

# Organocatalytic enantioselective conjugate addition of 2-naphthols to *ortho*-hydroxyphenyl substituted *para*-quinone methides: access to unsymmetrical triarylmethanes

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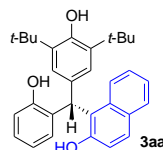
## Supporting Information

### Contents

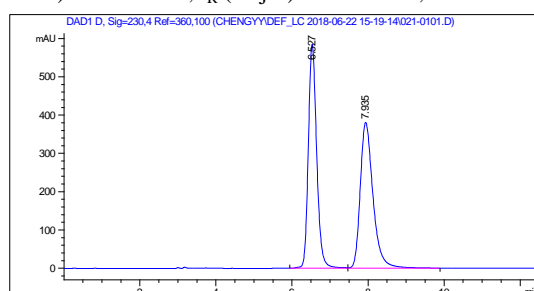
|   |     |
|---|-----|
| Compounds characterization of <b>3</b>                                  | S2  |
| Crystal structure and data for compound <b>3ha</b>                      | S10 |
| Transformation of <b>3aa</b> to <b>4aa</b>                              | S12 |
| Application of <b>3aa</b> as ligand in asymmetric 1,2-addition reaction | S13 |
| Asymmetric conjugate additions of <i>p</i> -QMs <b>5</b> and 2-naphthol | S14 |
| Copies of NMR spectra   | S16 |

## Compounds characterization of 3

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)naphthalen-2-ol (3aa)

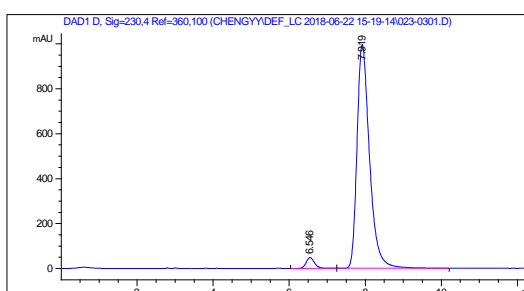


89.6 mg, 95% yield; White solid, mp 198.6-200.1 °C;  $[\alpha]_D^{20} = +104.00$  (c = 20 mg/mL, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ (ppm) 8.01 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.06-7.01 (m, 4H), 6.86-6.83 (m, 2H), 6.45 (s, 1H), 5.62 (s, 1H), 5.22 (s, 1H), 5.10 (s, 1H), 1.30 (s, 18H). <sup>13</sup>C NMR (126 Hz, CDCl<sub>3</sub>): δ (ppm) 153.6, 153.5, 153.4, 137.1, 133.5, 130.3, 130.1, 129.8, 128.8, 128.6, 128.2, 126.9, 125.4, 123.3, 123.1, 121.6, 119.9, 119.1, 116.2, 42.9, 34.6, 30.3. HRMS: exact mass calculated for [M-H]<sup>-</sup>(C<sub>31</sub>H<sub>33</sub>O<sub>3</sub>) requires *m/z* 453.24352, found *m/z* 453.24384. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 230 nm, retention time: *t*<sub>R</sub> (minor) = 6.546 min, *t*<sub>R</sub> (major) = 7.919 min, 94% ee.



Racemic

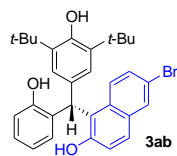
| # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|
| 1 | 6.527 | 8923.1 | 584.8  | 0.234  | 50.193 | 0.787    |
| 2 | 7.935 | 8854.5 | 380.6  | 0.3555 | 49.807 | 0.682    |



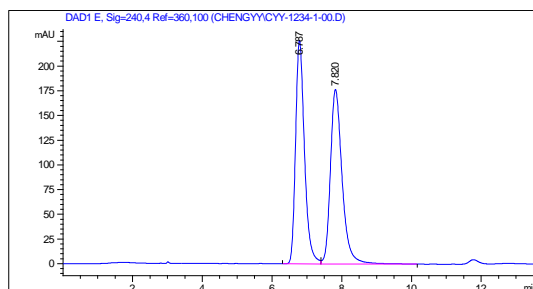
Chiral

| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 6.546 | 739.1   | 48     | 0.2355 | 3.145  | 0.808    |
| 2 | 7.919 | 22757.5 | 997    | 0.3483 | 96.855 | 0.65     |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-6-bromonaphthalen-2-ol (3ab)

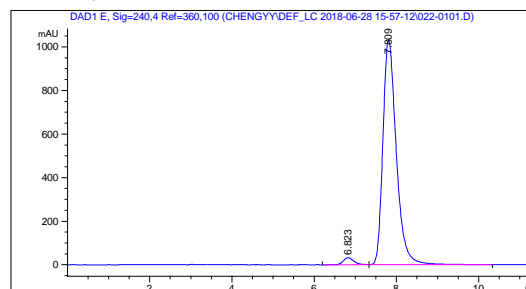


(3ab) 74.0 mg, 70% yield; White solid, mp 183.8-185.4 °C;  $[\alpha]_D^{20} = +102.5$  (c = 20 mg/mL, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ (ppm) 7.91-7.86 (m, 2H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.45 (dd, *J* = 2.0, 9.5 Hz, 1H), 7.17-7.13 (m, 1H), 7.07-6.99 (m, 4H), 6.86-6.83 (m, 2H), 6.42 (s, 1H), 5.41 (br s, 2H), 5.23 (s, 1H), 1.32 (s, 18H). <sup>13</sup>C NMR (126 Hz, CDCl<sub>3</sub>): δ (ppm) 153.7, 153.4, 137.1, 132.1, 131.0, 130.6, 130.1, 130.0, 128.8, 128.0, 125.3, 125.1, 121.7, 121.0, 119.7, 117.0, 116.2, 42.7, 34.6, 30.3. HRMS: exact mass calculated for [M-H]<sup>-</sup>(C<sub>31</sub>H<sub>32</sub>O<sub>3</sub>Br) requires *m/z* 531.15403, found *m/z* 533.15198. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 240 nm, retention time: *t*<sub>R</sub> (minor) = 6.823 min, *t*<sub>R</sub> (major) = 7.809 min, 95% ee.



Racemic

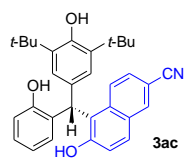
| # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|
| 1 | 6.787 | 4011.9 | 226.2  | 0.2709 | 49.343 | 0.723    |
| 2 | 7.82  | 4118.8 | 176.6  | 0.3541 | 50.657 | 0.705    |



Chiral

| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 6.823 | 584.3   | 32.6   | 0.273  | 2.437  | 0.766    |
| 2 | 7.809 | 23391.2 | 1032.7 | 0.3462 | 97.563 | 0.678    |

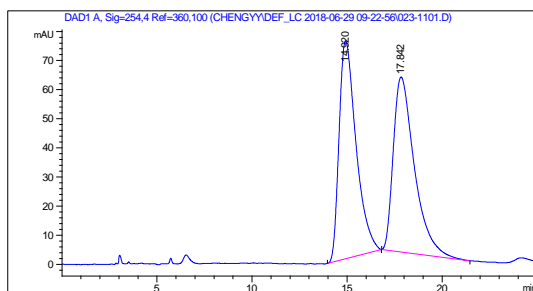
**5-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-6-hydroxynaphthalene-2-**



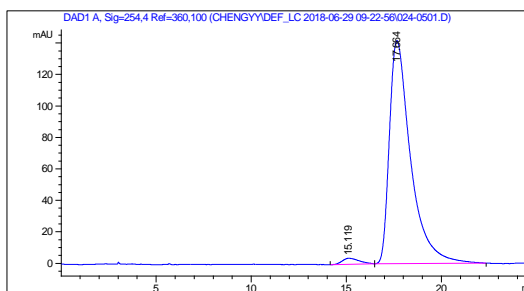
**carbonitrile (3ac)** 76.1 mg, 80% yield; White solid, mp 94.6-96.2 °C;  $[\alpha]_D^{20} = +147.0$

(c = 20 mg/mL, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ (ppm) 8.11-8.07 (m, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.17-7.15 (m, 2H), 7.01-6.99 (m, 3H), 6.88-6.84 (m, 2H), 6.49 (s, 1H), 5.08 (br s, 2H), 5.25 (s, 1H), 1.32 (s, 18H). <sup>13</sup>C NMR (126 Hz, CDCl<sub>3</sub>): δ

(ppm) 156.1, 153.5, 153.4, 137.2, 135.5, 134.7, 130.0, 129.8, 128.8, 128.6, 127.7, 127.4, 125.3, 124.6, 121.7, 121.5, 120.4, 119.7, 116.1, 106.2, 42.4, 34.6, 30.3. HRMS: exact mass calculated for [M-H]<sup>-</sup> (C<sub>32</sub>H<sub>32</sub>NO<sub>3</sub>) requires *m/z* 478.23877, found *m/z* 478.23953. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: *t*<sub>R</sub> (minor) = 15.119 min, *t*<sub>R</sub> (major) = 17.664 min, 96% ee.



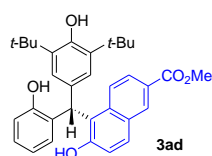
Racemic



Chiral

| # | Time   | Area   | Height | Width  | Area%  | Symmetry | # | Time   | Area    | Height | Width  | Area%  | Symmetry |
|---|--------|--------|--------|--------|--------|----------|---|--------|---------|--------|--------|--------|----------|
| 1 | 14.92  | 4639.6 | 74.9   | 0.9349 | 50.055 | 0.574    | 1 | 15.119 | 234.4   | 3.9    | 0.7314 | 2.088  | 0.589    |
| 2 | 17.842 | 4629.3 | 60.1   | 1.1592 | 49.945 | 0.542    | 2 | 17.664 | 10992.3 | 141.7  | 1.1553 | 97.912 | 0.501    |

**methyl 5-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-6-**



**hydroxynaphthalene-2-carboxylate (3ad)**

85.5 mg, 85% yield; White solid, mp 212.4-213.8 °C;  $[\alpha]_D^{20} = +75.0$  (c = 20 mg/mL,

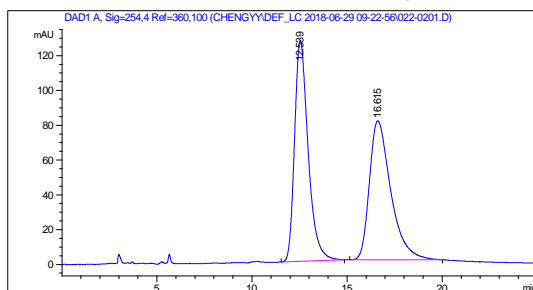
CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ (ppm) 8.52 (s, 1H), 8.04-7.97 (m, 2H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.19-7.16 (m, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 7.02-6.97 (m, 3H), 6.88-6.84 (m,

2H), 6.48 (s, 1H), 5.24 (s, 1H), 3.94 (s, 3H), 1.32 (s, 18H). <sup>13</sup>C NMR (126 Hz, CDCl<sub>3</sub>): δ (ppm) 167.4, 155.6,

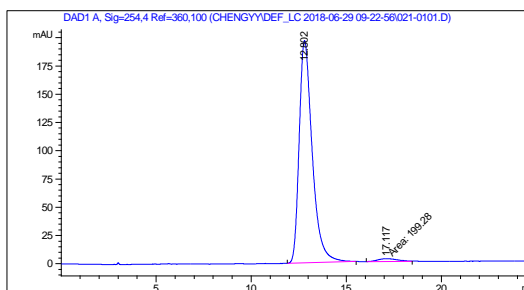
153.4, 137.1, 136.0, 131.7, 131.1, 129.9, 128.7, 127.9, 126.3, 125.3, 124.7, 123.3, 121.6, 120.7, 119.5, 116.1, 52.2,

42.7, 34.5, 30.2. HRMS: exact mass calculated for [M-H]<sup>-</sup> (C<sub>33</sub>H<sub>35</sub>O<sub>5</sub>) requires *m/z* 511.24900, found *m/z*

511.24982. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: *t*<sub>R</sub> (major) = 12.802 min, *t*<sub>R</sub> (minor) = 17.117 min, 96% ee.



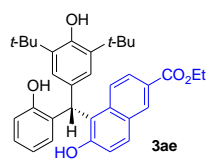
Racemic



Chiral

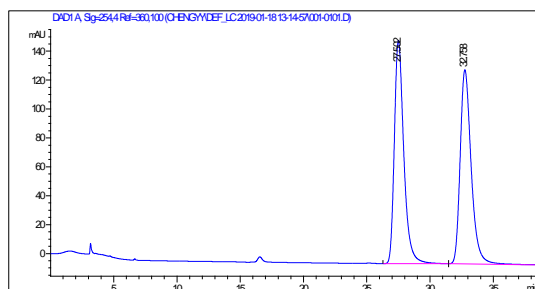
| # | Time   | Area   | Height | Width  | Area%  | Symmetry | # | Time   | Area   | Height | Width  | Area%  | Symmetry |
|---|--------|--------|--------|--------|--------|----------|---|--------|--------|--------|--------|--------|----------|
| 1 | 12.539 | 6290.5 | 126.9  | 0.7545 | 50.219 | 0.678    | 1 | 12.802 | 9362.7 | 196.7  | 0.7193 | 97.916 | 0.639    |
| 2 | 16.615 | 6235.5 | 79.9   | 1.1824 | 49.781 | 0.602    | 2 | 17.117 | 199.3  | 2.6    | 1.2685 | 2.084  | 0.761    |

**ethyl 5-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-6-**

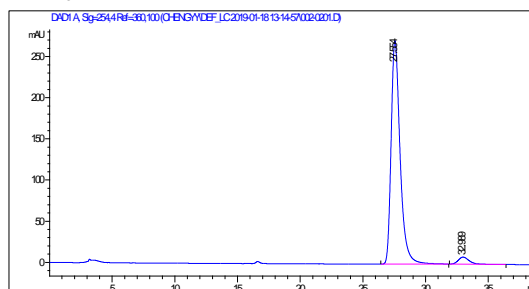


**hydroxynaphthalene-2-carboxylate (3ae)**

86.1 mg, 84% yield. White solid, mp 105.1-106.8 °C;  $[\alpha]_D^{20} = +134.5$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.51 (s, 1H), 8.08-7.98 (m, 2H), 7.80 (d,  $J = 9.2$  Hz, 1H), 7.16-7.10 (m, 2H), 7.02-7.01 (m, 3H), 6.89-6.82 (m, 2H), 6.53 (s, 1H), 5.23 (s, 1H), 4.40 (q,  $J = 7.2$  Hz, 2H), 1.40 (t,  $J = 7.2$  Hz, 3H), 1.32 (s, 18H).  $^{13}\text{C NMR}$  (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.4, 155.6, 153.7, 153.4, 137.1, 136.2, 131.8, 131.0, 130.2, 130.0, 128.8, 128.6, 128.0, 126.3, 125.4, 125.0, 123.5, 121.4, 120.7, 120.0, 116.1, 61.2, 42.6, 34.6, 30.3, 14.5. HRMS: exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{34}\text{H}_{39}\text{O}_5$ ) requires  $m/z$  527.2792, found  $m/z$  527.2798. HPLC conditions: Daicel Chiralpak IA column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time:  $t_R$  (major)=27.554 min,  $t_R$  (minor)= 32.989min, 93% ee.



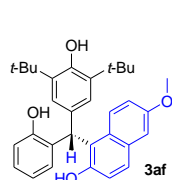
Racemic



Chiral

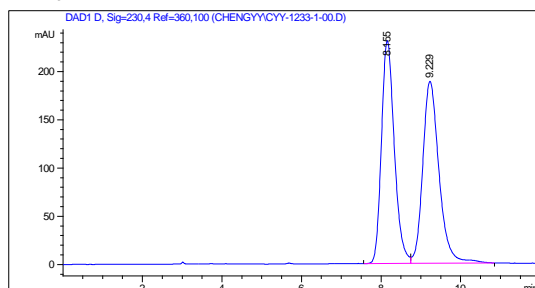
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|---|--------|--------|--------|--------|--------|----------|---|--------|---------|--------|--------|--------|----------|
| 1 | 27.502 | 8031.3 | 154.4  | 0.7889 | 49.766 | 0.684    | 1 | 27.554 | 13498.4 | 271.4  | 0.7562 | 96.376 | 0.673    |
| 2 | 32.758 | 8106.9 | 134.3  | 0.9161 | 50.234 | 0.695    | 2 | 32.989 | 507.5   | 8.6    | 0.8538 | 3.624  | 0.739    |

**1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-6-methoxynaphthalen-2-ol**

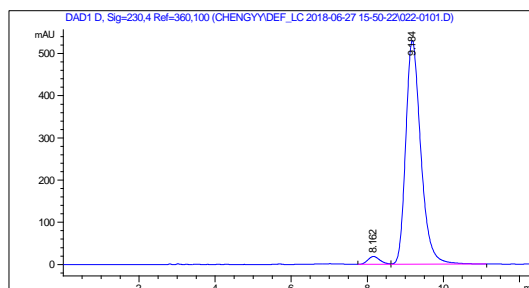


(3af) 87.7 mg, 92% yield; White solid, mp 105.3-107.2 °C;  $[\alpha]_D^{20} = +84.0$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 Hz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  (ppm) 7.96 (d,  $J = 9.5$  Hz, 1H), 7.63 (d,  $J = 9.0$  Hz, 1H), 7.20-7.05 (m, 6H), 6.95 (dd,  $J = 2.5, 9.0$  Hz, 1H), 6.88 (dd,  $J = 1.0, 8.0$  Hz, 1H), 6.76-6.73 (m, 1H), 6.66 (s, 1H), 5.94 (s, 1H), 3.83 (s, 3H), 1.30 (s, 18H).  $^{13}\text{C NMR}$  (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 155.8, 153.7, 153.3, 151.9, 137.0, 130.8, 130.3, 130.1, 128.6, 128.5, 128.3,

125.4, 124.7, 121.6, 120.4, 119.5, 119.0, 116.3, 107.3, 55.5, 43.0, 34.6, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{32}\text{H}_{35}\text{O}_4)$  requires  $m/z$  483.25408, found  $m/z$  483.25461. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 8.162 min,  $t_R$  (major) = 9.184 min, 95% ee.



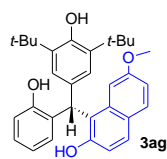
Racemic



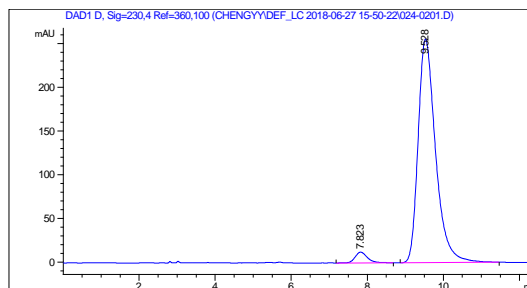
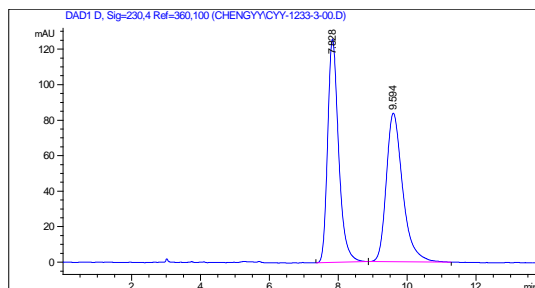
Chiral

| # | Time  | Area   | Height | Width  | Area%  | Symmetry | # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|---|-------|---------|--------|--------|--------|----------|
| 1 | 8.155 | 5194.4 | 231.2  | 0.3461 | 49.201 | 0.774    | 1 | 8.162 | 411.6   | 18.6   | 0.3457 | 2.748  | 0.813    |
| 2 | 9.229 | 5363.2 | 188.7  | 0.4336 | 50.799 | 0.743    | 2 | 9.184 | 14563.5 | 530.2  | 0.4204 | 97.252 | 0.715    |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-7-methoxynaphthalen-2-ol



**(3ag)** 84.5 mg, 85% yield; White solid, mp 107.5-109.2 °C;  $[\alpha]_D^{20} = +77.5$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.00 (s, 2H), 7.65-7.61 (m, 2H), 7.27 (d,  $J = 2.0$  Hz, 1H), 7.16 (dd,  $J = 1.3, 7.8$  Hz, 1H), 7.09-7.02 (m, 4H), 6.90 (dd,  $J = 1.0, 3.0$  Hz, 1H), 6.84 (dd,  $J = 2.3, 8.8$  Hz, 1H), 6.76-6.71 (m, 2H), 5.91 (s, 1H), 3.52 (s, 3H), 1.29 (s, 18H).  $^{13}\text{C NMR}$  (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 158.3, 153.7, 153.2, 136.9, 134.8, 130.5, 130.2, 129.4, 128.5, 125.5, 125.1, 121.5, 118.5, 117.1, 116.1, 115.3, 103.1, 55.2, 42.9, 34.5, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-$  ( $\text{C}_{32}\text{H}_{35}\text{O}_4$ ) requires  $m/z$  483.25408, found  $m/z$  483.25476. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 7.823 min,  $t_R$  (major) = 9.528 min, 93% ee.

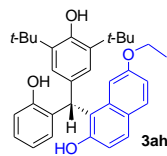


Racemic

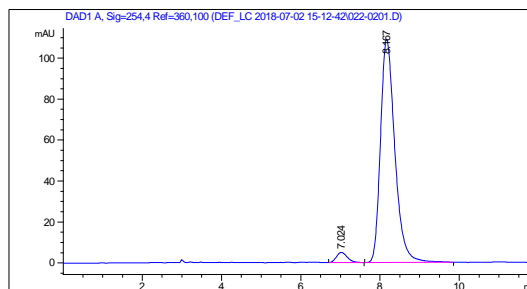
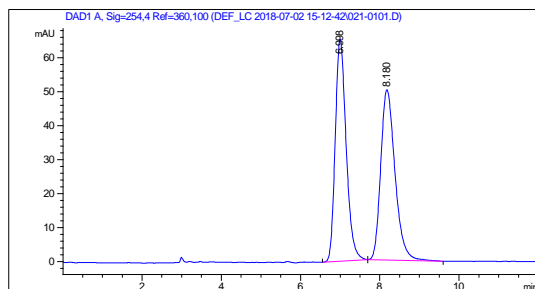
Chiral

| # | Time  | Area   | Height | Width  | Area%  | Symmetry | # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|---|-------|--------|--------|--------|--------|----------|
| 1 | 7.828 | 2774.4 | 125.8  | 0.3373 | 50.105 | 0.726    | 1 | 7.823 | 283.2  | 12.4   | 0.3494 | 3.360  | 0.785    |
| 2 | 9.594 | 2762.8 | 83.7   | 0.503  | 49.895 | 0.698    | 2 | 9.528 | 8146.6 | 256.1  | 0.4852 | 96.640 | 0.675    |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-7-ethoxynaphthalen-2-ol



**(3ah)** 87.9 mg, 89% yield; White solid, mp 169.6-171.4 °C;  $[\alpha]_D^{20} = +70.5$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.64-7.59 (m, 2H), 7.30 (s, 1H), 7.14-7.05 (m, 4H), 6.96-6.80 (m, 4H), 6.37 (s, 1H), 5.55 (br s, 2H), 5.19 (s, 1H), 3.03-3.9 (m, 2H), 1.34-1.31 (m, 21H).  $^{13}\text{C NMR}$  (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 157.6, 153.8, 153.7, 153.2, 136.9, 134.8, 130.6, 130.2, 129.4, 128.5, 125.5, 125.1, 121.5, 118.4, 116.9, 116.2, 115.6, 103.9, 63.3, 42.9, 34.5, 30.3, 14.8. HRMS: exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{33}\text{H}_{39}\text{O}_4$ ) requires  $m/z$  499.2848, found  $m/z$  499.2842. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time:  $t_R$  (minor) = 7.024 min,  $t_R$  (major) = 8.167 min, 93% ee.

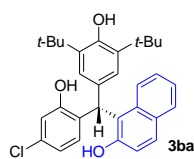


Racemic

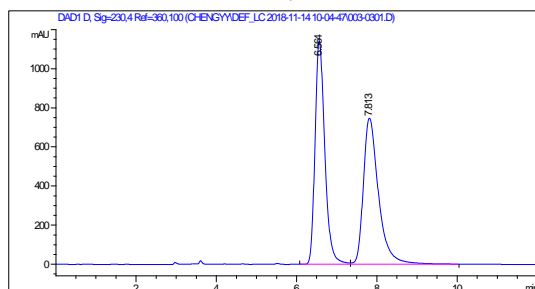
Chiral

| # | Time  | Area   | Height | Width  | Area%  | Symmetry | # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|---|-------|--------|--------|--------|--------|----------|
| 1 | 6.998 | 1247.9 | 65.3   | 0.2949 | 49.922 | 0.754    | 1 | 7.024 | 92.3   | 4.9    | 0.2956 | 3.267  | 0.778    |
| 2 | 8.18  | 1251.8 | 50.1   | 0.3836 | 50.078 | 0.722    | 2 | 8.167 | 2734.2 | 109    | 0.3848 | 96.733 | 0.696    |

**1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(4-chloro-2-hydroxyphenyl)methyl)naphthalen-2-ol**

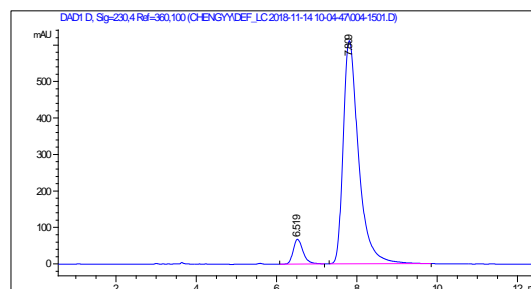


**(3ba)** 83.8 mg, 83% yield; White solid, mp 105.6-107.3 °C;  $[\alpha]_D^{20} = +97.5$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.94 (d,  $J = 9.0$  Hz, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.71 (d,  $J = 9.0$  Hz, 1H), 7.40 (t,  $J = 7.8$  Hz, 1H), 7.31 (t,  $J = 7.3$  Hz, 1H), 7.04-7.02 (m, 3H), 6.97 (d,  $J = 8.5$  Hz, 1H), 6.86 (d,  $J = 1.5$  Hz, 1H), 6.82 (d,  $J = 8.0$  Hz, 1H), 6.42 (s, 1H), 5.60 (br s, 2H), 5.24 (s, 1H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 154.4, 153.5, 153.2, 137.2, 133.4, 133.3, 131.2, 130.0, 129.9, 128.9, 127.0, 125.3, 123.5, 123.1, 121.5, 119.7, 118.9, 116.5, 42.4, 34.6, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{31}\text{H}_{32}\text{O}_3\text{Cl})$  requires  $m/z$  487.20455, found  $m/z$  487.20454. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 6.519 min,  $t_R$  (major) = 7.809 min, 87% ee.



Racemic

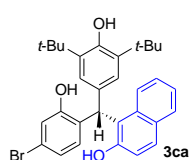
| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 6.564 | 19350.7 | 1143.8 | 0.2594 | 49.724 | 0.721    |
| 2 | 7.813 | 19565.7 | 746.9  | 0.3956 | 50.276 | 0.614    |



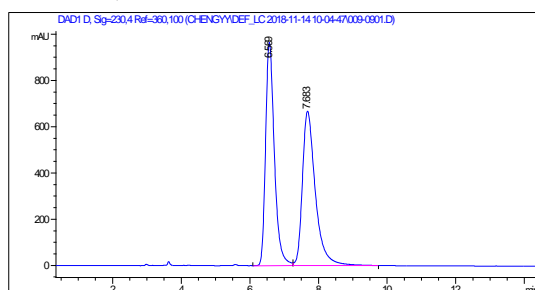
Chiral

| # | Time  | Area  | Height | Width  | Area%  | Symmetry |
|---|-------|-------|--------|--------|--------|----------|
| 1 | 6.519 | 1147  | 67.8   | 0.2593 | 6.592  | 0.745    |
| 2 | 7.809 | 16252 | 611.4  | 0.4001 | 93.408 | 0.597    |

**1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(4-bromo-2-hydroxyphenyl)methyl)naphthalen-2-ol**

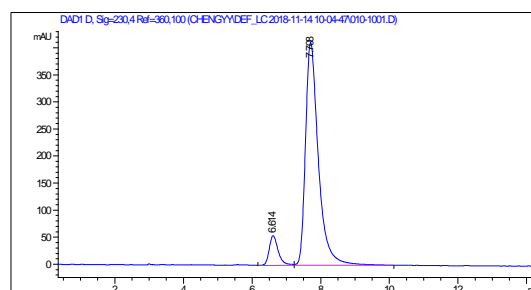


**(3ca)** 83.9 mg, 79% yield; White solid, mp 104.1-105.3 °C;  $[\alpha]_D^{20} = +99.0$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.97 (d,  $J = 8.8$  Hz, 1H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.74 (d,  $J = 8.8$  Hz, 1H), 7.43 (t,  $J = 7.4$  Hz, 1H), 7.35 (t,  $J = 7.4$  Hz, 1H), 7.08-7.05 (m, 4H), 7.01-6.93 (m, 2H), 6.45 (s, 1H), 5.67 (br s, 2H), 5.28 (s, 1H), 1.35 (s, 18H).  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 154.5, 153.5, 153.2, 137.2, 133.3, 131.6, 130.0, 129.8, 128.9, 127.6, 127.0, 125.3, 124.4, 123.5, 123.1, 121.2, 119.7, 119.3, 118.9, 42.4, 34.6, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{31}\text{H}_{32}\text{O}_3\text{Br})$  requires  $m/z$  531.15403, found  $m/z$  531.15253. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 6.614 min,  $t_R$  (major) = 7.708 min, 83% ee.



Racemic

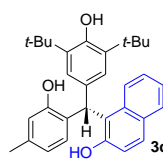
| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 6.569 | 17181.3 | 965.9  | 0.2715 | 49.549 | 0.694    |
| 2 | 7.683 | 17494.1 | 667.5  | 0.3938 | 50.451 | 0.609    |



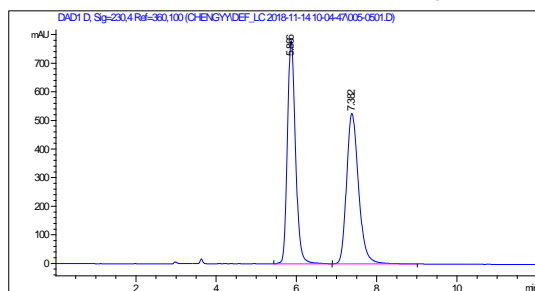
Chiral

| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 6.614 | 1005.6  | 55     | 0.2774 | 8.558  | 0.702    |
| 2 | 7.708 | 10744.9 | 412.1  | 0.3922 | 91.442 | 0.604    |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxy-4-methylphenyl)methyl)naphthalen-2-ol

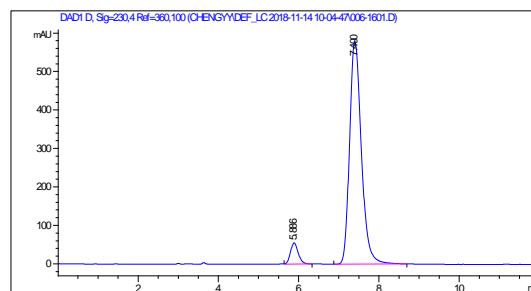


**(3da)** 78.7 mg, 83% yield; White solid, mp 88.8-90.5 °C;  $[\alpha]_D^{20} = +55.5$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.02 (d,  $J = 8.5$  Hz, 1H), 7.76 (d,  $J = 8.0$  Hz, 1H), 7.70 (d,  $J = 9.0$  Hz, 1H), 7.40 (t,  $J = 7.8$  Hz, 1H), 7.30 (t,  $J = 7.3$  Hz, 1H), 7.05-7.03 (m, 3H), 6.88 (d,  $J = 8.0$  Hz, 1H), 6.66 (s, 2H), 6.40 (s, 1H), 5.68 (br s, 1H), 5.20 (s, 1H), 5.04 (br s, 1H), 2.25 (s, 3H), 1.32 (s, 18H).  $^{13}\text{C NMR}$  (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.6, 153.4, 153.2, 138.7, 136.9, 133.4, 130.5, 129.8, 129.7, 128.8, 126.9, 125.4, 125.2, 123.3, 123.1, 122.4, 119.8, 119.1, 117.0, 42.7, 34.5, 30.3, 21.2. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{32}\text{H}_{35}\text{O}_3)$  requires  $m/z$  467.25917, found  $m/z$  467.25943. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 5.886 min,  $t_R$  (major) = 7.4 min, 88% ee.



Racemic

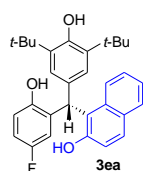
| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 5.866 | 10948.3 | 780.3  | 0.2177 | 50.082 | 0.79     |
| 2 | 7.382 | 10912.4 | 525.7  | 0.3182 | 49.918 | 0.753    |



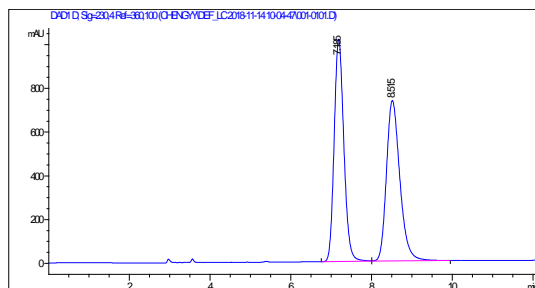
Chiral

| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 5.886 | 744.3   | 55.1   | 0.2097 | 5.918  | 0.822    |
| 2 | 7.4   | 11831.4 | 581.2  | 0.3115 | 94.082 | 0.746    |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(5-fluoro-2-hydroxyphenyl)methyl)naphthalen-2-ol

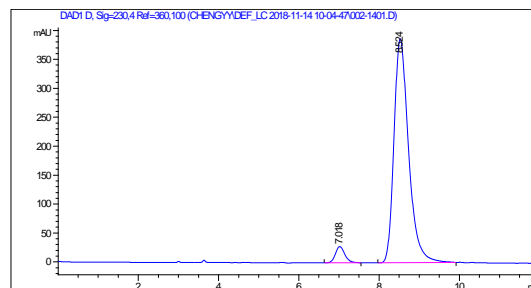


**(3ea)** 86.6 mg, 95% yield; White solid, mp 193.2-194.3 °C;  $[\alpha]_D^{20} = +116.0$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.95 (d,  $J = 8.5$  Hz, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.72 (d,  $J = 9.0$  Hz, 1H), 7.40 (t,  $J = 7.8$  Hz, 1H), 7.32 (t,  $J = 7.5$  Hz, 1H), 7.06-7.03 (m, 3H), 6.84-6.76 (m, 3H), 6.45 (s, 1H), 5.64 (br s, 1H), 5.30 (br s, 1H), 5.23 (s, 1H), 1.32 (s, 18H).  $^{13}\text{C NMR}$  (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 158.5 ( $J = 238.8$  Hz), 153.5, 153.2, 149.6, 137.2, 133.3, 130.1, 130.0 ( $J = 7.6$  Hz), 129.8, 129.7, 128.8, 126.9, 125.2, 123.4, 123.0, 119.8, 118.7, 117.0 ( $J = 8.2$  Hz), 116.7 ( $J = 24.2$  Hz), 114.7 ( $J = 23.1$  Hz), 42.8, 34.5, 30.2. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{31}\text{H}_{32}\text{O}_3\text{F})$  requires  $m/z$  471.23410, found  $m/z$  471.23459. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 7.018 min,  $t_R$  (major) = 8.524 min, 91% ee.



Racemic

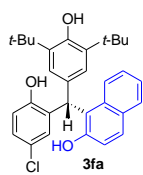
| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 7.185 | 16929   | 1017   | 0.2582 | 49.976 | 0.814    |
| 2 | 8.515 | 16945.2 | 734.3  | 0.3552 | 50.024 | 0.734    |



Chiral

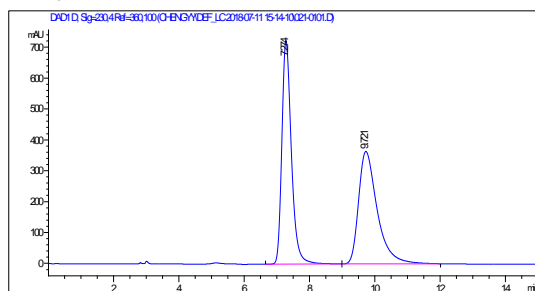
| # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|
| 1 | 7.018 | 459.5  | 27.8   | 0.2526 | 4.480  | 0.828    |
| 2 | 8.524 | 9795.3 | 387    | 0.3853 | 95.520 | 0.693    |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(5-chloro-2-hydroxyphenyl)methyl)naphthalen-2-ol



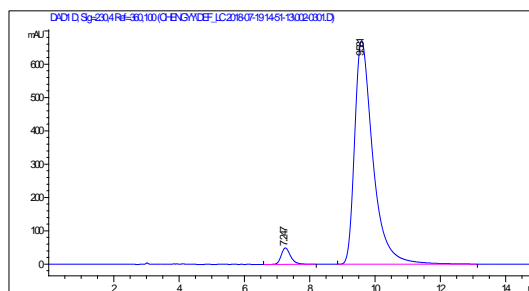
**(3fa)** 87.3 mg, 90% yield; White solid, mp 100.7-102.0 °C;  $[\alpha]_D^{20} = +109.0$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.94 (d,  $J = 8.5$  Hz, 1H), 7.79 (d,  $J = 8.0$  Hz, 1H), 7.73 (d,  $J = 9.0$  Hz, 1H), 7.42 (t,  $J = 7.5$  Hz, 1H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.10-7.01 (m, 5H), 6.78 (d,  $J = 8.5$  Hz, 1H), 6.44 (s, 1H), 5.46 (br s, 1H), 5.25 (s, 1H), 1.32 (s, 18H).  $^{13}\text{C NMR}$  (126 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.5, 153.3, 152.4, 137.2, 133.4, 130.1, 130.0, 129.8, 129.6, 128.9, 128.4,

127.0, 126.2, 125.2, 123.5, 123.0, 119.9, 118.6, 117.4, 42.7, 34.6, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{31}\text{H}_{32}\text{O}_3\text{Cl})$  requires  $m/z$  487.20455, found  $m/z$  487.20453. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 7.247 min,  $t_R$  (major) = 9.581 min, 93% ee.



Racemic

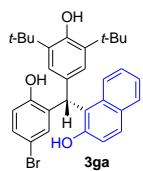
| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 7.274 | 14676.5 | 723.6  | 0.3106 | 50.436 | 0.705    |
| 2 | 9.721 | 14422.5 | 364.3  | 0.5959 | 49.564 | 0.599    |



Chiral

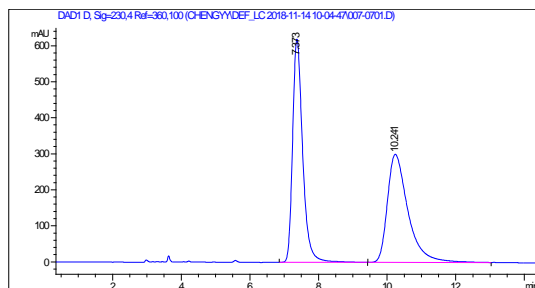
| # | Time  | Area    | Height | Width  | Area%  | Symmetry |
|---|-------|---------|--------|--------|--------|----------|
| 1 | 7.247 | 991.2   | 49.4   | 0.3082 | 3.657  | 0.749    |
| 2 | 9.581 | 26108.8 | 671.2  | 0.5858 | 96.343 | 0.56     |

### 1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(5-bromo-2-hydroxyphenyl)methyl)naphthalen-2-ol



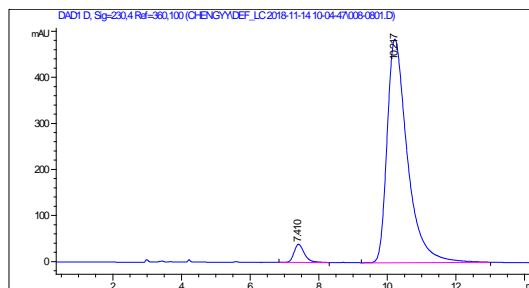
**(3ga)** 60.9 mg, 58% yield; White solid, mp 92.9-93.9 °C;  $[\alpha]_D^{20} = +118.0$  ( $c = 20$  mg/mL,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.94 (d,  $J = 8.8$  Hz, 1H), 7.79 (d,  $J = 7.2$  Hz, 1H), 7.74 (d,  $J = 8.8$  Hz, 1H), 7.44-7.40 (m, 1H), 7.33 (t,  $J = 7.0$  Hz, 1H), 7.26-7.23 (m, 1H), 7.14 (d,  $J = 2.4$  Hz, 1H), 7.05 (d,  $J = 8.8$  Hz, 1H), 7.01 (s, 2H), 6.74 (d,  $J = 8.4$  Hz, 1H), 6.43 (s, 1H), 5.52 (br s, 1H), 5.33 (br s, 1H), 5.25 (s, 1H), 1.32 (s, 18H).  $^{13}\text{C NMR}$  (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.5,

153.2, 152.9, 137.2, 133.4, 132.9, 131.3, 130.6, 130.1, 129.8, 129.6, 128.9, 127.0, 125.2, 123.5, 123.0, 119.9, 118.6, 117.9, 113.6, 42.7, 34.6, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-(\text{C}_{31}\text{H}_{32}\text{O}_3\text{Br})$  requires  $m/z$  531.15403, found  $m/z$  531.15334. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 230$  nm, retention time:  $t_R$  (minor) = 7.41 min,  $t_R$  (major) = 10.217 min, 92% ee.



Racemic

| # | Time   | Area    | Height | Width  | Area%  | Symmetry |
|---|--------|---------|--------|--------|--------|----------|
| 1 | 7.373  | 12603.3 | 619.5  | 0.3093 | 50.236 | 0.686    |
| 2 | 10.241 | 12484.7 | 300    | 0.6276 | 49.764 | 0.576    |

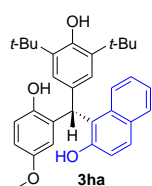


Chiral

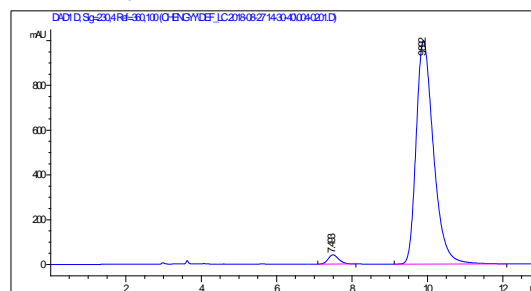
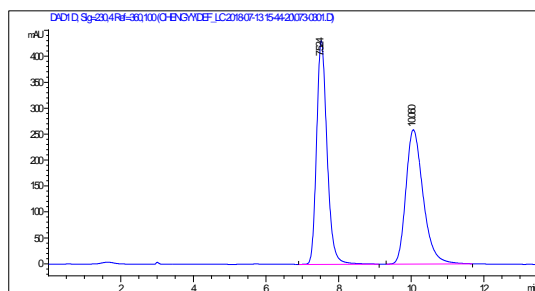
| # | Time   | Area    | Height | Width  | Area%  | Symmetry |
|---|--------|---------|--------|--------|--------|----------|
| 1 | 7.41   | 829.7   | 39.4   | 0.3198 | 4.011  | 0.724    |
| 2 | 10.217 | 19853.9 | 485    | 0.6136 | 95.989 | 0.568    |



**1-((S)-(3,5-di-*t*-butyl-4-hydroxyphenyl)(2-hydroxy-5-methoxyphenyl)methyl)naphthalen-2-ol**



**(3ha)** 87.7 mg, 91% yield; White solid, mp 106.3-107.5 °C;  $[\alpha]_D^{20} = +70.5$  (c = 20 mg/mL, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ (ppm) 8.01 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.05-7.04 (m, 3H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.70-6.68 (m, 1H), 6.60 (s, 1H), 6.42 (s, 1H), 5.66 (br s, 1H), 5.21 (s, 1H), 4.81 (br s, 1H), 3.60 (s, 3H), 1.32 (s, 18H). <sup>13</sup>C NMR (126 Hz, CDCl<sub>3</sub>): δ (ppm) 154.2, 153.5, 153.4, 147.7, 137.0, 133.4, 130.1, 129.9, 129.8, 129.7, 128.8, 126.9, 125.4, 123.3, 123.1, 119.9, 118.8, 117.2, 115.8, 113.2, 55.7, 43.2, 34.6, 30.3. HRMS: exact mass calculated for [M-H]<sup>-</sup>(C<sub>32</sub>H<sub>35</sub>O<sub>4</sub>) requires *m/z* 483.25408, found *m/z* 483.25406. HPLC conditions: Daicel Chiralpak OD-H column, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 230 nm, retention time: *t*<sub>R</sub> (minor) = 7.493 min, *t*<sub>R</sub> (major) = 9.892 min, 95% ee.

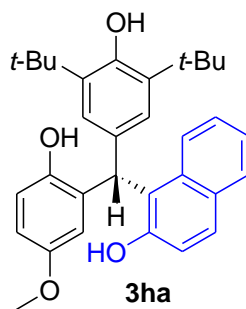
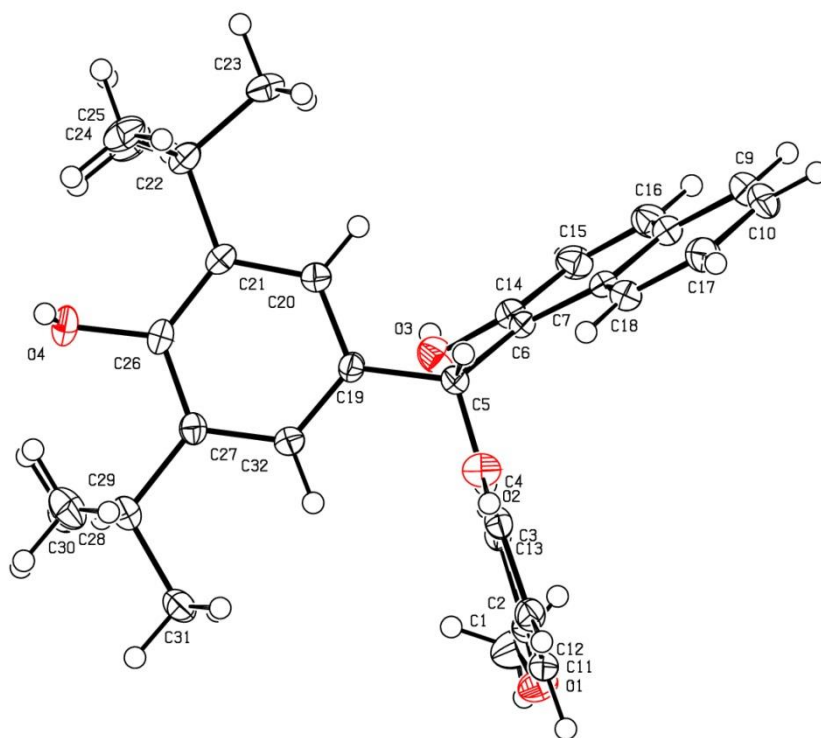


Racemic

Chiral

| # | Time  | Area   | Height | Width  | Area%  | Symmetry | # | Time  | Area  | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|---|-------|-------|--------|--------|--------|----------|
| 1 | 7.524 | 8637.6 | 431.2  | 0.3077 | 50.291 | 0.76     | 1 | 7.493 | 817.9 | 41.1   | 0.3059 | 2.507  | 0.793    |
| 2 | 10.06 | 8537.7 | 258.8  | 0.5048 | 49.709 | 0.711    | 2 | 9.892 | 31807 | 997.5  | 0.49   | 97.493 | 0.663    |

## Crystal Structure and data for compound 3ha



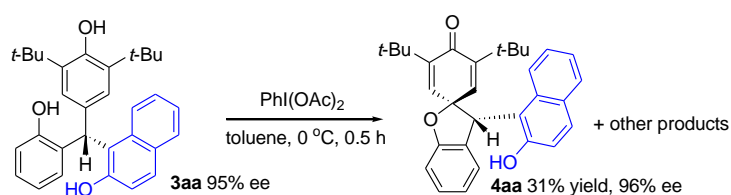
CCDC 1908826

**cxy0594\_0m (3ha) CCDC 1908826**

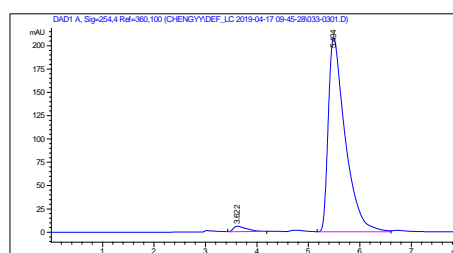
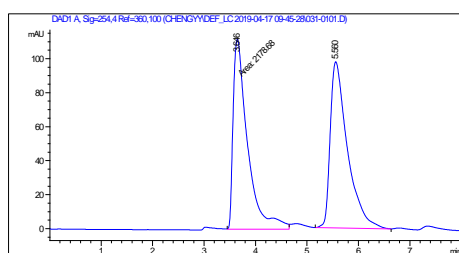
**Table 1 Crystal data and structure refinement for cxy0594\_0m.**

|   |   |
|---|---|
| Identification code                         | cxy0594_0m  |
| Empirical formula                           | C <sub>32</sub> H <sub>36</sub> O <sub>4</sub>                |
| Formula weight                              | 484.61  |
| Temperature/K                               | 100.0   |
| Crystal system                              | orthorhombic  |
| Space group                                 | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                 |
| a/Å   | 10.6683(3)  |
| b/Å   | 11.9783(3)  |
| c/Å   | 20.8929(6)  |
| α/°   | 90  |
| β/°   | 90  |
| γ/°   | 90  |
| Volume/Å <sup>3</sup>                       | 2669.86(13)   |
| Z   | 4   |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.206   |
| μ/mm <sup>-1</sup>                          | 0.617   |
| F(000)                                      | 1040.0  |
| Crystal size/mm <sup>3</sup>                | 0.43 × 0.39 × 0.37  |
| Radiation                                   | CuKα (λ = 1.54178)  |
| 2θ range for data collection/°              | 8.508 to 136.81   |
| Index ranges                                | -12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -24 ≤ l ≤ 25                      |
| Reflections collected                       | 18651   |
| Independent reflections                     | 4860 [R <sub>int</sub> = 0.0435, R <sub>sigma</sub> = 0.0408] |
| Data/restraints/parameters                  | 4860/4/336  |
| Goodness-of-fit on F <sup>2</sup>           | 1.026   |
| Final R indexes [I >= 2σ (I)]               | R <sub>1</sub> = 0.0400, wR <sub>2</sub> = 0.0998             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0417, wR <sub>2</sub> = 0.1012             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.35/-0.32  |
| Flack parameter                             | 0.04(13)  |

## Transformation of **3aa** to **4aa**



To a solution of **3aa** (90.8 mg, 0.2 mmol) in toluene (2.0 mL) was added iodosobenzene diacetate (70.8 mg, 0.22 mmol). The reaction mixture was stirred at  $0\text{ }^\circ\text{C}$  for 30 min. Upon completion, the mixture was purified by silica gel column chromatography to afford pure **4aa** as a yellow oil (28.0 mg, 31% yield).  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.88-7.84 (m, 2H), 7.32-7.29 (m, 2H), 7.27-7.22 (m, 2H), 7.09-7.05 (m, 1H), 6.81 (d,  $J = 3.2$  Hz, 1H), 6.72-6.66 (m, 2H), 6.56-6.54 (m, 1H), 6.18 (d,  $J = 2.8$  Hz, 1H), 5.48 (s, 1H), 5.15 (s, 1H), 1.25 (s, 9H), 0.95 (s, 9H).  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 187.2, 156.8, 153.6, 146.2, 145.5, 139.4, 138.2, 131.0, 130.7, 130.0, 129.5, 129.0, 128.5, 127.1, 125.4, 123.6, 123.4, 120.8, 119.2, 115.3, 112.8, 86.2, 50.4, 34.8, 34.7, 29.5, 29.1. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-$  ( $\text{C}_{31}\text{H}_{31}\text{O}_3$ ) requires  $m/z$  451.2268, found  $m/z$  451.2269; HPLC conditions: Daicel Chiralpak AD-3 column, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time:  $t_R$  (minor) = 3.622 min,  $t_R$  (major) = 5.494 min, 96% ee.



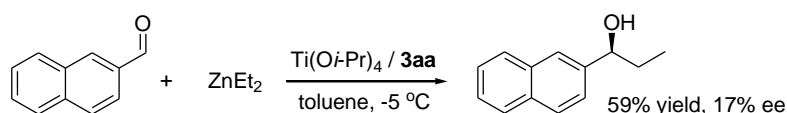
Racemic

| # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|
| 1 | 3.646 | 2178.7 | 111.7  | 0.3251 | 48.989 | 0.39     |
| 2 | 5.56  | 2268.6 | 97.7   | 0.3388 | 51.011 | 0.44     |

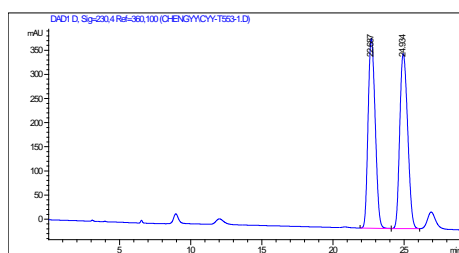
Chiral

| # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|
| 1 | 3.622 | 105.3  | 5.9    | 0.2588 | 2.169  | 0.409    |
| 2 | 5.494 | 4748.7 | 208    | 0.3363 | 97.831 | 0.435    |

### Application of **3aa** as ligand in asymmetric 1,2-addition reaction

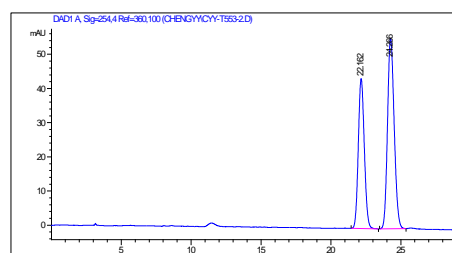


According to reference (J. Am. Chem. Soc. 2015, 137, 15062), Titanium tetraisopropoxide (427.6 mg, 1.5 mmol) was added to a solution of **3aa** (45.3 mg, 0.1 mmol) in toluene (1.0 mL) at  $-5\text{ }^\circ\text{C}$  under  $\text{N}_2$  and the mixture was stirred for 1 h followed by addition of diethylzinc (3.0 mL, 1.0 mol/mL in hexane). After 2 h, 2-naphthylaldehyde (156.3 mg, 1.0 mmol) in toluene (1.0 mL) was added and the mixture stirred at  $-5\text{ }^\circ\text{C}$  under  $\text{N}_2$  for 24 h. The reaction was quenched with saturated  $\text{NH}_4\text{Cl}$  solution (2.0 mL), the organic layer was separated and the water layer was extracted with ethyl acetate (3.0 mL \* 2). The organic layer and extraction were combined. The combined solution was dried over anhydrous  $\text{MgSO}_4$ , and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to obtain adduct in 59% yield (110.3 mg). HPLC conditions: Daicel Chiralpak OD-H column, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min,  $\lambda = 230\text{ nm}$ , retention time:  $t_R$  (minor) = 22.162 min,  $t_R$  (major) = 24.266 min, 17% ee.



Racemic

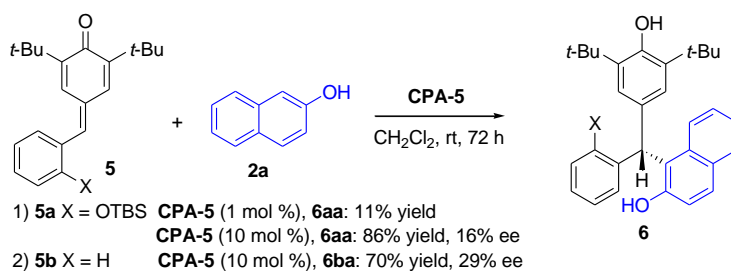
| # | Time   | Area    | Height | Width  | Area%  | Symmetry |
|---|--------|---------|--------|--------|--------|----------|
| 1 | 22.687 | 13638.2 | 393.2  | 0.5586 | 49.383 | 0.787    |
| 2 | 24.934 | 13978.8 | 362.5  | 0.6219 | 50.617 | 0.769    |



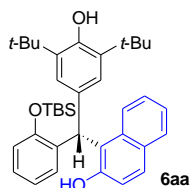
Chiral

| # | Time   | Area   | Height | Width  | Area%  | Symmetry |
|---|--------|--------|--------|--------|--------|----------|
| 1 | 22.162 | 1307.7 | 43.9   | 0.4636 | 41.551 | 0.864    |
| 2 | 24.266 | 1839.5 | 55.7   | 0.5134 | 58.449 | 0.813    |

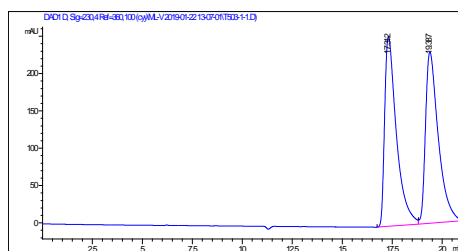
## Asymmetric conjugate addition of *p*-QMs **5** and 2-naphthol



To a mixture of *p*-QMs **5** (0.20 mmol), 2-naphthol **2a** (0.24 mmol), catalyst **CPA-5** in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was stirred at room temperature for 72 h. After removal of the solvent, the crude residue was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to give the corresponding products **6**.

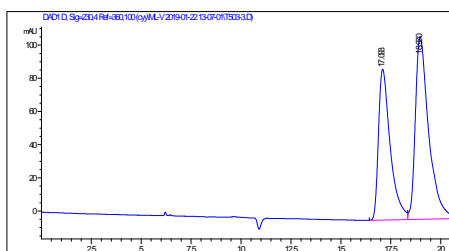


96.4 mg, 86% yield. Yellow solid, mp 90.2-92.3 °C; <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>): δ (ppm) 8.02 (d, *J* = 8.4 Hz, 1H), 7.85-7.83 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.39-7.35 (m, 1H), 7.23-7.18 (m, 1H), 7.14-7.10 (m, 2H), 7.02-6.88 (m, 4H), 6.66 (s, 1H), 5.83 (s, 1H), 5.25 (s, 1H), 1.38 (s, 18H), 0.88 (s, 9H), 0.38 (s, 3H). <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ (ppm) 153.9, 153.3, 153.1, 137.0, 133.8, 132.0, 131.9, 130.4, 129.6, 129.3, 128.6, 128.0, 126.8, 125.6, 123.1, 123.0, 121.5, 120.2, 120.1, 117.9, 42.7, 35.4, 30.3, 25.7, 18.2. HRMS: exact mass calculated for [M-H]<sup>-</sup> (C<sub>37</sub>H<sub>47</sub>O<sub>3</sub>Si) requires *m/z* 567.33000, found *m/z* 567.33111; HPLC conditions: Daicel Chiralpak OD-H column, n-hexane/2-propanol = 99.8/0.2, flow rate = 1.0 mL/min, λ = 230 nm, retention time: *t*<sub>R</sub> (minor) = 17.093 min, *t*<sub>R</sub> (major) = 18.97 min, 16% ee.



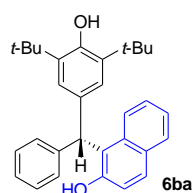
Racemic

| # | Time   | Area    | Height | Width  | Area%  | Symmetry |
|---|--------|---------|--------|--------|--------|----------|
| 1 | 17.312 | 10392.3 | 254.3  | 0.6068 | 50.443 | 0.431    |
| 2 | 19.387 | 10209.9 | 229.4  | 0.6633 | 49.557 | 0.488    |

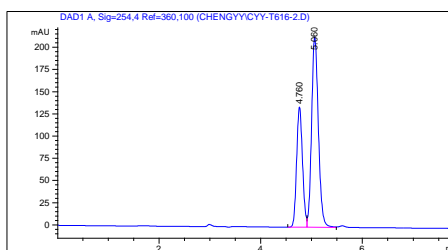
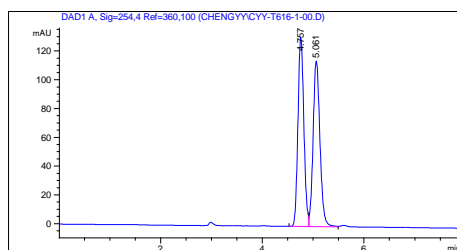


Chiral

| # | Time   | Area   | Height | Width  | Area%  | Symmetry |
|---|--------|--------|--------|--------|--------|----------|
| 1 | 17.093 | 3738   | 91     | 0.6151 | 42.114 | 0.507    |
| 2 | 18.97  | 5137.8 | 110.2  | 0.6959 | 57.886 | 0.518    |



61.0 mg, 70% yield. White solid, mp 199.1-200.9 °C;  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.02 (d,  $J = 8.4$  Hz, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.32-7.21 (m, 6H), 7.07 (d,  $J = 8.8$  Hz, 1H), 7.00 (s, 2H), 6.29 (s, 1H), 5.40 (s, 1H), 5.20 (s, 1H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.2, 142.2, 136.9, 133.6, 131.9, 129.7, 129.1, 129.0, 128.8, 127.0, 126.8, 125.8, 123.2, 123.0, 120.4, 120.1, 48.7, 34.6, 30.3. HRMS: exact mass calculated for  $[\text{M}-\text{H}]^-$  ( $\text{C}_{31}\text{H}_{33}\text{O}_2$ ) requires  $m/z$  437.24860, found  $m/z$  437.24902; HPLC conditions: Daicel Chiralpak OD-H column, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm, retention time:  $t_R$  (minor) = 4.76 min,  $t_R$  (major) = 5.06 min, 29% ee.

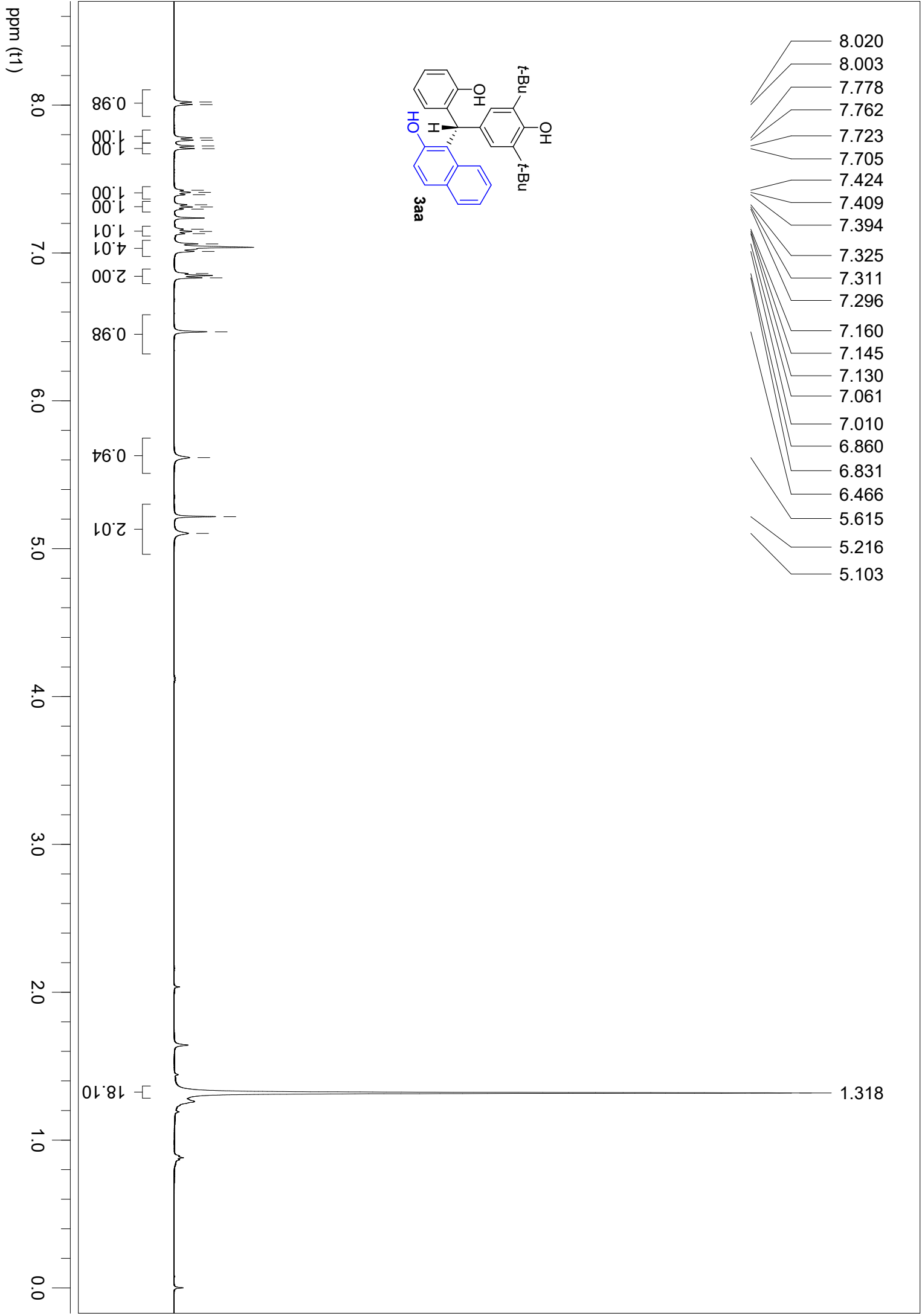


#### Racemic

| # | Time  | Area   | Height | Width  | Area%  | Symmetry |
|---|-------|--------|--------|--------|--------|----------|
| 1 | 4.757 | 1058.3 | 131.5  | 0.1259 | 49.523 | 0.89     |
| 2 | 5.061 | 1078.7 | 115.3  | 0.1452 | 50.477 | 0.819    |

#### Chiral

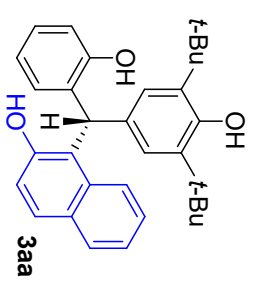
| # | Time | Area   | Height | Width  | Area%  | Symmetry |
|---|------|--------|--------|--------|--------|----------|
| 1 | 4.76 | 1084.8 | 135.4  | 0.1254 | 35.338 | 0.893    |
| 2 | 5.06 | 1984.9 | 214.4  | 0.142  | 64.662 | 0.802    |



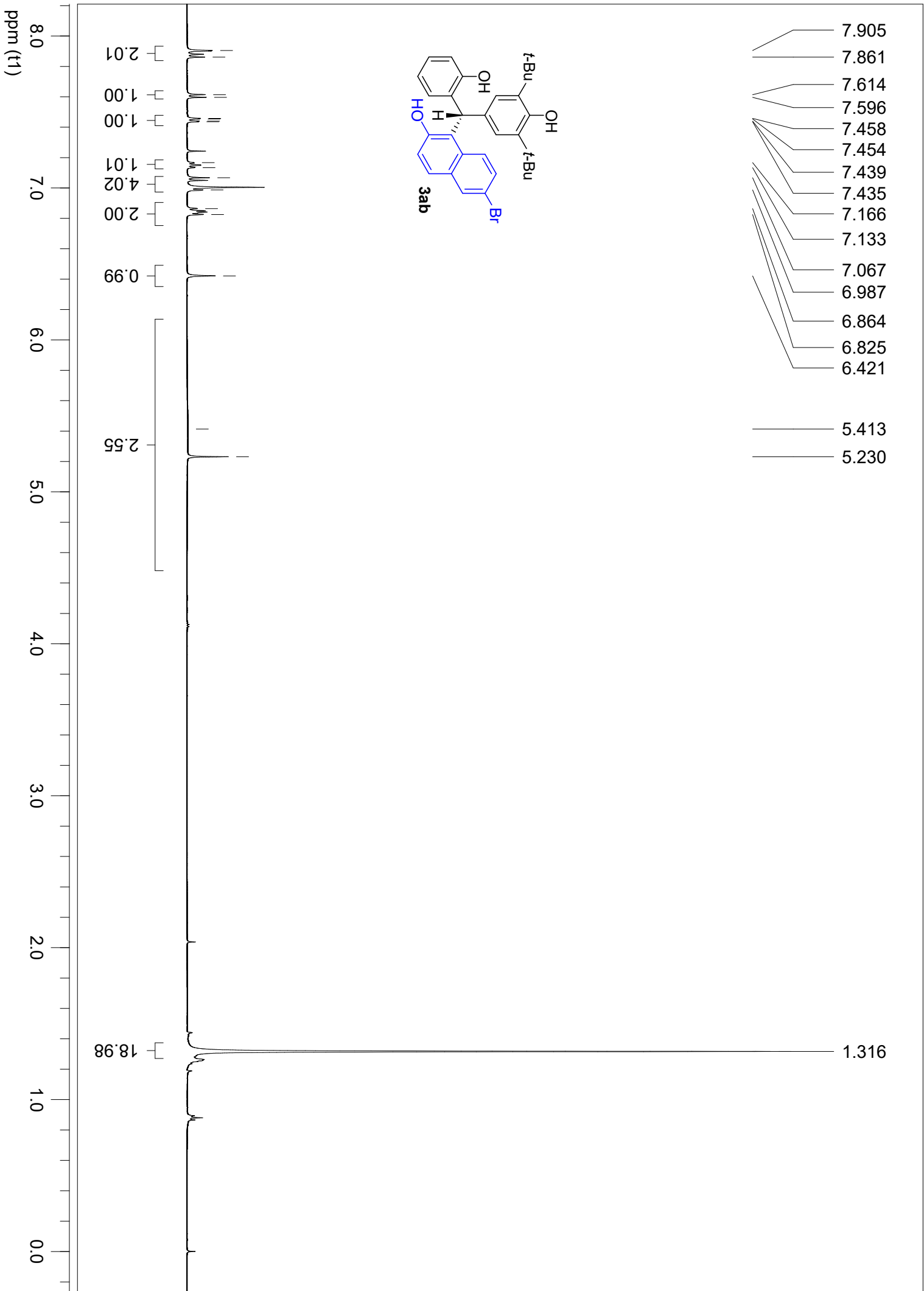


ppm (t1)

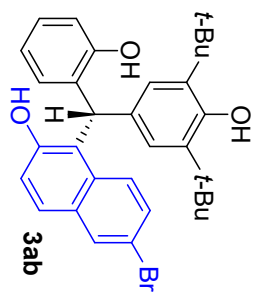
200  
150  
100  
50  
0



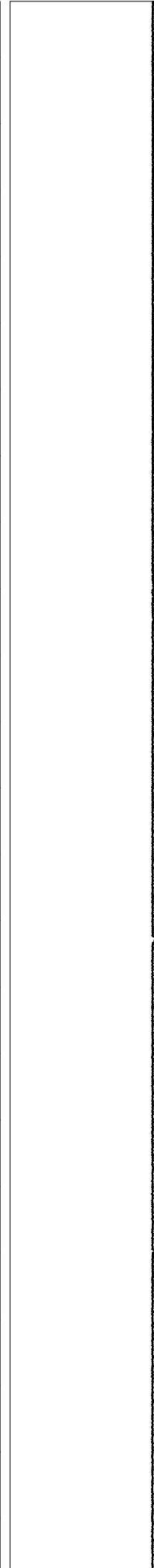
- 153.639
- 153.490
- 153.364
- 137.051
- 133.451
- 130.332
- 130.095
- 129.798
- 128.815
- 128.607
- 128.247
- 126.939
- 125.411
- 123.334
- 123.106
- 121.632
- 119.876
- 119.101
- 116.236
- 77.414
- 77.160
- 76.906
- 42.870
- 34.562
- 30.317

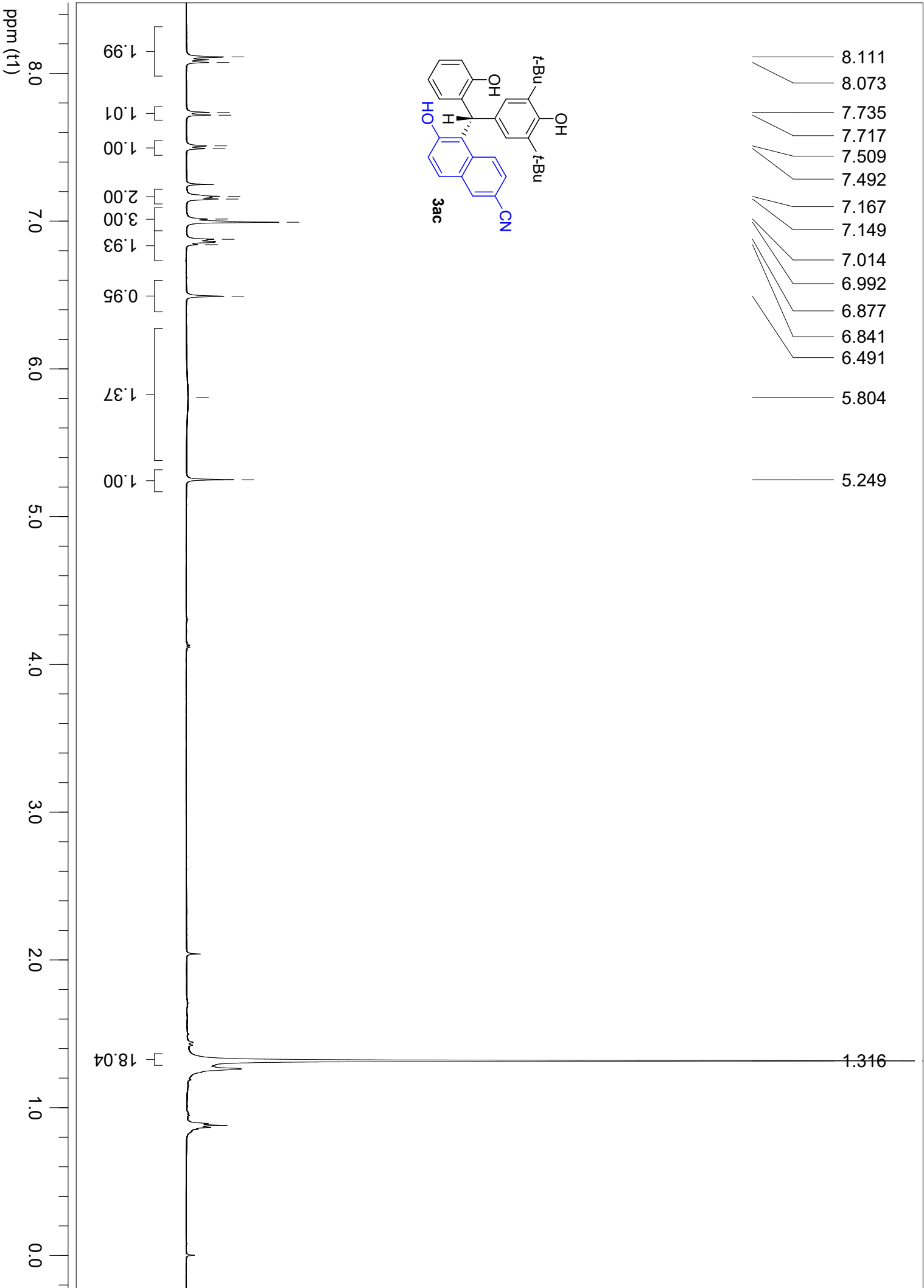


ppm (t1)



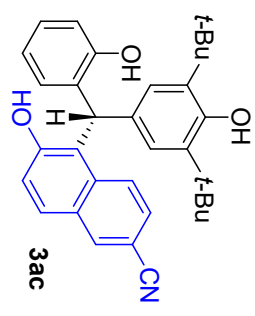
- 153.699
- 153.438
- 137.132
- 132.078
- 130.986
- 130.596
- 130.062
- 130.005
- 128.755
- 128.711
- 128.003
- 125.331
- 125.117
- 121.684
- 121.037
- 119.705
- 117.048
- 116.177
- 77.414
- 77.160
- 76.906
- 42.739
- 34.563
- 30.295



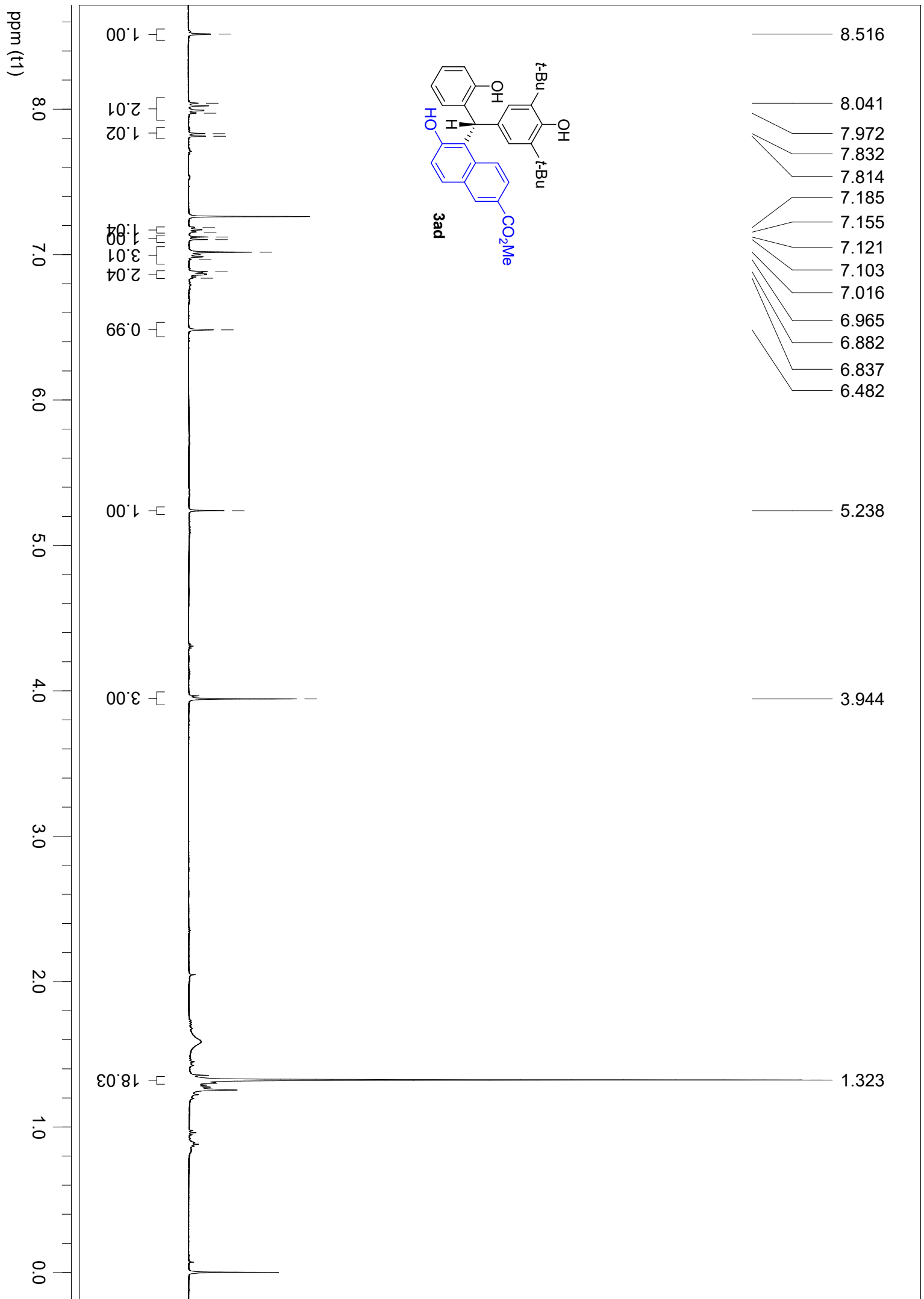


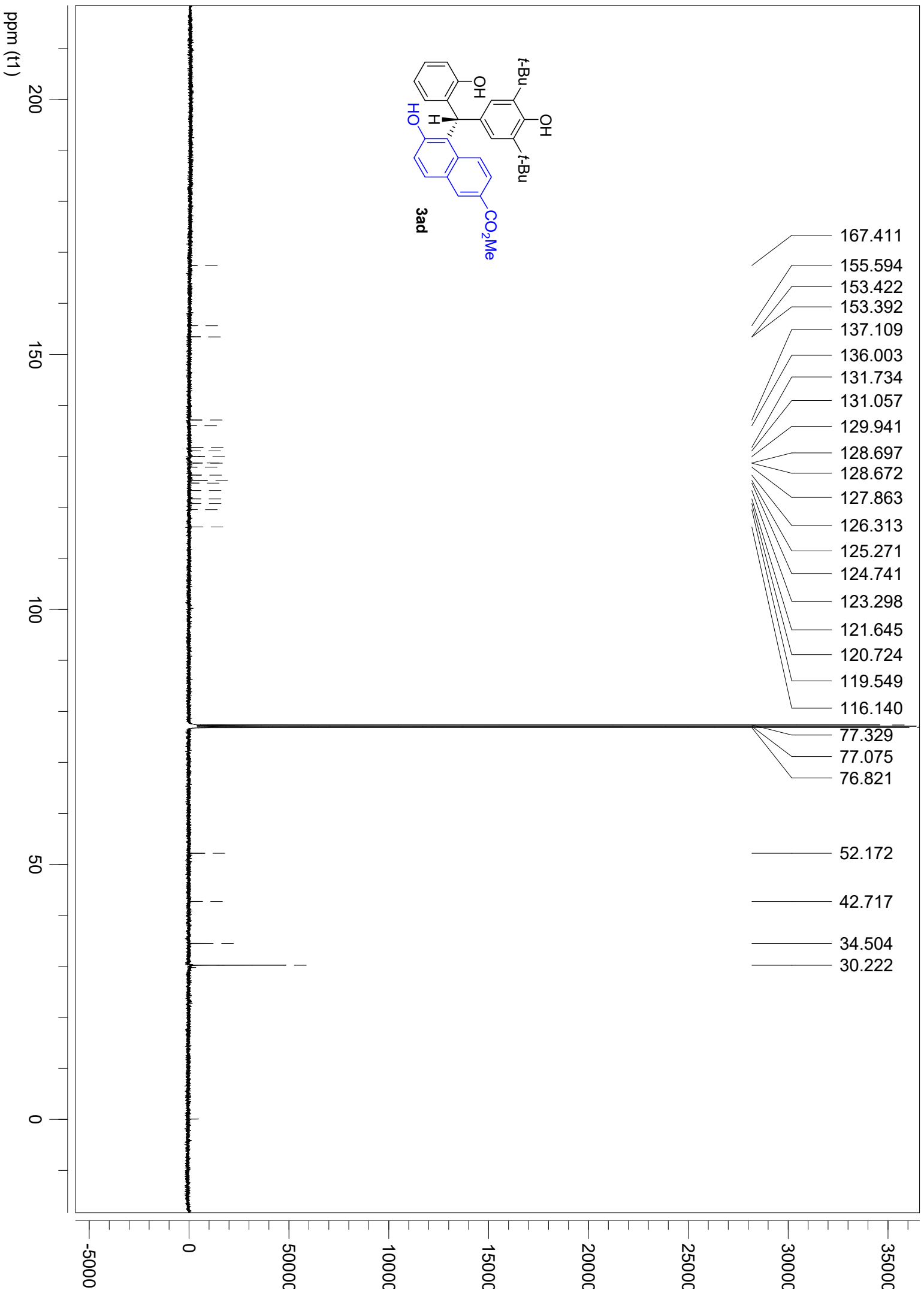
ppm (t1)

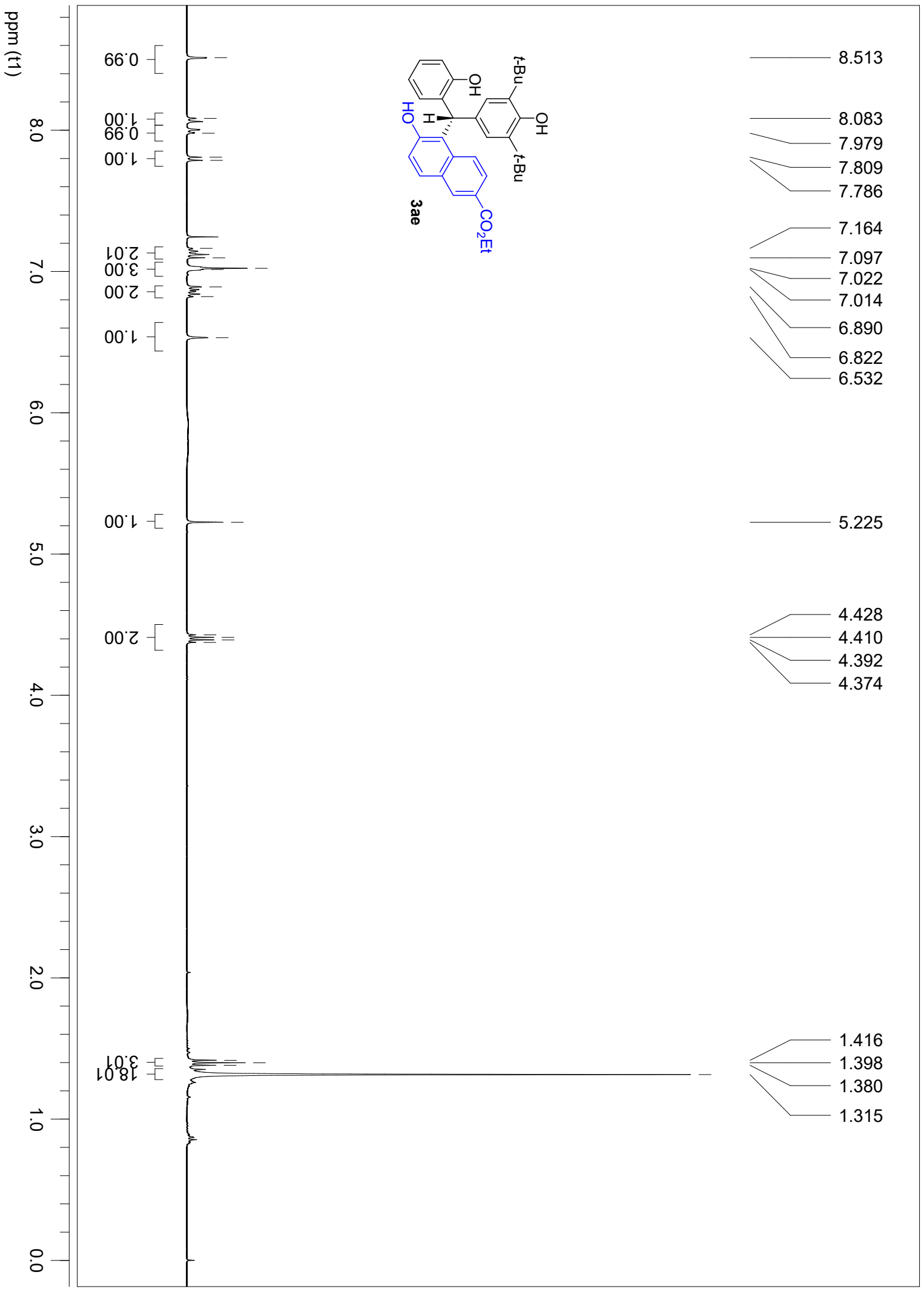
200  
150  
100  
50  
0



- 156.121
- 153.479
- 153.444
- 137.179
- 135.493
- 134.687
- 129.987
- 129.820
- 128.761
- 128.584
- 127.728
- 127.371
- 125.293
- 124.617
- 121.748
- 121.532
- 120.422
- 119.663
- 116.091
- 106.153
- 77.414
- 77.160
- 76.906
- 42.409
- 34.552
- 30.262

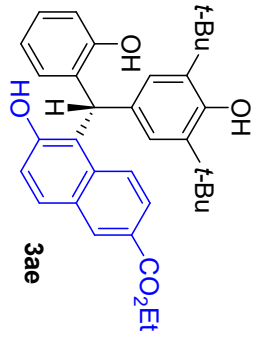




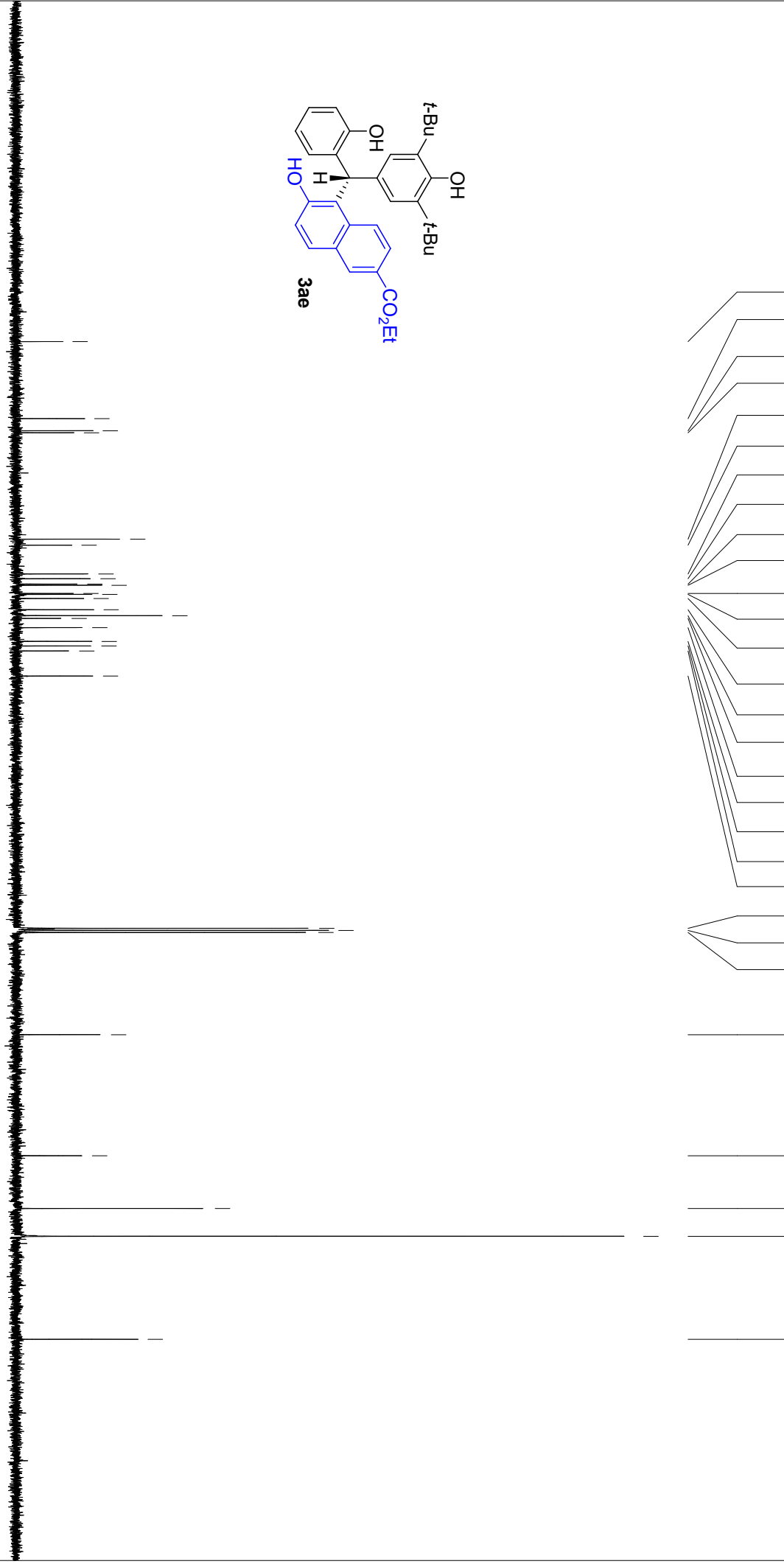


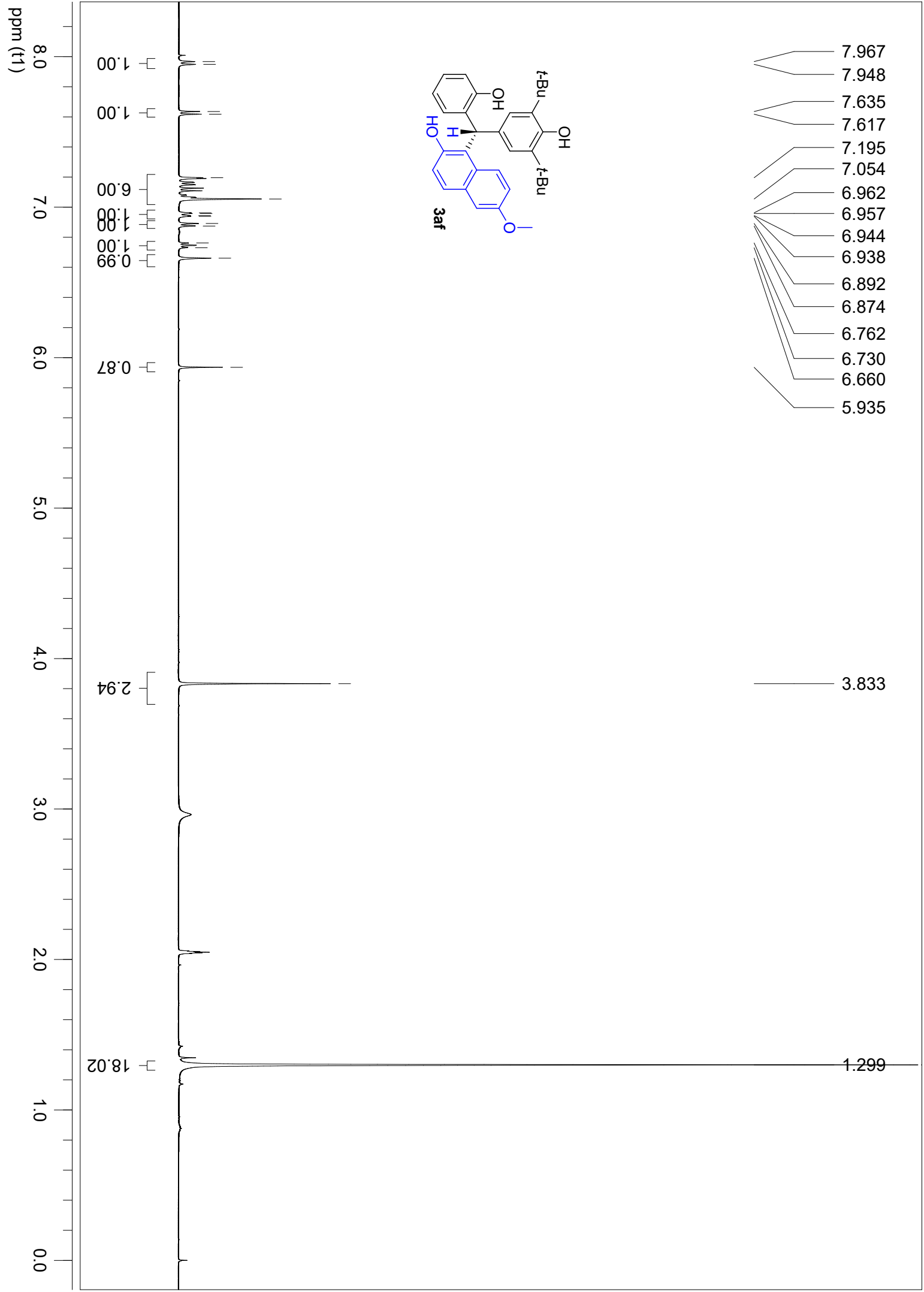


ppm (t1)



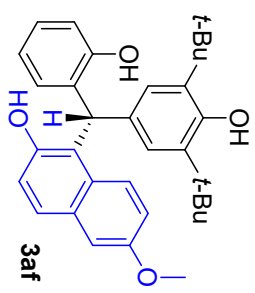
- 167.353
- 155.562
- 153.696
- 153.395
- 137.088
- 136.167
- 131.761
- 131.029
- 130.209
- 130.028
- 128.768
- 128.638
- 128.002
- 126.287
- 125.378
- 124.951
- 123.537
- 121.433
- 120.729
- 119.969
- 116.122
- 77.478
- 77.160
- 76.843
- 61.188
- 42.646
- 34.558
- 30.301
- 14.513



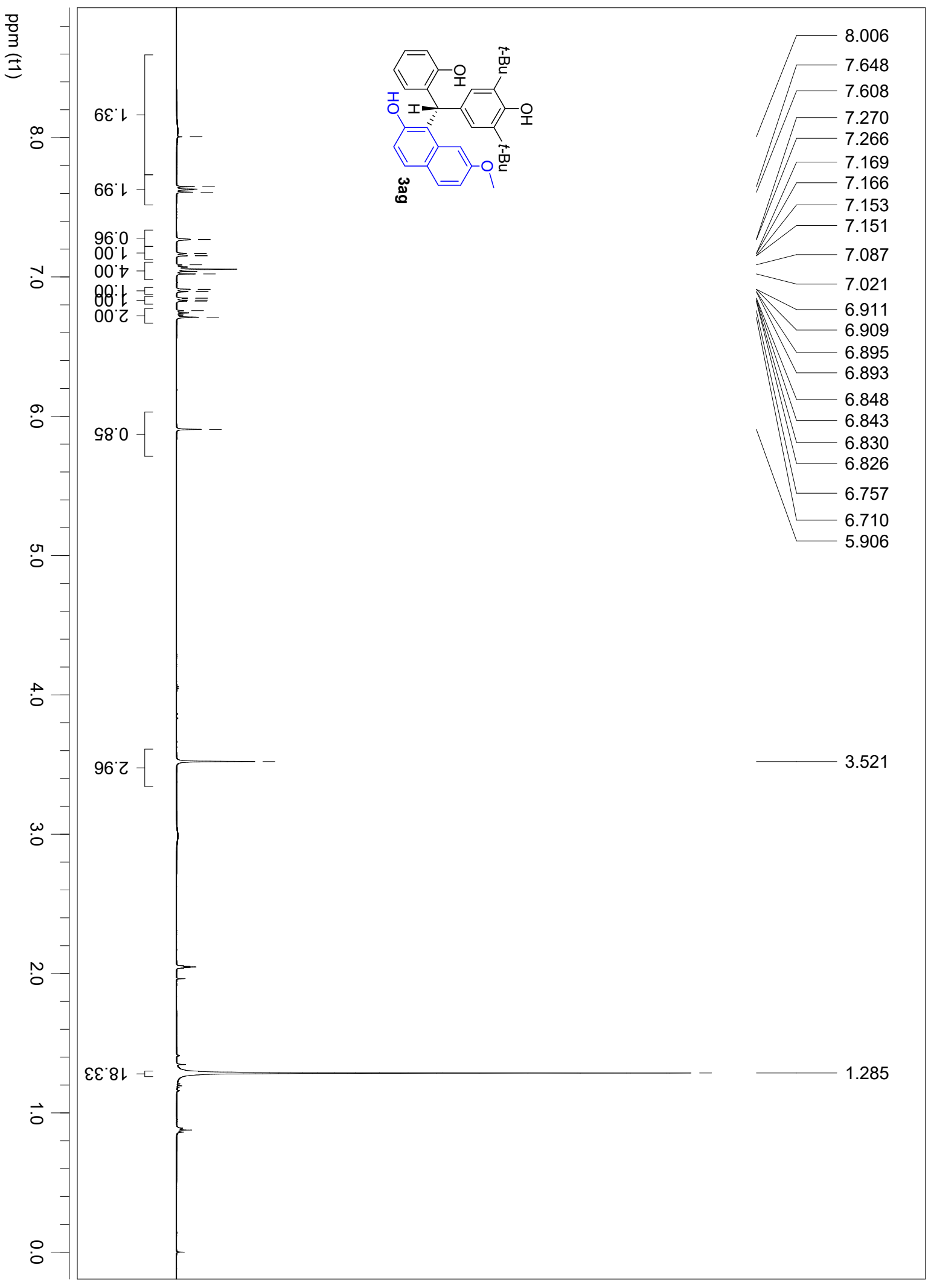


ppm (t1)

200  
150  
100  
50  
0



- 155.775
- 153.668
- 153.320
- 151.852
- 136.996
- 130.762
- 130.347
- 130.109
- 128.586
- 128.512
- 128.326
- 125.409
- 124.746
- 121.608
- 120.387
- 119.488
- 119.039
- 116.267
- 107.310
- 77.414
- 77.160
- 76.906
- 55.458
- 43.048
- 34.562
- 30.324



ppm (t1)

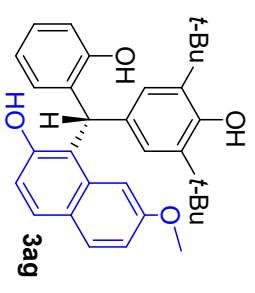
200

150

100

50

0



158.313

153.741

153.711

153.218

136.912

134.804

130.492

130.216

129.394

128.512

128.456

125.522

125.126

121.532

118.467

117.077

116.128

115.273

103.106

77.414

77.160

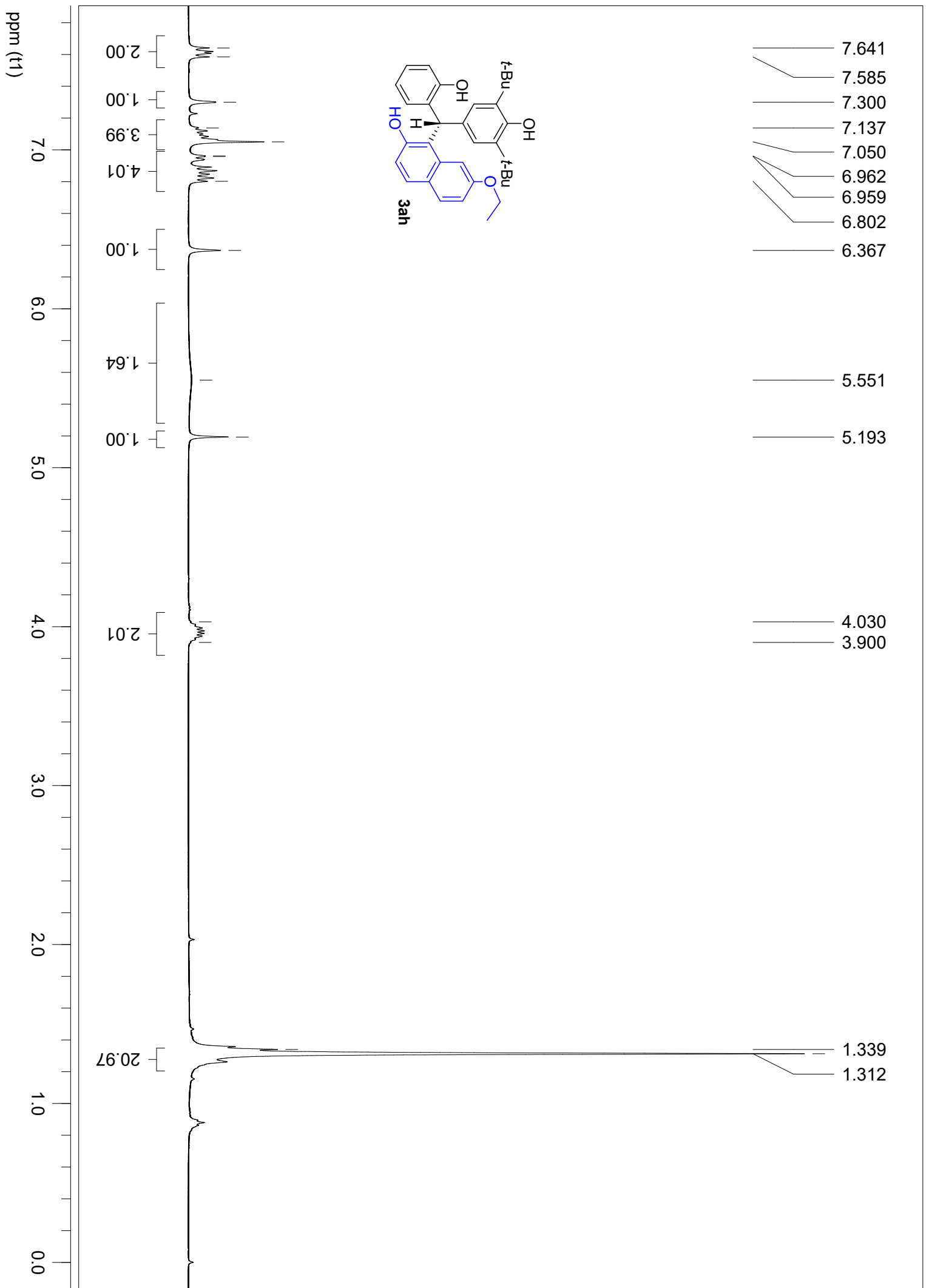
76.905

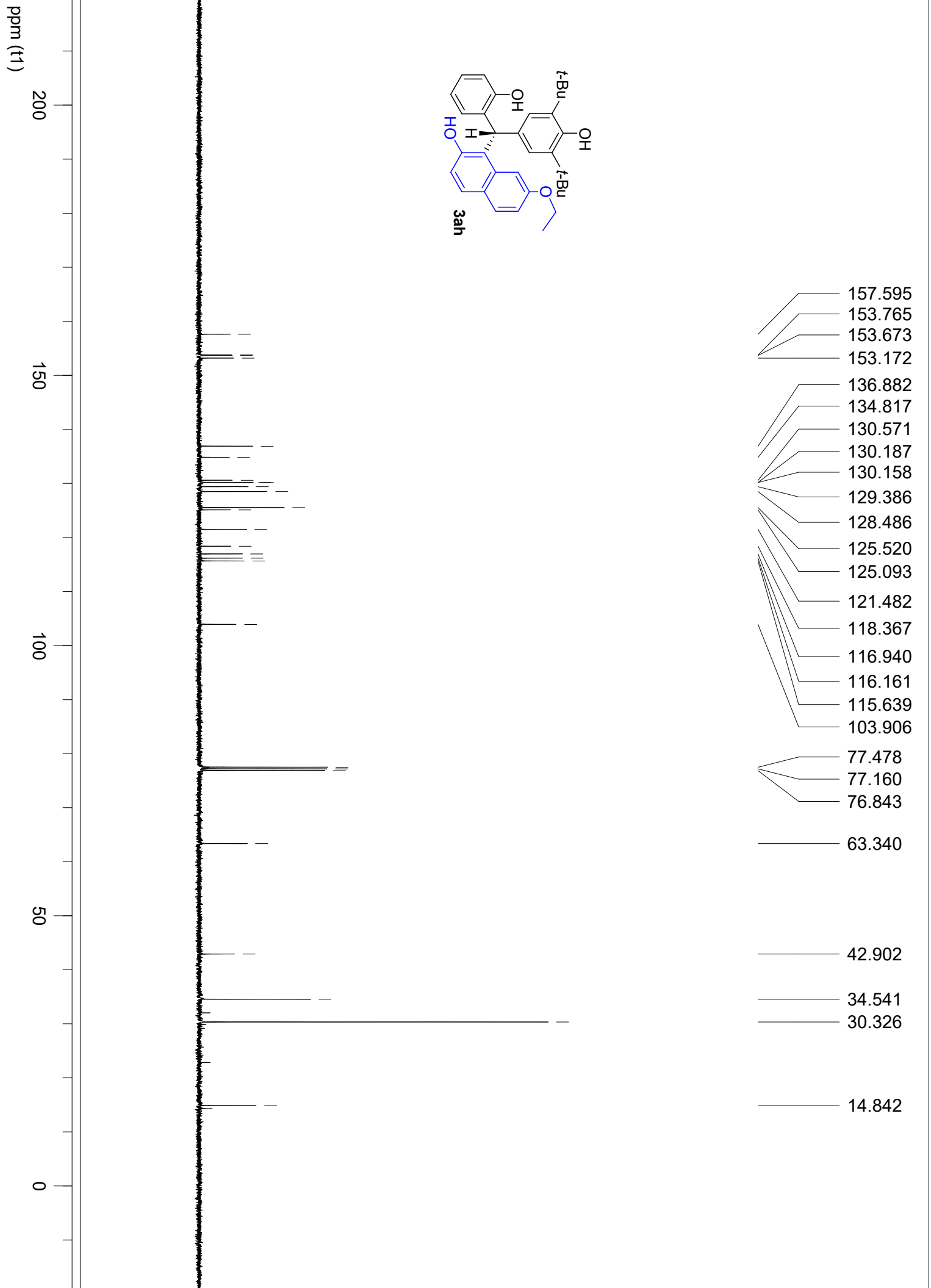
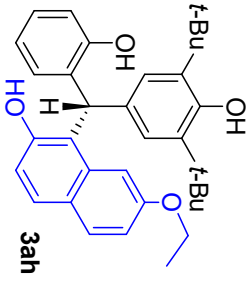
55.175

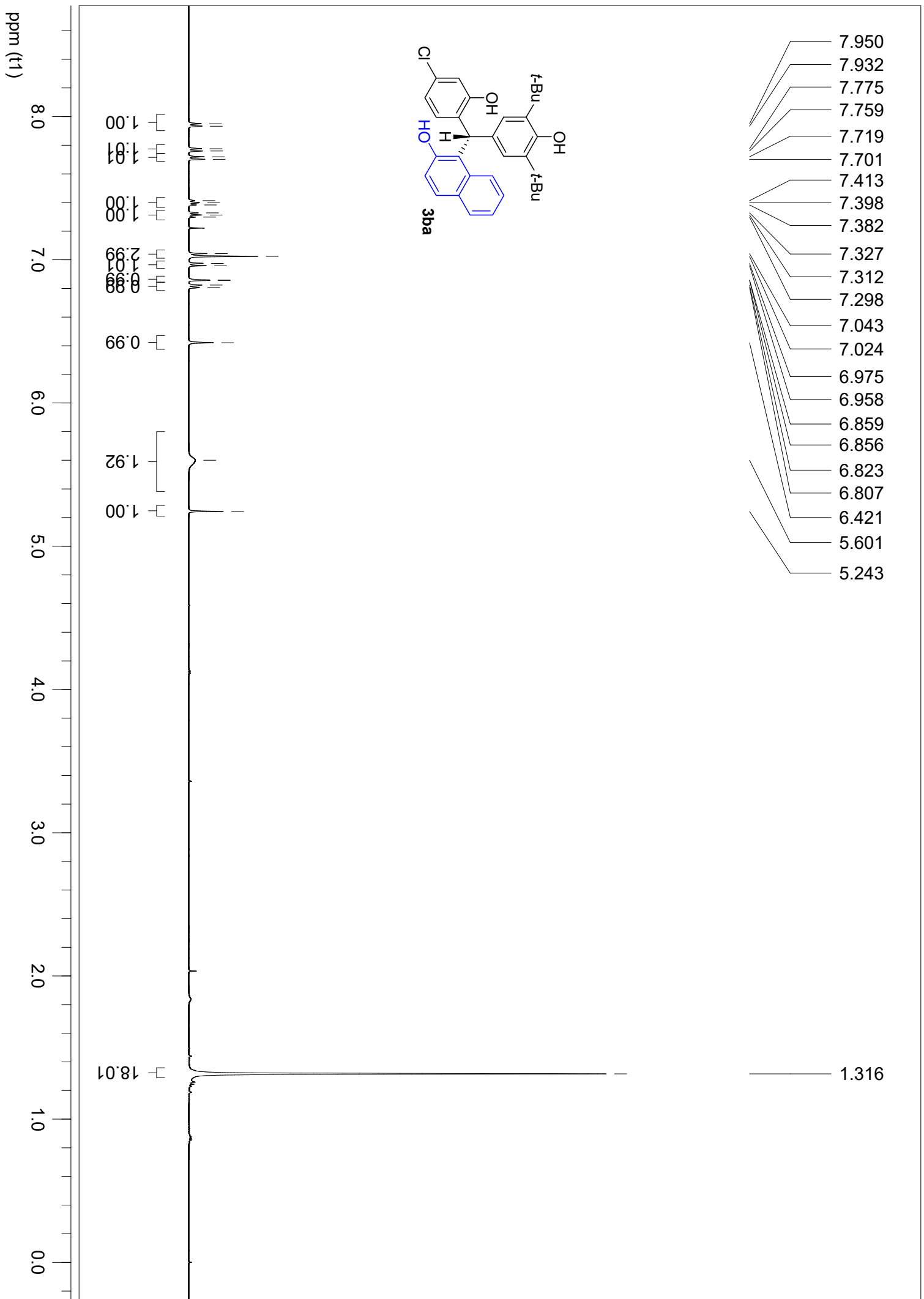
42.909

34.546

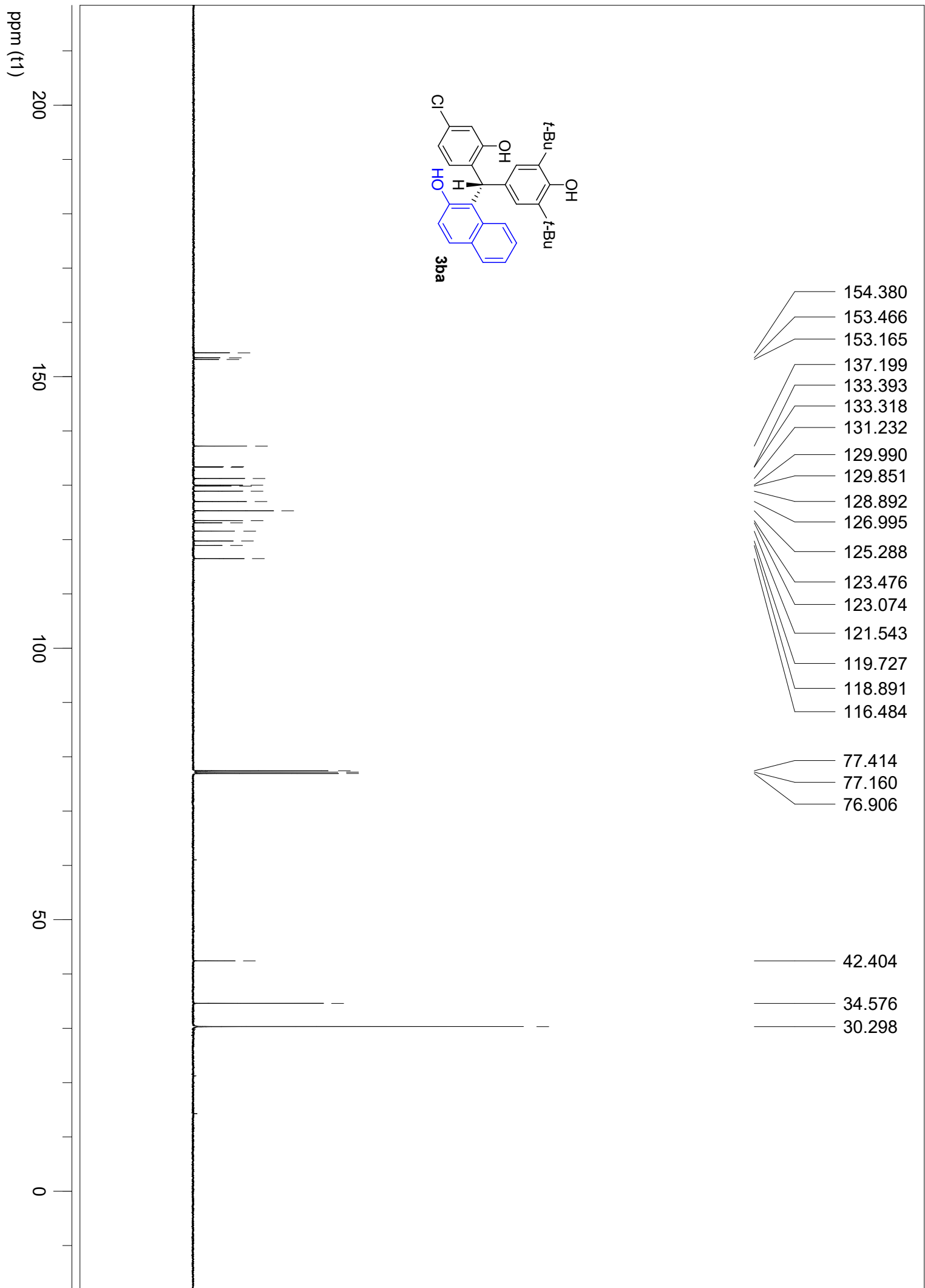
30.326

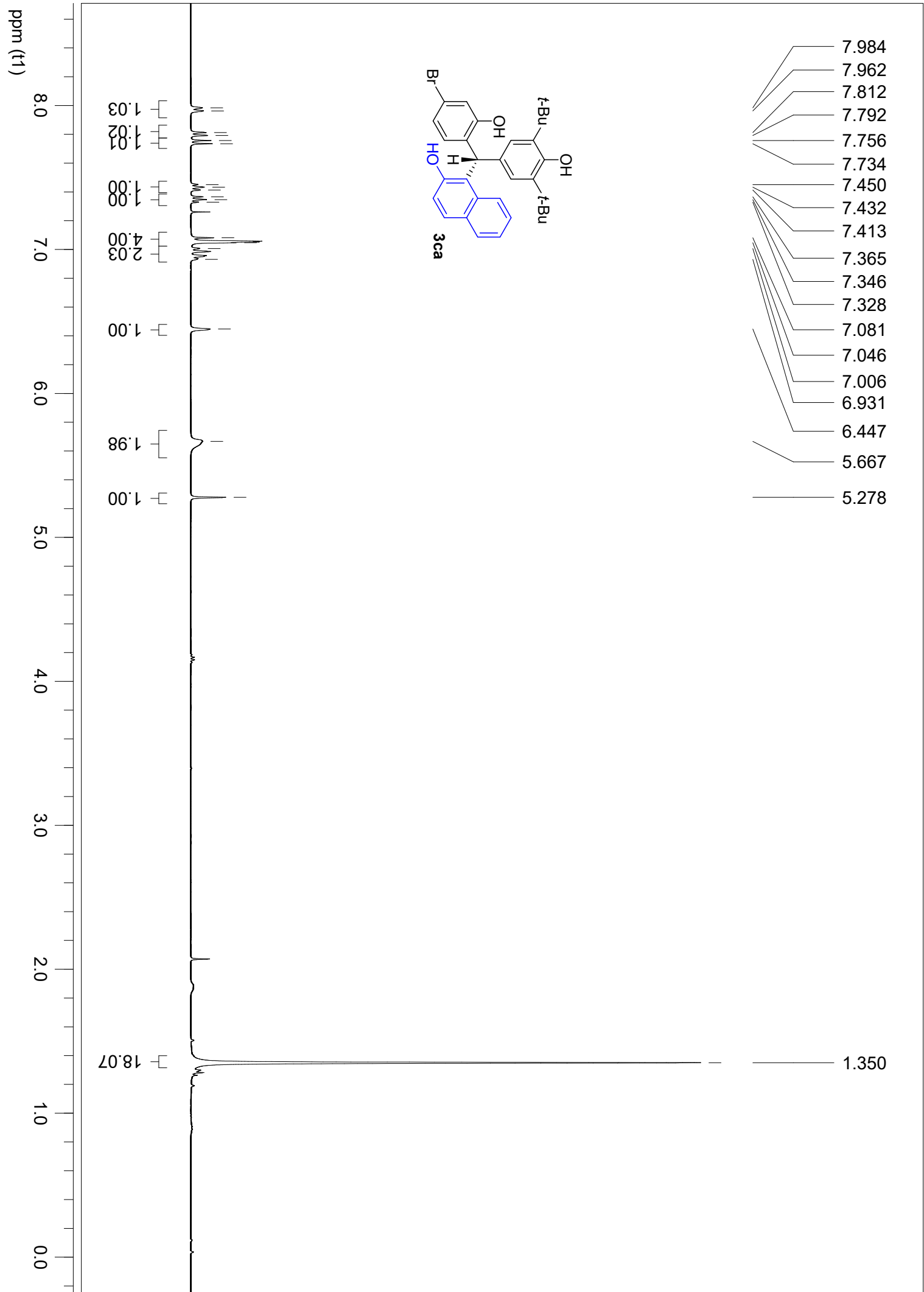












ppm (t1)

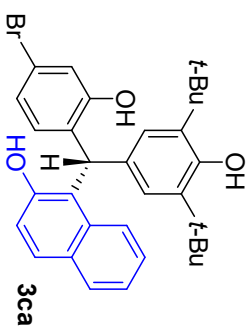
200

150

100

50

0



154.525

153.451

153.157

137.177

133.312

131.579

129.984

129.826

129.775

128.888

127.566

126.981

125.294

124.447

123.470

123.090

121.196

119.716

119.326

118.850

77.478

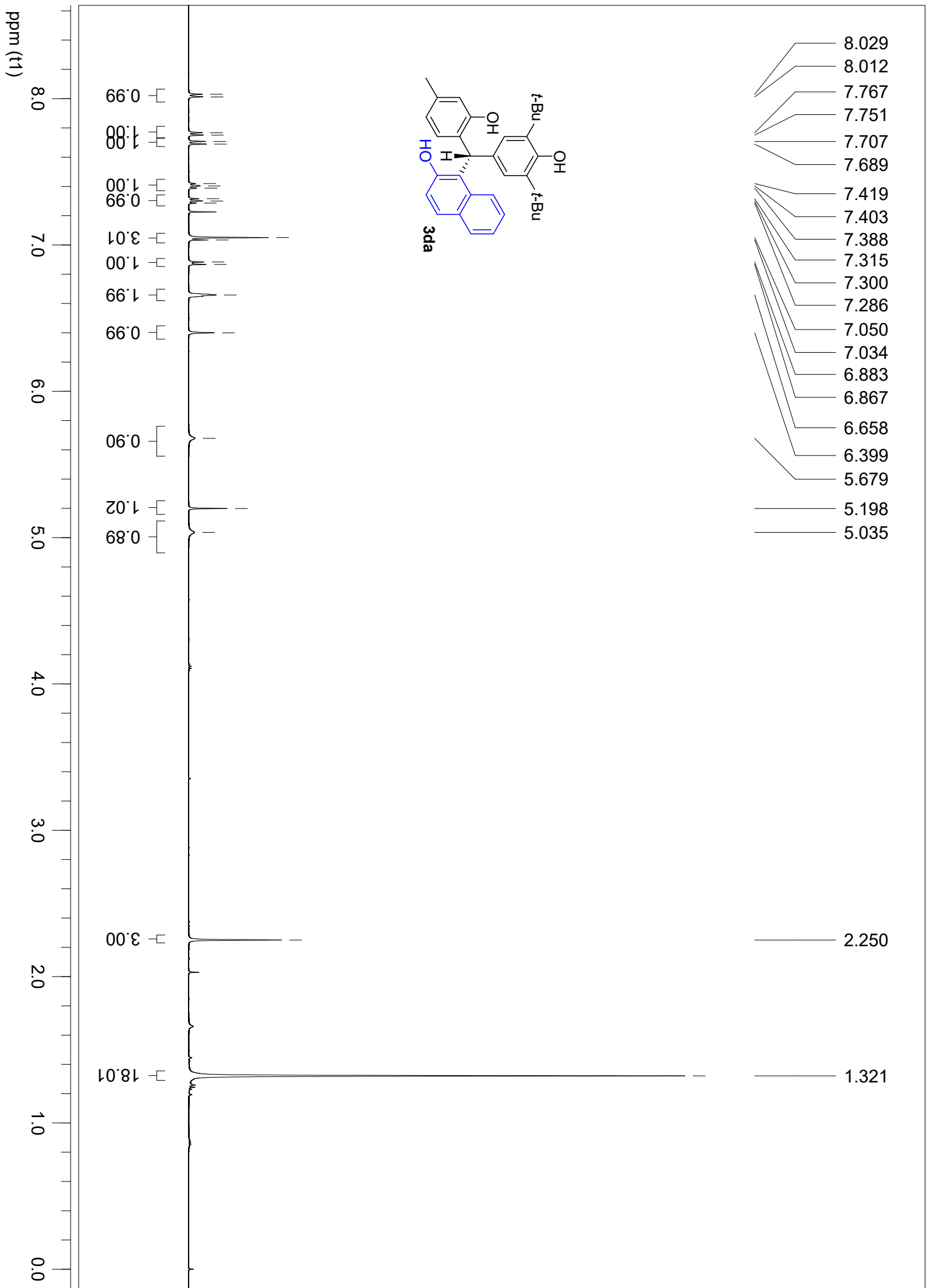
77.160

76.843

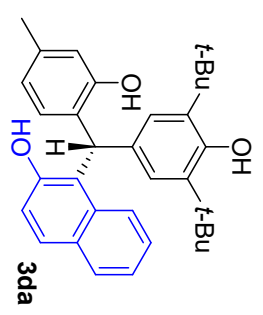
42.440

34.572

30.299

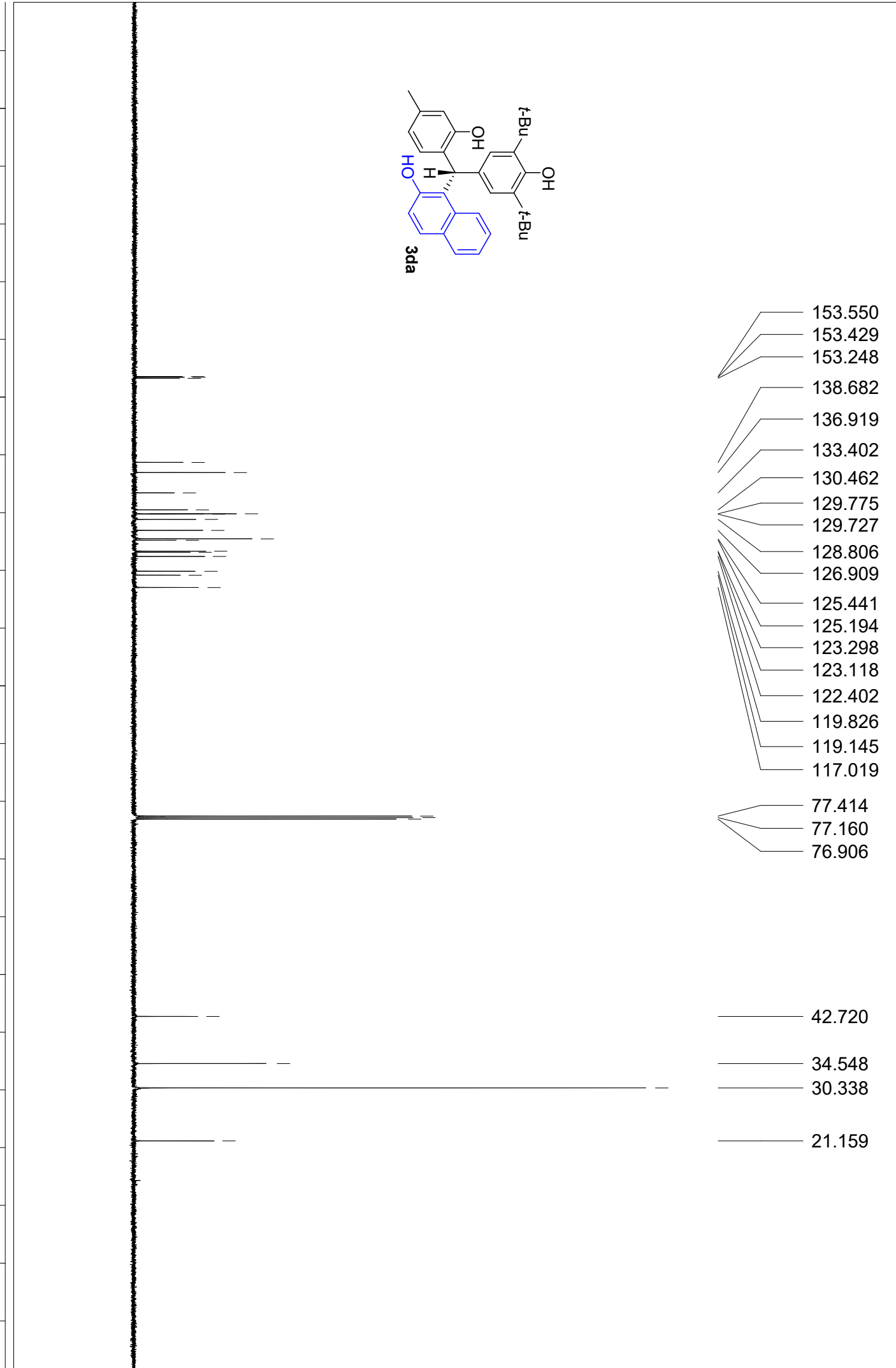


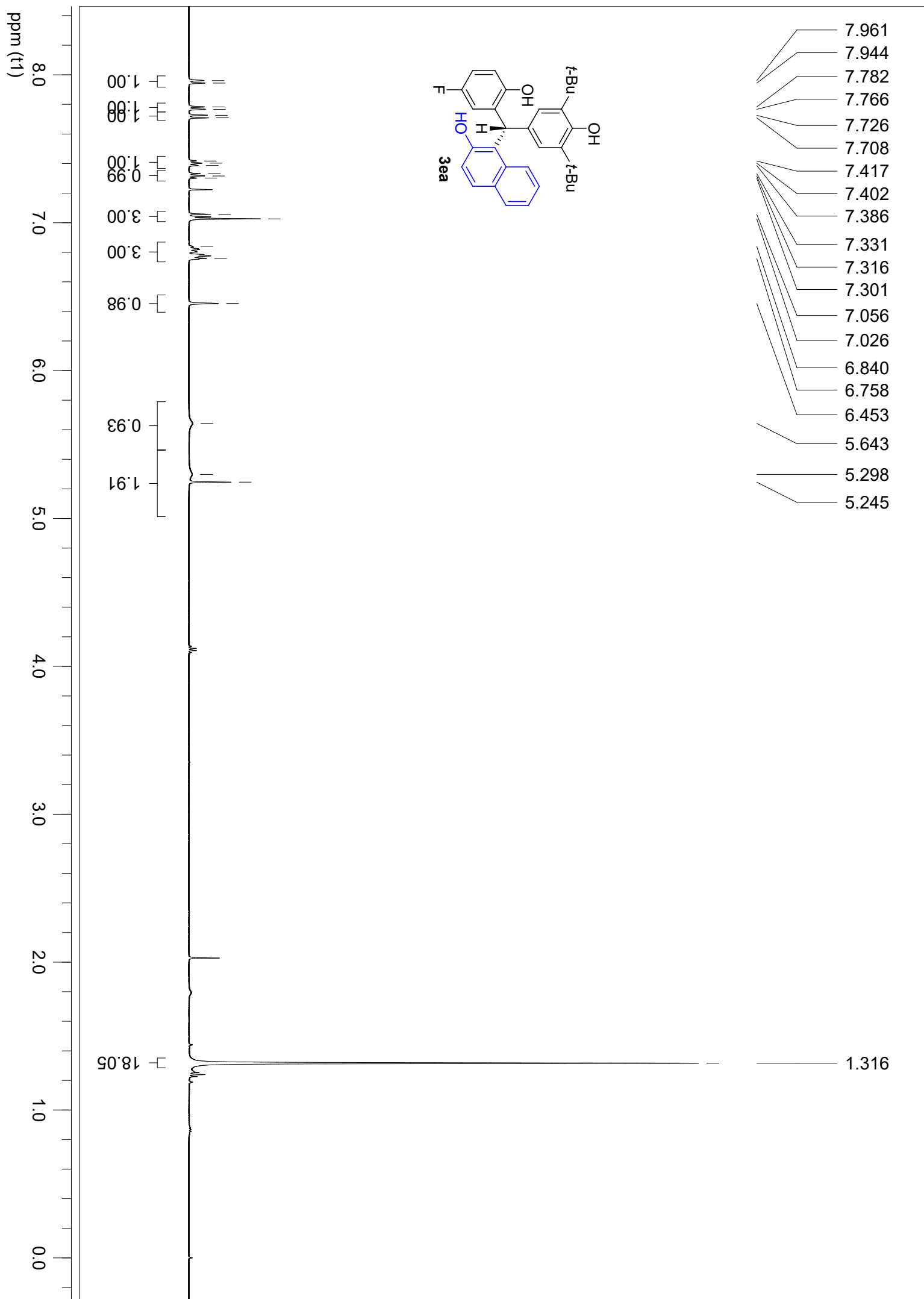
ppm (t1)



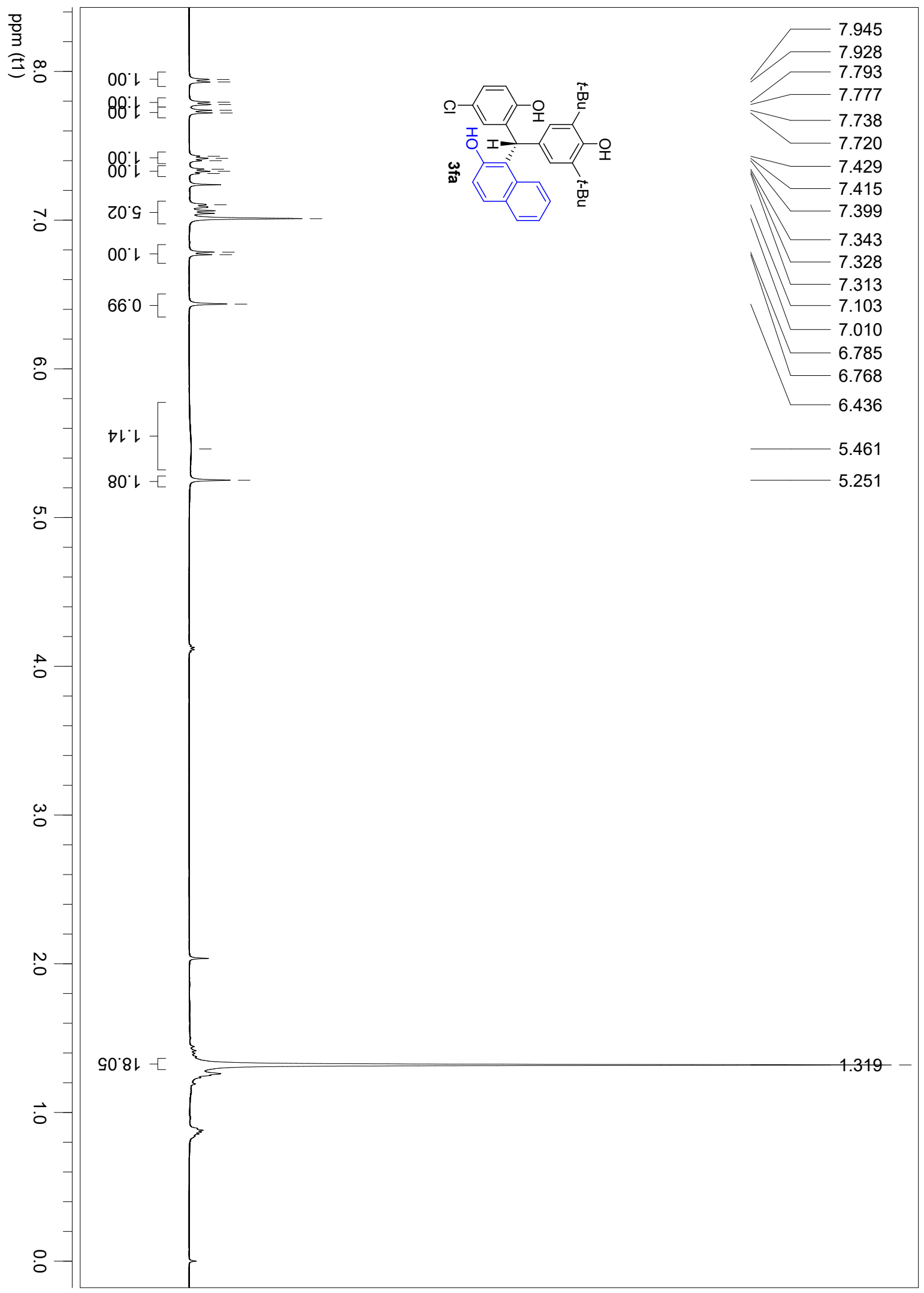
200  
150  
100  
50  
0

- 153.550
- 153.429
- 153.248
- 138.682
- 136.919
- 133.402
- 130.462
- 129.775
- 129.727
- 128.806
- 126.909
- 125.441
- 125.194
- 123.298
- 123.118
- 122.402
- 119.826
- 119.145
- 117.019
- 77.414
- 77.160
- 76.906
- 42.720
- 34.548
- 30.338
- 21.159

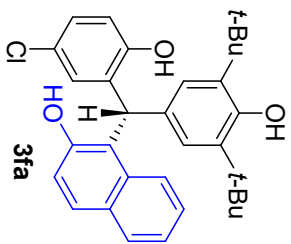












ppm ( $t_1$ )

200

150

100

50

0

153.534

153.258

152.380

137.234

133.370

130.113

130.081

130.004

129.840

129.600

128.917

128.373

127.021

126.241

125.236

123.467

123.003

119.859

118.608

117.448

77.414

77.160

76.906

42.741

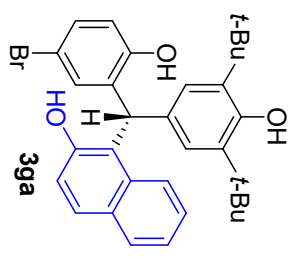
34.584

30.285

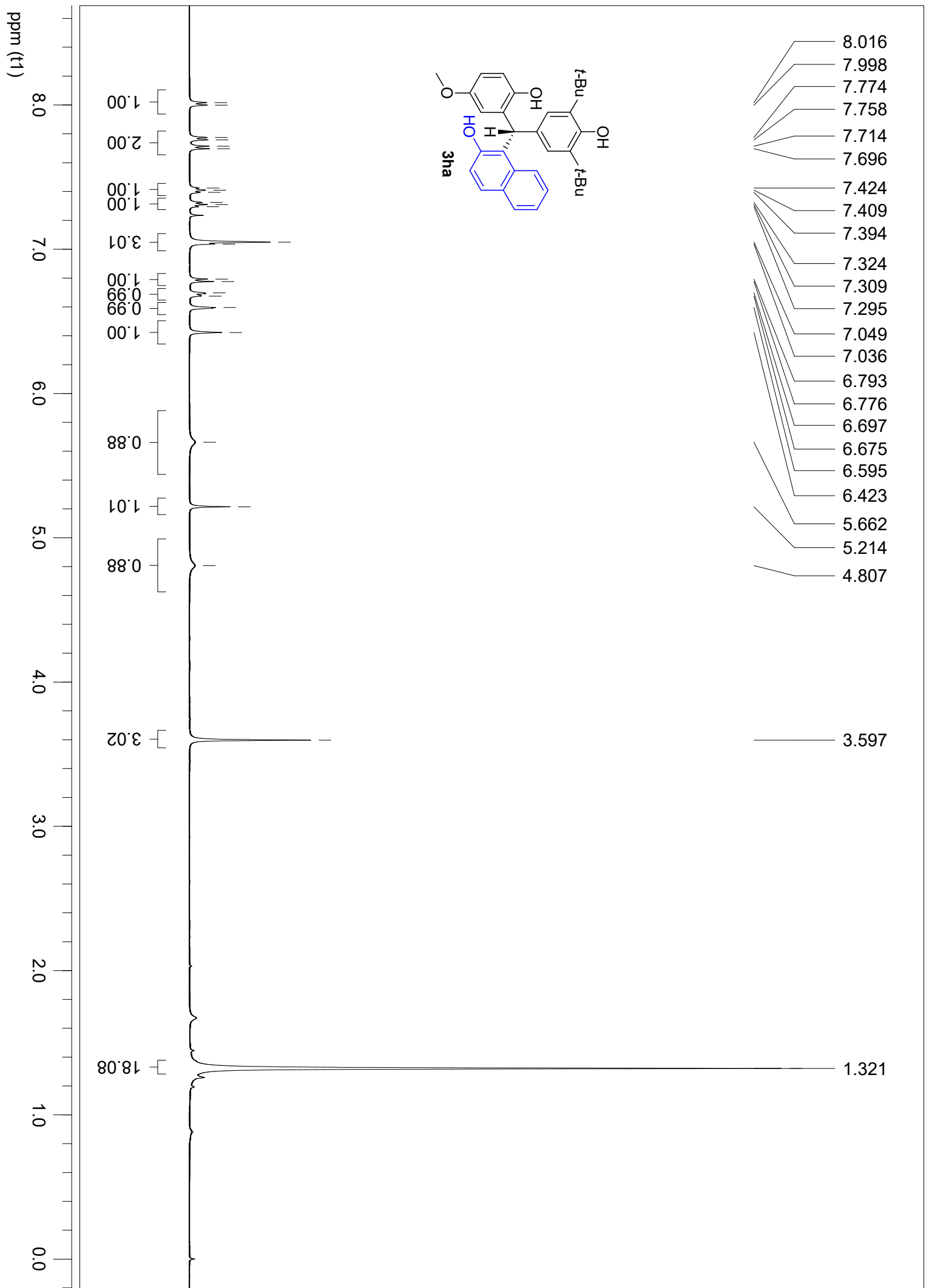


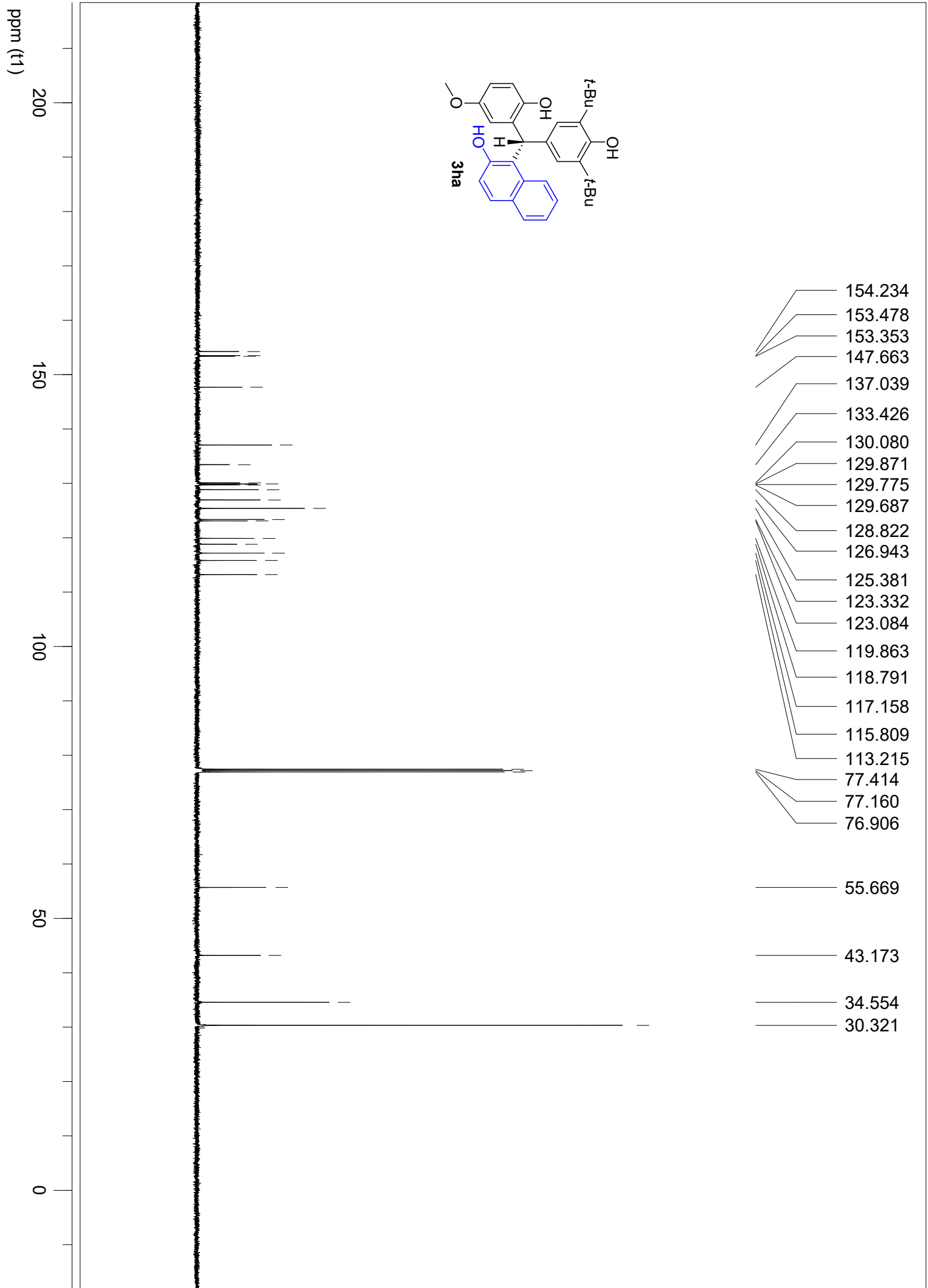
ppm (t1)

200  
150  
100  
50  
0

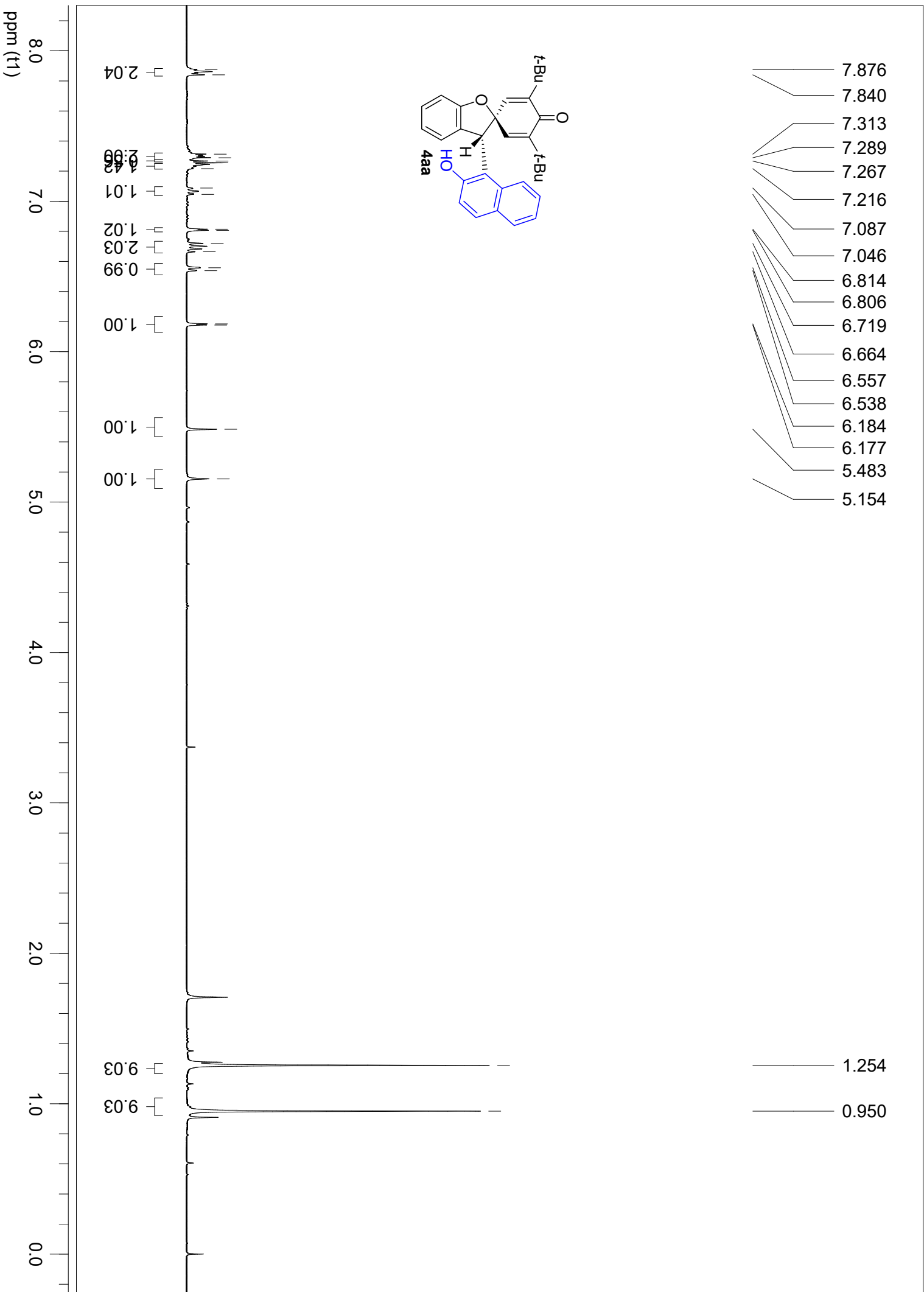


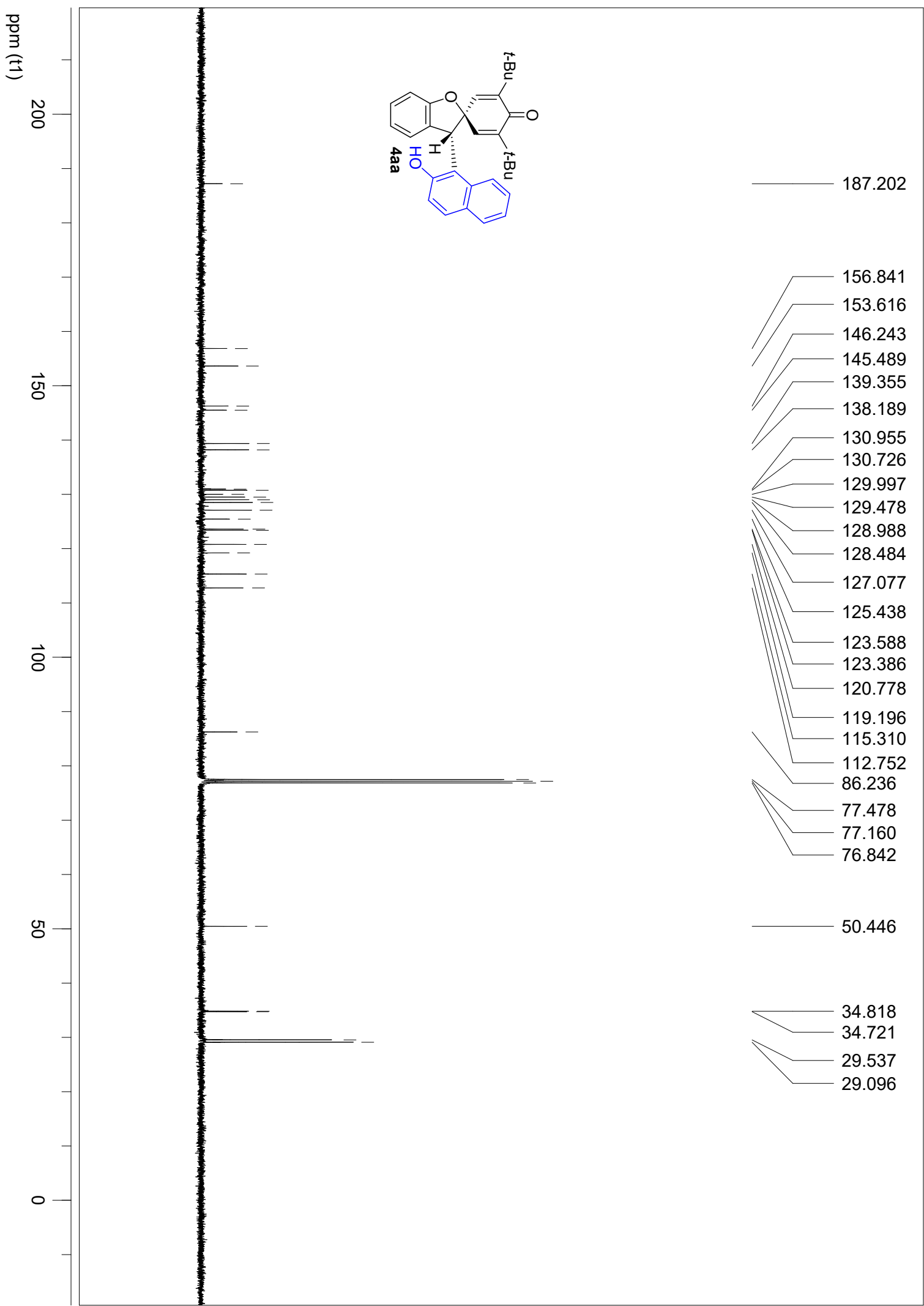
- 153.521
- 153.224
- 152.902
- 137.210
- 133.354
- 132.866
- 131.333
- 130.590
- 130.086
- 129.834
- 129.555
- 128.912
- 127.018
- 125.225
- 123.461
- 122.989
- 119.859
- 118.554
- 117.941
- 113.579
- 77.467
- 77.150
- 76.832
- 42.709
- 34.578
- 30.277

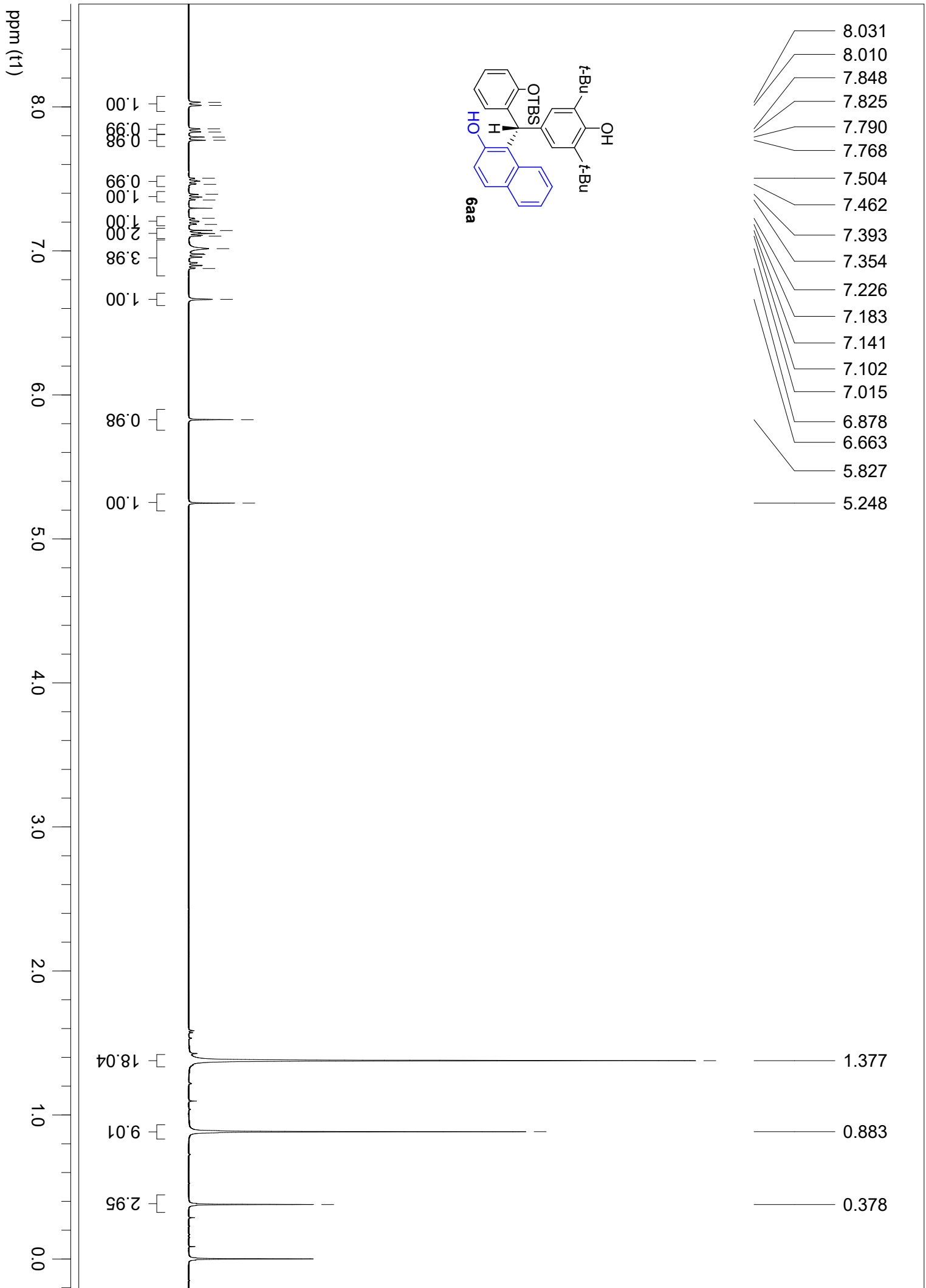




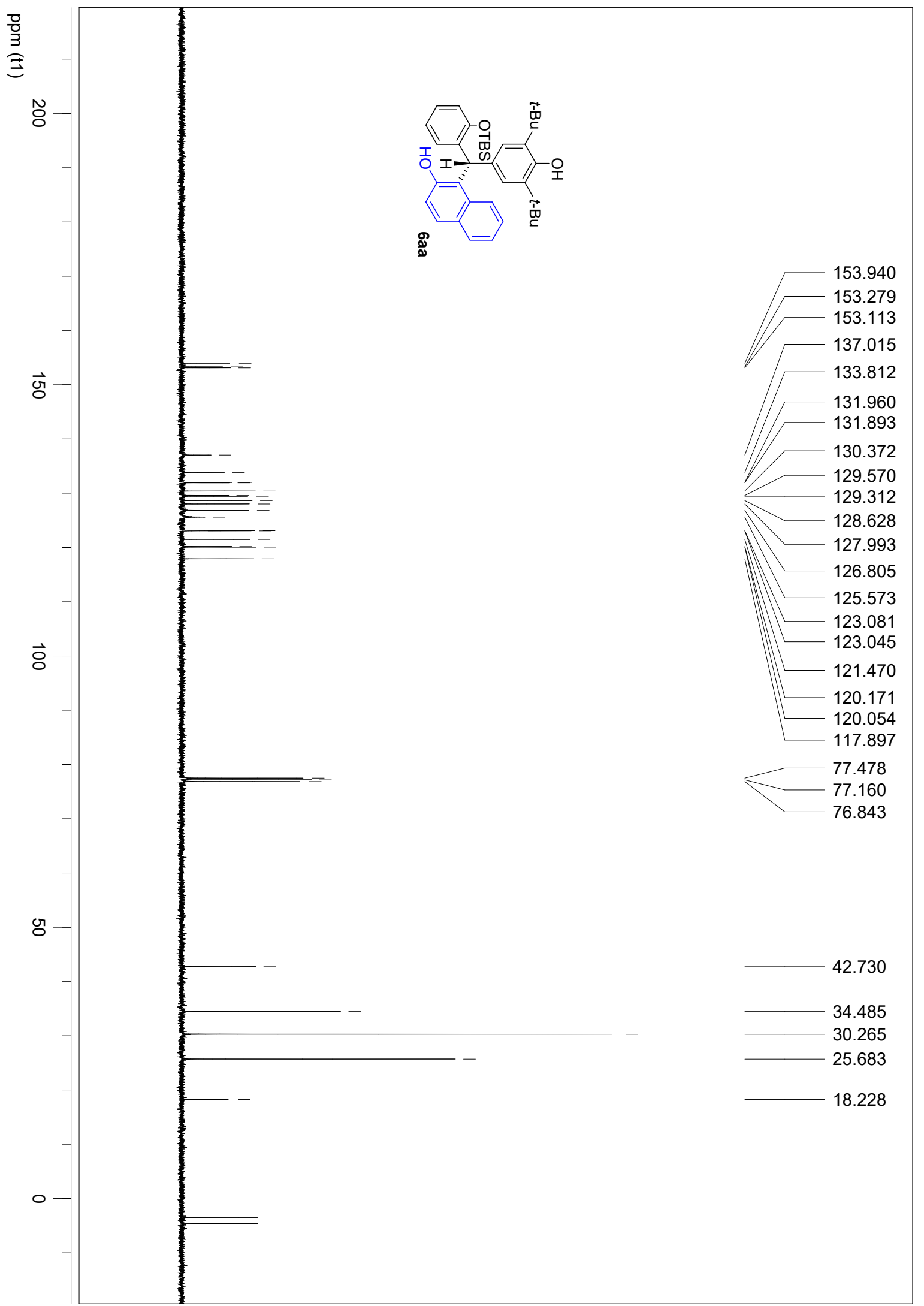
- 154.234
- 153.478
- 153.353
- 147.663
- 137.039
- 133.426
- 130.080
- 129.871
- 129.775
- 129.687
- 128.822
- 126.943
- 125.381
- 123.332
- 123.084
- 119.863
- 118.791
- 117.158
- 115.809
- 113.215
- 77.414
- 77.160
- 76.906
- 55.669
- 43.173
- 34.554
- 30.321

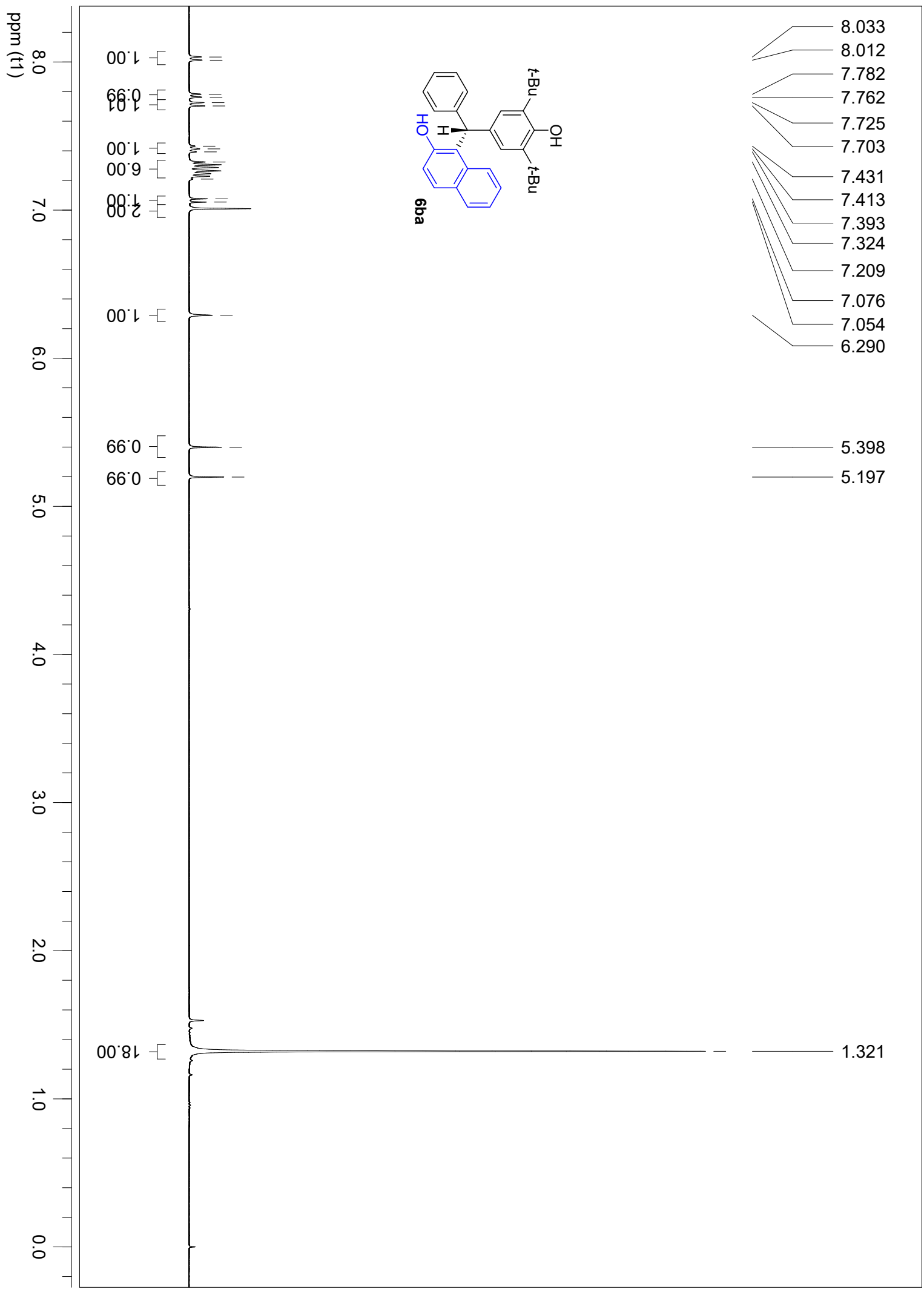












ppm (t1)

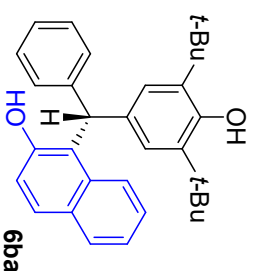
200

150

100

50

0



153.234

153.180

142.229

136.878

133.623

131.932

129.686

129.577

129.137

129.020

128.802

127.038

126.798

125.789

123.168

123.015

120.384

120.083

77.477

77.160

76.842

48.732

34.564

30.336