

## Supporting Information of

### A Comparative Study of Thallium(III) and Iodine(III)-Mediated Ring Contraction Reactions for the Synthesis of Indane

Ajmir Khan,<sup>\*a,b</sup> Luiz F. Silva Jr.,<sup>at</sup> Muhammad Rabnawaz<sup>\*b</sup>

<sup>a</sup>Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes, 748, São Paulo, SP CEP 05508-000, Brazil

<sup>b</sup>School of Packaging, Michigan State University, 448 Wilson Road, East Lansing, MI 48824-1223, USA.

\*Corresponding authors:

Muhammad Rabnawaz [rabnawaz@msu.edu](mailto:rabnawaz@msu.edu) ORCID: [orcid.org/0000-0002-4576-1810](https://orcid.org/0000-0002-4576-1810)

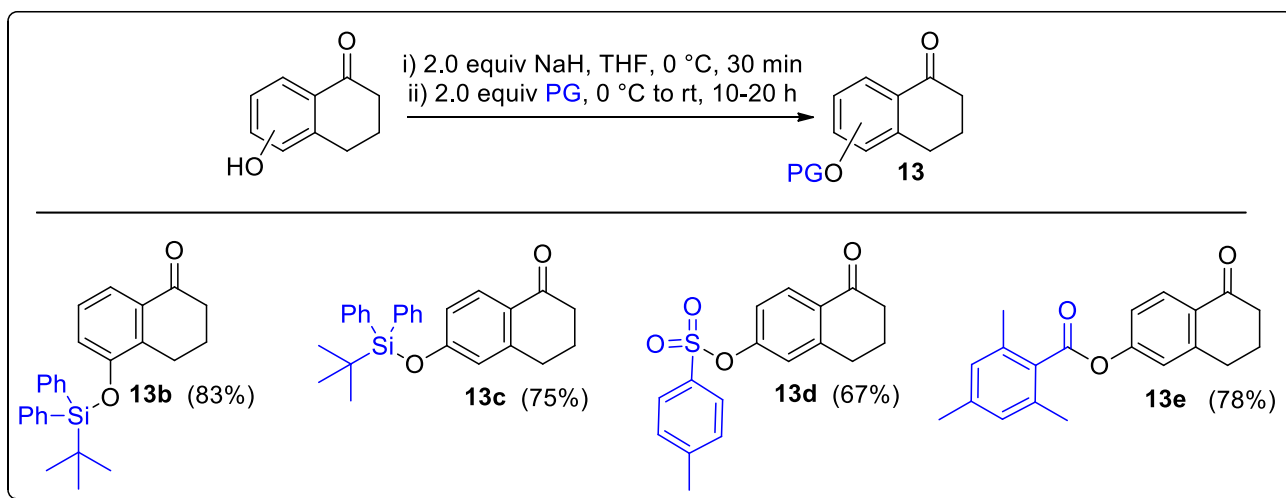
Ajmir Khan [khanajmi@msu.edu](mailto:khanajmi@msu.edu) ORCID: [orcid.org/0000-0002-5561-6609](https://orcid.org/0000-0002-5561-6609)

Supporting information includes

- 1) Substrate Preparation
- 2) Experimental
- 3) References
- 4) Spectra

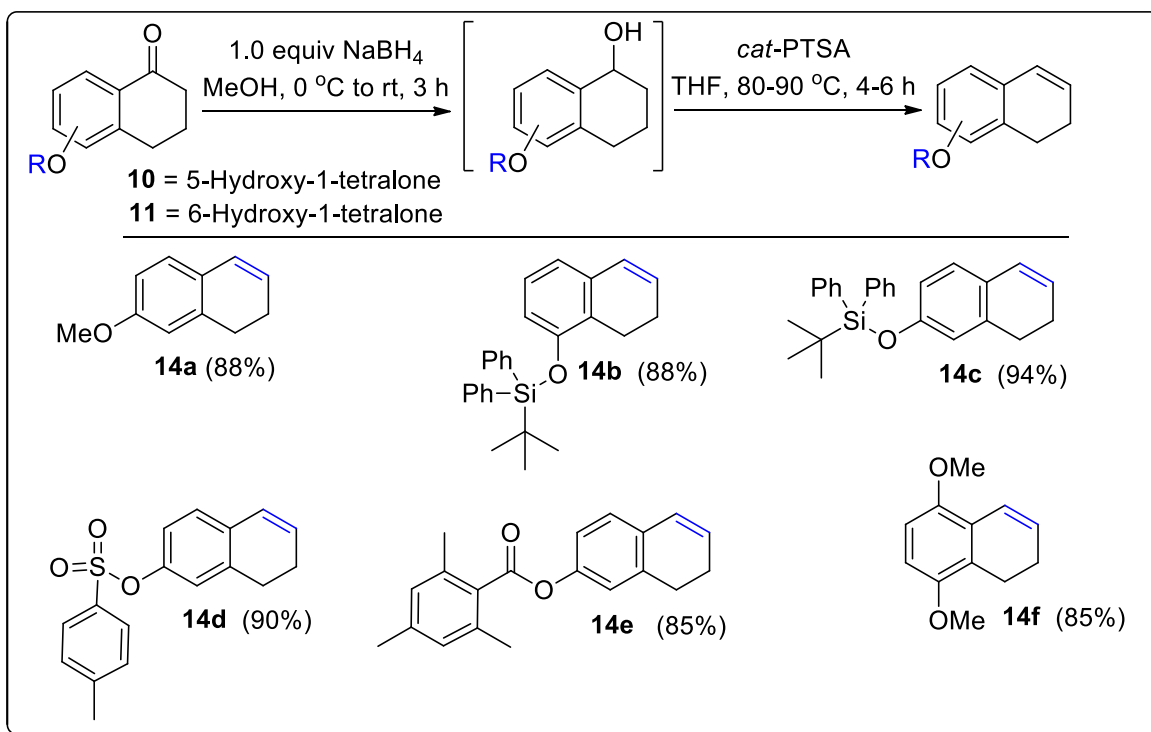
#### 1. Substrate Preparation:

TTN- and HTIB-mediated ring contraction reactions were studied for selected derivatives of tetralones. Tetralones having -OH or -NH<sub>2</sub> groups were commercially acquired and were protected to prevent any side reactions with these oxidative agents (HTIB and TTN). Different protecting groups were introduced, aiming to investigate their tolerance as well as their electronic and steric effects in the ring contraction reactions. The protected compounds (**13b-e**) were obtained in reasonable to good yields from the corresponding tetralones (**Scheme 1**).



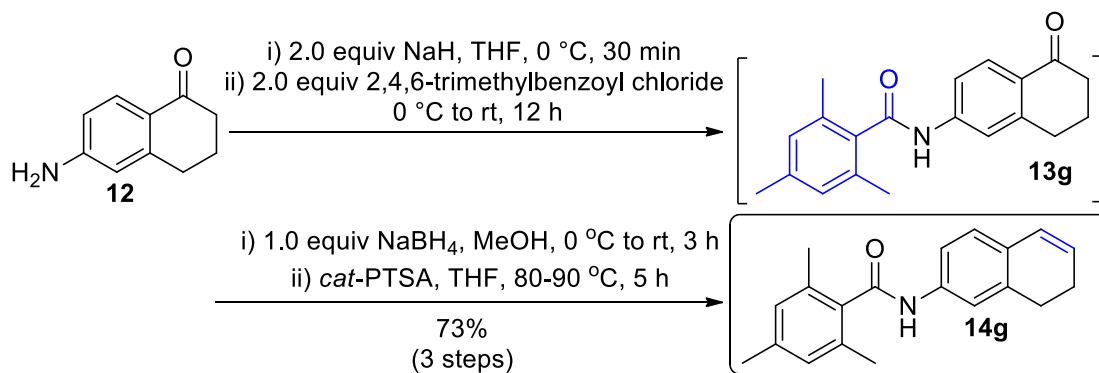
**Scheme 1.** Illustration of the chemistry utilized for the protection of the OH group.

Subsequently, commercially available tetralones **10** and **11**, and protected tetralones (**13b-e**) were reacted with NaBH<sub>4</sub> in MeOH in order to reduce to the corresponding alcohols which were transformed into the corresponding alkenes **14a-14f** and proceeded without purification via dehydration reaction using catalytic amount *p*-TsOH.H<sub>2</sub>O in THF. These results, along with the relevant reaction conditions, are summarized in **Scheme 2**.



**Scheme 2.** Reduction of protected tetralones.

Similarly, 6-amino-tetralone (**12**) was protected with 2,4,6-trimethylbenzoyl chloride to produce the corresponding protected ketone **13g**, which was directly converted to alkene **14g** via the reduction and dehydration protocol (**Scheme 3**).



**Scheme 3** Preparation of compound **14g**.

## 2. Experimental:

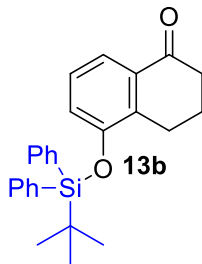
The described compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and melting point (for solids) and compared with literature data when available. All novel compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, HRMS, and melting point (for solids). All protection reactions, as well as reduction reactions, have been performed in septum-sealed flasks under the nitrogen atmosphere. Similarly, all dehydration reactions have been performed using the round bottom flask, fitted with Dean-Stark apparatus. The progress of these reactions was monitored by thin-layer chromatographic (TLC) analysis. The TLC employed silica gel plates (Merck Type 60 F<sub>254</sub> on aluminum), with detection by UV light (254 nm) and stained with phosphomolybdic acid solution, vanillin,  $\text{KMnO}_4$  solution or *p*-anisaldehyde. Chromatographic purifications in flash column chromatography were performed using 200-400 mesh silica gel. The reagents and solvents have been treated and/or dried, when necessary, according to the usual methods.

Chemical shifts are reported in parts per million (ppm) and coupling constants ( $J$ ) in Hertz. Standard and peak multiplicities are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quin; br s, broad singlet; and m, multiplet. All NMR samples were prepared using  $\text{CDCl}_3$  as a solvent.

### Protection of tetralones; General procedure

To the 2-neck round bottom flask (under  $\text{N}_2$  atmosphere), NaH (0.160 g, 4.00 mmol, 60% dispersed in mineral oil) was added in a portion-wise fashion to a magnetically stirred solution of **10** or **11** (0.324 g, 2.00 mmol) dissolved in THF (6 mL) at 0 °C. After 30 min *t*-butyl(chloro)diphenylsilane (1.100 g, 4.00 mmol) was added and the mixture was allowed to rt and stirred for 10 h. After completion of the reaction, distilled  $\text{H}_2\text{O}$  (10 mL) was added followed by extraction with EtOAc (3 x 10 mL). The organic layers were combined, washed with brine (10 mL), dried over  $\text{MgSO}_4$ , filtered and under reduced pressure all solvents were removed. The crude organic residue was purified by flash column chromatography (10-30% EtOAc in hexane).

### 5-((*t*-Butyldiphenylsilyl)oxy)-3,4-dihydronaphthalen-1(2*H*)-one (**13b**)



The title compound was prepared according to the general procedure (stirred at 0 °C to rt for 10 h), as described above.

Yield: 0.665 g, 1.66 mmol, (83%); white crystal; 115-116 °C.

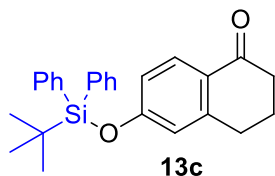
IR (film): 3341, 3134, 3072, 3050, 2999, 2953, 2932, 2891, 2859, 2709, 2590, 1961, 1891, 1824, 1777, 1678, 1596, 1569, 1490, 1472, 1462, 1428, 1391, 1361, 1348, 1333, 1318, 1275, 1253, 1186, 1157, 1114, 1067, 1025, 1007, 998, 972, 938, 900, 880, 823, 701, 660 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.81 (d, *J* = 8.5 Hz, 1 H), 7.70 (dd, *J* = 1.5 and 8.2 Hz, 4 H), 7.41 (t, *J* = 7.5 Hz, 2 H), 7.36, (t, *J* = 7.2 Hz, 4 H), 6.64 (dd, *J* = 2.5 and 8.5 Hz, 1 H), 6.60 (d, *J* = 2.0 Hz, 1 H), 2.71 (t, *J* = 6.0 Hz, 2 H), 2.52 (t, *J* = 6.5 Hz, 2 H), 2.00 (quin, *J* = 6.4 Hz, 2 H), 1.11 (s, 9H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 197.2, 160.1, 146.7, 135.4, 132.2, 130.2, 129.4, 128.0, 126.7, 119.0, 118.6, 39.0, 29.9, 26.5, 23.3, 19.5.

HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>28</sub>O<sub>2</sub>SiNa: 423.1756; found: 423.1734.

### 6-((*t*-Butyldiphenylsilyl)oxy)-3,4-dihydronaphthalen-1(2*H*)-one (13c)



The title compound was prepared according to the general procedure (stirred at 0 °C to rt for 10 h), as described above.

Yield: 0.601 g, 1.50 mmol (75%); colorless oil.

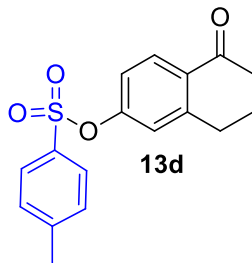
IR (film): 3134, 3072, 3050, 2999, 2653, 2932, 2891, 2859, 2709, 2590, 1961, 1891, 1824, 1777, 1678, 1596, 1569, 1490, 1472, 1462, 1428, 1391, 1361, 1348, 1333, 1318, 1275, 1253, 1186, 1157, 1114, 1067, 1025, 1007, 998, 972, 938, 900, 880, 823, 742, 710, 701 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.80 (d, *J* = 8.4 Hz, 1 H), 7.70 (dd, *J* = 1.8 and 8.1 Hz, 4 H), 7.33-7.45, (m, 6 H), 6.60-6.66 (m, 2 H), 2.72 (t, *J* = 6.0 Hz, 2 H), 2.53 (t, *J* = 6.4 Hz, 2 H), 2.00 (quin, *J* = 6.3 Hz, 2 H). 1.10 (s, 9H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 197.3, 160.1, 146.7, 135.5, 132.3, 130.2, 129.4, 128.0, 126.7, 119.0, 118.6, 39.0, 29.9, 26.5, 23.4, 19.5.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>28</sub>O<sub>2</sub>S: 401.1937; found: 401.1915.

### 3.5-Oxo-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (13d)



The title compound was prepared according to the general procedure (stirred at 0 °C to rt for 20 h), as described above.

Yield: 0.423 g, 1.34 mmol (67%); light red oil.

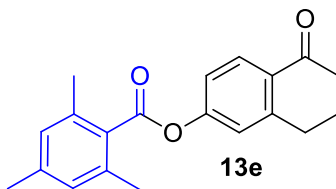
IR (film): 3368, 3067, 2948, 2873, 1923, 1686, 1601, 1577, 1482, 1455, 1433, 1403, 1376 1350, 1323, 1308, 1276, 1228, 1213, 1190, 1178, 1134, 1114, 1092, 1027, 945, 893, 865, 835, 816, 786, 748, 716, 691, 665, 643  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.93 (d,  $J$  = 8.4 Hz, 1 H), 7.74 (d,  $J$  = 8.4 Hz, 2 H), 7.33 (d,  $J$  = 8.1 Hz, 2 H), 7.05 (d,  $J$  = 2.4 Hz, 1 H), 6.78 (dd,  $J$  = 2.2 and 8.4 Hz, 1 H), 2.93 (t,  $J$  = 6.1 Hz, 2 H), 2.64 (t,  $J$  = 6.6 Hz, 2 H), 2.46 (s, 3 H), 2.13 (quin,  $J$  = 6.4 Hz, 2 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.2, 153.1, 146.7, 145.9, 132.5, 131.4, 130.0, 129.4, 128.6, 122.6, 120.6, 39.0, 29.9, 23.2, 21.9.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{17}\text{SO}_4$ : 317.0848; found: 317.0838.

### 5-Oxo-5,6,7,8-tetrahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (13e)



The title compound was prepared according to the general procedure (stirred at 0 °C to rt for 10 h), as described above.

Yield: 0.480 g, 1.56 mmol (78%); light-yellow solid; mp 113-115 °C.

IR (film): 3466, 3350, 2943, 2876, 2739, 2418, 1912, 1743, 1689, 1607, 1578, 1486, 1448, 1434, 1380, 1349, 1323, 1280, 1260, 1248, 1229, 1215, 1186, 1165, 1142, 1115, 1069, 1051, 1023, 956, 935, 901, 889, 856, 807, 755, 713, 691, 649, 609, 584, 571, 528, 506  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12 (d,  $J$  = 8.0 Hz, 1 H), 7.14-7.17 (m, 2 H), 6.92 (2 H, s), 2.99 (t,  $J$  = 6.2 Hz, 2 H), 2.65 (t,  $J$  = 6.5 Hz, 2 H), 2.44 (s, 6 H), 2.31 (s, 3 H), 2.15 (quin,  $J$  = 6.4 Hz, 2 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.1, 167.8, 154.5, 146.5, 140.4, 135.8, 130.6, 129.5, 129.4, 128.8, 121.5, 120.2, 39.0, 29.9, 23.2, 21.2, 20.1.

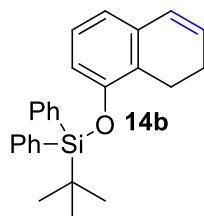
HRMS (ESI):  $m/z$  [ $M + H$ ] $^+$  calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_3$ : 309.1491; found: 309.1478.

### Reduction and dehydration reactions; General procedure

A 2-neck round bottom flask was charged with ketone **13b** (0.600 g, 1.50 mmol) dissolved in anhydrous MeOH (6 mL) under nitrogen atmosphere. To this solution  $\text{NaBH}_4$  (0.057 g, 1.50 mmol) was added in portion wise at 0 °C. After 30 min the reaction mixture was allowed to rt and stirred for another 3 hours. To the reaction mixture, distilled  $\text{H}_2\text{O}$  (10 mL) was added followed by extraction with EtOAc (3 x 10 mL). The organic extracts were combined, washed with brine (10 mL), dried over  $\text{MgSO}_4$ , filtered and under reduced pressure all solvents were removed. The crude alcohol **13bb** (was obtained as a colorless oil which was used in the next step without purification and characterization.

The crude alcohol **13bb** dissolved in THF (10 mL) and few crystals of PTSA ( $p$ -TsOH. $\text{H}_2\text{O}$ ) were added to the round bottom flask, fitted with Dean-Stark apparatus. The reaction was heated at 80-90 °C for 6 h. After completion of the reaction (analyzed by TLC) the mixture was quenched by the addition of a saturated aqueous solution of  $\text{NaHCO}_3$  followed by extraction with EtOAc (3 x 10 mL). The organic extracts were combined, washed with brine (10 mL), dried over  $\text{MgSO}_4$ , filtered and under reduced pressure all solvents were removed. The crude residue was purified by flash column chromatography (5-10% EtOAc in hexane).

### *t*-Butyl((7,8-dihydronaphthalen-1-yl)oxy)diphenylsilane (14b)



Yield: 0.504 g, 1.32 mmol (88%); colorless oil.

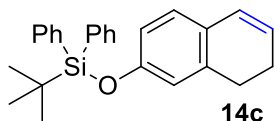
R (film): 3071, 3053, 3009, 3001, 2953, 2931, 2895, 2860, 1960, 1888, 1825, 1740, 1610, 1583, 1472, 1435, 1393, 1362, 1299, 1267, 1192, 1170, 1145, 1111, 1033, 999, 974, 855, 823, 700, 672  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.70-7.73 (m, 4 H), 7.32-7.41 (m, 6 H), 6.70 (d,  $J$  = 8.1 Hz, 1 H), 6.58 (s, 1 H), 6.46 (dd,  $J$  = 1.8 and 8.1 Hz, 1 H), 6.32 (d,  $J$  = 9.6 Hz, 1 H), 5.83 (quin,  $J$  = 4.6 Hz, 1 H), 2.61 (t,  $J$  = 8.1 Hz, 2 H), 2.18-2.24 (m, 2 H), 1.09 (s, 9 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 154.6, 137.0, 135.6, 133.2, 130.0, 127.9, 127.7, 127.3, 126.7, 126.0, 119.3, 117.3, 27.8, 26.7, 23.0, 19.6.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{28}\text{OSiNa}$ : 407.1807; found: 407.1801.

#### ***t*-Butyl((7,8-dihydronaphthalen-2-yl)oxy)diphenylsilane (14c)**



The reaction was heated at 80-90 °C for 6 h in dehydration step.

Yield: 1.082 g, 2.82 mmol (94%); colorless oil.

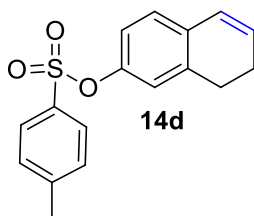
IR (film): 3071, 3049, 3016, 2999, 2956, 2932, 2893, 2858, 1960, 1888, 1822, 1738, 1607, 1582, 1487, 1472, 1428, 1390, 1361, 1294, 1269, 1189, 1167, 1143, 1113, 1029, 998, 973, 855, 822, 742, 701, 683  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.70-7.74 (m, 4H), 7.32-7.44 (m, 6H), 6.69 (d,  $J$  = 8.1 Hz, 1 H), 6.58 (s, 1 H), 6.47 (dd,  $J$  = 2.7 and 8.1 Hz, 1 H), 6.30-6.34 (m, 1 H), 5.82 (quin,  $J$  = 4.6 Hz, 1 H), 2.61 (t,  $J$  = 8.2 Hz, 2 H), 2.16-2.24 (m, 2 H), 1.09 (s, 9 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 154.6, 137.0, 135.7, 133.3, 130.0, 127.9, 127.7, 127.3, 126.7, 126.1, 119.3, 117.3, 27.9, 26.7, 23.6, 19.6.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{28}\text{OSiNa}$ : 407.1807; found: 407.1812.

#### **7,8-Dihydronaphthalen-2-yl 4-methylbenzenesulfonate (14d)**



The reaction was heated at 80-90 °C for 5 h in dehydration step.

Yield: 0.810 g, 2.70 mmol (90%); off-white solid; mp 102-104 °C.

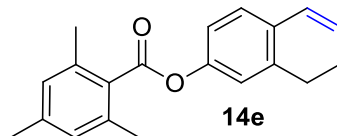
IR (film): 3033, 2930, 2883, 2829, 1921, 1600, 1566, 1490, 1458, 1378, 1291, 1243, 1230, 1207, 1188, 1177, 1120, 1099, 1080, 1030, 1000, 966, 901, 875, 819, 767, 703, 671  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.71, (d,  $J$  = 8.4 Hz, 2 H), 7.29, (d,  $J$  = 8.4 Hz, 2 H), 6.85 (d,  $J$  = 8.1 Hz, 1 H), 6.79 (s, 1 H), 6.65 (m, 1 H), 6.37 (m, 1 H), 6.00 (quin,  $J$  = 4.6 Hz, 1 H), 2.70 (t,  $J$  = 8.2 Hz, 2 H), 2.42 (s, 3 H), 2.21-2.30 (m, 2 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.1, 145.3, 137.2, 133.1, 132.7, 129.7, 129.3, 128.5, 126.7, 126.6, 121.6, 119.4, 27.4, 22.7, 21.7.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{SNa}$ : 323.0712; found: 323.0715.

### 7,8-Dihydronaphthalen-2-yl 2,4,6-trimethylbenzoate (**14e**)



The reaction was heated at 80-90 °C for 5 h in dehydration step.

Yield: 0.495 g, 1.70 mmol (85%); colorless oil.

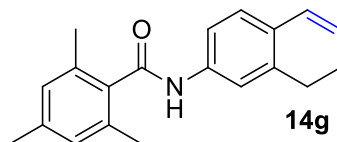
IR (film): 3468, 3032, 2930, 2884, 2830, 2737, 2105, 1870, 1744, 1611, 1576, 1491, 1437, 1425, 1395, 1379, 1335, 1322, 1297, 1254, 1221, 1199, 1164, 1141, 1113, 1053, 955, 888, 849, 815, 785, 754, 707, 688, 676  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.05 (d,  $J$  = 8.0 Hz, 1 H), 6.97-7.00 (m, 2 H), 6.91 (s, 2 H), 6.44-6.47 (m, 1 H), 6.02 (quin,  $J$  = 4.5 Hz, 1 H), 2.83 (t,  $J$  = 8.2 Hz, 2 H), 2.45 (s, 6H), 2.30-2.34 (m, 5 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.7, 149.4, 140.0, 137.2, 135.7, 132.3, 130.2, 128.7, 128.6, 127.1, 126.9, 120.9, 119.4, 27.7, 22.9, 21.3, 20.1.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_2\text{Na}$ : 315.1361; found: 315.1344.

### *N*-(7,8-Dihydronaphthalen-2-yl)-2,4,6-trimethylbenzamide (**14g**)



Tetralone **12** was protected according to the general procedure as for the protection of tetralones **10** and **11** (stirred at 0 °C to rt for 12 h). The protected ketone **13g** was proceeded to the next step of reduction and dehydration without purification and characterization as described above. The reaction mixture was heated at 80-90 °C for 5 h in dehydration step.

Yield: 0.425 g, 1.46 mmol (73%); off-white solid; mp 142-143 °C.



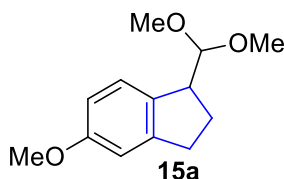
IR (film): 3270, 3097, 3031, 2928, 2883, 2829, 1888, 1649, 1610, 1584, 1525, 1420, 1378, 1328, 1312, 1285, 1266, 1248, 1223, 1178, 1123, 1094, 1030, 1015, 953, 882, 848, 833, 789, 755, 714, 692, 677, 605  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47 (s, 1 H), 7.33 (br, 1 H), 7.29 (dd,  $J$  = 2.0 and 8.0 Hz, 1 H), 6.98 (d,  $J$  = 8.0 Hz, 1 H), 6.87 (s, 2H), 6.42-6.44 (m, 1 H), 5.99 (quin,  $J$  = 4.6 Hz, 1 H), 2.81 (t,  $J$  = 8.0 Hz, 2 H), 2.28-2.33 (m, 11 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.8, 139.0, 136.8, 136.5, 135.2, 134.4, 131.0, 128.5, 128.0, 127.2, 126.5, 119.3, 117.7, 27.9, 23.1, 21.2, 19.3.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}$ : 292.1701; found: 292.1704.

### 1-(Dimethoxymethyl)-5-methoxy-2,3-dihydro-1*H*-indene (15a)<sup>1</sup>

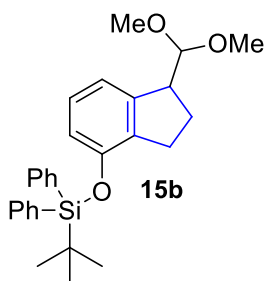


Yield: 0.032 g, 0.14 mmol (29%); colorless oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.31 (d,  $J$  = 9.6 Hz, 1 H), 6.75 (s, 1 H), 6.71 (d,  $J$  = 8.2 Hz, 1 H), 4.27 (d,  $J$  = 7.5 Hz, 1 H), 3.76 (s, 3 H), 3.41 (s, 3 H), 3.35 (s, 3 H), 2.75-2.96 (m, 2 H), 2.14-2.25 (m, 1 H), 1.89-2.02 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.1, 146.4, 134.8, 126.1, 112.2, 109.7, 107.4, 55.3, 54.2, 52.9, 46.6, 31.6, 27.8.

### *t*-Butyl((1-(dimethoxymethyl)-2,3-dihydro-1*H*-inden-4-yl)oxy)diphenylsilane (15b)



Yield: 0.033 g, 0.07 mmol (28%); colorless oil.

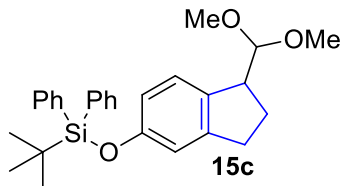
IR (film): 3429, 3072, 3049, 2957, 2932, 2893, 2858, 2829, 2711, 1961, 1888, 1822, 1724, 1607, 1582, 1486, 1473, 1428, 1390, 1361, 1298, 1272, 1188, 1172, 1144, 1114, 1079, 1059, 1008, 997, 967, 940, 904, 852, 822, 743, 701, 685  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.63-7.66 (m, 4 H), 7.25-7.37 (m, 6 H), 7.00 (d,  $J$  = 8.1 Hz, 1 H), 6.57 (d,  $J$  = 2.4 Hz, 1 H), 6.46 (dd,  $J$  = 2.4 and 8.1 Hz, 1 H), 4.15 (d,  $J$  = 7.5 Hz, 1 H), 3.29 (s, 3 H), 3.24 (s, 3 H), 2.54-2.74 (m, 2 H), 2.00-2.12 (m, 1 H), 1.78-1.88 (m, 1 H), 1.01 (s, 9 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.0, 146.2, 135.7, 135.2, 133.4, 129.9, 127.8, 125.7, 117.6, 115.7, 107.6, 54.1, 53.2, 46.8, 31.5, 27.8, 26.7, 19.6.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SiNa}$ : 469.2175; found: 469.2148.

***t*-Butyl((1-(dimethoxymethyl)-2,3-dihydro-1*H*-inden-5-yl)oxy)diphenylsilane (15c)**



Yield: 0.039 g, 0.09 mmol (34%); colorless oil.

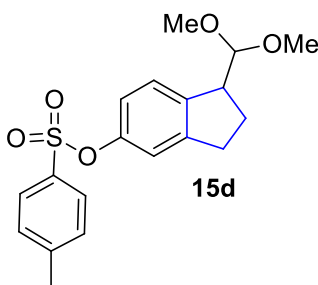
IR (film): 3430, 3070, 3048, 2958, 2931, 2892, 2857, 2830, 2710, 1963, 1888, 1820, 1720, 1604, 1580, 1488, 1477, 1433, 1390, 1360, 1300, 1271, 1188, 1171, 1144, 1111, 1080, 1069, 1005, 999, 966, 943, 902, 850, 823, 743, 700, 681  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (800 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.72 (d,  $J$  = 7.2 Hz, 4 H), 7.41 (t,  $J$  = 7.2 Hz, 2 H), 7.35 (t,  $J$  = 7.2 Hz, 4 H), 7.09 (d,  $J$  = 8.0 Hz, 1 H), 6.65 (s, 1 H), 6.54 (d,  $J$  = 8.0 Hz, 1 H), 4.23 (d,  $J$  = 8.0 Hz, 1 H), 3.36 (s, 3 H), 3.30-3.33 (m, 4 H), 2.73-2.77 (m, 1 H), 2.65-2.69 (m 1 H), 2.11-2.15 (m 1 H), 1.87-1.91 (m, 1 H), 1.09 (s, 9 H).

$^{13}\text{C}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 154.9, 146.1, 135.7, 135.2, 133.3, 129.9, 127.9, 125.7, 117.6, 115.7, 107.5, 54.0, 53.1, 46.7, 31.5, 27.8, 26.7, 19.6.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SiNa}$ : 469.2175; found: 469.2172.

**1-(Dimethoxymethyl)-2,3-dihydro-1*H*-inden-5-yl 4-methylbenzenesulfonate (15d)**



Yield: 0.027 g, 0.07 mmol (29%); light yellow oil.

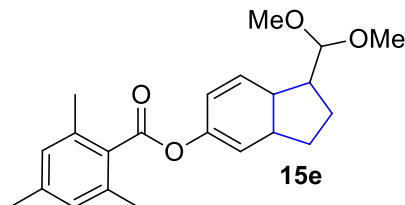
IR (film): 3468, 2925, 2853, 2380, 2346, 1921, 1733, 1597, 1478, 1455, 1372, 1306, 1292, 1257, 1224, 1190, 1178, 1159, 1122, 1091, 1058, 1019, 988, 931, 904, 873, 833, 814, 774, 729, 706, 691, 662  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.72 (d,  $J$  = 8.5 Hz, 2 H), 7.29 (dd,  $J$  = 8.2 and 16.7 Hz, 3 H), 6.89 (s, 1 H), 6.67 (dd,  $J$  = 2.2 and 8.2 Hz, 1 H), 4.26 (d,  $J$  = 7.5 Hz, 1 H), 3.34-3.42 (m, 7 H), 2.85-2.90 (m, 1 H), 2.75-2.82 (m, 1 H), 2.45 (s, 3 H), 2.17-2.24 (m, 1 H), 1.93-2.00 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.9, 146.7, 145.2, 141.8, 132.9, 129.8, 128.6, 126.2, 120.0, 118.5, 107.0, 54.3, 53.1, 47.1, 31.4, 27.7, 21.8.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_5\text{Na}$ : 385.1086; found: 385.1083.

### 1-(Dimethoxymethyl)-2,3,3a,7a-tetrahydro-1H-inden-5-yl 2,4,6-trimethylbenzoate (15e)



Yield: 0.022 g, 0.06 mmol (31%); colorless oil.

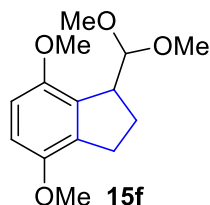
IR (film): 3468, 2925, 2831, 2736, 1743, 1611, 1592, 1483, 1428, 1378, 1254, 1226, 1189, 1163, 1129, 1095, 1051, 987, 956, 924, 887, 852, 806, 711, 601  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 (d,  $J$  = 8.1 Hz, 1 H), 7.07 (d,  $J$  = 2.0 Hz, 1 H), 6.99 (dd,  $J$  = 2.2 and 8.2 Hz, 1 H), 6.91 (s, 2 H), 4.32 (d,  $J$  = 7.5 Hz, 1 H), 3.37-3.50 (m, 7 H), 2.83-3.03 (m, 2 H), 2.44 (s, 6 H), 2.31 (s, 3 H), 2.19-2.29 (m, 1 H), 1.98-2.08 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.9, 150.0, 146.6, 140.7, 140.0, 135.7, 130.3, 128.7, 126.4, 119.4, 107.7, 107.2, 54.5, 52.9, 47.1, 31.6, 27.9, 21.3, 20.1.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{Na}$ : 377.1729; found: 377.1725.

### 1-(Dimethoxymethyl)-4,7-dimethoxy-2,3-dihydro-1H-indene (15f)



Yield: 0.023 g, 0.09 mmol (18%); colorless oil.

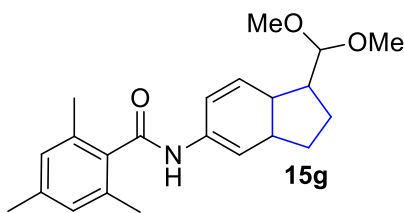
IR (film): 3368, 2931, 2826, 2872, 1733, 1669, 1608, 1574, 1488, 1433, 1369, 1255, 1094, 1078, 816  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.63 (dd,  $J$  = 9.0 and 11.4 Hz, 2 H), 4.70 (d,  $J$  = 3.0 Hz, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.56-3.60 (m, 1 H), 3.45 (s, 3 H), 3.20 (s, 3 H), 2.88-2.99 (m, 1 H), 2.75-2.84 (m, 1 H), 2.28-2.39 (m, 1 H), 1.98-2.11 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.7, 150.4, 135.3, 132.3, 109.4, 108.6, 107.1, 57.4, 55.7, 55.7, 55.5, 48.0, 29.5, 24.9.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Na}$ : 273.1461; found: 273.1458.

***N*-(1-(Dimethoxymethyl)-2,3,3a,7a-tetrahydro-1*H*-inden-5-yl)-2,4,6-trimethylbenzamide (15g)**



Yield: 0.031 g, 0.09 mmol (32%); yellow oil.

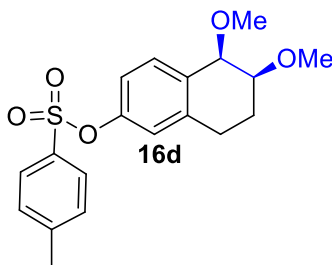
IR (film): 3748, 3276, 3120, 2924, 2854, 2830, 2734, 1728, 1651, 1611, 1597, 1530, 1491, 1454, 1425, 1377, 1329, 1286, 1251, 1177, 1154, 1122, 1076, 1058, 987, 954, 887, 850, 729, 600  $\text{cm}^{-1}$

$^1\text{H}$  NMR (800 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.65 (s, 1 H), 7.38 (d,  $J$  = 8.0 Hz, 1 H), 7.32 (s, 1 H), 7.22 (d,  $J$  = 8.8 Hz, 1 H), 6.88 (s, 2 H), 4.30 (d,  $J$  = 8.0 Hz, 1 H), 3.43 (s, 3 H), 3.38 (s, 3 H), 2.95-2.99 (m, 1 H), 2.85-2.89 (m, 1 H), 2.34 (s, 6 H), 2.30 (s, 3 H), 2.18-2.28 (m, 2 H), 1.98-2.02 (m, 1 H).

$^{13}\text{C}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.8, 146.2, 139.4, 139.0, 136.5, 135.2, 134.4, 128.5, 126.0, 118.1, 116.3, 107.3, 54.5, 52.9, 47.1, 31.7, 27.7, 21.2, 19.3.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{28}\text{O}_3\text{N}$ : 354.2069; found: 354.2056.

**(5*R*,6*S*)-5,6-Dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (16d)**



Yield: 0.015 g, 0.04 mmol (16%); light yellow oil.

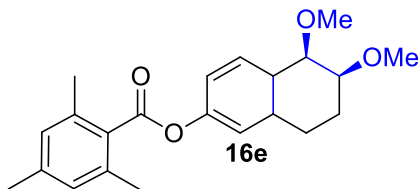
IR (film): 2927, 2825, 1923, 1726, 1607, 1597, 1492, 1456, 1372, 1307, 1294, 1251, 1210, 1190, 1178, 1137, 1115, 1093, 1046, 1018, 983, 944, 920, 879, 816, 773, 721, 708, 663  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.72 (d,  $J$  = 8.5 Hz, 2 H), 7.31 (d,  $J$  = 8.0 Hz, 2 H), 7.24 (d,  $J$  = 8.5 Hz, 1 H), 6.82 (d,  $J$  = 2.0 Hz, 1 H), 6.72 (dd,  $J$  = 2.5 and 8.0 Hz, 1 H), 4.28 (d,  $J$  = 2.5 Hz, 1 H), 3.64-3.67 (dt,  $J$  = 3.0 and 9.5 Hz, 1 H), 3.46 (s, 3 H), 3.45 (s, 3 H), 2.91-2.97 (m, 1 H), 2.66-2.73 (m, 1 H), 2.45 (s, 3 H), 2.14-2.23 (m, 1 H), 1.86-1.92 (m, 1 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.3, 145.4, 138.7, 133.8, 132.7, 130.7, 129.9, 128.6, 122.5, 119.5, 77.7, 77.1, 57.4, 56.7, 26.8, 22.3, 21.8.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_5\text{SNa}$ : 385.1086; found: 385.1080.

**(5R,6S)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (16e)**



Yield: 0.011 g, 0.03 mmol (15%); colorless oil.

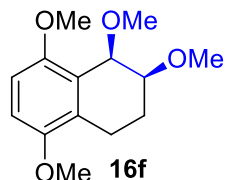
IR (film): 3469, 2926, 2824, 2086, 1743, 1611, 1587, 1494, 1456, 1427, 1378, 1245, 1219, 1190, 1164, 1144, 1116, 1100, 1082, 1052, 984, 942, 914, 888, 853, 802, 778, 708, 668  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.37 (d,  $J$  = 8.4 Hz, 1 H), 7.00-7.06 (m, 2 H), 6.91 (s, 2 H), 4.36 (d,  $J$  = 2.7 Hz, 1 H), 3.65 (dt,  $J$  = 3.3 and 10.2 Hz, 1 H), 3.48 (s, 6 H), 3.01-3.10 (m, 1 H), 2.77-2.89 (m, 1 H), 2.44 (s, 6 H), 2.31 (s, 3 H), 2.19-2.27 (m, 1 H), 1.92-2.00 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.5, 150.6, 140.1, 138.6, 135.7, 132.5, 131.1, 130.0, 128.8, 121.6, 118.9, 78.0, 77.7, 57.3, 56.6, 27.3, 22.3, 21.3, 20.1

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{Na}$ : 377.1729; found: 377.1722.

**(1R,2S)-1,2,5,8-Tetramethoxy-1,2,3,4-tetrahydronaphthalene (16f)**



Yield: 0.026 g, 0.10 mmol (21%); colorless oil.

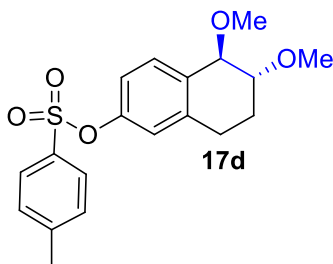
IR (film): 2935, 2900, 2832, 2034, 1726, 1602, 1481, 1464, 1439, 1364, 1331, 1257, 1202, 1184, 1153, 1091, 1070, 1016, 977, 947, 913, 829, 799, 767, 714, 660  $\text{cm}^{-1}$

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.71 (t,  $J$  = 6.3 Hz, 2 H), 4.86 (dd,  $J$  = 1.2, 2.7 Hz, 1 H), 3.82 (s, 3 H), 3.76 (s, 3 H), 3.56 (s, 3 H), 3.50 (s, 3 H), 3.38 (dt,  $J$  = 5.3 and 12.3 Hz, 1 H), 2.96-3.04 (m, 1 H), 2.46-2.60 (m, 1 H), 2.04-2.18 (m, 1 H), 1.93-2.00 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.2, 151.1, 127.6, 124.0, 109.5, 108.0, 74.8, 71.0, 58.1, 56.6, 56.0, 55.8, 20.3, 18.0.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Na}$ : 273.1461; found: 273.1458.

**(5R,6R)-5,6-Dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (17d)**



Yield: 0.017 g, 0.05 mmol (18%); light yellow oil.

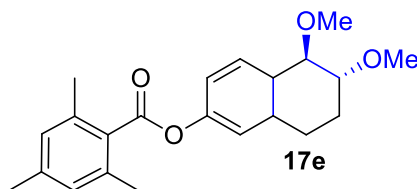
IR (film): 2929, 2824, 1922, 1727, 1608, 1598, 1492, 1455, 1401, 1373, 1307, 1295, 1249, 1213, 1189, 1178, 1137, 1113, 1093, 1042, 1009, 928, 914, 879, 831, 816, 776, 726, 694, 661  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.72 (2H, d,  $J$  = 8.0 Hz), 7.31 (2H, d,  $J$  = 8.0 Hz), 7.24 (1H, d,  $J$  = 8.5 Hz), 6.80 (1H, d,  $J$  = 2.5 Hz), 6.73 (1H, dd,  $J$  = 2.2 and 8.2 Hz), 4.16 (1H, d,  $J$  = 5.0 Hz), 3.67-3.70 (1H, m), 3.50 (3H, s), 3.43 (3H, s), 2.74-2.80 (1H, m), 2.63-2.69 (1H, dt,  $J$  = 5.5 and 17.0 Hz), 2.45 (3H, s), 2.03-2.08 (1H, m), 1.87-1.93 (1H, m).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.0, 145.3, 139.0, 133.8, 132.7, 131.3, 129.8, 128.7, 122.2, 119.8, 79.2, 77.6, 58.0, 56.8, 25.4, 23.1, 21.8.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_5\text{Na}$ : 385.1086; found: 385.1082.

### (5R,6R)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (17e)



Yield: 0.011 g, 0.03 mmol (17%); colorless oil.

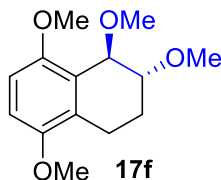
IR (film): 2928, 2822, 1744, 1611, 1586, 1494, 1455, 1427, 1377, 1320, 1299, 1244, 1222, 1164, 1144, 1115, 1096, 1053, 1010, 954, 918, 888, 852, 809, 787, 705, 660  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.41 (d,  $J$  = 8.4 Hz, 1 H), 7.05 (dd,  $J$  = 2.4 and 8.1 Hz, 1 H), 6.98 (d,  $J$  = 2.1 Hz, 1 H), 6.91 (s, 2 H), 4.26 (d,  $J$  = 4.8 Hz, 1 H), 3.70-3.75 (m, 1 H), 3.51 (s, 3 H), 3.45 (s, 3 H), 2.72-2.94 (m, 2 H), 2.43 (s, 6 H), 2.30 (s, 3 H), 2.08-2.18 (m, 1 H), 1.87-1.98 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.3, 150.1, 139.9, 138.7, 135.5, 132.5, 131.0, 130.0, 128.6, 121.1, 119.2, 79.2, 77.7, 57.4, 56.6, 25.5, 23.3, 21.1, 20.0.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{Na}$ : 377.1729; found: 377.1720.

### (1R,2R)-1,2,5,8-Tetramethoxy-1,2,3,4-tetrahydronaphthalene (17f)



Yield: 0.031 g, 0.12 mmol (25%); colorless oil.

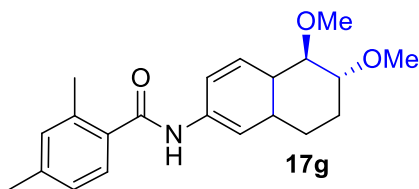
IR (film): 2939, 2831, 2029, 1726, 1602, 1481, 1464, 1438, 1378, 1358, 1339, 1319, 1292, 1258, 1194, 1154, 1112, 1086, 1052, 1019, 951, 870, 840, 799, 758, 723, 710  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.69 (dd,  $J$  = 9.0 and 10.5 Hz, 2 H), 4.47 (d,  $J$  = 1.5 Hz, 1 H), 3.75 (s, 3 H), 3.74-3.81 (m, 7 H), 3.53 (s, 3 H), 3.40 (s, 3 H), 2.68-2.77 (m, 1 H), 2.45-2.60 (m, 1 H), 2.06-2.14 (m, 1 H), 1.89-2.00 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 152.1, 151.5, 127.2, 125.7, 109.6, 108.0, 80.6, 70.0, 55.8, 59.8, 56.6, 56.0, 23.3, 21.1.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Na}$ : 273.1461; found: 273.1458.

***N*-((5*R*,6*R*)-5,6-Dimethoxy-4*a*,5,6,7,8,8*a*-hexahydronaphthalen-2-yl)-2,4,6-trimethylbenzamide (17g)**



Yield: 0.020 g, 0.05 mmol (19%); yellow oil.

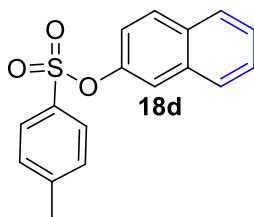
IR (film): 3748, 3282, 3118, 2925, 2855, 2824, 1656, 1611, 1594, 1530, 1504, 1455, 1418, 1376, 1331, 1279, 1177, 1096, 1084, 989, 954, 916, 884, 850, 828, 791, 755, 665, 603  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52 (s, 1 H), 7.33 (s, 2 H), 7.23 (br, 1 H), 6.88 (s, 2 H), 4.24 (d,  $J$  = 4.5 Hz, 1 H), 3.71-3.74 (m, 1 H), 3.49 (s, 3 H), 3.45 (s, 3 H), 2.84-2.90 (m, 1 H), 2.74-2.79 (m, 1 H), 2.33 (s, 6 H), 2.30 (s, 3 H), 2.10-2.16 (m, 1 H), 1.89-1.96 (m, 1 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.8, 139.0, 138.4, 137.4, 135.2, 134.4, 131.1, 130.9, 128.5, 119.5, 117.5, 79.3, 77.8, 57.4, 56.8, 25.6, 23.4, 21.3, 19.3.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{28}\text{O}_3\text{N}$ : 354.2069; found: 354.2059.

**Naphthalen-2-yl 4-methylbenzenesulfonate (18d).<sup>2</sup>**

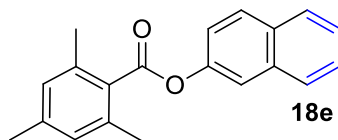


Yield: 0.003 g, 0.01 mmol (3%); pale yellow crystals mp 119-120  $^{\circ}\text{C}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.80 (t,  $J$  = 4.7 Hz, 1 H), 7.71-7.76 (m, 4 H), 7.46-7.50 (m, 3 H), 7.29 (d,  $J$  = 8.0 Hz, 2 H), 7.09 (dd,  $J$  = 2.5 and 9.0 Hz, 1 H), 2.43 (s, 3 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1326, 147.3, 145.5, 133.6, 132.0, 129.9, 129.9, 128.7, 128.0, 127.9, 127.0, 126.5, 121.3, 120.1, 21.8.

### Naphthalen-2-yl 2,4,6-trimethylbenzoate (18e)



Yield: 0.03 g, 0.01 mmol (4%); colorless oil.

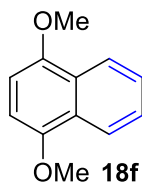
IR (film): 3450, 3051, 2920, 2851, 2346, 1736, 1629, 1599, 1581, 1510, 1461, 1426, 1377, 1354, 1267, 1254, 1236, 1207, 1165, 1154, 1137, 1119, 1048, 959, 943, 898, 886, 863, 855, 848, 827, 804, 777, 751, 735, 701, 639  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.91 (d,  $J$  = 9.0 Hz, 1 H), 7.86 (dd,  $J$  = 8.0 and 13.0 Hz, 2 H), 7.69 (d,  $J$  = 2.0 Hz, 1 H), 7.47-7.53 (m, 2 H), 7.37 (dd,  $J$  = 2.2 and 9.2 Hz, 1 H), 6.95 (s, 2 H), 2.50 (s, 6 H), 2.33 (s, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.7, 148.5, 140.2, 135.8, 134.0, 131.7, 130.1, 129.7, 128.8, 127.9, 127.8, 126.8, 125.9, 121.3, 118.7, 21.4, 20.2.

HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Na}$ : 313.1204; found: 313.1193.

### 1,4-Dimethoxynaphthalene (18f).<sup>3</sup>



Yield: 0.002 g, 0.01 mmol (2%); colorless solid; mp 88-90 °C.

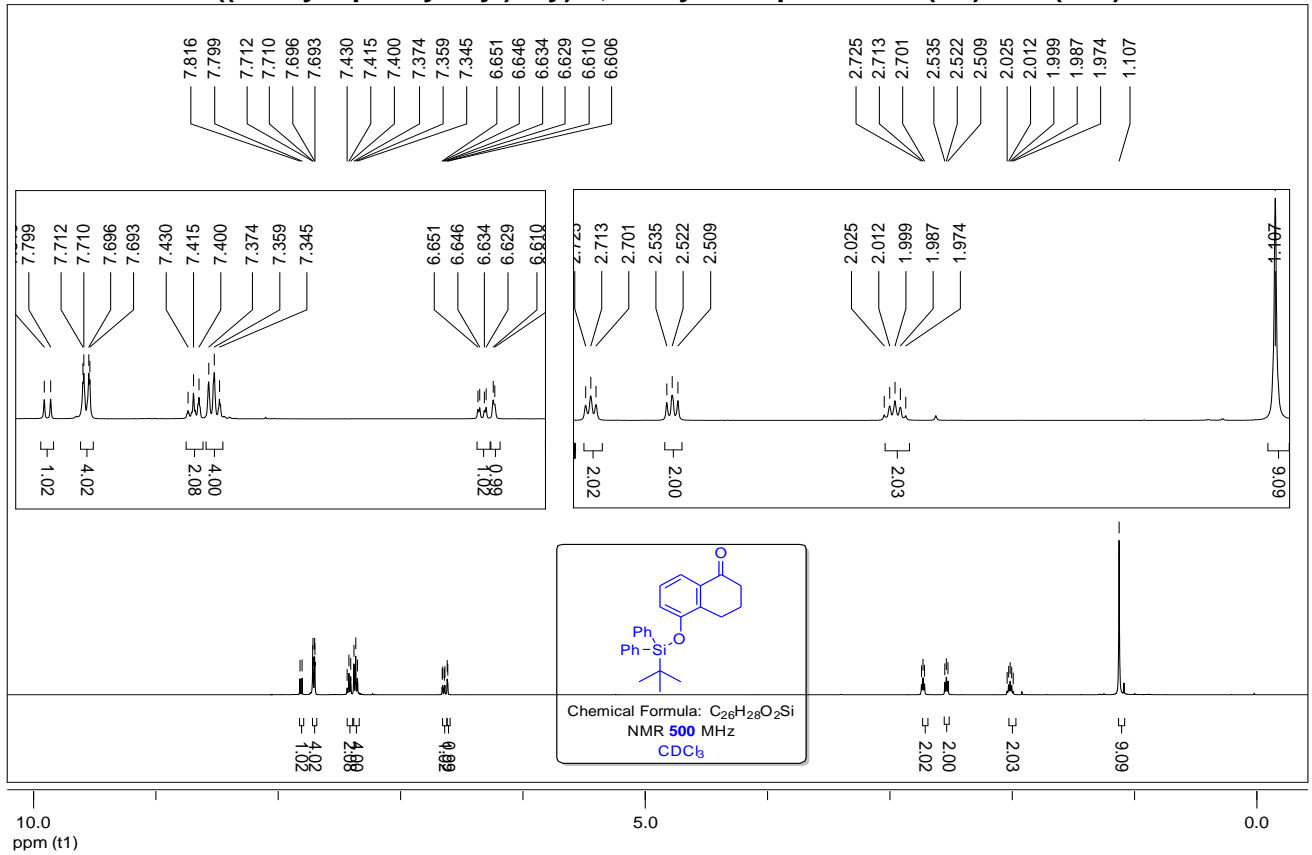
### 3. References.

- 1 H. M. C. Ferraz, A. M. Aguilar and L. F. Silva, *Synthesis (Stuttg)*, 2003, **2003**, 1031–1034.
- 2 R. L. Jezorek, N. Zhang, P. Leowanawat, M. H. Bunner, N. Gutsche, A. K. R. Pesti, J. T. Olsen and V. Percec, *Org Lett*, 2014, **16**, 6326–6329.
- 3 S. M. Rafiq, R. Sivasakthikumar and A. K. Mohanakrishnan, *Org Lett*, 2014, **16**, 2720–2723.

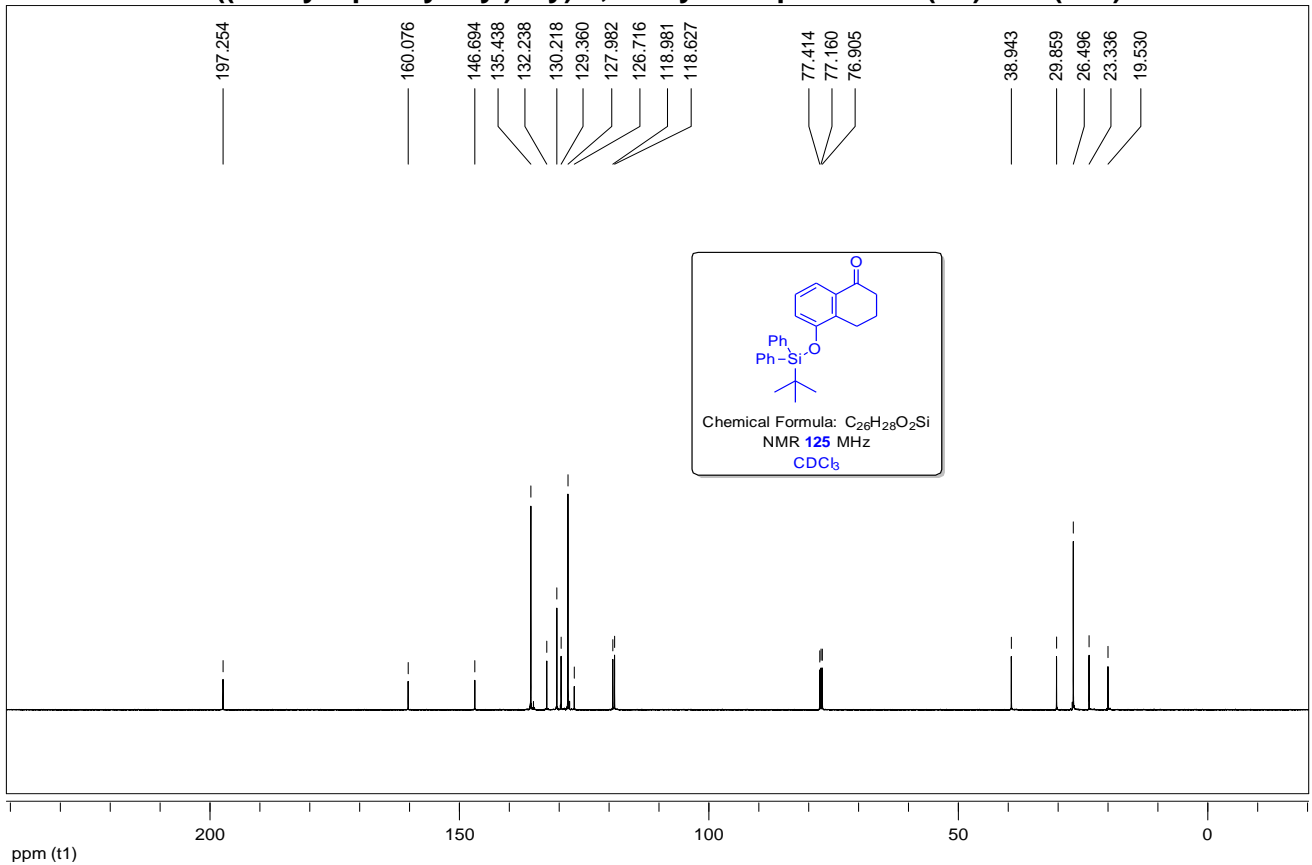
### 4. Spectra:



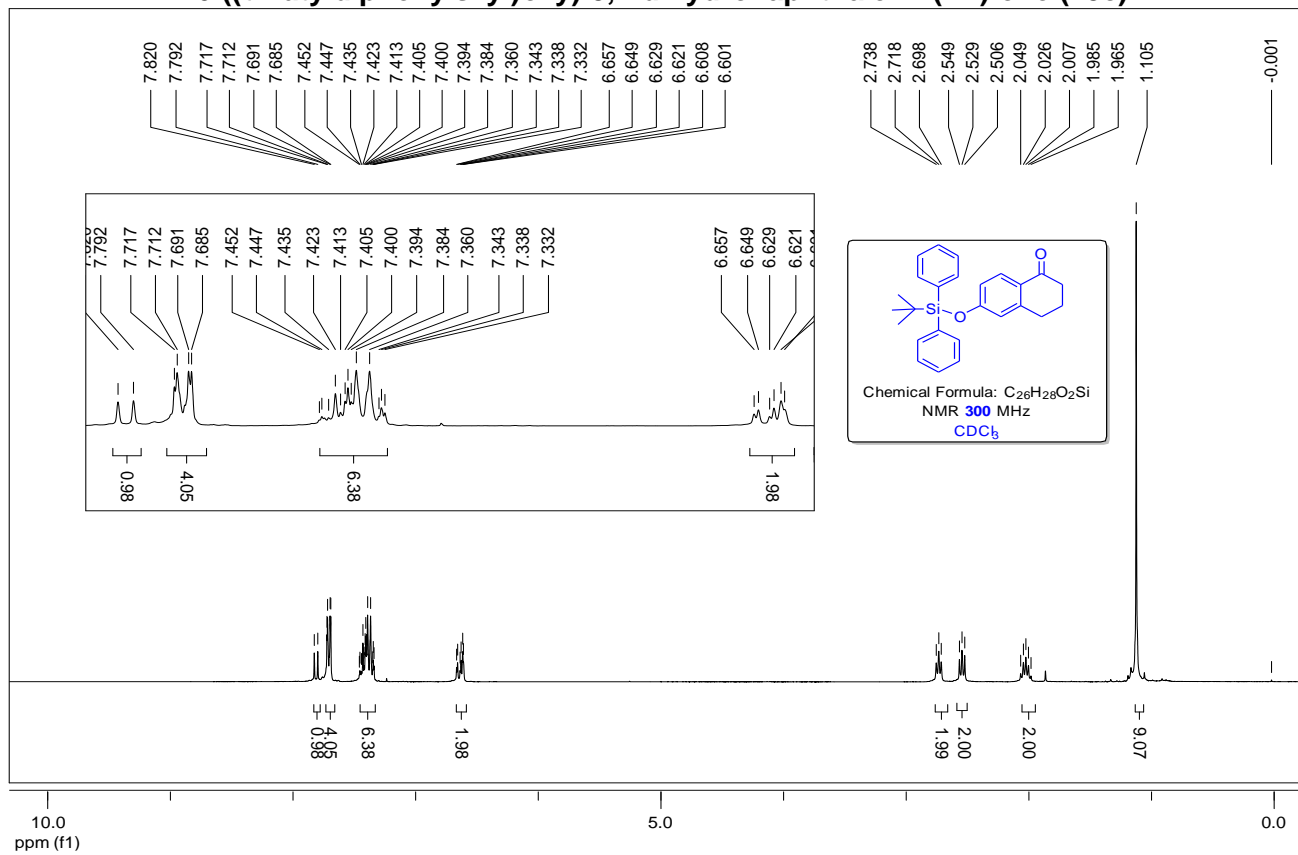
**5-((*t*-Butyldiphenylsilyl)oxy)-3,4-dihydronaphthalen-1(2*H*)-one (13b).**



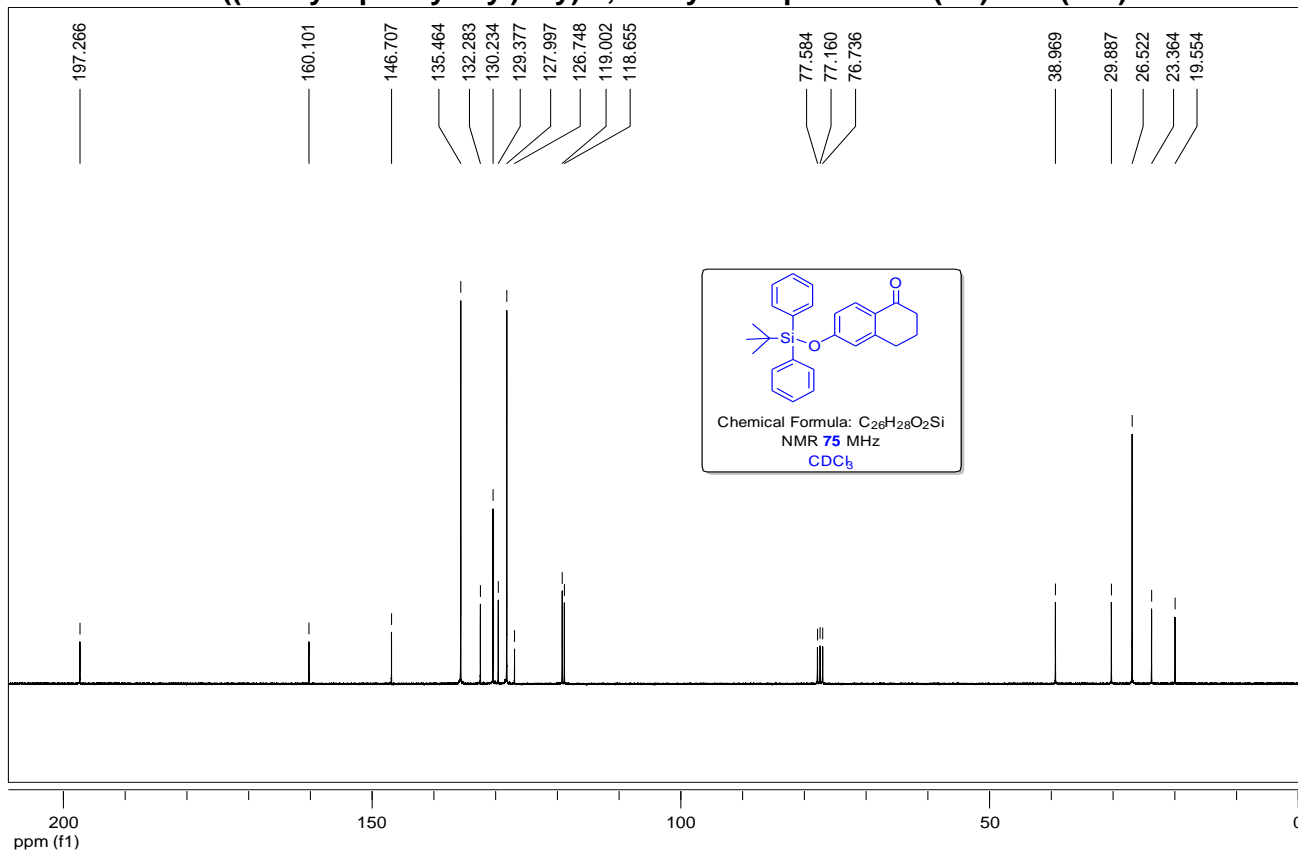
**5-((*t*-Butyldiphenylsilyl)oxy)-3,4-dihydronaphthalen-1(2*H*)-one (13b).**



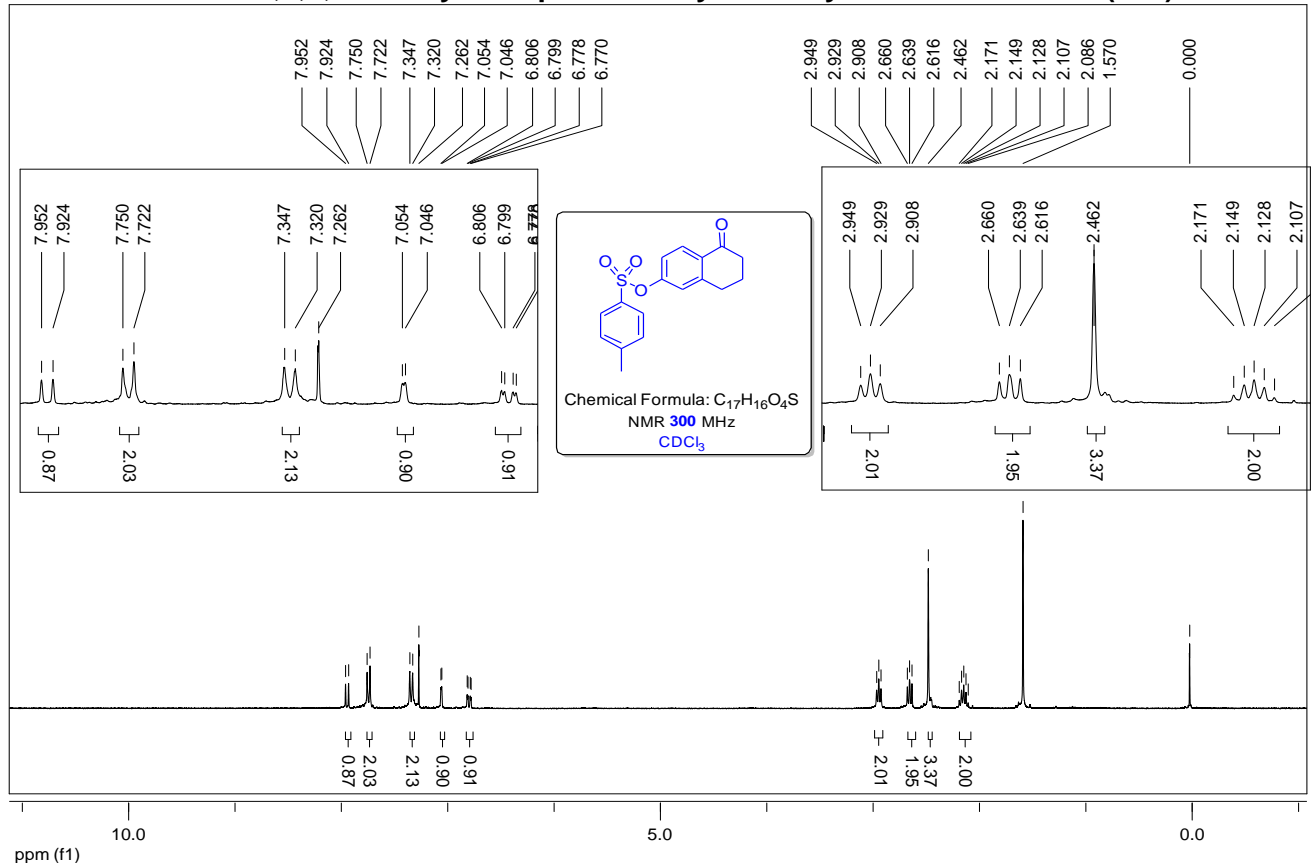
**6-((*t*-Butyldiphenylsilyl)oxy)-3,4-dihydronaphthalen-1(2H)-one (13c)**



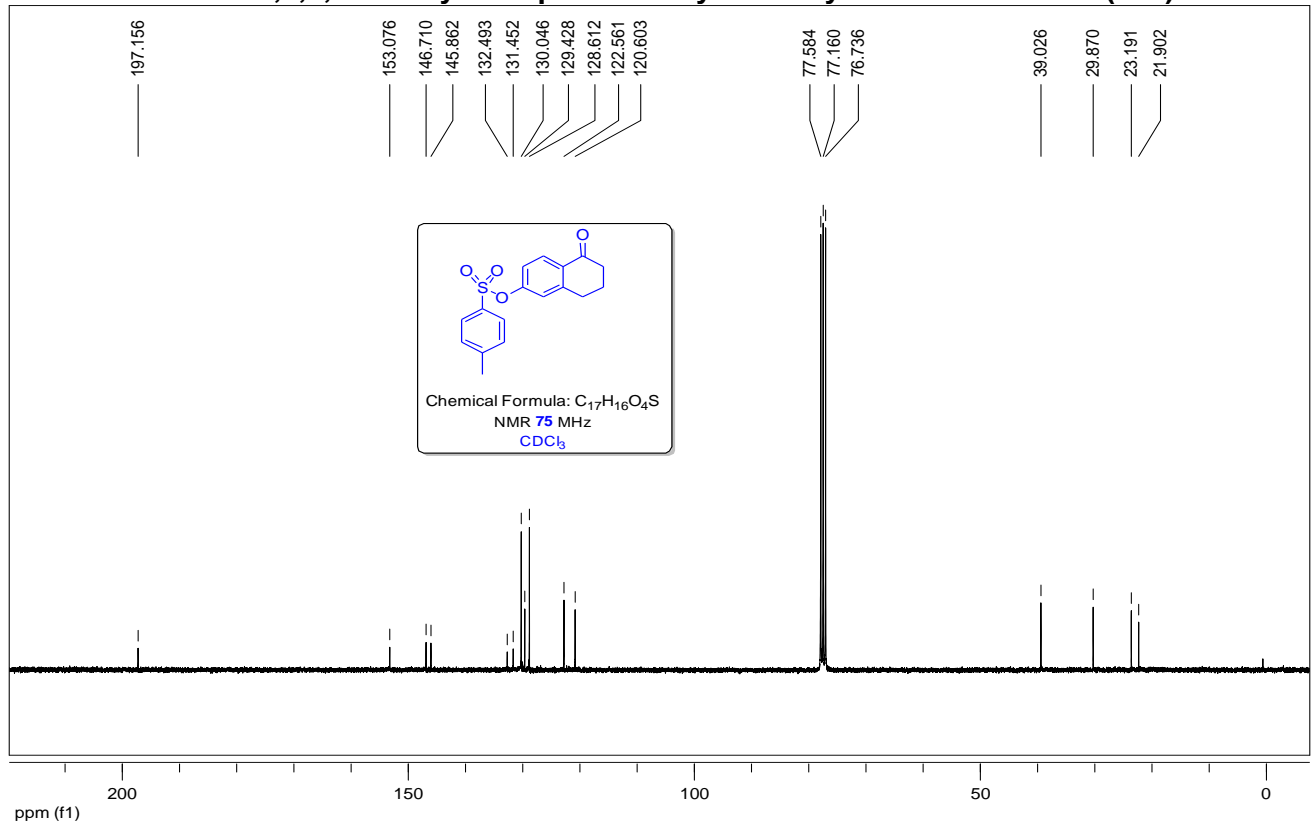
**6-((*t*-Butyldiphenylsilyl)oxy)-3,4-dihydronaphthalen-1(2H)-one (13c)**



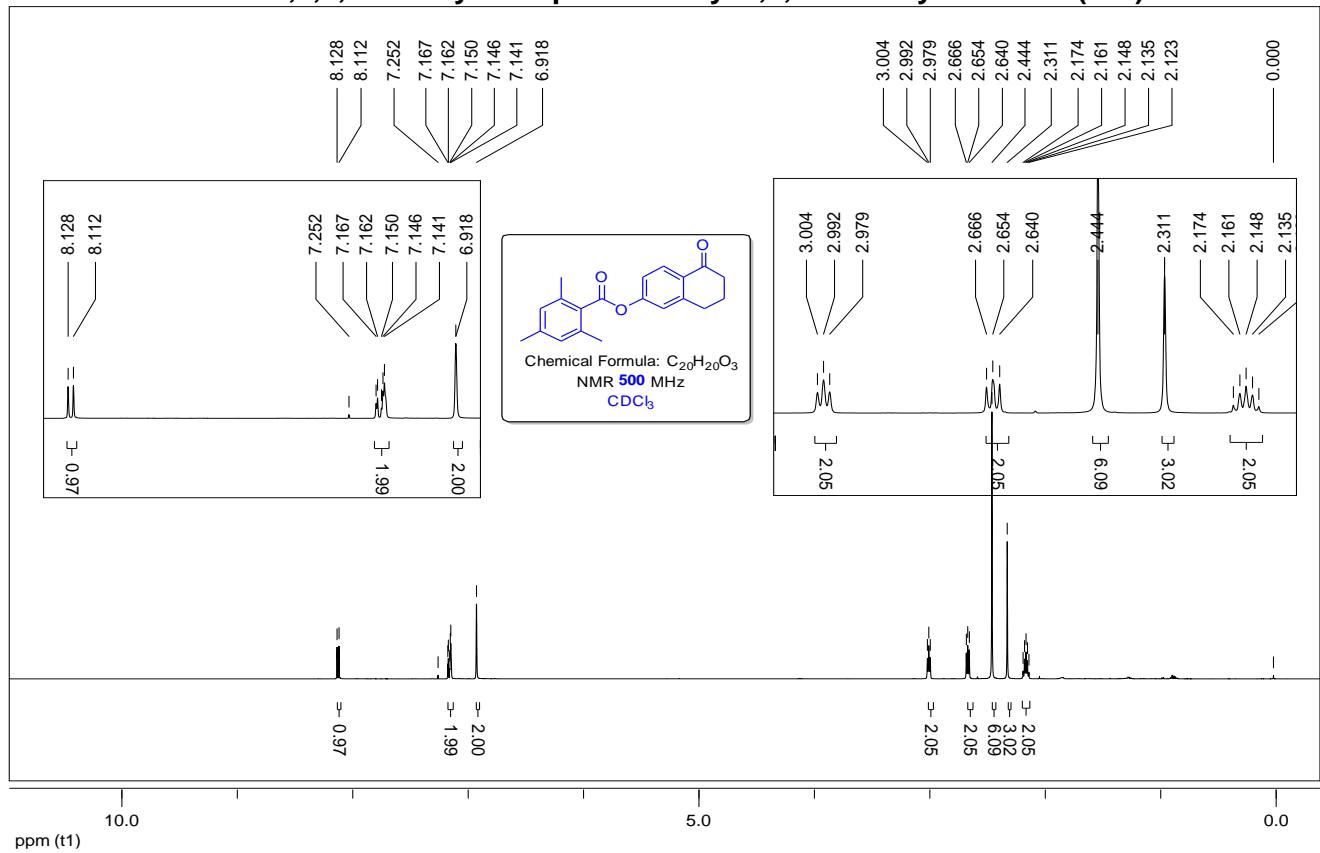
**3.5-Oxo-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (13d).**



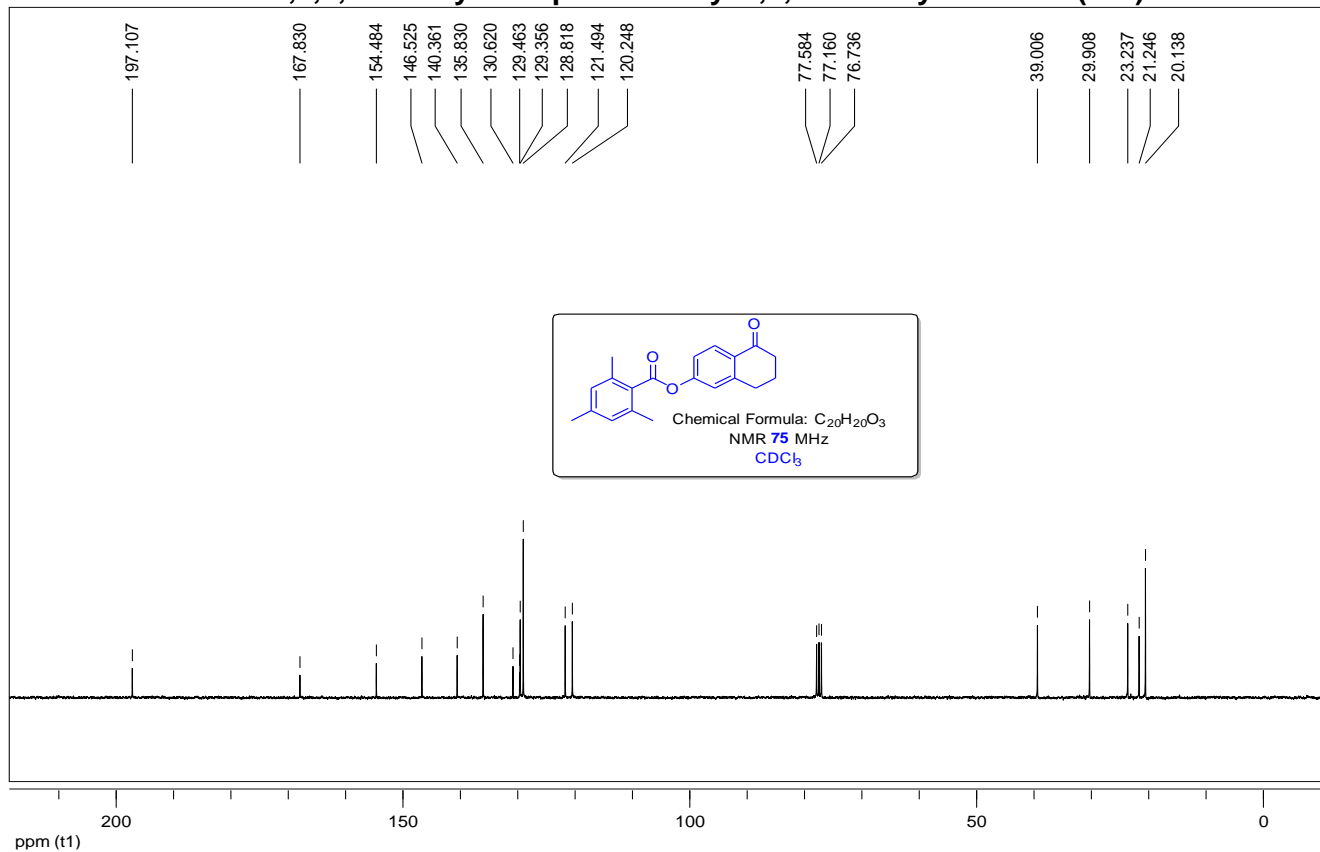
**3.5-Oxo-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (13d).**



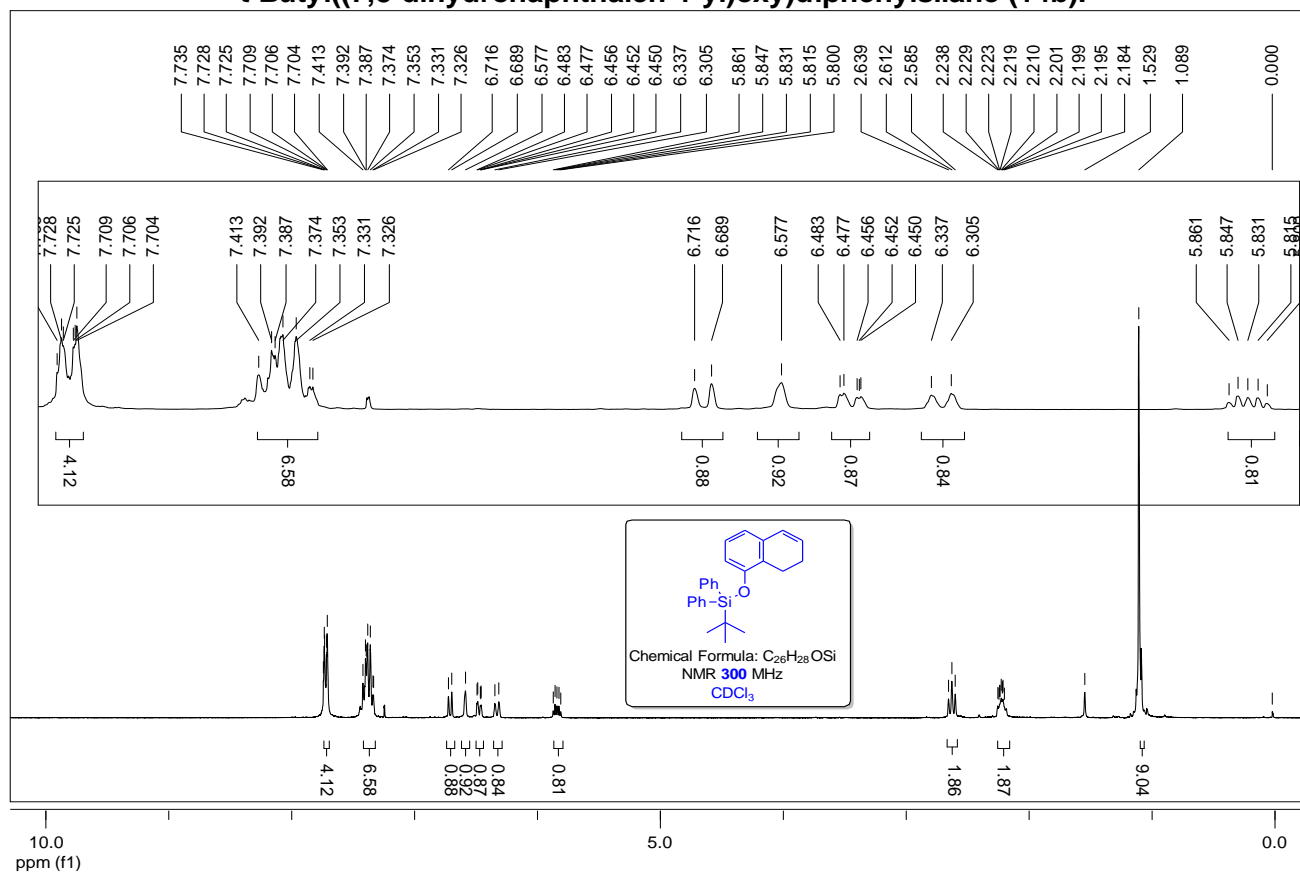
**5-Oxo-5,6,7,8-tetrahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (13e)**



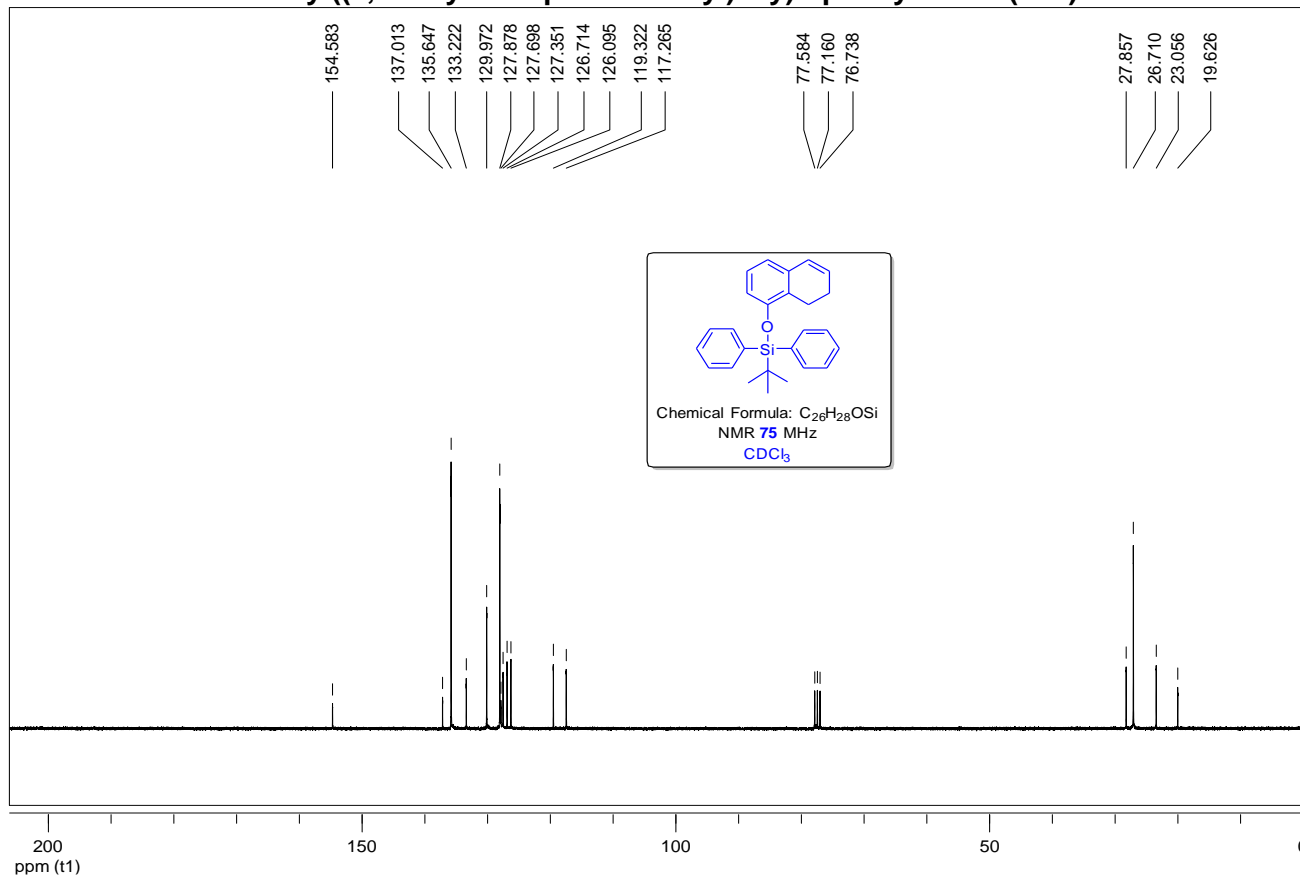
**5-Oxo-5,6,7,8-tetrahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (13e)**



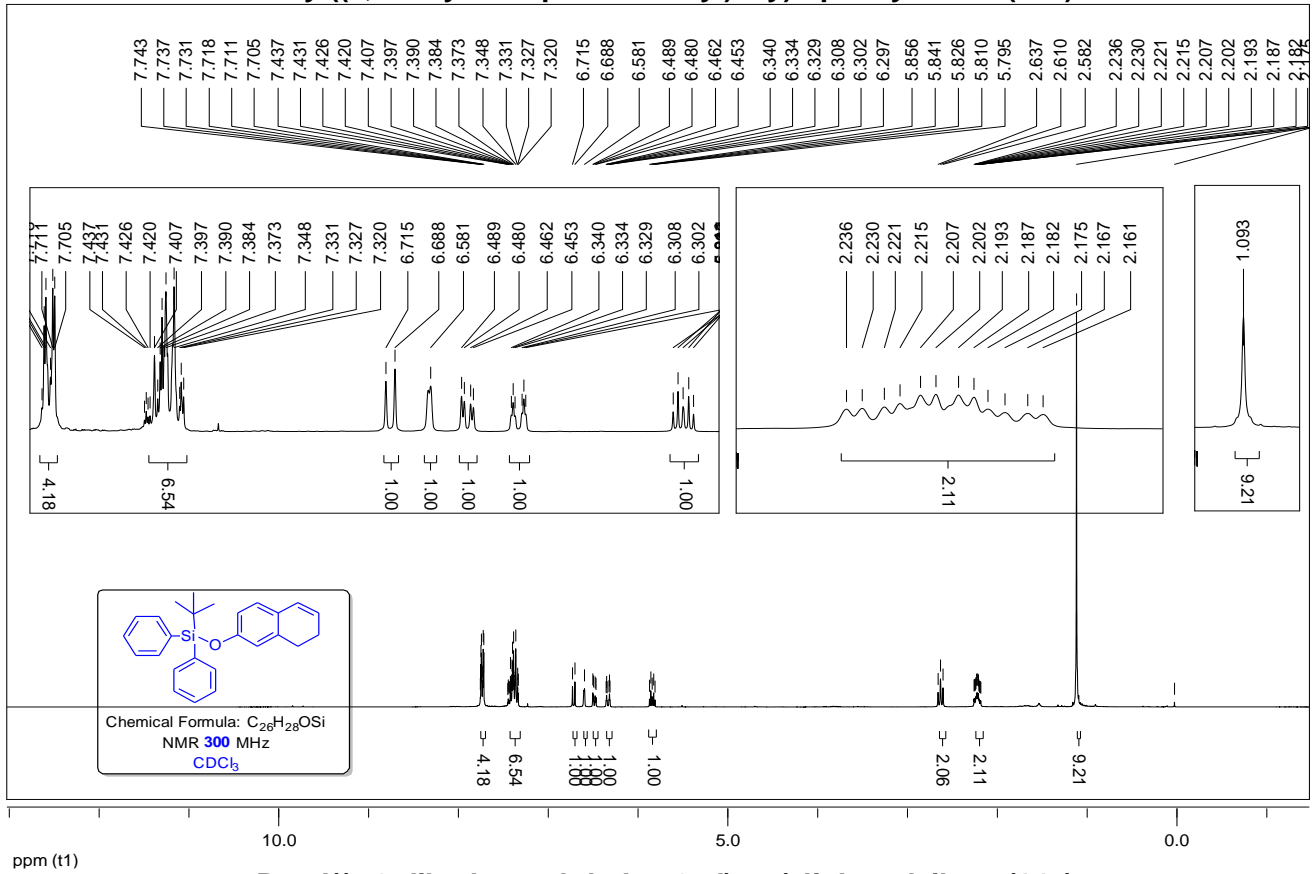
***t*-Butyl((7,8-dihydronaphthalen-1-yl)oxy)diphenylsilane (14b).**



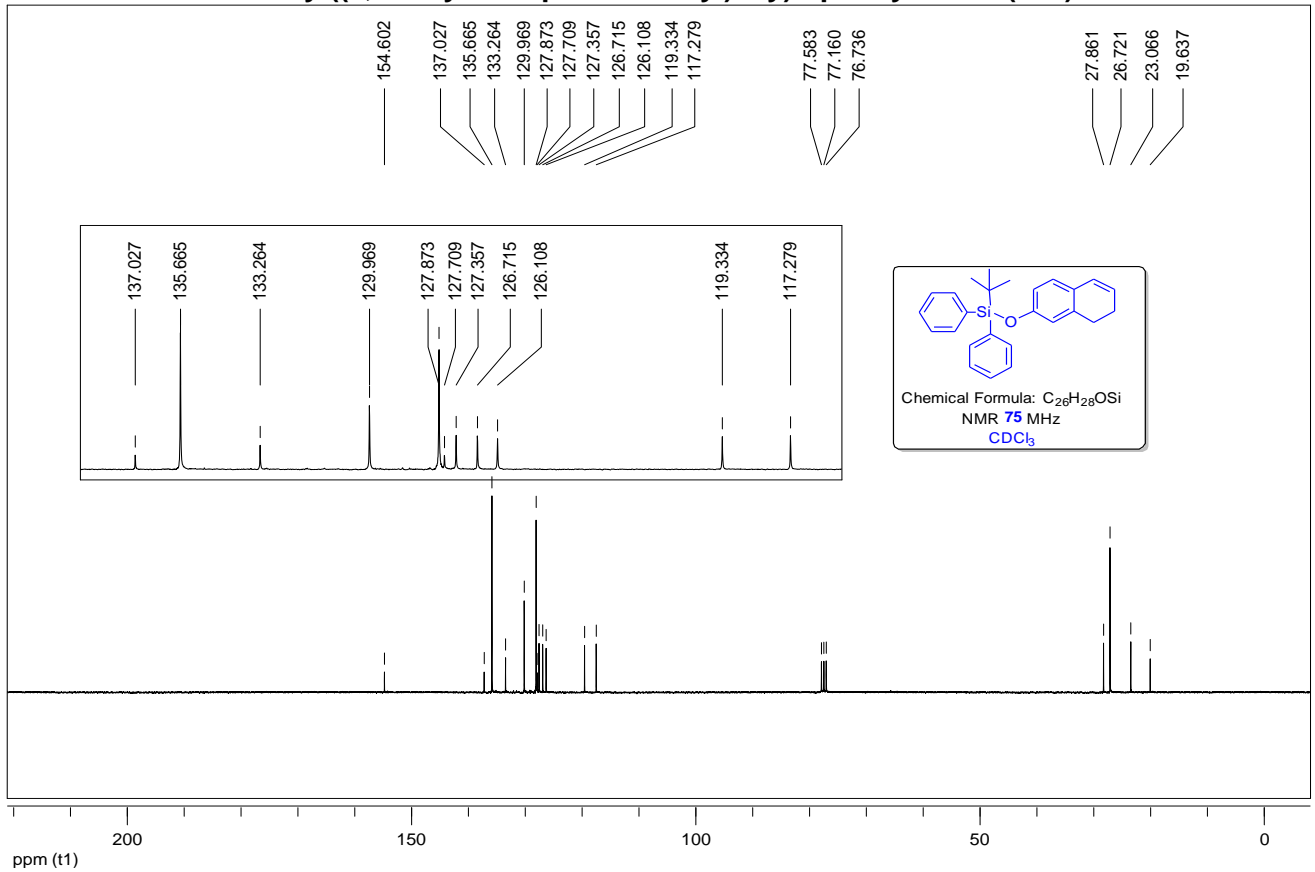
***t*-Butyl((7,8-dihydronaphthalen-1-yl)oxy)diphenylsilane (14b).**



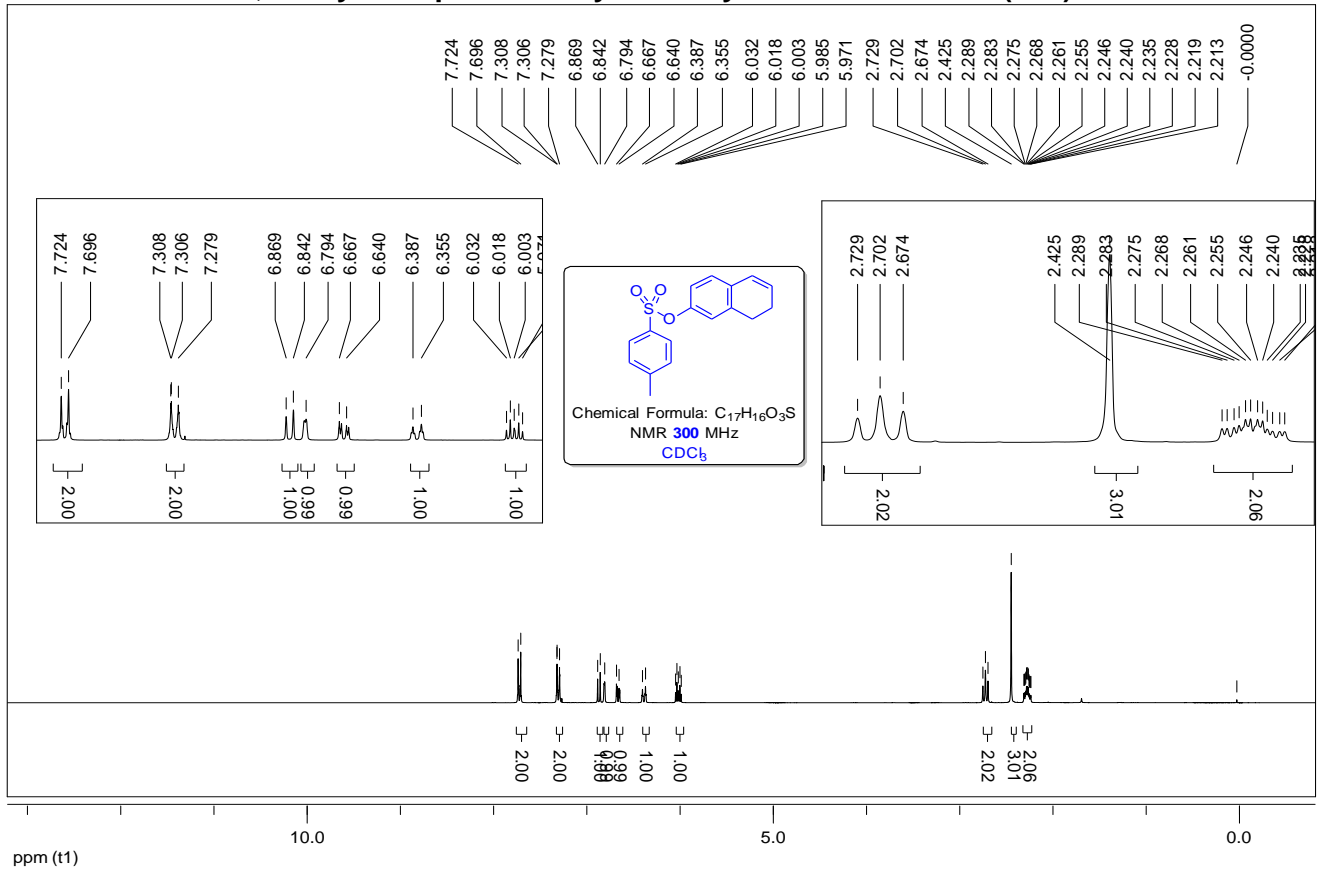
***t*-Butyl((7,8-dihydronaphthalen-2-yl)oxy)diphenylsilane (14c).**



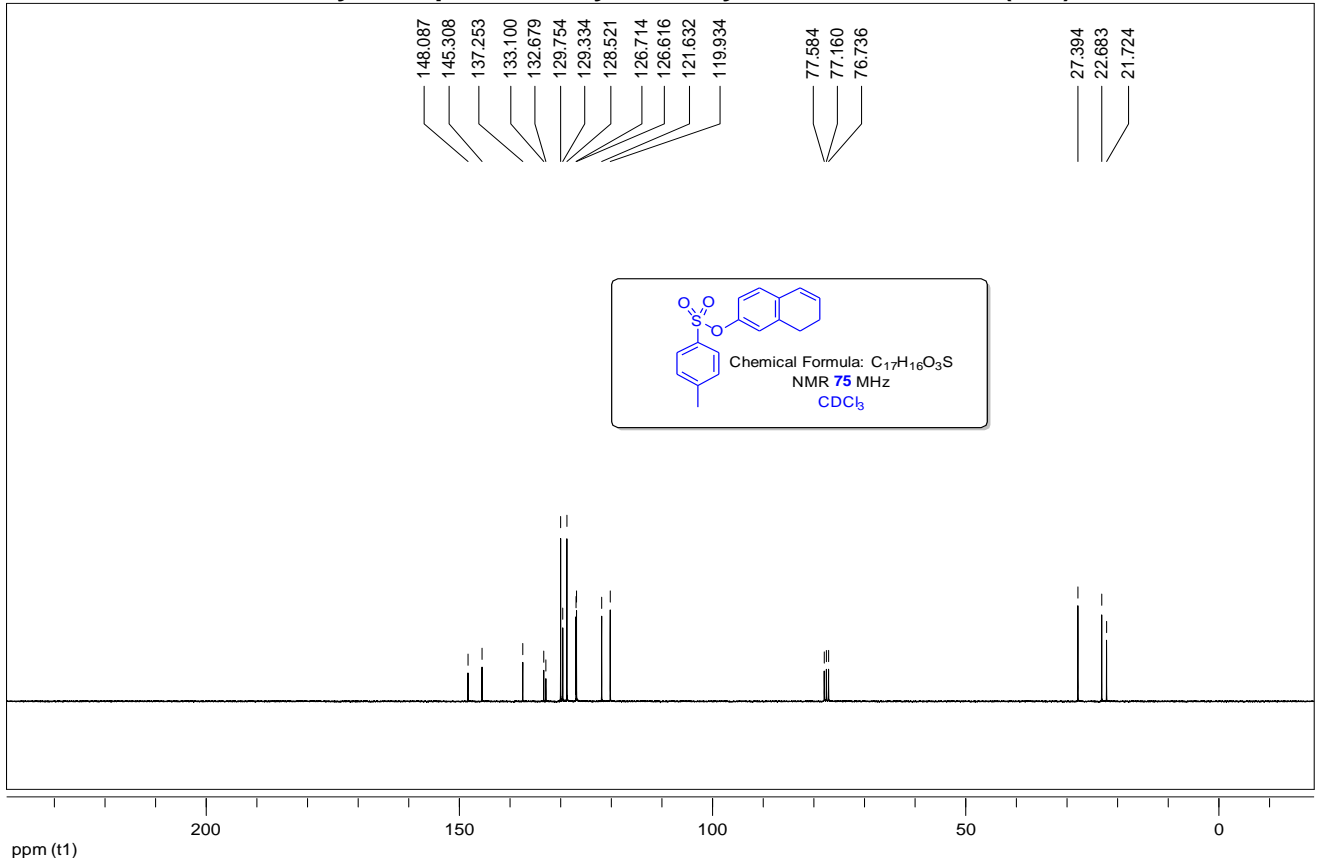
***t*-Butyl((7,8-dihydronaphthalen-2-yl)oxy)diphenylsilane (14c).**



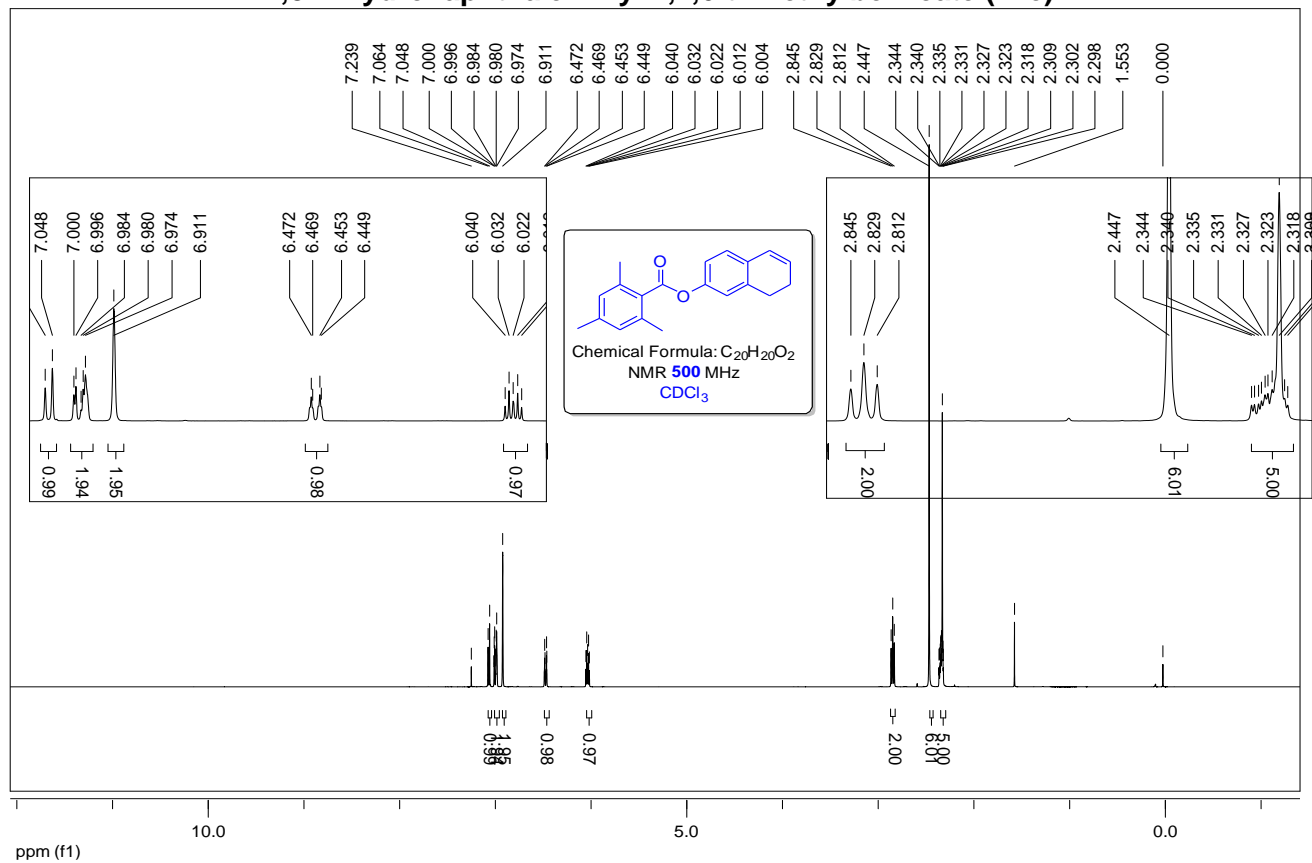
**7,8-Dihydronaphthalen-2-yl 4-methylbenzenesulfonate (14d).**



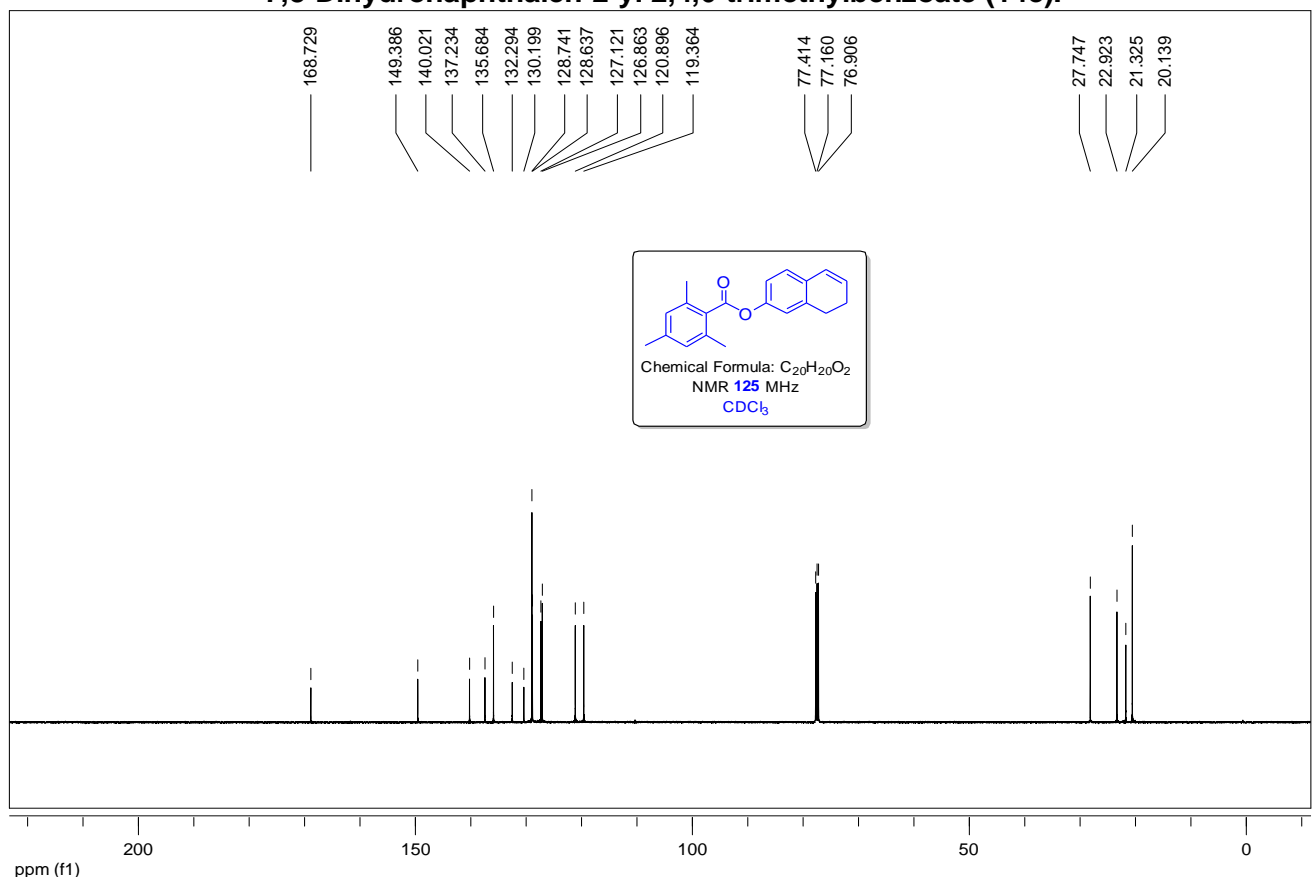
**7,8-Dihydronaphthalen-2-yl 4-methylbenzenesulfonate (14d).**



**7,8-Dihydronaphthalen-2-yl 2,4,6-trimethylbenzoate (14e).**

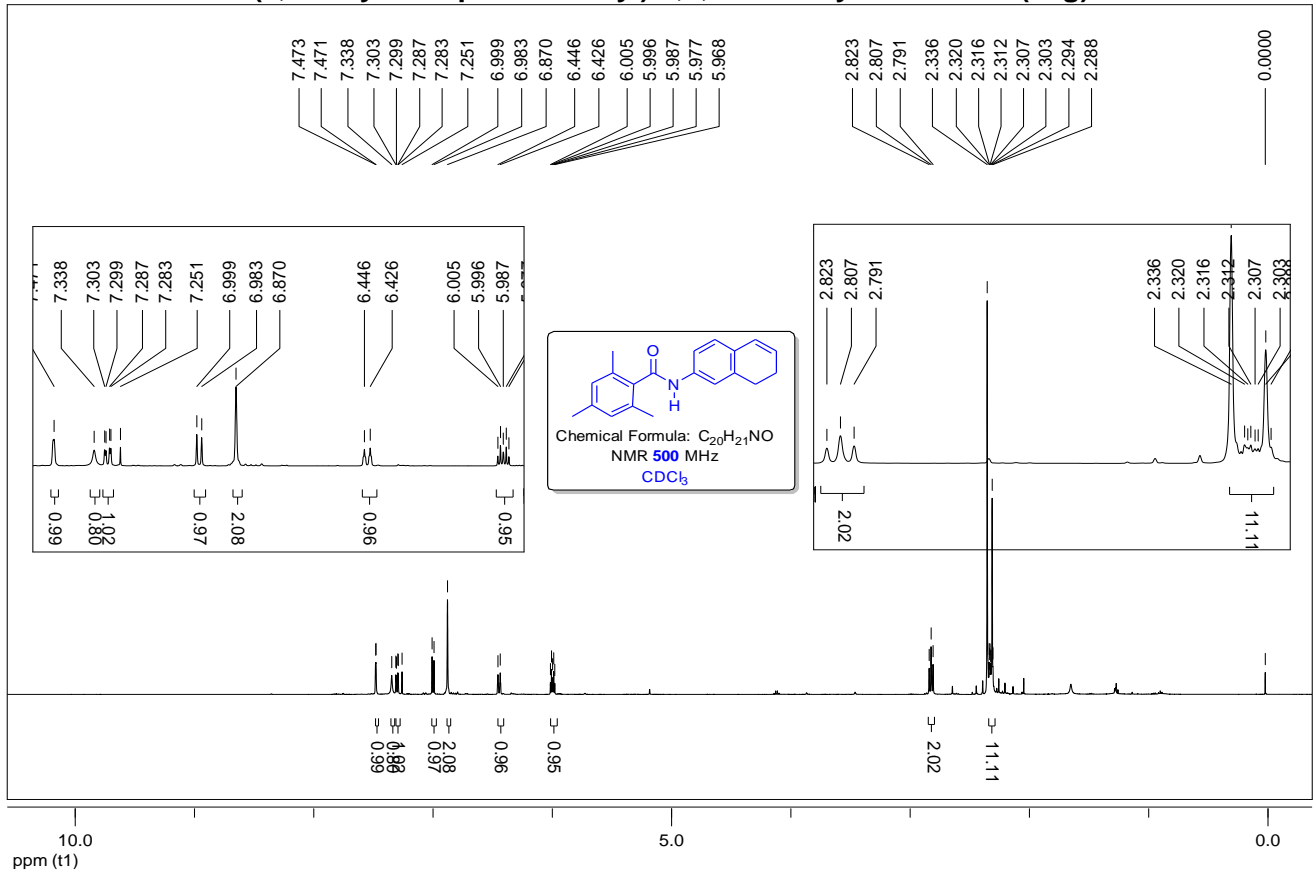


**7,8-Dihydronaphthalen-2-yl 2,4,6-trimethylbenzoate (14e).**

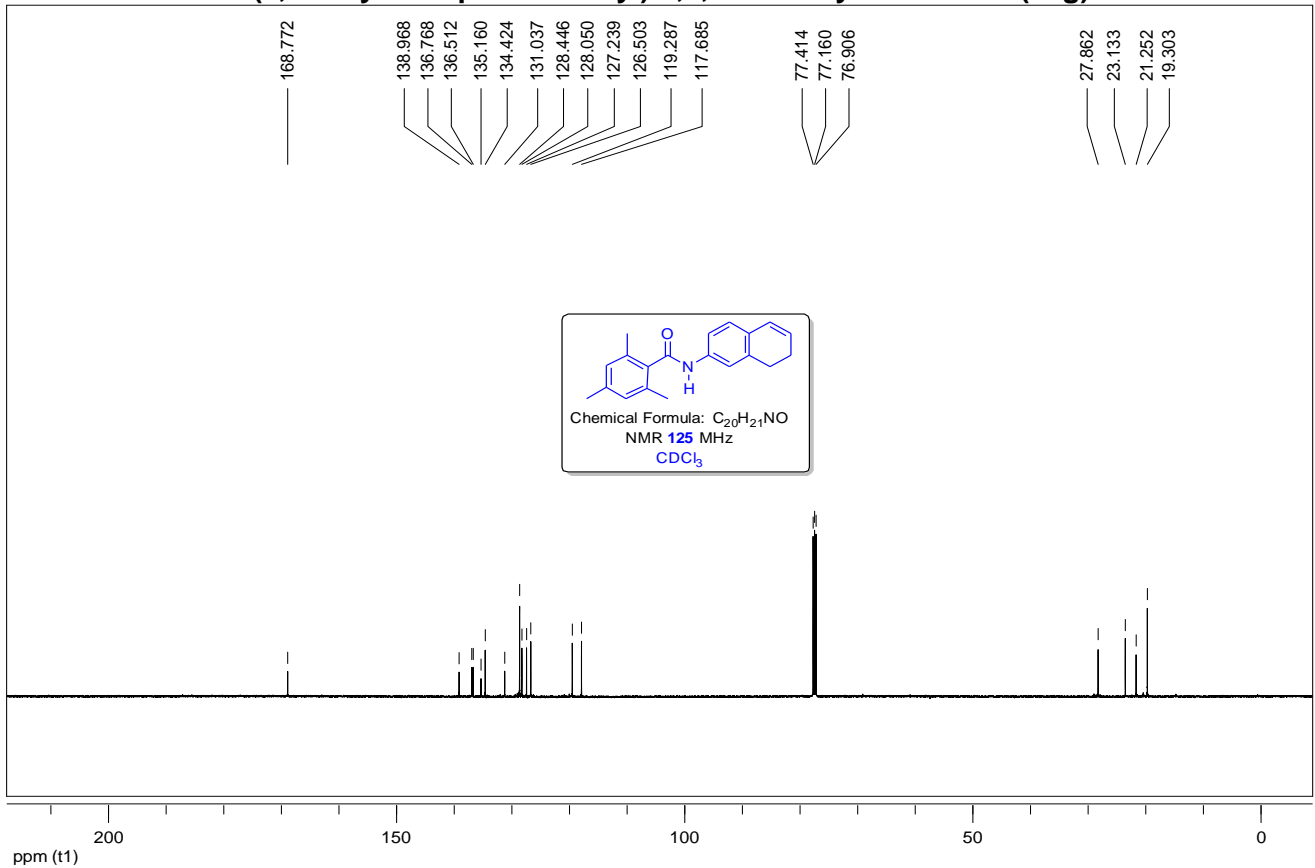




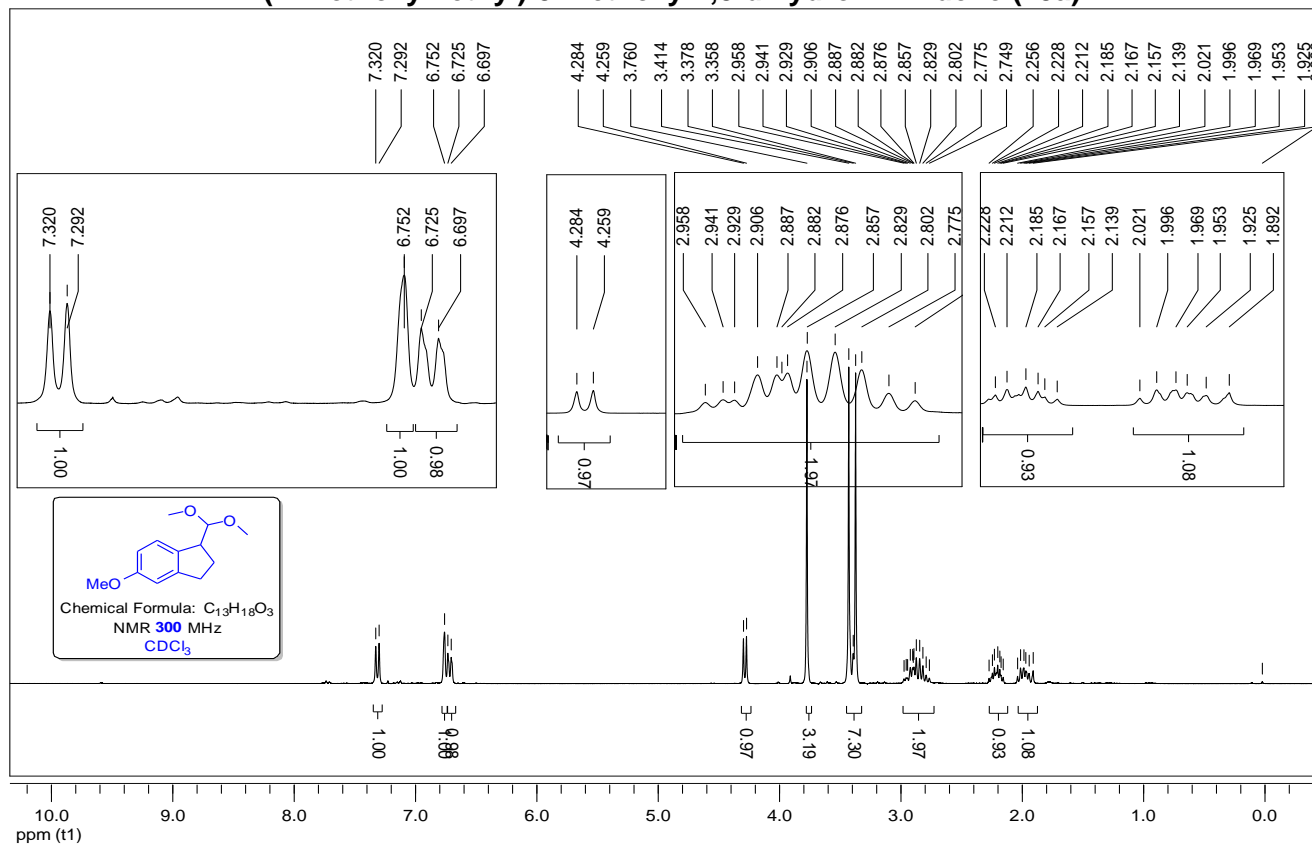
***N*-(7,8-Dihydronaphthalen-2-yl)-2,4,6-trimethylbenzamide (14g).**



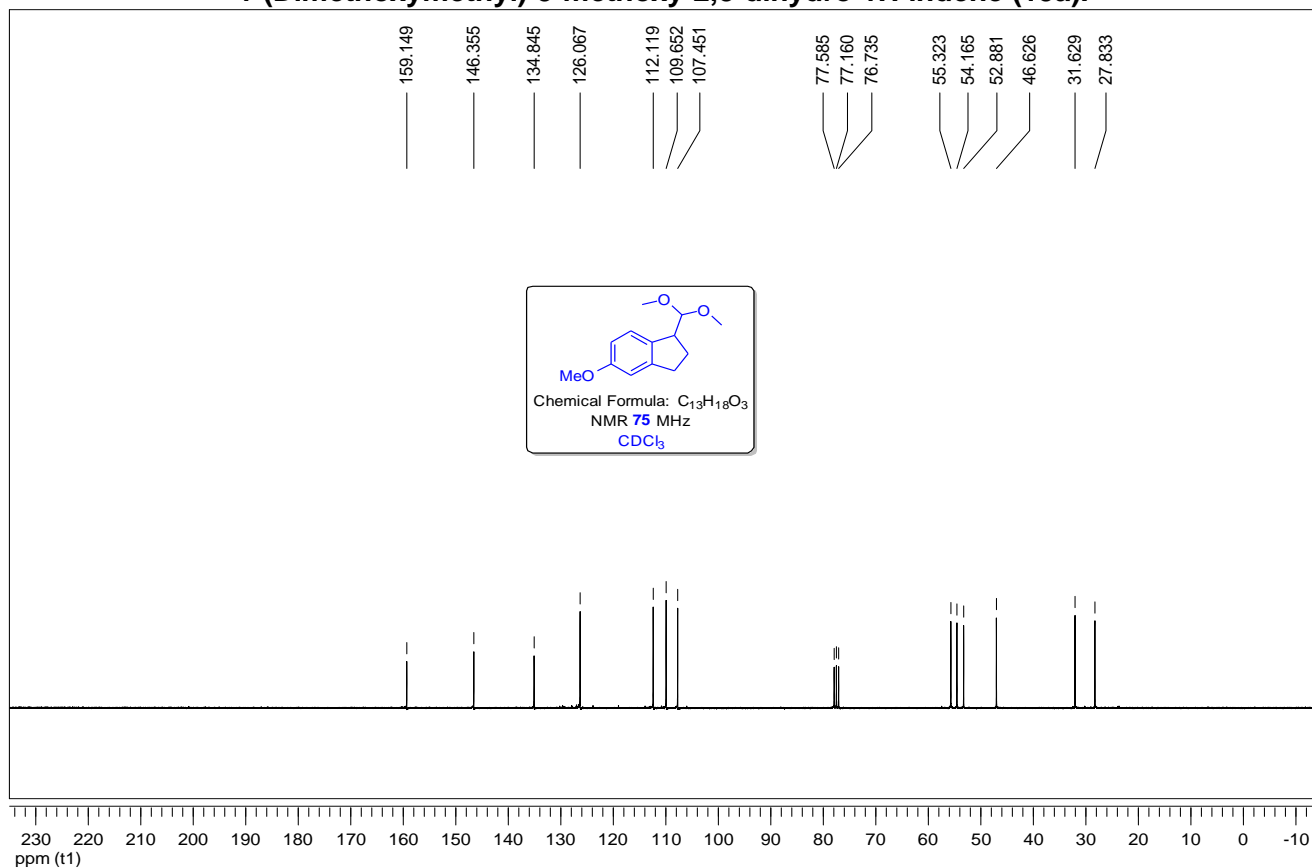
***N*-(7,8-Dihydronaphthalen-2-yl)-2,4,6-trimethylbenzamide (14g).**



**1-(Dimethoxymethyl)-5-methoxy-2,3-dihydro-1H-indene (15a).**

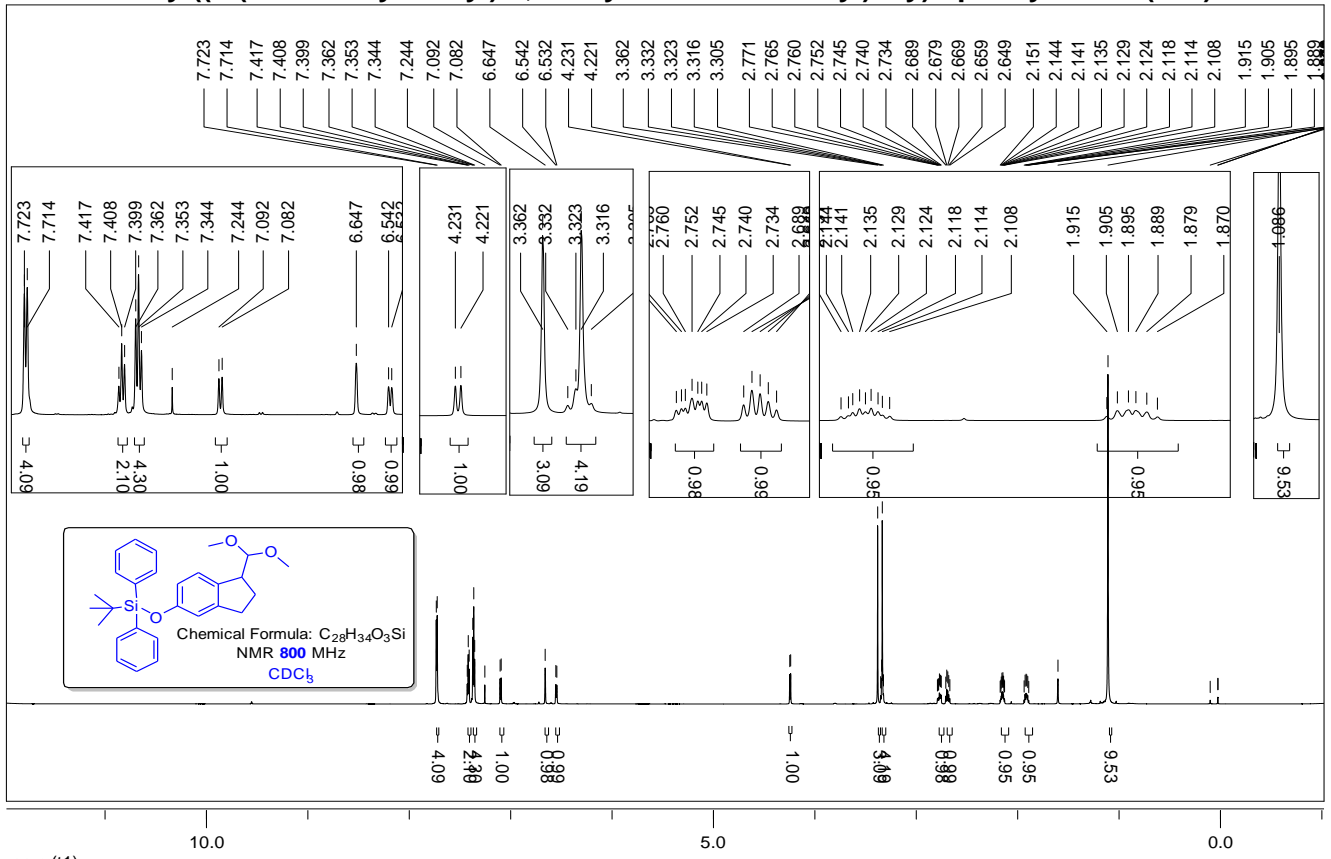


**1-(Dimethoxymethyl)-5-methoxy-2,3-dihydro-1H-indene (15a).**

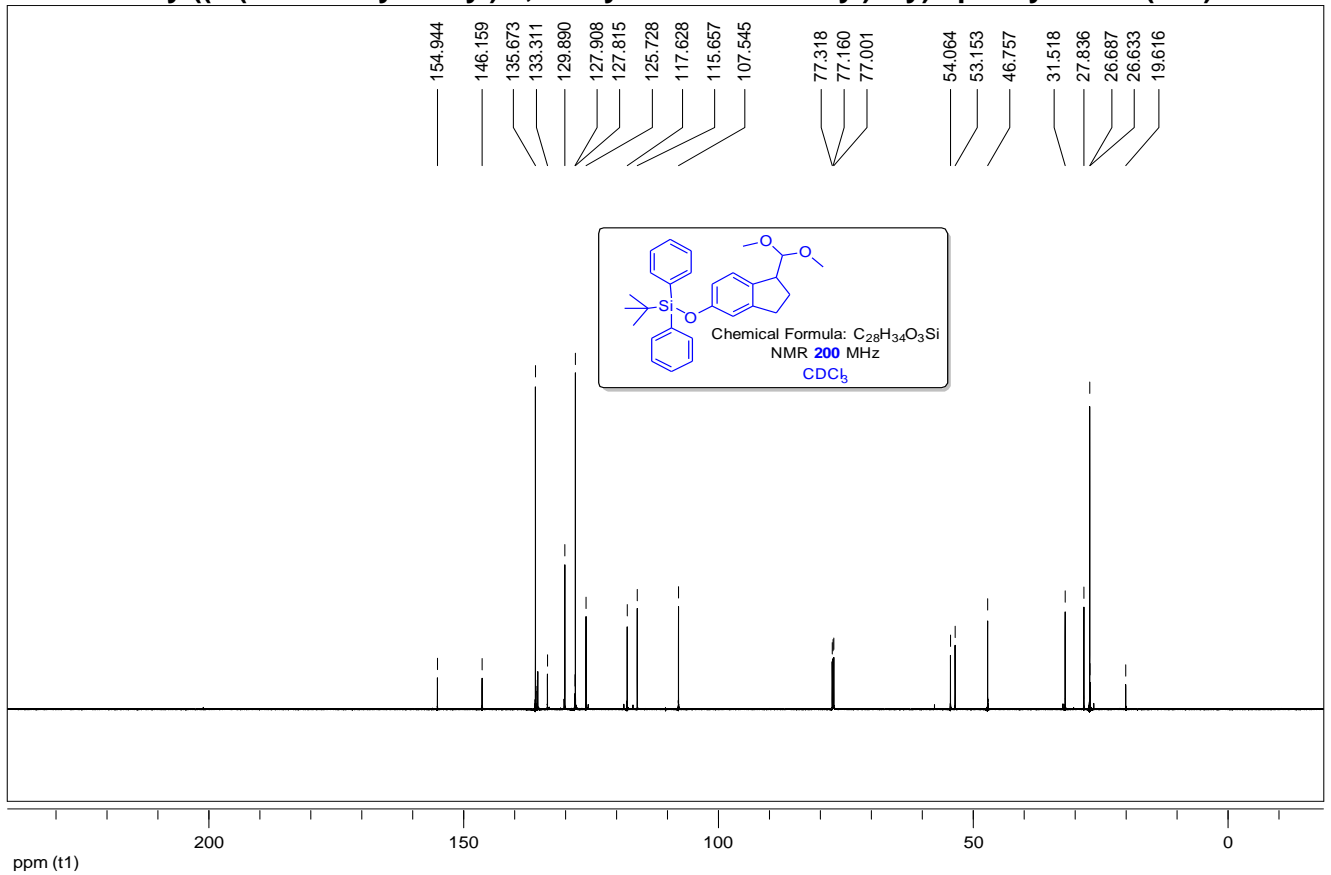




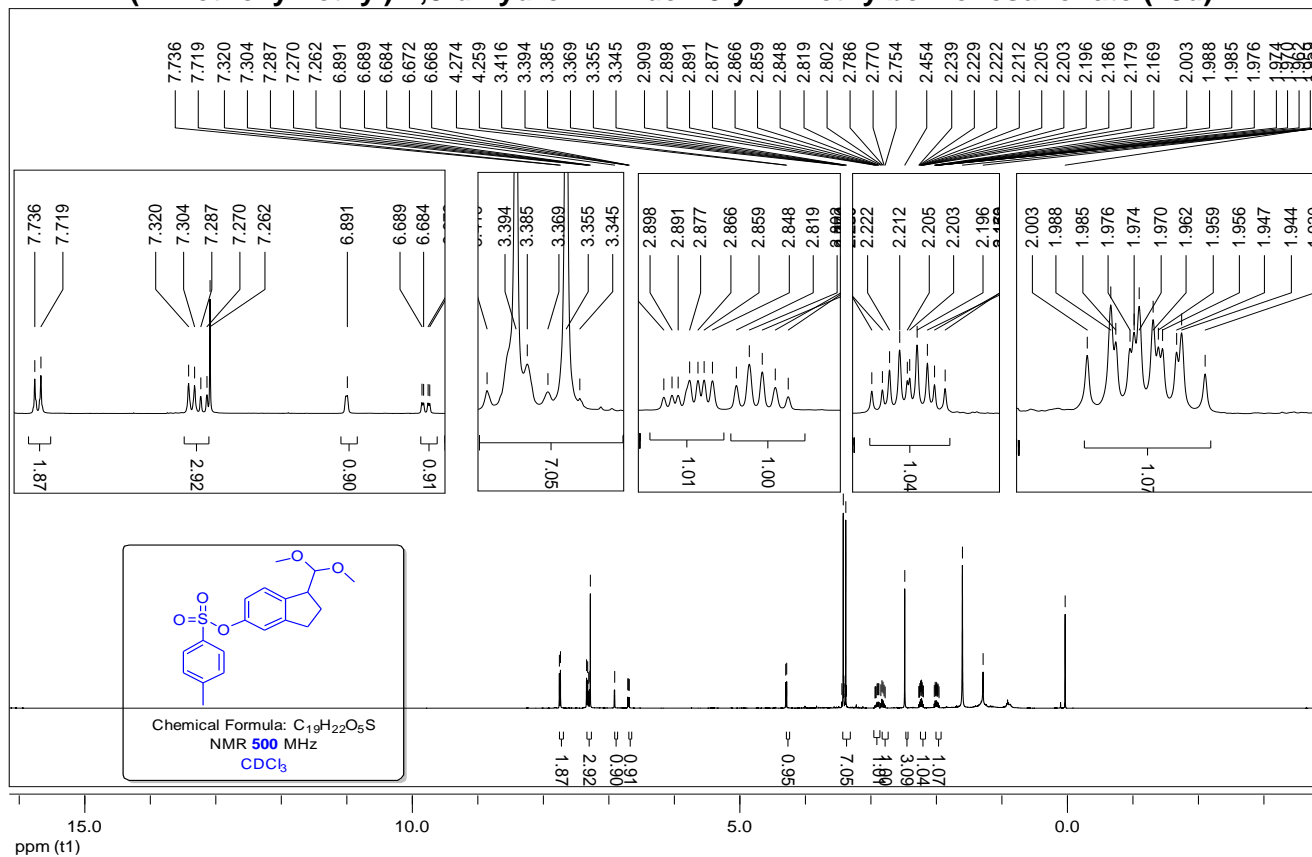
***t*-Butyl((1-(dimethoxymethyl)-2,3-dihydro-1*H*-inden-5-yl)oxy)diphenylsilane (15c).**



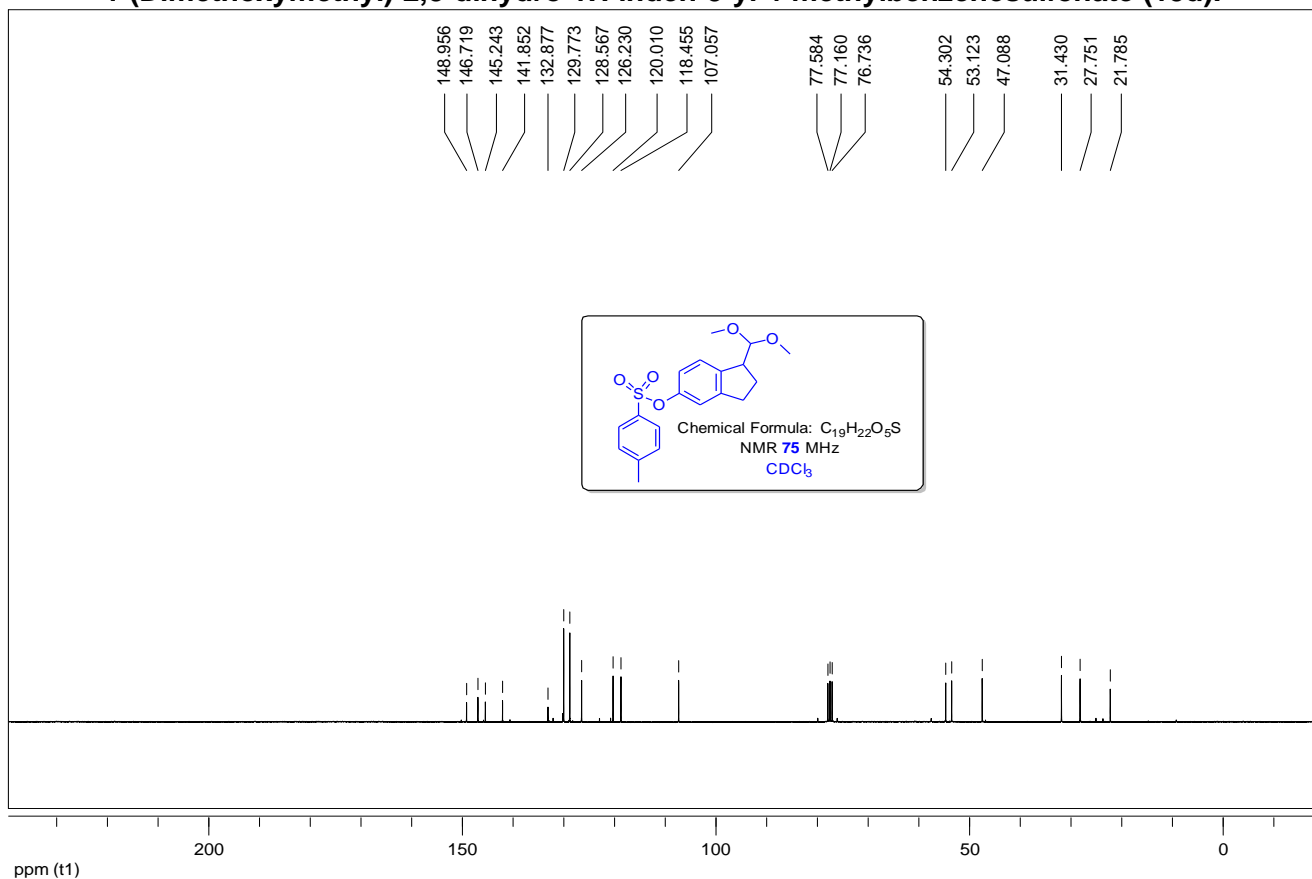
***t*-Butyl((1-(dimethoxymethyl)-2,3-dihydro-1*H*-inden-5-yl)oxy)diphenylsilane (15c).**



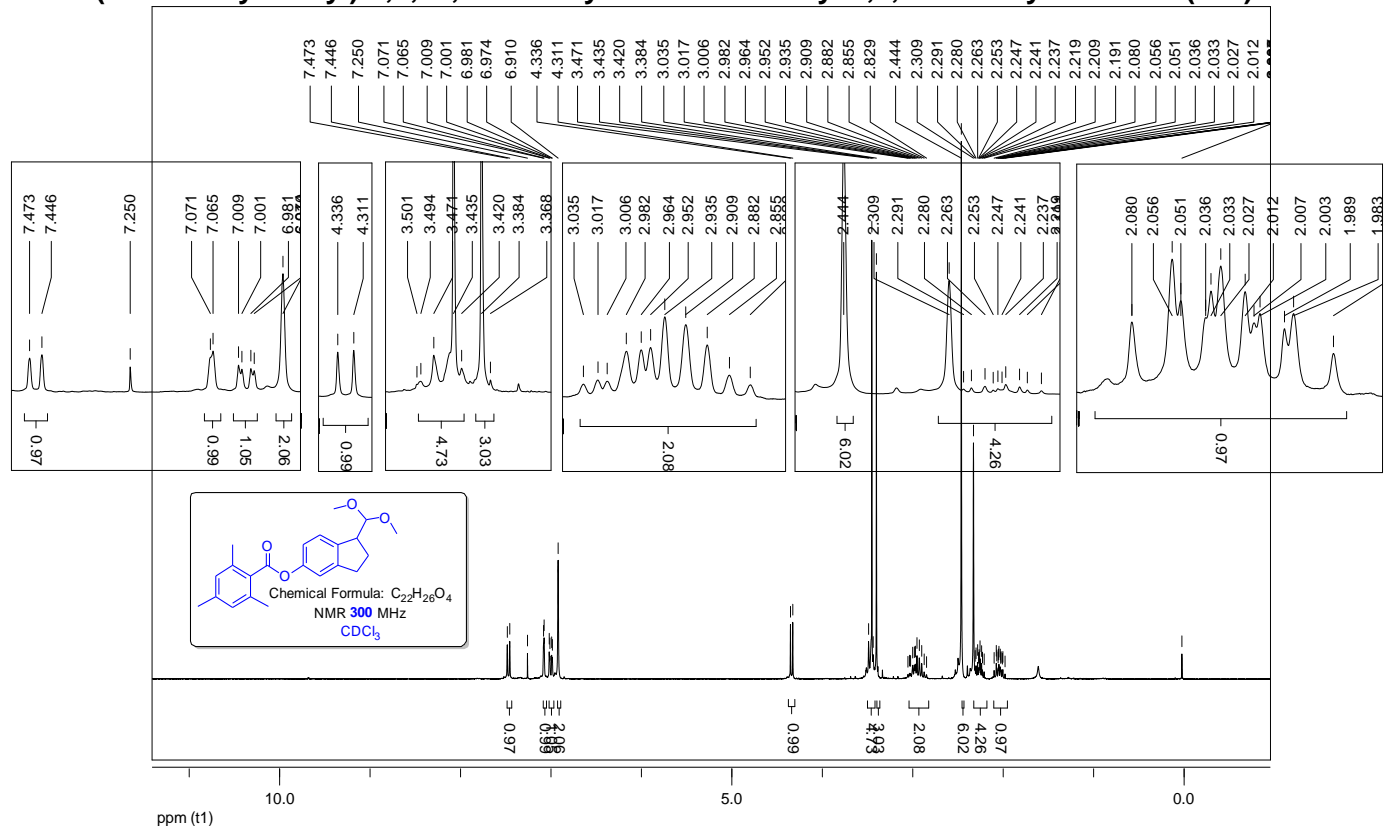
**1-(Dimethoxymethyl)-2,3-dihydro-1H-inden-5-yl 4-methylbenzenesulfonate (15d).**



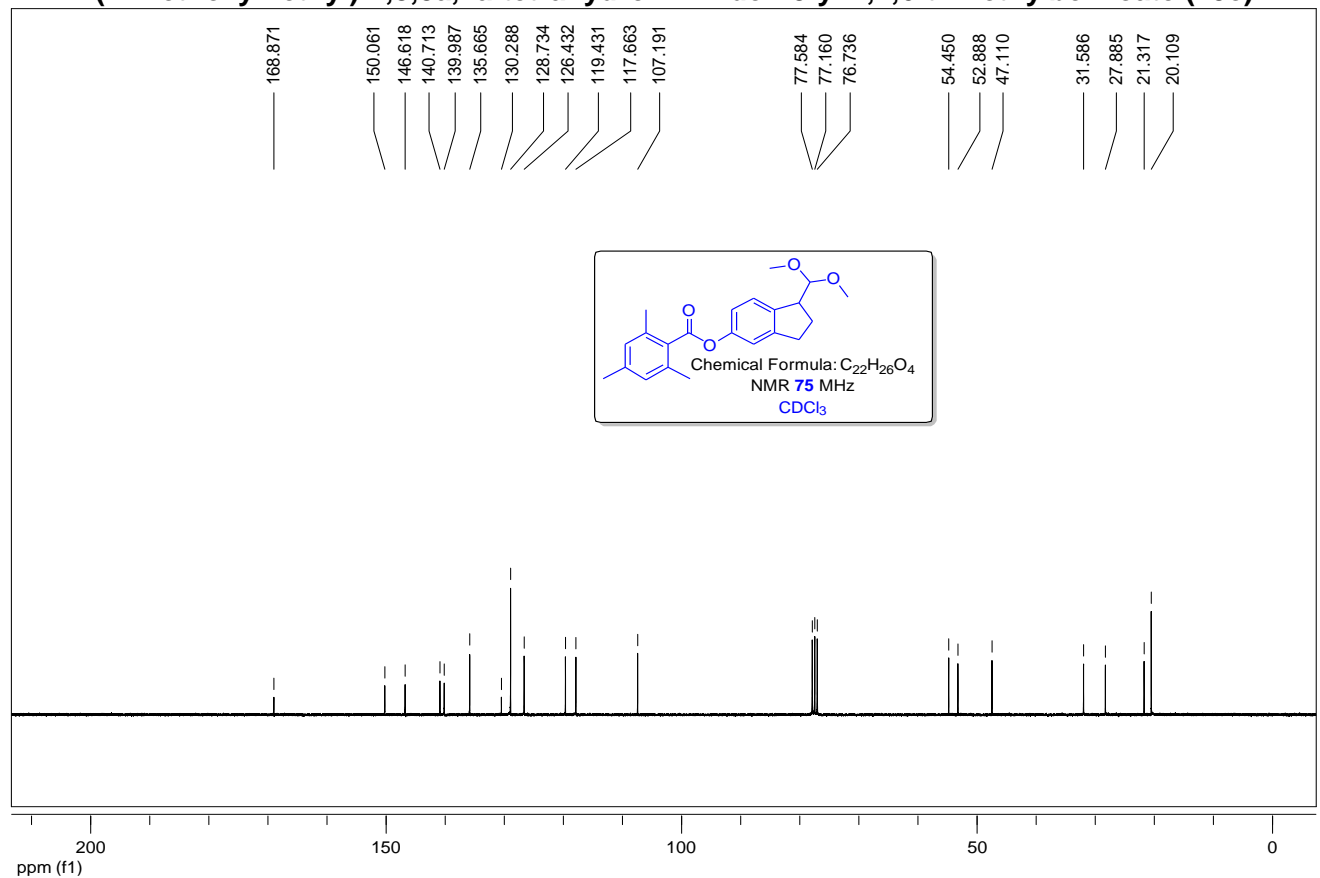
**1-(Dimethoxymethyl)-2,3-dihydro-1H-inden-5-yl 4-methylbenzenesulfonate (15d).**



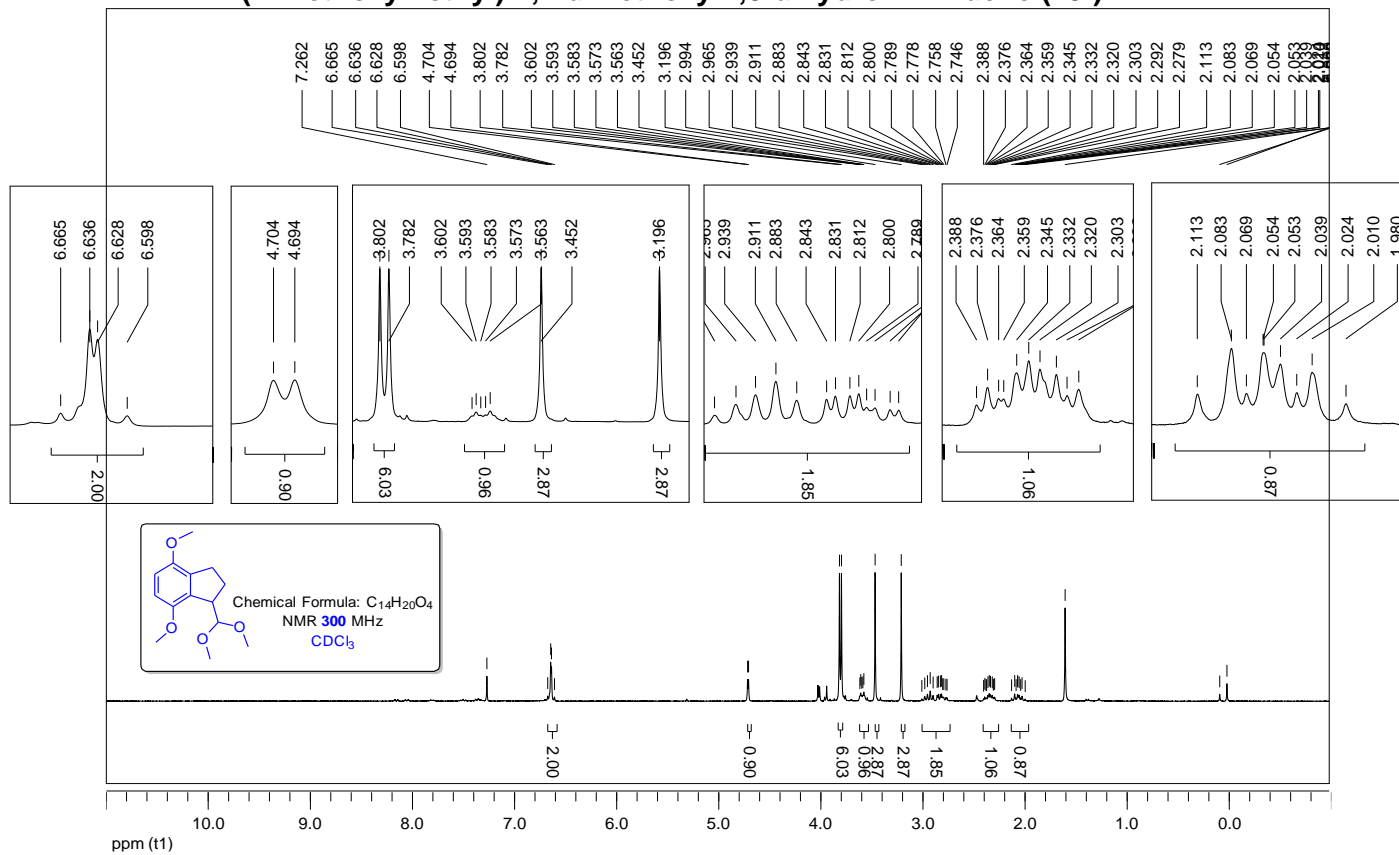
**1-(Dimethoxymethyl)-2,3,3a,7a-tetrahydro-1H-inden-5-yl 2,4,6-trimethylbenzoate (15e).**



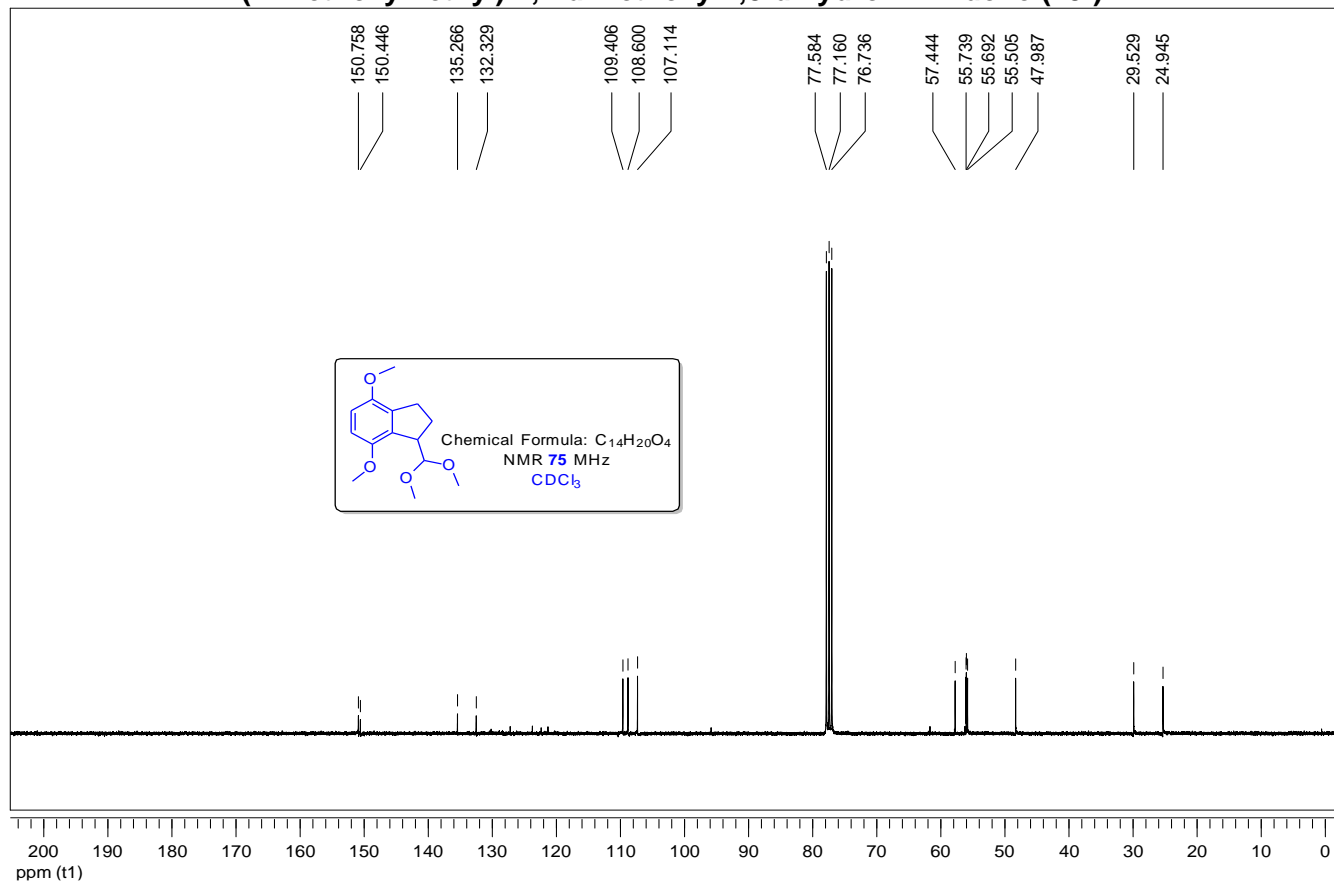
**1-(Dimethoxymethyl)-2,3,3a,7a-tetrahydro-1H-inden-5-yl 2,4,6-trimethylbenzoate (15e).**



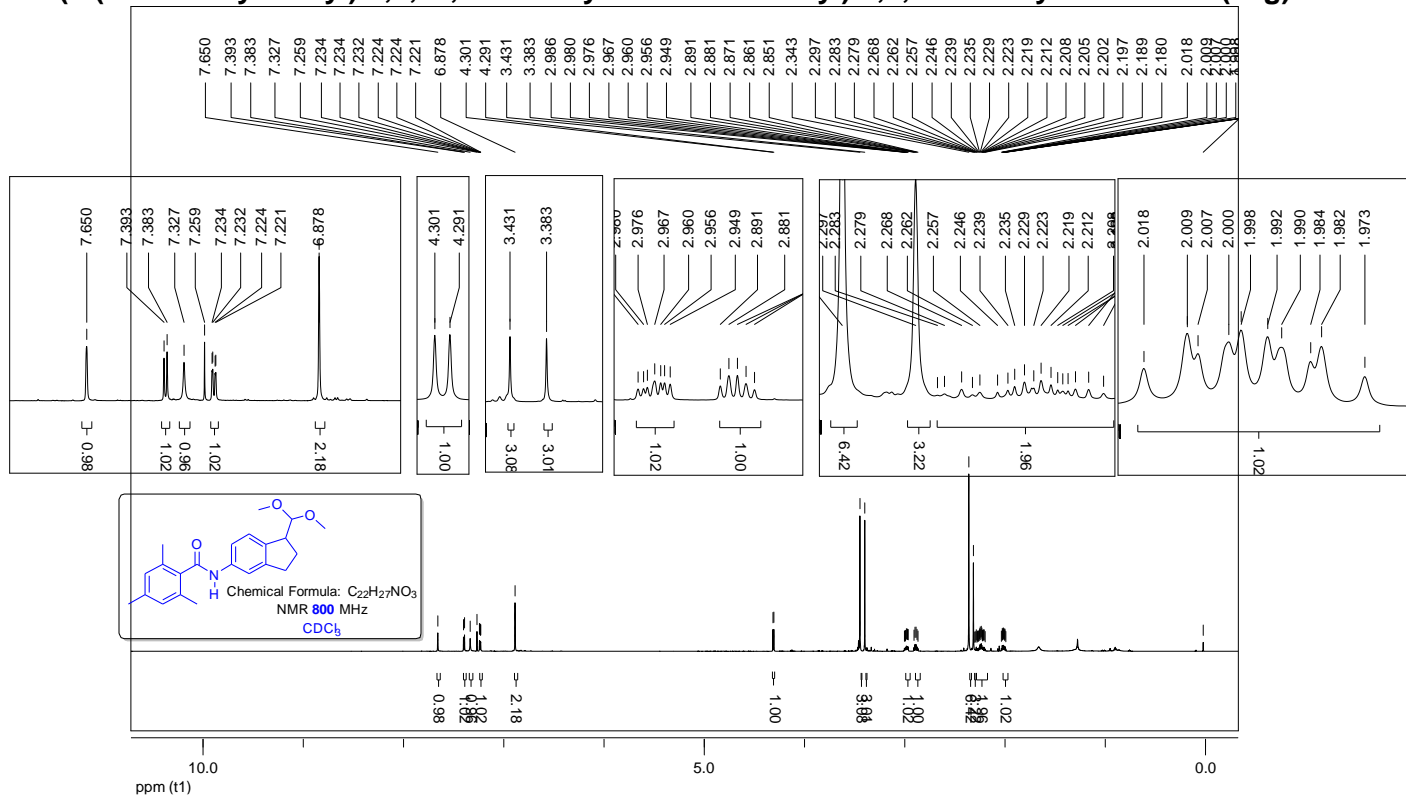
**1-(Dimethoxymethyl)-4,7-dimethoxy-2,3-dihydro-1*H*-indene (15f).**



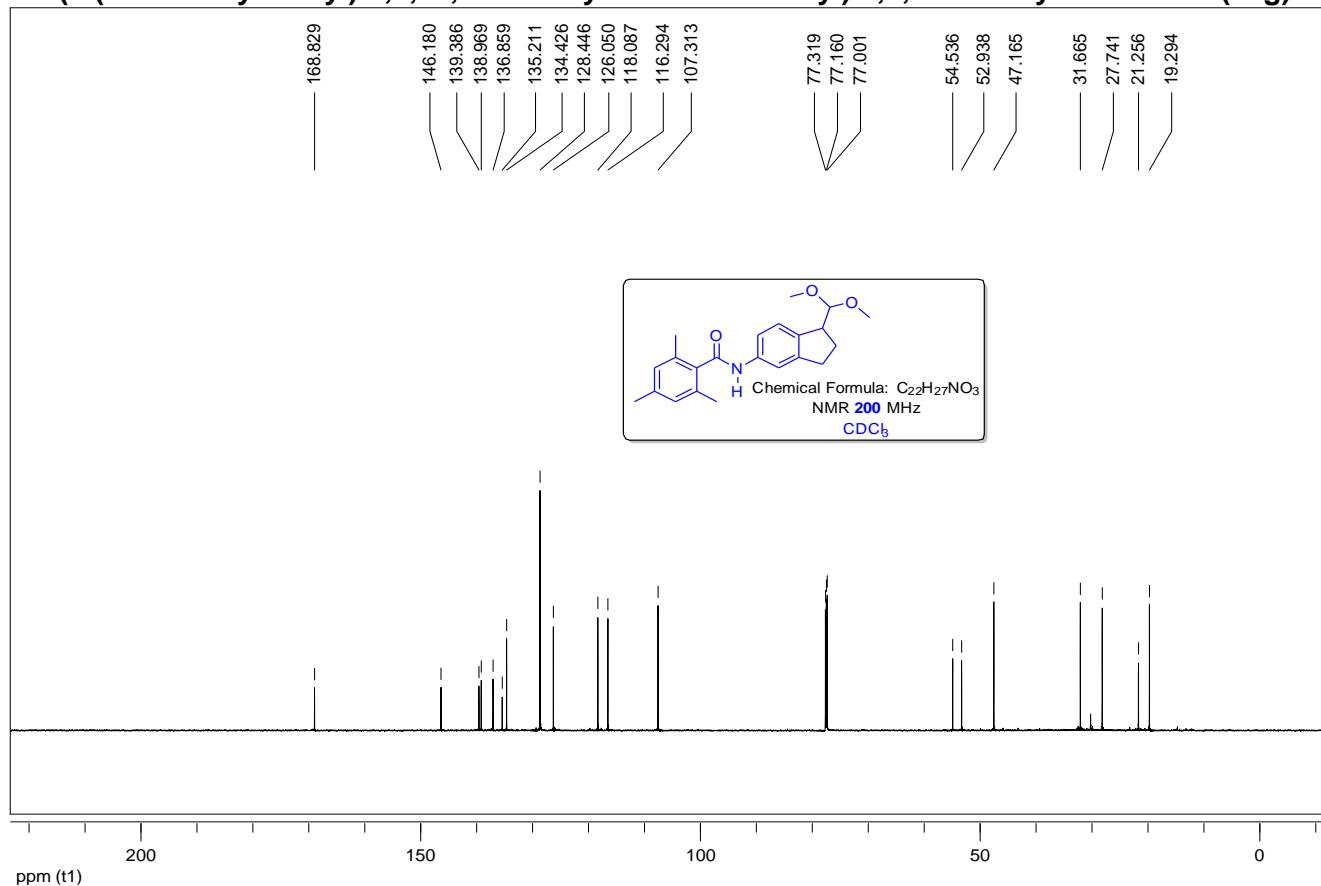
**1-(Dimethoxymethyl)-4,7-dimethoxy-2,3-dihydro-1*H*-indene (15f).**



***N*-(1-(Dimethoxymethyl)-2,3,3a,7a-tetrahydro-1*H*-inden-5-yl)-2,4,6-trimethylbenzamide (15g).**

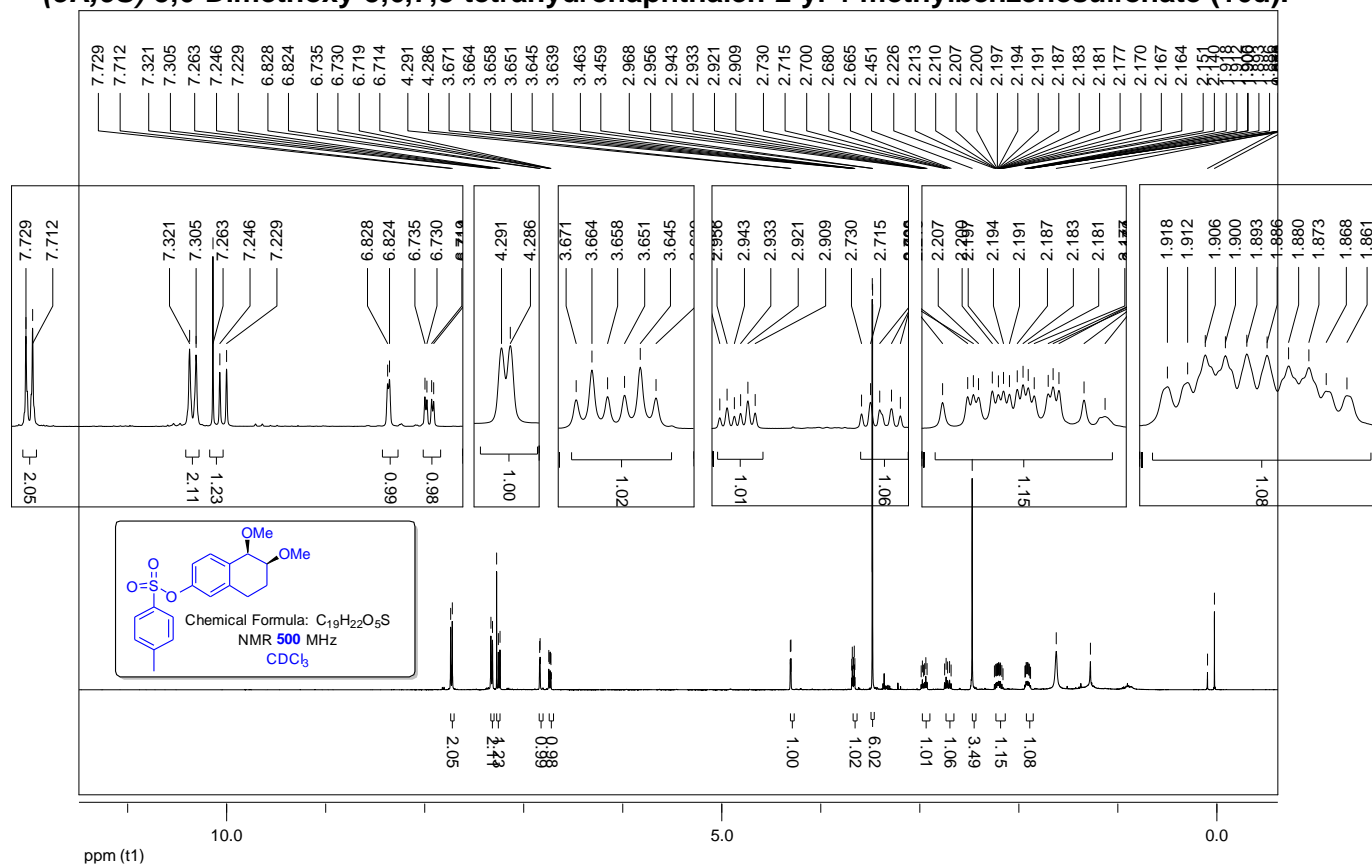


***N*-(1-(Dimethoxymethyl)-2,3,3a,7a-tetrahydro-1*H*-inden-5-yl)-2,4,6-trimethylbenzamide (15g).**

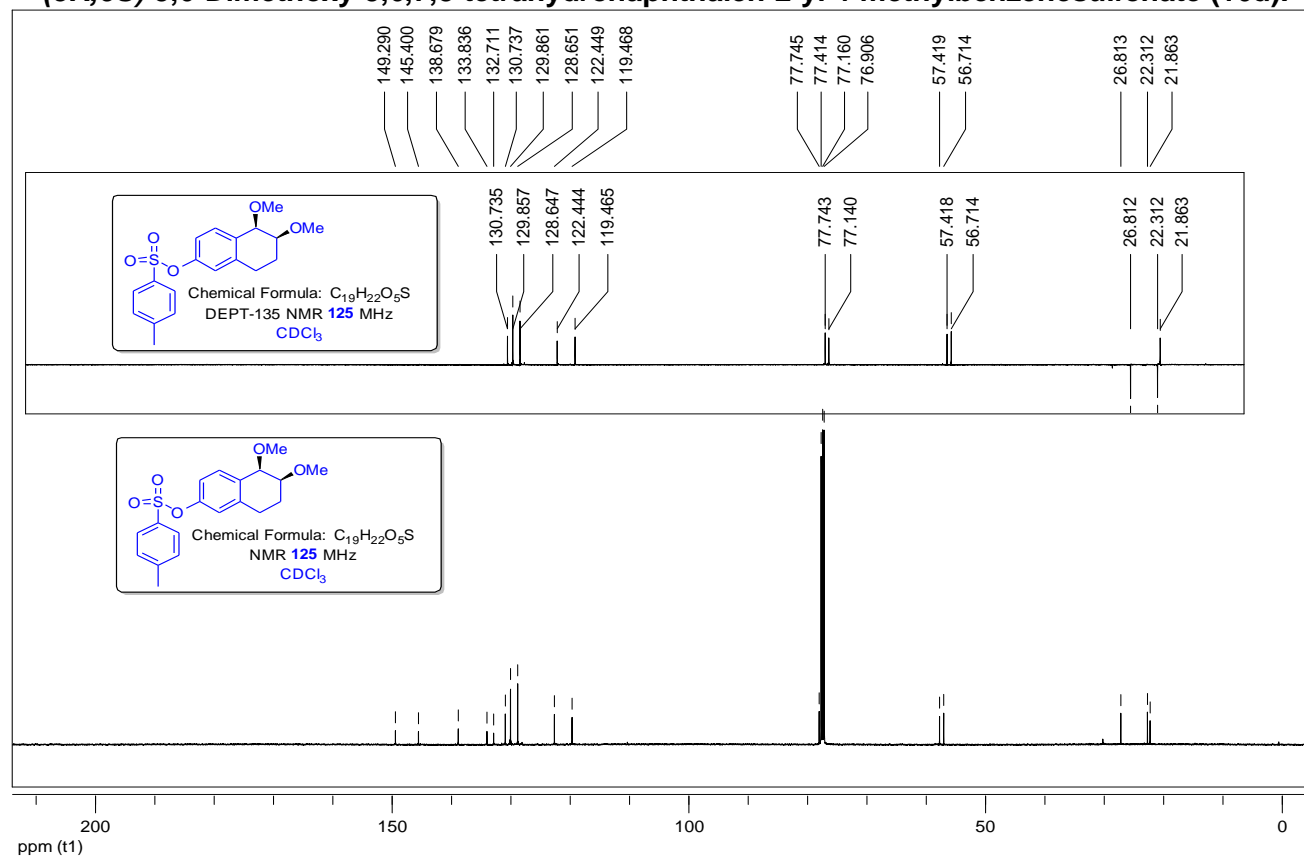




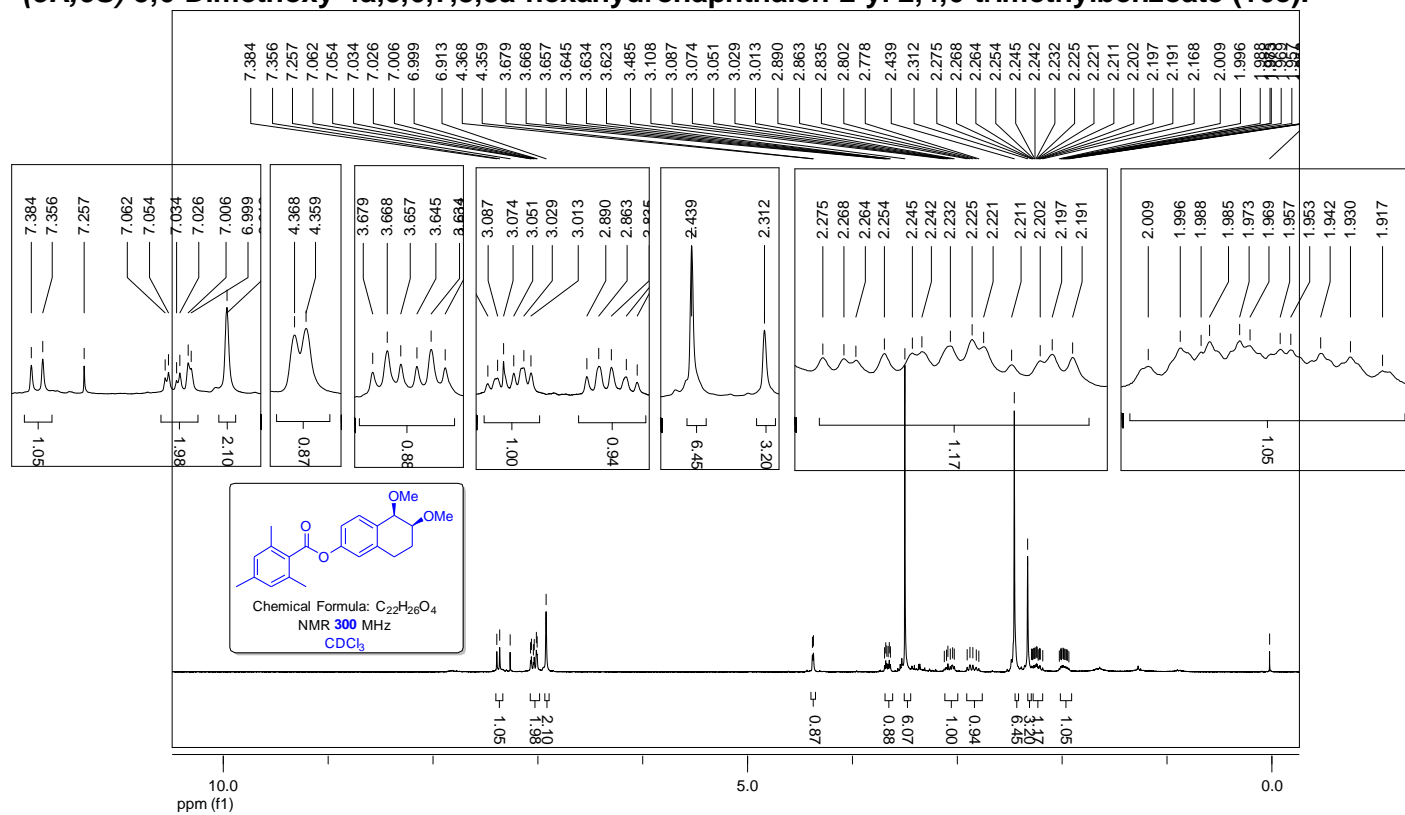
**(5R,6S)-5,6-Dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (16d).**



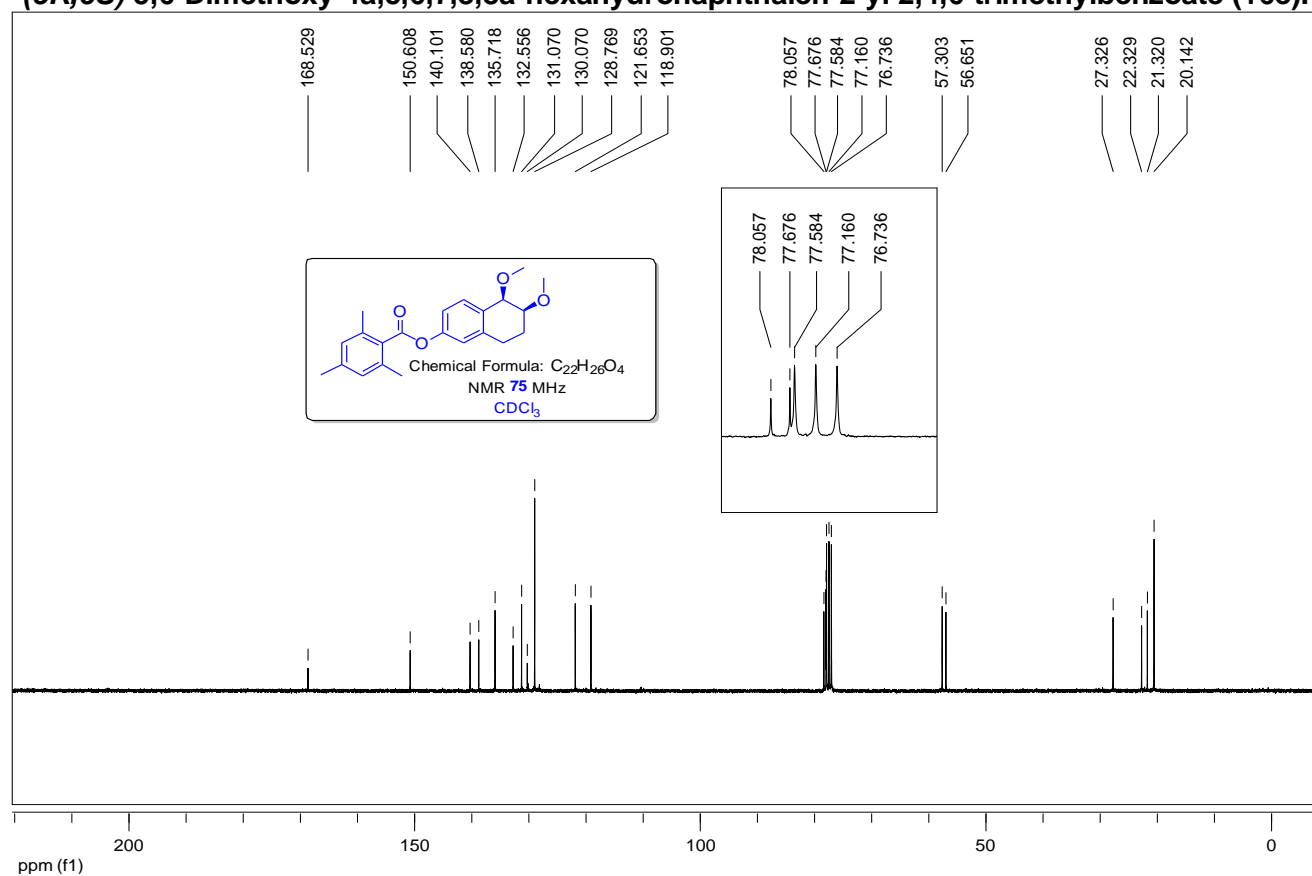
**(5R,6S)-5,6-Dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (16d).**



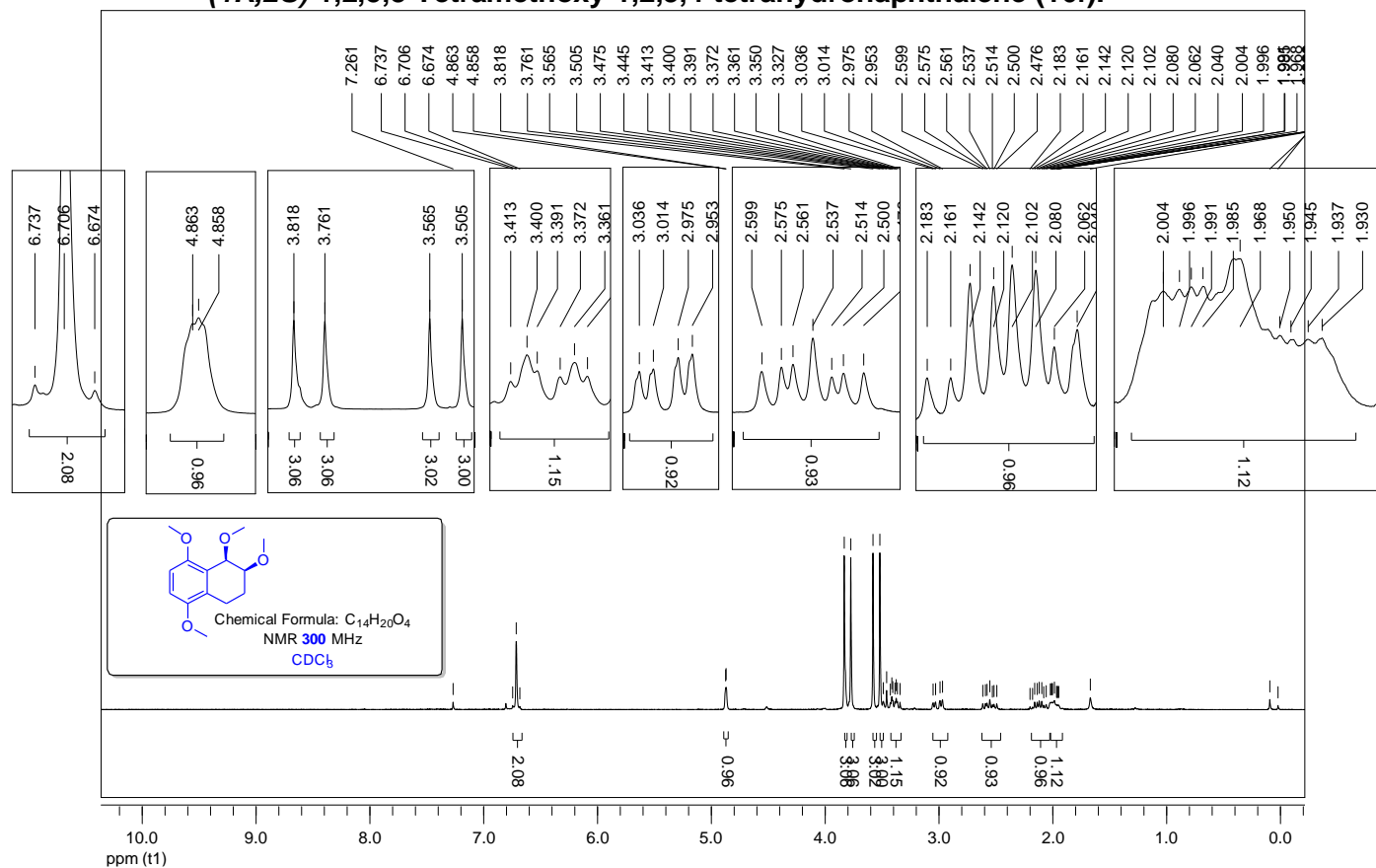
**(5R,6S)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (16e).**



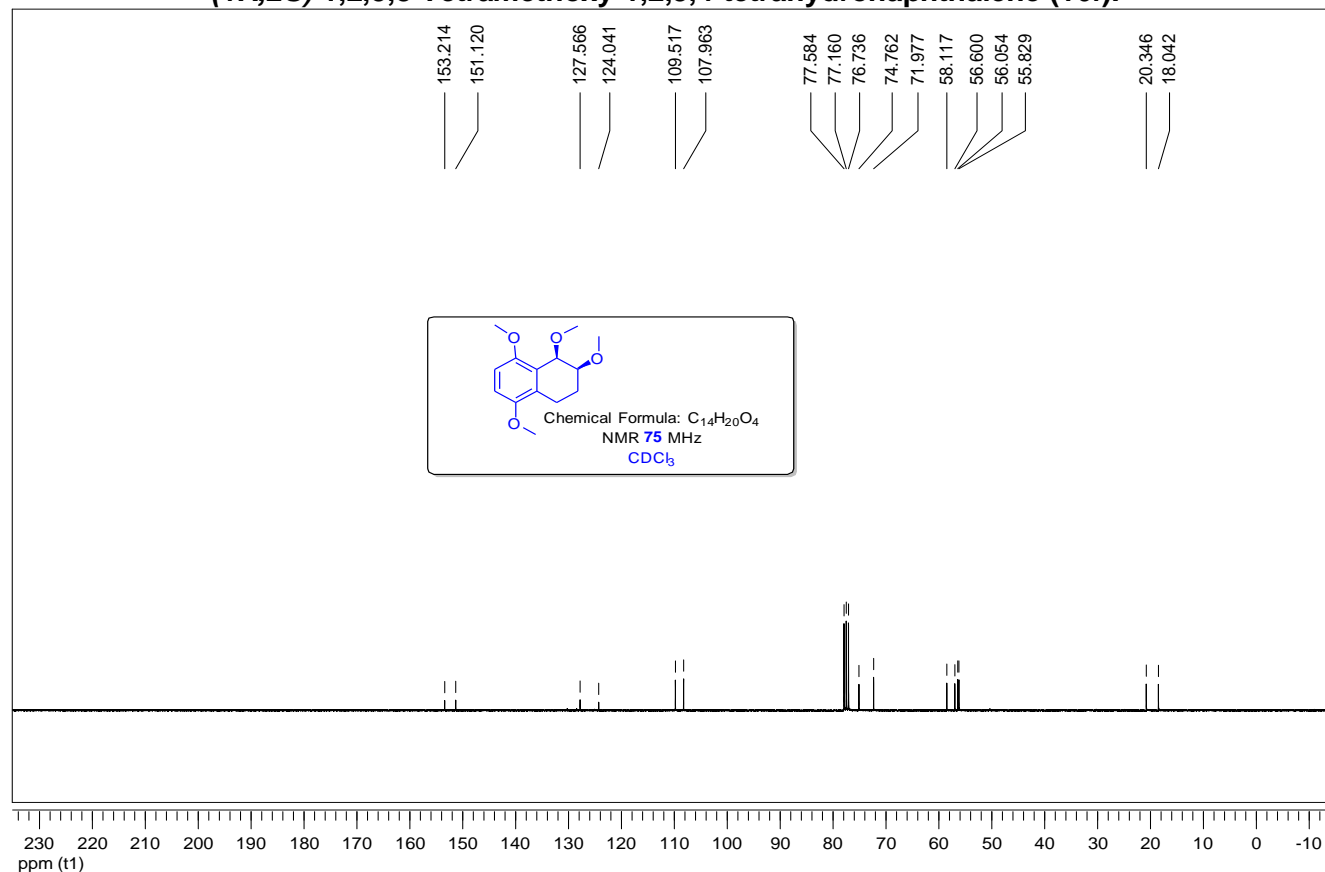
**(5R,6S)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (16e).**



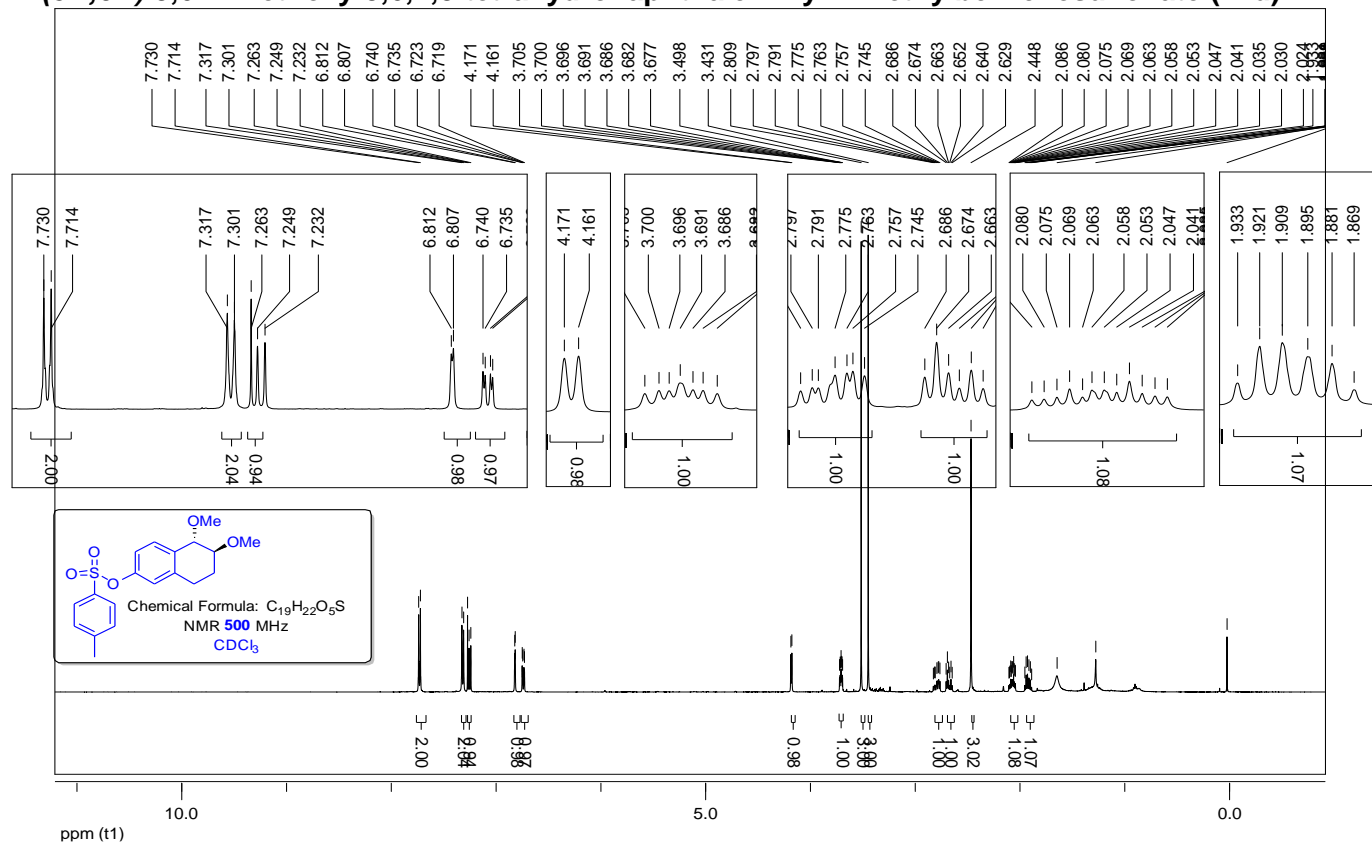
**(1R,2S)-1,2,5,8-Tetramethoxy-1,2,3,4-tetrahydronaphthalene (16f).**



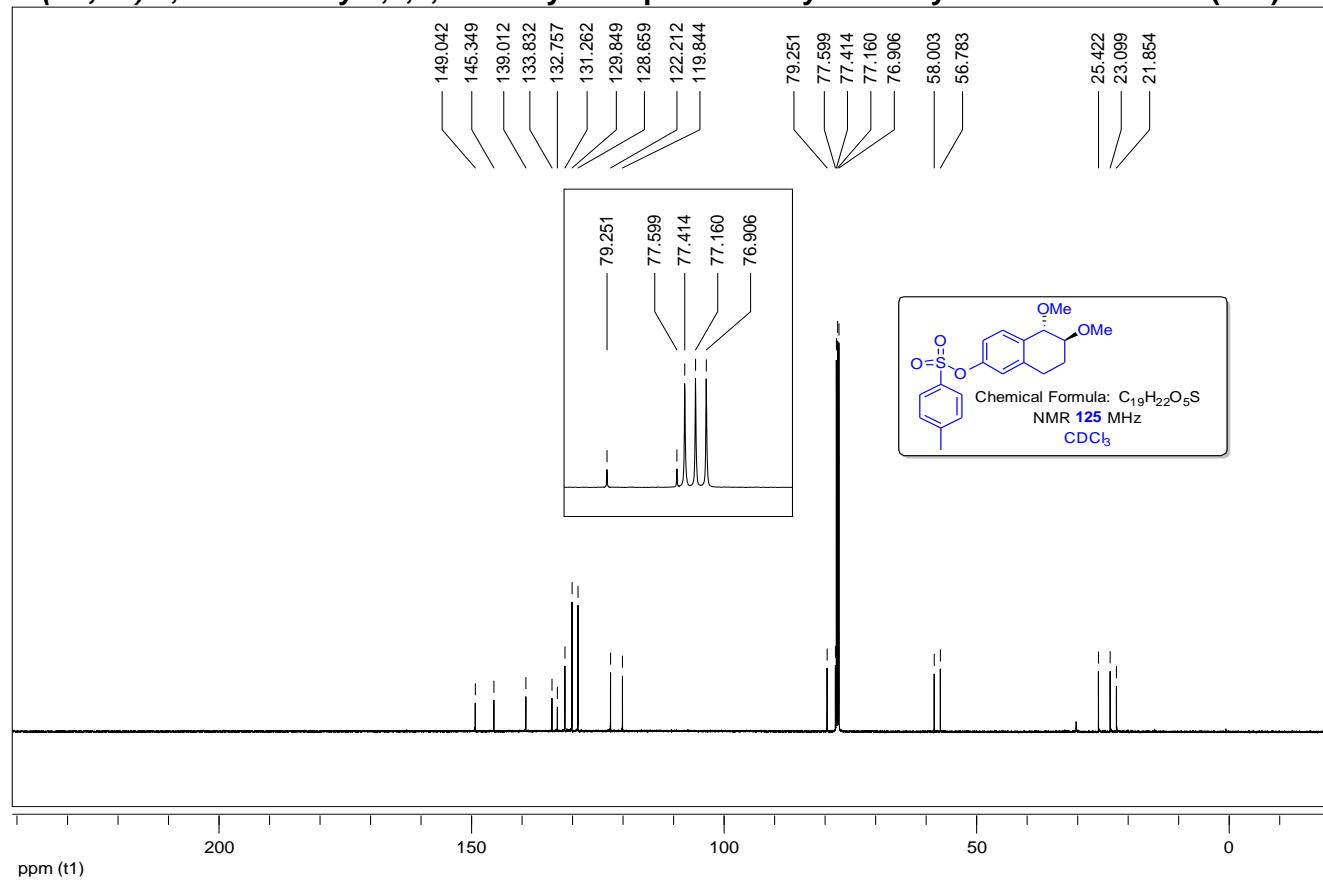
**(1R,2S)-1,2,5,8-Tetramethoxy-1,2,3,4-tetrahydronaphthalene (16f).**



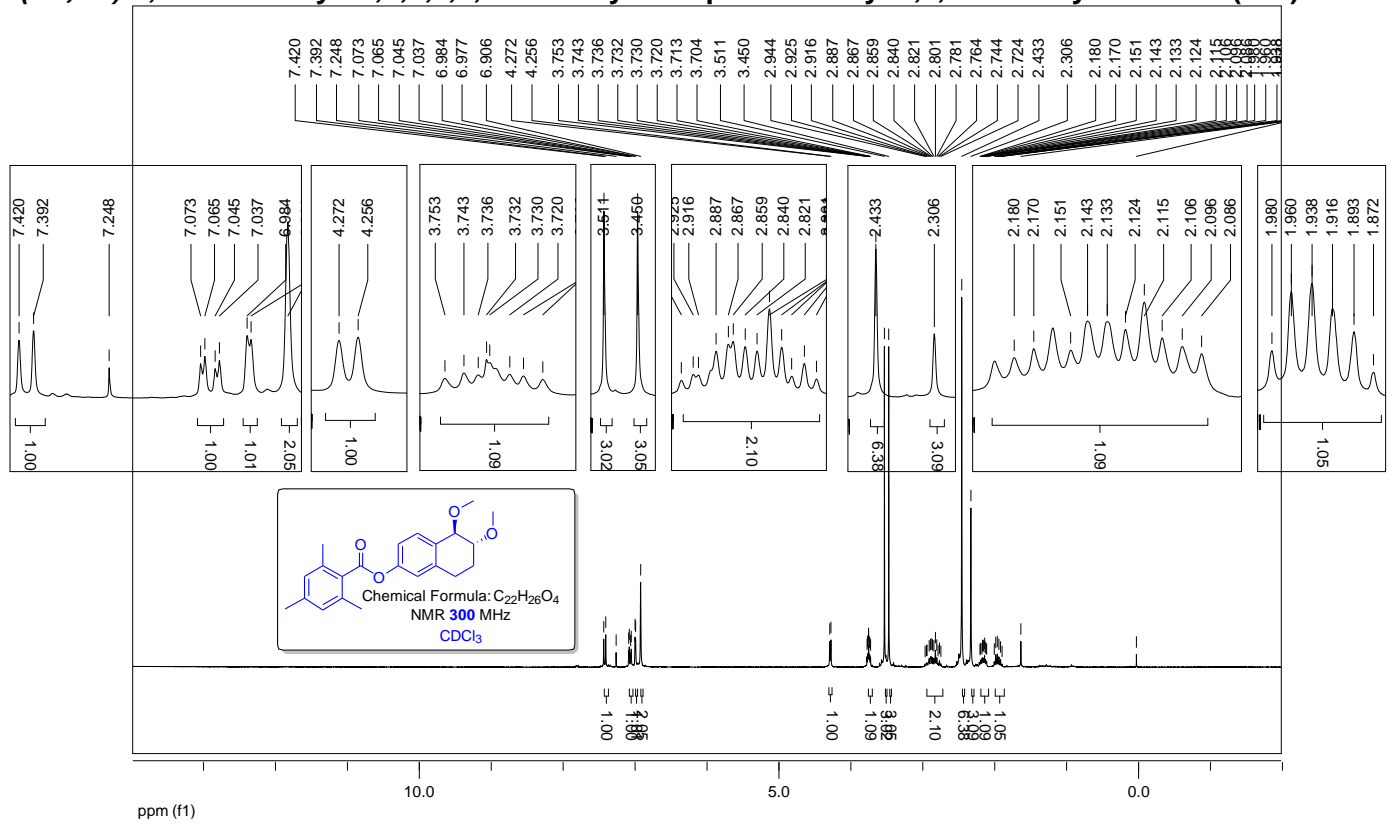
**(5*R*,6*R*)-5,6-Dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (17d).**



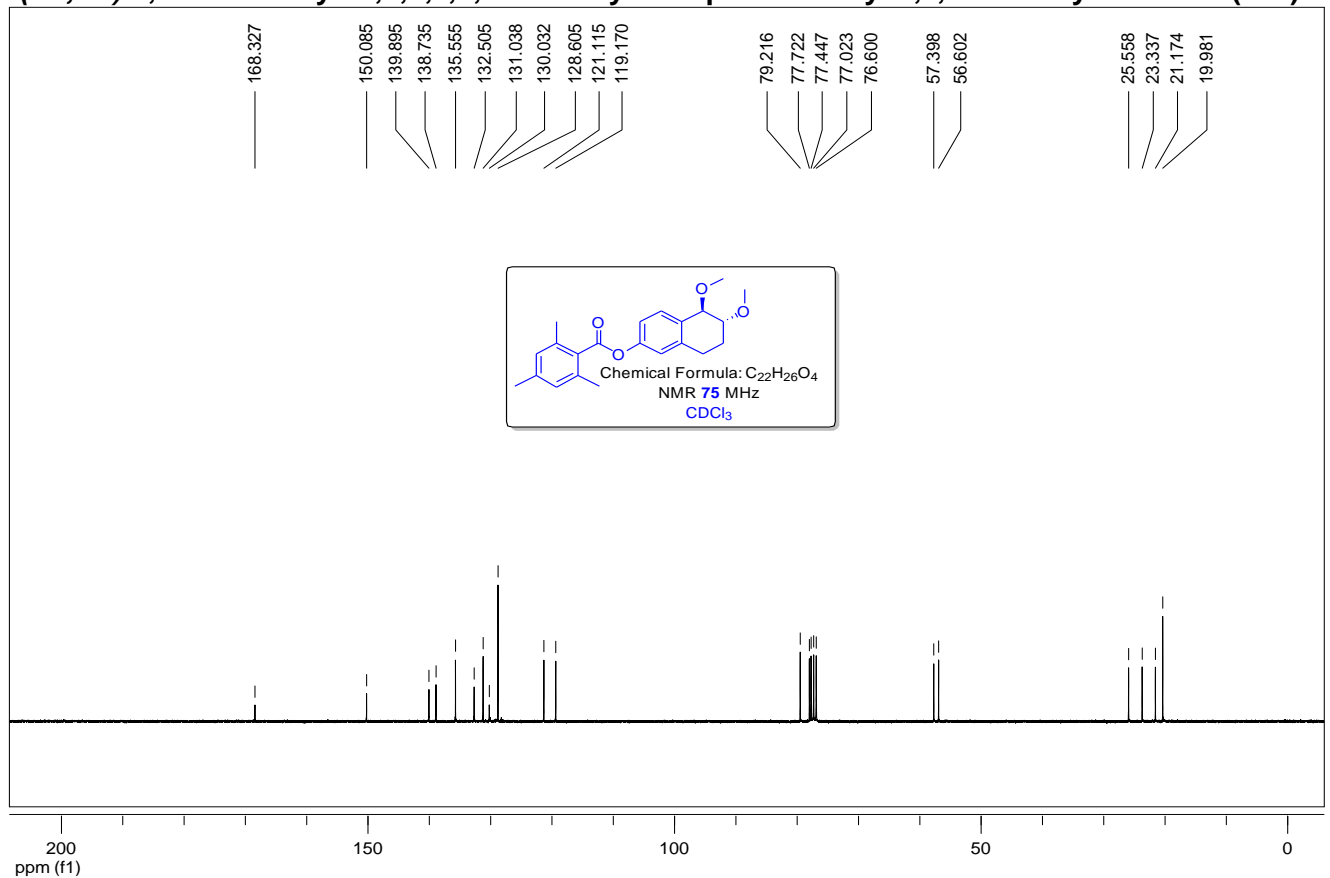
**(5*R*,6*R*)-5,6-Dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (17d).**



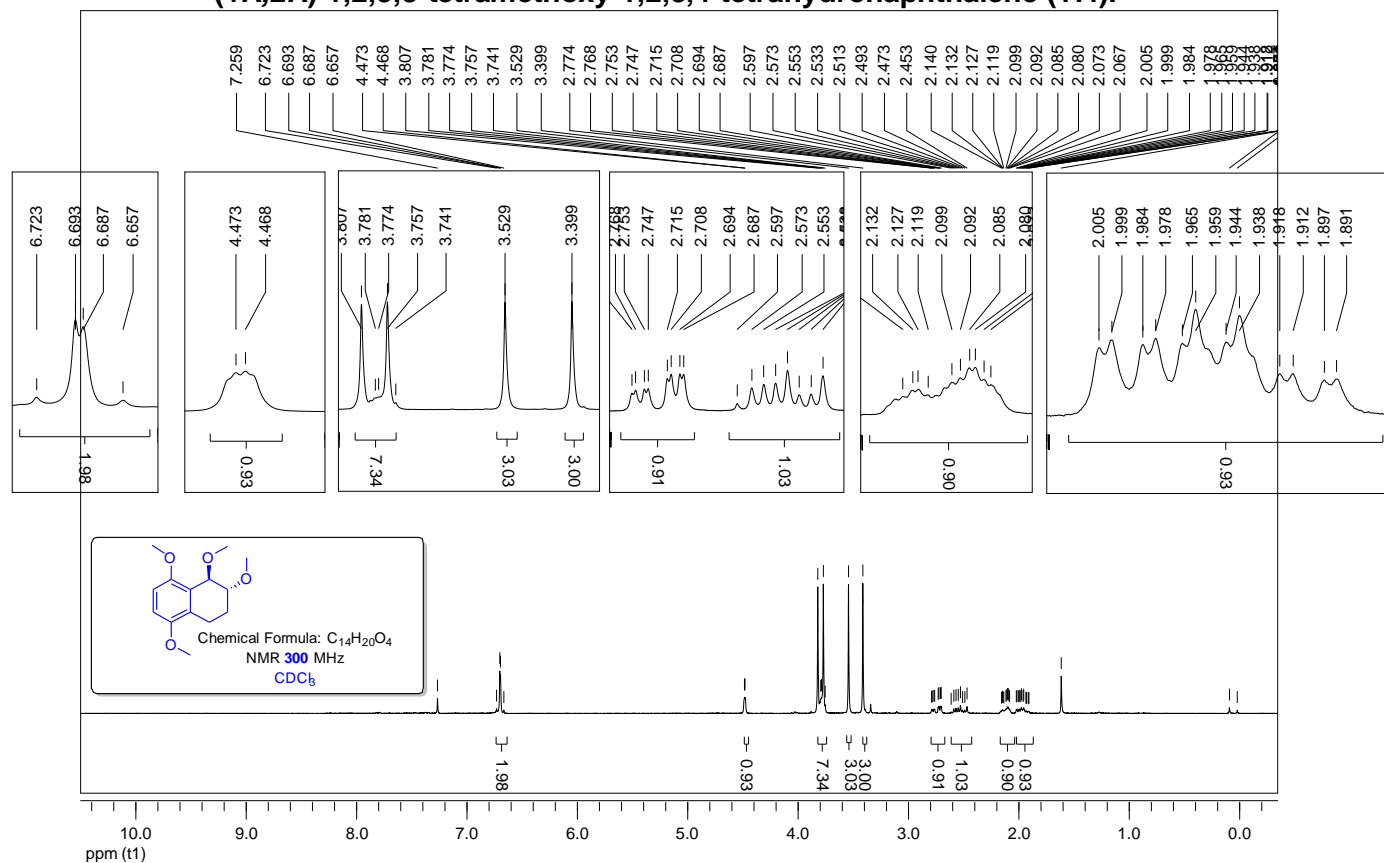
**(5R,6R)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (17e).**



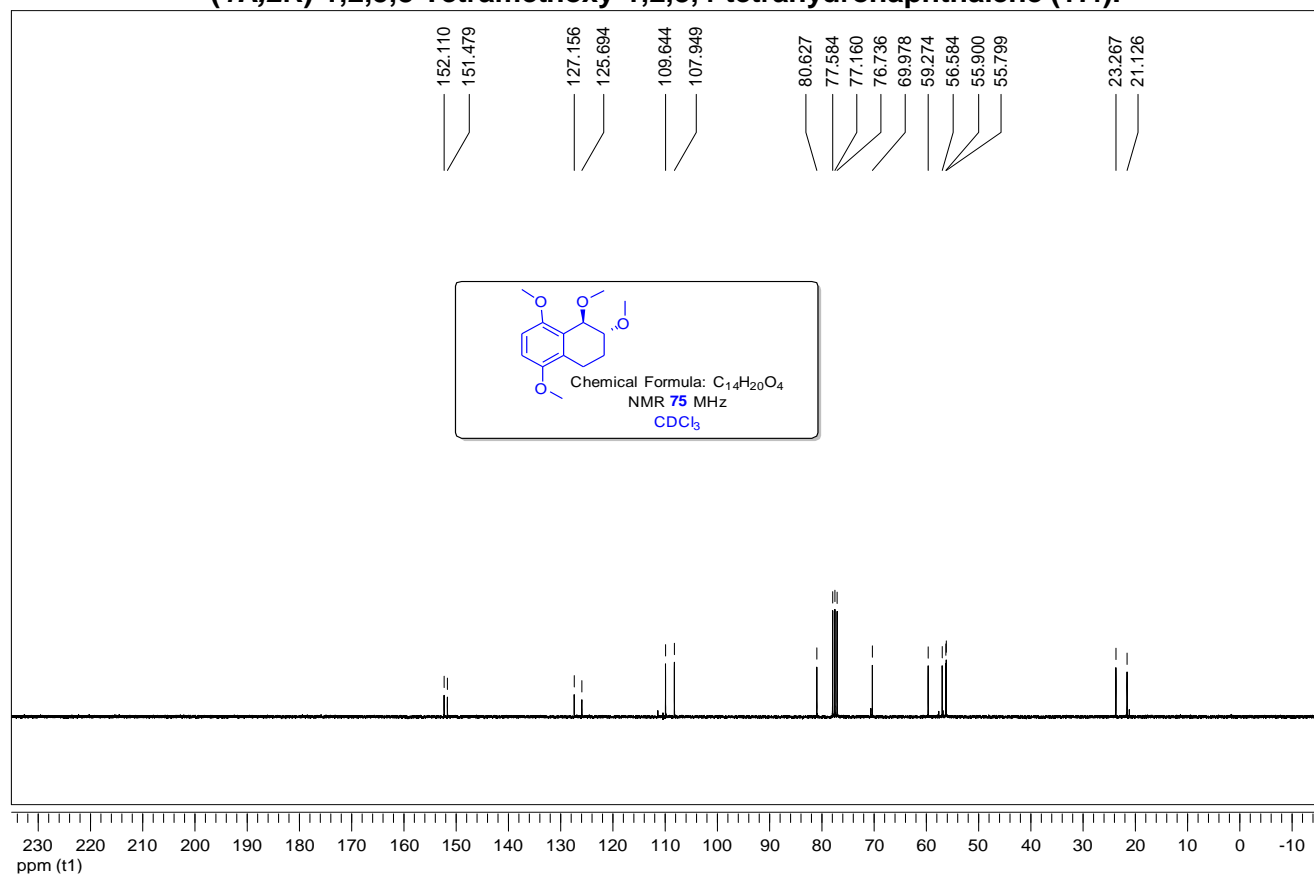
**(5R,6R)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl 2,4,6-trimethylbenzoate (17e).**



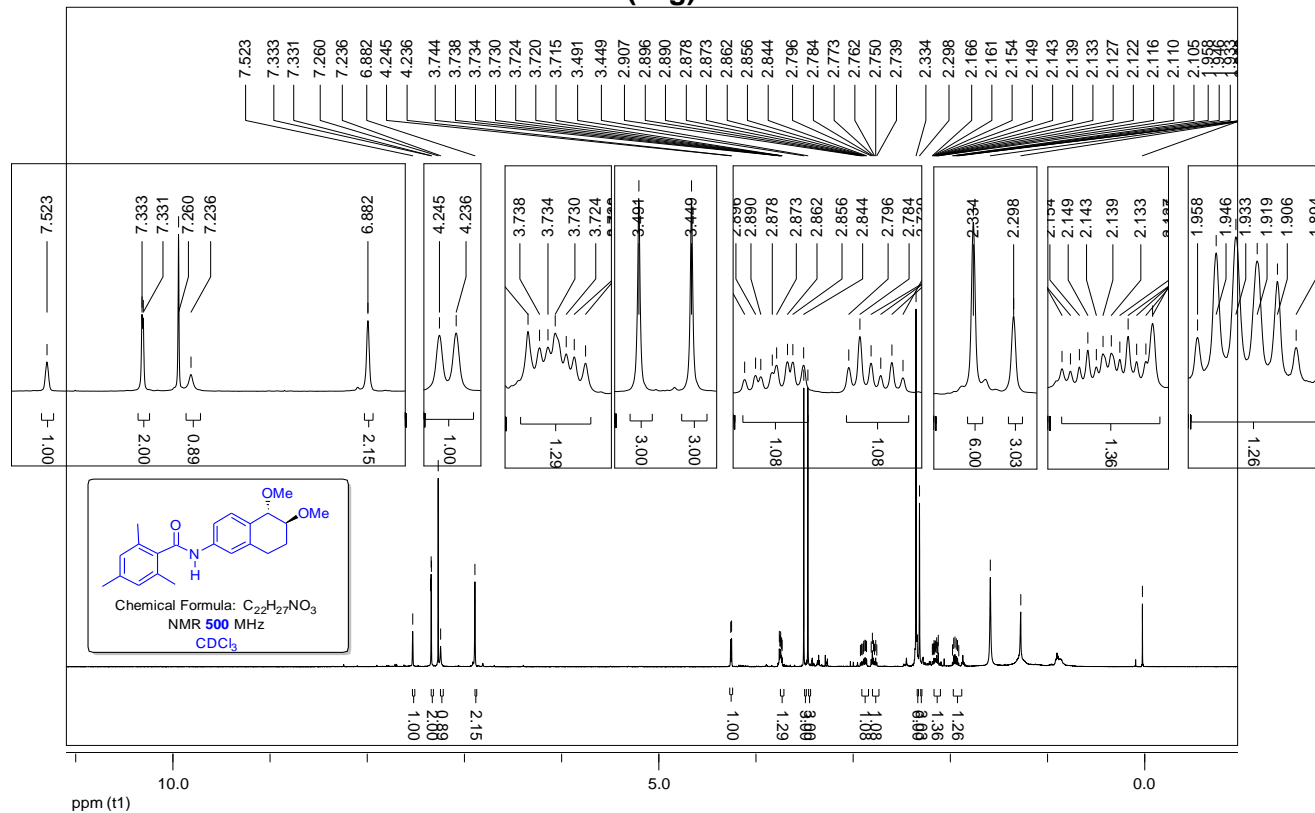
**(1R,2R)-1,2,5,8-tetramethoxy-1,2,3,4-tetrahydronaphthalene (17f).**



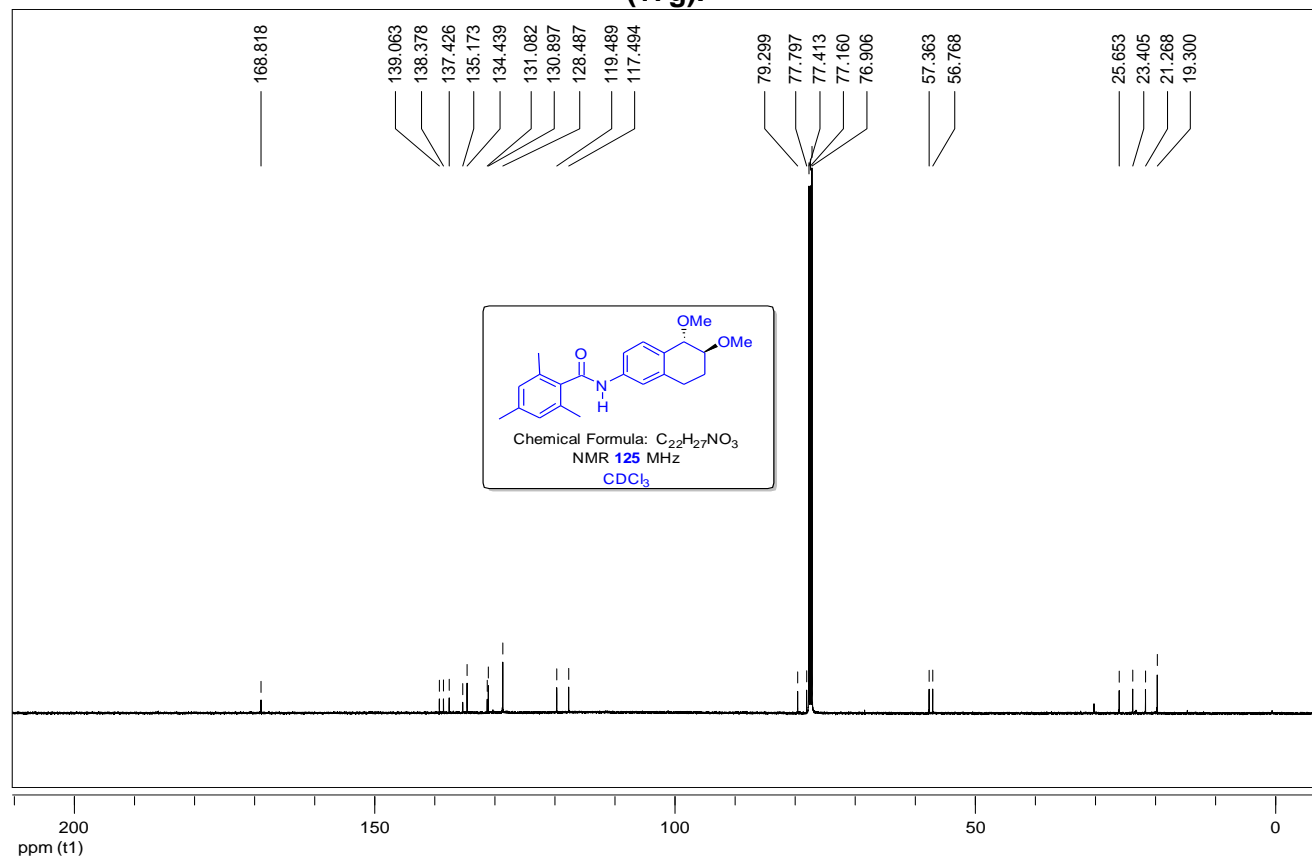
**(1R,2R)-1,2,5,8-Tetramethoxy-1,2,3,4-tetrahydronaphthalene (17f).**



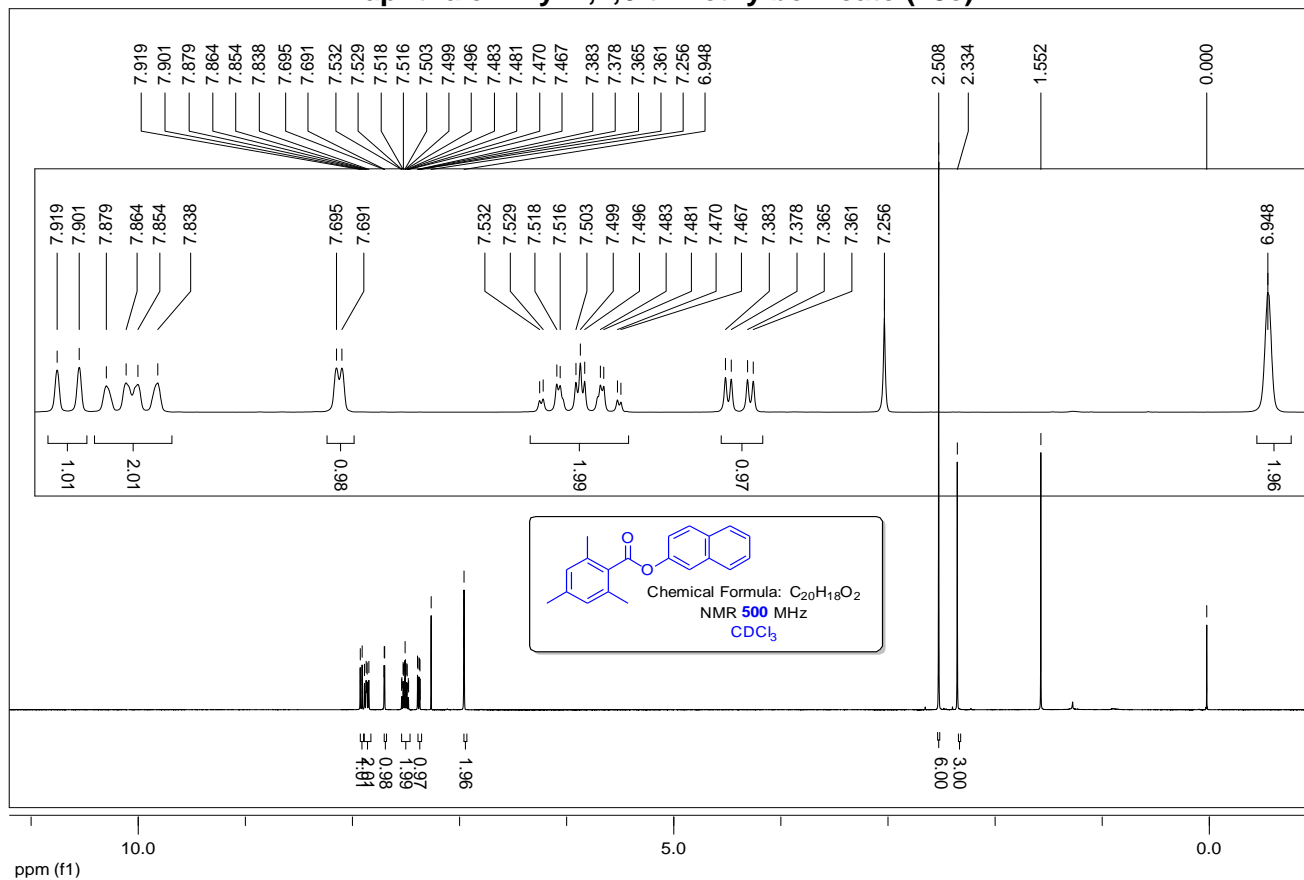
***N*-((5*R*,6*R*)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl)-2,4,6-trimethylbenzamide (17g).**



***N*-((5*R*,6*R*)-5,6-Dimethoxy-4a,5,6,7,8,8a-hexahydronaphthalen-2-yl)-2,4,6-trimethylbenzamide (17g).**



Naphthalen-2-yl 2,4,6-trimethylbenzoate (18e).



Naphthalen-2-yl 2,4,6-trimethylbenzoate (18e).

