Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Intramolecular transport of small-molecule cargo in a nanoscale device operated by light

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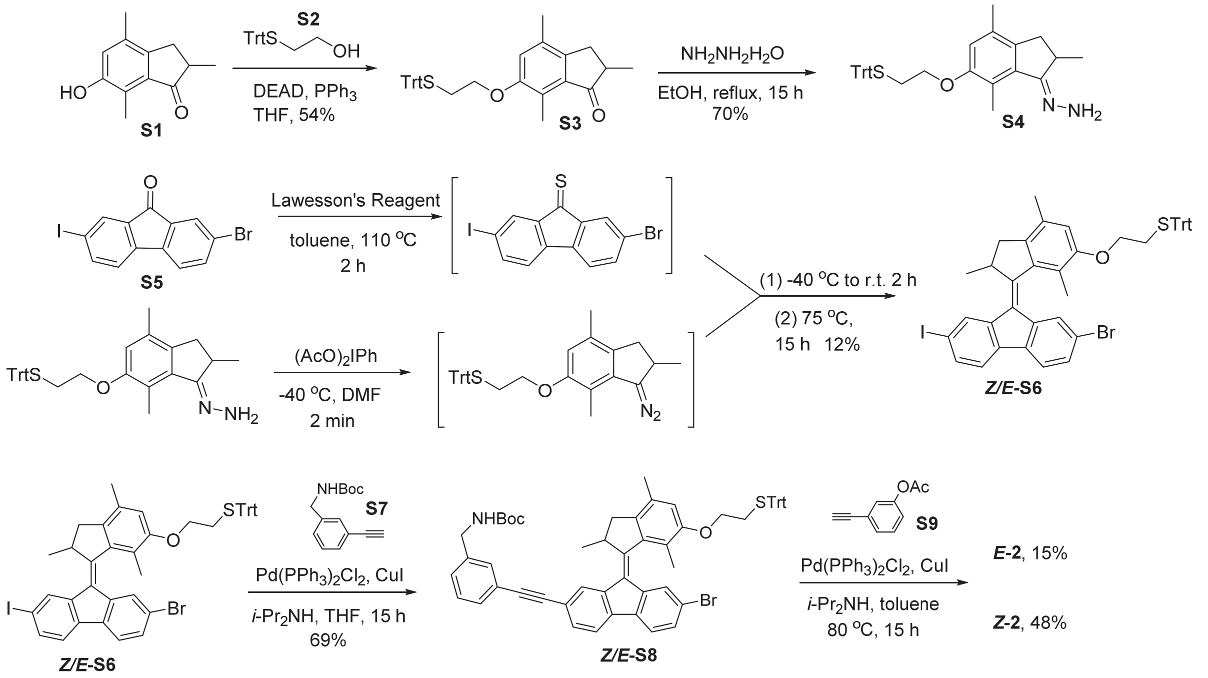
1 General:

Chemicals were purchased from Acros, Aldrich, Fluka or Merck and were used as received. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All reactions were performed under inert atmosphere (Ar). Analytical TLC was performed with Merck silica gel 60 F254 plates and visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM). Solvents for spectroscopic studies were of spectrophotometric grade (UVASOL Merck). Melting points were taken on a Mettler FP-2 melting point apparatus equipped with a Melttler FP-21 microscope. NMR spectra were recorded on Varian AMX400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) and Varian Unity Plus (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers. The deuterated solvents (CD_2Cl_2 and $CDCl_3$) were treated with Na_2CO_3, molecular sieves (4 Å) and degassed by argon prior to use. Chemical shifts are denoted in parts per million (ppm) relative to the residual solvent peak (CD_2Cl_2: ^{1}H $\delta = 5.32$ ppm, ^{13}C $\delta = 53.84$ ppm; $CDCl_3$: ^{1}H $\delta = 7.26$ ppm, ^{13}C $\delta = 77.0$ ppm). The splitting parameters are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. High-resolution mass spectrometry (ESIMS) was performed on a LTQ Orbitrap XL spectrometer with ESI ionization. UV/Vis measurements were performed on a JASCO V-630 spectrophotometer using a 1 cm quartz cuvette. UV irradiation experiments were carried out using a Spectroline model ENB-280C/FE lamp.

2 Synthesis



Scheme S1. Synthetic route towards the light-driven molecular motors *E*-**2** and *Z*-**2**.

Compounds 6-hydroxyl-2,4,7-trimethyl-2,3-dihydro-1-H-inden-1-one (**S1**), [1] 2-(tritylthio)ethanol (**S2**), [2] 2-bromo-7-iodo-9*H*-fluoren-9-one (**S5**), [3] *tert*-butyl 3-ethynylbenzylcarbamate (**S7**), [4] 3-ethynylphenyl acetate (**S9**)[5] were prepared according to procedures described in the literature.

2,4,7-trimethyl-6-(2-(tritylthio)ethoxy)-2,3-dihydro-1*H*-inden-1-one (S3)

A mixture of **S1** (263 mg, 1.38 mmol), **S2** (660 mg, 2.07 mmol) and triphenylphosphine (452 mg, 1.73 mmol) in THF (10 mL) was cooled to 0 °C. Diethyl azodicarboxylate (40 wt.% in toluene, 0.7 mL, 1.73 mmol) was added dropwise and the mixture was allowed to warm to r.t. and stirred for 15 h. The solvent was evaporated and the residue was purified by column chromatography (SiO_2, pentane:ether = 5:1) to yield **S3** as a white solid (370 mg, 54%). Mp. 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 7H), 7.28 (dt, *J* = 15.2, 7.2 Hz, 9H), 3.74 (t, *J* = 6.7 Hz, 2H), 3.16 (dd, *J* = 16.7, 8.0 Hz, 1H), 2.68 (s, 3H), 2.51 (s, 4H), 2.26 (s, 3H), 1.30 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 155.8, 145.0, 144.7, 134.2, 132.6, 129.6, 128.7, 127.9, 127.7, 126.72, 124.7, 119.5, 67.8, 66.7, 42.7, 32.5, 31.5, 17.8, 16.5, 9.9. HRMS (ESI): calcd. for $C_{33}H_{33}O_2S$ [M+H] 493.2123, found 493.2118.

(2,4,7-trimethyl-6-(2-(tritylthio)ethoxy)-2,3-dihydro-1*H*-inden-1-ylidene)hydrazine (S4)

A mixture of **S3** (200 mg, 0.41 mmol), hydrazine monohydrate (5 mL) and ethanol (25 mL) was heated at reflux overnight. After cooling, ethyl acetate (50 mL) and water (50 mL) were added to the mixture. The water layer was extracted with ethyl acetate (50 mL) and the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash column (SiO_2, pentane:ethyl acetate = 3:1) to yield **S4** (145 mg, 70%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.38 (m, 7H), 7.26 (dt, *J* = 15.0, 7.2 Hz, 9H), 5.24 (br, 2H), 3.74 (t, *J* = 6.7 Hz, 2H), 3.34 – 3.17 (m, 1H), 3.05 (dd, *J* = 16.2, 7.9 Hz, 1H), 2.63 (t, *J* = 6.7 Hz, 2H), 2.44 (s, 4H), 2.17 (s, 3H), 1.21 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 135.6, 133.7, 133.2, 131.6, 129.6, 129.2, 127.8, 127.6, 126.9, 125.8, 125.5, 124.4, 72.5, 63.5, 35.5, 32.7, 19.2, 14.1. HRMS (ESI): calcd. for $C_{33}H_{35}N_2OS$ [M+H] 507.2392, found 507.23787.

Compound S6

Lawesson's reagent (322 mg, 0.8 mmol) was added to a solution of **S5** (136 mg, 0.4 mmol) in toluene (10 mL). The mixture was stirred at 110 °C for 2 h after which the solvent was evaporated. The residue was purified by flash column (SiO_2, pentane:CH_2Cl_2 = 3:2) to obtain the thioketone as a brown oil. Meanwhile, to a solution of **S4** (100 mg, 0.2 mmol) in DMF (5 mL) at -40 °C, (diacetoxyiodo)benzene (64 mg, 0.2 mmol) in DMF (2 mL) was added dropwise. After complete addition, the mixture was stirred for 2 min followed by addition of the thioketone in DMF (2 mL). The resulting mixture was allowed to warm to rt and stirred for 2 h, and then heated at 75 °C overnight. After cooling to rt, the solvent was evaporated and the residue was purified by flash column (SiO_2, pentane:CH_2Cl_2 = 4:1) to yield **S6** (20 mg, 12%) as a yellow solid, as a mixture of *Z* and *E* isomers in a 1:1 ratio. Mp. 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.96 (s, 1H), 7.65 (d, *J* = 10.1 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 3H), 7.41 – 7.13 (m, 7H), 6.81 (s, 1H), 4.50 – 4.25 (m, 1H), 4.05 (d, *J* = 8.3 Hz, 1H), 3.84 (dd, *J* = 8.6, 4.0 Hz, 1H), 3.26 – 3.07 (m, 1H), 2.69 (d, *J* = 7.9 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.29 (d, *J* = 7.2 Hz, 2H), 2.07 (d, *J* = 7.1 Hz, 2H), 1.29 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 152.1, 144.6, 142.2, 141.4, 140.0, 139.1, 137.0, 134.1, 134.0, 133.7, 132.6, 130.4, 129.6, 127.9, 127.8, 127.5, 127.4, 126.8, 124.1, 123.8, 121.1, 120.4, 119.4, 43.8, 39.7, 35.0, 22.7, 18.3, 18.0, 15.0. HRMS (ESI): calcd. for $C_{46}H_{39}BrIOS$ [M+H] 845.0871, found 845.0869.

Compound S8

A mixture of **S6** (20 mg, 0.024 mmol), **S7** (5.1 mg, 0.025 mmol), $Pd(PPh_3)_2Cl_2$ (2.5 mol%) and CuI (5 mol%) in dry and degassed THF (2 mL) and $(i\text{-Pr})_2NH$ (2 mL) was stirred for 15 h at rt and then poured into an aqueous NH_4Cl solution. After extraction with $CHCl_3$ (3 x 5 mL), the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash column (SiO_2, pentane:$CHCl_3$ = 3:1) to yield **S8** (16 mg, 69%) as a brown oil, as a mixture of *E* and *Z* isomers in a 1:3 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.74 (m, 4H), 7.66 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.49 – 7.34 (m, 5H), 7.34 – 7.11 (m, 11H), 5.80 (s, 2H), 4.86 (s, 1H), 4.37 – 4.11 (m, 4H), 3.65 (t, *J* = 7.5 Hz, 1H), 3.17 (dd, *J* = 15.2, 5.7 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 1H), 2.59 (d, *J* = 15.2 Hz, 2H), 2.37 – 2.22 (m, 6H), 1.46 (s, 9H), 1.40 – 1.30 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 167.2, 152.2, 151.1, 144.64, 144.5, 142.3, 141.4, 140.0, 139.1, 137.0, 134.7, 134.0, 134.0, 133.8, 133.7, 133.7, 132.6, 130.4, 130.1, 129.6, 128.7, 128.5, 128.5, 127.9, 127.8, 127.5, 127.4, 126.8, 126.1, 124.2, 123.9, 122.2, 121.2, 120.4, 120.02, 119.4, 43.8, 39.7, 35.0, 31.3, 22.7, 21.0, 18.9, 18.1, 15.1. HRMS (ESI): calcd. for $C_{60}H_{54}BrNO_3S$ [M+H] 948.3008, found 948.3003.

Motor 2

A mixture of **S8** (32 mg, 0.034 mmol), **S9** (6.5 mg, 0.04 mmol), $Pd(PPh_3)_2Cl_2$ (2.5 mol%) and CuI (5 mol%) in dry and degassed toluene (2 mL) and $(i\text{-Pr})_2NH$ (2 mL) was heated at 80 ^{o}C for 15 h and then poured into an aqueous NH_4Cl solution. After extraction with $CHCl_3$ (3 x 5 mL), the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (SiO_2, pentane:$CHCl_3$ = 1:1) to yield *Z*-**2** (17 mg, 48%) and *E*-**2** (5.3 mg, 15%) as brown solids. Mp. 83-85 °C; *Z*-**2**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.99 – 7.93 (m, 1H), 7.93 – 7.88 (m, 1H), 7.87 – 7.79 (m, 2H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.53 (s, 1H), 7.46 (dt, *J* = 7.7, 2.2 Hz, 5H), 7.40 – 7.21 (m, 14H), 5.94 (s, 1H), 4.31 (d, *J* = 6.2 Hz, 2H), 4.27 – 4.16 (m, 1H), 3.71 (t, *J* = 7.4 Hz, 1H), 3.22 (dd, *J* = 15.2, 5.9 Hz, 1H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.66 (d, *J* = 15.2 Hz, 1H), 2.34 (d, *J* = 16.5 Hz, 6H), 2.16 (s, 3H), 1.48 (s, 9H), 1.39 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 167.2, 152.2, 151.1, 144., 144.5, 142.2, 141.4, 140.0, 139.1, 137.0, 134.6, 134.1, 134.0, 133.7, 132.6, 130.4, 130.1, 129.6, 127.9, 127.8, 127.5, 127.4, 126.8, 126.1, 124.1, 123.9, 122.2, 121.2, 120.4, 120.0, 119.4, 43.8, 39.7, 35.0, 31.2, 28.4, 22.7, 21.0, 18.9, 18.0, 15.0. *E*-**2**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.94 – 7.81 (m, 2H), 7.77 – 7.67 (m, 1H), 7.52 – 7.43 (m, 4H), 7.43 – 7.13 (m, 16H), 4.31 (d, *J* = 6.2 Hz, 2H), 4.25 (t, *J* = 6.5 Hz, 1H), 3.71 (td, *J* = 7.5, 1.1 Hz, 2H), 3.22 (dd, *J* = 15.2, 5.9 Hz, 1H), 2.76 (td, *J* = 7.5, 1.1 Hz, 2H), 2.65 (dd, *J* = 15.2, 1.1 Hz, 1H), 2.39 – 2.26 (m, 9H), 1.48 (s, 9H), 1.41 (dd, *J* = 6.8, 1.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 167.2, 152.18, 151.1, 144.6, 144.5, 142.3, 141.4, 140.0, 139.1, 137.1, 134.7, 134.1, 134.0, 133.7, 132.7, 130.4, 130.2, 129.6, 128.0, 127.9, 127.5, 127.4, 126.8, 126.1, 124.2, 123.9, 122.3, 121.2, 120.4, 120.0, 119.4, 43.8, 39.7, 35.0, 31.3, 28.4, 22.7, 21.1, 18.9, 18.1, 15.0. HRMS (ESI): calcd. for $C_{70}H_{65}N_2O_5S_1$ [M+NH$_4$] 1045.4608, found 1045.4604.

Conversion of *Z*-2 into *E*-1-NHAc

Motor ***Z*-2** (10 mg, 0.01 mol) was placed in a Young NMR tube under argon and CD_2Cl_2 (2 mL was added. The obtained yellow solution was kept at 0 ^{o}C and trifluoroacetic acid (2 equiv.) was added. After 5 min, the NMR tube was transferred to a glove box. The solution was filtered over a short pad of celite that was washed with CD_2Cl_2 and the yellow filtrate was collected. The obtained solution was transferred to another Young NMR tube containing Et_3N (1.5 equiv.), and taken out of the glove box. The tube was heated at 40 ^{o}C for 2 h. The solution was then further cooled to -50 ^{o}C and irradiated (λ = 312 nm) for 3 h. The solution was then kept in the dark for 0.5 h at rt followed by heating at 40 ^{o}C for 1 h under exclusion of light. The obtained yellow mixture was passed over a short pad of silica which was washed with $CHCl_3$. The yellow filtrate was collected. After solvent evaporation, ***E*-1-**

NHAc was obtained as a light-yellow solid (4.6 mg, 70%). Mp. 68-69 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.86 (dd, J = 19.4, 7.7 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.50 (s, 1H), 7.39 (d, J = 7.3 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.29 – 7.16 (m, 3H), 6.98 – 6.88 (m, 1H), 6.86 – 6.74 (m, 1H), 5.94 (s, 1H), 4.43 (d, J = 6.0 Hz, 2H), 4.29 – 4.23 (m, 1H), 4.20 (t, J = 6.7 Hz, 2H), 3.21 (dd, J = 15.2, 5.9 Hz, 1H), 3.01 (dt, J = 8.5, 6.7 Hz, 2H), 2.65 (d, J = 15.1 Hz, 1H), 2.32 (d, J = 21.0 Hz, 6H), 2.04 (s, 3H), 1.79 (t, J = 8.5 Hz, 1H), 1.40 (d, J = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 168.7, 157.41, 153.2, 144.8, 142.9, 141.3, 139.9, 139.6, 138.3, 138.2, 134.6, 134.5, 134.1, 133.9, 133.8, 133.7, 132.6, 130.4, 130.2, 129.9, 127.8, 127.7, 127.6, 127.5, 126.0, 125.8, 125.0, 124.1, 123.5, 120.1, 119.8, 119.3, 115.9, 113.9, 64.0, 44.4, 39.8, 35.3, 27.6, 23.1, 22.2, 19.1, 17.9, 14.9. HRMS (ESI): calcd. for $C_{46}H_{40}NO_3S$ [M+H] 686.4698, found 686.4696 and 708.4511 [M+Na].

3 Assignment of *Z*-2 and *E*-2

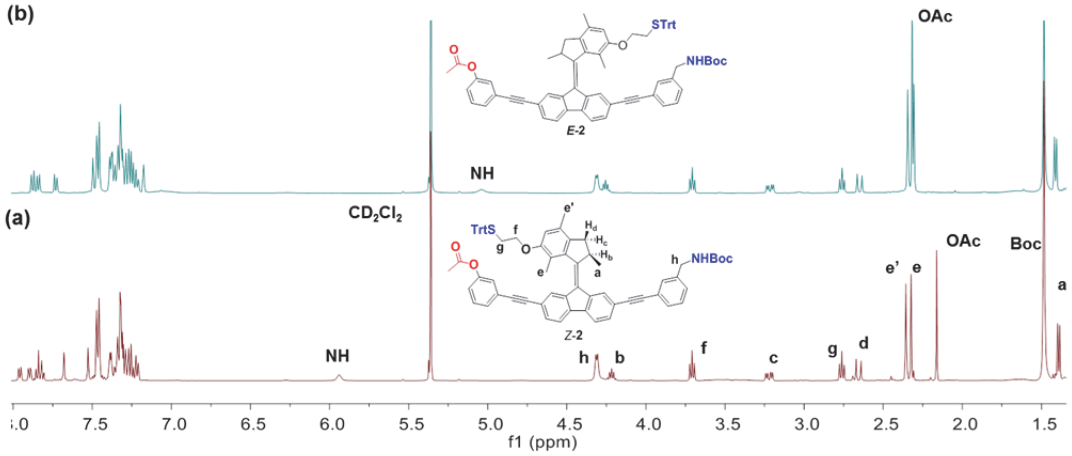


Figure S1. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of (a) ***Z*-2**; (b) ***E*-2**.

In ***Z*-2** isomer, the Trt group in the upper half and the phenyl acetate group are in close proximity (Figure S1a). Due to the shielding effect of the Trt group, the signal of the acetyl group (OAc) was found to have an upfield shift (2.16 ppm) than that of ***E***-2 (2.33 ppm) where the acetyl group is kept apart from the Trt group (Figure S1b). The upfield shift caused by the shielding of the upper half is in accordance with the previously reported motors bearing an unsymmetrical lower half.[6,7,8,9,10] The same upfield shift is also observed for the NH proton of Boc-protected benzyl amine. In ***E*-2** isomer, the Trt group in the upper half and NH-Boc group are in close proximity (Figure S1b). Due to the shielding effect of the Trt group, the signal of NH group was found to have an upfield shift (5.1 ppm) compared to ***Z*-2** (5.91 ppm) where NH group is apart from the Trt group (Figure S1a).

Distinctive features of the central motor core in ***Z*-2** are the signals of the methyl group (doublet at 1.40 ppm, a), aliphatic protons H_b, H_c and H_d.[7,10] The doublet at 2.65 ppm can be assigned to H_d, since there is only a negligible coupling between H_b and H_d due to their relative orientations as a result of the conformation of the five membered ring.[7,10] As H_c does not only couple to its geminal proton H_d but also to vicinal proton H_b, the double doublet at 3.22 ppm can be assigned to H_c. The absorption at

4.22 ppm corresponds to H_b, which shows a multiplet signal due to the coupling with the protons of the methyl group and proton H_c. The triplets at 2.76 ppm (H_g) and 3.71 ppm (H_f) can be assigned to the methylenes in the upper half next to S and O, respectively. The singlet at 2.16 ppm (OAc) can be assigned to the acetyl group. The doublet at 4.31 ppm (H_h) and the broad absorption at 5.95 ppm correspond to the benzylic methylene and NH proton at site C, respectively.

4 UV-vis spectral studies of ***Z*→*E*** isomerization

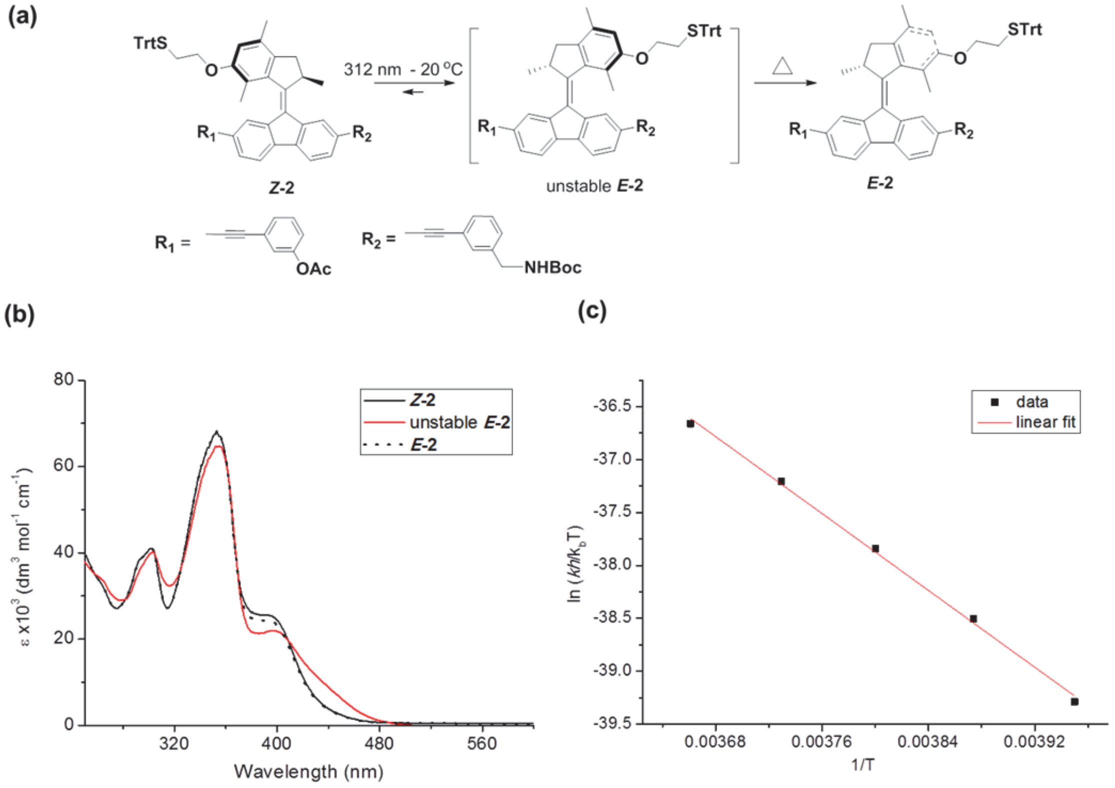


Figure S2. (a) Photochemical and thermal isomerization steps from ***Z*-2** to ***E*-2**. (Single enantiomer shown) (b) UV-vis spectra (CH_2Cl_2, -20 °C) of motor **2**: ***Z*-2** (black solid line), unstable ***E*-2** at PSS (red solid line), ***E*-2** (black dashed line). (c) Eyring analysis of thermal helix inversion of unstable ***E***-2 to ***E***-2.

When motor ***Z*-2** is irradiated with UV light, a photochemical *Z*-*E* isomerization takes place (Figure S2a). This photochemical step results in an unstable ***E*-2** isomer, in which the methyl group at the stereogenic center is forced to adopt a less favored pseudoequatorial orientation.[7] An irreversible thermal helix inversion (THI) takes place , in which both the upper and lower part slip past each other, to release the steric strain, generating the ***E*-2** isomer (Figure S2a). When a solution of compound ***Z*-2** in CH_2Cl_2 (Figure S2b, black solid line) was irradiated with UV light (λ_{max} = 312 nm) at –20 °C, an increase in the absorption between 420 nm to 480 nm was observed with concomitant decrease in the absorption from 370 nm to 410 nm (Figure S2b, red solid line). The solution was kept in the dark at rt for 0.5 h to allow the THI occur, resulting in a hypsochromic shift in the UV-vis spectra (Figure S2b, black dashed line).

The thermal helix inversion of unstable ***E***-2 to ***E***-2 was followed by monitoring the UV-vis absorption change at 460 nm (Figure S2c) with respect to time at five different temperatures (-20 °C, -15 °C, -10 °C, -5 °C, 0 °C). From these data, Gibbs free energy of activation ($\Delta^{\ddagger}G^{\circ}$ = 84.0 kJ/mol) , the half-life ($t_{1/2}$ = 96 s) at room temperature (20 °C) and at -50 ^{o}C (> 300 h) could be obtained by means of an Eyring analysis (Figure S2c), as well as the enthalpy of activation ($\Delta^{\ddagger}H^{\circ}$ = 72.2 kJ/mol) and entropy of activation ($\Delta^{\ddagger}S^{\circ}$ = -40.1 J/K.mol).

5 ^{1}H NMR spectra of the *S*→*N* acylation step

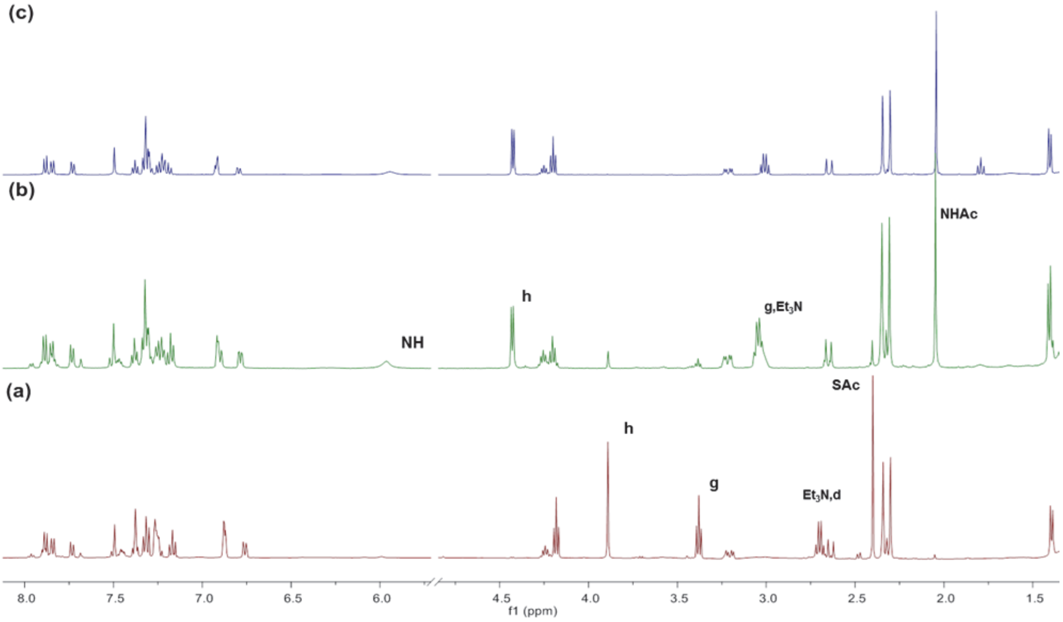
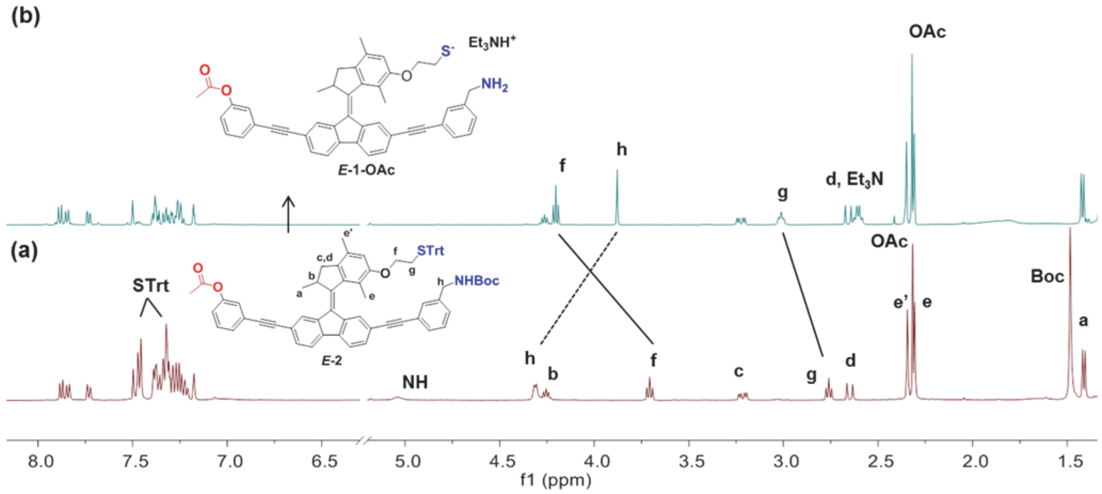


Figure S3. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of (a) ***E*-1-SAc**; (b) after 40 ^{o}C for 1 h; (c) after filtration over a short pad of silica.

Figure S3a shows the ^{1}H NMR spectrum of a mixture (5:1) of ***E*-1-SAc**/***Z*-1-SAc** (the same as Figure 3d). The sample was kept at 40 ^{o}C for 1 h (Figure S3b). Decreased absorptions at 2.4 ppm (SAc), 3.4 ppm (H_g) and 3.9 ppm (H_h) were found, together with increased absorptions at 2.0 ppm, 3.0 ppm, 4.4 ppm and 5.9 ppm. These spectral changes supported the cleavage of the thioacetate and the formation of benzylacetamide. After filtration over a short pad of silica, isomer ***E*-1-NHAc** could be isolated (Figure S3c, the same as Figure 3e).

6 Control experiment with isomer *E*-2



(i) CF_3COOH (2 equiv.), 0 °C, 5 min; (ii) Et_3N (1.5 equiv.), 40 °C, 2 h.

Figure S4. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of (a) ***E*-2**; (b) ***E*-1-OAc**, after 40 ^{o}C for 2 h.

A control experiment was performed starting with isomer ***E*-2** in which phenyl acetate (site A) and Trt-protected thiol (site B) are seperated from each other. Figure S4a shows the partial ^{1}H-NMR spectrum of a solution of ***E*-2** (10 mg, 0.01 mmol) in CD_2Cl_2 (0.5 mL). The solution of ***E*-2** was treated with CF_3COOH (2 equiv.) at 0 ^{o}C for 5 min and filtrated over Celite. The collected yellow fraction was added Et_3N (1.5 equiv.) and kept at 40 ^{o}C for 2 h (Figure. S4b). It was found that the signals of Trt (7.5 ppm, 7.3 ppm), proton NH (5.1 ppm) and Boc (1.5 ppm) disappeared (Figure S4b), indicating the cleavage of the Trt and Boc groups. In addition, downfield shifts of H_g (2.8 ppm to 3.0 ppm) and H_f (3.7 ppm to 4.4 ppm) and upfield shift of H_h (4.4 ppm to 3.9 ppm) were observed. These spectral changes are in accordance with those observed for ***Z*-1-OAc** (Figure 3b), and thus indicate the formation of ***E*-1-OAc** in this case. However, no spectral evidences could be found for formation of the thioacetate, suggesting that the intramolecular *O*→*S* acylation does not occur in isomer ***E*-1-OAc**. The signal for the OAc group (δ = 2.32 ppm) remains intact and the absence of thioacetate or benzylacetamide formation indicate that no intermolecular reaction takes place under these conditions.

7 ^{1}H NMR, ^{13}C NMR and Mass spectra

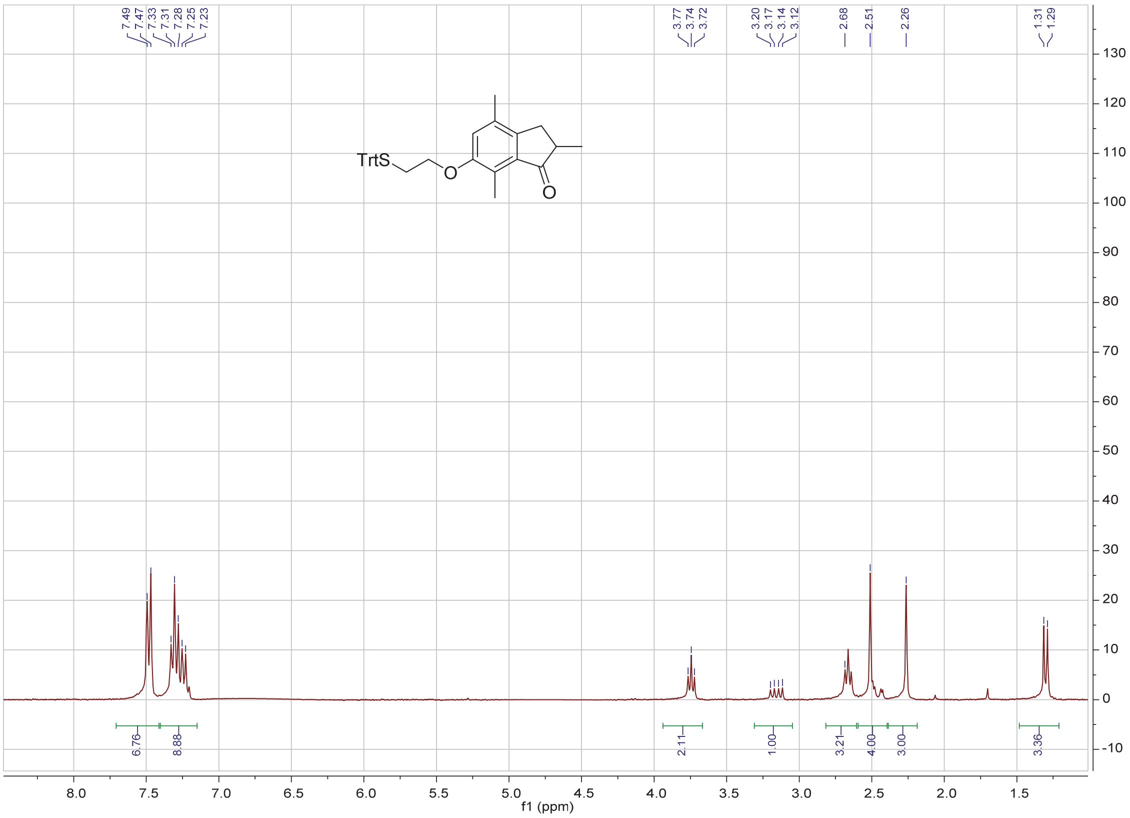


Figure S5. ^{1}H NMR spectrum of **S3** in $CDCl_3$ at 400 MHz.

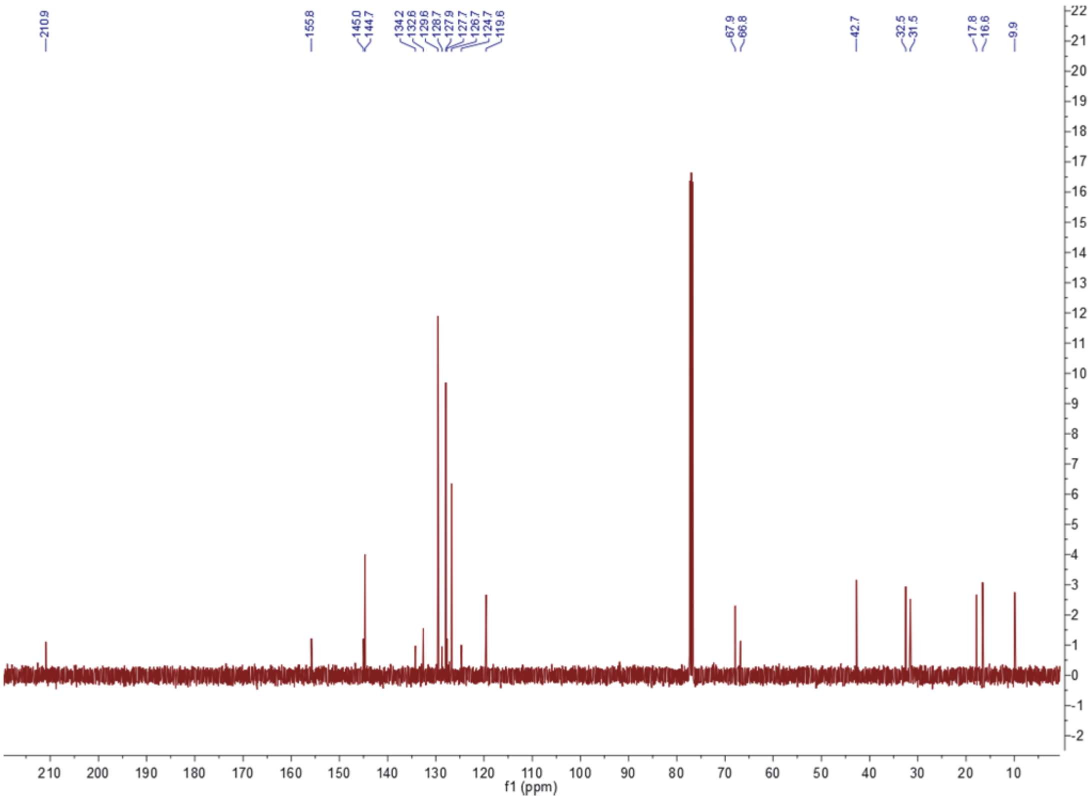


Figure S6. ^{13}C NMR spectrum of **S3** in $CDCl_3$ at 100 MHz.

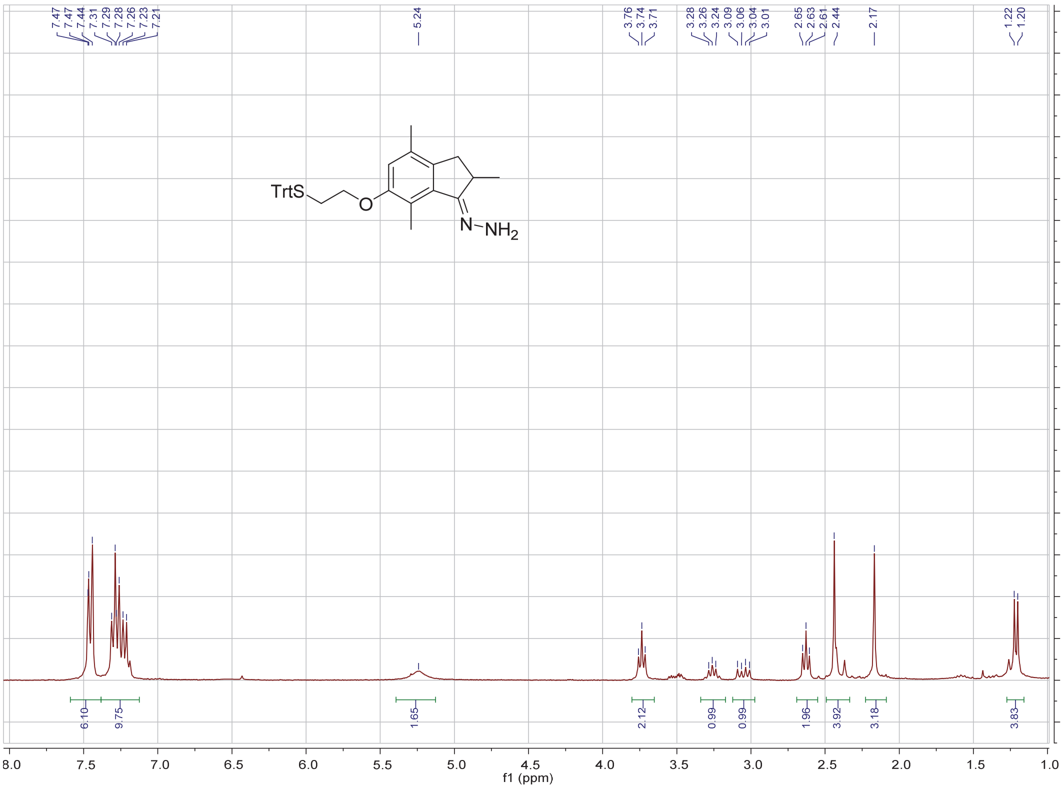


Figure S7. ^{1}H NMR spectrum of **S4** in $CDCl_3$ at 400 MHz.

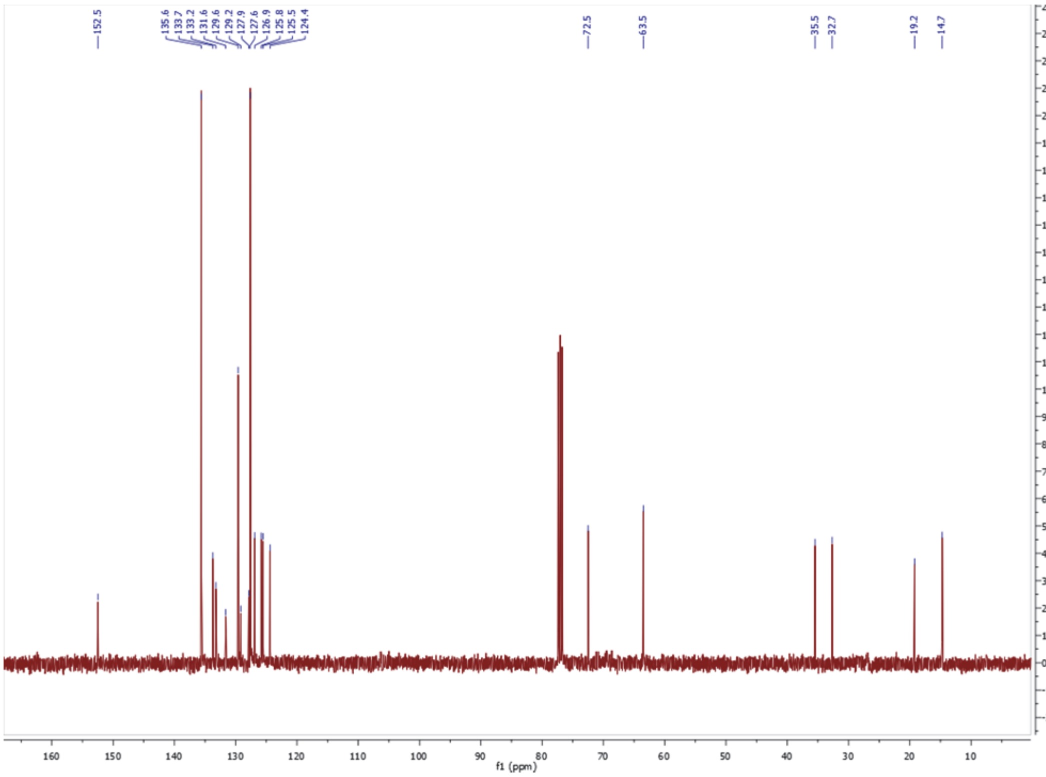


Figure S8. ^{13}C NMR spectrum of **S4** in $CDCl_3$ at 100 MHz.

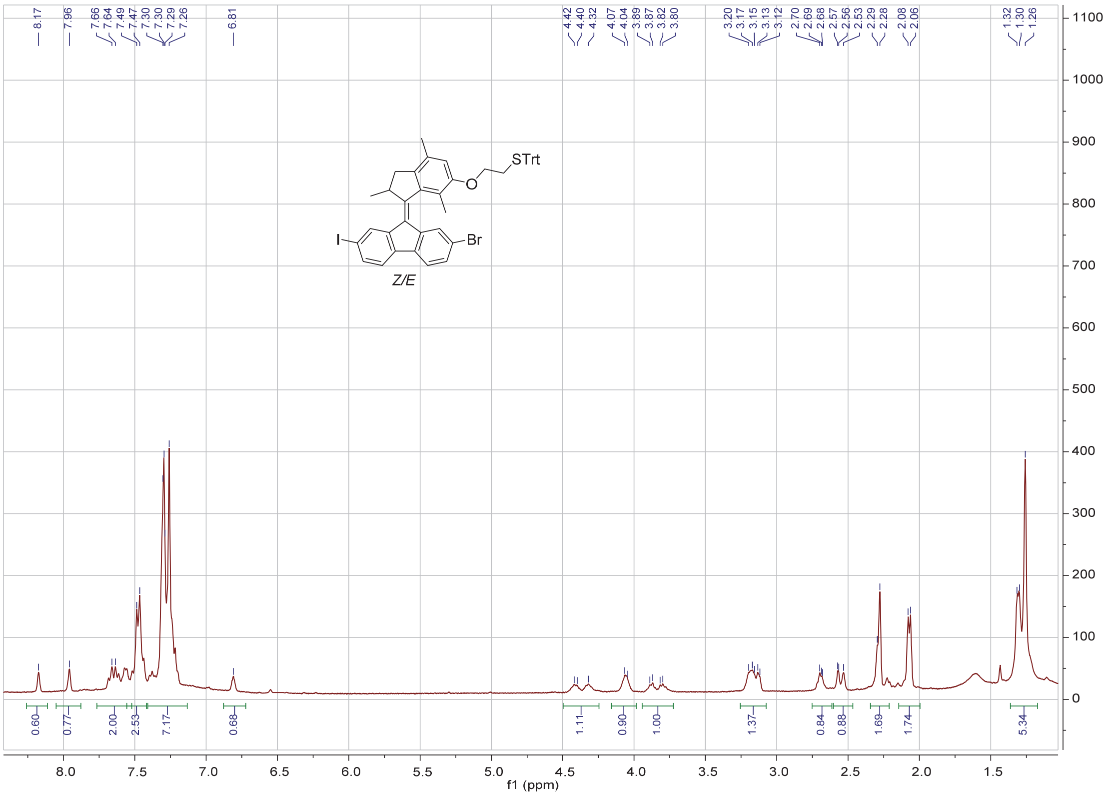


Figure S9. ^{1}H NMR spectrum of **S6** in $CDCl_3$ at 400 MHz.

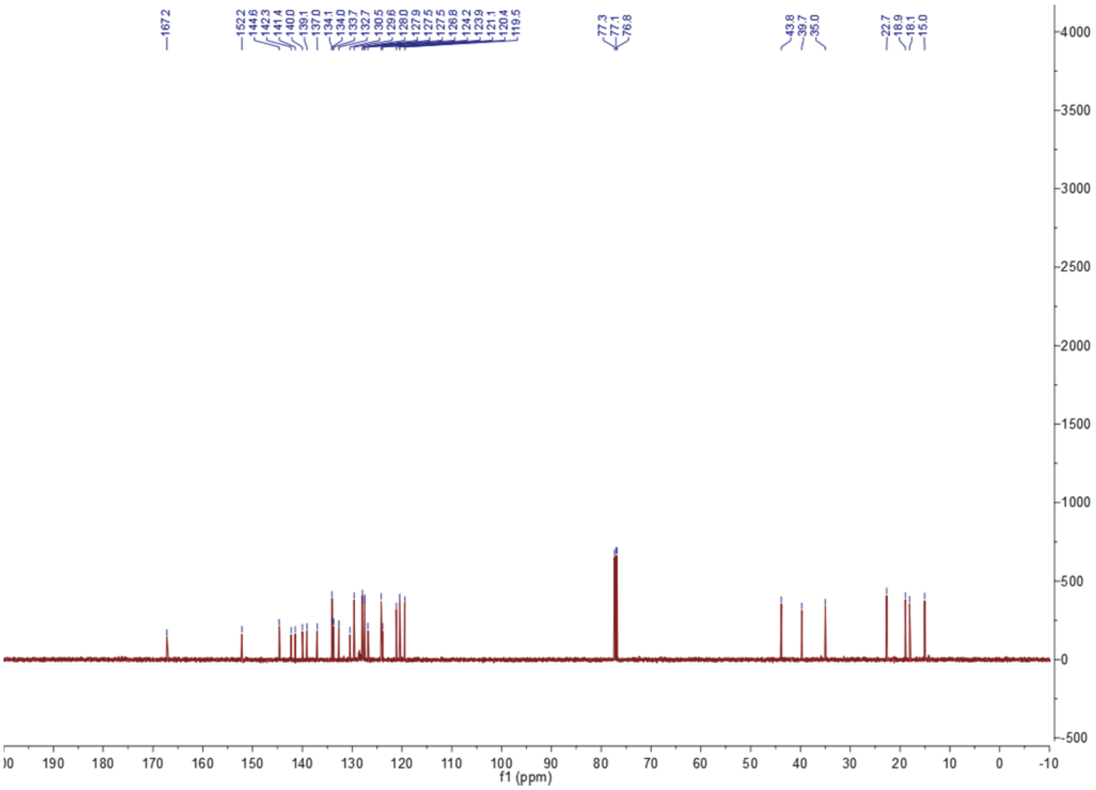


Figure S10. ^{13}C NMR spectrum of **S6** in $CDCl_3$ at 100 MHz.

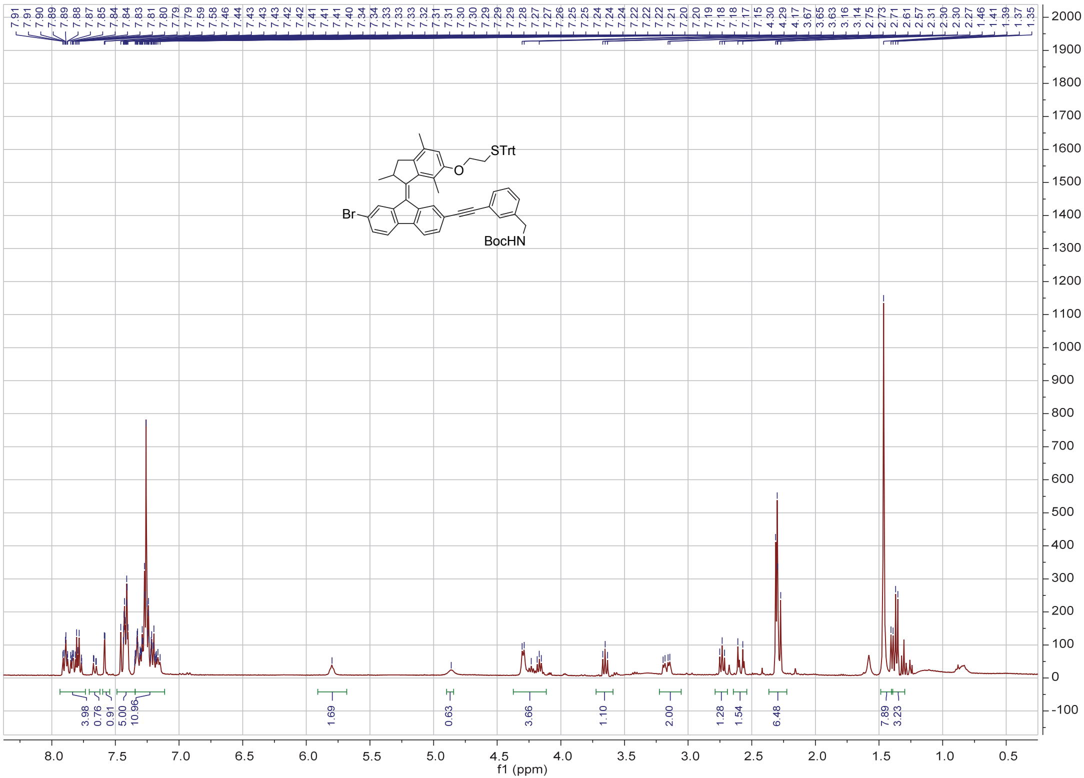


Figure S11. ^{1}H NMR spectrum of **S8** in $CDCl_3$ at 400 MHz.

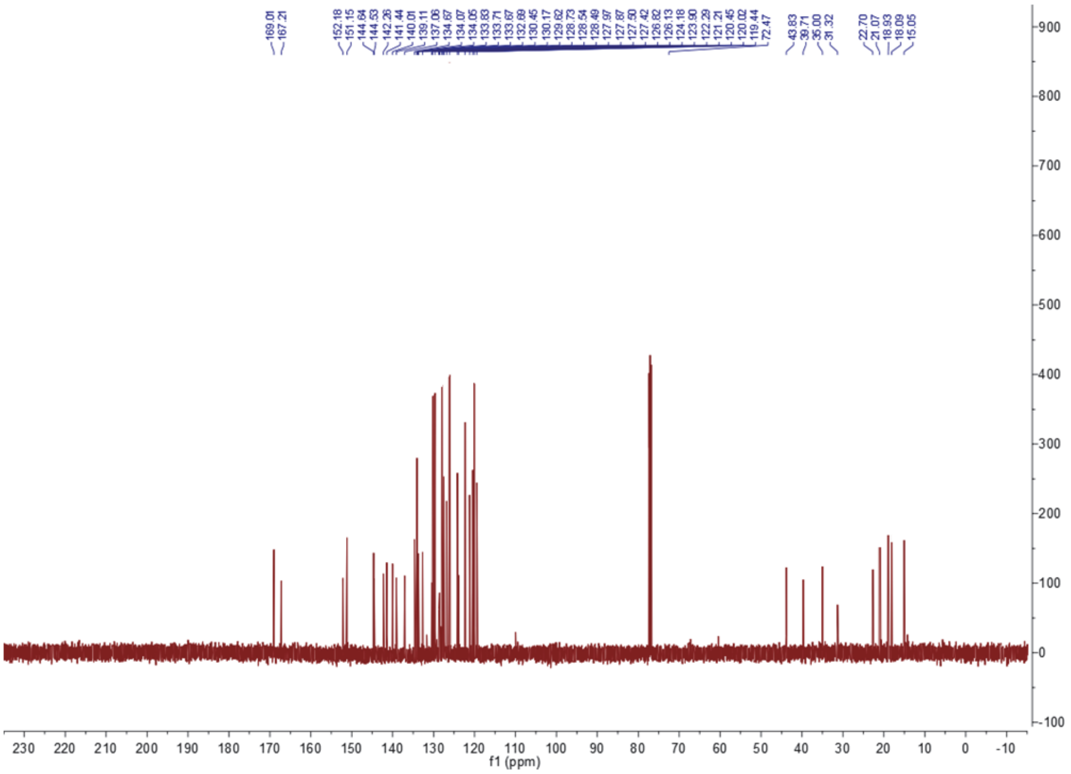


Figure S12. ^{13}C NMR spectrum of **S8** in $CDCl_3$ at 100 MHz.

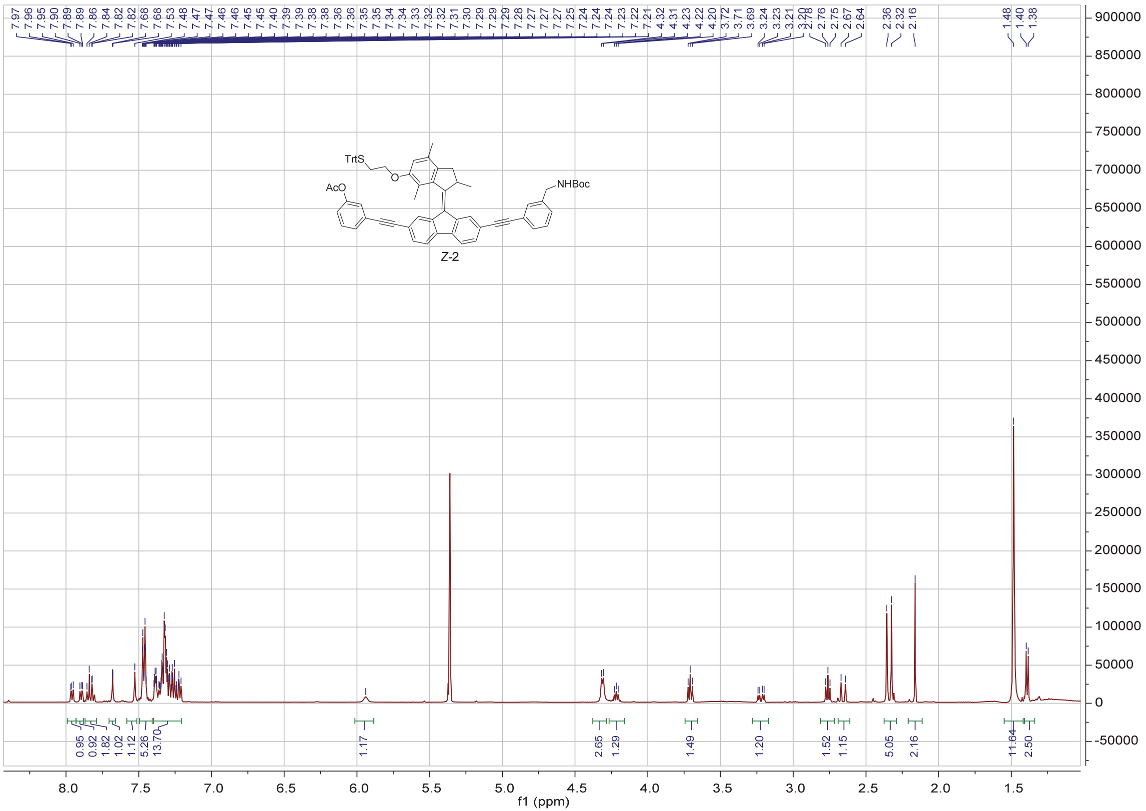


Figure S13. ^{1}H NMR spectrum of ***Z*-2** in CD_2Cl_2 at 500 MHz.

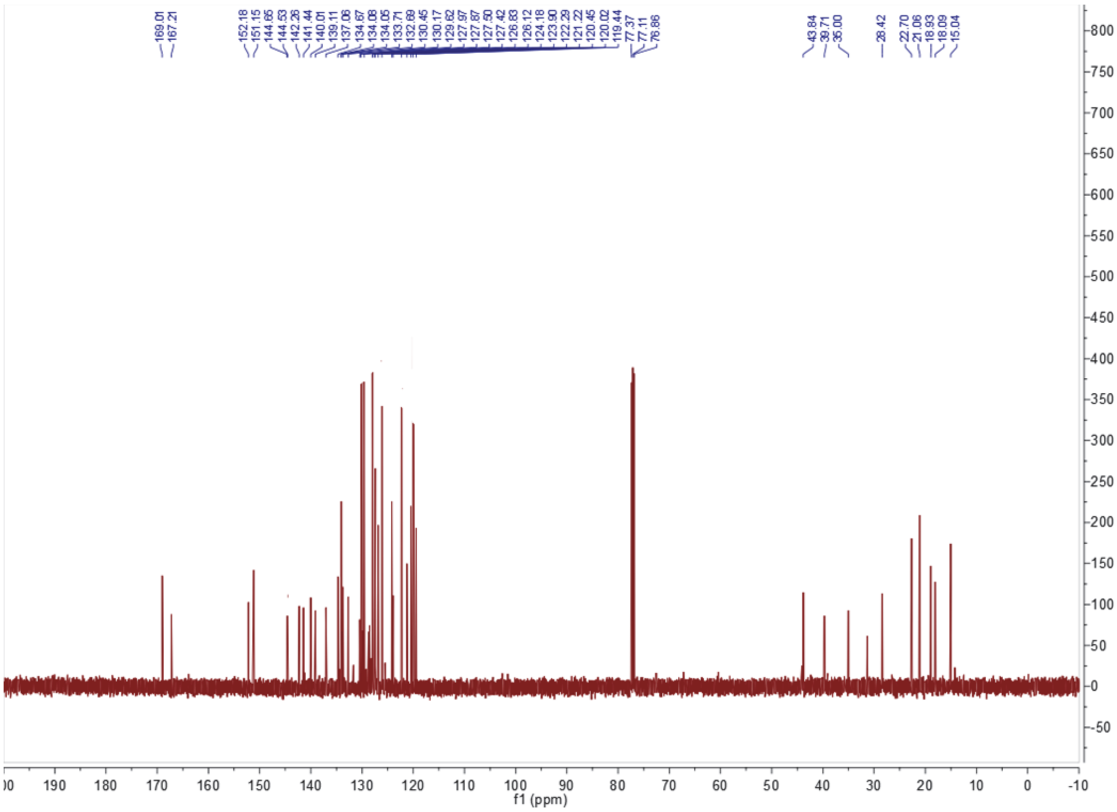


Figure S14. ^{1}H NMR spectrum of ***Z*-2** in $CDCl_3$ at 125 MHz.

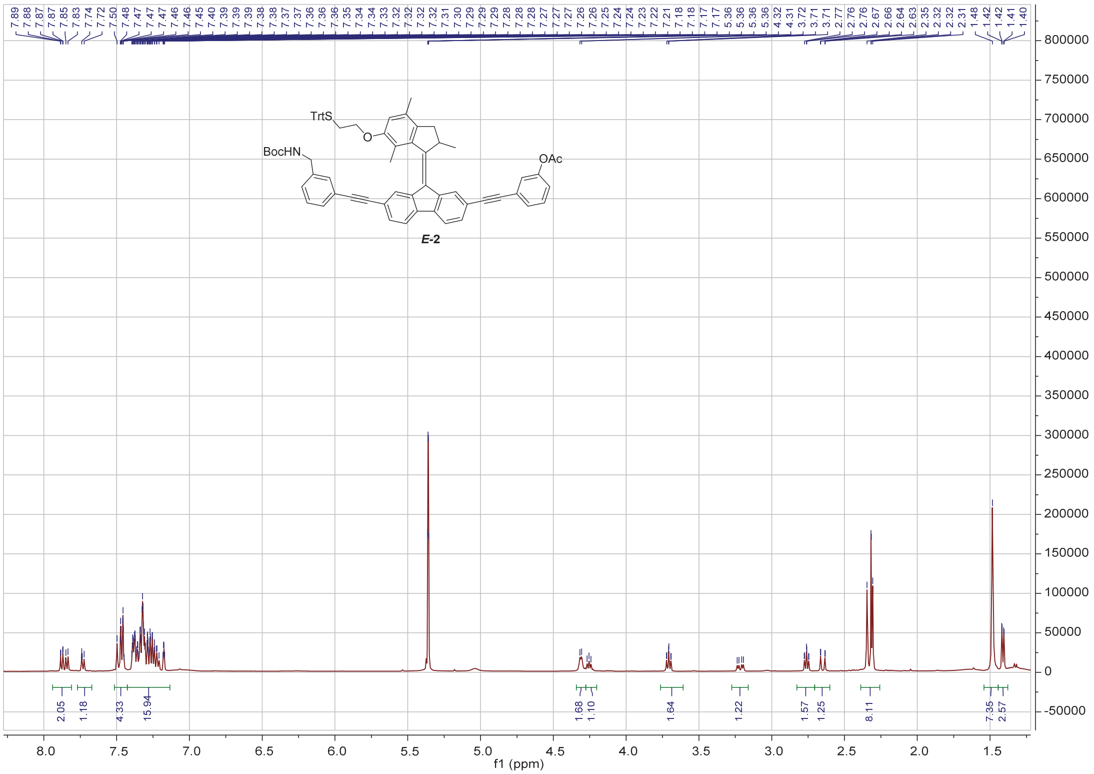


Figure S15. ^{1}H NMR spectrum of ***E*-2** in CD_2Cl_2 at 500 MHz.

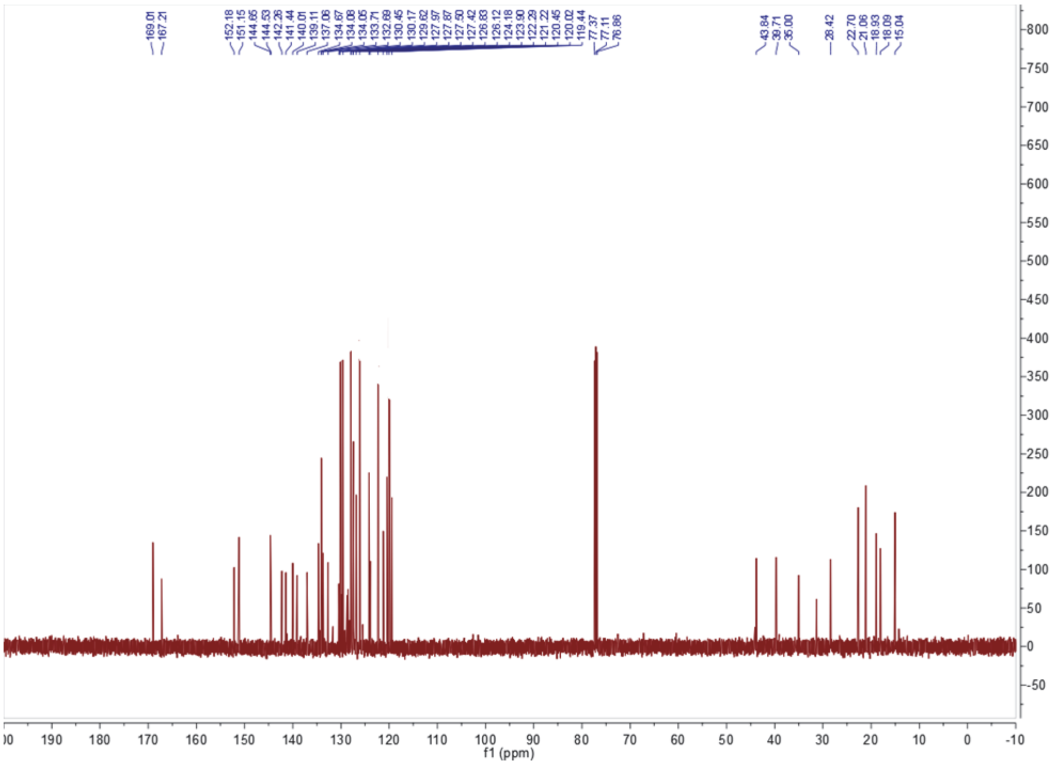


Figure S16. ^{13}C NMR spectrum of ***E*-2** in $CDCl_3$ at 125 MHz.

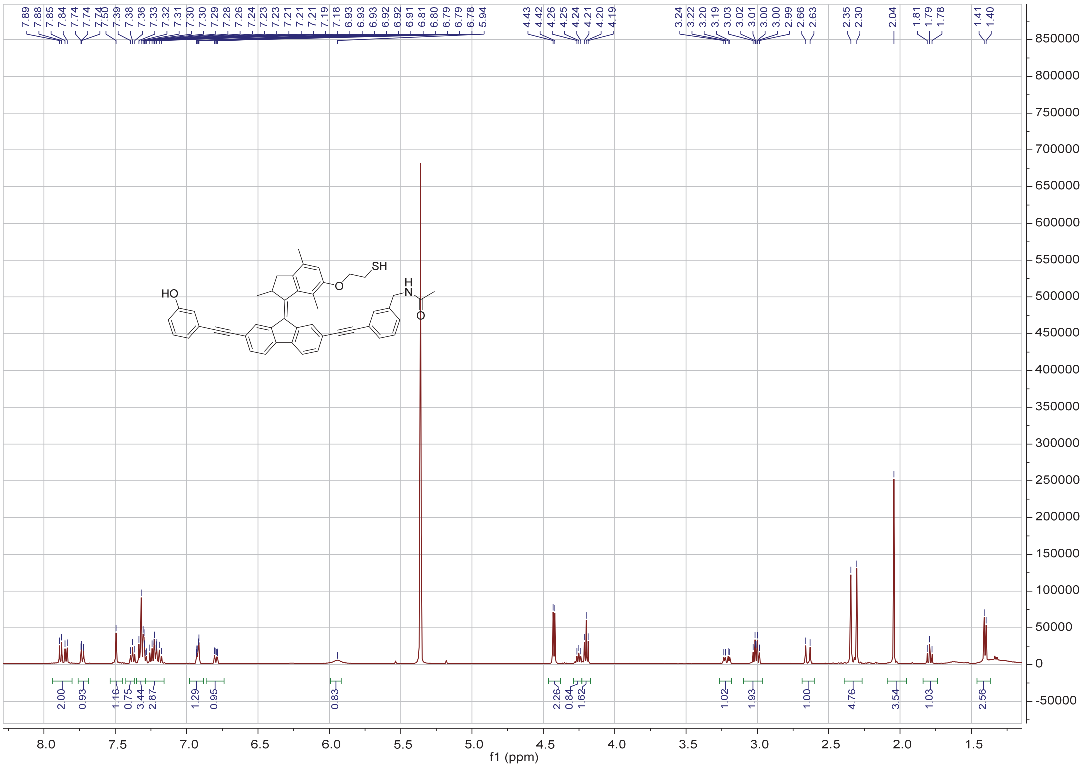


Figure S17. ^{1}H NMR spectrum of ***E*-1-NHAc** in CD_2Cl_2 at 500 MHz.

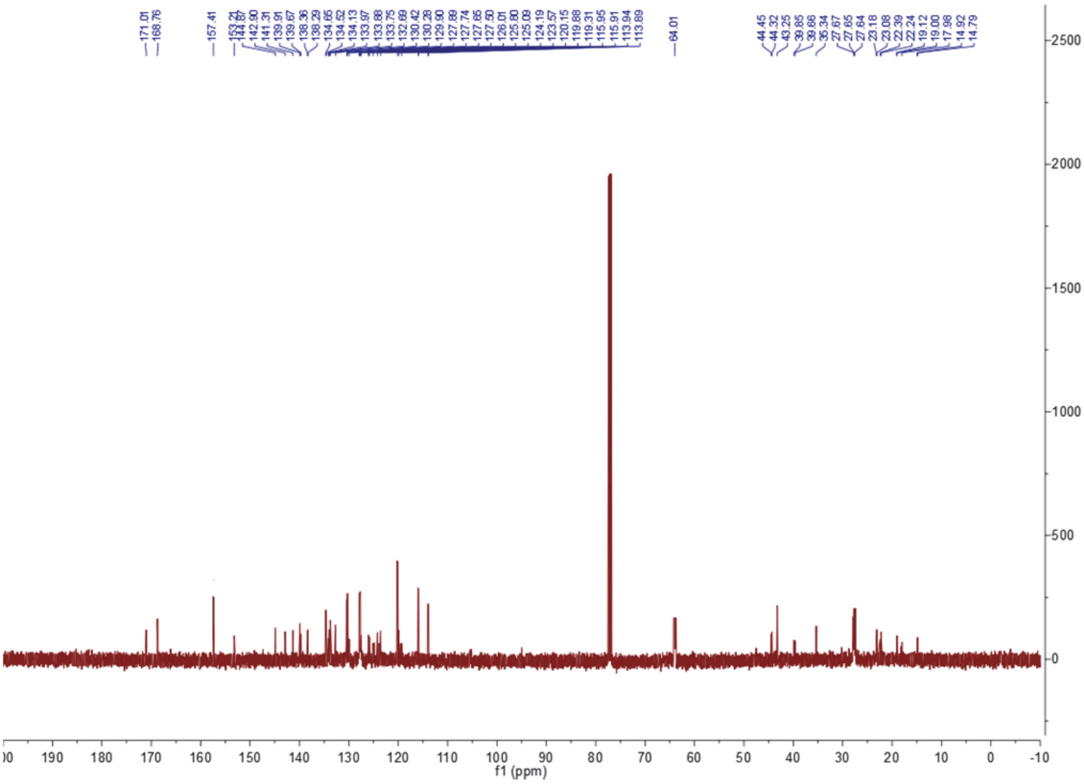


Figure S18. ^{13}C NMR spectrum of ***E*-1-NHAc** in $CDCl_3$ at 125 MHz.

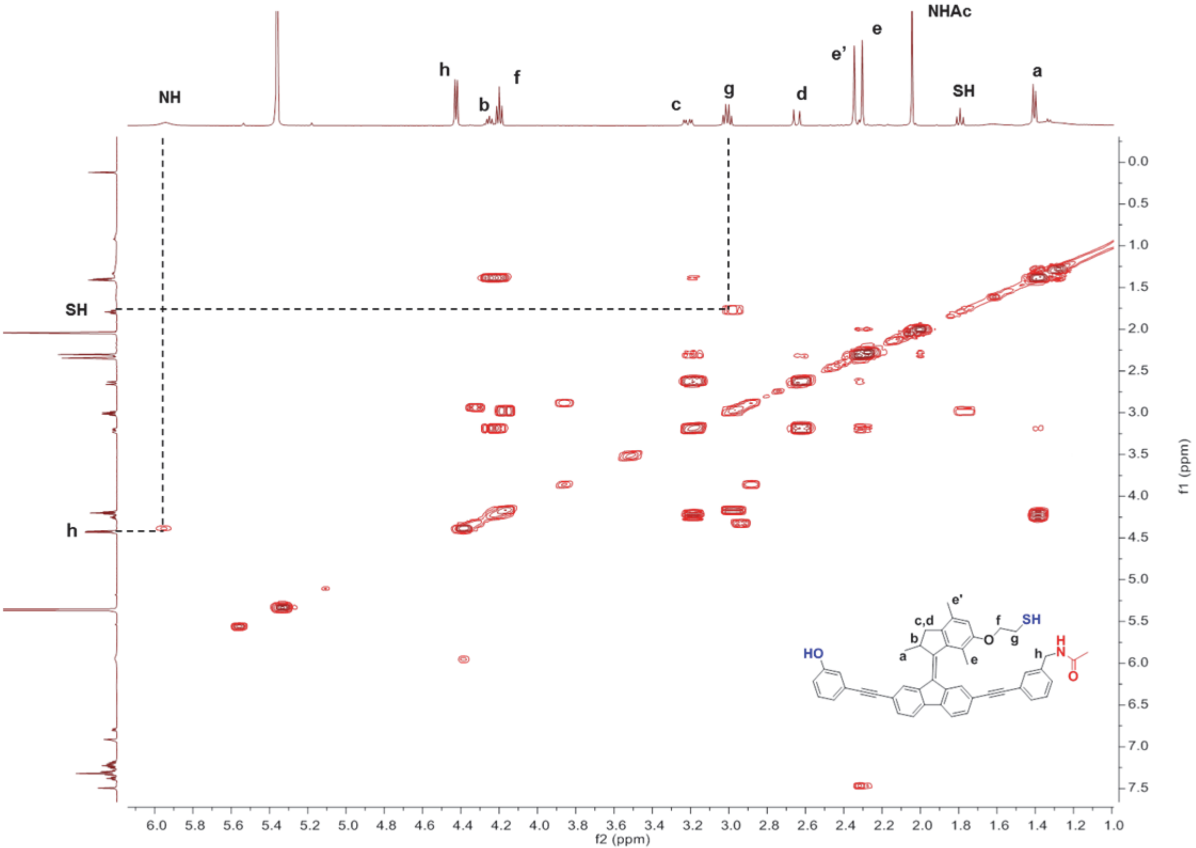


Figure S19. Partial ^{1}H-^{1}H COSY spectrum of ***E*-1-NHAc** (500 M, CD_2Cl_2).

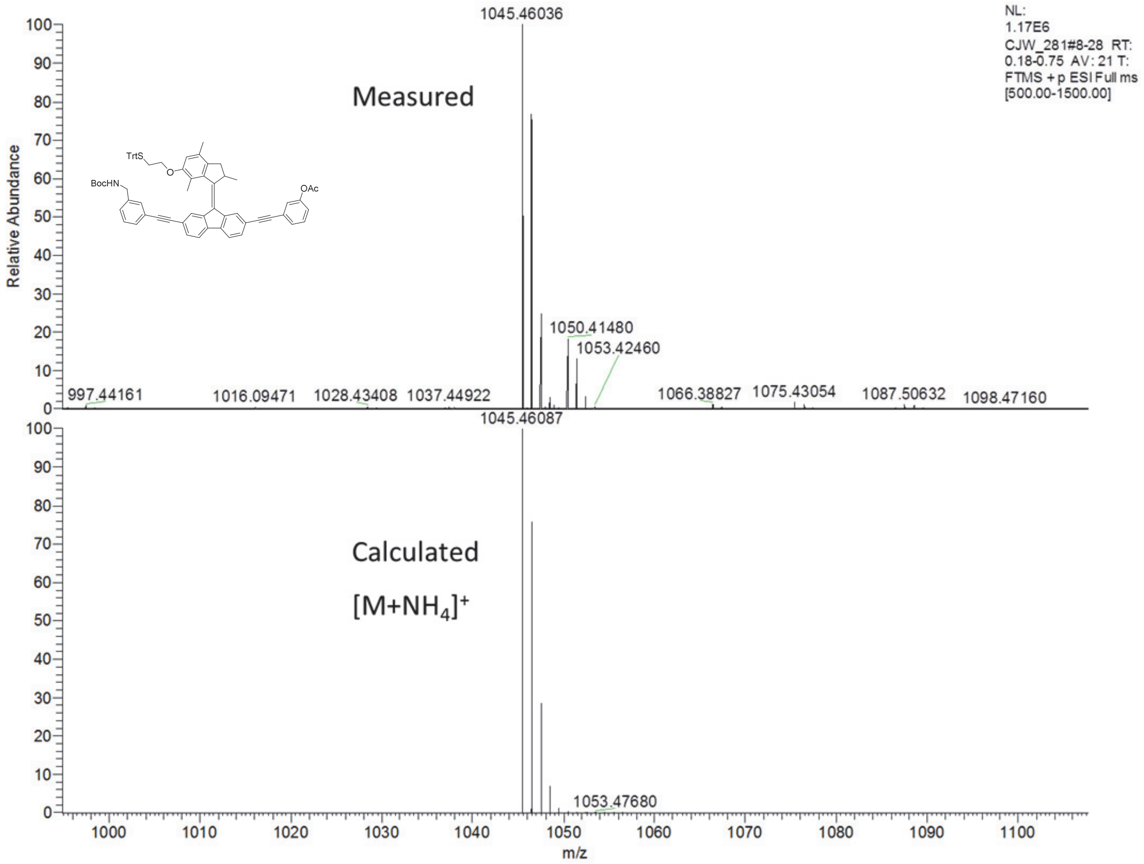


Figure S20. High-resolution mass spectrum of motor **2**.

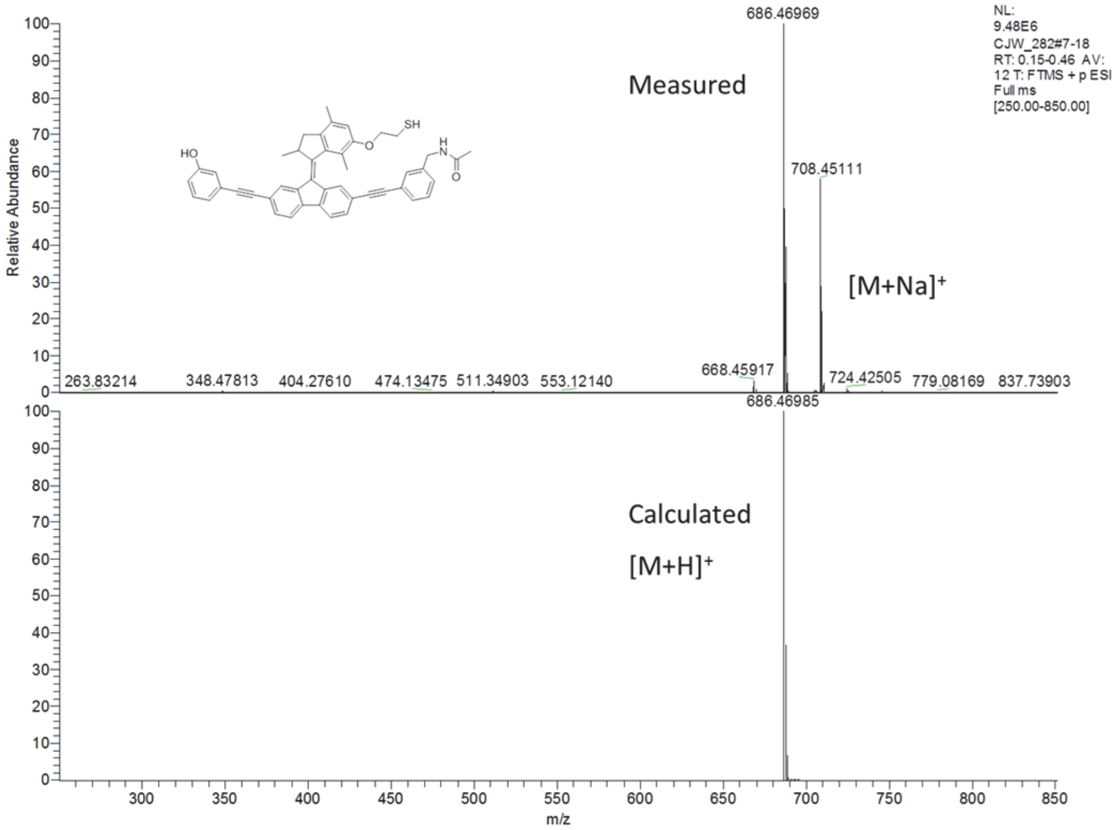
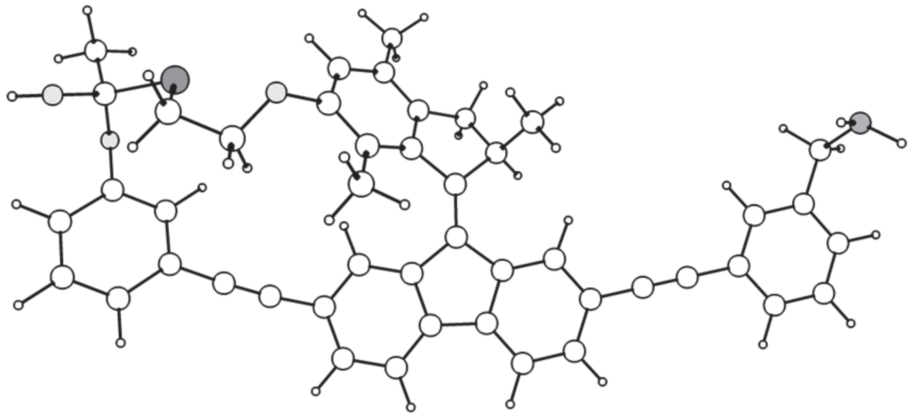


Figure S21. High-resolution mass spectrum of motor ***E*-1-NHAc**.

DFT Calculations

The Gaussian 09 program[11] was used for geometry optimizations and the calculation of energies. Initially, different input geometries were optimized at the semi-empirical PM6 level to find the global minima. Further geometry optimizations were performed at the DFT B3LYP/6-31G+(d,p) level using tight convergence criteria and an IEFPCM CH_2Cl_2 solvation model. All geometries were found to have zero imaginary frequencies.

Table S1. Cartesian coordinates of *Z*-**1** tetrahedral carbon intermediate.



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C	1.119125000	-0.224713000	2.091198000
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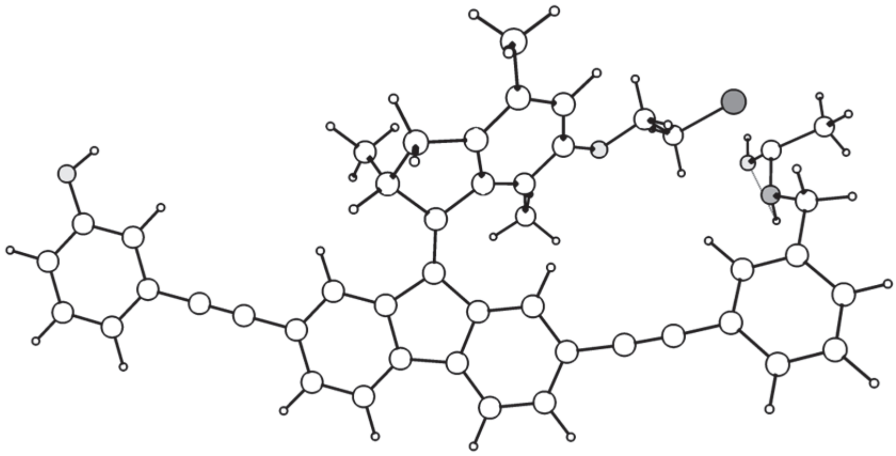
Sum of electronic and zero-point Energies = –2454.312035

Table S2. Cartesian coordinates of *E*-**1** tetrahedral carbon intermediate.



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Sum of electronic and zero-point Energies = –2454.327076

9 References and notes

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