Supporting Information

Photocatalyzed dehalogenative deuteration with silacarboxylic acids as halogen-atom transfer agents

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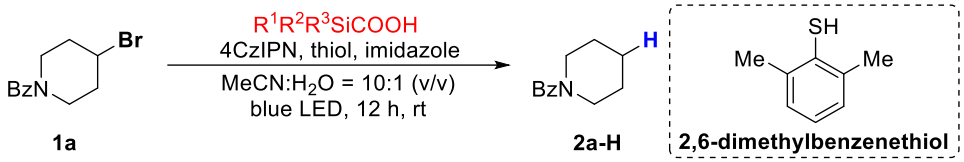
General information

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere in glass reaction tubes. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (300-400 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. Precoated silica gel plates F-254 were used for thin-layer analytical chromatography and visualized by UV fluorescence (254 nm) then one of the following: $KMnO_4$, phosphomolybdic acid. NMR spectra were recorded on a Bruker Avance (400 MHz or 500 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard. Chemical shifts (δ) were reported in parts per million (ppm) relative to residual solvent peaks rounded to the nearest 0.01 for proton and 0.1 for carbon (*ref: $CHCl_3$ ^1H: 7.26, ^{13}C: 77.16)*. Coupling constants (*J)* were reported in Hz to the nearest 0.1 Hz. Peak multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet) and br (broad). High resolution mass spectrometry (HRMS) was performed on a Waters Micromass (APCI-TOF or ESI-TOF).

Optimization of reaction conditions

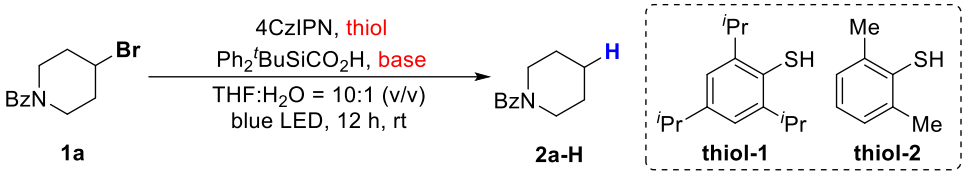
Table S1. Screening of silacarboxylic acids[a]



entry	$R^1R^2R^3SiCOOH$	yield of **2a** [%][b]	recovered **1a** [%][b]
1	$Ph_2{}^tBuSiCO_2H$	66	32
2	Ph_3SiCO_2H	23	68
3	$Ph_2MeSiCO_2H$	34	59
4	$PhMe_2SiCO_2H$	0	84

[a]Conditions: **1a** (0.2 mmol), $R^1R^2R^3SiCOOH$ (0.3 mmol), 4CzIPN (5 mol%), thiol (20 mol%), and imidazole (0.2 mmol), MeCN/H_2O (10:1, v/v, 0.2 M), 15 W blue LEDs, 12 h. [b]Yields were determined by ^1H NMR spectroscopy and gas chromatography.

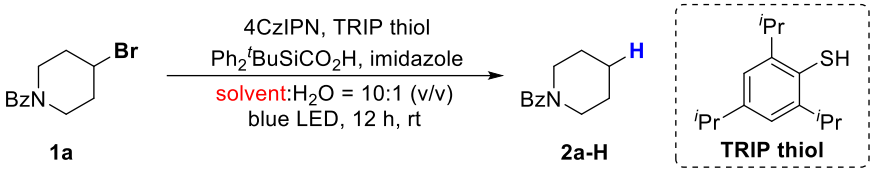
Table S2. Screening of bases and thiols[a]



entry	base	thiol	yield of **1b** [%][b]	recovered **1a** [%][b]
1	DBU	**thiol-1**	9	89
2	Na_2CO_3	**thiol-1**	14	67
3	NaOAc	**thiol-1**	22	47
4	imidazole	**thiol-2**	75	15
5	imidazole	**thiol-1**	90	8

Conditions: **1a** (0.2 mmol), 4CzIPN (5 mol%), thiol (20 mol%), $Ph_2{}^tBuSiCO_2H$ (0.3 mmol), base (0.2 mmol), and THF/H_2O (10:1, v/v, 0.2 M), 15 W blue LEDs, 12 h. [b]Yields were determined by ^1H NMR spectroscopy and gas chromatography.

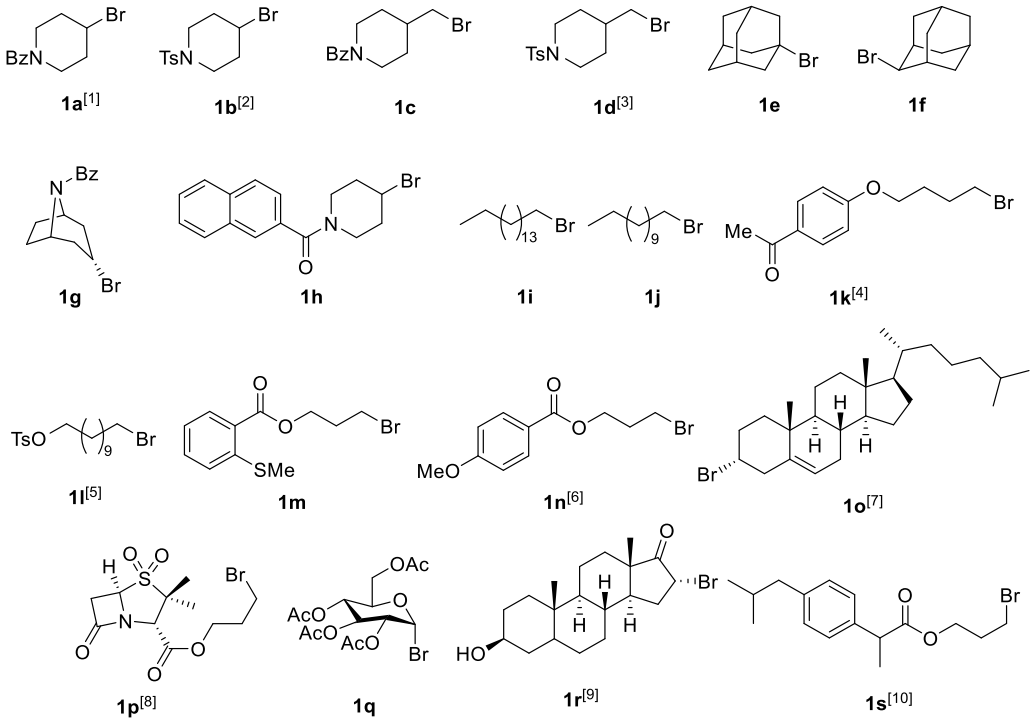
Table S3. Screening of solvents[a]



entry	solvent	yield of **2a** [%][b]	recovered **1a** [%][b]
1	MeCN	75	15
2	1,4-Dioxane	80	< 1
3	NMP	19	75
4[c]	1,4-Dioxane	80[d]	< 1
5	DMF	33	62

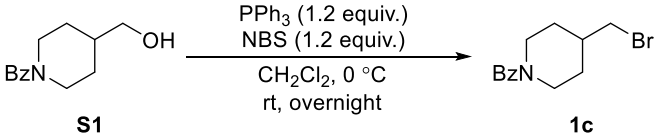
[a]Conditions: **1a** (0.2 mmol), 4CzIPN (5 mol%), TRIP thiol (20 mol%), $Ph_2{}^tBuSiCO_2H$ (0.3 mmol), imidazole (0.2 mmol), and solvent/H_2O (10:1, v/v, 0.2 M), 15 W blue LEDs, 12 h. [b]Yields were determined by ^1H NMR spectroscopy and gas chromatography. [c]The amount of thiol was reduced to 15 mol%. [d]Isolated Yields.

Preparation of substrates



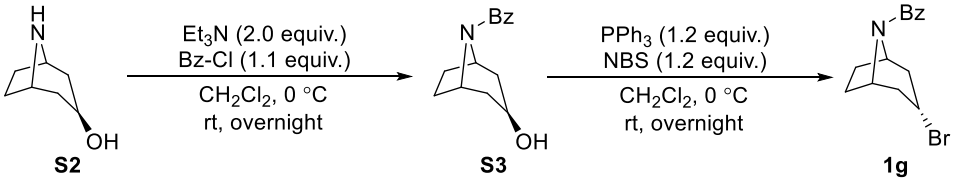
Alkyl bromides **1e, 1f, 1i, 1j, 1q** were obtained from commercial sources, alkyl bromides **1c**, **1g**, **1h** and **1m** were prepared by following methods, and other alkyl bromides were prepared using reported literature procedure[1~10].

Synthesis of 1c, 1g, 1h and 1m

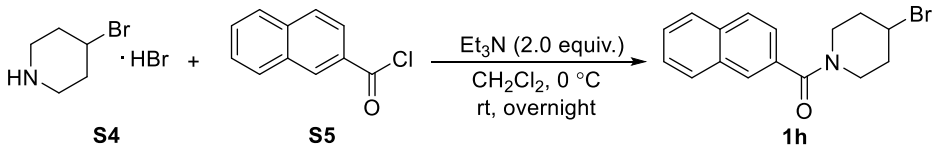


To a solution of (4-(hydroxymethyl)piperidin-1-yl)(phenyl)methanone (9 mmol, 1.99 g) and PPh_3 (10 mmol, 2.62 g) in CH_2Cl_2 (20 mL) was added NBS (10 mmol, 1.78 g) at 0 °C. The reaction was stirred at rt overnight. The reaction mixture was quenched with $NaHCO_3$ solution (50 mL) and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (PE:EA = 1:1) to afforded the product as a white powder (mp 86~88 °C), 0.635g, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.25 (m, 5H), 4.90-4.62 (m, 1H), 3.84-3.70 (m, 1H), 3.39-3.25 (m, 2H), 3.09-2.69 (m, 2H), 1.99-1.76 (m, 3H), 1.35-1.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 136.1, 129.6, 128.5, 126.8, 47.5, 41.9, 38.6,

38.5, 31.5, 30.7. HRMS (ESI) *m/z* calculated for $C_{13}H_{16}BrNO+Na^+$: 304.0307 $[M+Na]^+$; found: 304.0302.

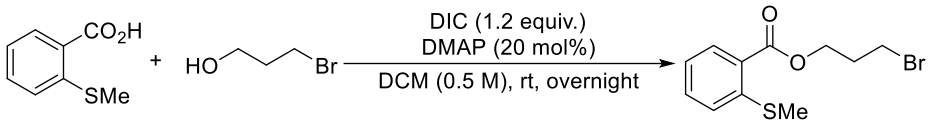


Benzoyl chloride (22 mmol, 3.04 g) was added dropwise to a solution of (1*R*,3*s*,5*S*)-8-azabicyclo[3.2.1]octan-3-ol (20 mmol, 2.54 g) and Et_3N (40 mmol, 4.04 g) in CH_2Cl_2 (40 mL) at 0 °C. The mixture was stirred overnight at rt. The reaction was quenched with water (80 mL). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (PE:EA = 1:1) to give product **3** as a white soild, 2.56 g, 55% yield. To a solution of **3** (10 mmol, 2.31g) and NBS (12 mmol, 2.14 g) in CH_2Cl_2 (40 mL) was added PPh_3 (12 mmol, 3.14 g) at 0 °C. The mixture was stirred overnight in rt. The reaction mixture was quenched with $NaHCO_3$ solution (50 mL) and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (petroleum ether and EtOAc) to afforded **1g** as a white powder (mp 93~95 °C), 0.54g, 19% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 3H), 7.45-7.37 (m, 2H), 4.83-4.75 (m, 1H), 4.50-4.34 (m, 1H), 4.12-4.05 (m, 1H), 2.44-1.89 (m, 6H), 1.82-1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 135.8, 130.2, 128.5, 127.1, 57.7, 53.0, 44.4, 42.6, 42.5, 28.2, 26.8. HRMS (ESI) *m/z* calculated for $C_{14}H_{16}BrNO+Na^+$: 316.0307 $[M+Na]^+$; found: 316.0304.



To a solution of 4-bromopiperidine hydrobromide (10 mmol, 5.02 g) and 2-naphthoyl chloride (22 mmol, 4.18 g) in CH_2Cl_2 (40 mL) was added Et_3N (40 mmol, 4.04 g) dropwise at 0 °C. The mixture was stirred overnight at rt. Then the reaction was quenched with water (80 mL). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over

Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (PE:EA = 1:1) to give **1h** as a white powder (mp 77~80 °C), 1.91 g, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.72 (m, 4H), 7.48-7.41 (m, 2H), 7.38 (dd, J = 8.4, 1.6 Hz, 1H), 4.43-4.24 (m, 1H), 4.03-3.17 (m, 4H), 2.28-1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 133.7, 132.9, 132.7, 128.4, 128.4, 127.8, 127.2, 126.8, 126.7, 124.1, 48.9, 45.9, 40.5, 36.1, 35.4. HRMS (ESI) m/z calculated for $C_{16}H_{16}BrNO+Na^+$: 340.0307 $[M+Na]^+$; found: 340.0301.

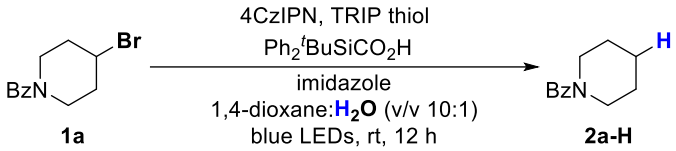


S6 **S7** **1m**

To a solution of 2-(methylthio)benzoic acid (5mmol, 0.84 g) and DMAP (1 mmol, 0.12 g) in dry CH_2Cl_2 (10 mL) was added 3-bromopropan-1-ol (6 mmol, 0.84 g, 0.46 mL) at rt. Then DIC (6 mmol, 0.76 g, 1.0 mL) was added dropwise. The mixture was stirred overnight. The mixture was filtered, concentrated under reduce pressure, and purified by flash chromatography on silica gal (PE:EA = 20:1) to give a white solid (mp 39~41°C), 1.30 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.6, 1.6 Hz, 1H), 7.46-7.34 (m, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.12-7.05 (m, 1H), 4.40 (t, J = 6.0 Hz, 2H), 3.49 (t, J = 6.4 Hz, 2H), 2.38 (s, 3H), 2.30-2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 143.4, 132.7, 131.4, 126.7, 124.5, 123.5, 62.9, 31.9, 29.7, 15.7; HRMS (ESI) m/z calculated for $C_{11}H_{13}BrO_2S+Na^+$: 310.9712 $[M+Na]^+$; found: 310.9712.

Radical dehalogenation

Typical procedure for the synthesis of 2a-H



1a **2a-H**

Under N_2 atmosphere, a tube equipped with a magnetic stirrer bar was charged sequentially with **1a** (53.6 mg, 0.2 mmol, 1.0 equiv.), $Ph_2{}^tBuSiCOOH$ (85.2 mg, 0.3 mmol, 1.5 equiv.), imidazole (13.6 mg, 0.2 mmol, 1.0 equiv.), and 4CzIPN (7.9 mg, 0.01 mmol, 5 mol%). Then 1,4-dioxane (0.1 M, 2 mL), TRIP thiol (7.1 mg, 0.03 mmol, 15 mol%) and H_2O (0.2 mL) was injected into the reaction tube successively. The solution was stirred under irradiation with 15 W blue LED at room temperature for 12 h. Upon completion, the mixture was quenched with H_2O, washed by EtOAc and brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to afford the product **2a-H**.

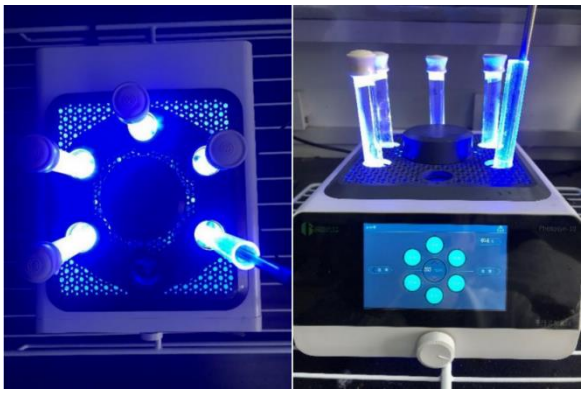
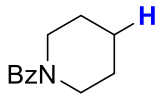


Figure S1. Experimental setup



2a-H

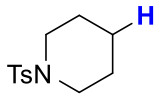
phenyl(piperidin-1-yl)methanone (2a-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (30.7 mg, 80% yield) was isolated as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 5H), 3.75-3.62 (m, 2H), 3.38-3.26 (m, 2H), 1.68-1.45 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 136.5, 129.4, 128.5, 126.8, 48.9, 43.2, 26.6, 25.7, 24.6.

HRMS (ESI) *m*/*z* calculated for $C_{12}H_{15}NO+Na^+$: 212.1046 $[M+Na]^+$; found: 212.1043.



2b-H

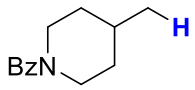
1-tosylpiperidine (2b-H)

Flash chromatography on silica gel (PE:EA = 20:1). The product (39.9 mg, 84% yield) was isolated as a white solid, mp 78~80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.95 (t, J = 5.6 Hz, 4H), 2.42 (s, 3H), 1.67-1.55 (m, 4H), 1.46-1.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 133.3, 129.6, 127.8, 47.1, 25.3, 23.6, 21.6.

The data is in accordance with the literature[11].



2c-H

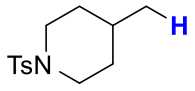
(4-methylpiperidin-1-yl)(phenyl)methanone (2c-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (37.7 mg, 93% yield) was isolated as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 5H), 4.71-4.58 (m, 1H), 3.75-3.58 (m, 1H), 3.05-2.62 (m, 2H), 1.83-1.43 (m, 3H), 1.36-1.02 (m, 2H), 0.95 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 136.5, 129.4, 128.4, 126.8, 48.1, 42.5, 34.8, 33.9, 31.2, 21.8.

HRMS (ESI) *m*/*z* calculated for $C_{13}H_{17}NO+Na^+$:226.1202 $[M+Na]^+$; found: 226.1203.



2d-H

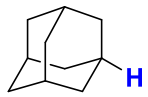
4-methyl-1-tosylpiperidine (2d-H)

Flash chromatography on silica gel (PE:EA = 20:1). The product (42.5 mg, 84% yield) was isolated as a white solid, mp 79~82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 3.76-3.60 (m, 2H), 2.42 (s, 3H), 2.20 (t, J = 11.2 Hz, 2H), 1.71-1.58 (m, 2H), 1.35-1.19 (m, 3H), 0.89 (d, J = 5.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 133.3, 129.6, 127.8, 46.5, 33.4, 30.2, 21.6.

The data is in accordance with the literature[12].



2e-H

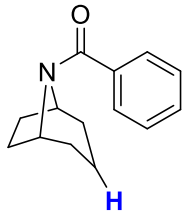
adamantane (2e-H)

Flash chromatography on silica gel (*n*-hexane). The product (16.3 mg, 60% yield) was isolated as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-1.85 (m, 4H), 1.76-1.73 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8, 28.3.

The data is in accordance with the literature[13].



2g-H

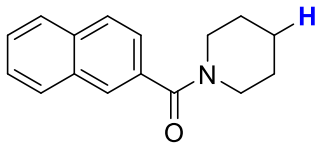
((1*R*,5*S*)-8-azabicyclo[3.2.1]octan-8-yl)(phenyl)methanone (2g-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (39.8 mg, 92% yield) was isolated as a white solid, mp 82~84 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2H), 7.41-7.33 (m, 3H), 4.87-4.70 (m, 1H), 4.12-3.89 (m, 1H), 2.05-1.86 (m, 3H), 1.83-1.59 (m, 5H), 1.59-1.51 (m, 1H), 1.46-1.39 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 136.8, 129.7, 1284, 127.0, 57.0, 52.1, 32.6, 30.9, 28.4, 27.1, 16.9.

HRMS (ESI) *m*/*z* calculated for $C_{14}H_{17}NO+Na^{+}$: 238.1202 $[M+Na]^{+}$; found: 238.1197.



2h-H

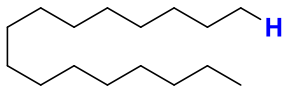
naphthalen-2-yl(piperidin-1-yl)methanone (2h-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (36.0 mg, 75% yield) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.69 (m, 4H), 7.49-7.33 (m, 3H), 3.85-3.66 (m, 2H), 3.48-3.31 (m, 2H), 1.71-1.32 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 133.8, 133.6, 132.8, 128.4, 128.2, 127.8, 126.9, 126.6, 126.5, 124.3, 48.9, 43.3, 26.6, 25.7, 24.6.

HRMS (ESI) *m/z* calculated for $C_{16}H_{17}NO+Na^+$: 262.1202 $[M+Na]^+$; found: 262.1201.



2i-H

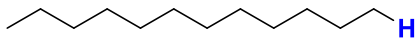
hexadecane (2i-H)

The mixture was treated with water, washed by EtOAc and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure, then purified by flash chromatography on silica gel (Petroleum Ether) to afford the product (40.7 mg, 90% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.17 (m, 28H), 0.81 (t, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 31.9, 29.74, 29.70, 29.4, 22.7, 14.1.

The data is in accordance with the literature[14].



2j-H

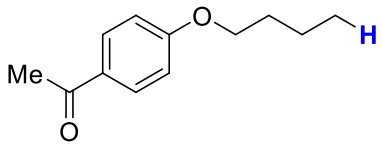
dodecane (2j-H)

Flash chromatography on silica gel (Petroleum Ether). The product (19.4 mg, 57% yield) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.22 (m, 20H), 0.88 (t, J = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 29.9, 29.8, 29.5, 22.9, 14.3.

The data was in accordance with the literature[15].



2k-H

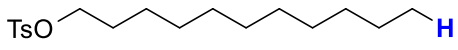
1-(4-butoxyphenyl)ethan-1-one (2k-H)

Flash chromatography on silica gel (PE:EA = 20:1). The product (31.4 mg, 81% yield) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.94 (t, J = 6.4 Hz, 2H), 2.47 (s, 3H), 1.77-1.66 (m, 2H), 1.49-1.36 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 163.2, 130.6, 130.1, 114.2, 68.0, 31.2, 26.4, 19.3, 13.9.

The data is in accordance with the literature[16].



2l-H

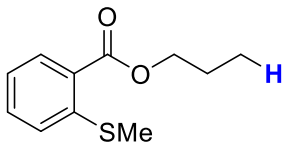
undecyl 4-methylbenzenesulfonate (2l-H)

Flash chromatography on silica gel (PE:EA = 20:1). The product (59.3 mg, 91% yield) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 3.94 (t, J = 6.4 Hz, 2H), 2.38 (s, 3H), 1.61-1.48 (m, 2H), 1.31-1.02 (m, 16H), 0.80 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 133.3, 129.9, 128.0, 70.8, 32.0, 29.7, 29.6, 29.5, 29.4, 29.0, 28.9, 25.4, 22.8, 21.7, 14.2.

HRMS (ESI) m/z calculated for $C_{18}H_{30}O_3S+Na^+$: 349.1808 $[M+Na]^+$; found: 349.1805.



2m-H

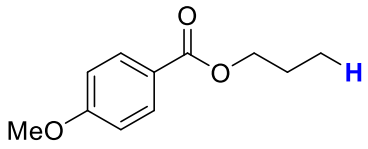
propyl 2-(methylthio)benzoate (2m-H)

Flash chromatography on silica gel (PE:EA = 20:1). The product (28.1 mg, 67% yield) was isolated as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.6, 1.6 Hz, 1H), 7.43-7.36 (m, 1H), 7.23-7.16 (m, 1H), 7.12-7.03 (m, 1H), 4.21 (t, J = 6.4 Hz, 2H), 2.38 (s, 3H), 1.81-1.65 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 143.3, 132.5, 131.4, 127.2, 124.4, 123.5, 66.8, 22.2, 15.7, 10.7.

HRMS (ESI) *m*/*z* calculated for $C_{11}H_{14}O_2S+Na^+$: 233.0607 $[M+Na]^+$; found: 233.0607.



2n-H

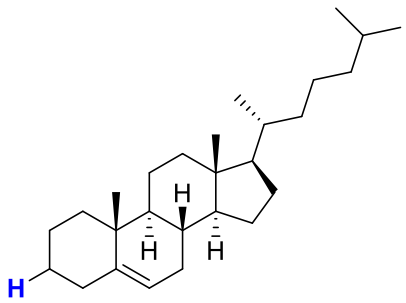
propyl 4-methoxybenzoate (2n-H)

Flash chromatography on silica gel (PE:EA = 20:1). The product (32.9 mg, 86% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.17 (t, J = 6.4 Hz, 2H), 3.78 (s, 3H), 1.84-1.61 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.3, 131.6, 123.1, 113.6, 66.4, 55.5, 22.3, 10.7.

HRMS (ESI) *m*/*z* calculated for $C_{11}H_{14}O_3+Na^+$: 217.0835 $[M+Na]^+$; found: 217.0835.



2o-H

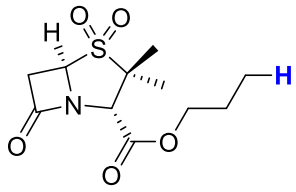
(8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (2o-H)

Flash chromatography on silica gel (Petroleum Ether). The product (52.2 mg, 70% yield) was isolated as a white solid, mp 65~68 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32-5.24 (m, 1H), 2.34-2.17 (m, 1H), 2.05-1.93 (m, 3H), 1.88-1.79 (m, 2H), 1.75-1.68 (m, 1H), 1.63-1.31 (m, 12H), 1.26-1.09 (m, 7H), 1.05-0.98 (m, 7H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.87 (dd, *J* = 6.4, 2.0 Hz, 6H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 119.2, 57.0, 56.3, 50.7, 42.5, 40.1, 39.7, 37.7, 36.4, 36.0, 33.1, 32.1, 32.0, 28.4, 28.3, 28.2, 24.4, 24.0, 23.0, 22.7, 20.9, 19.6, 18.9, 12.0.

The data is in accordance with the literature[17].



2p-H

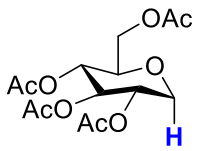
propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (2p-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (31.5 mg, 57% yield) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (dd, *J* = 4.4, 2.0 Hz, 1H), 4.32 (s, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.48-3.34 (m, 2H), 1.70-1.60 (m, 2H), 1.56 (s, 3H), 1.35 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 167.1, 68.2, 63.4, 62.8, 61.2, 38.4, 21.9, 20.5, 18.7, 10.5.

HRMS (ESI) *m*/*z* calculated for $C_{11}H_{17}NO_5S+Na^+$: 298.0720 $[M+Na]^+$; found: 298.0716.



2q-H

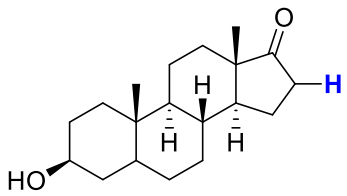
(2*R*,3*R*,4*S*,5*S*)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2q-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (48.9 mg, 73% yield) was isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, *J* = 9.6 Hz, 1H), 5.02-4.93 (m, 2H), 4.19-4.13 (m, 1H), 4.10-4.04 (m, 2H), 3.60-3.52 (m, 1H), 3.25 (t, *J* = 10.9 Hz, 1H), 2.04 (s, 3H), 1.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.4, 169.8, 169.6, 76.4, 73.7, 68.9, 68.4, 66.8, 62.2, 20.7, 20.7, 20.6.

HRMS (ESI) *m*/*z* calculated for $C_{14}H_{20}O_9$+Na^+: 355.1000 $[M+Na]^+$; found: 355.0993.



2r-H

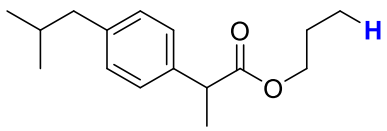
(3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-3-hydroxy-10,13-dimethylhexadecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2r-H)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (34.5 mg, 59% yield) was isolated as a white solid, mp 172~174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62-3.41 (m, 1H), 2.37 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.12-2.02 (m, 1H), 1.98 (dd, *J* = 18.8, 9.2 Hz, 1H), 1.90-1.84 (m, 1H), 1.80-1.70 (m, 3H), 1.68-1.54 (m, 2H), 1.52-1.00 (m, 11H), 0.92 (td, *J* = 12.8, 4.0 Hz, 2H), 0.79 (s, 3H), 0.76 (s, 3H), 0.68-0.57 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.7, 71.0, 54.4, 51.4, 47.9, 44.9, 38.0, 37.0, 35.9, 35.7, 35.1, 31.6, 31.4, 30.9, 28.4, 21.8, 20.5, 13.9, 12.3.

HRMS (ESI) *m*/*z* calculated for $C_{19}H_{30}O_2$+Na^+: 313.2138 $[M+Na]^+$; found: 313.2127.



2s-H

propyl 2-(4-isobutylphenyl)propanoate (2s-H)

Flash chromatography on silica gel (PE:EA = 50:1). The product (40.1 mg, 81% yield) was isolated as a colorless oil.

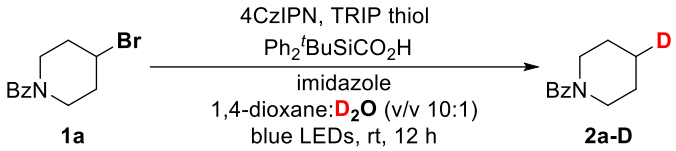
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.61 (q, *J* = 7.2 Hz, 1H), 2.37 (d, *J* = 7.2 Hz, 2H), 1.82-1.69 (m, 1H), 1.58-1.45 (m, 2H), 1.41 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 6H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 140.5, 138.0, 129.4, 127.2, 66.3, 45.3, 45.1, 30.3, 22.5, 22.0, 18.6, 10.4.

HRMS (ESI) *m*/*z* calculated for $C_{16}H_{24}O_2$+Na^+: 271.1669 $[M+Na]^+$; found: 271.1669.

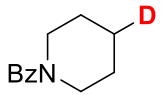
Radical deuteration

Typical procedure for the synthesis of 2a-D



1a **2a-D**

Under N_2 atmosphere, a tube equipped with a magnetic stirrer bar was charged sequentially with **1a** (53.6 mg, 0.2 mmol, 1.0 equiv.), $Ph_2{}^tBuSiCOOH$ (85.2 mg, 0.3 mmol, 1.5 equiv.), imidazole (13.6 mg, 0.2 mmol, 1.0 equiv.), and 4CzIPN (7.9 mg, 0.01 mmol, 5 mol%). Then 1,4-dioxane (0.1 M, 2 mL), TRIP thiol (7.1 mg, 0.03 mmol, 15 mol%) and D_2O (0.2 mL) was injected into the reaction tube successively. The solution was stirred under irradiation with 15 W blue LED at room temperature for 12 h. Upon completion, the mixture was treated with H_2O, washed by EtOAc and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure, then purified by flash chromatography on silica gel to afford the product **2a-D**.



2a-D

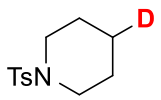
phenyl(piperidin-1-yl-4-*d*)methanone (2a-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (32.6 mg, 86% yield) was isolated as a yellowish oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 5H), 3.75-3.63 (m, 2H), 3.37-3.26 (m, 2H), 1.73-1.43 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 136.6, 129.4, 128.5, 126.9, 48.8, 43.2, 26.5, 25.6, 24.3 (t, J = 19.5 Hz, C-D).

HRMS (ESI) m/z calculated for $C_{12}H_{14}DNO+Na^+$: 213.1109 $[M+Na]^+$; found: 213.1106



2b-D

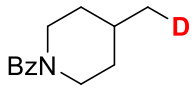
1-tosylpiperidine-4-*d* (2b-D)

Flash chromatography on silica gel (PE:EA = 20:1). The product (38.6 mg, 81% yield) was isolated as white solid, mp 77~79 °C, 85% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.96 (t, J = 6.0 Hz, 4H), 2.43 (s, 3H), 1.67-1.61 (m, 4H), 1.43-1.35 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 133.2, 129.6, 127.8, 47.0, 25.1, 23.2 (t, J = 19.6 Hz, C-D), 21.6.

HRMS (ESI) m/z calculated for $C_{12}H_{16}DNO_2S+Na^+$: 263.0935 $[M+Na]^+$; found: 263.0934.



2c-D

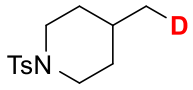
(4-(methyl-*d*)piperidin-1-yl)(phenyl)methanone (2c-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (36.7 mg, 90% yield) was isolated as a yellowish oil, 85% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 5H), 4.74-4.47 (m, 1H), 3.77-3.49 (m, 1H), 3.06-2.60 (m, 2H), 1.74-1.44 (m, 3H), 1.17 (d, J = 11.4 Hz, 2H), 0.92-0.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 136.6, 129.4, 128.4, 126.8, 48.1, 42.5, 34.8, 33.9, 31.1, 21.5 (t, J = 19.2 Hz, C-D).

HRMS (ESI) m/z calculated for $C_{13}H_{16}DNO+Na^+$: 227.1265 $[M+Na]^+$; found: 227.1263.



2d-D

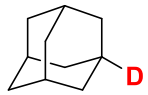
4-(methyl-*d*)-1-tosylpiperidine (2d-D)

Flash chromatography on silica gel (PE:EA = 20:1). The product (38.2 mg, 75% yield) was isolated as white solid, mp 79~82 °C, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.73 (d, J = 11.2 Hz, 2H), 2.43 (s, 3H), 2.22 (t, J = 11.2 Hz, 2H), 1.70-1.59 (m, 2H), 1.34-1.21 (m, 3H), 0.93-0.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 133.3, 129.6, 127.8, 46.5, 33.4, 30.1, 21.6, 21.3 (t, J = 19.6 Hz, C-D).

HRMS (ESI) m/z calculated for $C_{13}H_{18}DNO_2S+Na^+$: 277.1091 $[M+Na]^+$; found: 277.1085.



2e-D

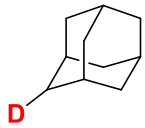
adamantane-1-*d* (2e-D)

Flash chromatography on silica gel (*n*-hexane). The product (15.2 mg, 55% yield) was isolated as a white solid, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-1.85 (m, 3H), 1.77-1.73 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9, 37.8, 28.4, 28.0 (t, J = 20.1 Hz).

The data is in accordance with the literature[18].



2f-D

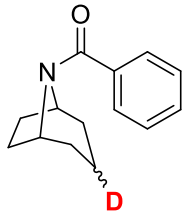
adamantane-2-*d* (2f-D)

Flash chromatography on silica gel (*n*-hexane). The product (16.3 mg, 59% yield) was isolated as a white solid, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89-1.85 (m, 4H), 1.77-1.73 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9, 37.5 (t, J = 19.6 Hz, C-D), 28.5, 28.4.

Data in accordance with the literature[19].



2g-D

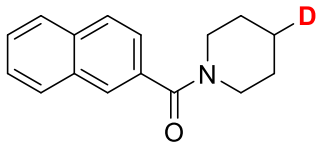
((1*R*,5*S*)-8-azabicyclo[3.2.1]octan-8-yl-3-*d*)(phenyl)methanone (2g-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (38.6 mg, 89% yield) was isolated as a white solid, 90% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.31 (m, 5H), 4.80-4.73 (m, 1H), 4.02-3.95 (m, 1H), 2.06-1.83 (m, 3H), 1.79-1.47 (m, 5H), 1.44-1.32 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 136.7, 129.6, 128.3, 126.9, 57.0, 52.1, 32.5, 30.8, 28.3, 27.1, 16.6 (t, J = 19.2 Hz).

HRMS (ESI) *m*/*z* calculated for $C_{14}H_{16}DNO+Na^+$: 239.1265 $[M+Na]^+$; found: 239.1261.



2h-D

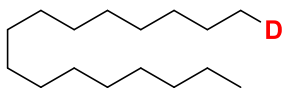
naphthalen-2-yl(piperidin-1-yl-4-*d*)methanone (2h-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (37.4 mg, 78% yield) was isolated as a colorless oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.62 (m, 4H), 7.56-7.28 (m, 3H), 3.75-3.60 (m, 2H), 3.35-3.23 (m, 2H), 1.65-1.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 133.8, 133.5, 132.7, 128.3, 128.2, 127.8, 126.9, 126.6, 126.5, 124.3, 48.8, 43.2, 26.5, 25.6, 24.2 (t, J = 19.8 Hz, C-D).

HRMS (ESI) *m*/*z* calculated for $C_{16}H_{16}DNO+Na^+$: 263.1265 $[M+Na]^+$; found: 263.1259.



2i-D

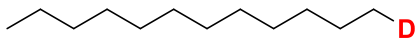
hexadecane-1-*d* (2i-D)

Flash chromatography on silica gel (Petroleum Ether). The product (31.9 mg, 70% yield) was isolated as a colorless oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20-1.17 (m, 28H), 0.81 (t, J = 6.8 Hz, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 31.9, 29.74, 29.70, 29.4, 22.7, 22.6, 14.1, 13.8 (t, J = 19.2 Hz, C-D).

Data in accordance with the literature[20].



2j-D

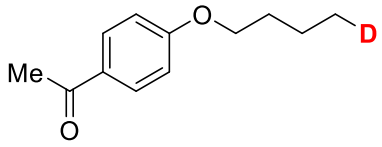
dodecane-1-*d* (2j-D)

Flash chromatography on silica gel (Petroleum Ether). The product (18.9 mg, 55% yield) was isolated as a colorless oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35-1.26 (m, 20H), 0.90 (t, J = 6.8 Hz, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2, 29.97, 29.93, 29.6, 22.9, 22.8, 14.3, 13.9 (t, J = 19.2 Hz, C-D).

Data in accordance with the literature[21].



2k-D

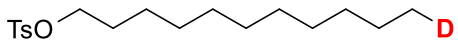
1-(4-(butoxy-4-*d*)phenyl)ethan-1-one (2k-D)

Flash chromatography on silica gel (PE:EA = 20:1). The product (30.8 mg, 79% yield) was isolated as a colorless oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 9.6 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 3.95 (t, J = 6.4 Hz, 2H), 2.47 (s, 3H), 1.77-1.63 (m, 2H), 1.50-1.35 (m, 2H), 0.97-0.81 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 163.2, 130.6, 130.2, 114.2, 68.0, 31.2, 26.4, 19.2, 13.6 (t, J = 18.4 Hz, C-D).

Data in accordance with the literature[22].



2l-D

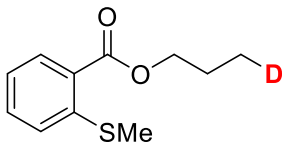
undecyl-11-*d* 4-methylbenzenesulfonate (2l-D)

Flash chromatography on silica gel (PE:EA = 20:1). The product (55.3 mg, 85% yield) was isolated as a colorless oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 2.44 (s, 3H), 1.71-1.57 (m, 2H), 1.47-1.07 (m, 16H), 0.95-0.79 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 133.2, 129.9, 127.9, 70.8, 31.9, 29.67, 29.61, 29.5, 29.4, 29.0, 28.9, 25.4, 22.7, 21.7, 13.9 (t, J = 19.0 Hz, C-D).

HRMS (ESI) m/z calculated for $C_{18}H_{29}DO_3S+Na^+$: 350.1871 $[M+Na]^+$; found: 350.1874.



2m-D

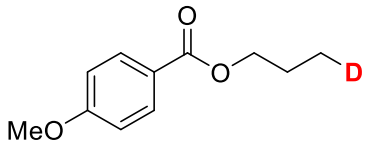
propyl-3-*d* 2-(methylthio)benzoate (2m-D)

Flash chromatography on silica gel (PE:EA = 20:1). The product (26.1 mg, 62% yield) was isolated as a yellowish oil, 92% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.6, 1.6 Hz, 1H), 7.43-7.35 (m, 1H), 7.22-7.16 (m, 1H), 7.12-7.03 (m, 1H), 4.21 (t, J = 6.4 Hz, 2H), 2.37 (s, 3H), 1.79-1.65 (m, 2H), 1.00-0.88 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.1, 131.4, 130.2, 126.0, 123.2, 122.4, 65.6, 21.0, 14.6, 9.3 (t, J = 19.3 Hz, C-D).

HRMS (ESI) m/z calculated for $C_{11}H_{13}DO_2S+Na^+$: 234.0669 $[M+Na]^+$; found: 234.0672.



2n-D

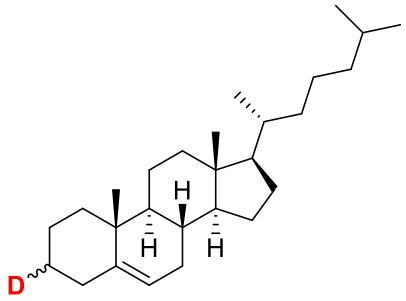
propyl-3-*d* 4-methoxybenzoate (2n-D)

Flash chromatography on silica gel (PE:EA = 20:1). The product (31.0 mg, 79% yield) was isolated as a colorless oil, 87% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.24 (t, J = 6.4 Hz, 2H), 3.84 (s, 3H), 1.82-1.71 (m, 2H), 1.06-0.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.3, 131.6, 123.0, 113.6, 66.3, 55.5, 22.2, 10.4 (t, J = 19.1 Hz, C-D).

Data in accordance with the literature[22].



2o-D

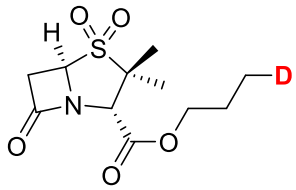
(8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-3-*d* (2o-D)

Flash chromatography on silica gel (Petroleum Ether). The product (55.4 mg, 74% yield) was isolated as a white solid, mp 66~68 °C, 90% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (dd, J = 5.1, 2.3 Hz, 1H), 2.29-2.16 (m, 1H), 2.07-1.91 (m, 3H), 1.89-1.76 (m, 2H), 1.75-1.68 (m, 1H), 1.64-1.26 (m, 12H), 1.25-1.06 (m, 6H), 1.05-0.97 (m, 7H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (dd, J = 6.4, 2.0 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 119.1, 57.0, 56.3, 50.7, 42.4, 40.0, 39.7, 37.7, 36.4, 36.0, 33.0, 32.1, 32.0, 28.4, 28.2, 27.8 (t, J = 19.0 Hz, C-D), 24.5, 24.0, 23.0, 22.7, 22.6, 20.9, 19.6, 18.9, 12.0.

Data in accordance with the literature[23].



2p-D

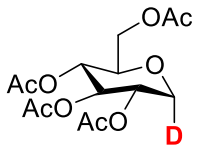
propyl-3-*d* (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (2p-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (38.6 mg, 70% yield) was isolated as a colorless oil, > 95% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (dd, J = 4.0, 2.0 Hz, 1H), 4.32 (s, 1H), 4.11 (t, J = 6.4 Hz, 2H), 3.49-3.34 (m, 2H), 1.73-1.68 (m, 2H), 1.56 (s, 3H), 1.35 (s, 3H), 0.94-0.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 167.1, 68.2, 63.4, 62.8, 61.2, 38.4, 21.9, 20.5, 18.7, 10.3 (t, J = 20.0 Hz, C-D).

Data in accordance with the literature[18].



2q-D

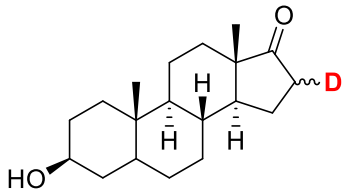
(2*R*,3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl-6-*d* triacetate (2q-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (53.0 mg, 79% yield) was isolated as a colorless oil, 85% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, J = 9.6 Hz, 1H), 5.02-4.93 (m, 2H), 4.19-4.13 (m, 1H), 4.10-4.04 (m, 2H), 3.60-3.52 (m, 1H), 2.04 (s, 3H), 1.99 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.4, 169.8, 169.6, 76.4, 73.7, 68.9, 68.4, 66.5 (t, J = 21.8 Hz, C-D), 62.2, 20.8, 20.7, 20.6.

Data in accordance with the literature[23].



2r-D

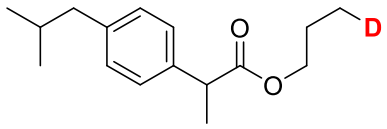
(3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-3-hydroxy-10,13-dimethylhexadecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one-16-*d* (2r-D)

Flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1). The product (38.5 mg, 66% yield) was isolated as a white soild, mp 171~173 °C, 90% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66-3.44 (m, 1H), 2.47-2.30 (m, 1H), 2.16 (s, 1H), 1.94-1.84 (m, 1H), 1.82-1.72 (m, 3H), 1.71-1.59 (m, 2H), 1.58-1.04 (m, 10H), 0.94 (td, J = 12.8, 5.2 Hz, 2H), 0.81 (s, 3H), 0.79 (s, 3H), 0.70-0.59 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.7, 71.0, 54.4, 51.4, 47.8, 44.8, 38.0, 37.0, 35.9, 35.7, 35.1, 31.5, 31.4, 30.9, 28.4, 21.7 (t, J = 10.4 Hz, C-D), 20.5, 13.8, 12.4.

HRMS (ESI) m/z calculated for $C_{19}H_{29}DO_2$+Na^+: 314.2201 $[M+Na]^+$; found: 314.2191.



2s-D

propyl-3-*d* 2-(4-isobutylphenyl)propanoate (2s-D)

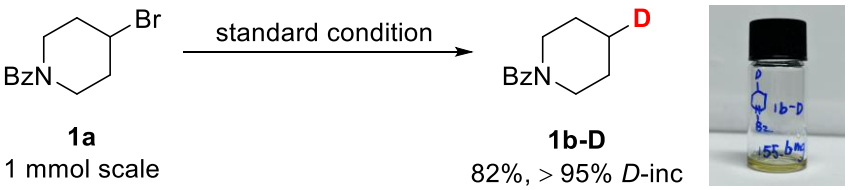
Flash chromatography on silica gel (PE:EA = 50:1). The product (37.4 mg, 75% yield) was isolated as a colorless oil, 92% D-inc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 3.94 (t, J = 6.4 Hz, 2H), 3.61 (q, J = 7.2 Hz, 1H), 2.36 (d, J = 7.2 Hz, 2H), 1.84-1.69 (m, 1H), 1.57-1.46 (m, 2H), 1.41 (d, J = 7.2 Hz, 3H), 0.81 (d, J = 6.4 Hz, 6H), 0.78-0.72 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 140.4, 137.9, 129.3, 127.2, 66.2, 45.2, 45.1, 30.2, 22.4, 21.9, 18.5, 10.0 (t, J = 19.0 Hz, C-D).

HRMS (ESI) m/z calculated for $C_{16}H_{23}DO_2$+Na^+: 272.1731 $[M+Na]^+$; found: 272.1732.

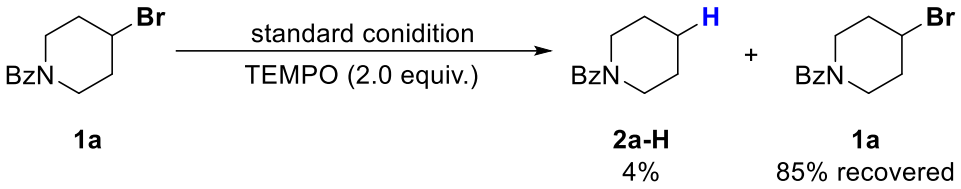
1 mmol-scale reaction



To a solution of **1a** (1.0 mmol), imidazole (1.0 mmol), $Ph_2{}^tBuSiCO_2H$ (1.5 mmol) and 4CzIPN (5 mol%) in 1,4-dioxane (10 mL) was added TRIP thiol (15 mol%) and D_2O (2.0 mL). The mixture was stirred under 15 W blue LED for 12 h at room temperature. The mixture was treated with water, washed by EtOAc and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure, then purified by flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1) to afford product as a yellowish oil, 155.6 mg, 82% yield. D-inc.: > 95%.

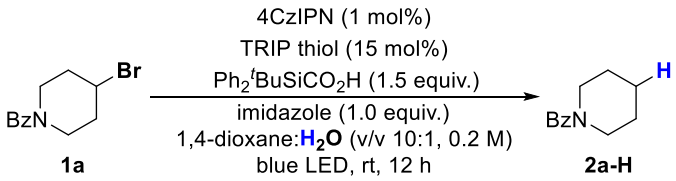
Mechanistic Studies

Radical trapping experiments



To a solution of **1a** (0.2 mmol), imidazole (0.2 mmol), $Ph_2{}^tBuSiCO_2H$ (0.3 mmol), 4CzIPN (5 mol%) and TEMPO (0.4 mmol) in 1,4-dioxane (2 mL) was added TRIP thiol (15 mol%) and H_2O (0.2 mL). The mixture was stirred under 15 W blue LED for 12 h at rt. The mixture was treated with water, washed by EtOAc and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure, then purified by flash chromatography on silica gel (PE:EA = 20:1, PE:EA = 5:1, PE:EA = 2:1) to afford 4% **2a-H**, recovered 85% **1a** (determined by gas chromatography).

Light on/off experiments



Under N_2 atmosphere, six tubes (No.1-6) equipped with magnetic stirrer bars were charged sequentially with **1a** (0.2 mmol), ^{t}BuPh$_2$SiCO$_2$H (0.3 mmol), imidazole (0.2 mmol) and 4CzIPN (1 mol%). Then 1,4-dioxane (0.1 M, 2 mL), H_2O (0.2 mL) and TRIP thiol (15 mol%) was added into the reaction tube and the reaction mixtures were stirred under 15 W blue LED. After 20 min, the blue LED was turned off, and No.1 vial was removed from the irradiation setup for analysis. The remaining vials were stirred in the absence of light for an additional 20 min. Then, No.2 vial was removed for analysis, and the blue LED was turned back on to irradiate the remaining reaction mixtures. After an additional 20 min of irradiation, the blue LED was turned off, and No. 3 vial was removed for analysis. The remaining vials were stirred in the absence of light for an additional 20 min. Then, No. 4 vial was removed for analysis, and the blue LED was turned back on to irradiate the remaining last reaction mixture for 20 min, and then it was analyzed. Finaly the blue LED was turned off and No.6 was analyzed after 20 min. Yields were determined by gas chromatography.

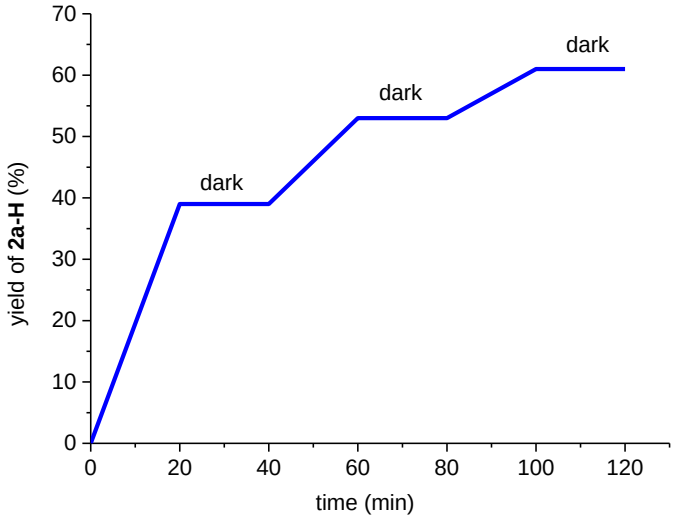


Figure S2. Light on/off experiments

Emission Quenching Studies

Fluorescence spectra was collected on Horiba Jobin Yvon Fluorescence Spectrophotometer Fluorolog-3 for all experiments. All test solutions were excited at 460 nm and the emission intensity was collected at 525 nm. In a typical experiment, the sample was degassed with a stream of N_2 for 15 minutes, then the emission spectrum of the sample was collected. First, the emission spectrum of a 1×10^{-5} M solution of 4CzIPN in a mixture solution of 1,4-dioxane and H_2O (10:1, v/v) was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

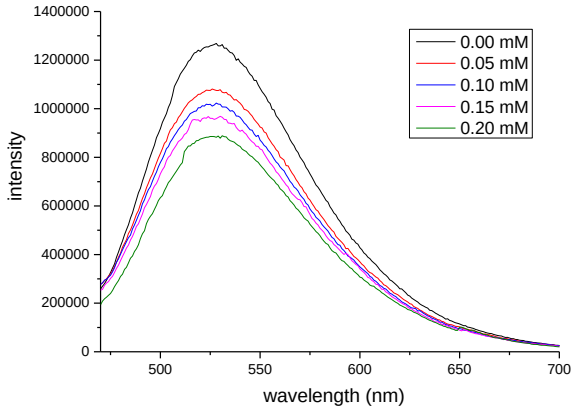


Figure S3. Emission quenching of 4CzIPN (5×10^{-6} M) in the presence of increasing amounts of $Ph_2{}^tBuSiCO_2H$.

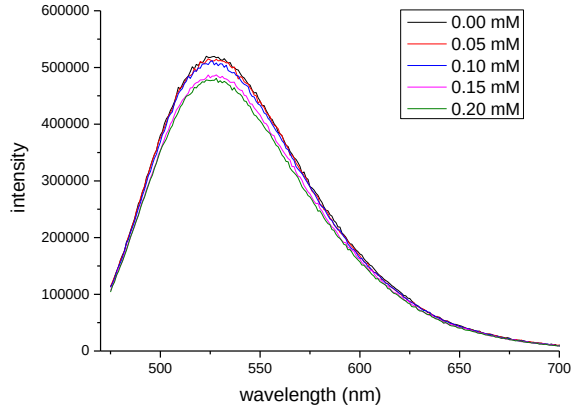


Figure S4. Emission quenching of 4CzIPN (5×10^{-6} M) in the presence of increasing amounts of Imidazole.

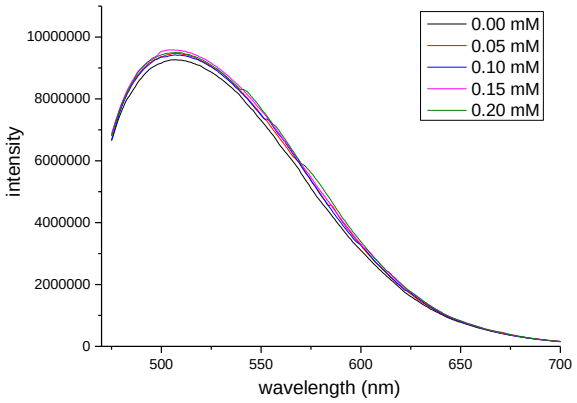


Figure S5. Emission quenching of 4CzIPN (5×10^{-6} M) in the presence of increasing amounts of **1a**.

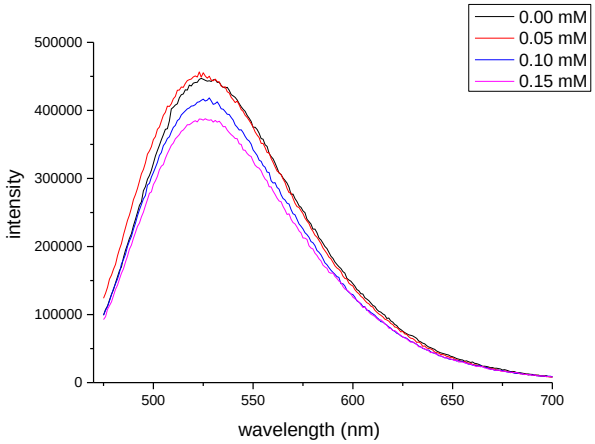


Figure S6. Emission quenching of 4CzIPN (5×10^{-6} M) in the presence of increasing amounts of **TRIP thiol**.

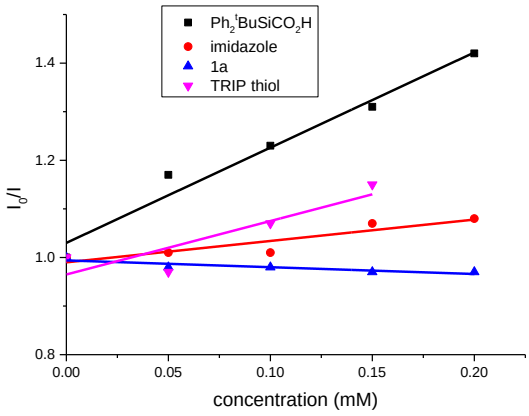


Figure S7. Stern-Volmer plots. I_0 and I are respective luminescence intensities in the absence and presence of the indicated concentrations of the corresponding quencher.

Reference

[1] A. Chollet, G. Mori, C. Menendez, F. Rodriguez, I. Fabing, M. R. Pasca, J Madacki, J. Korduláková, P. Constant, A. Quémard, V. B. Génisson, C. Lherbet and M. Baltas, Design, Synthesis and Evaluation of New GEQ Derivatives as Inhibitors of InhA Enzyme and Mycobacterium Tuberculosis Growth, *Eur. J. Med. Chem.,* 2015, **101**, 218-235.

[2] H. Zhao, A. J. McMillan, T. Constantin, R. C. Mykura, F. Juliá and D. Leonori, Merging Halogen-Atom Transfer (XAT) and Cobalt Catalysis to Override E2-Selectivity in the Elimination of Alkyl Halides: A Mild Route toward Contra-Thermodynamic Olefins, *J. Am. Chem. Soc.*, 2021, **143**, 14806−14813.

[3] K.-J. Bian, Y. Li, K.-F. Zhang, Y. He, T.-R. Wu, C.-Y. Wang and X.-S. Wang, Iron-catalyzed Remote Functionalization of Inert C(sp^3)-H Bonds of Alkenes via 1,*n*-Hydrogen-Atom-Transfer by C-centered Radical Relay, *Chem. Sci.*, 2020, **11**, 10437-10443.

[4] L. Zhong, Q. Liu, Y. S. Ting, V. Y. Thien, N. S. B. Kalong, D. Yang and M.-W. Wang, Adenine Derivatives Invert High Glucose-induced Thioredoxin-interacting Protein Over expression, *Chem. Biol. Drug. Des.*, 2018, **92**, 1998-2008.

[5] Y. Zou, H. Mouhib, W. Stahl, A. Goeke, Q. Wang and P. Kraft, Efficient Macrocyclization by a Novel Oxy-Oxonia-Cope Reaction: Synthesis and Olfactory Properties of New Macrocyclic Musks, *Chem. Eur. J.*, 2012, **18**, 7010-7015.

[6] H. Nelson, W. Richard, H. Brown, A. Medlin, C. Light and S. T. Heller, Practical Chemoselective Acylation: Organocatalytic Chemodivergent Esterification and Amidation of Amino Alcohols with *N*-Carbonylimidazoles, *Angew. Chem.*, *Int. Ed.*, 2021, **60**, 22818-2282.

[7] N. Iranpoor, H. Firouzabadi, A. Jamalian and F. Kazemi, Silicaphosphine (Silphos): a Filterable Reagent for the Conversion of Alcohols and Thiols to Alkyl Bromides and Iodides, *Tetrahedron*, 2005, **23**, 5699-5704.

[8] T. Yang, Y. Jiang, Y. Luo, J. J. H. Lim, Y. Lan and M. J. Koh, Chemoselective Union of Olefins, Organohalides and Redox-Active Esters Enables Regioselective Alkene Dialkylation, *J. Am. Chem. Soc.*, 2020, **142**, 21410-21419.

[9] H. Hu, Z. Rao, J. Xu, Q. Zhu, H.-J. Altenbach, H. Chen, D. Zhou, Y. Xiao, X. Ke, H. Guo, Z. Wu, P. Liu and X. Hu, 16-Morpholino Quaternary Ammonium Steroidal Derivatives as Neuromuscular Blocking Agents: Synthesis, Biological Evaluation and in Silico Probe of Ligand-

Receptor Interaction, *Eur. J. Med. Chem*., 2012, **56**, 332-347.

[10] J. Sheng, H.-Q. Ni, S.-X. Ni, Y. He, R. Cui, G.-X. Liao, K.-J. Bian, B.-B. Wu and X.-S. Wang, Diversity-Oriented Synthesis of Aliphatic Fluorides via Reductive C(sp^3)-C(sp^3) Cross-Coupling Fluoroalkylation, *Angew. Chem.*, *Int. Ed.*, 2021, **60**, 15020-15027.

[11] A. R. Katritzky, G. Zhang and J. Wu, 1-Phenylsulfonylbenzotriazole: A Novel and Convenient Reagent for the Preparation of Benzenesulfonamides and Aryl Benzenesulfonates, *Synth. Commun.*, 1994, **24**, 205-216.

[12] G. Kundu and T. H. Lambert, Electrochemical Vicinal C-H Difunctionalization of Saturated Azaheterocycles, *J. Am. Chem. Soc.*, 2024, **3**, 1794-1798.

[13] T. Fukuyama, Y. Fujita, H. Miyoshi, I. Ryu, S.-C. Kao and Y.-K. Wu, Electron Transfer-induced Reduction of Organic Halides with Amines, *Chem. Commun.*, 2018, **54**, 5582−5585.

[14] C. Chatgilialoglu, D. Griller and M. Lesage, Tris(trimethylsilyl)silane: A new reducing agent, *J. Org. Chem.*, 1988, **53**, 15, 3641-3642.

[15] Y.-C. Lu and J. G. West, Chemoselective Decarboxylative Protonation Enabled by Cooperative Earth-Abundant Element Catalysis, *Angew. Chem.*, *Int. Ed.*, 2023, **62**, e202213055.

[16] Y. Gu, H. Yin, M. Wakeling, J. An and R. Martin, Defunctionalization of sp^3 C-Heteroatom and sp^3 C-C Bonds Enabled by Photoexcited Triplet Ketone Catalysts, *ACS Catal.*, 2022, **12**, 1031-1036.

[17] X. Pan, E. Lacôte, J. Lalevée and D. P. Curran, Polarity Reversal Catalysis in Radical Reductions of Halides by *N*-Heterocyclic Carbene Boranes, *J. Am. Chem. Soc.*, 2012, **134**, 5669-5674.

[18] T. Constantin, M. Zanini, A. Regni, N. S. Sheikh, F. Juliá and D. Leonori, Aminoalkyl Radicals as Halogen-atom Transfer Agents for Activation of Alkyl and Aryl Halides, *Science*, 2020, **367**, 1021-1026.

[19] A. Xia, X. Xie, X. Hu, W. Xu and Y. Liu, Dehalogenative Deuteration of Unactivated Alkyl Halides Using D_2O as the Deuterium Source, *J. Org. Chem.*, 2019, **84**, 13841-13857.

[20] W. Knörr and G. Spiteller, Simple Method for the Analysis of Glycerol Enol Ethers Derived from Plasmalogens in Complex Lipid Mixtures and Subsequent Determination of the Aldehydic Components by Gas Chromatography-Mass Spectrometry, *J. Chromatogr. B.*, 1990, **526**, 303-318.

[21] Y.-Li Sun, F.-F. Tan, R.-G. Hu, C.-H. Hu and Y. Li, Visible-Light Photoredox-Catalyzed Hydrodecarboxylation and Deuterodecarboxylation of Fatty Acids, *Chin. J. Chem.*, **2022**, 40, 1903-

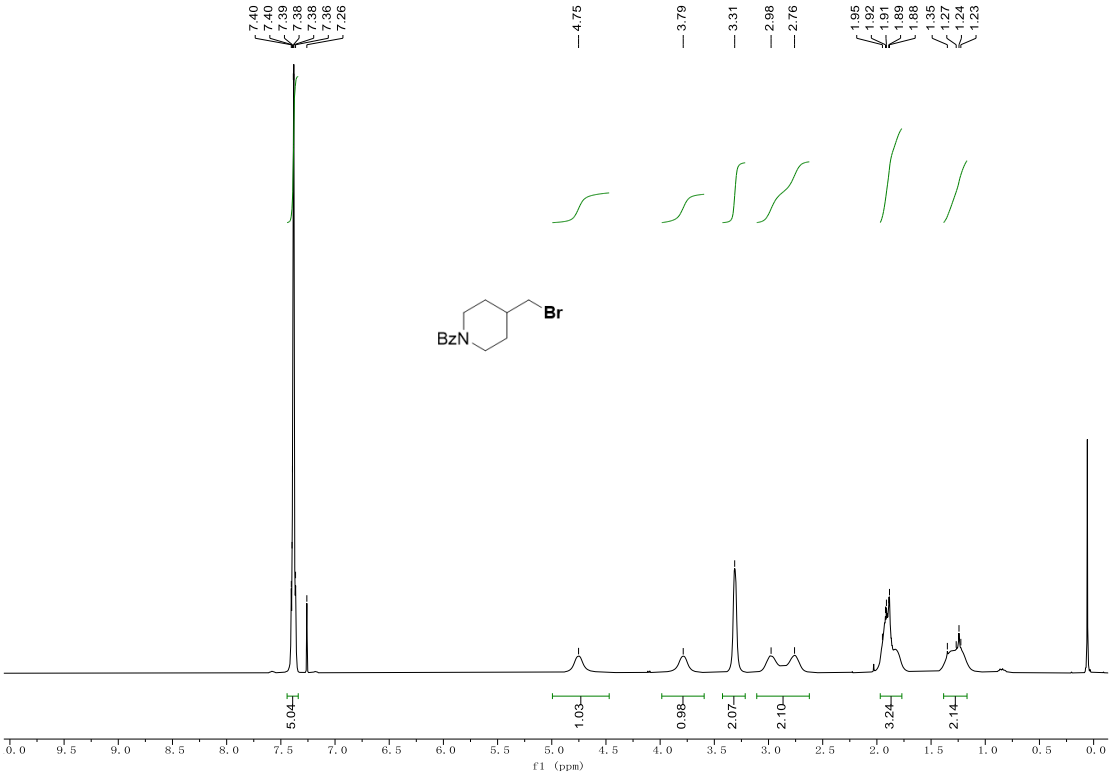
1908.

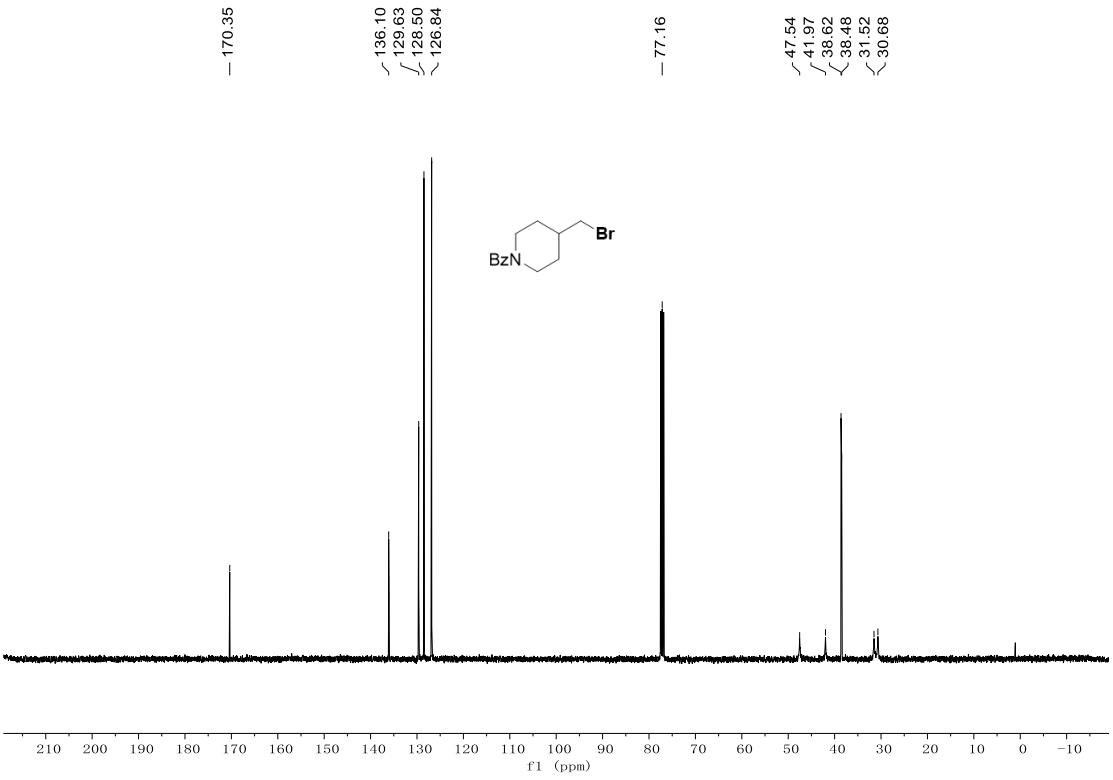
[22] J. Lee and S. Lee, Dehalogenative Deuteration of Alkyl and Arylbromides by Thiyl Radical Catalysis under Visible-Light Irradiation, *Chem. Commun.*, 2024, **60**, 5526-5529.

[23] S. Shi, R. Li, L. Rao and Z. Sun. A Mild, General, and Metal-Free Method for Sitespecific Deuteration Induced by Visible Light Using D_2O as the Source of Deuterium Atoms, *Green Chem.*, **2020**, 22, 669-672.

NMR spectra

1c; ^{1}H-NMR (400 MHz, $CDCl_3$); ^{13}C-NMR (100 MHz, $CDCl_3$)





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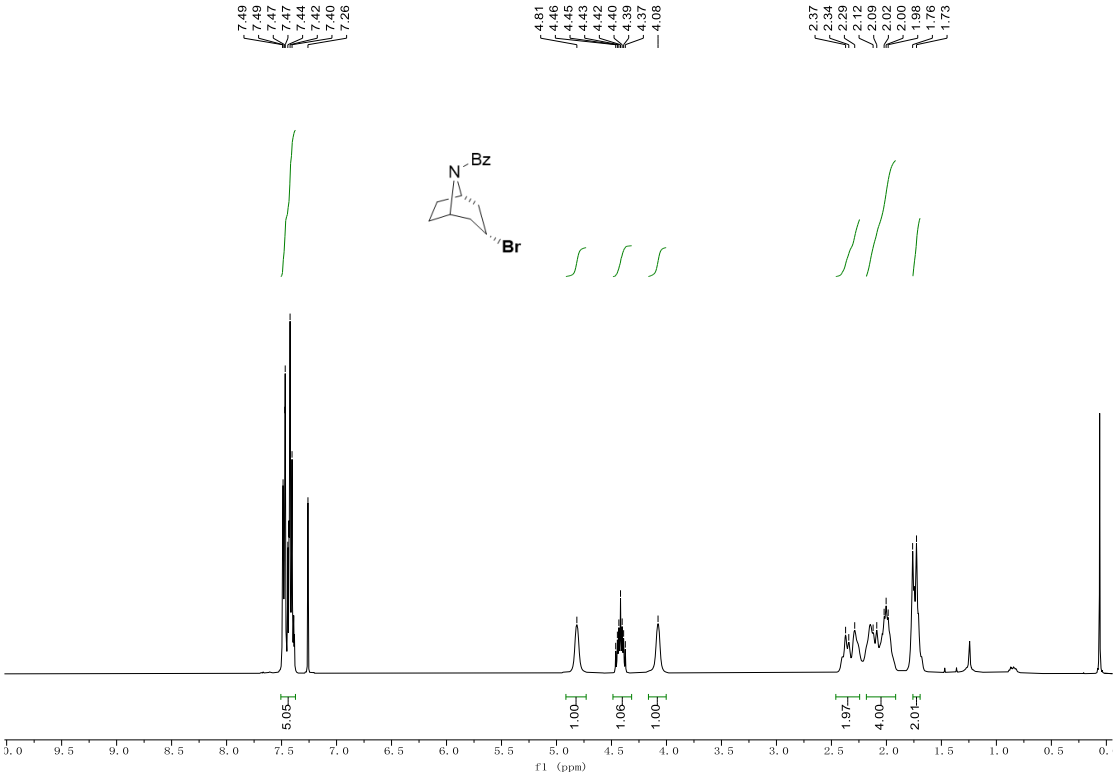

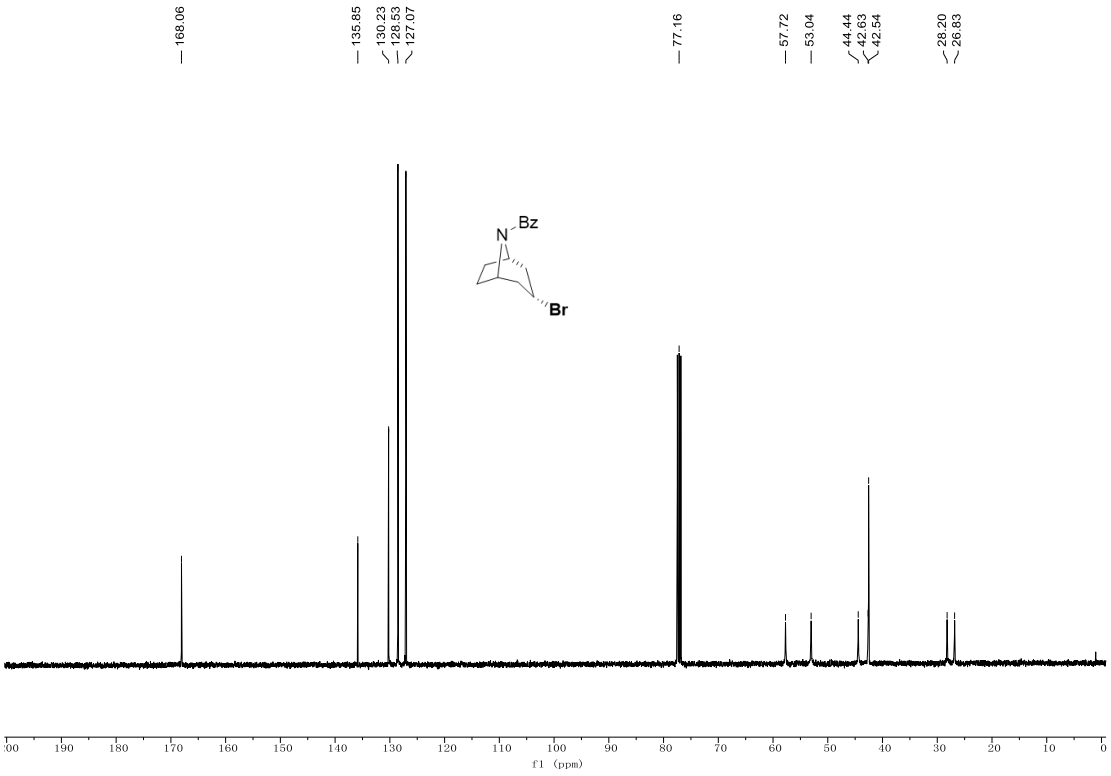

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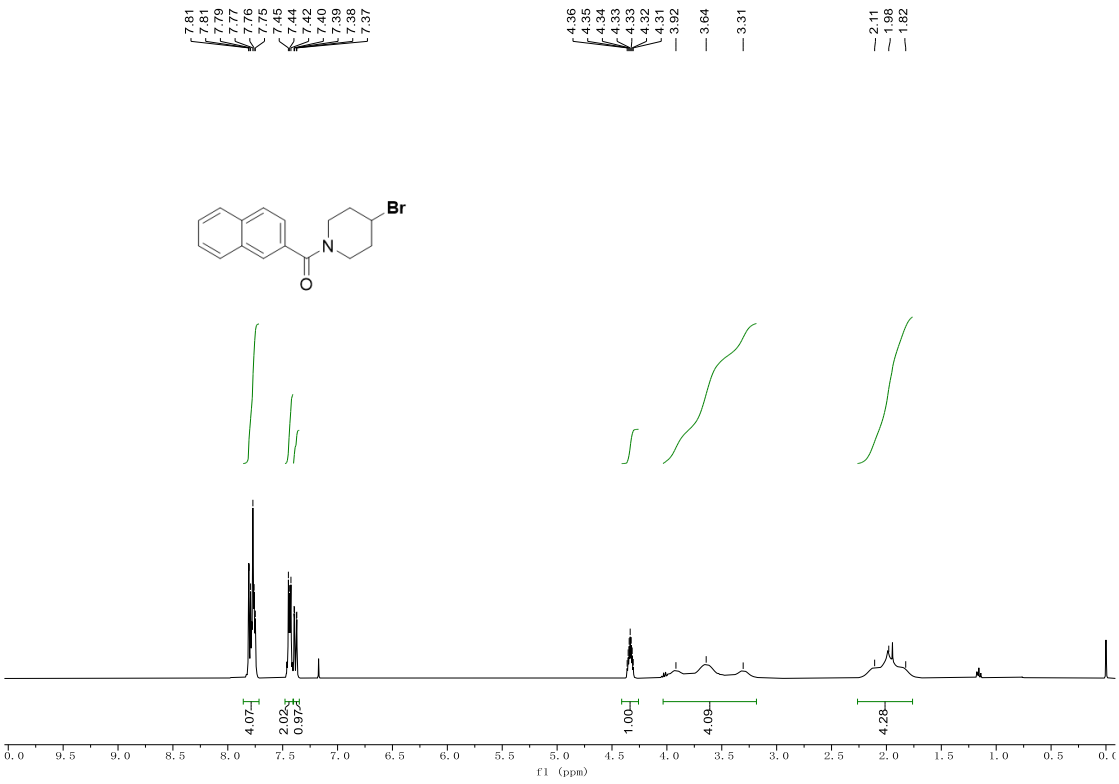

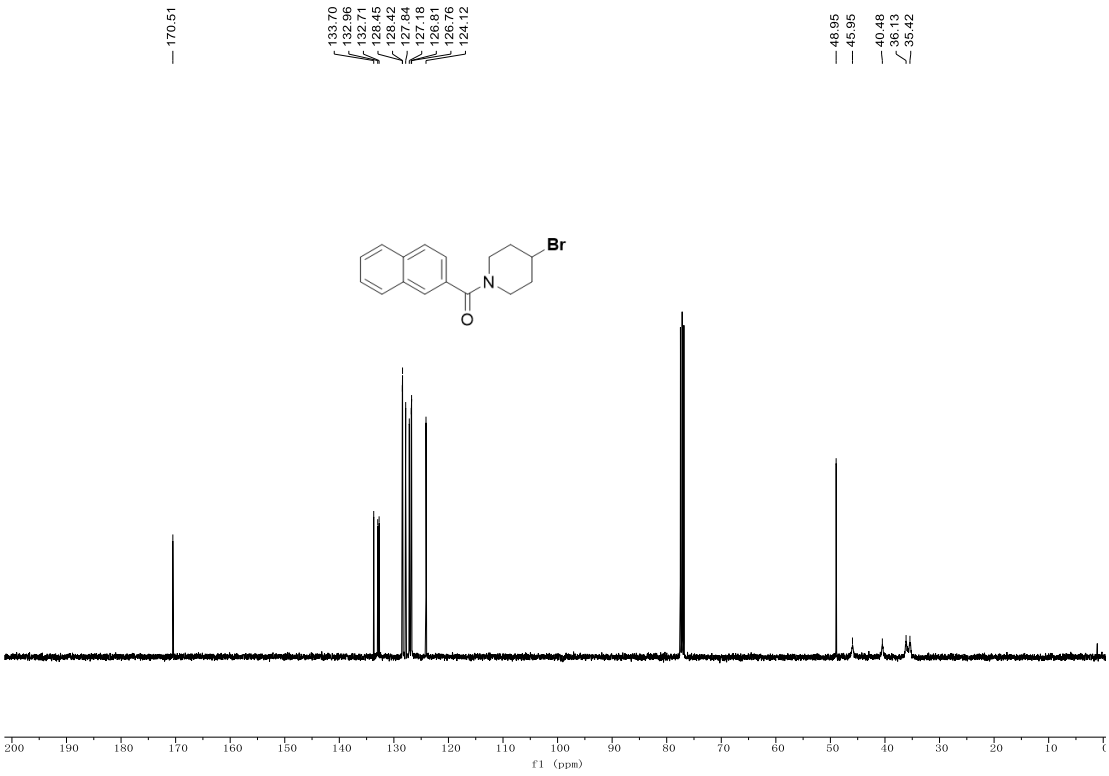

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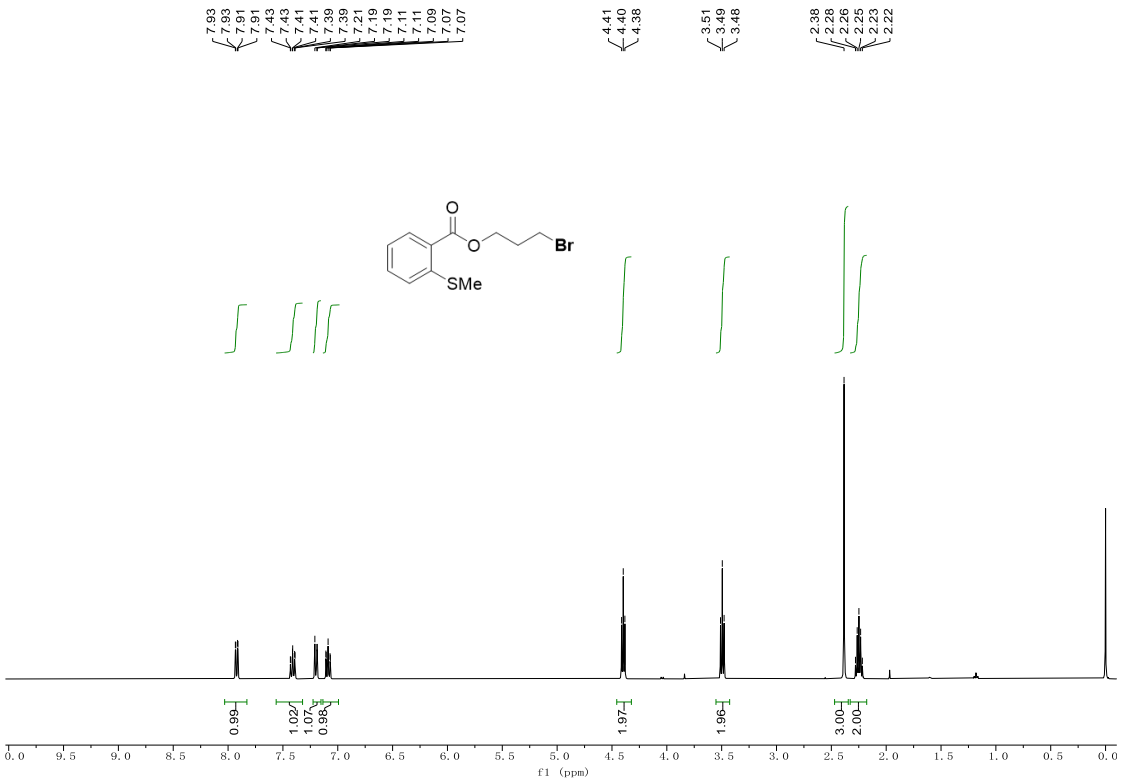

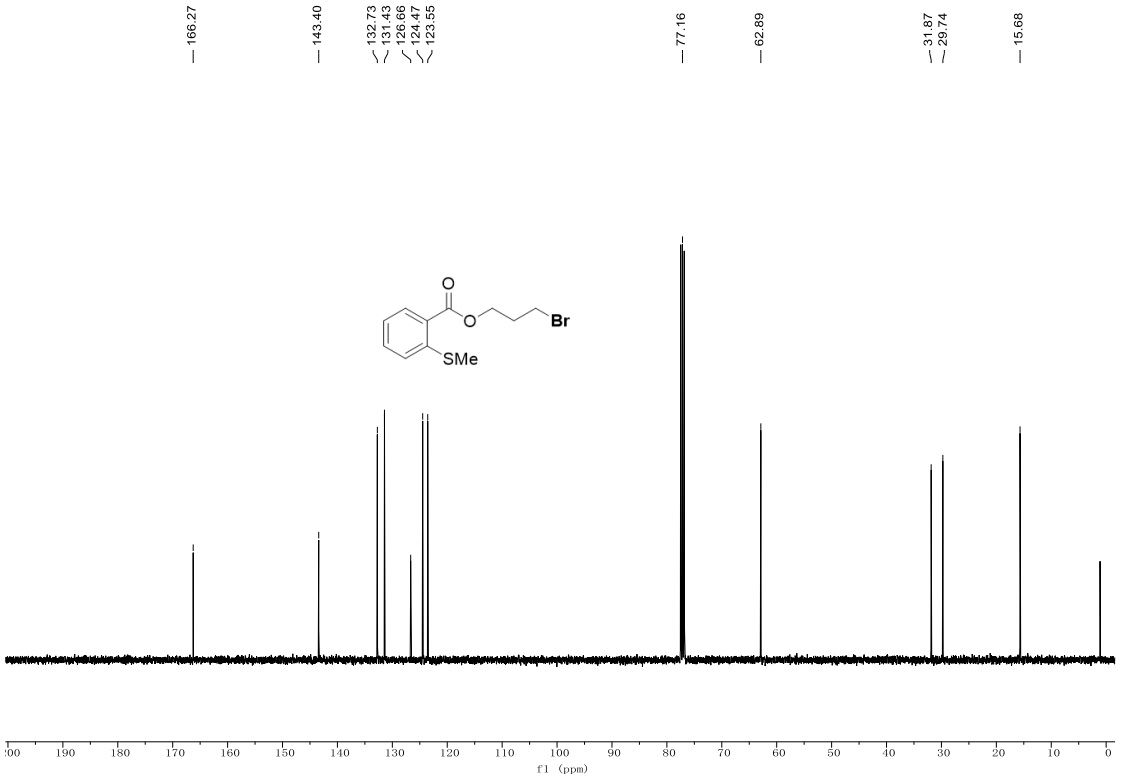

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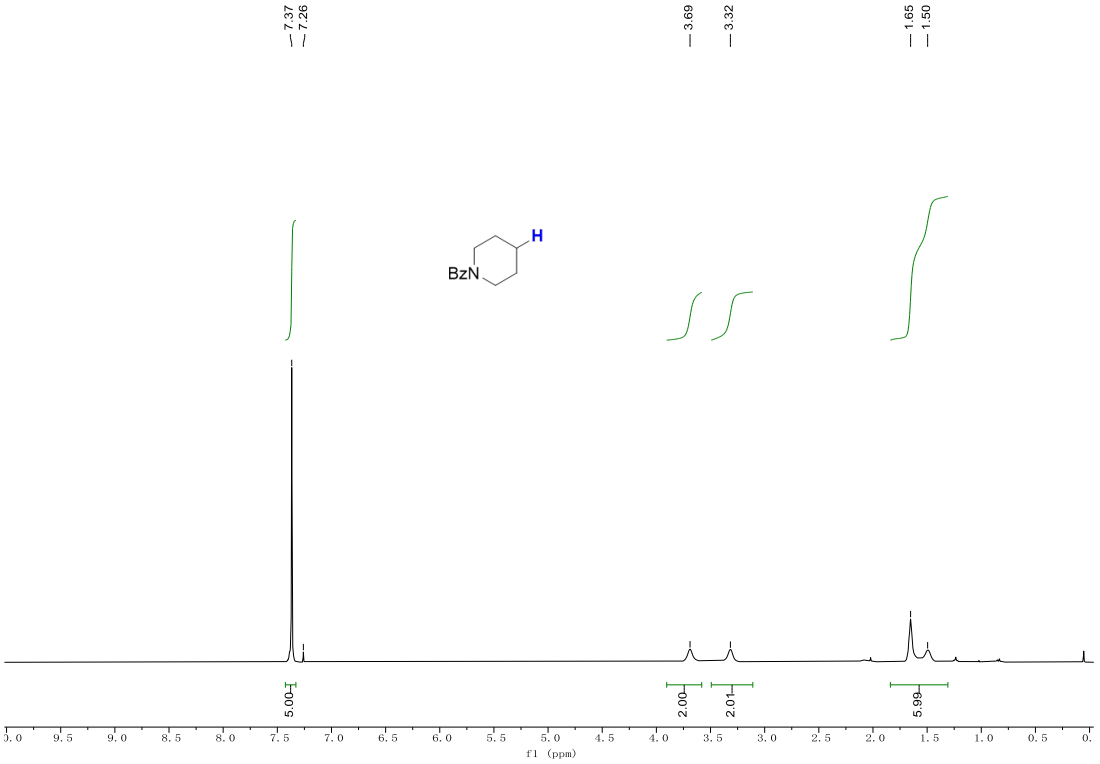

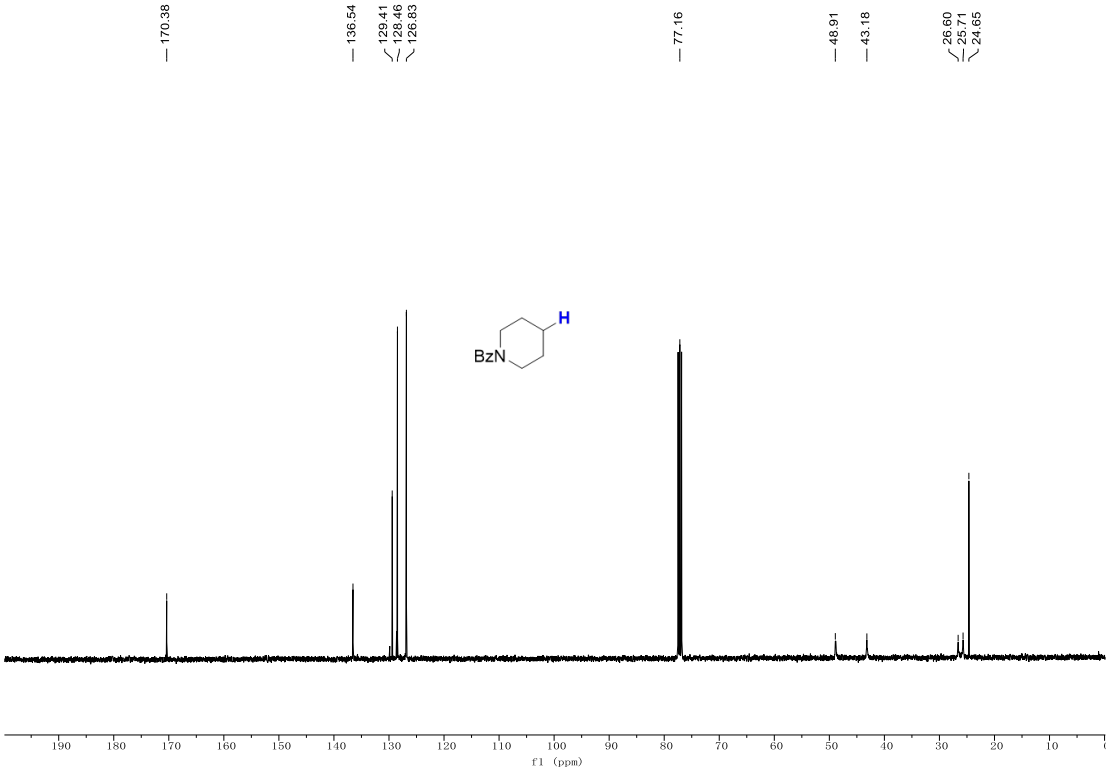

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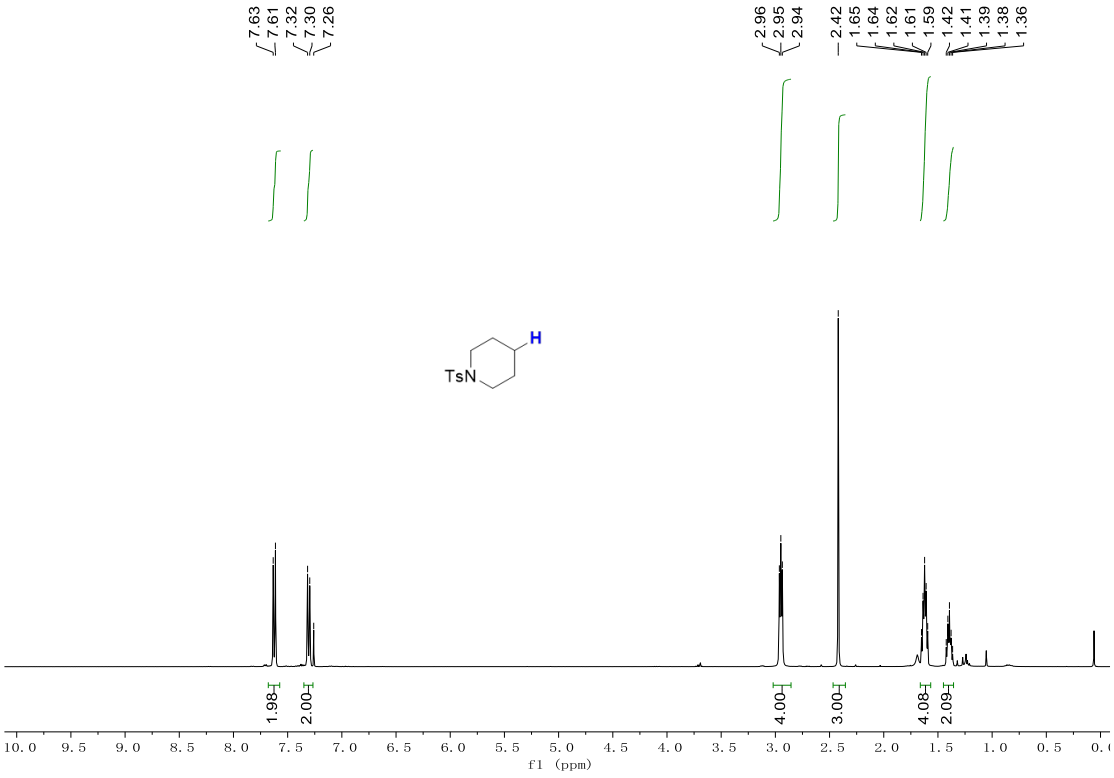

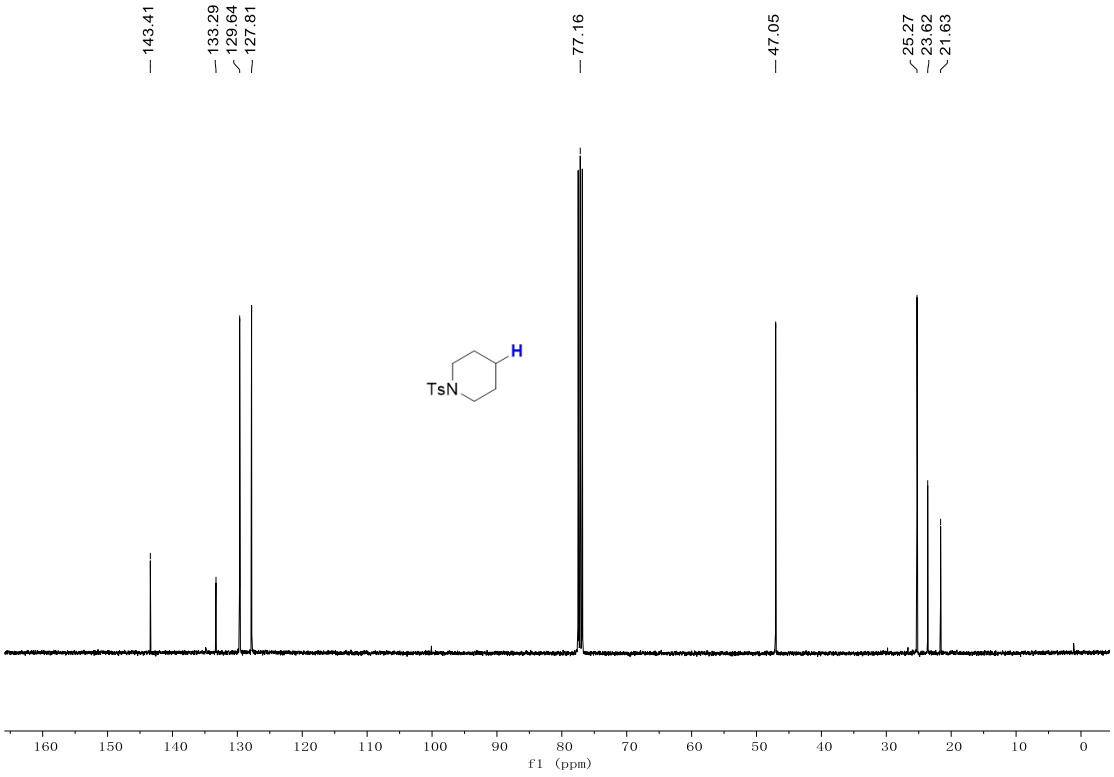

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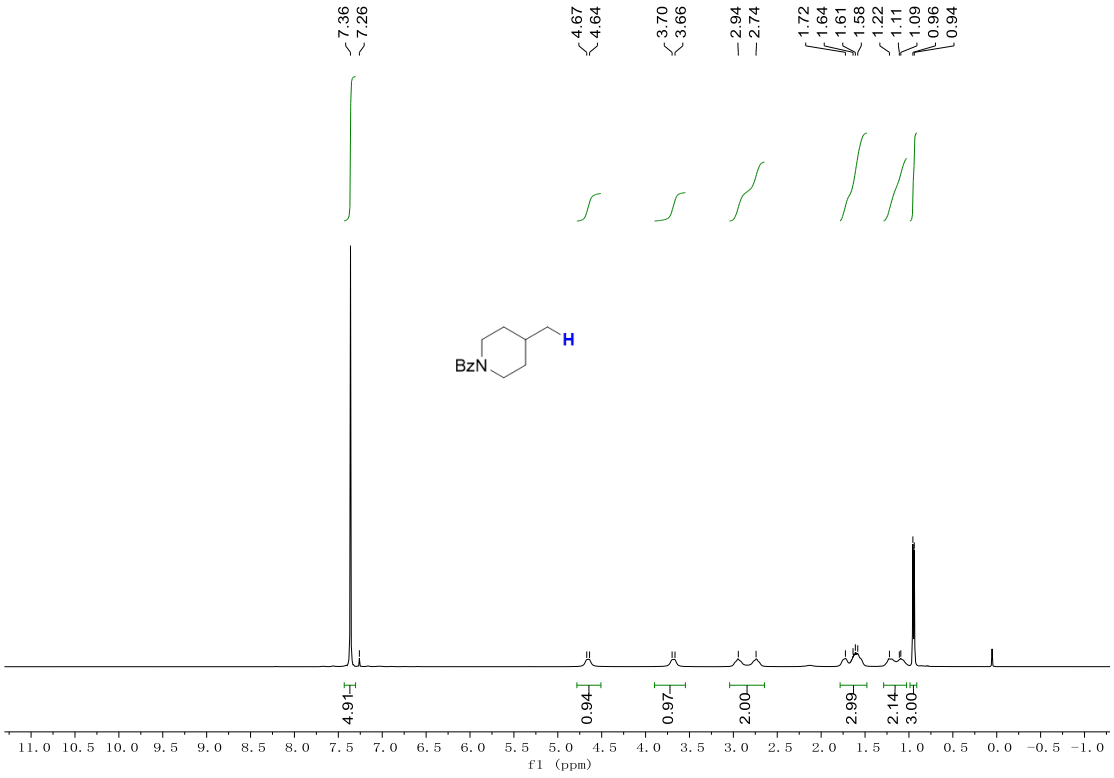

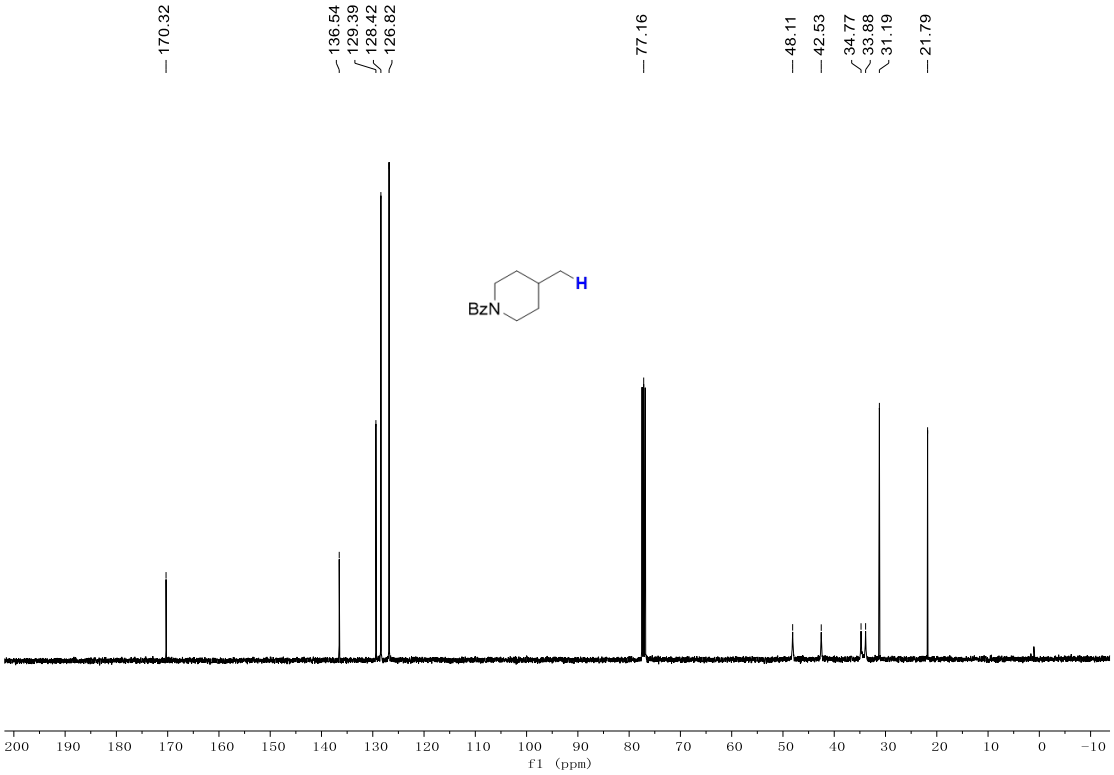

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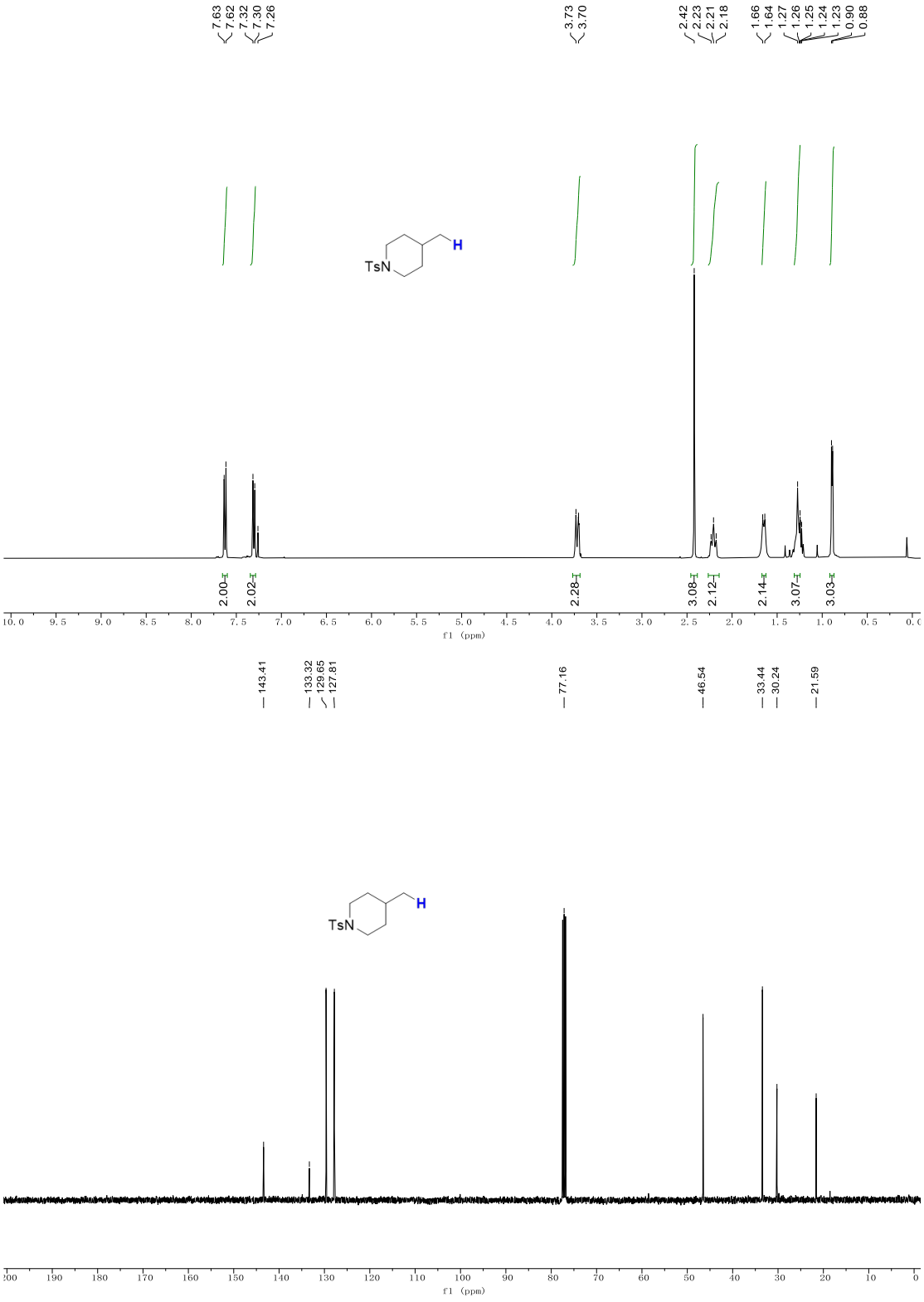

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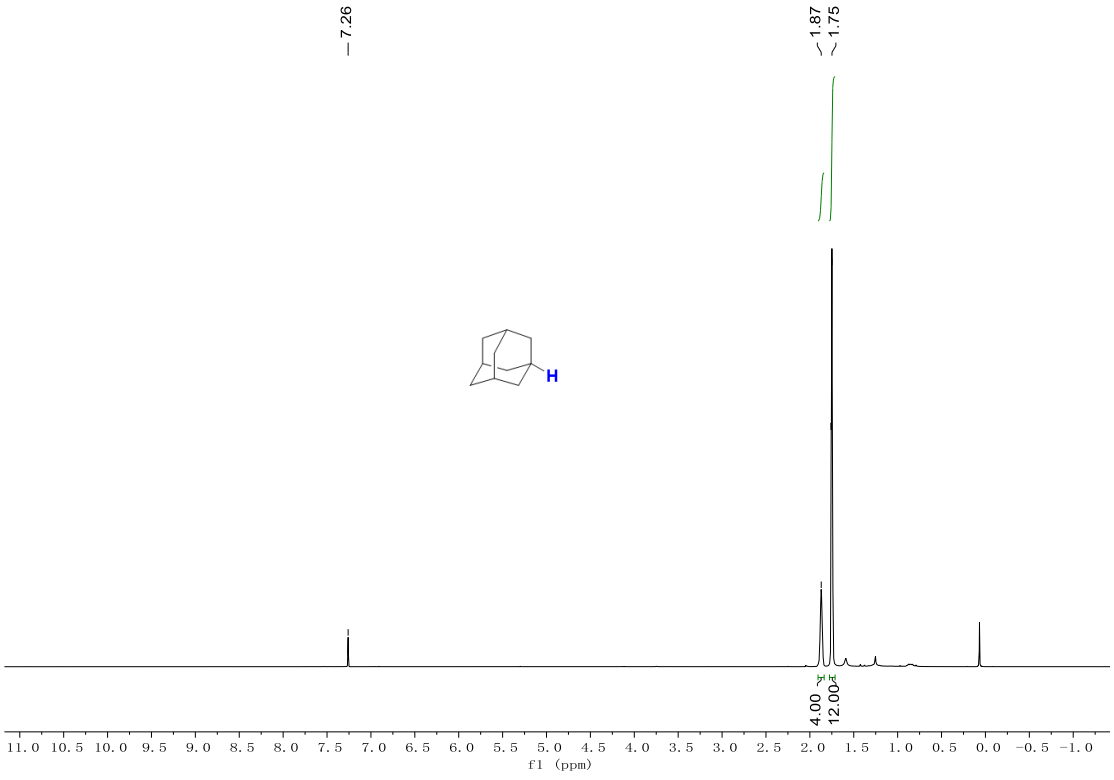

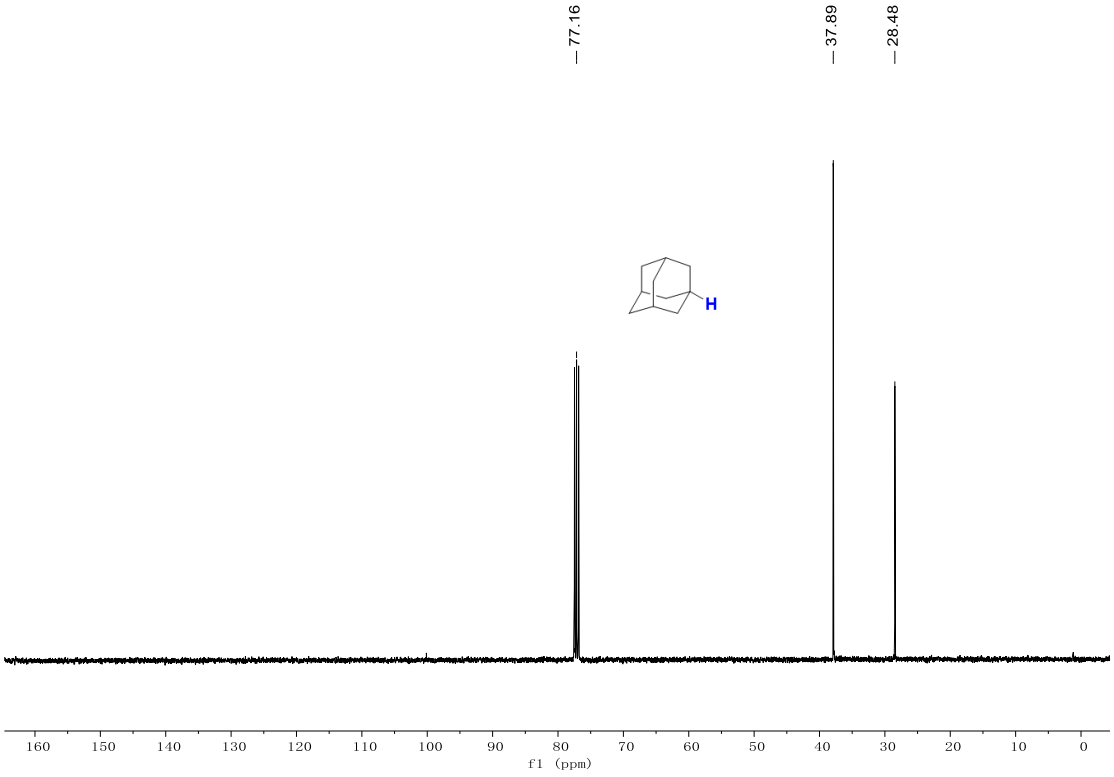

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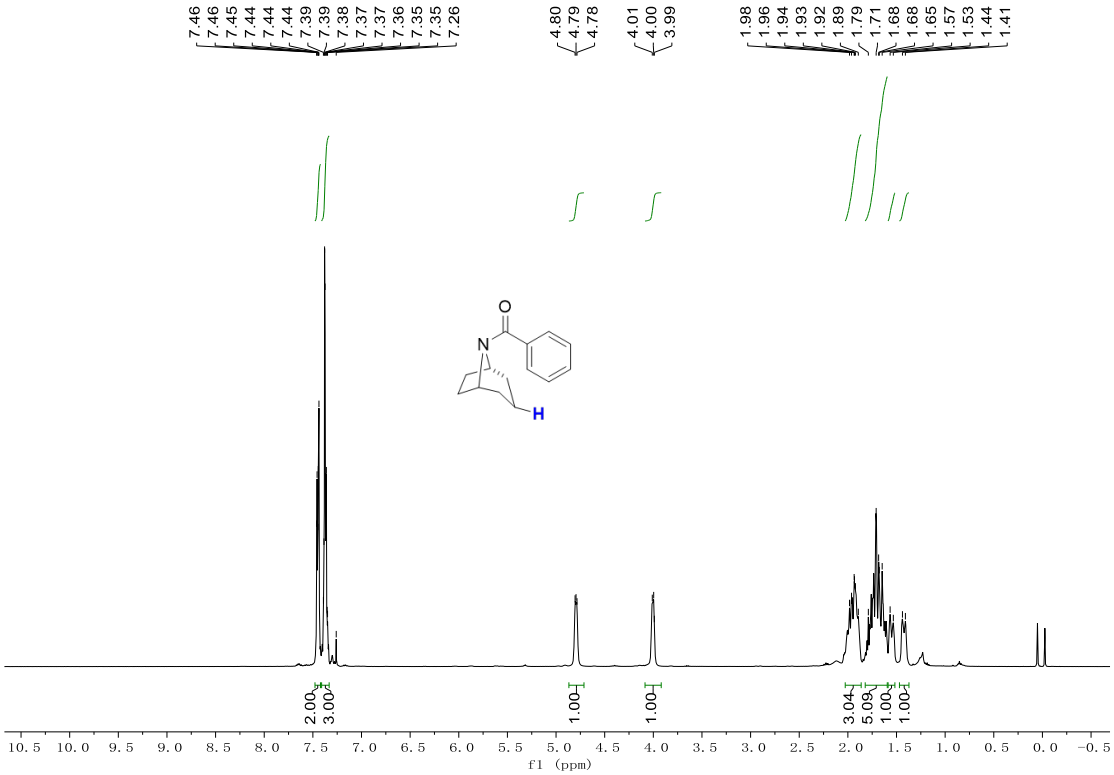

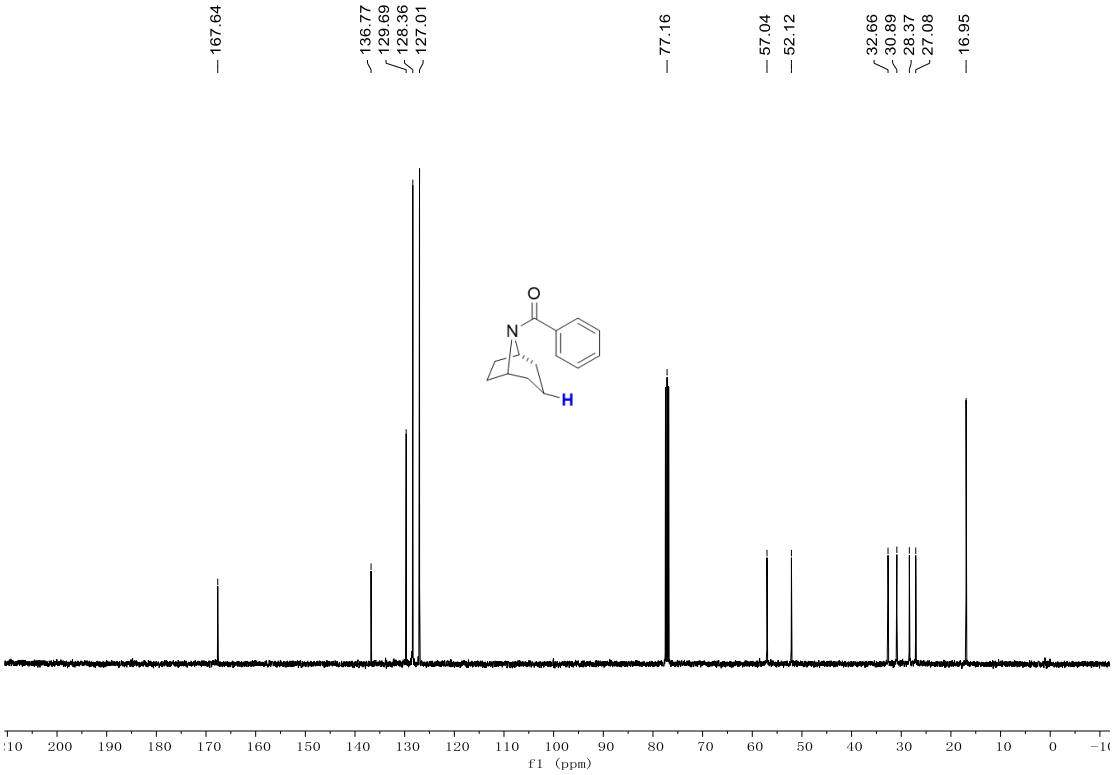

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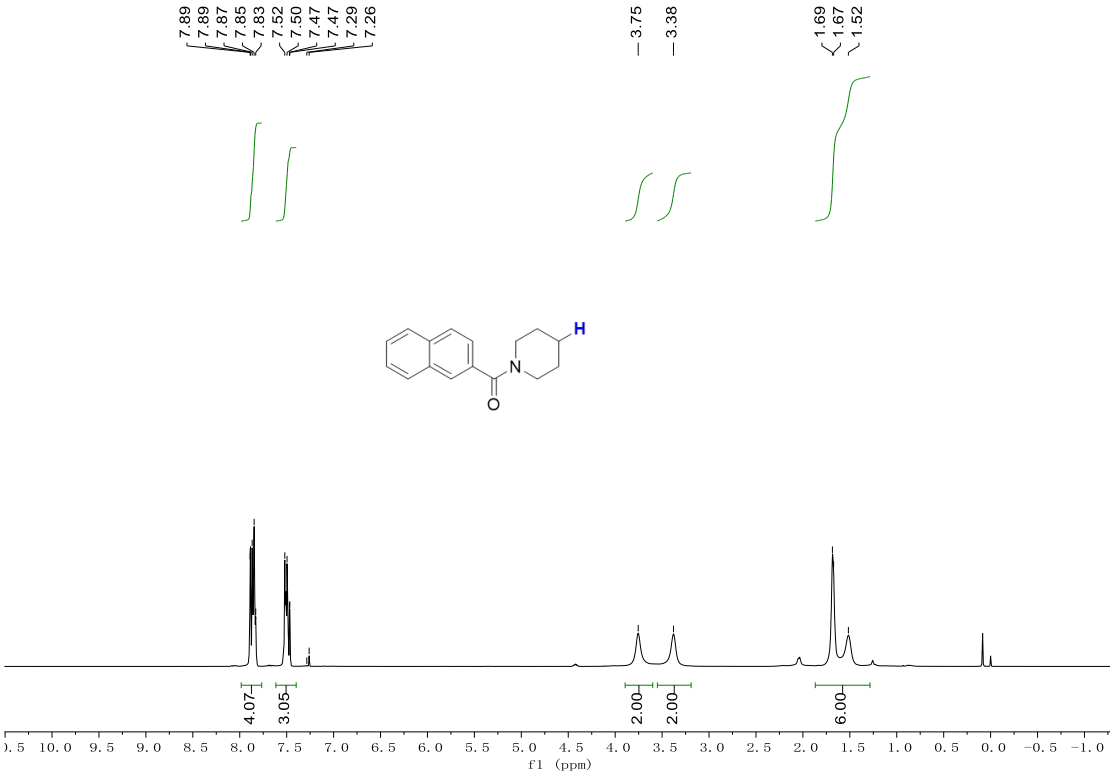

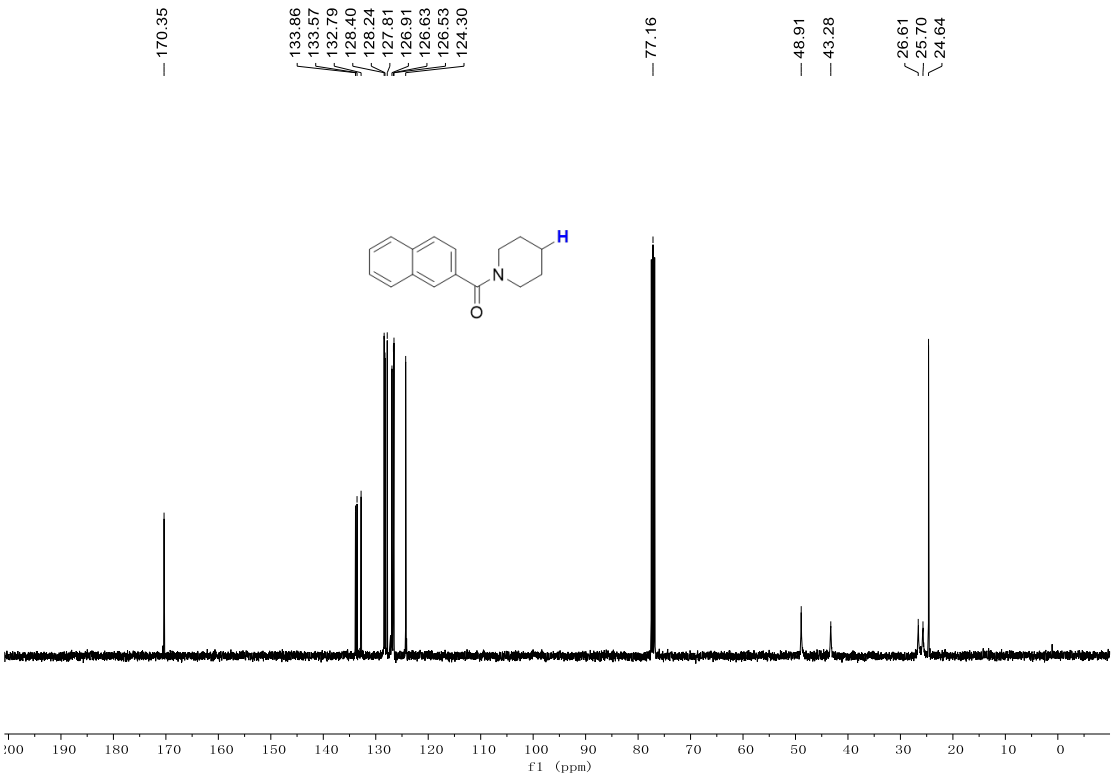

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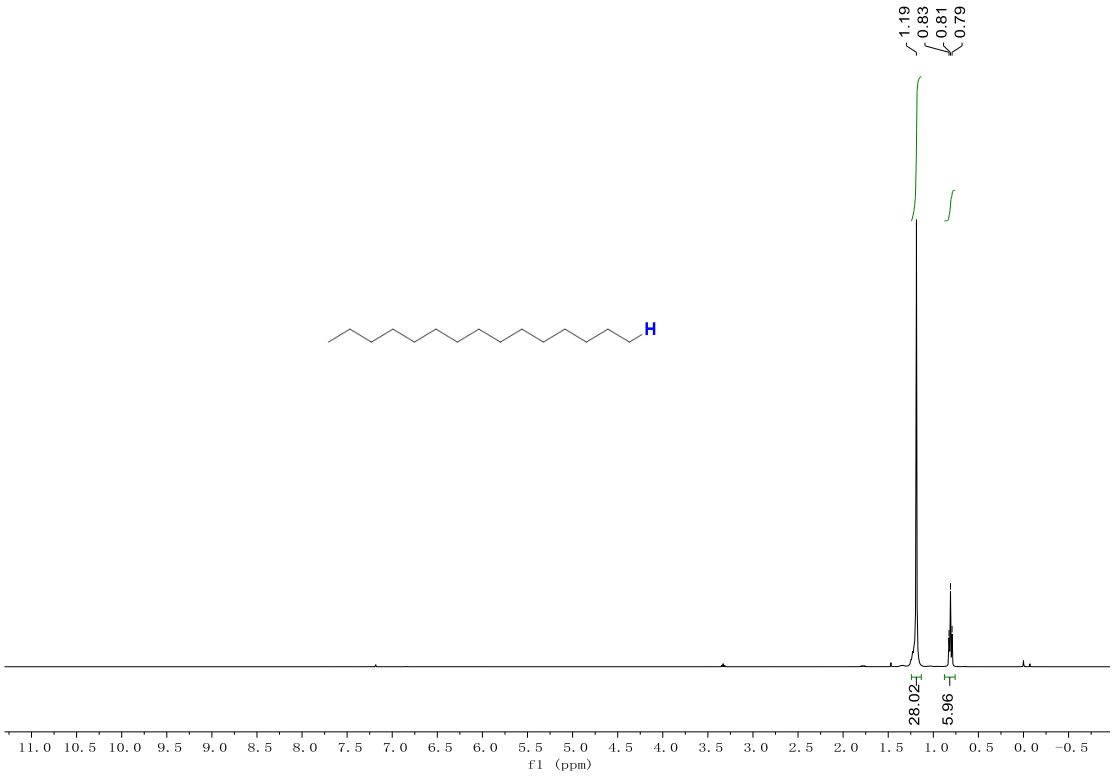

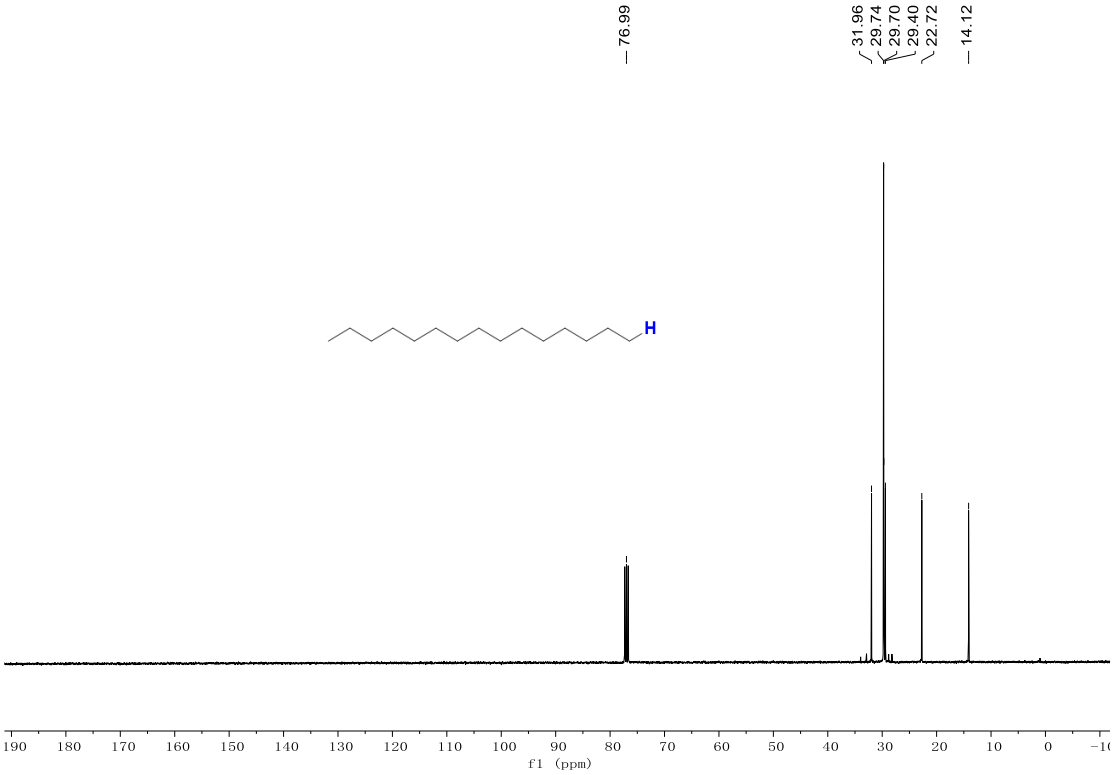

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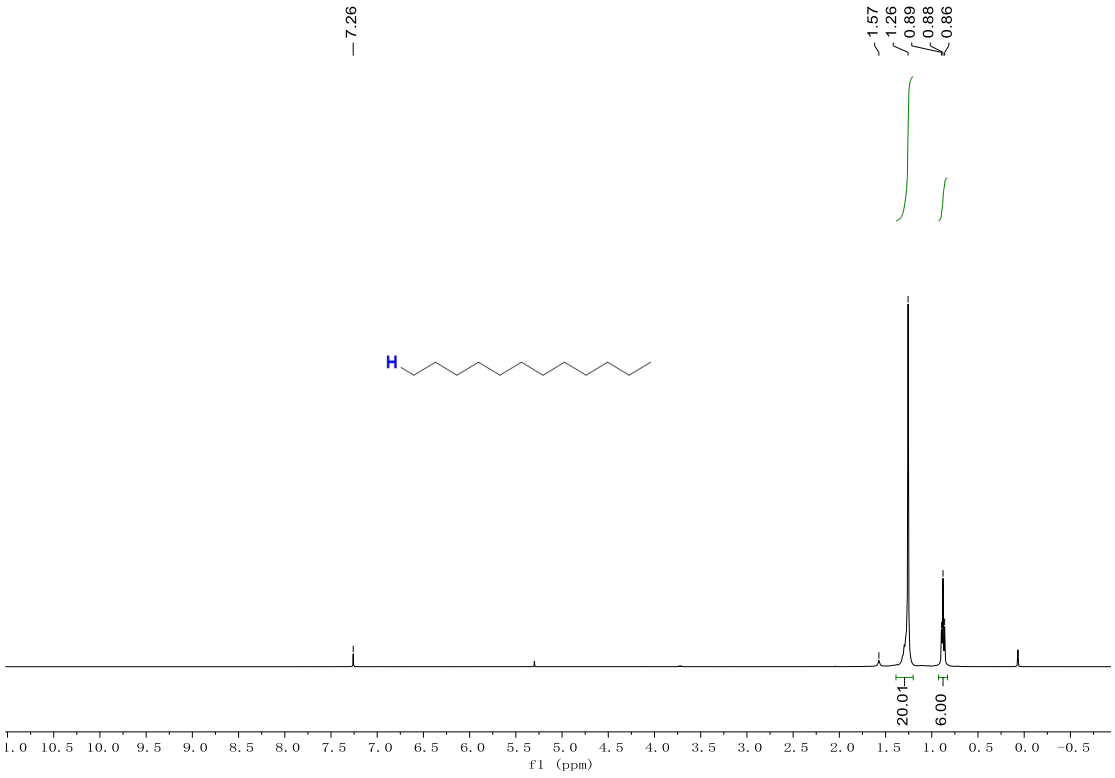

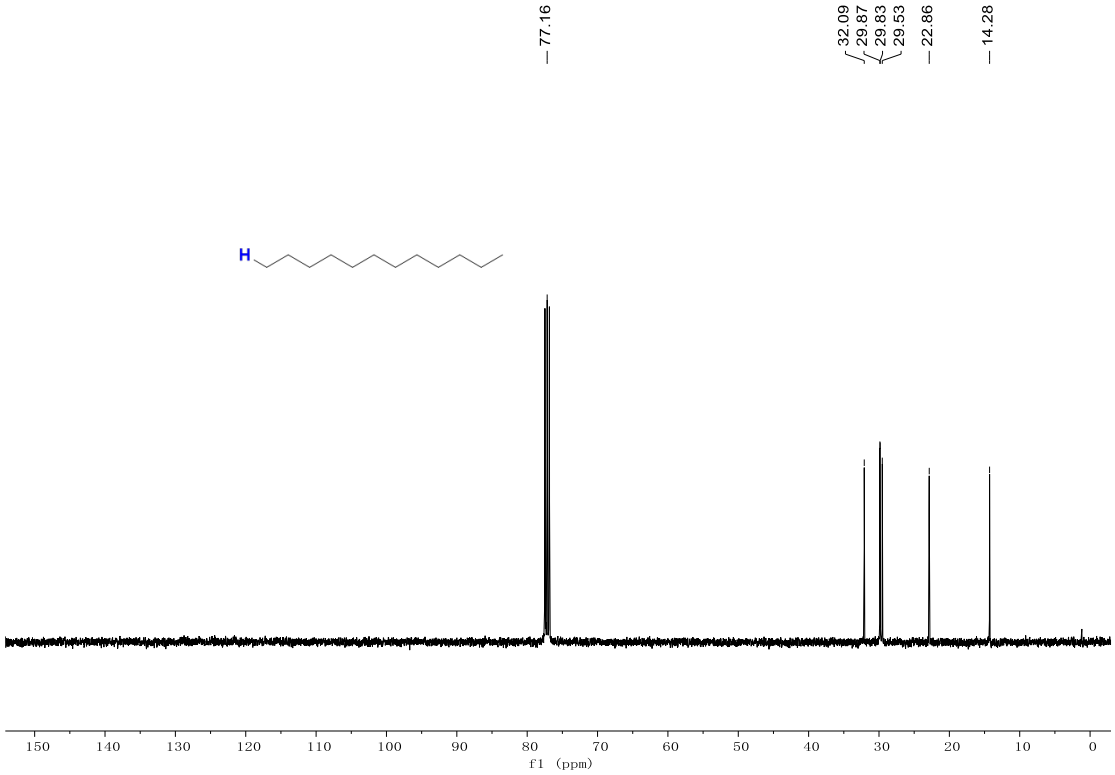

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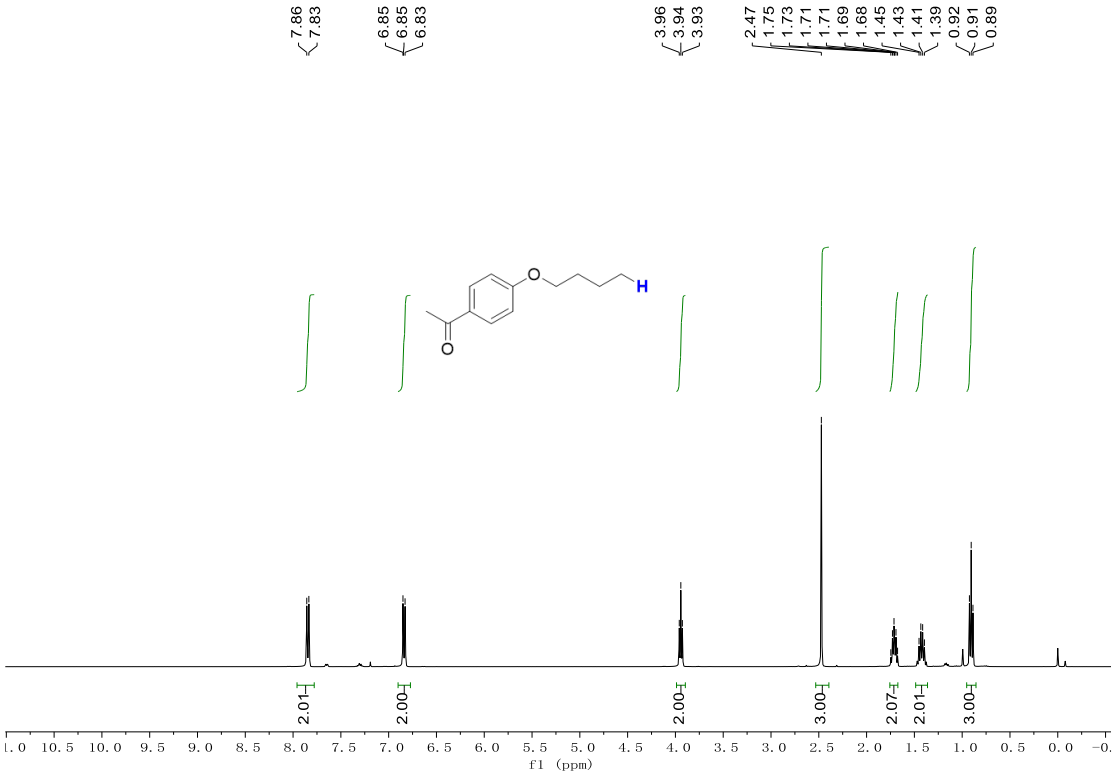

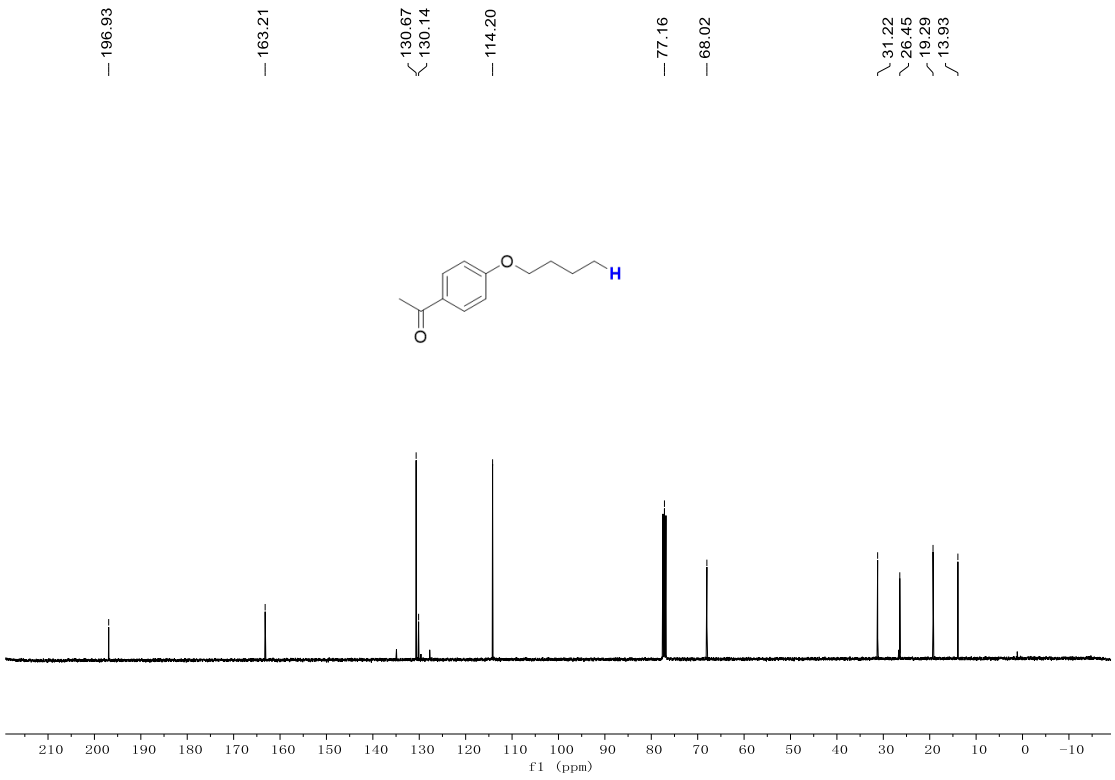

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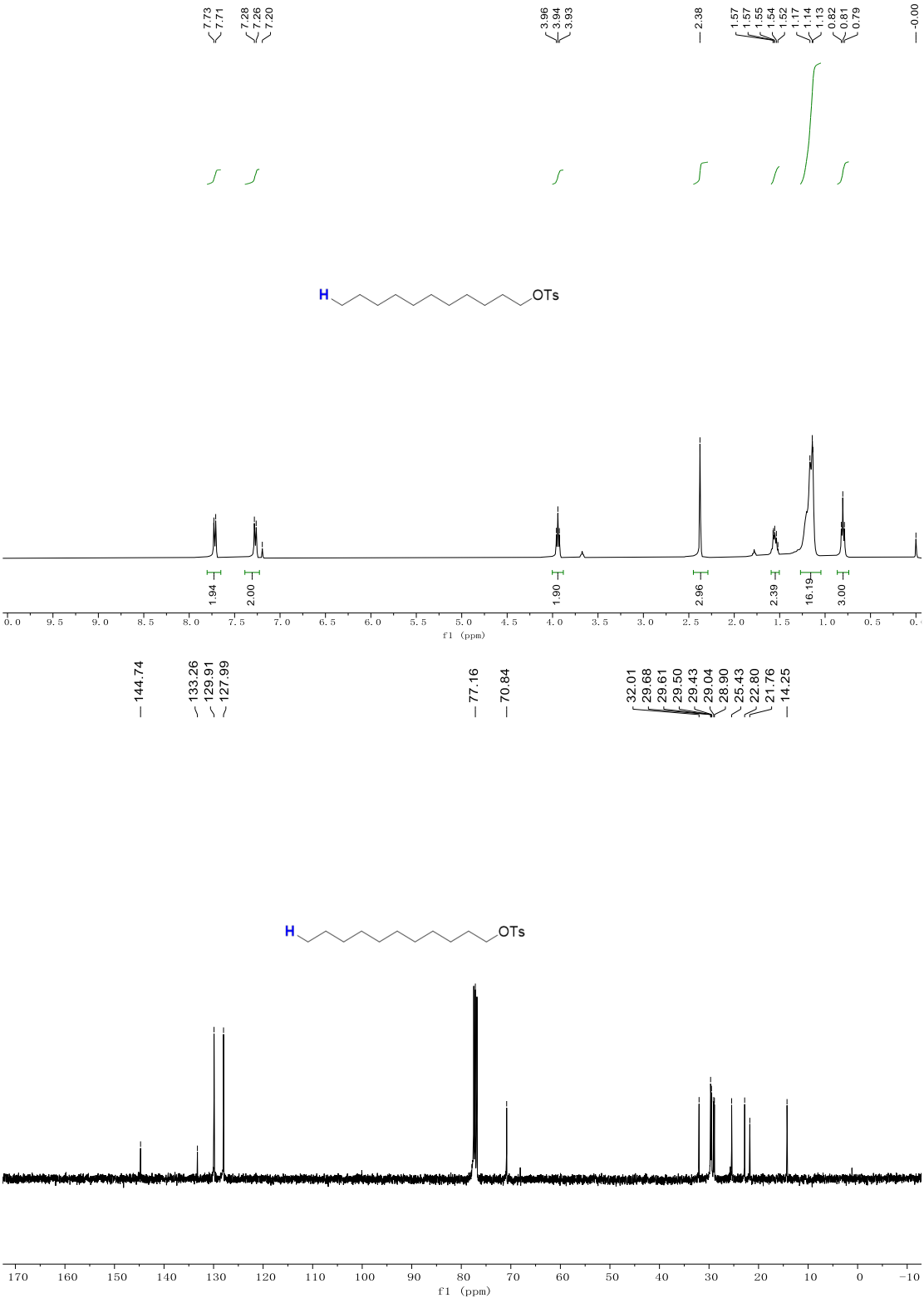

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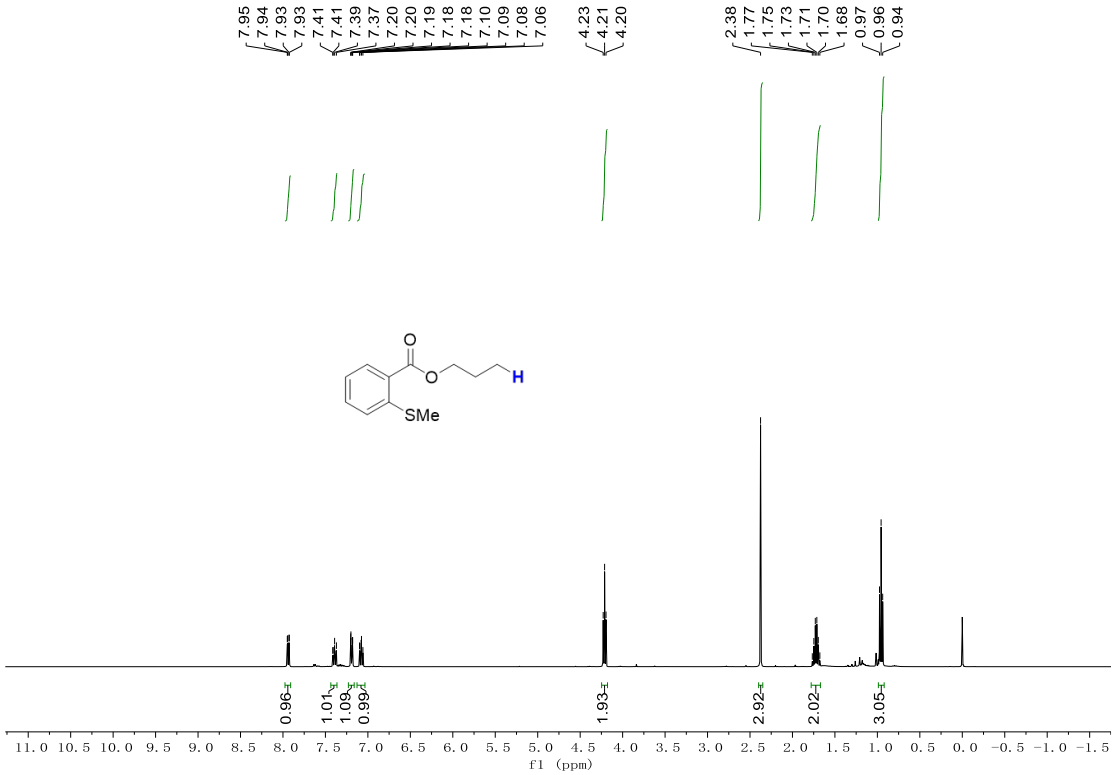

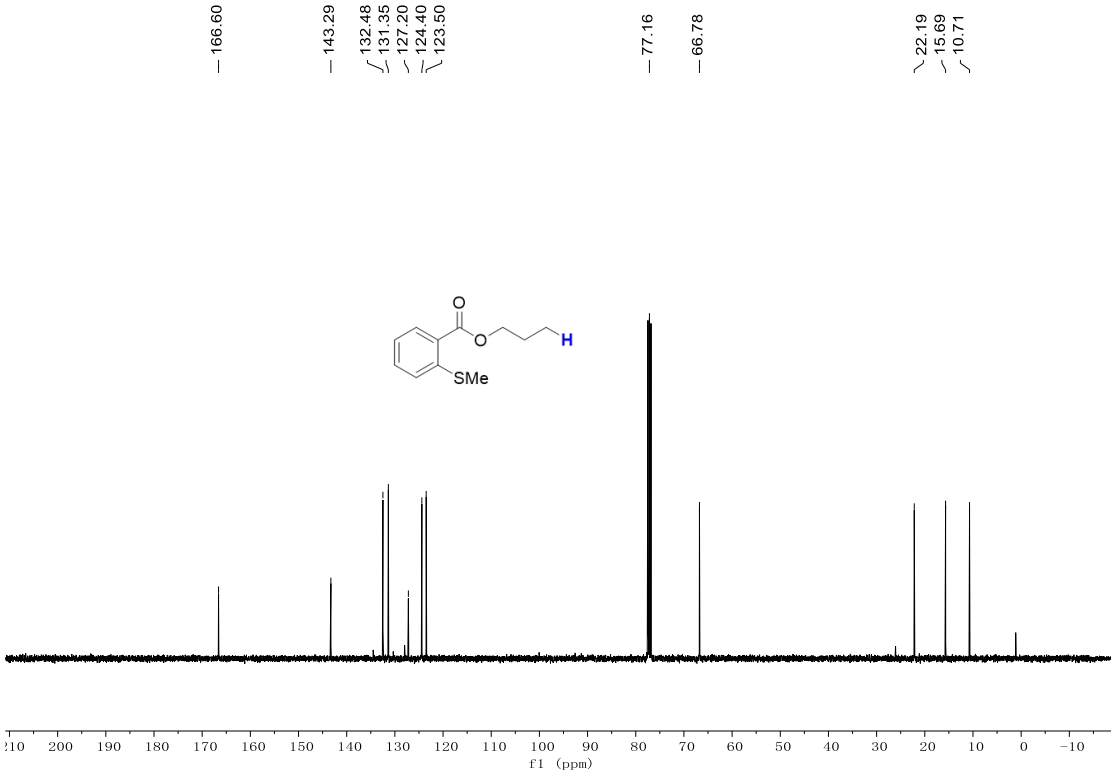

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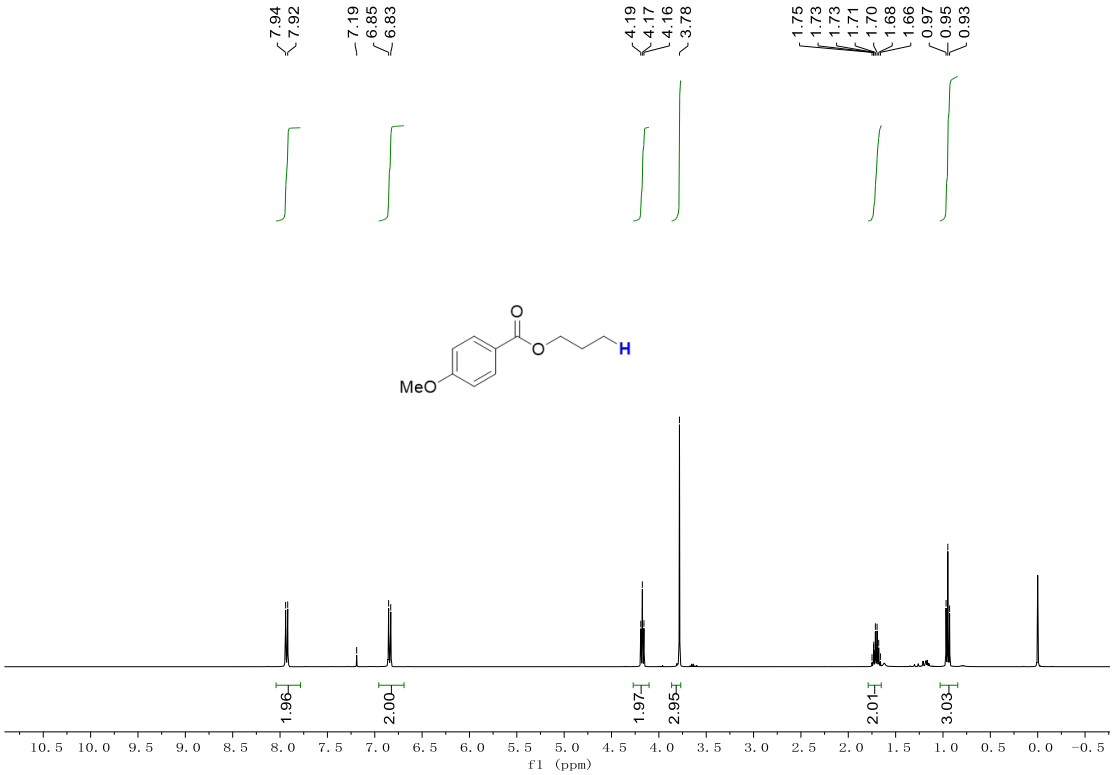

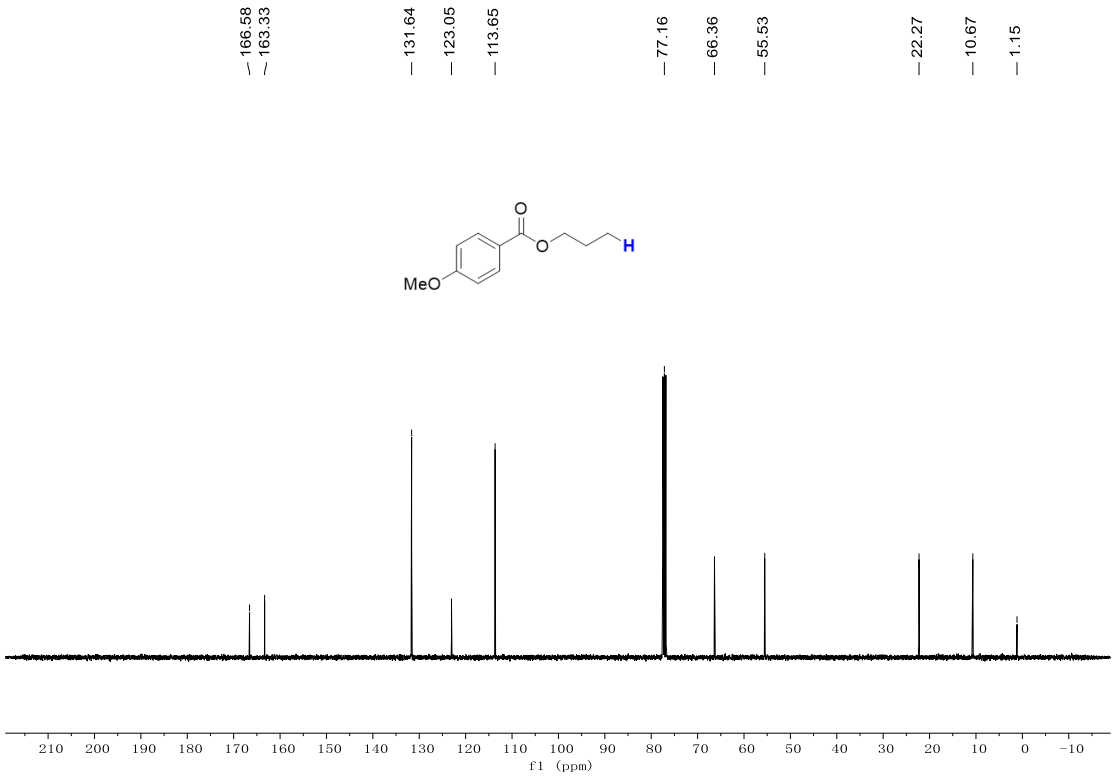

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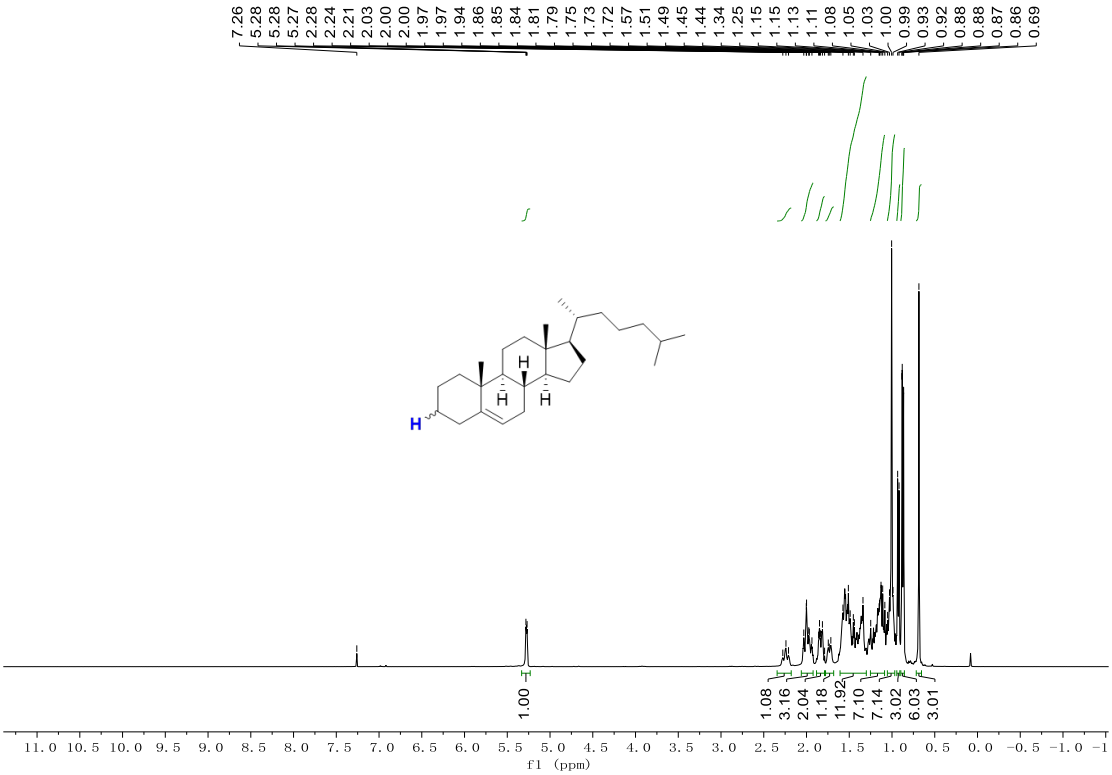

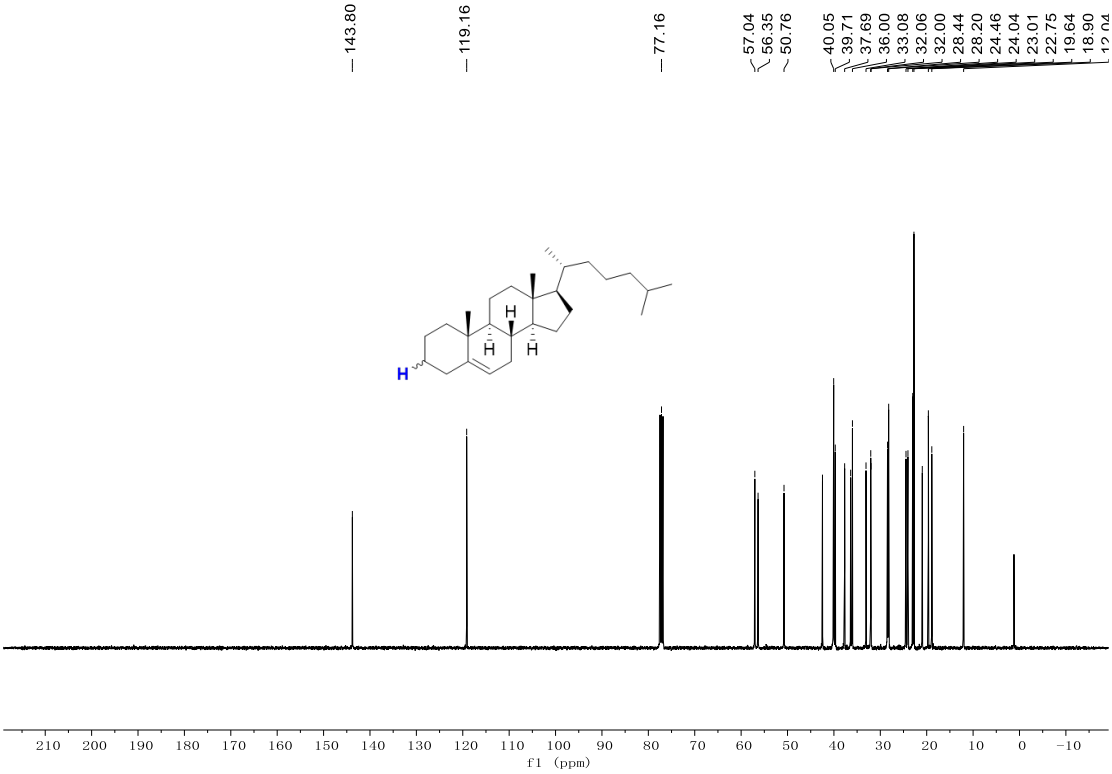

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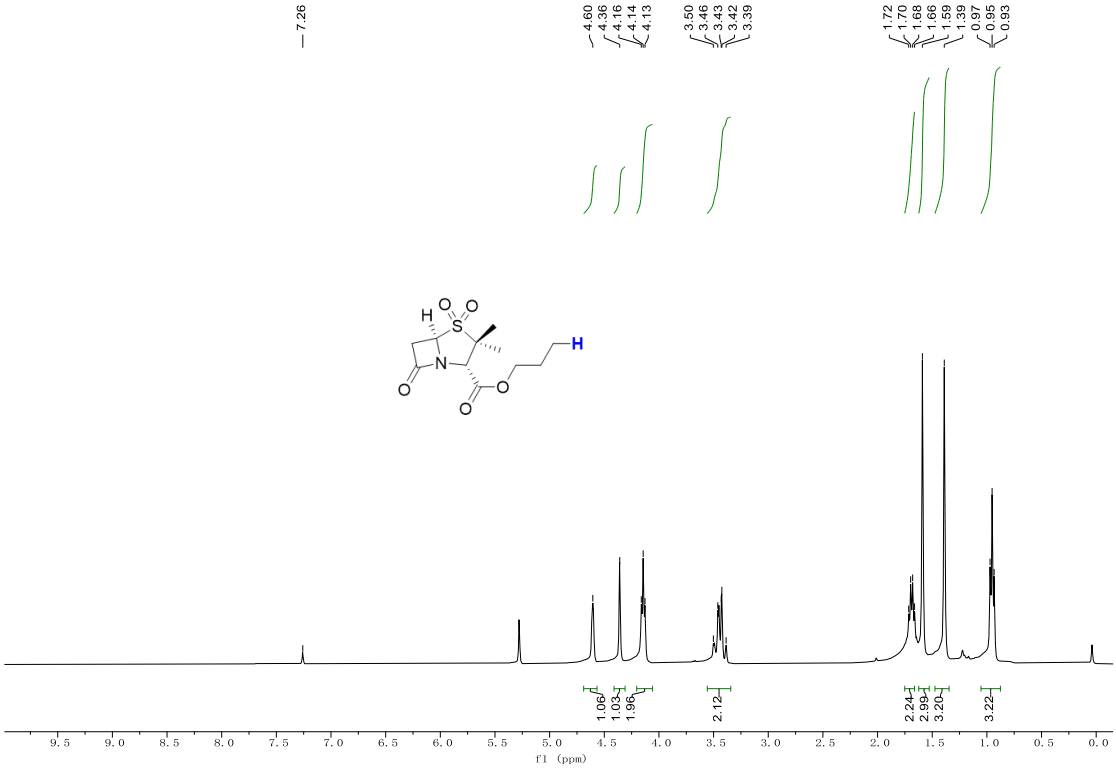

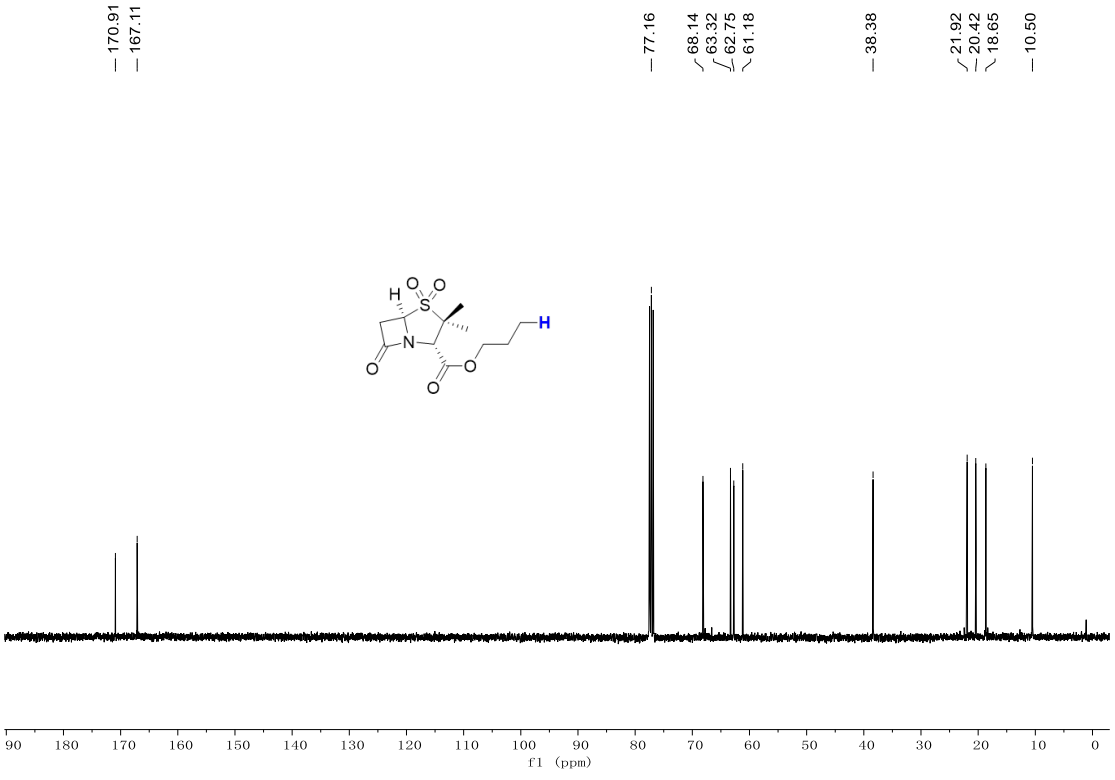

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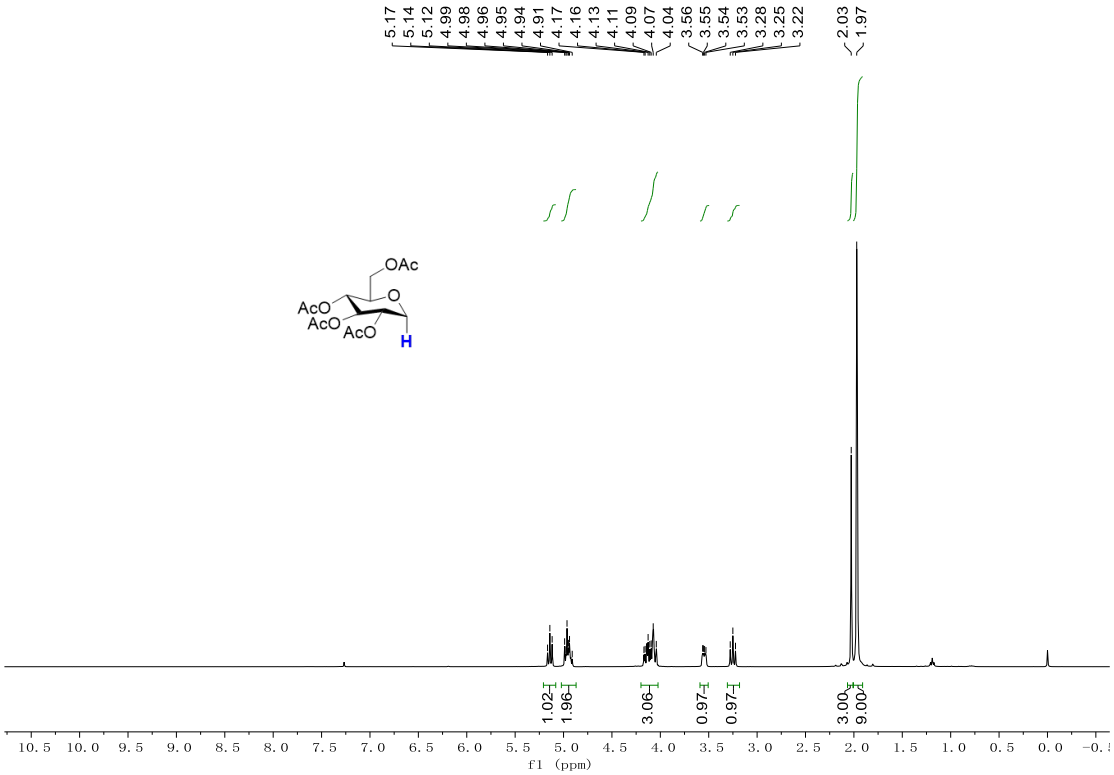

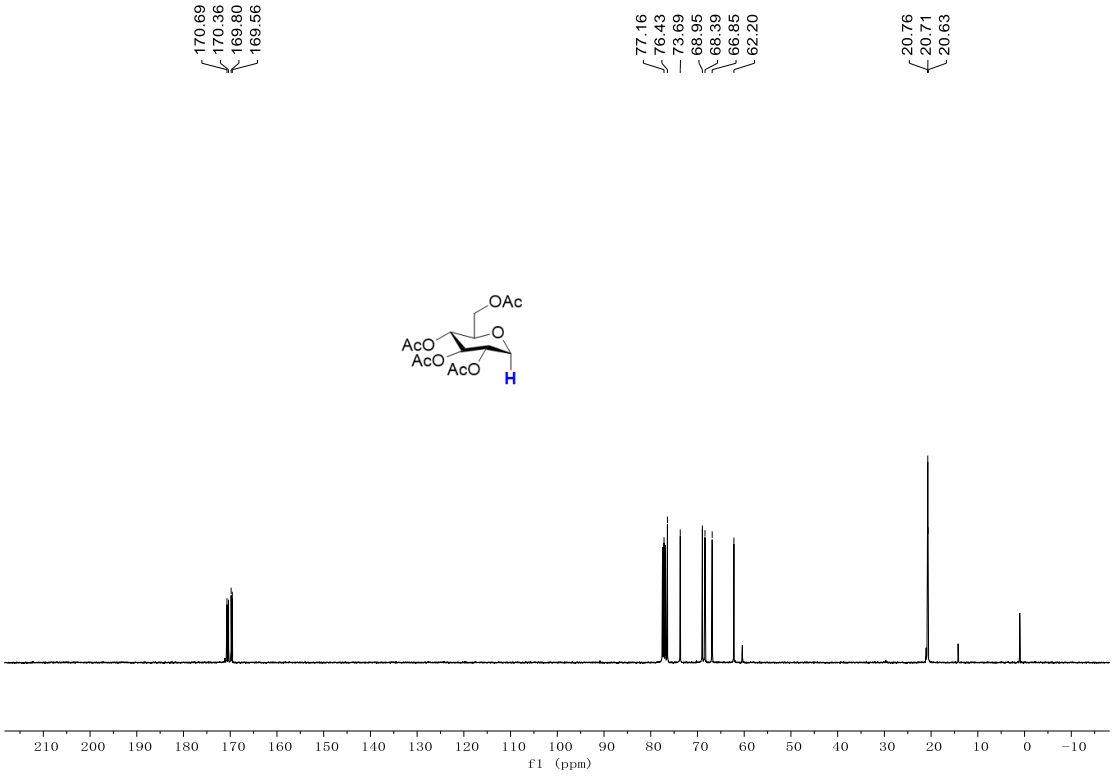

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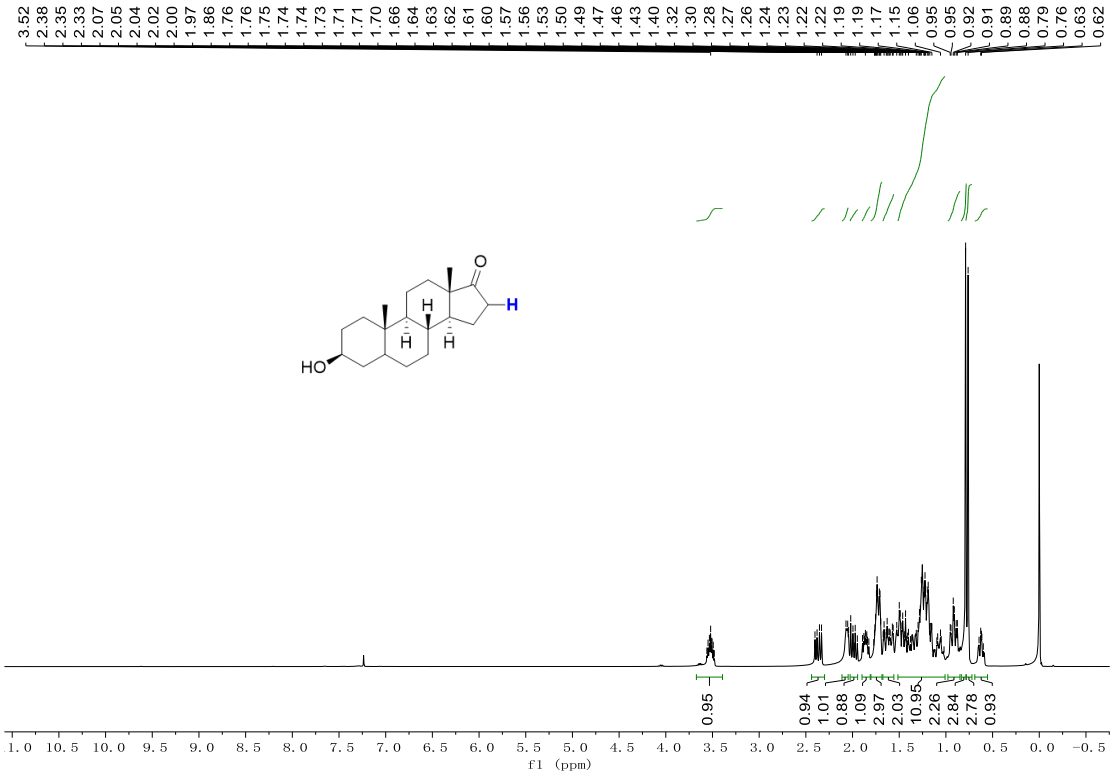

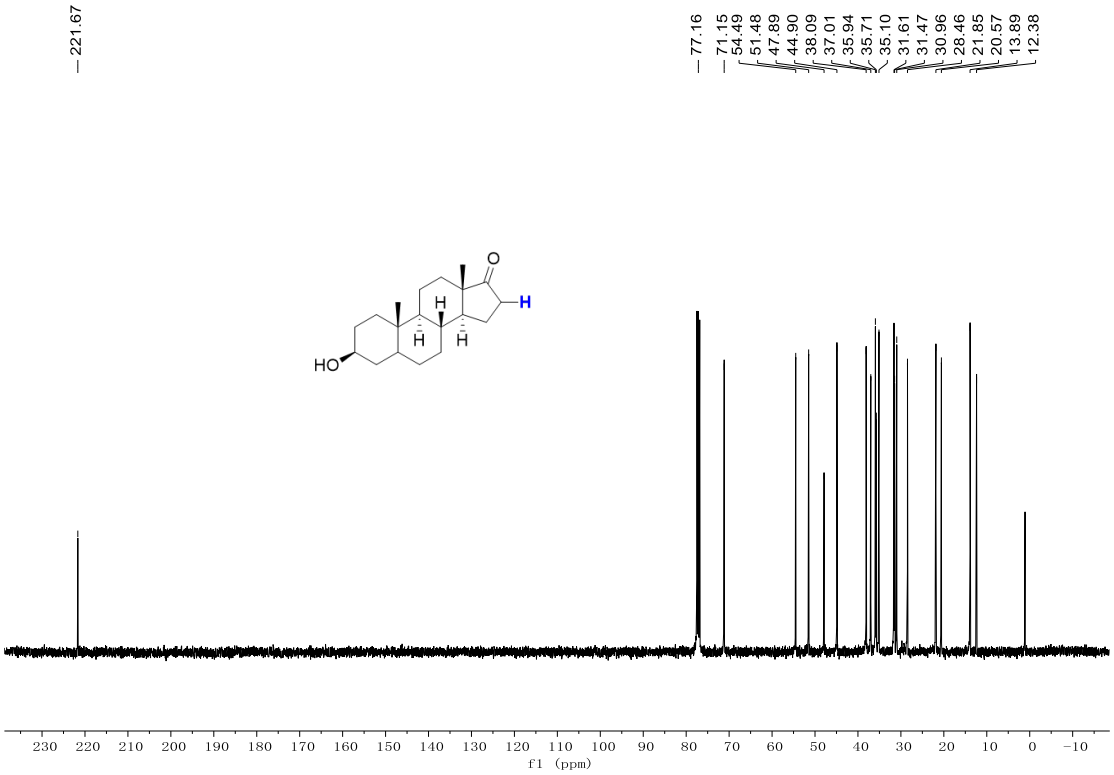

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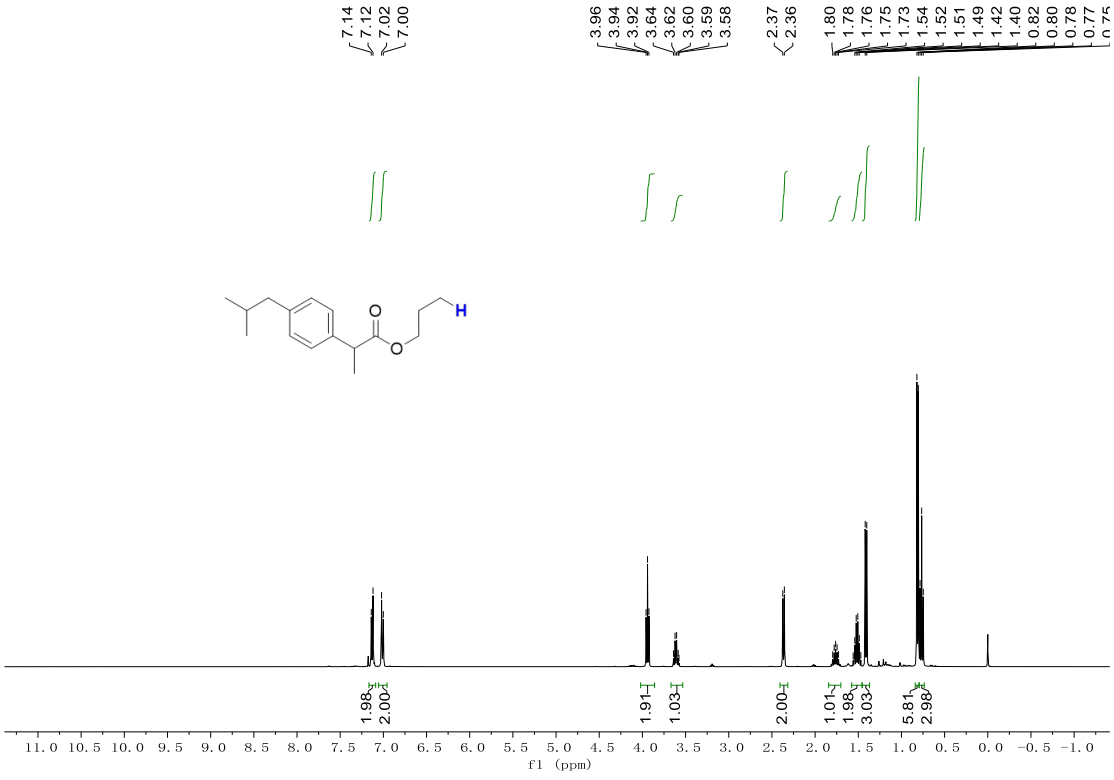

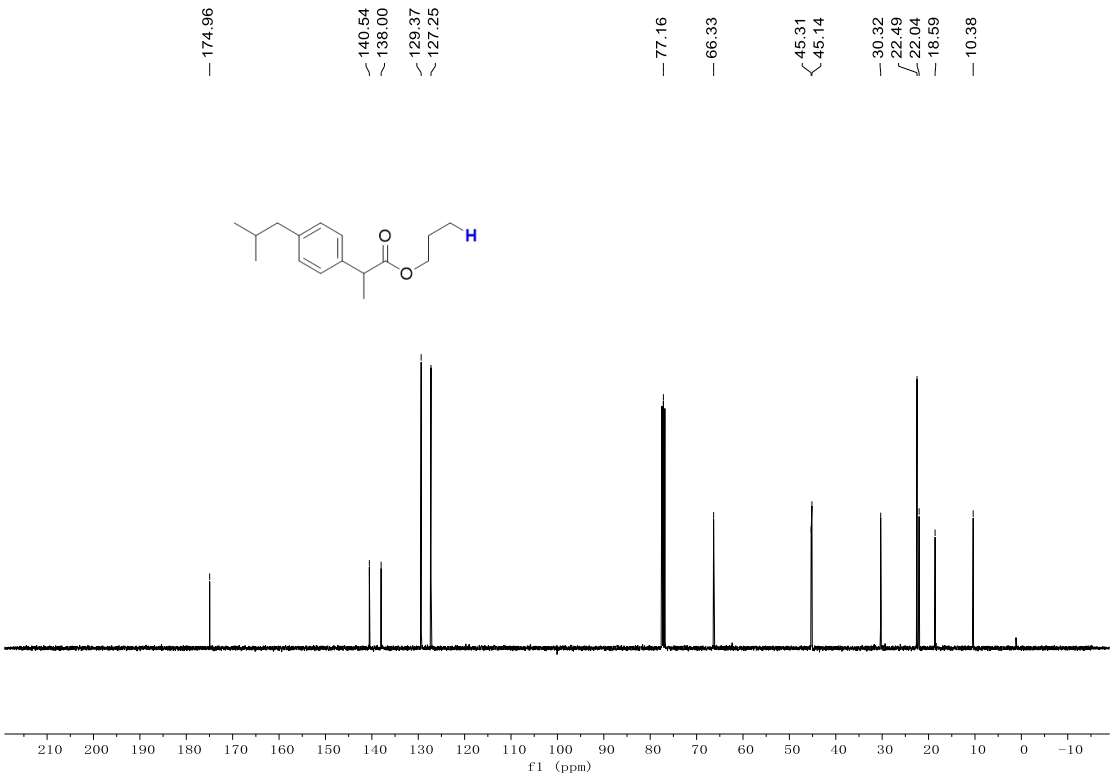

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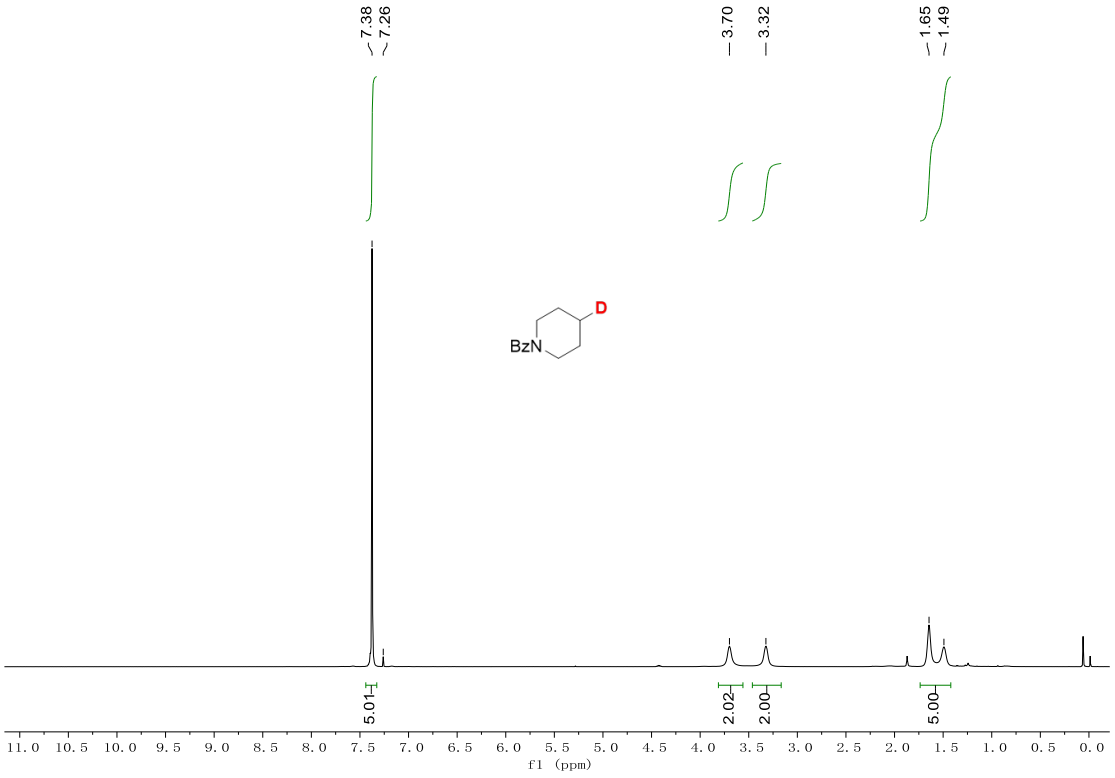

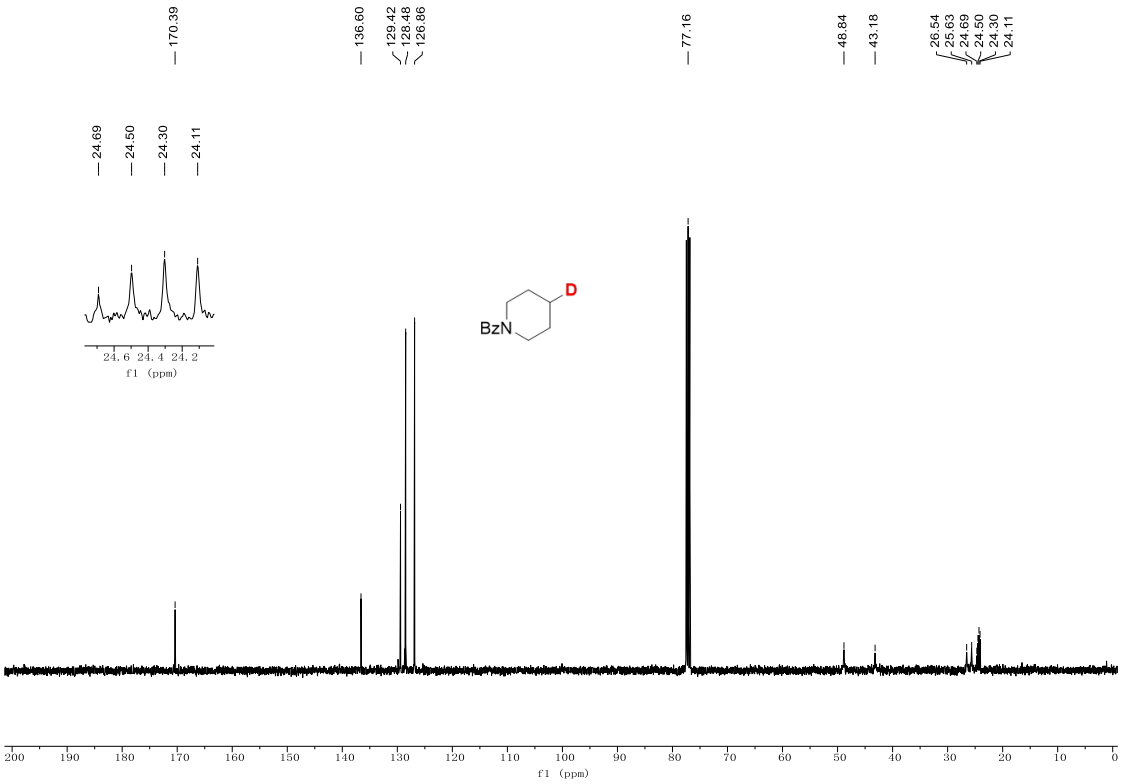

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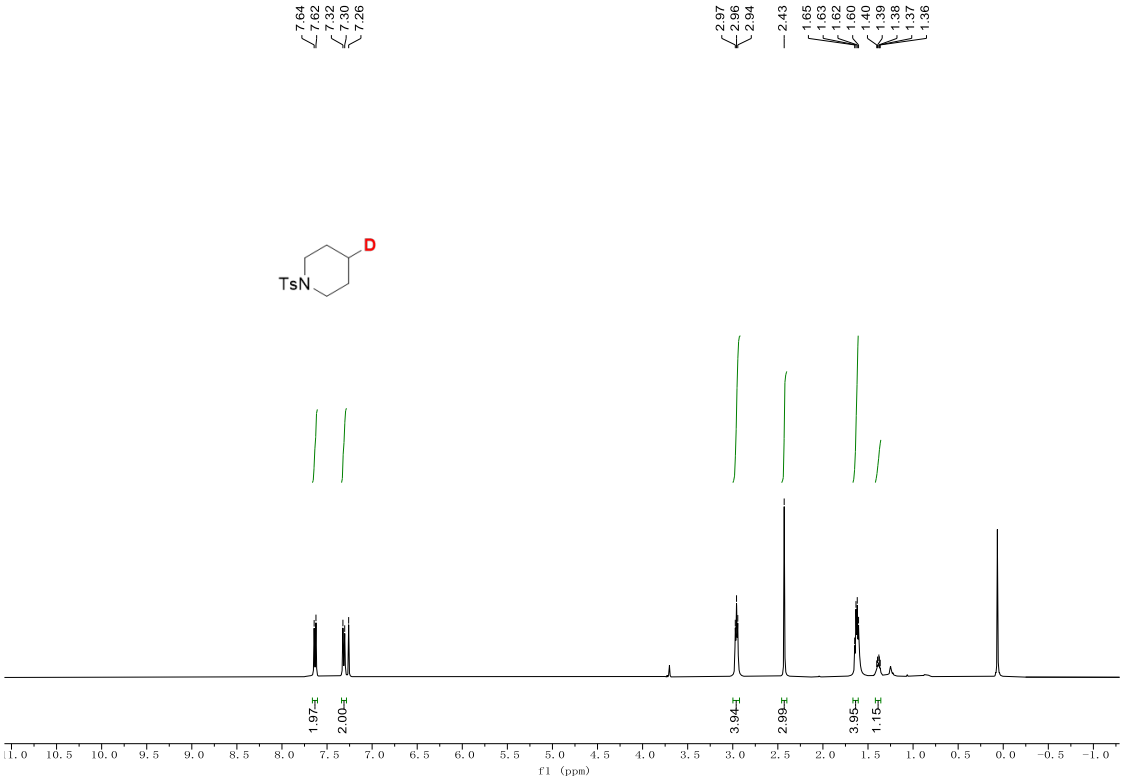

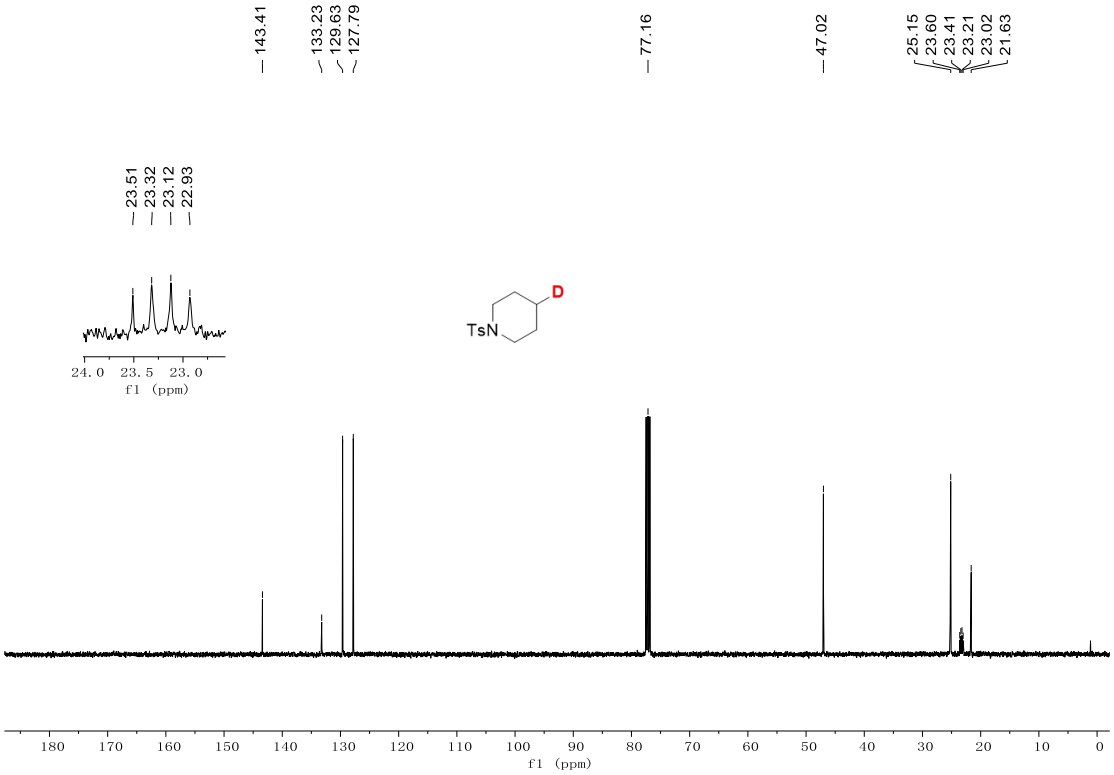

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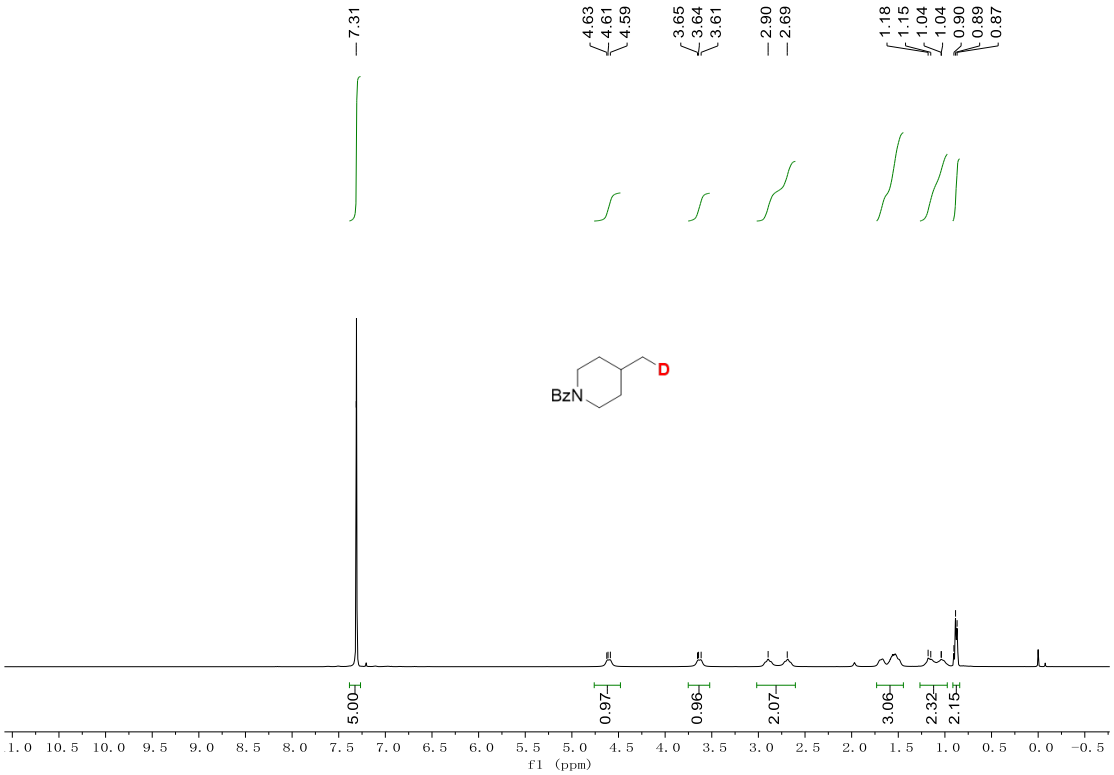

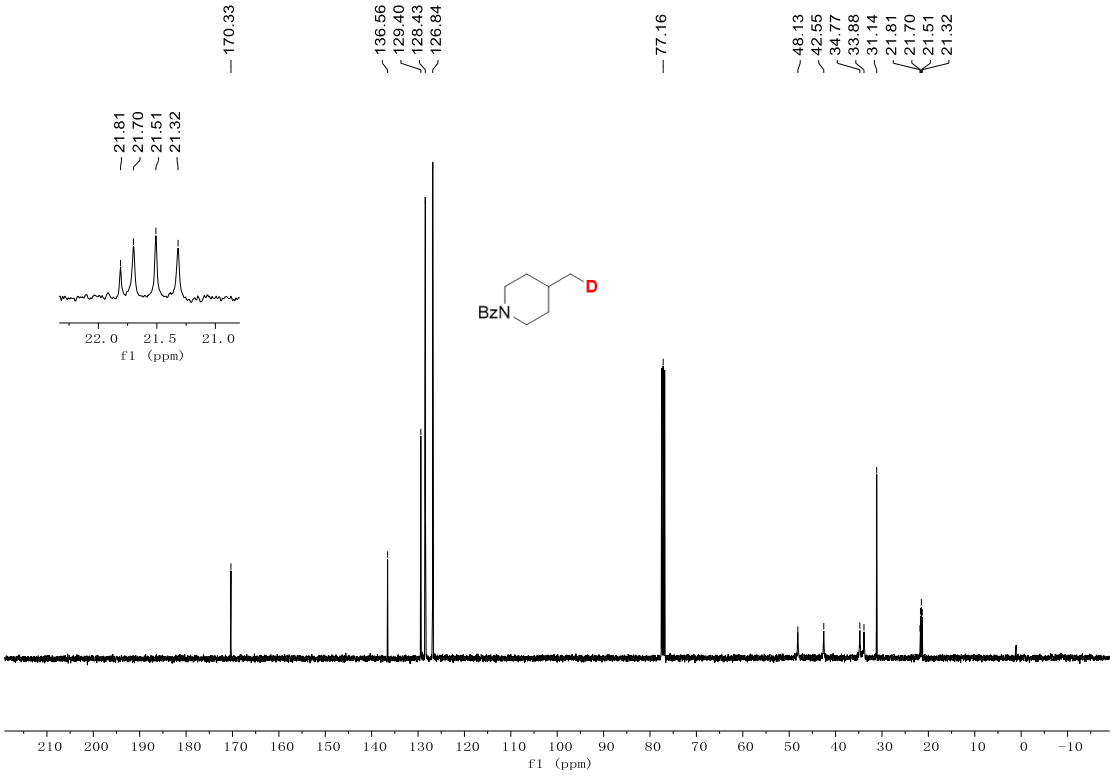

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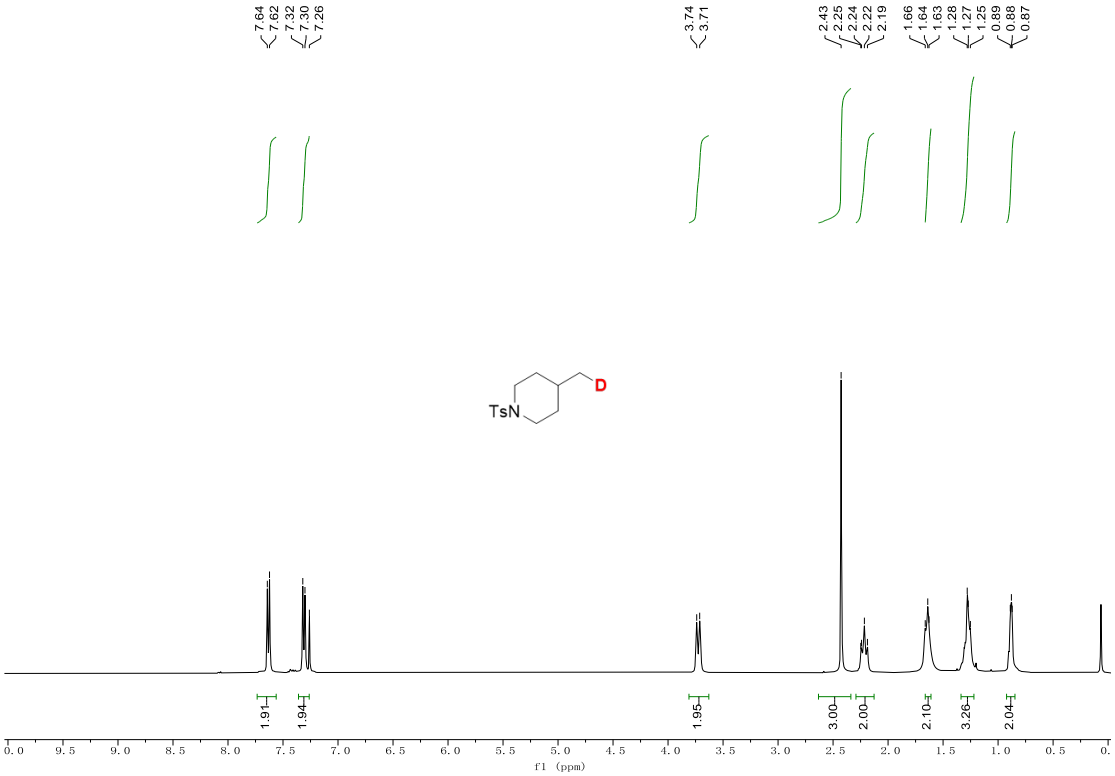

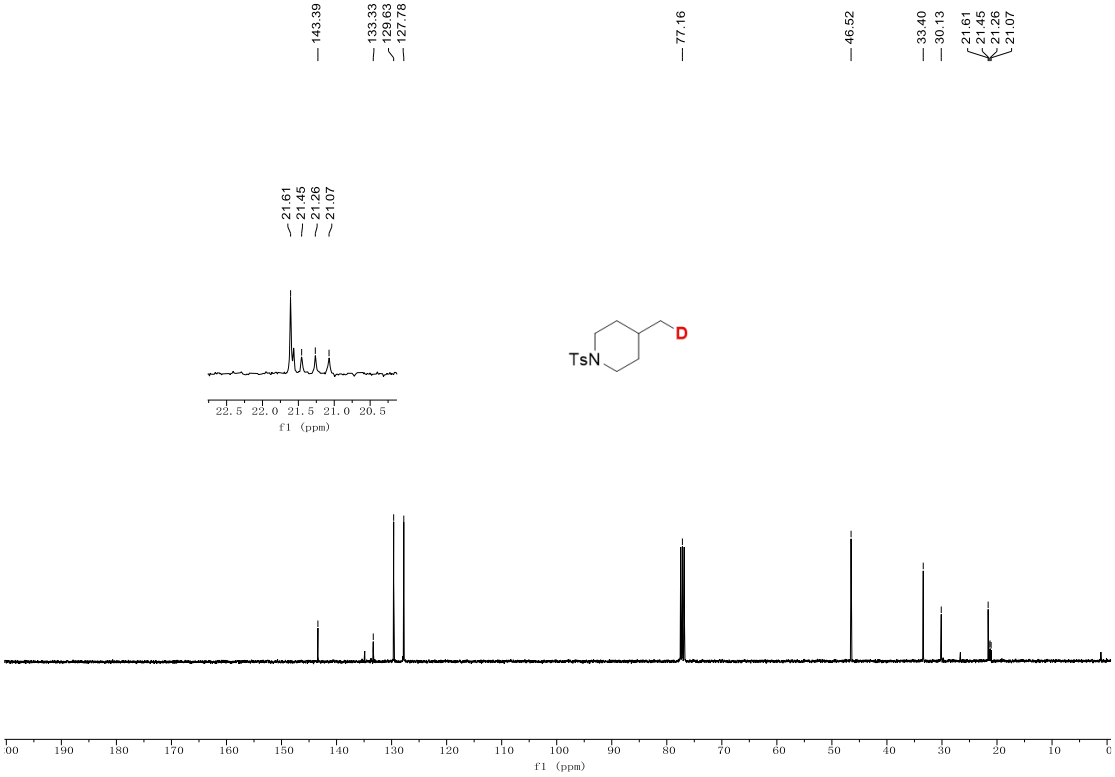

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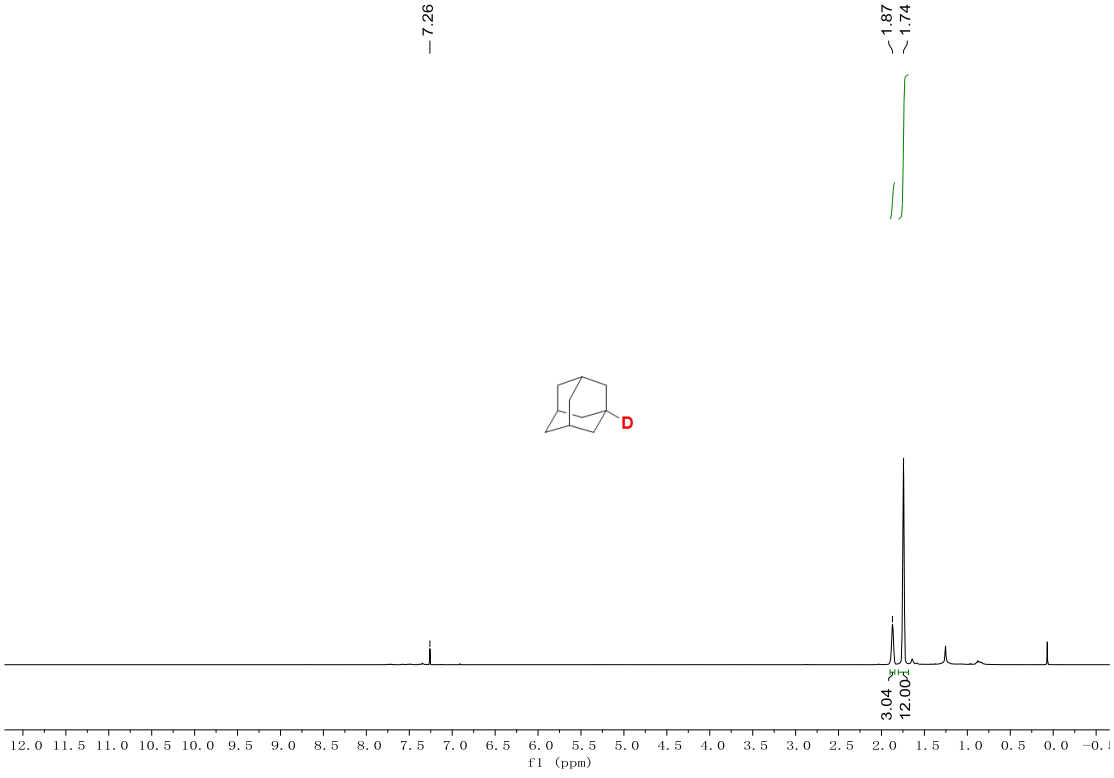

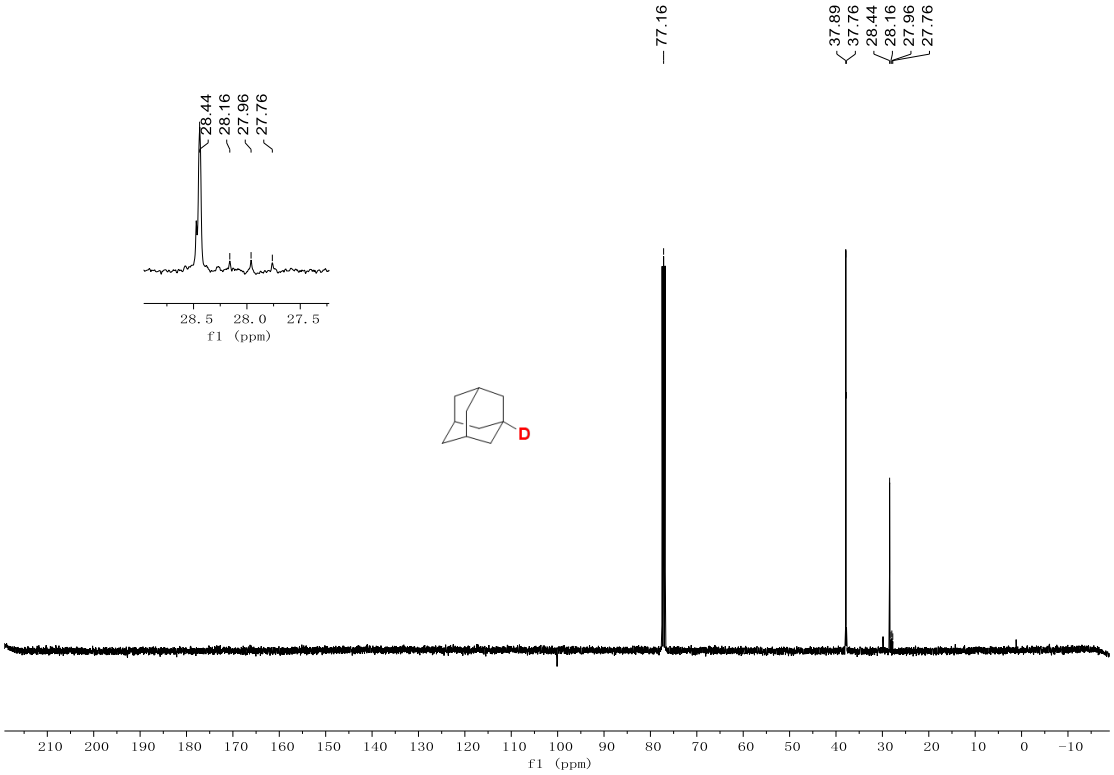

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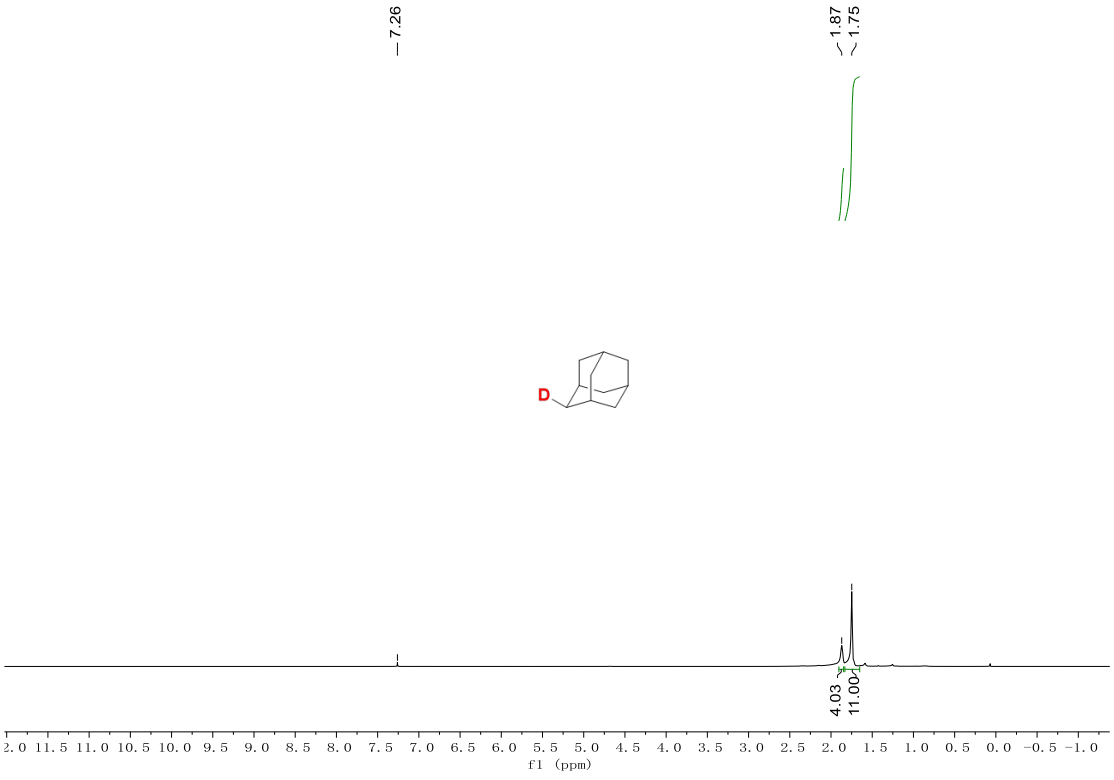

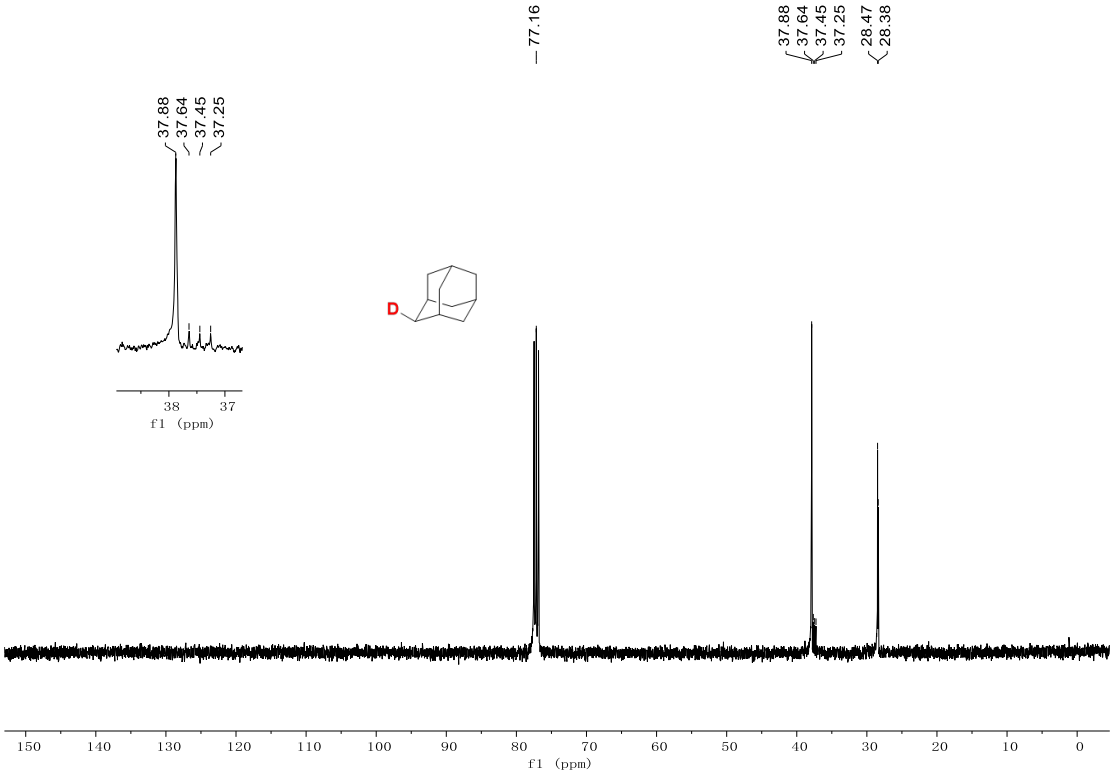

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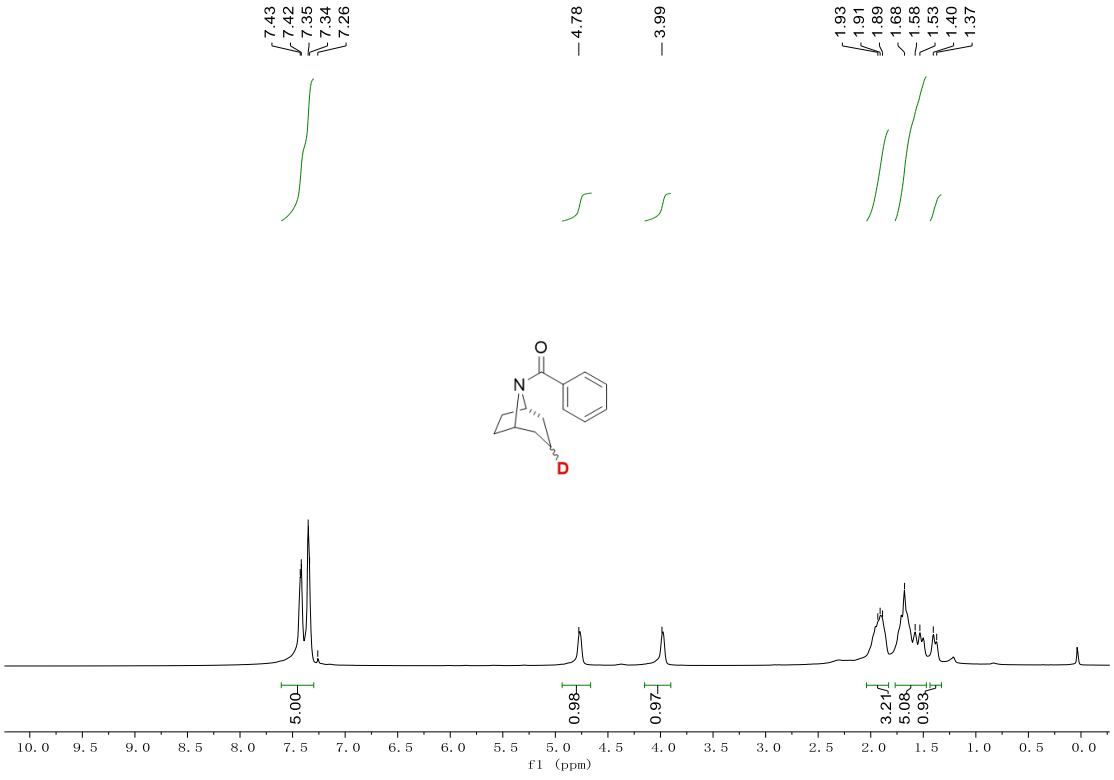

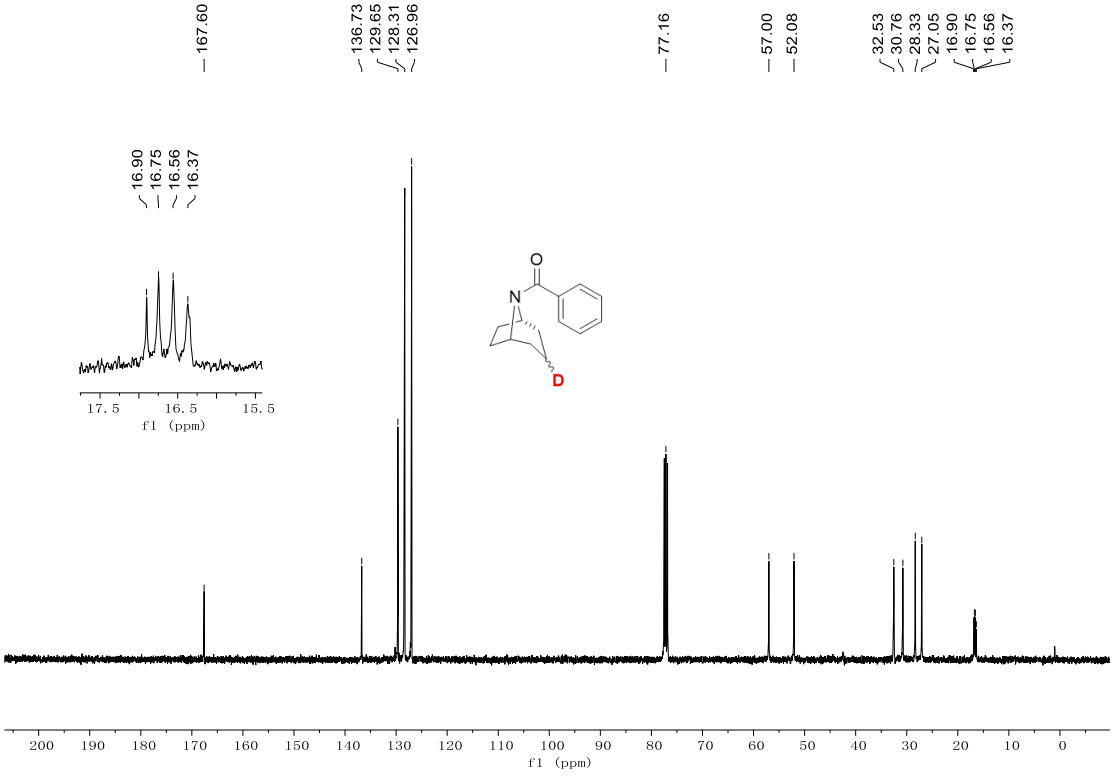

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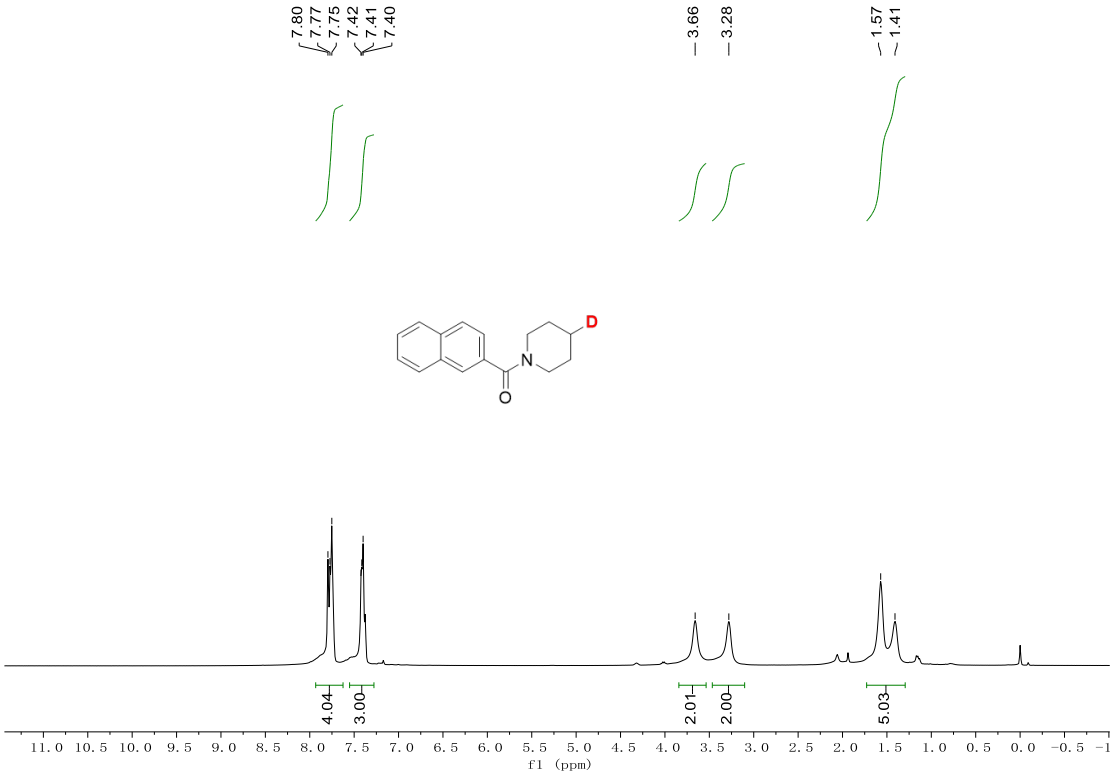

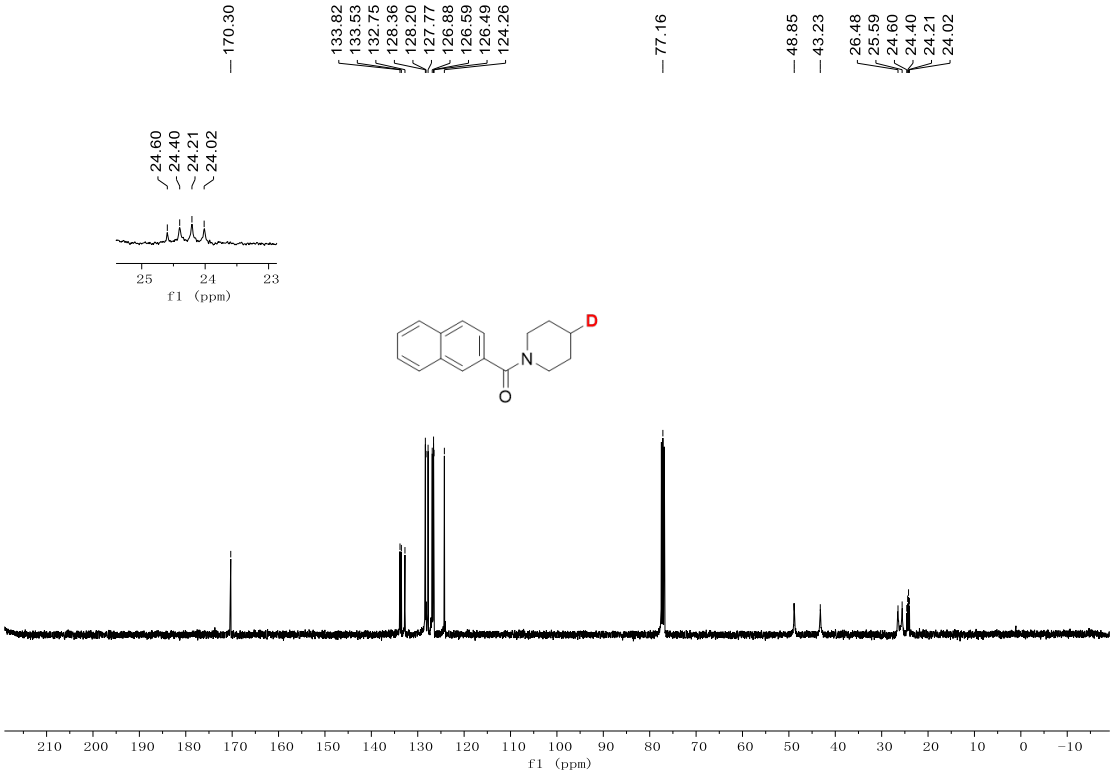

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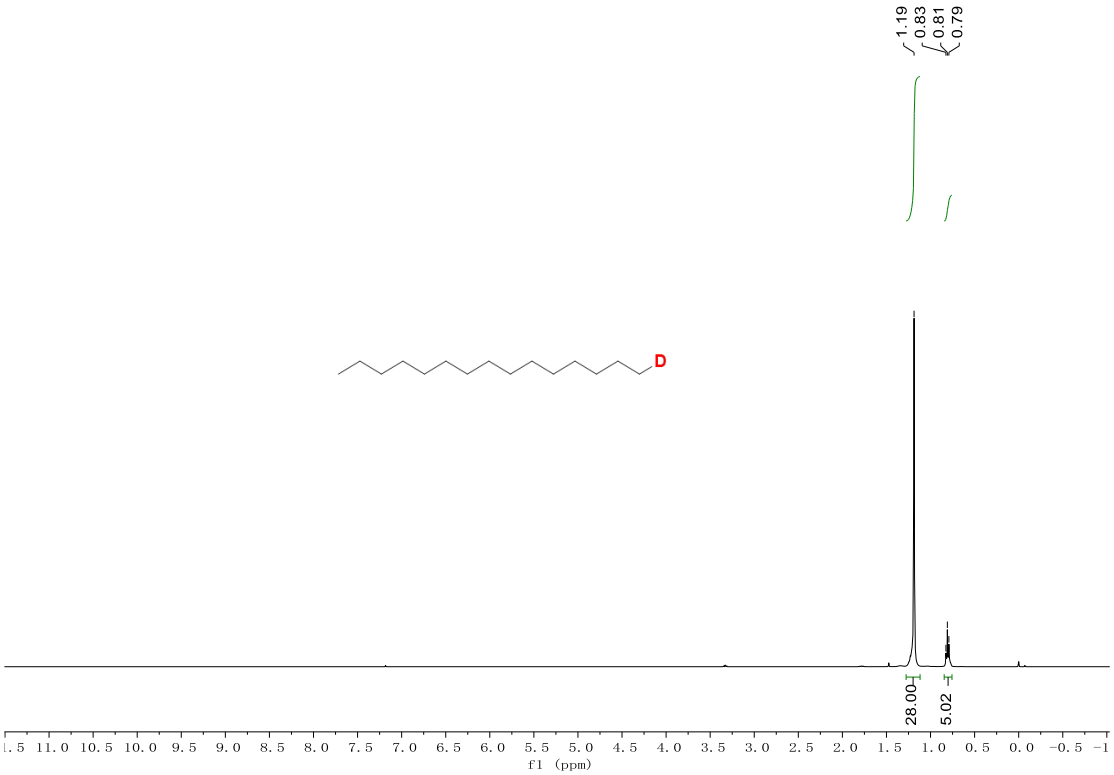

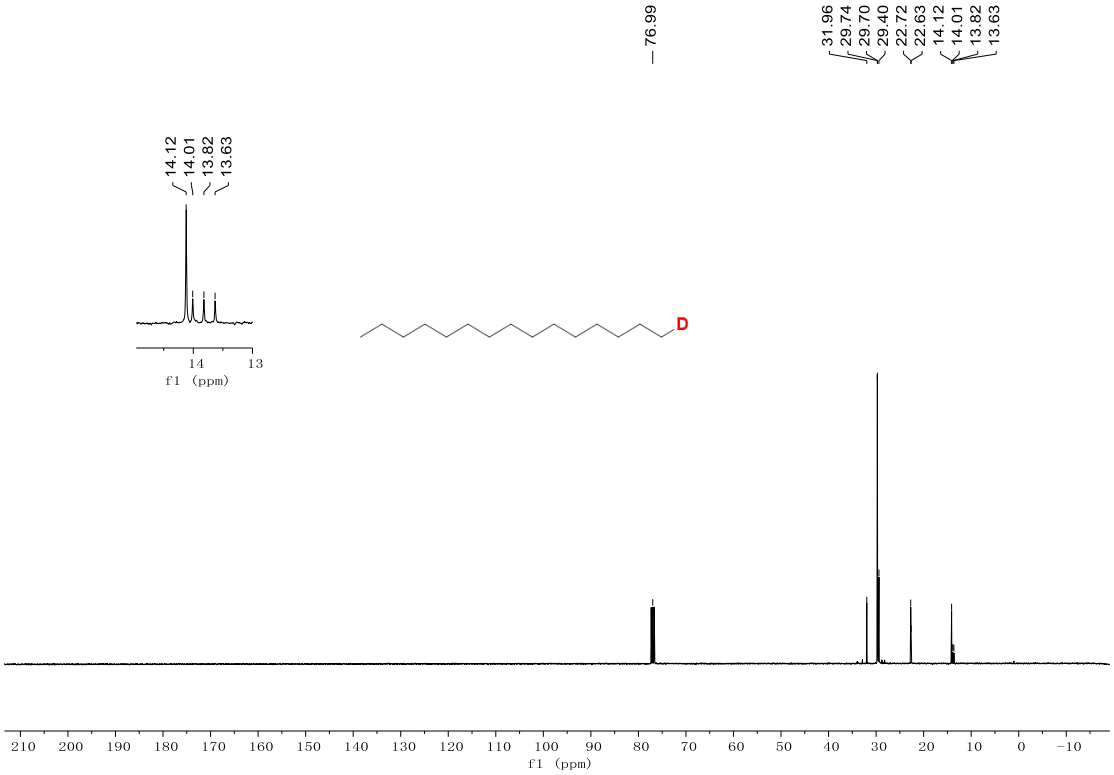

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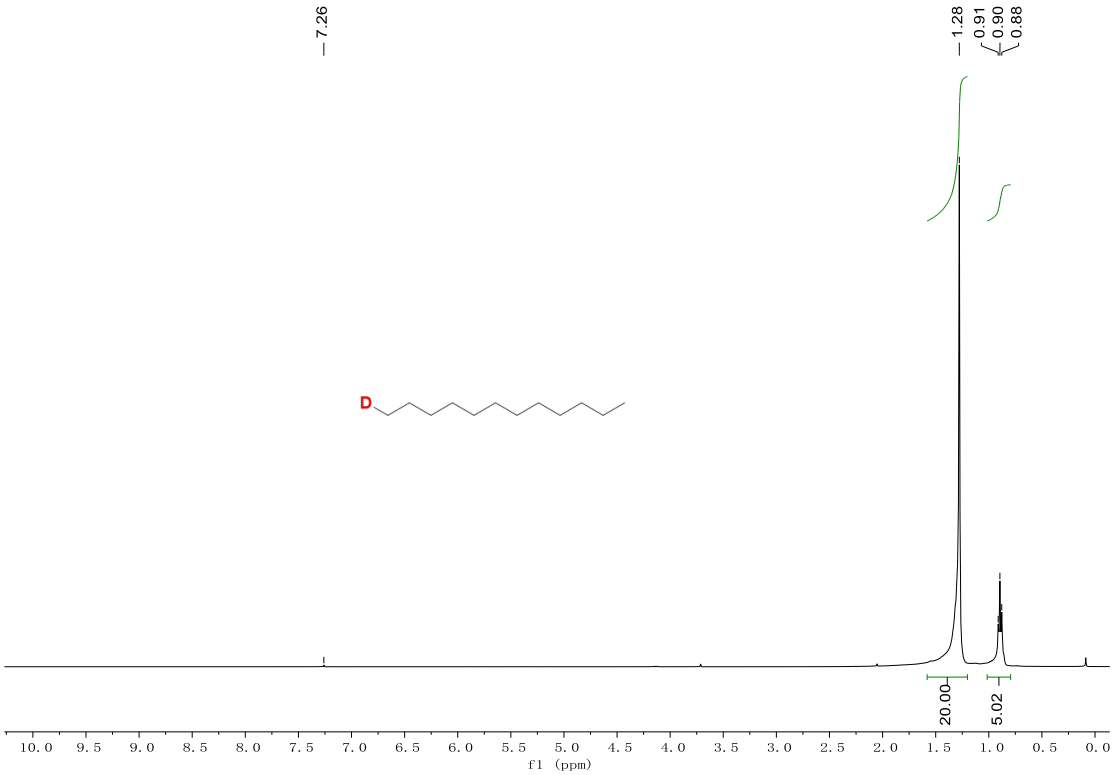

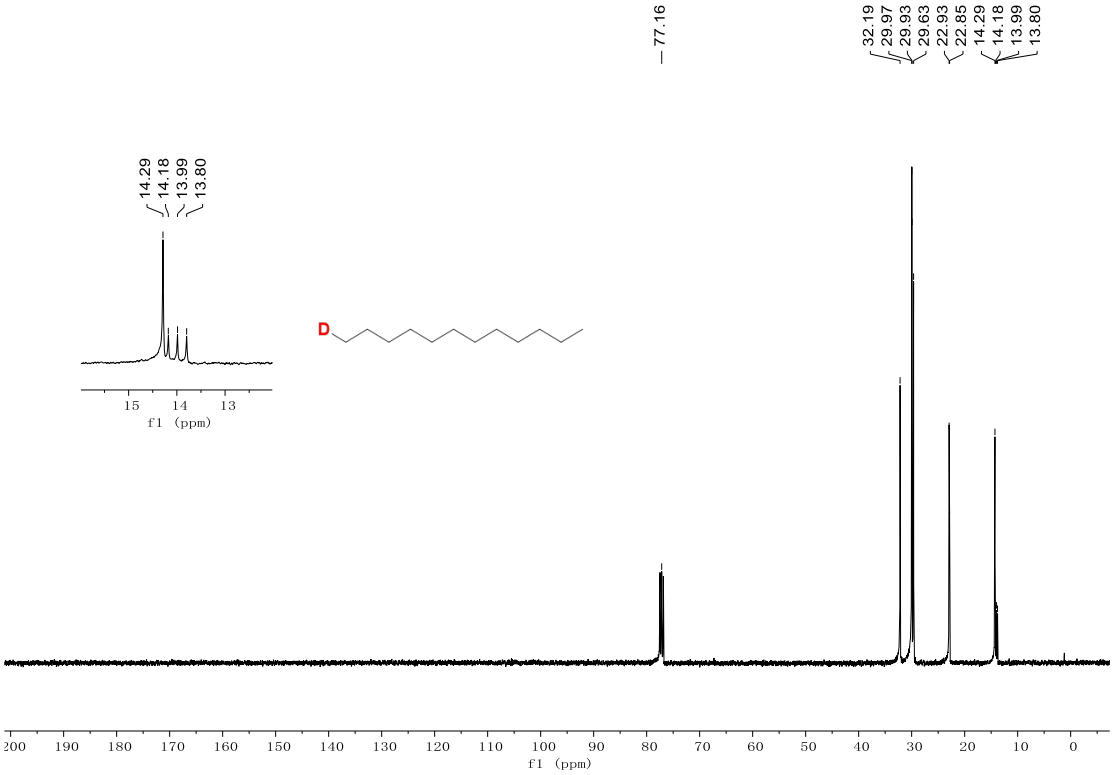

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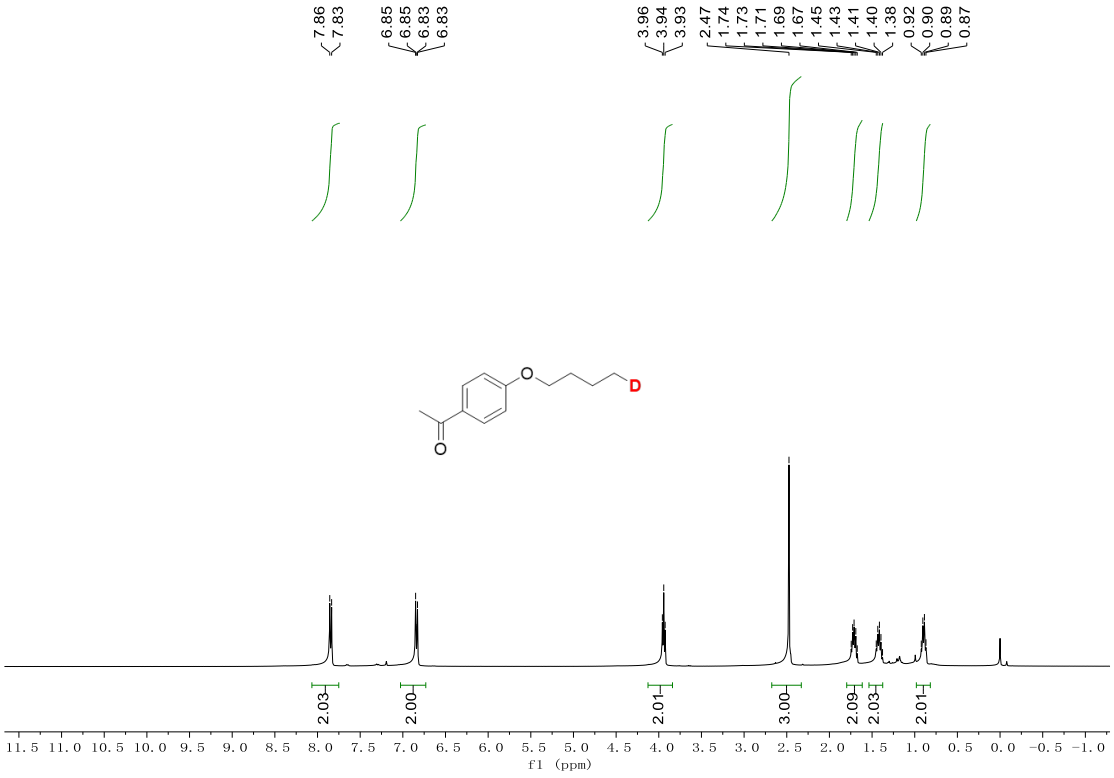

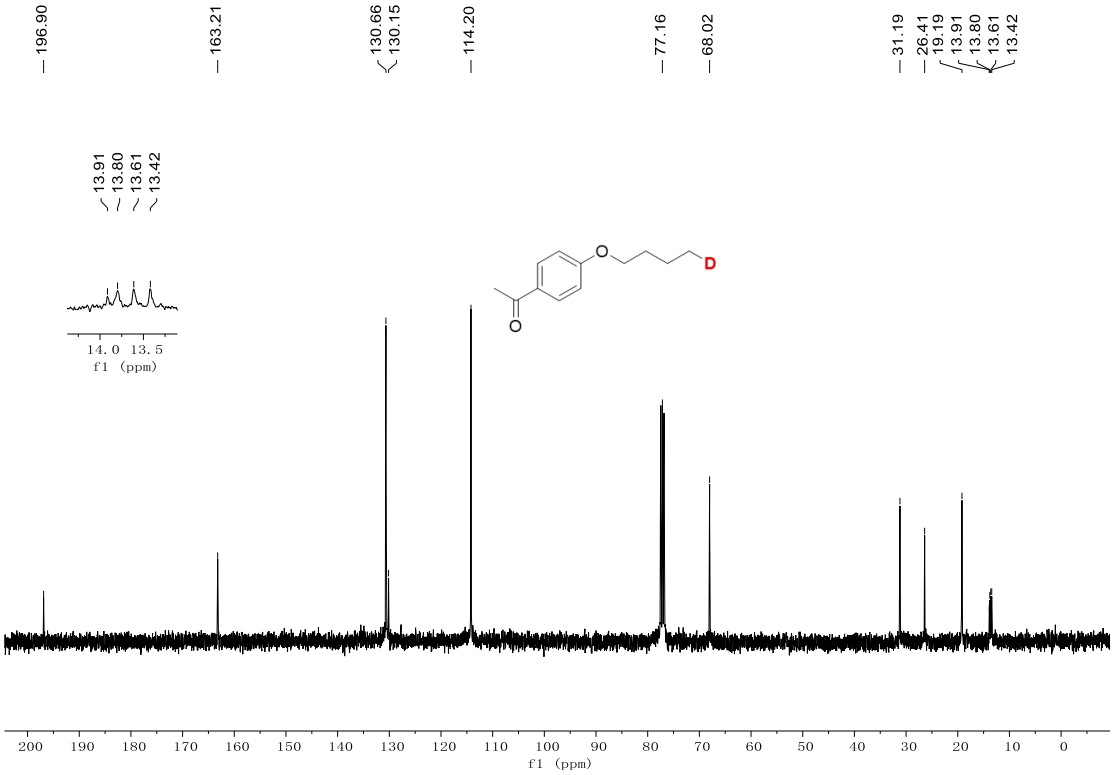

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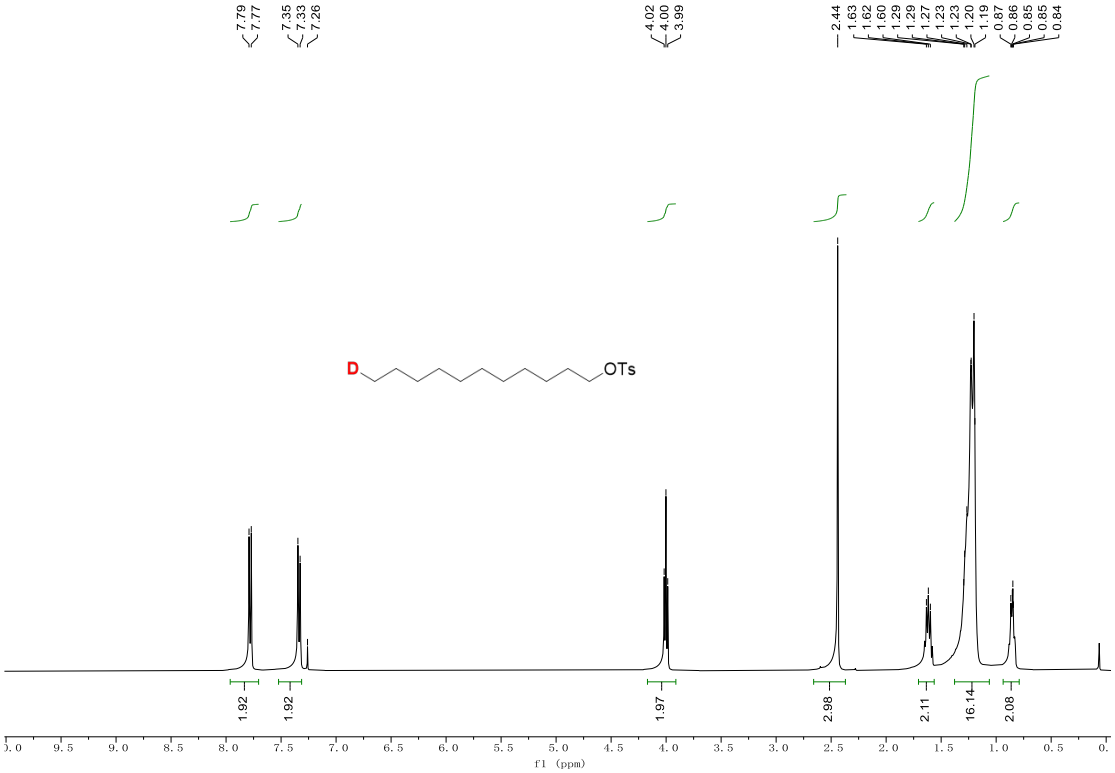

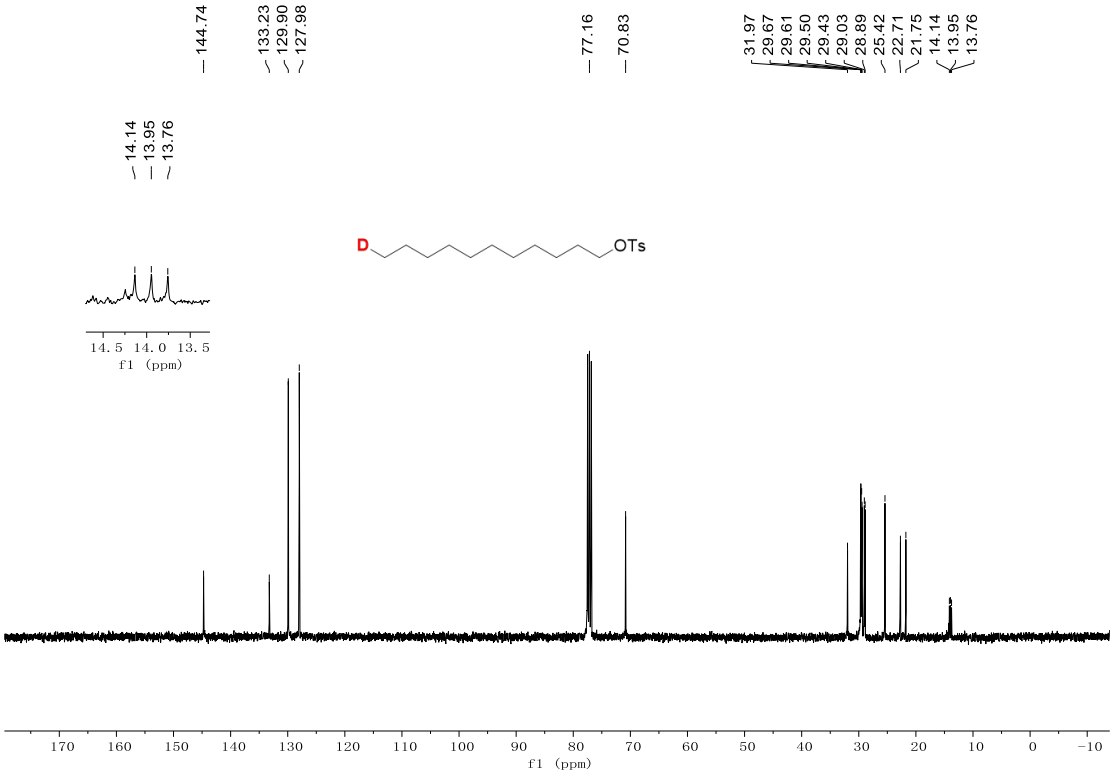

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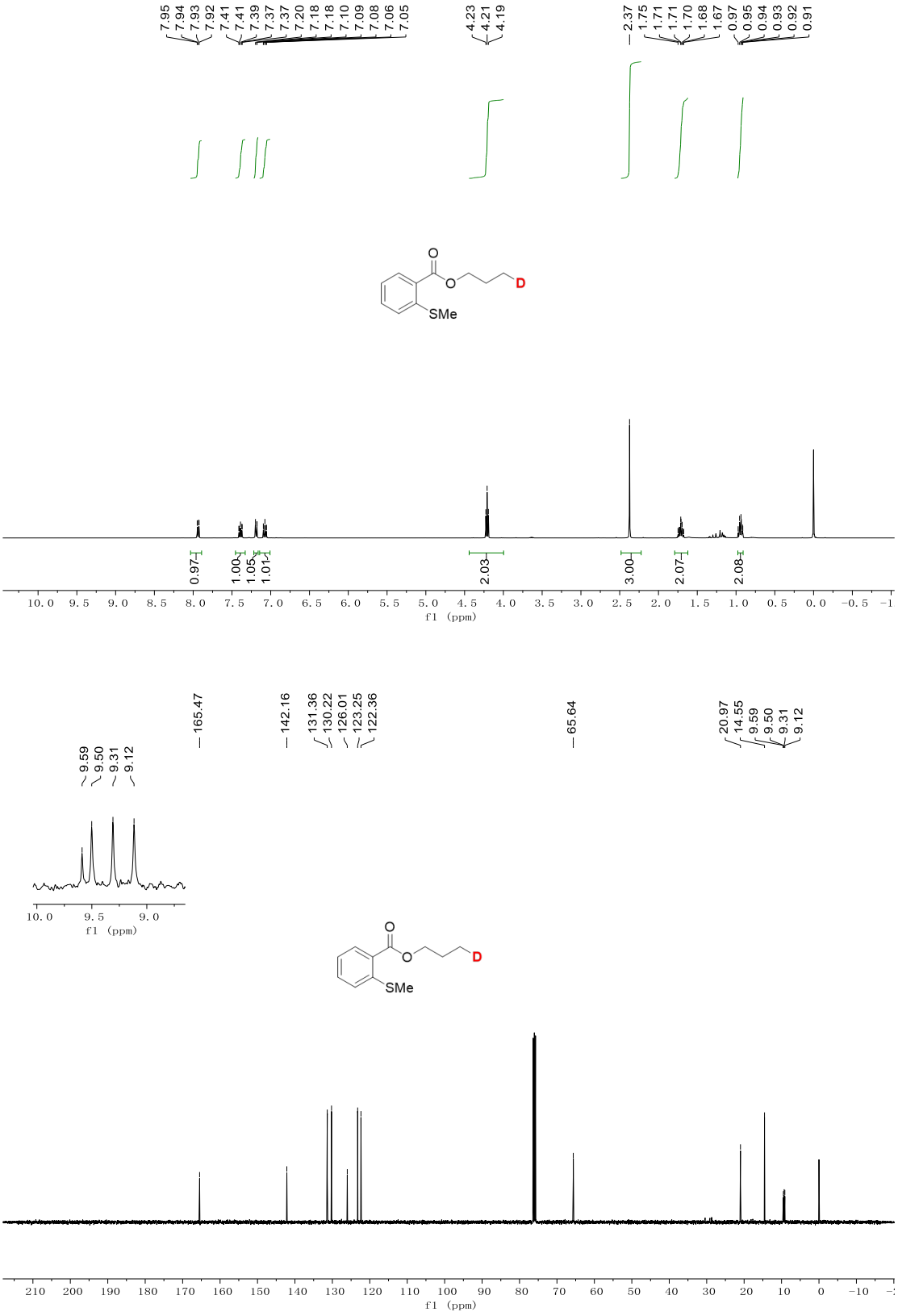

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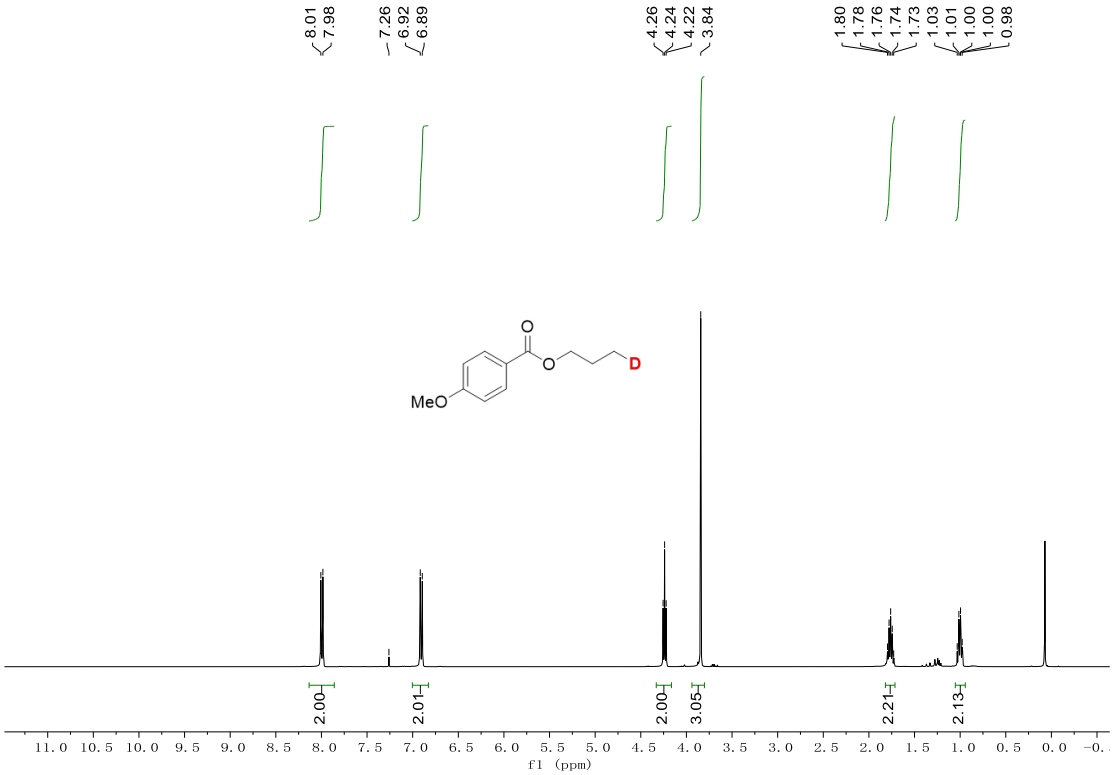

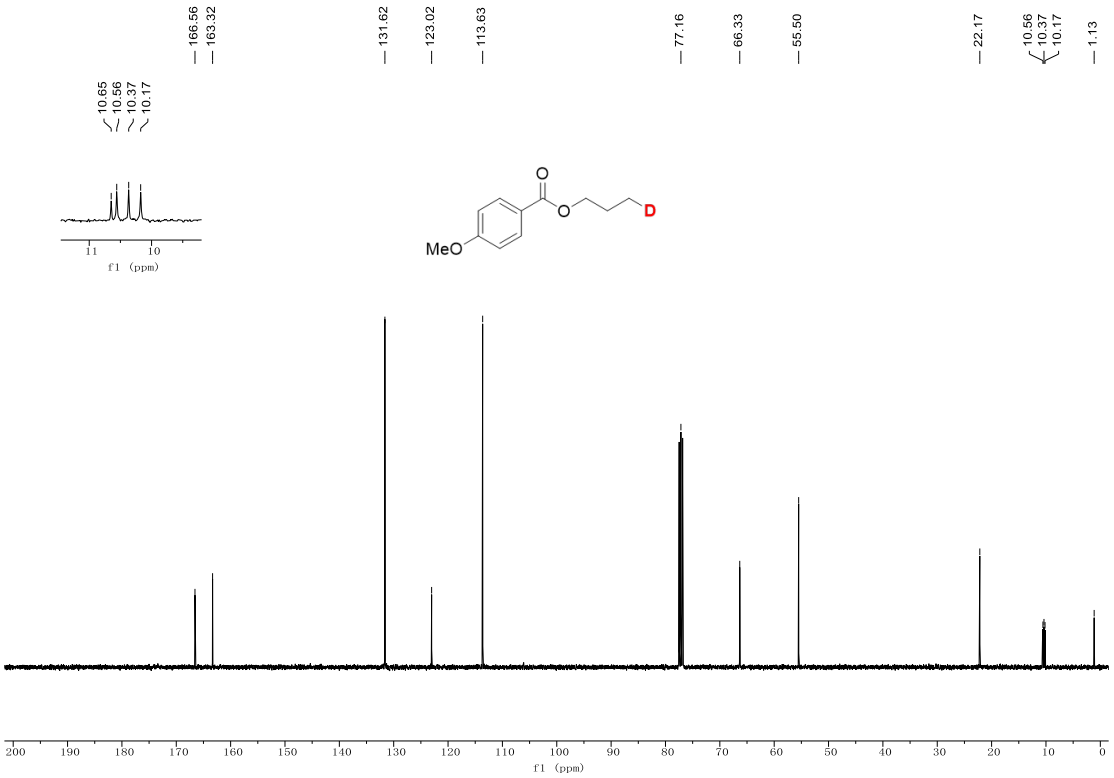

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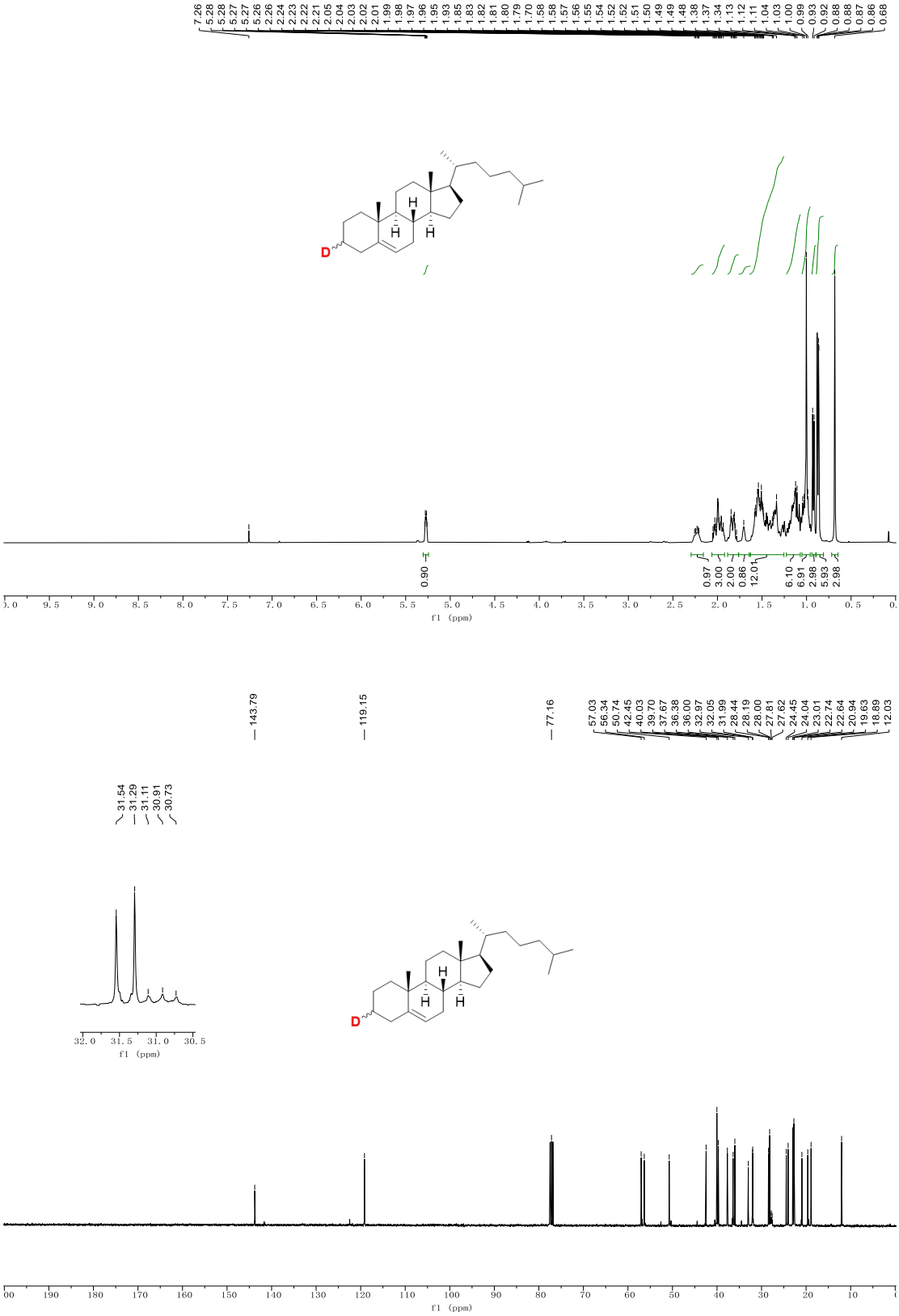

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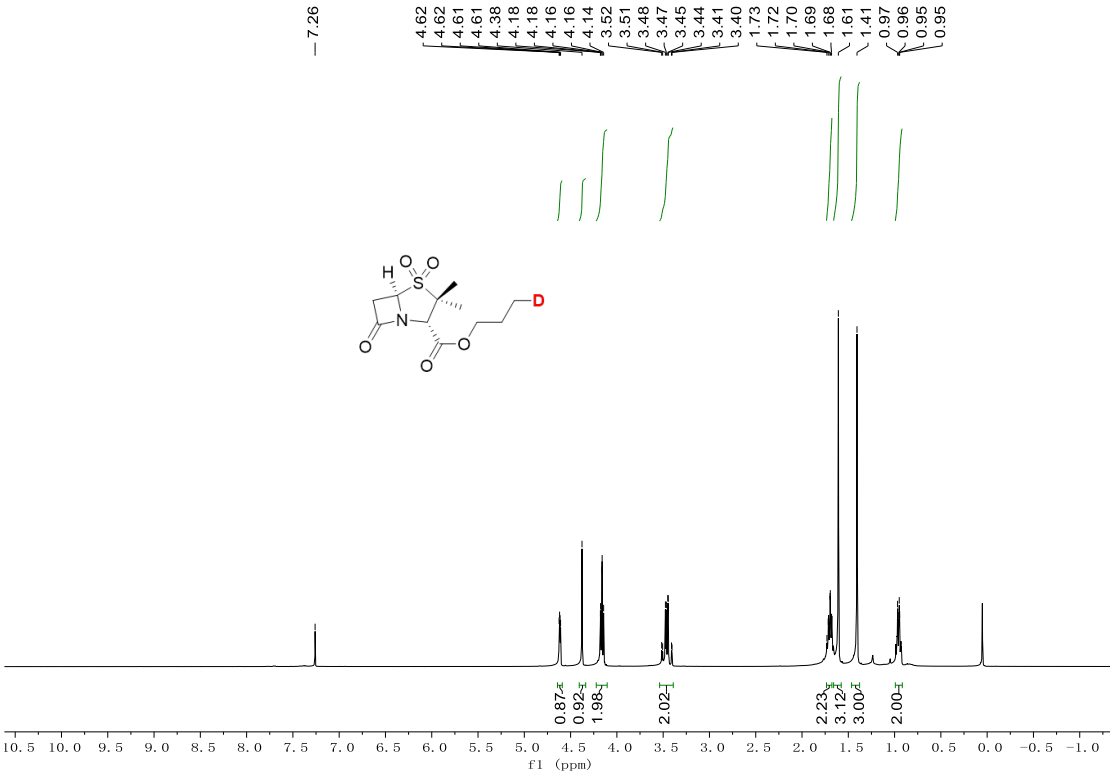

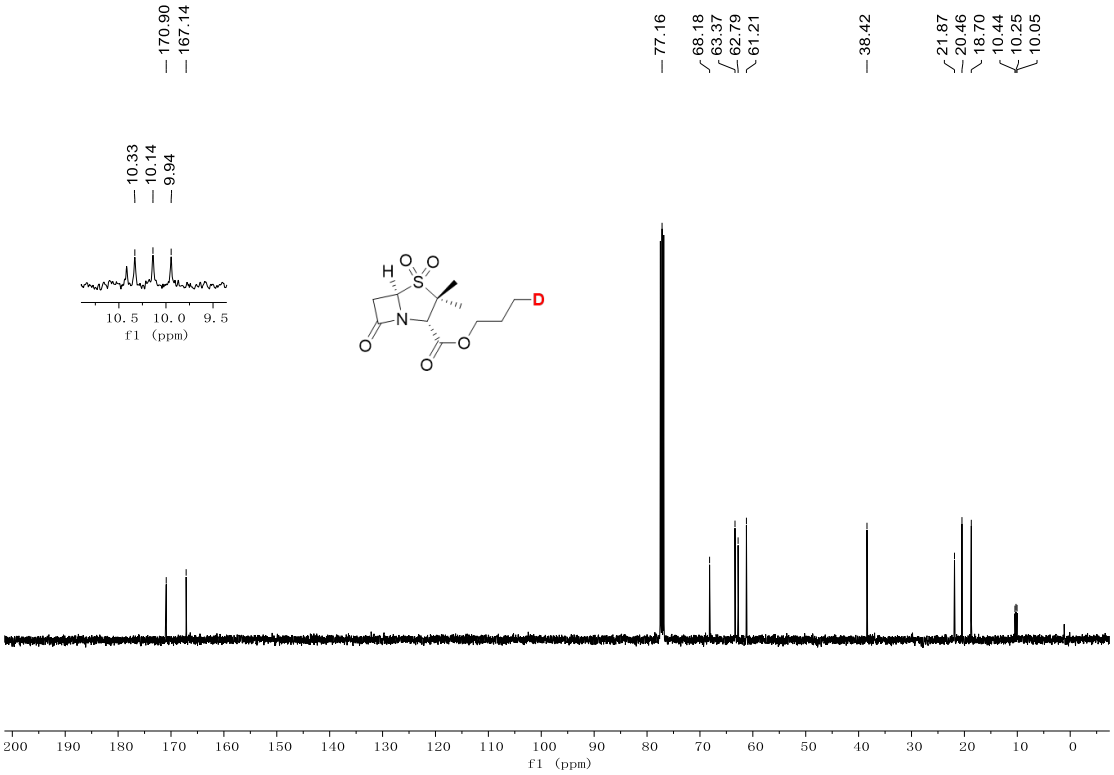

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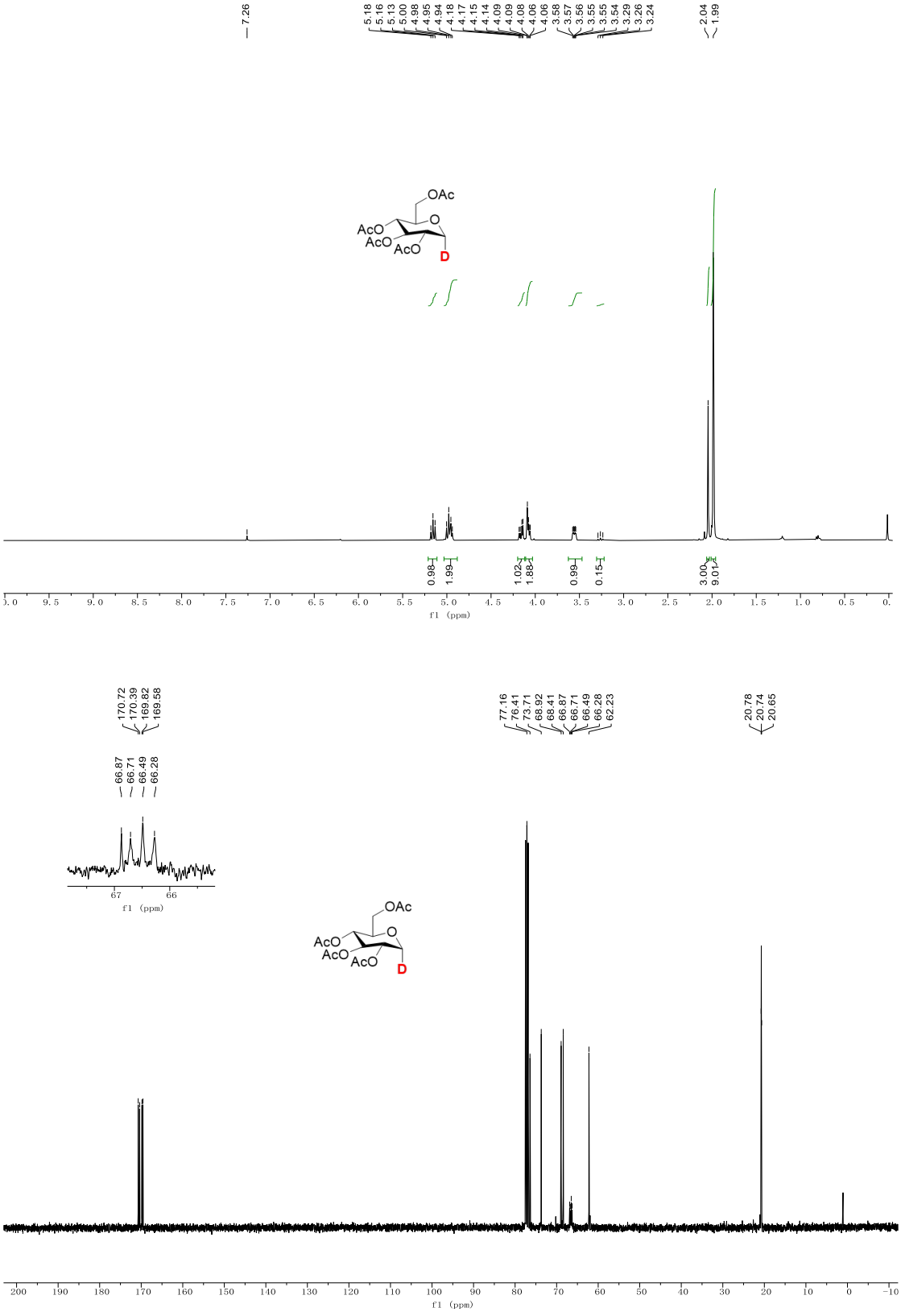

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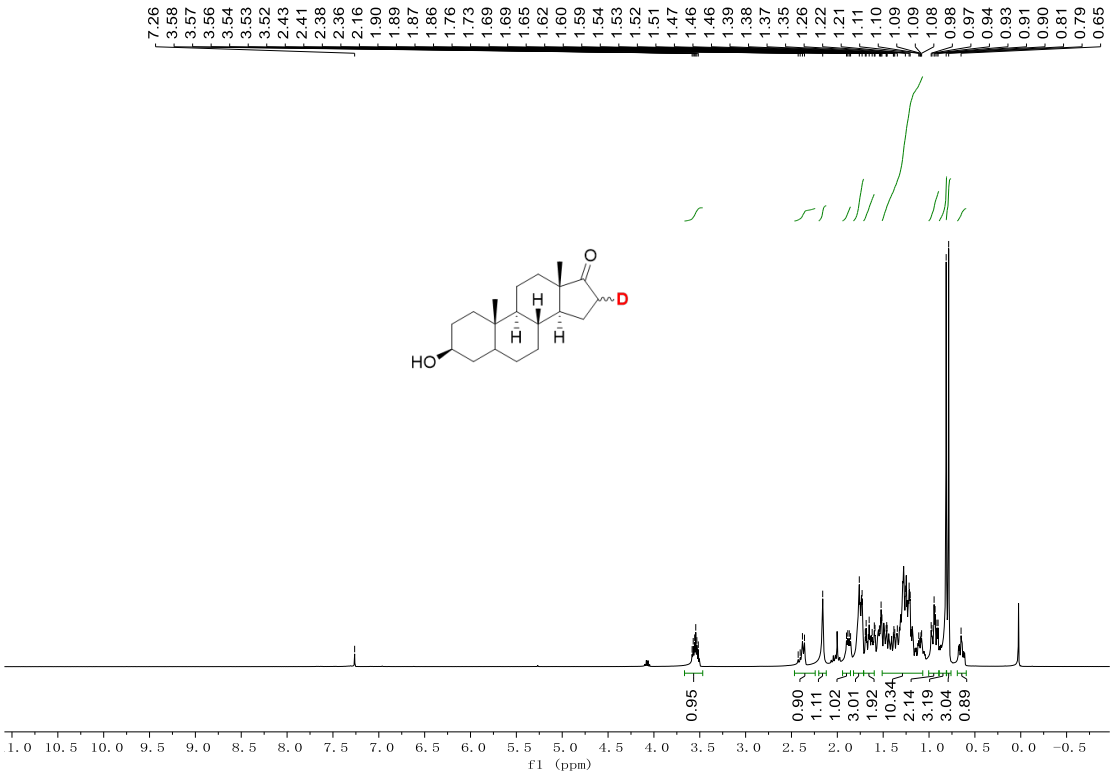

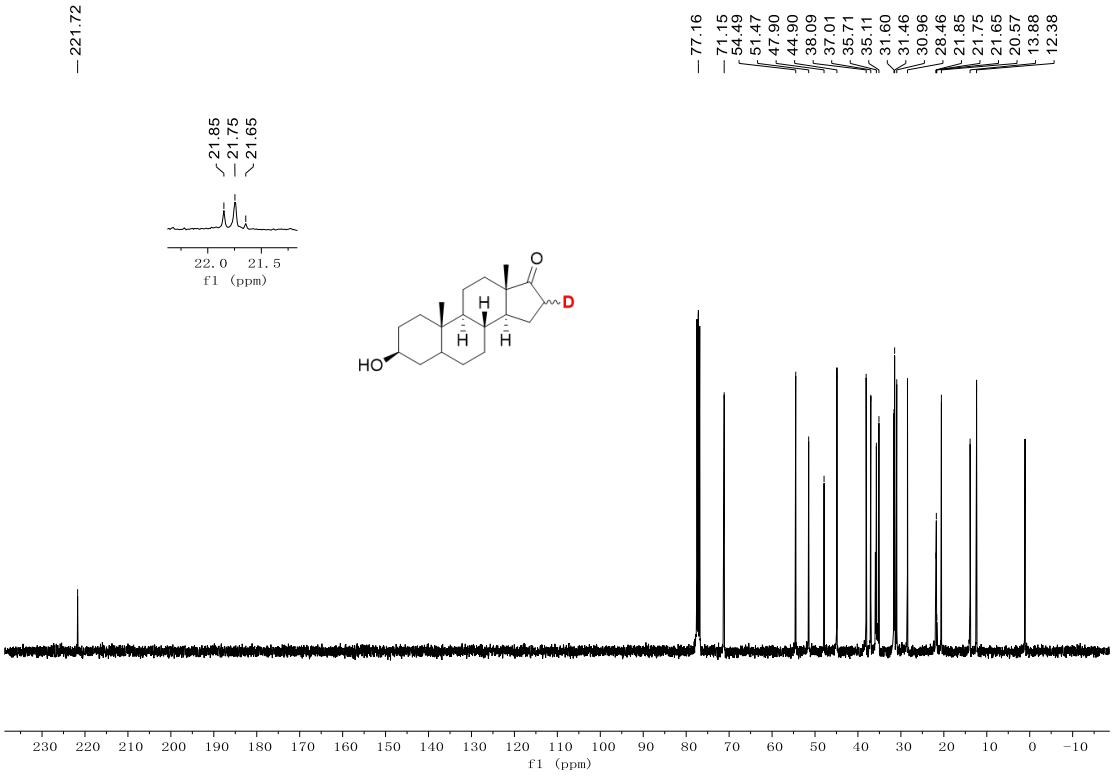

2s-D; ^{1}H-NMR (400 MHz, $CDCl_3$); ^{13}C-NMR (100 MHz, $CDCl_3$)