Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

# Supporting Information

# Silanization of quartz, silicon and mica surfaces with light-driven molecular motors: construction of a surface-bound photo-active nanolayer

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# General remarks

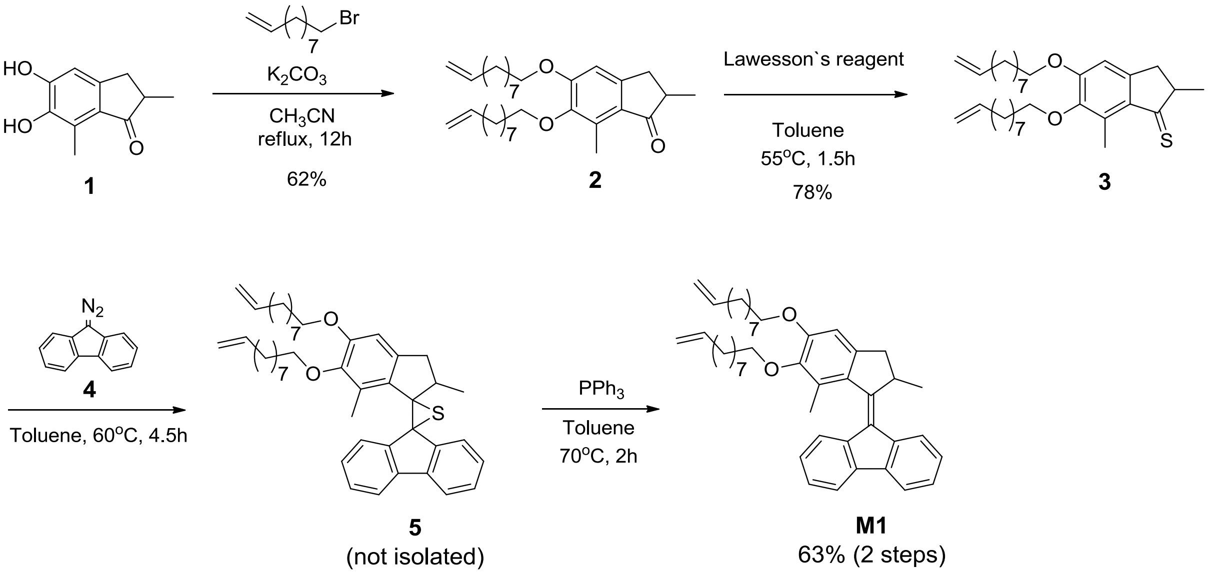
## General remarks for synthetic procedures:

Reagents were purchased from Aldrich, Acros, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. All reactions were performed in oven- or flame-dried round bottomed flasks fitted with rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at 30–40 °C. Flash column chromatography was performed as described by Still et al. (Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43, 2923-2925.) Chromatography: silica gel, Merck type 9385 230-400 mesh.
TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm).

## General remarks for instrumentation:

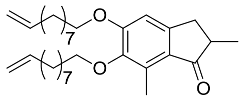
Mass spectra (HRMS) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus. $^{1}$H and $^{13}$C NMR spectra were recorded on a Varian VXR-300 a Varian Mercury Plus, or a Varian Inova 500 operating at 299.97, 399.93, and 499.98 MHz, respectively, for the $^{1}$H nucleus, and at 75.43, 100.57 and 124.98 MHz for the $^{13}$C nucleus.
Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents $CHCl_3$: δ 7.26, $CDHCl_2$: δ 5.32). Chemical shifts for carbon are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant in Hz, integration. Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at $\lambda$ = 365 nm, ± 30 nm. NMR samples were placed 2-3 cm from the lamp. Solution UV spectra were obtained using Hewlet-Packard HP 8543 FT or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette.

## Synthesis of compounds and intermediates



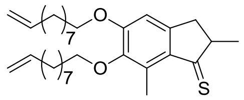
**Scheme S1** Synthesis of compound **M1.**

### 5,6-bis(dec-9-enyloxy)-2,7-dimethyl-2,3-dihydro-1*H*-inden-1-one (2)



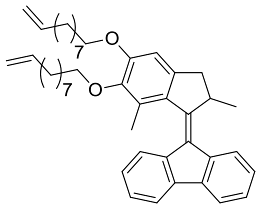
$K_2CO_3$ (2.5 g, 18 mmol) and 10-bromo-1-decene (2.3 mL, 11.5 mmol) were added to a solution of 5,6-dihydroxy-2,7-dimethyl-indane-1-one (**1**)[1] (0.70 g, 3.64 mmol) in acetonitrile (30 mL) and the mixture was heated at reflux overnight. The reaction was quenched by the addition of water (50 mL). The mixture was extracted with EtOAc (3×50 mL). The combined organic layers were washed with water and brine and dried ($Na_2SO_4$). After the evaporation of the solvent the crude product was purified by flash chromatography ($SiO_2$, *n*-heptane : EtOAc = 7 : 1) to give 1.05 g (2.24 mmol, 62 %) of colourless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, *J* = 7.2 Hz, 3H), 1.33-1.42 (m, 16H), 1.45-1.53 (m, 4H), 1.77 (quin, *J* = 8.0 Hz, 2H), 1.85 (quin, *J* = 8.0 Hz, 2H), 2.04 ($q_{apparent}$, *J* = 6.8 Hz, 4H), 2.55 (s, 3H), 2.59-2.67 (m, 2H), 3.23 (dd, *J* = 7.6, 16.4 Hz, 1H), 3.85 (t, *J* = 6.4 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 4.91-4.92 (m, 1H), 4.93-495 (m, 1H), 4.96-4.97 (m, 1H), 5.00-5.02 (m, 1H), 5.76-5.86 (m, 2H), 6.71 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 10.87, 16.65, 26.08, 26.11, 28.88, 28.91, 29.04, 29.10, 29.11, 29.27, 29.41, 29.46, 29.48, 30.32, 33.76, 33.78, 34.50, 42.61, 68.47, 72.99, 106.43, 114.11, 114.16, 126.95, 132.18, 139.05, 139.12, 146.06, 151.57, 157.70, 208.99. HRMS (APCI) calcd for $C_{31}H_{48}O_3$ 469.3676 ($M^+$), found 469, 3658 ($M^+$).

### 5,6-bis(dec-9-enyloxy)-2,7-dimethyl-2,3-dihydro-1H-indene-1-thione (3)



Lawesson`s reagent (202 mg, 0.5 mmol) was added to a solution of **2** (110 mg, 0.23 mmol) in toluene (10 ml). The mixture was heated to 75°C for 2 h and then filtered over celite. The solid residue was washed with toluene until it became colorless. The filtrate was concentrated *in vacuo* and purified by flash chromatography ($SiO_2$, *n*-pentane : diethyl ether = 10 : 1) to give 86 mg (0.18 mmol, 78 %) of a purple oil . $^1$H NMR (400 MHz, $CDCl_3$) δ 1.33-1.42 (m, 19H), 1.45-1.54 (m, 4H), 1.75-1.82 (m, 2H), 1.83-1.90 (m, 2H), 2.05 (q, *J* = 6.7 Hz, 4H), 2.70-2.75 (m, 1H), 2.73 (s, 3H), 2.97-3.05 (m, 1H), 3.32 (dd, *J* = 7.0, 17.3 Hz, 1H), 3.84 (t, *J* = 6.6 Hz, 2H), 4.06 (t, *J* = 6.4 Hz, 2H), 4.92-4.97 (m, 3H), 5.01 (s, 1H), 5.76-5.86 (m, 2H), 6.76 (s, 1H). $^{13}$C NMR (APT, 100 MHz, $CDCl_3$) δ 13.1, 21.7, 26.0, 26.1, 28.8, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 30.2, 33.7, 33.8, 39.0, 55.3, 68.5, 73.1, 105.7, 114.1, 114.2, 134.2, 137.5, 139.0, 139.1, 146.3, 153.5, 157.5, 248.2. (1 C not observed due to overlap.) HRMS (ESI) calcd for $C_{31}H_{48}O_2S$ 485.3448 ($MH^+$), found 485.3627 ($MH^+$).

**Dialkene-motor (M1)**



Diazofluorenone **3** (577 mg, 3.0 mmol) was added to a solution of thioketone **2** (700 mg, 1.45 mmol) in toluene (10 mL). The mixture was heated to 75ºC for 3 h. The formation of the episulfide was monitored by $^1$H NMR spectroscopy by following the shift of the aromatic proton of the thioketone from 6.76 ppm to 6.41 ppm. $PPh_3$ (650 mg, 2.5 mmol) was added to the reaction mixture and it was heated for additional 2 h at 75ºC. The reaction mixture was concentrated *in vacuo.* Diethyl ether (20 mL) was added to the mixture which resulted in the precipitation of $PPh_3S$ as yellow crystals. The precipitate was filtered and the procedure was repeated once more. To remove the excess $PPh_3$, $CH_3I$ (1.0 mL, 16.1 mmol) was added to the ether phase and the mixture was stirred for 1 h. The resulting precipitate was filtered. After the evaporation of the solvent the crude product was purified by flash chromatography ($SiO_2$, *n*-heptane : toluene = 5 : 1) to give alkene **M1** as yellow oil which solidified to a waxy solid upon standing in the fridge (560 mg, 0.91 mmol, 63 %).

$^1$H NMR (500 MHz, $CDCl_3$) δ 1.33-1.42 (m, 19H), 1.49-1.56 (m, 4H), 1.82 (quin, *J* = 8.0 Hz, 2H), 1.88 (quin, *J* = 8.0 Hz, 2H), 2.06 (quin, *J* = 7.5 Hz, 4H), 2.18 (s, 3H), 2.53 (d, *J* = 14.5 Hz, 1H), 3.30 (dd, *J* = 5.5, 14.5 Hz, 1H), 3.92 ($q_{apparent}$, *J* = 6.5 Hz, 1H), 4.00-4.15 (m, 4H), 4.92-5.03 (m, 4H), 5.77-5.87 (m, 2H), 6.83 (s, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.34-7.36 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.81-7.83 (m, 1H), 7.86-7.88 (m, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 16.33, 19.34, 26.49, 29.22, 29.39, 29.43, 29.66, 29.71, 29.77, 29.80, 29.85, 30.76, 34.09, 41.83, 45.07, 68.70, 72.99, 107.92, 114.41, 114.46, 119.36, 119.86, 123.72, 123.87, 126.63, 126.67, 126.89, 126.98, 128.77, 132.06, 133.33, 138.23, 139.35, 139.42, 139.46, 139.87, 139.99, 143.45, 145.95, 152.74, 153.76. (3 C not observed due to overlap.) HRMS (ESI) calcd for $C_{44}H_{56}O_2Na$ 639.4173, found 639.4194.

**Irradiation experiment to generate unstable isomer of dialkene-motor M1:**

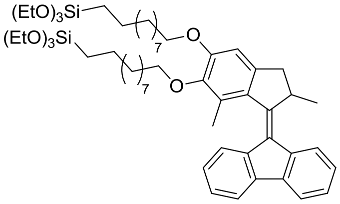
Motor **M1** (~2 mg) was dissolved in $CD_2Cl_2$ (~1 ml). This sample was placed in an NMR tube and irradiated with 365 nm light at -50ºC at a distance of 2-3 cm from the centre of the lamp. $^1$H NMR spectra of the sample were taken before, during and after irradiation at -50ºC. No further changes were observed after 4 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of unstable-**M1** to stable-**M1** with a ratio of 1 : 2. After warming the sample to rt, only the stable form was observed by $^1$H NMR spectroscopy.

stable-**M1** $^1$H NMR (500 MHz, $CD_2Cl_2$, -50°C) δ 1.19-1.36 (m, H), 1.37-1.50 (br m, H), 1.69-1.76 (br m, 2H), 1.76-1.84 (br m, 2H), 1.98 (br q, *J* = 6.5 Hz, 4H), 2.05 (s, 3H), 2.52 (d, *J* = 14.8 Hz, 1H), 3.23 (dd, *J* = 5.6, 14.6 Hz, 1H), 3.78 ($q_{apparent}$, *J* = 6 Hz, 1H), 3.96-4.07 (m, 4H), 4.87 (m, 2H), 4.93 (d, *J* = 5.2 Hz, 1H), 4.97 (d, *J* = 5.6 Hz, 1H), 5.73-5.83 (m, 2H), 6.85 (s, 1H), 7.10 (t, *J* = 5.9 Hz, 1H), 7.25-7.27 (m, 2H), 7.31-7.36 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 6.8 Hz, 1H)

unstable-**M1** $^1$H NMR (500 MHz, $CD_2Cl_2$, -50°C) δ 1.25-1.82 (absorptions in this region could not be resolved due to overlap with remaining stable-**M1**), 1.90 (s, 3H), 1.97-2.00 (absorptions in this region could not be resolved due to overlap with remaining stable-**M1**), 2.93 (dd, *J* = 5.8, 15.9 Hz, 1H), 3.37 (dd, *J* = 8.1, 16.3 Hz, 1H), 3.69 ($q_{apparent}$, *J* = 7.1 Hz, 1H), 3.90-5.82 (absorptions in this region could not be resolved due to overlap with remaining stable-**M1**), 6.80 (s, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.22-7.36 (absorptions in this region could not be resolved due to overlap with remaining stable-**M1**), 7.68

(d, *J* = 7.0 Hz, 1H) 7.75-7.85 (absorptions in this region could not be resolved due to overlap with remaining stable-**M1**).

## Disilane motor (M2)



A mixture of dialkene-motor **M1** (50 mg, 0.081 mmol) triethoxysilane (0.5 ml, 2.7 mmol) and $PtO_2$ (5 mg, 0.022 mmol) under inert atmosphere (Ar) was heated to 75°C for 30 min. The crude mixture was purified by column chromatography ($SiO_2$, heptane : EtOAc 10 : 1) to give alkene **M2** as a yellow oil. (The isolated yields varied between 30-50%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 0.61-0.67 (m, 2H), 0.89 (q, *J*= 6.0 Hz, 2H), 1.21 (d, *J*= 4.0 Hz, 3H,), 1.25 (t, *J*= 6.8 Hz, 18H), 1.24-1.46 (br m, 24H), 1.48-1.55 (m, 4H), 1.78-1.91 (m, 4H), 2.18 (s, 3H), 2.53 (d, *J*= 14.8 Hz, 1H), 3.29 (dd, *J*= 5.7, 14.6 Hz, 1H), 3.86 (q, *J*= 7.2 Hz, 12H), 3.99-4.15 (m, 5H), 6.83 (s, 1H), 7.11 (t, *J*= 7.5 Hz, 1H), 7.27 (t, *J*= 7.4 Hz, 1H), 7.32-7.37 (m, 2H), 7.39 (d, *J*= 7.9 Hz, 1H), 7.75 (d, *J*= 7.5 Hz, 1H), 7.79-7.82 (m, 1H), 7.86-7.89 (m, 1H). HRMS (ESI) calcd for $C_{56}H_{88}O_8Si_2Na$ 967.5910, found 967.5909.

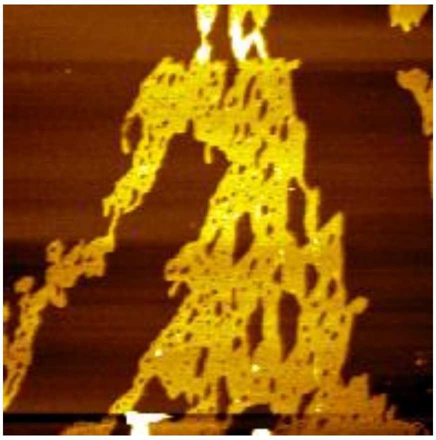
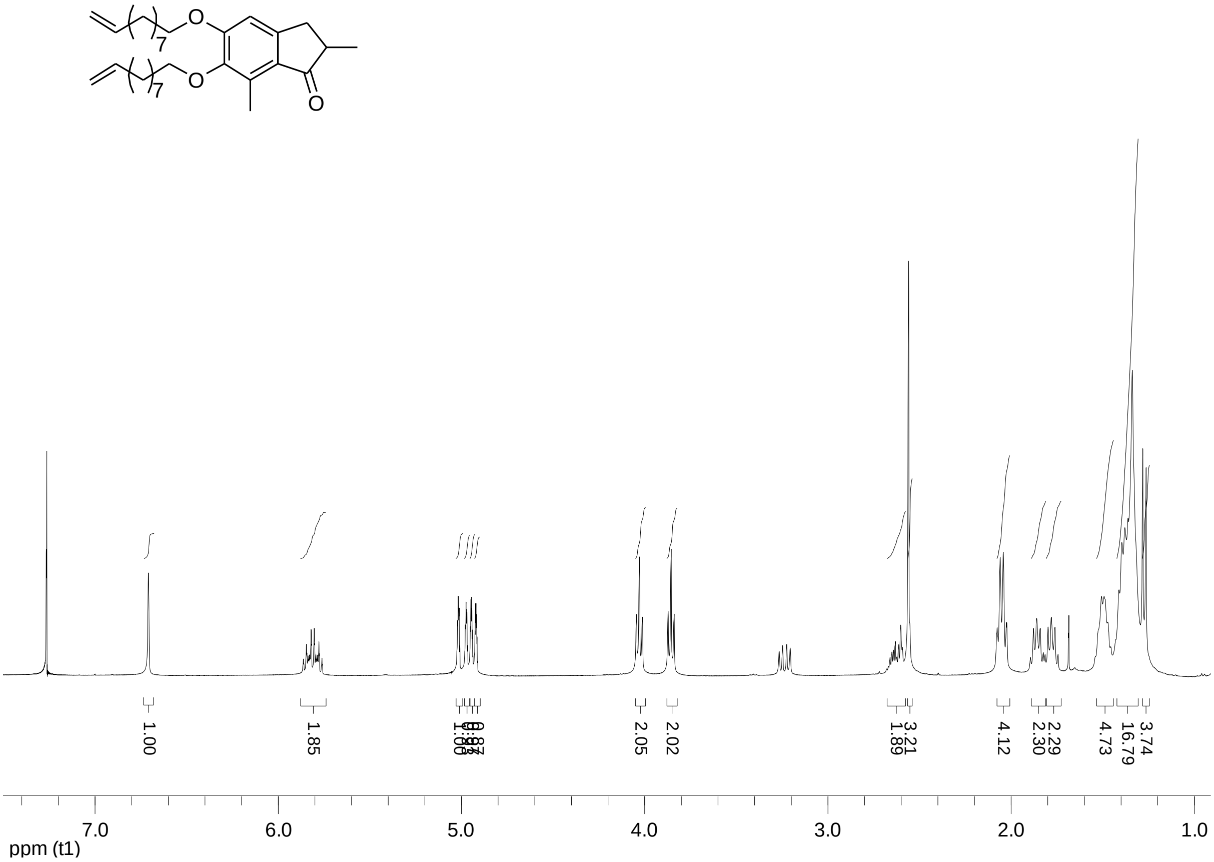


**Figure S1** Further irradiation (365 nm) of **MS-2** followed by standing in the dark resulted in further morphological changes. (Image size 10×10 µm)

## References

(1) For the synthesis of compound **1** see: G. London, G. T. Carroll, T. F. Landaluce, M. M. Pollard, P. Rudolf, B. L. Feringa, *Chem. Commun.* **2009**, 1712. (Supp. Inf.)

# NMR Spectra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2.30
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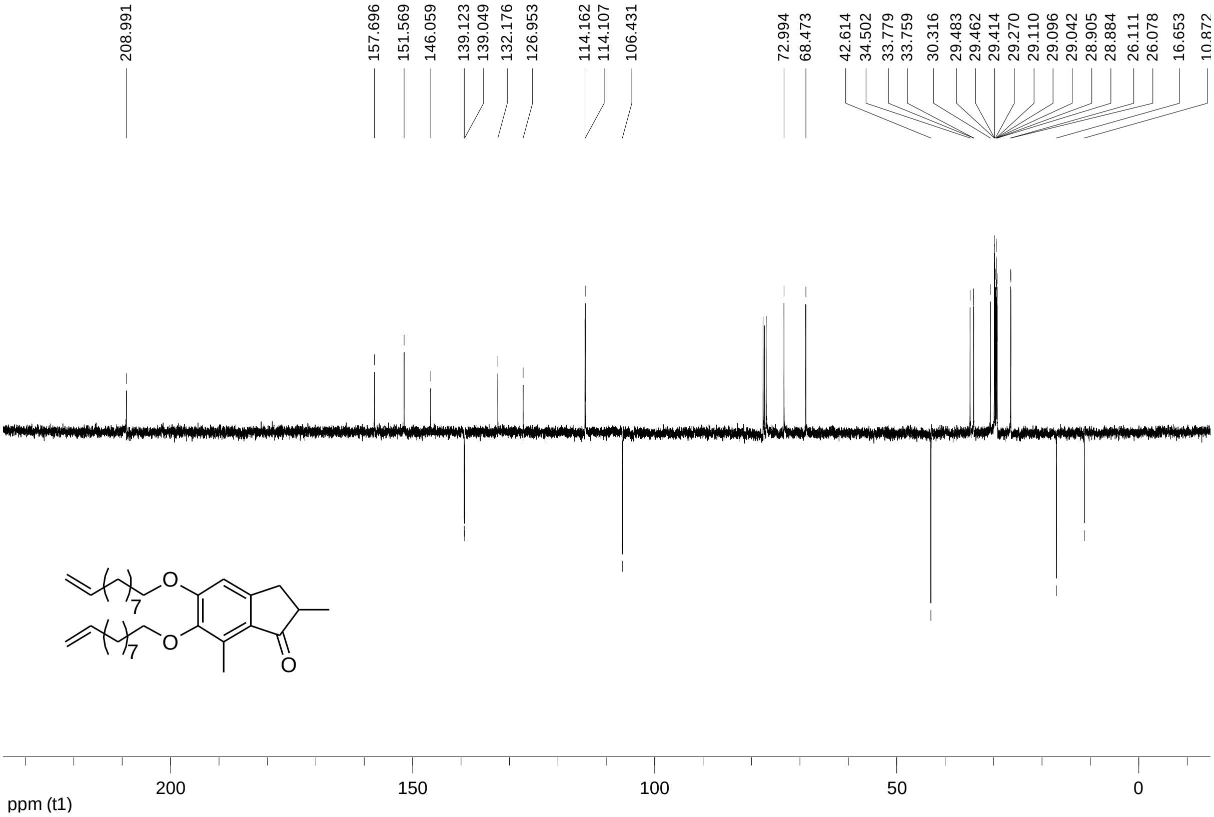
2.0
1.0
ppm (t1)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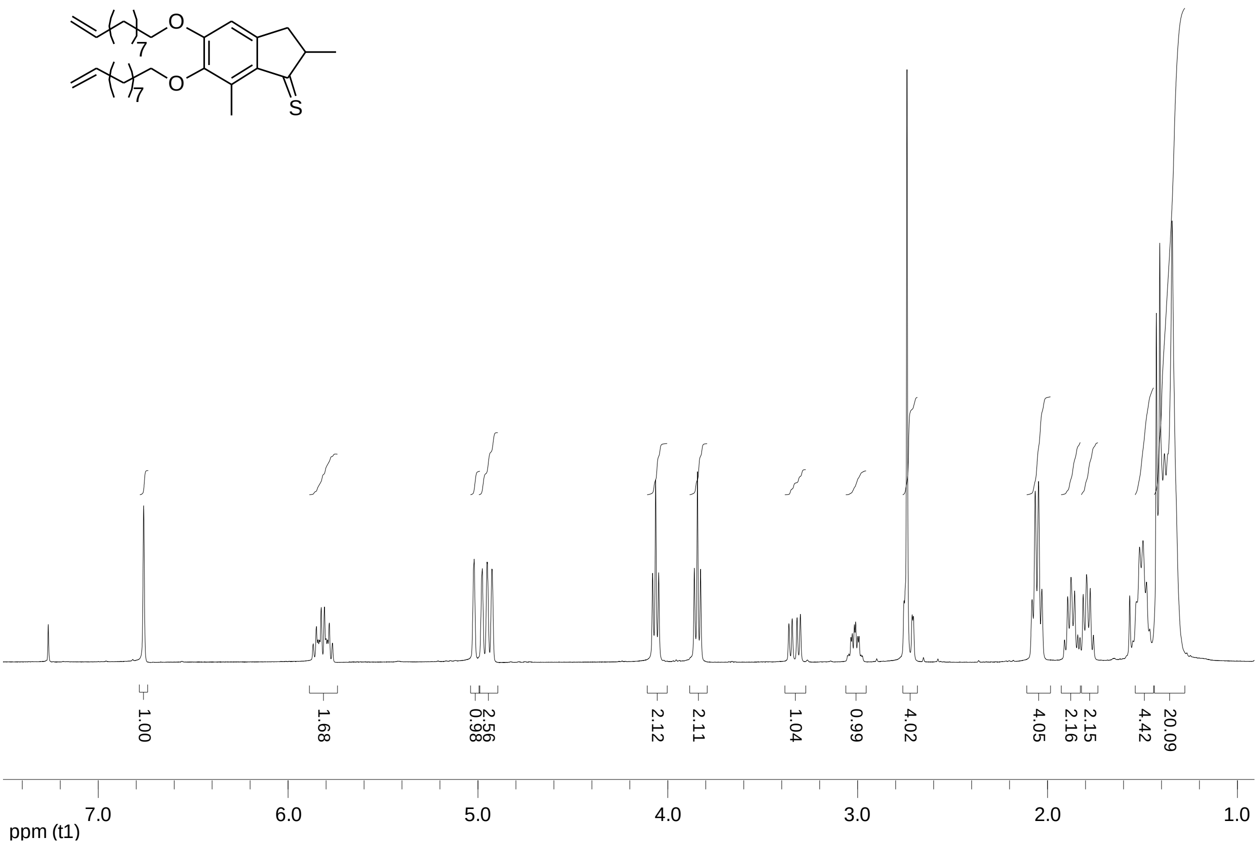
0
ppm (t1)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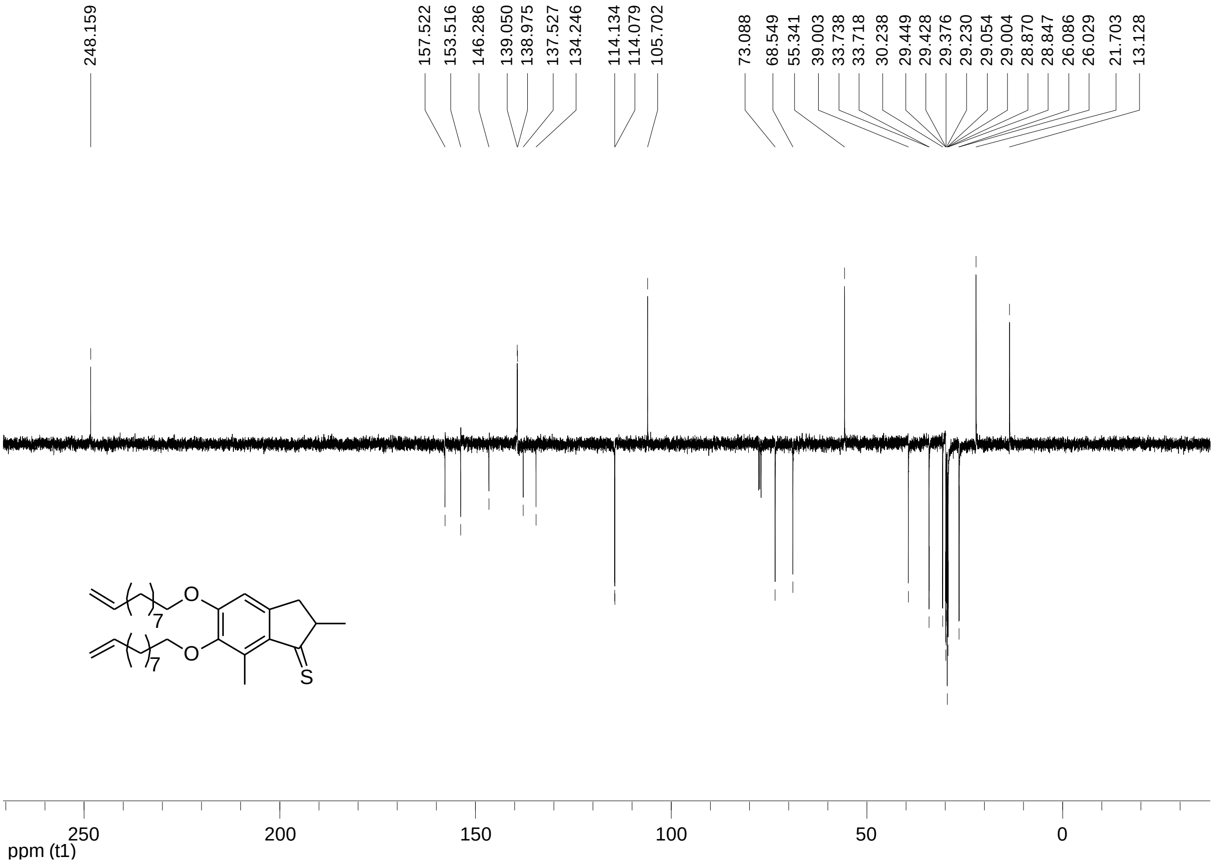
3.0
2.0
1.0
ppm (t1)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29.054
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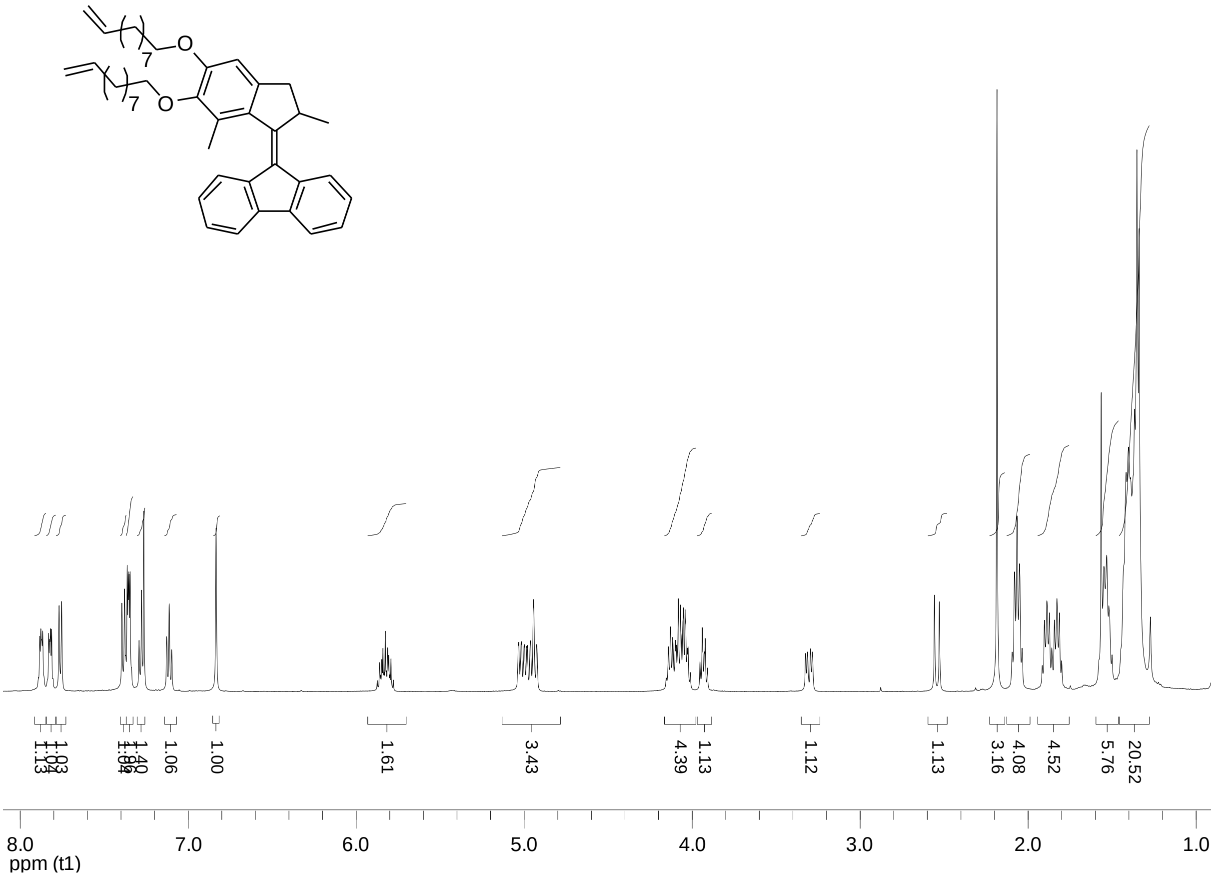
ppm (t1)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1.12
1.13
3.16
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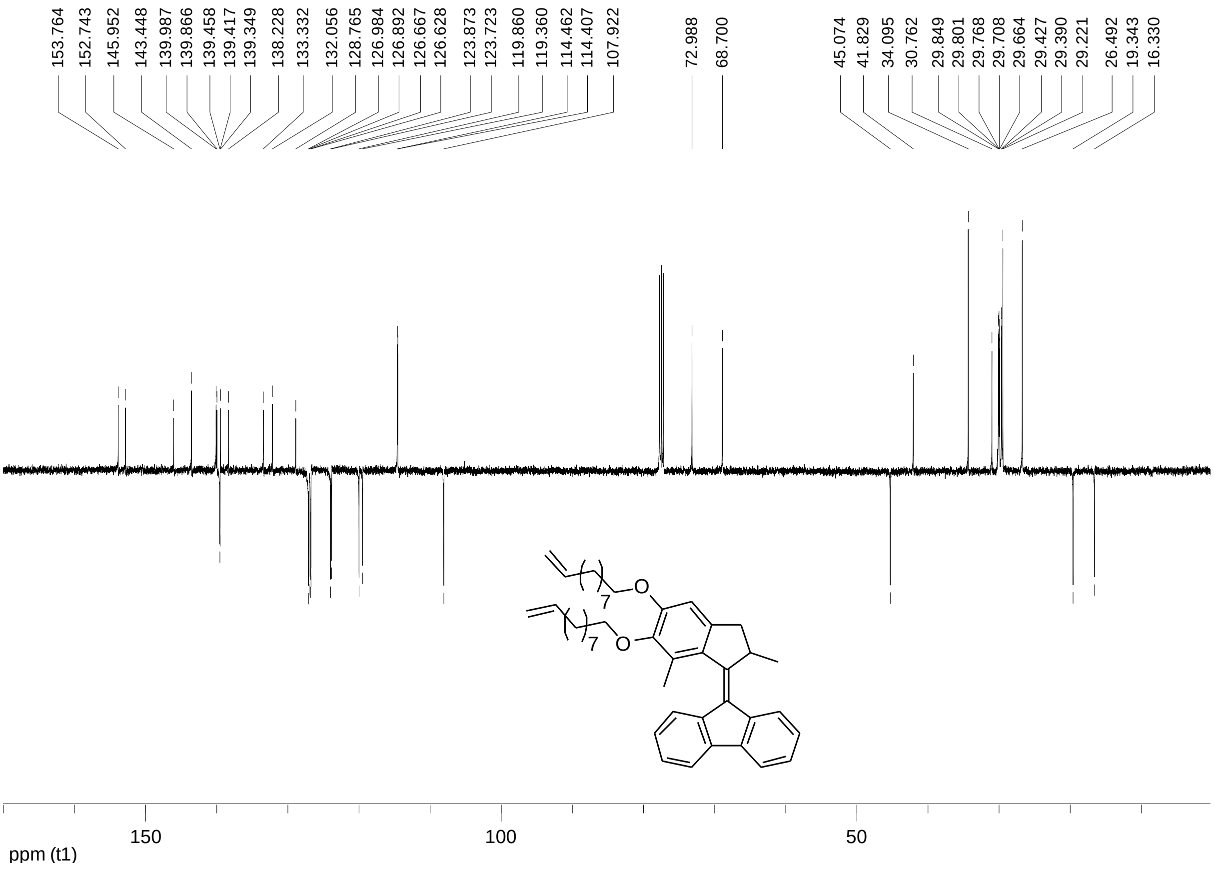
ppm (t1)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126.984
126.892
126.667
126.628
123.873
123.723
119.860
119.360
114.462
114.407
107.922
72.988
68.700
45.074
41.829
34.095
30.762
29.849
29.801
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29.390
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19.343
16.330
7
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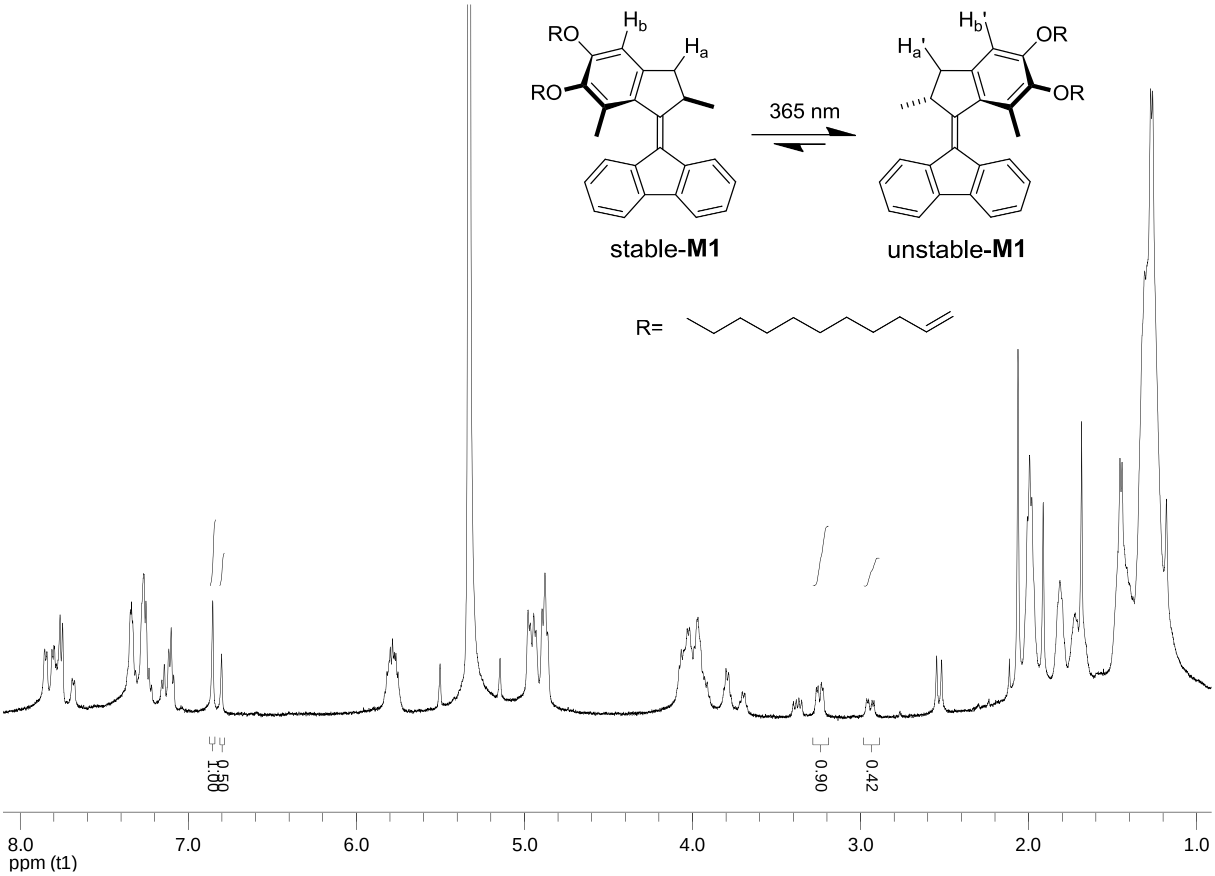
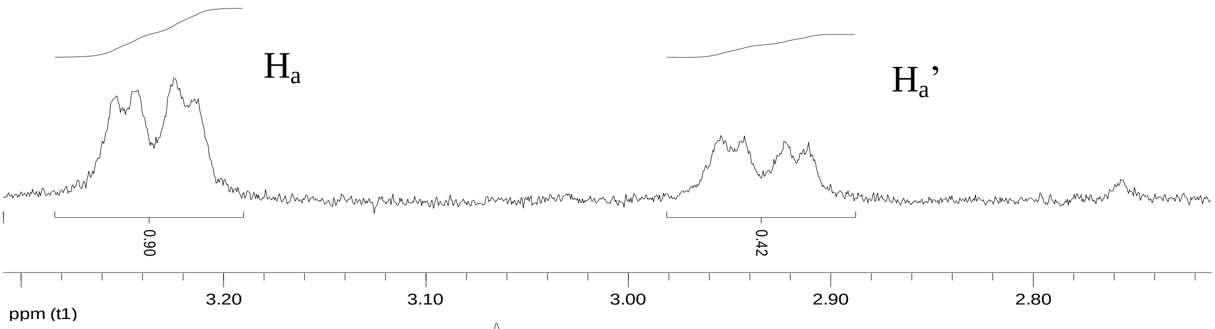
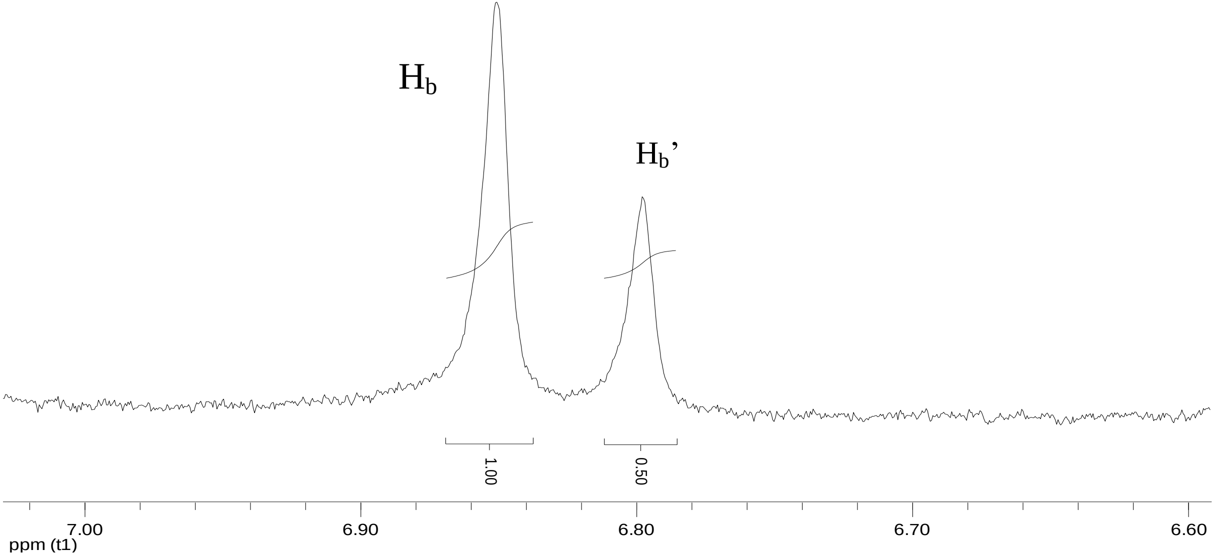
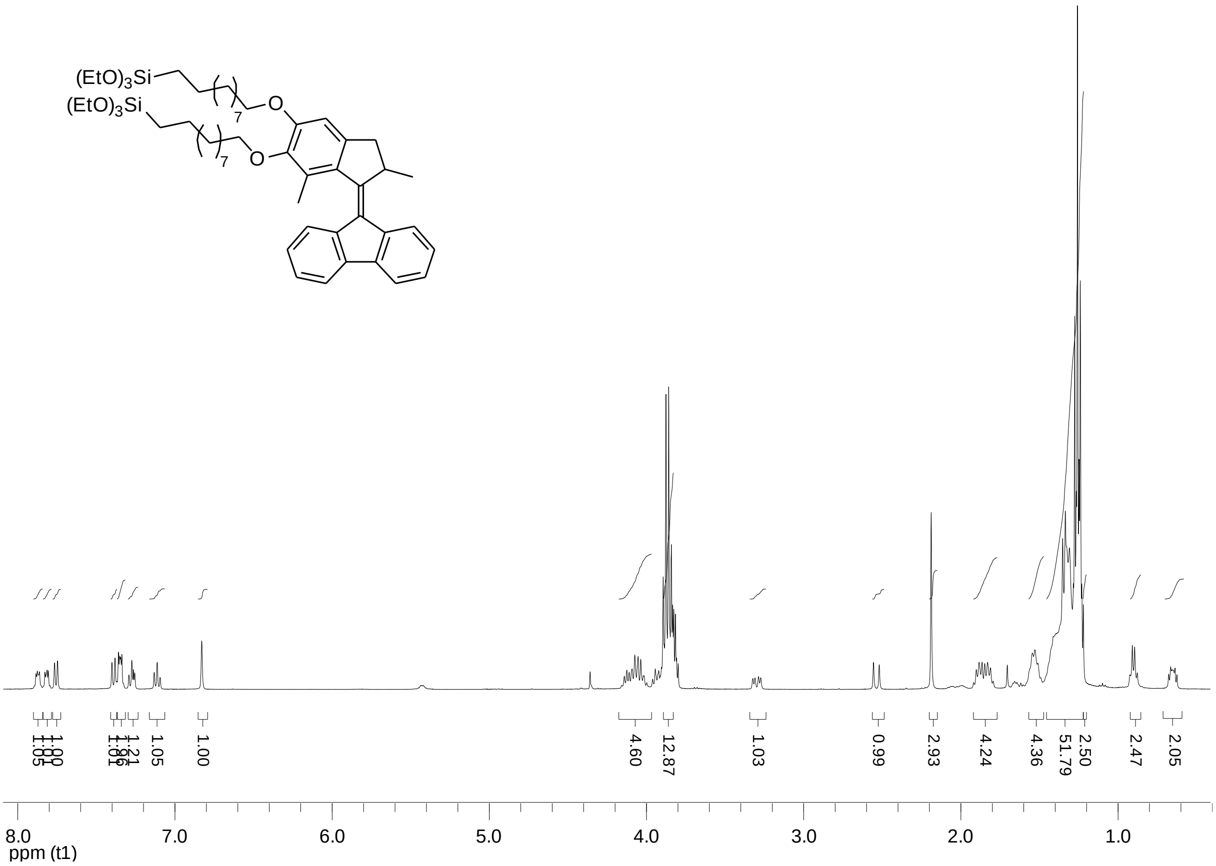
ppm (t1)

$^{1}$H-NMR spectrum of the photostationary state (λ= 365 nm) of stable-**M1** and unstable-**M1**





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(EtO)3Si
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O
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1.00
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1.00
4.60
12.87
1.03
0.99
2.93
4.24
4.36
51.79
2.50
2.47
2.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)