Supporting Information

Trideuteromethylation Enabled by a Sulfoxonium Metathesis Reaction.

Zuyuan Shen,[†] Shilei Zhang,[‡] Huihui Geng,[†] Jiarui Wang,[†] Xinyu Zhang,[†] Anqi Zhou,[†] Cheng Yao,[†] Xiaobei Chen,*[,†] Wei Wang*[,†, §]

[†]State Key Laboratory of Bioengineering Reactor, and Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science & Technology, Shanghai 200237, China

[‡]Jiangsu Key Laboratory of Neuropsychiatric Diseases and College of Pharmaceutical Sciences, Soochow University, 199 Ren'ai Road, Suzhou, Jiangsu, 215123, China

[§]Department of Pharmacology and Toxicology, and BIO5 Institute, University of Arizona, 1703 E. Mabel St., P. O. Box 210207, Tucson, AZ 85721-0207, USA

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1. General

1.1 General Experimental Considerations

Commercial reagents and solvents were used as received, unless otherwise stated. Organic solution was concentrated under reduced pressure on a Büchi rotary evaporator. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography was performed on silica gel 200–300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas-beta®). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 Spectrometer (400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively) and are internally referenced to residual solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.00 ppm in ^{1}H and ^{13}C NMR, respectively; DMSO-d_6 referenced at 2.50 and 39.52 ppm in ^{1}H and ^{13}C NMR, respectively). Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for ^{13}C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer.

1.2 General procedure for deuteration of substrates

TMSOI, DMSO-d_6 (40.0 equiv) were added in a sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added a base and a substrate (phenol, thiophenol, acidic amine, or enolizable methylene). The resulting solution was stirred at specified temperature for specified time. After cooling to room temperature, it was extracted, and the residue was purified by flash chromatography on silica gel using the indicated solvent system to give the desired product.

The level of deuterium incorporation of the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against a peak corresponding to a position not expected to be labelled.[1]

Equation 1 was then used to calculate the extent of labelling:

$$\%\ \text{Deuteration} = 100 - \left[\left(\frac{\text{residual integral}}{\text{number of labelling sites}} \right) \times 100 \right]$$

Equation 1

In HRMS, the intensity ratio of fully deuterated compound and non-deuterated compound is shown as:

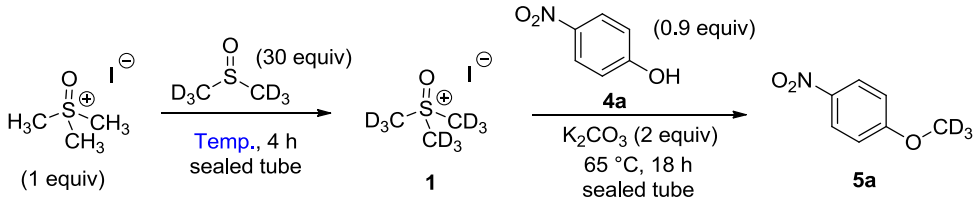
I_D:I_H = 100:X

I_D = EI-MS intensity of fully deuterated compound

I_H = EI-MS intensity of non-deuterated compound

2. The Screening of Reaction Condition

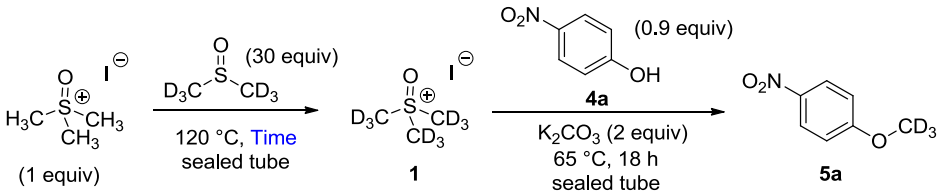
Table S1 The screening of reaction temperature.[a]



entry	temp (°C)	yield (%)[b]	% D[c]
1	80	94.3	35.6
2	100	86.7	75.5
3	120	49.3	94.0
4	130	44.8	93.2

[a]Reaction conditions: TMSOI (0.5 mmol) and DMSO-d_6 (15.0 mmol) in sealed tube was stirred at specified temperature for 16 h, then **4a** (0.45 mmol) and K_2CO_3 (1.0 mmol) was added, stirred in sealed tube at 65 °C for 18 h. [b]Yields of isolated products are given. [c]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy.

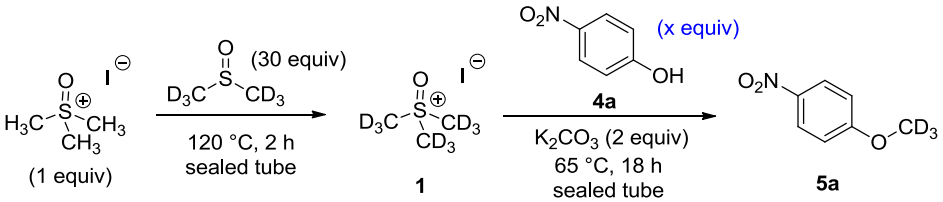
Table S2 The screening of reaction time.[a]



entry	*t* (h)	yield (%)[b]	% D[c]
1	1	65.8	88.7
2	1.5	62.3	91.2
3	2	58.3	94.4
4	3	55.6	94.4
5	4	49.3	94.0
6	8	42.8	93.5
7	16	40.9	90.6

[a]Reaction conditions: TMSOI (0.5 mmol) and DMSO-d_6 (15.0 mmol) in sealed tube was stirred at 120 °C for specified time, then **4a** (0.45 mmol) and K_2CO_3 (1.0 mmol) was added, stirred in sealed tube at 65 °C for 18 h. [b]Yields of isolated products are given. [c]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy.

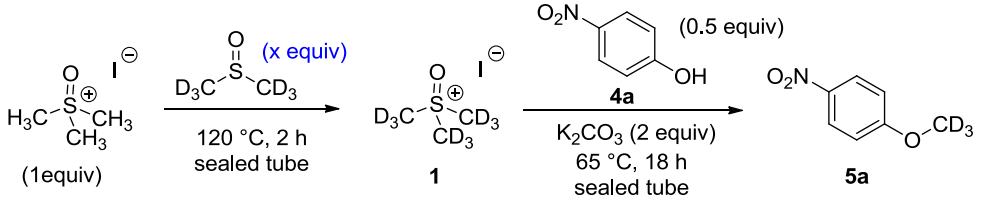
Table S3 The screening of the amount of **4a.**[a]



entry	4a (equiv)	yield (%)[b]	% D[c]
1	0.2	> 99	94.4
2	0.4	> 99	94.4
3	0.5	> 99	94.4
4	0.6	73.6	94.4
5	0.8	62.3	94.4

[a]Reaction conditions: TMSOI (0.5 mmol) and DMSO-d_6 (15.0 mmol) in sealed tube was stirred at 120 °C for 2h, then **4a** (x mmol) and K_2CO_3 (1.0 mmol) was added, stirred in sealed tube at 65 °C for 18 h. [b]Yields of isolated products are given. [c]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy.

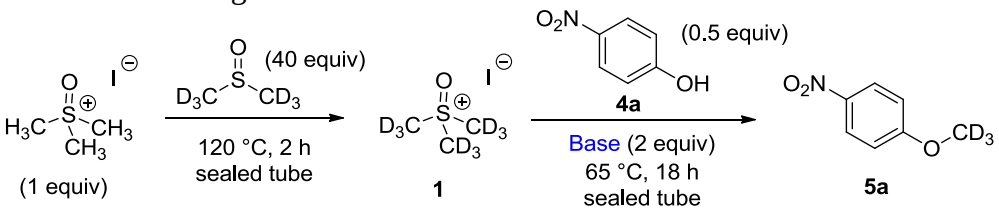
Table S4 The screening of the amount of DMSO-d_6.[a]



entry	*d*-DMSO (equiv)	yield (%)[b]	% D[c]
1	30	> 99	94.4
2	40	> 99	95.8
3	50	> 99	95.8

[a]Reaction conditions: TMSOI (0.5 mmol) and DMSO-d_6 (x mmol) in sealed tube was stirred at 120 °C for 2h, then **4a** (0.25 mmol) and K_2CO_3 (1.0 mmol) was added, stirred in sealed tube at 65 °C for 18 h. [b]Yields of isolated products are given. [c]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy.

Table S5 The screening of different bases.[a]

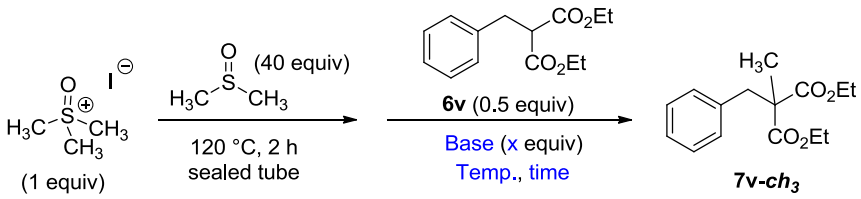


entry	base	yield (%)[b]	% D[c]
1	K_2CO_3	> 99	95.8
2	Powdered K_2CO_3	86.5	93.0
3	KOH	90.1	71.0
4	*t*-BuOK	88.0	84.3
5	Cs_2CO_3	90.6	91.0
6	$NaHCO_3$	> 99	93.4
7	K_3PO_4	90.6	85.4
8	K_2HPO_4	n.d[d]	n.d[d]
9	DIPEA	n.d[d]	n.d[d]
10	DBU	10.0	93.0

11	TBD	n.d[d]	n.d[d]

[a]Reaction conditions: TMSOI (0.5 mmol) and DMSO-d_6 (20.0 mmol) in sealed tube was stirred at 120 ºC for 2h, then **4a** (0.25 mmol) and base (1.0 mmol) was added, stirred in sealed tube at 65 ºC for 18 h. [b]Yields of isolated products are given. [c]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy. [d]not detected.

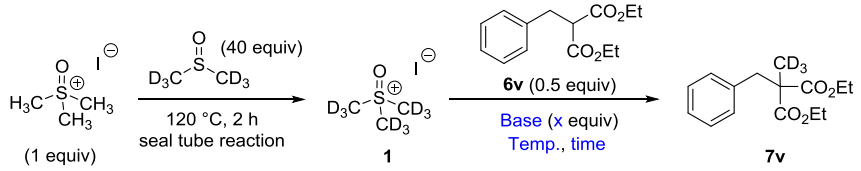
Table S6 The reaction conditions screening with diethyl 2-benzylmalonate **6v.**[a]



entry	base (x equiv)	temp (℃)	*t* (h)	yield (%)[c]
1	KOH (1.0)	25	12	87.5
2[b]	NaH (0.5)	reflux	8	24.8
3[b]	NaH (0.6)	reflux	8	62.1
4[b]	NaH (0.75)	reflux	8	99.0
5[b]	NaH (2.0)	reflux	8	-

[a]Reaction conditions: TMSOI (0.75 mmol) and DMSO-h_6 (30.0 mmol) in sealed tube was stirred at 120 ºC for 2h, then **6v** (0.375 mmol) and base (x equiv) was added, stirred in sealed tube at specified temperature for specified time. [b]To an solution of **6v** (0.375 mmol) in dry THF (3 mL) was added NaH (x equiv) at 0 ºC. After stirring at 25 ºC for 30 min, the solution of TMSOI in DMSO was added and heated to reflux for 8 h. [c]Yields of isolated products are given.

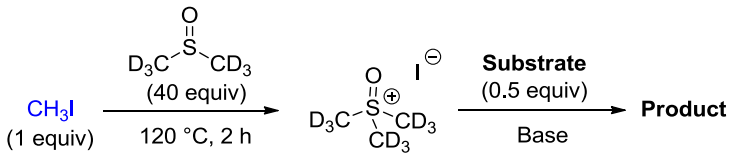
Table S7 Further reaction conditions screening with diethyl 2-benzylmalonate **6v.**[a]



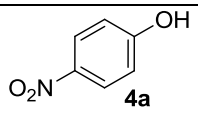
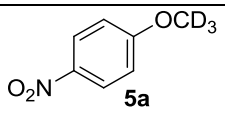
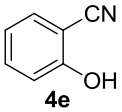
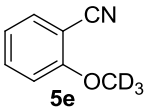
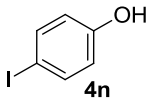
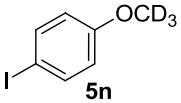
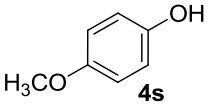
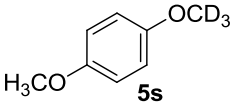
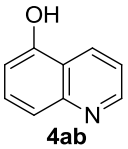
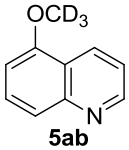
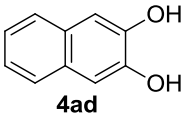
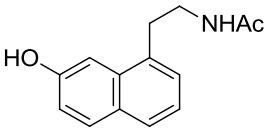
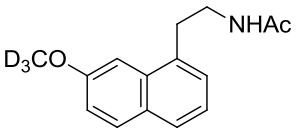
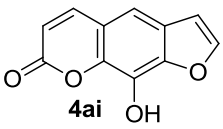
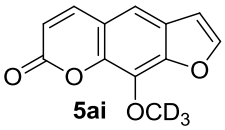
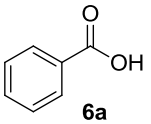
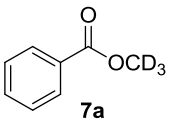
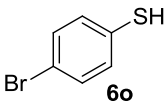
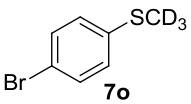
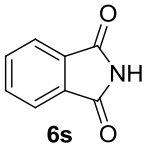
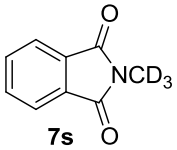
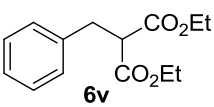
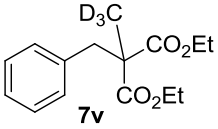
entry	base (x equiv)	temp. (℃)	*t* (h)	yield (%)[c]	% D[d]
1	KOH (1.0)	25.	12	87.3	95.3
2[b]	NaH (0.75)	reflux	8	98.2	95.3

[a]Reaction conditions: TMSOI (0.75 mmol), DMSO-d_6 (30.0 mmol) in sealed tube was stirred at 120 ºC for 2h, then **6v** (0.375 mmol) and base (x equiv) was added, stirred in sealed tube at specified temperature for specified time. [b]To an solution of **6v** (0.375 mmol) in dry THF (3 mL) was added NaH (0.563 mmol) at 0 ºC. After stirring at 25 ºC for 30 min, the solution of **1** was added and heated to reflux for 8 h. [c]Yields of isolated products are given. [d]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy.

3. The Results of Trideuteromethylation When MeI was Used in the Metathesis Reaction[a]



1

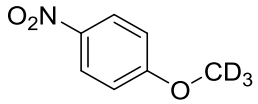
entry	substrate	product	yield (%)[b]	% D[c]
1	 **4a**	 **5a**	89	98
2	 **4e**	 **5e**	93	96
3	 **4n**	 **5n**	88	98
4	 **4s**	 **5s**	95	93
5	 **4ab**	 **5ab**	63	97
6	 **4ad**	 **5ad**	60	97
7	 **4ag**	 **5ag**	94	94
8	 **4ai**	 **5ai**	52	97
9	 **6a**	 **7a**	87	98
10	 **6o**	 **7o**	75	98
11	 **6s**	 **7s**	90	94
12	 **6v**	 **7v**	70	97

[a]Reaction conditions: MeI (0.50 mmol) and DMSO-d_6 (20.0 mmol) in sealed tube was stirred at 120 ºC for 2h, then substrate (0.25 mmol) and base (1.0 mmol) was added to the sealed tube, and stirred at specified temperature for specified time (these reaction conditions are same as the cases where TMSOI were used). [b]Yields of isolated products are given. [c]Deuterium incorporations (%) were determined by ^{1}H NMR spectroscopy.

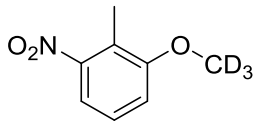
4. Experiment Procedures and Product Characterization

4.1 General procedure for substituted methoxy-d_3

TMSOI (0.5 mmol, 1.0 equiv), DMSO-d_6 (20.0 mmol, 40.0 equiv) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added a substituted phenol (0.25 mmol, 0.5 equiv), base (1.0 mmol, 2.0 equiv). The resulting solution was stirred at 65 ºC for 18 h. The solution was cooled to room temperature and the desired product was obtained by flash chromatography on silica gel using the indicated solvent system. The level of deuterium incorporation in the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against **equation1**.

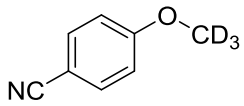


1-(Methoxy-d_3)-4-nitrobenzene (5a): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-d_6 (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-Nitrophenol (34.8 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (39.5 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.8% D. IR (film): ν_{max} (cm^{-1}) 3118, 3082, 3057, 1586, 1494, 1331, 1275, 1095, 986, 842, 749, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.20 - 8.12 (m, 2H), 6.96 - 6.88 (m, 2H), 3.88 - 3.85 (m, 0.13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.7, 141.6, 126.0 (2C), 114.1 (2C), 56.0 - 54.8 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3NO_3$: 156.0614, Found: 156.0615; I_D:I_H = 100:0.

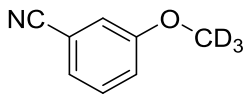


1-(Methoxy-d_3)-2-methyl-3-nitrobenzene (5b): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol,), DMSO-d_6 (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-Methyl-3-nitrophenol (38.3 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (2% ethyl acetate/petroleum ether) to provide the title compound as a yellow solid (42.6 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.8% D. IR

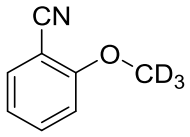
(film): ν_{max} (cm^{-1}) 3090, 2940, 2857, 1516, 1461, 1348, 1274, 1108, 874, 794, 768, 732; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 (d, *J* = 8.2 Hz, 1H), 7.25 (dd, *J* = 9.9, 6.6 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 3.88 - 3.84 (m, 0.13H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.4, 151.1, 126.7, 121.9, 115.7, 113.7, 56.4 - 55.1 (m, C-D_3), 11.50; HRMS (EI): m/z caled for $C_8H_6D_3NO_3$: 170.0771, Found: 170.0772; I_D:I_H = 100:4.02.



4-(Methoxy-*d*$_3$)benzonitrile (5c): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-d_6 (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-Cyanophenol (29.8 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (34.4 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.8% D. IR (film): ν_{max} (cm^{-1}) 3104, 2941, 2220, 2075, 1605, 1509, 1271, 1177, 1104, 990, 828, 735; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 - 7.53 (m, 2H), 6.95 - 6.90 (m, 2H), 3.83 - 3.79 (s, 0.16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.9, 134.0 (2C), 119.3, 114.8 (2C), 103.9, 55.6 - 54.3 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_4D_3NO$: 136.0716, Found: 136.0717; I_D:I_H = 100:4.98.

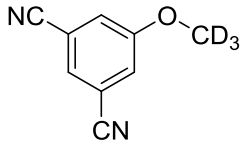


3-(Methoxy-*d*$_3$)benzonitrile (5d): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-d_6 (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-Cyanophenol (29.8 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (34.6 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.4% D. IR (film): ν_{max} (cm^{-1}) 3075, 2860, 2230, 2074, 1579, 1482, 1431, 1291, 1107, 1011, 871, 784, 680; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 - 7.33 (m, 1H), 7.23 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.15 - 7.08 (m, 2H), 3.82 - 3.78 (m, 0.14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.6, 130.4, 124.5, 119.3, 118.8, 116.8, 113.2, 55.2 - 55.0 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_4D_3NO$: 136.0716, Found: 136.0717; I_D:I_H = 100:3.67.

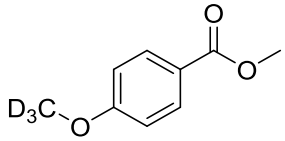


2-(Methoxy-*d*$_3$)benzonitrile (5e): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-d_6 (1.4 mL, 20.0 mmol) was stirred

at 120 ºC for 2 h. After cooling to room temperature, added 2-Cyanophenol (29.8 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (34.8 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.8% D. IR (film): v_{max} (cm^{-1}) 3078, 2859, 2227, 2076, 1598, 1449, 1290, 1266, 1102, 988, 753; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53 (td, *J* = 7.5, 1.6 Hz, 2H), 6.98 (dd, *J* = 16.6, 9.1 Hz, 2H), 3.92 - 3.88 (m, 0.13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.3, 134.5, 133.8, 120.8, 116.6, 111.4, 101.9, 56.1 - 54.6 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_4D_3NO$: 136.0716, Found: 136.0717; I_D:I_H = 100:4.11.

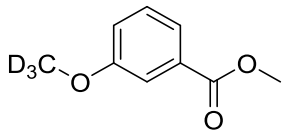


5-(Methoxy-*d*$_3$)isophthalonitrile (5f): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 5-Hydroxy-isophthalonitrile (36.0 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a white wastepaper solid (40.2 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.4% D. IR (film): v_{max} (cm^{-1}) 3086, 2922, 2239, 2078, 1591, 1441, 1333, 1173, 1096, 878, 675; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (t, *J* = 1.3 Hz, 1H), 7.37 (d, *J* = 1.3 Hz, 2H), 3.89 - 3.85 (m, 0.17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.2, 127.3 (2C), 121.9 (2C), 116.7, 115.1 (2C), 56.0 - 54.1 (m, C-D_3); HRMS (EI): m/z caled for $C_9H_3D_3N_2O$: 161.0668, Found: 161.0669; I_D:I_H = 100:4.57.

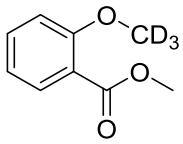


Methyl 4-(methoxy-*d*$_3$)benzoate (5g): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added Methyl 4-hydroxybenzoate (38.0 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow oil (43.5 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.1% D. IR (film): v_{max} (cm^{-1}) 2951, 1702, 1602, 1509, 1426, 1257, 1168, 1099, 845, 767, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.01 - 7.95 (m, 2H), 6.93 - 6.86 (m, 2H), 3.87 (s, 3H), 3.84 - 3.80 (m, 0.21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.9, 163.4, 131.7 (2C),

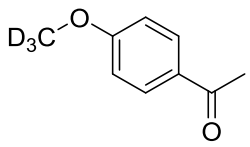
122.7, 113.7 (2C), 55.4 - 54.2 (m, C-D_3), 51.9; HRMS (EI): m/z caled for $C_9H_7D_3O_3$: 169.0818, Found: 169.0819; I_D:I_H = 100:4.83.



Methyl 3-(methoxy-*d_3*)benzoate (5h): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d_6* (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added Methyl 3-hydroxybenzoate (38.0 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow oil (42.5 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 89.2% D. IR (film): ν_{max} (cm^{-1}) 2954, 1720, 1586, 1447, 1280, 1225, 1106, 1019, 875, 754, 683; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.65 - 7.60 (m, 1H), 7.55 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.09 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 3.90 (s, 3H), 3.84 - 3.80 (m, 0.33H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.1, 159.6, 131.5, 129.5, 122.0, 119.6, 114.0, 55.5 - 54.3 (m, C-D_3), 52.3; HRMS (EI): m/z caled for $C_9H_7D_3O_3$: 169.0818, Found: 169.0819; I_D:I_H = 100:7.82.

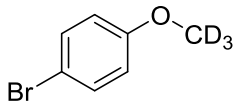


Methyl 2-(methoxy-*d_3*)benzoate (5i): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d_6* (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added Methyl 2-hydroxybenzoate (38.0 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow oil (42.8 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.1% D. IR (film): ν_{max} (cm^{-1}) 2952, 1725, 1600, 1489, 1452, 1249, 1082, 991, 753; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.48 -7.42 (m, 1H), 6.99 - 6.93 (m, 2H), 3.88 - 3.85 (s, 3.31H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.8, 159.1, 133.6, 131.7, 120.2, 120.1, 112.0, 56.0 - 54.8 (m, C-D_3), 52.1; HRMS (EI): m/z caled for $C_9H_7D_3O_3$: 169.0818, Found: 169.0819; I_D:I_H = 100:5.49.

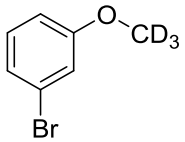


1-(4-(methoxy-*d_3*)phenyl)ethan-1-one (5j): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d_6* (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added

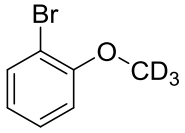
1-(4-hydroxyphenyl)ethan-1-one (34.0 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow oil (40.2 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.4% D (α of ketone: 8.0%). IR (film): v_{max} (cm^{-1}) 2998, 1665, 1597, 1504, 1417, 1357, 1264, 1174, 1102, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.95 - 7.87 (m, 2H), 6.97 - 6.84 (m, 2H), 3.84 - 3.80 (m, 0.14H), 2.53 - 2.49 (m, 2.80H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 196.8, 163.6, 130.7 (2C), 130.4, 113.7 (2C), 55.5 - 54.1 (m, C-D_3), 26.4; HRMS (EI): m/z caled for $C_9H_7D_3O_2$: 153.0869, Found: 153.0870; I_D:I_H = 100:4.05.



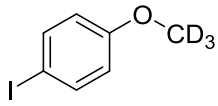
1-Bromo-4-(methoxy-*d*$_3$)benzene (5k): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-Bromophenol (43.3 mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a yellow liquid (40.8 mg, 85.8% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.1% D. IR (film): v_{max} (cm^{-1}) 2924, 1484, 1251, 1109, 990, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 - 7.34 (m, 2H), 6.81 - 6.75 (m, 2H), 3.78 (s, 0.15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.8, 132.4 (2C), 115.9 (2C), 112.9, 58.6 - 56.8 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3BrO$: 188.9869, Found: 188.9871; I_D:I_H = 100:3.92.



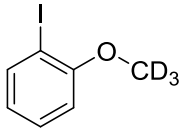
1-Bromo-3-(methoxy-*d*$_3$)benzene (5l): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-Bromophenol (43.3 mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a yellow liquid (42.3 mg, 89.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.2% D. IR (film): v_{max} (cm^{-1}) 2925, 1589, 1475, 1288, 1234, 1107, 1004, 858, 763, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.15 (t, *J* = 8.0 Hz, 1H), 7.11 - 7.03 (m, 2H), 6.84 (ddd, *J* = 8.2, 2.3, 0.9 Hz, 1H), 3.79 - 3.76 (m, 0.21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.4, 130.6, 123.8, 122.8, 117.2, 113.1, 55.4 - 54.2 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3BrO$: 188.9869, Found: 188.9871; I_D:I_H = 100:5.30.



1-Bromo-2-(methoxy-*d*$_3$)benzene (5m): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-Bromophenol (43.3 mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow oil (42.3 mg, 89.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.2% D. IR (film): ν_{max} (cm^{-1}) 3066, 1474, 1283, 1103, 1030, 992, 743, 655; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32 - 7.24 (m, 1H), 6.90 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.84 (td, *J* = 7.7, 1.4 Hz, 1H), 3.90 - 3.86 (m, 0.24H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.0, 133.4, 128.6, 121.9, 112.1, 111.8, 56.2 - 55.0 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3BrO$: 188.9869, Found: 188.9871; I_D:I_H = 100:6.57.

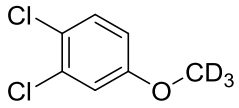


1-Iodo-4-(methoxy-*d*$_3$)benzene (5n): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-Iodophenol (55.0 mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (56.3 mg, 95.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.5% D. IR (film): ν_{max} (cm^{-1}) 3080, 1586, 1481, 1284, 1251, 1102, 987, 807; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 - 7.53 (m, 2H), 6.71 - 6.64 (m, 2H), 3.77 - 3.73 (m, 0.17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.6, 138.3, 138.2, 116.5 (2C), 82.8, 55.2 - 55.0 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3IO$: 236.9730, Found: 236.9732; I_D:I_H = 100:4.71.

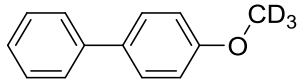


1-Iodo-2-(methoxy-*d*$_3$)benzene (5o): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-Iodophenol (55.0 mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a yellow liquid (54.0 mg, 91.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.2% D. IR (film): ν_{max} (cm^{-1}) 3060,

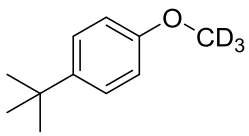
1469, 1281, 1102, 1016, 744, 643; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.71 (td, *J* = 7.6, 1.3 Hz, 1H), 3.88 - 3.84 (m, 0.24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.0, 138.4, 128.5, 121.4, 109.9, 84.9, 55.2 - 54.0 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3IO$: 236.9730, Found: 236.9732; I_D:I_H = 100:6.93.



1,2-Dichloro-4-(methoxy-*d*$_3$)benzene (5p): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3,4-Dichlorophenol (40.7 mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (36.1 mg, 80.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 90.6% D. IR (film): v_{max} (cm^{-1}) 2972, 1591, 1473, 1289, 1104, 999, 860, 841, 801, 626; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 (d, *J* = 8.9 Hz, 1H), 6.98 (d, *J* = 2.9 Hz, 1H), 6.75 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.78 - 3.74 (m, 0.29H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 133.0, 130.8, 124.0, 115.8, 114.2, 55.7 - 54.5 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_3D_3Cl_2O$: 178.9984, Found: 178.9982; I_D:I_H = 100:7.59.

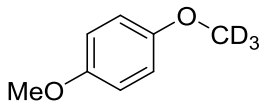


4-(Methoxy-*d*$_3$)-1,1'-biphenyl (5q): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added [1,1'-Biphenyl]-4-ol (42.6 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a white wastepaper solid (44.8 mg, 95.8% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.2% D. IR (film): v_{max} (cm^{-1}) 3035, 1602, 1519, 1482, 1270, 1105, 988, 831, 757, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 - 7.52 (m, 4H), 7.49 - 7.41 (m, 2H), 7.37 - 7.30 (m, 1H), 7.07 - 6.92 (m, 2H), 3.87 - 3.84 (m, 0.21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.3, 141.0, 133.9, 128.9 (2C), 128.3 (2C), 126.9 (2C), 126.8, 114.3 (2C), 55.5 - 54.4 (m, C-D_3); HRMS (EI): m/z caled for $C_{13}H_9D_3O$: 187.1076, Found: 187.1077; I_D:I_H = 100:0.

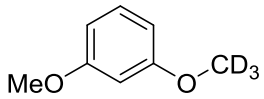


1-(*tert*-Butyl)-4-(methoxy-*d*$_3$)benzene (5r): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added

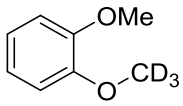
4-(*tert*-Butyl)phenol (37.6 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (44.8 mg, 85.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.5% D. IR (film): ν_{max} (cm^{-1}) 2954, 1507, 1238, 1107, 995, 823; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.82 - 3.78 (m, 0.17H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.4, 143.4, 126.4 (2C), 113.4 (2C), 55.4 - 53.6 (m, C-D_3), 34.2, 31.7 (3C); HRMS (EI): m/z caled for $C_{11}H_{13}D_3O$: 167.1389, Found: 167.1390; I_D:I_H = 100:0.



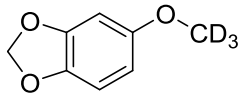
1-Methoxy-4-(methoxy-*d*$_3$)benzene (5s): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-Methoxyphenol (31.0 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a yellow solid (30.5 mg, 86.3% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 88.9% D. IR (film): ν_{max} (cm^{-1}) 2953, 2837, 1507, 1293, 1239, 1109, 1033, 824, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.76 (s, 4H), 3.69 -3.64 (m, 3.41H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.9 (2C), 114.8 (2C), 114.8 (2C), 55.9, 55.2 - 54.8 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_7D_3O_2$: 141.0869, Found: 141.0871; I_D:I_H = 100:8.06.



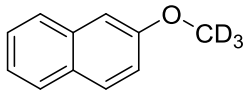
1-Methoxy-3-(methoxy-*d*$_3$)benzene (5t): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-Methoxyphenol (31.0 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a yellow solid (30.8 mg, 87.4% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.8% D. IR (film): ν_{max} (cm^{-1}) 2928, 2837, 1591, 1490, 1291, 1203, 1153, 1109, 1040, 878, 758, 685; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.19 (t, *J* = 8.2 Hz, 1H), 6.52 (dd, *J* = 8.3, 2.2 Hz, 2H), 6.48 (t, *J* = 2.3 Hz, 1H), 3.80 - 3.76 (m, 3.29H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.0, 130.0 (2C), 106.3 (2C), 100.6, 55.4, 54.8 - 54.3 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_7D_3O_2$: 141.0869, Found: 141.0871; I_D:I_H = 100:5.82.



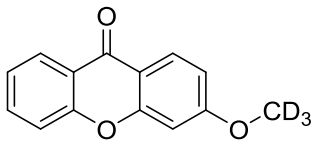
1-Methoxy-2-(methoxy-*d*$_3$)benzene (5u): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-Methoxyphenol (31.0 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a yellow solid (29.8 mg, 84.3% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.5% D. IR (film): ν_{max} (cm^{-1}) 2946, 2837, 1502, 1256, 1108, 1024, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.95 - 6.86 (m, 4H), 3.88 - 3.86 (m, 3.27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.1 (2C), 120.9, 120.9, 111.4, 55.9, 55.5 - 54.4 (m, C-D$_3$); HRMS (EI): m/z caled for $C_8H_7D_3O_2$: 141.0869, Found: 141.0871; I_D:I_H = 100:5.63.



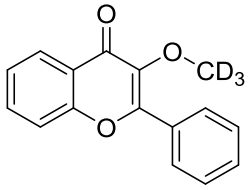
5-(methoxy-*d*$_3$)benzo[*d*][1,3]dioxole (5v): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added sesamol (34.5 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (1% ethyl acetate/petroleum ether) to provide the title compound as a brown oil (25.5 mg, 65.8% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.2% D. IR (film): ν_{max} (cm^{-1}) 2889, 1483, 1183, 1035, 932, 897, 813, 786; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.71 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.31 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.91 (s, 2H), 3.74 - 3.70 (m, 0.21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.3, 148.5, 141.7, 108.0, 104.8, 101.2, 97.6, 56.1 - 54.9 (m, C-D$_3$); HRMS (EI): m/z caled for $C_8H_5D_3O_3$: 155.0662, Found: 155.0664; I_D:I_H = 100:0.



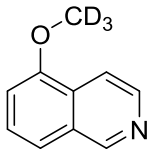
2-(Methoxy-*d*$_3$)naphthalene (5w): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-Naphthol (36.0mg, 0.25 mmol), KOH (56.1 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a yellow solid (37.6 mg, 93.4% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.5% D. IR (film): ν_{max} (cm^{-1}) 3056, 1626, 1594, 1503, 1466, 1389, 1259, 1180, 1105, 872, 835, 814, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78 (dd, *J* = 12.2, 8.5 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 11.2, 2.2 Hz, 2H), 3.94 - 3.91 (m, 0.23H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.7, 134.7, 129.5, 129.1, 127.8, 126.9, 126.5, 123.7, 118.8, 105.9, 54.9 - 54.2 (m, C-D$_3$); HRMS (EI): m/z caled for $C_{11}H_7D_3O$: 161.0920, Found: 161.0921; I_D:I_H = 100:6.67.



3-(Methoxy-*d*$_3$)-9H-xanthen-9-one (5x): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added sieber linker (53.1 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a light yellow solid (51.9 mg, 90.5% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.1% D. IR (film): ν_{max} (cm^{-1}) 2921, 1650, 1607, 1437, 1279, 1261, 1092, 867, 838, 829, 762, 751, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.27 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 7.63 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.34 - 7.28 (m, 1H), 6.87 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 3.87 - 3.84 (m, 0.12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 176.3, 165.1, 158.1, 156.2, 134.3, 128.2, 126.6, 123.9, 122.0, 117.7, 115.8, 113.3, 100.2, 55.9 - 54.7 (m, C-D_3); HRMS (ESI): m/z caled for $C_{14}H_7D_3O_3$ [(M+H)$^+$]: 230.0896, Found: 230.0892; I_D:I_H = 100:3.69.

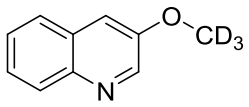


3-(Methoxy-*d*$_3$)-2-phenyl-4H-chromen-4-one (5y): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-hydroxyflavone (59.6 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (62.5 mg, 98.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 2923, 1638, 1606, 1464, 1240, 1203, 758, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.14 - 8.06 (m, 2H), 7.67 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.56 - 7.49 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 1H), 3.90 - 3.85 (m, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 175.3, 155.7, 155.4, 141.6, 133.6, 131.1, 130.8, 128.7 (2C), 128.6 (2C), 125.9, 124.8, 124.3, 118.1, 59.9 - 58.8 (m, C-D_3); HRMS (ESI): m/z caled for $C_{16}H_9D_3O_3$ [(M+H)$^+$]: 256.1053, Found: 256.1050; I_D:I_H = 100:3.20.

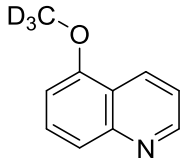


5-(Methoxy-*d*$_3$)isoquinoline (5z): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred

at 120 ºC for 2 h. After cooling to room temperature, added 5-Hydroxyisoquinoline (36.3 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a brown oil (20.7 mg, 51.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.8% D. IR (film): ν_{max} (cm^{-1}) 3068, 1572, 1467, 1400, 1316, 1268, 1067, 792; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.89 (d, *J* = 2.7 Hz, 1H), 8.57 (ddd, *J* = 8.5, 1.7, 0.7 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.63 - 7.57 (m, 1H), 7.37 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.84 (dd, *J* = 7.7, 0.8 Hz, 1H), 3.98 - 3.94 (m, 0.19H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.3, 150.8, 149.2, 130.9, 129.5, 121.6, 121.0, 120.3, 104.3, 55.3 - 54.6 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_6D_3NO$: 162.0872, Found: 162.0873; I_D:I_H = 100:5.06.

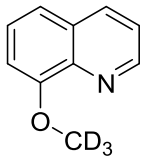


3-(Methoxy-*d*$_3$)quinoline (5aa): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-Hydroxyquinoline (36.3 mg, 0.25 mmol), K_3PO_4 (212.3 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a brown oil (34.2 mg, 84.3% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.8% D. IR (film): ν_{max} (cm^{-1}) 3061, 3010, 1601, 1423, 1346, 1277, 1213, 1104, 848, 780, 747, 611; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.67 (d, *J* = 2.9 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.57 - 7.46 (m, 2H), 7.34 (d, *J* = 2.8 Hz, 1H), 3.91 - 3.88 (m, 0.16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.2, 144.7, 143.6, 129.3, 128.9, 127.2, 126.8, 126.7, 112.3, 55.6 - 54.5 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_6D_3NO$: 162.0872, Found: 162.0873; I_D:I_H = 100:4.28.

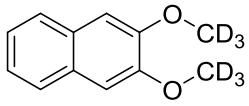


5-(Methoxy-*d*$_3$)quinoline (5ab): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 5-Hydroxyquinoline (36.3 mg, 0.25 mmol), K_3PO_4 (212.3 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a brown oil (38.6 mg, 95.2% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.4% D. IR (film): ν_{max} (cm^{-1}) 3067, 2925, 1574, 1468, 1400, 1269, 1171, 1106, 791; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.88 (d, *J* = 1.7 Hz, 1H), 8.61 - 8.52 (m, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.59 (t, *J* = 8.1 Hz, 1H), 7.35 (ddd,

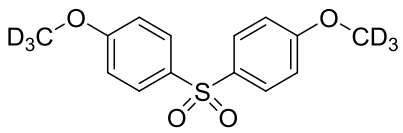
J = 8.5, 4.2, 0.6 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 3.98 (s, 0.14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.2, 150.7, 149.1, 131.0, 129.5, 121.5, 120.9, 120.3, 104.3, 55.3 - 54.7 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_6D_3NO$: 162.0872, Found: 162.0873; I_D:I_H = 100:3.48.



8-(Methoxy-*d*$_3$)quinoline (5ac): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 8-Hydroxyquinoline (36.3 mg, 0.25 mmol), K_3PO_4 (212.3 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a brown oil (40.0 mg, 98.6% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.8% D. IR (film): v_{max} (cm^{-1}) 3042, 3008, 1570, 1498, 1376, 1320, 1269, 1112, 822, 789, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.46 - 7.32 (m, 3H), 7.01 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.06 - 4.02 (m, 0.13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.4, 149.3, 140.2, 136.0, 129.4, 126.8, 121.8, 119.6, 107.6, 55.6 - 54.8 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_6D_3NO$: 162.0872, Found: 162.0873; I_D:I_H = 100:3.81.

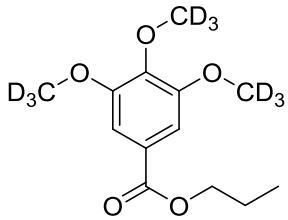


2,3-bis(Methoxy-*d*$_3$)naphthalene (5ad): According to the general procedure, the mixture solution of TMSOI (220.1 mg, 1.0 mmol), DMSO-*d*$_6$ (2.8 mL, 40.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2,3-dihydroxynaphthalene (40.1 mg, 0.25 mmol), KOH (112.2 mg, 2.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a yellow solid (44.5 mg, 91.7% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.1% D. IR (film): v_{max} (cm^{-1}) 2923, 1505, 1478, 1251, 1179, 1099, 969, 850, 749, 618; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.72 - 7.67 (m, 2H), 7.37 - 7.32 (m, 2H), 7.12 (s, 2H), 4.01 - 3.97 (m, 0.24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.6 (2C), 129.3 (2C), 126.4 (2C), 124.3 (2C), 106.4 (2C), 55.9 - 54.7 (m, C-D_3); HRMS (EI): m/z caled for $C_{12}H_6D_6O_2$: 194.1214, Found: 194.1215; I_D:I_H = 100:0.

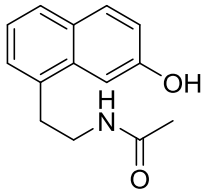


4,4'-Sulfonylbis((methoxy-*d*$_3$)benzene) (5ae): According to the general procedure, the mixture solution of TMSOI (220.1 mg, 1.0 mmol), DMSO-*d*$_6$ (2.8 mL, 40.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added

4,4'-sulfonyldiphenol (62.6 mg, 0.25 mmol), K_2CO_3 (276.4 mg, 2.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (20% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow solid (68.9 mg, 96.9% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 89.2% D. IR (film): ν_{max} (cm^{-1}) 2923, 1595, 1495, 1272, 1150, 1102, 794, 670; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.88 - 7.78 (m, 4H), 6.98 - 6.86 (m, 4H), 3.81 - 3.78 (m, 0.66H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.2 (2C), 134.0 (2C), 129.6 (4C), 114.5 (4C), 55.8 - 54.8 (m, 2C-D_3); HRMS (EI): m/z caled for $C_{14}H_8D_6O_4S$: 284.0989, Found: 284.0990; I_D:I_H = 100:0.

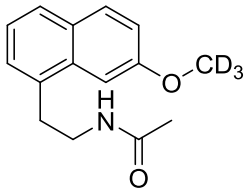


Propyl 3,4,5-tris(methoxy-*d*$_3$)benzoate (5af): According to the general procedure, the mixture solution of TMSOI (330.2 mg, 1.5 mmol), DMSO-*d*$_6$ (4.2 mL, 60.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added propyl gallate (53.1mg, 0.25 mmol), K_2CO_3 (414.6 mg, 3.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a white solid (60.6 mg, 92.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 87.4% D. IR (film): ν_{max} (cm^{-1}) 2967, 1710, 1586, 1428, 1348, 1220, 1129, 863, 765; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.27 (s, 2H), 4.25 (t, *J* = 6.7 Hz, 2H), 3.88 - 3.84 (m, 1.20H), 1.82 - 1.72 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 153.0 (2C), 142.1, 125.6, 106.8 (2C), 66.7, 60.5 - 59.6 (m, C-D_3), 56.3 - 55.4 (m, 2C-D_3), 22.2, 10.5; HRMS (EI): m/z caled for $C_{13}H_9D_9O_5$: 263.1719, Found: 263.1720; I_D:I_H = 100:0.

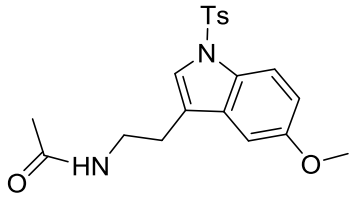


N-(2-(7-hydroxynaphthalen-1-yl)ethyl)acetamide (4ag)[2]: To N-(2-(7-methoxynaph -thalen-1-yl)ethyl)acetamide (243.3 mg, 1.0 mmol) in 5 mL of CH_2Cl_2, boron tribromide (375.8 mg, 1.5 mmol) was added dropwise at −10 ºC. After 0.5 h the reaction was brought to room temperature and stirred for an additional 1.5 h. The reaction was cooled to 0 ºC, 10 mL of water was carefully added, and the organic layer was separated. The aqueous phase was saturated with NaCl and extracted with 3 × 20 mL of ethyl acetate. The combined organic phase was dried with Na_2SO_4, and evaporated. The residue was purified by column chromatography with eluent (10% MeOH/CH_2Cl_2) on silica gel to give an off-white solid (214.0 mg, yield: 93.3%). ^{1}H

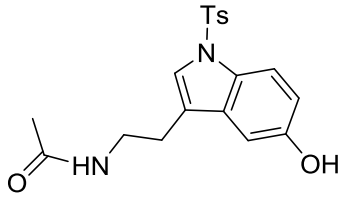
NMR (400 MHz, $CDCl_3$) δ ppm 8.72 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.66 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.20 (dt, *J* = 8.8, 6.2 Hz, 3H), 5.88 (s, 1H), 3.58 (dd, *J* = 14.4, 6.5 Hz, 2H), 3.18 (t, *J* = 7.4 Hz, 2H), 1.98 (s, 3H). Spectral data match those previously reported.



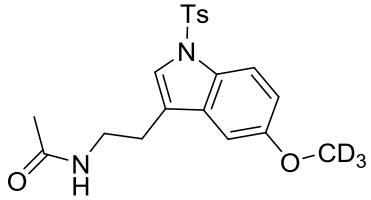
N-(2-(7-(Methoxy-*d*$_3$)naphthalen-1-yl)ethyl)acetamide (5ag): TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added **4ag** (57.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) The resulting solution was stirred at 40 ºC for 18 h. the reaction mixture was cooled to room temperature and was purified by flash chromatography (2% MeOH/CH_2Cl_2) to provide the title compound as a pale yellow solid (49.3 mg, 80.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.8% D. IR (film): ν_{max} (cm^{-1}) 3241, 3058, 2932, 1637, 1543, 1436, 1365, 1303, 1257, 1216, 1106, 867, 835, 825, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.77 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.29 (d, *J* = 9.1 Hz, 2H), 7.18 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.92 (s, 1H), 4.00 - 3.97 (m, 0.22H), 3.61 (dd, *J* = 14.2, 6.5 Hz, 2H), 3.25 (t, *J* = 7.3 Hz, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.6, 158.0, 133.7, 133.2, 130.3, 129.3, 127.1, 127.1, 123.2, 118.4, 102.4, 55.4 - 53.5 (m, C-D_3), 40.2, 33.2, 23.3; HRMS (EI): m/z caled for $C_{15}H_{14}D_3NO_2$: 246.1448, Found: 246.1447; I_D:I_H = 100:3.99.



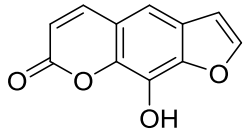
N-(2-(5-hydroxy-1H-indol-3-yl)ethyl)acetamide (5ah[1])[3]: N-(2-(5-methoxy-1H-indol-3-yl)ethyl)acetamide (232.3 mg, 1.0 mmol), NaOH (120.0 mg, 3.0 mmol), TBAB (32.2 mg, 0.1 mmol), CH_2Cl_2 (5 mL) were added a round flask. Afer strring 30 min at room temperature, to the reaction was added tosyl chloride (209.7 mg, 1.1 mmol) and the resulting solution was sttired at the temperature for 6 h. The mixture was evaporated to remove ethanol and then was treated with CH_2Cl_2 (20 mL), and the organic layer was washed with H_2O (2 × 20 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (2% MeOH/CH_2Cl_2) to provide the pure product as a colorless oil (349.8 mg, 90.5% yield). ^{1}H NMR (400 MHz, CD_3OD) δ ppm 7.90 - 7.86 (m, 1H), 7.70 (s, 2H), 7.32 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 12.2 Hz, 2H), 5.50 (s, 1H), 3.82 (s, 3H), 3.53 (q, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.94 (s, 3H). Spectral data match those previously reported.



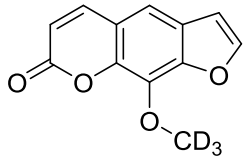
N-(2-(5-hydroxy-1-tosyl-1H-indol-3-yl)ethyl)acetamide (4ah)[3]**:** To **5ah**[1] (342.0 mg, 0.89 mmol) in 5 mL of CH_2Cl_2, boron tribromide (334.4 mg, 1.5 mmol) was added dropwise at −78 ºC. After 1 h the reaction was brought to room temperature and stirred for an additional 1 h. The reaction was cooled to 0 ºC, 20 mL of water was carefully added, and the organic layer was separated. The aqueous phase was saturated with NaCl and extracted with 3 × 20 mL of ethyl acetate. The combined organic phase was dried with Na_2SO_4, and evaporated. The residue was purified by column chromatography with eluent (2% MeOH/CH_2Cl_2) on silica gel to give an white solid (281.5 mg, yield: 85.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.93 (s, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.25 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 2.1 Hz, 1H), 6.88 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.04 (s, 1H), 3.44 (dd, *J* = 12.9, 6.6 Hz, 2H), 2.73 (t, *J* = 6.8 Hz, 2H), 2.27 (s, 3H), 1.90 (s, 3H). Spectral data match those previously reported.



N-(2-(5-(methoxy-d3)-1-tosyl-1H-indol-3-yl)ethyl)acetamide (5ah): TMSOI (110.0 mg, 1.0 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added **4ah** (93.1 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) The resulting solution was stirred at 65 ºC for 18 h. the reaction mixture was cooled to room temperature, 10 mL of water was carefully added, and the organic layer was separated. The aqueous phase was saturated with NaCl and extracted with 2 × 10 mL of ethyl acetate. The combined organic phase was dried with Na_2SO_4, and evaporated. The residue was purified by column chromatography with eluent (2% MeOH/ CH_2Cl_2) to provide the title compound as a colorless oil (90.4 mg, 92.8% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.5% D. IR (film): ν_{max} (cm^{-1}) 3265, 3087, 2924, 1632, 1569, 1448, 1363, 1309, 1172, 1109, 981, 831, 806, 789, 667, 583, 566, 537; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.85 (d, *J* = 9.8 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 9.5 Hz, 2H), 5.87 (s, 1H), 3.77 (m, 0.2H), 3.49 (q, *J* = 6.8 Hz, 2H), 2.81 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.4, 156.5, 144.9, 135.1, 131.8, 130.0, 129.9(2C), 126.7(2C), 124.1, 120.2, 114.7, 113.9, 101.99, 55.4 - 53.5 (m, C-D_3), 38.9, 25.182, 23.3, 21.6; HRMS (EI): m/z caled for $C_{20}H_{19}D_3N_2O_4S$: 389.1489, Found 389.1488; I_D:I_H = 100:4.65.



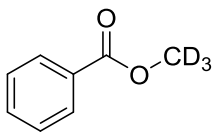
9-Hydroxy-7H-furo[3,2-g]chromen-7-one (xanthotoxol) (4ai)[4]: To 9-methoxy-7H-furo[3,2-g]chromen-7-one (232.3 mg, 1.0 mmol) in 5 mL of CH_2Cl_2, boron tribromide (375.8 mg, 1.5 mmol) was added dropwise at 0 ºC, and stirred for 4 h at this temperature. Then 10 mL of water was carefully added, and the organic layer was separated. The aqueous phase was saturated with NaCl and extracted with 3 × 20 mL of ethyl acetate. The combined organic phase was dried with Na_2SO_4, and evaporated. The residue was purified by column chromatography with eluent (10% MeOH/CH_2Cl_2) on silica gel to give **4ai** (194.1 mg, 96.0%) as a off-white solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.66 (s, 1H), 8.12 (d, *J* = 9.6 Hz, 1H), 8.08 (d, *J* = 2.2 Hz, 1H), 7.45 (s, 1H), 7.04 (d, *J* = 2.2 Hz, 1H), 6.40 (d, *J* = 9.6 Hz, 1H). Spectral data match those previously reported.



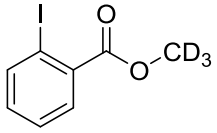
9-(Methoxy-*d*$_3$)-7H-furo[3,2-g]chromen-7-one (5ai): TMSOI (110.0 mg, 1.0 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added **4ai** (50.5 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) The resulting solution was stirred at 65 ºC for 18 h. the reaction mixture was cooled to room temperature and was purified by flash chromatography (CH_2Cl_2) to provide the title compound as a pale yellow solid (49.5 mg, 90.3% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 3118, 3922, 1705, 1583, 1401, 1335, 1298, 1158, 1106, 1024, 996, 870, 819, 788, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74 (d, *J* = 9.6 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.31 (s, 1H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.33 (d, *J* = 9.6 Hz, 1H), 4.26 - 4.21 (m, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.5, 147.6, 146.7, 144.5, 142.9, 132.8, 126.2, 116.5, 114.7, 113.0, 106.8, 61.4 - 59.9 (m, C-D_3); HRMS (EI): m/z caled for $C_{12}H_5D_3O_4$: 219.0611, Found: 219.0606; I_D:I_H = 100:5.99.

4.2 General procedure for substituted methyl-*d*$_3$ benzoate

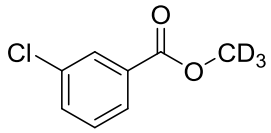
TMSOI (0.5 mmol, 1.0 equiv), DMSO-*d*$_6$ (20.0 mmol, 40.0 equiv) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added a substituted benzoic acid (0.25 mmol, 0.5 equiv), K_2CO_3 (0.5 mmol, 1.0 equiv). The resulting solution was stirred at rt for 3 h. The desired product was obtained by flash chromatography on silica gel using the indicated solvent system. The level of deuterium incorporation in the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against **equation1**.



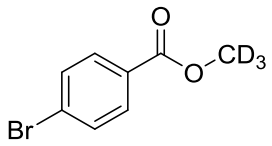
Methyl-*d*$_3$ benzoate (7a): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added benzoic acid (30.5 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (petroleum ether) to provide the title compound as a pale yellow liquid (33.0 mg, 94.9% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 1717, 1291, 1127, 1085, 707; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.04 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.58 - 7.51 (m, 1H), 7.47 - 7.39 (m, 2H), 3.91 (s, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.3, 133.0, 130.3, 129.7 (2C), 128.5 (2C), 52.2 - 51.0 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_5D_3O_2$: 139.0713, Found: 139.0712; I_D:I_H = 100:3.56.



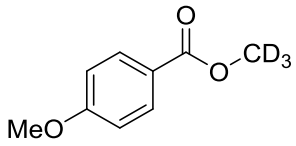
Methyl-*d*$_3$ 2-iodobenzoate (7b): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-iodobenzoic acid (62.0 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a white liquid (69.0 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 1721, 1292, 1252, 1141, 1083, 1016, 735; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.98 (d, *J* = 7.9 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.14 (ddd, *J* = 9.1, 5.3, 1.7 Hz, 1H), 3.92 (s, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.0, 141.4, 135.2, 132.7, 131.0, 128.0, 94.2, 52.6 - 51.4 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_4D_3IO_2$: 139.0713, Found: 264.9677; I_D:I_H = 100:3.34.



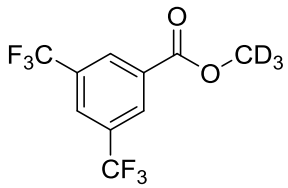
Methyl-*d*$_3$ 3-chlorobenzoate (7c): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-chlorobenzoic acid (39.1 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (32.9 mg, 75.9% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 1719, 1291, 1258, 1140, 1087, 746, 713; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.20 (t, *J* = 8.0 Hz, 1H), 8.01 (t, *J* = 1.8 Hz, 1H), 7.94 -7.87 (m, 1H), 7.52 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 3.92 (s, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.0, 134.6, 133.1, 132.0, 129.8, 129.8, 127.8, 52.5 - 51.3 (m，CD_3); HRMS (EI): m/z caled for $C_8H_4D_3ClO_2$: 173.0323, Found: 173.0321; I_D:I_H = 100:3.11.



Methyl-*d*$_3$ 4-bromobenzoate (7d): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-bromobenzoic acid (50.3 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (petroleum ether) to provide the title compound as a pale yellow liquid (45.7 mg, 83.8% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 1711, 1305, 1279, 1132, 1085, 1010, 844, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.93 - 7.83 (m, 2H), 7.61 - 7.52 (m, 2H), 3.90 (s, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.5, 131.8 (2C), 131.2 (2C), 129.1, 128.1, 52.1 - 51.2 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_4D_3BrO_2$: 216.9818, Found: 216.9816; I_D:I_H = 100:3.38.

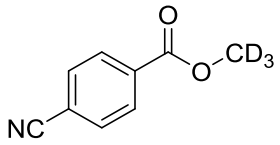


Methyl-*d*$_3$ 4-methoxybenzoate (7e): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-methoxybenzoic acid (38.0 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (petroleum ether) to provide the title compound as a off-white solid (31.7 mg, 75.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.1% D. IR (film): ν_{max} (cm^{-1}) 2931, 2843, 1709, 1606, 1511, 1291, 1250, 1169, 1088, 1027, 846, 766, 730; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.98 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 0.12H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.0, 163.4, 131.7 (2C), 122.7, 113.7 (2C), 55.5, 51.7 -50.7 (m, C-D_3); HRMS (EI): m/z caled for $C_9H_7D_3O_3$: 169.0818, Found: 169.0816; I_D:I_H = 100:3.31.

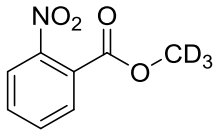


Methyl-*d*$_3$ 3,5-bis(trifluoromethyl)benzoate (7f): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3,5-bis(trifluoromethyl)benzoic acid (64.5 mg, 0.25 mmol,), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (42.8 mg, 62.2% yield). Deuterium

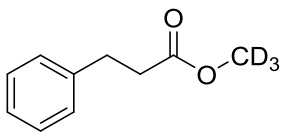
incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 1735, 1271, 1126, 913, 847, 768, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.49 (s, 2H), 8.06 (s, 1H), 4.00 (s, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 132.9 - 131.8 (m, 1C), 129.9 (2C), 127.1, 126.6 -126.4 (m, 1C), 124.4, 121.7, 119.0, 52.6 - 52.2 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_3D_3F_6O_2$: 275.0460, Found: 275.0459; I_D:I_H = 100:2.84.



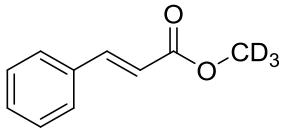
Methyl-*d_3* 4-cyanobenzoate (7g): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d_6* (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-cyanobenzoic acid (36.8 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a off-white solid (32.3 mg, 78.7% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 2230, 1715, 1283, 1130, 1081, 863, 760, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.17 - 8.09 (m, 2H), 7.78 - 7.69 (m, 2H), 3.95 (s, 0.11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 134.0, 132.3 (2C), 130.2 (2C), 118.1, 116.5, 52.9 - 52.7 (m, C-D_3); HRMS (EI): m/z caled for $C_9H_4D_3NO_2$: 164.0665, Found: 164.0663; I_D:I_H = 100:3.07.



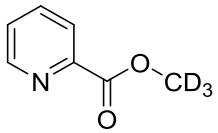
Methyl-*d_3* 2-nitrobenzoate (7h): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d_6* (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-nitrobenzoic acid (41.8 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (46.2 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.4% D. IR (film): ν_{max} (cm^{-1}) 1729, 1527, 1350, 1298, 1140, 1078, 854, 730; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.89 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.73 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.5 Hz, 1H), 7.65 - 7.60 (m, 1H), 3.91 (s, 0.11H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.0, 148.3, 133.0, 131.9, 129.9, 127.6, 124.0, 53.4 - 52.2 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_4D_3NO_4$: 184.0563, Found: 184.0562; I_D:I_H = 100:3.45.



Methyl-*d*$_3$ 3-phenylpropanoate (7i): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-phenylpropanoic acid (37.5 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at 40 ºC for 4 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (41.8 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.7% D. IR (film): ν_{max} (cm^{-1}) 1733, 1194, 1087, 747, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 - 7.28 (m, 2H), 7.22 (dd, *J* = 7.1, 4.9 Hz, 3H), 3.68 (s, 0.12H), 2.97 (t, *J* = 7.9 Hz, 2H), 2.65 (t, *J* = 7.9 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 140.6, 128.6 (2C), 128.4 (2C), 126.3, 51.7 - 50.5 (m, C-D_3), 35.8, 31.1; HRMS (EI): m/z caled for $C_{10}H_9D_3O_2$: 167.1026, Found: 167.1025; I_D:I_H = 100:3.94.

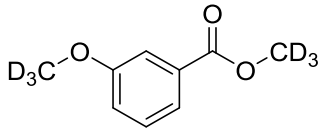


Methyl-*d*$_3$ cinnamate (7j): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol, 1.0 equiv), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added cinnamic acid (37.0 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a pale yellow liquid (39.3 mg, 95.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.1% D. IR (film): ν_{max} (cm^{-1}) 1707, 1638, 1332, 1316, 1189, 1085, 982, 769, 713, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, *J* = 16.0 Hz, 1H), 7.56 - 7.49 (m, 2H), 7.43 - 7.34 (m, 3H), 6.49 - 6.40 (m, 1H), 3.80 (s, 0.12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.6, 145.0, 134.5, 130.4, 129.0 (2C), 128.2 (2C), 117.9, 51.8 - 50.7 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_7D_3O_2$: 165.0869, Found: 165.0868; I_D:I_H = 100:5.80.



Methyl-*d*$_3$ picolinate (7k): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added picolinic acid (30.8 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at rt for 3 h, the reaction mixture was purified by flash chromatography (20% ethyl acetate/petroleum ether) to provide the title compound as a yellow liquid (30.8 mg, 87.6% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.1% D. IR (film): ν_{max} (cm^{-1}) 1719, 1312, 1248, 1146, 1085, 748, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.71 (ddd, *J* = 4.7, 1.7, 0.8 Hz, 1H), 8.10 (dt, J = 7.8, 1.0 Hz, 1H), 7.81 (td, *J* = 7.8, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 3.97 (s, 0.12H); ^{13}C

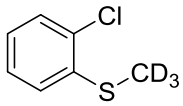
NMR (100 MHz, $CDCl_3$) δ ppm 165.8, 149.9, 147.9, 137.1, 127.0, 125.2, 53.0 - 51.8 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3NO_2$: 140.0665, Found: 140.0663; I_D:I_H = 100:3.87.



Methyl-*d*$_3$ 3-(methoxy-*d*$_3$)benzoate (7l): According to the general procedure, the mixture solution of TMSOI (220.1 mg, 1.0 mmol), DMSO-*d*$_6$ (2.8 mL, 40.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-hydroxybenzoic acid (34.5 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 16 h, the reaction mixture was purified by flash chromatography (10% ethyl acetate/petroleum ether) to provide the title compound as a yellow liquid (39.5 mg, 83.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: methoxy-*d*$_3$ benzene: 87.5% D; Methyl-*d*$_3$ benzoate: 93.8% D. IR (film): v_{max} (cm^{-1}) 2926, 1717, 1296, 1226, 1109, 1084, 873, 750, 680; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1H NMR (400 MHz, CDCl3) δ 7.66 - 7.61 (m, 1H), 7.55 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.10 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 3.91 (s, 0.17H), 3.85 - 3.81 (m, 0.38H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.1, 159.6, 131.5, 129.5 (2C), 122.0, 119.6, 114.0, 55.4 - 54.2 (m, C-D_3), 52.3 - 51.2 (m, C-D_3); HRMS (EI): m/z caled for $C_9H_4D_6O_3$: 172.1007, Found: 172.1008; I_D:I_H = 100:0.

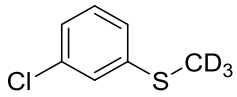
4.3 General procedure for substituted methylthio-*d*$_3$ benzene

TMSOI (0.5 mmol, 1.0 equiv), DMSO-*d*$_6$ (20.0 mmol, 40.0 equiv) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h. After cooling to room temperature, to the reaction mixture were added a substituted thiophenol (0.25 mmol, 0.5 equiv), base (1.0 mmol, 2.0 equiv). The resulting solution was stirred at 65 ºC for 18 h. The solution was cooled to room temperature and the desired product was obtained by flash chromatography on silica gel using the indicated solvent system. The level of deuterium incorporation in the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against **equation1**.

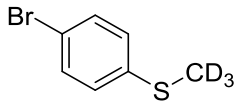


(2-Chlorophenyl)(methyl-*d*$_3$)sulfane (7m): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-chlorobenzenethiol (36.3 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (petroleum ether) to provide the title compound as a pale yellow oil (35.0 mg, 86.7% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.8% D. IR (film): v_{max} (cm^{-1}) 3060,

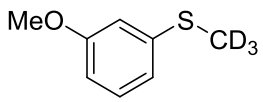
2922, 2853, 1452, 1431, 1035, 741; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.28 - 7.20 (m, 1H), 7.16 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.12 - 7.03 (m, 1H), 2.47 - 2.44 (m, 0.13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 137.8, 132.0, 129.5, 127.3, 125.7, 125.6, 14.9 - 14.4 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3ClS$: 161.0145, Found: 161.0143; I_D:I_H = 100:3.97.



(3-Chlorophenyl)(methyl-*d*$_3$)sulfane (7n): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-chlorobenzenethiol (36.3 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (petroleum ether) to provide the title compound as a pale yellow oil (38.6 mg, 95.4% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.2% D. IR (film): v_{max} (cm^{-1}) 3056, 2920, 2850, 1576, 1561, 1460, 1087, 856, 768, 675; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.23 - 7.17 (m, 2H), 7.14 - 7.06 (m, 2H), 2.48 - 2.44 (m, 0.21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 140.8, 134.9, 129.9, 126.0, 125.1, 124.6, 15.6 - 14.8 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3ClS$: 161.0145, Found: 161.0143; I_D:I_H = 100:4.14.

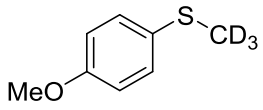


(3-Bromophenyl)(methyl-*d*$_3$)sulfane (7o): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol, 1.0 equiv), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-bromobenzenethiol (47.3 mg, 0.25 mmol), K_2CO_3 (138.2 mg) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (petroleum ether) to provide the title compound as a yellow solid (42.3 mg, 82.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.1% D. IR (film): v_{max} (cm^{-1}) 2926, 2852, 1469, 1092, 1001, 803; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 - 7.36 (m, 2H), 7.16 - 7.07 (m, 2H), 2.46 - 2.42 (m, 0.18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 137.8, 131.9 (2C), 128.2 (2C), 118.7, 15.6 - 15.0 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_4D_3BrS$: 204.9640, Found: 204.9642; I_D:I_H = 100:4.91.

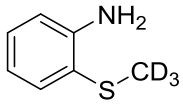


(3-Methoxyphenyl)(methyl-*d*$_3$)sulfane (7p): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 3-methoxybenzenethiol (35.1 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (petroleum ether) to

provide the title compound as a pale yellow liquid (37.7 mg, 96.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 94.7% D. IR (film): ν_{max} (cm^{-1}) 3001, 2937, 2833, 1588, 1572, 1475, 1282, 1246, 1228, 1037, 862, 847, 760, 683; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.20 (t, *J* = 8.0 Hz, 1H), 6.87 - 6.78 (m, 2H), 6.69 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.80 (s, 3H), 2.48 - 2.45 (m, 0.16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.0, 139.9, 118.8, 112.2, 110.7, 55.3, 15.8 - 14.5 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_7D_3OS$: 157.0641, Found: 157.0642; I_D:I_H = 100:0.

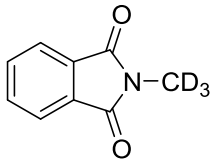


(4-Methoxyphenyl)(methyl-*d*$_3$)sulfane (7q): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 4-methoxybenzenethiol (35.1 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (petroleum ether) to provide the title compound as a pale yellow liquid (34.7 mg, 88.2% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.5% D. IR (film): ν_{max} (cm^{-1}) 3000, 2940, 2834, 1491, 1239, 1027, 818, 618; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29 - 7.22 (m, 2H), 6.89 - 6.79 (m, 2H), 3.78 (s, 3H), 2.44 - 2.40 (m, 0.23H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.3, 130.3 (2C), 128.8, 114.7 (2C), 55.5, 18.2 - 17.2 (m, C-D_3); HRMS (EI): m/z caled for $C_8H_7D_3OS$: 157.0641, Found: 157.0642; I_D:I_H = 100:6.35.

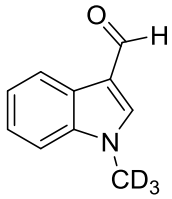


2-((Methyl-*d*$_3$)thio)aniline (7r): According to the general procedure, the mixture solution of TMSOI (110.0 mg, 0.5 mmol), DMSO-*d*$_6$ (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-aminobenzenethiol (31.3 mg, 0.25 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (petroleum ether) to provide the title compound as a pale yellow oil (13.5 mg, 38.0% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.2% D. IR (film): ν_{max} (cm^{-1}) 3449, 3349, 3063, 2922, 1605, 1478, 1447, 1296, 1194, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.35 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.09 (td, *J* = 7.5, 1.5 Hz, 1H), 6.74 - 6.68 (m, 2H), 4.27 (s, 2H), 2.36 - 2.32 (m, 0.24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 147.2, 133.5, 129.0, 120.3, 118.9, 115.0, 54.4 - 53.6 (m, C-D_3); HRMS (EI): m/z caled for $C_7H_6D_3NS$: 142.0644, Found: 142.0645; I_D:I_H = 100:5.49.

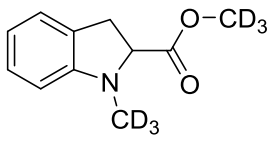
4.4 Experimental procedure for N-methylation-d_3 of amino compounds



2-(Methyl-d_3)isoindoline-1,3-dione (7s): The mixture solution of trimethylsulfo -xonium iodide (110.0 mg, 0.5 mmol), DMSO-d_6 (1.4 mL, 20.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added isoindoline-1,3-dione (36.3 mg, 0.25 mmol), K_2CO_3 (69.1 mg, 0.5 mmol) to the reaction mixture. After stirring at 40 ºC for 12 h, the reaction mixture was cooled to room temperature and was purified by flash chromatography (50% dichloromethane/petroleum ether) to provide the title compound as a white solid (57.0 mg, 77.4% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 93.4% D. IR (film): ν_{max} (cm^{-1}) 1707, 1403, 1186, 915, 710, 527; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.85 - 7.76 (m, 2H), 7.71 - 7.65 (m, 2H), 3.15 - 3.12 (m, 0.20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.5 (2C), 133.9 (2C), 132.3 (2C), 123.2 (2C), 23.9 - 22.7 (m, C-D_3); HRMS (EI): m/z caled for $C_9H_4D_3NO_2$: 164.0665, Found: 164.0664; I_D:I_H = 100:5.26.



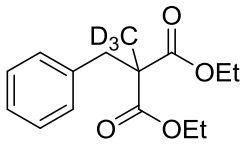
1-(Methyl-d_3)-1H-indole-3-carbaldehyde (7t): The mixture solution of TMSOI (165.1 mg, 0.75 mmol,), DMSO-d_6 (2.1 mL, 30.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (3 mL) solution of 1H-indole-3-carbaldehyde (54.4 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 15.0 mg, 0.375 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-d_6 solution of TMSOI was added and was heated to reflux for 6 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (50% ethyl acetate/petroleum ether) to provide the title compound as a white solid (64.4 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.5% D. IR (film): ν_{max} (cm^{-1}) 3102-2735, 1637, 1530, 1470, 1359, 1326, 780, 741, 715; ^{1}H NMR δ ppm 9.92 (s, 1H), 8.33 - 8.26 (m, 1H), 7.59 (s, 1H), 7.36 - 7.28 (m, 3H), 3.80 - 3.76 (m, 0.14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 184.5, 139.5, 137.9, 125.2, 123.9, 122.9, 122.0, 118.0, 110.0, 33.7 - 32.3 (m, C-D_3); HRMS (EI): m/z caled for $C_{10}H_6D_3NO$: 162.0872, Found: 162.0873; I_D:I_H = 100:4.38.



Methyl-*d*$_3$ 1-(methyl-*d*$_3$)indoline-2-carboxylate (7u): The mixture solution of TMSOI (220.1 mg, 1.0 mmol), DMSO-*d*$_6$ (2.8 mL, 40.0 mmol) was stirred at 120 ºC for 2 h. After cooling to room temperature, added 2-hydroxybenzoic acid (40.8 mg, 0.25 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) to the reaction mixture. After stirring at 65 ºC for 18 h before cooling to room temperature, the reaction mixture was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a white solid (19.2 mg, 38.9% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 1-(methoxy-*d*$_3$) indoline: 94.3% D; Methyl-*d*$_3$ benzoate: 95.7% D. IR (film): ν_{max} (cm^{-1}) 1698, 1478, 1410, 1255, 1223, 1085, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.11 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.70 (td, *J* = 7.4, 0.7 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 4.05 (t, *J* = 9.8 Hz, 1H), 3.80 (s, 0.12H), 3.35 (dd, *J* = 15.7, 9.8 Hz, 1H), 3.13 (dd, *J* = 15.7, 9.7 Hz, 1H), 2.84 - 2.80 (m, 0.16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 173.3, 152.3, 128.0, 127.2, 124.2, 118.6, 107.6, 68.2, 55.8 - 54.6 (m, C-D_3), 52.1 - 51.1 (m, C-D_3) 33.64; HRMS (EI): m/z caled for $C_{11}H_7D_6NO_2$: 197.1323, Found: 197.1322; I_D:I_H = 100:0.

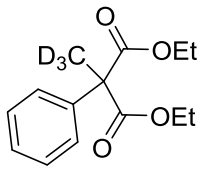
4.5 General procedure for methylation-*d*$_3$ of active methylene compounds

TMSOI (0.75 mmol, 1.0 equiv), DMSO-*d*$_6$ (30.0 mmol, 40.0 equiv) were added in a 15 mL sealed reaction tube. The mixture solution was stirred at 120 ºC for 2 h before being cooled to room temperature. To an anhydrous THF (3 mL) solution of active methylene compound (0.375 mmol, 0.5 equiv) was added sodium hydride (60% dispersion in mineral oil, 0.563 mmol, 0.75 equiv) was added at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature and evaporating to remove THF and, it was extracted by a conventional method, the residue was purified by flash chromatography on silica gel using the indicated solvent system. The level of deuterium incorporation in the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against **equation1**.

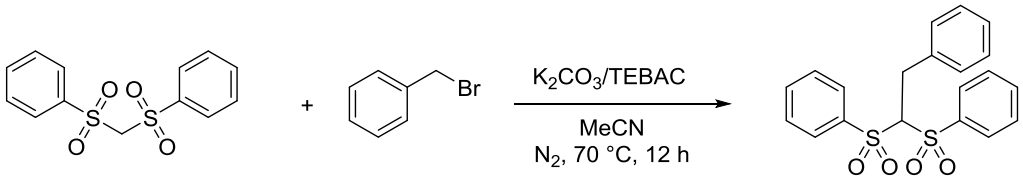


Diethyl 2-benzyl-2-(methyl-*d*$_3$)malonate (7v): According to the general procedure, the mixture solution of TMSOI (165.1 mg, 0.75 mmol,), DMSO-*d*$_6$ (2.1 mL, 30.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (3 mL) solution of diethyl 2-benzylmalonate (93.8 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 22.5 mg, 0.563 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then

brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a colourless liquid (97.2 mg, 98.2% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.7% D. IR (film): ν_{max} (cm^{-1}) 2981, 1727, 1271, 1236, 1180, 1098, 1043, 737, 670; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29 - 7.20 (m, 3H), 7.16 - 7.09 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.24 (s, 2H), 1.35 (s, 0.13H), 1.26 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.0 (2C), 136.3, 130.3 (2C), 128.2 (2C), 127.0, 61.4 (2C), 54.7, 41.1, 19.8 - 18.6 (m, C-D_3), 14.1 (2C); HRMS (EI): m/z caled for $C_{15}H_{17}D_3O_4$: 267.1550, Found: 267.1551; I_D:I_H = 100:3.87.

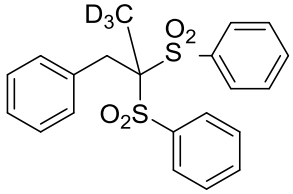


Diethyl 2-(methyl-*d*$_3$)-2-phenylmalonate (7w): According to the general procedure, the mixture solution of TMSOI (165.1 mg, 0.75 mmol,), DMSO-*d*$_6$ (2.1 mL, 30.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (3 mL) solution of diethyl 2-phenylmalonate (59.0 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 22.5 mg, 0.563 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a colourless liquid (62.8 mg, > 99% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.6% D. IR (film): ν_{max} (cm^{-1}) 2983, 1729, 1242, 1197, 1045, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 - 7.26 (m, 5H), 4.27 - 4.19 (m, 4H), 1.87 (s, 0.10H), 1.26 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.6 (2C), 138.4, 128.2 (2C), 127.6, 127.5 (2C), 61.8 (2C), 58.7, 22.4 - 21.2 (m, C-D_3), 14.1 (2C); HRMS (EI): m/z caled for $C_{14}H_{15}D_3O_4$: 253.1393, Found: 253.1394; I_D:I_H = 100:3.51.

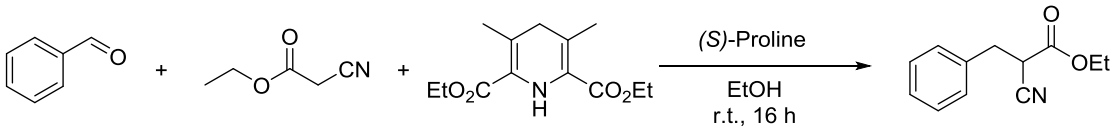


(2-Phenylethane-1,1-diyldisulfonyl)dibenzene (6x)[5]**:** To a stirred suspension of bis(phenylsulfonyl)methane (593 mg, 2.0 mmol), K_2CO_3 (304 mg, 2.2 mmol), TEBAC (91 mg, 0.4 mmol) in dry acetonitrile (10 mL) was added benzyl bromide (285 µL, 2.4 mmol) dropwise under N_2 atomosphere. The mixture was stirred at 70 ºC for 12 h. The reaction was monitored by TLC and after completion of the reaction it

was cooled to room temperature and filtered through a celite pad. The filtrate was evaporated under vacuo and the residue was purified by flash chromatography (25% ethyl acetate/petroleum ether) to provide the pure product as a white solid (737 mg, 95.3% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.87 (d, *J* = 7.5 Hz, 4H), 7.66 (t, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 4H), 7.17 (s, 3H), 7.02 (s, 2H), 4.75 (t, *J* = 5.0 Hz, 1H), 3.53 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 138.2, 136.3 (2C), 134.7 (2C), 129.6 (4C), 129.3 (4C), 128.8 (2C), 128.8 (2C), 127.3, 31.4. Spectral data match those previously reported.

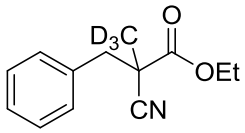


(1-Phenylpropane-2,2-diyldisulfonyl-3,3,3-*d*$_3$)dibenzene (7x): According to the general procedure, the mixture solution of TMSOI (165.1 mg, 0.75 mmol,), DMSO-*d*$_6$ (2.1 mL, 30.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (3 mL) solution of **6x** (144.9 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 22.5 mg, 0.563 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (50% dichloromethane /petroleum ether) to provide the title compound as a white solid (135.2 mg, 89.2% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 92.0% D. IR (film): ν_{max} (cm^{-1}) 2922, 1447, 1309, 1135, 1073, 759, 737, 715, 688, 625; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.03 (dd, *J* = 8.4, 1.1 Hz, 4H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 4H), 7.26 (dd, *J* = 6.4, 3.2 Hz, 3H), 7.24 - 7.16 (m, 2H), 3.61 (s, 2H), 1.64 - 1.62 (m, 0.26H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 136.4, 134.7 (2C), 133.3 (2C), 131.6 (4C), 131.5 (4C), 128.8 (2C), 128.2 (2C), 127.6, 87.5, 36.1, 17.9 - 16.2 (m, C-D_3); HRMS (EI): m/z caled for $C_{21}H_{17}D_3O_4S_2$: 403.0991, Found: 403.0992; I_D:I_H = 100:7.25.

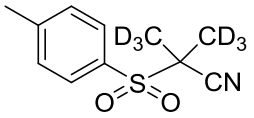


Ethyl 2-cyano-3-phenylpropanoate (6y)[6]**:** To a stirred suspension of benzaldehyde (0.53 g, 5.0 mmol), ethyl 2-cyanoacetate (0.53 mL, 5.0mmol), Hantzsch ester (1.27g, 5.0 mmol) was added anhydrous ethanol (10 mL), and then the catayst proline (58 mg, 0.5mmol) was added and the reaction was sttired at rt for 16 h. The mixture was evaporated to remove ethanol and then was treated with ethyl acetate (50 mL), and the organic layer was washed with 1M HCl (8 × 20 mL), H_2O (50 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was

purified by flash chromatography (10% ethyl acetate/petroleum ether) to provide the pure product as a pale yellow oil (0.98 g, 96.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 - 7.27 (m, 5H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.72 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.24 (ddd, *J* = 22.3, 13.8, 7.1 Hz, 2H), 1.27 (dd, *J* = 9.0, 5.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.7, 135.4, 129.2 (2C), 129.0 (2C), 127.9, 116.3, 63.1, 39.8, 35.9, 14.1. Spectral data match those previously reported.

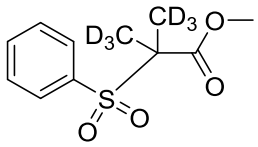


Ethyl 2-benzyl-2-cyanopropanoate-3,3,3-*d*$_3$ (7y): According to the general procedure, the mixture solution of TMSOI (165.1 mg, 0.75 mmol,), DMSO-*d*$_6$ (2.1 mL, 30.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (3 mL) solution of **6y** (76.2 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 15.0 mg, 0.375 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (5% ethyl acetate/petroleum ether) to provide the title compound as a white solid (65.2 mg, 78.9% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 96.0% D. IR (film): ν_{max} (cm^{-1}) 3034, 2985, 2931, 2855, 1738, 1223, 1089, 1048, 733, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 - 7.28 (m, 5H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 13.5 Hz, 1H), 3.07 (d, *J* = 13.5 Hz, 1H), 1.65 (s, 0.12H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.1, 134.3, 130.1 (2C), 128.7 (2C), 128.0, 119.9, 62.909, 45.3, 43.7, 23.3 - 22.0 (m, C-D_3), 14.0; HRMS (EI): m/z caled for $C_{13}H_{12}D_3NO_2$: 220.1291, Found: 220.1292; I_D:I_H = 100:3.69.



2-(Methyl-*d*$_3$)-2-tosylpropanenitrile-3,3,3-*d*$_3$ (7z): According to the general procedure, the mixture solution of TMSOI (330.1 mg, 1.5 mmol,), DMSO-*d*$_6$ (4.2 mL, 60.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (5 mL) solution of 2-tosylacetonitrile (73.2 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 45.0 mg, 1.125 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10 mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (10% ethyl acetate/petroleum ether) to provide the title compound as a off-white solid (75.8 mg, 90.5% yield). Deuterium

incorporation based on ^{1}H NMR spectroscopy: 95.9% D. IR (film): ν_{max} (cm^{-1}) 2924, 2853, 1323, 1152, 1084, 1051, 1009, 813, 665; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.87 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 3H), 1.68 (s, 0.25H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.7, 130.8 (2C), 130.5, 130.1 (2C), 118.4, 57.3, 21.9 (s), 21.1 - 19.9 (m, 2C-D_3); HRMS (EI): m/z caled for $C_{11}H_7D_6NO_2S$: 229.1044, Found: 229.1045; I_D:I_H = 100:0.



Methyl 2-(methyl-*d*$_3$)-2-(phenylsulfonyl)propanoate-3,3,3-*d*$_3$ (7aa): According to the general procedure, the mixture solution of TMSOI (330.1 mg, 1.5 mmol,), DMSO-*d*$_6$ (4.2 mL, 60.0 mmol) was stirred at 120 ºC for 2 h before being cooled. To an anhydrous THF (5 mL) solution of 2-(phenylsulfonyl)acetate (80.3 mg, 0.375 mmol) was added sodium hydride (60% dispersion in mineral oil, 45.0 mg, 1.125 mmol) at 0 ºC. After 30 minutes of stirring, the previous DMSO-*d*$_6$ solution of TMSOI was added and was heated to reflux for 8 hours at 80 ºC. After cooling to room temperature, the reaction mixture was evaporated to remove THF and then was treated with water (10 mL) and ethyl acetate (10mL). The organic layer was washed with water (2 × 10 mL), then brine, and dryed over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (10% ethyl acetate/petroleum ether) to provide the title compound as a yellow oil (85.5 mg, 94.1% yield). Deuterium incorporation based on ^{1}H NMR spectroscopy: 95.9% D. IR (film): ν_{max} (cm^{-1}) 2959, 2922, 2851, 1735, 1447, 1266, 1141, 1073, 791, 719, 695, 633; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.87 (dd, *J* = 42.7, 7.9 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 3.65 (s, 3H), 1.59 (s, 0.25H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.3, 135.6, 134.2, 133.8 (2C), 130.3, 129.4 (2C), 128.8, 127.4, 68.8, 53.1, 20.2 - 19.0 (m, 2C-D_3); HRMS (EI): m/z caled for $C_{11}H_8D_6O_4S$: 248.0989, Found: 248.0990; I_D:I_H = 100:0.

5. References

(1) William, J. K.; Marc, R.; Tell, T. *Angew. Chem. Int. Ed.* **2017**, *129*, 7916.

(2) Ettaoussi, M.; Sabaouni, A.; Rami, M.; Boutin, J. A.; Delagrange, P.; Renard, P.; Spedding, M.; Caignard, D. H.; Berthelot, P.; Yous, S. *Eur. J. Org. Chem.* **2012**, *49*, 310.

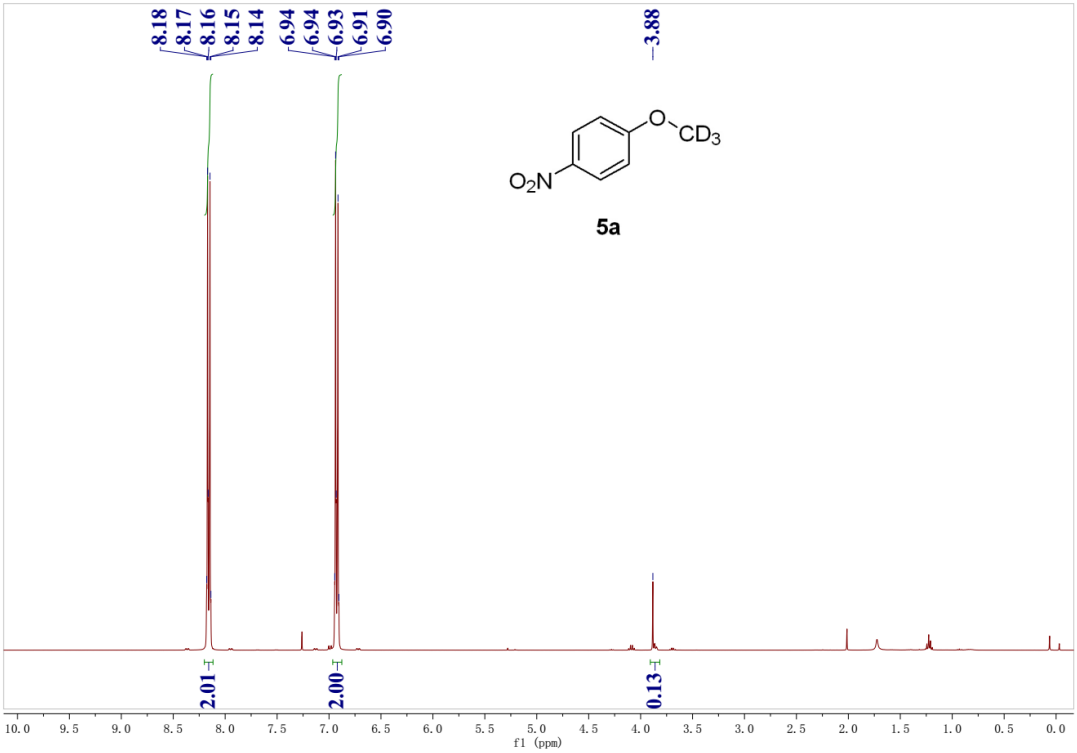
(3) Matsumoto, Shunichiro, *et al.* Preparation of indole compounds and their salts as peripheral MT1 and/or MT2 receptor agonists, and preventive and therapeutic compositions containing them for urinary incontinence: IN2015108039 [P]. 2015-7-23.

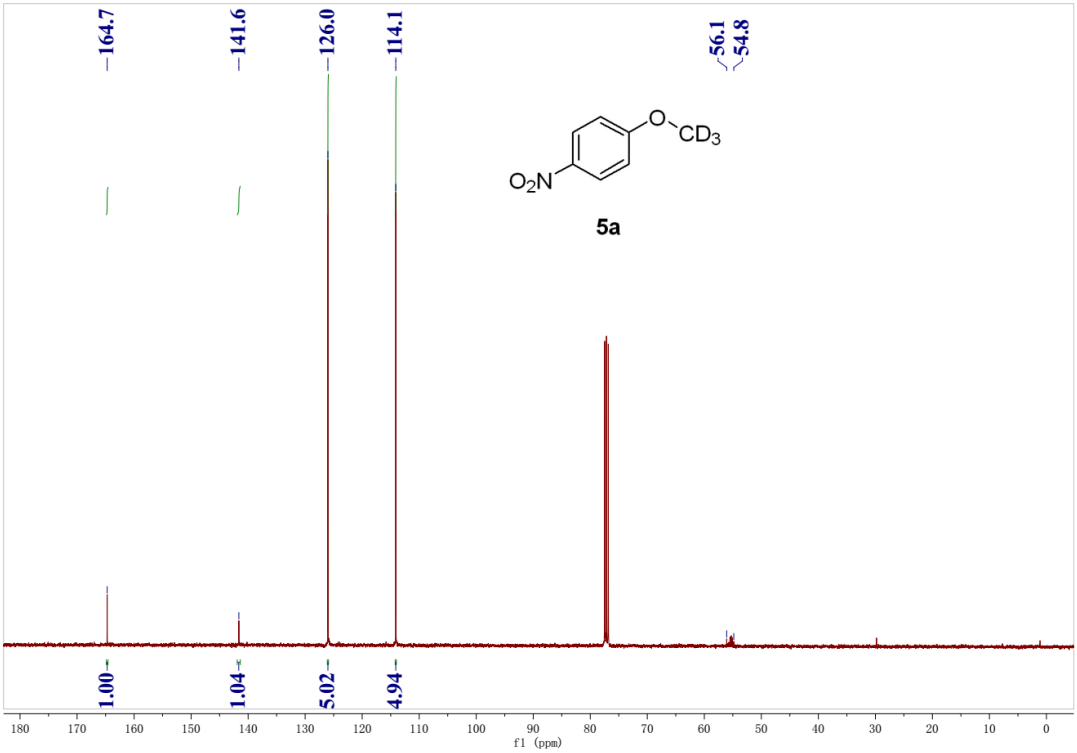
(4) Zhang, B.; Fan, C.; Dong, L.; Wang, F.; Yue, J. *Eur. J. Org. Chem.*, **2010**, *45*, 5258.

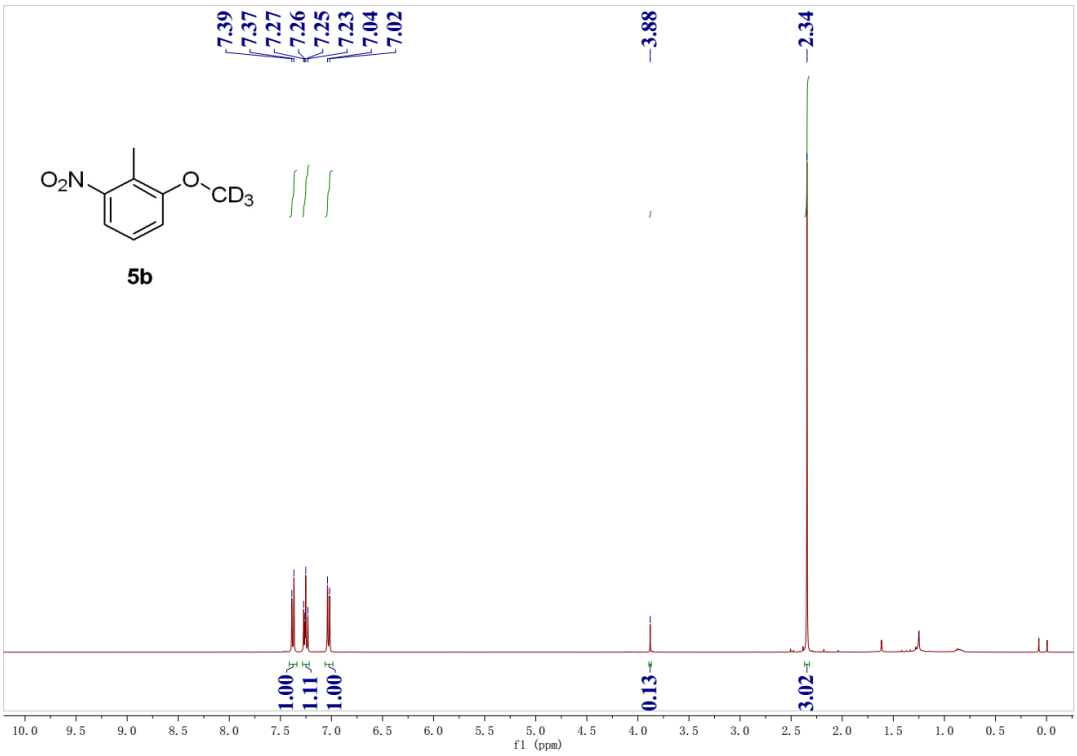
(5) Wang, Y.; Huang, X. *Chemical Research in Chinese Universities* **1993**, *9*, 91.

(6) Che, J.; Lam, Y. L. *Adv. Synth. Catal.* **2010**, *352*, 1752.

6. Spectral Data for the Products



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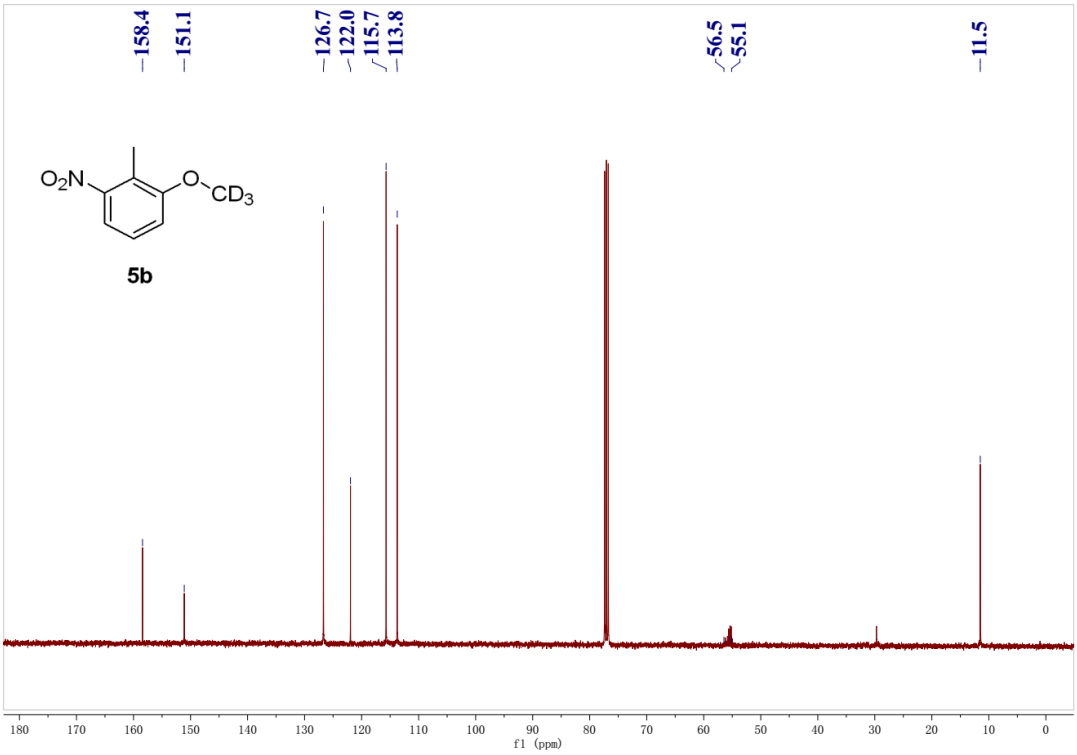
f1 (ppm)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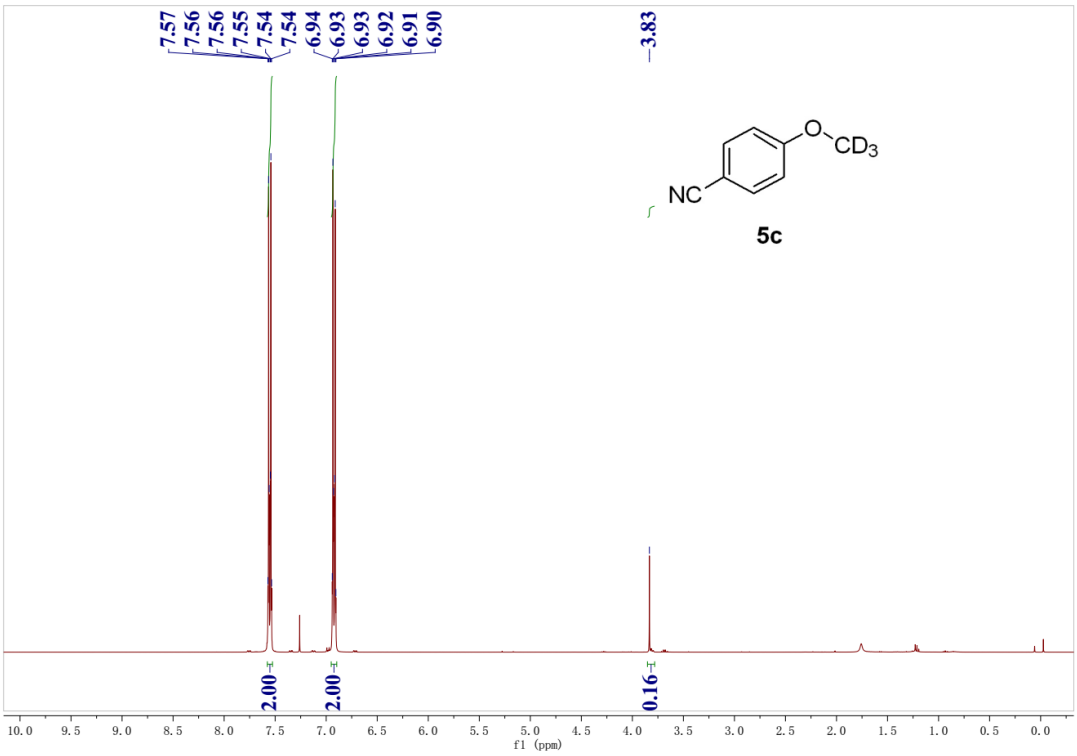
f1 (ppm)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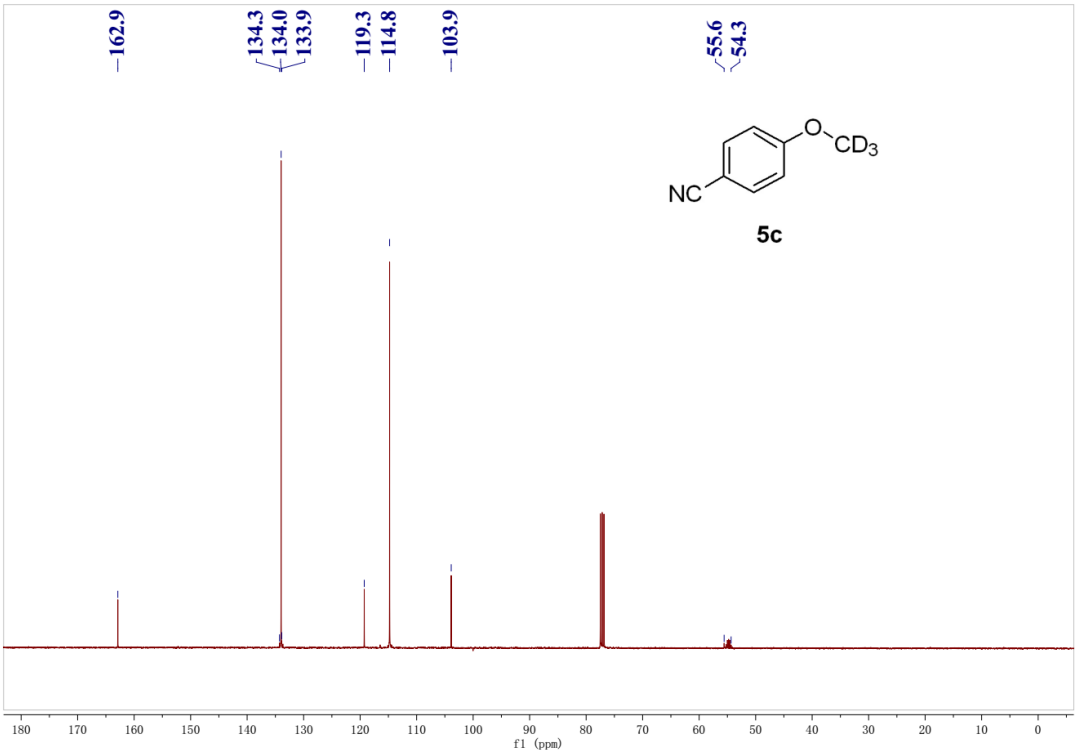
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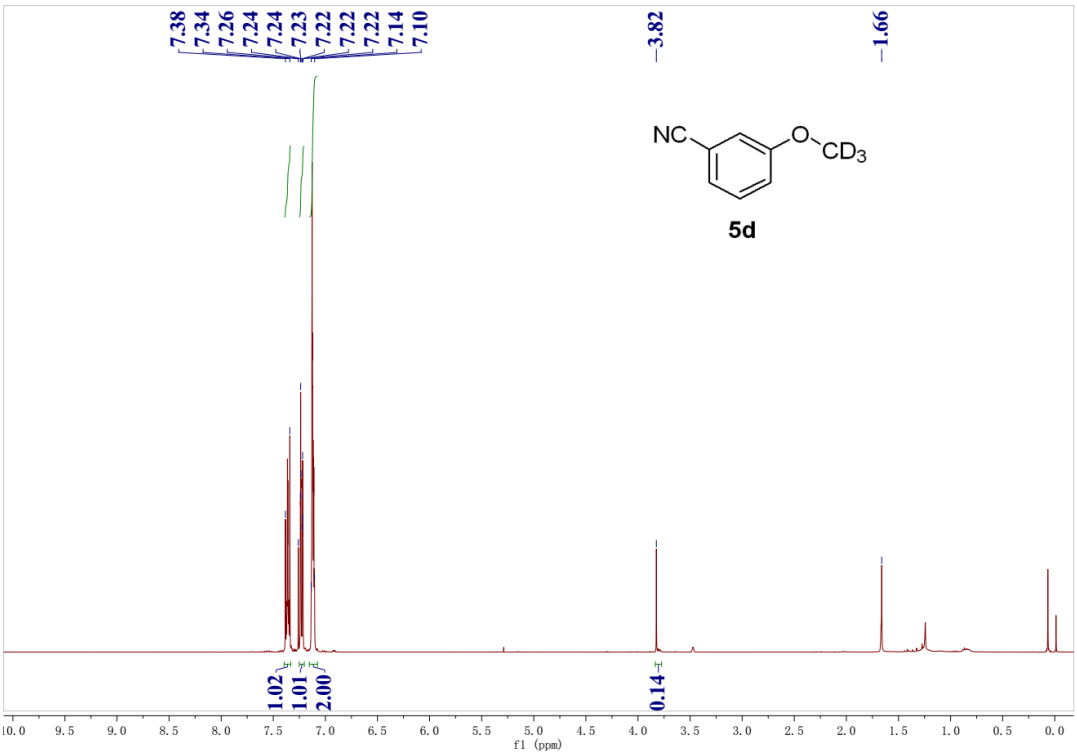
5c
f1 (ppm)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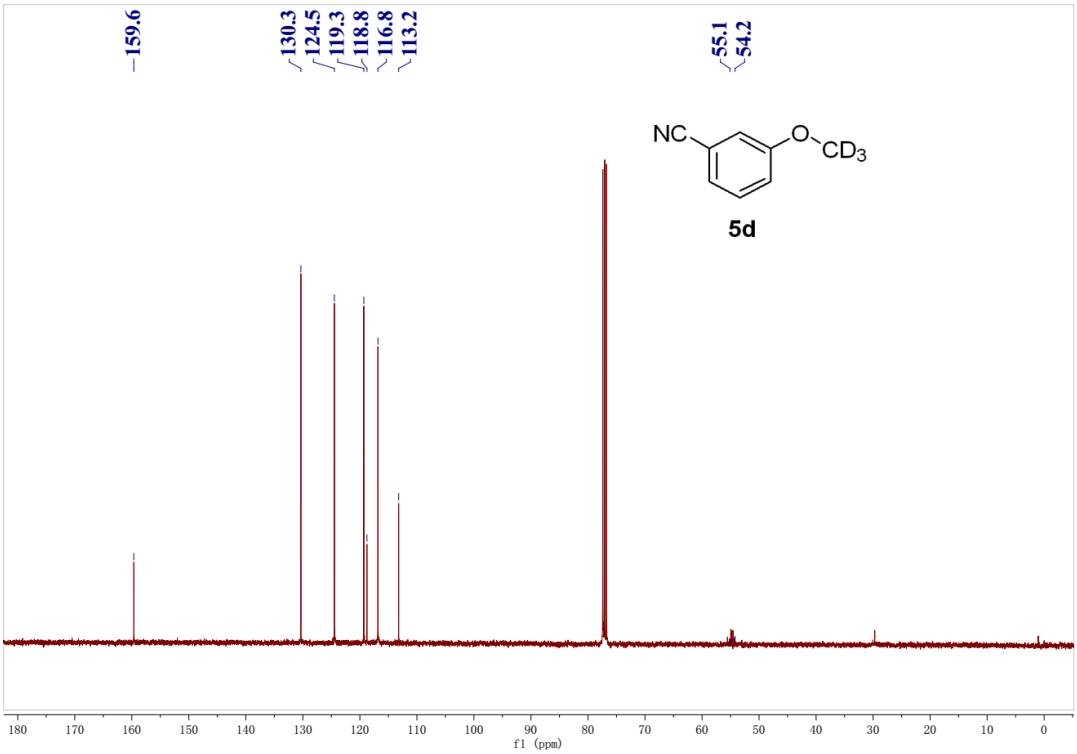
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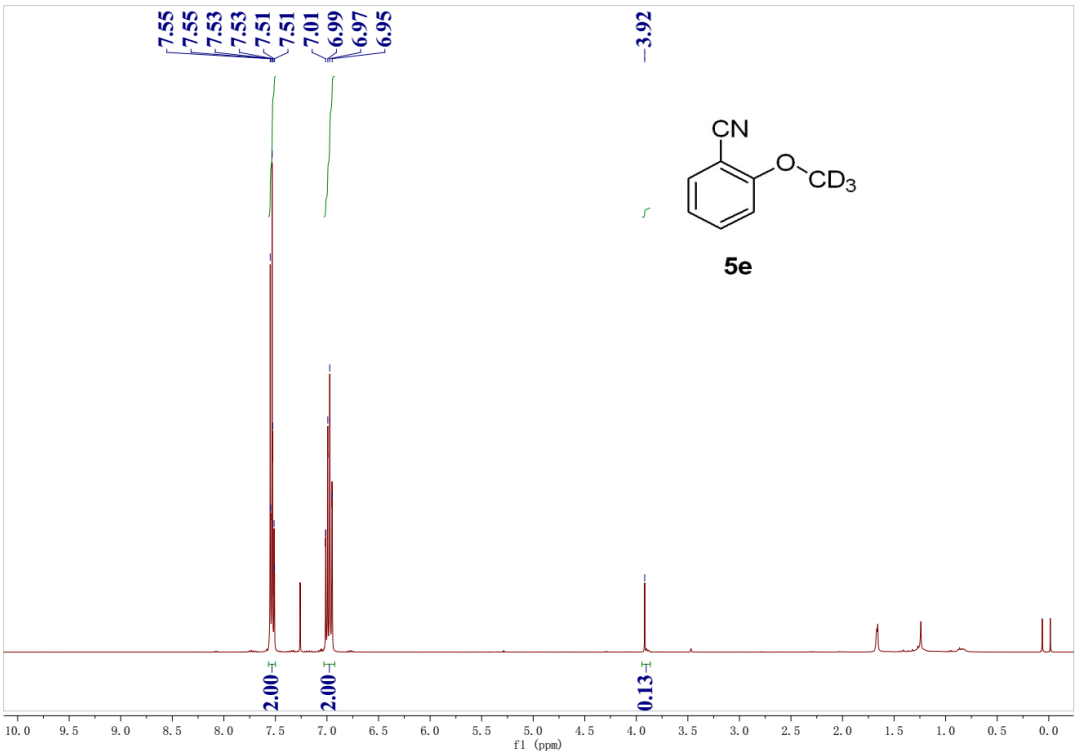
f1 (ppm)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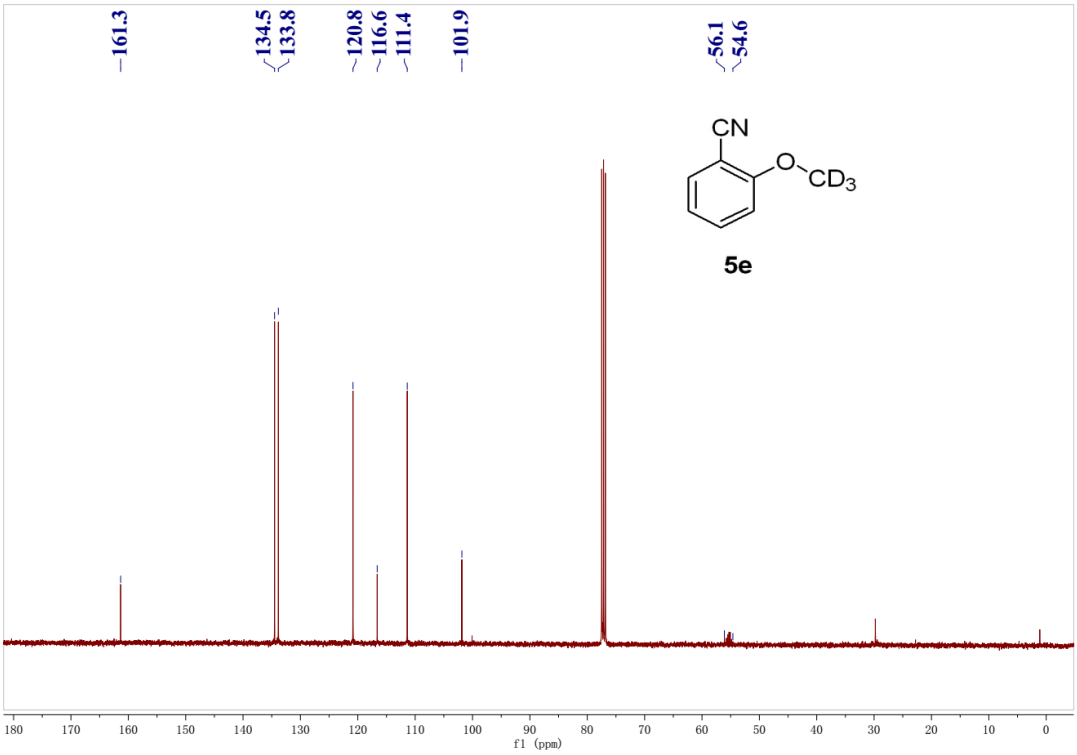
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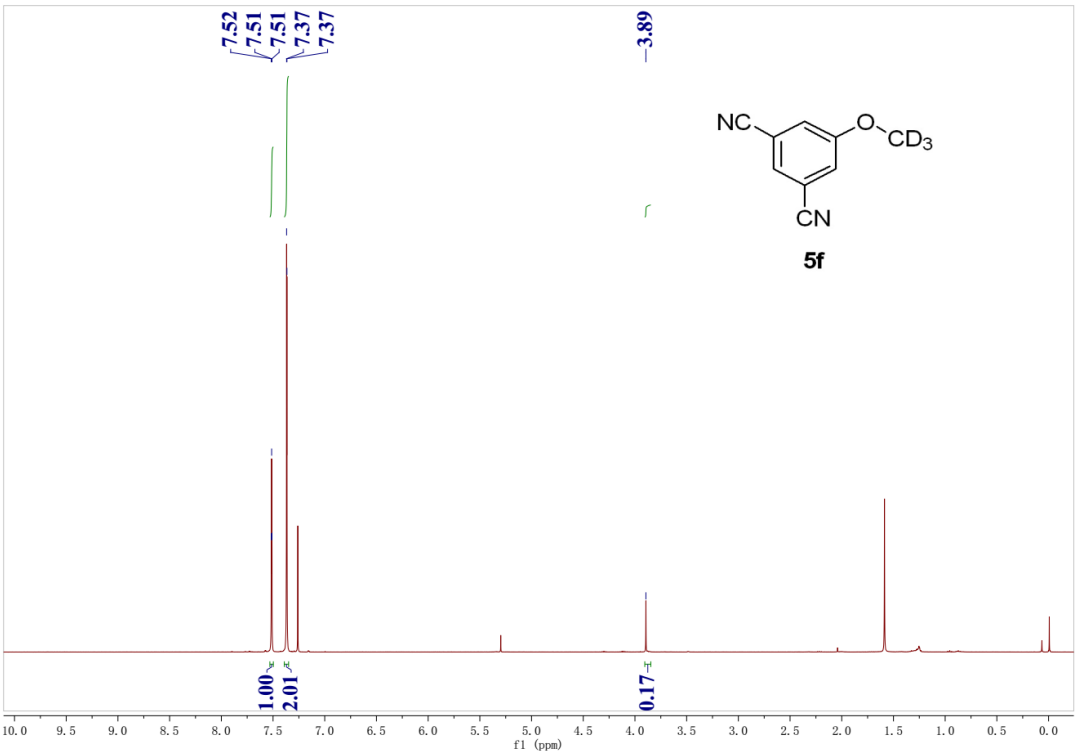
CD3
5e
f1 (ppm)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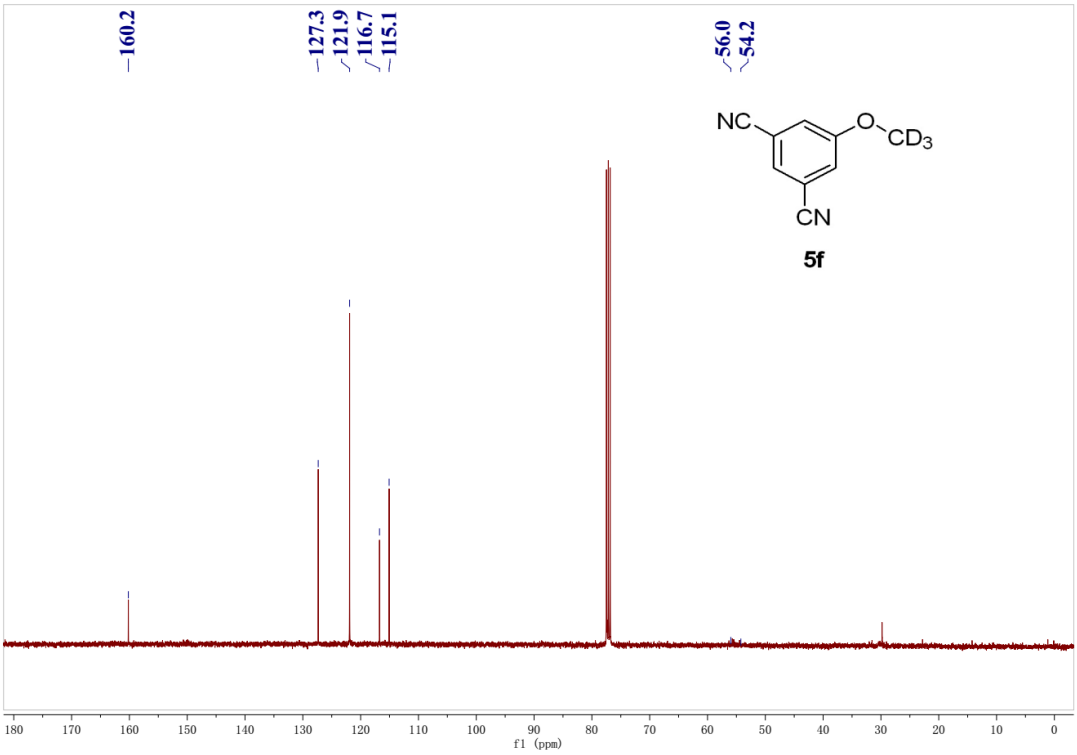
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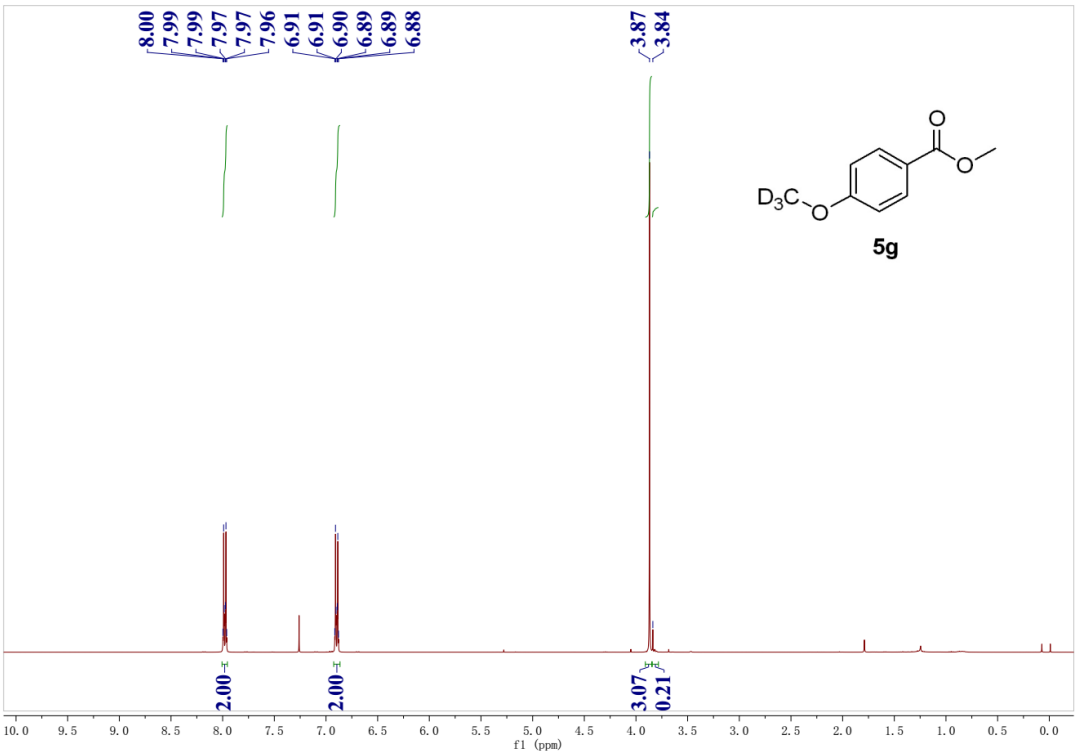
CN
5f
f1 (ppm)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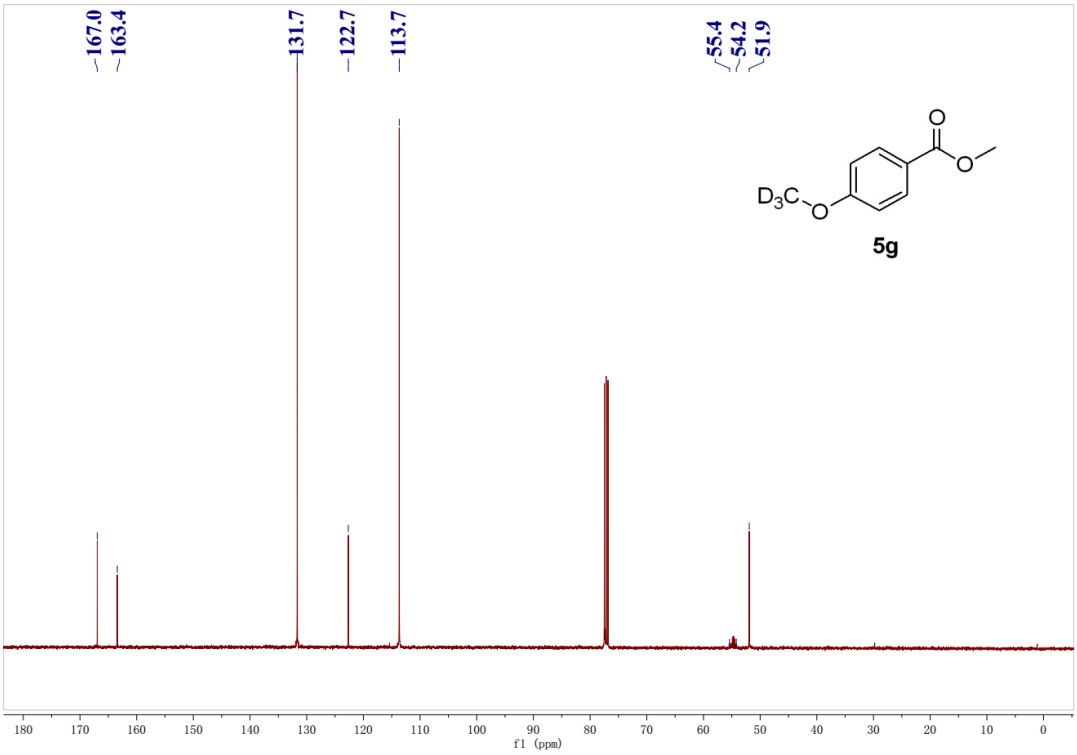
O
O
5g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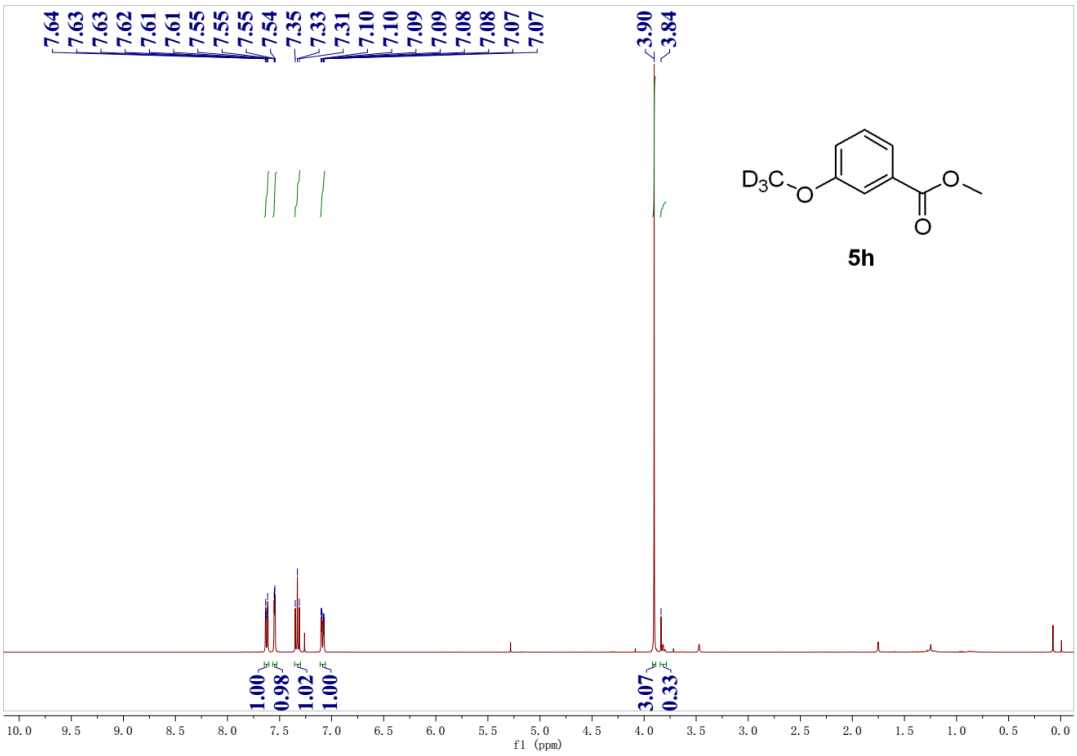
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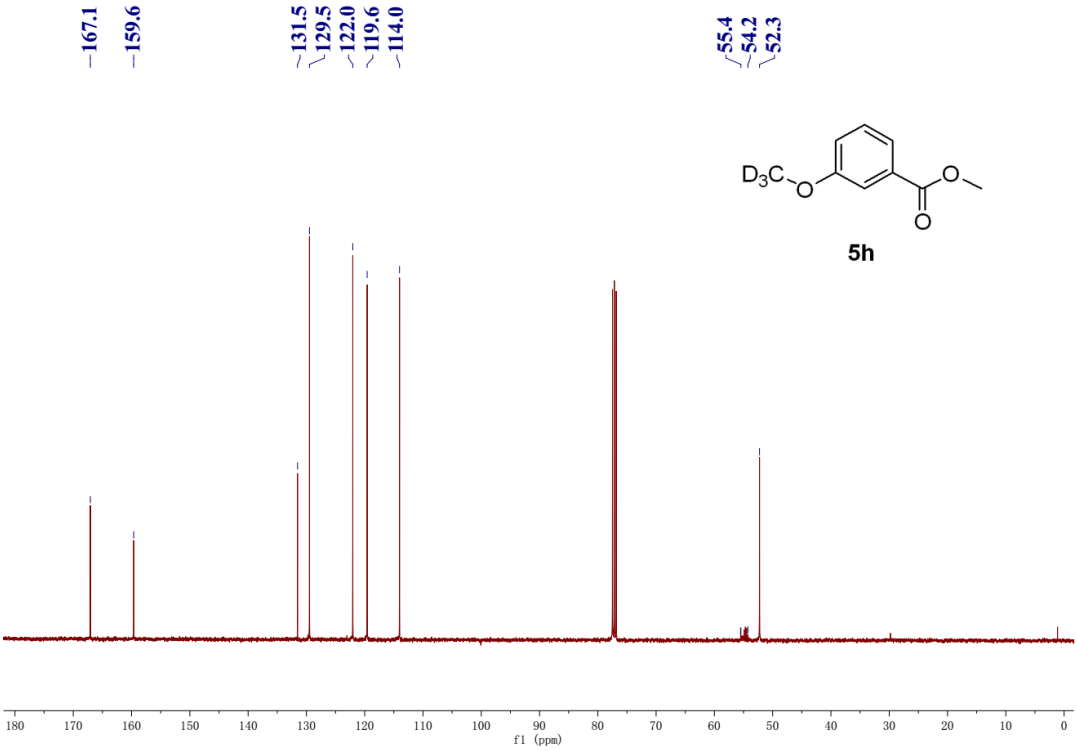
O

5h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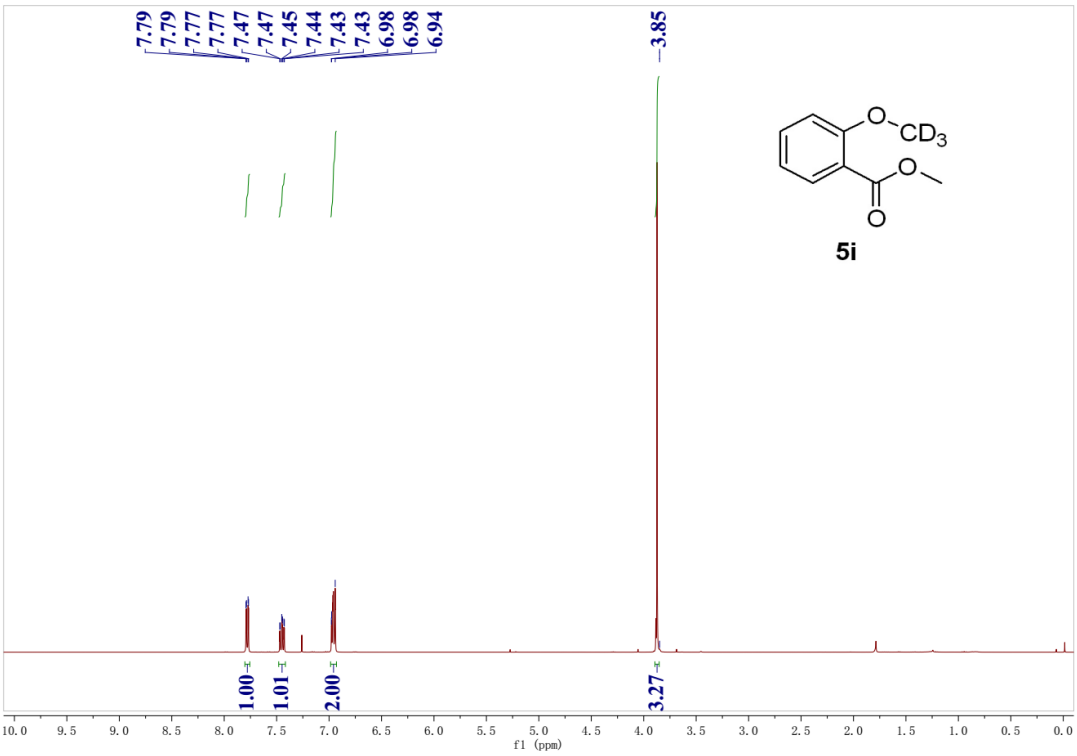
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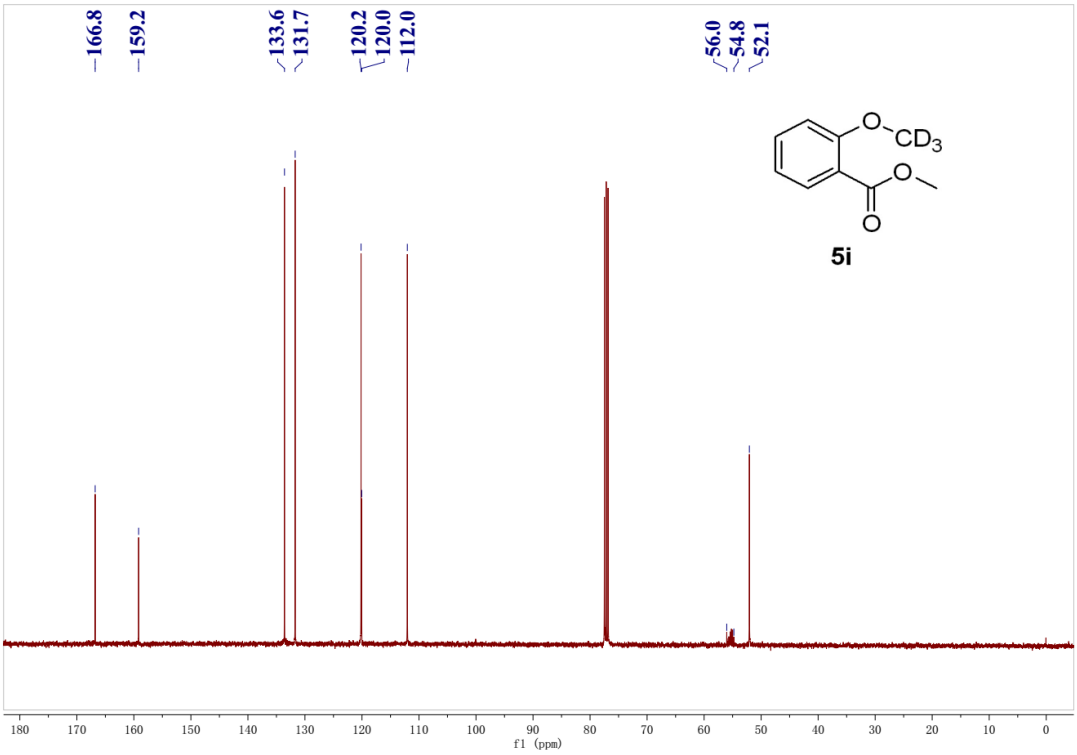
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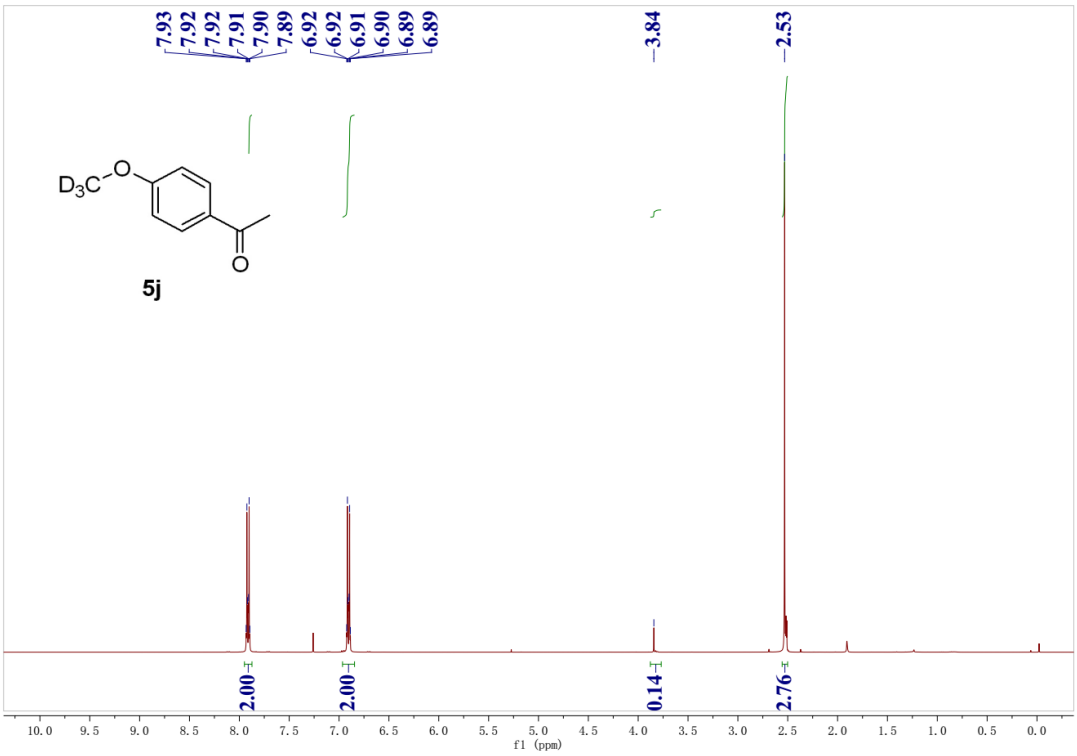
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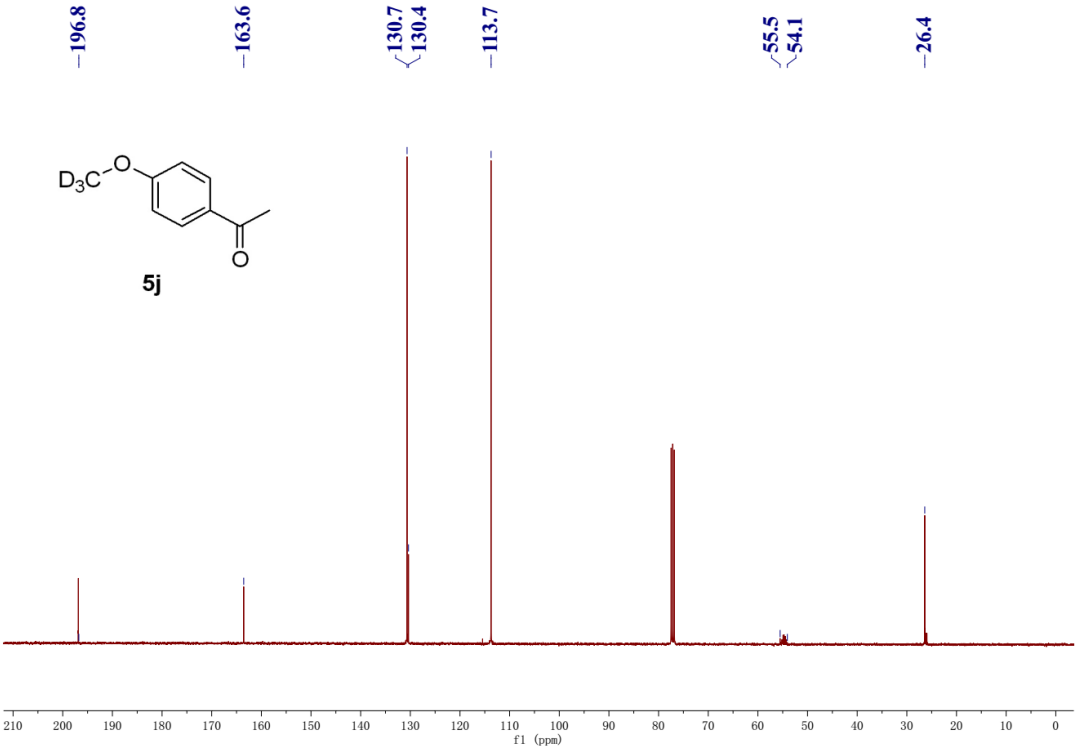
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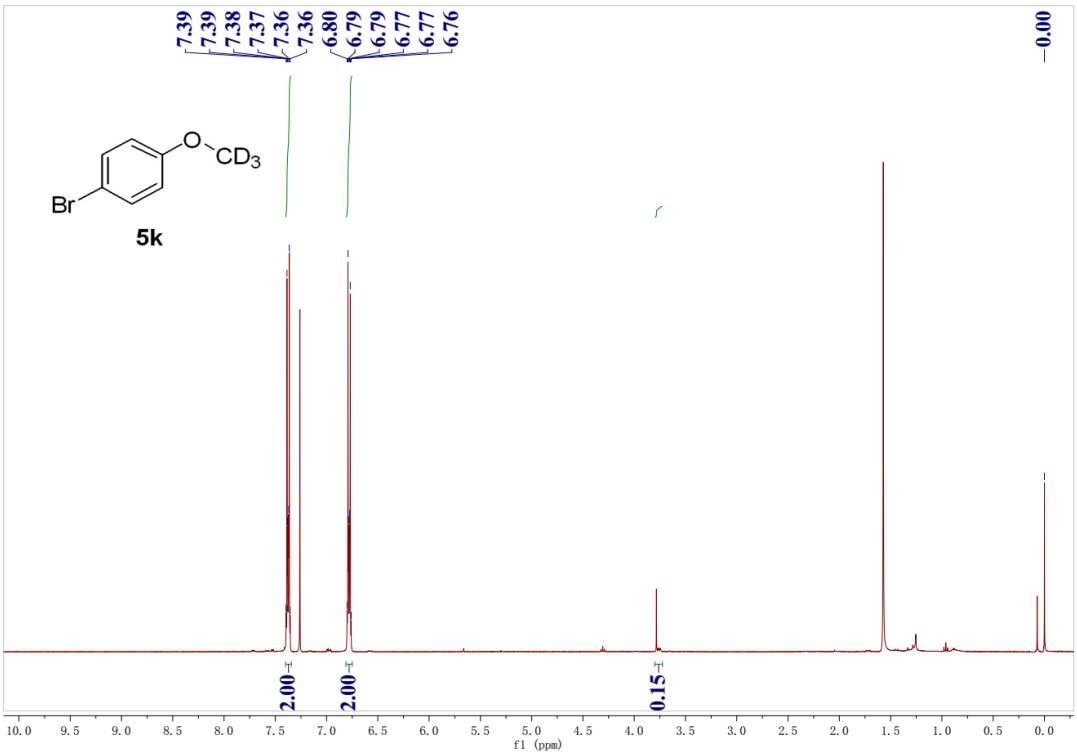
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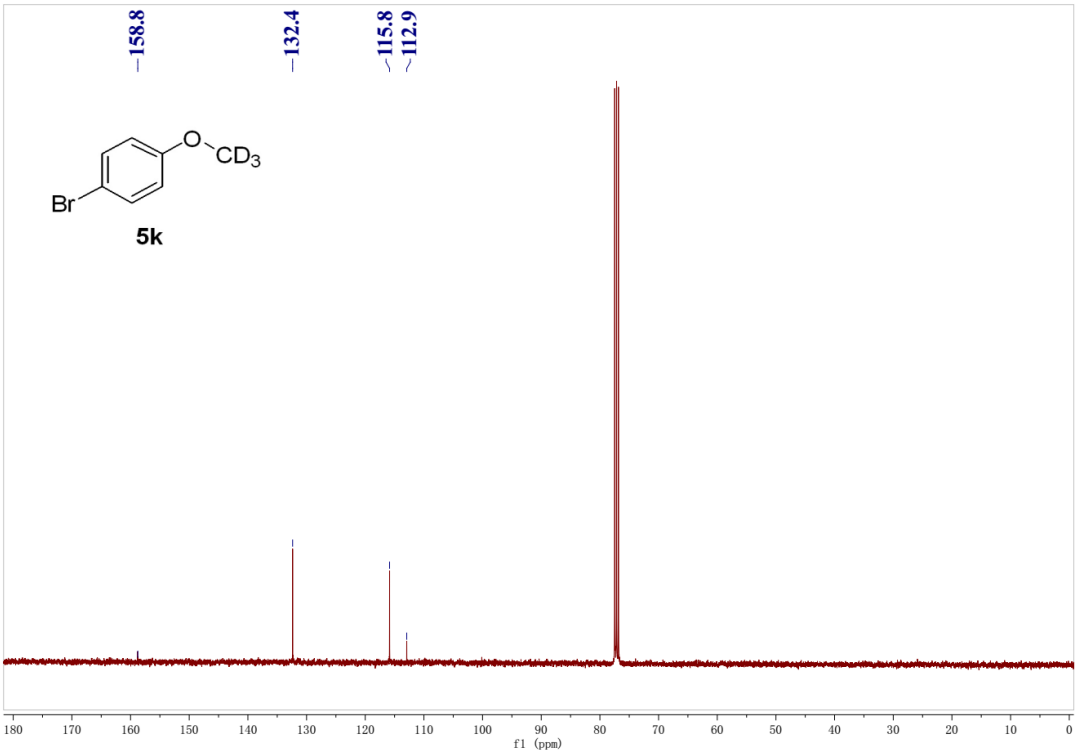
f1 (ppm)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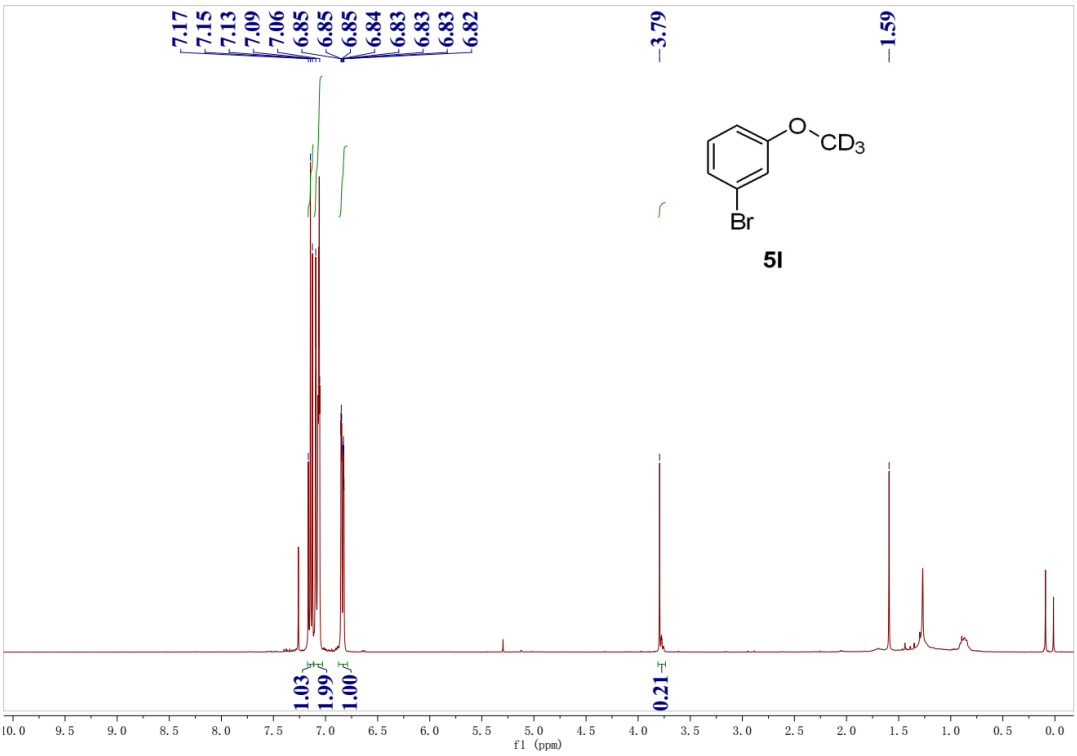
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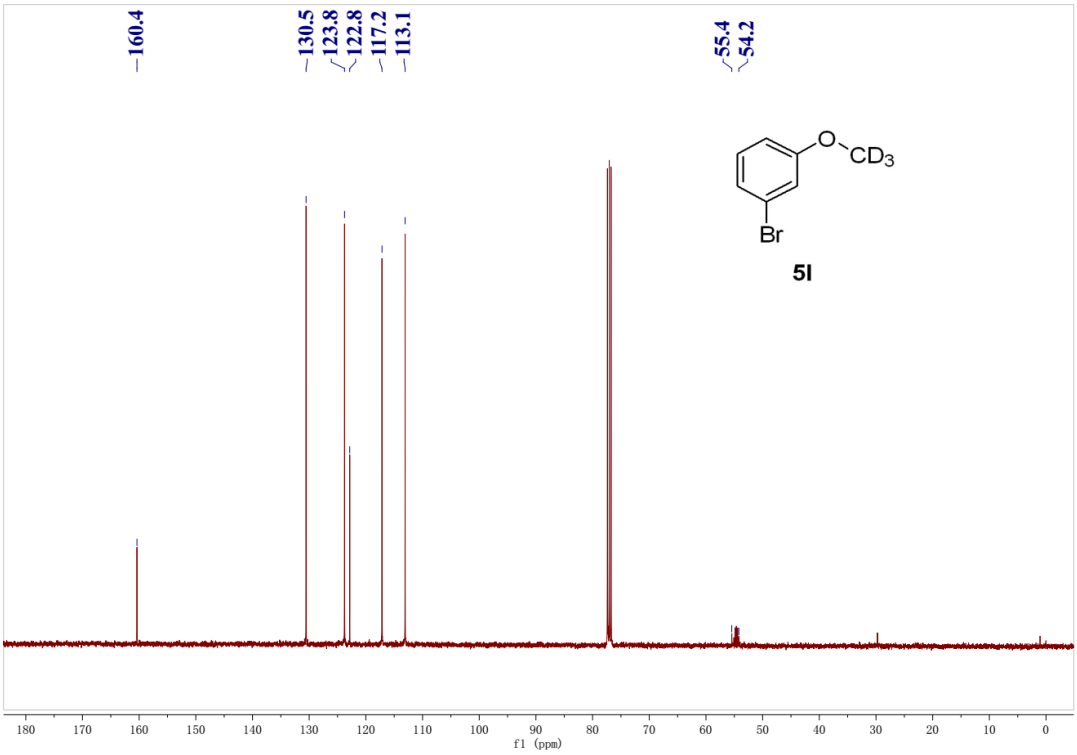
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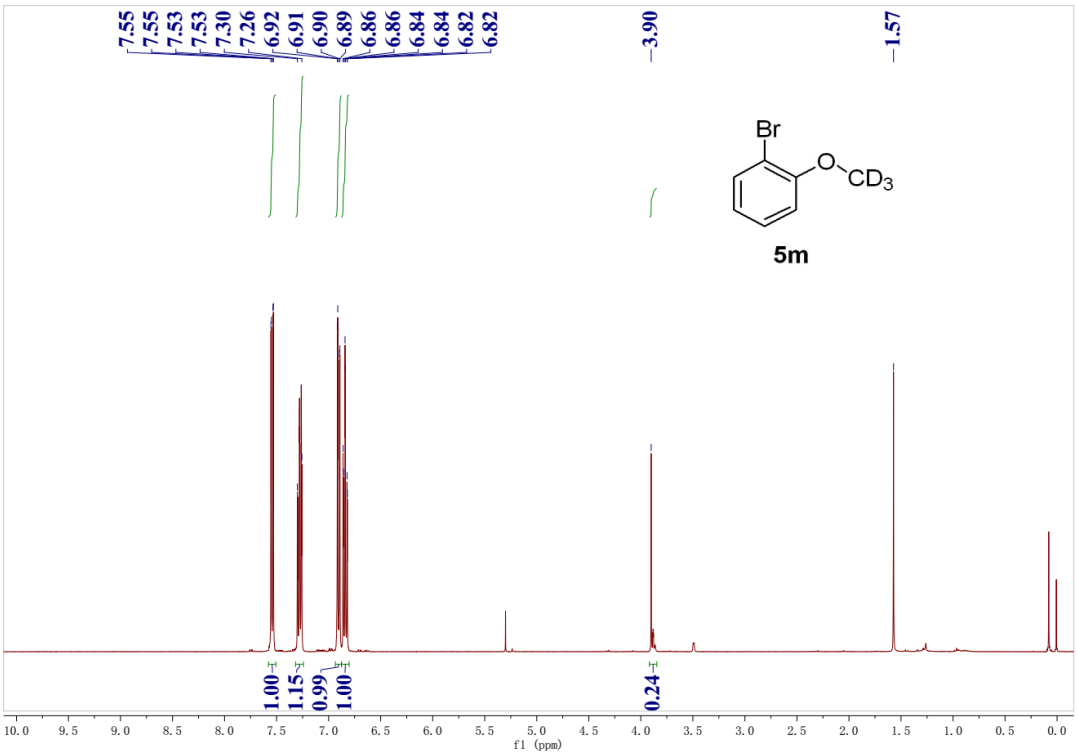
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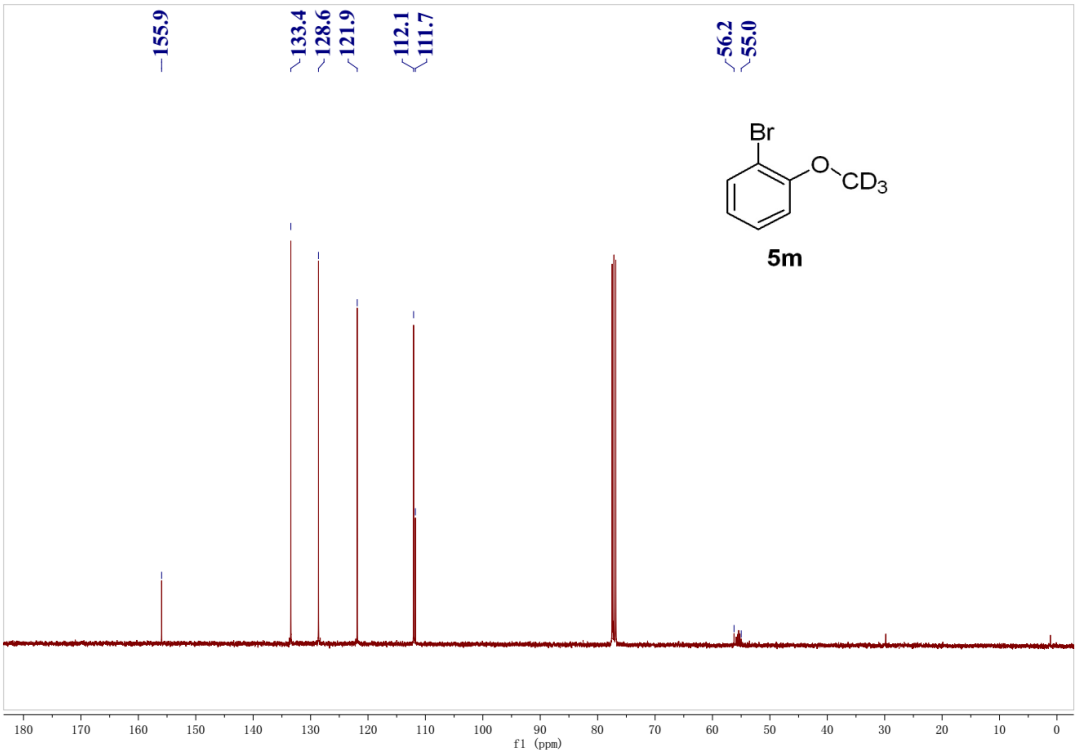
0.24
f1 (ppm)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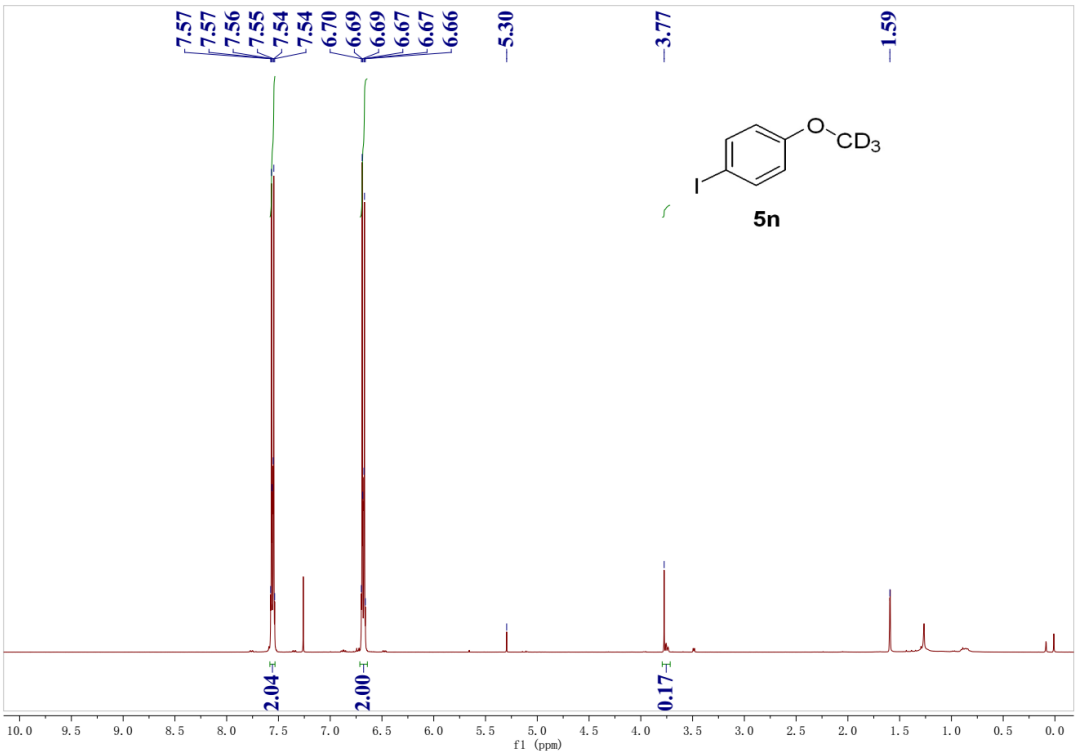
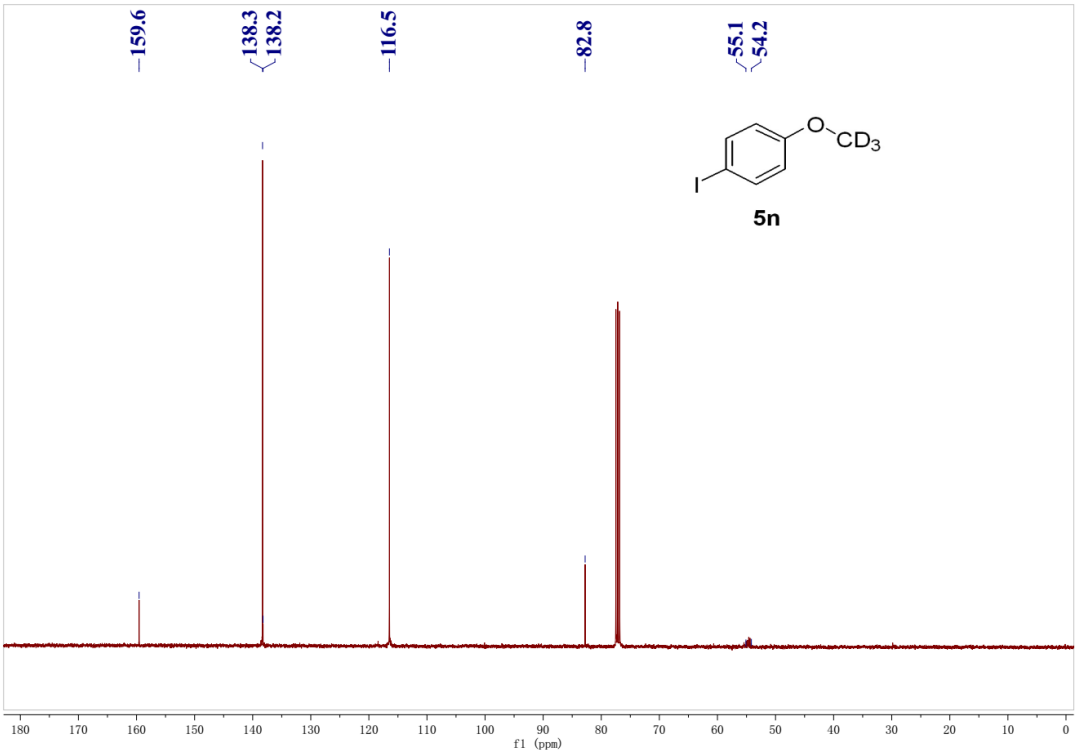
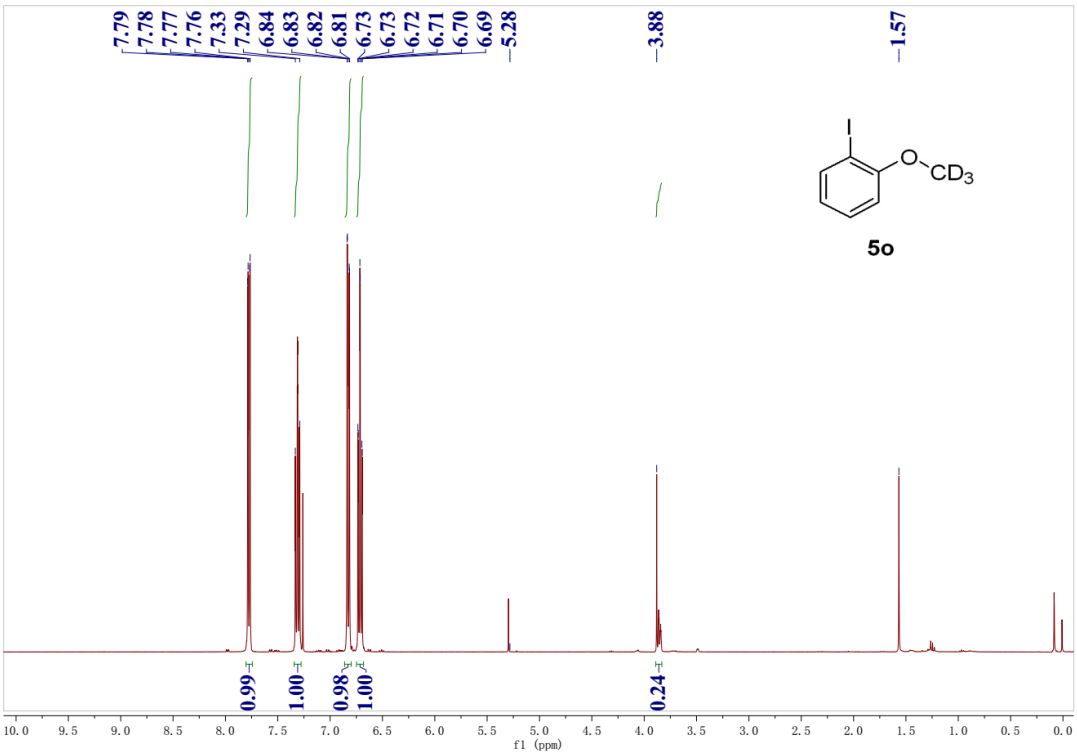
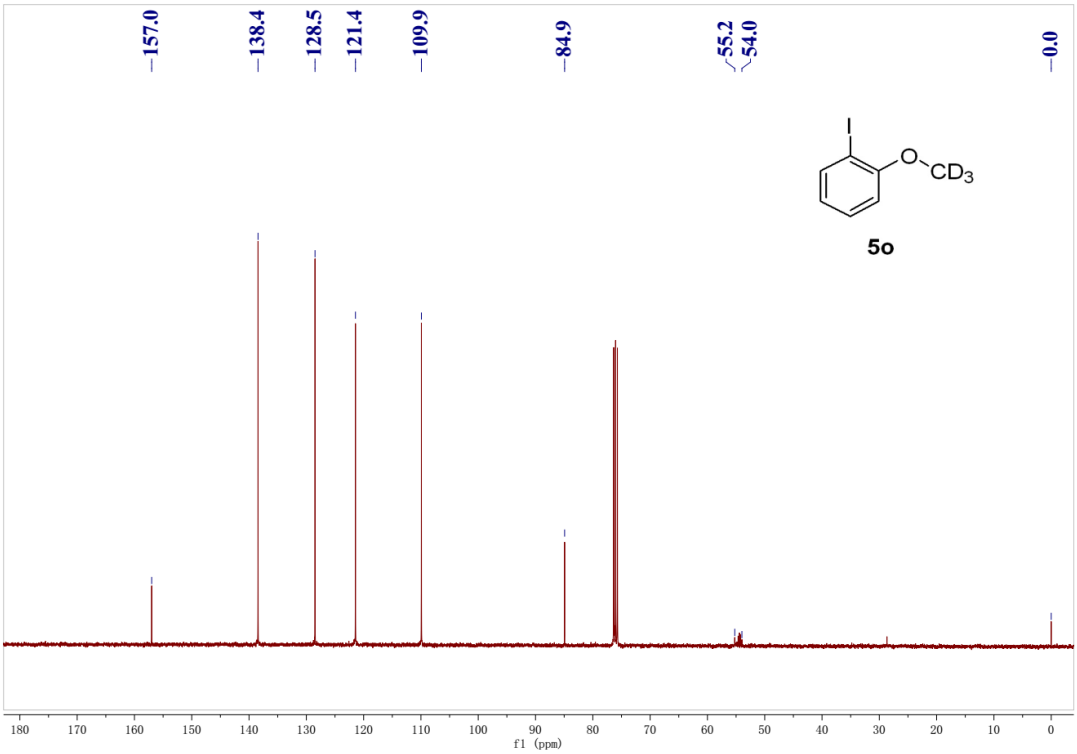
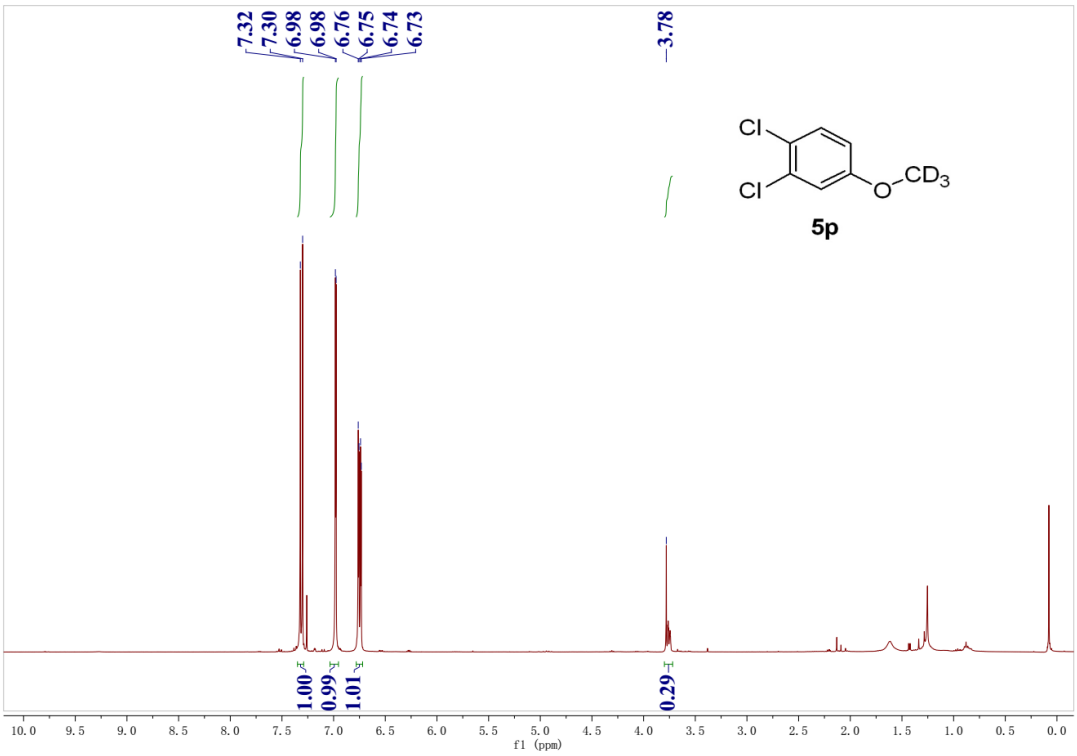
133.4
128.6
121.9
112.1
111.7
56.2
55.0
Br
O
CD3
5m
f1 (ppm)

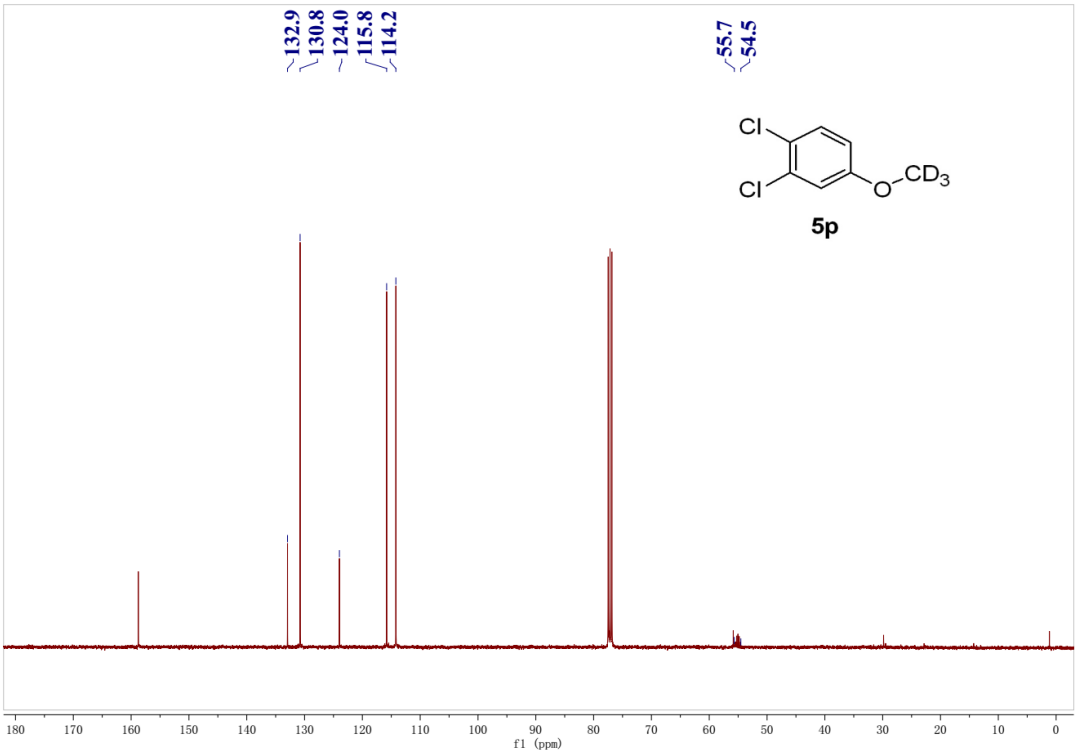

7.57
7.57
7.56
7.55
7.54
7.54
6.70
6.69
6.69
6.67
6.67
6.66
5.30
3.77
1.59
O
CD3
I
5n
2.04
2.00
0.17
f1 (ppm)

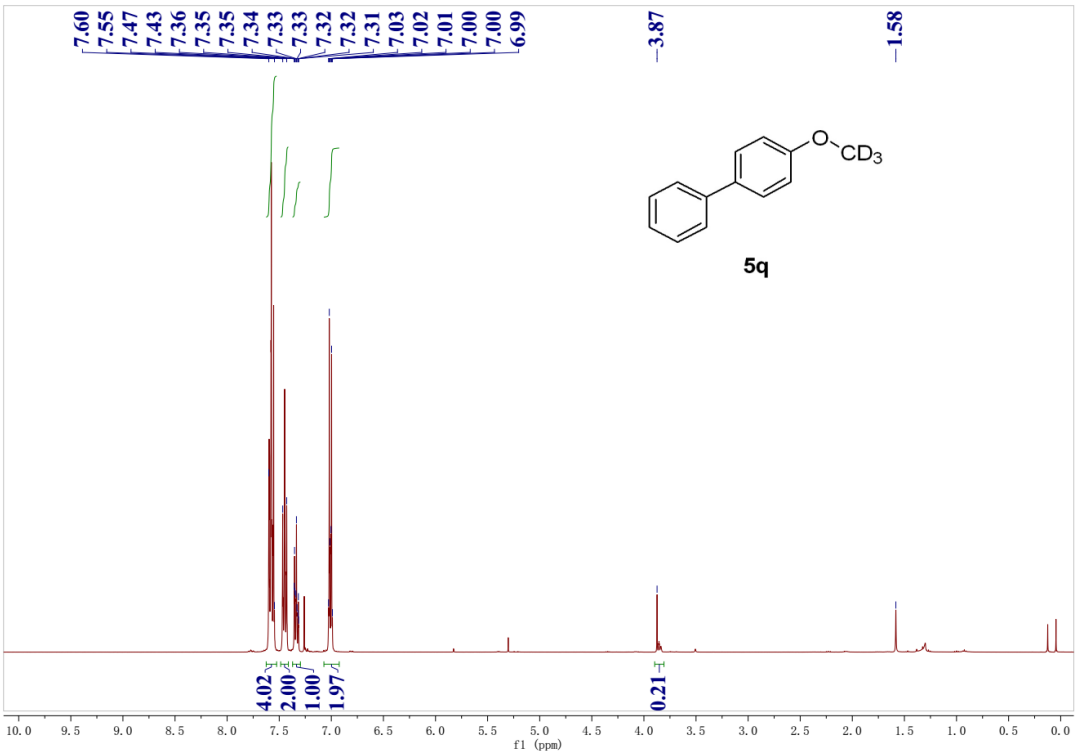

159.6
138.3
138.2
116.5
82.8
55.1
54.2
O
CD3
I
5n
f1 (ppm)

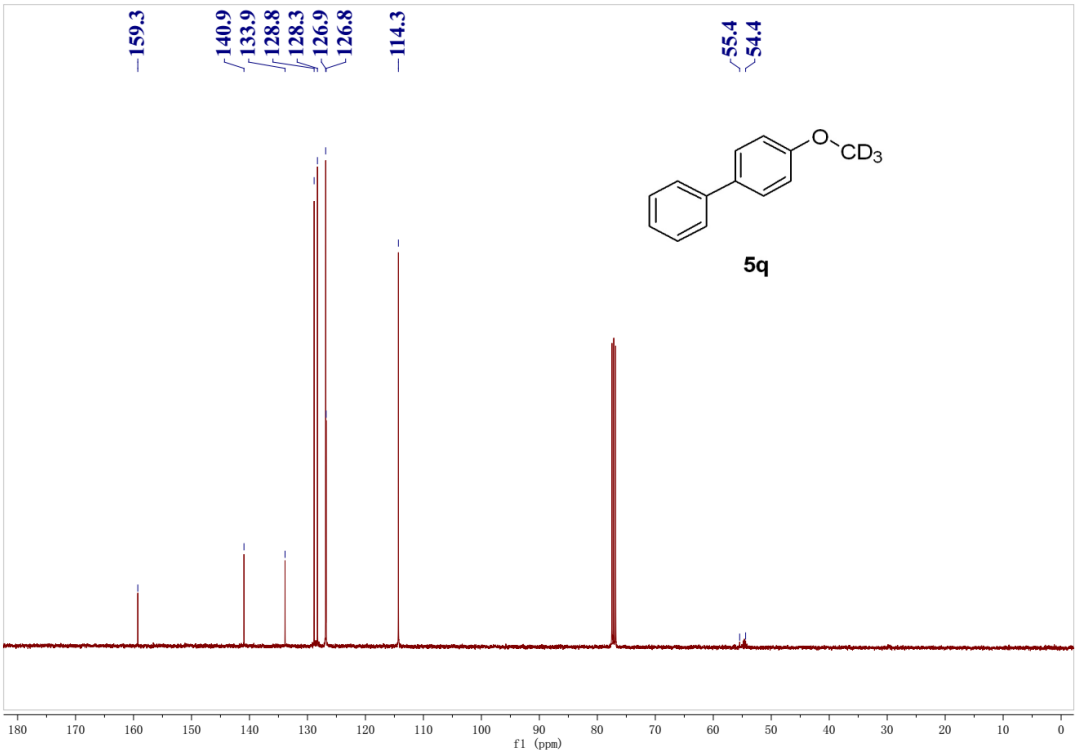

7.79
7.78
7.77
7.76
7.33
7.29
6.84
6.83
6.82
6.81
6.73
6.73
6.72
6.71
6.70
6.69
5.28
3.88
1.57
0.99
1.00
0.98
1.00
0.24
I
O
CD3
5o
f1 (ppm)

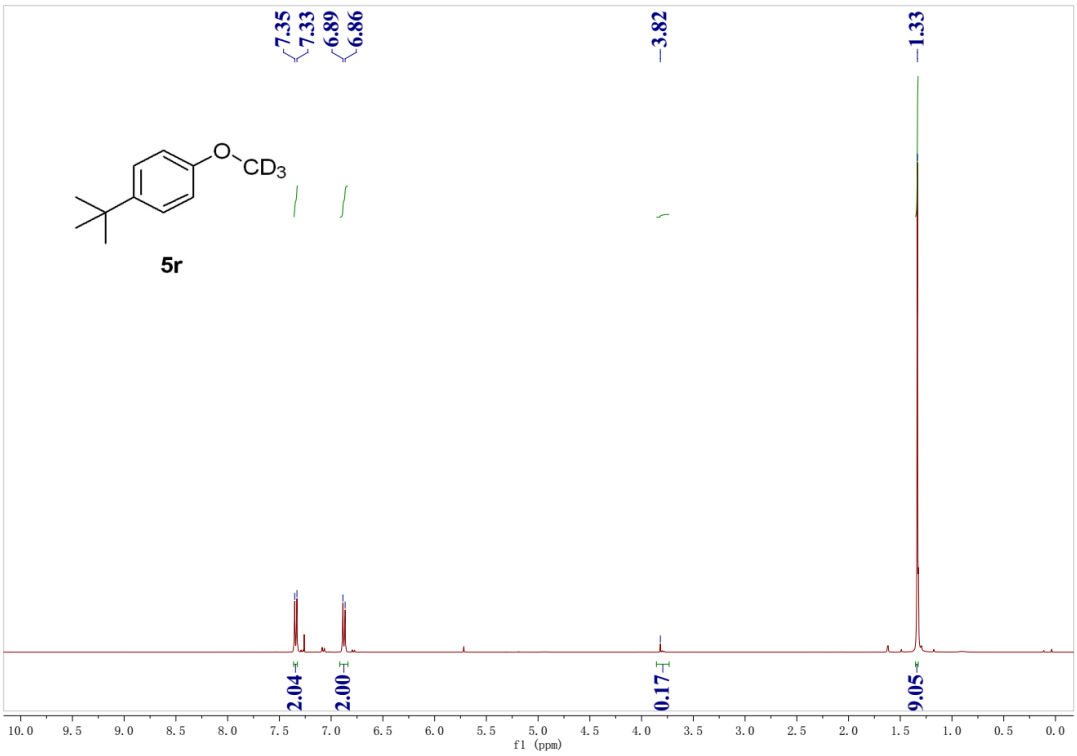

157.0
138.4
128.5
121.4
109.9
84.9
55.2
54.0
0.0
I
O
CD3
5o
f1 (ppm)

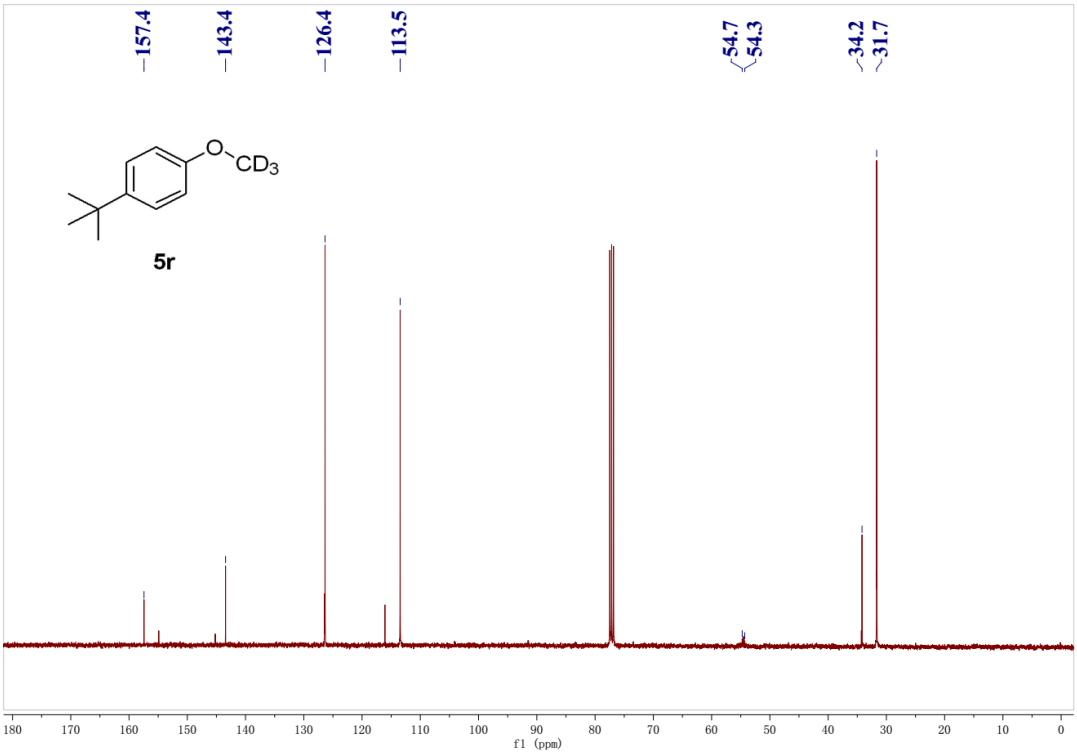

7.32
7.30
6.98
6.98
6.76
6.75
6.74
6.73
3.78
Cl
Cl
O
CD3
5p
1.00
0.99
1.01
0.29
f1 (ppm)

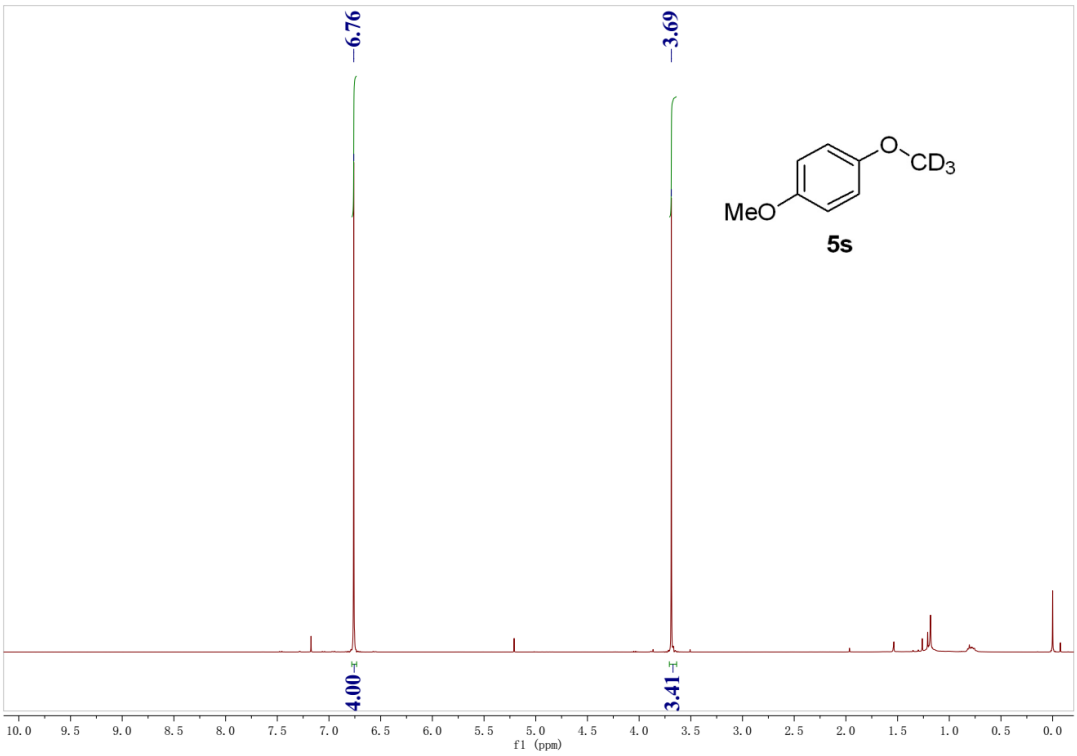

132.9
130.8
124.0
115.8
114.2
55.7
54.5
Cl
Cl
O
CD3
5p
f1 (ppm)

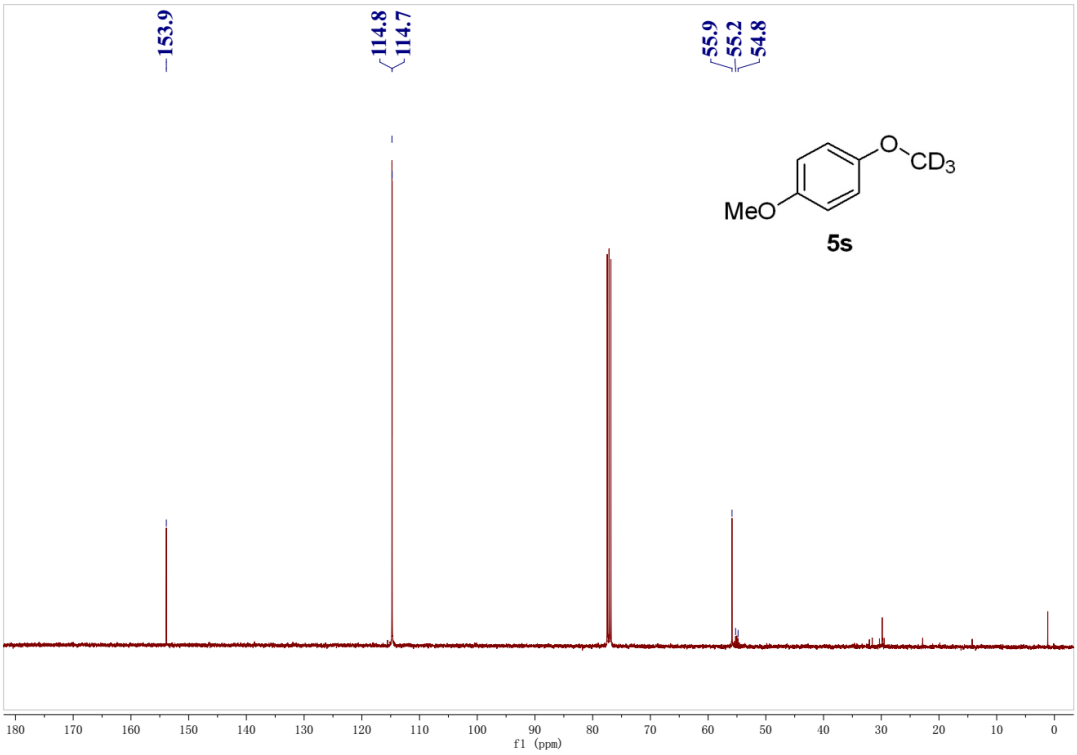

7.60
7.55
7.47
7.43
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.03
7.02
7.01
7.00
7.00
6.99
3.87
1.58
O
CD3
5q
4.02
2.00
1.00
1.97
0.21
f1 (ppm)

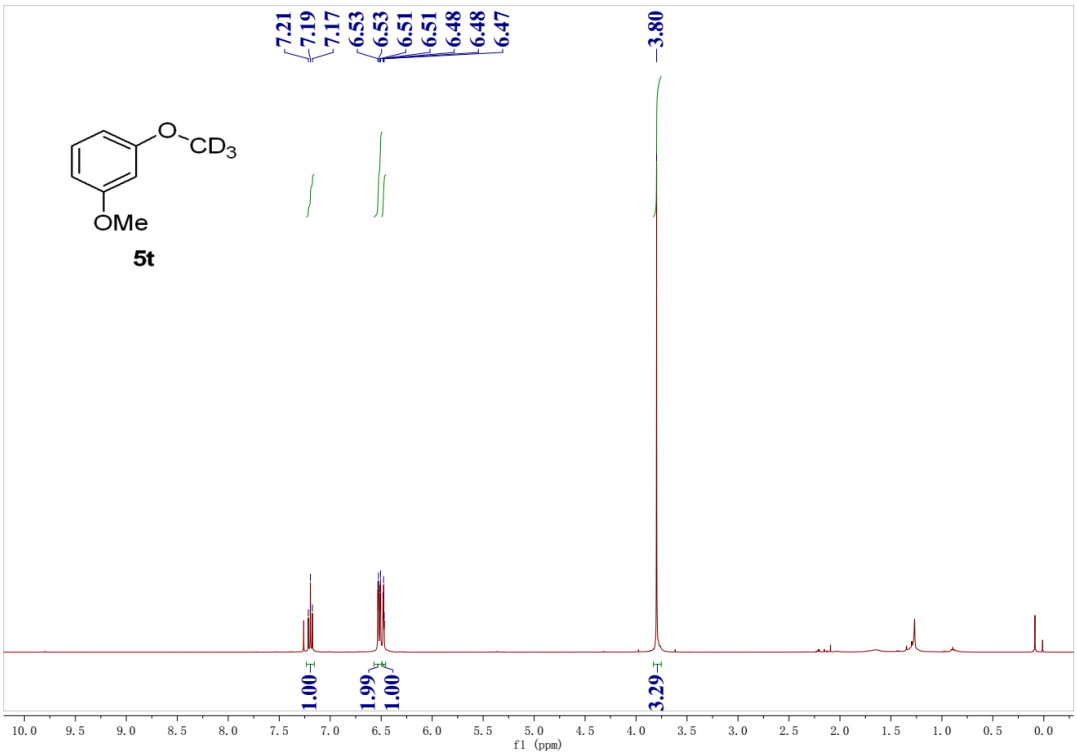

159.3
140.9
133.9
128.8
128.3
126.9
126.8
114.3
55.4
54.4
O
CD3
5q
f1 (ppm)

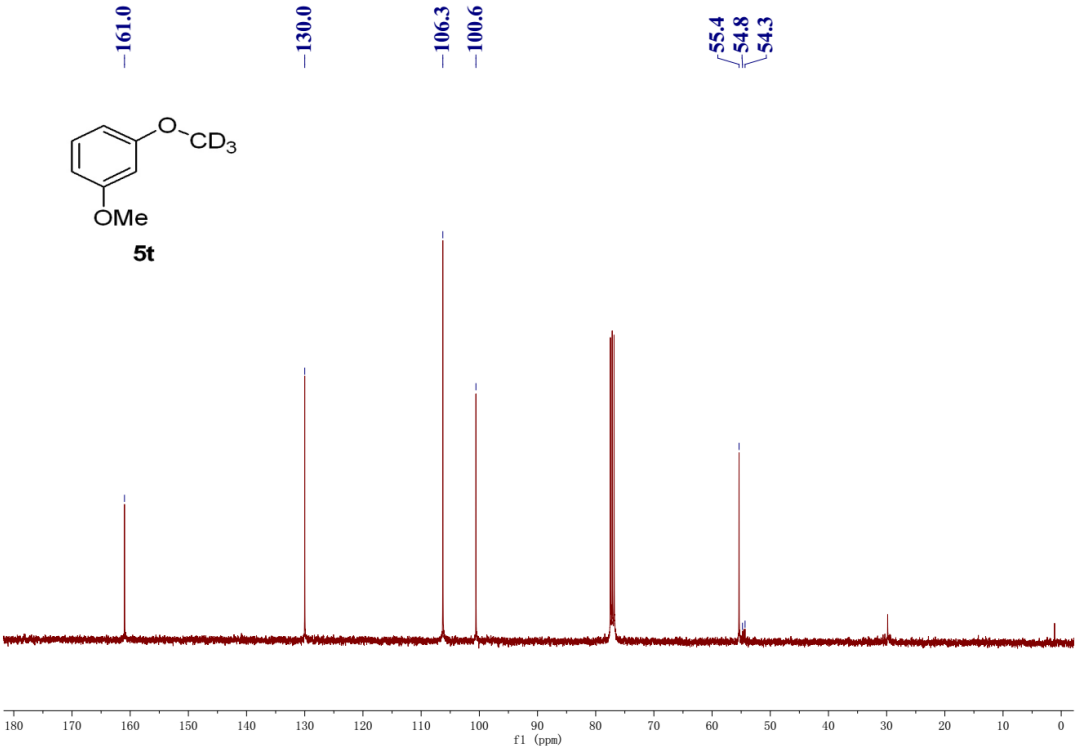

7.35
7.33
6.89
6.86
3.82
1.33
O
CD3
5r
2.04
2.00
0.17
9.05
f1 (ppm)

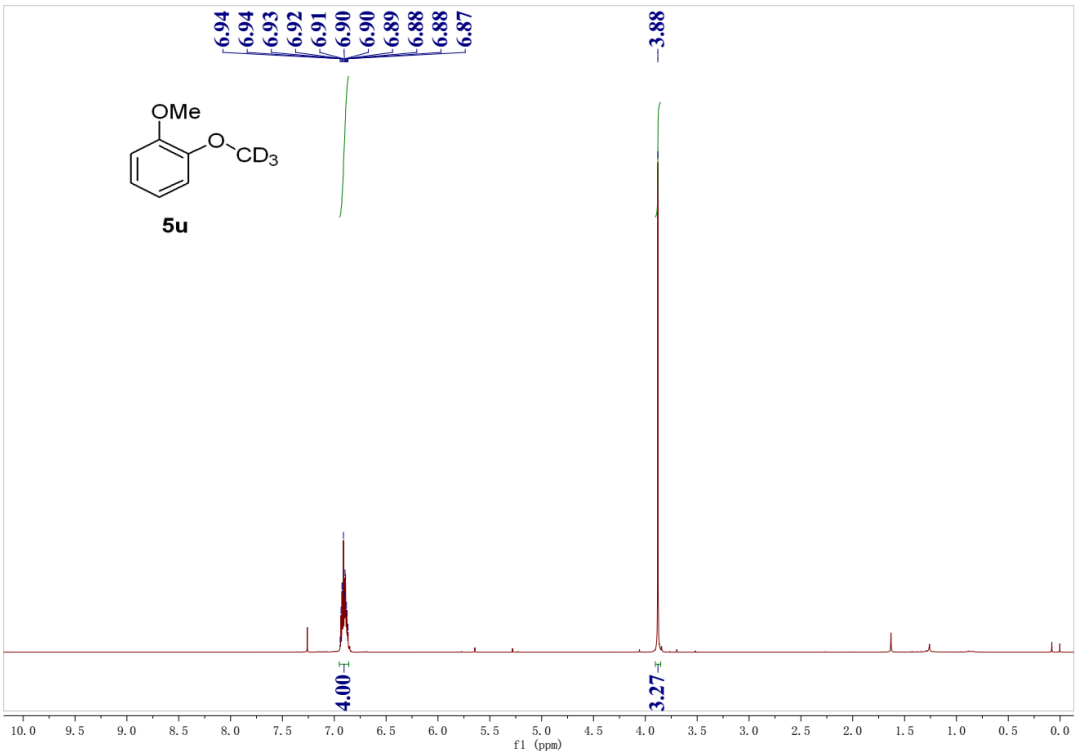

157.4
143.4
126.4
113.5
54.7
54.3
34.2
31.7
O
CD3
5r
f1 (ppm)

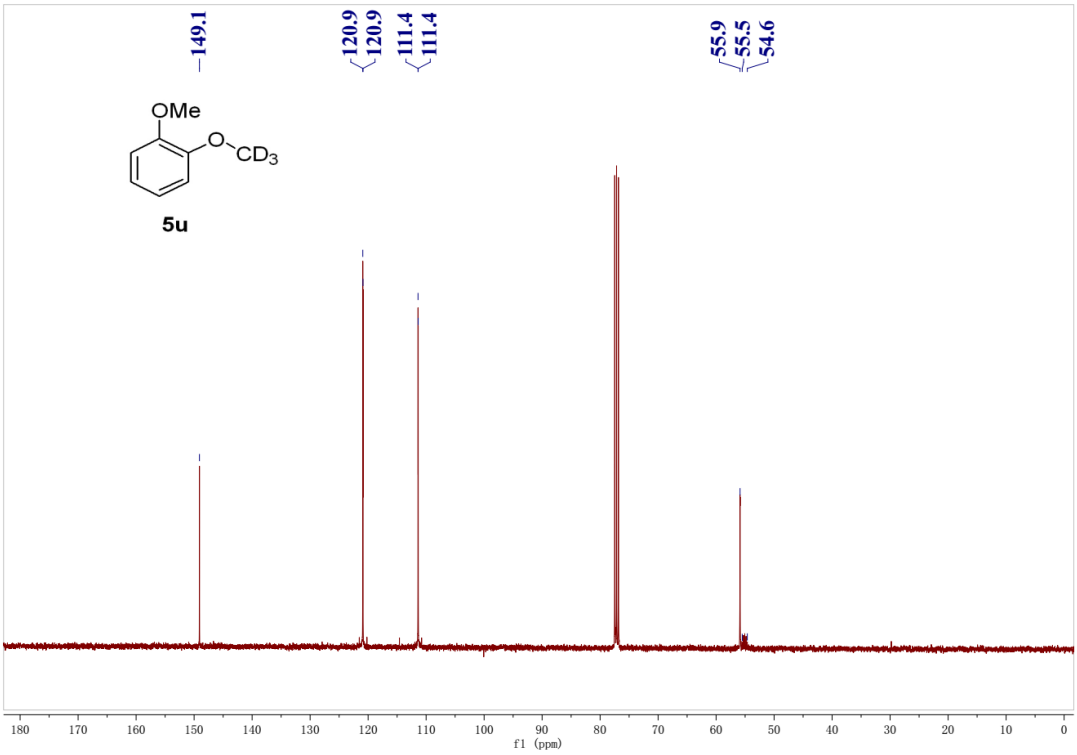

6.76
3.69
4.00
3.41
MeO
O
CD3
5s
f1 (ppm)

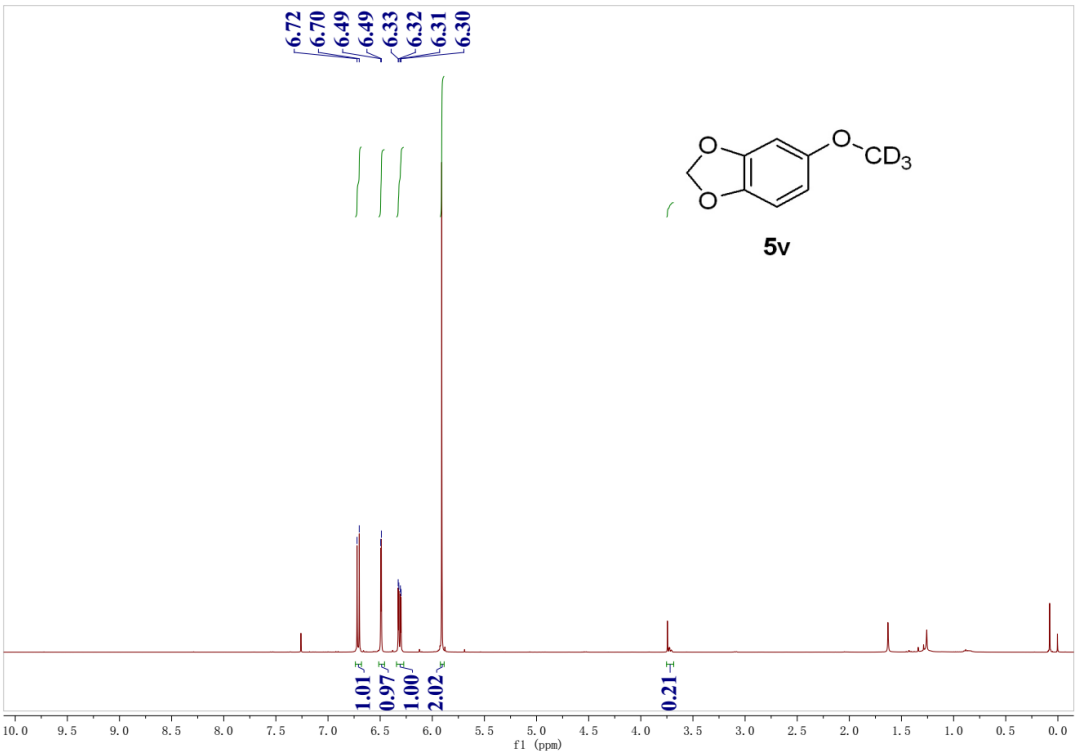

153.9
114.8
114.7
55.9
55.2
54.8
MeO
O
CD3
5s
f1 (ppm)

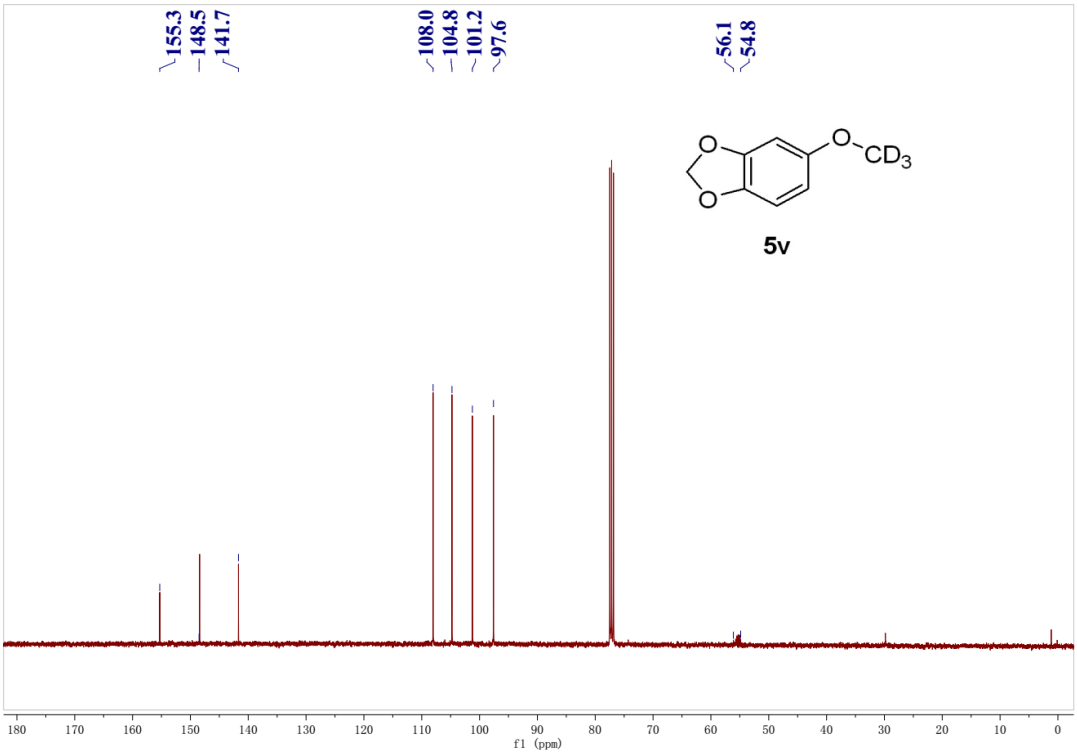

7.21
7.19
7.17
6.53
6.53
6.51
6.51
6.48
6.48
6.47
3.80
O
CD3
OMe
5t
1.00
1.99
1.00
3.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

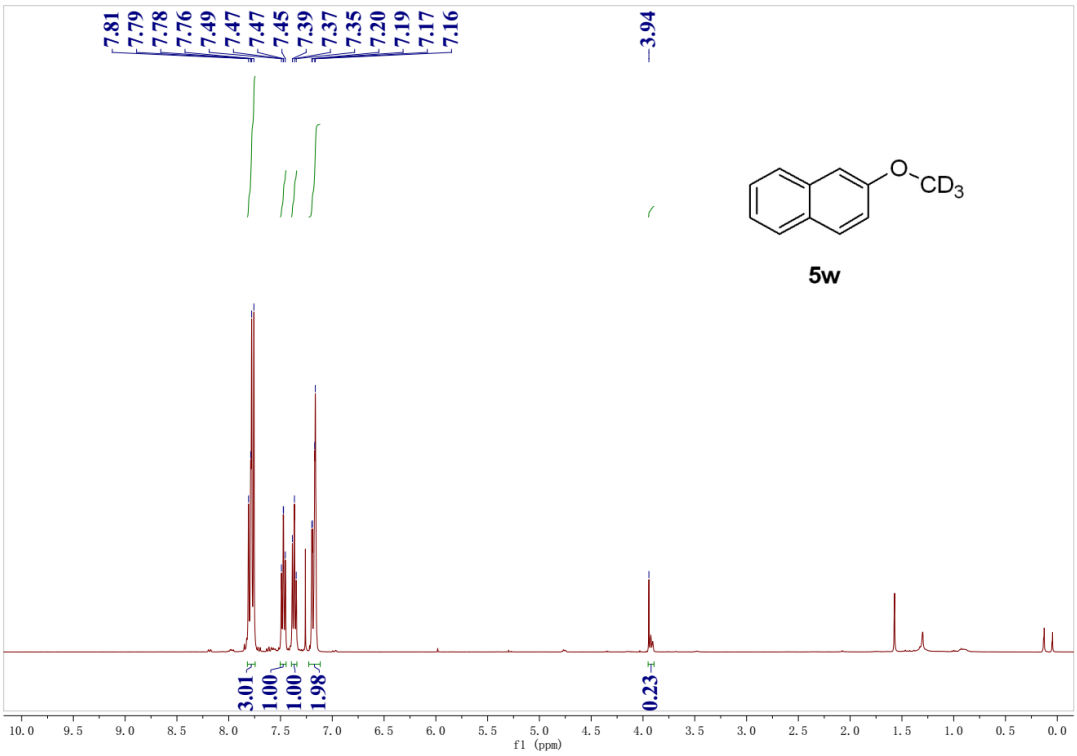

161.0
130.0
106.3
100.6
55.4
54.8
54.3
O
CD3
OMe
5t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

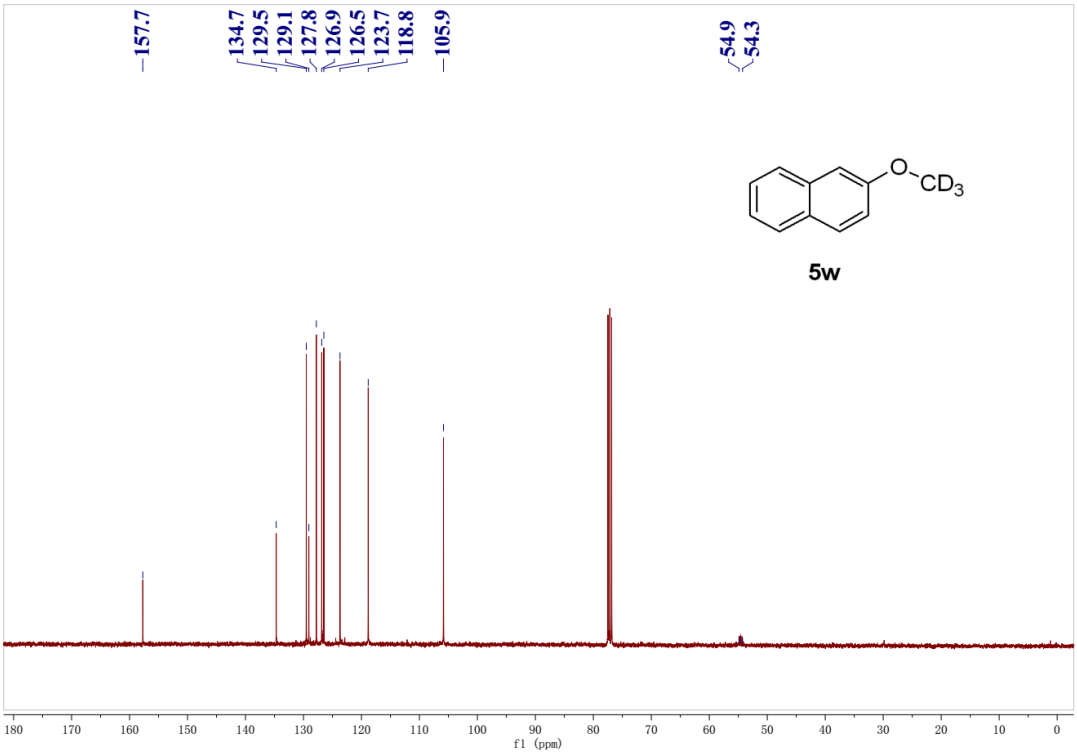

6.94
6.94
6.93
6.92
6.91
6.90
6.90
6.89
6.88
6.88
6.87
3.88
OMe
O
CD3
5u
4.00
3.27
f1 (ppm)

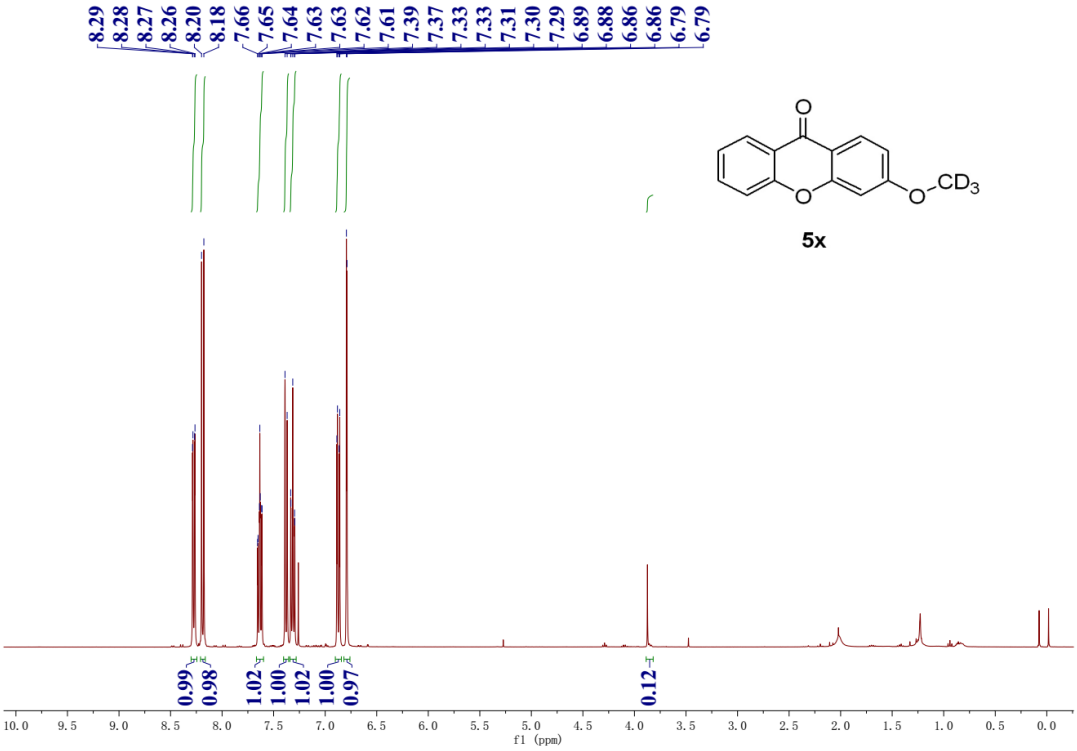

149.1
120.9
120.9
111.4
111.4
55.9
55.5
54.6
OMe
O
CD3
5u
f1 (ppm)

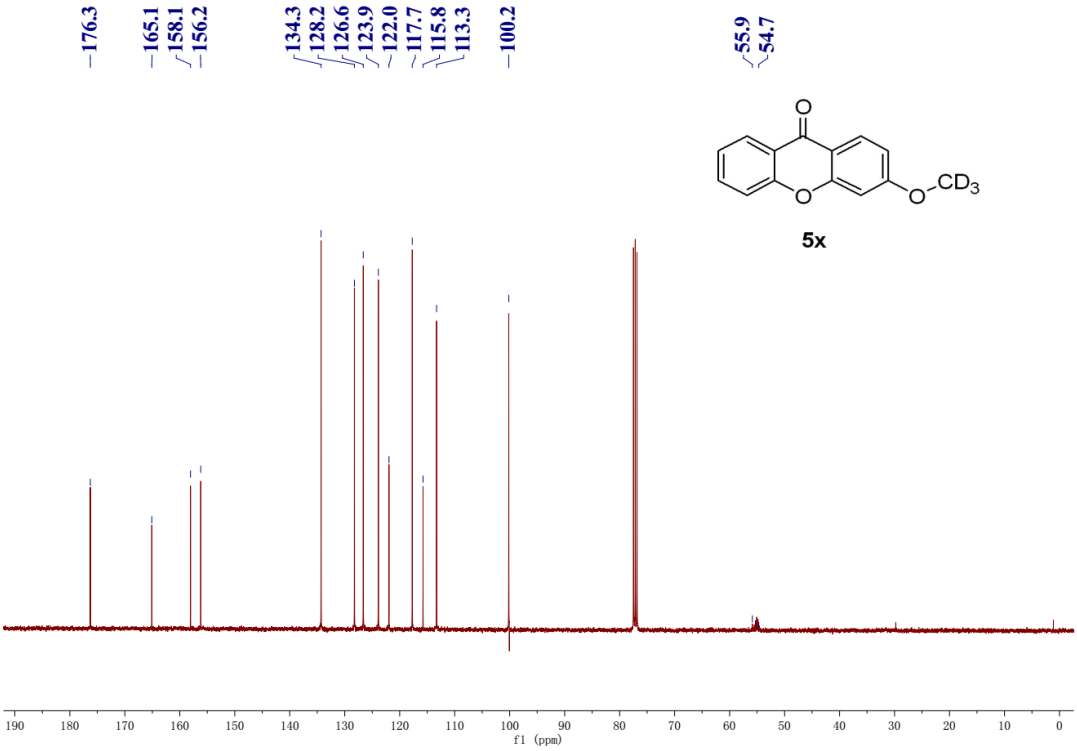

6.72
6.70
6.49
6.49
6.33
6.32
6.31
6.30
O
O
O
CD3
5v
1.01
0.97
1.00
2.02
0.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

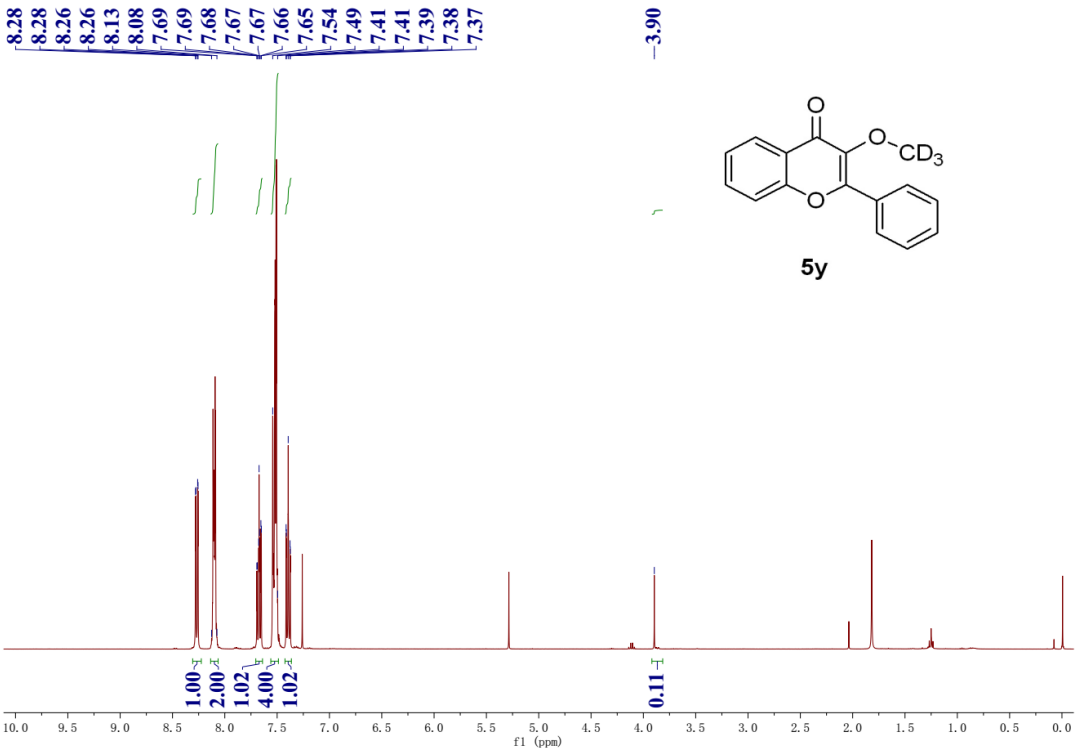

155.3
148.5
141.7
108.0
104.8
101.2
97.6
56.1
54.8
O
O
O
CD3
5v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.81
7.79
7.78
7.76
7.49
7.47
7.47
7.45
7.39
7.37
7.35
7.20
7.19
7.17
7.16
3.94
O
CD3
5w
3.01
1.00
1.00
1.98
0.23
f1 (ppm)

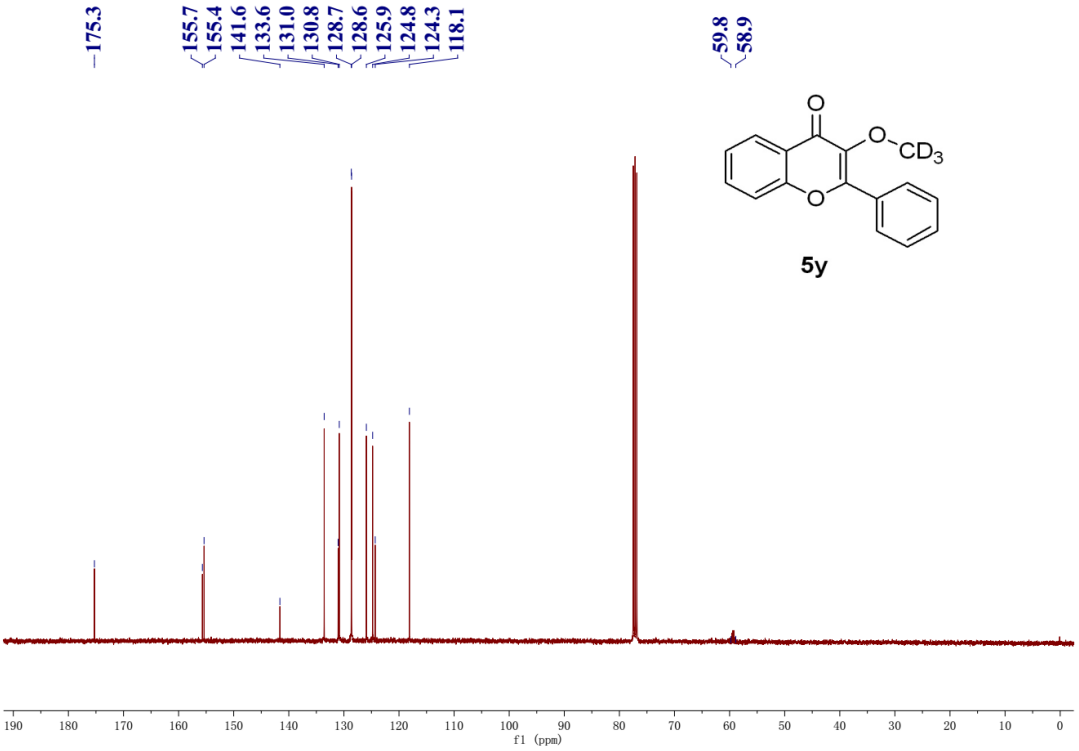

157.7
134.7
129.5
129.1
127.8
126.9
126.5
123.7
118.8
105.9
54.9
54.3
O
CD3
5w
f1 (ppm)


8.29
8.28
8.27
8.26
8.20
8.18
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.39
7.37
7.33
7.33
7.31
7.30
7.29
6.89
6.88
6.86
6.86
6.79
6.79
O
O
O
CD3
5x
0.99
0.98
1.02
1.00
1.02
1.00
0.97
0.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

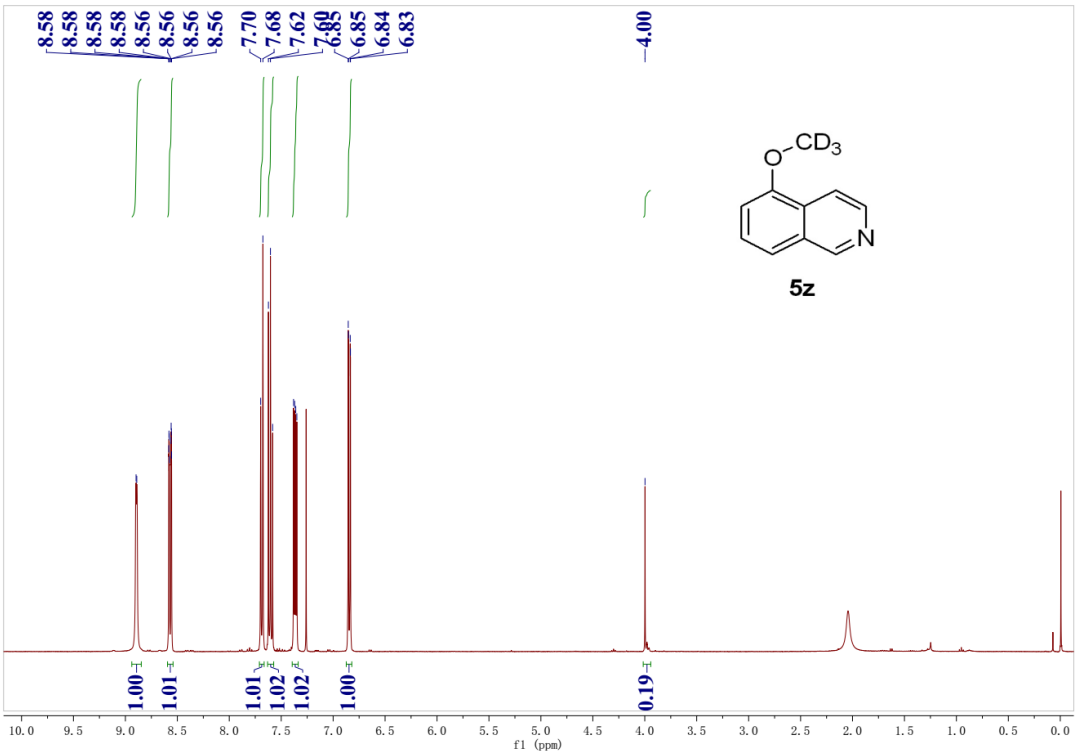

176.3
165.1
158.1
156.2
134.3
128.2
126.6
123.9
122.0
117.7
115.8
113.3
100.2
55.9
54.7
O
O
O
CD3
5x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

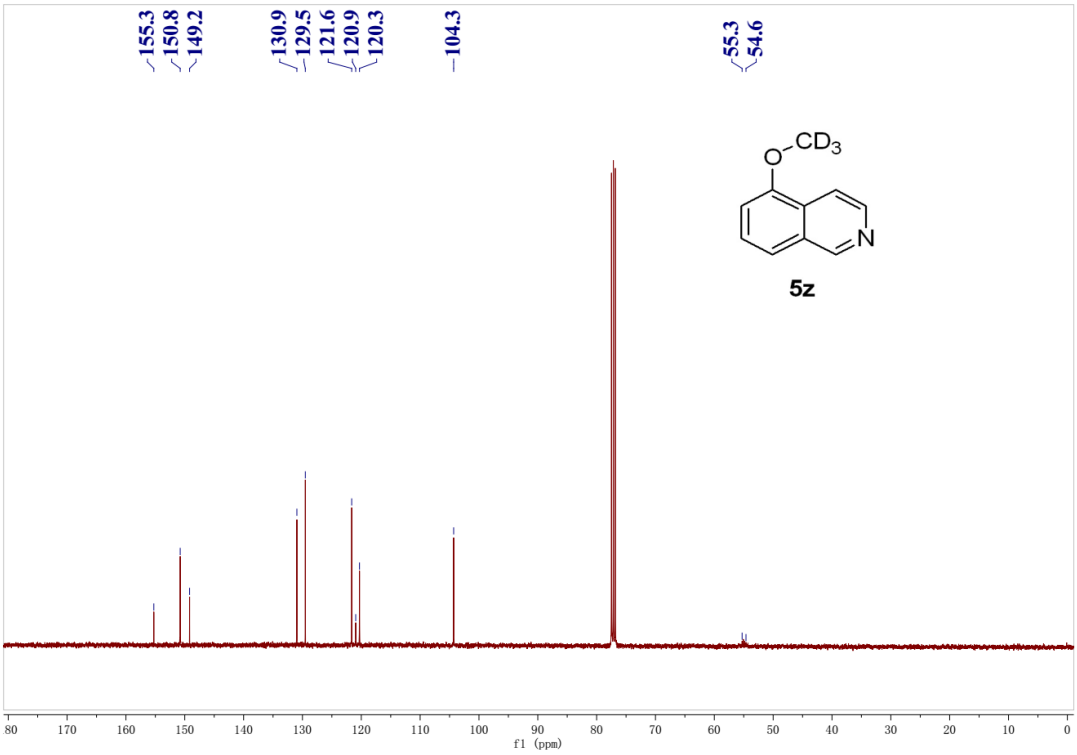

8.28
8.28
8.26
8.26
8.13
8.08
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.54
7.49
7.41
7.41
7.39
7.38
7.37
3.90
O
O
CD3
O
1.00
2.00
1.02
4.00
1.02
0.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

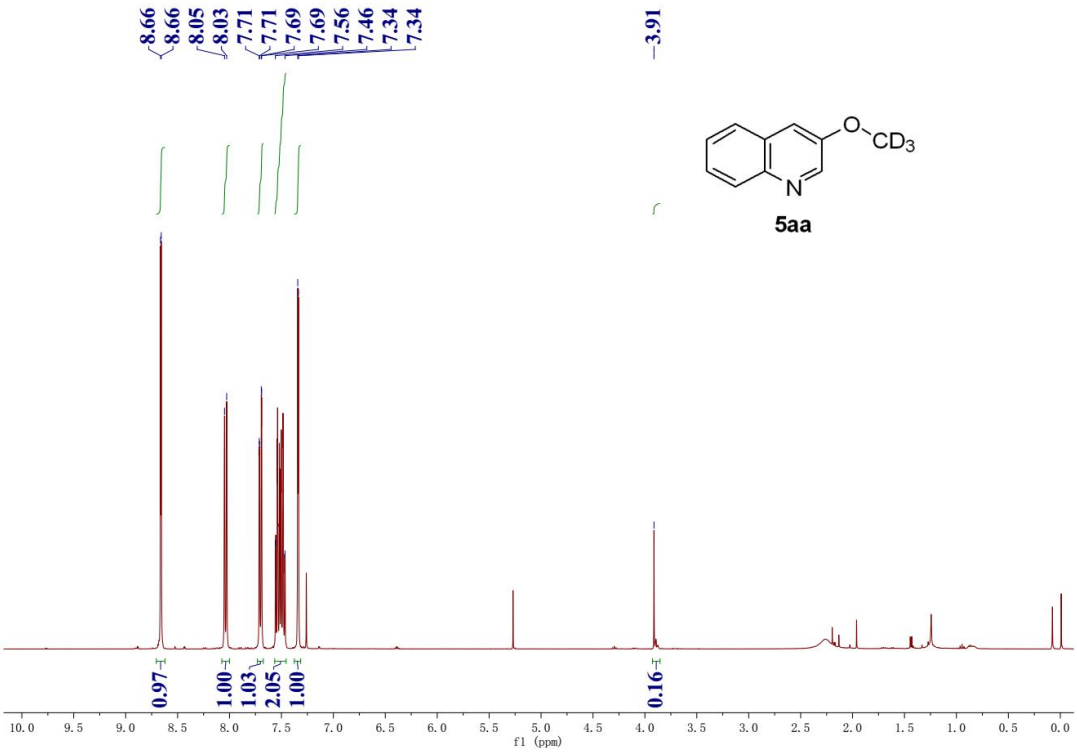
5y

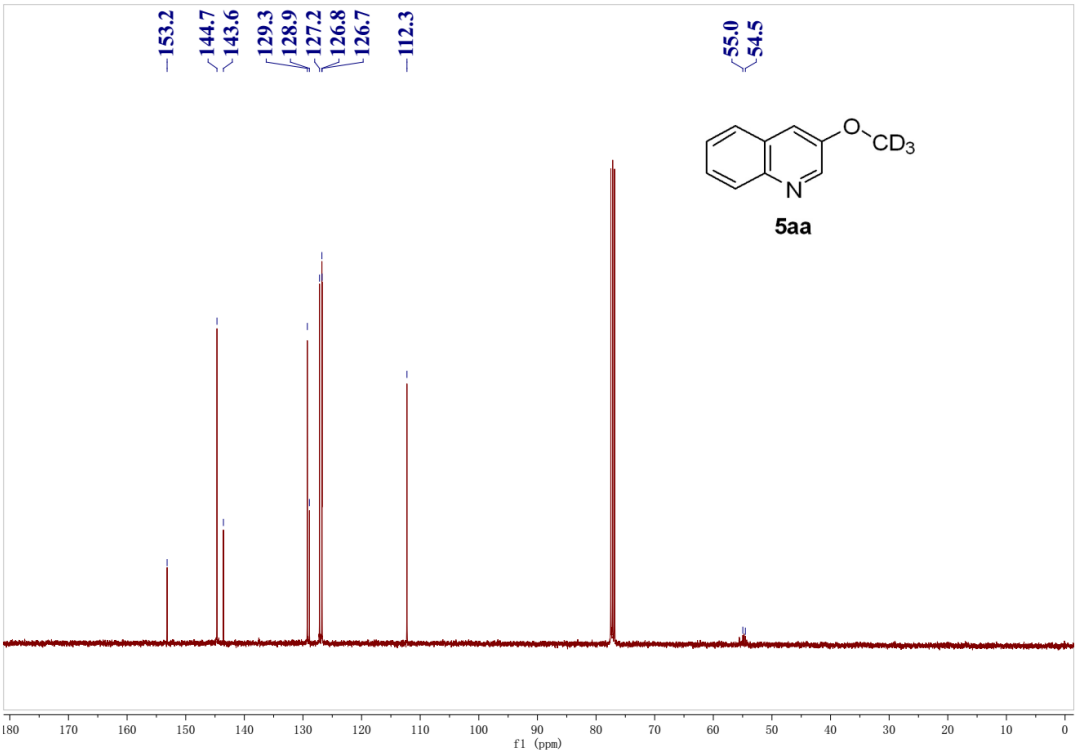

175.3
155.7
155.4
141.6
133.6
131.0
130.8
128.7
128.6
125.9
124.8
124.3
118.1
59.8
58.9
O
O
CD3
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

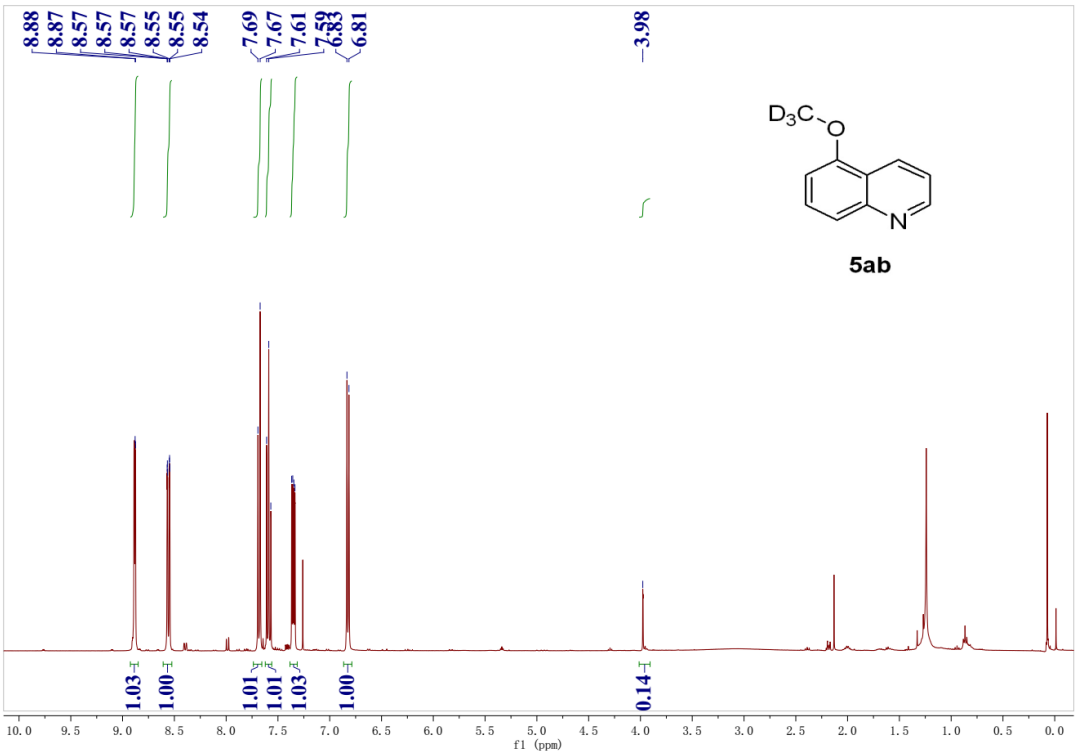
5y


8.58
8.58
8.58
8.58
8.56
8.56
8.56
8.56
7.70
7.68
7.62
7.60
6.85
6.84
6.83
4.00
1.00
1.01
1.01
1.02
1.02
1.00
0.19
f1 (ppm)


155.3
150.8
149.2
130.9
129.5
121.6
120.9
120.3
104.3
55.3
54.6
f1 (ppm)


8.66
8.66
8.05
8.03
7.71
7.71
7.69
7.69
7.56
7.46
7.34
7.34
3.91
O
CD3
N
5aa
0.97
1.00
1.03
2.05
1.00
0.16
f1 (ppm)


153.2
144.7
143.6
129.3
128.9
127.2
126.8
126.7
112.3
55.0
54.5
O
CD3
N
5aa
f1 (ppm)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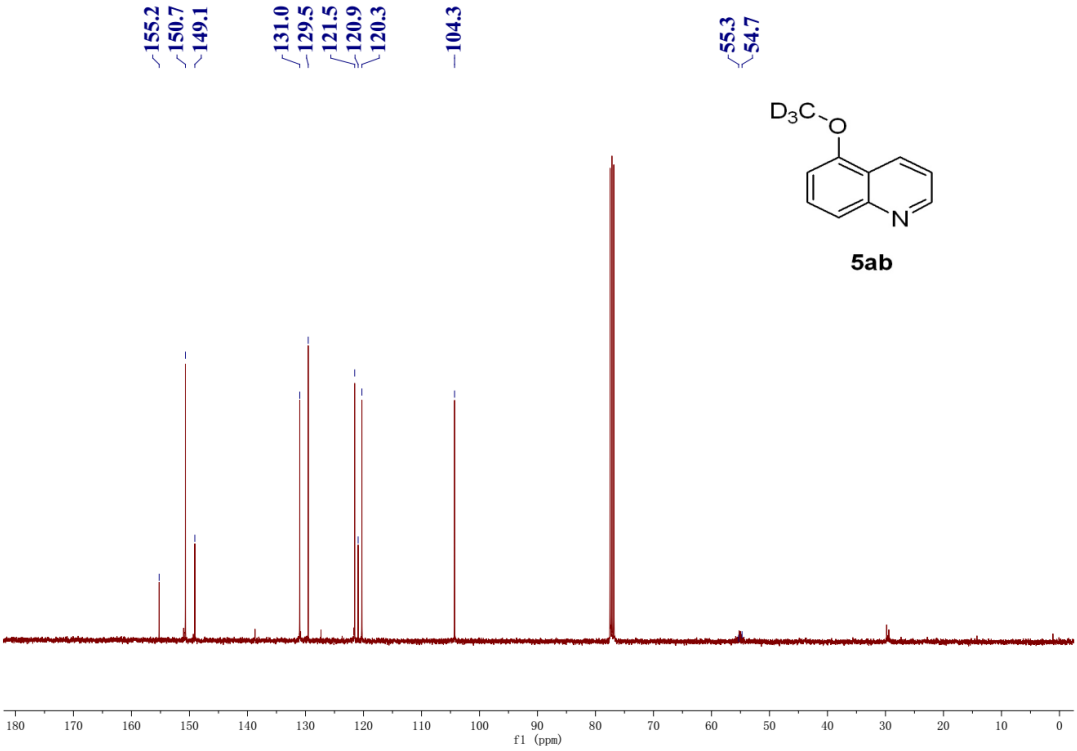
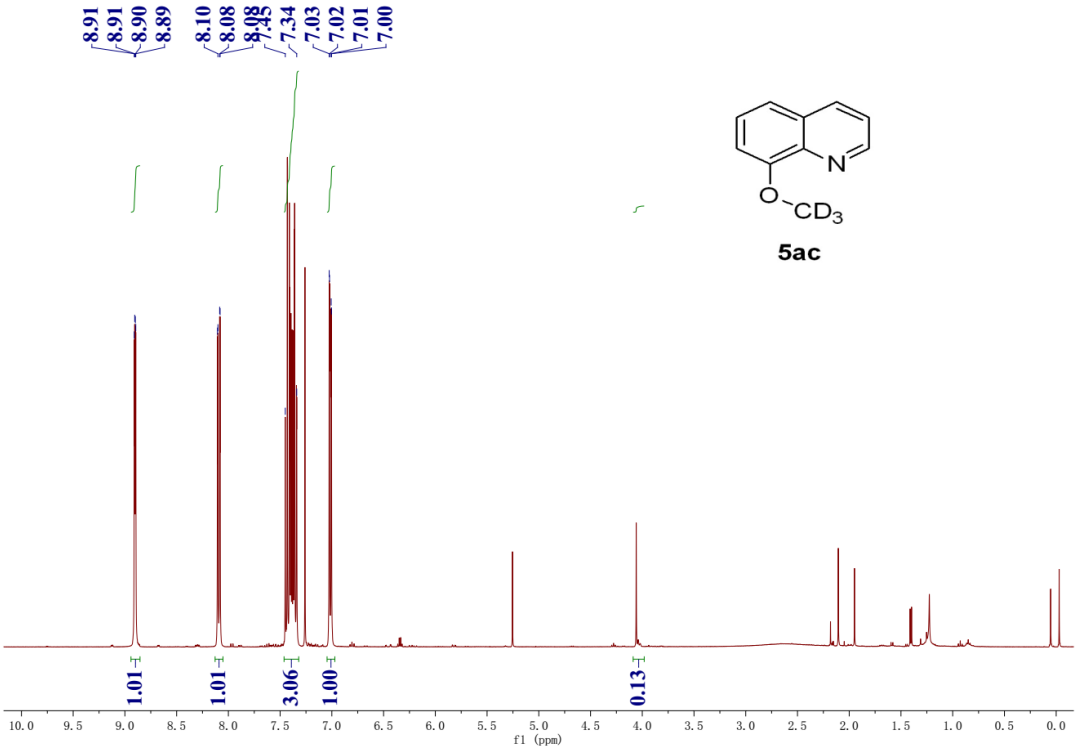
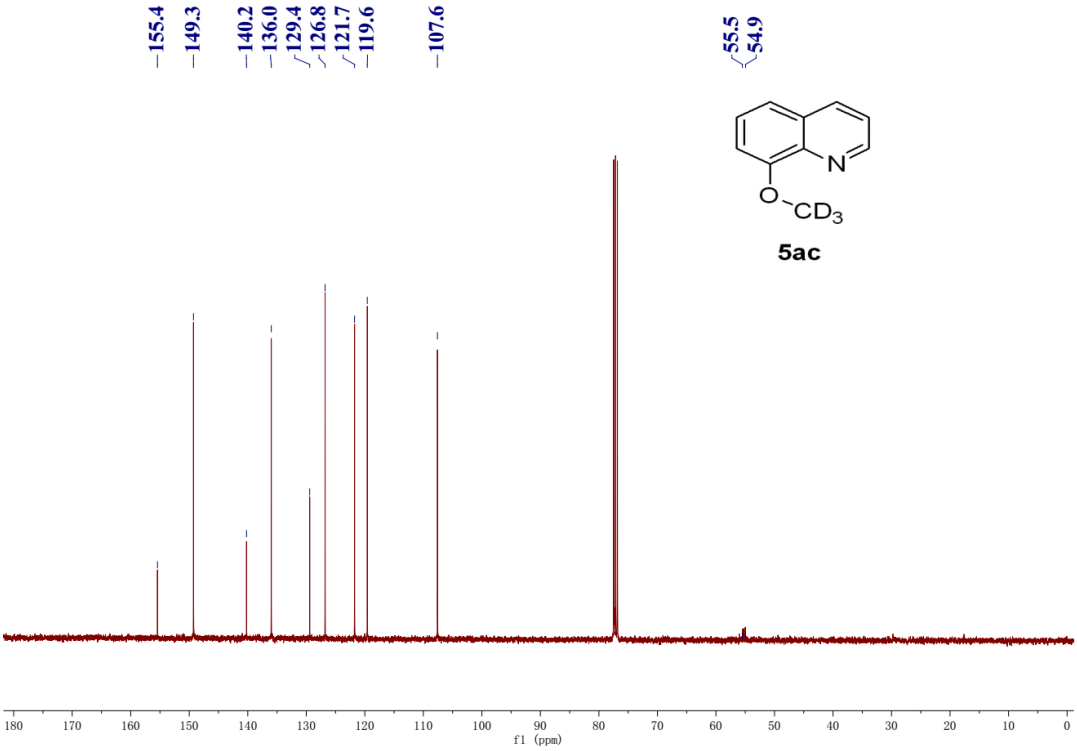
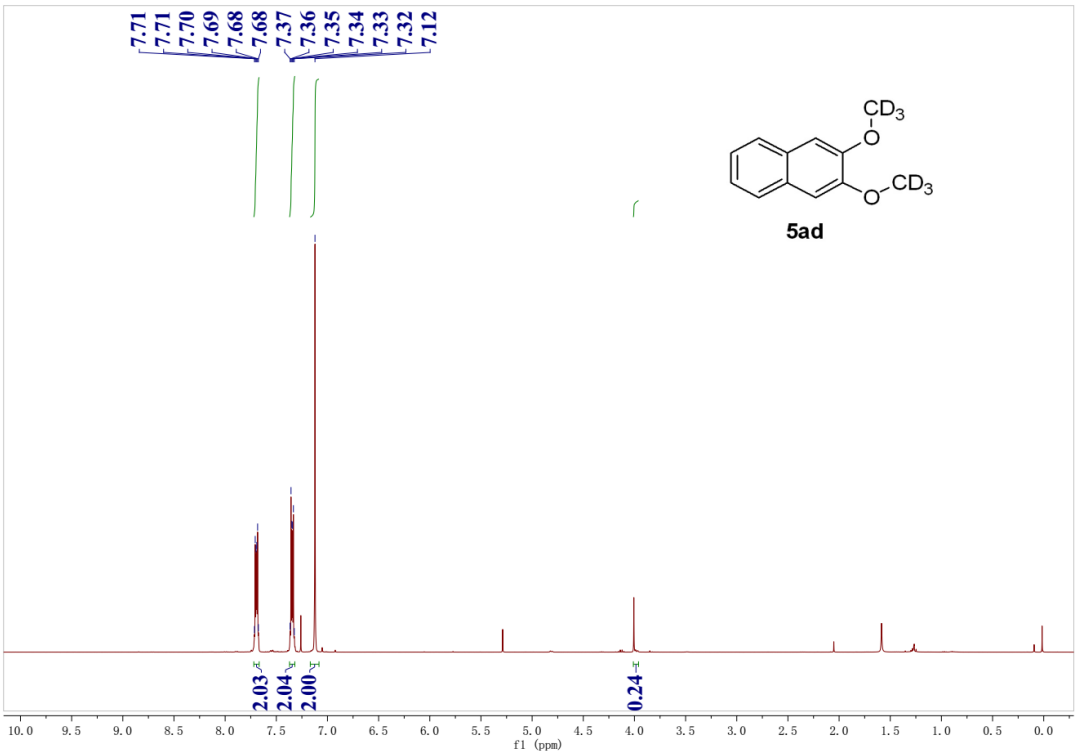
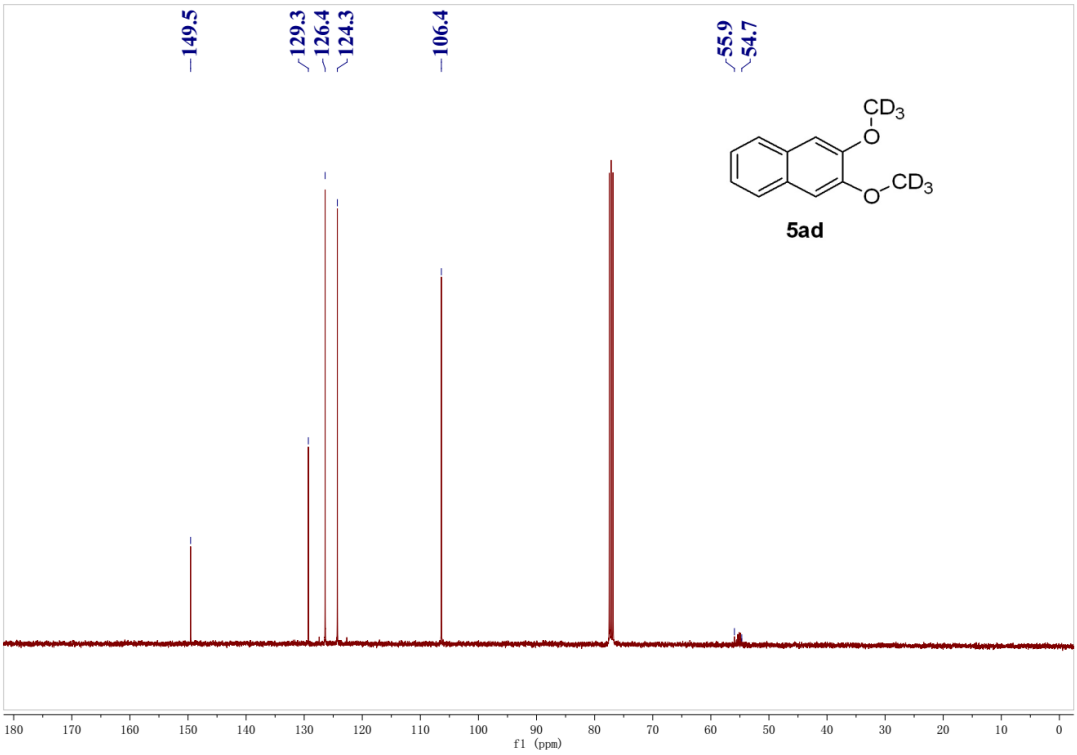
8.57
8.55
8.55
8.54
7.69
7.67
7.61
7.59
6.83
6.81
3.98
D3C
O
N
5ab
1.03
1.00
1.01
1.01
1.03
1.00
0.14
f1 (ppm)

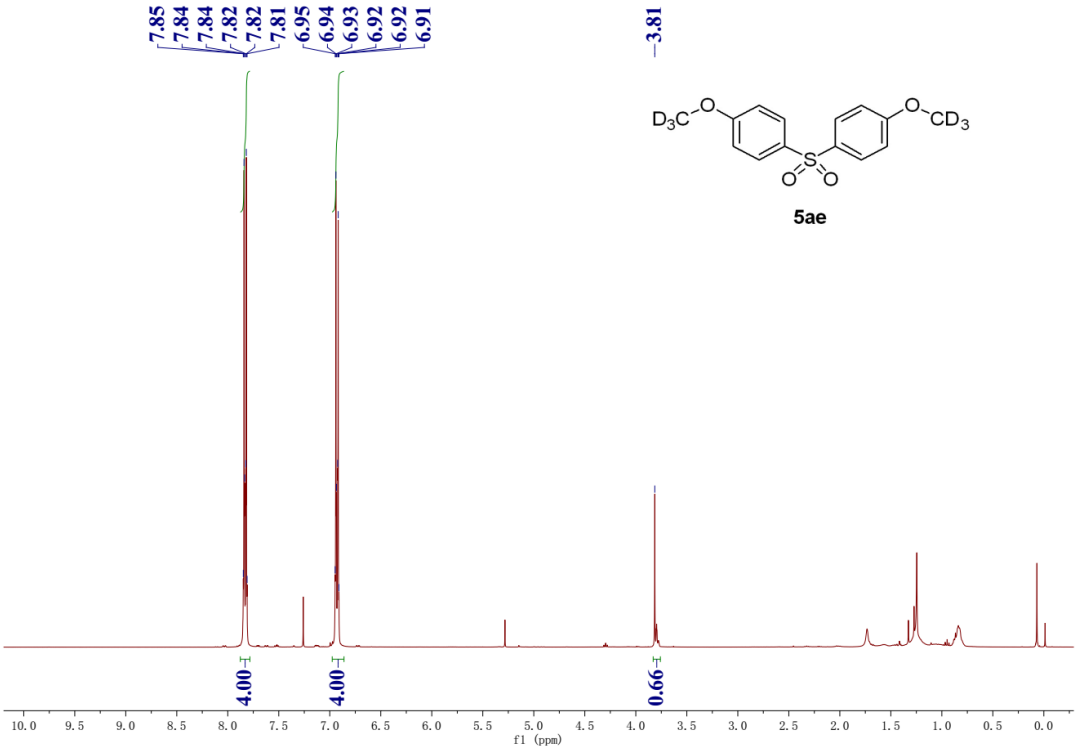

155.2
150.7
149.1
131.0
129.5
121.5
120.9
120.3
104.3
55.3
54.7
D3C
O
N
5ab
f1 (ppm)


8.91
8.91
8.90
8.89
8.10
8.08
7.34
7.03
7.02
7.01
7.00
1.01
1.01
3.06
1.00
0.13
f1 (ppm)
N
O
CD3
5ac

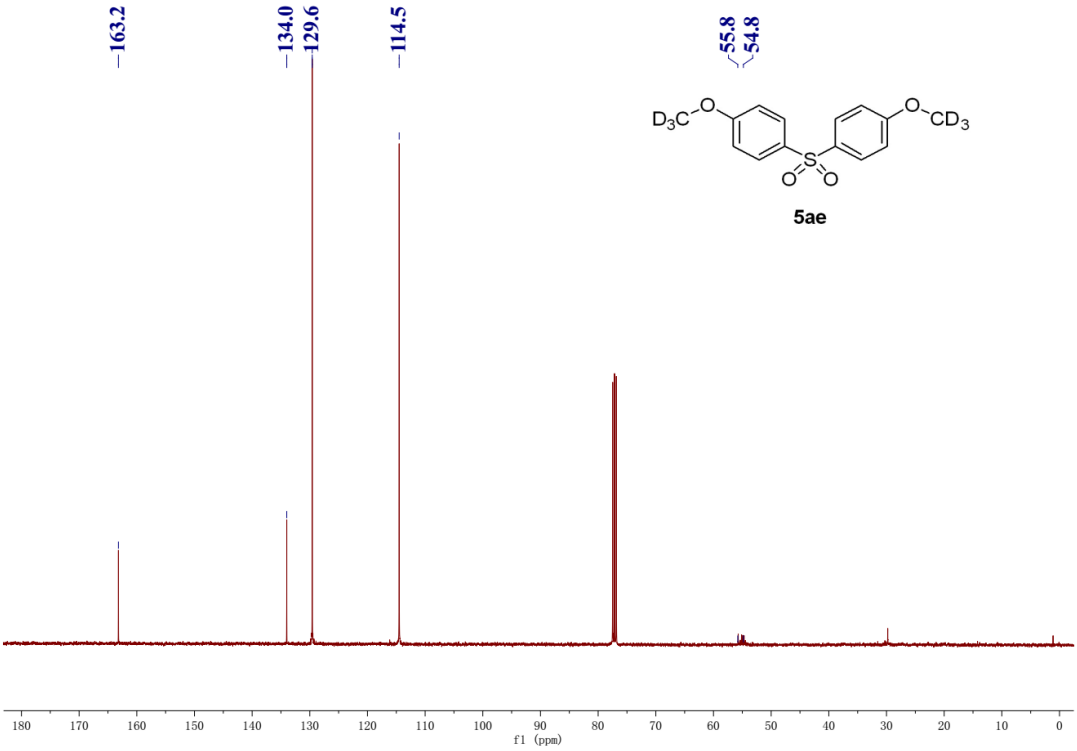

155.4
149.3
140.2
136.0
129.4
126.8
121.7
119.6
107.6
55.5
54.9
f1 (ppm)
N
O
CD3
5ac


7.71
7.71
7.70
7.69
7.68
7.68
7.37
7.36
7.35
7.34
7.33
7.32
7.12
CD3
O
O
CD3
5ad
2.03
2.04
2.00
0.24
f1 (ppm)

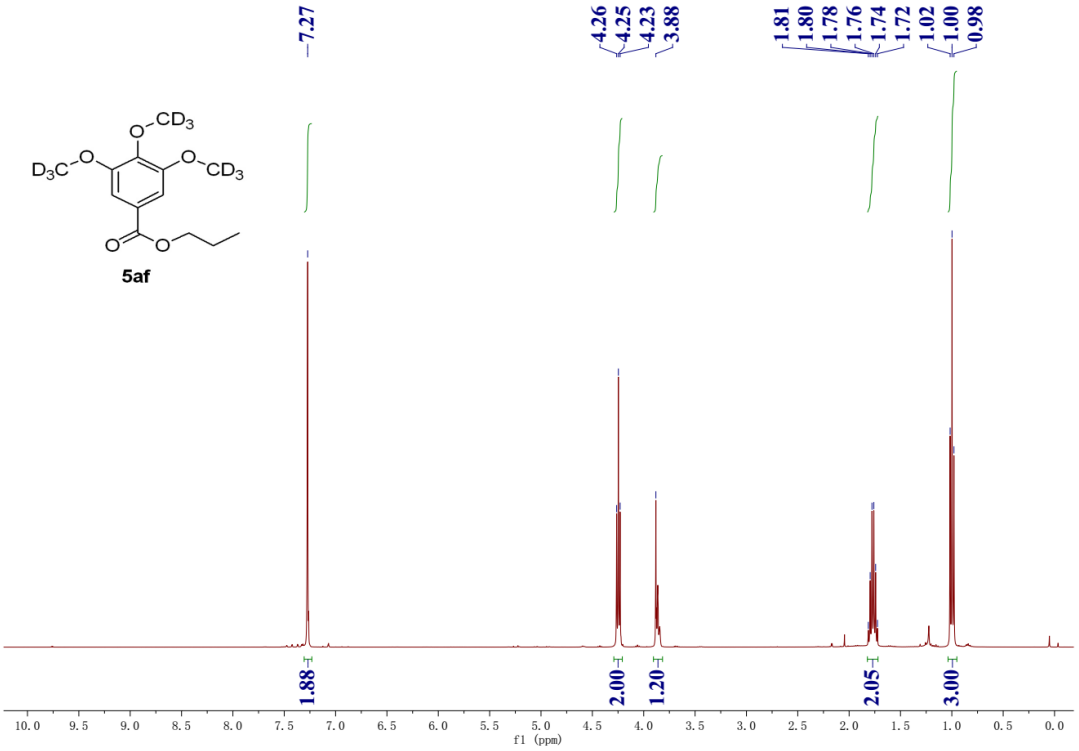

149.5
129.3
126.4
124.3
106.4
55.9
54.7
CD3
O
O
CD3
5ad
f1 (ppm)


7.85
7.84
7.84
7.82
7.82
7.81
6.95
6.94
6.93
6.92
6.92
6.91
3.81
4.00
4.00
0.66
f1 (ppm)

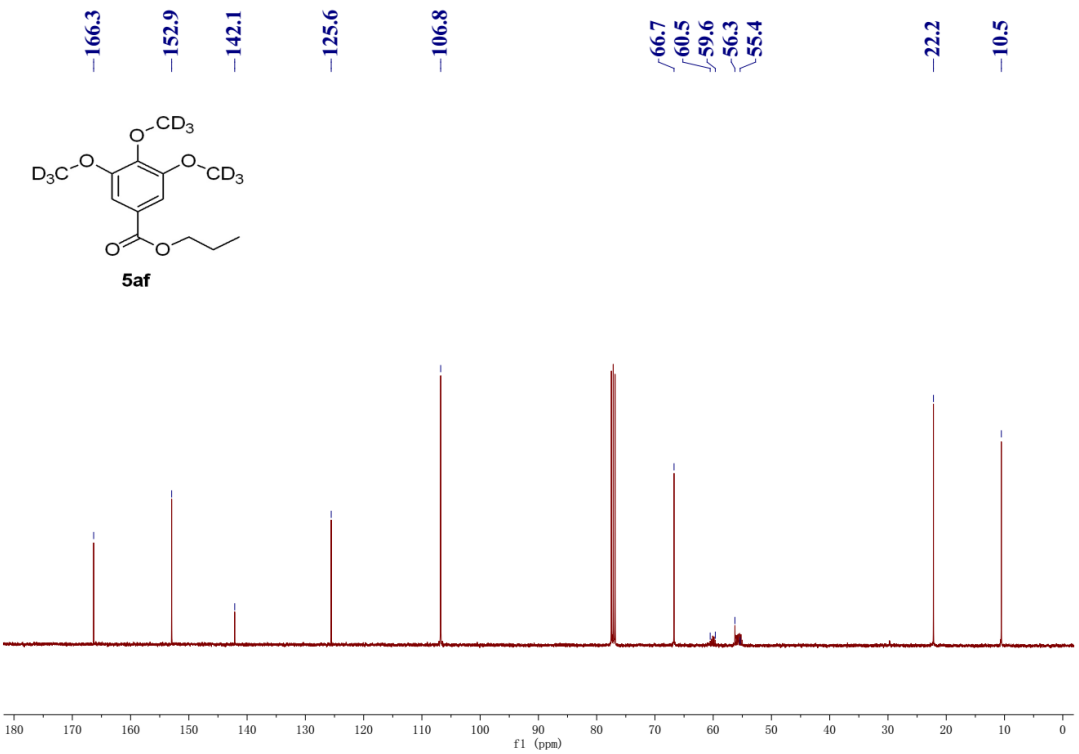
5ae


163.2
134.0
129.6
114.5
55.8
54.8
f1 (ppm)

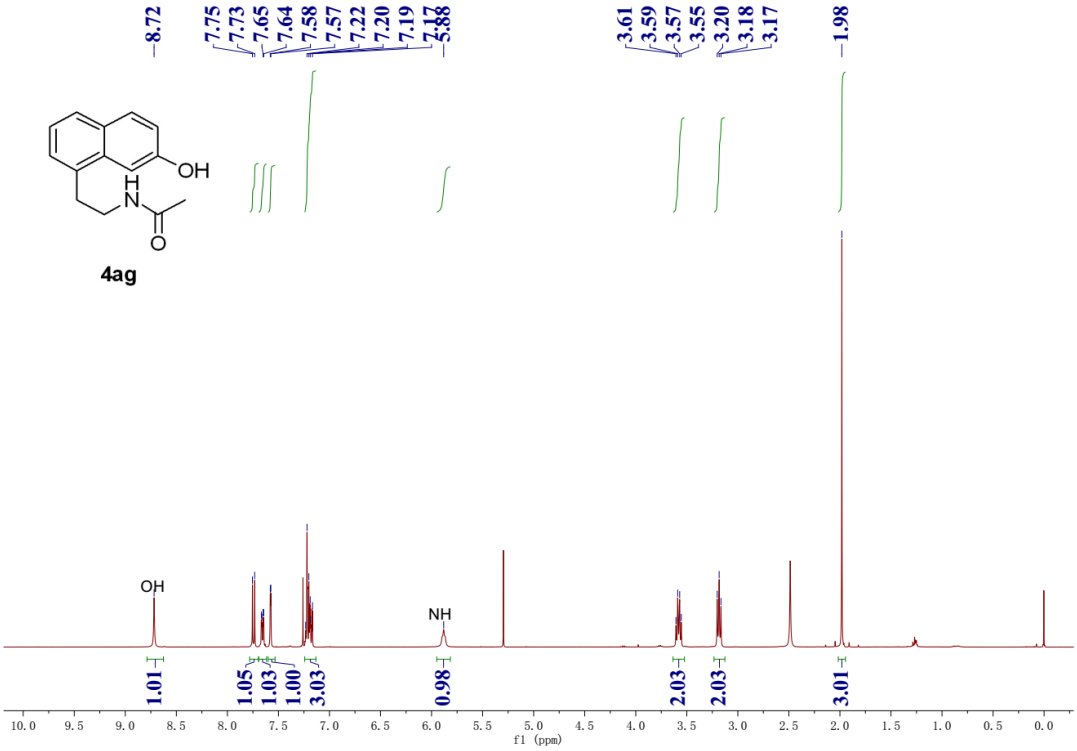
5ae


7.27
4.26
4.25
4.23
3.88
1.81
1.80
1.78
1.76
1.74
1.72
1.02
1.00
0.98
1.88
2.00
1.20
2.05
3.00
f1 (ppm)

5af


166.3
152.9
142.1
125.6
106.8
66.7
60.5
59.6
56.3
55.4
22.2
10.5
f1 (ppm)

5af


8.72
7.75
7.73
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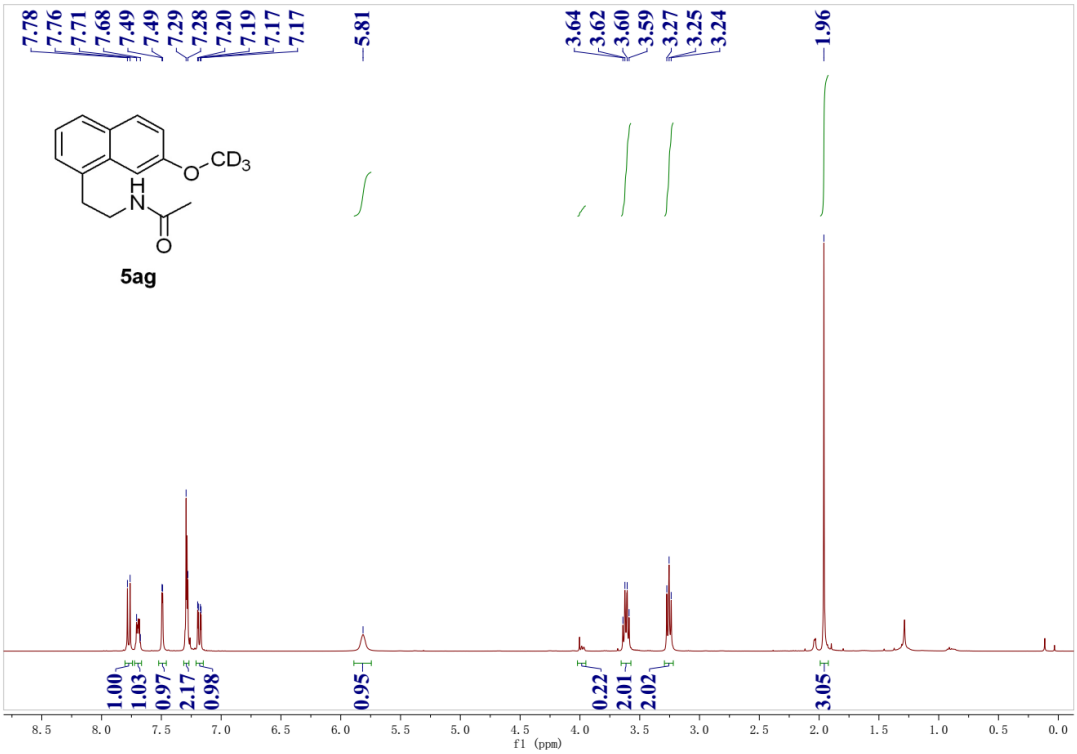
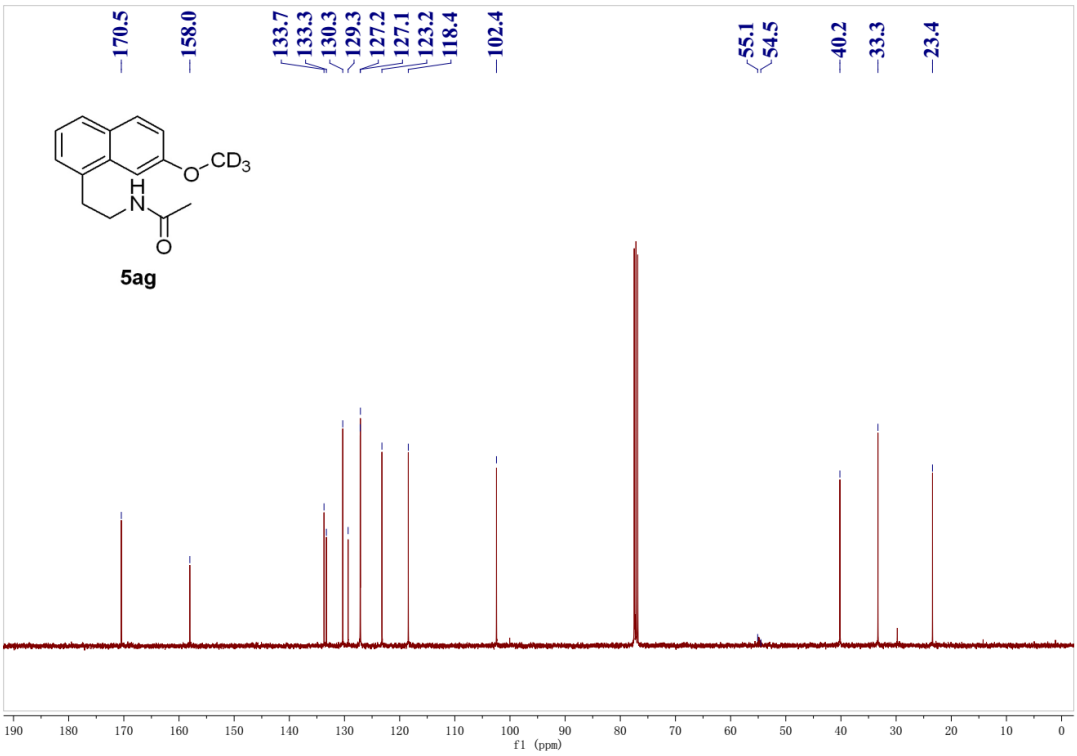
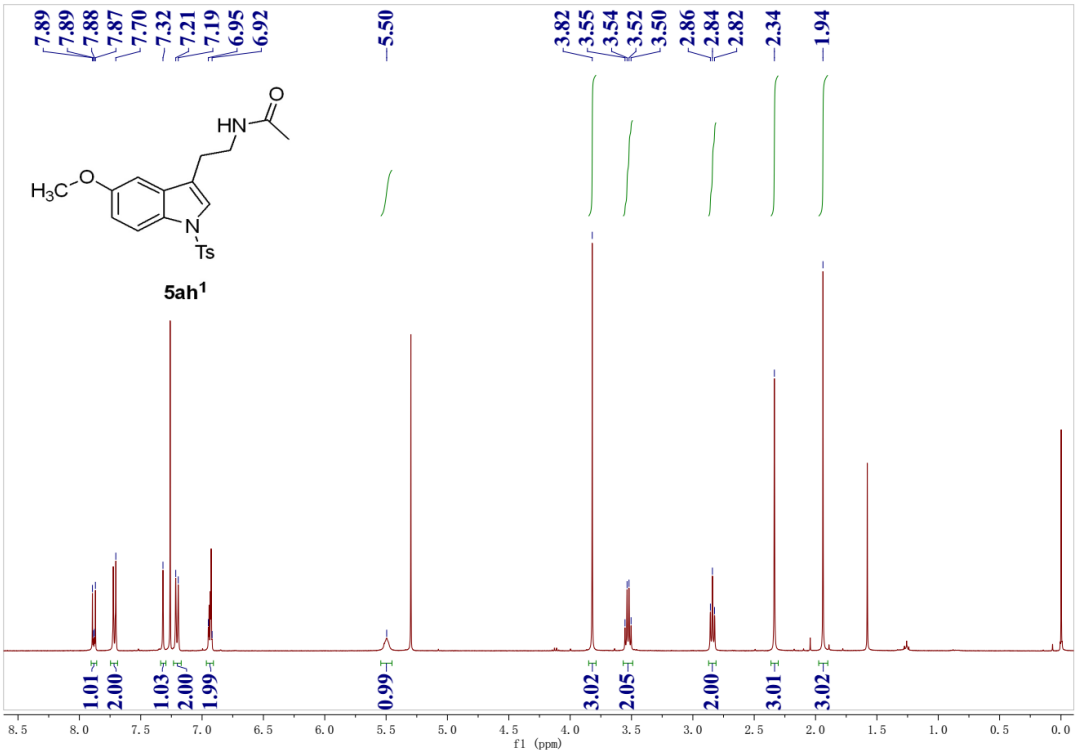
7.64
7.58
7.57
7.22
7.20
7.19
5.88
3.61
3.59
3.57
3.55
3.20
3.18
3.17
1.98
OH
NH
1.01
1.05
1.03
1.00
3.03
0.98
2.03
2.03
3.01
f1 (ppm)

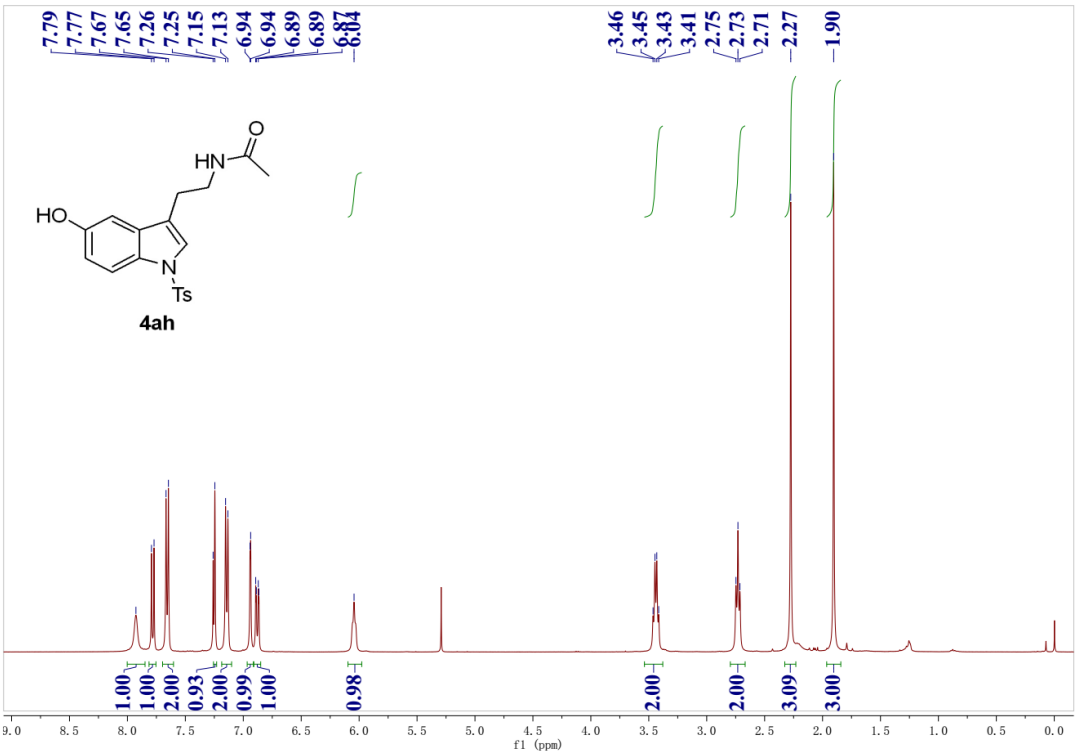
4ag

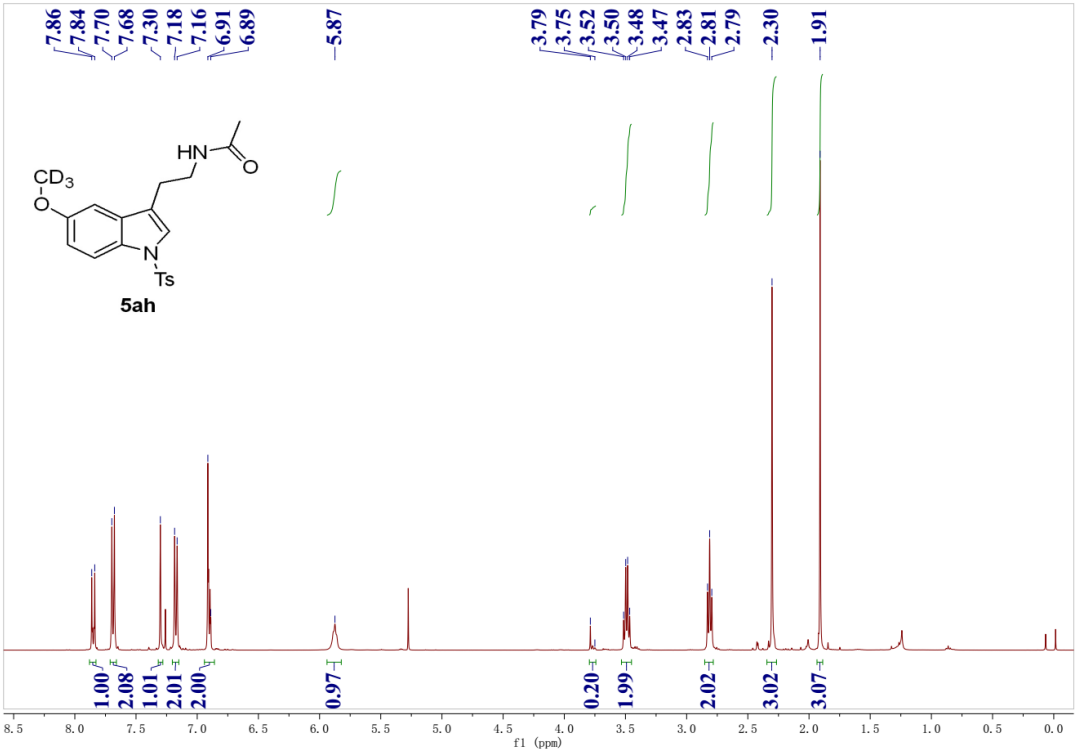

7.78
7.76
7.71
7.68
7.49
7.49
7.29
7.28
7.20
7.19
7.17
7.17
5.81
3.64
3.62
3.60
3.59
3.27
3.25
3.24
1.96
1.00
1.03
0.97
2.17
0.98
0.95
0.22
2.01
2.02
3.05
f1 (ppm)

5ag


170.5
158.0
133.7
133.3
130.3
129.3
127.2
127.1
123.2
118.4
102.4
55.1
54.5
40.2
33.3
23.4
CD3
O
H
N
O
5ag
f1 (ppm)


7.89
7.89
7.88
7.87
7.70
7.32
7.21
7.19
6.95
6.92
5.50
3.82
3.55
3.54
3.52
3.50
2.86
2.84
2.82
2.34
1.94
HN
O
H3C
O
N
Ts
5ah1
1.01
2.00
1.03
2.00
1.99
0.99
3.02
2.05
2.00
3.01
3.02
f1 (ppm)


7.79
7.77
7.67
7.65
7.26
7.25
7.15
7.13
6.94
6.94
6.89
6.89
6.87
6.84
3.46
3.45
3.43
3.41
2.75
2.73
2.71
2.27
1.90
HO
HN
O
N
Ts
4ah
1.00
1.00
2.00
0.93
2.00
0.99
1.00
0.98
2.00
2.00
3.09
3.00
f1 (ppm)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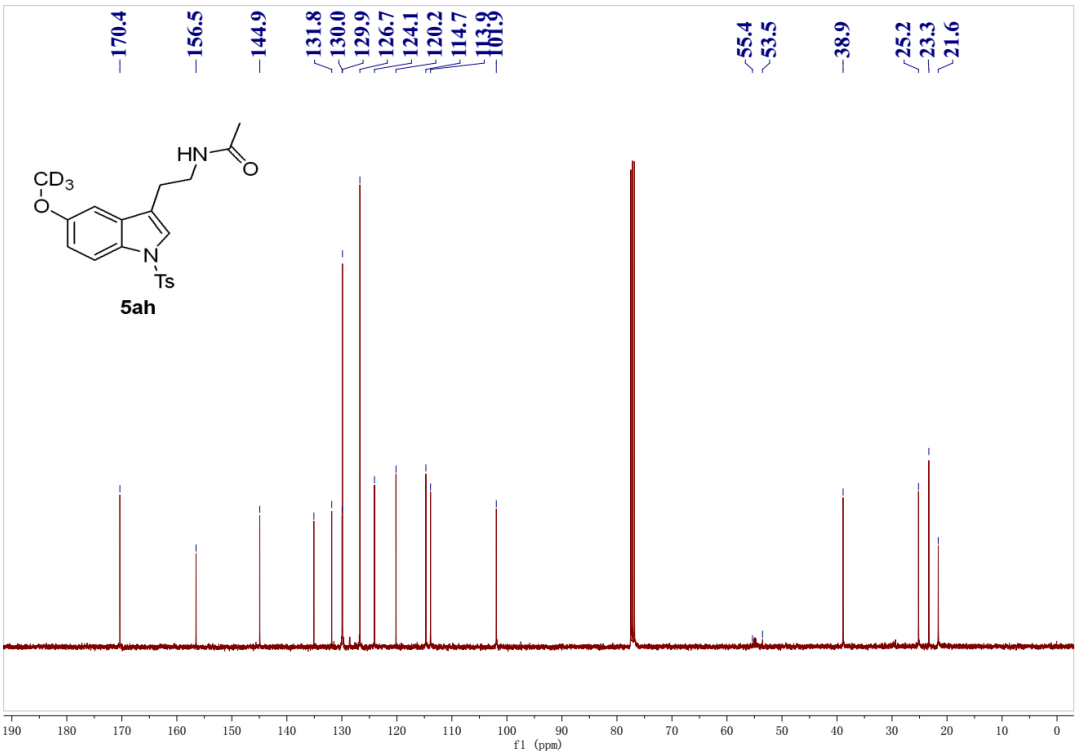
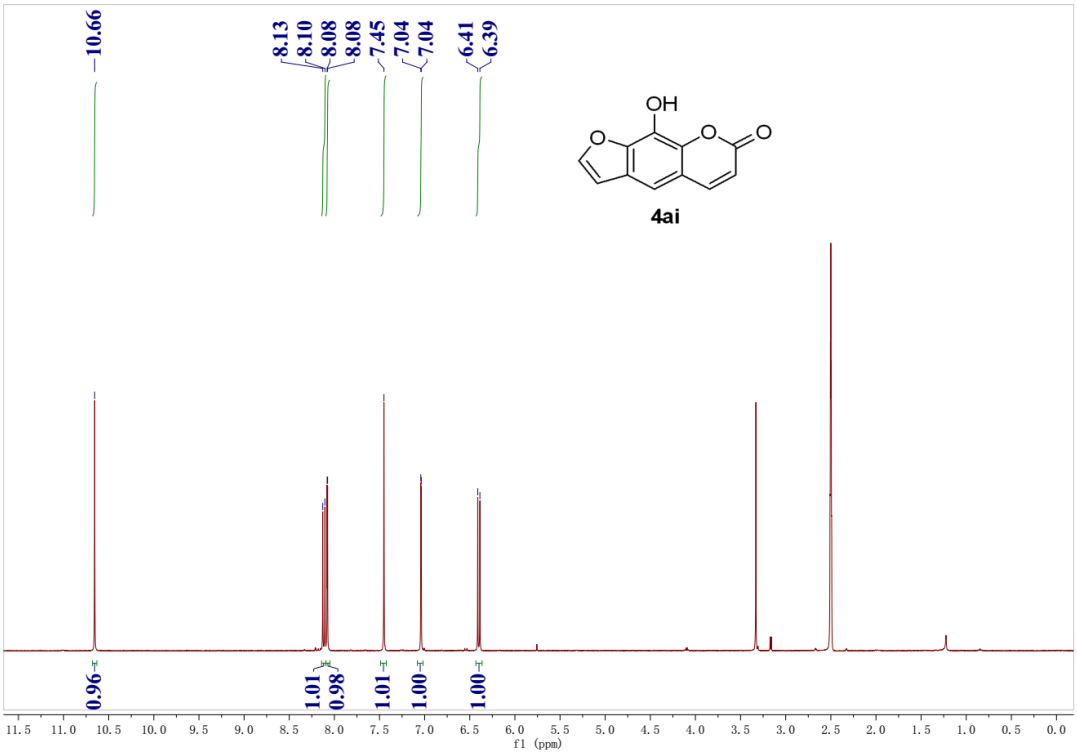
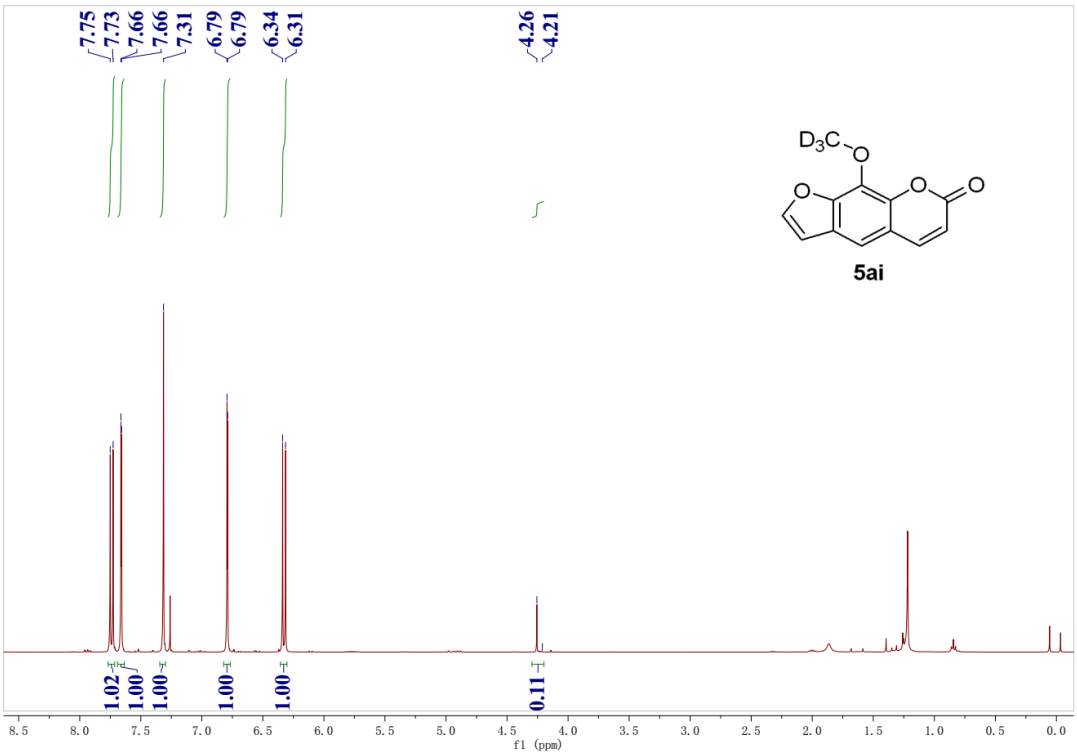
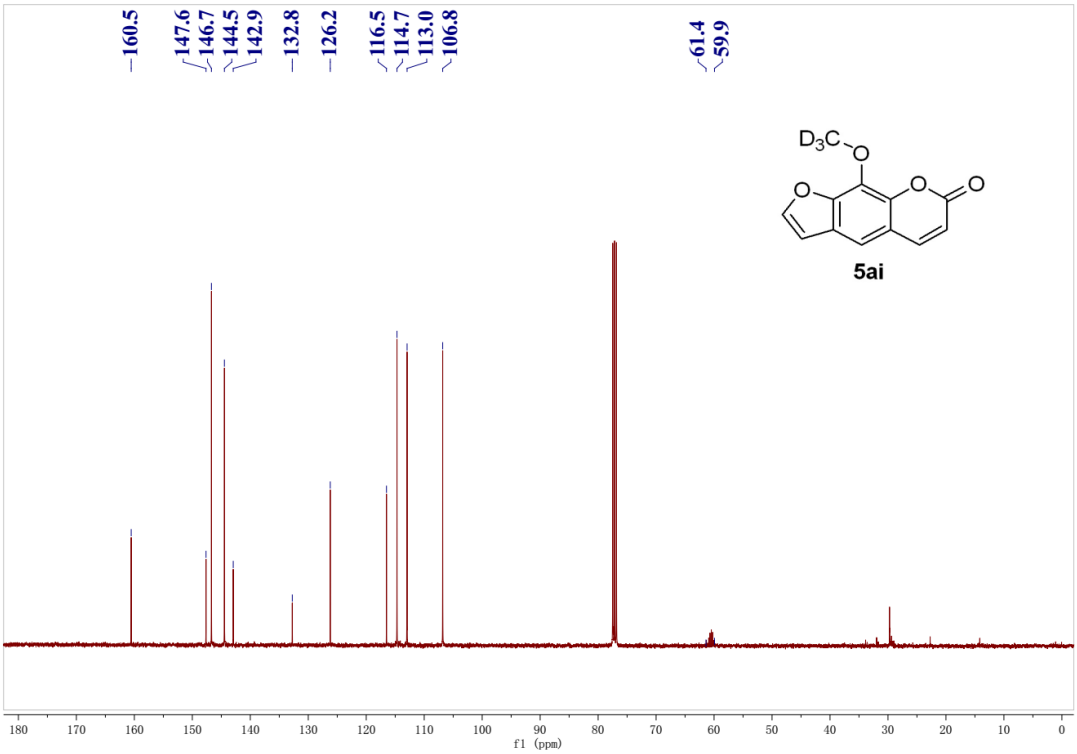
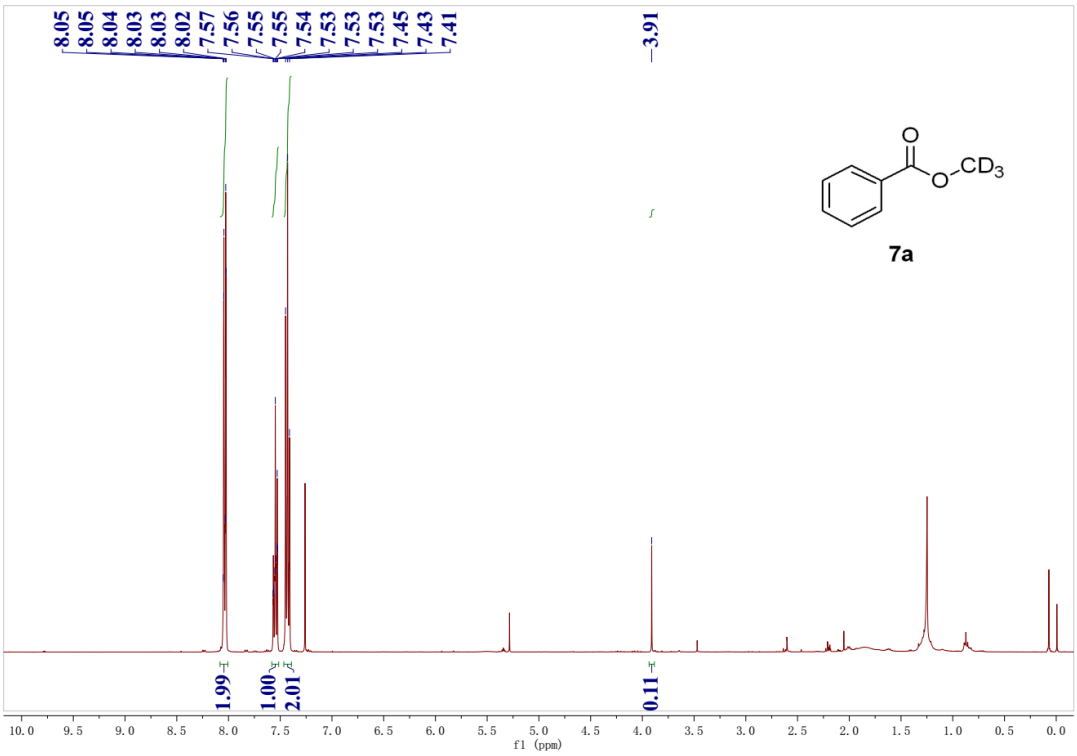
7.84
7.70
7.68
7.30
7.18
7.16
6.91
6.89
5.87
3.79
3.75
3.52
3.50
3.48
3.47
2.83
2.81
2.79
2.30
1.91
CD3
O
HN
O
N
Ts
5ah
1.00
2.08
1.01
2.01
2.00
0.97
0.20
1.99
2.02
3.02
3.07
f1 (ppm)

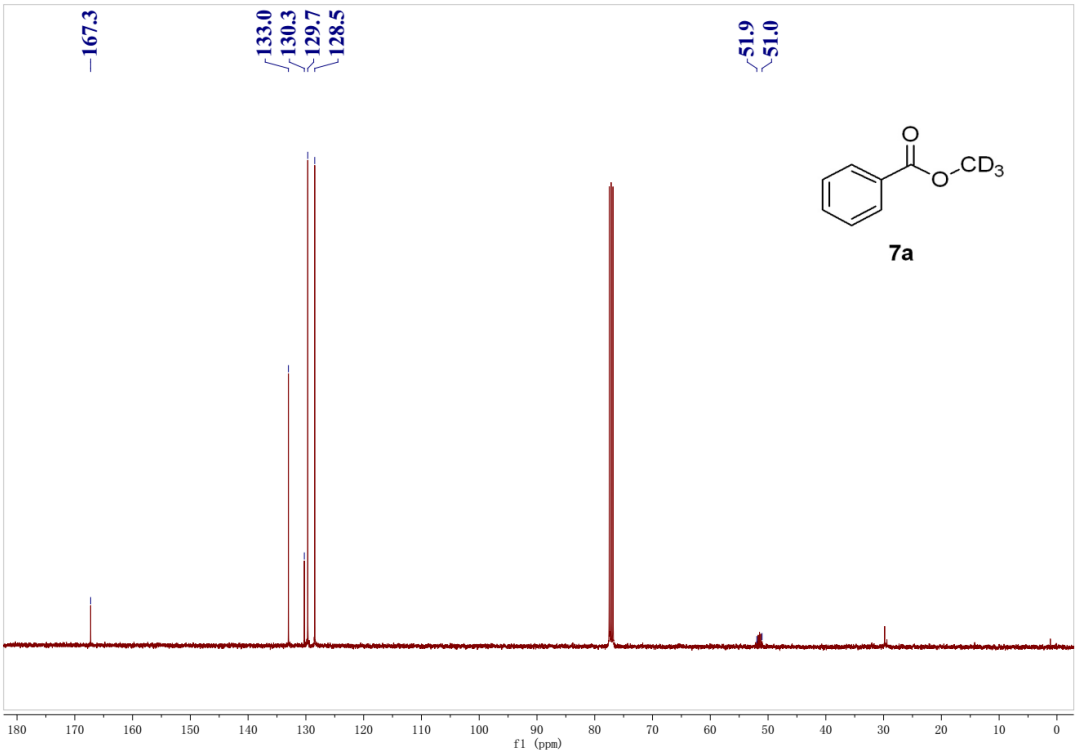

170.4
156.5
144.9
131.8
130.0
129.9
126.7
124.1
120.2
114.7
113.9
101.9
55.4
53.5
38.9
25.2
23.3
21.6
HN
O
CD3
O
N
Ts
5ah
f1 (ppm)

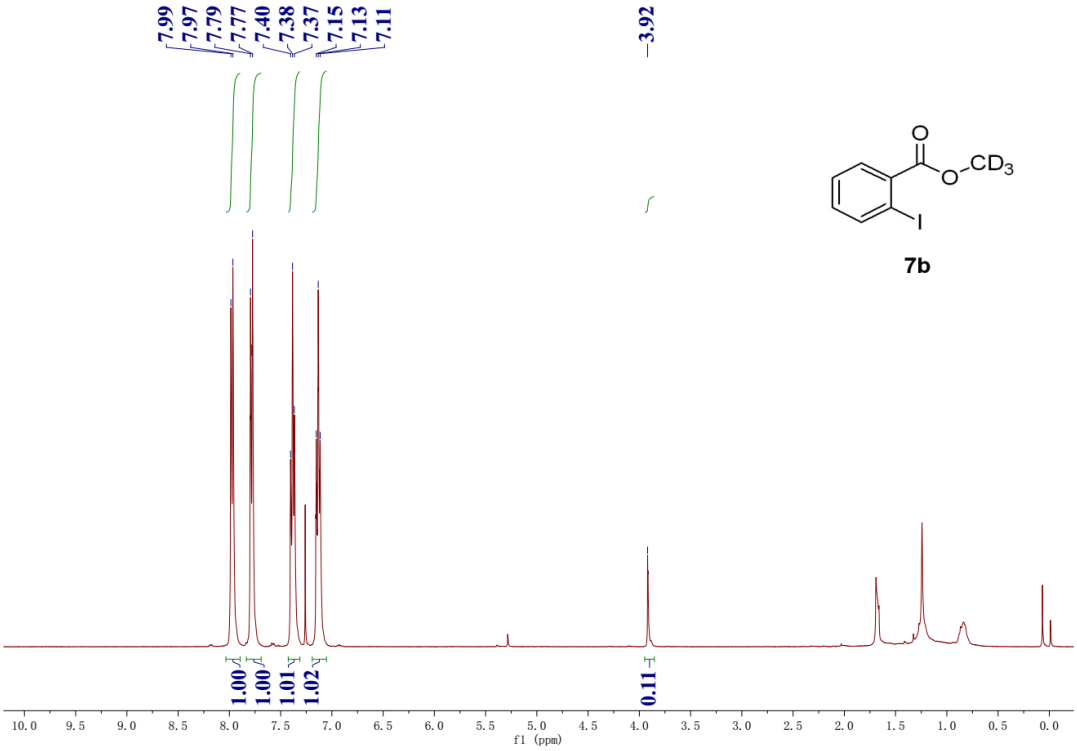

10.66
8.13
8.10
8.08
8.08
7.45
7.04
7.04
6.41
6.39
OH
O
O
O
4ai
0.96
1.01
0.98
1.01
1.00
1.00
f1 (ppm)


7.75
7.73
7.66
7.66
7.31
6.79
6.79
6.34
6.31
4.26
4.21
D3C
O
O
O
O
5ai
1.02
1.00
1.00
1.00
1.00
0.11
f1 (ppm)


160.5
147.6
146.7
144.5
142.9
132.8
126.2
116.5
114.7
113.0
106.8
61.4
59.9
D3C
O
O
O
O
5ai
f1 (ppm)

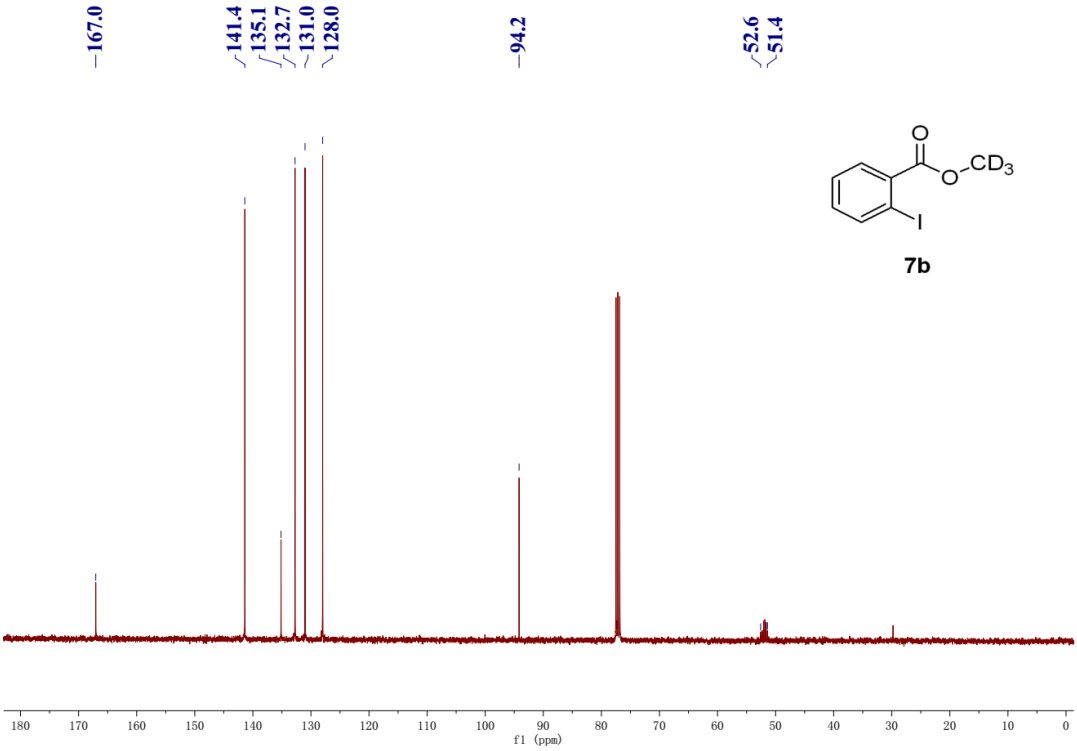

8.05
8.05
8.04
8.03
8.03
8.02
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.45
7.43
7.41
3.91
1.99
1.00
2.01
0.11
f1 (ppm)
O
O
CD3
7a


167.3
133.0
130.3
129.7
128.5
51.9
51.0
f1 (ppm)
O
O
CD3
7a


7.99
7.97
7.79
7.77
7.40
7.38
7.37
7.15
7.13
7.11
3.92
1.00
1.00
1.01
1.02
0.11
f1 (ppm)

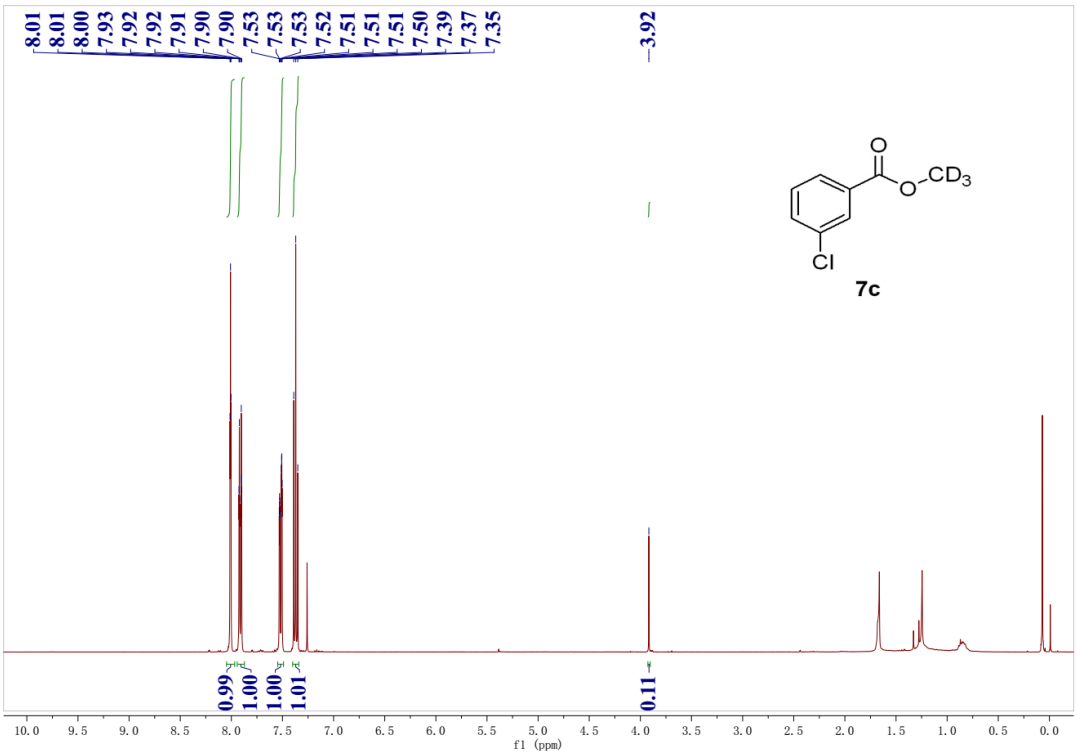
O
O
CD3
I

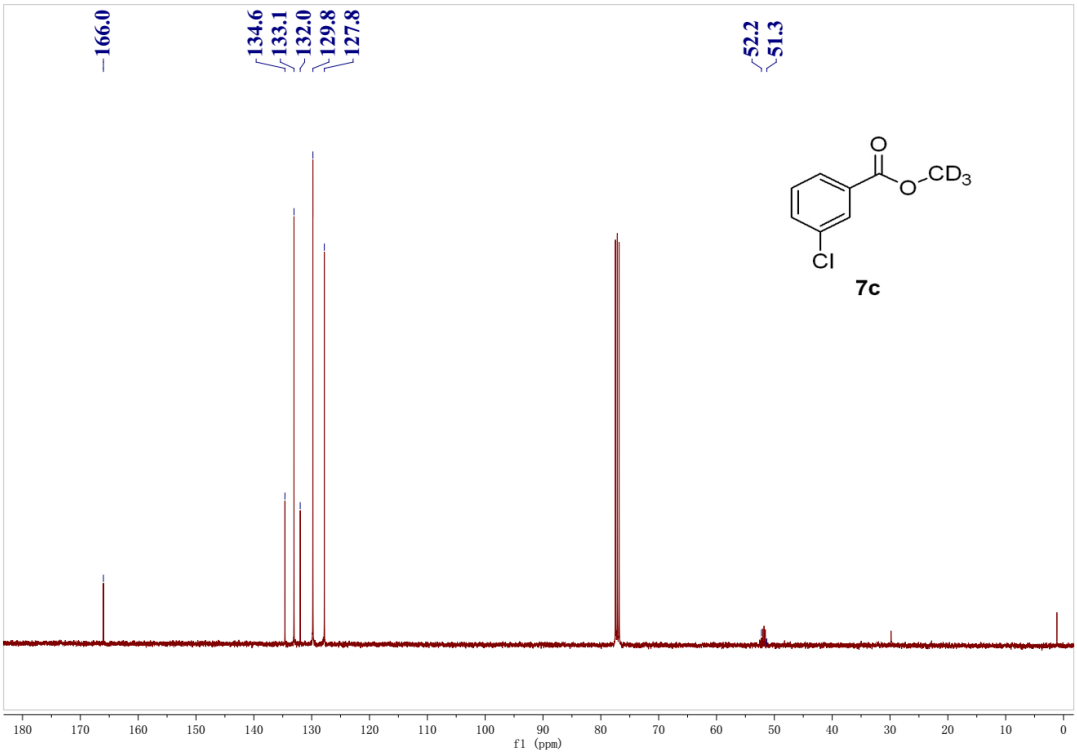
7b

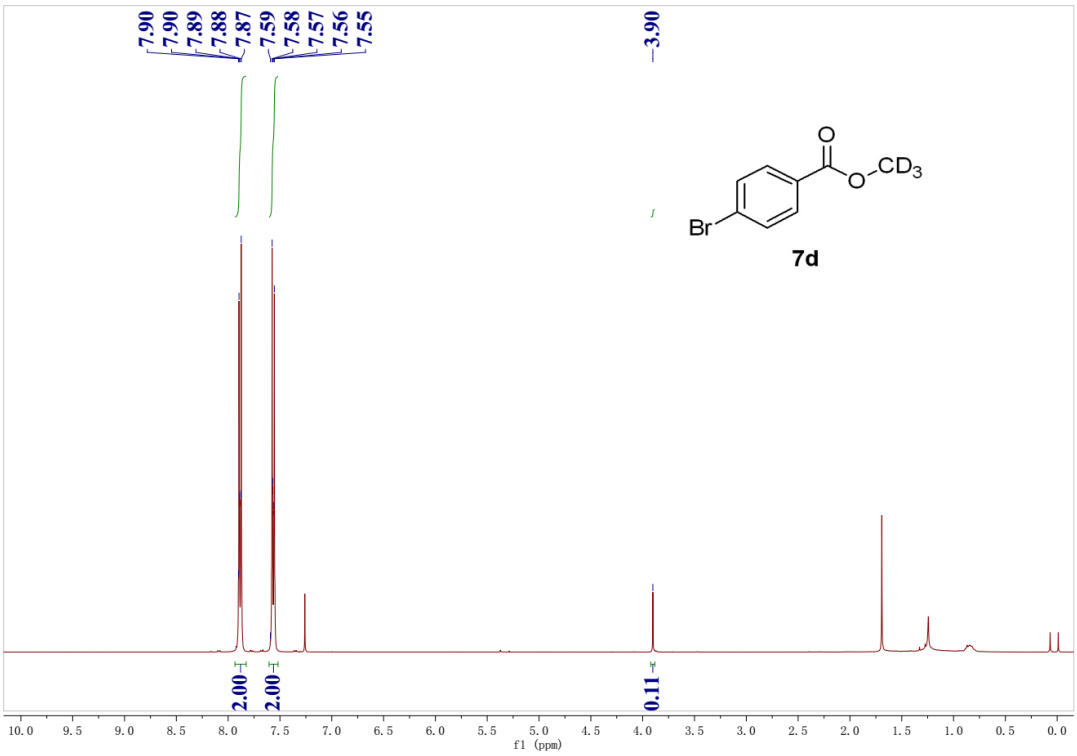

167.0
141.4
135.1
132.7
131.0
128.0
94.2
52.6
51.4
f1 (ppm)

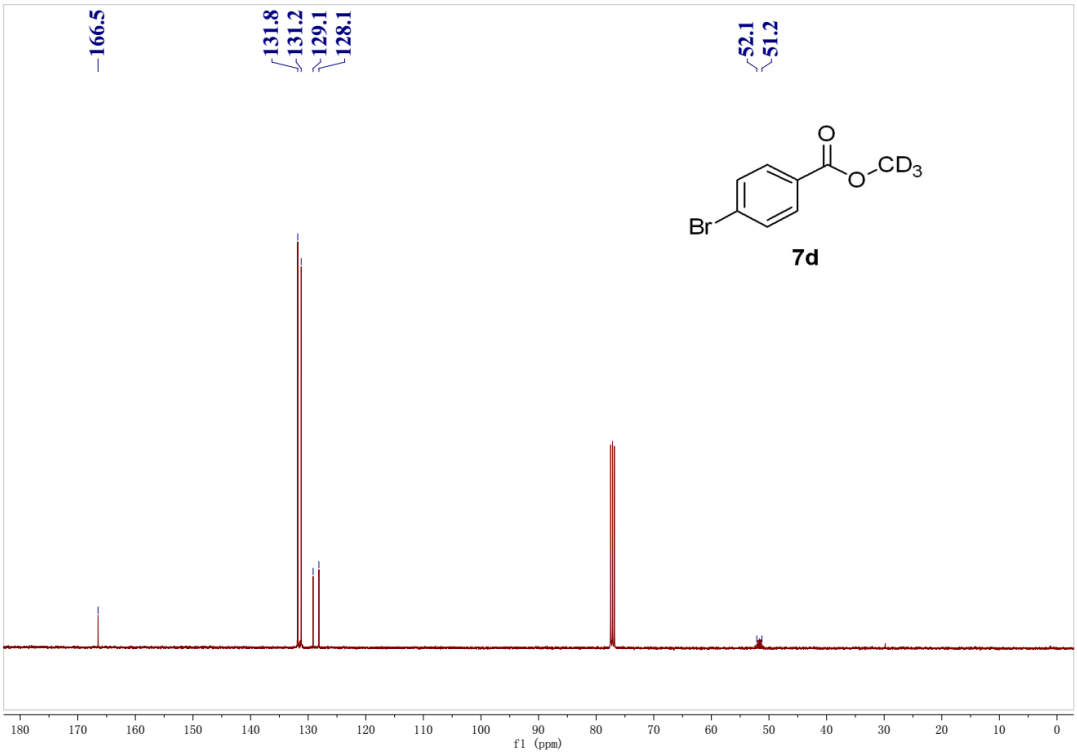
O
O
CD3
I

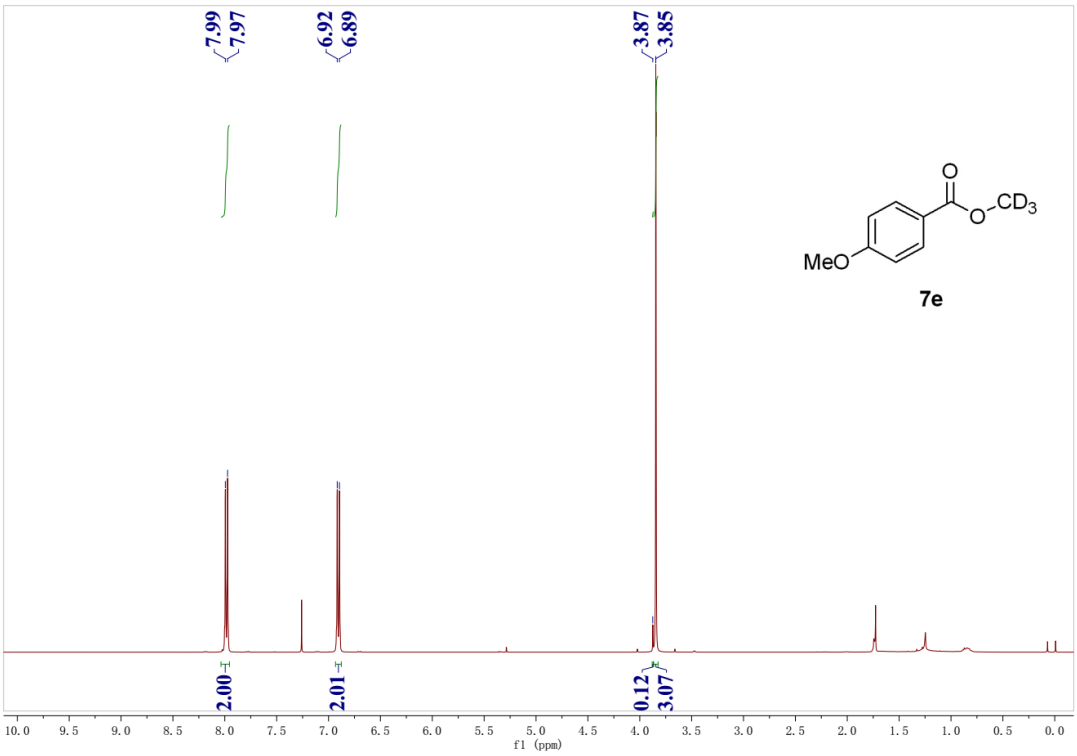
7b

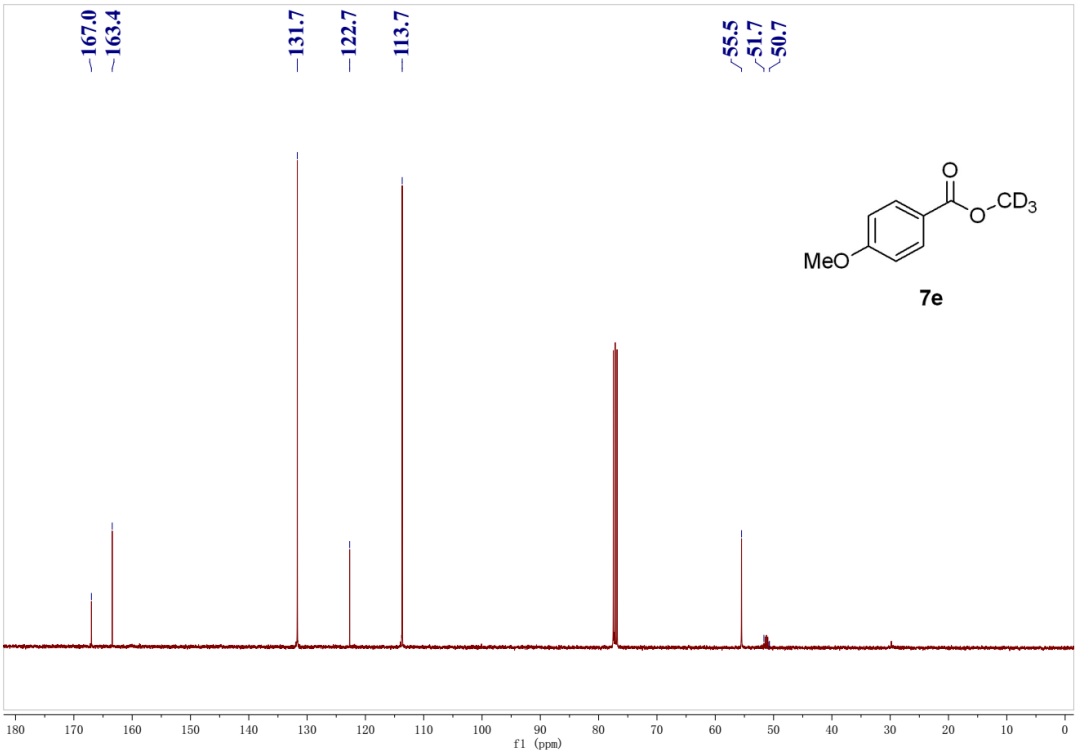

8.01
8.01
8.00
7.93
7.92
7.92
7.91
7.90
7.90
7.53
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.39
7.37
7.35
3.92
0.99
1.00
1.00
1.01
0.11
O
O
CD3
Cl
7c
f1 (ppm)

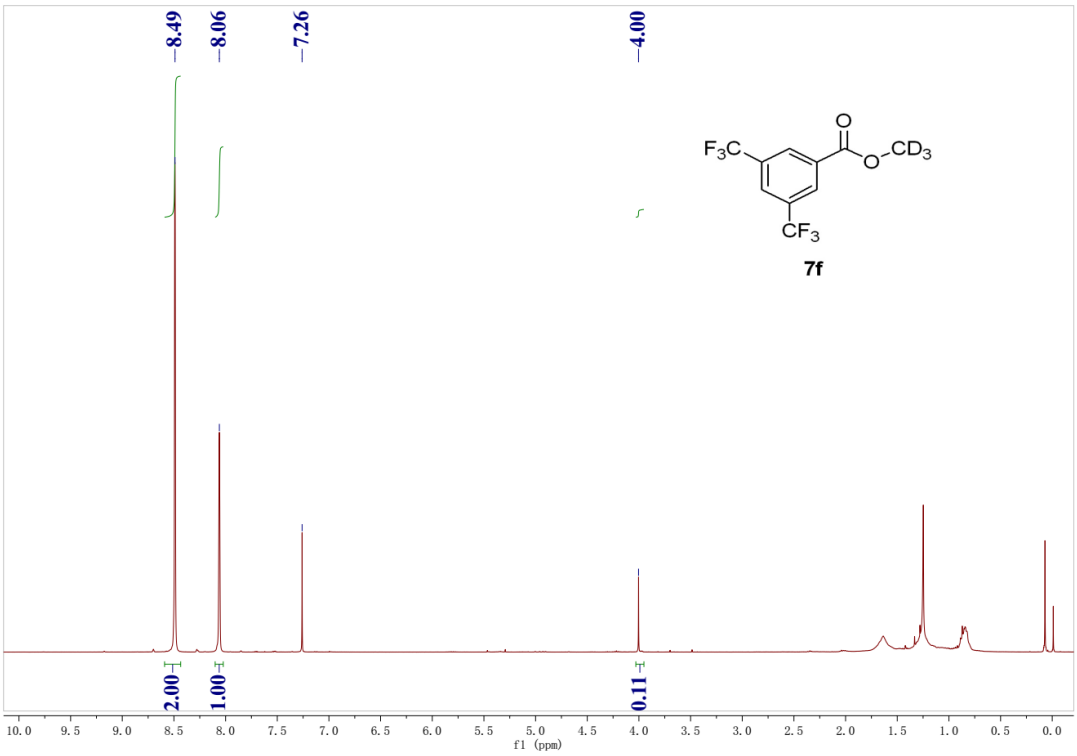

166.0
134.6
133.1
132.0
129.8
127.8
52.2
51.3
O
O
CD3
Cl
7c
f1 (ppm)

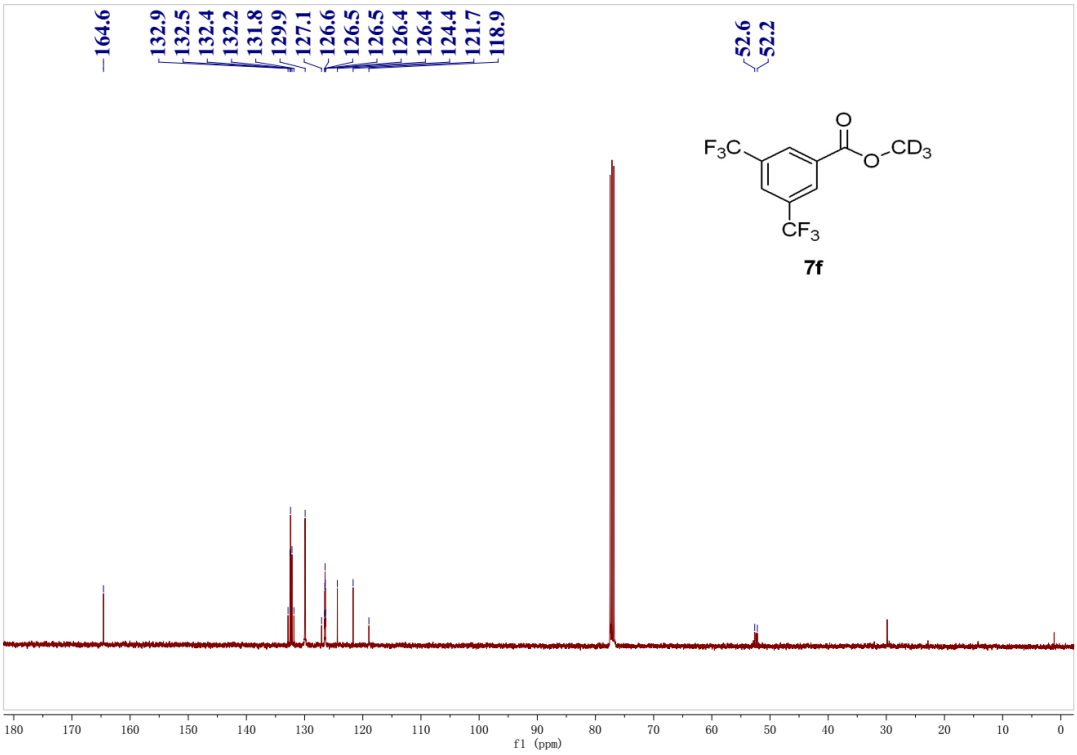

7.90
7.90
7.89
7.88
7.87
7.59
7.58
7.57
7.56
7.55
3.90
2.00
2.00
0.11
f1 (ppm)
Br
O
O
CD3
7d

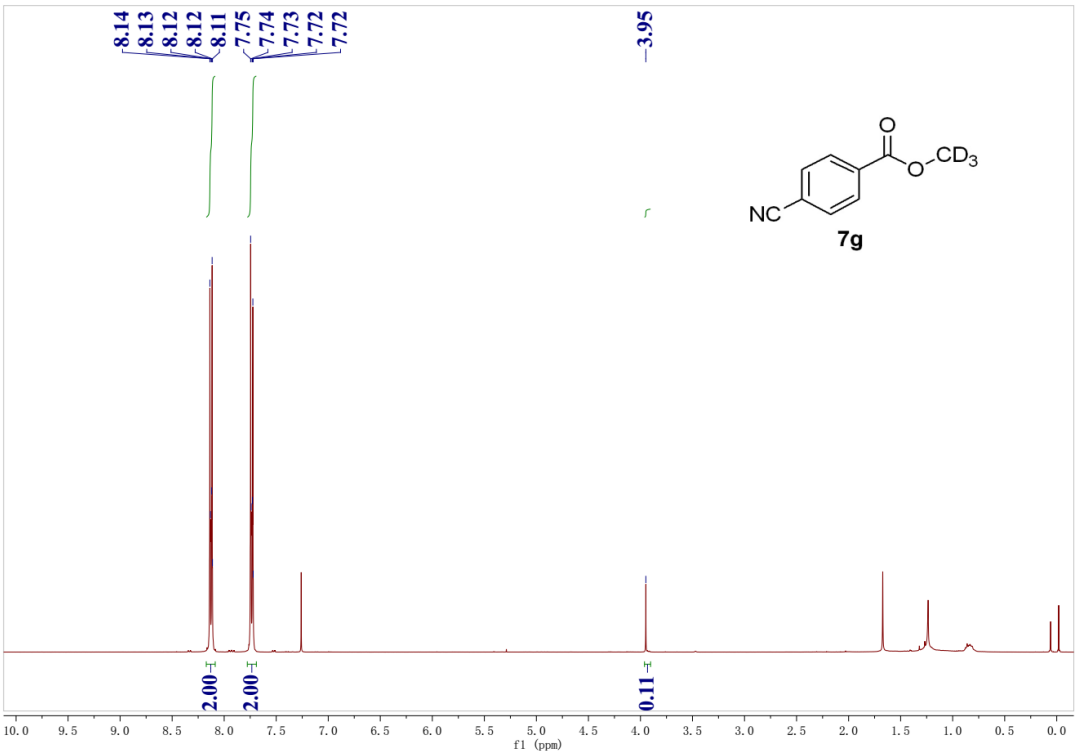

166.5
131.8
131.2
129.1
128.1
52.1
51.2
f1 (ppm)
Br
O
O
CD3
7d

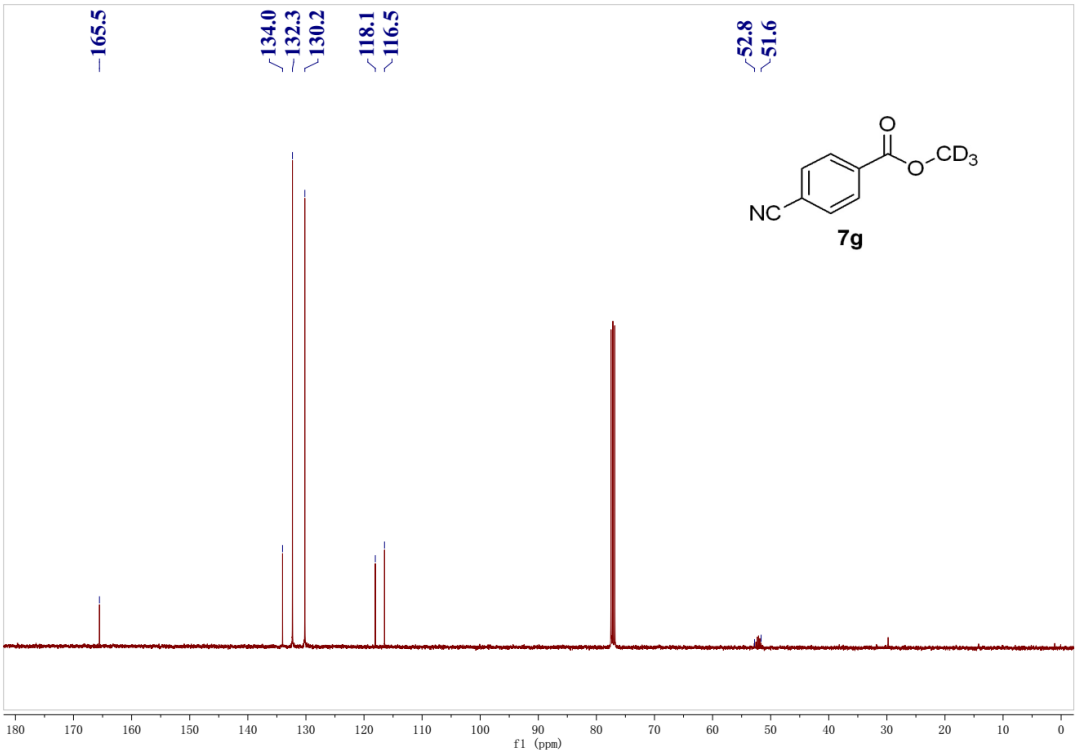

7.99
7.97
6.92
6.89
3.87
3.85
2.00
2.01
0.12
3.07
f1 (ppm)
MeO
CD3
7e

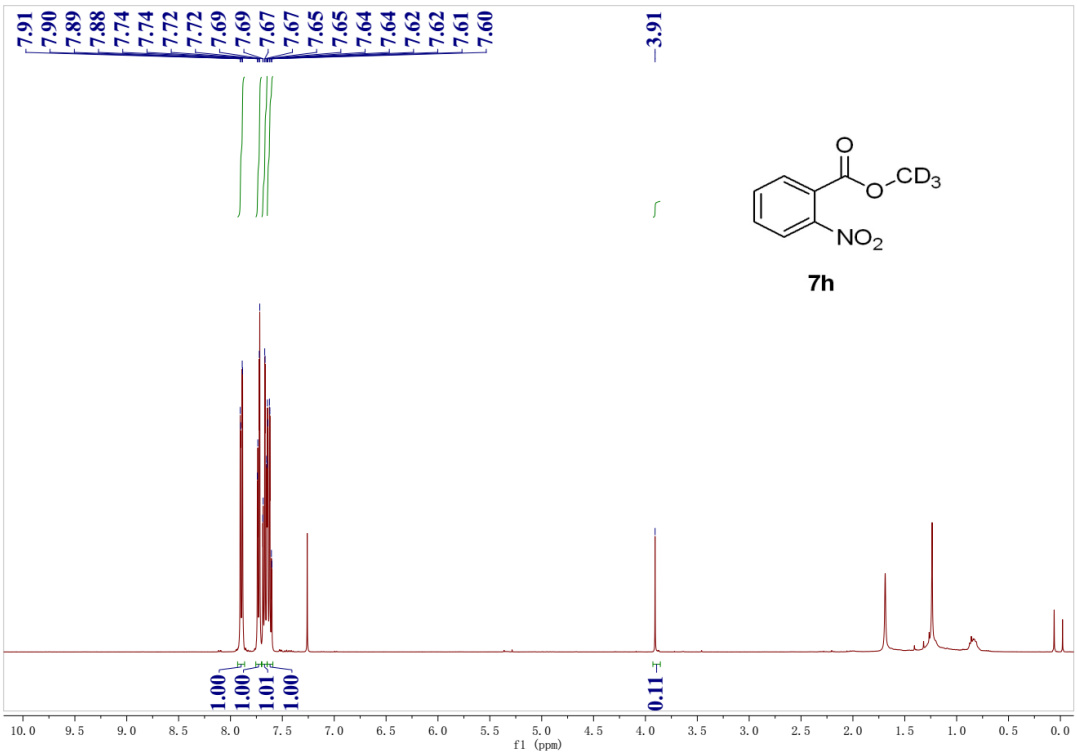

167.0
163.4
131.7
122.7
113.7
55.5
51.7
50.7
f1 (ppm)
MeO
CD3
7e

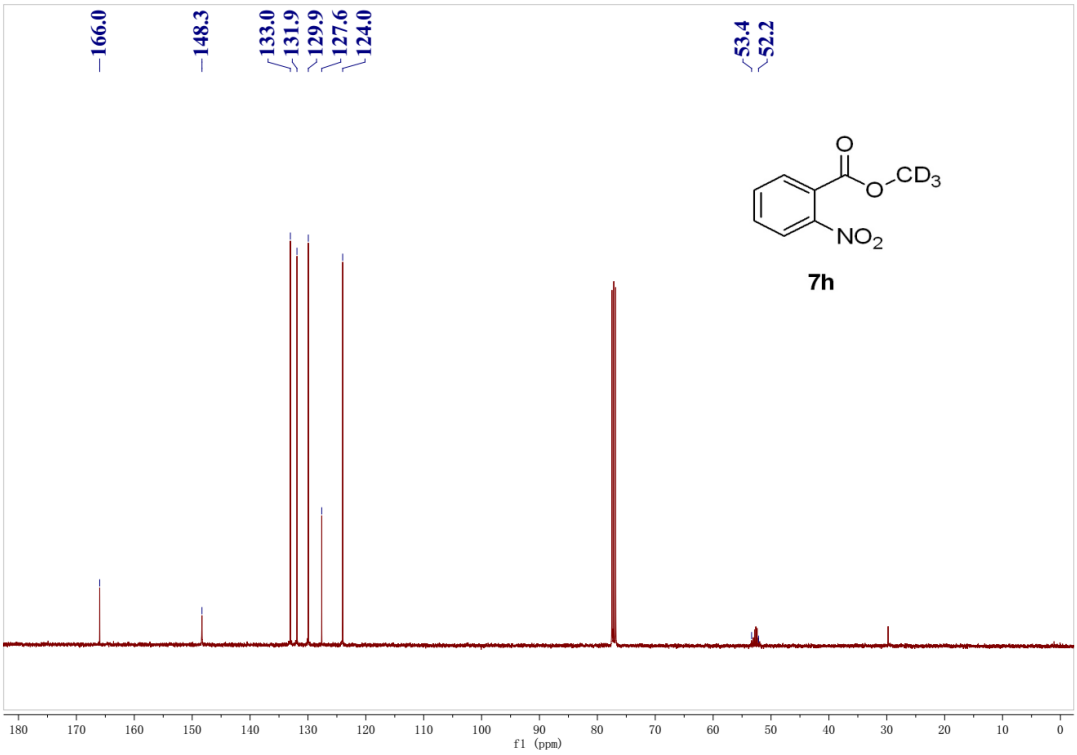

8.49
8.06
7.26
4.00
F3C
O
O
CD3
CF3
7f
2.00
1.00
0.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

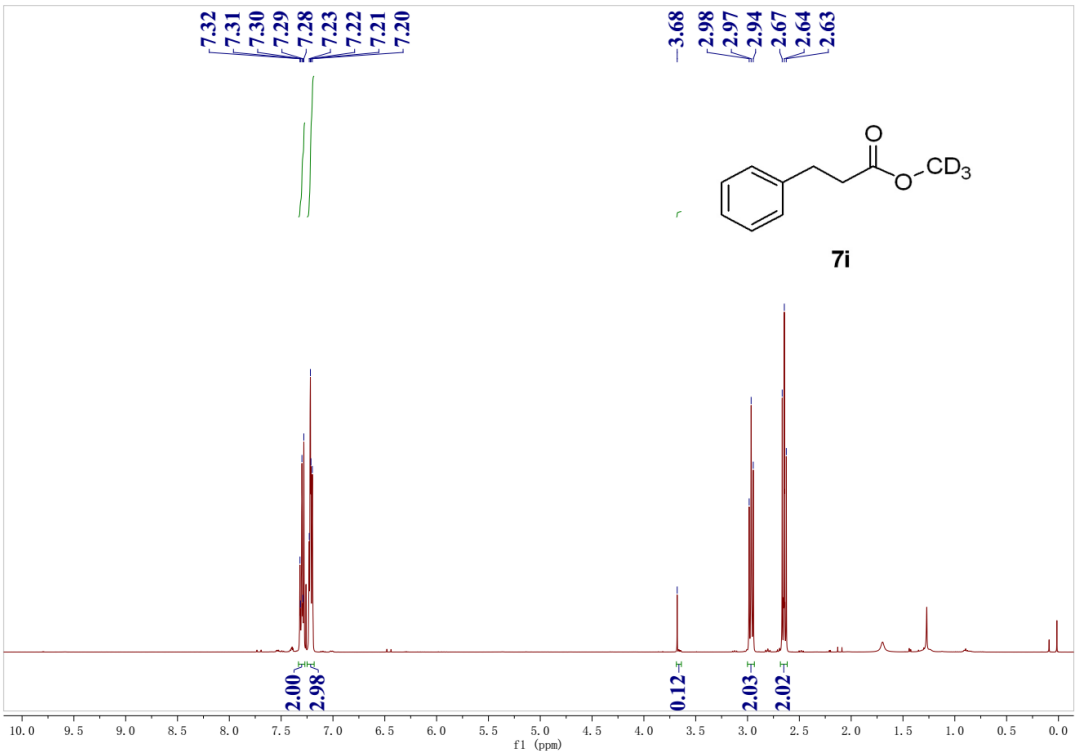

164.6
132.9
132.5
132.4
132.2
131.8
129.9
127.1
126.6
126.5
126.5
126.4
126.4
124.4
121.7
118.9
52.6
52.2
F3C
O
O
CD3
CF3
7f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

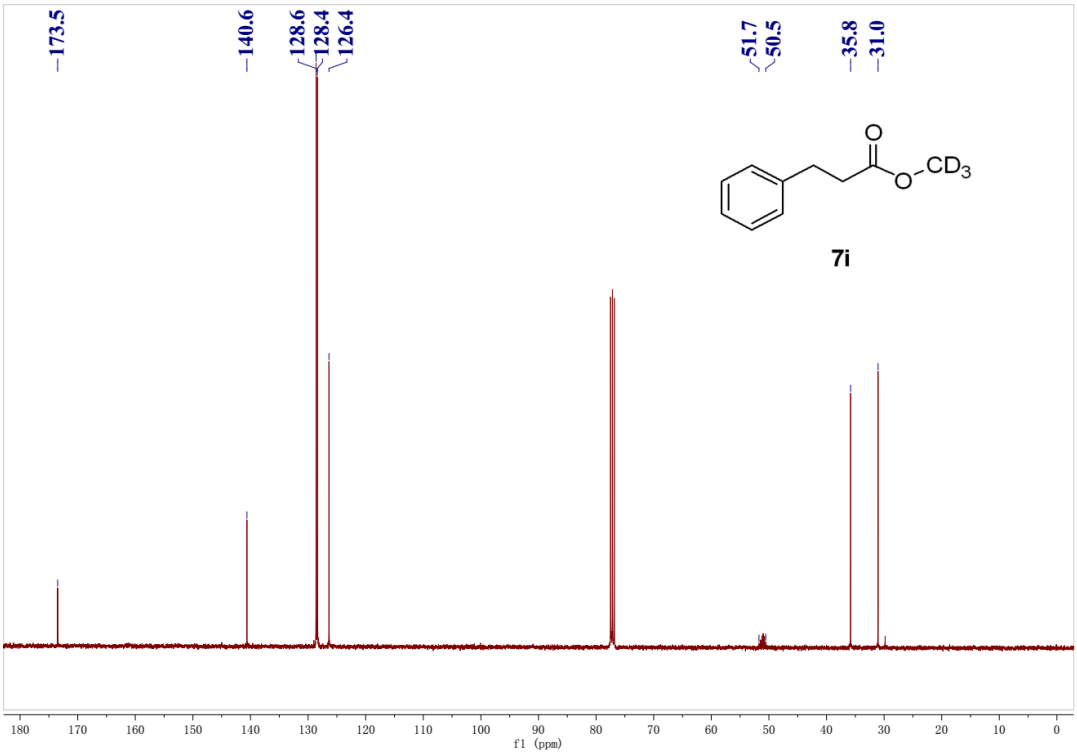

8.14
8.13
8.12
8.12
8.11
7.75
7.74
7.73
7.72
7.72
3.95
2.00
2.00
0.11
f1 (ppm)
NC
O
O
CD3
7g

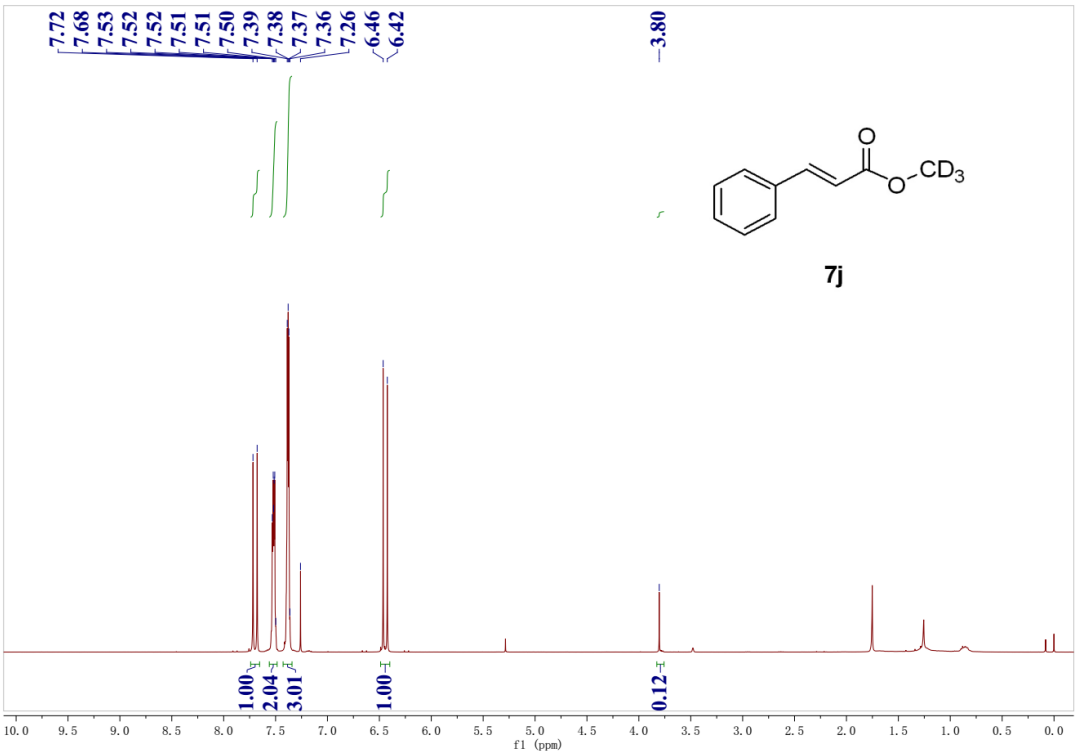

165.5
134.0
132.3
130.2
118.1
116.5
52.8
51.6
f1 (ppm)
NC
O
O
CD3
7g


7.91
7.90
7.89
7.88
7.74
7.74
7.72
7.72
7.69
7.69
7.67
7.67
7.65
7.65
7.64
7.64
7.62
7.62
7.61
7.60
3.91
O
O
CD3
NO2
7h
1.00
1.00
1.01
1.00
0.11
f1 (ppm)


166.0
148.3
133.0
131.9
129.9
127.6
124.0
53.4
52.2
O
O
CD3
NO2
7h
f1 (ppm)


7.32
7.31
7.30
7.29
7.28
7.23
7.22
7.21
7.20
3.68
2.98
2.97
2.94
2.67
2.64
2.63
O
O
CD3
7i
2.00
2.98
0.12
2.03
2.02
f1 (ppm)


173.5
140.6
128.6
128.4
126.4
51.7
50.5
35.8
31.0
O
O
CD3
7i
f1 (ppm)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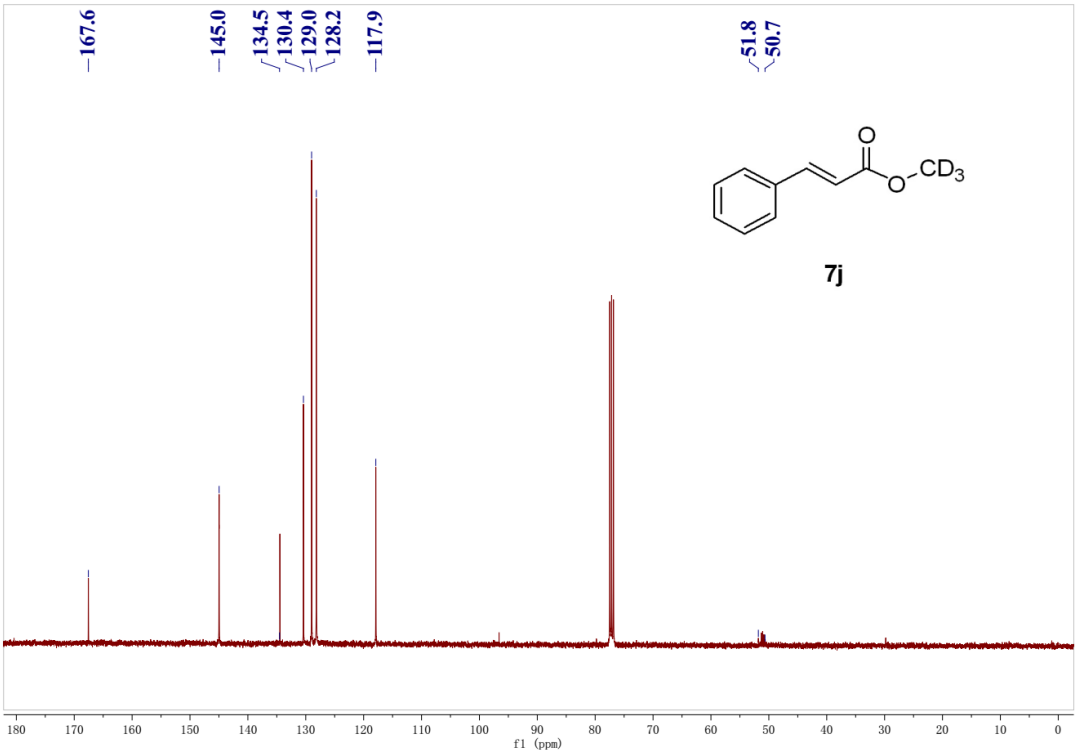
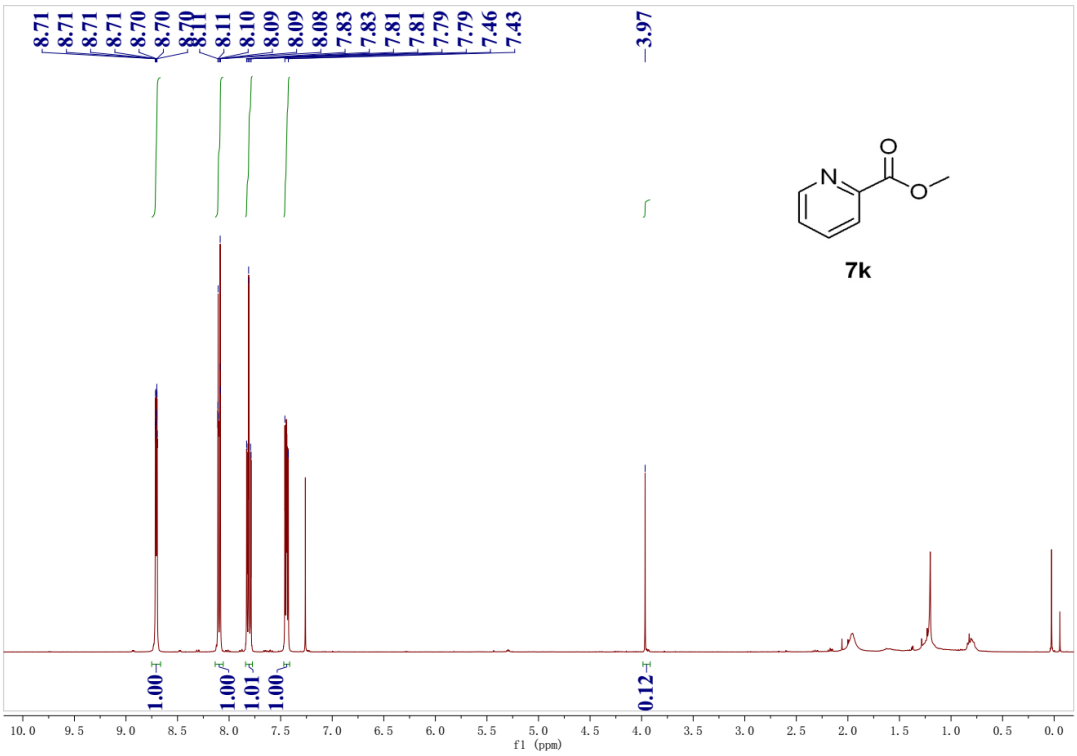
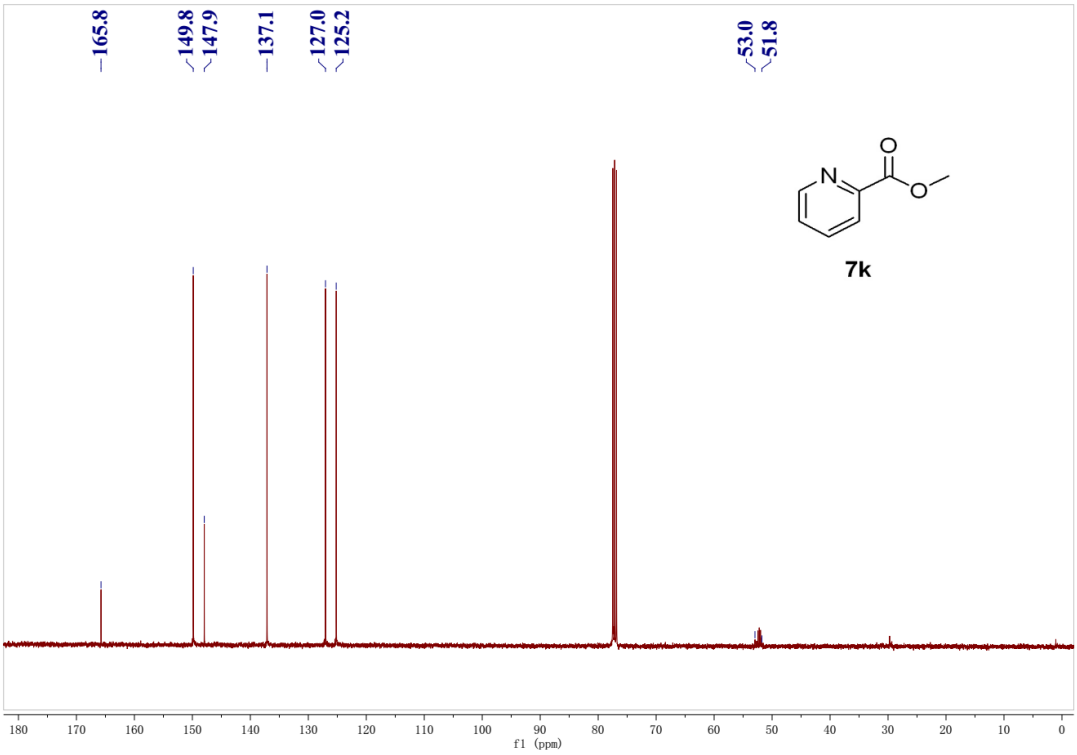
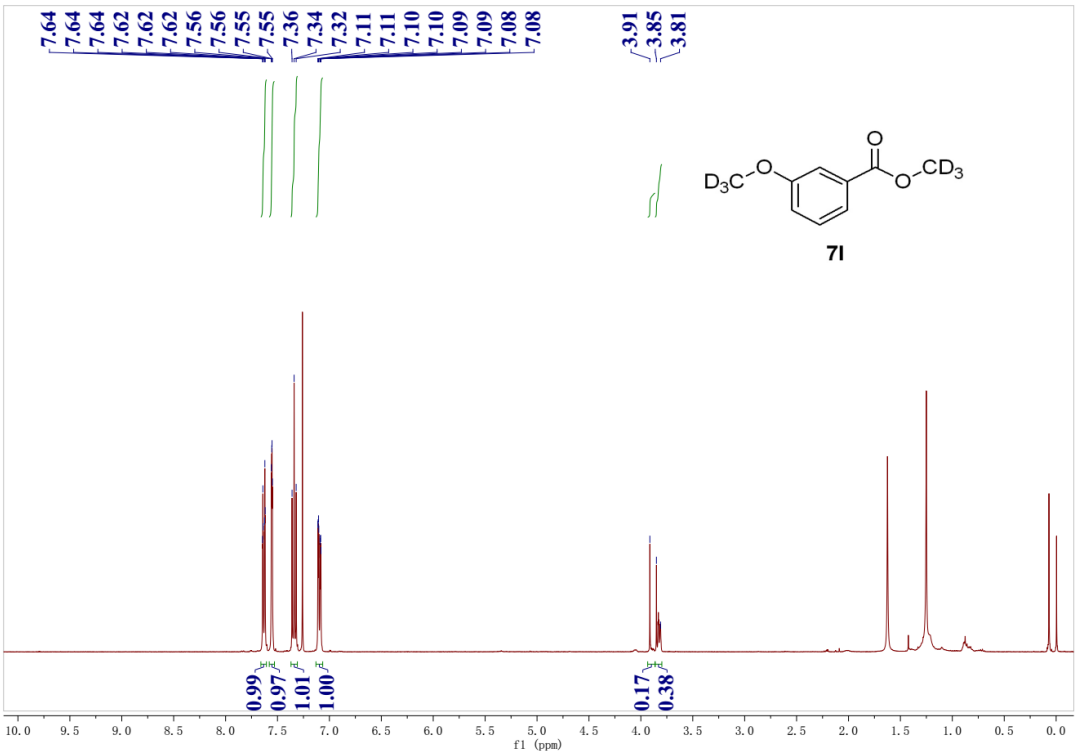
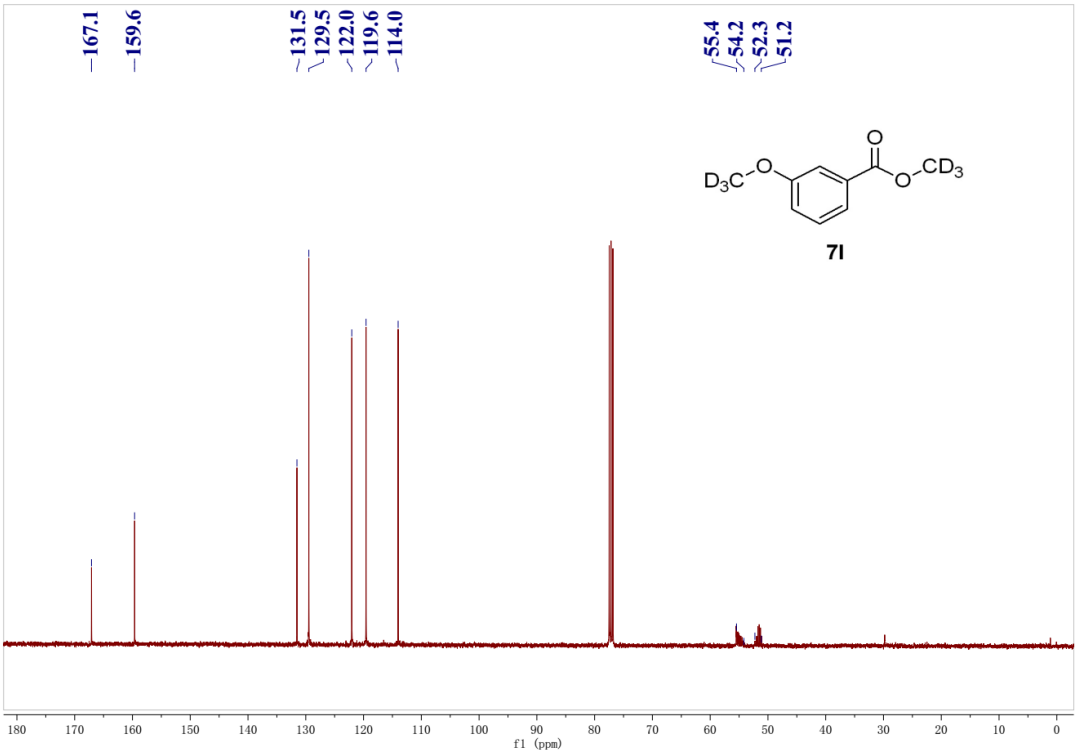
7.52
7.52
7.51
7.51
7.50
7.39
7.38
7.37
7.36
7.26
6.46
6.42
3.80
O
O
CD3
7j
1.00
2.04
3.01
1.00
0.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

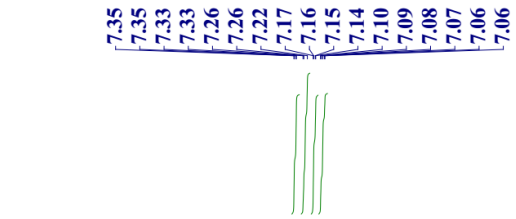

167.6
145.0
134.5
130.4
129.0
128.2
117.9
51.8
50.7
O
O
CD3
7j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

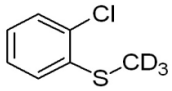

8.71
8.71
8.71
8.71
8.70
8.70
8.70
8.11
8.11
8.10
8.09
8.09
8.08
7.83
7.83
7.81
7.81
7.79
7.79
7.46
7.43
3.97
1.00
1.00
1.01
1.00
0.12
f1 (ppm)
7k


165.8
149.8
147.9
137.1
127.0
125.2
53.0
51.8
f1 (ppm)
7k

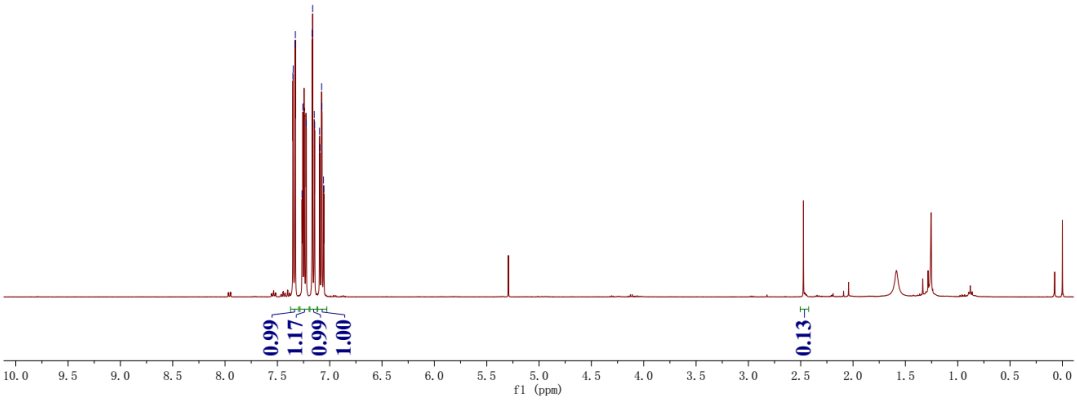

7.64
7.64
7.64
7.62
7.62
7.62
7.56
7.56
7.55
7.55
7.36
7.34
7.32
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
3.91
3.85
3.81
D3C
O
O
CD3
7l
0.99
0.97
1.01
1.00
0.17
0.38
f1 (ppm)

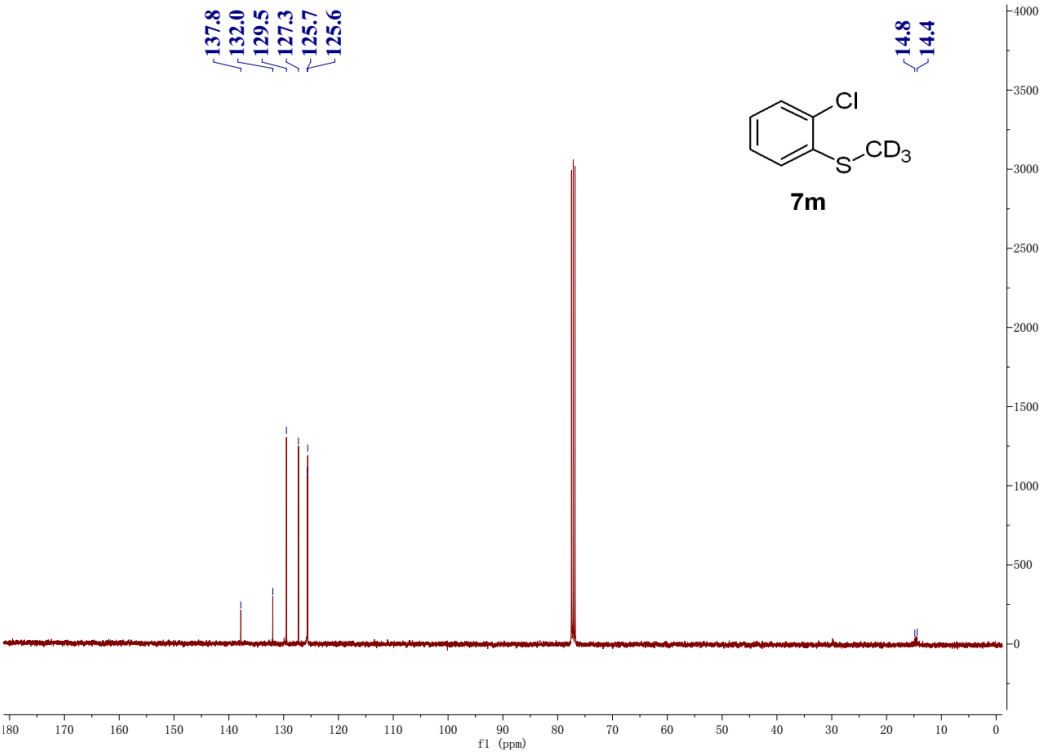

167.1
159.6
131.5
129.5
122.0
119.6
114.0
55.4
54.2
52.3
51.2
D3C
O
O
CD3
7l
f1 (ppm)

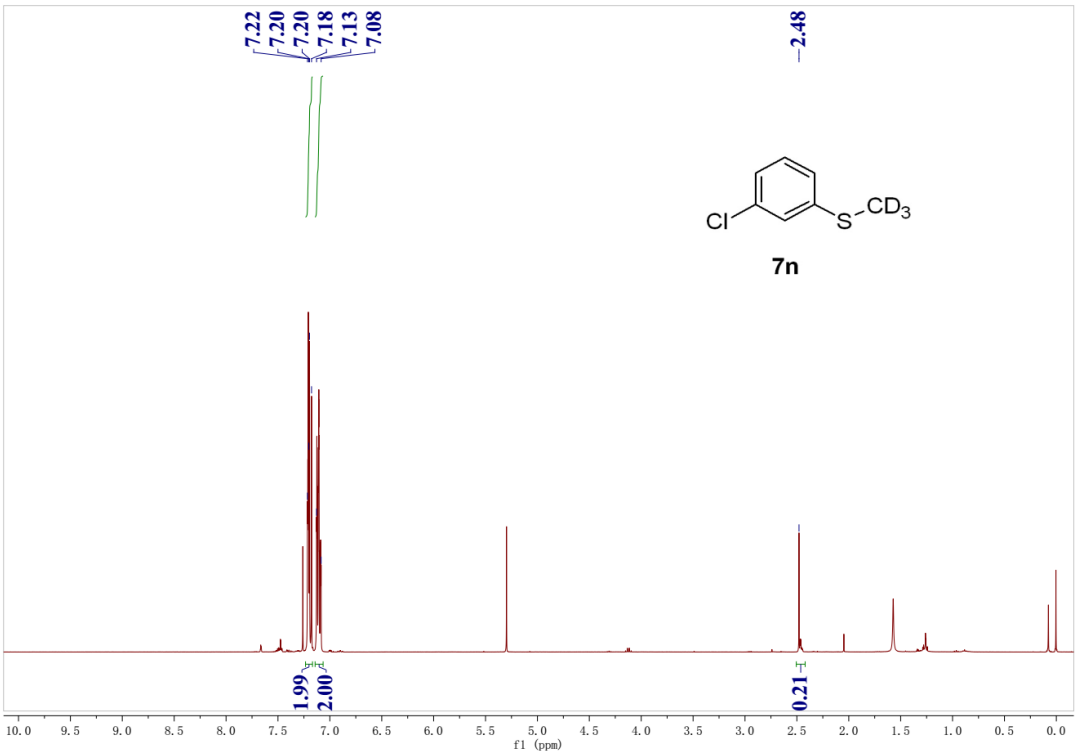

7.35
7.35
7.33
7.33
7.26
7.26
7.22
7.17
7.16
7.15
7.14
7.10
7.09
7.08
7.07
7.06
7.06

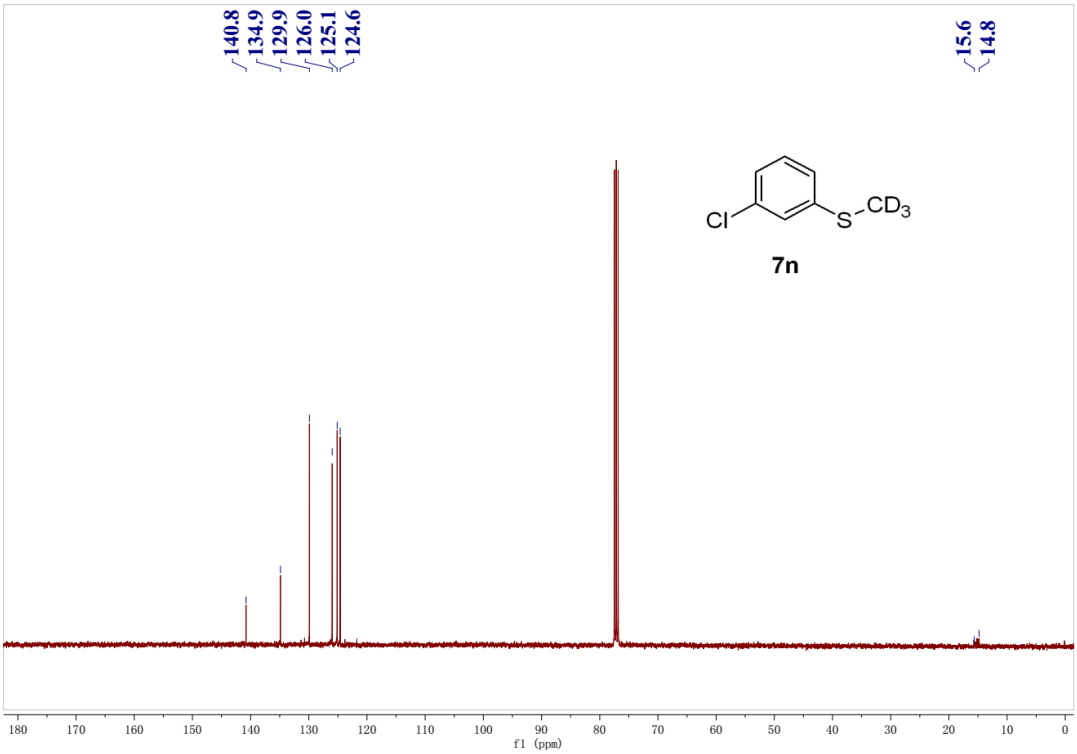

Cl
S
CD3

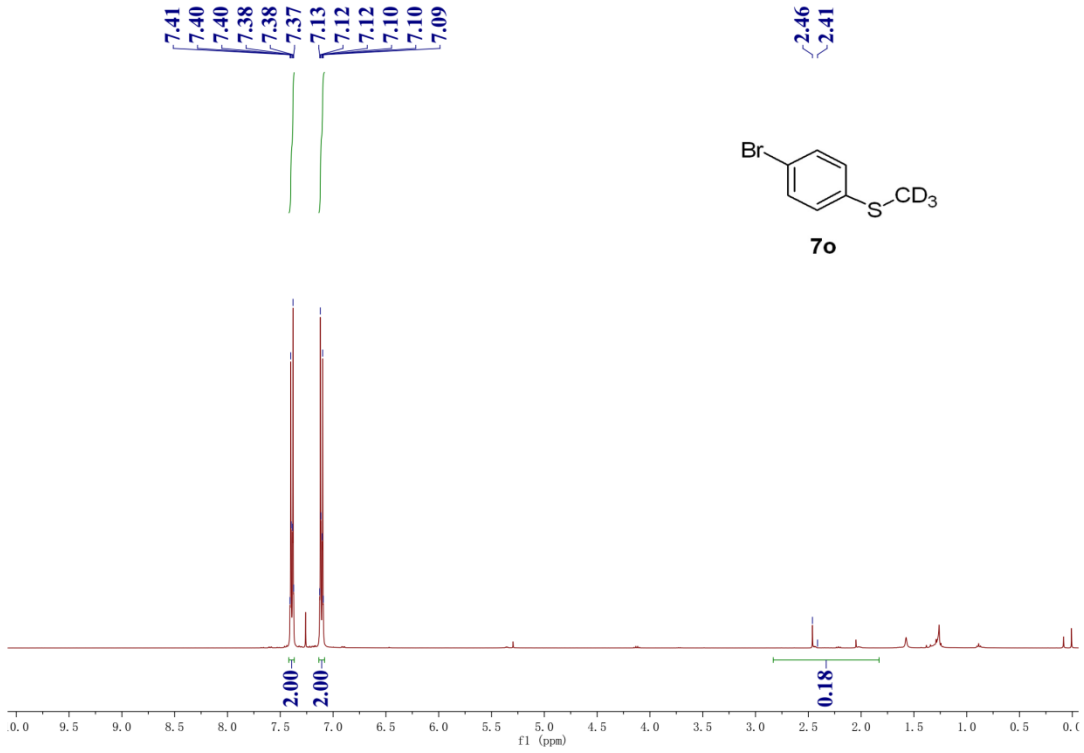
7m

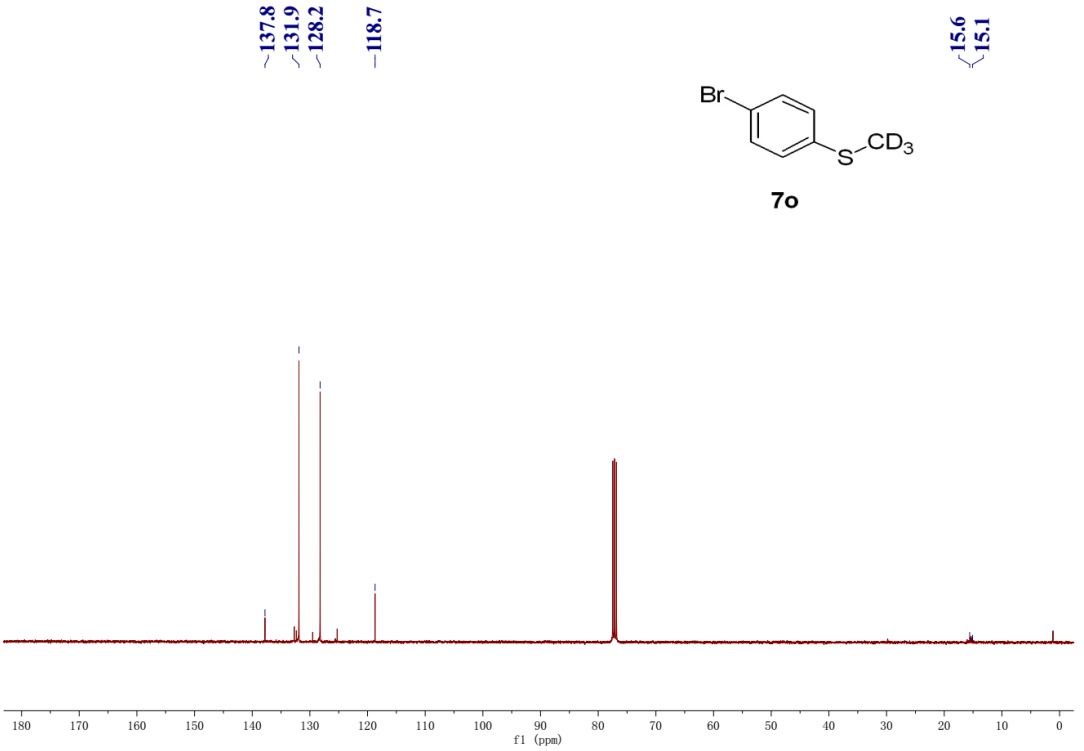

0.99
1.17
0.99
1.00
0.13
f1 (ppm)

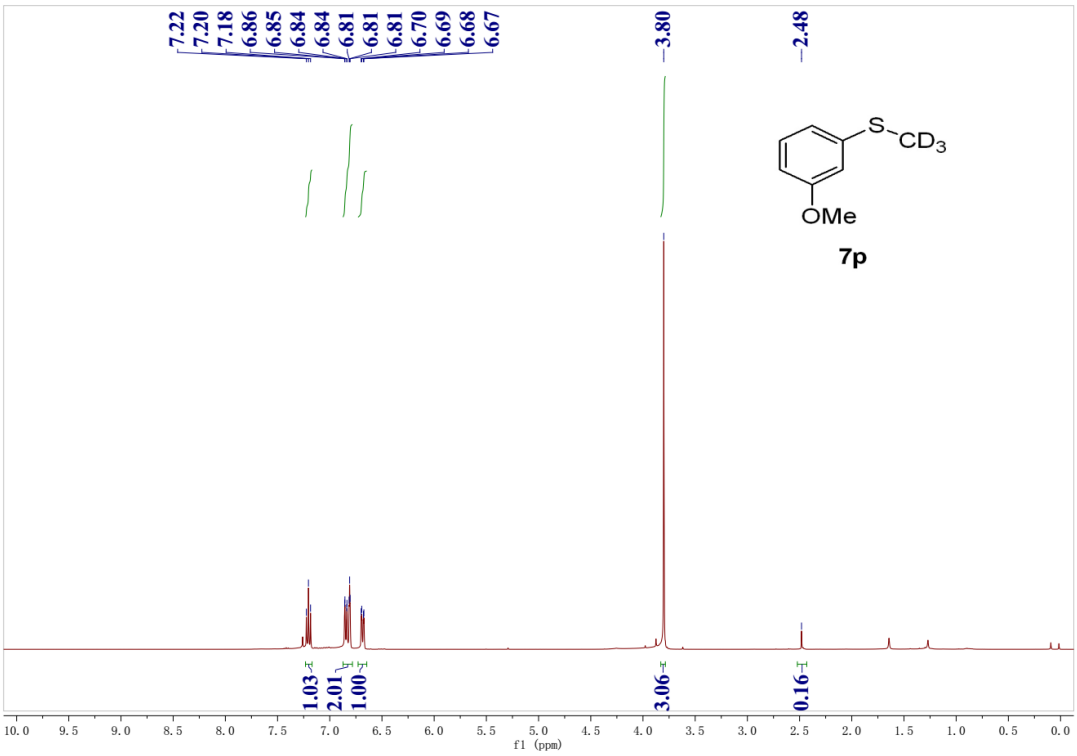

137.8
132.0
129.5
127.3
125.7
125.6
14.8
14.4
Cl
S
CD3
7m
f1 (ppm)

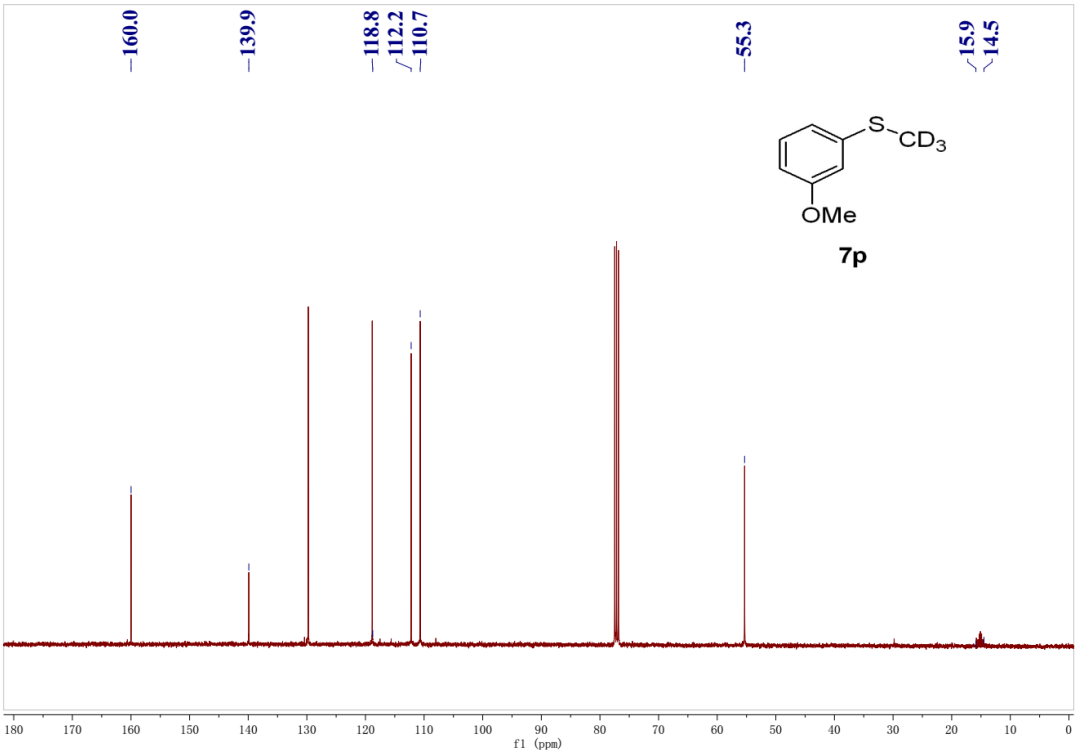

7.22
7.20
7.20
7.18
7.13
7.08
2.48
Cl
S
CD3
7n
1.99
2.00
0.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

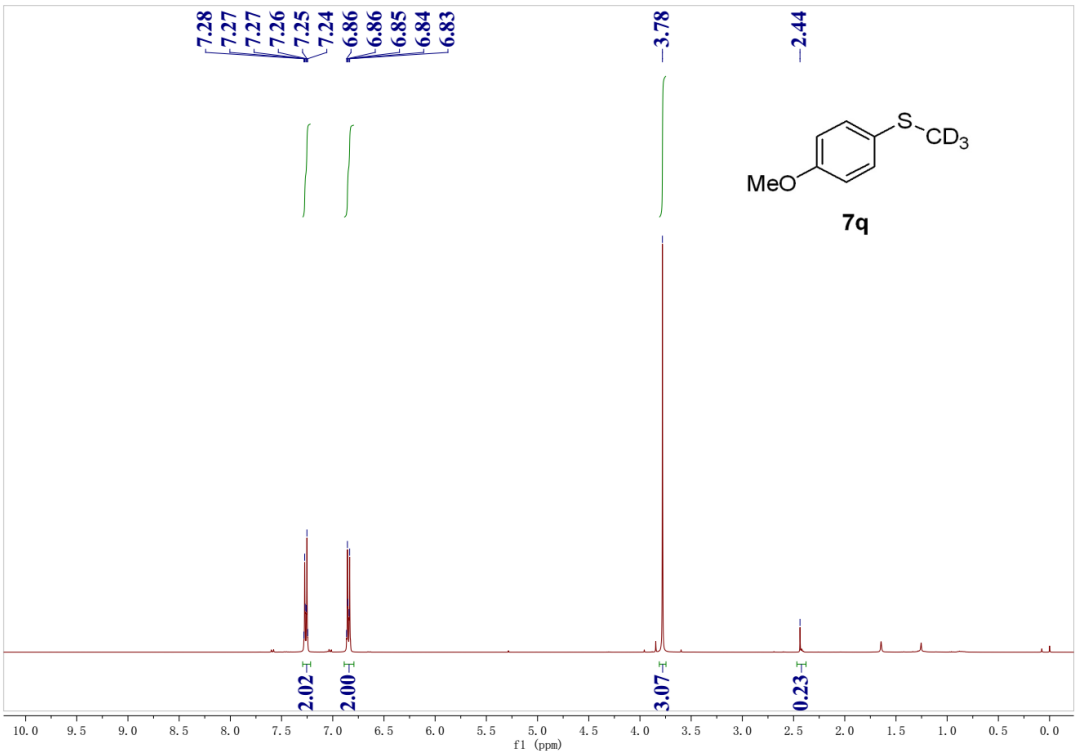

140.8
134.9
129.9
126.0
125.1
124.6
15.6
14.8
Cl
S
CD3
7n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

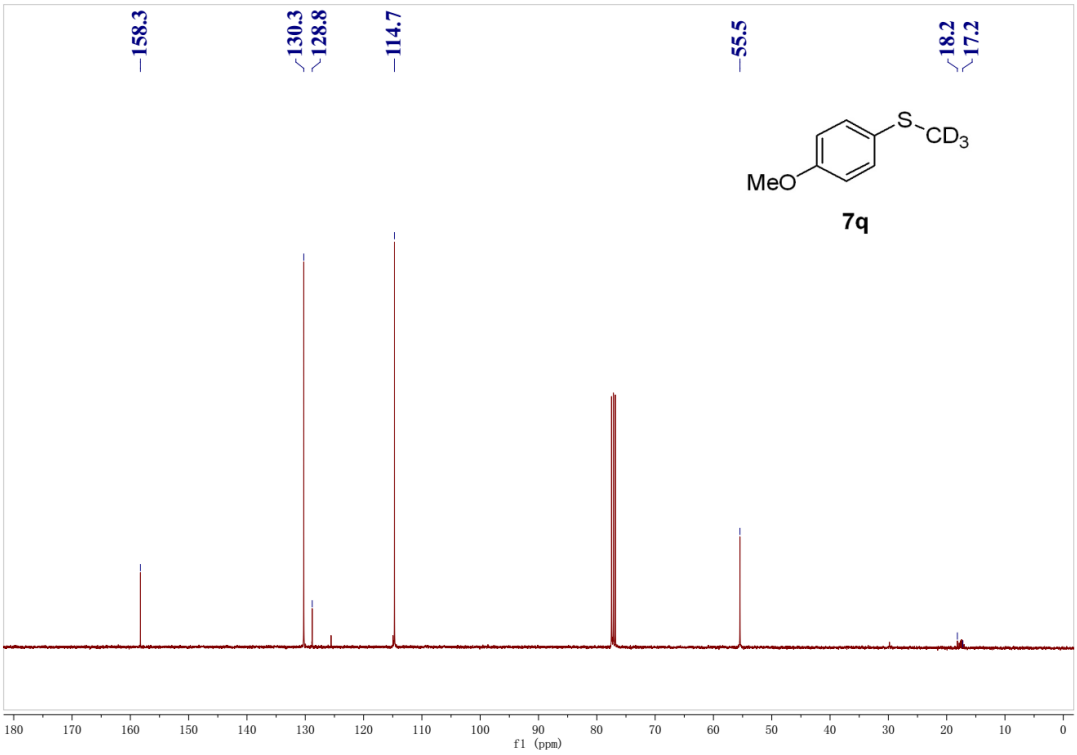

7.41
7.40
7.40
7.38
7.38
7.37
7.13
7.12
7.12
7.10
7.10
7.09
2.46
2.41
Br
S
CD3
7o
2.00
2.00
0.18
f1 (ppm)

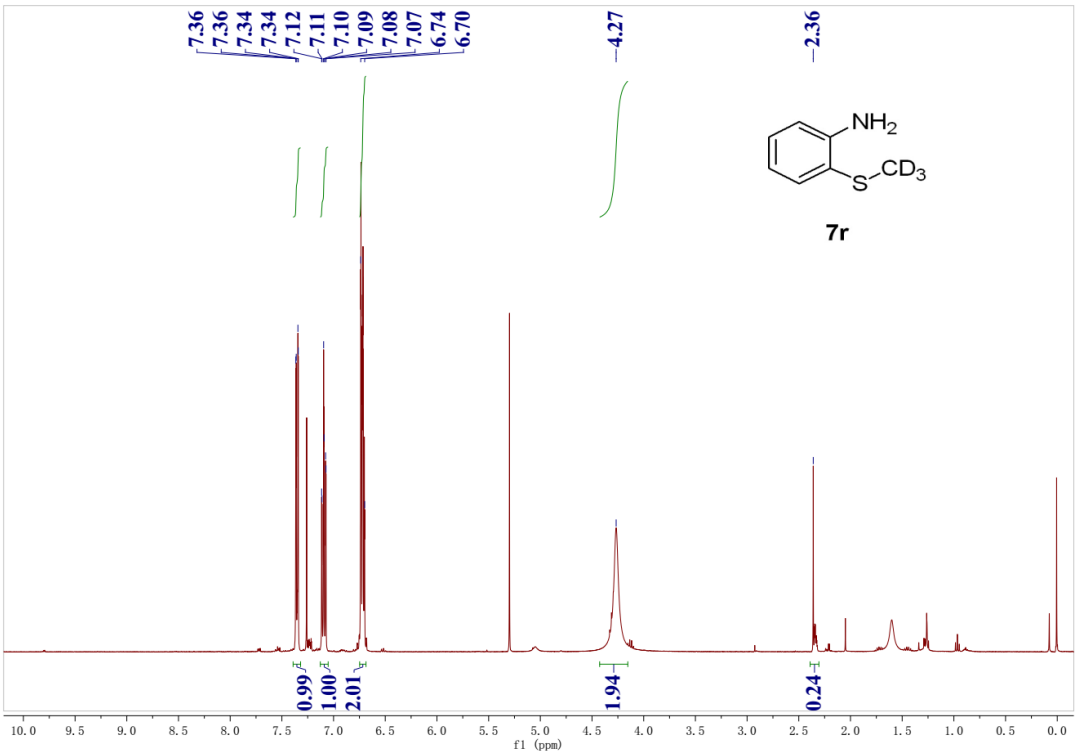

137.8
131.9
128.2
118.7
15.6
15.1
Br
S
CD3
7o
f1 (ppm)

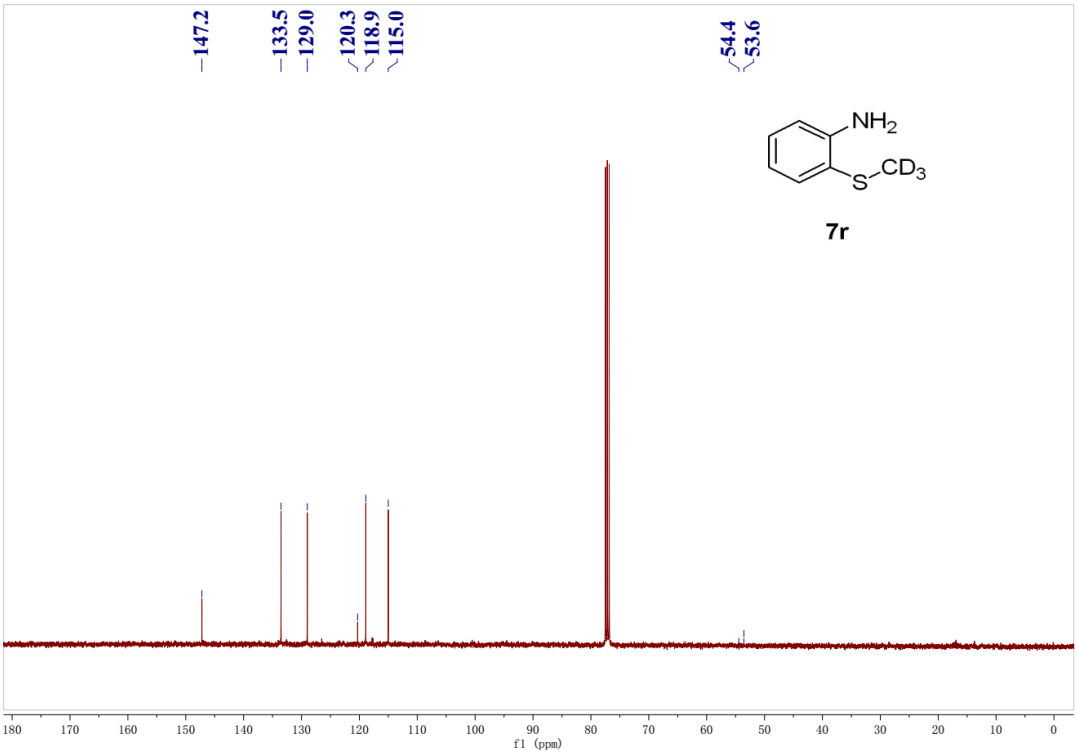

7.22
7.20
7.18
6.86
6.85
6.84
6.84
6.81
6.81
6.81
6.70
6.69
6.68
6.67
3.80
2.48
S
CD3
OMe
7p
1.03
2.01
1.00
3.06
0.16
f1 (ppm)

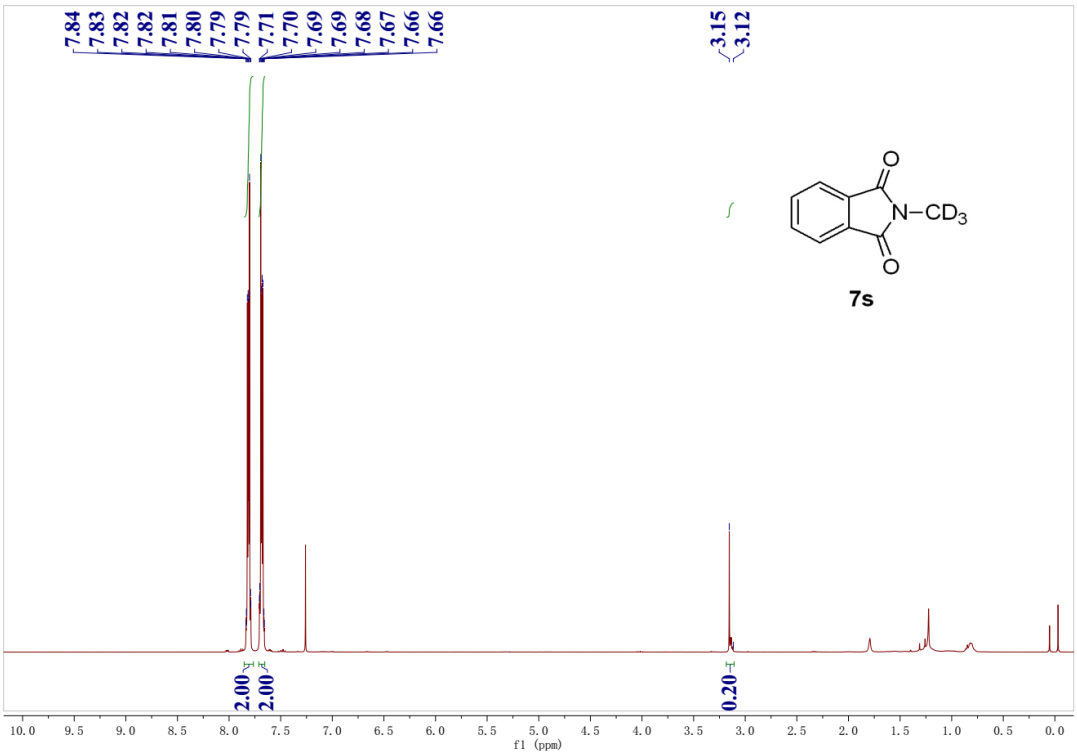

160.0
139.9
118.8
112.2
110.7
55.3
15.9
14.5
S
CD3
OMe
7p
f1 (ppm)

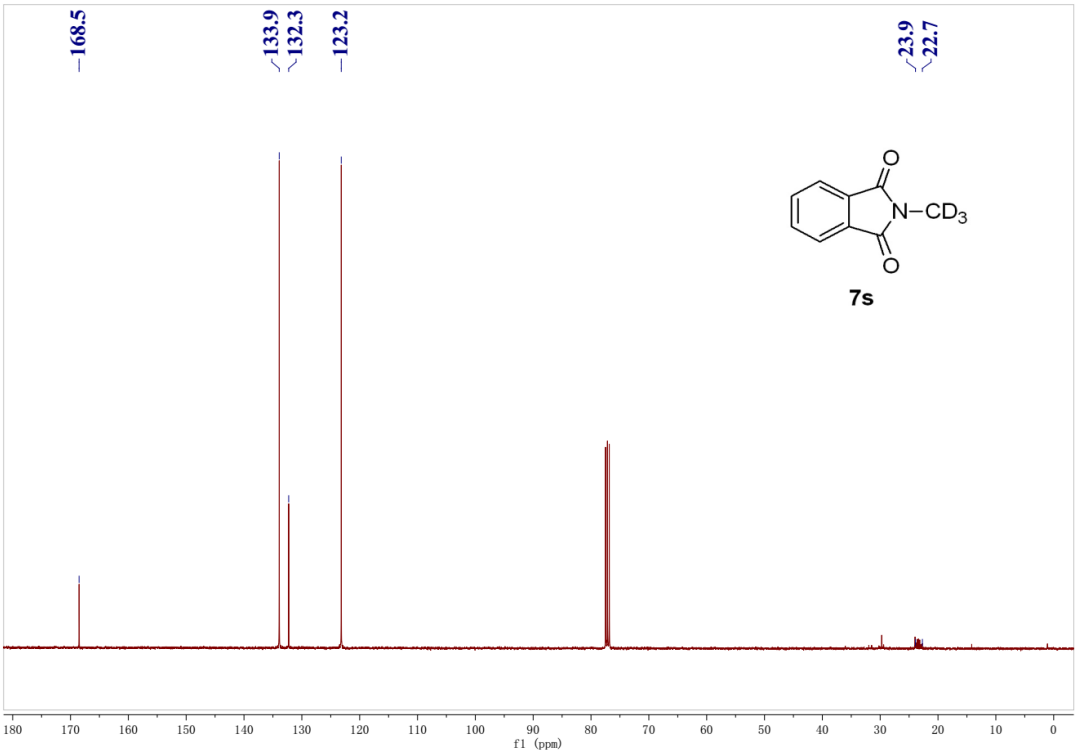

7.28
7.27
7.27
7.26
7.25
7.24
6.86
6.86
6.85
6.84
6.83
3.78
2.44
S
CD3
MeO
7q
2.02
2.00
3.07
0.23
f1 (ppm)

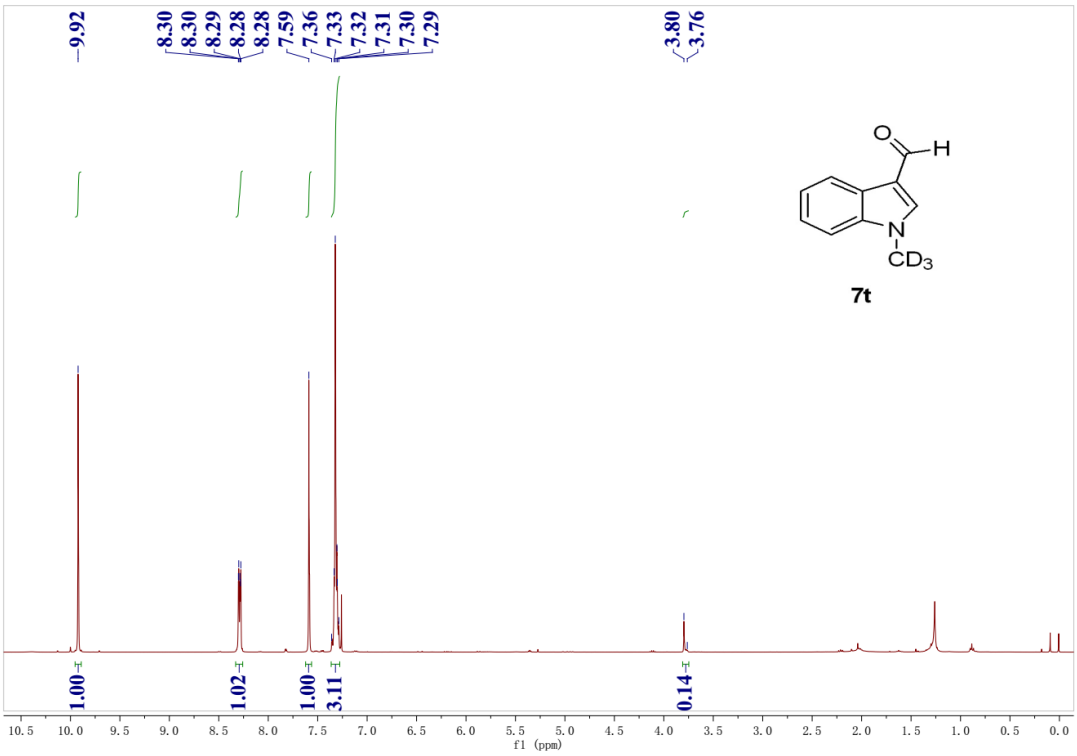

158.3
130.3
128.8
114.7
55.5
18.2
17.2
S
CD3
MeO
7q
f1 (ppm)

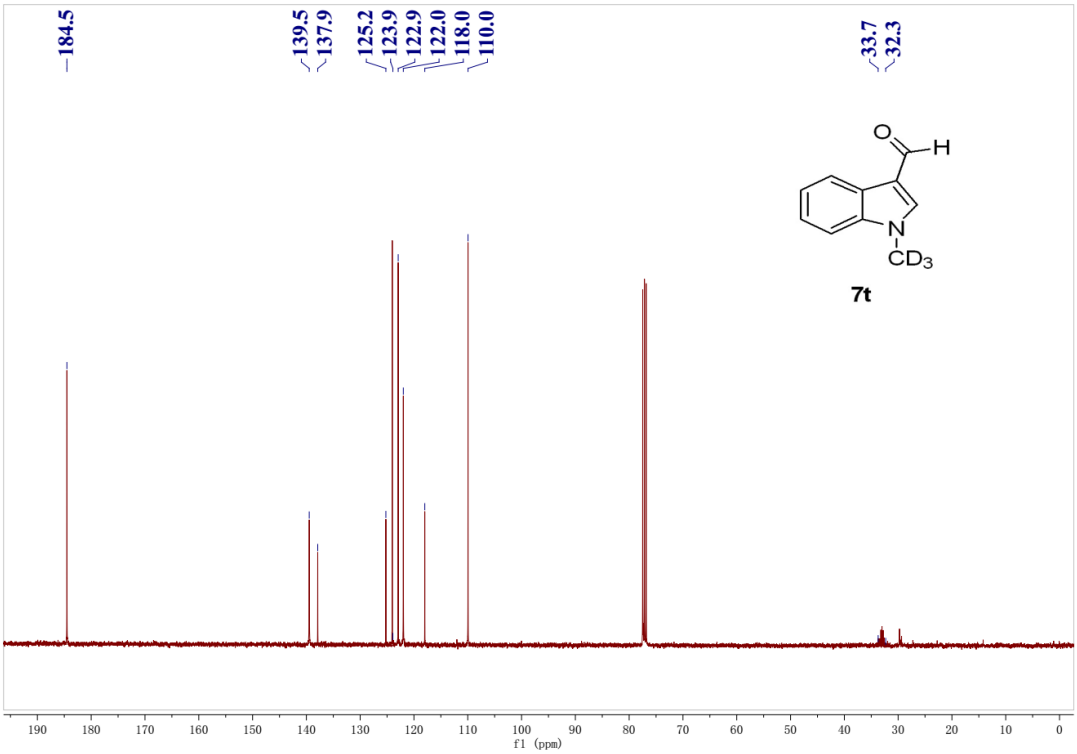

7.36
7.36
7.34
7.34
7.12
7.11
7.10
7.09
7.08
7.07
6.74
6.70
4.27
2.36
NH2
S
CD3
7r
0.99
1.00
2.01
1.94
0.24
f1 (ppm)

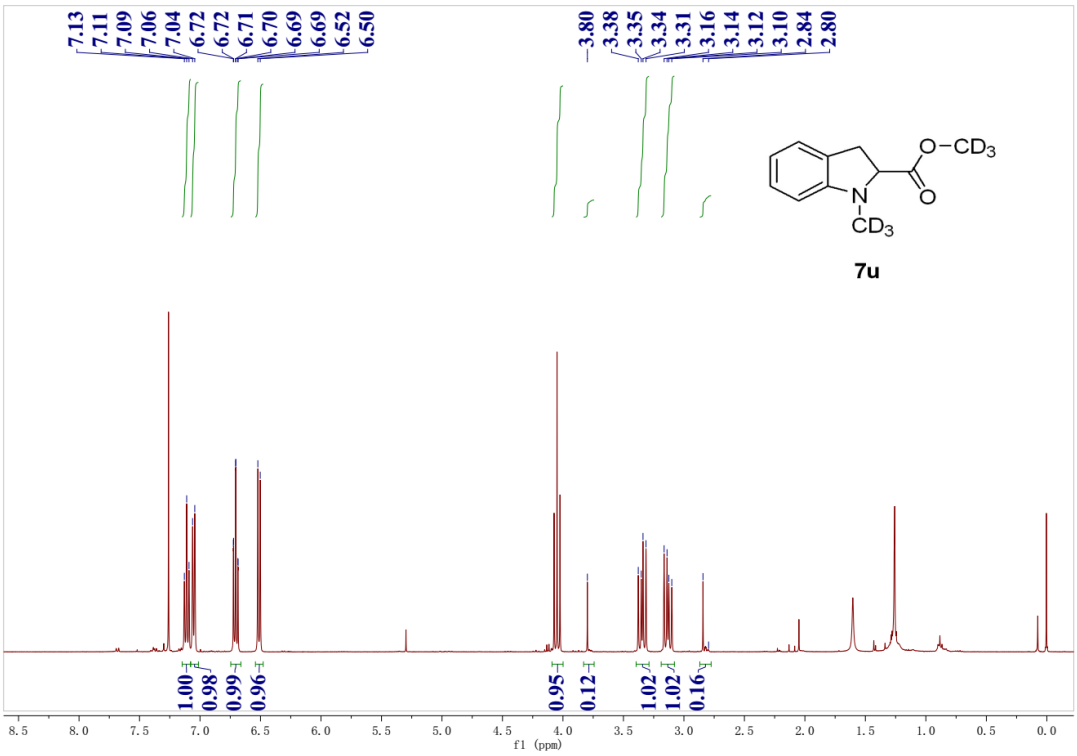

147.2
133.5
129.0
120.3
118.9
115.0
54.4
53.6
NH2
S
CD3
7r
f1 (ppm)

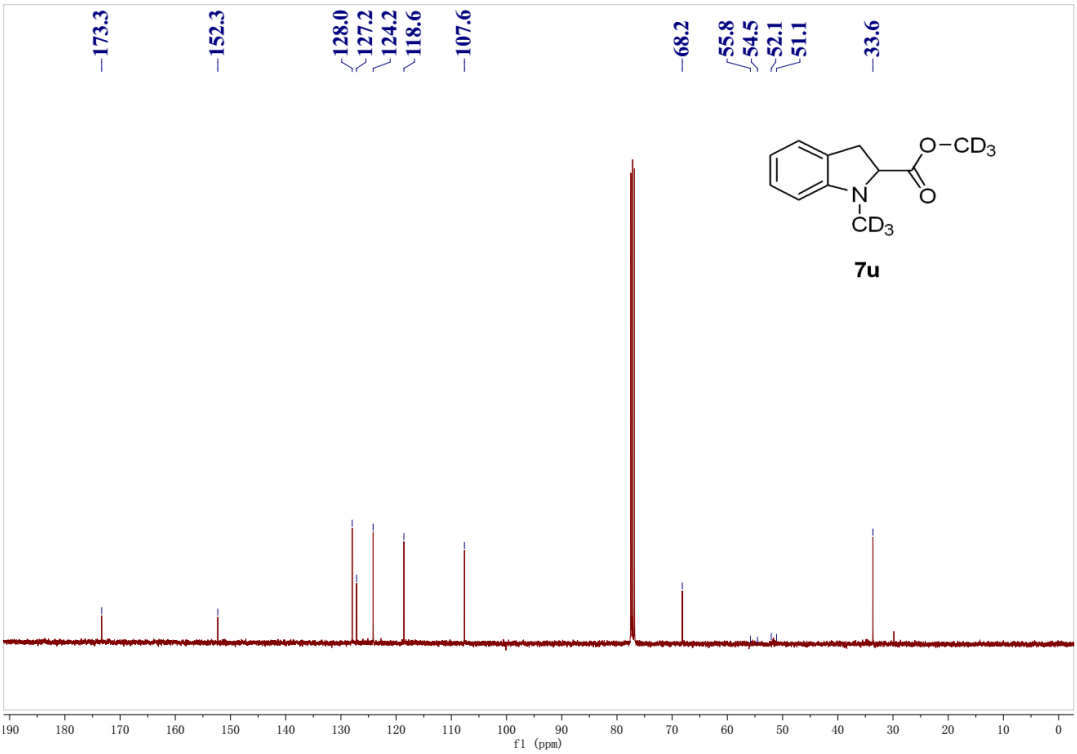

7.84
7.83
7.82
7.82
7.81
7.80
7.79
7.79
7.71
7.70
7.69
7.69
7.68
7.67
7.66
7.66
3.15
3.12
N–CD3
7s
2.00
2.00
0.20
f1 (ppm)

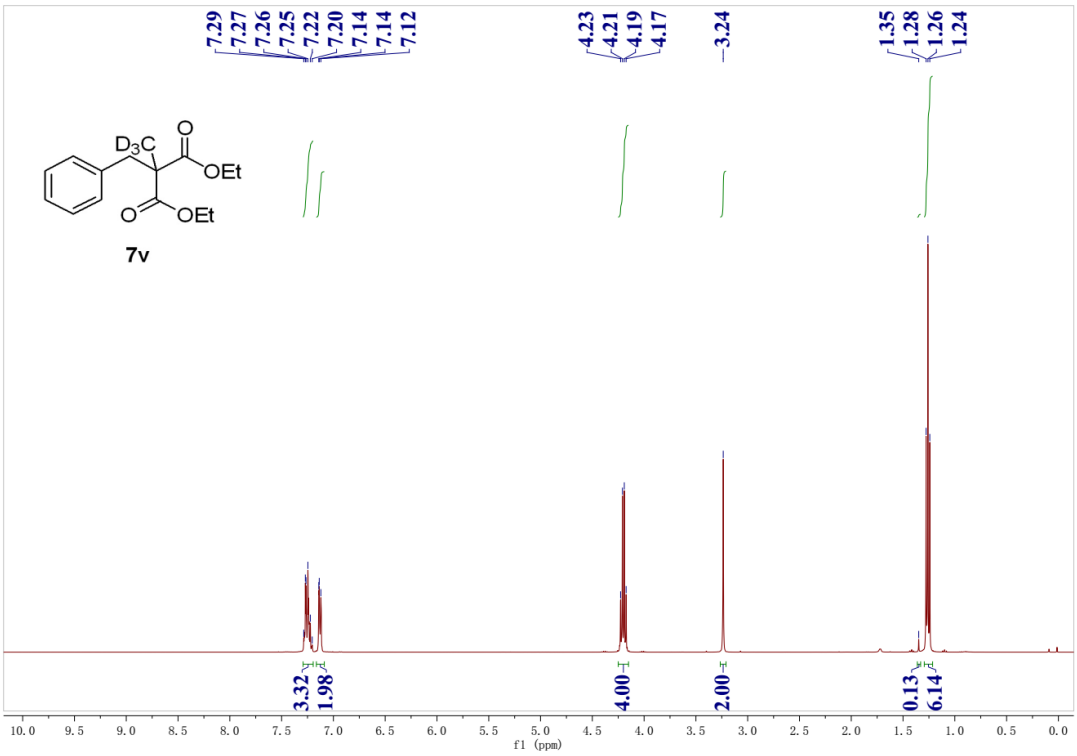

168.5
133.9
132.3
123.2
23.9
22.7
N–CD3
7s
f1 (ppm)

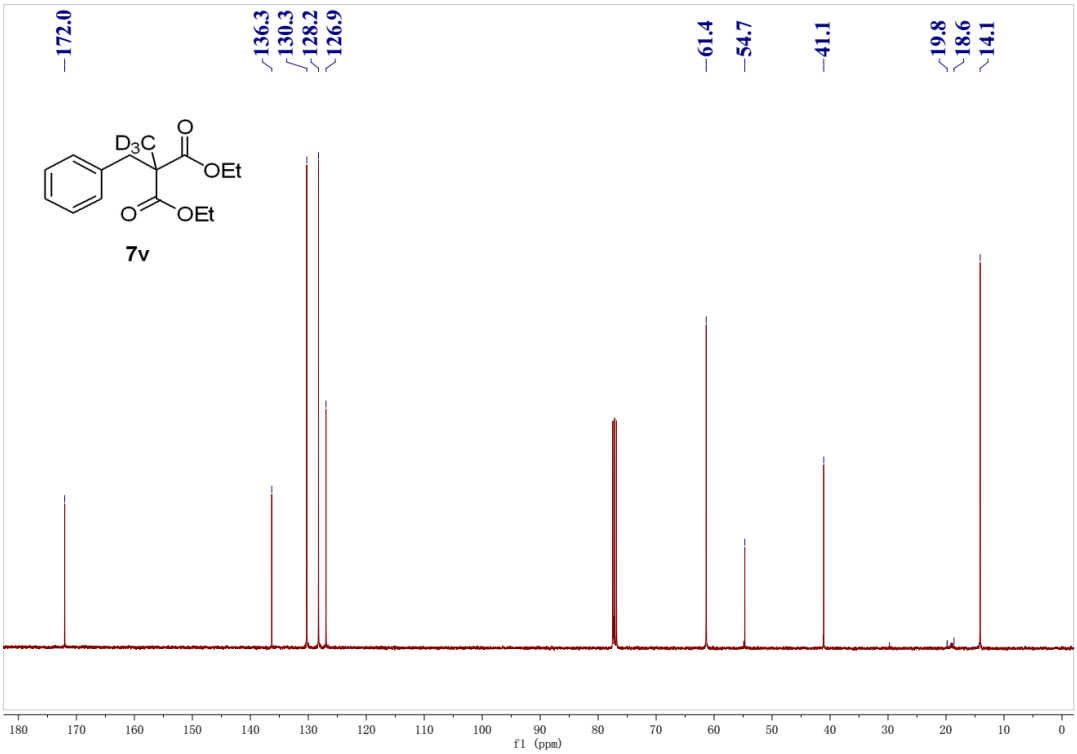

9.92
8.30
8.30
8.29
8.28
8.28
7.59
7.36
7.33
7.32
7.31
7.30
7.29
3.80
3.76
1.00
1.02
1.00
3.11
0.14
f1 (ppm)
7t

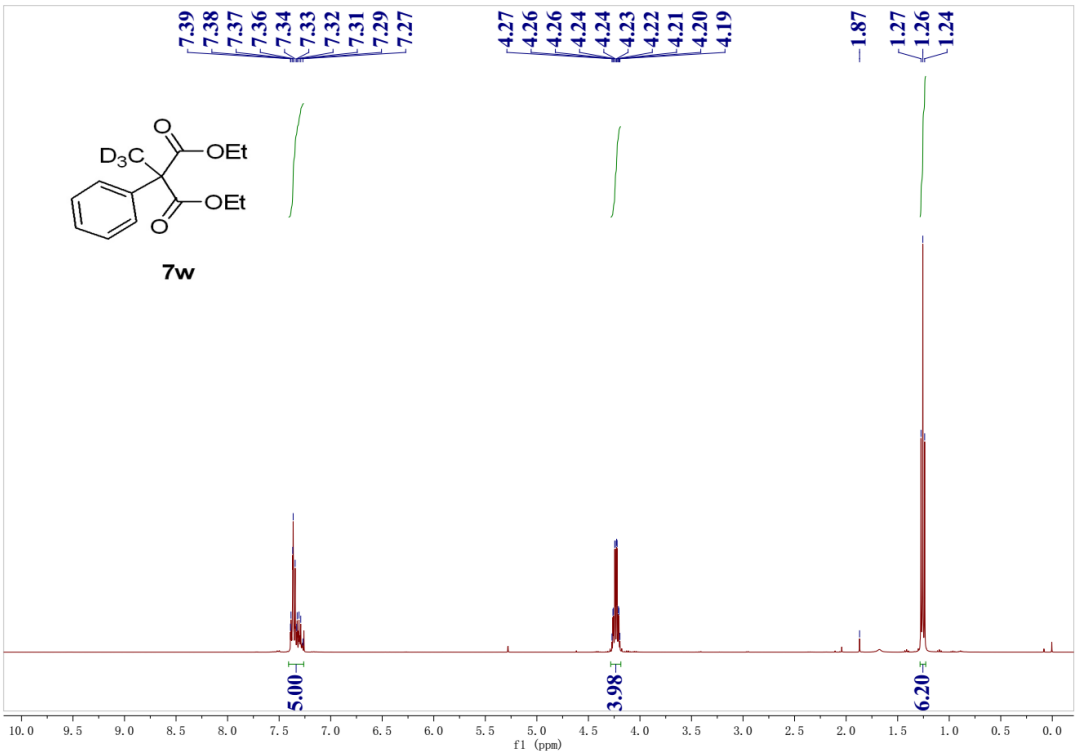

184.5
139.5
137.9
125.2
123.9
122.9
122.0
118.0
110.0
33.7
32.3
f1 (ppm)
7t

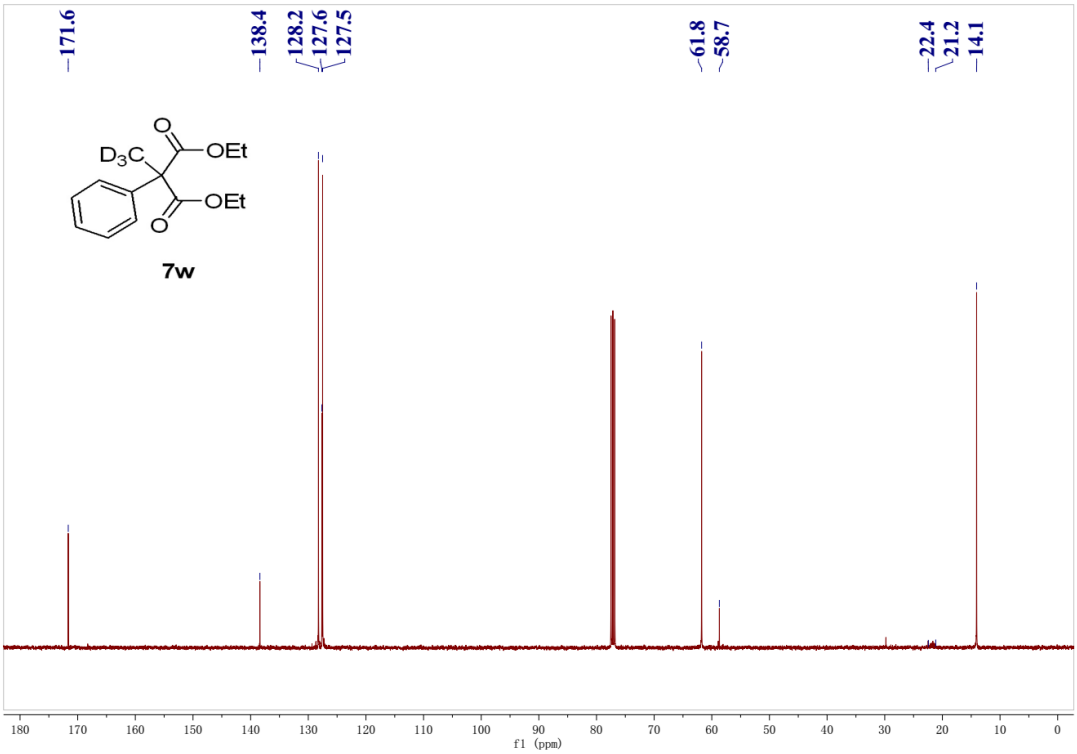

7.13
7.11
7.09
7.06
7.04
6.72
6.72
6.71
6.70
6.69
6.69
6.52
6.50
3.80
3.38
3.35
3.34
3.31
3.16
3.14
3.12
3.10
2.84
2.80
O−CD3
O
N
CD3
7u
1.00
0.98
0.99
0.96
0.95
0.12
1.02
1.02
0.16
f1 (ppm)

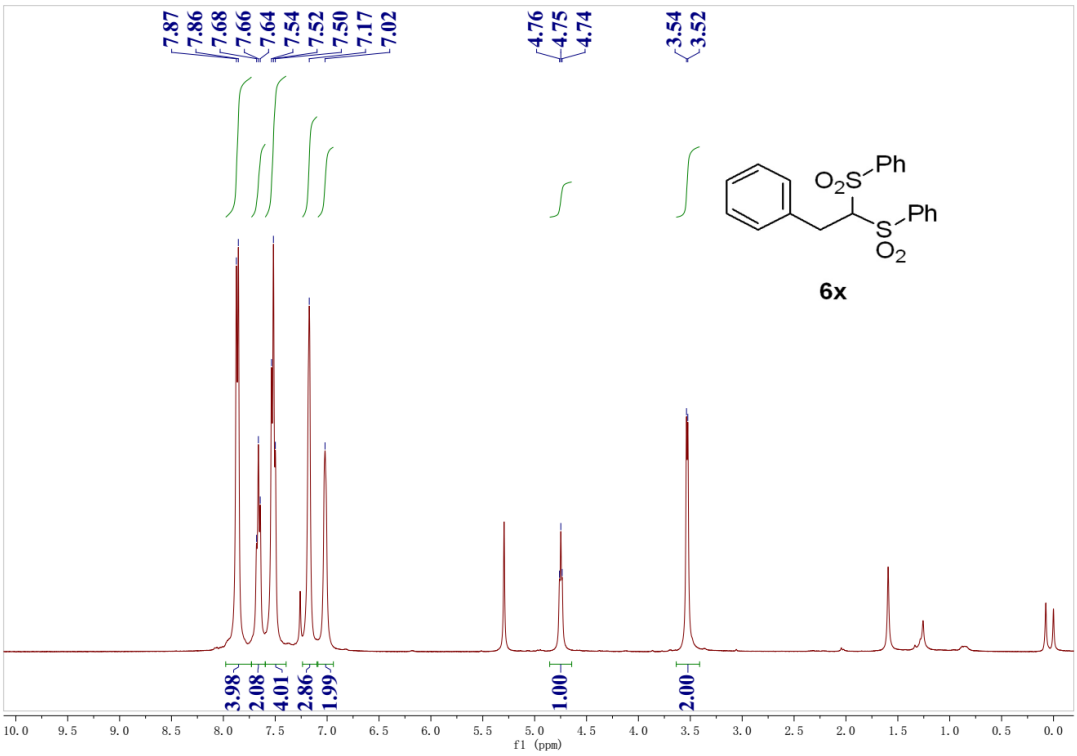

173.3
152.3
128.0
127.2
124.2
118.6
107.6
68.2
55.8
54.5
52.1
51.1
33.6
O−CD3
O
N
CD3
7u
f1 (ppm)

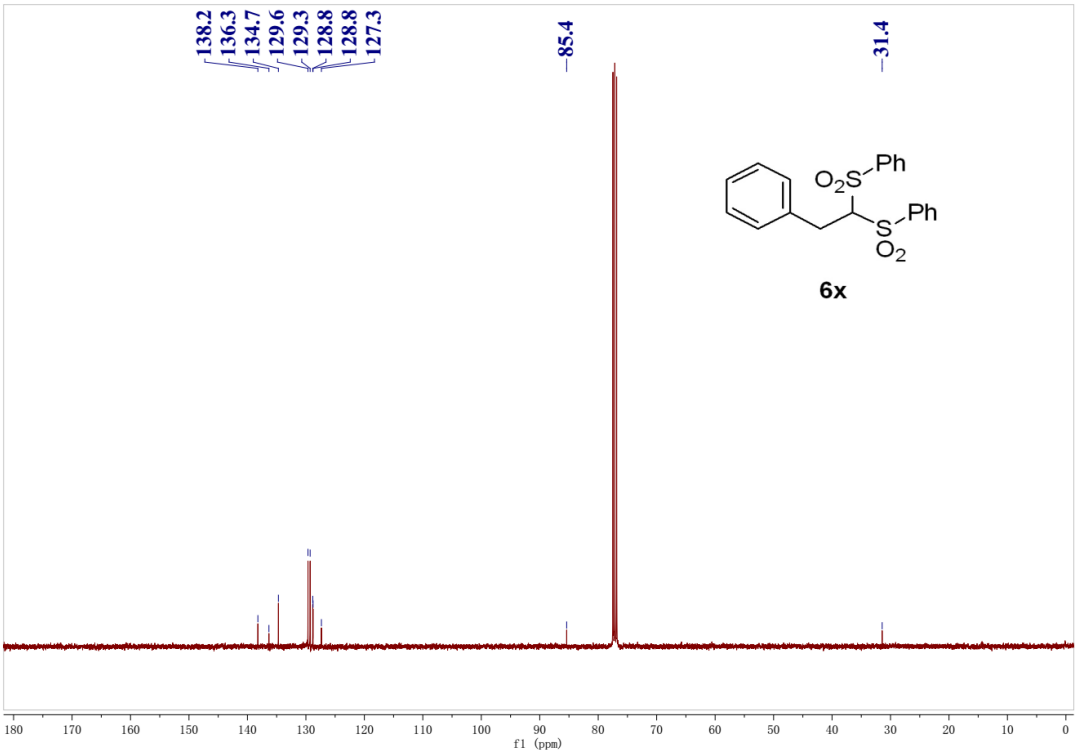

7.29
7.27
7.26
7.25
7.22
7.20
7.14
7.14
7.12
4.23
4.21
4.19
4.17
3.24
1.35
1.28
1.26
1.24
D3C
O
OEt
O
OEt
7v
3.32
1.98
4.00
2.00
0.13
6.14
f1 (ppm)

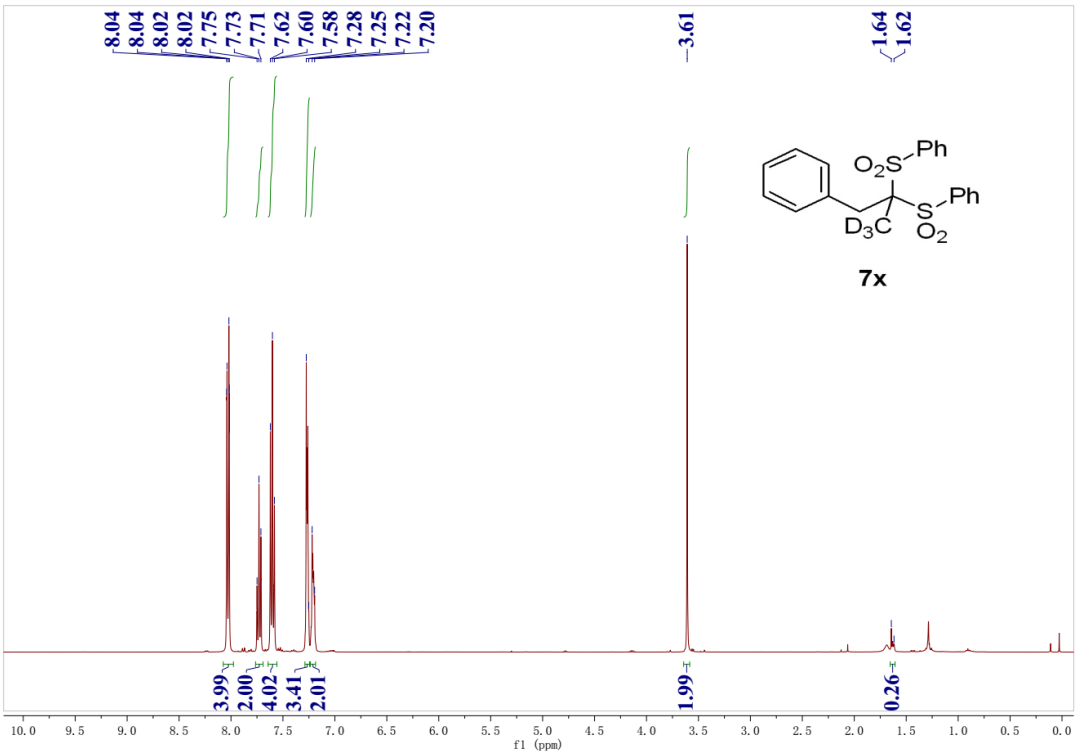

172.0
136.3
130.3
128.2
126.9
61.4
54.7
41.1
19.8
18.6
14.1
D3C
O
OEt
O
OEt
7v
f1 (ppm)

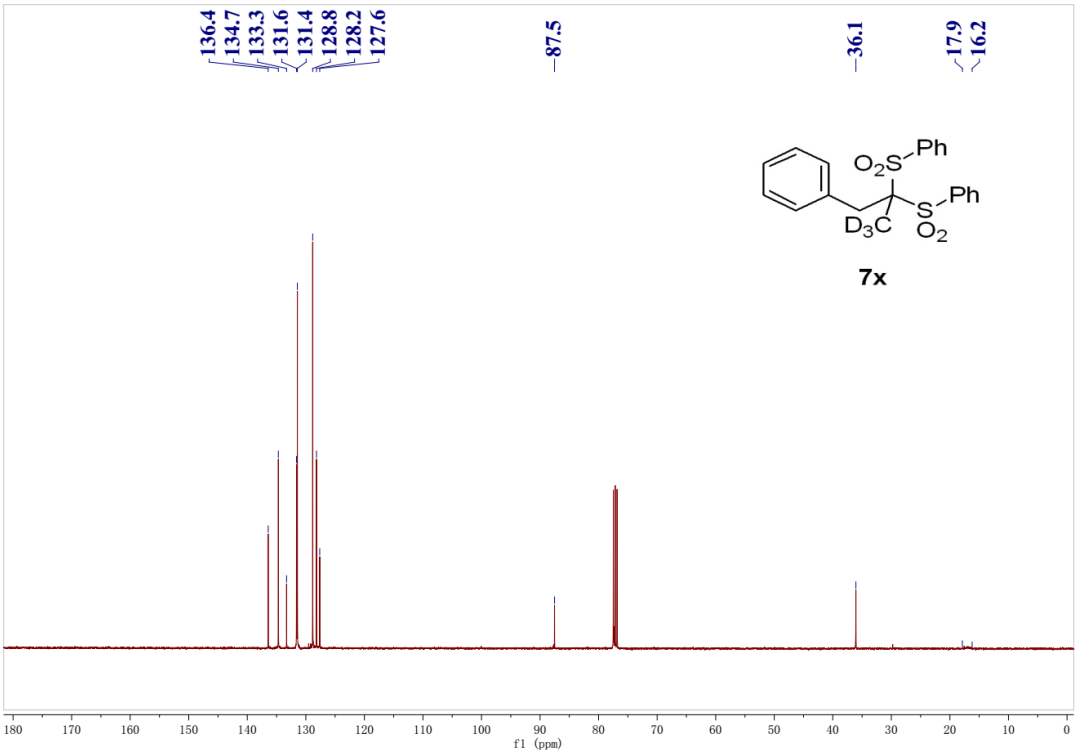

7.39
7.38
7.37
7.36
7.34
7.33
7.32
7.31
7.29
7.27
4.27
4.26
4.26
4.24
4.24
4.23
4.22
4.21
4.20
4.19
1.87
1.27
1.26
1.24
D3C
OEt
OEt
O
O
7w
5.00
3.98
6.20
f1 (ppm)

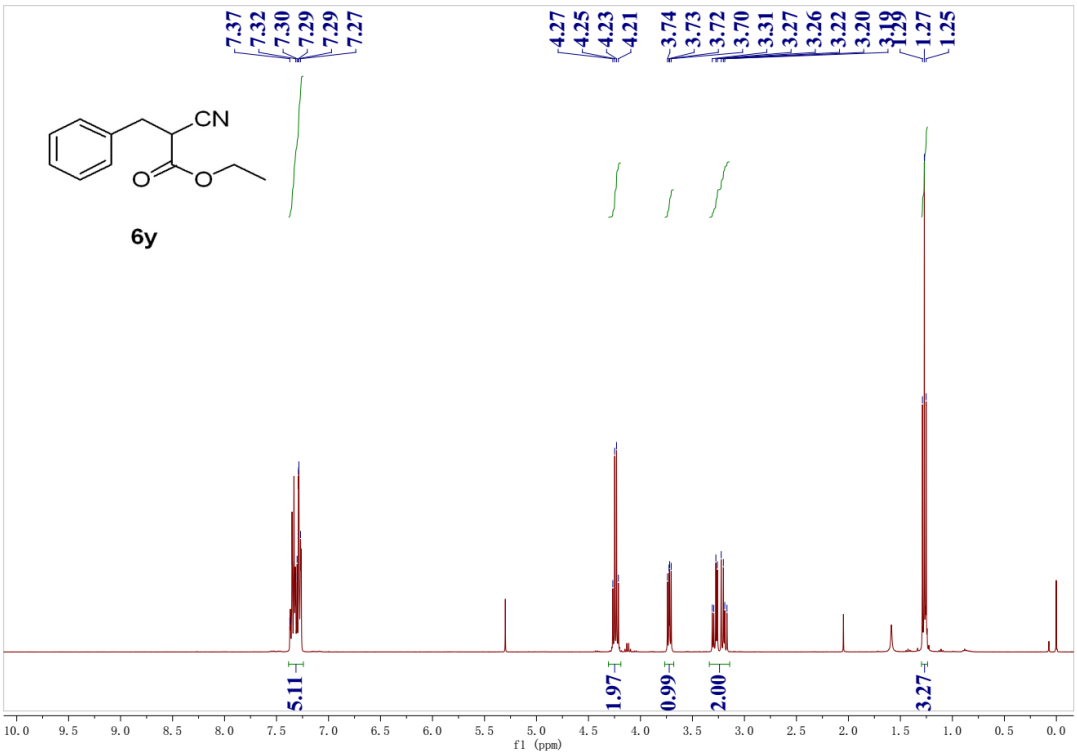

171.6
138.4
128.2
127.6
127.5
61.8
58.7
22.4
21.2
14.1
D3C
OEt
OEt
O
O
7w
f1 (ppm)

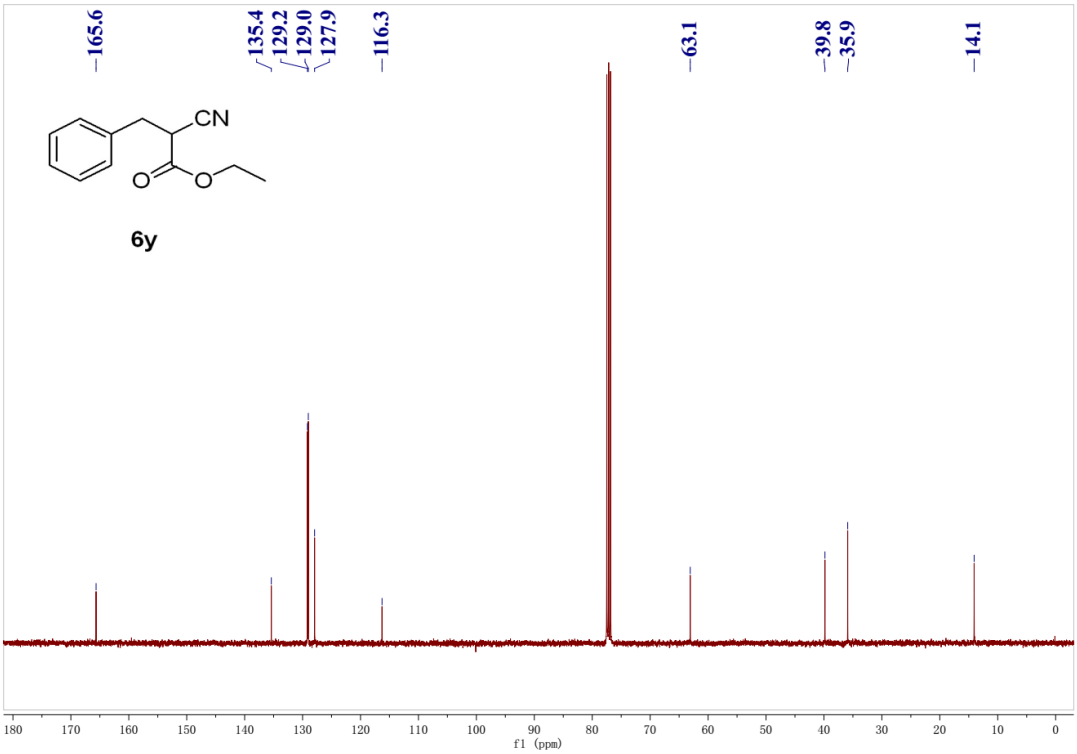

7.87
7.86
7.68
7.66
7.64
7.54
7.52
7.50
7.17
7.02
4.76
4.75
4.74
3.54
3.52
Ph
O2S
Ph
S
O2
6x
3.98
2.08
4.01
2.86
1.99
1.00
2.00
f1 (ppm)

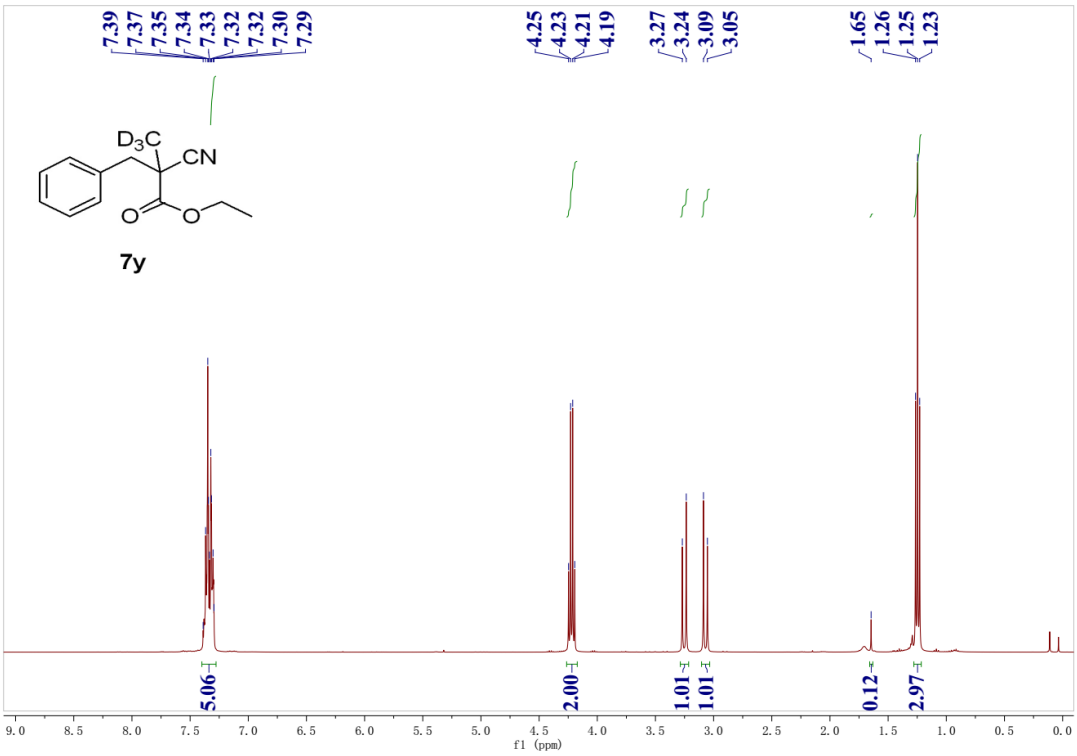

138.2
136.3
134.7
129.6
129.3
128.8
128.8
127.3
85.4
31.4
Ph
O2S
Ph
S
O2
6x
f1 (ppm)

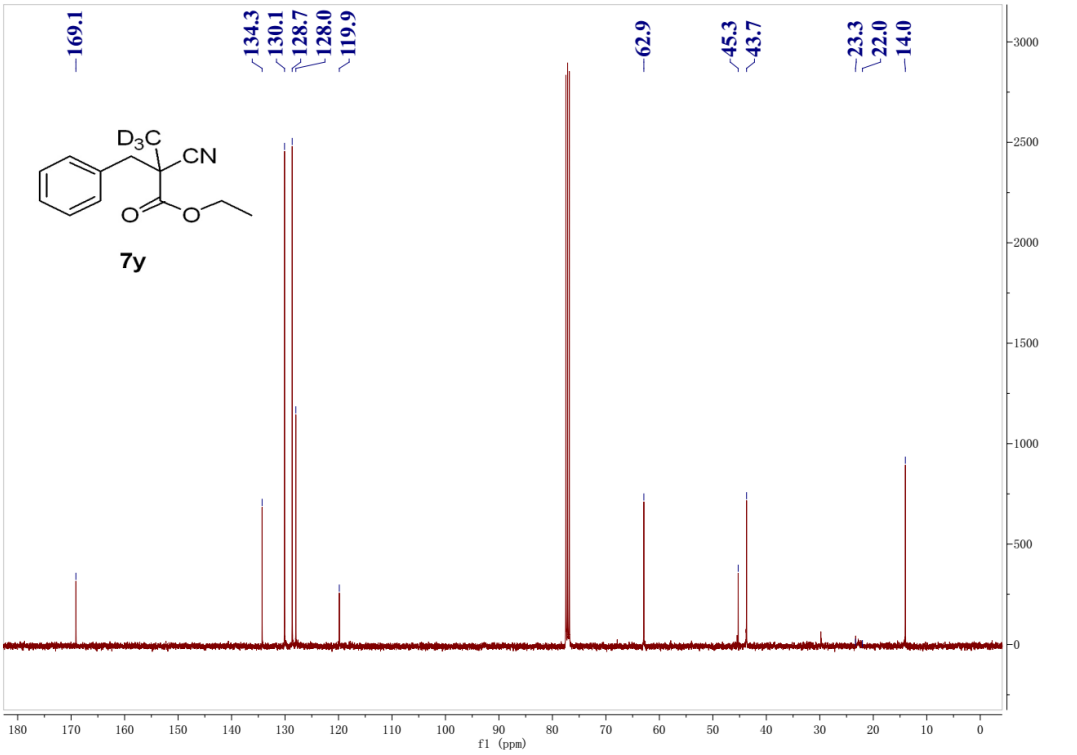

8.04
8.04
8.02
8.02
7.75
7.73
7.71
7.62
7.60
7.58
7.28
7.25
7.22
7.20
3.61
1.64
1.62
Ph
O2S
Ph
S
O2
D3C
7x
3.99
2.00
4.02
3.41
2.01
1.99
0.26
f1 (ppm)

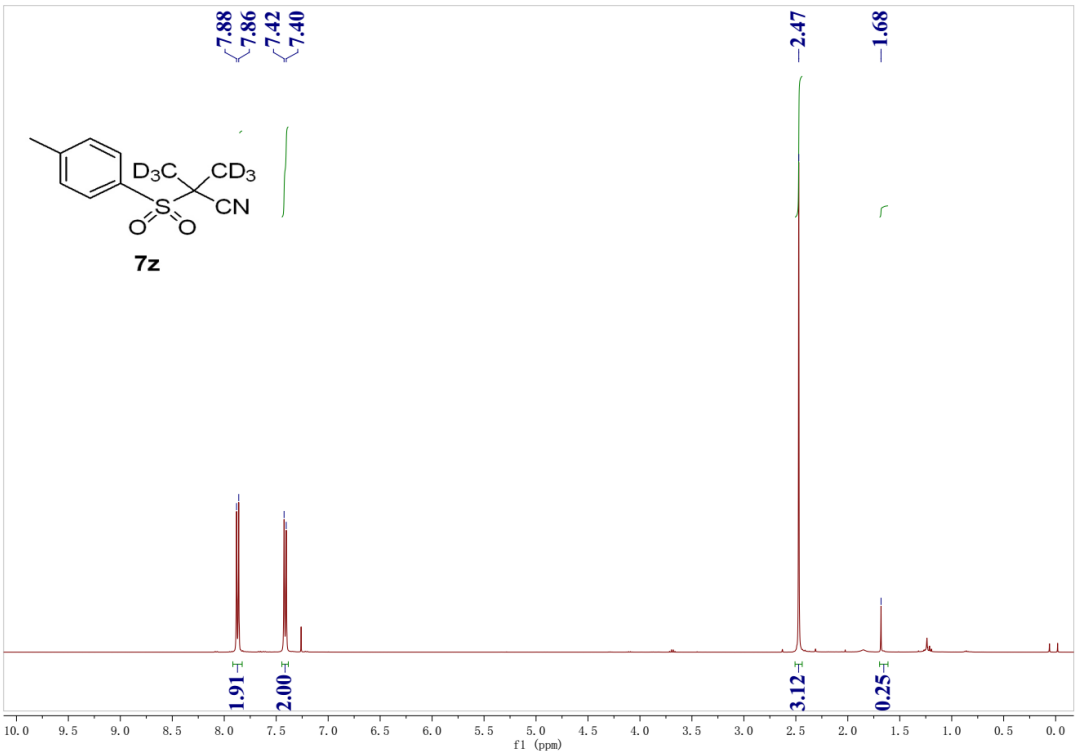

136.4
134.7
133.3
131.6
131.4
128.8
128.2
127.6
87.5
36.1
17.9
16.2
Ph
O2S
Ph
S
O2
D3C
7x
f1 (ppm)

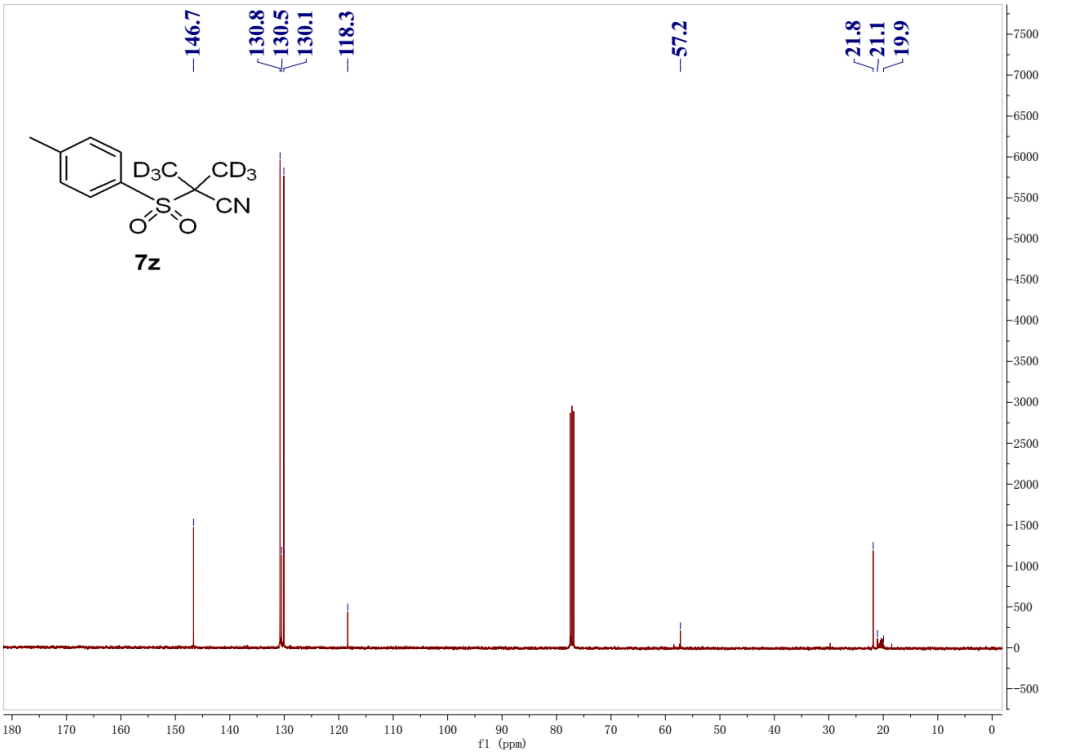

7.37
7.32
7.30
7.29
7.29
7.27
4.27
4.25
4.23
4.21
3.74
3.73
3.72
3.70
3.31
3.27
3.26
3.22
3.20
1.27
1.25
CN
O
O
6y
5.11
1.97
0.99
2.00
3.27
f1 (ppm)

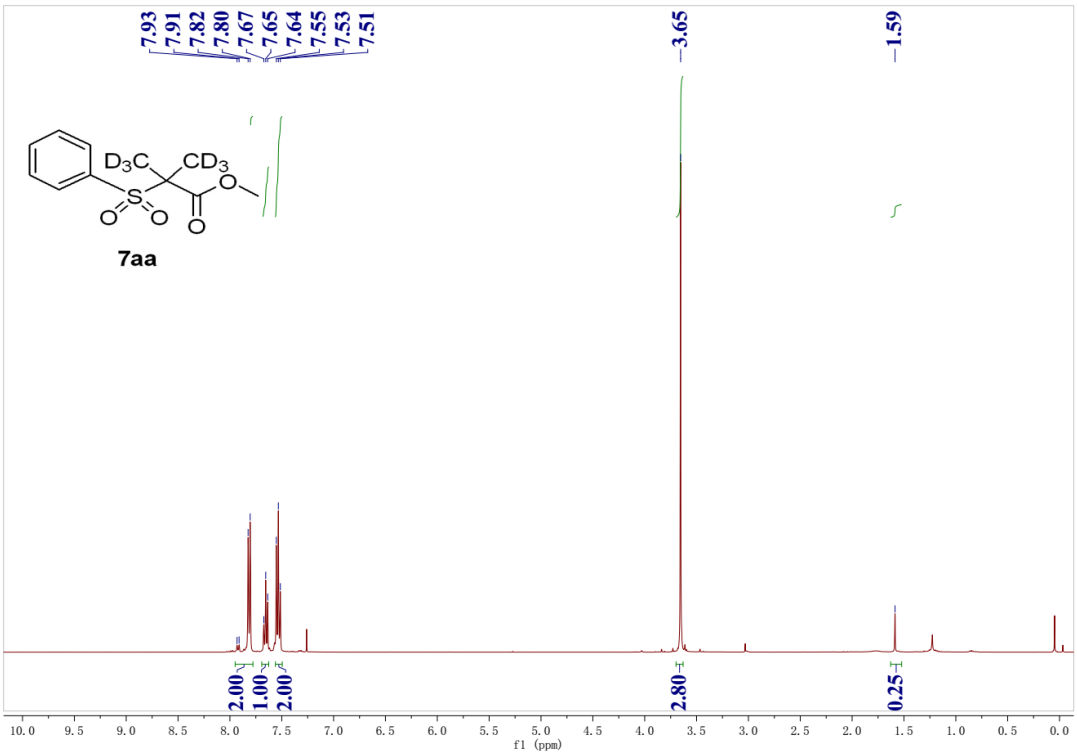

165.6
135.4
129.2
129.0
127.9
116.3
63.1
39.8
35.9
14.1
CN
O
O
6y
f1 (ppm)

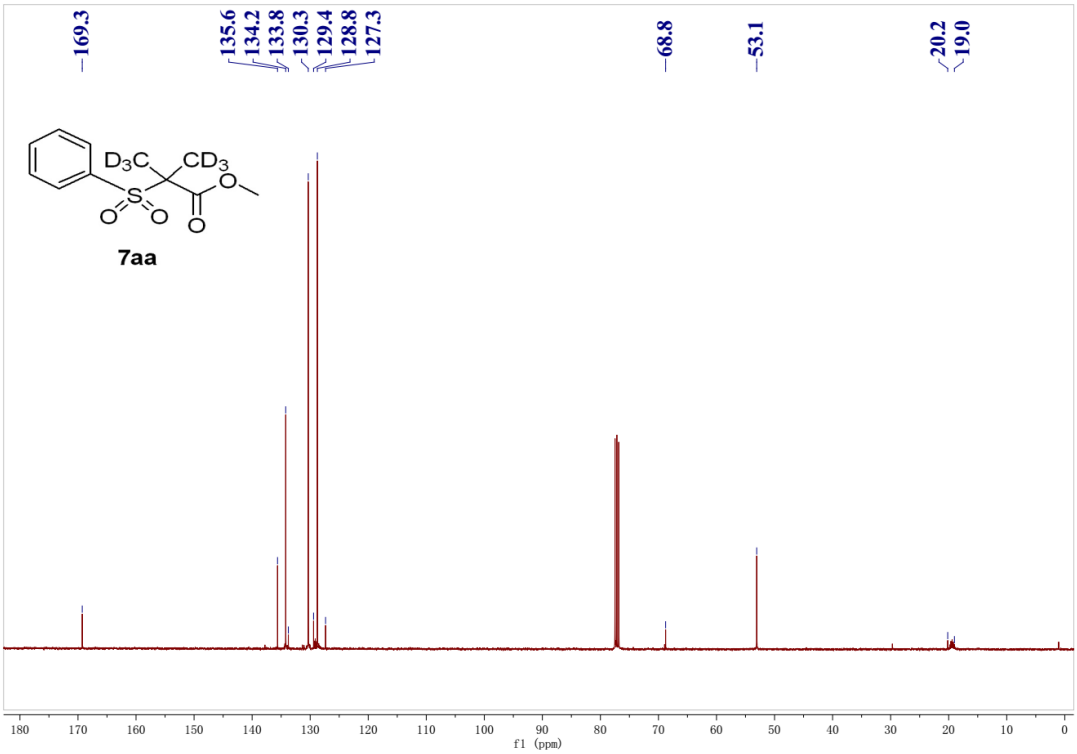

7.39
7.37
7.35
7.34
7.33
7.32
7.32
7.30
7.29
4.25
4.23
4.21
4.19
3.27
3.24
3.09
3.05
1.65
1.26
1.25
1.23
D3C
CN
O
O
7y
5.06
2.00
1.01
1.01
0.12
2.97
f1 (ppm)


169.1
134.3
130.1
128.7
128.0
119.9
62.9
45.3
43.7
23.3
22.0
14.0
D3C
CN
O
O
7y
f1 (ppm)


7.88
7.86
7.42
7.40
2.47
1.68
D3C
CD3
CN
O
O
7z
1.91
2.00
3.12
0.25
f1 (ppm)


146.7
130.8
130.5
130.1
118.3
57.2
21.8
21.1
19.9
D3C
CD3
CN
O
O
7z
f1 (ppm)


7.93
7.91
7.82
7.80
7.67
7.65
7.64
7.55
7.53
7.51
3.65
1.59
D3C
CD3
O
S
O
O
O
7aa
2.00
1.00
2.00
2.80
0.25
f1 (ppm)


169.3
135.6
134.2
133.8
130.3
129.4
128.8
127.3
68.8
53.1
20.2
19.0
D3C
CD3
O
S
O
O
O
7aa
f1 (ppm)