Supporting Information

Molybdenum-Mediated Reductive Deuteration of Nitroarenes with D_2O: Synthesis of *ortho*- and *para*-Deuterated Anilines

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1.General Information

Reagents, solvents and analytical methods:

Unless otherwise noted, all reactions were carried out under a carbon monoxide or nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz and ^{19}F NMR at 471 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl3(^{1}H NMRδ7.27,^{13}C NMRδ77.0) as solvent. High-resolution mass spectra (HRMS) is produced by Thermo Fisher Scientific. Its main body is composed of two parts: Thermo Scientific's UltiMate 3000 Series liquid system and Thermo Scientific Q-Exactive combined quadrupole Orbitrap mass spectrometer. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. NMR analyses of the unlabelled anilines and labelled anilines were recorded using the same deuterated solvent. After referencing the spectra to the residual solvent signal, integration of the signals on the unlabelled aniline spectra was performed. The same integration areas were applied to the deuterated product spectra, and calibration of the integration was carried out on the same signal. Deuterium content was calculated by the decrease of the area of a specific signal, using the following formula, where $A_{unlabelled}$ is the area in the unlabelled aniline's spectra and $A_{labelled}$ is the area in the product spectra: $D\% = (1-A_{labelled} / A_{unlabelled})*100\%$.

2.General Procedure for the Starting Materials

The Substrates of nitrocompounds (1a-1ad)

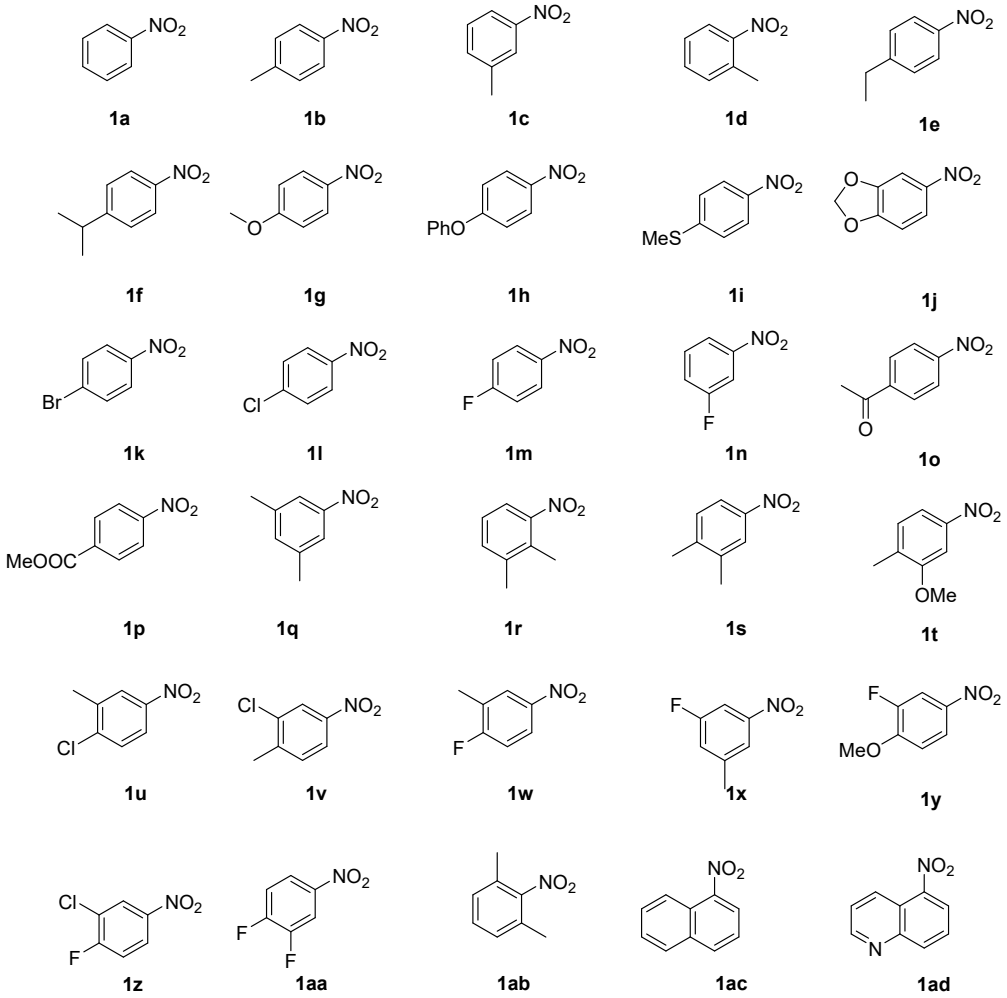
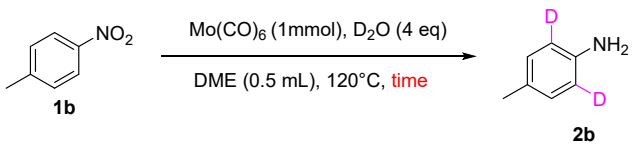


Figure S0 Substrates of nitrocompounds.

3.Optimization of Reaction Conditions

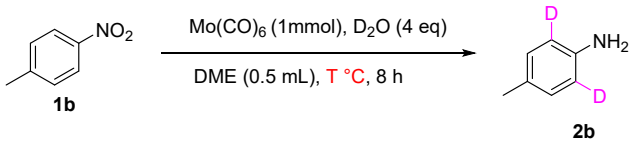
Table S1. Optimization of reaction time.[a]



Entry	Time	Yield (%)[b]	D%
1	1 h	37%	47%
2	2 h	53%	66%
3	4 h	71%	66%
4	8 h	87%	69%
5	12 h	86%	67%

[a] Reaction conditions: **1b** (1 mmol), D_2O (4 eq), $Mo(CO)_6$ (1 mmol), DME (0.5 mL), N_2 atmosphere, 120 ºC for time. [b] Isolated yield.

Table S2. Optimization of temperature.[a]

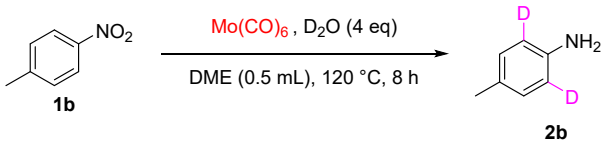


1b **2b**

Entry	Temperature	Yield (%)[b]	D%
1	60 ℃	trace	
2	80 ℃	trace	
3	100 ℃	75%	57%
4	120 ℃	87%	69%
5	130 ℃	85%	67%

[a] Reaction conditions: **1b** (1 mmol), D_2O (4 eq), $Mo(CO)_6$ (1 mmol), DME (0.5 mL), N_2 atmosphere, T ºC for 8 h. [b] Isolated yield.

Table S3. Optimization of the amount of $Mo(CO)_6$.[a]

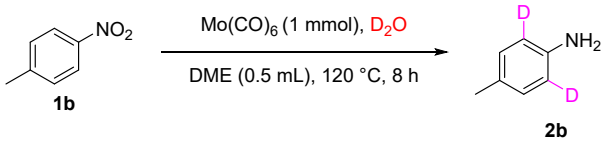


1b **2b**

Entry	$Mo(CO)_6$	Yield (%)[b]	D%
1	0.5 mmol	53%	45%
2	1 mmol	87%	69%
3	1.5 mmol	85%	65%

[a] Reaction conditions: **1b** (1 mmol), D_2O (4 eq), $Mo(CO)_6$, DME (0.5 mL), N_2 atmosphere, 120 ºC for 8 h. [b] Isolated yield.

Table S4. Optimization of the equivalent of D_2O.[a]



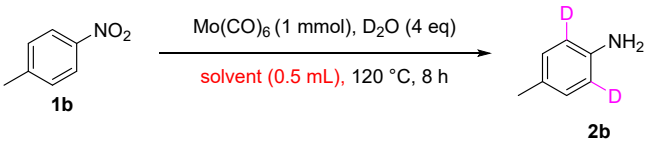
1b **2b**

Entry	D_2O	Yield (%)[b]	D%
1	NO D_2O	NR	
2	1 equiv.	50%	13%
3	2 equiv.	65%	55%
4	3 equiv.	83%	67%
5	4 equiv.	87%	69%
6	5 equiv.	85%	68%

7	10 equiv.	89%	94%
8	15 equiv.	76%	92%
9	30 equiv.	NR	

[a] Reaction conditions: **1b** (1 mmol), D_2O, $Mo(CO)_6$ (1 mmol), DME (0.5 mL), N_2 atmosphere, 120 ºC for 8 h. [b] Isolated yield.

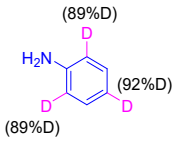
Table S5. Optimization of solvent.[a]



Entry	Solvent	Yield (%)[b]	D%
1	1,4-dioxane	62%	60%
2	THF	63%	92%
3	MeCN	69%	39%
4	toluene	60%	87%
5	DCE	ND	
6	MTBE	83%	91%
7	DME	89%	94%
8	CpME	50%	90%
9	D_2O	NR	

[a] Reaction conditions: **1b** (1 mmol), D_2O (10 eq), $Mo(CO)_6$ (1 mmol), solvent (0.5 mL), N_2 atmosphere, 120 ºC for 8 h. [b] Isolated yield.

4.Spectroscopic Data of Products



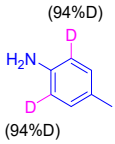
Benzen-2,4,6-*d*$_3$-amine (2a)

The title compound was prepared from Nitrobenzene (123.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid. (general procedure: 83.6 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 2H), 6.77 (t, *J* = 7.4 Hz, 0.08H), 6.70 (d, *J* = 8.4 Hz, 0.23H), 3.31 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 129.2 (d, *J* = 13.9 Hz), 118.4 (dd, *J* = 41.6, 16.7 Hz), 115.0 (dd, *J* = 41.6, 17.9 Hz).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5D_3N^+$ 97.0840; Found 97.0845.



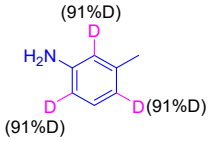
2,6-*d*$_2$*p*-*Toluidine* (2b)

The title compound was prepared from 1-Methyl-4-nitrobenzene (137.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 97.1 mg, 89%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.01 (s, 2H), 6.65 (d, *J* = 8.6 Hz, 0.11H), 3.46 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 143.7, 129.7, 127.9, 116.2 – 113.8 (m), 20.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_8D_2N^+$ 110.0933; Found 110.0937.



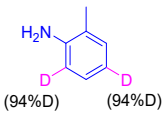
2,4,6-*d*$_3$-*m*-Toluidine (2c)

The title compound was prepared from 1-Methyl-3-nitrobenzene (137.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 91.3 mg, 83%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.09 (s, 1H), 6.63 (d, *J* = 7.5 Hz, 0.09H), 6.57 – 6.52 (m, 0.17H), 3.44 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 146.2, 139.0, 129.0, 119.3 (dd, *J* = 42.2, 18.1 Hz), 115.8 (dd, *J* = 42.6, 19.0 Hz), 112.1 (dd, *J* = 41.4, 17.3 Hz), 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7D_3N^+$ 111.0996; Found 111.1000.



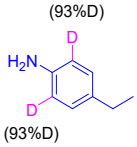
4,6-*d*$_2$-*o*-Toluidine (2d)

The title compound was prepared from 1-Methyl-2-nitrobenzene (137.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 97.1 mg, 89%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.09 (d, *J* = 6.6 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 0.06H), 6.72 (d, *J* = 7.7 Hz, 0.06H), 3.44 (s, 2H), 2.21 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.5, 130.4, 126.8, 122.4, 118.5 (dd, *J* = 41.9, 17.4 Hz), 114.8 (dd, *J* = 41.7, 18.1 Hz), 17.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_8D_2N^+$ 110.0933; Found 110.0938.



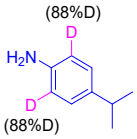
4-Ethylbenzen-*2,6*-*d*$_2$-amine (2e)

The title compound was prepared from 1-Ethyl-4-nitrobenzene (151.1 mg, 0.9 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 109.5 mg, 89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 2H), 6.67 (d, *J* = 8.6 Hz, 0.15H), 3.33 (s, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 134.5, 128.5, 115.1 (dd, *J* = 41.1, 17.3 Hz), 28.0, 16.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{10}D_2N^+$ 124.1090; Found 124.1091.



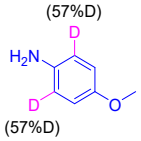
4-Isopropylbenzen-*2,6-d*$_2$-amine (2f)

The title compound was prepared from 1-Isopropyl-4-nitrobenzene (165.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 121.9 mg, 89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 6.68 (d, *J* = 8.6 Hz, 0.24H), 3.26 (s, 2H), 2.90 – 2.78 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 139.2, 127.0, 115.1 (dd, *J* = 41.3, 17.8 Hz), 33.3, 24.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{12}D_2N^+$ 138.1246; Found 138.1247.



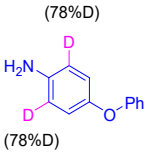
4-Methoxybenzen-*2,6-d*$_2$-amine (2g)

The title compound was prepared from 1-Methoxy-4-nitrobenzene (153.1mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a brown solid (general procedure: 112.6 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (s, 2H), 6.68 (d, *J* = 12.3 Hz, 0.87H), 3.77 (s, 3H), 3.12 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 139.8, 116.5, 114.8 (dd, *J* = 12.2, 2.0 Hz), 55.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_8D_2NO^+$ 126.0882; Found 126.0885.

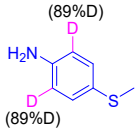


4-Phenoxybenzen-*2,6-d*$_2$-amine (2h)

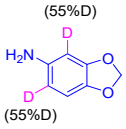
The title compound was prepared from 1-Nitro-4-phenoxybenzene (215.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a yellow solid (general procedure: 162.7 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.92 (s, 2H), 6.71 (d, *J* = 9.1 Hz, 0.44H), 3.51 (s, 2H).

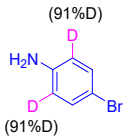
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 148.6, 142.6, 129.6, 122.1, 121.1, 117.3, 116.1 (dd, *J* = 41.0, 16.9 Hz).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}D_2NO^+$ 188.1039; Found 188.1040.



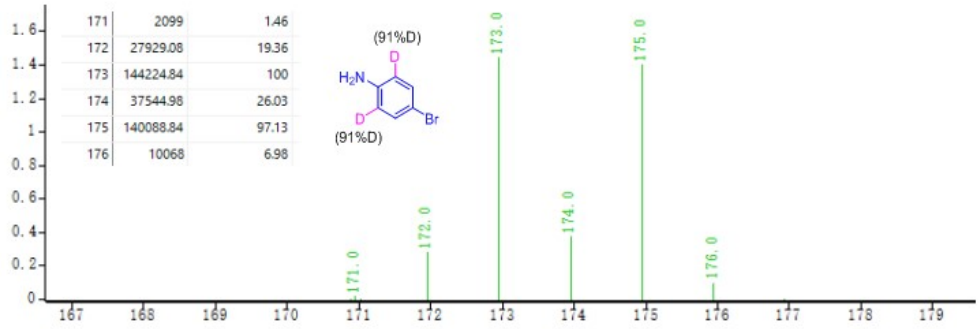
4-(Methylthio)benzen-*2,6-d*$_2$-amine (2i)
The title compound was prepared from Methyl(4-nitrophenyl)sulfane (169.2 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a yellow solid (general procedure: 108.6 mg, 77%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.65 (d, *J* = 8.8 Hz, 0.22H), 3.51 (s, 2H), 2.44 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 138.9, 120.3 (dd, *J* = 43.5, 19.6 Hz), 112.9 (dd, *J* = 42.3, 18.8 Hz), 21.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_8D_2NS^+$ 142.0654; Found 142.0655.

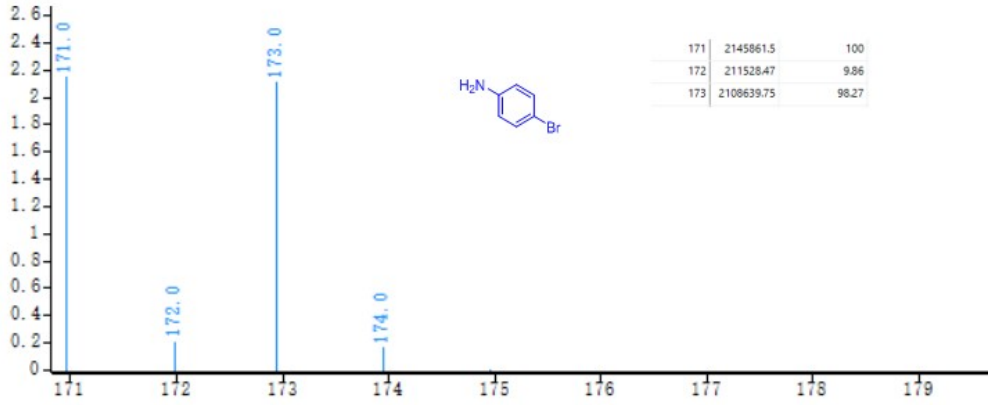


Benzo[d][1,3]dioxol-*4,6-d*$_2$-5-amine (2j)
The title compound was prepared from 4-Nitrobenzo[d][1,3]dioxole (167.5 mg, 1.5 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a yellow solid (general procedure: 115.5 mg, 83%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (s, 1H), 6.30 (s, 0.9H), 5.86 (s, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 108.5 (d, *J* = 11.0 Hz), 100.7, 98.2
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_6D_2NO^+$ 140.0675; Found 140.0684.

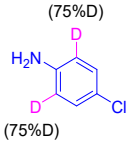


4-Bromobenzen-*2,6-d*$_2$-amine (2k)
The title compound was prepared from 1-Bromo-4-nitrobenzene (201.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a red solid (general procedure: 143.6 mg, 83%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 2H), 6.57 (d, *J* = 9.1 Hz, 0.18H), 3.59 (s, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 131.9, 116.6 (dd, *J* = 41.4, 17.2 Hz), 110.1.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5D_2BrN^+$ 173.9882; Found 173.9882.
The 2 mg of 4-Bromoaniline and **2k** was weighed separately into a 2 mL glass bottle. Then 2 mL DCM was added and the sample concentration was 1 mg/mL. Measure the sample using GCMS and calculate the deuteratation rate based on the results of GCMS.





2k: 0D%=1%; 1D%=2%; 2D%=97%



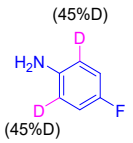
4-Chlorobenzen-*2,6-d*$_2$-amine (2l)

The title compound was prepared from 1-Chloro-4-nitrobenzene (157.0 mg, 0.9 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 104.5 mg, 81%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.13 (s, 2H), 6.62 (d, *J* = 9.0 Hz, 0.51H), 3.58 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.9, 129.0, 123.1, 116.4 – 115.7 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5ClD_2N^+$ 130.0387; Found 130.0388.



4-Fluorobenzen-*2,6-d*$_2$-amine (2m)

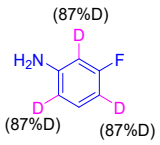
The title compound was prepared from 1-Fluoro-4-nitrobenzene (141.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 96.1 mg, 85%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.88 (ddd, *J* = 8.6, 4.4, 1.0 Hz, 2H), 6.68 – 6.59 (m, 1.1H), 3.40 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 156.5 (d, *J* = 235.8 Hz), 142.3, 115.9 (d, *J* = 60.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -126.79 (td, *J* = 8.6, 3.3 Hz).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5D_2FN^+$ 114.0683; Found 114.0686.



3-Fluorobenzen-*2,4,6-d*$_3$-amine (2n)

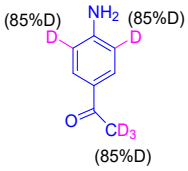
The title compound was prepared from 1-Fluoro-3-nitrobenzene (141.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 76.8 mg, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 6.6 Hz, 1H), 6.47 (t, *J* = 8.7 Hz, 0.25H), 6.40 (d, *J* = 11.0 Hz, 0.13H), 3.58 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8 (d, *J* = 243.3 Hz), 148.1 (d, *J* = 10.08 Hz), 130.2 (d, *J* = 9.7 Hz), 110.9–110.1 (m), 105.4–104.5 (m), 102.5–101.4 (m).

^{19}F NMR (471 MHz, $CDCl_3$) δ -111.43 – -116.46 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_4D_3FN^+$ 115.0745; Found 115.0749.



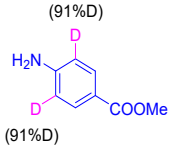
1-(4-Aminophenyl-*3,5-d*$_2$)ethan-1-one (2o)

The title compound was prepared from 1-(4-Aminophenyl)ethan-1-one (165.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a red solid (general procedure: 112.3 mg, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 2H), 6.64 (d, *J* = 9.0 Hz, 0.3H), 4.27 (s, 2H), 2.46 (s, 0.45H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 151.4, 130.7, 127.5, 113.5 (dd, *J* = 41.7, 17.6 Hz), 29.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_5D_5NO^+$ 141.0502; Found 141.0511.



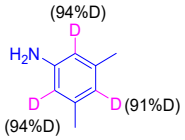
Methyl-4-aminobenzoate-*3,5-d*$_2$ (2p)

The title compound was prepared from methyl-4-nitrobenzoate (181.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.30) to give the product as a brown solid (general procedure: 147.1 mg, 96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 2H), 6.62 (d, *J* = 8.9 Hz, 0.18H), 4.05 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 138.1, 116.6 (d, *J* = 12.8 Hz), 115.7 (d, *J* = 13.7 Hz), 42.3, 29.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_8D_2NO_2^+$ 153.0831; Found 153.0833.



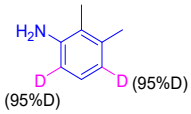
3,5-Dimethylbenzen-*2,4,6-d*$_3$-amine (2q)

The title compound was prepared from 1,3-Dimethyl-5-nitrobenzene (151.2 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 100.5 mg, 81%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.48 (s, 0.09H), 6.38 (s, 0.12H), 3.41 (s, 2H), 2.28 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 145.0, 131.0, 125.8, 115.6 (dd, *J* = 41.2, 17.2 Hz), 18.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_9D_3N^+$ 125.1153; Found 125.1154.



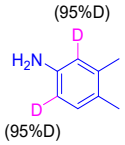
2,3-Dimethylbenzen-*4,6-d*$_2$-amine (2r)

The title compound was prepared from 1,2-Dimethyl-3-nitrobenzene (151.2 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 102.1 mg, 83%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.00 (s, 1H), 6.71 (d, *J* = 7.5 Hz, 0.05H), 6.63 (d, *J* = 7.9 Hz, 0.05H), 3.53 (s, 2H), 2.35 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.5, 137.1, 125.9, 120.7 (d, *J* = 72.5 Hz), 113.0, 20.5, 12.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{10}D_2N^+$ 124.1090; Found 124.1092.



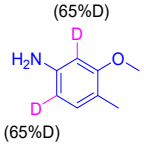
2,3-Dimethylbenzen-*4,6-d*$_2$-*amine* (2s)

The title compound was prepared from 1,2-Dimethyl-4-nitrobenzene (151.2 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 104.7 mg, 85%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.96 (s, 1H), 6.56 (s, 0.05H), 6.50 (d, *J* = 7.9 Hz, 0.05H), 3.33 (s, 2H), 2.22 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.1, 137.3, 130.2, 126.6, 116.7 (dd, *J* = 43.0, 19.5 Hz), 112.5 (dd, *J* = 41.5, 17.2 Hz), 19.8, 18.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{10}D_2N^+$ 124.1090; Found 124.1092.



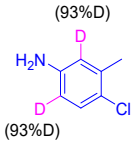
3-Methoxy-4-methylbenzen-*2,6-d*$_2$-amine (2t)

The title compound was prepared from 2-Methoxy-1-methyl-4-nitrobenzene (167.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a yellow solid (general procedure: 126.5 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 – 6.92 (m, 1H), 6.26 (d, *J* = 7.8 Hz, 0.7H), 3.81 (s, 3H), 3.47 (s, 2H), 2.16 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 145.5, 131.0, 116.5, 106.8, 98.4 (dd, *J* = 40.2, 16.5 Hz), 55.2, 15.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{10}D_2NO^+$ 140.1039; Found 140.1039.



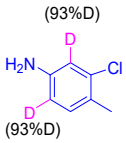
4-Chloro-3-methylbenzen-*2,6-d*$_2$-amine (2u)

The title compound was prepared from 1-Chloro-2-methyl-4-nitrobenzene (171.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 115.9 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 1H), 6.57 (s, 0.07H), 6.48 (d, *J* = 8.4 Hz, 0.07H), 3.53 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 136.6, 129.4, 123.5, 117.3 (dd, *J* = 42.6, 18.8 Hz), 113.7 (dd, *J* = 40.9, 16.8 Hz), 20.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7D_2ClN^+$ 144.0544; Found 144.0544.



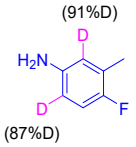
3-Chloro-4-methylbenzen-*2,6-d*$_2$-amine (2v)

The title compound was prepared from 2-Chloro-1-methyl-4-nitrobenzene (171.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a yellow solid (general procedure: 123.0 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.73 (s, 0.07H), 6.52 (d, *J* = 8.1 Hz, 0.07H), 3.51 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 134.5, 131.3, 125.5, 115.4 (dd, *J* = 42.2, 17.8 Hz), 113.6 (dd, *J* = 41.3, 17.2 Hz), 19.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7D_2ClN^+$ 144.0544; Found 144.0545.



4-Fluoro-3-methylbenzen-*2,6-d*$_2$-amine (2w)

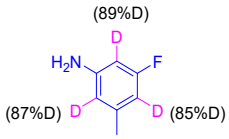
The title compound was prepared from 1-fluoro-2-methyl-4-nitrobenzene (155.0 mg, 0.9 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a red oil (general procedure: 110.5 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (d, *J* = 9.4 Hz, 1H), 6.52 (d, *J* = 6.4 Hz, 0.1H), 6.47 (dd, *J* = 8.6, 4.0 Hz, 0.1H), 3.35 (s, 2H), 2.22 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1 (d, *J* = 234.0 Hz), 141.9 (d, *J* = 2.52 Hz), 125.2 (d, *J* = 18.9 Hz), 117.8, 115.2 (d, *J* = 23.94 Hz), 113.4, 14.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -130.23 – -132.59 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7D_2FN^+$ 128.0839; Found 128.0841.



3-Fluoro-5-methylbenzen-*2,4,6-d*$_3$-amine (2x)

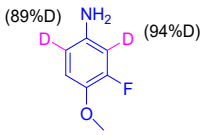
The title compound was prepared from 1-Fluoro-3-methyl-5-nitrobenzene (155.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a yellow solid (general procedure: 101.2 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 (d, *J* = 9.9 Hz, 0.13H), 6.29 (s, 0.15H), 6.22 (d, *J* = 10.7 Hz, 0.11H), 3.60 (s, 2H), 2.27 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8 (d, *J* = 242.6 Hz), 147.7 (d, *J* = 11.34 Hz), 140.8 (d, *J* = 10.08 Hz), 111.2, 105.9, 99.1, 21.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.42 – -118.13 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_6D_3FN^+$ 129.0902; Found 129.0903.



3-Fluoro-4-methoxybenzen-*2,6-d*$_2$-amine (2y)

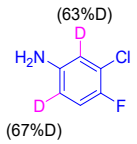
The title compound was prepared from 2-Fluoro-1-methoxy-4-nitrobenzene (171.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a yellow solid (general procedure: 128.7 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (d, *J* = 11.3 Hz, 1H), 6.32 (d, *J* = 7.2 Hz, 0.06H), 6.17 (dd, *J* = 8.5, 3.4 Hz, 0.11H), 3.83 (s, 3H), 3.49 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9 (d, *J* = 11.34 Hz), 147.1, 145.2, 143.0, 116.1 (d, *J* = 18.9 Hz), 106.4, 56.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -144.08 – -153.51 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7D_2FNO^+$ 144.0788; Found 144.0802.



3-Chloro-4-fluorobenzen-*2,6-d*$_2$-amine (2z)

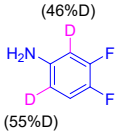
The title compound was prepared from 2-Chloro-1-fluoro-4-nitrobenzene (175.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a red solid (general procedure: 127.9 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 8.8, 4.4 Hz, 1H), 6.70 (d, *J* = 6.1 Hz, 0.37H), 6.51 (dd, *J* = 8.8, 3.8 Hz, 0.33H), 3.53 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6 (d, *J* = 238.2 Hz), 143.2, 120.8, 116.7 (d, *J* = 21.42 Hz), 114.3 (d, *J* = 6.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -128.55 – -131.60 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_4D_2ClFN^+$ 148.0293; Found 148.0282.



3,4-Difluorobenzen-*2,6-d*$_2$-amine (2aa)

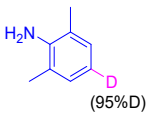
The title compound was prepared from 3,4-Difluoro-1-nitrobenzene (159.0 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a brown solid (general procedure: 108.9 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (t, *J* = 9.1 Hz, 1.45H), 6.50 (dd, *J* = 12.0, 6.7 Hz, 0.54H), 3.57 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7 (dd, *J* = 10.2, 5.9 Hz), 150.7 (dd, *J* = 10.3, 5.8 Hz), 133.9 (t, *J* = 15.4 Hz), 132.0 (t, *J* = 15.6 Hz), 98.5 (dd, *J* = 47.7, 22.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -130.23 – -140.35 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_4D_2F_2N^+$ 132.0588; Found 132.0581.



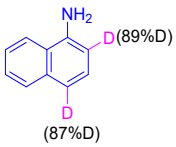
2,6-Dimethylbenzen-4-*d*-amine (2ab)

The title compound was prepared from 1,3-Dimethyl-2-nitrobenzene (151.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a yellow oil (general procedure: 85.5 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.67 (t, *J* = 7.4 Hz, 0.05H), 3.41 (s, 2H), 2.20 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 128.2, 121.8, 117.9 (dd, *J* = 41.0, 16.8 Hz), 17.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{11}DN^+$ 123.1027; Found 123.1030.



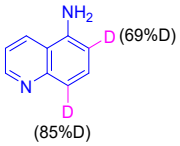
Naphthalen-*2,4-d*$_2$-1-amine (2ac)

The title compound was prepared from 1-nitronaphthalene (173.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.30) to give the product as a yellow solid (general procedure: 123.3 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 2H), 7.57 – 7.46 (m, 2.13H), 7.37 (s, 1H), 6.83 (d, *J* = 7.4 Hz, 0.11H), 3.98 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 134.4, 128.6, 126.2, 125.9, 124.9, 123.7, 120.9, 118.8 (dd, *J* = 43.7, 19.1 Hz), 109.6 (dd, *J* = 41.6, 17.6 Hz).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_8D_2N^+$ 146.0933; Found 146.0934.



Quinolin-*6,8-d*$_2$-5-amine (2ad)

The title compound was prepared from 5-Nitroquinoline (174.1 mg, 1 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.20) to give the product as a red solid (general procedure: 112.5 mg, 77%).

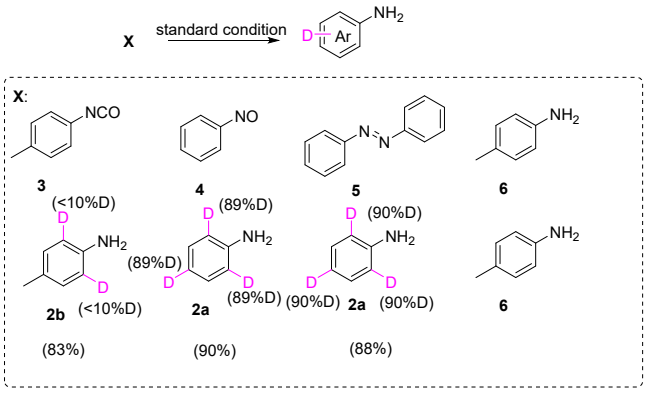
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.17 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 0.15H), 7.50 (s, 1H), 7.30 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 0.3H), 4.22 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 149.0, 142.4, 130.0, 129.9, 129.7, 119.7 (d, *J* = 42.8 Hz), 118.7, 110.1 – 109.4 (m).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_7D_2N_2^+$ 147.0886; Found 147.0889.

5.Mechanistic Experiments

Control experiments



X (1 mmol), $Mo(CO)_6$ (1 mmol) were transferred into an 15 mL tube which was filled with nitrogen. Then, DME (0.5 mL) and D_2O (10 equiv.) were added to the reaction tube by syringe or microsyringe. The tube was sealed and the mixture was stirred at 120 °C for 8 h. After the reaction was completed, the reaction mixture was filtered and concentrated under vacuum. The crude pr-

oduct was purified by column chromatography on silica gel to afford the corr-esponding product.

6.References

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[2] Atzrodt, J., Derdau, V., Fey, T., et al., The renaissance of H/D exchange[J]. Angew. Chem. Int. Ed. **2007**, *46*, 7744-7765.

[3] Florian B., Nils R., Stephan B., et al., Manganese-Catalysed Deuterium Lab elling of Anilines and Electron-Rich (Hetero)Arenes[J]. Angew. Chem. Int. Ed. **2022**, *61*, e202202423.

[4] Hironao S., Nobuhiro I., Hiroyoshi E., et al., Aromatic ring favorable and efficient H–D exchange reaction catalyzed by Pt/C[J]. Tetrahedron Letters **2005**, *46,* 6995-6998.

7.Copies of NMR Spectra for Compounds

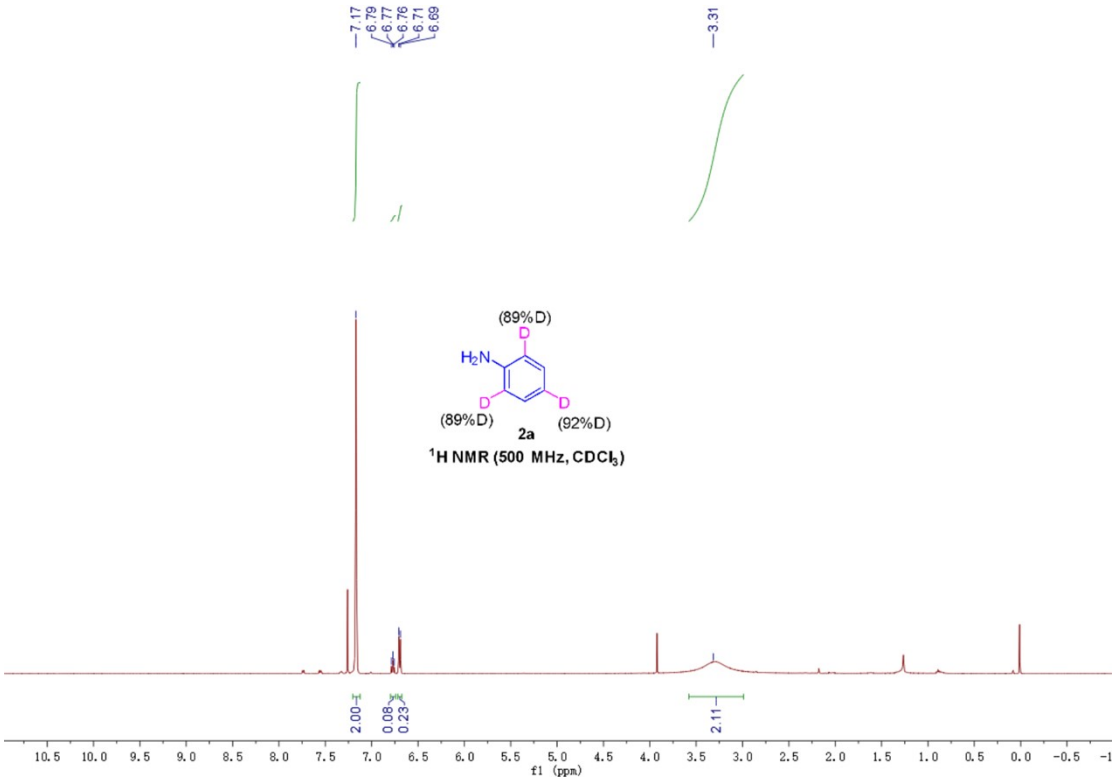

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2a

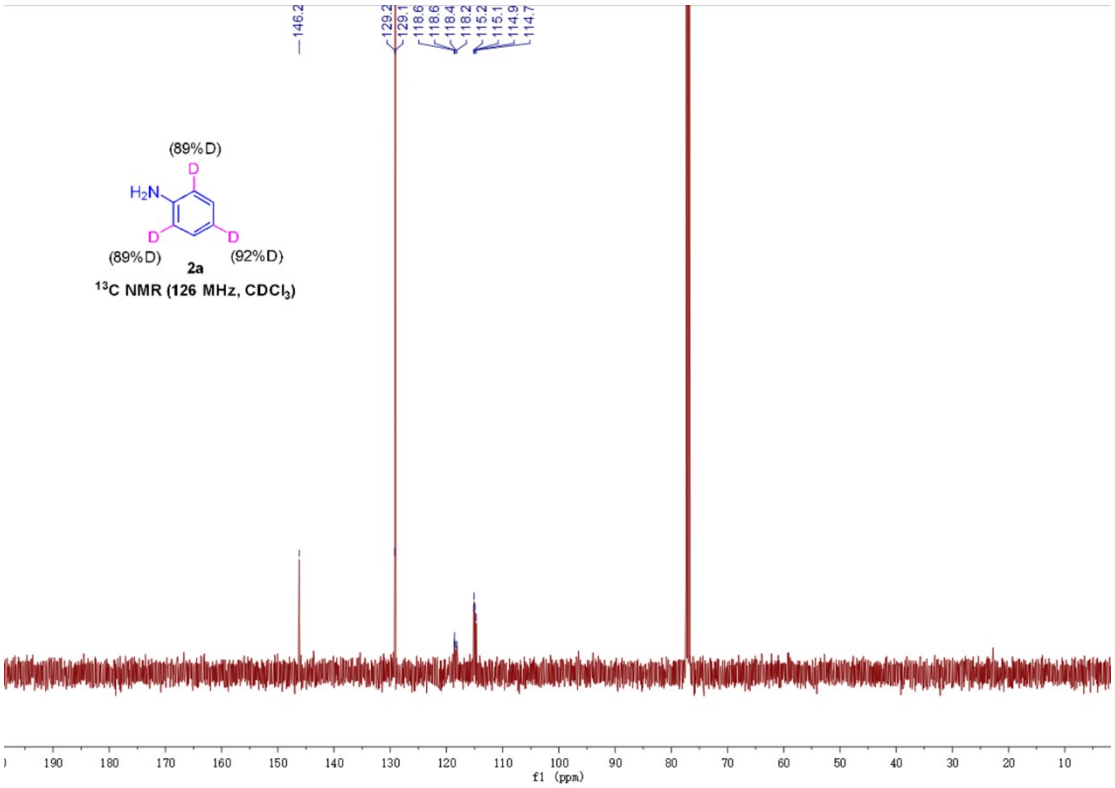

Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2a

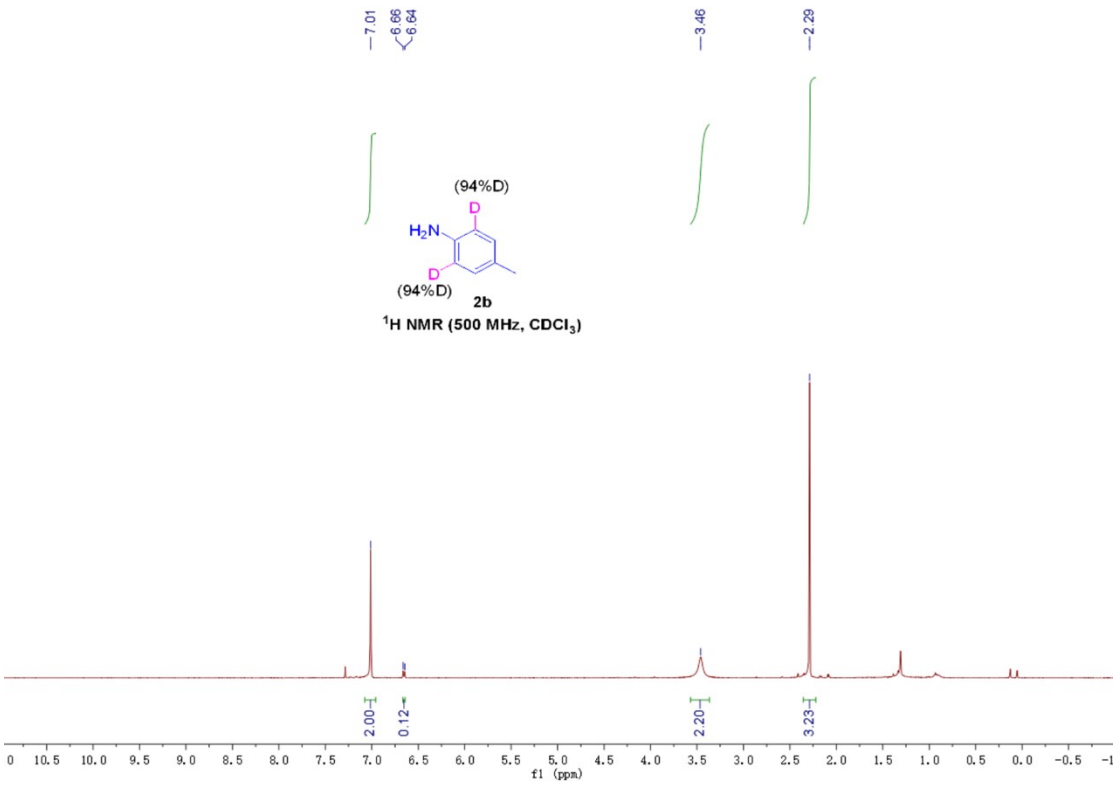

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2b

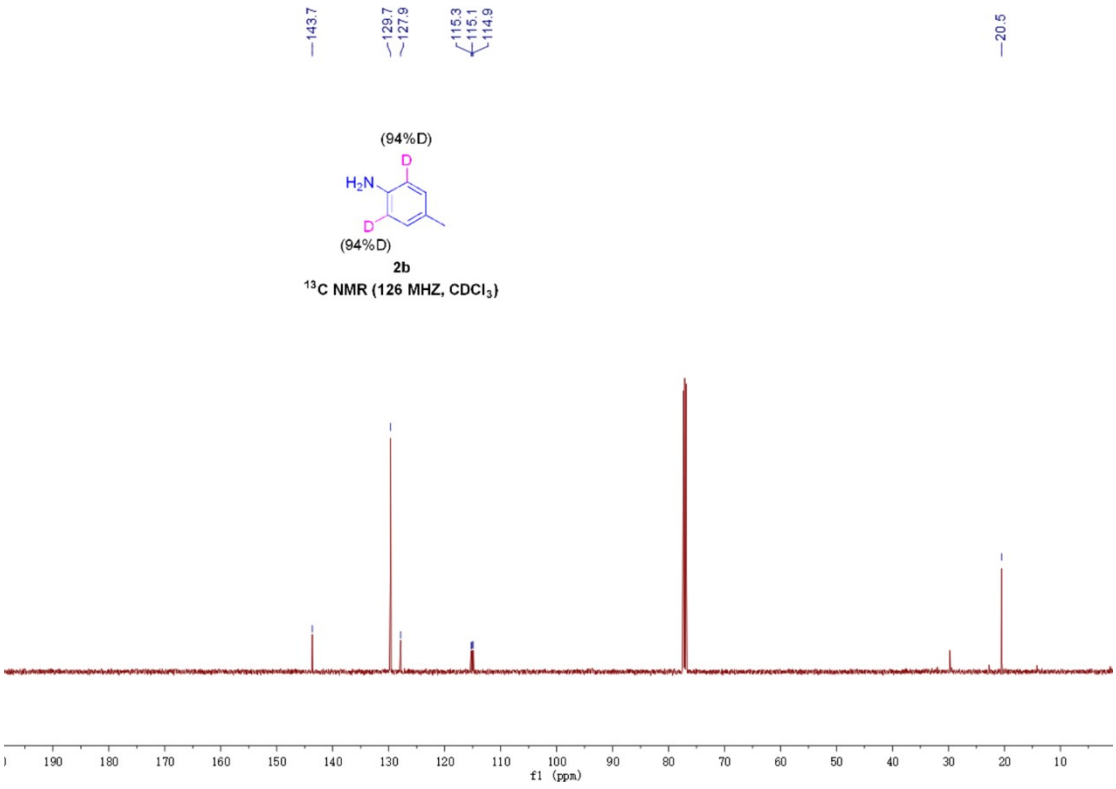

Figure S4. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2b

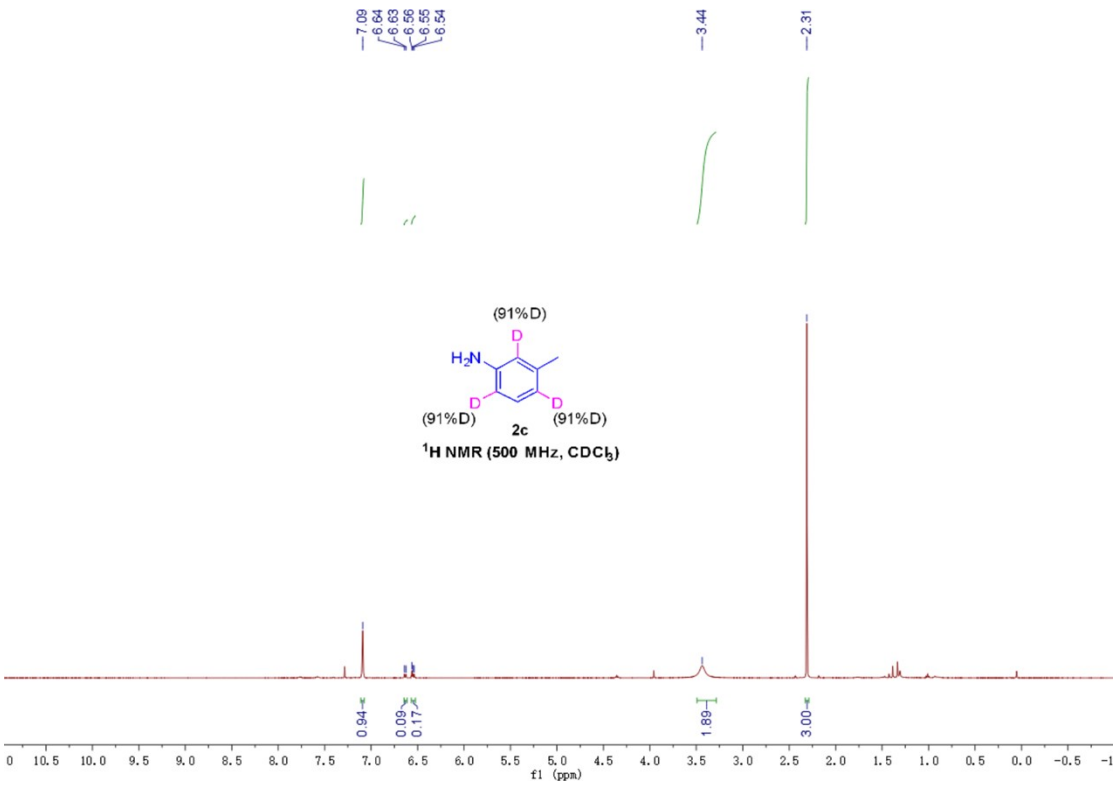

Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2c

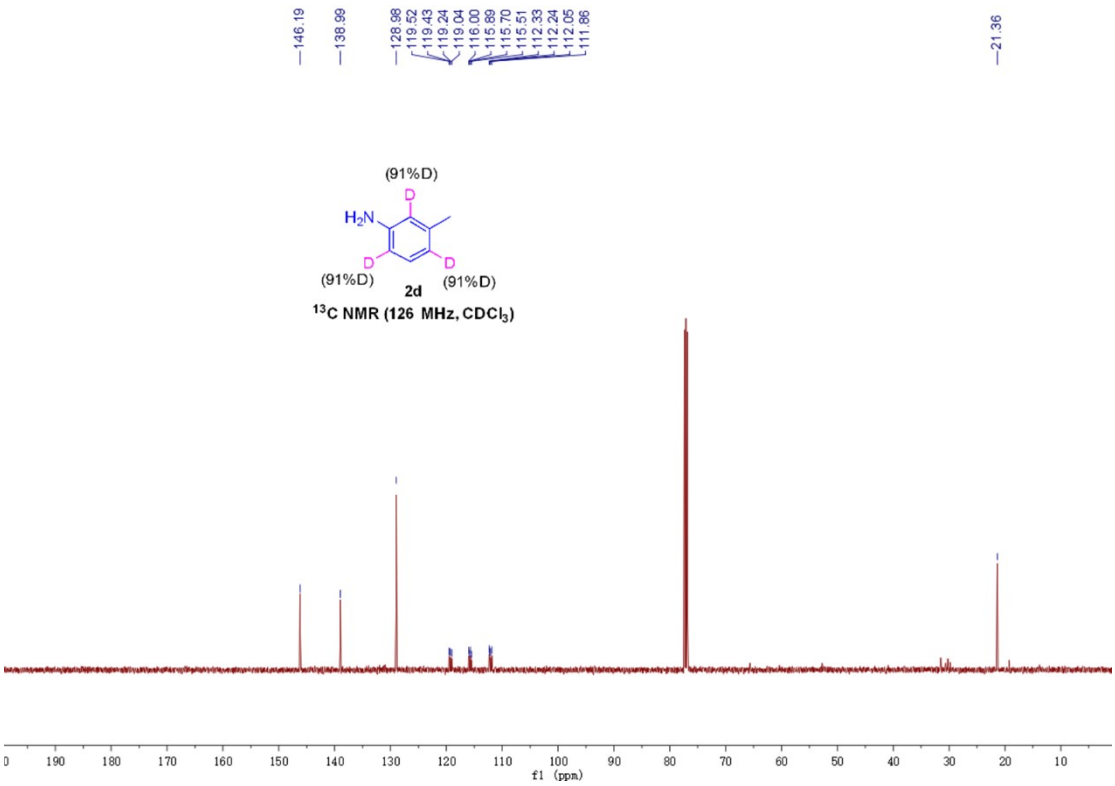

Figure S6. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2c

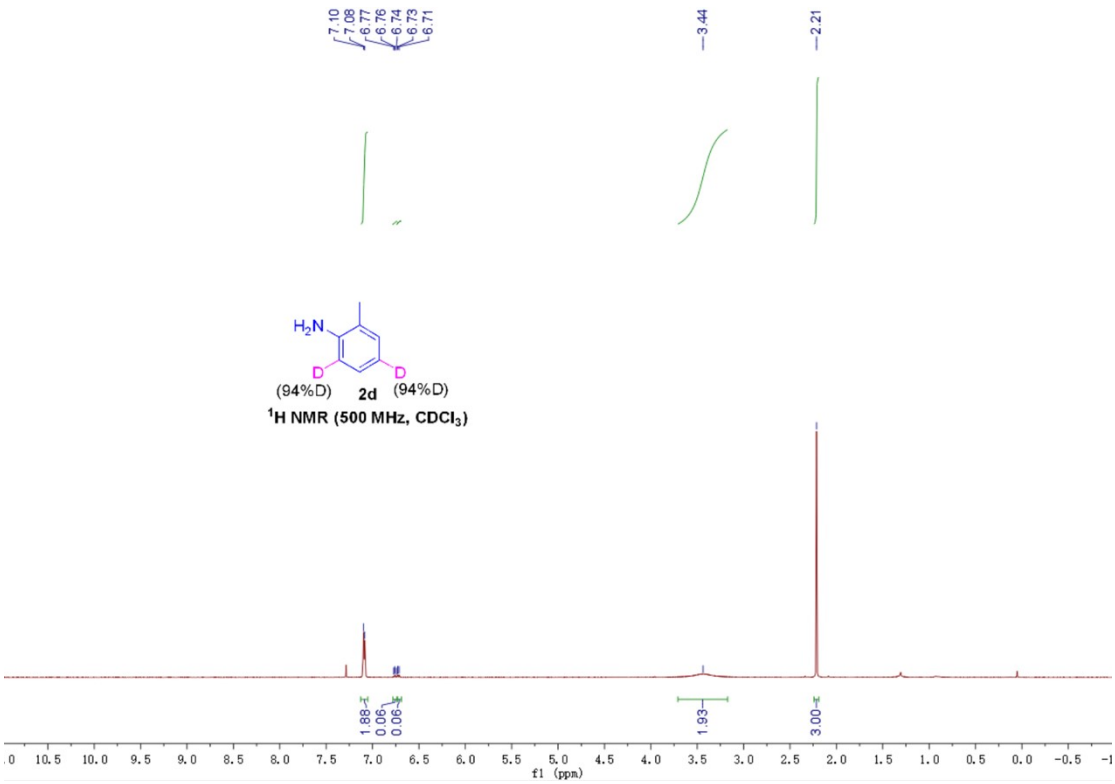

Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2d

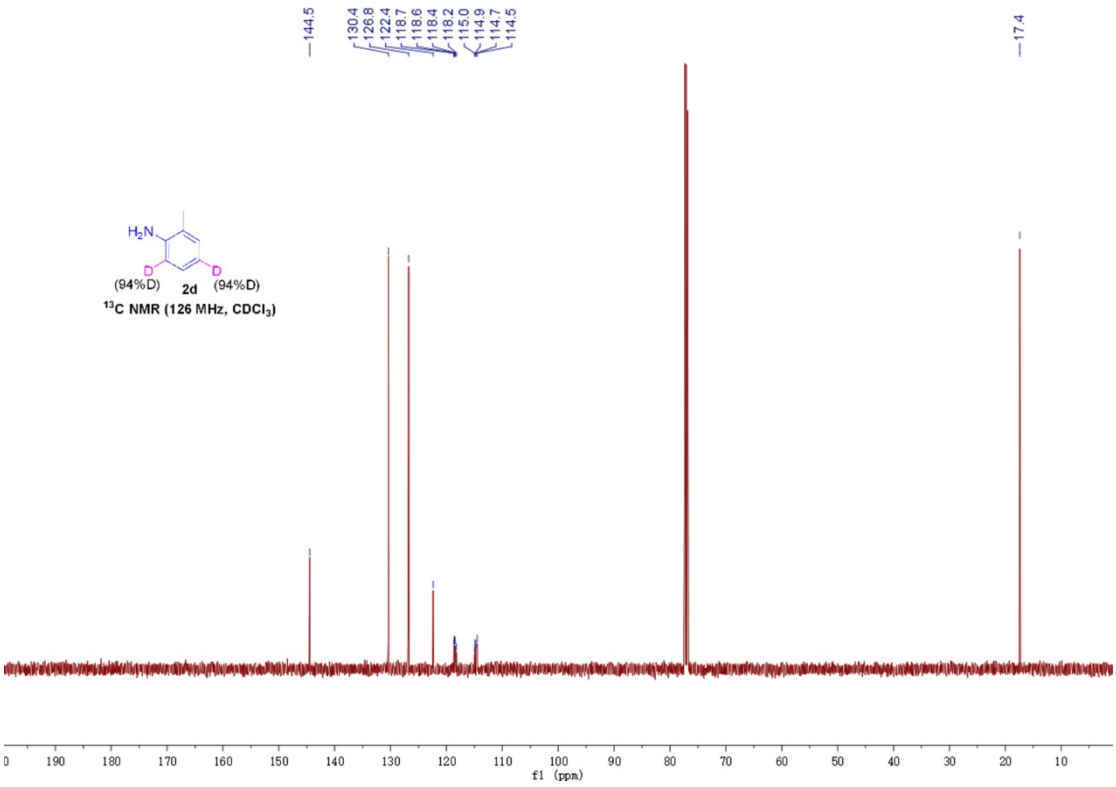

Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2d

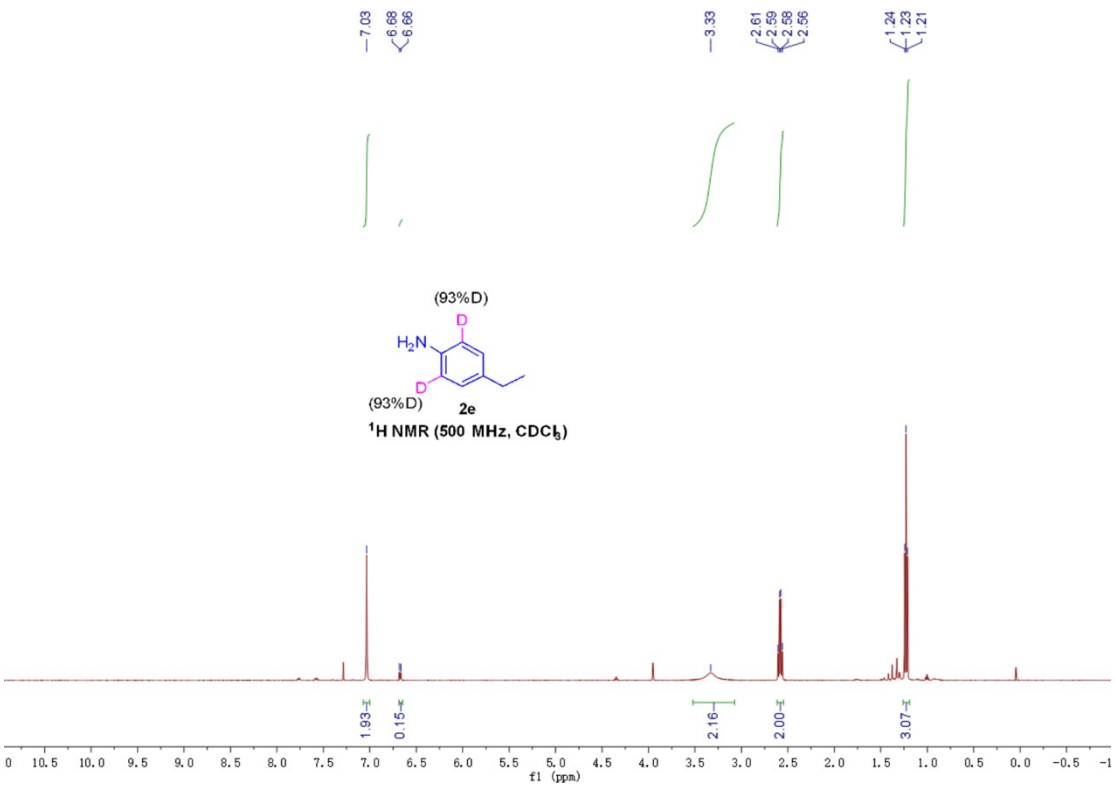

Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2e

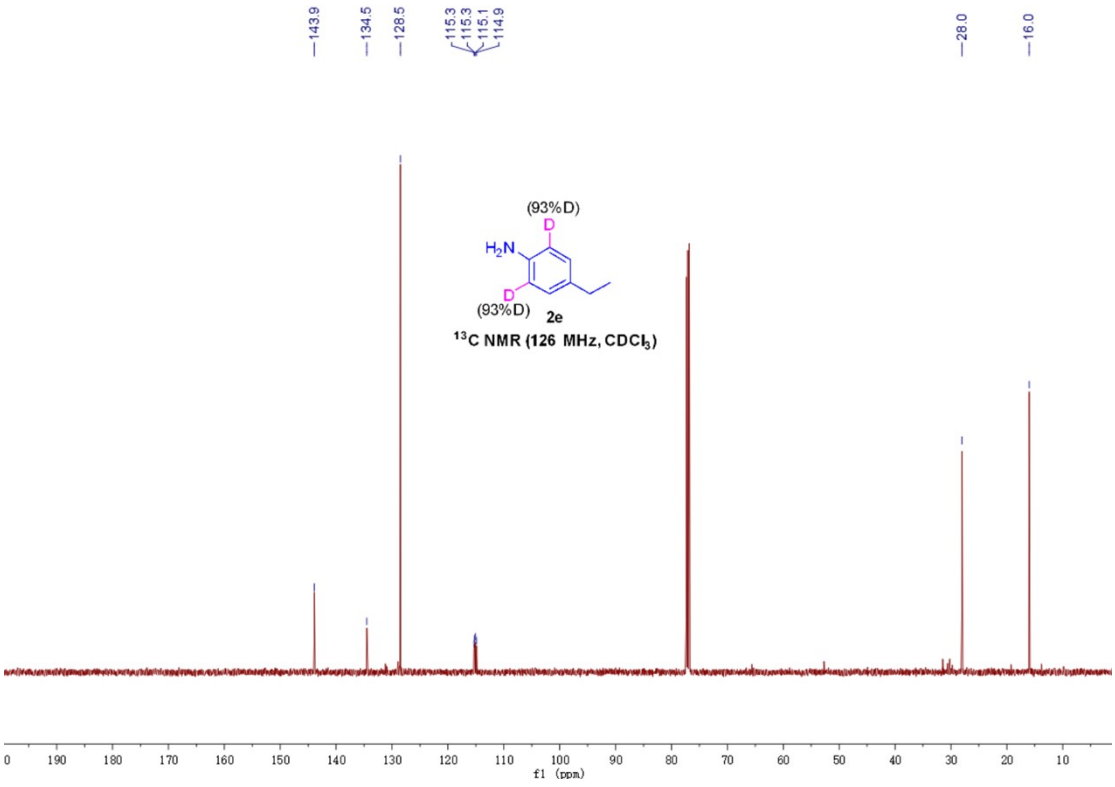

Figure S10. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2e

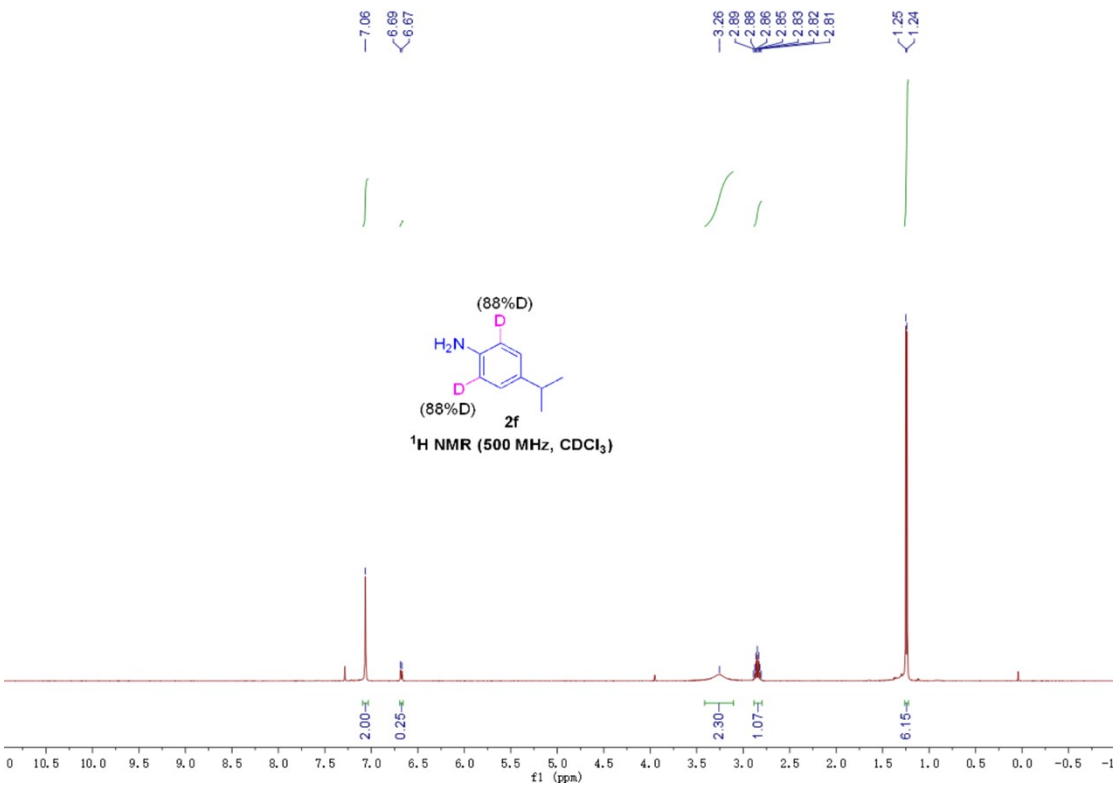

Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2f

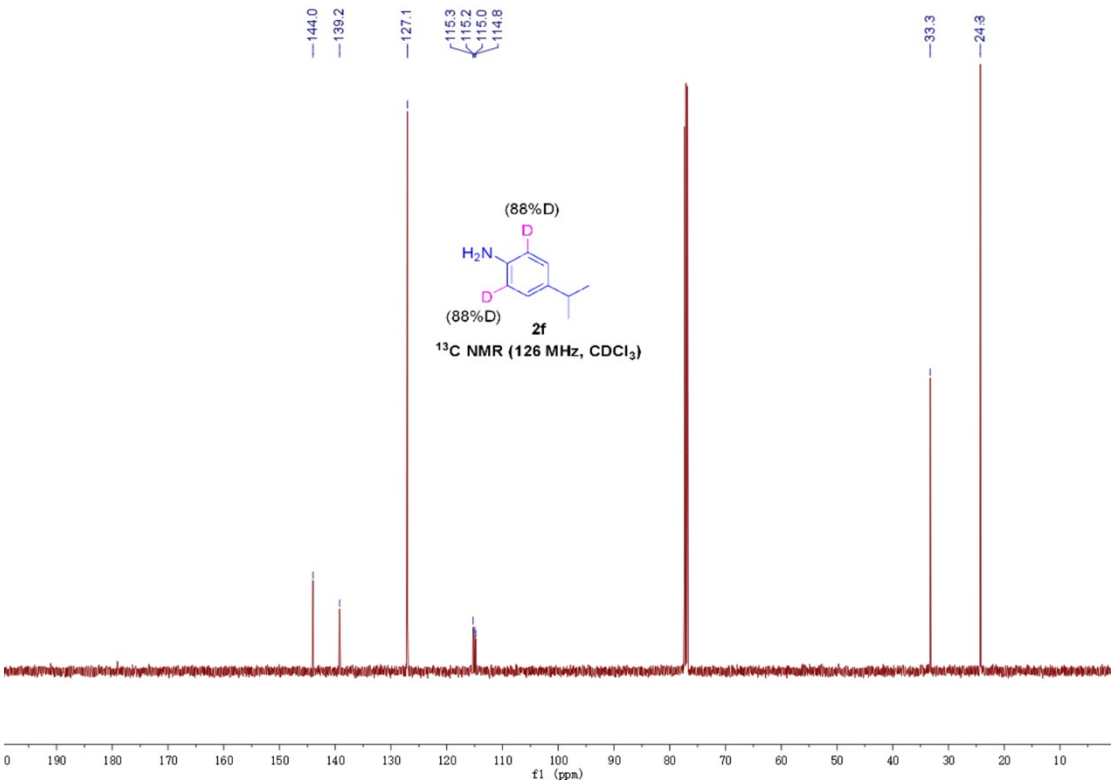

Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2f

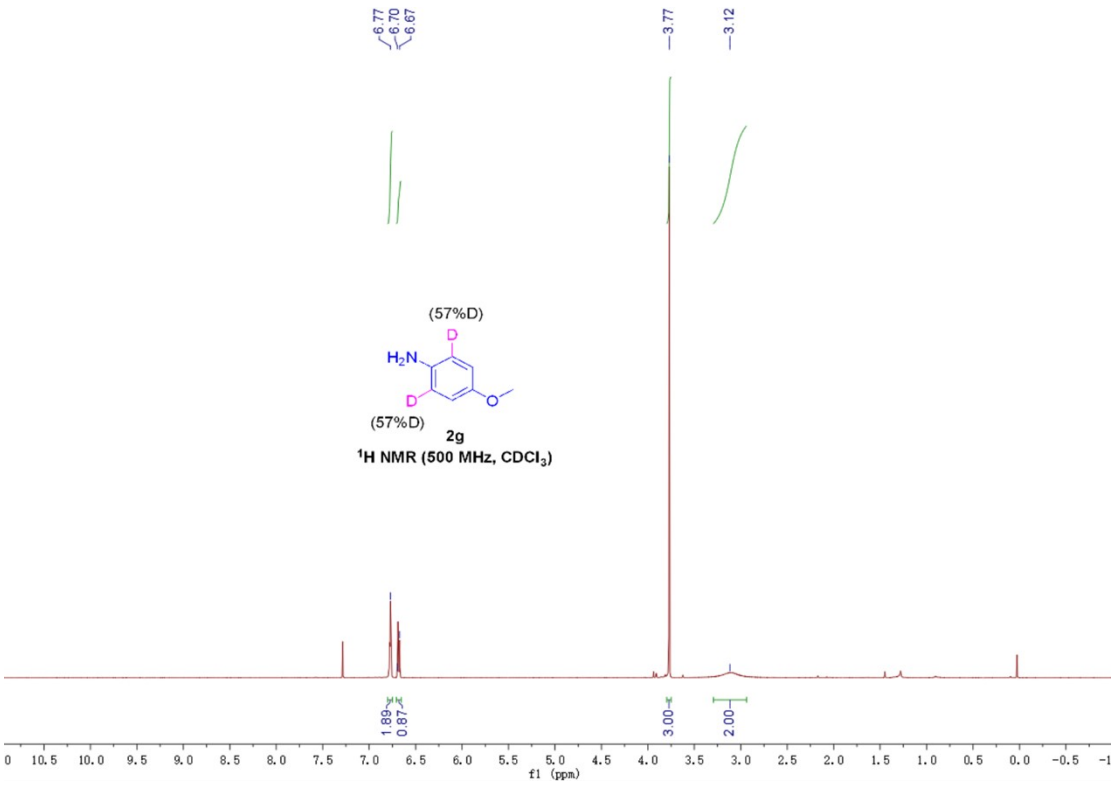

Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2g

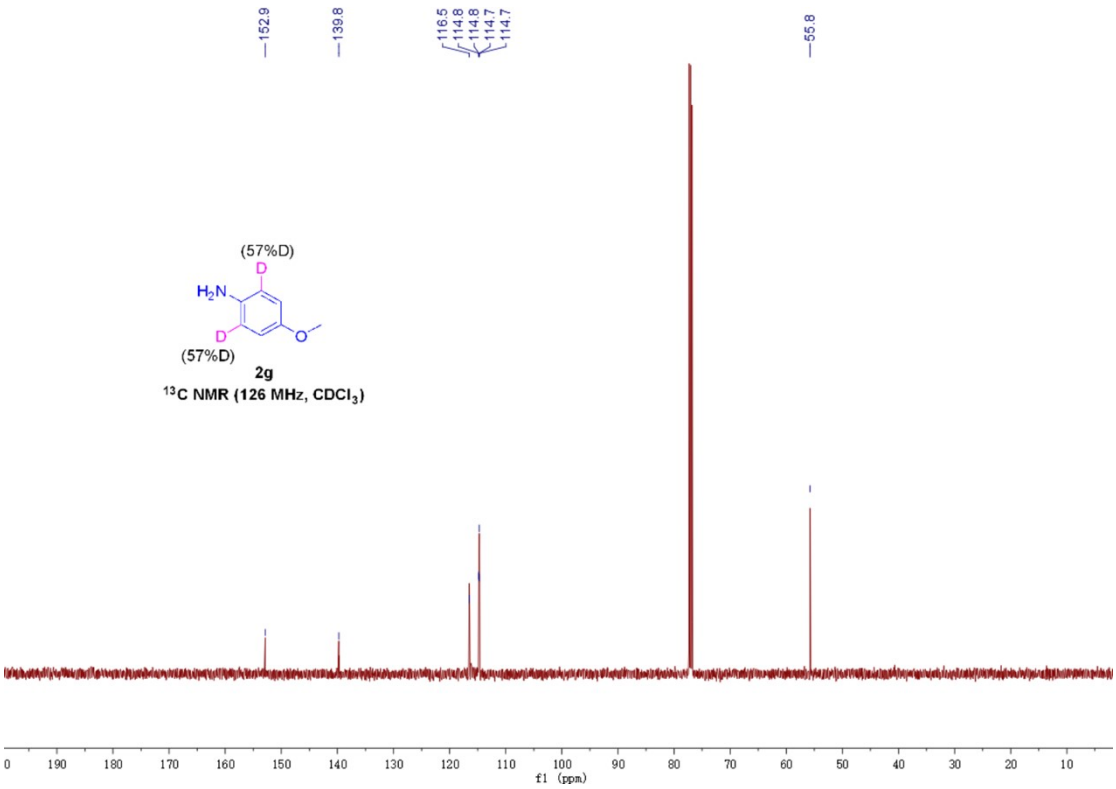

Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2g

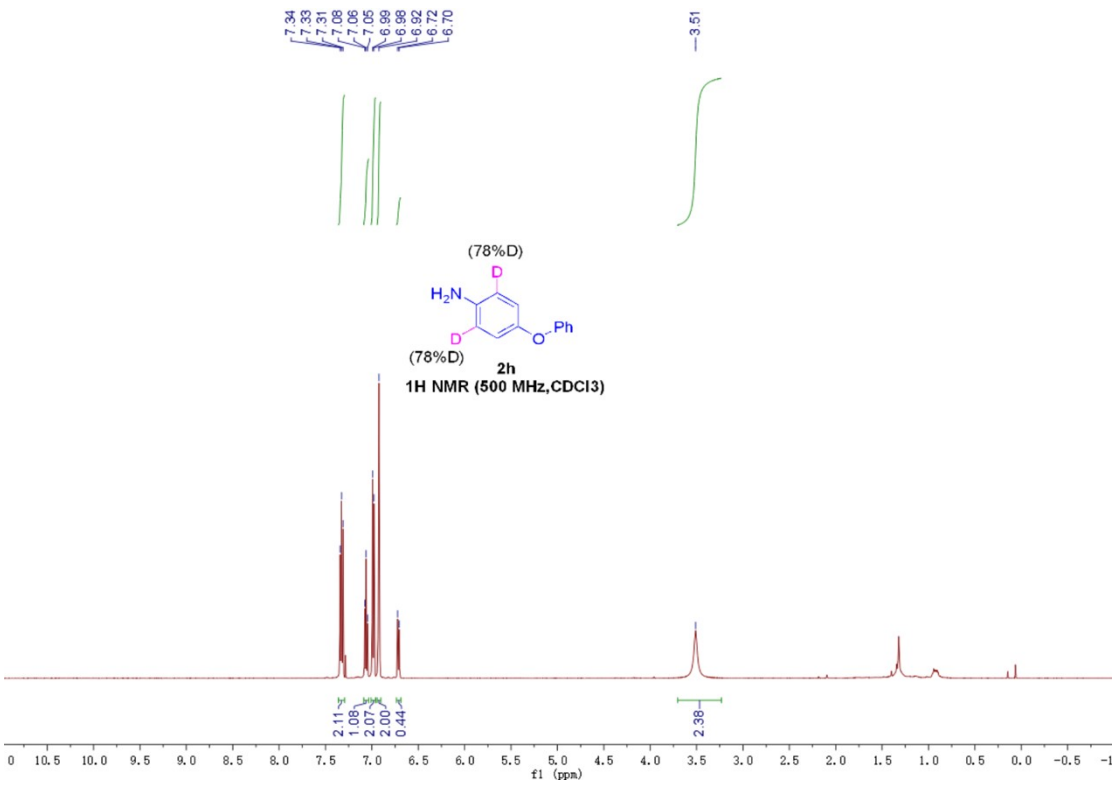

Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2h

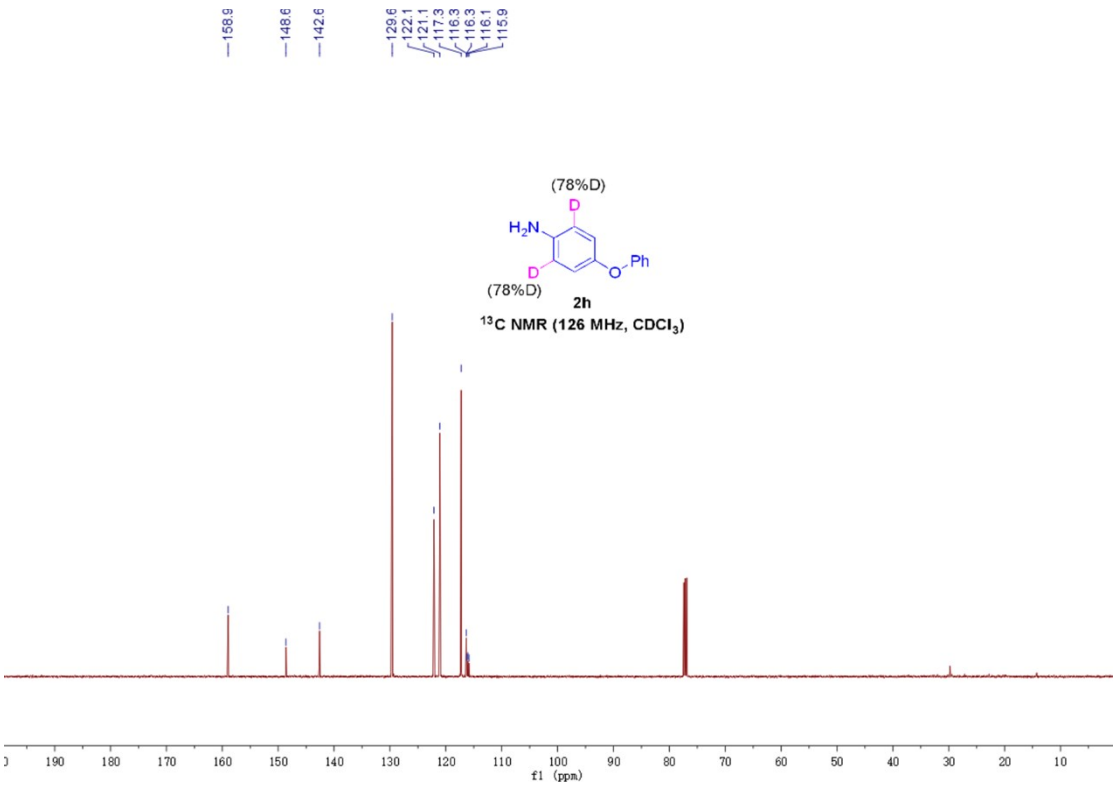

Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2h

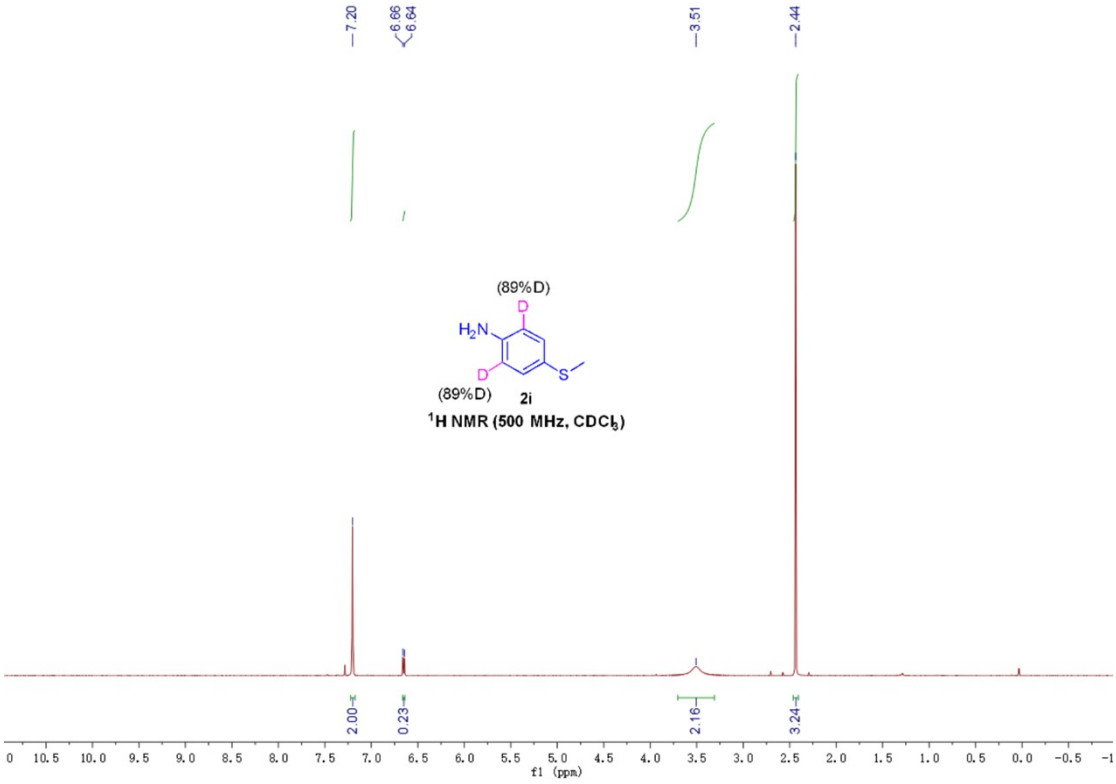

Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2i

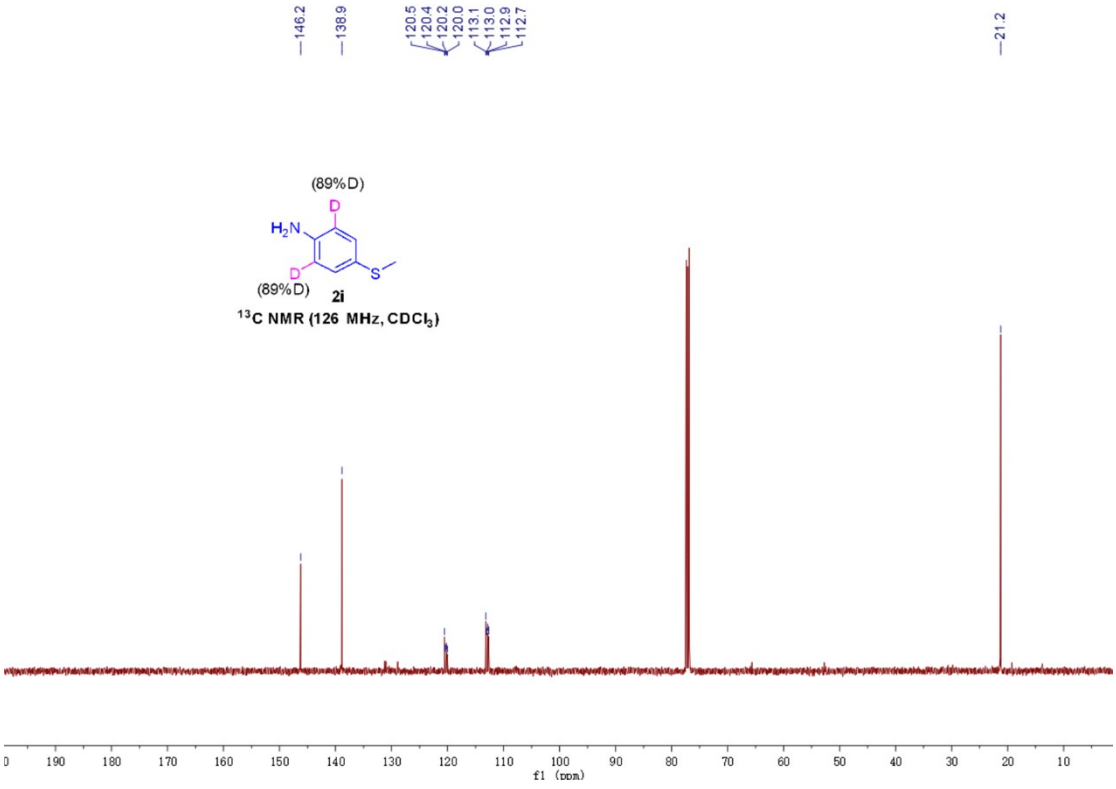

Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2i

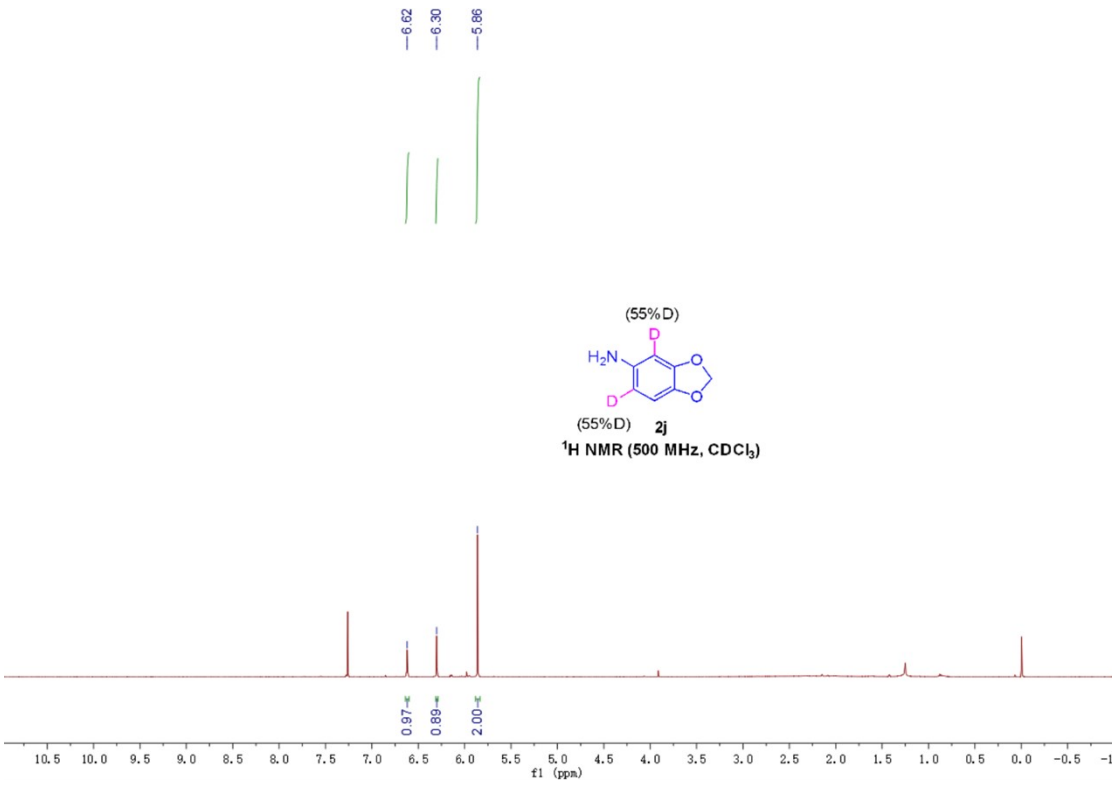

Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2j

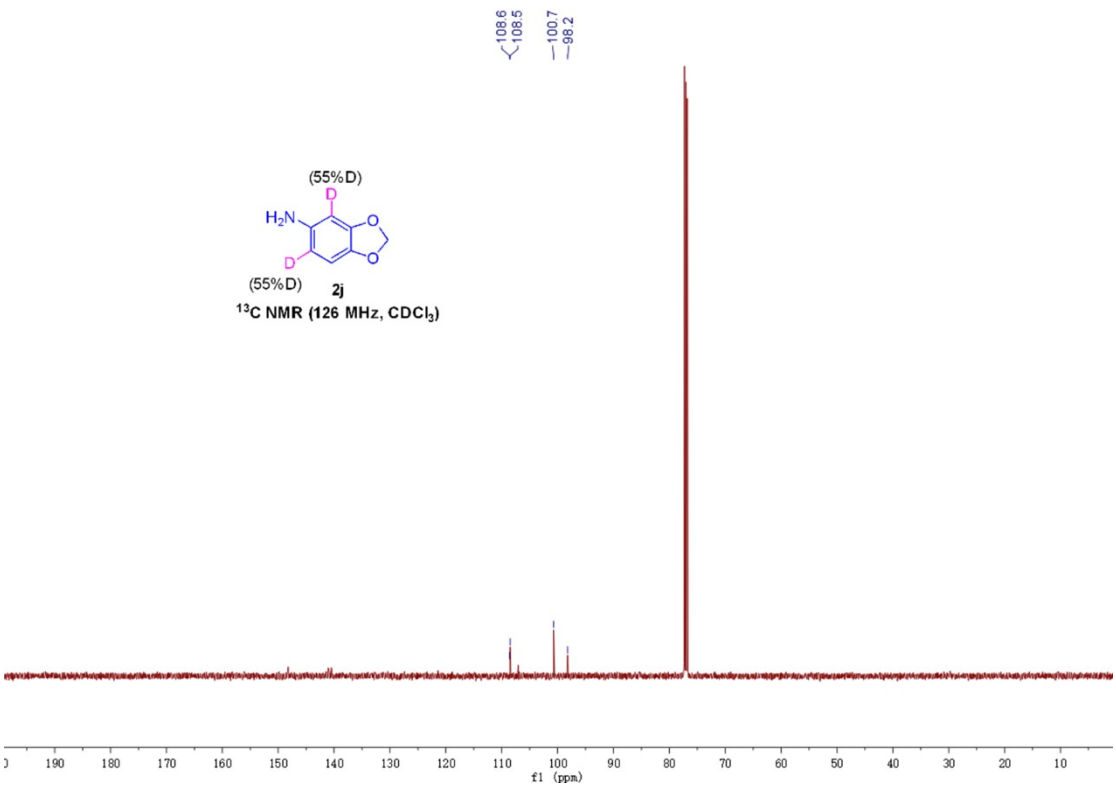

Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2j

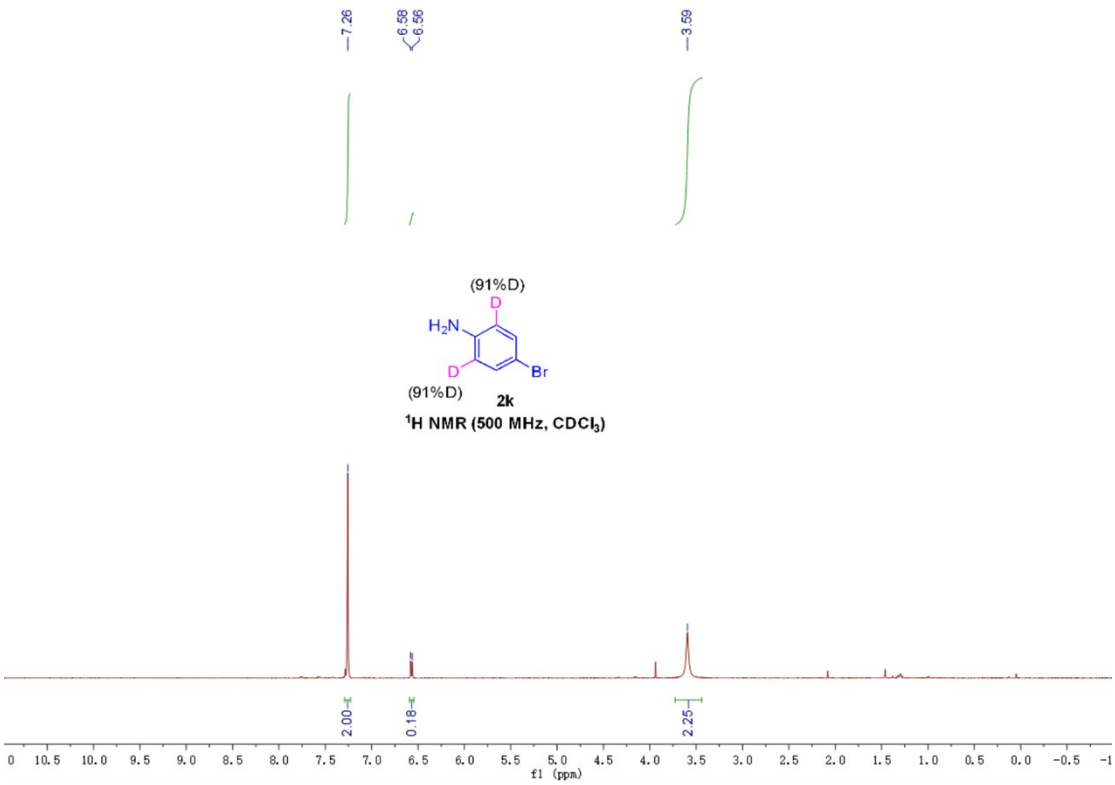

Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2k

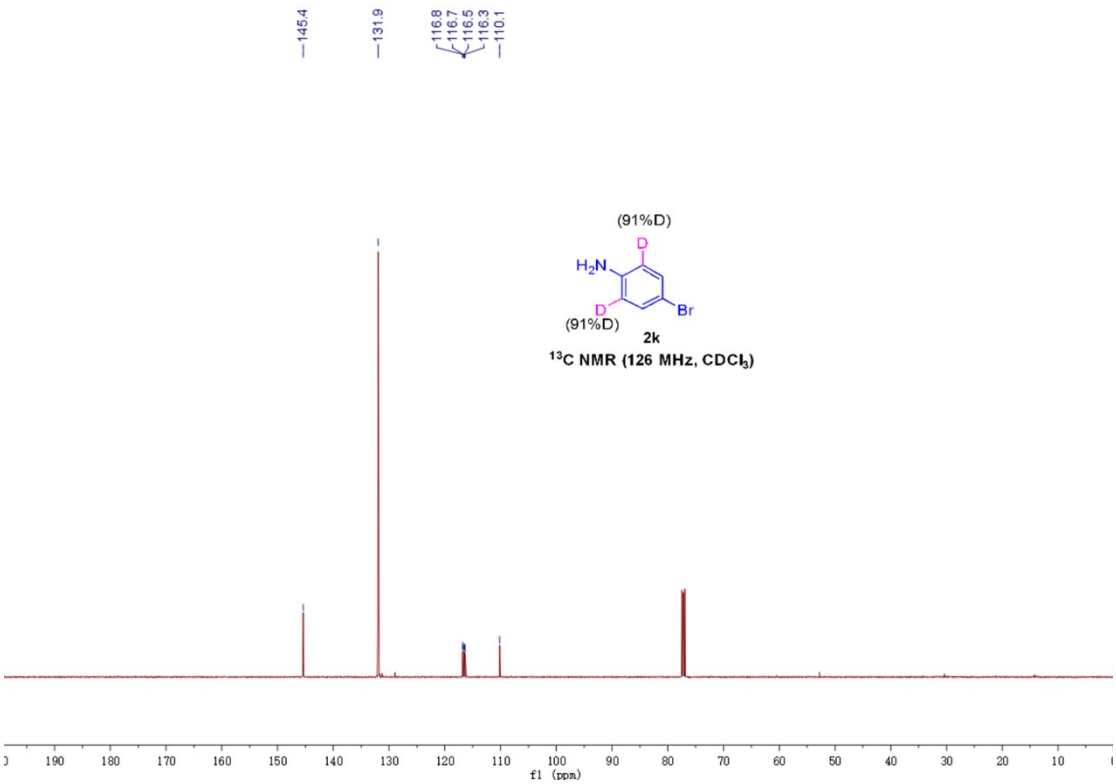

Figure S22. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2k

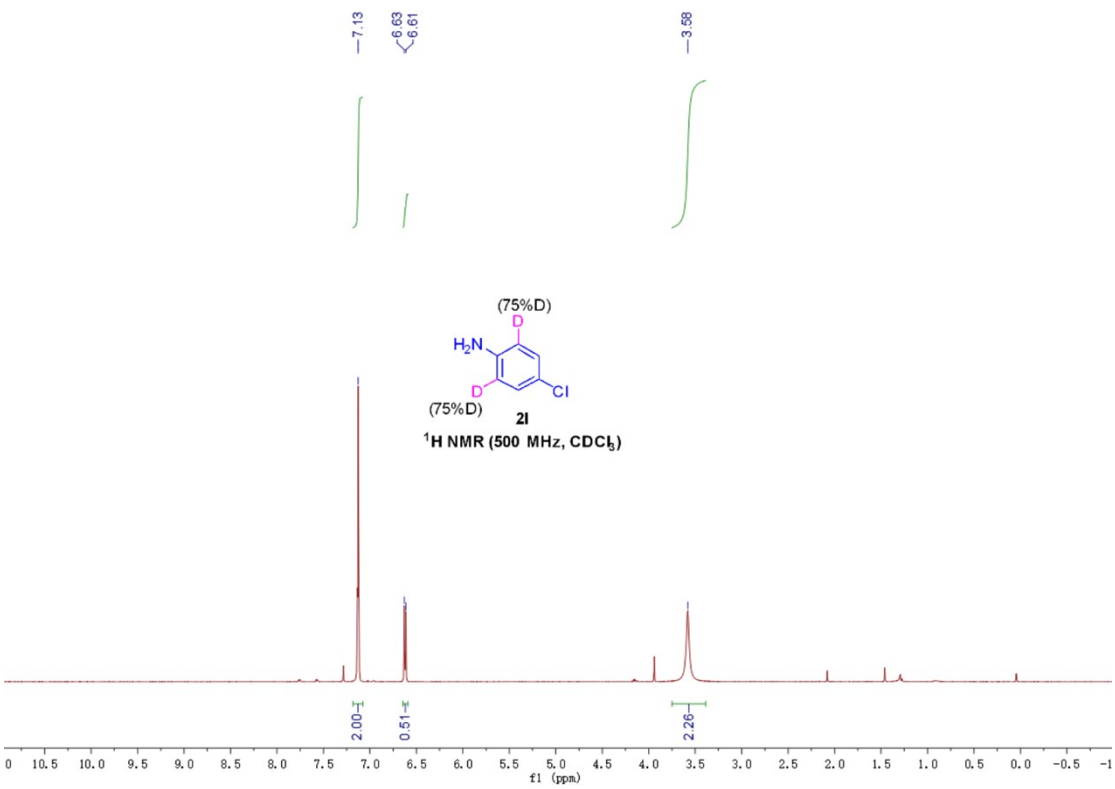

Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2l

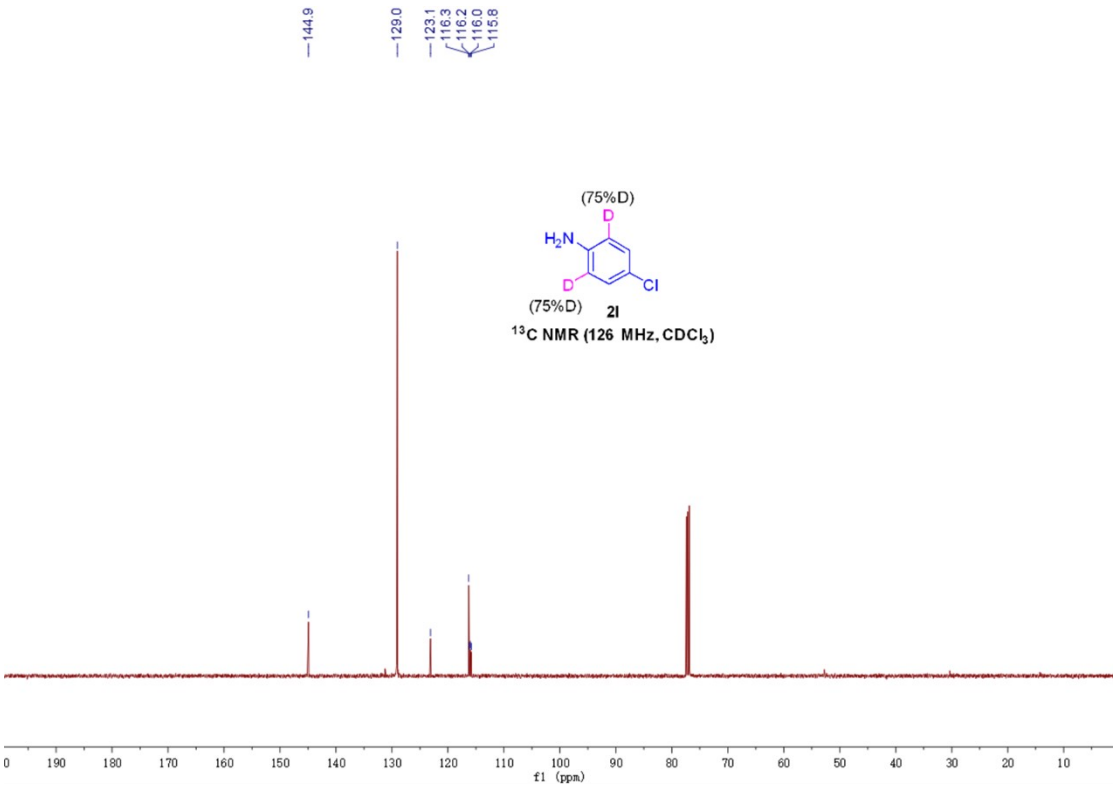

Figure S24. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2l

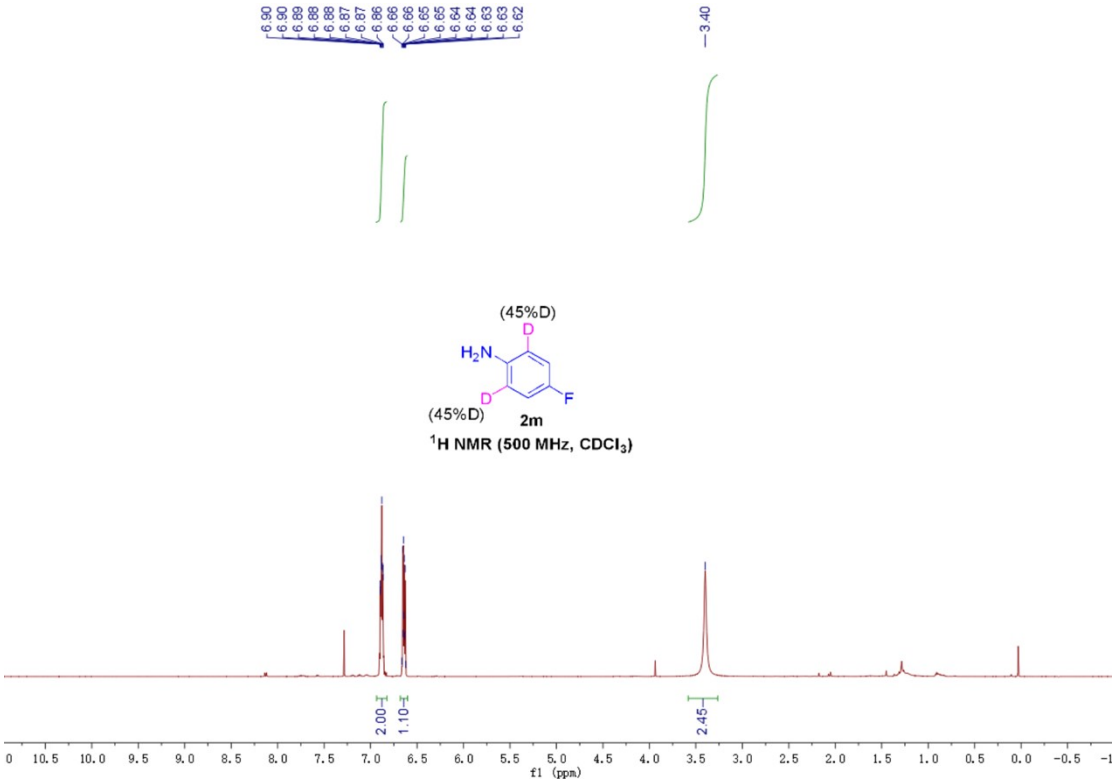

Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2m

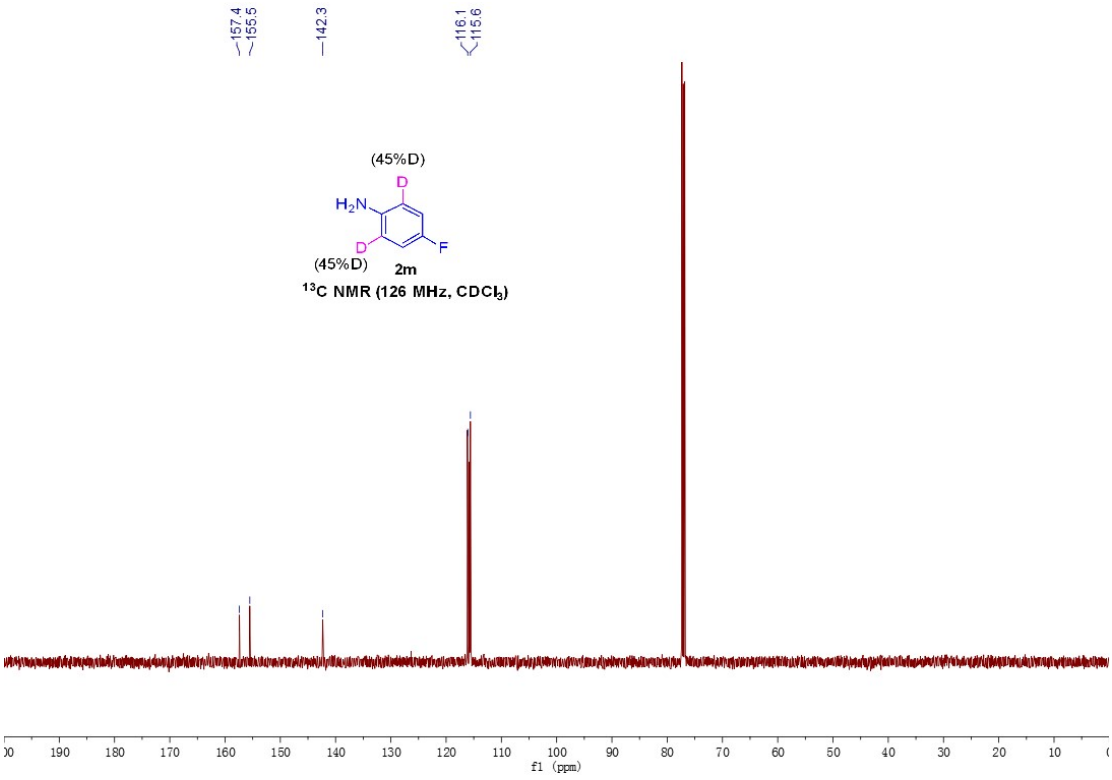

Figure S26. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2m

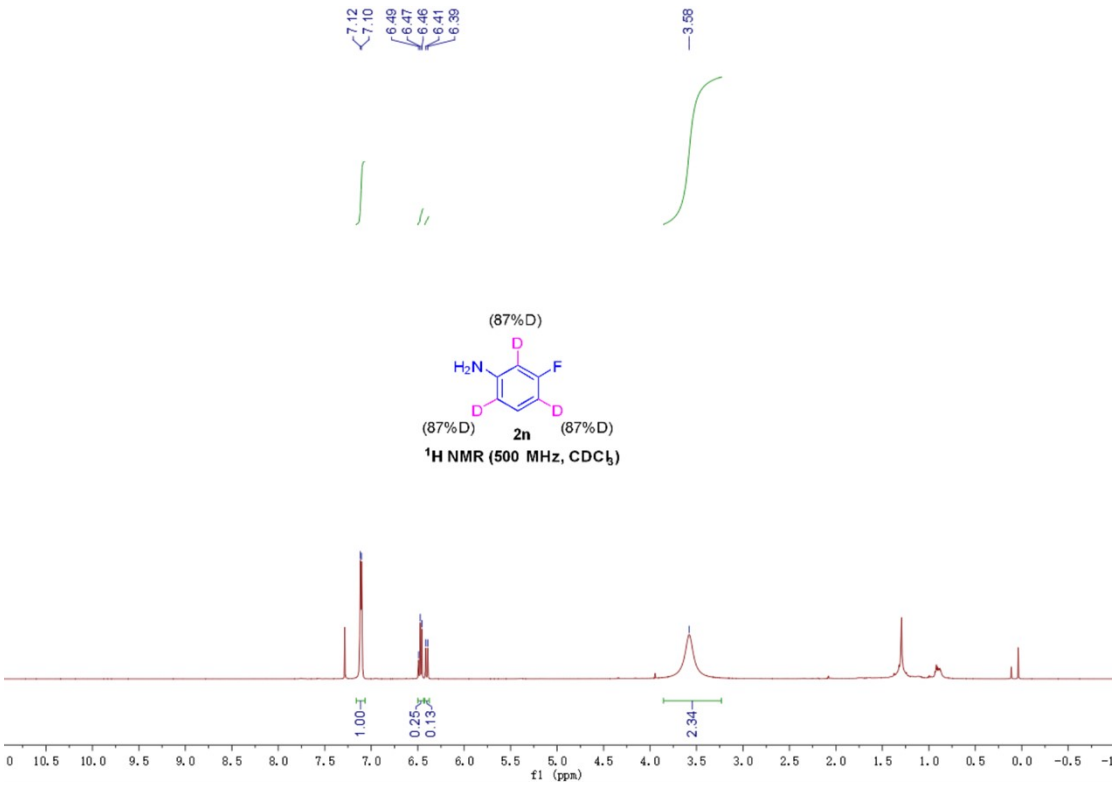

Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2n

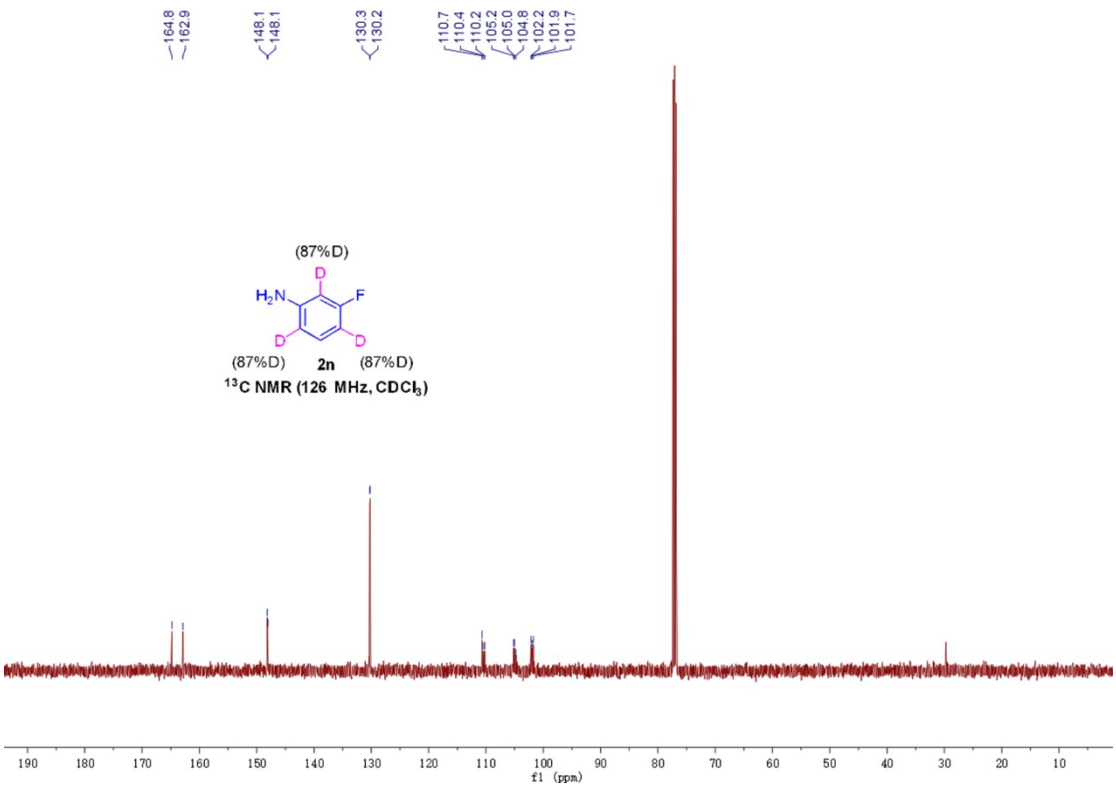

Figure S28. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2n

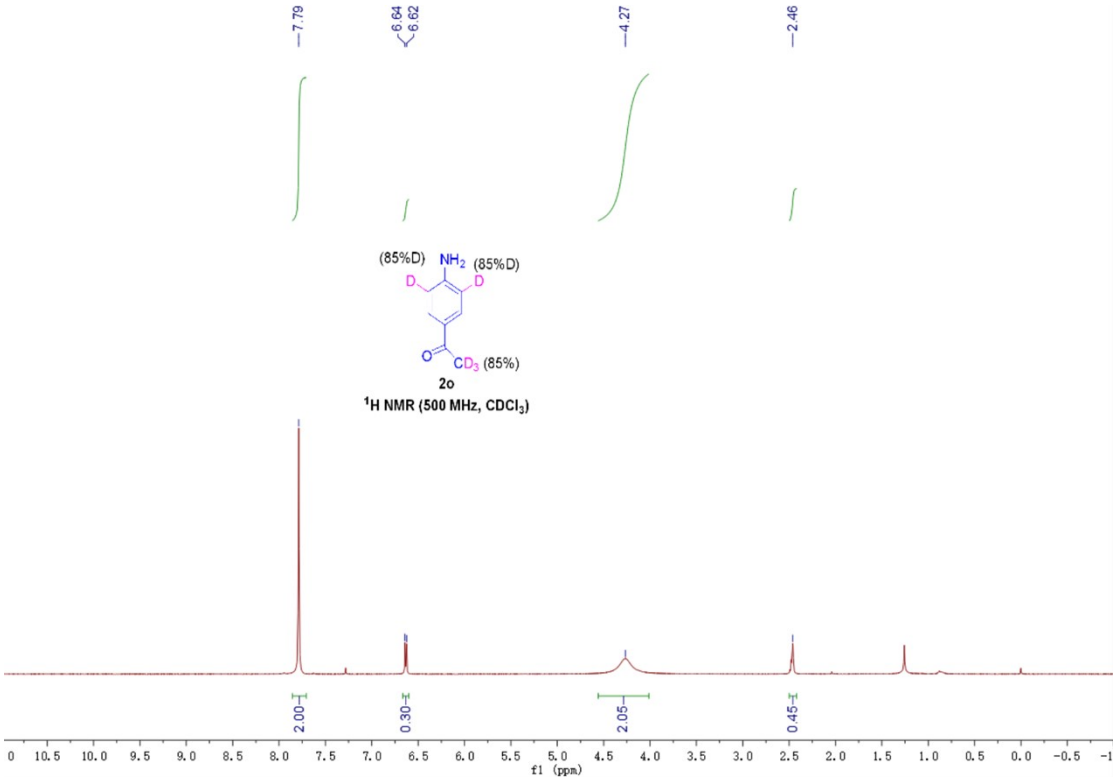

Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2o

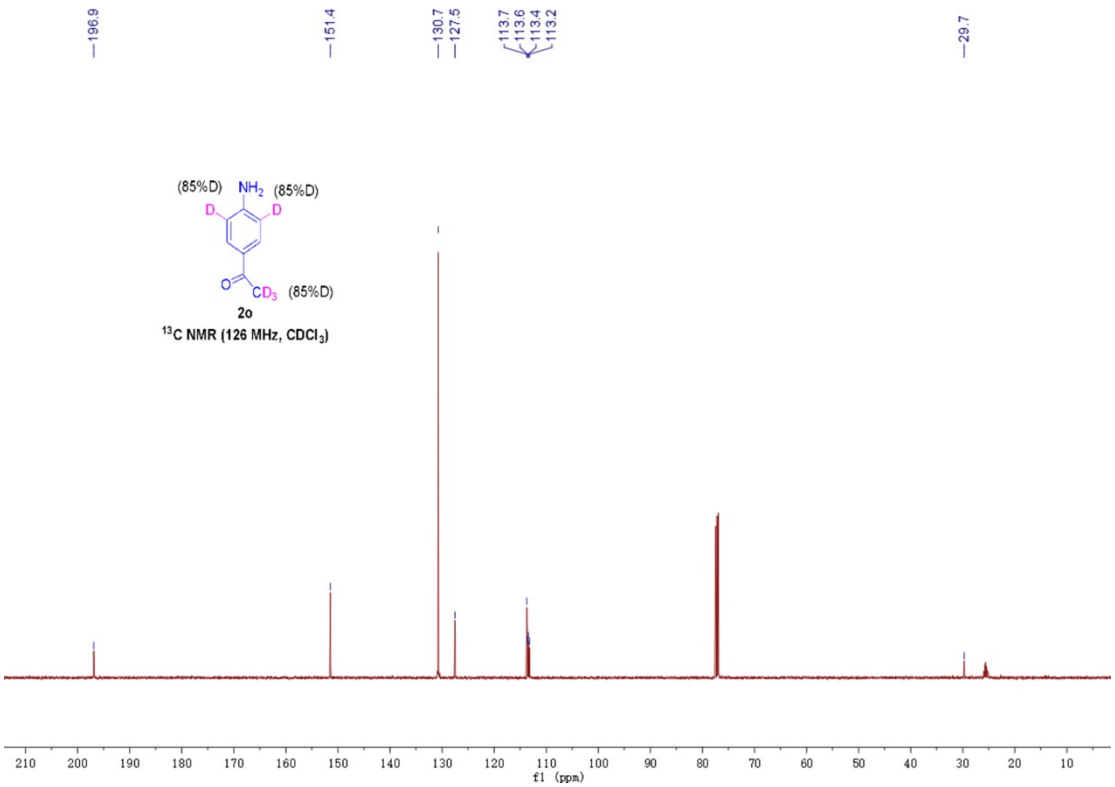

Figure S30. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2o

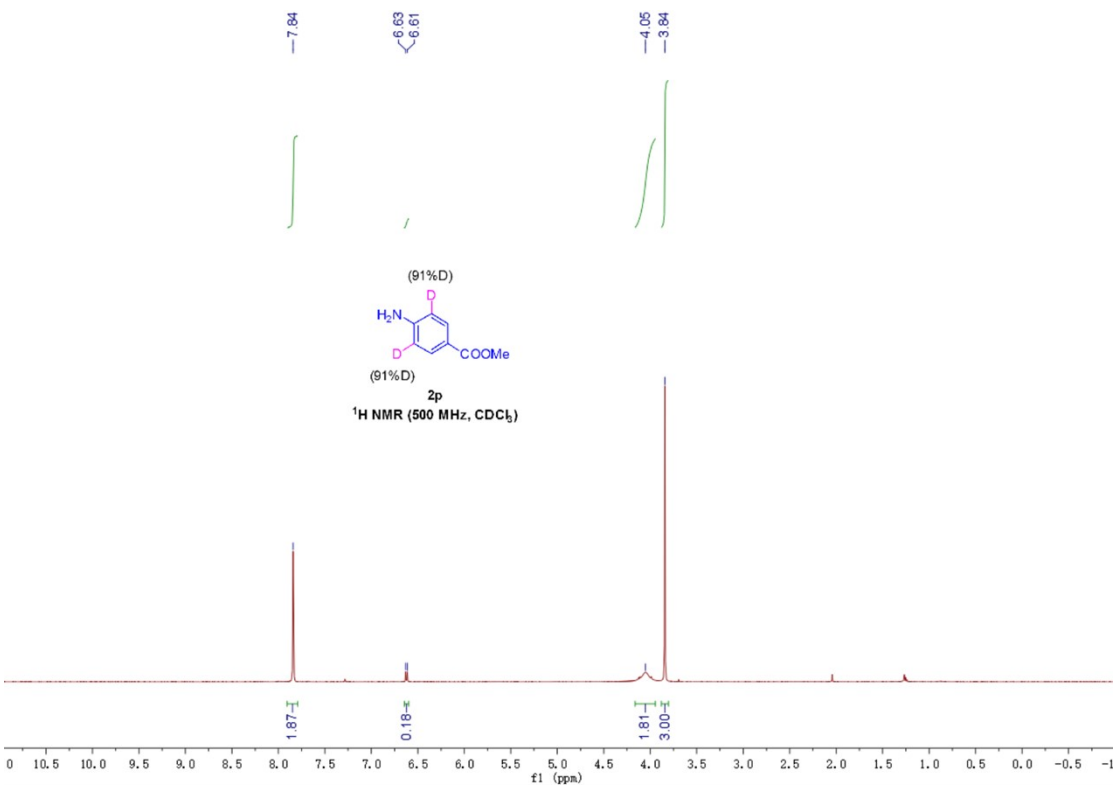

Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2p

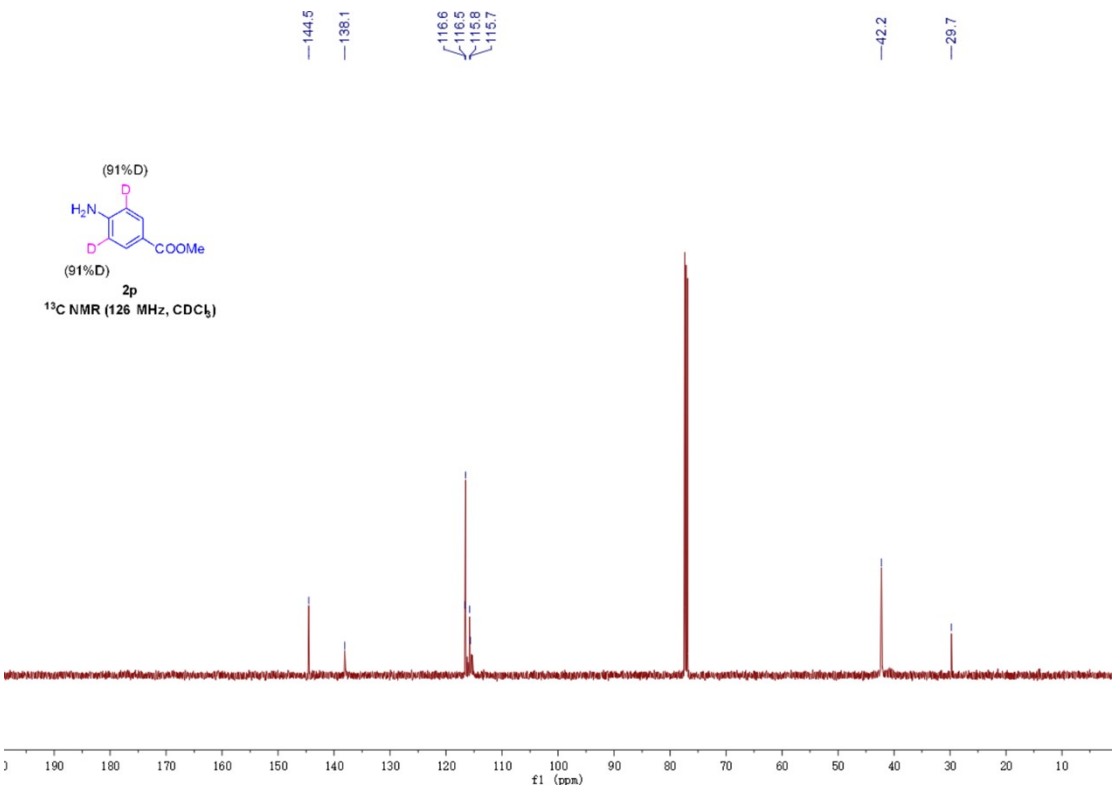

Figure S32. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2p

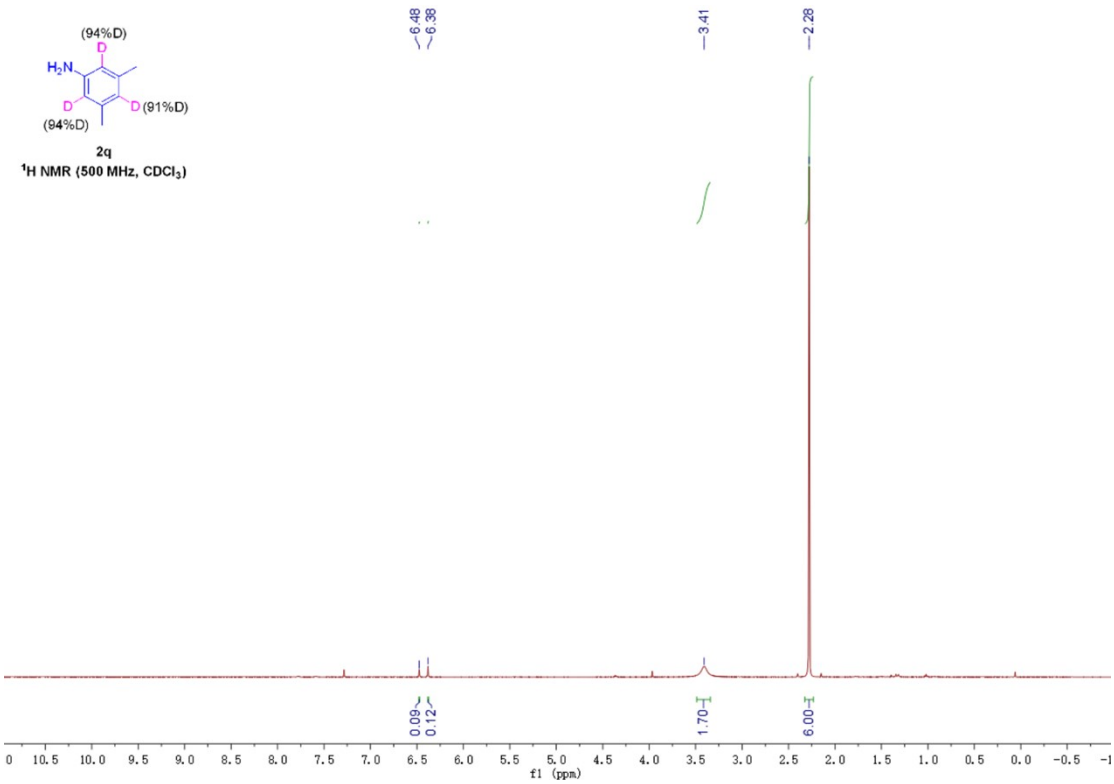

Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2q

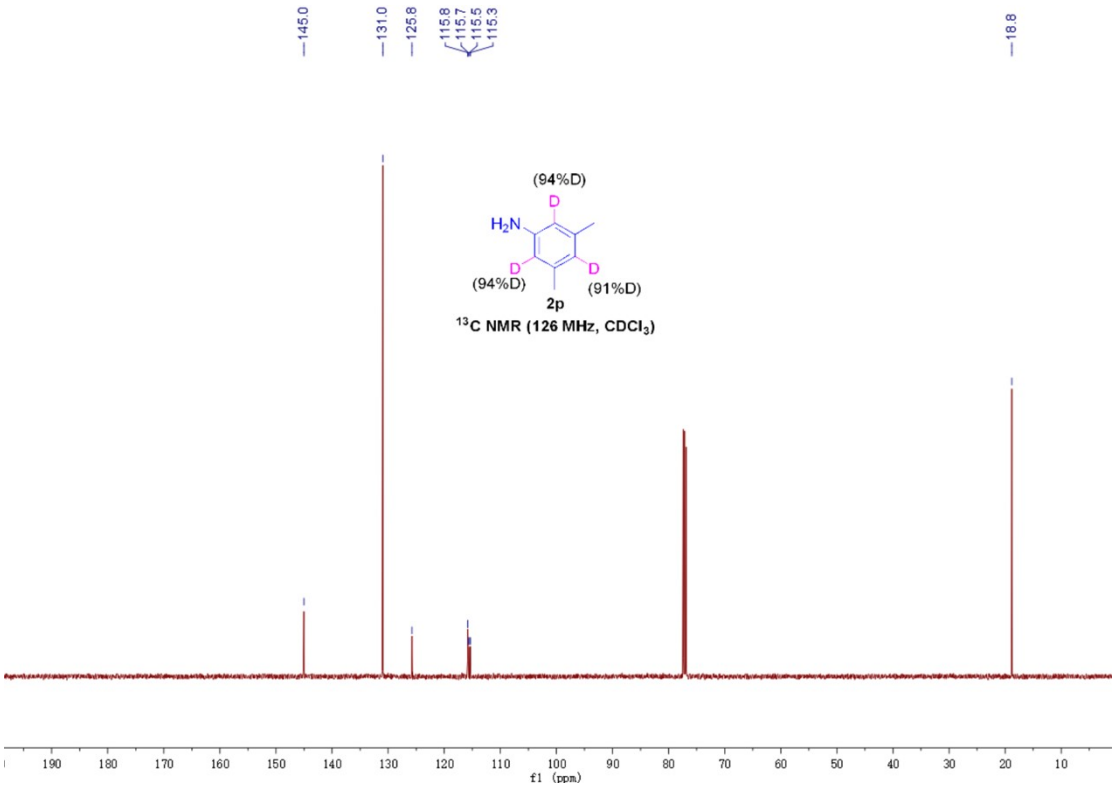

Figure S34. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2q

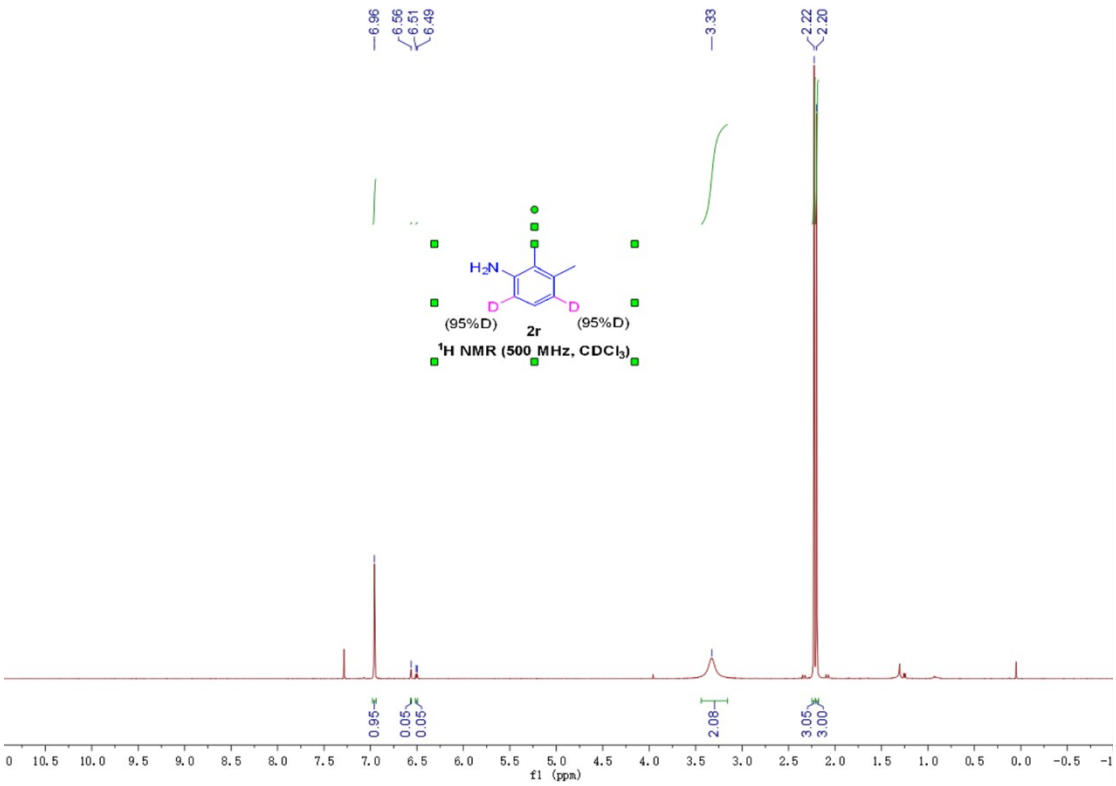

Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2r

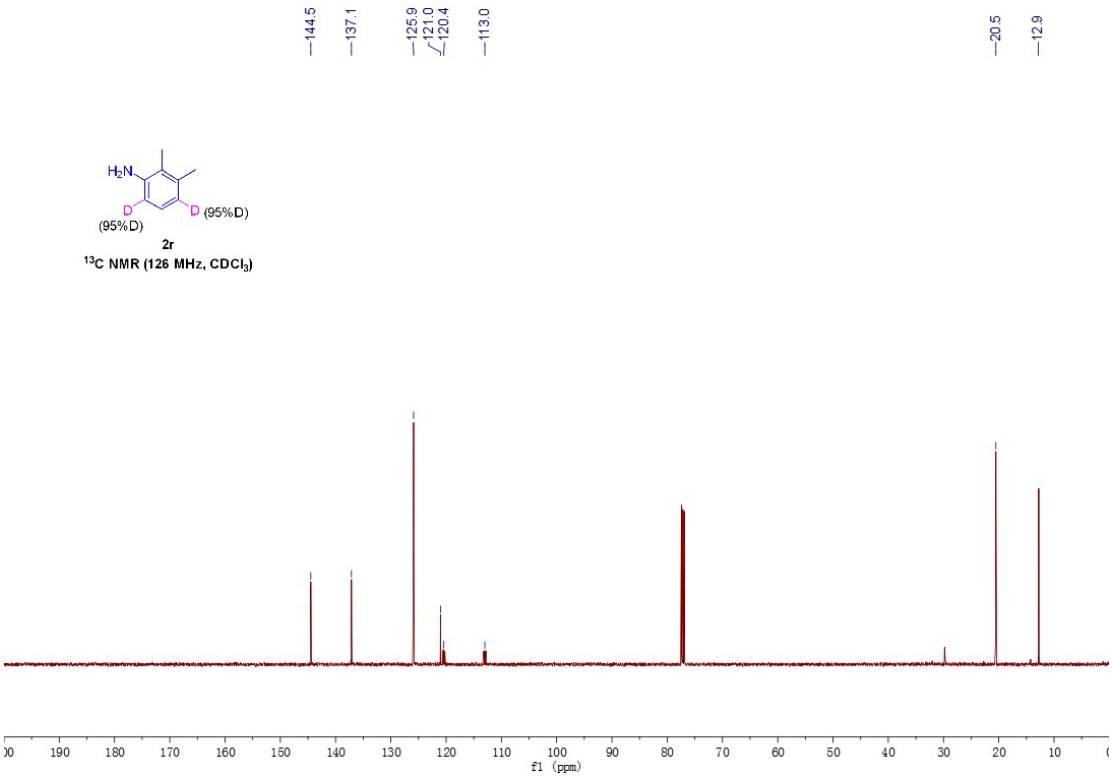

Figure S36. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2r

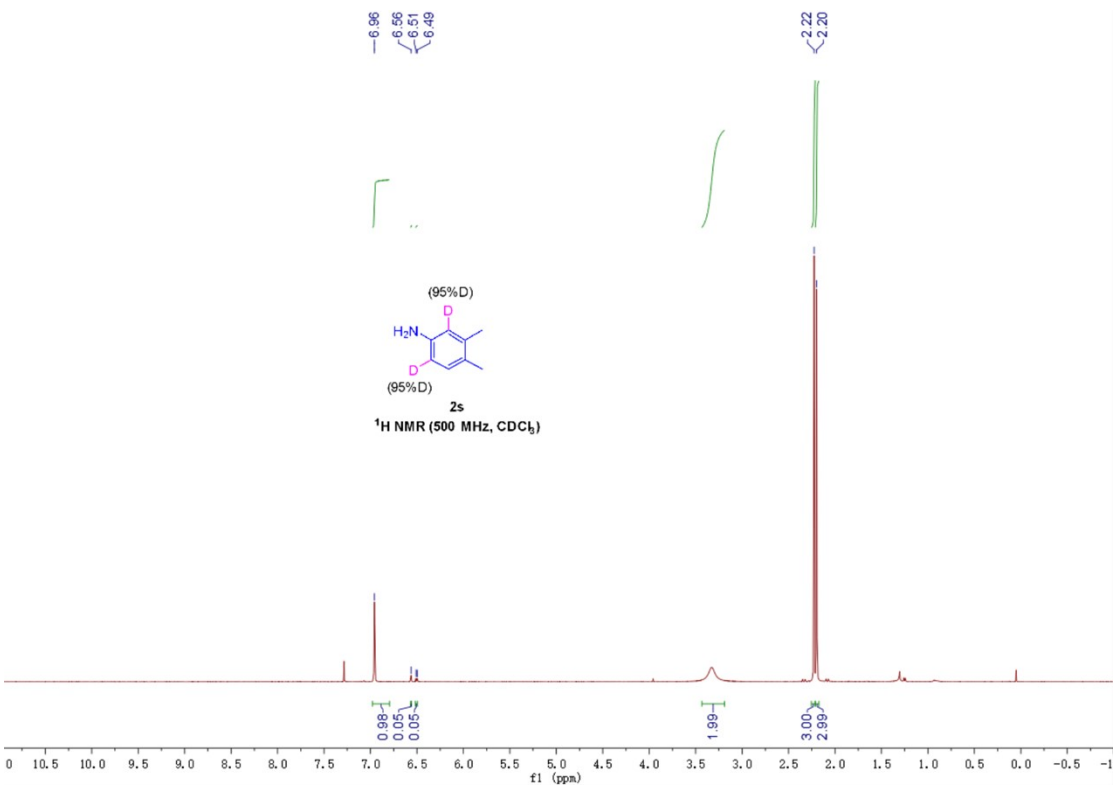

Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2s

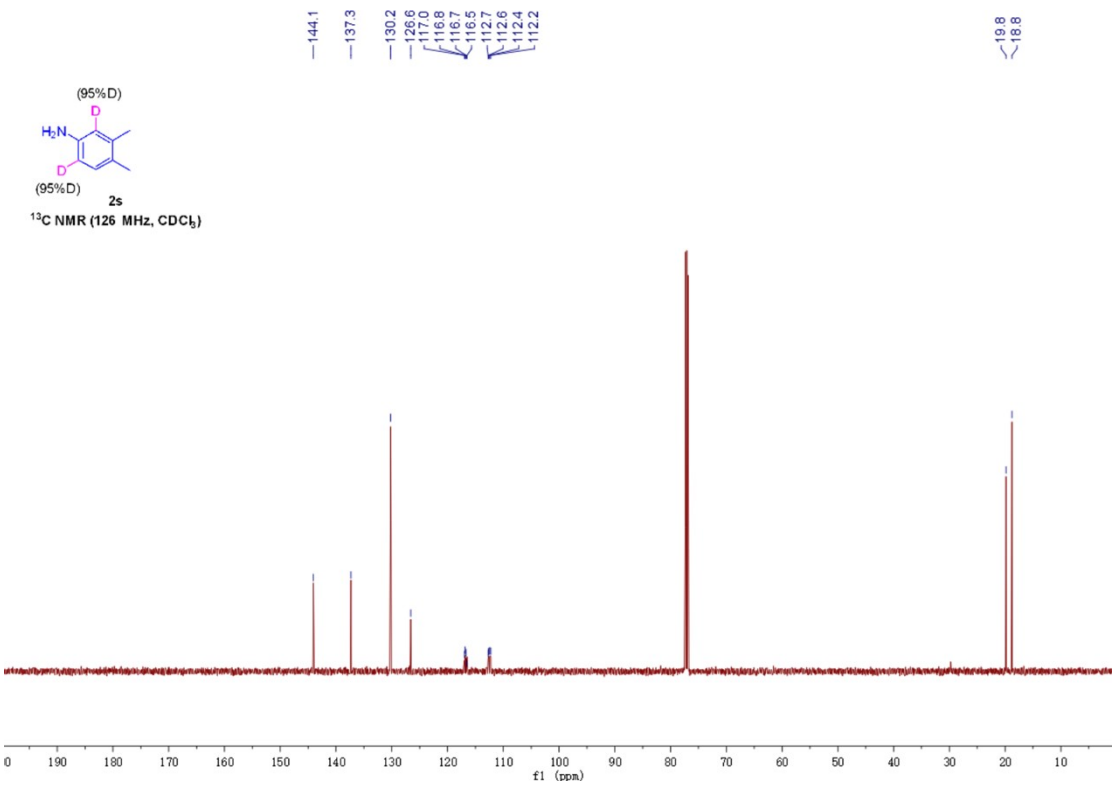

Figure S38. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2s

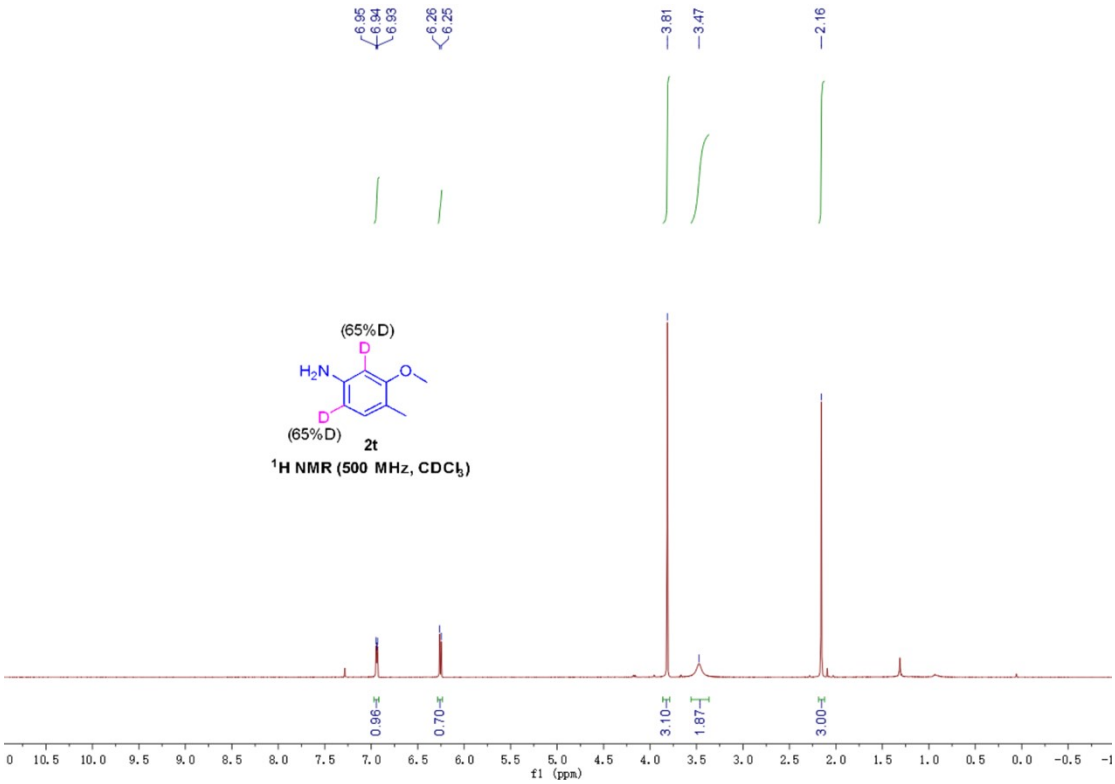

Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2t

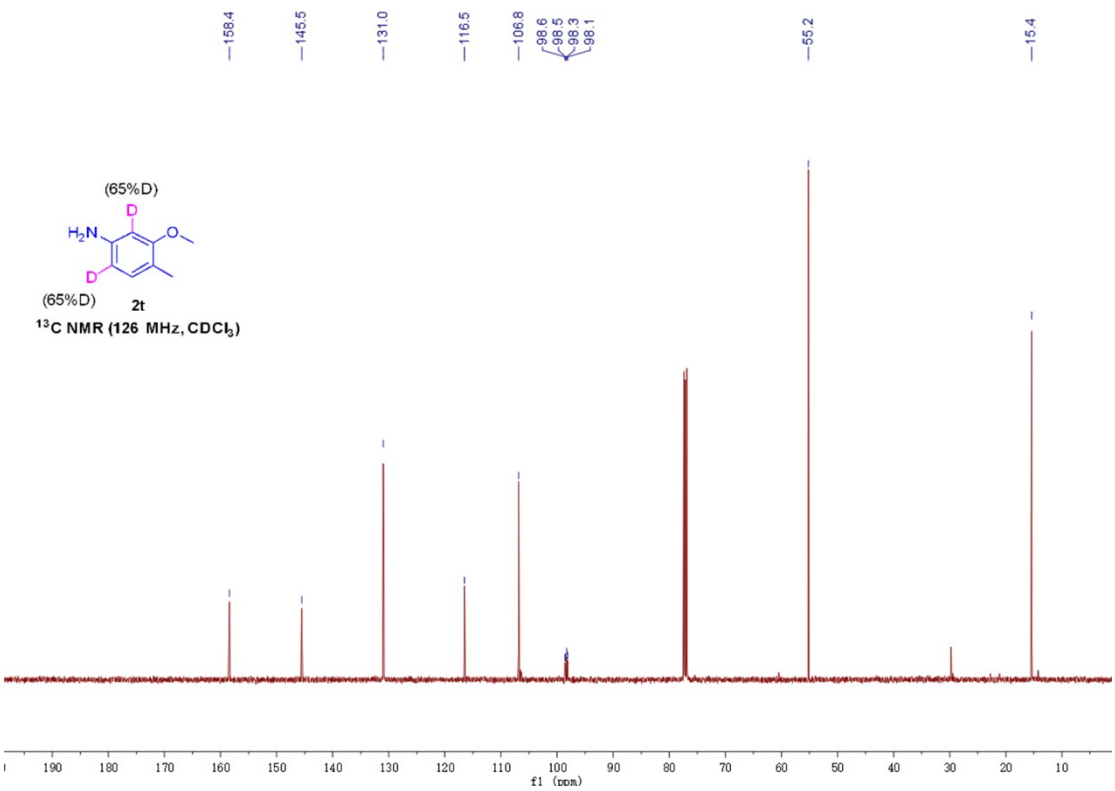

Figure S40. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2t

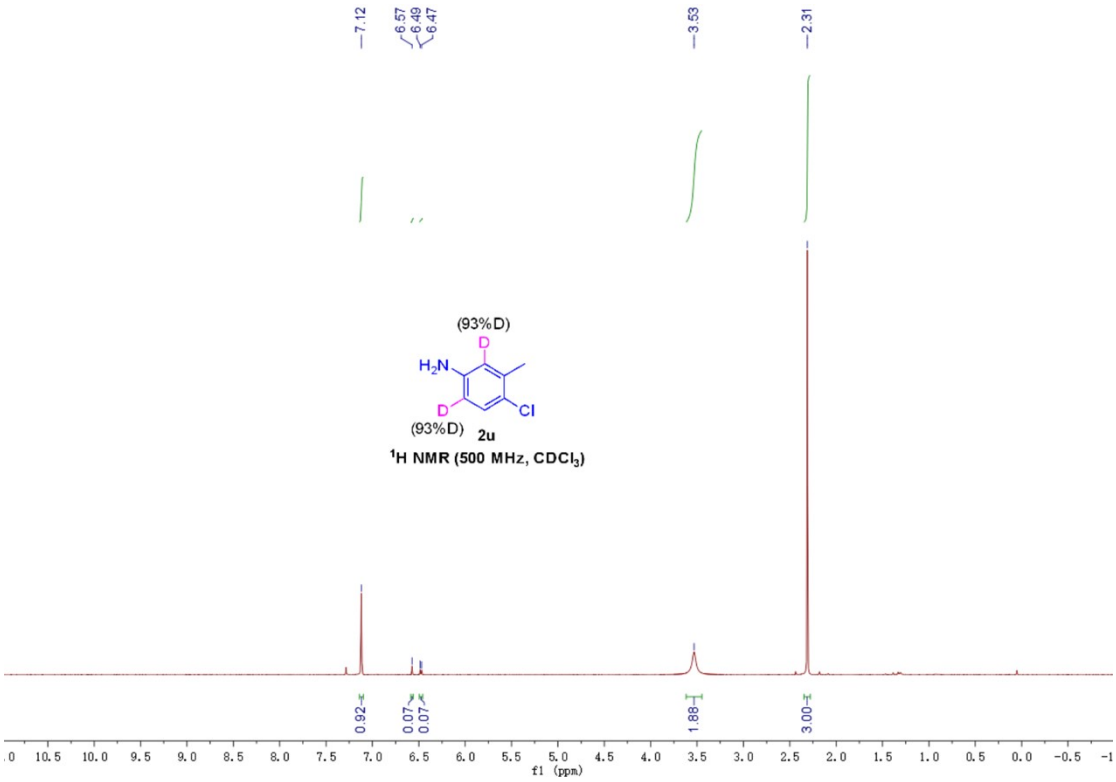

Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2u

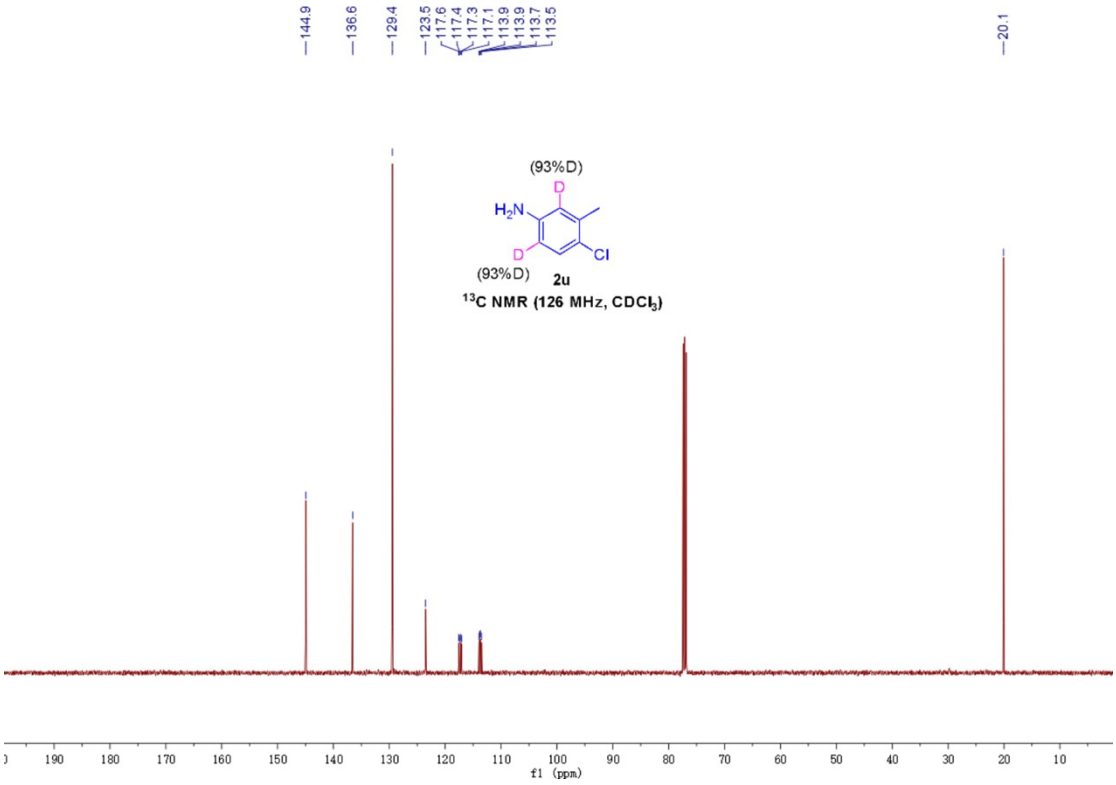

Figure S42. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2u

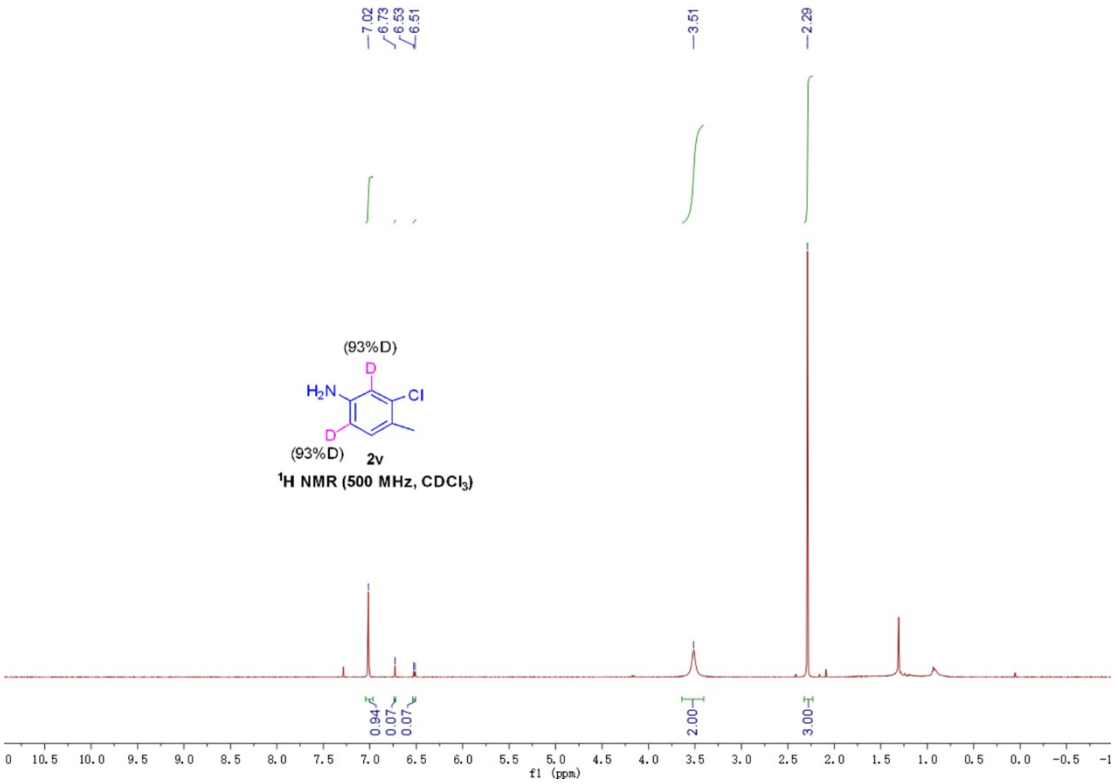

Figure S43. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2v

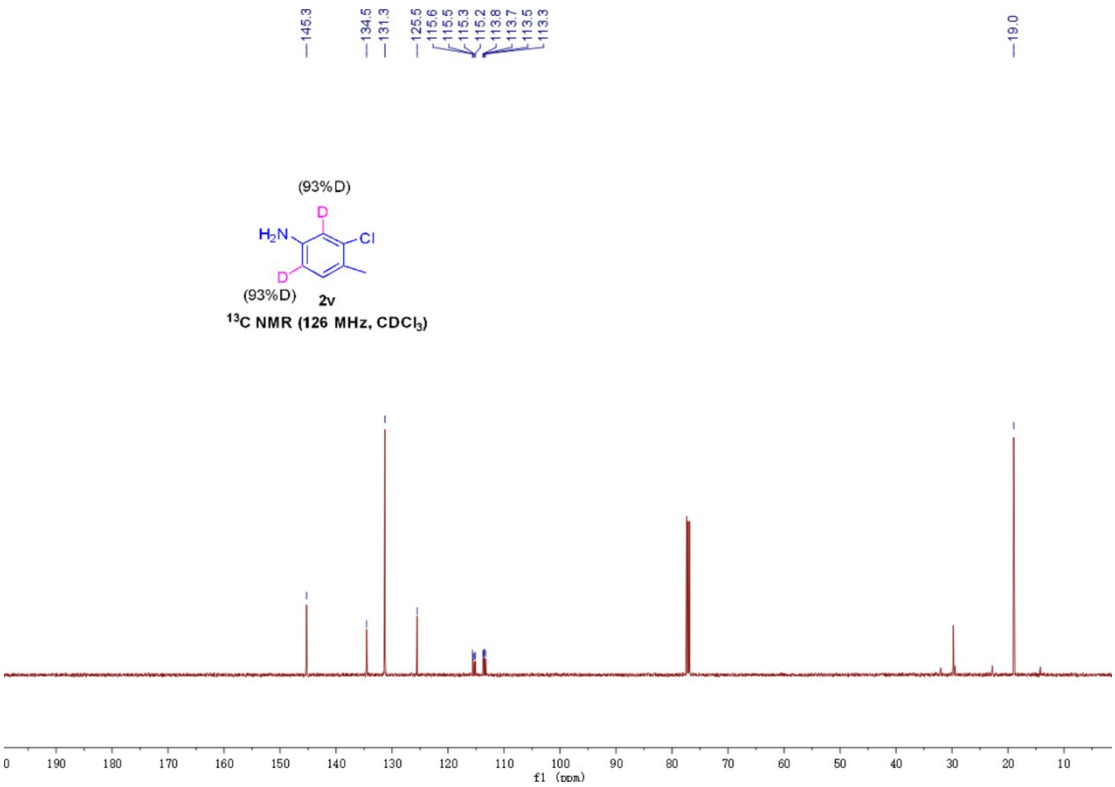

Figure S44. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2v

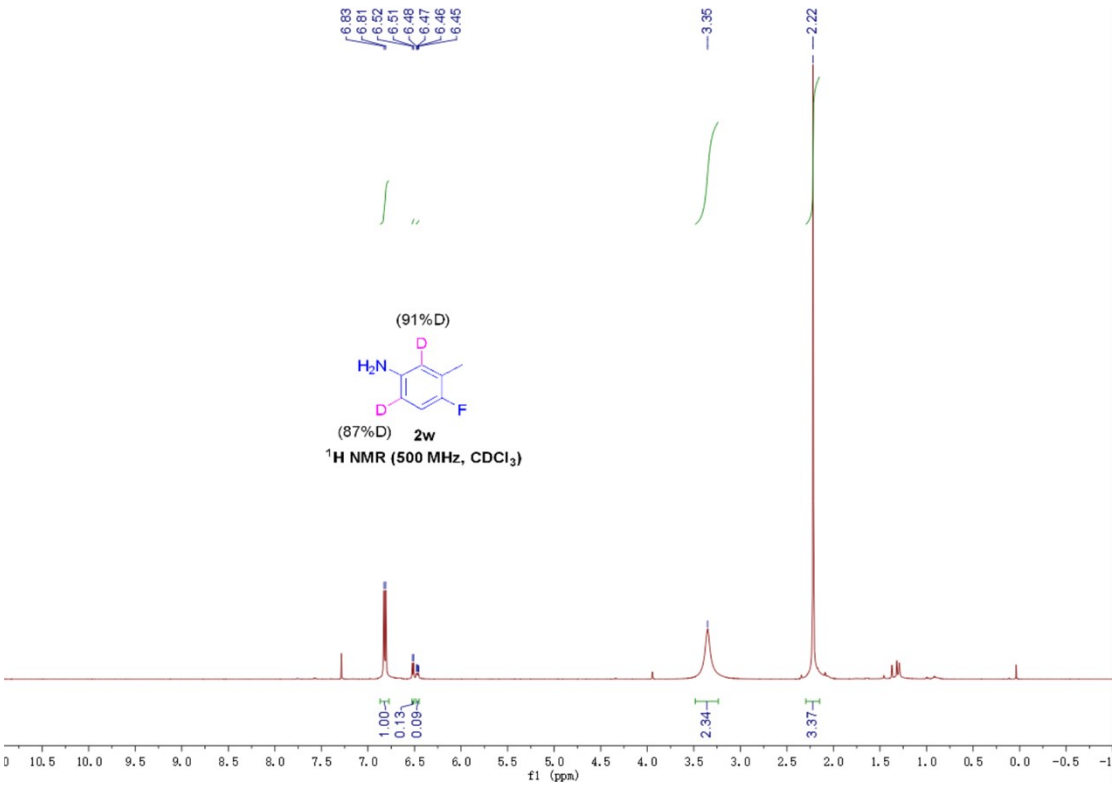

Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2w

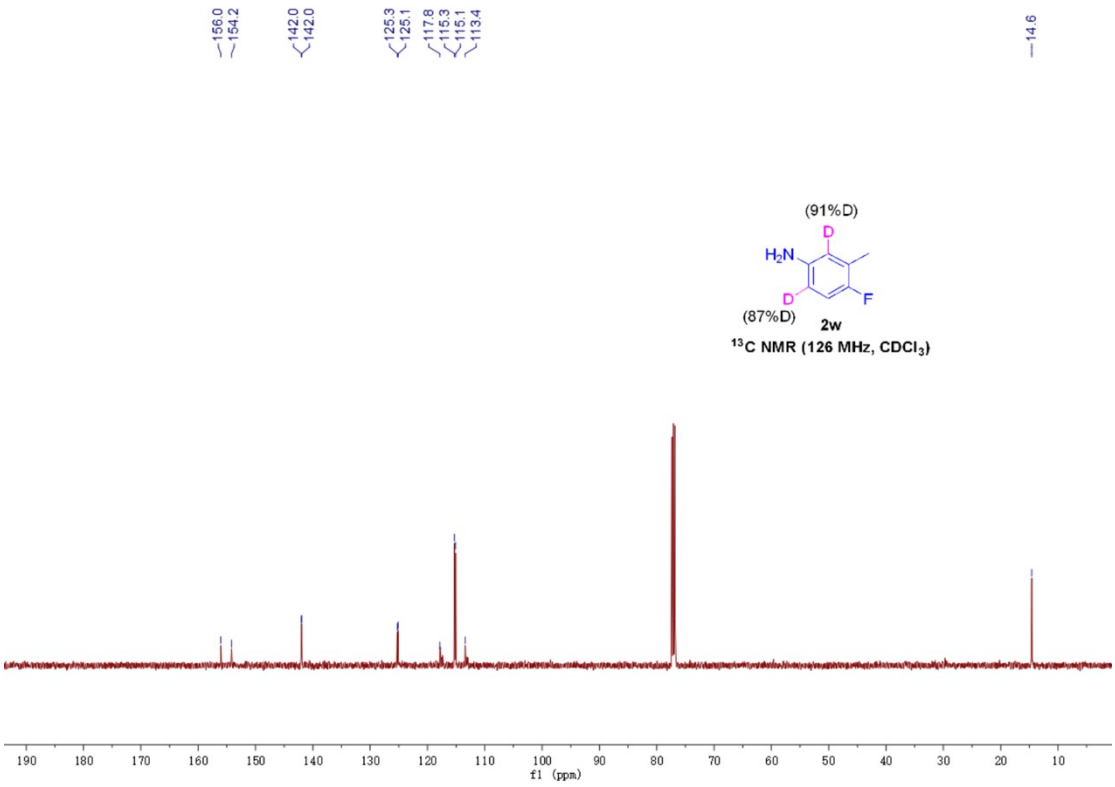

Figure S46. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2w

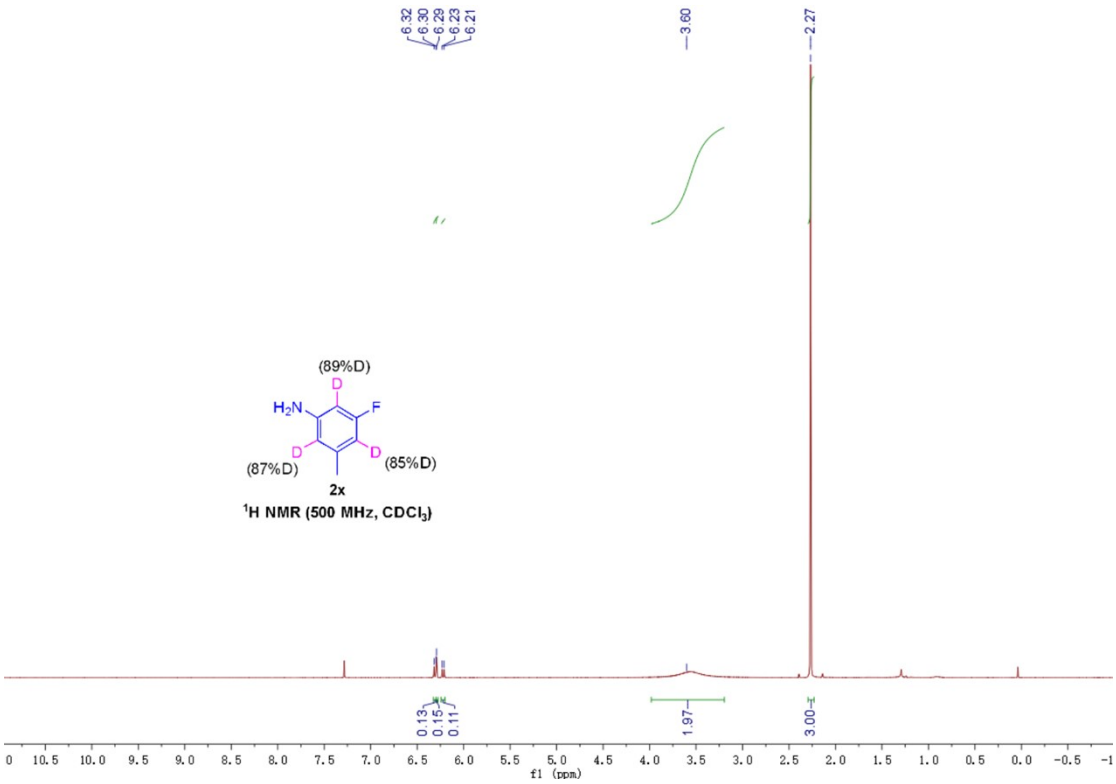

Figure S47. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2x

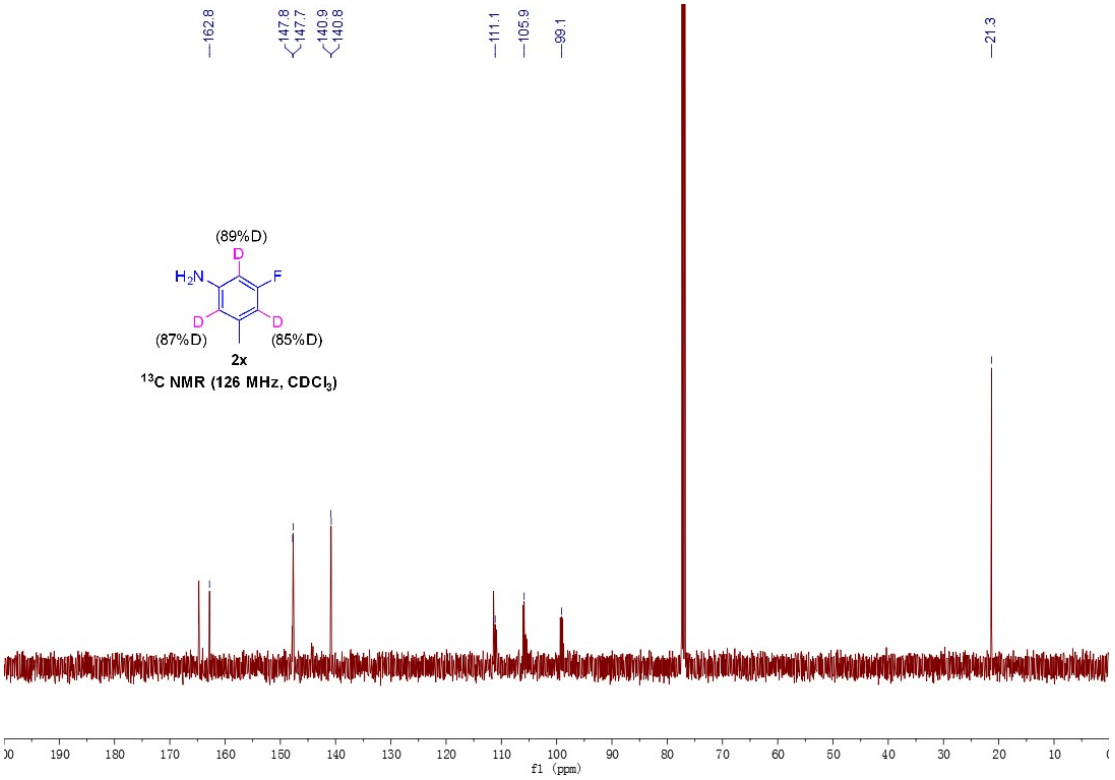

Figure S48. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2x

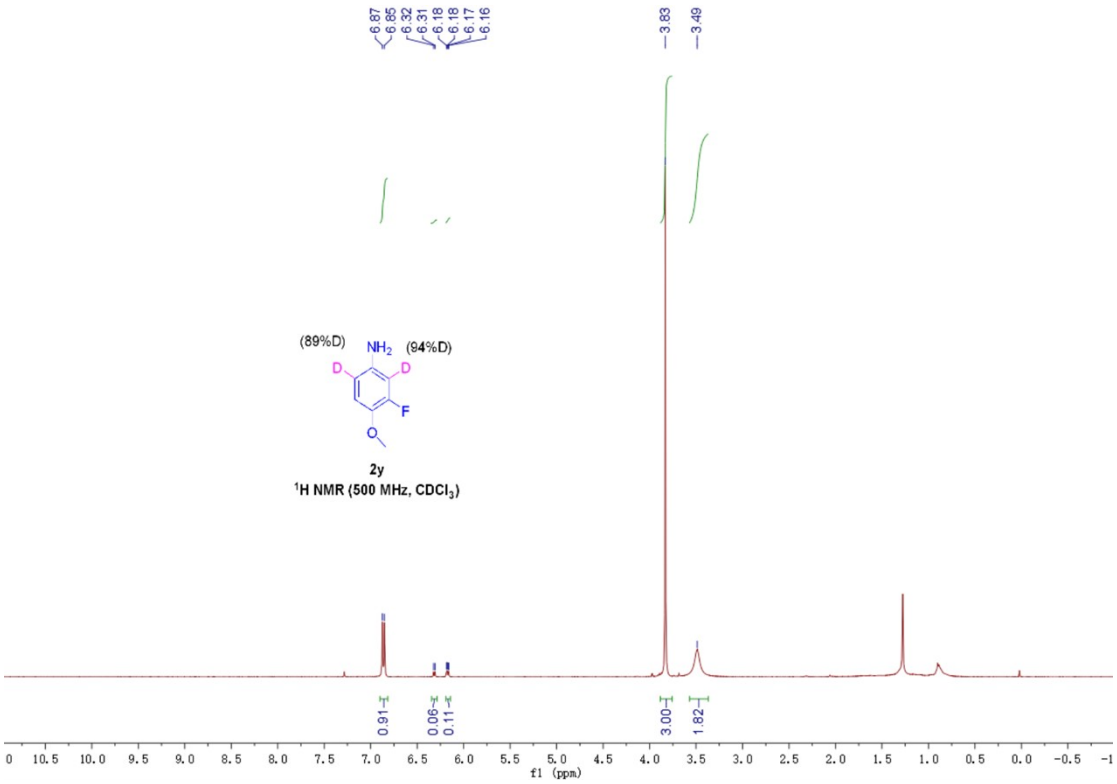

Figure S49. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2y

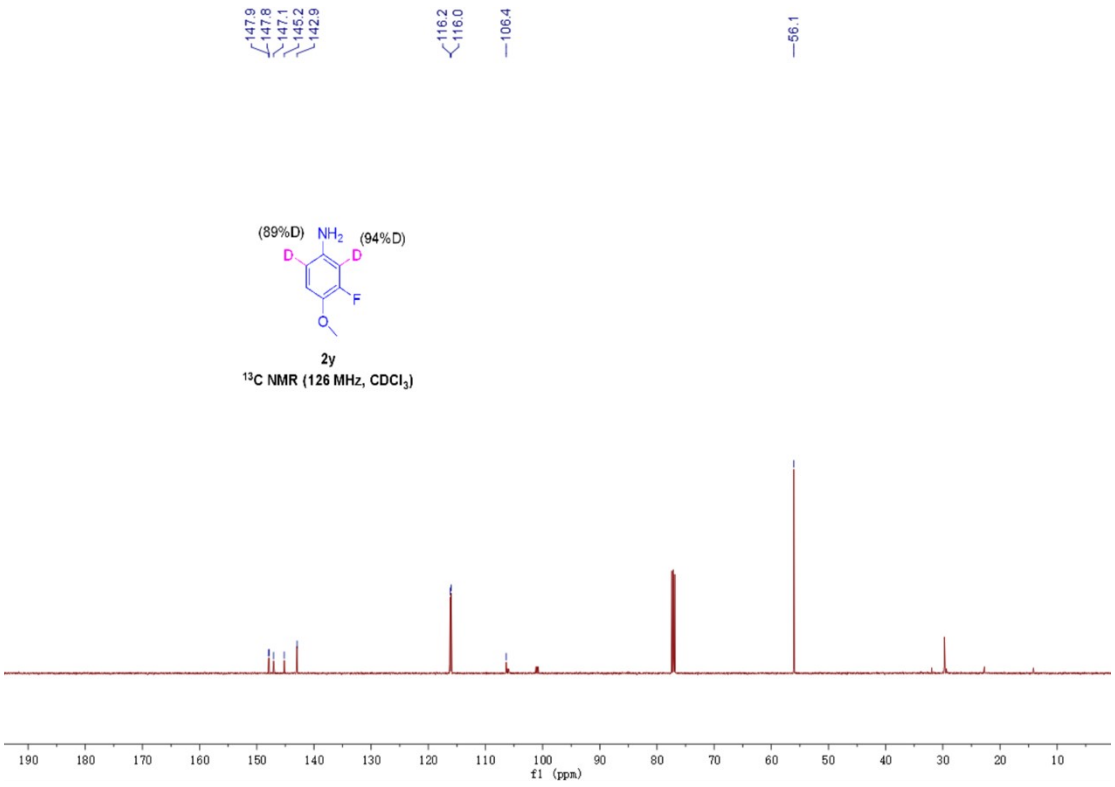

Figure S50. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2y

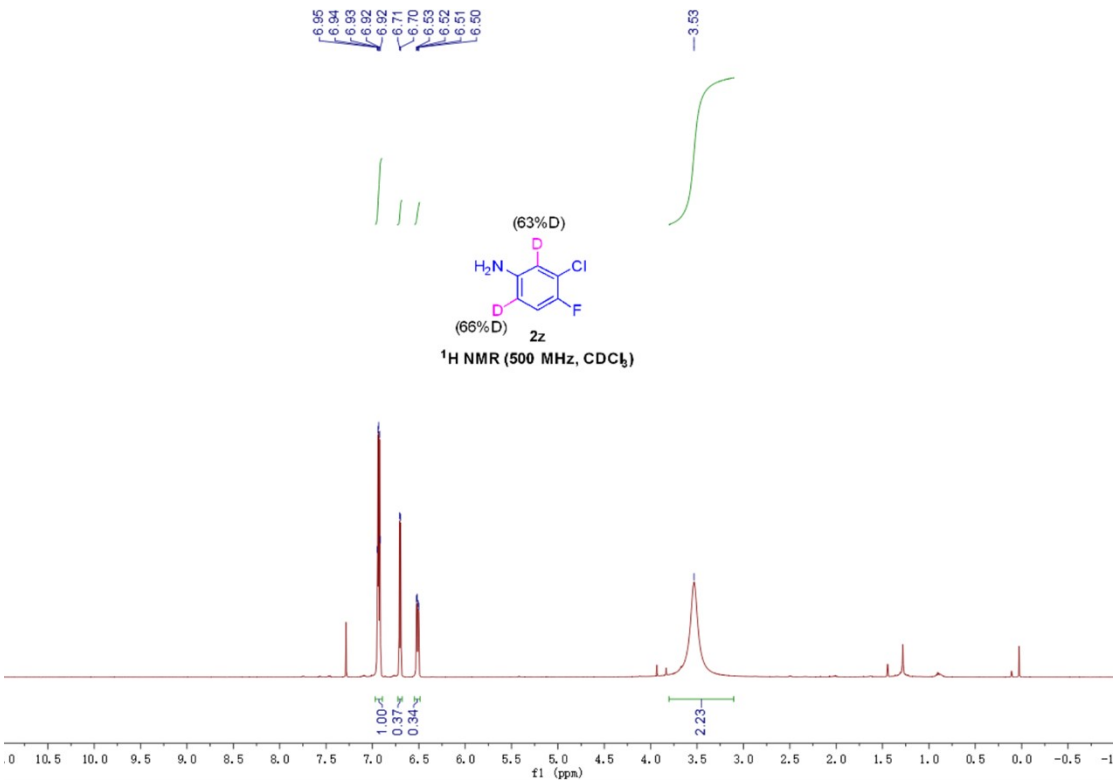

Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2z

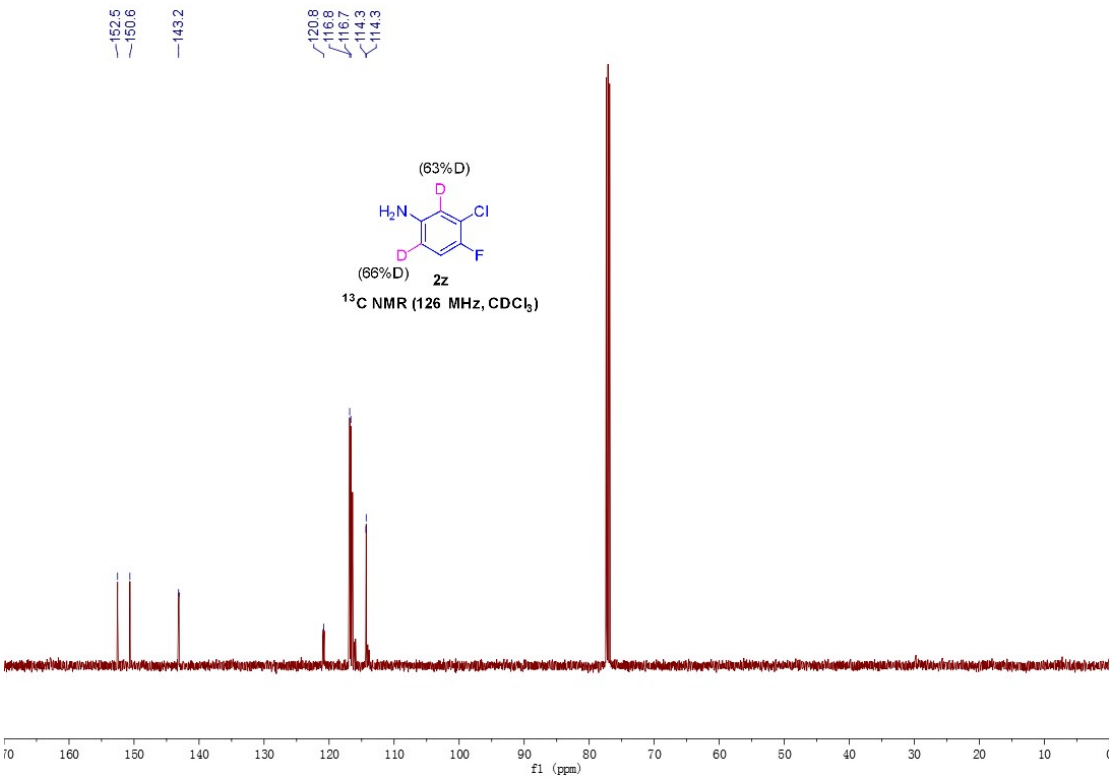

Figure S52. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2z

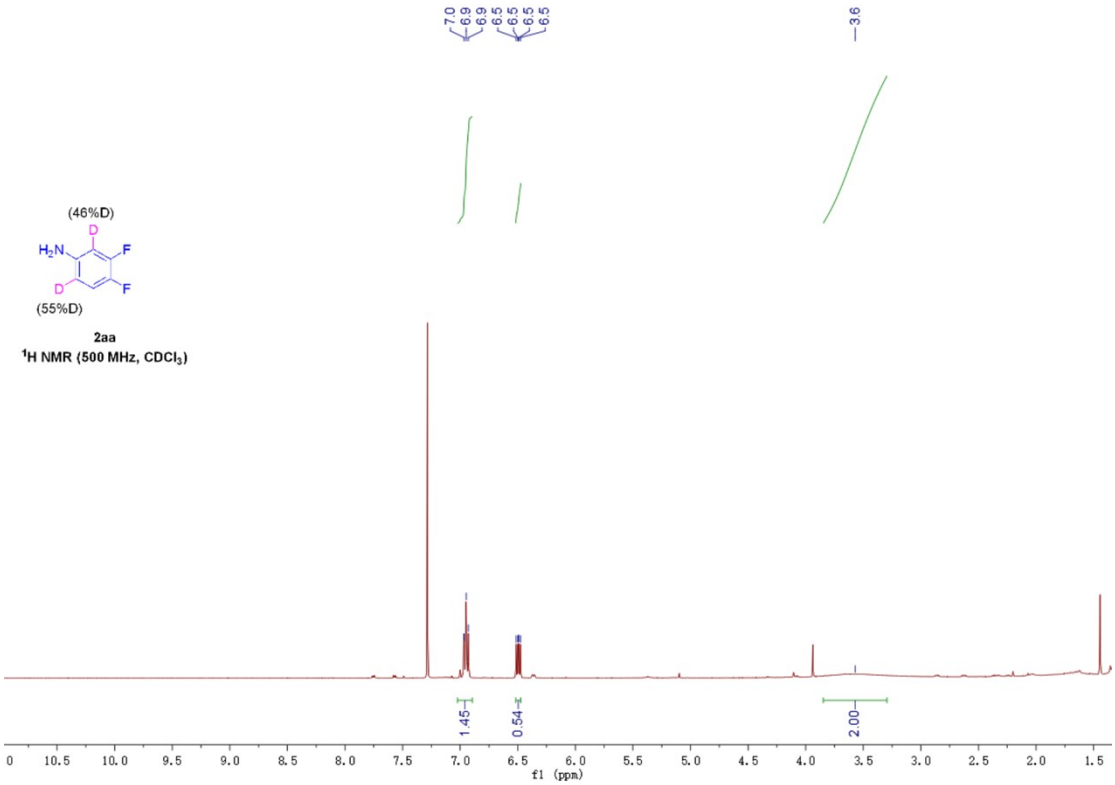

Figure S53. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2aa

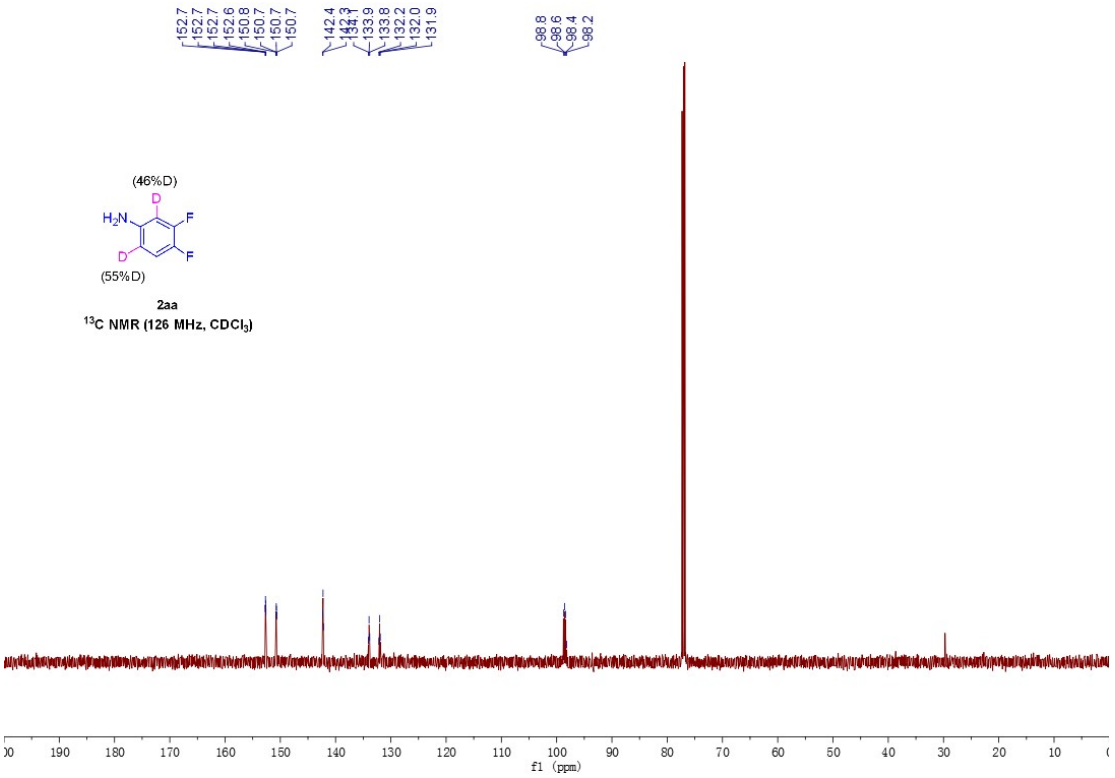

Figure S54. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2aa

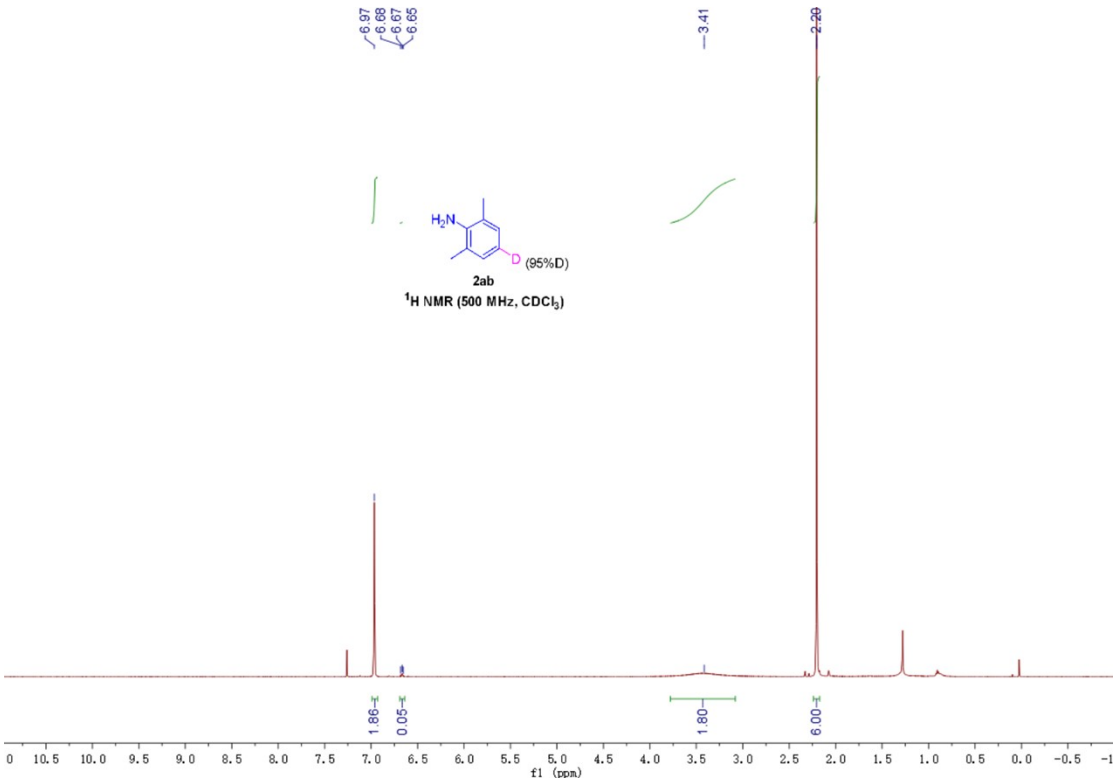

Figure S55. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2ab

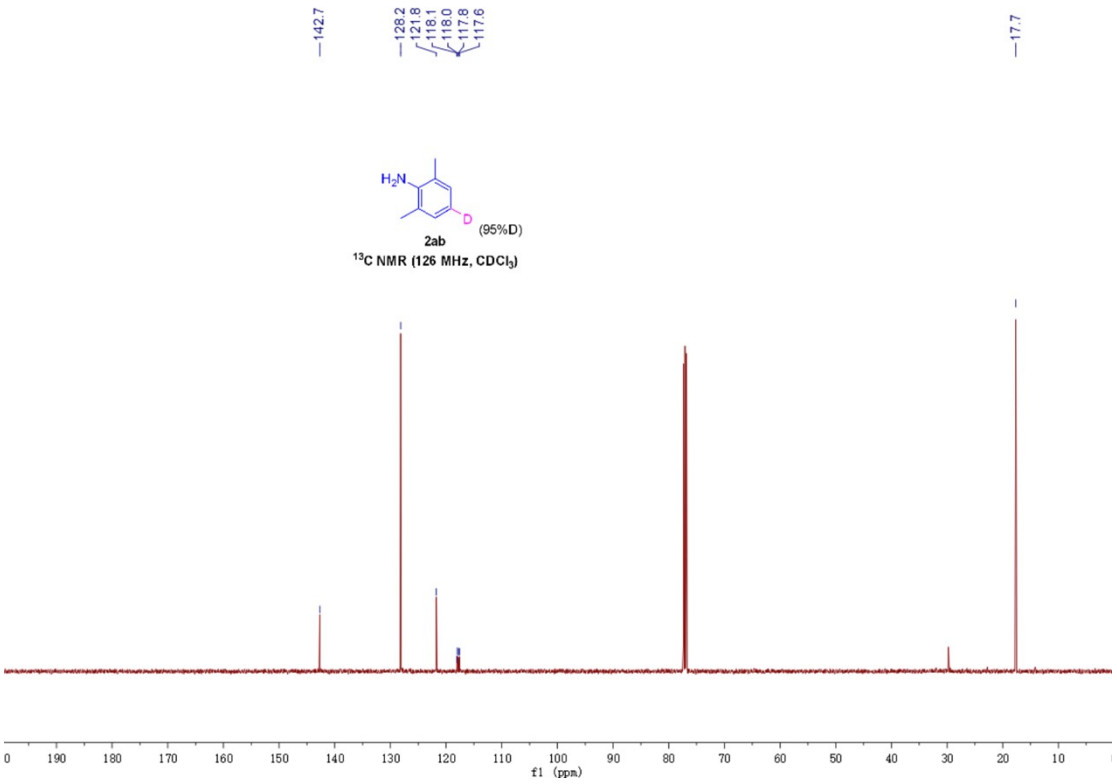

Figure S56. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2ab

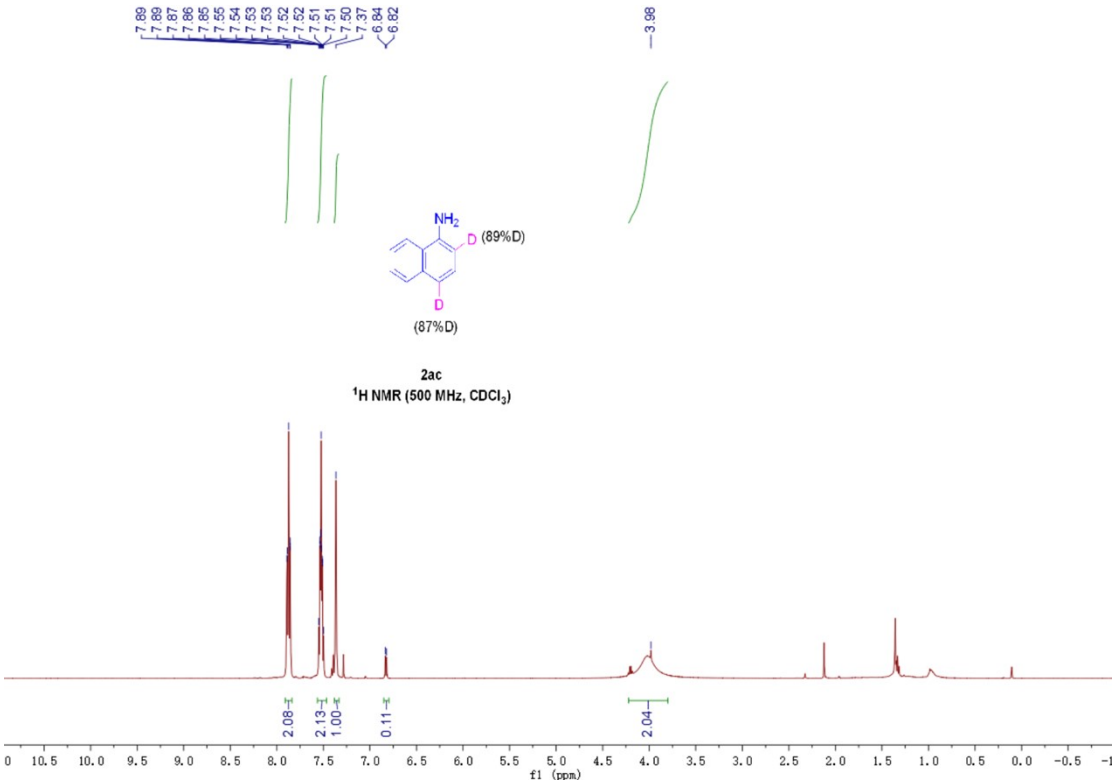

Figure S57. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2ac

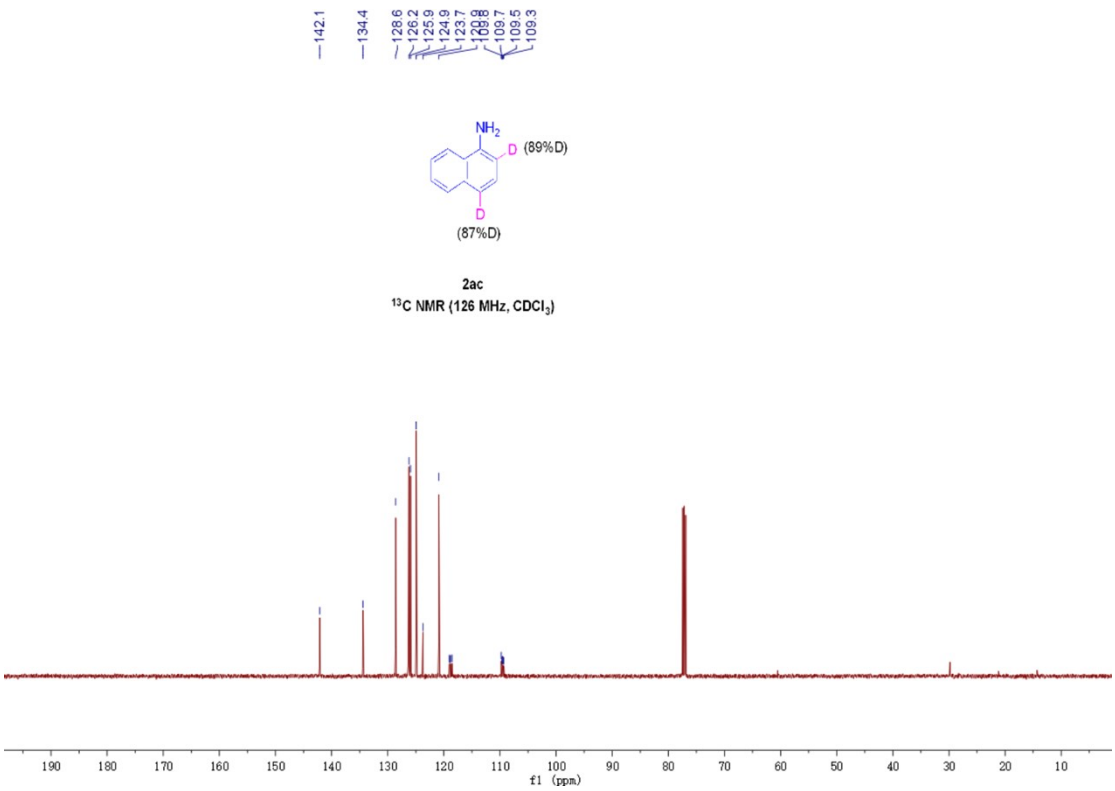

Figure S58. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2ac

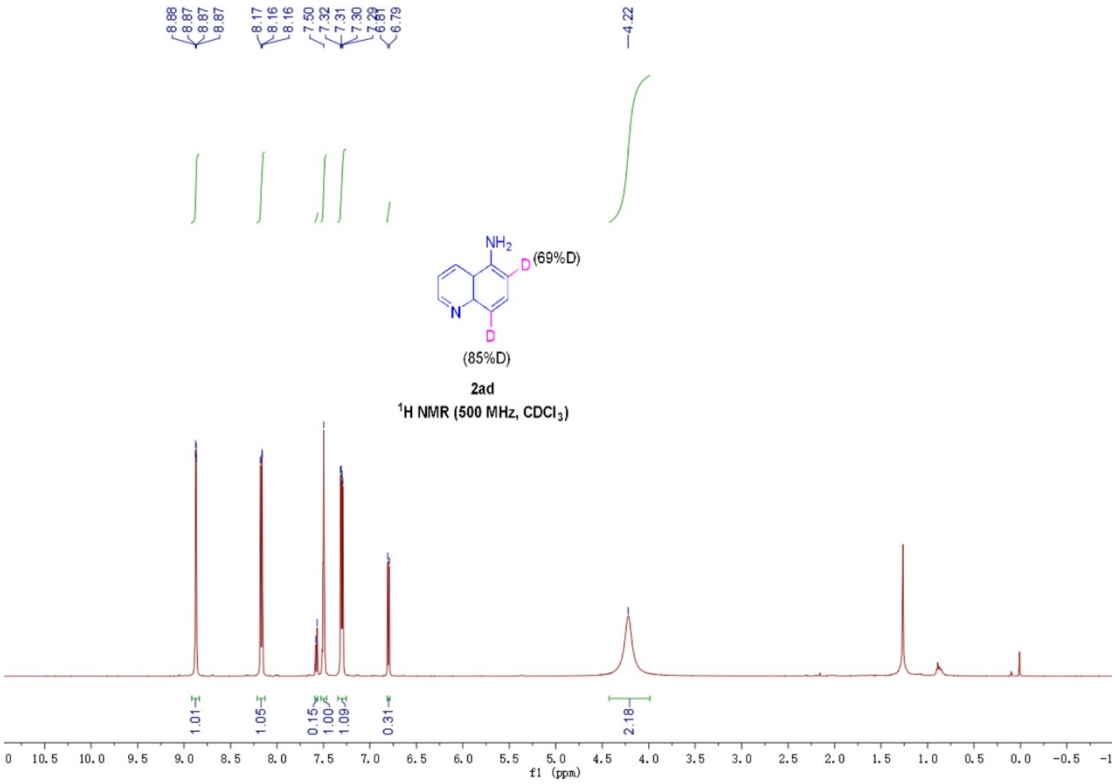

Figure S59. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2ad

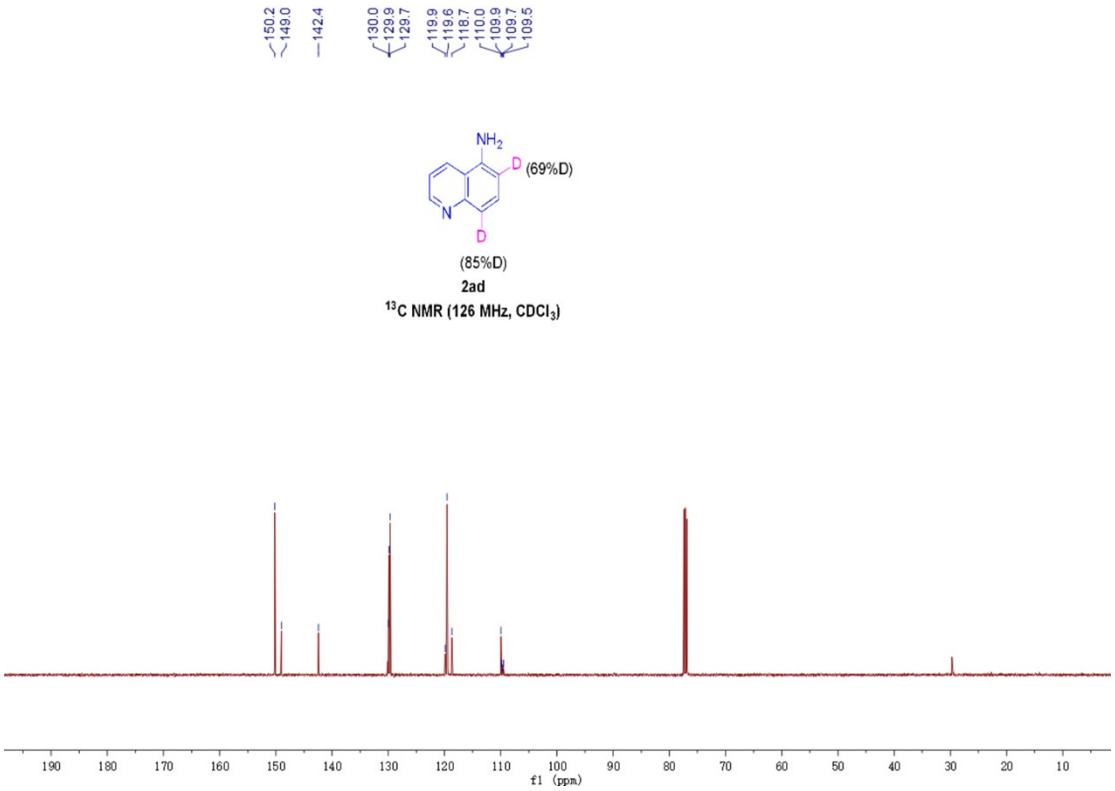

Figure S60. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2ad