Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Hemithioindigo Molecular Motor for Metal Surface Attachment

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Supplementary Material

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Materials and General Methods

Reagents and solvents were obtained from *ABCR*, *Acros*, *Aldrich*, *Fluka*, *Merck*, *Sigma-Aldrich* or *TCI* in the qualities *puriss*., *p.a*., or *purum* and used as received. Technical solvents for column chromatography and extraction were distilled prior to use on a rotary evaporator (*Vacuubrand* CVC 3000). Reactions were monitored on *Merck* Silica 60 F254 TLC plates and detection was done by irradiation with UV light (254 nm or 366 nm).

Column chromatography was performed with silica gel 60 (*Merck*, particle size 0.063- 0.200 mm) and distilled technical solvents.

High Performance Liquid Chromatography (HPLC) was performed on a Shimadzu HPLC system consisting of a LC-20AP solvent delivery module, a CTO-20A column oven, a SPD-M20A photodiode array UV/vis detector and a CBM-20A system controller using a semipreparative CHIRALPAK® IC column (particle size 5 µm) from Diacel and HPLC grade solvents (EtOAc and *n*-heptane) from *Sigma-Aldrich* an *ROTH.*

^{1}H NMR and ^{13}C NMR spectra were measured on a Varian VNMRS 400 (400 MHz), Varian VNMRS 600 (600 MHz), or Bruker AVANCE III HD 800 (800 MHz) NMR spectrometer. Deuterated solvents were obtained from *Cambridge Isotope Laboratories* and used without further purification. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) relative to tetramethylsilane as external standard. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as internal reference. CD_2Cl_2: δ_H = 5.320 ppm, δ_C = 54.00 ppm; toluene-d_8: δ_H = 2.090 ppm, δ_C = 20.40 ppm. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad signal). The coupling constant values (J) are given in hertz (Hz). Signal assignments are given in the experimental part with the arbitrary numbering indicated.

Electron Impact (EI) mass spectra were measured on a *Finnigan MAT95Q* or on a *Finnigan MAT90* mass spectrometer. The found masses from *high resolution* measurements are reported in m/z units with M as the molecular ion.

Elemental analyses were performed on an *Elementar Vario EL* apparatus.

Infrared spectra were recorded on a *Perkin Elmer Spectrum BX-FT-IR* instrument equipped with a Smith *DuraSamplIR II* ATR-device. Transmittance values are qualitatively described by wavenumber (cm^{-1}) as very strong (*vs*), strong (*s*), medium (*m*), weak (*w*), and very weak (*vw*).

UV/vis spectra were measured on a *Varian Cary 5000* spectrophotometer. The spectra were recorded in a quartz cuvette (1 cm). Spectral grade solvents were obtained from *VWR* and *Merck*. Absorption wavelengths (λ) are reported in nm and the molar absorption coefficients (ε) $L \cdot mol^{-1} \cdot cm^{-1}$ in brackets.

Melting points (m.p.) were measured on a *Büchi B-540 melting point* apparatus in open capillaries.

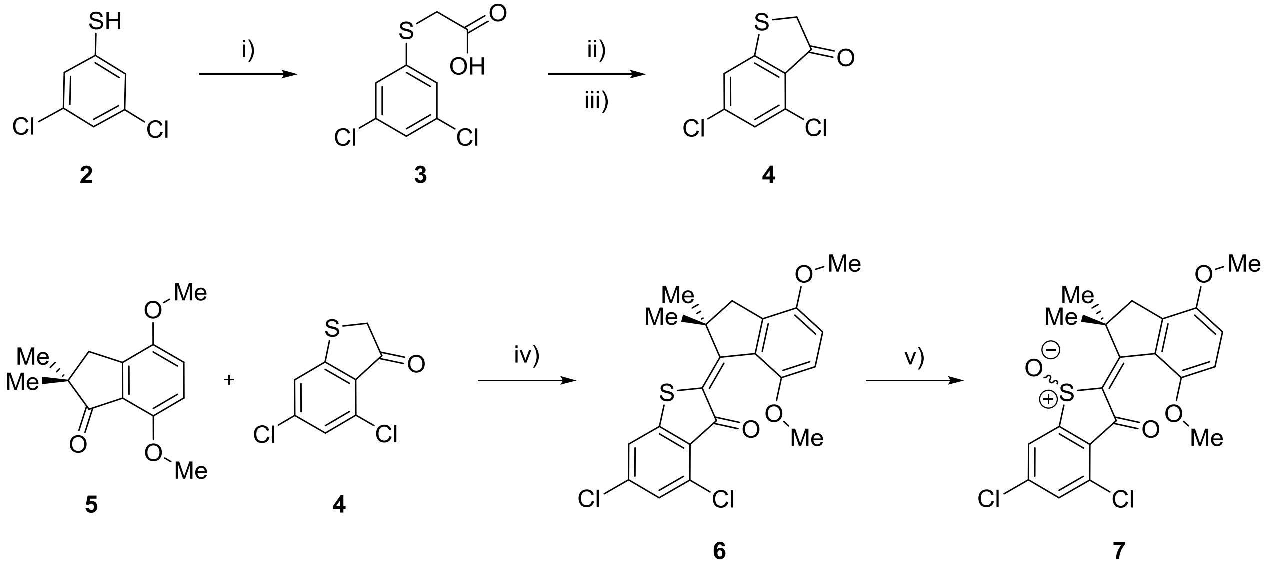
Photoisomerization experiments were conducted using LEDs from *Roithner Lasertechnik GmbH* (365 nm, 385 nm, 405 nm, 420 nm, 435 nm, 450 nm, 470 nm, 490 nm, 505 nm, 515 nm) for illumination. For specifying the isomer composition in the pss at different wavelengths continuous irradiation of the solutions were carried out in NMR tubes in CD_2Cl_2 at 23 °C and the ratio of the species were determined by integration of the corresponding ^{1}H NMR signals. For low temperature studies a *Prizmatix UHP-T-LED-450* (450 nm) was used as light source and the light beam was guided by a fiber-optic cable from *Thorlabs* (FT1500UMT, 0.39 NA, 1500 µm, one SMA, one blank end) and pointed directly into the NMR tube during NMR measurements.

Synthesis

3,5-Dichlorobenzenethiol (**2**) and 3,5-bis(tert-butylthio)-1-chlorobenzene were purchased from *TCI* and used as received. 4,7-Dimethoxy-2,2-dimethyl-1-indanone (**5**) used for the condensation reaction was prepared from commercially available 4,7-dimethoxyphenylpropionic acid according to literature procedures.[1] [2]

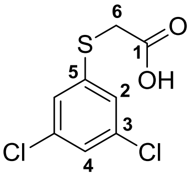
Building Block Synthesis: Motor Unit of 1

Precursor **7** represents the molecular motor unit of **1**. Its synthesis is shown in Supplementary Figure 1. Detailed experimental procedures are given below.



Supplementary Figure 1 Synthesis of precursor **7** starting from commercially available 3,5-dichlorobenzenethiol (**2**). Conditions: i) 2-Bromoacetic acid, K_2CO_3, acetone, 23 °C, 17 h, 99%; ii) Oxalyl chloride, DMF, CH_2Cl_2, 23 °C, 2h; iii) $AlCl_3$, 1,2-dichloroethane, 23 °C, 30 min, 83%; iv) BCl_3, CH_2Cl_2, 0 °C, 85%, v) Sodium perborate, AcOH, 23 °C, 5 h, 88%

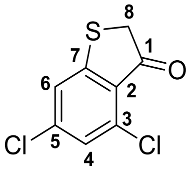
2-((3,5-Dichlorophenyl)thio)acetic acid (3)



2-Bromoacetic acid (1.73 g, 12.45 mmol) and K_2CO_3 (4.62 g, 33.41 mmol) were dissolved in acetone (50.0 mL) and the solution was cooled to 0 °C. 3,5-Dichlorobenzenethiol (**2**) (2.08 g, 11.63 mmol) was added and the reaction mixture warmed to 23 °C. After stirring for 17 h 1M aqueous HCl solution (200 mL) was added until pH 2 was reached. The aqueous phase was extracted with EtOAc (3x 200 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified by recrystallization from *n*-heptane. Compound **3** (2.75 g, 11.60 mmol, 99%) was obtained as colorless needles.

m.p: 105 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.30 (d, ^4J(H,H) = 1.8 Hz, 2H, H-C(2), 7.25 (t, ^4J(H,H) = 1.8 Hz, 1H, H-C(4)), 3.75 (s, 2H, H_2-C(6)) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 174.3 (C(1)), 139.1 (C(5)), 135.9 (C(3)), 127.6 (C(2)), 127.5 (C(4)), 36.1 (C(6)) ppm; IR: $\tilde{\nu}$ = 3077*vw*, 3060*vw*, 2959*vw*, 1685*m*, 1555*s*, 1417*w*, 1405*m*, 1387*m*, 1370*w*, 1355*w*, 1312*w*, 1272*w*, 1245*w*, 1200*m*, 1135*w*, 1109*w*, 1099*m*, 1048*vw*, 987*w*, 921*m*, 890*m*, 869*m*, 845*s*, 818*s*, 792*vs*, 673*w*, 659*vs* cm^{-1}; HR-EI-MS calc. [$C_8H_6Cl_2O_2S^+$]: 235.9466, found: 235.9460; elemental analysis calc. (%) for $C_8H_6Cl_2O_2S$: C 40.53, H 2.55, S 13.52; found: C 40.64, H 2.70, S 13.63.

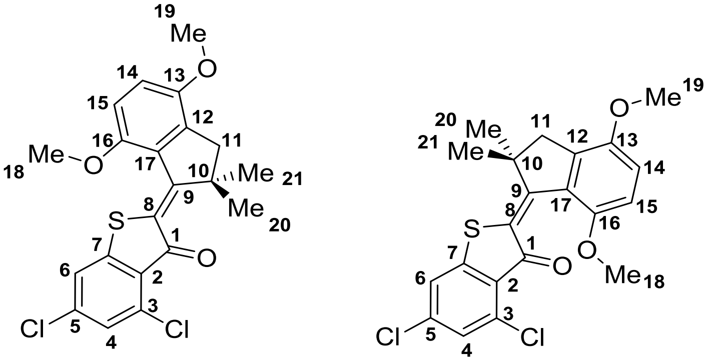
4,6-Dichlorobenzo[*b*]thiophen-3(2*H*)-one (4)



Oxalyl chloride (1.18 mL, 13.73 mmol) and *N,N*-dimethylformamide (5 drops) were added under N_2 to a 0 °C cold solution of 2-((3,5-dichlorophenyl)thio)acetic acid (**3**) (2.71 g, 11.43 mmol) in dry CH_2Cl_2 (50 mL). The reaction mixture was allowed to warm up to 23 °C and stirred for 2 h. After removing the volatiles *in vacuo* the residue was dissolved in 1,2-dichloroethane (50 mL) and the solution cooled to 0 °C. $AlCl_3$ (4.58 g, 34.34 mmol) was added slowly under N_2 atmosphere and the reaction mixture was allowed to warm to 23 °C. After stirring for 30 min saturated aqueous solution of $NaHCO_3$ (400 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3x 300 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, *i*Hex:EtOAc, 98:2 v/v) to afford product **4** (2.07 g, 9.45 mmol, 83%) as a slightly beige solid.

R$_f$ = 0.22 (*i*Hex:EtOAc 95:5 v/v); m.p: 158 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.35 (d, ^4J(H,H) = 1.7 Hz, 1H, H-C(6)), 7.19 (d, ^4J(H,H) = 1.7 Hz, 1H, H-C(4)), 3.86 (s, 2H, H_2-C(8)) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 196.1 (C(1), 158.8 (C(7)), 142.21 (C(5)), 135.7 (C(3)), 127.5 (C(4)), 125.7 (C(2)), 123.6 (C(6)), 40.8 (C(8)) ppm; IR: $\tilde{\nu}$ = 3075*vw*, 2978*vw*, 2930*vw*, 2220*vw*, 2170*vw*, 2161*vw*, 1686*s*, 1569*m*, 1546*vs*, 1412*vw*, 1384*m*, 1366*m*, 1294*m*, 1221*m*, 1205*m*, 1172*s*, 1145*w*, 1119*w*, 1078*m*, 1017*w*, 872*w*, 840*vs*, 833*vs*, 823*vs*, 781*m*, 721*vw*, 707*m*, 667*vw* cm^{-1}; HR-EI-MS calc. [$C_8H_4Cl_2OS^+$]: 217.9360, found: 217.9349.

(*Z*)/(*E*)-4,6-Dichloro-2-(4,7-dimethoxy-2,2-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)benzo[*b*]thiophen-3(2*H*)-one (6)

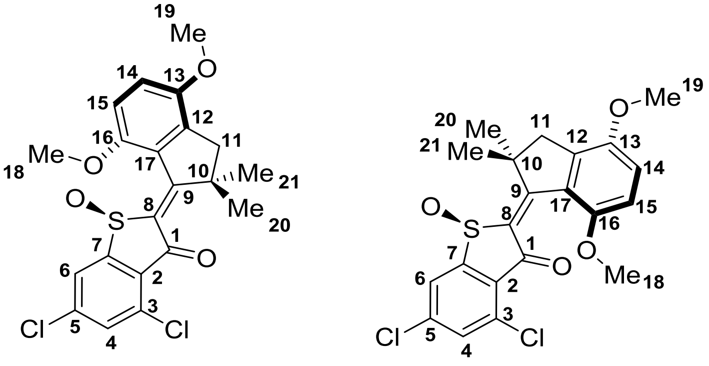


4,6-Dichlorobenzo[*b*]thiophen-3(2*H*)-one (**4**) (0.82 g, 3.74 mmol) was dissolved in dry CH_2Cl_2 (23 mL) under N_2 atmosphere and cooled to -78 °C, before BCl_3 (3.73 mL, 3.73 mmol, 1.0M in CH_2Cl_2) was added. The mixture was rapidly added to a solution of 4,7-dimethoxy-2,2-dimethyl-1-indanone (**5**) (0.59 g, 2.68 mmol) in dry CH_2Cl_2 (6 mL) precooled to 0 °C. After stirring the reaction for 50 min at this temperature saturated aqueous $NaHCO_3$ solution (250 mL) was added and the mixture extracted with CH_2Cl_2 (3x 200 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, *i*Hex:EtOAc, 99:1 v/v) to afford compound **6** (0.96 g, 2.28 mmol, 85%) as a yellow solid.

E isomer: *R*$_f$ = 0.30 (*i*Hex:EtOAc 9:1 v/v); m.p: 185 °C; ^{1}H NMR (599 MHz, CD_2Cl_2) δ = 7.38 (d, ^4J(H,H) = 1.8 Hz, 1H, H-C(4/6)), 7.23 (d, ^4J(H,H) = 1.8 Hz, 1H, H-C(6/4)), 6.91 (d, ^3J(H,H) = 8.9 Hz, 1H, H-C(15)), 6.74 (d, ^{3}J(H,H) = 8.8 Hz, 1H, H-C(14)), 3.82 (s, 3H, H_3-C(19)), 3.80 (s, 3H, H_3-C(18)), 3.00 (d, ^{2}J(H,H) = 15.8 Hz, 1H, H_2-C(11)), 2.85 (d, ^{2}J(H,H) = 15.6 Hz, 1H, H_2-C(11)), 1.66 (s, 3H, H_3-C(20)), 1.19 (s, 3H, H_3-C(21)) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 184.3 (C(1)), 157.6 (C(9)), 152.9 (C(16)), 150.2 (C(13)), 147.9 (C(8)), 139.7 (C(2/5)), 136.8 (C(17)), 134.7 (C(3/7)), 129.4 (C(12)), 127.2 (C(4/6)), 126.7 (C(5/2)), 125.3 (C(7/3)), 122.4 (C(6/4)), 114.5 (C(15)), 110.0 (C(14)), 56.5 (C(19)), 55.6 (C(18)), 50.8 (C(10)), 46.2 (C(11)), 26.8 (C(20)), 26.2 (C(21)) ppm; IR: $\tilde{\nu}$ = 2954*w*, 2931*w*, 283*vw*, 1668*s*, 1573*vs*, 1554*w*, 1535*vs*, 1491*s*, 1464*m*, 1433*m*, 1396*vw*, 1338*w*, 1293*w*, 1274*m*, 1265*vs*, 1218*s*, 1200*m*, 1172*m*, 1151*w*, 1118*s*, 1097*m*, 1079*vs*, 1068*vs*, 1042*m*, 1014*w*, 998*m*, 961*m*, 942*w*, 927*w*, 908*vw*, 870*m*, 848*w*, 836*vs*, 824*s*, 796*vs*, 782*w*, 765*s*, 750*m*, 733*w*, 718*s*, 682*w*, 658*m* cm^{-1}; HR-EI-MS calc. [$C_{21}H_{18}Cl_2O_3S^{+}$]: 420.0354, found: 420.0343.

Z isomer: R_f = 0.35 (*i*Hex:EtOAc 9:1 v/v); m.p: 178 °C; ^{1}H NMR (599 MHz, CD_2Cl_2) δ = 7.29 (d, ^{4}J(H,H) = 1.7 Hz, 1H, H-C(4/6)), 7.16 (d, ^{4}J(H,H) = 1.7 Hz, 1H, H-C(6/4)), 6.96 (d, ^{3}J(H,H) = 8.8 Hz, 1H, H-C(14)), 6.78 (d, ^{3}J(H,H) = 8.8 Hz, 1H, H-C(15)), 3.90 (s, 3H, H_3-C(18)), 3.81 (s, 3H, H_3-C(19)), 2.91 (s, 2H, H_2-C(11)), 1.53 (s, 6H, H_3-C(20), H_3-C(21)) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 186.2 (C(1)), 163.6 (C(9)), 150.8 (C(16)), 150.6 (C(8)), 150.5 (C(13)), 140.0 (C(2/5)), 138.1 (C(12)), 134.6 (C(3/7)), 129.1 (C(17)), 128.4 (C(7/3)), 126.8 (C(4/6)), 126.5 (C(5/2)), 121.8 (C(6/4)), 115.6 (C(14)), 110.5 (C(15)), 56.4 (C(19)), 55.4 (C(18)), 51.9 (C(10)), 48.1 (C(11)), 27.0 (C(20), C(21)) ppm; IR: $\tilde{\nu}$ = 3075*vw*, 2932*vw*, 2832*vw*, 1719*vw*, 1667*m*, 1572*vs*, 1538*s*, 1491*s*, 1460*m*, 1450*m*, 1435*m*, 1372*m*, 1337*w*, 1294*w*, 1262*vs*, 1219*m*, 1196*w*, 1171*m*, 1116*w*, 1101*m*, 1086*s*, 1069*vs*, 1061*vs*, 992*m*, 956*w*, 889*w*, 846*s*, 829*s*, 817*s*, 805*vs*, 782*m*, 765*w*, 753*w*, 717*s*, 686*m*, 661*m* cm^{-1}; HR-EI-MS calc. [$C_{21}H_{18}Cl_2O_3S^{+}$]: 420.0354, found: 420.0347. elemental analysis calc. (%) for $C_{21}H_{18}Cl_2O_3S$: C 59.87, H 4.31, S 7.61; found: C 59.89, H 4.37, S 7.48.

(*Z*)/(*E*)-4,6-Dichloro-2-(4,7-dimethoxy-2,2-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)benzo[*b*]thiophen-3(2*H*)-one 1-oxide (7)



(*Z*)/(*E*)-4,6-Dichloro-2-(4,7-dimethoxy-2,2-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)benzo[*b*]thiophen-3(2*H*)-one (**6**) (112 mg, 0.26 mmol) was dissolved in concentrated acetic acid (20 mL) and EtOAc (1 mL) and sodium perborate tetrahydrate (164 mg, 1.07 mmol) were added. After the reaction mixture was stirred for 5 h at 23 °C saturated aqueous $NaHCO_3$ solution (250 mL) was added. The aqueous phase was extracted with EtOAc (3x 200 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (SiO_2, *i*Hex:EtOAc, 9:1 v/v) to obtain both configurational isomers of motor **7** (102 mg, 0.23 mmol, 88% combined yield) as yellow (*Z* isomer) and orange (*E* isomer) solids.

E isomer: R_f = 0.41 (*i*Hex:EtOAc 7:3 v/v); m.p: 213 °C; ^{1}H NMR (599 MHz, CD_2Cl_2) δ = 7.96 (br, 1H, H-C(6)), 7.67 (d, ^4J(H,H) = 1.7 Hz, 1H, H-C(4)), 7.00 (d, ^3J(H,H) = 8.8 Hz, 1H, H-C(14)), 6.76 (d, ^3J(H,H) = 8.8 Hz, 1H, H-C(15)), 3.83 (s, 3H, H_3-C(19)), 3.79 (s, 3H, H_3-C(18)), 3.08 (d, ^2J(H,H) = 15.6 Hz, 1H, H_2-C(11)), 2.91 (d, ^2J(H,H) = 15.5 Hz, 1H, H_2-C(11)), 1.92 (s, 3H, H_3-C(21)), 1.36 (s, 3H, H_3-C(20)) ppm; ^{13}C NMR (201 MHz, CD_2Cl_2) δ = 179.8 (C(1)), 170.4 (C(9)), 153.5 (C(16)), 153.3 (C(8)), 150.4 (C(13)), 141.1 (C(5)), 140.2 (C(7)), 138.1 (C(12)), 134.4 (C(4)), 133.8 (C(3)), 130.7 (C(2)), 128.8 (C(17)), 126.2 (C(6)), 116.5 (C(14)), 110.1 (C(15)), 56.6 (C(19)), 55.7 (C(18)), 52.7 (C(10)), 46.8 (C(11)), 28.9 (C(21)), 26.0 (C(20)) ppm; IR: $\tilde{\nu}$ = 3043*vw*, 2956*vw*, 1692*m*, 1575*m*, 1548*m*, 1491*m*, 1459*w*, 1434*m*, 1379*vw*, 1361*vw*, 1336*vw*, 1302*vw*, 1291*vw*, 1276*w*, 1264*s*, 1215*m*, 1187*m*, 1172*w*, 1162*w*, 1134*w*, 1117*w*, 1082*s*, 1061*vs*, 1036*m*, 1000*m*, 962*w*, 941*w*, 913*vw*, 889*w*, 864*m*, 828*w*, 796*s*, 776*w*, 731*w*, 716*m*, 687*w*, 662*s* cm^{-1}; HR-EI-MS calc. [$C_{21}H_{18}Cl_2O_4S^+$]: 436.0303, found: 436.0295.

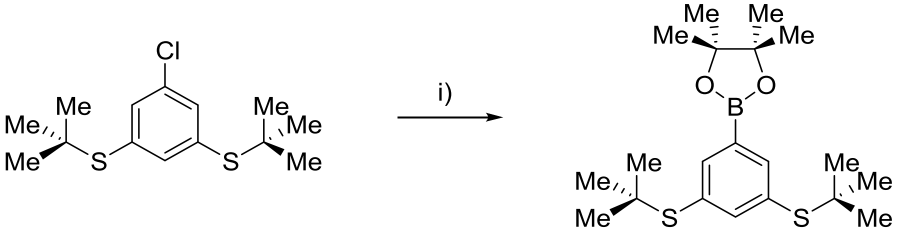
Z isomer: R_f = 0.11 (*i*Hex:EtOAc 7:3 v/v); m.p: 210 °C; ^{1}H NMR (599 MHz, CD_2Cl_2) δ = 7.89 (d, ^4J(H,H) = 1.7 Hz, 1H, H-C(6)), 7.62 (d, ^4J(H,H) = 1.7 Hz, 1H, H-C(4)), 7.06 (d, ^3J(H,H) = 8.9 Hz, 1H, H-C(14)), 6.85 (d, ^3J(H,H) = 8.8 Hz, 1H, H-C(15)), 4.03 (s, 3H, H_3-C(18)), 3.83 (s, 3H, H_3-C(19)), 2.99 (d, ^2J(H,H) = 16.4 Hz, 1H, H_2-C(11)), 2.91 (d, ^2J(H,H) = 16.4 Hz, 1H, H_2-C(11)), 1.53 (s, 3H, H_3-C(20)), 1.52 (s, 3H, H_3-

C(21)) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 182.1 (C(1)), 171.2 (C(9)), 155.1 (C(8)), 151.9 (C(16)), 150.7 (C(13)), 143.5 (C(7)), 141.5 (C(5)), 139.3 (C(12)), 134.0 (C(4)), 133.7 (C(3)), 130.7 (C(2)), 126.6 (C(17)), 125.7 (C(6)), 117.2 (C(14)), 110.0 (C(15)), 56.5 (C(18)), 55.6 (C(19)), 52.5 (C(10)), 47.7 (C(11)), 28.8 (C(20)), 25.7 (C(21)) ppm; IR: $\tilde{\nu}$ = 2941*vw*, 1673*m*, 1572*m*, 1537*s*, 1491*m*, 1473*w*, 1443*w*, 1416*w*, 1383*w*, 1337*vw*, 1292*w*, 1275*w*, 1261*s*, 1215*m*, 1196*m*, 1180*s*, 1135*w*, 1116*w*, 1086*m*, 1066*vs*, 1044*vs*, 992*m*, 955*w*, 936*w*, 919*w*, 876*w*, 859*s*, 824*m*, 802*s*, 777*w*, 757*w*, 717*m*, 691*m*, 658*m* cm^{-1}; HR-EI-MS calc. [$C_{21}H_{18}Cl_2O_4S^+$]: 436.0303, found: 436.0298.

elemental analysis calc. (%) for $C_{21}H_{18}Cl_2O_4S$: C 57.68, H 4.15, S 7.33; found: C 57.86, H 4.23, S 7.37.

Building Block Synthesis: Feet Precursor 8

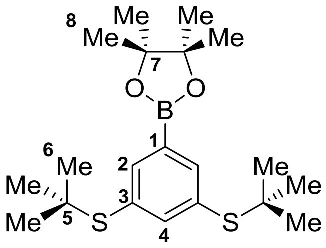
The Synthesis of the feet precursor **8** is shown in Supplementary Figure 2. The experimental procedure is based on a published literature procedure and described below.[3]



8

Supplementary Figure 2 Synthesis of the feet precursor **8**. Conditions: i) Bis(pinakolato)diboron, NaOAc, Pd(dba)$_2$, XPhos, neat, 110 °C, 18 h, 99%.

3,5-Bis(tert-butylthio)phenylboronic acid pinacol ester (8)



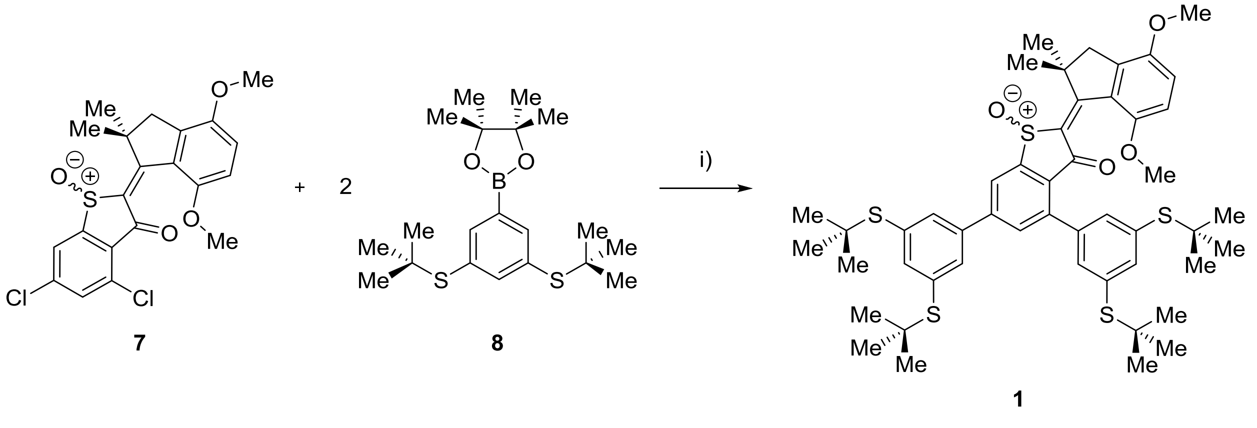
3,5-Bis(tert-butylthio)-1-chlorobenzene (1003 mg, 3.47 mmol), Sodiumacetate (568 mg, 6.82 mmol), Bis(pinakolato)diboron (889 mg, 3.50 mmol), Bis(dibenzylideneacetone)palladium (20 mg, 0.04 mmol) and

XPhos (33 mg, 0.07 mmol) were combined under N_2 atmosphere. After stirring the neat reaction mixture for 18 h at 110 °C dest. water (300 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3x 200 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed *in vacuo*. Compound **8** (1304 mg, 3.43 mmol, 99%) was obtained as a colorless solid.

R_f = 0.01 (*i*Hex); m.p: 122 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.89 (d, ^4J(H,H)= 1.8 Hz, 2H, H-C(2)), 7.81 (t, ^4J(H,H) = 1.8 Hz, 1H, H-C(4)), 1.34 (s, 12H, H_3-C(8)), 1.28 (s, 18H, H_3-C(6)) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = (C(1) not observed because of very pronounced signal broadening), 149.2 (C(4)), 144.2 (C(2)), 133.2 (C(3)), 84.7 (C(7)), 46.5 (C(5)), 31.4 (C(6)), 25.2 (C(8)) ppm; IR: $\tilde{\nu}$ = 3013*vw*, 2972*w*, 2925*vw*, 2899*vw*, 2862*vw*, 1877*vw*, 1576*vw*, 1546*vw*, 1472*vw*, 1460*vw*, 1446*vw*, 1428*vw*, 1412*w*, 1387*s*, 1369*m*, 1361*s*, 1339*vs*, 1311*s*, 1283*vw*, 1271*w*, 1212*w*, 1160*s*, 1141*s*, 1124*s*, 1112*m*, 1028*vw*, 998*vw*, 962*w*, 948*vw*, 932*vw*, 896*w*, 870*m*, 842*m*, 829*vw*, 799*w*, 722*w*, 713*vs*, 676*vw*, 663*vw* cm^{-1}; HR-EI-MS calc. [$C_{20}H_{33}BO_2S_2^+$]: 380.2015, found: 380.2012; elemental analysis calc. (%) for $C_{20}H_{33}BO_2S_2$: C 63.15, H 8.74, S 16.86; found: C 63.35, H 8.65, S 17.02.

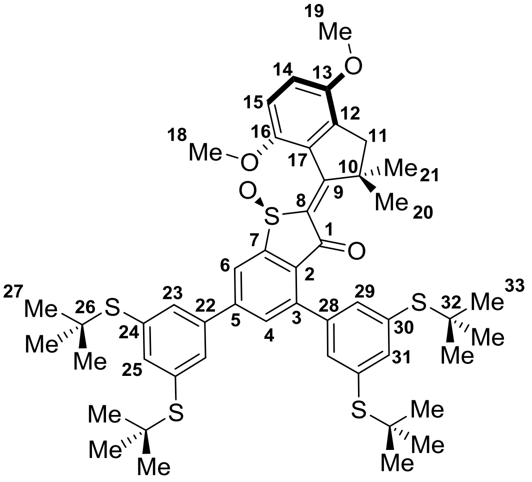
Synthesis of motor 1

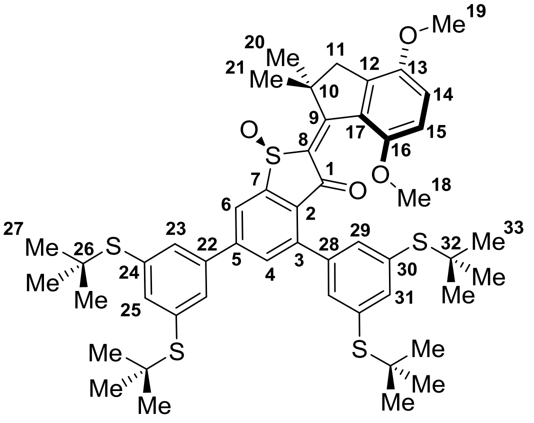
Supplementary Figure 3 displays the last steps in the convergent synthesis of motor **1**. Fragment **7**, the motor unit of **1** (see Supplementary Figure 1), is connected to the two feet moieties in a twofod Suzuki cross coupling reaction with the feet precursor **8** (see Supplementary Figure 2). Reaction conditions were choosen based on known literature procedures and are specified below.[4]



Supplementary Figure 3 Synthesis of motor **1** via twofold Suzuki cross coupling between precursor **7** (motor part of **1**) and two feet precursors **8**. Conditions: i) Na_2CO_3, $Pd(OAc)_2$, H_2O:DMF (3.5:3), 110 °C, 3 h, 45%.

(*Z*)/(*E*)-4,6-Bis(3,5-bis(tert-butylthio)phenyl)-2-(4,7-dimethoxy-2,2-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)benzo[*b*]thiophen-3(2*H*)-one 1-oxide (1)





4,5-Dichloro-2-(4,7-dimethoxy-2,2-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)benzo[*b*]thiophen-3(2H)-one 1-oxide (**7**) (40 mg, 0.09 mmol) was dissolved in a 3.5:3 mixture of H_2O: *N*,*N* dimethylformamide (2.6 mL) under N_2 atmosphere. Sodium carbonate (39 mg, 0.36 mmol), 3,5-Bis(tert-butylthio)phenylboronic acid pinacol ester (**8**) (104 mg, 0.27 mmol) and $Pd(OAc)_2$ (0.5 mg, 0.002 mmol) were added. After heating the mixture for 3 h at 110 °C without stirring a saturated aqueous NH_4Cl solution (50 mL) was added. The aqueous phase was extracted with EtOAc (3x 50 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (SiO_2, *i*Hex:EtOAc, 9:1) to obtain *Z*-**1** and *E*-**1** (36 mg, 0.04 mmol, 45%) as yellow to orange solids. Further purification and isomer separation was achieved using HPLC.

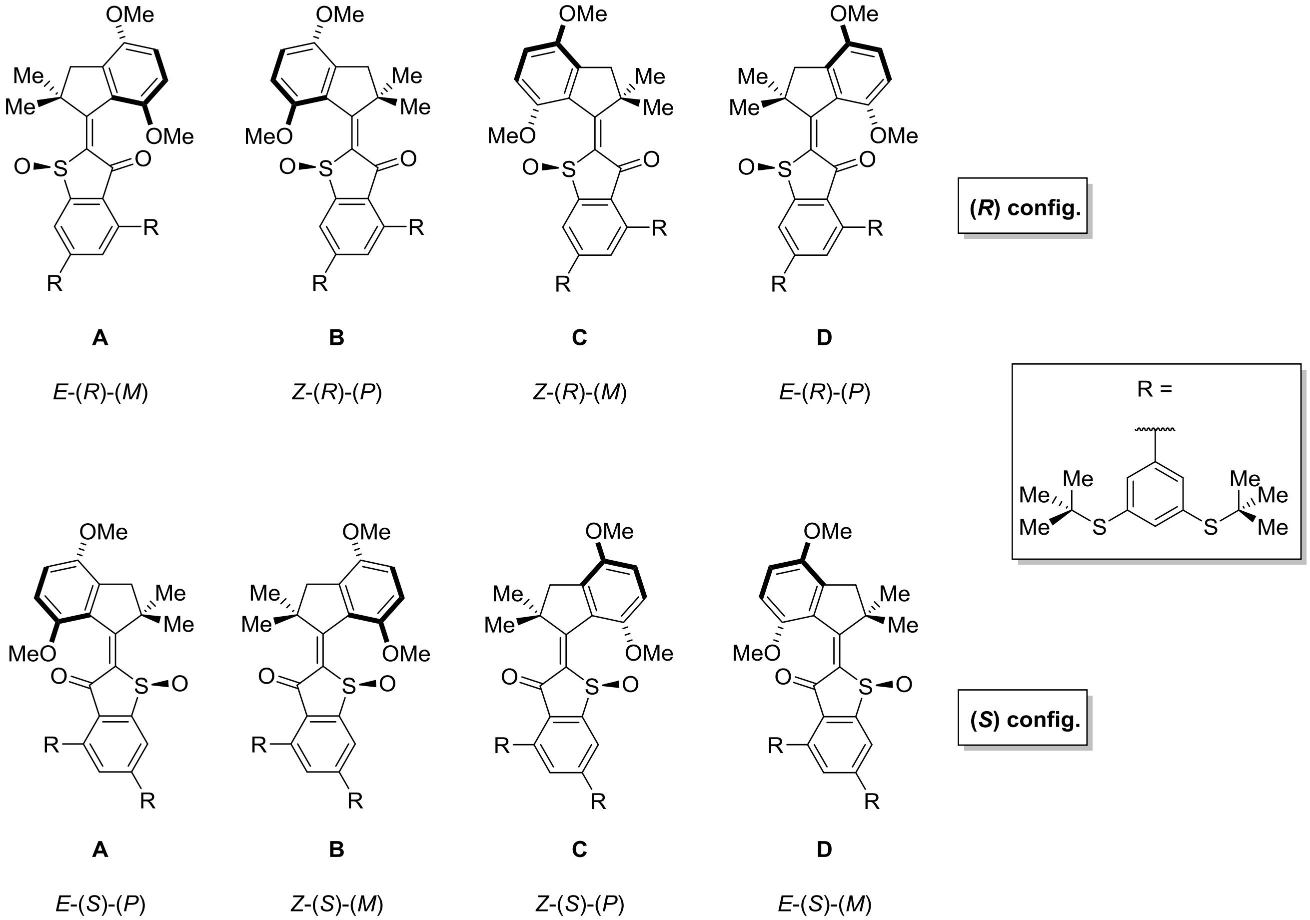
E isomer: R_f = 0.51 (*i*Hex:EtOAc 7:3 v/v); m.p: 159 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ = 8.29 (d, ^4J(H,H) = 1.6 Hz, 1H, H-C(6)), 7.93 (d, ^4J(H,H) = 1.6 Hz, 2H, H-C(23)), 7.85 (t, ^4J(H,H) = 1.6 Hz, 1H, H-C(25)), 7.82 (t, ^4J(H,H) = 1.6 Hz, 1H, H-C(31)), 7.77 (d, ^4J(H,H) = 1.6 Hz, 2H, H-C(29)), 7.76 (d, ^4J(H,H) = 1.6 Hz, 1H, H-C(4)), 6.95 (d, ^3J(H,H) = 8.8 Hz, 1H, H-C(14)), 6.67 (d, ^3J(H,H) = 8.9 Hz, 1H, H-C(15)), 3.82 (s, 3H, H_3-C(19)), 3.63 (s, 3H, H_3-C(18)), 3.07 (d, ^2J(H,H) = 15.5 Hz, 1H, H_2-C(11)), 2.91 (d, ^2J(H,H) = 15.4 Hz, 1H, H_2-C(11)), 1.97 (s, 3H, H_3-C(20/21)), 1.40 (s, 3H, H_3-C(21/20)), 1.36 (s, 18H, , H_3-C(27)), 1.33 (s, 18H, H_3-C(33)) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 181.8 (C(1)), 169.4 (C(9)), 153.3 (C(16)), 152.4 (C(8)), 150.2 (C(13)), 146.8 (C(25)), 146.2 (C(31)), 146.1 (C(5)), 141.8 (C(3), C(7)), 139.8 (C(22)), 139.3 (C(29)), 138.8 (C(28)), 137.8 (C(12)), 137.1 (C(23)), 134.8 (C(24)), 134.2 (C(4)), 132.9 (C(30)), 131.2 (C(2)), 129.2 (C(17)), 125.2 (C(6)), 116.0 (C(14)), 110.1 (C(15)), 56.5 (C(19)), 56.4 (C(18)), 52.9 (C(10)), 47.0 (C(26)), 46.8 (C(32)), 46.8 (C(11)), 31.4 (C(27), C(33)), 28.8 (C(20/ 21)), 26.3 (C(21/20)) ppm; IR: $\tilde{\nu}$ = 2958*m*, 2896*w*, 2860*w*, 1685*m*, 1597*w*, 1572*m*, 1544*vs*, 1493*m*, 1456*m*, 1392*w*, 1362*s*, 1311*vw*, 1265*vs*, 1118*w*, 1077*s*, 1058*vs*, 1002*w*, 964*vw*, 948*vw*, 874*m*, 859*w*, 801*w*, 749*vw*, 701*s*, 675*w* cm^{-1}; HR-EI-MS calc. [$C_{49}H_{60}O_4S_5^+$]: 872.3095, found: 872.3111.

Z isomer: R_f = 0.10 (*i*Hex:EtOAc 7:3 v/v); m.p: 163 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.21 (d, ^4J(H,H) = 1.6 Hz, 1H, H-C(6)), 7.90 (d, ^4J(H,H) = 1.6 Hz, 2H, H-C(23)), 7.83 (t, ^4J(H,H) = 1.6 Hz, 1H, H-C(31)), 7.82 (t, ^4J(H,H) = 1.5 Hz, 1H, H-C(25)), 7.70 (d, ^4J(H,H) = 1.6 Hz, 1H, H-C(4)), 7.68 (d, ^4J(H,H) = 1.6 Hz, 2H, H-C(29)), 7.05 (d, ^3J(H,H) = 8.9 Hz, 1H, H-C(14)), 6.86 (d, ^3J(H,H) = 8.9 Hz, 1H, H-C(15)), 4.06 (s, 3H, H_3-C(18)), 3.83 (s, 3H, H_3-C(19)), 2.99 (d, ^2J(H,H) = 16.4 Hz, 1H, H_2-C(11)), 2.88 (d, ^2J(H,H) = 16.4 Hz, 1H, H_2-C(11)), 1.50 (s, 3H, H_3-C(20/21)), 1.44 (s, 3H, H_3-C(21/20)), 1.35 (s, 18H, H_3-C(33)), 1.33 (s, 18H, H_3-C(27)) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 184.4 (C(1)), 169.5 (C(9)), 153.7 (C(8)), 151.9 (C(16)), 150.7 (C(13)), 146.8 (C(25)), 146.5 (C(5)), 146.1 (C(31)), 144.3 (C(7)), 141.3 (C(3)), 140.0 (C(22)), 139.1 (C(12)), 139.0 (C(28)), 139.0 (C(29)), 137.1 (C(23)), 134.9 (C(24)), 133.5 (C(30)), 133.3 (C(4)), 131.9 (C(2)), 127.0 (C(17)), 124.7 (C(6)), 116.8 (C(14)), 110.0 (C(15)), 56.5 (C(19)), 55.6 (C(18)), 52.4 (C(10)), 47.6 (C(11)), 47.0 (C(26)), 47.0 (C(32)), 31.5 (C(33)), 31.4 (C(27)), 28.7 (C(21/20)), 26.1 (C(20/21)) ppm; IR: $\tilde{\nu}$ = 2958*m*, 2938*w*, 2921*w*, 2896*w*, 2860*w*, 1675*m*, 1596*w*, 1541*vs*, 1493*s*, 1470*w*, 1455*m*, 1391*w*, 1362*s*, 1338*vw*, 1310*vw*, 1294*w*, 1265*vs*, 1218*s*, 1184*m*, 1160*vs*, 1116*vw*, 1082*vs*, 1066*vs*, 1046*m*, 993*vw*, 955*vw*, 939*vw*, 913*vw*, 887*w*, 872*m*, 798*w*, 759*vw*, 745*vw*, 720*vw*, 700*s*, 675*vw* cm^{-1}; HR-EI-MS calc. [$C_{49}H_{60}O_4S_5^+$]: 872.3095, found: 872.3100.

Motor Analysis

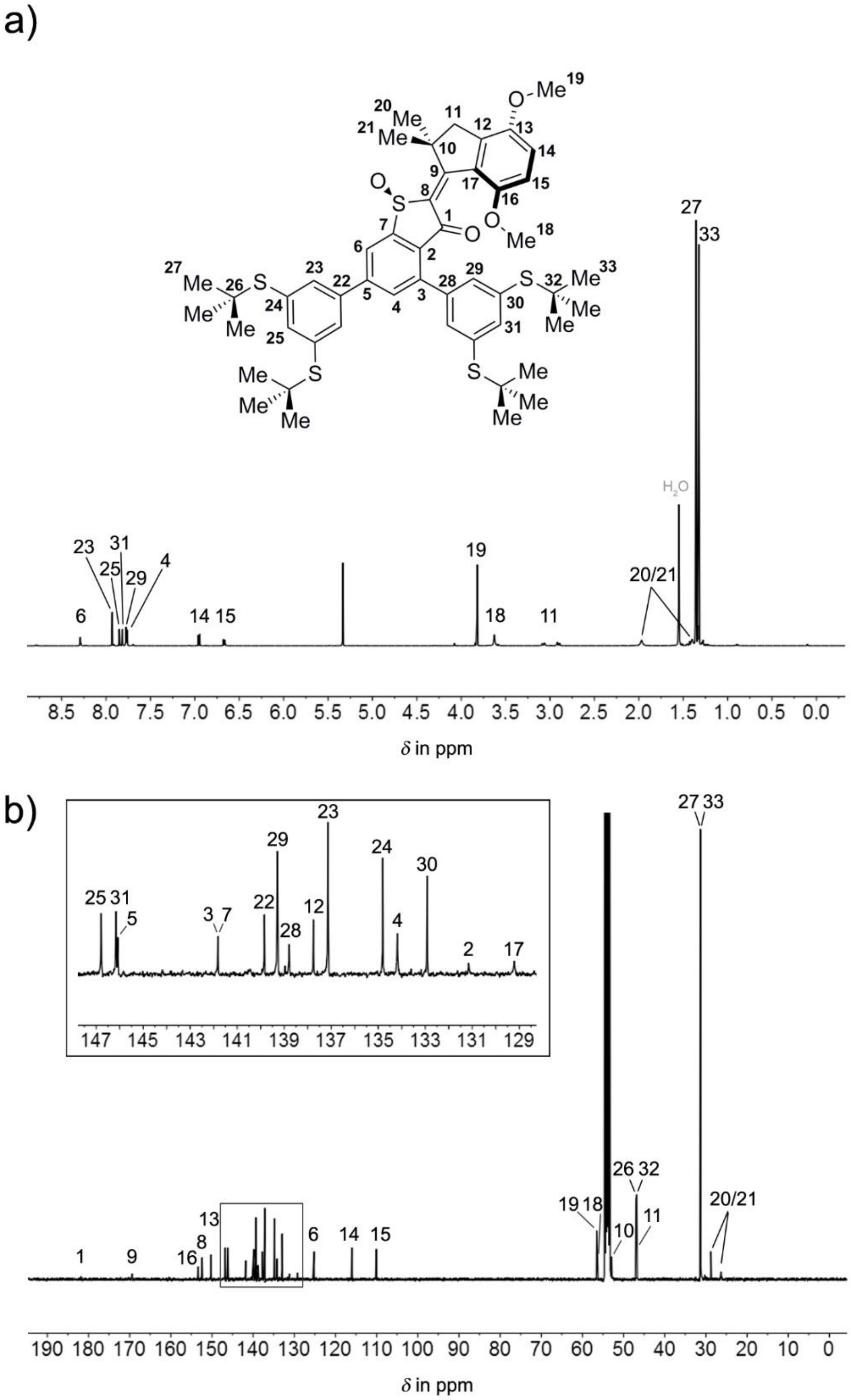
Conformational Analysis in Solution

Supplementary Figure 4 shows the four different intermediates **A**, **B**, **C** and **D** of motor **1** adapted during rotation for (*R*) and (*S*) configuration of the sulfoxide.

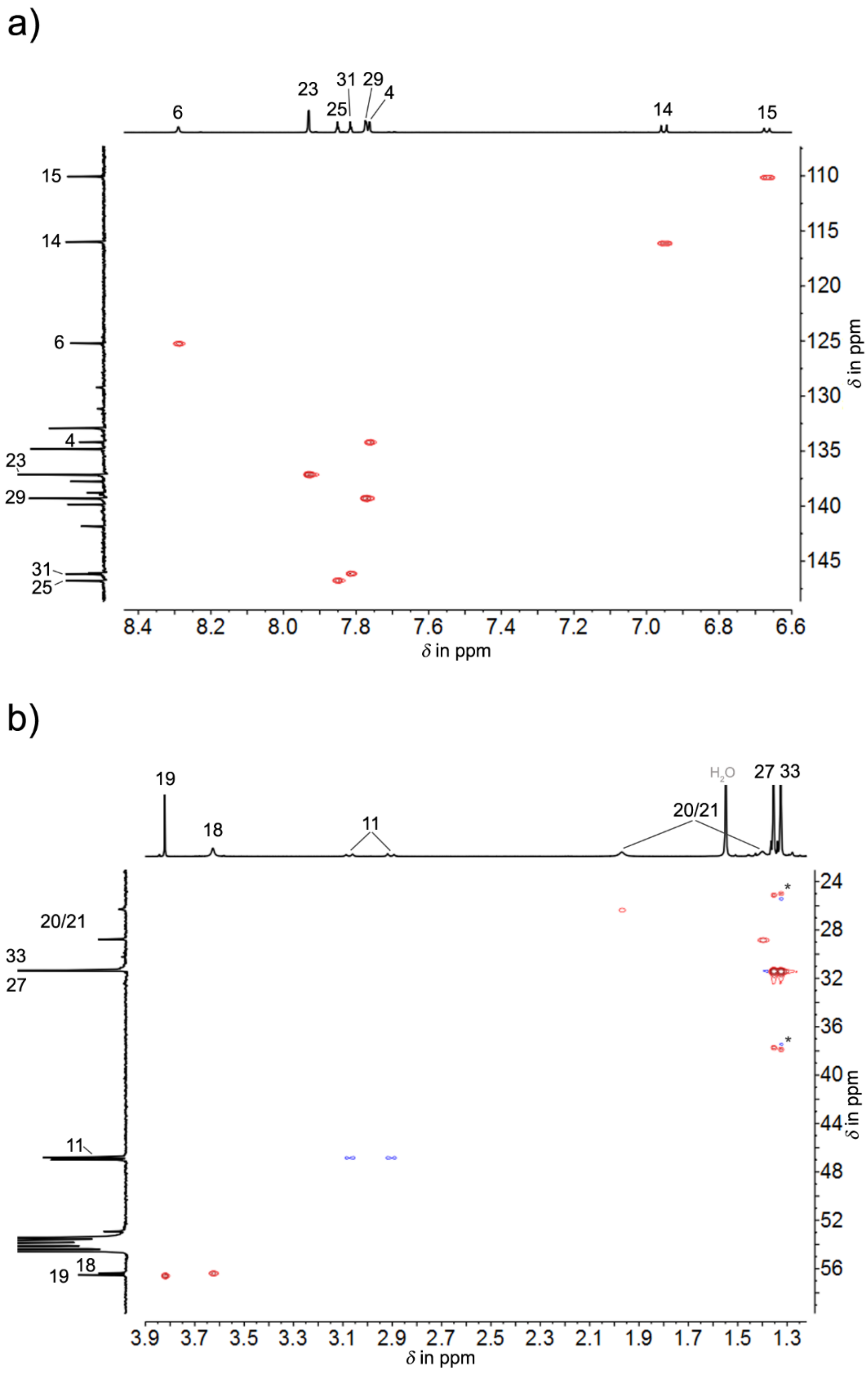


Supplementary Figure 4 Absolute stereo configuration of the different isomers **A**, **B**, **C** and **D** of motor **1**.

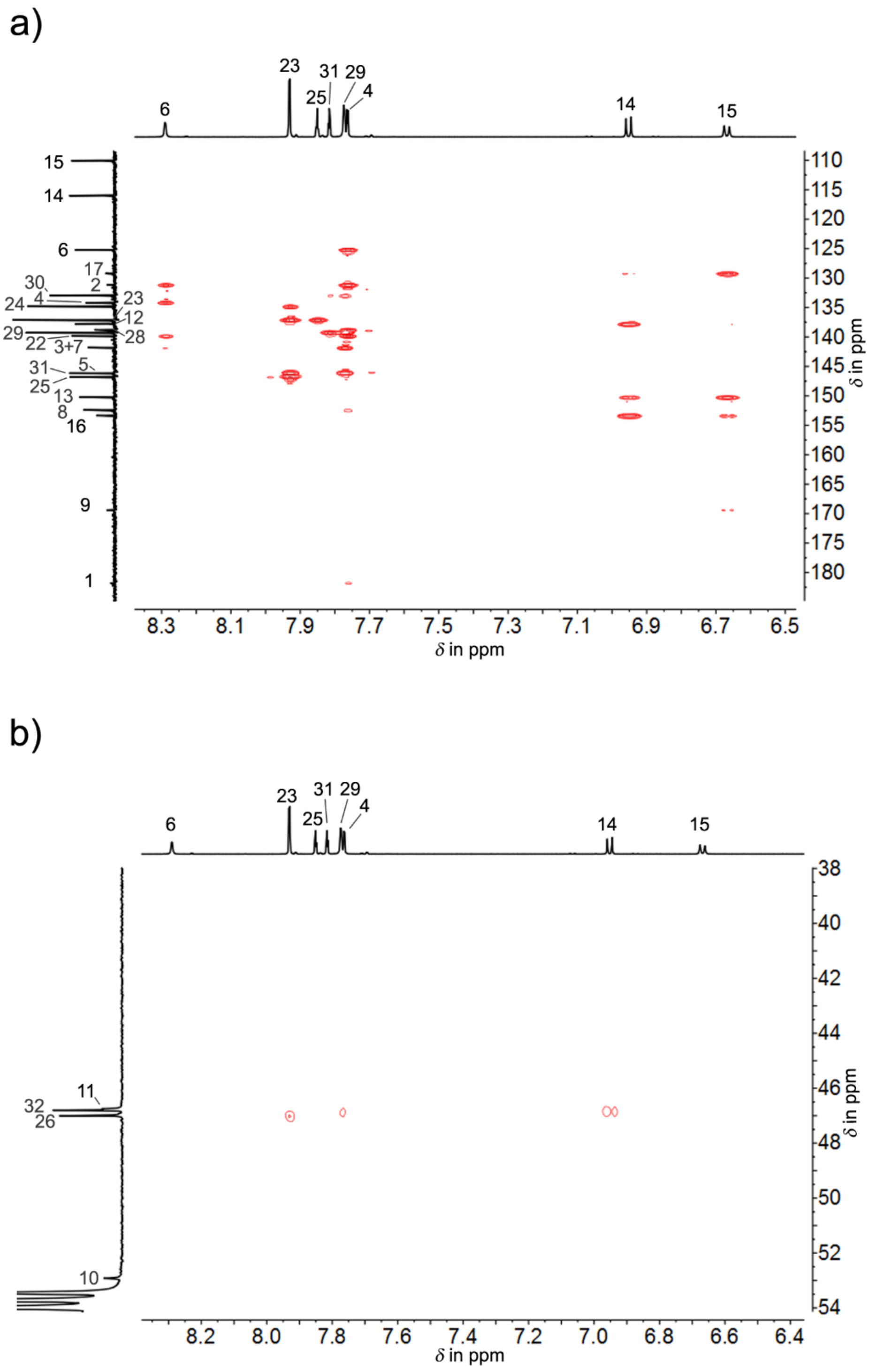
Supplementary Figure 5 till Supplementary Figure 16 display the 1D- and 2D-NMR spectra of **A-1** (*Z* isomer) and **C-1** (*E* isomer) and give important structural information.



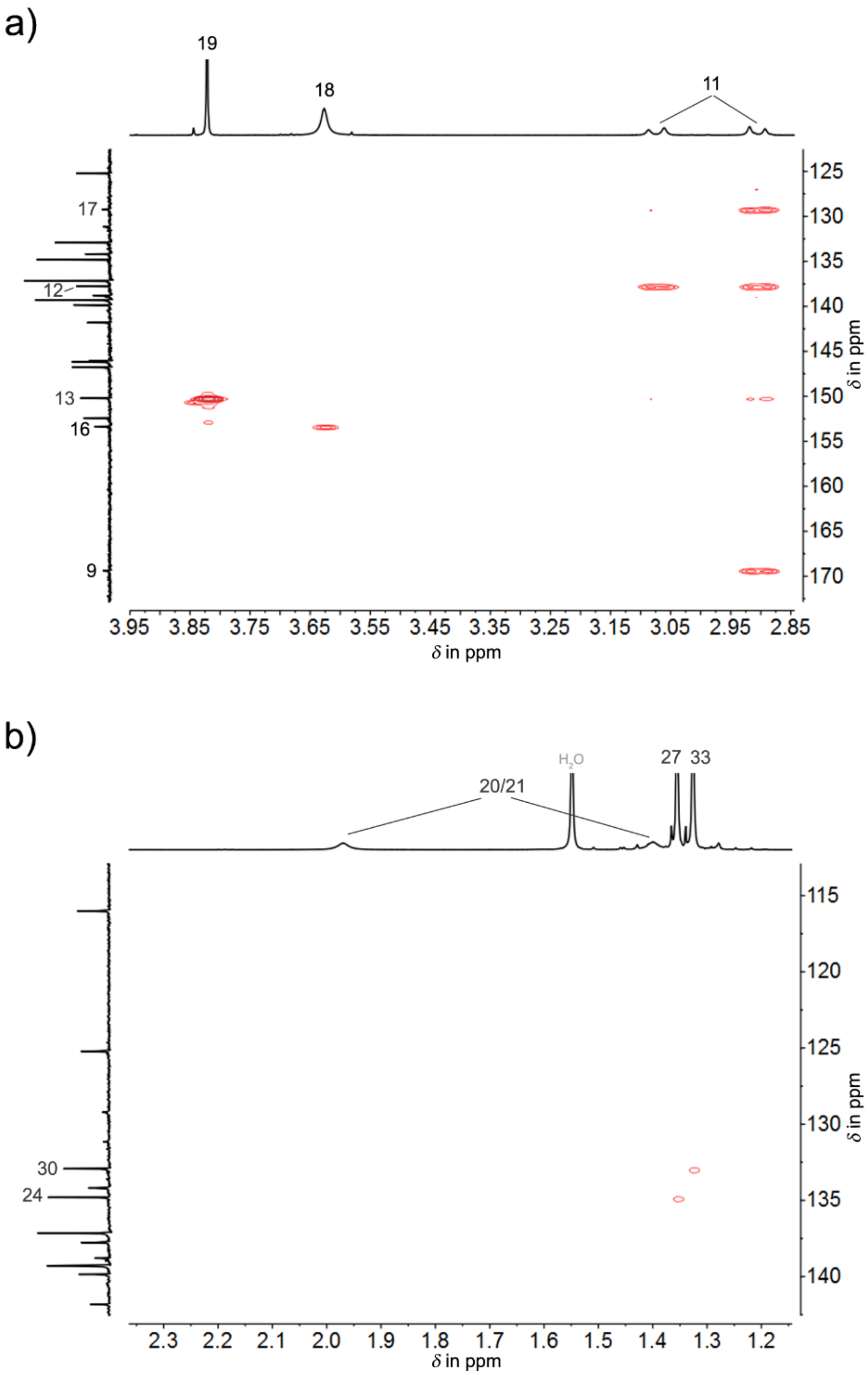
Supplementary Figure 5 NMR spectra of the **A** isomer of motor **1** and assignments of the signals to the molecular structure (exemplarily shown in the (*R*)-**A**-**1** configuration). **a)** ^{1}H NMR spectrum (CD$_2$Cl$_2$, 600 MHz, 30 °C). **b)** ^{13}C NMR spectrum (CD$_2$Cl$_2$, 1001MHz, 20 °C).



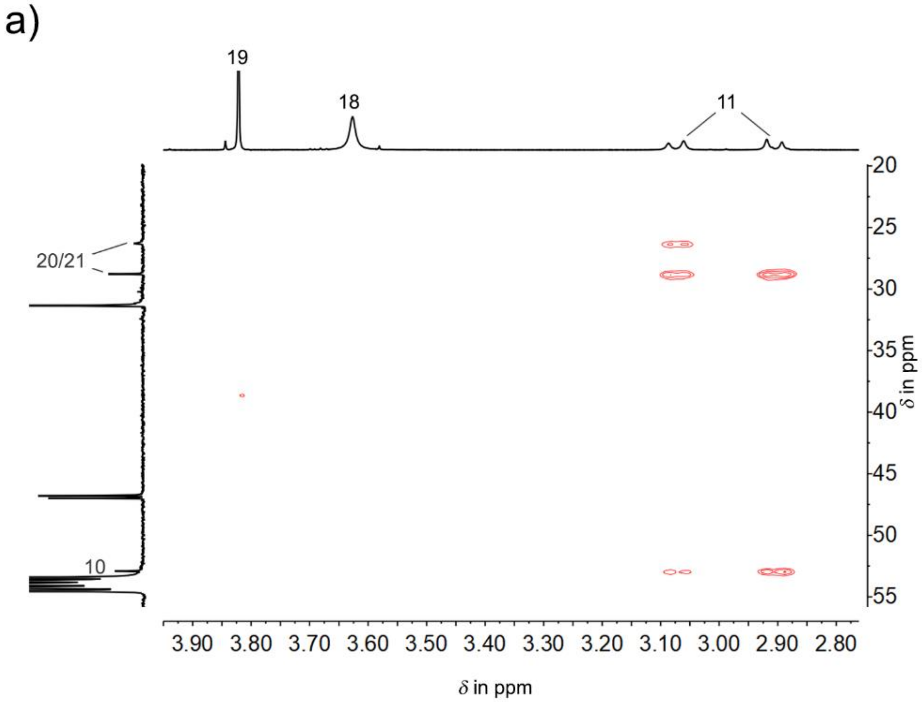
Supplementary Figure 6 HSQC NMR spectra of the **A** isomer of motor **1** (CD_2Cl_2, 600 MHz, 30 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 5*. **a)** Aromatic region of the spectrum. **b)** Aliphatic region of the spectrum.

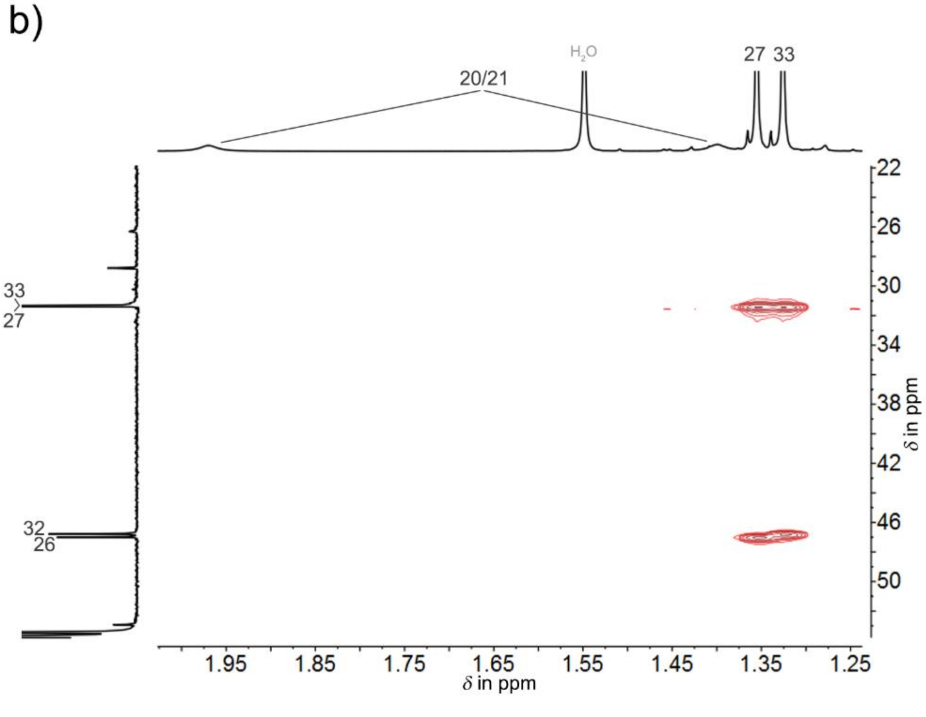


Supplementary Figure 7 HMBC NMR spectra of the **A** isomer of motor **1** (CD_2Cl_2, 600 MHz, 30 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 5*. **a)** Aromatic-aromatic region of the spectrum. **b)** Aromatic-aliphatic region of the spectrum.

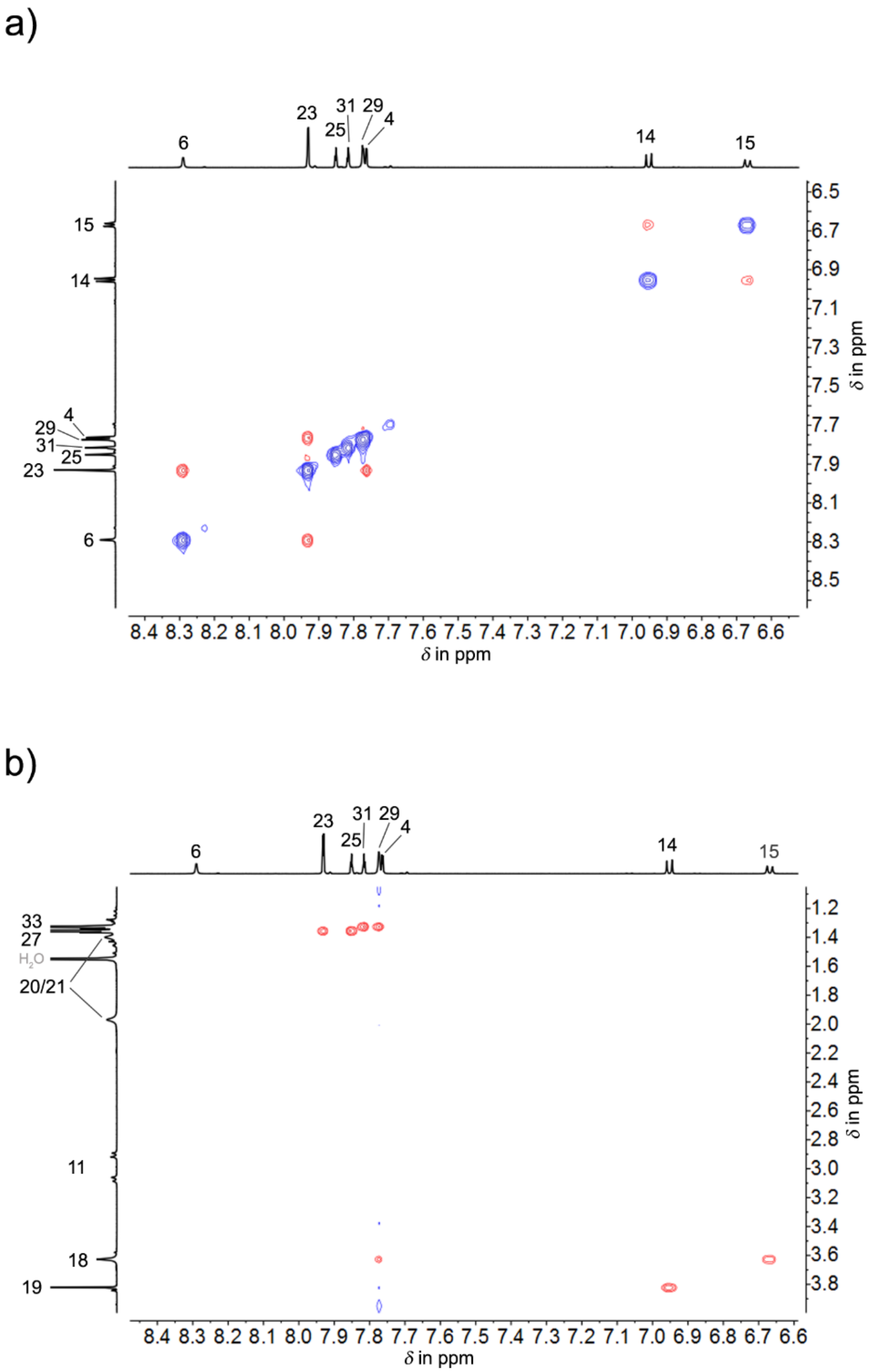


Supplementary Figure 8 HMBC NMR spectra of the **A** isomer of motor **1** (CD_2Cl_2, 600 MHz, 30 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 5*. **a)** Aliphatic-aromatic region of the spectrum. **b)** Different aliphatic-aromatic region of the spectrum. The cross peak signals between one hydrogen 11 and carbon 9 are not seen because one C(9)-C(10)-C(11)-H(11) dihedral angle is close to 90.0°. A similar behavior is seen for the original HTI motor **9**.

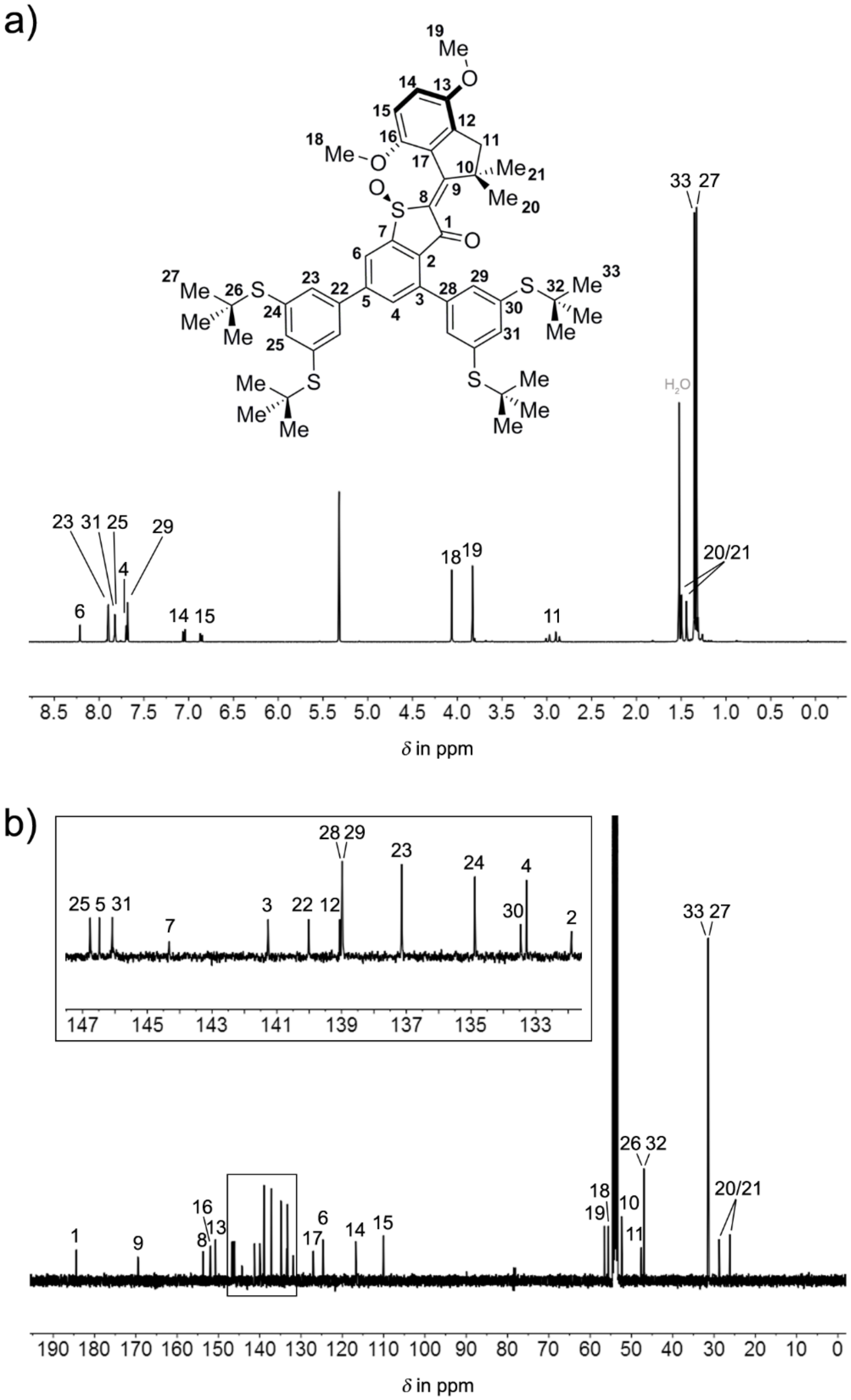




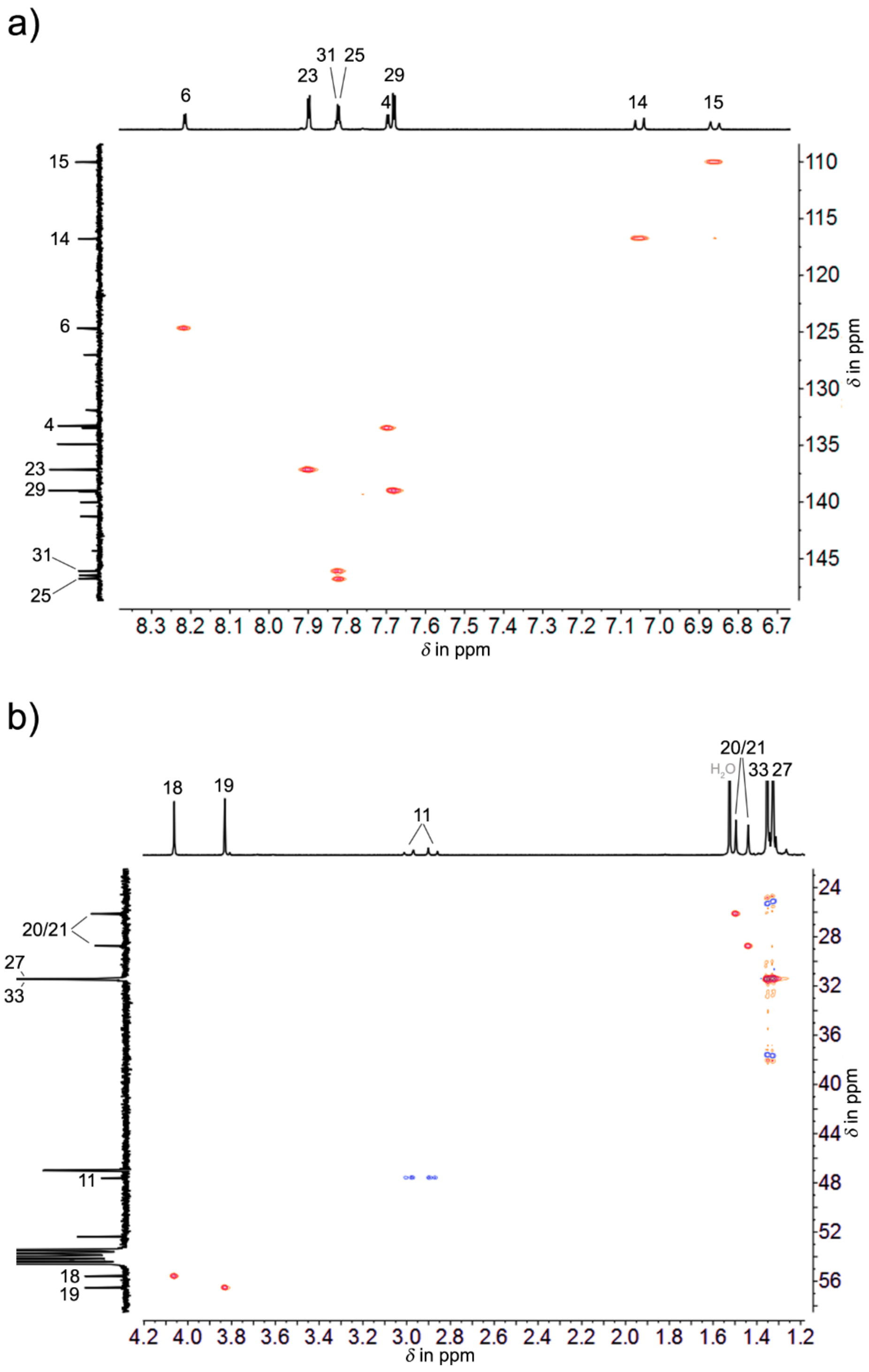
Supplementary Figure 9 HMBC NMR spectra of the **A** isomer of motor **1** (CD_2Cl_2, 600 MHz, 30 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 5*. **a)** Aliphatic-aliphatic region of the spectrum. **b)** Different aliphatic-aliphatic region of the spectrum. The cross peak signals between one hydrogen 11 and one carbon of 20/21 are not seen because one C(20/21)-C(10)-C(11)-H(11) dihedral angle is close to 90.0°. A similar behavior is seen for the original HTI motor **9**.



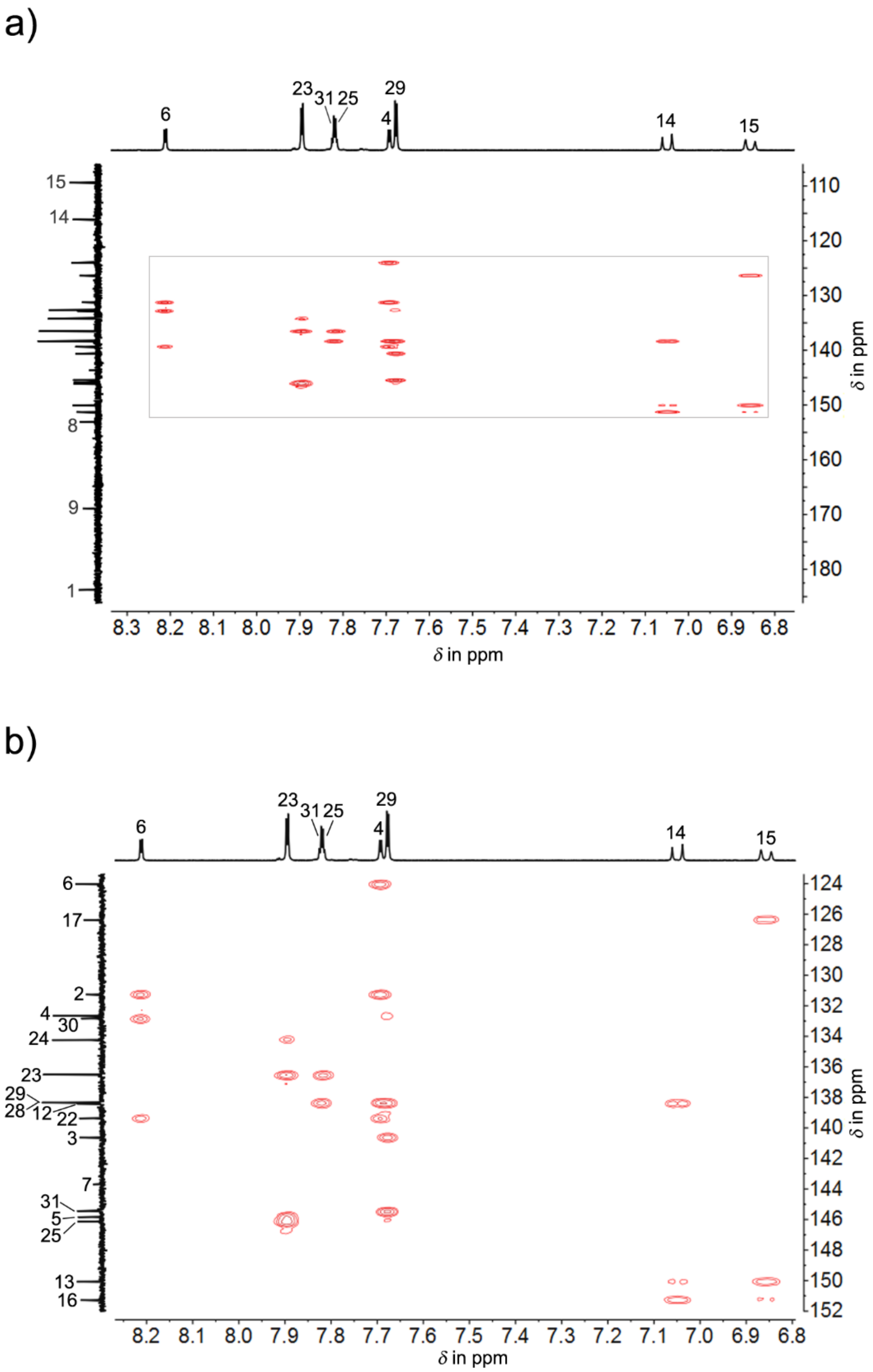
Supplementary Figure 10 NOESY NMR spectra of the **A** isomer of motor **1** (CD_2Cl_2, 600 MHz, 30 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 5*. **a)** Aromatic-aromatic region of the spectrum. **b)** Aromatic-aliphatic region of the spectrum. The cross peak signals between hydrogen 18 and hydrogen 29 prove the *E* configuration of the central double bond.



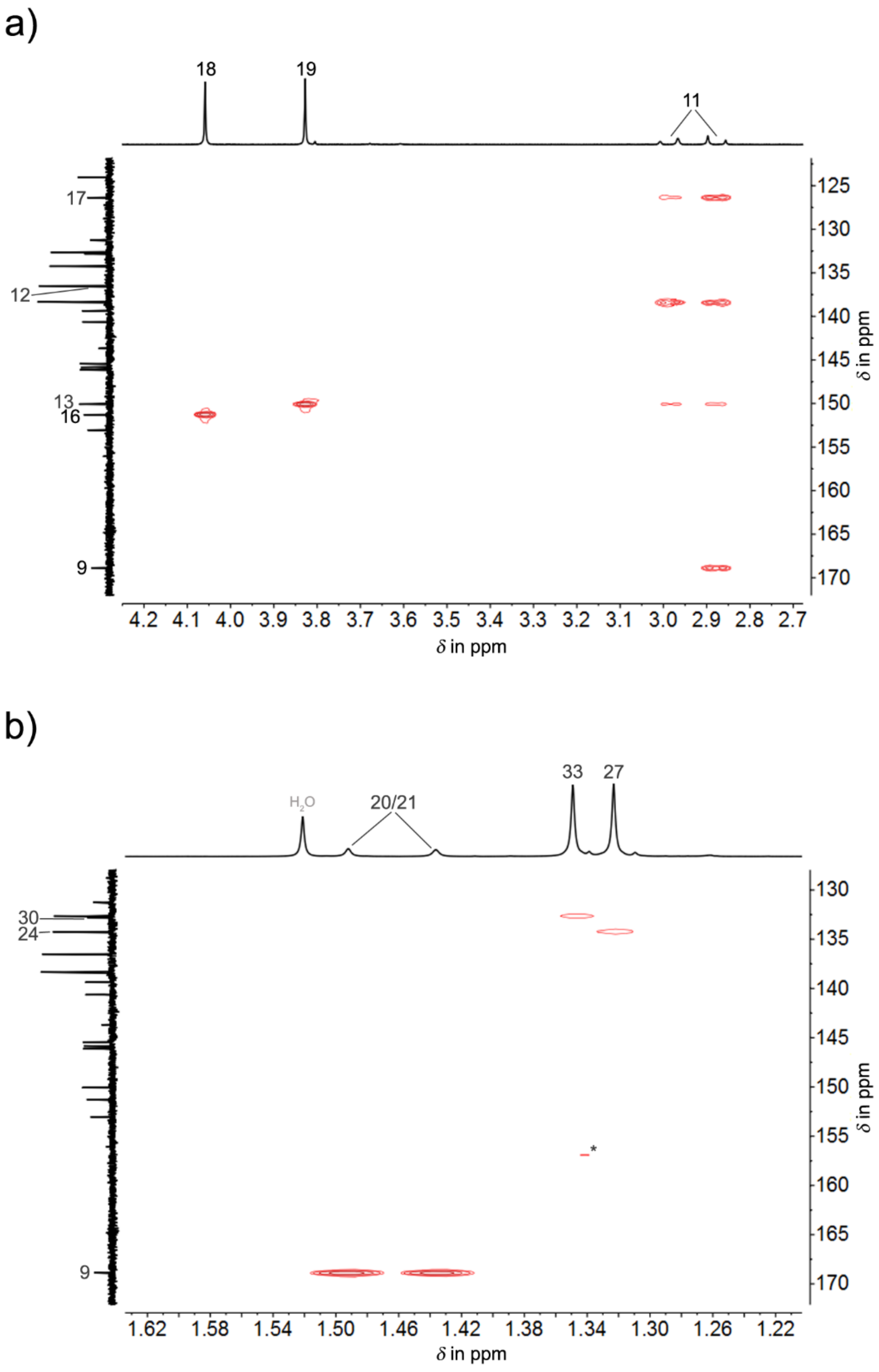
Supplementary Figure 11 NMR spectra of the **C** isomer of motor **1** and assignments of the signals to the molecular structure (exemplarily shown in the (*R*)-**C**-1 configuration). **a)** ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 27 °C). **b)** ^{13}C NMR spectrum (CD_2Cl_2, 101 MHz, 27 °C).



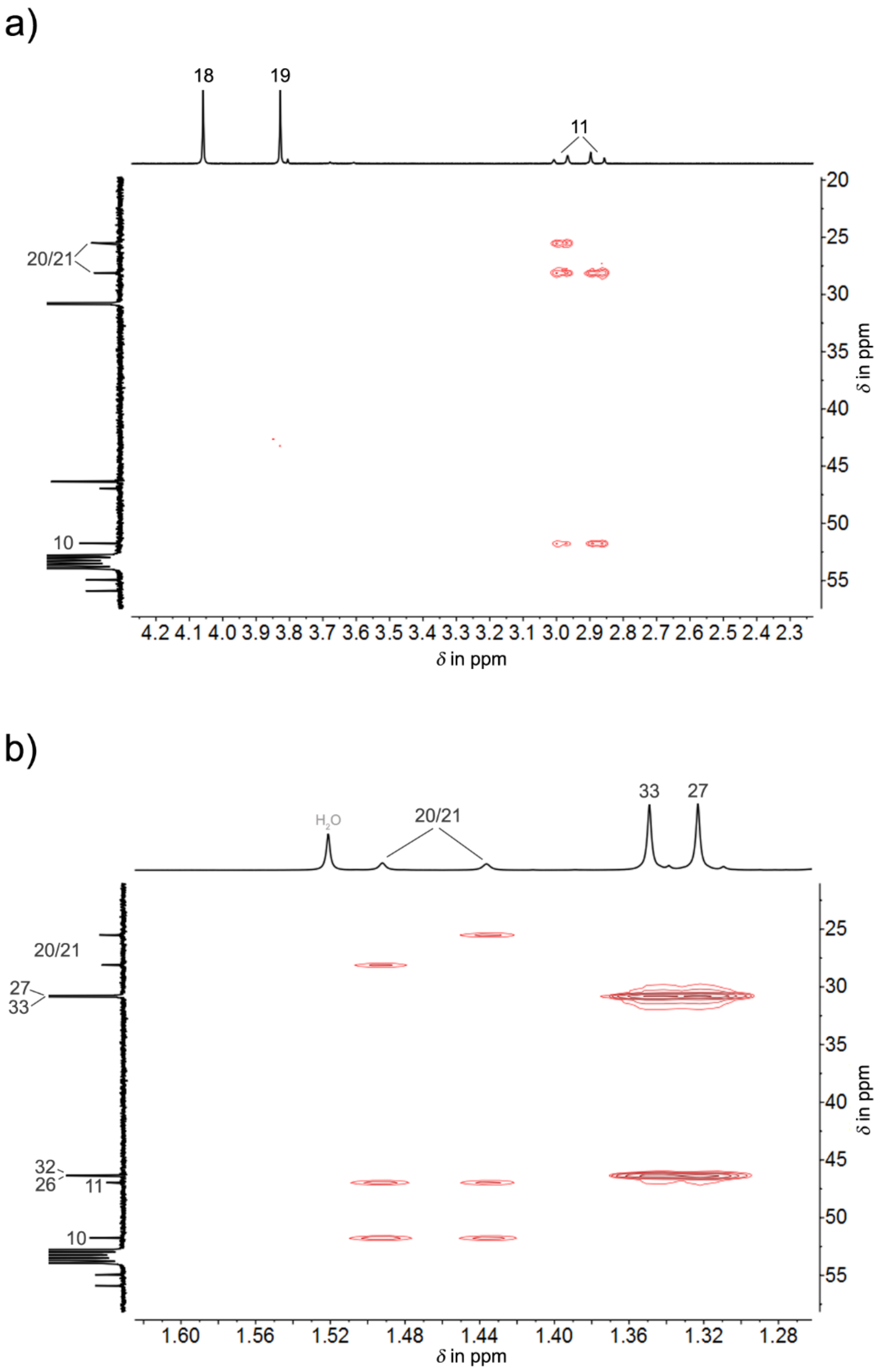
Supplementary Figure 12 HSQC NMR spectra of the **C** isomer of motor **1** (CD_2Cl_2, 600 MHz, 27 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 11*. **a)** Aromatic region of the spectrum. **b)** Aliphatic region of the spectrum.



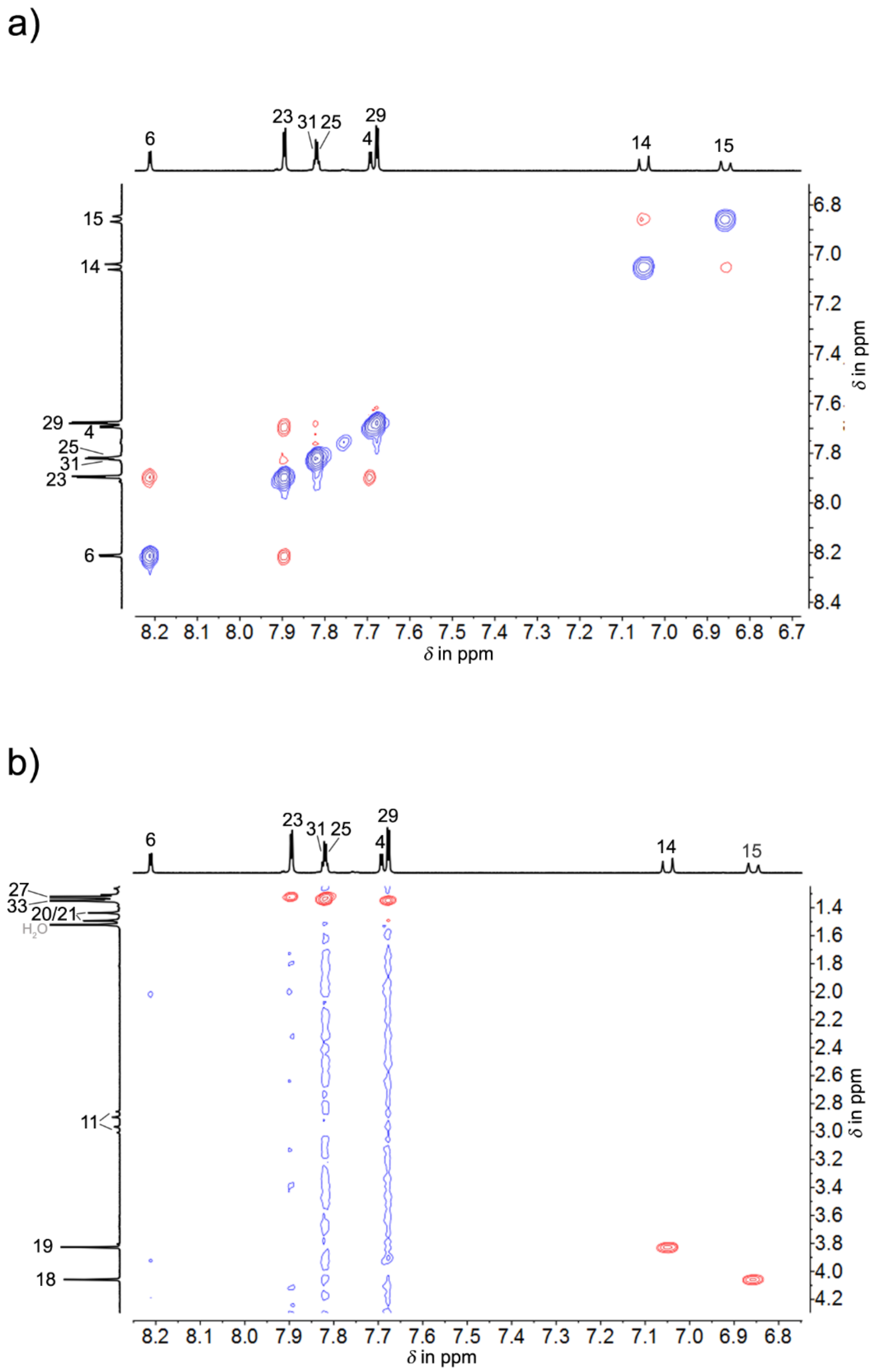
Supplementary Figure 13 HMBC NMR spectra of the **C** isomer of motor **1** (CD_2Cl_2, 600 MHz, 27 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 11*. **a)** Aromatic region of the spectrum. **b)** Zoom of the aromatic-aromatic region of the spectrum (see grey box in **a)**).



Supplementary Figure 14 HMBC NMR spectra of the **C** isomer of motor **1** (CD_2Cl_2, 600 MHz, 27 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 11*. **a)** Aliphatic-aromatic region of the spectrum. **b)** Different aliphatic-aromatic region of the spectrum. The cross peak signals between one hydrogen 11 and carbon 9 are not seen because one C(9)-C(10)-C(11)-H(11) dihedral angle is close to 90.0°. A similar behavior is seen for the original HTI motor **9**.



Supplementary Figure 15 HMBC NMR spectra of the **C** isomer of motor **1** (CD_2Cl_2, 600 MHz, 27 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 11*. **a)** Aliphatic-aliphatic region of the spectrum. **b)** Different aliphatic-aliphatic region of the spectrum. The cross peak signals between one hydrogen 11 and one carbon of 20/21 are not seen because one C(20/21)-C(10)-C(11)-H(11) dihedral angle is close to 90.0°. A similar behavior is seen for the original HTI motor **9**.

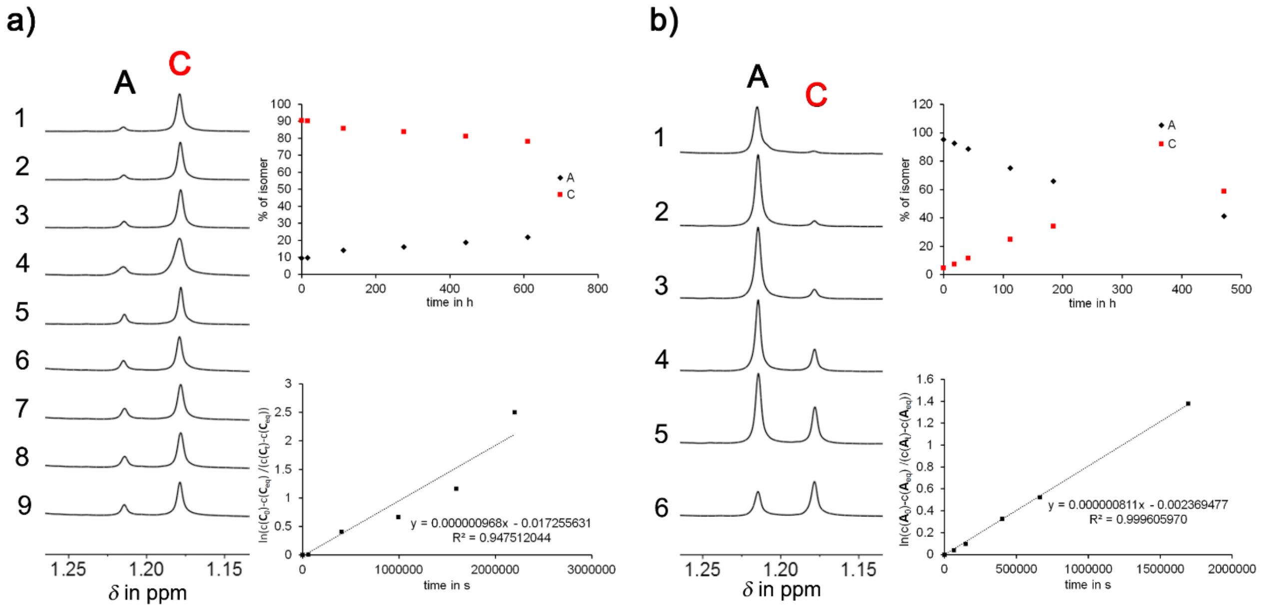


Supplementary Figure 16 NOESY NMR spectra of the **C** isomer of motor **1** (CD_2Cl_2, 600 MHz, 27 °C) and assignments of the signals to the molecular structure as depicted in *Supplementary Figure 11*. **a)** Aromatic-aromatic region of the spectrum. **b)** Aromatic-aliphatic region of the spectrum. The weak cross peak signals between one methylgroup hydrogen 20/21 and hydrogen 29 confirm the *Z* configuration of the central double bond.

Temperature and Irradiation Dependent Behavior of Motor 1

Elevated Temperature Behavior

The **C** isomer is the thermodynamically most stable form of motor **1**. At elevated temperatures the **A** isomer interconverts with the **C** isomer and *vice versa*. Supplementary Figure 17 shows the ^{1}H NMR spectra of **1** during heating to 100 °C in toluene-d_8 and the corresponding kinetic plots.



Supplementary Figure 17 Kinetic and thermodynamic analysis of the thermal isomerization of **a) C-1** to **A-1** and **b) A-1** to **C-1** at 100°C in the dark. For demonstration of the gradual conversion ^{1}H NMR signals (toluene-d_8, 400 MHz) of the *tert*-butyl groups are shown. Spectra were taken at different time points over the course of 610 h (**a**)) and 470 h (**b**)). Decrease and increase of the respective isomers are shown over time. Data points were obtained from integration of indicative NMR signals. Starting point of **a)** is a mixture of **C** : **A** isomer in a ratio of 90 : 10, of **b)** 5 : 95, respectively. After heating the solutions to 100 °C until the equilibrium is reached a stable ratio of 77 : 23 (**C** : **A**) is established (for thermodynamic equilibrium see **a)**; **b)** only for kinetic informations, meassurement was stopped before equilibrium was reached), which can be translated to an energy difference of 0.9 kcal/mol. A first order kinetic analysis taking into account the dynamic equilibrium gives linear relationships. The slopes m (0.000000968 for **a)** and 0.000000811 for **b)**) can each be translated into both rate constants $k_{(C\rightarrow A)}$ and $k_{(A\rightarrow C)}$ and further into the Gibbs energies of activation for the respective isomerizations.

The first-order rate constant for the thermal **A** to **C** and **C** to **A** isomerizations of motor **1** were determined from the decay kinetics of the **A** and **C** isomer during prolonged heating at 100 °C (see Supplementary Figure 17). As the thermal isomerization is a dynamic equilibrium between both isomerization processes **A** to **C** and *vice versa* it has to be described according to equation 1:

$$\ln\left(\frac{c(0)-c(\mathrm{eq})}{c(t)-c(\mathrm{eq})}\right) = (k(\mathbf{A} \rightarrow \mathbf{C}) + k(\mathbf{C} \rightarrow \mathbf{A}))t \qquad \text{(eq. 1)}$$

with $c(0)$ = initial concentration of the decreasing isomer, $c(\mathrm{eq})$ = concentration of the decreasing isomer at equilibrium, $c(t)$ = concentration of the decreasing isomer at the particular point in time, $k(\mathbf{A} \rightarrow \mathbf{C})$ = rate constant of the **A** to **C** isomerization, $k(\mathbf{C} \rightarrow \mathbf{A})$ = rate constant of the **C** to **A** isomerization, and t = elapsed time.

The slopes obtained from the log-plots according to equation 1 are m = 0.000000968 s^{-1} from the **A** to **C** isomerization and m = 0.000000811 s^{-1} from the **C** to **A** isomerization of motor **1** (see Supplementary Figure 17). Both slopes contain the rate constants for both isomerization directions and therefore are fairly the same. From each slope the rate constants $k(\mathbf{A} \rightarrow \mathbf{C})$ and $k(\mathbf{C} \rightarrow \mathbf{A})$ can be calculated according to equation 2 and 3:

$$k(\mathbf{A} \rightarrow \mathbf{C}) = \frac{m}{1+\frac{c(\mathbf{A}\mathrm{eq})}{c(\mathbf{C}\mathrm{eq})}} \qquad \text{(eq. 2)}$$

$$k(\mathbf{C} \rightarrow \mathbf{A}) = \frac{m}{1+\frac{c(\mathbf{C}\mathrm{eq})}{c(\mathbf{A}\mathrm{eq})}} \qquad \text{(eq. 3)}$$

When taking into account the law of mass action (equation 4):

$$\frac{c(\mathbf{A}\mathrm{eq})}{c(\mathbf{C}\mathrm{eq})} = \frac{k(\mathbf{C}\rightarrow\mathbf{A})}{k(\mathbf{A}\rightarrow\mathbf{C})} \qquad \text{(eq. 4)}$$

with $c(\mathbf{C}\mathrm{eq})$ = concentration of the **C** isomer at equilibrium and $c(\mathbf{A}\mathrm{eq})$ = concentration of the **A** isomer at equilibrium.

Using the Eyring equation the Gibbs energy of activation ΔG^* for the thermal isomerizations can be calculated according to equation 5 for each rate constant $k(\mathbf{A} \rightarrow \mathbf{C})$ and $k(\mathbf{C} \rightarrow \mathbf{A})$:

$$k = \frac{k_B\ T}{h}\ \mathrm{e}^{\frac{-\Delta G*}{RT}} \qquad \text{(eq. 5)}$$

with k_B = Boltzmann constant ($1.381 \cdot 10^{-23}$ J·K^{-1})

T = temperature in K

h = Planck constant ($6.626 \cdot 10^{-34}$ J·s)

After rearranging equation 5 and insertion of the numerical values of the constants $\Delta G*$ is given by:

$$\Delta G* \text{ (in J mol}^{-1}\text{)} = 8.314\ \cdot T\ \cdot \left[23.760 + \ln\left(\frac{T}{k}\right)\right] \qquad \text{(eq. 6)}$$

Supplementary table 1 displays all calculated values according to the described procedure.

Supplementary table 1 Calculated values of *k* and corresponding ΔG* from kinetic and thermodynamic data (see *Supplementary Figure 17*) according to equations 1-6.

	$k(\mathbf{C} \rightarrow \mathbf{A})$ (s^{-1})	$\Delta G*(\mathbf{C} \rightarrow \mathbf{A})$ (kcal·mol^{-1})	$k(\mathbf{A} \rightarrow \mathbf{C})$ (s^{-1})	$\Delta G*(\mathbf{A} \rightarrow \mathbf{C})$ (kcal·mol^{-1})
a) **C** to **A** isomerization	$2.2264 \cdot 10^{-7}$	33.37	$7.4536 \cdot 10^{-7}$	32.47
b) **A** to **C** isomerization	$1.8653 \cdot 10^{-7}$	33.50	$6.2447 \cdot 10^{-7}$	32.60

The stationary isomer composition of motor **1** at 100 °C is 77% **C** isomers and 23% **A** isomers. This equilibrium reflects the relative energy difference $-\Delta G$ between the two isomeric states. $-\Delta G$ can be calculated according to:

$$-\Delta G = \ln K \cdot R \cdot T \qquad \text{(eq. 7)}$$

with K = equilibrium constant = [**C**]/[**A**]

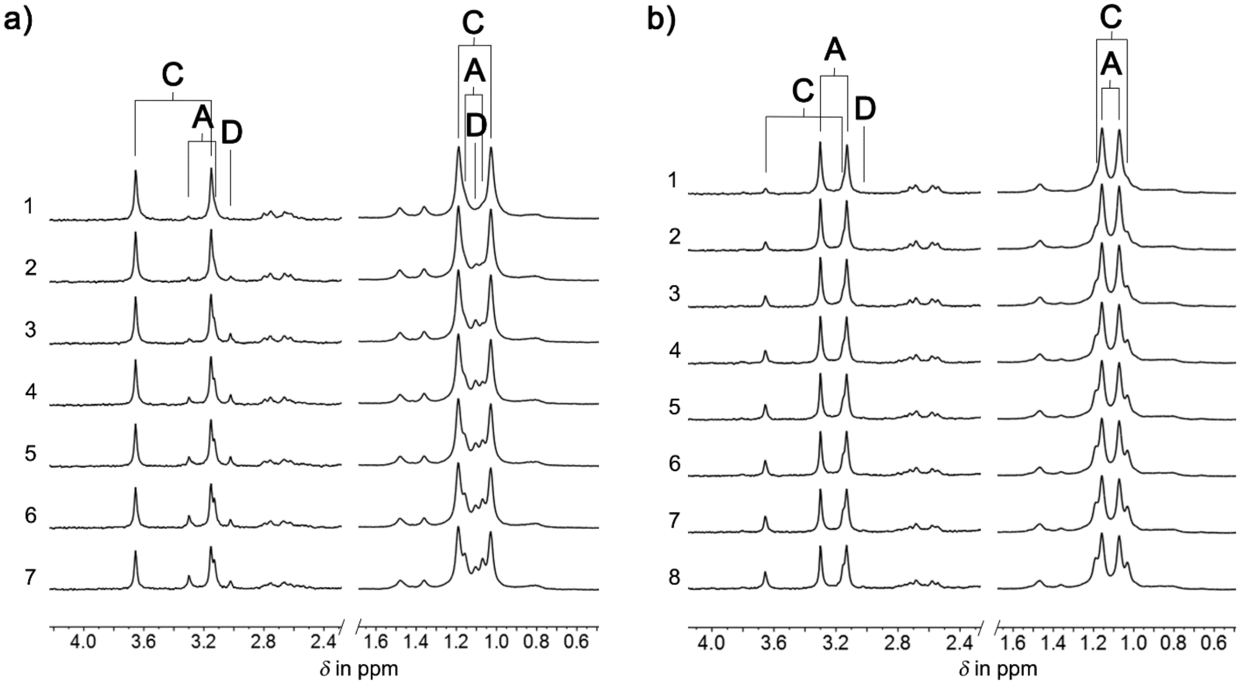
R = ideal gas constant = (8.314 J·K^{-1}·mol^{-1})

T = temperature in K

Using K = 77/23 for the equilibrium constant at 100 °C gives an energy difference between the **C** and **A** isomer of 0.90 kcal·mol^{-1} for motor **1**.

Irradiation at Low Temperature

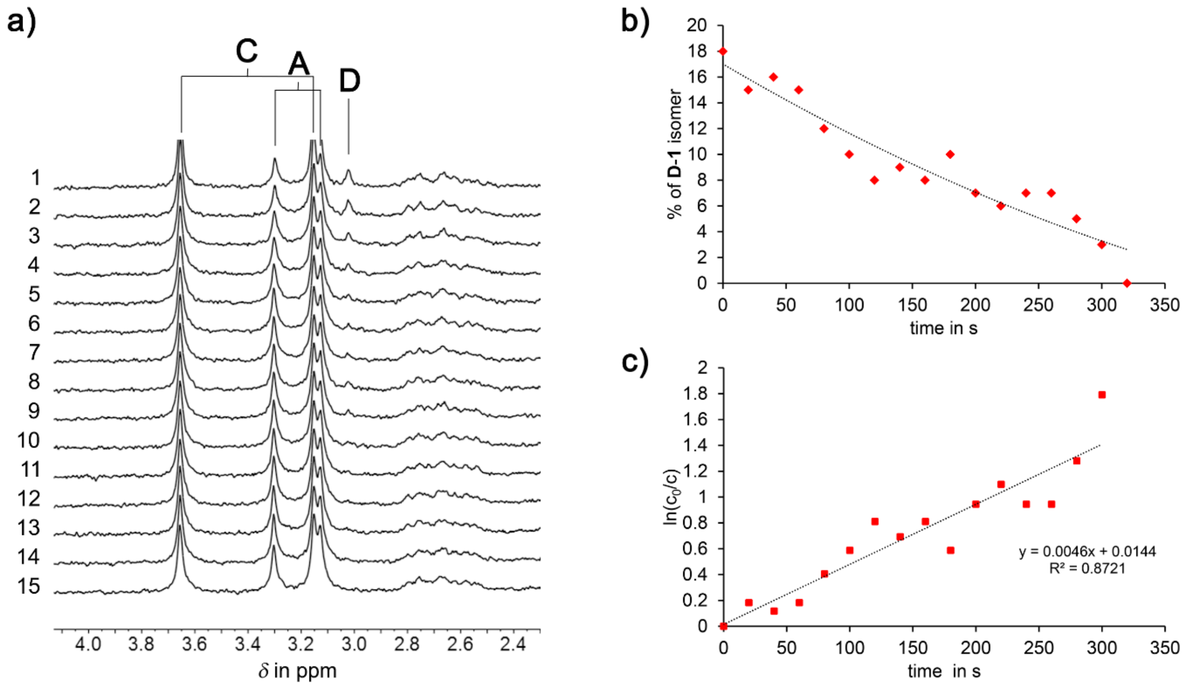
Supplementary Figure 18 shows ^{1}H NMR spectra of the **C** and **A** isomer of motor **1** in toluene-d_8 acquired at -80°C during high power 450 nm irradiation.



Supplementary Figure 18 ^{1}H NMR spectra of motor **1** (toluene-d_8, 1.5 mM, 400 MHz) acquired at -80 °C during high power 450 nm irradiation. Indicative signals of the methoxy groups (2.4-4.0 ppm) and *tert*-butyl groups (0.6-1.6 ppm) are assigned exemplarily. **a)** Irradiation of **A-1** illustrated by spectra recorded with 1 min time intervals. **b)** Irradiation of **C-1** illustrated by spectra recorded with 20 s time intervals.

Supplementary Figure 18 **a)** illustrates the photoisomerization process of **C-1** at -80 °C. Upon irradiation **C-1** interconverts into **D-1**. Only after the signals of metastable **B-1** (see Supplementary Figure 19) are present the signals of **C-1** start rising. The signals of the *tert*-butyl groups display this chronological order especially clearly. Supplementary Figure 18 **b)** shows the isomerization of **A-1** at -80 °C. At this temperature the signals of **A-1** convert directly into the signals of **C-1** upon irradiation. No other metastable species can be observed. After enough **C-1** has accumulated, signal **D-1** increases slowly.

Supplementary Figure 19 shows the thermal conversion of **D-1** to **A-1**.



Supplementary Figure 19 Kinetic analysis of the thermal conversion of **D-1** to **A-1**. **a)** ^{1}H NMR spectra (toluene-*d*$_8$, 1.5 mM, 400 MHz) acquired during thermal conversion of the photo generated species **D-1** at -80 °C in the dark. For demonstration of the gradual conversion signals of the methoxy groups are shown. Spectra were taken in 20 s time intervals (spectra 1-15). **b)** Decrease of **D-1** over time. **c)** First order kinetic analysis of the ^{1}H NMR data. The slope of the linear fit (formula given in the diagram) is the first order rate constant $k_{(B\rightarrow C)}$ = 0.0046 s^{-1}.

The thermal **D-1** to **C** isomerization process of motor **1** was followed via ^{1}H NMR spectroscopy in toluene-*d*$_8$. Supplementary Figure 19 **a)** shows full conversion of **D-1** to **A-1**, while signals of **C-1** stay constant. The thermal helix inversion can be analyzed using a first-order kinetics description.

At –80 °C the first-order rate constant of the thermal **D** to **A** isomerization of motor **1** is $k_{(\mathbf{B}\rightarrow\mathbf{C})} = 0.0046\ \mathrm{s}^{-1}$. The Gibbs energy of activation Δ*G** for this thermal helix inversion can be calculated from the rate constant $k_{(\mathbf{B}\rightarrow\mathbf{C})}$ of the reaction using the Eyring equation:

$$k_{(\mathbf{D}\rightarrow\mathbf{A})} = \frac{k_B\ T}{h}\ \mathrm{e}^{\frac{-\Delta G*}{RT}} \qquad \text{(eq. 8)}$$

with k_B = Boltzmann constant ($1.381\cdot10^{-23}$ J·K^{-1})

T = temperature in K

h = Planck constant ($6.626\cdot10^{-34}$ J·s)

$k_{(\mathbf{D}\rightarrow\mathbf{A})}$ = rate constant of the thermal **D** to **A** isomerization

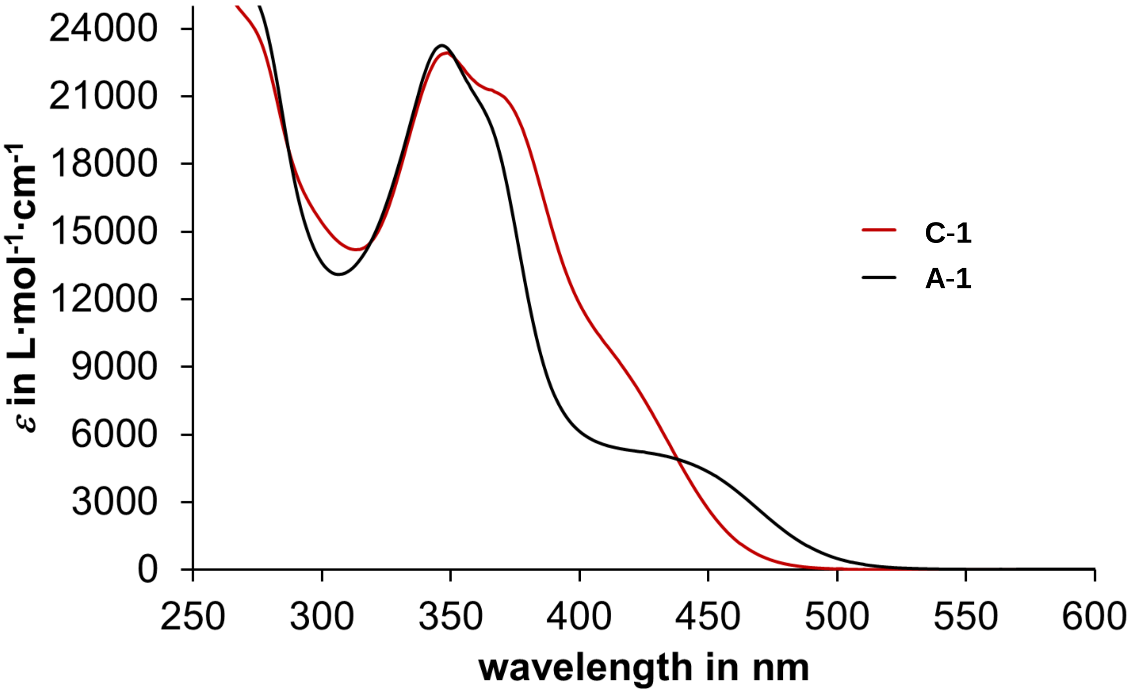
After rearranging equation 8 and insertion of the numerical values of the constants Δ*G** is given by:

$$\Delta G^* \text{ (in J mol}^{-1}) = 8.314\ \cdot T\ \cdot\ \left[23.760 + \ln\left(\frac{T}{k(\mathbf{D}\rightarrow\mathbf{A})}\right)\right] \qquad \text{(eq. 9)}$$

In this way Δ*G** = 55.25 kJ·mol^{-1} = 13.20 kcal·mol^{-1} was obtained for the thermal **D** to **A** isomerization of motor **1**.

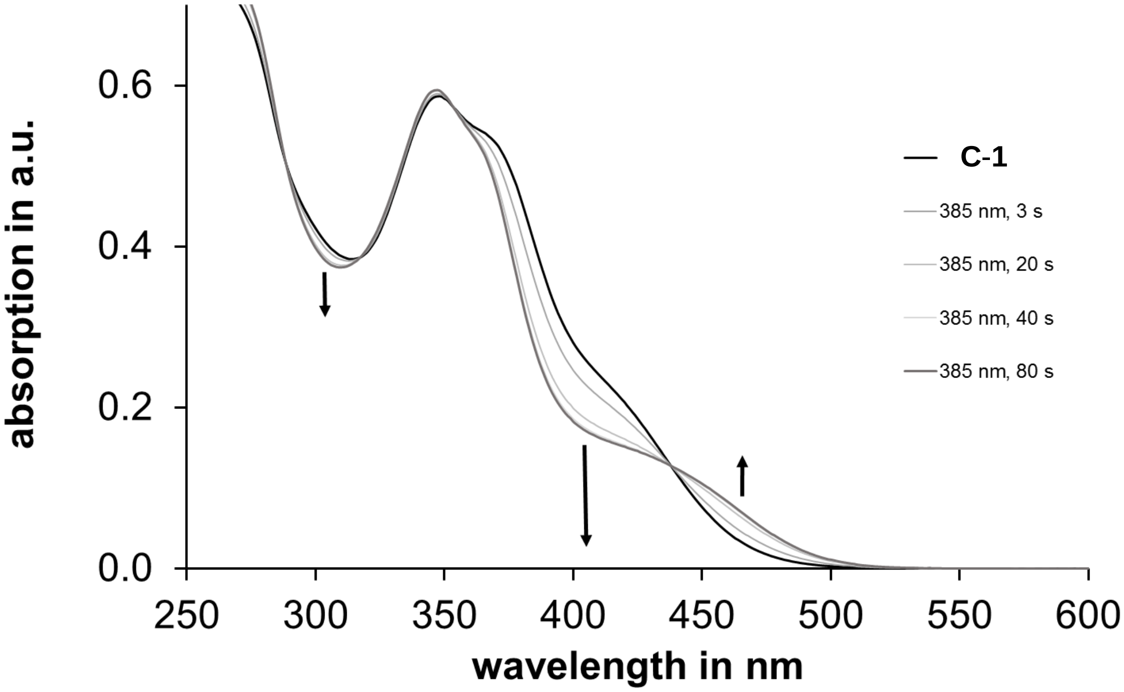
Photophysical Properties

Supplementary Figure 20 shows the molar absorption coefficients of the **A** and **C** isomer of motor **1**.



Supplementary Figure 20 Molar absorption coefficients of **A-1** (black) and **C-1** (red) in CH_2Cl_2 at 23 °C.

Supplementary Figure 21 shows the photoisomerization of **C-1** to **A-1** at 23 °C monitored via UV/vis spectroscopy. Spectra were measured after different irradiation intervals using a 385 nm LED for illumination.



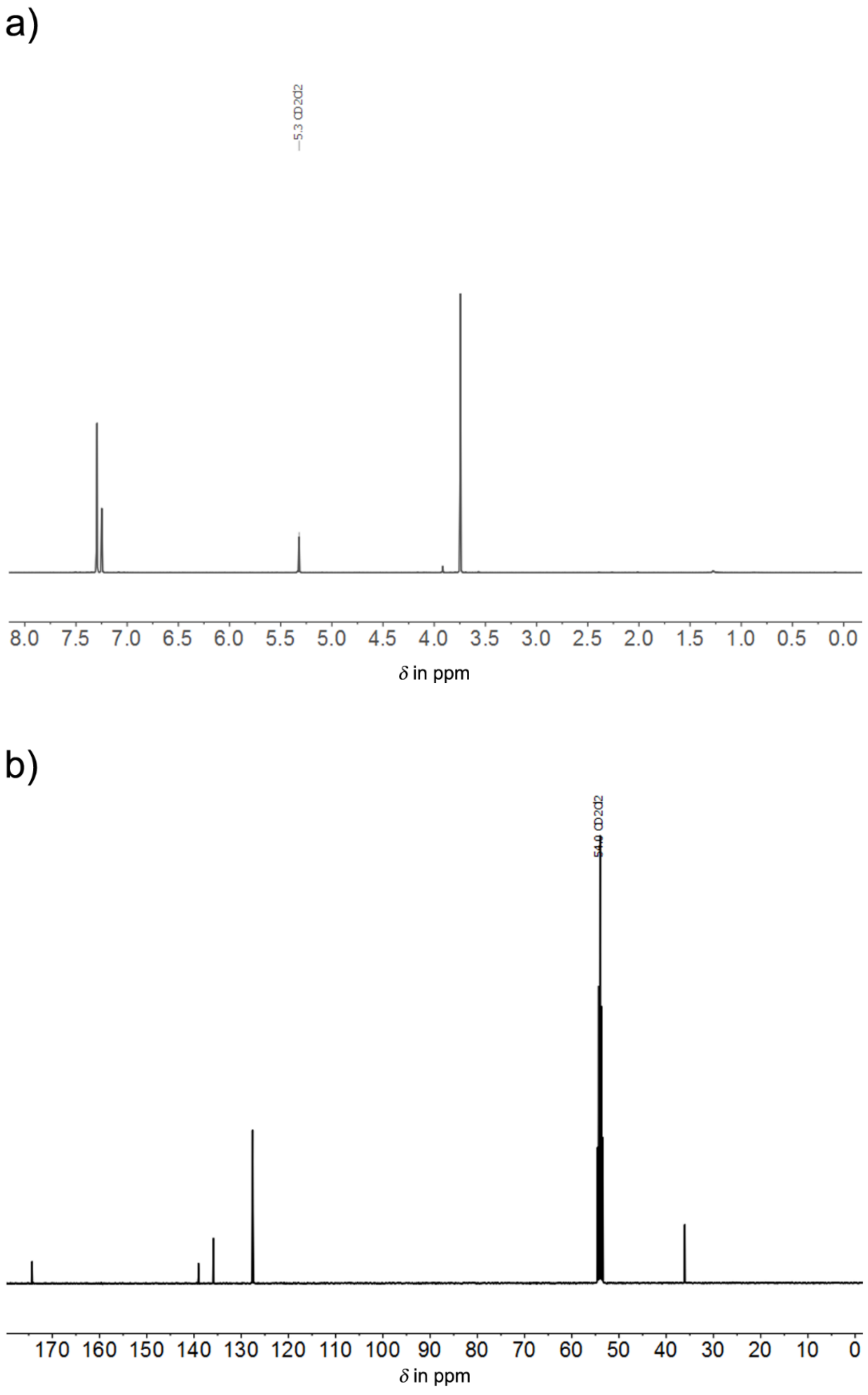
Supplementary Figure 21 Irradiation of **C-1** in CH_2Cl_2 solution with 385 nm light at 23 °C for 3 s, 20 s, 40 s and 80 s.

Supplementary table 2 gives an overview over the isomer yields of **1** obtained after irradiation to the photostationary state at different wavelengths at 23 °C.

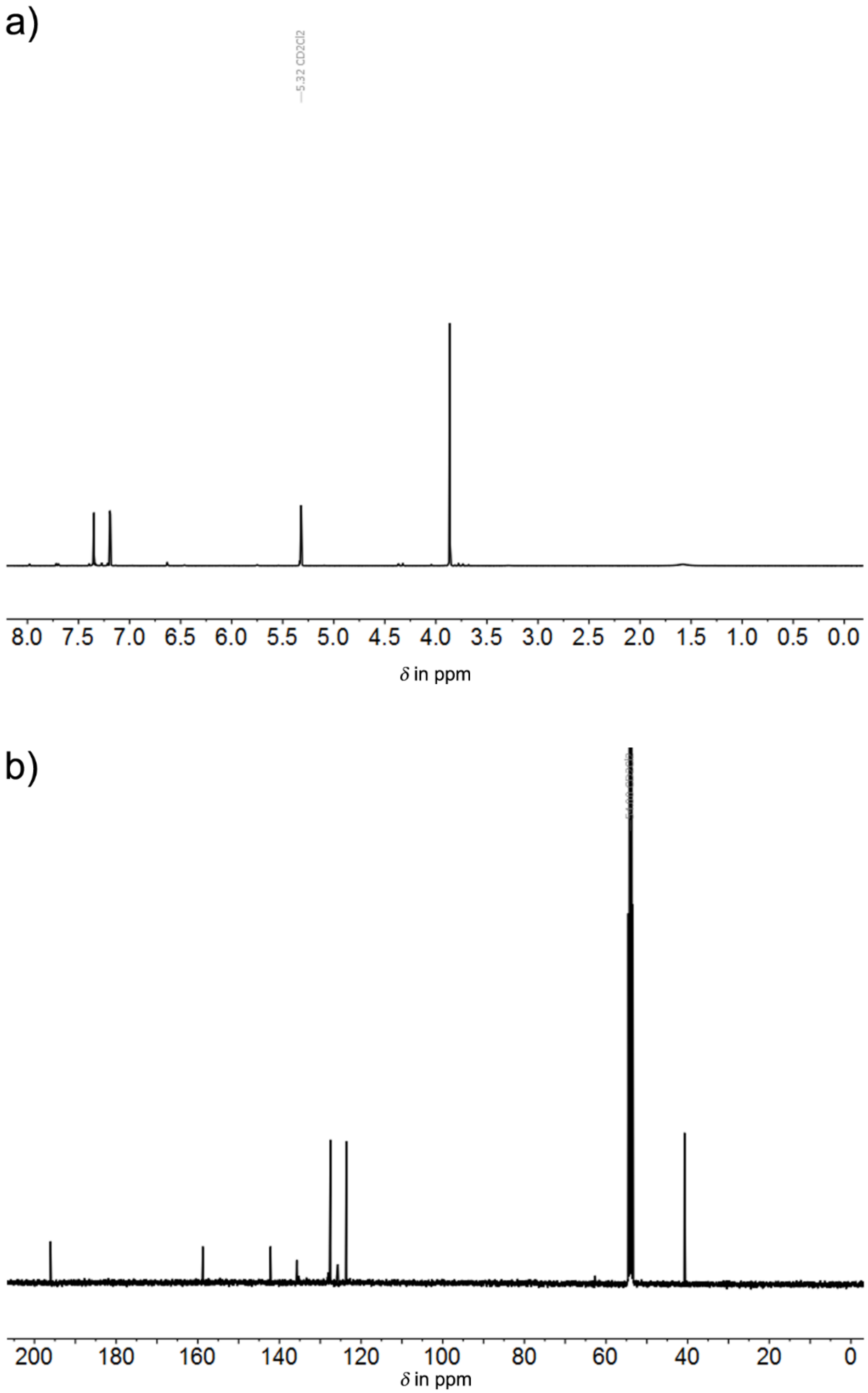
Supplementary table 2 Isomer yields of motor **1** obtained in the photostationary state at different wavelengths in CD_2Cl_2 at 23 °C. Isomeric yields were determined using ^1H NMR spectroscopy.

wavelength in nm	% of **A** isomer	% of **C** isomer
365	74	26
385	**81**	**19**
405	**81**	**19**
420	78	22
435	69	31
450	64	36
470	41	59
490	18	82
505	16	84
515	**13**	**87**

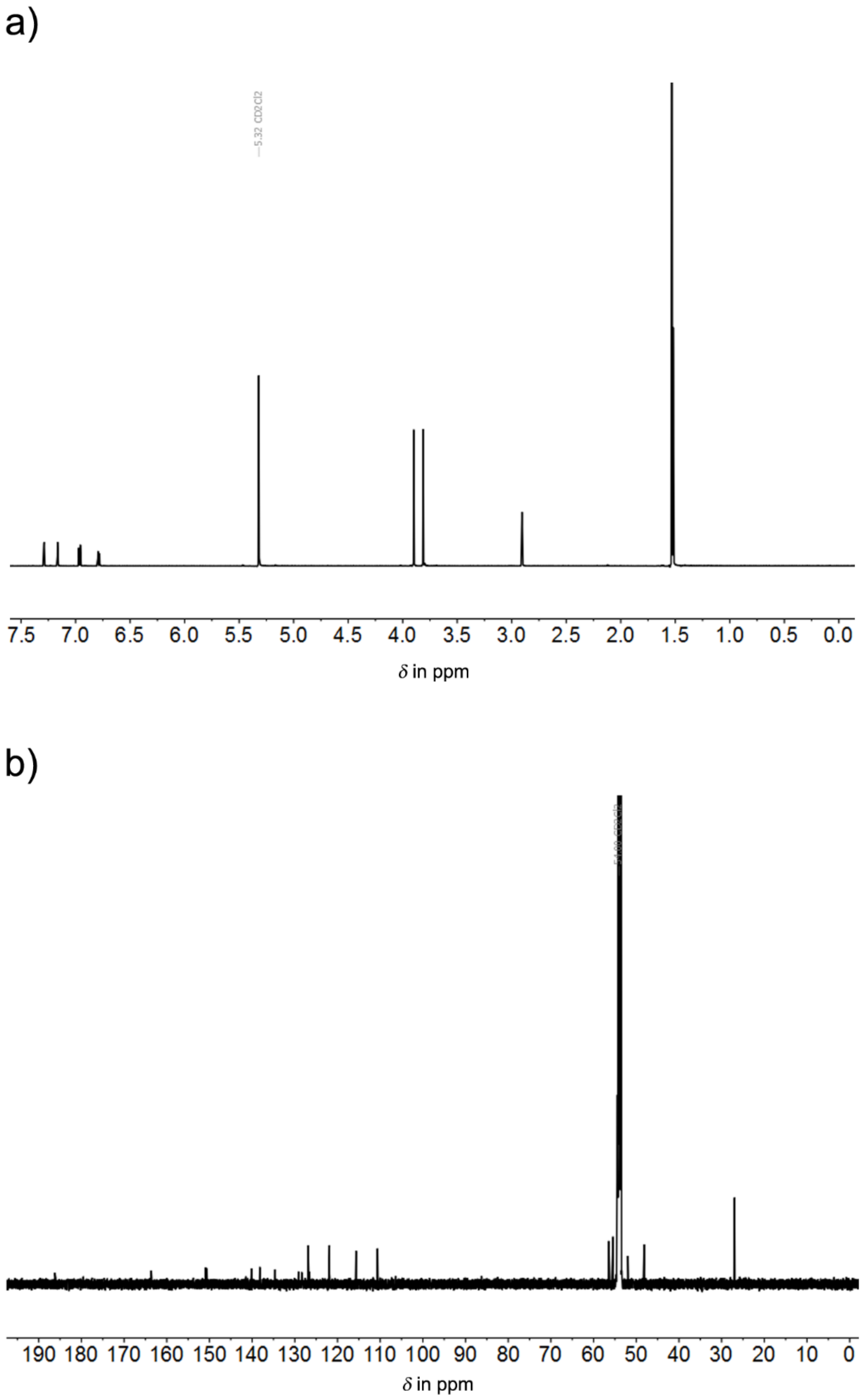
NMR Spectra of synthetic intermediates



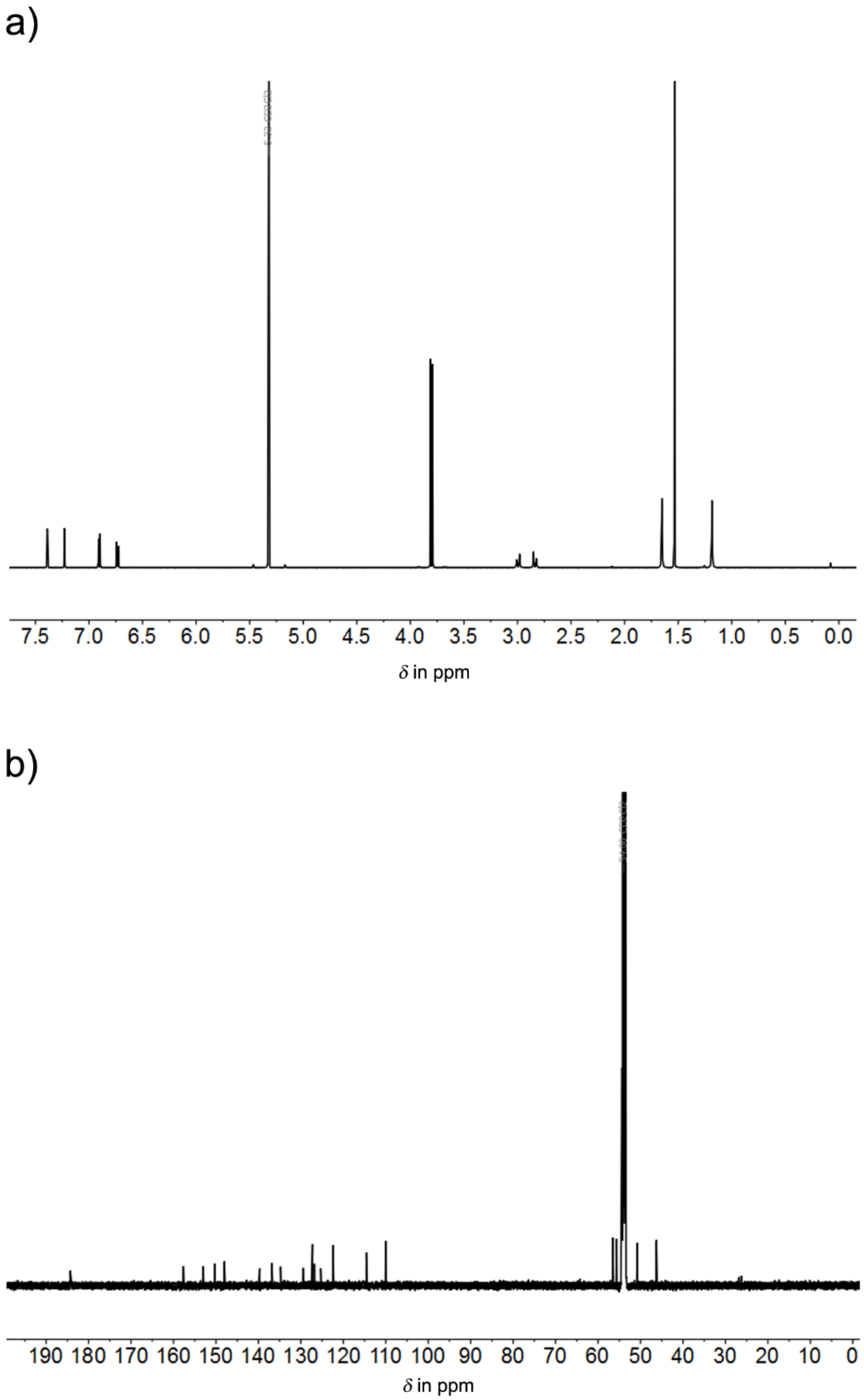
Supplementary Figure 22 NMR spectra of compound **3** (CD_2Cl_2, 400 MHz, 27 °C). a) ^{1}H NMR spectrum. b) ^{13}C NMR spectrum.



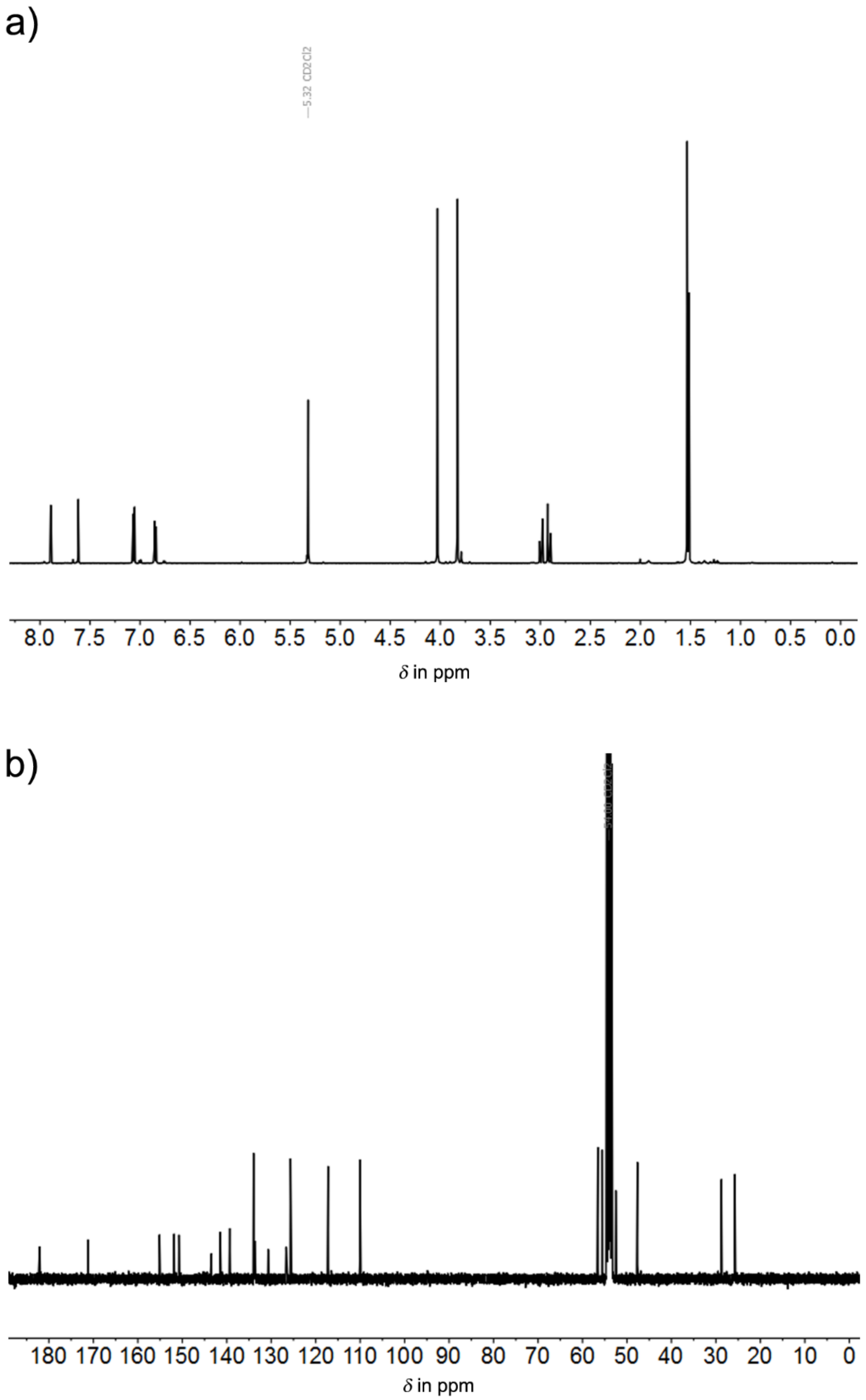
Supplementary Figure 23 NMR spectra of compound **4** (CD_2Cl_2, 400 MHz, 27 °C). a) ^1H NMR spectrum. b) ^{13}C NMR spectrum.



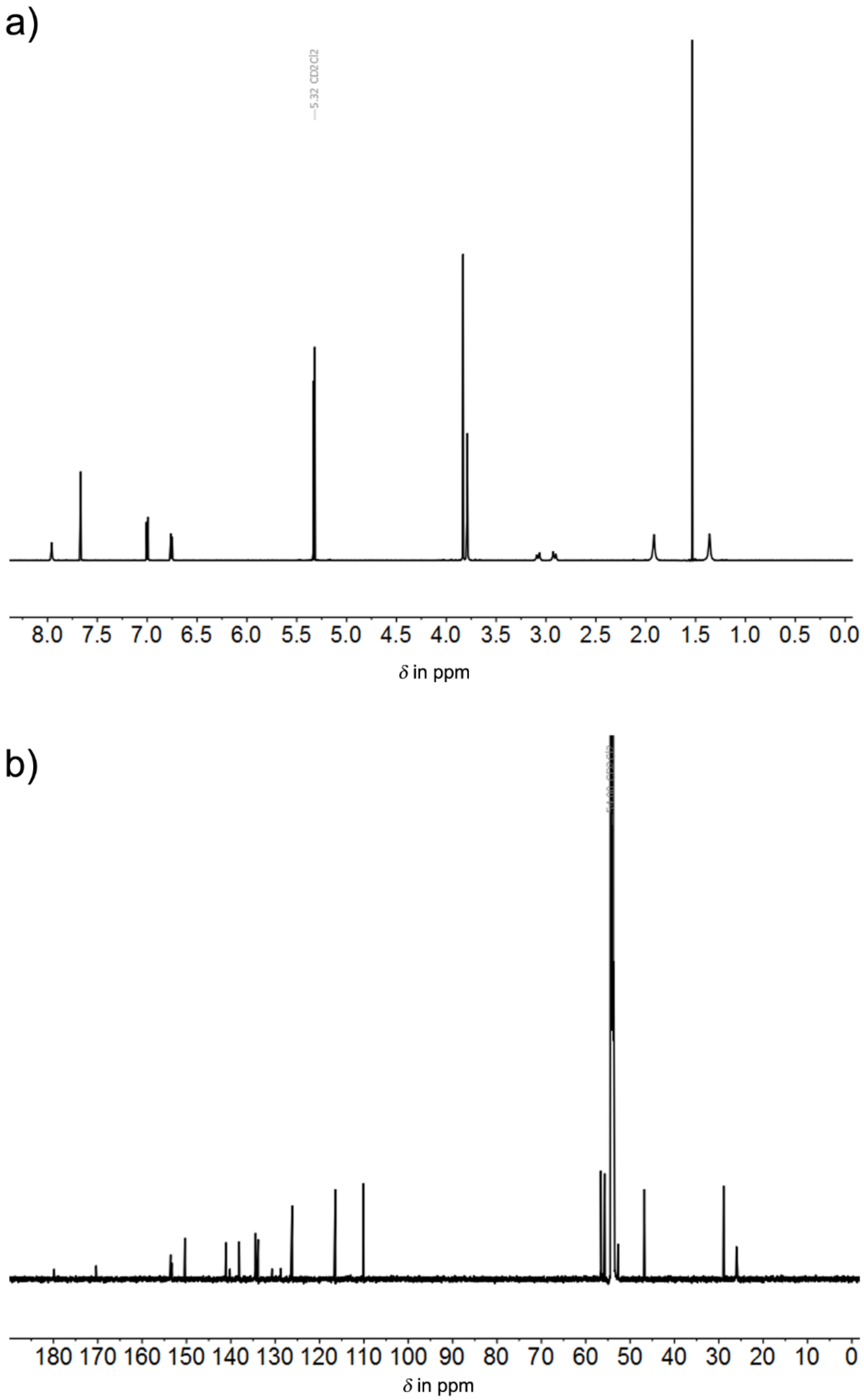
Supplementary Figure 24 NMR spectra of compound **Z-6** (CD_2Cl_2, 600 MHz, 30 °C). a) ^1H NMR spectrum. b) ^{13}C NMR spectrum.



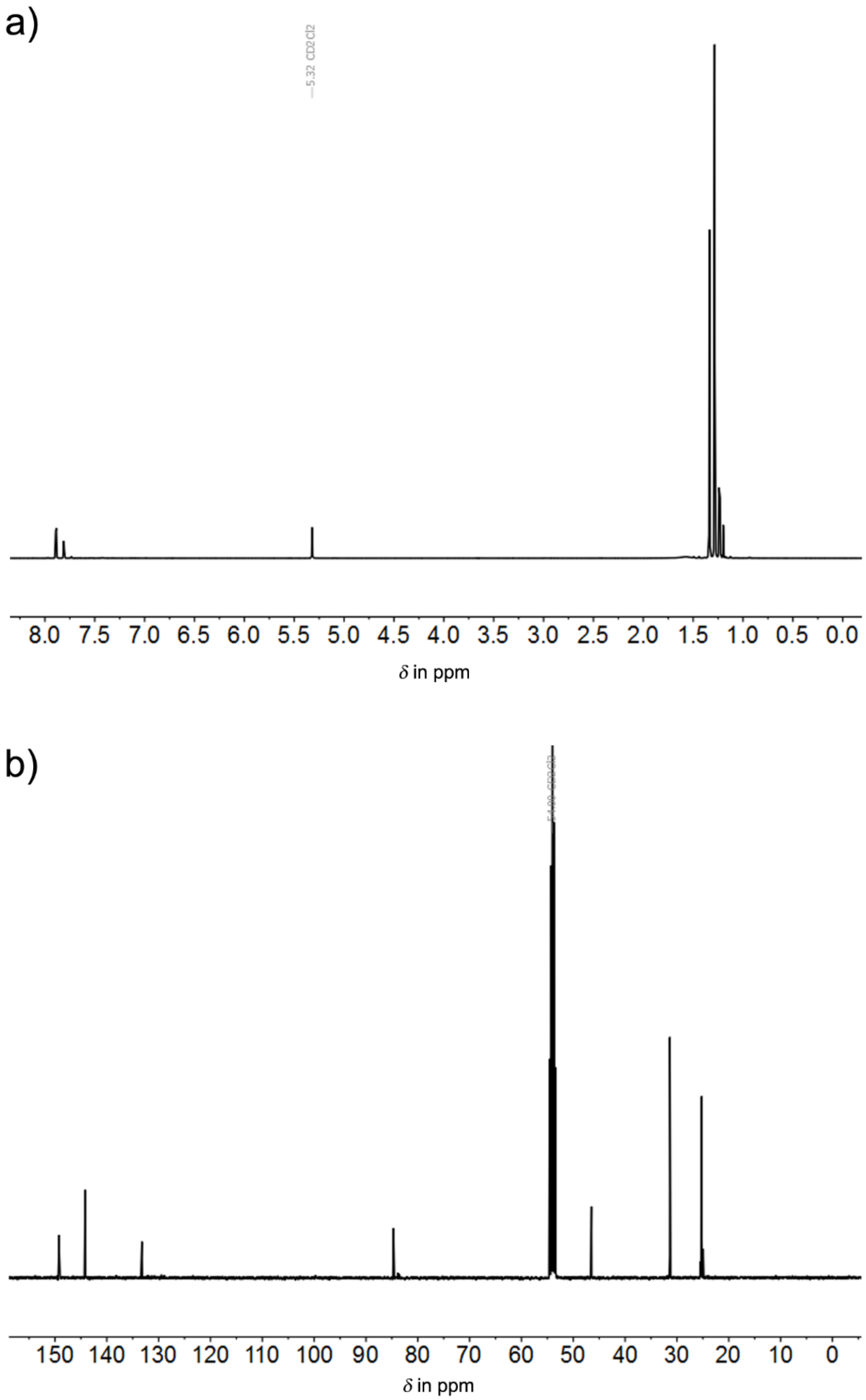
Supplementary Figure 25 NMR spectra of compound ***E*-6** (CD_2Cl_2, 600 MHz, 27 °C). a) ^{1}H NMR spectrum. b) ^{13}C NMR spectrum.



Supplementary Figure 26 NMR spectra of compound **Z-7** (CD_2Cl_2, 27 °C). a) ^1H NMR spectrum (600 MHz). b) ^{13}C NMR spectrum (400 MHz).

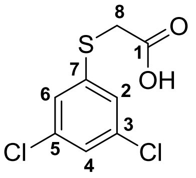


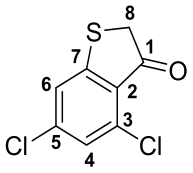
Supplementary Figure 27 NMR spectra of compound ***E*-7** (CD_2Cl_2). a) ^{1}H NMR spectrum (600 MHz, 27 °C). b) ^{13}C NMR spectrum (200 MHz, 30 °C).



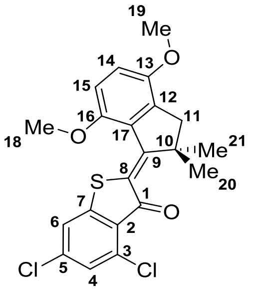
Supplementary Figure 28 NMR spectra of compound **8** (CD_2Cl_2, 400 MHz, 27 °C). a) ^1H NMR spectrum. b) ^{13}C NMR spectrum.

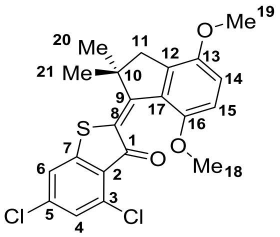
Crystal Structural Data



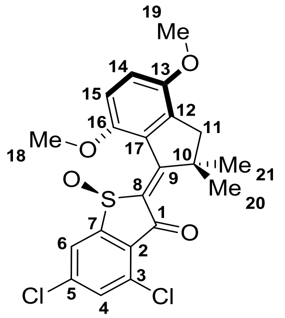


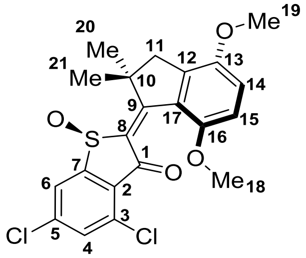
Compound	**3 (CCDC 1869283)**	**4 (CCDC 1873825)**
net formula	$C_8H_6Cl_2O_2S$	$C_8H_4Cl_2OS$
M_r/g mol^{-1}	237.09	219.07
crystal size/mm	0.264 × 0.247 × 0.068	0.100 × 0.010 × 0.010
T/K	143(2)	107.(2)
radiation	MoKα	MoKα
diffractometer	'Oxford XCalibur'	'Bruker D8 Venture TXS'
crystal system	triclinic	monoclinic
space group	'P -1'	'P 1 21/c 1'
a/Å	4.9268(4)	26.058(2)
b/Å	7.7000(7)	3.9096(4)
c/Å	12.5316(10)	16.8317(18)
α/°	89.531(7)	90
β/°	82.298(7)	108.831(6)
γ/°	77.518(7)	90
V/Å^3	459.87(7)	1623.0(3)
Z	2	8
calc. density/g cm^{-3}	1.712	1.793
μ/mm^{-1}	0.891	0.993
absorption correction	multi-scan	multi-Scan
transmission factor range	0.94560–1.00000	0.87–0.99
refls. measured	2551	9503
R_{int}	0.0205	0.0773
mean σ(I)/I	0.0493	0.0949
θ range	4.212–26.356	2.393–25.026
observed refls.	1555	2136
x, y (weighting scheme)	0.0300, 0.0147	0.0480,
hydrogen refinement	H(C) constr, H(O) restr	constr
refls in refinement	1853	2831
parameters	122	218
restraints	1	0
$R(F_{obs})$	0.0361	0.0550
$R_w(F^2)$	0.0828	0.1099
S	1.069	1.029
shift/error$_{max}$	0.001	0.001
max electron density/e Å^{-3}	0.326	0.528
min electron density/e Å^{-3}	−0.288	−0.602



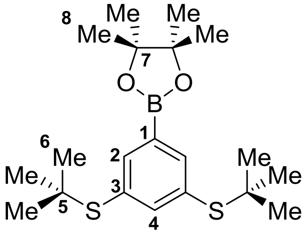


Compound	***Z*-6 (CCDC 1869284)**	***E*-6 (CCDC 1869285)**
net formula	$C_{21}H_{18}Cl_2O_3S$	$C_{21}H_{18}Cl_2O_3S$
M_r/g mol^{-1}	421.31	421.31
crystal size/mm	0.100 × 0.060 × 0.010	0.090 × 0.080 × 0.020
T/K	123.(2)	106.(2)
radiation	MoKα	MoKα
diffractometer	'Bruker D8 Venture TXS'	'Bruker D8 Venture TXS'
crystal system	monoclinic	orthorhombic
space group	'P 1 21/n 1'	'P c a 21'
a/Å	12.7042(13)	16.0174(11)
b/Å	7.6415(7)	15.9817(10)
c/Å	19.807(2)	7.3482(6)
α/°	90	90
β/°	102.369(4)	90
γ/°	90	90
V/Å^3	1878.2(3)	1881.0(2)
Z	4	4
calc. density/g cm^{-3}	1.490	1.488
μ/mm^{-1}	0.477	0.476
absorption correction	Multi-Scan	Multi-Scan
transmission factor range	0.8585–0.9705	0.86–0.99
refls. measured	3318	8980
R_{int}	0.0593	0.0328
mean σ(I)/I	0.0542	0.0377
θ range	3.189–25.339	3.306–26.372
observed refls.	2804	2871
x, y (weighting scheme)	0.0326, 1.0426	0.0160, 2.1696
hydrogen refinement	constr	constr
Flack parameter	3318	0.07(4)
refls in refinement	249	3025
parameters	0	248
restraints	0.0417	1
$R(F_{obs})$	0.0928	0.0374
$R_w(F^2)$	1.152	0.0829
S	0.001	1.156
shift/error$_{max}$	0.320	0.001
max electron density/e Å^{-3}	−0.345	0.340
min electron density/e Å^{-3}	$C_{21}H_{18}Cl_2O_3S$	−0.270





Compound	**C-1 (CCDC 1869286)**	**A-1 (CCDC 1869287)**
net formula	$C_{21}H_{18}Cl_2O_4S$	$C_{21}H_{18}Cl_2O_4S$
M_r/g mol^{-1}	437.31	437.31
crystal size/mm	0.100 × 0.020 × 0.020	0.100 × 0.050 × 0.040
T/K	293.(2)	103.(2)
radiation	MoKα	MoKα
diffractometer	'Bruker D8 Venture TXS'	'Bruker D8 Venture TXS'
crystal system	monoclinic	monoclinic
space group	'P 1 21/n 1'	'P 1 21/c 1'
a/Å	9.3294(2)	12.7347(14)
b/Å	21.9444(6)	14.3201(15)
c/Å	10.2119(3)	22.210(2)
α/°	90	90
β/°	104.3420(10)	106.007(3)
γ/°	90	90
V/Å^3	2025.51(9)	3893.2(7)
Z	4	8
calc. density/g cm^{-3}	1.434	1.492
μ/mm^{-1}	0.448	0.467
absorption correction	Multi-Scan	Multi-Scan
transmission factor range	0.92–0.99	0.8927–0.9705
refls. measured	19899	22336
R_{int}	0.0378	0.0442
mean σ(I)/I	0.0270	0.0468
θ range	3.235–25.350	3.192–24.999
observed refls.	2832	5757
x, y (weighting scheme)	0.0406, 1.2983	0.0359, 2.0380
hydrogen refinement	constr	constr
refls in refinement	3697	6798
parameters	257	513
restraints	0	0
$R(F_{obs})$	0.0429	0.0339
$R_w(F^2)$	0.1068	0.0932
S	1.037	1.076
shift/error$_{max}$	0.001	0.001
max electron density/e Å^{-3}	0.478	0.243
min electron density/e Å^{-3}	−0.451	−0.402



Compound	**8 (CCDC 1869288)**
net formula	$C_{20}H_{33}BO_2S_2$
M_r/g mol^{-1}	380.39
crystal size/mm	0.090 × 0.070 × 0.050
T/K	103.(2)
radiation	MoKα
diffractometer	'Bruker D8 Venture TXS'
crystal system	monoclinic
space group	'C 1 2/c 1'
a/Å	19.3829(7)
b/Å	11.6584(4)
c/Å	12.0827(4)
α/°	90
β/°	127.8800(10)
γ/°	90
V/Å^3	2155.08(13)
Z	4
calc. density/g cm^{-3}	1.172
μ/mm^{-1}	0.257
absorption correction	Multi-Scan
transmission factor range	0.8971–0.9705
refls. measured	14630
R_{int}	0.0307
mean σ(I)/I	0.0204
θ range	3.495–27.103
observed refls.	2110
x, y (weighting scheme)	0.0257, 2.2115
hydrogen refinement	constr
refls in refinement	2368
parameters	120
restraints	0
R(F$_{obs}$)	0.0282
R_w(F^2)	0.0719
S	1.079
shift/error$_{max}$	0.001
max electron density/e Å^{-3}	0.317
min electron density/e Å^{-3}	−0.223

Theoretically Obtained Geometries

(*R*)-**B-1**				(*R*)-**C-1**				(*R*)-**B-1** to (*R*)-**C-1** TS			
S	0.8273	-2.6712	-1.2015	S	-1.4437	-2.643	-1.1015	S	-1.1975	-2.8714	0.0302
O	0.5854	-2.5497	-2.6906	O	-1.2709	-3.8232	-0.1771	O	-1.1888	-3.4878	1.4158
O	2.9075	0.5634	-0.7724	O	-2.8481	0.9378	-0.5866	O	-2.6773	0.7442	0.422
O	2.6222	-4.3823	-2.2081	O	-3.6064	-3.9146	-2.0871	O	-2.6958	-4.8413	-0.6319
O	6.2568	-5.6092	1.7808	O	-7.0382	-4.5706	2.2161	O	-8.1312	-3.8956	-0.8625
C	-0.1233	-1.266	-0.5148	C	-0.1787	-1.4035	-0.7088	C	0.0072	-1.5221	0.0809
C	-1.4785	-1.3322	-0.262	C	1.1642	-1.7145	-0.609	C	1.371	-1.7524	0.0504
H	-2.0166	-2.2662	-0.3737	H	1.4952	-2.743	-0.6867	H	1.7582	-2.7613	-0.0312
C	-2.151	-0.158	0.114	C	2.0756	-0.6695	-0.4061	C	2.2378	-0.6528	0.0896
C	-1.4227	1.0394	0.1796	C	1.5882	0.6478	-0.3521	C	1.6815	0.6361	0.1685
H	-1.9336	1.9491	0.472	H	2.2905	1.4593	-0.2034	H	2.3442	1.4914	0.2237
C	-0.055	1.1173	-0.1119	C	0.2315	0.9663	-0.4662	C	0.3051	0.8676	0.2232
C	0.6052	-0.0788	-0.4486	C	-0.6756	-0.1039	-0.6193	C	-0.5454	-0.2553	0.1764
C	2.0675	-0.3086	-0.641	C	-2.163	-0.073	-0.5472	C	-2.0348	-0.2658	0.1926
C	2.3523	-1.773	-0.651	C	-2.7054	-1.4542	-0.4596	C	-2.5831	-1.6381	-0.0971
C	3.4568	-2.3965	-0.1586	C	-3.8865	-1.8607	0.0792	C	-3.8942	-1.9769	-0.3419
C	3.8253	-3.8198	-0.2698	C	-4.5164	-3.1836	-0.029	C	-4.5266	-3.312	-0.5444
C	3.4643	-4.7886	-1.2359	C	-4.3979	-4.1866	-1.0186	C	-4.03	-4.6481	-0.5697
C	4.0271	-6.0587	-1.1545	C	-5.138	-5.3556	-0.8751	C	-4.9248	-5.7141	-0.589
H	3.768	-6.8155	-1.8822	H	-5.0567	-6.1468	-1.6072	H	-4.5479	-6.7267	-0.5746
C	4.948	-6.3776	-0.1488	C	-6.0157	-5.5299	0.2012	C	-6.3053	-5.5189	-0.6596
H	5.3582	-7.3785	-0.1231	H	-6.5693	-6.4568	0.2701	H	-6.956	-6.383	-0.6786
C	5.3434	-5.4179	0.7806	C	-6.1868	-4.5211	1.147	C	-6.8103	-4.2276	-0.7369
C	4.7853	-4.1413	0.6933	C	-5.4398	-3.3515	1.0081	C	-5.9169	-3.1566	-0.681
C	5.1174	-2.951	1.5313	C	-5.4887	-2.1398	1.8798	C	-6.3172	-1.733	-0.7846
H	6.19	-2.8579	1.7179	H	-4.9522	-2.3234	2.8177	H	-7.1851	-1.4991	-0.1641
H	4.6307	-3.0232	2.511	H	-6.51	-1.8584	2.1484	H	-6.6103	-1.5113	-1.8172
C	4.551	-1.7362	0.7306	C	-4.7682	-1.0296	1.0517	C	-5.0631	-0.9268	-0.3633
C	2.2261	-5.2674	-3.2496	C	-3.3037	-4.9573	-3.0079	C	-2.1395	-6.1147	-0.3168
H	1.5323	-4.6849	-3.8509	H	-2.5884	-4.5299	-3.7083	H	-1.0633	-5.9601	-0.2837
H	1.7205	-6.1514	-2.8464	H	-4.1987	-5.2754	-3.5524	H	-2.3817	-6.8513	-1.0895
H	3.0892	-5.5761	-3.8486	H	-2.8501	-5.8106	-2.496	H	-2.4841	-6.4591	0.6612
C	6.8794	-6.881	1.8849	C	-7.8252	-5.7392	2.3918	C	-9.0832	-4.9484	-0.9021
H	7.5648	-6.8099	2.7278	H	-8.4205	-5.5665	3.2869	H	10.0554	-4.4684	-0.9996
H	7.4448	-7.1275	0.9788	H	-7.1992	-6.6264	2.5407	H	-9.0645	-5.5419	0.0192
H	6.1468	-7.6722	2.0819	H	-8.4943	-5.9058	1.5396	H	-8.918	-5.6075	-1.7622
C	4.0726	-0.6665	1.7252	C	-5.8127	-0.2383	0.2312	C	-4.8785	0.2127	-1.386
H	4.8632	-0.4984	2.4629	H	-6.4852	0.2946	0.9104	H	-5.8175	0.7715	-1.4534
H	3.1818	-0.9984	2.2664	H	-6.416	-0.9056	-0.39	H	-4.6697	-0.1988	-2.3781
H	3.8585	0.285	1.2462	H	-5.3152	0.4882	-0.4108	H	-4.0936	0.9098	-1.1168

C	5.6567	-1.1618	-0.1847	C	-4.0186	-0.0924	2.0106	C	-5.3239	-0.4102	1.0729
H	6.4689	-0.7592	0.4283	H	-4.7054	0.2206	2.8031	H	-6.1695	0.2843	1.0531
H	5.2536	-0.3605	-0.8036	H	-3.6519	0.8021	1.5139	H	-4.4662	0.1085	1.4868
H	6.0734	-1.9347	-0.8359	H	-3.1768	-0.6054	2.4841	H	-5.5892	-1.2436	1.73
C	0.6116	2.4494	-0.0391	C	-0.1692	2.4001	-0.3953	C	-0.1668	2.2821	0.3294
C	1.1734	3.0308	-1.1805	C	-0.8291	3.0157	-1.4642	C	-0.0679	3.1312	-0.7749
C	0.5972	3.1721	1.1577	C	0.1982	3.1715	0.7118	C	-0.617	2.7963	1.5484
C	1.7219	4.3136	-1.1298	C	-1.1243	4.3796	-1.43	C	-0.4372	4.4776	-0.6773
H	1.1578	2.4943	-2.1196	H	-1.089	2.4374	-2.3404	H	0.306	2.7503	-1.7173
C	1.1561	4.4525	1.2275	C	-0.1032	4.5361	0.767	C	-0.9807	4.1394	1.6636
H	0.1467	2.7416	2.0438	H	0.7234	2.7114	1.5397	H	-0.6673	2.1537	2.4177
C	1.7076	5.023	0.0772	C	-0.755	5.1381	-0.3125	C	-0.884	4.9794	0.5476
H	2.1076	6.0277	0.1127	H	-0.9581	6.2007	-0.2952	H	-1.137	6.0272	0.6411
C	-3.604	-0.1821	0.4166	C	3.5272	-0.9459	-0.2623	C	3.7099	-0.841	0.0507
C	-4.4375	0.8736	0.0238	C	4.4815	-0.0956	-0.837	C	4.526	0.0373	-0.6748
C	-4.1687	-1.259	1.1134	C	3.9695	-2.0674	0.4528	C	4.3113	-1.9032	0.7398
C	-5.8049	0.8565	0.3092	C	5.8482	-0.3461	-0.6924	C	5.9128	-0.128	-0.7053
H	-4.0252	1.7172	-0.5148	H	4.1646	0.7565	-1.4249	H	4.0821	0.8449	-1.2429
C	-5.5339	-1.2902	1.4082	C	5.3324	-2.3436	0.5859	C	5.6944	-2.0955	0.6987
H	-3.5373	-2.0631	1.4696	H	3.2519	-2.72	0.9339	H	3.7054	-2.5727	1.3375
C	-6.3486	-0.2242	1.012	C	6.2701	-1.4758	0.0164	C	6.4934	-1.2006	-0.0206
H	-7.3993	-0.2245	1.2697	H	7.327	-1.6793	0.1247	H	7.5661	-1.3381	-0.0467
S	1.0511	5.399	2.7507	S	0.4539	5.5245	2.1597	S	-1.4561	4.8193	3.2571
S	2.3224	5.1157	-2.6211	S	-1.8516	5.1969	-2.8553	S	-0.2186	5.575	-2.0826
S	-6.2086	-2.6206	2.4106	S	7.0511	0.7156	-1.5007	S	6.9316	0.9663	-1.7013
S	-6.8319	2.2688	-0.1141	S	5.8772	-3.7431	1.572	S	6.4508	-3.4171	1.652
C	-7.4477	1.908	-1.8646	C	7.4562	2.036	-0.2082	C	7.4124	2.3643	-0.5211
C	-6.7346	-3.9398	1.1638	C	6.0187	-5.1642	0.3324	C	6.5225	-4.8785	0.4548
C	-6.2743	1.8038	-2.8425	C	6.2021	2.8315	0.1631	C	6.1676	3.1015	-0.0208
H	-5.6238	0.96	-2.603	H	5.4535	2.1982	0.644	H	5.5282	2.4483	0.577
H	-6.6547	1.6499	-3.8585	H	6.4655	3.626	0.87	H	6.4681	3.9413	0.6155
H	-5.6731	2.7154	-2.8387	H	5.7512	3.2948	-0.7171	H	5.5799	3.4972	-0.8518
C	-8.2918	0.6311	-1.885	C	8.0869	1.3985	1.0328	C	8.2339	1.8203	0.6508
H	-8.6845	0.4642	-2.8942	H	8.362	2.1812	1.7486	H	8.5473	2.6487	1.296
H	-7.6987	-0.2444	-1.6121	H	7.3924	0.7215	1.5346	H	7.6525	1.1273	1.2625
H	-9.1364	0.7037	-1.1967	H	8.9887	0.8391	0.7754	H	9.1296	1.3032	0.3002
C	-8.3144	3.1321	-2.1923	C	8.4711	2.9348	-0.9283	C	8.2693	3.2875	-1.3987
H	-8.7287	3.0244	-3.1996	H	8.7799	3.743	-0.258	H	8.6087	4.1412	-0.8039
H	-9.1476	3.2305	-1.4923	H	9.3644	2.376	-1.2179	H	9.1522	2.769	-1.7804
H	-7.7291	4.0543	-2.1644	H	8.0395	3.3857	-1.8252	H	7.6999	3.6723	-2.2482
C	-5.5302	-4.4393	0.3612	C	4.663	-5.4507	-0.3187	C	5.1142	-5.2794	0.0072
H	-4.7539	-4.8364	1.0188	H	4.7525	-6.3112	-0.9911	H	5.171	-6.1609	-0.6413
H	-5.8455	-5.2392	-0.318	H	3.9029	-5.6809	0.4307	H	4.4816	-5.5248	0.8629
H	-5.0957	-3.6428	-0.2468	H	4.3173	-4.6024	-0.9134	H	4.6332	-4.4811	-0.5623

C	-7.8235	-3.3982	0.2339	C	7.0791	-4.8513	-0.7268	C	7.4052	-4.5458	-0.7513
H	-8.155	-4.1897	-0.4475	H	8.0512	-4.6575	-0.2685	H	8.4143	-4.2694	-0.4387
H	-8.6897	-3.0492	0.7999	H	7.1846	-5.7052	-1.4054	H	7.4776	-5.4207	-1.4072
H	-7.4539	-2.5707	-0.3753	H	6.8026	-3.9832	-1.3289	H	6.9898	-3.7252	-1.3399
C	-7.293	-5.0617	2.0506	C	6.4593	-6.3493	1.2032	C	7.1578	-5.994	1.2966
H	-7.6348	-5.888	1.4195	H	5.7179	-6.5763	1.973	H	6.546	-6.2329	2.1699
H	-6.5313	-5.4486	2.7318	H	6.5783	-7.2373	0.5746	H	7.2505	-6.8998	0.6892
H	-8.1427	-4.7155	2.644	H	7.4161	-6.151	1.6924	H	8.1565	-5.7144	1.6408
C	4.0933	4.4881	-2.8311	C	-3.7136	4.9252	-2.6723	C	-1.8537	5.4734	-3.0246
C	4.1056	2.9898	-3.1477	C	-0.979	5.4643	3.3906	C	-3.3102	4.4741	3.3847
H	5.1364	2.6647	-3.3318	C	-4.0643	3.4437	-2.8371	C	-2.1254	4.0393	-3.4869
H	3.7159	2.3936	-2.3212	H	-3.6283	2.8292	-2.048	H	-2.2511	3.3617	-2.6399
H	3.5174	2.7719	-4.0419	H	-5.1526	3.3192	-2.7902	H	-3.0499	4.0112	-4.0747
C	4.9197	4.7883	-1.5782	H	-3.722	3.0649	-3.803	H	-1.3122	3.6647	-4.1125
H	4.9192	5.856	-1.3478	C	-4.3048	5.7514	-3.8232	C	-1.6271	6.3951	-4.2311
H	4.5375	4.2454	-0.7113	H	-3.9361	5.406	-4.7925	H	-0.7992	6.0435	-4.8516
H	5.9566	4.4717	-1.7376	H	-5.3945	5.6477	-3.8215	H	-2.5301	6.4143	-4.8494
C	4.6131	5.2968	-4.028	H	-4.0636	6.8121	-3.7203	H	-1.4114	7.419	-3.9159
H	5.6417	4.9951	-4.25	C	-4.2029	5.4551	-1.3223	C	-3.0043	5.9943	-2.1593
H	4.0103	5.1177	-4.922	H	-3.7625	4.8973	-0.4934	H	-3.1493	5.3742	-1.2724
H	4.6104	6.3692	-3.8187	H	-3.9593	6.5126	-1.1982	H	-2.8223	7.0214	-1.8358
C	2.6423	4.9836	3.6811	H	-5.291	5.3434	-1.2566	H	-3.9371	5.9755	-2.7343
C	2.7187	3.484	3.9807	C	-1.2682	4.0219	3.8149	C	-3.5831	2.9675	3.3853
H	3.6209	3.2706	4.565	H	-0.3836	3.553	4.2515	H	-3.0536	2.4714	4.2017
H	1.8525	3.1514	4.5569	H	-2.0662	4.0122	4.5659	H	-4.6566	2.7908	3.5191
H	2.7709	2.8938	3.0633	H	-1.6004	3.4141	2.9708	H	-3.2865	2.5007	2.4442
C	3.8668	5.4443	2.8859	C	-2.2277	6.1186	2.7934	C	-4.0623	5.1638	2.2435
H	3.824	6.5158	2.6799	H	-3.0346	6.1198	3.5351	H	-5.1396	5.0004	2.3605
H	4.778	5.2414	3.4601	H	-2.0308	7.152	2.5005	H	-3.8776	6.2403	2.2399
H	3.9494	4.914	1.9351	H	-2.5845	5.5741	1.9168	H	-3.7696	4.7587	1.2728
C	2.5128	5.7868	4.9829	C	-0.4596	6.2827	4.581	C	-3.6936	5.0937	4.7358
H	1.6344	5.4794	5.5557	H	-1.2269	6.3184	5.3608	H	-4.7636	4.9455	4.9128
H	3.3985	5.6193	5.6039	H	0.4397	5.8349	5.011	H	-3.1476	4.6252	5.5584
H	2.437	6.8587	4.7843	H	-0.2275	7.3097	4.2882	H	-3.4923	6.1677	4.7552

(*S*)-**D-1**				(*S*)-**A-1**				(*S*)-**D-1** to (*S*)-**A-1** TS			
S	-0.7757	-3.3233	-0.9524	S	0.7857	-3.2665	-1.0277	C	0.4254	-1.5688	-1.1143
O	-0.5713	-3.4319	-2.4483	O	0.437	-4.396	-0.0832	O	-2.6038	-0.1083	-1.9169
O	-2.946	-0.1191	-0.7175	O	2.9595	-0.0851	-0.6614	O	-4.8569	-1.0449	-1.3083
O	-3.6618	-0.8237	1.774	O	3.6875	-0.879	1.8057	C	1.789	-1.4318	-0.932
O	-8.0486	-3.8656	0.2741	O	8.0814	-3.7689	0.0409	C	0.0033	0.7444	-0.5719
C	0.1473	-1.8326	-0.433	C	-0.1519	-1.7883	-0.5567	C	1.3814	0.8779	-0.3604
C	1.5161	-1.8392	-0.2489	C	-1.5214	-1.8086	-0.37	C	2.2865	-0.1809	-0.5359
H	2.0831	-2.7576	-0.346	H	-2.075	-2.7354	-0.4592	C	-0.4701	-0.5197	-0.959
C	2.1608	-0.6255	0.0353	C	-2.1669	-0.6034	-0.0643	C	-1.8671	-0.899	-1.3883
C	1.3886	0.5447	0.092	C	-1.3994	0.5719	0.0078	C	-2.0039	-2.3997	-1.1555
H	1.8778	1.4837	0.3221	H	-1.8958	1.5054	0.2449	C	-2.9007	-3.2226	-0.5426
C	0.0059	0.5584	-0.1289	C	-0.0162	0.5945	-0.1957	C	-2.5322	-4.6848	-0.092
C	-0.6235	-0.6735	-0.3845	C	0.6224	-0.6347	-0.4603	C	-6.929	-3.126	0.9115
C	-2.0842	-0.9553	-0.5431	C	2.0853	-0.9208	-0.5357	C	-6.0293	-4.1417	1.2102
C	-2.3181	-2.4275	-0.5203	C	2.3186	-2.3923	-0.5223	C	-4.7406	-4.0688	0.6775
C	-3.4754	-3.0769	-0.227	C	3.484	-3.0468	-0.28	C	-3.6796	-5.0914	0.8737
C	-4.6595	-2.5124	0.4373	C	4.6755	-2.4925	0.3767	C	-5.2554	-2.0002	-0.4573
C	-4.7892	-1.446	1.361	C	4.8129	-1.4673	1.3434	C	-6.5405	-2.0738	0.0765
C	-6.0622	-1.15	1.8459	C	6.0944	-1.1754	1.809	C	-2.5467	-5.6245	-1.3178
H	-6.2048	-0.3295	2.535	H	6.2438	-0.3875	2.5338	C	-4.3084	-3.0048	-0.1229
C	-7.178	-1.9126	1.4828	C	7.2108	-1.9007	1.3777	C	-5.7244	0.0248	-1.6481
H	-8.1429	-1.6395	1.8894	H	8.1823	-1.6325	1.7717	C	-1.2109	-4.8196	0.6965
C	-7.04	-3.0197	0.6481	C	7.0682	-2.9649	0.4888	H	-7.9384	-3.1366	1.301
C	-5.7705	-3.3158	0.154	C	5.7904	-3.2586	0.0159	H	-7.2658	-1.3092	-0.164
C	-5.3777	-4.492	-0.6819	C	5.3876	-4.3934	-0.8729	H	-5.1373	0.6646	-2.3024
H	-5.6684	-4.3422	-1.728	H	5.8997	-5.3248	-0.6203	H	-6.6126	-0.3357	-2.1794
H	-5.8542	-5.4173	-0.3484	H	5.6231	-4.1704	-1.9203	H	-6.029	0.5878	-0.7592
C	-3.8223	-4.5481	-0.5638	C	3.8414	-4.4968	-0.6782	H	-3.3373	-5.0919	1.9144
C	-3.773	0.3066	2.6315	C	3.8013	0.2051	2.7194	H	-4.048	-6.1017	0.6744
H	-2.7575	0.6674	2.779	H	2.784	0.5418	2.9069	H	-2.3596	-6.6537	-0.9963
H	-4.2065	0.0313	3.5993	H	4.379	1.0273	2.2868	H	-3.519	-5.5955	-1.8164
H	-4.3708	1.0965	2.1679	H	4.2584	-0.1145	3.6623	H	-1.7876	-5.3585	-2.0551
C	-9.3523	-3.6151	0.7769	C	9.3921	-3.5267	0.5288	H	-0.3269	-4.7396	0.0707
H	-9.9869	-4.3982	0.3654	H	10.0286	-4.2757	0.0603	H	-1.1502	-4.0647	1.4852
H	-9.7281	-2.6384	0.4508	H	9.4436	-3.6389	1.618	H	-1.187	-5.8032	1.1754
H	-9.3786	-3.6665	1.8716	H	9.7469	-2.5276	0.2504	H	1.7629	1.8464	-0.0583
C	-3.2322	-5.1107	-1.866	C	3.5266	-5.4404	0.5087	H	2.4553	-2.2751	-1.0718
H	-3.7659	-6.0319	-2.1201	H	3.8343	-6.4598	0.2567	S	-0.3828	-3.0754	-1.754
H	-2.1755	-5.3622	-1.7892	H	2.4567	-5.4354	0.7202	O	-0.3915	-2.9738	-3.2624
H	-3.3422	-4.4098	-2.6953	H	4.066	-5.1339	1.4083	O	-6.2915	-5.2379	1.9896
C	-3.4184	-5.444	0.6298	C	3.1877	-5.0329	-1.96	C	-7.5973	-5.3738	2.5284

H	-3.7204	-6.4777	0.4384
H	-3.8917	-5.1138	1.5577
H	-2.3353	-5.427	0.7713
C	-0.7122	1.8646	-0.0561
C	-1.3556	2.3989	-1.1775
C	-0.6863	2.6035	1.1308
C	-1.9783	3.6469	-1.1139
H	-1.3634	1.8469	-2.1075
C	-1.3048	3.8562	1.2094
H	-0.1945	2.1997	2.0076
C	-1.9554	4.3701	0.0848
H	-2.4447	5.3336	0.1383
C	3.6277	-0.58	0.259
C	4.396	0.4839	-0.2323
C	4.2709	-1.5956	0.9792
C	5.7757	0.5345	-0.0196
H	3.9222	1.2801	-0.792
C	5.6497	-1.559	1.2015
H	3.6919	-2.4028	1.4097
C	6.3986	-0.4854	0.7078
H	7.4604	-0.4322	0.9081
S	6.4297	-2.8065	2.2334
S	6.7216	1.9597	-0.5697
S	-1.3477	4.7434	2.7707
S	-2.7142	4.3818	-2.5788
C	-4.4768	3.6963	-2.6334
C	0.1737	5.8655	2.7256
C	-5.109	4.4507	-3.8116
H	-4.5702	4.2586	-4.743
H	-6.1416	4.113	-3.945
H	-5.1233	5.5292	-3.6366
C	-5.2153	4.015	-1.3313
H	-4.7502	3.5183	-0.4774
H	-5.2365	5.09	-1.138
H	-6.2492	3.6584	-1.4004
C	-4.4647	2.1891	-2.9024
H	-3.939	1.9606	-3.8322
H	-3.9965	1.6287	-2.0922
H	-5.4957	1.8288	-2.9987
C	0.0662	6.8715	1.5763
H	-0.8389	7.4763	1.6634
H	0.9309	7.5443	1.5938
H	0.0548	6.3726	0.6051
C	1.4535	5.0341	2.6054

H	3.717	-5.9391	-2.27
H	3.2517	-4.3123	-2.7796
H	2.1451	-5.3127	-1.8087
C	-3.6325	-0.5679	0.1708
C	-4.4117	0.4928	-0.31
C	-4.2611	-1.5902	0.8943
C	-5.7897	0.5335	-0.0841
H	-3.9483	1.2945	-0.8708
C	-5.6383	-1.5634	1.1289
H	-3.671	-2.393	1.3181
C	-6.3988	-0.4933	0.6452
H	-7.459	-0.4485	0.856
C	0.7	1.8982	-0.0871
C	1.3961	2.4322	-1.1767
C	0.6226	2.6361	1.0986
C	2.0175	3.6788	-1.0842
H	1.4462	1.8813	-2.1059
C	1.2386	3.8877	1.206
H	0.0941	2.2307	1.9529
C	1.9403	4.4016	0.1124
H	2.428	5.3643	0.1889
S	-6.7478	1.9558	-0.6206
S	-6.404	-2.8153	2.166
S	1.2125	4.7744	2.768
S	2.822	4.4124	-2.5133
C	-6.8646	-4.2087	0.9749
C	-7.3343	1.5118	-2.3619
C	4.5847	3.7263	-2.4847
C	-0.3057	5.896	2.6554
C	-0.1488	6.9007	1.5106
H	-0.0965	6.4006	0.5413
H	-1.0132	7.5739	1.4906
H	0.7521	7.5051	1.6354
C	-1.579	5.0642	2.4813
H	-1.5695	4.5121	1.5391
H	-1.7018	4.3511	3.2994
H	-2.4529	5.725	2.4691
C	-0.3147	6.6187	4.0096
H	0.5983	7.2009	4.1571
H	-1.1649	7.3069	4.0488
H	-0.4121	5.913	4.8382
C	5.2584	4.0354	-1.1456
H	6.2944	3.6789	-1.1666
H	5.2703	5.109	-0.9441

H	-7.8445	-4.5428	3.1993
H	-8.3541	-5.4379	1.738
H	-7.5919	-6.3028	3.0963
C	3.74	0.0179	-0.3036
C	4.6828	-0.5482	-1.172
C	4.1963	0.7885	0.7738
C	6.0524	-0.3582	-0.9701
H	4.3516	-1.1037	-2.0404
C	5.5622	0.9874	0.9893
H	3.4865	1.2374	1.4571
C	6.4885	0.4202	0.1075
H	7.5457	0.604	0.2452
C	-0.8877	1.9197	-0.3709
C	-1.9846	1.8528	0.495
C	-0.6184	3.1217	-1.0321
C	-2.7969	2.9683	0.7063
H	-2.2097	0.9297	1.0139
C	-1.4463	4.2353	-0.861
H	0.2238	3.1879	-1.7095
C	-2.5307	4.1569	0.0169
H	-3.1697	5.0179	0.161
S	7.2376	-0.9828	-2.1679
S	6.1143	2.0654	2.3167
S	-1.0793	5.7697	-1.7179
S	-4.2355	2.8453	1.775
C	7.642	-2.7309	-1.5755
C	6.3636	0.9164	3.7963
C	-2.0354	5.6252	-3.3449
C	-3.6126	3.3916	3.474
C	-1.6648	6.9157	-4.0886
H	-2.1812	6.94	-5.0534
H	-1.9631	7.8025	-3.5237
H	-0.5903	6.9722	-4.2783
C	-3.5421	5.5722	-3.0769
H	-4.0839	5.5398	-4.0289
H	-3.8171	4.6805	-2.5099
H	-3.877	6.4517	-2.5226
C	-1.5786	4.3962	-4.1354
H	-0.5053	4.4296	-4.3348
H	-1.8041	3.4678	-3.6067
H	-2.1028	4.3642	-5.097
C	-2.5014	2.4592	3.964
H	-1.6252	2.5044	3.3137
H	-2.185	2.7594	4.9693

H	2.3269	5.6951	2.6317
H	1.5412	4.32	3.4271
H	1.4847	4.4832	1.663
C	0.1241	6.5865	4.0798
H	0.9711	7.2755	4.1562
H	-0.7949	7.1677	4.1887
H	0.1866	5.8799	4.911
C	6.9362	-4.1743	1.031
C	7.9469	-3.6458	0.0099
H	8.2702	-4.4618	-0.6461
H	7.5096	-2.8686	-0.6203
H	8.8294	-3.2334	0.5034
C	7.5898	-5.2219	1.9433
H	6.8847	-5.5974	2.6889
H	7.9276	-6.0697	1.3391
H	8.4576	-4.8111	2.4648
C	5.7091	-4.7635	0.3302
H	4.9879	-5.1502	1.0534
H	5.2091	-4.0207	-0.2952
H	6.0172	-5.5894	-0.3204
C	7.2601	1.5295	-2.3303
C	8.1436	0.2794	-2.3319
H	8.49	0.074	-3.351
H	9.0192	0.4122	-1.6932
H	7.5942	-0.5988	-1.9864
C	8.0683	2.7612	-2.7623
H	8.4336	2.6159	-3.7837
H	7.4554	3.6657	-2.7483
H	8.9328	2.9196	-2.1129
C	6.0427	1.3402	-3.2392
H	5.4131	2.2324	-3.2493
H	6.3759	1.146	-4.2648
H	5.4331	0.4905	-2.9246
H	4.752	3.5329	-0.3192
C	5.2753	4.4873	-3.6253
H	6.3125	4.1482	-3.7105
H	4.7823	4.3032	-4.5834
H	5.2831	5.5645	-3.4421
C	4.5849	2.2206	-2.7634
H	4.075	1.6558	-1.9818
H	4.1073	2	-3.7209
H	5.619	1.8592	-2.8092
C	-8.2335	0.2734	-2.3275
H	-8.6064	0.0599	-3.3355
H	-7.6882	-0.6077	-1.983
H	-9.0922	0.4258	-1.6704
C	-6.1412	1.2957	-3.2967
H	-5.5339	0.4438	-2.9832
H	-6.5008	1.0909	-4.3113
H	-5.5021	2.1804	-3.334
C	-8.1371	2.7483	-2.7902
H	-7.5124	3.6447	-2.8038
H	-8.5306	2.5943	-3.7998
H	-8.9825	2.9267	-2.1212
C	-7.8663	-3.7115	-0.0707
H	-8.1634	-4.5414	-0.7216
H	-8.7646	-3.3084	0.4015
H	-7.4311	-2.9346	-0.703
C	-5.6159	-4.7871	0.3039
H	-4.8974	-5.1462	1.0435
H	-5.8988	-5.6306	-0.3356
H	-5.1209	-4.0466	-0.3282
C	-7.5158	-5.2545	1.891
H	-7.8282	-6.1165	1.2935
H	-6.817	-5.607	2.6534
H	-8.3994	-4.8515	2.3919
H	-2.8451	1.4236	4.0087
C	-3.1284	4.8435	3.4307
H	-3.92	5.5145	3.0908
H	-2.8193	5.1587	4.4337
H	-2.2689	4.9612	2.7676
C	-4.8552	3.2647	4.3664
H	-5.2225	2.2359	4.3951
H	-4.6011	3.5626	5.3885
H	-5.6643	3.911	4.0175
C	6.8133	1.8697	4.9124
H	6.0508	2.6229	5.1253
H	6.9911	1.2986	5.829
H	7.7411	2.3832	4.6487
C	7.4551	-0.1155	3.5003
H	7.1688	-0.7766	2.6797
H	8.3978	0.3696	3.2389
H	7.6239	-0.739	4.3855
C	5.0492	0.2283	4.1749
H	4.2699	0.9599	4.3988
H	4.6914	-0.423	3.3745
H	5.2014	-0.3926	5.065
C	8.2803	-2.6932	-0.1844
H	8.5569	-3.708	0.1232
H	9.1815	-2.0766	-0.179
H	7.5881	-2.298	0.5621
C	8.6511	-3.2324	-2.6182
H	8.959	-4.2518	-2.3654
H	8.2146	-3.2495	-3.6197
H	9.5453	-2.6049	-2.6421
C	6.3882	-3.6098	-1.5773
H	6.6544	-4.6321	-1.286
H	5.6441	-3.2469	-0.8649
H	5.9309	-3.6457	-2.5682

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