Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Selective Oxidation of Unactivated C-H Bonds by Supramolecular Control

*Yat-Sing Fung, Siu-Cheong Yan and Man-Kin Wong**

State Key Laboratory of Chirosciences and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China.

SUPPORTING INFORMATION

Table S1. Oxidation of Adamantane (**1**) at Different Temperature[a]

Entry	Temperature (°C)	**1** : **2a** : **2a'**[b]
1	0	87 : 13 : 0
2	**25**	**48 : 47 : 5**
3	40	60 : 33 : 7

[a] Reactions were carried out by **1** (0.1 mmol) and 1,1,1-trifluoroacetone (0.1 mmol) in H_2O (1 mL) and CH_3CN (1.5 mL), with Oxone (0.5 mmol) and $NaHCO_3$ (1.55 mmol). [b] Determined by ^1H NMR analysis of the crude reaction mixture.

Table S2. Oxidation of **1** with Different Bases[a]

Entry	Base	pH	**1** : **2a** : **2a'**[b]
1	**$NaHCO_3$**	**6.9**	**48 : 47 : 5**
2	$CaCO_3$	6.4	44 : 41 : 15
3	Na_2CO_3	9.0	98 : 2 : 0
4	K_2CO_3	8.7	97 : 3 : 0
5	Cs_2CO_3	9.1	100 : 0 : 0

[a] Reactions were carried out by **1** (0.1 mmol) and 1,1,1-trifluoroacetone (0.1 mmol) in H_2O (1 mL) and CH_3CN (1.5 mL) at room temperature, with Oxone (0.5 mmol) and base (1.55 mmol). [b] Determined by ^1H NMR analysis of the crude reaction mixture.

Table S3. Oxidation of **1** with Different Amounts of Oxone and $NaHCO_3$[a]

Entry	Oxone (mmol)	$NaHCO_3$ (mmol)	Time	**1** : **2a** : **2a'**[b]
1	0.5	1.55	2 h	48 : 47 : 5
2	0.5×2	1.55×2	4 h	24 : 67 : 9
3	**0.5×3**	**1.55×3**	**6 h**	**7 : 50 : 43**
4	0.5×4	1.55×4	8 h	16 : 59 : 25
5	0.25×8	0.775×8	8 h	12 : 54 : 34

[a] Reactions were carried out by **1** (0.1 mmol) and 1,1,1-trifluoroacetone (0.1 mmol) in H_2O (1 mL) and CH_3CN (1.5 mL) at room temperature, with different amounts of Oxone and $NaHCO_3$. [b] Determined by ^1H NMR analysis of the crude reaction mixture.

Table S4. Effect of Loading of 1,1,1-Trifluoroacetone on Oxidation of **1**[a]

Entry	1,1,1-trifluoroacetone (equiv)	**1** : **2a** : **2a'**[b]
1	2	23 : 52 : 25
2	**1**	**7 : 50: 43**
3	0.5	51 : 38 : 11
4	0.1	64 : 31 : 5

[a] Reactions were carried out by **1** (0.1 mmol) and different amounts of 1,1,1-trifluoroacetone in H_2O (1 mL) and CH_3CN (1.5 mL) at room temperature with Oxone (0.5 mmol × 3) and $NaHCO_3$ (1.55 mmol × 3). (total reaction time: 6 h). [b] Determined by ^1H NMR analysis of the crude reaction mixture.

Table S5. Oxidation of **3a** with Different Loading of Oxone and $NaHCO_3$[a]

Entry	Oxone (mmol)	$NaHCO_3$ (mmol)	Time	**3a** : **4a** : **4a'**[b]
1	1×4	3.1×4	8 h	69 : 27 : 4
2[c]	**0.5×8**	**1.55×8**	**8 h**	**44 : 48 : 8**

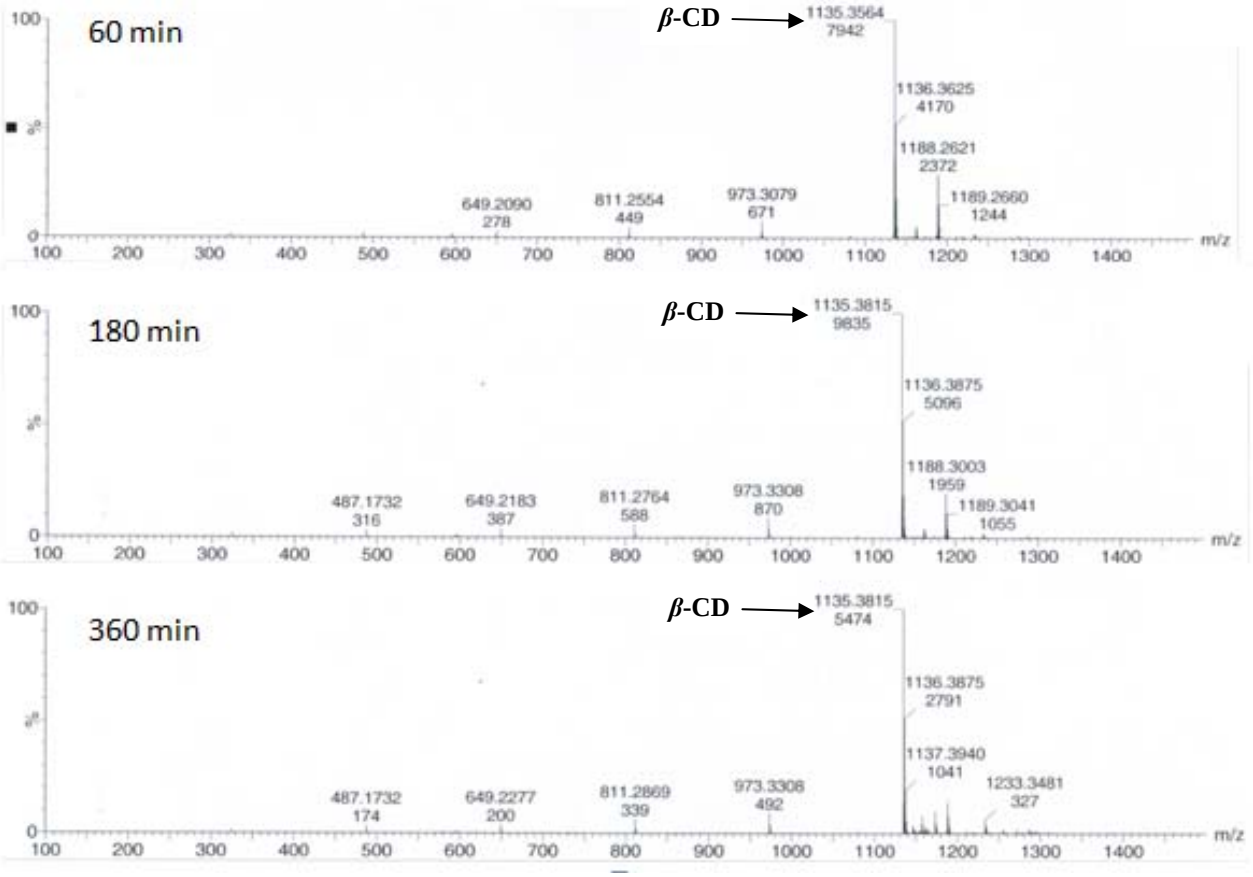
[a] Reactions were carried out by **3a** (0.2 mmol) and 1,1,1-trifluoroacetone (0.2 mmol) in H_2O (4 mL) and CH_3CN (6 mL) at room temperature with Oxone (1 mmol × 4) and $NaHCO_3$ (3.1 mmol × 4). [b] Determined by ^1H NMR analysis of the crude reaction mixture. [c] The reaction was conducted with Oxone (0.5 mmol × 8) and $NaHCO_3$ (1.55 mmol × 8).

Table S6. Oxidation of **3a** with Different Amounts of *β*-CD[a]

Entry	*β*-CD (equiv)	Conversion (%)[b]	Yield (%)[c]	**4a** : **4a'**[d]
1	0.1	23	40	7 : 1
2	0.5	32	50	8 : 1
3	**1.1**	**40**	**71**	**20 : 1**
4	2	34	42	25 : 1
5	5	49	20	29 : 1
6	10	47	29	30 : 1

[a] Reactions were conducted with **3a** (0.2 mmol), 1,1,1-trifluoroacetone (0.2 mmol) and different loadings of *β*-CD in H_2O (10 mL) at room temperature with Oxone (0.5 mmol × 8) and $NaHCO_3$ (1.55 mmol × 8). [b] Conversion was calculated from the amount of substrate recovered by flash column chromatography. [c] Yield based on conversion. [d] Determined by ^1H NMR.

Figure S1. LC-MS (ESI+) spectra of *β*-CD (*m/z* = 1135.38) in dioxirane-based oxidation of **3a**



Calculation of the difference of activation energy for the improvement of the site-selectivity of C-H bond oxidation of 3a using Arrhenius equation ($\ln k = -(E_a/RT) + \ln A$)

The calculation was based on two assumptions. (i) There is no change in ΔS. (ii) The activation energy for the formation of **4a** remains unchanged, and the activation energy for the formation of **4a'** is increased due to the induced steric hindrance by *β*-CD. The steps of calculation were shown as follows:

Let the Arrhenius equation for the C-H bond oxidation of **3a** in a mixture of H_2O and CH_3CN be:

$$\ln k_1 = -(E_{a1}/RT) + \ln A \quad (1)$$

And let the Arrhenius equation for the C-H bond oxidation of **3a** in H_2O with *β*-CD be:

$$\ln k_2 = -(E_{a2}/RT) + \ln A \quad (2)$$

where k_1 and k_2 are the rate constants for the C-H bond oxidation of **3a** in a mixture of H_2O and CH_3CN and that in H_2O with *β*-CD, respectively; Ea_1 and Ea_2 are the activation energies for the C-H bond oxidation of **3a** in a mixture of H_2O and CH_3CN and that in H_2O with *β*-CD, respectively; R is gas constant (1.987 cal K^{-1} mol^{-1}); T is absolute temperature, assumed to be 298 K; A is the pre-exponential factor.

The difference of Ea_1 and Ea_2 is calculated by (1) - (2):

$$\ln k_1 - \ln k_2 = \left[-\left(\frac{Ea_1}{RT}\right) + \ln A\right] - \left[-\left(\frac{Ea_2}{RT}\right) + \ln A\right]$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{Ea_2 - Ea_1}{RT} \quad (3)$$

The C-H bond oxidation of **3a** in a mixture of H_2O and CH_3CN gave **4a** and **4a'** in the ratio of 1 : 1/7, and the C-H bond oxidation of **3a** in H_2O with *β*-CD gave **4a** and **4a'** in the ratio of 1 : 1/20.

Therefore,

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\frac{\frac{1}{7}}{\frac{1}{20}} = \ln 2.857 \quad (4)$$

Substitute (4) into (3):

$$\ln 2.857 = \frac{Ea_2 - Ea_1}{RT}$$

$$Ea_2 - Ea_1 = RT\ln 2.857$$

$$Ea_2 - Ea_1 = 1.987 \text{ cal } K^{-1}mol^{-1} \times 298K \times \ln 2.857$$
$$Ea_2 - Ea_1 = 0.622 \text{ kcal } mol^{-1}$$

Therefore, the difference in the activation energy for the improvement of the site-selectivity of C-H bond oxidation of **3a** is 0.622 kcal mol^{-1}.

Details of ^{1}H NMR titration experiments and Scott's plots of 3a-c

The mixtures of **3a-c** and *β*-CD for the ^{1}H NMR titration experiments were prepared by mixing indicated volume of (i) **3a-c** stock solutions (0.5 M, 0.25 mmol of **3a-c** in 0.5 mL of D_6-acetone), (ii) *β*-CD stock solution (0.01 M, 0.1 mmol of *β*-CD in 10 mL of D_2O), and (iii) D_2O according to the following table. The final volumes of the mixtures were ~ 0.5 mL.

Entry	Ratio of **3a-c** : *β*-CD	Volume of **3a-c** stock solutions (*μ*L)	Volume of *β*-CD stock solution (mL)	Volume of D_2O (mL)
1	0 : 10	0	0.50	0
2	1 : 9	1	0.45	0.05
3	2 : 8	2	0.40	0.10
4	3 : 7	3	0.35	0.15
5	4 : 6	4	0.30	0.20
6	5 : 5	5	0.25	0.25
7	5.5 : 4.5	6	0.25	0.25
8	6 : 4	6	0.20	0.30
9	6.7 : 3.3	6	0.15	0.35
10	7 : 3	7	0.15	0.35

Remarks: In general, the mixtures with high ratio of *β*-CD are opaque and viscous (entries 1-7) while transparent solutions are observed in the mixtures with low ratio of *β*-CD (entries 8-10).

The mixtures were subjected to ^{1}H NMR analysis. The changes of the chemical shift of H3 of *β*-CD (with the chemical shift of H4 of *β*-CD as the internal reference) are obtained as $\Delta\delta_{obs}$ which is used for the calculation of the binding constant.

The binding constants (K) of **3a-c** to *β*-CD were calculated by fitting $\Delta\delta_{obs}$ into Scott's plot as the equation shown below (R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 787):

$$[\mathbf{3a\text{-}c}] / \Delta\delta_{obs} = [\mathbf{3a\text{-}c}] / \Delta\delta_{max} + \Delta\delta_{max} / K$$

where [**3a-c**] is the concentration of **3a-c** with normalized concentration of *β*-CD, $\Delta\delta_{obs}$ is the observed change of the chemical shift of H3 of *β*-CD at different concentrations of **3a-c**, $\Delta\delta_{max}$ is the maximum change of the chemical shift of H3 of *β*-CD.

Figure S2. Scott's plot of ^{1}H NMR titration of **3a** and β-CD

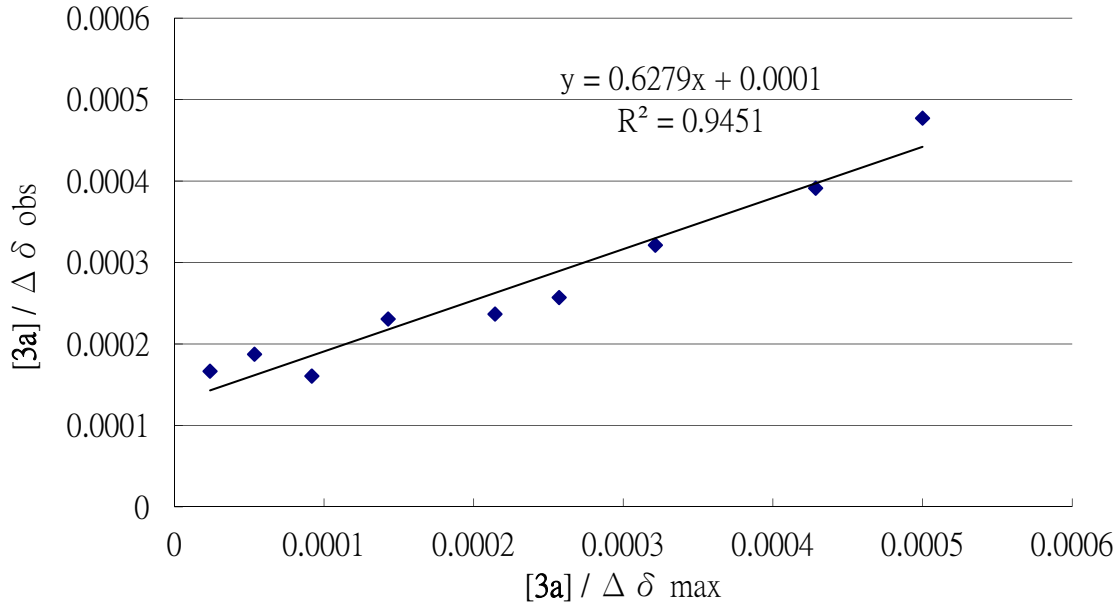


Figure S3. Scott's plot of ^{1}H NMR titration of **3b** and β-CD

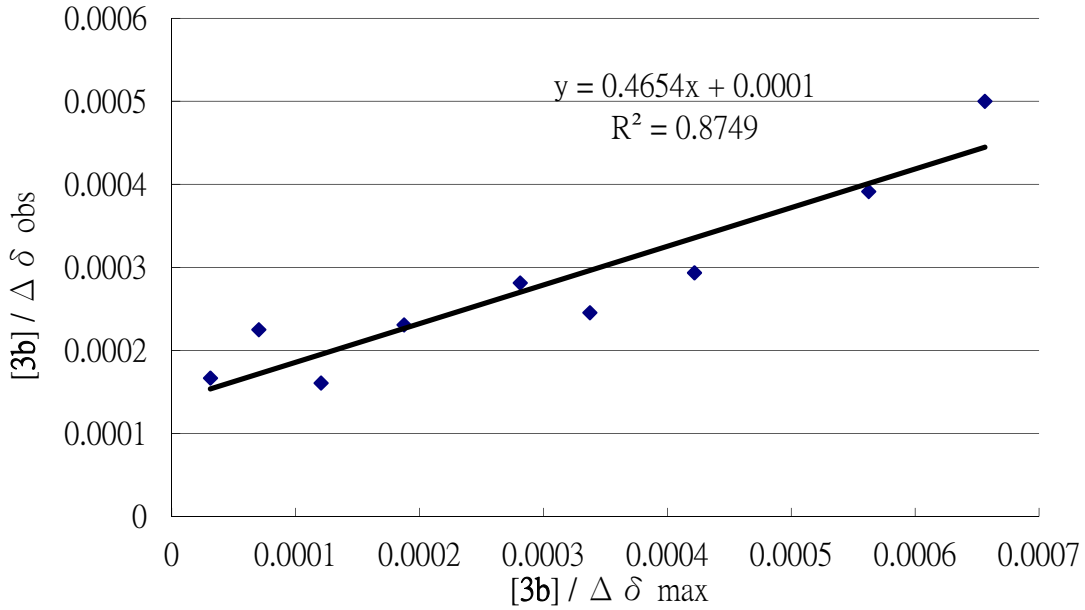


Figure S4. Scott's plot of ^{1}H NMR titration of **3c** and β-CD

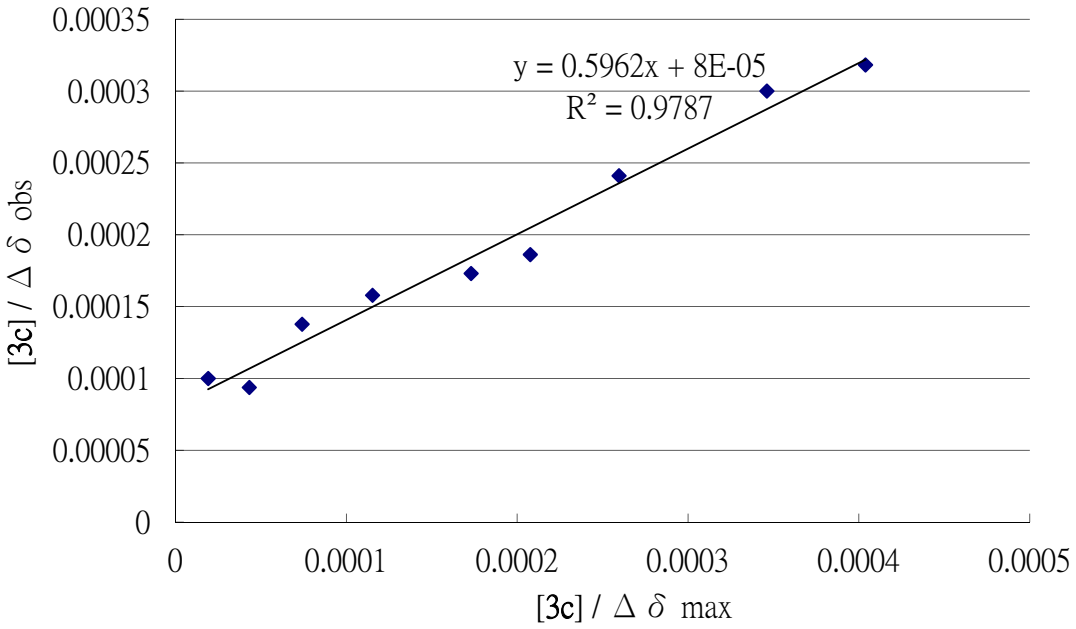


Figure S5. ^{1}H NMR titration curve for **3b** and β-CD

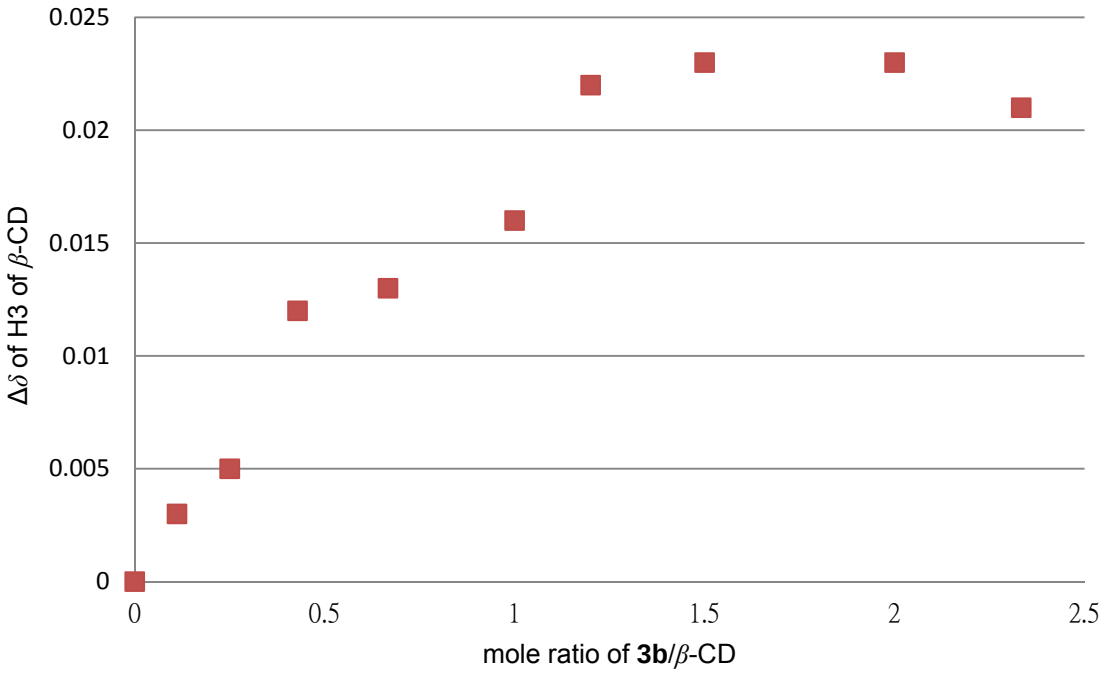


Figure S6. ^{1}H NMR titration curve for **3c** and β-CD

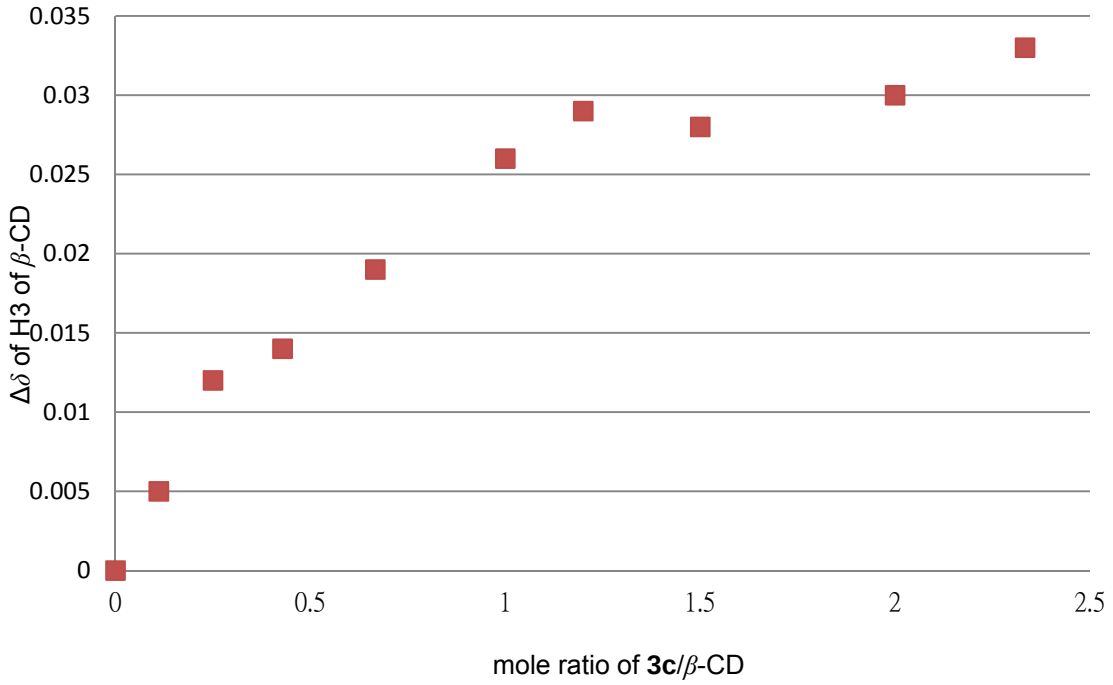


Figure S7. ^{1}H NMR titration curve for **3d** and β-CD

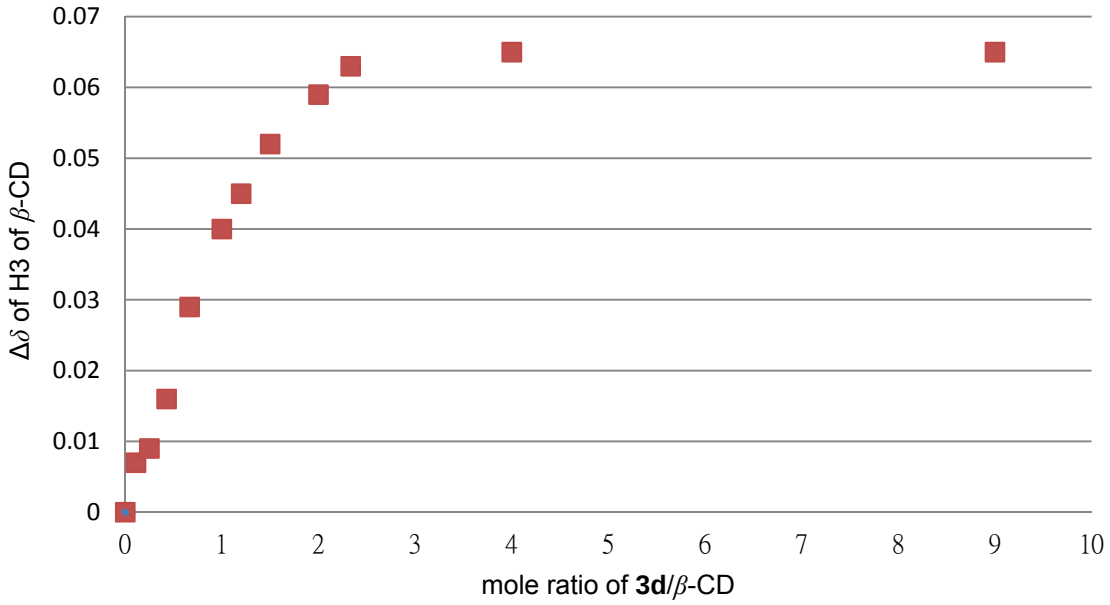


Figure S8. ^{1}H NMR titration curve for **3a** and α-CD

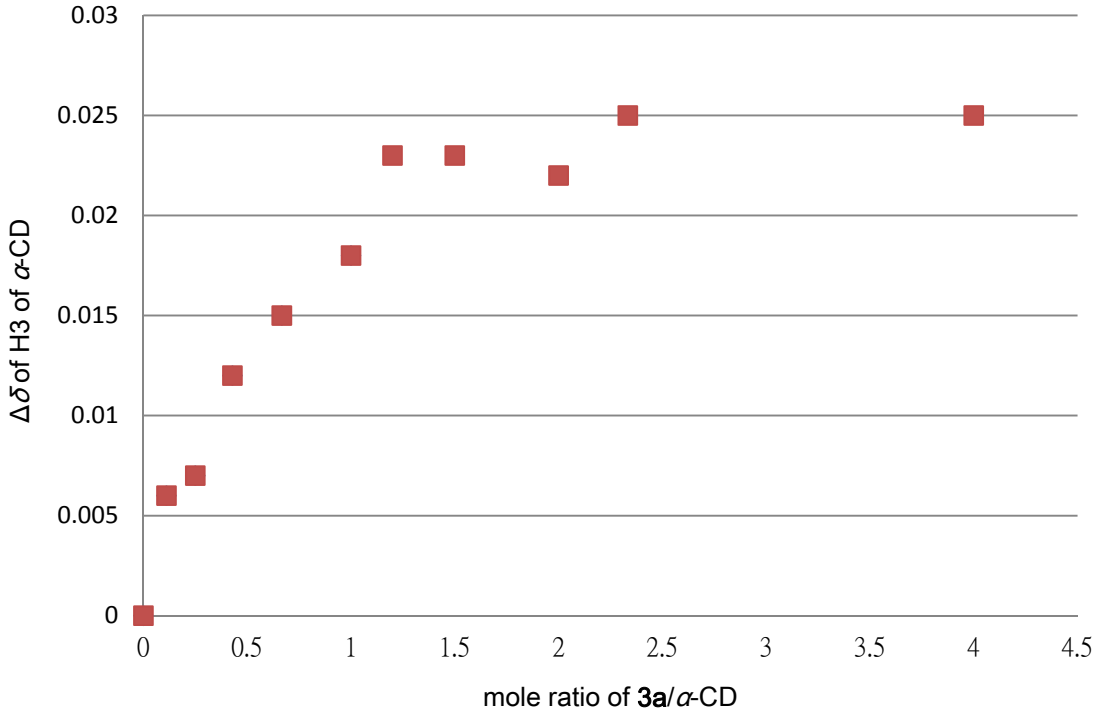


Figure S9. ^{1}H NMR titration curve for **3b** and α-CD

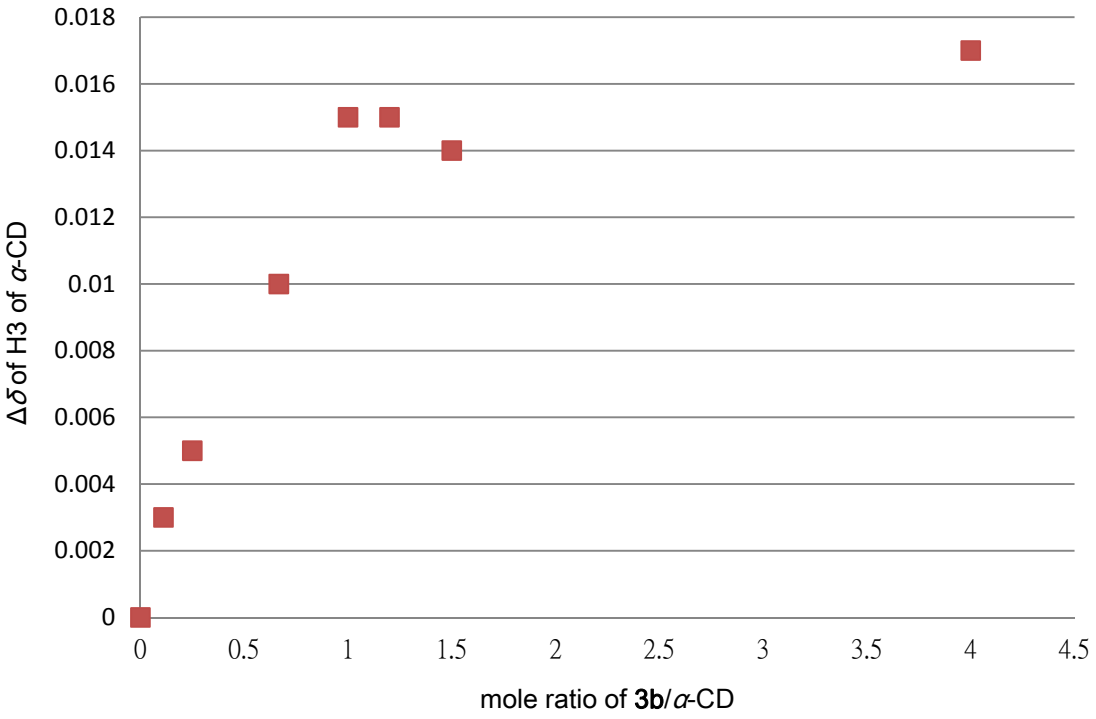


Figure S10. ^{1}H NMR titration curve for **3c** and α-CD

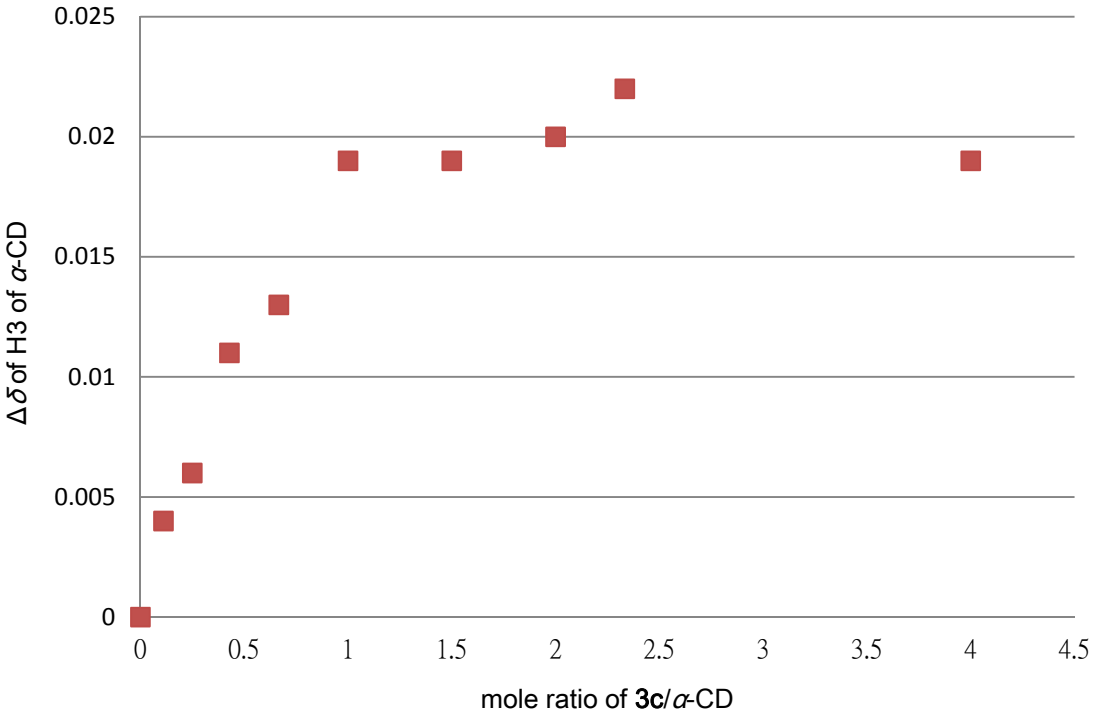


Figure S11. ^{1}H NMR titration curve for **3d** and α-CD

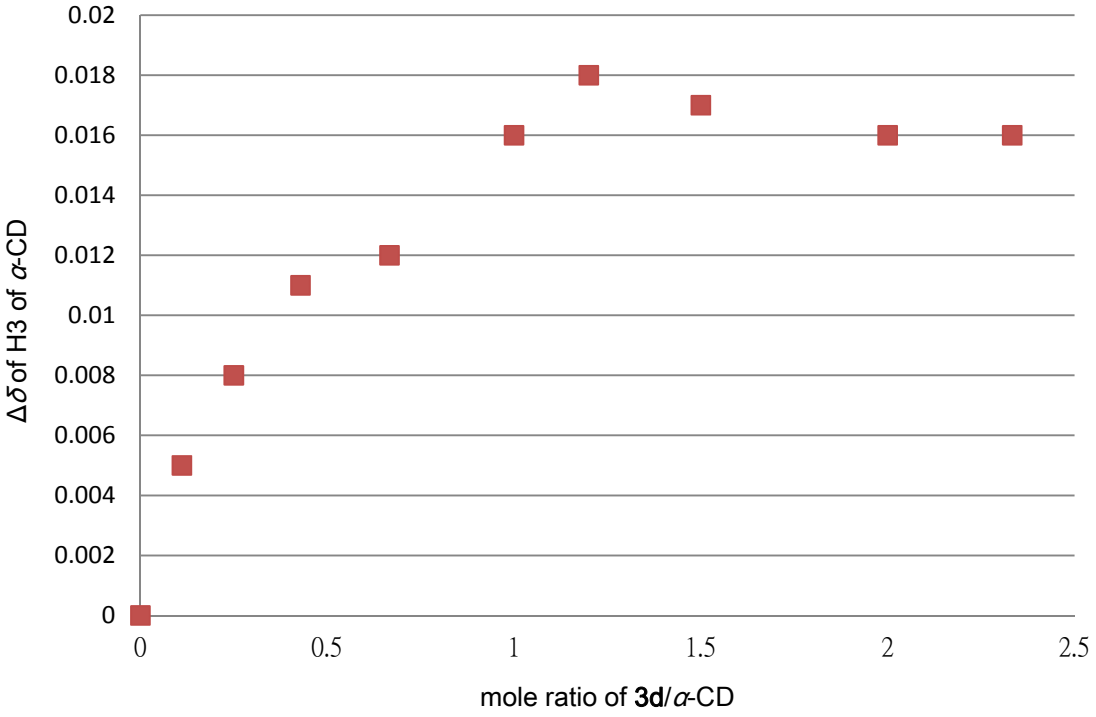


Figure S12. ^{1}H NMR titration curve for **3a** and γ-CD

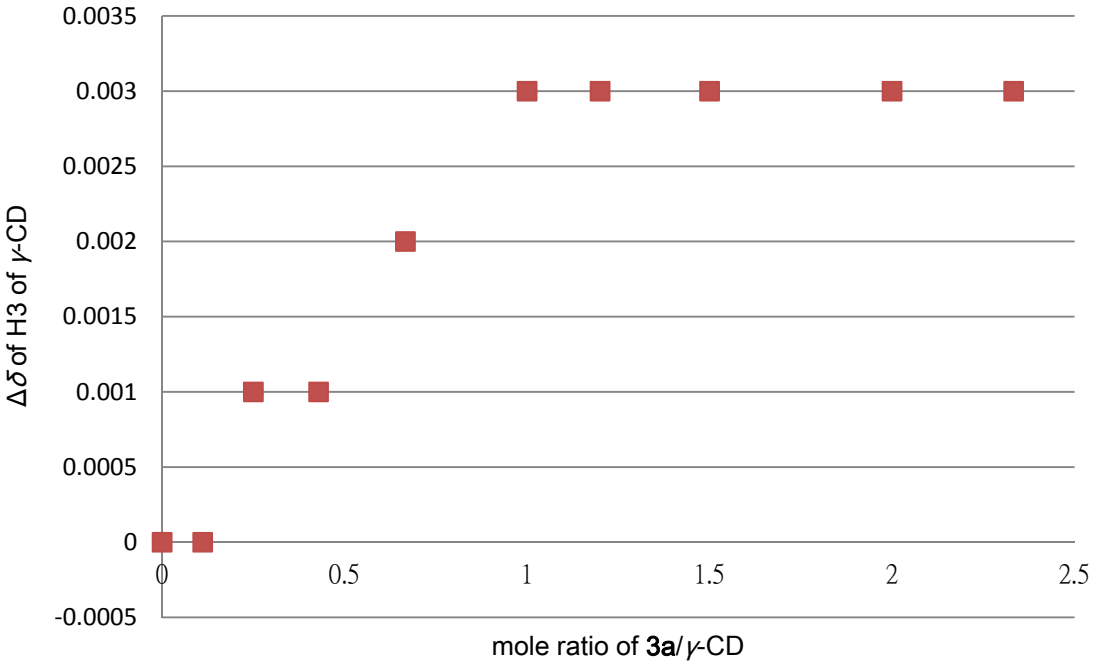


Figure S13. ^{1}H NMR titration curve for **3b** and γ-CD

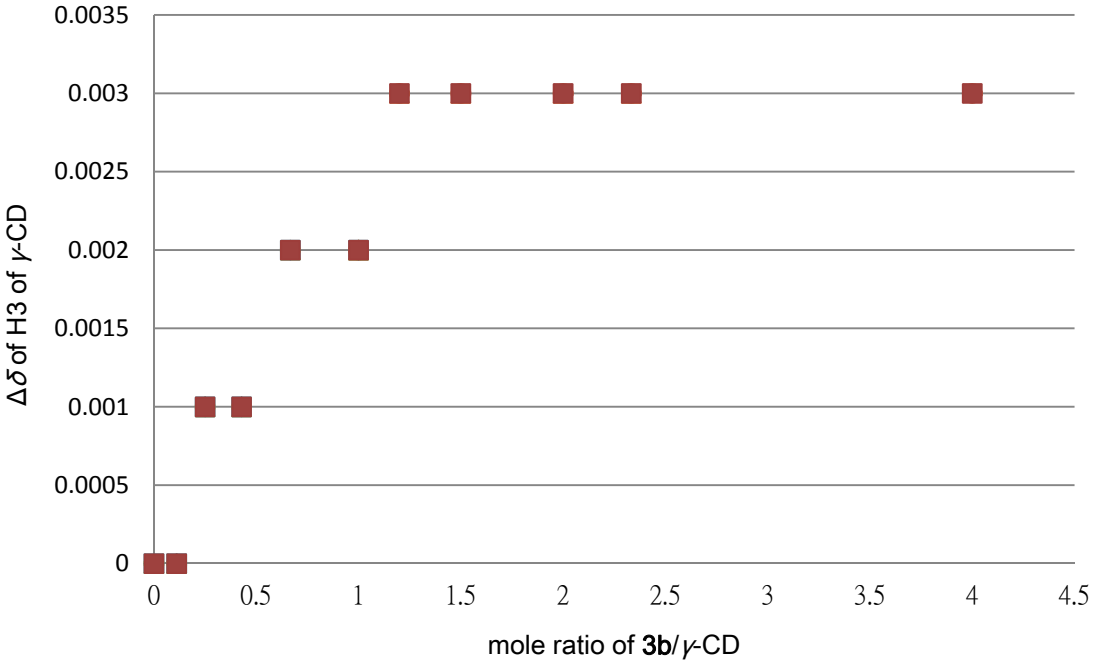


Figure S14. ^{1}H NMR titration curve for **3c** and γ-CD

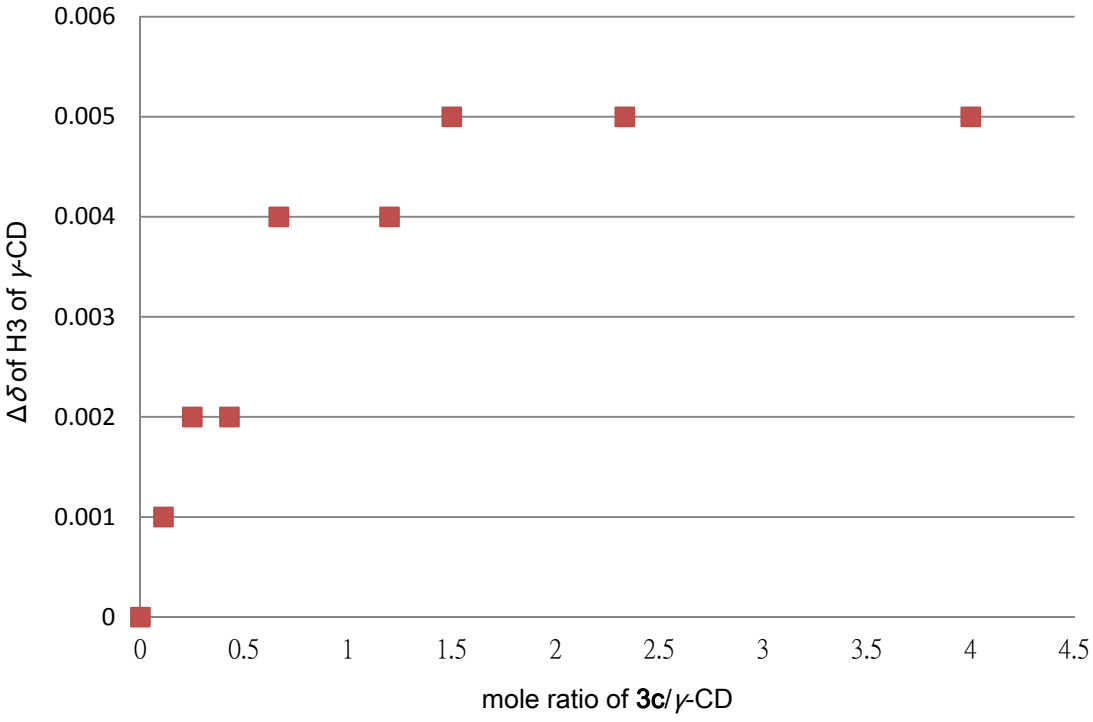
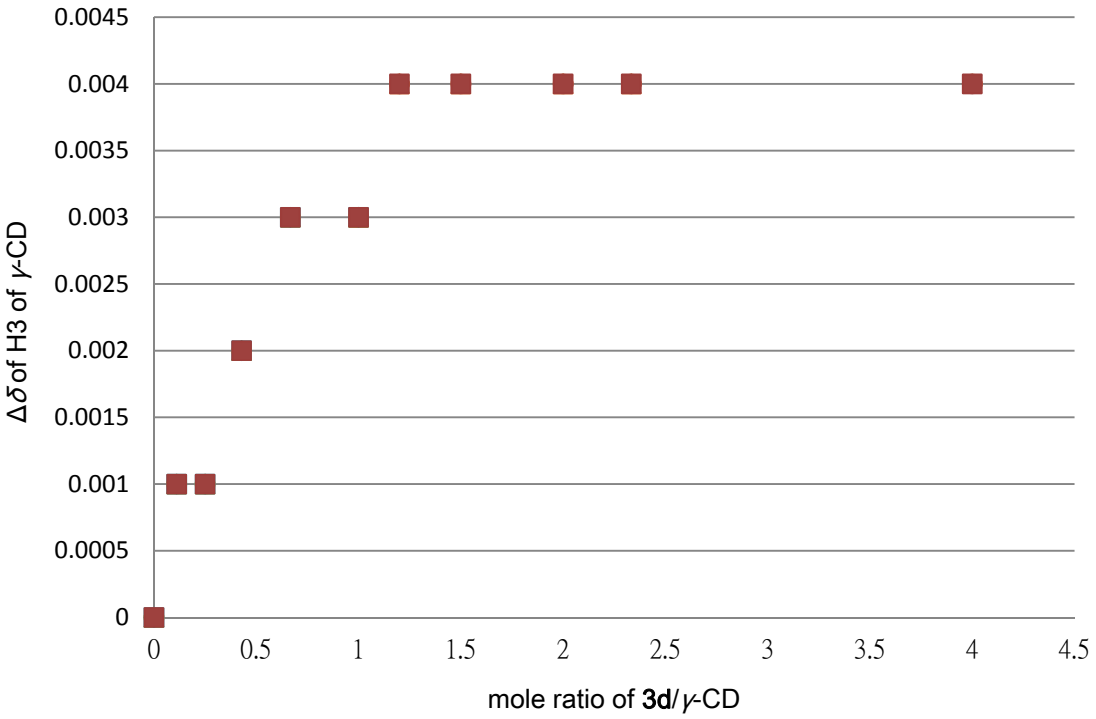
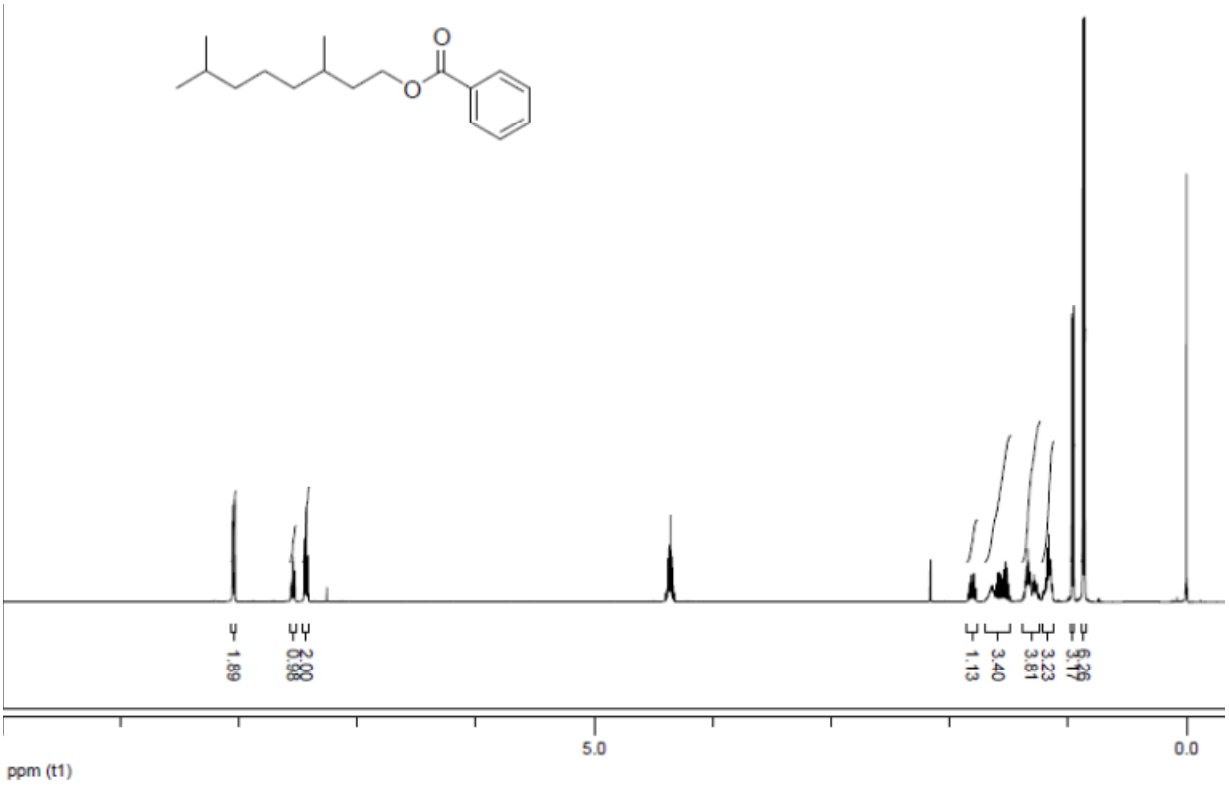
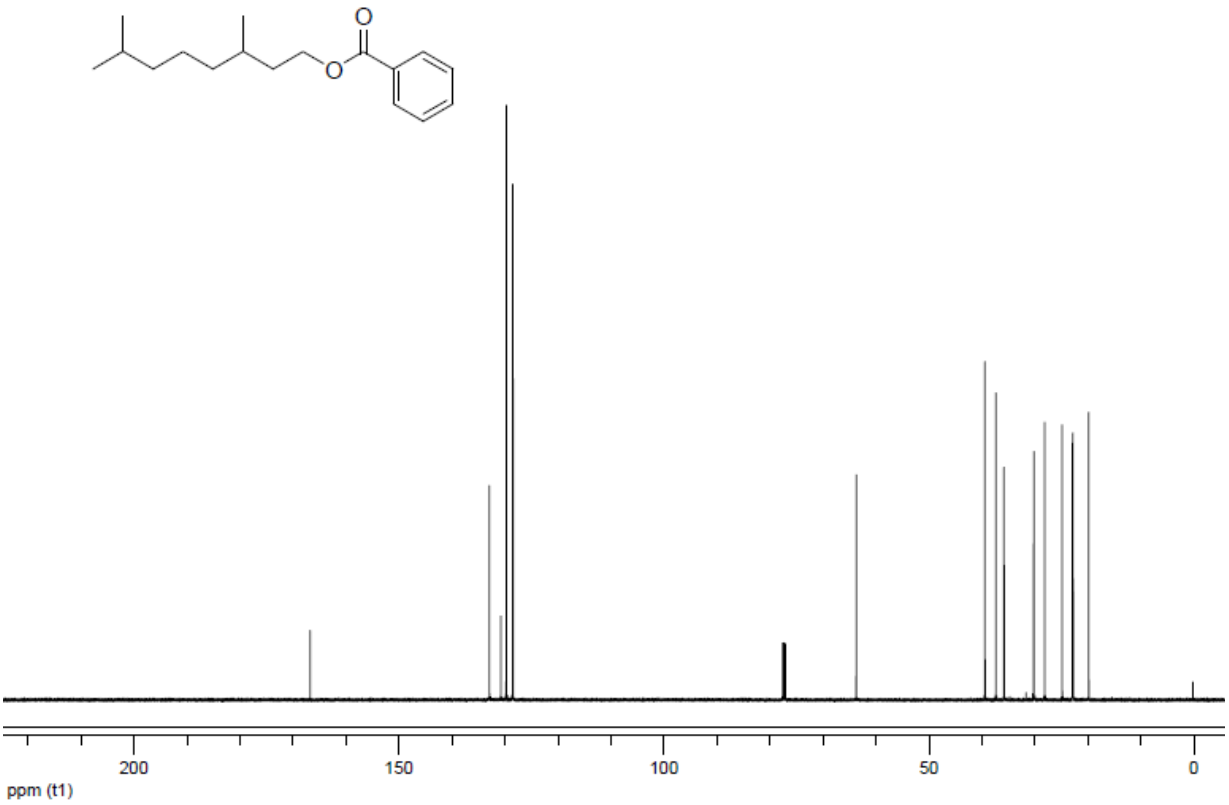


Figure S15. ^{1}H NMR titration curve for **3d** and γ-CD

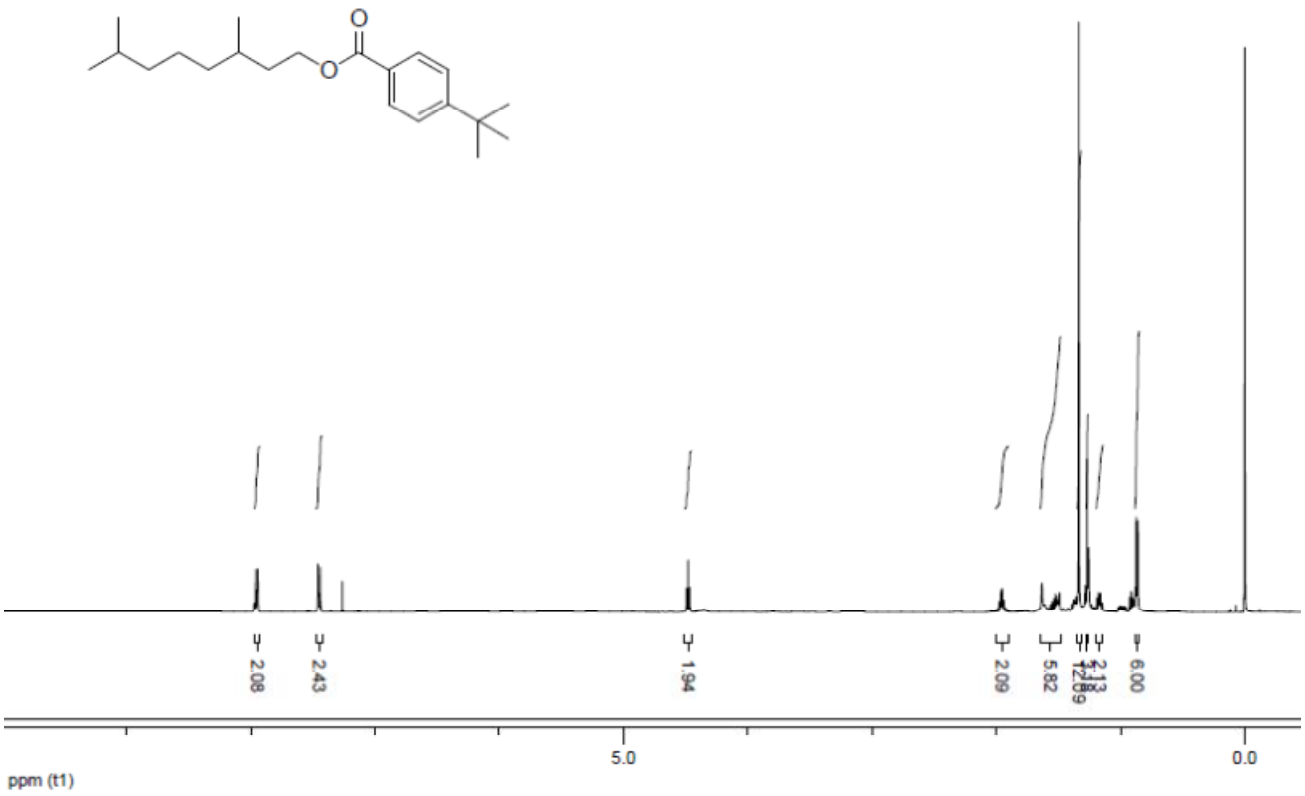


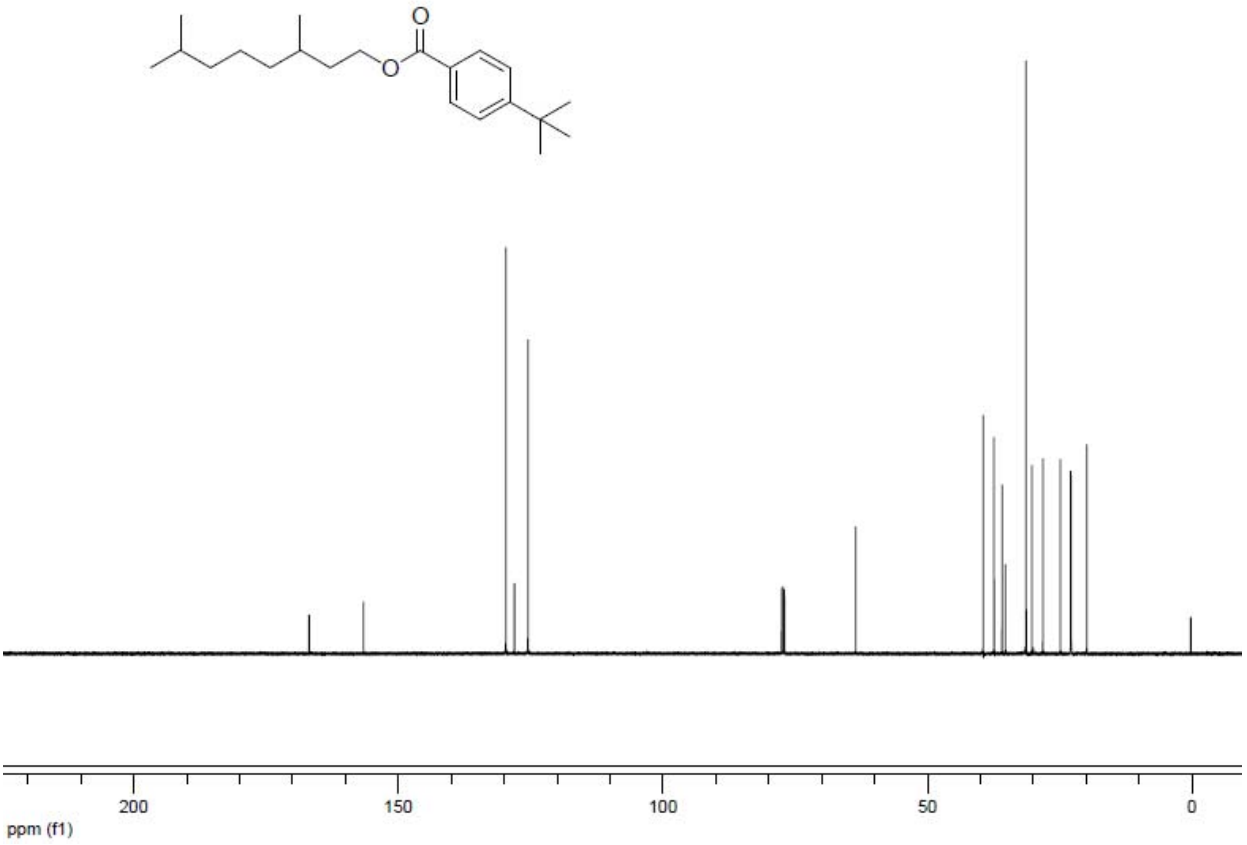
3,7-dimethyloctyl benzoate (3a)



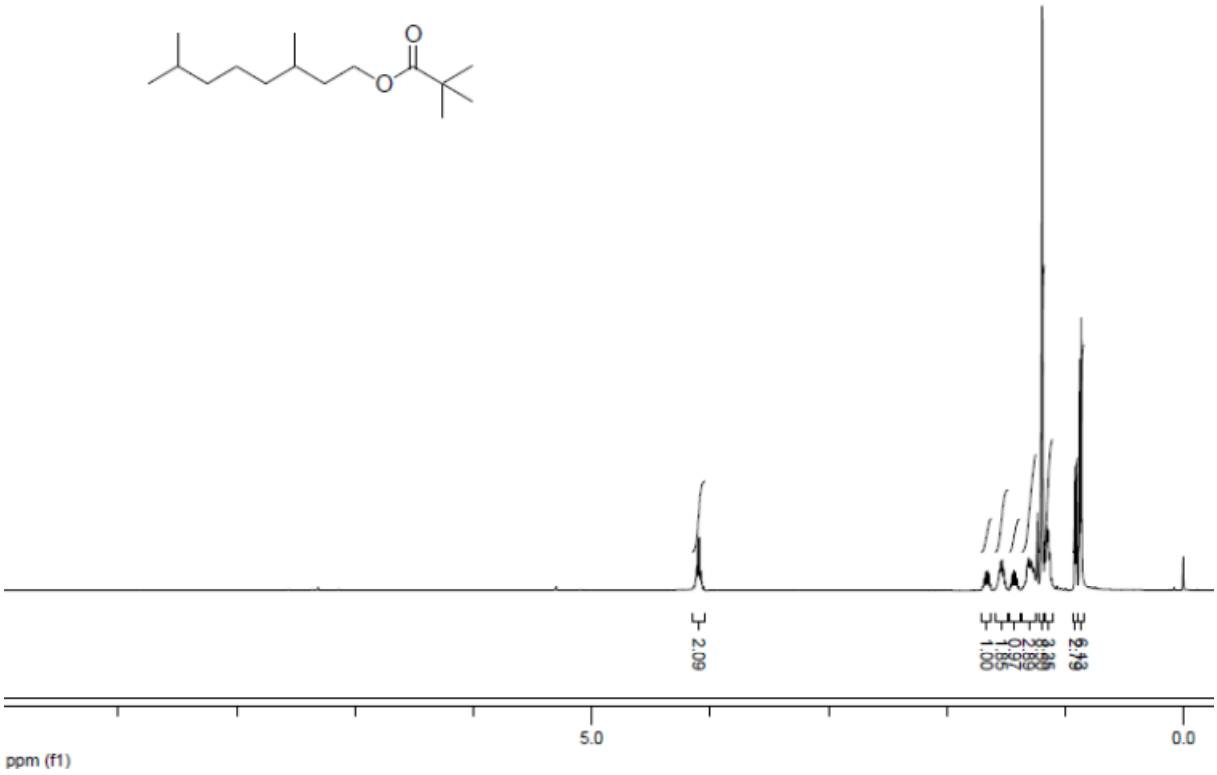


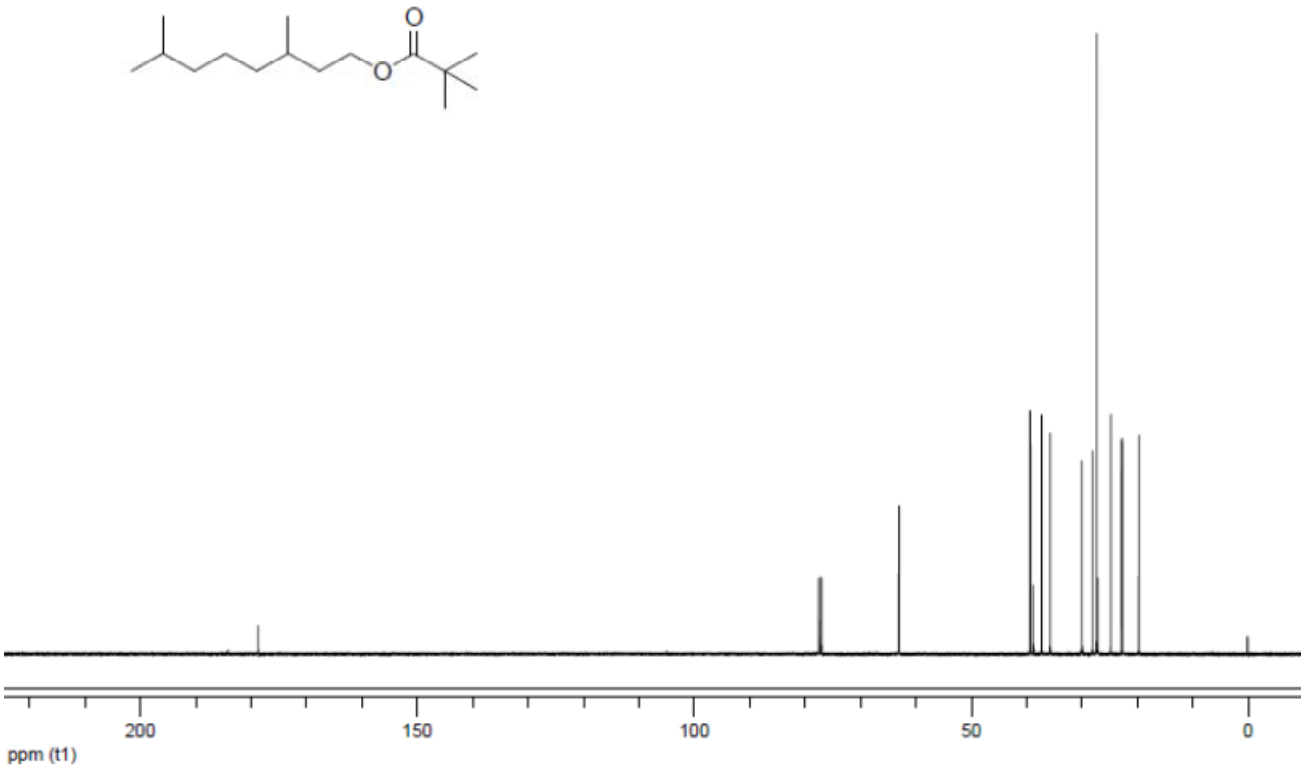
3,7-dimethyloctyl 4-*tert*-butylbenzoate (3b)



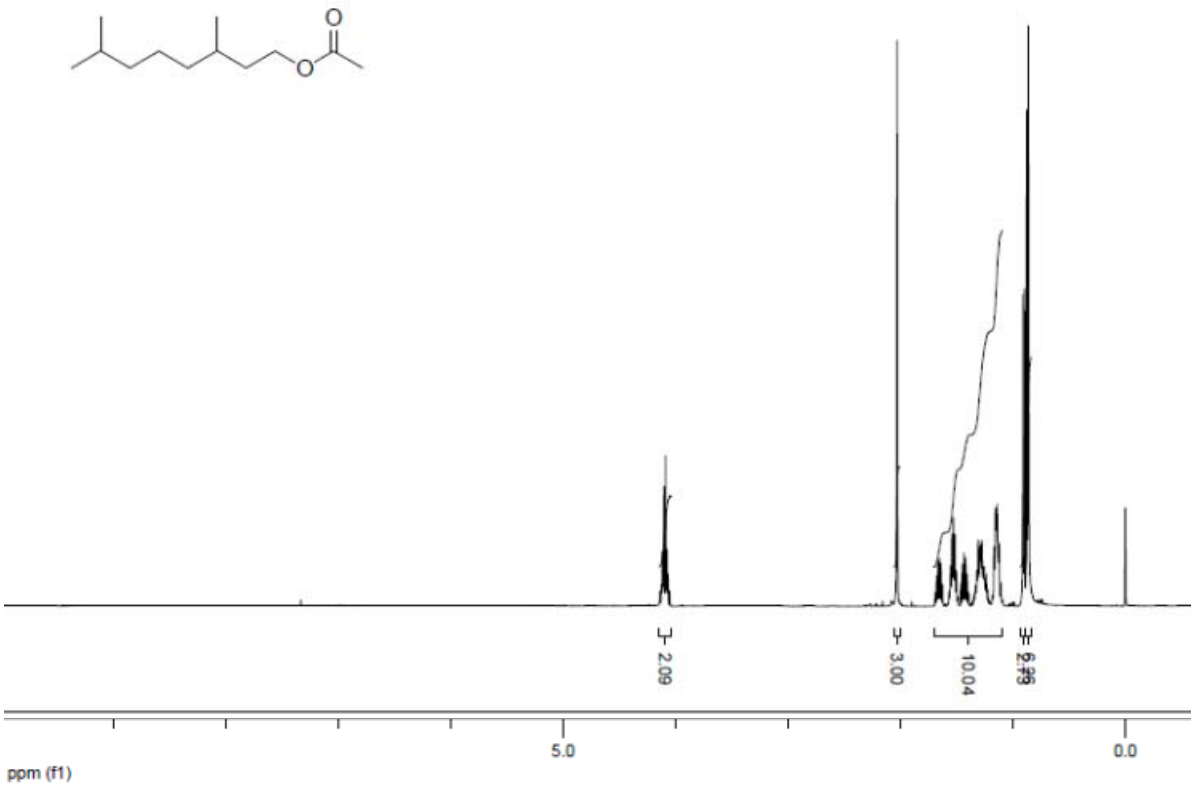


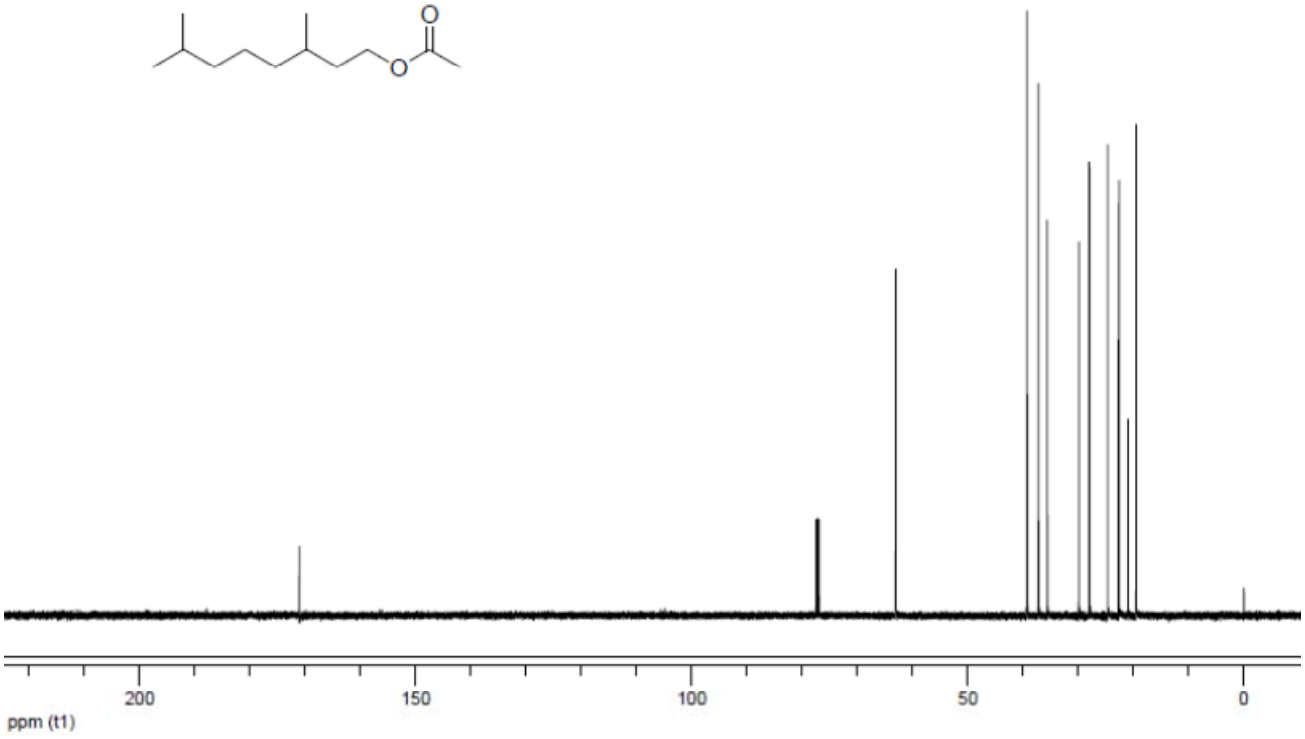
3,7-dimethyloctyl pivalate (3c)



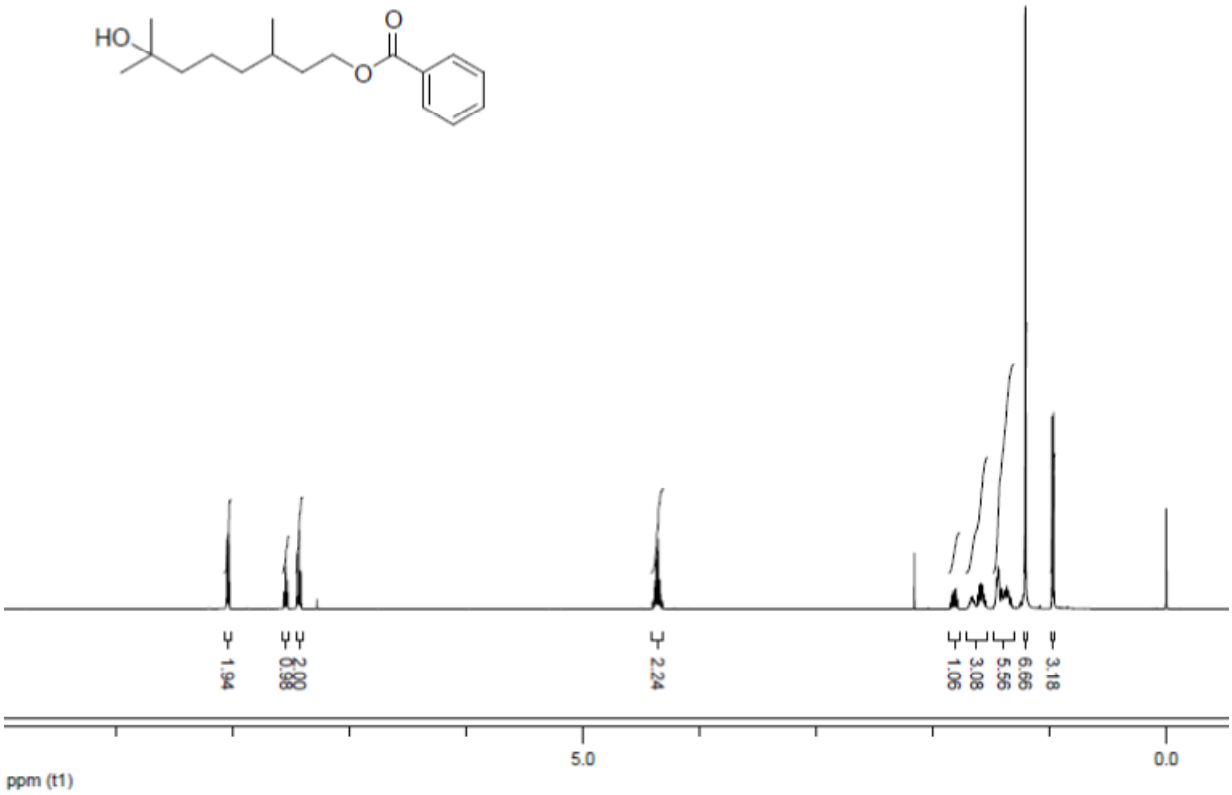


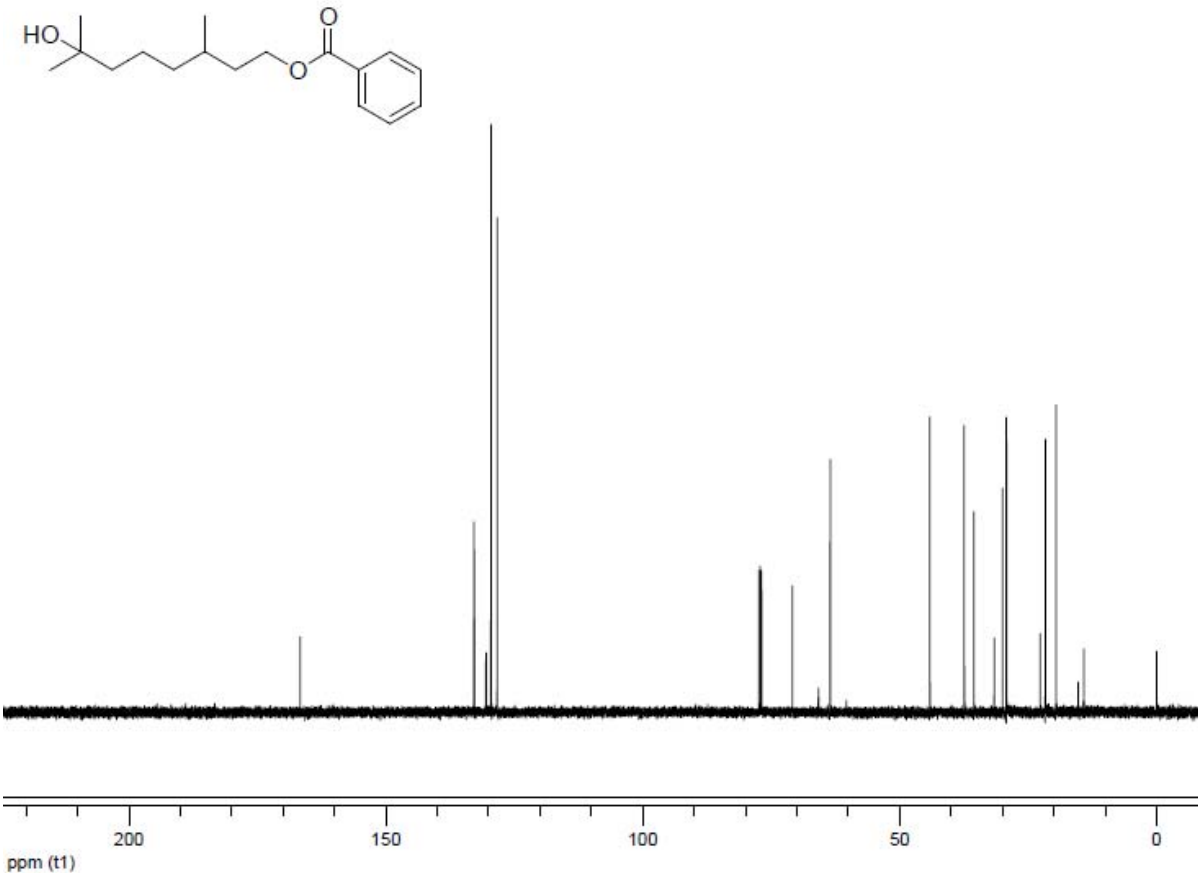
3,7-dimethyloctyl acetate (3d)



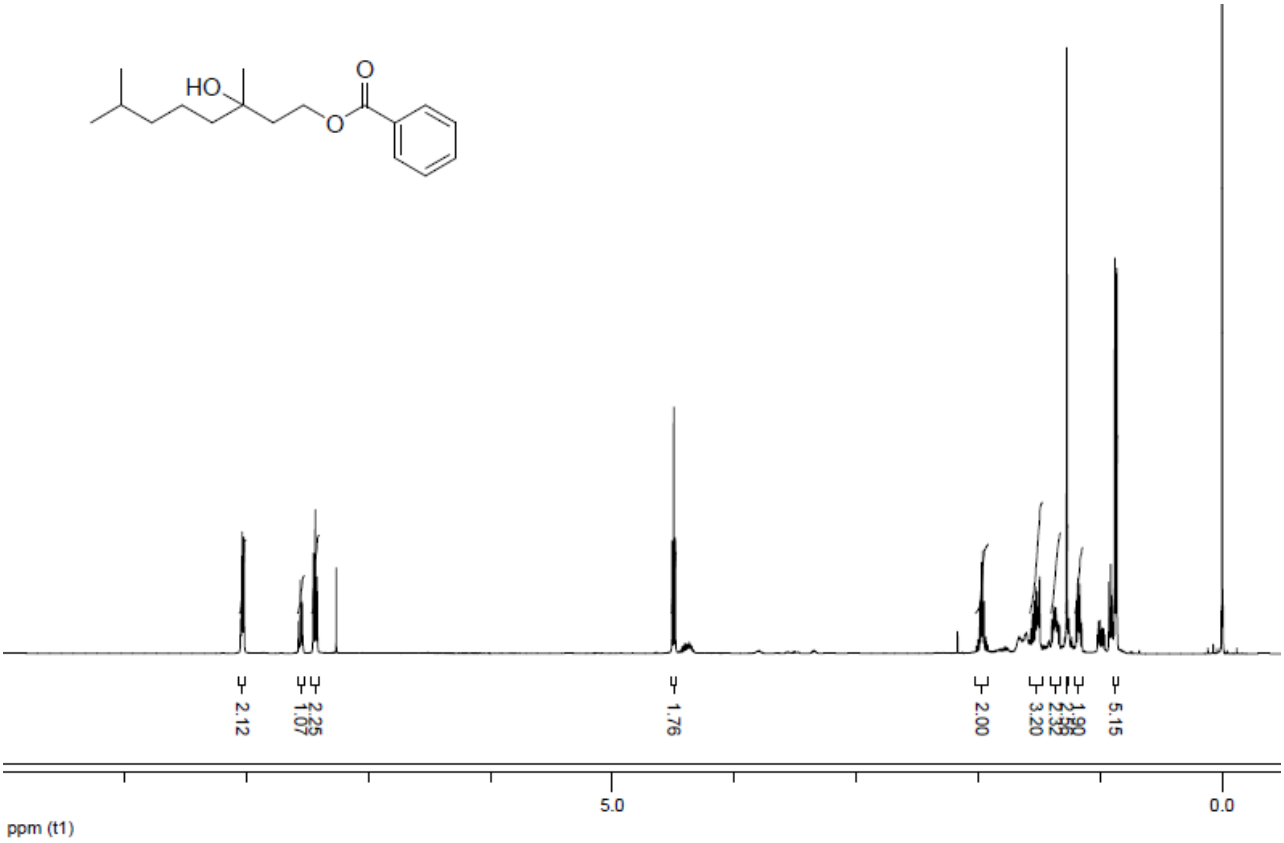


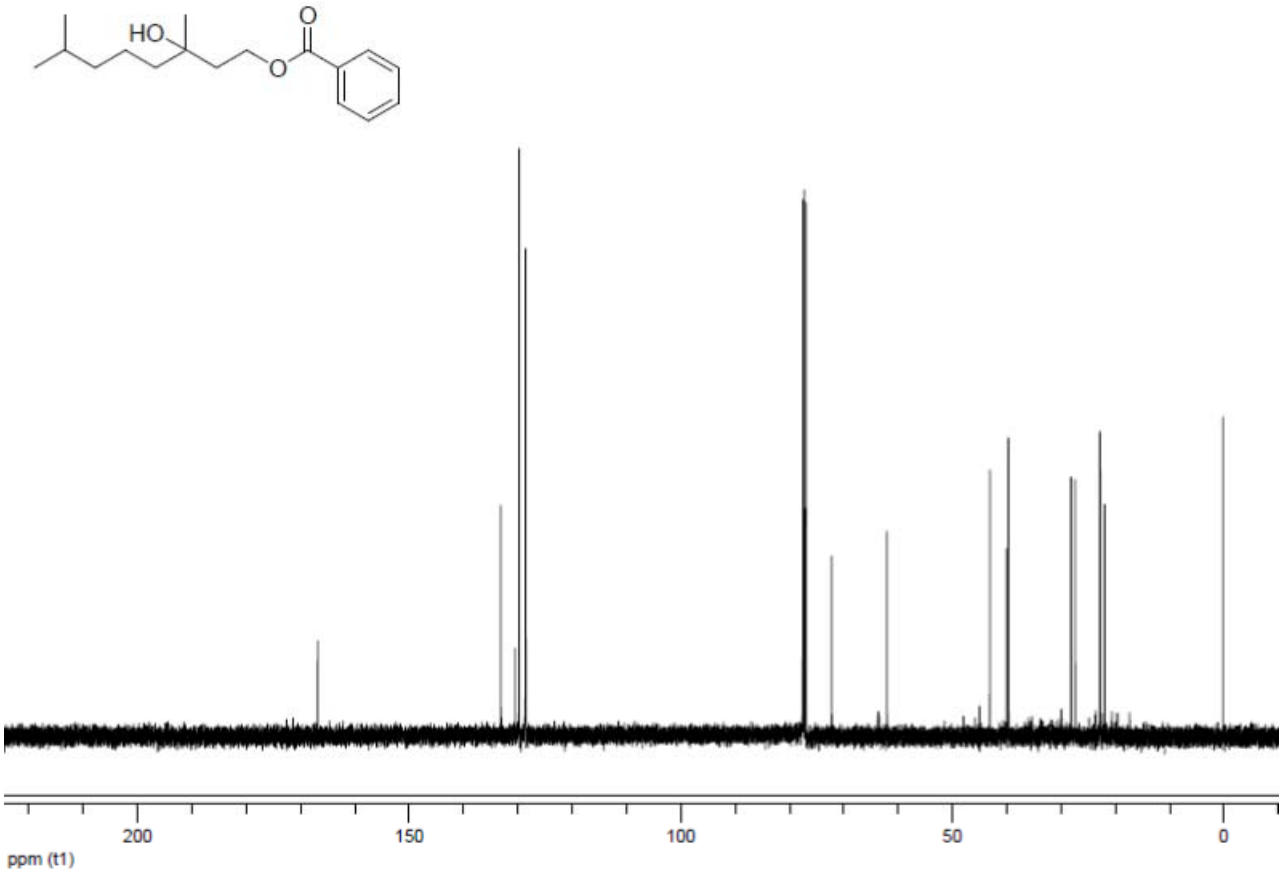
7-hydroxy-3,7-dimethyloctyl benzoate (4a)



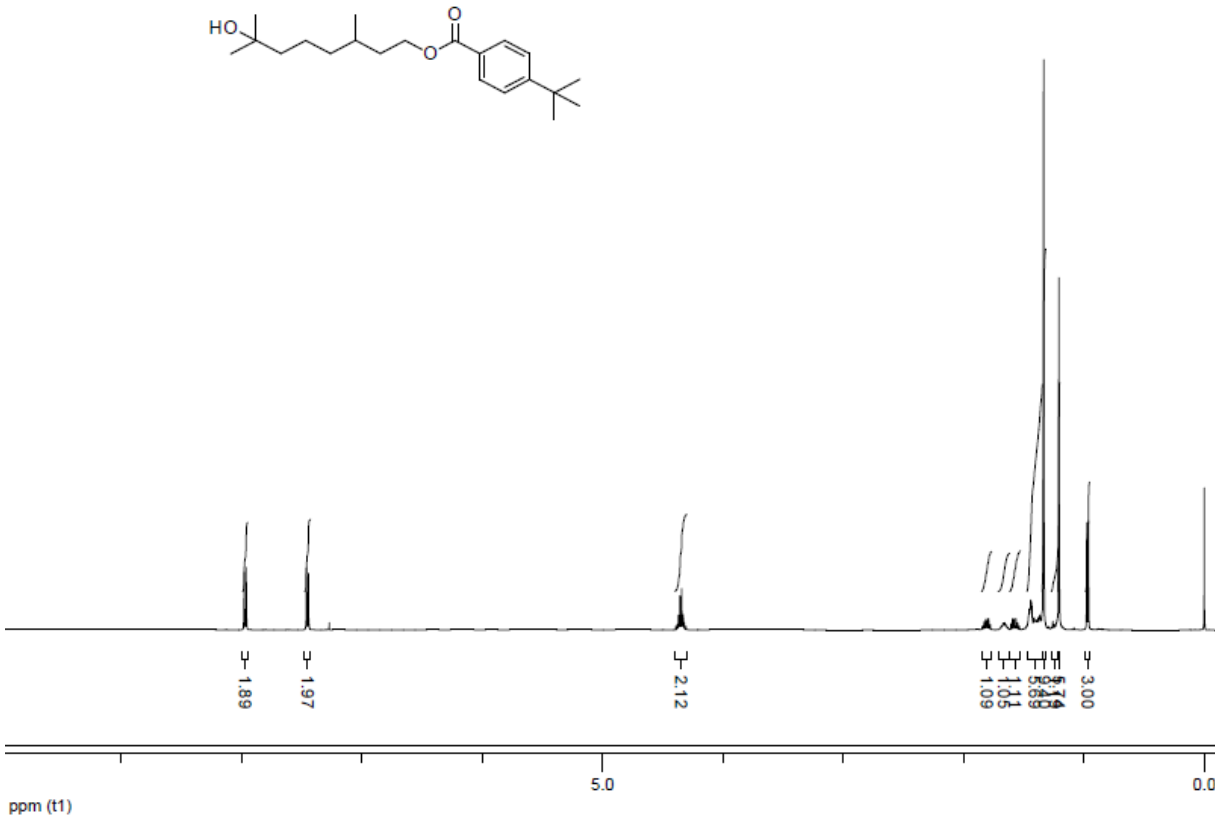


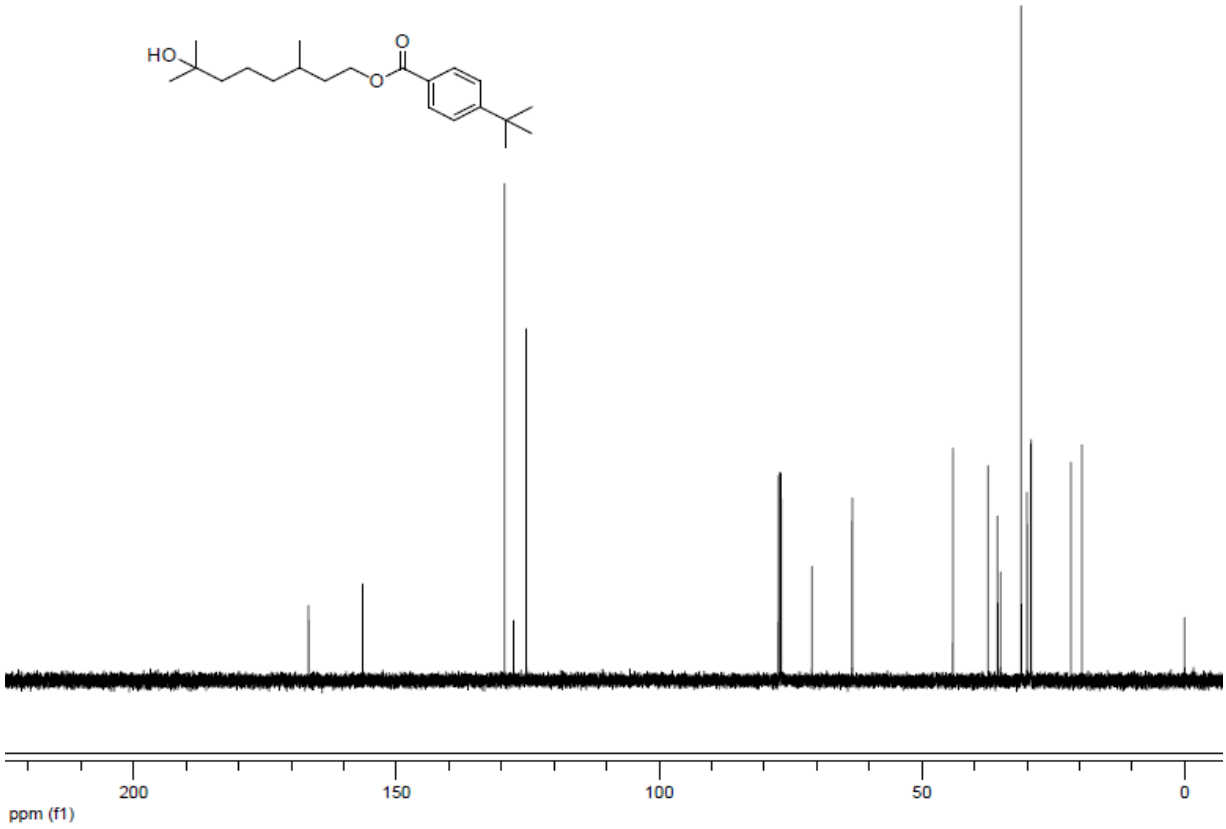
3-hydroxy-3,7-dimethyloctyl benzoate (4a')



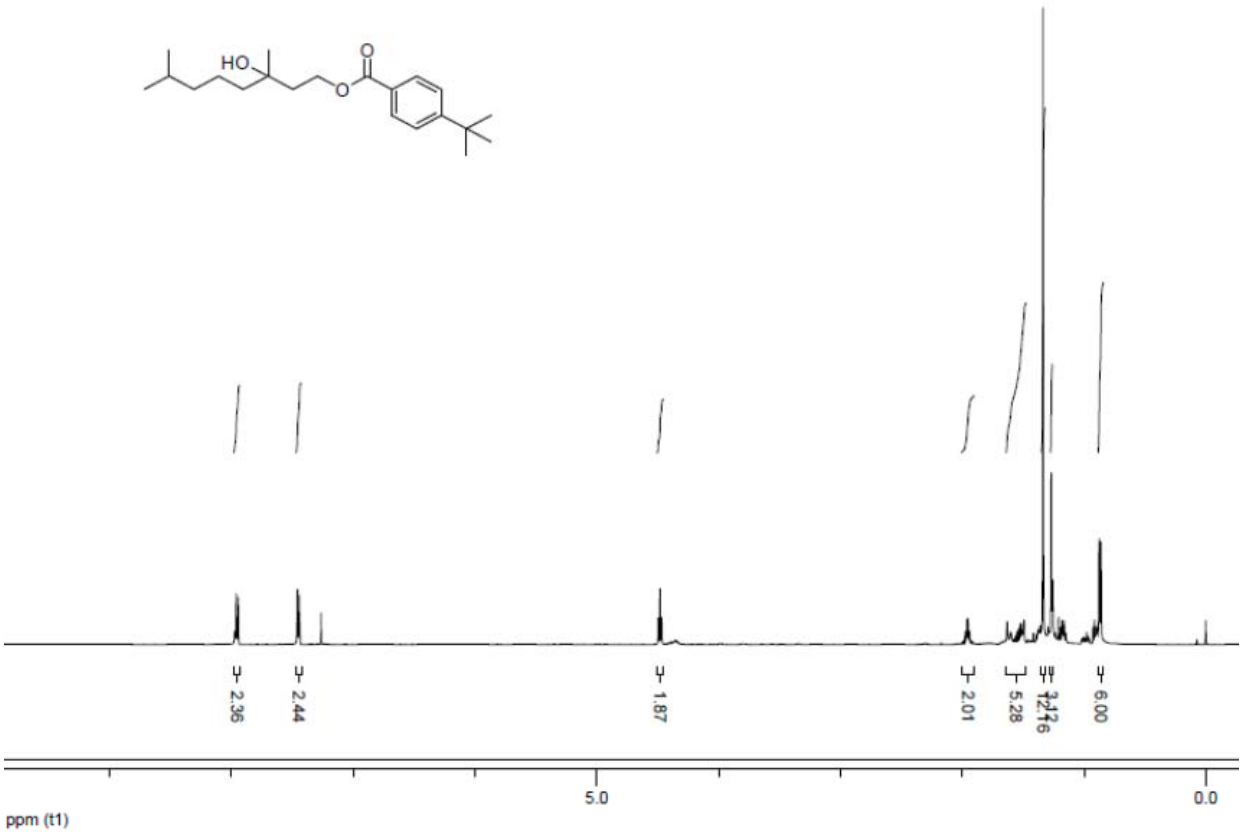


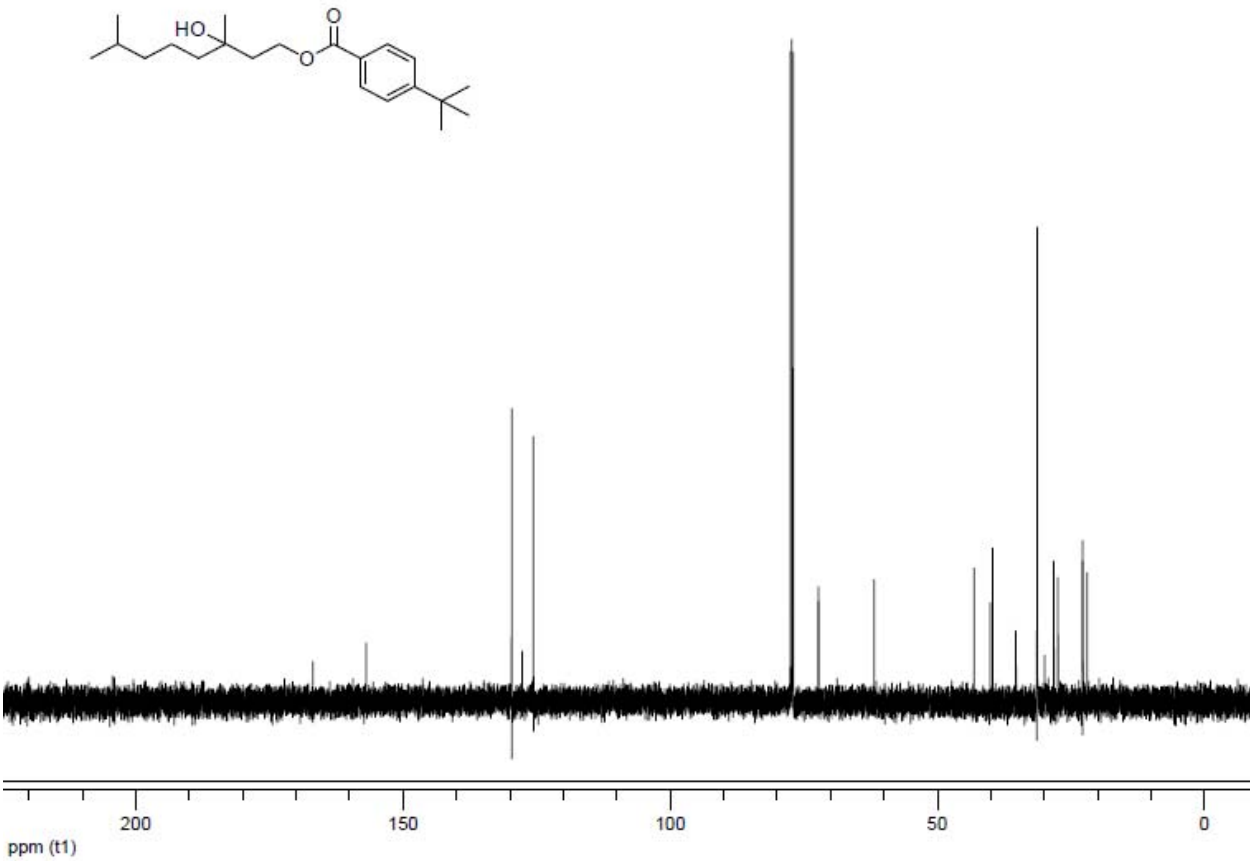
7-hydroxy-3,7-dimethyloctyl 4-*tert*-butylbenzoate (4b)



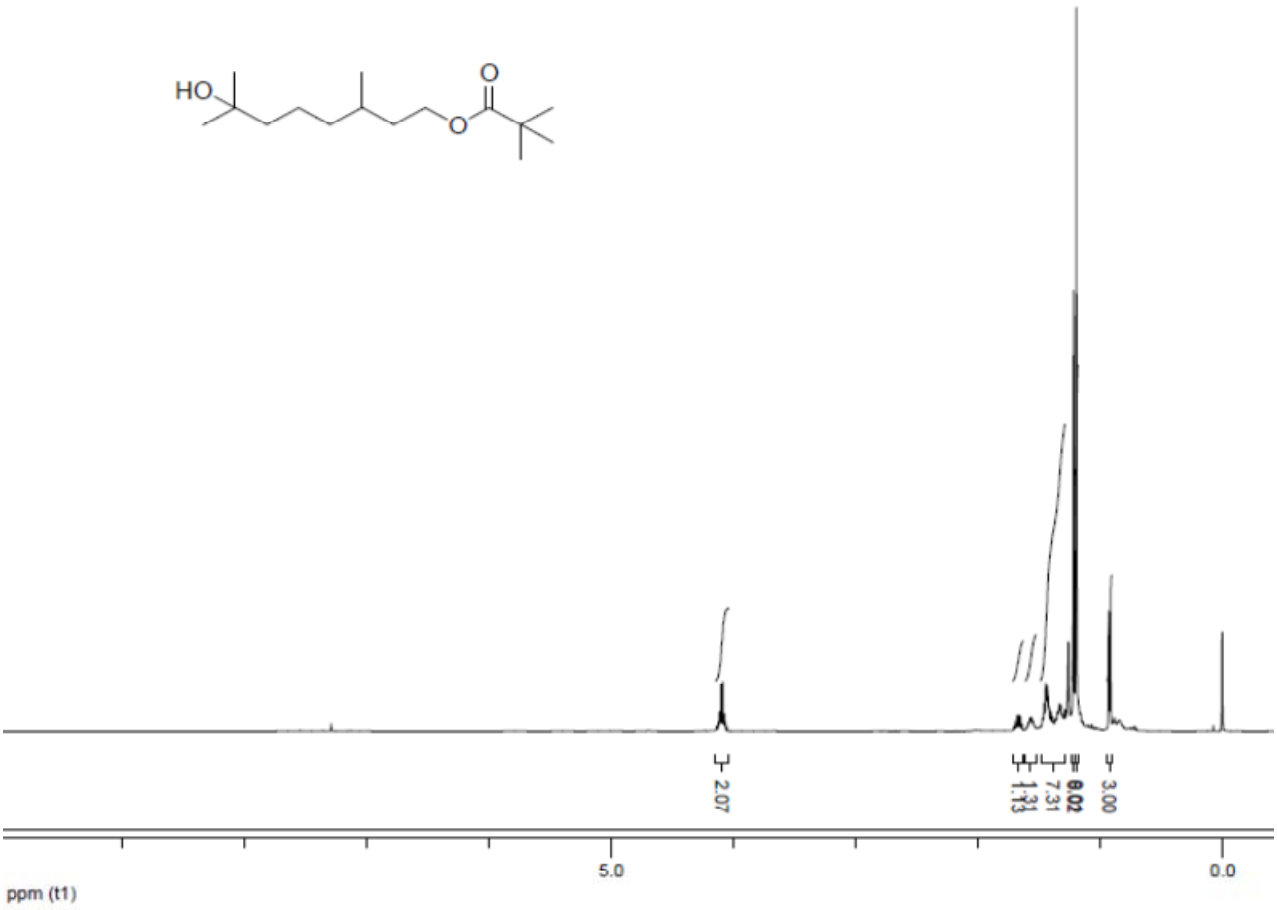


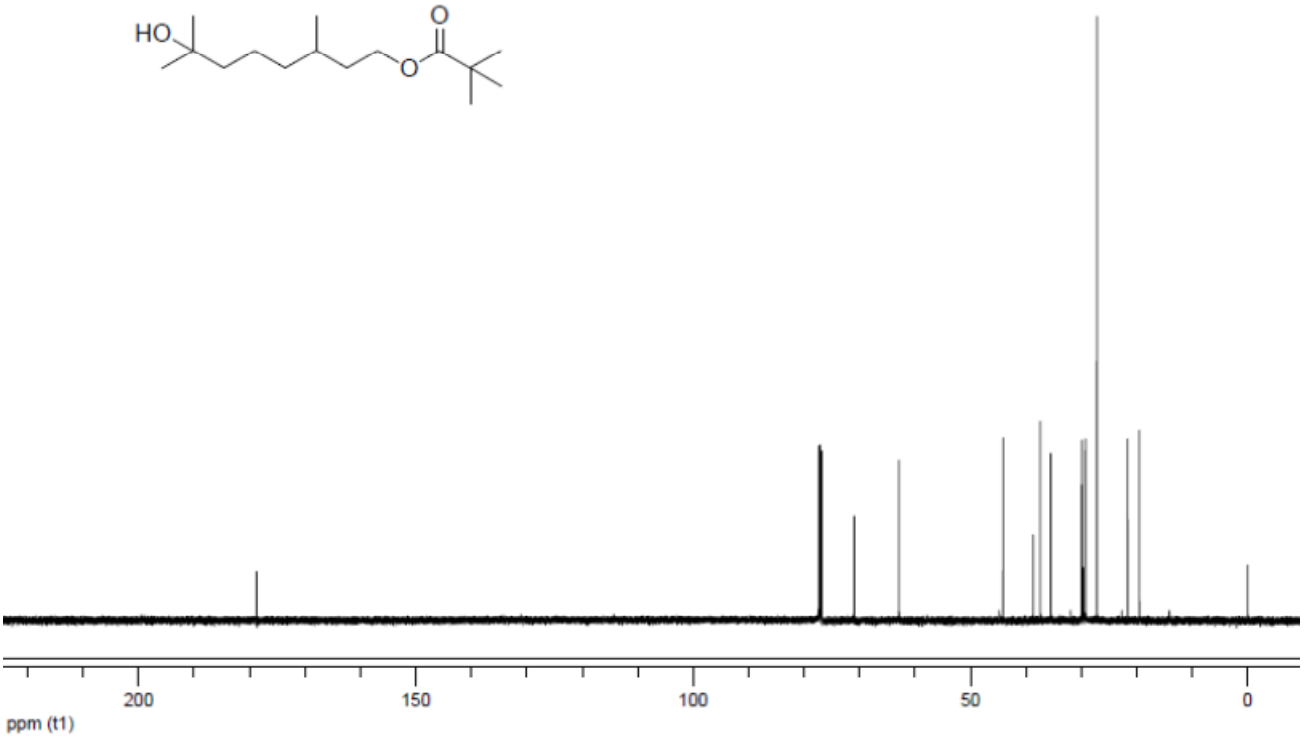
3-hydroxy-3,7-dimethyloctyl 4-*tert*-butylbenzoate (4b')



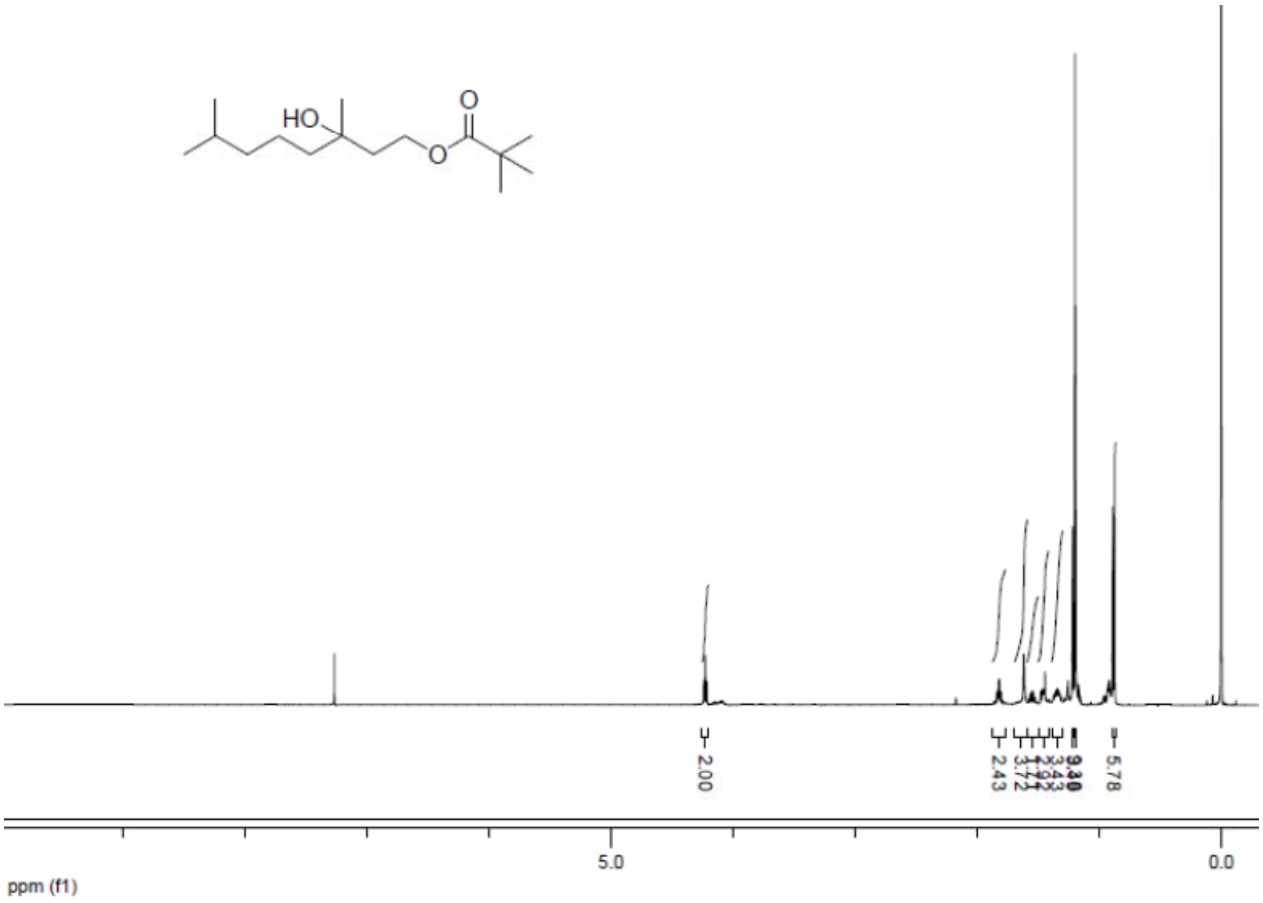


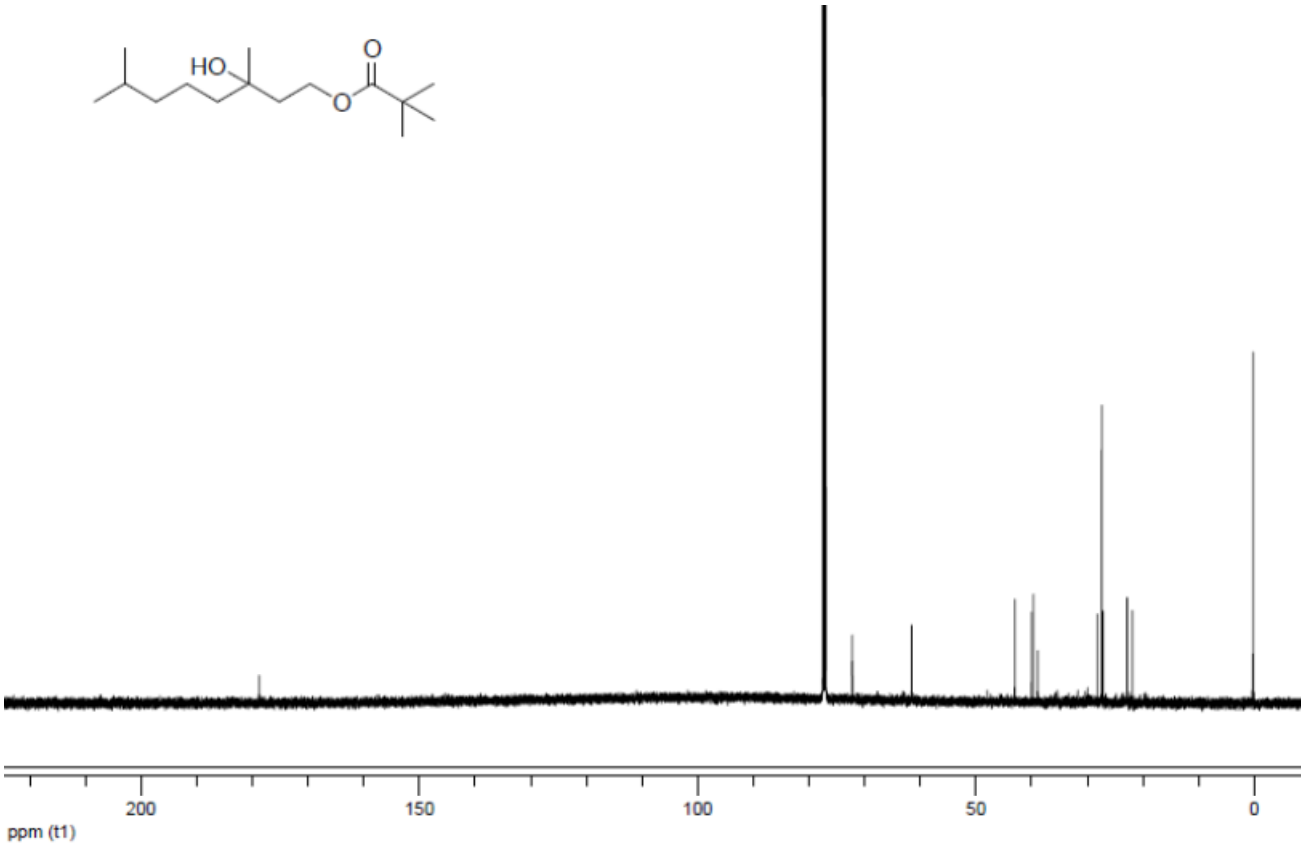
7-hydroxy-3,7-dimethyloctyl pivalate (4c)



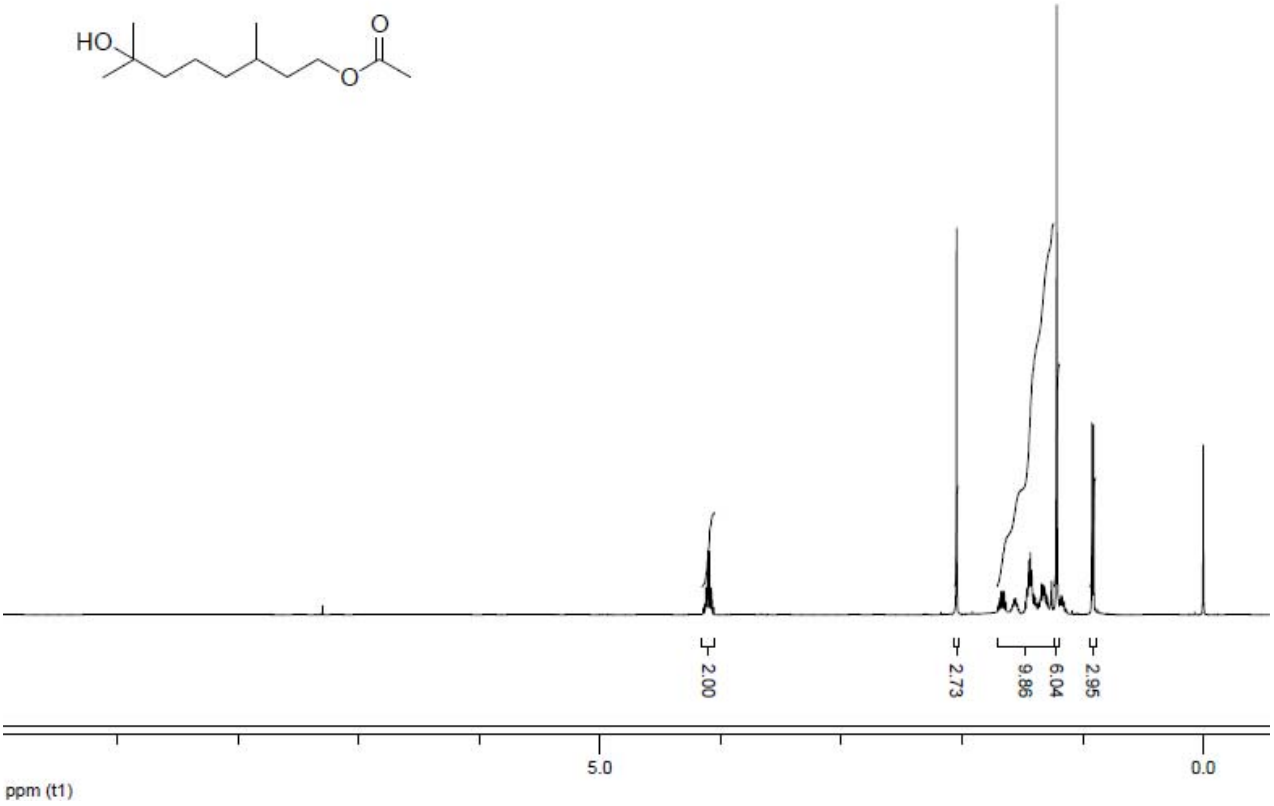


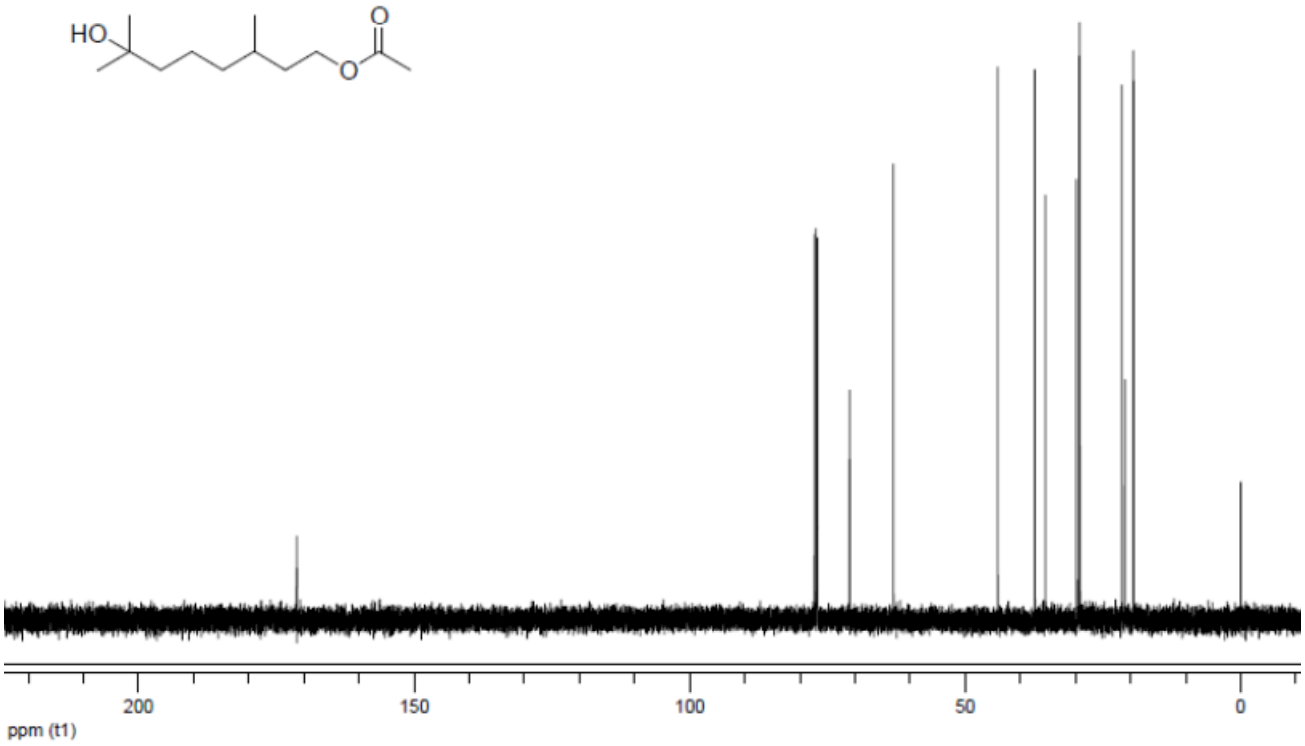
3-hydroxy-3,7-dimethyloctyl pivalate (4c')



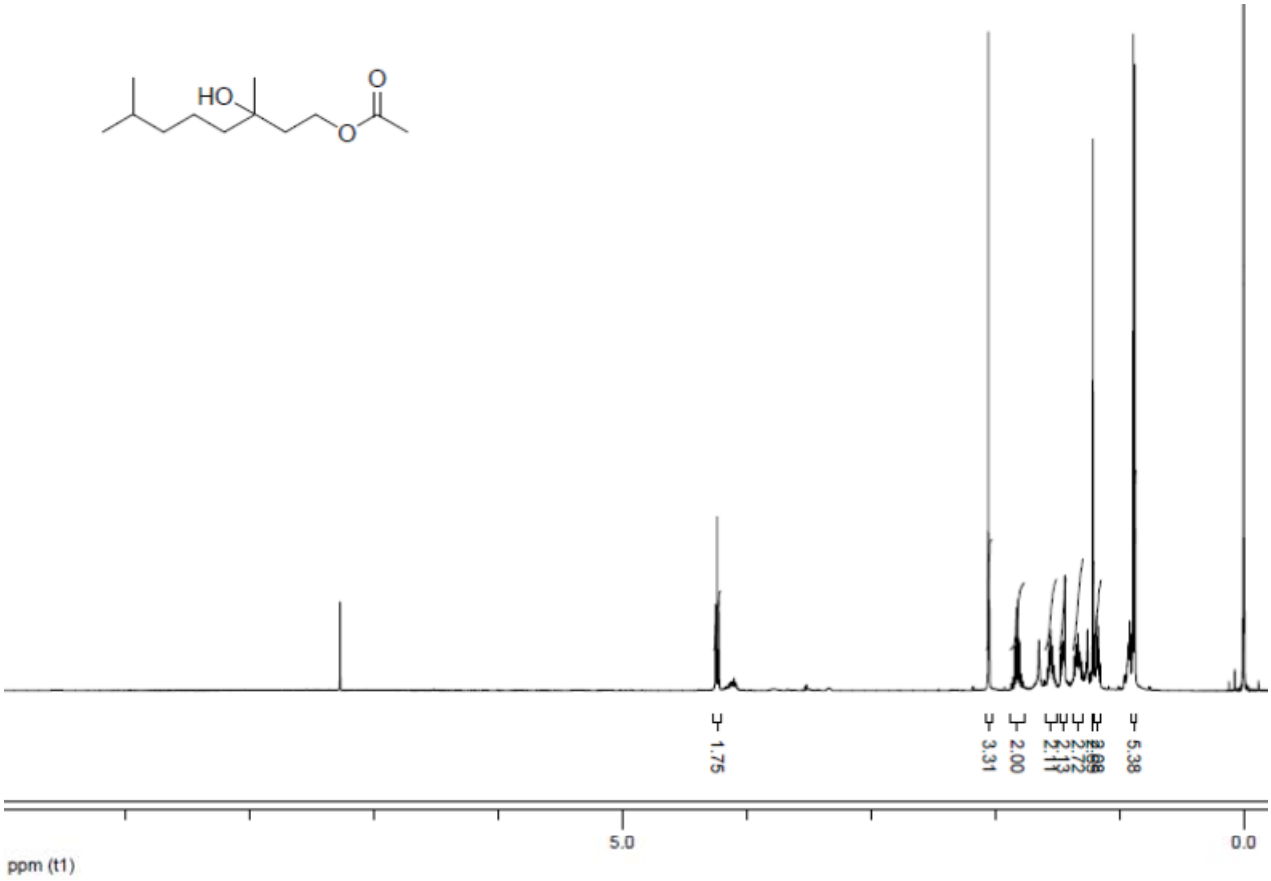


7-hydroxy-3,7-dimethyloctyl acetate (4d)





3-hydroxy-3,7-dimethyloctyl acetate (4d')



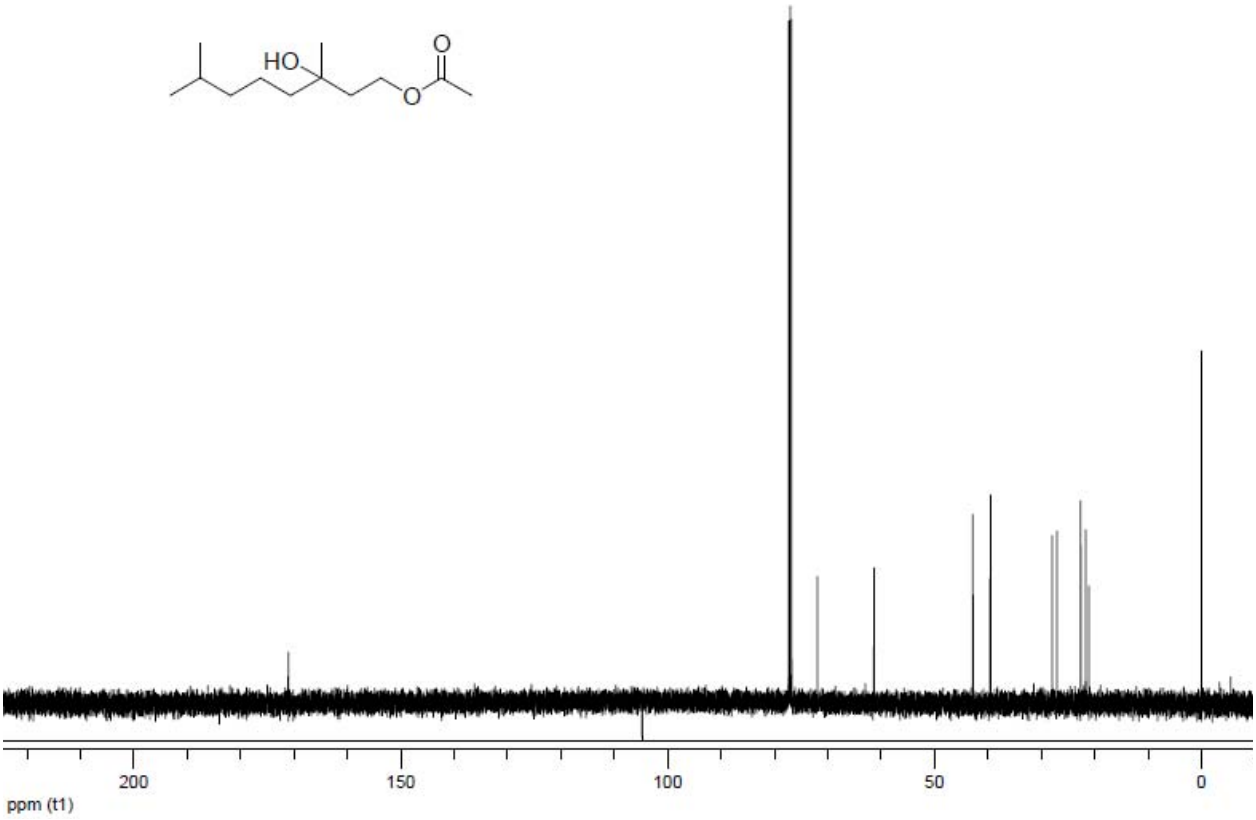
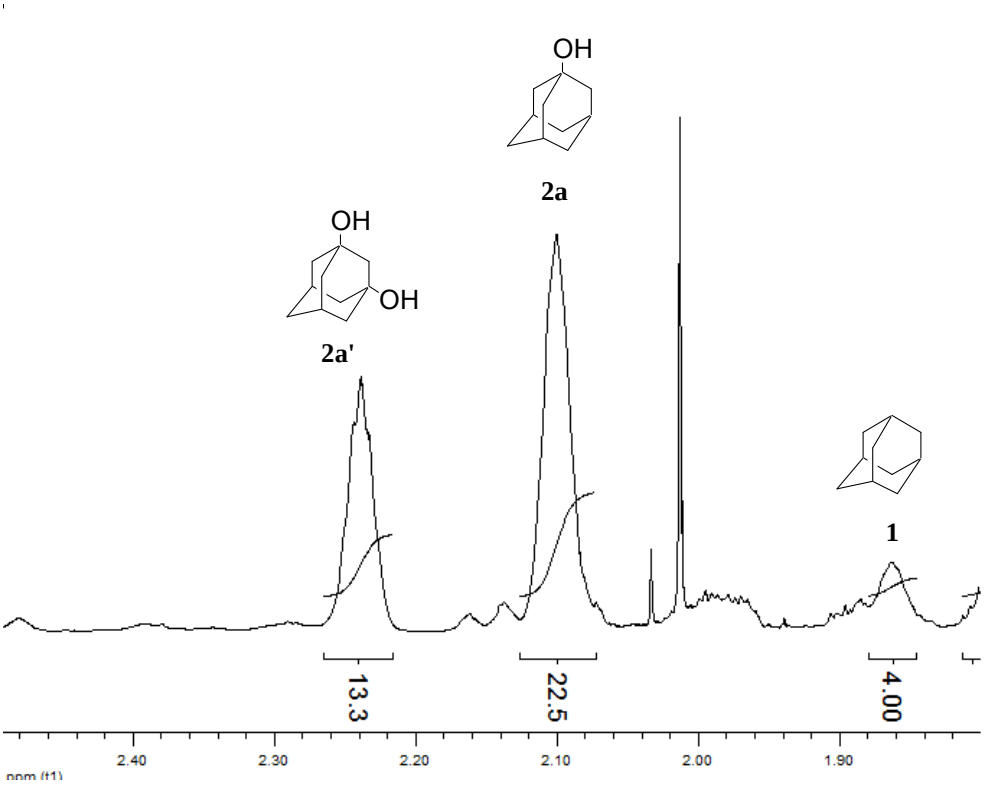


Table 1, entry 1 (Table S3, entry 3; Table S4, entry 2)



Calculation of the ratio of adamantane (1) to products (Table 1, entry 1)

1 : **2a** : **2a'**

= [4/4 ÷ (4/4 + 22.5/3 + 13.3/2) × 100] : [22.5/3 ÷ (4/4 + 22.5/3 + 13.3/2) × 100] : [13.3/2 ÷ (4/4 + 22.5/3 + 13.3/2) × 100]

= 7 : 50 : 43

Table 1, entry 2

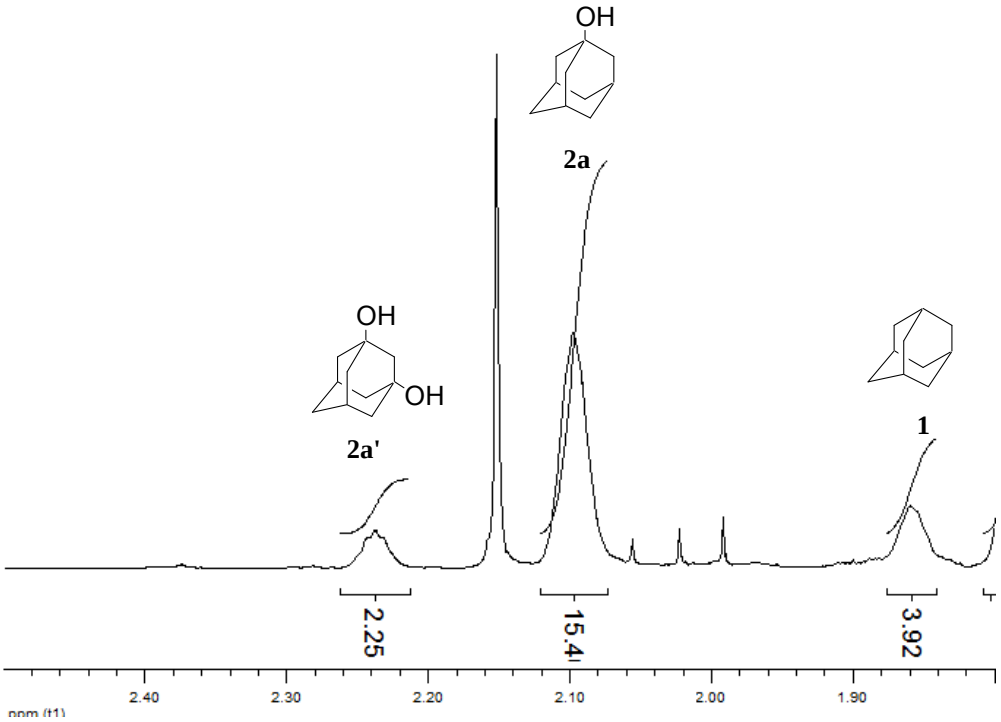


Table 1, entry 3

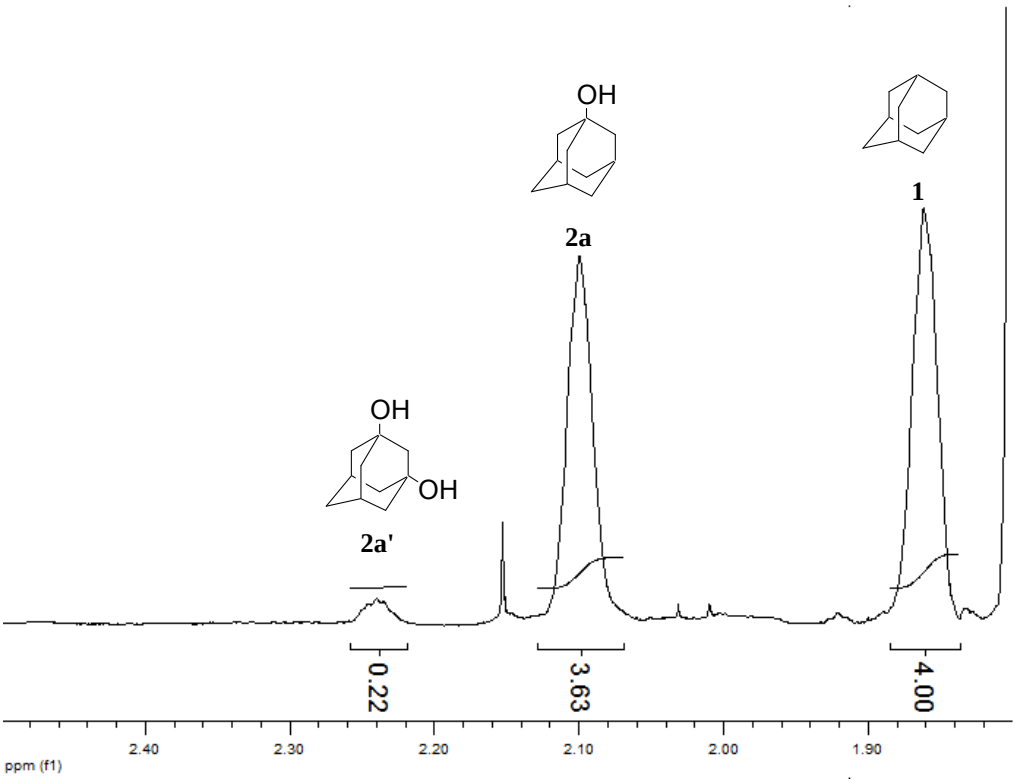


Table 1, entry 4

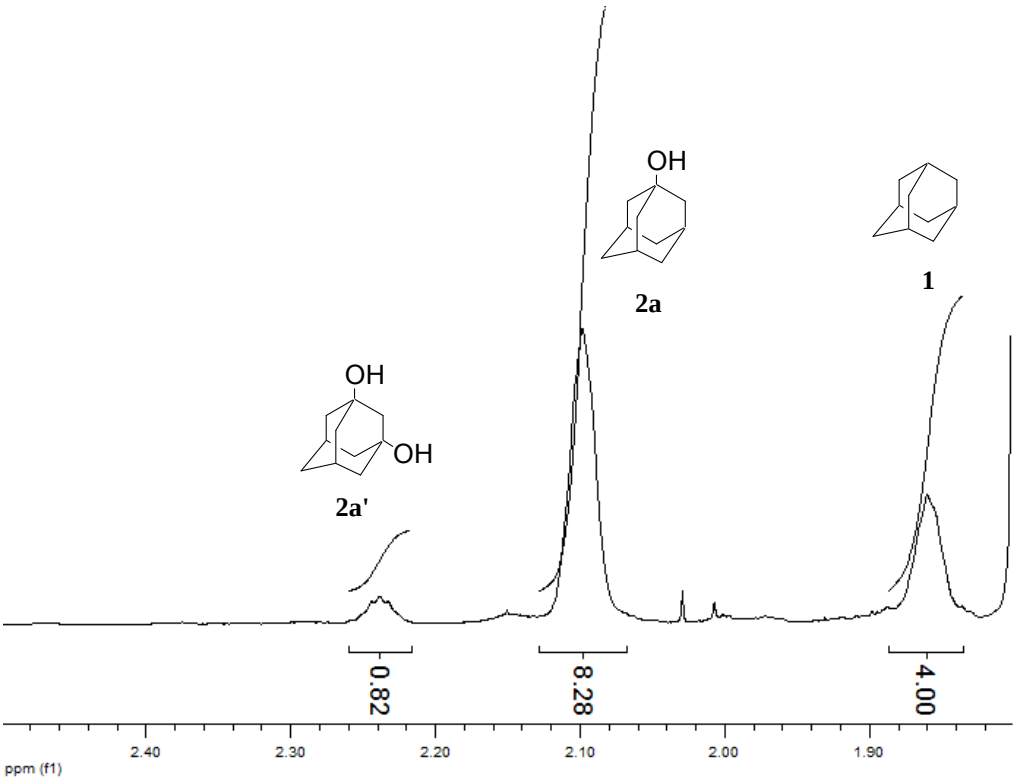


Table 1, entry 5

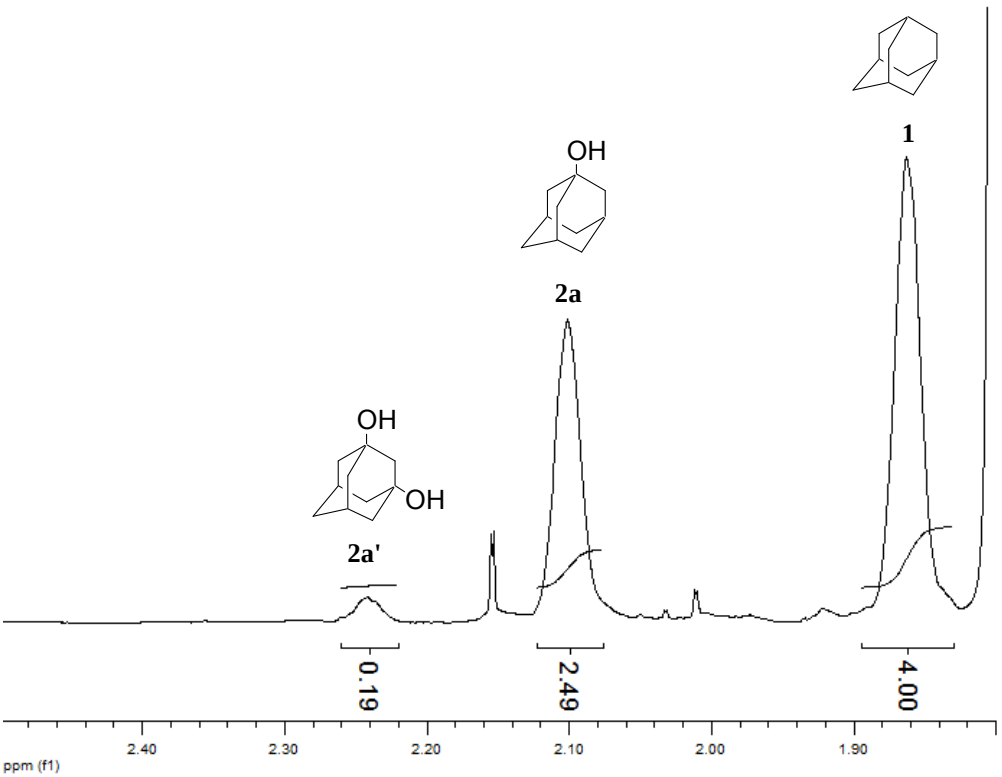


Table 1, entry 6

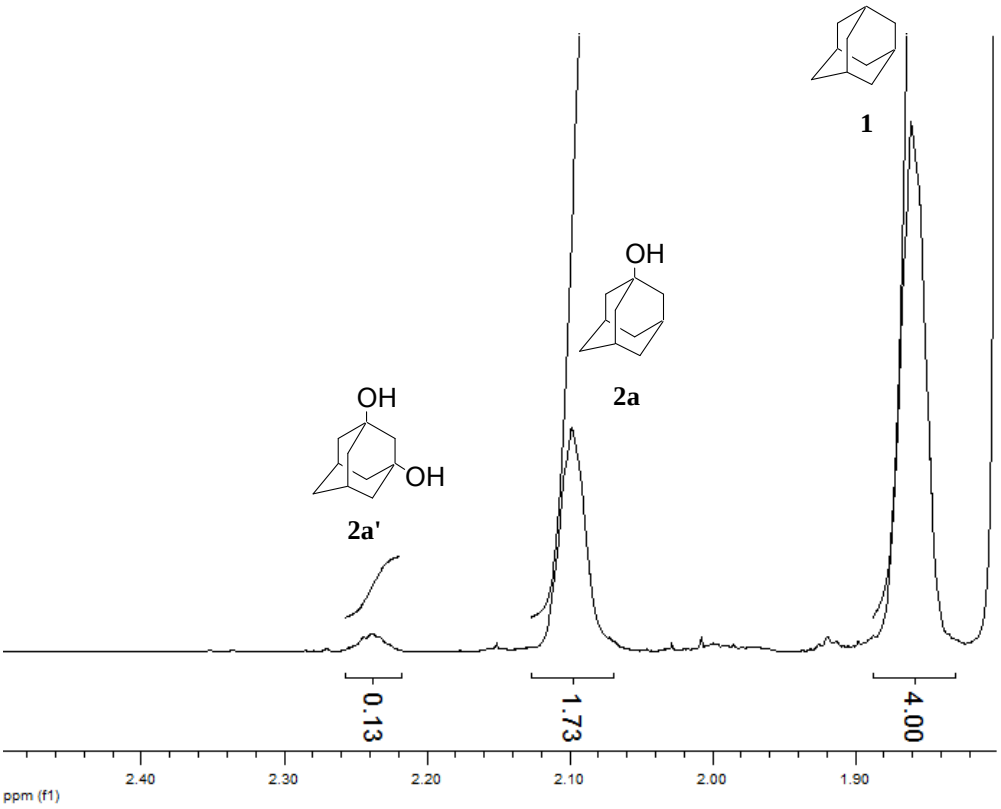


Table 1, entry 7

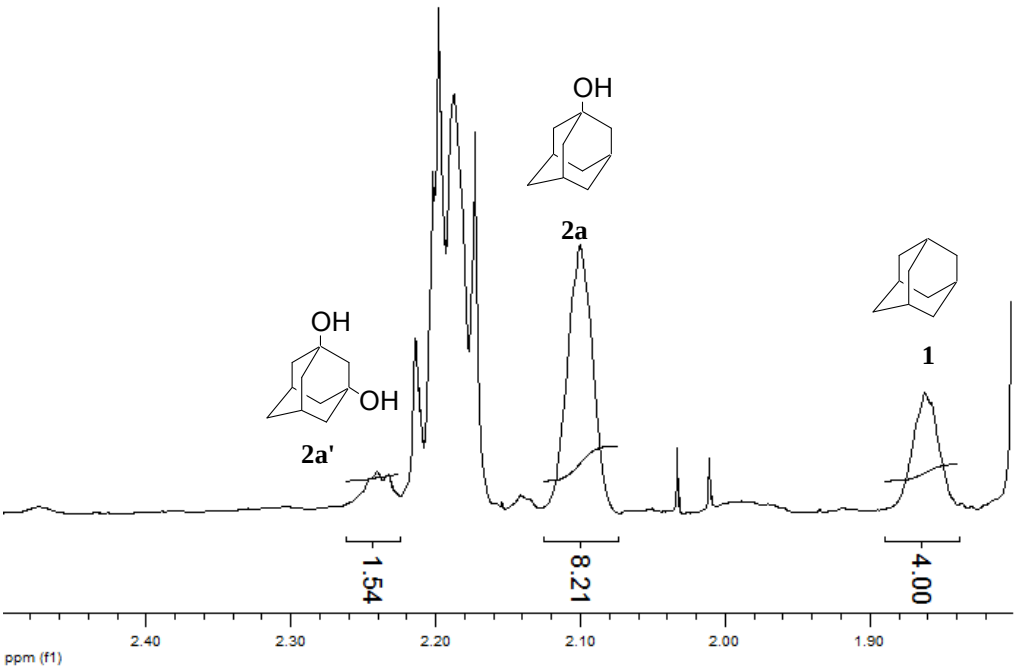


Table 1, entry 8

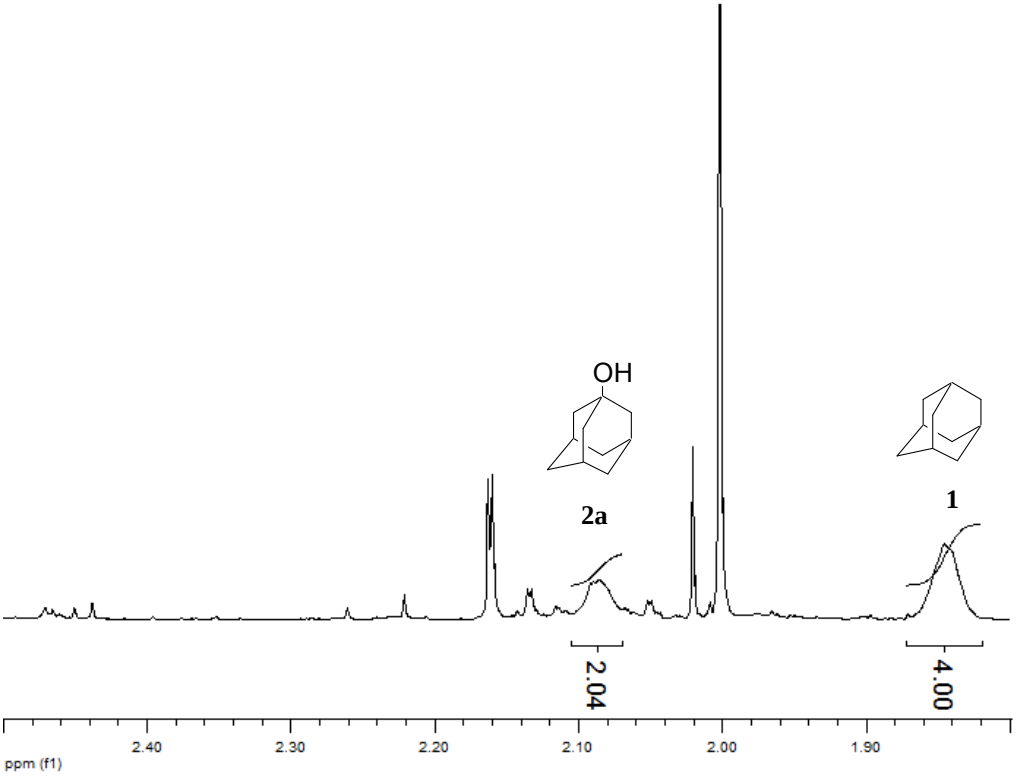


Table 2, entry 1 (Table 3, entry 2; Table S6, entry 3)

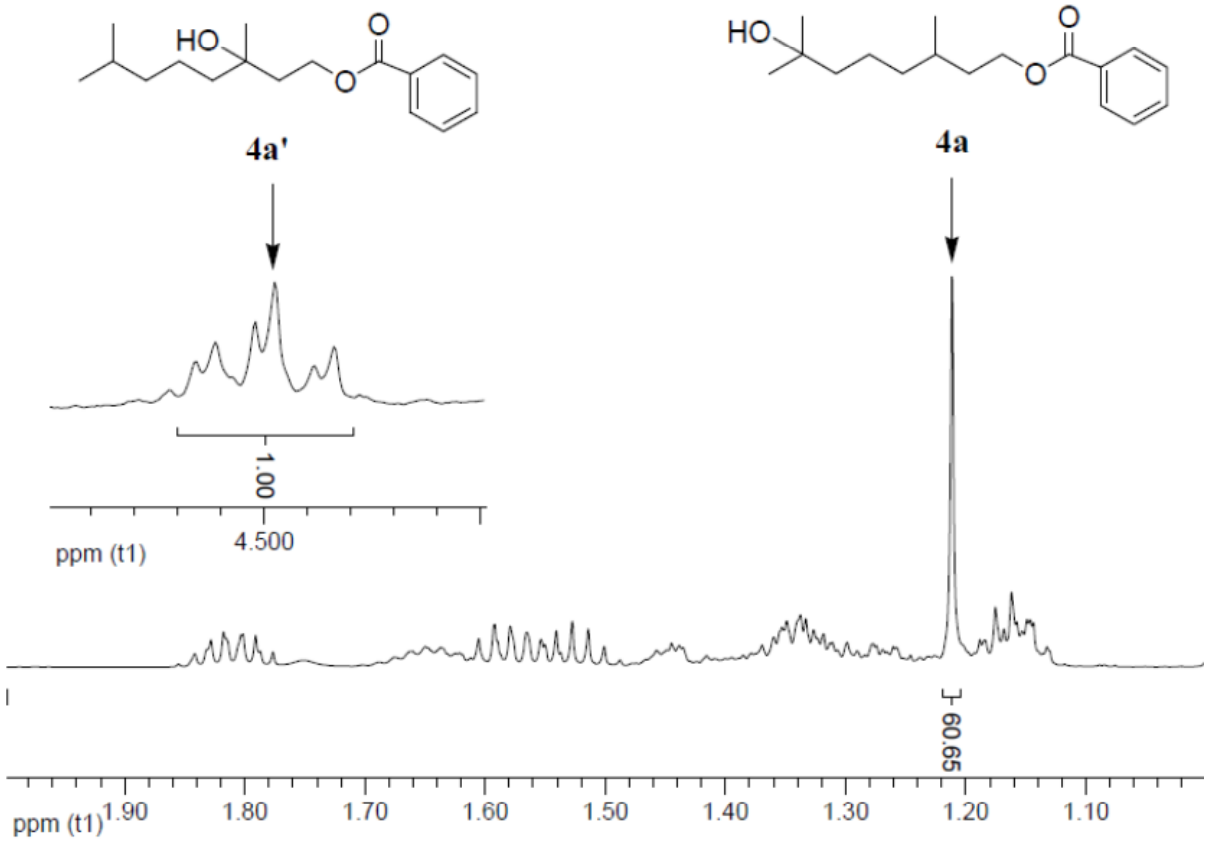


Table 2, entry 2 (Table 3, entry 4)

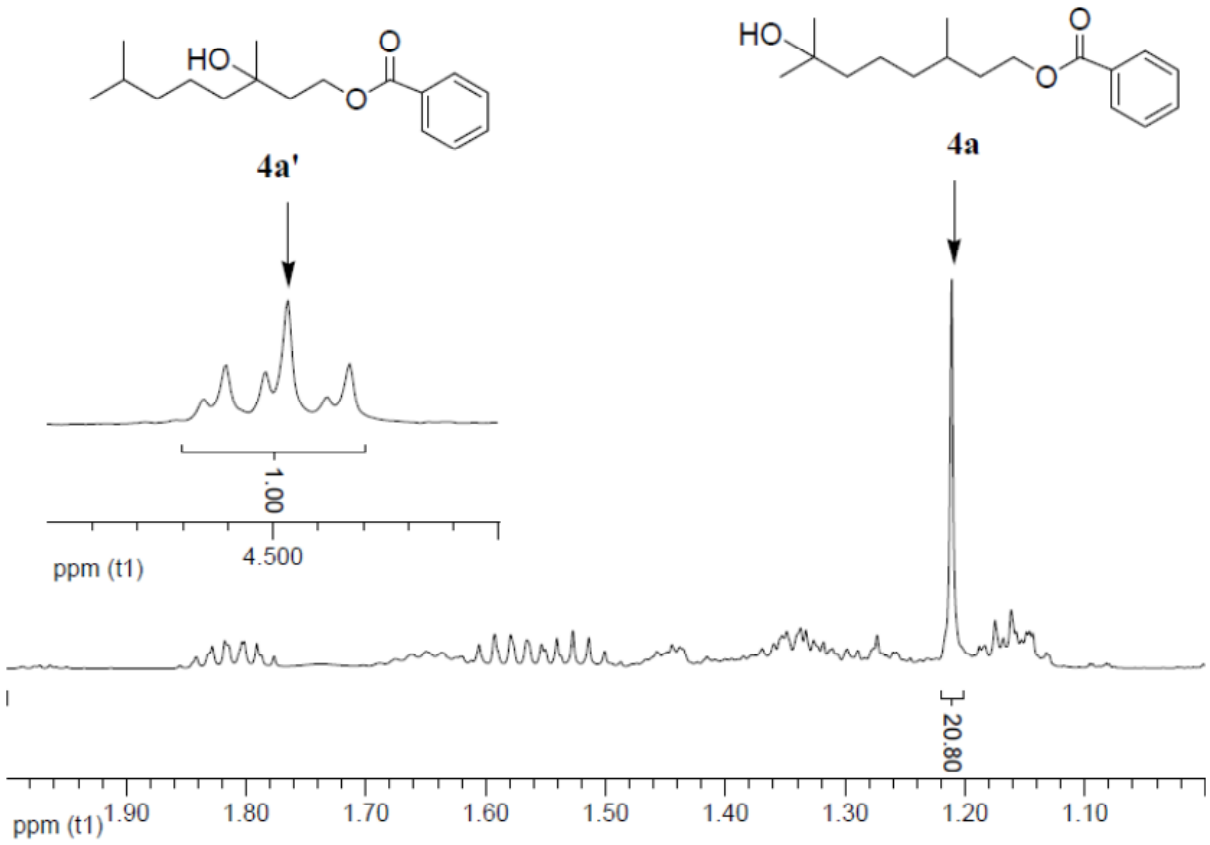


Table 2, entry 3

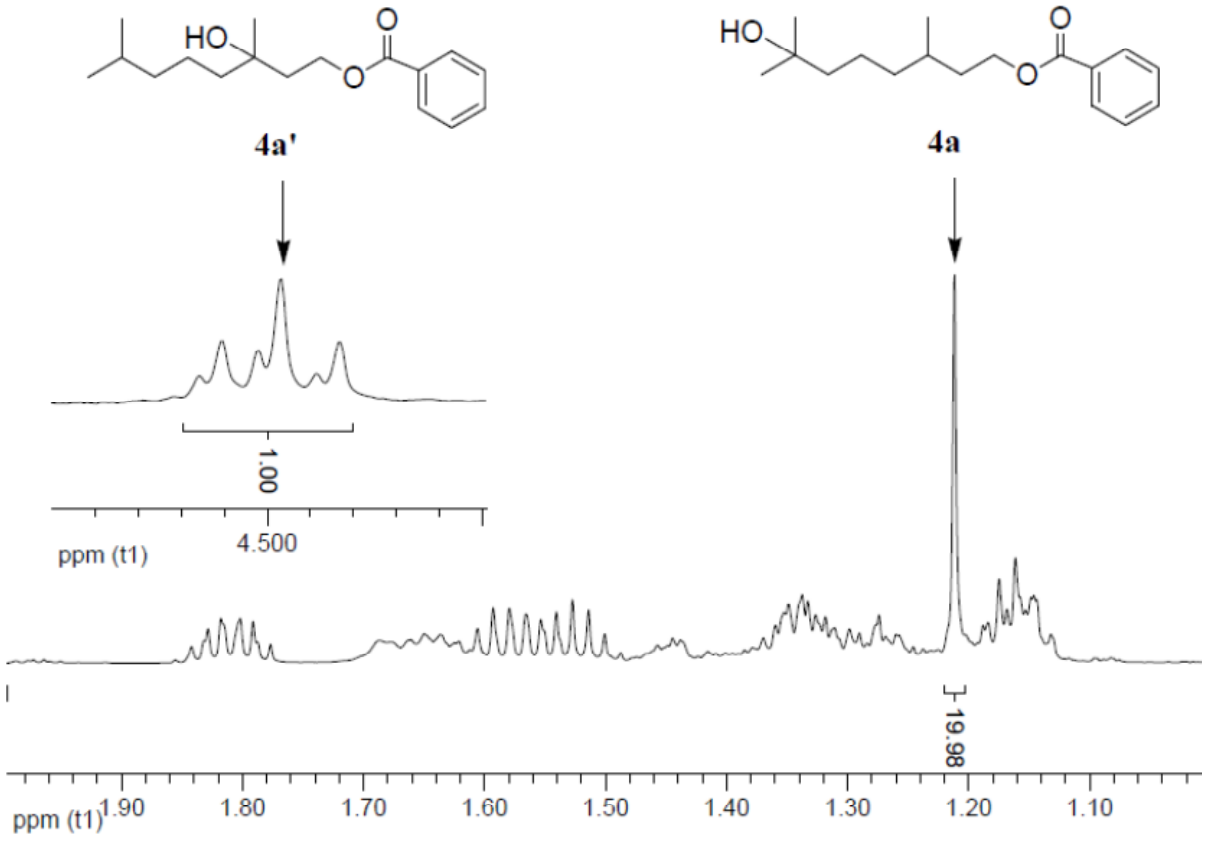


Table 2, entry 4

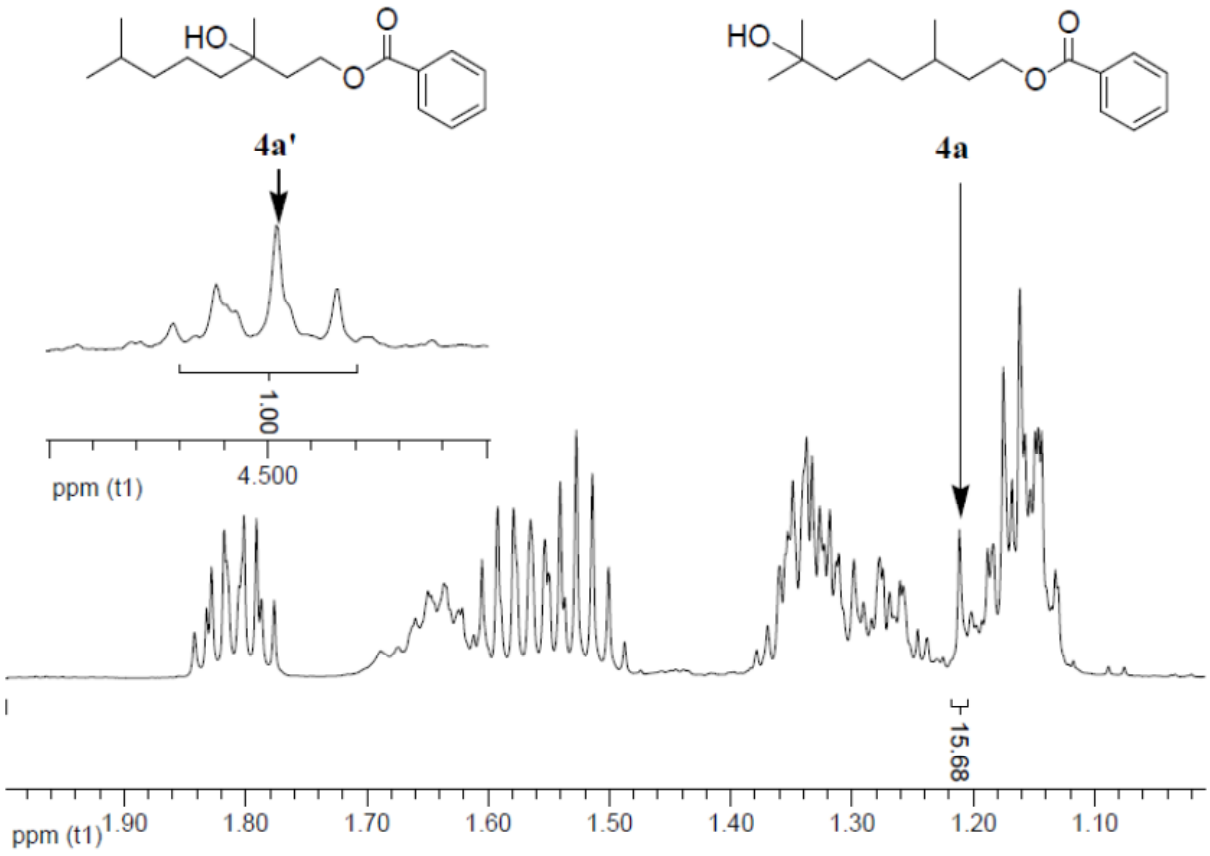


Table 3, entry 1

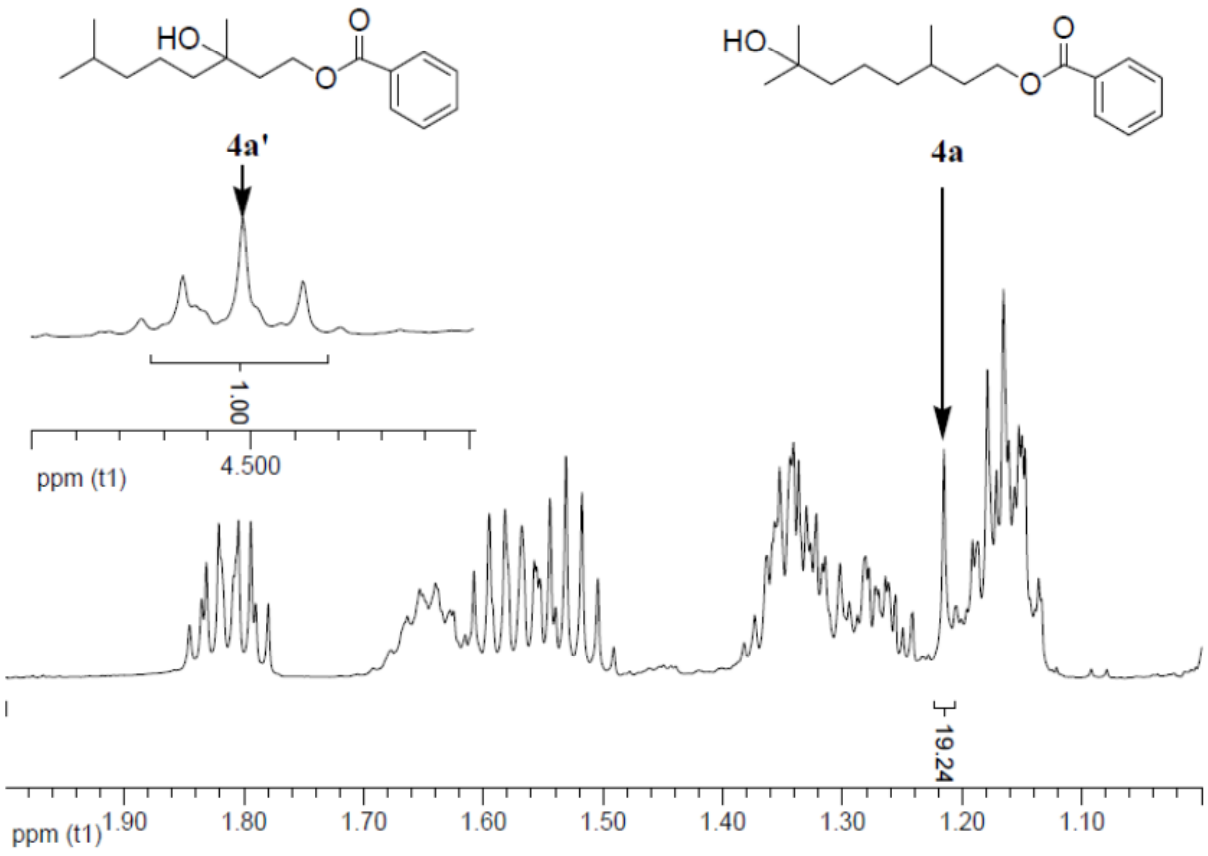


Table 3, entry 3

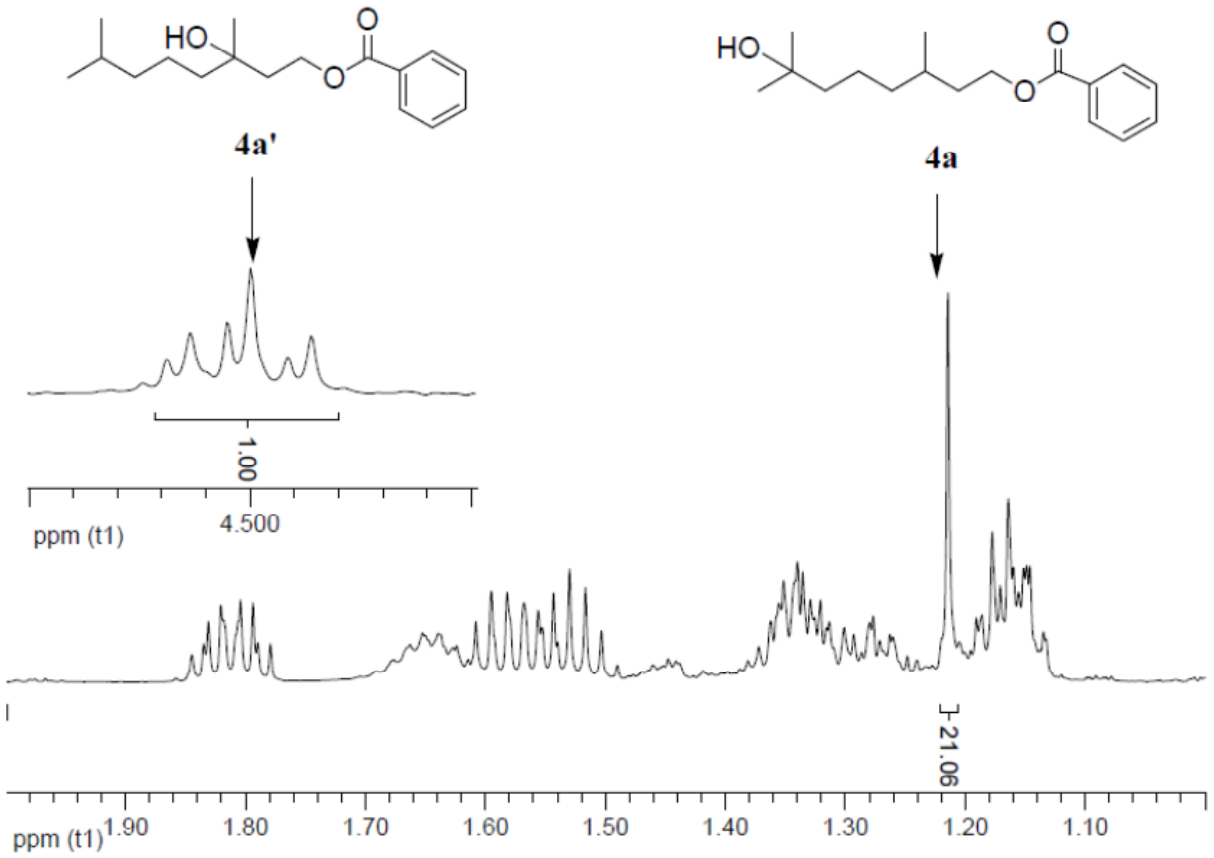


Table 3, entry 5

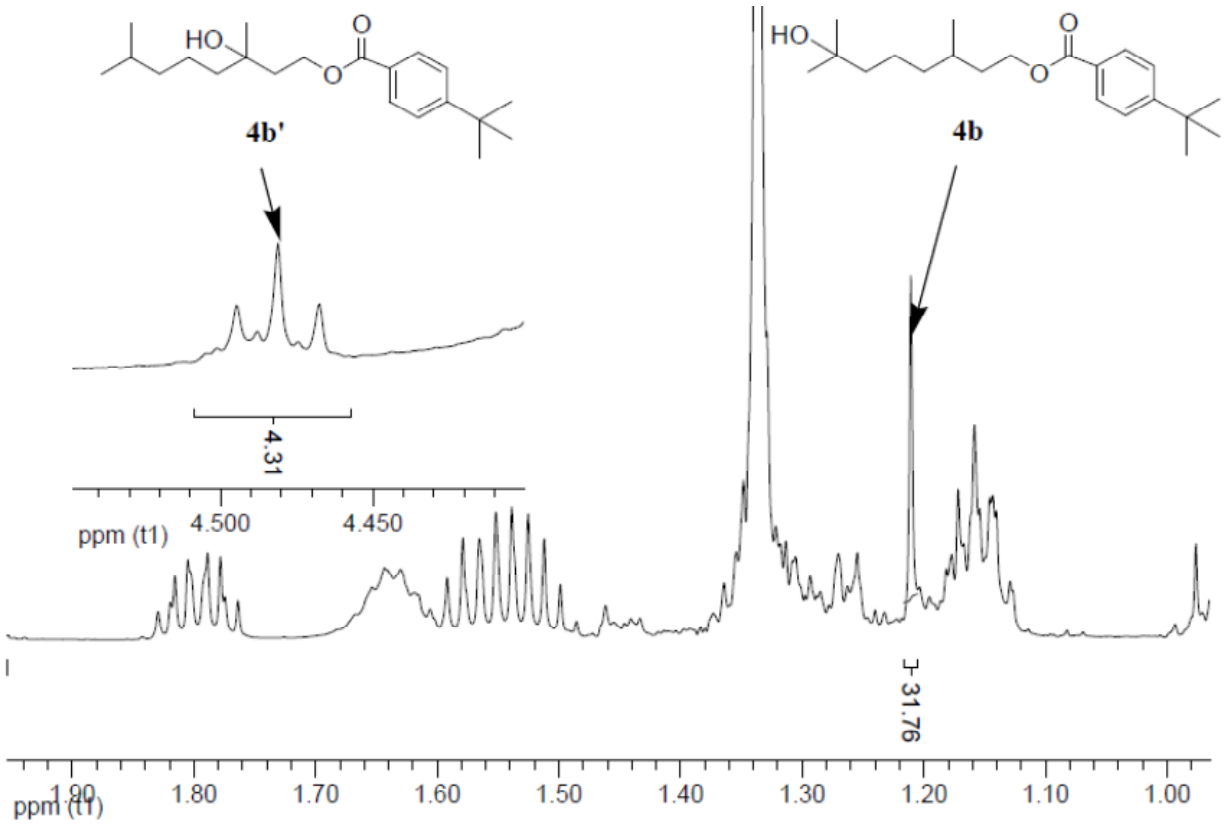


Table 3, entry 6

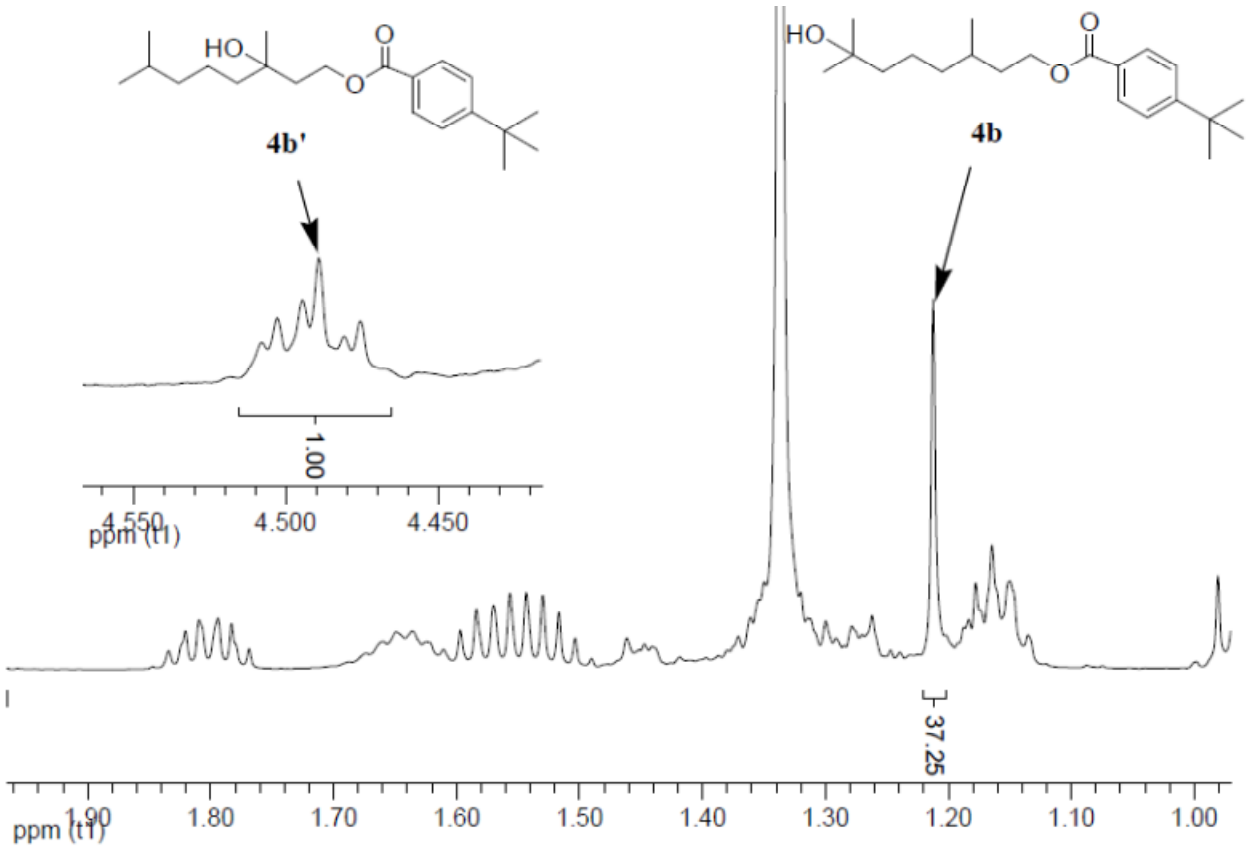


Table 3, entry 7

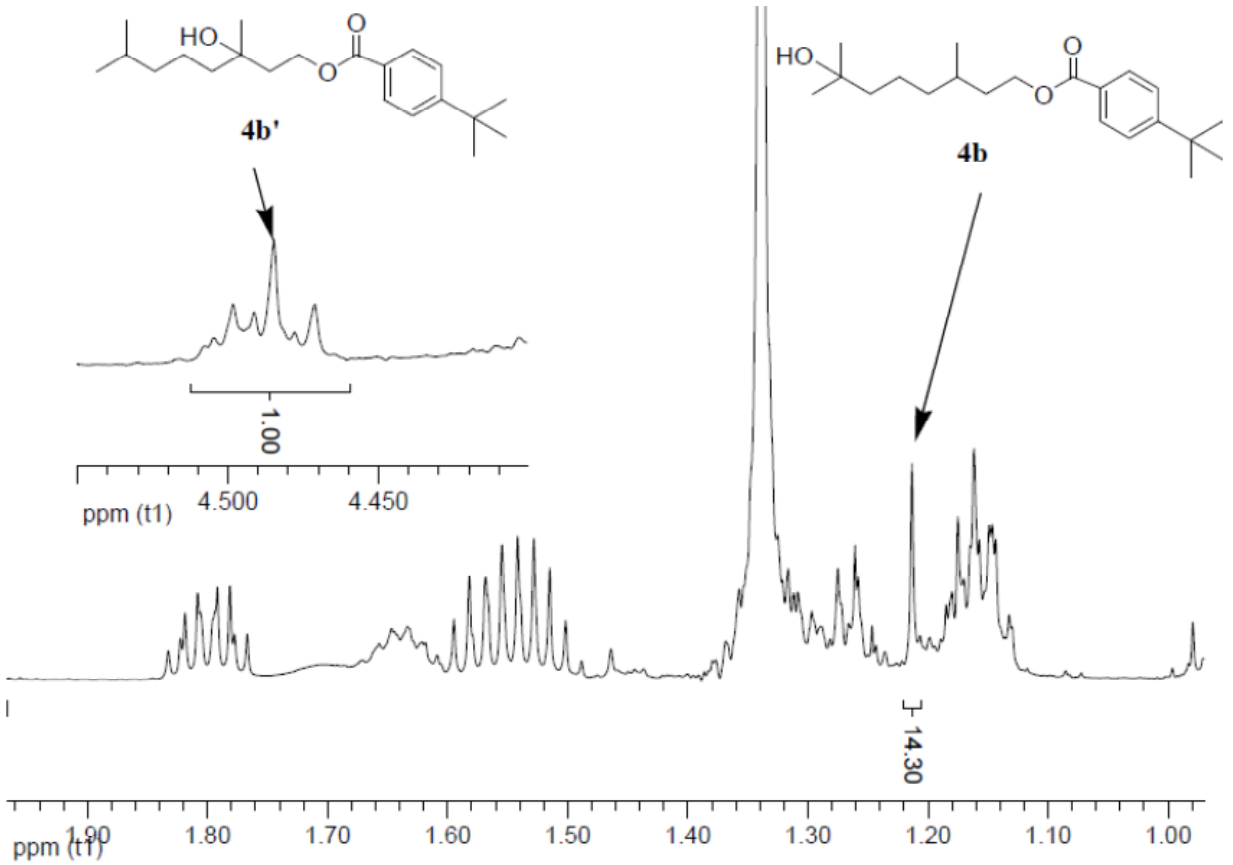


Table 3, entry 8

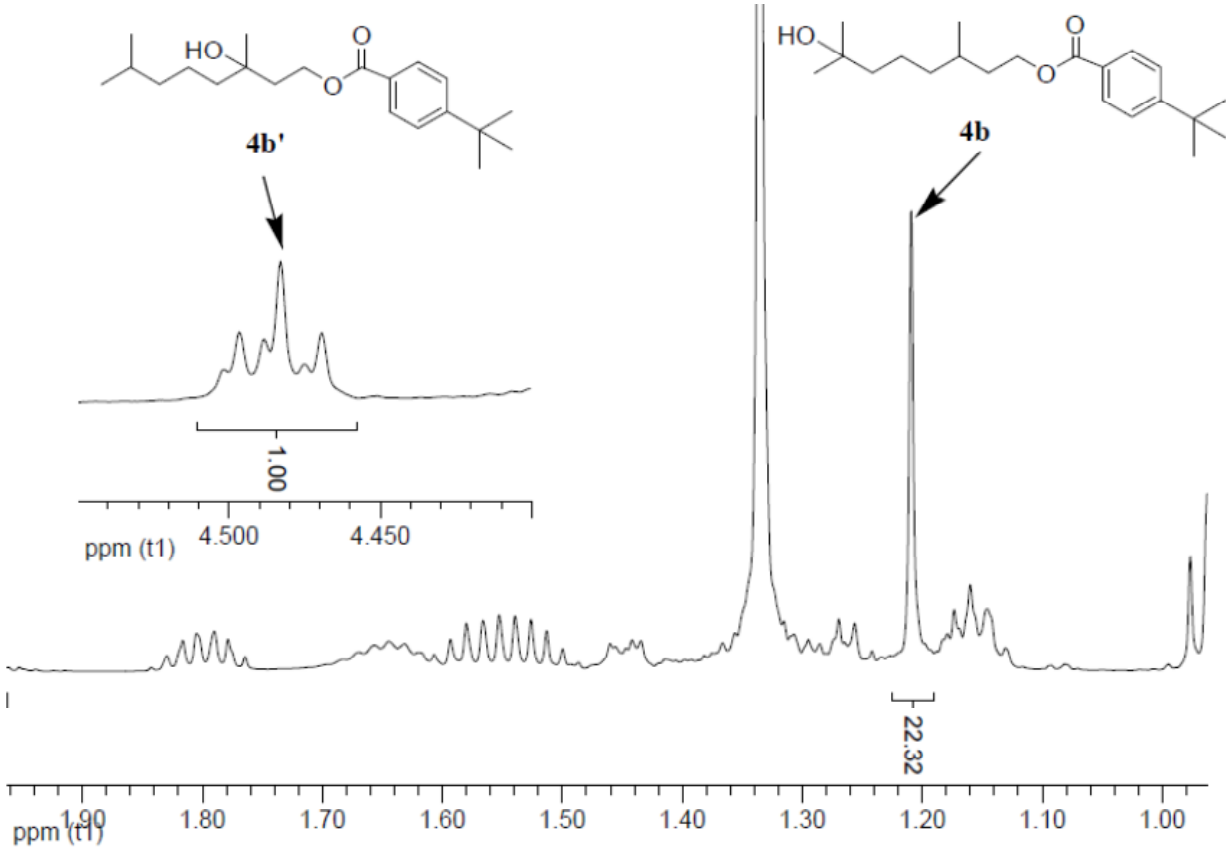


Table 3, entry 9

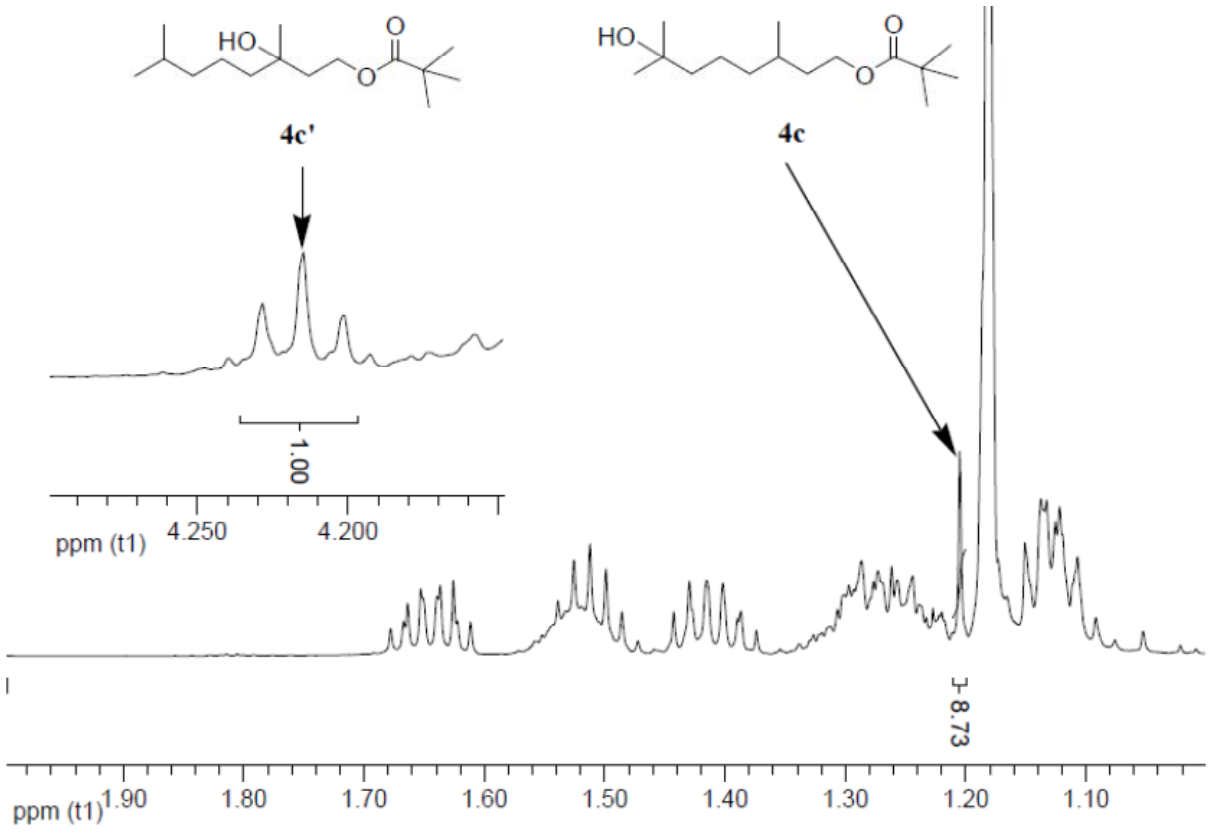


Table 3, entry 10

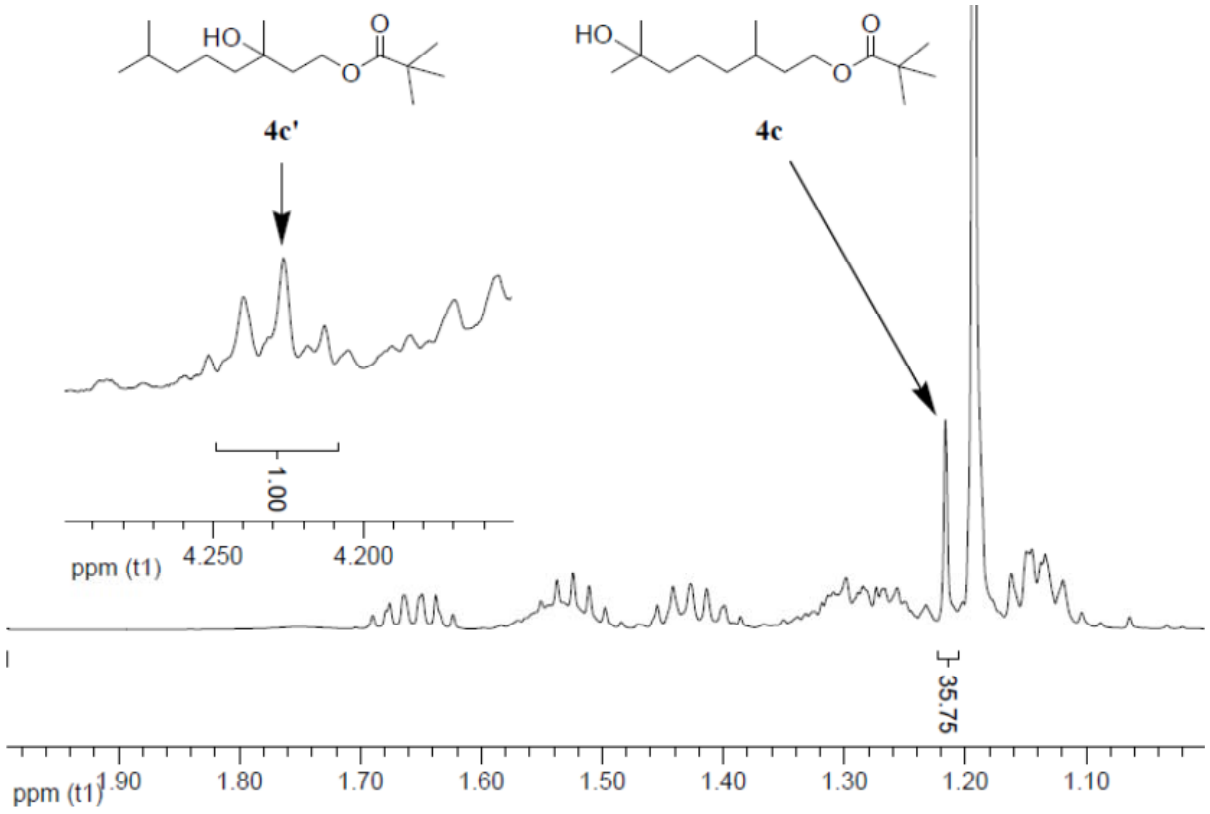


Table 3, entry 11

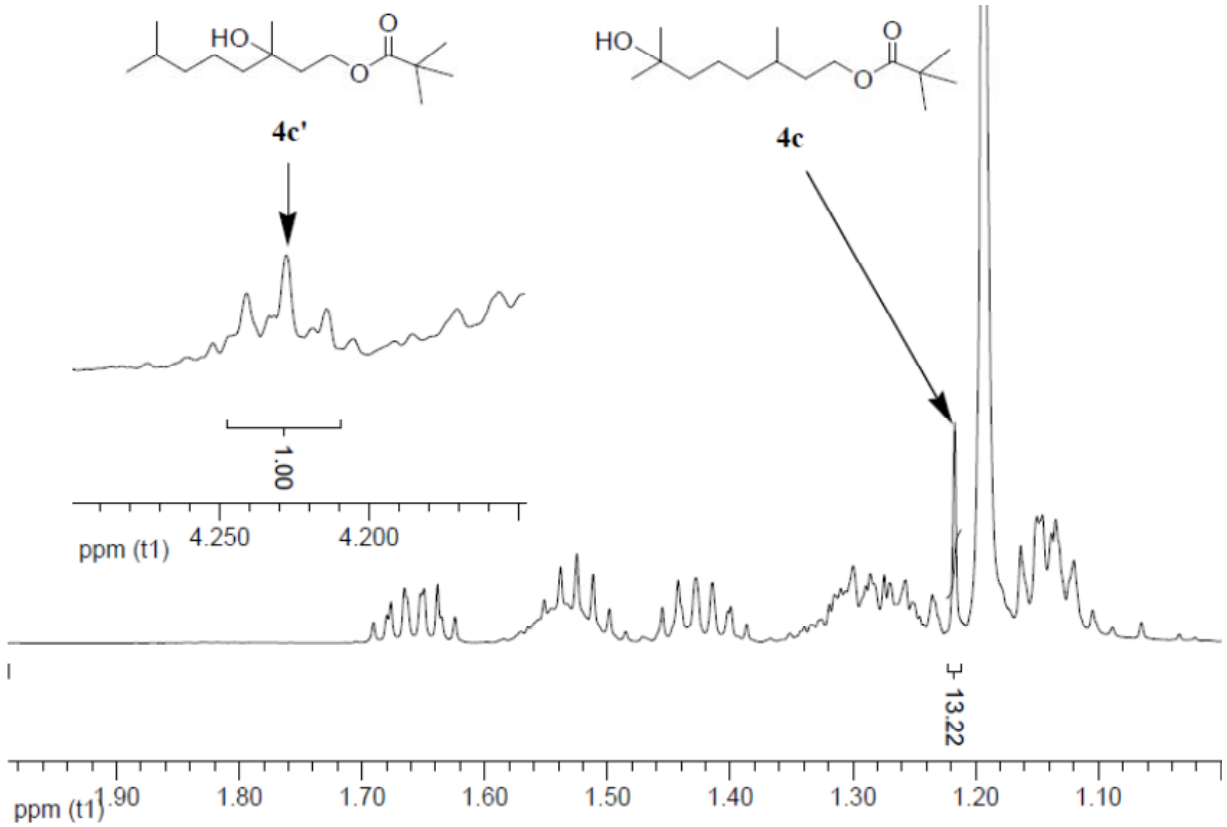


Table 3, entry 12

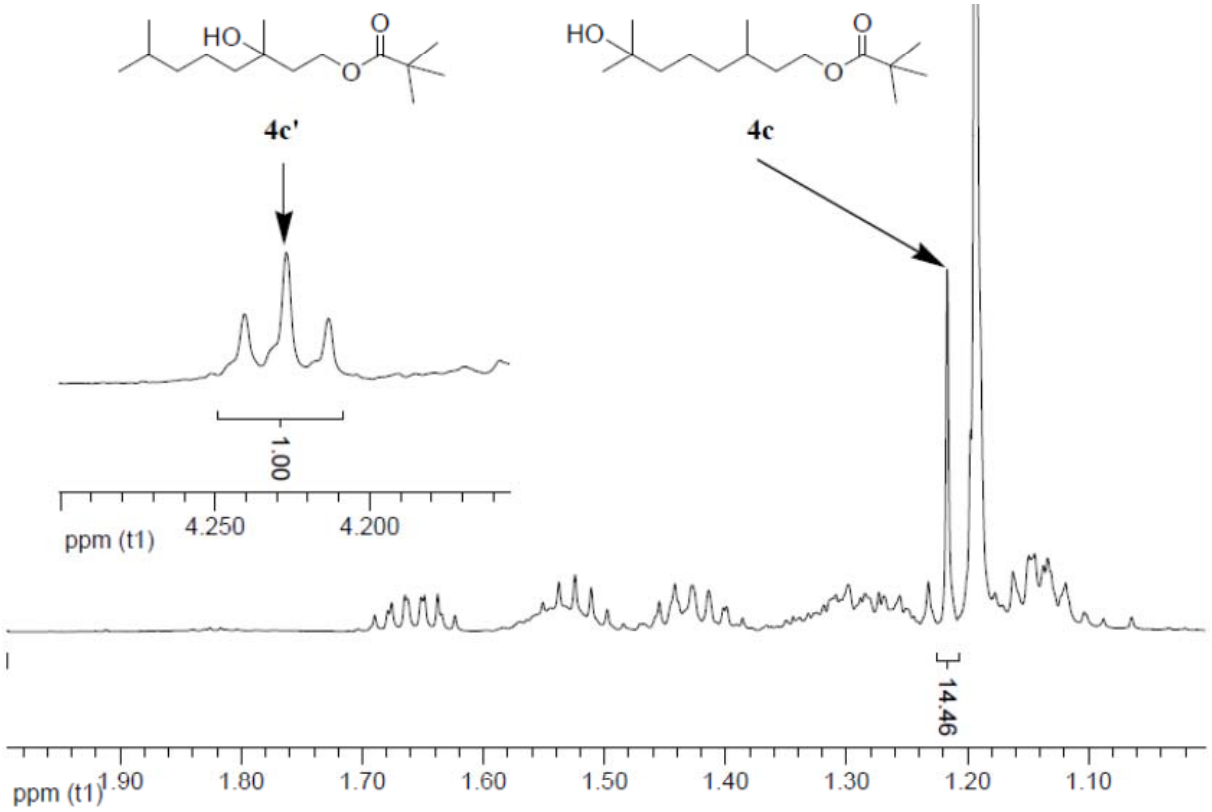


Table 3, entry 14

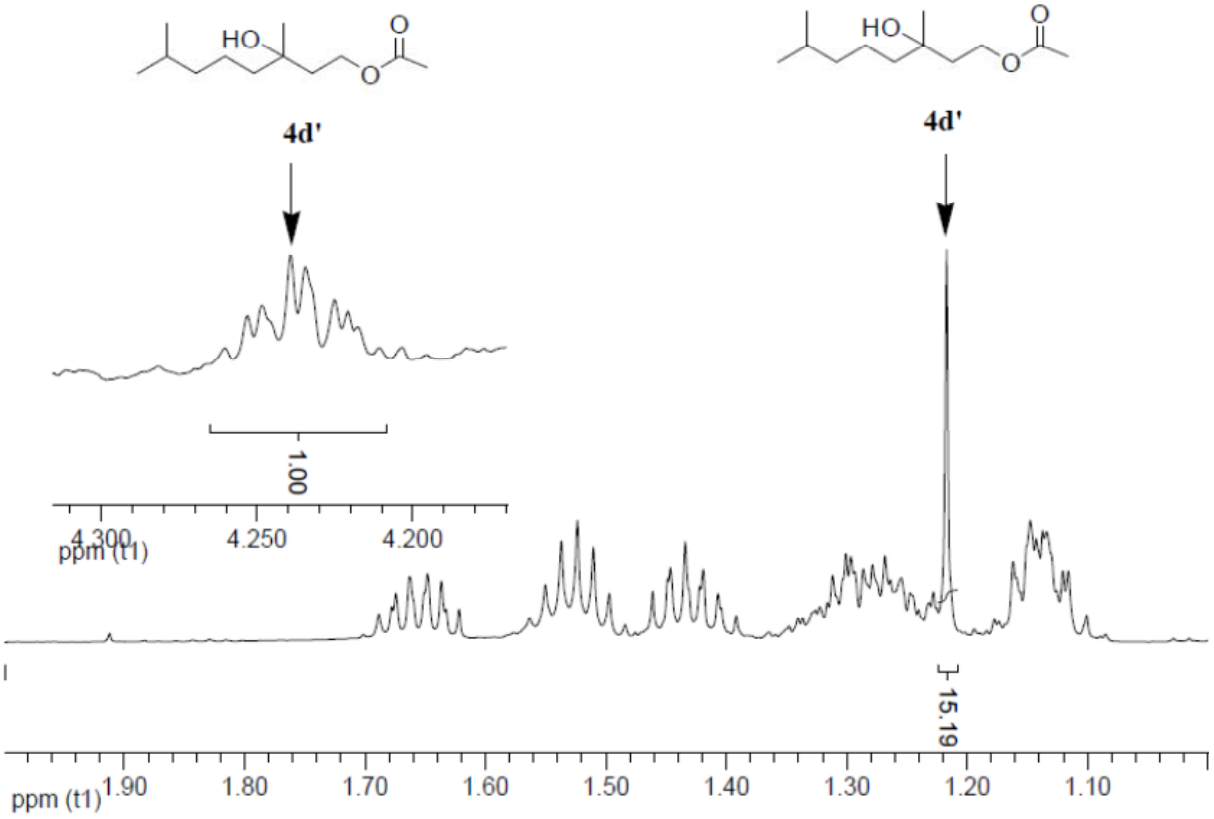


Table 3, entry 15

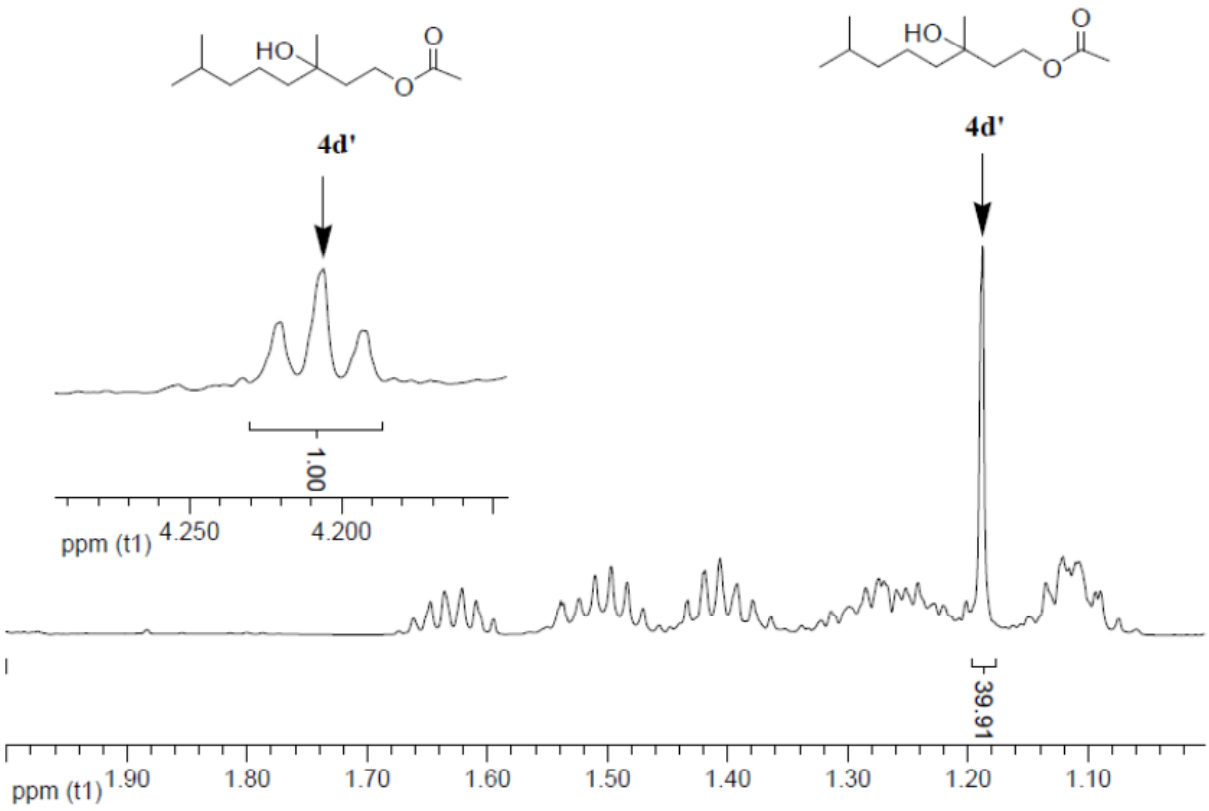


Table 3, entry 16

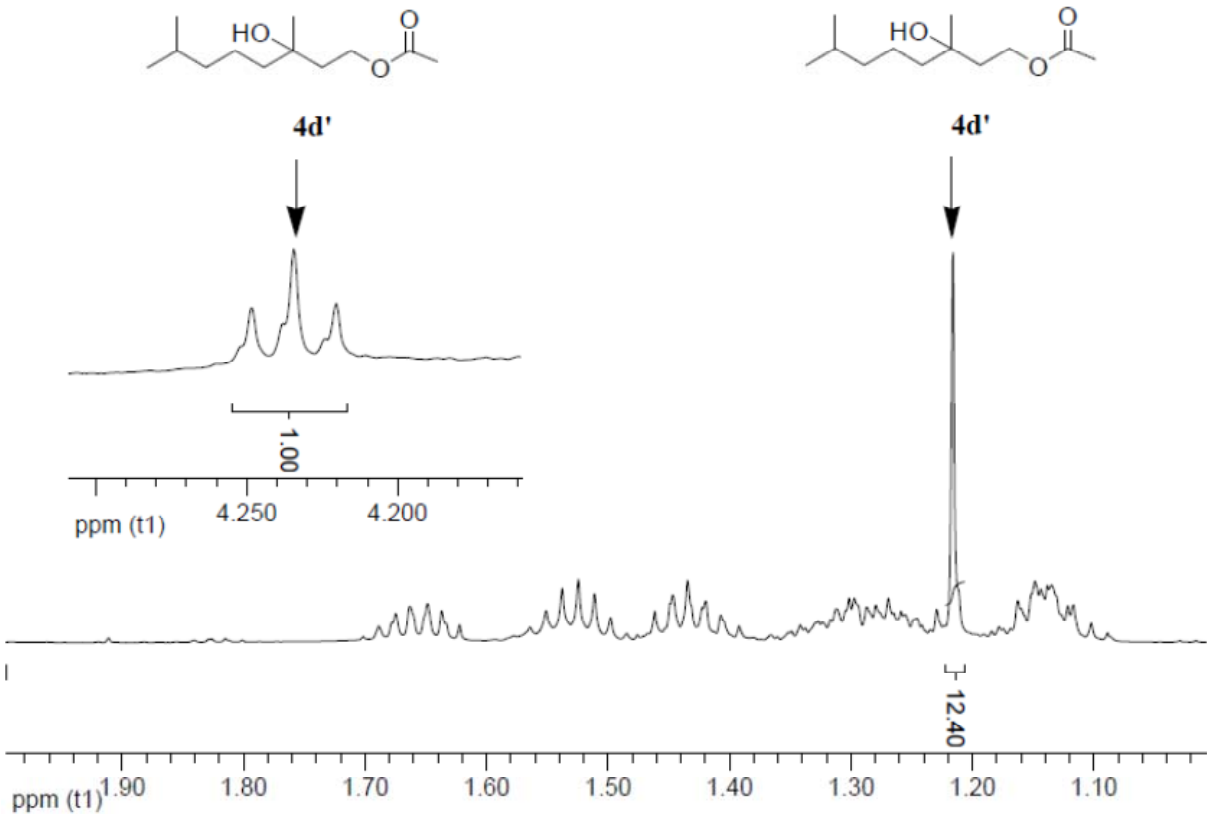


Table S1, entry 1 (Table S2, entry 1; Table S3, entry 1)

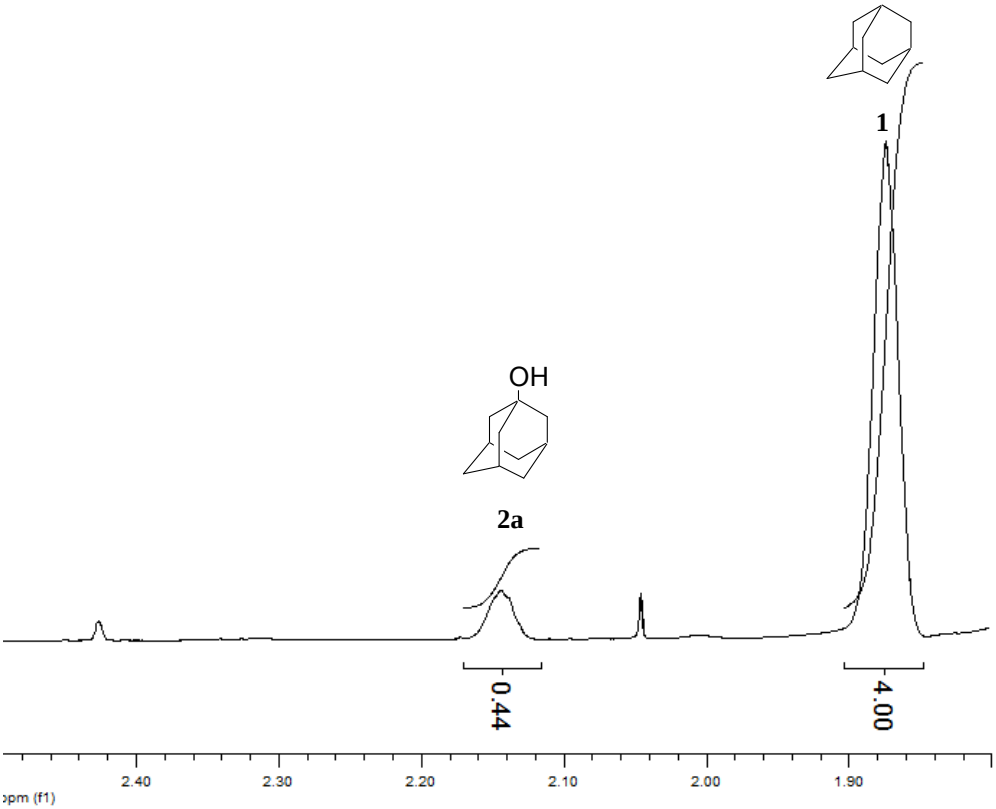


Table S1, entry 2

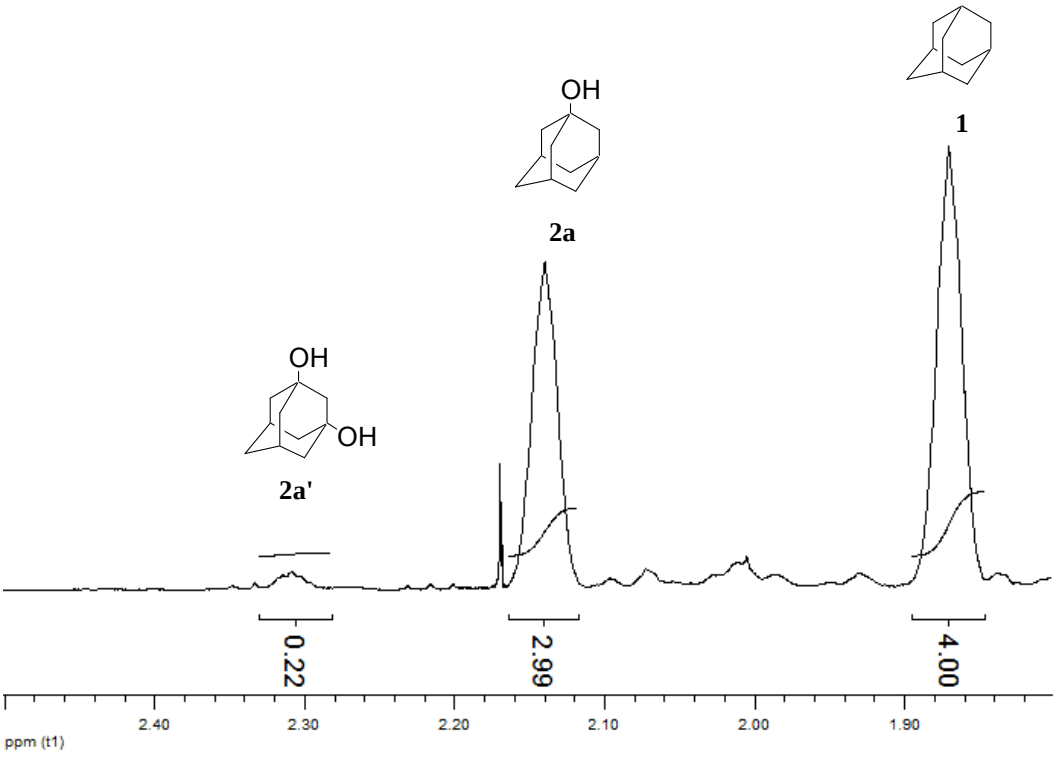


Table S1, entry 3

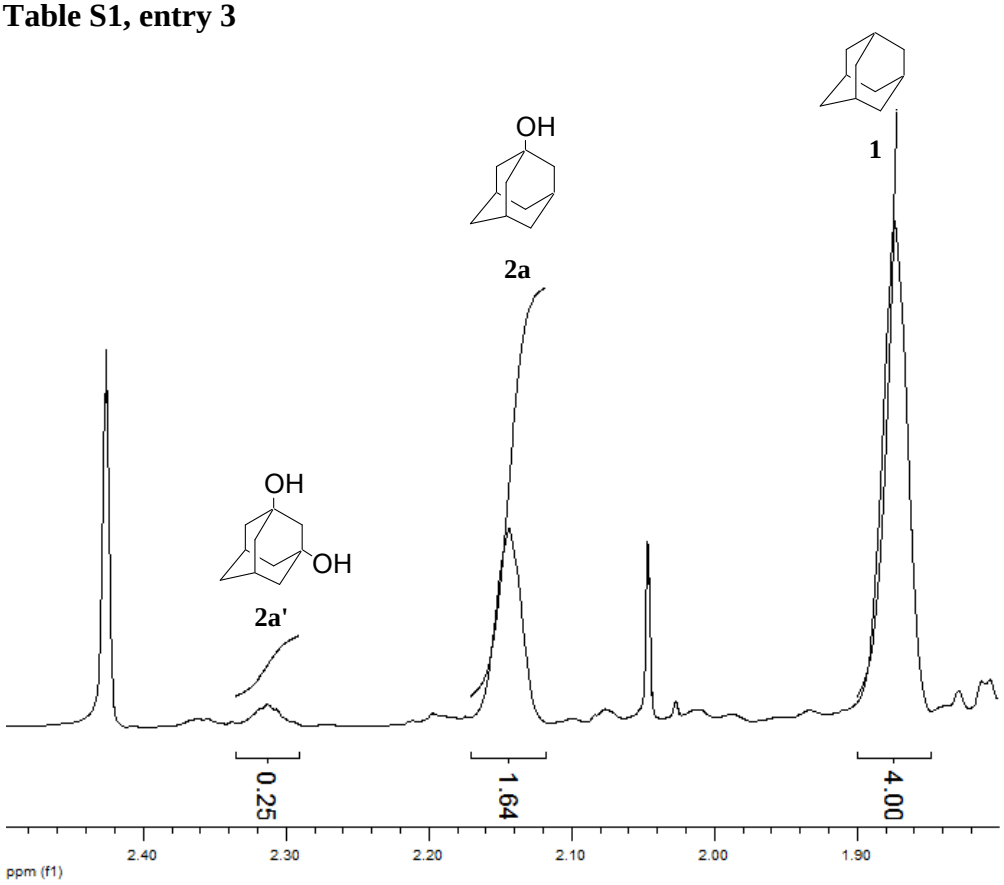


Table S2, entry 2

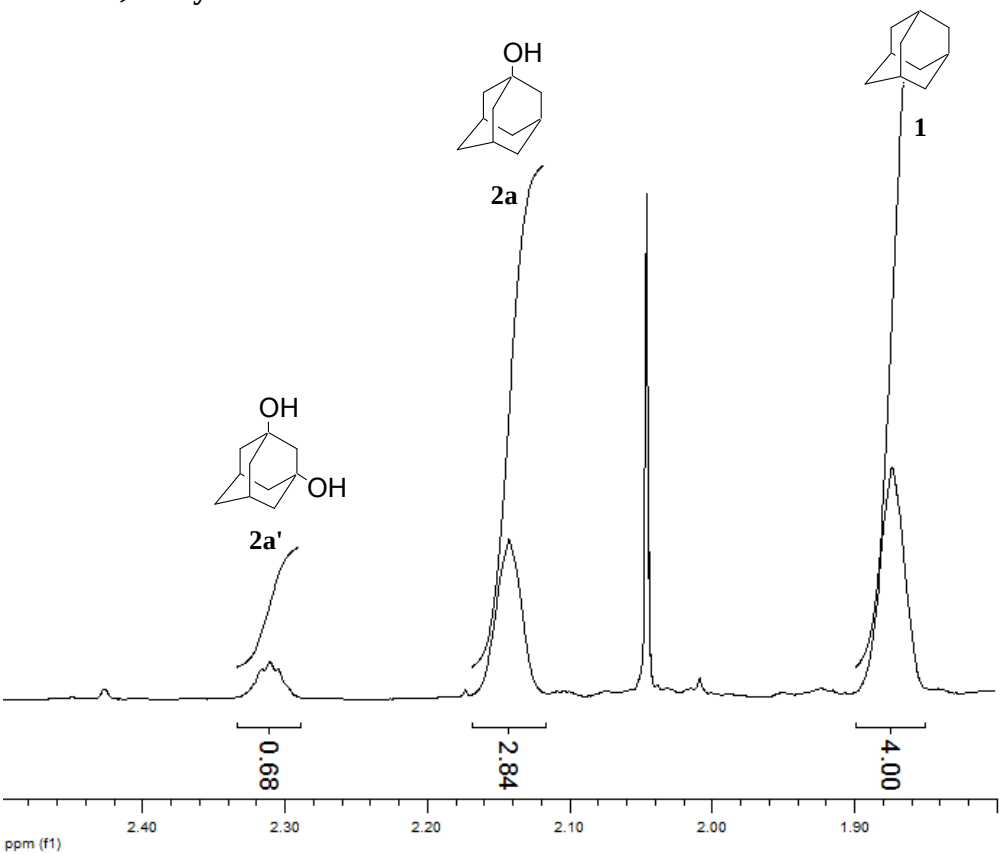


Table S2, entry 3

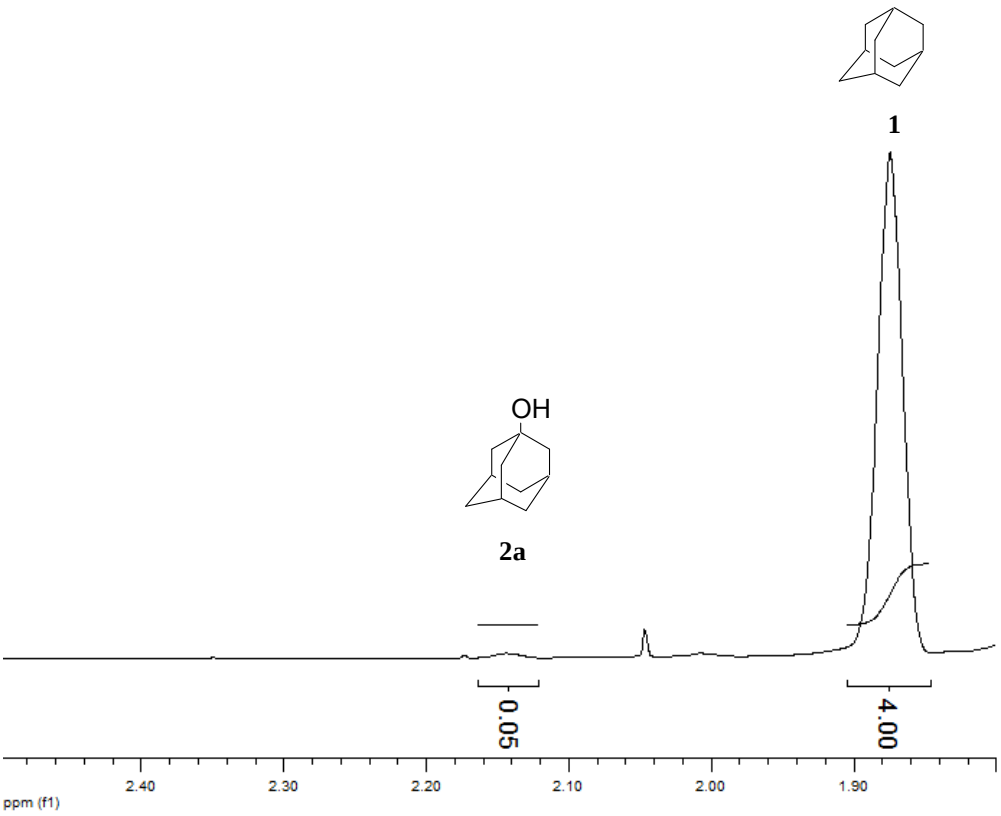


Table S2, entry 4

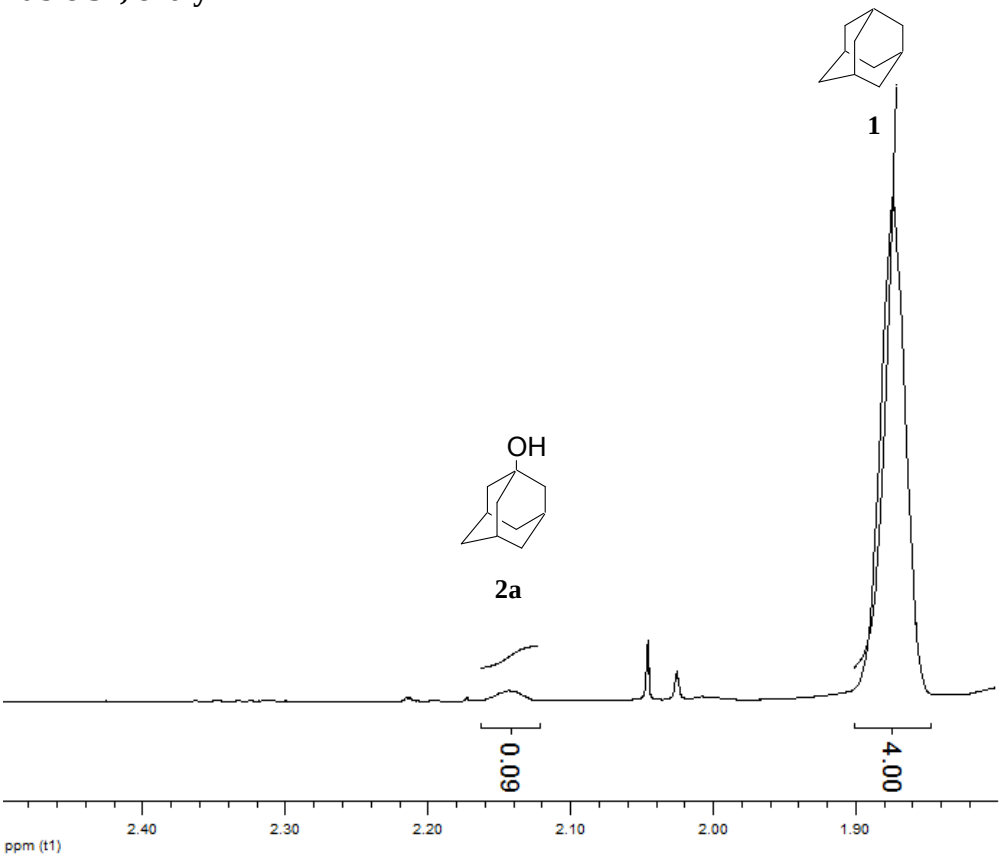


Table S2, entry 5

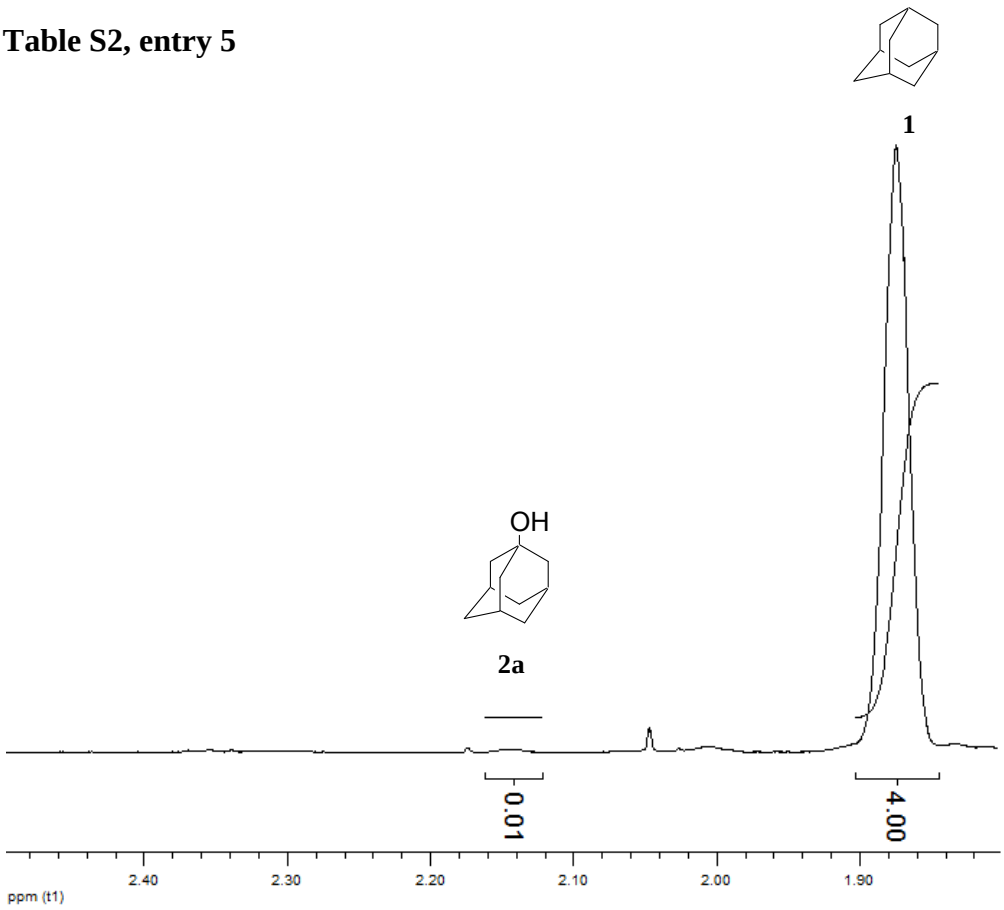


Table S3, entry 2

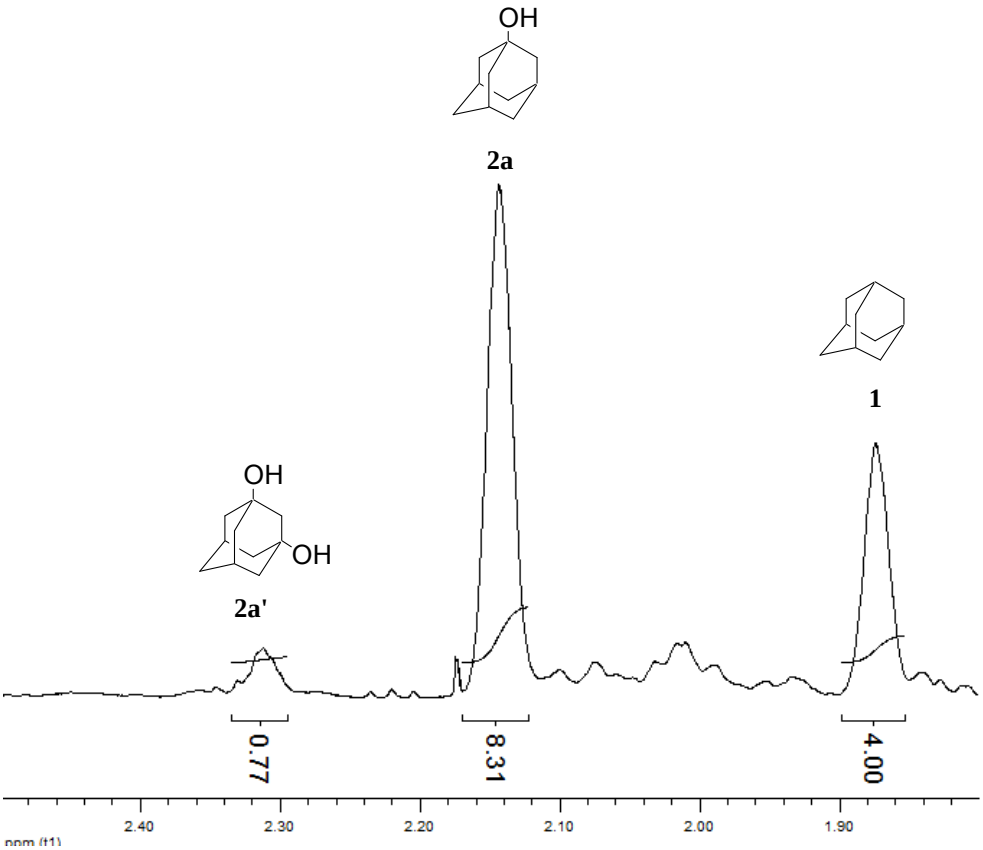


Table S3, entry 4

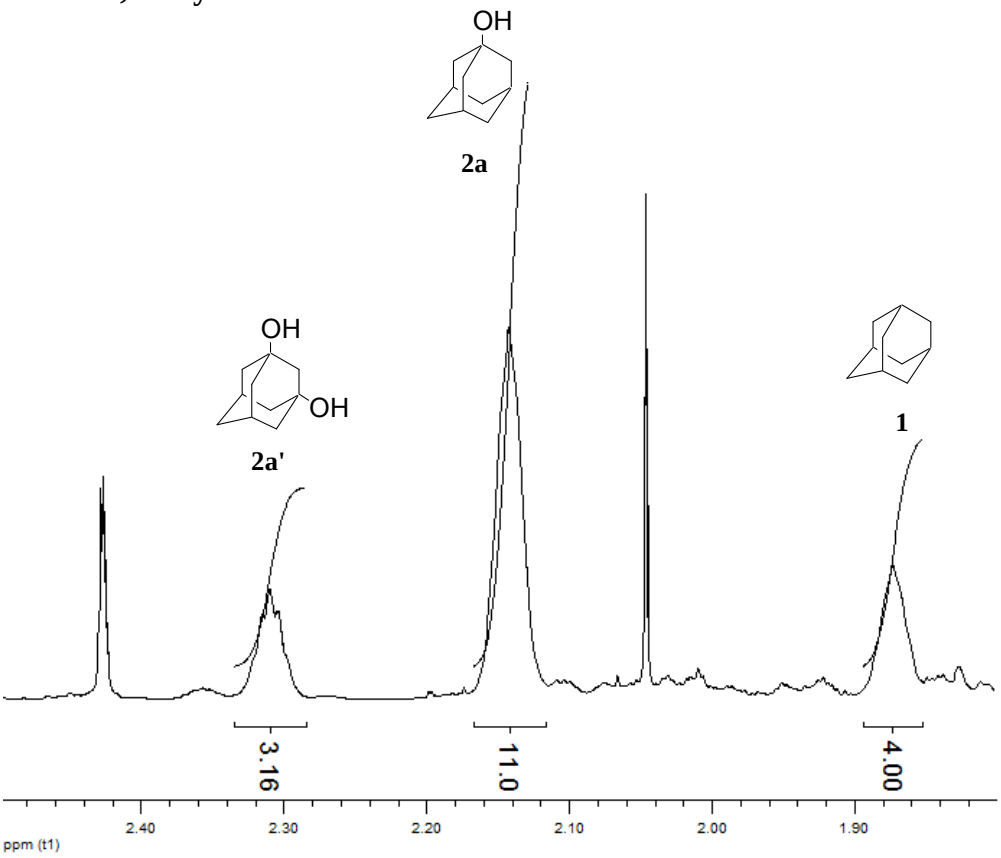


Table S3, entry 5

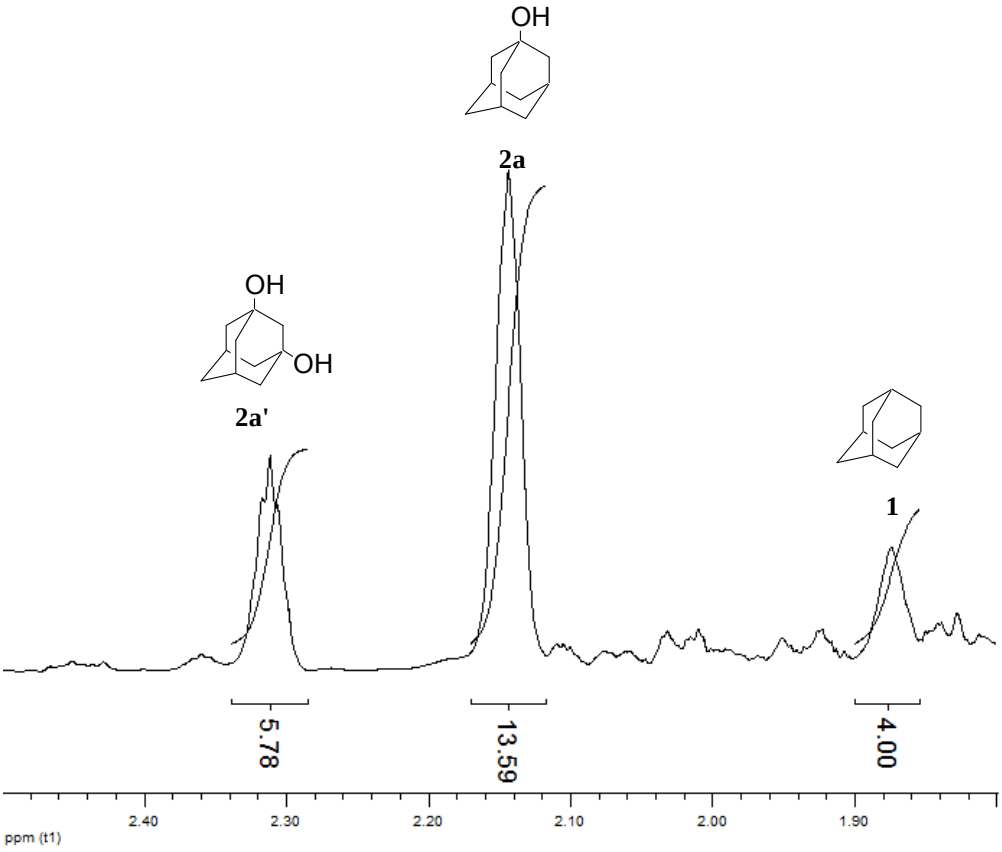


Table S4, entry 1

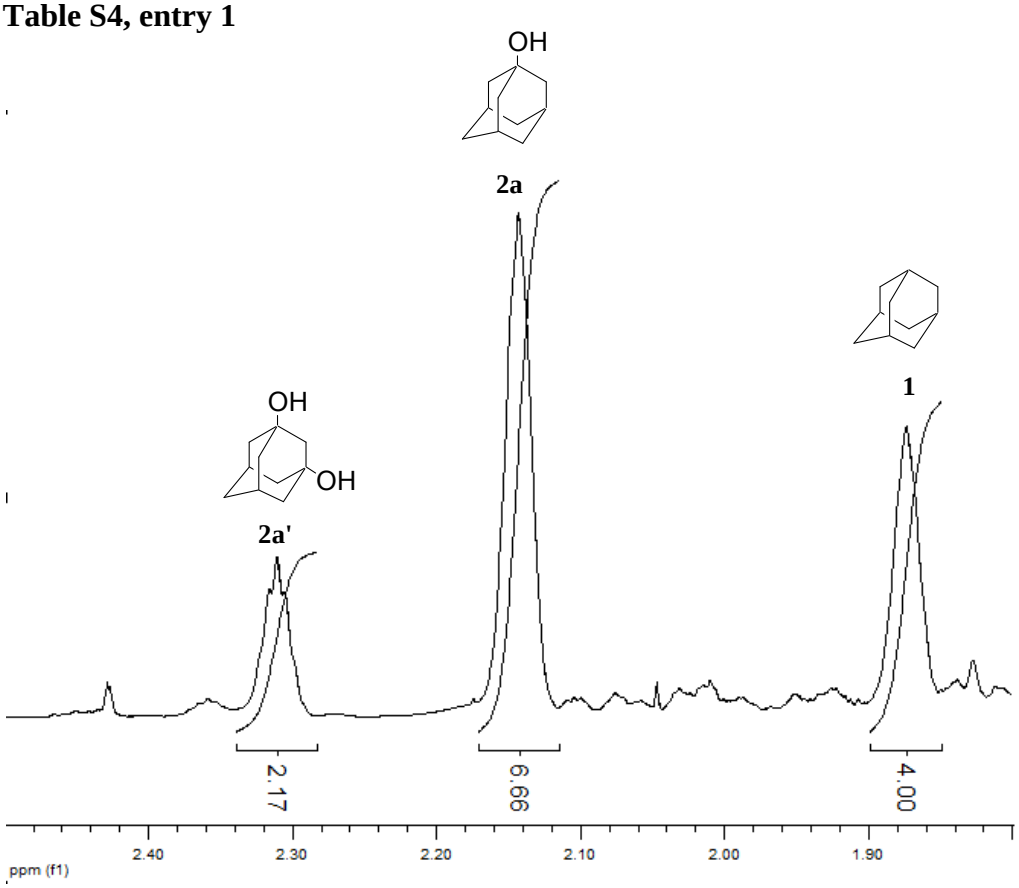


Table S4, entry 3

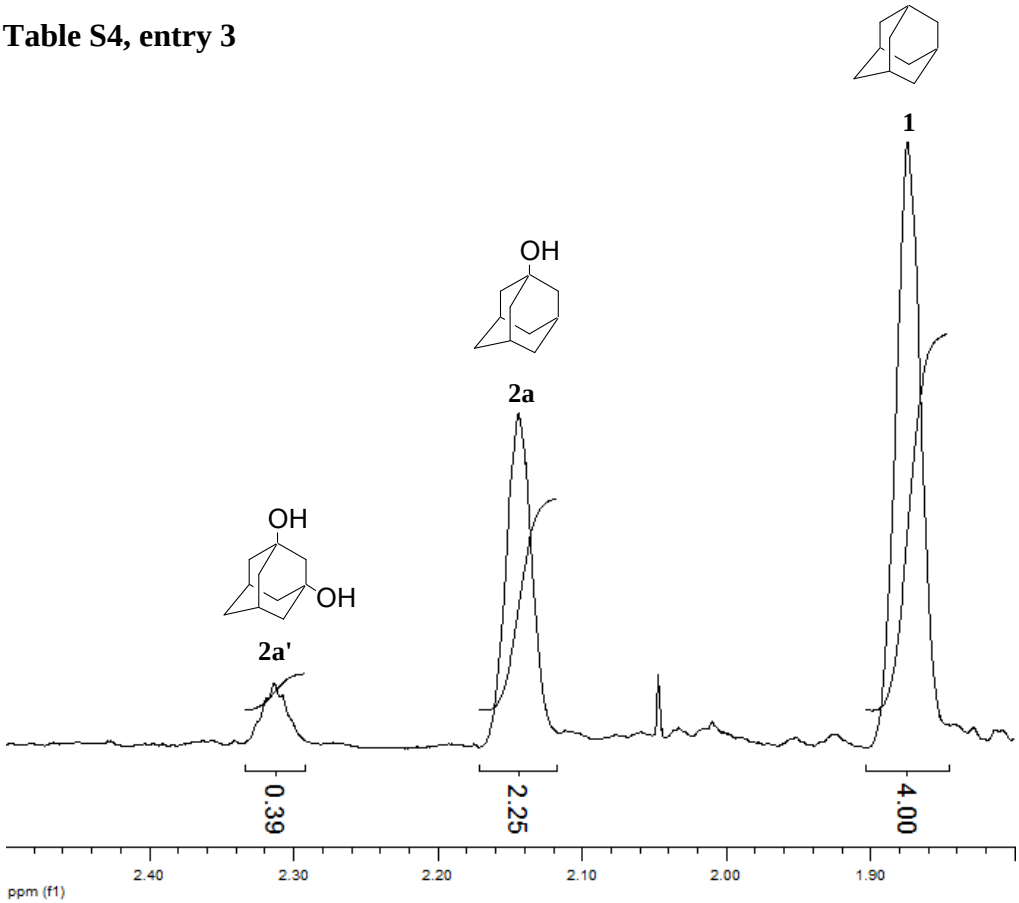


Table S4, entry 4

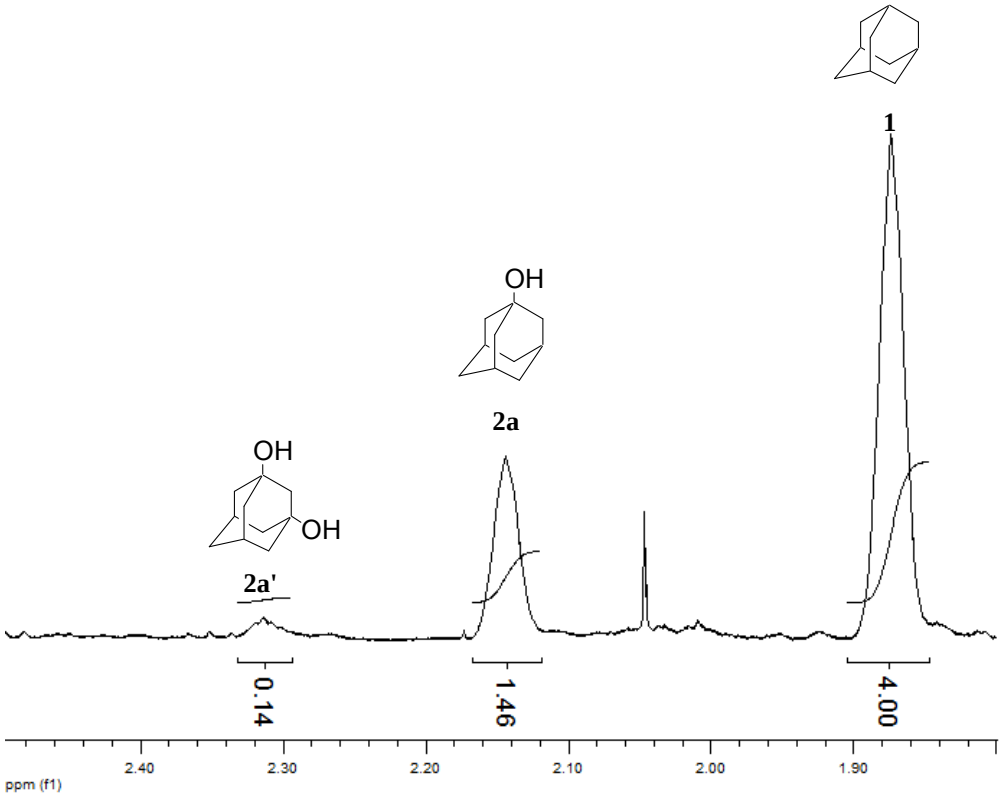
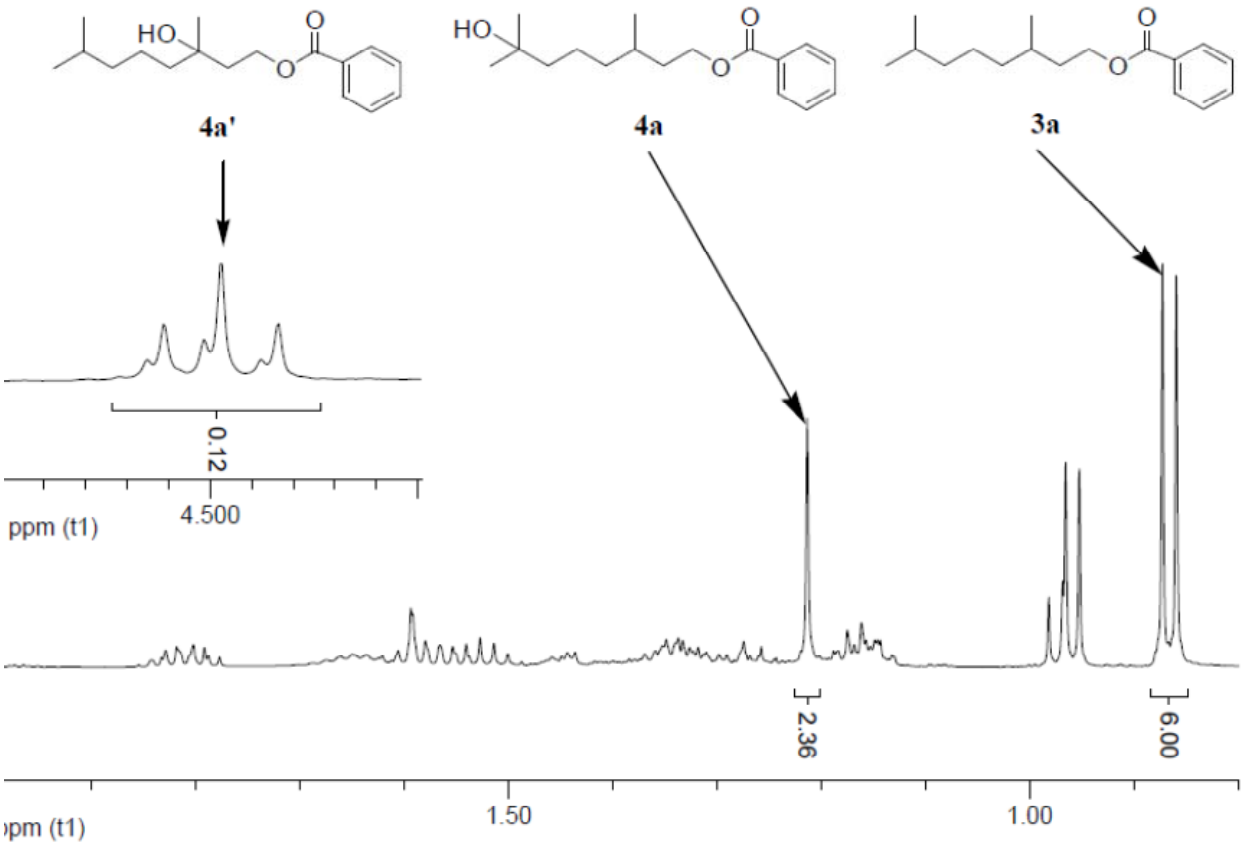


Table S5, entry 1



Ratio of 3a : 4a : 4a'(Table S5, entry 1)

= [6/6 ÷ (6/6 + 2.36/6 + 0.12/2) × 100] : [2.36/6 ÷ (6/6 + 2.36/6 + 0.12/2) × 100] : [0.12/2 ÷ (6/6 + 2.36/6 + 0.12/2) × 100]

= 69 : 27 : 4

Table S5, entry 2

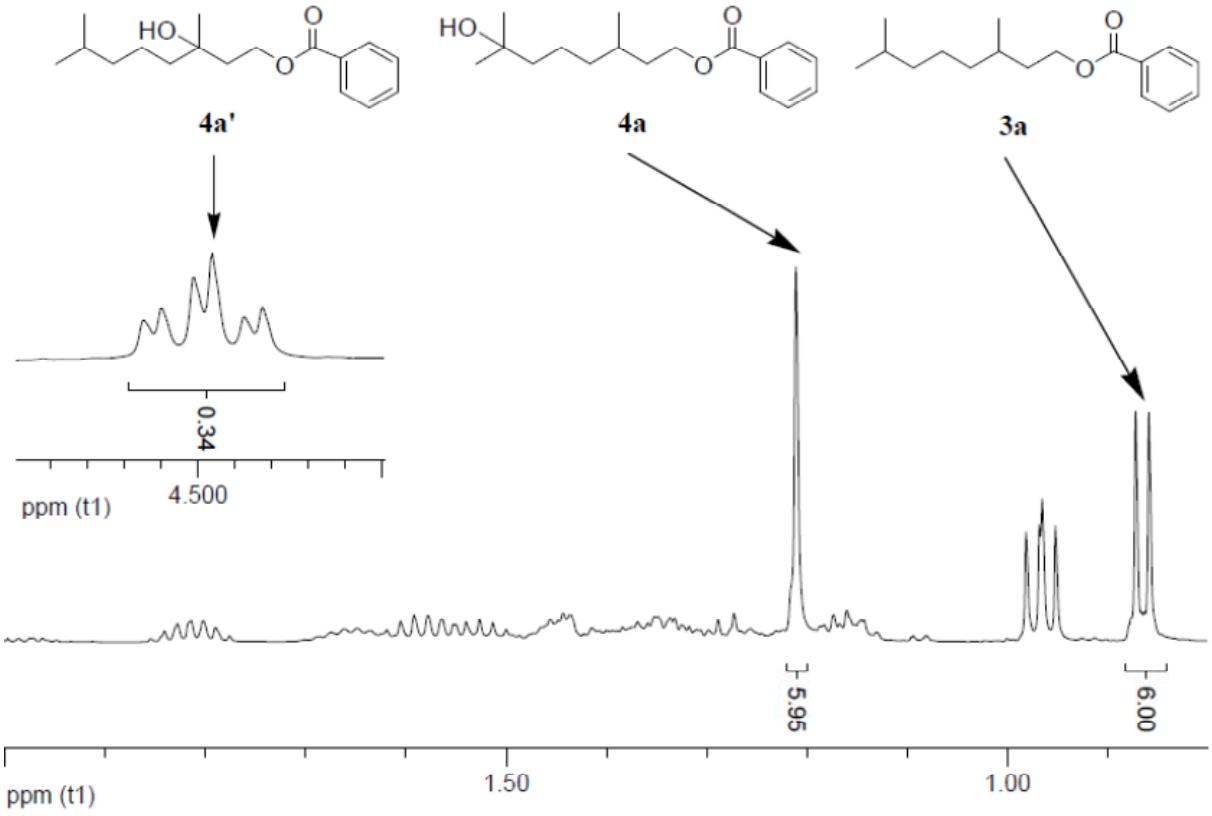


Table S6, entry 1

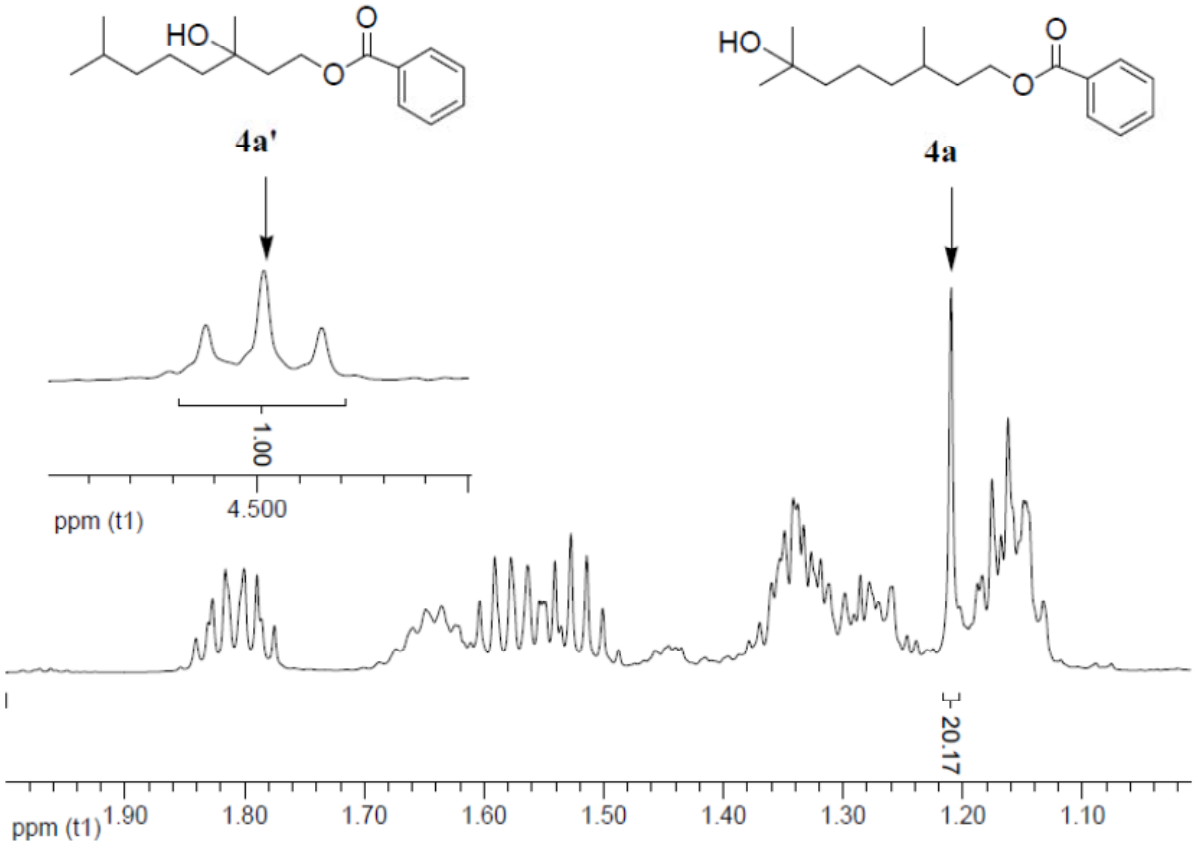


Table S6, entry 2

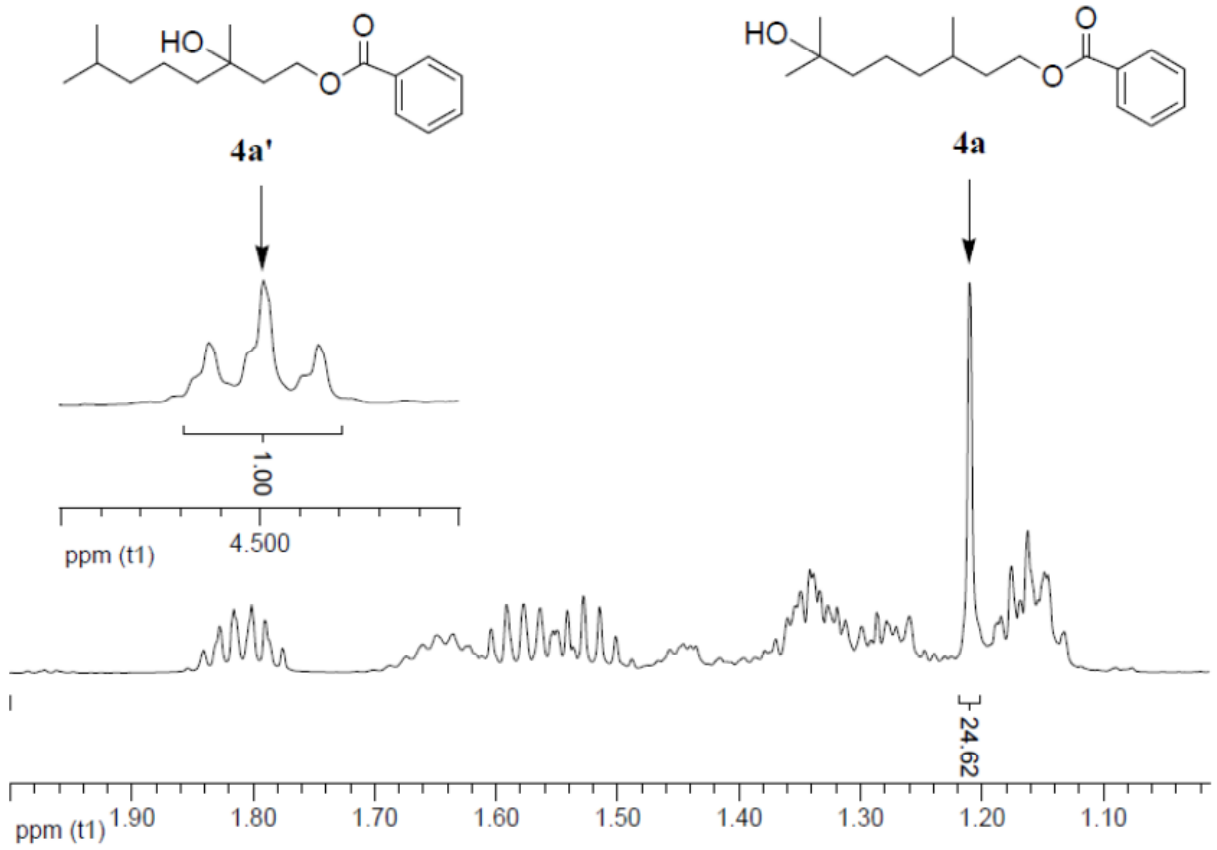


Table S6, entry 4

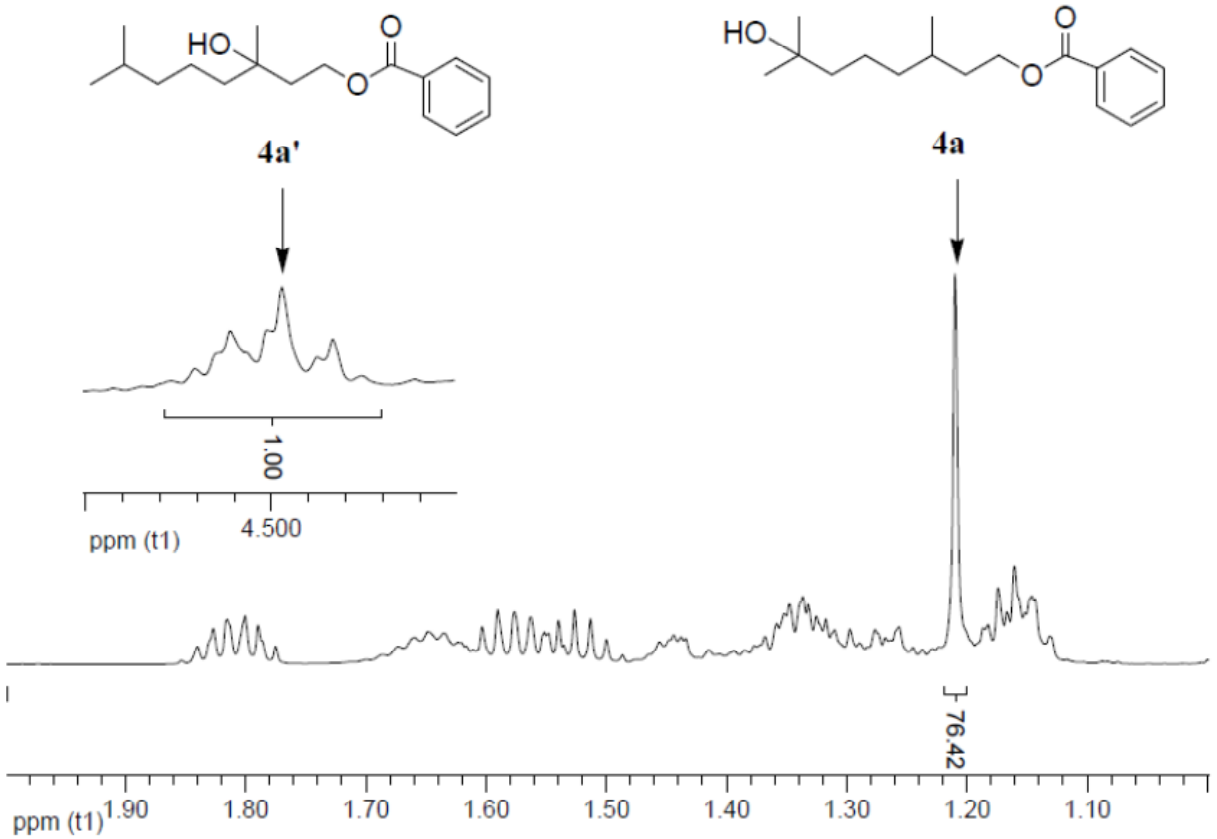


Table S6, entry 5

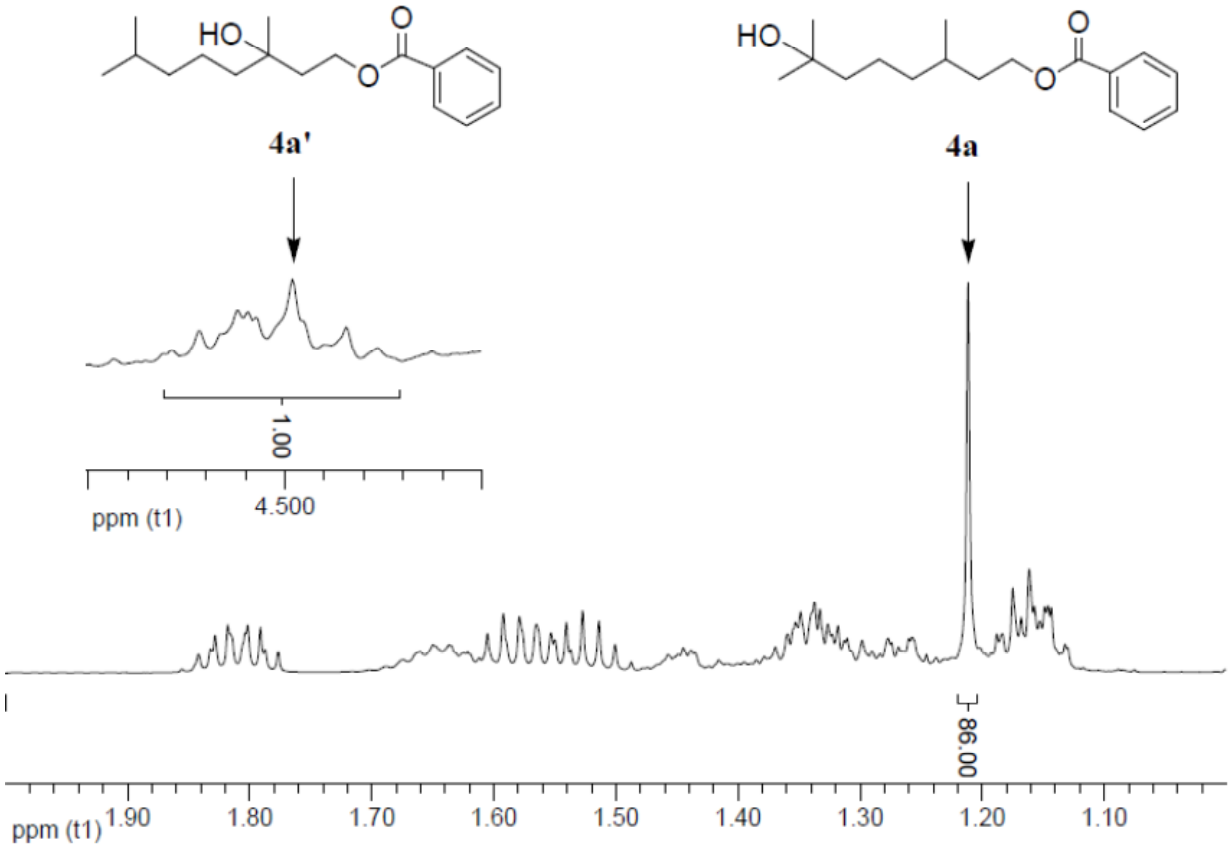
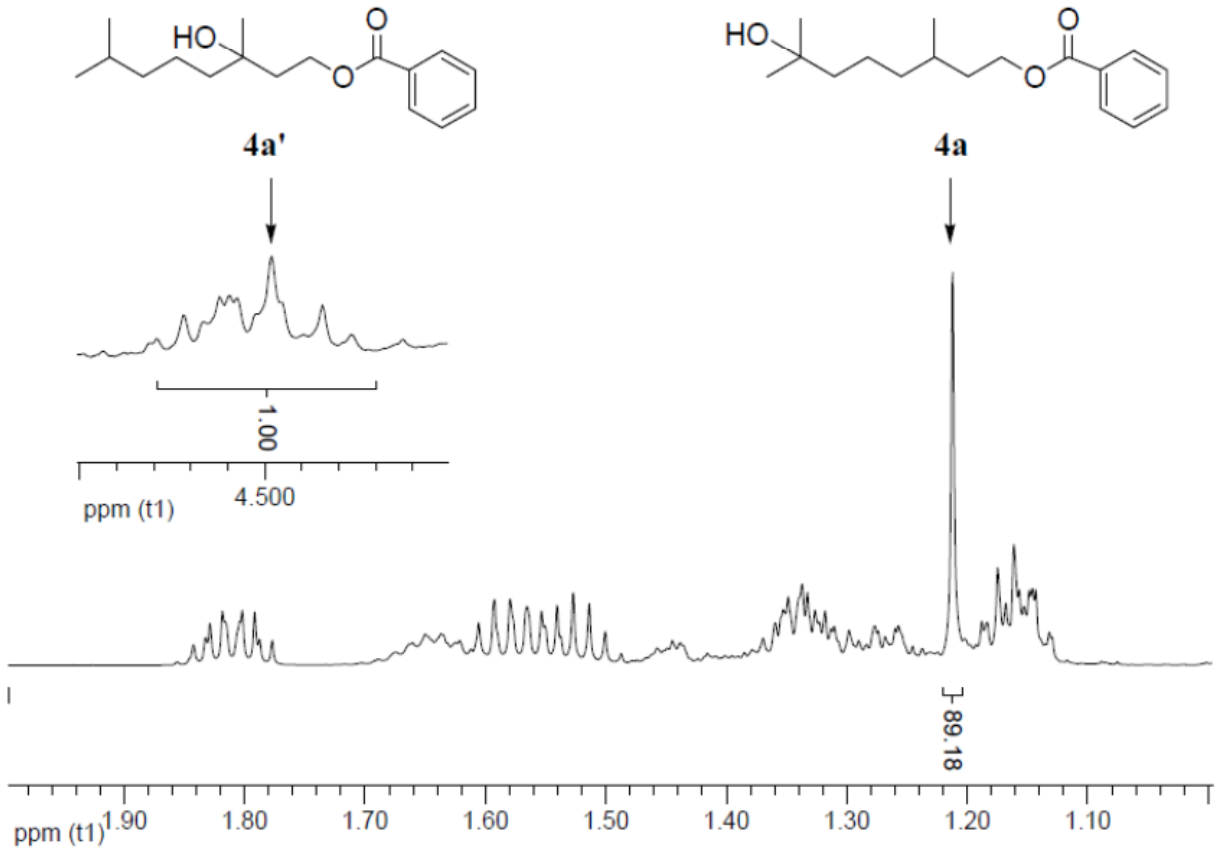
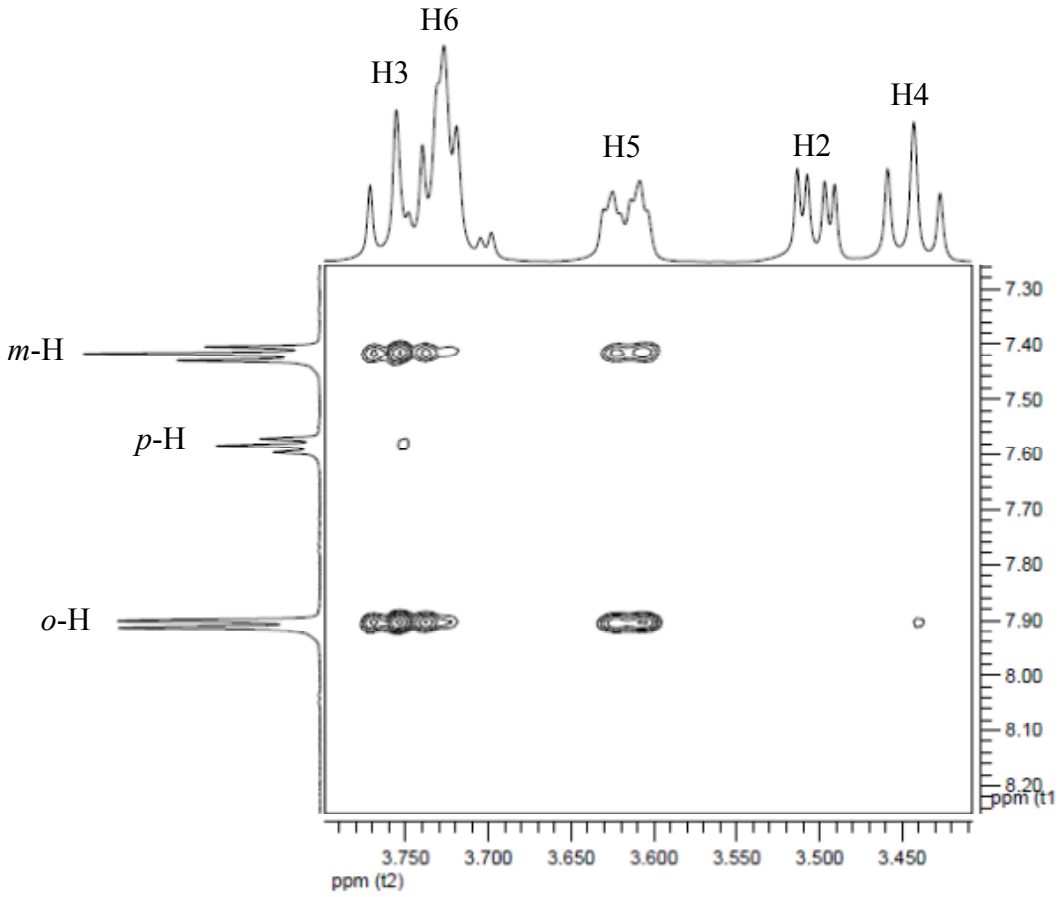


Table S6, entry 6



Partial contour plot of 2D ROESY spectrum for binding of 5a to *β*-CD in D_2O.



Based on the 2D ROESY spectrum of the binding of **5a** to *β*-CD, strong NOE correlation signals of *o*-H and *m*-H of **5a** with H3 and H5 of *β*-CD and the absence of correlation signal of *p*-H of **5a** with protons of *β*-CD suggest that the phenyl group of **5a** is deeply inserted into the *β*-CD cavity and *p*-H of **5a** is exposed outside of the cavity. H6 of *β*-CD shows no NOE correlation signal with any protons of the phenyl group of **5a**, revealing that *p*-H of **5a** is exposed outside the secondary face of *β*-CD. Considering the 1 : 1 stoichiometry of the inclusion complexation between **3a** and *β*-CD, the possible binding geometry of the benzoate group of **5a** is proposed (Figure S16).

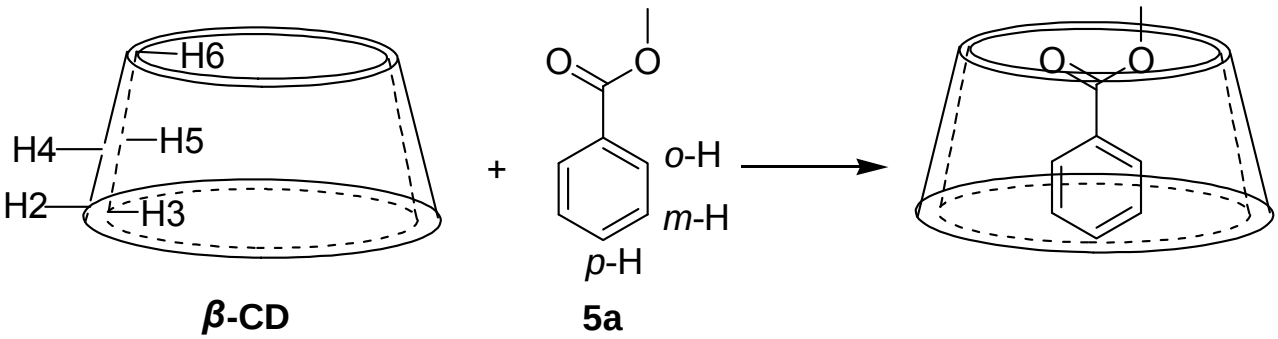
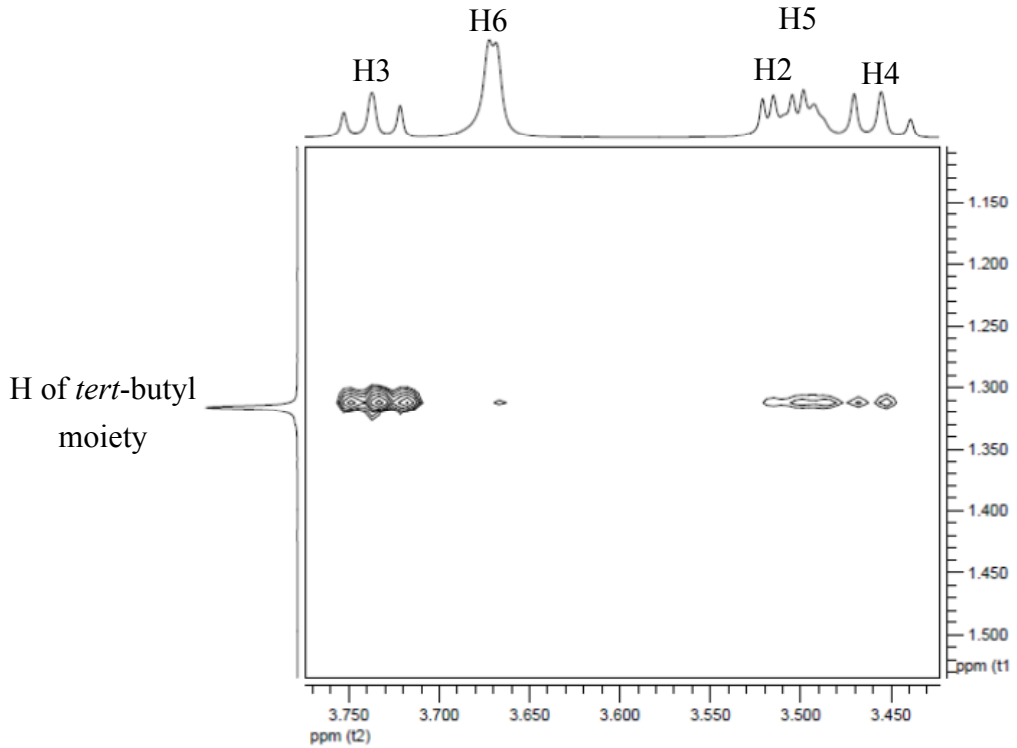
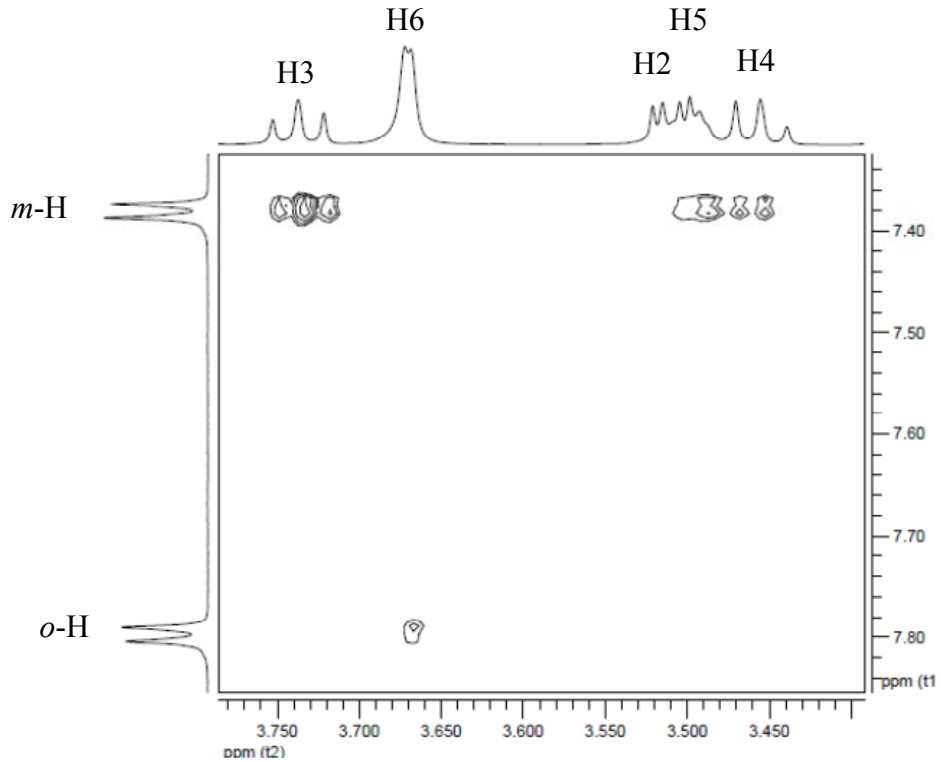


Figure S16. Proposed binding geometry for the inclusion of **5a** in *β*-CD.

Partial contour plot of 2D ROESY spectrum for binding of 5b (*tert*-butyl moiety) to *β*-CD in D_2O.



Partial contour plot of 2D ROESY spectrum for binding of 5b (phenyl ring moiety) to *β*-CD in D_2O.



In the 2D ROESY spectrum for binding of **5b** to *β*-CD, the protons of the *tert*-butyl group and the protons at the *m*-position of the phenyl ring of **5b** have strong NOE correlation signals with H3 and H5 of *β*-CD while the protons at the *o*-position of the phenyl ring of **5b** only exhibits weak correlation signal with H6 of *β*-CD. This suggests that **5b** inserts into *β*-CD from the primary face. The *tert*-butyl group of **5b** is included in the *β*-CD cavity, and just half of the phenyl ring is inserted to the *β*-CD cavity. As the stoichiometry for the formation of inclusion complex of **3b** and *β*-CD is 1 : 1, the possible binding geometry of the 4-*tert*-butylbenzoate moiety of **5b** is proposed in Figure S17.

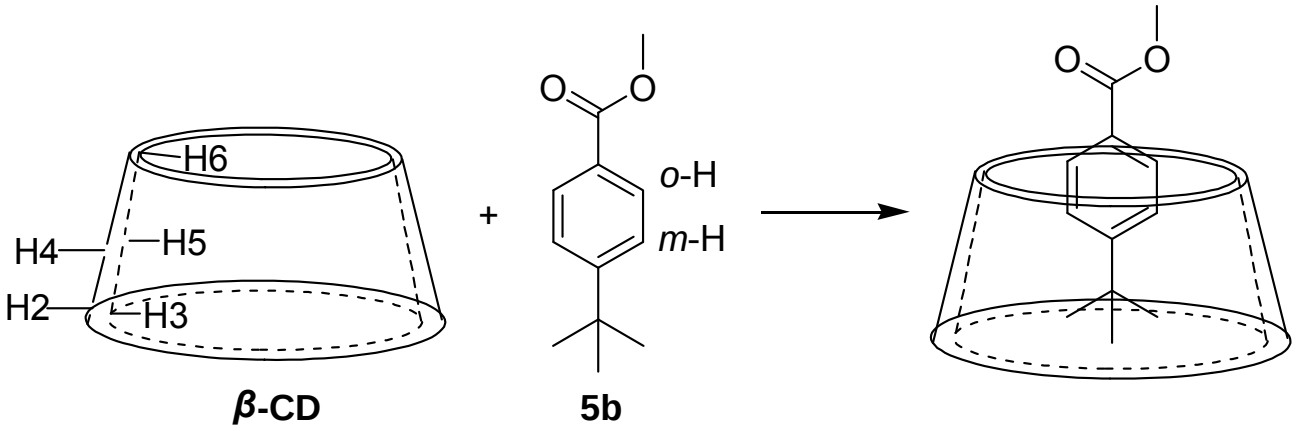
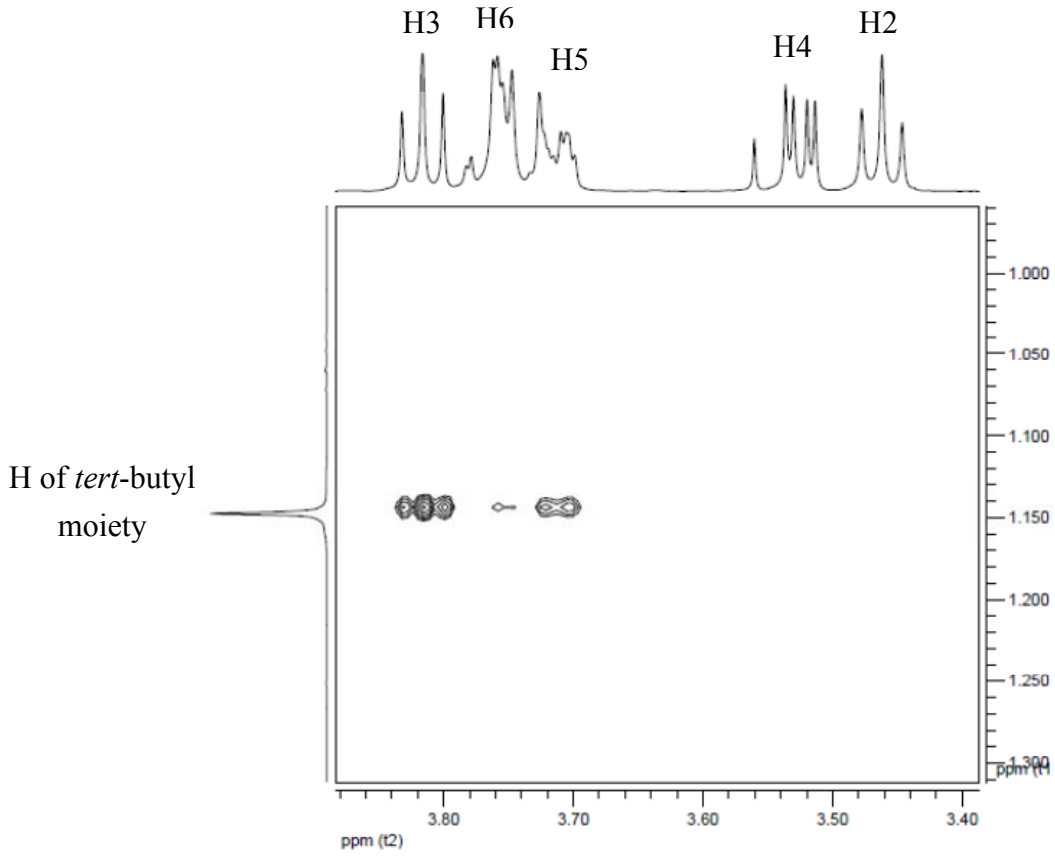


Figure S17. Proposed binding geometry for the inclusion of **5b** in *β*-CD.

Partial contour plot of 2D ROESY spectrum for binding of 5c to *β*-CD in D_2O.



From the 2D ROESY spectrum for binding of **5c** to *β*-CD, the protons of the *tert*-butyl group of **5c** have NOE correlation signals with H3, H5, and H6 of *β*-CD with different intensities. The NOE signal between the protons of the *tert*-butyl group and H3 is the strongest, and that between the protons of the *tert*-butyl group and H5 is moderate, while that between the protons of the *tert*-butyl group and H5 is the weakest. Based on these findings, it was proposed that the *tert*-butyl group of **5c** enters the cavity of *β*-CD from the secondary face, unlike **5a** and **5b**. As the stoichiometry for formation of inclusion complex of **3c** and *β*-CD is 1 : 1, the possible binding geometry of the *tert*-butyl group of **5c** to *β*-CD is suggested (Figure S18).

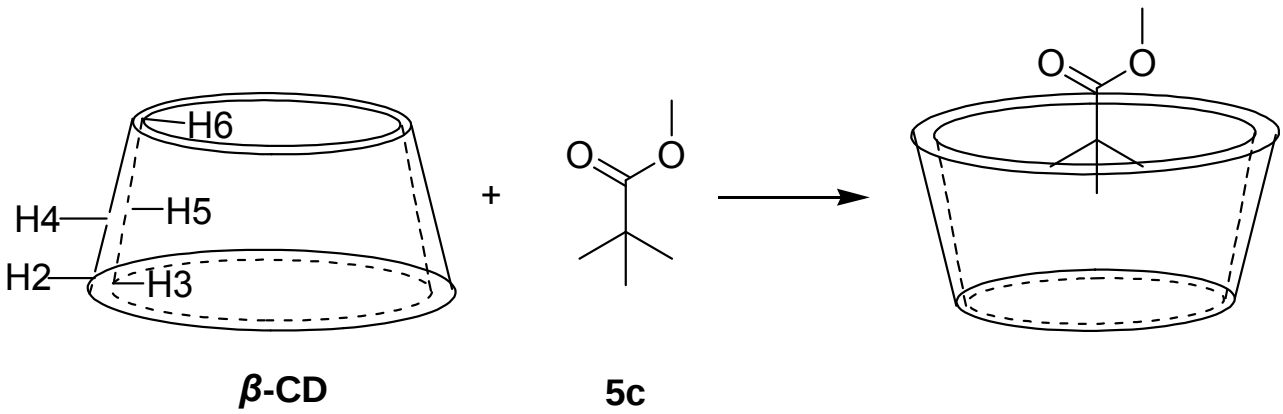
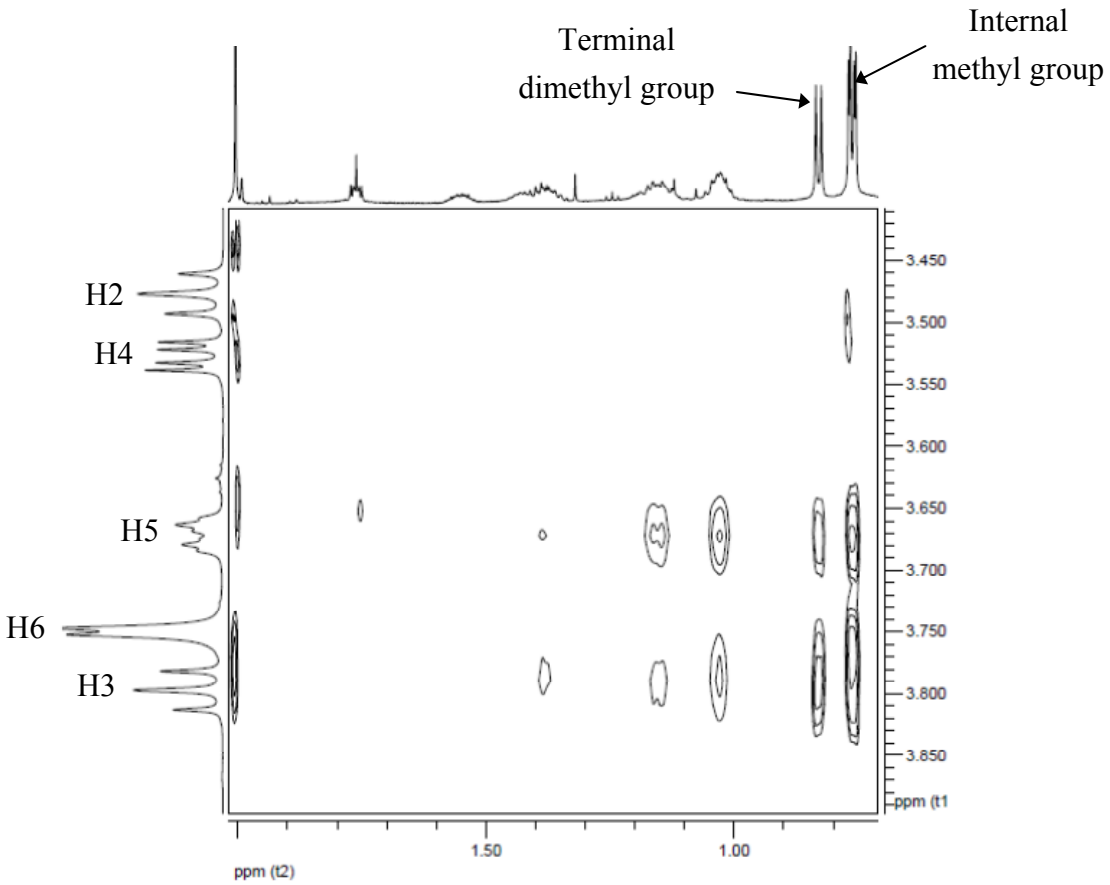


Figure S18. Proposed binding geometry for the inclusion of **5c** in *β*-CD.

Partial contour plot of 600 MHz 2D ROESY spectrum for binding of 3d to *β*-CD in D_2O.



From the 2D ROESY spectrum of the binding of **3d** to *β*-CD, strong NOE signals of the 3,7-dimethyloctyl chain of **3d** with H3, H5, and H6 of *β*-CD suggest that the 3,7-dimethyloctyl chain of **3d** is included into the cavity of *β*-CD. The NOE signal of the terminal dimethyl group of **3d** with H5 and H6 of *β*-CD is more intense than that with H3 of *β*-CD, and the internal methyl group of **3d** have more intense signal with H3 than with H5. This reveals that the terminal dimethyl group is close to the primary face, and the internal methyl group is close to the secondary face. Based on the 2 : 1 stoichiometry of the inclusion complex between **3d** and *β*-CD, the binding geometry is proposed as Figure S19.

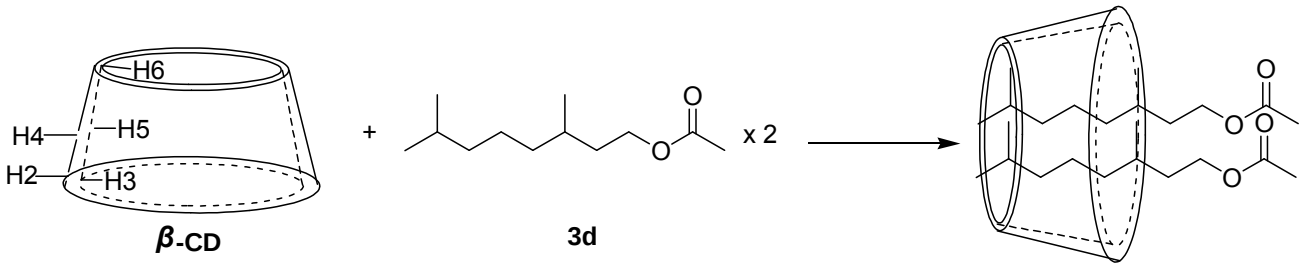
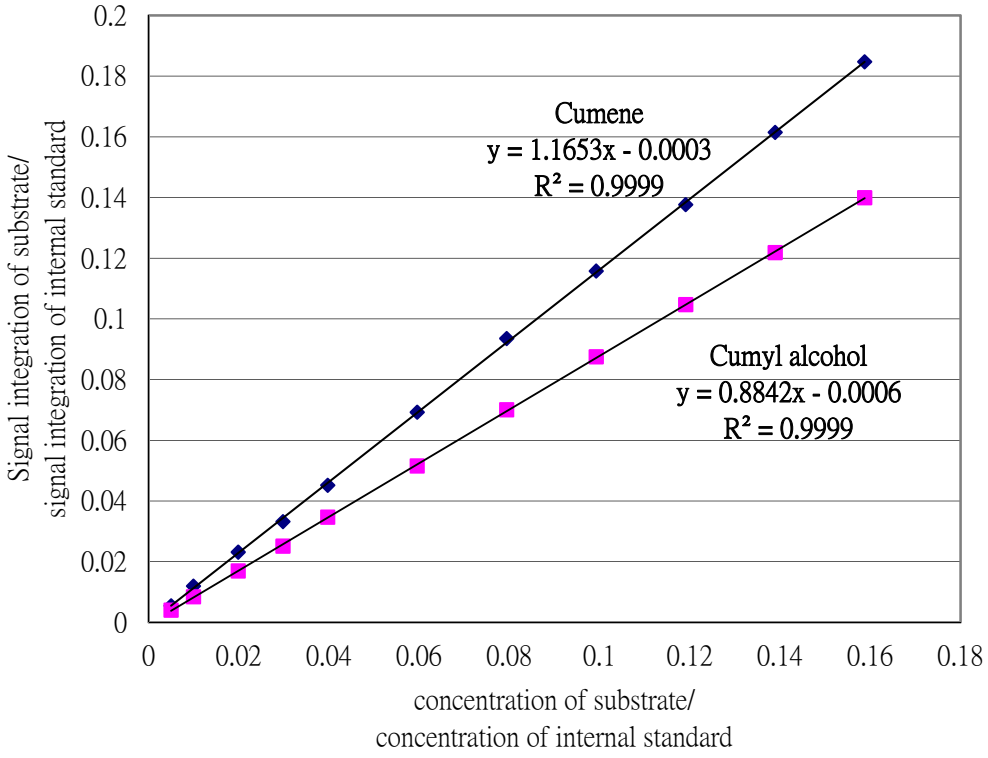


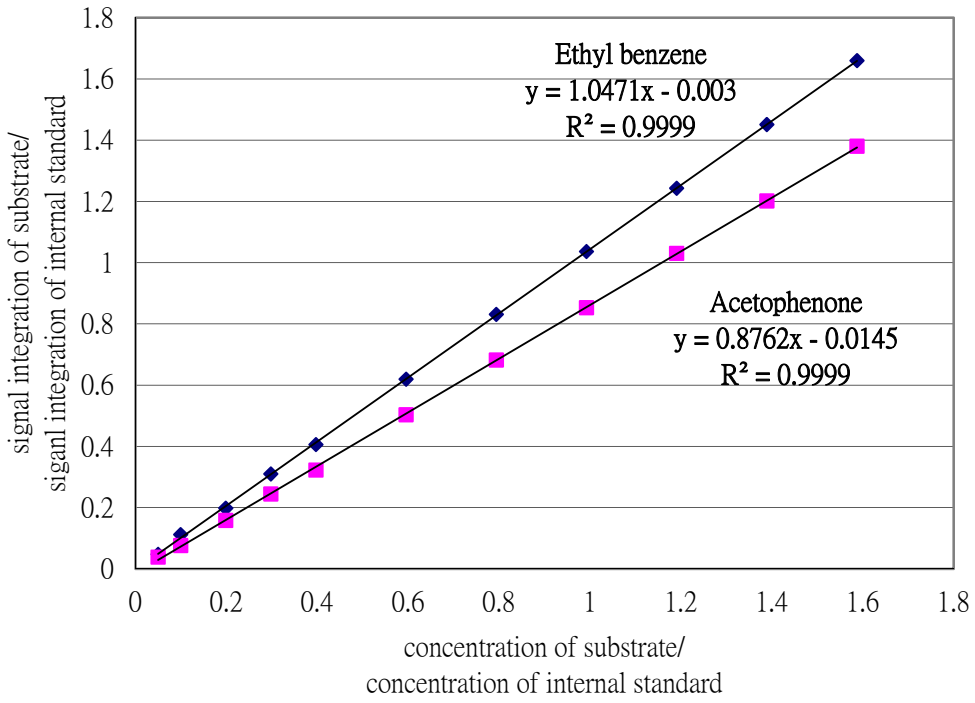
Figure S19. Proposed binding geometry for the inclusion of **3d** in *β*-CD.

Calibration Curve for GC Analysis

(a) Cumene (**6a**) and cumyl alcohol (**7a**) (25 – 800 ppm), internal standard: n-decane (5040 ppm)



(b) Ethyl benzene (**6b**) and acetophenone (**7b**) (25 – 975 ppm), internal standard: n-decane (504 ppm)

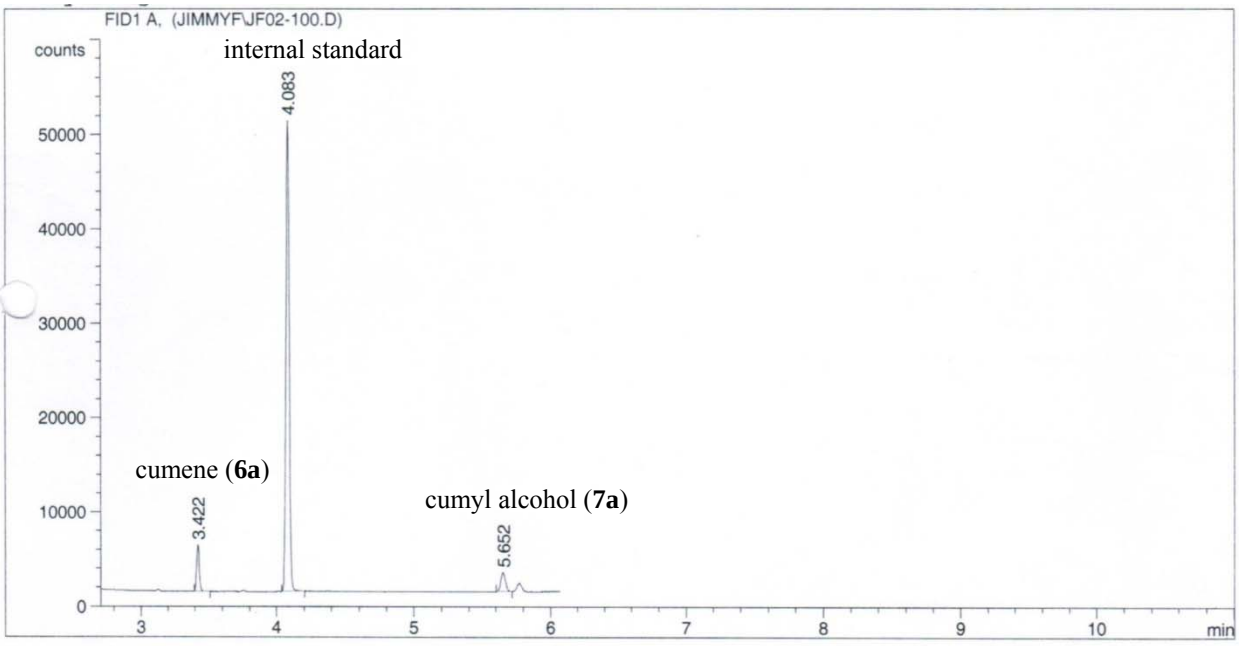


Chromatogram of C-H bond Oxidation of 6a and 6b

(a) Oxidation of 6a in H_2O with *β*-CD

Temperature program: The temperature initially stayed at 105 °C for 3 min, then rose to 110 °C at the rate of 70 °C per min, and finally stayed at 110 °C for 3 min.

Concentration of internal standard: 3111 ppm

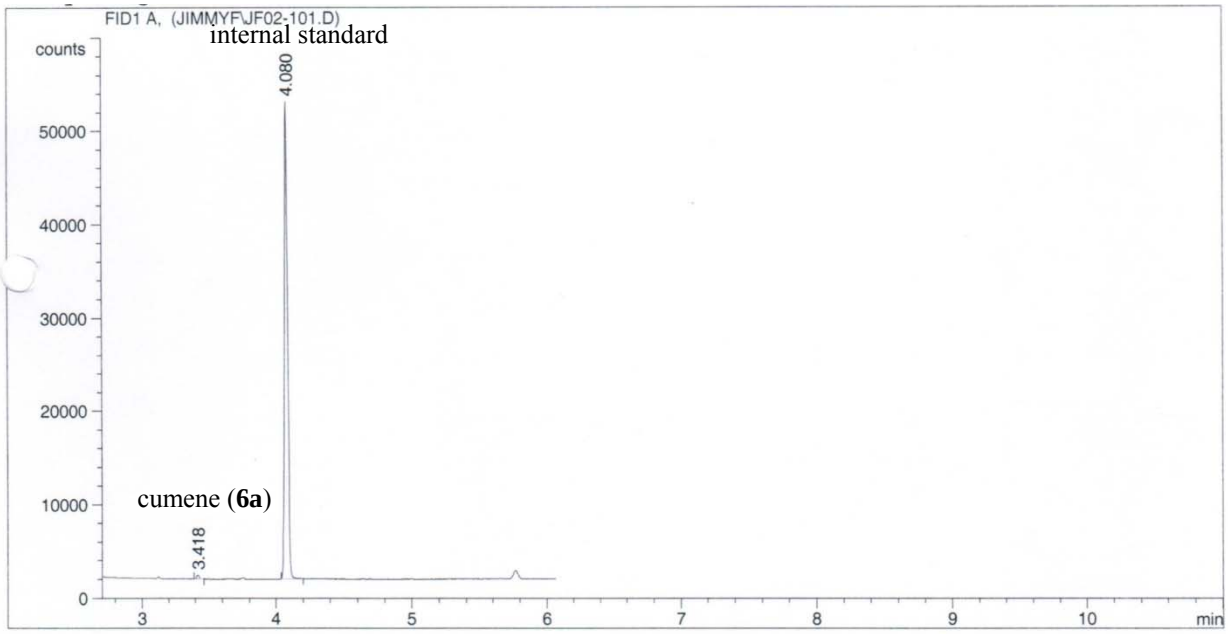



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.422 BB    0.0220 6805.32422 4972.39062  7.14136
   2   4.083 BB    0.0265 8.35267e4  4.99685e4  87.65111
   3   5.652 BV    0.0362 4962.49072 2050.17944  5.20753

Totals :                  9.52945e4  5.69911e4

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
```

(b) Oxidation of 6a in H_2O

Temperature program: The temperature initially stayed at 105 °C for 3 min, then rose to 110 °C at the rate of 70 °C per min, and finally stayed at 110 °C for 3 min.

Concentration of internal standard: 3111 ppm

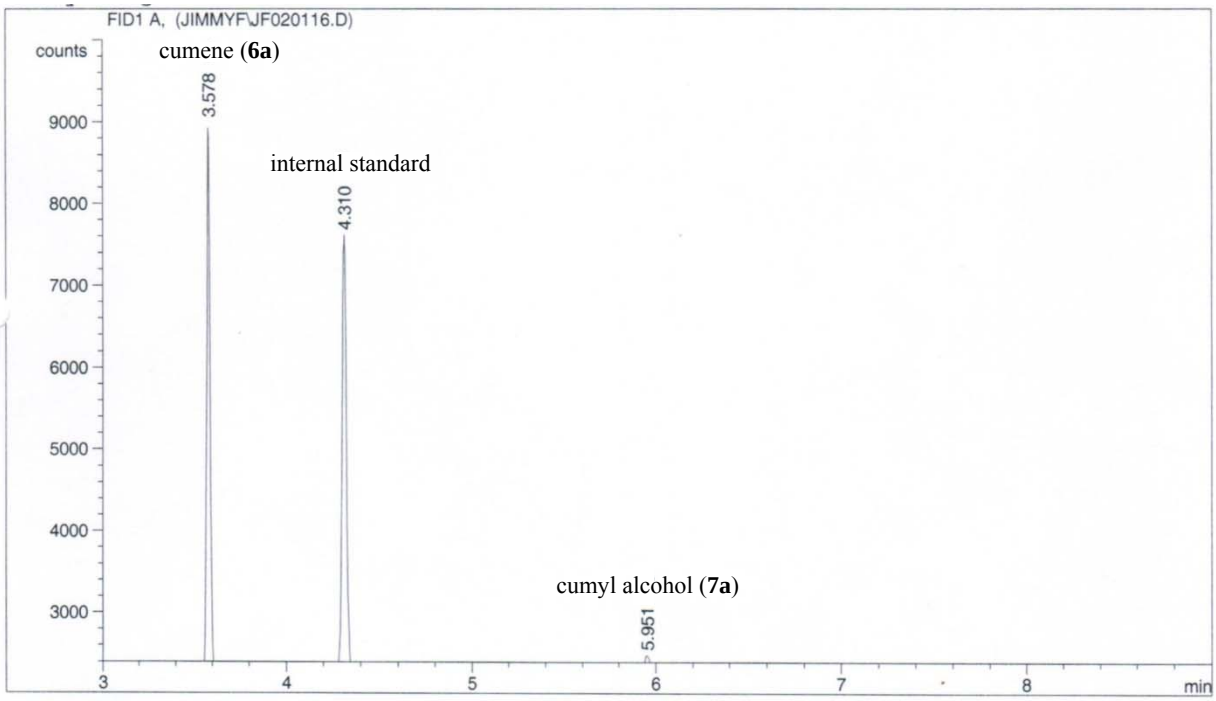



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.418 PB    0.0211  553.42493  426.21051  0.65376
   2   4.080 BB    0.0262 8.40989e4  5.11577e4  99.34624

Totals :                  8.46523e4  5.15840e4

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
```

(c) Oxidation of 6a in H_2O/CH_3CN without β-CD

Temperature program: The temperature initially stayed at 100 °C for 3 min, then rose to 110 °C at the rate of 70 °C per min, and finally stayed at 110 °C for 3 min.

Concentration of internal standard: 311 ppm

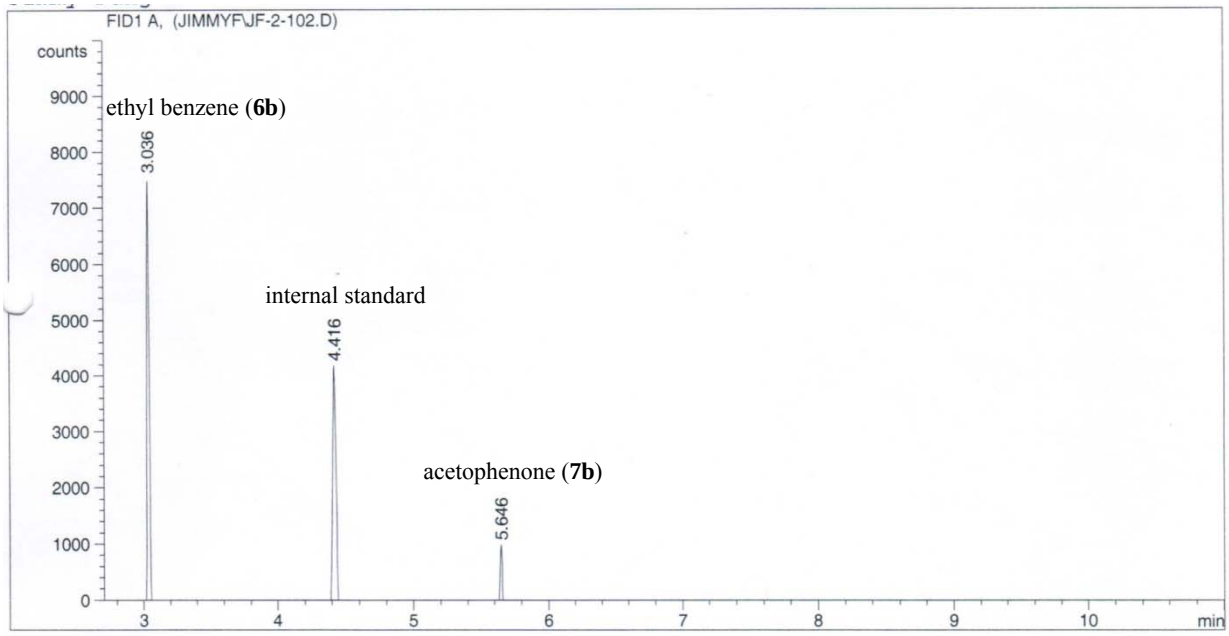



```
================================================================================
                              Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.578 BV    0.0198 8487.38379 6696.82227 47.50764
   2   4.310 VB    0.0262 8798.01367 5352.95313 49.24637
   3   5.951 BP    0.0315  579.90680  246.19954  3.24599

Totals :                  1.78653e4  1.22960e4

 Results obtained with enhanced integrator!
================================================================================
                              *** End of Report ***
```

(d) Oxidation of 6b in H_2O with β-CD

Temperature program: The temperature initially stayed at 100 °C for 3 min, then rose to 180 °C at the rate of 70 °C per min, and finally stayed at 180 °C for 3 min.

Concentration of internal standard: 311 ppm

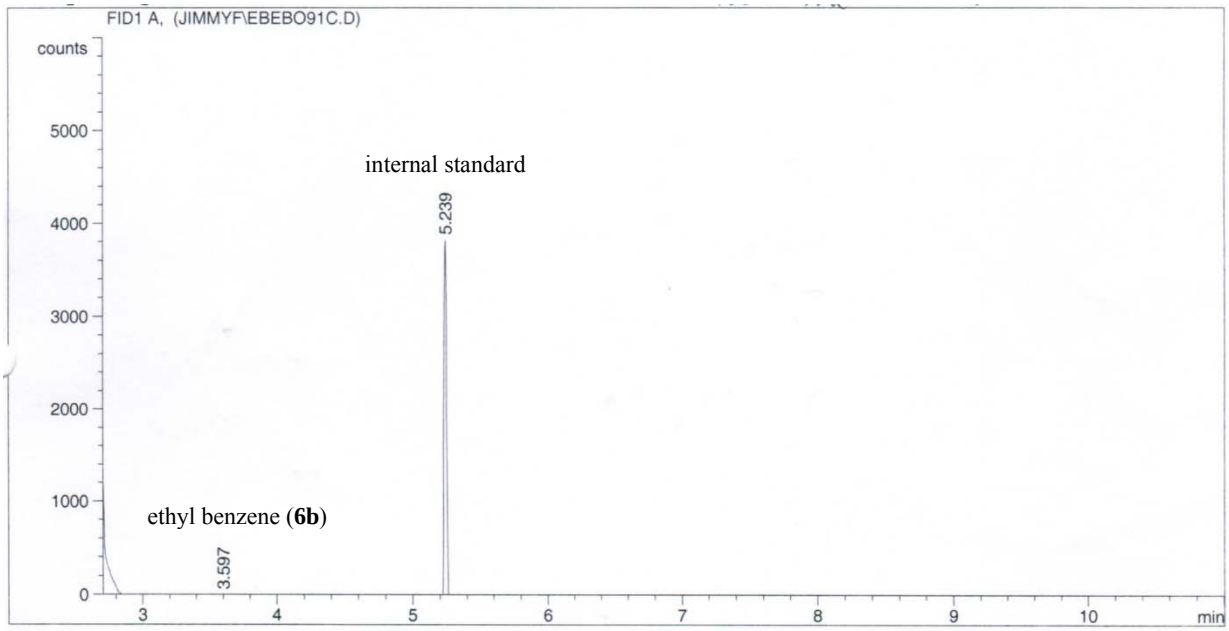



```
================================================================================
                          Area Percent Report
================================================================================

 orted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000
Sample Amount          :      1.00000  [ng/ul]   (not used in calc.)

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.036 PB    0.0191 9496.75781 7858.29980 46.45183
   2   4.416 VB    0.0305 8946.07324 4647.00146 43.75825
   3   5.646 BP    0.0211 2001.48279 1447.86682  9.78992

Totals :                  2.04443e4  1.39532e4

 Results obtained with enhanced integrator!
================================================================================

trument 1 12/15/10 4:37:11 PM Jimmy                          Page 1 of 1
```

(e) Oxidation of 6b in H_2O

Temperature program: The temperature initially stayed at 100 °C for 5 min, then rose to 180 °C at the rate of 70 °C per min, and finally stayed at 180 °C for 2 min.

Concentration of internal standard: 311 ppm

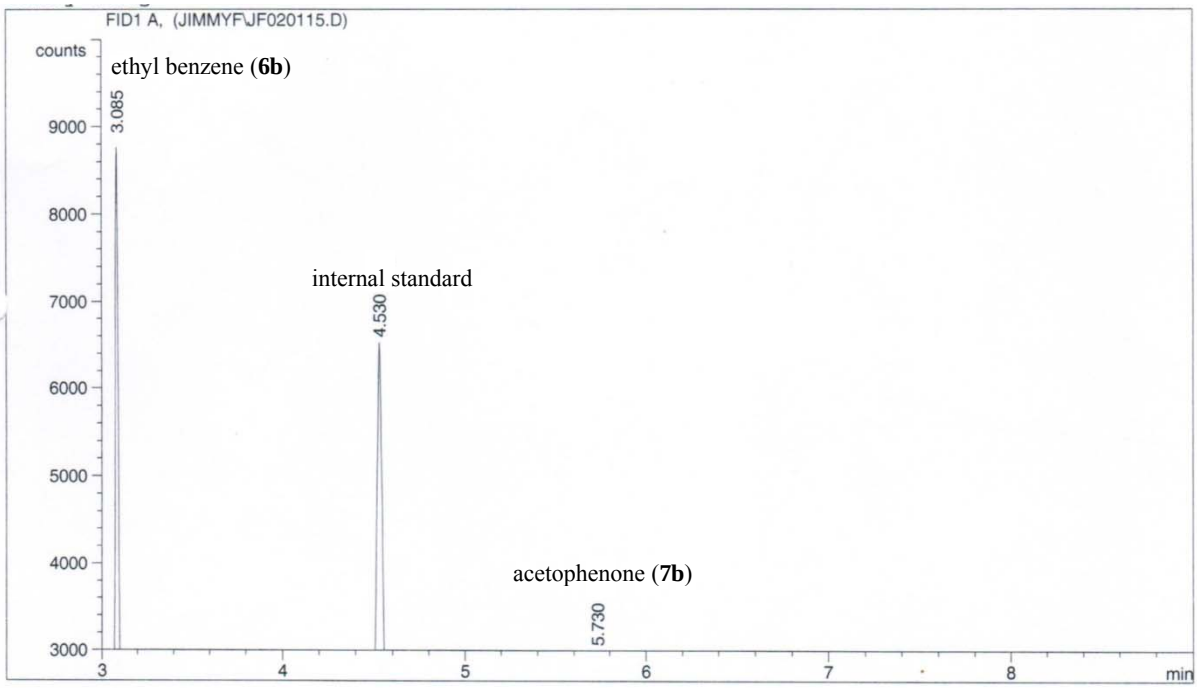



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
ample Amount          :      1.00000  [ng/ul]   (not used in calc.)

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.597 BP    0.0217  354.67297  248.26387  4.74011
   2   5.239 BV    0.0247 7127.70703 4452.40576 95.25989

Totals :                  7482.38000 4700.66963

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

(f) Oxidation of 6b in H_2O/CH_3CN without β-CD

Temperature program: The temperature initially stayed at 100 °C for 3 min, then rose to 180 °C at the rate of 70 °C per min, and finally stayed at 180 °C for 3 min.

Concentration of internal standard: 311 ppm

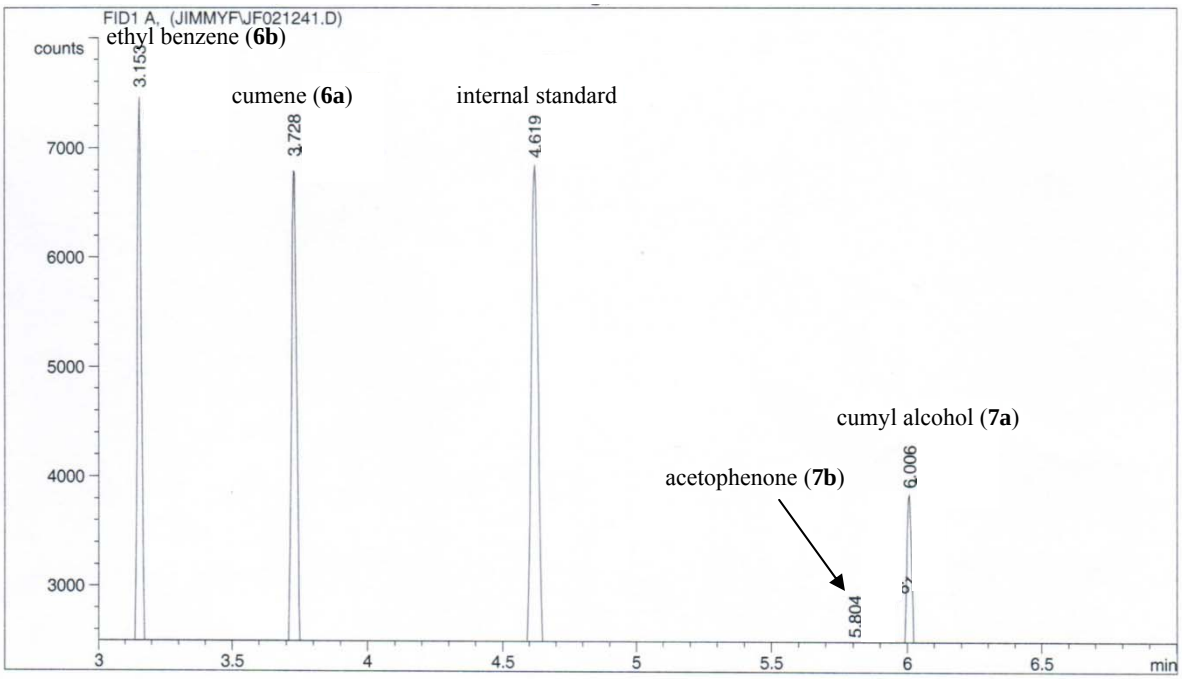



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.085 BP    0.0172 7318.51367 6479.84033 46.57081
   2   4.530 PB    0.0296 8169.40381 4209.70801 51.98538
   3   5.730 BV    0.0219  226.89276  148.01051  1.44381

Totals :                  1.57148e4  1.08376e4

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
```

(g) Oxidation of a mixture of 6a and 6b in H_2O with β-CD

Temperature program: The temperature initially stayed at 100 °C for 3 min, then rose to 180 °C at the rate of 70 °C per min, and finally stayed at 180 °C for 2 min.

Concentration of internal standard: 311 ppm

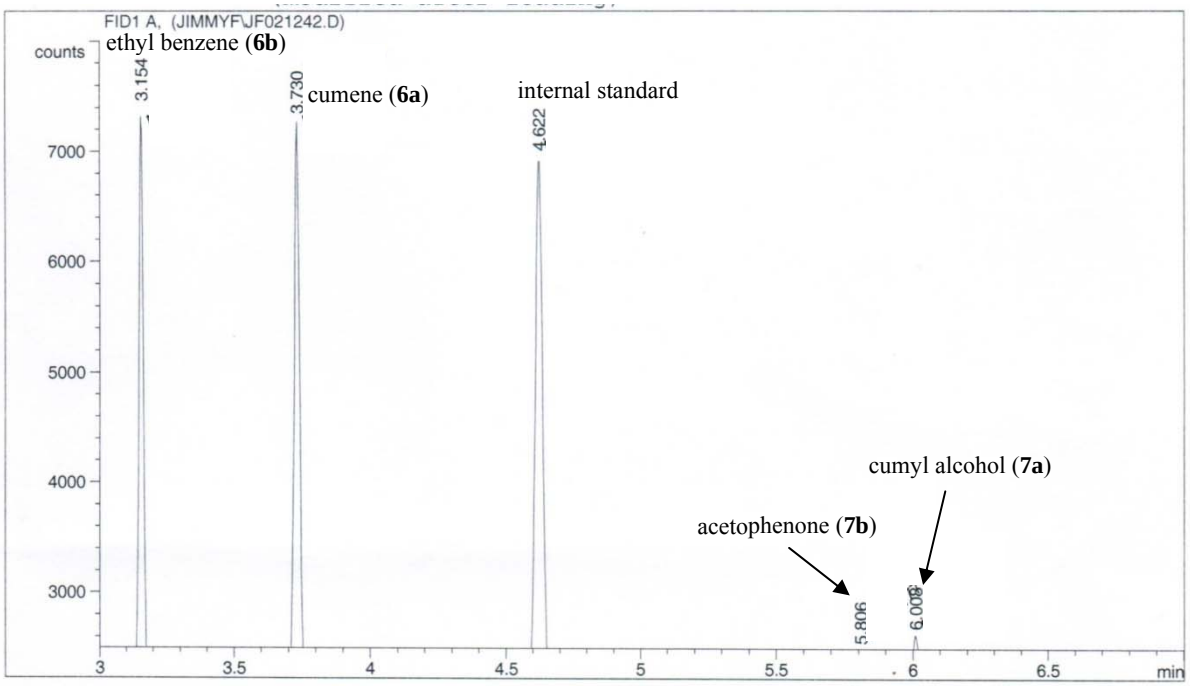



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.153 MM    0.0191 6220.30762 5415.76953 24.50126
   2   3.728 MM    0.0241 6983.68750 4834.27930 27.50815
   3   4.619 MM    0.0323 9355.64746 4820.53369 36.85110
   4   5.804 MM    0.0236  161.70407  114.41843  0.63694
   5   6.006 MM    0.0249 2666.35620 1786.06433 10.50255

Totals :                  2.53877e4  1.69711e4

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

(h) Oxidation of a mixture of 6a and 6b in H_2O/CH_3CN without *β*-CD

Temperature profile: The temperature initially stayed at 100 °C for 3 min, then rose to 180 °C at the rate of 70 °C per min, and finally stayed at 180 °C for 2 min.

Concentration of internal standard: 311 ppm




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   3.154 MM    0.0189 5984.56348 5269.64111 24.83551
   2   3.730 MM    0.0238 7451.79248 5213.46387 30.92440
   3   4.622 MM    0.0329 9665.46289 4899.29199 40.11098
   4   5.806 MM    0.0211  177.60823  140.13611  0.73706
   5   6.008 MM    0.0260  817.37604  523.15692  3.39205

Totals :                  2.40968e4  1.60457e4

 Results obtained with enhanced integrator!
---------------------------------
```