Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2013

Towards Dynamic Control of Wettability by Using Functionalized Altitudinal Molecular Motors on Solid Surfaces

Gábor London, Kuang-Yen Chen, Gregory T. Carroll, and Ben L. Feringa*[a]

chem_201300500_sm_miscellaneous_information.pdf
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 Schlenk 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. ‘H and 13C 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 ‘H nucleus, and at 75.43, 100.57 and 124.98 MHz for the 13C nucleus. Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from residual protium in the NMR solvents CHCl3: δ 7.26, CDCl3: δ 5.32, DMSO δ 2.5). 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 (CDCl3: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet), coupling constant in Hz, integration. Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at λ = 365 nm, ± 30 nm. NMR samples were placed 2-3 cm from the lamp. UV spectra were obtained using Hewlet-Packard HP 8543 FT or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette. Contact angles were measured on a LINOS contact angle goniometer. The contact angle was measured at three different locations on each surface and the results averaged.

Preparation of azide terminated monolayer
1.25 mL of the hydrolysis solution containing 0.04 g 11-azidoundecyltrimethoxy silane2 6 ml THF and 31 µl double-distilled H2O and 4 µl 37% HCl was added to 25 mL cyclohexane to give a slightly 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 Ar.

Procedure for the interfacial 1,3-dipolar cycloaddition
Compounds 16 and 17 were grafted to the azide monolayer SAM-1 by immersing the slide into a 1 mM solution of cis- and trans-16 and 17 in DMF containing 1 mol% CuSO4•5H2O and 5 mol% sodium-ascorbate relative to the alkyne moieties. The azide functionalized slides were immersed for 12 h at rt. The modified quartz substrates (MS-1 and MS-2) were sonicated in DMF, water and MeOH for 2 min each and then dried under a stream of Ar.
Figure S1 (a) Partial $^1$H NMR spectra of cis-15 and trans-15 in CDCl$_3$. (b) Partial $^1$H NMR spectra of cis-16 and trans-16 in CDCl$_3$. Cis- and trans-isomers were assigned based on the singlet absorption of H$_a$ of the aromatic lower half. In previously reported motors containing substituted fluorene lower halves the absorption of H$_a$ appears at higher field in the cis-form compared to the trans-isomer.$^{3-6}$
Figure S2 (a) Eyring plot of the conversion of unstable-trans-16 to stable-trans-16 and (b) Eyring plot of the conversion of unstable-cis-16 to stable-cis-16 via thermal helix inversion.

Figure S3 (a) Eyring plot of the conversion of unstable-trans-17 to stable-trans-17 and (b) Eyring plot of the conversion of unstable-cis-17 to stable-cis-17 via thermal helix inversion.

Figure S4 Water droplets on quartz surfaces modified by the attachment of (a) cis-16 and (b) trans-16 containing a cyano-group on the rotor part. Water contact angles of 67(±1°) and 60(±1°) were measured for cis-16 and trans-16 isomers, respectively.
Figura S5 Water droplets on quartz surfaces modified by the attachment of perfluorobutyl-motor cis-17 (a) and trans-17 (b). Water contact angles of 80(±2°) and 92(±1°) were measured for cis-17 and trans-17 isomers, respectively.

Synthesis of compounds and intermediates

The synthesis of compounds 24,7, 34, 44 and 51 has been reported earlier.

(Cis/trans)-Diester-bromo motor (7) 2-bromodiazofluorenone (4) (1.23 g, 4.7 mmol) was added to a solution of thioketone 5 (1.64 g, 4.3 mmol) in toluene (30 mL). The mixture was heated up to 55°C for 3 h. The formation of the episulfide was monitored by 1H NMR spectroscopy by following the shift of the aromatic proton of the thioketone from 6.66 ppm to 6.35 and 6.37 ppm (E/Z isomers of the episulfide). After the conversion of the thioketone was complete, PPh3 (1.2 g, 4.7 mmol) was added to the episulfide solution and the mixture was heated for an additional 2 h at 75°C. The reaction mixture was cooled to rt and concentrated in vacuo. EtOAc (60 mL) was added to the mixture, which resulted in the precipitation of PPh3S as yellow crystals. The precipitate was filtered and the procedure was repeated once more. The solvent was removed under reduced pressure. The product was obtained as a mixture of cis and trans isomers (42 : 58) after column chromatography (SiO2, n-hexane : EtOAc = 4 : 1) as a yellow solid (1.6 g, 2.93 mmol, 68 %). 1H NMR (400 MHz, CDCl3) δ 1.30-1.34 (m, 9H major, 9H minor), 2.23 (s, 3H, major), 2.24 (s, 3H, minor), 2.54 (d, J = 14.7 Hz, 1H major, 1H minor), 3.29 (dd, J = 5.8, 14.76 Hz, 1H major, 1H minor), 4.04-4.15 (m, 1H major, 1H minor), 4.26-4.33 (m, 4H major, 4H minor), 4.67 (d, J = 15.8 Hz, 1H major), 4.70 (d, J = 15.7 Hz, 1H minor), 4.79 (s, 2H, major), 4.75 (s, 2H, minor), 4.83 (d, J = 15.7 Hz, 1H, minor), 4.90 (d, J = 15.8 Hz, 1H, major), 6.75 (s, 1H, major), 6.77 (s, 1H, minor), 7.17 (t, J = 7.6 Hz, 1H, major), 7.29 (t, J = 7.5 Hz, 1H, major), 7.32-7.41 (m, 1H major, 3H minor), 7.45-7.48 (m, 1H major, 1H minor), 7.61 (d, J = 8.1 Hz, 1H, minor), 7.66 (d, J = 8.1 Hz, 1H, major), 7.71 (d, J = 7.3 Hz, 1H, major), 7.76-7.79 (m, 1H minor), 7.82-7.85 (m, 1H, minor), 7.95 (s, 1H, major); 13C NMR (100 MHz, CDCl3) δ 14.1, 14.2, 16.2, 18.8, 18.9, 41.3, 41.4, 44.7, 44.8, 60.9, 61.0, 61.4, 65.8, 65.9, 68.1, 69.3, 69.7, 108.2, 108.4, 119.1, 119.6, 120.2, 120.3, 120.4, 120.7, 123.6, 123.7, 126.4, 126.7, 126.8, 126.9, 127.0, 127.1, 128.1, 128.4, 129.3, 129.4, 131.9, 132.1, 134.0, 134.2, 137.4, 137.9,
138.4, 138.7, 139.2, 139.3, 141.3, 143.5, 143.7, 145.1, 145.6, 151.2, 151.7, 152.8, 152.9, 168.4, 168.5, 169.3, 169.5; HRMS (ESI) calcd for C_{32}H_{32}O_{6}Br 591.1377 (MH^+), found 591.1379.

One of the isomers (trans) could be crystallized from Et_2O. ^1H NMR (400 MHz, CDCl_3) δ 1.29-1.35 (m, 9H), 2.23 (s, 3H), 2.55 (d, J = 14.9 Hz, 1H), 3.29 (dd, J = 5.5, 15.1 Hz, 1H), (quin, J = 6.5 Hz, 1H), 4.26-4.33 (m, 4H), 4.67 (d, J = 15.9 Hz, 1H), 4.74 (s, 2H), 4.90 (d, J = 15.8 Hz, 1H), 6.75 (s, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.4 Hz, 1H) 7.95 (s, 1H); ^13C NMR (100 MHz, CDCl_3) δ 14.1, 14.2, 16.2, 18.9, 41.4, 44.8, 60.9, 61.4, 65.8, 69.3, 108.2, 119.1, 120.5, 120.8, 123.6, 126.7, 127.0, 127.1, 128.5, 129.3, 132.1, 134.3, 137.5, 138.2, 138.5, 141.3, 143.5, 145.1, 151.3, 152.8, 168.5, 169.6.

(Cis/trans)-Diester-cyano motor (8) A solution of (cis/trans)-7 (546 mg, 1.00 mmol) in N,N-dimethylacetamide (22 mL) was added to a mixture of Pd_2(dba)_3 (18.5 mg, 0.02 mmol, 2 mol%), dppf (22.3 mg, 0.04 mmol, 4 mol%), Zn powder (13.1 mg, 0.20 mmol, 20 mol%) and Zn(CN)_2 (235.0 mg, 2.00 mmol, 200 mol%) purged with argon and the mixture was heated at 150°C for 5 h. The reaction mixture was cooled to rt, diluted with EtOAc (50 mL), and washed with saturated aq Na_2CO_3 (60 mL), brine (20 mL), dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography (SiO_2, n-hexane : EtOAc = 4 : 1) afforded the product as a mixture of trans and cis isomers (~2 : 1) as a yellow solid (479 mg, 0.89 mmol, 89%). Cis/trans mixture: ^1H NMR (400 MHz, CDCl_3) δ 1.29-1.36 (m, 9H major, 9H minor), 2.23 (s, 3H, major), 2.25 (s, 3H, minor), 2.57 (d, J = 14.8 Hz, 1H, minor), 2.58 (d, J = 14.8 Hz, 1H, major), 3.31 (dd, J = 5.7, 14.6 Hz, 1H major, 1H minor), 4.04-4.16 (m, 1H major, 1H minor), 4.26-4.34 (m, 4H major, 4H minor), 4.68 (d, J = 15.9 Hz, 1H, major), 4.75 (s, 2H, major), 4.76 (s, 2H, minor), 4.84 (d, J = 3.6 Hz, 2H, minor), 4.92 (d, J = 15.9 Hz, 1H, major), 6.76 (s, 1H, major), 6.79 (s, 1H, minor), 7.26 (m, 1H, major), 7.35 (dt, J = 1.0, 7.5 Hz, 1H, major), 7.40 (d, J = 7.7 Hz, 1H, major), 7.43-7.47 (m, 2H, minor) 7.57 (dd, J = 1.4, 7.9 Hz, 1H minor), 7.63 (dd, J = 1.3, 7.9 Hz, 1H, major), 7.65 (br s, 1H, minor), 7.80 (d, J = 7.3 Hz, 1H, major), 7.83 (d, J = 7.4 Hz, 1H, minor), 7.85-7.91 (m, 2H, minor) 7.88 (d, J = 7.9 Hz, 1H, major), 8.09 (s, 1H, major); ^13C NMR (125 MHz, CDCl_3) δ 14.1, 14.2, 16.2, 18.9, 19.2, 41.4, 44.9, 45.2, 60.9, 61.0, 61.5, 65.7, 65.9, 69.2, 69.3, 108.2, 108.5, 109.4, 109.5, 119.6, 119.8, 120.0, 120.1, 120.2, 120.6, 123.8, 123.82, 127.0, 127.1, 127.2, 127.3, 127.5, 127.6, 128.4, 128.5, 130.1, 130.4, 132.1, 132.3, 133.6, 133.9, 137.3, 137.7, 138.3, 139.5, 140.1, 142.6, 143.3, 143.8, 143.9, 145.1, 145.4, 151.6, 151.8, 154.5, 154.7, 168.4, 169.5, 169.6; HRMS (ESI) calcd for C_{33}H_{31}NO_{6}Na 560.2044 (MNa^+), found 560.2022.

One of the isomers (trans) could be crystallized from Et_2O: ^1H NMR (400 MHz, CDCl_3) δ 1.30-1.36 (m, 9H), 2.23 (s, 3H), 2.58 (d, J = 14.8 Hz, 1H), 3.31 (dd, J = 5.9, 14.7 Hz, 1H), 4.07 (quin, J = 6.4 Hz, 1H), 4.30 (m, 4H), 4.68 (d, J = 15.9 Hz, 1H), 4.75 (s, 2H), 4.92 (d, J = 15.9 Hz, 1H), 6.76 (s, 1H), 7.26 (m, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H), 7.63 (dd, J = 1.2, 7.9 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 8.09 (s, 1H).
2-(Perfluorobutyl)-9H-fluoren-9-one (10) A suspension of Cu-bronze (2.6 g, 40.6 mmol) in DMSO (30 mL, dried over 4 Å molecular sieves for 12 h) was heated at 125 °C for 15 min. Iodononafluorobutane (3.5 mL, 20.3 mmol) in DMSO (5 mL) was added dropwise and the mixture was stirred for 45 min at 125 °C. Next, 2-bromofluorenone 2 (1.0 g, 3.9 mmol) in DMSO (10 mL) was added dropwise and the mixture was stirred for an additional 6 h at the same temperature. The mixture was diluted with diethyl ether (50 mL), and was filtered over celite to remove Cu-bronze. The organic phase was washed with water (5 × 100 mL) and brine, dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO₂, n-heptane : dichloromethane 10 : 1 → 5 : 1, dry-loaded on celite) to give 10 as yellow crystals (1.1 g, 2.8 mmol, 72 %). Mp 96-97 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.1 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.7 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.88 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 120.4, 121.2, 122.7 (t, J = 6.5 Hz), 124.7, 129.6 (t, J = 24.6 Hz), 130.3, 133.2 (t, J = 6.5 Hz), 134.3, 134.4, 135.1, 142.9, 147.7, 192.1. Peaks corresponding to CF₃ are not observed due to the low intensity of the peaks in the region they are expected (~ 115 ppm). HRMS (APCI) calcd for C₁₇H₈F₉O 399.0433 (MH⁺), found 399.0423.

(E/Z)-(2-(Perfluorobutyl)-9H-fluoren-9-ylidene)hydrazine (11) To a solution of ketone 10 (1.0 g, 2.5 mmol) in MeOH : DCM (4:1, 25 mL), N₂H₄ • H₂O (8 mL) was added and the solution was heated at 45°C for 3 h. Addition of water (10 mL) to the hot mixture followed by cooling to room temperature resulted in the precipitation of a pale yellow solid. The solid was filtered, washed with cold MeOH and dried on air. The product 11 (151 mg, 0.37 mmol, 64 %) was obtained as a mixture of E/Z isomers (~ 1 : 1.5) as a pale yellow solid and was used without further purification. ¹H NMR (300 MHz, CDCl₃) δ 6.52 (br s, 2H, major), 6.58 (br s, 2H, minor), 7.36-7.42 (m, 2H, major), 7.43-7.53 (m, 2H, minor), 7.56 (d, J = 8.0 Hz, 1H, minor), 7.67 (d, J = 8.0 Hz, 1H, major), 7.71-7.74 (m, 1H, major), 7.76-7.79 (m, 1H major, 1H minor), 7.87 (t, J = 8.7 Hz, 1H major, 1H minor), 7.94 (d, J = 7.1 Hz, 1H, minor), 7.98 (s, 1H, minor), 8.07 (s, 1H, major); ¹³C NMR (100 MHz, CDCl₃) δ 119.4 (t, J = 5.6 Hz), 119.5, 120.3, 120.4, 121.0, 121.3, 123.3 (t, J = 6.3 Hz), 125.3, 126.7 (t, J = 6.6 Hz), 128.3 (d, J = 7.1 Hz), 128.7, 128.9, 129.2, 129.8, 130.0, 130.6, 136.9, 138.0, 138.4, 139.6, 141.4, 143.4, 143.8, 144.5; HRMS (ESI) calcd for C₁₇H₁₀F₉N₂ 413.0695 (MH⁺), found 413.0690. Minor-isomer was isolated (SiO₂, n-heptane : EtOAc 5 : 1). ¹H NMR (400 MHz, CDCl₃) δ 6.58 (br s, 2H) 7.44-7.53 (m, 2H), 7.56 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.98 (s, 1H).

9-diazo-2-(Perfluorobutyl)-9H-fluorene (12) MnO₂ (0.5 g, 5.75 mmol) was added to a stirred solution of hydrazone 11 (760 mg, 1.84 mmol) in THF (10 mL) after which the color of the
solution turned to red. The mixture was stirred for an additional 30 min and then filtered over a plug of celite. The solvent was removed under reduced pressure and the solid residue was immediately used in the next step.

(Cis/trans)-Diester-perfluorobutyl motor (9) Diazofluorene 12 was dissolved in toluene (5 mL) and added to a solution of thioacetone 5\(^1\) (560 mg, 1.47 mmol) in toluene (10 mL). The mixture was heated at 75°C for 3 h. The formation of the episulfide was monitored by \(^1\)H NMR spectroscopy by following the shift of the absorption of the aromatic proton of the thioacetone from 6.66 to 6.34 and 6.39 ppm in the episulfide isomers (cis/trans). After the conversion of the thioacetone was complete, PPh\(_3\) (0.8 g, 3.05 mmol) was added to the episulfide solution, followed by an additional 1 h stirring at 75°C. The mixture was cooled to rt and the solvent was evaporated under reduced pressure. The crude product was dissolved in Et\(_2\)O and CH\(_3\)I (2 mL, 32 mmol) was added. The solution was stirred for 2 h at rt, the precipitate was filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (SiO\(_2\), n-heptane → n-heptane : Et\(_2\)O 3 :1) to give 9 as a mixture of isomers (1.4 : 1) as a yellow oil (792 mg, 1.08 mmol, 73%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.28-1.36 (m, 9H major, 9H minor), 2.21 (s, 3H major), 2.25 (s, 3H minor), 2.56 (d, \(J = 14.8\) Hz, 1H major), 2.58 (d, \(J = 14.7\) Hz, 1H minor), 3.32 (dd, \(J = 4.7, 14.8\) Hz, 1H major, 1H minor), 4.06-4.18 (m, 1H major, 1H minor), 4.24-4.34 (m, 4H major, 4H minor), 4.52 (d, \(J = 15.6\) Hz, 1H major), 4.68 (d, \(J = 15.8\) Hz, 1H minor), 4.75 (s, 2H major, 2H minor), 4.87 (d, \(J = 15.8\) Hz, 1H major), 4.92 (d, \(J = 16.1\) Hz, 1H minor), 6.77 (s, 1H minor), 6.79 (s, 1H major), 7.24 (t, \(J = 7.4\) Hz, 1H minor), 7.34 (t, \(J = 7.4\) Hz, 1H major), 7.39-7.46 (m, 3H major, 1H minor), 7.50 (d, \(J = 7.9\) Hz, 1H major), 7.56-7.59 (m, 1H major, 1H minor), 7.81 (d, \(J = 7.6\) Hz, 1H minor), 7.85-7.91 (m, 2H major, 1H minor), 8.06 (s, 1H minor); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.7, 13.8, 13.9, 15.5, 16.1, 18.5, 18.6, 41.2, 41.3, 44.8, 44.9, 60.6, 60.7, 61.1, 61.2, 65.5, 65.6, 69.1, 69.3, 108.0, 108.4, 115.6-116.6 (m, CF\(_3\)), 119.1, 119.4, 119.8, 120.3, 121.5 (t, \(J = 6.9\) Hz), 121.8 (t, \(J = 6.4\) Hz), 123.6, 123.7, 124.8 (t, \(J = 6.2\) Hz), 125.1 (t, \(J = 4.8\) Hz), 126.0 (t, \(J = 23.7\) Hz), 126.3 (t, \(J = 23.6\) Hz), 126.8, 127.1, 127.7, 127.9, 128.0, 128.2, 131.6, 132.1, 133.7, 133.9, 137.5, 137.9, 138.2, 139.3, 139.9, 142.2, 142.7, 143.6, 143.9, 145.0, 145.5, 151.3, 151.9, 153.3, 153.7, 168.2, 169.1, 169.4; HRMS (ESI) calcd for C\(_{36}\)H\(_{31}\)F\(_9\)O\(_6\)Na 753.6039 (MNa\(^+\)), found 753.1856.

(Cis/trans)-Dihydroxy-cyano motor (14) A solution of (cis/trans)-8 (339 mg, 0.63 mmol) in THF (22 mL) was added to a suspension of LiBH\(_4\) (14.4 mg, 0.66 mmol) in THF (3 mL) and the mixture was stirred at rt for 90 min. The mixture was diluted with EtOAc (25 mL) and washed with H\(_2\)O (20 mL), brine (10mL), dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. Purification by flash column chromatography (SiO\(_2\), EtOAc) afforded 14 as a mixture of isomers (1 : 1.7) as a yellow solid (152 mg, 0.34 mmol, 55%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.36 (d, \(J = 6.6\) Hz, 3H, minor), 1.37 (d, \(J = 6.7\) Hz, 3H, major), 2.18 (s, 3H, minor), 2.19 (s, 3H, major), 2.61 (d, \(J = 14.9\) Hz, 3H, minor), 5.07 (s, 2H, major), 5.10 (s, 2H, minor).
(Cis/trans)-Dihydroxy-perfluorobutyl motor (15) A suspension of LiBH₄ (66 mg, 3 mmol) in THF (5 mL) was added to a solution of motor (cis/trans)-9 (660 mg, 0.9 mmol) in THF (15 mL) and the mixture was heated at 40 °C for 3 h. The reaction was quenched with H₂O (10 mL) and the mixture was extracted with EtOAc until the aqueous phase was colorless. The combined organic layers were washed with water and brine and dried (Na₂SO₄). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO₂, Et₂O → EtOAc). One of the isomers could be precipitated by adding Et₂O to the product mixture. The rest of the cis and trans isomer mixture was separated by column chromatography (SiO₂, Et₂O).

**Cis-15** (140 mg, 0.22 mmol, 24 %) was obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 1.35 (d, J = 6.7 Hz, 3H), 2.18 (s, 3H), 2.59 (d, J = 14.7 Hz, 1H), 3.35 (dd, J = 5.6, 14.91 Hz, 1H), 3.37 (br s, OH), 3.75 (br s, OH), 3.86 (t, J = 10.4 Hz, 1H), 3.91-4.00 (m, 3H), 4.04-4.10 (m, 1H), 4.12-4.27 (m, 4H), 6.90 (s, 1H), 7.39-7.47 (m, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.87-7.92 (m, 3H). The protons of the terminal OH-groups could be observed in DMSO-d₆. ¹H NMR (400 MHz, DMSO-d₆) δ 1.29 (d, J = 6.5 Hz, 3H), 2.07 (s, 3H), 2.61 (d, J = 14.8 Hz, 1H), 3.69 (br dd, J = 5.1, 9.7 Hz, 2H), 3.81 (br dd, J = 4.1, 8.6 Hz, 2H), 3.94-4.02 (m, 2H), 4.09 (q, J = 6.5 Hz, 1H), 4.12-4.18 (m, 2H), 4.75 (t, J = 5.3, OH), 4.93 (t, J = 5.2 Hz, OH), 7.13 (s, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.51-7.55 (m, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 8.11 (d, J = 7.4 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H). (1H is not observed due to overlap with DMSO peak at 3.33 ppm.) ¹³C NMR (100 MHz, CDCl₃) δ 15.6, 18.9, 41.6, 45.1, 60.9, 61.8, 70.5, 74.4, 108.3, 119.3, 120.4, 121.6 (t, J = 7.1 Hz), 123.8, 125.3 (t, J = 5.3 Hz), 126.1 (t, J = 23.6 Hz), 126.9, 127.9, 128.1, 131.9, 133.3, 137.7, 138.0, 140, 142.4, 144.6, 145.7, 153.2, 154.2.

**Trans-15** (200 mg, 0.31 mmol, 34%) was obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 1.36 (d, J = 6.7 Hz, 3H), 2.21 (s, 3H), 2.62 (d, J = 14.7 Hz, 1H), 3.54 (dd, J = 5.7, 14.9 Hz, 1H), 3.73 (br s, OH), 3.91-4.24 (m, 9H), 6.89 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H, minor), 2.62 (d, J = 14.8 Hz, 1H, major), 3.34 (dd, J = 5.7, 14.8 Hz, 1H major, 1H minor), 3.92-4.23 (m, 9H major, 8H minor), 4.28-4.32 (m, 1H, minor) 6.90 (s, 1H, major) 6.91 (s, 1H, minor), 7.22 (t, J = 7.6 Hz, 1H, major), 7.33-7.38 (m, 2H, major), 7.41-7.49 (m, 2H, minor), 7.56 (dd, J = 1.3, 7.9 Hz, 1H, minor), 7.63-7.65 (m, 1H major, 1H minor), 7.81-7.85 (m, 1H major, 1H minor), 7.87-7.89 (m, 1H, minor) 7.89 (d, J = 7.9 Hz, 1H, major), 7.91 (d, J = 7.8 Hz, 1H, minor), 8.10 (s, 1H, major); ¹³C NMR (125 MHz, CDCl₃) δ 155.0, 154.8, 153.4, 153.0, 145.6, 144.6, 144.5, 143.2, 142.8, 140.2, 139.6, 138.5, 137.8, 137.4, 133.3, 133.0, 132.2, 131.9, 130.1, 129.985, 128.6, 128.1, 127.3, 127.3, 127.2, 127.1, 127.0, 123.8, 123.4, 120.7, 120.3, 120.2, 120.1, 119.9, 119.8, 109. 6, 109.1, 108.3, 108.1, 74.4, 74.3, 70.6, 70.6, 64.4, 62.2, 62.0, 61.0, 45.0, 44.8, 41.6, 41.5, 19.2, 18.9, 16.1, 15.9; HRMS (ESI) calcd for C₂⁹H₇⁷NO₁₄Na 476.1832 (MNa⁺), found 476.1843.
Hz, 1H), 7.33 (t, \( J = 7.5 \) Hz, 1H), 7.37 (d, \( J = 7.9 \) Hz, 1H), 7.57 (d, \( J = 8.0 \) Hz, 1H), 7.83 (d, \( J = 8.0 \) Hz, 1H), 7.91 (d, \( J = 7.9 \) Hz, 1H), 8.07 (s, 1H).

The protons of the terminal OH-groups could be observed in DMSO-\( d_6 \). \( ^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 1.29 (d, \( J = 6.6 \) Hz, 3H), 2.09 (s, 3H), 2.63 (d, \( J = 15.1 \) Hz, 1H), 3.70 (q, \( J = 5.2 \) Hz, 2H), 3.79 (q, \( J = 5.0 \) Hz, 2H), 3.92-3.97 (m, 1H), 3.98-4.05 (m, 1H), 4.08-4.19 (m, 3H), 4.77 (t, \( J = 5.4 \) Hz, \( \text{OH} \)), 4.91 (t, \( J = 5.4 \) Hz, \( \text{OH} \)), 7.11 (s, 1H), 7.30-7.33 (m, 2H), 7.37-7.41 (m, 1H), 7.69 (d, \( J = 7.8 \) Hz, 1H), 8.02 (s, 1H), 8.04 (d, \( J = 7.6 \) Hz, 1H), 8.22 (d, \( J = 7.9 \) Hz, 1H). (1H is not observed due to overlap with DMSO peak at 3.33 ppm.); \(^{13}\)C NMR (100 MHz, CDC\( \text{Cl}_3 \)) \( \delta \) 15.9, 18.8, 41.6, 44.9, 61.0, 62.1, 70.5, 74.4, 108.1, 119.5, 120.0, 121.9 (t, \( J = 7.0 \) Hz), 123.4, 124.9 (t, \( J = 6.3 \) Hz), 126.6 (t, \( J = 23.7 \) Hz), 127.1, 127.6, 128.0, 132.1, 133, 5, 137.8, 138.5, 139.5, 142.6, 144.4, 145.6, 152.9, 153.7; HRMS (ESI) calcd for C\(_{32}\)H\(_{27}\)F\(_4\)O\(_4\)Na 669.5304 (MNa\(^+\)), found 669.1622.

\((\text{Cis/trans})\)-Dialkyne-cyano motor (16) A solution of \((\text{cis/trans})\)-14 (160 mg, 0.35 mmol) in THF (14 mL) was added dropwise to the suspension of NaH (95%, 35 mg, 1.36 mmol) in THF (6 mL) and the mixture was stirred at rt for 30 min. To this mixture propargyl bromide (80% in toluene, 170 \( \mu \)L, 1.53 mmol) was added. The solution was stirred at rt for 12 h. The mixture was diluted with EtOAc (25 mL) and washed with H\(_2\)O (20 mL), brine (10 mL), dried \((\text{Na}_2\text{SO}_4)\) and concentrated \textit{in vacuo}. Purification by column chromatography (SiO\(_2\), n-hexane : EtOAc = 4 : 1) afforded the product as a mixture of \textit{cis} and \textit{trans} isomers as a yellow solid (118 mg, 0.22 mmol, 63%).

85 mg (0.16 mmol) of the isomer mixture was separated by column chromatography (SiO\(_2\), toluene : EtO\(_2\)O 20 : 1).

\textbf{Cis-16} (26 mg, 0.05 mmol, 31%, \( R_e = 0.45 \)) was obtained as a yellow solid. \(^1\)H NMR (400 MHz, CDC\( \text{Cl}_3 \)) \( \delta \) 1.34 (d, \( J = 6.7 \) Hz, 3H), 2.16 (s, 3H), 2.41 (t, \( J = 2.4 \) Hz, 1H), 2.49 (t, \( J = 2.4 \) Hz, 1H), 2.58 (d, \( J = 14.8 \) Hz, 1H), 3.32 (dd, \( J = 5.7, 14.7 \) Hz, 1H), 3.92-3.94 (m, 2H), 4.00 (t, \( J = 4.77 \) Hz, 2H), 4.12 (quinapparent, \( J = 8.0 \) Hz, 1H), 4.23-4.30 (m, 4H), 4.31-4.32 (m, 4H), 6.88 (s, 1H), 7.40 (dt, \( J = 1.1, 7.4 \) Hz, 1H), 7.45 (dt, \( J = 1.5, 7.6 \) Hz, 1H), 7.55 (dd, \( J = 1.4, 7.9 \) Hz, 1H), 7.65 (dapparent, \( J = 0.8 \) Hz, 1H), 7.83 (dd, \( J = 0.5, 7.9 \) Hz, 1H), 7.87 (dapparent, \( J = 0.9, 7.3 \) Hz, 1H), 7.90 (d, \( J = 7.6 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDC\( \text{Cl}_3 \)) \( \delta \) 16.1 19.0, 41.5, 45.0, 58.4, 58.6, 68.1, 68.2, 69.3, 72.0, 74.4, 74.8, 108.5, 109.2, 119.7, 119.9, 120.7, 123.8, 126.8, 127.2, 128.5, 130.0, 131.8, 132.8, 137.7, 137.9, 140.2, 142.6, 144.0, 146.2, 153.7, 155.5.

\textbf{Trans-16} (40 mg, 0.075 mmol, 47%, \( R_e =0.55 \)) was obtained as a yellow solid. \(^1\)H NMR (400 MHz, CDC\( \text{Cl}_3 \)) \( \delta \) 1.36 (d, \( J = 6.7 \) Hz, 3H), 2.18 (s, 3H), 2.43 (t, \( J = 2.3 \) Hz, 1H), 2.49 (t, \( J = 2.3 \) Hz, 1H), 2.59 (d, \( J = 14.8 \) Hz, 1H), 3.32 (dd, \( J = 5.9, 14.8 \) Hz, 1H), 3.89-3.93 (m, 2H), 3.99 (t, \( J = 4.7 \) Hz, 2H), 4.03-4.16 (m, 2H), 4.22-4.38 (m, 3H), 4.30 (d, \( J = 2.3 \) Hz, 2H), 4.32 (d, \( J = 2.4 \) Hz, 2H), 6.87 (s, 1H), 7.22 (t, \( J = 7.3 \) Hz, 1H), 7.33 (t, \( J = 7.3 \) Hz, 1H), 7.38 (d, \( J = 7.9 \) Hz, 1H), 7.63 (dd, \( J = 0.8, 7.9 \) Hz, 1H), 7.81 (d, \( J = 7.6 \) Hz, 1H), 7.88 (d, \( J = 7.9 \) Hz, 1H), 8.09 (s, 1H); \(^{13}\)C NMR (125 MHz, CDC\( \text{Cl}_3 \)) \( \delta \) 16.0, 19.3, 41.5, 45.0, 58.3, 58.6, 68.0, 68.2, 69.3, 71.6, 74.6,
Irradiation experiment to generate unstable isomer of motor trans-16:

Motor cis-16 (~2 mg) was dissolved in CD$_2$Cl$_2$ (~1 mL). This sample was placed in an NMR tube and irradiated at 365 nm at -55°C at a distance of 2-3 cm from the centre of the lamp. 1H NMR spectra of the sample were taken before, during and after irradiation at -55°C. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of unstable-trans-16 to stable-cis-16 of 5 : 1. After warming the sample to rt, only the stable forms were observed by $^1$H NMR spectroscopy.

stable-cis-16 $^1$H NMR (500 MHz, CD$_2$Cl$_2$, -55°C) $\delta$ 1.28 (d, $J = 6.5$ Hz, 3H), 2.08 (s, 3H), 2.51 (s, 1H), 2.56-2.60 (m, 2H), 3.28 (dd, $J = 5.4$, 14.7 Hz, 1H), 3.80-3.88 (m, 2H), 3.95 (t, $J = 3.6$ Hz, 2H), 4.06-4.13 (m, 2H), 4.27 (s, 2H), 4.29 (d, $J = 1.4$ Hz, 2H), 6.89 (s, 1H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.57 (s, 2H), 7.85-7.91 (m, 3H).

unstable-trans-16 $^1$H NMR (500 MHz, CD$_2$Cl$_2$, -55°C) $\delta$ 1.42 (d, $J = 6.4$ Hz, 3H), 1.93 (s, 3H), 2.50-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-cis-16), 2.98 (dd, $J = 5.30$, 16.4 Hz, 1H), 3.42 (dd, $J = 8.2$, 16.3 Hz, 1H), 3.72-4.13 (absorptions in this region could not be resolved due to overlap with remaining stable-cis-16), 4.20 (d, $J = 2.2$ Hz, 2H), 4.21-4.25 (absorptions in this region could not be resolved due to overlap with remaining stable-cis-16), 4.28 (d, $J = 2.2$ Hz, 2H), 6.83 (s, 1H), 7.19-7.23 (m, 2H), 7.30 (t, $J = 7.7$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.98 (s, 1H).

Irradiation experiment to generate unstable isomer of motor cis-16:

Motor trans-16 (~2 mg) was dissolved in CD$_2$Cl$_2$ (~1 mL). This sample was placed in an NMR tube and irradiated at 365 nm at -55°C at a distance of 2-3 cm from the centre of the lamp. 1H NMR spectra of the sample were taken before, during and after irradiation at -55°C. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of unstable-cis-16 to stable-trans-16 of 3.5 : 1. After warming the sample to rt, only the stable forms were observed by $^1$H NMR spectroscopy.

stable-trans-16 $^1$H NMR (500 MHz, CD$_2$Cl$_2$, -55°C) $\delta$ 1.29 (d, $J = 6.5$ Hz, 3H), 2.09 (s, 3H), 2.52 (s, 1H), 2.57-2.60 (m, 2H), 3.28 (dd, $J = 5.5$, 14.7 Hz, 1H), 3.77-3.86 (m, 2H), 3.92-3.95 (m, 2H), 3.99-4.06 (m, 2H), 4.18-4.32 (m, 3H), 4.24 (s, 2H), 4.29 (s, 2H), 6.88 (s, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.3-7.34 (m, 2H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 8.09 (s, 1H).

unstable-cis-16 $^1$H NMR (500 MHz, CD$_2$Cl$_2$, -55°C) $\delta$ 1.45 (d, $J = 6.4$ Hz, 3H), 1.92 (s, 3H), 2.48-2.50 (m, 1H), 2.55-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-trans-16), 2.98 (dd, $J = 5.3$, 16.0 Hz, 1H), 3.41 (dd, $J = 8.2$, 16.3 Hz, 1H), 7.23 (m, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.98 (s, 1H).
3.74-4.31 (absorptions in this region could not be resolved due to overlap with remaining stable-trans-16), 4.22 (d, \(J = 2.2\) Hz, 2H), 6.83 (s, 1H), 7.30-7.35 (absorptions in this region could not be resolved due to overlap with remaining stable-trans-16), 7.39 (t, \(J = 7.7\) Hz, 1H), 7.47 (s, 1H), 7.53 (dd, \(J = 0.7, 7.9\) Hz, 1H), 7.74 (d, \(J = 7.8\) Hz, 1H), 7.87 (d, \(J = 7.8\) Hz, 2H)

**Cis-Dialkyne-perfluorobutyl motor (cis-17)** A suspension of NaH (100 mg, 50% in oil, 2.1 mmol) in THF (2 mL) was cooled to 0°C and a solution of cis-15 (140 mg, 0.22 mmol) in THF (5 mL) was added dropwise. Then, propargyl bromide (0.15 mL, 80% in toluene, 1.35 mmol) was added to this mixture and the resulting solution was stirred at rt for 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\(_2\)SO\(_4\)). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO\(_2\), n-pentane : DCM 2 : 1 \(\rightarrow\) 2 : 3) to give the product as a yellow solid (100 mg, 0.14 mmol, 64%).

\[\text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 1.33 (d, \(J = 6.7\) Hz, 3H), 2.16 (s, 3H), 2.42 (t, \(J = 2.3\) Hz, 1H), 2.49 (t, \(J = 2.3\) Hz, 1H), 2.57 (d, \(J = 14.6\) Hz, 1H), 3.33 (dd, \(J = 5.8, 14.4\) Hz, 1H), 3.92 (t, \(J = 4.5\) Hz, 2H), 3.99-4.01 (m, 2H), 4.07-4.18 (m, 2H), 4.23-4.37 (m, 2H), 6.88 (s, 1H), 7.38-7.46 (m, 2H), 7.50 (d, \(J = 7.9\) Hz, 1H), 7.61 (s, 1H), 7.86-7.92 (m, 3H); \[\text{13C NMR (100 MHz, CDCl}_3\text{)} \delta 15.6, 19.0, 41.5, 45.1, 58.3, 58.6, 67.9, 68.2, 69.2, 71.8, 74.2, 74.7, 108.5, 119.1, 120.4, 121.7 (t, \(J = 6.5\) Hz), 123.8, 125.1 (t, \(J = 5.8\) Hz), 126.1 (t, \(J = 23.2\) Hz), 126.7, 127.5, 128.0, 131.7, 133.0, 137.7, 138.0, 140.2, 142.2, 144.0, 146.2, 153.5, 154.7; HRMS (APCI) calcd for C\(_{38}\)H\(_{32}\)F\(_9\)O\(_4\) 723.2151 (MH\(^+\)), found 723.2152.

**Irradiation experiment to generate unstable isomer of motor trans-17:** Motor cis-17 (~2 mg) was dissolved in CD\(_2\)Cl\(_2\) (~1 mL). This sample was placed in an NMR tube and irradiated at 365 nm at -55°C 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 -55°C. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of stable-cis-17 to unstable-trans-17 of 1 : 2.5. After warming the sample to rt, only the stable form was observed by \(^1\)H NMR spectroscopy.

stable-cis-17 \[^1\text{H NMR (500 MHz, CD}_2\text{Cl}_2, -55\text{°C)} \delta 1.29 (d, \(J = 6.6\) Hz, 3H), 2.06 (s, 3H), 2.52 (t, \(J = 2.3\) Hz, 1H), 2.55-2.58 (m, 2H), 3.28 (dd, \(J = 5.3, 14.6\) Hz, 1H), 3.79-3.85 (m, 2H), 3.9-4.0 (m, 4H), 4.10 (quin, \(J = 6.0\) Hz, 1H), 4.14-4.25 (m, 2H), 4.26 (t, \(J = 2.4\) Hz, 2H), 4.29 (d, \(J = 2.3\) Hz, 2H), 6.88 (s, 1H), 7.39 (t, \(J = 7.3\) Hz, 1H), 7.44 (t\(_{\text{apparent}}, J = 8.0\) Hz, 1H), 7.48 (d, \(J = 8.5\) Hz, 1H), 7.51 (s, 1H), 7.89-7.92 (m, 3H).

unstable-trans-17 \[^1\text{H NMR (500 MHz, CD}_2\text{Cl}_2, -55\text{°C)} \delta 1.41 (d, \(J = 6.3\) Hz, 3H), 1.95 (s, 3H), 2.5-2.51 (m, 1H), 2.55-2.59 (absorptions in this region could not be resolved due to overlap with remaining stable-cis-17), 3.40 (dd, \(J = 8.4, 16.1\) Hz, 1H), 3.72-4.29 (absorptions in this
region could not be resolved due to overlap with remaining stable-cis-17), 6.82 (s, 1H), 7.19-7.22 (m, 2H), 7.28-7.31 (m, 1H), 7.32-7.51 (absorptions in this region could not be resolved due to overlap with remaining stable-cis-17), 7.82 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.89-7.94 (absorptions in this region could not be resolved due to overlap with remaining stable-cis-17).

Trans-Dialkyne-perfluorobutyl motor (trans-17) A suspension of NaH (100 mg, 50% in oil, 2.1 mmol) in THF (2 mL) was cooled to 0°C and a solution of trans-15 (90 mg, 0.14 mmol) in THF (4 mL) was added dropwise. Then, propargyl bromide (0.1 mL, 80 % in toluene, 0.9 mmol) was added to this mixture and the resulting solution was stirred at rt for 5 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 (Na₂SO₄). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO₂, n-pentane : DCM 1 : 1 → 1 : 2) to give the product as a yellow solid (80 mg, 0.11 mmol, 78 %).

**1H NMR (400 MHz, CDCl₃)**

δ 1.35 (d, J = 6.7 Hz, 3H), 2.19 (s, 3H), 2.43 (t, J = 2.4 Hz, 1H), 2.49 (t, J = 2.4 Hz, 1H), 2.59 (d, J = 14.7 Hz, 1H), 3.33 (dd, J = 6.0, 14.6 Hz, 1H), 3.88-3.95 (m, 2H), 3.99 (t, J = 4.7 Hz, 2H), 4.06-4.17 (m, 3H), 4.22-4.37 (m, 2H), 4.30 (d, J = 2.4 Hz, 2H) 4.32 (d, J = 2.4 Hz, 2H), 4.30 (t, J = 4.7 Hz, 1H), 4.32 (d, J = 2.4 Hz, 2H), 6.87 (s, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H); **13C NMR (100 MHz, CDCl₃)** δ 16.1, 18.9, 41.5, 44.9, 58.3, 58.6, 68.0, 68.2, 69.3, 71.6, 74.5, 74.7, 108.3, 119.5, 119.9, 121.9 (t, J = 7.1 Hz), 123.6, (t, J = 6.6 Hz), 126.5 (t, J = 23.8 Hz), 127.0, 127.7, 127.8, 132.0, 133.2, 137.6, 138.5, 139.5, 142.6, 143.7, 145.8, 153.1, 154.2; HRMS (APCI) calcd for C₃₈H₃₂F₉O₄ 723.2151 (MH⁺), found 723.2152.

Irradiation experiment to generate unstable isomer of motor cis-17:
Motor trans-17 (~2 mg) was dissolved in CD₂Cl₂ (~1 ml). This sample was placed in an NMR tube and irradiated at 365 nm at -55°C at a distance of 2-3 cm from the centre of the lamp. **1H NMR spectra of the sample were taken before, during and after irradiation at -55°C. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of stable-trans-17 to unstable-cis-17 of 1 : 2. After warming the sample to rt, only the stable forms were observed by **1H NMR spectroscopy.**

stable-trans-17 **1H NMR (500 MHz, CD₂Cl₂, -55°C)** δ 1.29 (d, J = 6.6 Hz, 3H), 2.09 (s, 3H), 2.52 (t, J = 2.3 Hz, 1H), 2.58 (d, J = 14.7 Hz, 1H), 2.59 (t, J = 2.5 Hz, 1H), 3.28 (dd, J = 5.6, 14.7 Hz, 1H), 3.77-3.86 (m, 3H), 3.94 (t, J = 3.9 Hz, 2H), 3.98-4.02 (m, 1H), 4.06 (t, J = 6.5 Hz, 1H), 4.17-4.32 (m, 2H) 4.24 (d, J = 2.0 Hz, 2H), 4.28 (d, J = 2.3 Hz, 2H), 6.87 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.30-7.34 (m, 2H), 7.55 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H).

unstable-cis-17 **1H NMR (500 MHz, CD₂Cl₂, -55°C)** δ 1.46 (d, J = 6.2 Hz, 3H), 1.89 (s, 3H), 2.49-2.51 (m, 1H), 2.55-2.60 (absorptions in this region could not be resolved due to overlap
with remaining stable-\textit{trans-17}, 3.00 (dd, $J = 5.7$, 16.4 Hz, 1H), 3.41 (dd, $J = 8.4$, 16.3 Hz, 1H), 3.74-4.32 (absorptions in this region could not be resolved due to overlap with remaining stable-\textit{trans-17}), 4.22 (s, 2H), 6.83 (s, 1H), 7.19-7.39 (absorptions in this region could not be resolved due to overlap with remaining stable-\textit{trans-17}), 7.37 (s, 2H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.87 (d, $J = 7.4$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 1H).
NMR Spectra
Spectrum 1 $^1$H NMR spectrum of (cis/trans)-7 in CDCl$_3$. 

(cis/trans)-7
Spectrum 2 APT $^{13}$C NMR spectrum of (cis/trans)-7 in CDCl$_3$. 
Spectrum 3 $^1$H NMR spectrum of trans-7 in CDCl$_3$. 
Spectrum 4 APT $^{13}$C NMR spectrum of \textit{trans-7} in CDCl$_3$. 
Spectrum $^1$H NMR spectrum of (cis/trans)-8 in CDCl$_3$. 
Spectrum 6 Expansion of $^1$H NMR spectrum of (cis/trans)-8 in CDCl$_3$. 
Spectrum 7 APT $^{13}$C NMR spectrum of (cis/trans)-8 in CDCl$_3$. 
Spectrum 8 $^1$H NMR spectrum of trans-8 in CDCl$_3$. 
Spectrum 9 $^1$H NMR spectrum of (cis/trans)-9 in CDCl$_3$. 
Spectrum 10 APT $^{13}$C NMR spectrum of (cis/trans)-9 in CDCl$_3$. 
Spectrum 1H-NMR spectrum of 10 in CDCl₃.
Spectrum 12 APT $^1$H NMR spectrum of 10 in CDCl$_3$. 
Spectrum 13 $^1$H NMR spectrum of (E/Z)-11 in CDCl$_3$. 

(E/Z)-11

Spectrum 13 $^1$H NMR spectrum of (E/Z)-11 in CDCl$_3$. 

(E/Z)-11
Spectrum 14 APT $^{13}$C NMR spectrum of (E/Z)-11 in CDCl$_3$. 
Spectrum $^{1}H$ NMR spectrum of the minor isomer of 11 in CDCl$_3$. 

11 (minor)
Spectrum 16 $^1$H NMR spectrum of (cis/trans)-14 in CDCl$_3$. 
Spectrum 17 Expansion of $^1$H NMR spectrum of (cis/trans)-14 in CDCl$_3$. 
Spectrum 18 APT $^{13}$C NMR spectrum of (cis/trans)-14 in CDCl$_3$. 
Spectrum 1H NMR spectrum of cis-15 in CDCl$_3$. 

Spectrum 19
**Spectrum 20** $^1$H NMR spectrum of cis-15 in DMSO-$d_6$. (The inset shows the OH proton signals.)
Spectrum 21 APT $^{13}$C NMR spectrum of cis-15 in CDCl$_3$. 
Spectrum 22 $^1$H NMR spectrum of trans-15 in CDCl$_3$. 

\[ \text{trans-15} \]
Spectrum 23 $^1$H NMR spectrum of trans-15 in DMSO-$d_6$. (The inset shows the OH proton signals.)
Spectrum 24 APT 13C NMR spectrum of trans-15 in CDCl3.
Spectrum 25 H NMR spectrum of cis-16 in CDCl3.
Spectrum 26 Expansion of $^1$H NMR spectrum of cis-16 in CDCl$_3$. 
Spectrum 27 APT $^{13}$C NMR spectrum of cis-16 in CDCl$_3$. 

cis-16
Spectrum 28 $^1$H NMR spectrum of cis-16 in CD$_2$Cl$_2$ at -55°C.
Spectrum 29 \(^1\)H NMR spectrum of the photostationary state (\(\lambda=365\) nm) of stable-\textit{cis}-16 and unstable-\textit{trans}-16 in CD\(_2\)Cl\(_2\) at -55°C.
Spectrum 30 $^1$H NMR spectrum of trans-16 in CDCl$_3$. 

trans-16
Spectrum 31 APT $^{13}$C NMR spectrum of trans-16 in CDCl$_3$. 

trans-16
Spectrum 32 $^1$H NMR spectrum of \textit{trans-16} in CD$_2$Cl$_2$ at -55°C.
Spectrum 33 $^1$H NMR spectrum of the photostationary state ($\lambda=365$ nm) of stable-trans-16 and unstable-cis-16 in CD$_2$Cl$_2$ at -55°C.
Spectrum 34: H NMR spectrum of cis-17 in CDCl₃.
Spectrum 35 APT $^{13}$C NMR spectrum of cis-17 in CDCl$_3$. 
Spectrum 36 \(^1\)H NMR spectrum cis-17 in CD\(_2\)Cl\(_2\) at -55°C.
Spectrum 37 \( ^1\text{H} \) NMR spectrum of the photostationary state (\( \lambda = 365 \text{ nm} \)) of stable-cis-17 and unstable-trans-17 in CD\(_2\)Cl\(_2\) at -55°C.
Spectrum $^1$H NMR spectrum of trans-17 in CDCl$_3$. 

trans-17
Spectrum 39 APT $^{13}$C NMR spectrum of trans-17 in CDCl$_3$. 

trans-17
Spectrum 40 $^1$H NMR spectrum *trans-17* in CD$_2$Cl$_2$ at -55°C.
Spectrum 41 $^1$H NMR spectrum of the photostationary state ($\lambda=365$ nm) of stable-trans-17 and unstable-cis-17 in CD$_2$Cl$_2$ at -55°C.
References


