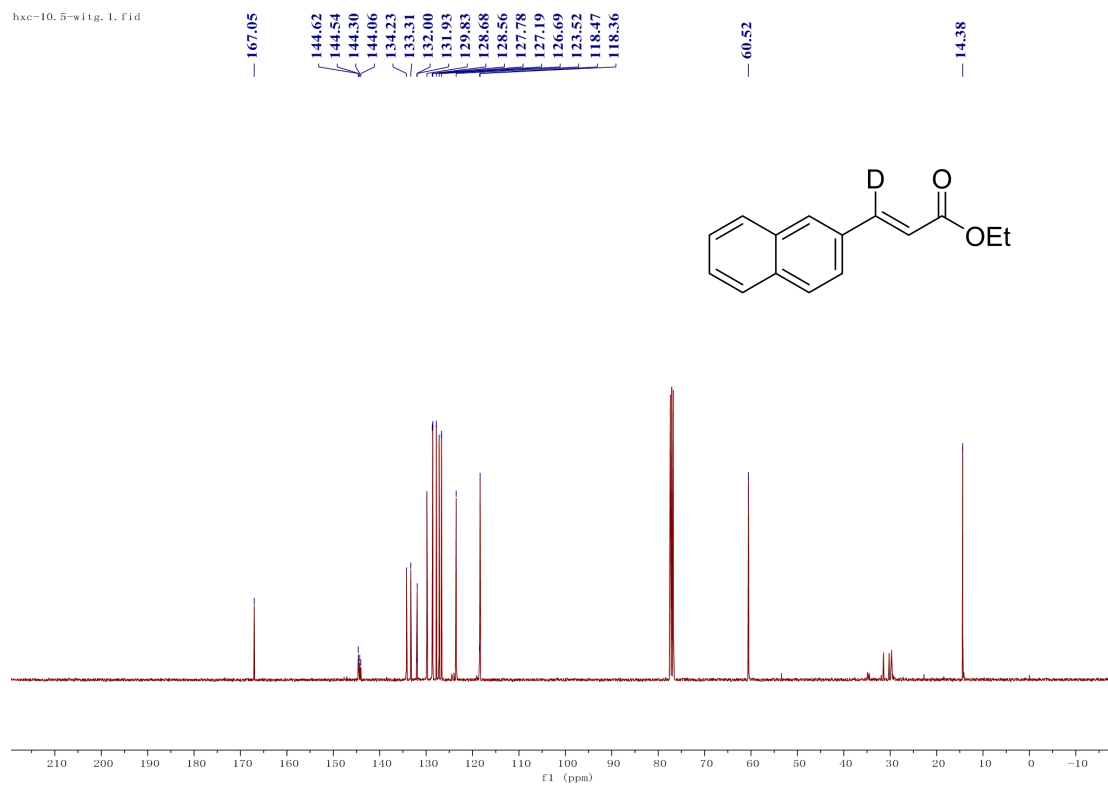


Substrate 7: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)

hxc-wittig-pr.1.fid



hxc-10.5-wittg.1.fid



References

1. Xu, J.; Lou, Y.; Wang, L.; Wang, Z.; Xu, W.; Ma, W.; Chen, Z.; Chen, X.; Wu, Q. Rational Design of Biocatalytic Deuteration Platform of Aldehydes. *ACS Catal.* **2021**, *11*, 13348-13354.
2. Zhang, Y.; Ji, P.; Dong, Y.; Wei, Y.; Wang, W. Deuteration of Formyl Groups Via a Catalytic Radical H/D Exchange Approach. *ACS Catal.* **2020**, *10*, 2226-2230.
3. Kuang, Y.; Cao, H.; Tang, H.; Chew, J.; Chen, W.; Shi, X.; Wu, J. Visible Light Driven Deuteration of Formyl C-H and Hydridic C(sp³)-H Bonds in Feedstock Chemicals and Pharmaceutical Molecules. *Chem Sci.* **2020**, *11*, 8912-8918.
4. Liu, W.; Zhao, L.-L.; Melaimi, M.; Cao, L.; Xu, X.; Bouffard, J.; Bertrand, G.; Yan, X. Mesoionic Carbene (Mic)-Catalyzed H/D Exchange at Formyl Groups. *Chem.* **2019**, *5*, 2484-2494.
5. Geng, H.; Chen, X.; Gui, J.; Zhang, Y.; Shen, Z.; Qian, P.; Chen, J.; Zhang, S.; Wang, W. Practical Synthesis of C-1 Deuterated Aldehydes Enabled by NHC Catalysis. *Nat Catal.* **2019**, *2*, 1071-1077.
6. Li, X.; Wu, S.; Chen, S.; Lai, Z.; Luo, H. B.; Sheng, C. One-Pot Synthesis of Deuterated Aldehydes from Arylmethyl Halides. *Org. Lett.* **2018**, *20*, 1712-1715.
7. Kerr, W. J.; Reid, M.; Tuttle, T. Iridium-Catalyzed Formyl-Selective Deuteration of Aldehydes. *Angew. Chem. Int. Ed.* **2017**, *56*, 7808-7812.