Supporting Information

A 1,3-Carbonyl Shift in the Platinum-catalyzed Aromatization of 2-Epoxy-1-(methoxyalk-2-ynyl)benzenes

Rupsha Chaudhuri , Arindam Das, Hsin-Yi Liao and Rai-Shung Liu*

[†]*Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, ROC and*
[‡]*Department of Science Education, National Taipei University of Education, Taipei, Taiwan, ROC*

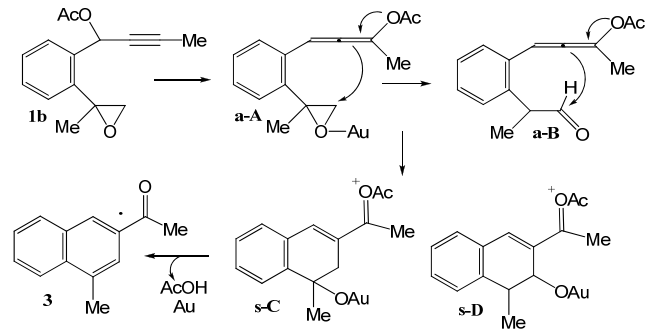
---------- ***rsliu@mx.nthu.edu.tw***

Contents

(I) Mechanistic discussion of 2-naphthyl ketone 3.

Scheme S1 shows a proposed mechanism for formation of 2-naphthyl ketone **3** from epoxide **1b** (see Table 1, entry 7). We envisage that $PPh_3AuCl/AgSbF_6$ catalyzed 1,3-acetate shift of species 1b to form allenyl acetate **a-A**, which subsequently undergoes carbocyclization as shown by species **a-B,** ultimately giving desired product **3** through an aromatization of species **s-C** and **s-D**.

Scheme S1

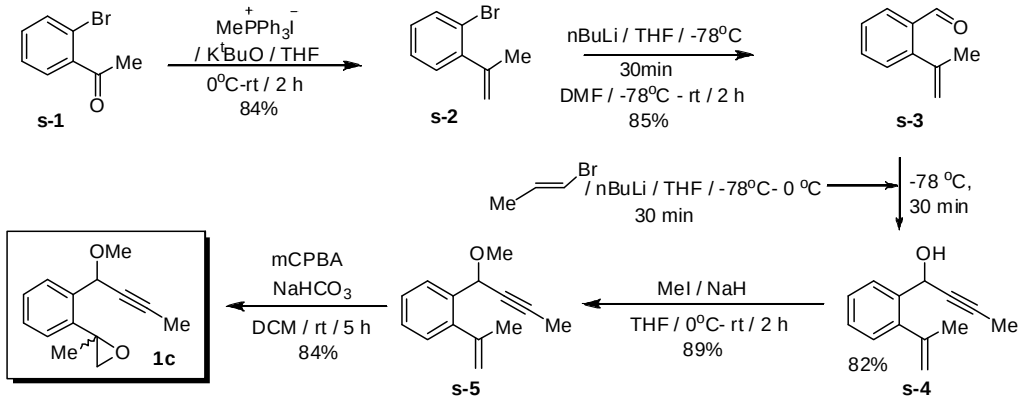


(II) Experimental procedures for the synthesis of 2 -Epoxy-1-(methoxyalk-2-ynyl)benzenes:

(a) General Sections

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glasswares using standard syringe and other apparatus. Diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was distilled over CaH_2 before use. All spectra were run at 400 / 500 / 600 MHz (^{1}H NMR) or 100 / 125 / 150 MHz (^{13}C NMR) in $CDCl_3$ solution.

(b) Typical procedure for the synthesis of 2-(2-{1-methoxybut-2-ynyl}phenyl)-2-methyloxirane (1c).



(1) Synthesis of 1-bromo-2-(prop-1-en-2-yl)benzene (s-2).

A THF solution of $MePPh_3I$ (10 g, 24.7 mmol) was cooled to 0 ^oC, and to this solution was added K^tBuO (4.16 gm, 37.1 mmol). The solution was stirred for 0.5 h at 0 ^oC, and to this mixture was added 1-(2-bromophenyl)ethanone (2.45 g, 1.66 ml, 12.4 mmol) at the same temperature before it was continued to stir for 2 h. The reaction was quenched with water, extracted with diethyl ether (25 ml). The extract was washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-2** (2.03 g, 10.3 mmol, 84%) as colorless liquid.

(2) Synthesis of 2-(prop-1-en-2-yl)benzaldehyde (s-3).

A THF solution of **s-2** (1.2 g, 6.1 mmol) was cooled to –78 ^oC, and to this solution was added n-BuLi (2.5 M in hexane, 3.7 ml, 9.2 mmol) slowly. The mixture was stirred for 0.5 h at –78 ^oC, and to this mixture *N*,*N*-dimethylformamide (0.89 g, 0.94 ml, 12.2 mmol) was added at the same temperature. The mixture was continued to stir for 2 h at room temperature before it was quenched with water. The organic layer was extracted with diethyl ether (25 ml), washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-3** (0.76 g, 5.2 mmol, 85%) as yellow liquid.

(3) Synthesis of 1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-ol (s-4).

A THF solution of 1-bromo-1-propene (0.93 g, 0.7 ml, 7.7 mmol) was cooled to –78 ^oC, and to this solution was added n-BuLi (2.5 M in hexane, 6.2 ml, 15.4 mmol) slowly. The mixture was warmed to –20 ^oC, and stirred for 0.5 h. The solution was again cooled to –78 ^oC before addition of compound **s-3** (0.7 g, 4.8 mmol), and this mixture was stirred for 1 h at room temperature. The reaction was quenched with water, extracted with ethyl acetate (25 ml). The extract was washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-4** (0.73 g, 3.9 mmol, 82%) as yellow liquid.

(4) Synthesis of 1-(1-methoxybut-2-ynyl)-2-(prop-1-en-2-yl)benzene (s-5).

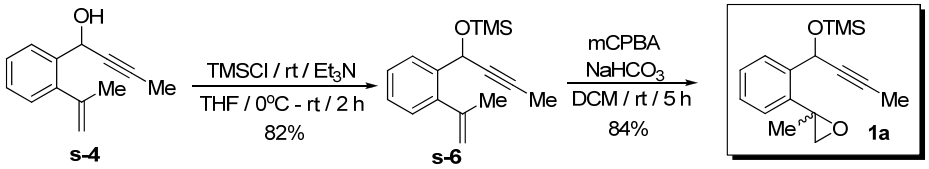
A THF solution of NaH (60%) (0.19 g, 4.7 mmol) was cooled to 0^oC and to this solution was added **s-4** (0.73 g, 3.9 mmol). The mixture was continued to stir for 0.5 h. MeI (2.76 g, 3.0 ml, 19.5 mmol) was added to the mixture and stirred for additional 2 h.

The reaction was quenched with water, extracted with ethyl acetate (25 ml). The extract was washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-5** (0.7 g, 3.5 mmol, 89%) as yellow liquid.

(5) Synthesis of 2-Epoxy-1-(methoxyalk-2-ynyl)benzene)(1c).

mCPBA (0.905g, 5.2 mmol), and $NaHCO_3$ (0.588 g, 7.0 mmol), was added to a DCM solution of **s-5** (0.7 g, 3.5 mmol) and stirred for 5 h. The reaction was quenched with water, extracted with DCM (25 ml). The extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **1c** (0.635 g, 2.9 mmol, 84%) as colorless liquid.

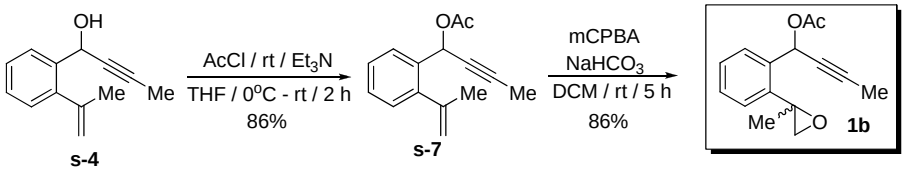
(c) Typical procedure for the synthesis of trimethyl(1-{2-{2-methyloxiran-2-yl}phenyl}but-2-ynyloxy)silane(1a).



Synthesis of 1-(2-(prop-1-en-2-yl)phenyl)but-2-ynyl acetate (s-6).

To alcohol **s-4** (0.73 g, 3.9 mmol) in THF was added Et_3N (1.2 g, 1.6 ml, 11.7 mmol) and trimethylsilylchoride (0.640 g, 0.75 ml, 5.9 mmol) at 0 ^oC, and the resulting mixture was continued to stir for 2 h. The reaction was quenched with water, extracted with diethyl ether (25 ml). The extract was washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-6** (0.622 g, 2.4 mmol, 82%) as yellow liquid.

(d) Typical procedure for the synthesis of 1-(2-(2-methyloxiran-2-yl)phenyl)but-2-ynyl acetate(1b).

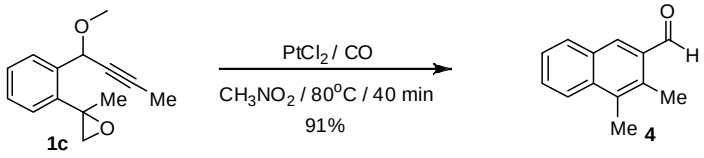


Synthesis of 1-(2-(prop-1-en-2-yl)phenyl)but-2-ynyl acetate (s-7):

To alcohol **s-4** (0.73 g, 4.3 mmol) in THF was added Et_3N (1.2 g, 1.6 ml, 11.7 mmol) and acetyl chloride (0.652 g, 0.6 ml, 5.9 mmol) at 0 ^oC, and the resulting mixture was continued to stir for 2 h. The reaction was quenched with water, extracted with diethyl

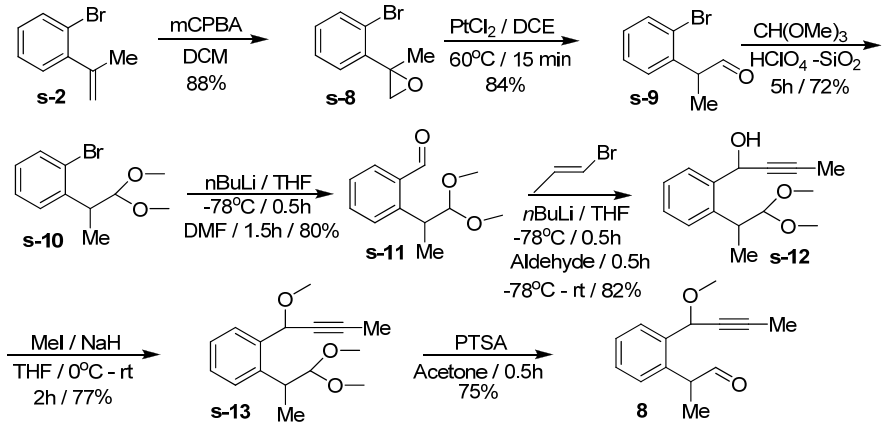
ether (25 ml). The extract was washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-7** (0.769 g, 3.4 mmol, 86%) as yellow liquid.

(III) Standard procedure for catalytic operations-------Synthesis of 3,4-dimethyl-2-naphthaldehyde (4).



To a long tube containing $PtCl_2$ (8.6 mg, 0.03 mmol) was added dry dichloroethane (1.0 ml). To this solution was added a dichloroethane solution (3.0 ml) of epoxide **1c** (100 mg, 0.46 mmol), and the resulting suspension was stirred for 40 min at 80°C. The solution was concentrated, and eluted through a silica column (hexane) to afford compound **4** (77.4 mg, 0.42 mmol, 91%) as a yellow liquid.

(IV) Synthetic route for 2-(2-(1-methoxybut-2-ynyl)phenyl)propanal (8).



(a) Synthesis of 2-(2-bromophenyl)-2-methyloxirane (s-8):

mCPBA (1.3 g, 7.6 mmol), and $NaHCO_3$ (0.85 g, 10.2 mmol), was added to a DCM solution of **s-2** (1.0 g, 5.1 mmol) and stirred for 5 h. The reaction was quenched with water, extracted with DCM (25 ml). The extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a silica column to afford compound **s-8** (0.95 g, 4.4 mmol, 88%) as colorless liquid.

(b) Synthesis of 2-(2-bromophenyl)propanal (s-9):

To a round bottom flask containing $PtCl_2$ (25 mg, 0.09 mmol) was added dry dichloroethane (5.0 ml). To this solution was added a dichloroethane solution (5.0 ml) of

s-8 (200 mg, 0.9 mmol), and the resulting suspension was stirred for 15 min at 60^{o}C. The solution was passed through a celite bed and concentrated under reduced pressure to afford compound **s-9** (168 mg, 0.78 mmol, 84%).

(c) Synthesis of 1-bromo-2-(1,1-dimethoxypropan-2-yl)benzene (s-10):

$HClO_4$-SiO_2 was added in catalytic amount to a trimethylorthoformate solution of **s-9** (0.4 g, 1.8 mmol) and stirred for 5 h. The reaction was quenched with water, extracted with ethyl acetate. The extract was washed with water, dried over K_2CO_3, and concentrated under reduced pressure. The residue was eluted through a neutral silica column to afford compound **s-10** (0.35 g, 1.35 mmol, 72%) as colorless liquid.

(d) Synthesis of 2-(1,1-dimethoxypropan-2-yl)benzaldehyde (s-11):

A THF solution of **s-10** (0.9 g, 3.5 mmol) was cooled to –78 ^{o}C, and to this solution was added n-BuLi (2.5 M in hexane, 2.1 ml, 5.2 mmol) slowly. The mixture was stirred for 0.5 h at –78 ^{o}C, and to this mixture *N*,*N*-dimethylformamide (0.5 g, 0.54 ml, 6.9 mmol) was added at the same temperature. The mixture was continued to stir for 1.5 h at room temperature before it was quenched with water. The organic layer was extracted with diethyl ether (25 ml), washed with water, dried over K_2CO_3, and concentrated under reduced pressure. The residue was eluted through a neutral silica column to afford compound **s-11** (0.578 g, 2.7 mmol, 80%) as yellow liquid.

(e) Synthesis of 1-(2-(1,1-dimethoxypropan-2-yl)phenyl)but-2-yn-1-ol (s-12):

A THF solution of 1-bromo-1-propene (0.3 g, 0.21 ml, 2.4 mmol) was cooled to –78 ^{o}C, and to this solution was added n-BuLi (2.5 M in hexane, 1.9 ml, 4.9 mmol) slowly. The mixture was warmed to –20 ^{o}C, and stirred for 0.5 h. The solution was again cooled to –78 ^{o}C before addition of compound **s-11** (0.32 g, 1.5 mmol), and this mixture was stirred for 0.5 h at room temperature. The reaction was quenched with water, extracted with ethyl acetate (25 ml). The extract was washed with water, dried over K_2CO_3, and concentrated under reduced pressure. The residue was eluted through a neutral silica column to afford compound **s-12** (0.31 g, 1.25 mmol, 82%) as yellow liquid.

(f) Synthesis of 1-(2-(1,1-dimethoxypropan-2-yl)phenyl)-2-(1-methoxybut-2-ynyl) (s-13):

A THF solution of NaH (60%) (0.08 g, 2.1 mmol) was cooled to 0^{o}C and to this solution was added **s-12** (0.4 g, 1.6 mmol). The mixture was continued to stir for 0.5 h.

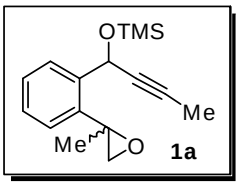
MeI (1.14 g, 1.22 ml, 8.0 mmol) was added to the mixture and stirred for additional 2 h. The reaction was quenched with water, extracted with ethyl acetate (25 ml). The extract was washed with water, dried over K_2CO_3, and concentrated under reduced pressure. The residue was eluted through a neutral silica column to afford compound **s-13** (0.32 g, 1.24 mmol, 77%) as yellow liquid.

(g) Synthesis of 2-(2-(1-methoxybut-2-ynyl)phenyl)propanal (8):

PTSA (0.04 g, 0.02 mmol) was added to a acetone solution of s-13 (0.1 g, 0.4 mmol) and stirred for 0.5 h. After completion acetone was removed under reduced pressure. Residue was diluted with ethyl acetate, washed with water, dried over K_2CO_3, and concentrated under reduced pressure. The residue was eluted through a neutral silica column to afford compound **8** (0.06 g, 0.27 mmol, 75%) as yellow liquid.

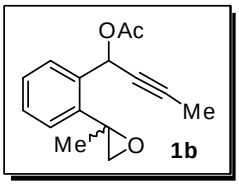
(V) Spectral data for all compounds.

Spectral data for trimethyl(1-{2-{2-methyloxiran-2-yl}phenyl}but-2-ynyloxy)silane(**1a**).



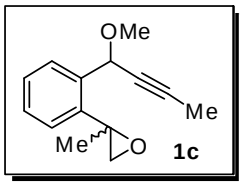
Yellow liquid ; IR (neat, cm^{-1}): 3035 (s), 2105 (s), 1582 (s), 1450 (s), 1262(s), 1253 (s), 1150, 1022(s), (s), 890 (s), 810 (s); ^1H NMR (400 MHz , $CDCl_3$): Major isomer: δ 7.67 (t, *J* = 7.4 Hz, 1 H), 7.38 - 7.22 (m, 3 H), 5.86 (d, *J* = 1.4 Hz, 1 H), 2.97 - 2.94 (m, 2 H), 1.80 (s, 3 H), 1.65 (s, 3 H), 0.16 (s, 9H) ; Minor isomer (selected peaks): δ 5.77 (d, *J* = 1.4 Hz, 1 H), 2.89 - 2.87 (m, 2 H), 1.81 (s, 3 H), 0.17 (s, 9H);^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 139.3, 137.8, 137.3, 128.0 (2x CH), 127.8, 127.6, 127.3, 127.2, 127.1, 126.9, 82.5, 82.3, 80.3, 80.1, 61.4, 61.1, 58.0, 57.8, 55.1, 54.8, 24.8, 24.6, 3.7 ($2xCH_3$), 0.34 ($3xCH_3$), 0.26 ($3xCH_3$); HRMS calcd for $C_{16}H_{22}O_2Si$: 274.1389; found: 274.1390.

Spectral data for 1-(2-{2-methyloxyran-2-yl}phenyl)but-2-ynyl acetate**(1b).**



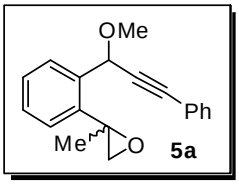
Yellow liquid ; IR (neat, cm^{-1}): 3033 (s), 2101 (s), 1720 (s),1588 (s), 1450 (s), 1255 (s), 1020(s), 1150 (s), 888 (s), 810 (s); ^1H NMR (400 MHz , $CDCl_3$): Major isomer:δ 7.63 (dt, *J* = 3.2, 5.8 Hz 1 H), 7.4 (dt, *J* = 2.0, 5.4 Hz, 1 H), 7.35 - 7.28 (m, 2 H), 6.70 (q, *J* = 2.2 Hz, 1 H), 2.98 ($d_{a,b}$, *J* = 5.2 Hz, 2 H), 2.08 (s, 3H), 1.83 (d, *J* = 2.2 Hz, 3 H), 1.60 (s, 3 H) ; Minor isomer (selected peaks): δ 6.72 (q, *J* = 2.2 Hz, 1 H), 2.93 ($d_{a,b}$, *J* = 5.1 Hz, 2 H), 2.06 (s, 3H), 1.84 (d, *J* = 2.3 Hz, 3 H), 1.63 (s, 3 H) ;^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 169.5, 138.9, 138.7, 135.1, 134.8, 128.8, 128.7, 128.2, 128.1, 127.6 (2xCH), 127.5, 127.0, 83.9, 83.8, 76.2 (2xC), 62.6, 62.5, 57.4, 57.3, 54.8, 54.6, 24.6, 24.3, 21.0 (2xCH_3), 3.7 (2xCH_3); HRMS calcd for $C_{15}H_{16}O_3$: 244.1099; found: 244.1098.

Spectral data for 2-(2-{1-methoxybut-2-ynyl}phenyl)-2-methyloxirane**(1c).**



Yellow liquid ; IR (neat, cm^{-1}): 3030 (s), 2109 (s),1555 (s), 1451 (s), 1251 (s), 1150 (s), 1050 (s), 888 (s), 812 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers:δ 7.65 - 7.62 (m, 2 H), 7.47 - 7.44 (m, 1 H), 7.37 - 7.23 (m, 5 H), 5.40 (t, *J* = 2.0 Hz, 1 H), 5.35 (d, *J* = 2.2 Hz, 1 H), 3.40 (s, 3 H), 3.39 (s, 3 H), 2.95 - 2.93 (m, 2H), 2.89 ($d_{a,b}$, *J* = 5.2 Hz, 1 H), 2.87 ($d_{a,b}$, *J* = 5.2 Hz, 1 H), 1.86 (d, *J* = 2.1 Hz, 3 H), 1.84 (d, *J* = 2.2 Hz, 3 H), 1.61 (s, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.7, 136.6, 136.4, 127.9 (2xCH), 127.8, 127.6, 127.5, 127.4, 127.1 (2xCH), 83.7(2xC), 77.3 (2xC), 69.6, 69.4, 57.8, 57.7, 55.9 (2xOCH_3), 54.6, 54.5, 24.6 (2xCH_3), 3.5 (2xCH_3); HRMS calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1148.

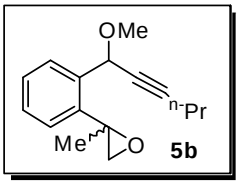
Spectral data for 2-(2-{1-methoxy-3-phenylprop-2-ynyl}phenyl)-2-methyloxirane**(5a).**



Yellow liquid ; IR (neat, cm^{-1}): 3036 (s), 2107 (s),1584 (s), 1455 (s), 1253 (s), 1151 (s), 1048 (s), 893 (s), 812 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers : δ 7.79 - 7.76 (m, 2 H), 7.48 - 7.29 (m, 16 H), 5.74 (s, 1 H), 5.66 (s, 1 H), 3.54 (s, 3 H), 3.53 (s, 3 H), 3.03 - 2.93 (m, 4 H), 1.70 (s, 3 H), 1.69 (s, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ

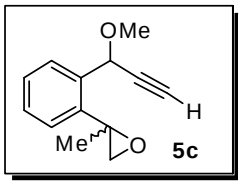
139.1, 138.9, 136.1, 136.0, 131.8, 131.7 (2xCH), 131.6 (2xCH), 128.5 (3xCH), 128.2 (6xCH), 128.0, 127.7, 127.4 (2xCH), 122.5, 122.4, 87.6, 87.5, 86.9, 86.7, 70.0, 69.8, 58.0, 57.8, 56.3 (2xOCH_3), 54.7 (2xCH_2), 24.8, 24.7; HRMS calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1309.

Spectral data for 2-(2-{1-methoxyhex-2-ynyl}phenyl)-2-methyloxirane**(5b).**



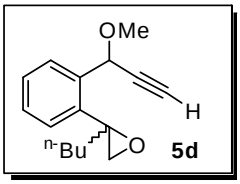
Yellow liquid ; IR (neat, cm^{-1}): 3030 (s), 2100 (s),1596 (s), 1454 (s), 1251 (s), 1153 (s), 1049 (s), 893 (s), 815 (s); ^{1}H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.66 (t, *J* = 6.0 Hz 2 H), 7.38 (t, *J* = 6.1 Hz, 2 H), 7.33 - 7.25 (m, 4 H), 5.45 (s, 1 H), 5.38 (s, 1H), 3.43 (s, 3H), 3.41 (s, 3H), 2.97 - 2.96 (m, 2 H), 2.95 - 2.87 (m, 2 H), 2.24 - 2.17 (m, 4 H), 1.63 (s, 6 H), 1.57 - 1.46 (m, 4 H), 0.99 - 0.94 (m, 6 H);^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.8, 136.7, 136.5, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.2, 127.1, 88.3 (2xC), 78.0, 77.8, 69.6, 69.5, 57.9, 57.8, 55.9 (2xOCH_3), 54.7, 54.6, 24.6 (2xCH_3), 21.9, 21.8, 20.7 (2xCH_2), 13.4 (2xCH_3); HRMS calcd for $C_{16}H_{20}O_2$: 244.1463; found: 244.1465.

Spectral data for 2-(2-{1-methoxyprop-2-ynyl}phenyl)-2-methyloxirane**(5c).**



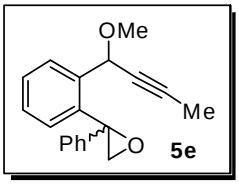
Yellow liquid ; IR (neat, cm^{-1}): 3100 (s), 2105 (s),1599 (s), 1452 (s), 1251 (s), 1150 (s), 1050 (s), 893 (s), 815 (s); ^{1}H NMR (600 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.68 (d, *J* = 1.2 Hz, 2 H), 7.38 - 7.29 (m, 6 H), 5.50 (d, *J* = 1.9 Hz, 1 H), 5.42 (d, *J* = 2.0 Hz, 1 H), 3.46 (s, 6 H), 2.97 - 2.87 (m, 4 H), 2.63 (d, *J* = 2.1 Hz, 1 H), 2.62 (d, *J* = 2.2 Hz, 1 H),1.63 (s, 6 H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.0, 138.8, 135.6, 135.4, 128.5 (2xCH), 128.0, 127.9, 127.7, 127.5, 127.3 (2xCH), 81.5, 81.3, 75.7, 75.6, 69.2, 68.9, 57.9, 57.7, 56.2 (2xOCH_3), 54.5 (2xCH_2), 24.7, 24.6; HRMS calcd for $C_{13}H_{14}O_2$: 202.0994; found: 202.0996.

Spectral data for 2-butyl-2-(2-{1-methoxyprop-2-ynyl}phenyl)-2-methyloxirane**(5d)**.



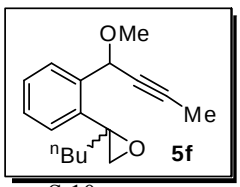
Yellow liquid ; IR (neat, cm^{-1}): 3095 (s), 2110 (s),1600 (s), 1452 (s), 1253 (s), 1150 (s), 1050 (s), 887 (s), 815 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.69 - 7.66 (m, 2 H), δ7.35 - 7.26 (m, 6 H), 5.43 (d, *J* = 1.8 Hz, 1 H), 5.39 (d, *J* = 2.0 Hz, 1 H), 3.45 (s, 3 H), 3.44 (s, 3 H), 2.99 - 2.96 (m, 2 H), 2.86 - 2.82 (m, 2 H), 2.60 (d, *J* = 2.1 Hz, 1 H), 2.59 (d, *J* = 2.2 Hz, 1 H), 1.94 - 1.76 (m, 4 H), 1.29 - 1.26 (m, 8 H), 0.92 - 0.75 (m, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.7, 136.2, 135.9, 128.2 (4xCH), 128.1, 128.0, 127.8, 127.6, 81.8, 81.5, 75.4 (2xCH), 69.3, 69.0, 60.6, 60.5, 56.3 (2xOCH_3), 53.2 (2xCH_2), 37.1 (2xCH_2), 26.8 (2xCH_2), 22.6 (2xCH_2), 13.8 (2xCH_3); HRMS calcd for $C_{16}H_{20}O_2$: 244.1463; found: 244.1466.

Spectral data for 2-(2-{1-methoxybut-2-ynyl}phenyl)-2-phenyloxirane**(5e)**.



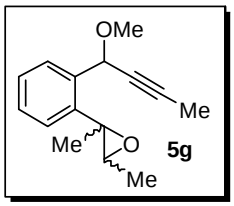
Yellow liquid ; IR (neat, cm^{-1}): 3015 (s), 2112 (s),1601 (s), 1454 (s), 1255 (s), 1150 (s), 1050 (s), 881 (s), 815 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.76 (dd, *J* = 1.0, 7.6 Hz, 2 H), 7.00 - 7.18 (m, 16 H), 5.20 (d, *J* = 2.1 Hz, 1 H), 5.16 (d, *J* = 2.0 Hz, 1 H), 3.42 ($d_{a,b}$, *J* = 5.7 Hz, 1 H), 3.40 ($d_{a,b}$, *J* = 5.7 Hz, 1 H), 3.32 (s, 3 H), 3.26 ($d_{a,b}$, *J* = 5.7 Hz, 1 H), 3.22 ($d_{a,b}$, *J* = 5.7 Hz, 1 H), 3.00 (s, 3 H), 1.86 (d, *J* = 2.2 Hz, 3 H), 1.68 (d, *J* = 3.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 139.6, 139.1, 138.7, 136.2, 135.7, 128.9 (2xCH), 128.8 (2xCH), 128. 3 - 128.0 (7xCH), 127.7 (2xCH), 127.4, 126.0 (2xCH), 125.9 (2xCH), 83.3 (2xC), 77.3 (2xC), 69.6 (2xCH), 60.6, 60.3, 57.6, 57.5, 56.5, 55.9, 3.7, 3.5; HRMS calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1305.

Spectral data for 2-butyl-(2-{1-methoxybut-2-ynyl}phenyl)oxirane**(5f).**



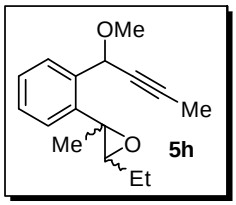
Yellow liquid ; IR (neat, cm^{-1}): 3020 (s), 2100 (s), 1597 (s), 1458 (s), 1255 (s), 1156 (s), 1090 (s), 881 (s), 815 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.66 - 7.63 (m, 2 H), δ7.33 - 7.23 (m, 6 H), δ5.34 - 5.32 (m, 2 H), 3.41 (s, 3 H), 3.38 (s, 3 H), 2.97 ($d_{a,b}$, J = 5.3 Hz, 2 H), 2.86 ($d_{a,b}$, J = 5.3 Hz, 1 H), 2.82 ($d_{a,b}$, J = 5.3 Hz, 1 H), 1.98 - 1.73 (m, 10 H), 1.28 - 1.25 (m, 8 H), 0.84 - 0.81 (m, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.5, 137.1, 136.8, 128.0 (2xCH), 127.9 (3xCH), 127.8, 127.5 (2xCH), 83.5 (2xC), 77.3 (2xC), 69.6, 69.3, 60.5 (2xC), 56.1 ($2xOCH_3$), 53.2 ($2xCH_2$), 37.0 ($2xCH_2$), 26.8 ($2xCH_2$), 22.6 ($2xCH_2$), 13.7 ($2xCH_3$), 3.6 ($2xCH_3$); HRMS calcd for $C_{17}H_{22}O_2$: 258.1620; found: 258.1623.

Spectral data for 2-(2-(1-methoxybut-2-ynyl)phenyl)-2,3-dimethyloxirane(**5g**).



Yellow liquid ; IR (neat, cm^{-1}): 3033 (s), 2109 (s),1581 (s), 1457 (s), 1253 (s), 1150 (s), 1048 (s), 881 (s), 815 (s); ^1H NMR (400 MHz, $CDCl_3$), Major isomer: δ 7.67 - 7.65 (m, 1 H), 7.40 - 7.36 (m, 1 H), 7.32 - 7.20 (m, 2 H), 5.06 (s, 1 H), 3.43 (s, 3 H), 3.21 - 3.19 (m, 1 H), 1.85 (s, 3 H), 1.56 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 140.9, 139.4, 137.9, 137.4, 136.8, 136.1, 135.5, 128.7, 128.5, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 127.1, 126.8, 126.7, 126.5, 83.6, 83.5, 82.3, 78.6, 77.3, 77.2, 77.0, 76.8, 76.7, 69.7, 69.6, 69.5, 69.4, 69.3, 68.0, 63.1, 62.7, 61.9, 61.8, 61.1, 61.0, 59.7, 59.5, 59.4, 56.2, 55.9, 55.8, 55.7, 25.7, 25.2, 25.0, 19.6, 19.5, 16.1, 15.0, 14.9, 13.8, 13.7, 3.5, 3.4; HRMS calcd for $C_{15}H_{18}O_2$: 230.1307, found: 230.1309.

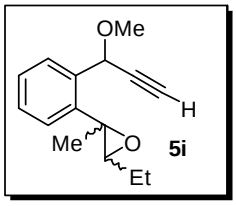
Spectral data for 3-ethyl-2(2-(1-methoxybut-2-ynyl)phenyl)-2-methyloxirane(**5h**).



Yellow liquid ; IR (neat, cm^{-1}): 3030 (s), 2106 (s),1584 (s), 1454 (s), 1260 (s), 1150 (s), 1048 (s), 880 (s), 813 (s); ^1H NMR (400 MHz, $CDCl_3$), Major isomer: δ 7.68 - 7.67 (m, 1 H), 7.39 - 7.37 (m, 1 H), 7.31 - 7.27 (m, 2 H), 5.08 - 5.09 (m, 1 H), 3.46 (s, 3 H), 3.07 -

3.04 (m, 1 H), 1.91 - 1.80 (m, 5 H), 1.57 (s, 3 H), 0.98 - 0.89 (m, 3 H); Selected peaks of others isomers: δ 7.77 - 7.82 (m, 1 H), 7.59 - 7.57 (m, 1 H), 7.09 - 7.05 (m, 2 H), 5.78 (s, 1 H), 5.71 (s, 1 H), 5.02 (s, 1 H), 3.45 (s, 3 H), 1.61 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 138.0, 137.9, 137.3, 136.9, 136.7, 135.6, 128.7, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 126.9, 83.9, 83.7, 69.8, 69.7, 69.6, 68.3, 67.0, 65.5, 65.3, 62.3, 62.2, 56.4, 55.9, 26.0, 25.5, 25.3, 23.8, 22.9, 22.8, 10.5, 10.4, 3.6; HRMS calcd for $C_{16}H_{20}O_2$: 244.1463, found: 244.1465.

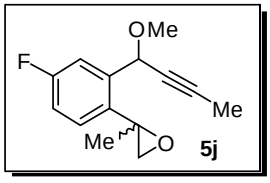
Spectral data for 3-ethyl-2-(2-(1-methoxyprop-2-ynyl)phenyl)-2-methyloxirane(**5i**).



5i

Yellow liquid ; IR (neat, cm^{-1}): 3044 (s), 2107 (s),1581 (s), 1451 (s), 1251 (s), 1150 (s), 1049 (s), 881 (s), 810 (s); ^{1}H NMR (400 MHz, $CDCl_3$), Major isomer: δ 7.71 - 7.67 (m, 1 H), 7.42 - 7.39 (m, 1 H), 7.32 - 7.29 (m, 2 H), 5.13 (s, 1 H), 3.49 (s, 3 H), 3.09 - 3.06 (m, 1 H), 2.54 (s, 1 H), 1.61 (s, 3 H), 1.40 - 1.35 (m, 2 H), 0.97 - 0.86 (m, 3 H); Selected peaks of others isomers: δ 7.81 (d, J = 7.1 Hz, 1 H), 7.61 (d, J = 7.0 Hz, 1 H), 7.11 - 7.07 (m, 2 H), 5.85 (s, 1 H), 5.78 (s, 1 H), 5.07 (s, 1 H), 3.43 (s, 3 H), 2.95 - 2.89 (m, 1 H), 2.54 (s, 1 H), 1.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 138.3, 138.0, 137.4, 137.1, 136.9, 136.1, 135.6, 134.5, 129.0, 128.6, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 127.0, 83.2, 81.7, 81.5, 81.2, 75.8, 75.7, 75.6, 74.4, 69.5, 69.3, 69.2, 67.9, 66.9, 65.5, 65.4, 63.8, 63.3, 62.2, 62.0, 56.7, 56.6, 56.1, 25.9, 25.5, 25.2, 23.8, 23.7, 22.8, 22.7, 10.4, 10.3, 10.2; HRMS calcd for $C_{15}H_{18}O_2$: 230.1307, found: 230.1309.

Spectral data for 2-(4-fluoro-2-{1-methoxybut-2-ynyl}methyl)oxirane**(5j).**

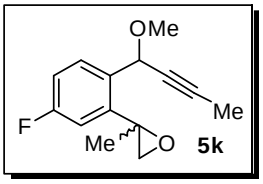


5j

Yellow liquid ; IR (neat, cm^{-1}): 3065 (s), 2110 (s),1602 (s), 1455 (s), 1256 (s), 1159 (s), 1132 (s), 1100 (s), 881 (s), 816 (s), 768 (s), 288 (s); ^{1}H NMR (400 MHz, $CDCl_3$): (1:1) Mixture of isomers: δ 7.34 - 7.30 (m, 4 H), δ6.94 - 6.90 (m, 2 H), 5.36 (s, 1 H), 5.31 (s, 1

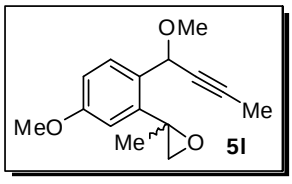
H), 3.39 (s, 3 H), 3.37 (s, 3 H), 2.92 - 2.90 (m, 2 H), 2.84 ($d_{a,b}$, J = 5.1 Hz, 1 H), 2.80 ($d_{a,b}$, J = 5.1 Hz, 1 H), 1.85 (d, J = 1.6 Hz, 3 H), 1.83 (d, J = 1.7 Hz, 3 H), 1.57 (s, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, J_{CF} = 245.0 Hz, 2 C), 139.1 (d, J_{CF} = 21.0 Hz, 2C), 134.8 (d, J_{CF} = 23.0 Hz, 2 C), 129.2 - 129.0 (2xC), 115.2, 114.9, 114.6 - 114.0 (2xCH), 84.2 (2xC), 76.4 (2xC), 69.1, 68.9, 57.4, 57.2, 56.0 (2xOCH_3), 54.6 (2xCH_2), 24.6 (2xCH_3), 3.5 (2xCH_3) ; HRMS calcd for $C_{14}H_{15}FO_2$: 234.1056; found: 234.1060.

.Spectral data for 2-(5-fluoro-2-{1-methoxybut-2-ynyl}methyl)oxirane**(5k).**



Yellow liquid ; IR (neat, cm^{-1}): 3070 (s), 2112 (s),1585 (s), 1457 (s), 1251 (s), 1159 (s), 1133 (s), 1100 (s), 881 (s), 820 (s), 769 (s), 288 (s); ^{1}H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.63 - 7.59 (m, 2 H), 7.08 - 6.94 (m, 4 H), 5.33 (d, J = 1.5 Hz, 1 H), 5.27 (d, J = 1.6 Hz, 1 H), 3.39 (s, 3 H), 3.37 (s, 3 H), 2.95 - 2.92 (m, 2 H), 2.86 ($d_{a,b}$, J = 5.2 Hz, 1H), 2.84 ($d_{a,b}$, J = 5.2 Hz, 1H), 1.85 (d, J = 1.9 Hz, 3 H), 1.84 (d, J = 1.7 Hz, 3 H), 1.60 (s, 3 H), 1.59 (s, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, J_{CF} = 246.0 Hz, 2 C), 141.3 (d, J_{CF} = 15.0 Hz, 2 C), 132.5 (2xC), 129.8 (d, J_{CF} = 18.0 Hz, 2 CH), 114.8 (d, J_{CF} = 21.0 Hz, 2 CH), 114.1 (d, J_{CF} = 22.0 Hz, 2 CH), 84.0 (2xC), 76.6 (2xC), 69.1, 68.9, 57.4, 57.2, 55.9 (2xCH_2), 54.6, 54.5, 24.2, 24.1, 3.4 (2xCH_3); HRMS calcd for $C_{14}H_{15}FO_2$: 234.1056; found: 234.1060.

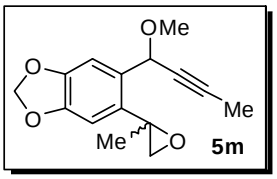
Spectral data for 2-(5-methoxy-2-{1-methoxybut-2-ynyl}methyl)oxirane**(5l).**



Yellow liquid ; IR (neat, cm^{-1}): 3045 (s), 2106 (s),1599 (s), 1454 (s), 1256 (s), 1154 (s), 1072 (s), 881 (s), 817 (s); ^{1}H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.55 (d, J = 8.6 Hz, 2 H), 6.89 (dd, J = 2.4, 6.0 Hz, 2 H), 6.82 (d, J = 8.5 Hz, 2 H), 5.31 (s, 1 H), 5.25 (s, 1 H), 3.75 (s, 6 H), 3.37 (s, 3 H), 3.35 (s, 3 H), δ2.94 - 2.92 (m, 2 H), δ2.88 - 2.85 (m, 2 H), 1.85 (d, J = 1.9 Hz, 3 H), 1.84 (d, J = 1.3 Hz, 3 H), 1.60 (s, 6 H); ^{13}C NMR

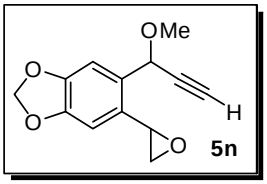
(100 MHz, $CDCl_3$): δ 159.3 (2xC), 140.4, 140.3, 129.2, 129.1, 128.6 (2xC), 113.7, 113.5, 112.0 (2xCH), 83.5, 83.4, 77.3 (2xC), 69.2, 69.1, 57.8, 57.6, 55.7 (2xOCH_3), 55.1 (2xOCH_3), 54.7, 54.6, 24.5, 24.4. 3.5 (2xCH_3); HRMS calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1254.

Spectral data for 5-(1-methoxybut-2-ynyl)-6-(2-methyloxiran-2-yl)benzo[*d*][1,3]dioxole**(5m).**



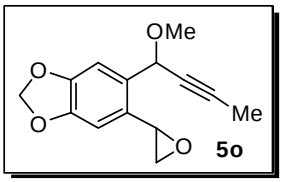
Yellow liquid ; IR (neat, cm^{-1}): 3051 (s), 2102 (s),1601 (s), 1454 (s), 1256 (s), 1153 (s), 1072 (s), 881 (s), 817 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.08 (s, 2 H), 6.81 (s, 2 H), 5.89 (s, 4 H), 5.27 (q, *J* = 2.1 Hz, 1 H), 5.24 (q, *J* = 2.1 Hz, 1 H), 3.37 (s, 3 H), 3.35 (s, 3 H), δ2.92 - 2.90 (m, 2 H), δ2.87 ($d_{a,b}$, *J* = 5.3 Hz, 1 H), δ2.83 ($d_{a,b}$, *J* = 5.3 Hz, 1 H), 1.86 (d, *J* = 2.1 Hz, 3 H), 1.85 (d, *J* = 2.2 Hz, 3 H), 1.57 (s, 3 H), 1.56 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3 (2xC), 147.2 (2xC), 133.1, 132.9, 130.6, 130.5, 107.6, 107.5, 107.2, 107.1, 101.1 (2xCH_2), 83.5 (2xC), 77.3 (2xC), 69.2, 69.1, 57.6 (2xC), 56.0, 55.9, 54.8 (2xCH_2), 24.7 (2xCH_3), 3.5 (2xCH_3); HRMS calcd for $C_{15}H_{16}O_4$: 260.1049; found: 260.1050.

Spectral data for 5-(1-methoxyprop-2-ynyl)-6-(oxiran-2-yl)benzo[*d*][1,3]dioxole**(5n).**



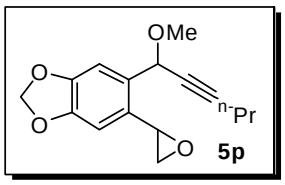
Yellow liquid ; IR (neat, cm^{-1}): 3066 (s), 2110 (s),1586 (s), 1471 (s), 1259 (s), 1152 (s), 1076 (s), 889 (s), 817 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.08 (s, 1 H), 7.06 (s, 1 H), 6.73 (s, 1 H), 6.72 (s, 1 H), 5.91 (d, *J* = 1.2 Hz, 2 H), 5.90 (d, *J* = 1.4 Hz, 2 H), 5.23 (d, *J* = 1.8 Hz, 1 H), 5.22 (d, *J* = 1.8 Hz, 1 H), 4.14 - 4.13 (m, 1 H), 4.08 - 4.07 (m, 1 H), 3.39 (s, 3 H), 3.37 (s, 3 H), 3.08 - 3.06 (m, 2 H), 2.68 - 2.58 (m, 4 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 148.0, 147.1, 147.0, 130.4, 130.2, 129.8 (2xC), 108.3, 108.0, 105.1 (2xCH), 101.3 (2xCH_2), 80.7, 80.5, 76.4, 75.9, 70.2, 69.8, 55.9, 55.7, 50.6, 50.4, 49.7, 49.5; HRMS calcd for $C_{13}H_{12}O_4$: 232.0736; found: 232.0733.

Spectral data for 5-(1-methoxybut-2-ynyl)-6-(oxiran-2-yl)benzo[*d*][1,3]dioxole**(5o).**



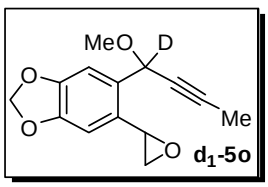
Yellow liquid ; IR (neat, cm^{-1}): 3071 (s), 2112 (s),1600 (s), 1466 (s), 1251 (s), 1151 (s), 1079 (s), 889 (s), 819 (s); ^{1}H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.07 (s, 1 H), 7.06 (s, 1 H), 6.72 (s, 1 H), 6.70 (s, 1 H), 5.90 - 5.89 (m, 4 H), 5.18 - 5.15 (m, 2 H), 4.18 - 4.17 (m, 1 H), 4.10 - 4.08 (m, 1 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.08 - 3.06 (m, 2 H), 2.62 - 2.57 (m, 2 H), 1.88 - 1.21 (m, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 147.7, 146.9 (2xC), 130.9 (2xC), 130.1, 130.0, 108.2, 107.9, 104.9, 104.8, 101.1 ($2xCH_2$), 84.5, 84.0, 76.3, 76.2, 70.4, 70.3, 55.6, 55.4, 50.6, 50.4, 49.6, 49.5, 3.5 ($2xCH_3$); HRMS calcd for $C_{14}H_{14}O_4$: 246.0892; found: 246.0890.

Spectral data for 5-(1-methoxyhex-2-ynyl)-6-(oxiran-2-yl)benzo[*d*][1,3]dioxole**(5p).**



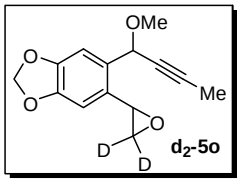
Yellow liquid ; IR (neat, cm^{-1}): 3066 (s), 2110 (s),1584 (s), 1475 (s), 1256 (s), 1155 (s), 1076 (s), 880 (s), 817 (s); ^{1}H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.07 (s, 1 H), 7.05 (s, 1 H), 6.71 (s, 1 H), 6.70 (s, 1 H), 5.90 - 5.88 (m, 4 H), 5.21 - 5.19 (m, 2 H), 4.18 - 4.17 (m, 1 H), 4.10 - 4.09 (m, 1 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 3.07 ($d_{a,b}$, J = 5.6 Hz, 1 H), 3.06 ($d_{a,b}$, J = 5.6 Hz, 1 H), 2.61 ($dd_{a,b}$, J = 2.6, 5.6 Hz, 1 H), 2.57 ($dd_{a,b}$, J = 2.6, 5.6 Hz, 1 H), 2.24 - 2.18 (m, 4 H), 1.57 - 1.47 (m, 4 H), 0.97 - 0.93 (m, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 147.7, 146.8 (2xC), 131.0 (2xC), 130.2, 130.1, 108.3, 108.0, 104.9, 104.8, 101.1 ($2xCH_2$), 89.0, 88.5, 76.6 (2xC), 70.5, 70.3, 55.5, 55.3, 50.6, 50.4, 49.6, 49.4, 22.0, 21.9, 20.6 ($2xCH_2$), 13.4 ($2xCH_3$); HRMS calcd for $C_{16}H_{18}O_4$: 274.1205; found: 274.1202.

Spectral data for compound**(d_1-5o).**



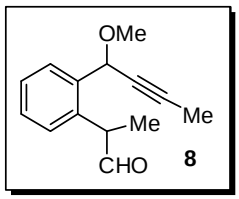
Yellow liquid ; IR (neat, cm^{-1}): 3071 (s), 2111 (s),1605 (s), 1466 (s), 1251 (s), 1151 (s), 1079 (s), 889 (s), 819 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.09 (s, 1 H), 7.05 (s, 1 H), 6.74 (s, 1 H), 6.72 (s, 1 H), 5.93 - 5.91 (m, 4 H), 4.20 - 4.19 (m, 1 H), 4.12 - 4.10 (m, 1 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 3.10 ($d_{a,b}$, J = 5.6 Hz, 1 H), 3.09 ($d_{a,b}$, J = 5.6 Hz, 1 H), 2.65 - 2.59 (m, 2 H), 1.90 (s, 3 H), 1.88 (s, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 147.4, 146.6 (2xC), 130.6 (2xC), 129.9, 129.8, 107.9, 107.6, 104.5 (2xCH), 100.9 (2xCH_2), 84.1, 83.6, 76.1, 75.9, 70.0 - 69.4 (m, 2 CD), 55.2, 55.0, 50.2, 50.0, 49.3, 49.1, 3.1 (2xCH_3); HRMS calcd for $C_{14}H_{13}DO_4$: 247.0955; found: 247.0950.

Spectral data for compound**(d_2-5o).**



Yellow liquid ; IR (neat, cm^{-1}): 3076 (s), 2112 (s),1600 (s), 1460 (s), 1252 (s), 1157 (s), 1072 (s), 892 (s), 819 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 7.08 (s, 1 H), 7.04 (s, 1 H), 6.73 (s, 1 H), 6.71 (s, 1 H), 5.91 - 5.90 (m, 4 H), 5.18 - 5.16 (m, 2 H), 4.18 (s, 1 H), 4.09 (s, 1 H), 3.35 (s, 3 H), 3.34 (s, 3 H), 1.89 (d, J = 2.2 Hz, 3 H), 1.87 (d, J = 2.2 Hz, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8 (2xC), 146.9 (2xC), 130.9 (2xC), 130.1 (2xC), 108.3, 108.0, 105.0, 104.9, 101.2 (2xCH_2), 84.5, 84.0, 76.3, 76.2, 70.5, 70.4, 55.7, 55.5, 49.5, 49.4, 3.6 (2xCH_3); HRMS calcd for $C_{14}H_{12}D_2O_4$: 248.1018; found: 248.0999.

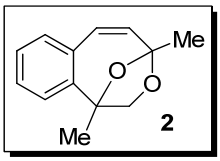
Spectral data for 2-(2-(1-methoxybut-2-ynyl)phenyl)propanal**(8).**



Yellow liquid ; IR (neat, cm^{-1}): 3035 (s), 2821 (s), 2717 (s), 2112 (s),1702 (s), 1600 (s), 1466 (s), 1151 (s), 1079 (s); ^1H NMR (400 MHz , $CDCl_3$): (1:1) Mixture of isomers: δ 9.67 (s, 1 H), 9.65 (s, 1 H), 7.35 - 7.20 (m, 8 H), 5.14 (d, J = 2.3 Hz, 1 H), 5.09 (d, J = 2.2 Hz, 1 H), 4.35 (q, J = 7.0 Hz, 1 H), 4.27 (q, J = 7.0 Hz, 1 H), 3.38 (s, 3 H), 3.37 (s, 3 H), 1.89 (d, J = 2.1 Hz, 3 H), 1.88 (d, J = 2.3 Hz, 3 H), 1.42 (d, J = 7.0 Hz, 3 H), 1.40 (d, J =

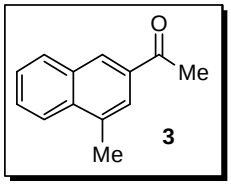
7.0 Hz, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 201.2, 137.6, 137.3, 137.2, 136.9, 129.1 (2xCH), 129.0, 128.9, 128.6, 128.3 (2xCH), 127.9, 127.4, 127.3, 85.2, 84.7, 72.5, 72.0, 56.0, 55.7, 48.4, 47.9, 15.1, 14.8, 3.6 (2xCH_3); $C_{14}H_{16}O_2$: 216.1150; found: 216.1153.

Spectral data for compound(**2**).



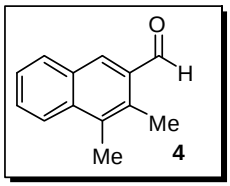
Colourless liquid ; IR (neat, cm^{-1}): 3070 (s), 2805 (s), 1582 (s), 1472 (s), 1021 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.30 - 7.21 (m, 4 H), 6.50 (d, *J* = 11.8 Hz, 1 H), 5.79 (d, *J* = 11.8 Hz, 1 H), 3.94 ($d_{a,b}$, *J* = 8.2 Hz, 1 H), 3.81 ($d_{a,b}$, *J* = 8.2 Hz, 1 H), 1.79 (s, 3 H), 1.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 144.4, 134.0, 133.0, 131.8, 131.3, 127.7, 127.6, 124.7, 107.8, 80.9, 76.5, 25.3, 23.0; HRMS calcd for $C_{13}H_{14}O_2$: 202.0994, found: 202.0996.

Spectral data for 1-(4-methylnaphthalen-2-yl)ethanone(**3**):

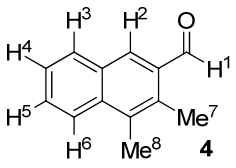


Colourless liquid ; IR (neat, cm^{-1}): 3070 (s), 2808 (s), 1752 (s), 1590 (s), 1472 (s); ^{1}H NMR (600 MHz, $CDCl_3$) : δ 8.31 (s, 1 H), 7.98 (dd, *J* = 8.4, 30.2 Hz, 1 H), 7.94 (dd, *J* = 6.8, 7.5 Hz, 1 H), 7.86 (s, 1H), 7.62 (t, *J* = 8.3 Hz, 1 H), 7.54 (t, *J* = 6.9 Hz, 1 H), 2.70 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 198.4, 134.9, 134.0, 133.5, 132.6, 130.2, 128.8, 128.3, 126.4, 124.1 (2xCH), 26.6, 19.4; HRMS calcd for $C_{13}H_{12}O_2$: 184.0888, found: 184.0891.

Spectral data for 3,4-dimethyl-2-naphthaldehyde(**4**).



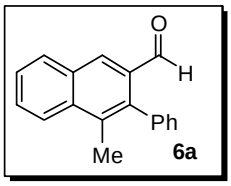
Colourless liquid ; IR (neat, cm^{-1}): 3078 (s), 2833 (s), 2809 (s), 2705 (s), 1730 (s), 1585 (s), 1452 (s); ^1H NMR (600 MHz, $CDCl_3$) : δ 10.33 (s, 1 H), 8.16 (s, 1 H), 8.06 (d, *J* = 8.5 Hz, 1 H), 7.93 (d, *J* = 8.1 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 2.76 (s, 3 H), 2.63 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 193.8, 135.1, 134.9, 133.5, 133.0, 132.5, 130.9, 130.0, 129.0, 125.6, 124.0, 15.5, 14.5; HRMS calcd for $C_{13}H_{12}O$: 184.0888, found: 184.0889.



4

irradiation	intensity increase
H^1 (δ 10.33)	H^2 (δ 8.16, 7.88%), Me^7 (δ 2.76, 1.52%),
H^2 (δ 8.16)	H^1 (δ 10.33, 9.58%), H^3 (δ 7.93, 3.62%),
H^6 (δ 8.06)	Me^8 (δ 2.63, 9.59%), H^5 (δ 7.63, 5.98%),
Me^7 (δ 2.76)	H^1 (δ 10.33, 1.35%), Me^8 (δ 2.63, 0.06%),
Me^8 (δ 2.63)	H^6 (δ 8.06, 3.07%), Me^7 (δ 2.76, 0.75%).

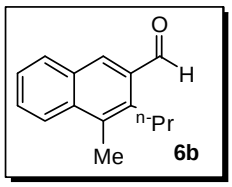
Spectral data for 4-methyl-3-phenyl-2-naphthaldehyde(**6a**).



6a

Yellow liquid ; IR (neat, cm^{-1}): 3079 (s), 3031 (s), 2831 (s), 2807 (s), 2707 (s), 1736 (s), 1580 (s), 1450 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 9.76 (s, 1 H), 8.41 (s, 1 H), 8.09 (d, *J* = 8.5 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.68 (t, *J* = 7.1 Hz, 1 H), 7.57 (t, *J* = 7.1 Hz, 1 H), 7.50 - 7.43 (m, 5 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.0, 139.4, 137.8, 135.2, 133.1, 132.2, 131.7, 130.7, 130.3 (2xCH), 129.0, 128.3 (2xCH), 127.6, 127.4, 126.5, 124.6, 15.9; HRMS calcd for $C_{18}H_{14}O$: 246.1045, found: 246.1048.

Spectral data for 4-methyl-3-propyl-2-naphthaldehyde(**6b**).

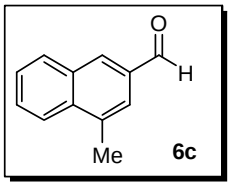


6b

Colourless liquid ; IR (neat, cm^{-1}): 3064 (s), 2830 (s), 2809 (s), 2705 (s), 1737 (s), 1585 (s), 1454 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 10.32 (s, 1 H), 8.18 (s, 1 H), 8.04 (d, *J* =

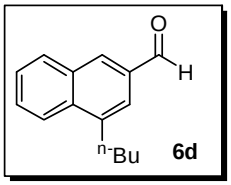
8.6 Hz, 1 H), 7.91 (d, *J* = 7.8 Hz, 1 H), 7.62 (t, *J* = 7.1 Hz, 1 H), 7.49 (t, *J* = 7.1 Hz, 1 H), 3.20 (t, *J* = 2.6 Hz, 2 H), 2.65 (s, 3 H), 1.65 - 1.56 (m, 2 H), 1.06 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.3, 137.3, 135.3, 134.6, 132.9, 132.5, 130.9, 130.0, 128.9, 125.6, 124.1, 30.5, 24.6, 14.3, 14.0; HRMS calcd for $C_{15}H_{16}O$: 212.1201, found: 212.1205.

Spectral data for 4-methyl-2-naphthaldehyde(**6c**).



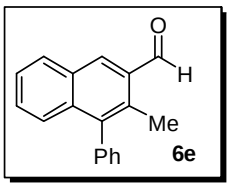
Colourless liquid ; IR (neat, cm^{-1}): 3055 (s), 2833 (s), 2809 (s), 2709 (s), 1740 (s), 1587 (s), 1455 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 10.10 (s, 1 H), 8.18 (s, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 7.7 Hz, 1 H), 7.78 (s, 1 H), 7.67 (t, *J* = 7.3 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 2.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 192.5, 135.9, 135.8, 133.6, 133.4, 132.7, 130.2, 129.0, 126.7,124.4, 122.8, 19.4; HRMS calcd for $C_{12}H_{10}O$: 170.0732, found: 170.0735.

Spectral data for 4-butyl-2-naphthaldehyde(**6d**).



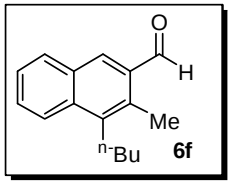
Colourless liquid ; IR (neat, cm^{-1}): 3055 (s), 2841 (s), 2808 (s), 2710 (s), 1737 (s), 1590 (s), 1451 (s); ^{1}H NMR (600 MHz, $CDCl_3$) : δ 10.11 (s, 1 H), 8.17 (s, 1 H), 8.08 (d, *J* = 8.5 Hz, 1 H), 7.99 (d, *J* = 7.9 Hz, 1 H), 7.78 (s, 1 H), 7.65 (t, *J* = 7.5 Hz, 1 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 3.09 (t, *J* = 7.8 Hz, 2 H), 1.75 - 1.71 (m, 2 H), 1.47 - 1.43 (m, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 192.5, 140.5, 135.2, 133.7, 133.3, 133.1, 130.4, 128.9, 126.5, 124.2, 122.1, 32.7, 32.6, 22.8, 13.9; HRMS calcd for $C_{15}H_{16}O$: 212.1201, found: 212.1203.

Spectral data for 3-methyl-4-phenyl-2-naphthaldehyde(**6e**).



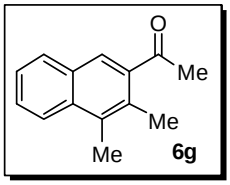
Yellow liquid ; IR (neat, cm^{-1}): 3088 (s), 3033 (s), 2831 (s), 2809 (s), 2708 (s), 1736 (s), 1593 (s), 1456 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 10.40 (s, 1 H), 8.35 (s, 1 H), 7.97 (d, *J* = 7.3 Hz, 1 H), 7.52 - 7.43 (m, 5 H), 7.34 (d, *J* = 7.9 Hz, 1 H), 7.23 - 7.21 (m, 2 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.4, 140.3, 138.9, 135.6, 135.4, 132.9, 132.7, 130.9, 130.1 (2xCH), 129.3, 129.0, 128.5 (2xCH), 127.4, 126.6, 125.9, 17.1; HRMS calcd for $C_{18}H_{14}O$: 246.1045, found: 246.1046.

Spectral data for 4-butyl-3-methyl-2-naphthaldehyde(**6f**).

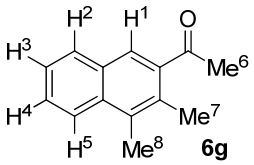


Colourless liquid ; IR (neat, cm^{-1}): 3052 (s), 2843 (s), 2804 (s), 2710 (s), 1734 (s), 1590 (s), 1451 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 10.32 (s, 1 H), 8.14 (s, 1 H), 8.03 (d, *J* = 8.6 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.62 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 3.09 (t, *J* = 7.1 Hz, 2 H), 2.75 (s, 3 H), 1.60 - 1.51 (m, 4 H), 0.99 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.8, 138.3, 135.0, 134.5, 133.1, 132.1, 131.2, 130.1, 129.0, 125.5, 124.0, 32.1, 28.0, 23.2, 15.1, 13.9; HRMS calcd for $C_{16}H_{18}O$: 226.1358, found: 226.1359.

Spectral data for 1-(3,4-dimethylnaphthalen-2-yl)ethanone(**6g**).



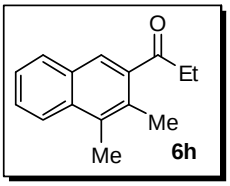
Colourless liquid ; IR (neat, cm^{-1}): 3071 (s), 2805 (s), 1742 (s), 1595 (s), 1472 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.02 (d, *J* = 8.6 Hz, 1 H), 7.89 (s, 1 H), 7.82 (d, *J* = 8.2 Hz, 1 H), 7.55 (dt, *J* = 1.2 , 7.6 Hz, 1 H), 7.45 (dt, *J* = 0.76, 7.8 Hz, 1 H), 2.66 (s, 3 H), 2.61 (s, 3 H), 2.51 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 203.8, 138.9, 133.7, 133.4, 130.7, 130.5, 129.1, 127.6, 126.5, 125.4, 123.8, 30.4, 17.4, 14.7; HRMS calcd for $C_{14}H_{14}O$: 198.1045, found: 198.1043.



6g

irradiation	intensity increase
H^2 (δ 7.82)	H^1 (δ 7.89, 1.04%),
H^1 (δ 7.89)	Me^6 (δ 2.66, 4.28%),
H^5 (δ 8.02)	Me^8 (δ 2.61, 2.24%),
Me^8 (δ 2.61)	H^5 (δ 8.02, 3.50%),
Me^6 (δ 2.66)	H^1 (δ 7.89, 1.76%).

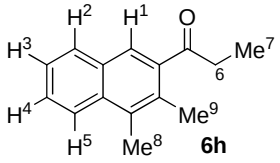
Spectral data for 1-(3,4-dimethylnaphthalen-2-yl)propan-1-one(**6h**).



6h

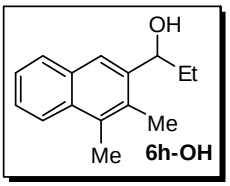
Colourless liquid ; IR (neat, cm^{-1}): 3076 (s), 2803 (s), 1745 (s), 1599 (s), 1474 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.01 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 8.9 Hz, 1 H), 7.78 (s, 1 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 1 H), 2.97 (q, *J* = 7.1 Hz, 2 H), 2.59 (s, 3 H), 2.46 (s, 3 H), 1.25 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 207.3, 139.3, 133.3, 133.1, 130.7, 130.0, 128.9, 127.2, 125.2, 125.1, 123.7, 35.9, 17.2, 14.6, 8.3; HRMS calcd for $C_{15}H_{16}O$: 212.1201, found: 212.1203.

irradiation	intensity increase
H^1 (δ 7.78)	CH_2^6 (δ 2.97, 3.47%),
H^5 (δ 8.01)	Me^8 (δ 2.59, 8.73%), H^4 (δ 7.54, 4.42%),
CH_2^6 (δ 2.97)	H^1 (δ 7.78, 2.99 %), Me^7 (δ 1.25, 2.64%),
Me^8 (δ 2.59)	H^5 (δ 8.01, 3.59%).



6h

Spectral data for 1-(3,4-dimethylnaphthalen-2-yl)propan-1-ol(**6h-OH**).

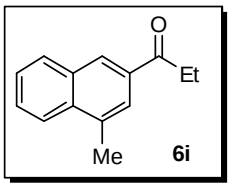


6h-OH

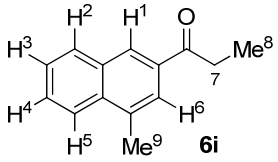
White Solid ; IR (neat, cm^{-1}): 3555 (br), 3072 (s), 2808 (s), 1592 (s), 1477 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.00 (d, *J* = 8.4 Hz, 1 H), 7.82 (s, 1 H), 7.79 (d, *J* = 7.9 Hz, 1 H), 7.47 - 7.38 (m, 2 H), 5.03 (dd, *J* = 4.5, 3.3 Hz, 1 H), 2.61 (s, 3 H), 2.42 (s, 3 H), 1.91 -

1.73 (m, 2 H), 1.03 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 141.2, 131.9, 131.8 (2xC), 130.8, 128.4, 125.5, 124.6, 123.6, 122.3, 72.9, 30.9, 15.5, 14.8, 10.4; HRMS calcd for $C_{15}H_{18}O$: 214.1358, found: 214.1360.

Spectral data for 1-(4-methylnaphthalen-2-yl)propan-1-one(**6i**).

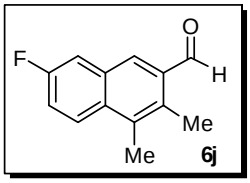


Colourless liquid ; IR (neat, cm^{-1}): 3081 (s), 2803 (s), 1749 (s), 1598 (s), 1471 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.31 (s, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 7.94 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 0.5 Hz, 1 H), 7.61 (dt, J = 1.4, 7.6 Hz, 1 H), 7.53 (dt, J = 1.2, 7.5 Hz, 1 H), 3.11 (q, J = 7.2 Hz, 2 H), 2.71 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 201.0, 135.0, 134.8, 133.8, 132.7, 130.1, 128.2, 128.1, 126.3, 124.2, 124.1, 31.7, 19.4, 8.4; HRMS calcd for $C_{14}H_{14}O$: 198.1045, found: 198.1047.



irradiation	intensity increase
H^1 (δ 8.31)	H^2 (δ 7.94, 2.31%), CH_2^7 (δ 3.11, 4.16%),
H^6 (δ 7.86)	CH_2^7 (δ 3.11, 1.37%), Me^9 (δ 2.71, 3.18%),
CH_2^7 (δ 3.11)	Me^9(δ 2.71, 4.80%), Me^8 (δ 1.26, 3.98%), H^1 (δ 8.31, 2.23%), H^6 (δ 7.86, 1.15%),
Me^8 (δ1.26)	CH_2^7 (δ 3.11, 1.22%),
Me^9 (δ 2.71)	H^5 (δ 7.99, 1.67%),H^6 (δ 7.86, 1.14%).

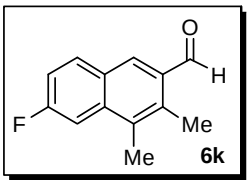
Spectral data for 7-fluoro-3,4-dimethyl-2-naphthaldehyde(**6j**).



Colourless liquid ; IR (neat, cm^{-1}): 3052 (s), 2843 (s), 2809 (s), 2710 (s), 1733 (s), 1597 (s), 1451 (s), 1115 (s); ^{1}H NMR (600 MHz, $CDCl_3$) : δ 10.33 (s, 1 H), 8.09 (s, 1 H), 8.06 (dd, J = 5.3, 6.2 Hz, 1 H), 7.53 (dd, J = 2.7, 9.1 Hz, 1 H), 7.39 (dt, J = 1.7, 8.0 Hz, 1 H), 2.74 (s, 3 H), 2.63 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 193.6, 160.2 (d, J_{CF} = 246.0 Hz), 133.9, 133.8, 133.5, 133.4, 132.1, 131.8 (d, J_{CF} = 14.7 Hz), 126.7 (d, J_{CF} = 8.5 Hz),

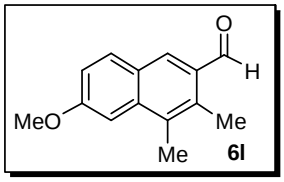
119.0 (d, J_{CF} = 24.7 Hz), 112.6 (d, J_{CF} = 19.9 Hz), 15.4, 14.7; HRMS calcd for $C_{13}H_{11}FO$: 202.0794, found: 202.0796.

Spectral data for 6-fluoro-3,4-dimethyl-2-naphthaldehyde(**6k**).

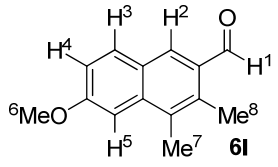


Colourless liquid ; IR (neat, cm^{-1}): 3055 (s), 2844 (s), 2809 (s), 2712 (s), 1739 (s), 1598 (s), 1455 (s), 1118 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 10.29 (s, 1 H), 8.12 (s, 1 H), 7.91 (dd, *J* = 6.0, 9.0 Hz, 1 H), 7.62 (dd, *J* = 2.3, 11.5 Hz, 1 H), 7.25 (dt, *J* = 2.2, 8.5 Hz, 1 H), 2.74 (s, 3 H), 2.55 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.3, 162.8 (d, J_{CF} = 248.0 Hz), 136.5 (d, J_{CF} = 10.0 Hz), 134.4, 133.7 (2xC), 132.9, 132.6 (d, J_{CF} = 10 Hz), 127.9, 116.0 (d, J_{CF} = 25.0 Hz), 108.1 (d, J_{CF} = 22.0 Hz), 15.6, 14.6; HRMS calcd for $C_{13}H_{11}FO$: 202.0794, found: 202.0797.

Spectral data for 6-methoxy-3,4-dimethyl-2-naphthaldehyde(**6l**).

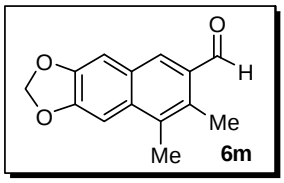


Colourless liquid ; IR (neat, cm^{-1}): 3059 (s), 2844 (s), 2812 (s), 2707 (s), 1735 (s), 1590 (s), 1456 (s), 1218 (s); ^1H NMR (400 MHz, $CDCl_3$) : δ 10.24 (s, 1 H), 8.02 (s, 1 H), 7.80 (d, *J* = 8.9 Hz, 1 H), 7.24 (s, 1 H), 7.14 (dd, *J* = 2.4, 8.9 Hz, 1 H), 3.94 (s, 3 H), 2.74 (s, 3 H), 2.55 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.4, 160.3, 136.8, 134.8, 133.2, 131.8, 131.6, 131.1, 126.2, 118.0, 102.9, 55.3, 15.6, 14.5; HRMS calcd for $C_{14}H_{14}O_2$: 214.0994, found: 214.0998.



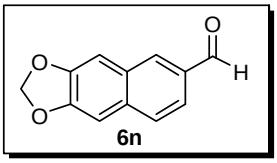
irradiation	intensity increase
H^2 (δ 8.05)	H^1 (δ 10.24, 2.32%), H^3 (δ 7.80, 1.51%),
H^3 (δ7.80)	H^2 (δ 8.05, 1.37%), H^4 (δ 7.14, 4.05%),
Me^7 (δ 2.55)	H^5 (δ 7.24, 0.93%), Me^8 (δ 2.74, 0.90%),
Me^8 (δ 2.74)	H^1 (δ 10.24, 0.33%).

Spectral data for 7,8-dimethylnaphtho[2,3-*d*][1,3]dioxole-6-carbaldehyde(**6m**).



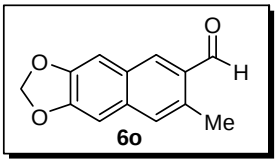
Colourless liquid ; IR (neat, cm^{-1}): 3058 (s), 2846 (s), 2811 (s), 2710 (s), 1739 (s), 1597 (s), 1459 (s), 1222 (s);^{1}H NMR (400 MHz, $CDCl_3$) : δ 10.23 (s, 1 H), 7.90 (s, 1 H), 7.27 (s, 1 H), 7.11 (s, 1 H), 6.04 (s, 2 H), 2.68 (s, 3 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 193.4, 150.4, 147.1, 133.1, 132.9, 132.4, 131.6, 131.5, 127.8, 105.2, 101.4, 100.8, 15.2, 14.8; HRMS calcd for $C_{14}H_{12}O_3$: 228.0786, found: 228.0789.

Spectral data for naphtho[2,3-*d*][1,3]dioxde-6-carbaldehyde(**6n**).



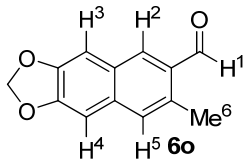
Colourless liquid ; IR (neat, cm^{-1}): 3066 (s), 2846 (s), 2711 (s), 1731 (s), 1592 (s), 1457 (s), 1225 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 10.05 (s, 1 H), 8.12 (d, J = 0.6 Hz, 1 H), 7.78 (dd, J = 1.6, 8.5 Hz, 1 H), 7.72 (d, J = 8.3 Hz, 1 H), 7.23 (s, 1 H), 7.15 (s, 1 H), 6.08 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 192.1, 150.2, 148.5, 134.5, 132.9, 132.5, 129.8, 127.9, 122.2, 105.1, 104.1, 101.6; HRMS calcd for $C_{12}H_8O_3$: 200.0473, found: 232.0479.

Spectral data for 7-methylnaphtho[2,3-*d*][1,3]dioxde-6-carbaldehyde(**6o**).



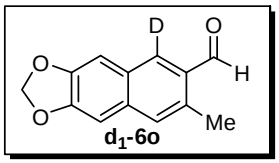
Colourless liquid ; IR (neat, cm^{-1}): 3049 (s), 2846 (s), 2811 (s), 2714 (s), 1732 (s), 1599 (s), 1451 (s), 1224 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 10.23 (s, 1 H), 8.07 (s, 1 H), 7.44 (s, 1 H), 7.17 (s, 1 H), 7.04 (s, 1 H), 6.05 (s, 2 H), 2.71 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 192.9, 150.3, 147.8, 134.4, 134.1, 133.8, 131.5, 129.1, 128.0, 104.7, 103.2, 101.4, 20.0; HRMS calcd for $C_{13}H_{10}O_3$: 214.063, found: 214.066.

irradiation	intensity increase
H^1 (δ 10.23)	H^2 (δ 8.07, 1.59%),
H^2 (δ 8.07)	H^1 (δ 10.23, 1.77%), H^3 (δ 7.17, 1.28%),
H^5 (δ 7.44)	H^4 (δ 7.04, 1.98%), Me^6 (δ 2.71, 2.56%),
Me^6 (δ 2.71)	H^1 (δ 10.23, 0.23%), H^5 (δ 7.44, 0.48%).



6o

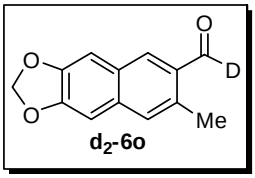
Spectral data for compound(**d_1-6o**).



d_1-6o

Yellow liquid ; IR (neat, cm^{-1}): 3042 (s), 2849 (s), 2817 (s), 2711 (s), 1735 (s), 1596 (s), 1459 (s), 1220 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 10.22 (s, 1 H), 7.42 (s, 1 H), 7.15 (s, 1 H), 7.03 (s, 1 H), 6.04 (s, 2 H), 2.70 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 192.81, 150.3, 147.8, 134.1 (2xC), 133.8, 131.4, 129.0, 128.0, 104.6, 103.2, 101.4, 19.9; HRMS calcd for $C_{13}H_9DO_3$: 215.0693, found: 215.0695.

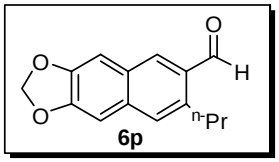
Spectral data for compound(**d_2-6o**).



d_2-6o

Yellow liquid ; IR (neat, cm^{-1}): 3049 (s), 2847 (s), 2812 (s), 2717 (s), 1741 (s), 1599 (s), 1453 (s), 1222 (s); ^{1}H NMR (600 MHz, $CDCl_3$) : δ 8.07 (s, 1 H), 7.44 (s, 1 H), 7.17 (s, 1 H), 7.04 (s, 1 H), 6.05 (s, 2 H), 2.71 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 192.7 (t, $J_{C\text{-}D}$ = 21 Hz), 150.3, 147.9, 134.3, 134.2, 133.9, 131.5, 129.1, 128.1, 104.7, 103.2, 101.4, 19.9; HRMS calcd for $C_{13}H_9DO_3$: 215.0693, found: 215.0698.

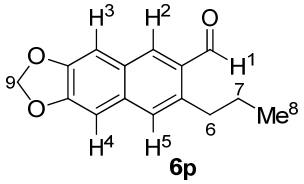
Spectral data for 7-propylnaphtho[2,3-*d*][1,3]dioxde-6-carbaldehyde(**6p**).



6p

Colourless liquid ; IR (neat, cm^{-1}): 3056 (s), 2848 (s), 2816 (s), 2714 (s), 1740 (s), 1599 (s), 1453 (s), 1222 (s); ^{1}H NMR (600 MHz, $CDCl_3$) : δ 10.25 (s, 1 H), 8.11 (s, 1 H), 7.42

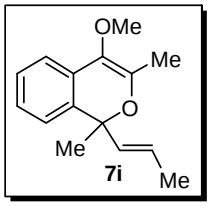
(s, 1 H), 7.17 (s, 1 H), 7.06 (s, 1 H), 6.05 (s, 2 H), 3.05 (t, *J* = 1.4 Hz, 2 H), 1.68 - 1.64 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 192.4, 150.2, 147.9, 139.0, 133.9, 131.0, 128.4, 128.3, 128.2, 104.7, 103.3, 101.4, 34.7, 25.1, 13.9; HRMS calcd for $C_{15}H_{14}O_3$: 242.0943, found: 242.0945.



6p

irradiation	intensity increase
H^1 (δ 10.25)	H^2 (δ 8.11, 1.89%),
H^2 (δ 8.11)	H^1 (δ 10.25, 2.45%), H^3 (δ 7.17, 1.63%),
H^3 (δ 7.17)	H^1 (δ 10.25, 1.68%), H^2 (δ 8.11, 2.53%), CH_2^9 (δ 6.06, 2.61%),
CH_2^6(δ 3.05)	H^1 (δ 10.25, 0.67%), H^5 (δ 7.45, 0.59%), CH_2^7(δ 1.66, 1.63%), Me^8(δ 0.98, 0.67%).

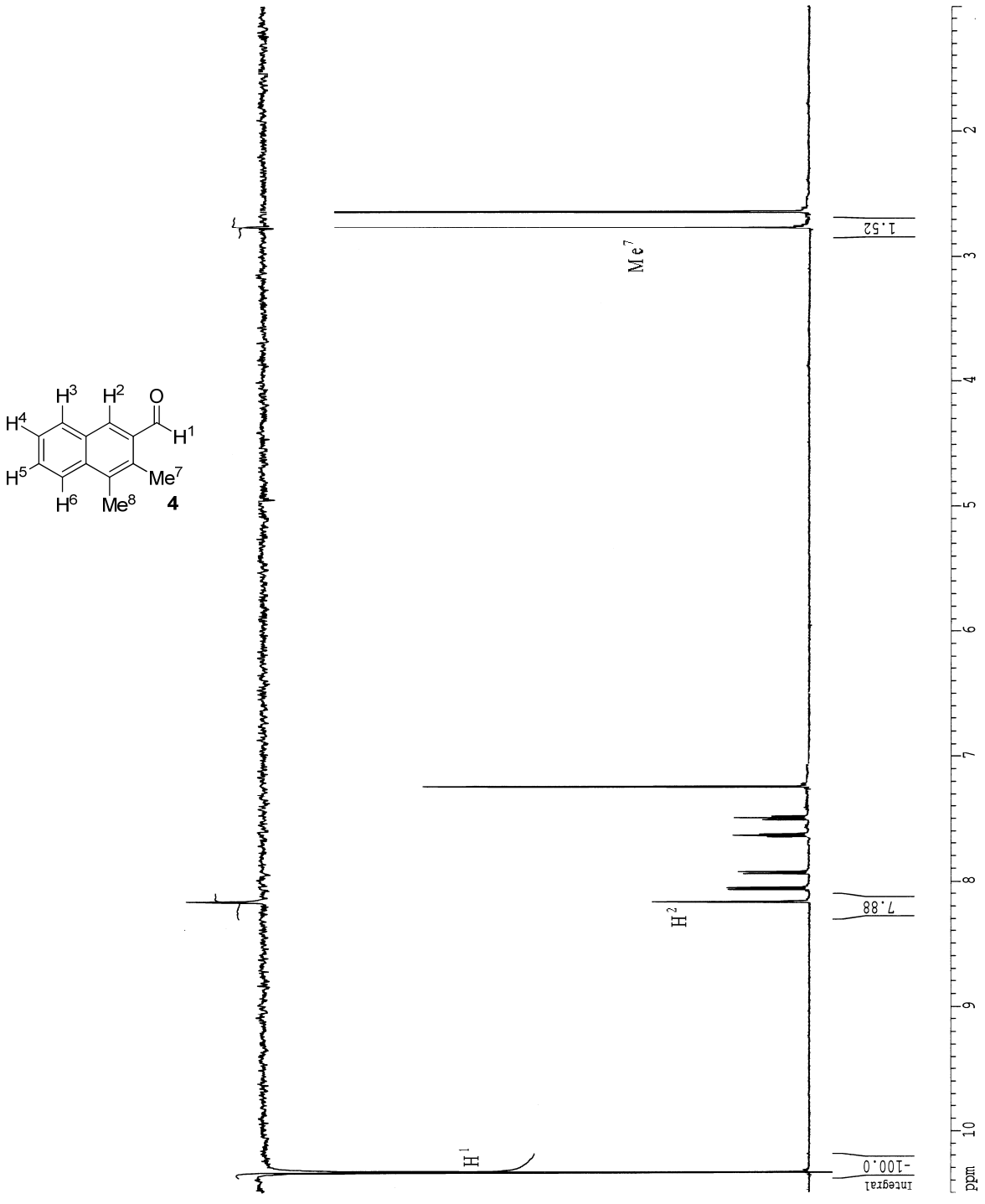
Spectral data for (*E*)-4-methoxy-1,3-dimethyl-1-(prop-1-enyl)-1*H*-isochromene(**7i**).

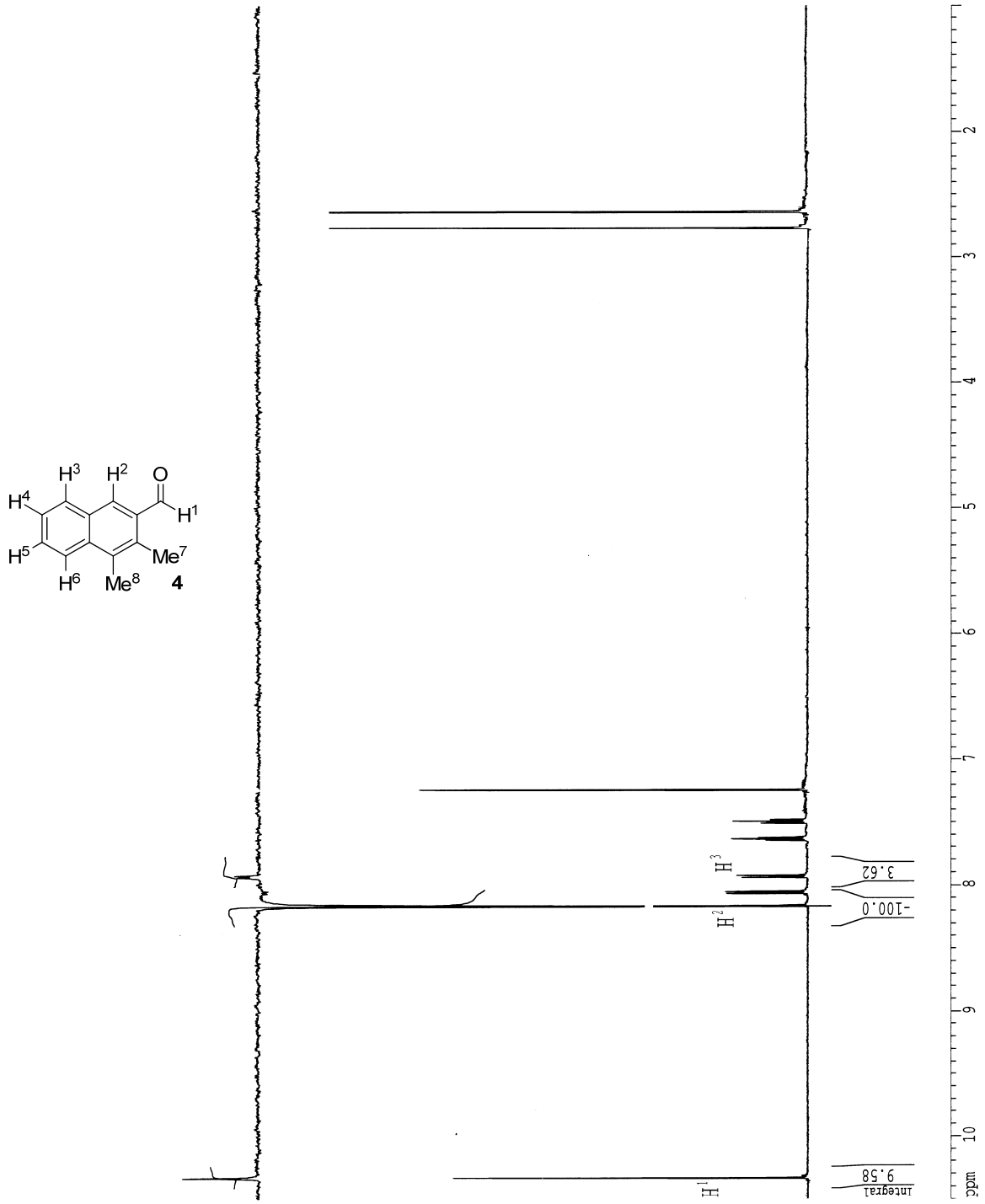


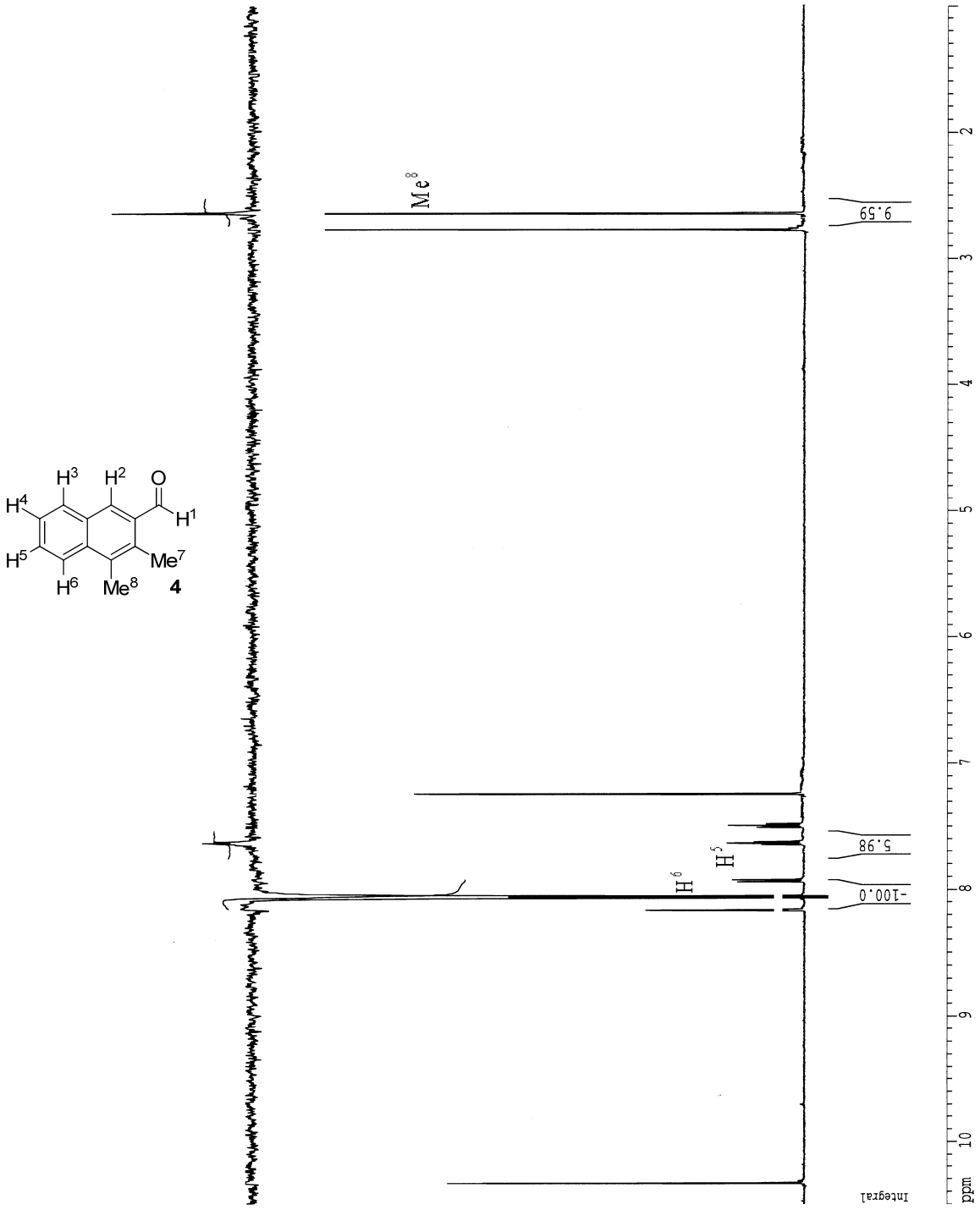
7i

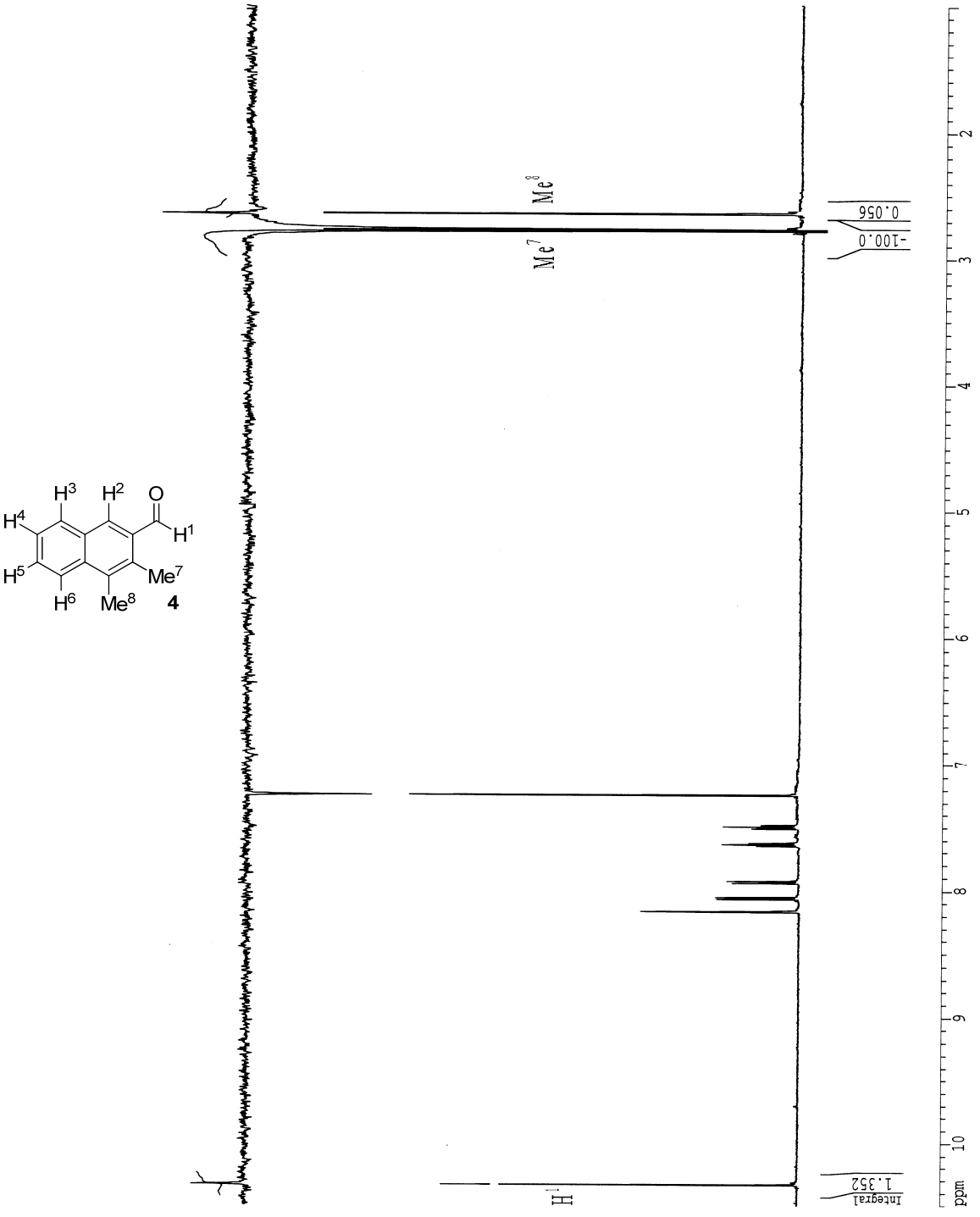
Colourless liquid ; IR (neat, cm^{-1}): 3068 (s), 3020 (s), 2844 (s), 2819 (s), 1621(s), 1589 (s), 1452 (s), 1221 (s); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.26 - 7.19 (m, 2 H), 7.13 (dt, *J* = 1.7, 7.5 Hz, 1 H), 7.01 (dd, *J* = 0.7, 7.4 Hz, 1 H), 5.65 - 5.60 (m, 1 H), 5.43 - 5.34 (m, 1 H), 3.60 (s, 3 H), 1.94 (s, 3 H), 1.66 (t, *J* = 1.6 Hz, 3 H), 1.65 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) : δ 142.6, 136.0, 134.4, 128.4 (2xC), 127.4, 126.1 (2xCH), 123.9, 118.5, 79.3, 60.4, 25.0, 17.6, 14.4; HRMS calcd for $C_{15}H_{18}O_2$: 230.1307, found: 230.1310.

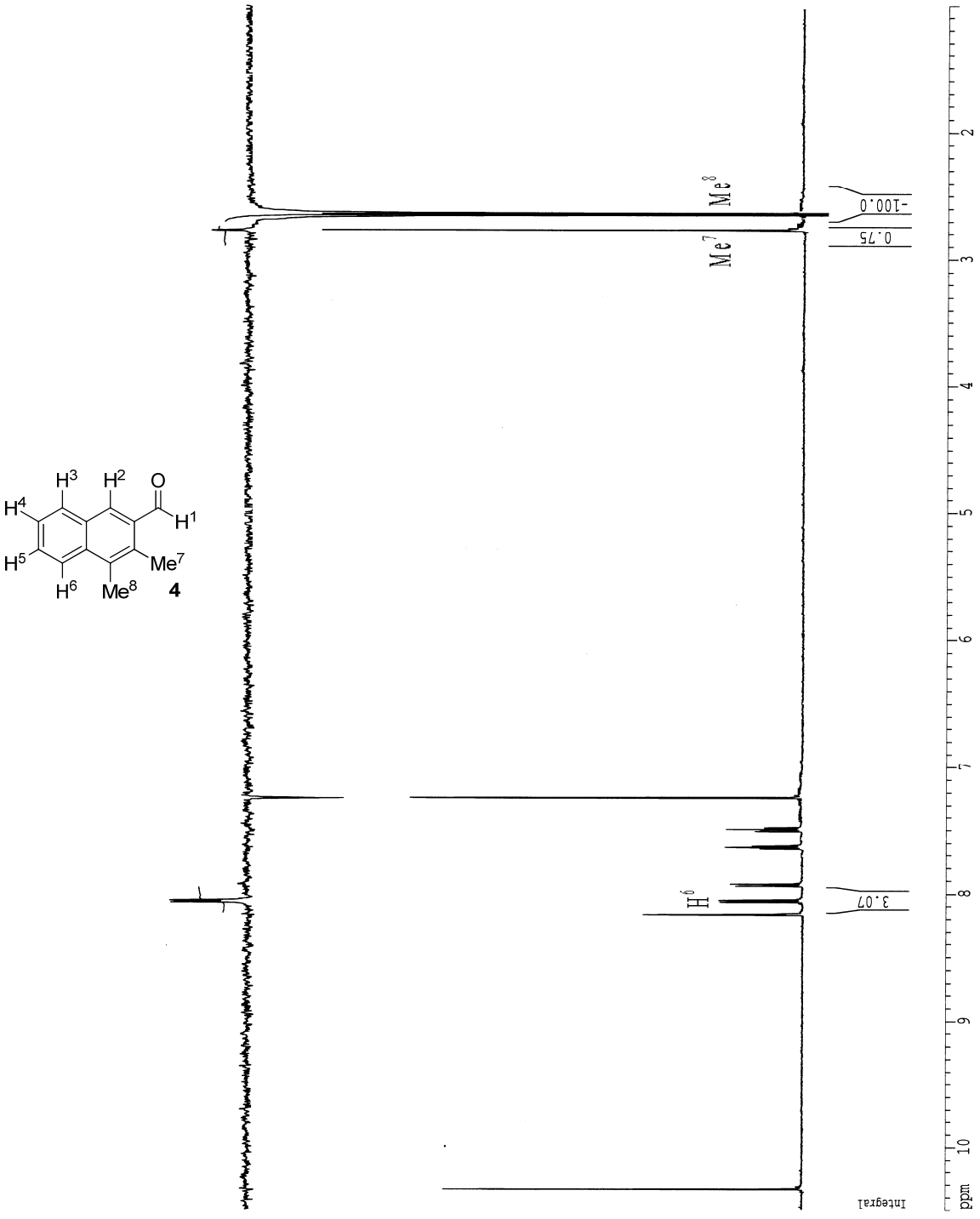
(VI) NOE spectra for compound 4.




H3
H2
O
H4
H1
H5
Me7
H6
Me8
4
H3
H2
H1
3.62
-100.0
9.58
integral
ppm


H3
H2
O
H4
H1
H5
Me7
H6
Me8
4
Me8
H6
H5
9.59
5.98
100.0
Integral
ppm


H3
H2
O
H4
H1
H5
Me7
H6
Me8
4
Me8
Me7
H1
0.056
-100.0
1.352
Integral
ppm


H3
H2
O
H4
H1
H5
Me7
H6
Me8
4
Me8
Me7
H6
-100.0
0.75
3.07
Integral
ppm

(VII) X-Ray crystal structure and data of compound 6h-OH.

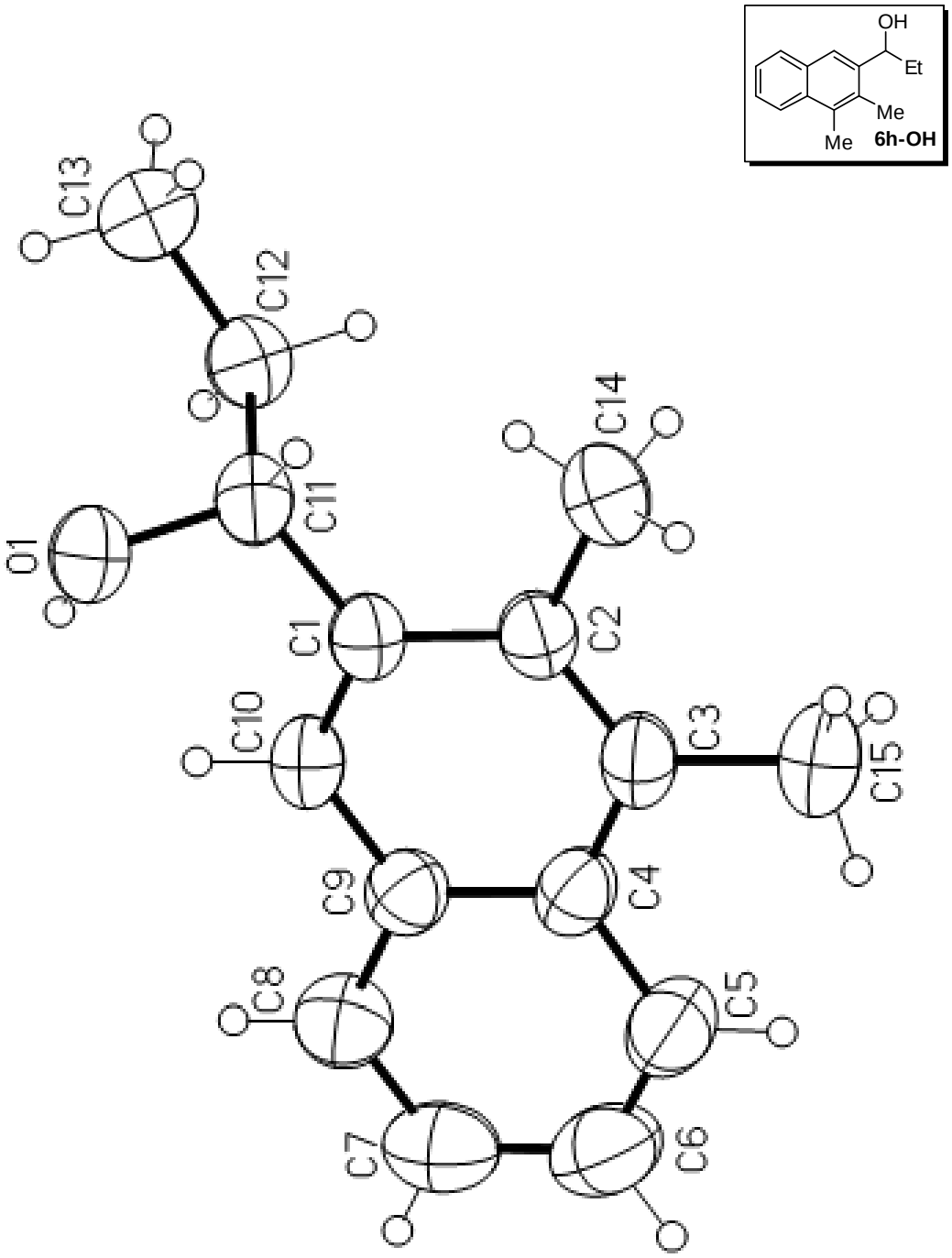


Figure 1

Table 1. Crystal data and structure refinement for 090725_0M.

Identification code	090725_0m	
Empirical formula	C15 H18 O	
Formula weight	214.29	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.5257(13) Å	α= 86.572(7)°.
	b = 11.462(2) Å	β= 75.395(6)°.
	c = 13.094(2) Å	γ = 86.188(6)°.
Volume	1234.2(4) $Å^3$	
Z	4	
Density (calculated)	1.153 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	464	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.61 to 26.40°.	
Index ranges	-10<=h<=10, -14<=k<=14, 0<=l<=16	
Reflections collected	5034	
Independent reflections	5034 [R(int) = 0.0455]	
Completeness to theta = 26.40°	99.1 %	
Absorption correction	Empirical	
Max. and min. transmission	0.745372 and 0.668054	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5034 / 0 / 298	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0622, wR2 = 0.1491	
R indices (all data)	R1 = 0.1429, wR2 = 0.1911	
Largest diff. peak and hole	0.215 and -0.226 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 090725_0M. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5410(3)	2632(2)	1215(2)	47(1)
C(2)	5857(3)	1520(2)	1647(2)	49(1)
C(3)	5135(3)	1198(2)	2681(2)	53(1)
C(4)	3951(3)	1955(2)	3322(2)	52(1)
C(5)	3159(4)	1691(3)	4401(2)	72(1)
C(6)	2035(4)	2440(3)	4977(3)	80(1)
C(7)	1586(4)	3501(3)	4534(3)	74(1)
C(8)	2313(3)	3801(3)	3508(2)	64(1)
C(9)	3506(3)	3050(2)	2885(2)	51(1)
C(10)	4266(3)	3352(2)	1826(2)	51(1)
C(11)	6165(3)	3004(2)	74(2)	51(1)
C(12)	5192(3)	2623(2)	-664(2)	58(1)
C(13)	5987(4)	2891(3)	-1826(2)	73(1)
C(14)	7104(4)	705(2)	969(2)	70(1)
C(15)	5580(4)	19(3)	3155(3)	81(1)
C(16)	8590(3)	3954(2)	2264(2)	44(1)
C(17)	7772(3)	3639(2)	3324(2)	49(1)
C(18)	8126(3)	2563(3)	3768(2)	52(1)
C(19)	9293(3)	1755(2)	3174(2)	49(1)
C(20)	9730(4)	633(3)	3572(2)	66(1)
C(21)	10855(4)	-100(3)	2977(3)	74(1)
C(22)	11644(4)	231(3)	1944(3)	69(1)
C(23)	11261(3)	1286(2)	1530(2)	60(1)
C(24)	10094(3)	2077(2)	2121(2)	47(1)
C(25)	9712(3)	3183(2)	1699(2)	47(1)
C(26)	8290(3)	5160(2)	1783(2)	50(1)
C(27)	9369(3)	6052(2)	2041(2)	59(1)
C(28)	8953(4)	7304(3)	1706(3)	86(1)
C(29)	6513(3)	4487(3)	3959(2)	71(1)
C(30)	7270(4)	2234(3)	4906(2)	82(1)
O(2)	8512(2)	5176(2)	668(1)	62(1)

O(1)	6323(2)	4244(2)	-76(2)	63(1)

Table 3. Bond lengths [Å] and angles [°] for 090725_0M.

C(1)-C(10)	1.360(4)
C(1)-C(2)	1.431(3)
C(1)-C(11)	1.517(4)
C(2)-C(3)	1.379(4)
C(2)-C(14)	1.510(4)
C(3)-C(4)	1.422(4)
C(3)-C(15)	1.518(4)
C(4)-C(9)	1.417(4)
C(4)-C(5)	1.427(4)
C(5)-C(6)	1.352(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.388(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.364(4)
C(7)-H(7)	0.9300
C(8)-C(9)	1.410(4)
C(8)-H(8)	0.9300
C(9)-C(10)	1.408(4)
C(10)-H(10)	0.9300
C(11)-O(1)	1.434(3)
C(11)-C(12)	1.522(4)
C(11)-H(11)	0.9800
C(12)-C(13)	1.524(4)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600

C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(25)	1.361(3)
C(16)-C(17)	1.425(3)
C(16)-C(26)	1.517(3)
C(17)-C(18)	1.379(4)
C(17)-C(29)	1.515(4)
C(18)-C(19)	1.423(4)
C(18)-C(30)	1.522(4)
C(19)-C(24)	1.414(3)
C(19)-C(20)	1.422(4)
C(20)-C(21)	1.352(4)
C(20)-H(20)	0.9300
C(21)-C(22)	1.393(4)
C(21)-H(21)	0.9300
C(22)-C(23)	1.349(4)
C(22)-H(22)	0.9300
C(23)-C(24)	1.410(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.404(3)
C(25)-H(25)	0.9300
C(26)-O(2)	1.423(3)
C(26)-C(27)	1.527(4)
C(26)-H(26)	0.9800
C(27)-C(28)	1.521(4)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600

C(30)-H(30C)	0.9600
O(2)-H(2)	0.8200
O(1)-H(1)	0.8200

C(10)-C(1)-C(2)	119.6(2)
C(10)-C(1)-C(11)	119.6(2)
C(2)-C(1)-C(11)	120.7(2)
C(3)-C(2)-C(1)	119.5(2)
C(3)-C(2)-C(14)	120.4(2)
C(1)-C(2)-C(14)	120.1(3)
C(2)-C(3)-C(4)	120.8(2)
C(2)-C(3)-C(15)	120.5(3)
C(4)-C(3)-C(15)	118.7(3)
C(9)-C(4)-C(3)	119.3(2)
C(9)-C(4)-C(5)	116.5(3)
C(3)-C(4)-C(5)	124.2(3)
C(6)-C(5)-C(4)	122.0(3)
C(6)-C(5)-H(5)	119.0
C(4)-C(5)-H(5)	119.0
C(5)-C(6)-C(7)	121.0(3)
C(5)-C(6)-H(6)	119.5
C(7)-C(6)-H(6)	119.5
C(8)-C(7)-C(6)	119.5(3)
C(8)-C(7)-H(7)	120.3
C(6)-C(7)-H(7)	120.3
C(7)-C(8)-C(9)	121.2(3)
C(7)-C(8)-H(8)	119.4
C(9)-C(8)-H(8)	119.4
C(10)-C(9)-C(8)	121.7(3)
C(10)-C(9)-C(4)	118.4(3)
C(8)-C(9)-C(4)	119.8(3)
C(1)-C(10)-C(9)	122.3(2)
C(1)-C(10)-H(10)	118.8
C(9)-C(10)-H(10)	118.8
O(1)-C(11)-C(1)	112.6(2)
O(1)-C(11)-C(12)	108.5(2)

C(1)-C(11)-C(12)	111.6(2)
O(1)-C(11)-H(11)	108.0
C(1)-C(11)-H(11)	108.0
C(12)-C(11)-H(11)	108.0
C(11)-C(12)-C(13)	113.2(2)
C(11)-C(12)-H(12A)	108.9
C(13)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12B)	108.9
C(13)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(2)-C(14)-H(14A)	109.5
C(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(3)-C(15)-H(15A)	109.5
C(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(25)-C(16)-C(17)	119.3(2)
C(25)-C(16)-C(26)	119.9(2)
C(17)-C(16)-C(26)	120.7(2)
C(18)-C(17)-C(16)	119.9(2)
C(18)-C(17)-C(29)	120.3(2)
C(16)-C(17)-C(29)	119.8(3)
C(17)-C(18)-C(19)	120.7(2)
C(17)-C(18)-C(30)	119.9(3)

C(19)-C(18)-C(30)	119.4(3)
C(24)-C(19)-C(20)	116.9(3)
C(24)-C(19)-C(18)	118.9(2)
C(20)-C(19)-C(18)	124.2(3)
C(21)-C(20)-C(19)	121.9(3)
C(21)-C(20)-H(20)	119.0
C(19)-C(20)-H(20)	119.0
C(20)-C(21)-C(22)	120.5(3)
C(20)-C(21)-H(21)	119.7
C(22)-C(21)-H(21)	119.7
C(23)-C(22)-C(21)	119.6(3)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(22)-C(23)-C(24)	121.7(3)
C(22)-C(23)-H(23)	119.2
C(24)-C(23)-H(23)	119.2
C(25)-C(24)-C(23)	121.9(2)
C(25)-C(24)-C(19)	118.8(2)
C(23)-C(24)-C(19)	119.3(2)
C(16)-C(25)-C(24)	122.4(2)
C(16)-C(25)-H(25)	118.8
C(24)-C(25)-H(25)	118.8
O(2)-C(26)-C(16)	113.4(2)
O(2)-C(26)-C(27)	108.7(2)
C(16)-C(26)-C(27)	111.6(2)
O(2)-C(26)-H(26)	107.6
C(16)-C(26)-H(26)	107.6
C(27)-C(26)-H(26)	107.6
C(28)-C(27)-C(26)	113.5(2)
C(28)-C(27)-H(27A)	108.9
C(26)-C(27)-H(27A)	108.9
C(28)-C(27)-H(27B)	108.9
C(26)-C(27)-H(27B)	108.9
H(27A)-C(27)-H(27B)	107.7
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5

H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(17)-C(29)-H(29A)	109.5
C(17)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(17)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(18)-C(30)-H(30A)	109.5
C(18)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(18)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(26)-O(2)-H(2)	109.5
C(11)-O(1)-H(1)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 090725_0M. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	48(2)	42(2)	52(2)	2(1)	-14(1)	-5(1)
C(2)	52(2)	42(2)	56(2)	0(1)	-18(1)	-4(1)
C(3)	59(2)	44(2)	62(2)	8(1)	-27(2)	-8(1)
C(4)	57(2)	53(2)	49(2)	6(1)	-20(1)	-13(1)
C(5)	91(2)	69(2)	58(2)	11(2)	-23(2)	-14(2)
C(6)	89(2)	95(3)	54(2)	-3(2)	-10(2)	-15(2)
C(7)	68(2)	87(3)	65(2)	-19(2)	-7(2)	-6(2)
C(8)	62(2)	66(2)	63(2)	-6(2)	-15(2)	-4(2)
C(9)	52(2)	50(2)	51(2)	0(1)	-14(1)	-8(1)
C(10)	55(2)	42(2)	57(2)	6(1)	-17(1)	0(1)

C(11)	50(2)	44(2)	57(2)	4(1)	-11(1)	-2(1)
C(12)	67(2)	50(2)	58(2)	-1(1)	-15(2)	-9(1)
C(13)	91(2)	72(2)	56(2)	-3(2)	-18(2)	-4(2)
C(14)	80(2)	52(2)	76(2)	-2(2)	-20(2)	9(2)
C(15)	104(3)	60(2)	79(2)	17(2)	-27(2)	2(2)
C(16)	39(1)	51(2)	43(2)	-6(1)	-7(1)	-4(1)
C(17)	42(1)	63(2)	41(2)	-12(1)	-3(1)	-6(1)
C(18)	49(2)	68(2)	38(2)	0(1)	-4(1)	-15(1)
C(19)	52(2)	50(2)	47(2)	4(1)	-14(1)	-9(1)
C(20)	77(2)	65(2)	58(2)	13(2)	-19(2)	-13(2)
C(21)	95(2)	53(2)	78(2)	5(2)	-32(2)	4(2)
C(22)	75(2)	56(2)	75(2)	-9(2)	-20(2)	10(2)
C(23)	65(2)	53(2)	57(2)	-4(2)	-10(2)	5(2)
C(24)	47(2)	48(2)	46(2)	-3(1)	-10(1)	-5(1)
C(25)	50(2)	51(2)	35(1)	0(1)	-1(1)	-4(1)
C(26)	46(2)	52(2)	48(2)	-5(1)	-10(1)	4(1)
C(27)	67(2)	55(2)	56(2)	-8(1)	-17(2)	0(1)
C(28)	107(3)	51(2)	107(3)	-9(2)	-39(2)	-2(2)
C(29)	62(2)	87(2)	57(2)	-22(2)	3(2)	1(2)
C(30)	88(2)	99(3)	50(2)	8(2)	2(2)	-15(2)
O(2)	81(1)	56(1)	50(1)	-2(1)	-21(1)	5(1)
O(1)	76(1)	49(1)	61(1)	7(1)	-11(1)	-13(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 090725_0M.

	x	y	z	U(eq)
H(5)	3425	982	4716	86
H(6)	1555	2241	5680	96
H(7)	796	4003	4933	89
H(8)	2017	4514	3214	76
H(10)	3977	4069	1535	62
H(11)	7254	2622	-131	61

H(12A)	4121	3016	-486	70
H(12B)	5056	1788	-553	70
H(13A)	6030	3723	-1956	109
H(13B)	5363	2582	-2254	109
H(13C)	7068	2537	-2000	109
H(14A)	7839	373	1368	105
H(14B)	7698	1134	357	105
H(14C)	6566	89	751	105
H(15A)	6672	-226	2804	122
H(15B)	4851	-548	3066	122
H(15C)	5499	86	3894	122
H(20)	9228	396	4263	80
H(21)	11105	-832	3260	89
H(22)	12429	-272	1542	83
H(23)	11781	1497	836	71
H(25)	10244	3396	1008	57
H(26)	7160	5415	2095	59
H(27A)	9271	6008	2797	71
H(27B)	10491	5847	1693	71
H(28A)	9110	7367	952	129
H(28B)	9646	7824	1911	129
H(28C)	7841	7513	2041	129
H(29A)	5449	4208	4037	107
H(29B)	6581	5243	3598	107
H(29C)	6710	4546	4644	107
H(30A)	7325	2858	5350	124
H(30B)	7790	1533	5135	124
H(30C)	6154	2101	4950	124
H(2)	9271	4719	411	92
H(1)	5465	4585	217	95