Supplementary Material (ESI) for Chemical Communications

Supporting Information

Light-Driven Altitudinal Molecular Motors on Surfaces

Gábor London,[a] Gregory T Carroll,[a] Tatiana Fernández Landaluce,[a,b] Michael M. Pollard,[a] Petra Rudolf[b] and Ben L. Feringa*[a,b]

[a]*Centre for Systems Chemistry,*
Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands.
[b] *Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen,The Netherlands*
[c]*Department of Chemistry, York University, 4700 Keele Street, Toronto, ON Canada M3J 1P3.*

General remarks

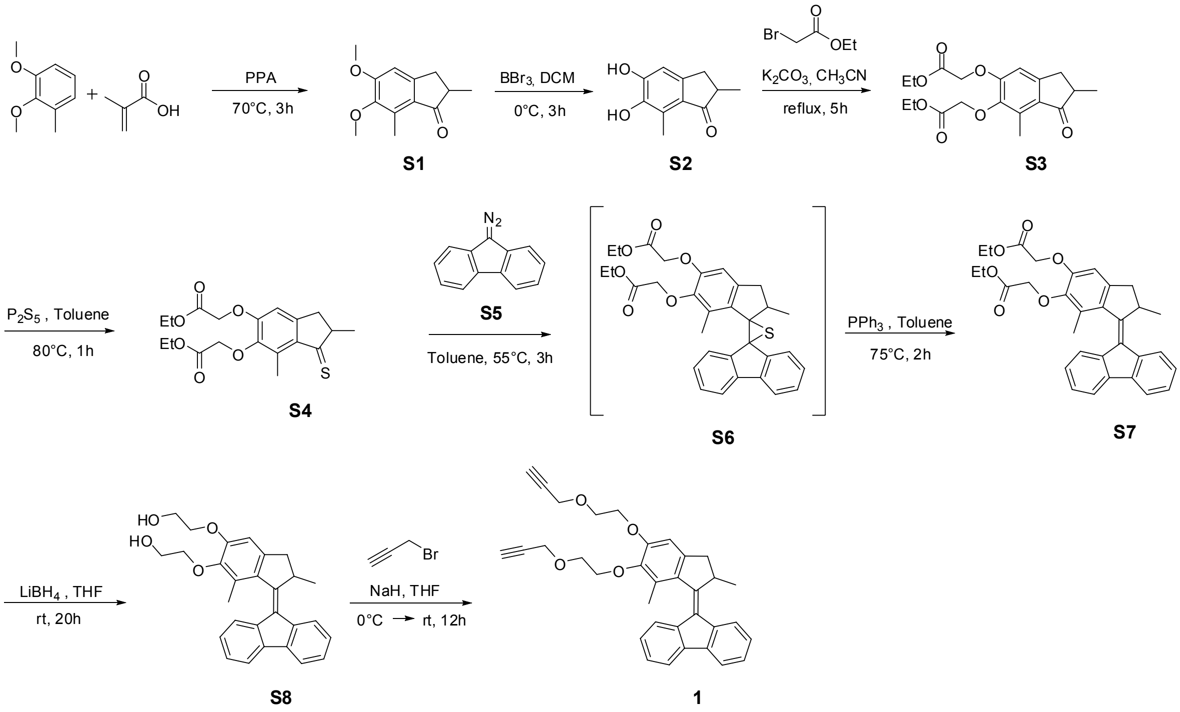
General remarks for synthetic procedures:

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 or modified Schlenk (Kjeldahl shape) 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 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).

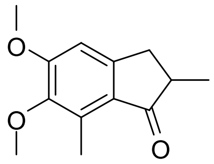
General remarks for instrumentation:

Mass spectra (HRMS) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. ^{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, DMSO δ 2.5, CD_2HCOD δ 3.31). 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, DMSO-d_6: δ 39.4). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet), integration, coupling constant in Hz. 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 CD spectra were recorded on a JASCO J-715 spectropolarimeter using UVASOL grade methanol in a 1.0 cm quartz cell at $T \leq -20$ºC temperature. UV spectra were obtained using Hewlet-Packard HP 8543 FT or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette. Spectroscopic ellipsometry measurements were performed on a J.A. Woollam VASE ellipsometer. Samples for analysis by XPS were prepared on silicon wafers (Wafer World Inc.) containing a thin layer of SiO_2 (approximately 2 nm, exact value measured for each sample) and measured in three different locations and the results averaged. A refractive index value of 1.5 was used for the organic layer. Contact angles were measurured on a LINOS contact angle goniometer. The contact angle was calculated using home-made software. The contact angle was measured at three different locations on each surface and the results averaged.

Synthesis of compounds and intermediates

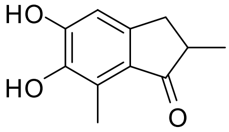


(Enantiomers resolved at this stage.)



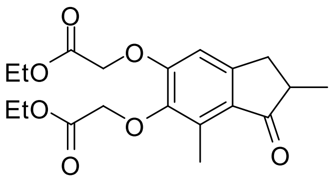
5,6-dimethoxy-2,7-dimethyl-indane-1-one **S1**

To mechanically stirred polyphosphoric acid (30 mL) heated at 70°C, were added methacrylic acid (12.9 ml, 150 mmol) and 2,3-dimethoxytoluene (12 ml, 89 mmol). After stirring at 70°C for 3 h, the mixture was poured onto ice and stirred overnight. The water layer was extracted with EtOAc (3 x 50 ml). The combined organic layers were washed with aqueous $NaHCO_3$ (30 mL), water (30 mL) and brine (30 mL) and dried (Na_2SO_4). The solution was concentrated *in vacuo* to a damp solid which was recrystallized from *n*-heptane to give brown crystals (13.5 g , 61.3 mmol, 76%). Mp 106-107 °C; ^1H NMR (400MHz, $CDCl_3$) δ 1.27 (d, 3H, *J* = 6.8 Hz), 2.62 (s, 3H), 2.60-2.70 (m, 2H), 3.26 (dd, 1H, *J* = 7.0, 16.8 Hz), 3.76 (s, 3H), 3.93 (s, 3H), 6.75 (s, 1H); ^{13}C NMR (APT, 125 MHz, $CDCl_3$) δ 10.5, 16.5, 34.3, 42.5, 55.7, 60.2, 105.8 127.0, 131.8, 146.6, 151.8, 157.9, 208.8. HRMS (EI) calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1097. Elemental analysis calcd: (%) C, 70.89; H, 7.32; found: C, 70.94; H, 7.31.



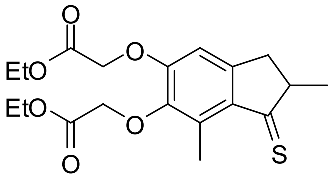
5,6-dihydroxy-2,7-dimethyl-indane-1-one **S2**

BBr_3 (1.9 ml, 20 mmol) was added slowly to a stirred solution of **S1** (3.00 g, 13.4 mmol) in CH_2Cl_2 (10 ml) at 0°C under inert atmosphere (N_2). After 3 h at this temperature, the reaction was quenched by adding water (20 mL) slowly. The water layer was extracted with ethyl acetate until the water phase became colorless. The organic layer was washed with water (20 mL) and brine (20 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give the crude product as a brown solid. The solid was suspended in diethyl ether (2 x 20 ml) followed by filtration gave 2.10 g (10.9 mmol, 82 %) of grey powder. Mp 229.5-230.5 °C; ^1H NMR (500MHz, Methanol-*d*$_4$) δ 1.20 (d, 3H, *J* = 7.0 Hz), 2.46 (s, 3H), 2.50 (dd, 1H, *J*= 3.5, 16.5 Hz), 2.54-2.61 (m, 1H), 3.18 (dd, 1H, *J* = 7.8, 16.8 Hz), 6.67 (s, 1H); ^{13}C NMR (APT, 100 MHz, DMSO-*d*$_6$) δ 10.3, 16.5, 33.4, 42.0, 108.9, 123.2, 125.3, 142.9, 147.2, 151.8, 208.0. HRMS (EI) calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0776. Elemental analysis calcd: (%) C, 68.74; H, 6.29; found: C, 68.37; H, 6.30.



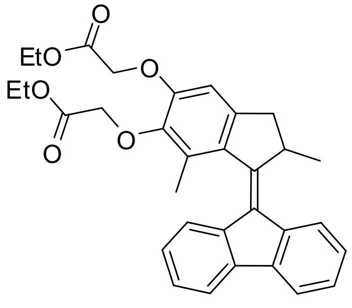
Diethyl 2,2'-(2,7-dimethylindane-1-one-5,6-diyl)bis(oxy)diacetate **S3**

To the solution of **S2** (1.96 g, 10.2 mmol) in acetonitrile (15 mL) were added K_2CO_3 (3.5 g, 25 mmol) and ethyl bromoacetate (3.5 mL, 30 mmol) and the mixture was heated at reflux for 5 h. The reaction was quenched by the addition of water (25 mL). The mixture was extracted with ethyl acetate (3 x 30 ml). The combined organic layers were washed with water (30 mL) and brine (30 mL), and dried (Na_2SO_4). After the evaporation of the solvent the crude product was purified by flash chromatography (SiO_2, *n*-heptane : EtOAc = 2 : 1). For analytical purposes the product was purified further by recrystallization from *n*-heptane to give 2.84 g (7.80 mmol, 76 %) of white crystals.
Mp 81–81.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, 3H, *J* = 6.8 Hz), 1.29-1.33 (m, 6H), 2.58 (dd, 1H, *J* = 4.2, 17.0 Hz), 2.63 (s, 3H), 3.23 (dd, 1H, *J* = 7.8, 16.6 Hz), 4.28 (q, 4H, *J* = 7.2 Hz), 4.66 (s, 2H), 4.73 (s, 2H), 6.62 (s, 1H); ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 10.9, 14.0, 14.1, 16.4, 34.3, 42.6, 60.9, 61.5, 65.2, 69.4, 106.7, 128.2, 132.8, 145.1, 151.4, 155.2, 167.9, 169.2, 208.7. HRMS (EI) calcd for $C_{19}H_{24}O_7$ 364.1522, found 364.1533.



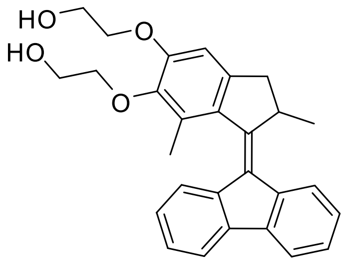
Diethyl 2,2'-(2,7-dimethyl-1-thioxo-2,3-dihydro-1H-indene-5,6-diyl)bis(oxy)diacetate **S4**

P_2S_5 (1.35 g, 3.00 mmol) was added to a solution of **S3** (750 mg, 2.00 mmol) in toluene (10 ml). The mixture was heated to 80ºC for 1 h and then filtered. The solid residue was washed with EtOAc until its color became pale yellow. The filtrate was concentrated *in vacuo* and purified by flash chromatography (SiO_2, *n*-heptane : ethyl acetate = 4 : 1) to give 320 mg (0.85 mmol, 42 %) of a purple oil that solidified to a waxy solid upon standing in the fridge. (*Note*: this compound is not stable towards air or moisture and slowly decomposes to ketone **S3**.)
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29-1.33 (m, 6H), 1.40 (d, 3H, *J* = 7.2 Hz), 2.72 (dd, 1H, *J* = 3.2, 17.2 Hz) 2.95-3.04 (m, 1H), 3.33 (dd, 1H, *J* = 6.8, 17.2 Hz), 4.28 (q, 4H, *J* = 6.8 Hz), 4.64 (s, 2H), 4.75 (s, 2H), 6.66 (s, 1H); ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 13.2, 14.0, 21.5, 38.9, 55.5, 60.9, 61.6, 65.1, 69.5, 105.96, 134.7, 138.1, 145.3, 153.2, 154.8, 167.7, 169.1, 248.8. HRMS (EI) calcd for $C_{19}H_{24}O_6S$ 380.1294, found 380.1289.



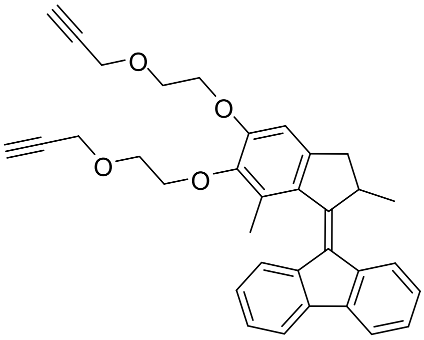
Diester-motor **S7**

Diazofluorenone **S5**[1] (500 mg, 2.5 mmol) was added to a solution of **S4** (630 mg, 1.67 mmol) in toluene (10 ml). The mixture was heated up to 55ºC 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 6.66 ppm to 6.35 ppm[2]. To the episulfide solution PPh_3 (650 mg, 2.5 mmol) was added and was heated for additional 2 h at 75ºC. The reaction mixture was concentrated *in vacuo.* EtOAc (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. After the evaporation of the solvent the crude product was purified by flash chromatography (SiO_2, *n*-heptane : ethyl acetate = 5 : 1) to give alkene **5** as yellow solid (570 mg, 1.11 mmol, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.34 (m, 9H), 2.25 (s, 3H), 2.52 (d, 1H, *J* = 14.4 Hz), 3.28 (dd, 1H, *J* = 5.8, 14.2 Hz), 4.12 (quin, 1H, *J* = 6.2 Hz), 4.26-4.33 (m, 4H), 4.66 (d, 1H, *J* = 16.0 Hz), 4.73 (s, 2H), 4.88 (d, 1H, *J* = 16.0 Hz), 6.74 (s, 1H), 7.14 (t, 1H, *J* = 7.6 Hz), 7.28 (t, 1H, *J* = 7.4 Hz), 7.32-7.38 (m, 3H), 7.74 (d, 1H, *J* = 8.0 Hz), 7.79-7.81 (m, 1H), 7.84-7.86 (m, 1H); ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 14.0, 14.1, 16.1, 18.8, 41.3, 44.7, 60.8, 61.3, 65.7, 69.2, 108.2, 119.0, 119.5, 123.6, 126.5, 126.6, 126.7, 126.9, 129.4, 131.9, 134.6, 137.6, 139.1, 139.4, 139. 7, 143.2, 145.0, 150.9, 151.1, 168.4, 169.5 (1 C not observed due to overlap.) HRMS (EI) calcd for $C_{32}H_{32}O_6$ 512.2199, found 512.2188.



Diol-motor **S8**

A solution of **S7** (90 mg, 0.21 mmol) in THF (5 mL) was added to a suspension of $LiBH_4$ (22 mg, 1 mmol) in THF (3 mL) and the mixture was stirred at r.t. for 20 h. The reaction was quenched with aqueous HCl solution (5 mL, 0.1 M) and the mixture was extracted with EtOAc until the aqueous phase was colourless. The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was recrystallized from toluene : *n*-heptane 5 : 1 to give yellow crystals (70 mg, 0.14 mmol, 67 %). Mp 187.5-188.0ºC. ^{1}H NMR (500 MHz, DMSO-*d$_6$*) δ 1.26 (d, 3H, *J* = 6.5 Hz), 2.10 (s, 3H), 2.55 (d, 1H, *J* = 15.0 Hz), 3.24 (dd, 1H, *J* = 5.8, 14.8 Hz), 3.71 (q, 2H, *J* = 5.5 Hz), 3.80 (q, 2H, *J* = 5.5 Hz), 3.92-3.96 (m, 1H), 4.03 (quin., 1H, *J* = 6.5 Hz), 4.06-4.10 (m, 1H), 4.12-4.17 (m, 2H), 4.80 (t, 1H, *J* = 5.0 Hz, O*H*), 4.93 (t, 1H, *J* = 5.0 Hz, O*H*), 7.06 (s, 1H), 7.17 (t, 1H, *J* = 7.8 Hz), 7.26-7.31 (m, 2H), 7.35-7.40 (m, 2H), 7.83 (d, 1H, *J* = 7.0 Hz), 7.87 (d, 1H, *J* = 7.5 Hz), 7.91-7.93 (m, 1H); ^{13}C NMR (APT, 125 MHz, $CDCl_3$) δ 15.91, 18.92, 41.54, 44.81, 60.99, 62.09, 70.49, 108.02, 119.22, 119.63, 123.22, 123.66, 126.37, 126.66, 126.83, 126.90, 129.14, 131.94, 133.97, 137.77, 139.29, 139.55, 139.64, 143.92, 145.41, 151.54, 152.34. HRMS (EI) calcd for $C_{28}H_{28}O_4$ 428.1987, found 428.1998.



Dialkyne-motor **1**

A suspension of NaH (30 mg, 1.3 mmol) in THF (3 mL) was cooled to 0ºC and a solution of **S8** (67 mg, 0.16 mmol) in THF (7 mL) was added dropwise (under N_2 atmosphere). To this mixture propargyl bromide (50 μL, 0.45 mmol, 80 % in toluene) was added. The solution was stirred at room temperature 12 h. The reaction was quenched with water (10 mL) and the mixture was extracted with EtOAc until the yellow color of the aqueous phase had disappeared. The organic phase was washed with water (10 mL) and brine (10 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was recrystallized from *n*-heptane to give yellow crystals (55 mg, 0.11 mmol, 69 %). Mp 138.0-139.0ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, 3H, *J* = 6.8 Hz), 2.20 (s, 3H), 2.43 (t, 1H, *J* = 2.0 Hz), 2.49 (t, 1H, *J* = 2.4 Hz), 2.53 (d, 1H, *J* = 14.8 Hz), 3.29 (dd, 1H, *J* = 5.8, 14.6 Hz), 3.91 (t, 2H, *J* = 4.6 Hz), 3.98 (t, 2H, *J* = 4.2 Hz), 4.09-4.16 (m, 2H), 4.21-4.36 (m, 3H), 4.31 (dd, 2H, *J* = 0.6, 2.2 Hz), 4.32 (dd, 2H, *J* = 0.8, 2.4 Hz), 6.84 (s, 1H), 7.11 (t, 1H, *J* = 7.4 Hz), 7.23 (t, 1H, *J* = 7.4 Hz), 7.33-7.37 (m, 3H), 7.75 (d, 1H, *J* = 7.2 Hz), 7.80-7.82 (m, 1H), 7.85-7.87 (m, 1H); ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 16.0, 19.0, 41.5, 44.8, 58.3, 58.6, 68.00, 68.2, 69.3, 71.5, 74.5, 74.7, 108.3, 119.1, 119.6, 123.5, 123.6, 126.5, 126.5, 126.7, 128.9, 131.9, 133.8, 137.8, 139.1, 139.6, 143.2, 145.7, 152.0, 152.6. (4 C not observed due to overlap.) HRMS (EI) calcd for $C_{34}H_{32}O_4$ 504.2301, found 504.2286.

Irradiation experiment to generate unstable isomer of 1

Motor **1** (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 -60ºC at a distance of 2-3 cm from the centre of the lamp. ^{1}H-NMR spectra of the sample was taken before, during and after irradiation at -60ºC. No further changes were observed after 6 h of irradiation. After warming the sample to room temperature, only the stable form was observed by ^{1}H-NMR.

Stable-**1**: ^{1}H NMR (500 MHz, -60ºC, CD_2Cl_2) δ 1.25 (d, 3H, *J*= 6.5 Hz), 2.08 (s, 3H), 2.52 (d, 1H, *J*= 15 Hz), 2.52 (t, 1H, *J*= 2.5 Hz), 2.58 (t, 1H, *J*= 2.5 Hz), 3.23 (dd, 1H, *J*= 5.5, 14.8 Hz), 3.76-3.85 (m, 2H), 3.92 (t, 2H, *J*= 4 Hz), 3.96-4.00 (m, 1H), 4.06 (quin, 1H, *J*= 6.5 Hz), 4.14-4.27 (m, 7H), 6.84 (s, 1H), 7.1 (t, 1H, *J*= 7 Hz), 7.23-7.27 (m, 2H), 7.30-7.35 (m, 2H), 7.74 (d, 1H, *J*= 7.5Hz), 7.78-7.80 (m, 1H), 7.83-7.84 (m, 1H)

Unstable-**1**: ^{1}H NMR (500 MHz, -60ºC, CD_2Cl_2) δ 1.44 (d, 3H, *J*= 6.5 Hz), 1.93 (s, 3H), 2.94 (dd, 1H, *J*= 6, 16.5 Hz), 2.51 (t, 1H, *J*= 2.5 Hz), 2.59 (t, 1H, *J*= 2.5 Hz), 3.37 (dd, 1H, *J*= 8.5, 16.5 Hz), 3.71-4.29 (peaks in this region could not be resolved due to overlap with remaining stable-**1**), 6.80 (s, 1H), 7.09-7.35 (peaks in this region could not be resolved due to overlap with remaining stable-**1**), 7.67-7.69 (m, 1H), 7.74-7.85 (peaks in this region could not be resolved due to overlap with remaining stable-**1**).

Materials and methods (surfaces)

Quartz microscope slides were obtained from UQG Optics. Toluene and THF were reagent grade and were dried and distilled before use according to standard procedures. Other solvents used were reagent grade chemicals (LAB-SCAN analytical sciences, Poland), and were used as received. All water and aqueous solutions used with surfaces was doubly distilled.

Silicon wafers: XPS analysis on insulating surfaces (like quartz) generates surface charging. Since compensation with a flood gun rapidly destroys organic molecules, the charging effect was minimized by employing a very thin SiOx layer on a conducting silicon substrate which mimics the quartz surface.[3]

Experimental procedures for surface modification

11-azidoundecyltrimethoxysilane monolayer on quartz

Quartz microscope slides were cut into pieces so as to fit into measurement cell of UV/Vis spectrometer. They were cleaned using a 3/7 ratio of 30% H_2O_2 in H_2SO_4 (*Caution! This mixture is extremely corrosive and reactive toward organics*) at 80 °C. These samples were then rinsed with water (3 times) and with MeOH and dried under a stream of N_2.

Azide terminated monolayer was prepared according to two different methods:

Method A (direct assembly)

A piranha-cleaned quartz slides immersed in a 1 mM solution of the silane in toluene for 1 d at rt. After the assembly the slides were sonicated twice in toluene and once in MeOH 2 min each and dried under a stream of N_2.

Method B (chemical pretreatement)

1.25 mL of the hydrolysis solution containing 0.04 g 11-azidoundecyltrimethoxy silane, 6 ml THF and 31 µl double-distilled H_2O and 4 µl 37% HCl was added to 25 mL cyclohexane to give a slighty hazy solution. The piranha-cleaned quartz slides were immersed into this solution overnight. After the assembly the slides were sonicated in DMF, toluene and MeOH for 2 min each and dried under a stream of N_2.

Attaching 1 to azide-functionalized surfaces:

Compound **1** was grafted to the azide monolayer in DMF at room temperature by immersing the slide into a 2 mM solution of **1** containing 1 mol% $CuSO_4 \cdot 5H_2O$ and 5 mol% Na-ascorbate relative to the alkyne moieties. Although the reaction time depended on the method of preparing the azide surface slides were typically immersed for 12 h. The modified quartz substrate or silicon wafer was sonicated in DMF, water and MeOH for 2 min each, and then dried under a stream of N_2.

Higher coverages were obtained when the motor was reacted with azide surfaces prepared by method B. Photochemical experiments were performed on motor surfaces prepared from azide surfaces that were assembled using method A.

XPS measurements

For the X-ray photoelectron spectroscopy (XPS) measurements, the samples were introduced through a load look system into an SSX-100 (Surface Science Instruments) photoemission spectrometer with a monochromatic Al Kα X-ray source ($h\nu$=1486.6 eV). The base pressure in the spectrometer during the measurements was 10^{-10} mbar. The photoelectron takeoff angle was 37°. The energy resolution was set to 1.3 eV to minimize measuring time. XPS binding energies were referenced to the Si 2p core level set to the SiO_2 reference value of 103.0 eV.[4] Spectral analysis included a linear background subtraction and a peak deconvolution that employed mixed Gaussian-Lorentzian functions in a least-square curve-fitting program (WinSpec) developed at the LISE, University of Namur, Belgium. For each sample, a survey scan and the C 1s, O 1s, N 1s and Si 2p narrow scan spectra were collected. The photoemission peak areas of each element, used to estimate the amount of each species on the surface, were normalized by the sensitivity factors of each element tabulated for the spectrometer used. Four different points on each sample were analyzed to check for homogeneity of the monolayer. The same elemental composition for all points of the same sample were obtained, suggesting that all samples were homogeneous.

XPS of 11-azidoundecyltrimethoxysilane monolayer on silicon wafers

The survey scan of the azide self-assembled monolayer (SAM) (Figure 1) shows the core levels of silicon, carbon, nitrogen and oxygen. The presence of the carbon and the nitrogen peaks is clear evidence of the modification of the surface with the azide. The ratio of the peak areas of carbon 1*s* and nitrogen 1*s* matches the stoichiometry of the 11-azidoundecyltrimethoxysilane, namely 11 to 3.

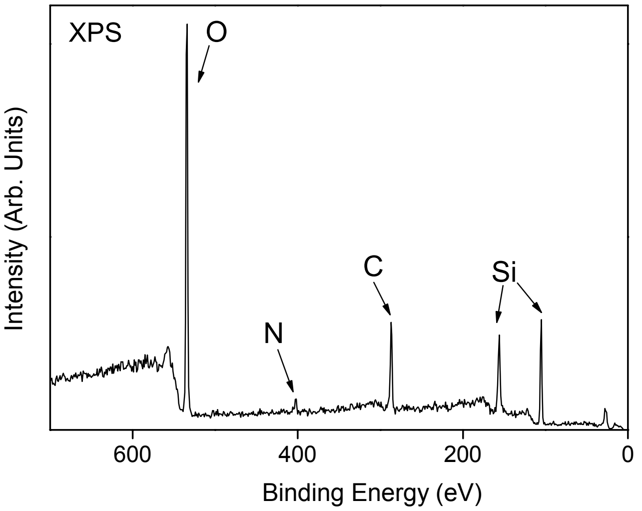


Fig.1 X-ray photoelectron survey spectrum of the azide SAM on silicon oxide.

XPS of 1 after 1,3-dipolar cycloaddition on azide-modified silicon wafers

Figure 2 represents the XPS survey spectrum of dialkyne-motor 1 after 1,3-dipolar cycloaddition on an azide-modified silicon wafer. The absence of a copper peak at 933 eV, sulphur peak at 164 eV and sodium peak at 1072 eV indicates the perfect elimination of the catalyst and the ascorbate after the formation of the dialkyne-motor monolayer.
Comparing the survey spectrum before (Fig. 1) and after (Fig. 2) the dialkyne-motor attachment, we can see an increase in the intensity of the carbon peak, which corresponds with the motor monolayer on the surface.

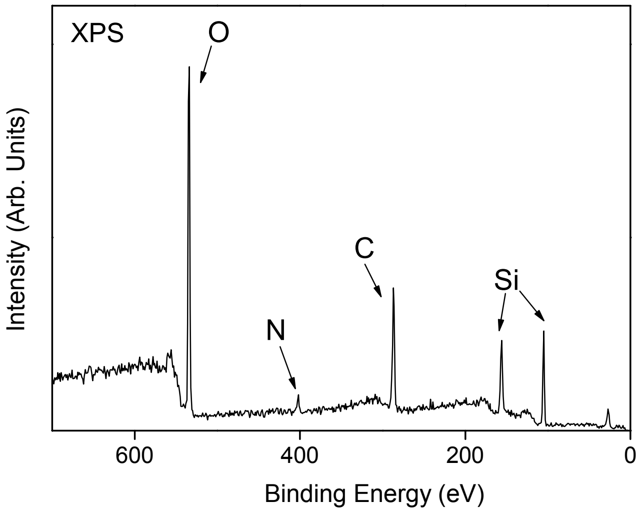
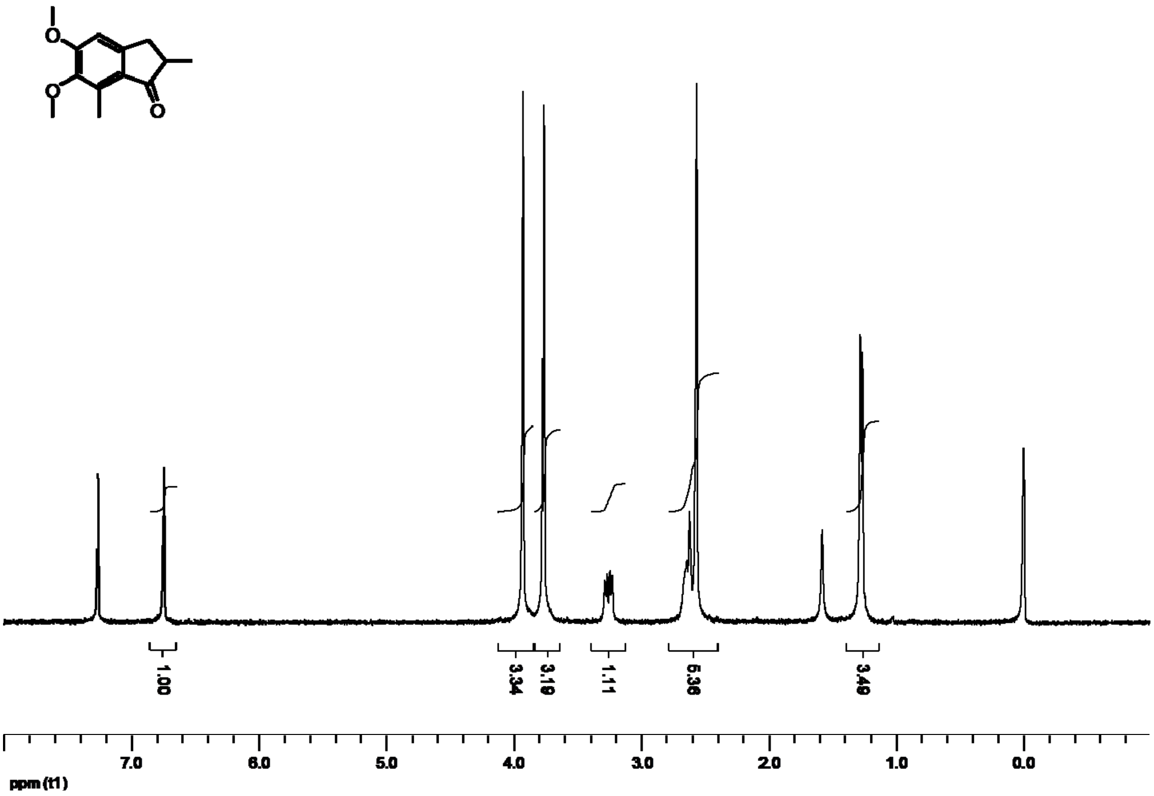
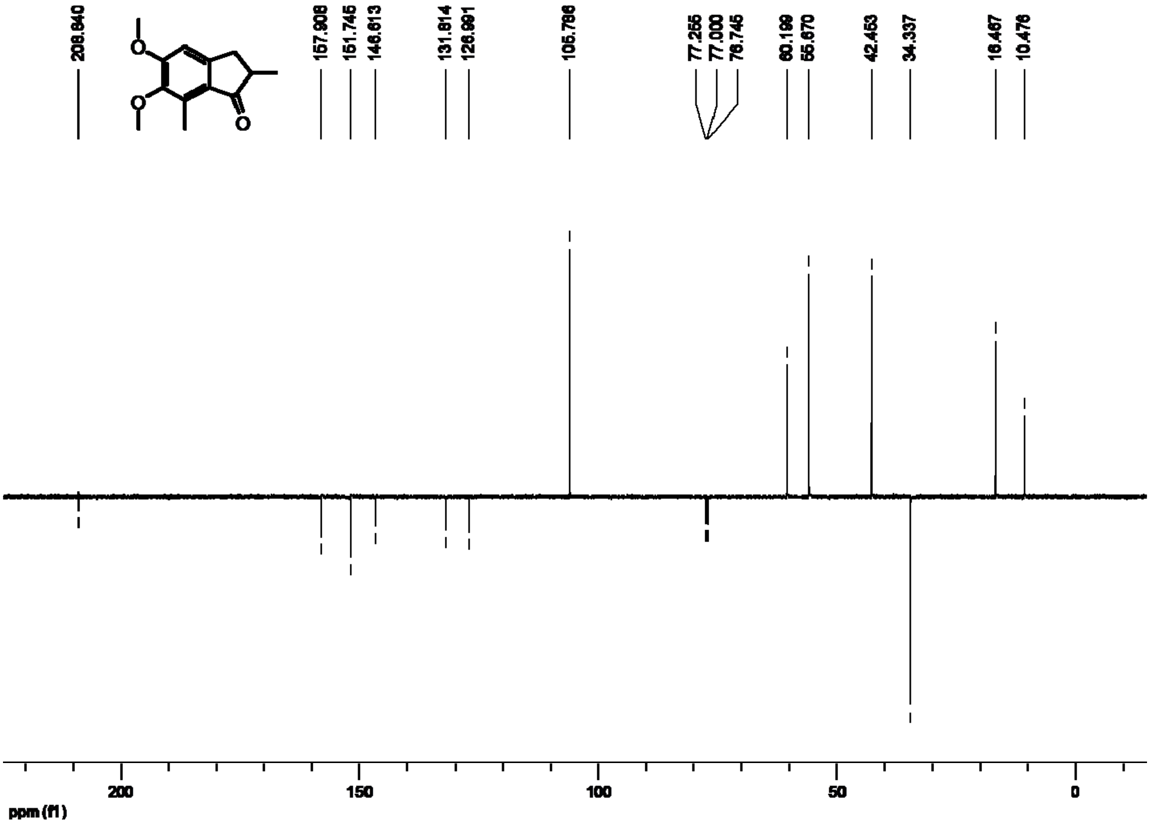
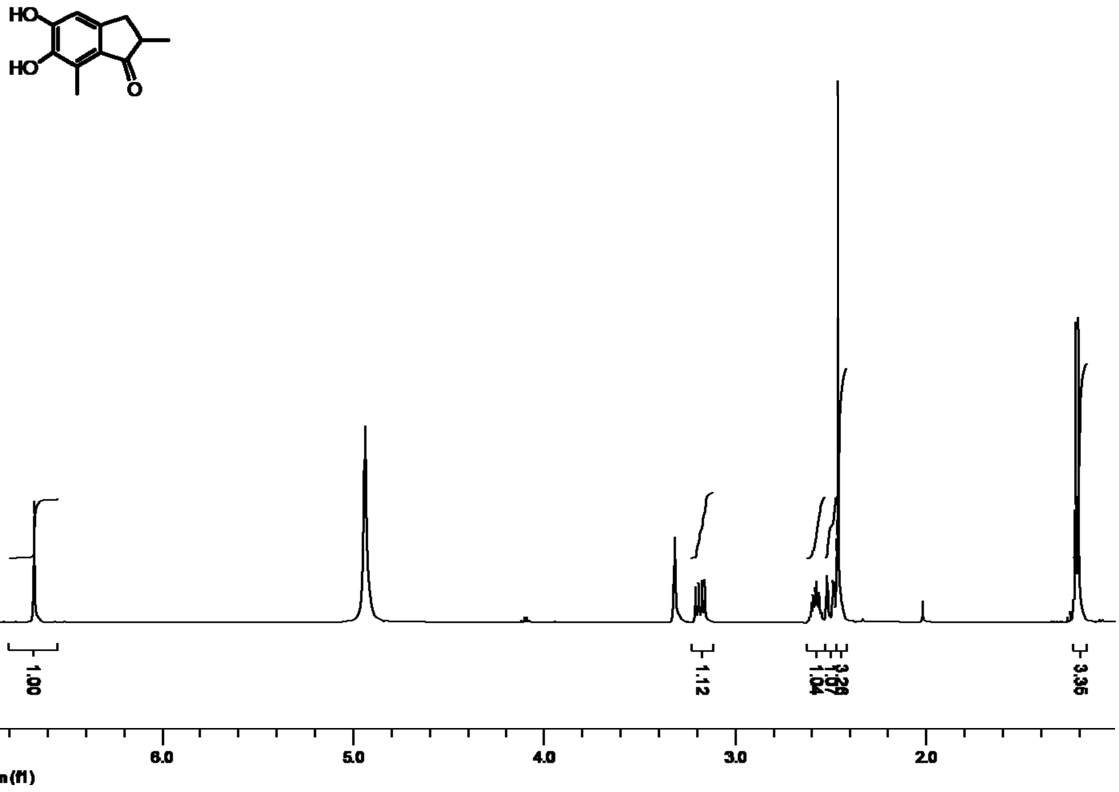


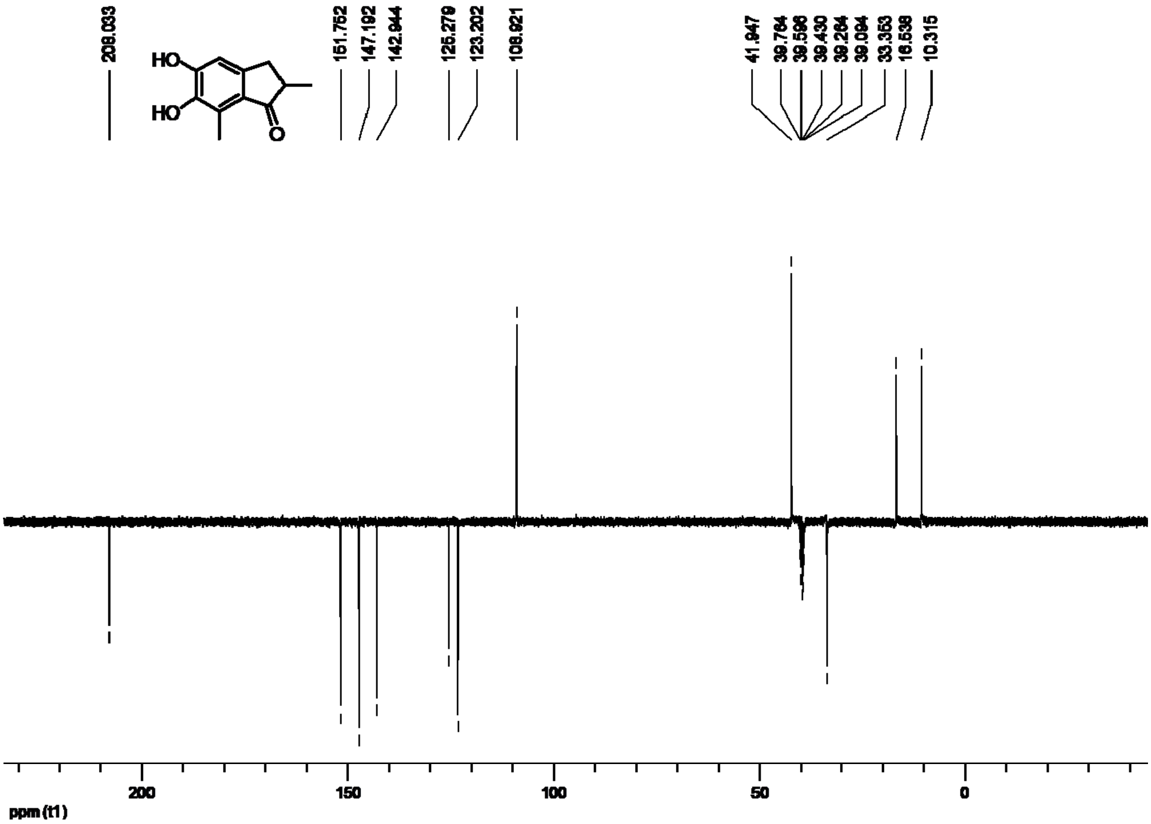
Fig. 2 X-ray photoelectron survey spectrum of **1** after 1,3-cycloaddition on azide-modified silicon wafers.

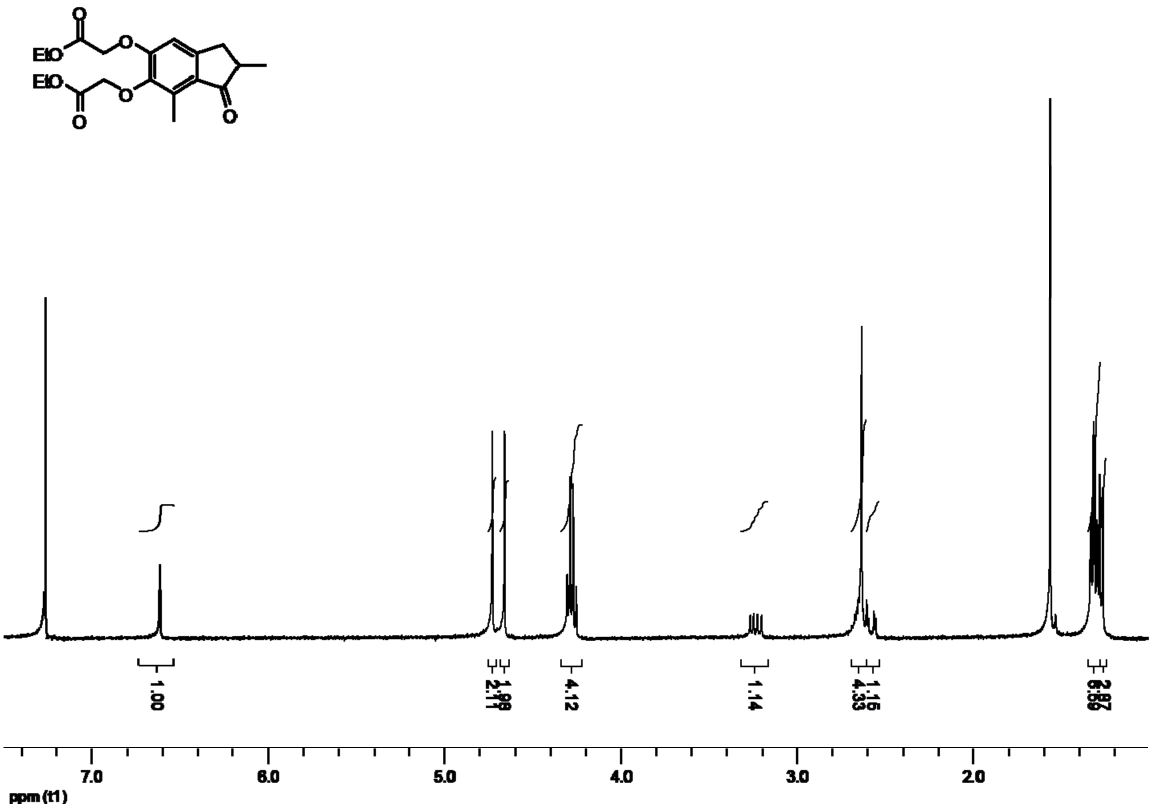
NMR Spectra

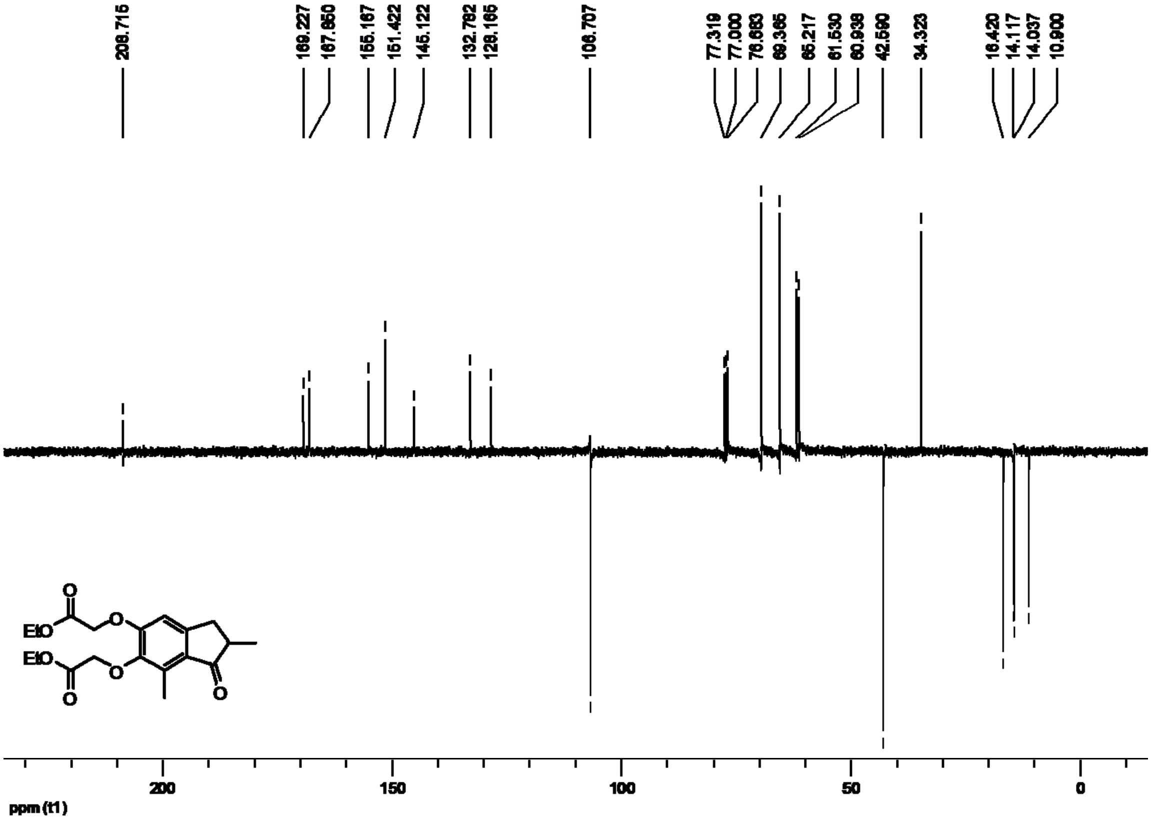

1.00
3.34
3.19
1.11
5.36
3.46
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

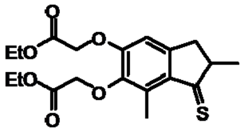

209.840
157.908
151.745
146.613
131.614
126.991
105.786
77.255
77.000
76.745
60.199
55.670
42.453
34.337
16.467
10.476
200
150
100
50
0
ppm (f1)

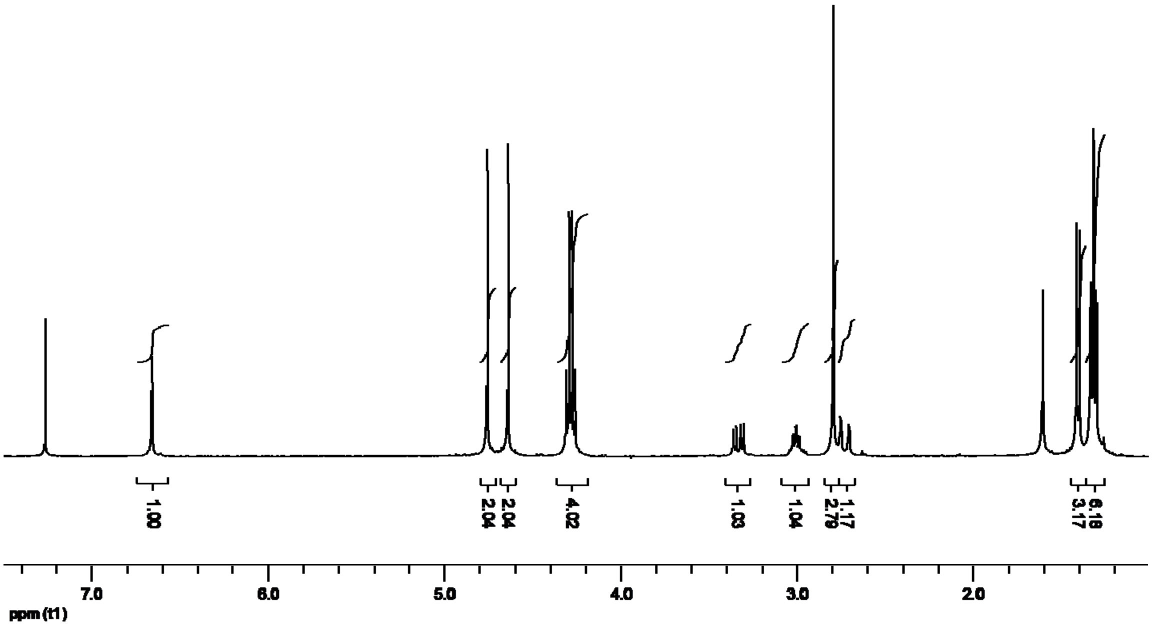

HO
HO
O
1.00
1.12
1.04
1.07
3.28
3.35
6.0
5.0
4.0
3.0
2.0
ppm (f1)

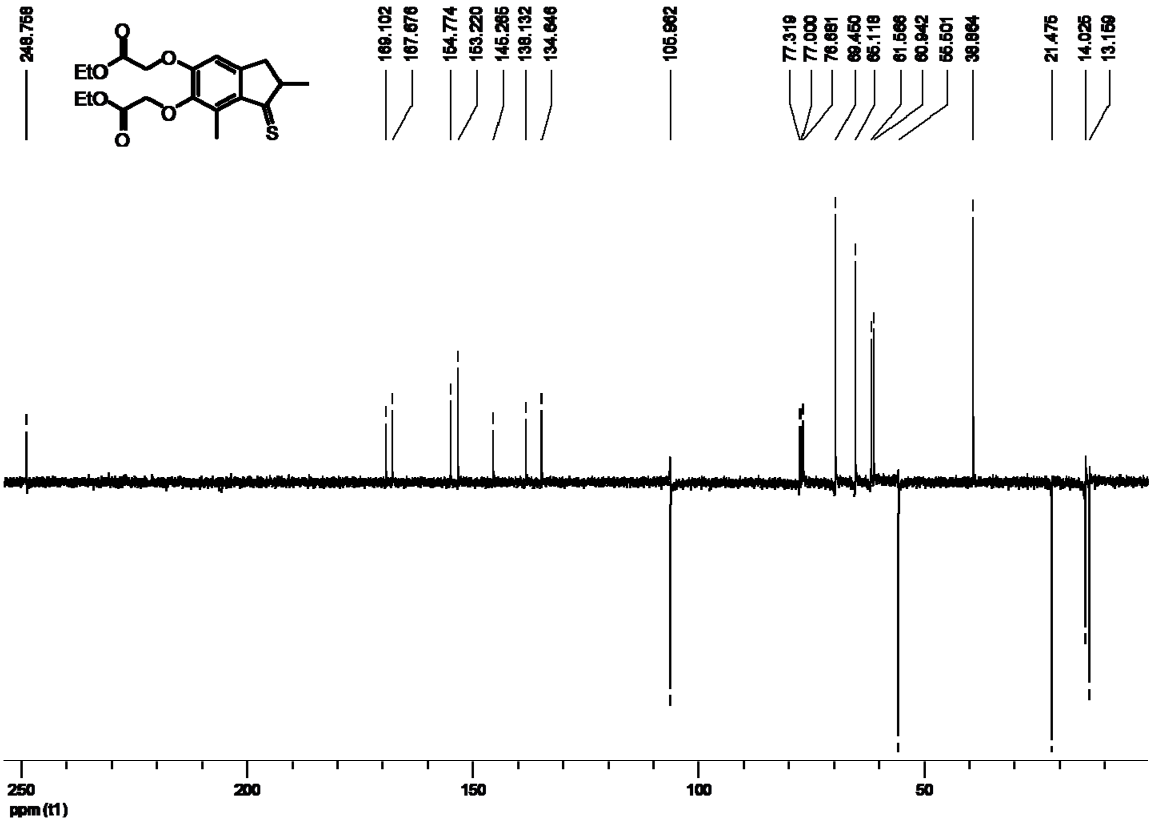

208.033
HO
HO
O
151.752
147.192
142.944
126.279
123.202
108.921
41.947
39.764
39.598
39.430
39.264
39.094
33.353
16.538
10.315
200
150
100
50
0
ppm (t1)

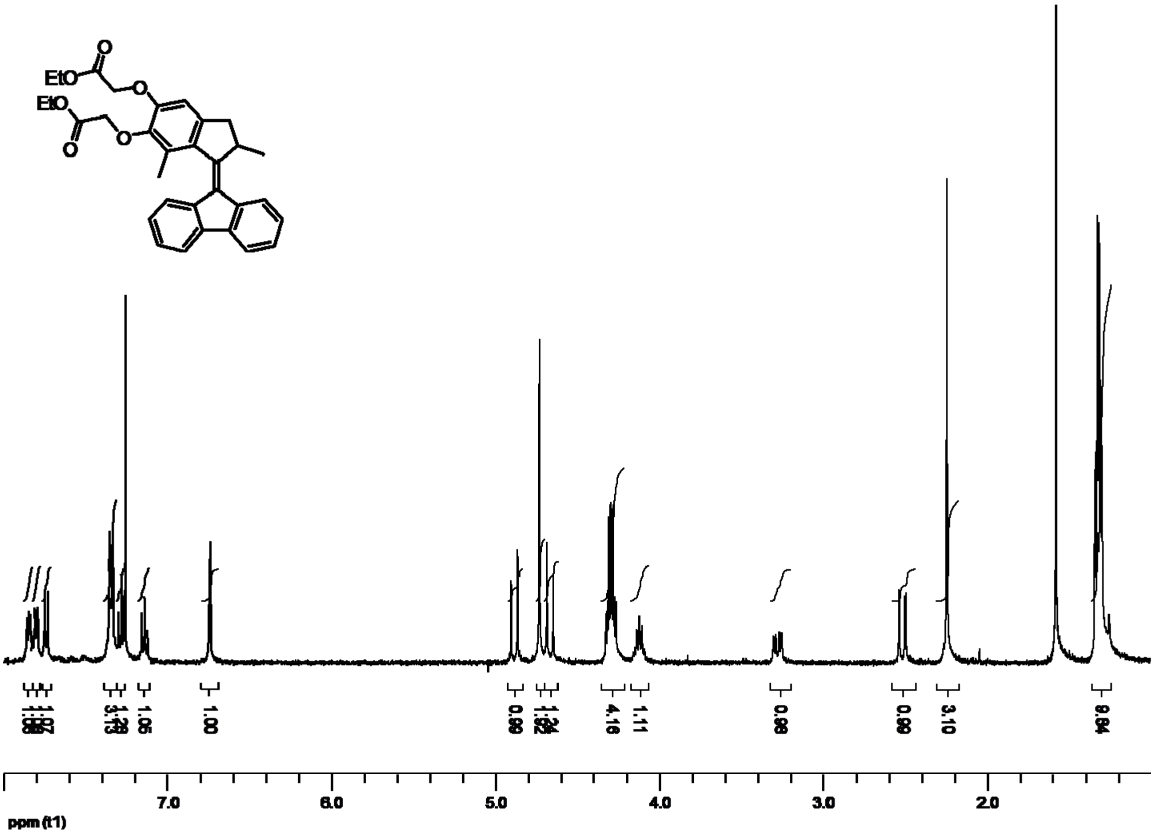

EtO
EtO
O
O
O
O
O
1.00
2.11
1.99
4.12
1.14
4.33
1.15
6.89
2.87
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

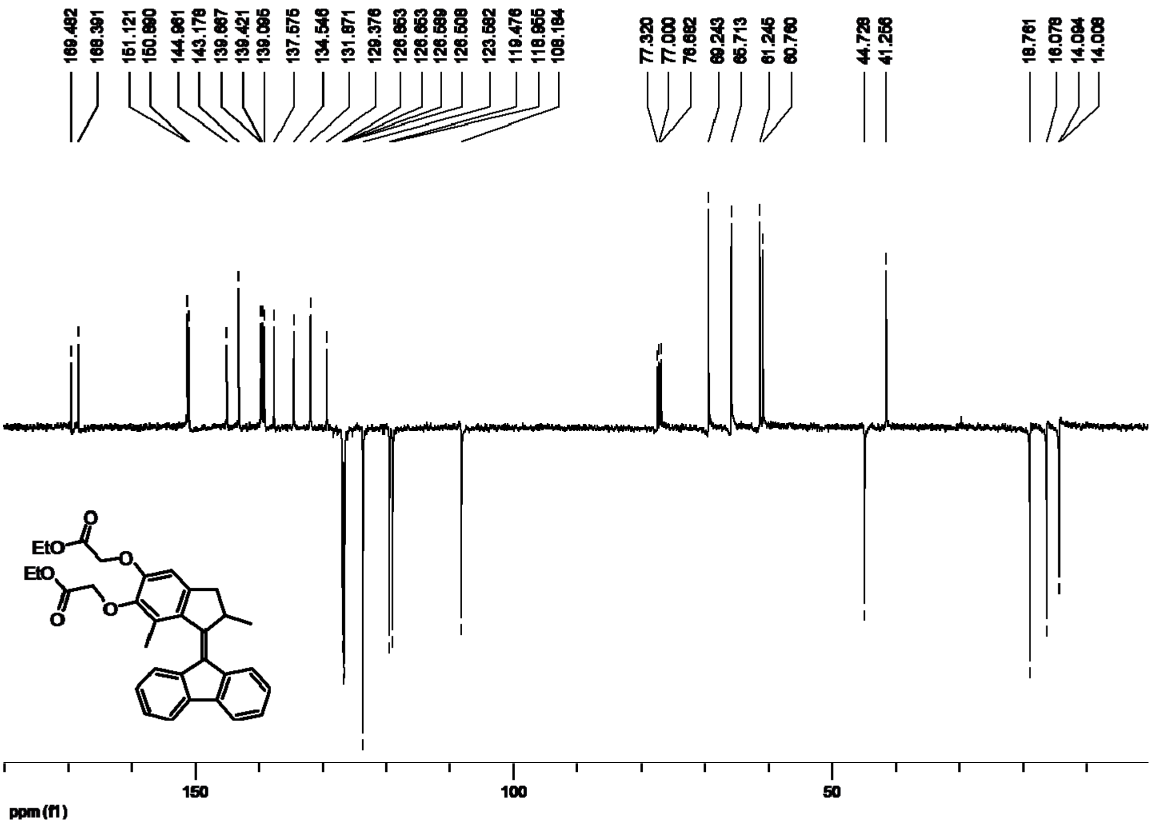

208.715
169.227
167.850
155.167
151.422
145.122
132.782
128.165
106.707
77.319
77.000
76.683
69.365
65.217
61.530
60.938
42.580
34.323
16.420
14.117
14.037
10.900
EtO
EtO
O
O
O
O
O
200
150
100
50
0
ppm (t1)

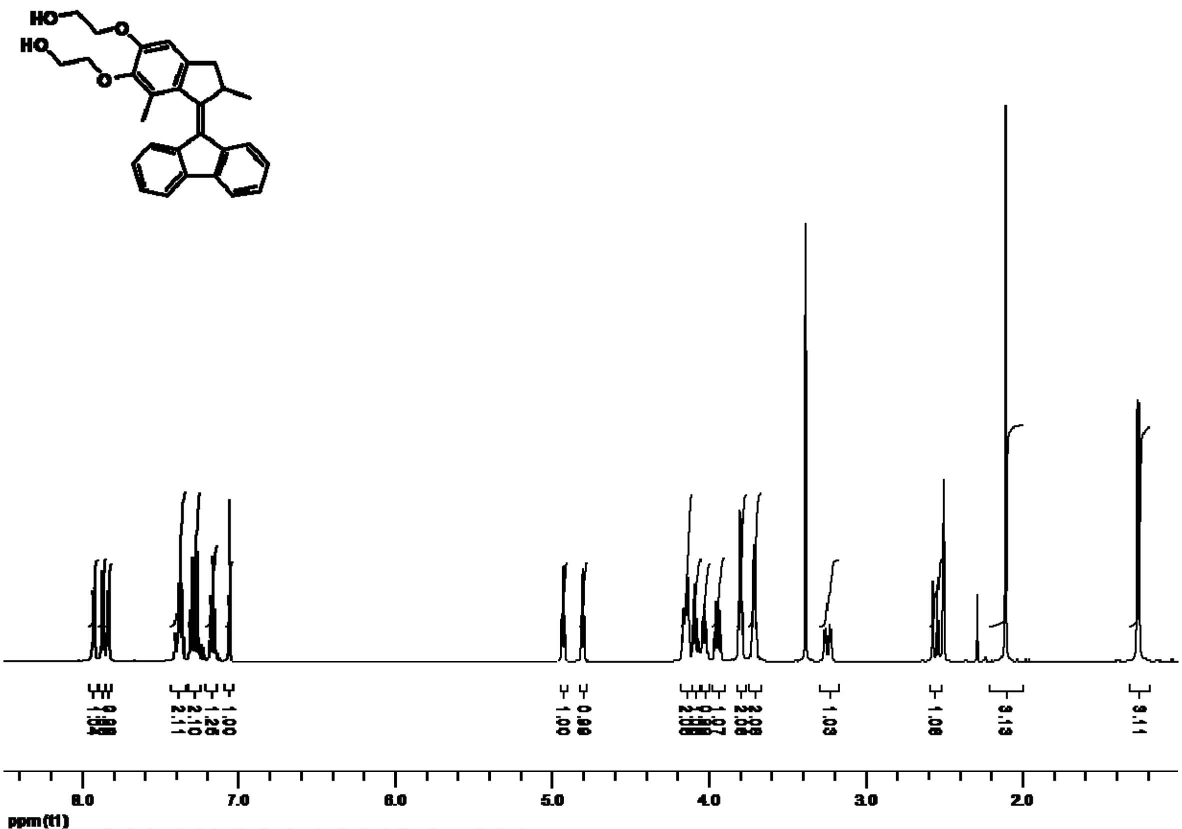

EtO
EtO
O
O
O
O
S

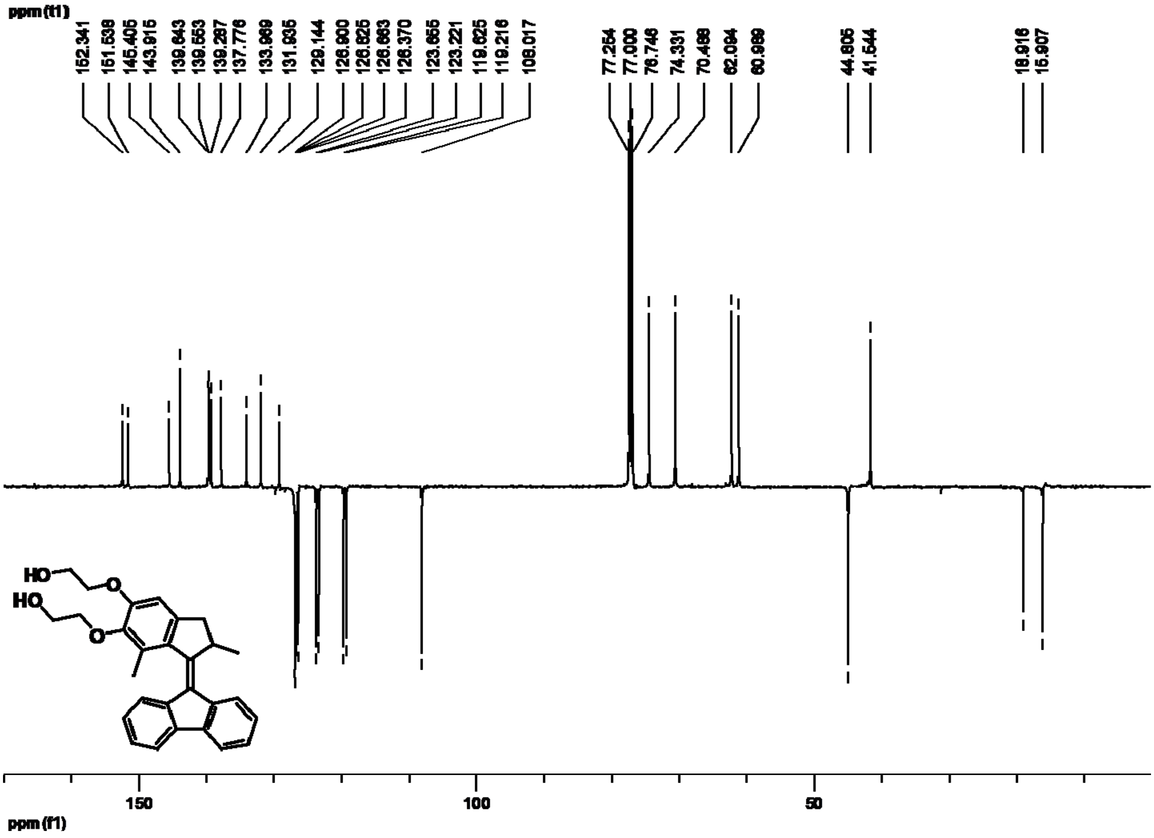

1.00
2.04
2.04
4.02
1.03
1.04
2.79
1.17
3.17
6.18
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

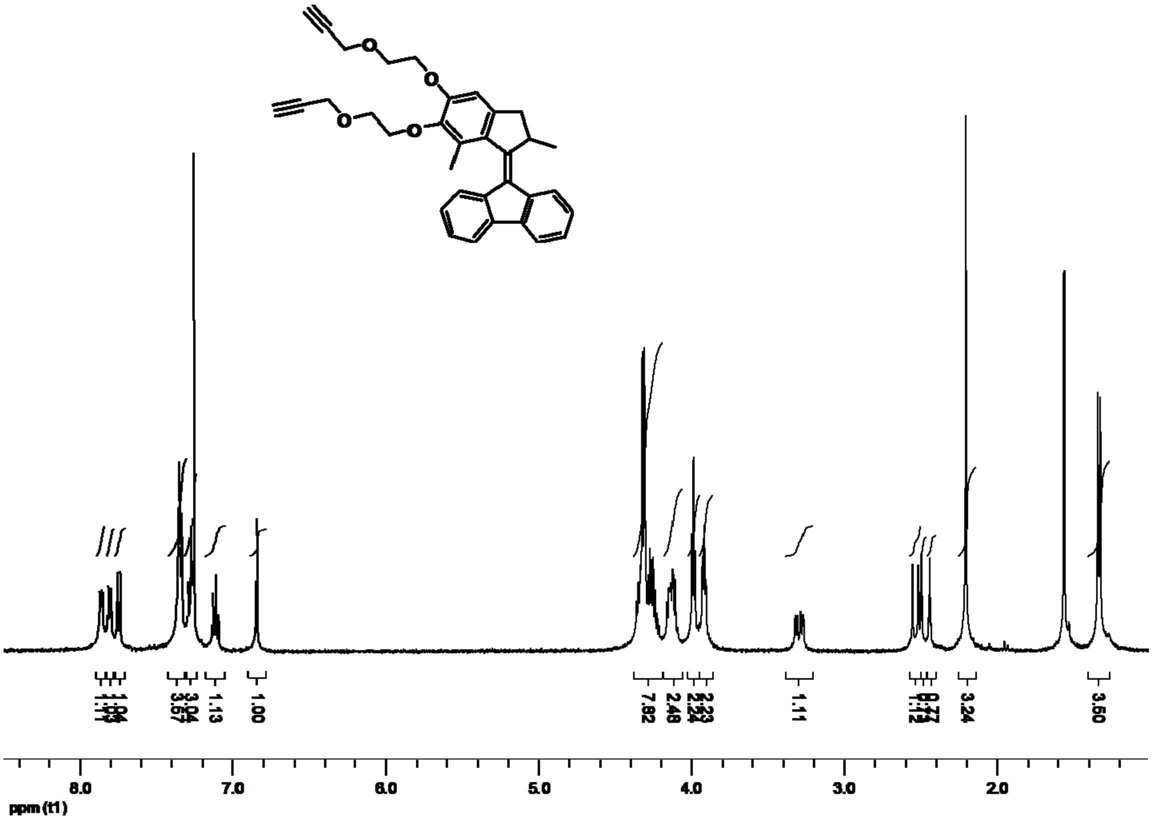

249.758
169.102
167.676
154.774
153.220
145.285
139.132
134.846
105.862
77.319
77.000
76.681
69.450
65.118
61.568
60.942
55.501
39.864
21.475
14.025
13.159
EtO
EtO
O
O
O
O
S
250
200
150
100
50
ppm (t1)

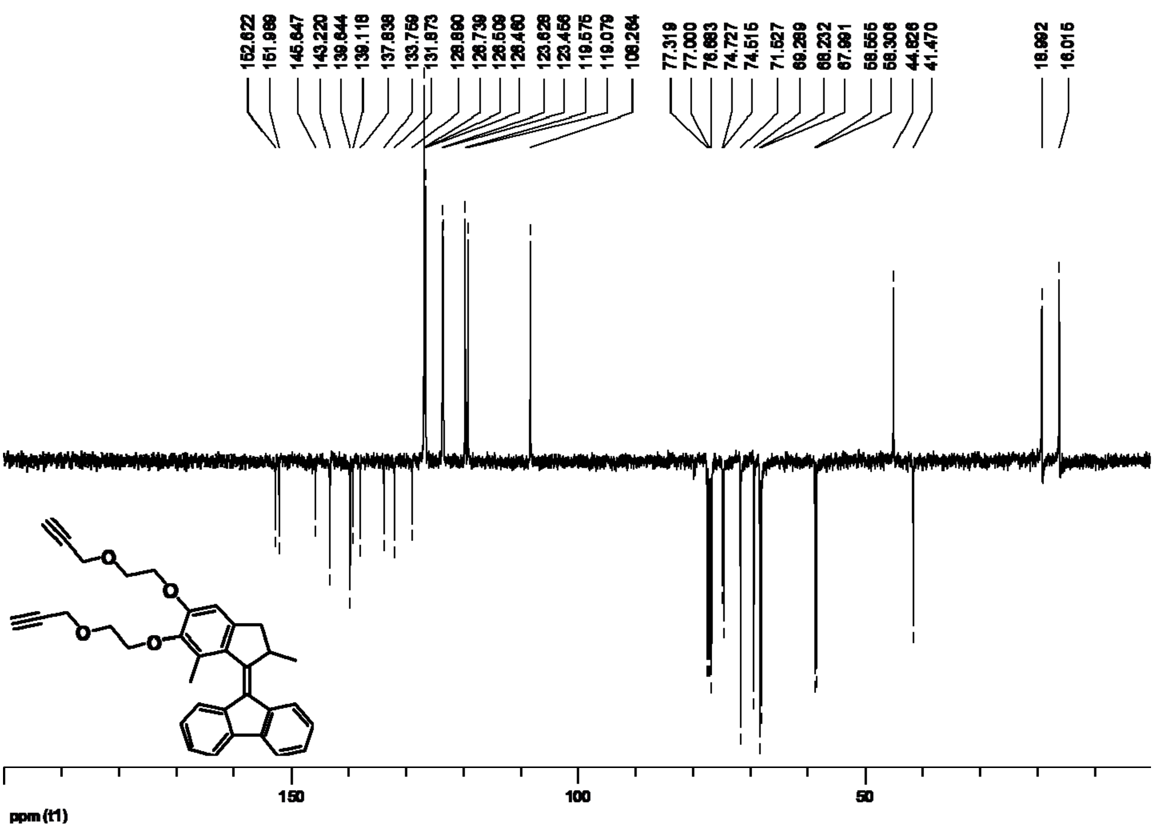

EtO
O
O
EtO
O
O
1.07
3.13
1.05
1.00
0.99
1.24
4.16
1.11
0.98
0.99
3.10
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


169.482
169.391
151.121
150.890
144.961
143.178
139.667
139.421
139.095
137.575
134.546
131.671
129.376
126.953
126.863
126.589
126.508
123.582
119.476
118.955
109.184
77.320
77.000
76.682
69.243
65.713
61.245
60.780
44.728
41.256
18.761
16.078
14.094
14.008
EtO
O
O
EtO
O
O
150
100
50
ppm (f1)

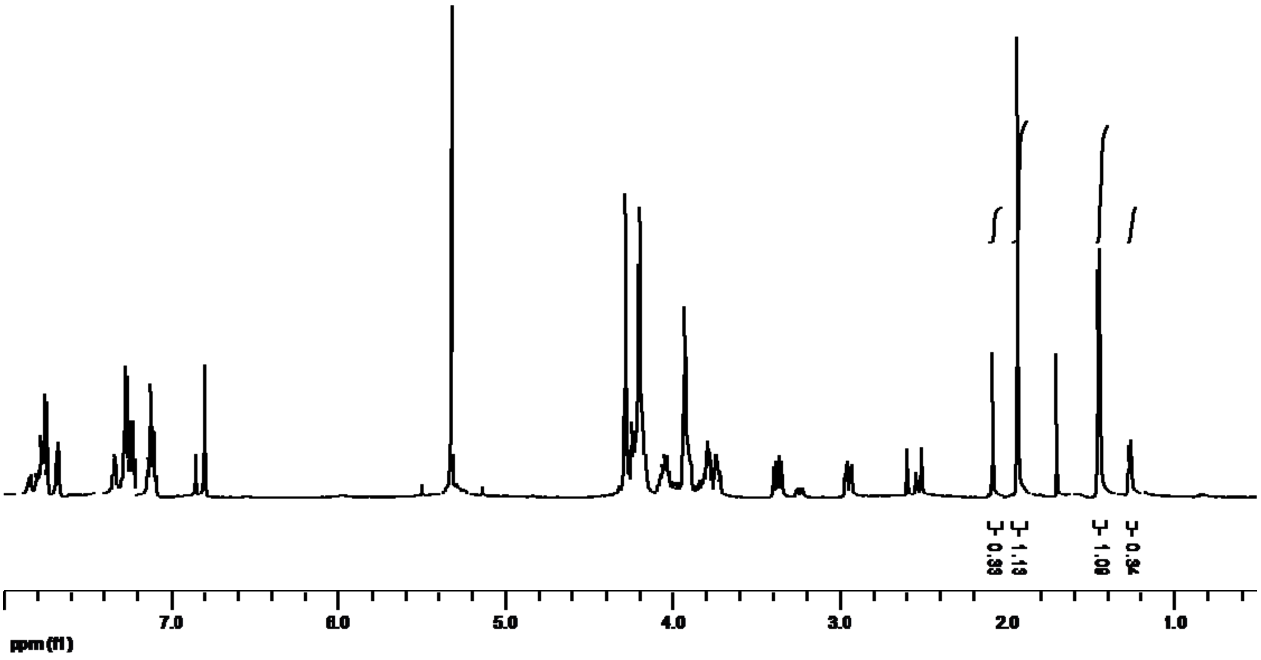

HO
HO
O
O
2.11
2.10
1.25
1.00
1.00
0.99
1.07
2.08
2.08
1.03
1.08
3.13
3.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

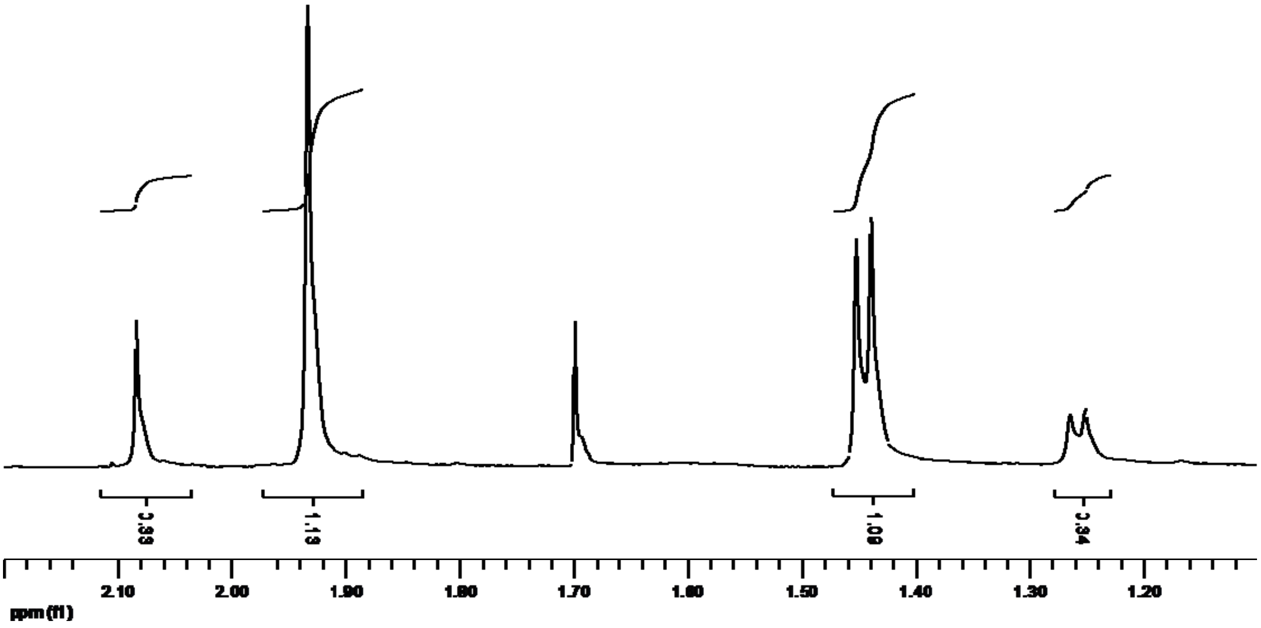

152.341
151.538
145.405
143.915
139.643
139.553
139.287
137.776
133.989
131.935
129.144
126.900
126.826
126.683
126.370
123.655
123.221
119.625
119.216
108.017
77.254
77.000
76.746
74.331
70.488
62.084
60.989
44.805
41.544
18.916
15.907
HO
HO
O
O
150
100
50
ppm (f1)


1.04
1.11
3.67
3.04
1.13
1.00
7.82
2.48
2.24
2.23
1.11
0.77
1.12
3.24
3.50
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


152.622
151.989
145.647
143.220
139.644
139.118
137.838
133.759
131.873
128.890
128.739
128.508
128.460
123.628
123.456
119.575
119.079
108.264
77.319
77.000
76.683
74.727
74.515
71.527
69.289
68.232
67.991
58.555
58.306
44.626
41.470
18.992
16.015
150
100
50
ppm (t1)

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

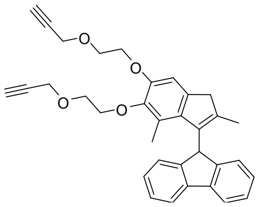




Notes and references

(1) For the synthesis of **S5** see: J. Vicario, M. Walko, A. Meetsma, B. L. Feringa, *J. Am.Chem. Soc.* 2006, **128**, 5127.

(2) Prolonged heating of the formed episulfide resulted in spontaneous desulfurization which yielded not only alkene **S7** but also also a product which is suggested to be the result of the isomerization of the olefin. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 6H, *J*= 7.2 Hz), 1.97 (s, 3H), 2.93 (s, 3H), 3.40 (s, 2H), 4.26 (q, 4H, *J*= 7.2 Hz), 4.67 (s, 4H), 5.08 (s, 1H), 6.86 (s, 1H), 7.14-7.23 (m, 3H), 7.28-7.37 (m, 3H), 7.72 (d, 2H, *J*=7.5 Hz)



(3) D. Briggs, M. P. Seah (Ed.) Practical Surface Analysis by Auger and X-ray Photoemission spectroscopy, John Wiley & Sons Ltd.: Chichester 1983.

(4) J.K. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Inc., 1995.