Supplementary information

Spontaneous conversion of prenyl halides to acid: Application for metal-free preparation of deuterated compounds under mild conditions

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Contents

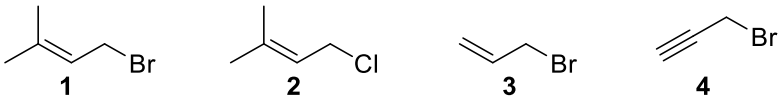
1. Materials and methods

Chemicals were purchased from Tokyo Chemical Industry Co., Ltd (TCI) or Sigma-Aldrich Co., Ltd unless otherwise mentioned. All deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories, Inc. Analytical reagent grade (both reagents and solvents) were used as received without any further purification. Reactions were performed either in NMR tubes or in flasks (10 mL) with glass stoppers. Semi-preparative HPLC was performed using Waters Binary HPLC Pump, connected with 2998 Photodiode Array Detector and C_{18} reversed phase column (250 x 20.5 mm), if further purification was required (for compound **18**). NMR spectra were recorded at 24 °C either on a Bruker AVANCE 300 MHz spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) or on Bruker AVANCE 400 MHz spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts were recorded in ppm with reference to the residual CHD_2OD (quintet at 3.31 ppm) or $CHCl_3$ (singlet at 7.26 ppm) or DMSO-d_6 (quintet at 2.5 ppm) signal for ^{1}H NMR, to the CD_3OD (septet at 49.0 ppm) or $CDCl_3$ (triplet at 77.0 ppm) or DMSO-*d*6 (septet at 39.5 ppm) signal for ^{13}C NMR. Multiplicities of NMR signals were reported as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublets of doublet), td (triplets of doublet), and m (multiplet), while the coupling constants were in Hz. Mass spectrometry (MS) data were obtained from high resolution mass spectrometer either on Thermo Scientific, orbitrap, Q Exactive Focus spectrometer or on Bruker micro TOF mass spectrometer.

Because of the catalysts being liquid, the volume and weight of catalysts are calculated from their density, and thus giving the volume required for the reaction. The stock solution of each catalyst was freshly prepared in CD_3OD, and this solution was pre-diluted in CD_3OD just before using for the reaction. Percentage of deuterium incorporation was determined by the ^{1}H NMR integrals relative to the unlabeled positions of the product unless otherwise stated.

$$\%\ \textbf{Deuteration} = \left[\mathbf{1} - \left(\frac{\textbf{Residual integral}}{\textbf{Integral of labelled position before deuteration}}\right)\right] \times \mathbf{100}$$

Splitting pattern of ^{13}C NMR signals of deuterium-labelled positions and MS data were used for verification of deuteration. Structures of catalysts **1**-**4** are shown below (in Supplementary Figure 1).

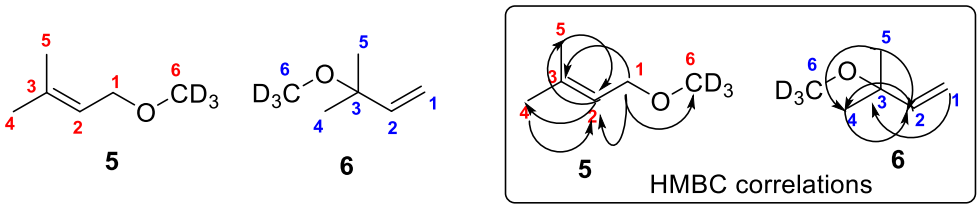


Supplementary Figure 1. Structures of catalysts **1**-**4**

2. Mechanism of *in situ* generation of DBr and proposed structures of compounds 5 and 6

To investigate the mechanism of *in situ* generation of DBr from prenyl bromide (**1**) in CD_3OD, 39 µL (0.3 mmol) of catalyst **1** was dissolved in CD_3OD, and NMR data were recorded after 24 h. ^{13}C NMR, DEPT 135, DEPT 90, and 2D NMR techniques were used to identify the compounds generated from prenyl bromide (**1**) in CD_3OD. Analysis of ^{1}H NMR spectrum revealed that compound **1** had structural changes in CD_3OD, suggesting the formation of compounds **5** and **6**. Analysis of 1D and 2D NMR data revealed the proposed structures of

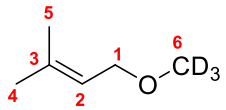
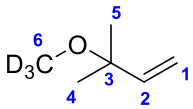
compounds **5** and **6** (Supplementary Figure 2), which are present as a mixture with approximately in 3:1 ratio.



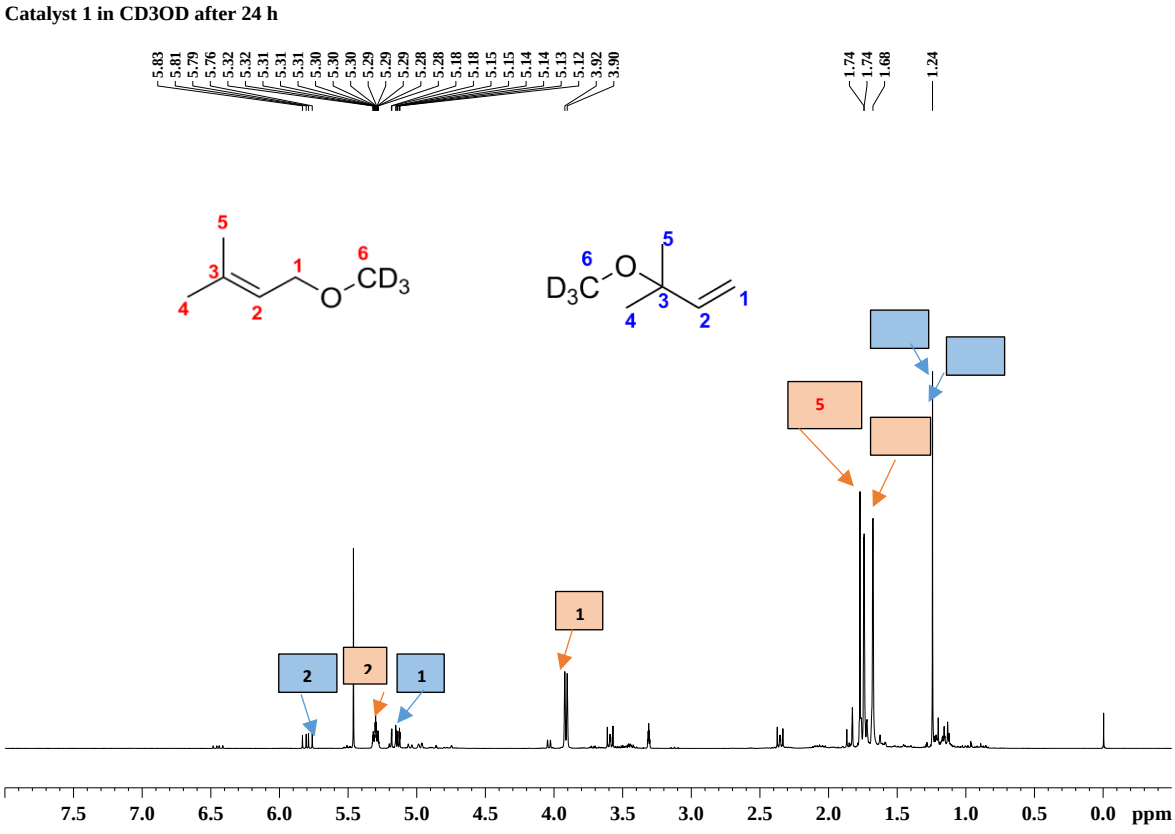
Supplementary Figure 2. Proposed structures and HMBC correlations of compounds **5** and **6**

^{1}H and ^{13}C spectra of compounds **5** and **6** are shown in Supplementary Figures 3 and 4. ^{1}H and ^{13}C spectral data of compounds **5** and **6** are listed in Supplementary Table 1. ^{1}H NMR spectrum of **5** showed signals at δ_H 5.30 (H-2), 3.91 (H_2-1), 1.74 (H_3-4), and1.68 (H_3-5), while ^{1}H NMR spectrum of **6** showed signals at δ_H 5.80 (H-2), 5.16 (H-1a), 5.14 (H-1b), and 1.24 (H_3-4 and H_3-5). DEPT experiments showed that C-1 (at δ_C 114.68) of compound **6** was a methylene carbon, while the chemical shift at δ_C 76.48 of C-3 of **6** suggested it was sp3 carbon attached to an oxygen atom. ^{1}H-^{1}H COSY spectrum showed correlation of H-1 and H-2 of compound **5** and correlation of H-1a/H-1b with H-2 of compound **6** (Supplementary Figure 5). Proton(s) attached to carbon in **5** and **6** were assigned by HSQC spectrum (Supplementary Figure 6). HMBC correlations of compound **5** were observed from H_2-1 to C-6 of CD_3 carbon that has a typical multiplicity of carbon-deuterium coupling (see the expansion of HMBC spectrum in Supplementary Figure 7). Moreover, HMBC spectrum of compound **5** also showed the correlations from H_2-1 to C-2 and C-3; H-2 to C-4 and C-5; and H_3-4 and H_3-5 to C-2 (Supplementary Figures 2 and 7). HMBC correlations of compound **6** were observed from H-1a/1b to C-3 and H-2 to C-4 and C-5; H_3-4 and H_3-5 to C-2 (Supplementary Figures 2 and 7).

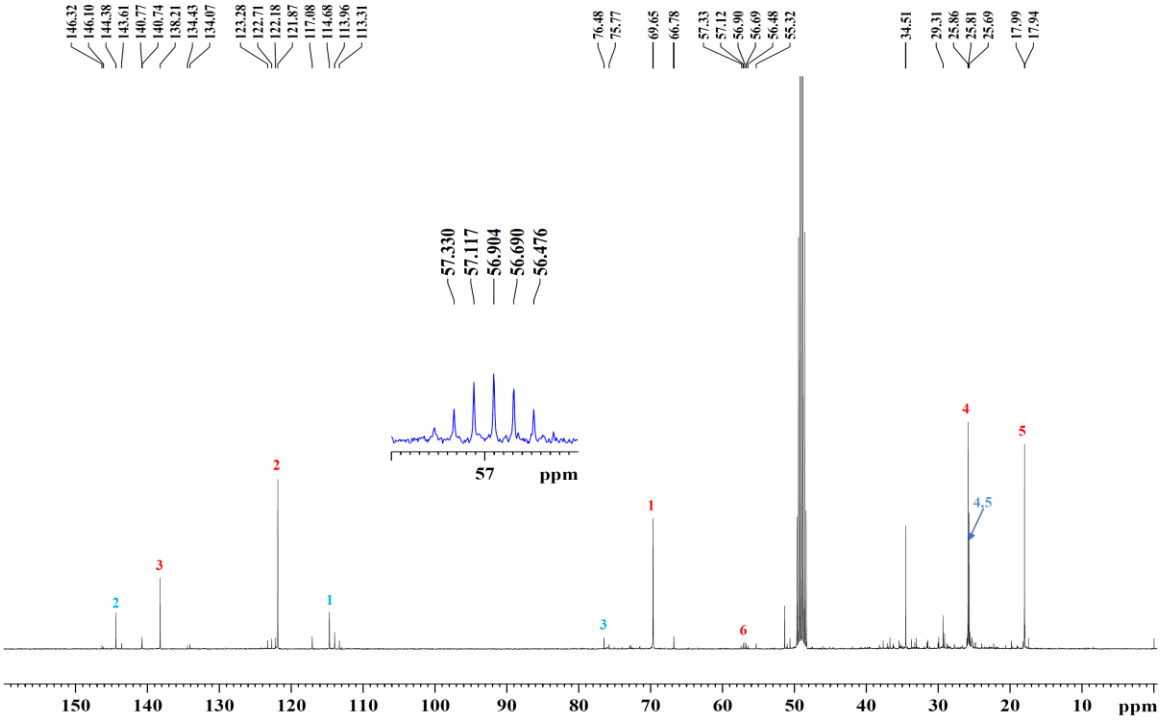
Supplementary Table 1. ^{1}H and ^{13}C NMR spectral data (CD_3OD) of compounds **5** and **6**

 **5**			 **6**		
Position	δ_C ppm, Type	δ_H ppm, multiplicity (*J* in Hz)	Position	δ_C ppm, Type	δ_H ppm, multiplicity (*J* in Hz)
1	69.65, CH_2	3.91, d (6.9)	1	114.68, CH_2	(H-1a) 5.14, dd (17.7, 1.2); (H-1b) 5.16, dd (10.9, 1.2)
2	121.87, CH	5.30, m	2	144.38, CH	5.80, dd (17.7, 10.8)
3	138.21, C	-	3	76.48, C	-
4	17.99, CH_3	1.68, s [a]	4	25.69, CH_3	1.24, s
5	25.86, CH_3	1.74, s [a]	5	25.69, CH_3	1.24, s
6	56.90, CD_3	Not observed [b]	6	Not observed [b]	Not observed [b]

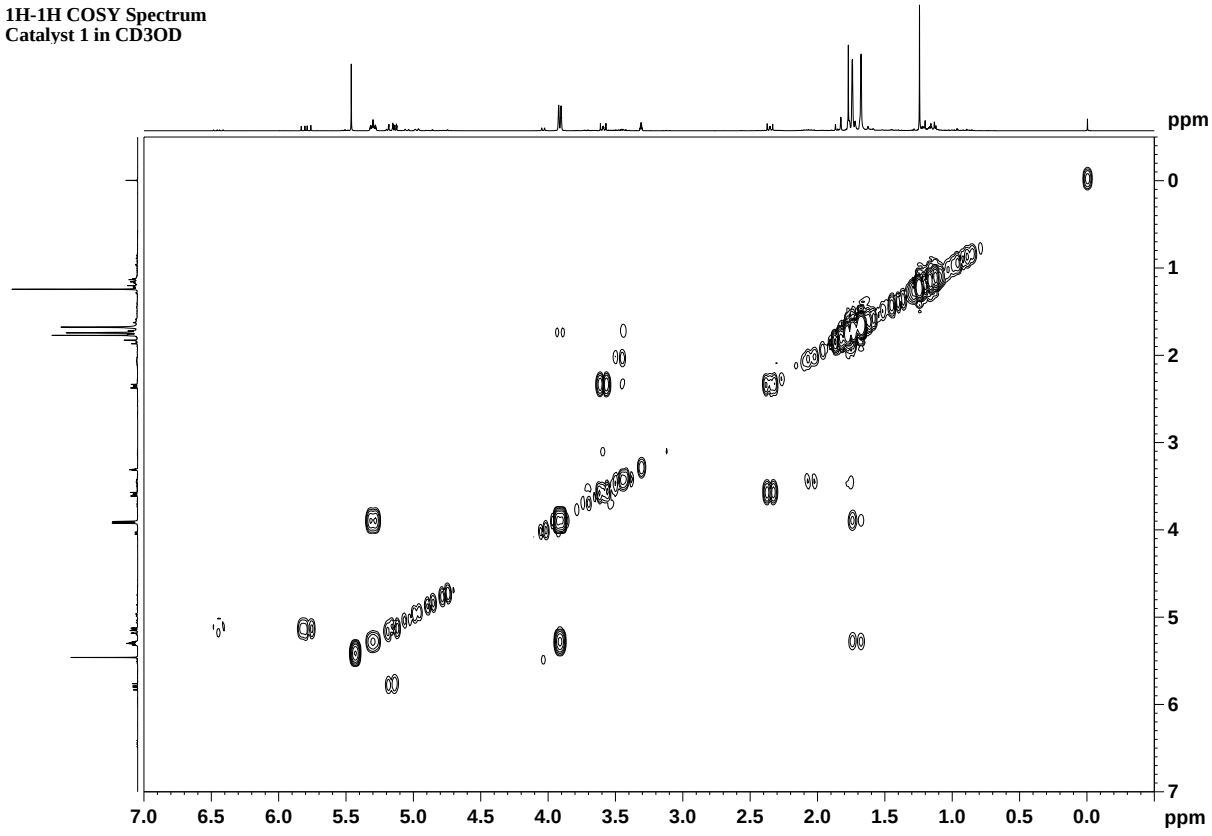
[a] May be interchangeable in the same column.
[b] Not observed: this could be because these signals are overlapping with NMR solvent, CD_3OD.



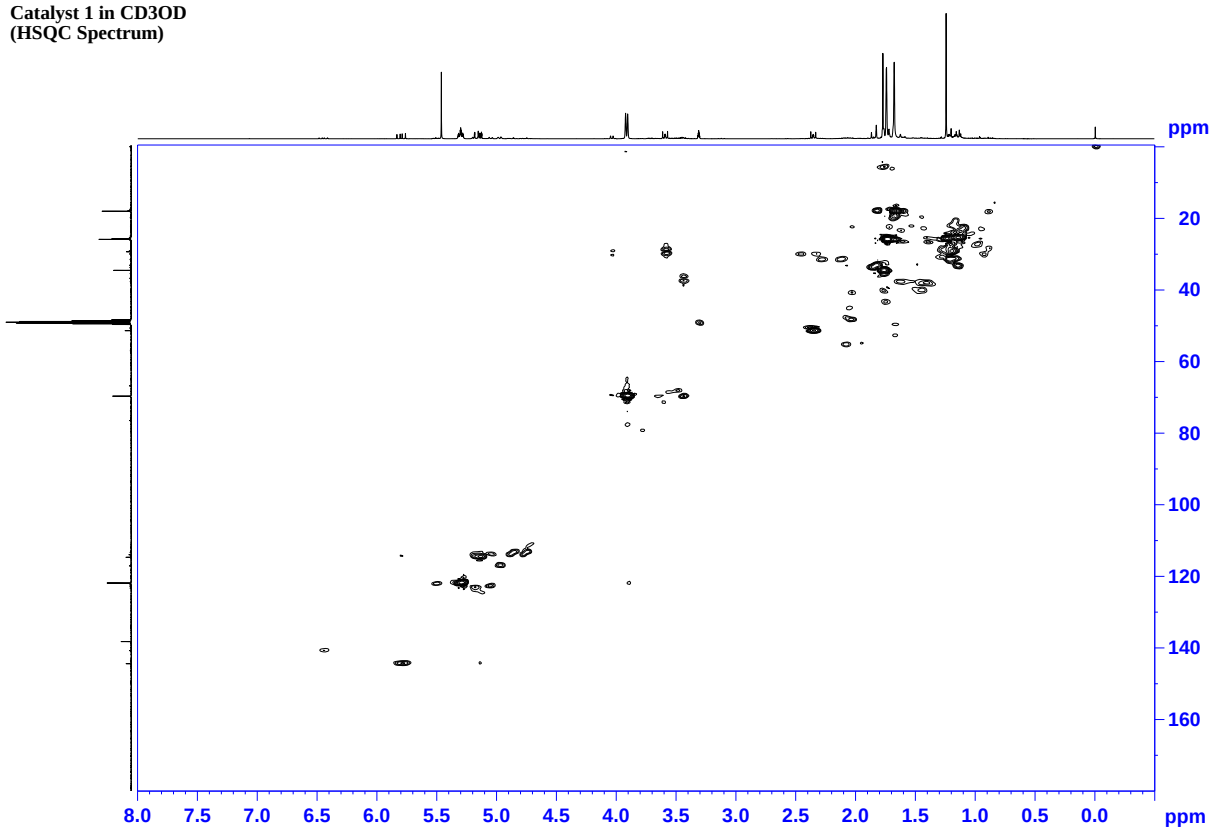
Supplementary Figure 3. ^{1}H NMR spectrum of compounds **5** and **6** in (400 MHz, CD_3OD)



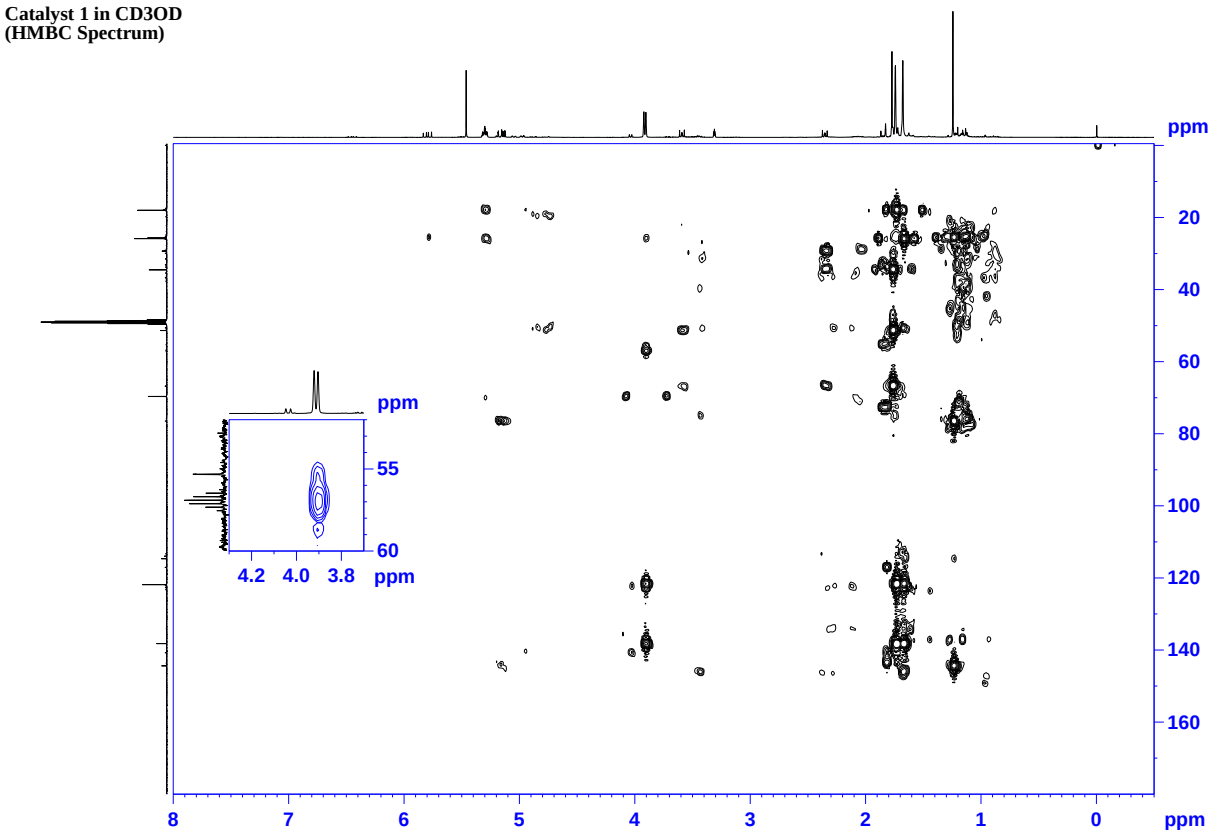
Supplementary Figure 4. ^{13}C NMR spectrum of compounds **5** and **6** in (100 MHz, CD_3OD)



Supplementary Figure 5. ^{1}H-^{1}H COSY spectrum of compounds **5** and **6** in CD_3OD



Supplementary Figure 6. HSQC spectrum of compounds **5** and **6** in CD_3OD



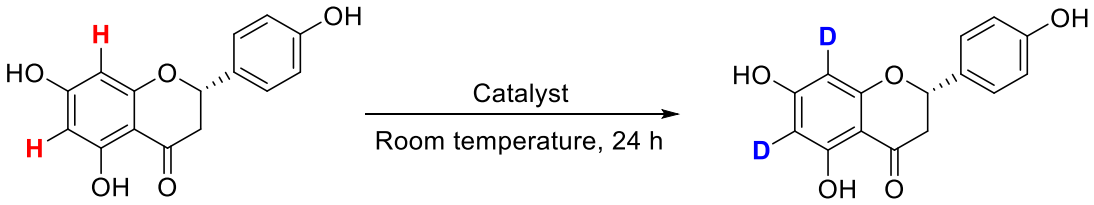
Supplementary Figure 7. HMBC spectrum of compounds **5** and **6** in CD_3OD

3. Optimization of reaction conditions for phenolic compounds

To investigate the catalytic ability of catalysts **1**, **3**, and **4** and the catalyst amounts for deuteration of naringenin (**12**), an NMR tube was charged with **12** (29.2 mg, 0.1 mmol), CD_3OD (0.6 mL) and catalyst (as indicated in entries 1-5, Supplementary Table 2). NMR tube was vortexed and kept at room temperature for 24 h. ^1H NMR spectrum was used to assess deuteration percentages. Catalyst **1** (2-3 mol%) gave >95% deuteration (entries 1-3, Supplementary Table 2), which was better than catalysts **3** and **4** (giving 45% and <5% deuteration, entries 4 and 5). Catalyst **1** at 2 or 3 mol% was therefore chosen as the optimum catalyst loading.

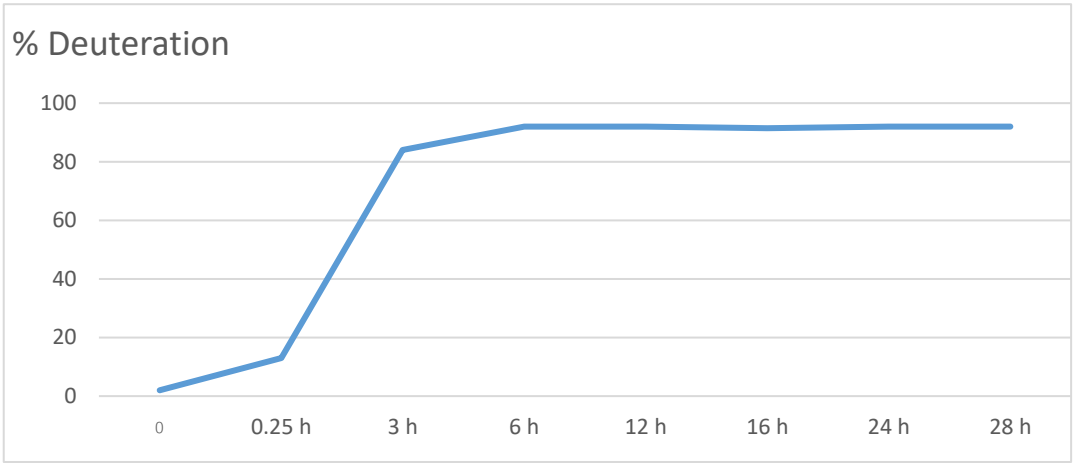
In order to assess the effect of co-solvent on deuteration, an NMR tube was charged with **12** (29.2 mg, 0.1 mmol), co-solvent (0.3 mL), CD_3OD (0.6 mL) and 2 mol% of catalyst **1** (entries 6-8, Supplementary Table 2). An NMR tube was vortexed and kept at room temperature for 24 h. ^1H NMR spectrum was used to assess deuteration percentages. Acetone d_6, $CHCl_3$, THF could be used as co-solvents for deuteration, giving 93-95% deuterium incorporation (entries 6 and 8, Supplementary Table 2). Therefore, these solvents can be used as co-solvents for substrates with poor solubility in CD_3OD.

Supplementary Table 2. Catalyst and co-solvents for deuteration of naringenin (**12**)



Entry	Catalyst (mol%)	D source/Co-solvent	D-incorporation (%)	Yield (%)
1	**1** (10)	CD_3OD	>95	>97
2	**1** (3)	CD_3OD	>95	>97
3	**1** (2)	CD_3OD	>95	>97
4	**3** (10)	CD_3OD	45	>97
5	**4** (10)	CD_3OD	<5	>97
6	**1** (2)	CD_3OD/Acetone d_6	>95	>97
7	**1** (2)	$CD_3OD/CHCl_3$	>93	>97
8	**1** (2)	CD_3OD/THF	>95	>97
9	No catalyst	CD_3OD	<5	>97

To study the time required for deuteration, the reaction was monitored in an NMR tube; plot of % deuteration and time is in Supplementary Figure 8. An NMR tube was charged with **12** (29.2 mg, 0.1 mmol), CD_3OD (0.6 mL) and catalyst **1** (2 mol%). An NMR tube was vortexed and kept at room temperature. ^1H NMR spectra were recorded at different time intervals (0, 0.25 h, 3 h, 6 h, 12 h, 24 h, and 28 h). It was found that 84% deuteration was obtained within 3 h, and 92% deuteration was observed at 12 h (Supplementary Figure 8). Therefore, the time required for deuteration is at least 12 h.

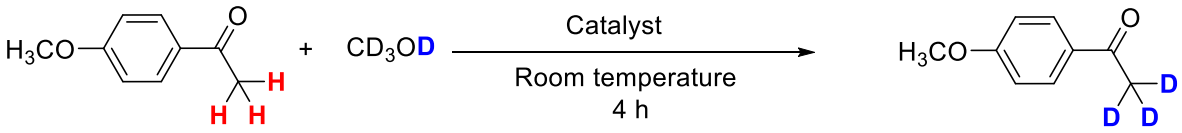


Supplementary Figure 8. Percentage deuterium incorporation of naringenin (**12**) with time

4. Optimization of reaction conditions for carbonyl compounds

An NMR tube was charged with compound **20** (47.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and catalyst (entries 1-4 of Supplementary Table 3). NMR tube was vortexed and kept at room temperature for 4 h. ^1H NMR spectrum was used to assess deuteration percentages. Catalyst **1** with 1 mol% and 5 mol% gave >95% deuteration (entries 1 and 2, Supplementary Table 3), which was better than catalysts **3** and **4** (entries 3 and 4). It was found that when using THF and $CHCl_3$ as co-solvents, >95% deuteration (entries 5 and 6) was obtained for these conditions, suggesting that both THF and $CHCl_3$ could be used as co-solvents for substrates with poor solubility in CD_3OD.

Supplementary Table 3. Catalyst and co-solvents for deuteration of carbonyl compounds

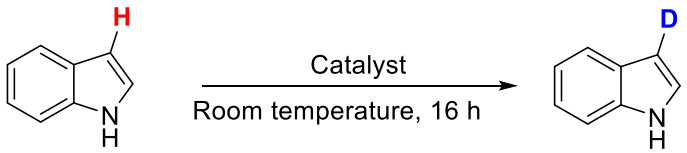


Entry	Catalyst (mol%)	D source/Co-solvent	D-incorporation (%)	Yield (%)
1	**1** (5)	CD_3OD	>95	>98
2	**1** (1)	CD_3OD	>95	>98
3	**3** (10)	CD_3OD	<35	>98
4	**4** (10)	CD_3OD	<5	>98
5	**1** (1)	CD_3OD/THF	>95	>98
6	**1** (1)	$CD_3OD/CHCl_3$	>95	>98
7	No catalyst	CD_3OD	0	>99

5. Optimization of reaction conditions for pyrroles and indoles

An NMR tube was charged with indole (**58**) (37.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and catalyst (Supplementary Table 4). NMR tube was vortexed and kept at room temperature for 16 h. ^1H NMR was used to assess deuteration percentages. Catalyst **1** (1 mol%), catalyst **3** (10 mol%) and catalyst **4** (10 mol%) gave >95% deuteration (entries 1, 3, and 4). However, catalyst **4** with 1 mol% gave only <40% deuteration (entry 2). Therefore, catalyst **1** with 1 mol% is sufficient for deuteration that gave >95% deuterium incorporation. THF and $CHCl_3$ were found to be suitable as co-solvents for substrates with poor solubility (giving >95% deuteration, entries 5 and 6).

Supplementary Table 4. Catalyst and co-solvents for deuteration of indoles

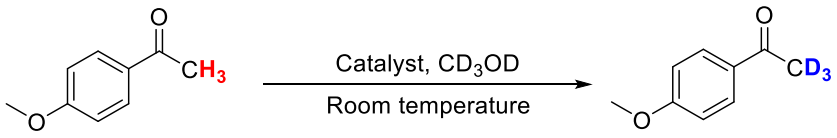


Entry	Catalyst (mol%)	D source/Co-solvent	D-incorporation (%)	Yield (%)
1	**1** (1)	CD_3OD	>95	>97
2	**4** (1)	CD_3OD	<40	>97
3	**3** (10)	CD_3OD	>95	>97
4	**4** (10)	CD_3OD	>95	>97
5	**1** (1)	CD_3OD/THF	>95	>97
6	**1** (1)	$CD_3OD/CHCl_3$	>95	>97
7	No catalyst	CD_3OD	<5	>98

6. Catalyst loading required for deuteration

In order to study the minimum catalyst amount required for deuteration of a carbonyl compound **20**, different amounts of catalyst **1** were used with various catalyst loading (0.1 mol%, 0.5 mol%, 1.0 mol%, 3.0 mol%, 5.0 mol%, 10.0 mol%, and 20.0 mol%; entries 1-7, Supplementary Table 5). It was found that the amount of 0.5 mol% of catalyst **1** gave 82% of deuteration after 24 h (entry 6), which was slightly lower than those with 1.0-20.0 mol% (entries 1-5). However, the catalyst at 0.1 mol% gave only <5% (entry 7). Therefore, catalyst **1** is required at least 0.5 mol% for deuteration.

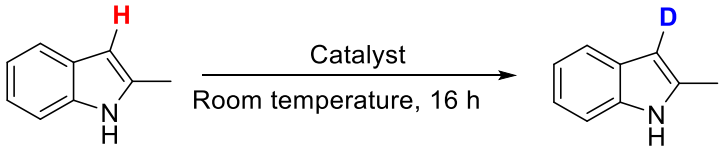
Supplementary Table 5. Effects of amounts of catalyst **1** on the deuteration of compound **20**



Entry	Catalyst	Catalyst amount (mol%)	Time	% Deuteration	Yield
1	**1**	20	4 h	>95%	>98%
2	**1**	10	4 h	>95%	>98%
3	**1**	5	4 h	>95%	>98%
4	**1**	3	4 h	>95%	>98%
5	**1**	1	4 h	>95%	>98%
6	**1**	0.5	24 h	>82%	>98%
7	**1**	0.1	24 h	<5%	<98%

The amount of catalyst **1** required for deuteration of 2-methylindole (**60**) was investigated, and it was found that 1.0 mol% and 0.5 mol% gave >95% deuteration (entries 1 and 2, Supplementary Table 6). The catalyst amount of 0.1 mol% provided >94% deuteration (entry 3), which was relatively similar to that of 1.0 mol% and 0.5 mol% (entries 1 and 2), suggesting that deuteration of indole **60** required at least 0.1 mol%.

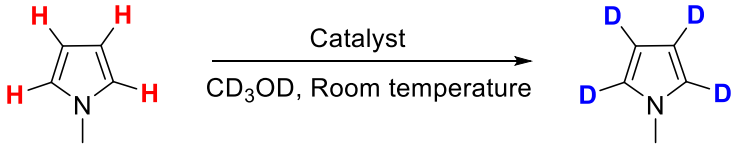
Supplementary Table 6. Effects of amounts of catalyst **1** on the deuteration of indole **60**



Entry	Catalyst (mol%)	D source	D-incorporation (%)	Yield (%)
1	**1** (1)	CD_3OD	>95	>97
2	**1** (0.5)	CD_3OD	>95	>97
3	**1** (0.1)	CD_3OD	>94	>97

To investigate the amount of catalyst **1** required for deuteration of pyrrole **71**, deuteration was performed with 1.0 mol%, 0.5 mol%, and 0.1 mol% (Supplementary Table 7). It was found that catalyst **1** with 1 mol% and 0.5 mol% gave >90% deuteration (entries 1 and 2), while that with 0.1 mol% gave 81%-87% deuteration (entry 3). Therefore, deuteration of pyrrole **71** required at least 0.1 mol%.

Supplementary Table 7. Effects of amounts of catalyst **1** on the deuteration of pyrrole **71**



Entry	Catalyst (mol%)	Time	%Deuteration	
			Positions 2,5	Positions 3,4
1	**1** (1)	4 h	>90%	>90%
2	**1** (0.5)	24 h	>90%	>90%
3	**1** (0.1)	24 h	>81%	>87%

7. Amount of deuterium source required for deuteration

To investigate the amounts of the deuterium source (D) required for deuteration, compound **20** (0.3 mmol) and catalyst **1** (3 mol%) were used as model compound and catalyst model, respectively. Amounts of a deuterium source (CD_3OD), i.e., 3 eq, 5 eq, 10 eq, 20 eq, and 50 eq were used for deuteration of compound **20** (entries 1-5, Supplementary Table 8). It was found that 3-10 eq of a deuterium source provided 70%-83% deuteration (entries 1-3), while 20 eq and 50 eq of a deuterium source gave 92% and 96% deuteration, respectively (entries 4 and 5). Therefore, it is recommended that at least 50 eq of CD_3OD should be used for deuteration.

Supplementary Table 8. Effects of amounts of deuterium source on deuteration of compound **20**

Entry	Catalyst	CD_3OD amount	Time	% Deuteration	Yield
1	Cat **1**	3 eq	16 h	>70%	>98%
2	Cat **1**	5 eq	16 h	>79%	>98%
3	Cat **1**	10 eq	16 h	>83%	>98%
4	Cat **1**	20 eq	16 h	>92%	>98%
5	Cat **1**	50eq	16 h	>96%	>98%

8. Gram scale synthesis of deuterated compounds

*Naringenin (**12**)*

1 g scale

A reaction flask (25 mL) with a glass stopper was charged with naringenin (**12**) (1 g, 3.5 mmol), CD_3OD (8 mL), and 1 mol% of catalyst **1**. A reaction mixture was stirred at room temperature for 24 h. Then a reaction mixture was evaporated under vacuum to remove catalyst and solvent. Deuterated naringenin (**12**) was obtained as a pale yellowish white solid (0.993 g) in >98% yield with >95% deuterium incorporation.

2.7 g scale

A reaction flask (25 mL) with a glass stopper was charged with naringenin (2.7 g, 9.4 mmol), 3.0 mL of dry THF, CD_3OD (5 mL), and 1 mol% of catalys **1**. A reaction mixture was stirred at room temperature for 24 h. Then a reaction mixture was evaporated under vacuum to remove catalyst and solvents. Deuterated naringenin (**12**) was obtained as a yellowish white solid (2.7 g) in >99% yield with >80% incorporation of deuterium.

*Progesterone (**49**)*

A reaction flask (25 mL) with a glass stopper was charged with progesterone (**49**) (1 g, 3.17 mmol), CD_3OD (10 mL), and 1 mol% of catalyst **1**. A reaction mixture was stirred at room temperature for 24 h. Then a reaction mixture was evaporated under vacuum to remove catalyst and solvent. Deuterated progesterone (**49**) was obtained as a white solid (1 g) in >99% yield with 86%-97%% deuterium ncorporation.

*1-Phenylpyrrole (**73**)*

A reaction flask (25 mL) with a glass stopper was charged with 1-phenylpyrrole (**73**) (1 g, 7.0 mmol), CD_3OD (6 mL), and 1 mol% of cat **1**. A reaction mixture was stirred at room temperature for 8 h. Then a reaction mixture was evaporated under vacuum to remove catalyst and solvent. Deuterated 1-phenylpyrrole (**73**) was obtained as a brownish yellow solid (0.997 g) in >98% yield with >94% incorporation of deuterium.

9. Deuteration by acetyl chloride and DCl

Deuteration by acetyl chloride

Deuteration was performed using acetyl chloride which can potentially generate deuterium chloride (DCl) *in situ*. Reaction flask was added with CD_3OD (600 µL, 50 eq) and acetyl chloride (0.6 µL, 0.03 eq) followed by addition of 4'methoxyacetophenone (**20**) (47.4 mg, 0.3 mmol). Reaction mixture was stirred for 4 h and then it was evaporated under reduced pressure to remove acetyl chloride and solvent. Deuterated 4'-methoxyacetophenone (**20**) was obtained as pale yellow solids (47.2 mg) with >98% yield (>95% incorporation of deuterium).

Deuteration by DCl

Deuteration reaction was performed using commercially available DCl (20% solution in D_2O with 99 atom %D). A reaction flask was added CD_3OD (600 µL, 50 eq) and DCl in D_2O (1.5 µL, 0.03 eq) followed by addition of 4'methoxyacetophenone (**20**) (47.3 mg, 0.3 mmol). Reaction mixture was stirred for 4 h, then it was evaporated under reduced pressure to remove DCl and solvent. Deuterated 4'-methoxyacetophenone (**20**) was obtained as pale yellow solids (47.0 mg; >98% yield) with >95% deuteration.

10. Effects of light and temperature on deuteration

Effects of light on deuteration

Deuteration reaction by initiator **1** or acetyl chloride was performed under three conditions, under dark condition, normal day light, and tungsten light. 4'-Methoxyacetophenone (**20**) and 5-nitroindole (**65**) were used as model substrates. Deuteration with initiator **1** and acetyl chloride gave >95% or >97% deuteration of **20** or **65** under dark condition, normal day light, and tungsten light (Supplementary Table 9). These results indicated that deuteration using initiator **1** or acetyl chloride is independent of light.

Effects of temperature on deuteration

Deuteration of the model compounds, 4'-methoxyacetophenone (**20**) and 5-nitroindole (**65**), was conducted at -10 ˚C and at room temperature using initiator **1** or acetyl chloride. Interestingly, less than 8% or 2% deuteration of **20** or **65** were observed at -10 ˚C, while >95% or >97% deuteration for **20** or **65** observed at room temperature (Supplementary Table 9), suggesting that the generation of DBr from initiator **1** is more likely to depend on temperature. When using acetyl chloride as a catalyst, >97% deuteration were obtained both at -10 ˚C and room temperature (Supplementary Table 9), suggesting that deuteration by acetyl chloride did not depend on temperature.

Supplementary Table 9. Effect of light and temperature on deuteration using **1** and acetyl chloride as catalysts and compounds **20** and **65** as model substrates. Experiments were performed in duplicate; [a] 4 h reaction time, [b] 24 h reaction time.

Compound/ Catalyst	Effects of light, %Deuteration			Effects of temperature, %Deuteration	
	Dark	Day light	Tungsten light	Room temperature	-10 ˚C
4'-Methoxyacetophenone **(20)**/ Initiator **1**, experiment 1[a]	>95	>95	>95	>95	<7
4'-Methoxyacetophenone **(20)**/ Initiator **1**, experiment 2[a]	>95	>95	>95	>95	<8
5-Nitroindole (**65)**/ Initiator **1**, experiment 1[b]	>97	>97	>97	>97	<2
5-Nitroindole (**65)/** Initiator **1,** experiment 2**[b]**	>97	>97	>97	>97	<2
4'-Methoxyacetophenone **(20)**/ Acetyl chloride, experiment 1[a]	>95	>95	>95	>95	>95
4'-Methoxyacetophenone **(20)**/ Acetyl chloride, experiment 2[a]	>95	>95	>95	>95	>95
5-Nitroindole (**65)**/Acetyl chloride, experiment 1[b]	>97	>97	>97	>97	>97
5-Nitroindole (**65)/**Acetyl chloride**,** experiment 2**[b]**	>97	>97	>97	>97	>97

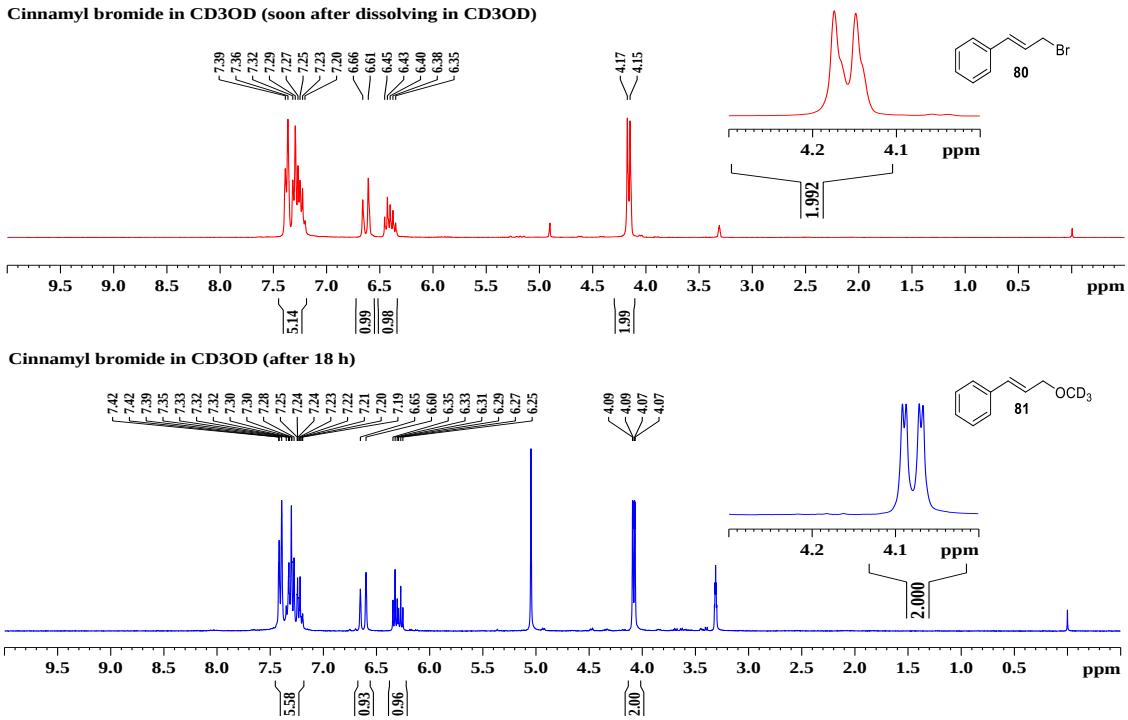
11. Deuteration by cinnamyl bromide (80)

A reaction vessel with a glass stopper was charged with 4'-methoxyacetophenone (**20**) (47.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of cinnamyl bromide (**80)**. The reaction mixture was stirred at room temperature for 4 h, and it was transferred to an NMR tube. Deuteration was observed at a methyl group next to carbonyl carbon with >90% deuteration.

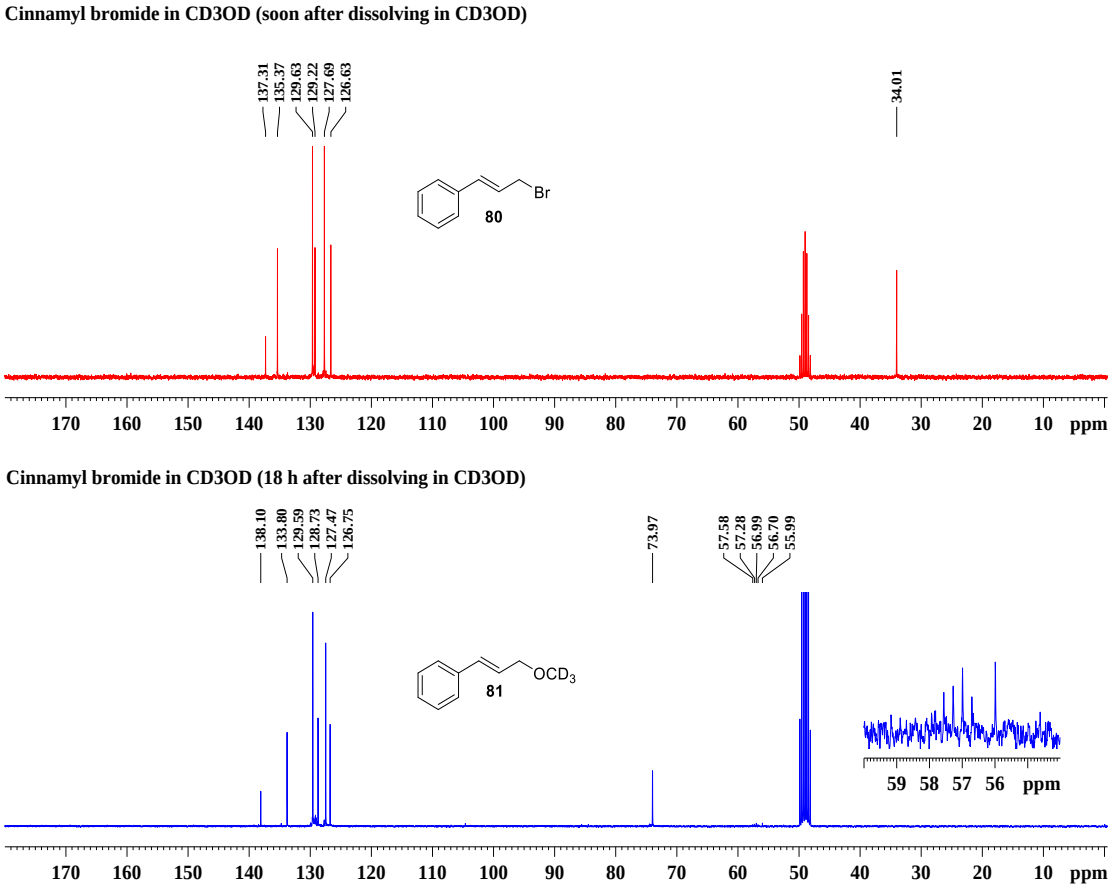
12. Conversion of cinnamyl bromide (80) to a product 81 in CD_3OD

Cinnamyl bromide (**80**) (25 mg) was dissolved in CD_3OD. With this amount (25 mg) of **80** in CD_3OD, it was found that **80** was transformed to a product **81** completely after 18 h, as indicated by ^1H and ^{13}C NMR spectra (Supplementary Figure C1 and Supplementary Figure C2). Therefore, compound **80** spontaneously converted to **81** after 18 h. ^1H NMR resonance (at δ_H 4.16) of methylene protons in cinnamyl bromide (**80**) had similar chemical shift to that (δ_H 4.07) of the product **81**. However, and ^{13}C NMR resonance of a methylene carbon of a products **81** at δ_C 73.97 was far different than that at δ_C 34.01 of cinnamyl bromide (**80**) (Supplementary Figure C2). The resonance at δ_C 73.97 of **81** suggested that this carbon bearing an oxygen atom. ^{13}C NMR of a carbon in $-OCD_3$ moiety of **81** resonated at δ_C 57.0 with characteristics of a carbon bearing D atom (Supplementary Figure C2). HMBC spectrum showed the correlation from methylene protons ($-CH_2-O$) to a carbon of $-OCD_3$ (Supplementary Figure C3). These NMR data established the structure of **81**.

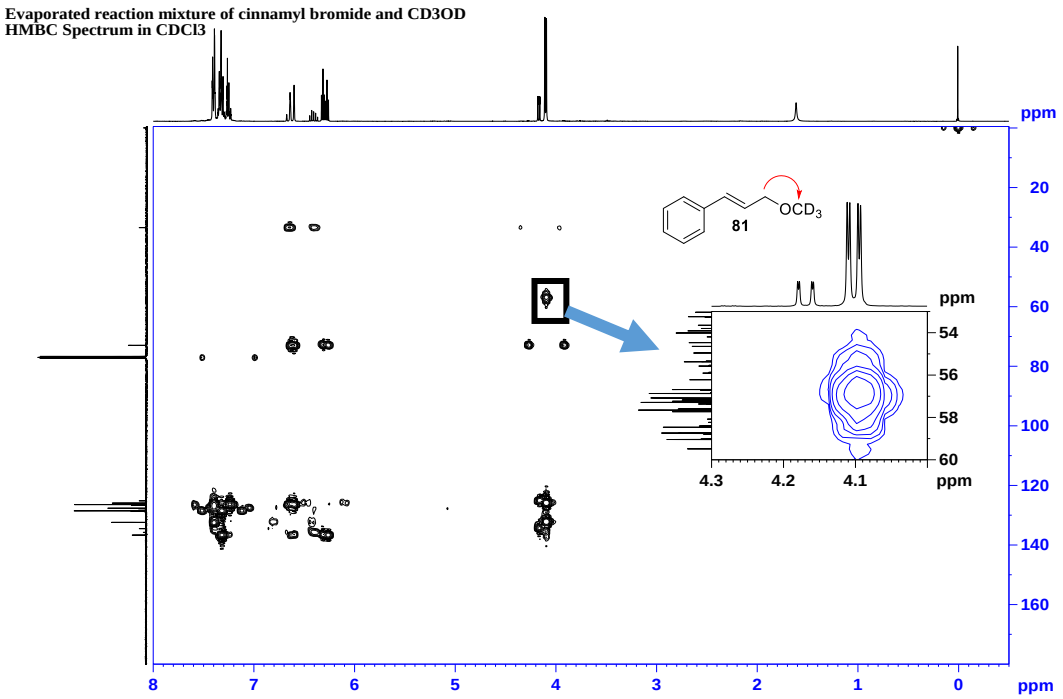
Solution of **81** in CD_3OD was evaporated to dryness using a rotary evaporator, then $CDCl_3$ was used as NMR solvent. ^1H NMR spectrum of **81** in $CDCl_3$ was acquired and shown in Supplementary Figure C4. It was found that a protion of compound **81** was converted back to **80** possibly during evaporation of CD_3OD.



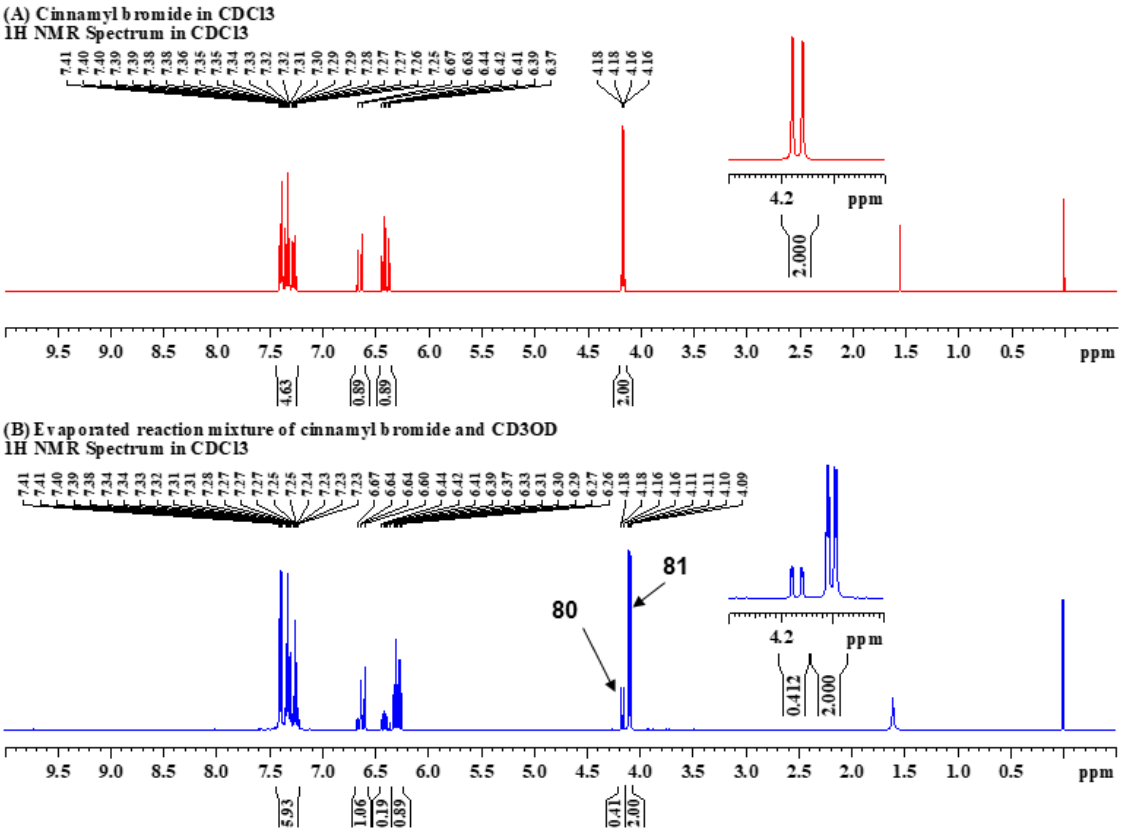
Supplementary Figure C1. ^1H NMR spectrum of cinnamyl bromide (**80**) (25 mg) (300 MHz, in CD_3OD) (top), and ^1H NMR spectrum product **81** obtained after leaving an NMR tube containg **80** at room temperature for 18 h (bottom), indicating that **80** spontaneously converted to **81** after 18 h



Supplementary Figure C2. ^{13}C NMR spectrum (in CD_3OD) of cinnamyl bromide (**80**) (25 mg) (top), and ^{13}C NMR spectrum (in CD_3OD) of a product **81** obtained after leaving an NMR tube containg **80** at room temperature for 18 h (bottom). ^{13}C NMR of a carbon in -OCD_3 moiety of **81** resonated at δ_C 57.0 (expansion) with characteristics of a carbon bearing D atom.



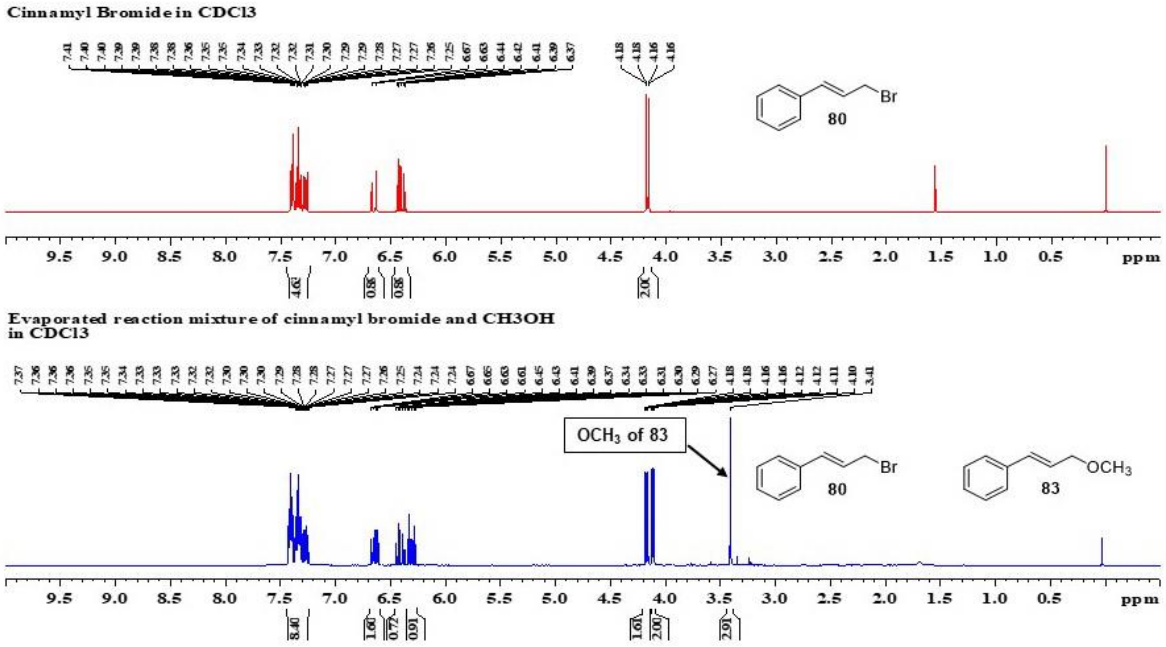
Supplementary Figure C3. HMBC spectrum of a product **81**. HMBC correlation was observed from -CH_2-O protons to a carbon of -OCD_3 group at δ_C 57.0 (expansion).



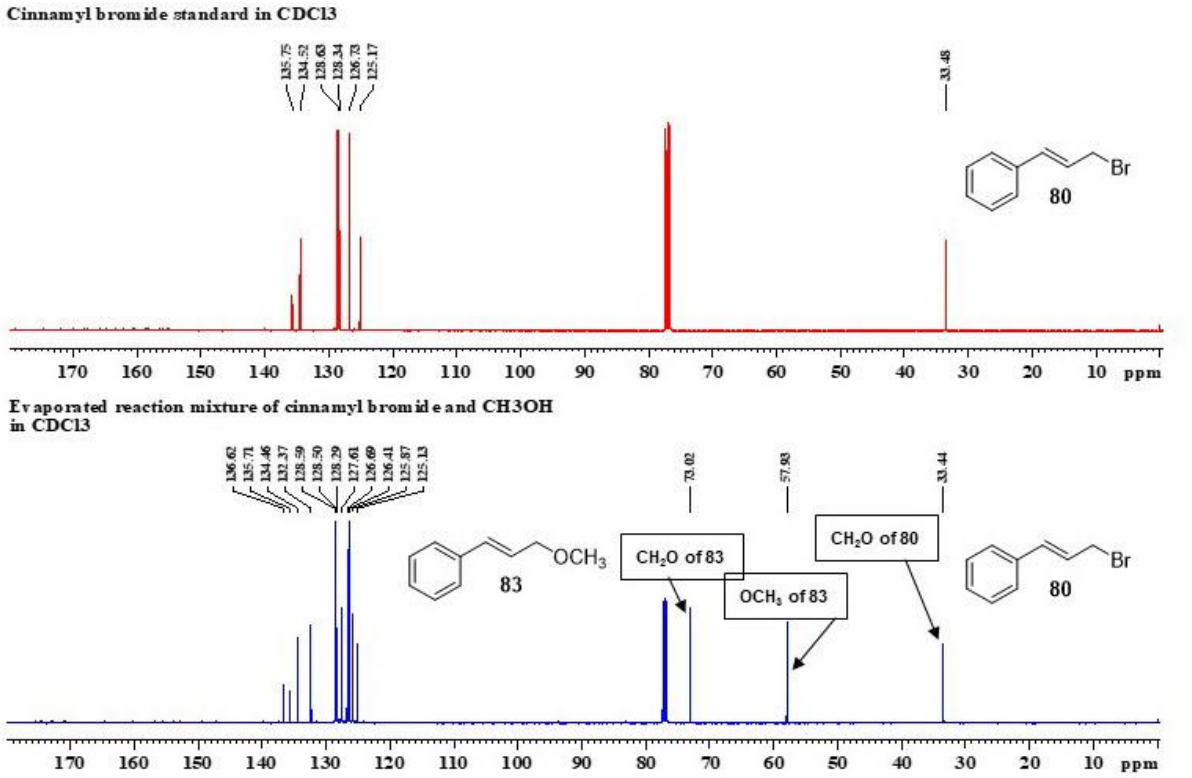
Supplementary Figure C4. ^{1}H NMR spectrum of cinnamyl bromide (**80**) (25 mg) (300 MHz, in CD_3Cl) (top), and ^{1}H NMR spectrum (300 MHz, in CD_3Cl) of **81** after evaporation of CD_3OD and changing NMR solvent to CD_3Cl (bottom). Signals of cinnamyl bromide (**80**) were observed in a sample of **81** after evaporation, indicating that a protion of **81** was converted back to **80** possibly during evaporation of CD_3OD.

13. Conversion of cinnamyl bromide (80) to a product 83 in CH_3OH

Cinnamyl bromide (25 mg) (**80**) was dissolved in CH_3OH (0.6 mL), and this solution was stirred at room temperature for 24 h. After evaporation of CH_3OH, ^{1}H NMR spectrum of this sample was acquired and shown in Supplementary Figure C5. ^{13}C NMR spectrum of this sample is displayed in Supplementary Figure C6. It was found that around 50% of cinnamyl bromide (**80**) converted to a product **83**, as indicated by ^{1}H NMR spectrum (Supplementary Figure C5). ^{1}H NMR resonance (δ_H 4.19) of methylene protons (-CH_2-O) of a product **83** was close to that (δ_H 4.17) of cinnamyl bromide (**80**) (Supplementary Figure C5), but ^{13}C NMR resonance of the methylene carbon of **83** at δ_C 73.02 (a characteristic δ_C for carbon bearing an oxygen atom) was much different from that (δ_C 33.44) of cinnamyl bromide (**80**) (Supplementary Figure C6). Moreover, NMR signals for OCH_3 group in **83** were observed at δ_H 3.41 and δ_C 57.93 (Supplementary Figures C5 and C6).



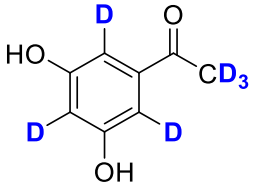
Supplementary Figure C5. ^{1}H NMR spectrum of cinnamyl bromide (**80**) (400 MHz, $CDCl_3$) (top), and ^{1}H NMR spectrum of a product **83** (400 MHz, $CDCl_3$) (bottom).



Supplementary Figure C6. ^{13}C NMR spectrum (in $CDCl_3$) of cinnamyl bromide (**80**) (top), and ^{13}C NMR spectrum (in $CDCl_3$) of a product **83** (bottom).

14. Deuteration procedure of individual compounds and spectroscopic data of deuterated compounds

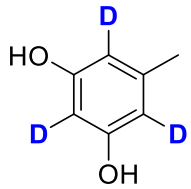
3',5'-Dihydroxyacetophenone-d_6 (**7**)



A reaction vessel with a glass stopper was charged with 3',5'-dihydroxyacetophenone (**7**) (46.6 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 3',5'-dihydroxyacetophenone (**7**) was obtained as a brownish

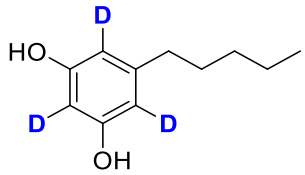
solid (46.6 mg) in >98% yield with >94% incorporation of deuterium. Mesitylene (0.15 mmol) was used as the internal standard. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.88 (s, 0.09H), 6.51 (s, 0.05H), 2.44 (m, *J*=2.2 Hz, 0.09H); ^{13}C NMR: (100 MHz, CD_3OD) δ 200.70, 159.81, 140.11, 108.25 (t, $J_{(C\text{-}D)}$=25.1Hz), 107.47 (t, $J_{(C\text{-}D)}$=26.4Hz), 26.29 (m, $J_{(C\text{-}D)}$=19.4Hz); HRMS (APCI) exact mass calculated for $[M\text{-}H]^-$ ($C_8HD_6O_3$) requires *m/z* 157.07663, found *m/z* 157.0768.

Orcinol-d_3 (**8**)



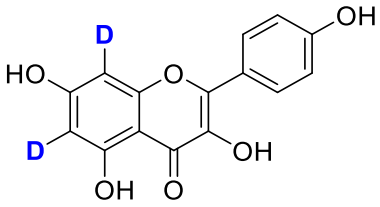
A reaction vessel with a glass stopper was charged with orcinol monohydrate (43 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated orcinol (**8**) was obtained as a light brown solid (42.7 mg) in >98% yield with >98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.11 (s, 0.02H), 6.06 (s, 0.01H), 2.16 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 159.13, 140.96, 108.24 (t, $J_{(C\text{-}D)}$=24.1 Hz), 100.40 (t, $J_{(C\text{-}D)}$=24.1 Hz), 21.44; HRMS (APCI) exact mass calculated for $[M\text{-}H]^-$ ($C_7H_4D_3O_2$) requires 126.06289, found *m/z* 126.0627.

Olivetol-d_3 (**9**)



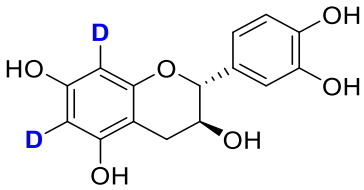
A reaction vessel with a glass stopper was charged with olivetol (38 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated olivetol (**9**) was obtained as a brownish yellow solid (38 mg) in 98% yield with >86% deuterium incorporation. ^{1}H NMR: (300 MHz, CD_3OD) δ 6.12 (s, 0.14H), 6.07 (s, 0.14H), 6.75 (s, 1H), 2.43 (t, *J*=7.6, 2H), 1.57 (quint, *J*=7.4 Hz, 2H), 1.39-1.29 (m, 4H), 0.90 (t, *J*=6.9 Hz, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 159.16, 146.15, 107.61 (t, $J_{(C\text{-}D)}$=23.5 Hz), 100.69 (t, $J_{(C\text{-}D)}$=21.6 Hz), 36.83, 32.61, 32.12, 23.59, 14.38; HRMS (APCI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}D_3O_2$) requires *m/z* 184.14114, found *m/z* 184.1414.

Kaempferol-d_2 **(10)**



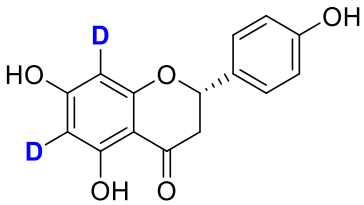
A reaction vessel with a glass stopper was charged with kaempferol (29.7 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated kaempferol (**10**) was obtained as a yellow solid in >98% yield with >92% deuterium incorporation. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.07 (d, *J*=8.9 Hz, 1H), 6.90 (d, *J*=8.9 Hz, 1H), 6.39 (s, 0.04H), 6.17 (s, 0.08H); ^{13}C NMR: (100 MHz, CD_3OD) δ 177.29, 165.47, 162.39, 160.54, 158.18, 148.10, 137.07, 130.68, 123.71, 116.30, 104.52, 99.03 (t, $J_{(C\text{-}D)}$=24.4 Hz), 94.25 (t, $J_{(C\text{-}D)}$=23.1 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_9D_2O_6$) requires *m/z* 289.06757, found *m/z* 289.0676.

Catechin-d_2 (**11**)



A reaction vessel with a glass stopper was charged with catechin (32.4 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated catechin (**11**) was obtained as a brown solid (32.3 mg) in >98% yield with >98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.84 (d, *J*=1.9 Hz, 1H), 6.77 (d, *J*=8.1 Hz, 1H), 6.72 (dd, *J*=8.2, 1.9 Hz, 1H), 5.93 (s, 0.01H), 5.86 (s, 0.01H), 4.56 (d, *J*=7.5 Hz, 1H), 4.01-3.94 (m, 1H), 2.85 (dd, *J*=16.2, 5.5, 1H), 2.50 (dd, *J*=16.1, 8.2, 1H); ^{13}C NMR: (100 MHz, CD_3OD) δ 157.74, 157.50, 156.85, 146.25, 146.22, 132.23, 120.04, 116.09, 115.27, 100.83, 96.06 (t, $J_{(C\text{-}D)}$=24.6 Hz), 95.28 (t, $J_{(C\text{-}D)}$=23.7 Hz), 82.85, 68.81, 28.51; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{13}D_2O_6$) requires *m/z* 293.09887, found *m/z* 293.0990.

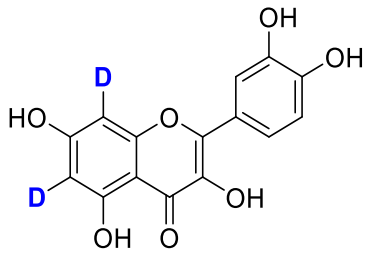
Naringenin-d_2 (**12**)



A reaction vessel with a glass stopper was charged with naringenin (29.2 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated naringenin (**12**) was obtained as a yellowish white solid (29.1 mg) in >98% yield

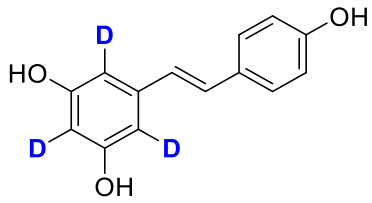
with >95% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.29 (d, *J*=8.6 Hz, 2H), 6.81 (d, *J*=8.6 Hz, 2H), 5.88 (d, *J*=2.0 Hz, 0.10H), 5.28 (dd, *J*=13.0, 2.9 Hz, 1H), 3.07 (dd, *J*=18.6, 13.0 Hz, 1H), 2.68 (dd, *J*=17.1, 3.0 Hz, 1H); ^{13}C NMR: (75 MHz, CD_3OD) δ 197.71, 168.16, 165.33, 164.74, 158.92, 131.03, 129.00, 116.29, 103.32, 96.78 (t, $J_{(C-D)}$=26.0 Hz), 95.89 (t, $J_{(C-D)}$=24.9 Hz), 80.39, 43.94; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{11}D_2O_5$) requires *m/z* 275.08830, found *m/z* 275.0884.

Quercetin-d_2 (**13**)



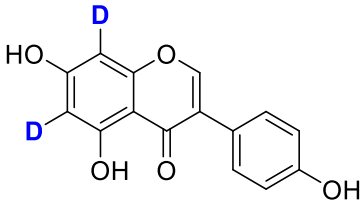
A reaction vessel with a glass stopper was charged with quercetin (31.5 mg, 0.1 mmol), dry THF (0.3 mL), CD_3OD (0.6 mL, 150eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvents. Deuterated quercetin (**13**) was obtained as a yellowish orange solid (31.5) in >98% yield with >94% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.73 (d, *J*=2.2 Hz, 1H), 7.63 (dd, *J*=8.5, 2.2 Hz, 1H), 6.88 (d, *J*=8.5 Hz, 1H), 6.39 (s, 0.02H), 6.18 (s, 0.06H); ^{13}C NMR: (100 MHz, CD_3OD) δ 177.32, 165.48, 162.44, 158.15, 148.77, 147.98, 146.22, 137.23, 124.12, 121.65, 116.20, 115.96, 104.49, 99.00 (t, $J_{(C-D)}$=25.2 Hz), 94.14 (t, $J_{(C-D)}$=23.25 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_9D_2O_7$) requires *m/z* 305.06248, found *m/z* 305.0625.

Resveratrol-d_3 (**14**)



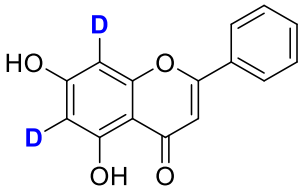
A reaction vessel with a glass stopper was charged with resveratrol (23 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated resveratrol (**14**) was obtained as a brown solid (22.9 mg) in >98% yield with >92% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.35 (d, *J*=8.6 Hz, 2H), 6.95 (d, *J*=16.3 Hz, 1H), 6.80 (d, *J*=17.2 Hz, 1H), 6.75 (d, *J*=8.7 Hz, 1H), 6.45 (s, 0.08H), 6.16 (s, 0.08H); ^{13}C NMR: (100 MHz, CD_3OD) δ 159.53, 158.34, 141.15, 130.44, 129.40, 128.79, 126.95, 116.48, 105.50 (t, $J_{(C-D)}$=24.2 Hz), 102.42 (t, $J_{(C-D)}$=23.5 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{10}D_3O_3$) requires *m/z* 232.10475, found *m/z* 232.1048.

Genistein-d_2 (**15**)



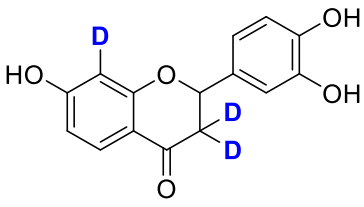
A reaction vessel with a glass stopper was charged with genistein (27.6 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated genistein (**15**) was obtained as a yellow solid in >98% yield with >95% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.06 (s, 1H), 7.37 (d, *J*= 8.0Hz, 2H), 6.84 (d, *J*= 8.0Hz, 2H), 6.34 (s, 0.03H), 6.22 (s, 0.05H); ^{13}C NMR: (100 MHz, CD_3OD) δ 182.26, 165.88, 163.80, 159.66, 158.84, 154.82, 131.39, 124.72, 123.29, 116.25, 106.27, 99.86 (t, $J_{(C\text{-}D)}$=24.4 Hz), 94.54 (t, $J_{(C\text{-}D)}$=25.8 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_9D_2O_5$) requires *m/z* 273.07265, found *m/z* 273.0727.

Chrysin-d_2 (**16**)



A reaction vessel with a glass stopper was charged with chrysin (26.7 mg, 0.1 mmol), dry THF (0.3 mL), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvents. Deuterated chrysin (**16**) was obtained as a yellow solid (26.5) in >98% yield with 60-98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.00 (m, *J*=7.8, 1.7 Hz, 2H), 7.61-7.54 (m, 3H), 6.75 (s, 1H), 6.49 (s, 0.01H), 6.23 (s, 0.40H); ^{13}C NMR: (100 MHz, CD_3OD) δ 183.93, 166.26, 165.69, 163.31, 159.51, 133.08, 132.55, 130.25, 127.46, 106.07, 105.56, 100.03 (t, $J_{(C\text{-}D)}$=24.9 Hz), 94.91 (t, $J_{(C\text{-}D)}$=25.5 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_9D_2O_4$) requires *m/z* 257.077739, found *m/z* 257.0783.

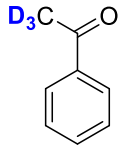
Butin-d_2 (**18**)



A reaction vessel with a glass stopper was charged with butein (**17**) (27.2 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Dried reaction mixture was purified by semi-preparative HPLC using C_{18} column and 25-80% Acetonitrile AR in water. Butin was eluted at 36 min retention time and was dried under reduced pressure. Deuterated butin (**18**) was obtained as a brown solid (14.6 mg) in 54% yield with >91% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.72 (d, *J*=8.7 Hz,

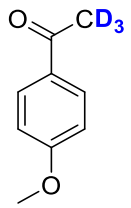
1H), 6.93 (s, 1H), 6.75-6.85 (m, 2H), 6.49 (dd, *J*=8.7, 2.0 Hz, 1H), 6.36 (d, *J*= 2.16 Hz, 0.83H), 5.31 (s, 1H), 2.99 (d, *J*=13.0 Hz, 0.08H), 2.67 (s, 0.08H); ^{13}C NMR: (100 MHz, CD_3OD) δ 193.59, 166.77, 165.52, 146.80, 146.47, 132.02, 129.81, 119.22, 116.24, 115.00, 114.70, 111.70, 103.82, 80.94, 44.48 (m, $J_{(C-D)}$=20.1 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{11}D_2O_5$) requires *m/z* 275.0883, found *m/z* 275.0883.

Acetophenone-d_3 (**19**)



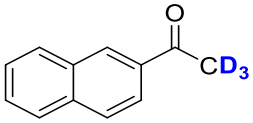
A reaction vessel (5 mL) with a glass stopper was charged with acetophenone (36.8 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq) and and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 4 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated acetophenone (**19**) was obtained as a yellowish oil (36.4 mg) in >97% yield with >91% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.98 (d, *J*=7.4Hz, 1H), 7.59 (t, *J*=7.4Hz, 1H), 7.48 (t, *J*=7.7 Hz, 1H), 2.54 (m, *J*=2.2 Hz, 0.27H); ^{13}C NMR: (100 MHz, CD_3OD) δ 200.59, 138.29, 134.39, 129.70, 129.40, 26.22 (m, $J_{(C-D)}$=19.5 Hz); HRMS (APCI) exact mass calculated for $[M+H]^+$ ($C_8H_6D_3O$) requires *m/z* 124.08362, found *m/z* 124.0837.

4'-Methoxyacetophenone-d_3 (**20**)



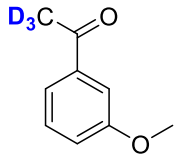
A reaction vessel with a glass stopper was charged with 4'-methoxyacetophenone (47.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 4 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 4'-methoxyacetophenone (**20**) was obtained as a pale yellow crystals (47.3 mg) in >98% yield with >98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.94 (d, *J*=8.8 Hz, 2H), 6.97 (d, *J*=8.9 Hz, 1H), 3.85 (s, 3H), 2.49 (quint, *J*=2.2 Hz, 0.05H); ^{13}C NMR: (100 MHz, CD_3OD) δ 199.46, 165.35, 131.81, 131.26, 114.82, 56.02, 25.64 (t, $J_{(C-D)}$=19.5Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_8D_3O_2$) requires *m/z* 154.09419, found *m/z* 154.0941.

2-Acetylnaphthalene-d_3 (**21**)



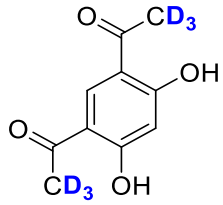
A reaction vessel with a glass stopper was charged with 2-acetylnaphthalene (34.7 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2-acetylnaphthalene (**21**) was obtained as a white solid (34.6 mg) in >98% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CDCl3) δ 8.43 (s, 1H), 8.01 (dd, *J*=8.6, 1.6Hz, 1H), 7.93 (d, *J*=8.0 Hz, 1H), 7.86 (d, *J*=8.6 Hz, 1H), 7.84 (d, *J*=8.0 Hz, 1H), 7.58 (td, *J*=6.9, 1.3 Hz, 1H), 7.53 (td, *J*=6.9, 1.2 Hz, 1H), 2.67 (m, *J*=2.2 Hz, 0.29H); ^{13}C NMR: (100 MHz, CDCl3) δ 198.27, 135.46, 134.28, 132.36, 130.12, 129.42, 128.37, 128.29, 127.64, 126.65, 123.70, 25.92 (m, $J_{(C\text{-}D)}$=19.5 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_8D_3O$) requires *m/z* 174.09927, found *m/z* 174.0994.

3'-Methoxyacetophenone-d_3 (**22**)



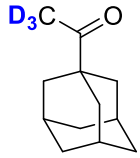
A reaction vessel with a glass stopper was charged with 3'-methoxyacetophenone (47.4mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 4 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 3'-methoxyacetophenone (**22**) was obtained as a yellowish brown oil (47.0mg) in >97% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.55 (d, *J*=7.7Hz, 1H), 7.46 (t, *J*=2.0Hz, 1H), 7.38 (t, *J*=7.9 Hz, 1H), 7.14 (dd, *J*=8.2, 2.6 Hz, 1H), 3.82 (s, 3H), 2.53 (m, *J*=2.3 Hz, 0.27H); ^{13}C NMR: (100 MHz, CD_3OD) δ 200.33, 161.30, 139.61, 130.77, 122.09, 120.41, 113.65, 55.82, 26.22 (m, $J_{(C\text{-}D)}$=19.5 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_8D_3O_2$) requires *m/z* 154.09419, found *m/z* 154.0942.

4,6-Diacetylresorcinol-d_6 (**23**)



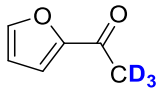
A reaction vessel with a glass stopper was charged with 4,6-diacetylresorcinol (9.7 mg, 0.05 mmol), CD_3OD (0.6 mL, 300 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 4,6-diacetylresorcinol (**23**) was obtained as white crystals (9.7 mg) in >98% yield with >85% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.46 (s, 1H), 6.33 (s, 1H), 3.85 (s, 3H), 2.63 (m, *J*=2.2 Hz, 0.89H); ^{13}C NMR: (100 MHz, CD_3OD) 204.93, 169.68, 138.63, 114.93, 104.86, 26.09 (m, $J_{(C\text{-}D)}$=19.6 Hz); HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{10}H_3D_6O_4$) requires *m/z* 199.08720, found *m/z* 199.0876.

1-Acetyladamantane-d_3 (**24**)



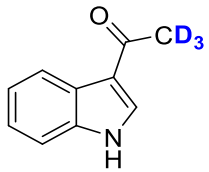
A reaction vessel with a glass stopper was charged with 1-acetyladamantane (36.4 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-acetyladamantane (**24**) was obtained as a yellowish white solid (36.3 mg) in 98% yield with 98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CDCl3) δ 2.19 (s, 0.02H), 2.03 (s, 3H), 1.79-1.65 (m, 12H); ^{13}C NMR: (100 MHz, CDCl3) δ 214.25, 46.43, 38.18, 36.51, 27.89, 23.52 (m, $J_{(C\text{-}D)}$=19.3 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{16}D_3O$) requires *m/z* 182.16187, found *m/z* 182.1620.

2-Acetylfuran-d_3 (**25**)



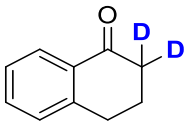
A reaction vessel with a glass stopper was charged with 2-acetylfuran (34.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2-acetylfuran (**25**) was obtained as a yellow viscous oil (33.8 mg) in >98% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.77 (d, *J*=1.1 Hz, 1H), 7.34 (d, *J*=3.6 Hz, 1H), 6.63 (dd, *J*=3.6, 1.7 Hz, 1H) 2.42 (m, *J*=2.3 Hz, 0.28H); ^{13}C NMR: (100 MHz, CD_3OD) δ 188.82, 153.93, 148.64, 119.45, 113.48, 25.29 (quint, $J_{(C\text{-}D)}$=19.6Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_6H_4D_3O_2$) requires *m/z* 114.06289, found *m/z* 114.0632.

3-Acetylindole-d_3 (**26**)



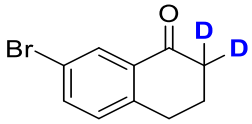
A reaction vessel with a glass stopper was charged with 3-acetylindole (32.5 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 4 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 3-acetylindole (**26**) was obtained as a pale yellow solid (34.6 mg) in >98% yield with >93% incorporation of deuterium. ^{1}H NMR: (400 MHz, CDCl3) δ 8.26-8.20 (m, 1H), 8.10 (s, 1H), 7.45-7.40 (m, 1H), 7.25-7.15 (m, 2H), 2.46 (m, *J*=2.2 Hz, 0.19H); ^{13}C NMR: (100 MHz, CDCl3) δ 196.64, 138.45, 135.54, 126.78, 124.26, 123.20, 122.79, 118.47, 112.84, 26.41 (m, $J_{(C\text{-}D)}$=19.5 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_7D_3ON$) requires *m/z* 163.09452, found *m/z* 163.0947.

1-Tetralone-d_2 (**27**)



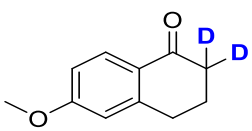
A reaction vessel with a glass stopper was charged with 1-tetralone (44.8 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-tetralone (**27**) was obtained as a brownish oil (44.5 mg) in >98% yield with >97% deuterium incorporation. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.92 (dd, *J*=8.4, 1.4 Hz, 1H), 7.49 (td, *J*=7.5, 1.3 Hz, 1H), 7.27-7.30 (m, 2H), 2.95 (t, *J*=6.1 Hz, 2H), 2.61-2.56 (m, *J*=2.5 Hz, 0.05H), 2.08 (t, *J*=6.0 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3OD) δ 200.75, 146.44, 134.82, 133.54, 130.04, 127.77, 127.60, 39.30 (quint, $J_{(C\text{-}D)}$=19.6 Hz), 30.42, 24.25; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_9D_2O$) requires *m/z* 149.0931, found *m/z* 149.0930.

7-Bromo-1-tetralone-d_2 (**28**)



A reaction vessel with a glass stopper was charged with 7-bromo-1-tetralone (47.4 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 7-bromo-1-tetralone (**28**) was obtained as a yellow solid (47.1 mg) in >98% yield with >98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.98 (d, *J*=2.2 Hz, 1H), 7.60 (dd, *J*=8.2, 2.2 Hz, 1H), 7.24 (d, *J*=8.2 Hz, 1H), 2.93 (t, *J*=6.1 Hz, 2H), 2.63-2.57 (m, *J*=2.8 Hz, 0.04H), 2.09 (t, *J*=6.1 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3OD) δ 199.02, 145.28, 137.28, 135.17, 132.24, 130.33, 121.30, 38.89 (quint, $J_{(C\text{-}D)}$=19.6 Hz), 29.84, 23.89; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_8D_2O^{79}Br$) requires *m/z* 227.00351, found *m/z* 227.0037, [M+H] ($C_{10}H_8D_2O\,^{81}Br$) requires *m/z* 229.0015, found *m/z* 229.0018.

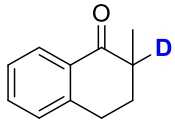
6-Methoxy-1-tetralone-d_2 (**29**)



A reaction vessel with a glass stopper was charged with 6-methoxy-1-tetralone (35.6 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 6-methoxy-1-tetralone (**29**) was obtained as a light brown solid (35.6 mg) in >98% yield with >97% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.88 (d, *J*=8.7 Hz, 1H), 6.82 (dd, *J*=8.7, 2.5 Hz, 1H), 6.78 (d, *J*=2.4 Hz, 1H), 3.84 (s, 3H), 2.92

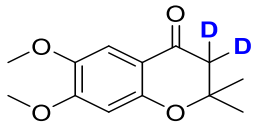
(t, *J*=6.1 Hz, 2H), 2.57-2.50 (m, 0.05H), 2.05 (t, *J*=6.1 Hz, 2H); ^{13}C NMR: (75 MHz, CD_3OD) δ 199.86, 165.50, 149.18, 130.30, 127.00, 114.33, 113.59, 55.99, 39.06 (quint, $J_{(C\text{-}D)}$=19.5 Hz), 30.85, 24.31; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{11}D_2O_2$) requires *m/z* 179.10356, found *m/z* 179.1033.

2-Methyl-1-tetralone-d_1 (**30**)



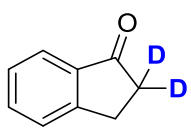
A reaction vessel with a glass stopper was charged with 2-methyl-1-tetralone (32.7 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2-methyl-1-tetralone (**30**) was obtained as a yellowish brown oil (32.4 mg) in 98% yield with >76% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.92 (dd, *J*=7.0, 1.6 Hz, 1H), 7.47 (dt, *J*=7.5, 1.5 Hz, 1H), 7.28 (t, *J*=7.5 Hz, 2H), 3.10-2.91 (m, 2H), 2.64-2.52 (m, 0.23H), 2.23-2.14 (m, 1H), 1.88-1.74 (m, 1H), 1.21 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 202.91, 146.05, 134.50, 133.35, 129.99, 127.97, 127.53, 43.30 (t, $J_{(C\text{-}D)}$=19.1 Hz), 32.47, 29.61, 15.60; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}DO$) requires *m/z* 162.10237, found *m/z* 162.1025.

6,7-Dimethoxy-2,2-dimethyl-4-chromanone-d_2 (**31**)



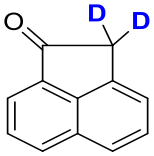
A reaction vessel with a glass stopper was charged with 6,7-dimethoxy-2,2-dimethyl-4-chromanone (24.8 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 6,7-dimethoxy-2,2-dimethyl-4-chromanone (**31**) was obtained as a yellowish white solid (24.8 mg) in 98% yield with >97% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.19 (s, 1H), 6.47 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.65 (s, 0.04H), 1.42 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 193.49, 158.46, 158.37, 145.51, 113.21, 107.56, 101.86, 80.58, 56.65, 56.61, 48.06 (overlapped m, $J_{(C\text{-}D)}$=19.5 Hz), 26.61; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}D_2O_4$) requires *m/z* 239.12469, found *m/z* 239.1245.

1-Indanone-d_2 (**32**)



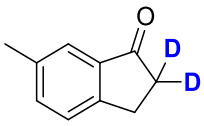
A reaction vessel with a glass stopper was charged with 1-indanone (27.8 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-indanone (**32**) was obtained as a white solid (27.6 mg) in 98% yield with 96% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.66 (d, *J*=7.7 Hz, 1H), 7.61 (t, *J*=7.6 Hz, 1H), 7.51 (d, *J*=7.7 Hz, 1H), 7.36 (t, *J*=7.4 Hz, 1H), 3.10 (s, 2H), 2.59-2.63 (m, *J*=2.9 Hz, 0.07H); ^{13}C NMR: (100 MHz, CD_3OD) δ 209.75, 157.26, 137.94, 136.07, 128.34, 127.99, 124.31, 36.44(m, $J_{(C-D)}$=20 Hz), 26.46; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_7D_2O$) requires *m/z* 135.07734, found *m/z* 135.0775.

1-Acenaphthenone-d_2 (**33**)



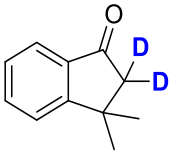
A reaction vessel with a glass stopper was charged with 1-acenapthenone (34.3 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-acenapthenone (**33**) was obtained as a yellowish brown solid (34.0 mg) in 98% yield with >95% incorporation of deuterium. ^{1}H NMR: (400 MHz, CDCl3) δ 8.07 (d, *J*=8.1 Hz, 1H), 7.95 (t, *J*=7.0 Hz, 1H), 7.81 (t, *J*=8.4 Hz 1H), 7.70 (t, *J*=7.3 Hz, 1H), 7.59 (d, *J*=7.0 Hz, 1H), 7.45 (d, *J*=6.8 Hz, 1H), 3.78 (br t, *J*=2.6 Hz, 0.1H); ^{13}C NMR: (100 MHz, CDCl3) δ 203.01, 142.96, 134.85, 134.65, 131.41, 130.87, 128.31, 127.92, 123.90, 121.34, 121.0, 41.63 (m, $J_{(C-D)}$=19.9 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_7D_2O$) requires *m/z* 171.07734, found *m/z* 171.0774.

6-Methyl-1-indanone-d_2 (**34**)



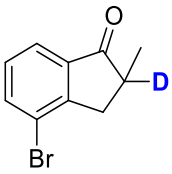
A reaction vessel with a glass stopper was charged with 6-methyl-1-indanone (30 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 6-methyl-1-indanone (**34**) was obtained as a yellowish white solid (29.9 mg) in >98% yield with 98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.43-7.34 (m, 3H), 3.01 (s, 2H), 2.59-2.55 (m, *J*=2.9 Hz, 0.03H), 2.34 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 209.74, 154.61, 138.46, 138.06, 137.27, 127.61, 124.14, 36.75(q, $J_{(C-D)}$=20 Hz), 26.05, 21.02; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{10}H_8D_2ONa$) requires *m/z* 171.0749, found *m/z* 171.0756.

3,3-Dimethyl-1-indanone-d_2 (**35**)



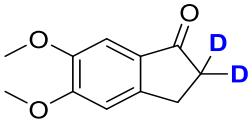
A reaction vessel with a glass stopper was charged with 3,3-dimethyl-1-indanone (32.7 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 3,3-dimethyl-1-indanone (**35**) was obtained as a brown oil (32.5 mg) in >98% yield with >88% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.72-7.58 (m, 3H), 7.39 (dt, *J*=7.6, 1.2 Hz, 1H), 2.56 (m, *J*=2.8 Hz, 0.23H), 1.41 (s, 6H); ^{13}C NMR: (75 MHz, CD_3OD) δ 208.33, 165.73, 136.56, 128.64, 124.96, 124.05, 53.43 (m, $J_{(C\text{-}D)}$=20.3 Hz), 39.48, 30.09; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{11}D_2O$) requires *m/z* 163.10865, found *m/z* 163.1086.

4-Bromo-2-methyl-1-indanone-d_1 (**36**)



A reaction vessel with a glass stopper was charged with 4-Bromo-2-methyl-1-indanone (46.0 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 4-bromo-2-methyl-1-indanone (**36**) was obtained as a yellowish oil (46.0 mg) in 98% yield with >85% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.79 (dd, *J*=7.8, 0.8 Hz, 1H), 7.63 (d, *J*=7.54 Hz, 1H), 7.31 (t, *J*=7.7 Hz, 1H), 3.32 (d, *J*=17.64 Hz, 1H), 2.78-2.65 (m, *J*=3.8 Hz, 0.15H), 2.61 (d, *J*=17.65 Hz, 1H), 1.26 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 210.47, 154.62, 139.37, 138.79, 130.54, 123.66, 123.10, 42.78 (t, $J_{(C\text{-}D)}$=19.8 Hz), 36.79, 16.18; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_9DO^{79}Br$) requires *m/z* 225.99723, found *m/z* 225.9969, $[M+H]^+$ ($C_{10}H_9DO^{81}Br$) requires *m/z* 227.9952, found *m/z* 227.9949.

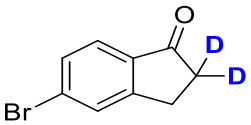
5,6-Dimethoxy-1-indanone-d_2 (**37**)



A reaction vessel with a glass stopper was charged with 5,6-dimethoxy-1-indanone (39.2 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5,6-dimethoxy-1-indanone (**37**) was obtained as a light brown solid (39.1 mg) in >98% yield with >98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.06 (s, 1H), 6.99 (s, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 2.99 (s,2H), 2.57(m, 0.03H); ^{13}C NMR:

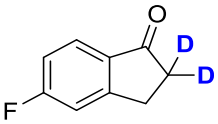
(100 MHz, CD_3OD) δ 208.55, 157.44, 153.02, 150.85, 130.39, 108.95, 104.95, 56.63, 56.35, 36.74 (q, $J_{(C-D)}$=19.98 Hz), 26.25; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{10}D_2O_3Na$) requires *m/z* 217.0804, found *m/z* 217.0804.

5-Bromo-1-indanone-d_2 (**38**)



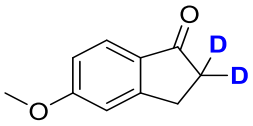
A reaction vessel with a glass stopper was charged with 5-bromo-1-indanone (21.5 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-bromo-1-indanone (**38**) was obtained as a brownish white solid (21.5 mg) in >98% yield with >95% incorporation of deuterium. ^1H NMR: (400 MHz, $CDCl_3$) δ 7.64 (dd, *J*=7.8 ,0.8 Hz, 1H), 7.59 (d, *J*=7.6 Hz, 1H), 7.49 (t, J=7.69, 1H), 3.10 (s, 2H), 2.65 (m, *J*=2.8Hz, 0.09H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 205.63, 156.70, 135.90, 130.90, 129.93, 124.87, 35.48 (quint, $J_{(C-D)}$=20.1 Hz), 25.30; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_6D_2O^{79}Br$) requires *m/z* 212.98786, found *m/z* 212.9879, $[M+H]^+$ ($C_9H_6D_2O^{81}Br$) requires *m/z* 214.9858, found *m/z* 214.9859.

5-Fluoro-1-indanone-d_2 (**39**)



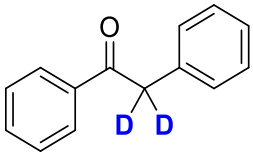
A reaction vessel with a glass stopper was charged with 5-fluoro-1-indanone (31.3 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-fluoro-1-indanone (**39**) was obtained as a white crystals (31.3 mg) in >98% yield with >97% incorporation of deuterium. ^1H NMR: (300 MHz, CD_3OD) δ 7.71 (dd, *J*=8.5, 5.39 Hz, 1H), 7.26 (dt, *J*=8.9, 1.0 Hz, 1H), 7.13 (td, *J*=8.8, 2.26, 1H), 3.14 (s, 2H), 2.70-2.64 (m, 0.06H); ^{13}C NMR: (75 MHz, CD_3OD) δ 207.76, 170.41, 167.03, 160.46 (d, $J_{(C-F)}$=10.4 Hz), 134.58 (d, $J_{(C-F)}$=1.6 Hz), 126.83(d, $J_{(C-F)}$=10.8 Hz), 116.49 (d, $J_{(C-F)}$=24.3 Hz), 114.4 (d, $J_{(C-F)}$=22.6 Hz), 36.71 (quint, $J_{(C-D)}$=21.6 Hz), 26.48 ((d, $J_{(C-F)}$=2.1 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_6D_2OF$) requires *m/z* 153.06792, found *m/z* 153.0679.

5-Methoxy-1-indanone-d_2 (**40**)



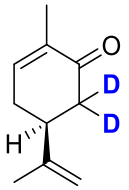
A reaction vessel with a glass stopper was charged with 5-methoxy-1-indanone (33.1 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of catalyst **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-methoxy-1-indanone (**40**) was obtained as a brownish white solid (32.9 mg) in >98% yield with >98% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.58 (d, *J*=8.6 Hz, 1H), 7.00 (s, 1H), 6.91 (dd, *J*=8.6, 2.2 Hz, 1H), 3.87 (s, 3H), 3.06 (s, 2H), 2.61-2.58 (m, *J*=2.7 Hz, 0.03H); ^{13}C NMR: (100 MHz, CD_3OD) δ 208.48, 167.34, 160.75, 130.97, 126.07, 116.69, 110.84, 56.28, 36.92(q, $J_{(C-D)}$=20 Hz), 26.58; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_9D_2O_2$) requires *m/z* 165.08791, found *m/z* 165.0881.

Deoxybenzoin-d_2 (**41**)



A reaction vessel with a glass stopper was charged with deoxybenzoin (20.7 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated deoxybenzoin (**41**) was obtained as a white solid (20.7 mg) in >98% yield with >88% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 8.10-8.00 (m, 2H), 7.65-7.40 (m, 3H), 7.40-7.15 (m, 5H), 4.28-4.34(m, *J*=2.1 Hz, 0.24H); ^{13}C NMR: (75 MHz, CD_3OD) δ 200.37, 134.41, 130.56, 129.75, 129.73, 129.57, 127.78, 45.95 (t, $J_{(C-D)}$=19.5 Hz); HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{14}H_{10}D_2ONa$) requires *m/z* 221.0905, found *m/z* 221.0906.

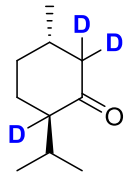
(S)-(+)-Carvone-d_2 (**42**)



A reaction vessel with a glass stopper was charged with (S)-(+)-Carvone (47.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated (S)-(+)-carvone (**42**) was obtained as a yellowish oil (47.2 mg) in >98% yield with >90% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 6.88 (m, *J*=1.4 Hz, 1H), 4.79 (d, *J*=12.2 Hz, 2H), 2.75-2.65 (m, 1H), 2.55-2.28 (m, 2H), 1.80-1.70 (m, 6H); ^{13}C NMR: (75 MHz, CD_3OD) δ 202.07, 148.26, 147.28, 136.08, 110.94, 43.68, 44.10-42.80 (m), 32.26,

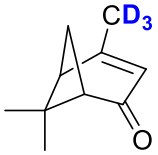
20.59, 15.72; HRMS (APCI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{13}D_2O$) requires *m/z* 153.12430, found *m/z* 153.1241.

(+)-Menthone-d_3 (**43**)



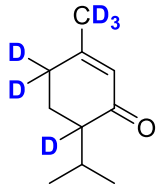
A reaction vessel with a glass stopper was charged with (+)-menthone (47.2 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated menthone (**43**) was obtained as a yellow oil (47.0 mg) in 98% yield with >90% incorporation of deuterium. NMR data suggested that deuterated menthone was obtained as a mixture of two diastereomers. ^{1}H NMR: (400 MHz, CD_3OD) δ 2.40-2.20 (m, 0.10H), 2.15-2.00 (m, 2H), 2.00-1.85 (m, 2H), 1.85-1.69 (m, 2H), 1.50-1.30 (m, 2H), 1.02 (d, *J*=6.5 Hz, 3H), 1.00 (d, *J*=6.7 Hz, 1.5H), 0.94 (d, *J*=6.6 Hz, 1.5H), 0.92 (d, *J*=6.8 Hz, 3H), 0.85 (d, *J*=6.9 Hz, 3H), 0.83 (d, *J*=6.7 Hz, 1.5H); ^{13}C NMR: (100 MHz, CD_3OD) δ 217.36, 215.14, 58.05 (t, $J_{(C\text{-}D)}$=19.8 Hz), 56.40 (t, $J_{(C\text{-}D)}$=18.9 Hz), 51.02 (m, $J_{(C\text{-}D)}$=19.4 Hz), 36.85, 35.64, 34.78, 30.33, 29.21, 27.88, 27.08, 22.53, 21.42, 21.27, 20.15, 19.11; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{16}D_3O$) requires *m/z* 158.16187, found *m/z* 158.1620.

(1S)-(-)-Verbenone-d_3 (**44**)



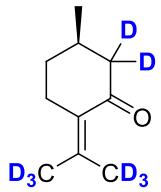
A reaction vessel with a glass stopper was charged with (1S)-(-)-verbenone (43.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated (1S)-(-)-verbenone (**44**) was obtained as a yellow oil (43.0 mg) in >98% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 5.72 (s, 1H), 2.89 (dt, *J*=5.5 Hz, 1H), 2.58 (td, *J*=5.9, 1.5 Hz, 1H), 2.51 (td, *J*=5.8, 1.1 Hz, 1H), 2.06 (d, *J*=9.2Hz, 1H), 2.04-2.00 (m, *J*=2.1 Hz, 0.50H), 1.53 (s, 3H), 1.00 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 206.87, 174.16, 121.66, 58.86, 55.64, 51.07, 42.11, 26.85, 23.09 (m, $J_{(C\text{-}D)}$=19.5 Hz), 22.27; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{12}D_3O$) requires *m/z* 154.13057, found *m/z* 154.1305.

(-)-Piperitone-d_6 (**45**)



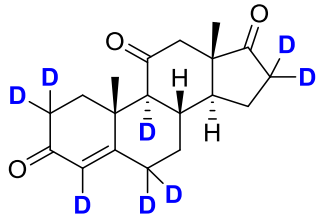
A reaction vessel with a glass stopper was charged with (-)-piperitone (48.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated (-)-piperitone (**45**) was obtained as a yellowish oil (48.1 mg) in >98% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 5.80 (s, 0.64H), 2.38-2.30 (m, 1.23H), 2.09-1.92 (m, 1.76H), 1.85-1.75 (m, 1H), 0.94 (d, *J*=7.0 Hz, 3H), 0.86 (d, *J*=6.8 Hz, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 204.18, 165.15, 126.77 (t, $J_{(C\text{-}D)}$=29.4 Hz), 52.31 (t, $J_{(C\text{-}D)}$=19.1 Hz), 30.57 (m, $J_{(C\text{-}D)}$=23.8 Hz), 27.08, 23.49 (m, $J_{(C\text{-}D)}$=20.4 Hz), 20.91, 19.02; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{11}D_6O$) requires *m/z* 159.16505, found *m/z* 159.1649.

(+)-Pulegone-d_8 (**46**)



A reaction vessel with a glass stopper was charged with (+)-pulegone (53.1 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated (+)-pulegone (**46**) was obtained as a yellow oil (53.3 mg) in >98% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 5.72 (s, 1H), 2.89 (m, 1H), 2.58 (td, *J*=5.9 Hz 1H), 2.51 (td, *J*=5.8 Hz 1H), 2.06 (d, *J*=9.2Hz, 1H), 2.02 (m, *J*=2.1 Hz, 0.48H), 1.53 (s, 3H), 1.00 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 206.87, 174.16, 121.66, 58.86, 55.64, 51.07, 42.11, 26.85, 23.09 (m, $J_{(C\text{-}D)}$=19.5 Hz), 22.27; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_9D_8O$) requires *m/z* 161.17761, found *m/z* 161.1775.

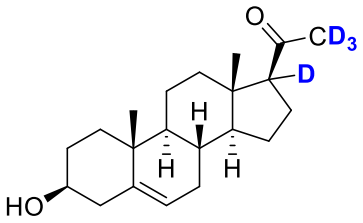
Adrenosterone-d_8 **(47)**



A reaction vessel with a glass stopper was charged with adrenosterone (30.6 mg, 0.1 mmol), CD_3OD (0.6 mL, 150eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent.

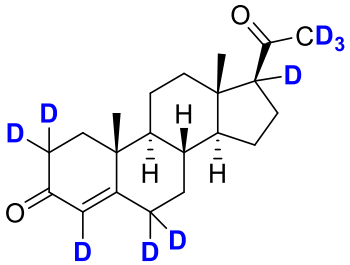
Deuterated adrenosterone (**47**) was obtained as a yellowish white solid (31.1 mg) in >96% yield with 78-90% incorporation of deuterium. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.72 (s, 0.22H), 2.72 (m, 1H), 2.55-2.41 (m, 1.87H), 2.33-2.20 (m, 1.82H), 2.15-2.00 (m, 3H), 1.92-1.84 (m, 2H), 1.71-1.59 (m, 2H), 1.41 (s, 3H), 1.31-1.23 (m, 1H), 0.85 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 216.81, 207.49, 199.62, 167.96, 124.39 (t, $J_{(C\text{-}D)}$=25.7 Hz), 61.72 (t, $J_{(C\text{-}D)}$=18.2 Hz), 50.33, 49.73, 38.17, 36.19, 36.12-35.00 (m), 34.45, 34.00-32.50 (m), 32.00-31.00 (m), 30.74, 30.65, 21.30, 17.23, 14.57; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{17}D_8O_3$) requires *m/z* 309.23004, found *m/z* 309.2283.

Pregnenolone-d_4 (**48**)



A reaction vessel with a glass stopper was charged with pregnenolone (32.3 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated pregnenolone (**48**) was obtained as a white solid (32.0 mg) in >96% yield with >94% incorporation of deuterium. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 5.38-5.30 (m, 1H), 3.60-3.46 (m, 1H), 2.52 (t, *J*=9.1 Hz, 0.06H), 2.35-2.10 (m, 3H), 2.08-1.94 (m, 2H), 1.90-1.79 (m, 2H), 1.79-1.43 (m, 10H), 1.30-0.97 (m, 7H), 0.63 (s, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 210.98, 140.67, 121.06, 71.09, 63.03 (t, $J_{(C\text{-}D)}$=19.9 Hz), 56.69, 48.92 (m, $J_{(C\text{-}D)}$=21.5 Hz), 43.88, 41.63, 38.53, 37.04, 36.31, 31.65, 31.54, 30.96, 24.26, 22.44, 20.85, 19.11, 12.95; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{29}D_4O_2$) requires *m/z* 321.27261, found *m/z* 321.2711.

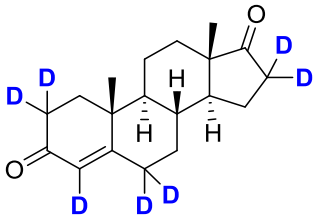
Progesterone-d_9 (**49**)



A reaction vessel with a glass stopper was charged with progesterone (32.4 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent.

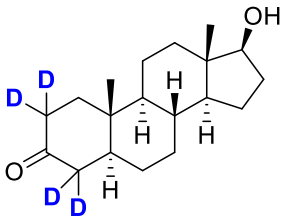
Deuterated progesterone (**49**) was obtained as a light yellow solid (32.5 mg) in 96% yield with 86%-97% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 5.71 (s, 0.03H), 2.65 (t, *J*=9.0 Hz, 0.05H), 2.52-2.41 (m, 0.08H), 2.37-2.25 (m, 0.20H), 2.21-2.00 (m, 3.42H), 1.89 (dd, *J*=3.5 Hz, 1H), 1.76-1.61 (m, 5H), 1.58-1.46 (m, 2H), 1.35-1.18 (m, 5H), 1.12-0.97 (m, 2H), 0.71-0.65 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 212.43, 202.42, 174.91, 123.87 (t, $J_{(C-D)}$=23.7 Hz), 64.01 (t, $J_{(C-D)}$=19.3 Hz), 57.20, 55.16, 45.01, 39.87, 39.65, 36.75, 36.57, 34.5-33.03 (m, $J_{(C-D)}$=20.62 Hz), 33.19, 30.99 (m, $J_{(C-D)}$=19.78 Hz), 25.33, 23.63, 22.13, 17.65, 13.66; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{22}D_9O_2$) requires *m/z* 324.28835, found *m/z* 324.2877.

Δ4-Androstene-3,17-dione-d_7 (**50**)



A reaction vessel with a glass stopper was charged with Δ4-Androstene-3,17-dione (29.5 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated Δ4-androstene-3,17-dione (**50**) was obtained as a white solid (29.8 mg) in >96% yield with 83-90% incorporation of deuterium. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.75 (s, 0.17H), 2.43-2.29 (m, 1H), 2.13-1.90 (m, 3.2H), 1.88-1.81 (td, *J*=3.2 Hz, 1H), 1.80-1.60 (m, 3H), 1.60-1.36 (m, 2H), 1.33-1.21 (m, 2H), 1.19 (s, 3H), 1.17-1.03 (m, 1H), 1.03-0.93 (m, 1H), 0.90 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 199.44, 170.51, 123.72 (t, $J_{(C-D)}$=28.0 Hz), 53.78, 50.77, 47.45, 38.53, 35.73-35.20 (m), 35.06, 33.80-32.94 (m), 32.55-31.39 (m), 31.22, 31.0-30.39 (m), 21.58, 21.48, 20.26, 17.32, 13.63; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{20}D_7O_2$) requires *m/z* 294.2445, found *m/z* 294.2431.

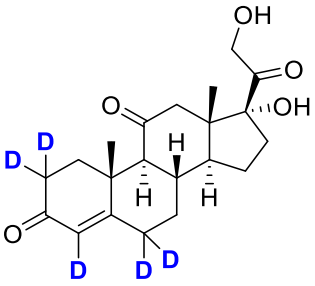
Stanolone-d_4 (**51**)



A reaction vessel with a glass stopper was charged with stanolone (30.6 mg, 0.1 mmol), $CHCl_3$ (0.3 mL), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvents. Deuterated stanolone (**51**) was obtained as a white solid (30.6 mg) in 96% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.63 (t, *J*=8.5 Hz, 1H),

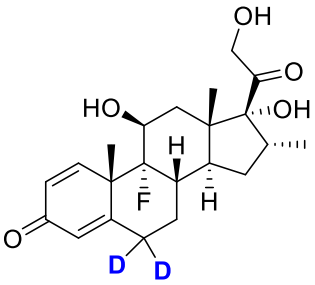
2.45-2.15 (m, 0.84H), 2.12-1.95(m, 2.3H), 1.92-1.74 (m, 1H), 1.74-1.11 (m, 12H), 1.11-0.64 (m, 10H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 212.18, 81.77, 53.85, 50.74, 46.62, 45.00-43.00(m), 42.92, 38.41, 38.10-36.60 (m), 36.59, 35.67, 35.44, 31.19, 30.15, 28.69, 23.32, 20.97, 11.44, 11.13; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{27}D_4O_2$) requires *m/z* 295.25696, found *m/z* 295.2570.

Cortisone-d_5 (**52**)



A reaction vessel with a glass stopper was charged with cortisone (18.4 mg, 0.05 mmol), CD_3OD (0.6 mL, 300 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated cortisone (**52**) was obtained as a white solid (18.3 mg) in 96% yield with 84%-94% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 5.72 (s, 0.05H), 4.61 (d, *J*=19.5 Hz, 1H), 4.23 (d, *J*=19.5 Hz, 1H), 2.96 (d, *J*=12.3 Hz, 1H), 2.80-2.65 (m, 2H), 2.56-2.36 (m, 1.34H), 2.3-2.20 (m, 0.28H), 2.20-1.85 (m, 5H), 1.80-1.60 (m, 2H), 1.55-1.23 (m, 5H), 0.61 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 212.78, 212.03, 202.56, 124.44 (t, $J_{(C-D)}$=24.9 Hz), 89.34, 67.87, 63.47, 52.23, 51.44, 50.97, 39.49, 37.82, 35.43, 35.22, 34.00-33.39 (m), 33.38, 33.18-32.00 (m), 24.12, 17.58, 16.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{24}D_5O_5$) requires *m/z* 366.23233, found *m/z* 366.2324.

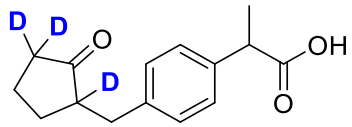
Dexamethasone-d_2 (**53**)



A reaction vessel with a glass stopper was charged with dexamethasone (20.0 mg, 0.05 mmol), CD_3OD (0.6 mL, 300 eq), and 3 mol% of catalyst **2**. A reaction mixture was stirred at room temperature for 48 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated dexamethasone (**53**) was obtained as a white solid (19.8mg) in 98% yield with 74% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.41 (d, *J*=10.1 Hz, 1H), 6.32-6.26 (dd, *J*=10.1, 1.9 Hz, 1H), 6.08 (m, (d, *J*=1.9 Hz, 1H), 4.60 (d, *J*=19.3 Hz, 1H), 4.25 (m, 2H), 3.20-3.00 (m, 1H), 2.75-2.60 (m, 0.23H), 2.55-2.15 (m, 3.30H), 2.00-1.65 (m, 2H), 1.55-1.40 (m, 5H), 1.30-1.15 (m, 1H), 1.00 (s, 3H), 0.86 (d, *J*=7.3 Hz, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 212.67, 189.01, 171.00, 155.95, 129.80, 125.14, 103.50, 101.17, 92.01, 73.14, 72.64, 68.05, 45.02, 37.46, 37.02, 35.67, 35.41, 33.43, 31.00-33.10 (m, $J_{(C-D)}$=18.5 Hz),

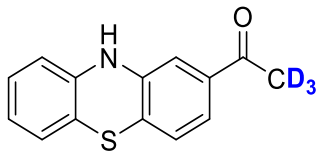
28.71, 23.61, 23.54, 17.49, 15.33 ; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{28}D_2O_5F$) requires *m/z* 395.21973, found *m/z* 395.2180.

Loxoprofen-d_3 (**54**)



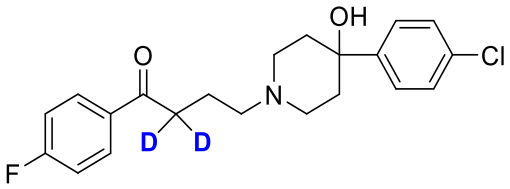
A reaction vessel with a glass stopper was charged with loxoprofen (25.1 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated loxoprofen (**54**) was obtained as a yellowish white solid (25.0 mg) in >97% yield with >90% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.18 (d, *J*=8.2 Hz, 2H), 7.11 (d, *J*=8.2 Hz, 1H), 3.71 (q, *J*=7.2 Hz, 1H), 3.03 (d, *J*=13.9 Hz, 1H), 2.49 (d, *J*=13.9 Hz, 1H), 2.43-2.30 (m, 0.10H), 2.30-2.20 (m, 0.12H), 2.10-1.85 (m, 2.09H), 1.80-1.46 (m, 2H), 1.42 (d, *J*=7.2 Hz, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 222.69, 176.70, 140.22, 139.82, 130.16, 128.46, 51.48 (t, $J_{(C\text{-}D)}$=19.3 Hz), 46.06, 38.57 (m, $J_{(C\text{-}D)}$=19.6 Hz), 35.95, 29.92, 21.19, 19.00; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{15}H_{14}D_3O_3$) requires *m/z* 248.13605, found *m/z* 248.1371.

2- Acetylphenothiazine-d_3 (**55**)



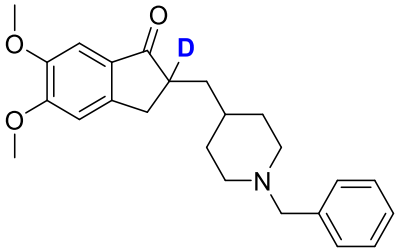
A reaction vessel with a glass stopper was charged with 2-acetylphenothiazine (24.6 mg, 0.1 mmol), dry THF (0.3 mL), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvents. Deuterated 2-acetylphenothiazine (**55**) was obtained as a yellow solid (24.5 mg) in 98% yield with >96% incorporation of deuterium. ^{1}H NMR: (300 MHz, DMSO-*d*6) δ 8.76 (s, 1H), 7.33 (dd, *J*=8.0, 1.7 Hz, 1H), 7.17 (d, *J*=1.7 Hz, 1H), 7.10-6.96 (m, 2H), 6.90 (dd, *J*=7.7, 1.4 Hz, 1H), 6.75 (t, *J*=7.2 Hz, 1H), 6.65 (dd, *J*=7.9, 1.0 Hz, 1H), 2.44 (m, *J*=2.0 Hz, 0.11H); ^{13}C NMR: (75 MHz, DMSO-*d*6) δ 196.94, 142.01, 141.22, 136.12, 127.98, 126.27, 126.12, 123.27, 115.22, 114.57, 112.66, 25.86 (m, $J_{(C\text{-}D)}$=19.5 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_9D_3ON^{32}S$) requires *m/z* 245.08224, found *m/z* 245.0819.

Haloperidol-d_2 (**56**)



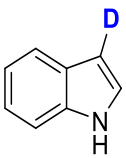
A reaction vessel with a glass stopper was charged with haloperidol (19.2 mg, 0.05 mmol), CD_3OD (0.6 mL, 300 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated haloperidol (**56**) was obtained as a white solid (19.0 mg) in >98% yield with >97% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.11-8.06 (m, 2H), 7.47-7.40 (m, 2H), 7.36-7.29 (m, 2H), 7.28-7.19 (m, 2H), 3.04 (t, 0.05H), 2.90-2.82 (m, 2H), 2.63-2.53 (m, 4H), 2.08-1.90 (m, 4H), 1.76-1.66 (m, 2H); ^{13}C NMR: (100 MHz, CD_3OD) δ 200.14, 168.42, 165.91, 148.95, 135.04, 135.01, 133.53, 132.11, 132.02, 129.18, 127.52, 116.71, 116.49, 71.26, 58.85, 50.37, 38.50, 36.35 (m, $J_{(C\text{-}D)}$=18.4 Hz), 22.19; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{22}D_2O_2N^{35}ClF$) requires *m/z* 378.15996, found *m/z* 378.1599.

Donepezil-d_1 (**57**)



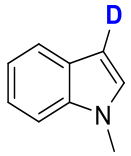
A reaction vessel with a glass stopper was charged with donepezil HCl (22.0 mg, 0.05 mmol), CD_3OD (0.6 mL, 300 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated donepezil (**57**) was obtained as a white solid (22.0 mg) in >98% yield with 95% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.59-7.48 (m, 5H), 7.12 (s, 1H), 7.05 (s, 1H), 4.34 (s, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 3.54-3.49 (m, 2H), 3.33-3.29 (overlapped), 3.08 (td, *J*=16.2, 5.5 Hz, 1H), 2.73 (d, *J*=17.2 Hz, 1H), 2.17-1.95 (m, 2H), 1.95-1.75 (m, 2H), 1.60-1.35 (m, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 209.77, 157.75, 151.37, 151.11, 132.48, 131.24, 130.34, 129.74, 108.99, 105.27, 61.77, 56.73, 56.45, 53.73, 45.72 (t, $J_{(C\text{-}D)}$=19.5 Hz), 38.88, 33.98, 33.13, 31.10, 30.14; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{24}H_{29}DO_3N$) requires *m/z* 381.22830, found *m/z* 381.2279.

Indole-d_1 (**58**)



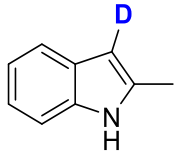
A reaction vessel with a glass stopper was charged with indole (37.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated indole (**58**) was obtained as a white solid (36.1 mg) in >97% yield with >97% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.55 (d, *J*=7.9 Hz, 1H), 7.37 (d, *J*=8.1 Hz, 1H), 7.19 (s, 1H), 7.09 (td, *J*=7.5, 1.1 Hz, 1H), 7.00 (td, *J*=7.4, 1.0 Hz, 1H), 6.43 (t, *J*=2.5 Hz, 0.03H); ^{13}C NMR: (100 MHz, CD_3OD) δ 137.56, 129.27, 125.30, 122.13, 121.10, 119.94, 112.06, 102.02 (t, $J_{(C\text{-}D)}$=26.2 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_8H_7DN) requires *m/z* 119.07140, found *m/z* 119.0715.

1-Methylindole-d_1 (**59**)



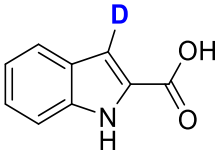
A reaction vessel with a glass stopper was charged with 1-methylindole (41.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 15 min, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-methylindole (**59**) was obtained as a brownish yellow oil (39.3 mg) in 95% yield with >98% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.52 (dt, *J*=7.8, 0.9 Hz, 1H), 7.30 (td, *J*=8.2, 0.9 Hz, 1H), 7.13 (dt, *J*=7.1, 1.1, 1H), 7.07 (s, 1H), 7.01 (td, *J*=7.0, 1.0 Hz, 1H), 6.39 (dd, *J*=3.1, 0.8 Hz, 0.02H), 3.71 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 138.20, 129.92, 129.76, 122.21, 121.44, 119.96, 110.05, 101.33 (t, $J_{(C\text{-}D)}$=26.5 Hz), 32.72; HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_9H_9DN) requires *m/z* 133.08705, found *m/z* 133.0870.

2-Methylindole-d_1 (**60**)



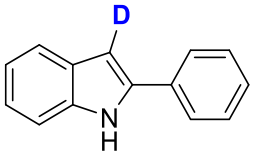
A reaction vessel with a glass stopper was charged with 2-methylindole (41.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 15 min, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2-methylindole (**60**) was obtained as a white solid (41.4 mg) in >98% yield with >97% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.38 (d, *J*=7.70 Hz, 1H), 7.24 (d, *J*=7.9 Hz, 1H), 6.98 (dt, *J*=7.4, 1.1, 1H), 6.92 (dt, *J*=7.9, 1.0 Hz, 1H), 6.09 (s, 0.03H), 2.39 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 137.92, 136.41, 130.45, 121.12, 120.02, 119.73, 111.24, 99.96 (t, $J_{(C\text{-}D)}$=26.0 Hz), 13.41; HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_9H_9DN) requires *m/z* 133.08705, found *m/z* 133.0872.

Indole-2-carboxylic acid-d_1 (**61**)



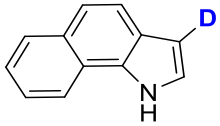
A reaction vessel with a glass stopper was charged with indole-2-carboxylic acid (49.8 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated indole-2-carboxylic acid (**61**) was obtained as a white solid (49.8 mg) in >98% yield with >87% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.62 (d, *J*=8.1 Hz, 1H), 7.44 (d, *J*=8.4 Hz, 1H), 7.24 (t, *J*=7.6 Hz 1H), 7.16 (s, 0.13H), 7.06 (dd, *J*=7.5 Hz, 1H); ^{13}C NMR: (100 MHz, CD_3OD) δ 165.14, 138.94, 129.06, 128.61, 125.77, 123.06, 121.22, 113.18, 109.08 (t, $J_{(C-D)}$=25.5 Hz), 95.33, 55.94; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_9H_5DO_2N$) requires *m/z* 161.04558, found *m/z* 161.0456.

2-Phenylindole-d_1 (**62**)



A reaction vessel with a glass stopper was charged with 2-phenylindole (39.4 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2-phenylindole (**62**) was obtained as a white solid (39.2 mg) in >98% yield with >99% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.78 (dd, *J*=8.6, 1.3 Hz, 2H), 7.52 (d, *J*=7.8 Hz, 1H), 7.37-7.43 (m, 3H), 7.26 (t, *J*=7.4 Hz, 1H), 7.09 (dt, *J*=7.4, 1.1 Hz, 1H), 6.99 (dt, *J*=7.9, 0.9 Hz, 1H), 6.78 (s, 0.01H); ^{13}C NMR: (75 MHz, CD_3OD) δ 139.22, 138.86, 134.20, 130.48, 129.84, 128.24, 126.10, 122.66, 121.12, 120.45, 112.05, 99.47 (t, $J_{(C-D)}$=26 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{11}DN$) requires *m/z* 195.10270, found *m/z* 195.1029.

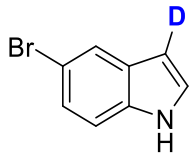
1H-Benzo[g]indole-d_1 (**63**)



A reaction vessel with a glass stopper was charged with benzo[g]indole (34.5 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated *1H*-benzo[g]indole (**63**) was obtained as a light brown solid (34.5 mg) in >98% yield with 93% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.21 (d, *J*=8.2 Hz, 1H), 7.85 (d, *J*=8.10 Hz, 1H), 7.64 (d, *J*=8.6, 1H), 7.48 (dt, *J*=7.6, 1.2 Hz, 1H), 7.41 (d, *J*=8.6,

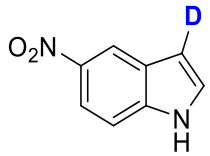
1H), 7.36 (dt, *J*=8.1, 1.1, 1H), 7.28(s, 0.5H), 6.58 (d, *J*=2.9, 0.07H); ^{13}C NMR: (100 MHz, CD_3OD) δ 132.03, 131.65, 129.46, 126.12, 125.13, 124.37, 123.72, 123.54, 121.68, 121.20, 120.82, 103.85 (t, $J_{(C\text{-}D)}$=26.2 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_9DN$) requires *m/z* 169.08705, found *m/z* 169.0870.

5-Bromoindole-d_1 (**64**)



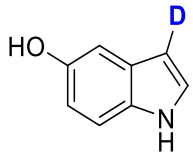
A reaction vessel with a glass stopper was charged with 5-bromoindole (39.6 mg, 0.2 mmol), CD_3OD (0.6 mL, 75 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-bromoindole (**64**) was obtained as a white solid (39.6 mg) in 98% yield with 97% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.67 (d, *J*=1.8 Hz, 1H), 7.29 (d, *J*=8.6 Hz, 1H), 7.24 (s, 1H), 7.16 (dd, *J*=8.6, 1.9 Hz, 1H), 6.40 (dd, *J*=3.1, 0.7 Hz, 0.03H); ^{13}C NMR: (75 MHz, CD_3OD) δ 136.26, 131.15, 126.94, 124.86, 123.53, 113.71, 113.06, 101.77 (t, $J_{(C\text{-}D)}$=26.5 Hz); HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_8H_4DN^{79}Br$) requires *m/z* 194.9663, found *m/z* 194.9666, $[M-H]^-$ ($C_8H_4DN^{81}Br$) requires *m/z* 196.9642, found *m/z* 196.9645.

5-Nitroindole-d_1 (**65**)



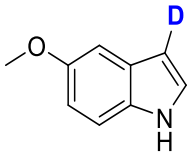
A reaction vessel with a glass stopper was charged with 5-nitroindole (17.1 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-nitroindole (**65**) was obtained as a deep yellow solid (16.9 mg) in >98% yield with >96% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 8.49 (d, *J*=2.2 Hz, 1H), 7.98 (dd, *J*=9.0, 2.2 Hz, 1H), 7.43 (s, 1H), 7.41 (d, *J*=2.4 Hz, 1H), 6.63 (d, *J*=3.1 Hz, 0.04H); ^{13}C NMR: (100 MHz, CD_3OD) δ 142.52, 140.62, 129.20, 128.52 118.30, 117.61, 112.17, 104.73 (t, $J_{(C\text{-}D)}$=26.8 Hz); HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_8H_4DO_2N_2$) requires *m/z* 162.04083, found *m/z* 162.0407.

5-Hydroxyindole-d_1 (**66**)



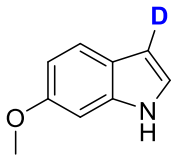
A reaction vessel with a glass stopper was charged with 5-hydroxyindole (41.2 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-hydroxyindole (**66**) was obtained as a white solid (41.2 mg) in >98% yield with >92% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.19 (d, *J*=8.7 Hz, 1H), 7.13 (s, 1H), 6.94 (d, *J*=2.3 Hz, 1H), 6.68 (dd, *J*=8.7, 2.3 Hz, 1H), 6.28 (d, *J*=3.0 Hz, 0.08H); ^{13}C NMR: (100 MHz, CD_3OD) δ 151.21, 132.64, 130.02, 126.09, 112.44, 112.24, 105.23, 101.37 (t, $J_{(C\text{-}D)}$=26.1 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_8H_7DON) requires *m/z* 135.06632, found *m/z* 135.0665.

5-Methoxyindole-d_1 (**67**)



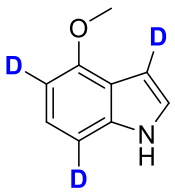
A reaction vessel with a glass stopper was charged with 5-methoxyindole (45.1 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 5-methoxyindole (**67**) was obtained as a white solid (45.0 mg) in 98% yield with 96% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.26 (d, *J*=8.8 Hz, 1H), 7.17 (s, 1H), 7.04 (d, *J*=2.1 Hz, 1H), 6.75 (d, *J*=8.8 Hz, 1H), 6.35 (dd, *J*=2.8 Hz, 0.04H), 3.76 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 155.07, 132.90, 129.68, 126.03, 112.67, 112.49, 103.09, 101.95 (t, $J_{(C\text{-}D)}$=25 Hz), 56.24; HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_9H_9DON) requires *m/z* 149.08197, found *m/z* 149.0820.

6-Methoxyindole-d_1 (**68**)



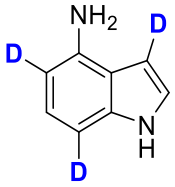
A reaction vessel with a glass stopper was charged with 6-methoxyindole (45.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 6-methoxyindole (**68**) was obtained as a white solid (44.8mg) in >98% yield with >98% incorporation of deuterium.. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.39 (d, *J*=8.6 Hz, 1H), 7.07 (s, 1H), 6.90 (d, *J*=2.2 Hz 1H), 6.67 (dd, *J*=8.6, 2.3 Hz, 1H), 6.34 (dd, *J*=3.2, 0.7 Hz, 0.01H), 3.78 (s, 3H); ^{13}C NMR: (75 MHz, CD_3OD) δ 157.37, 138.26, 124.19, 123.69, 121.58, 110.27, 101.92 (t, $J_{(C\text{-}D)}$=26.1 Hz), 95.40, 55.97; HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_9H_9DON) requires *m/z* 149.08197, found *m/z* 149.0820.

4-Methoxyindole-d_3 (**69**)



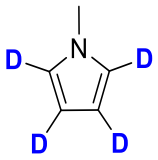
A reaction vessel with a glass stopper was charged with 4-methoxyindole (45.1 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 10 mol% of **4**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 4-methoxyindole (**69**) was obtained as a white solid (45.1 mg) in >98% yield with 68%-93% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.09 (s, 1H), 7.03-6.97 (m, 1H), 7.03-6.97 (m, 0.32H), 6.49 (d, *J*=3.1 Hz, 0.11H), 6.46 (d, *J*=7.8 Hz, 0.08H), 3.89 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 154.49, 139.02, 123.65, 123.78, 119.87, 105.47 (t, $J_{(C-D)}$=24.4 Hz), 99.60 (t, J(C-D)=25.0 Hz), 99.35 (t, $J_{(C-D)}$=26.5 Hz), 55.59; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_7D_3ON$) requires *m/z* 151.09452, found *m/z* 151.0945.

4-Aminoindole-d_3 (**70**)



A reaction vessel with a glass stopper was charged with 4-Aminoindole (40.5 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 4-aminoindole (**70**) was obtained as a brown solid (40.0 mg) in >98% yield with 80-83% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.09 (d, *J*=3.2 Hz, 1H), 6.95-6.87 (m, 1H), 6.86 (d, *J*=8.2 Hz, 0.19H), 6.49 (d, *J*=3.2 Hz, 0.16H), 6.40 (d, *J*=7.4 Hz, 0.17H); ^{13}C NMR: (100 MHz, CD_3OD) δ 139.80, 138.57, 123.65, 123.14, 119.58, 105.21 (t, $J_{(C-D)}$=24.5 Hz), 103.70 (t, $J_{(C-D)}$=24.1 Hz), 99.10; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_8H_6D_3N_2$) requires *m/z* 136.09486, found *m/z* 136.0949.

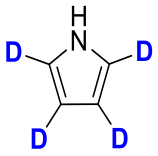
1-Methylpyrrole-d_4 (**71**)



A reaction vessel with a glass stopper was charged with 1-methylpyrrole (25.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-methylpyrrole (**71**) was obtained as a brown oil (20.3 mg) in 80% yield with >90% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.58 (s, 0.19H), 6.01 (s,

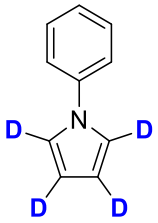
0.19H), 3.61 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 122.06 (t, $J_{(C\text{-}D)}$=27.3 Hz), 108.30 (t, $J_{(C\text{-}D)}$=26.1 Hz), 35.87.

Pyrrole-d_4 (**72**)



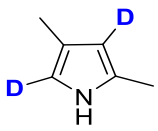
A reaction vessel with a glass stopper was charged with pyrrole (21.2 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated pyrrole (**72**) was obtained as a brown liquid (17.6 mg) in 82% yield with >90% incorporation of deuterium. Mesitylene (0.05 mmol) was used as the internal standard. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.72 (s, 0.20H), 6.10 (s, 0.20H); ^{13}C NMR: (100 MHz, CD_3OD) δ 117.93 (t, $J_{(C\text{-}D)}$=27.4 Hz), 107.61 (t, $J_{(C\text{-}D)}$=25.5 Hz); HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_4HD_4N^{23}Na$) requires *m/z* 94.05653, found *m/z* 94.0565.

1-Phenylpyrrole-d_4 (**73**)



A reaction vessel with a glass stopper was charged with 1-phenylpyrrole (44.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-phenylpyrrole (**73**) was obtained as a yellowish white solid (44.0 mg) in 98% yield with >93% incorporation of deuterium. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.50-7.39 (m, 4H), 7.25-7.19 (m, 1H), 7.16 (s, 0.14H), 6.27 (s, 0.14H); ^{13}C NMR: (75 MHz, CD_3OD) δ 142.13, 130.66, 126.40, 120.93, 119.60 (t, $J_{(C\text{-}D)}$=28.3 Hz), 110.87 (t, $J_{(C\text{-}D)}$=26.2 Hz); HRMS (APCI) exact mass calculated for $[M+H]^+$ ($C_{10}H_6D_4N$) requires *m/z* 148.10588, found *m/z* 148.1057.

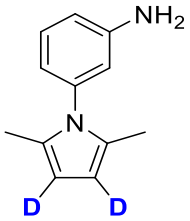
2,4-Dimethylpyrrole-d_2 (**74**)



A reaction vessel with a glass stopper was charged with 2,4-dimethylpyrrole (30.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room

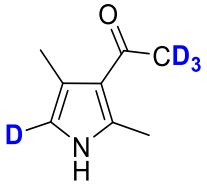
temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2,4-dimethylpyrrole (**74**) was obtained as a brown oil (29.5) mg) in >98% yield with >95% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.29 (s, 0.045H), 5.58 (s, 0.047H), 2.15 (s, 3H), 2.00 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 128.20, 118.59, 114.46 (t, $J_{(C-D)}$=26.6 Hz), 107.47 (t, $J_{(C-D)}$=24.8 Hz), 12.80, 12.05; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_6H_8D_2N$) requires *m/z* 98.09333, found *m/z* 98.0938.

1-(3-Aminophenyl)-2,5-dimethylpyrrole-d_2 (**75**)



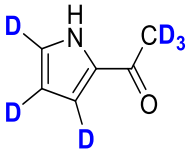
A reaction vessel with a glass stopper was charged with 1-(3-aminophenyl)-2,5-dimethylpyrrole (19.0 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 1-(3-aminophenyl)-2,5-dimethylpyrrole (**75**) was obtained as a dark brown solid (19.0 mg) in >98% yield with >97% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.18 (t, *J*=7.95 Hz, 1H), 6.75 (m, *J*=8.1, 0.9 Hz, 1H), 6.52 (t, *J*=2.04 Hz, 1H), 6.47 (m, *J*=8.0, 0.9 Hz, 1H), 5.75 (s, 0.06H); ^{13}C NMR: (100 MHz, CD_3OD) δ 149.93, 141.27, 130.57, 129.19, 118.53, 116.05, 115.61, 106.19 (t, $J_{(C-D)}$=25.4 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{13}D_2N_2$) requires *m/z* 189.13553, found *m/z* 189.1359.

3-Acetyl-2,4-dimethylpyrrole-d_4 (**76**)



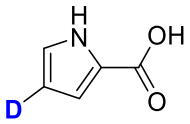
A reaction vessel with a glass stopper was charged with 3-acetyl-2,4-dimethylpyrrole (43.3 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 3-acetyl-2,4-dimethylpyrrole (**76**) was obtained as a brownish yellow solid (43.2 mg) in >98% yield with >97% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.35 (s, 0.01H), 2.44 (s, 3H), 2.35 (m, *J*=2.3 Hz, 0.13H), 2.21 (s, 3H); ^{13}C NMR: (100 MHz, CD_3OD) δ 198.12, 138.44, 121.55, 121.35, 116.47 (t, $J_{(C-D)}$=27.8 Hz), 29.71 (t, $J_{(C-D)}$=19.4 Hz), 15.14, 13.89; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_8H_8D_3NONa$) requires *m/z* 163.0921, found *m/z* 163.0914.

2-Acetylpyrrole-d_6 (**77**)



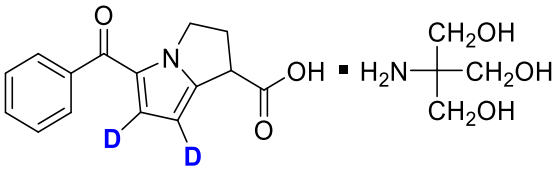
A reaction vessel with a glass stopper was charged with 2-acetylpyrrole (33.4 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 16 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated 2-acetylpyrrole (**77**) was obtained as a brown solid (33.4 mg) in >98% yield with >95% incorporation of deuterium. Mesitylene (0.1 mmol) was used as the internal standard for ^{1}H NMR. ^{1}H NMR: (300 MHz, CD_3OD) δ 7.05 (s, 0.05H), 6.99 (s, 0.07H), 6.22 (s, 0.05H) , 2.34 (m, J=2.2 Hz, 0.14H); ^{13}C NMR: (75 MHz, CD_3OD) δ 190.01, 133.08, 126.51 (t, $J_{(C-D)}$=28.1 Hz), 118.65 (t, $J_{(C-D)}$=26.3 Hz), 110.77 (t, $J_{(C-D)}$=26.5 Hz), 24.74 (m, $J_{(C-D)}$=25.9 Hz); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_6H_2D_6NO$) requires *m/z* 116.09770, found *m/z* 116.0979.

Pyrrole-2-carboxylic acid-d_1 (**78**)



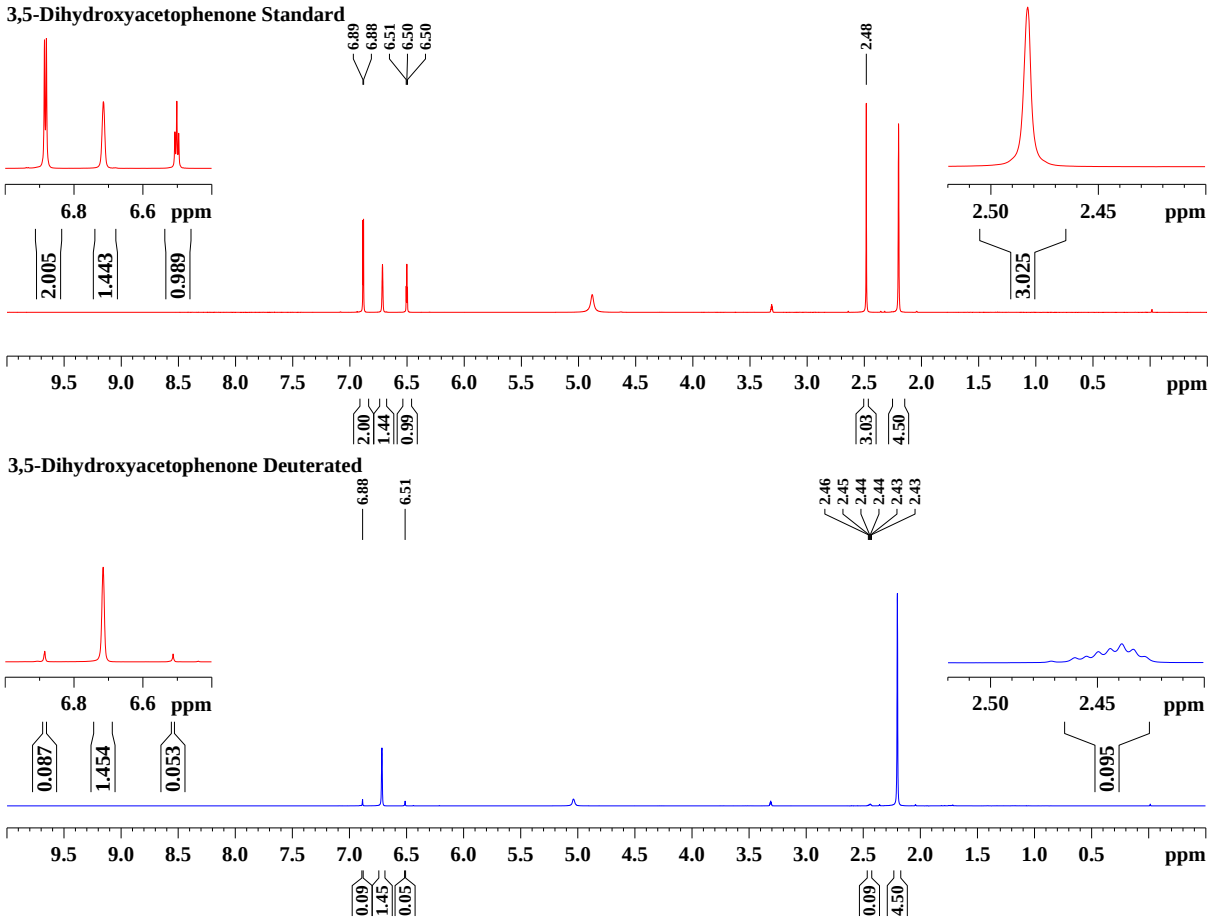
A reaction vessel with a glass stopper was charged with pyrrole-2-carboxylic acid (34.0 mg, 0.3 mmol), CD_3OD (0.6 mL, 50 eq), and 1 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated pyrrole-2-carboxylic acid (**78**) (33.9 mg) was obtained as a yellowish white solid in >98% yield with >81% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 6.95 (d, J=1.2 Hz, 1H), 6.86 (d, J=1.1 Hz, 1H), 6.18 (t, J=3.1 Hz, 0.19H); ^{13}C NMR: (100 MHz, CD_3OD) δ 164.50, 124.42, 123.79, 116.59, 110.46 (t, $J_{(C-D)}$=26.1 Hz); HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_5H_3DNO_2$) requires *m/z* 111.03103, found *m/z* 111.0313.

Ketorolac tromethamine-d_2 (**79**)

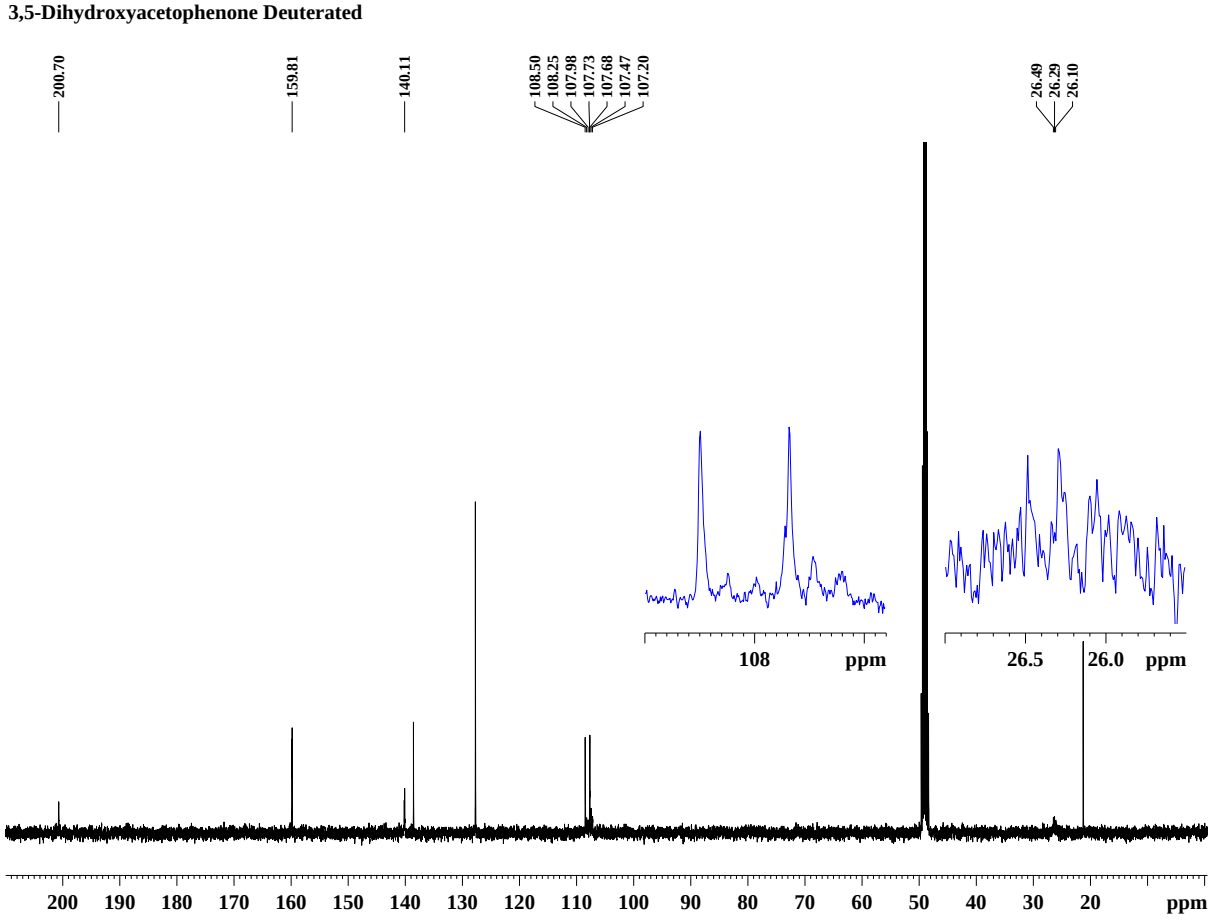


A reaction vessel with a glass stopper was charged with ketorolac tromethamine (38.4 mg, 0.1 mmol), CD_3OD (0.6 mL, 150 eq), and 3 mol% of **1**. A reaction mixture was stirred at room temperature for 24 h, and then it was evaporated under reduced pressure to remove the catalyst and solvent. Deuterated ketorolac tromethamine (**79**) was obtained as a white solid (38.2 mg) in >98% yield with 41%-97% incorporation of deuterium. ^{1}H NMR: (400 MHz, CD_3OD) δ 7.76 (d, J=7.5 Hz, 2H), 7.58 (t, J=7.3 Hz, 1H), 7.49 (t, J=7.4 Hz, 1H), 6.83 (s, 0.59H), 6.13-611 (m, 0.04H), 4.60-4.34 (m, 2H), 4.16 (t, J=7.2 Hz, 1H), 3.68 (s, 6H), 2.85 (m, J=6.7 Hz 2H); ^{13}C NMR: (100 MHz, CD_3OD) δ 186.87, 173.46, 145.04, 140.44, 132.72, 129.80, 129.35, 128.14, 126.93, 104.32 (t, $J_{(C-D)}$=26.9 Hz), 62.76, 60.97, 43.59, 32.08; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{13}DO_3N$) requires *m/z* 257.10310, found *m/z* 257.1032.

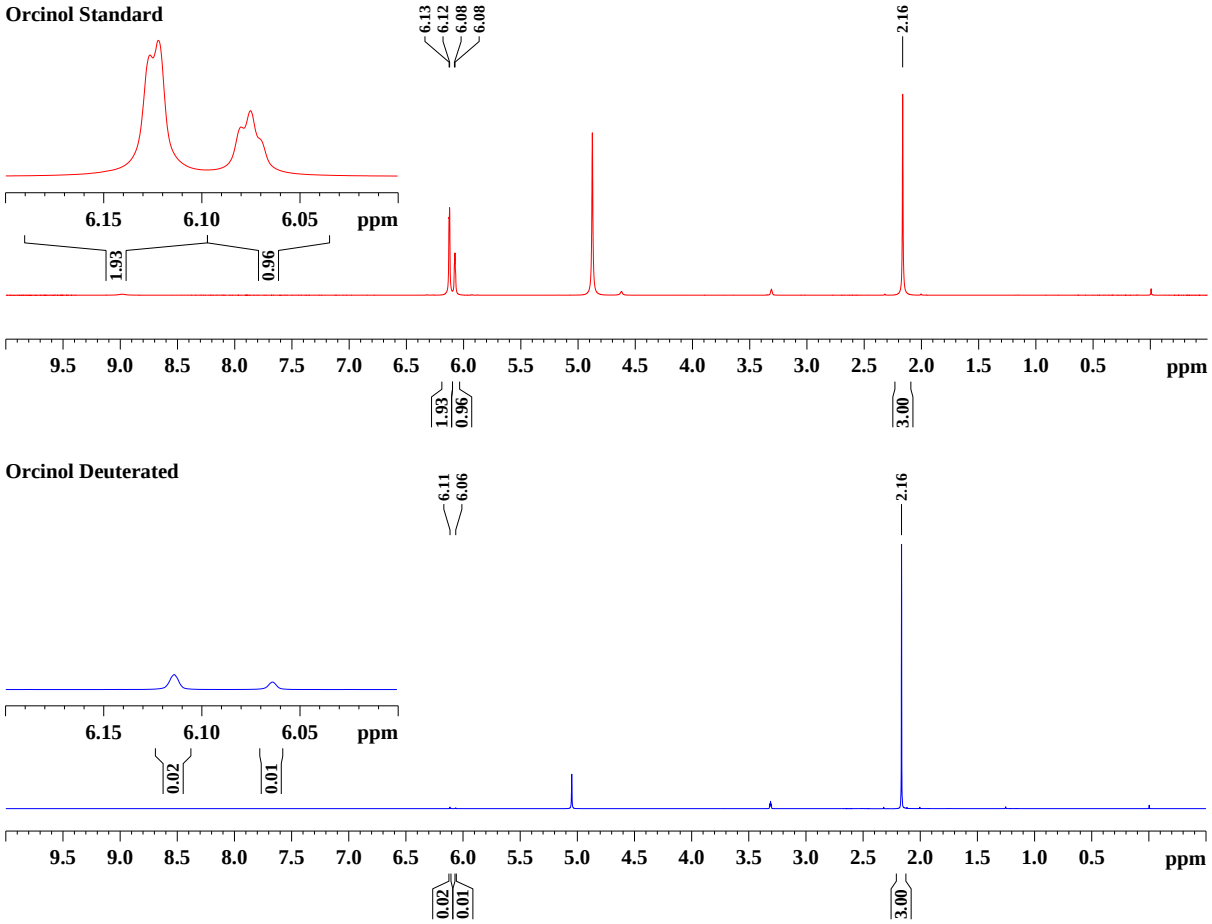
15. NMR spectra of the deuterated compounds



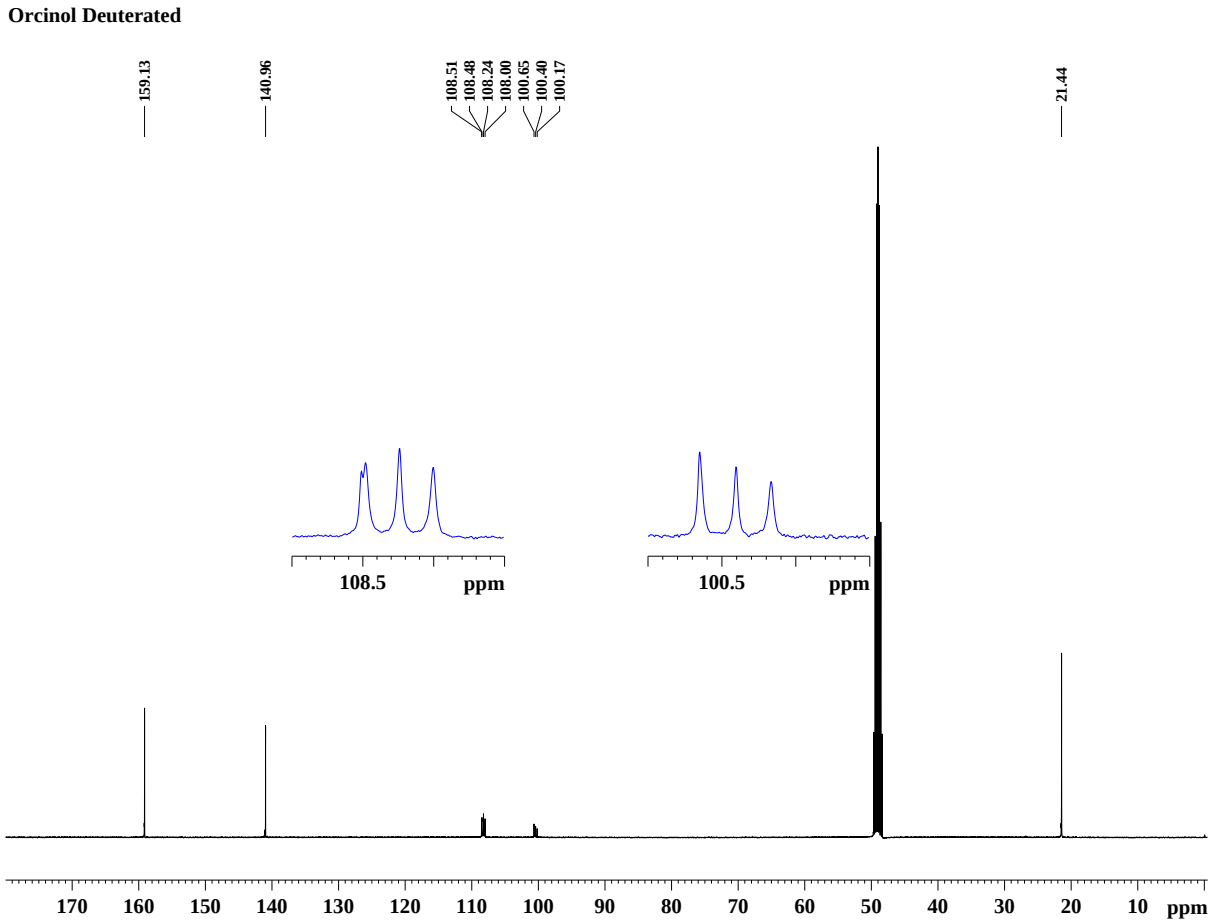
Supplementary Spectrum. ^{1}H NMR spectrum of 3',5'-dihydroxy acetophenone (**7**) with mesitylene as the internal standard (400 MHz, CD_3OD)



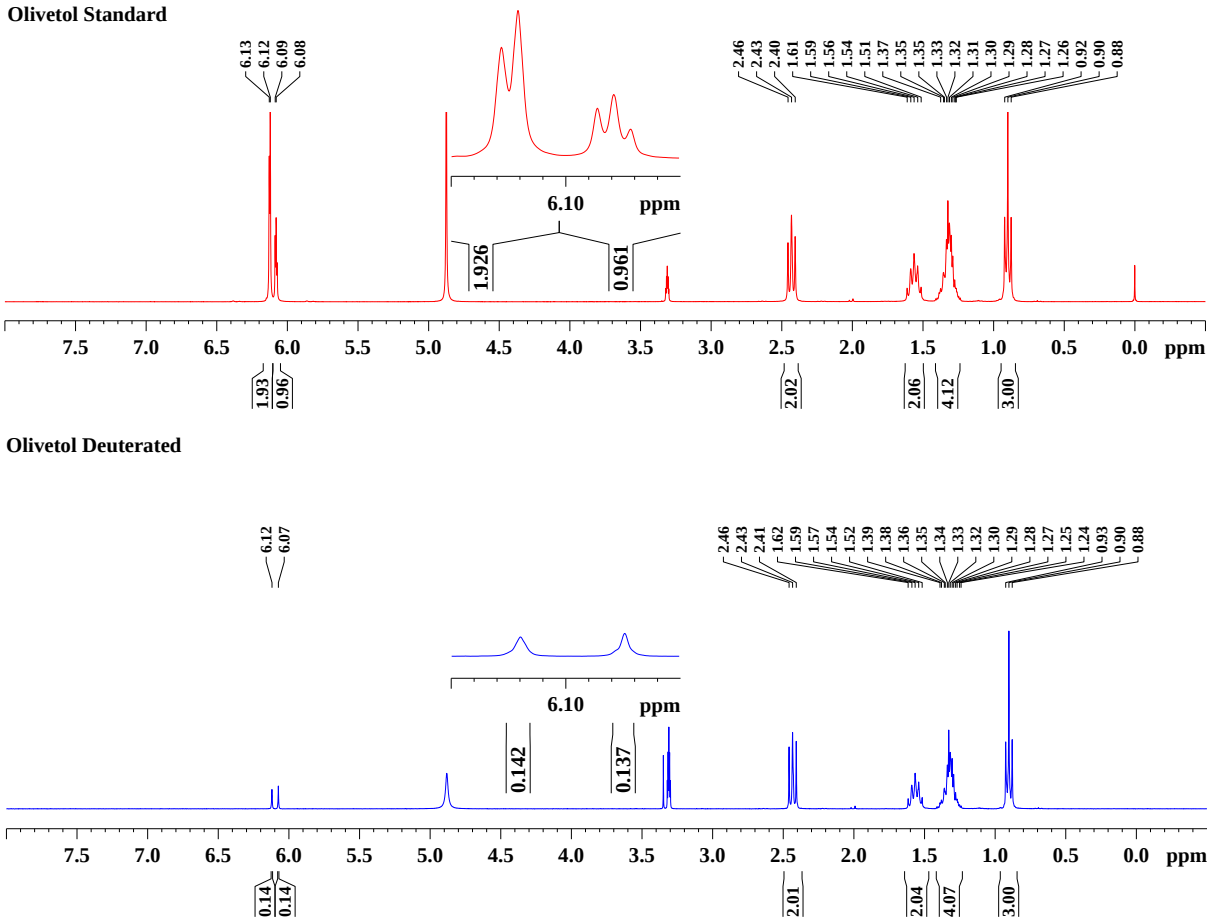
Supplementary Spectrum. ^{13}C NMR spectrum of 3',5'-dihydroxy acetophenone (**7**) with mesitylene as the internal standard (100 MHz, CD_3OD)



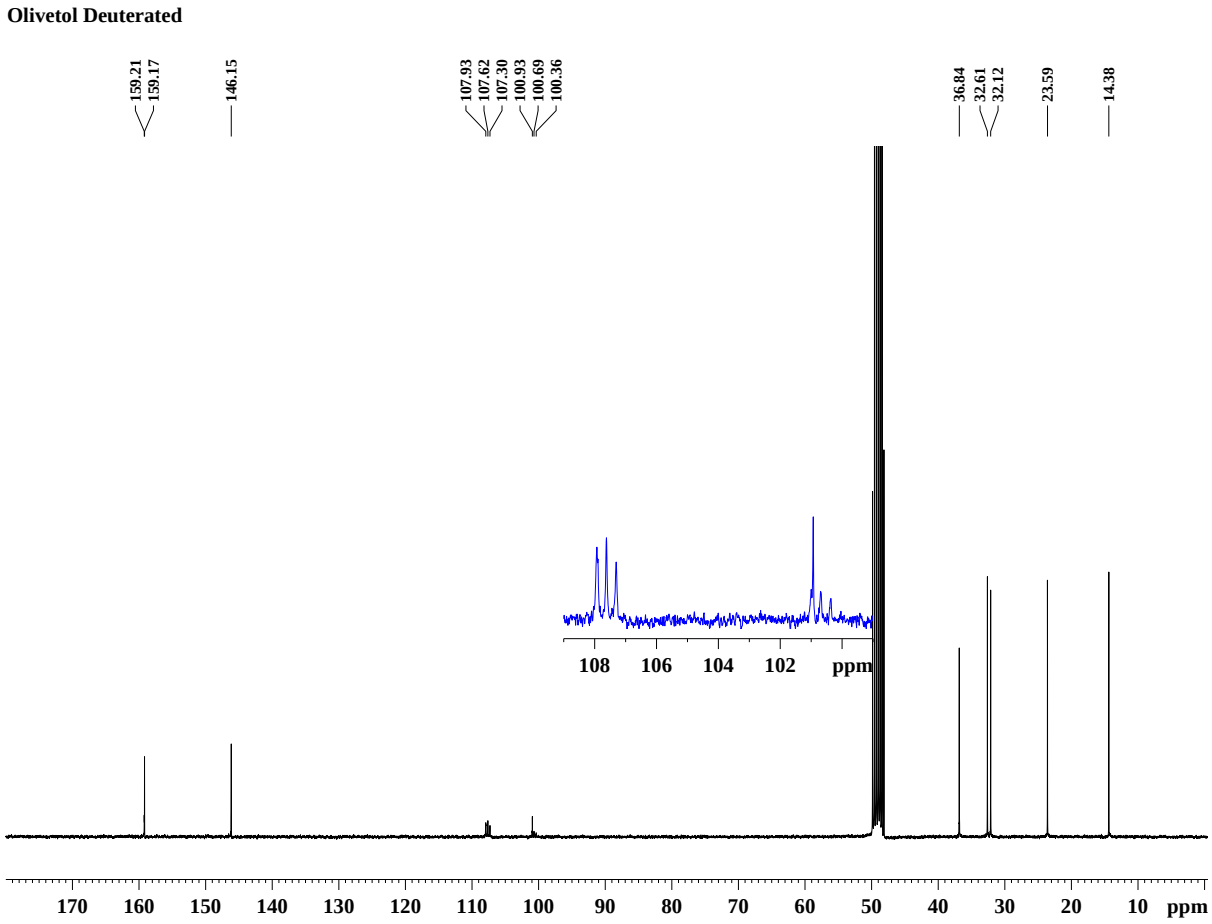
Supplementary Spectrum. ^{1}H NMR spectrum of orcinol (**8**) (400 MHz, CD_3OD)



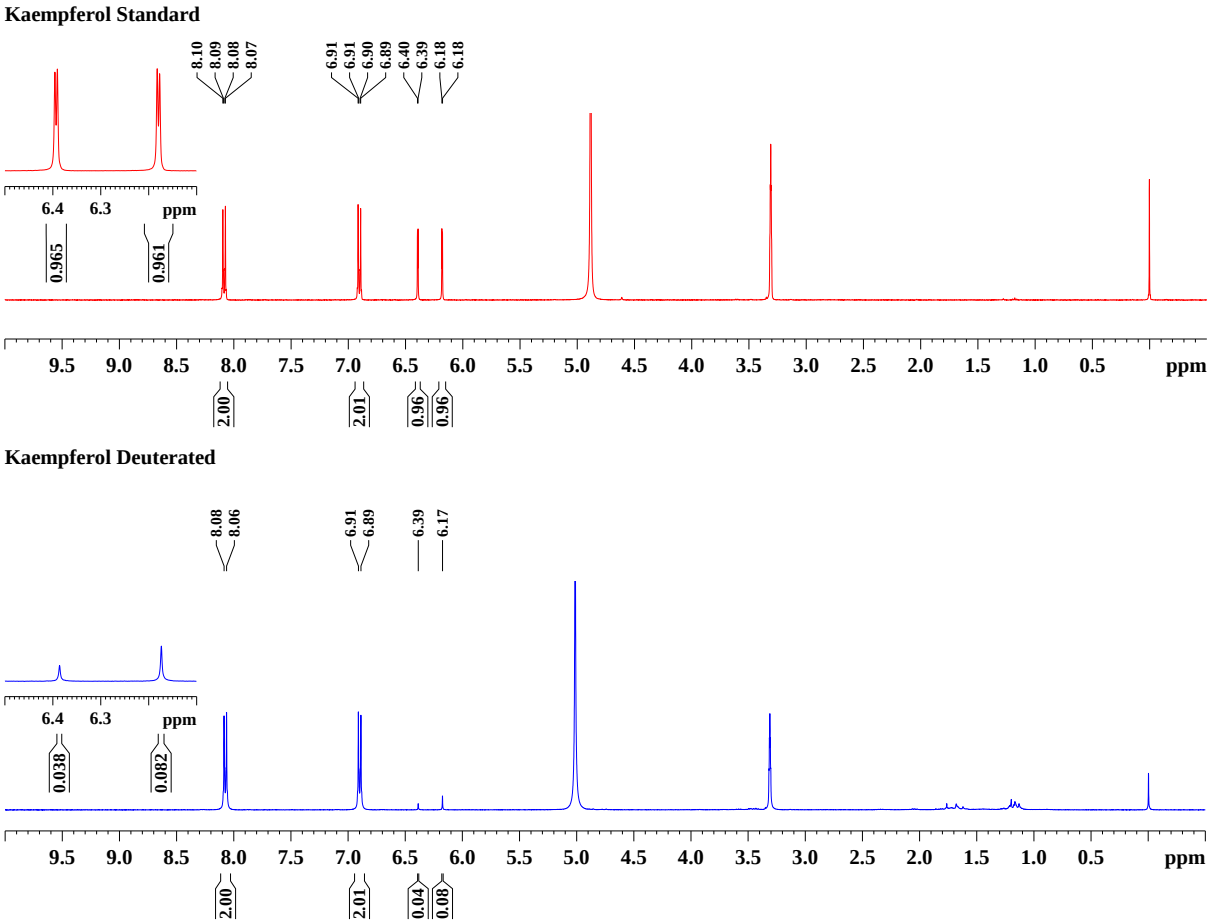
Supplementary Spectrum. ^{13}C NMR spectrum of orcinol (**8**) (100 MHz, CD_3OD)



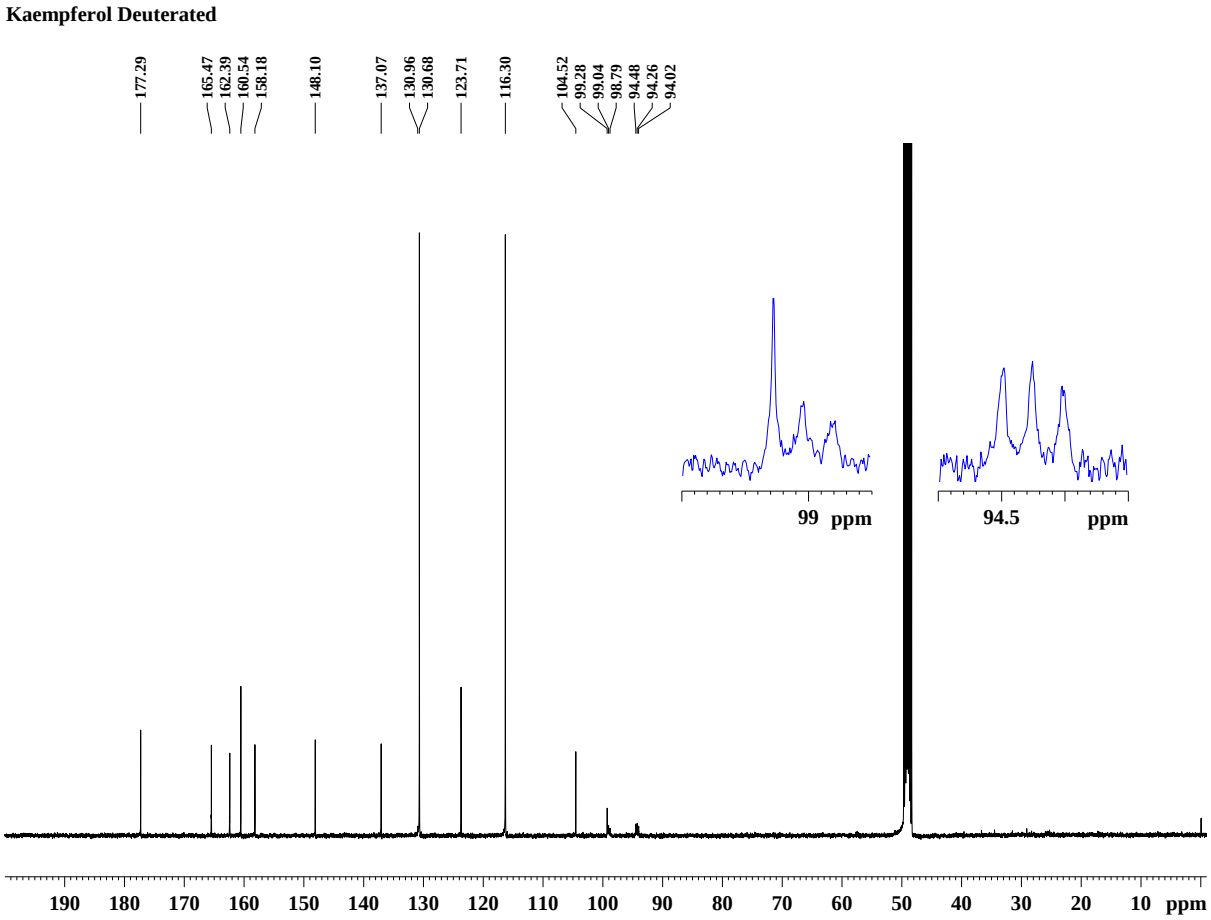
Supplementary Spectrum. ^{1}H NMR spectrum of olivetol (**9**) (300 MHz, CD_3OD)



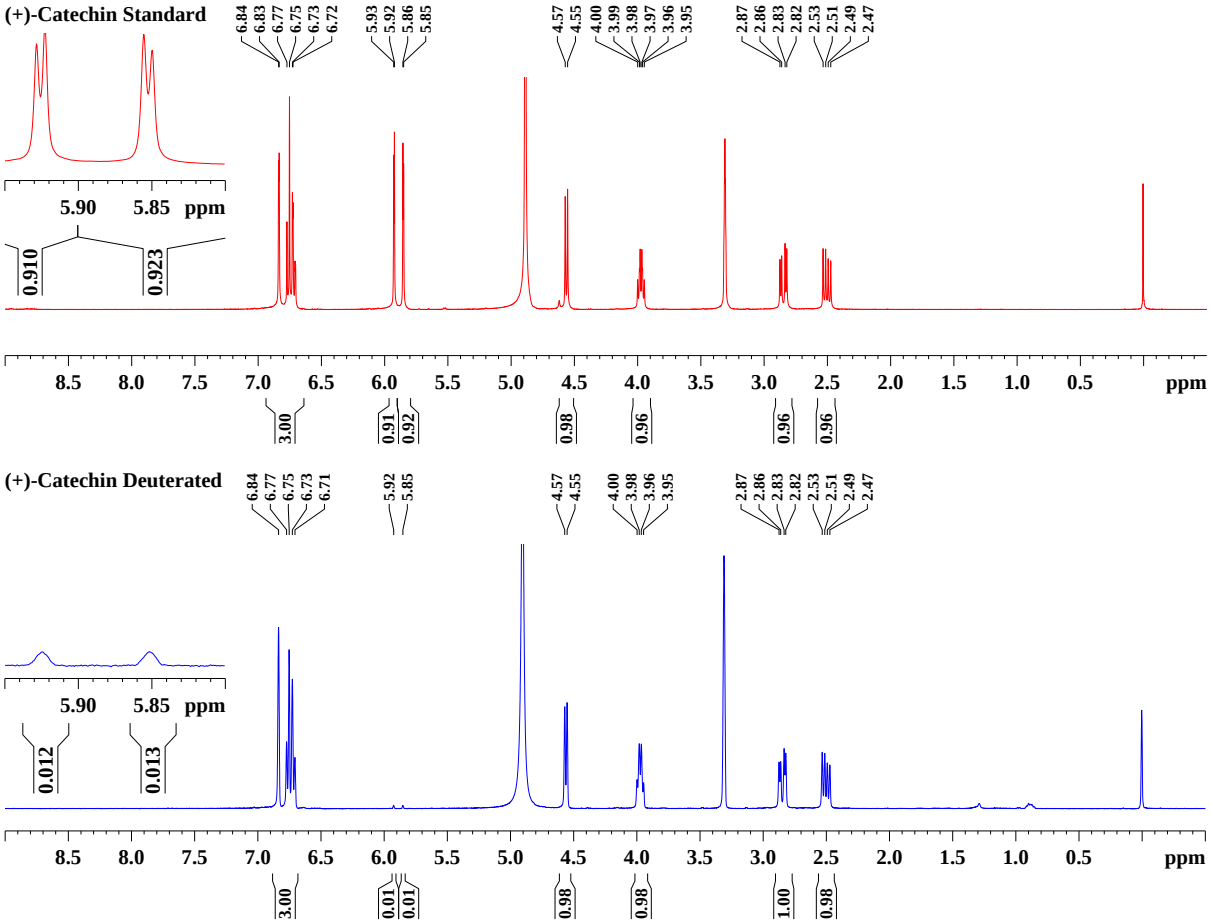
Supplementary Spectrum. ^{13}C NMR spectrum of olivetol (**9**) (75 MHz, CD_3OD)



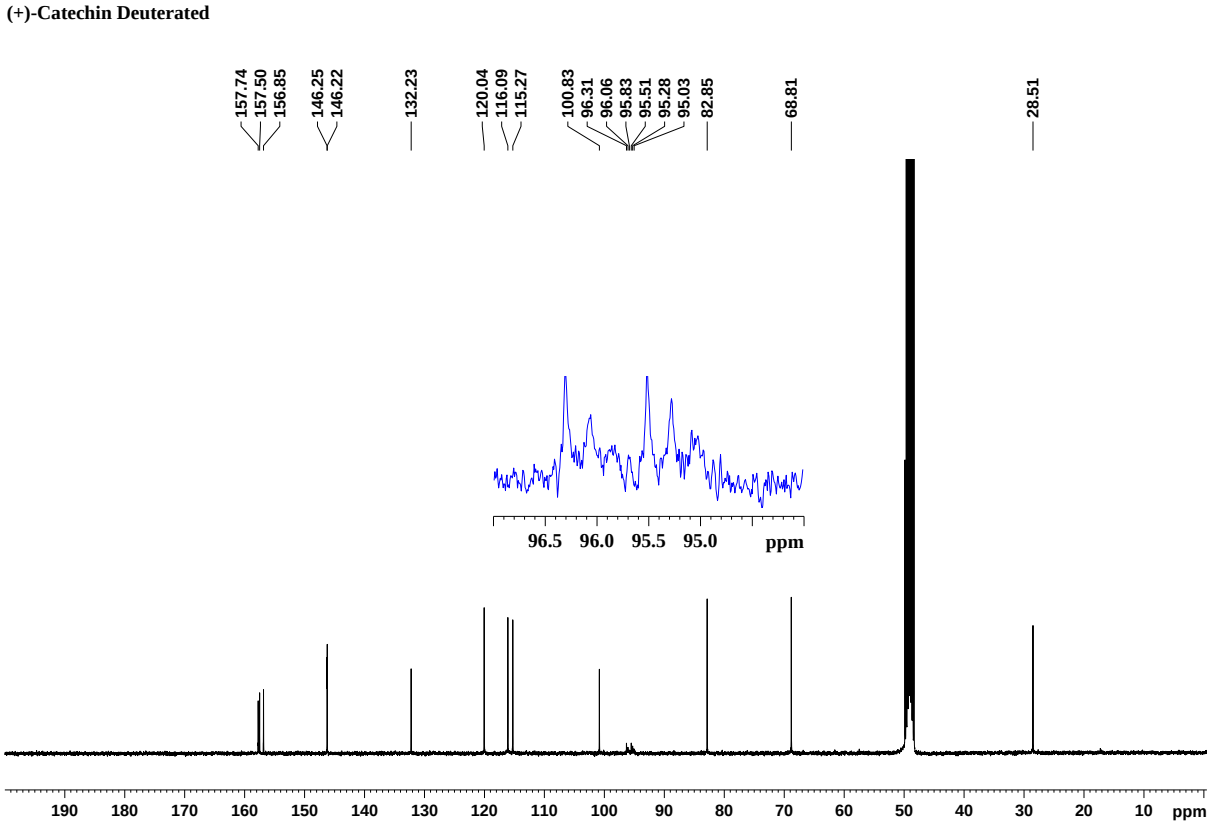
Supplementary Spectrum. ^{1}H NMR spectrum of kaempferol (**10**) (400 MHz, CD_3OD)



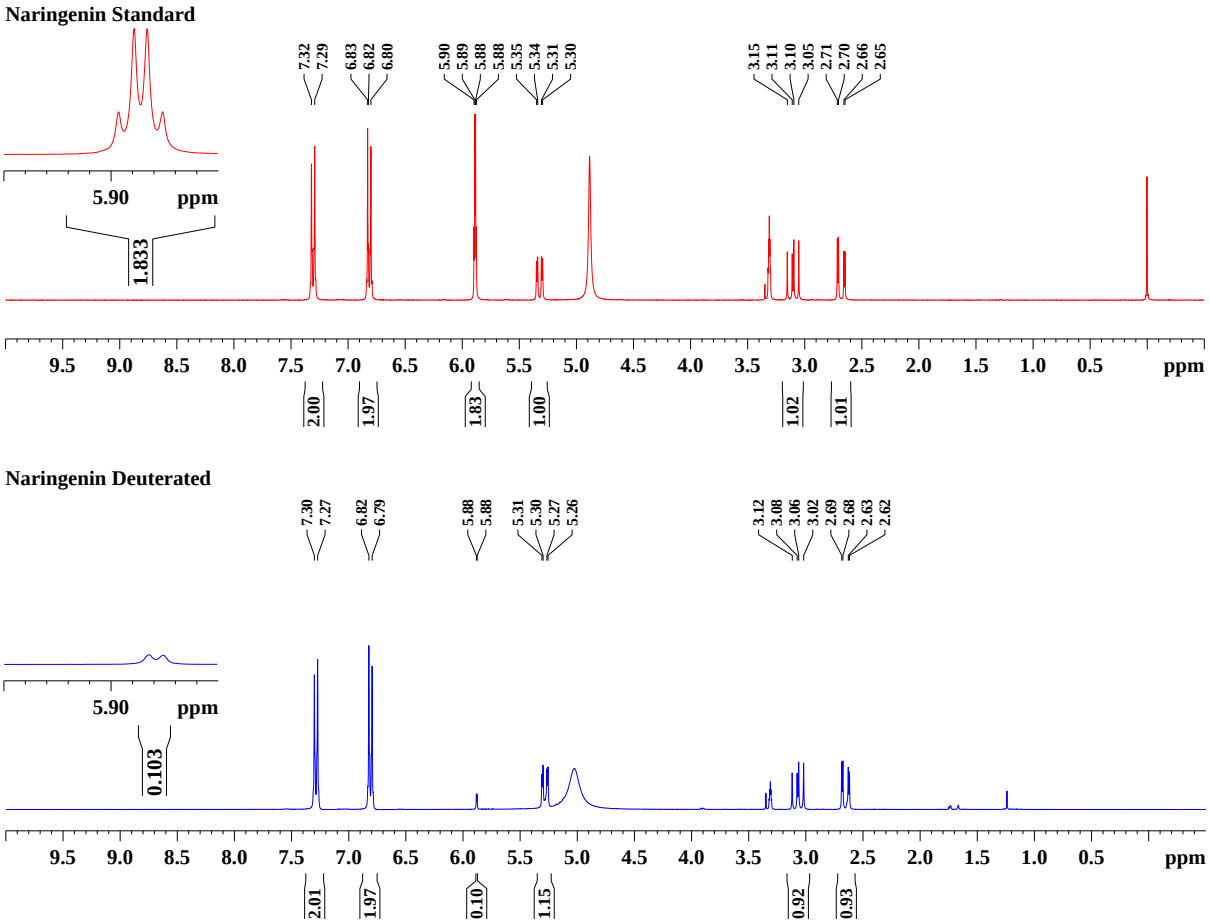
Supplementary Spectrum. ^{13}C NMR spectrum of kaempferol (**10**) (100 MHz, CD_3OD)



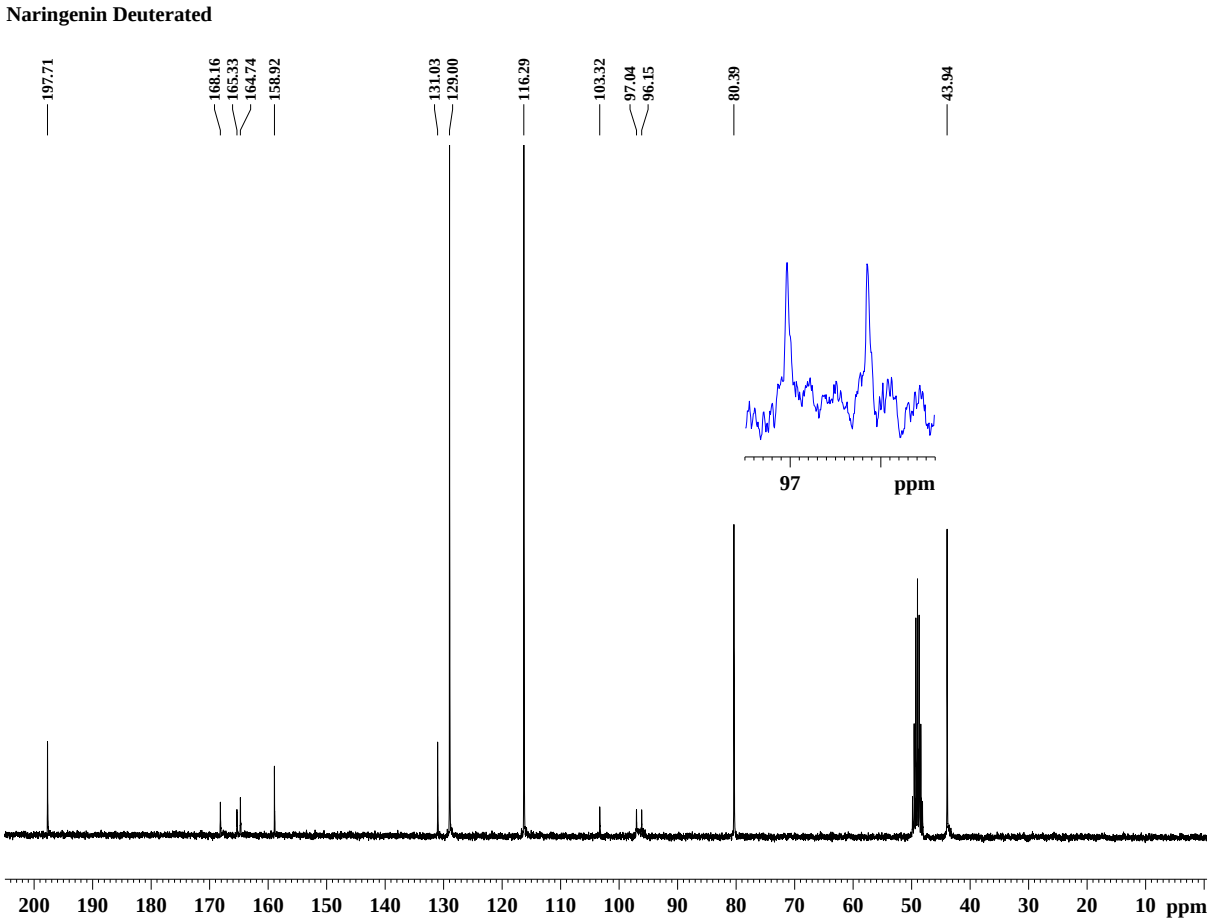
Supplementary Spectrum. ^{1}H NMR spectrum of catechin (**11**) (400 MHz, CD_3OD)



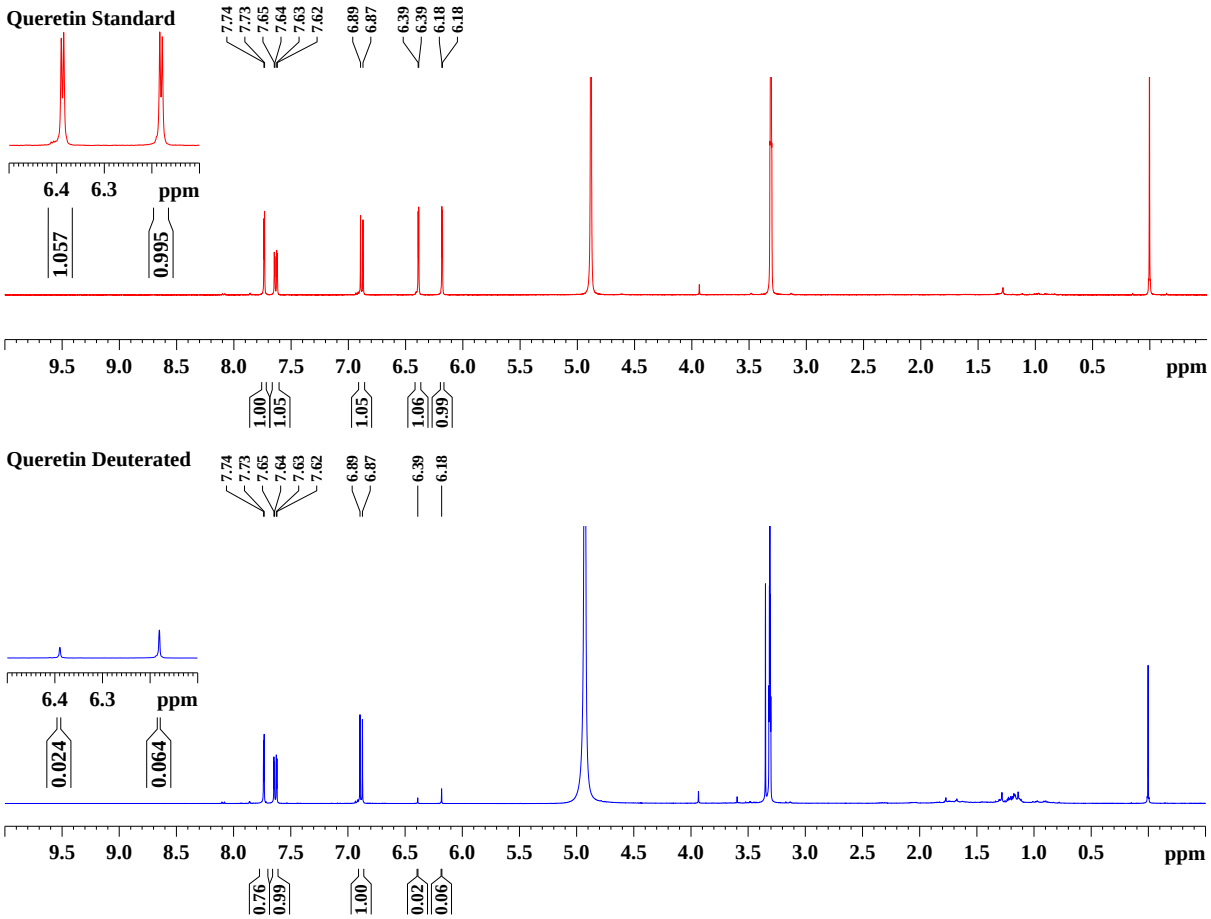
Supplementary Spectrum. ^{13}C NMR spectrum of catechin (**11**) (100 MHz, CD_3OD)



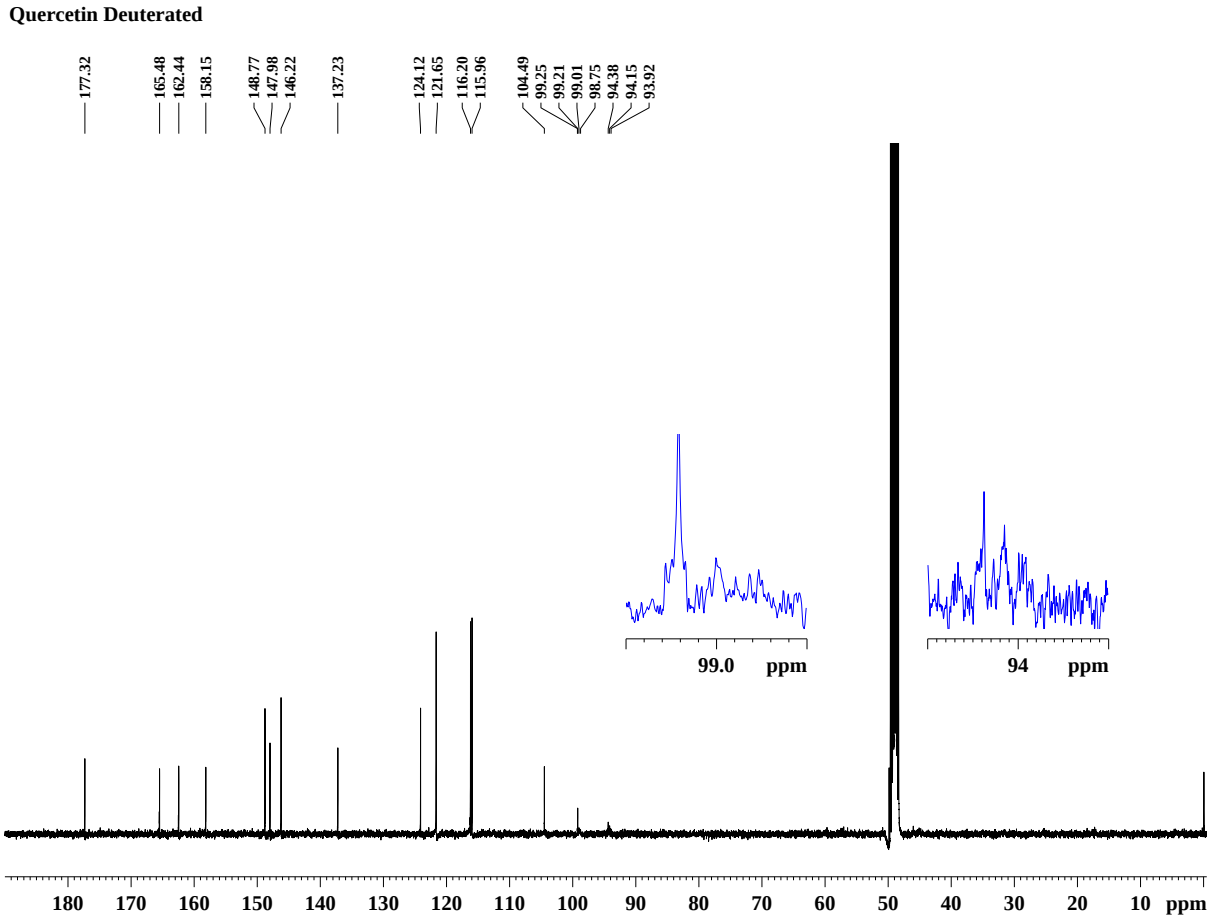
Supplementary Spectrum. ^{1}H NMR spectrum of naringenin (**12**) 300 MHz in CD_3OD



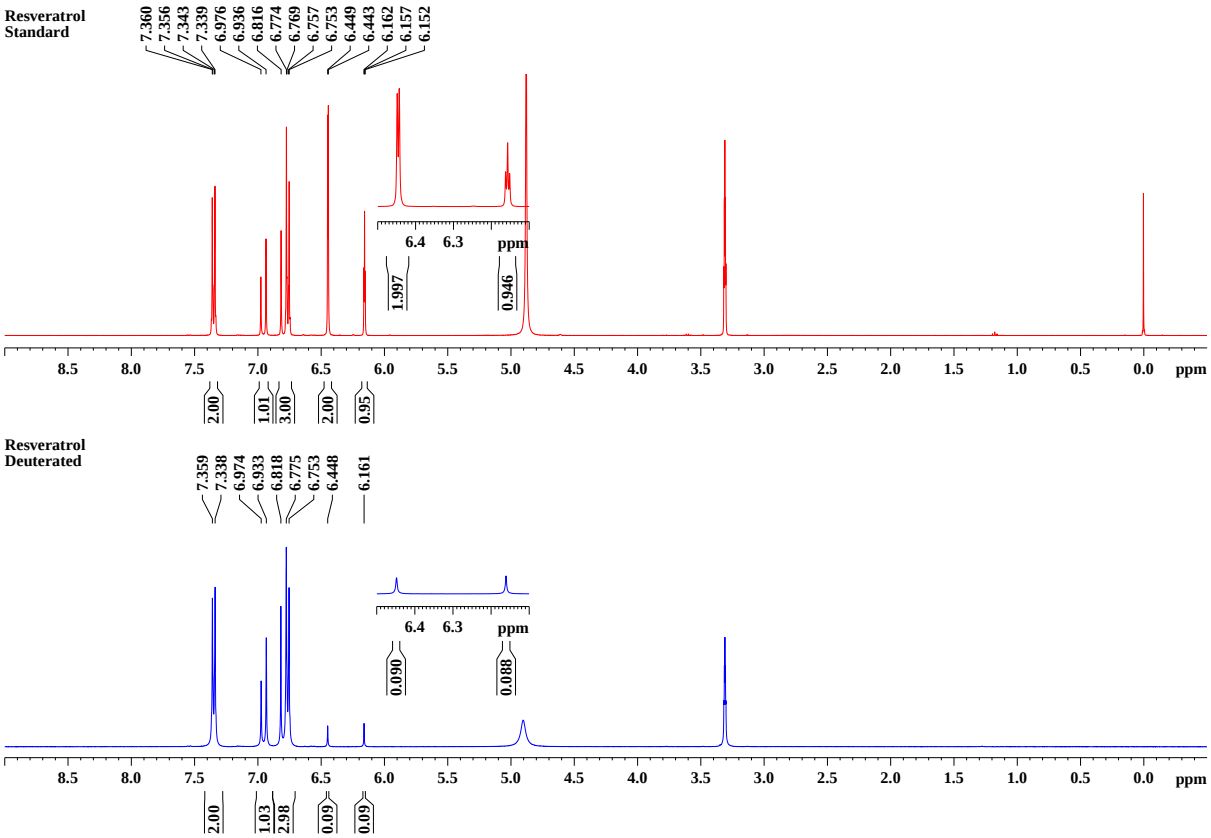
Supplementary Spectrum. ^{13}C NMR spectrum of naringenin (**12**) (75 MHz, CD_3OD)



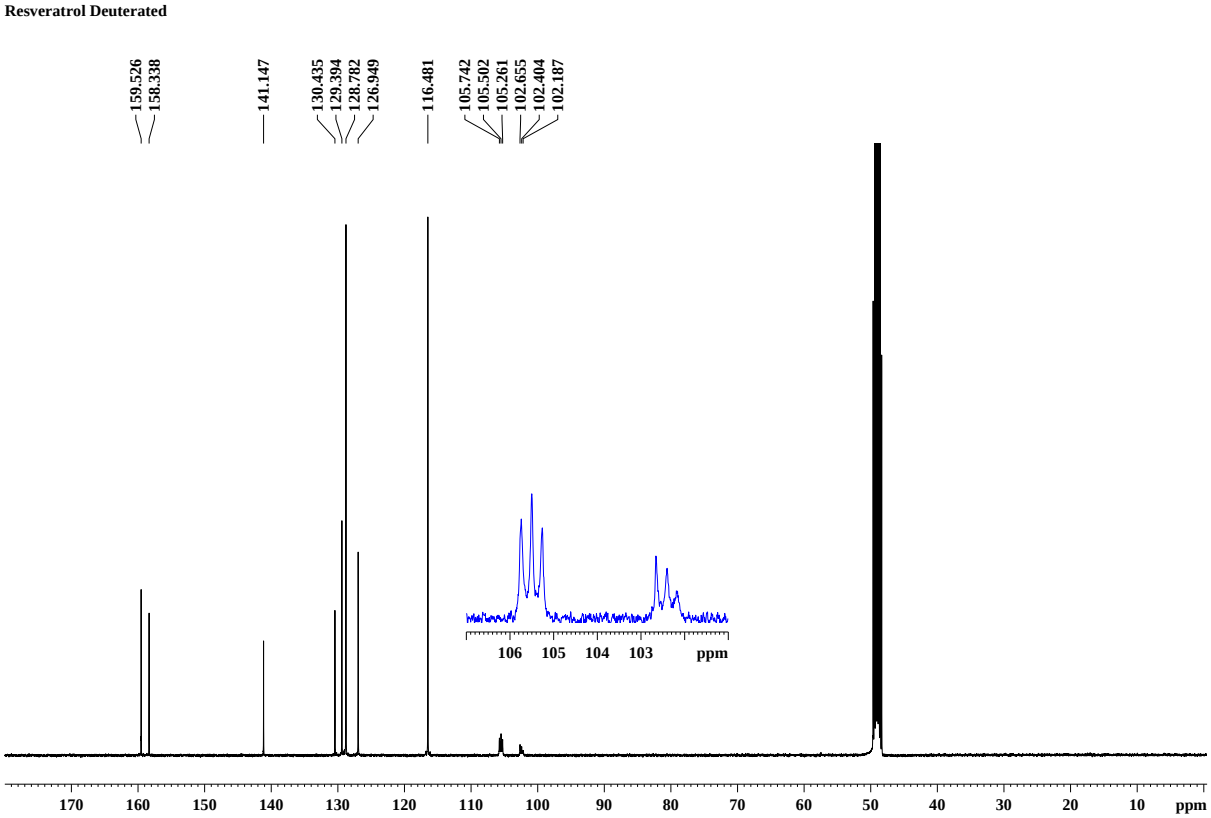
Supplementary Spectrum. ^{1}H NMR spectrum of quercetin (**13**) (400 MHz, CD_3OD)



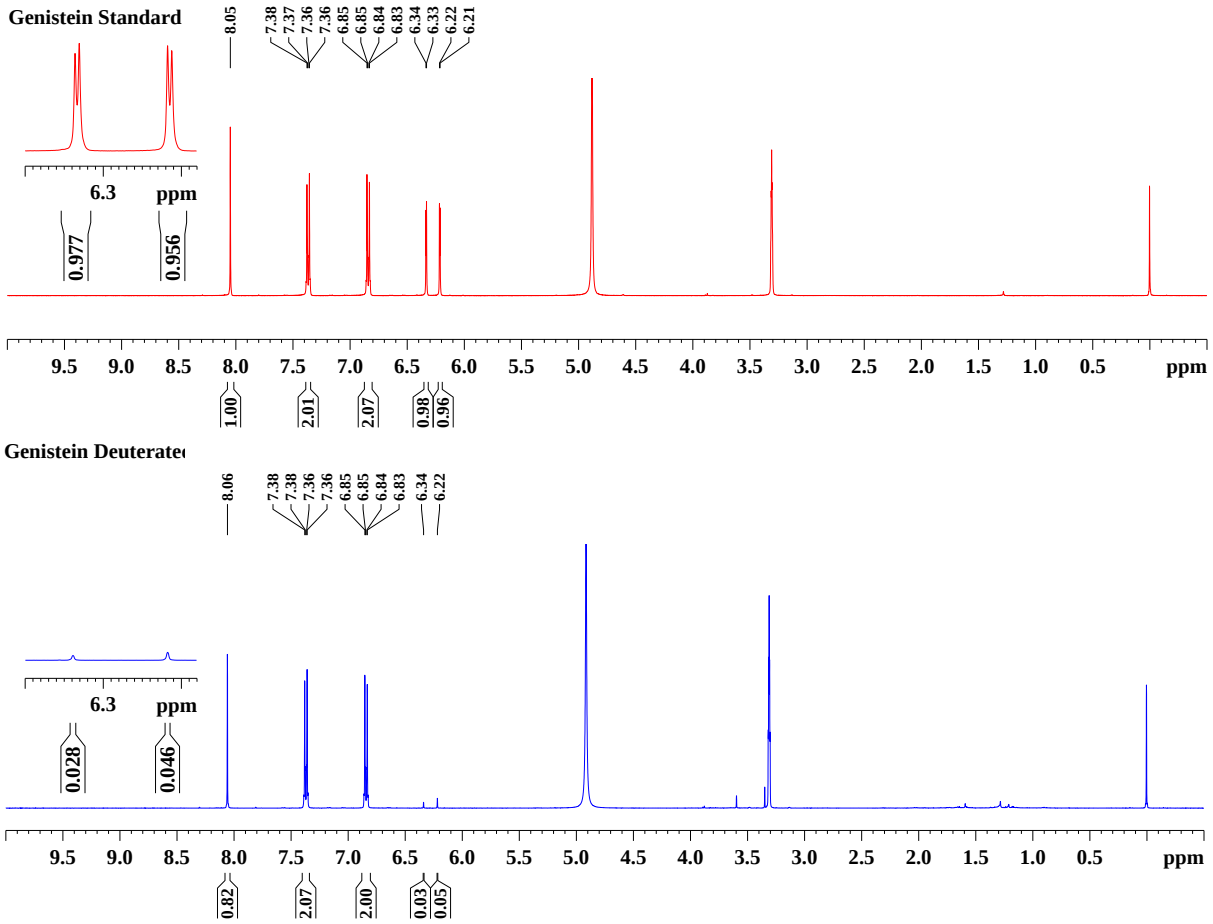
Supplementary Spectrum. ^{13}C NMR spectrum of quercetin (**13**) (100 MHz, CD_3OD)



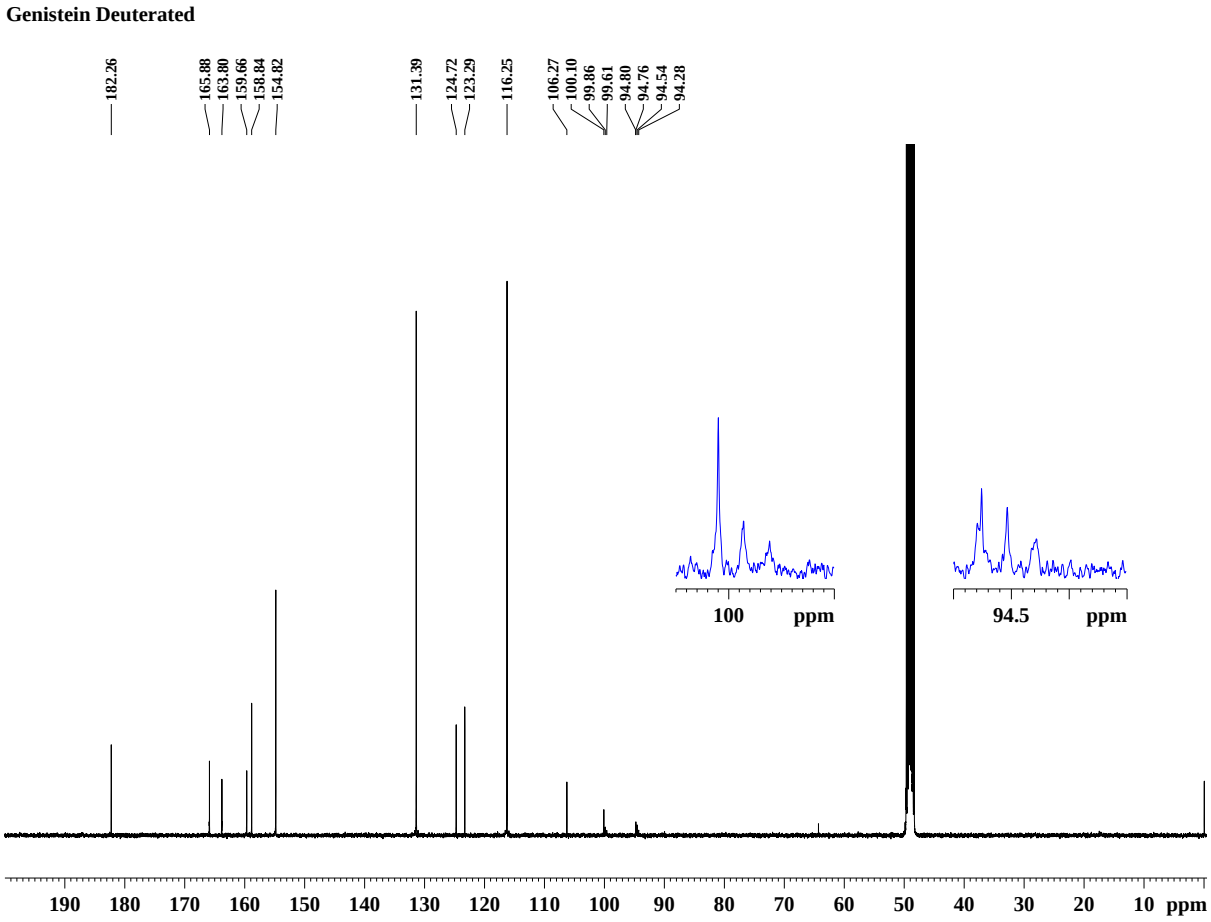
Supplementary Spectrum. ^{1}H NMR spectrum of resveratrol (**14**) (400 MHz, CD_3OD)



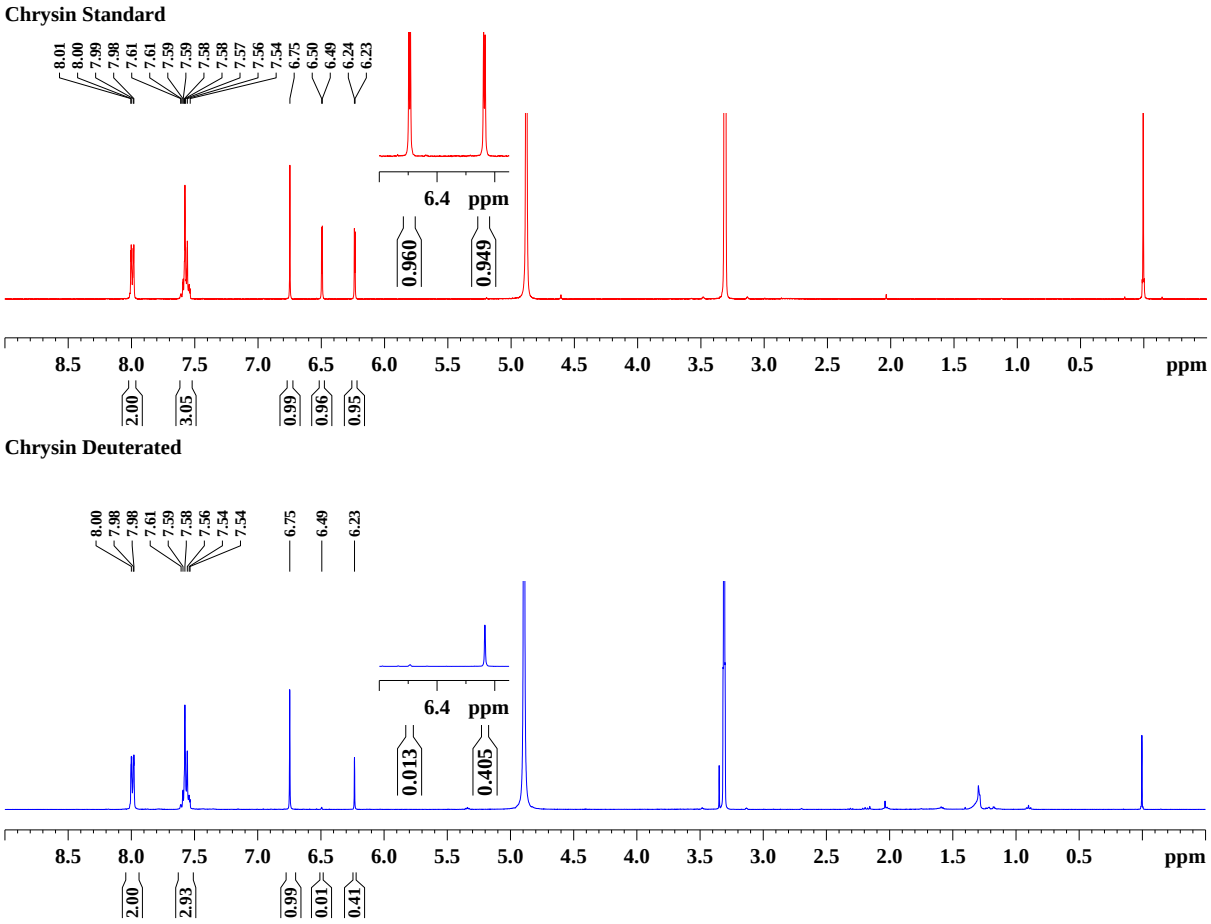
Supplementary Spectrum. ^{13}C NMR spectrum of resveratrol (**14**) (100 MHz, CD_3OD)



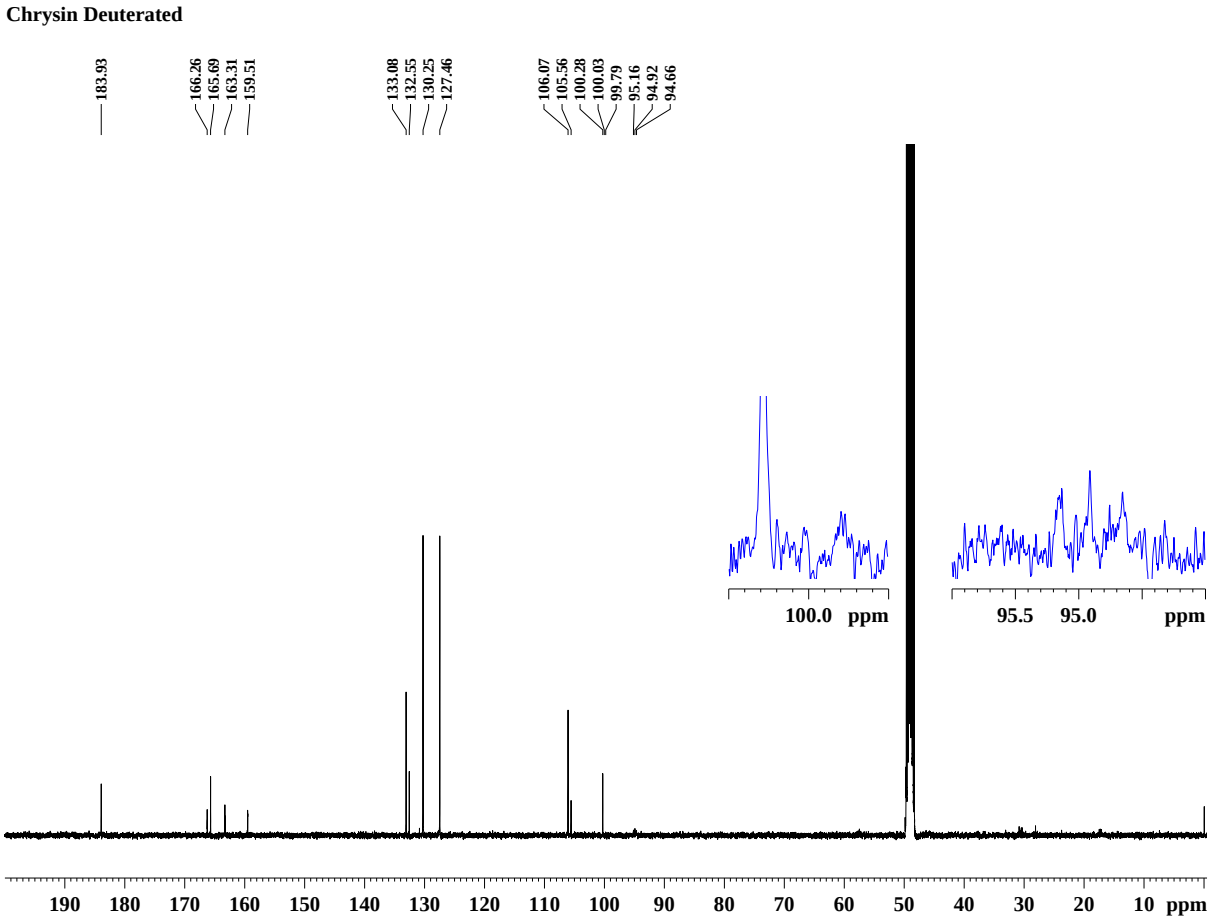
Supplementary Spectrum. ^{1}H NMR spectrum of genistein (**15**) (400 MHz, CD_3OD)



Supplementary Spectrum. ^{13}C NMR spectrum of genistein (**15**) (100 MHz, CD_3OD)

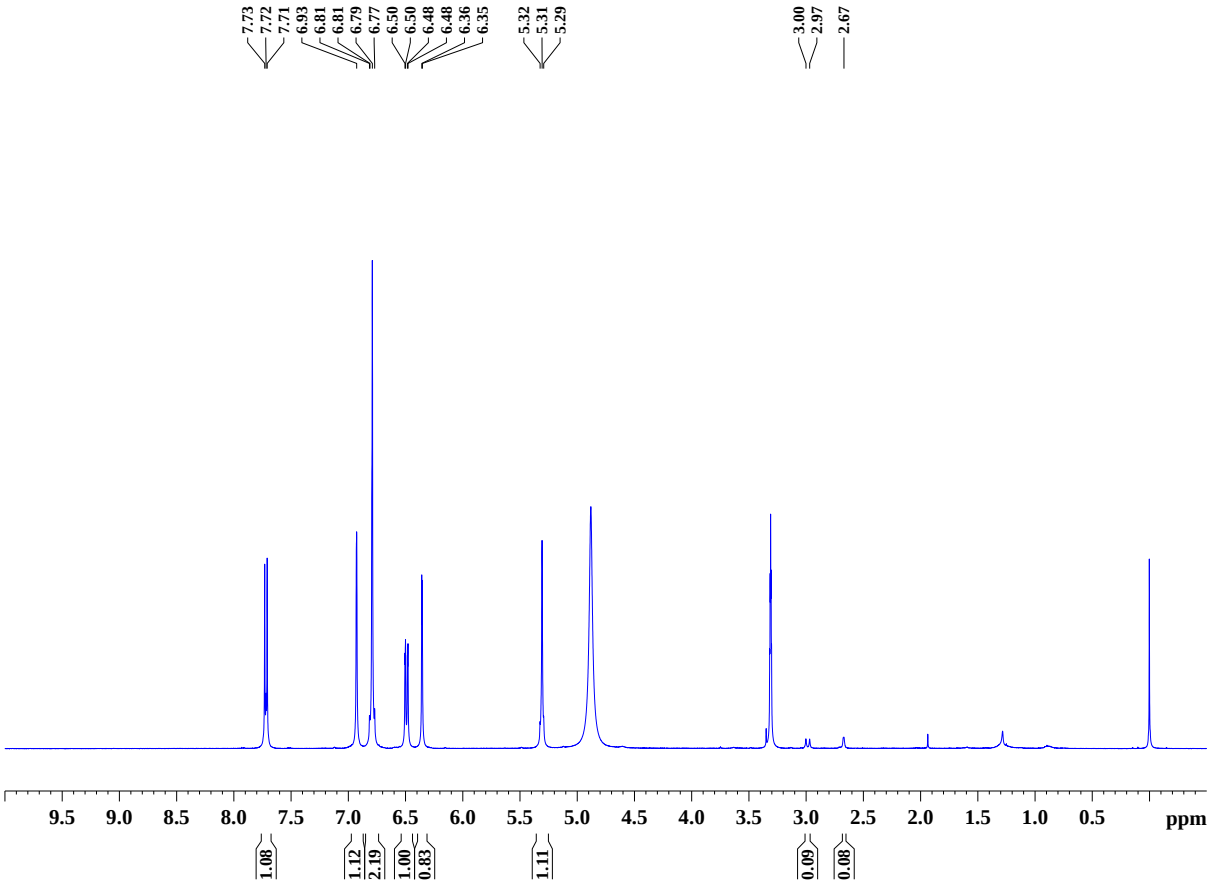


Supplementary Spectrum. ^{1}H NMR spectrum of chrysin (**16**) (400 MHz, CD_3OD)

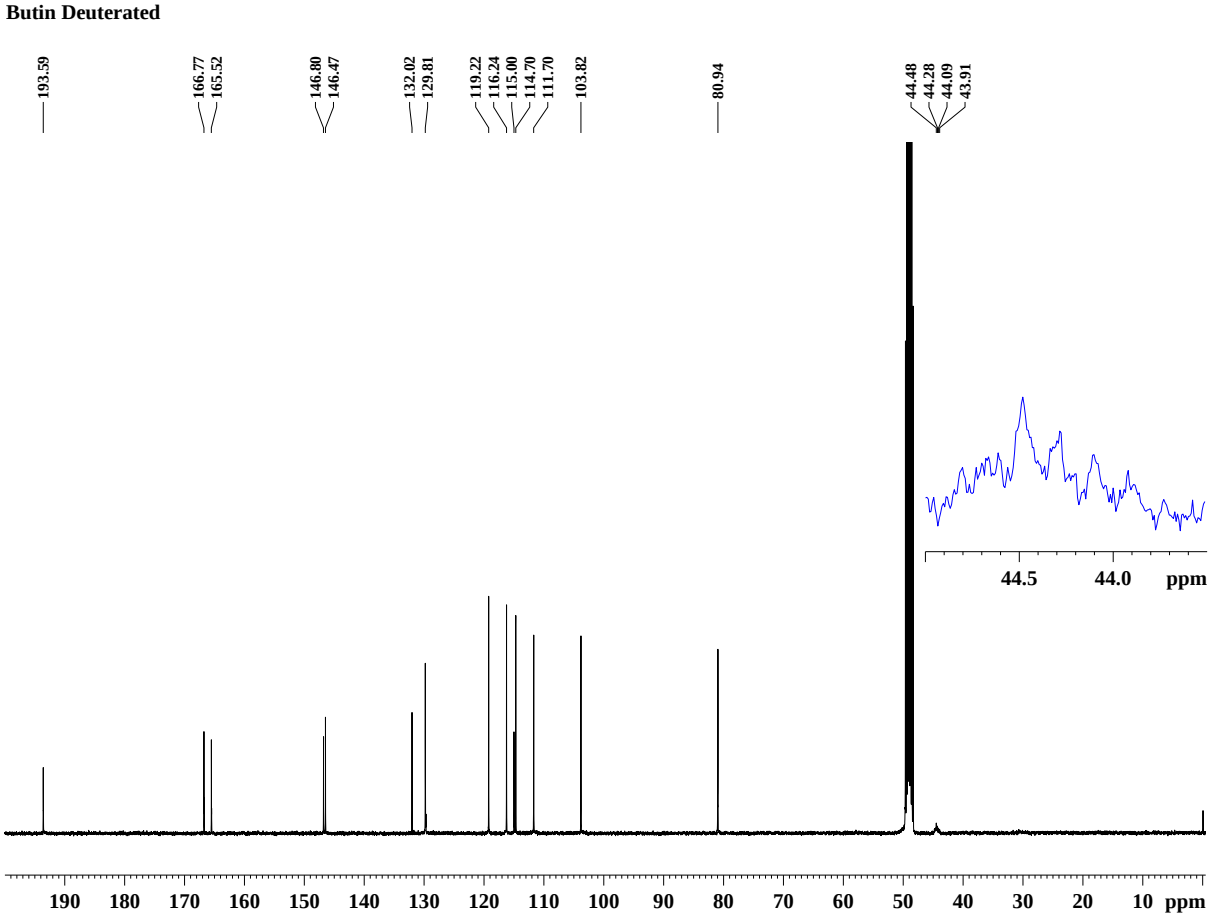


Supplementary Spectrum. ^{13}C NMR spectrum of chrysin (**16**) (100 MHz, CD_3OD)

Butin Deuterated

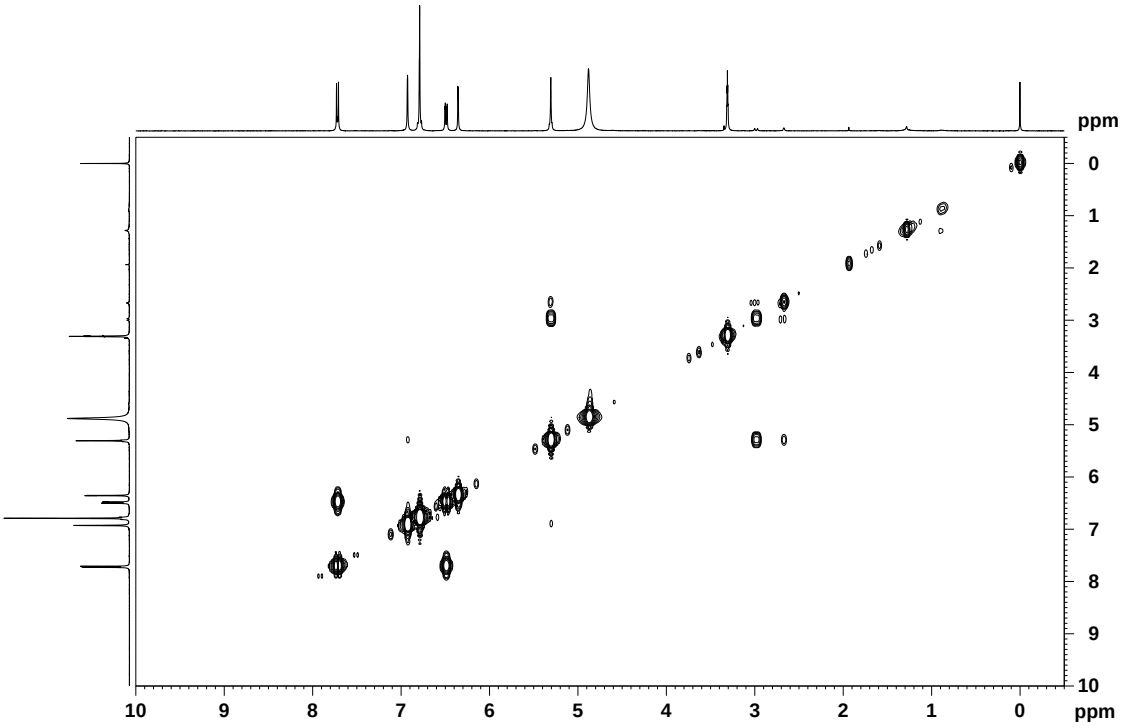


Supplementary Spectrum. ^{1}H NMR spectrum of butin (**18**) (400 MHz, CD_3OD)

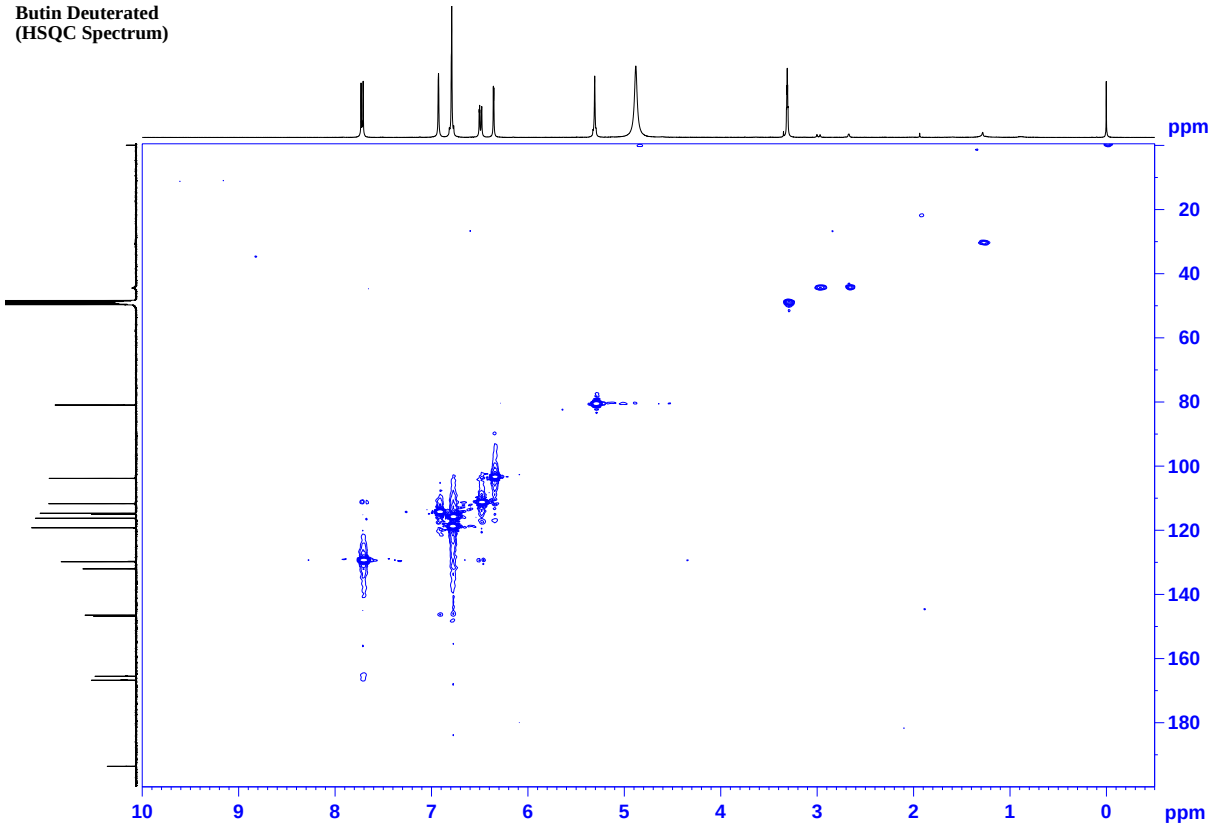


Supplementary Spectrum. ^{13}C NMR spectrum of butin (**18**) (100 MHz, CD_3OD)

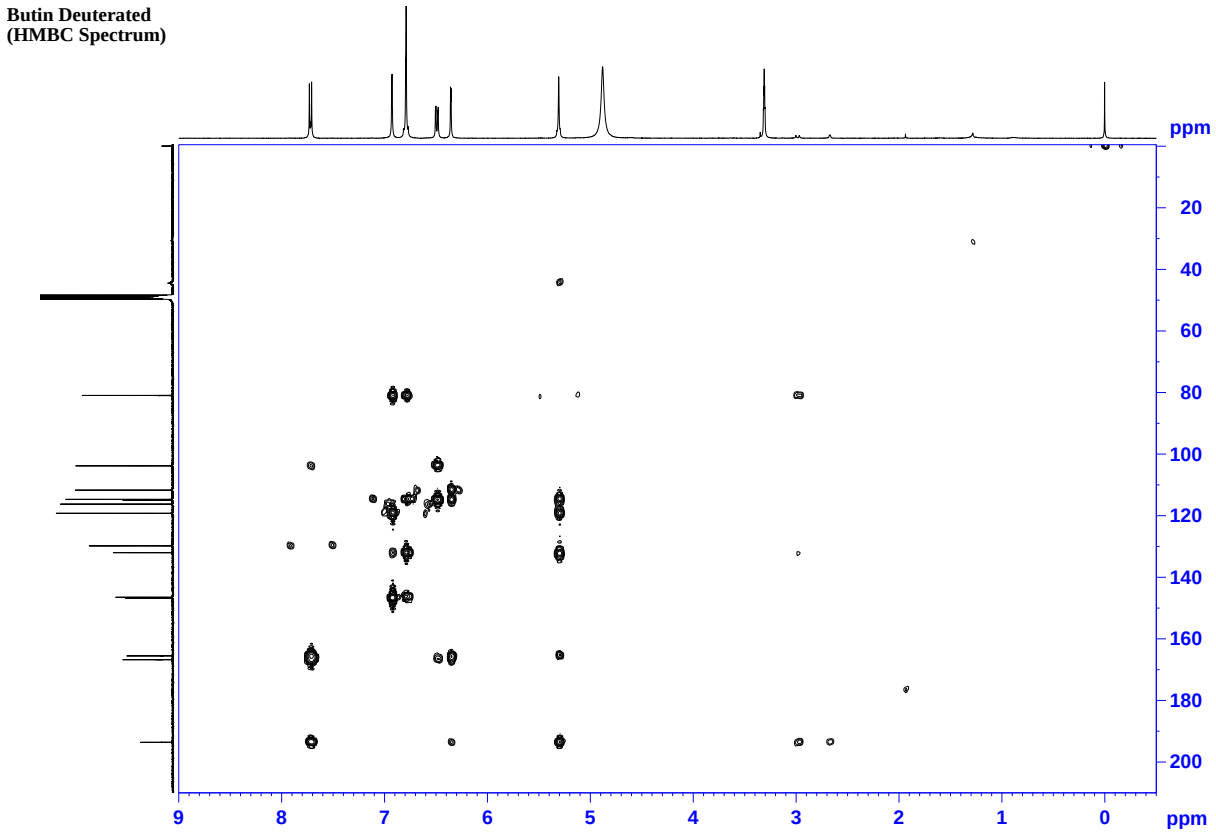
Butin Deuterated
(COSY Spectrum)



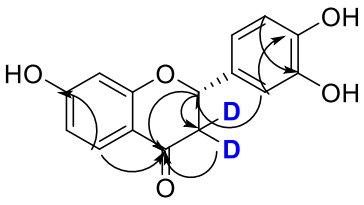
Supplementary Spectrum. ^{1}H-^{1}H COSY spectrum of butin (**18**) in CD_3OD



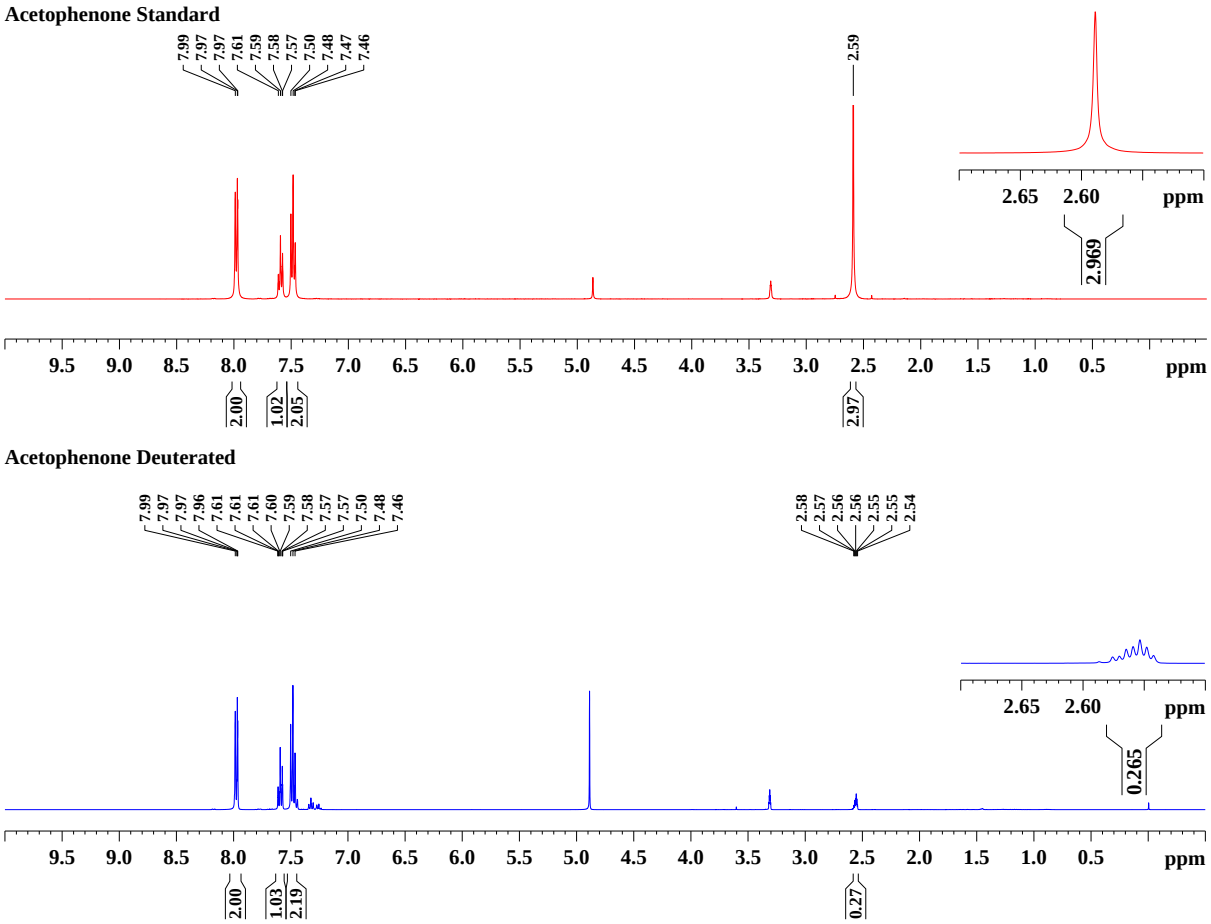
Supplementary Spectrum. HSQC spectrum of butin (**18**) in CD_3OD



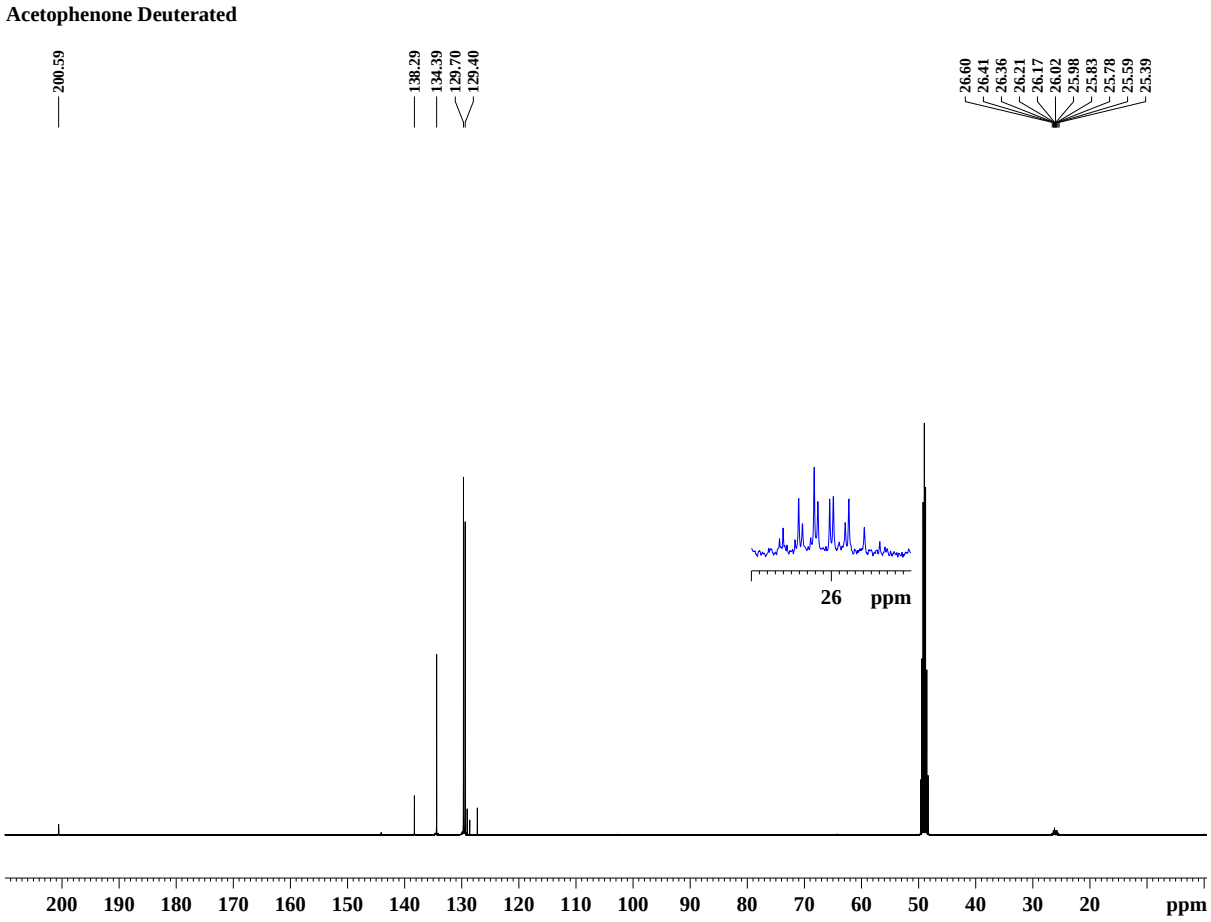
Supplementary Spectrum. HMBC spectrum of butin (**18**) in CD_3OD



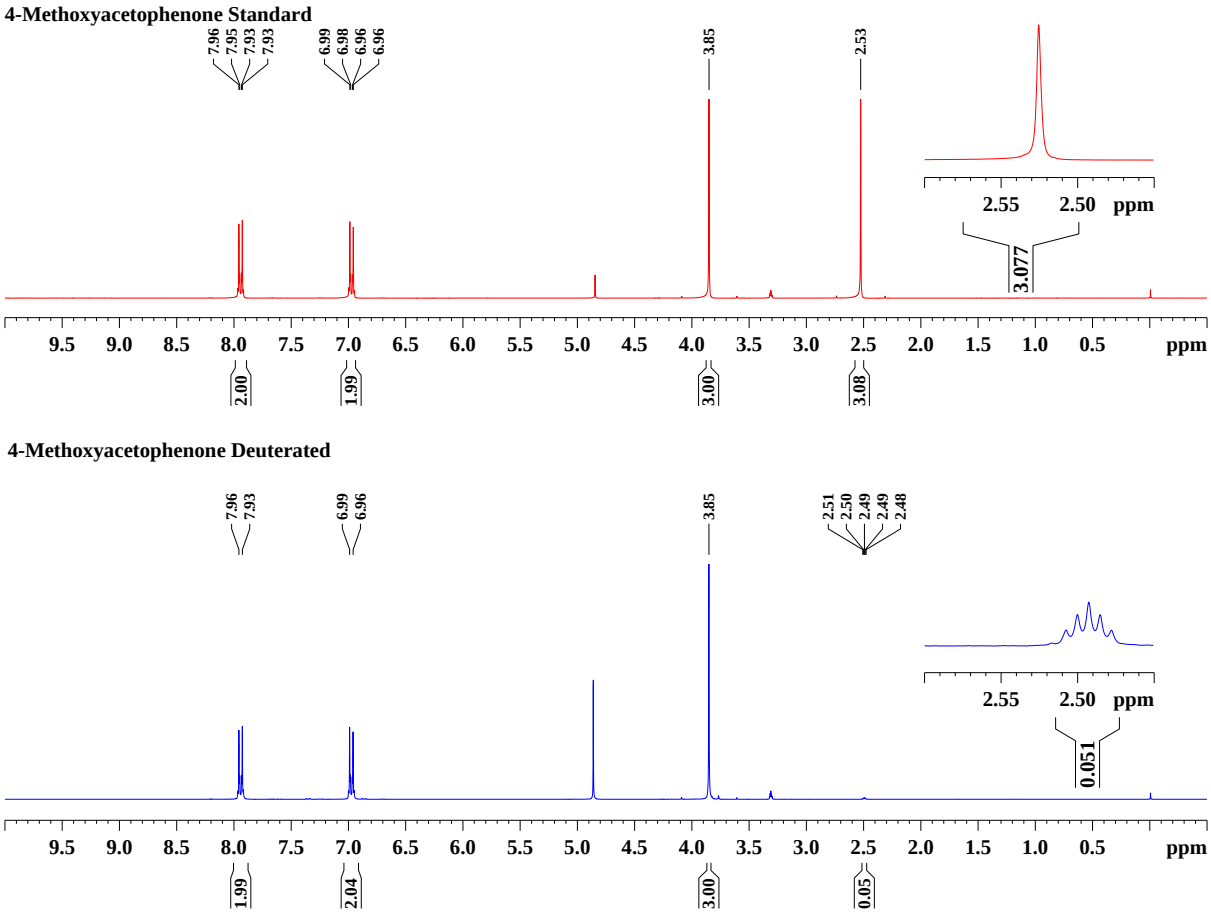
HMBC correlations of deuterated butin (**18**)



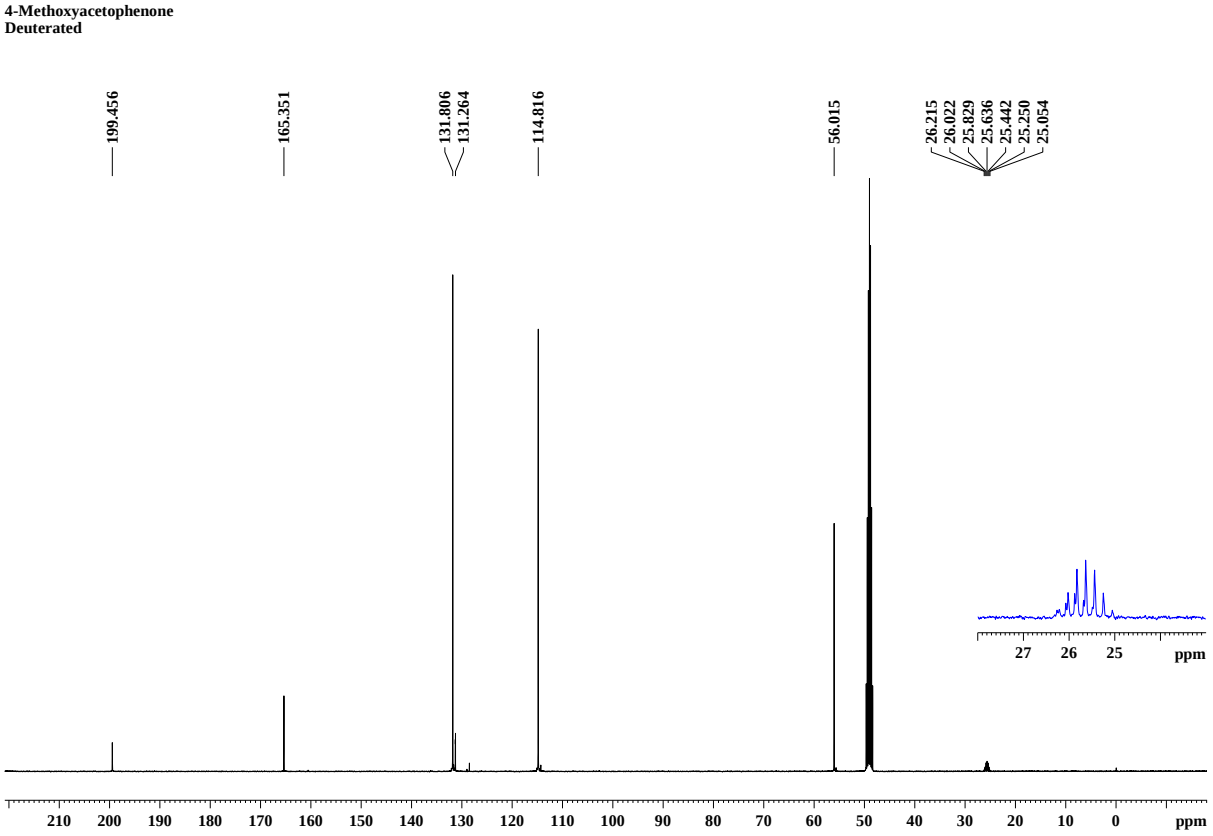
Supplementary Spectrum. ^{1}H NMR spectrum of acetophenone (**19**) (400 MHz, CD_3OD)



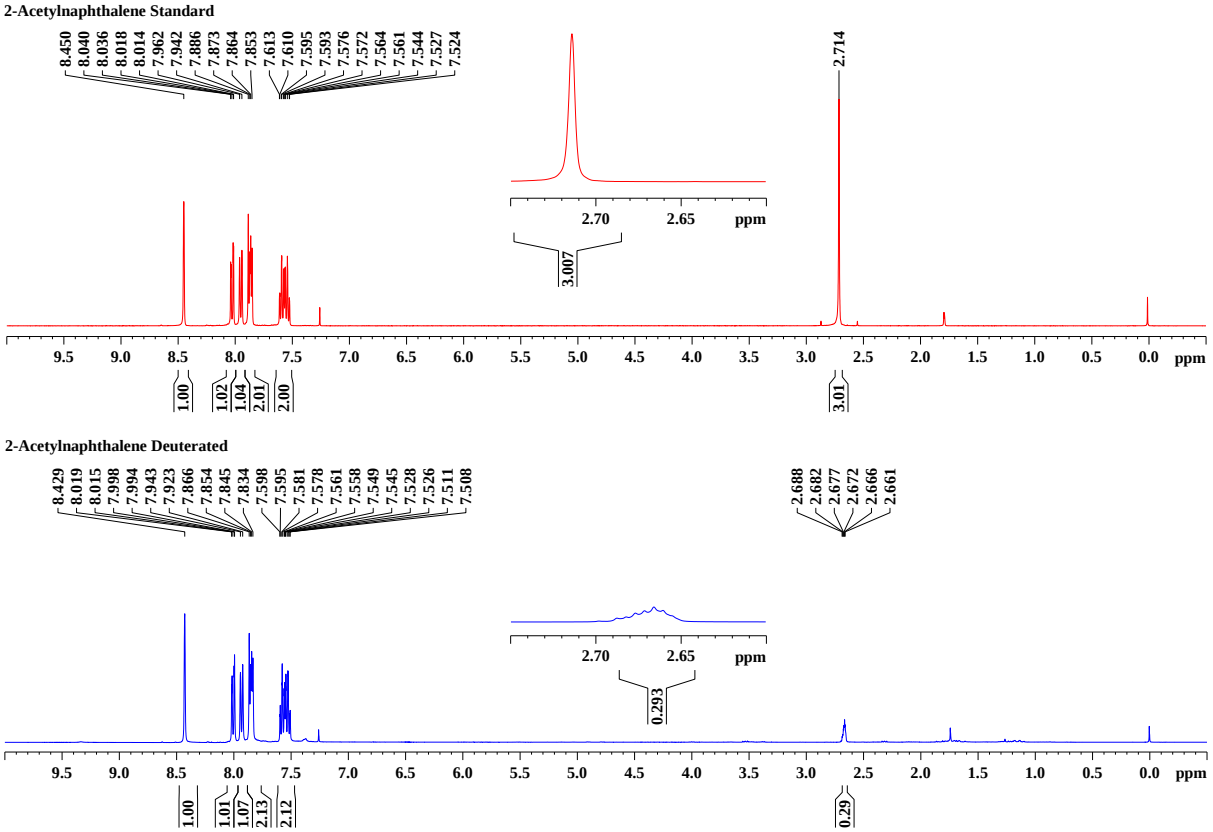
Supplementary Spectrum. ^{13}C NMR spectrum of acetophenone (**19**) (100 MHz, CD_3OD)



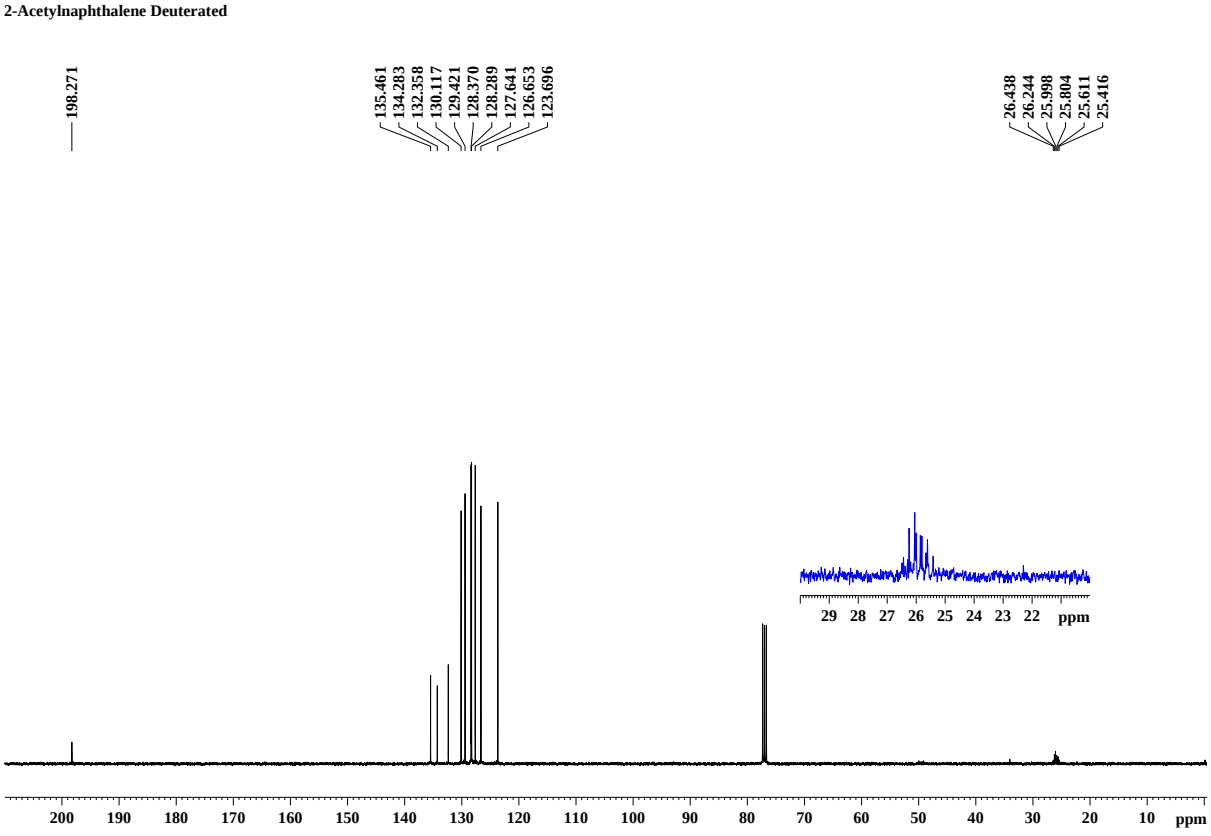
Supplementary Spectrum. ^{1}H NMR spectrum of 4'-methoxyacetophenone (**20**) (400 MHz, CD_3OD)



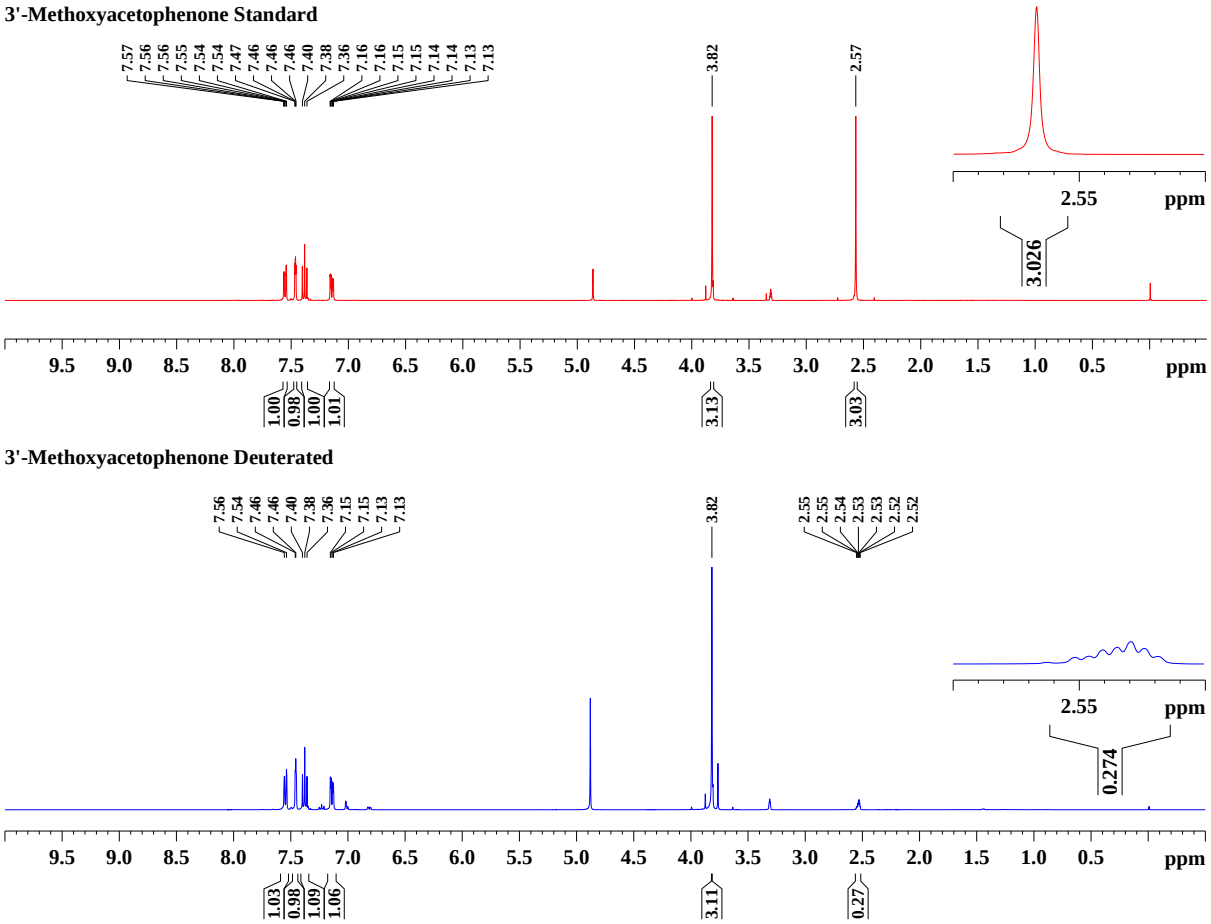
Supplementary Spectrum. ^{13}C NMR spectrum of 4'-methoxyacetophenone (**20**) (100 MHz, CD_3OD)



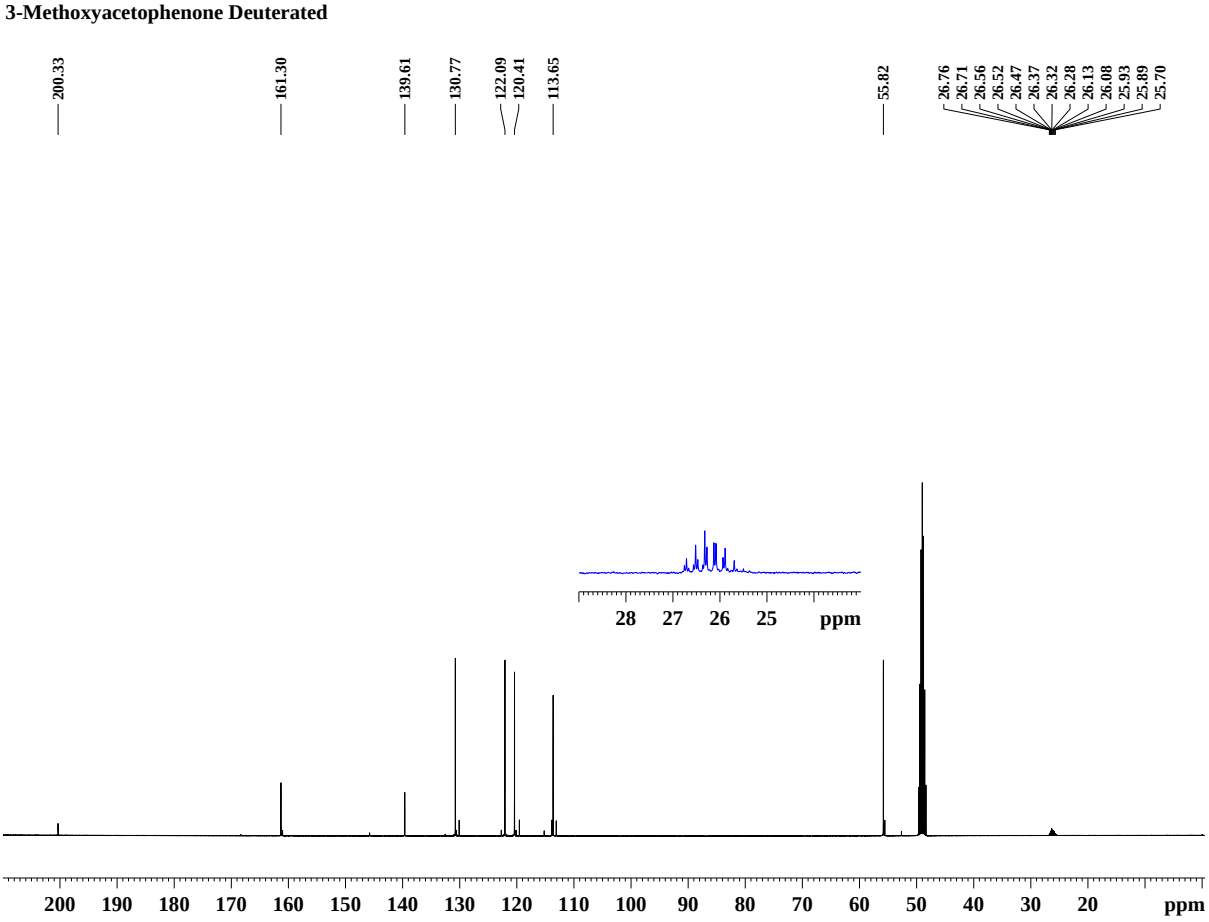
Supplementary Spectrum. ^{1}H NMR spectrum of 2-acetylnaphthalene (**21**) (400 MHz, $CDCl_3$)



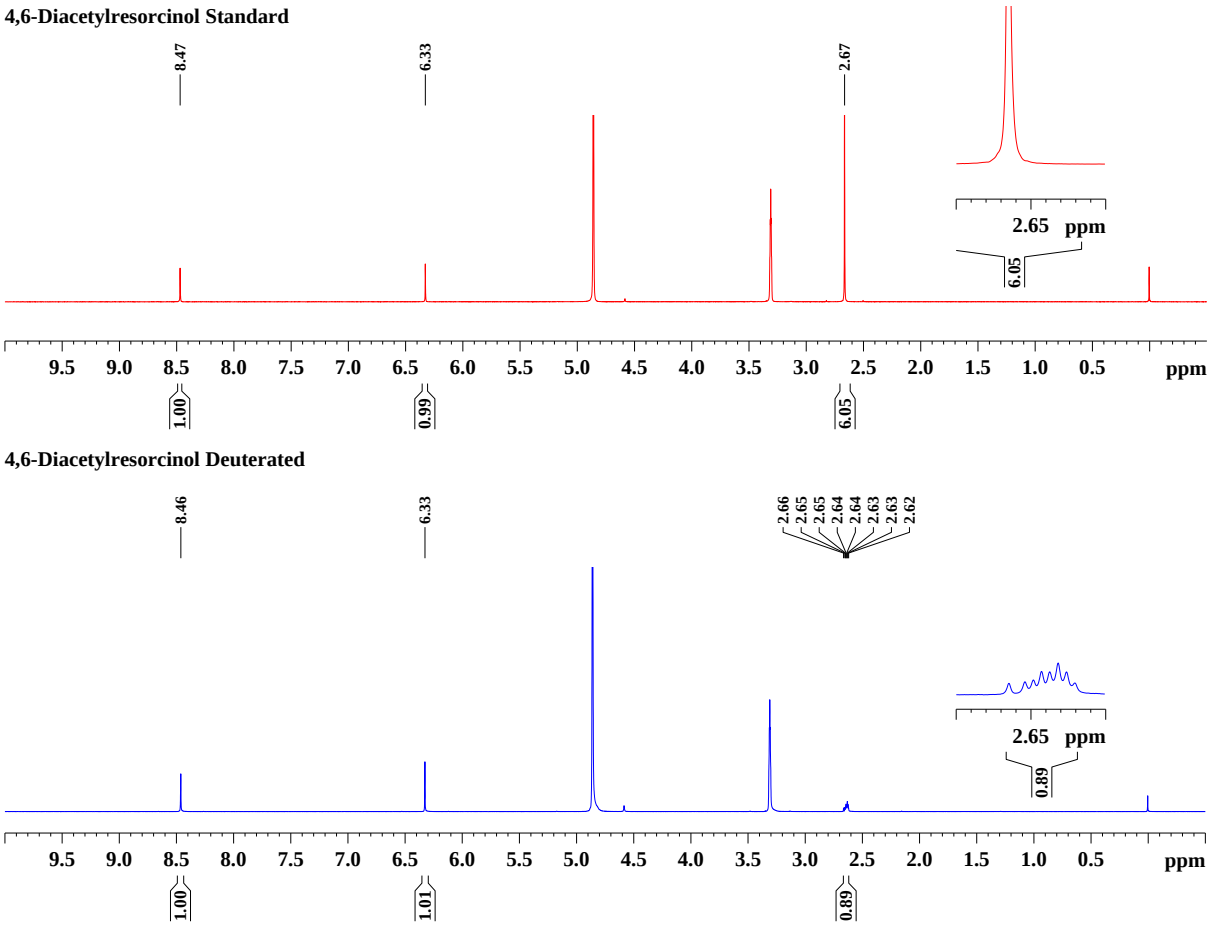
Supplementary Spectrum. ^{13}C NMR spectrum of 2-acetylnaphthalene (**21**) (100 MHz, $CDCl_3$)



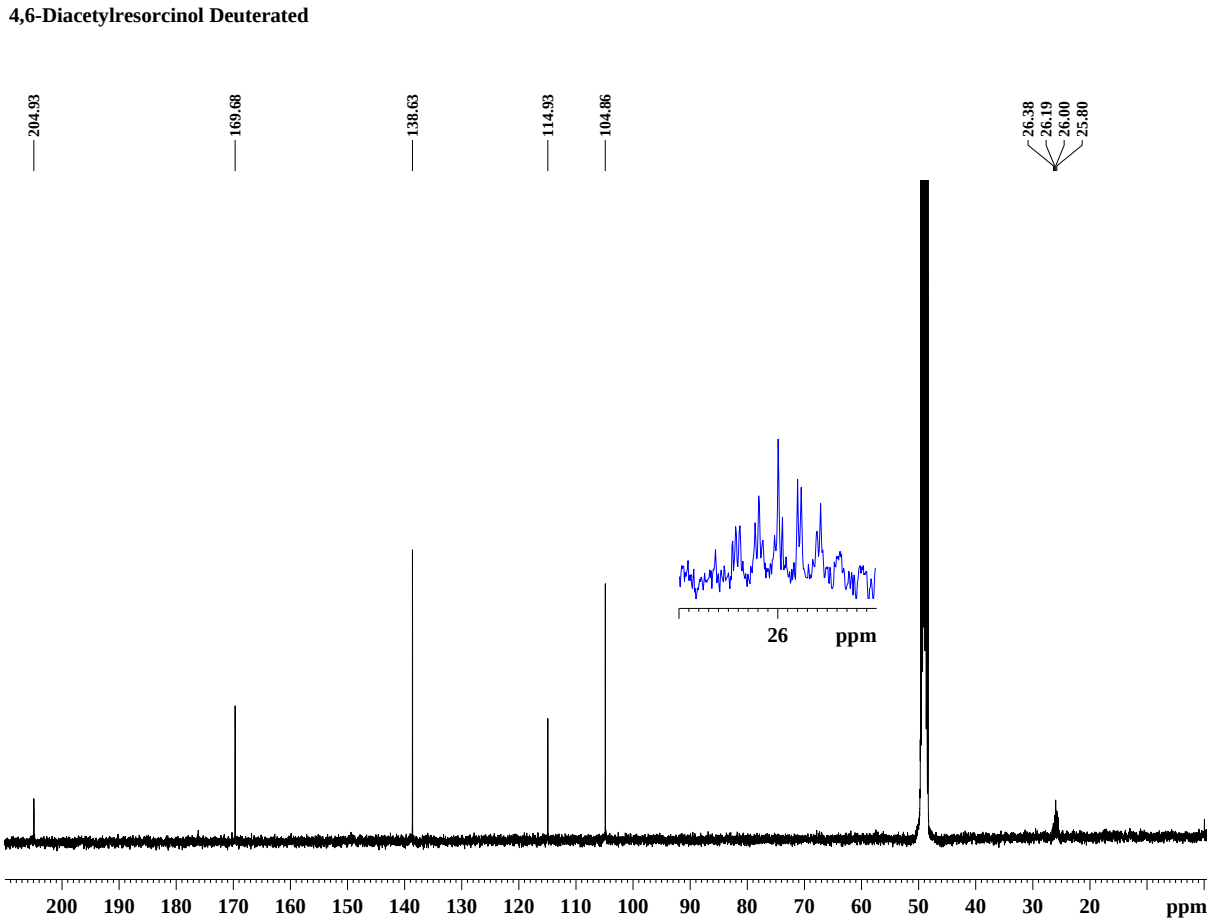
Supplementary Spectrum. ^{1}H NMR spectrum of 3'-methoxyacetophenone (**22**) (400 MHz, CD_3OD)



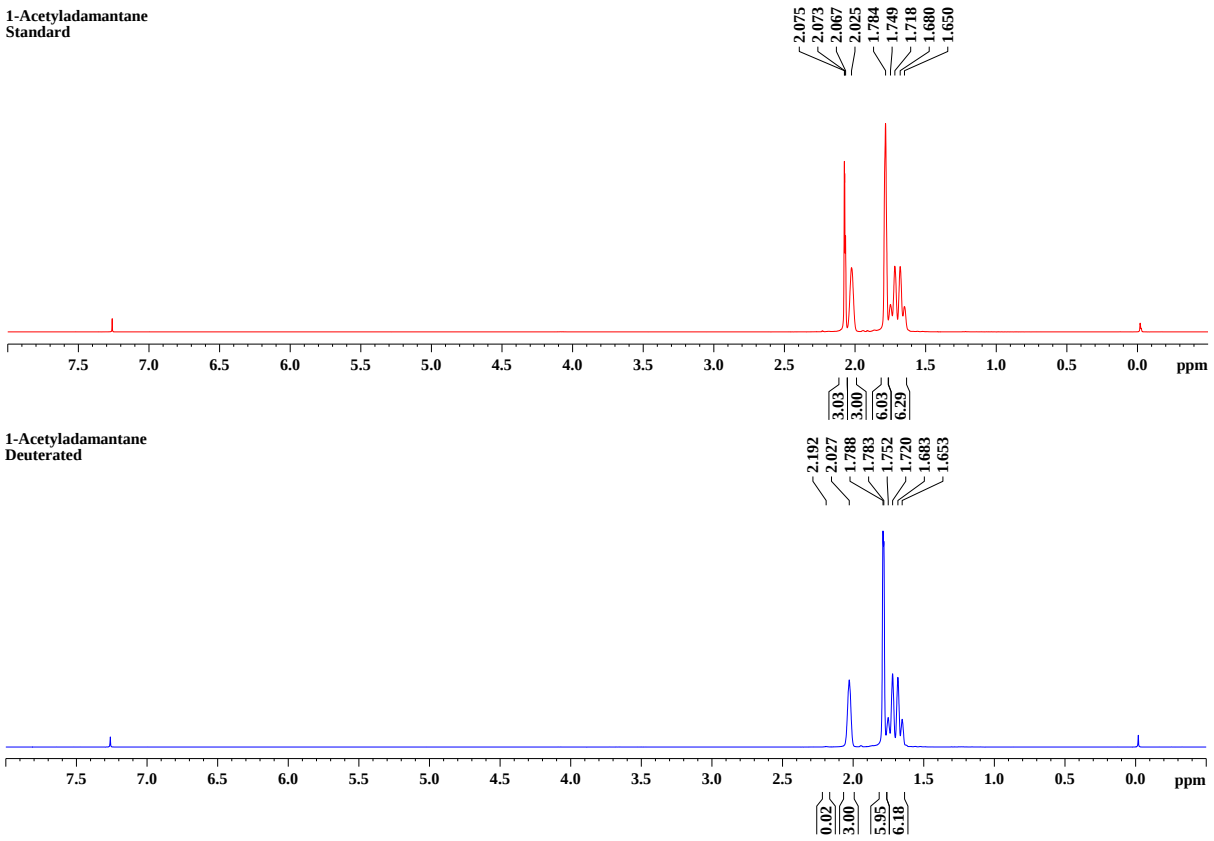
Supplementary Spectrum. ^{13}C NMR spectrum of 3'-methoxyacetophenone (**22**) (100 MHz, CD_3OD)



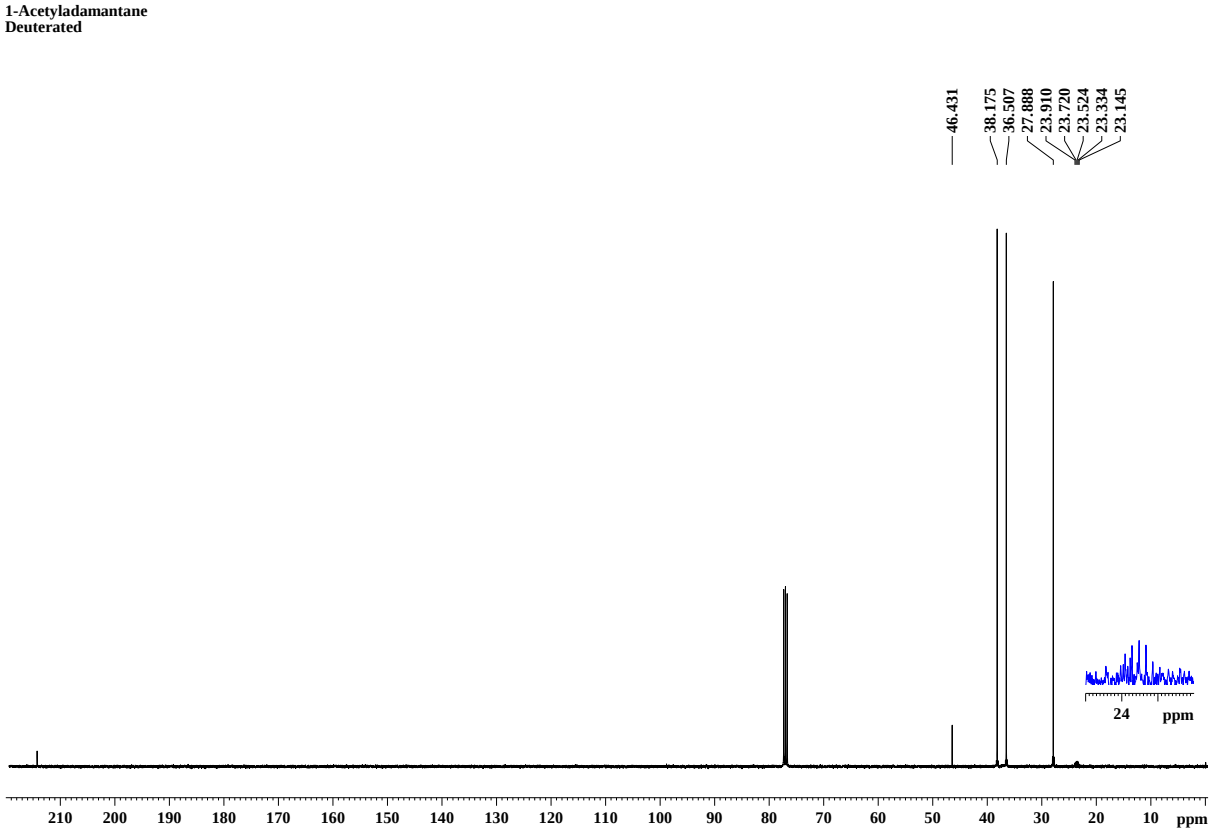
Supplementary Spectrum. ^{1}H NMR spectrum of 4,6-diacetylresorcinol (**23**) (400 MHz, CD_3OD)



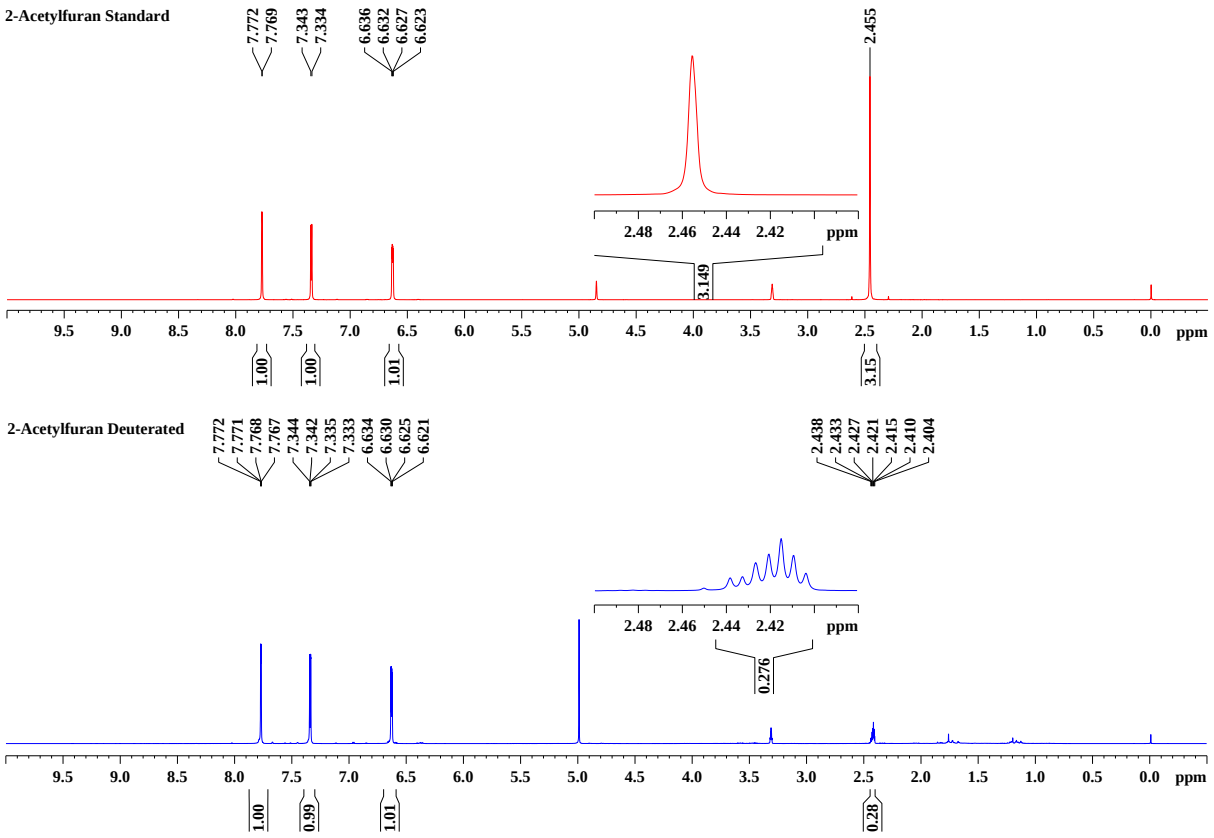
Supplementary Spectrum. ^{13}C NMR spectrum of 4,6-diacetylresorcinol (**23**) (100 MHz, CD_3OD)



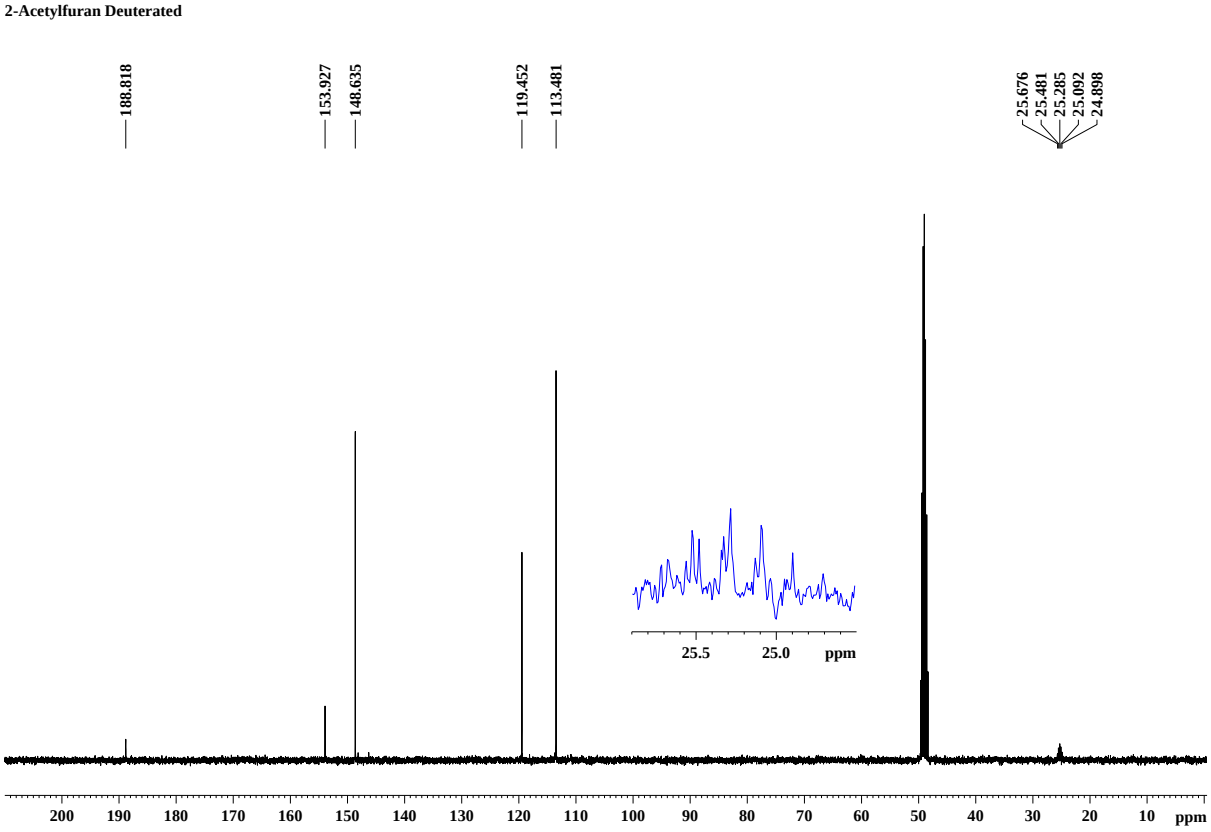
Supplementary Spectrum. ^{1}H NMR spectrum of 1-acetyladamantane (**24**) (400 MHz, $CDCl_3$)



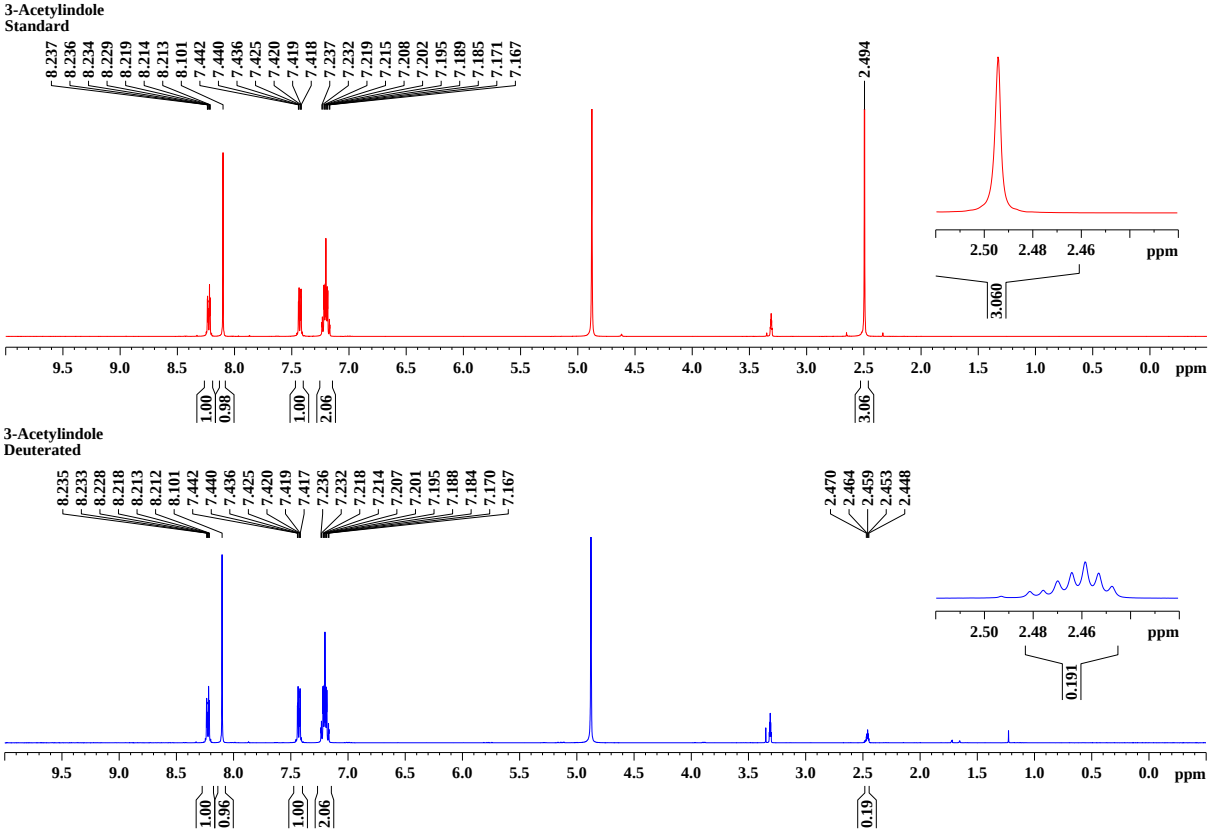
Supplementary Spectrum. ^{13}C NMR spectrum of 1-acetyladamantane (**24**) (100 MHz, $CDCl_3$)



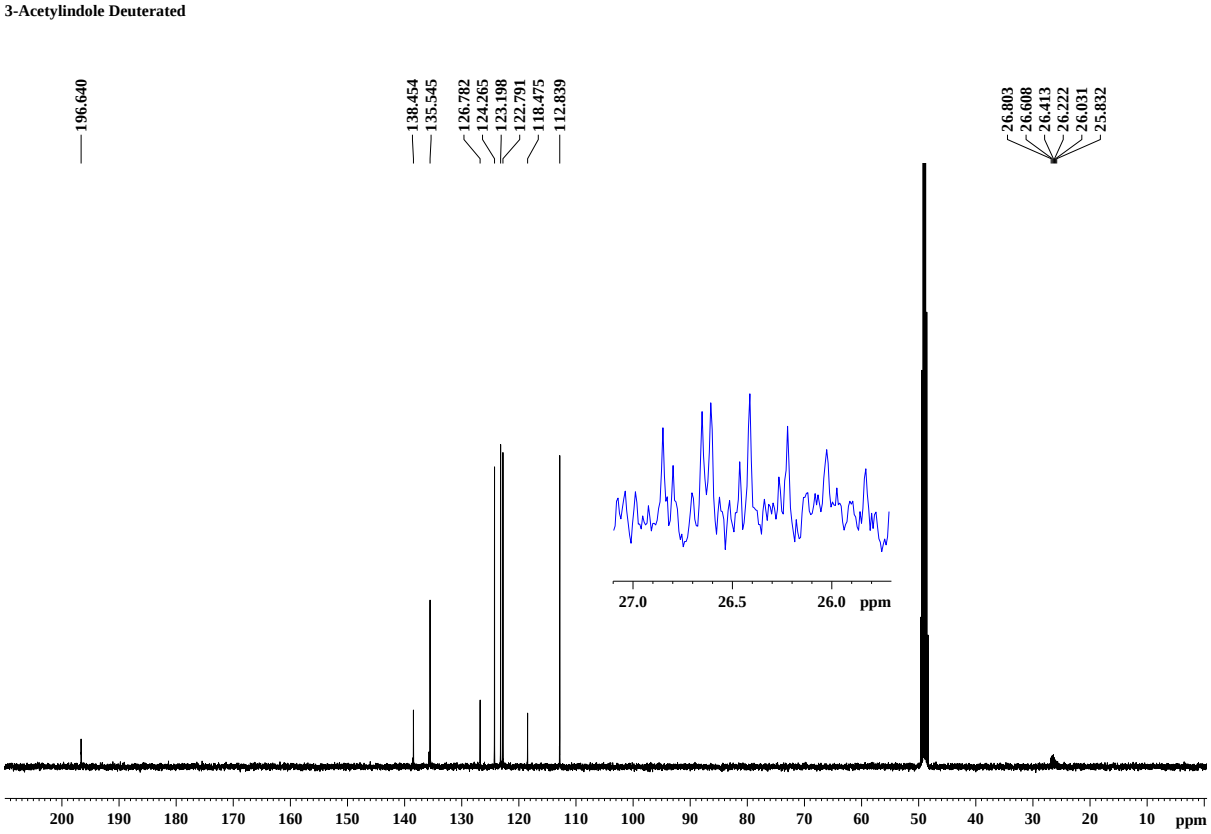
Supplementary Spectrum. ^{1}H NMR spectrum of 2-acetylfuran (**25**) (400 MHz, CD_3OD)



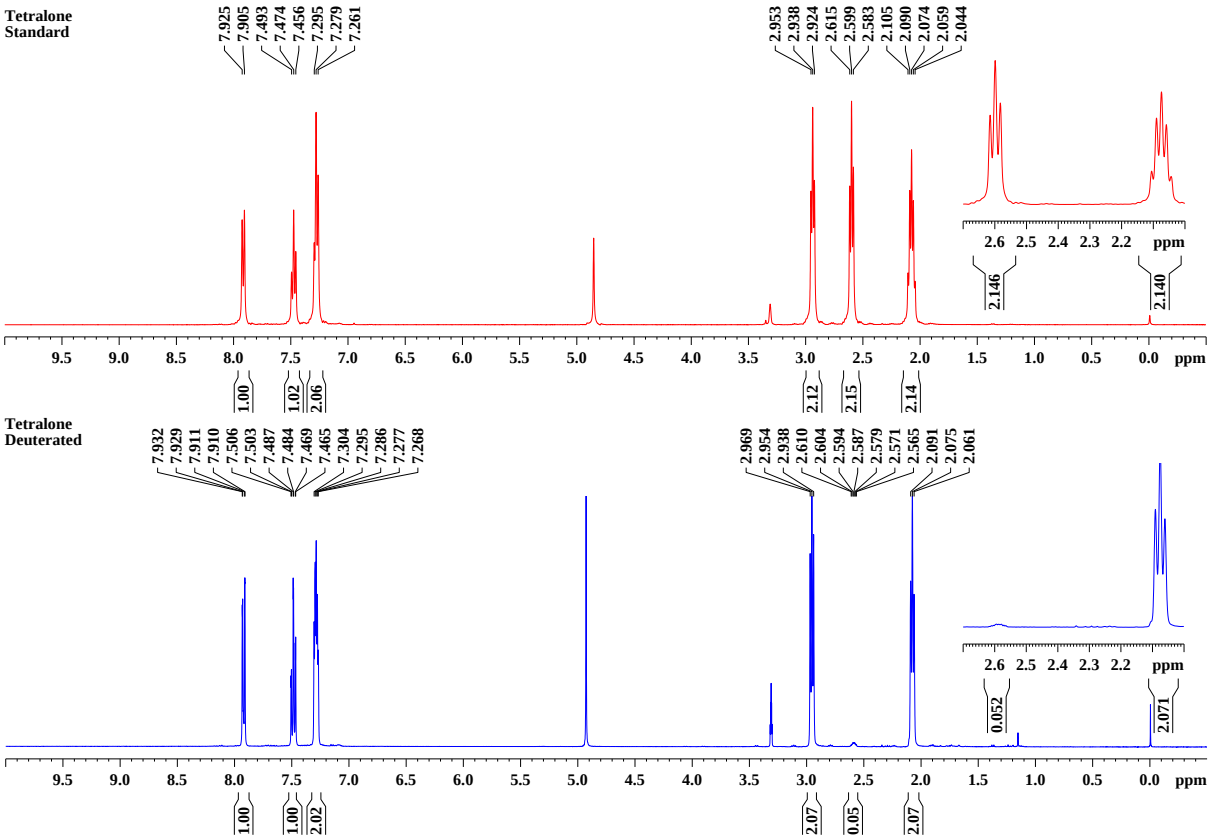
Supplementary Spectrum. ^{13}C NMR spectrum of 2-acetylfuran (**25**) (100 MHz, CD_3OD)



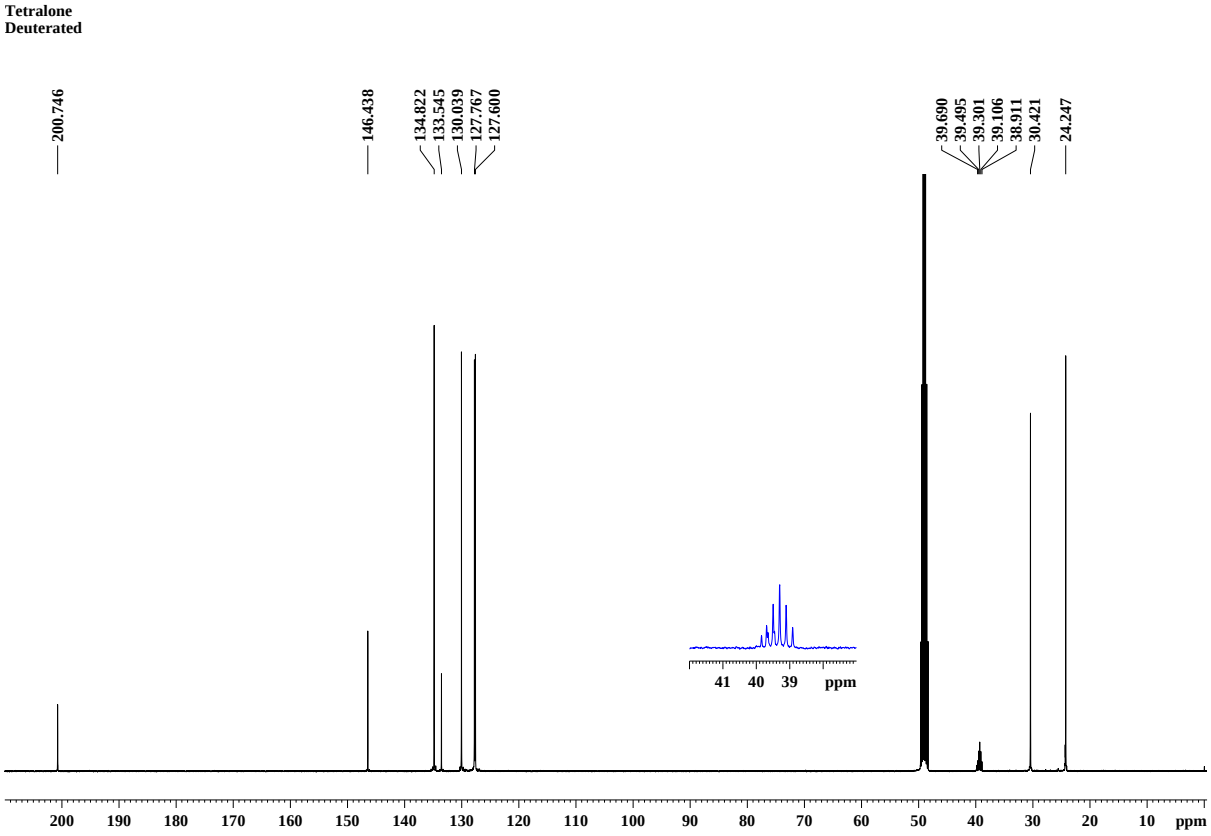
Supplementary Spectrum. ^{1}H NMR spectrum of 3-acetylindole (**26**) (400 MHz, CD_3OD)



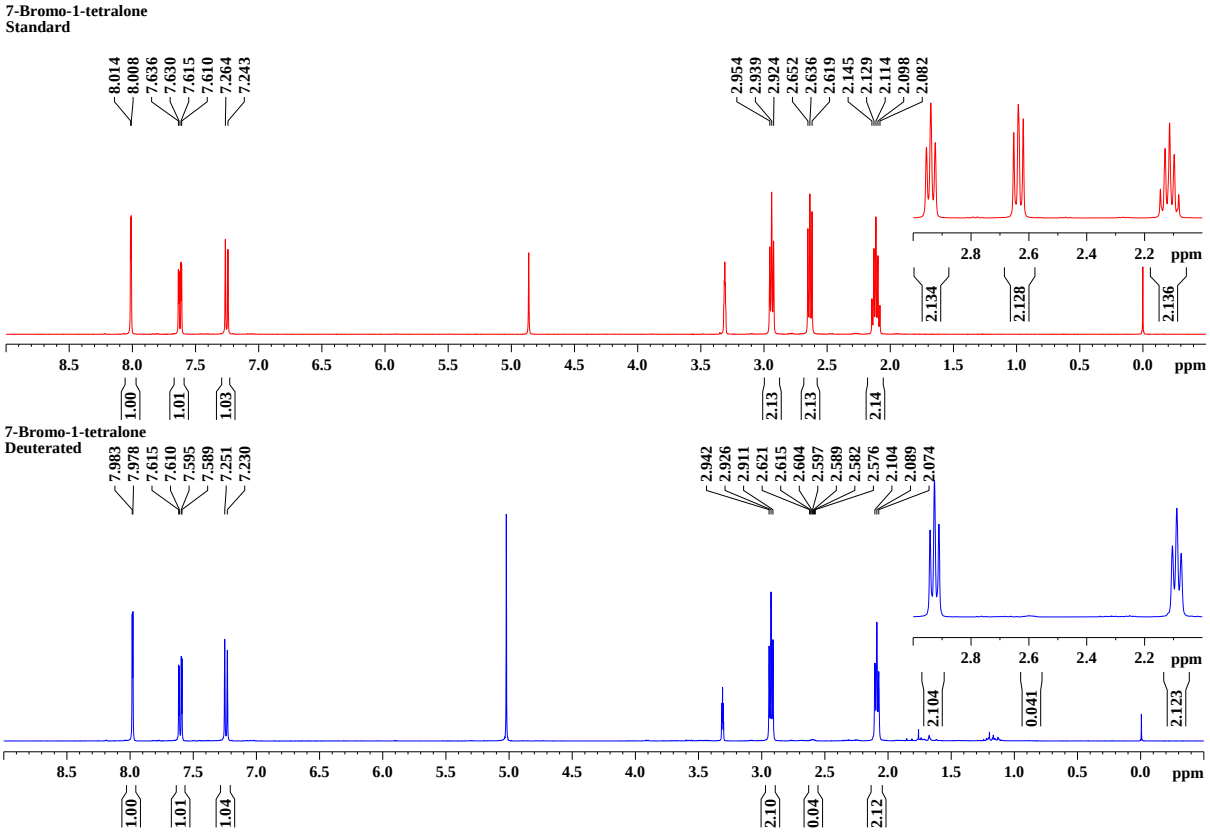
Supplementary Spectrum. ^{13}C NMR spectrum of 3-acetylindole (**26**) (100 MHz, CD_3OD)



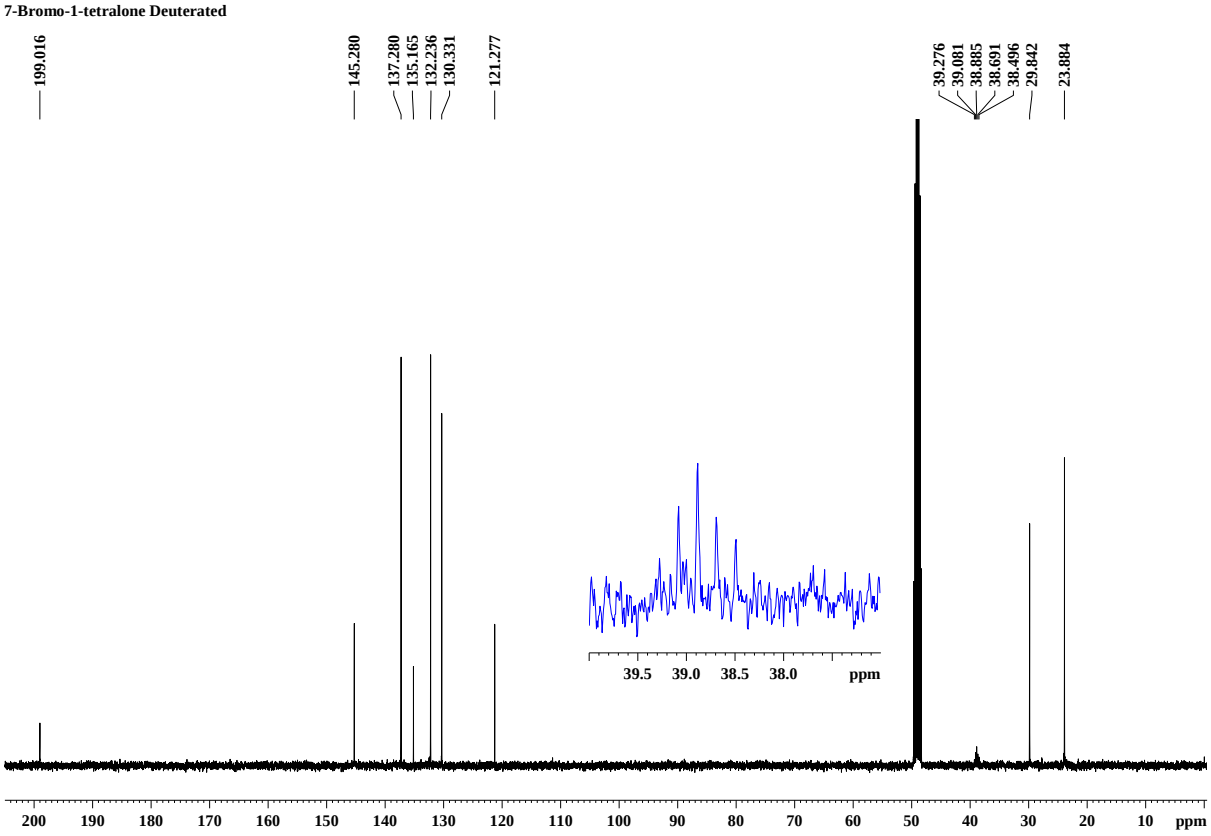
Supplementary Spectrum. ^{1}H NMR spectrum of 1-tetralone (**27**) (400 MHz, CD_3OD)



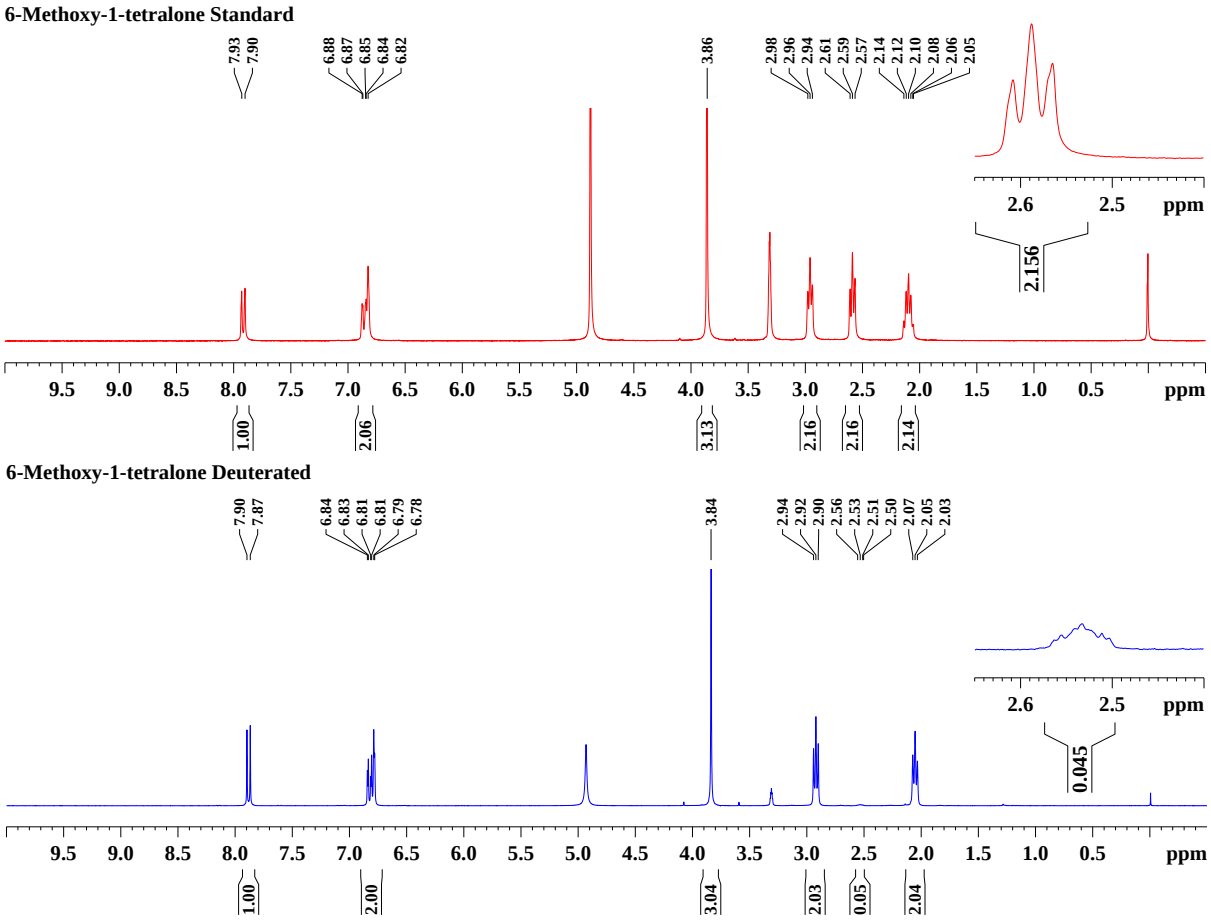
Supplementary Spectrum. ^{13}C NMR spectrum of 1-tetralone (**27**) (100 MHz, CD_3OD)



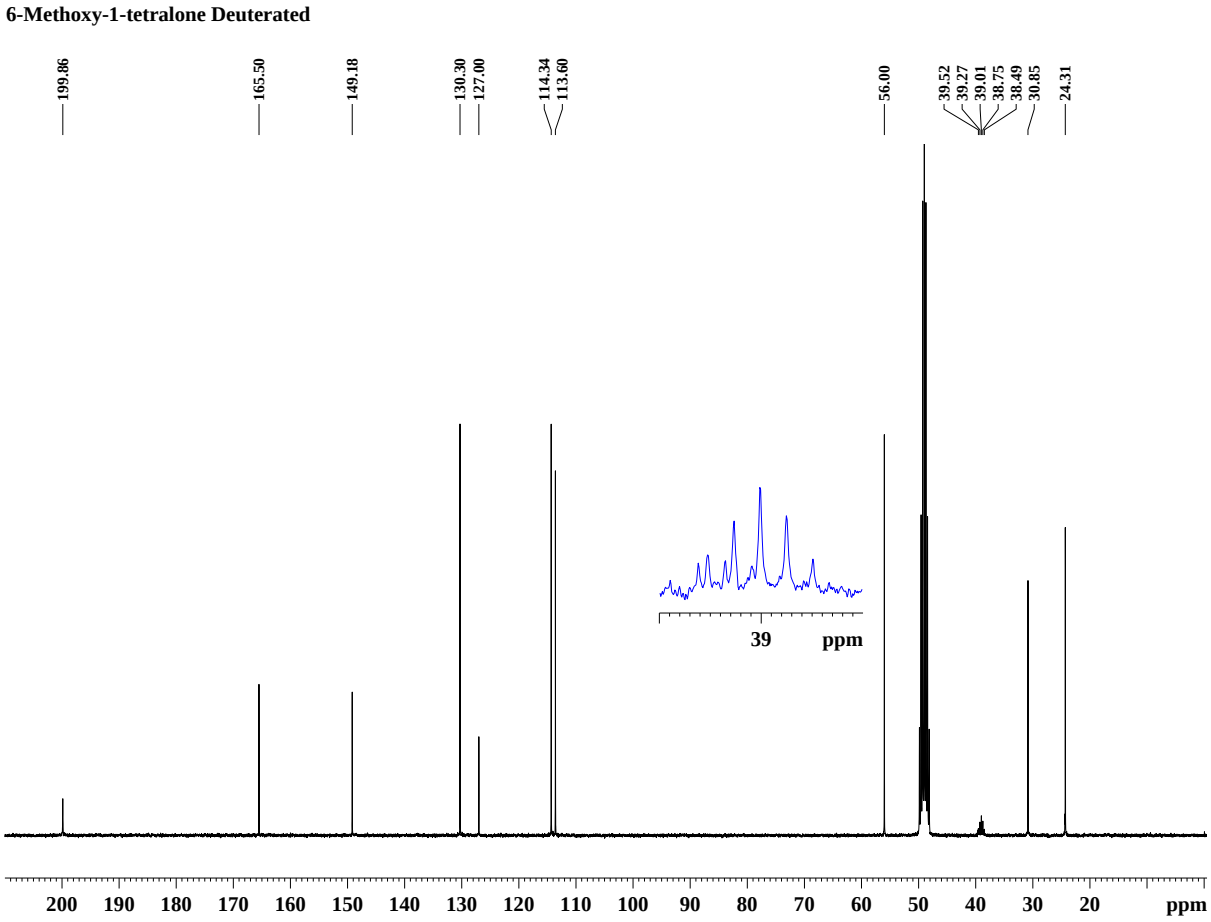
Supplementary Spectrum. ^{1}H NMR spectrum of 7-bromo-1-tetralone (**28**) (400 MHz, CD_3OD)



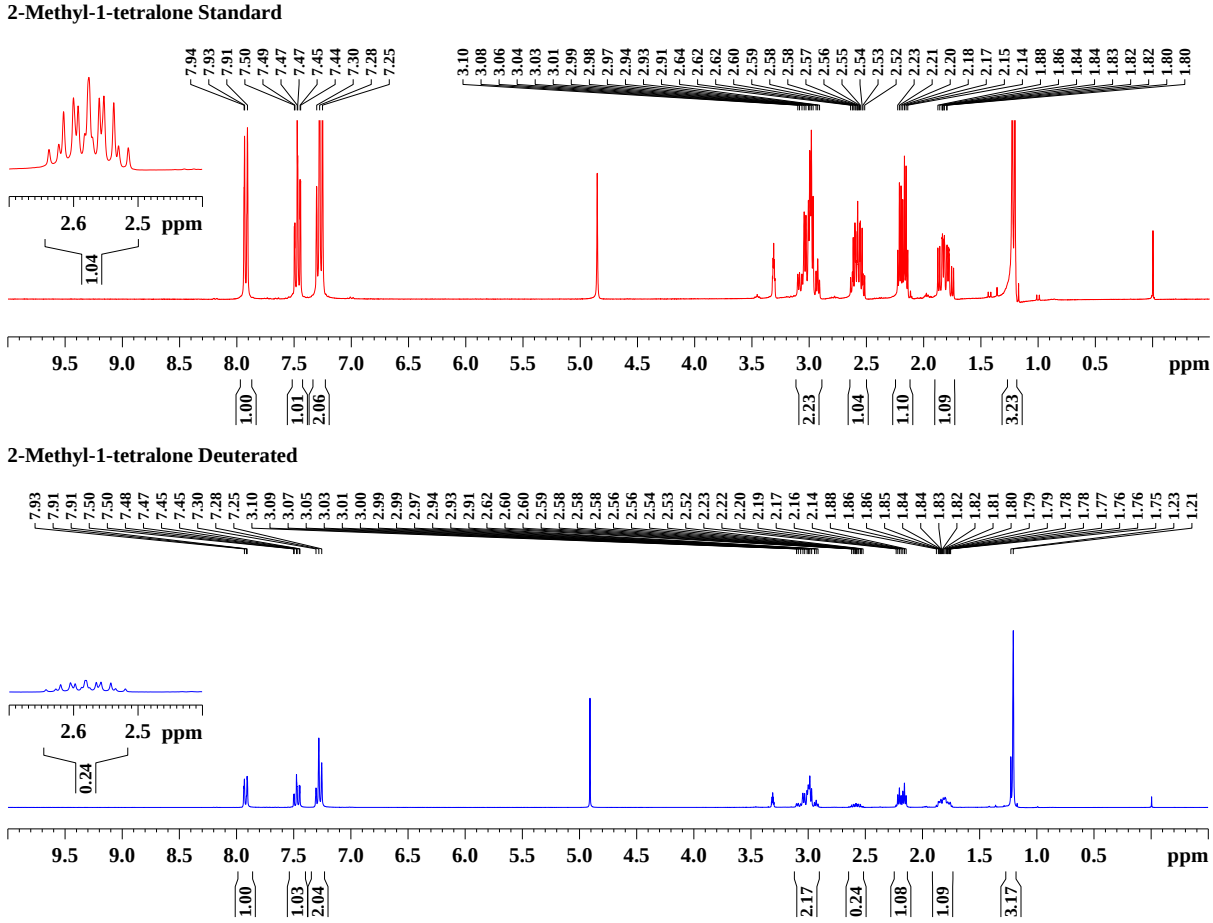
Supplementary Spectrum. ^{13}C NMR spectrum of 7-bromo-1-tetralone (**28**) (100 MHz, CD_3OD)



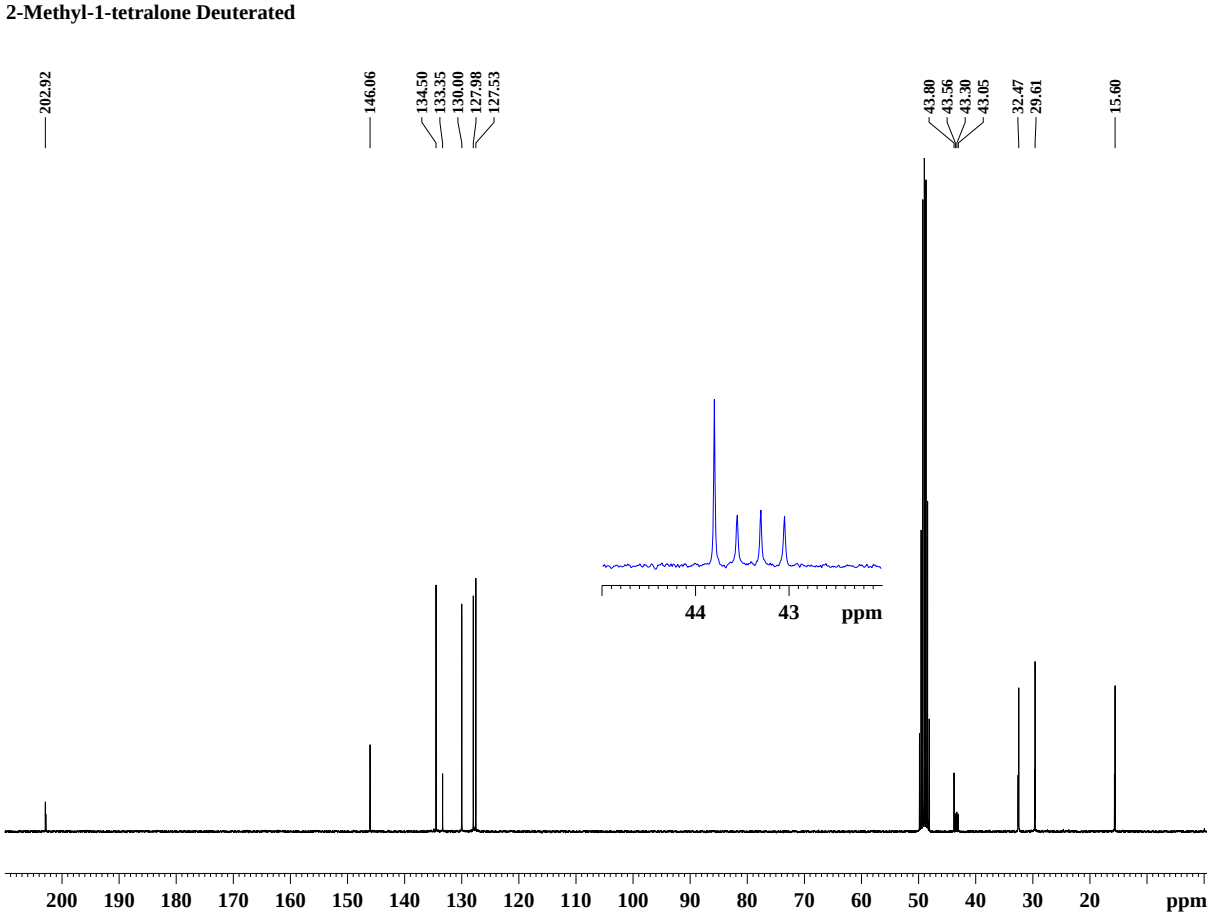
Supplementary Spectrum. ^{1}H NMR spectrum of 6-methoxy-1-tetralone (**29**) (300 MHz, CD_3OD)



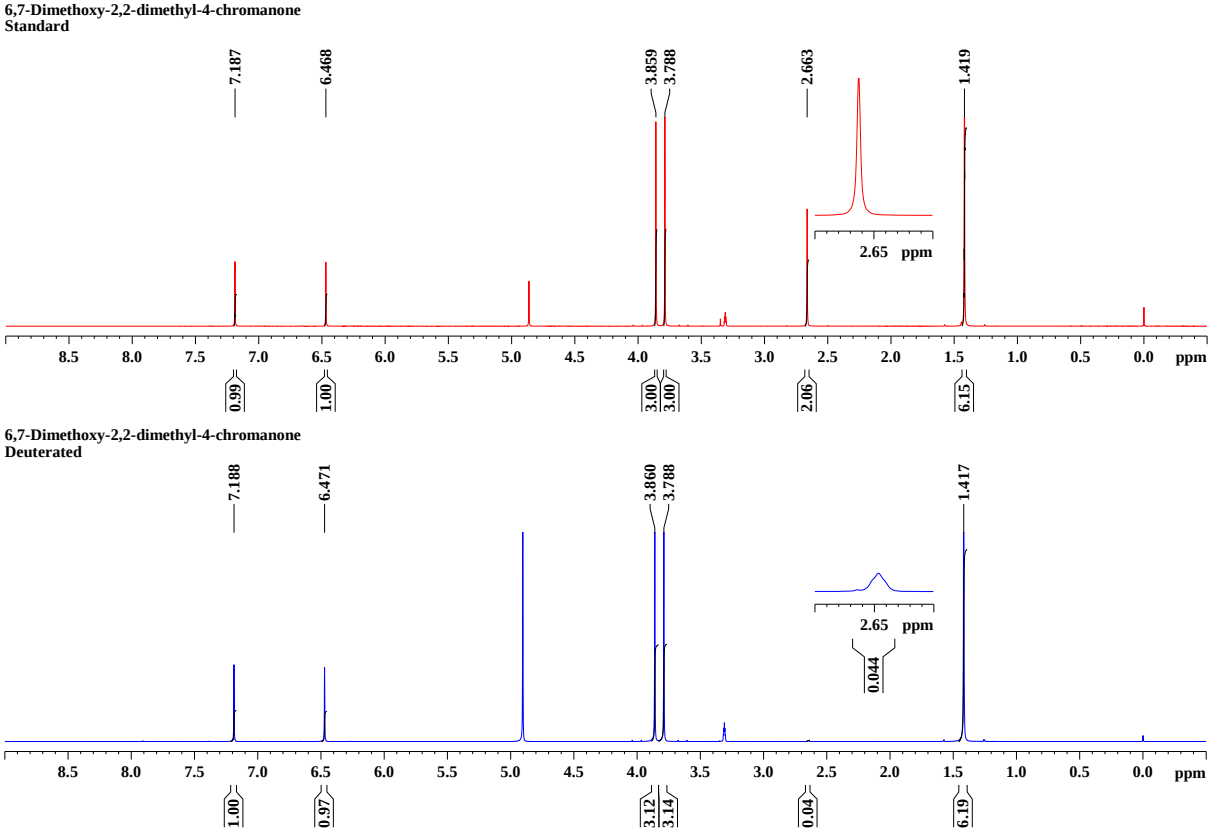
Supplementary Spectrum. ^{13}C NMR spectrum of 6-methoxy-1-tetralone (**29**) (75 MHz, CD_3OD)



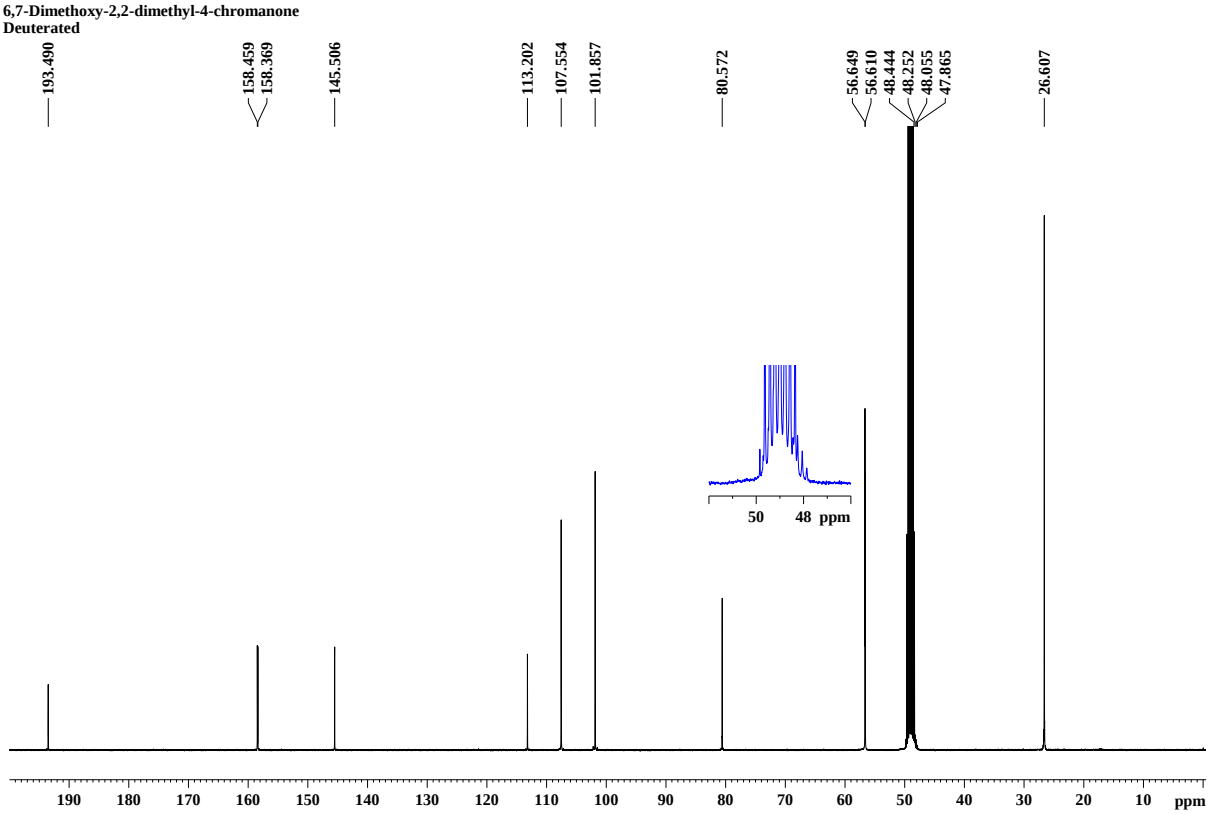
Supplementary Spectrum. ^{1}H NMR spectrum of 2-methyl-1-tetralone (**30**) (300 MHz, CD_3OD)



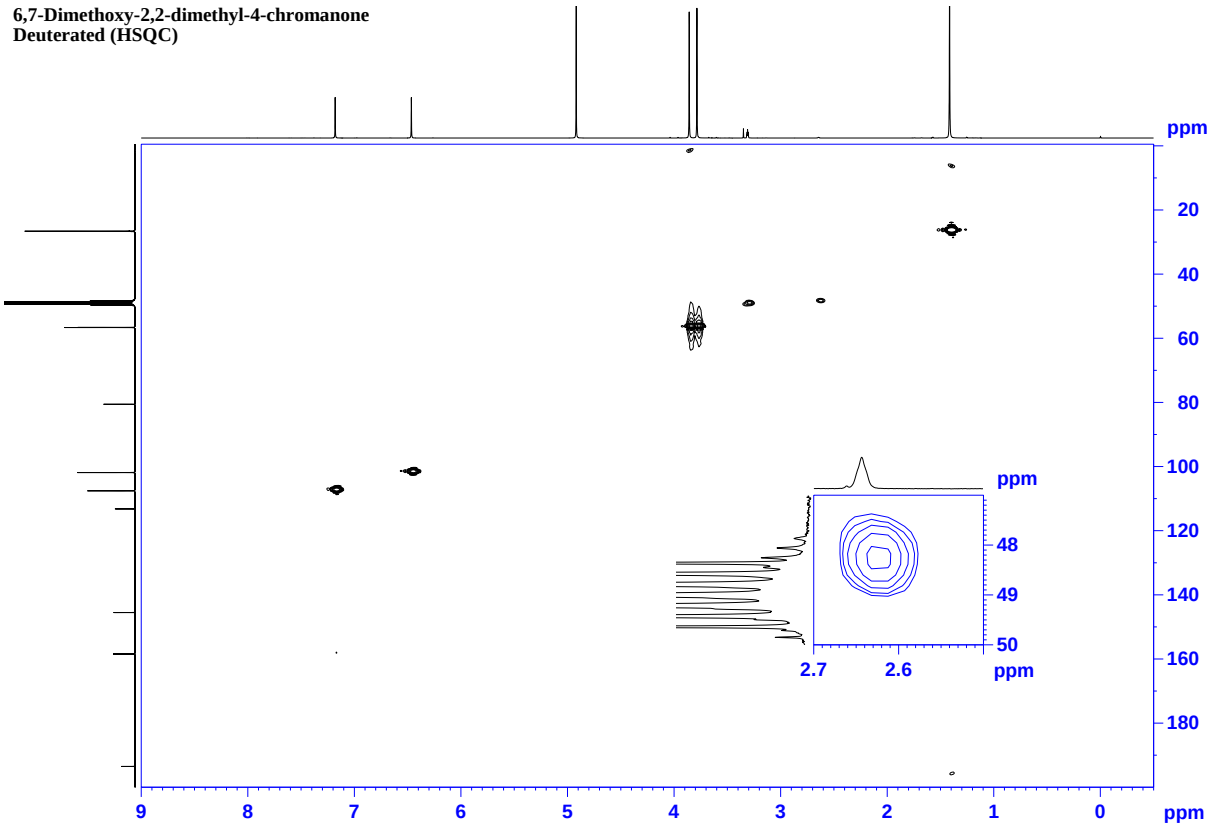
Supplementary Spectrum. ^{13}C NMR spectrum of 2-methyl-1-tetralone (**30**) (75 MHz, CD_3OD)



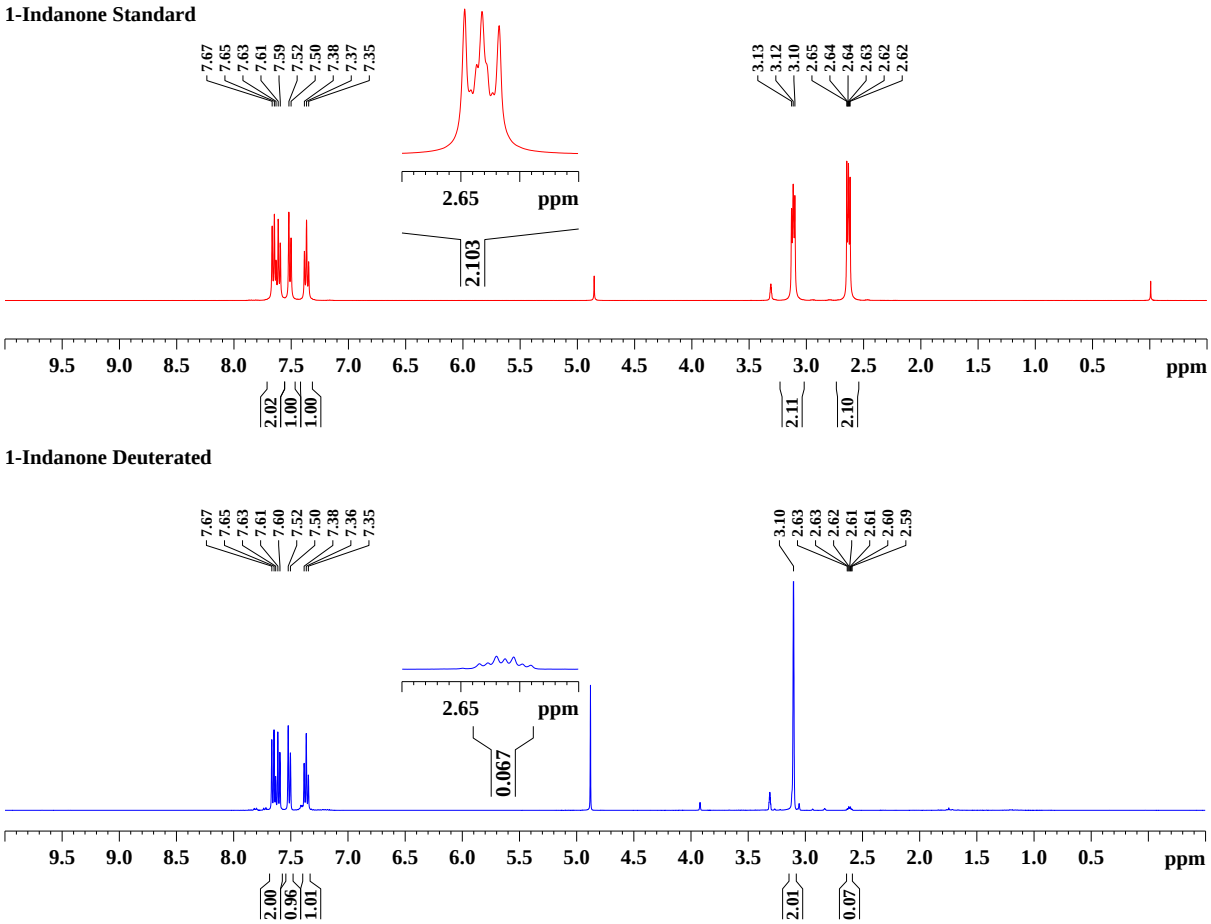
Supplementary Spectrum. ^{1}H NMR spectrum of 6,7-dimethoxy-2,2-dimethyl-4-chromanone (**31**) (400 MHz, CD_3OD)



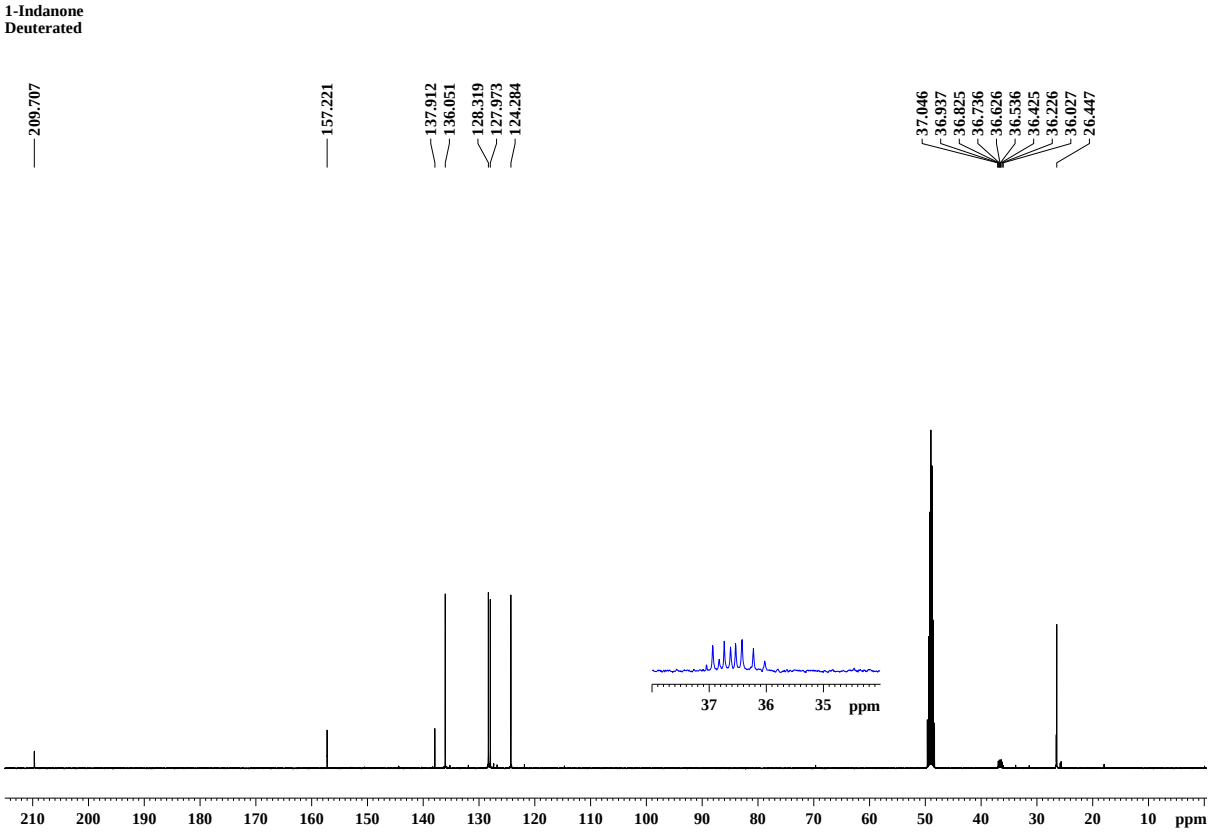
Supplementary Spectrum. ^{13}C NMR spectrum of 6,7-dimethoxy-2,2-dimethyl-4-chromanone (**31**) (100 MHz, CD_3OD)



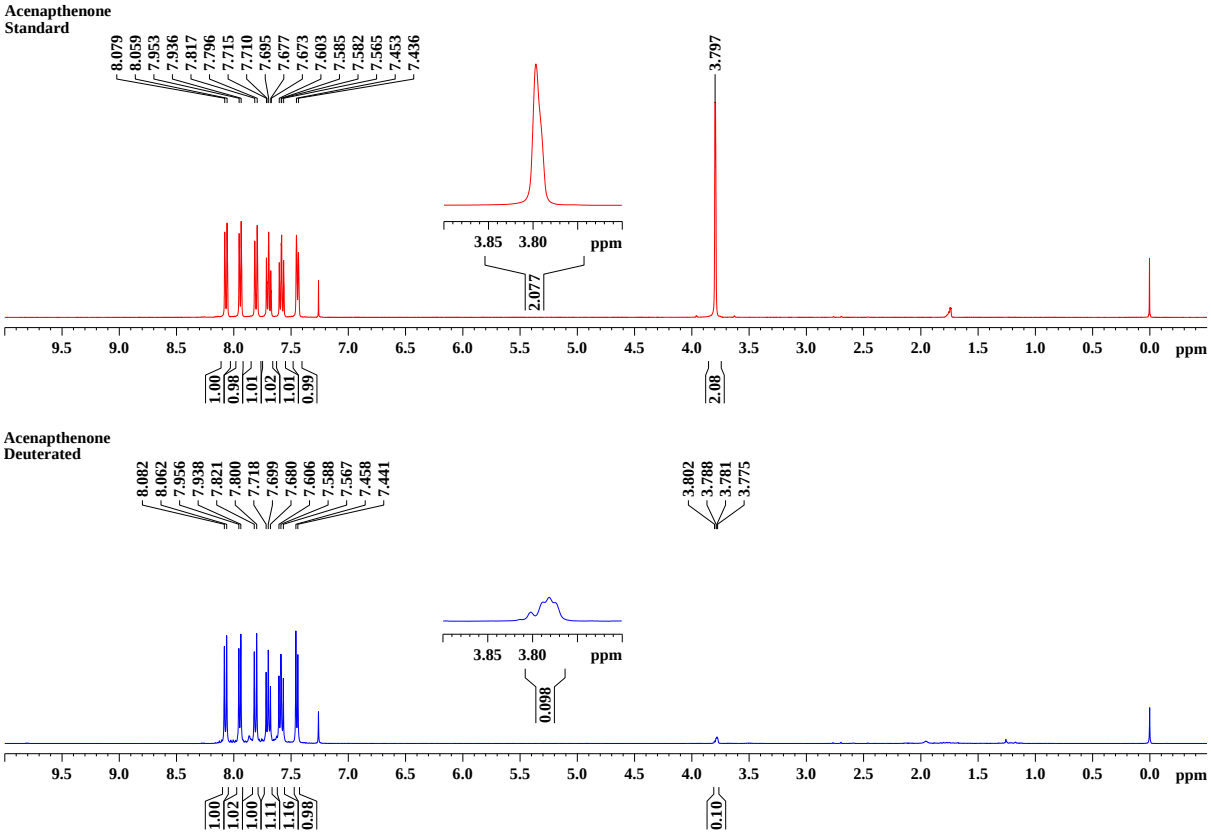
Supplementary Spectrum. HSQC spectrum of 6,7-dimethoxy-2,2-dimethyl-4-chromanone (**31**) in CD_3OD



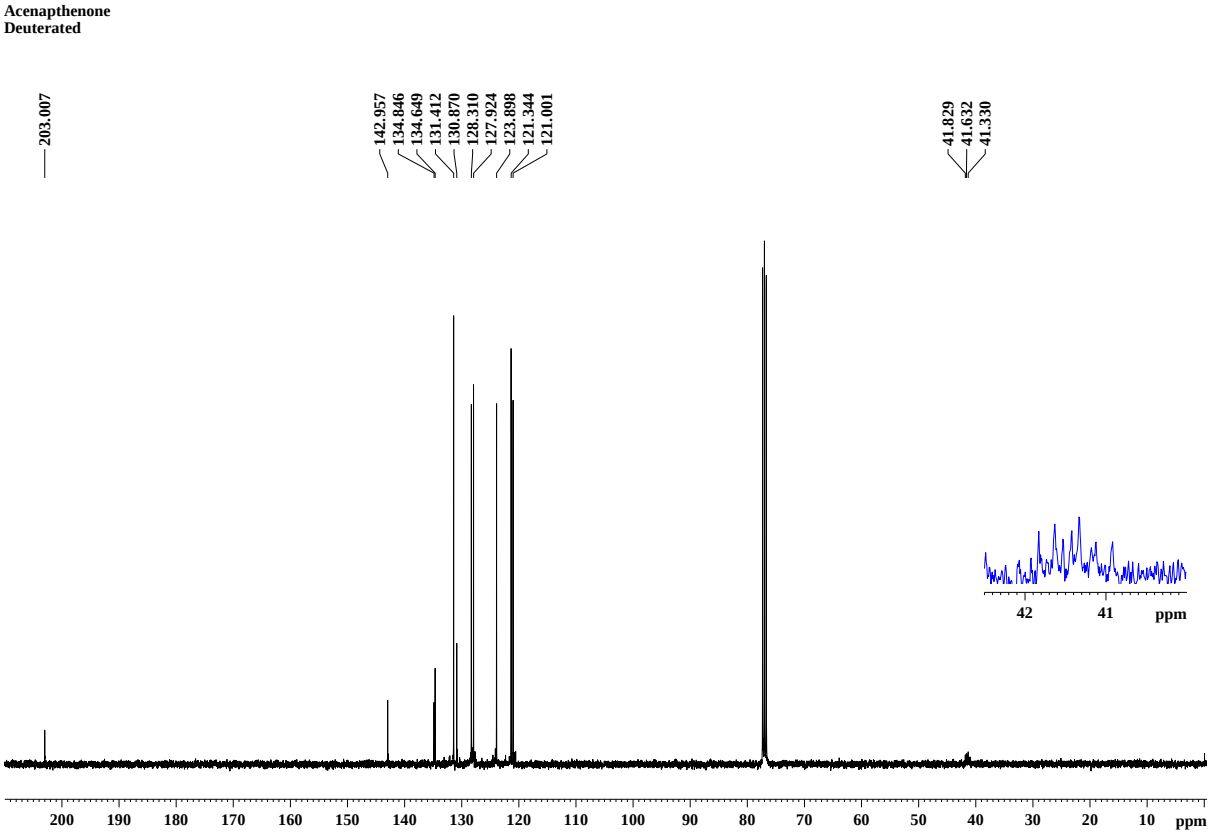
Supplementary Spectrum. ^{1}H NMR spectrum of 1-indanone (**32**) (400 MHz, CD_3OD)



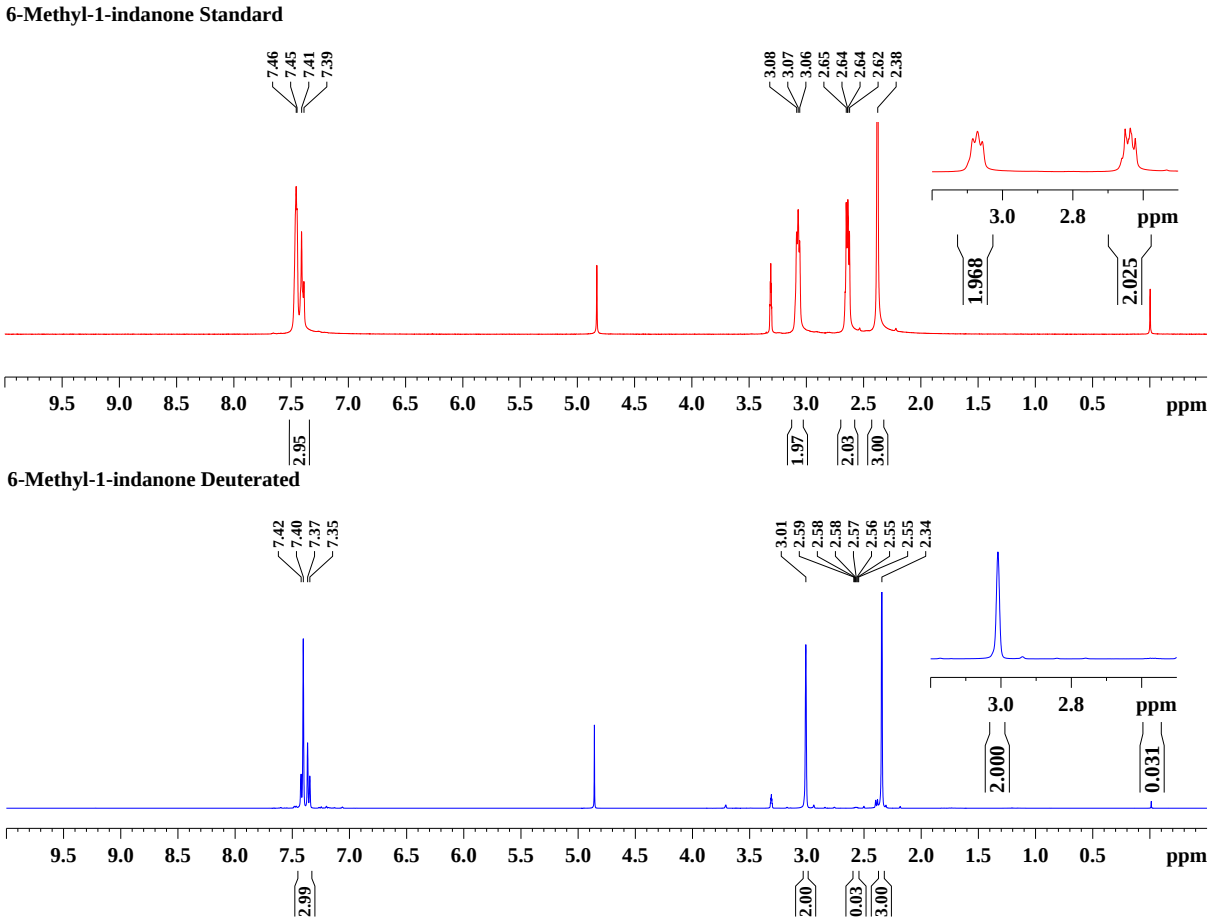
Supplementary Spectrum. ^{13}C NMR spectrum of 1-indanone (**32**) (100 MHz, CD_3OD)



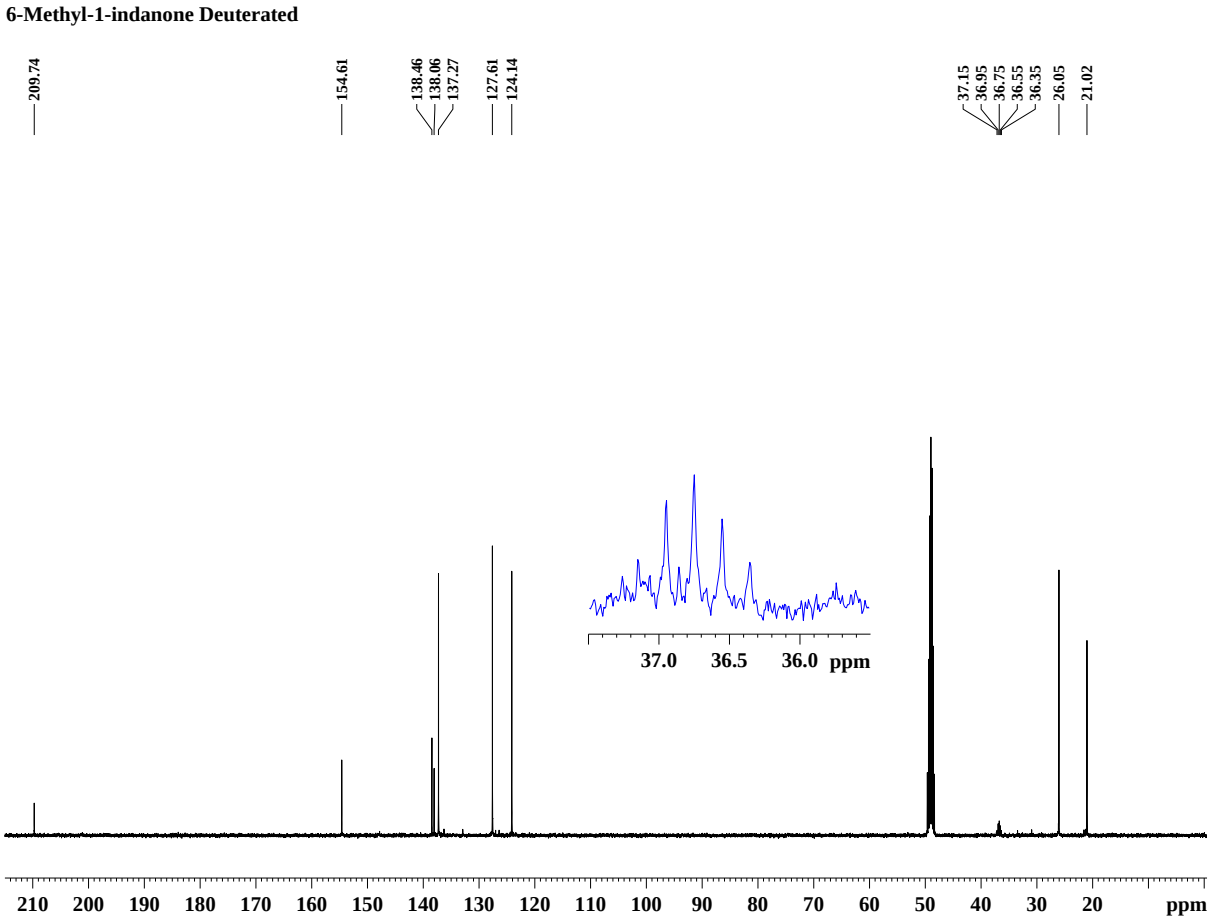
Supplementary Spectrum. ^{1}H NMR spectrum of 1-acenaphthenone (**33**) (400 MHz, $CDCl_3$)



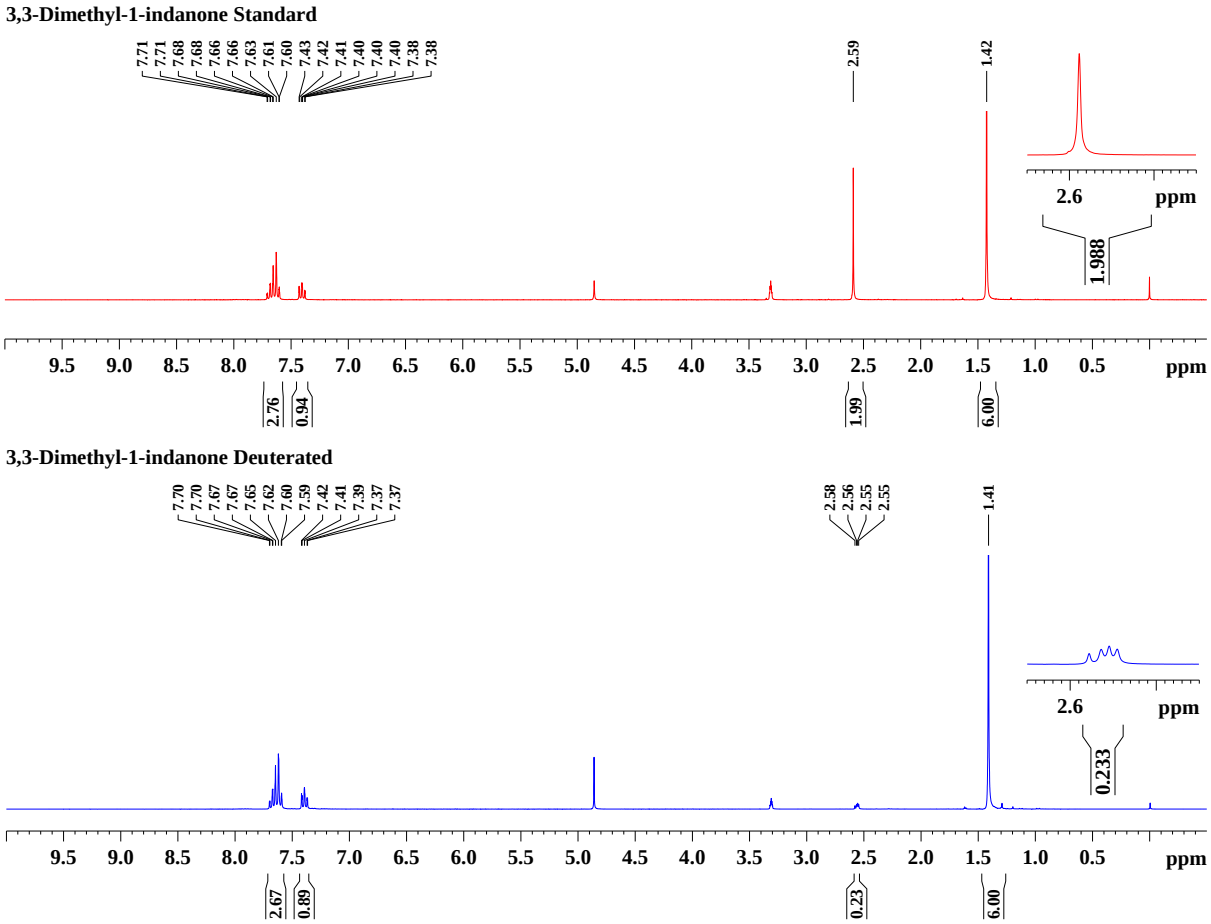
Supplementary Spectrum. ^{13}C NMR spectrum of 1-acenaphthenone (**33**) (100 MHz, $CDCl_3$)



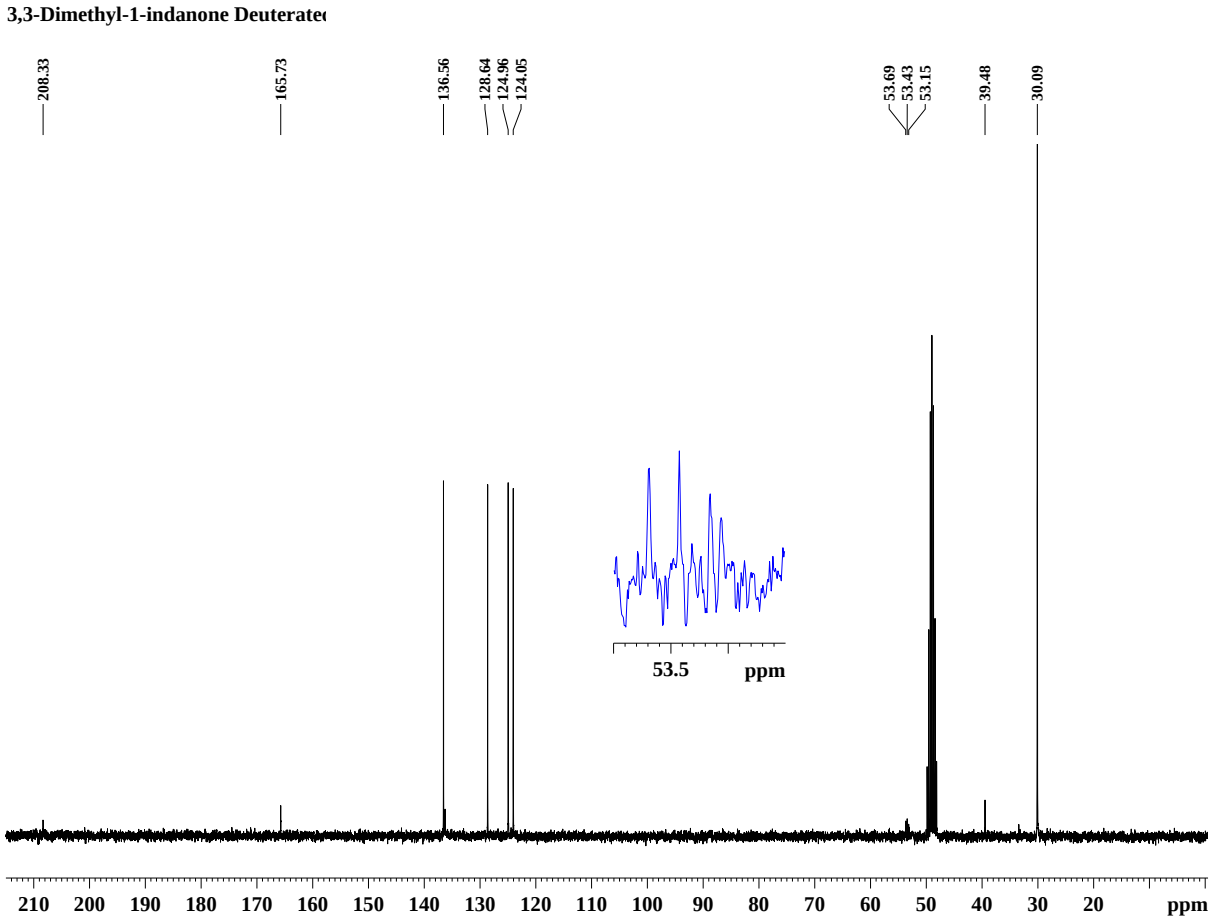
Supplementary Spectrum. ^{1}H NMR spectrum of 6-methyl-1-indanone (**34**) (400 MHz, CD_3OD)



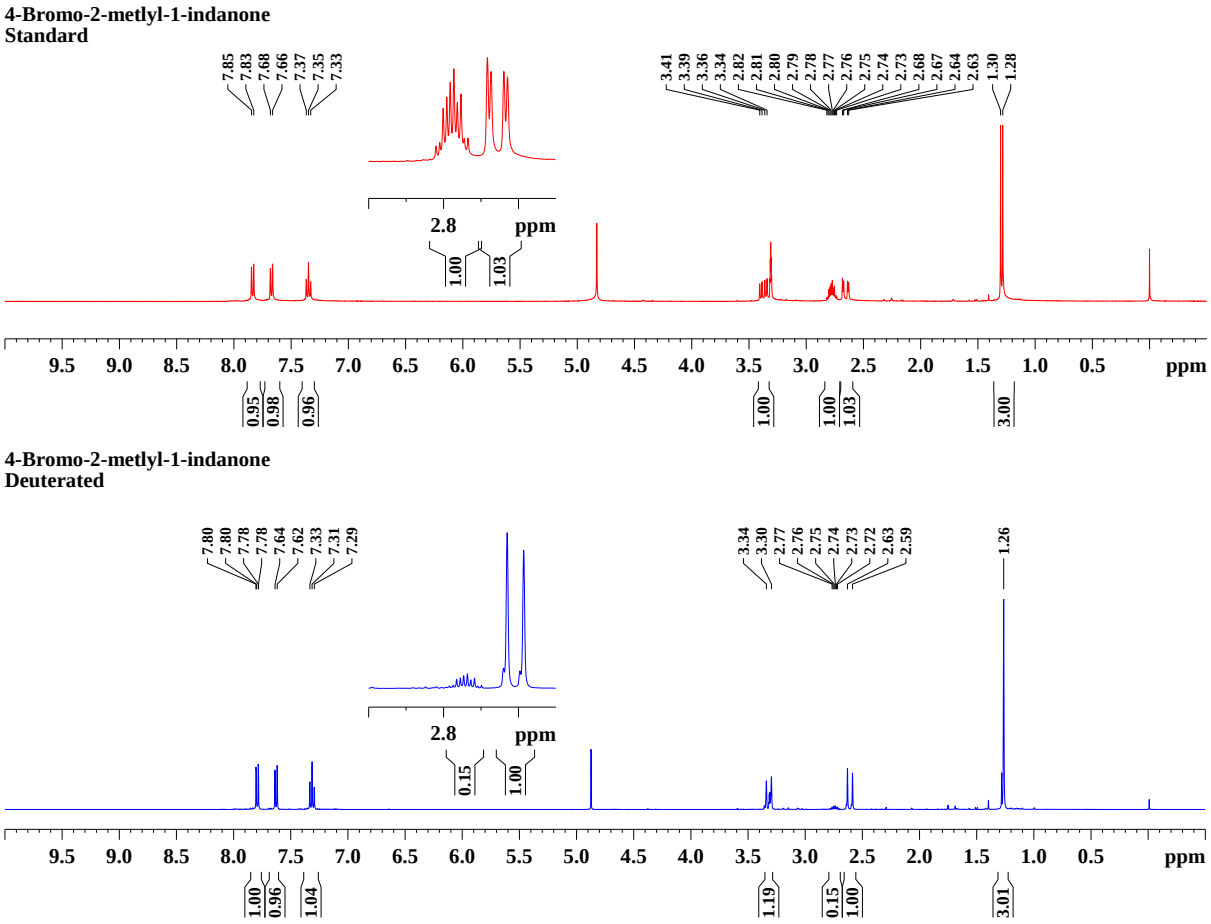
Supplementary Spectrum. ^{13}C NMR spectrum of 6-methyl-1-indanone (**34**) (100 MHz, CD_3OD)



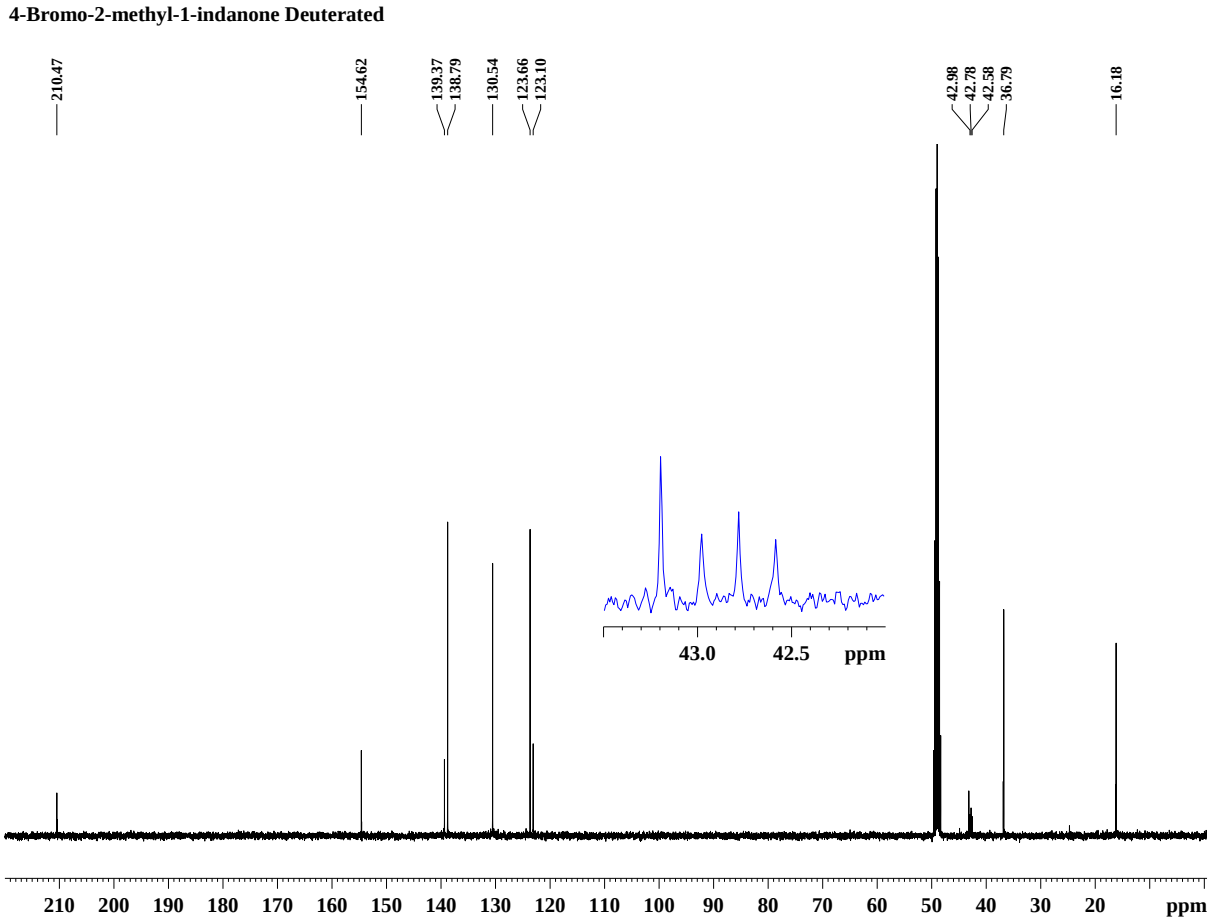
Supplementary Spectrum. ^{1}H NMR spectrum of 3,3-dimethyl-1-indanone (**35**) (300 MHz, CD_3OD)



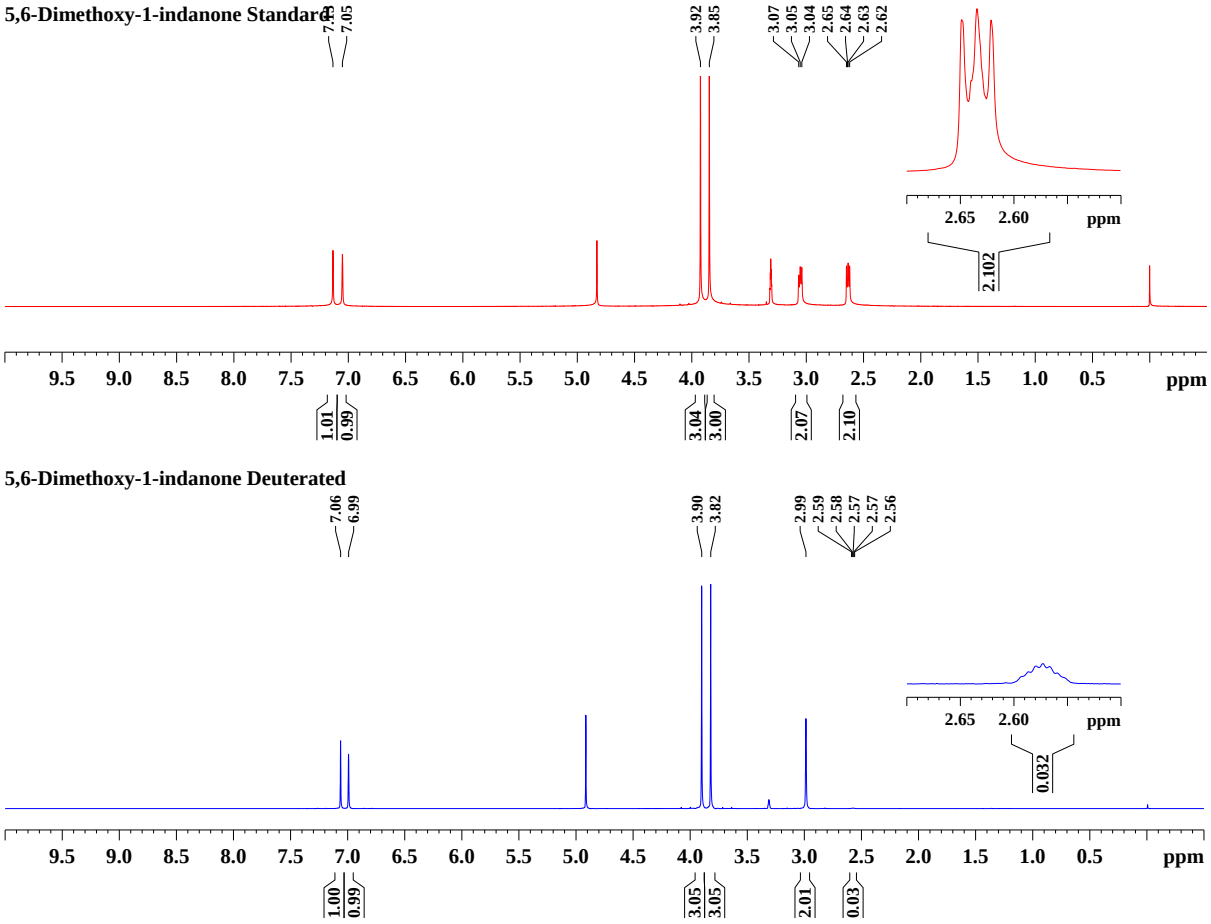
Supplementary Spectrum. ^{13}C NMR spectrum of 3,3-dimethyl-1-indanone (**35**) (75 MHz, CD_3OD)



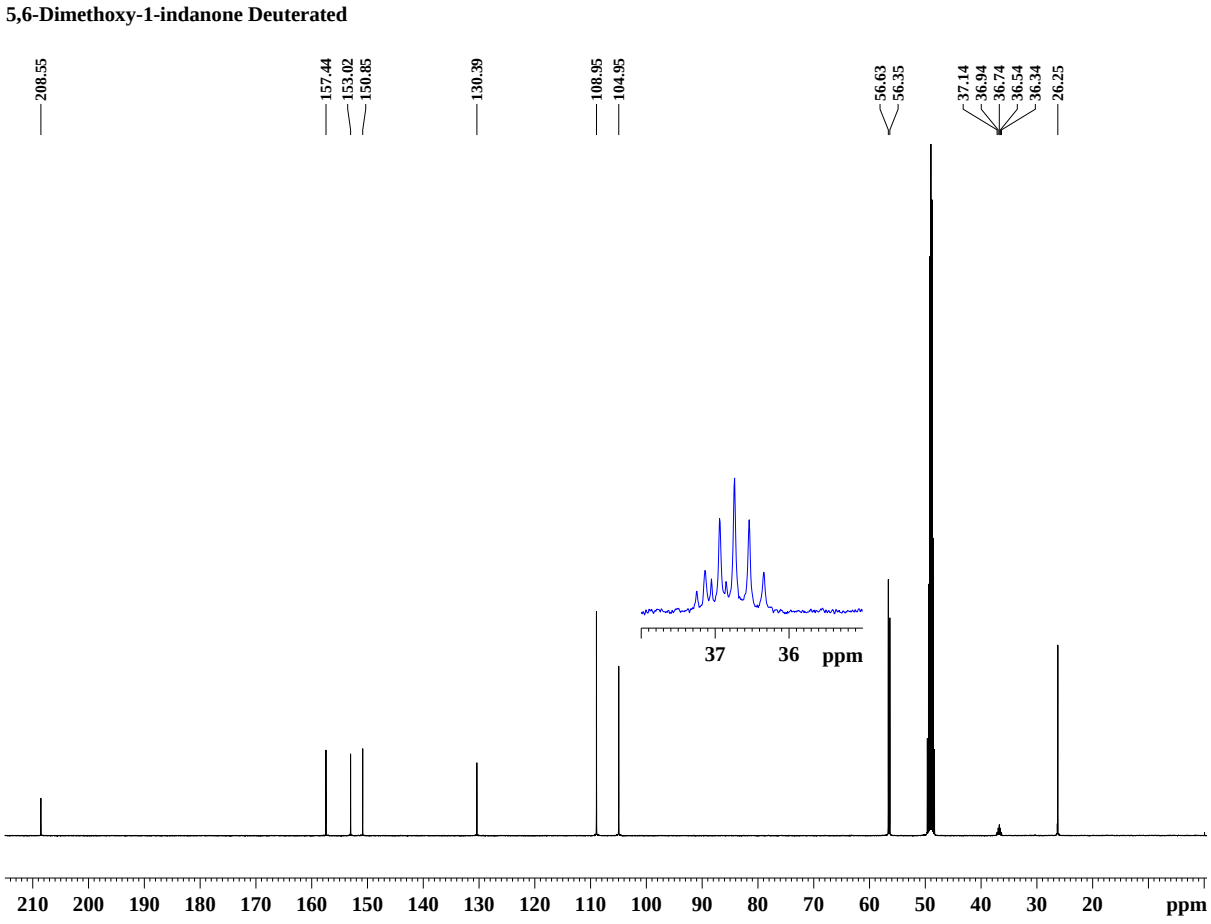
Supplementary Spectrum. ^{1}H NMR spectrum of 4-bromo-2-methyl-1-indanone (**36**) (400 MHz, CD_3OD)



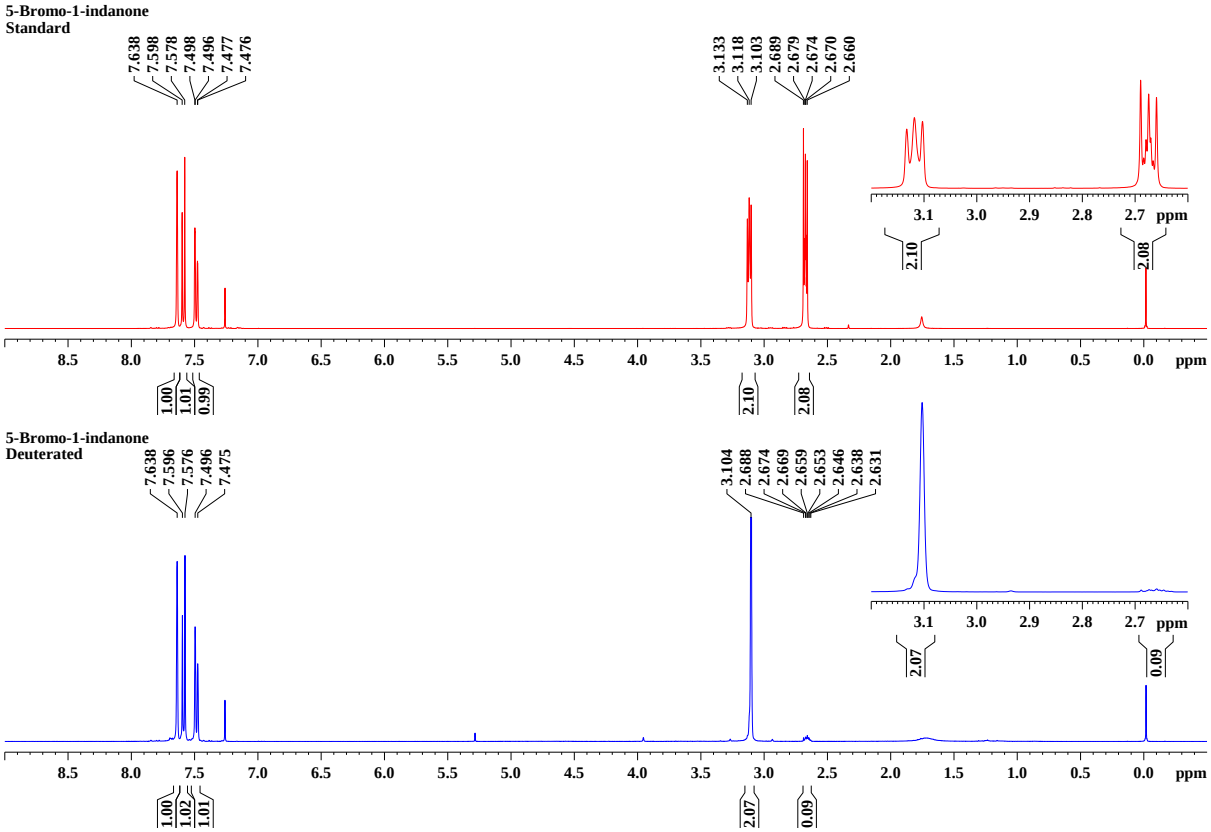
Supplementary Spectrum. ^{13}C NMR spectrum of 4-bromo-2-methyl-1-indanone (**36**) (100 MHz, CD_3OD)



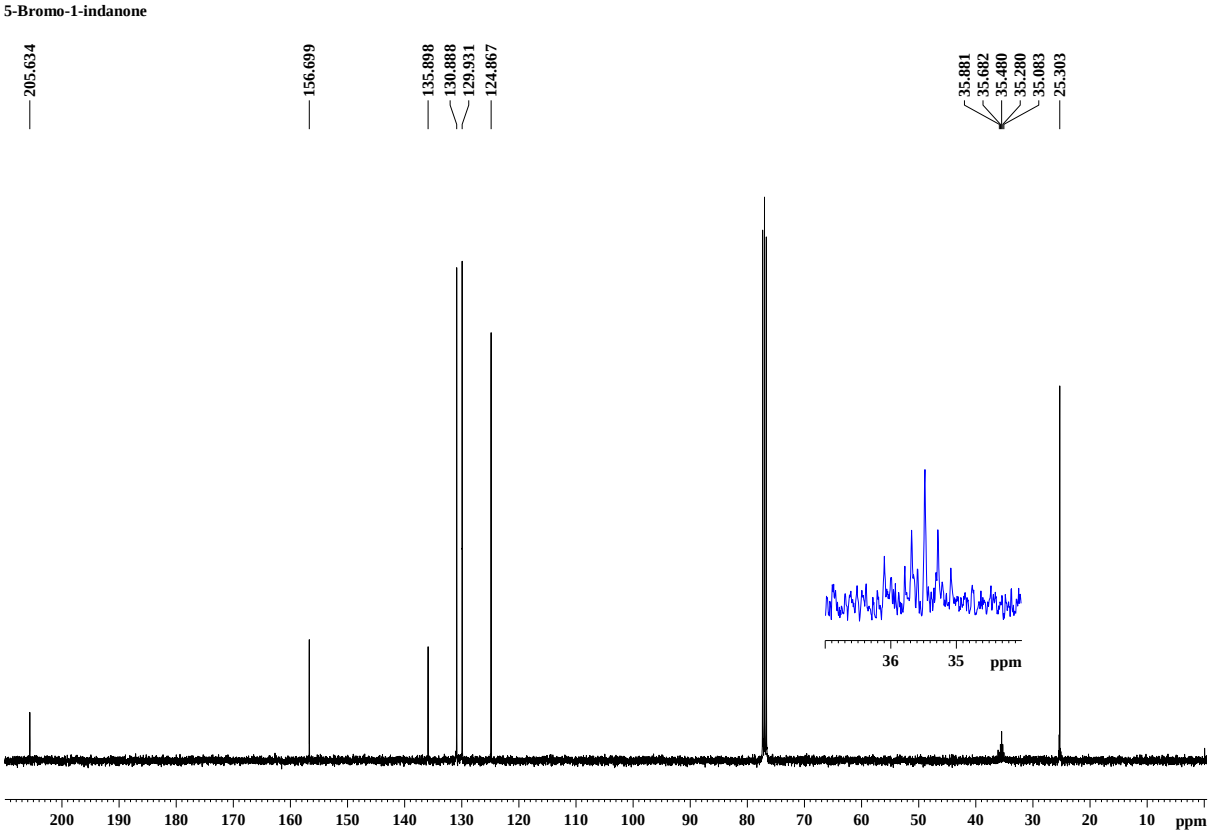
Supplementary Spectrum. ^{1}H NMR spectrum of 5,6-dimethoxy-1-indanone (**37**) (400 MHz, CD_3OD)



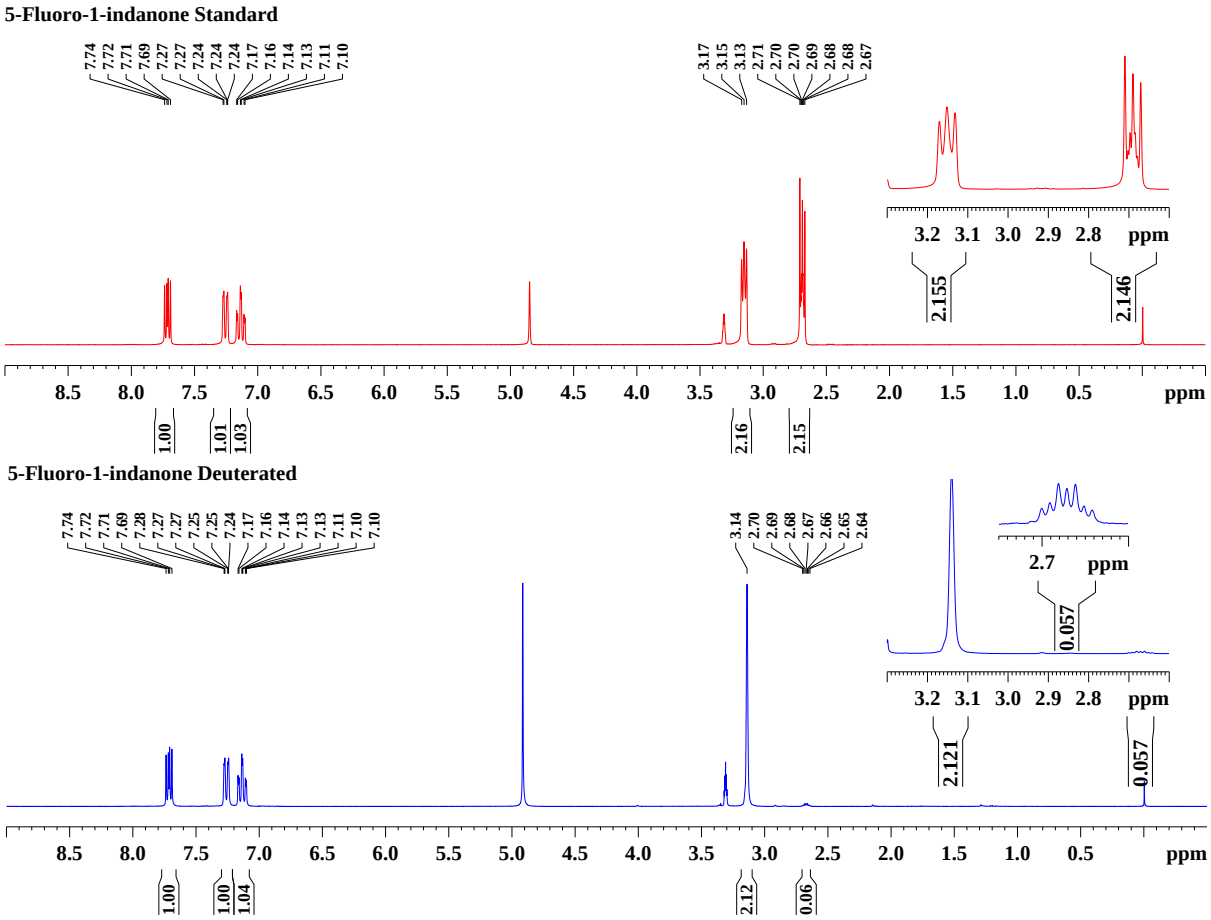
Supplementary Spectrum. ^{13}C NMR spectrum of 5,6-dimethoxy-1-indanone (**37**) (100 MHz, CD_3OD)



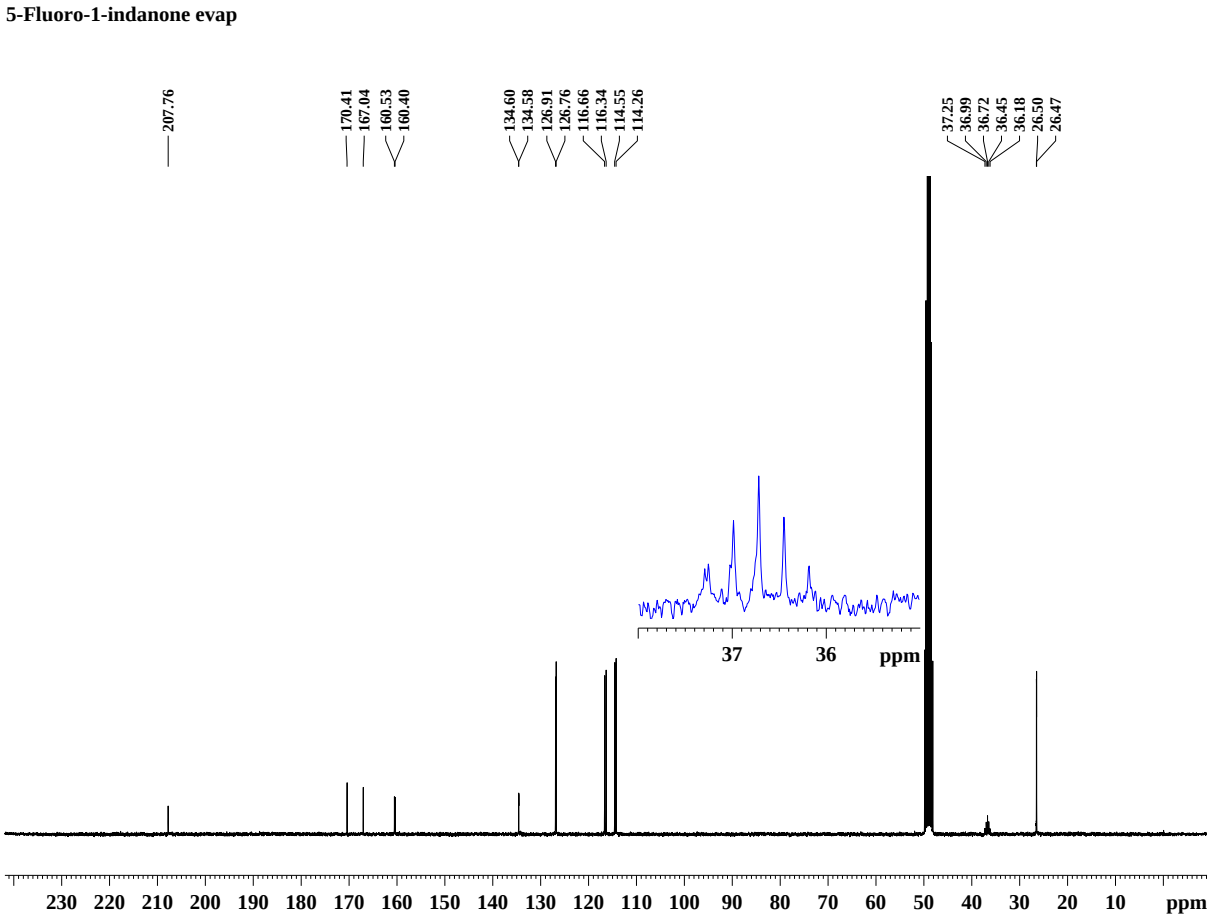
Supplementary Spectrum. ^{1}H NMR spectrum of 5-bromo-1-indanone (**38**) (400 MHz, $CDCl_3$)



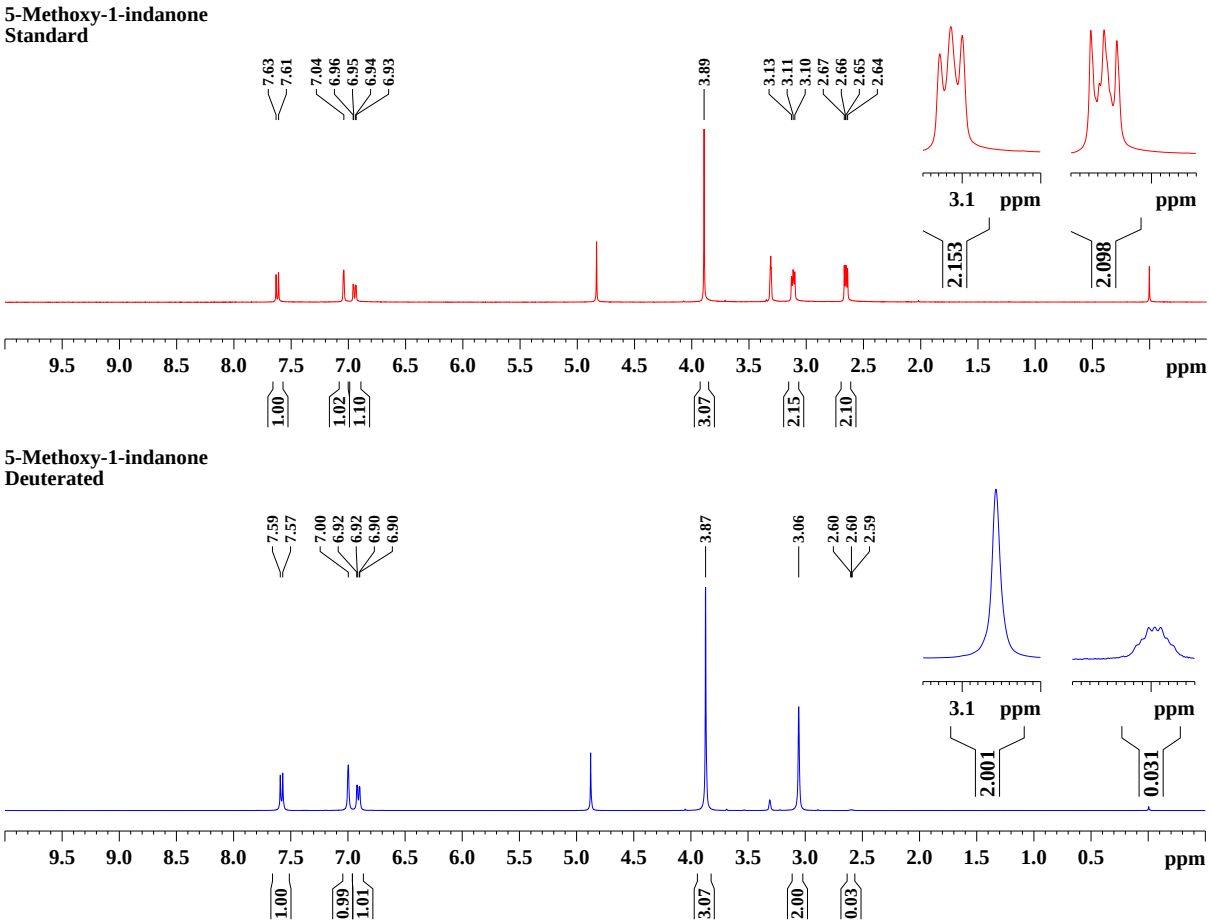
Supplementary Spectrum. ^{13}C NMR spectrum of 5-bromo-1-indanone (**38**) (100 MHz, $CDCl_3$)



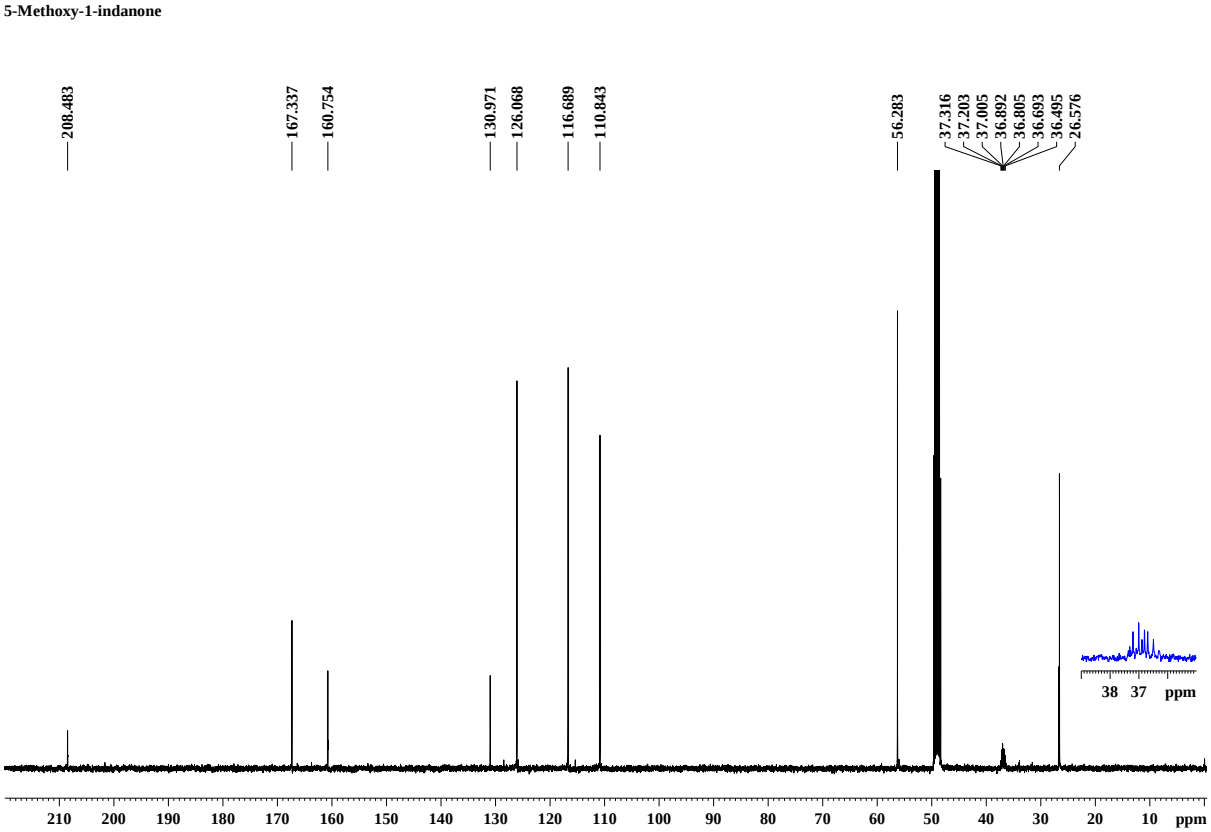
Supplementary Spectrum. ^{1}H NMR spectrum of 5-fluoro-1-indanone (**39**) (300 MHz, CD_3OD)



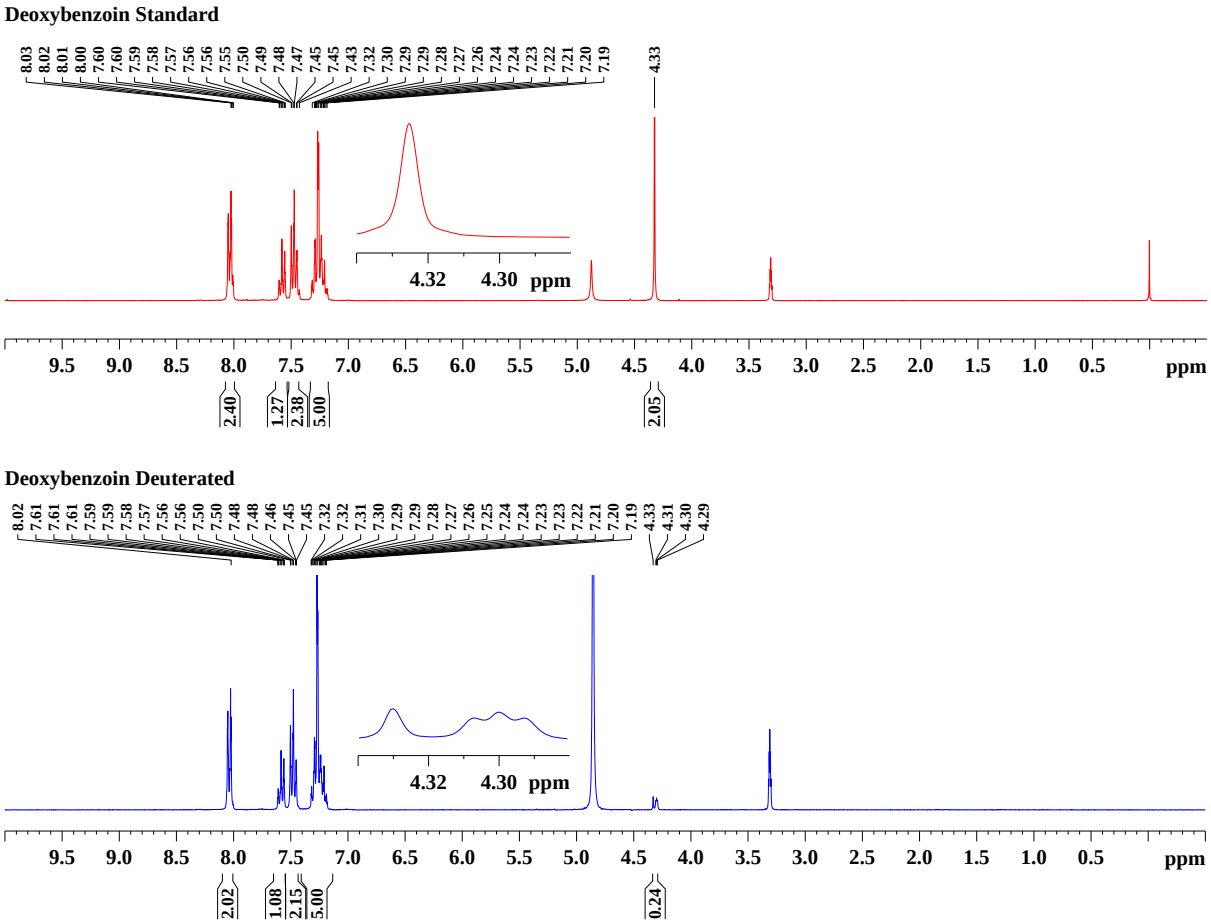
Supplementary Spectrum. ^{13}C NMR spectrum of 5-fluoro-1-indanone (**39**) (75 MHz, CD_3OD)



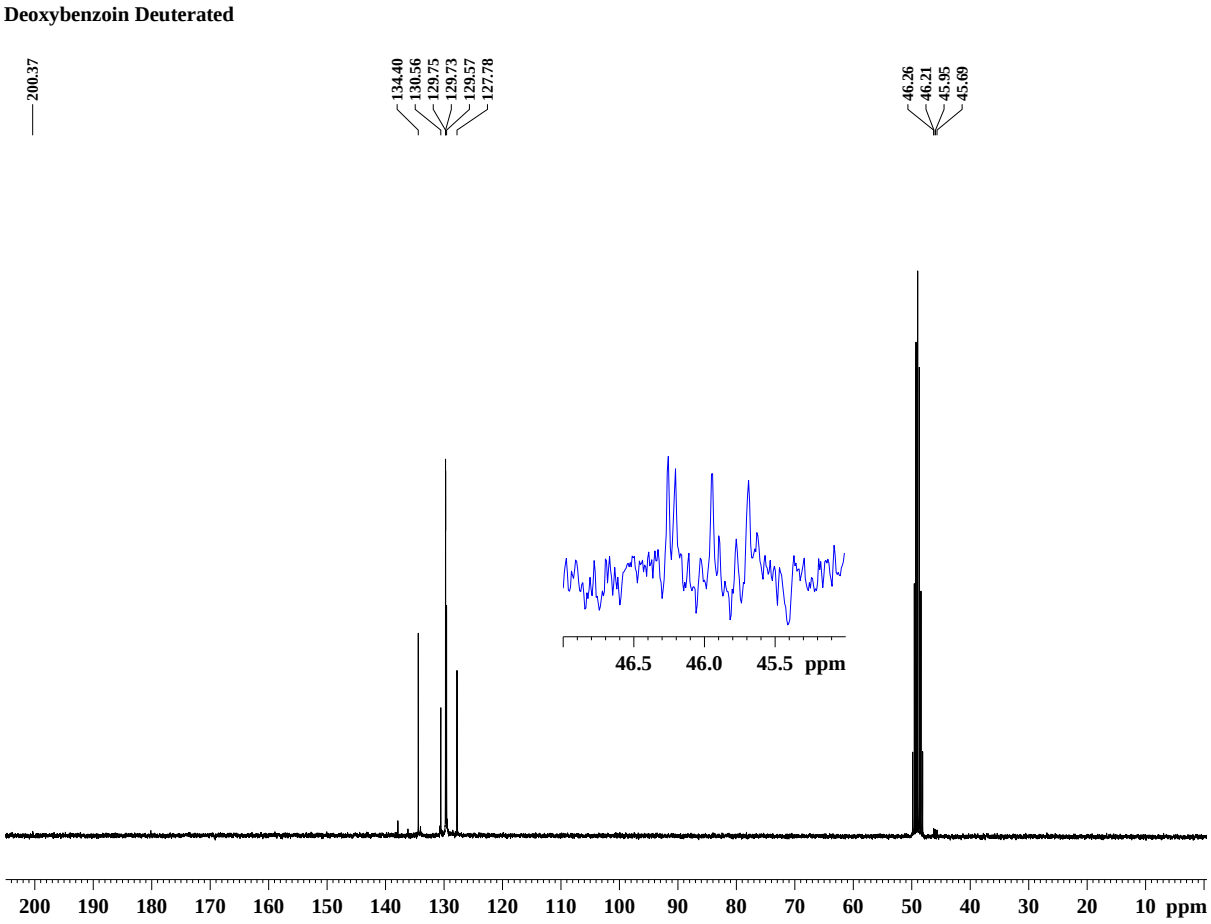
Supplementary Spectrum. ^{1}H NMR spectrum of 5-methoxy-1-indanone (**40**) (400 MHz, CD_3OD)



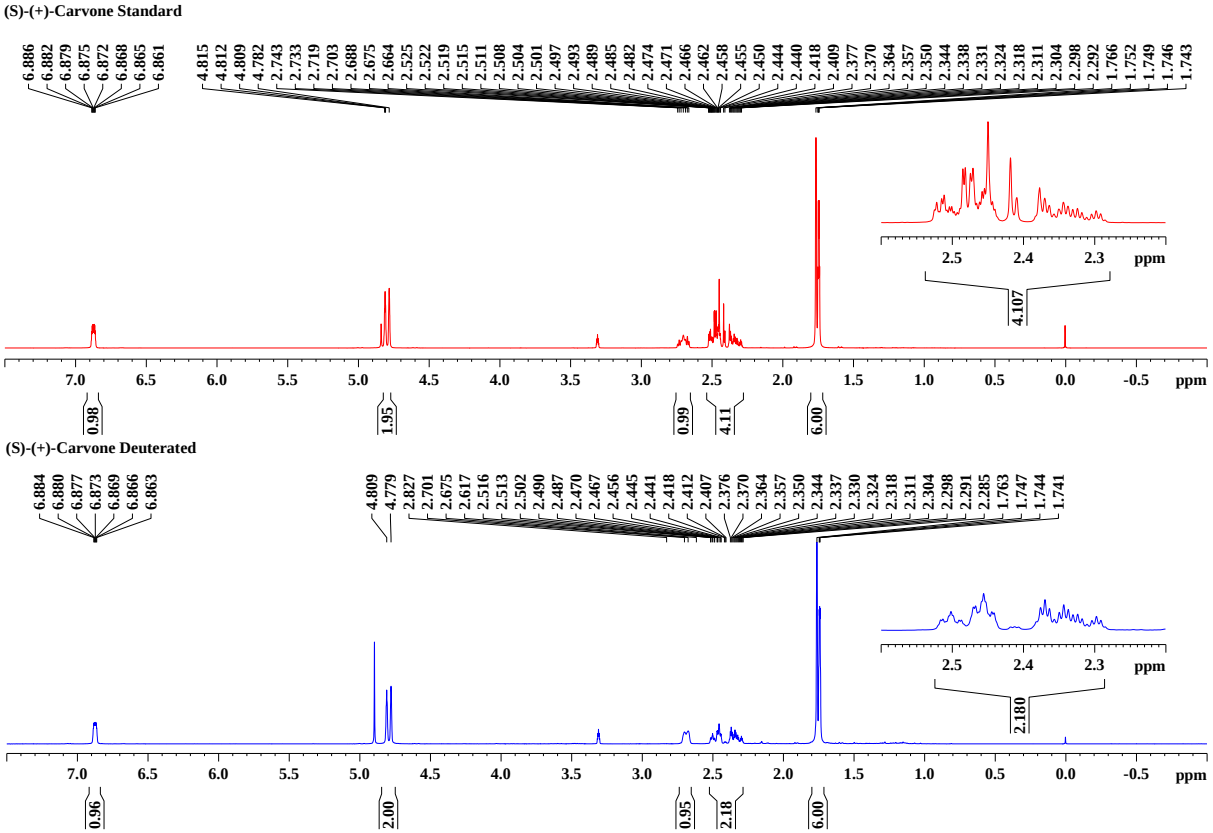
Supplementary Spectrum. ^{13}C NMR spectrum of 5-methoxy-1-indanone (**40**) (100 MHz, CD_3OD)



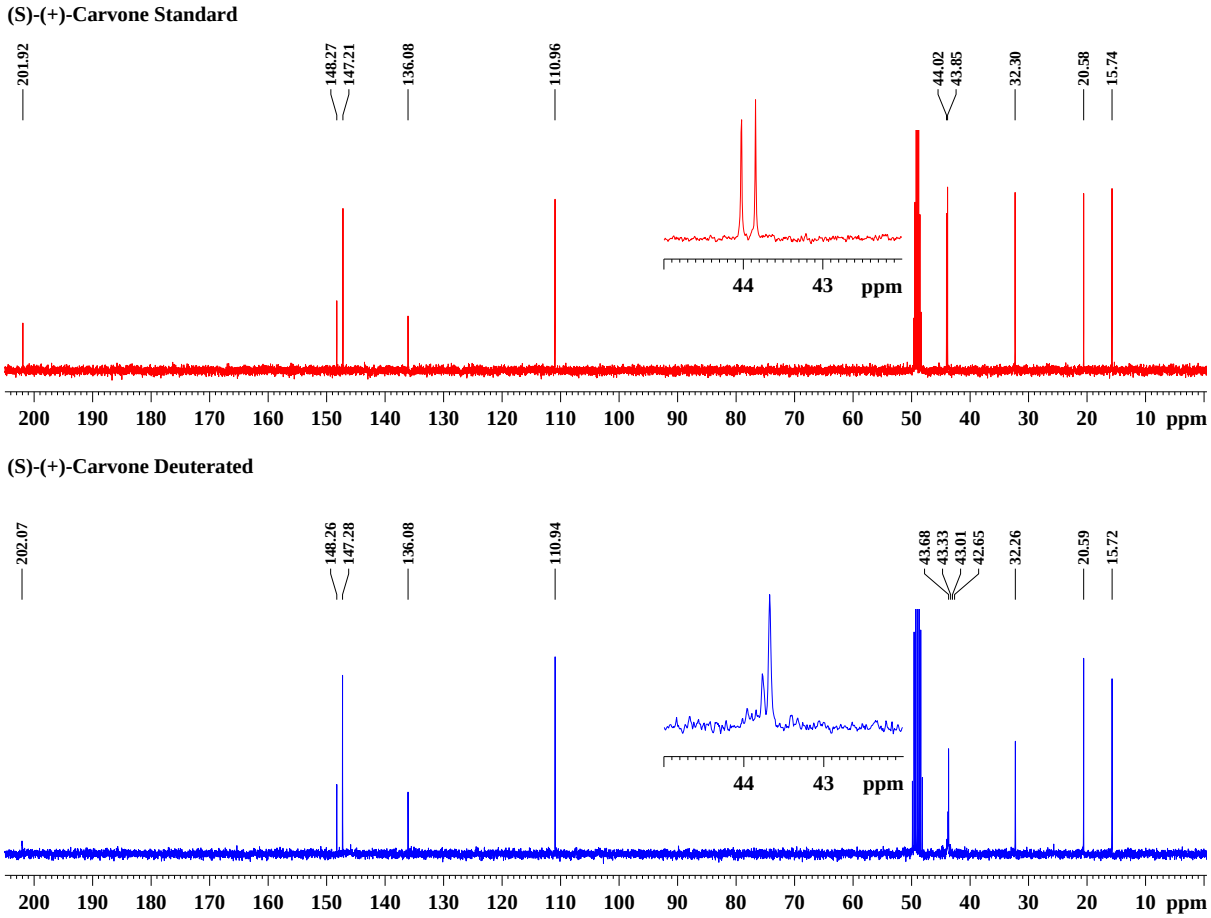
Supplementary Spectrum. ^{1}H NMR spectrum of deoxybenzoin (**41**) (300 MHz, CD_3OD)



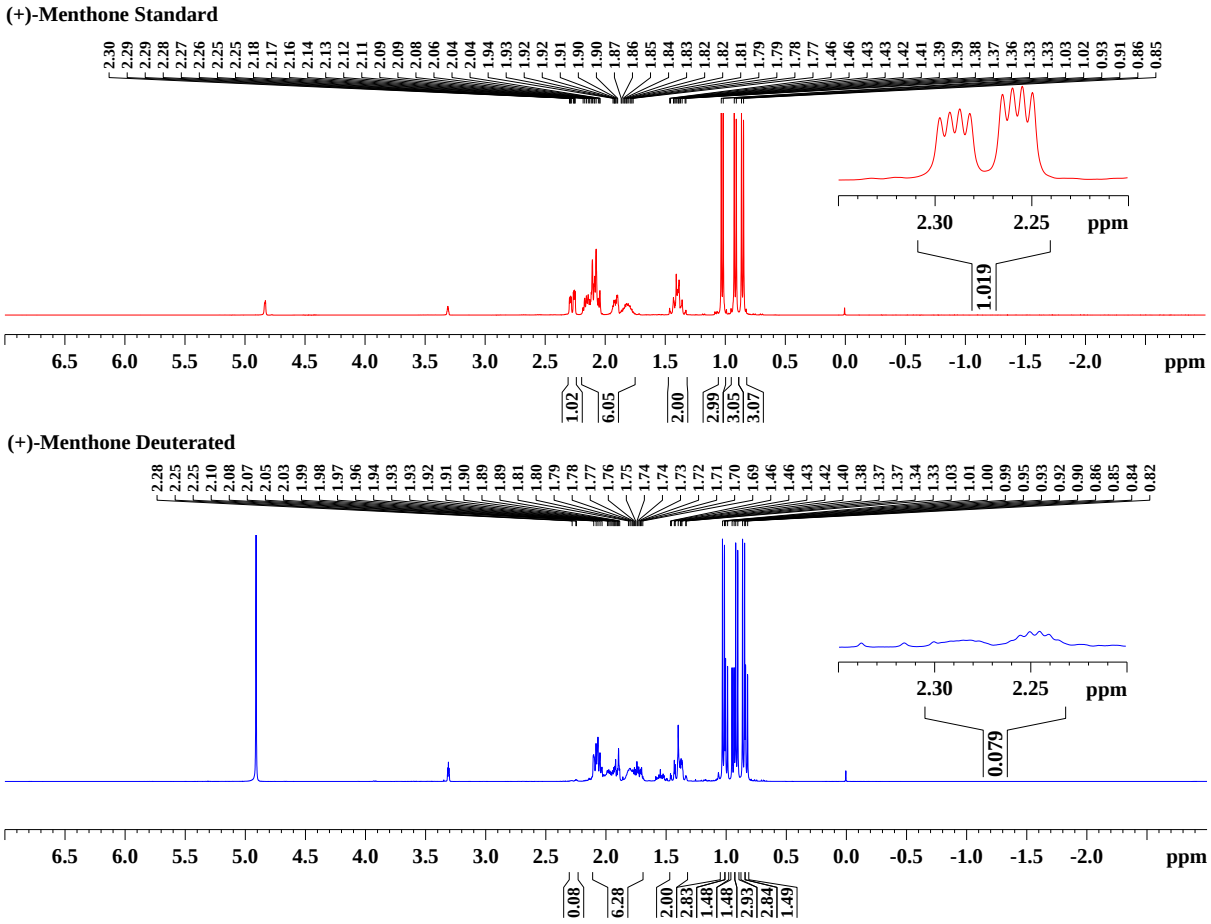
Supplementary Spectrum. ^{13}C NMR spectrum of deoxybenzoin (**41**) (75 MHz, CD_3OD)



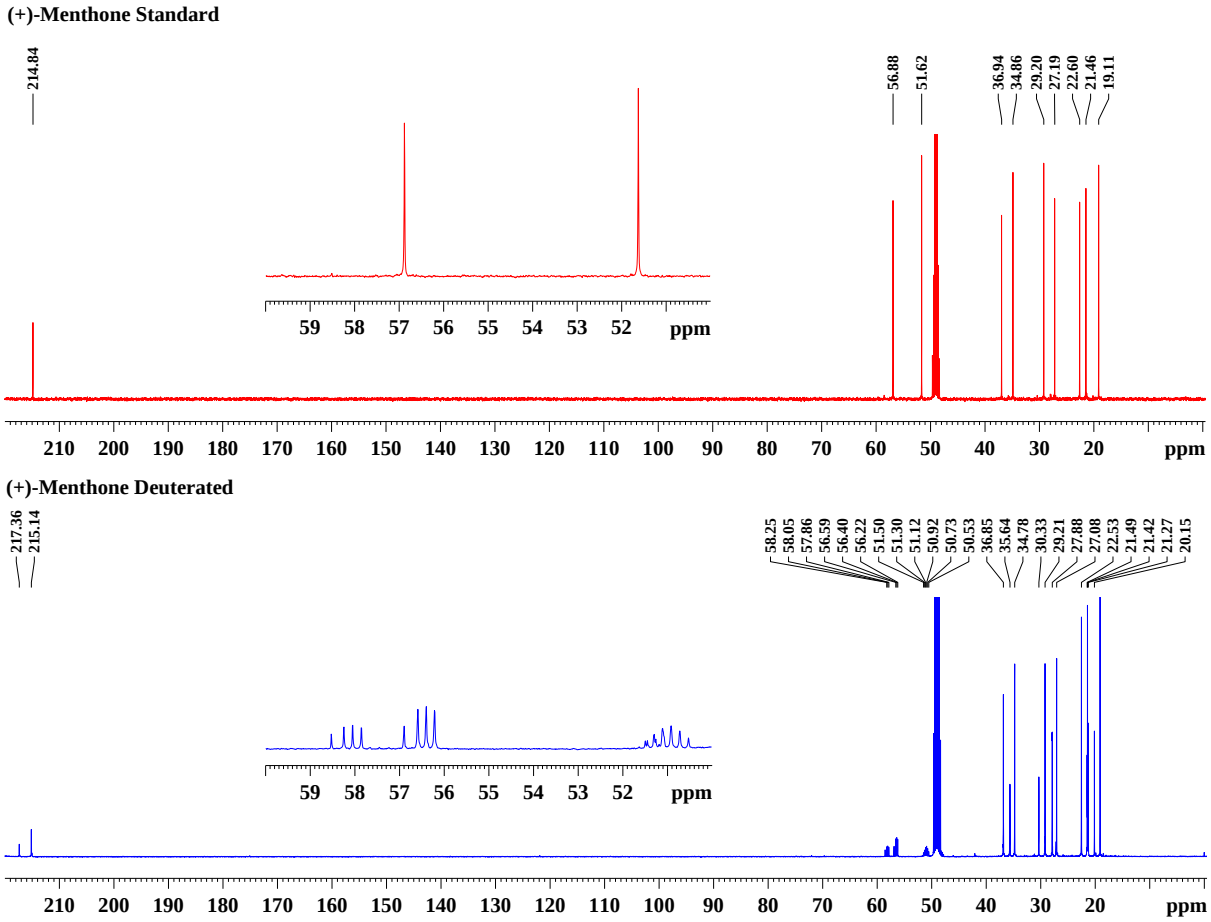
Supplementary Spectrum. ^{1}H NMR spectrum of (*S*)-(+)-carvone (**42**) (300 MHz, CD_3OD)



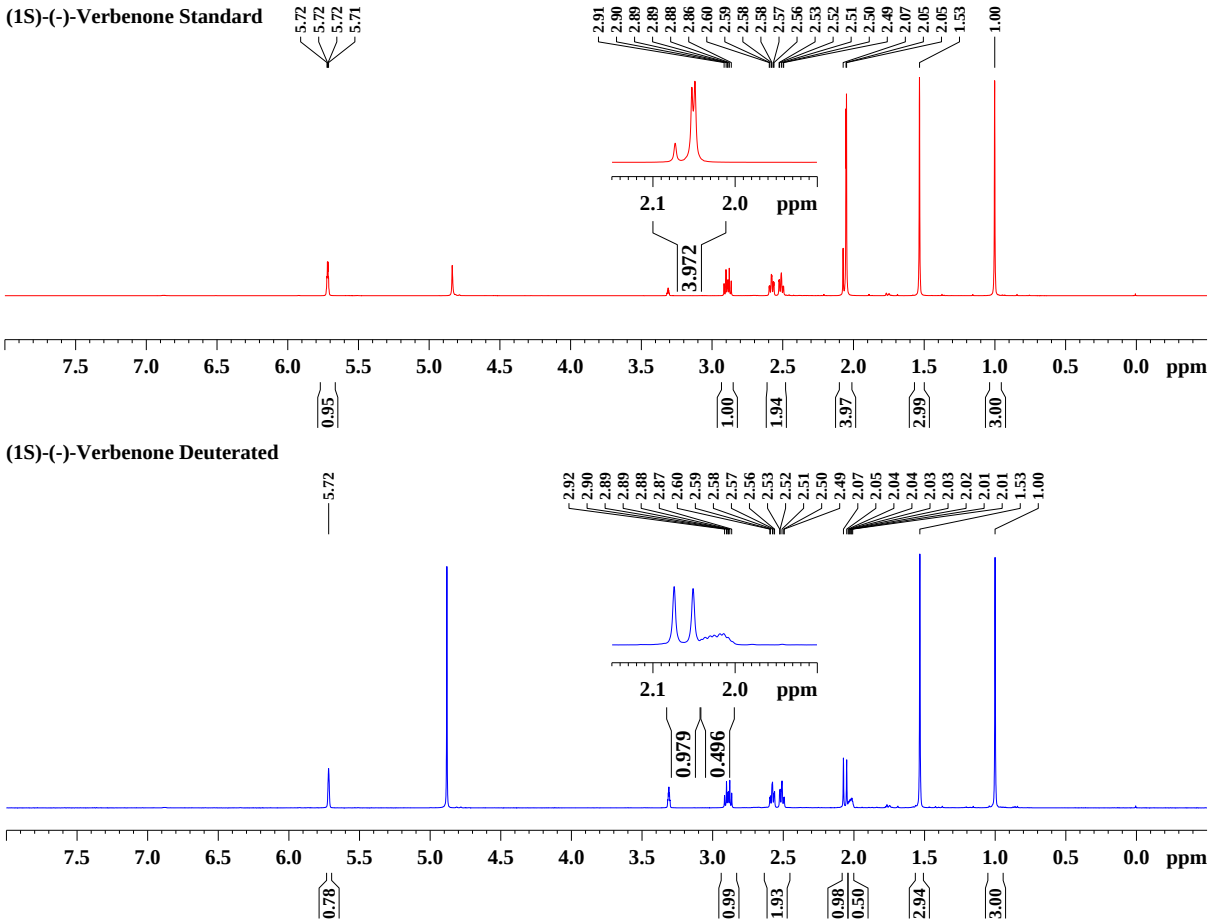
Supplementary Spectrum. ^{13}C NMR spectrum of (*S*)-(+)-carvone (**42**) (75 MHz, CD_3OD)



Supplementary Spectrum. ^{1}H NMR spectrum of (+)-menthone (**43**) (400 MHz, CD_3OD)

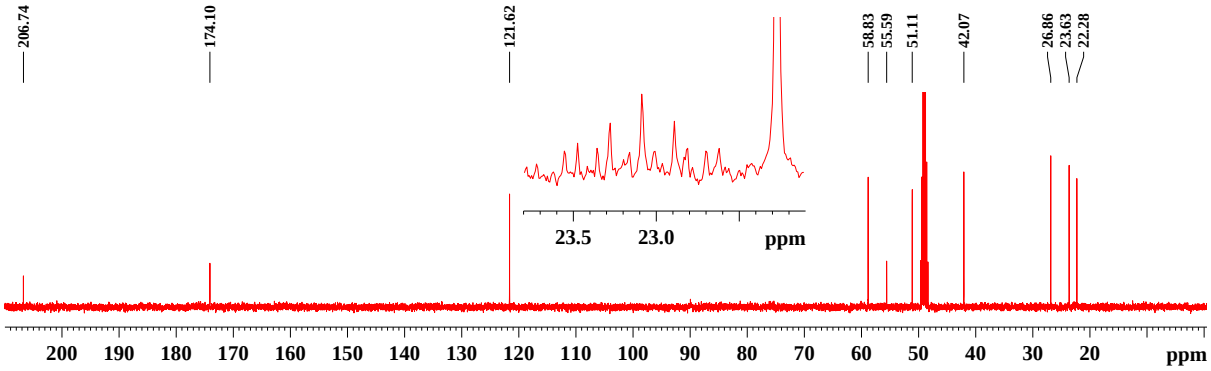


Supplementary Spectrum. ^{13}C NMR spectrum of (+)-menthone (**43**) (100 MHz, CD_3OD)

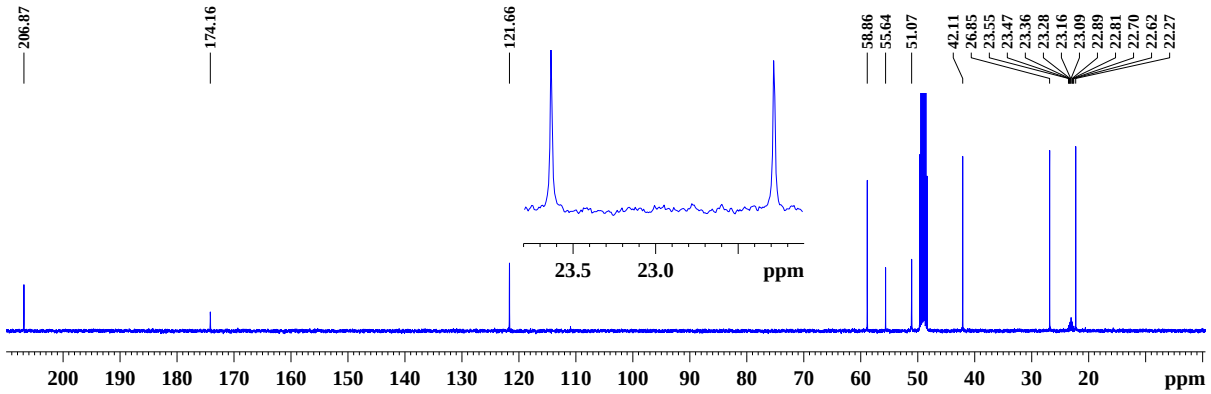


Supplementary Spectrum. ^{1}H NMR spectrum of (1*S*)-(-)-verbenone (**44**) (400 MHz, CD_3OD)

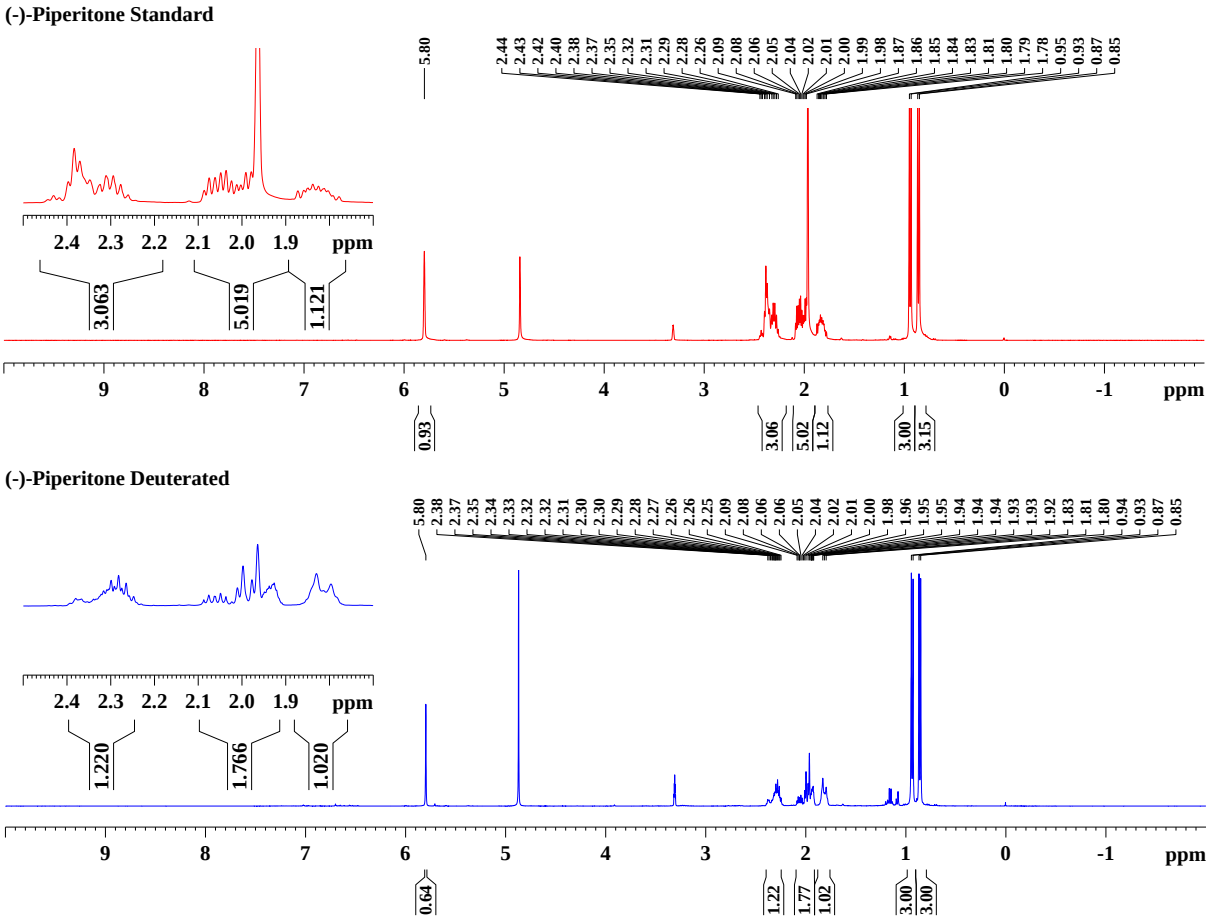
(1S)-(-)-Verbenone Standard



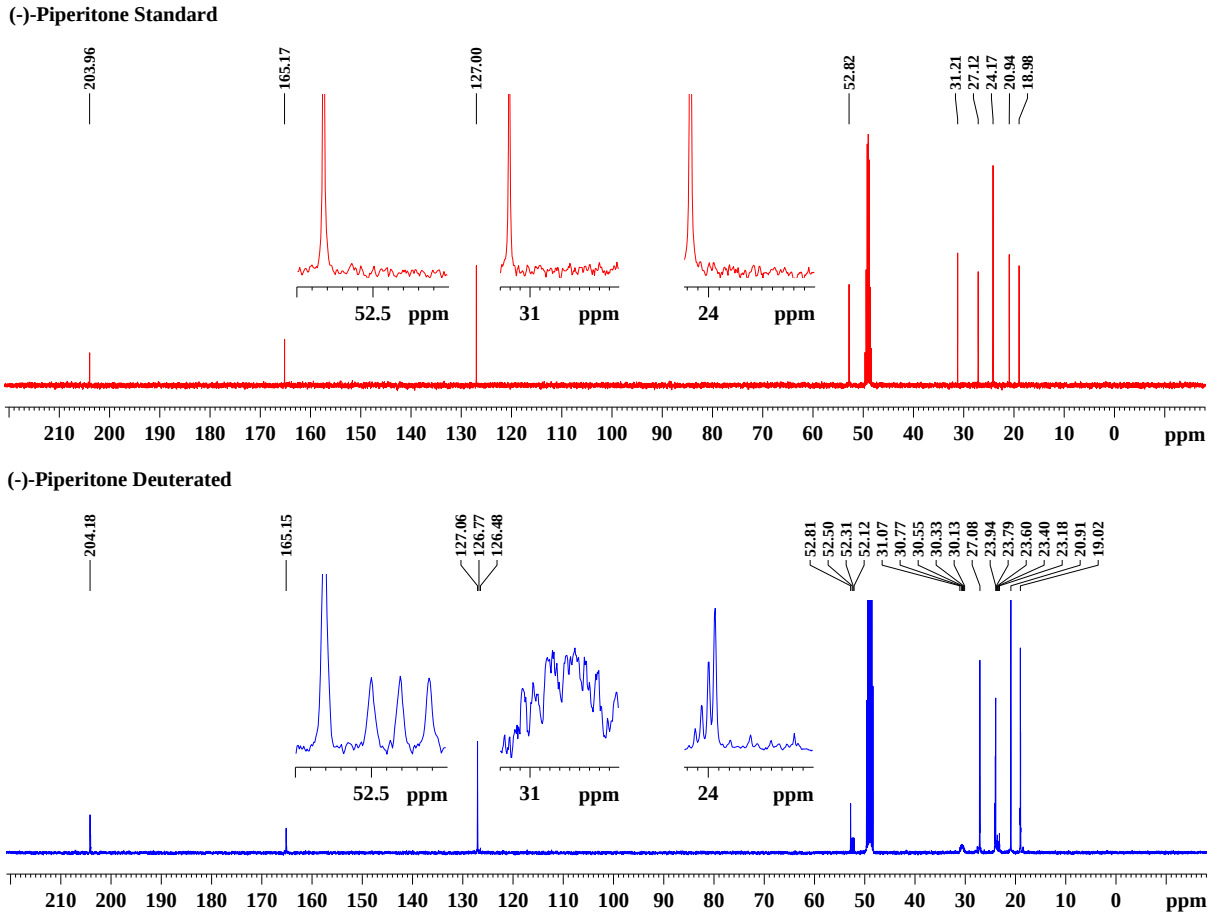
(1S)-(-)-Verbenone Deuterated



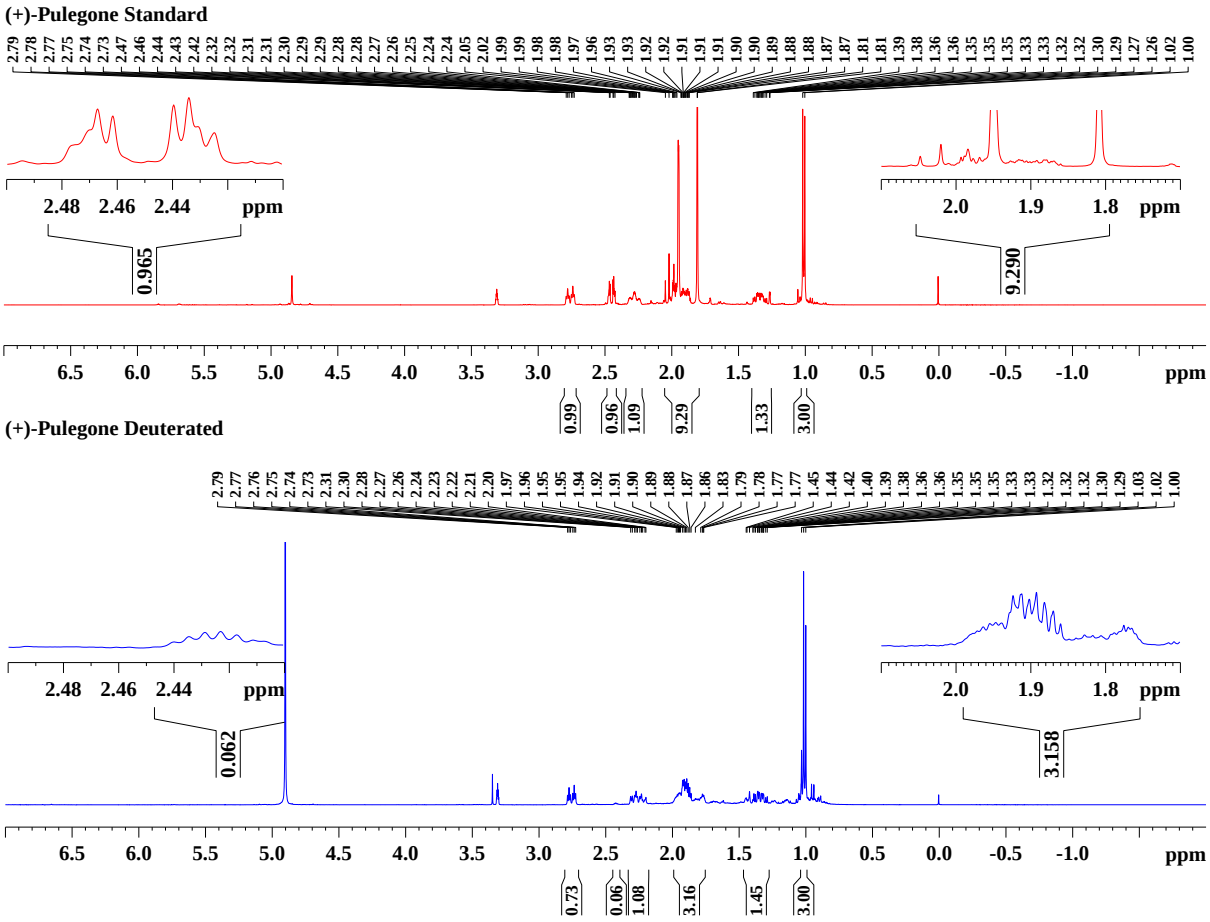
Supplementary Spectrum. ^{13}C NMR spectrum of (1*S*)-(-)-verbenone (**44**) (100 MHz, CD_3OD)



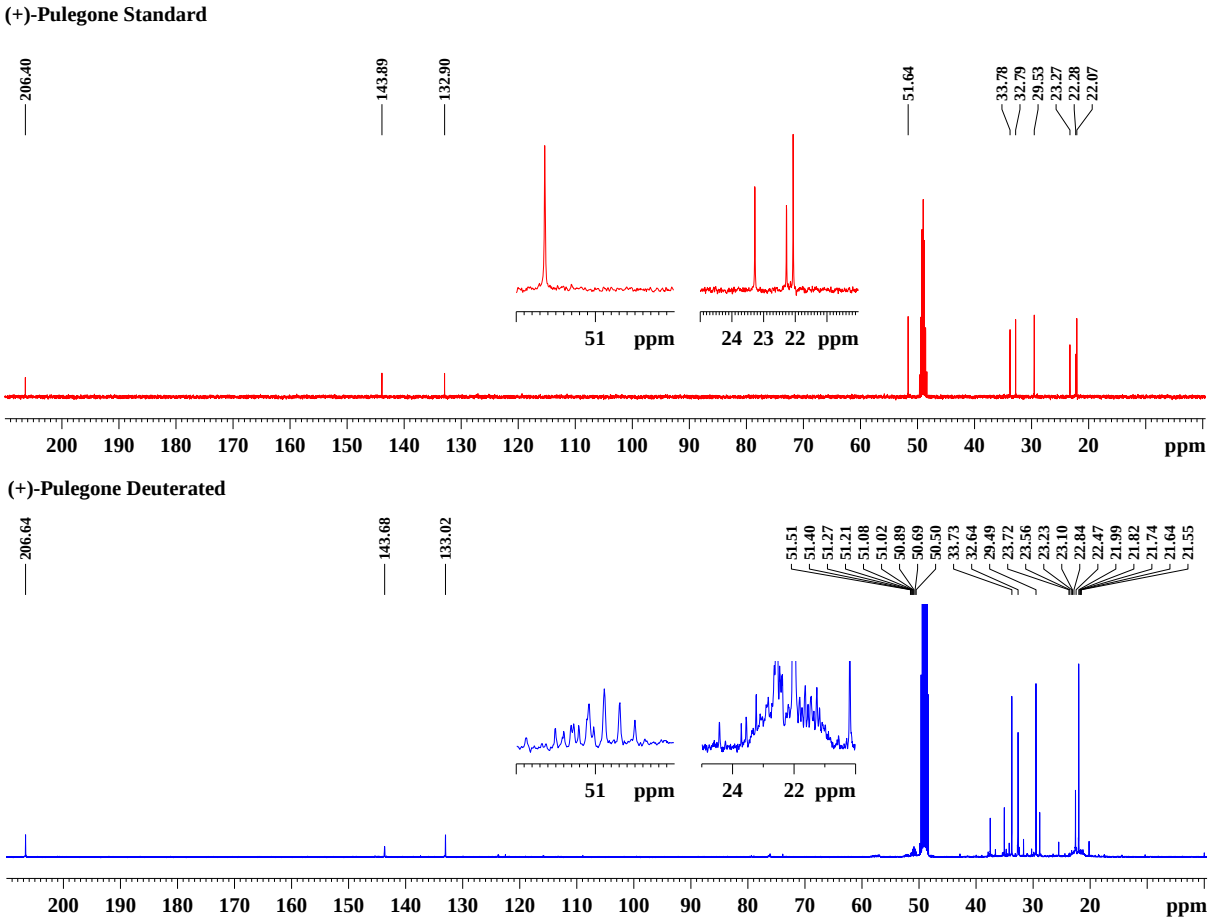
Supplementary Spectrum. ^{1}H NMR spectrum of (-)-piperitone (**45**) (400 MHz, CD_3OD)



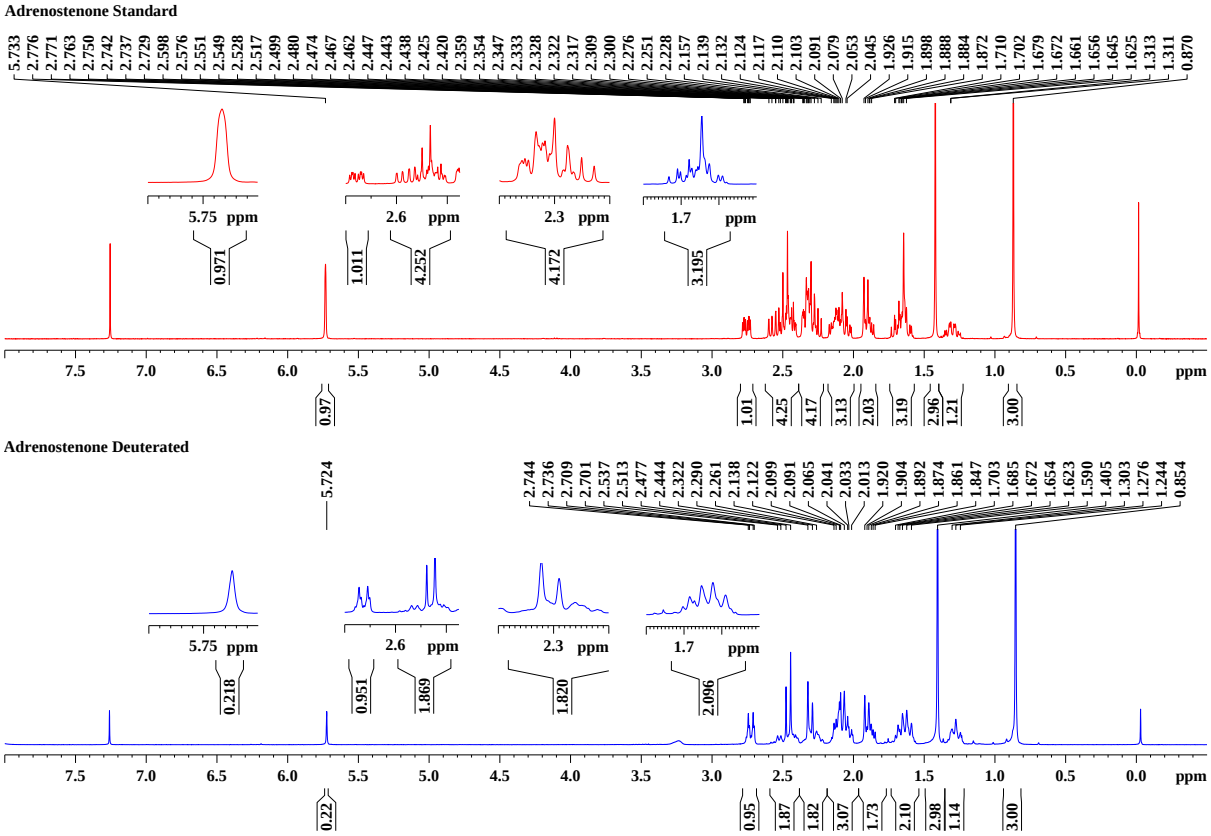
Supplementary Spectrum. ^{13}C NMR spectrum of (-)-piperitone (**45**) (100 MHz, CD_3OD)



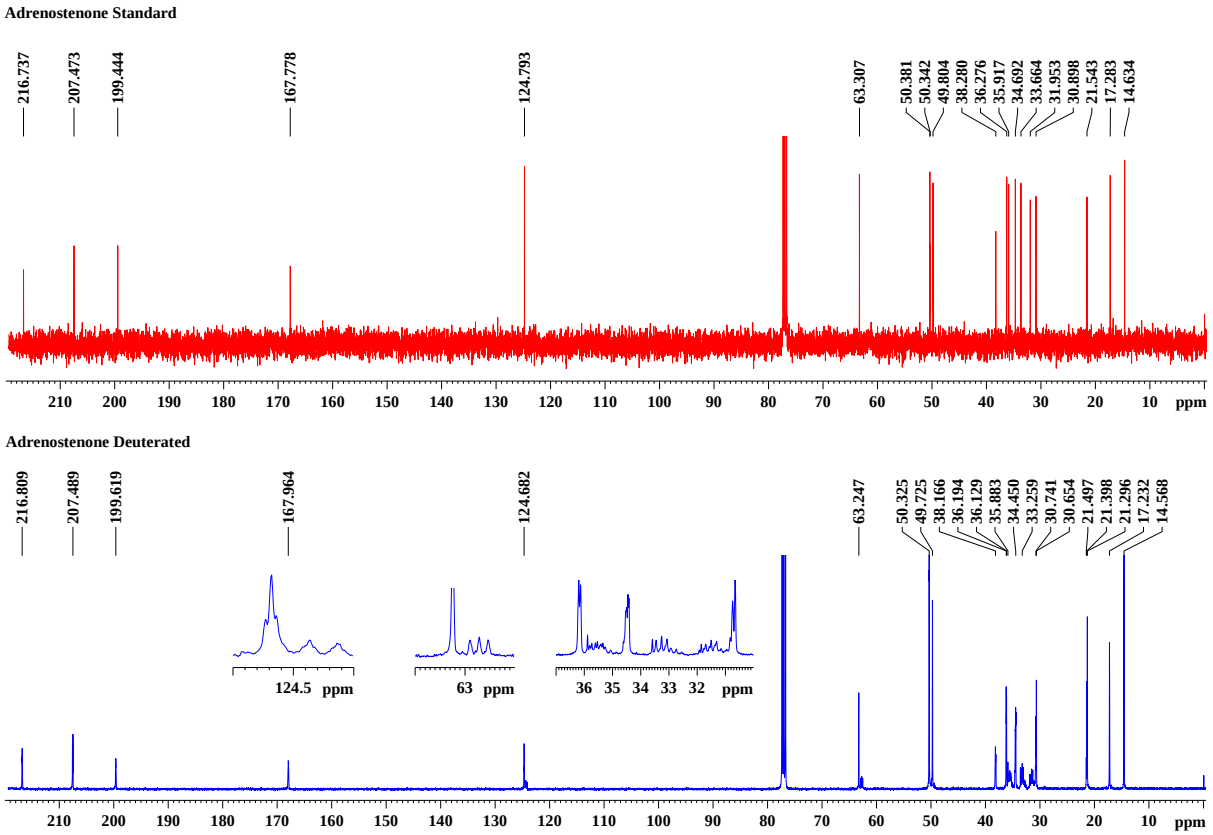
Supplementary Spectrum. ^{1}H NMR spectrum of (+)-pulegone (**46**) (400 MHz, CD_3OD)



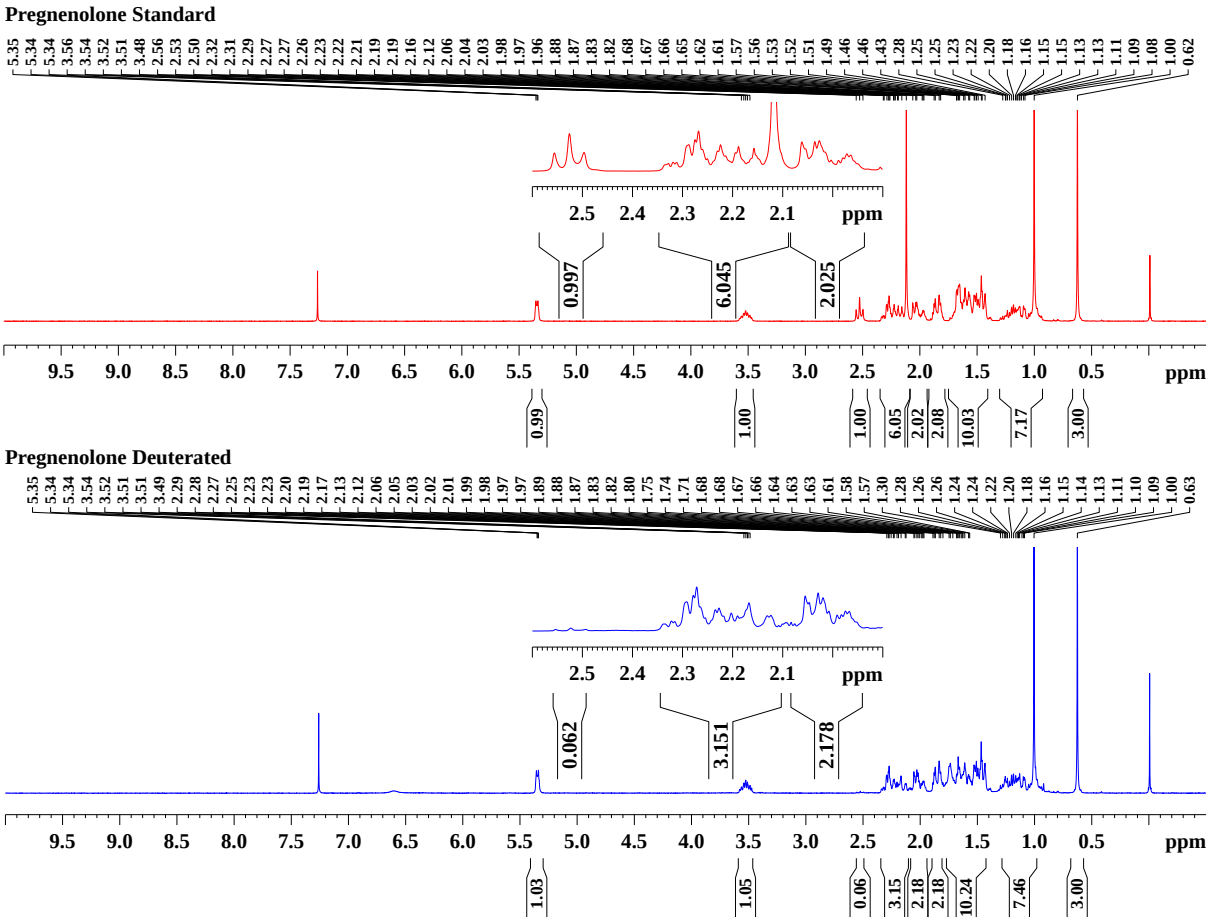
Supplementary Spectrum. ^{13}C NMR spectrum of (+)-pulegone (**46**) (100 MHz, CD_3OD)



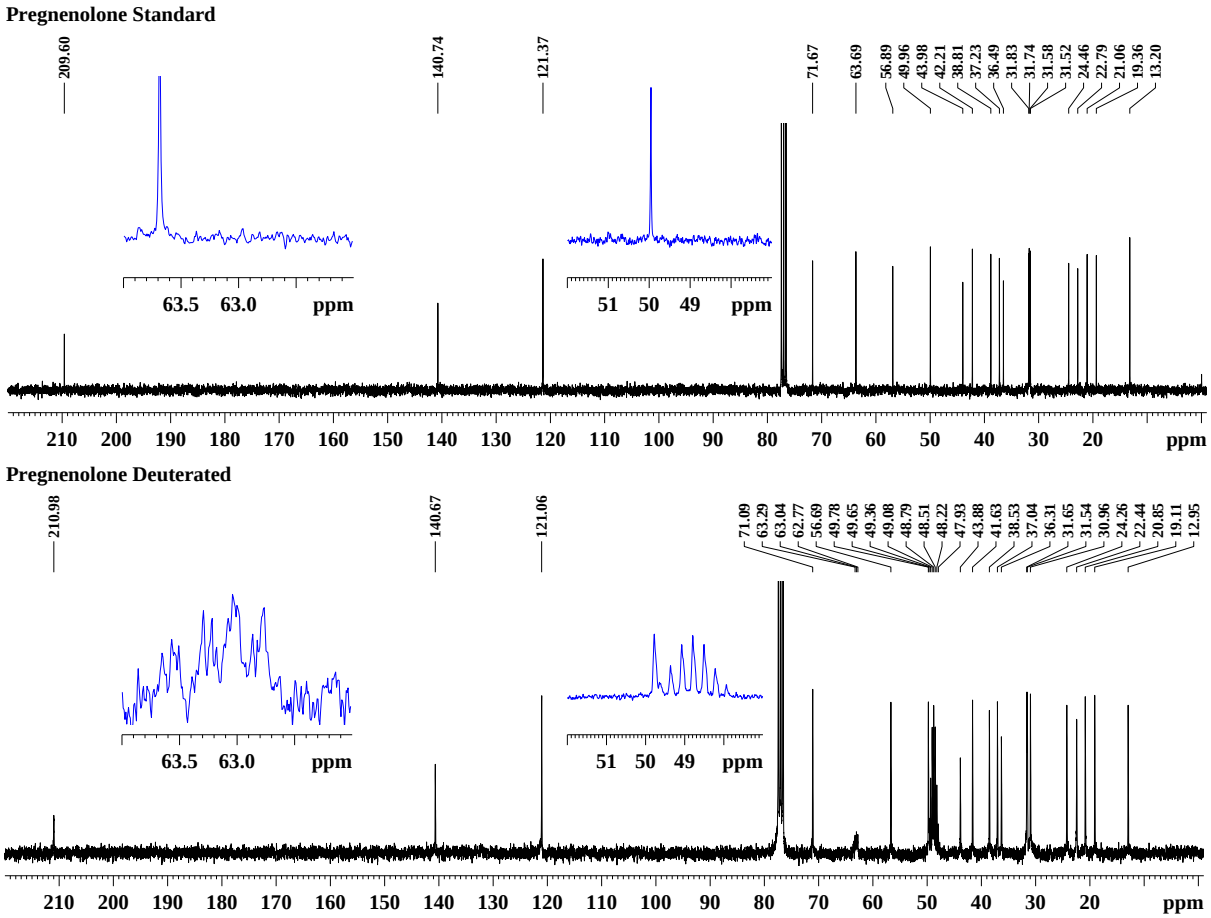
Supplementary Spectrum. ^{1}H NMR spectrum of adrenosterone (**47**) (400 MHz, $CDCl_3$)



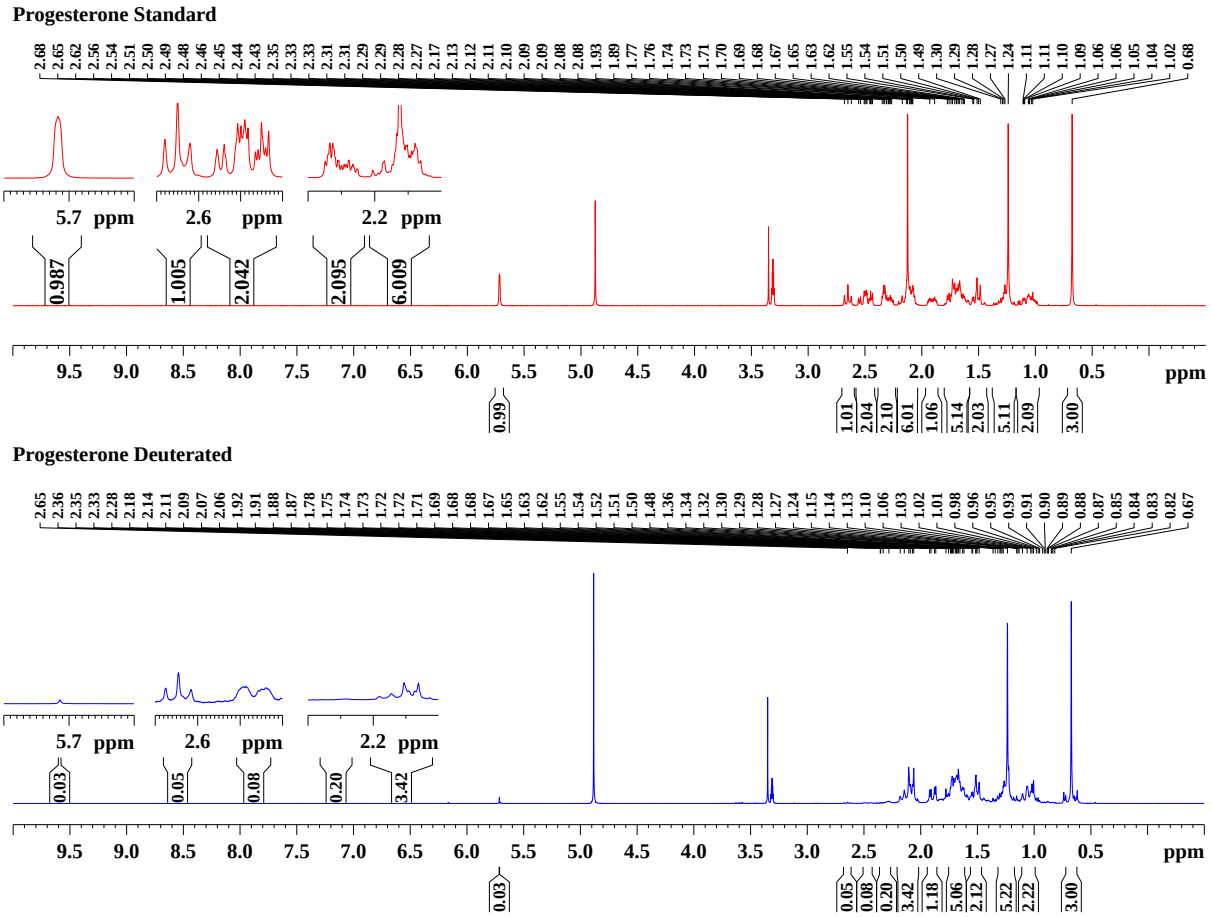
Supplementary Spectrum. ^{13}C NMR spectrum of adrenosterone (**47**) (100 MHz, $CDCl_3$)



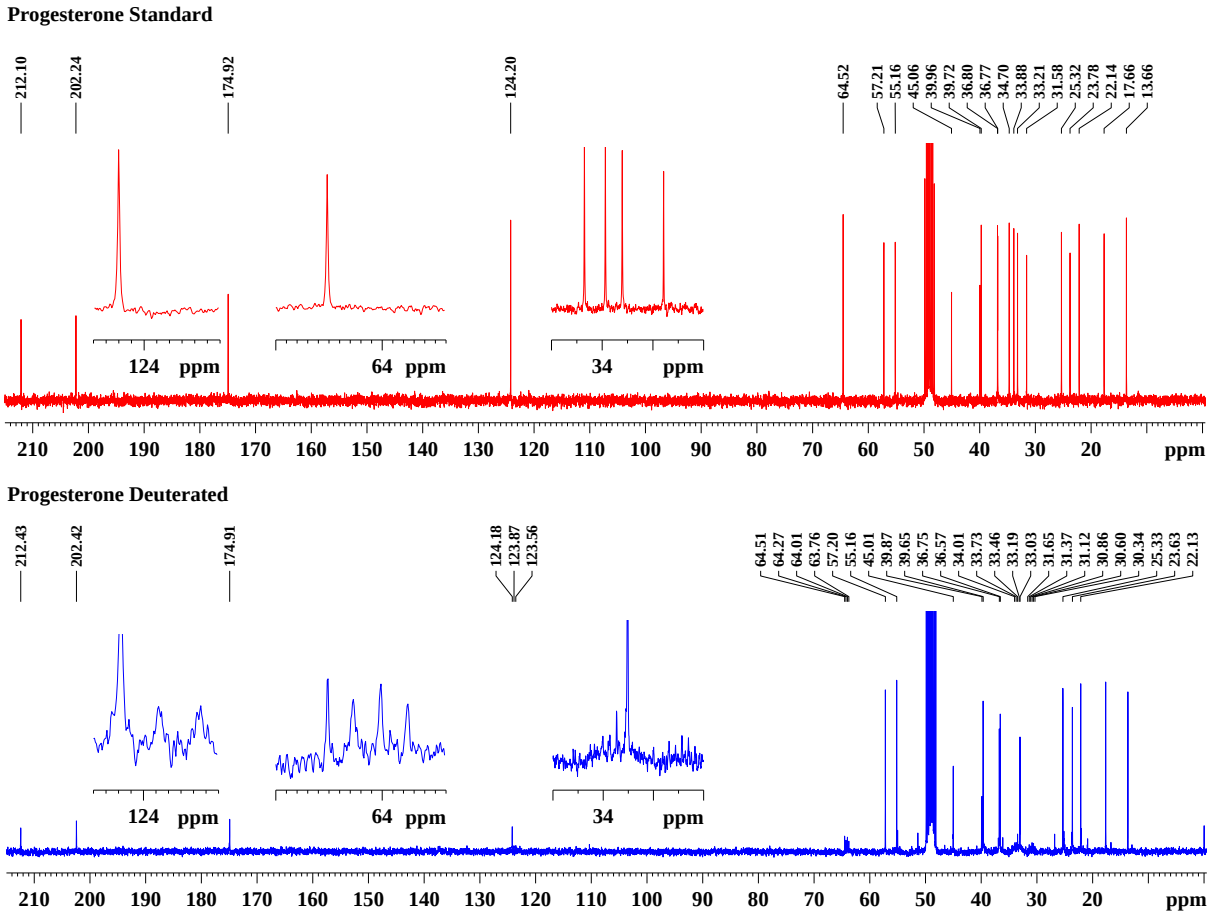
Supplementary Spectrum. ^{1}H NMR spectrum of pregnenolone (**48**) (300 MHz, $CDCl_3$)



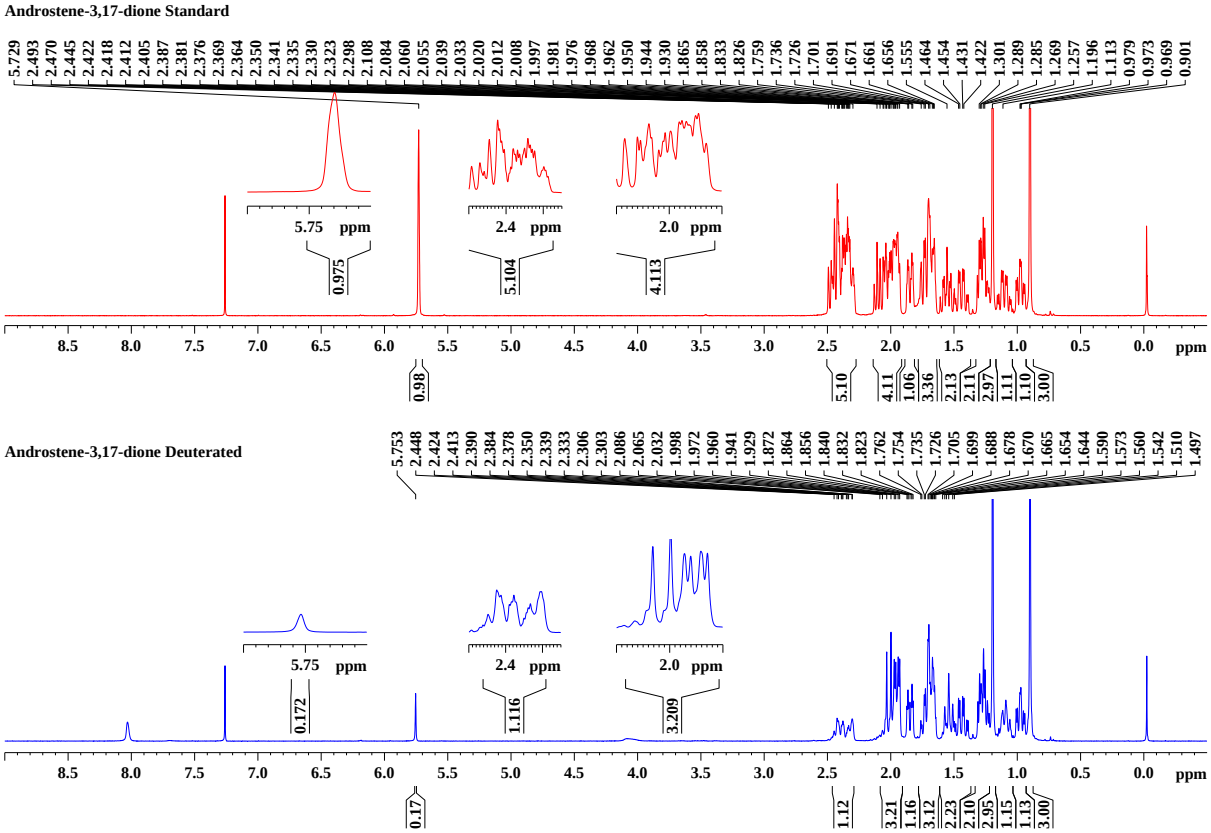
Supplementary Spectrum. ^{13}C NMR spectrum of pregnenolone (**48**) (75 MHz, $CDCl_3$)



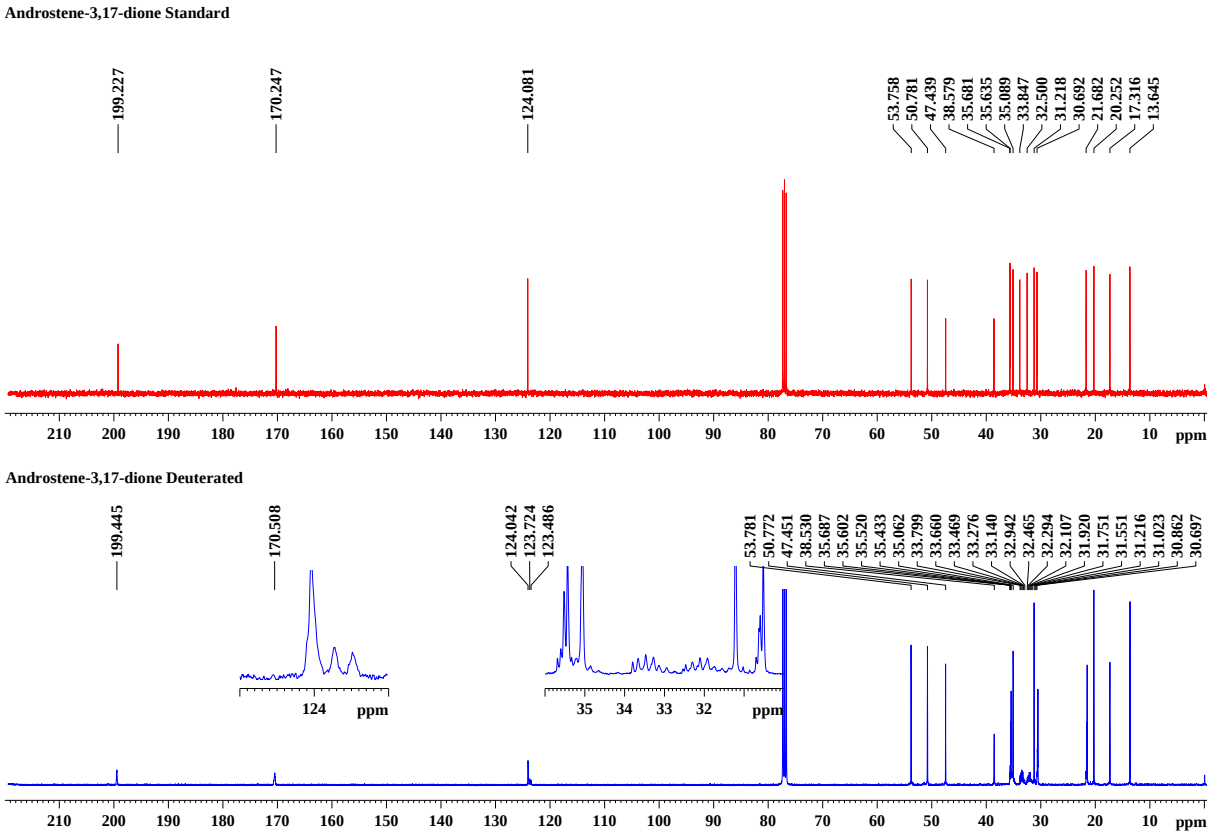
Supplementary Spectrum. ^{1}H NMR spectrum of progesterone (**49**) (300 MHz, CD_3OD)



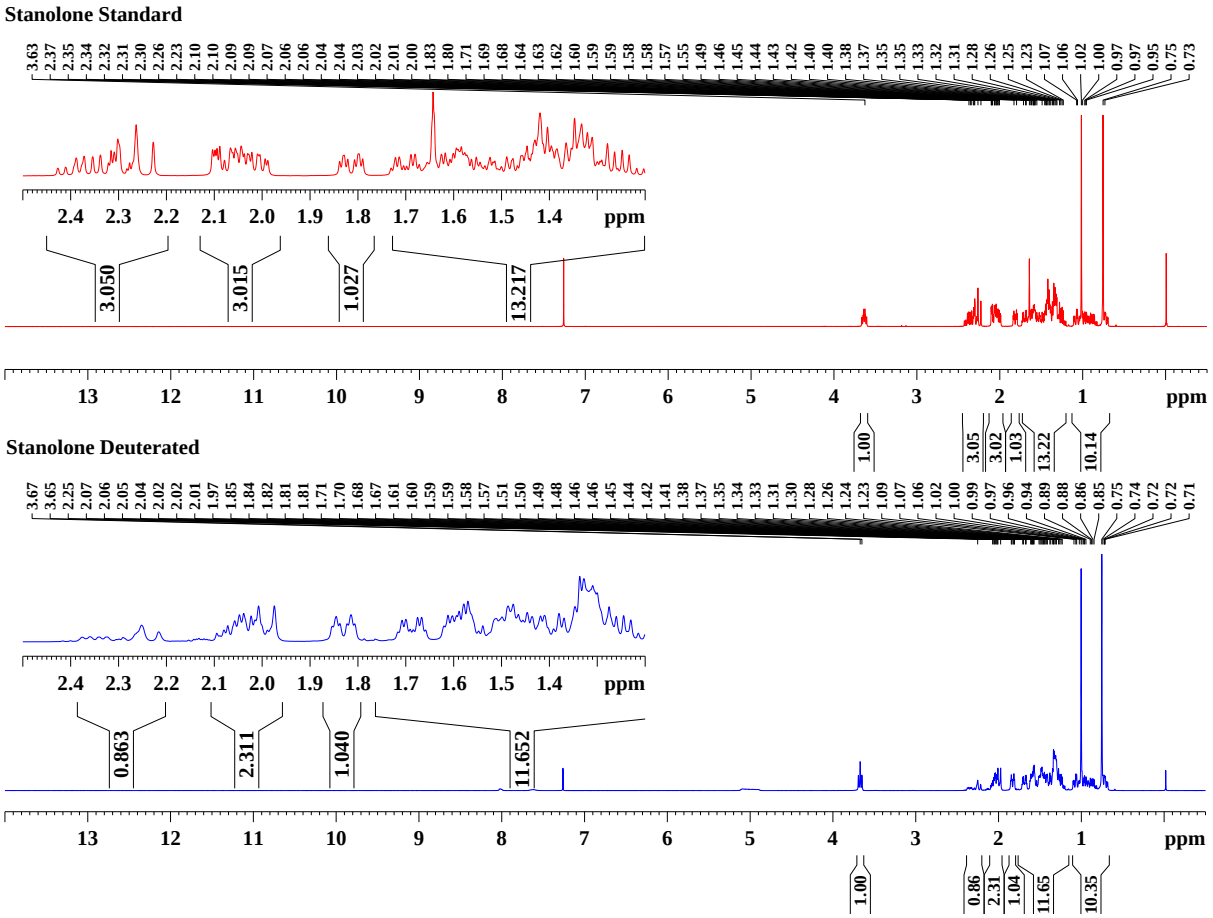
Supplementary Spectrum. ^{13}C NMR spectrum of progesterone (**49**) (75 MHz, CD_3OD)



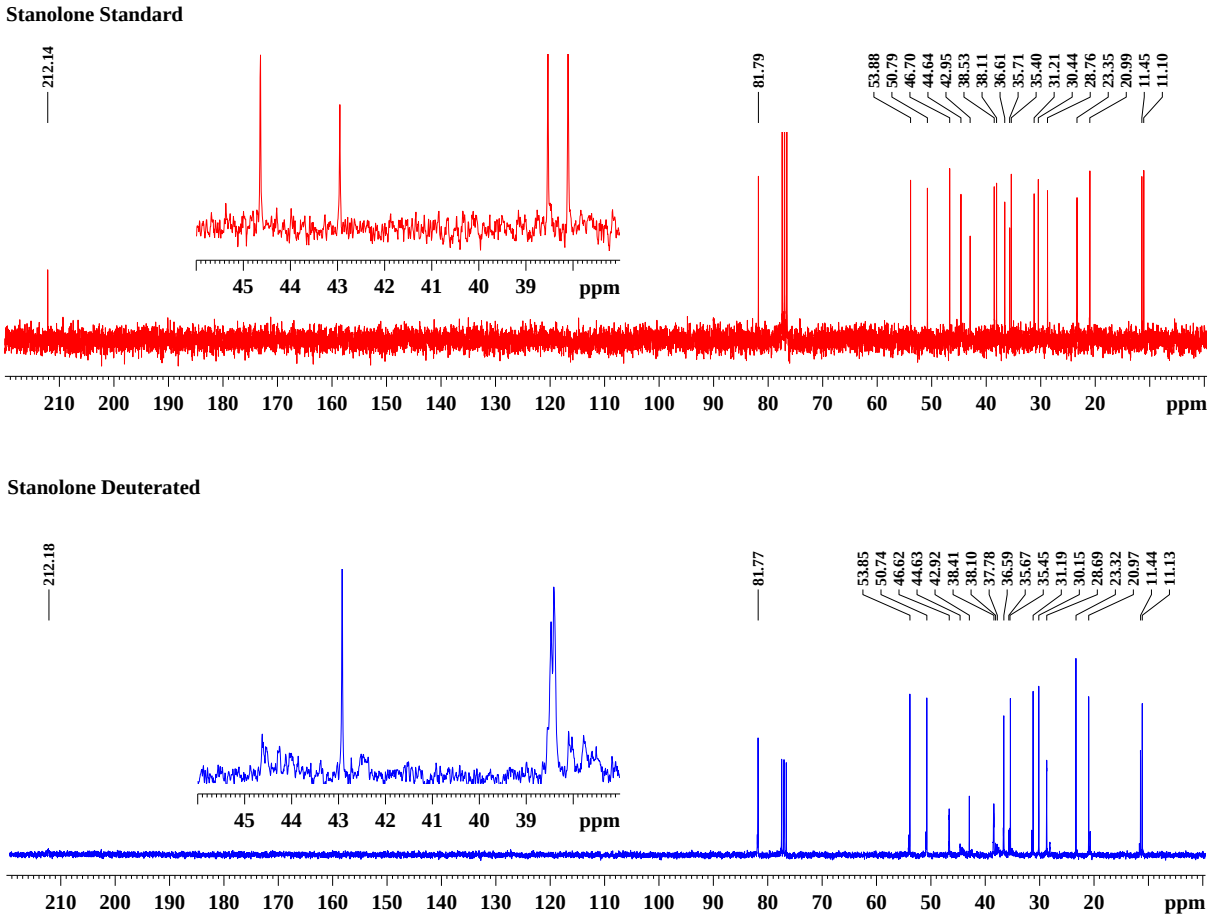
Supplementary Spectrum. ^{1}H NMR spectrum of Δ4-androstene-3,17-dione (**50**) (400 MHz, $CDCl_3$)



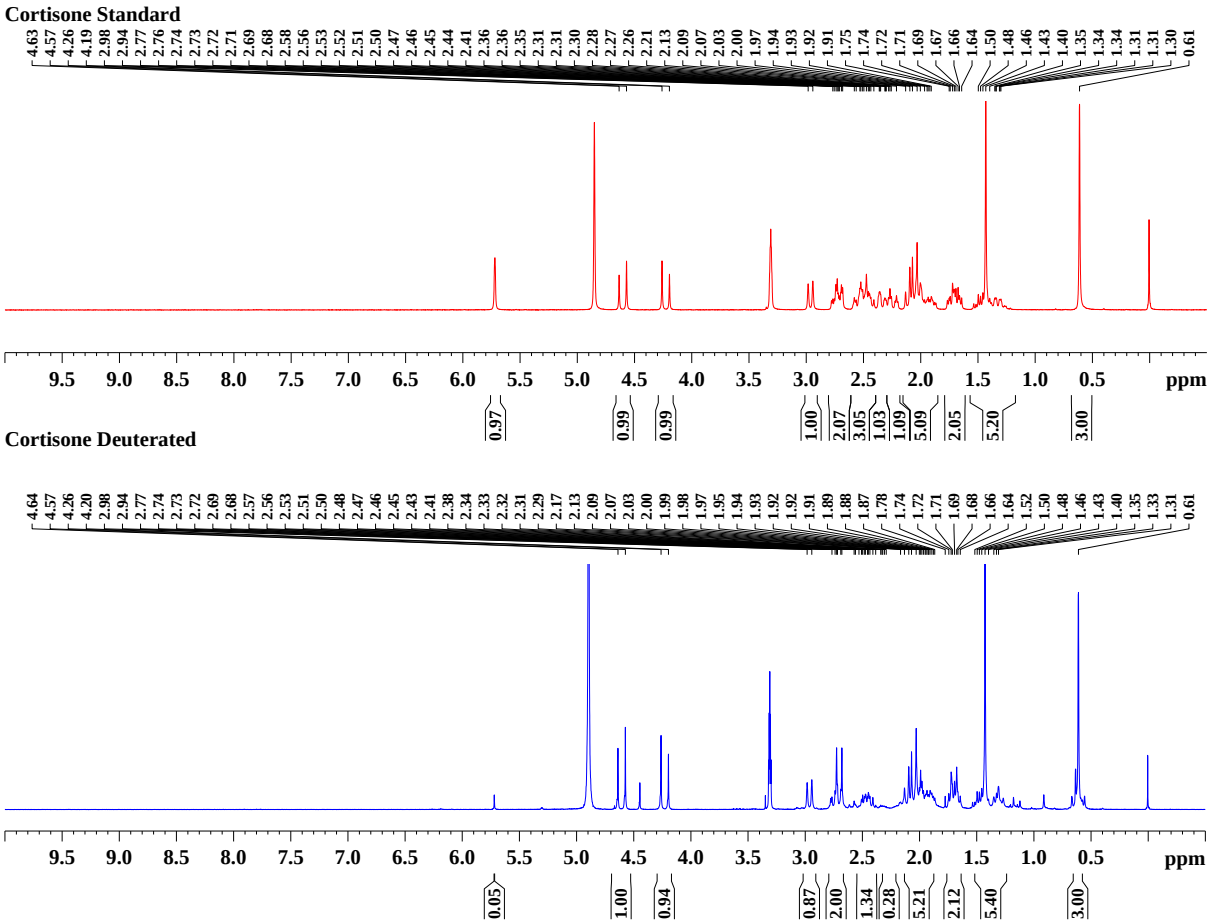
Supplementary Spectrum. ^{13}C NMR spectrum of Δ4-androstene-3,17-dione (**50**) (100 MHz, $CDCl_3$)



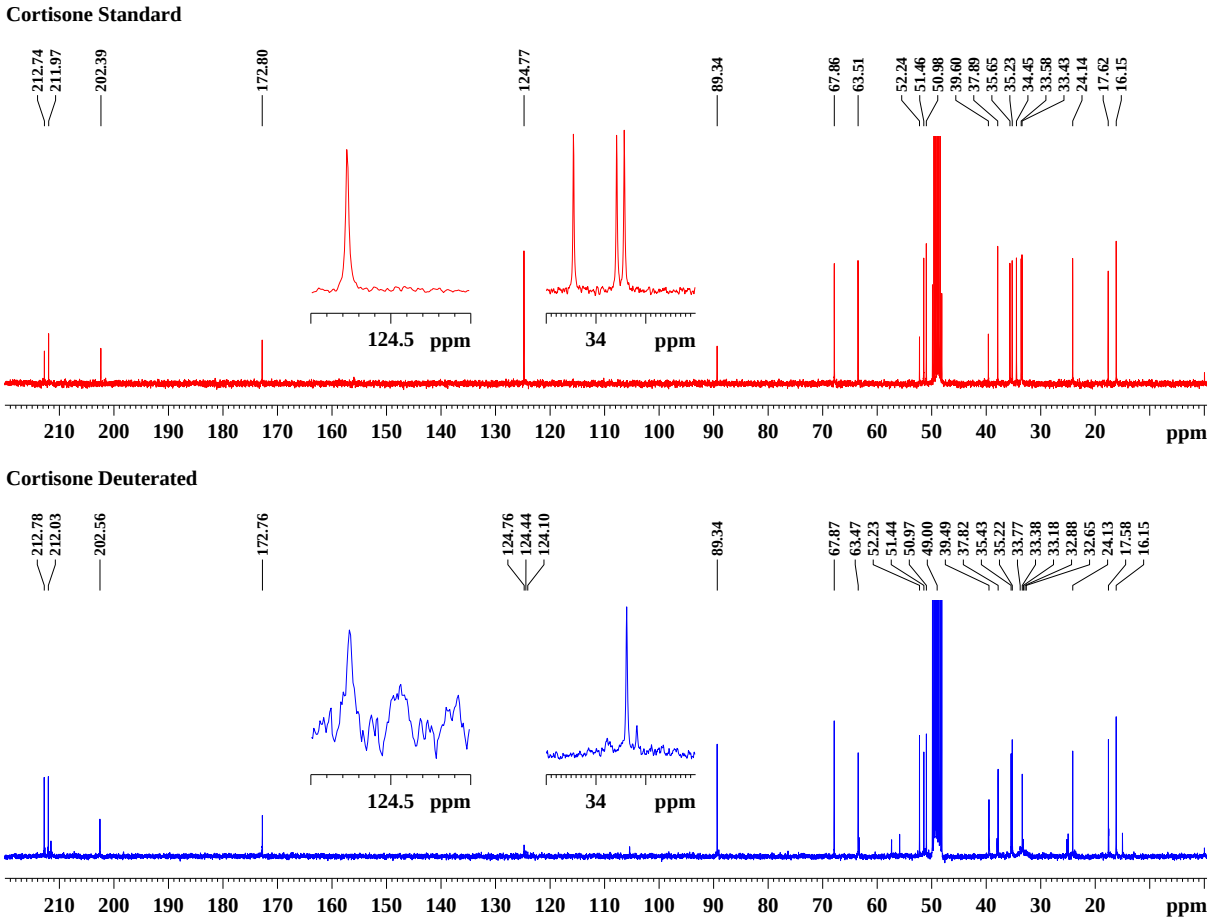
Supplementary Spectrum. ^{1}H NMR spectrum of stanolone (**51**) (400 MHz, $CDCl_3$)



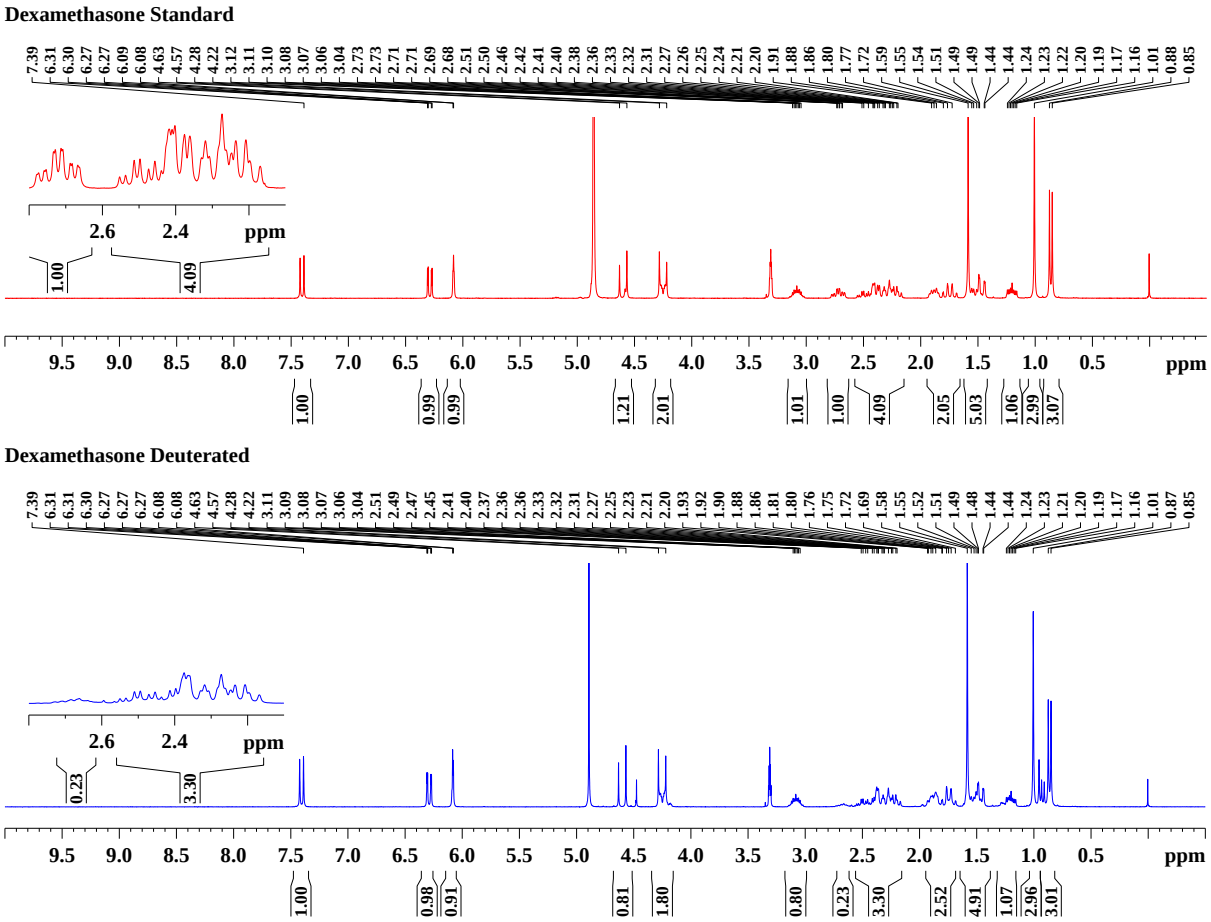
Supplementary Spectrum. ^{13}C NMR spectrum of stanolone (**51**) (100 MHz, $CDCl_3$)



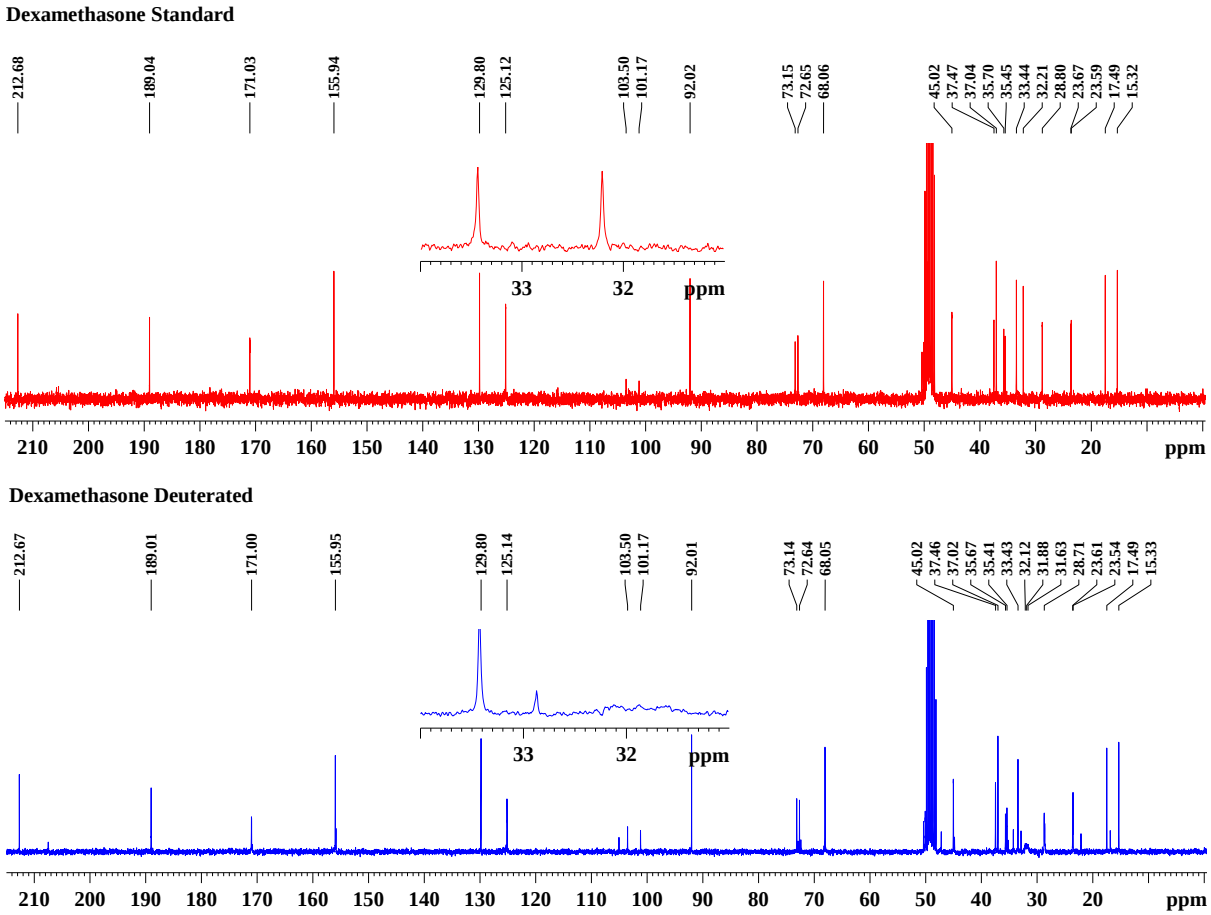
Supplementary Spectrum. ^{1}H NMR spectrum of cortisone (**52**) (300 MHz, CD_3OD)



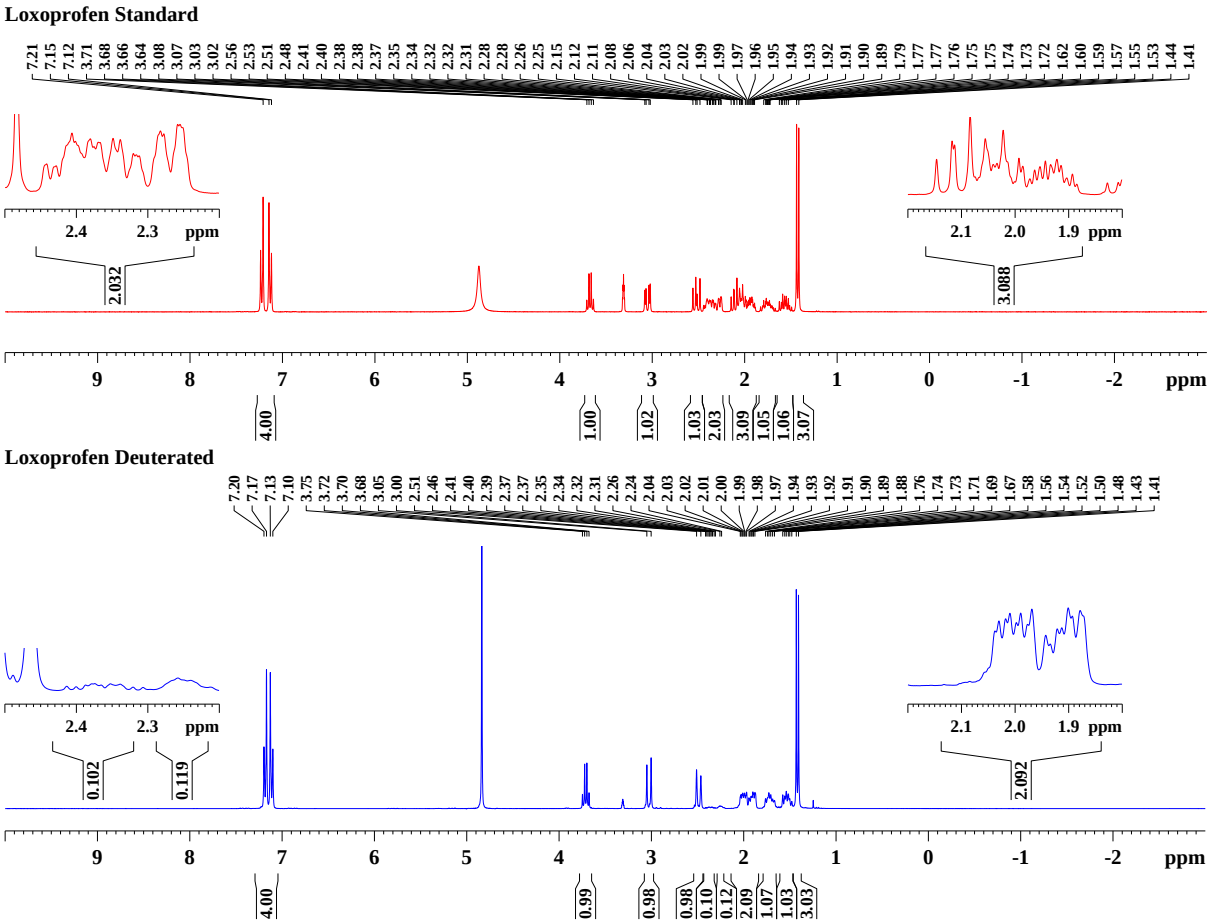
Supplementary Spectrum. ^{13}C NMR spectrum of cortisone (**52**) (75 MHz, CD_3OD)



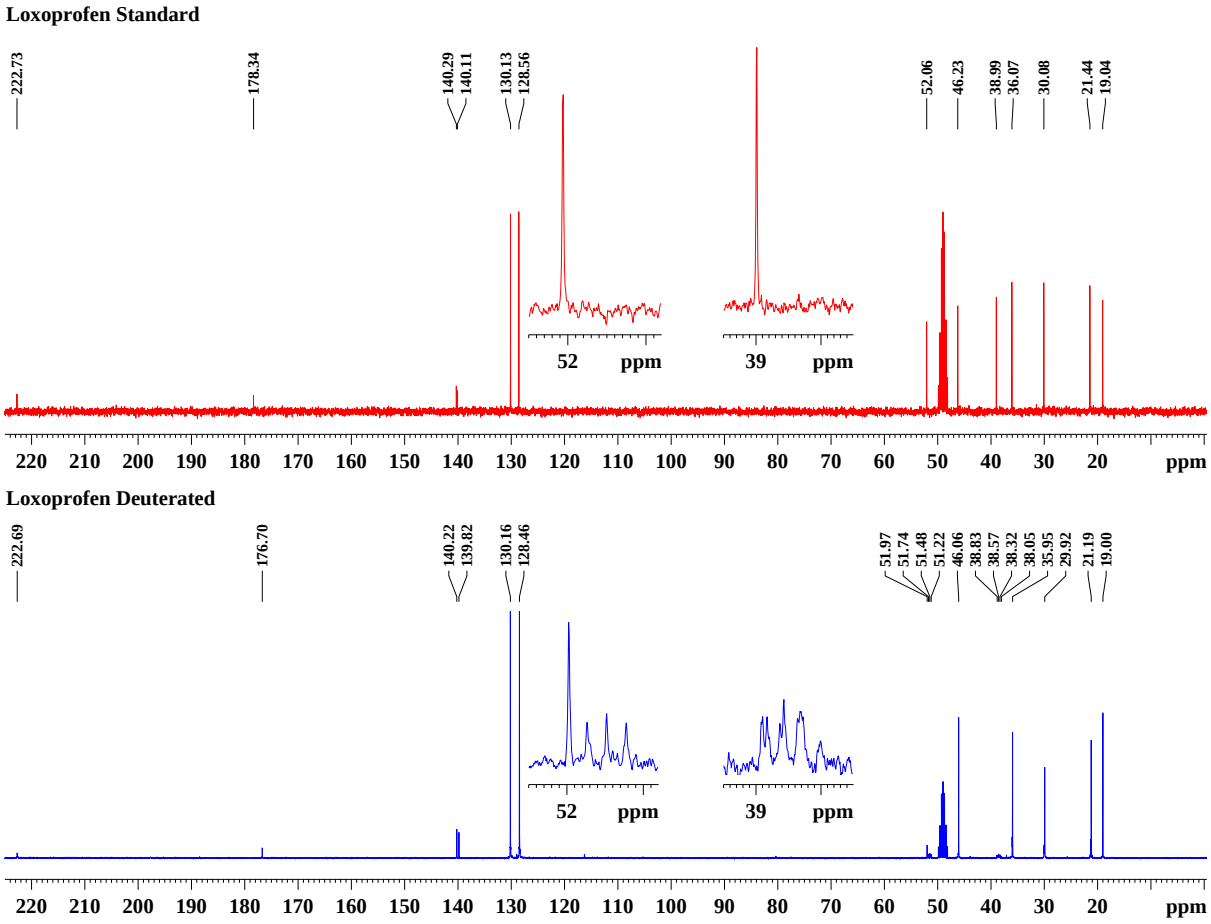
Supplementary Spectrum. ^{1}H NMR spectrum of dexamethasone (**53**) (300 MHz, CD_3OD)



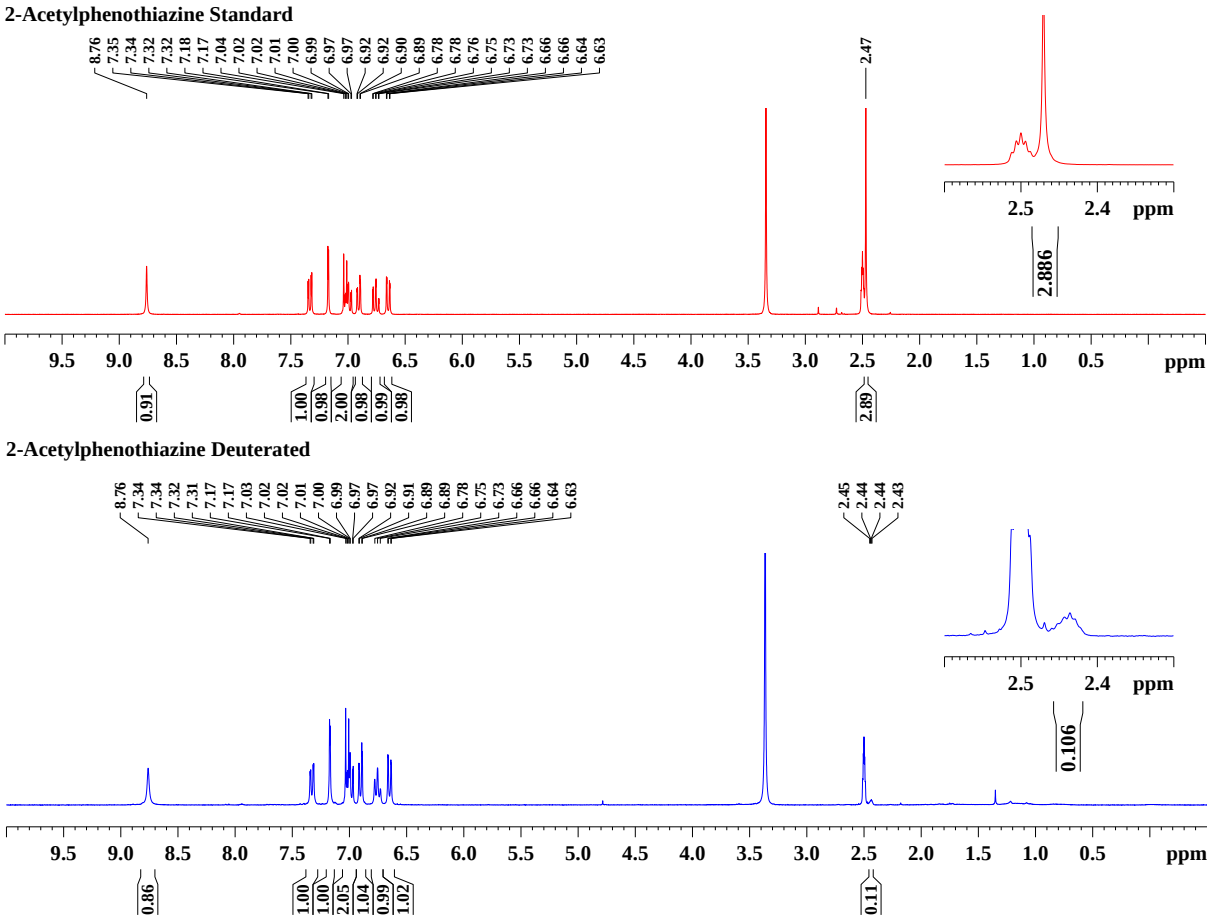
Supplementary Spectrum. ^{13}C NMR spectrum of dexamethasone (**53**) (75 MHz, CD_3OD)



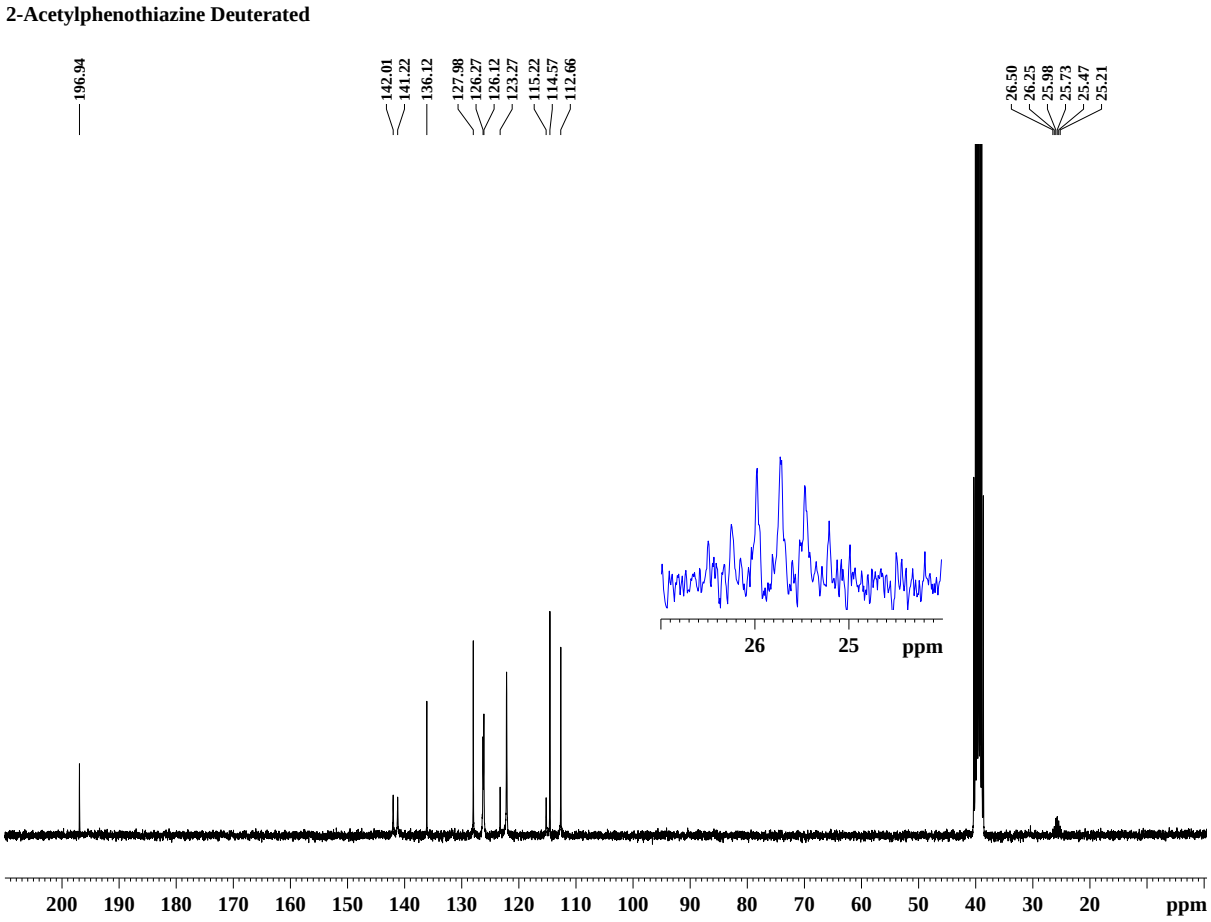
Supplementary Spectrum. ^{1}H NMR spectrum of loxoprofen (**54**) (300 MHz, CD_3OD)



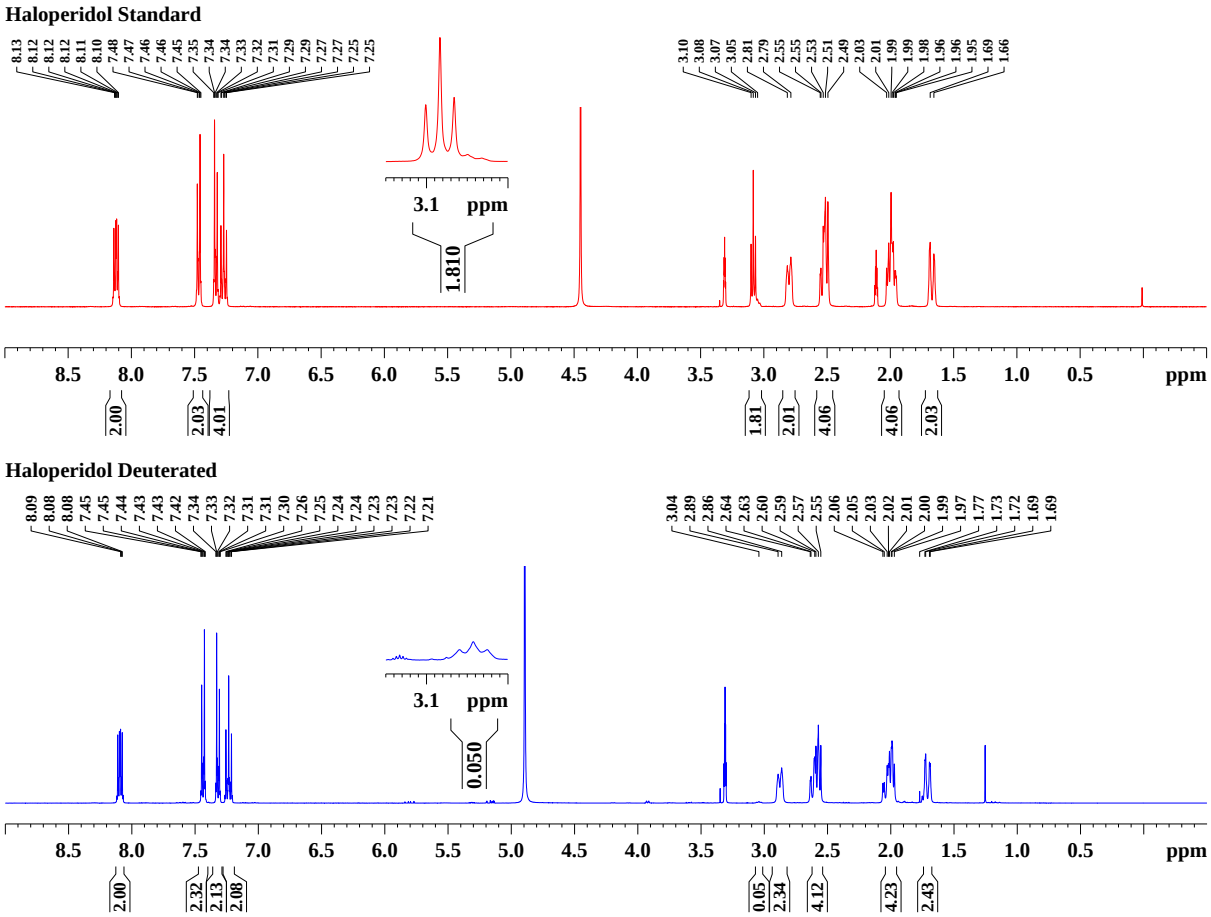
Supplementary Spectrum. ^{13}C NMR spectrum of loxoprofen (**54**) (75 MHz, CD_3OD)



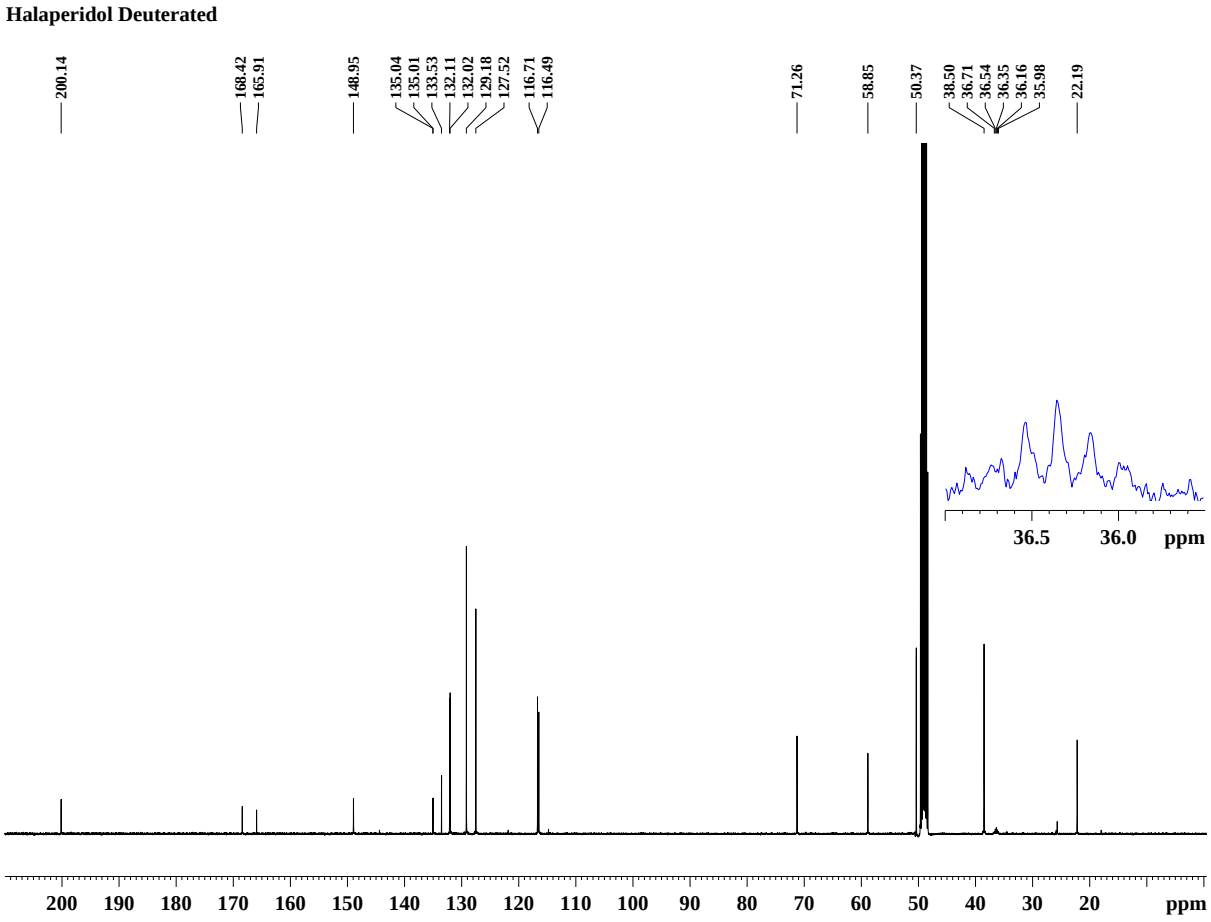
Supplementary Spectrum. ^{1}H NMR spectrum of 2-acetylphenothiazine (**55**) (300 MHz, DMSO-d_6)



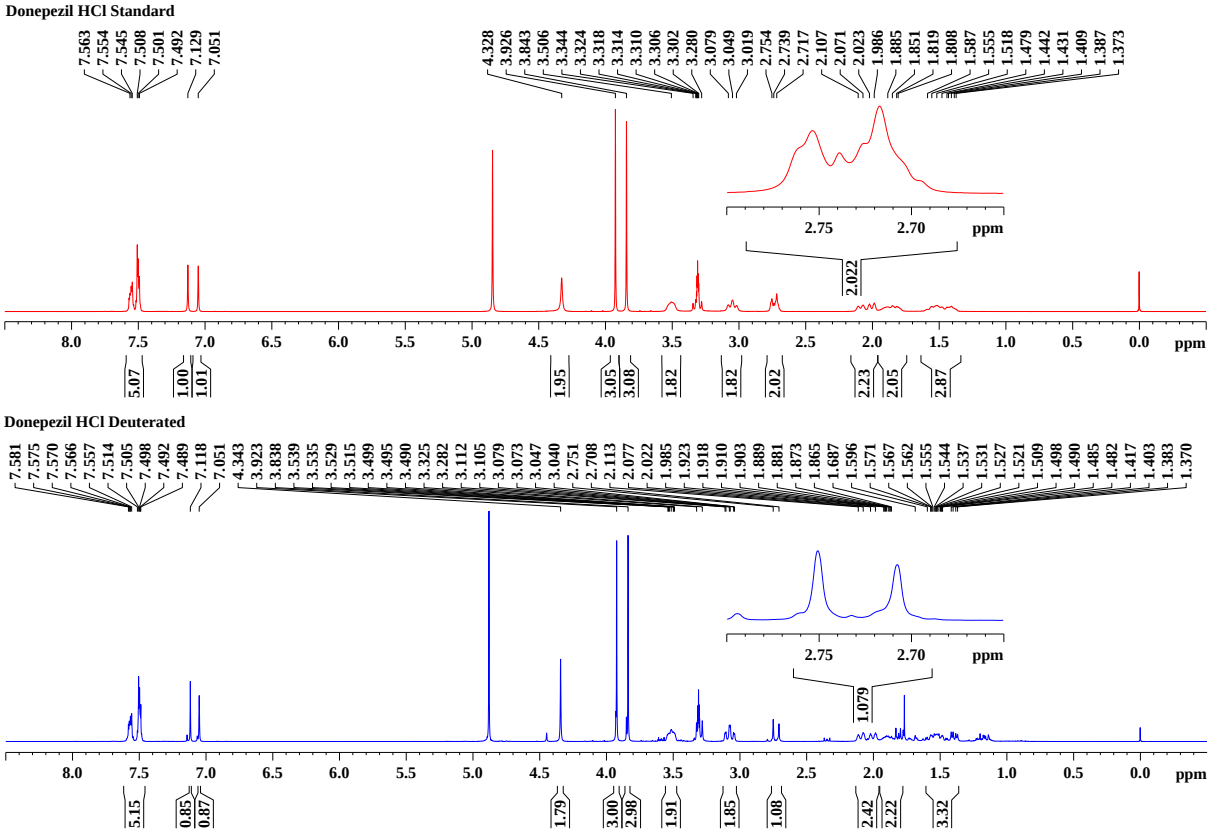
Supplementary Spectrum. ^{13}C NMR spectrum of 2-acetylphenothiazine (**55**) (75 MHz, DMSO-d_6)



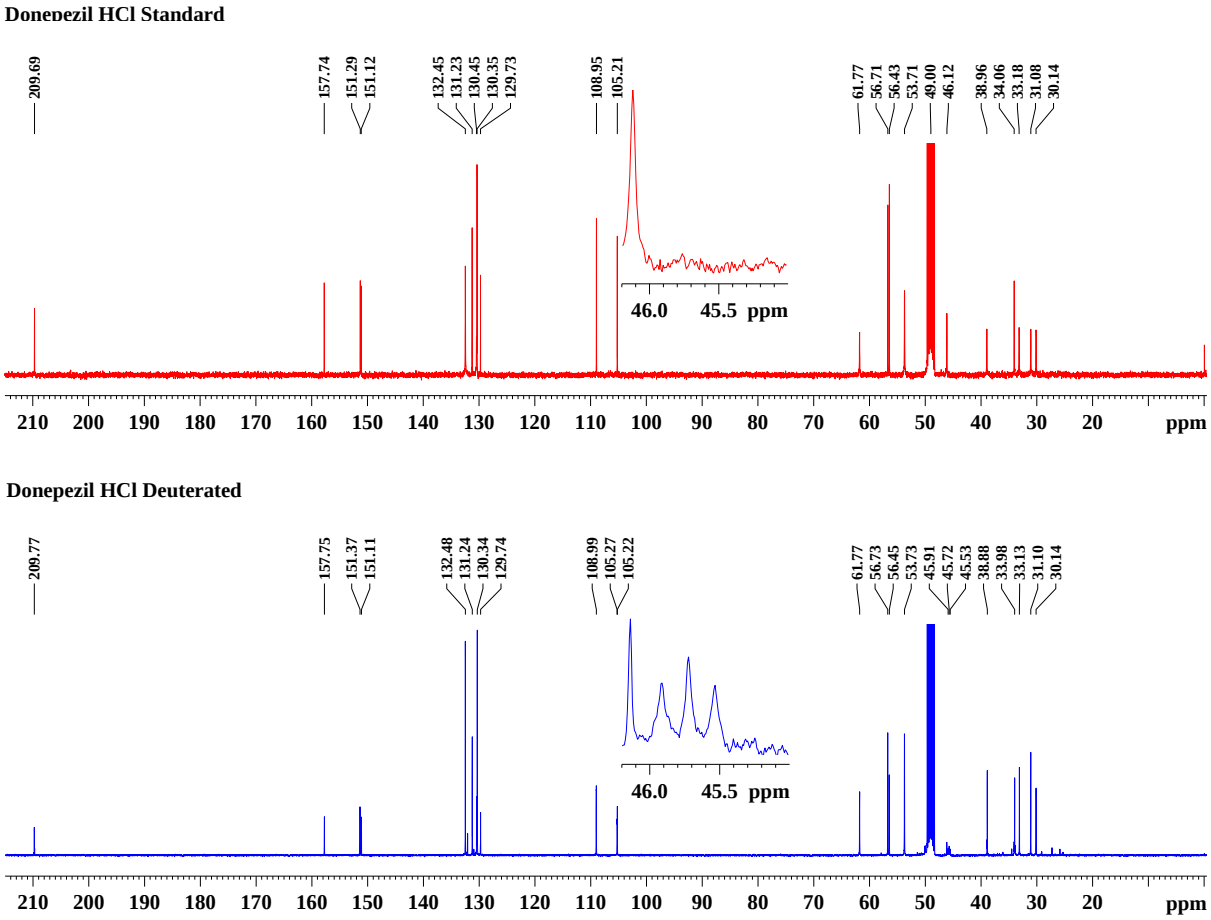
Supplementary Spectrum. ^{1}H NMR spectrum of haloperidol (**56**) (400 MHz, CD_3OD)



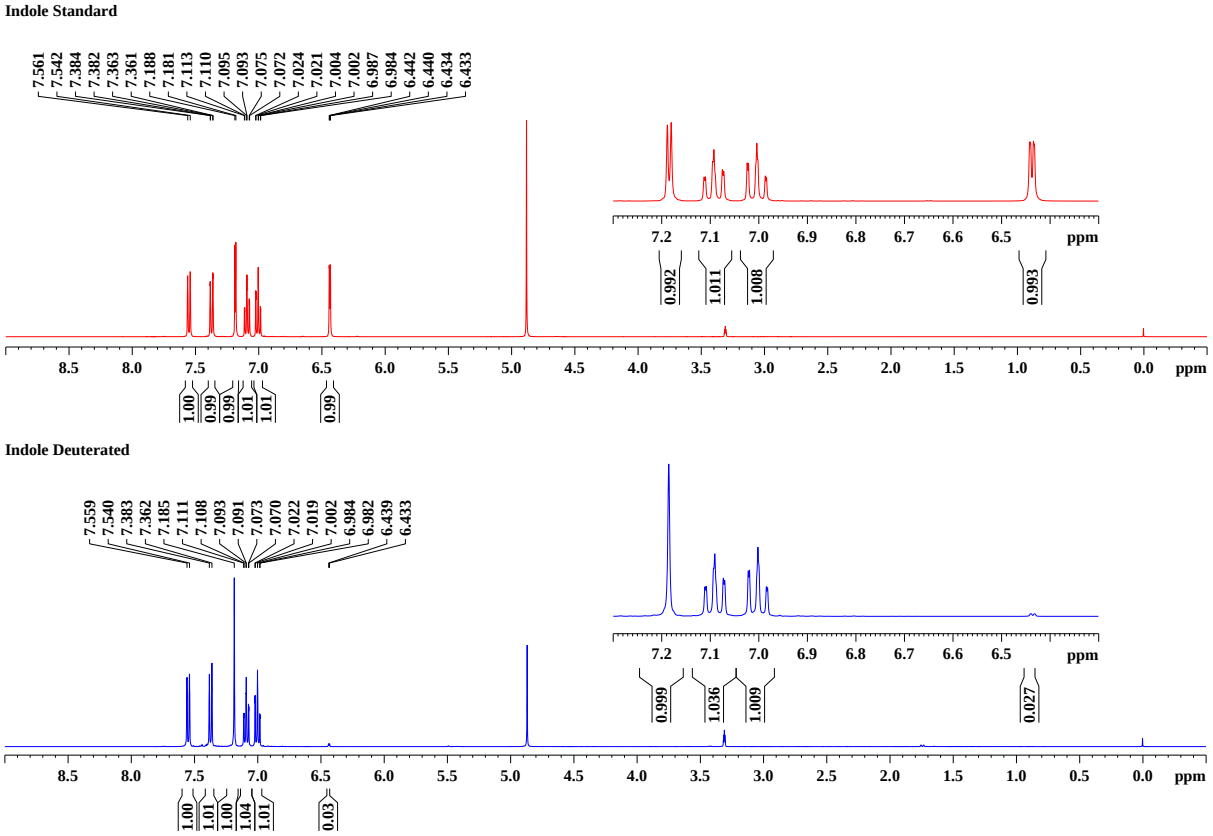
Supplementary Spectrum. ^{13}C NMR spectrum of haloperidol (**56**) (100 MHz, CD_3OD)



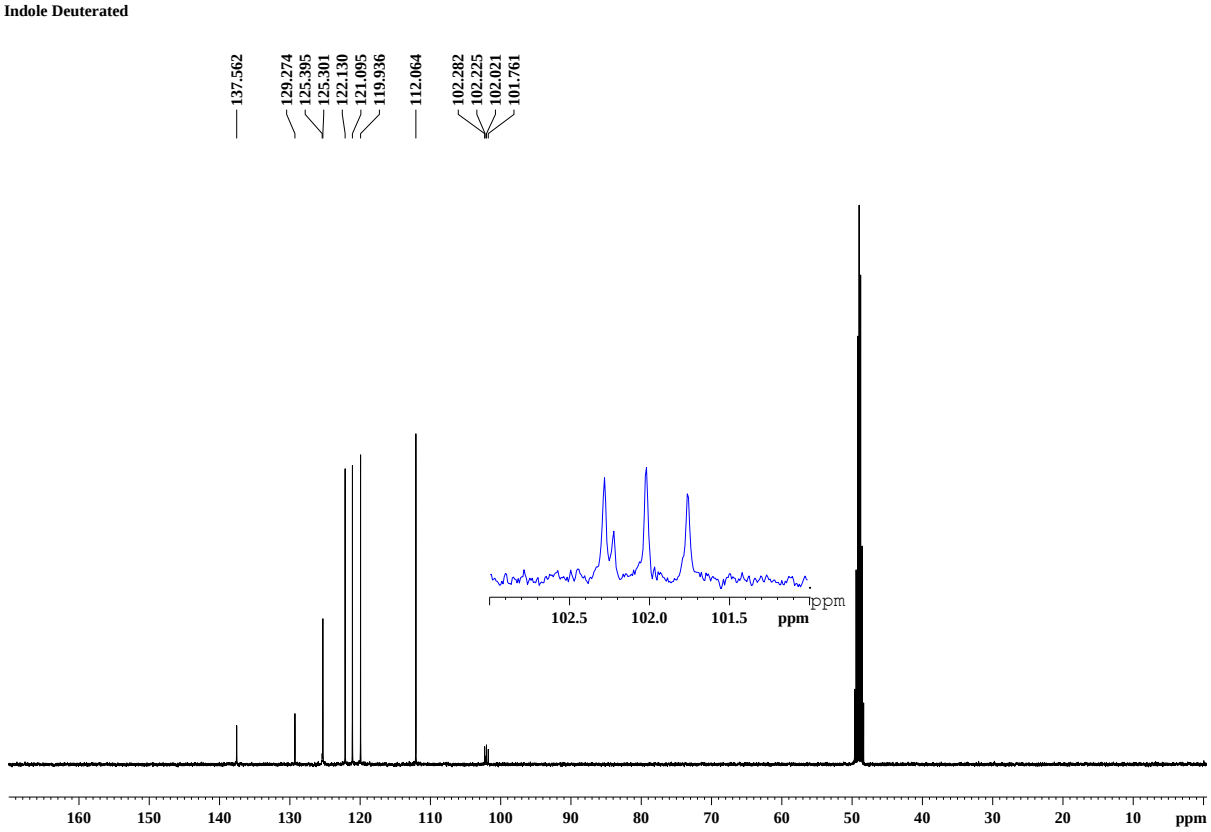
Supplementary Spectrum. ^{1}H NMR spectrum of donepezil (**57**) (400 MHz, CD_3OD)



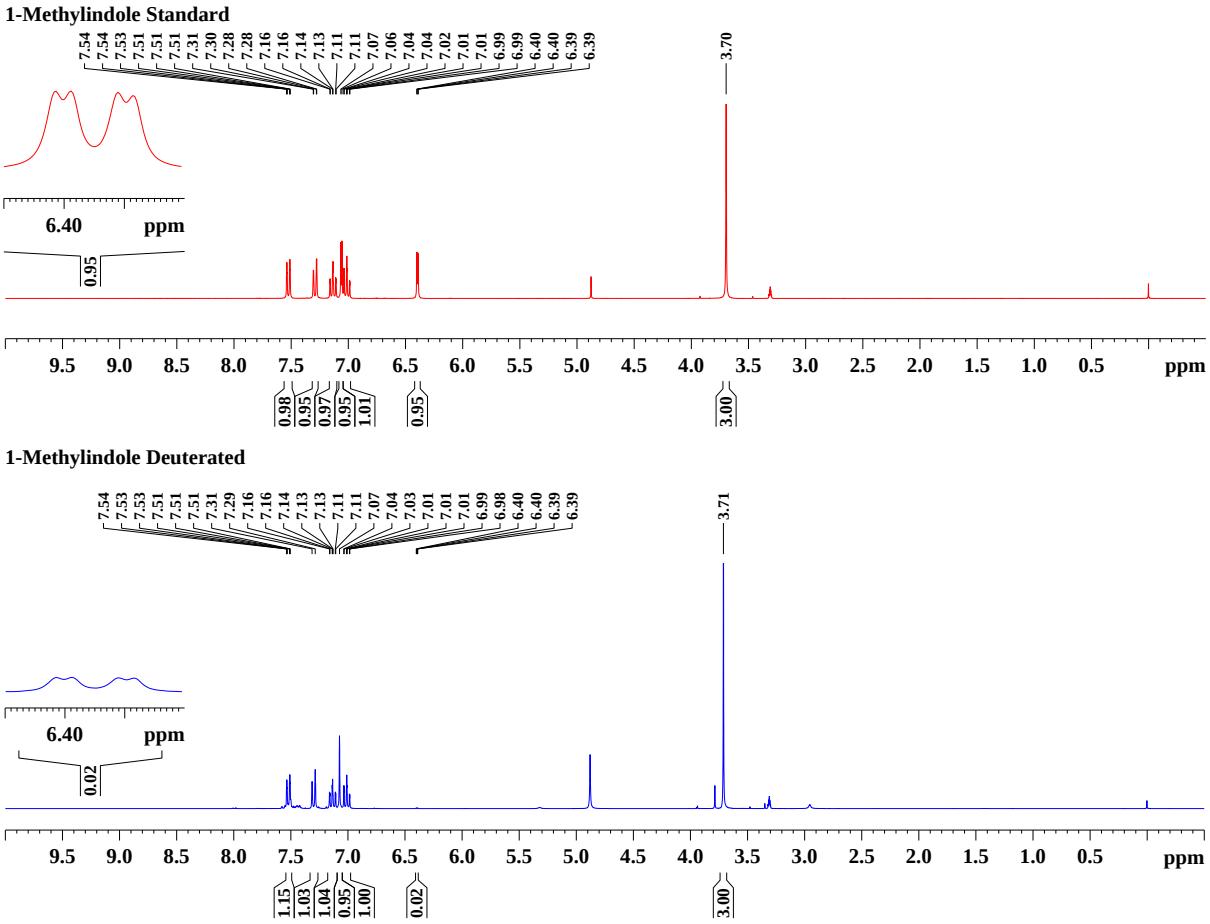
Supplementary Spectrum. ^{13}C NMR spectrum of donepezil (**57**) (100 MHz, CD_3OD)



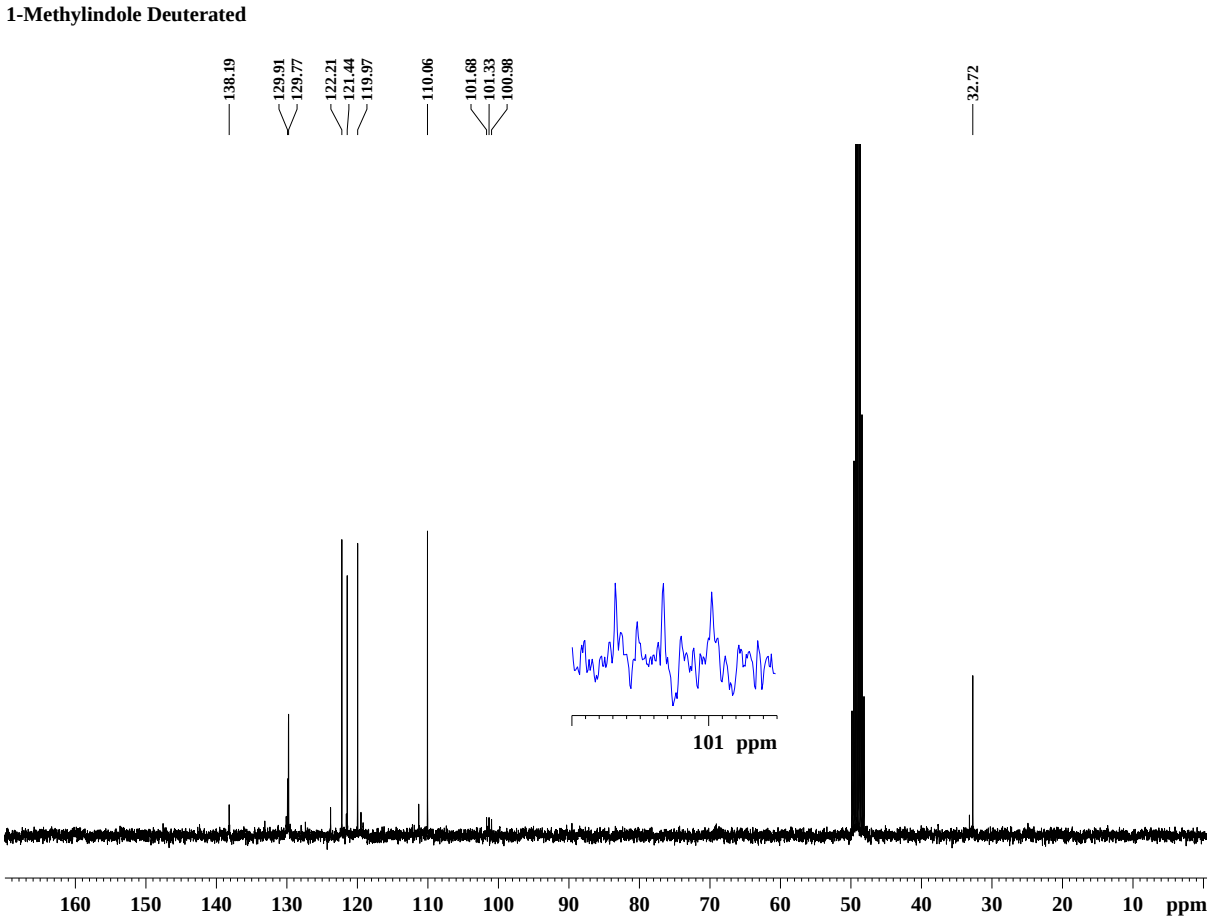
Supplementary Spectrum. ^{1}H NMR spectrum of indole (**58**) (400 MHz, CD_3OD)



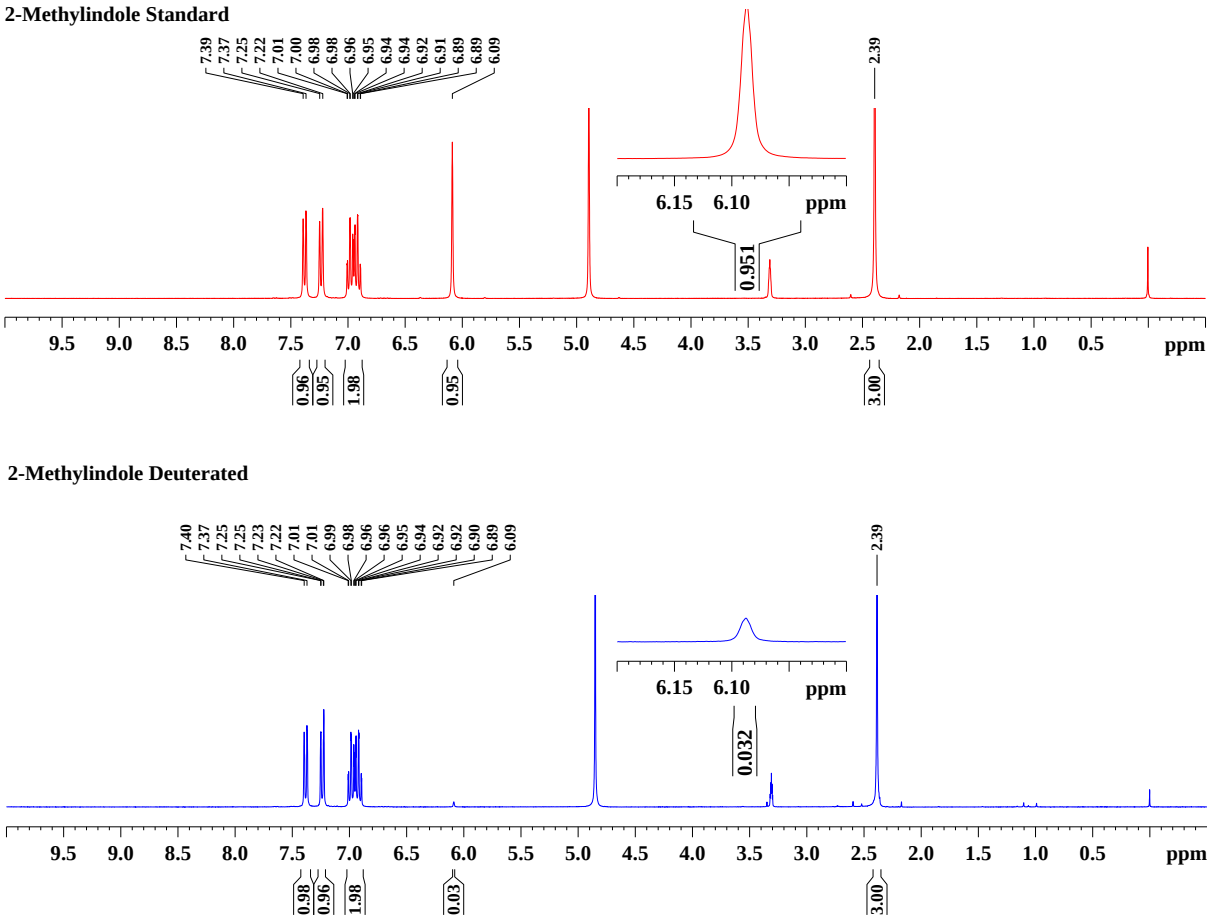
Supplementary Spectrum. ^{13}C NMR spectrum of indole (**58**) (100 MHz, CD_3OD)



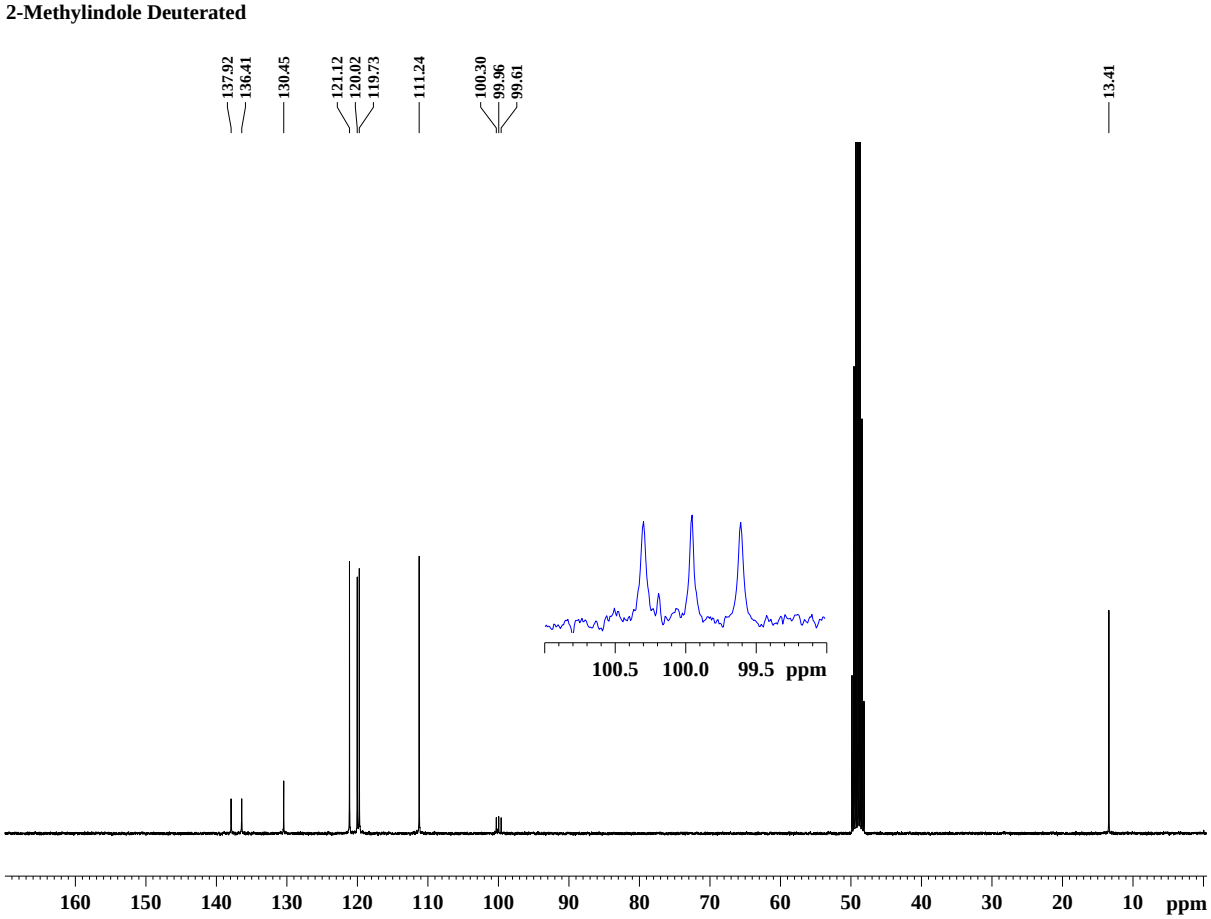
Supplementary Spectrum. ^{1}H NMR spectrum of 1-methylindole (**59**) (300 MHz, CD_3OD)



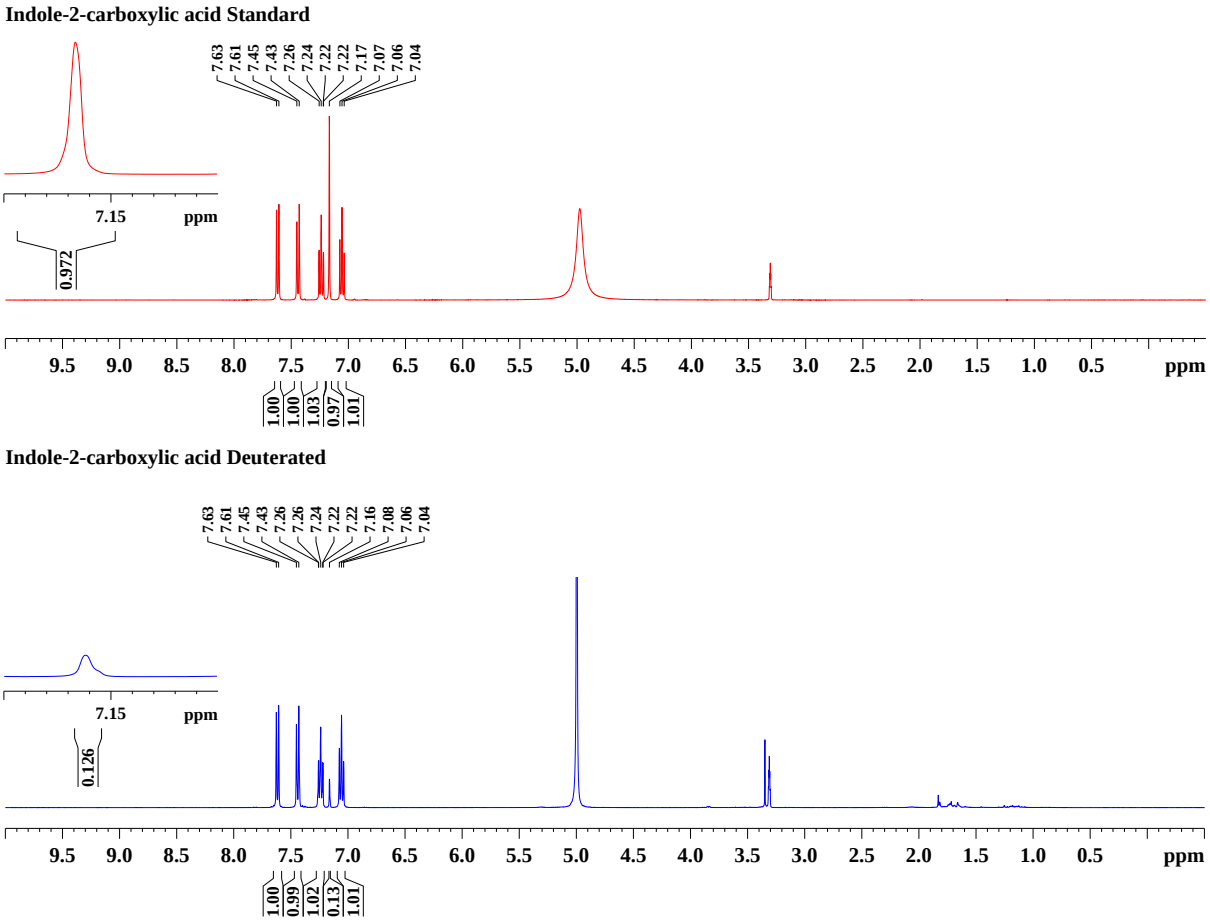
Supplementary Spectrum. ^{13}C NMR spectrum of 1-methylindole (**59**) (75 MHz, CD_3OD)



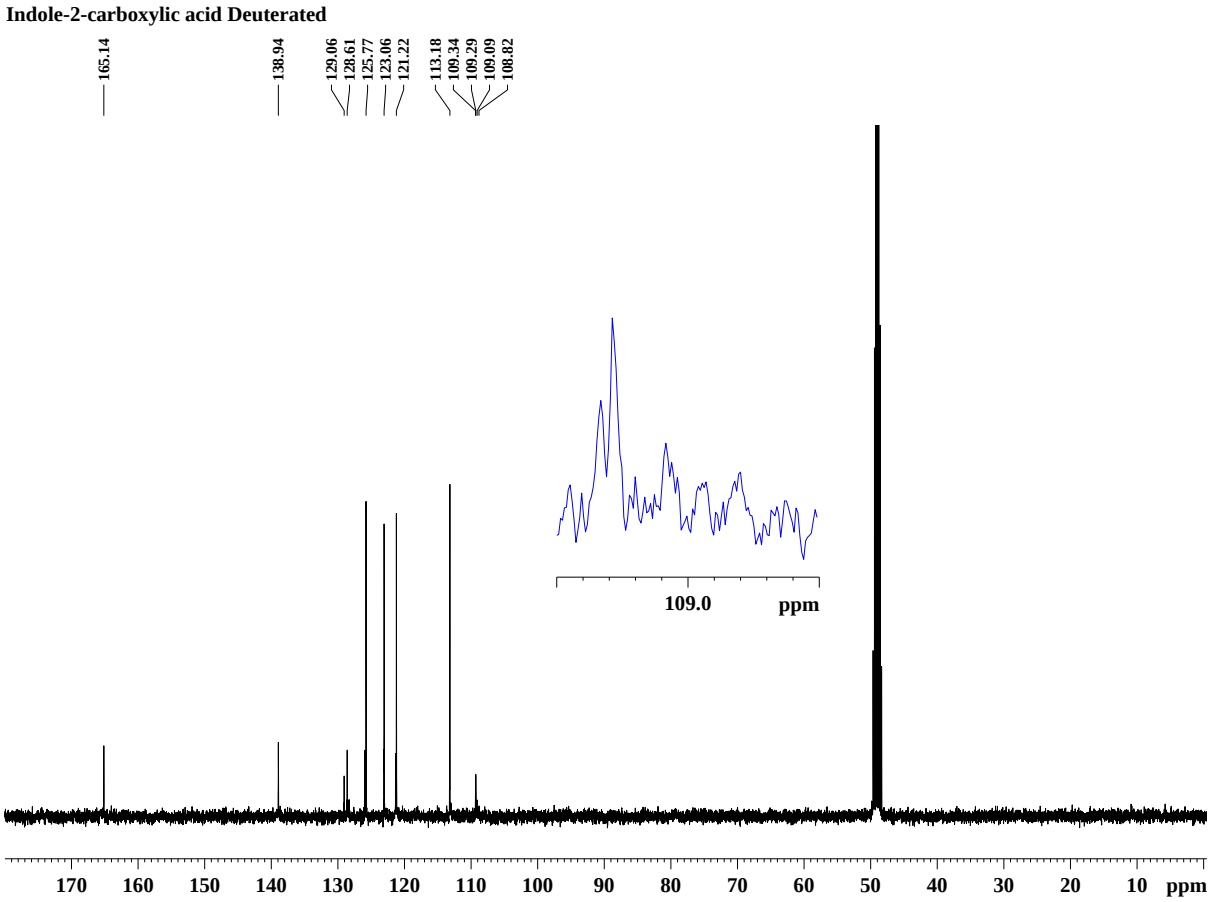
Supplementary Spectrum. ^{1}H NMR spectrum of 2-methylindole (**60**) (300 MHz, CD_3OD)



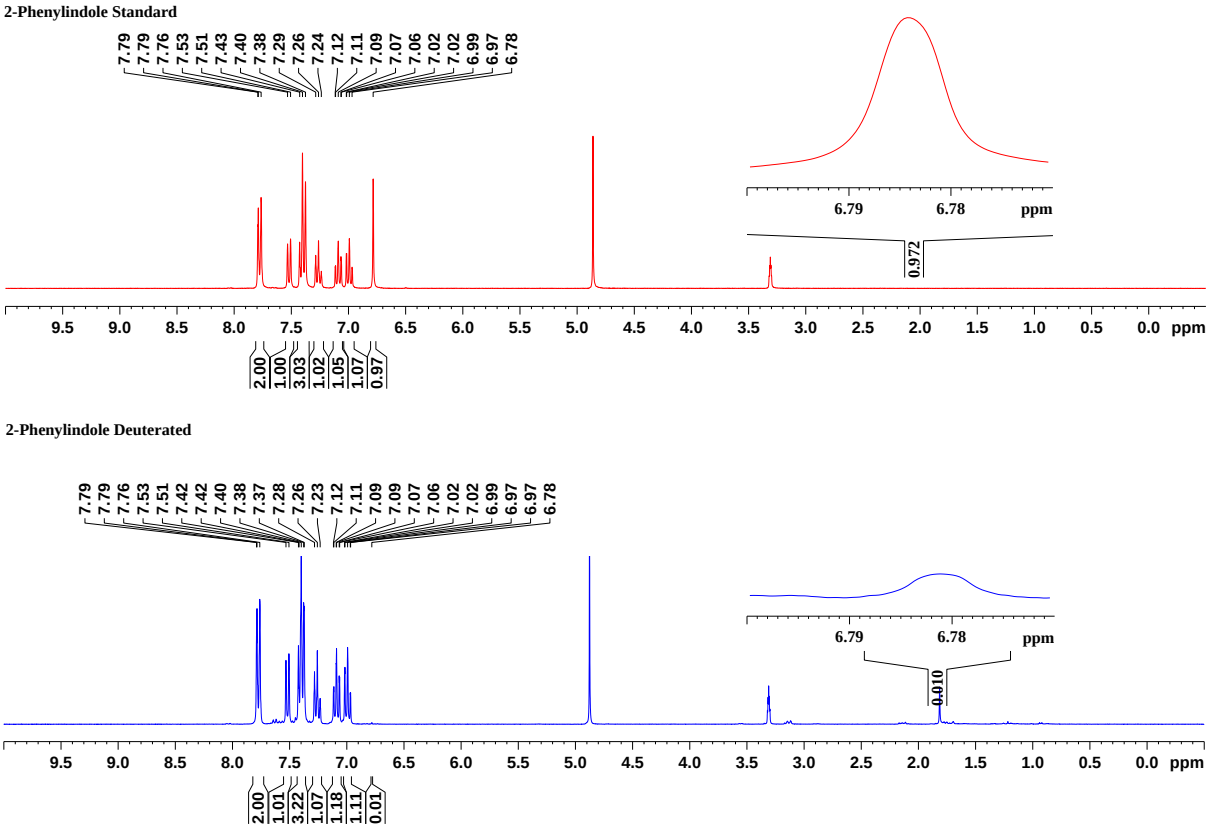
Supplementary Spectrum. ^{13}C NMR spectrum of 2-methylindole (**60**) (75 MHz, CD_3OD)



Supplementary Spectrum. ^{1}H NMR spectrum of indole-2-carboxylic acid (**61**) (400 MHz, CD_3OD)

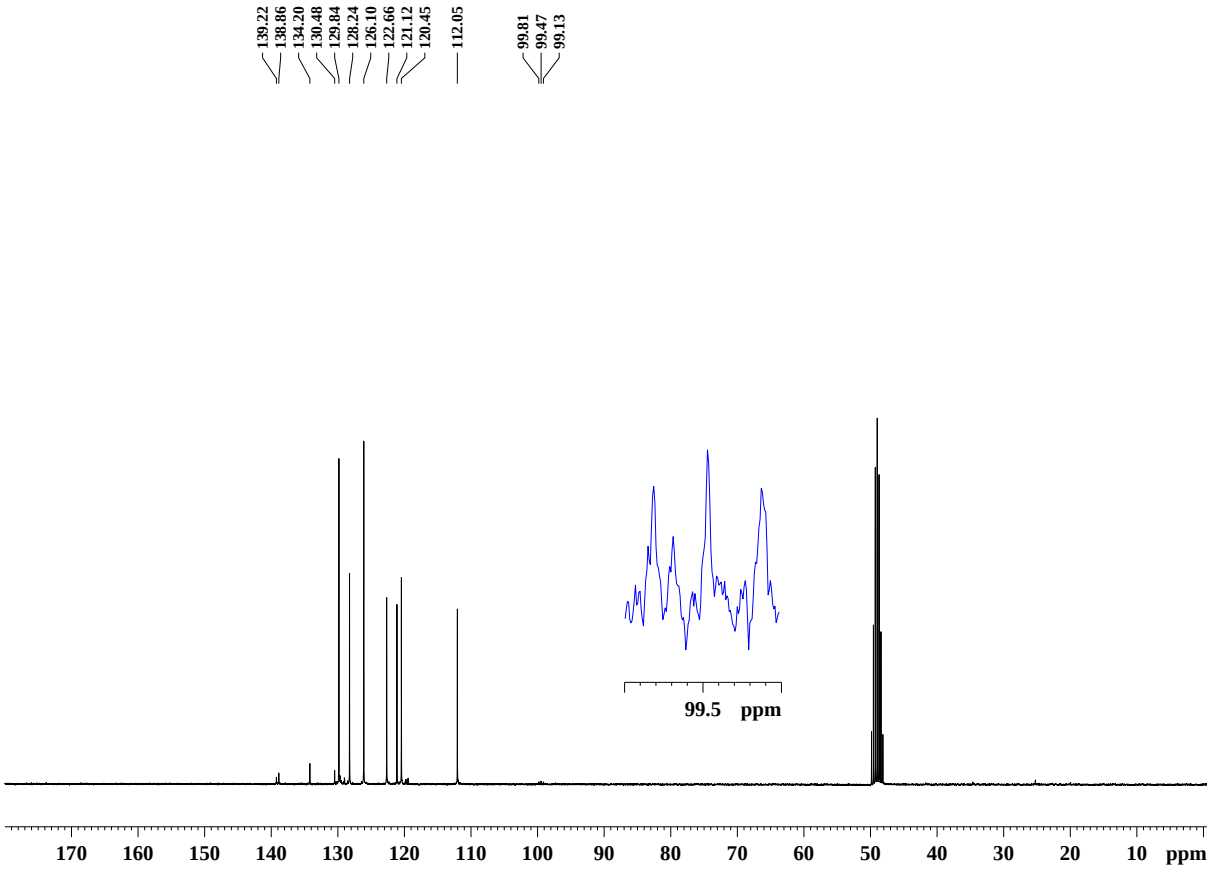


Supplementary Spectrum. ^{13}C NMR spectrum of indole-2-carboxylic acid (**61**) (100 MHz, CD_3OD)



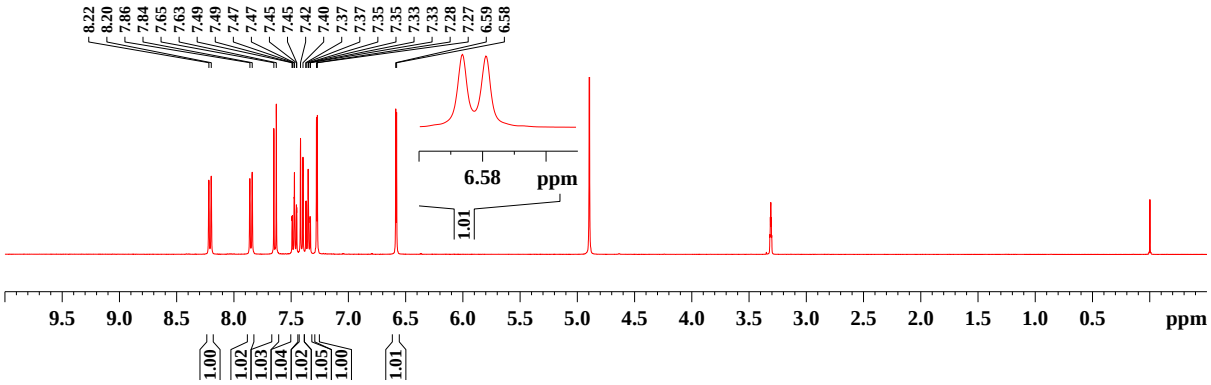
Supplementary Spectrum. ^{1}H NMR spectrum of 2-phenylindole (**62**) (300 MHz, CD_3OD)

2-Phenylindole Deuterated

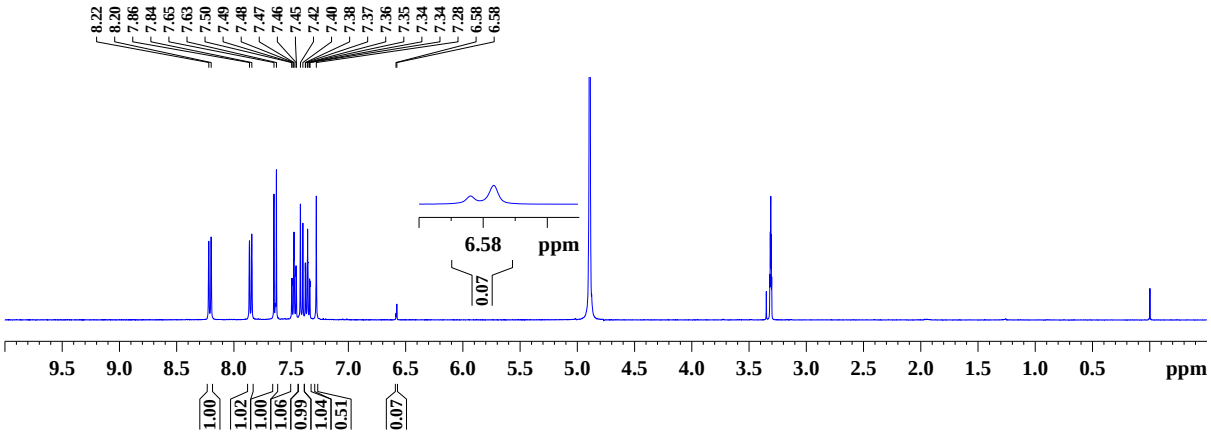


Supplementary Spectrum. ^{13}C NMR spectrum of 2-phenylindole (**62**) (75 MHz, CD_3OD)

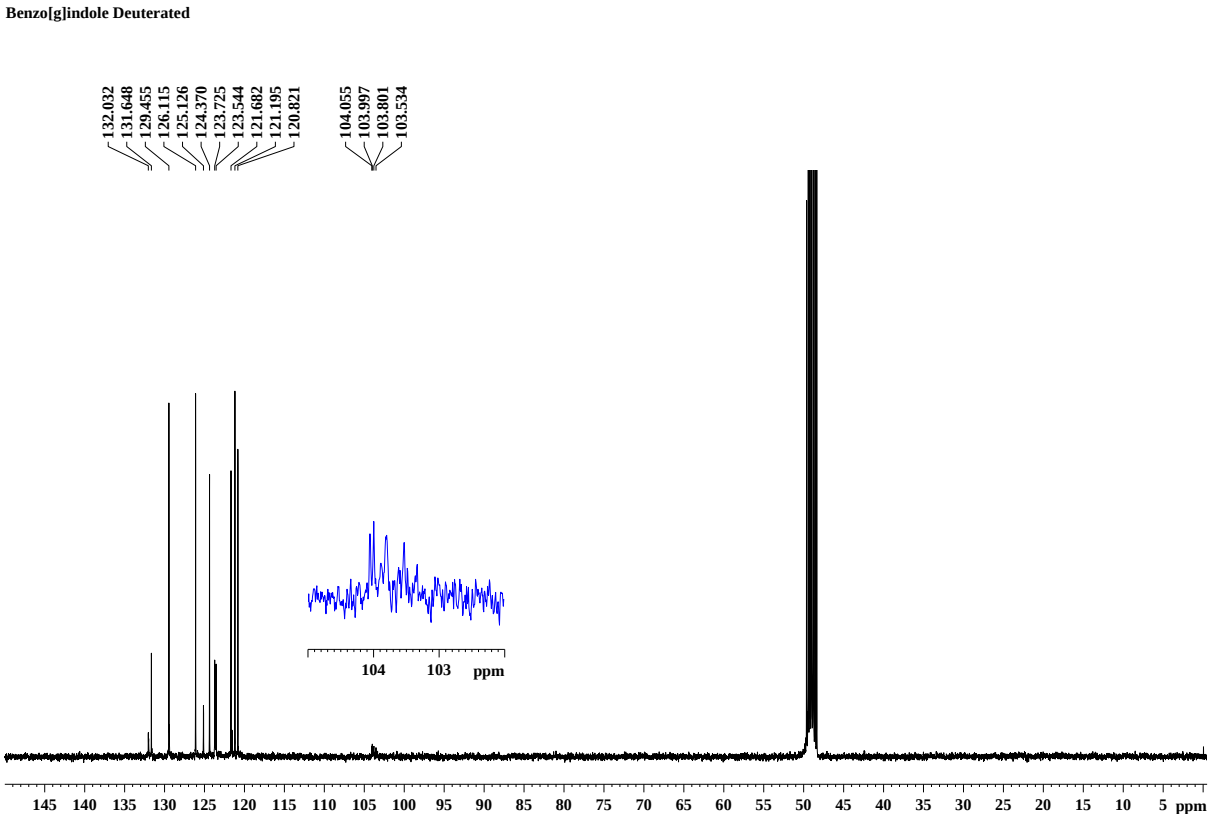
Benzo[g]indole Standard



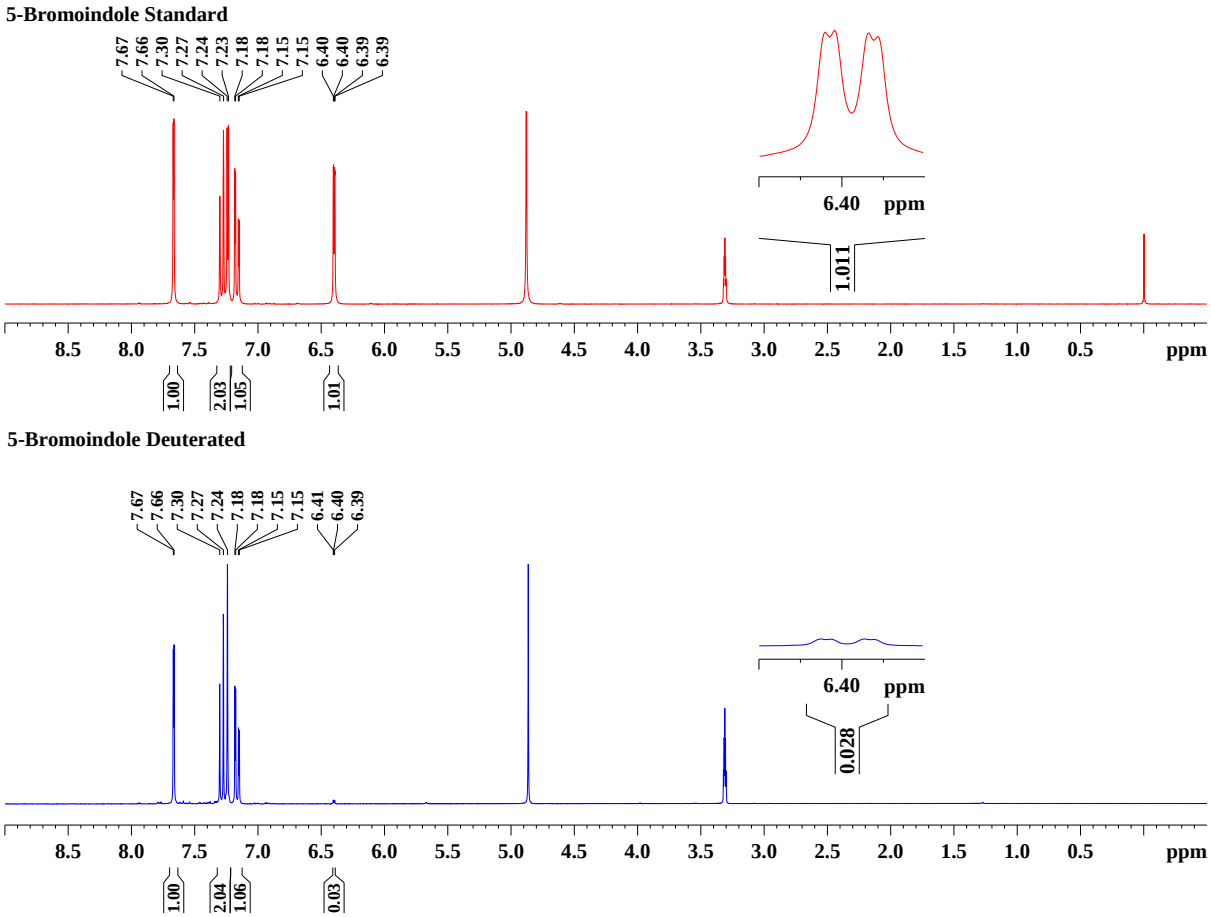
Benzo[g]indole Deuterated



Supplementary Spectrum. ^{1}H NMR spectrum of *1H*-benzo[g]indole (**63**) (400 MHz, CD_3OD)

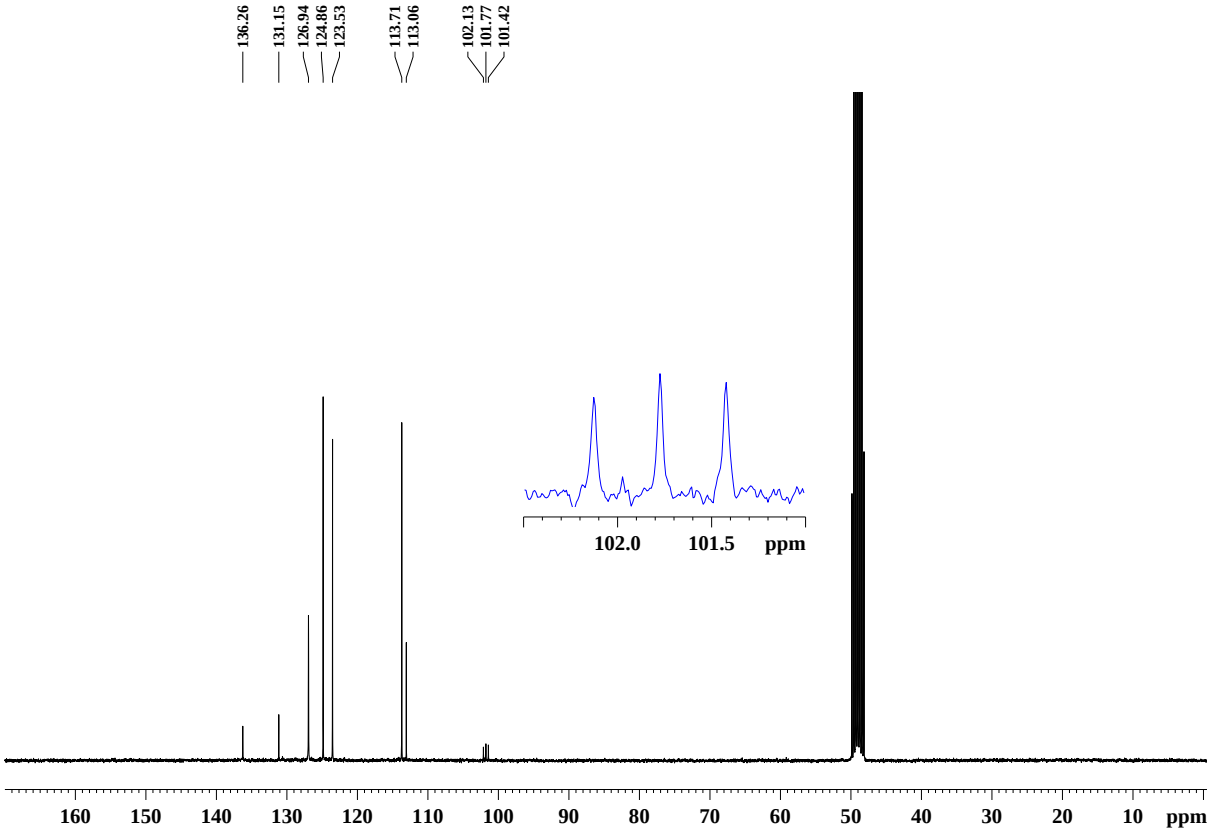


Supplementary Spectrum. ^{13}C NMR spectrum of *1H*-benzo[g]indole (**63**) (100 MHz, CD_3OD)

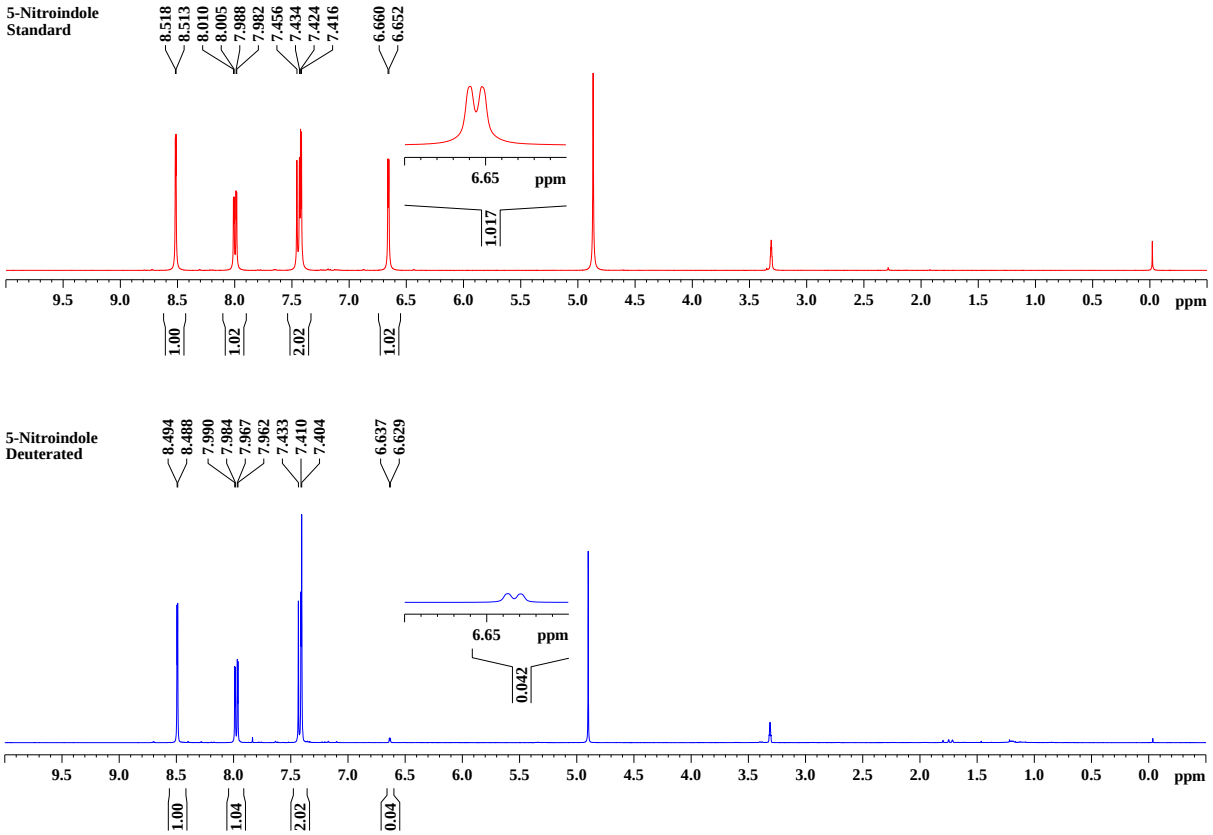


Supplementary Spectrum. ^{1}H NMR spectrum of 5-bromoindole (**64**) (300 MHz, CD_3OD)

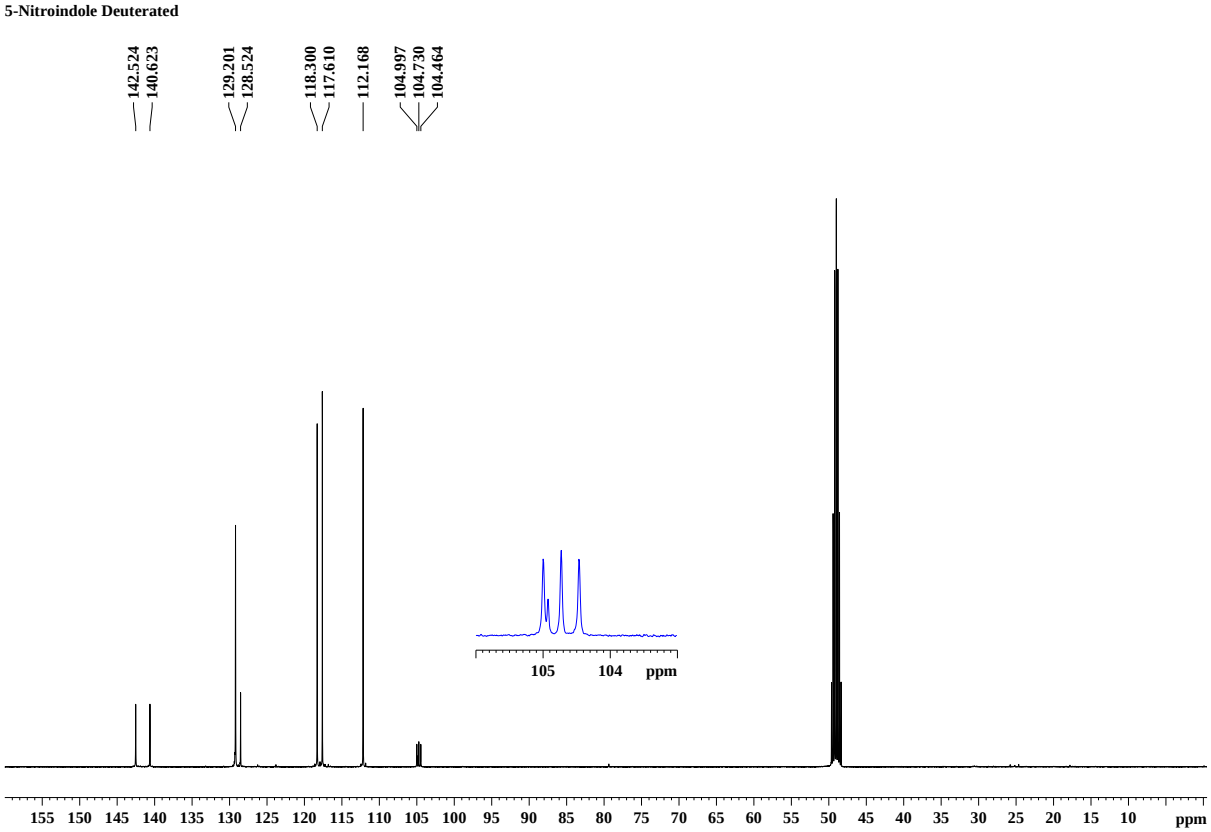
5-Bromoindole Deuterated



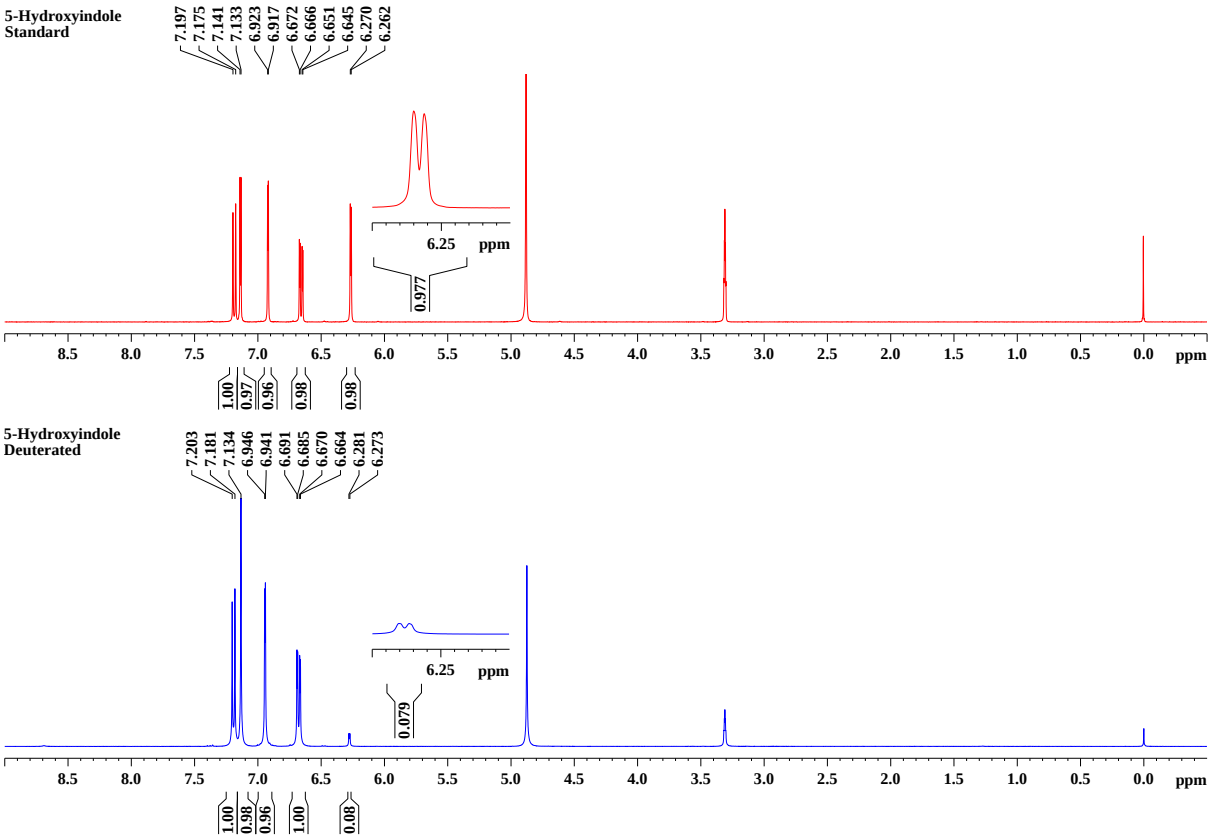
Supplementary Spectrum. ^{13}C NMR spectrum of 5-bromoindole (**64**) (75 MHz, CD_3OD)



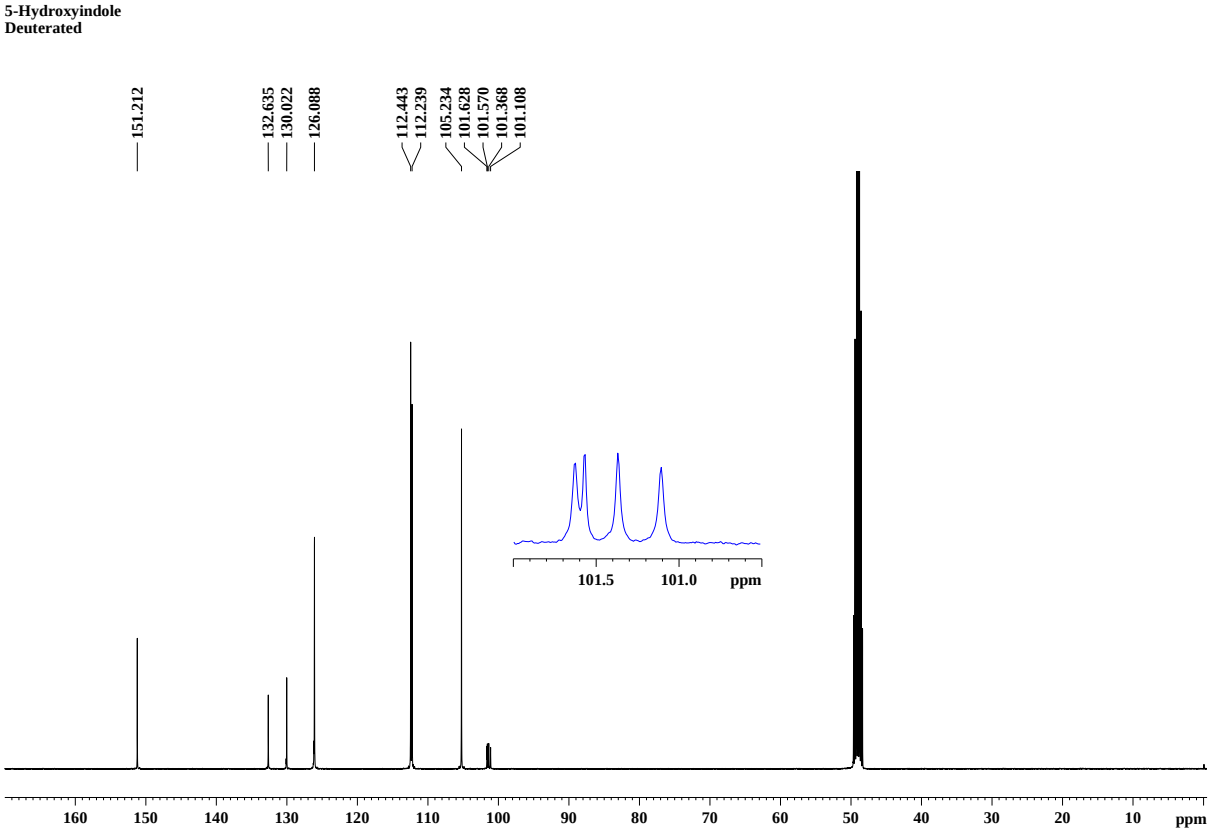
Supplementary Spectrum. ^{1}H NMR spectrum of 5-nitroindole (**65**) (400 MHz, CD_3OD)



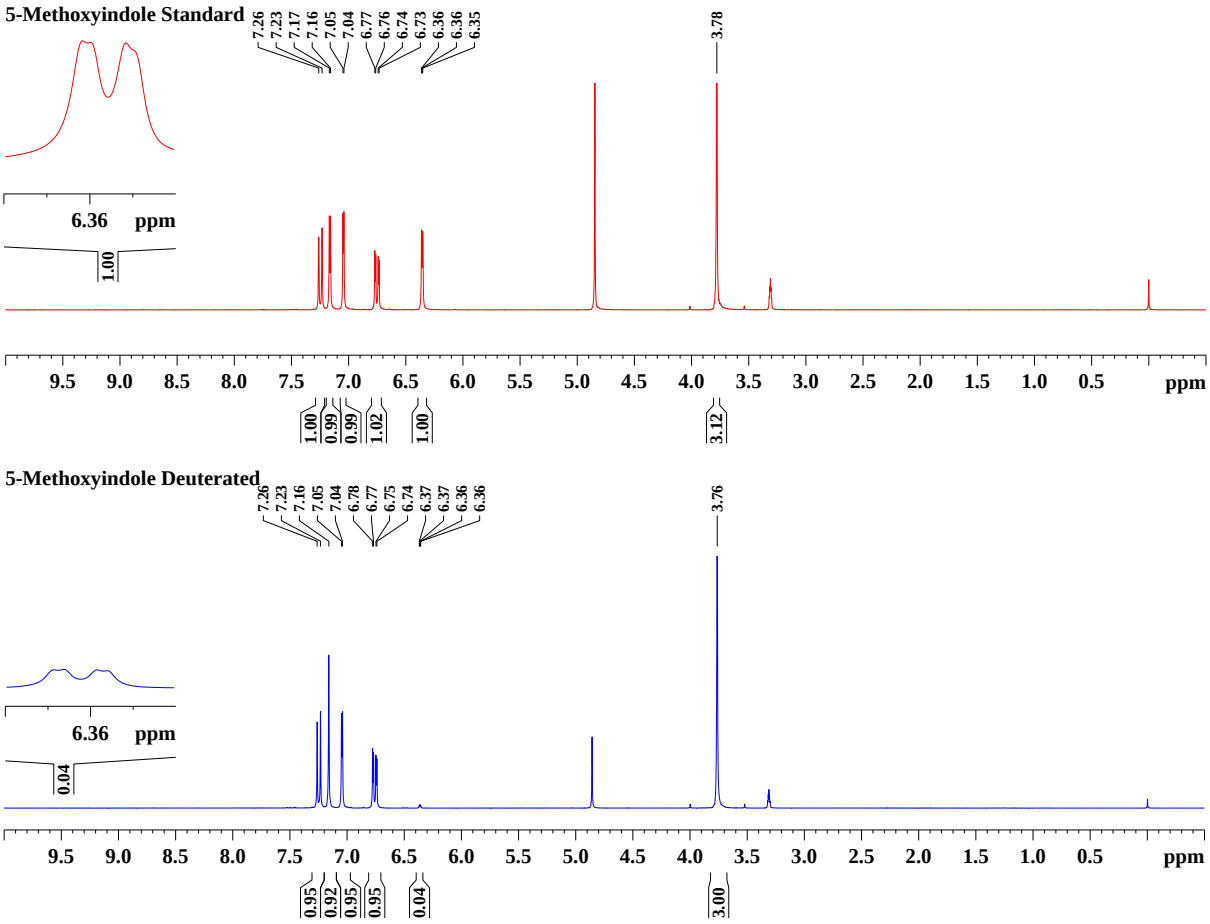
Supplementary Spectrum. ^{13}C NMR spectrum of 5-nitroindole (**65**) (100 MHz, CD_3OD)



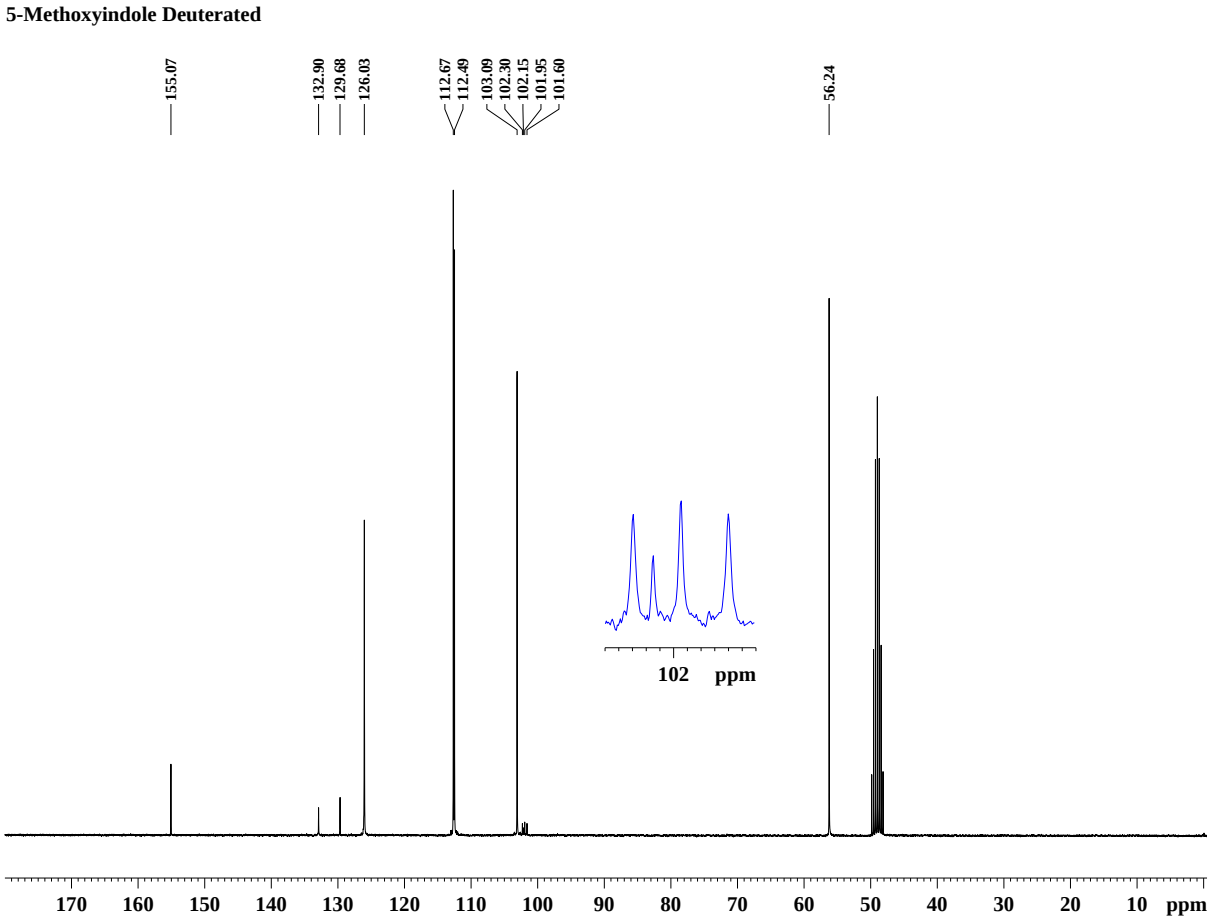
Supplementary Spectrum. ^{1}H NMR spectrum of 5-hydroxyindole (**66**) (400 MHz, CD_3OD)



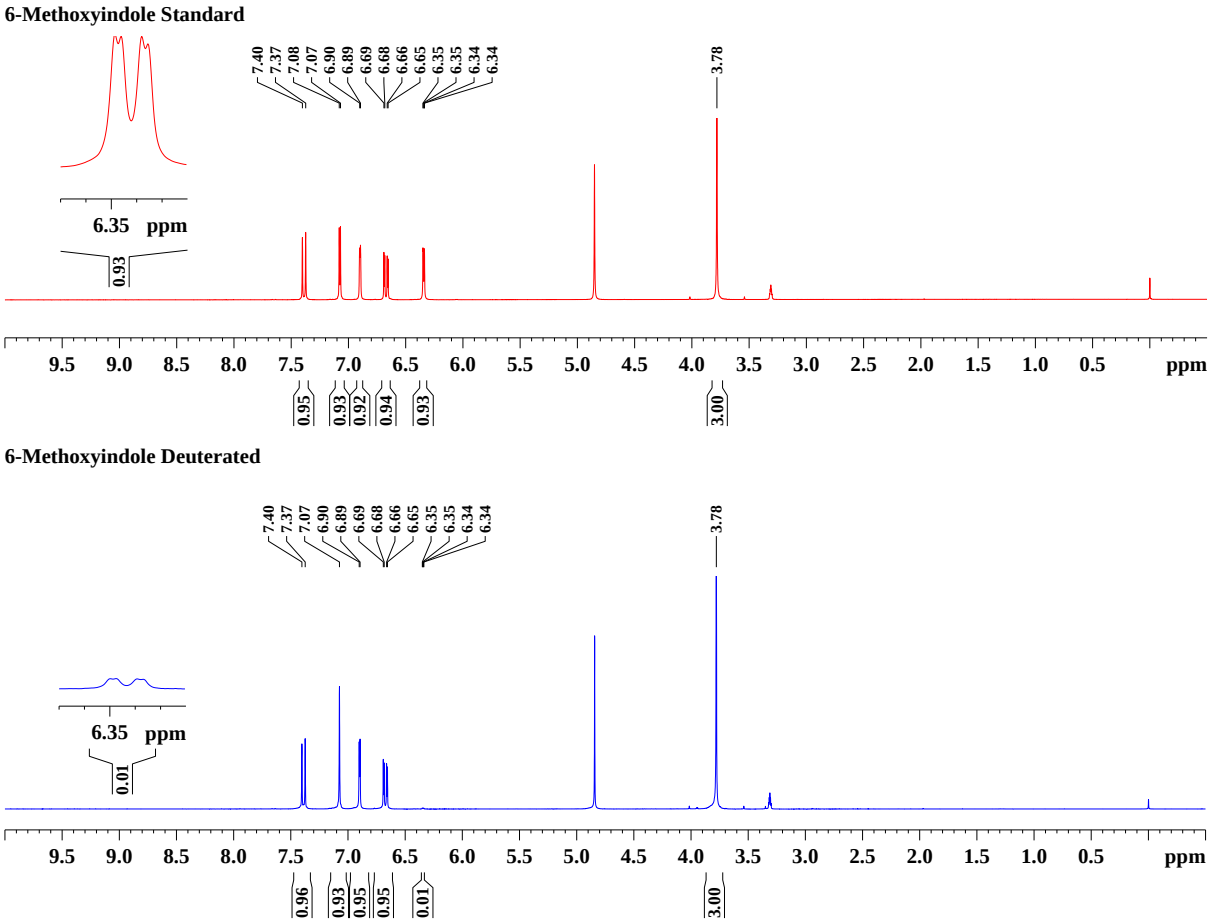
Supplementary Spectrum. ^{13}C NMR spectrum of 5-hydroxyindole (**66**) (100 MHz, CD_3OD)



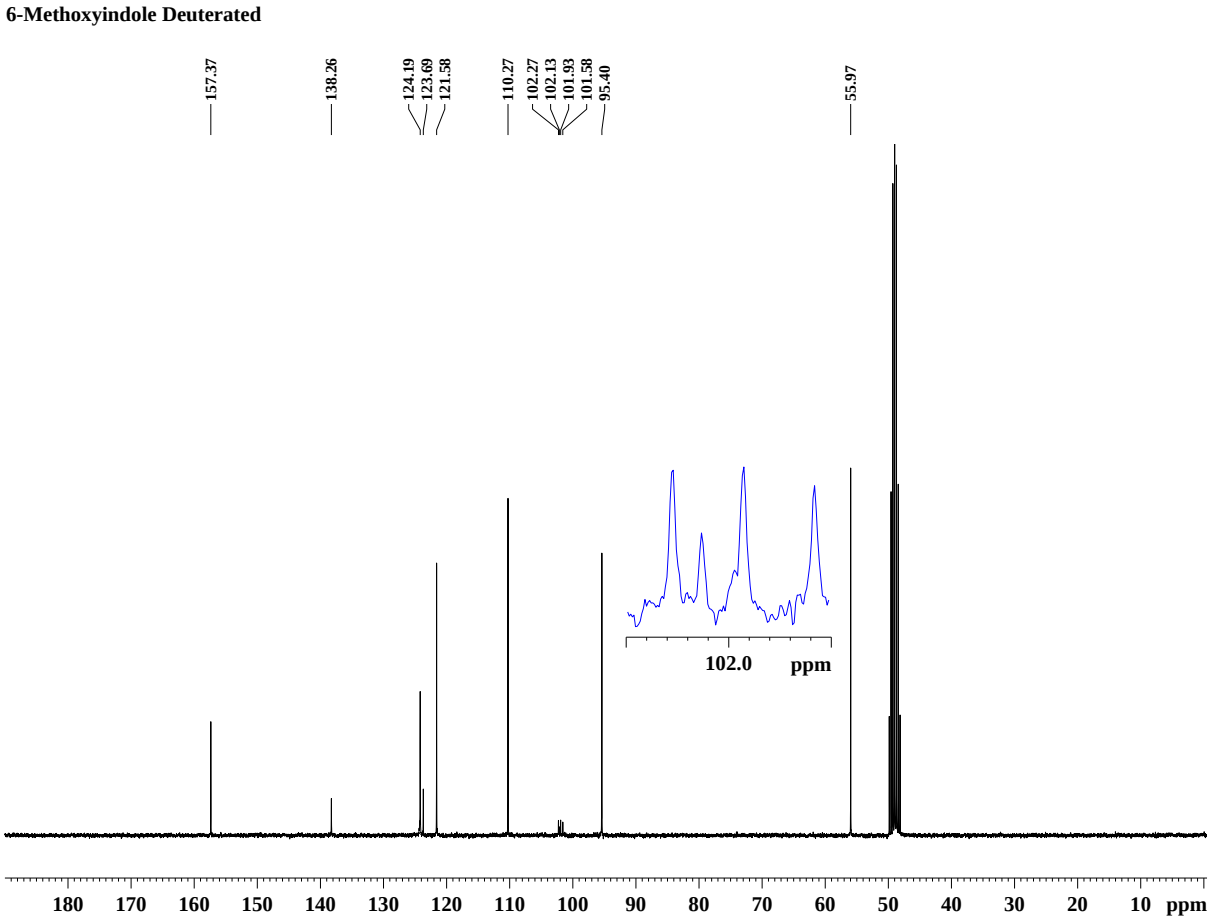
Supplementary Spectrum. ^{1}H NMR spectrum of 5-methoxyindole (**67**) (300 MHz, CD_3OD)



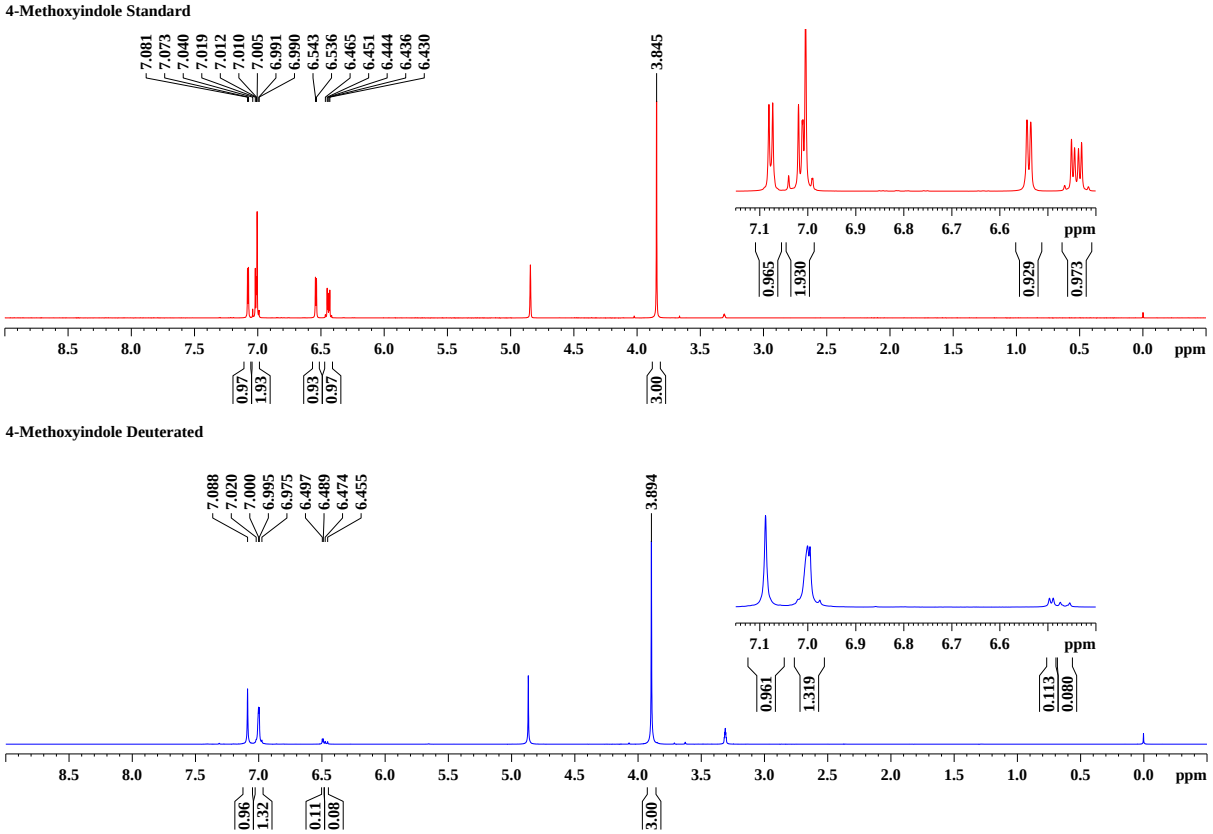
Supplementary Spectrum. ^{13}C NMR spectrum of 5-methoxyindole (**67**) (75 MHz, CD_3OD)



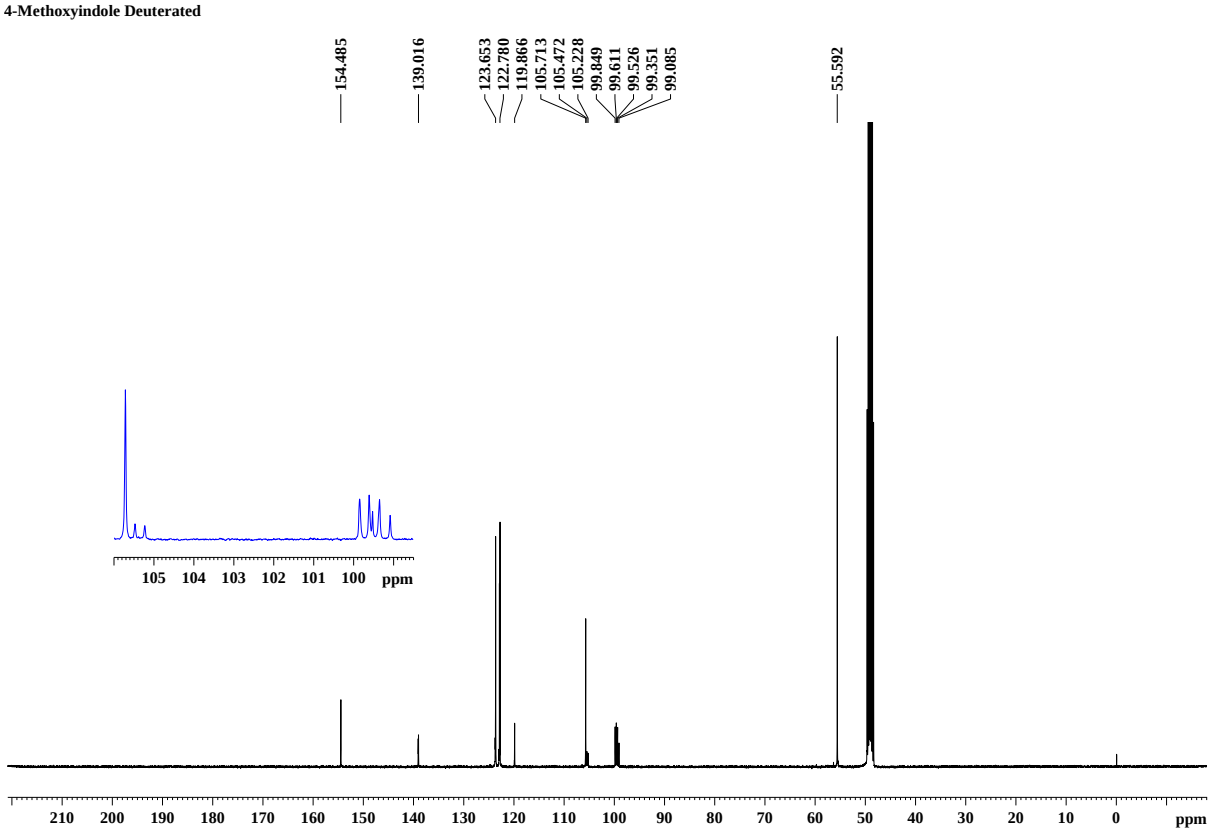
Supplementary Spectrum. ^{1}H NMR spectrum of 6-methoxyindole (**68**) (300 MHz, CD_3OD)



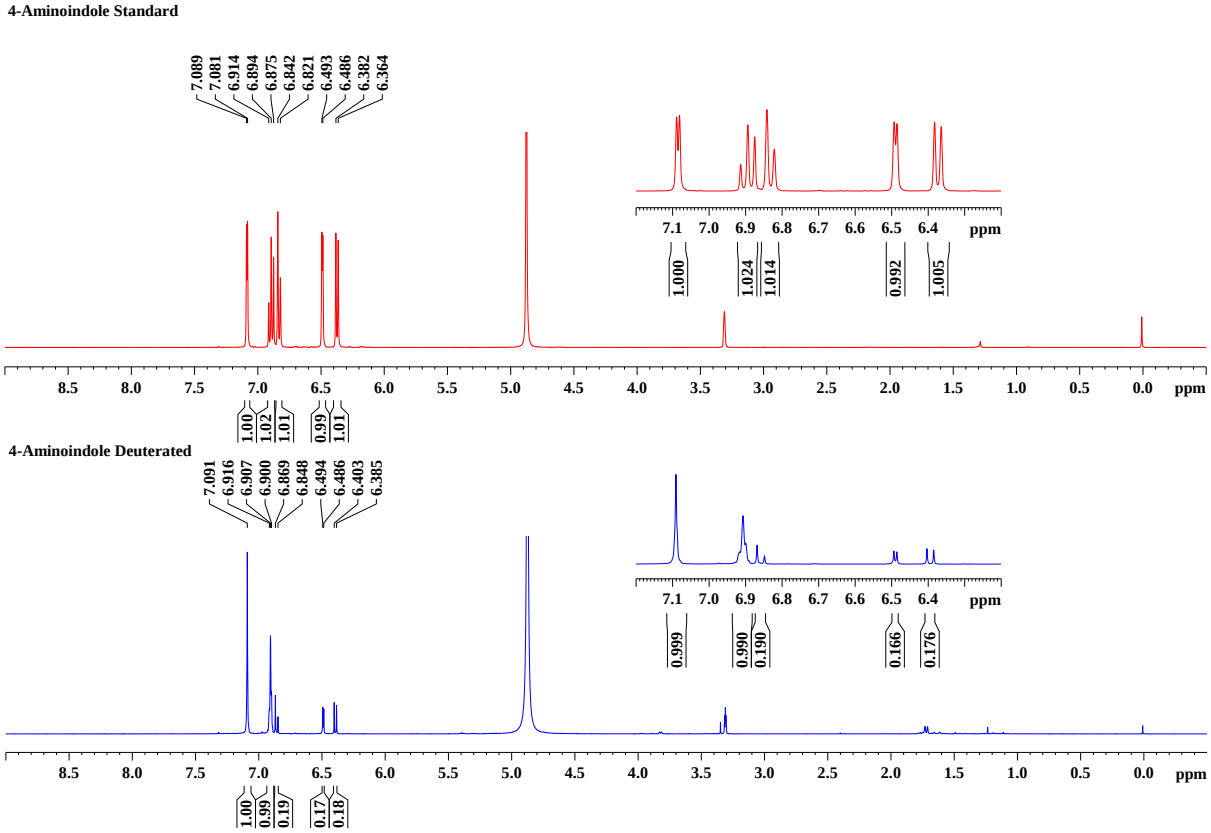
Supplementary Spectrum. ^{13}C NMR spectrum of 6-methoxyindole (**68**) (75 MHz, CD_3OD)



Supplementary Spectrum. ^{1}H NMR spectrum of 4-methoxyindole (**69**) (400 MHz, CD_3OD)

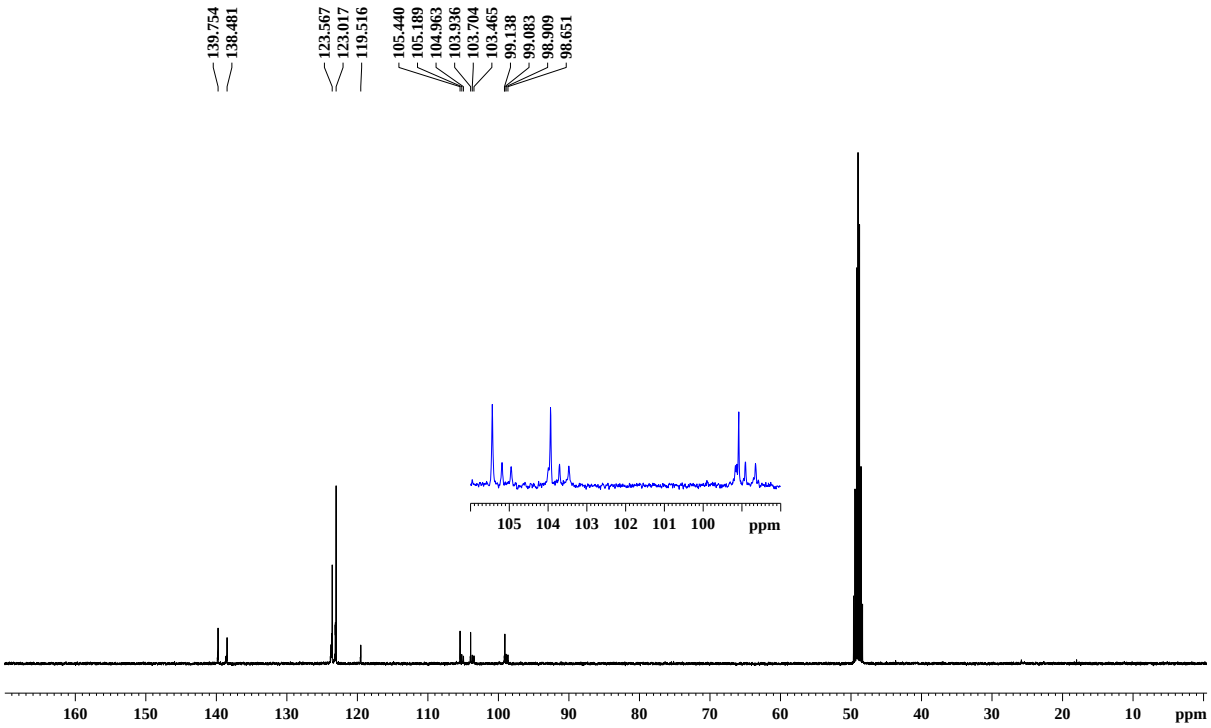


Supplementary Spectrum. ^{13}C NMR spectrum of 4-methoxyindole (**69**) (100 MHz, CD_3OD)

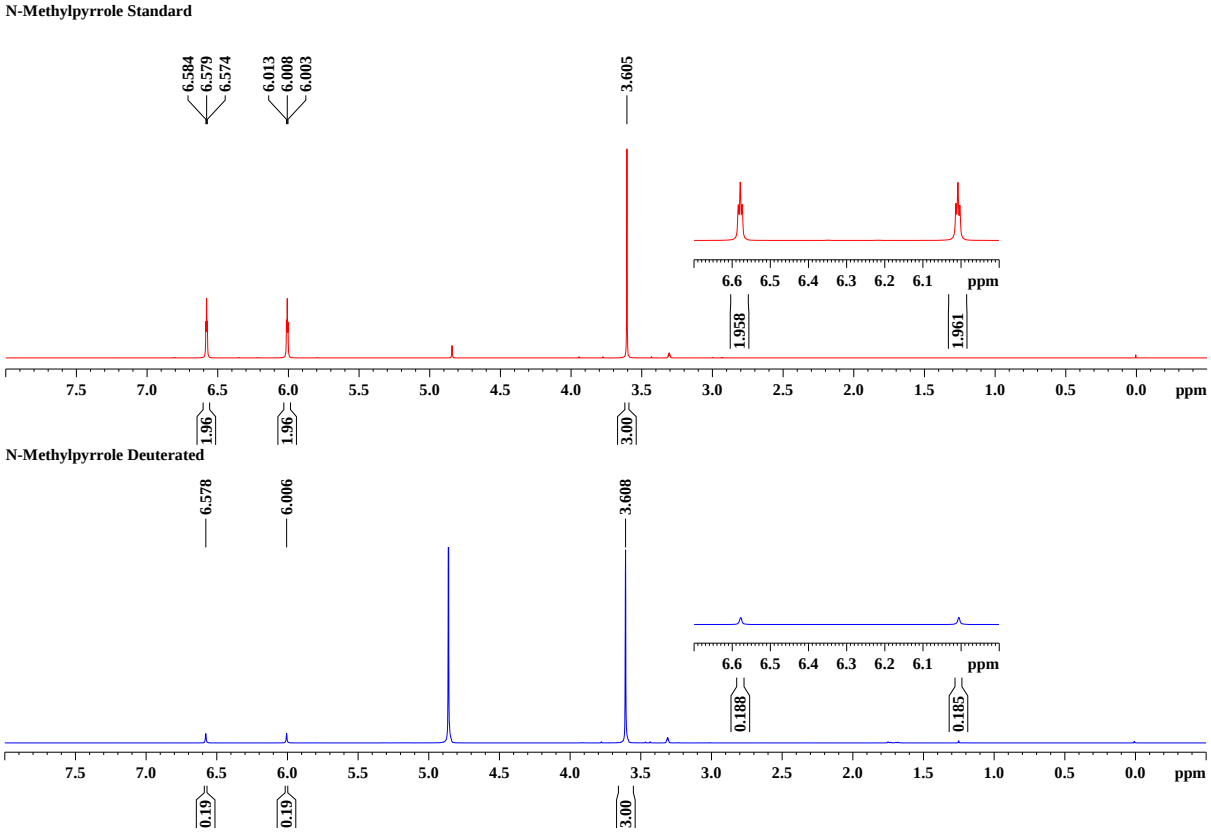


Supplementary Spectrum. ^{1}H NMR spectrum of 4-aminoindole (**70**) (400 MHz, CD_3OD)

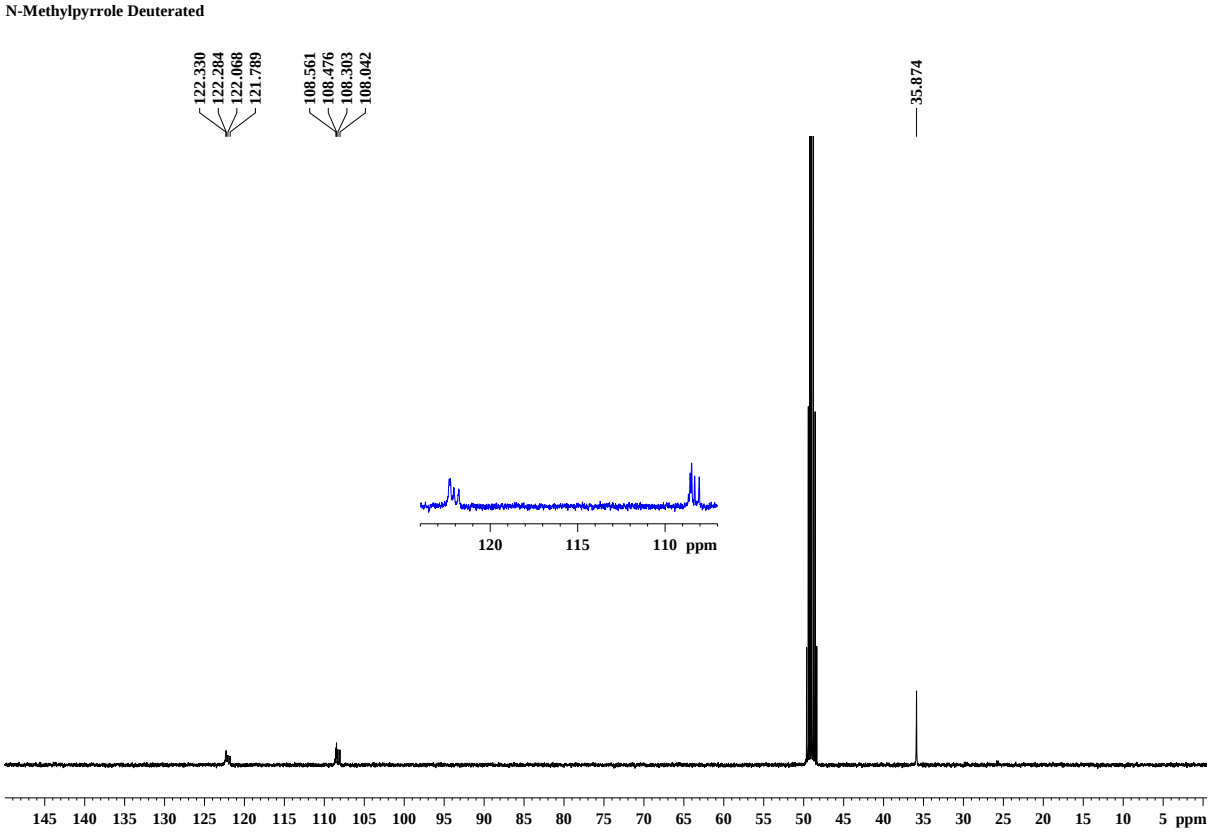
4-Aminoindole Deuterated



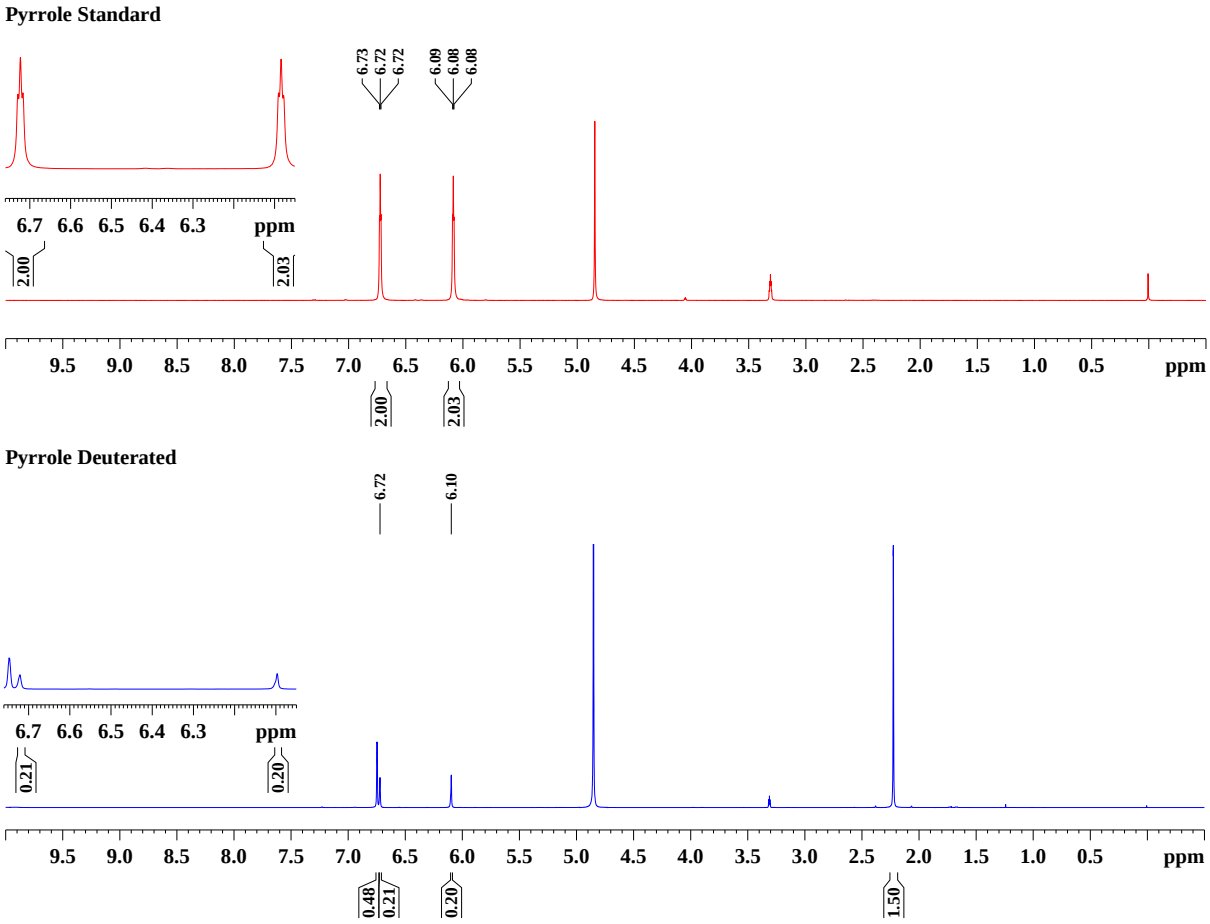
Supplementary Spectrum. ^{13}C NMR spectrum of 4-aminoindole (**70**) (100 MHz, CD_3OD)



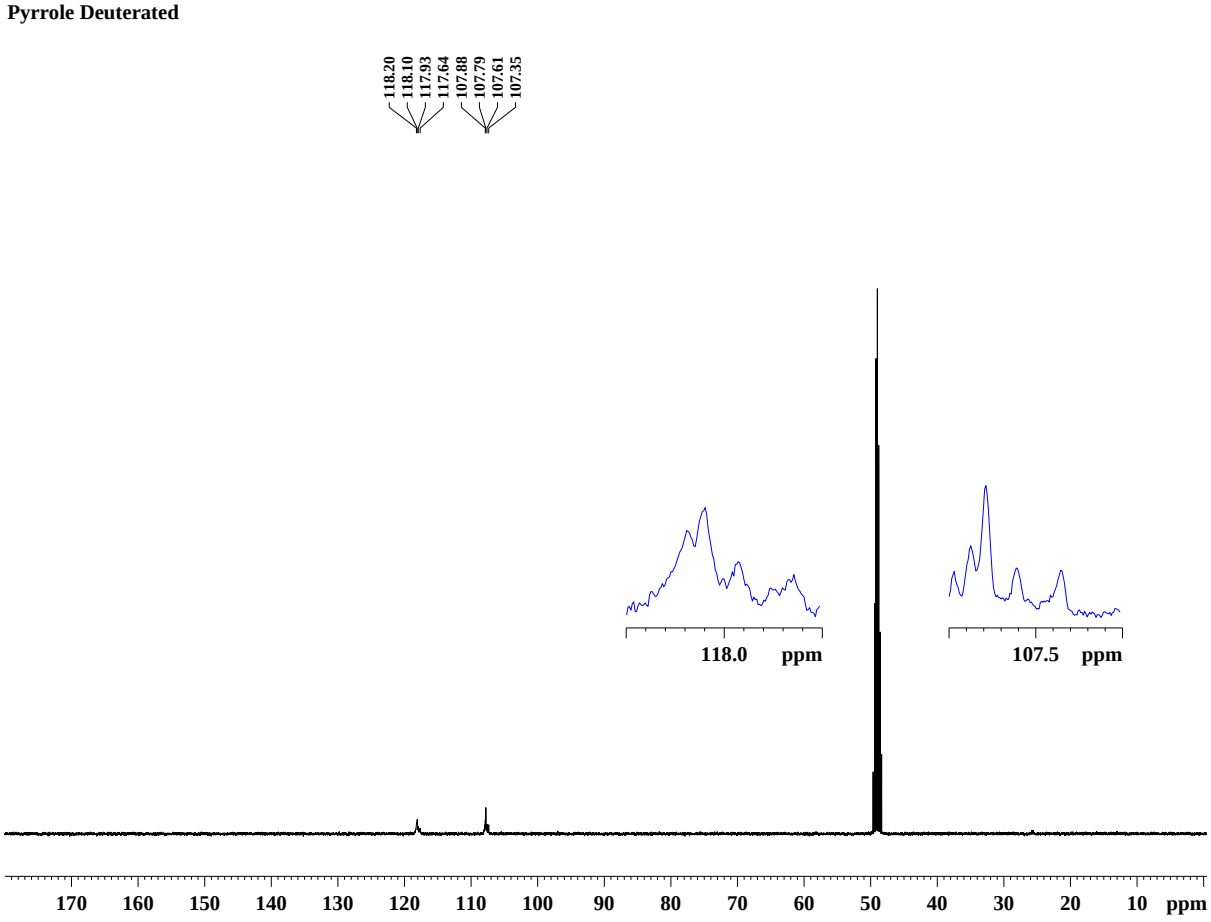
Supplementary Spectrum. ^{1}H NMR spectrum of 1-methylpyrrole (**71**) (400 MHz, CD_3OD)



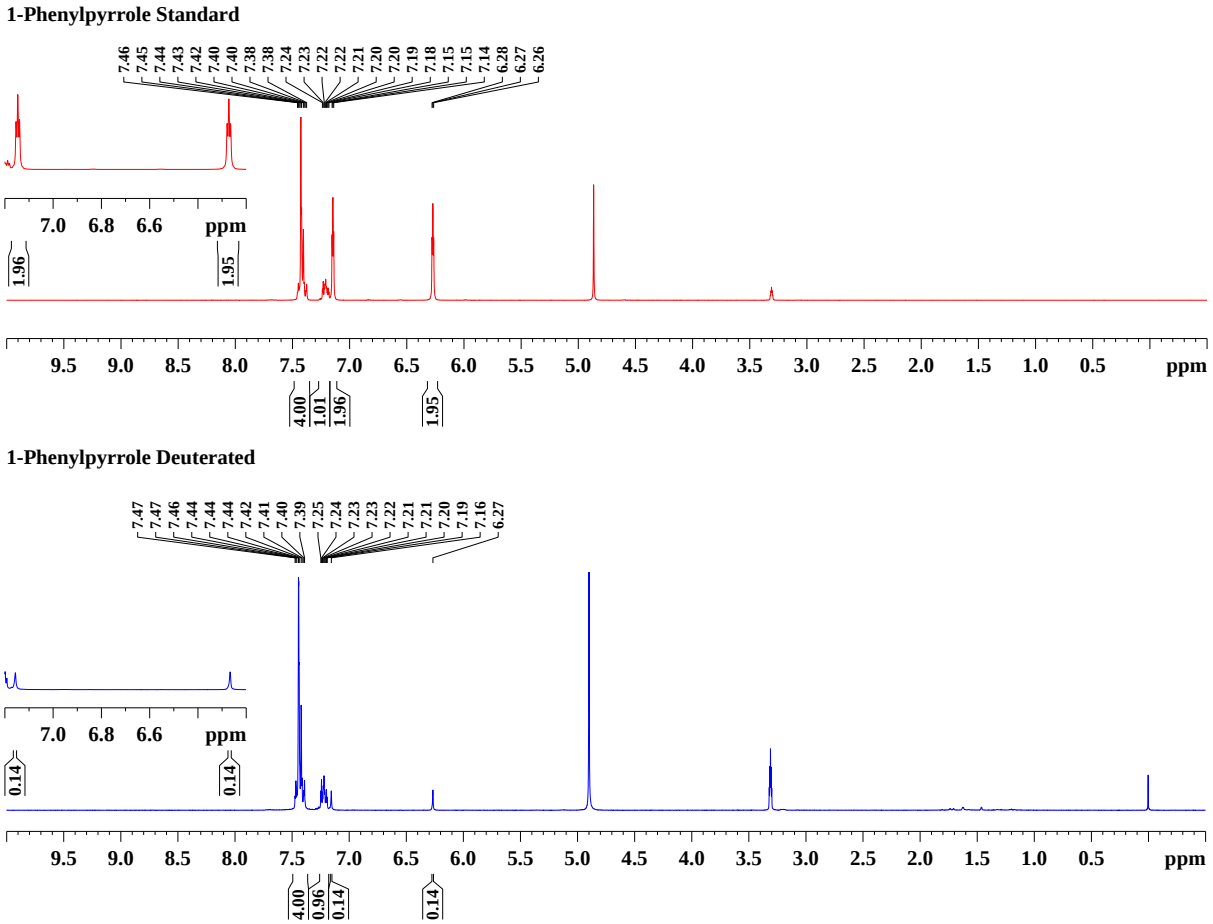
Supplementary Spectrum. ^{13}C NMR spectrum of 1-methylpyrrole (**71**) (100 MHz, CD_3OD)



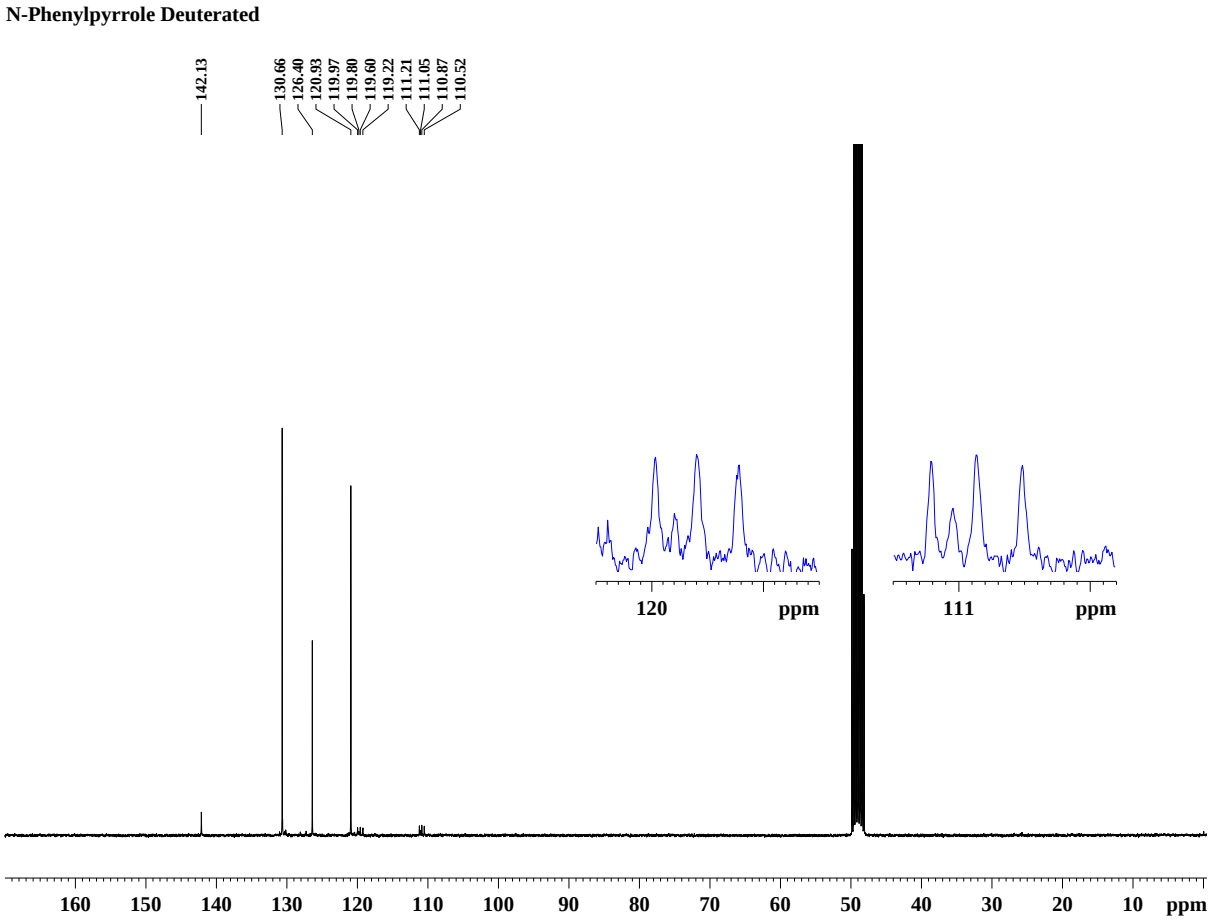
Supplementary Spectrum. ^{1}H NMR spectrum of pyrrole (**72**) (400 MHz, CD_3OD)



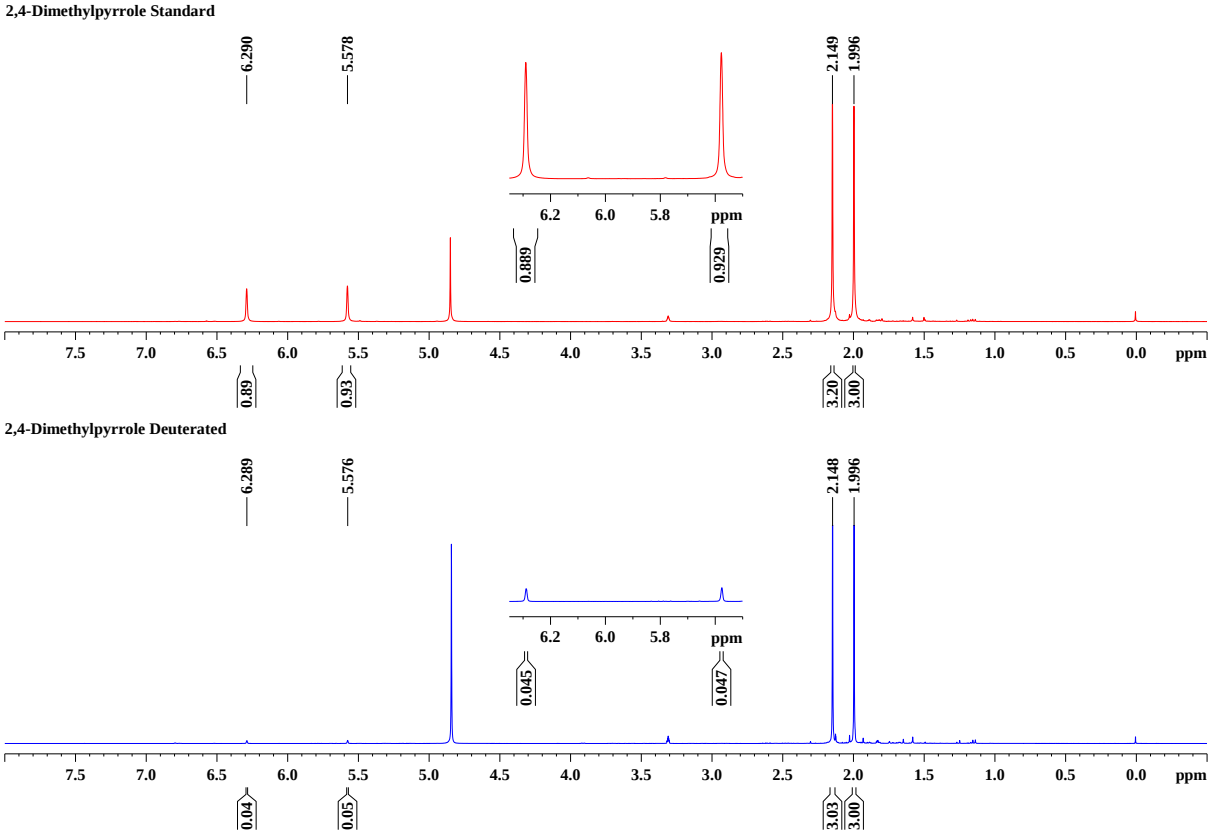
Supplementary Spectrum. ^{13}C NMR spectrum of pyrrole (**72**) (100 MHz, CD_3OD)



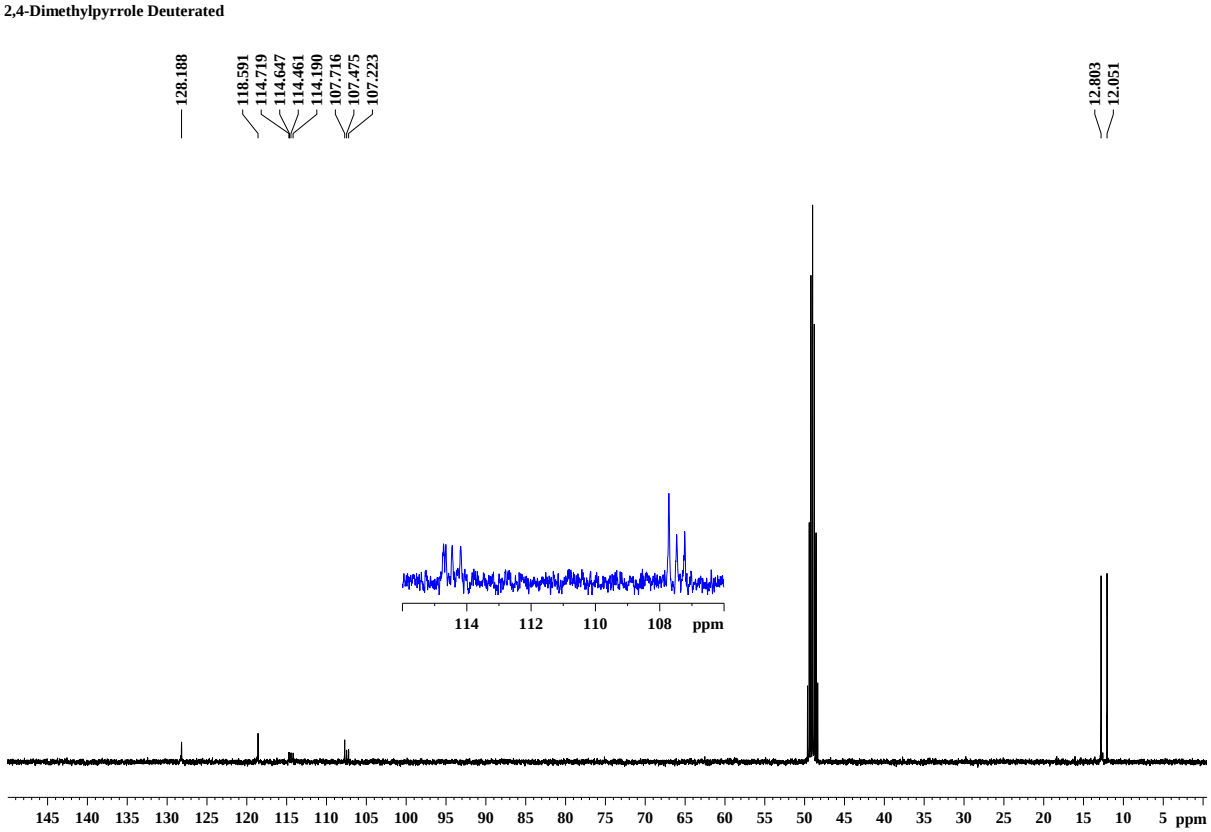
Supplementary Spectrum. ^{1}H NMR spectrum of 1-phenylpyrrole (**73**) (300 MHz, CD_3OD)



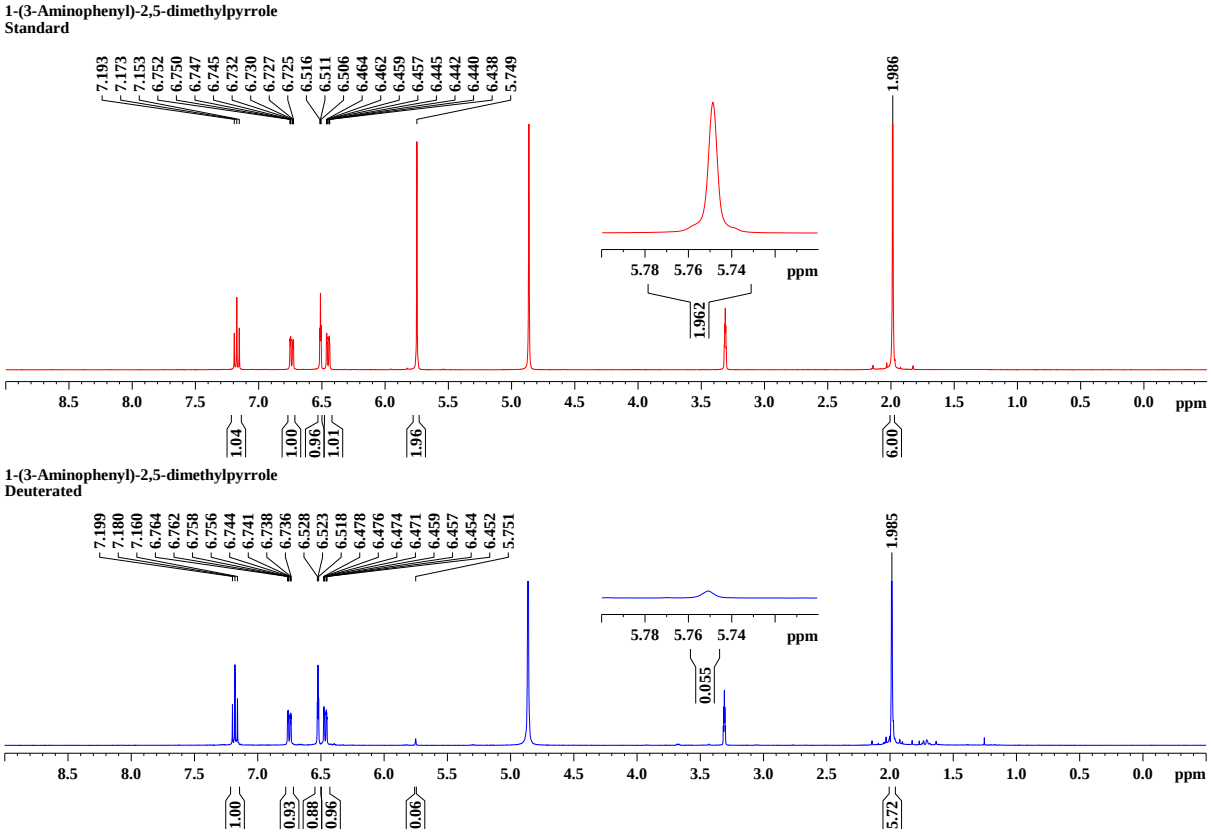
Supplementary Spectrum. ^{13}C NMR spectrum of 1-phenylpyrrole (**73**) (75 MHz, CD_3OD)



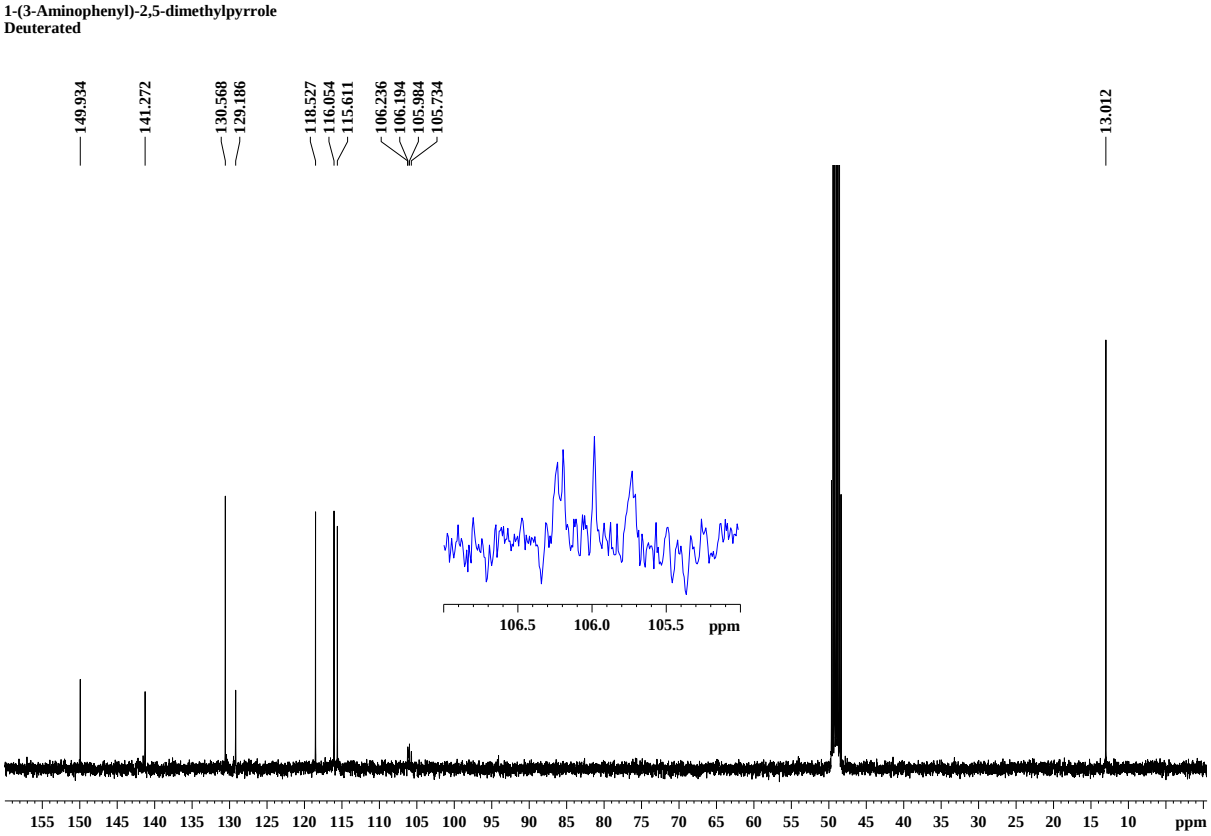
Supplementary Spectrum. ^{1}H NMR spectrum of 2,4-dimethylpyrrole (**74**) (400 MHz, CD_3OD)



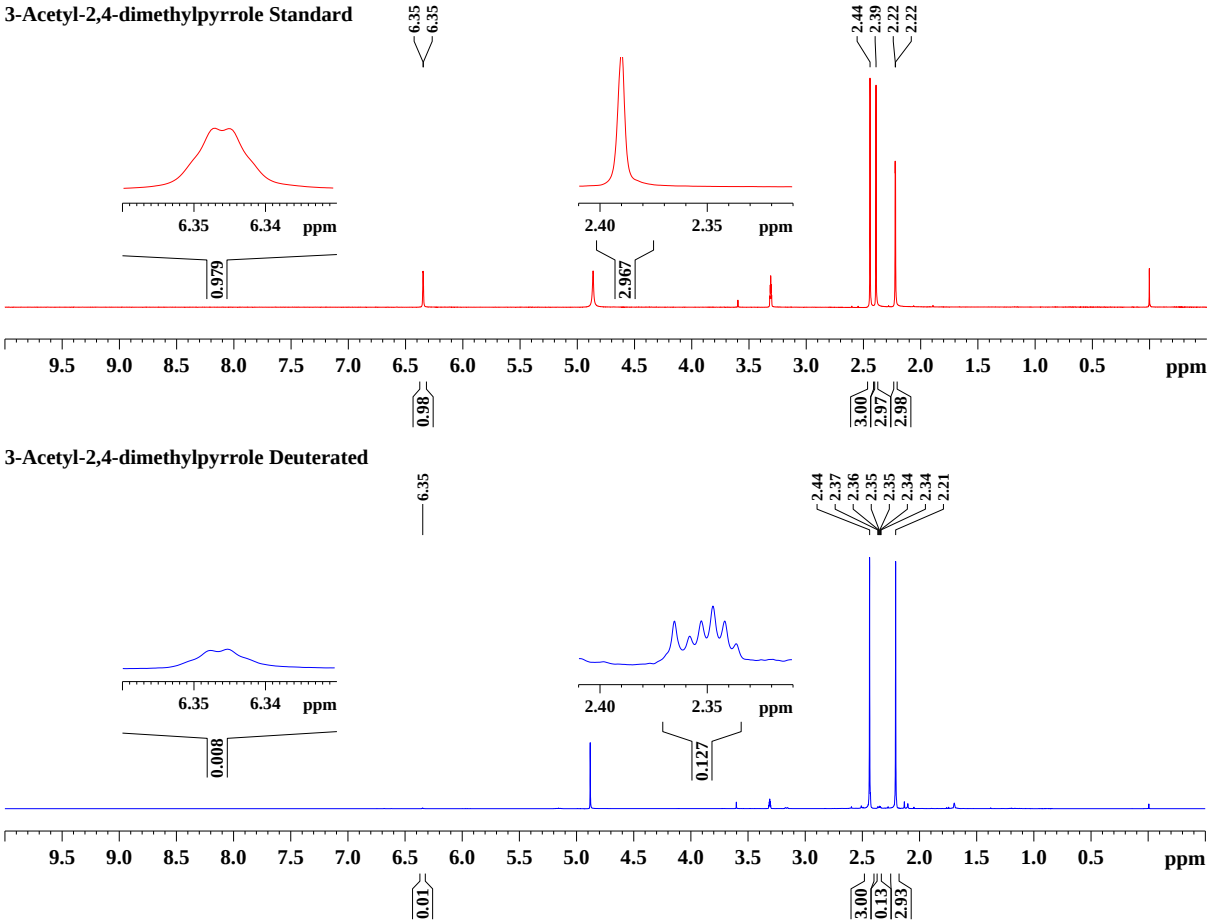
Supplementary Spectrum. ^{13}C NMR spectrum of 2,4-dimethylpyrrole (**74**) (100 MHz, CD_3OD)



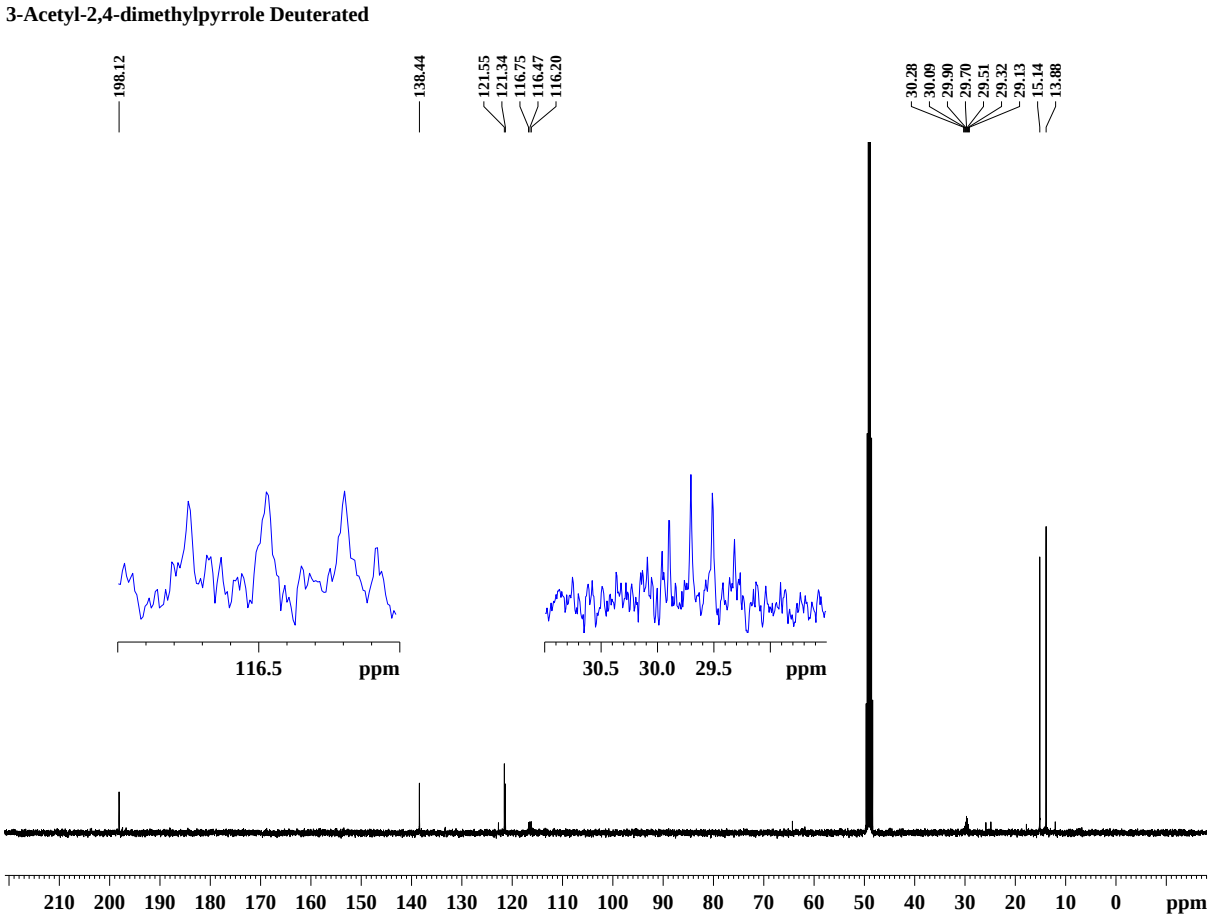
Supplementary Spectrum. ^{1}H NMR spectrum of 1-(3-aminophenyl)-2,5-dimethylpyrrole (**75**) (400 MHz, CD_3OD)



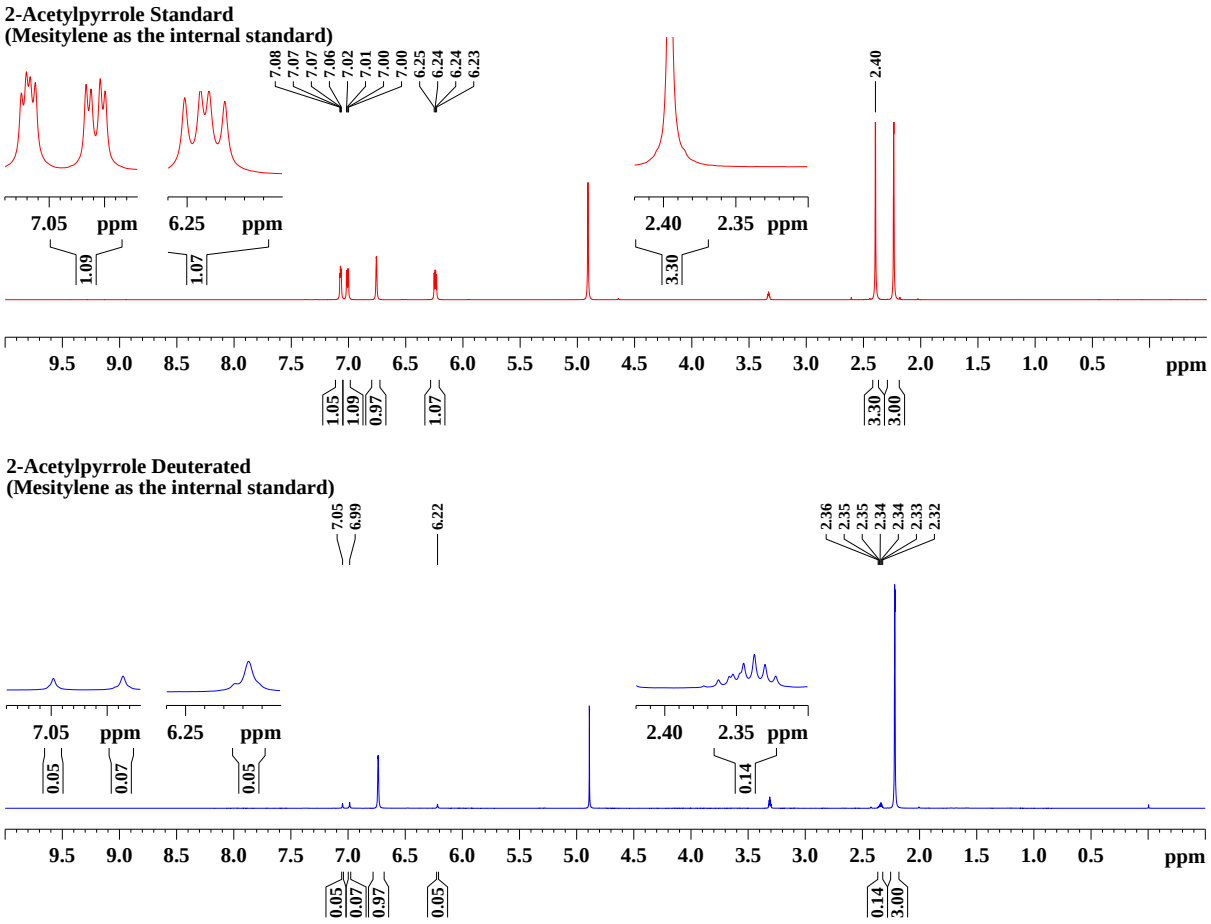
Supplementary Spectrum. ^{13}C NMR spectrum of 1-(3-aminophenyl)-2,5-dimethylpyrrole (**75**) (100 MHz, CD_3OD)



Supplementary Spectrum. ^{1}H NMR spectrum of 3-acetyl-2,4-dimethylpyrrole (**76**) (400 MHz, CD_3OD)

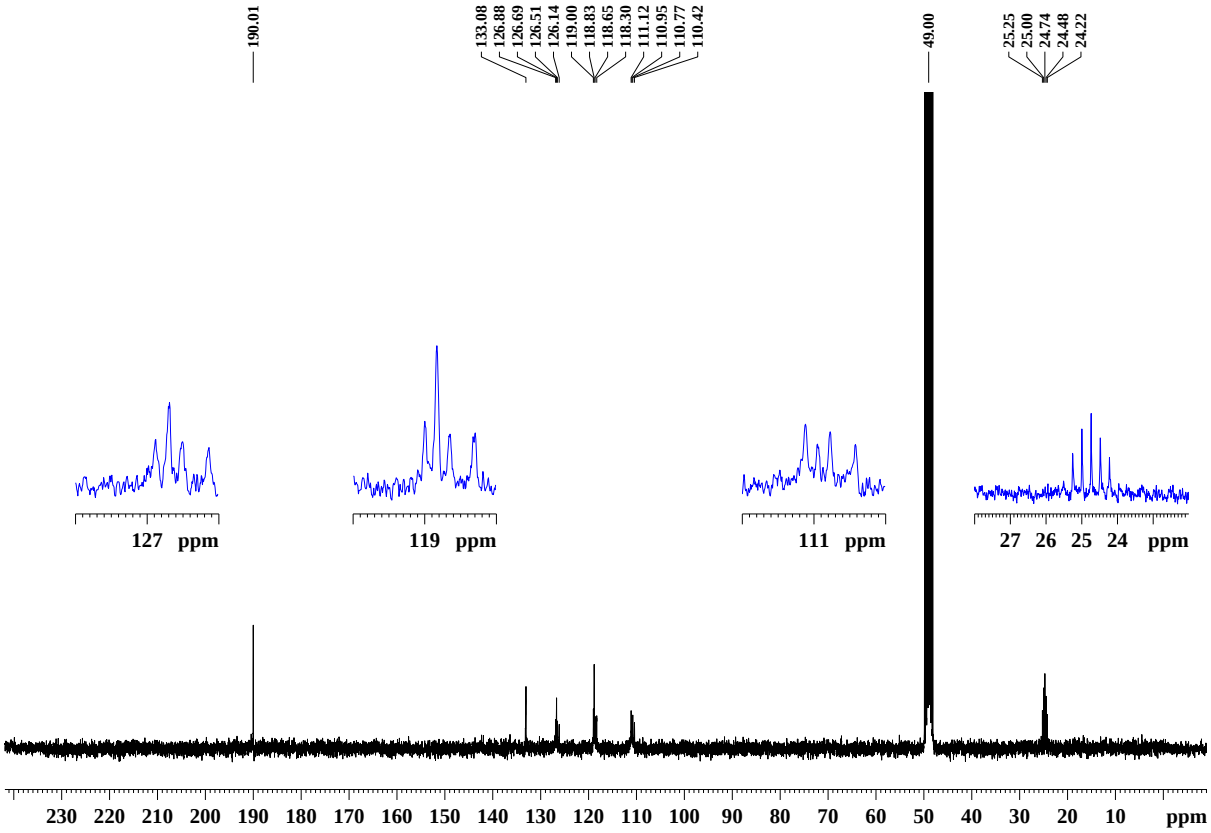


Supplementary Spectrum. ^{13}C NMR spectrum of 3-acetyl-2,4-dimethylpyrrole (**76**) (100 MHz, CD_3OD)

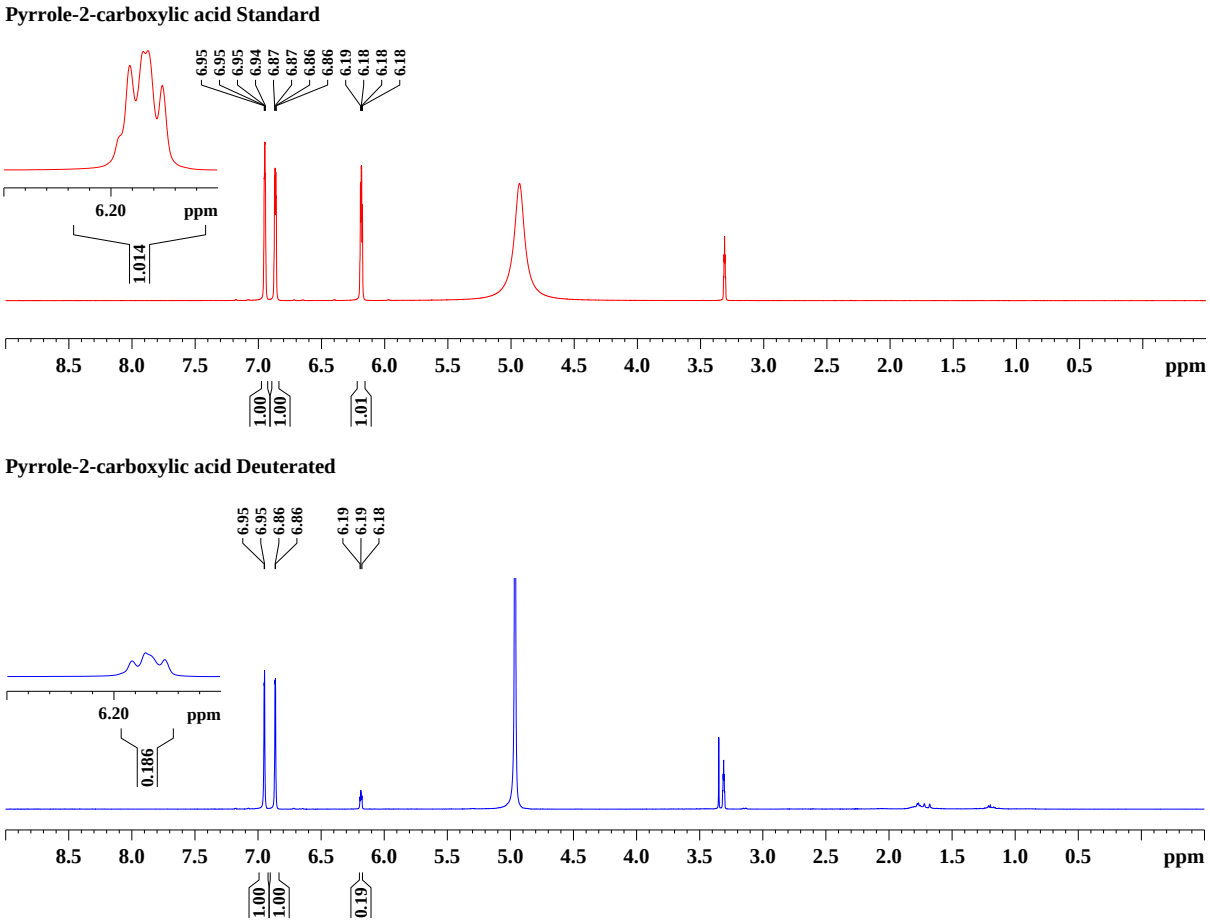


Supplementary Spectrum. ^{1}H NMR spectrum of 2-acetylpyrrole (**77**) (with mesitylene as the internal standard) (300 MHz, CD_3OD)

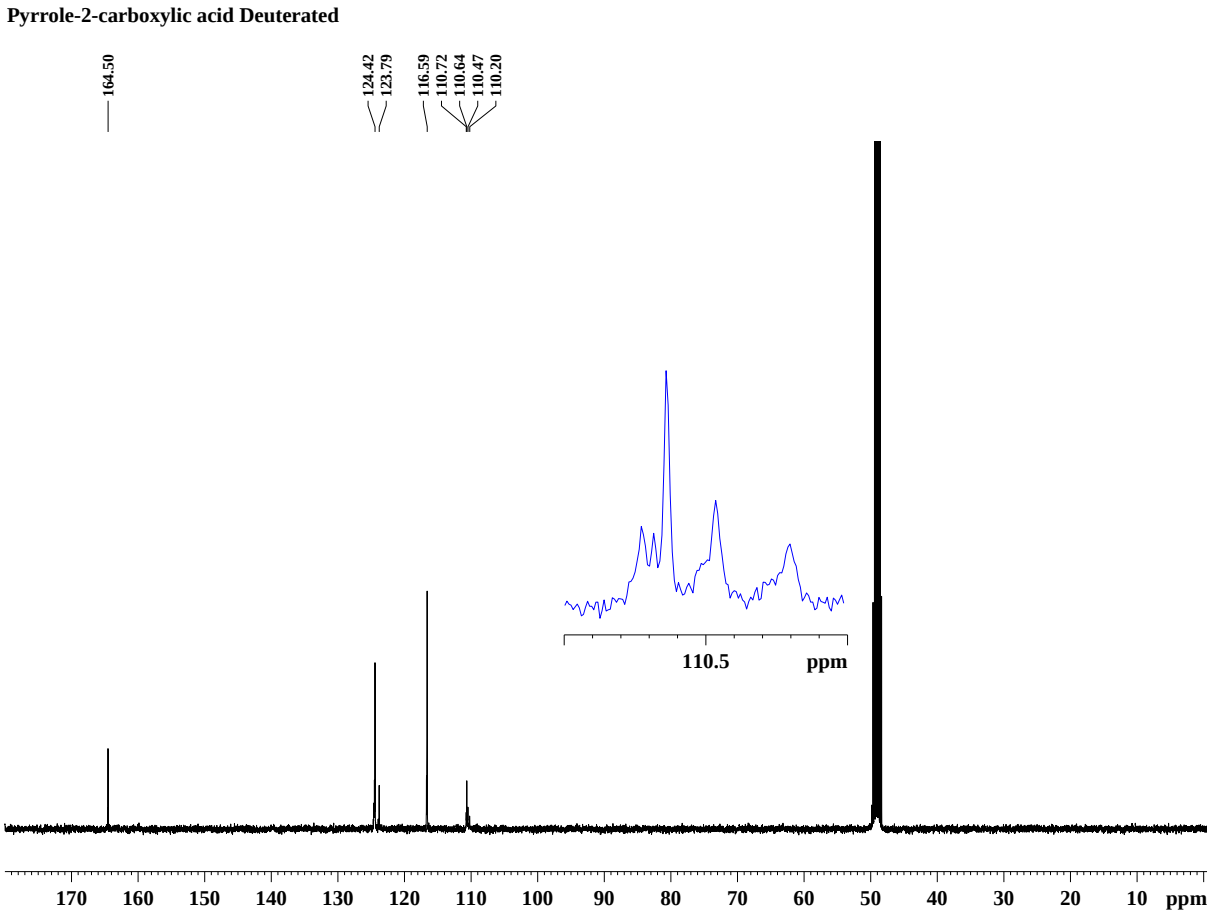
2-Acetylpyrrole Deuterated



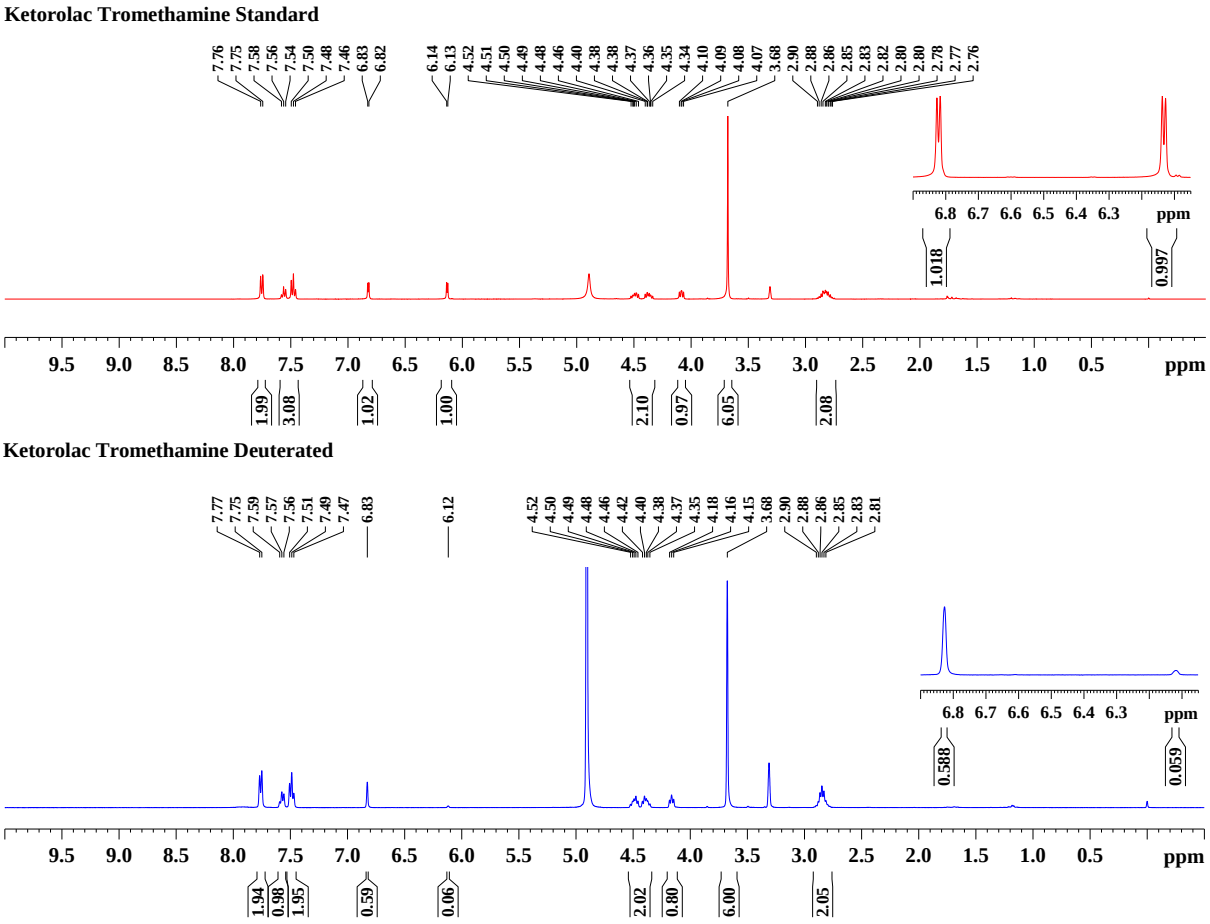
Supplementary Spectrum. ^{13}C NMR spectrum of 2-acetylpyrrole (**77**) (75 MHz, CD_3OD)



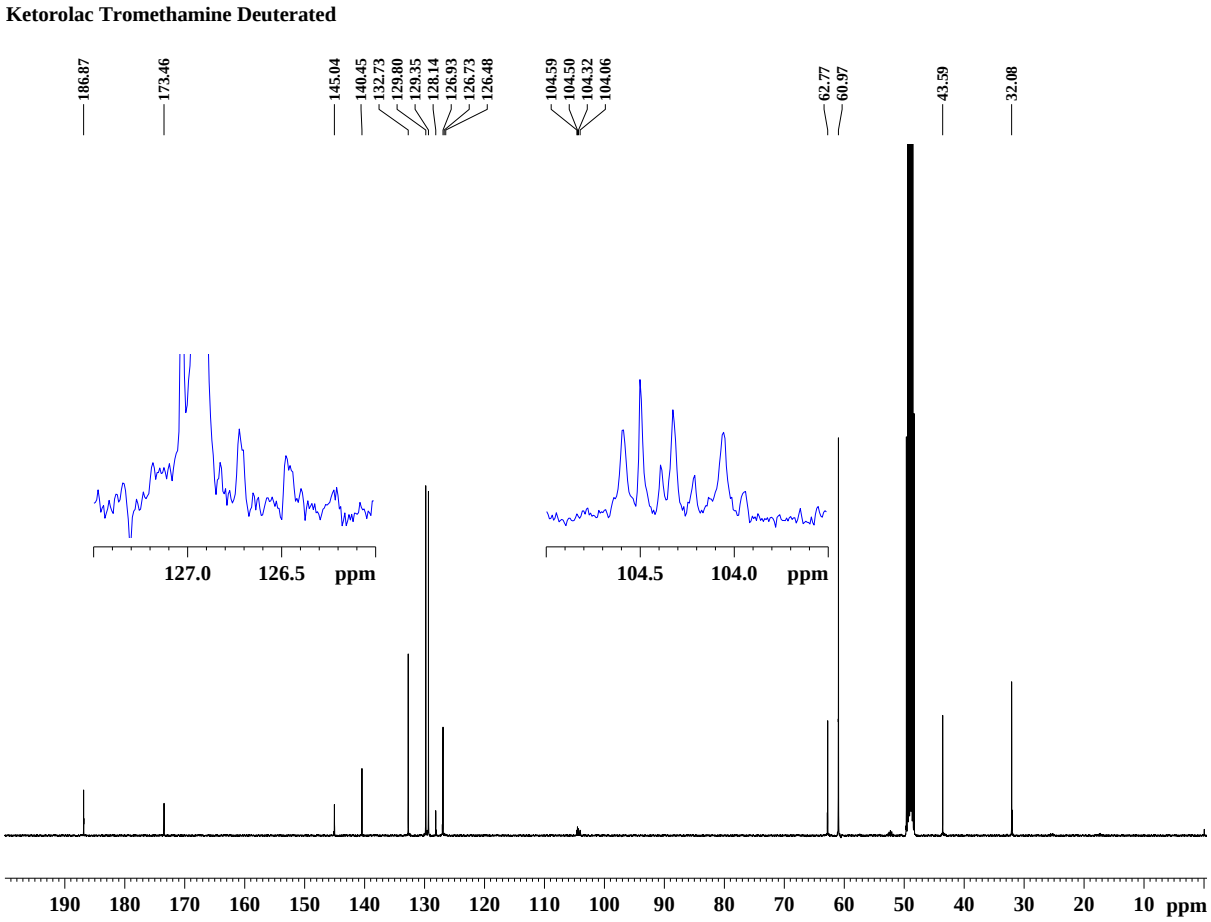
Supplementary Spectrum. ^{1}H NMR spectrum of pyrrole-2-carboxylic acid (**78**) (400 MHz, CD_3OD)



Supplementary Spectrum. ^{13}C NMR spectrum of pyrrole-2-carboxylic acid (**78**) (100 MHz, CD_3OD)



Supplementary Spectrum. ^{1}H NMR spectrum of ketorolac tromethamine (**79**) (400 MHz, CD_3OD)



Supplementary Spectrum. ^{13}C NMR spectrum of ketorolac tromethamine (**79**) (100 MHz, CD_3OD)