Supporting Information

Scalable Reductive Deuteration of (Hetero)Aryl Chlorides with D_2O

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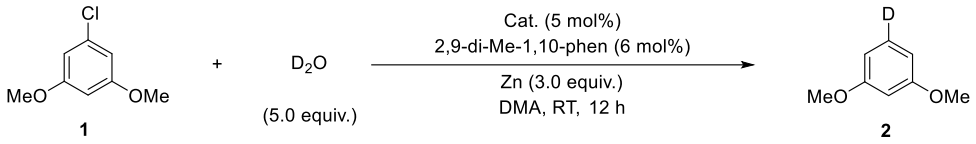
1. General remarks

^{1}H NMR, ^{13}C NMR data were obtained on AVANCE III Bruker 400 or 500 MHz nuclear resonance spectrometers unless otherwise noted. Chemical shifts (in ppm) were referenced to tetramethylsilane (TMS) (δ = 0.00 ppm) in $CDCl_3$ or dimethyl sulfoxide (δ = 2.50 ppm) in DMSO-d_6 as an internal standard. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. ^{13}C NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) or DMSO-d_6 (δ = 39.50 ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI) mode.

2. Optimization of reaction conditions

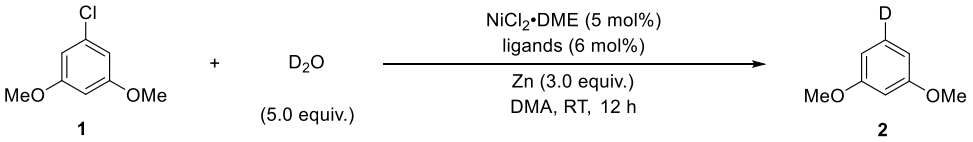
Table S1 | Optimization of catalysts



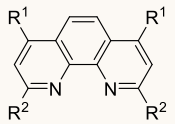
entry	Cat.	yield[a]	D-inc[b]
1	NiF_2	trace	-
2	$NiCl_2$	87%	90%
3	$NiBr_2$	80%	88%
4	NiI_2	76%	90%
5	**$NiCl_2$•DME**	**99%**	**>99%**
6	$NiBr_2$•DME	91%	95%
7	$Ni(OTf)_2$	54%	89%
8	$Ni(acac)_2$	68%	85%
9	$Fe(OTf)_3$	n.d.	-
10	$FeCl_2$	trace	-
11	$CoCl_2$	44%	64%
12	$CrCl_3$	23%	51%
13	none	n.d.	-

Reaction conditions: **1** (0.2 mmol), D_2O (2.0 mmol), catalyst (5 mol %), 2,9-di-Me-1,10-phen (6 mol %), Zn (3.0 equiv.) and DMA (1.0 mL) at room temperature for 12 h under N_2. [a]Determined by GC–MS analysis of the crude reaction mixture using benzophenone as an internal standard. [b]Deuterium incorporation was determined by ^1H NMR analysis.

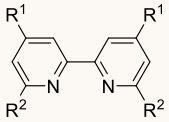
Table S2 | Optimization of ligands



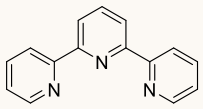
entry	ligand	yield[a]	D-inc[b]
1	**L1**	**99%**	**>99%**
2	L2	82%	90%
3	L3	71%	57%
4	L4	79%	58%
5	L5	53%	50%
6	L6	57%	52%
7	L7	41%	47%
8	L8	n.d.	-
9	w/o ligand	30%	27%
10	PCy_3	n.d.	-
11	PPh_3	trace	-



L1: R^1 = H, R^2 = Me
L2: R^1 = R^2 = H
L3: R^1 = Me, R^2 = H
L4: R^1 = Ph, R^2 = H



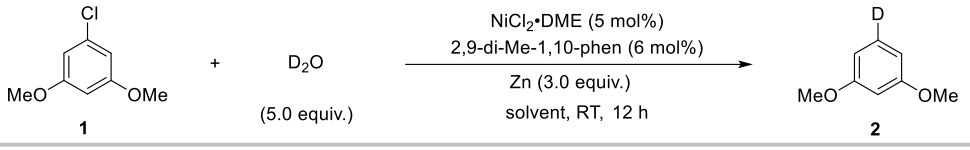
L5: R^1 = R^2 = H
L6: R^1 = H, R^2 = Me
L7: R^1 = R^2 = Me



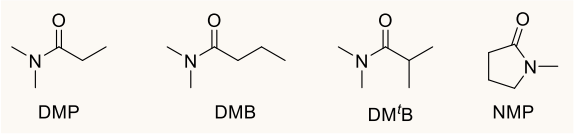
L8

Reaction conditions: **1** (0.2 mmol), D_2O (2.0 mmol), $NiCl_2$·DME (5 mol %), ligand (6 mol %), Zn (3.0 equiv.) and DMA (1.0 mL) at room temperature for 12 h under N_2. [a]Determined by GC–MS analysis of the crude reaction mixture using benzophenone as an internal standard. [b]Deuterium incorporation was determined by ^1H NMR analysis.

Table S3 | Optimization of solvents

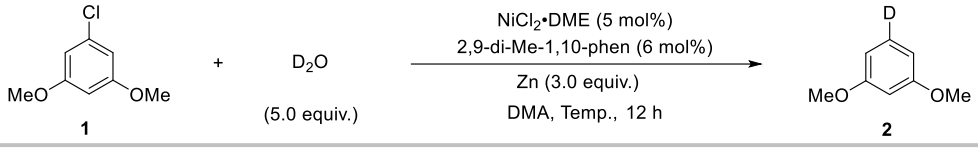


entry	solvent	yield[a]	D-inc[b]
1	DMF	97%	94%
2	**DMA**	**99%**	**>99%**
3	DMP	96%	>99%
4	DMB	90%	>99%
5	DM^{t}B	82%	>99%
6	DMSO	84%	80%
7	NMP	71%	82%
8	THF	32%	27%
9	MeCN	20%	15%
10	DCE	trace	-
11	1,4-dioxane	27%	20%



Reaction conditions: **1** (0.2 mmol), D_2O (2.0 mmol), $NiCl_2$·DME (5 mol %), 2,9-di-Me-1,10-phen (6 mol %), Zn (3.0 equiv.) and solvent (1.0 mL) at room temperature for 12 h under N_2. [a]Determined by GC–MS analysis of the crude reaction mixture using benzophenone as an internal standard. [b]Deuterium incorporation was determined by ^{1}H NMR analysis.

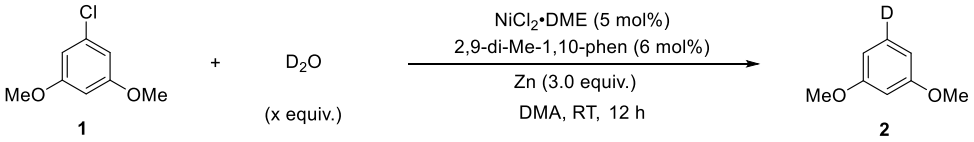
Table S4 | Optimization of temperature



entry	Temp.	yield[a]	D-inc[b]
1	0 °C	78%	92%
2	**RT (25 °C)**	**99%**	**>99%**
3	50 °C	81%	>99%
4	80 °C	65%	>99%
5	100 °C	23%	88%

Reaction conditions: **1** (0.2 mmol), D_2O (2.0 mmol), $NiCl_2$·DME (5 mol %), 2,9-di-Me-1,10-phen (6 mol %), Zn (3.0 equiv.) and DMA (1.0 mL) at different temperature for 12 h under N_2. [a]Determined by GC–MS analysis of the crude reaction mixture using benzophenone as an internal standard. [b]Deuterium incorporation was determined by ^{1}H NMR analysis.

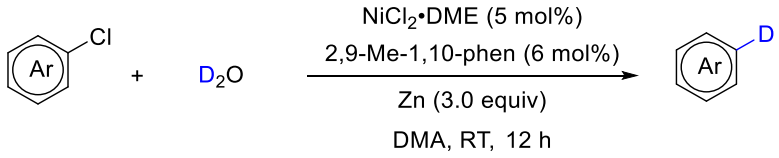
Table S5 | Optimization of the equivalents of D_2O



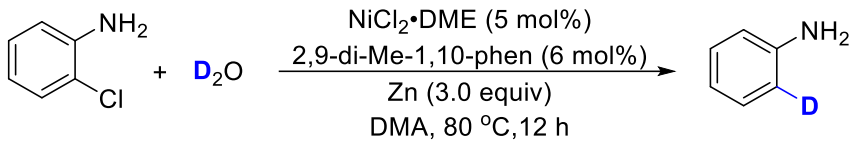
entry	equiv. of D_2O	yield[a]	D-inc[b]
1	1.0 equiv.	43%	63%
2	2.0 equiv.	61%	80%
3	3.0 equiv.	72%	95%
4	**5.0 equiv.**	**99%**	**>99%**
5	10.0 equiv.	99%	>99%

Reaction conditions: **1** (0.2 mmol), D_2O (1.0-10.0 equiv.), $NiCl_2$·DME (5 mol %), 2,9-di-Me-1,10-phen (6 mol %), Zn (3.0 equiv.) and DMA (1.0 mL) at room temperature for 12 h under N_2. [a]Determined by GC–MS analysis of the crude reaction mixture using benzophenone as an internal standard. [b]Deuterium incorporation was determined by ^1H NMR analysis.

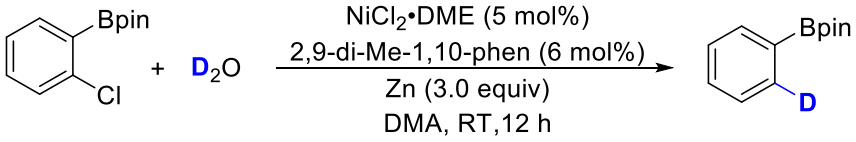
3. General procedure



General procedure for the nickel-catalyzed deuteration: To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.010 mmol), 2,9-dimethyl-1,10-phenanthroline (2.50 mg, 0.012 mmol), Zn powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 – 40.0 mg, 1.0 – 2.0 mmol) was added, followed by the addition of aryl chloride (0.2 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



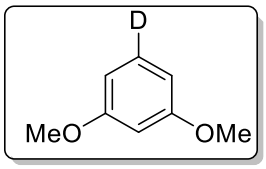
General procedure for the kilogram synthesis of benzen-2-*d*-amine: To a 50 L reaction kettle was added sequentially $NiCl_2$·DME (164.79 g, 0.75 mol), 2,9-dimethyl-1,10-phenanthroline (187.43 g, 0.90 mol), Zn powder (2.93 kg, 45.0 mol). The vessel was evacuated and filled with argon. DMA (8.0 L) was added and the mixture was stirred at room temperature for 10 min. The deuterated water (3.0 kg, 150 mol) was added, followed by the addition of 2-chloroaniline (1913.55 g, 15.0 mol) in one portion. DMA (4.0 L) was subsequently added. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (5.0 L) and washed with water (5.0 L), the additional zinc powder and solid byproduct was removed by filtrated. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by reduced pressure distillation, yielded desired product (1016.7 g, 72%) as a yellow oil. More than 99% Deuterium incorporation was determined by ^1H NMR.



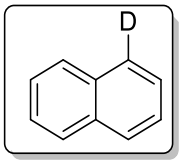
General procedure for the kilogram synthesis of 4,4,5,5-tetramethyl-2-(phenyl-2-*d*)-1,3,2-dioxaborolane: To a 50 L reaction kettle was added sequentially $NiCl_2$·DME (65.92 g, 0.3 mol), 2,9-dimethyl-1,10-phenanthroline (74.97 g, 0.36 mol), Zn powder (1.18 kg, 18.0 mol). The vessel was evacuated and filled with argon. DMA (4.0 L) was added and the mixture was stirred at room temperature for 10 min. The deuterated water (1.2 kg, 60 mol) was added, followed by the addition of 2-(2-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1431.12 g, 6.0 mol) in one portion. DMA (1.0 L) was subsequently added. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (5.0 L) and washed with water (5.0 L), the additional zinc powder and solid byproduct was removed

by filtrated. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by reduced pressure distillation, yielded desired product (1045.91 g, 85%) as a yellow oil. More than 99% Deuterium incorporation was determined by ^{1}H NMR.

4. Characterization data

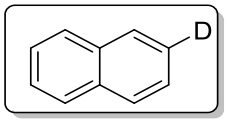


1,3-Dimethoxybenzene-5-*d* (2)[1]. The representative procedure was followed using 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **2** (27.5 mg, 99 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.52 – 6.51 (m, 2H), 6.48 – 6.47 (m, 1H), 3.79 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 160.78, 129.58 (t, J_{C-D} = 27.5 Hz), 105.97, 100.35, 55.22; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_8H_{10}DO_2$ 140.0816, found: 140.0809.

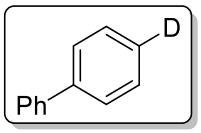


Naphthalene-1-*d* (3)[1]. The representative procedure was followed using 1-chloronaphthalene (32.52 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by

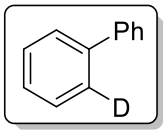
column chromatography (*n*-hexane) yielded **3** (23.5 mg, 91 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.85 – 7.83 (m, 3H), 7.48 – 7.46 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 133.41, 133.35, 127.85, 127.81, 127.53 (t, $J_{C–D}$ = 24.5 Hz), 125.79, 125.67; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{10}H_8D$ 130.0762, found: 130.0768.



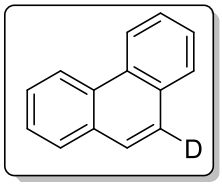
Naphthalene-2-*d* (4)[2]. The representative procedure was followed using 2-chloronaphthalene (32.52 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane) yielded **4** (22.7 mg, 88 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.85 – 7.83 (m, 4H), 7.49 – 7.47 (m, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 133.42, 127.86, 127.74, 125.79, 125.69, 125.51 (t, $J_{C–D}$ = 24.5 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{10}H_8D$ 130.0762, found: 130.0766.



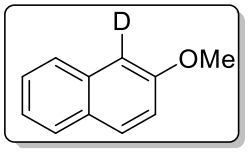
1,1'-Biphenyl-4-*d* (5)[2]. The representative procedure was followed using 4-chloro-1,1'-biphenyl (37.73 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane) yielded **5** (27.9 mg, 90 %) as a white solid. 98 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.52 – 7.50 (m, 4H), 7.37 – 7.34 (m, 4H), 7.28 – 7.24 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 141.22, 128.72, 128.61, 127.22, 127.14, 126.93 (t, $J_{C–D}$ = 24.5 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{10}D$ 156.0918, found: 156.0911.



1,1'-Biphenyl-2-*d* (6)[2]. The representative procedure was followed using 2-chloro-1,1'-biphenyl (37.73 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane) yielded **6** (24.8 mg, 80 %) as a white solid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.52 – 7.50 (m, 3H), 7.37 – 7.34 (m, 4H), 7.28 – 7.24 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 141.19, 141.14, 128.73, 128.62, 127.22, 127.14, 126.84 (t, $J_{C–D}$ = 23.5 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{10}D$ 156.0918, found: 156.0914.

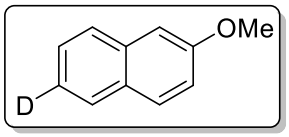


Phenanthrene-9-*d* (7)[2]. The representative procedure was followed using 9-chlorophenanthrene (42.54 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane) yielded **7** (26.9 mg, 75 %) as a white solid. 96 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.67 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.72 (s, 1H), 7.63 (t, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 132.02, 131.96, 130.27, 128.54, 128.48, 126.76, 126.57 (t, $J_{C–D}$ = 24.0 Hz), 126.52, 122.63; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{14}H_{10}D$ 180.0918, found: 180.0916.

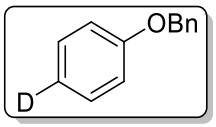


2-Methoxynaphthalene-1-*d* (8)[3]. The representative procedure was followed using 1-chloro-2-methoxynaphthalene (38.53 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **8** (30.6 mg, 96 %) as a white solid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.68 – 7.63 (m, 3H), 7.36 – 7.32 (m, 1H), 7.26 – 7.22 (m, 1H), 7.07 – 7.05 (m, 1H), 3.81 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 157.46, 134.43, 129.33, 128.86, 127.61, 126.63, 126.32, 123.53, 118.69, 105.32 (t,

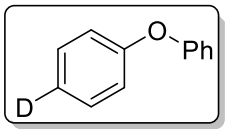
$J_{C–D}$ = 24.0 Hz), 55.22; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{11}H_{10}DO$ 160.0867, found: 160.0869.



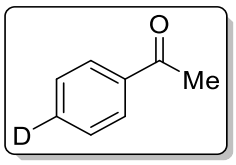
2-Methoxynaphthalene-6-*d* (9)[2]. The representative procedure was followed using 2-chloro-6-methoxynaphthalene (38.53 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **9** (28.7 mg, 90 %) as a white solid. 95 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.66 – 7.62 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.22 (m, 0.05H), 7.06 – 7.03 (m, 2H), 3.80 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 157.54, 134.54, 129.34, 128.91, 127.49, 126.69, 126.22, 123.54, 123.26 (t, $J_{C–D}$ = 24.5 Hz), 118.67, 105.70, 55.21; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{11}H_{10}DO$ 160.0867, found: 160.0871.



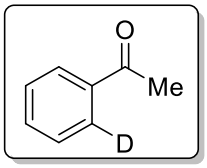
1-(Benzyloxy)benzene-4-*d* (10)[1]. The representative procedure was followed using 1-(benzyloxy)-4-chlorobenzene (43.74 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **10** (30.4 mg, 82 %) as a colorless oil. 90 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.36 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 7.25 – 7.24 (m, 1H), 7.22 – 7.20 (m, 2H), 6.91 – 6.89 (m, 2H), 4.98 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.73, 137.02, 129.34, 128.54, 127.90, 127.45, 120.62 (t, $J_{C–D}$ = 24.5 Hz), 114.78, 69.85; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{13}H_{12}DO$ 186.1024, found: 186.1031.



1-Phenoxybenzene-4-*d* (11)[1]. The representative procedure was followed using 1-chloro-4-phenoxybenzene (40.93 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **11** (27.7 mg, 81 %) as a colorless oil. 95 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.27 – 7.23 (m, 4H), 7.03 – 7.00 (m, 1.05H), 6.94 – 6.92 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 157.23, 129.70, 129.59, 123.18, 122.91 (t, $J_{C–D}$ = 24.5 Hz), 118.86; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{10}DO$ 172.0867, found: 172.0870.

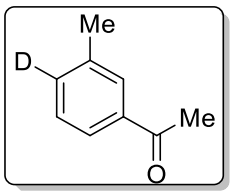


1-(Phenyl-4-*d*)ethan-1-one (12)[4]. The representative procedure was followed using 1-(4-chlorophenyl)ethan-1-one (30.92 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **12** (20.8 mg, 86 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.97 – 7.96 (m, 2H), 7.48 – 7.46 (m, 2H), 2.61(s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.14, 137.07, 132.77 (t, $J_{C–D}$ = 24.5 Hz), 128.42, 128.27, 26.60; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_8H_8DO 122.0711, found: 122.0713.

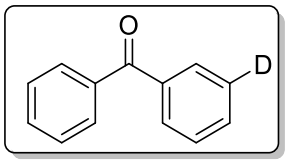


1-(Phenyl-2-*d*)ethan-1-one (13)[4]. The representative procedure was followed using 1-(4-chlorophenyl)ethan-1-one (30.92 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **13** (16.7 mg,

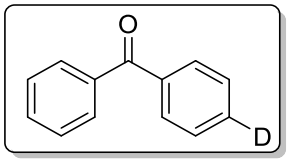
69 %) as a colorless oil. 95 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.97 – 7.96 (m, 1.05H), 7.59 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 2.61(s, 2.41H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 198.13, 137.04, 133.08, 128.55, 128.43, 128.26, 128.01 (t, $J_{C–D}$ = 24.5 Hz), 26.60; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_8H_8DO 122.0711, found: 122.07018.



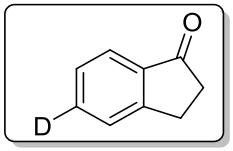
1-(3-Methylphenyl-4-*d*)ethan-1-one (14). The representative procedure was followed using 1-(4-chloro-3-methylphenyl)ethan-1-one (33.72 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **14** (25.4 mg, 94 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.69 – 7.66 (m, 2H), 7.27 – 7.25 (m, 1H), 2.50 (s, 3H), 2.32 (s, 3H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 198.33, 138.16, 137.03, 133.45 (t, $J_{C–D}$ = 24.5 Hz), 128.70, 128.24, 125.49, 26.60, 21.19; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_9H_{10}DO$ 136.0867, found: 136.0870.



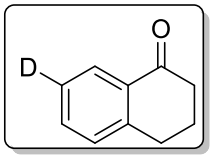
Phenyl(phenyl-3-*d*)methanone (15). The representative procedure was followed using (3-chlorophenyl)(phenyl)methanone (43.33 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **15** (27.9 mg, 76 %) as a white solid. 84 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.75 – 7.72 (m, 4H), 7.53 – 7.50 (m, 2H),7.43 – 7.30 (m, 3.16H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 196.73, 137.57, 132.39, 132.28, 130.03, 129.93, 128.25, 127.96 (t, $J_{C–D}$ = 24.5 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{13}H_{10}DO$ 184.0867, found: 184.0873.



Phenyl(phenyl-4-*d*)methanone (16)[5]. The representative procedure was followed using (4-chlorophenyl)(phenyl)methanone (43.33 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **16** (34.4 mg, 94 %) as a white solid. 96 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.74 – 7.73 (m, 4H), 7.54 – 7.50 (m, 1.04H) ,7.43 – 7.40 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 196.74, 137.57, 132.39, 132.09 (t, $J_{C–D}$ = 25.0 Hz), 130.04, 128.25, 128.14; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{13}H_{10}DO$ 184.0867, found: 184.0869.

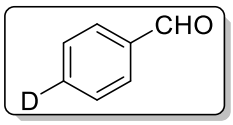


2,3-Dihydro-1*H*-inden-1-one-5-*d* (17). The representative procedure was followed using 5-chloro-2,3-dihydro-1*H*-inden-1-one (33.32 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 30 : 1) yielded **17** (24.5 mg, 92 %) as a white solid. 91 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.76 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 0.09H), 7.48 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 3.16 – 3.14 (m, 2H), 2.71 – 2.58 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 207.02, 155.12, 137.06, 134.25 (t, $J_{C–D}$ = 24.0 Hz), 127.13, 126.55, 123.68, 36.19, 25.77; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_9H_8DO 134.0711, found: 134.0716.

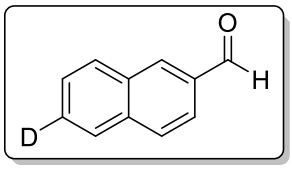


2,3-Dihydro-1*H*-inden-1-one-5-*d* (18). The representative procedure was followed using 5-chloro-2,3-dihydro-1*H*-inden-1-one (36.1 mg, 0.20 mmol) and D_2O (18 μL, 1.0

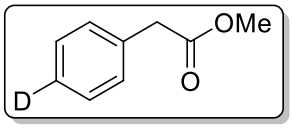
mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 30 : 1) yielded **18** (20.9 mg, 71 %) as a white solid. 89 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.95 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 0.11H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 6.0 Hz, 2H), 2.07 – 2.04 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.27, 144.40, 133.30, 132.99 (t, $J_{C–D}$ = 24.0 Hz), 132.53, 128.58, 127.06, 126.41, 39.08, 29.62, 23.21, 23.12; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{10}H_{10}DO$ 148.0867, found: 148.0861.



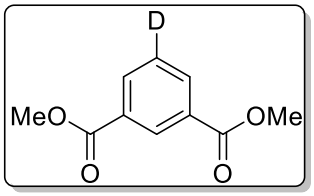
Benzaldehyde-4-*d* (19)[6]. The representative procedure was followed using 4-chlorobenzaldehyde (28.11 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **19** (18.6 mg, 87 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 10.03 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 192.38, 136.39, 134.45 (t, $J_{C–D}$ = 25.0 Hz), 129.73, 128.87; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_7H_6DO 108.0554, found: 108.0552.



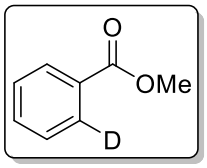
2-Naphthaldehyde-6-*d* (20). The representative procedure was followed using 6-chloro-2-naphthaldehyde (38.13 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **20** (20.4 mg, 65 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 10.10 (s, 1H), 8.28 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.88 (m, 2H), 7.84 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 192.22, 136.46, 134.52, 134.13, 132.66, 129.52, 129.10, 127.96, 126.98, 122.78; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{11}H_8DO$ 158.0711, found: 158.0710.



Methyl 2-(phenyl-4-*d*)acetate (21). The representative procedure was followed using methyl 2-(4-chlorophenyl)acetate (36.92 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **21** (25.1 mg, 83 %) as a green-yellow oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 (d, J = 8.0 Hz, 2H), 7.19 (s, J = 8.0 Hz, 2H), 3.60 (s, 3H), 3.55 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 171.96, 133.91, 129.18, 128.40, 126.75 (t, $J_{C–D}$ = 24.5 Hz), 51.97, 41.14; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_9H_{10}DO_2$ 152.0816, found: 152.0817.

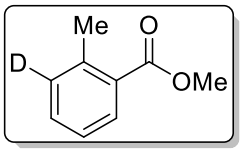


Dimethyl isophthalate-5-*d* (22)[7]. The representative procedure was followed using dimethyl 5-chloroisophthalate (45.70 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **22** (29.3 mg, 75 %) as a colorless oil. 96 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.61 – 8.60 (m, 1H), 8.15 – 8.14 (m, 2H), 7.45 (t, J = 7.5 Hz, 0.04 H), 3.87 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 166.16, 133.63, 130.62, 130.46, 128.28 (t, $J_{C–D}$ = 27.0 Hz), 52.32; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{10}H_{10}DO_4$ 196.0715, found: 196.0719.

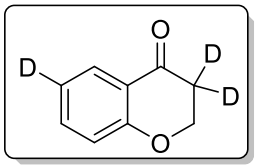


Methyl benzoate-2-*d* (23)[8]. The representative procedure was followed using methyl

2-chlorobenzoate (34.12 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **23** (23.3 mg, 85 %) as a colorless oil. 98 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.99 – 7.96 (m, 1H), 7.50 – 7.46 (m, 1H), 7.38 – 7.35 (m, 2H), 3.84 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 167.06, 132.87, 130.01, 129.51, 129.24 (t, $J_{C–D}$ = 24.5 Hz), 128.31, 128.19, 52.06; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_8H_8DO_2$ 138.0660, found: 138.0668.

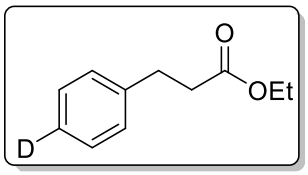


Methyl 2-methylbenzoate-3-*d* (24). The representative procedure was followed using methyl 3-chloro-2-methylbenzoate (36.8 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **24** (27.2 mg, 90 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.82 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H) ,3.80 (s, 3H), 2.51 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 167.00, 140.03, 131.77, 131.29 (t, $J_{C–D}$ = 24.5 Hz), 130.50, 129.50, 125.61, 51.71, 21.58; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_9H_{10}DO_2$ 152.0816, found: 152.0824.

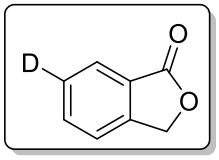


Chroman-4-one-3,3,6-*d*$_3$ (25). The representative procedure was followed using 6-chlorochroman-4-one (36.52 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **25** (22.9 mg, 77 %) as a colorless oil. 95 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.81 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 0.05H), 6.89 (d, *J* = 8.5 Hz, 1H) ,4.45 (s, 2H), 2.74 – 2.71 (m, 0.32H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 191.83, 161.81, 135.81, 126.94, 121.28, 121.02 (t, $J_{C–D}$ = 24.5 Hz), 117.81,

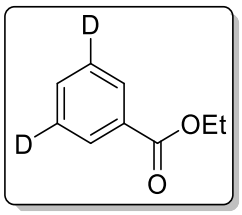
66.85, 37.30 (hexet, J_{C-D} = 20.0 Hz); **HRMS** (ESI) m/z ([M+ H]$^+$) Calcd. for $C_9H_6D_3O_2$ 152.0785, found: 152.0779.



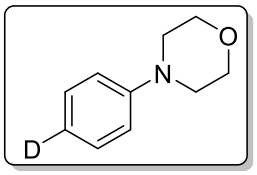
Ethyl 3-(phenyl-4-*d*)propanoate (26). The representative procedure was followed using ethyl 3-(4-chlorophenyl)propanoate (42.5 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **26** (29.4 mg, 82 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.20 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H) ,4.04 (q, *J* = 7.0 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 172.83, 140.51, 128.29, 128.22, 125.86 (t, J_{C-D} = 24.5 Hz), 60.33, 35.89, 30.92, 14.14; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{11}H_{14}DO_2$ 180.1129, found: 180.1130.



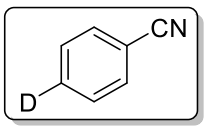
Isobenzofuran-1(3*H*)-one-6-*d* (27). The representative procedure was followed using 6-chloroisobenzofuran-1(3*H*)-one (33.7 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **27** (21.8 mg, 81 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.85 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 1H) , 7.44 (d, *J* = 7.5 Hz, 1H), 5.25 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 171.03, 146.47, 133.85, 128.68 (t, J_{C-D} = 24.5 Hz), 125.56, 122.05, 69.60; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_8H_6DO_2$ 136.0503, found: 136.0504.



Ethyl benzoate-3,5-*d*$_2$ (28). The representative procedure was followed using methyl ethyl 3,5-dichlorobenzoate (43.80 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **28** (24.4 mg, 80 %) as a yellow oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.51 (s, 2H), 7.55 (s, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 166.60, 132.54, 130.46, 129.38, 127.97 (t, $J_{C–D}$ = 24.0Hz), 60.91, 14.30; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_9H_9D_2O_2$ 153.0879, found: 153.0886.

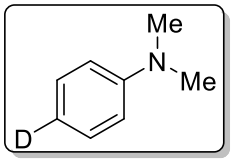


4-(Phenyl-4-*d*)morpholine (29)[9]. The representative procedure was followed using 4-(4-chlorophenyl)morpholine (46.34 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **29** (29.6 mg, 90 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.29 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.87 – 3.85 (m, 4H), 3.16 – 3.15 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 151.23, 129.04, 119.75 (t, $J_{C–D}$ = 24.5 Hz), 115.67, 66.91, 49.34; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{10}H_{13}DNO$ 165.1133, found: 165.1130.

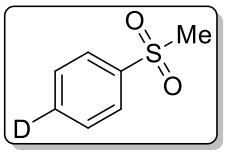


Benzonitrile-4-*d* (30)[10]. The representative procedure was followed using 4-chlorobenzonitrile (27.51 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by

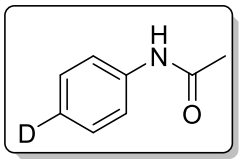
column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **30** (16.9 mg, 81 %) as a colorless oil. 90 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 0.1H), 7.48 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 132.64 (t, $J_{C–D}$ = 24.5 Hz), 132.13, 128.98, 118.83, 112.43; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_7H_5DN 105.0558, found: 105.0564.



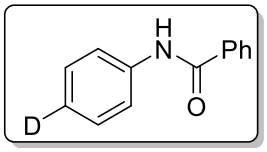
***N*,*N*-dimethylaniline-4-*d* (31)**[11]. The representative procedure was followed using 4-chloro-*N*,*N*-dimethylaniline (31.13 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **31** (21.7 mg, 89 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 (m, 2H), 6.75 (m, 2H), 2.94 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 150.58, 128.92, 116.63, 112.64, 40.62; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_8H_{11}DN$ 123.1027, found: 123.1020.



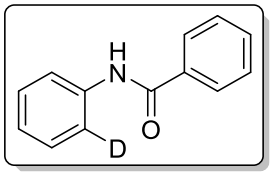
1-(Methylsulfonyl)benzene-4-*d* (32)[10]. The representative procedure was followed using 1-chloro-4-(methylsulfonyl)benzene (38.13 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **32** (27.4 mg, 87 %) as an orange oil. 96 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.88 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 3.00 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 140.38, 133.37 (t, $J_{C–D}$ = 24.5 Hz), 129.20, 127.26, 44.42; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_7H_8DO_2S$ 158.0381, found: 158.0384.



***N*-(Phenyl-4-*d*)acetamide (33)**[11]. The representative procedure was followed using *N*-(4-chlorophenyl)acetamide (33.92 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **33** (22.3 mg, 82 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.51 (br, 0.89H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 2.09 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 168.49, 137.89, 128.80, 123.98 (t, $J_{C–D}$ = 24.0 Hz), 119.92, 24.50; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_8H_9DNO 137.0820, found: 137.0816.

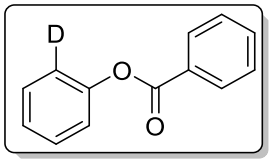


***N*-(Phenyl-4-*d*)benzamide (34)**[11]. The representative procedure was followed using *N*-(4-chlorophenyl)benzamide (46.34 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **34** (33.7 mg, 85 %) as a white solid. 90 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, DMSO-d_6) δ** 10.26 (s, 1H), 7.97 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 0.1H); **^{13}C NMR (125 MHz, DMSO-d_6) δ** 166.06, 139.67, 135.50, 132.03, 129.02 (t, $J_{C–D}$ = 25.0 Hz), 128.99, 128.87, 128.15, 120.85; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{13}H_{11}DNO$ 199.0976, found: 199.0970.

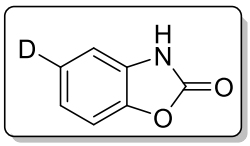


***N*-(Phenyl-2-*d*)benzamide (35)**. The representative procedure was followed using *N*-(2-chlorophenyl)benzamide (46.34 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol).

Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **35** (31.7 mg, 80 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ** 10.25 (s, 1H), 7.98 – 7.96 (m, 2H), 7.71 – 7.79 (m, 1H), 7.61 – 7.58 (m, 1H), 7.55 – 7.52 (m, 2H), 7.38 – 7.35 (m, 2H), 7.12 – 7.09 (m, 1H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ** 166.02, 139.58, 135.47, 131.97, 129.04, 128.94, 128.82, 128.11, 124.09, 120.81, 120.55 (t, $J_{C–D}$ = 25.0 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{13}H_{11}DNO$ 199.0976, found: 199.0979.

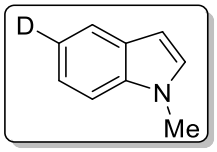


Phenyl-2-*d* benzoate (36). The representative procedure was followed using 2-chlorophenyl benzoate (46.53 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **36** (35.5 mg, 89 %) as a white solid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 8.21 – 8.19 (m, 2H), 7.62 – 7.59 (m, 1H), 7.50 – 7.47 (m, 2H), 7.43 – 7.39 (m, 2H), 7.27 – 7.23 (m, 1H), 7.22 – 7.20 (m, 1H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 165.07, 150.88, 133.48, 130.08, 129.54, 129.40, 129.30, 128.49, 125.79, 121.63, 121.37 (t, $J_{C–D}$ = 25.0 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{13}H_{10}DO_2$ 200.0816, found: 200.0821.

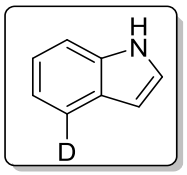


Benzo[*d*]oxazol-2(3*H*)-one-5-*d* (37). The representative procedure was followed using 5-chlorobenzo[*d*]oxazol-2(3*H*)-one (33.91 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **37** (18.7 mg, 69 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ** 11.84 (s, 1H), 7.32 – 7.27 (m, 1H), 7.16 – 7.09 (m, 2H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ** 154.70, 142.57, 132.15, 128.21, 121.97, 111.26,

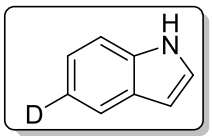
110.10 (t, $J_{C–D}$ = 22.0 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_7H_5DNO_2$ 137.0456, found: 137.0454.



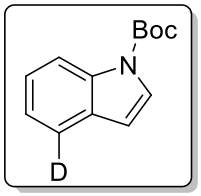
1-Methyl-1*H*-indole-5-*d* (38)[12]. The representative procedure was followed using 5-chloro-1-methyl-1*H*-indole (33.12 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 30 : 1) yielded **38** (23.8 mg, 90 %) as a green-yellow liquid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.56 – 7.54 (m, 1H), 7.25 – 7.23 (m, 1H), 7.15 – 7.13 (m, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 7.0 Hz, 1H), 3.70 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 136.65, 128.72, 128.42, 121.33, 120.70, 118.94 (t, $J_{C–D}$ = 24.5Hz), 109.12, 100.84, 32.76; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_9H_9DN 133.0871, found: 133.0877.



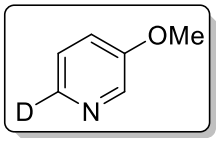
1*H*-Indole-4-*d* (39)[12]. The representative procedure was followed using 4-chloro-1*H*-indole (30.32 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **39** (16.5 mg, 70 %) as a yellow oil. 85 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.81 (br, 0.92H), 7.56 (d, *J* = 8.0 Hz, 0.15H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.04 – 7.03 (m, 1H), 7.01 – 6.99 (m, 1H), 6.45 – 6.44 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 135.68, 127.66, 124.11, 121.90, 120.66, 120.37 (t, $J_{C–D}$ = 25.5 Hz), 119.74, 119.62; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_8H_7DN 119.0714, found: 119.0723.



1*H*-Indole-5-*d* (40)[12]. The representative procedure was followed using 5-chloro-1*H*-indole (30.32 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **40** (17.0 mg, 72 %) as a yellow oil. 87 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.83 (br, 0.93H), 7.56 (s, 1H) 7.23 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.05 – 7.04 (m, 0.13H), 7.02 – 7.00 (m, 1H), 6.55 – 6.54 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 135.69, 127.64, 124.10, 121.64 (t, $J_{C–D}$ = 25.0 Hz), 120.67, 119.04, 110.88, 102.52; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_8H_7DN 119.0714, found: 119.0721.

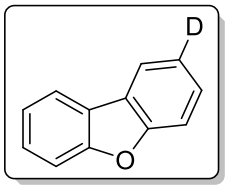


***tert*-Butyl 1*H*-indole-1-carboxylate-4-*d* (41)**[12]. The representative procedure was followed using *tert*-butyl 4-chloro-1*H*-indole-1-carboxylate (50.34 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **41** (31.4 mg, 72 %) as a yellow oil. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.08 – 8.06 (m, 1H), 7.52 (d, *J* = 4.0 Hz, 1H) 7.24 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 4.0 Hz, 1H), 1.60 (s, 9H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 149.81, 135.17, 130.46, 125.87, 124.15, 122.48, 120.61 (t, $J_{C–D}$ = 24.0 Hz), 115.13, 107.21, 83.61, 28.21; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{13}H_{15}DNO_2$ 219.1238, found: 219.1239.

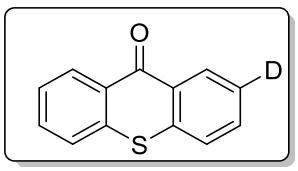


3-Methoxypyridine-6-*d* (42)[12]. The representative procedure was followed using 2-

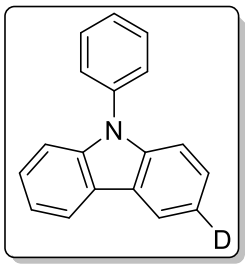
chloro-5-methoxypyridine (28.71 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **42** (14.7 mg, 67 %) as a yellow oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.35 (s, 1H), 7.27 – 7.20 (m, 2H), 3.87 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 155.67, 141.77 (t, $J_{C–D}$ = 27.5 Hz), 137.56, 123.63, 120.42, 55.47; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_7DNO 111.0663, found: 111.0667.



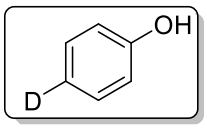
Dibenzo[*b*,*d*]furan-2-*d* (43)[13]. The representative procedure was followed using 2-chlorodibenzo[*b*,*d*]furan (40.53 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **43** (31.1 mg, 92 %) as a white solid. 97 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.94 – 7.92 (m, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.32 (t, *J* = 8.5 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 156.14, 127.08, 126.97, 124.19, 122.64, 122.36 (t, $J_{C–D}$ = 24.5 Hz), 120.60, 120.49, 111.62; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_8DO$ 170.0711, found: 170.0710.



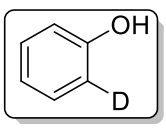
9*H*-Thioxanthen-9-one-2-*d* (44). The representative procedure was followed using 2-chloro-9*H*-thioxanthen-9-one (49.34 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : DCM = 1:1) yielded **44** (38.4 mg, 90 %) as a white solid. 90 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.63 – 8.61 (m, 2H), 7.63 – 7.56 (m, 4H), 7.50 – 7.46 (m, 1.1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 179.92, 137.23, 132.22, 132.12, 129.82, 129.71, 129.18, 126.26, 125.98 (t, $J_{C–D}$ = 25.5 Hz), 125.94; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{13}H_8DOS$ 214.0431, found: 214.0427.



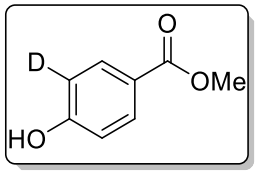
9-Phenyl-9*H*-carbazole-3-*d* (45)[14]. The representative procedure was followed using 3-chloro-9-phenyl-9*H*-carbazole (55.55 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 200 : 1) yielded **45** (23.3 mg, 90 %) as a white solid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.11 – 8.10 (m, 2H), 7.51 – 7.50 (m, 4H), 7.36 – 7.35 (m, 5H), 7.25 – 7.22 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 140.86, 137.67, 129.77, 127.34, 127.06, 125.87, 125.76, 123.32, 120.24, 120.13, 119.86, 119.59 (t, $J_{C–D}$ = 24.0 Hz), 109.70; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{18}H_{13}DN$ 245.1184, found: 245.1180.



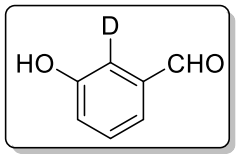
Phen-4-*d*-ol (46)[6]. The representative procedure was followed using 4-iodophenol (43.99 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **46** (17.5 mg, 92 %) as a white solid. 85 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.22 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 8.0 Hz, 0.15H), 6.83 (d, *J* = 8.0 Hz, 2H), 5.76 – 5.71 (br, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 155.29, 129.54, 120.79, 120.52 (t, $J_{C–D}$ = 25.5 Hz), 115.32; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_6H_6DO 96.0554, found: 96.0559.



Phen-2-*d*-ol (47). The representative procedure was followed using 2-iodophenol (43.99 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **47** (17.7 mg, 93 %) as a white solid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 – 7.21 (m, 2H), 6.94 – 6.90 (m, 1H), 6.84 – 6.82 (m, 1H), 5.67 (br, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 155.32, 129.63, 129.54, 120.75, 115.33, 115.06 (t, $J_{C–D}$ = 24.0 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_6DO 96.0554, found: 96.0552.

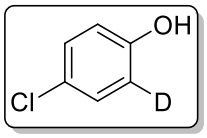


Methyl 4-hydroxybenzoate-3-*d* (48). The representative procedure was followed using methyl 4-hydroxy-3-iodobenzoate (55.61 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **48** (26.6 mg, 87 %) as a colorless liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.88 – 7. 86 (m, 2H), 6.83 – 6.81 (m, 1H), 6.73 (s, 1H), 3.82 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 167.58, 160.40, 131.93, 131.84, 122.09, 115.31, 115.05 (t, $J_{C–D}$ = 24.5 Hz), 52.09; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_8H_8DO_3$ 154.0609, found: 154.0616.

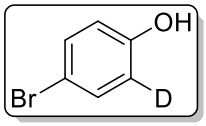


3-Hydroxybenzaldehyde-2-*d* (49). The representative procedure was followed using 2-bromo-3-hydroxybenzaldehyde (40.00 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **49** (20.9 mg, 85 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.96 (s, 1H), 7.46 – 7.41 (m, 2H), 7.13 (m, 1H), 5.79 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 192.27, 156.38, 137.81, 130.35, 123.35,

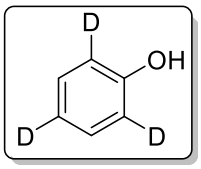
122.01, 114.77; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_7H_6DO_2$ 124.0503, found: 124.0500.



4-Chlorophen-2-*d*-ol (50). The representative procedure was followed using 4-chloro-2-iodophenol (50.69 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **50** (23.3 mg, 90 %) as a yellow liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.19 – 7.18 (m, 2H), 6.78 – 6.76 (m, 1H), 5.14 (br, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 154.28, 129.48, 129.40, 125.48, 116.72, 116.45 (t, $J_{C–D}$ = 24.5 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_6H_5DClO 130.0164, found: 130.0170.

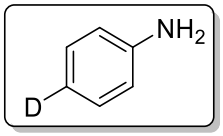


4-Bromophen-2-*d*-ol (51). The representative procedure was followed using 4-bromo-2-iodophenol (59.78 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **51** (21.9 mg, 63 %) as a pink liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.27 – 7.24 (m, 2H), 6.66 – 6.64 (m, 1H), 5.01 (br, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 154.57, 132.44, 132.36, 117.19, 116.92 (t, $J_{C–D}$ = 24.0 Hz), 112.84; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_6H_5DBrO 173.9659, found: 173.9663.

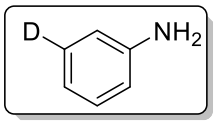


Phen-2,4,6-*d*$_3$-ol (52)[15]. The representative procedure was followed using 2,4,6-triiodophenol (94.36 mg, 0.20 mmol) and D_2O (108 μL, 6.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **52** (13.6 mg, 70 %) as yellow liquid.

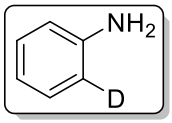
Series of deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.16 (s, 2H), 6.85 (t, *J* = 7.5 Hz, 0.11H), 6.76 (d, *J* = 7.5 Hz, 0.15H) 5.18 (br, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 155.35, 129.42, 120.71, 120.45 (t, $J_{C–D}$ = 25.0 Hz), 115.28, 115.00 (t, $J_{C–D}$ = 25.0 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_6H_4D_3O$ 98.0680, found: 98.0693.



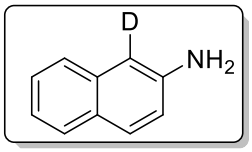
Benzen-4-*d*-amine (53)[6]. The representative procedure was followed using 4-chloroaniline (25.52 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **53** (16.3 mg, 87 %) as a white solid. 80 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.17 – 7.14 (m, 2H), 6.76 (t, *J* = 7.0 Hz, 0.2H), 6.70 – 6.68 (m, 2H), 3.61 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 146.27, 129.26, 129.14, 118.29 (t, $J_{C–D}$ = 24.5 Hz), 115.08; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_7DN 95.0714, found: 95.0711.



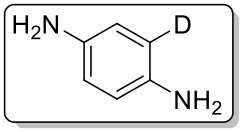
Benzen-3-*d*-amine (54). The representative procedure was followed using 3-chloroaniline (25.52 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **54** (15.4 mg, 82 %) as a white solid. 74 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.15 (t, *J* = 7.5 Hz, 1.26H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.69 – 6.67 (m, 2H), 3.44 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 146.30, 129.23, 128.95 (t, $J_{C–D}$ = 23.5 Hz), 118.40, 115.07, 114.97; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_7DN 95.0714, found: 95.0720.



Benzen-2-*d*-amine (55)[6]. The representative procedure was followed using 2-chloroaniline (25.52 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **55** (16.5 mg, 88 %) as a white solid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.10 – 7.06 (m, 2H), 6.68 (t, *J* = 7.0 Hz, 1H), 6.66 – 6.60 (m, 1H), 3.37 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 146.26, 129.24, 129.14, 118.53, 115.09, 114.80 (t, $J_{C–D}$ = 24.0 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_7DN 95.0714, found: 95.0715.

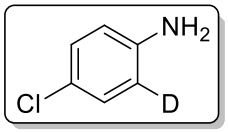


Naphthalen-1-*d*-2-amine (56). The representative procedure was followed using 1-chloronaphthalen-2-amine (35.41 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **56** (20.4 mg, 71 %) as a white solid. 75 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.23 – 7.19 (m, 1H), 6.96 – 6.95 (m, 0.25H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.76 (br, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 144.05, 134.89, 129.14, 127.95, 127.67, 126.29, 125.76, 122.42, 118.19, 108.56, 108.25 (t, $J_{C–D}$ = 24.0 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{10}H_9DN$ 145.0871, found: 145.0879.

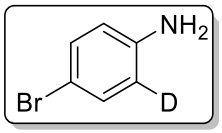


Benzene-2-*d*-1,4-diamine (57). The representative procedure was followed using 2-chlorobenzene-1,4-diamine (28.41 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 1 : 1) yielded **57** (19.4 mg,

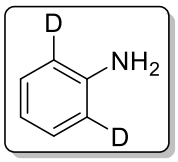
89 %) as a white solid. 54 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.92 (t, *J* = 8.0 Hz, 1H), 6.12 – 6.10 (m, 2H), 6.01 (t, *J* = 8.0 Hz, 0.46H), 3.45 (br, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 147.45, 130.11, 105.92, 101.90; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_6H_8DN_2$ 110.0823, found: 110.0830.



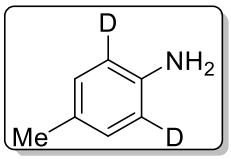
4-Chlorobenzen-2-*d*-amine (58). The representative procedure was followed using 4-chloro-2-iodoaniline (50.69 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **58** (18.2 mg, 71 %) as a yellow liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.03 – 7.00 (m, 2H), 6.53 – 6.51 (m, 1H), 3.48 (br, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 144.85, 129.06, 128.97, 123.11, 116.20, 115.91 (t, $J_{C–D}$ = 24.0 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_6DClN 129.0324, found: 129.0321.



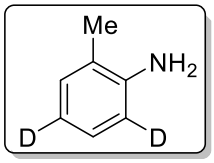
4-Bromobenzen-2-*d*-amine (59). The representative procedure was followed using 4-bromo-2-iodoaniline (59.58 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **59** (25.6 mg, 74 %) as a colorless liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.16 – 7.14 (m, 2H), 6.48 – 6.46 (m, 1H), 3.48 (br, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 145.31, 131.94, 131.85, 116.66, 116.38 (t, $J_{C–D}$ = 24.0 Hz), 110.12; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for C_6H_6DBrN 172.9819, found: 172.9826.



Benzen-2,6-*d*$_2$-amine (60)[16]. The representative procedure was followed using 2,6-dichloroaniline (32.41 mg, 0.20 mmol) and D_2O (72 μL, 4.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **60** (13.9 mg, 73 %) as an orange liquid. 93% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.08 (d, *J* = 7.5 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 0.15H), 3.54 (br, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 146.19, 129.13, 118.51, 115.07, 114.79 (t, $J_{C–D}$ = 24.0 Hz); **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_6H_6D_2N$ 96.0777, found: 96.0785.

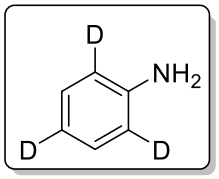


2,6-*d*$_2$-4-Methylaniline (61)[17]. The representative procedure was followed using 2,6-dichloro-4-methylaniline (35.21 mg, 0.20 mmol) and D_2O (72 μL, 4.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **61** (16.4 mg, 75 %) as an orange liquid. 96% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.88 (s, 2H), 6.52 (d, *J* = 8.5 Hz, 0.08H), 3.36 (br, 2H), 2.16 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 143.63, 129.58, 127.71, 115.21, 114.93 (t, $J_{C–D}$ = 23.5 Hz), 20.41; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_7H_8D_2N$ 110.0933, found: 110.0932.

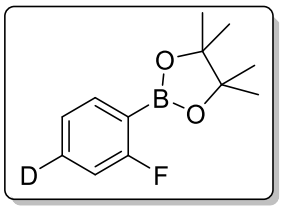


4,6-*d*$_2$-2-Methylaniline (62). The representative procedure was followed using 2,4-dichloro-6-methylaniline (35.21 mg, 0.20 mmol) and D_2O (72 μL, 4.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **62** (14.8 mg, 68 %) as an orange liquid. 92% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR**

(500 MHz, $CDCl_3$) δ 6.97 – 6.98 (m, 2H), 6.65 – 6.59 (m, 0.13H), 3.50 (br, 2H), 2.09 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 144.43, 130.27, 126.68, 122.26, 118.56, 118.30 (t, J = 24.5 Hz), 114.86, 114.58 (t, $J_{C–D}$ = 24.5 Hz), 17.29; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_7H_8D_2N$ 110.0933, found: 110.0943.

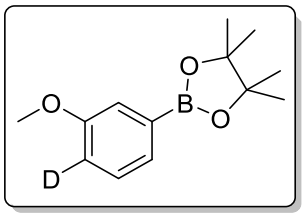


Benzen-2,4,6-*d*$_3$-amine (63)[15]. The representative procedure was followed using 2,4,6-trichloroaniline (39.29 mg, 0.20 mmol) and D_2O (108 μL, 6.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **63** (15.5 mg, 87 %) as yellow liquid. Series of deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.14 (s, 2H), 6.75 (t, J = 7.5 Hz, 0.13H), 6.67 (d, J = 7.5 Hz, 0.21H) 3.62 (br, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 146.20, 129.00, 118.47, 118.20 (t, $J_{C–D}$ = 25.0 Hz), 115.04, 114.76 (t, $J_{C–D}$ = 24.0 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_6H_5D_3N$ 97.0840, found: 97.0847.

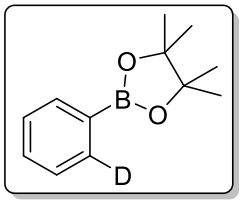


2-(2-Fluorophenyl-4-*d*)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64). The representative procedure was followed using 2-(4-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51.32 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **64** (37.0 mg, 83 %) as colorless liquid. 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.65 (t, J = 7.0 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 6.95 (d, J = 7.0 Hz, 1H), 1.29 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 167.17 (d, J = 249.0 Hz), 136.80 (d, J = 8.0 Hz), 132.91 (t, $J_{C–D}$ = 28.0 Hz), 123.44 (d, J = 3.0 Hz), 115.12

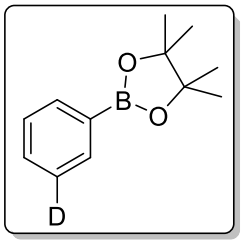
(d, J = 24.0 Hz), 83.86, 24.79; **^{19}F NMR (301 MHz, $CDCl_3$) δ** -102.626; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{16}DBFO_2$ 224.1363, found: 224.1359.



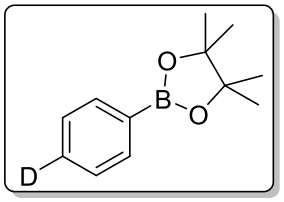
2-(3-Methoxyphenyl-4-*d*)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65). The representative procedure was followed using 2-(4-chloro-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53.71 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **65** (41.8 mg, 89 %) as orange liquid. 87% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.34 – 7.32 (m, 1H), 7.25 – 7.20 (m, 2H), 6.94 – 6.91 (m, 0.13H), 3.75 (s, 3H), 1.29 (s, 12H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.96, 128.78, 127.12, 118.72, 117.51 (t, $J_{C–D}$ = 23.0 Hz), 83.76, 55.16, 24.81; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{13}H_{19}DBO_3$ 236.1563, found: 236.1561.



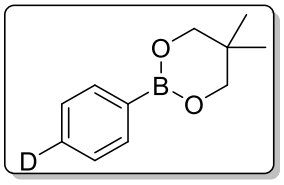
4,4,5,5-Tetramethyl-2-(phenyl-2-*d*)-1,3,2-dioxaborolane (66)[18]. The representative procedure was followed using 2-(2-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (47.70 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **66** (36.9 mg, 90 %) as yellow liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.73 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 – 7.27 (m, 2H), 1.27 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 134.70, 134.41 (t, $J_{C–D}$ = 24.0 Hz), 131.22, 127.68, 127.56, 83.73, 24.84; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{17}DBO_2$ 206.1457, found: 206.1451.



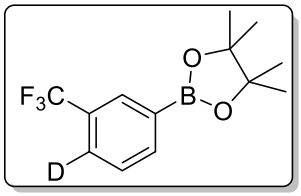
4,4,5,5-Tetramethyl-2-(phenyl-3-*d*)-1,3,2-dioxaborolane (67)[18]. The representative procedure was followed using 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (47.70 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **67** (35.7 mg, 87 %) as yellow liquid. 89% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.75 – 7.73 (m, 2H), 7.39 – 7.37 (m, 1H), 7.29 (t, *J* = 7.5 Hz, 1.11H), 1.27 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 134.72, 134.60, 131.22, 131.12, 127.68, 127.38 (t, $J_{C–D}$ = 24.0 Hz), 83.73, 24.85; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{17}DBO_2$ 206.1457, found: 206.1462.



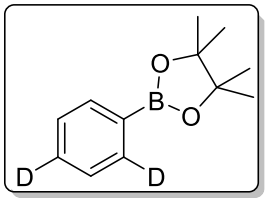
4,4,5,5-Tetramethyl-2-(phenyl-4-*d*)-1,3,2-dioxaborolane (68)[18]. The representative procedure was followed using 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (47.70 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **68** (37.7 mg, 92 %) as a colorless liquid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.74 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 1.27 (s, 12H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 134.69, 130.94 (t, $J_{C–D}$ = 30.0 Hz), 127.57, 83.73, 24.84; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{17}DBO_2$ 206.1457, found: 206.1454.



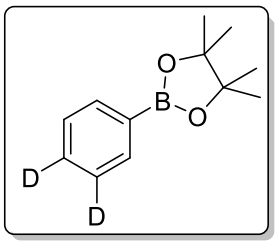
5,5-Dimethyl-2-(phenyl-4-*d*)-1,3,2-dioxaborinane (69). The representative procedure was followed using 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (44.90 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **69** (31.0 mg, 81 %) as yellow liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.72 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 3.69 (s, 4H), 0.95 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 133.79, 130.34 (t, $J_{C–D}$ = 24.0 Hz), 127.55, 127.44, 72.28, 31.86, 21.88; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{11}H_{15}DBO_2$ 192.1301, found: 192.1307.



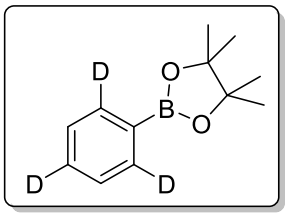
4,4,5,5-Tetramethyl-2-(3-(trifluoromethyl)phenyl-4-*d*)-1,3,2-dioxaborolane (70). The representative procedure was followed using 2-(4-chloro-3-(trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (61.30 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **70** (33.3 mg, 61 %) as colorless liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.99 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 1.29 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 137.97, 131.33 (q, *J* = 3.5 Hz), 129.90 (q, *J* = 40.0 Hz), 127.89, 124.27 (q, *J* = 240.0 Hz), 84.26, 24.85; **^{19}F NMR (301 MHz, $CDCl_3$) δ** -62.607; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{13}H_{16}DBF_3O_2$ 274.1331, found: 274.1340.



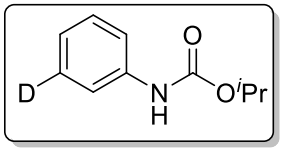
4,4,5,5-Tetramethyl-2-(phenyl-2,4-*d*$_2$)-1,3,2-dioxaborolane (71). The representative procedure was followed using 2-(2,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (54.59 mg, 0.20 mmol) and D_2O (72 μL, 4.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **71** (35.9 mg, 87 %) as colorless liquid. More than 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.73 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.28 (m, 2H), 1.27 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 134.70, 134.41 (t, $J_{C–D}$ = 24.0 Hz), 130.90 (t, $J_{C–D}$ = 24.0 Hz), 127.57, 127.45, 83.74, 24.85; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{12}H_{16}D_2BO_2$ 207.1520, found: 207.1521.



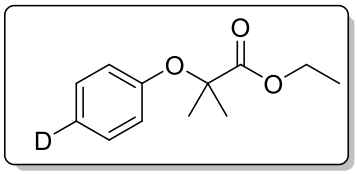
4,4,5,5-Tetramethyl-2-(phenyl-3,4-*d*$_2$)-1,3,2-dioxaborolane (72). The representative procedure was followed using 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (54.59 mg, 0.20 mmol) and D_2O (72 μL, 4.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **72** (31.7 mg, 77 %) as colorless liquid. 98% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.75 – 7.73 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1.06H), 1.27 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 134.72, 134.60, 130.81 (t, $J_{C–D}$ = 24.0 Hz), 127.56, 127.28 (t, $J_{C–D}$ = 24.0 Hz), 83.73, 24.85; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{12}H_{16}D_2BO_2$ 207.1520, found: 207.1525.



4,4,5,5-Tetramethyl-2-(phenyl-2,4,6-*d*$_3$)-1,3,2-dioxaborolane (73). The representative procedure was followed using 4,4,5,5-tetramethyl-2-(2,4,6-trichlorophenyl)-1,3,2-dioxaborolane (61.48 mg, 0.20 mmol) and D_2O (108 μL, 6.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **73** (29.4 mg, 71 %) as colorless liquid. Series of deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.29 (s, 2H), 1.27 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 127.46, 121.22, 83.74, 24.85; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{15}D_3BO_2$ 208.1583, found: 208.1580.

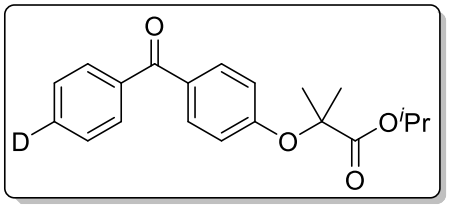


Isopropyl (phenyl-3-*d*)carbamate (74). The representative procedure was followed using isopropyl (3-chlorophenyl)carbamate (42.73 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **74** (30.6 mg, 85 %) as a white solid. 80 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.39 – 7.38 (m, 2H), 7.30 – 7.27 (m, 1.20H), 7.05 – 7.03 (m, 1H), 6.68 (s, 1H), 1.29 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 153.21, 138.06, 128.94, 128.66 (t, $J_{C–D}$ = 24.5 Hz), 123.14, 123.03, 118.51, 68.63, 22.04; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{10}H_{13}DNO_2$ 181.1082, found: 181.1089.

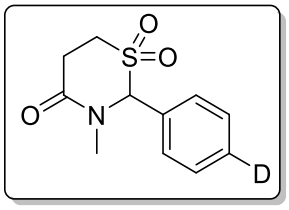


Ethyl 2-methyl-2-(phenoxy-4-*d*)propanoate (75)[19]. The representative procedure was followed using ethyl 2-(4-chlorophenoxy)-2-methylpropanoate (48.54 mg, 0.20 mmol)

and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **75** (31.4 mg, 75 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.24 (q, *J* = 7.5 Hz, 2H), 1.60 (s, 6H), 1.24 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 174.32, 155.38, 128.99, 121.77 (t, $J_{C–D}$ = 24.5 Hz), 119.05, 78.99, 61.37, 25.35, 14.04; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{12}H_{16}DO_3$ 210.1235, found: 210.1234.

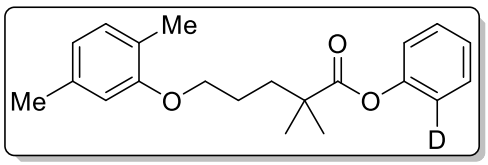


Isopropyl 2-(4-(benzoyl-4-*d*)phenoxy)-2-methylpropanoate (76) [1]. The representative procedure was followed using isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (72.17 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **76** (45.2 mg, 69 %) as a white solid. More than 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.76 (t, *J* = 9.0 Hz, 4H), 7.47 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.09 (sept, *J* = 8.0 Hz, 1H), 1.66 (s, 6H), 1.21 (d, *J* = 8.0 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 195.48, 173.11, 159.49, 138.10, 132.00, 131.60 (t, $J_{C–D}$ = 24.0 Hz), 130.55, 129.68, 128.03, 117.11, 79.32, 69.26, 25.33, 21.48; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{20}H_{22}DO_4$ 328.1654, found: 328.1659.

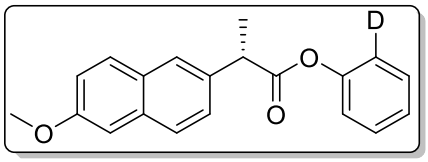


3-Methyl-2-(phenyl-4-*d*)-1,3-thiazinan-4-one 1,1-dioxide (77). The representative procedure was followed using 2-(4-chlorophenyl)-3-methyl-1,3-thiazinan-4-one 1,1-

dioxide (54.75 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 1 : 1) yielded **77** (37.5 mg, 78 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.22 (s, 1H), 3.29 – 3.25 (m, 1H), 3.12 – 3.04 (m, 3H), 2.90 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 166.11, 130.12 (t, $J_{C–D}$ = 24.5 Hz), 130.08, 129.15, 128.04, 80.57, 43.24, 36.20, 30.52; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{11}H_{13}DNO_3S$ 241.0752, found: 241.0757.

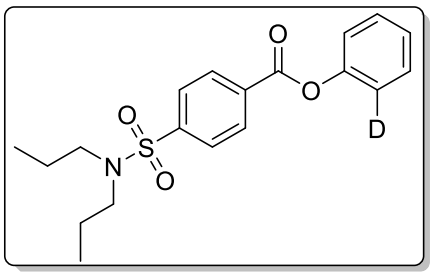


Phenyl-2-*d* 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (78). The representative procedure was followed using 2-chlorophenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (72.18 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **78** (40.6 mg, 62 %) as a white solid. 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.25 – 7.22 (m, 2H), 7.10 – 7.07 (m, 1H), 6.93 – 6.88 (m, 2H) 6.56 – 6.52 (m, 2H), 3.87 – 3.85 (m, 2H), 2.20 (s, 3H), 2.08 (s, 3H), 1.78 – 1.77 (m, 4H), 1.26 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 176.16, 156.80, 150.91, 136.33, 130.27, 129.24, 129.14, 125.52, 123.51, 121.42, 121.16 (t, $J_{C–D}$ = 25.0 Hz), 120.69, 111.88, 67.69, 42.31, 37.08, 25.20, 25.06, 21.31, 15.71; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{21}H_{26}DO_3$ 328.2017, found: 328.2020.

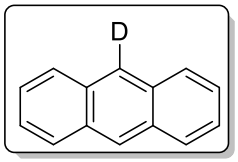


Phenyl-2-*d* (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (79). The representative procedure was followed using 2-chlorophenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (68.16 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **79** (43.0 mg, 70 %) as a white solid.

99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.89 – 7.82 (m, 3H), 7.63 – 7.61 (m, 1H), 7.42 – 7.39 (m, 2H), 7.29 – 7.23 (m, 3H), 7.12 – 7.10 (m, 1H), 4.20 (q, J = 7.0 Hz, 1H), 3.97 (s, 3H), 1.81 (d, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 173.01, 157.66, 150.72, 135.06, 133.74, 129.21, 129.18, 129.08, 128.90, 127.27, 126.03, 126.00, 125.60, 121.28, 121.00 (t, $J_{C–D}$ = 25.0 Hz), 118.99, 105.55, 55.12, 45.46, 18.41; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{20}H_{18}DO_3$ 308.1391, found: 308.1400.

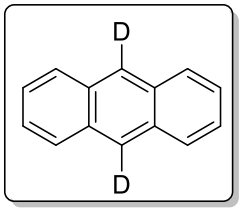


Phenyl-2-*d* 4-(*N*,*N*-dipropylsulfamoyl)benzoate (80). The representative procedure was followed using 2-chlorophenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (79.18 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **80** (47.8 mg, 66 %) as a white solid. 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.22 – 8.20 (m, 2H), 7.85 – 7.84 (m, 2H), 7.35 – 7.32 (m, 2H), 7.20 – 7.17 (m, 1H), 7.13 – 7.11 (m, 1H), 3.05 – 3.02 (m, 4H), 1.49 – 1.44 (m, 4H), 0.80 – 0.77 (m, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 163.64, 150.45, 144.74, 132.70, 130.60, 129.41, 129.31, 126.99, 126.03, 121.31, 121.05 (t, $J_{C–D}$ = 25.0 Hz), 49.80, 21.78, 11.00; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{19}H_{23}DNO_4S$ 363.1483, found: 363.1488.

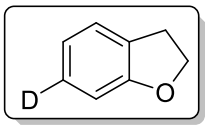


Anthracene-9-*d* (81)[2]. The representative procedure was followed using 9-chloroanthracene (42.54 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane) yielded **81** (30.8 mg, 86 %) as a colorless oil. 99%

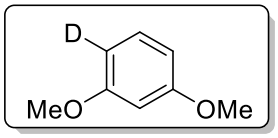
Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.33 (s, 1H), 7.91 (q, *J* = 3.5 Hz, 4H), 7.37 (q, *J* = 3.5 Hz, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 131.65, 131.58, 128.14, 128.09, 126.17, 125.83 (t, $J_{C–D}$ = 24.0 Hz), 125.31; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{14}H_{10}D$ 180.0918, found: 180.0921.



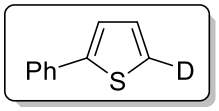
Anthracene-9,10-*d*$_2$ (82). The representative procedure was followed using 9,10-dichloroanthracene (49.2 mg, 0.20 mmol) and D_2O (36 μL, 2.0 mmol). Isolation by column chromatography (*n*-hexane) yielded **82** (29.2 mg, 81 %) as a colorless oil. 86% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.33 (s, 0.28H), 7.91 (q, *J* = 3.5 Hz, 4H), 7.37 (q, *J* = 3.5 Hz, 4H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 131.65, 131.57, 128.14, 128.09, 126.17, 125.81 (t, $J_{C–D}$ = 24.0 Hz), 125.30; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{14}H_9D_2$ 181.0981, found: 181.0990.



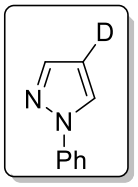
2,3-Dihydrobenzofuran-6-*d* (83). The representative procedure was followed using 6-chloro-2,3-dihydrobenzofuran (30.92 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **83** (18.9 mg, 78 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.21 – 7.20 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 4.49 (t, *J* = 9.0 Hz, 2H), 3.12 (t, *J* = 9.0 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.23, 130.65, 129.42, 127.83, 112.01, 110.81, 71.52, 29.63; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for C_8H_8DO 122.0711, found: 122.0715.



1,3-Dimethoxybenzene-4-*d* (84)[4]. The representative procedure was followed using 1-chloro-2,4-dimethoxybenzene (34.52 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **84** (17.8 mg, 64 %) as a colorless oil. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.33 (d, *J* = 9.0 Hz, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 6.32 (dd, *J* = 2.5Hz, 2.5 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 160.21, 156.52, 133.12, 105.87, 102.43, 99.97, 56.12, 55.54; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_8H_{10}DO_2$ 140.0816, found: 140.0821.

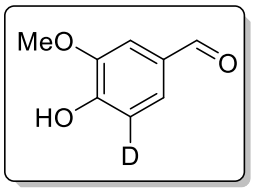


2-Phenylthiophene-5-*d* (85). The representative procedure was followed using 2-chloro-5-phenylthiophene (38.94 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **85** (26.1 mg, 81 %) as a colorless oil. 95 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.54 – 7.52 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 3.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1.05H), 6.99 (d, *J* = 3.5Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 144.31, 134.39, 128.85, 127.81, 127.42, 125.93, 124.80, 124.57 (t, $J_{C–D}$ = 24.5 Hz), 123.04; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{10}H_8DS$ 162.0482, found: 162.0485.

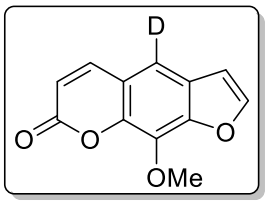


1-Phenyl-1*H*-pyrazole-4-*d* (86). The representative procedure was followed using 4-chloro-1-phenyl-1*H*-pyrazole (35.72 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 50 : 1) yielded **86** (23.8 mg, 82 %) as a colorless oil. More than 99 % Deuterium incorporation was determined by

^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.84 (s, 1H), 7.65 – 7.61 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 140.94, 140.18, 129.37, 126.61, 126.39, 119.17, 107.37 (t, $J_{C–D}$ = 21.0 Hz); **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_9H_8DN_2$ 146.0823, found: 146.0821.

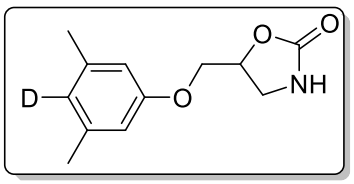


4-Hydroxy-3-methoxybenzaldehyde-5-*d* (87). The representative procedure was followed using 3-chloro-4-hydroxy-5-methoxybenzaldehyde (37.32 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded 87 (24.2 mg, 79 %) as a white solid. 88 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 9.76 (s, 0.72H), 7.36 (s, 2H), 6.98 – 6.96 (m, 0.12H), 6.15 (s, 1H), 3.90 (s, 3H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 190.85, 151.61, 147.12, 129.88, 127.40, 114.35, 114.10 (t, $J_{C–D}$ = 25.0 Hz), 108.74, 56.12; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_8H_8DO_3$ 154.0609, found: 154.0611.

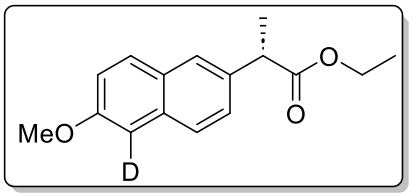


9-Methoxy-7*H*-furo[3,2-*g*]chromen-7-one-4-*d* (88). The representative procedure was followed using 4-chloro-9-methoxy-7*H*-furo[3,2-*g*]chromen-7-one (50.13 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 100 : 1) yielded **88** (29.5 mg, 68 %) as a white solid. 90 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.77 (d, *J* = 4.7 Hz, 1H), 7.69 (d, *J* = 1.3 Hz, 1H), 7.35 (s, 0.1H), 6.82 (d, *J* = 1.3 Hz, 1H), 6.37 (d, *J* = 4.7 Hz, 1H), 4.30 (s, 3H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** 160.39, 147.70, 146.60, 144.24, 142.99, 132.77, 126.00, 116.39, 114.71, 112.88, 112.59 (t, $J_{C–D}$ = 25.5 Hz), 106.66, 61.29; **HRMS** (ESI) m/z ([M+H]$^+$) Calcd. for $C_{12}H_8DO_4$ 218.0558, found:

218.0563.

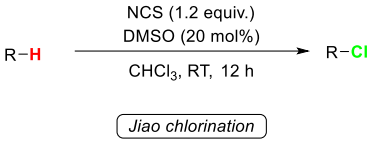


5-((3,5-Dimethylphenoxy-4-*d*)methyl)oxazolidin-2-one (89). The representative procedure was followed using 5-((4-chloro-3,5-dimethylphenoxy)methyl)oxazolidin-2-one (51.14 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 1 : 1) yielded **89** (27.6 mg, 62 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 6.65 (s, 2H), 6.11 (s, 1H), 4.97 – 4.92 (m, 1H), 4.10 – 4.09 (m, 2H), 3.76 (t, *J* = 8.5 Hz, 1H), 3.61 – 3.58 (m, 1H), 2.34 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.49, 155.89, 137.32, 127.16, 114.63, 74.13, 68.22, 42.65, 20.88; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{12}H_{15}DNO_3$ 223.1187, found: 223.1190.

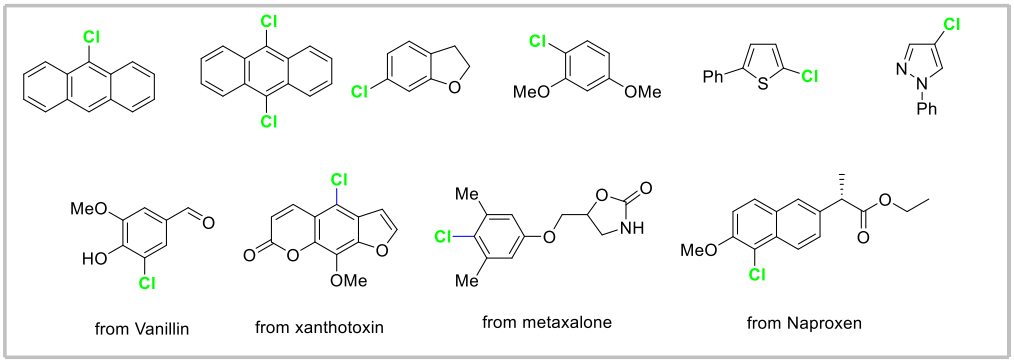


Ethyl (*S*)-2-(6-methoxynaphthalen-2-yl-5-*d*)propanoate (90). The representative procedure was followed using ethyl (*S*)-2-(5-chloro-6-methoxynaphthalen-2-yl)propanoate (58.55 mg, 0.20 mmol) and D_2O (18 μL, 1.0 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 1 : 1) yielded **90** (37.9 mg, 73 %) as a white solid. 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.60 (t, *J* = 9.0 Hz, 3H), 7.32 (d, *J* = 6.5 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 4.08 – 4.00 (m, 2H), 3.80 (s, 3H), 3.74 (q, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 174.62, 157.52, 135.80, 133.55, 129.20, 128.88, 126.99, 126.19, 125.85, 118.88, 105.24 (t, $J_{C–D}$ = 24.0 Hz), 60.68, 55.24, 45.45, 18.57, 14.09; **HRMS** (ESI) m/z ($[M+H]^+$) Calcd. for $C_{16}H_{18}DO_3$ 260.1391, found: 260.1394.

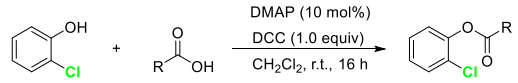
5. General procedure for the synthesis of aryl chlorides

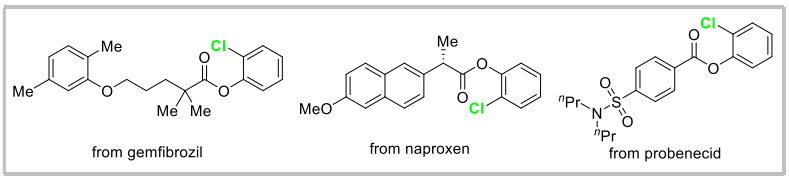


Jiao chlorination



Synthesis of aryl chlorides *via* Jiao chlorination: [20] Aromatic compound (0.5 mmol) and NCS (79.8 mg, 0.6 mmol) were dissolved in $CHCl_3$ (2 mL). DMSO (7 μL, 0.1 mmol) was added to the solution under air at 25 ºC and the mixture were stirred for the required time. After concentrating in vacuum, the residue was purified by chromatography on silica gel to afford the chlorinated product.





Synthesis of chloro-substituted esters:[21] In a 50 mL round-bottomed flask fitted with a magnetic stir bar, a mixture of 2-chlorophenol (0.5 mmol), corresponding acid (0.5 mmol), and DMAP (10 mol%) was dissolved in CH_2Cl_2. The mixture was placed in an ice bath and stirred for 10 min before DCC (0.5 mmol) was added. The mixture was allowed to stir at room temperature for 16 h. The solid precipitate was filtered and washed twice with CH_2Cl_2. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding products.

6. Mechanistic studies

1. Kinetic analysis experiment[22]:

1.1 Ordered in catalyst

To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (4.0, 5.0, 6.0, 7.5 mol%), 2,9-dimethyl-1,10-phenanthroline (7.5 mol%), Zn powder (40.0 mg, 0.60 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (1.0 mmol) was added, followed by the addition of chloride **1** (0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 5 h at room temperature. Over the course of the reaction a GC-MS analysis was acquired every half-an-hour. The 1,3,5-trimethoxybenzene as an internal standard to afford GC-MS yield.

Supplementary Table 1. Order with respect to $NiCl_2$·DME

($NiCl_2$·DME) / mol%	Δ[2a] Δt^{-1} / 10^{-4} s^{-1}	ln(Δ[2a] Δt^{-1} / 10^{-4} s^{-1})
4.0	0.4433	-0.8135
5.0	0.4478	-0.8034
6.0	0.4528	-0.7923
7.5	0.4539	-0.7899

1.2 Ordered in 1

To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (5.0 mol%), 2,9-dimethyl-1,10-phenanthroline (6.0 mol%), Zn powder (40.0 mg, 0.60 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (1.0 mmol) was added, followed by the addition of chloride **1** (0.10, 0.15, 0.20, 0.30 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The

resulting solution was stirred for 5 h at room temperature. Over the course of the reaction a GC-MS analysis was acquired every half-an-hour. The 1,3,5-trimethoxybenzene as an internal standard to afford GC-MS yield.

Supplementary Table 2. Order with respect to 1a

1 / mmol	Δ[2a] Δt^{-1} / 10^{-4} s^{-1}	ln(Δ[2a] Δt^{-1} / 10^{-4} s^{-1})
0.1	0.4712	-0.7525
0.15	0.4854	-0.7228
0.2	0.4757	-0.7430
0.3	0.4779	-0.7384

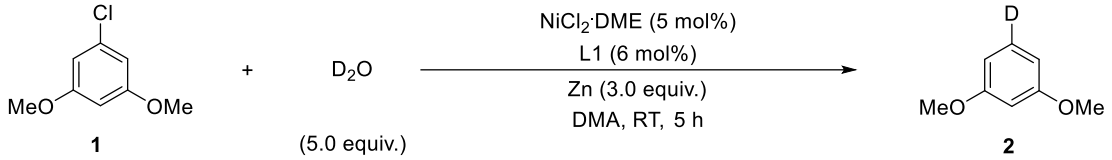
1.3 Ordered in D_2O

To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (5.0 mol%), 2,9-dimethyl-1,10-phenanthroline (6.0 mol%), Zn powder (40.0 mg, 0.60 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (0.6, 1.0, 1.6, 2.0 mmol) was added, followed by the addition of chloride **1** (0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 5 h at room temperature. Over the course of the reaction a GC-MS analysis was acquired every half-an-hour. The 1,3,5-trimethoxybenzene as an internal standard to afford GC-MS yield.

Supplementary Table 3. Order with respect to D_2O

D_2O / mmol	Δ[2a] Δt^{-1} / 10^{-4} s^{-1}	ln(Δ[2a] Δt^{-1} / 10^{-4} s^{-1})
0.6	0.3617	-1.0169
1.0	0.4557	-0.7859
1.6	0.4307	-0.8423
2.0	0.4266	-0.8519

1.4 Reaction profile



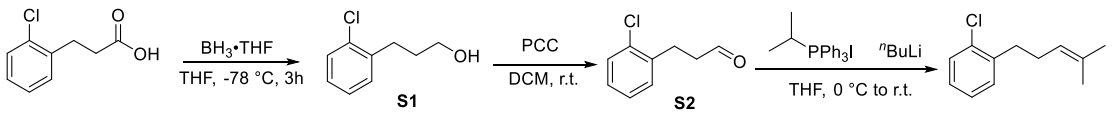
To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (5.0 mol%), 2,9-dimethyl-1,10-phenanthroline (6.0 mol%), Zn powder (40.0 mg, 0.60 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 mg, 1.0 mmol) was added, followed by the addition of chloride **1** (0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 5 h at room temperature. Over the course of the reaction a GC-MS analysis was acquired every half-an-hour. The 1,3,5-trimethoxybenzene as an internal standard to afford GC-MS yield.

Supplementary Table 3. Reaction profile

Time / min	GC-MS yield of **1** / %	GC-MS yield of **2** / %
30	96	4
60	83	17
90	71	28
120	56	44
150	29	71
180	18	81
210	1	99
240	0	99

2. Radical experiments:

2.1 Synthesis of 1-chloro-2-(4-methylpent-3-en-1-yl)benzene:



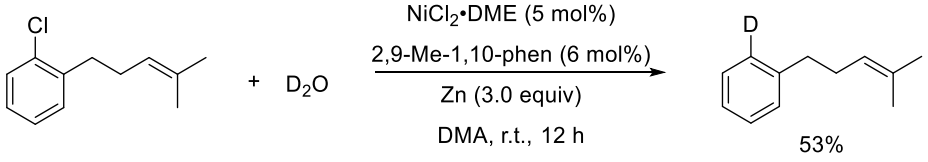
According to the reference[23], to a solution of acid (1.0 equiv.) in anhydrous THF (0.5 M) at –78 °C was added a 1 M solution of BH_3·THF in THF (1.2 equiv.) dropwise.

After stirring at −78 °C for 1 h, the reaction temperature was raised to 0 °C and the reaction was monitored by TLC. Upon completion, the reaction was quenched with excess MeOH. All volatiles were removed under reduced pressure and the residue was purified by flash column chromatography to afford **S1** as colorless oil.

According to the reference[24], to a mixture of pyridinium chlorochromate (PCC) (2.55 g, 11.8 mmol) and dichloromethane (50 mL), the corresponding alcohol **S1** was added. The resulting mixture was stirred for 1 h under room temperature, when TLC analysis indicated the disappearance of the starting material. The mixture was filtered over silica gel under vacuum, washing with dichloromethane. The solvent was totally removed under reduced pressure, resulting in a yellow oil, which was purified by column chromatography on silica-gel column to obtain the aldehyde **S2** as colorless oil.

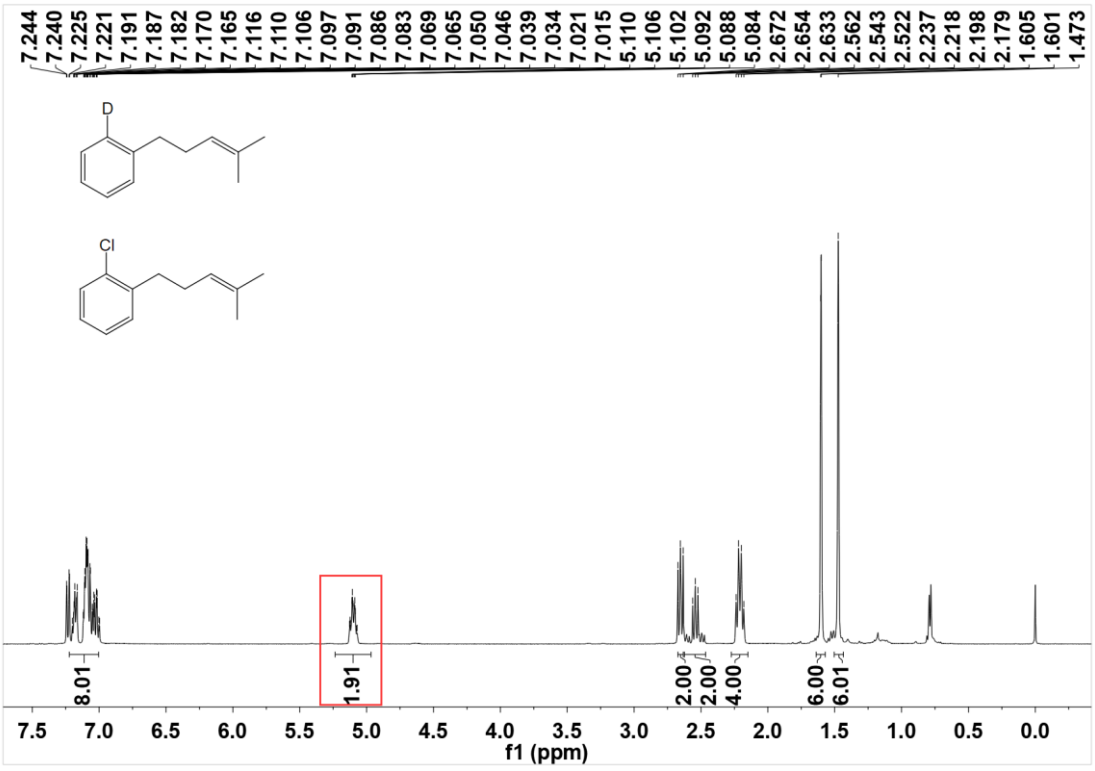
According to the reference[25], a Wittig reaction was conducted to give the final substrates. The phosphonium salt (4.8 mmol, 1.6 equiv) was suspended in THF (9.0 mL) under N_2 and cooled in an ice bath. A solution of ^{n}BuLi (3.0 mmol, 1.0 equiv) was added, and the reaction was stirred at 0 ^{o}C for 30 min. Then, the aldehyde **S2** was added to the flask, and the reaction was stirred at room temperature for 1 h. After this time, 15 mL of H_2O was added, and the reaction mixture was extracted with EtOAc (3 x 15 mL). The organic phase was then washed with brine and dried with Na_2SO_4, and the EtOAc was evaporated under reduced pressure. Purification to remove triphenylphosphine oxide by flash column chromatography yielded the final aryl halide containing the pendant alkene.

2.2 Radical trapping experiment:

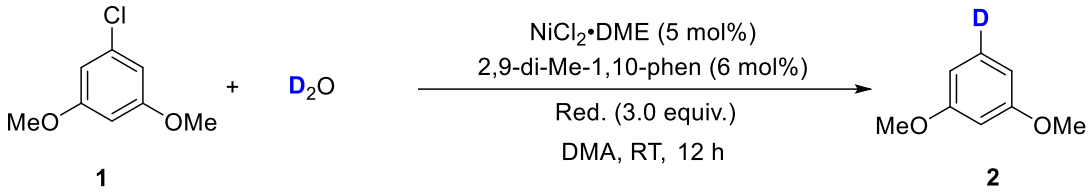


To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (4.41 mg, 0.02 mmol), 2,9-dimethyl-1,10-phenanthroline (5.50 mg, 0.02 mmol), Zn powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL)

was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (1.0 – 2.0 mmol) was added, followed by the addition of aryl chloride (0.2 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to get the mixture of aryl chloride and deuterated product. NMR test shown that, there is no cyclization product can be detected in the reaction. The peak in ^{1}H-NMR 5.10 (q, J = 2.0 Hz, 1.91 H) showed no cyclization product can be detected. Suggested that no aryl radical generated in this condition.



3. Reactions with various reductants:

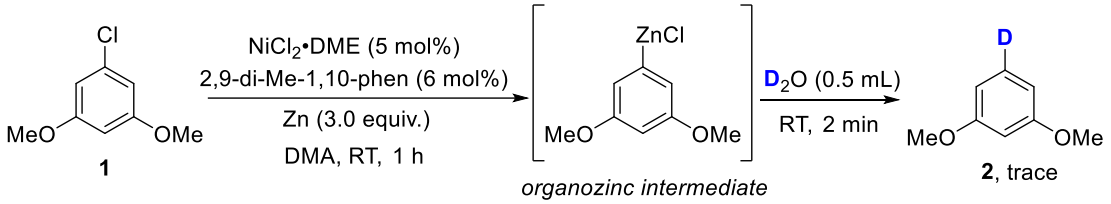


1 **2**

entry	Red.	yield (D inc-)
1	Zn	99% (>99%)
2	Mn	70% (80%)
3	Fe	8%
4	B_2Pin_2 + K_3PO_4	4%
5	TDAE	5%
6	none	n.d.

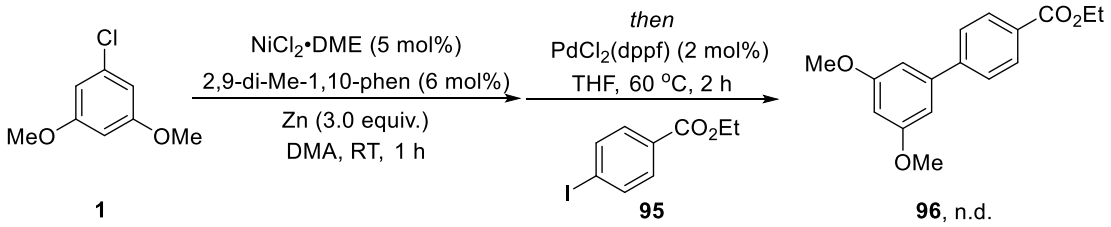
To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.010 mmol), 2,9-dimethyl-1,10-phenanthroline (2.50 mg, 0.012 mmol), reductant (3.0 equiv., 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 mg, 1.0 mmol, 5.0 equiv.) was added, followed by the addition of 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC. The yield was determined versus the internal standard (1,3,5-trimethoxybenzene), the D-incorporation was determined by GC-MS fragment peak.

4. Organozinc intermediate experiment:



To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.010 mmol), 2,9-dimethyl-1,10-phenanthroline (2.50 mg, 0.012 mmol), zinc powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 1 h at room temperature. After this time, deuterated water (20.0 mg, 1.0 mmol, 5.0 equiv.) was added under argon protect condition, and then stirred for 2 min. The crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC. The yield was determined versus the internal standard (1,3,5-trimethoxybenzene). The result showed that trace target substrate **2** was detected, suggesting that no organozinc intermediate was involved in this reaction.

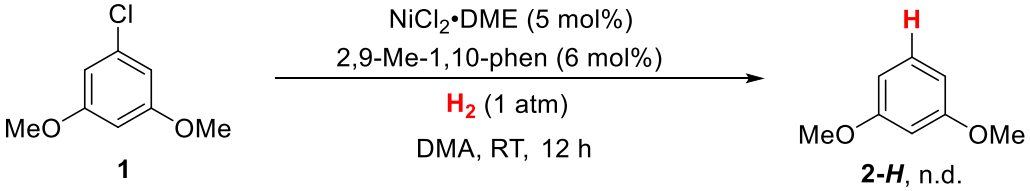
5. Sequential Negishi experiment[26]:



To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.01 mmol), 2,9-dimethyl-1,10-phenanthroline (2.80 mg, 0.01 mmol), Zn powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 mg, 1.0 mmol) was added, followed by the addition of 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. DMA (0.50 mL) was

subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the mixture was filtered, and the liquid was collected. To a reaction tube equipped with a stir bar was added $PdCl_2$(dppf) (4.4 mg, 0.02 mmol) and aryl iodide **96** (27.0 mg, 0.1 mmol). The vessel was evacuated and filled with argon (three times), THF (0.5 mL) and above obtained liquid was added, the mixture was stirred at 60 °C for 2 h, diluted with ethyl acetate (10 mL), washed with H_2O and brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The result showed that no target substrate **96** detected, further suggesting that no organic-zinc intermediate was involved in this reaction.

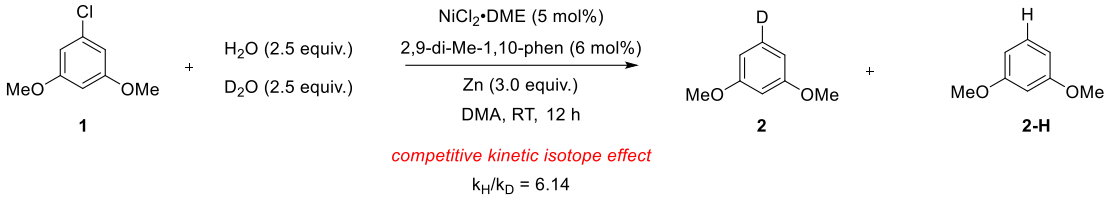
6. Hydrogen reduction experiment[27]:



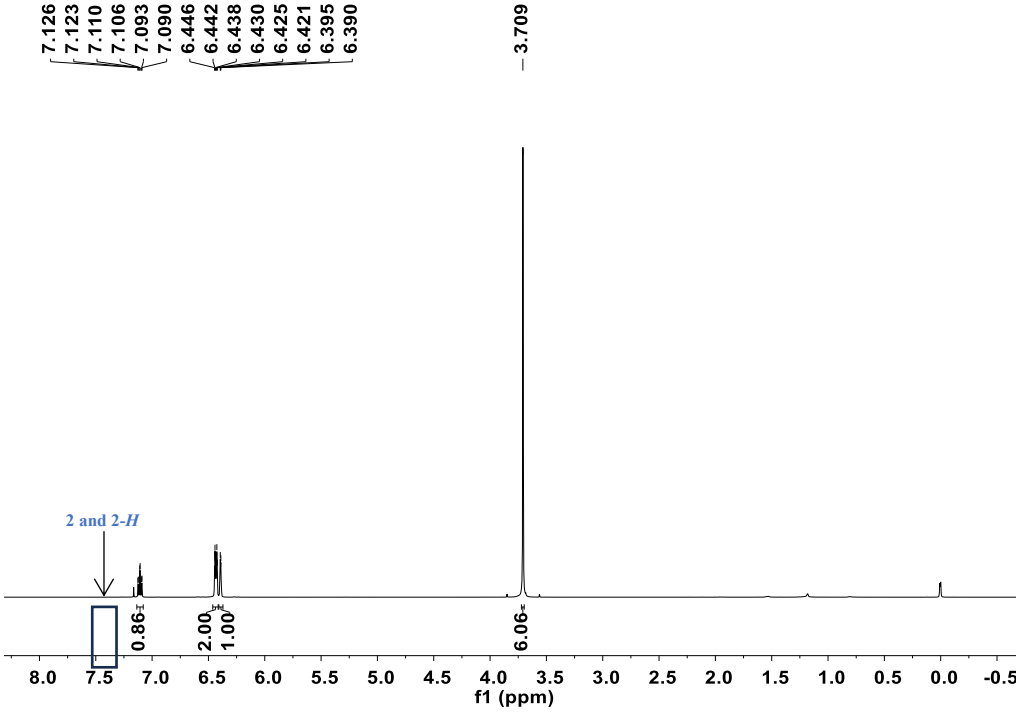
To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.010 mmol), 2,9-dimethyl-1,10-phenanthroline (2.50 mg, 0.012 mmol), zinc powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with H_2 (three times). DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The result showed that no target product **2** was formed.

7. Kinetic isotope effect experiments:

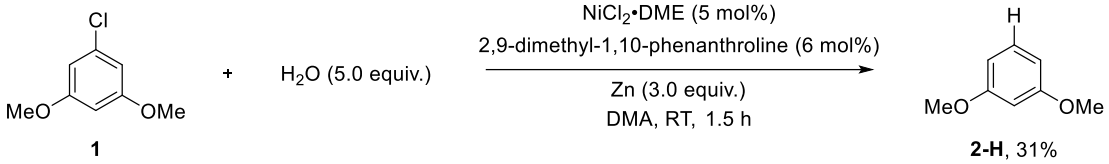
7.1 Competitive kinetic isotope effect experiments[28]:

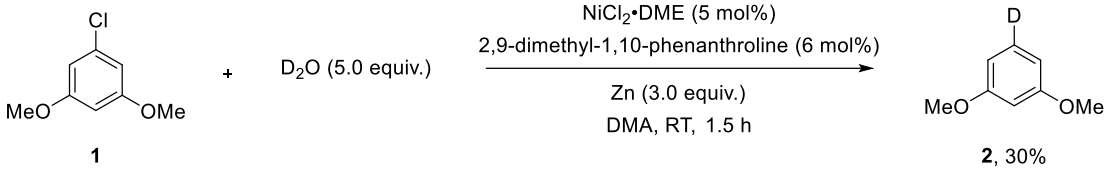


To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.01 mmol), 2,9-dimethyl-1,10-phenanthroline (2.80 mg, 0.01 mmol), Zn powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (10.0 mg, 0.5 mmol) and water (9.0 mg, 0.5 mmol) was added, followed by the addition of 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography. The KIE value was calculated according to the analysis of purified crude ^{1}H NMR: 14% deuterium incorporation was detected in **2**, indicated the KIE value is 0.86/0.14=6.14.



7.2 parallel kinetic isotope effect experiments[29]:



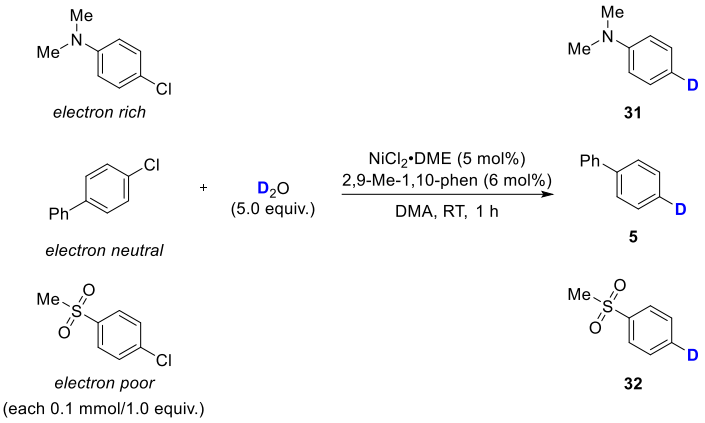


parallel kinetic isotope effect

k_H/k_D = 1.03

To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.01 mmol), 2,9-dimethyl-1,10-phenanthroline (2.80 mg, 0.01 mmol), Zn powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 mg, 1.0 mmol) or water (18.0 mg, 1.0 mmol) was added, followed by the addition of 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 1.5 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). 1,3,5-Trimethoxybenzene (33.6 mg, 0.2 mmol) was added as internal standard to afford GC-MS yield. The GC-MS yield of **2-H** is 31%. The GC-MS yield of **2** is 30%. The KIE value is 1.03, revealing that C–D bond formation is not the rate-determining step.

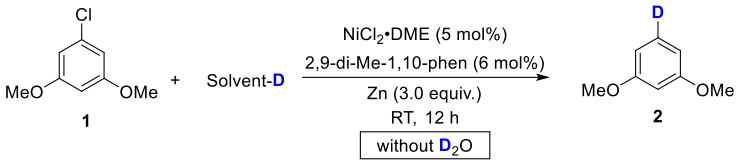
8. Competitive experiments:



	31	5	32
Yield	5%	10%	37%

To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (3.30 mg, 0.015 mmol), 2,9-dimethyl-1,10-phenanthroline (3.75 mg, 0.018 mmol), zinc powder (58.5 mg, 0.9 mmol). The vessel was evacuated and filled with argon (three times). DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (30.0 mg, 1.5 mmol, 5.0 equiv.) was added, followed by the addition of three aryl chlorides (each of 0.1 mmol, 1.0 equiv.) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 1 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The yields were determined versus the internal standard (1,3,5-trimethoxybenzene).

9. Experiments with deuterated solvents:

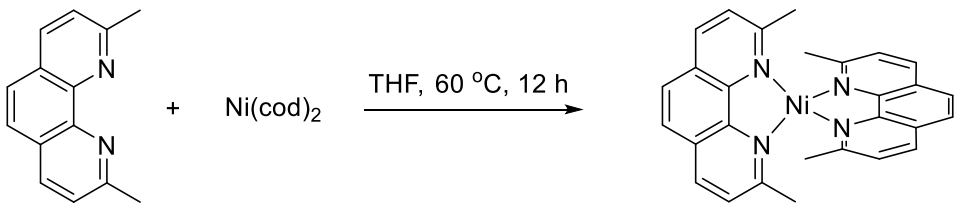


Entry	Solvent-D	Yield	D-inc.
1	acetone-d_6	45%	55%
2	$CDCl_3$	0%	0%
3	CH_3CN-d_3	23%	42%
4	CH_3OH-d_4	84%	92%
5	DMSO-d_6	82%	70%
6	DMF-d_7	87%	72%
7	DMA-d_9	76%	94%
8	DMA-d_9 + H_2O (10.0 equiv.)	99%	<1%

To a 10 mL Schlenk tube was added sequentially $NiCl_2$·DME (2.20 mg, 0.010 mmol), 2,9-dimethyl-1,10-phenanthroline (2.50 mg, 0.012 mmol), zinc powder (40.0 mg, 0.6 mmol). The vessel was evacuated and filled with argon (three times), Solvent-D (0.5 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min, followed by the addition of 1-chloro-3,5-dimethoxybenzene (34.52 mg, 0.20 mmol) in one portion. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The yield was determined versus the internal standard (1,3,5-trimethoxybenzene), the D-incorporation was determined by ^{1}H NMR.

10. Experiments for Ni(I) and Ni(0) catalysis:

10.1 Preparation of Ni(phen)$_2$:



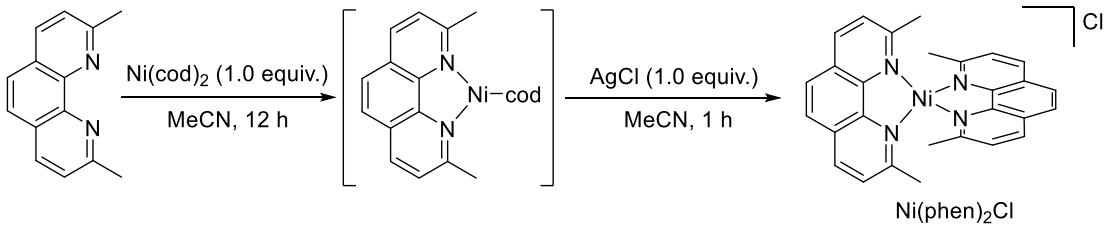
0.2 mmol 0.1 mmol Ni(phen)$_2$

This compound was prepared according to the literature procedure.[30] In an argon-filled glove box, to a 50 mL round bottom flask equipped with a magnetic stir bar was

added $Ni(cod)_2$ (27.5 mg, 0.1 mmol), 2,9-dimethyl-1,10-phenanthroline (41.7 mg, 0.2 mmol), and dry THF (5 mL). It was sealed and removed from the glove box. The reaction mixture was stirred at 60 °C for 12 h. The reaction mixture turned from a pale-yellow suspension to an inky purple solution. The reaction mixture was filtered through celite, and the celite was washed with THF in glove box. The filtrate was concentrated in vacuum to afford $Ni(phen)_2$ as an air-sensitive dark solid (33.3 mg, 70% yield).

Note: The complex is sensitive to air and moisture in the solid state and is unstable in solution at ambient temperature.

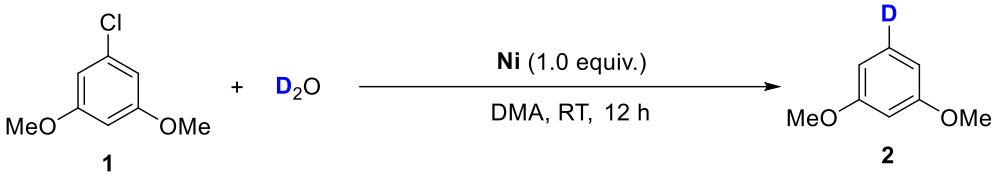
10.2 Preparation of $Ni(phen)_2Cl$:

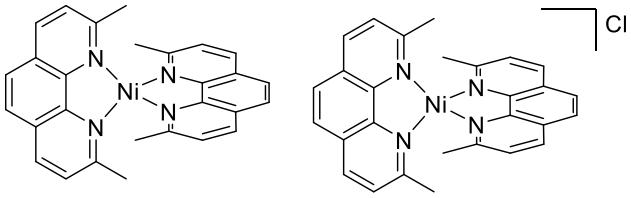


This compound was prepared according to the literature procedure.[30] In an argon-filled glove box, to a 50 mL round bottom flask equipped with a magnetic stir bar was added $Ni(cod)_2$ (54.8 mg, 0.2 mmol), 2,9-dimethyl-1,10-phenanthroline (72.0 mg, 0.2 mmol), and dry CH_3CN (10 mL). The reaction mixture was stirred for 12 h, and it was changed from a pale-yellow suspension to an inky purple solution. AgCl (28.6 mg, 1.0 equiv) was added. The reaction solution immediately turned from dark purple to deep blue. The reaction mixture was stirred for 1 h before being filtered through celite. The celite was washed with THF glove box, and the filtrate was concentrated in vacuum to afford a gray solid. It was treated with dry THF, and the insoluble powder was removed by filtration. The solvent was removed in vacuum to afford $Ni(phen)_2Cl$ as an air sensitive gray solid (56.1 mg, 55% yield).

Note: The complex is sensitive to air and moisture in the solid state and is unstable in solution at ambient temperature.

10.3 Stoichiometric reactions of 1 and deuterium water with $Ni(phen)_2$ or $Ni(phen)_2Cl$



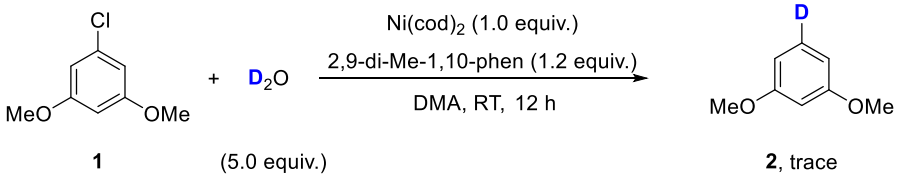


Ni(0): $Ni(phen)_2$ **Ni(I)**: $Ni(phen)_2Cl$

[Ni]	2	1
$Ni(phen)_2$	trace	99%
$Ni(phen)_2Cl$	11%	73%

The reaction was conducted in an Ar-filled glovebox. To a reaction tube equipped with a stir bar was added $Ni(phen)_2$ (47.4 mg, 0.1 mmol) or $Ni(phen)_2Cl$ (50.9 mg, 0.1 mmol). A solution of 1-chloro-3,5-dimethoxybenzene **1** (17.2 mg, 0.1 mmol) and deuterium water (9 μL, 0.5 mmol) in DMA (1.0 mL) was added. The reaction tube was sealed and removed from the glove box, and the reaction mixture was stirred at room temperature for 12 h. Diluted with ethyl acetate (10 mL), washed with H_2O and brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The yield was determined versus the internal standard (1,3,5-trimethoxybenzene).

11. Transformation of Ni^0 species

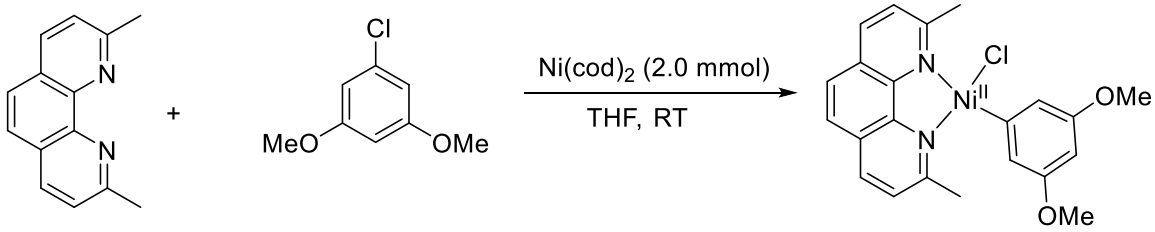


To a 10 mL Schlenk tube was added sequentially $Ni(cod)_2$ (55.0 mg, 0.20 mmol), 2,9-dimethyl-1,10-phenanthroline (50.0 mg, 0.24 mmol). The vessel was evacuated and filled with argon (three times), DMA (0.50 mL) was added *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 mg, 1.0 mmol) was added, followed by the addition of 1-chloro-3,5-dimethoxybenzene **1** (34.4 mg, 0.2

mmol) in one portion. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The result showed that trace target product **2** was detected.

12. Catalytic reactions with Ni^{II} complex

12.1 Preparation of Ar–Ni^{II}(2,9-di-Me-1,10-phen)Cl:

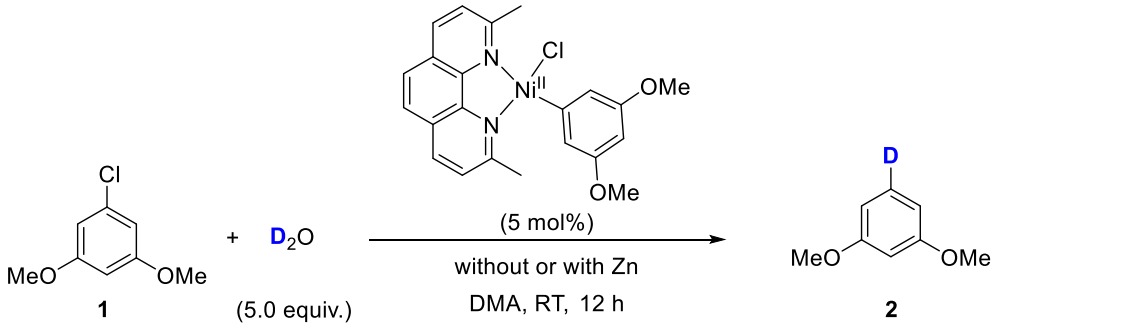


1.2 equiv. 1.2 equiv.

This compound was prepared according to the literature procedure.[31] In a nitrogen-filled glove box, $Ni(cod)_2$ (550 mg, 2 mmol), 2,9-dimethyl-1,10-phenanthroline (499.8 mg, 2.4 mmol), and THF (40 mL) were added to a dry round bottom flask. The resulting mixture was then stirred at RT for 20 h. After this time, 1-chloro-3,5-dimethoxybenzene (414 mg, 2.4 mmol) was added, and reaction was stirred in the glovebox at RT for 2 h. The resulting solution was concentrated in vacuo, and the resulting dark blue solid was triturated with pentanes to remove residual cyclooctadiene and aryl halide to afford complex in 35% yield.

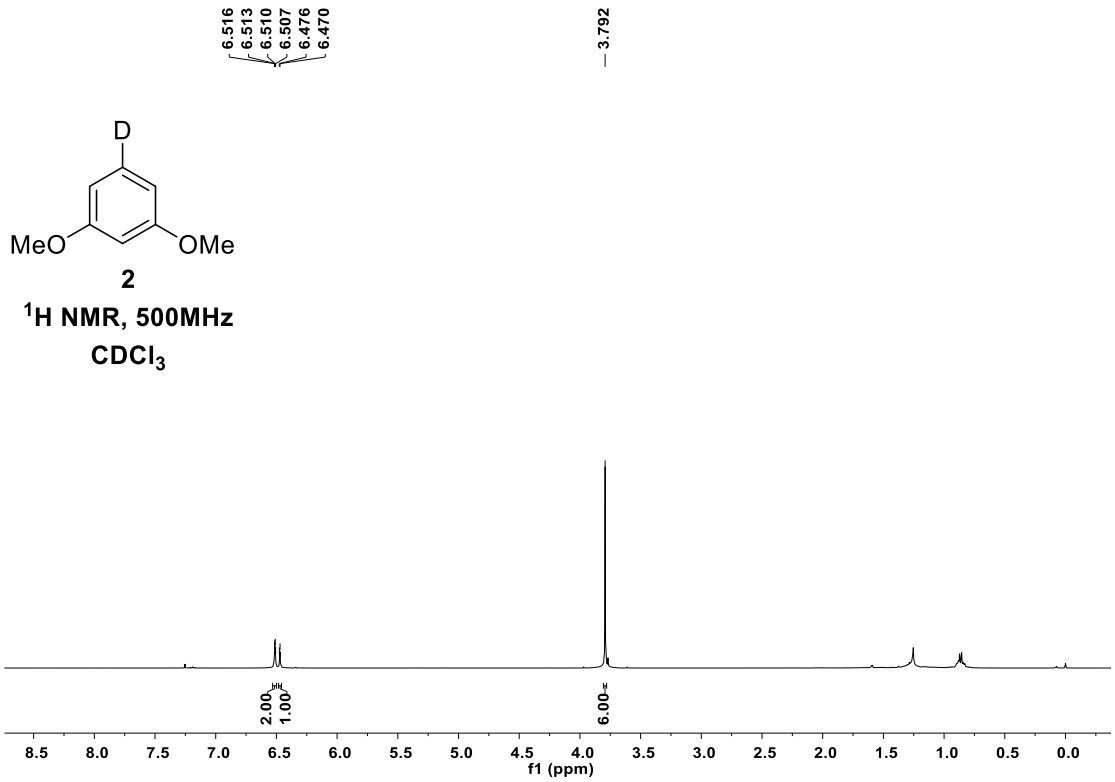
Note: The complex is sensitive to air and moisture in the solid state and is unstable in solution at ambient temperature.

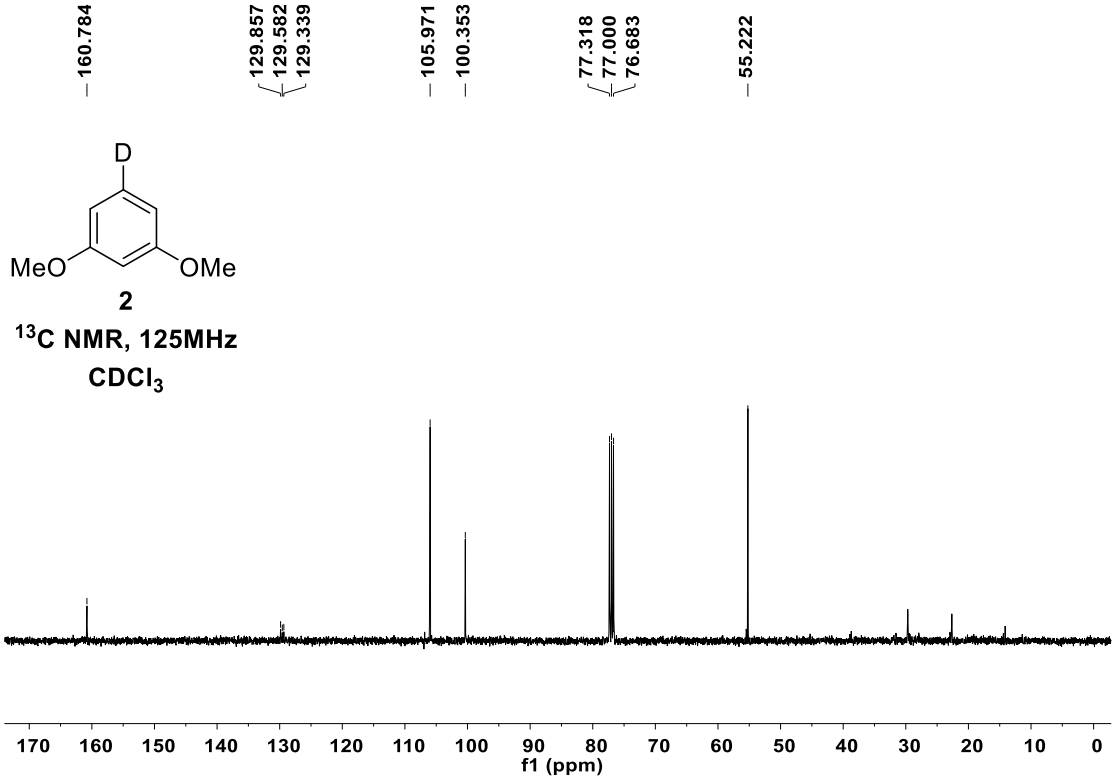
12.2 Stoichiometric reactions of 1 and deuterium water with Ar–Ni^{II}(2,9-di-Me-1,10-phen)Cl

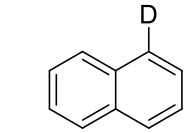


In an argon-filled glove box, prepare two 10 mL Schlenk tube, both of them added Ar–Ni^{II}(2,9-di-Me-1,10-phen)Cl (4.4 mg, 0.01 mmol), and one of tube added the additional of zinc powder (20.0 mg, 6.0 mmol). DMA (0.50 mL) was added in two tubes *via* syringe and the mixture was stirred at room temperature for 10 min. The deuterated water (20.0 mg, 1.0 mmol) and 1-chloro-3,5-dimethoxybenzene **1** (34.4 mg, 0.2 mmol) was added in two tubes. DMA (0.50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature. After this time, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL × 3). A 0.2 mL of solution was collected, diluted with ethyl acetate (1.0 mL), and analyzed by GC-MS. The yield was determined versus the internal standard (1,3,5-trimethoxybenzene), the D-incorporation was determined by ^{1}H NMR.

7. NMR Spectra



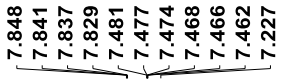


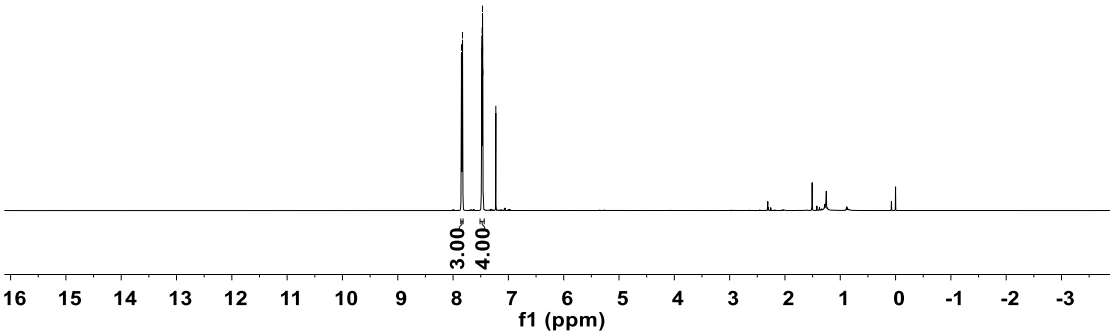


3

^{1}H NMR, 500MHz

$CDCl_3$

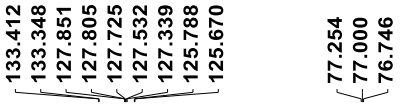


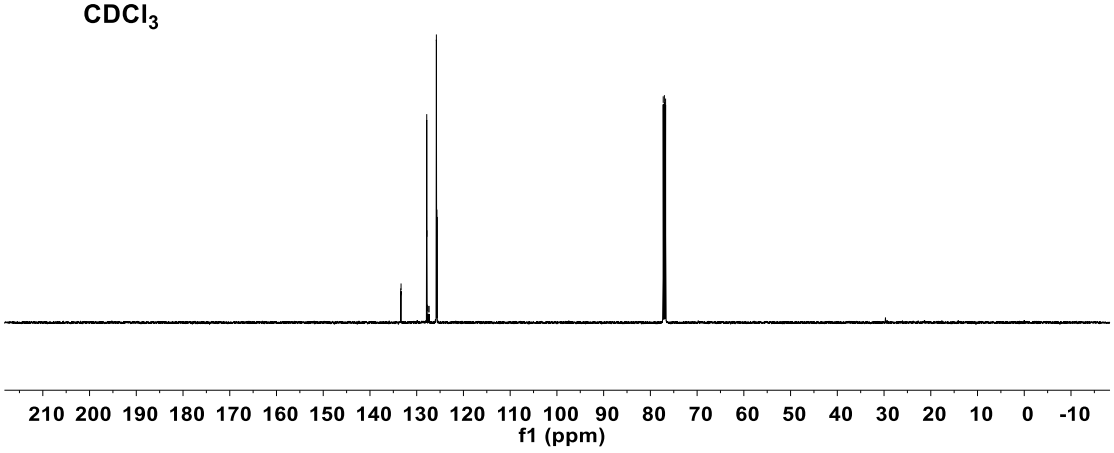


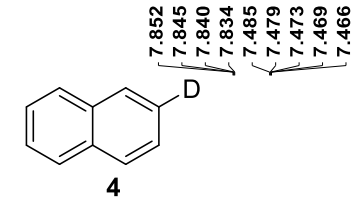
3

^{13}C NMR, 125MHz

$CDCl_3$



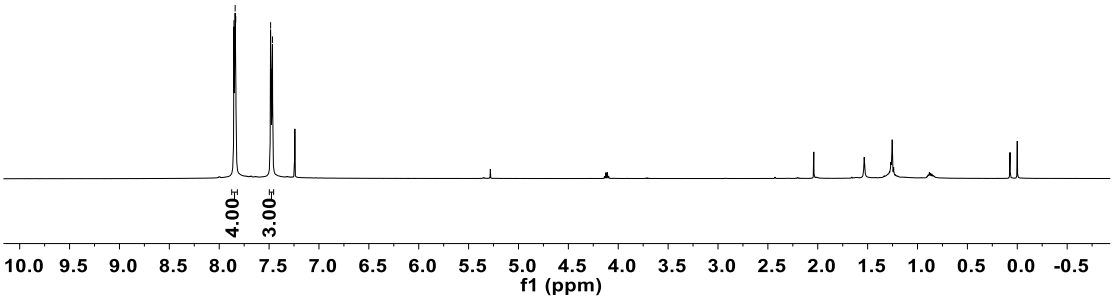


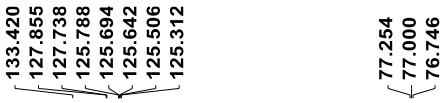


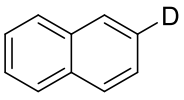
4

^{1}H NMR, 500MHz

$CDCl_3$



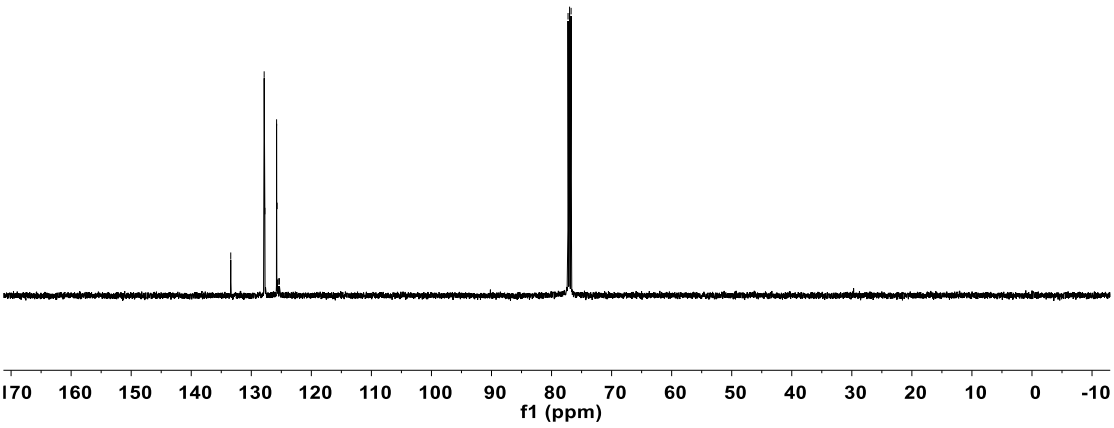


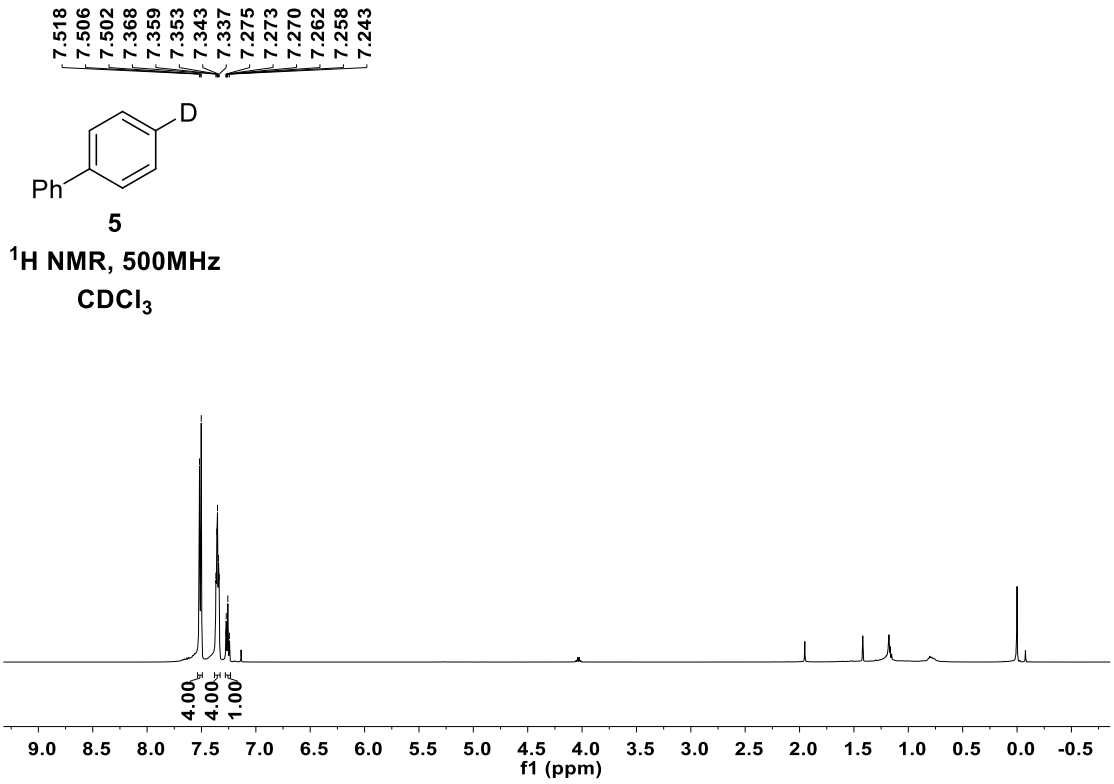


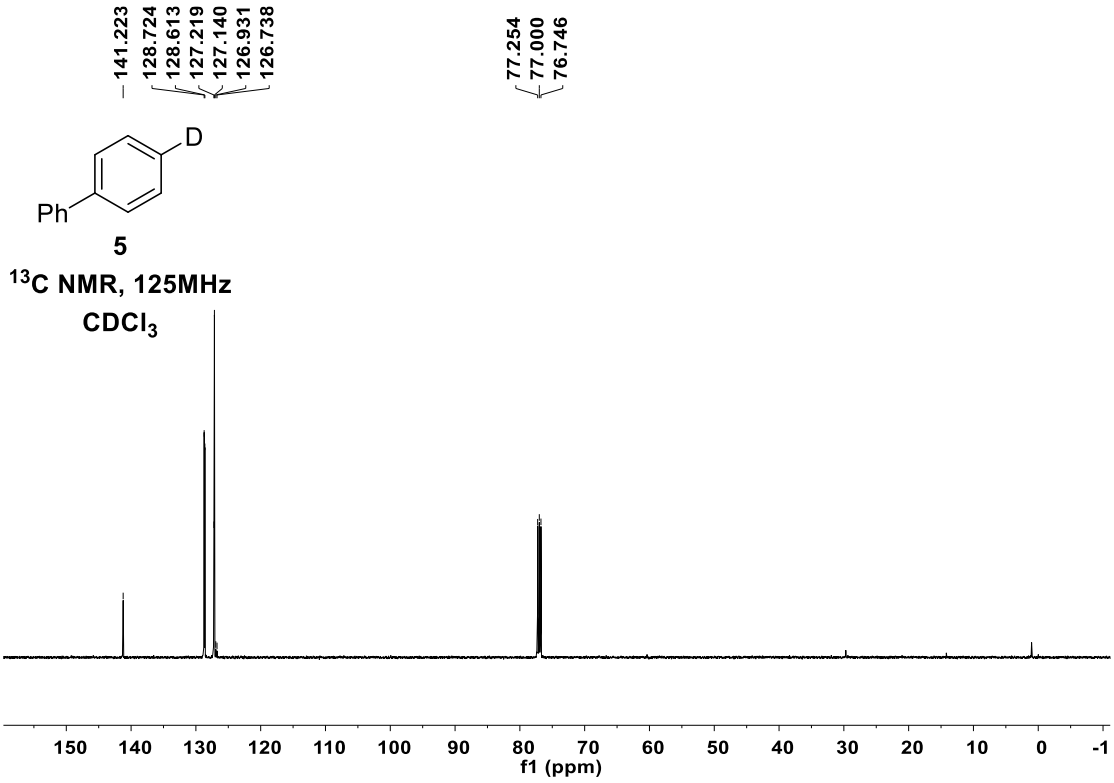
4

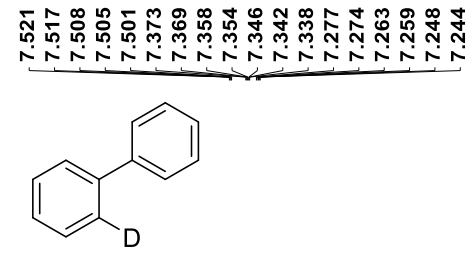
^{13}C NMR, 125MHz

$CDCl_3$




7.518
7.506
7.502
7.368
7.359
7.353
7.343
7.337
7.275
7.273
7.270
7.262
7.258
7.243
D
Ph
5
1H NMR, 500MHz
CDCl3
4.00
4.00
1.00
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 -0.5
f1 (ppm)

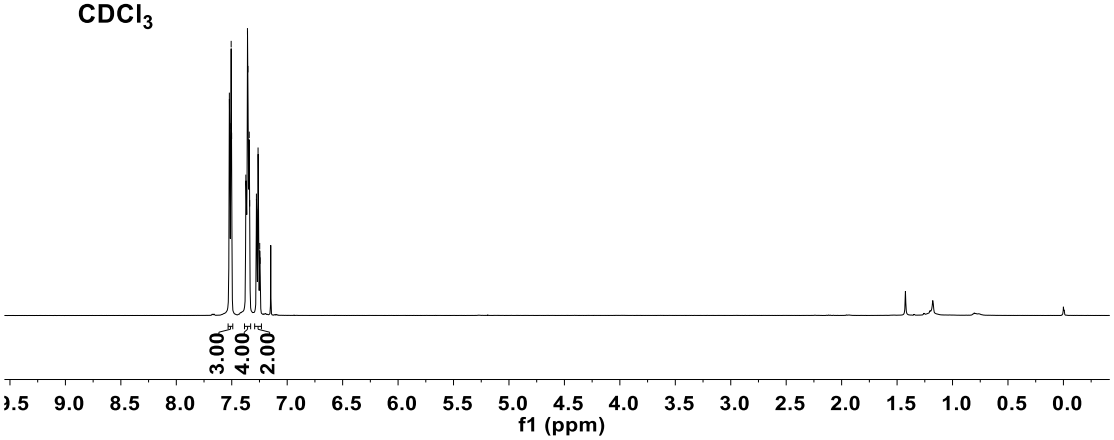

141.223
128.724
128.613
127.219
127.140
126.931
126.738
77.254
77.000
76.746
D
Ph
5
13C NMR, 125MHz
CDCl3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

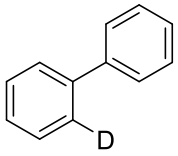


6

^{1}H NMR, 500MHz

$CDCl_3$

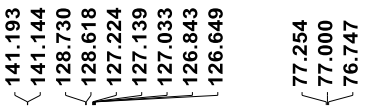


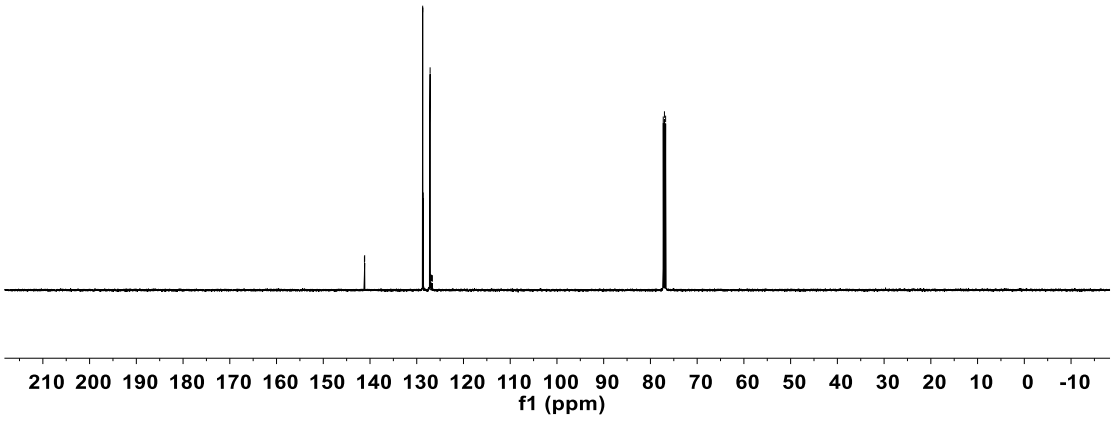


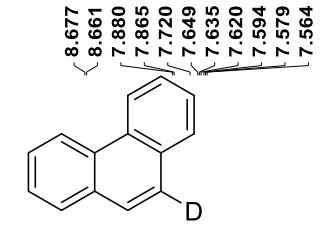
6

^{13}C NMR, 125MHz

$CDCl_3$



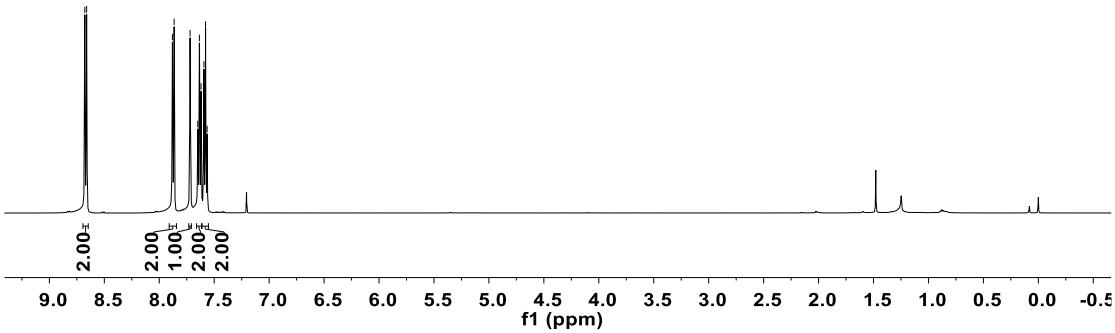


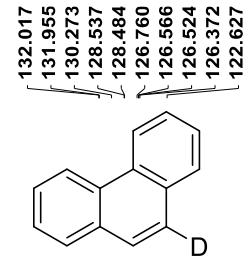


7

^{1}H NMR, 500MHz

$CDCl_3$

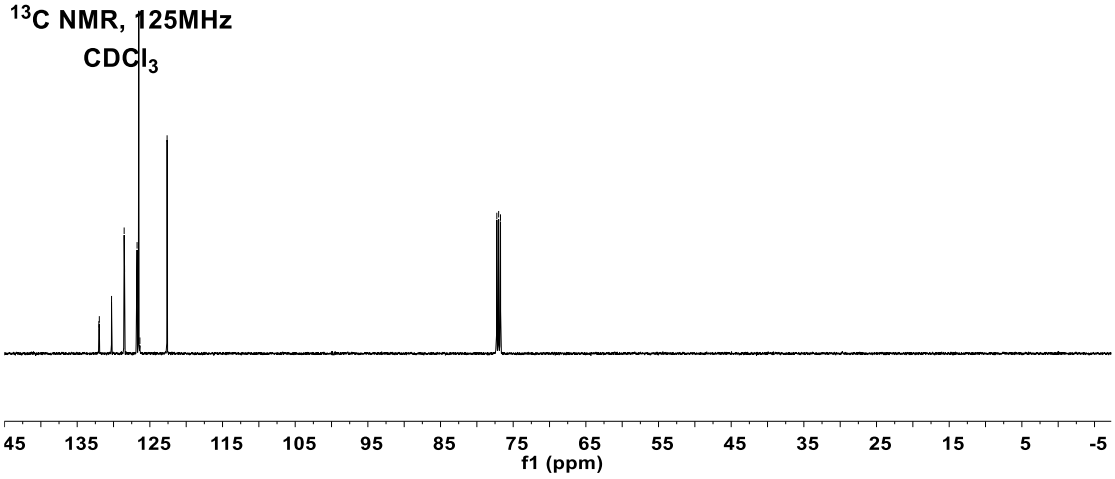


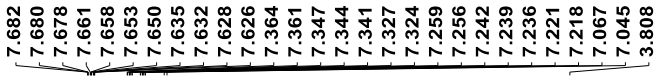


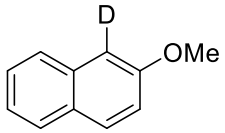
7

^{13}C NMR, 125MHz

$CDCl_3$



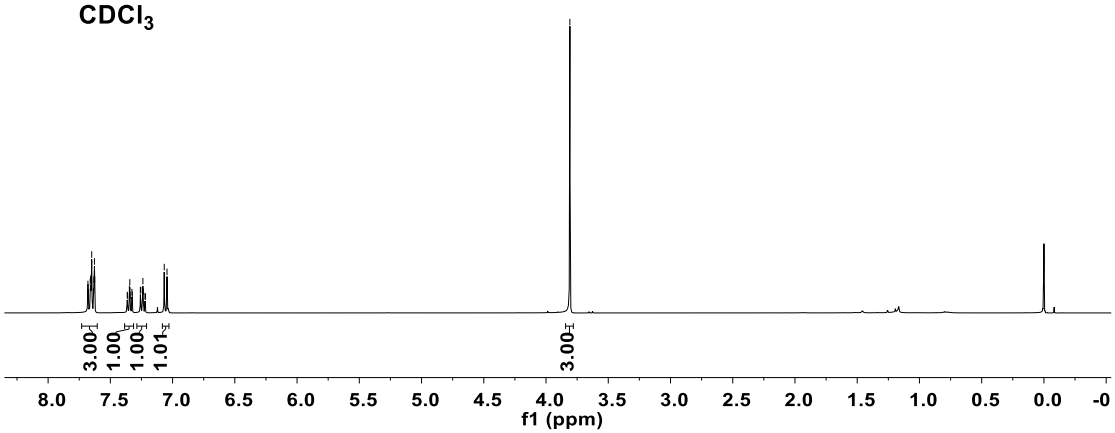


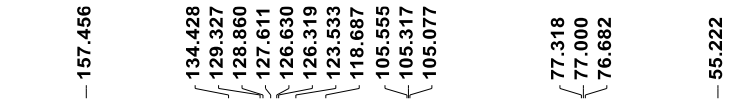


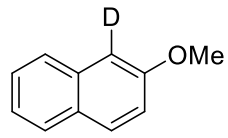
8

^{1}H NMR, 500MHz

$CDCl_3$



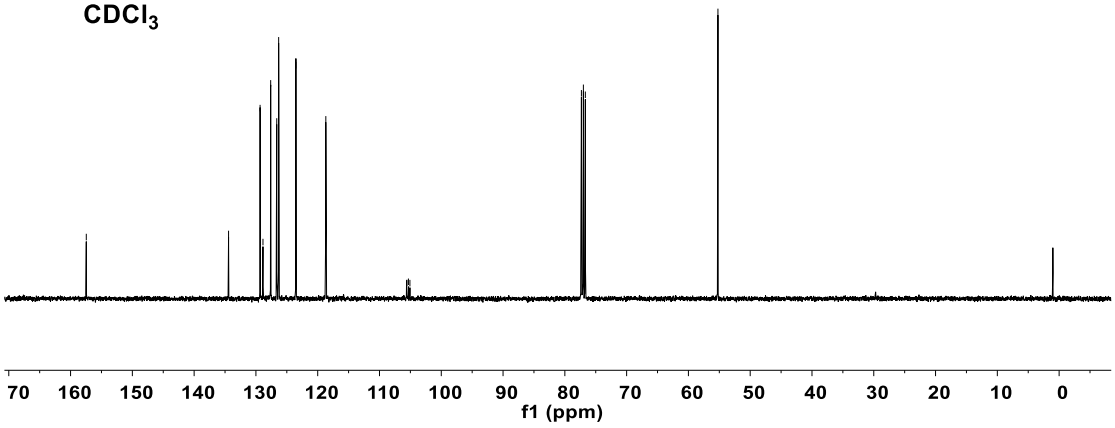


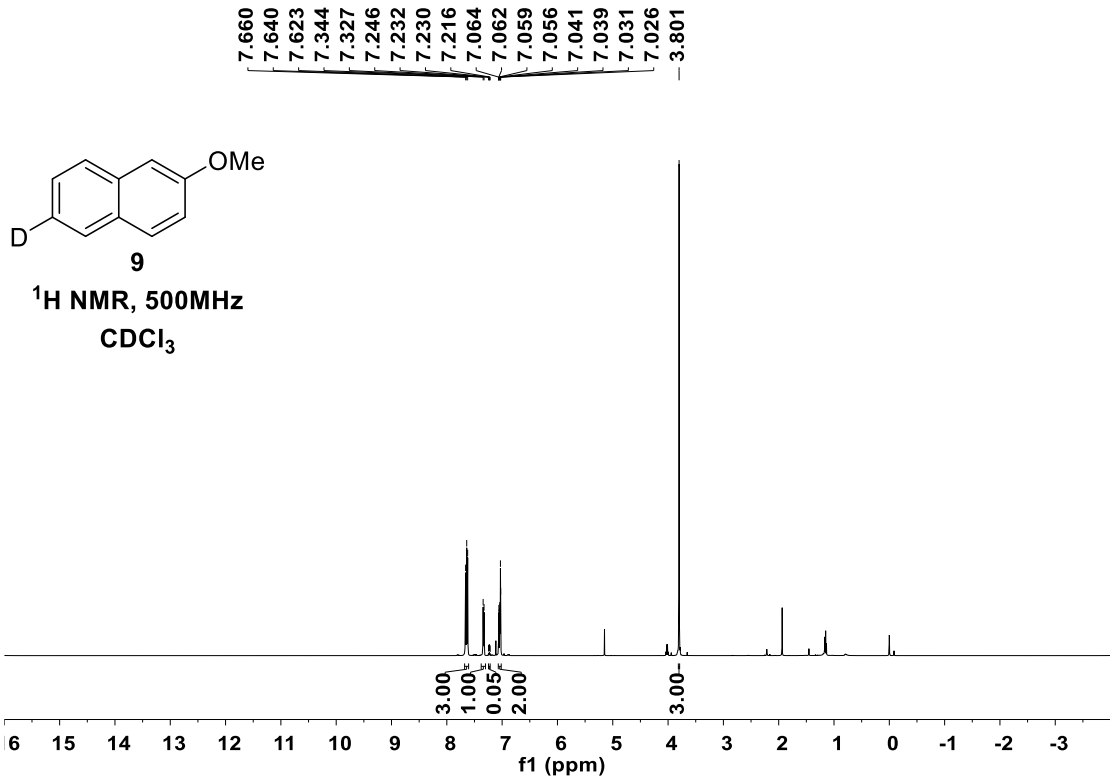


8

^{13}C NMR, 125MHz

$CDCl_3$





9

^{1}H NMR, 500MHz

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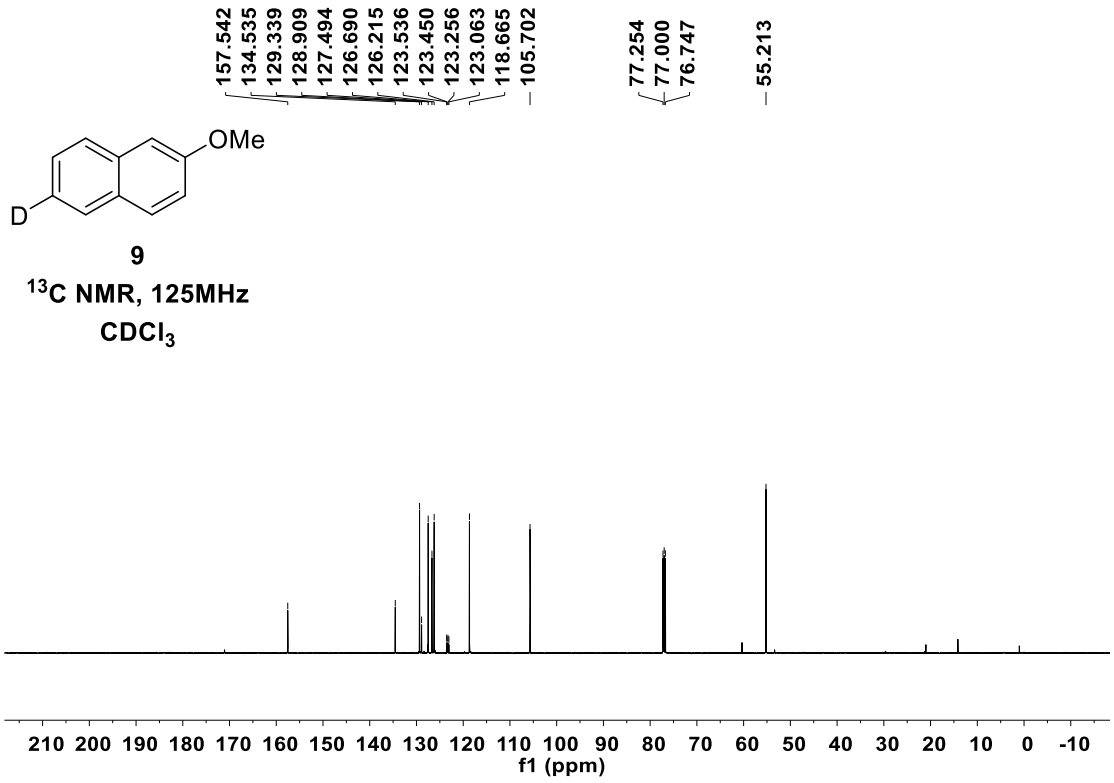
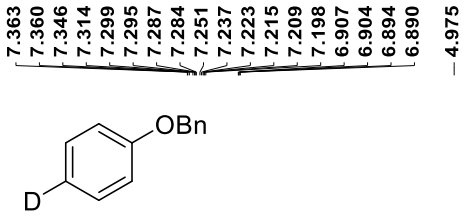


9

^{13}C NMR, 125MHz

$CDCl_3$



10

^{1}H NMR, 500MHz

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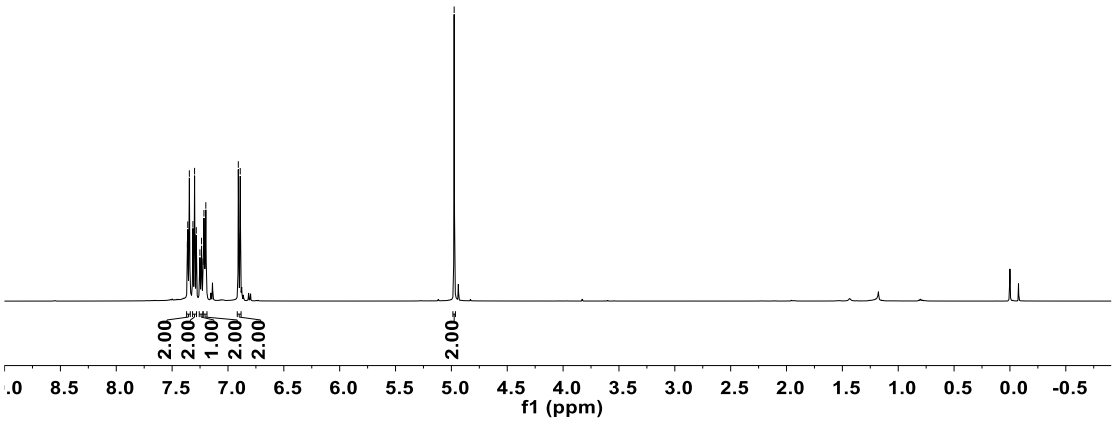
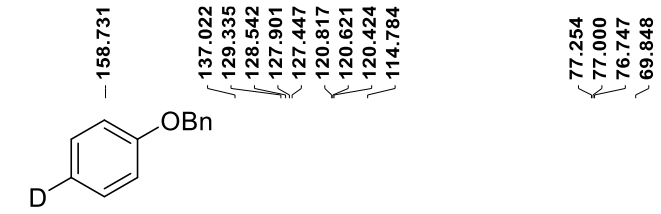
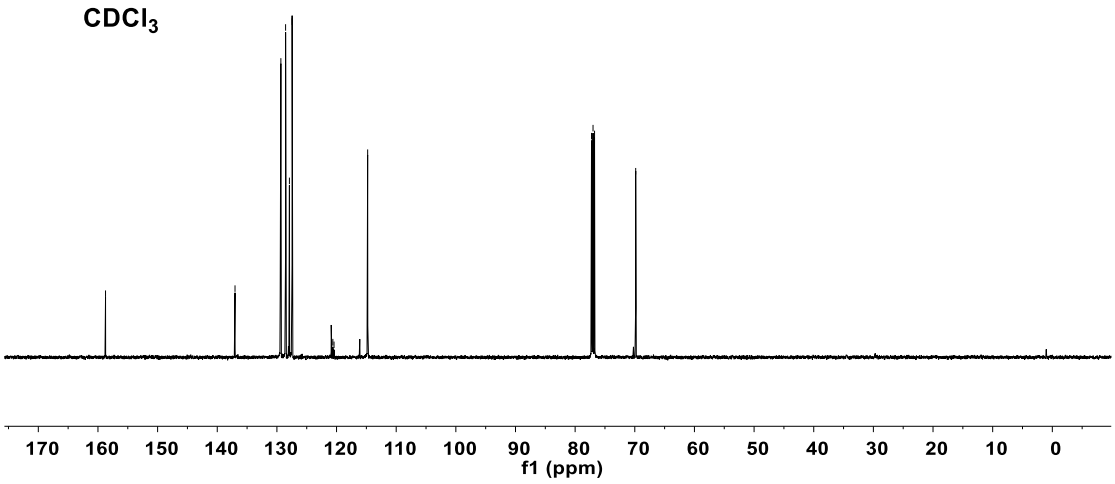


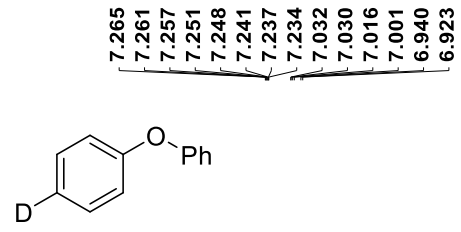


10

^{13}C NMR, 125MHz

$CDCl_3$

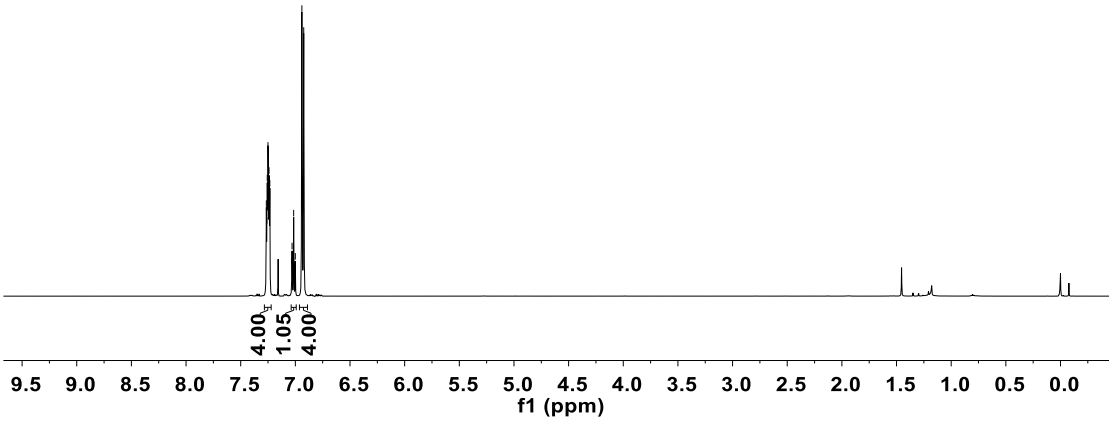


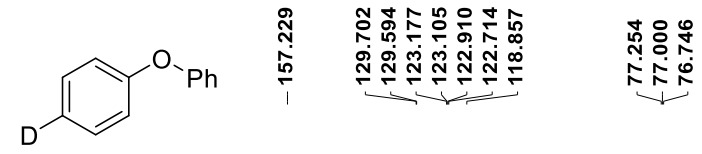


11

^{1}H NMR, 500MHz

$CDCl_3$

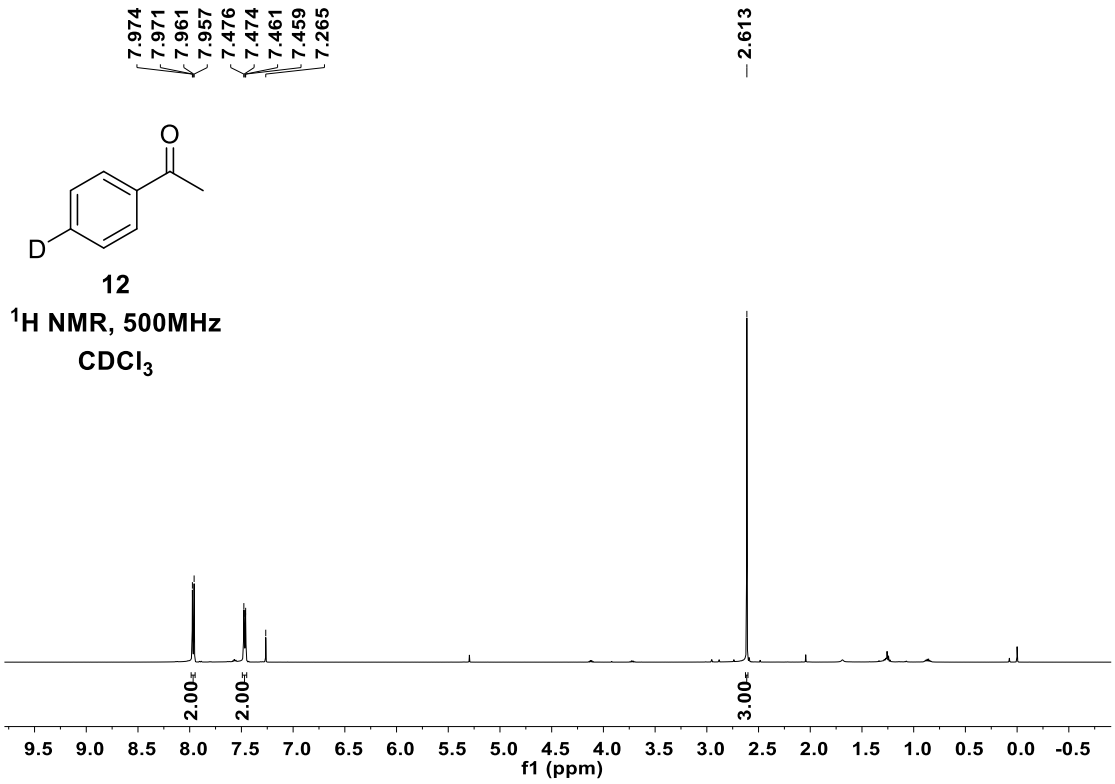




11

^{13}C NMR, 125MHz

$CDCl_3$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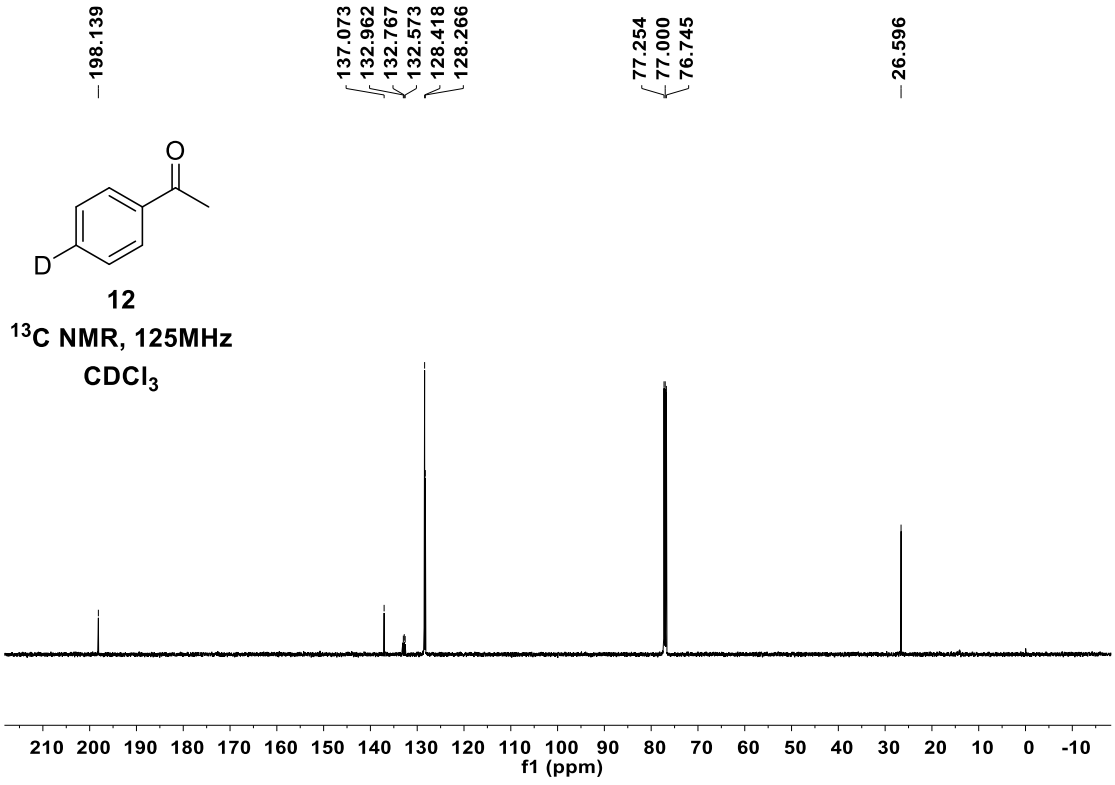
7.971
7.961
7.957
7.476
7.474
7.461
7.459
7.265
2.613
O
D
12
1H NMR, 500MHz
CDCl3
2.00
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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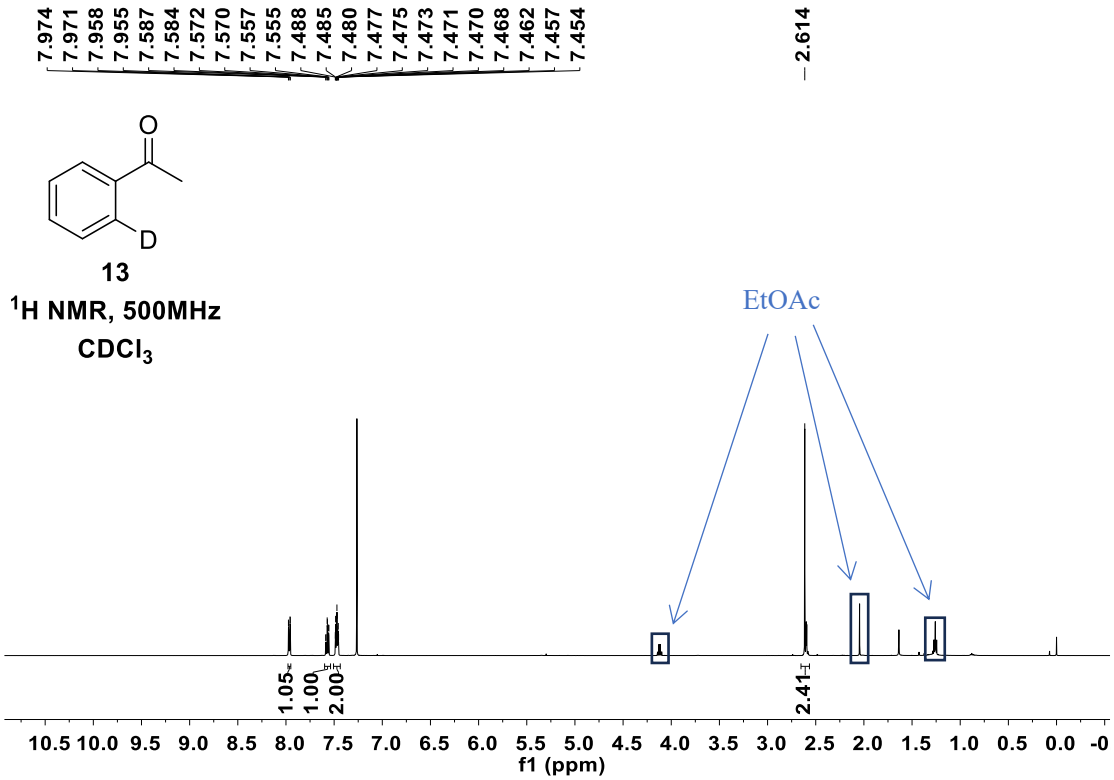
137.073
132.962
132.767
132.573
128.418
128.266
77.254
77.000
76.745
26.596
O
D
12
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.974
7.971
7.958
7.955
7.587
7.584
7.572
7.570
7.557
7.555
7.488
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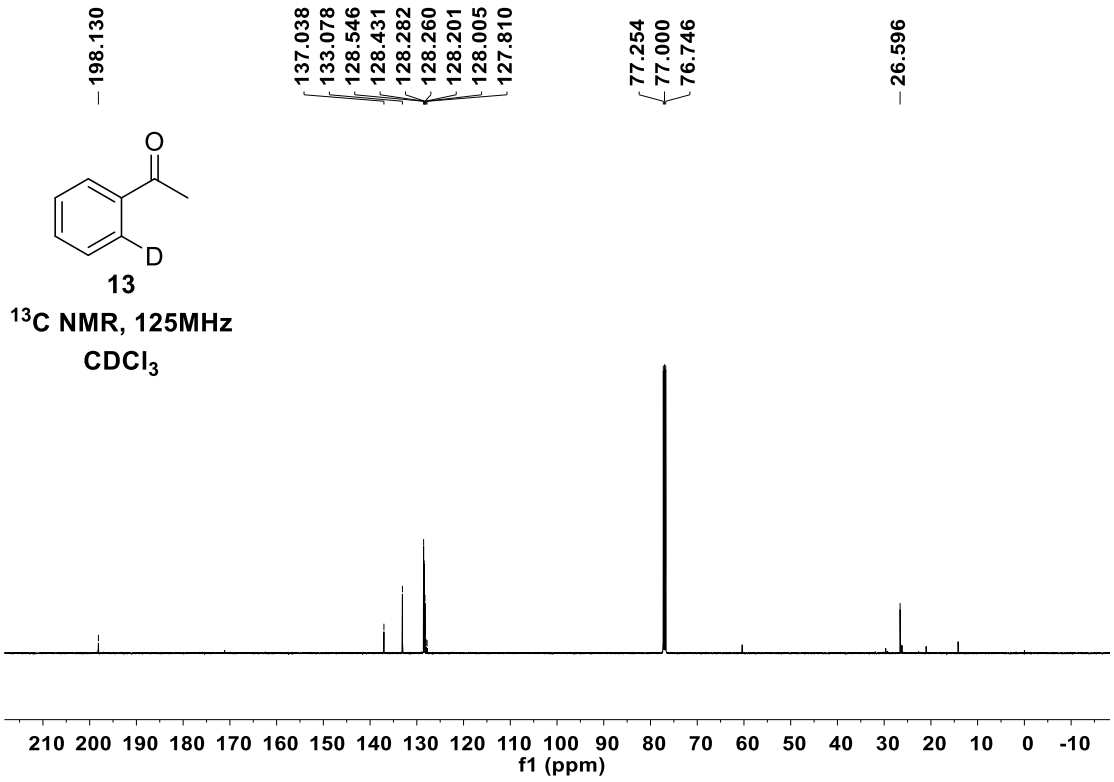
7.480
7.477
7.475
7.473
7.471
7.470
7.468
7.462
7.457
7.454
2.614
O
D
13
1H NMR, 500MHz
CDCl3
EtOAc
1.05
1.00
2.00
2.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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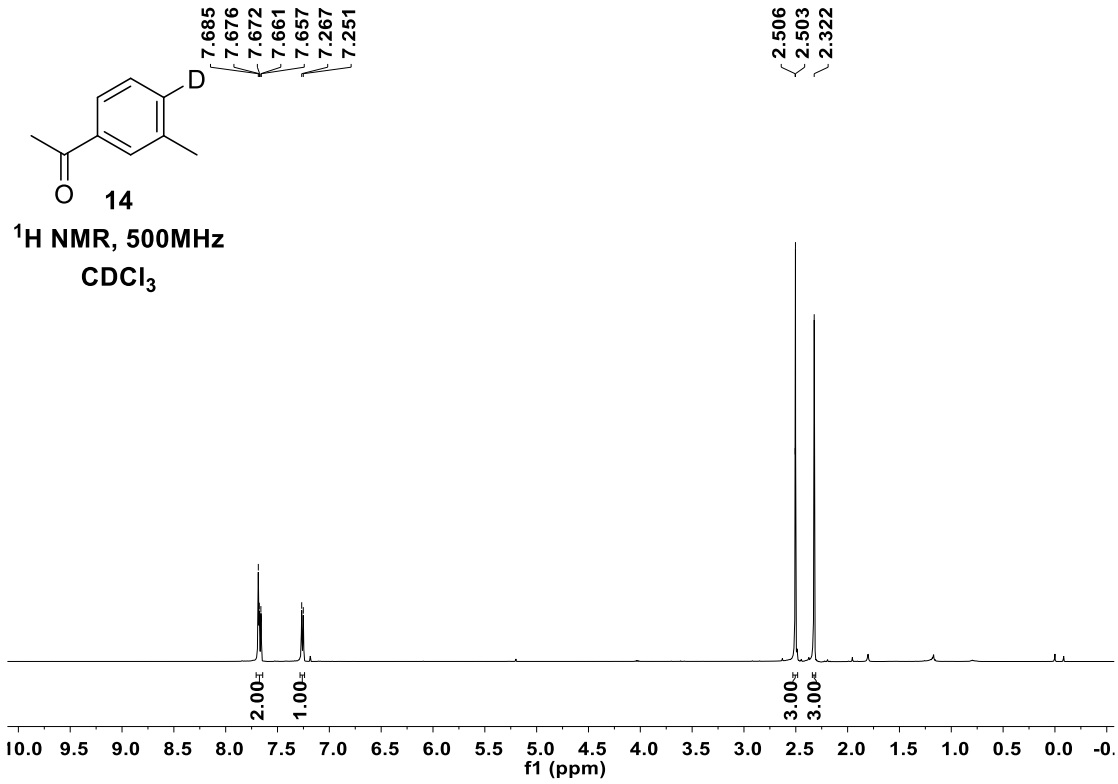
137.038
133.078
128.546
128.431
128.282
128.260
128.201
128.005
127.810
77.254
77.000
76.746
26.596
O
D
13
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.676
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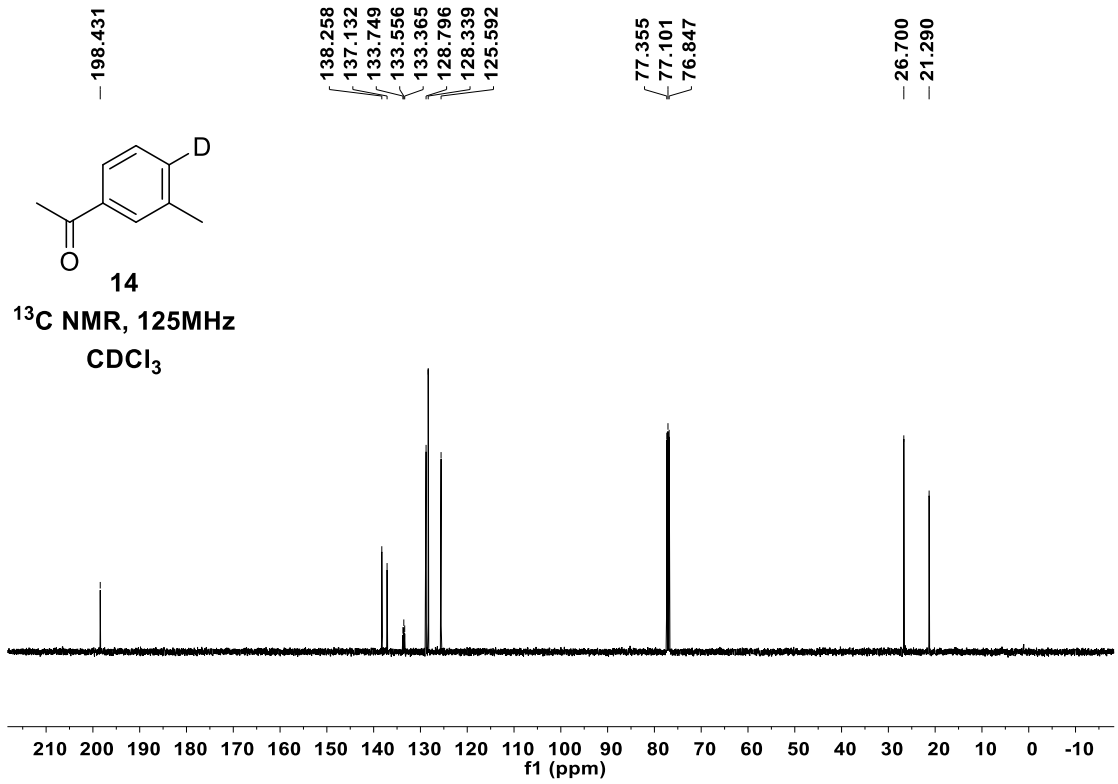
7.661
7.657
7.267
7.251
2.506
2.503
2.322
D
O
14
1H NMR, 500MHz
CDCl3
2.00
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


198.431
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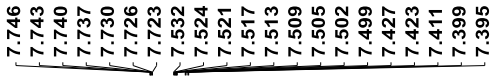
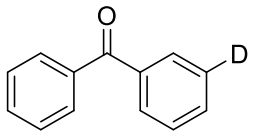
133.365
128.796
128.339
125.592
77.355
77.101
76.847
26.700
21.290
D
O
14
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

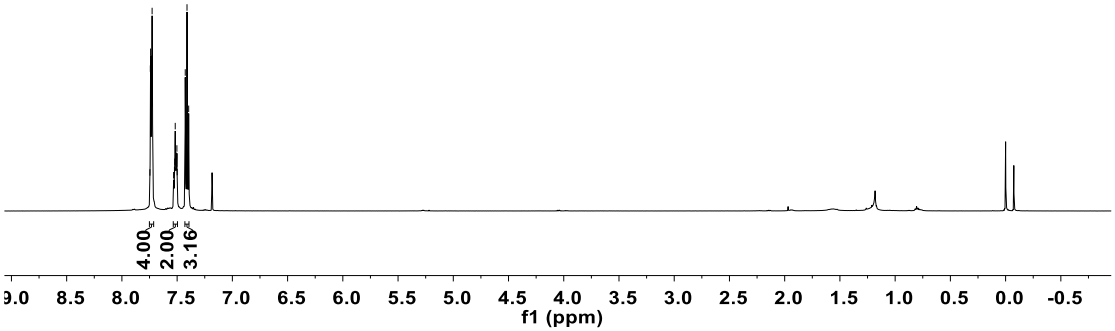


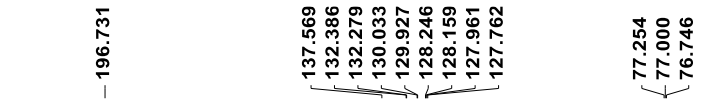


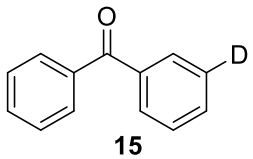
15

^{1}H NMR, 500MHz

$CDCl_3$



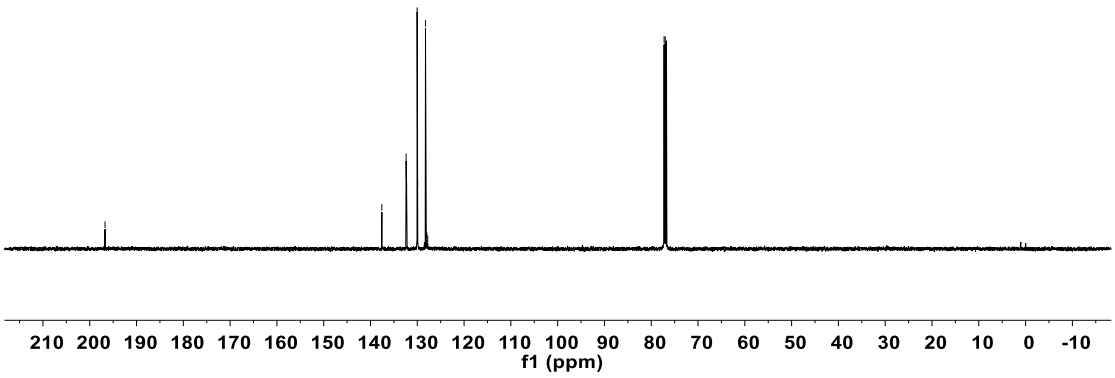


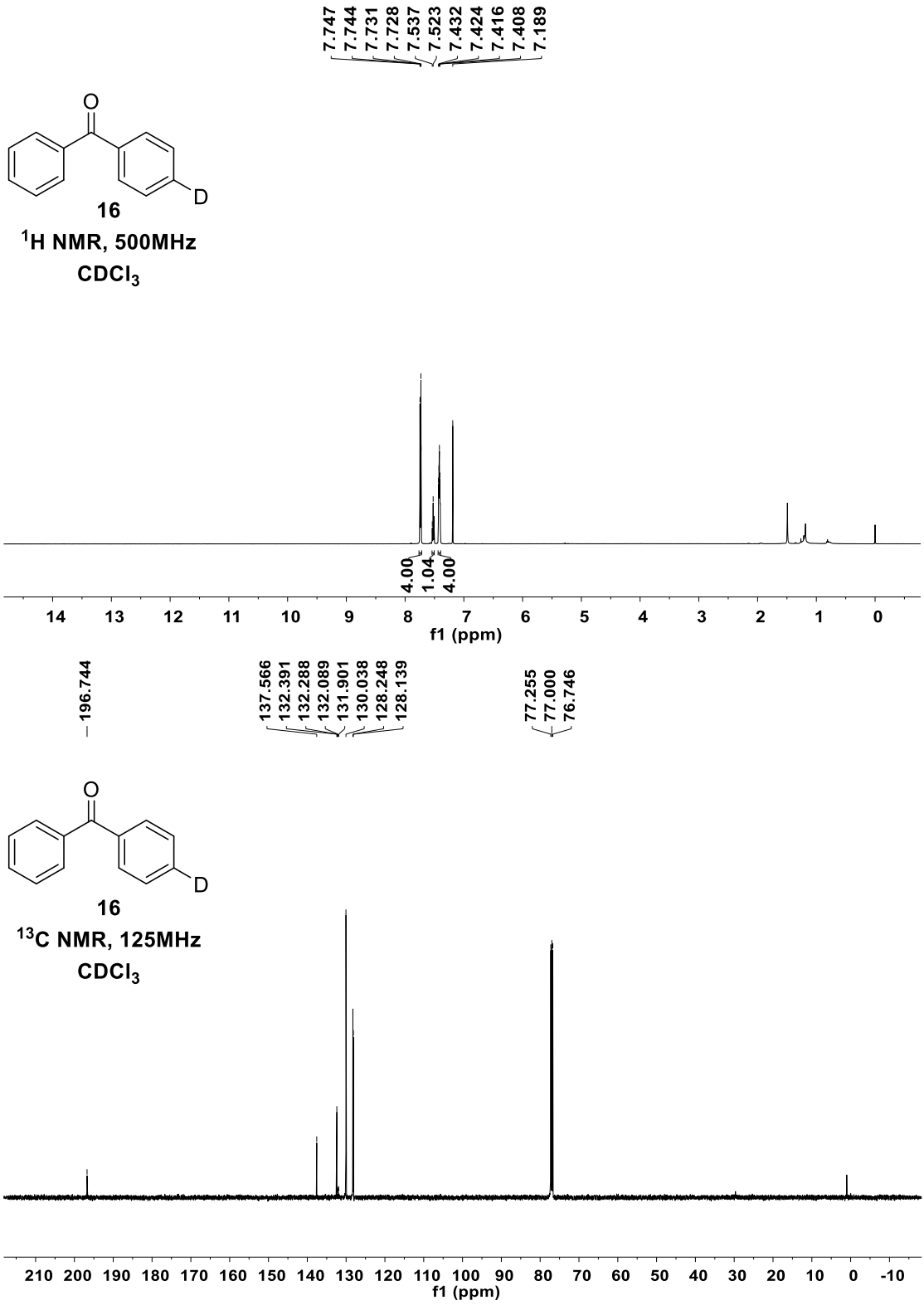


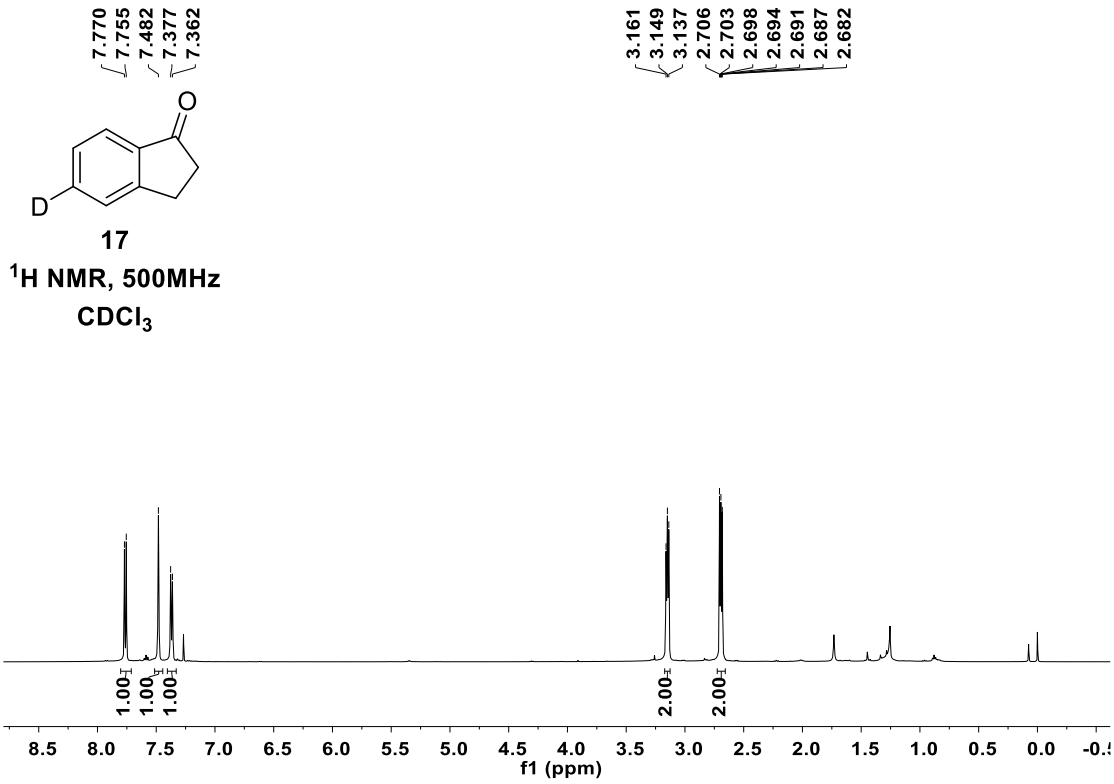
15

^{13}C NMR, 125MHz

$CDCl_3$



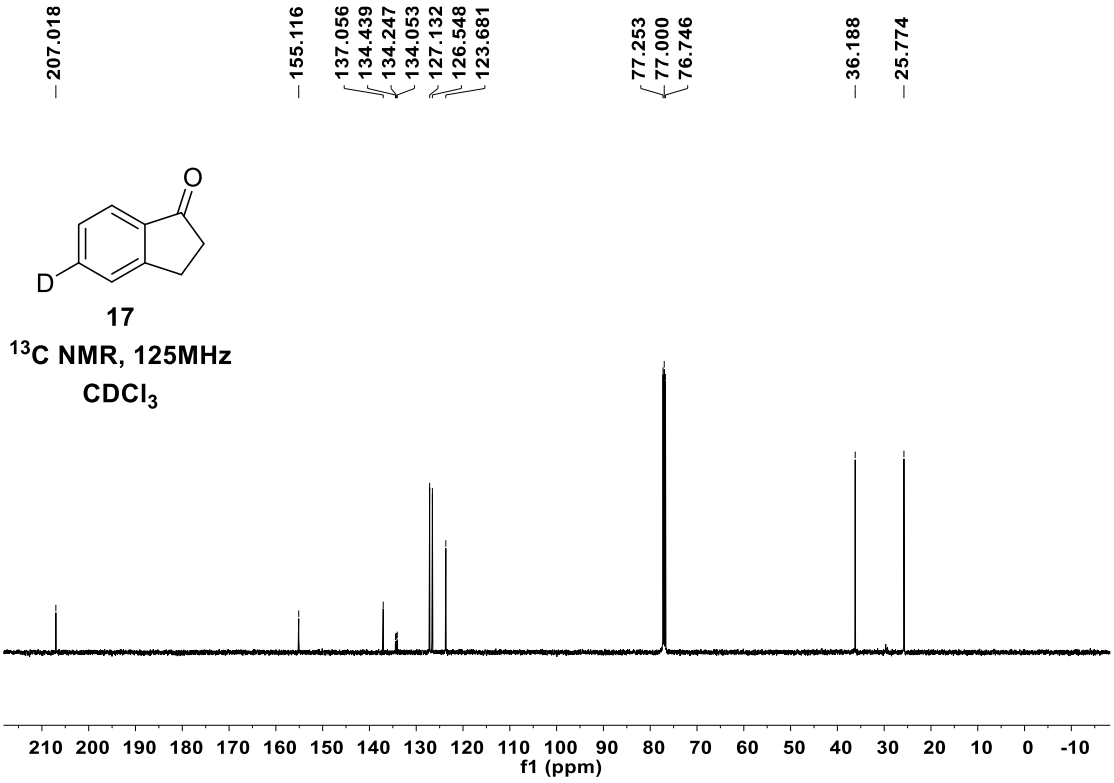

7.747
7.744
7.731
7.728
7.537
7.523
7.432
7.424
7.416
7.408
7.189
O
D
16
1H NMR, 500MHz
CDCl3
4.00
1.04
4.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.744
137.566
132.391
132.288
132.089
131.901
130.038
128.248
128.139
77.255
77.000
76.746
O
D
16
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



17

^{1}H NMR, 500MHz

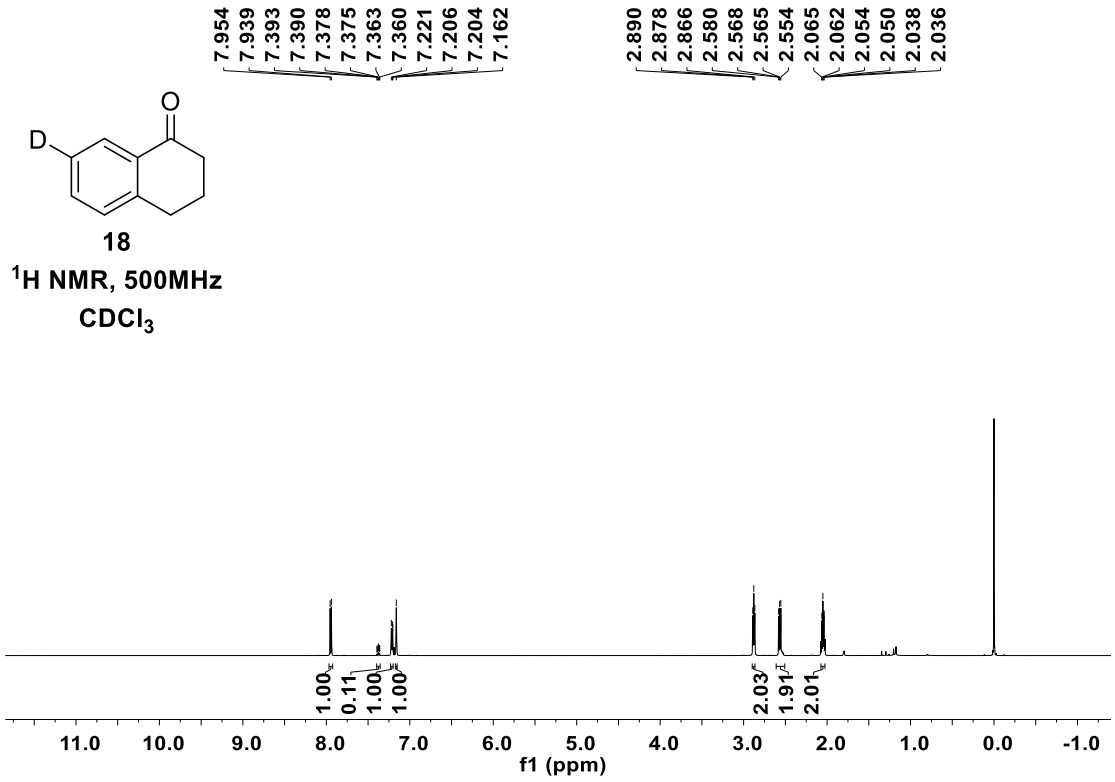
$CDCl_3$

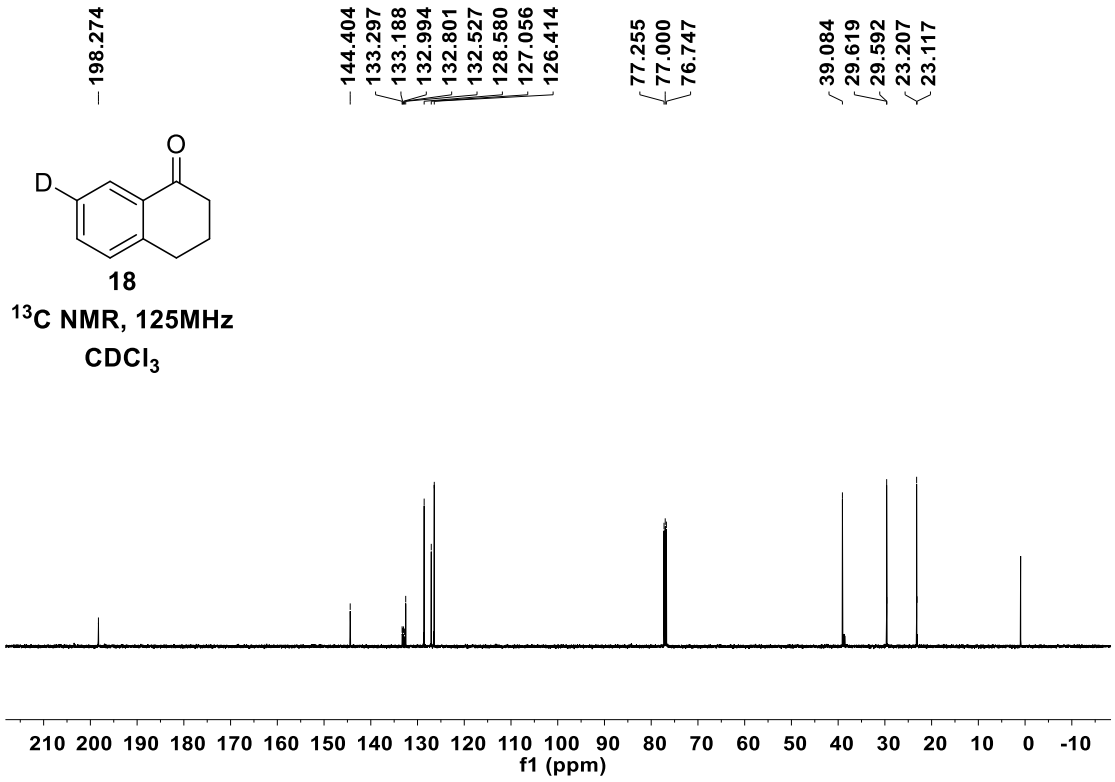


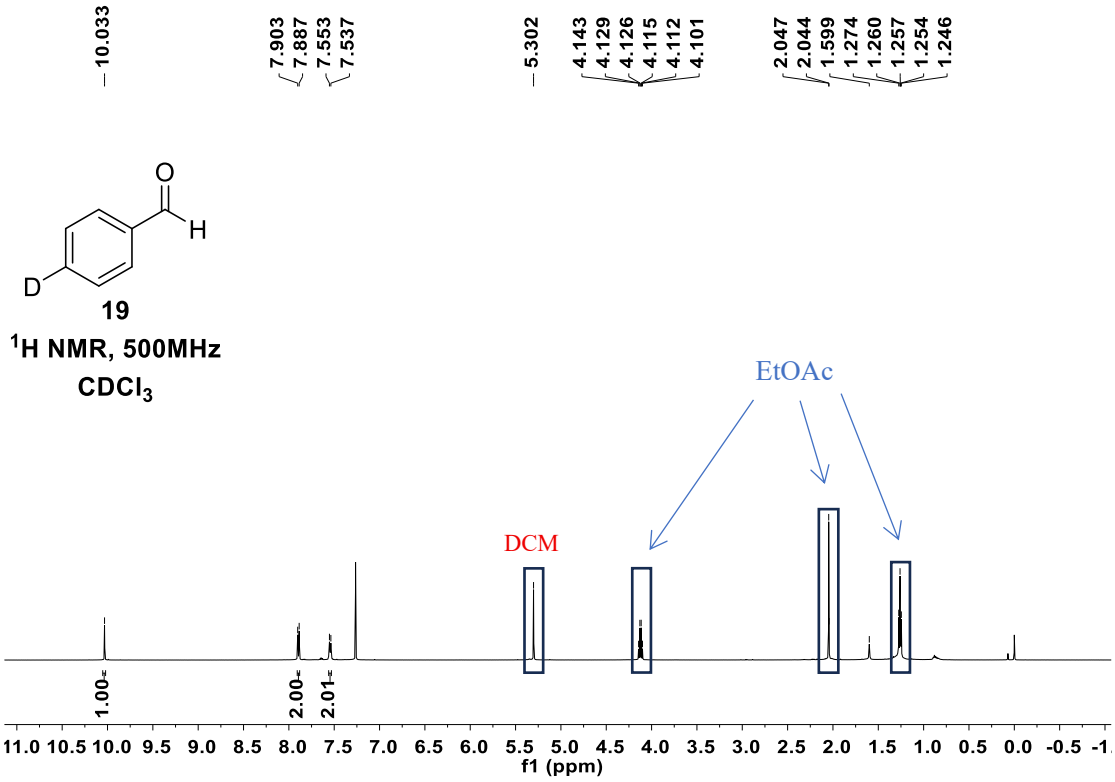
17

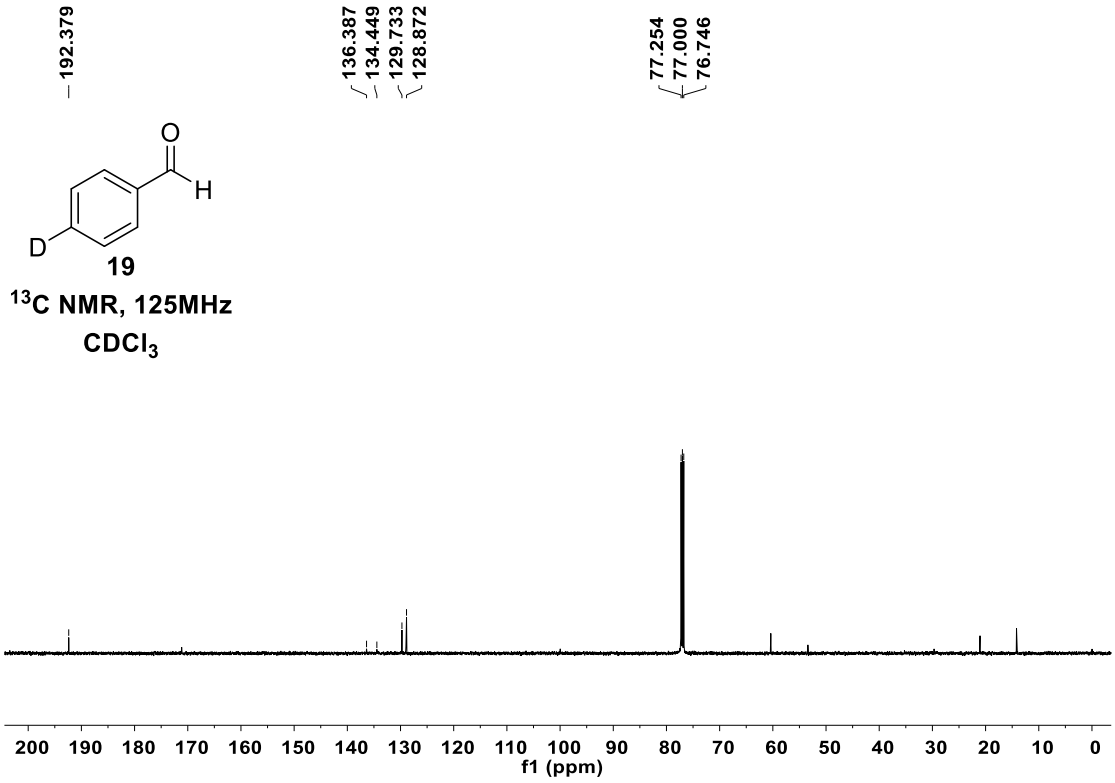
^{13}C NMR, 125MHz

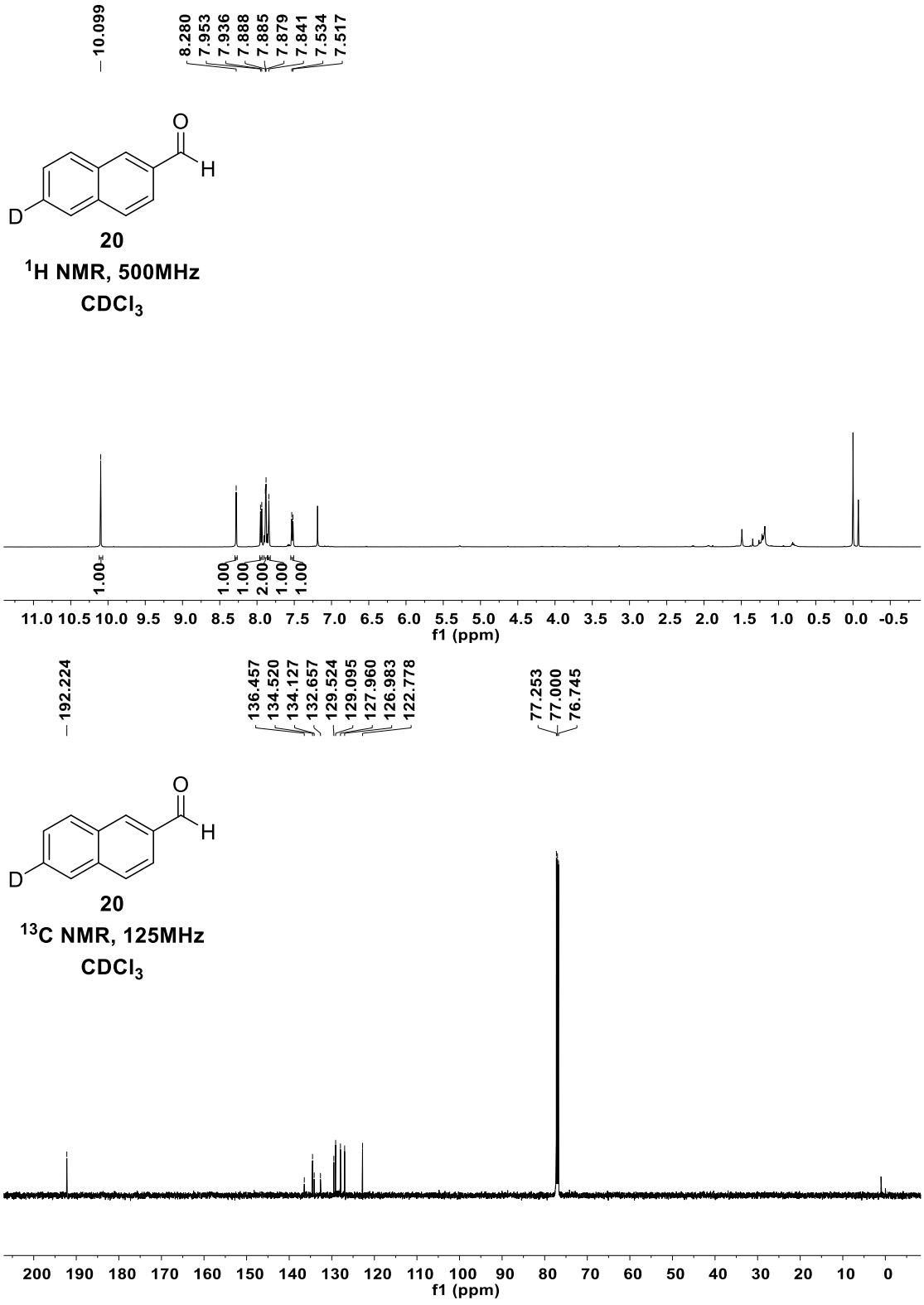
$CDCl_3$

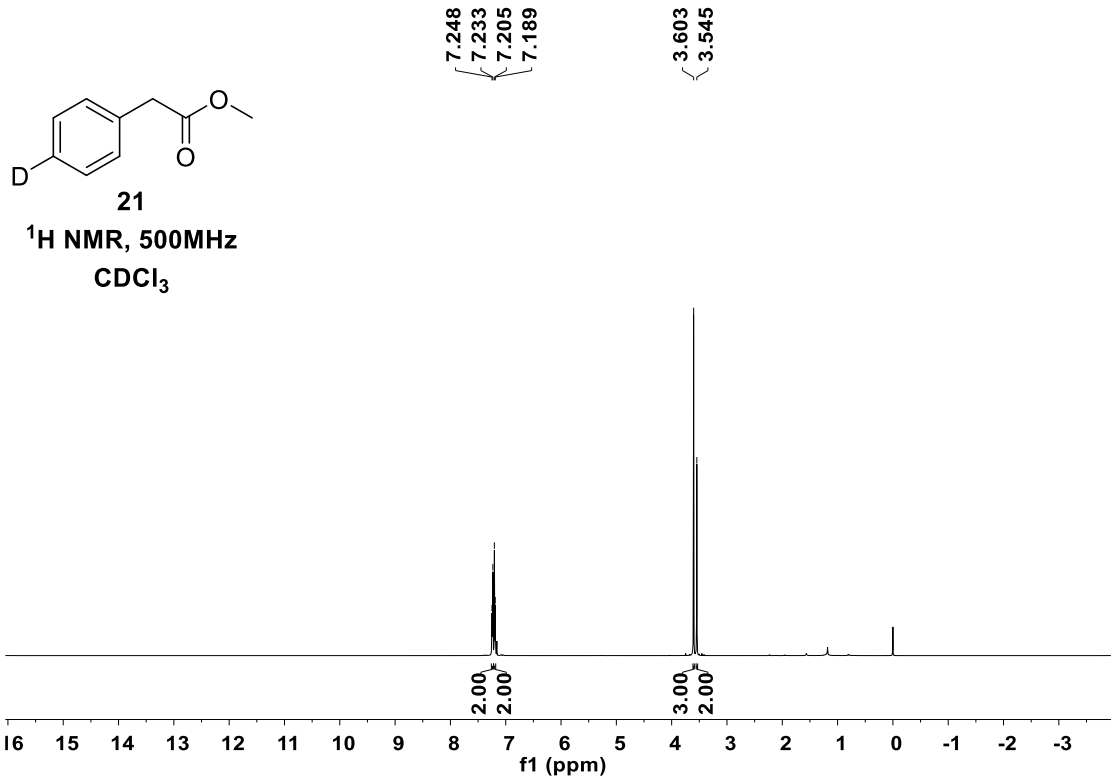

7.954
7.939
7.393
7.390
7.378
7.375
7.363
7.360
7.221
7.206
7.204
7.162
2.890
2.878
2.866
2.580
2.568
2.565
2.554
2.065
2.062
2.054
2.050
2.038
2.036
O
D
18
1H NMR, 500MHz
CDCl3
1.00
0.11
1.00
1.00
2.03
1.91
2.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

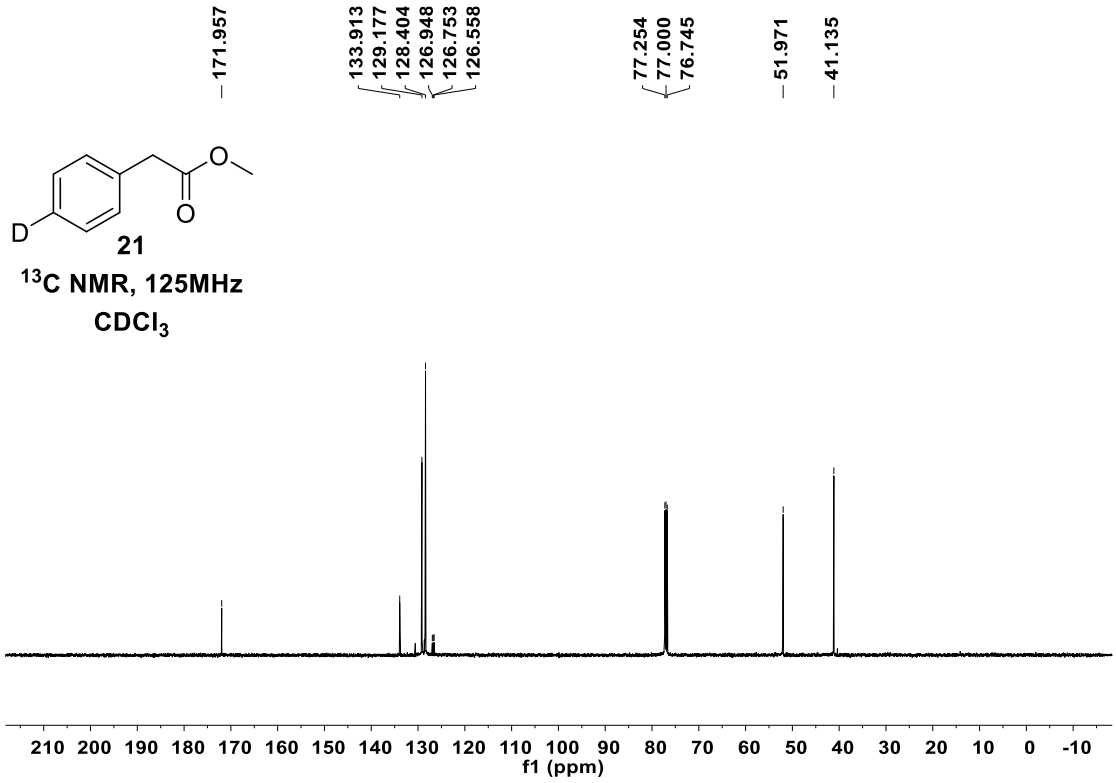

198.274
144.404
133.297
133.188
132.994
132.801
132.527
128.580
127.056
126.414
77.255
77.000
76.747
39.084
29.619
29.592
23.207
23.117
O
D
18
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

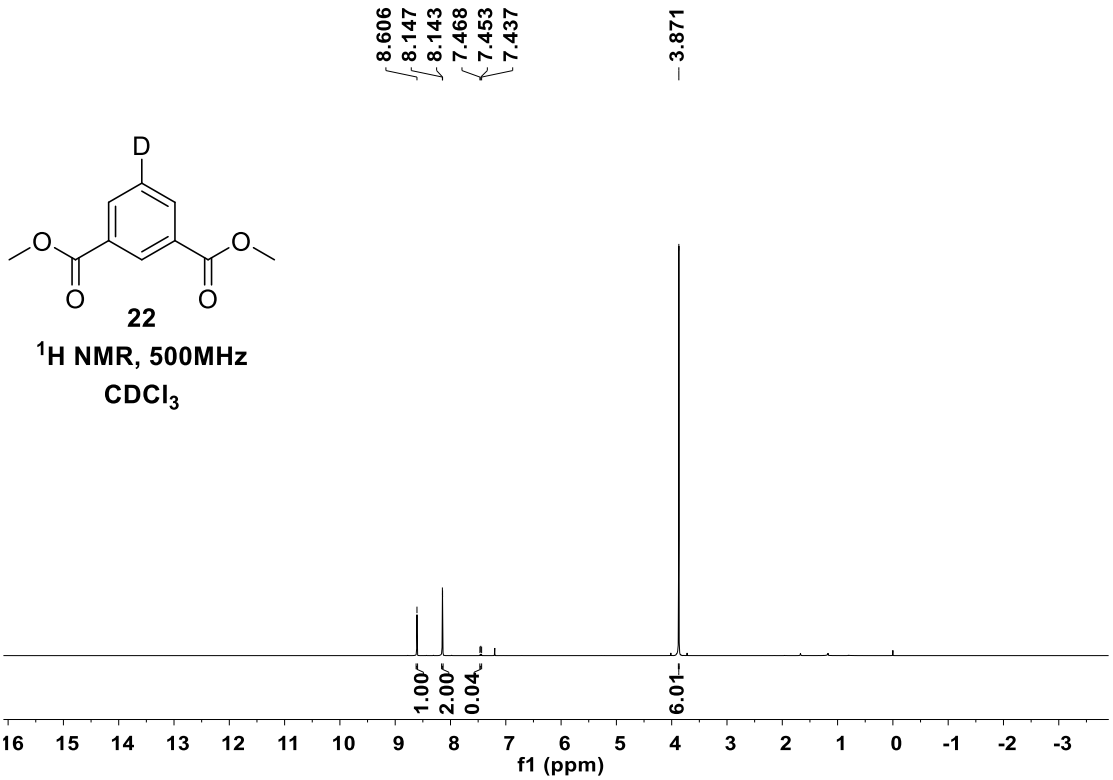

10.033
7.903
7.887
7.553
7.537
5.302
4.143
4.129
4.126
4.115
4.112
4.101
2.047
2.044
1.599
1.274
1.260
1.257
1.254
1.246
O
H
D
19
1H NMR, 500MHz
CDCl3
EtOAc
DCM
1.00
2.00
2.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

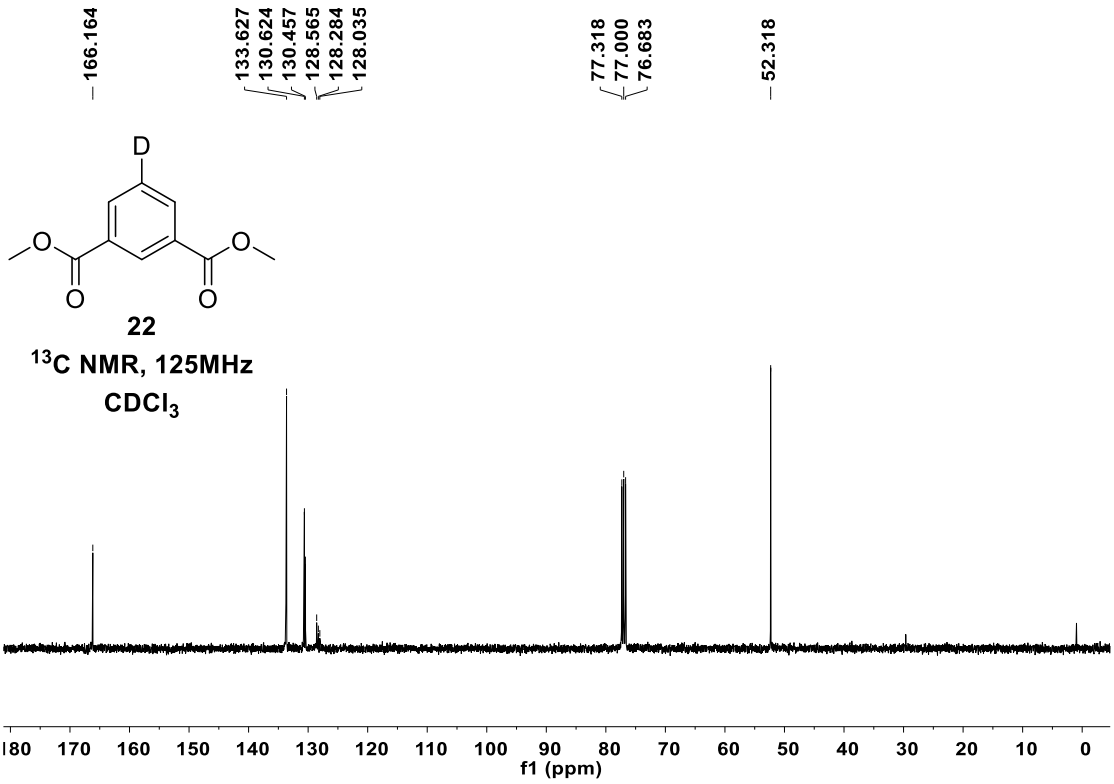

192.379
136.387
134.449
129.733
128.872
77.254
77.000
76.746
O
H
D
19
13C NMR, 125MHz
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

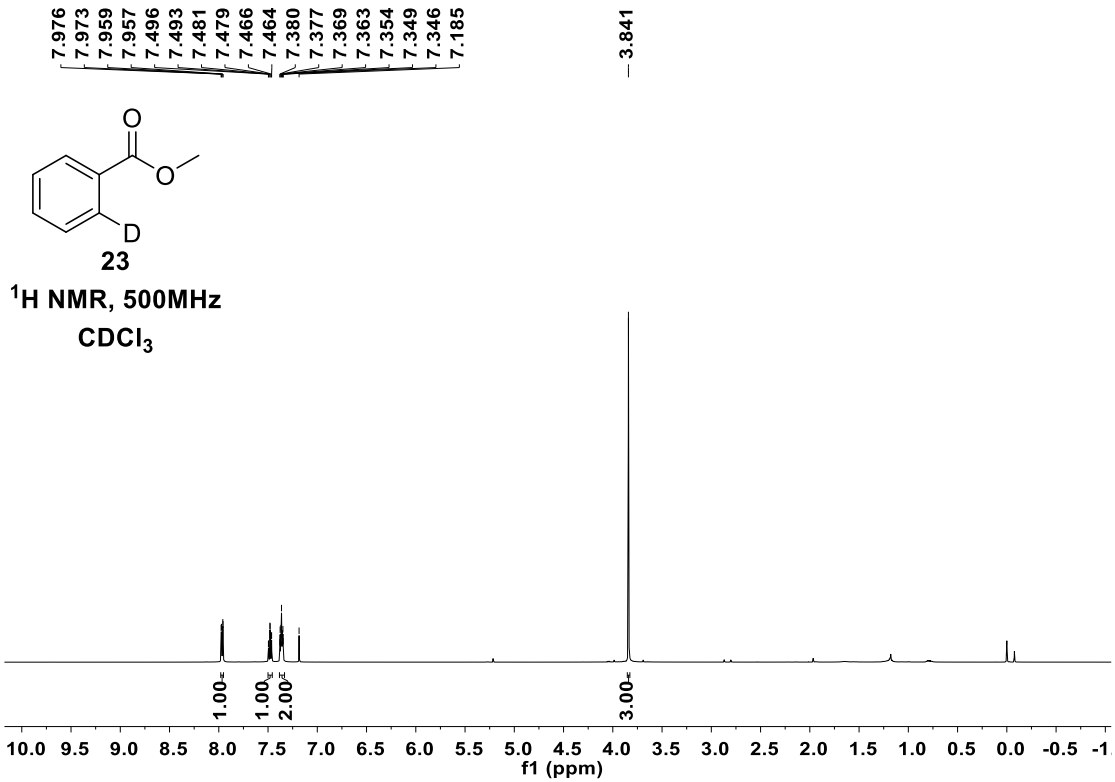

10.099
8.280
7.953
7.936
7.888
7.885
7.879
7.841
7.534
7.517
O
H
D
20
1H NMR, 500MHz
CDCl3
1.00
1.00
1.00
2.00
1.00
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
192.224
136.457
134.520
134.127
132.657
129.524
129.095
127.960
126.983
122.778
77.253
77.000
76.745
O
H
D
20
13C NMR, 125MHz
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.248
7.233
7.205
7.189
3.603
3.545
O
O
D
21
1H NMR, 500MHz
CDCl3
2.00
2.00
3.00
2.00
f1 (ppm)


171.957
133.913
129.177
128.404
126.948
126.753
126.558
77.254
77.000
76.745
51.971
41.135
O
O
D
21
13C NMR, 125MHz
CDCl3
f1 (ppm)


8.606
8.147
8.143
7.468
7.453
7.437
3.871
D
O
O
O
O
22
1H NMR, 500MHz
CDCl3
1.00
2.00
0.04
6.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

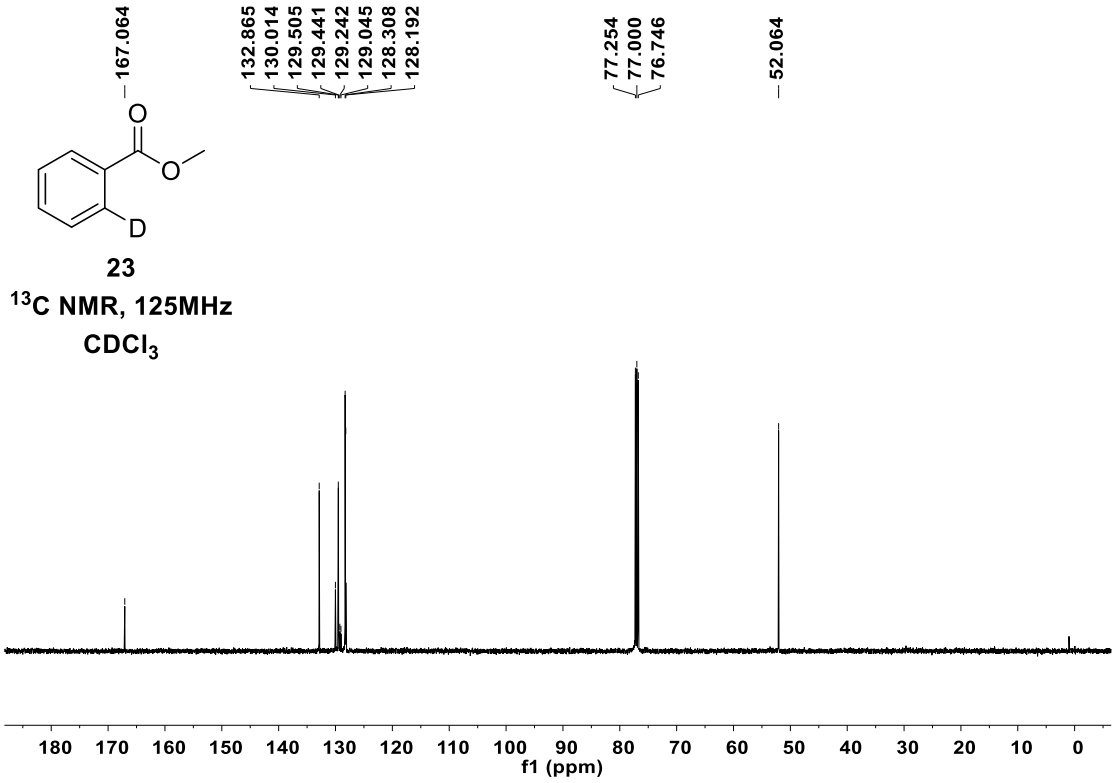

166.164
133.627
130.624
130.457
128.565
128.284
128.035
77.318
77.000
76.683
52.318
D
O
O
O
O
22
13C NMR, 125MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



23

^{1}H NMR, 500MHz

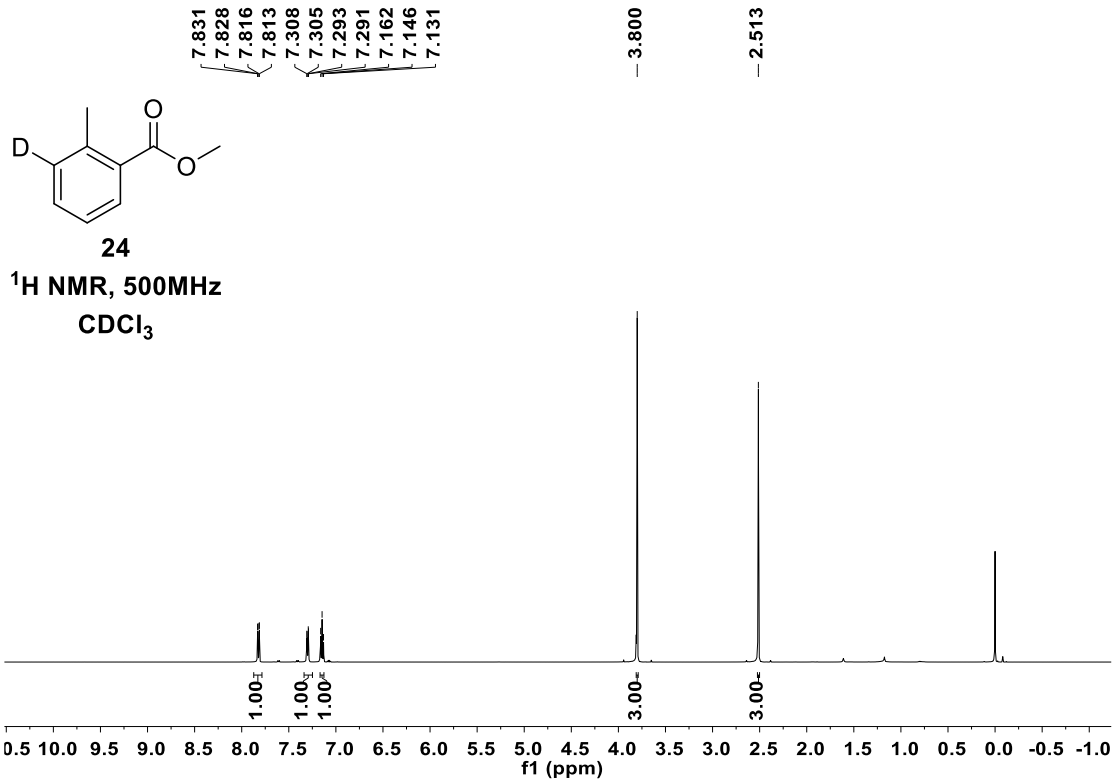
$CDCl_3$



23

^{13}C NMR, 125MHz

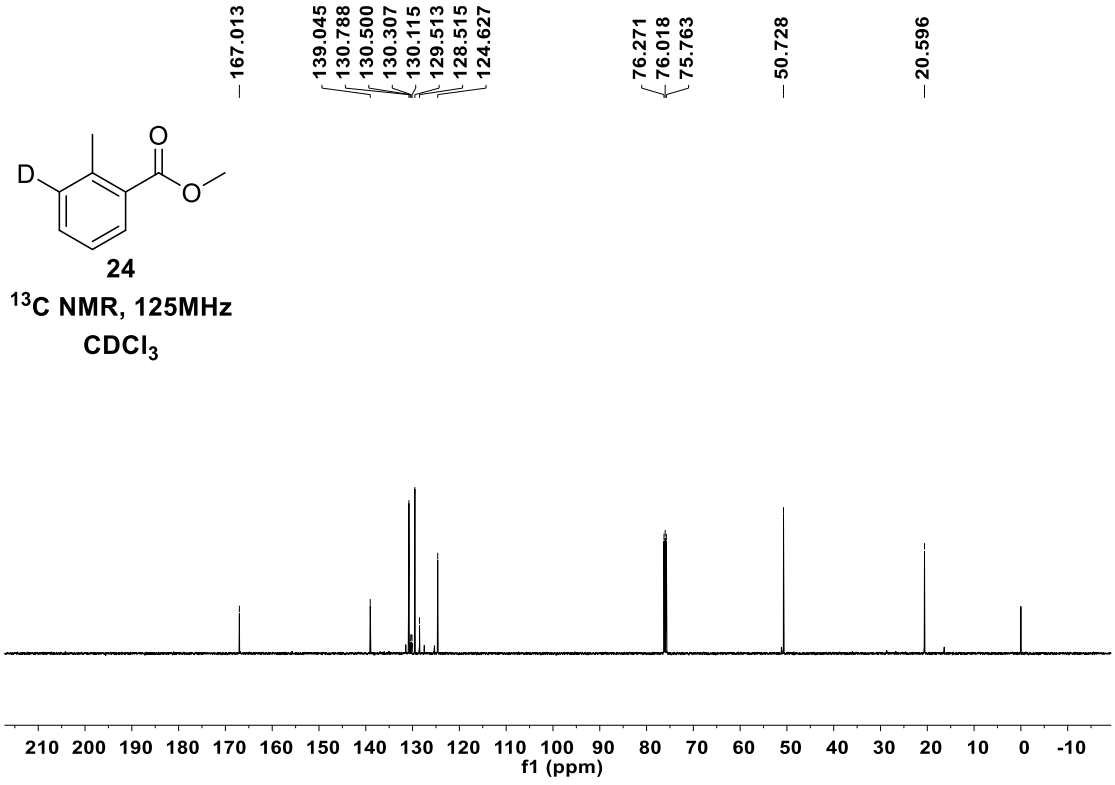
$CDCl_3$



24

^{1}H NMR, 500MHz

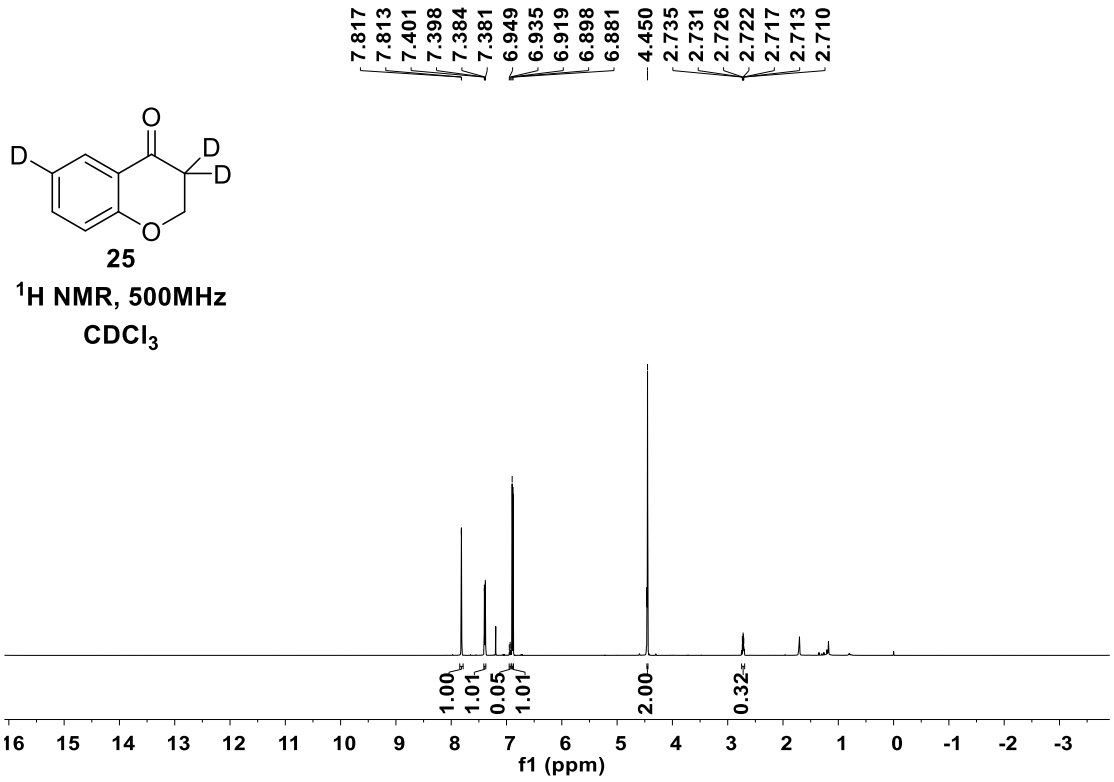
$CDCl_3$

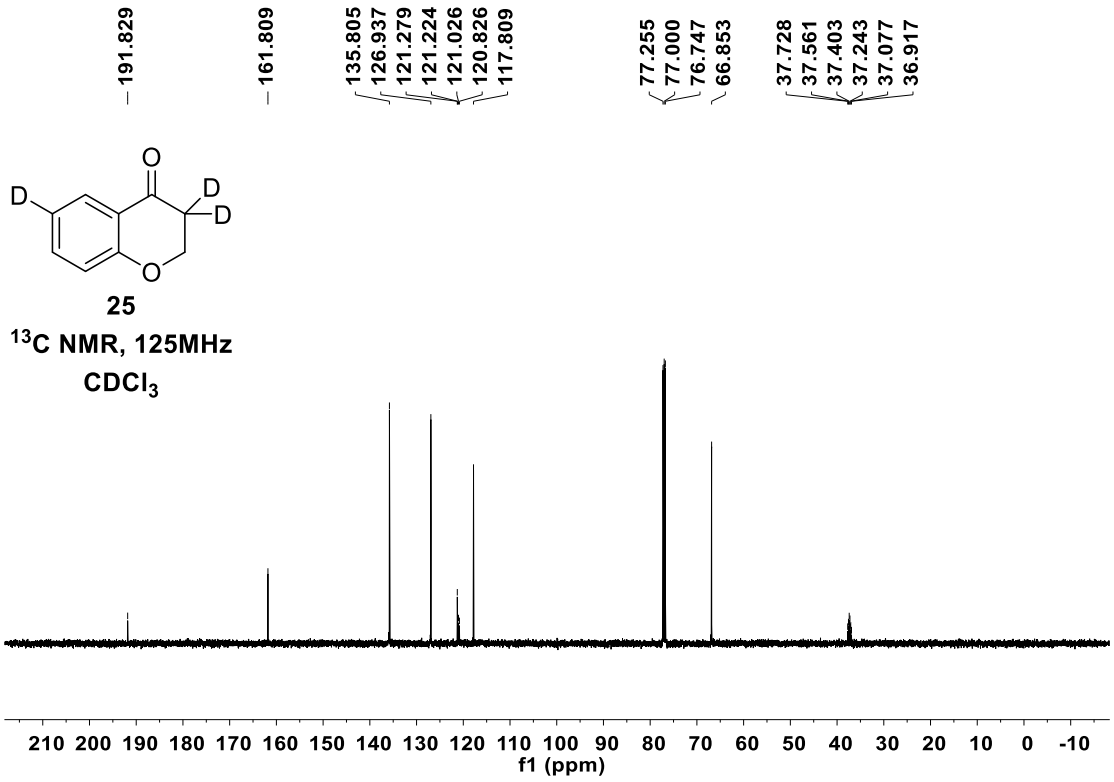


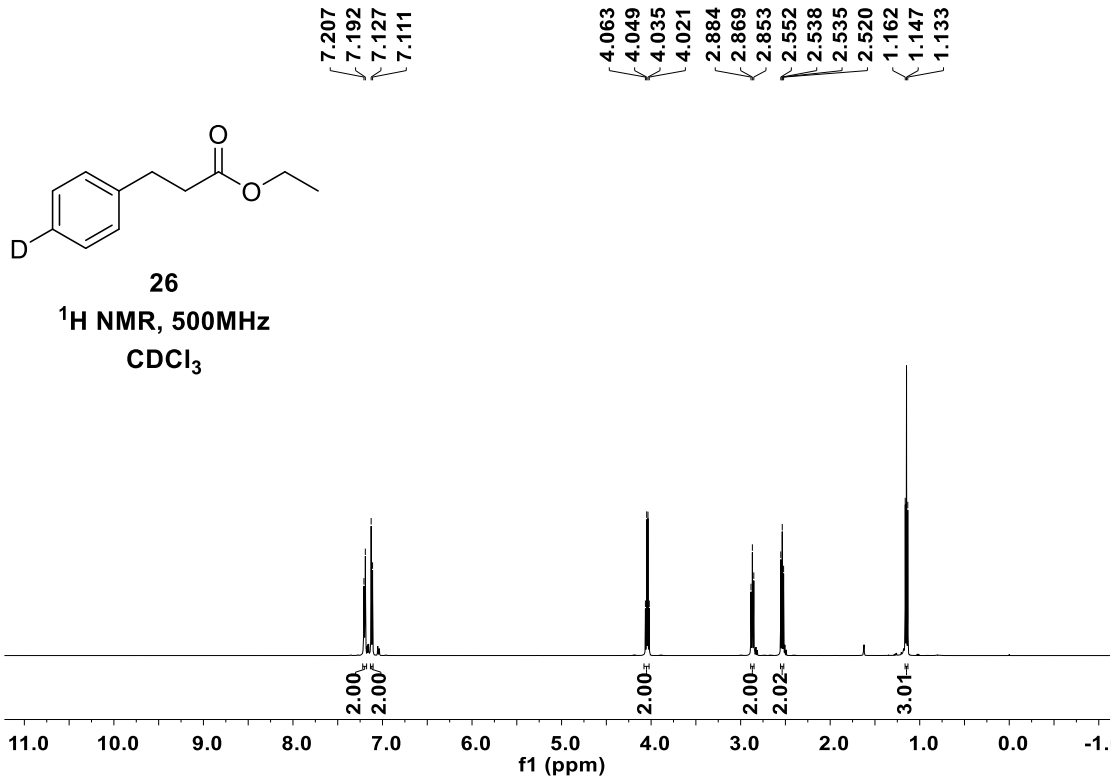
24

^{13}C NMR, 125MHz

$CDCl_3$


7.817
7.813
7.401
7.398
7.384
7.381
6.949
6.935
6.919
6.898
6.881
4.450
2.735
2.731
2.726
2.722
2.717
2.713
2.710
O
D
D
D
O
25
1H NMR, 500MHz
CDCl3
1.00
1.01
0.05
1.01
2.00
0.32
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

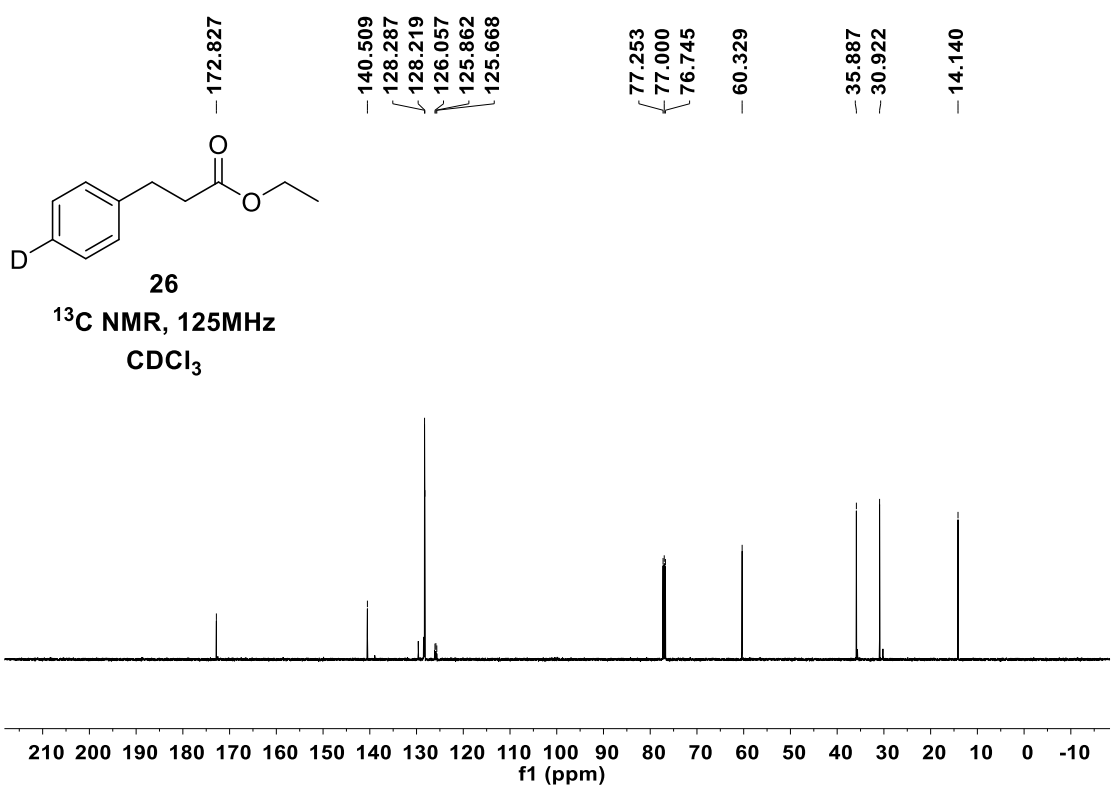

191.829
161.809
135.805
126.937
121.279
121.224
121.026
120.826
117.809
77.255
77.000
76.747
66.853
37.728
37.561
37.403
37.243
37.077
36.917
O
D
D
D
O
25
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



26

^{1}H NMR, 500MHz

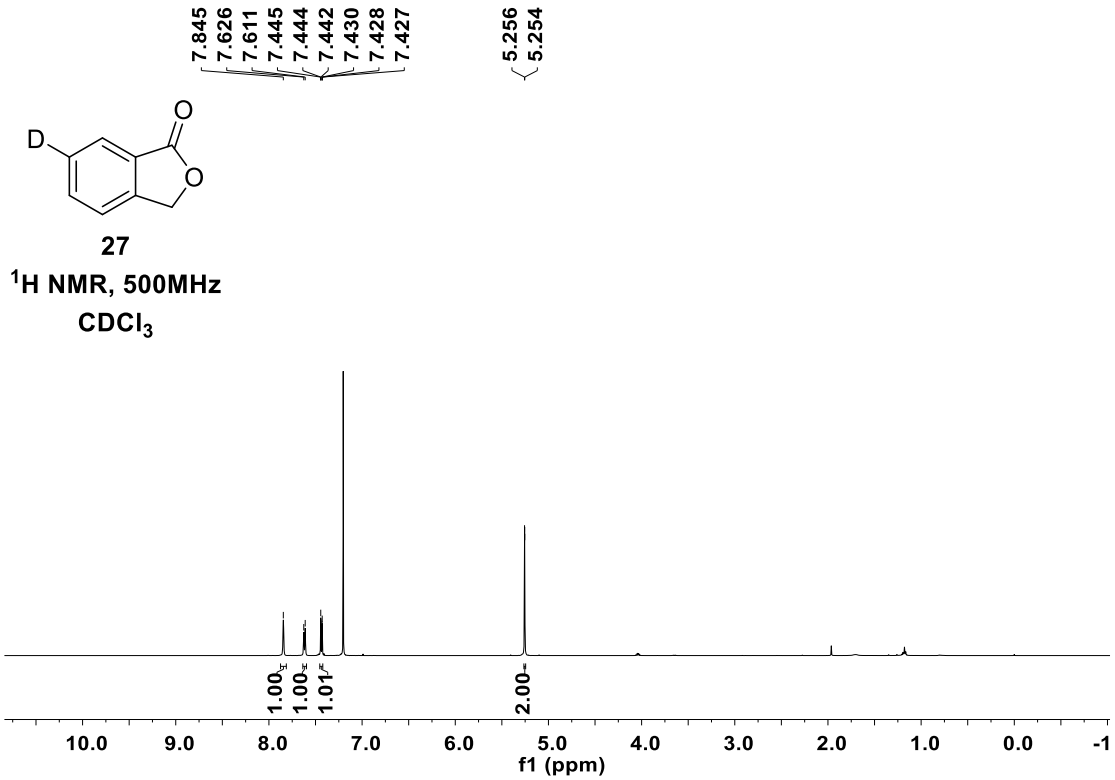
$CDCl_3$



26

^{13}C NMR, 125MHz

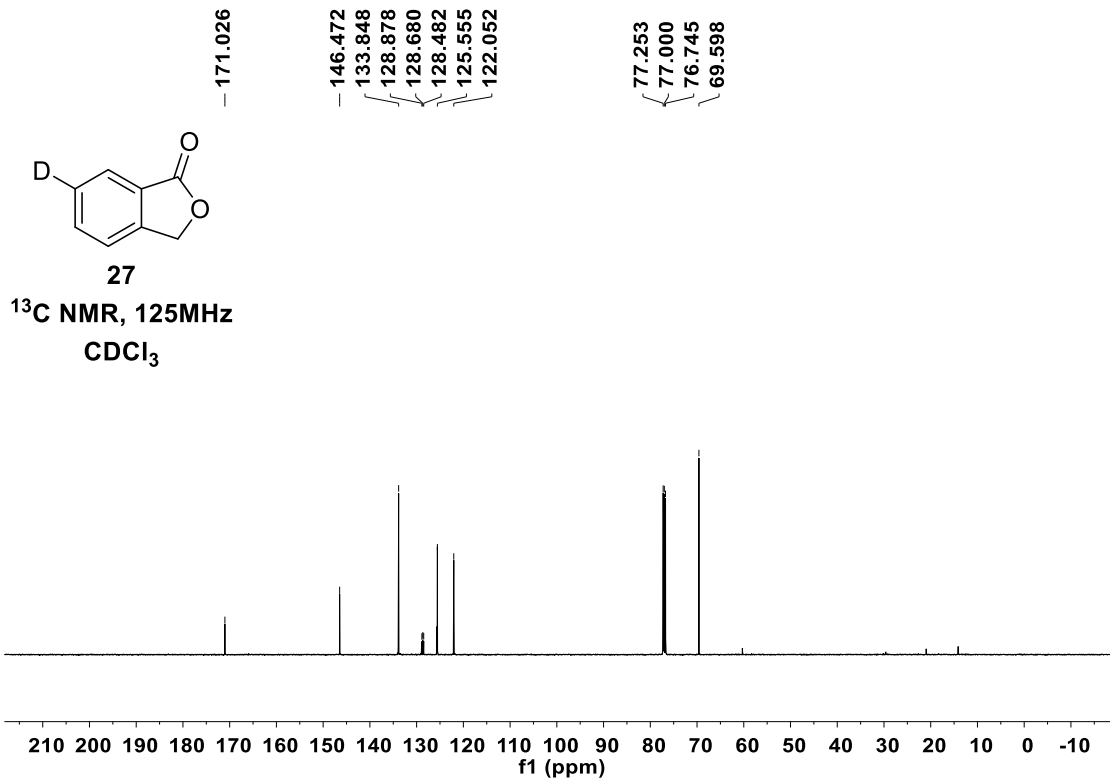
$CDCl_3$



27

^{1}H NMR, 500MHz

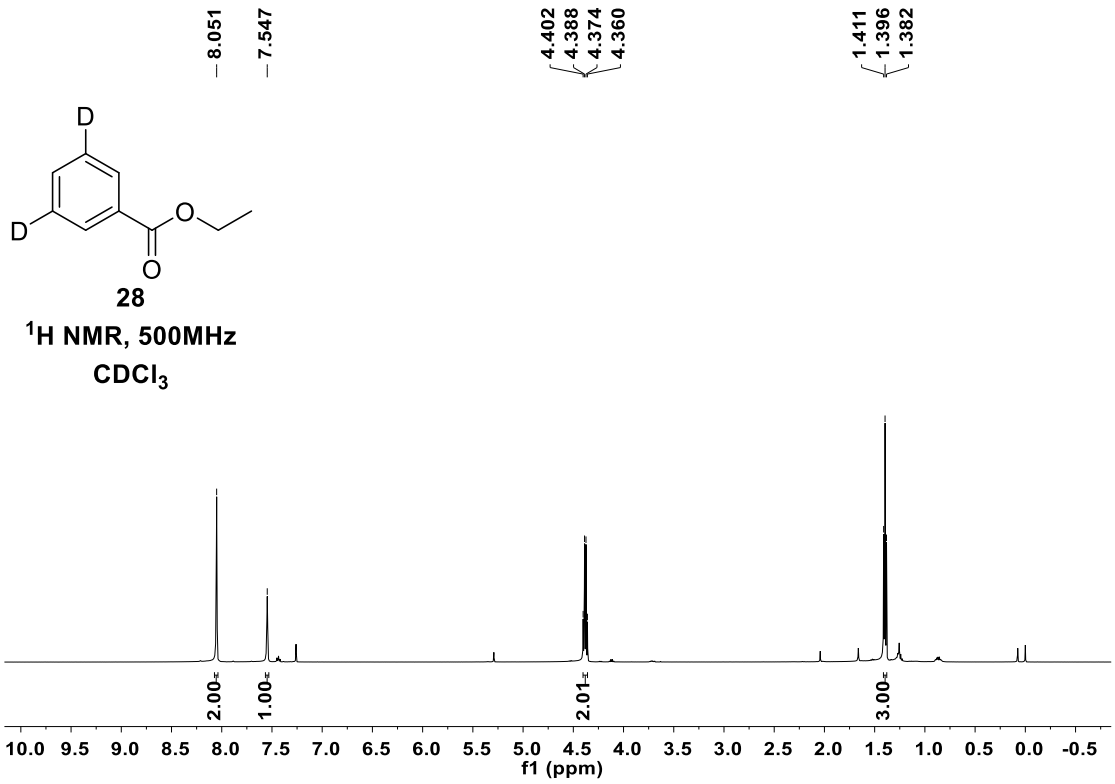
$CDCl_3$

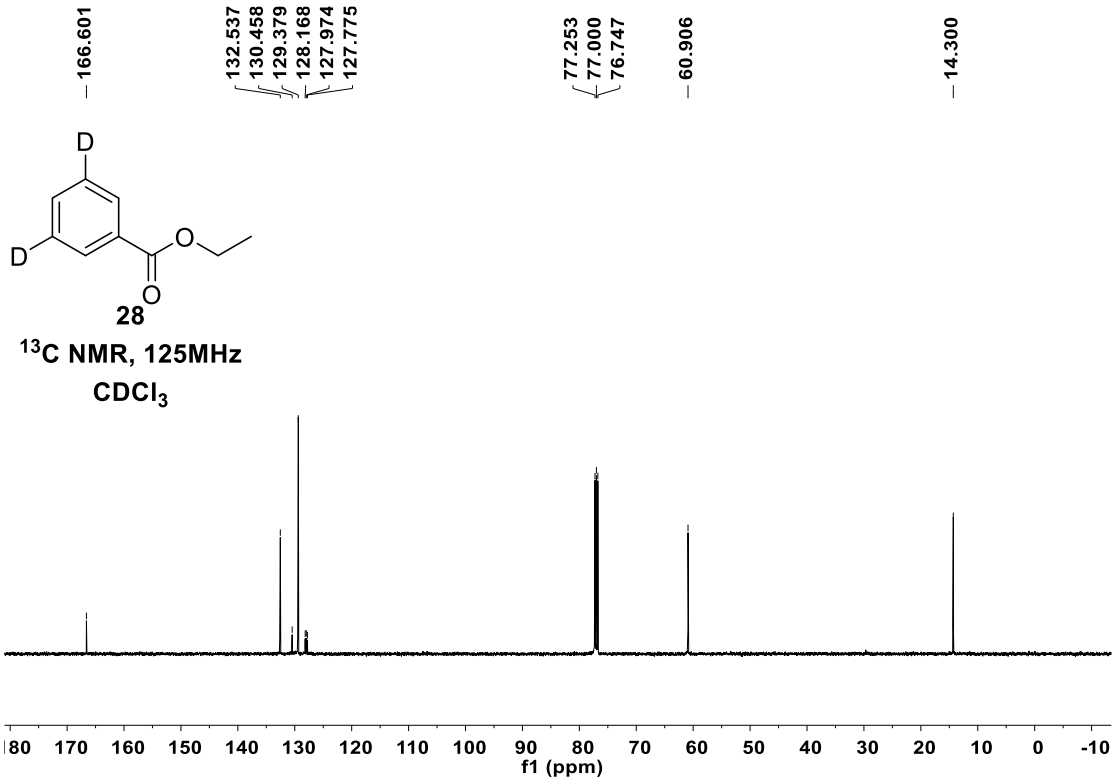


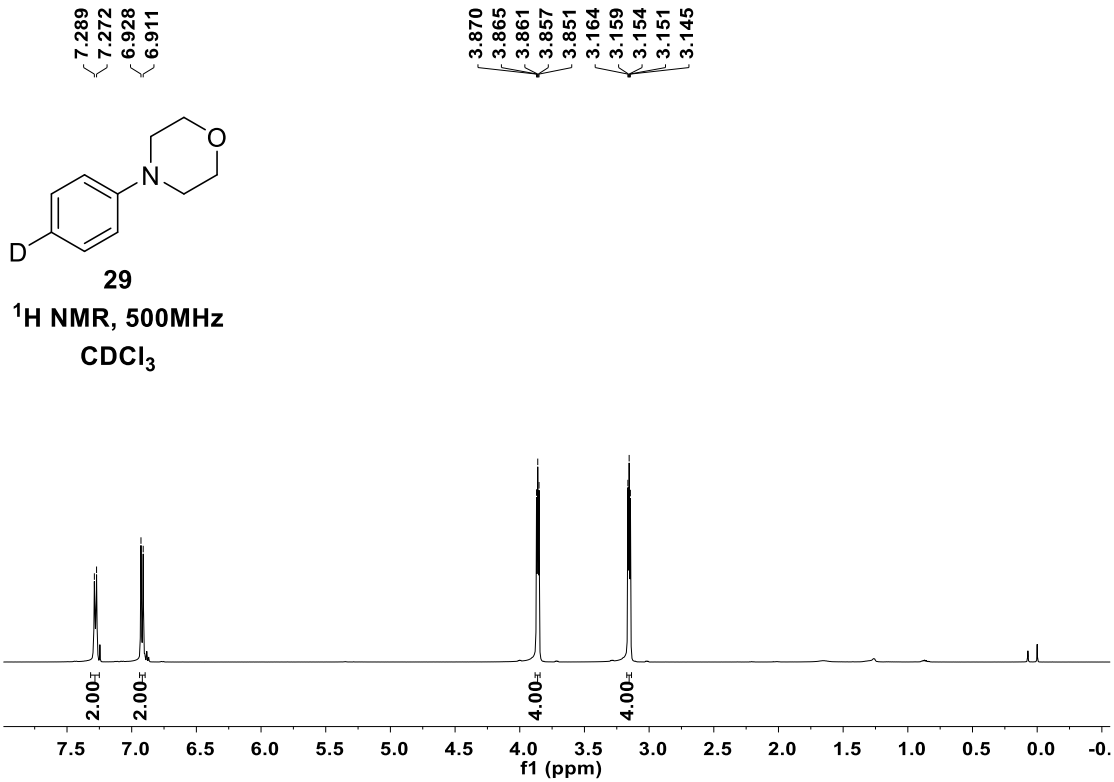
27

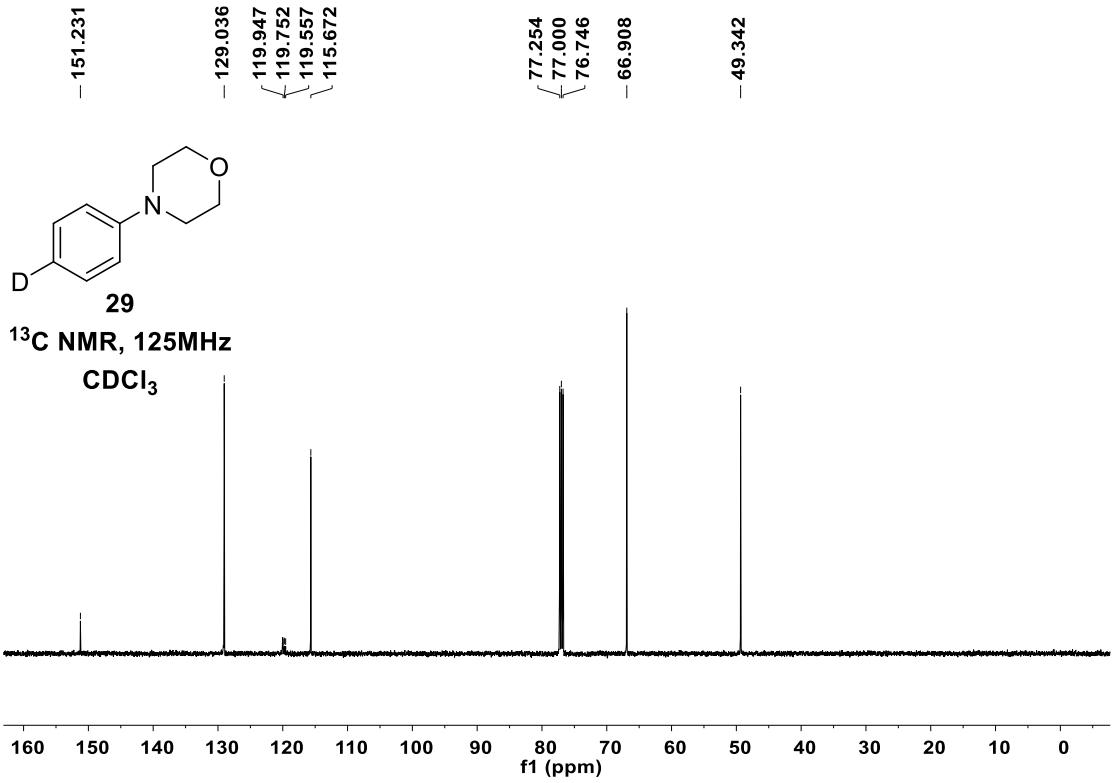
^{13}C NMR, 125MHz

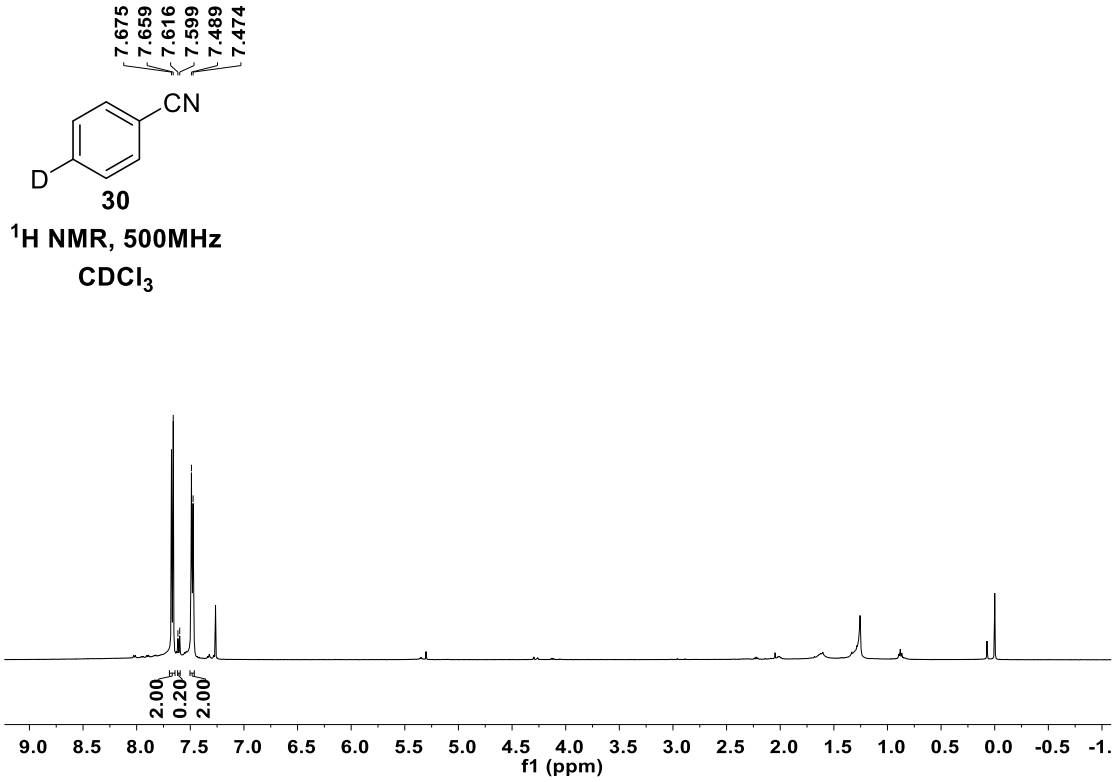
$CDCl_3$

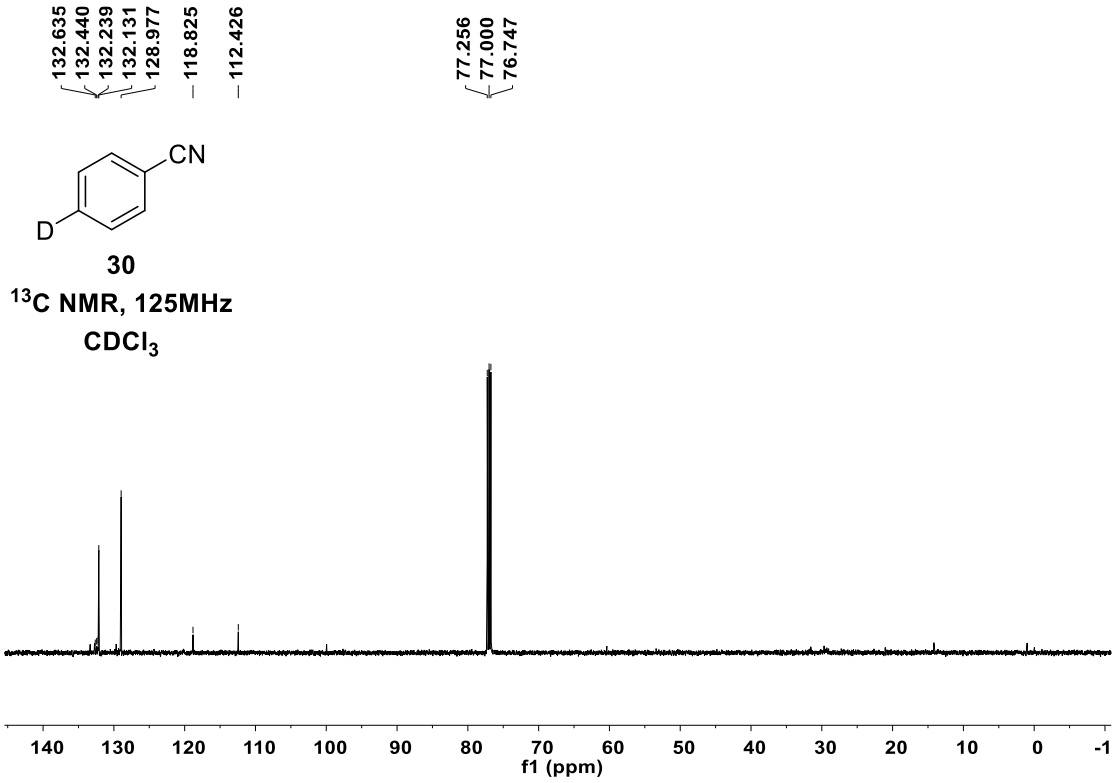

8.051
7.547
4.402
4.388
4.374
4.360
1.411
1.396
1.382
D
D
O
O
28
1H NMR, 500MHz
CDCl3
2.00
1.00
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

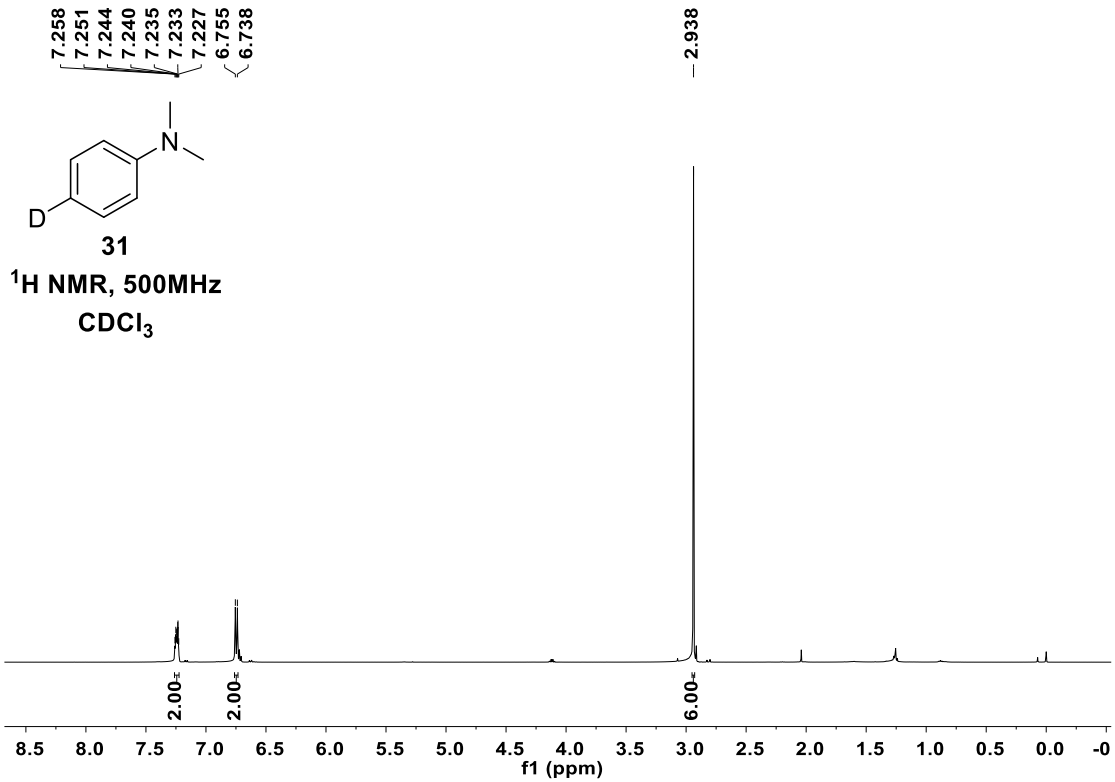

166.601
132.537
130.458
129.379
128.168
127.974
127.775
77.253
77.000
76.747
60.906
14.300
D
D
O
O
28
13C NMR, 125MHz
CDCl3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.289
7.272
6.928
6.911
3.870
3.865
3.861
3.857
3.851
3.164
3.159
3.154
3.151
3.145
O
N
D
29
1H NMR, 500MHz
CDCl3
2.00
2.00
4.00
4.00
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 -0.
f1 (ppm)


151.231
129.036
119.947
119.752
119.557
115.672
77.254
77.000
76.746
66.908
49.342
O
N
D
29
13C NMR, 125MHz
CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.675
7.659
7.616
7.599
7.489
7.474
CN
D
30
1H NMR, 500MHz
CDCl3
2.00
0.20
2.00
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 -0.5 -1.
f1 (ppm)

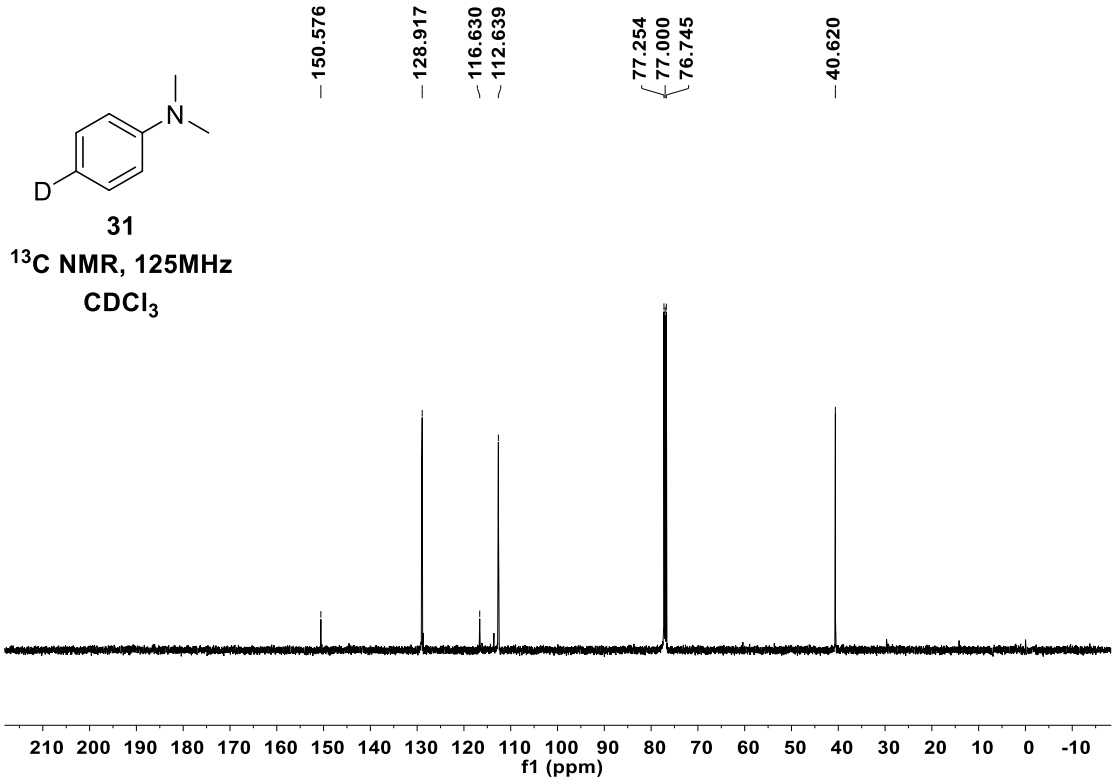

132.635
132.440
132.239
132.131
128.977
118.825
112.426
77.256
77.000
76.747
CN
D
30
13C NMR, 125MHz
CDCl3
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



31

^{1}H NMR, 500MHz

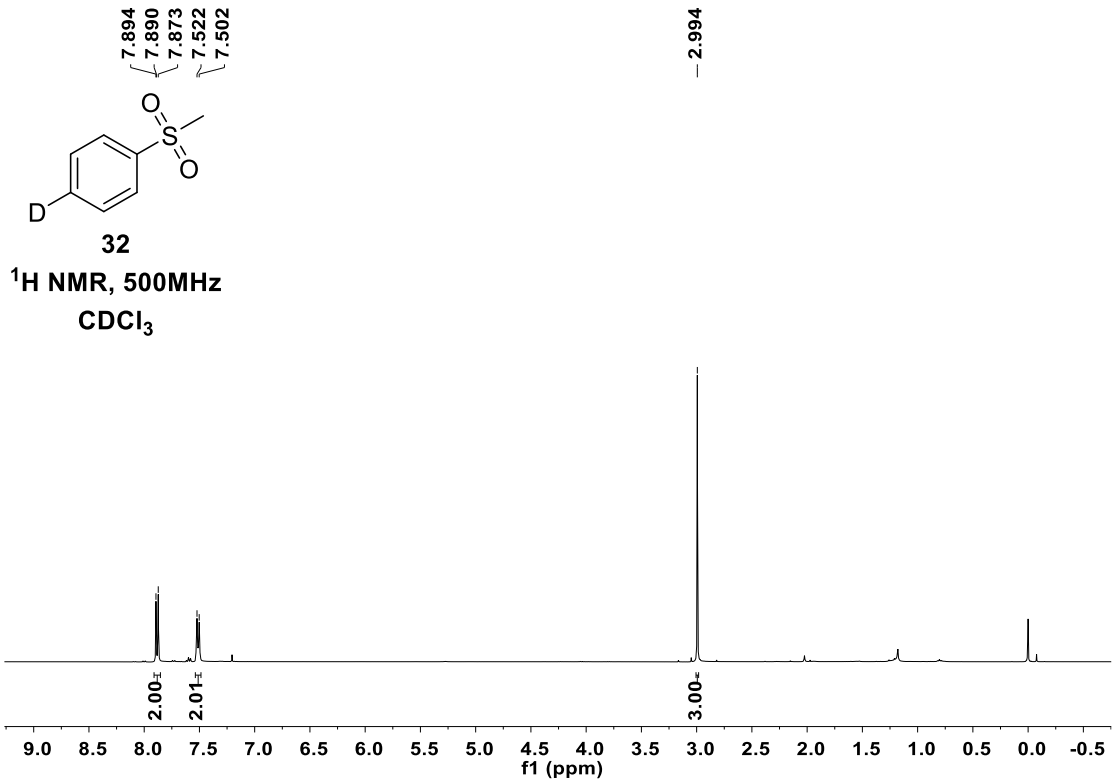
$CDCl_3$

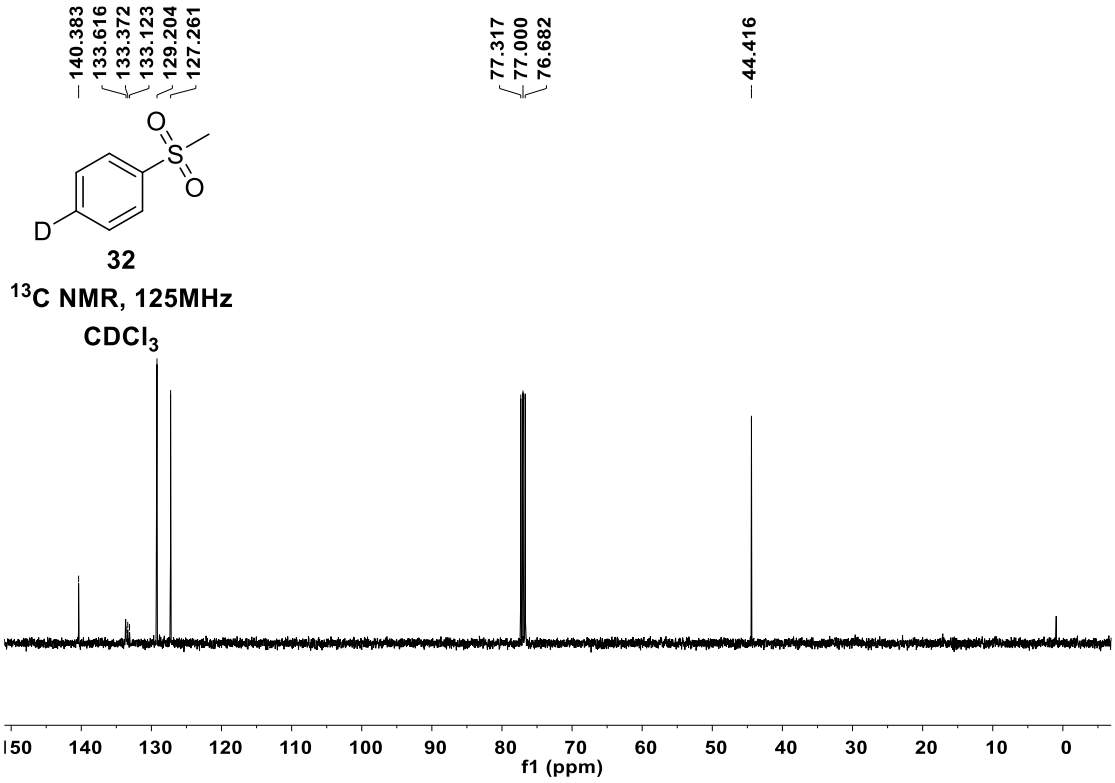


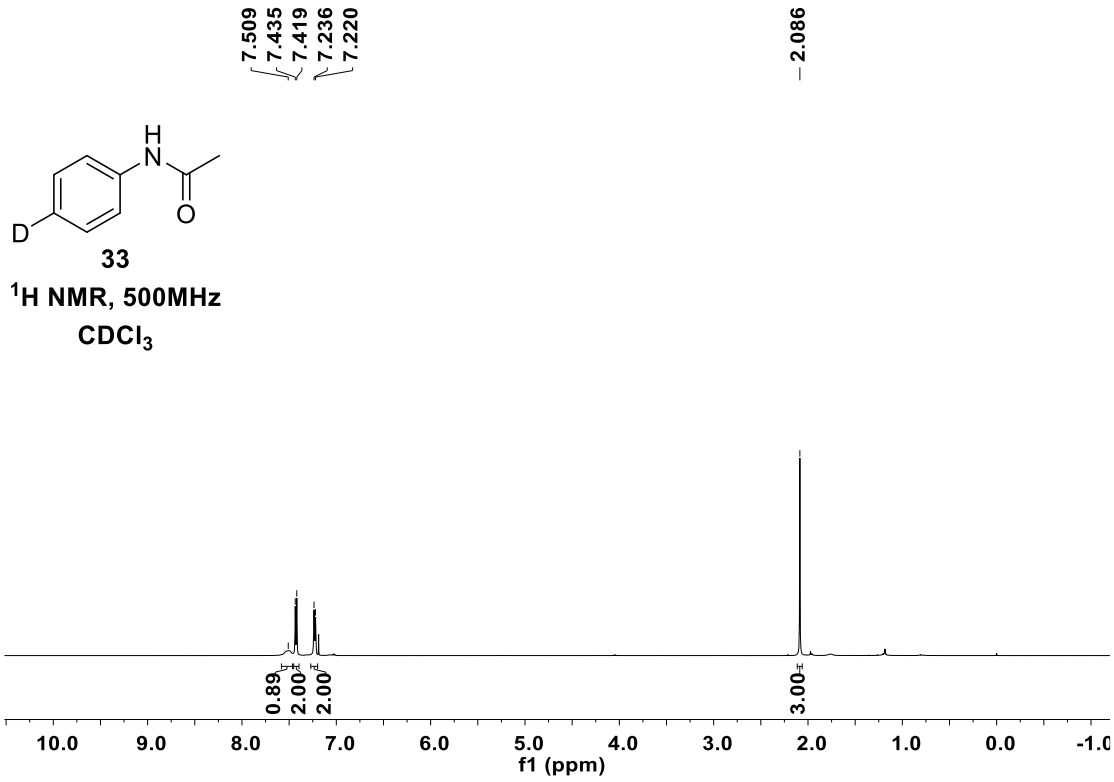
31

^{13}C NMR, 125MHz

$CDCl_3$


7.894
7.890
7.873
7.522
7.502
2.994
O
S
O
D
32
1H NMR, 500MHz
CDCl3
2.00
2.01
3.00
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 -0.5
f1 (ppm)

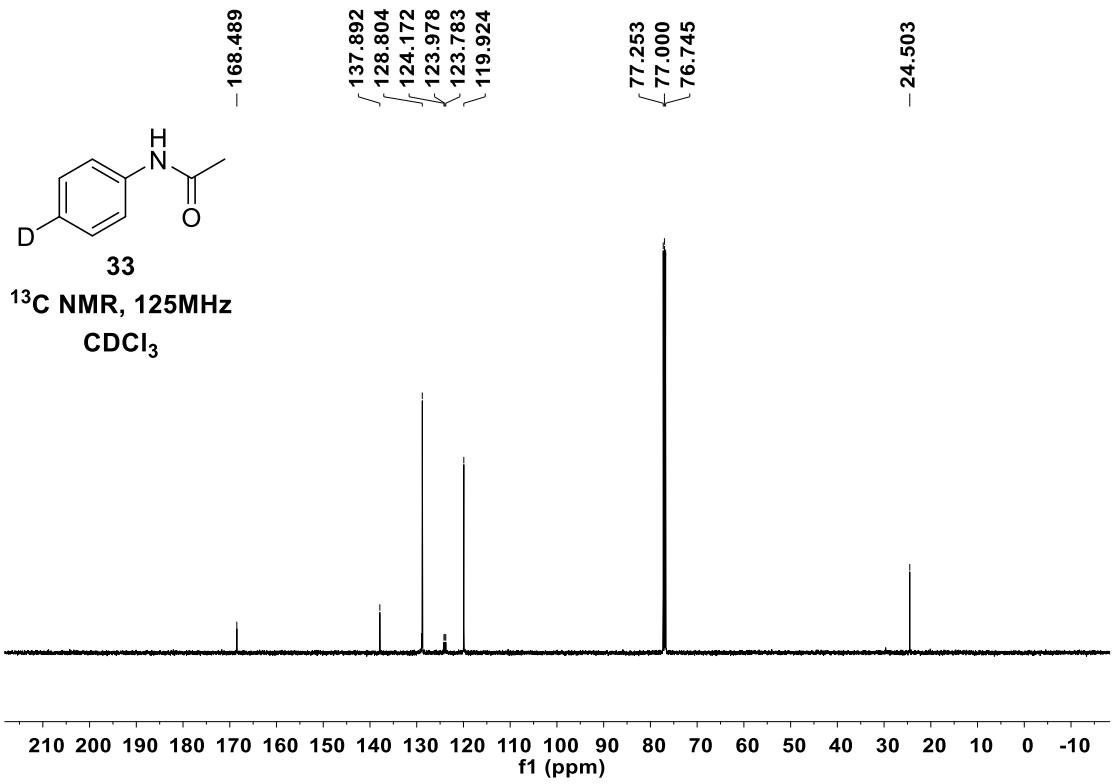

140.383
133.616
133.372
133.123
129.204
127.261
77.317
77.000
76.682
44.416
O
S
O
D
32
13C NMR, 125MHz
CDCl3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



33

^{1}H NMR, 500MHz

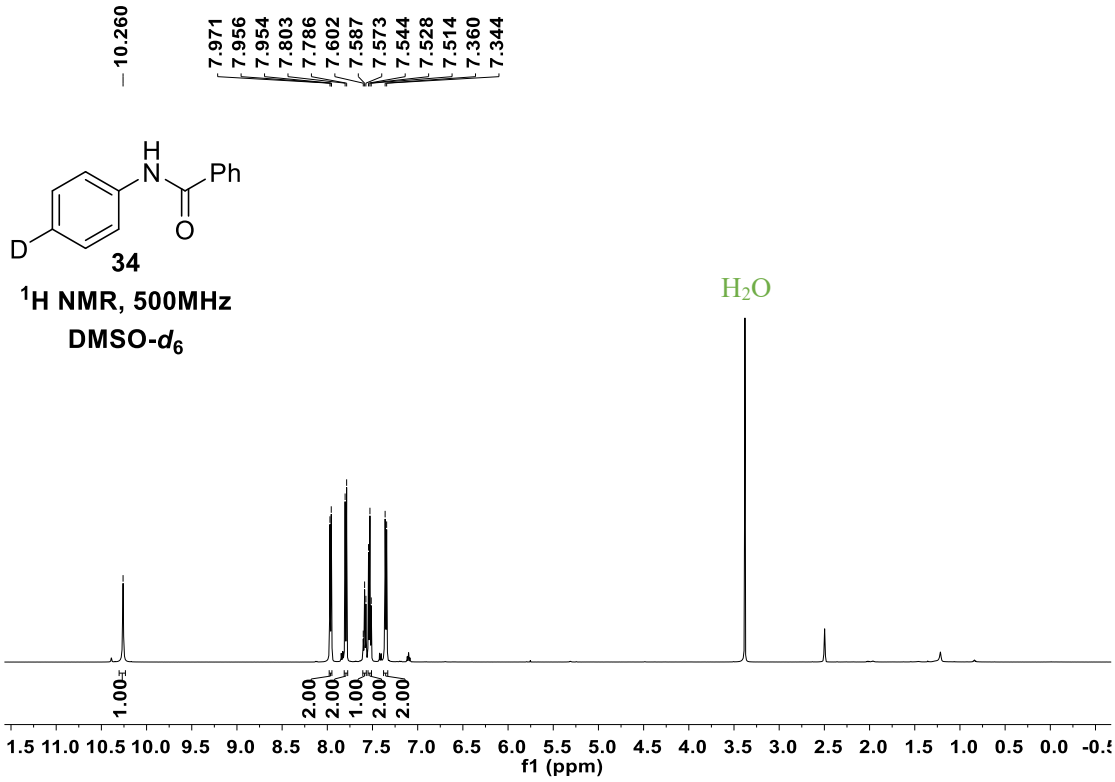
$CDCl_3$

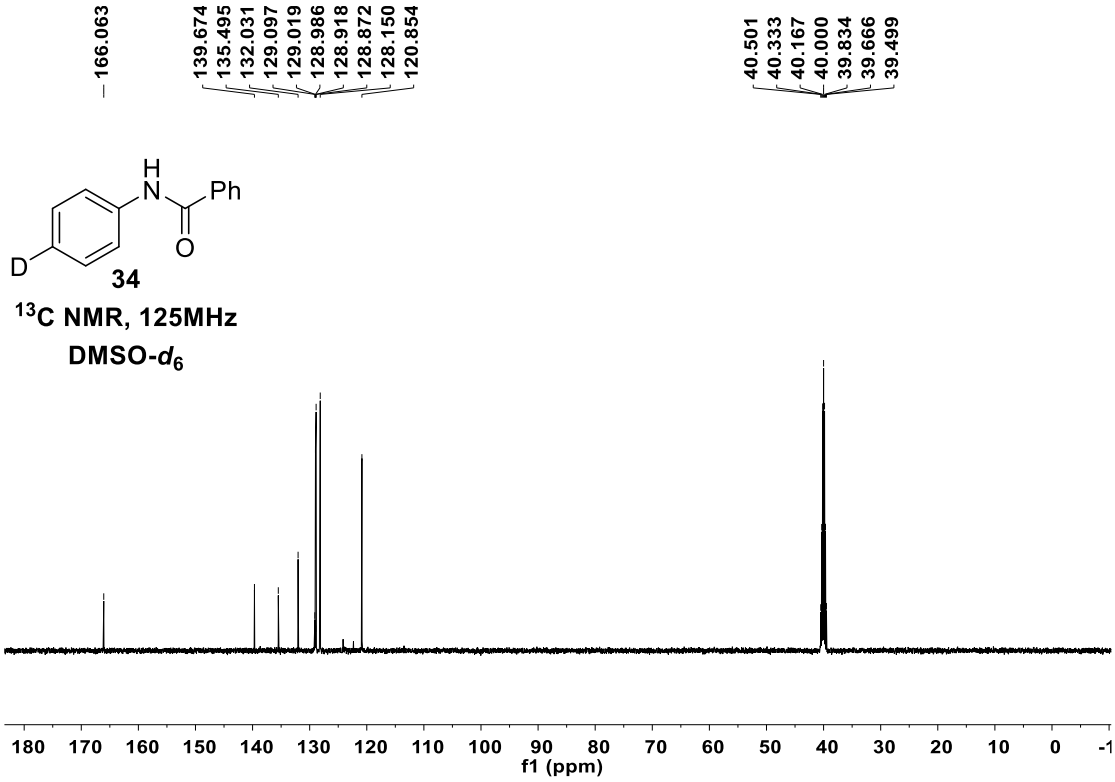


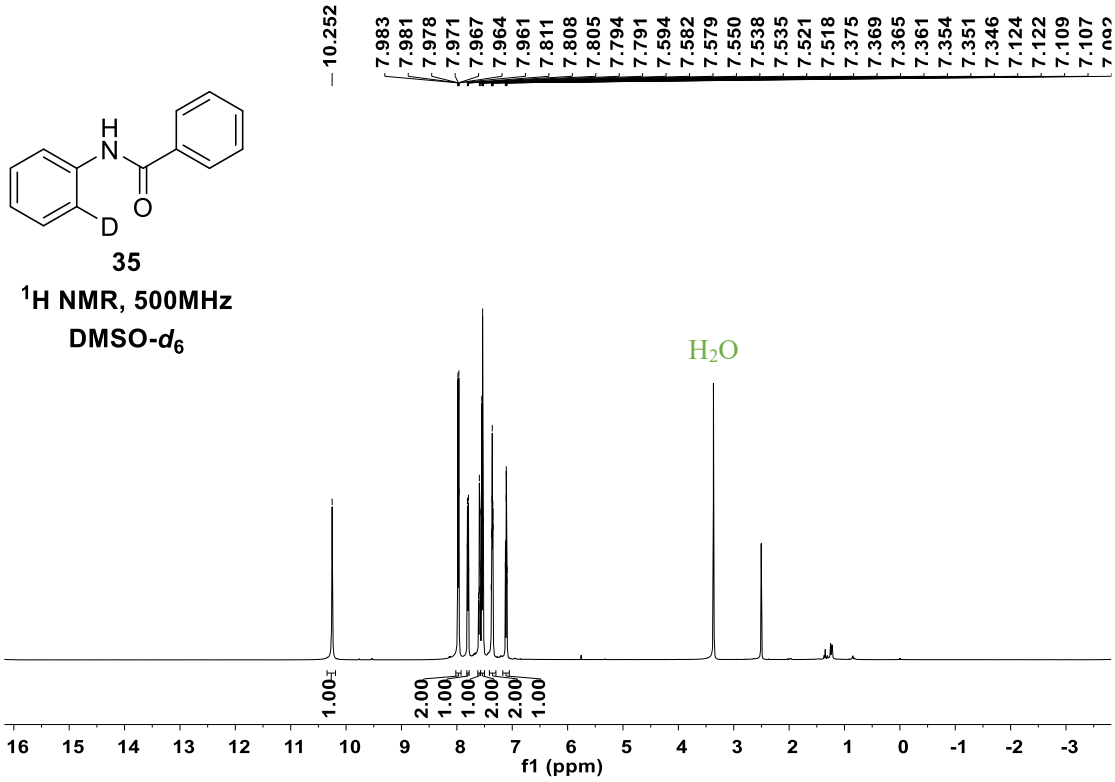
33

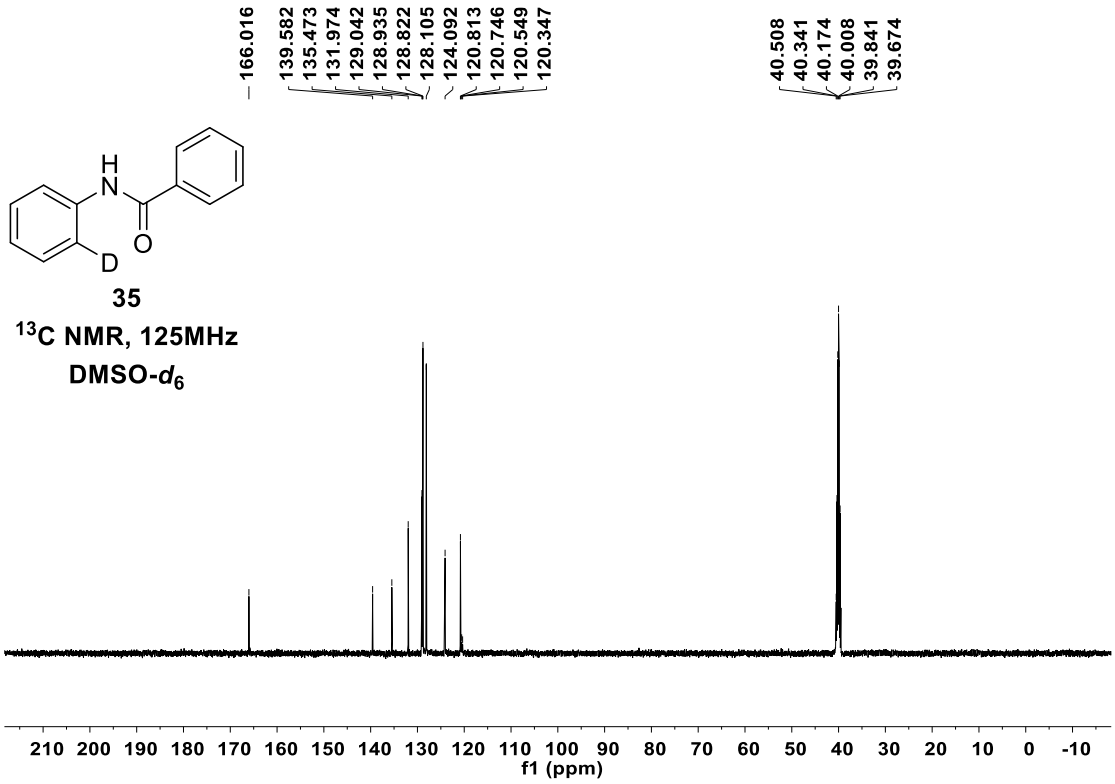
^{13}C NMR, 125MHz

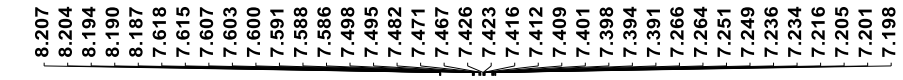
$CDCl_3$

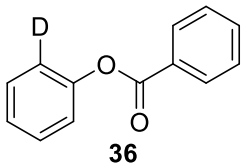

10.260
7.971
7.956
7.954
7.803
7.786
7.602
7.587
7.573
7.544
7.528
7.514
7.360
7.344
H
N
Ph
O
D
34
1H NMR, 500MHz
DMSO-d6
H2O
1.00
2.00
2.00
1.00
2.00
2.00
f1 (ppm)


166.063
139.674
135.495
132.031
129.097
129.019
128.986
128.918
128.872
128.150
120.854
40.501
40.333
40.167
40.000
39.834
39.666
39.499
H
N
Ph
O
D
34
13C NMR, 125MHz
DMSO-d6
f1 (ppm)


10.252
7.983
7.981
7.978
7.971
7.967
7.964
7.961
7.811
7.808
7.805
7.794
7.791
7.594
7.582
7.579
7.550
7.538
7.535
7.521
7.518
7.375
7.369
7.365
7.361
7.354
7.351
7.346
7.124
7.122
7.109
7.107
H
N
O
D
35
1H NMR, 500MHz
DMSO-d6
H2O
1.00
2.00
1.00
1.00
2.00
2.00
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


166.016
139.582
135.473
131.974
129.042
128.935
128.822
128.105
124.092
120.813
120.746
120.549
120.347
40.508
40.341
40.174
40.008
39.841
39.674
H
N
O
D
35
13C NMR, 125MHz
DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

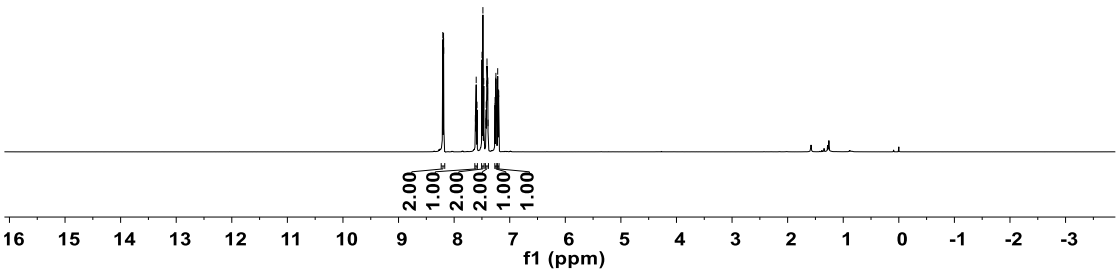


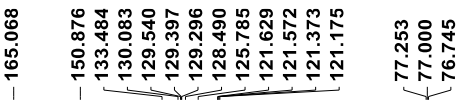


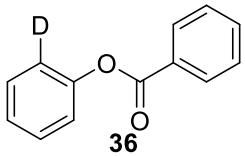
36

^{1}H NMR, 500MHz

$CDCl_3$



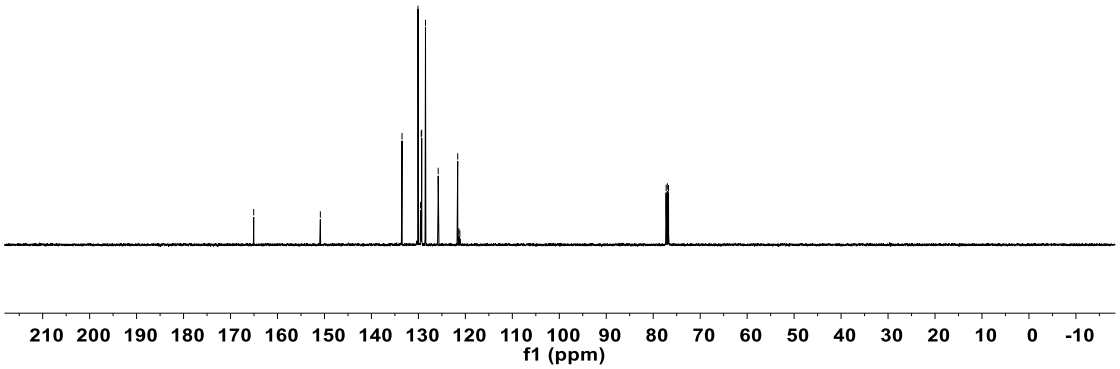


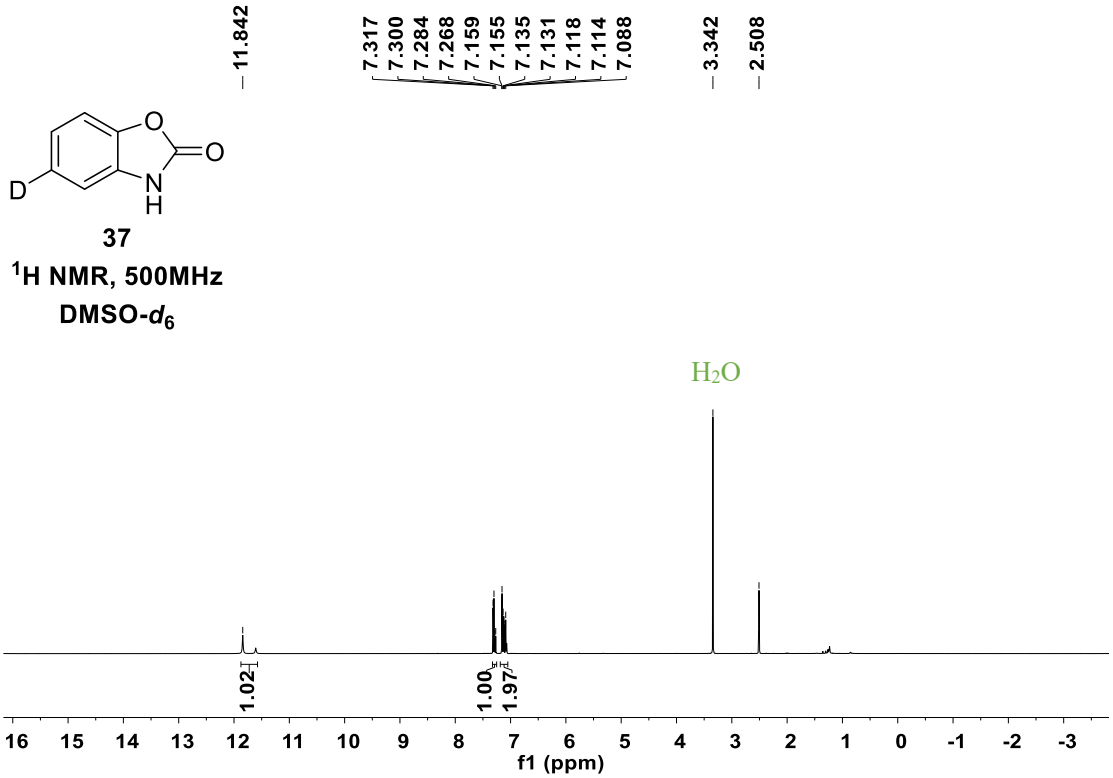


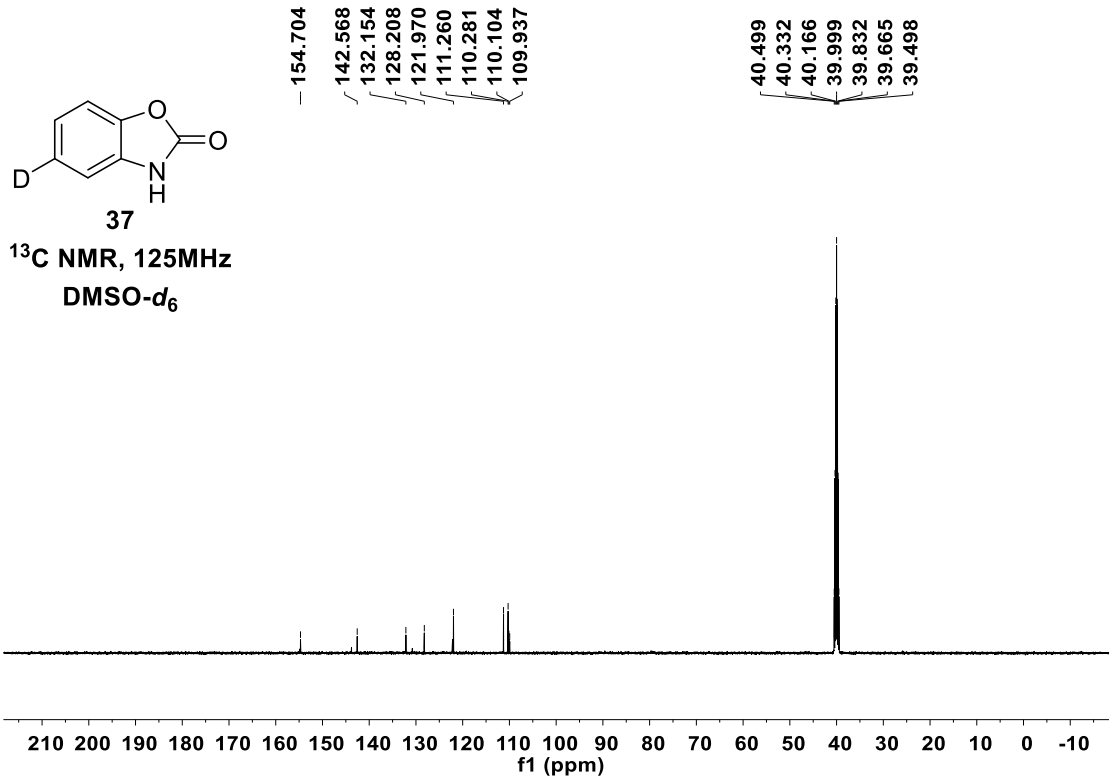
36

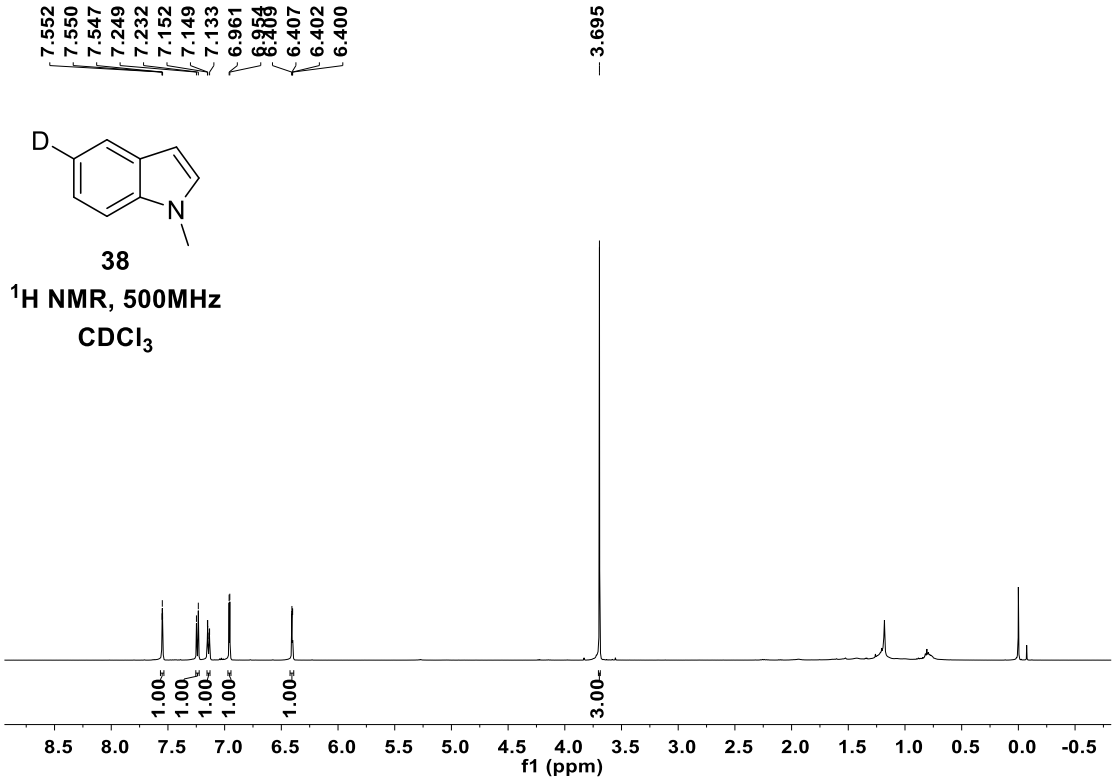
^{13}C NMR, 125MHz

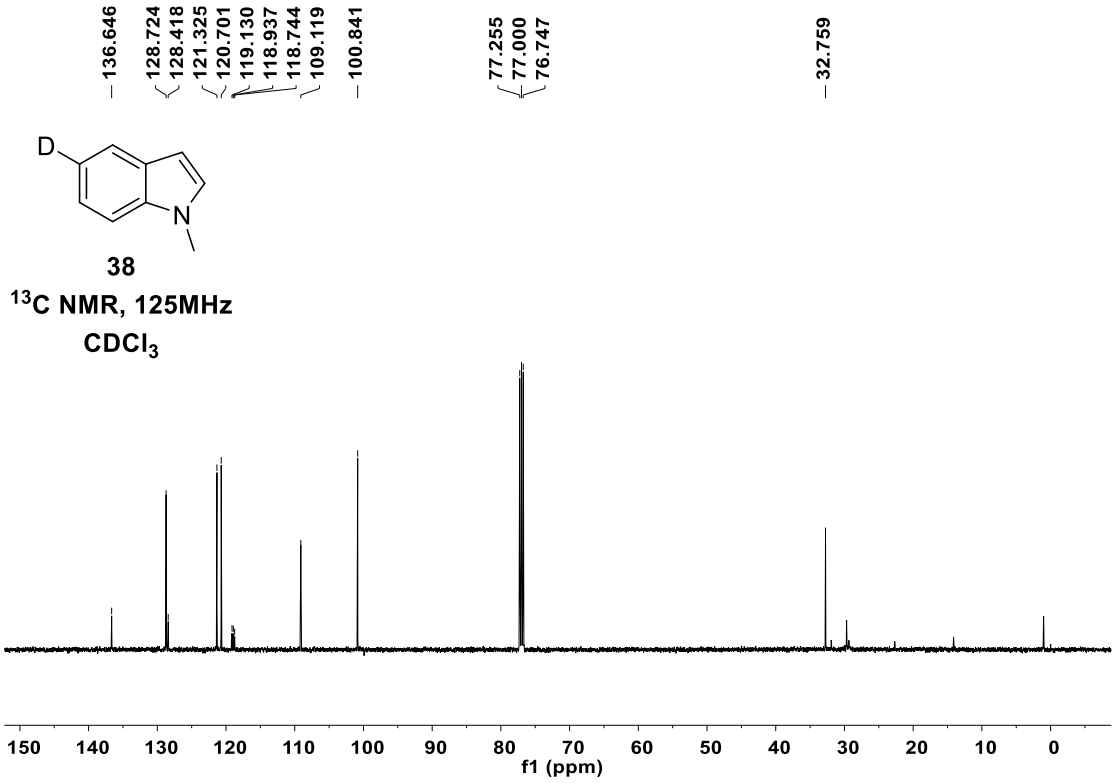
$CDCl_3$

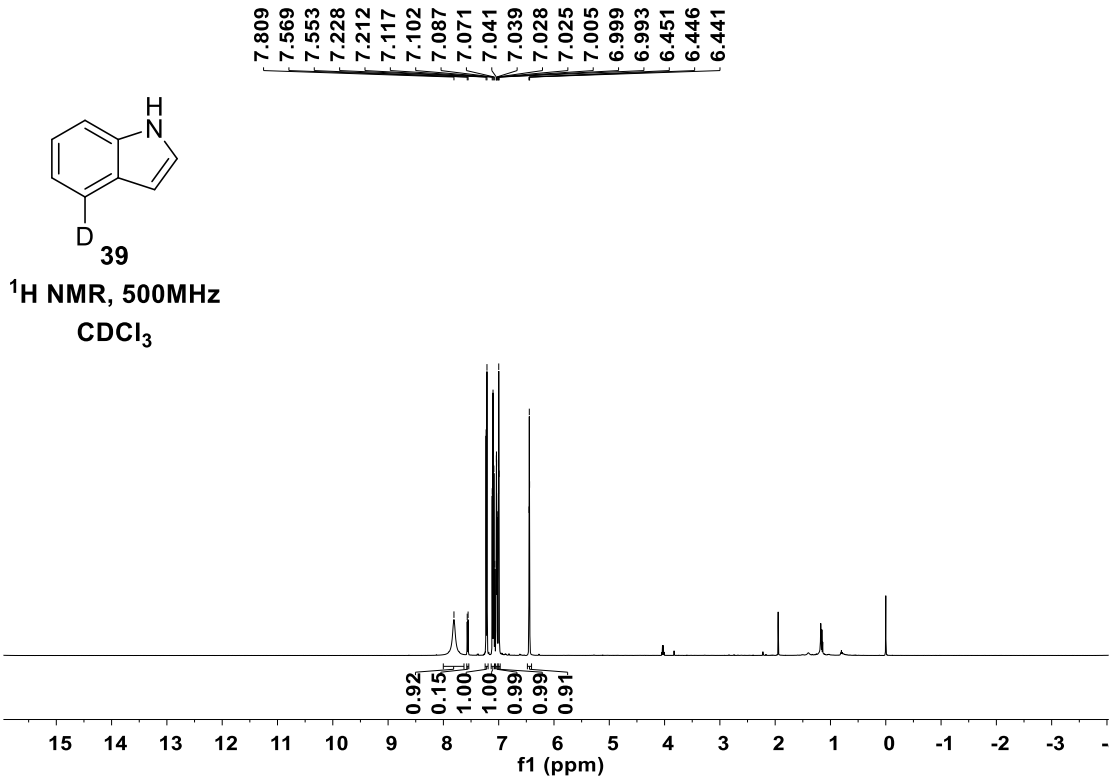



11.842
7.317
7.300
7.284
7.268
7.159
7.155
7.135
7.131
7.118
7.114
7.088
3.342
2.508
O
O
N
H
D
37
1H NMR, 500MHz
DMSO-d6
H2O
1.02
1.00
1.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


154.704
142.568
132.154
128.208
121.970
111.260
110.281
110.104
109.937
40.499
40.332
40.166
39.999
39.832
39.665
39.498
O
O
N
H
D
37
13C NMR, 125MHz
DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.552
7.550
7.547
7.249
7.232
7.152
7.149
7.133
6.961
6.954
6.409
6.407
6.402
6.400
3.695
D
N
38
1H NMR, 500MHz
CDCl3
1.00
1.00
1.00
1.00
1.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

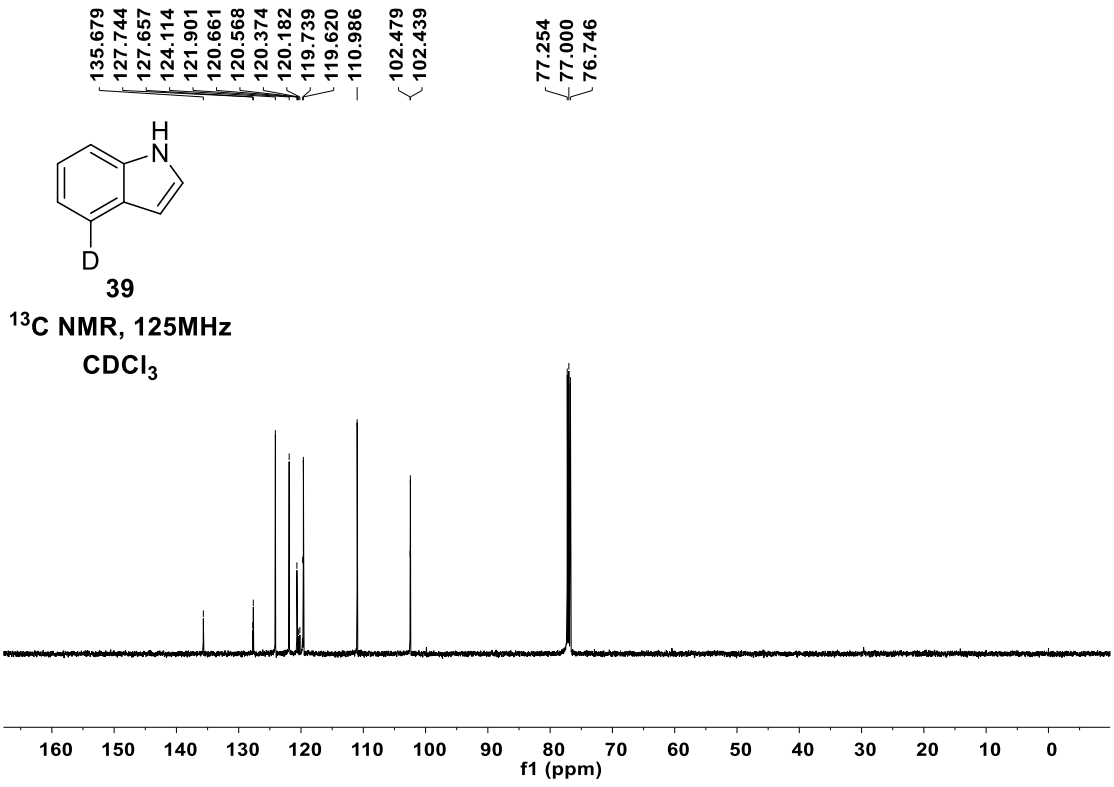

136.646
128.724
128.418
121.325
120.701
119.130
118.937
118.744
109.119
100.841
77.255
77.000
76.747
32.759
D
N
38
13C NMR, 125MHz
CDCl3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



39

^{1}H NMR, 500MHz

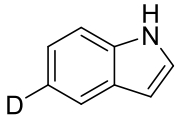
$CDCl_3$



39

^{13}C NMR, 125MHz

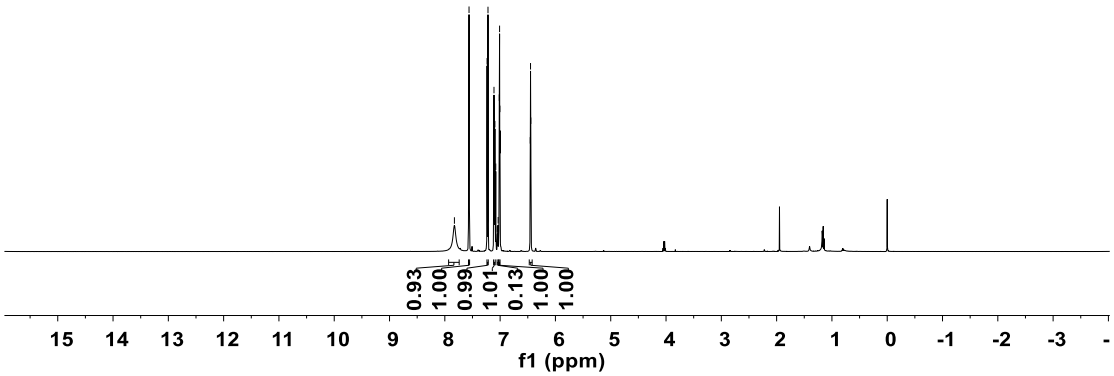
$CDCl_3$

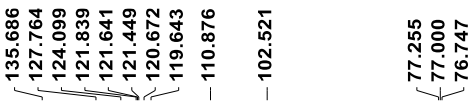


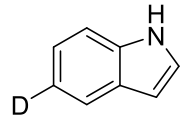
40

^{1}H NMR, 500MHz

$CDCl_3$



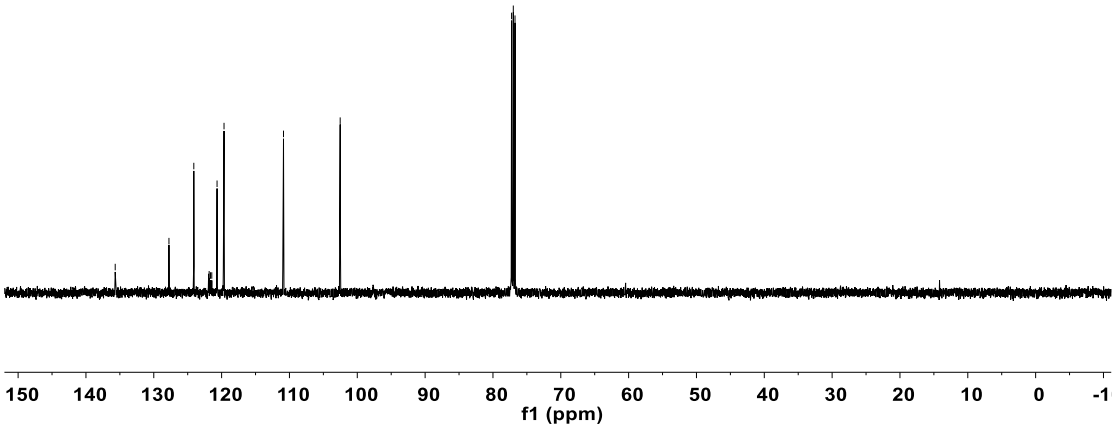


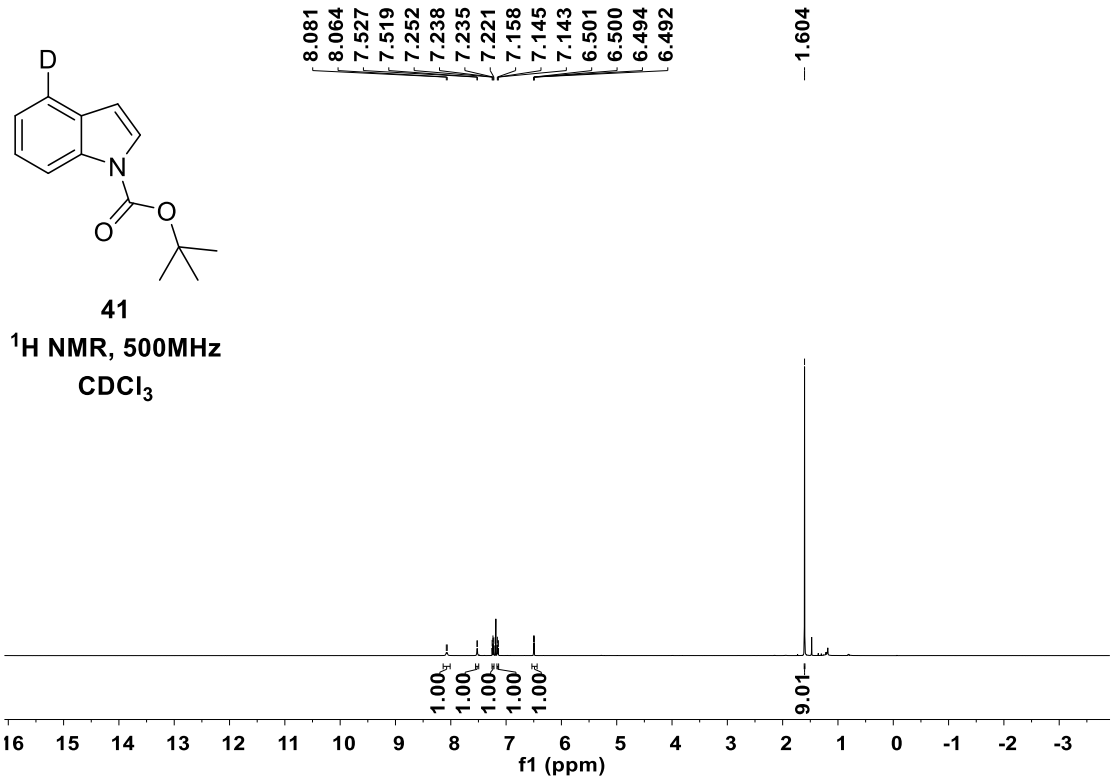


40

^{13}C NMR, 125MHz

$CDCl_3$

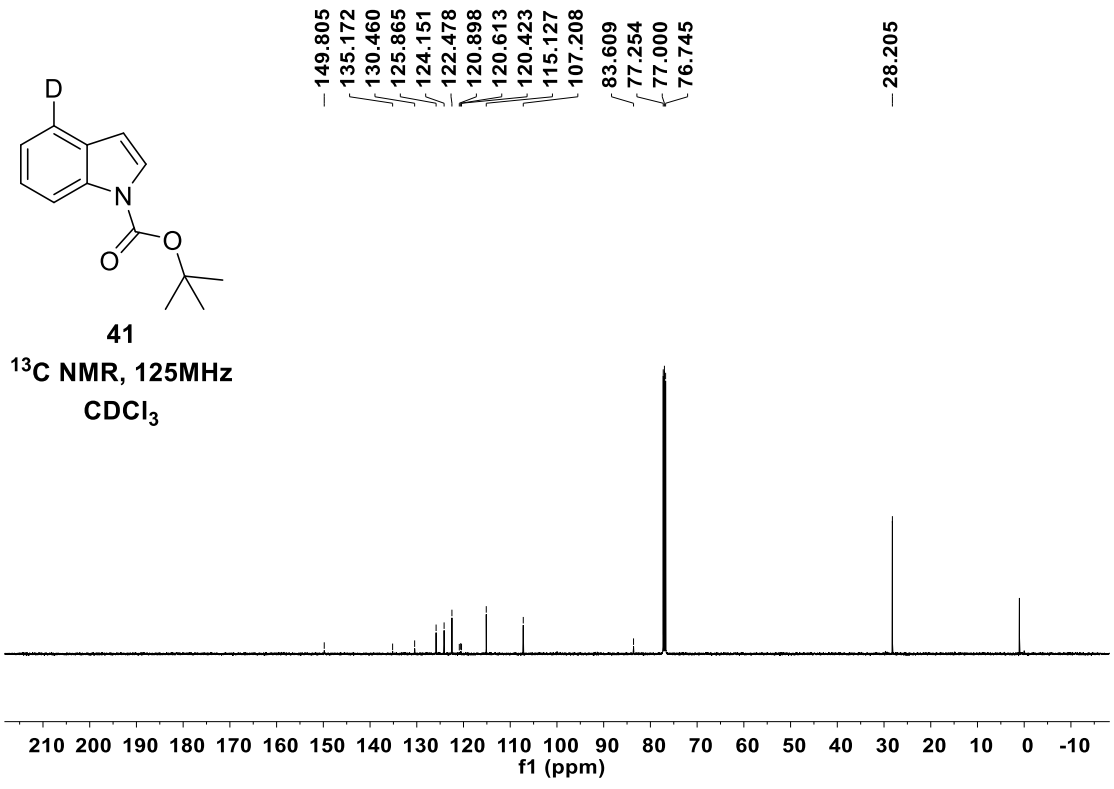




41

^{1}H NMR, 500MHz

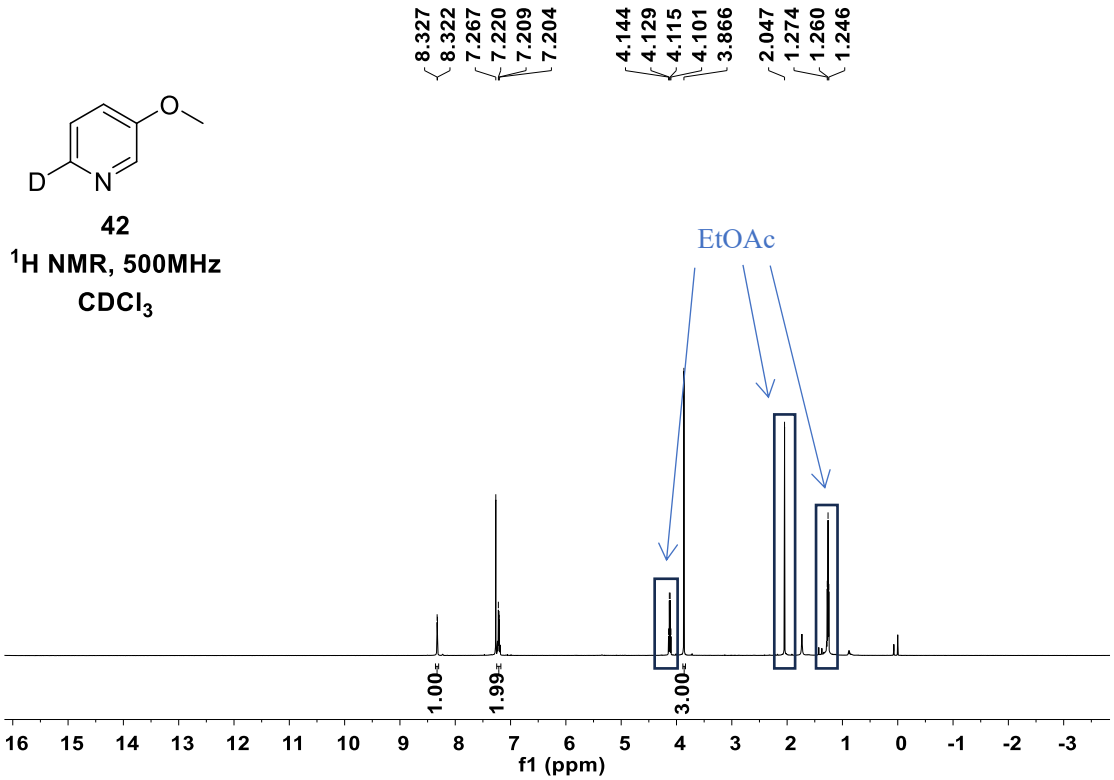
$CDCl_3$

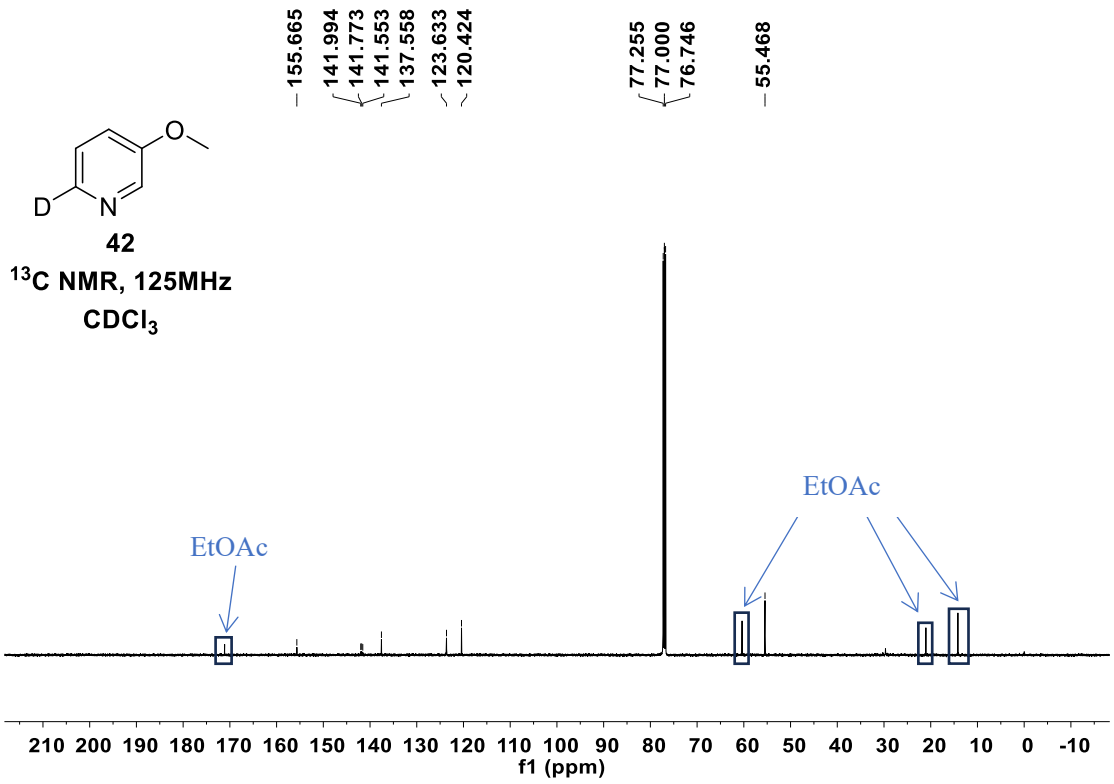


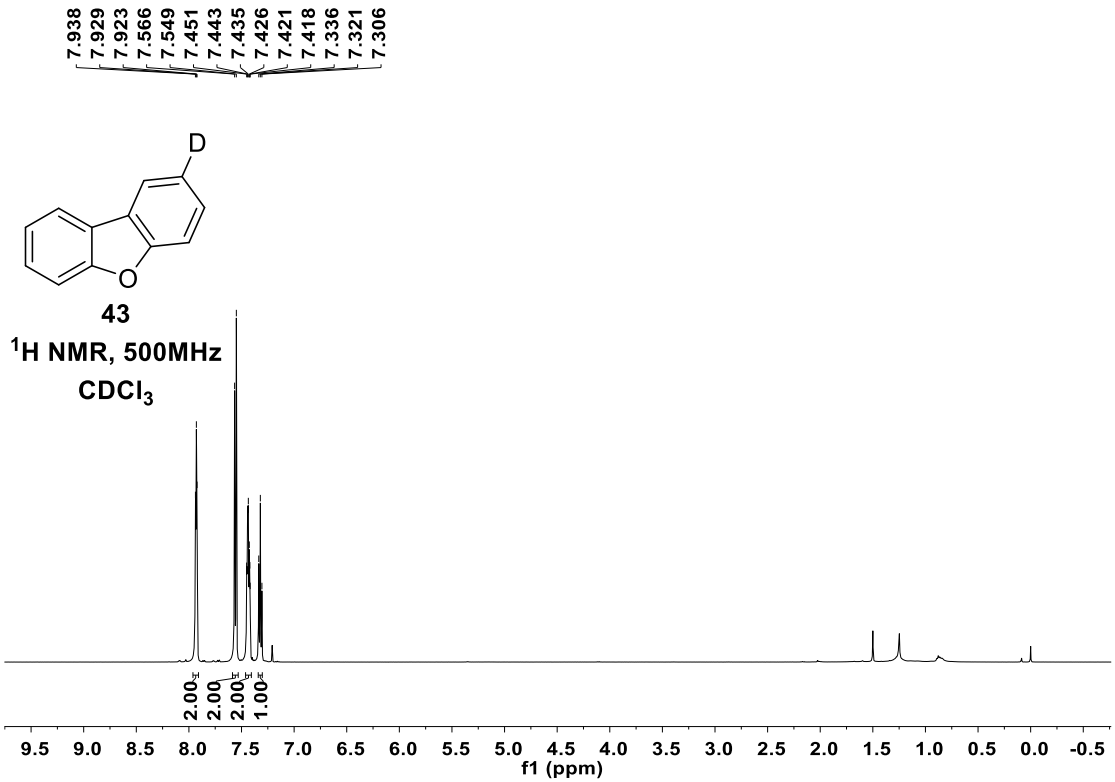
41

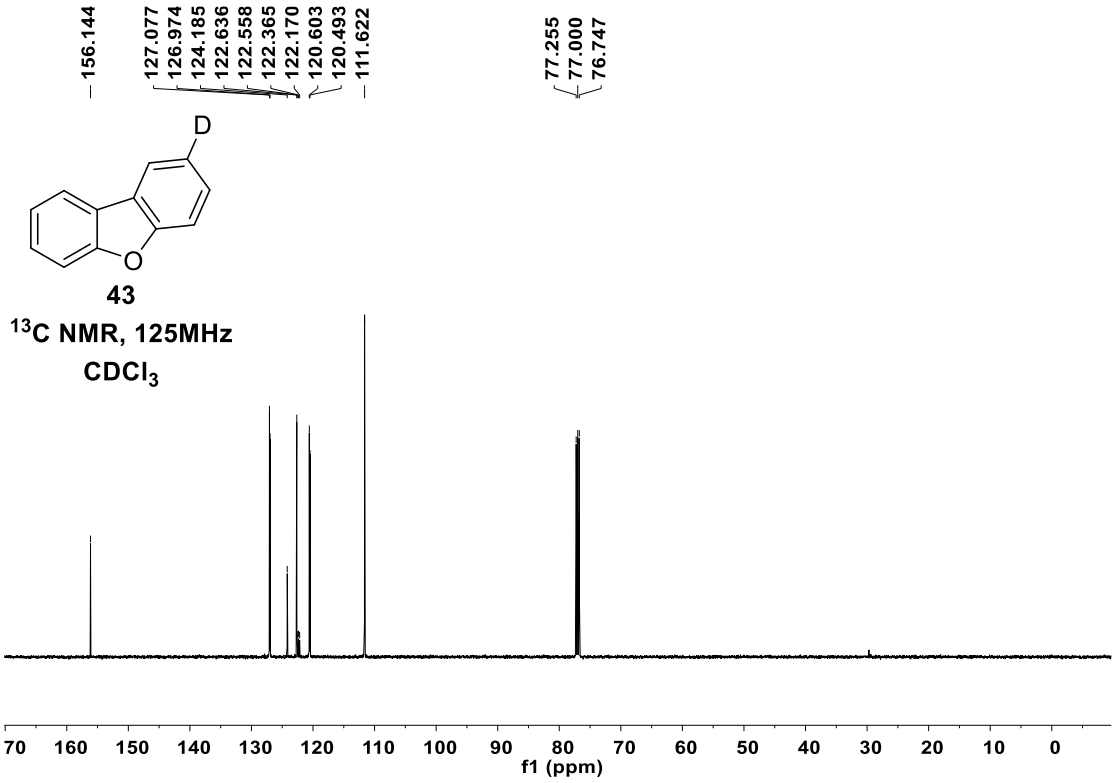
^{13}C NMR, 125MHz

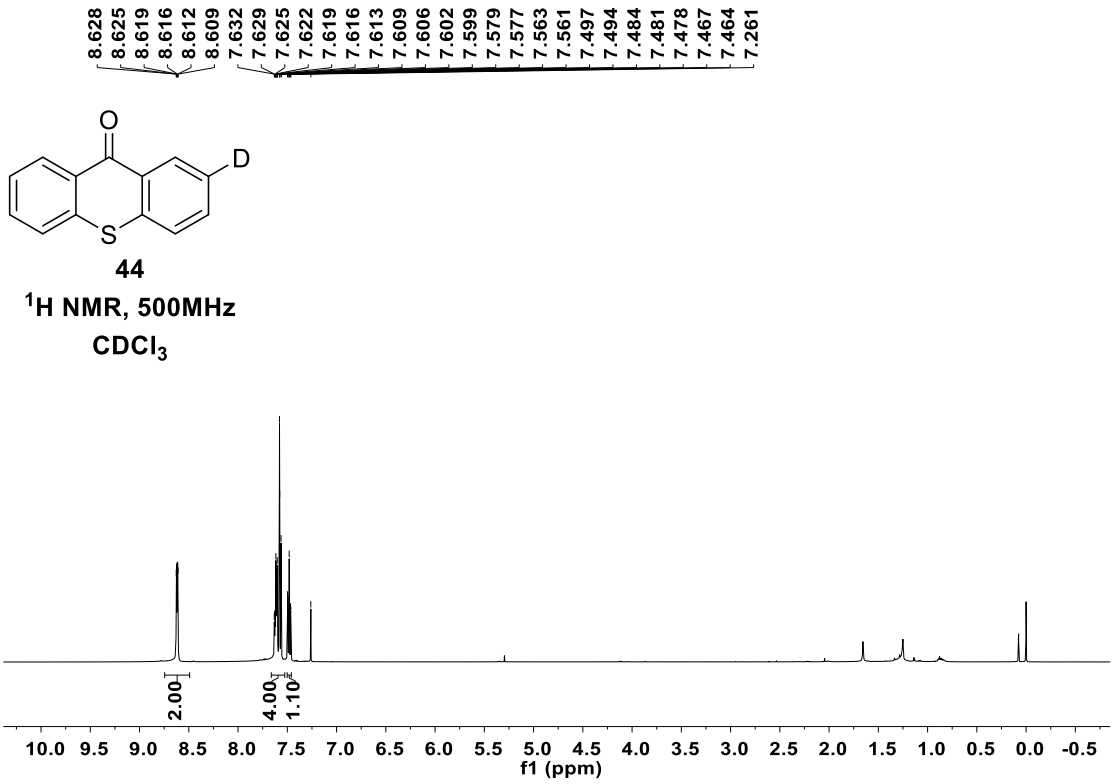
$CDCl_3$

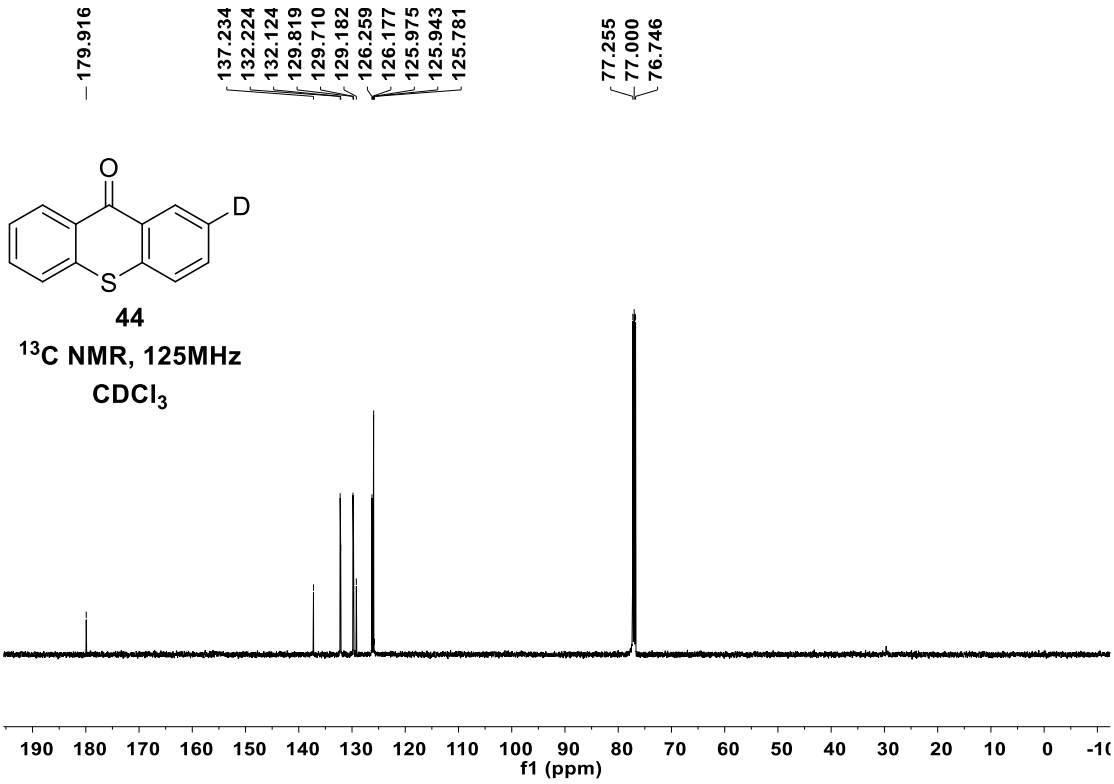

8.327
8.322
7.267
7.220
7.209
7.204
4.144
4.129
4.115
4.101
3.866
2.047
1.274
1.260
1.246
O
D
N
42
1H NMR, 500MHz
CDCl3
EtOAc
1.00
1.99
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

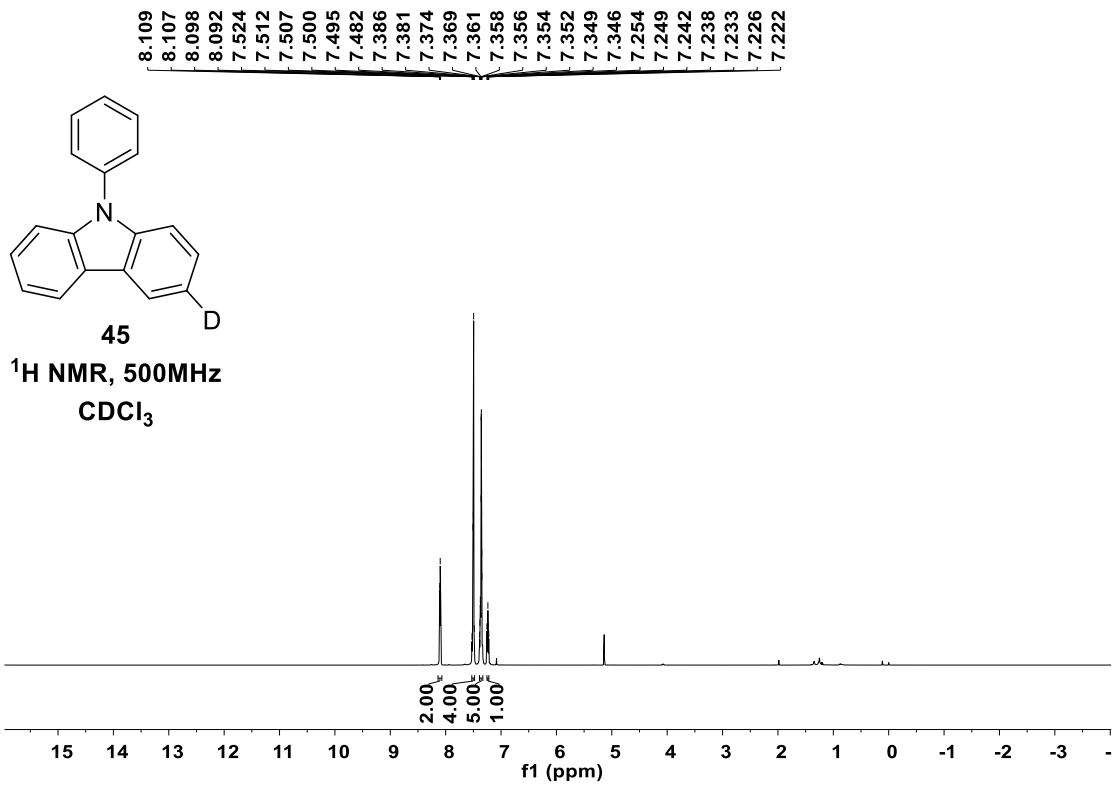

155.665
141.994
141.773
141.553
137.558
123.633
120.424
77.255
77.000
76.746
55.468
O
D
N
42
13C NMR, 125MHz
CDCl3
EtOAc
EtOAc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

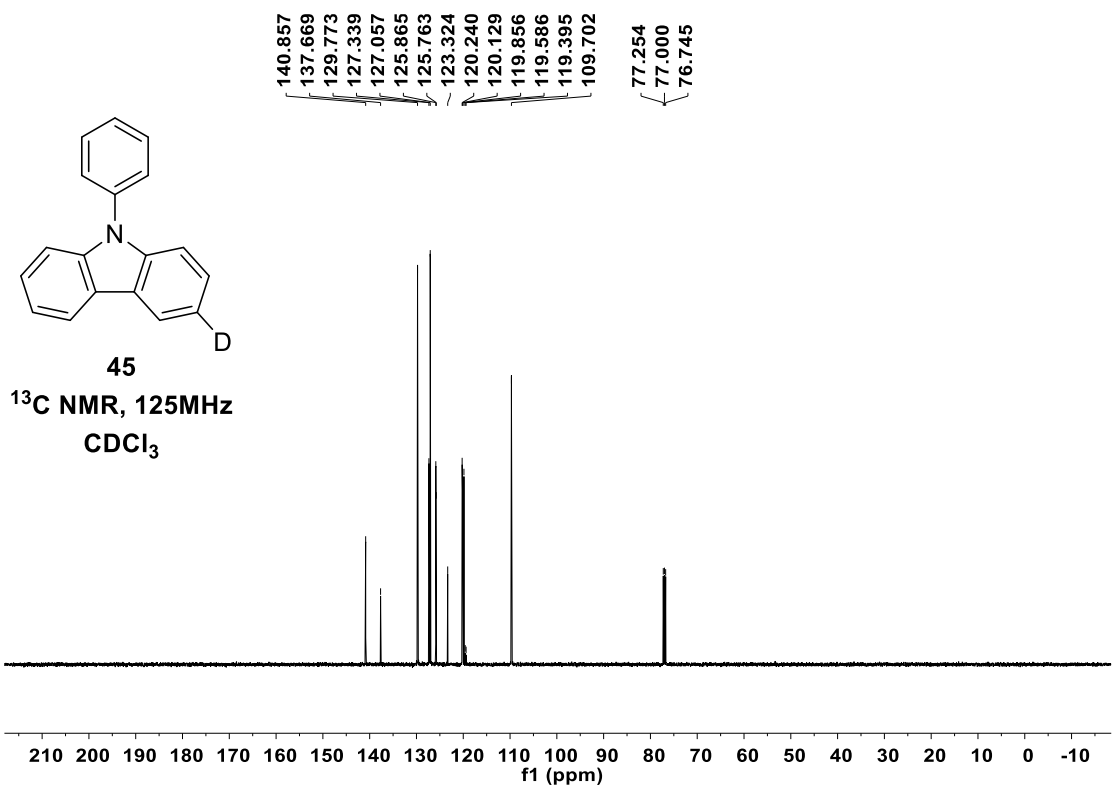

7.938
7.929
7.923
7.566
7.549
7.451
7.443
7.435
7.426
7.421
7.418
7.336
7.321
7.306
D
O
43
1H NMR, 500MHz
CDCl3
2.00
2.00
2.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

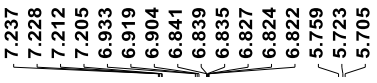

156.144
127.077
126.974
124.185
122.636
122.558
122.365
122.170
120.603
120.493
111.622
77.255
77.000
76.747
D
O
43
13C NMR, 125MHz
CDCl3
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

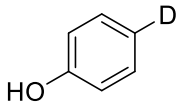

8.628
8.625
8.619
8.616
8.612
8.609
7.632
7.629
7.625
7.622
7.619
7.616
7.613
7.609
7.606
7.602
7.599
7.579
7.577
7.563
7.561
7.497
7.494
7.484
7.481
7.478
7.467
7.464
7.261
O
D
S
44
1H NMR, 500MHz
CDCl3
2.00
4.00
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.916
137.234
132.224
132.124
129.819
129.710
129.182
126.259
126.177
125.975
125.943
125.781
77.255
77.000
76.746
O
D
S
44
13C NMR, 125MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.109
8.107
8.098
8.092
7.524
7.512
7.507
7.500
7.495
7.482
7.386
7.381
7.374
7.369
7.361
7.358
7.356
7.354
7.352
7.349
7.346
7.254
7.249
7.242
7.238
7.233
7.226
7.222
N
D
45
1H NMR, 500MHz
CDCl3
2.00
4.00
5.00
1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


140.857
137.669
129.773
127.339
127.057
125.865
125.763
123.324
120.240
120.129
119.856
119.586
119.395
109.702
77.254
77.000
76.745
N
D
45
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

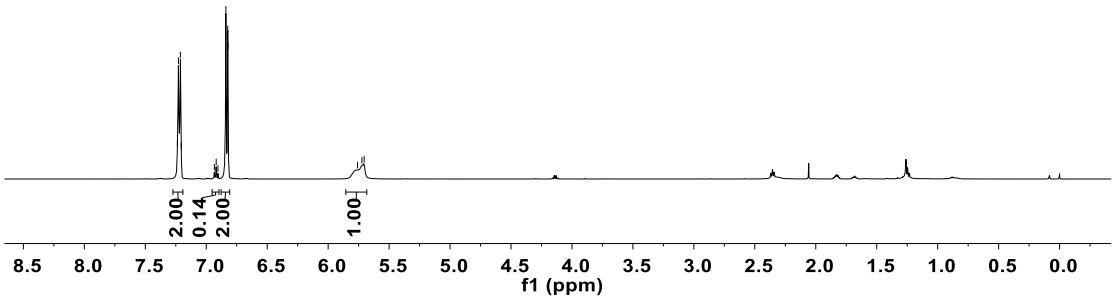


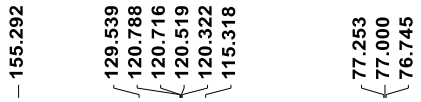


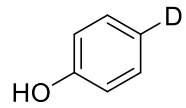
46

^{1}H NMR, 500MHz

$CDCl_3$



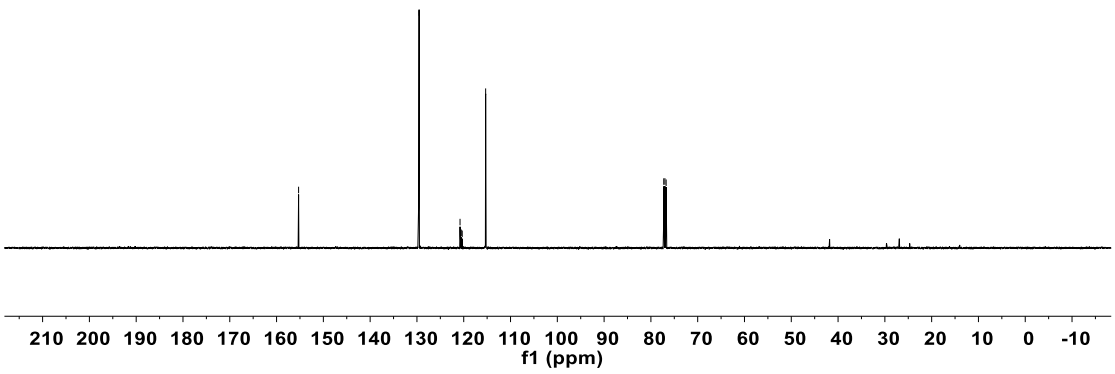


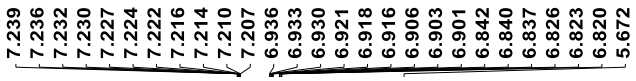


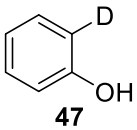
46

^{13}C NMR, 125MHz

$CDCl_3$



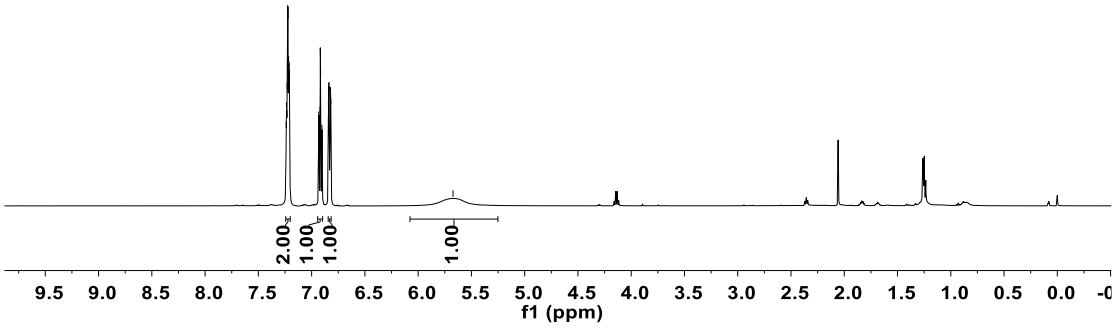


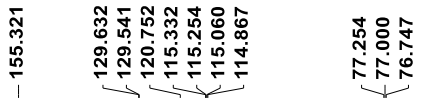


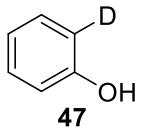
47

^{1}H NMR, 500MHz

$CDCl_3$



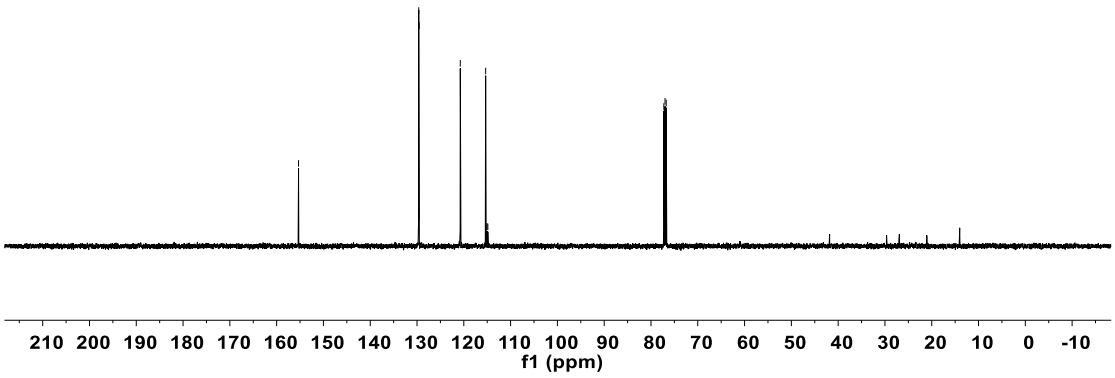


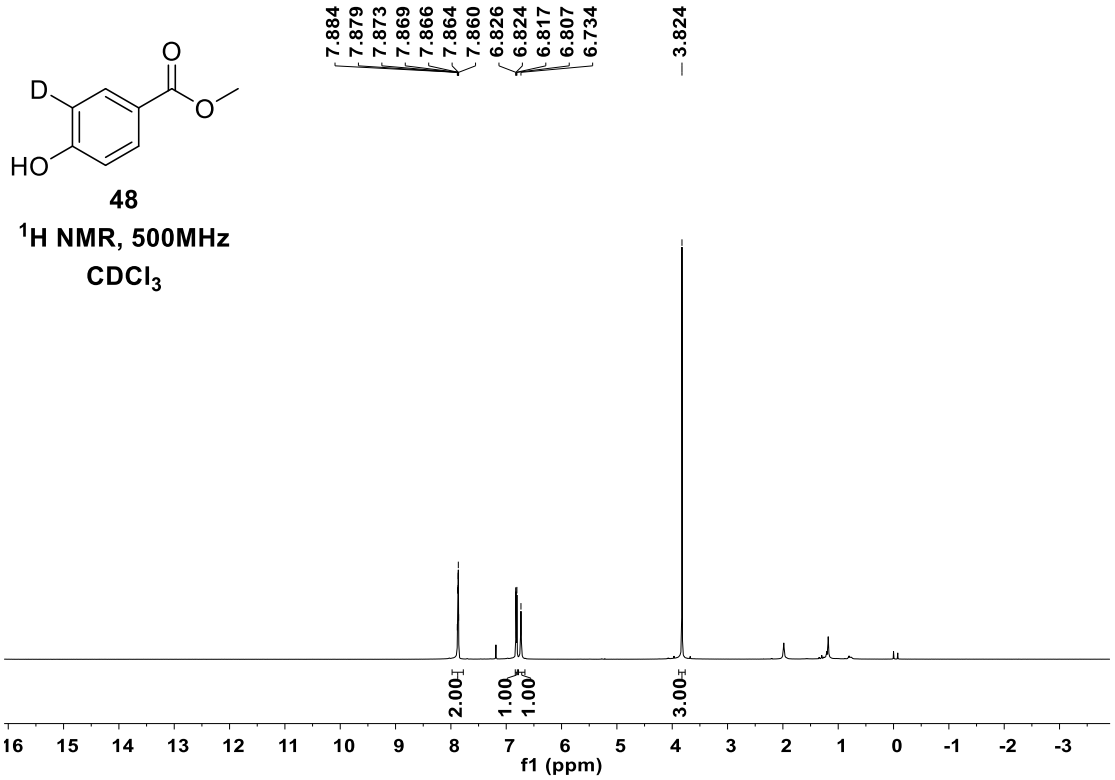


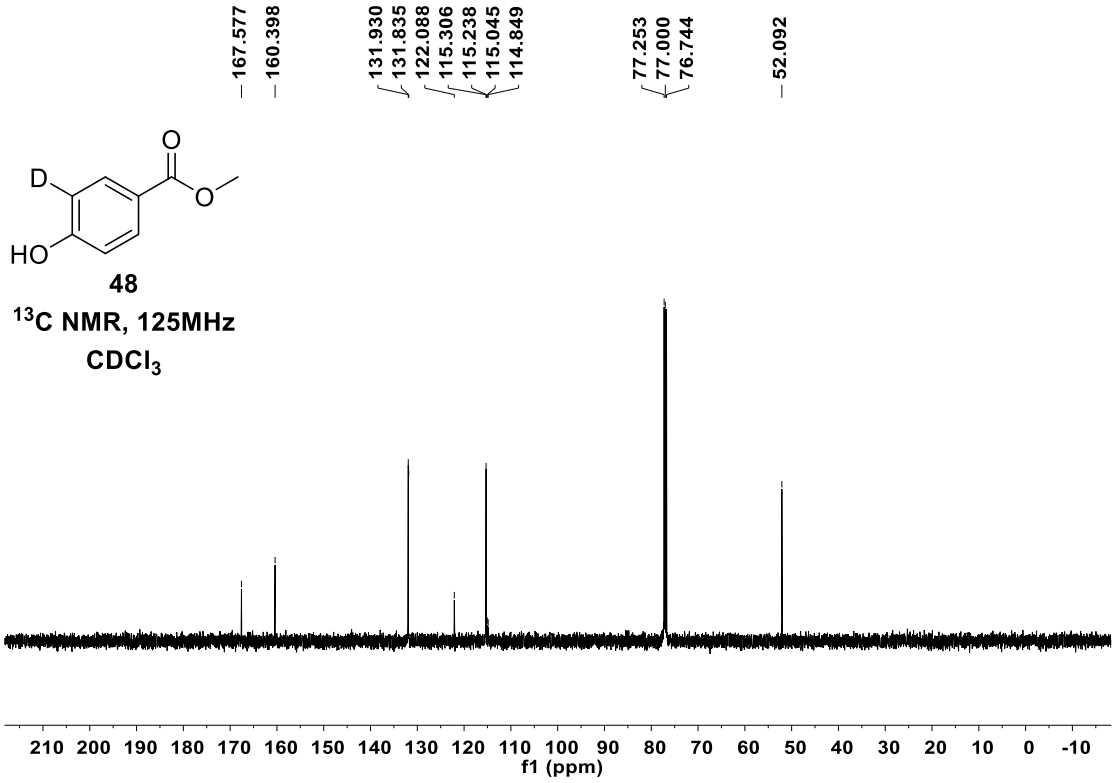
47

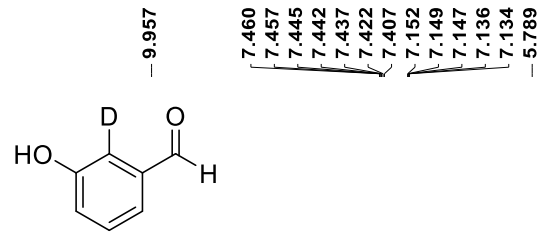
^{13}C NMR, 125MHz

$CDCl_3$




7.884
7.879
7.873
7.869
7.866
7.864
7.860
6.826
6.824
6.817
6.807
6.734
3.824
O
D
O
HO
48
1H NMR, 500MHz
CDCl3
2.00
1.00
1.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

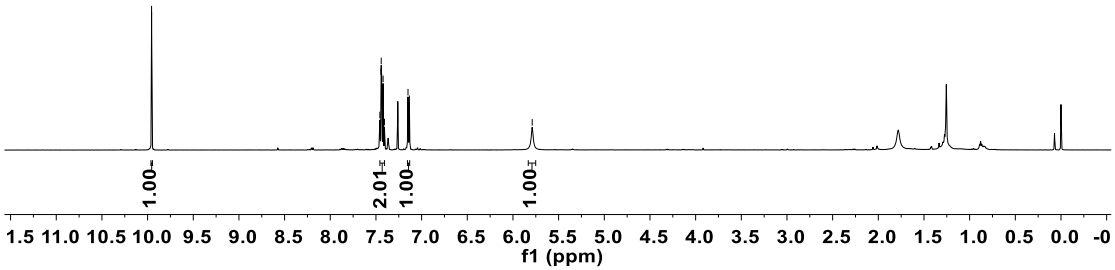

167.577
160.398
131.930
131.835
122.088
115.306
115.238
115.045
114.849
77.253
77.000
76.744
52.092
O
D
O
HO
48
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

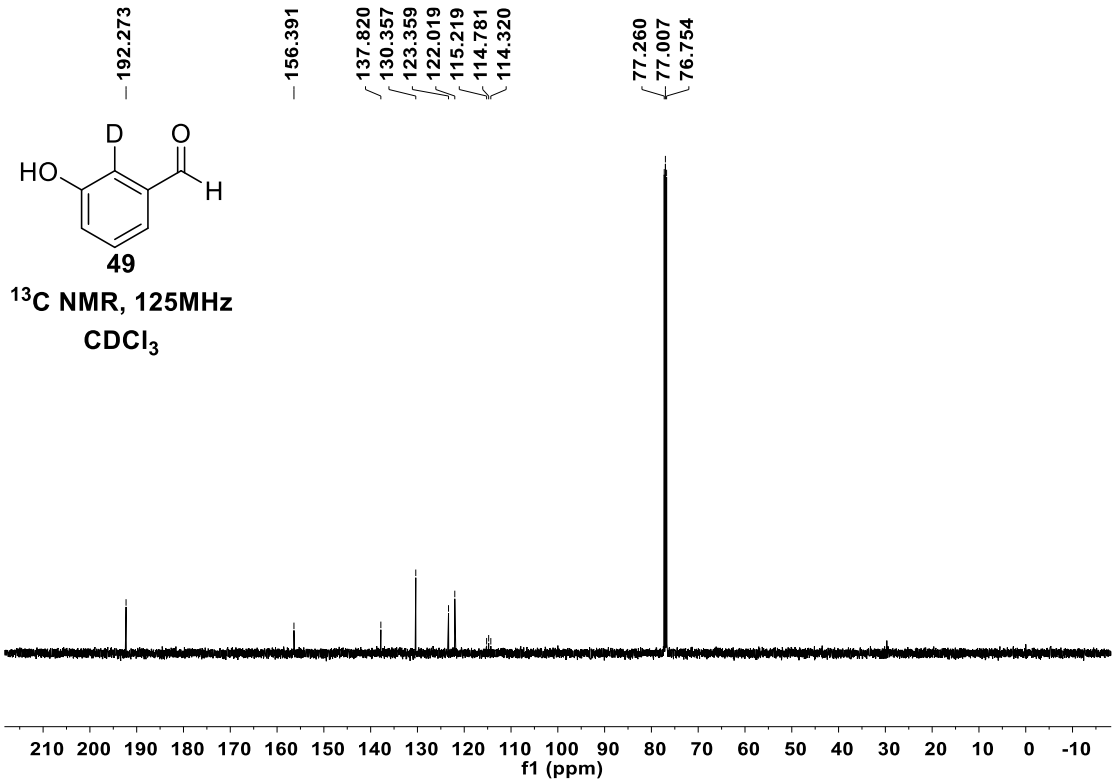


49

^{1}H NMR, 500MHz

$CDCl_3$

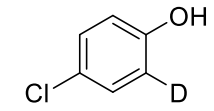




49

^{13}C NMR, 125MHz

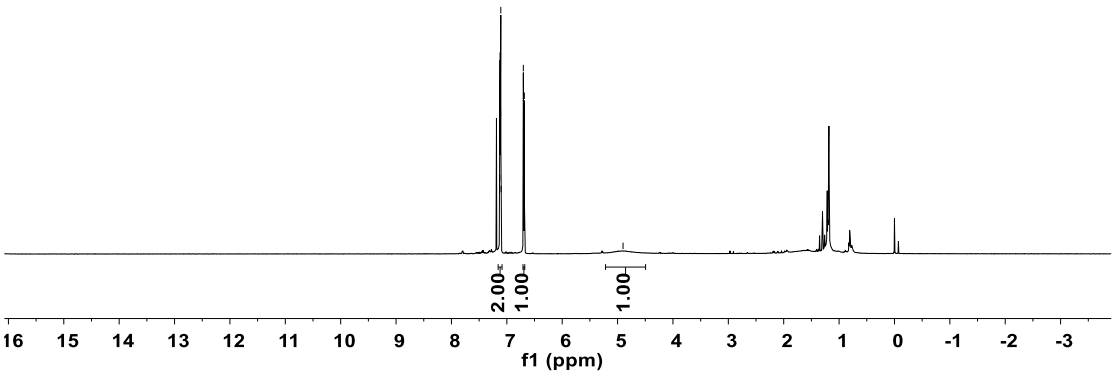
$CDCl_3$

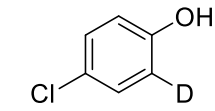


50

^{1}H NMR, 500MHz

$CDCl_3$

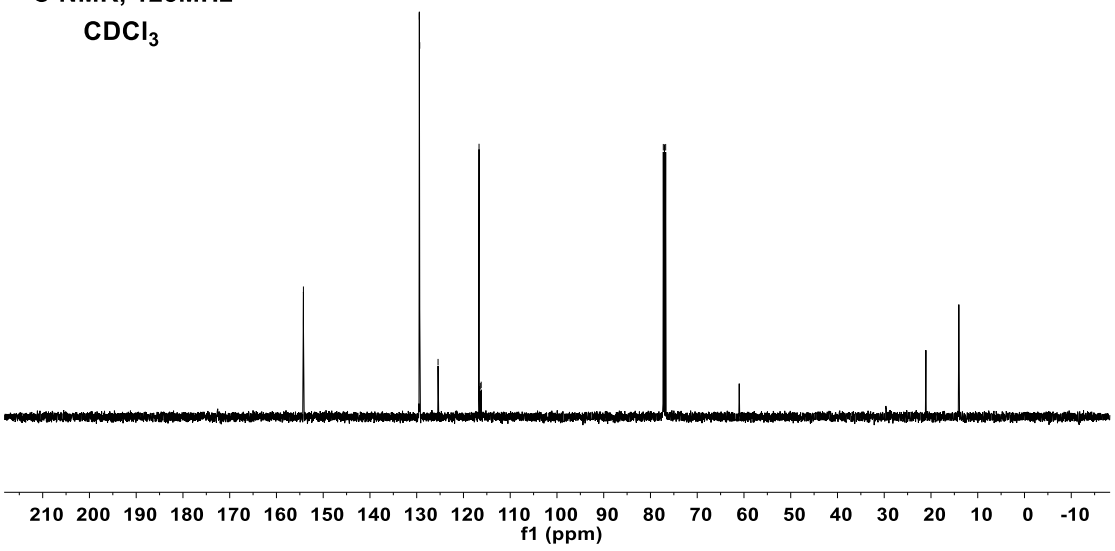


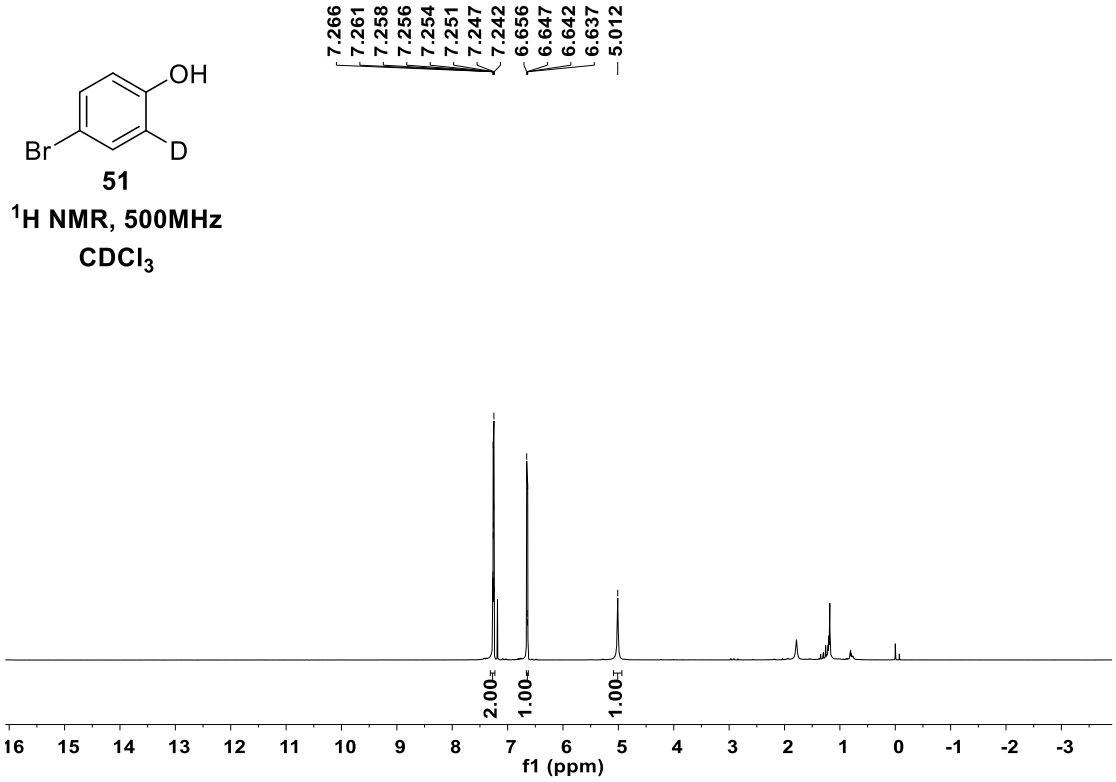


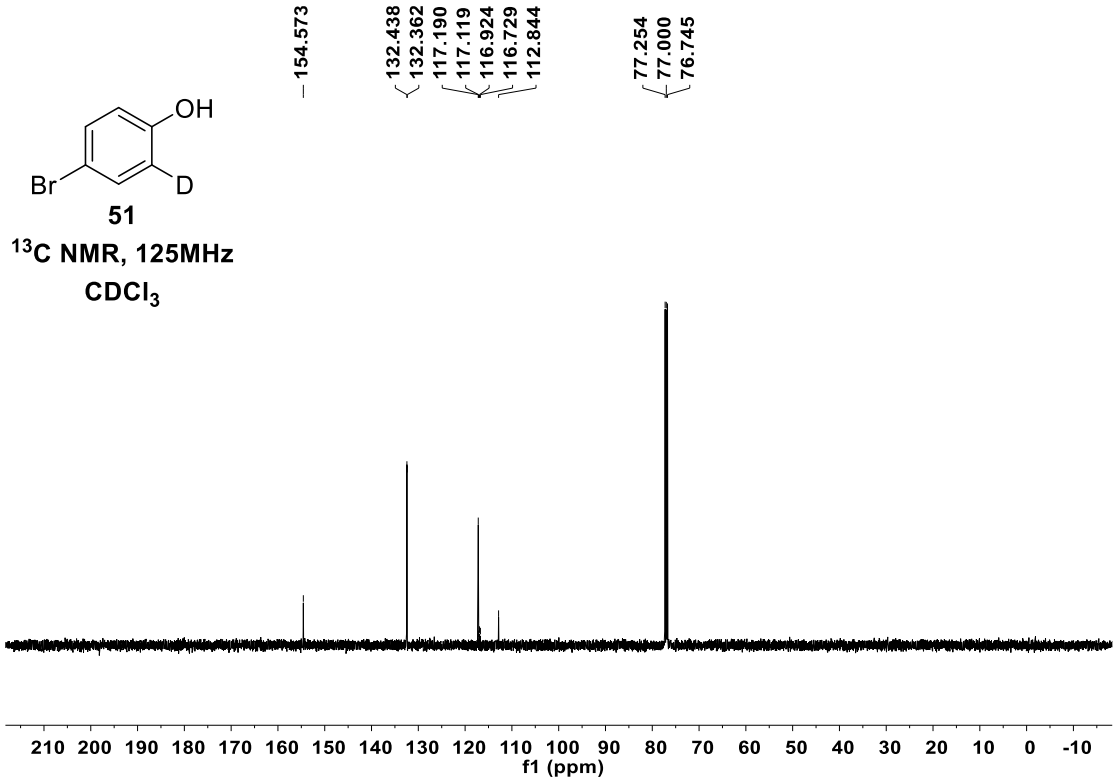
50

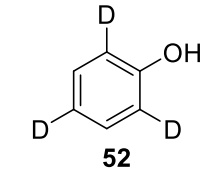
^{13}C NMR, 125MHz

$CDCl_3$




7.266
7.261
7.258
7.256
7.254
7.251
7.247
7.242
6.656
6.647
6.642
6.637
5.012
OH
Br
D
51
1H NMR, 500MHz
CDCl3
2.00
1.00
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

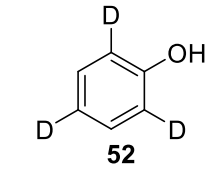

154.573
132.438
132.362
117.190
117.119
116.924
116.729
112.844
77.254
77.000
76.745
OH
Br
D
51
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



52

^{1}H NMR, 500MHz

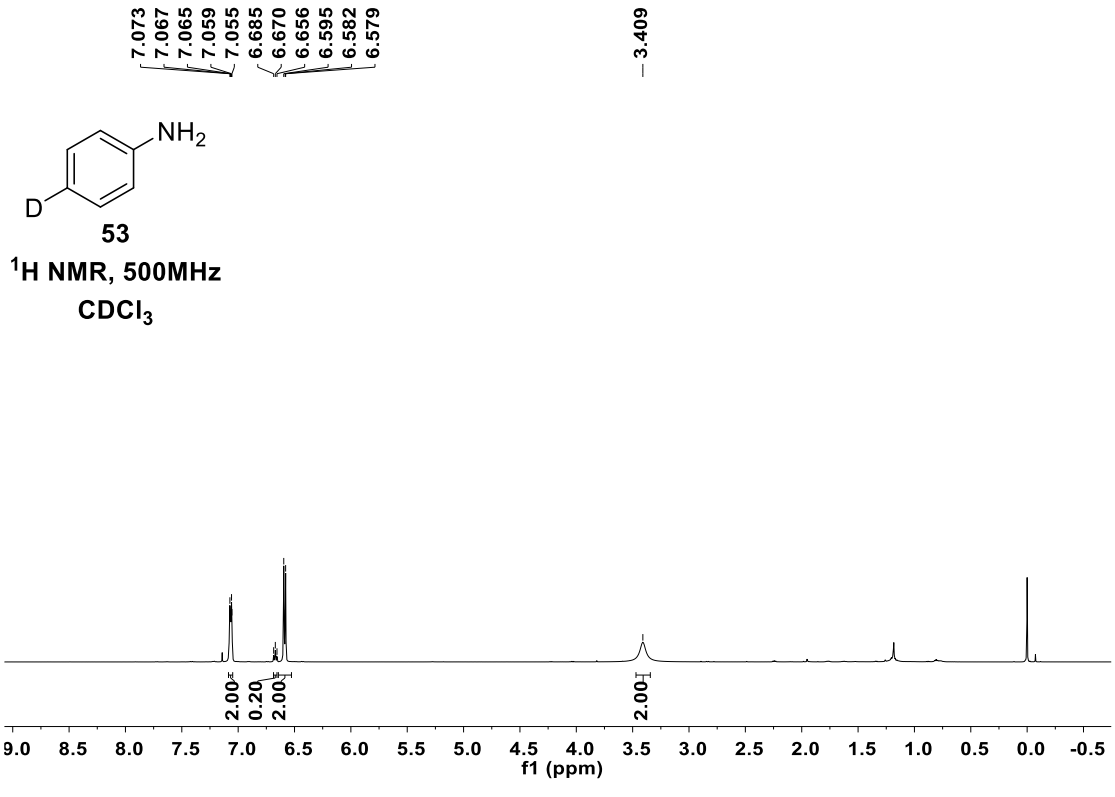
$CDCl_3$



52

^{13}C NMR, 125MHz

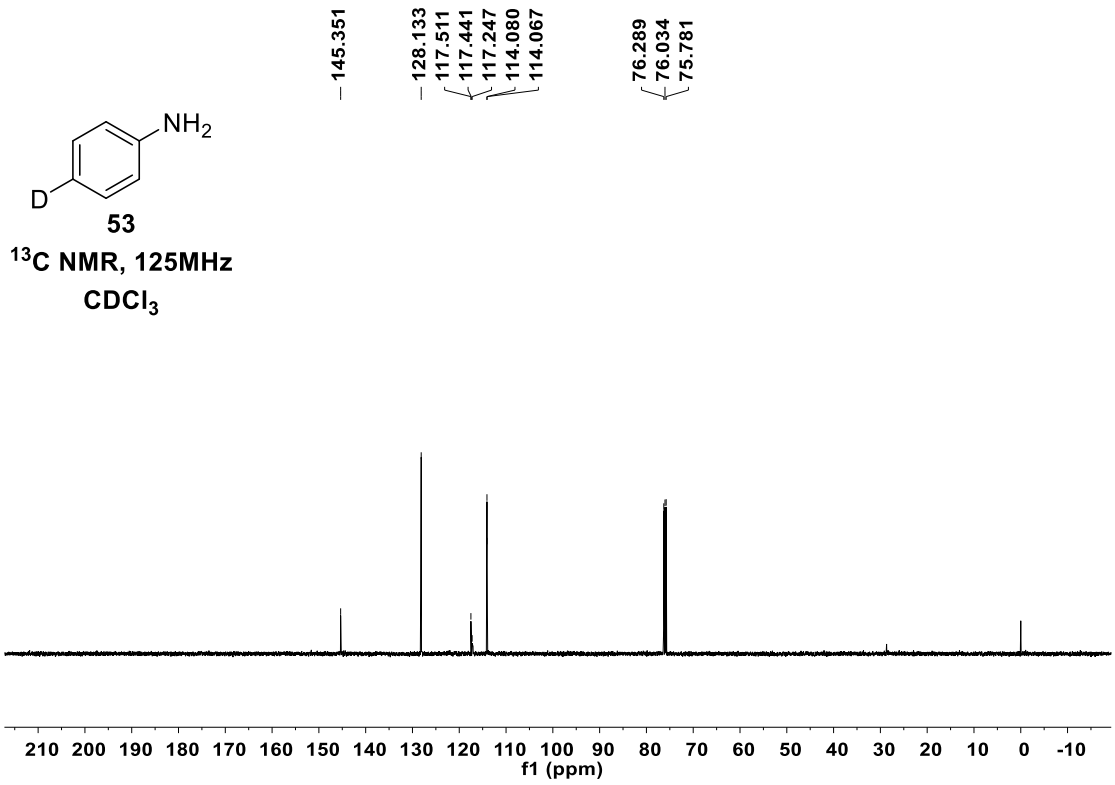
$CDCl_3$



53

^{1}H NMR, 500MHz

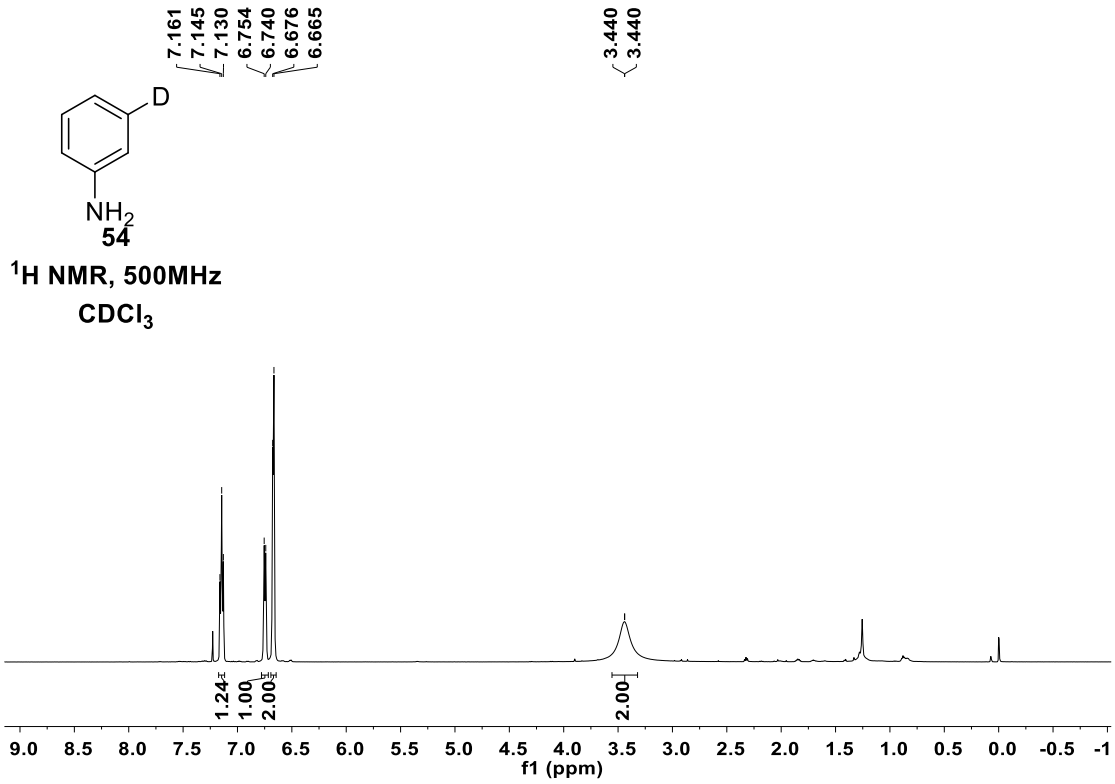
$CDCl_3$



53

^{13}C NMR, 125MHz

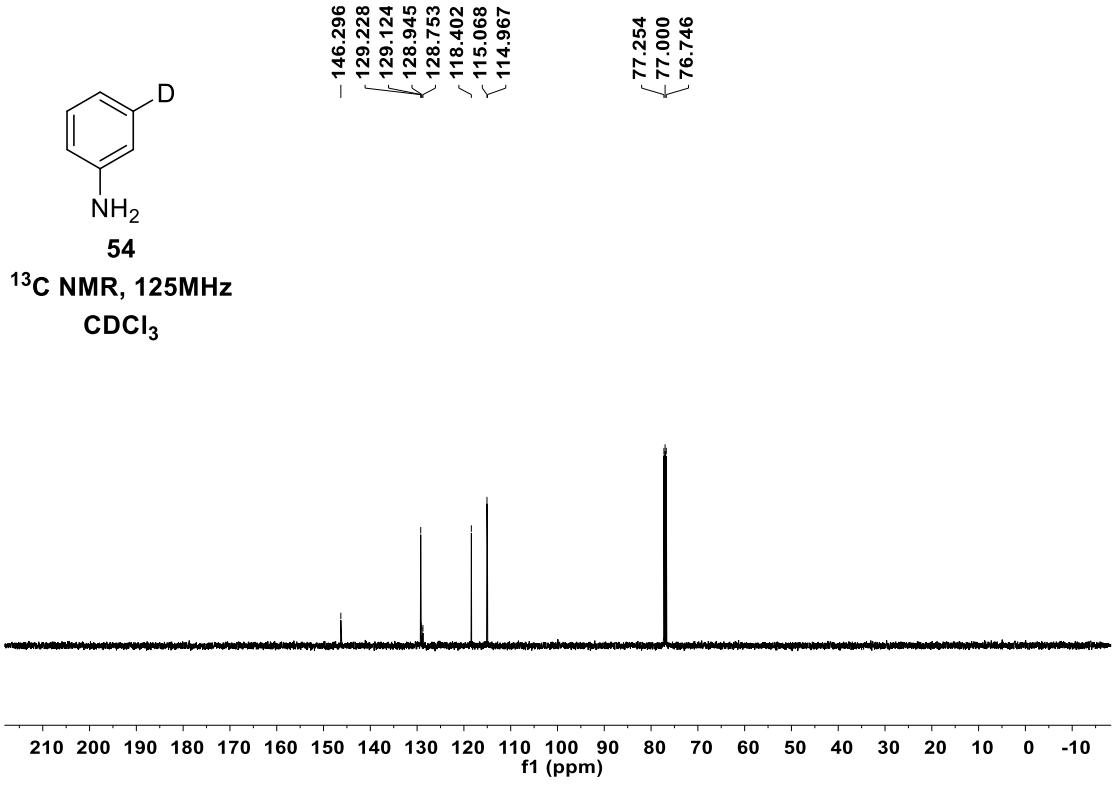
$CDCl_3$



54

^{1}H NMR, 500MHz

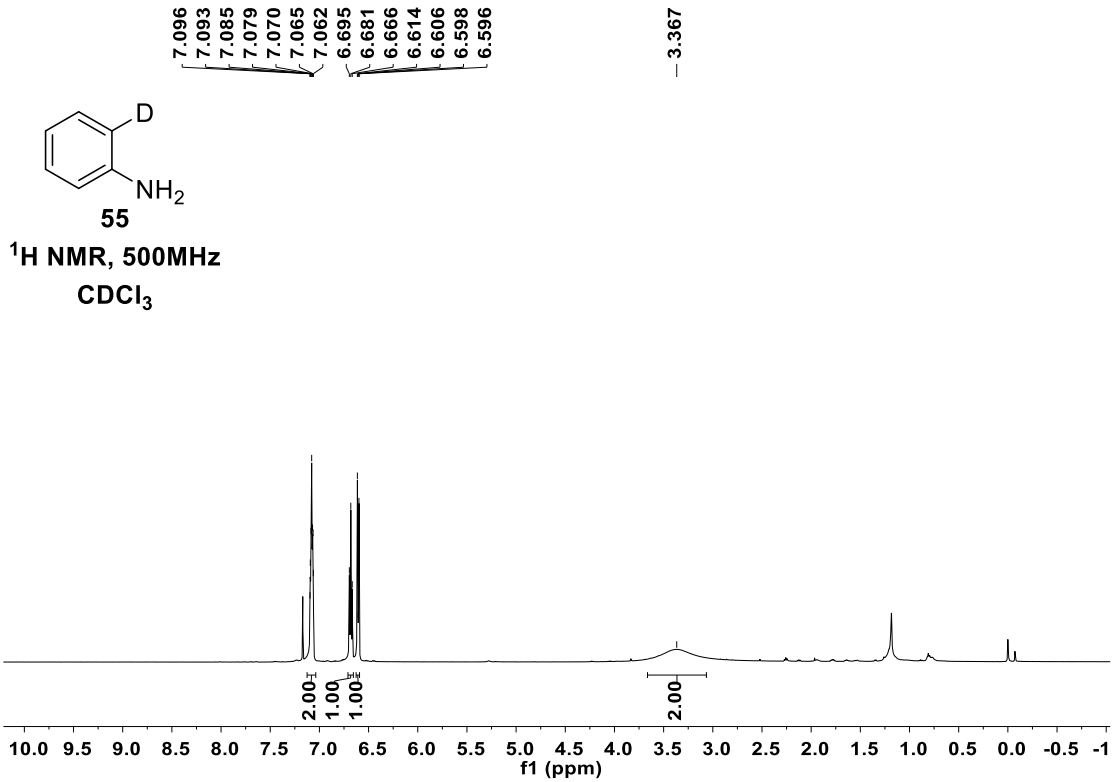
$CDCl_3$



54

^{13}C NMR, 125MHz

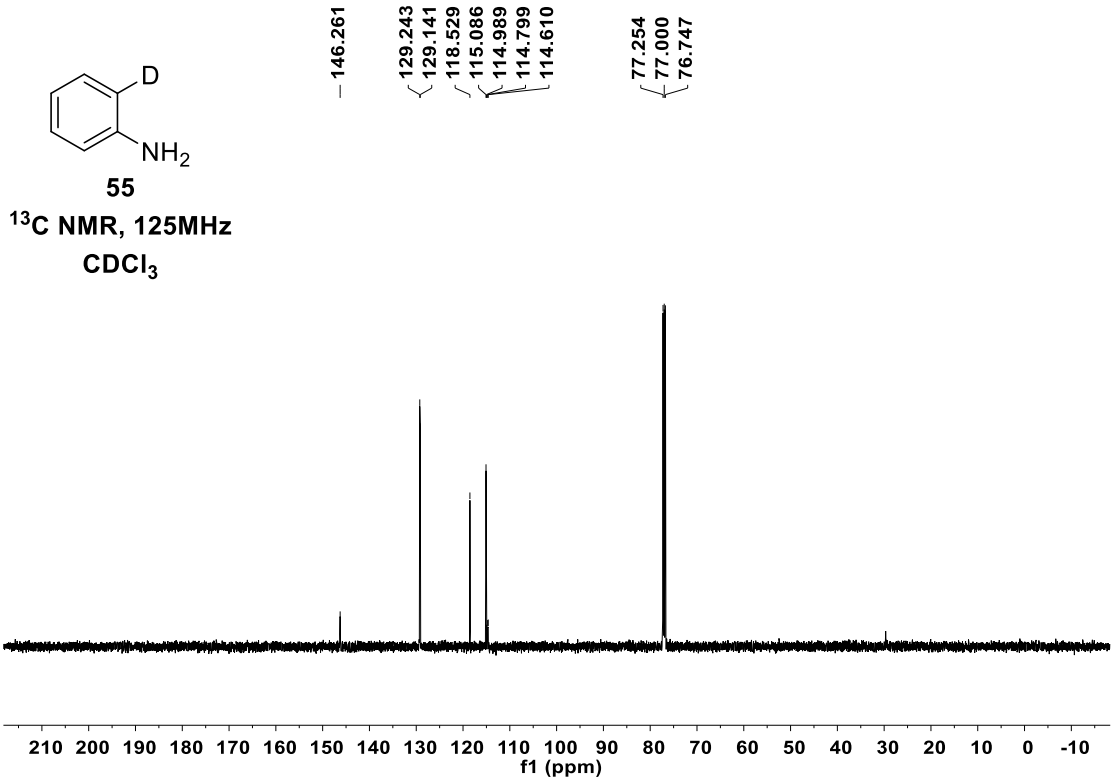
$CDCl_3$



55

^{1}H NMR, 500MHz

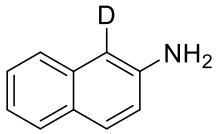
$CDCl_3$



55

^{13}C NMR, 125MHz

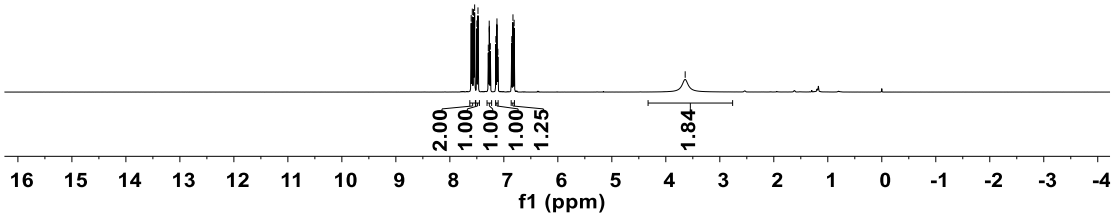
$CDCl_3$

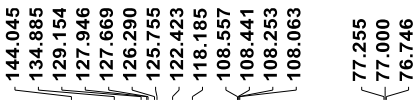


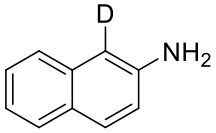
56

^{1}H NMR, 500MHz

$CDCl_3$



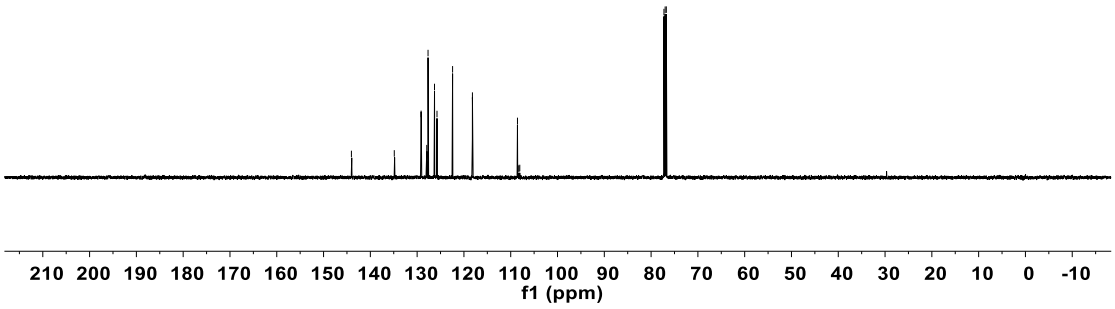


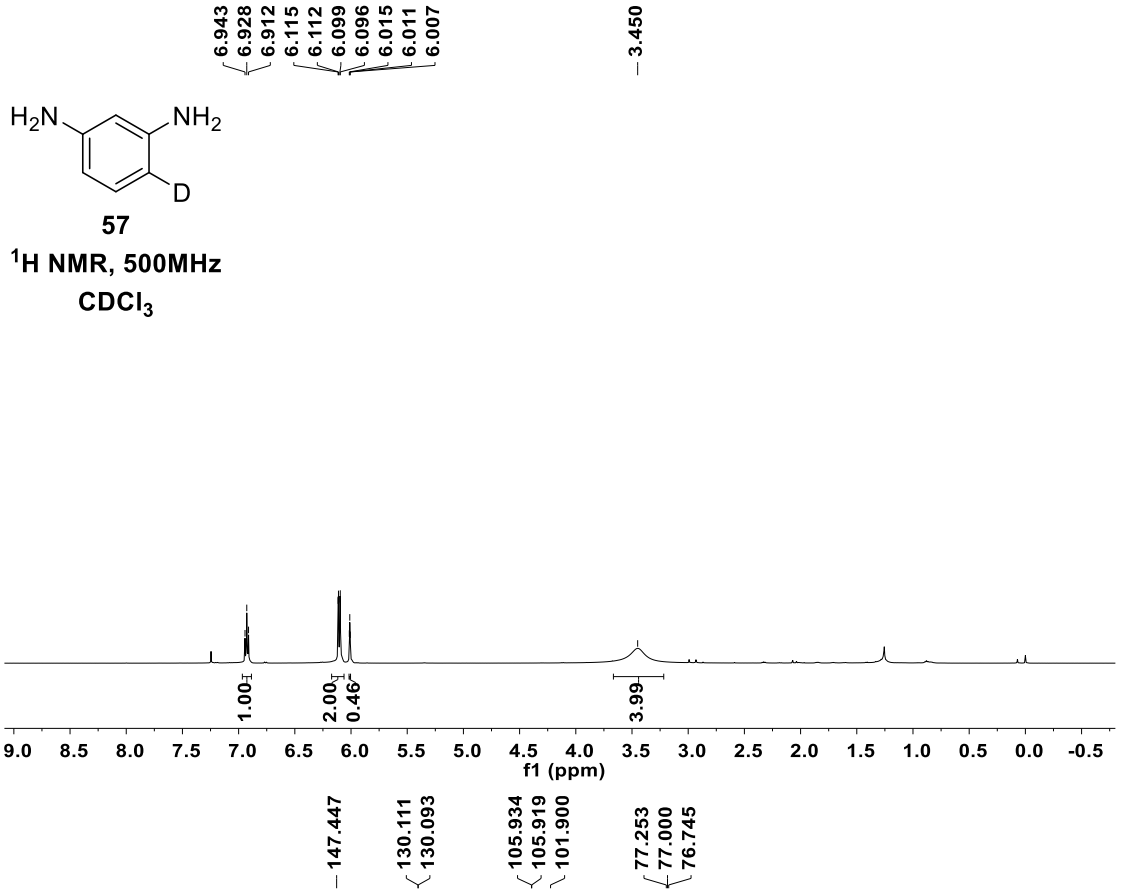


56

^{13}C NMR, 125MHz

$CDCl_3$





57

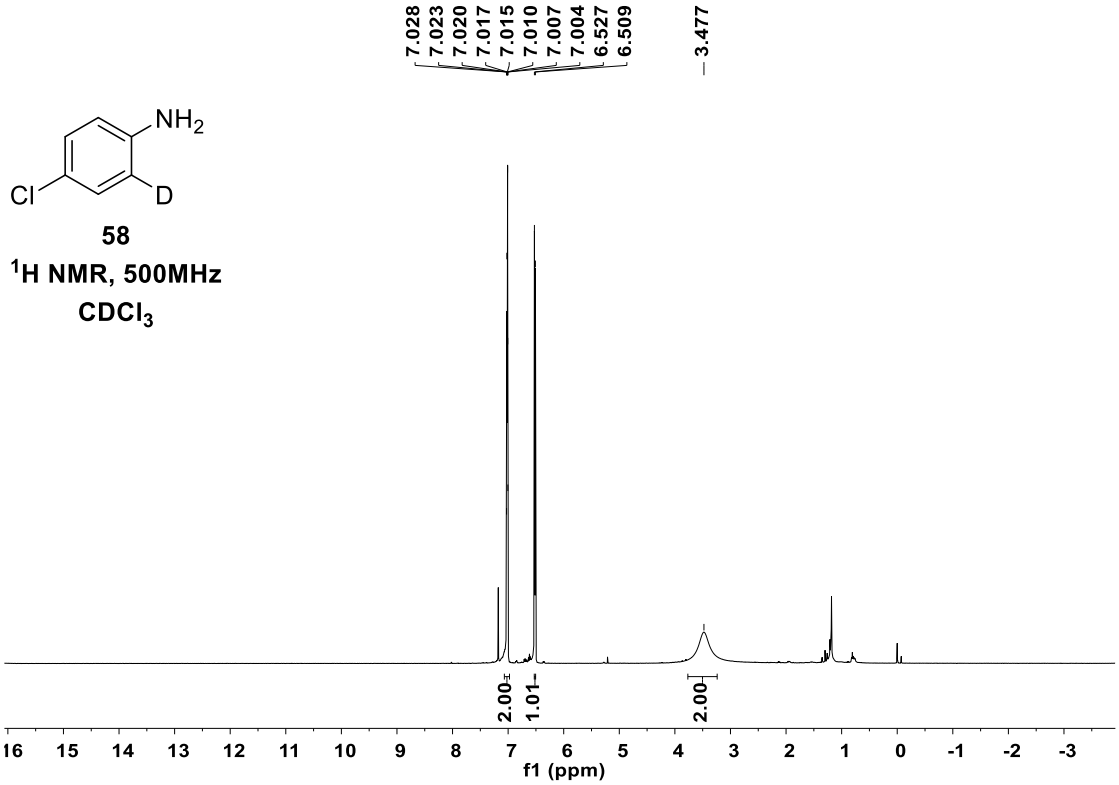
^{1}H NMR, 500MHz

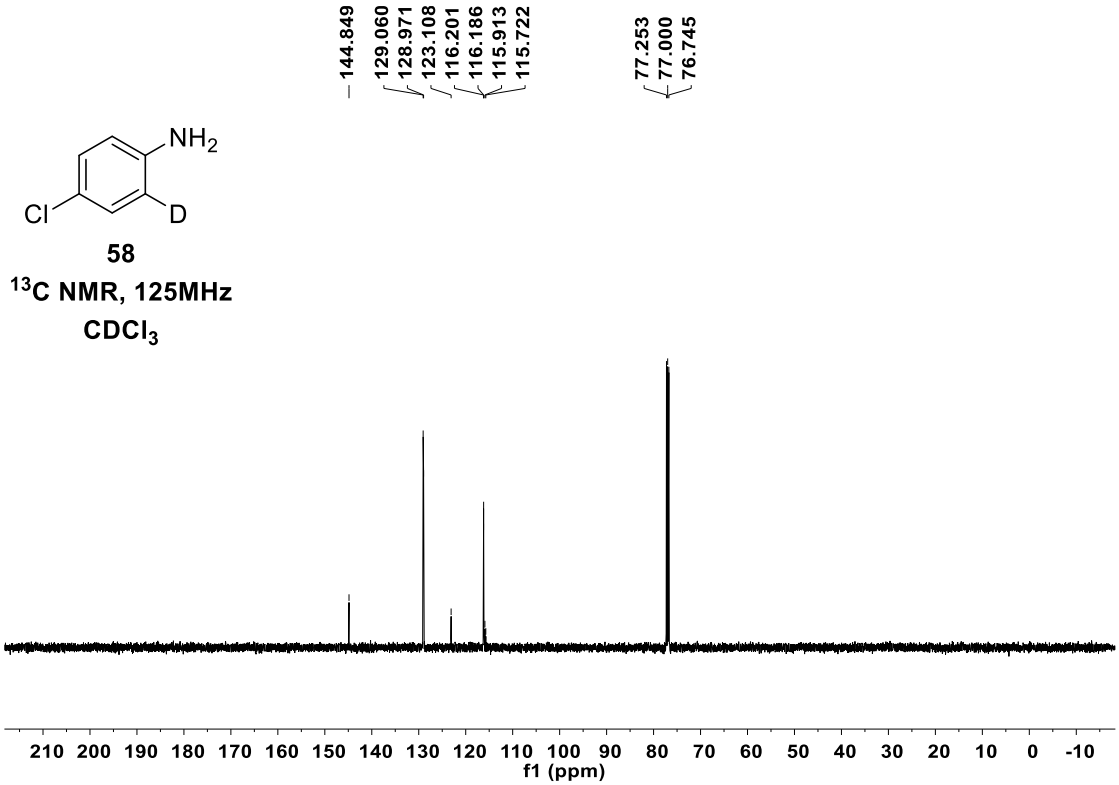
$CDCl_3$

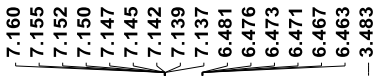
57

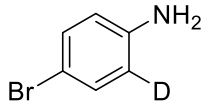
^{13}C NMR, 125MHz

$CDCl_3$


7.028
7.023
7.020
7.017
7.015
7.010
7.007
7.004
6.527
6.509
3.477
NH2
Cl
D
58
1H NMR, 500MHz
CDCl3
2.00
1.01
2.00
f1 (ppm)


144.849
129.060
128.971
123.108
116.201
116.186
115.913
115.722
77.253
77.000
76.745
NH2
Cl
D
58
13C NMR, 125MHz
CDCl3
f1 (ppm)

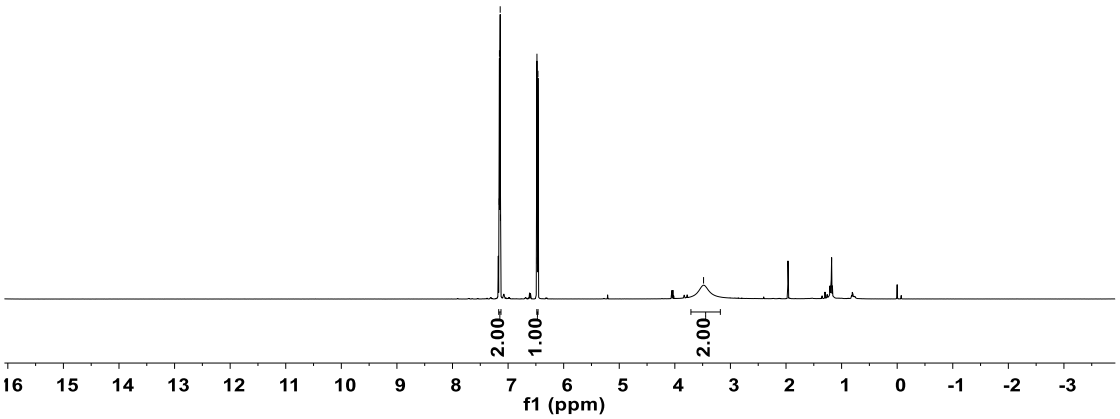


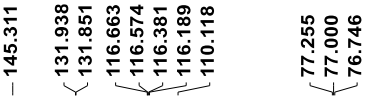


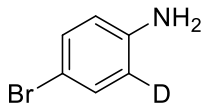
59

^{1}H NMR, 500MHz

$CDCl_3$



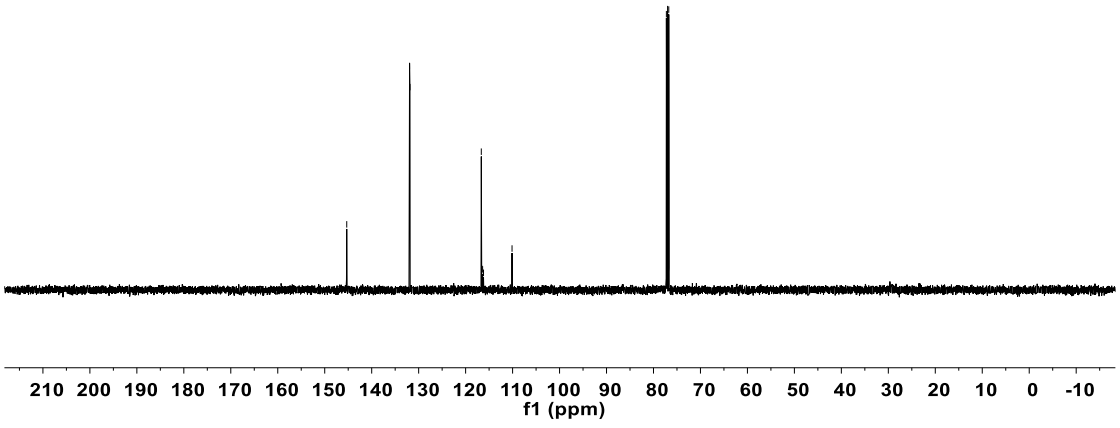


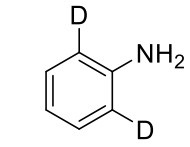


59

^{13}C NMR, 125MHz

$CDCl_3$

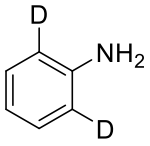




60

^{1}H NMR, 500MHz

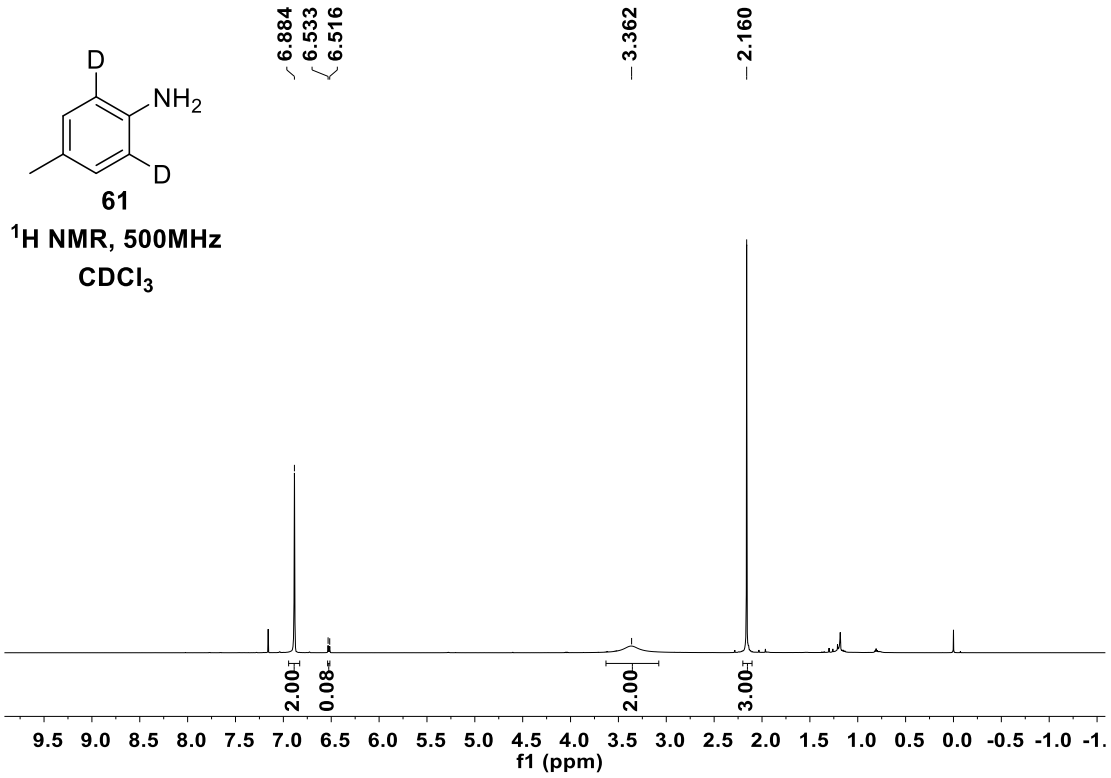
$CDCl_3$

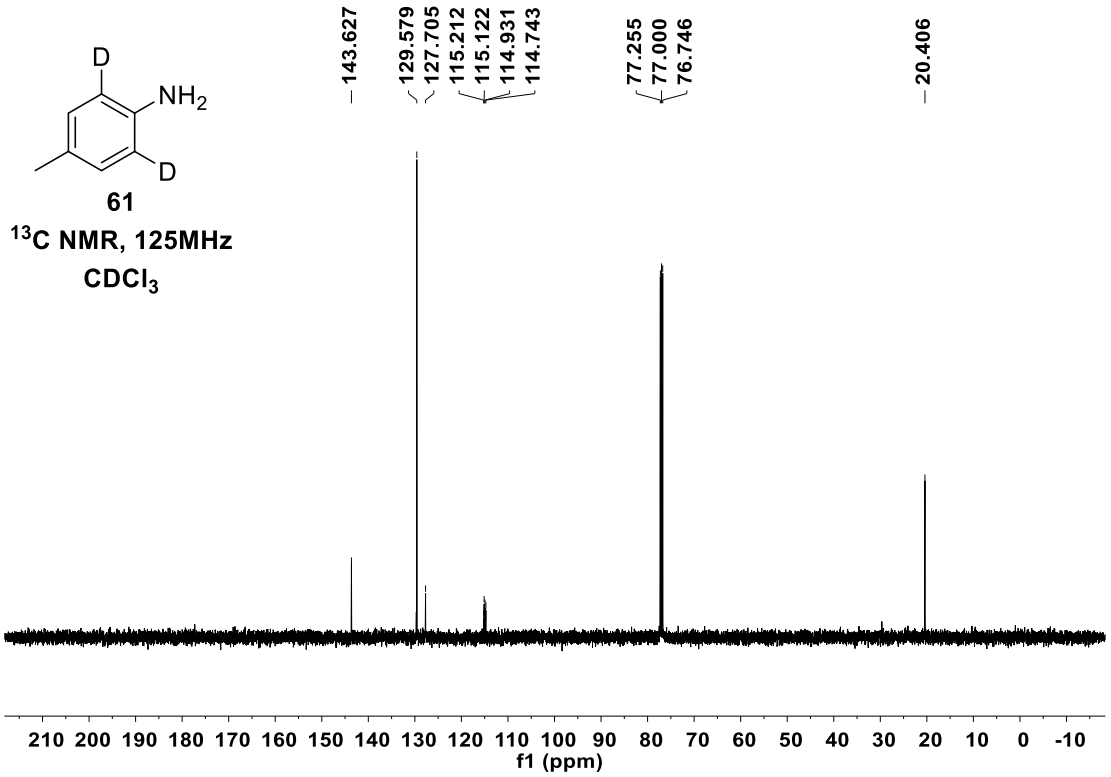


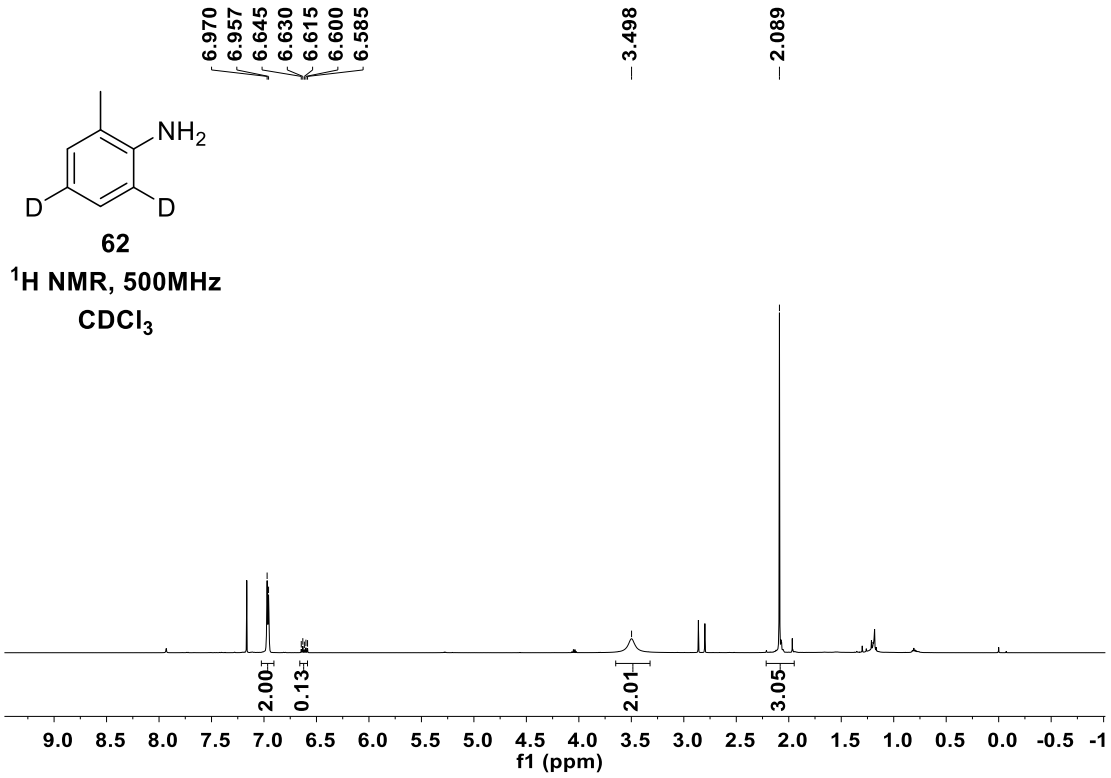
60

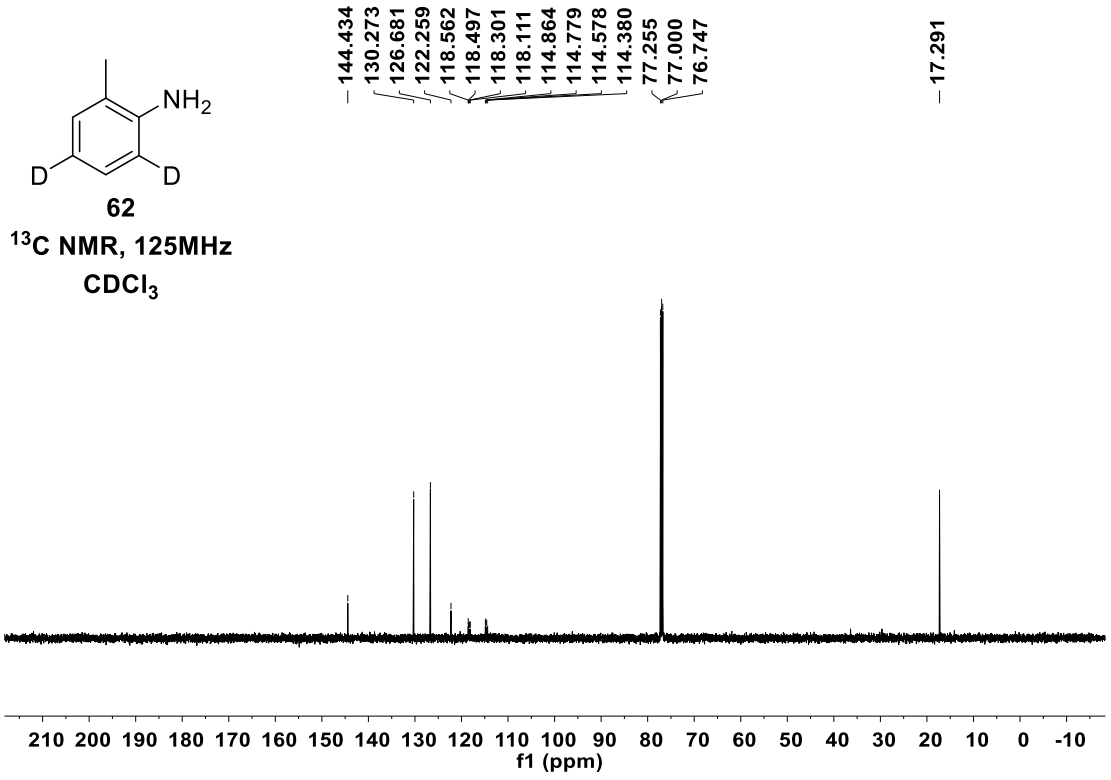
^{13}C NMR, 125MHz

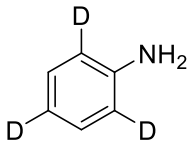
$CDCl_3$


D
NH2
D
61
1H NMR, 500MHz
CDCl3
6.884
6.533
6.516
3.362
2.160
2.00
0.08
2.00
3.00
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 -0.5 -1.0 -1.
f1 (ppm)


D
NH2
D
61
13C NMR, 125MHz
CDCl3
143.627
129.579
127.705
115.212
115.122
114.931
114.743
77.255
77.000
76.746
20.406
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


6.970
6.957
6.645
6.630
6.615
6.600
6.585
3.498
2.089
NH2
D
D
62
1H NMR, 500MHz
CDCl3
2.00
0.13
2.01
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

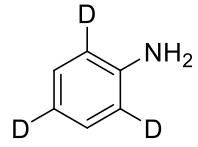

144.434
130.273
126.681
122.259
118.562
118.497
118.301
118.111
114.864
114.779
114.578
114.380
77.255
77.000
76.747
17.291
NH2
D
D
62
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



63

^{1}H NMR, 500MHz

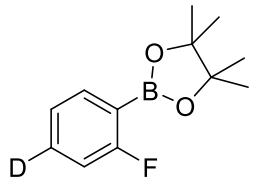
$CDCl_3$



63

^{13}C NMR, 125MHz

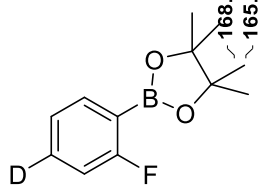
$CDCl_3$



64

^{1}H NMR, 400MHz

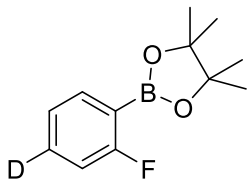
$CDCl_3$



64

^{13}C NMR, 100MHz

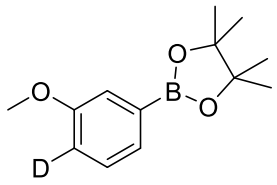
$CDCl_3$



64

^{19}F NMR, 301MHz

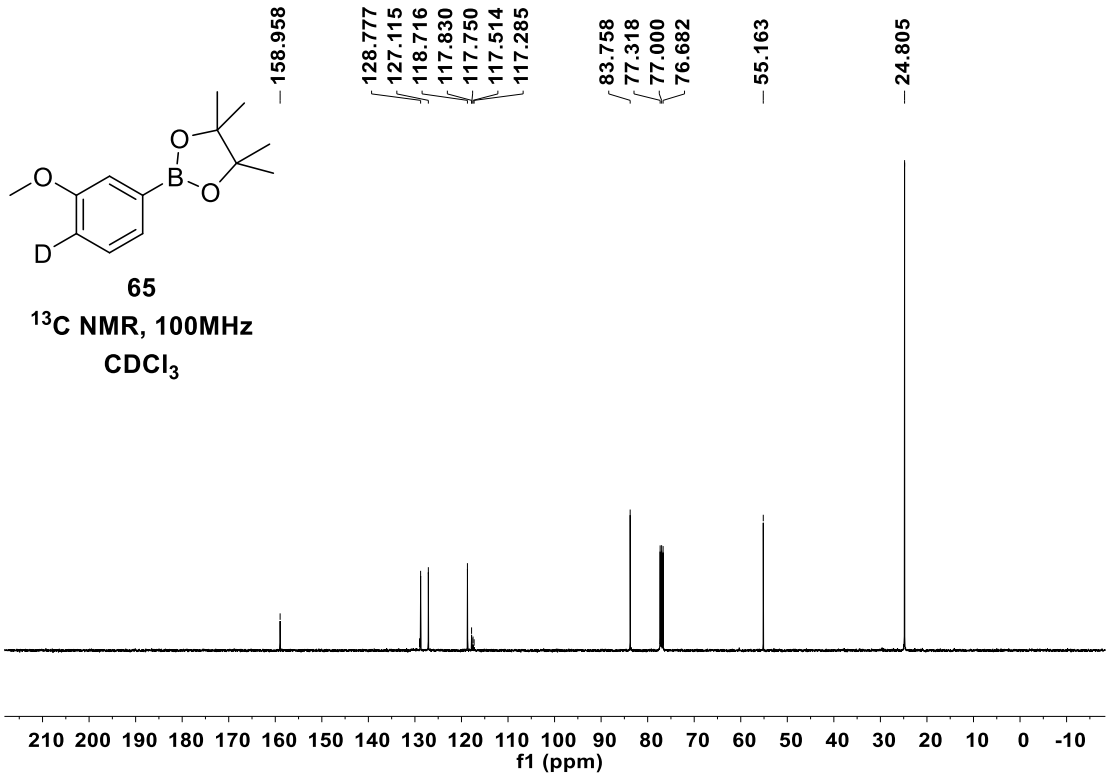
$CDCl_3$

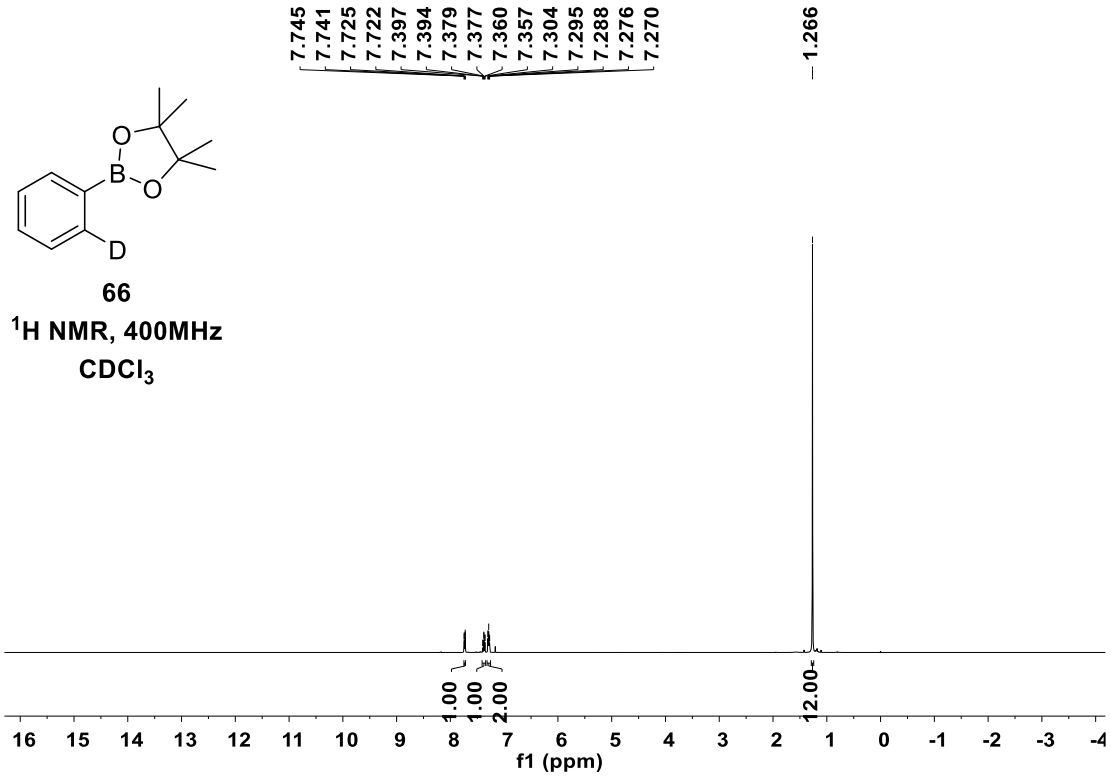


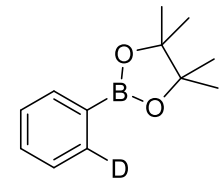
65

^{1}H NMR, 400MHz

$CDCl_3$


158.958
128.777
127.115
118.716
117.830
117.750
117.514
117.285
83.758
77.318
77.000
76.682
55.163
24.805
O
B
O
O
D
65
13C NMR, 100MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

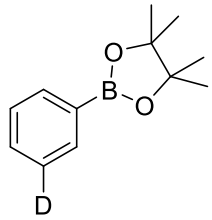

7.745
7.741
7.725
7.722
7.397
7.394
7.379
7.377
7.360
7.357
7.304
7.295
7.288
7.276
7.270
1.266
O
B
O
D
66
1H NMR, 400MHz
CDCl3
1.00
1.00
2.00
12.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)



66

^{13}C NMR, 100MHz

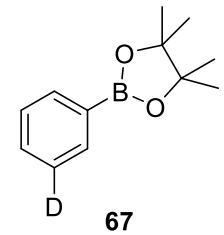
$CDCl_3$



67

^{1}H NMR, 400MHz

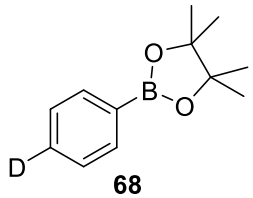
$CDCl_3$



67

^{13}C NMR, 100MHz

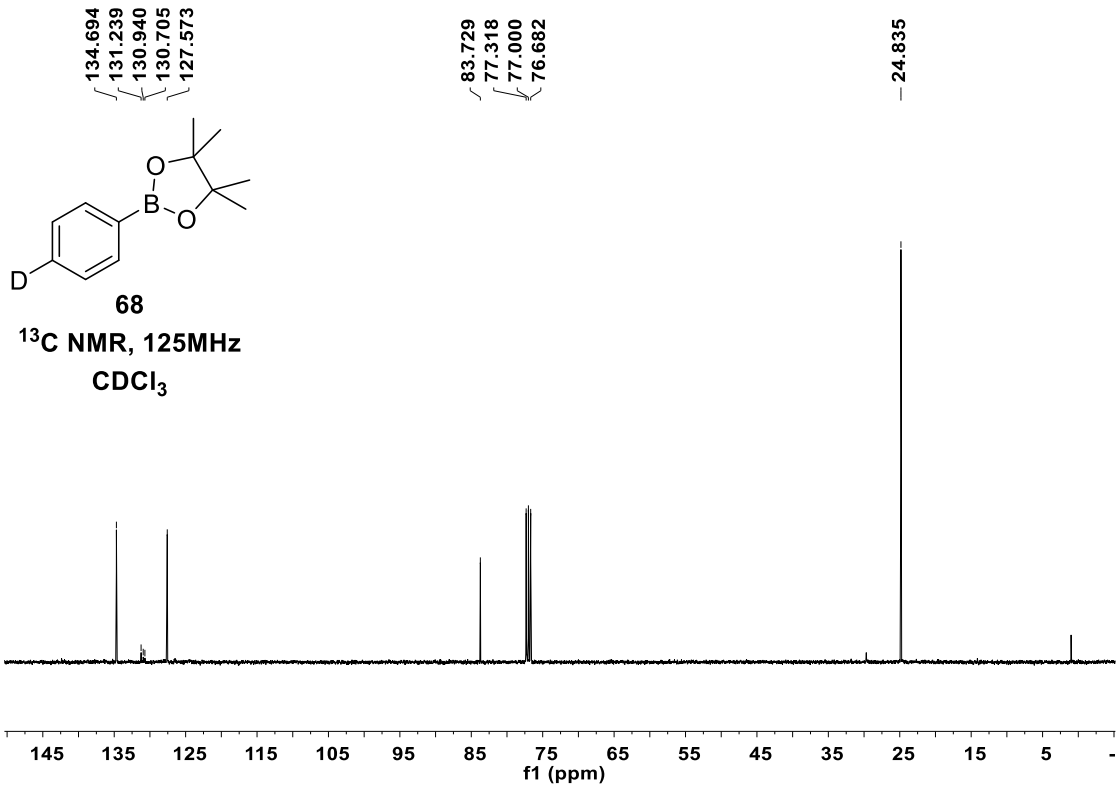
$CDCl_3$

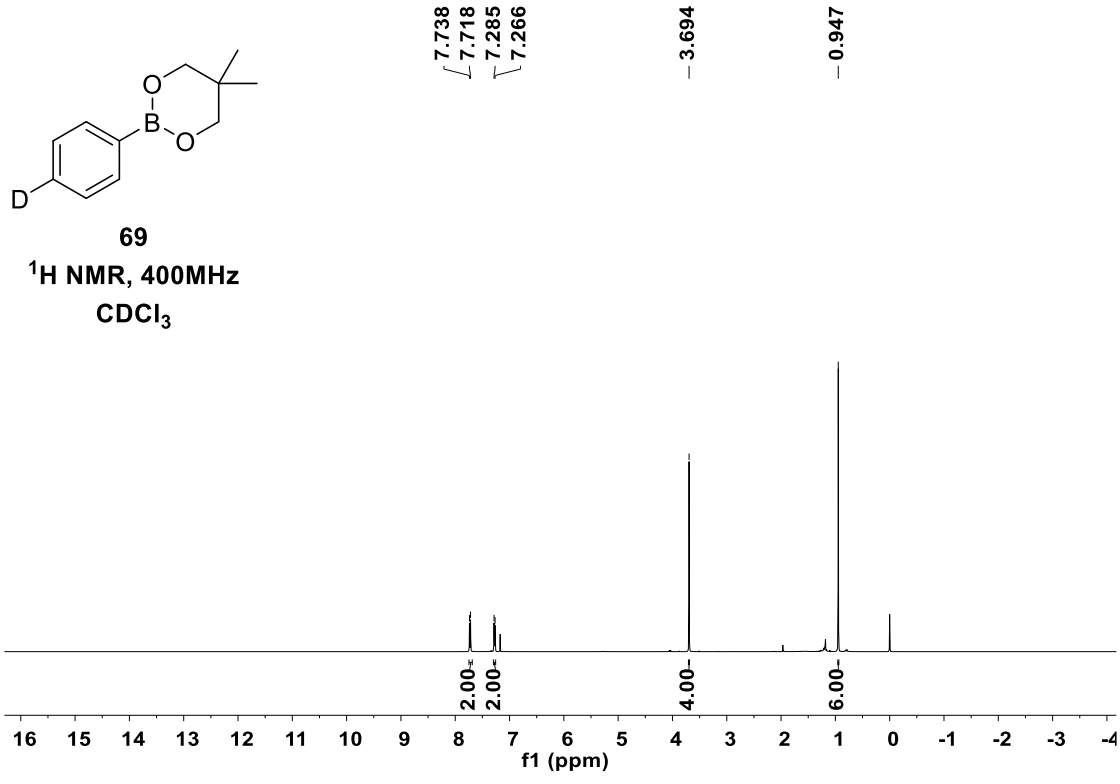


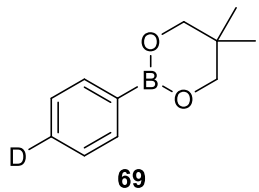
68

^{1}H NMR, 500MHz

$CDCl_3$


134.694
131.239
130.940
130.705
127.573
83.729
77.318
77.000
76.682
24.835
O
B
O
D
68
13C NMR, 125MHz
CDCl3
145 135 125 115 105 95 85 75 65 55 45 35 25 15 5
f1 (ppm)

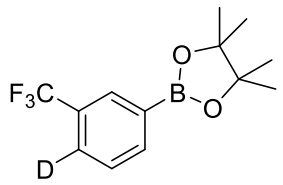

7.738
7.718
7.285
7.266
3.694
0.947
O
B
O
D
69
1H NMR, 400MHz
CDCl3
2.00
2.00
4.00
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)



69

^{13}C NMR, 100MHz

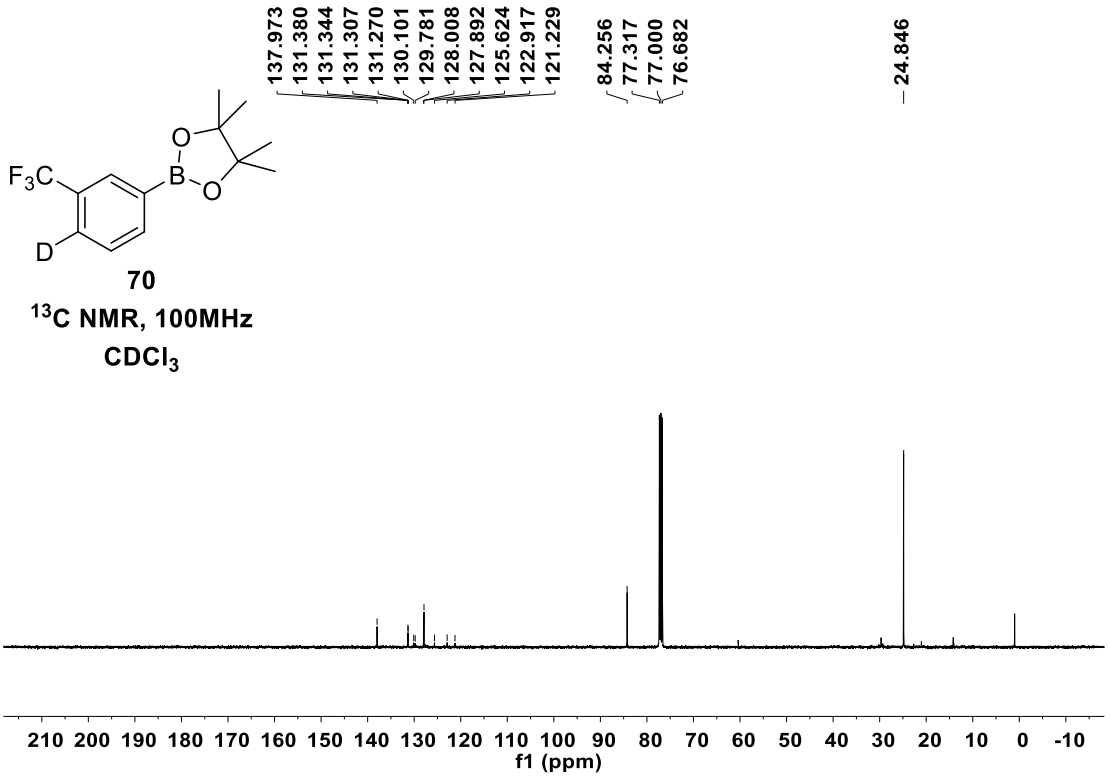
$CDCl_3$



70

^{1}H NMR, 400MHz

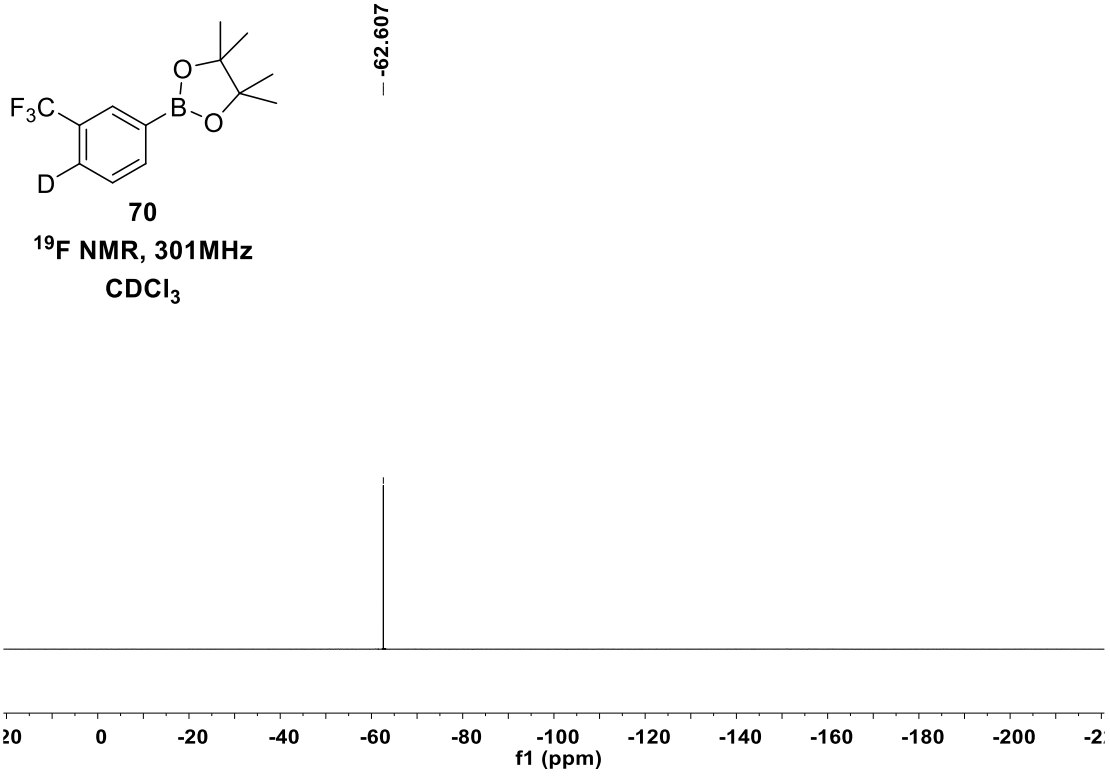
$CDCl_3$



70

^{13}C NMR, 100MHz

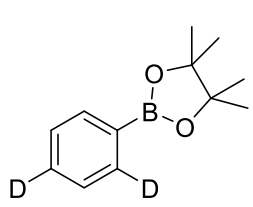
$CDCl_3$



70

^{19}F NMR, 301MHz

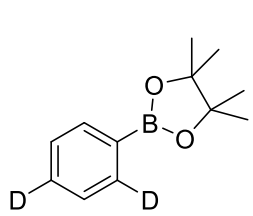
$CDCl_3$



71

^{1}H NMR, 400MHz

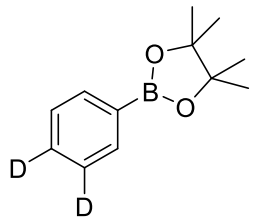
$CDCl_3$



71

^{13}C NMR, 100MHz

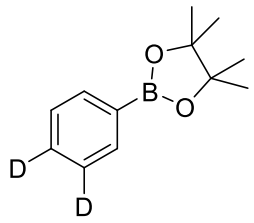
$CDCl_3$



72

^{1}H NMR, 400MHz

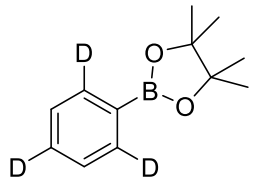
$CDCl_3$



72

^{13}C NMR, 100MHz

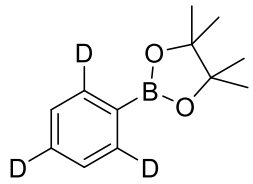
$CDCl_3$



73

^{1}H NMR, 400MHz

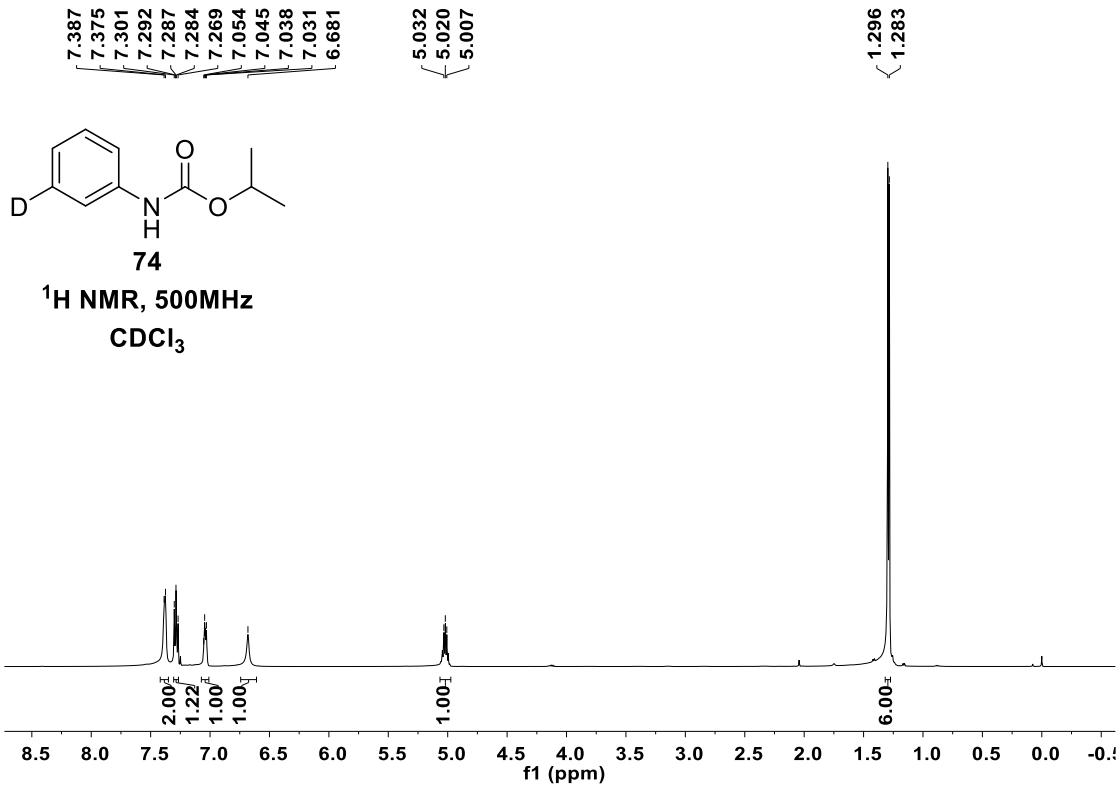
$CDCl_3$

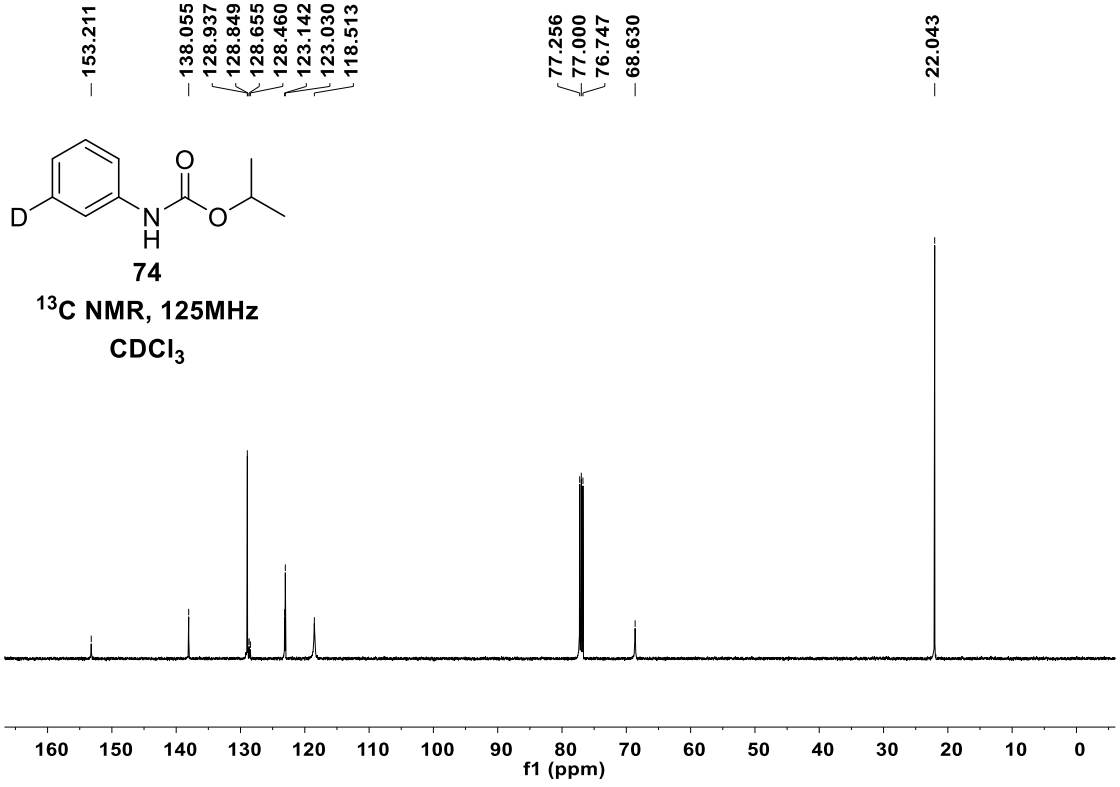


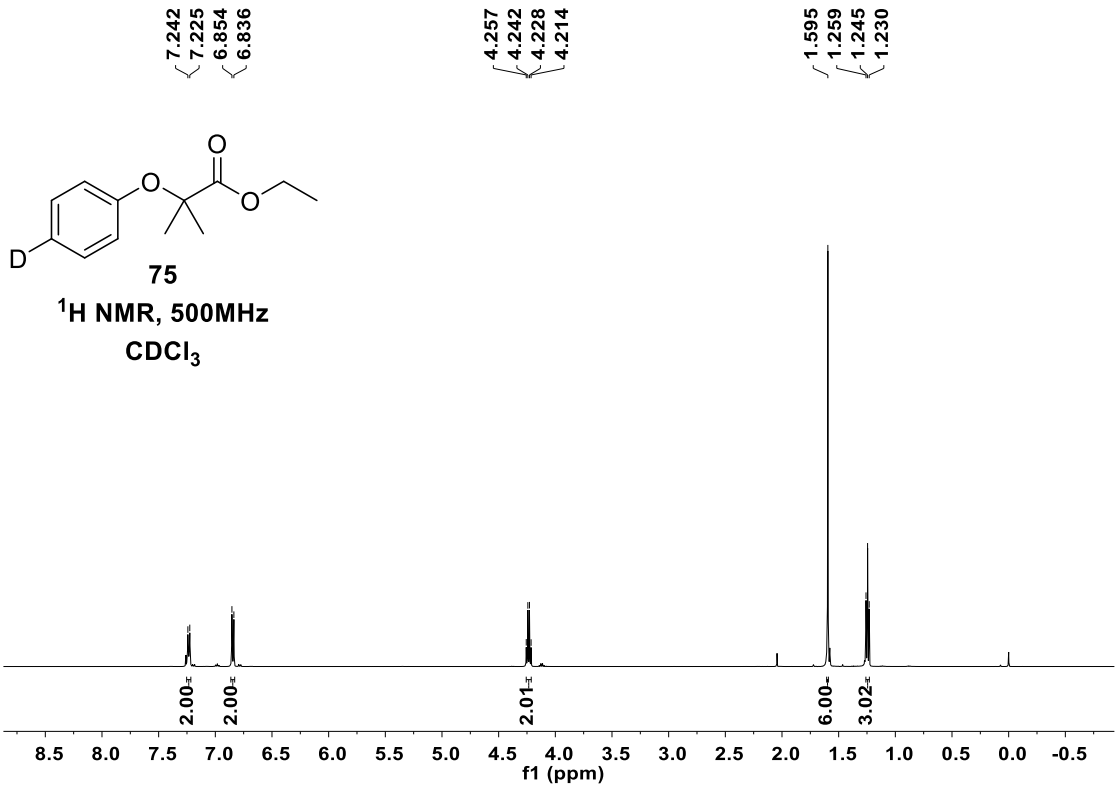
73

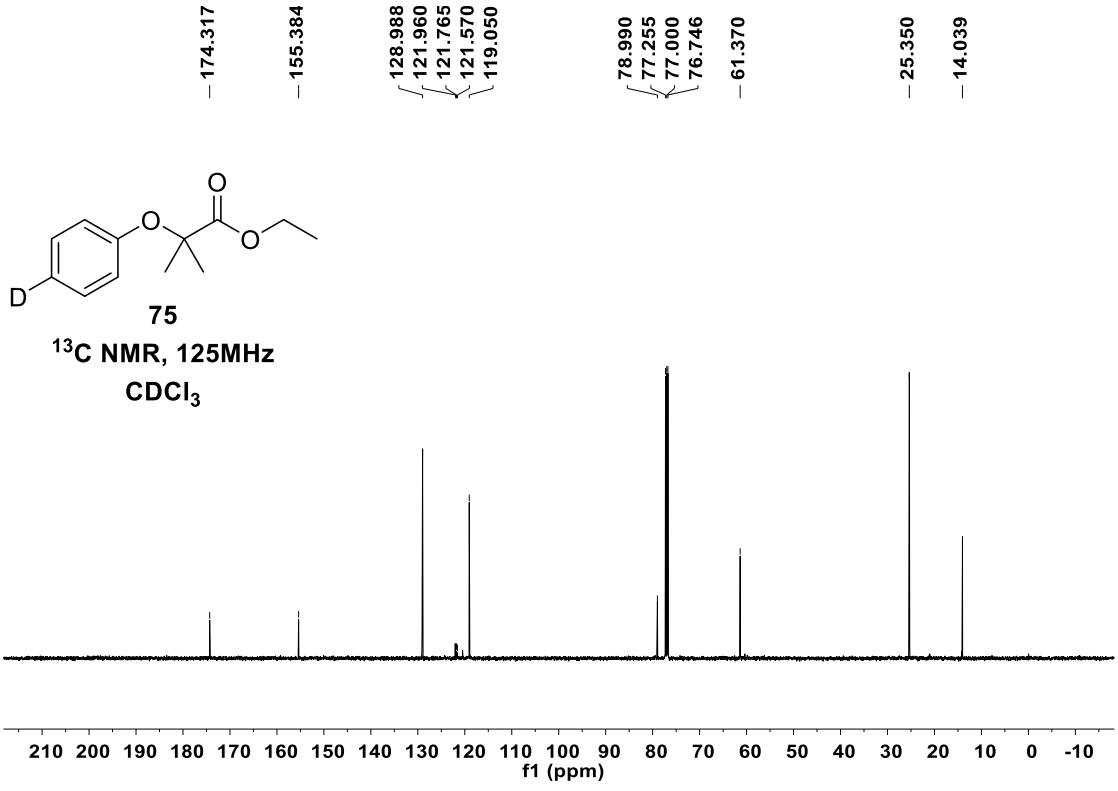
^{13}C NMR, 100MHz

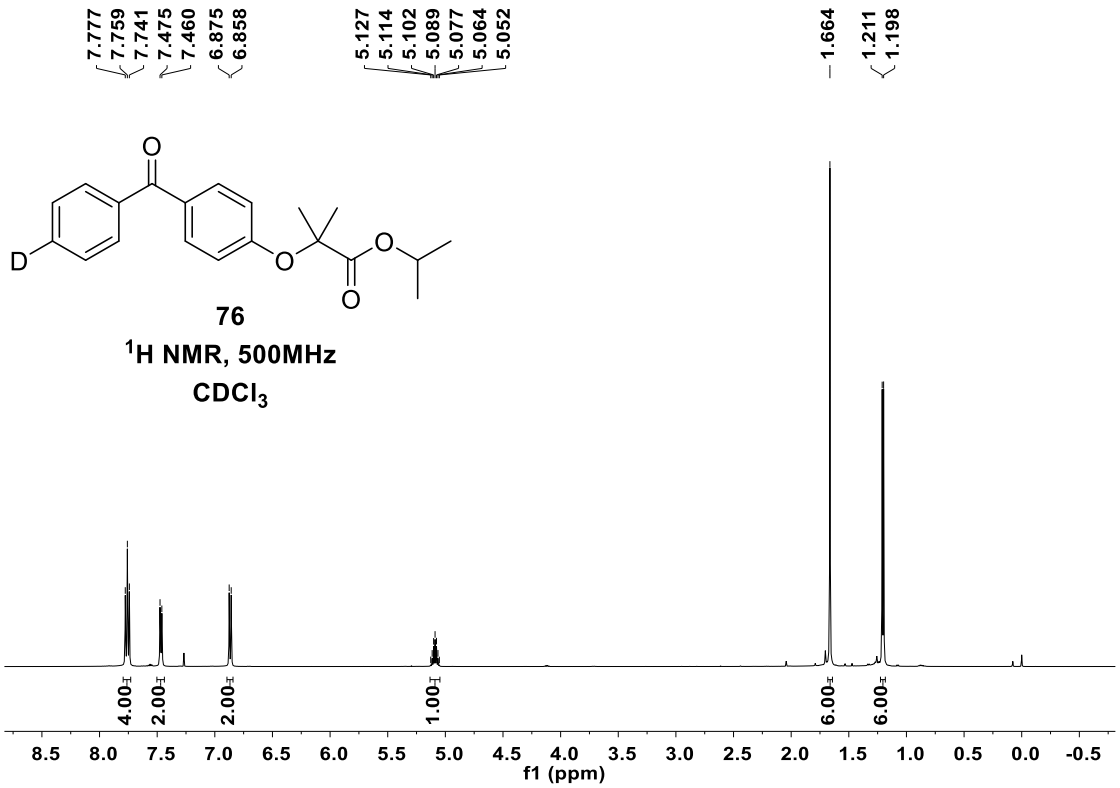
$CDCl_3$

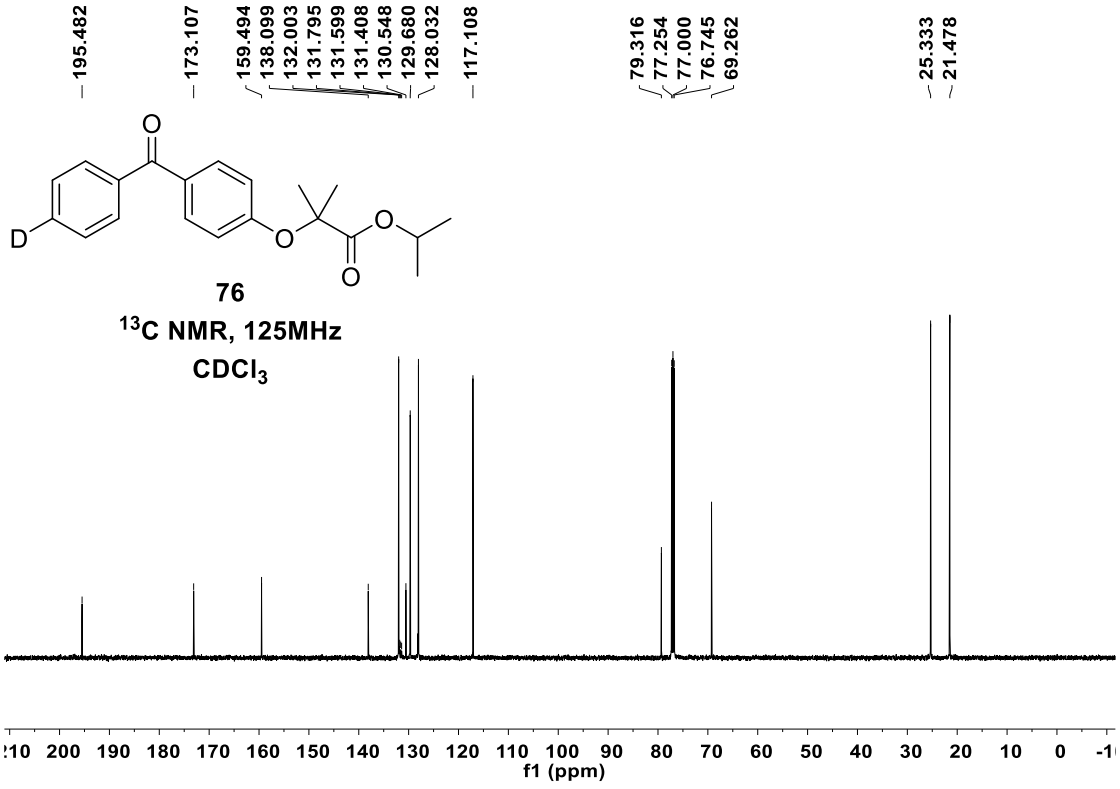

7.387
7.375
7.301
7.292
7.287
7.284
7.269
7.054
7.045
7.038
7.031
6.681
5.032
5.020
5.007
1.296
1.283
D
N
H
O
O
74
1H NMR, 500MHz
CDCl3
2.00
1.22
1.00
1.00
1.00
6.00
f1 (ppm)

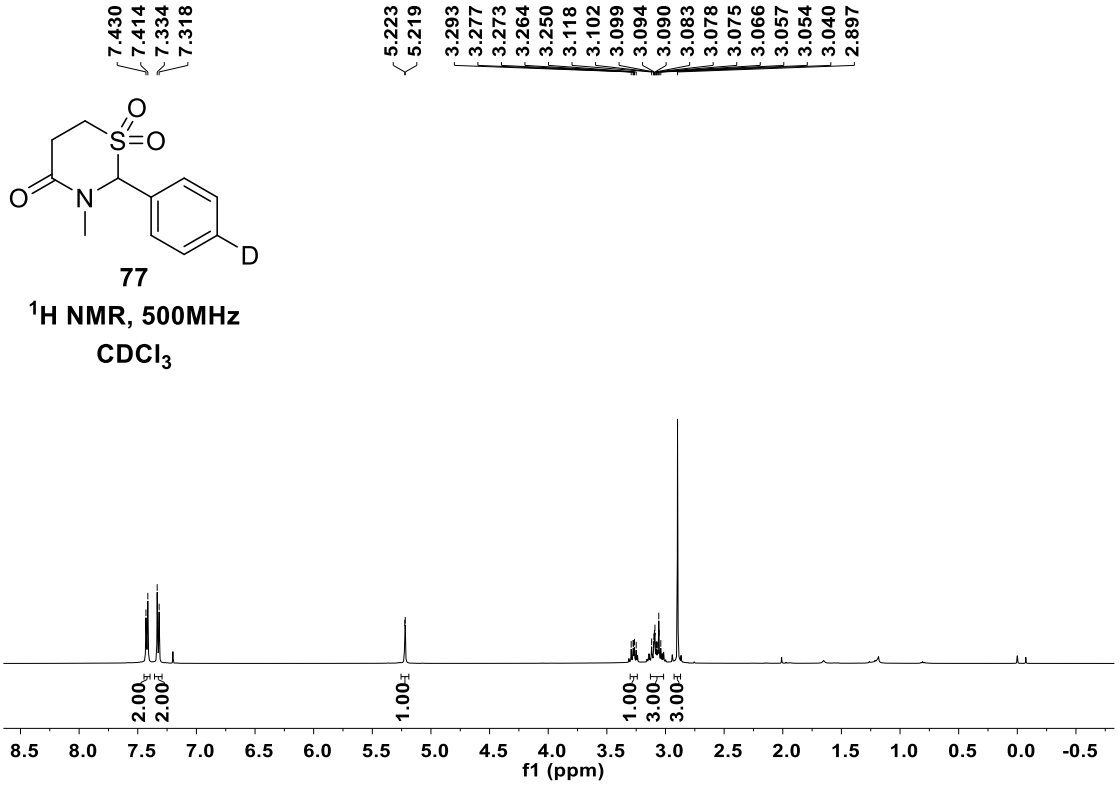

153.211
138.055
128.937
128.849
128.655
128.460
123.142
123.030
118.513
77.256
77.000
76.747
68.630
22.043
D
N
H
O
O
74
13C NMR, 125MHz
CDCl3
f1 (ppm)


7.242
7.225
6.854
6.836
4.257
4.242
4.228
4.214
1.595
1.259
1.245
1.230
O
O
O
D
75
1H NMR, 500MHz
CDCl3
2.00
2.00
2.01
6.00
3.02
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 -0.5
f1 (ppm)


174.317
155.384
128.988
121.960
121.765
121.570
119.050
78.990
77.255
77.000
76.746
61.370
25.350
14.039
O
O
O
D
75
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.777
7.759
7.741
7.475
7.460
6.875
6.858
5.127
5.114
5.102
5.089
5.077
5.064
5.052
1.664
1.211
1.198
O
D
O
O
O
76
1H NMR, 500MHz
CDCl3
4.00
2.00
2.00
1.00
6.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

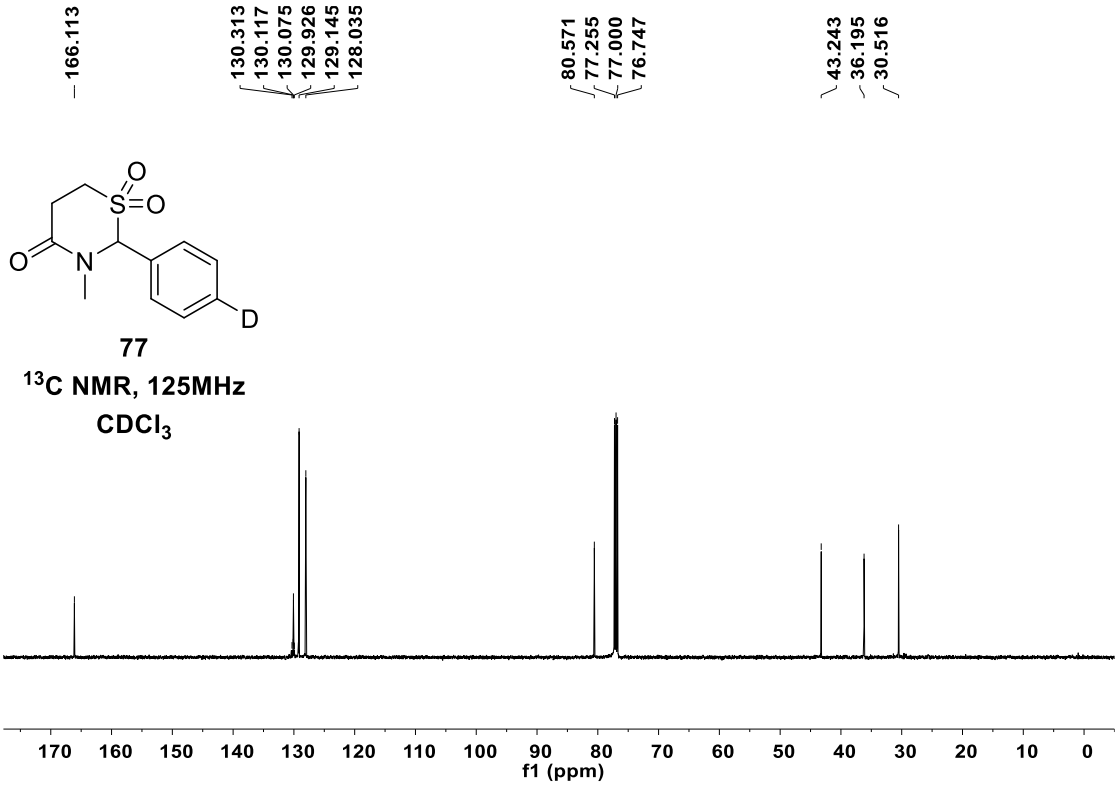

195.482
173.107
159.494
138.099
132.003
131.795
131.599
131.408
130.548
129.680
128.032
117.108
79.316
77.254
77.000
76.745
69.262
25.333
21.478
O
D
O
O
O
76
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



77

^{1}H NMR, 500MHz

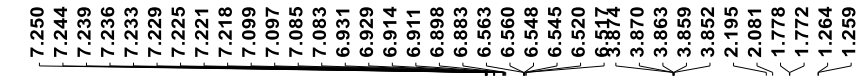
$CDCl_3$

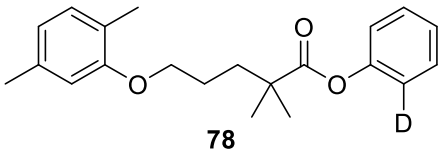


77

^{13}C NMR, 125MHz

$CDCl_3$

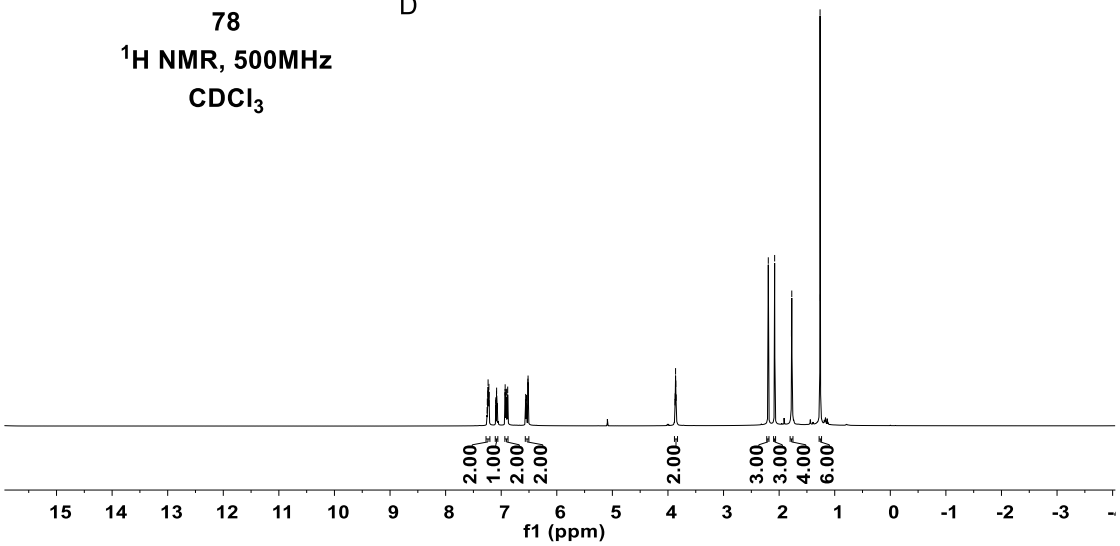


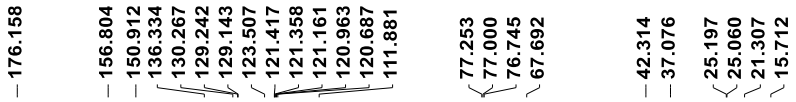


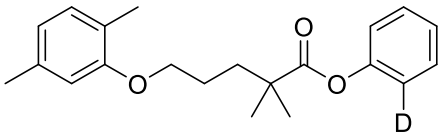
78

^{1}H NMR, 500MHz

$CDCl_3$



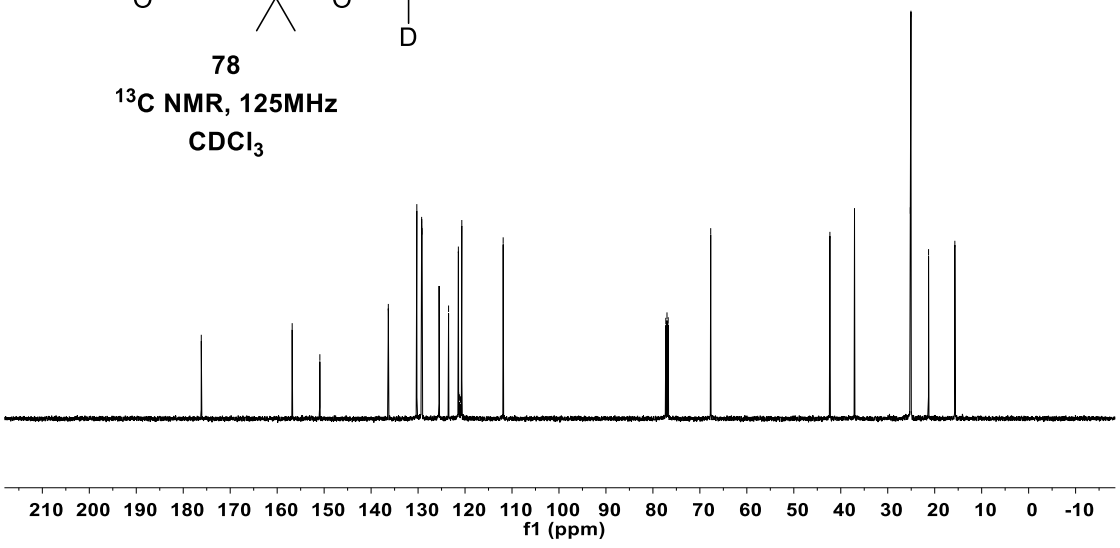


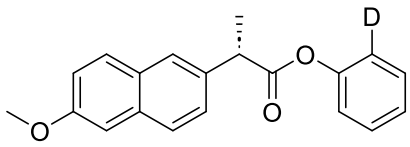


78

^{13}C NMR, 125MHz

$CDCl_3$

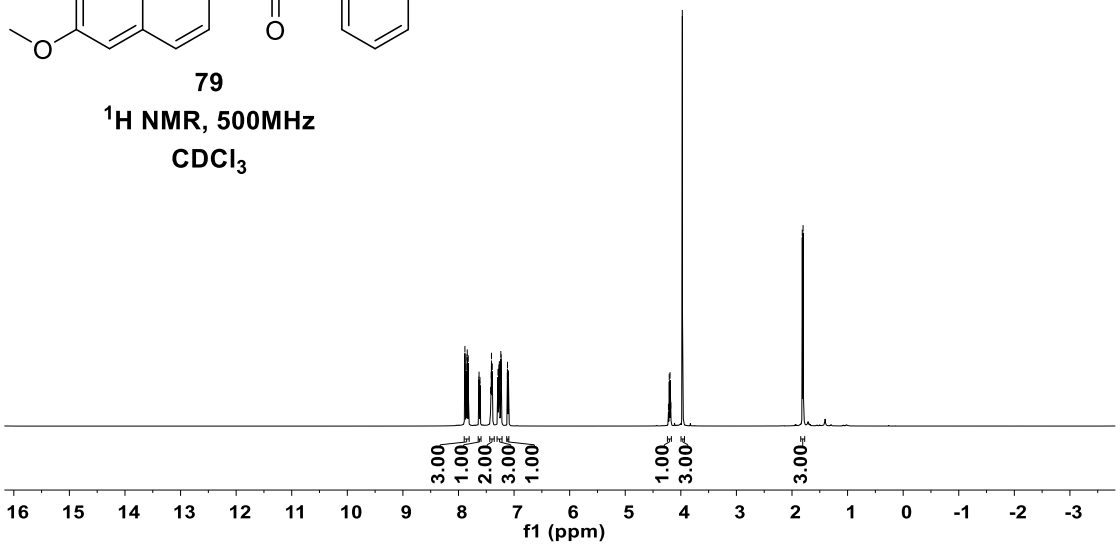


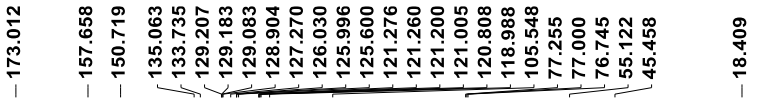


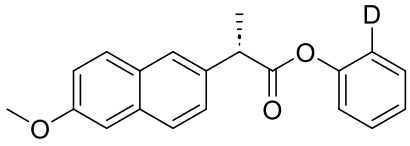
79

^{1}H NMR, 500MHz

$CDCl_3$



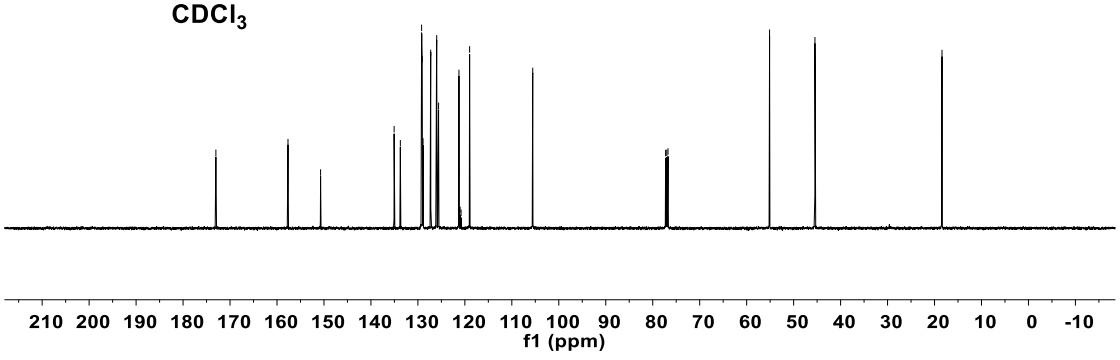


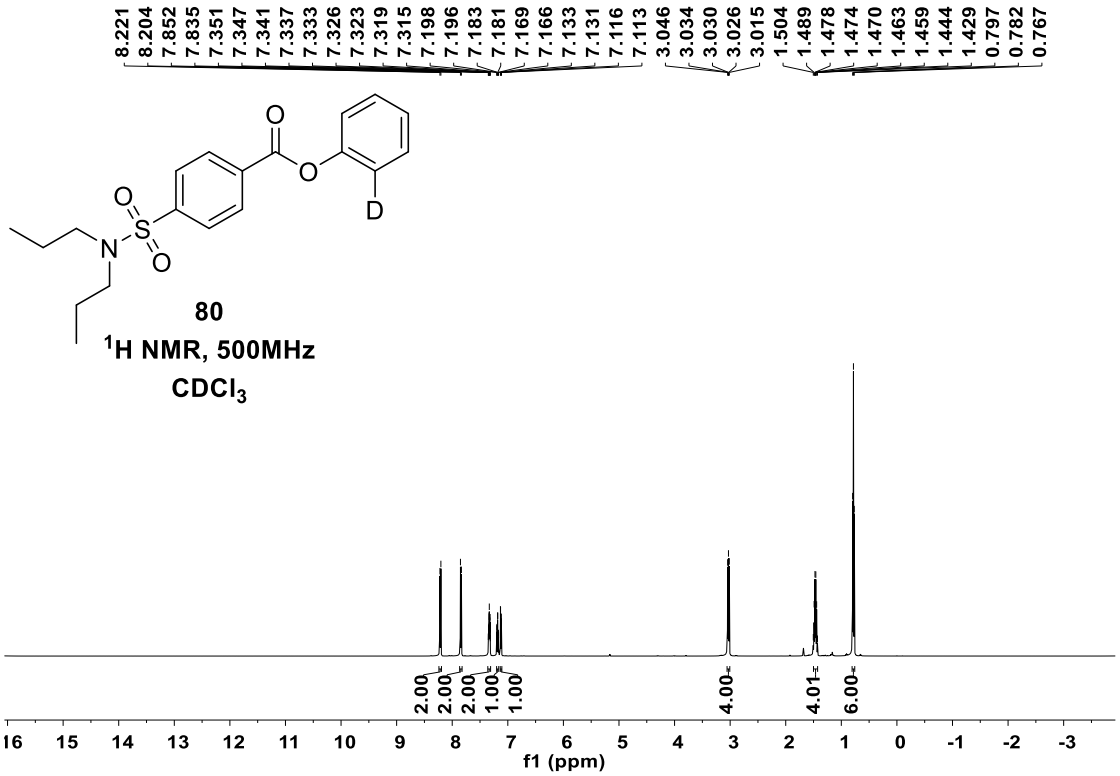


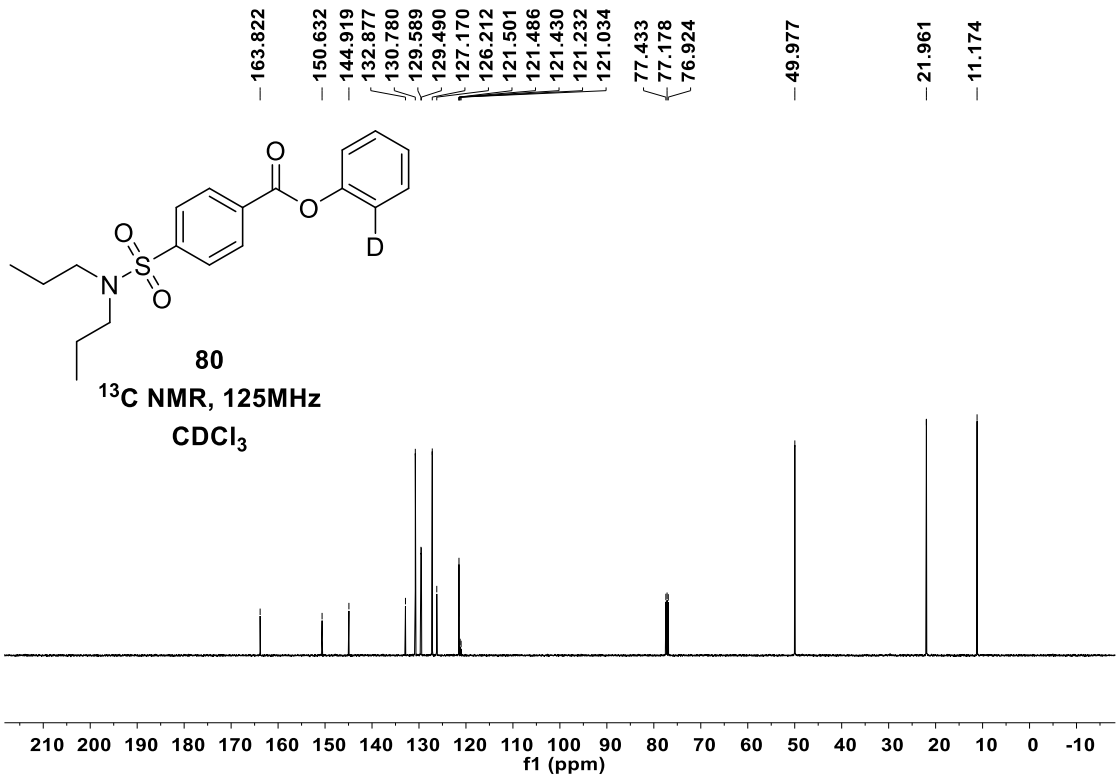
79

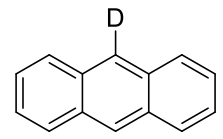
^{13}C NMR, 125MHz

$CDCl_3$




8.221
8.204
7.852
7.835
7.351
7.347
7.341
7.337
7.333
7.326
7.323
7.319
7.315
7.198
7.196
7.183
7.181
7.169
7.166
7.133
7.131
7.116
7.113
3.046
3.034
3.030
3.026
3.015
1.504
1.489
1.478
1.474
1.470
1.463
1.459
1.444
1.429
0.797
0.782
0.767
O
O
S
O
N
O
D
80
1H NMR, 500MHz
CDCl3
2.00
2.00
2.00
1.00
1.00
4.00
4.01
6.00
f1 (ppm)

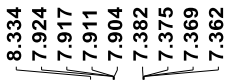

163.822
150.632
144.919
132.877
130.780
129.589
129.490
127.170
126.212
121.501
121.486
121.430
121.232
121.034
77.433
77.178
76.924
49.977
21.961
11.174
O
O
S
O
N
O
D
80
13C NMR, 125MHz
CDCl3
f1 (ppm)

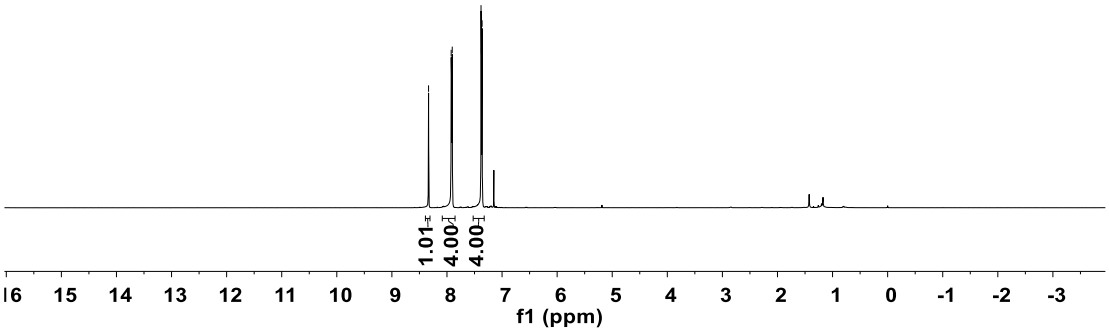


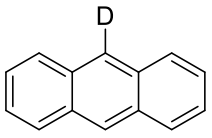
81

^{1}H NMR, 500MHz

$CDCl_3$



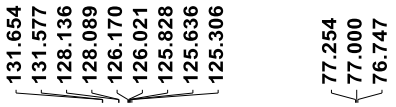


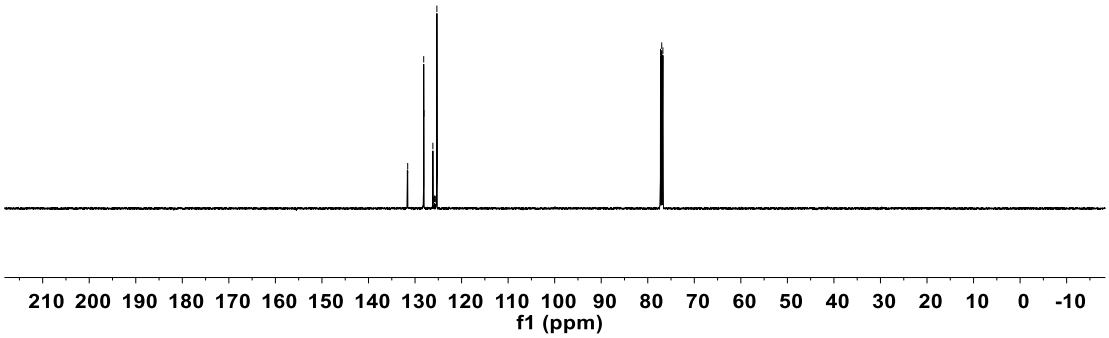


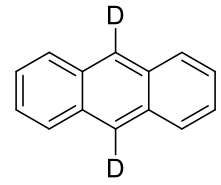
81

^{13}C NMR, 125MHz

$CDCl_3$



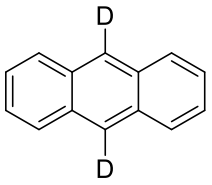




82

^{1}H NMR, 500MHz

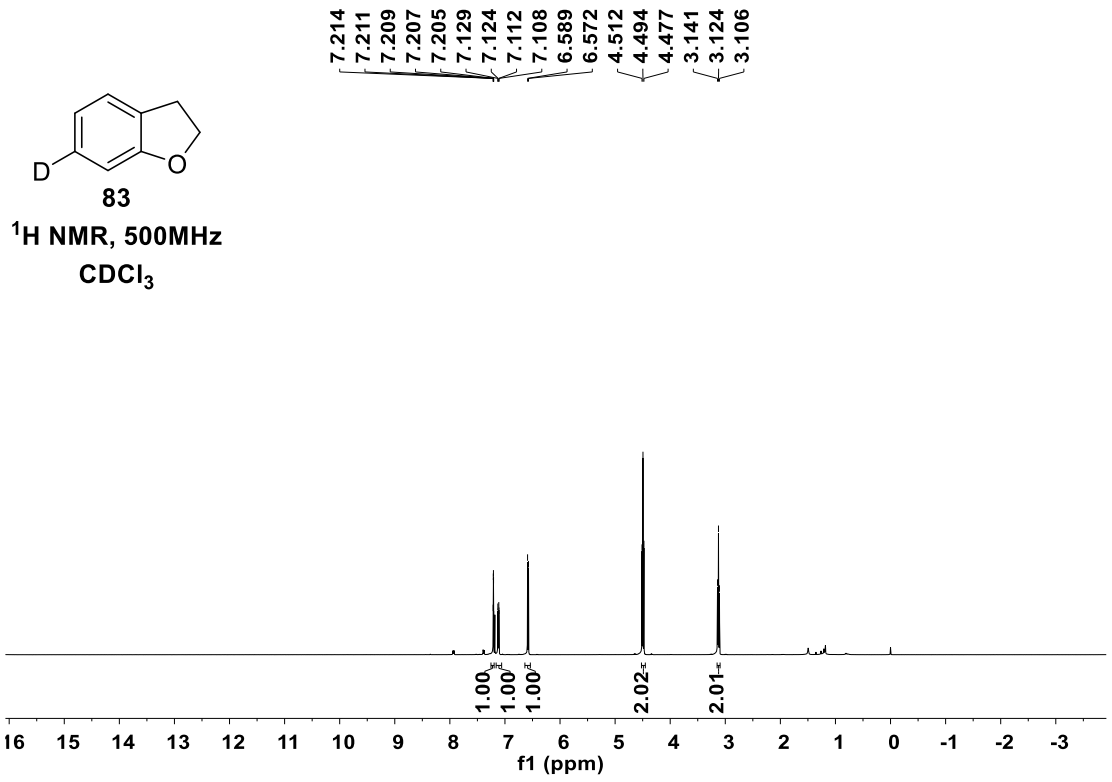
$CDCl_3$

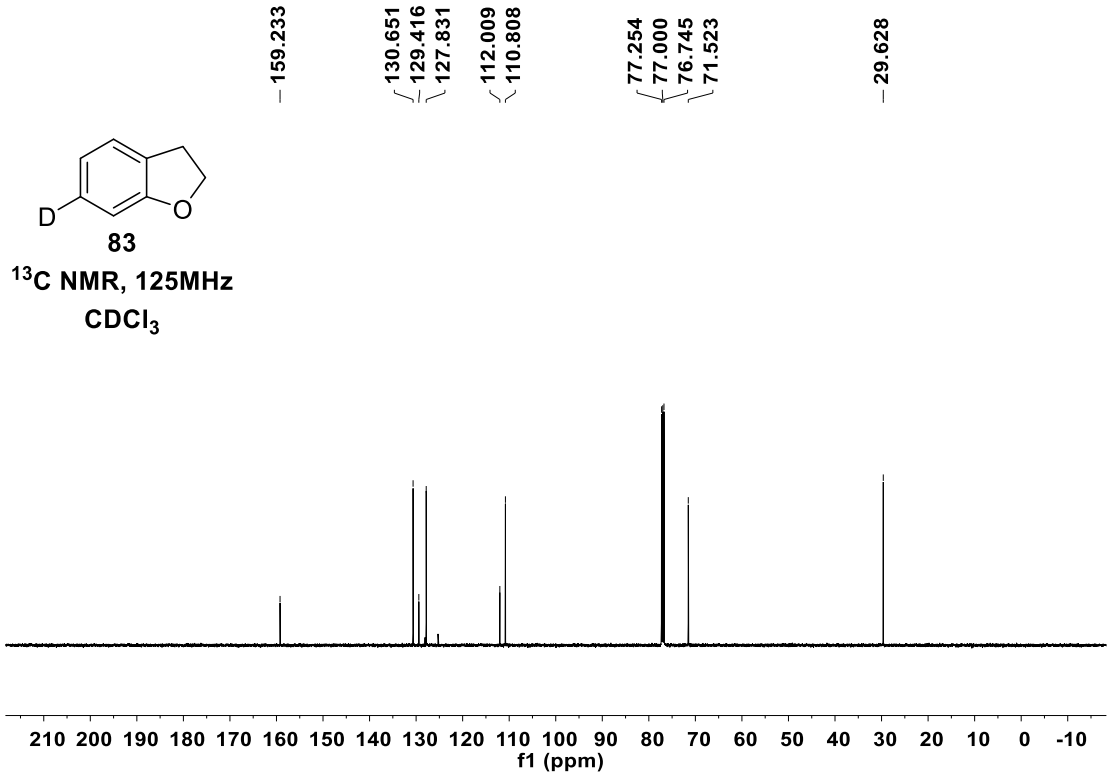


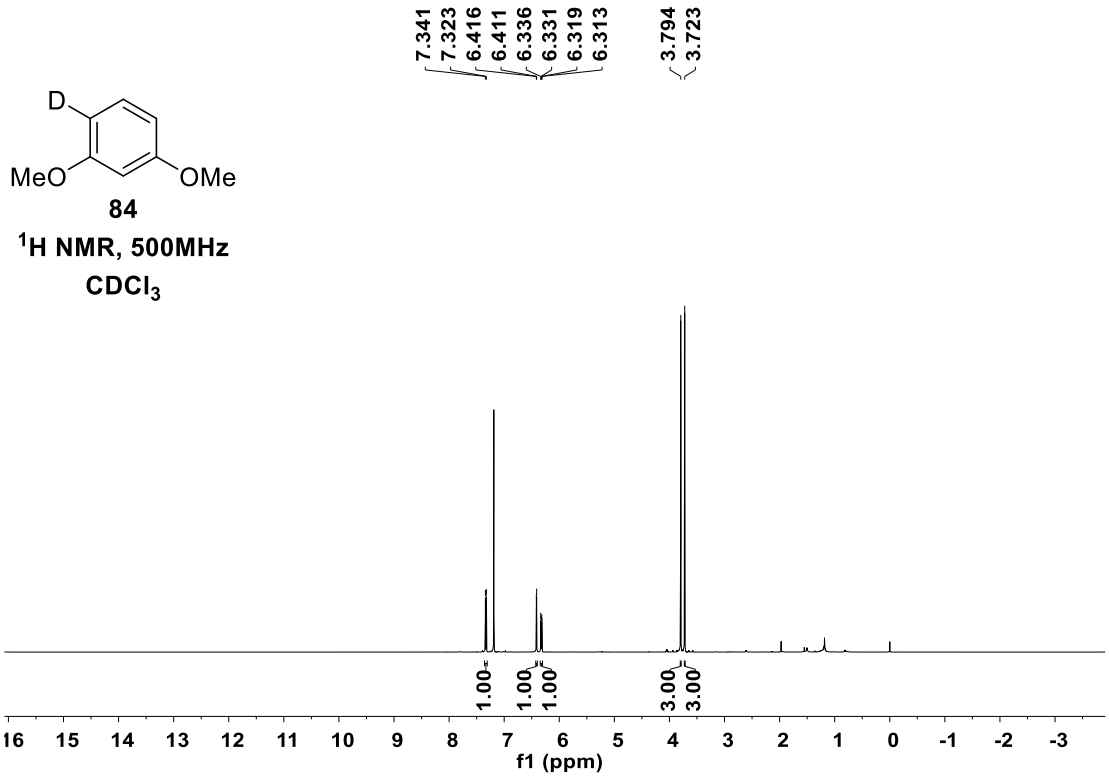
82

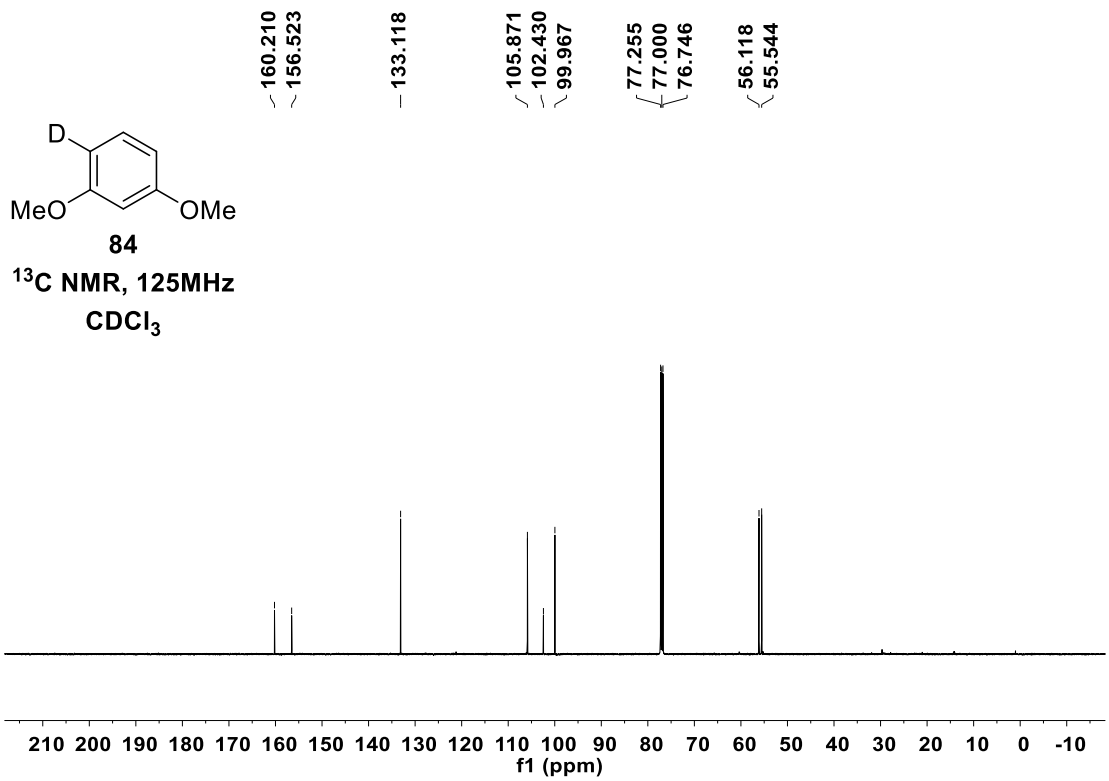
^{13}C NMR, 125MHz

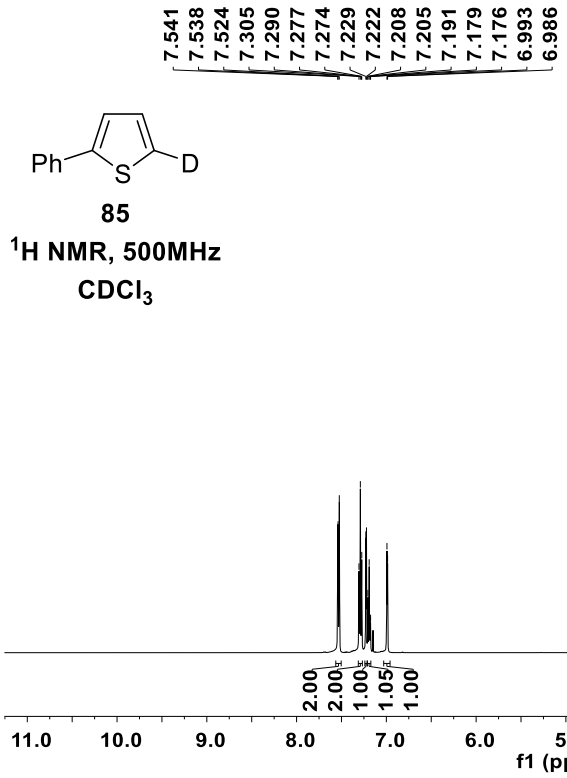
$CDCl_3$

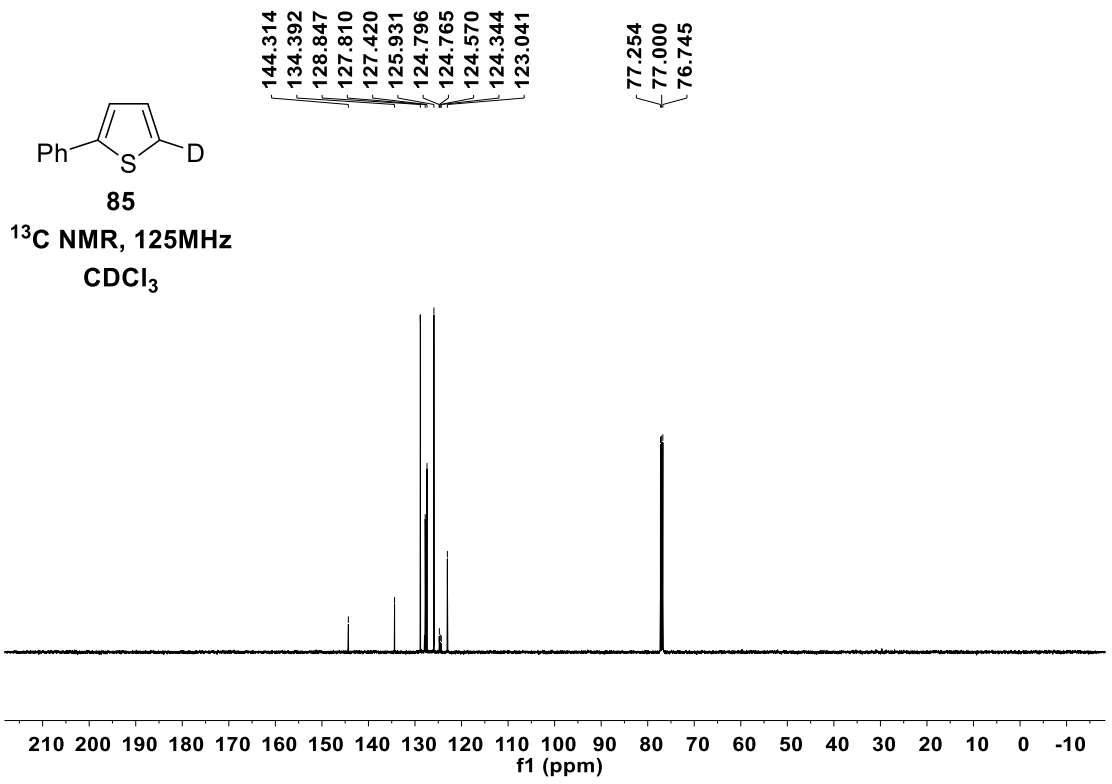

7.214
7.211
7.209
7.207
7.205
7.129
7.124
7.112
7.108
6.589
6.572
4.512
4.494
4.477
3.141
3.124
3.106
D
O
83
1H NMR, 500MHz
CDCl3
1.00
1.00
1.00
2.02
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

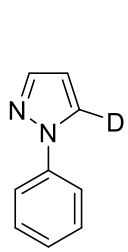

159.233
130.651
129.416
127.831
112.009
110.808
77.254
77.000
76.745
71.523
29.628
D
O
83
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.341
7.323
6.416
6.411
6.336
6.331
6.319
6.313
3.794
3.723
D
MeO
OMe
84
1H NMR, 500MHz
CDCl3
1.00
1.00
1.00
3.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


160.210
156.523
133.118
105.871
102.430
99.967
77.255
77.000
76.746
56.118
55.544
D
MeO
OMe
84
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.541
7.538
7.524
7.305
7.290
7.277
7.274
7.229
7.222
7.208
7.205
7.191
7.179
7.176
6.993
6.986
Ph
S
D
85
1H NMR, 500MHz
CDCl3
2.00
2.00
1.00
1.05
1.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

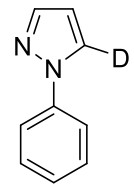

144.314
134.392
128.847
127.810
127.420
125.931
124.796
124.765
124.570
124.344
123.041
77.254
77.000
76.745
Ph
S
D
85
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



86

^{1}H NMR, 500MHz

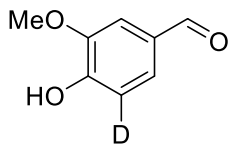
$CDCl_3$



86

^{13}C NMR, 125MHz

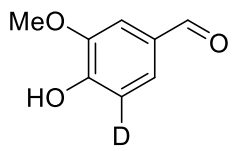
$CDCl_3$



87

^{1}H NMR, 500MHz

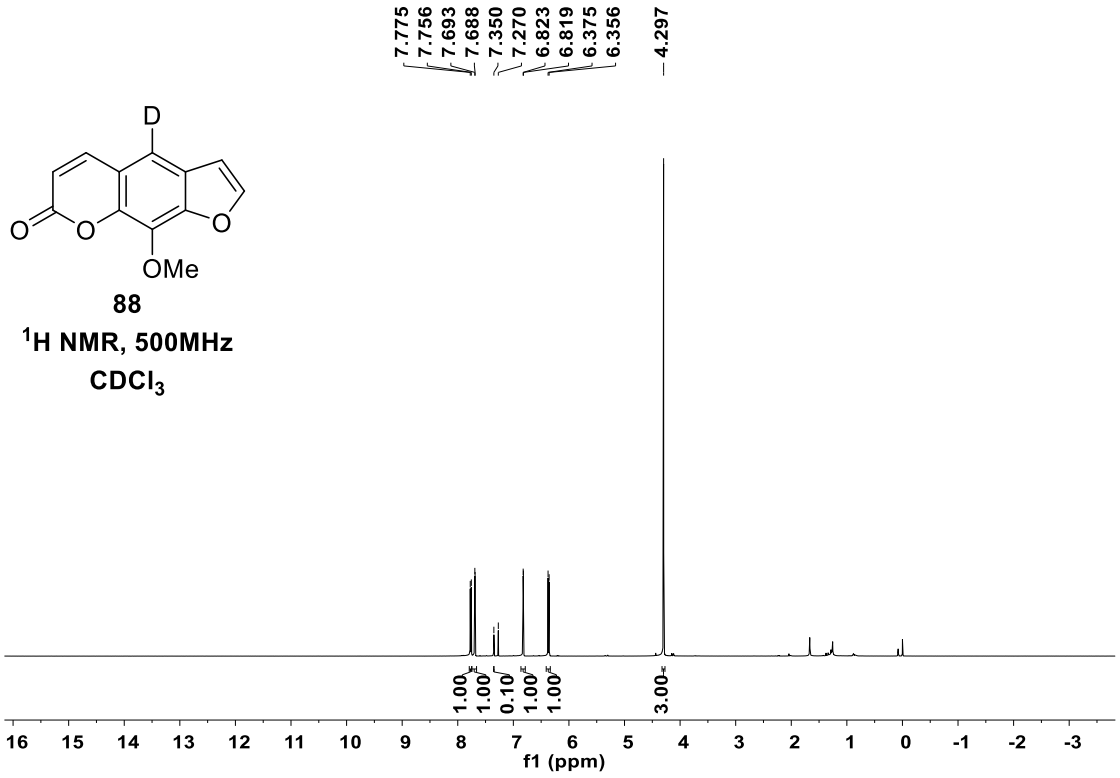
$CDCl_3$



87

^{13}C NMR, 125MHz

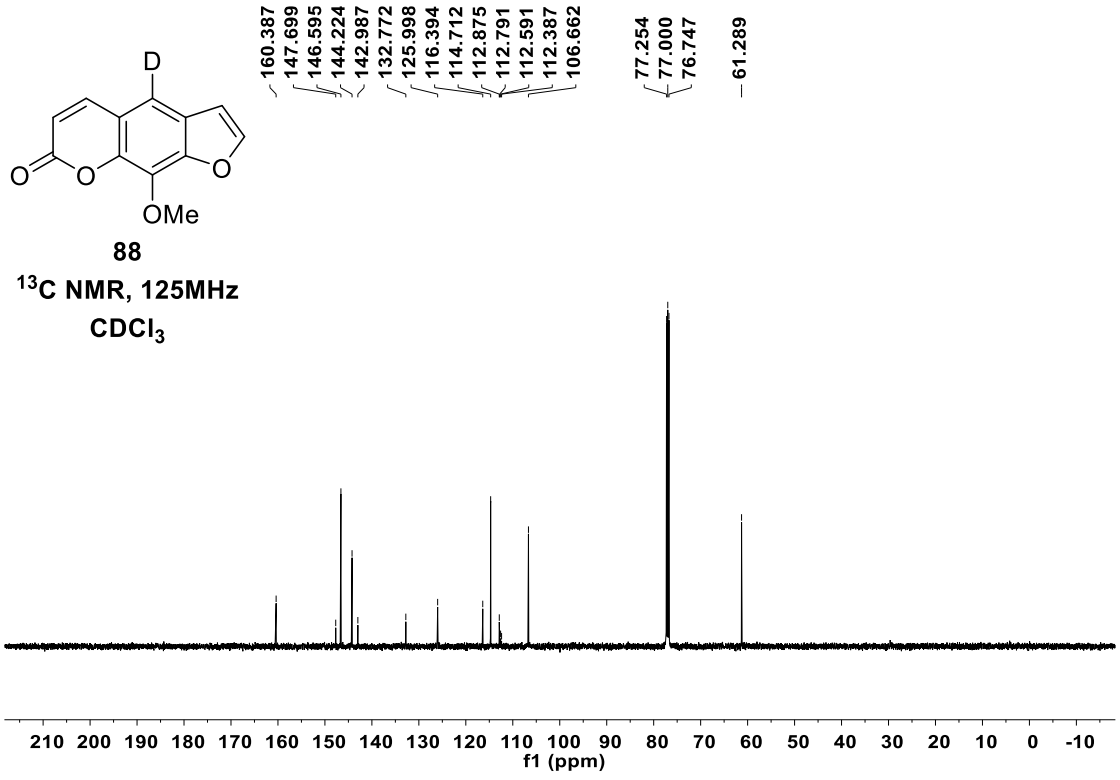
$CDCl_3$



88

^{1}H NMR, 500MHz

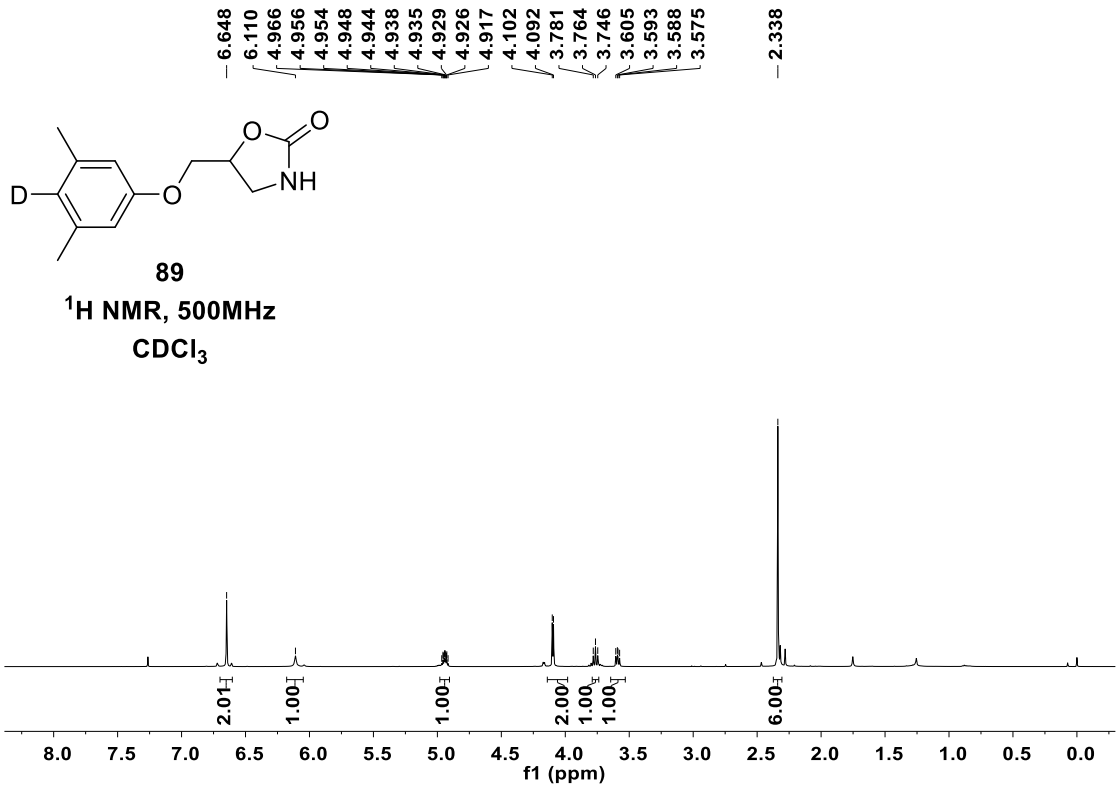
$CDCl_3$

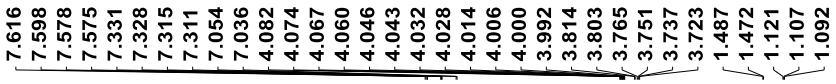


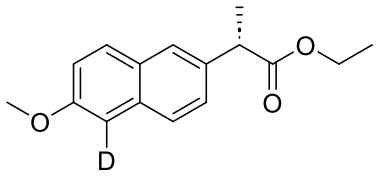
88

^{13}C NMR, 125MHz

$CDCl_3$


6.648
6.110
4.966
4.956
4.954
4.948
4.944
4.938
4.935
4.929
4.926
4.917
4.102
4.092
3.781
3.764
3.746
3.605
3.593
3.588
3.575
2.338
O
O
NH
D
O
89
1H NMR, 500MHz
CDCl3
2.01
1.00
1.00
2.00
1.00
1.00
6.00
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)
159.528
155.928
137.353
127.197
114.662
77.290
77.037
76.782
74.162
68.255
42.683
20.916
O
O
NH
D
O
89
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

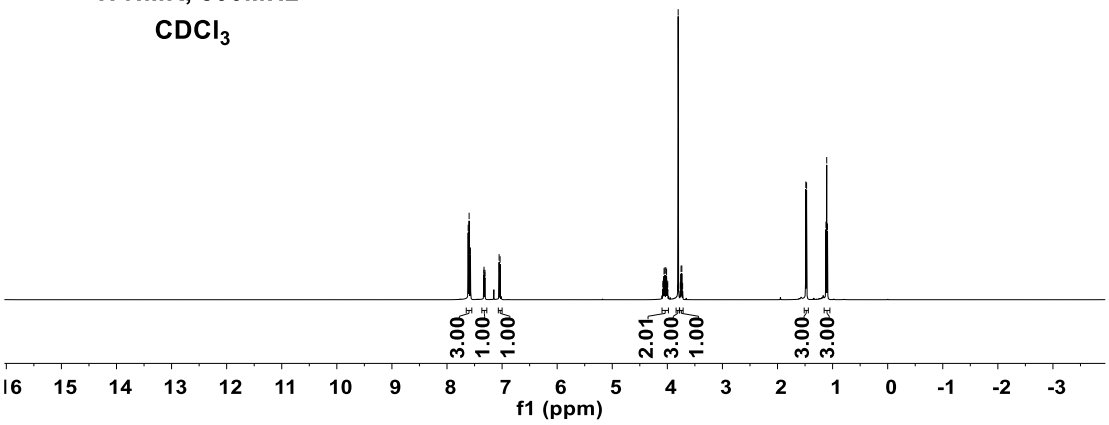


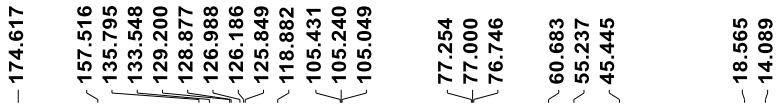


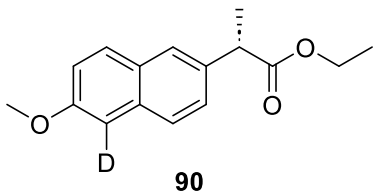
90

^{1}H NMR, 500MHz

$CDCl_3$



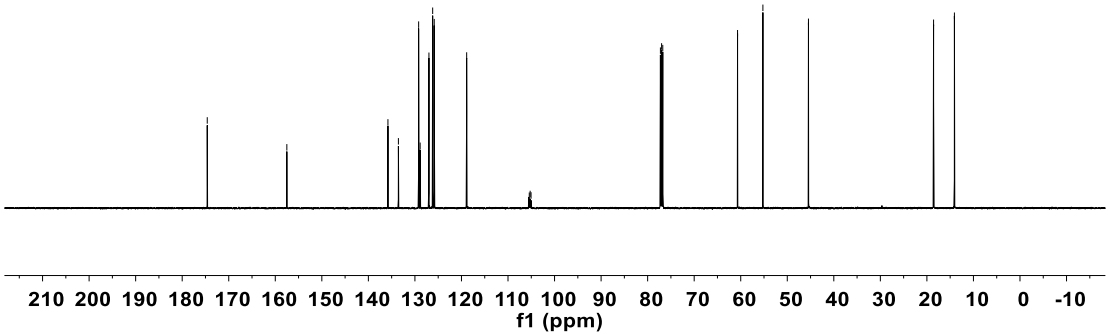




90

^{13}C NMR, 125MHz

$CDCl_3$



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