Electronic Supplementary Information (ESI)

Alkyl-substituted spiropyrans: Electronic effects, model compounds and synthesis of aliphatic main-chain copolymers

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Experimental

NMR spectroscopy

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Bruker ARX 300. All spectra were recorded at 303 K in $CDCl_3$ as solvent and were referenced to the residual solvent peak (δ = 7.26 ppm). ^{1}H–^{1}H and ^{1}H–^{13}C correlated 2D NMR spectra were recorded to verify the signal assignments using standard pulse sequences included in the Bruker TOPSPIN 2.1 software package.

UV-Vis-spectroscopy

The optical characterisation of solutions was carried out on a Shimadzu UV-1800 series UV-Vis-spectrometer, controlled by the UVProbe 2.30 software. The samples were measured in quartz cuvettes with Ethanol as a solvent. For thin films one drop of a polymer solution (25 mg/ml in $CHCl_3$) was solvent cast on a quartz substrate and measured on the Flame-S UV-Vis-spectrometer from Ocean Optics, controlled by the OceanView 1.5.2 software.

SEC measurements

SEC measurements were carried out on four SDV gel 5 µm columns, with pore sizes ranging from 10^3 to 10^6 Å (PSS), connected in series with a 254 nm UV-Detector detector and calibrated with polystyrene standards. THF was used as eluent at 30 °C at a flow rate of 1.0 ml/min.

Simulations

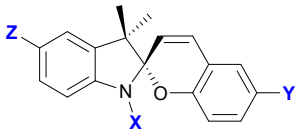


Figure 1: Definition of the substituent positions X, Y and Z

Similar to our previous strategy[1], we have determined the collective influence of different substitution positions on the gas-phase energy difference between MC and SP forms ΔU for an extended number of substituent positions. The substituent positions are labelled as depicted in Figure 1, where X is the N-position, Y the *para* position relative to the O-atom and Z the position *para* to the N-atom. The most general fit function for three substituents reads

$$\Delta U(X,Y,Z) = \Delta U_H + \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_Z\sigma_Z + \rho_{XY}\sigma_X\sigma_Y + \rho_{XZ}\sigma_X\sigma_Z + \rho_{YZ}\sigma_Y\sigma_Z + \rho_{XYZ}\sigma_X\sigma_Y\sigma_Z\,, \quad (1)$$

where the $\sigma_i, i = X,Y,Z$ are Hammett constants, and ΔU_H, ρ_X, ρ_Y ρ_Z, ρ_{XY}, ρ_{XZ}, ρ_{YY} and ρ_{XYZ} are system dependent parameters. Due to their *para*-position relative to nitrogen and oxygen, σ_Y and σ_Z are set to the *para* Hammett constant σ_p, while σ_X is described by a linear combination of inductive σ_I and resonance σ_R parameters. We extended our Hammett constants[1] by the new substituent C_6H_4OMe for which we obtained σ_p = -0.13, σ_I = 0.06 and σ_R = -0.19. We have calculated ΔU(X,Y,Z) for 87 substitution combinations, where in addition to the 63 combinations with hydrogen on Z[1], additional 24 combinations with ethyl on X and various substituents on Y and Z were modeled. We varied Z for fixed X substituent only, such that we cannot determine any correlation between X and Z. We consequently removed all terms proportional to $\sigma_X\sigma_Z$ in Equation (1) and obtain the reduced fit function

$$\Delta U(X,Y,Z) = \Delta U_H + \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_Z\sigma_Z + \rho_{XY}\sigma_X\sigma_Y + \rho_{YZ}\sigma_Y\sigma_Z\,. \quad (2)$$

The parameters from a least squares fit yielded ΔU_H = (0.14 ± 0.01) eV, ρ_X = (0.83 ± 0.02) eV, ρ_Y = (-0.11 ± 0.01) eV, ρ_Z = (0.20 ± 0.02) eV, ρ_{XY} = (0.16 ± 0.05) eV, ρ_{YZ} = (0.02 ± 0.05) eV with a correlation coefficient of R = 0.981. Using $\sigma_{X=Et}$ = -0.024 leads to Equation (1) in the main text.

The corresponding fit function surfaces ΔU(X,Y,Z=H) and ΔU(X=Et,Y,Z) are depicted in Figure 2. While the finite value of ρ_{XY} indicates a clear correlation between X and Y, the small ρ_{YZ} indicates that the correlation between Y and Z can be practically neglected. This is reasonable due to the larger spatial distance between substituent positions Y and Z.

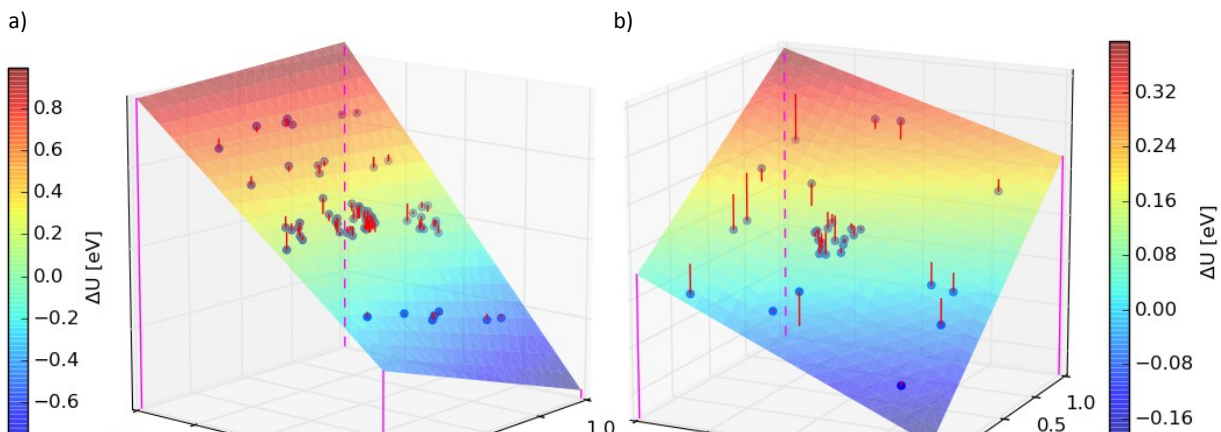
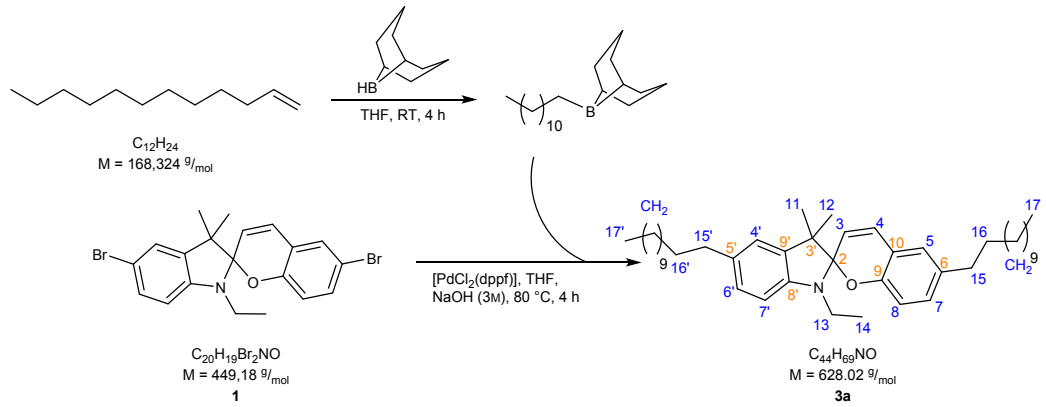


Figure 2: The fit function surfaces for a) ΔU(X,Y,Z=H) and b) ΔU(X=Et,Y,Z) compared to the gas phase energy differences ΔU between MC and SP (blue points). The deviations of the points to the surfaces are depicted by red lines. Note that image a) is very similar to fig. 3 of Brügner et. al[1] as only few substitution new combinations with Z = H were added.

Synthesis of compound 3a



A 5 ml Schlenk tube was loaded with 0.197 ml (0.891 mmol) 1-dodecene, sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). 1.78 ml (0.891 mmol) 9-borabicyclo(3.3.1)nonan (9-BBN) solution in THF (0.5M) was added and the mixture was stirred for 4 hours at room temperature. 99.8 mg (0.223 mmol) of monomer **1** and 3.30 mg (4.46 µmol) of [$PdCl_2$(dppf)] were mixed under nitrogen with the borane-solution, stirred for 5 minutes until 1.5 ml of a N_2 purged 3M aq. NaOH solution were added. Stirring rapidly, this reaction mixture was heated for 4 hours at 80 °C, cooled and extracted with 0.7 ml of a saturated aq. NH_4Cl-solution. The organic layer was separated and volatiles were removed under reduced pressure. The solid residue was filtrated over a short, deactivated (NEt_3) silica gel plug using *iso*-Hexane : Ethylacetate, 9 : 1, concentrated to dryness and dissolved in 7 ml of boiling methanol. The product precipitated over night while cooling to 5 °C. After decanting methanol, this washing process was repeated. The product **3a** was dried under high vacuum and was received as 71.3 mg (113 mmol, 51%) of a reddish, highly viscous oil.

entry	base	catalyst	# eq. 9-BBN	t / h	T / °C	crude yield / %
13	NaOH	$PdCl_2$(dppf)	4	4	75	97
14	NaOH	$Pd_2(dba)_3$ + PPh_3	4	4	75	90
15	Na_2CO_3	$PdCl_2$(dppf)	4	4	75	76
16	KF	$PdCl_2$(dppf)	4	4	75	0
17	NaOH	$PdCl_2$(dppf)	2.5	4	75	75
18	K_2CO_3	$PdCl_2$(dppf)	4	14	75	96
19	K_2CO_3	$PdCl_2$(dppf)	2	14	75	93
20	NaOH	$PdCl_2$(dppf)	4	4	90	87
21	NaOH	$PdCl_2$(dppf)	4	4	80	100

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.95 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 6'-H_1), 6.88 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 7-H_1), 6.87 (d, 1H, ^4J = 1.5 Hz, 4'-H_1), 6.83 (d, 1H, ^4J = 2.1 Hz, 5-H_1), 6.76 (d, 1H, ^3J = 10.1 Hz, 4-H_1), 6.60 (d, 1H, ^3J = 8.2 Hz, 8-H_1), 6.44 (d, 1H, ^3J = 7.8 Hz, 7'-H_1), 5.64 (d, 1H, ^3J = 10.1 Hz, 3-H_1), 3.38-3.06 (m, 2H, 13-H_2), 2.57 (dd, 2H, ^3J = 7.8 Hz, ^3J = 7.7 Hz, 15'-H_2), 2.51 (dd, 2H, ^3J = 7.8 Hz, ^3J = 7.7 Hz, 15-H_2), 1.66-1.50 (m, 4H, 16-H_2, 16'-H_2), 1.4-1.2 (m, 36H, 18·CH_2), 1.30 (s, 3H, 11-H_3), 1.15 (t, 3H, ^3J = 7.2 Hz, 14-H_3), 1.14 (s, 3H, 12-H_3), 0.89 (t, 6H, ^3J = 7.0 Hz, 17-H_3, 17'-H_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 152.53 (C_9), 145.48 ($C_{8'}$), 136.88 ($C_{9'}$), 134.32 (C_6), 133.19 ($C_{5'}$), 129.58 (C_7), 129.31 (C_4), 127.07 ($C_{6'}$), 126.45 (C_5), 121.99 ($C_{4'}$), 120.14 (C_3), 118.45 (C_{10}), 114.93 (C_8), 105.89 ($C_{7'}$), 104.68 (C_2), 52.25 ($C_{3'}$), 38.14 (C_{13}), 35.88 ($C_{15'}$) 35.23 (C_{15}), 32.23 ($C_{16/16'}$), 32.09 ($C_{16/16'}$), 32.09-29.52 (C_{CH2}), 26.28 (C_{12}), 22.85 (C_{CH2}), 20.36 (C_{11}), 14.70 (C_{14}), 14.27 (C_{17}, $C_{17'}$).
MS: (ESI); m/z = 460.36 (4) [$C_{32}H_{46}ON$ ≙ Dodecen-SP-H], 628.55 (100) [MH^+].

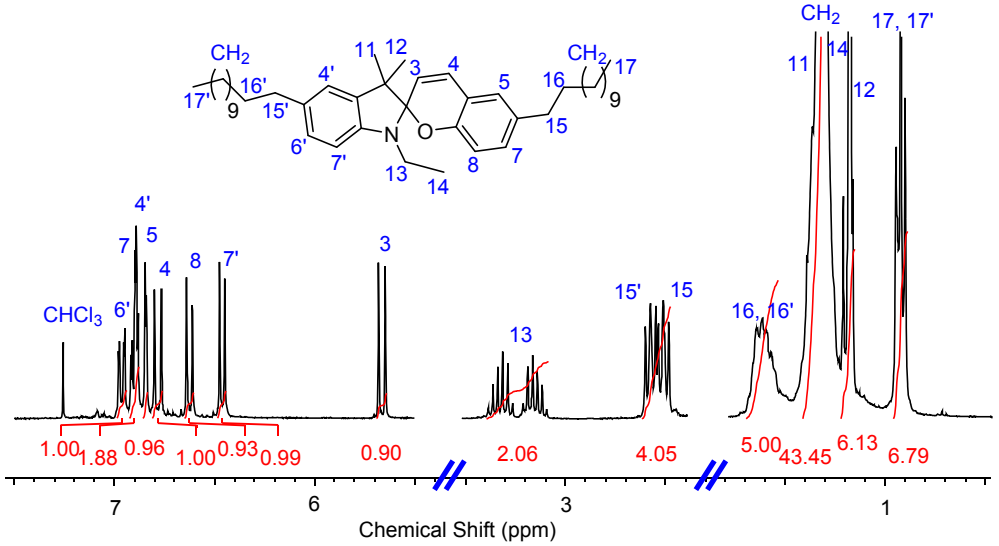


Figure 3: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **3a**.

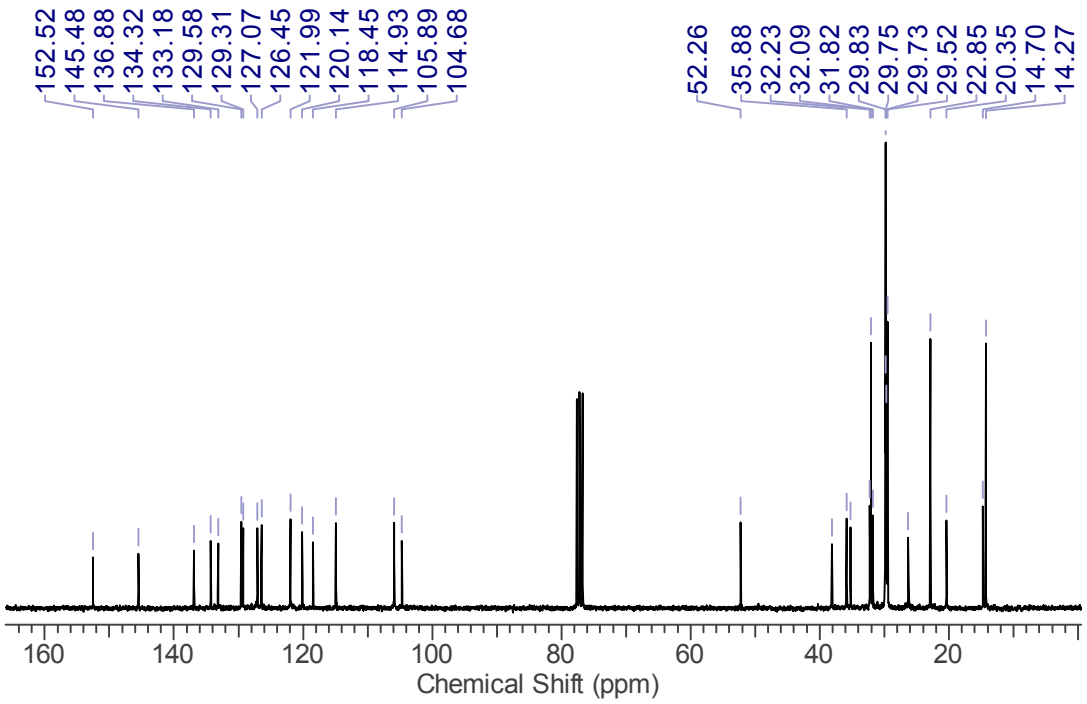
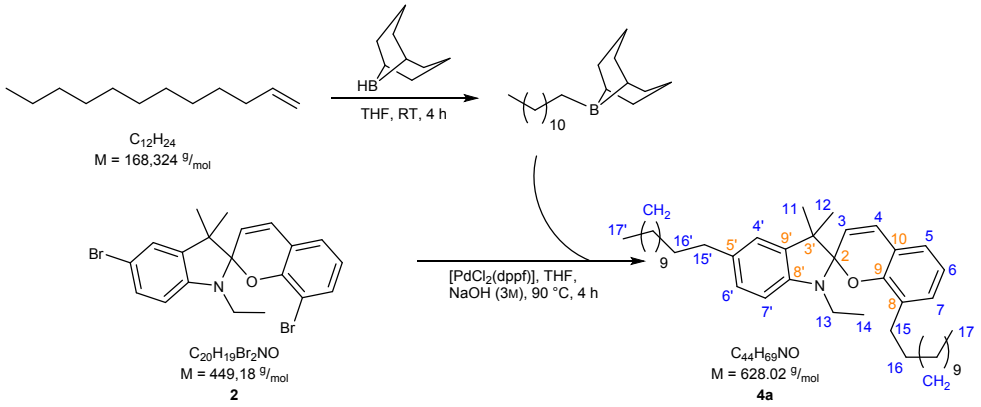


Figure 4: ^{13}C NMR (75 MHz, $CDCl_3$) of compound **3a**.

Synthesis of compound 4a



A 5 ml Schlenk tube was loaded with 0.197 ml (0.891 mmol) 1-dodecene, sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). 1.78 ml (0.891 mmol) 9-borabicyclo(3.3.1)nonan (9-BBN) solution in THF (0.5M) was added and the mixture was stirred for 4 hours at room temperature. 99.5 mg (0.223 mmol) of monomer **2** and 3.29 mg (4.46 µmol) of [$PdCl_2$(dppf)] were mixed under nitrogen with the borane-solution, stirred for 5 minutes until 1.5 ml of a N_2 purged 3M aq. NaOH solution were added. Stirring rapidly, this reaction mixture was heated for 4 hours at 90 °C, cooled and extracted with 0.7 ml of a saturated aq. NH_4Cl-solution. The organic layer was separated and volatiles were removed under reduced pressure. The residue was filtrated over a short, deactivated (NEt_3) silica gel plug using *iso*-Hexane : Ethylacetate, 9 : 1, concentrated to dryness and dissolved in 7 ml of boiling methanol. The product precipitated over night while cooling to 5 °C. After decanting methanol, this washing process was repeated. The product **4a** was dried under high vacuum and was received as 56.8 mg (90.4 mmol, 41%) of a reddish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.97 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 7-H_1), 6.94 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.9 Hz, 6'-H_1), 6.91 (dd, 1H, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 5-H_1), 6.89 (d, 1H, ^4J = 2.1 Hz, 4'-H_1), 6.83 (d, 1H, ^3J = 10.1 Hz, 4-H_1), 6.76 (dd, 1H, ^3J = 7.5 Hz, ^3J = 7.5 Hz, 6-H_1), 6.44 (d, 1H, ^3J = 7.7 Hz, 7'-H_1), 5.71 (d, 1H, ^3J = 10.1 Hz, 3-H_1), 3.28-2.97 (m, 2H, 13-H_2), 2.59 (dd, 2H, ^3J = 7.8 Hz, ^3J = 7.7 Hz, 15'-H_2), 2.49-2.22 (m, 2H, 15-H_2), 1.73-1.50 (m, 4H, 16-H_2, 16'-H_2), 1.4-1.2 (m, 36H, 18·CH_2), 1.30 (s, 3H, 11-H_3), 1.2 (s, 3H, 12-H_3), 1.15 (t, 3H, ^3J = 7.2 Hz, 14-H_3), 0.89 (t, 6H, ^3J = 7.0 Hz, 17-H_3, 17'-H_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 151.76 (C_9), 145.43 ($C_{8'}$), 137.04 ($C_{9'}$), 133.05 ($C_{5'}$), 130.32 (C_7), 129.50 (C_8), 129.32 (C_4), 126.86 ($C_{6'}$), 124.54 (C_5), 121.73 ($C_{4'}$), 119.43 (C_6), 119.30 (C_3), 118.48 (C_{10}), 105.84 ($C_{7'}$), 104.55 (C_2), 51.63 ($C_{3'}$), 38.21 (C_{13}), 35.88 ($C_{15'}$), 32.27 (C_{16}/$C_{16'}$), 32.13 (C_{16}/$C_{16'}$), 32.11 (C_{15}), 32.10-29.54 (C_{CH2}), 26.10 (C_{11}), 22.87 (C_{CH2}), 20.44 (C_{13}), 14.88 (C_{14}), 14.28 (C_{17}, $C_{17'}$).

MS: (ESI); m/z = 460.36 (6) [$C_{32}H_{46}ON$ ≙ Dodecen-SP-H], 628.55 (100) [MH^+].

entry	base	catalyst	# eq. 9-BBN	t / h	T / °C	crude yield / %
22	NaOH	$PdCl_2$(dppf)	4	4	75	72
23	NaOH	$PdCl_2$(dppf)	4	5	75	75
24	NaOH	$PdCl_2$(dppf)	4	7	80	77
25	NaOH	$PdCl_2$(dppf)	4	4	90	90

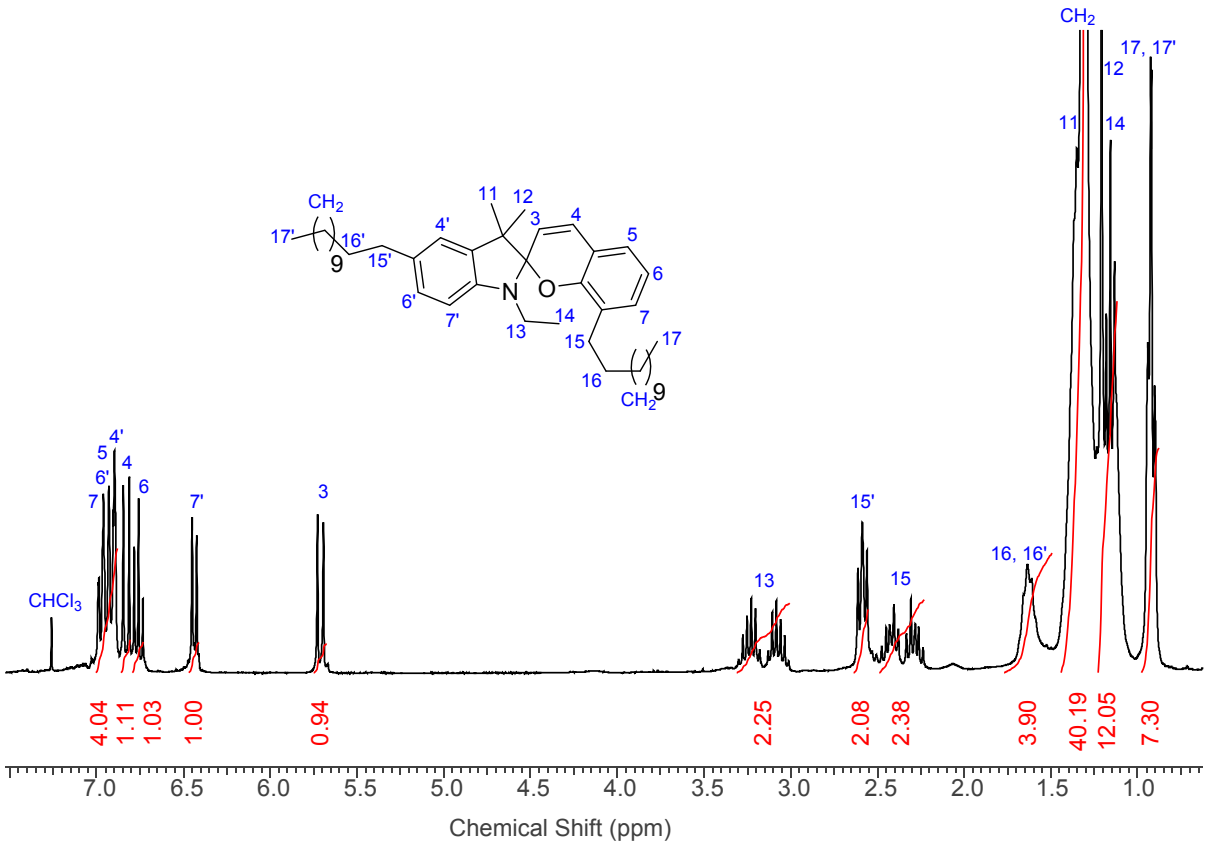


Figure 5: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **4a**.

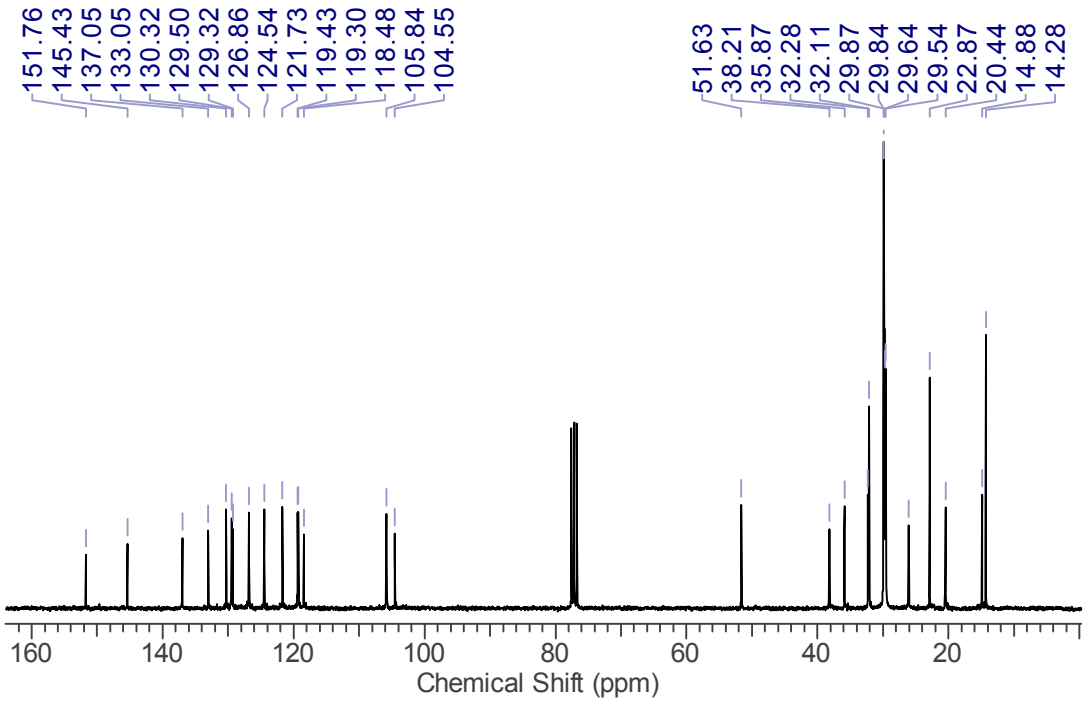
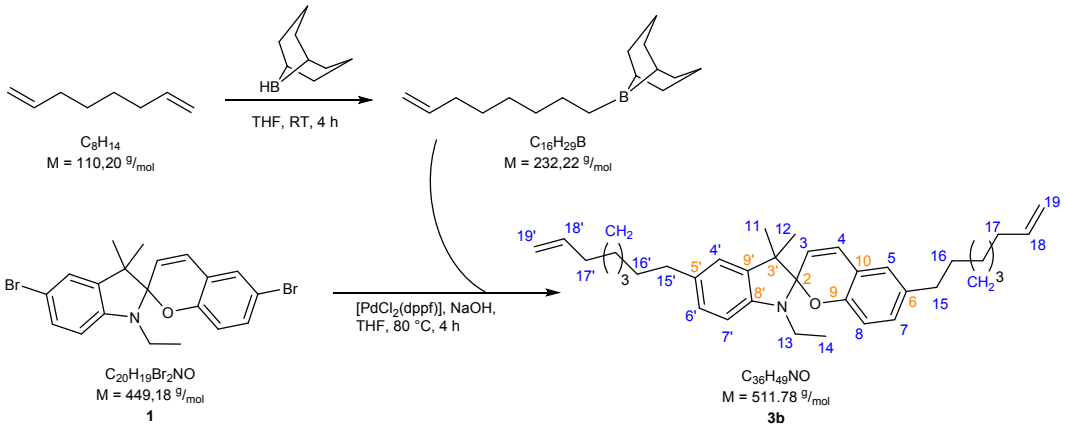


Figure 6: ^{13}C NMR (75 MHz, $CDCl_3$) of compound **4a**.

Synthesis of compound 3b



A 10 ml Schlenk tube was loaded with 0.526 ml (3.57 mmol) 1,7-octadiene, sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). 3.56 ml (1.78 mmol) 9-borabicyclo(3.3.1)nonan (9-BBN) solution in THF (0.5M) was added and the mixture was stirred for 4 hours at room temperature. 203.9 mg (0.446 mmol) of monomer **1** and 6.70 mg (8.92 µmol) of [$PdCl_2$(dppf)] were mixed under nitrogen with the borane-solution, stirred for 5 minutes until 3.0 ml of a N_2 purged 3M aq. NaOH solution were added. Stirring rapidly, this reaction mixture was heated for 4 hours at 80 °C, cooled and extracted with 1.4 ml of a saturated aq. NH_4Cl-solution. The organic layer was separated and volatiles were removed under reduced pressure. The residue was filtrated over a short, deactivated (NEt_3) silica gel plug using *iso*-Hexane : Ethylacetate, 9 : 1, concentrated to dryness and dissolved in 7 ml of boiling methanol. The product precipitated over night while cooling to 5 °C. After decanting methanol, this washing process was repeated. The product **3b** was dried under high vacuum and was received as 123 mg (0.24 mmol, 53%) of a reddish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.95 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 6'-H_1), 6.88 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 7-H_1), 6.87 (d, 1H, ^4J = 1.5 Hz, 4'-H_1), 6.83 (d, 1H, ^4J = 2.1 Hz, 5-H_1), 6.76 (d, 1H, ^3J = 10.1 Hz, 4-H_1), 6.60 (d, 1H, ^3J = 8.2 Hz, 8-H_1), 6.44 (d, 1H, ^3J = 7.8 Hz, 7'-H_1), 5.90-5.75 (m, 2H, 18-H_1, 18'-H_1), 5.64 (d, 1H, ^3J = 10.1 Hz, 3-H_1), 5.06-4.87 (m, 4H, 19-H_2, 19'-H_2) 3.38-3.06 (m, 2H, 13-H_2), 2.57 (dd, 2H, ^3J = 7.8 Hz, ^3J = 7.7 Hz, 15'-H_2), 2.51 (dd, 2H, ^3J = 7.8 Hz, ^3J = 7.7 Hz, 15-H_2), 2.14-1.93 (m, 4H, 17-H_2, 17'-H_2), 1.66-1.50 (m, 4H, 16-H_2, 16'-H_2), 1.4-1.2 (m, 12H, 6·CH_2), 1.30 (s, 3H, 11-H_3), 1.15 (t, 3H, ^3J = 7.2 Hz, 14-H_3), 1.14 (s, 3H, 12-H_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 152.53 (C_9), 145.48 ($C_{8'}$), 139.38 (C_{18}/$C_{18'}$), 139.30 (C_{18}/$C_{18'}$), 136.89 ($C_{9'}$), 134.22 (C_6), 133.08 ($C_{5'}$), 129.57 (C_7), 129.29 (C_4), 127.07 (C_6), 126.44 (C_5), 121.97 ($C_{4'}$), 120.15 (C_3), 118.45 (C_{10}), 114.93 (C_8), 114.31 (C_{19}/$C_{19'}$), 114.28 (C_{19}/$C_{19'}$), 105.89 ($C_{7'}$), 104.68 (C_2), 52.25 ($C_{3'}$), 38.13 (C_{13}), 35.83 ($C_{15'}$), 35.17 (C_{15}), 33.96 (C_{17}/$C_{17'}$), 33.92 (C_{17}/$C_{17'}$), 32.11 (C_{16}/$C_{16'}$), 31.71 (C_{16}/$C_{16'}$), 29.51-29.00 (C_{CH2}), 26.28 (C_{11}), 20.35 (C_{12}), 14.69 (C_{14}).

MS: (ESI); m/z = 512.39 (100) [MH^+].

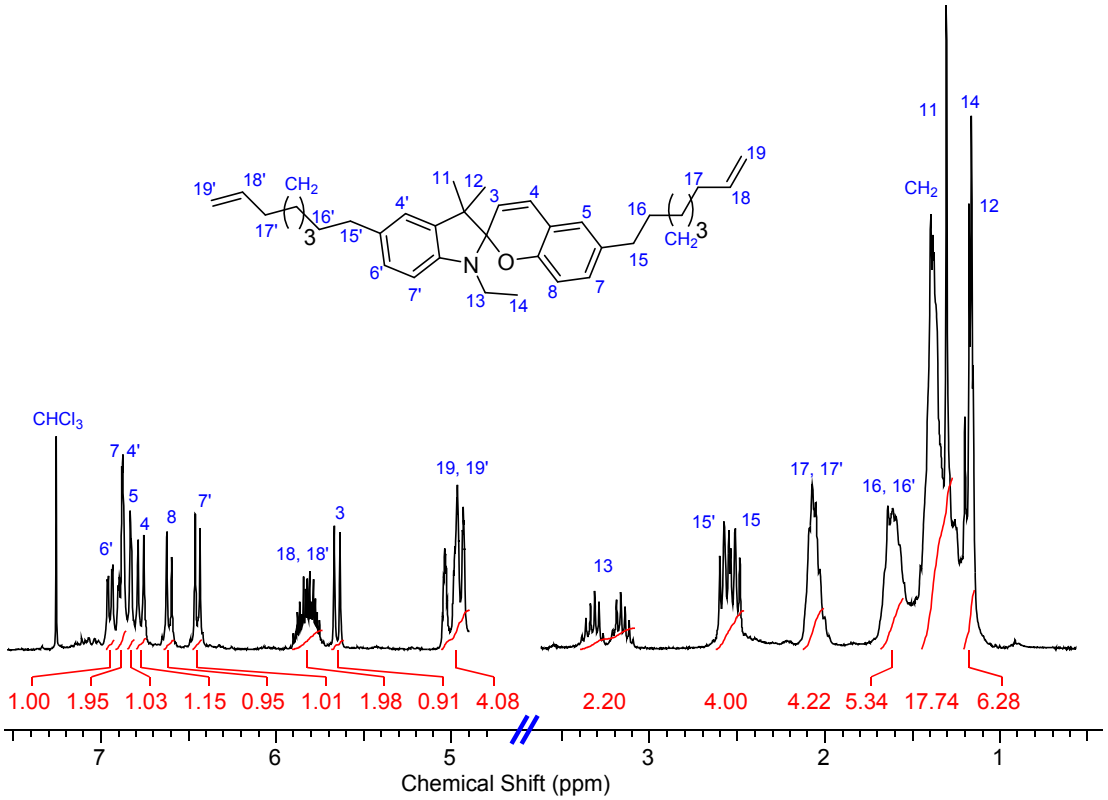


Figure 7: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **3b**.

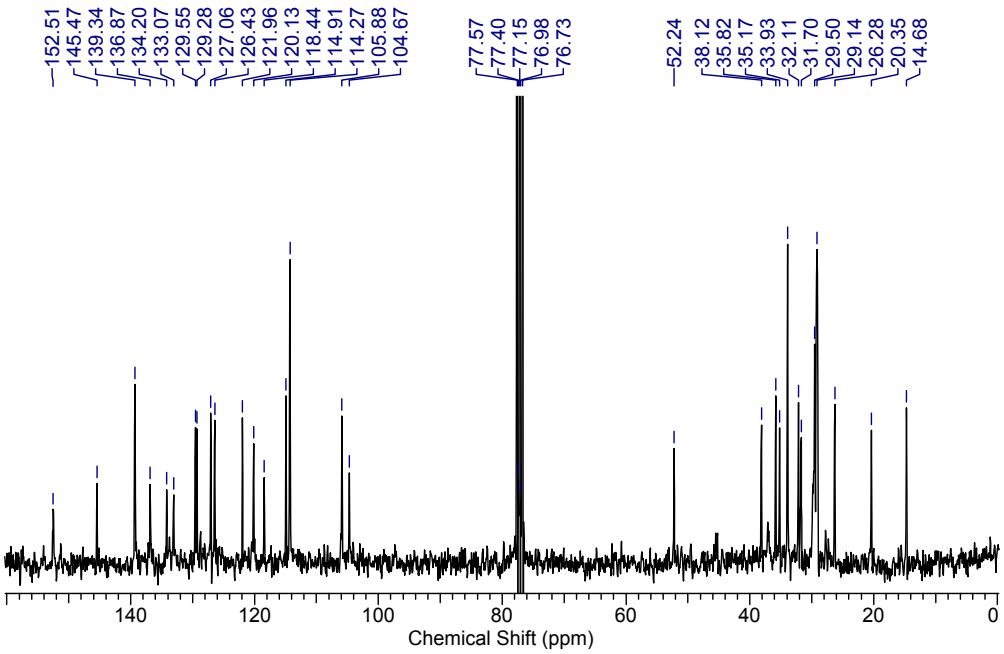
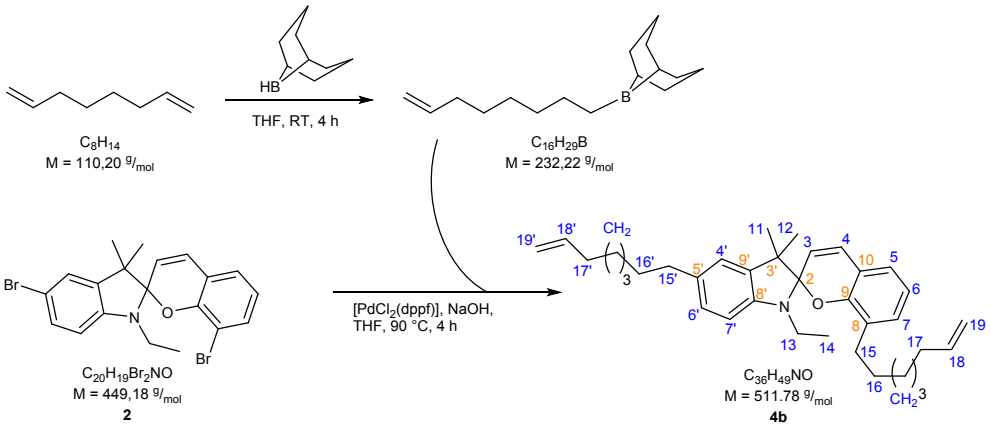


Figure 8: ^{13}C NMR (75 MHz, $CDCl_3$) of compound **3b**.

Synthesis of compound 4b



A 10 ml Schlenk tube was loaded with 0.513 ml (3.48 mmol) 1,7-octadiene, sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). 3.47 ml (1.74 mmol) 9-borabicyclo(3.3.1)nonan (9-BBN) solution in THF (0.5M) was added and the mixture was stirred for 4 hours at room temperature. 195.0 mg (0.434 mmol) of monomer **2** and 6.41 mg (8.70 µmol) of [$PdCl_2$(dppf)] were mixed under nitrogen with the borane-solution, stirred for 5 minutes until 3.0 ml of a N_2 purged 3M aq. NaOH solution were added. Stirring rapidly, this reaction mixture was heated for 4 hours at 90 °C, cooled and extracted with 1.4 ml of a saturated aq. NH_4Cl-solution. The organic layer was separated and volatiles were removed under reduced pressure. The residue was filtrated over a short, deactivated (NEt_3) silica gel plug using *iso*-Hexane : Ethylacetate, 9 : 1, concentrated to dryness and dissolved in 7 ml of boiling methanol. The product precipitated over night while cooling to 5 °C. After decanting methanol, this washing process was repeated. The product **4b** was dried under high vacuum and was received as 116 mg (0.226 mmol, 52%) of a reddish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.97 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 7-H_1), 6.94 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.9 Hz, 6'-H_1), 6.91 (dd, 1H, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 5-H_1), 6.89 (d, 1H, ^4J = 2.1 Hz, 4'-H_1), 6.83 (d, 1H, ^3J = 10.1 Hz, 4-H_1), 6.76 (dd, 1H, ^3J = 7.5 Hz, ^3J = 7.5 Hz, 6-H_1), 6.44 (d, 1H, ^3J = 7.7 Hz, 7'-H_1), 5.92-5.66 (m, 2H, 18-H, 18'-H), 5.71 (d, 1H, ^3J = 10.1 Hz, 3-H_1), 5.07-4.90 (m, 4H, 19-H, 19'-H), 3.28-2.97 (m, 2H, 113-H_2), 2.59 (dd, 2H, ^3J = 7.8 Hz, ^3J = 7.6 Hz, 15'-H_2), 2.49-2.22 (m, 2H, 15-H_2), 2.14-1.93 (m, 4H, 17-H_2, 17'-H_2), 1.66-1.50 (m, 4H, 16-H_2, 16'-H_2), 1.4-1.2 (m, 12H, 6·CH_2), 1.30 (s, 3H, 11-H_3), 1.20 (s, 3H, 14-H_3), 1.15 (t, 3H, ^3J = 7.2 Hz, 12-H_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 151.72 (C_9), 145.41 ($C_{8'}$), 139.42 (C_{18}/$C_{18'}$), 139.35 (C_{18}/$C_{18'}$), 137.03 ($C_{9'}$), 132.94 ($C_{5'}$), 130.30 (C_7), 129.49 (C_8), 129.20 (C_4), 126.85 ($C_{6'}$), 124.56 (C_5), 121.72 ($C_{4'}$), 119.43 (C_6), 119.29 (C_3), 118.46 (C_{10}), 114.28 (C_{19}/$C_{19'}$), 114.15 (C_{19}/$C_{19'}$), 105.81 ($C_{7'}$), 104.52 (C_2), 51.62 ($C_{3'}$), 38.18 (C_{13}), 35.81 ($C_{15'}$), 33.97 (C_{17}/$C_{17'}$), 33.91 (C_{17}/$C_{17'}$), 32.16 (C_{16}, $C_{16'}$), 29.85 (C_{15}), 29.62-28.92 (C_{CH2}), 26.11 (C_{11}), 20.43 (C_{14}), 14.86 (C_{12}).

MS: (ESI); m/z = 512.39 (100) [MH^+].

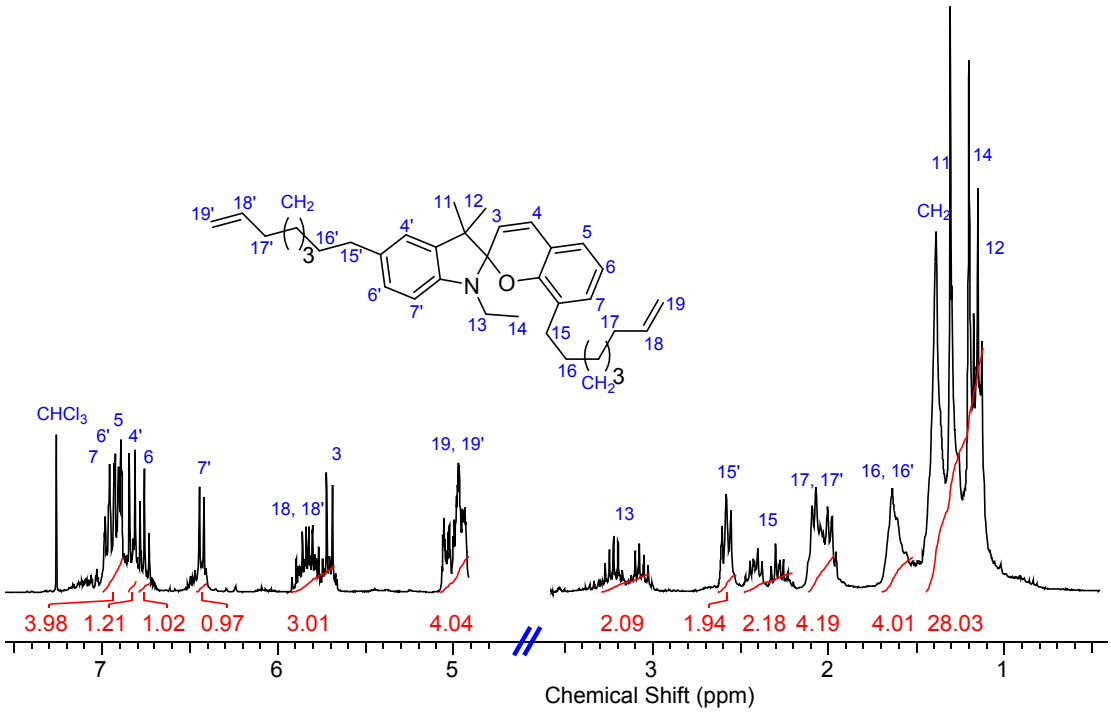


Figure 9: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **4b**.

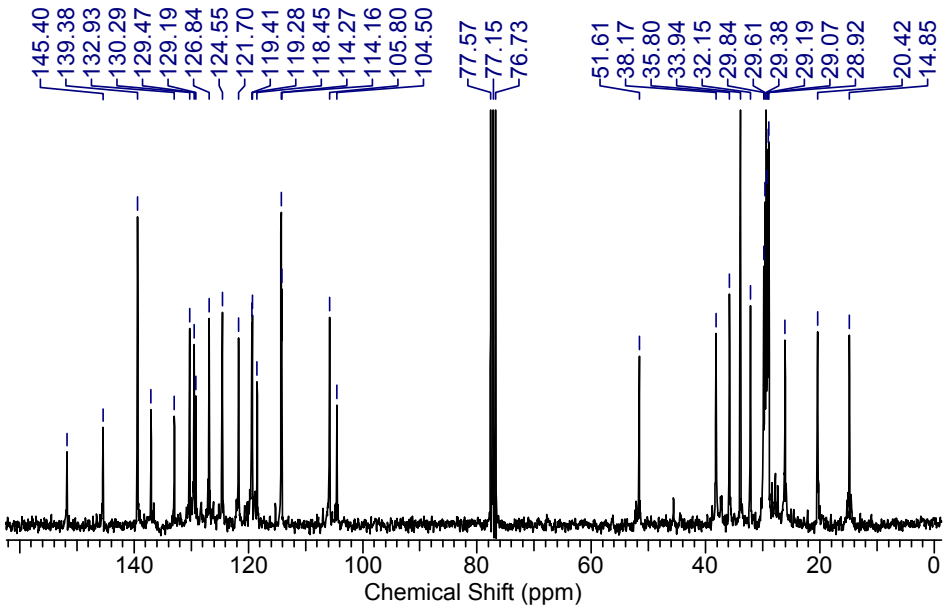
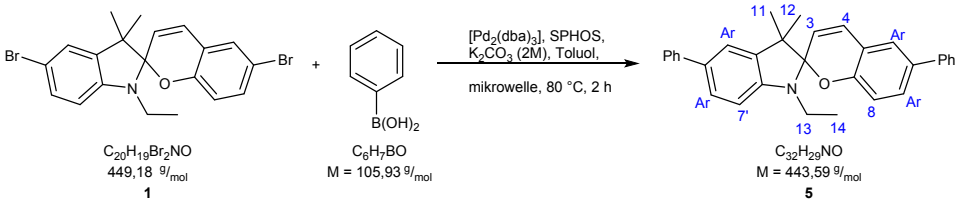


Figure 10: ^{13}C NMR (75 MHz, CDCl3) of compound **4b**.

Synthesis of compound 5



$C_{20}H_{19}Br_2NO$
449,18 g/mol
1

C_6H_7BO
M = 105,93 g/mol

$C_{32}H_{29}NO$
M = 443,59 g/mol
5

In a small microwave vial 101.3 mg (0.223 mmol) of monomer **2** and 68.9 mg (0.558 mmol) of phenylboronic acid were dissolved in 2.2 ml of toluene. 2.2 ml of 3M aq. K_2CO_3 solution and a small amount of Aliquat® were added then the mixture was purged with N_2 for 15 min. Under N_2 2.10 mg (2.23 µmol) of $[Pd_2(dba)_3]$ and 3.81 mg (8.92 µmol) of SPhos were added. By dielectric heating to 80 °C with an average of 30 W for 2 h the reaction was brought to completion. The mixture was extracted with 0.7 ml of a saturated aq. NH_4Cl-solution. The organic layer was separated and volatiles were removed under reduced pressure. The solid residue was filtrated over a short, deactivated (NEt_3) silica gel plug using *iso*-Hexane : Ethylacetate, 9 : 1, concentrated to dryness and recrystallized from Ethanol. The product **5** was dried under high vacuum and was received as 60.4 mg (0.136 mmol, 61%) of a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.61-7.51 (m, 4H, Ar-H_1), 7.45-7.24 (m, 10H, Ar-H_1), 6.91 (d, 1H, ^{3}J = 10.2 Hz, 4-H_1), 6.80 (d, 1H, ^{3}J = 8.40 Hz, 8-H_1), 6.63 (d, 1H, ^{3}J = 8.1 Hz, 7'-H_1), 5.75 (d, 1H, ^{3}J = 10.2 Hz, 3-H_1), 3.48-3.18 (m, 2H, 13-H_2), 1.38 (s, 3H, 11-H_3), 1.23 (t, 3H, ^{3}J = 7.1 Hz, 14-H_3), 1.23 (s, 3H, 12-H_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 153.93, 146.86, 142.06, 140.83, 137.41, 133.33, 132.12, 129.48, 128.85, 128.76, 128.56, 126.78, 126.75, 126.71, 126.68, 126.18, 125.45, 120.89, 120.23, 118.87, 115.61, 106.48, 105.02, 52.43, 38.08, 26.36, 20.28, 14.58.

MS: (ESI); m/z = 443.22 (100) [M].

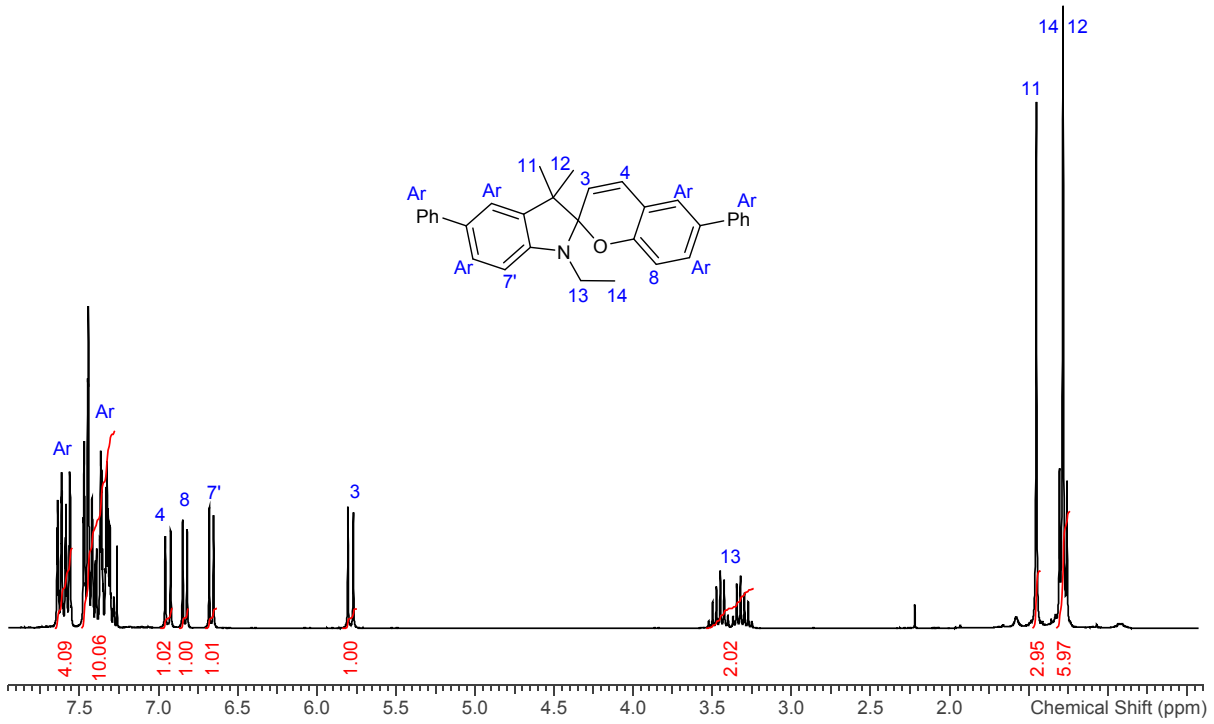


Figure 11: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **5**.

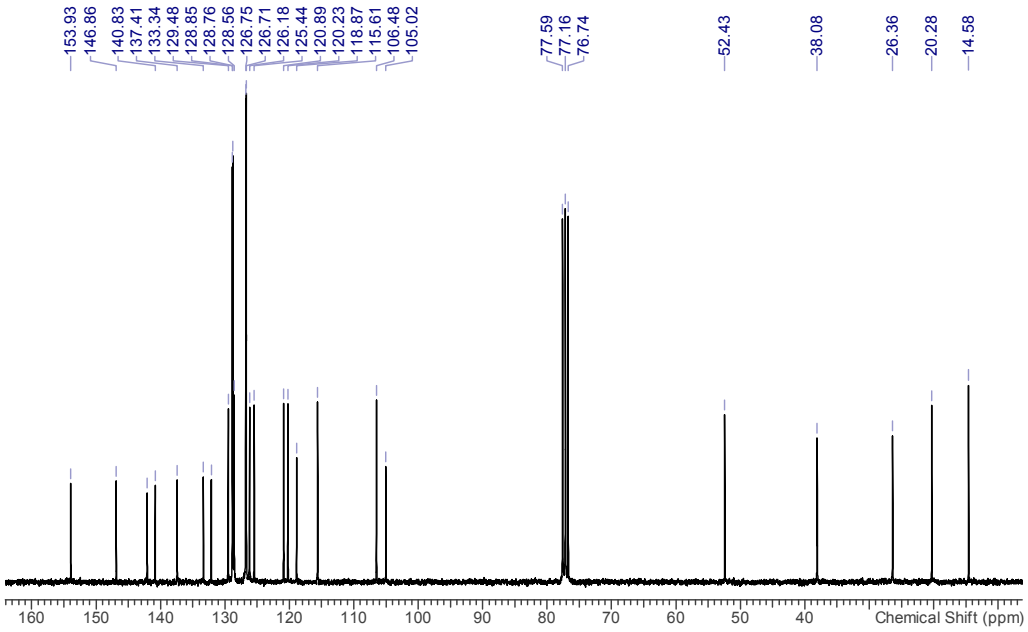
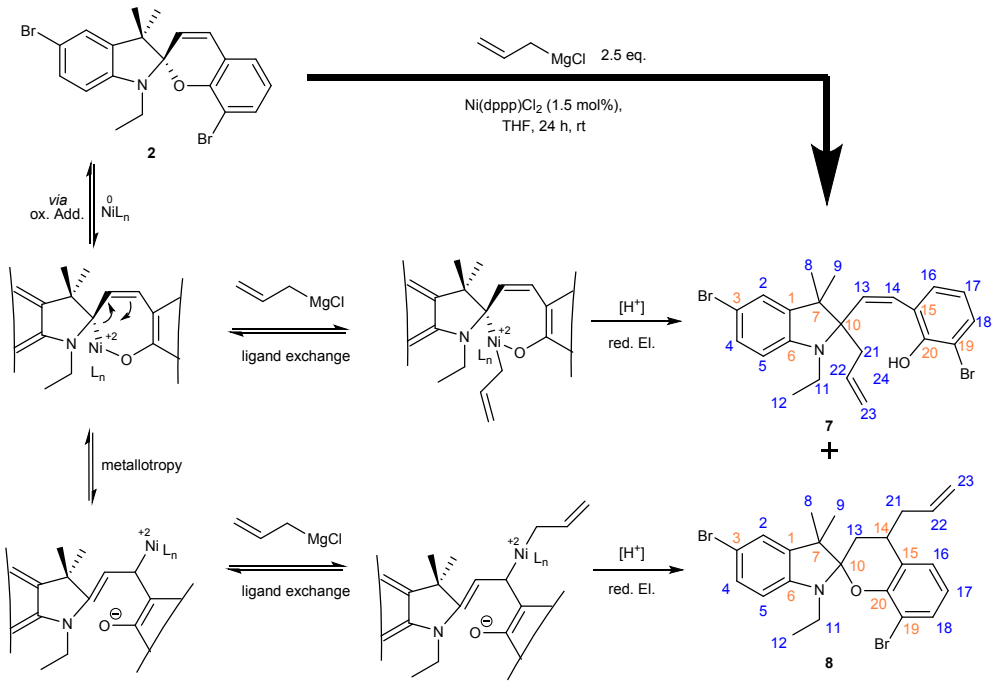


Figure 12: ^{13}C NMR (75 MHz, $CDCl_3$) of compound **5**.

Kumada coupling



Scheme 1: Kumada coupling reaction with a plausible reaction mechanism.

Under N_2 atmosphere 1.90 g (4.24 mmol) of compound **2** and 34.9 mg (0.0643 mmol) of $Ni(dppp)Cl_2$ were dissolved in 50 ml of dry THF, then 3.93 mL (10.6 mmol) of a allylmagnesium chloride solution (2.0M in THF) were added. The reaction mixture was stirred for 24 h at ambient temperature, cooled to 0 °C, then 15 ml of an aq. HCl solution (0.1M) were added. The organic phase was washed with 100 ml water, the aqueous layer was extracted two times with 25 ml of diethyl ether. All combined organic phases were dried with $MgSO_4$ and the volatiles were removed under reduced pressure. The crude products were purified by column chromatography (silica, *i*-Hexane : Et_2O, 9 : 1, deactivated with 5 vol% NEt_3).

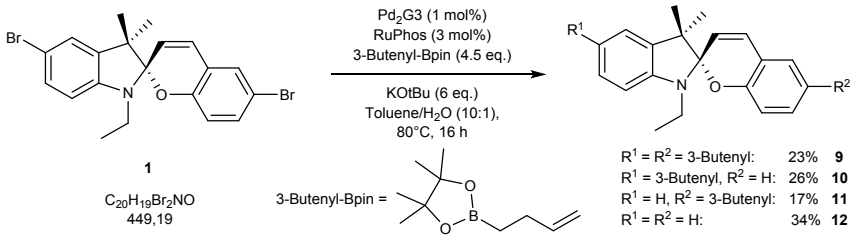
compound 7: **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.09 (dd [X-part of the ABX_3-signal], $^3J_{12,11}$ = 7.1 Hz, 3H, 12-H), 1.22 (s, 3H, 8/9-H), 1.29 (s, 3H, 9/8-H), 2.38 (m [AB-Teil des ABX-Signals], 2H, 21-H), 2.77 (m, [A-part of the ABX_3-signal], 1H, 11-H), 3.03 (m, [B-part of the ABX_3-signal], 1H, 11-H), 4.82 (dd, $^3J_{23,22}$ = 10.1 Hz, $^2J_{23,23}$ = 1.4 Hz, 1H, 23-H), 4.87 (dd, $^3J_{23,22}$ = 17.0 Hz, $^2J_{23,23}$ = 1.4 Hz, 1H, 23-H), 5.60 (m, 1H, 22-H), 5.84 (d, $^3J_{13,14}$ = 13.1 Hz 13-H), 6.53 (d, $^3J_{14,13}$ = 13.1 Hz, 1H, 14-H), 6.73 (dd, $^3J_{17,16}$ = 7.8 Hz, $^3J_{17,18}$ = 7.8 Hz, 1H, 17-H), 7.08 (d, $^4J_{2,4}$ = 1.9 Hz, 1H, 2-H), 7.23 (dd, $^3J_{4,5}$ = 8.3 Hz, $^4J_{4,2}$ = 1.9 Hz, 1H, 4-H) , 7.23 (dd, $^3J_{16,17}$ = 7.8 Hz, $^4J_{16,18}$ = 1.9 Hz, 1H, 16-H), 7.33 (dd, $^3J_{18,17}$ = 8.0 Hz, $^4J_{18,16}$ = 1.6 Hz, 1H, 18-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 14.72 (s, 1C, 12-C), 23.37 (s, 1C, 8/9-C), 25.90 (s, 1C, 9/8-C), 38.49 (s, 1C, 11-C), 39.27 (s, 1C, 21-C), 48.31 (s, 1C, 7-C), 103.61 (s, 1C, 10-C), 107.71 (s, 1C, 5-C), 107.42 (s, 1C, 3-C), 109.91 (s, 1C, 19-C), 118.10 (s, 1C, 23-C), 120.35 (s, 1C, 17-C) 124.54 (s, 1C, 2-C), 124.91 (s, 1C, 16-C), 125.75 (s, 1C, 14-C), 130.13 (s, 1C, 4-C), 131.62 (s, 1C, 18-C), 136.83 (s, 1C, 13-C), 139.42 (s, 1C, 1-C), 147.92 (s, 1C, 6-C), 149.10 (s, 1C, 20-C).

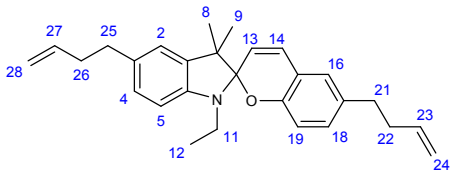
compound 8: **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.18 (s, 3H, 8/9-H), 1.21 (s, 3H, 9/8-H), 1.23 (dd [X-part of the ABX_3-signal], $^3J_{12,11}$ = 7.1 Hz, 3H, 12-H), 1.91 (dd, $^3J_{13,14}$ = 13.0 Hz, $^2J_{13,13}$ = 14.4 Hz, 1H, 13-H), 2.34 (dd, $^3J_{13,14}$ = 4.7 Hz, $^2J_{13,13}$ = 14.4 Hz, 1H, 13-H), 2.36 (m, 1H, 21-H), 2.89 (m, 1H, 21-H), 3.17 (m, 3H, 14-H), 3.22 (m, [A-part of the ABX_3-signal], 1H, 11-H), 3.35 (m, [B-part of the ABX_3-signal], 1H, 11-H), 5.17 (dd, $^3J_{23,22}$ = 10.3 Hz, $^2J_{23,23}$ = 2.1 Hz, 1H, 23-H), 5.21 (dd, $^3J_{23,22}$ = 17.1 Hz, $^2J_{23,23}$ = 2.1 Hz, 1H, 23-H), 5.86 (dd, $^3J_{22,23}$ = 17.1 Hz, $^3J_{22,23}$ = 10.3 Hz, 1H, 22-H), 6.43 (dd, $^3J_{5,4}$ = 8.3 Hz, 1H, 5-H), 6.73 (dd, $^3J_{17,16}$ = 7.8 Hz, $^3J_{17,18}$ = 7.8 Hz, 1H, 17-H), 7.08 (d, $^4J_{2,4}$ = 1.9 Hz, 1H, 2-H), 7.23 (dd, $^3J_{4,5}$ = 8.3 Hz, $^4J_{4,2}$ = 1.9 Hz, 1H, 4-H) , 7.23 (dd, $^3J_{16,17}$ = 7.8 Hz, $^4J_{16,18}$ = 1.9 Hz, 1H, 16-H), 7.35 (d, $^3J_{18,17}$ = 8.3 Hz, $^4J_{18,16}$ = 1.9 Hz, 1H, 18-H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 14.53 (s, 1C, 12-C), 21.98 (s, 1C, 8/9-C), 25.60 (s, 1C, 9/8-C), 31.01 (s, 1C, 13-C), 31.87 (s, 1C, 14-C), 37.24 (s, 1C, 11-C), 37.79 (s, 1C, 21-C), 49.41 (s, 1C, 7-C), 103.61 (s, 1C, 10-C), 107.71 (s, 1C, 5-C), 109.80 (s, 1C, 3-C), 110.97 (s, 1C, 19-C), 118.10 (s, 1C, 23-C), 120.35 (s, 1C, 17-C) 124.54 (s, 1C, 2-C), 124.91 (s, 1C, 16-C), 125.77 (s, 1C, 15-C), 130.13 (s, 1C, 4-C), 131.62 (s, 1C, 18-C), 134.91 (s, 1C, 22-C), 139.42 (s, 1C, 1-C), 146.80 (s, 1C, 6-C), 151.87 (s, 1C, 20-C).

Suzuki-Miyaura coupling with boronic esters



Under N_2 atmosphere a small Schlenk tube was loaded with 50.0 mg (111 µmol) of **1**, 74.9 mg (668 µmol) KOtBu, 0.82 mg (1.11 µmol) Pd_2G3 and 1.55 mg (3.33 µmol) of RuPhos. 90.9 mg (500 µmol) of 3-Butenyl-Bpin were dissolved in 0.5 ml toluene and 0.05 ml water. This solution was purged with N_2 then added to the reaction mixture, which was rapidly stirred at 80 °C for 16 h. The addition of 1.0 ml aqueous sat. NH_4Cl solution finished the reaction. The organic phase was separated, the aqueous layer was extracted two times with 2 ml of diethyl ether. All combined organic phases were dried with $MgSO_4$ and the volatiles were removed under reduced pressure. Suzuki-Miyaura couplings with boronic esters did not yield the desired dialkenylated spiropyran as the main product. This is mainly due to a competing debromination reaction, leading to mixtures of monoalkenylated or entirely debrominated SP, which were found to be hard to separate. Nevertheless, through purifying by HPLC (MeOH : aq. KH_2PO_4 (5.0 mM) 9 : 1) and comparison of obtained ^{1}H NMR signals with the fully characterised compound **4b** we could determine the different products and therefore their approx. ratios.



compound 9: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.135 (s, 3 H, 8-H), 1.149 (dd, AB*X*$_3$ signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H), 1.277 (s, 3 H, 9-H), 2.27-2.42 (m, 4 H, 22-H, 26-H), 2.56-2.70 (m, 4 H, 21-H, 25-H), 3.05-3.38 (m, *AB*X$_3$ signal, 2 H, 11-H), 4.93-5.12 (m, 4 H, 24-H, 28-H), 5.646 (d, $^{3}J_{13,14}$ = 10.3 Hz, 1 H, 13-H), 5.77-5.99 (m, 2 H, 23-H, 27-H), 6.448 (d, $^{3}J_{5,4}$ = 7.8 Hz, 1 H, 5-H), 6.612 (d, $^{3}J_{19,18}$ = 8.2 Hz, 1 H, 19-H), 6.770 (d, $^{3}J_{14,13}$ = 10.3 Hz, 1 H, 14-H), 6.840 (d, $^{4}J_{16,18}$ = 1.7 Hz, 1 H, 16-H), 6.889 (d, $^{4}J_{2,4}$ = 1.9 Hz, 1 H, 2-H), 6.896 (dd, $^{3}J_{18,19}$ = 8.2 Hz, $^{4}J_{18,16}$ = 1.7 Hz, 1 H, 18-H), 6.962 (dd, $^{3}J_{4,5}$ = 7.8 Hz, $^{4}J_{4,2}$ = 1.9 Hz, 1 H, 4-H).

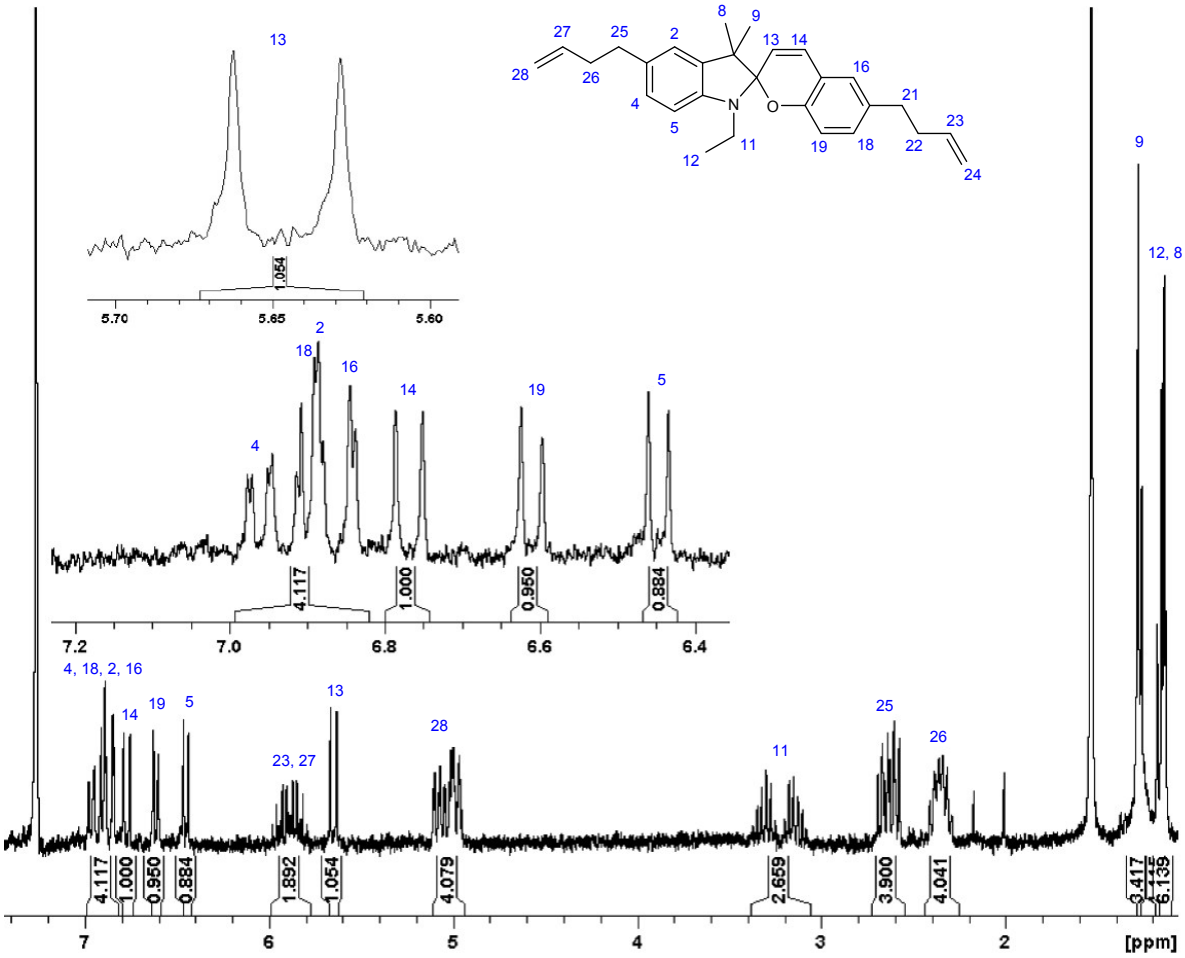
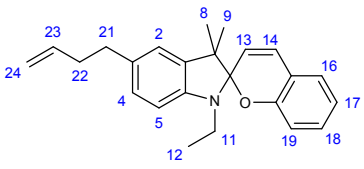
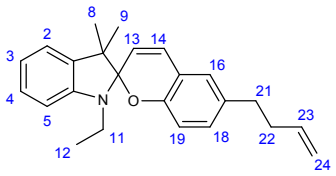


Figure 13: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **9**.



compound 10: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.14 (s, 3 H, 8-H / 9-H), 1.15 (dd, AB*X*$_3$ signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H,), 1.28 (s, 3 H, 9-H / 8-H), 2.34-2.42 (m, 2 H, 22-H), 2.63-2.70 (m, 2 H, 21-H), 3.08-3.40 (m, *AB*X$_3$ signal, 2 H, 11-H), 4.94-5.12 (m, 2 H, 24-H), 5.692 (d, $^{3}J_{13,14}$ = 10.3 Hz, 1 H, 13-H), 5.78-5.99 (m, 1 H, 23-H), 6.457 (d, ^{3}J = 7.8 Hz, 1 H, 5-H), 6.689 (d, ^{3}J = 8.2 Hz, 1 H, $H_{arom.}$), 6.77-6.83 (m, 2 H, $H_{arom.}$ / $H_{olef.}$), 6.887-6.916 (m, 1 H, 2-H), 6.94-7.11 (m, 3 H, $H_{arom.}$).



compound 11: **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.14 (s, 3 H, 8-H / 9-H), 1.15 (dd, ABX_3 signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H), 1.29 (s, 3 H, 9-H / 8-H), 2.28-2.36 (m, 2 H, 22-H), 2.56-2.64 (m, 2 H, 21-H), 3.08-3.40 (m, *AB*X_3 signal, 2 H, 11-H), 4.94-5.12 (m, 2 H, 24-H), 5.686 (d, $^{3}J_{13,14}$ = 10.2 Hz, 1 H, 13-H), 5.78-5.99 (m, 1 H, 23-H), 6.529 (d, ^{3}J = 7.8 Hz, 1 H, $H_{arom.}$), 6.600 (d, $^{3}J_{19,18}$ = 8.2 Hz, 1 H, 19-H), 6.76-6.86 (m, 2 H, $H_{arom.}$), 6.849 (d, $^{4}J_{16,18}$ = 1.8 Hz, 1 H, 16-H), 6.902 (d, $^{3}J_{14,13}$ = 10.3 Hz, 1 H, 14-H), 7.03-7.08 (m, 1 H, $H_{arom.}$), 7.146 (ddd, ^{3}J = 7.7 Hz, ^{3}J = 7.7 Hz, ^{5}J = 1.3 Hz, 1 H, $H_{arom.}$).

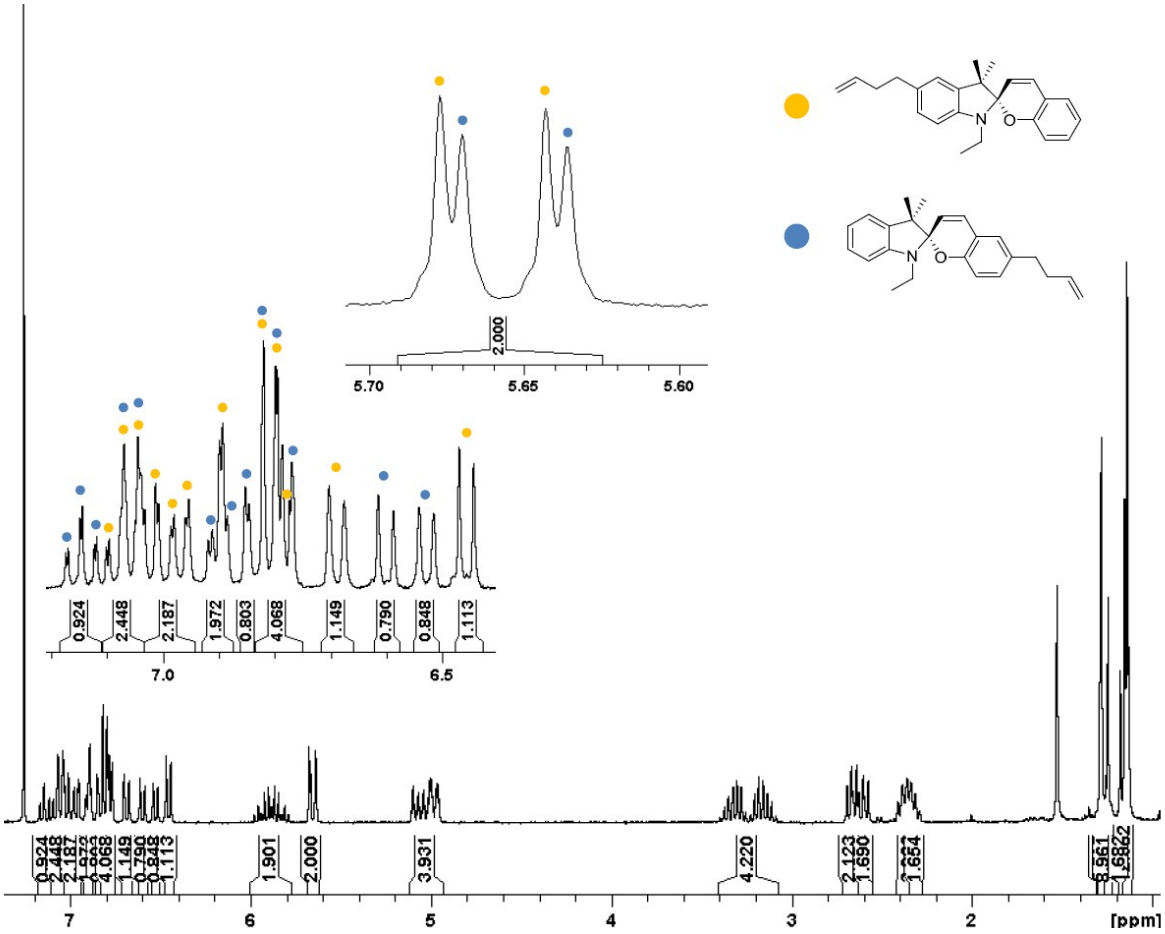
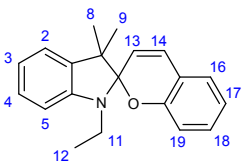


Figure 14: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **10** (yellow dot) and **11** (blue dot).



compound 12: **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.148 (s, 3 H, 8-H / 9-H), 1.161 (dd, ABX_3 signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H), 1.296 (s, 3 H, 9-H / 8-H), 3.11-3.41 (m, *AB*X_3 signal, 2 H, 11-H), 5.666 (d, $^{3}J_{13,14}$ = 10.2 Hz, 1 H, 13-H), 6.537 (d, ^{3}J = 7.8 Hz, 1 H, $H_{arom.}$), 6.677 (d, ^{3}J = 8.2 Hz, 1 H, $H_{arom.}$), 6.77-6.91 (m, 3 H, $H_{arom.}$ / $H_{olefin.}$), 7.00-7.11 (m, 3 H, $H_{arom.}$), 7.152 (ddd, ^{3}J = 7.7 Hz, ^{3}J = 7.7 Hz, ^{5}J = 1.3 Hz, 1 H, $H_{arom.}$).

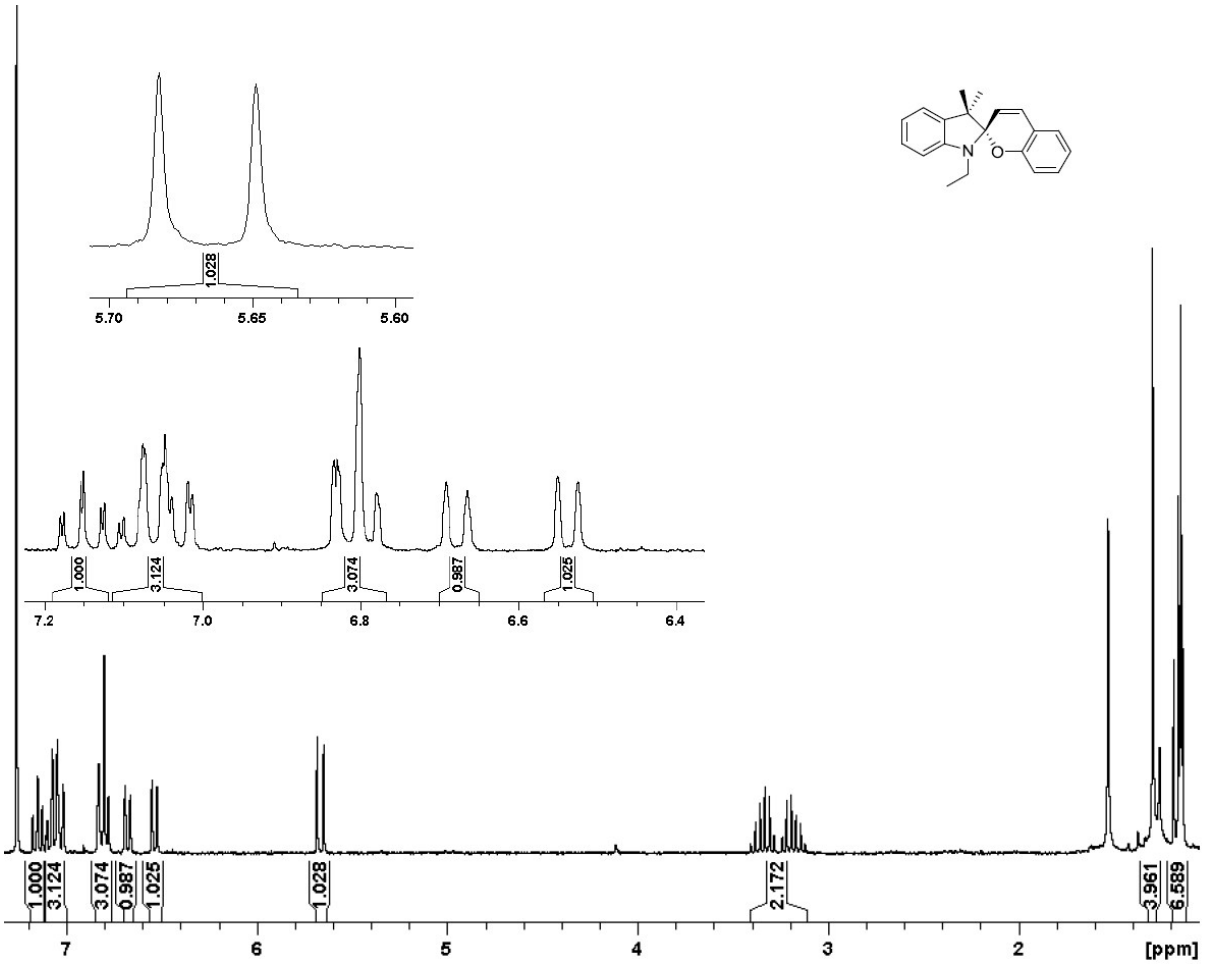
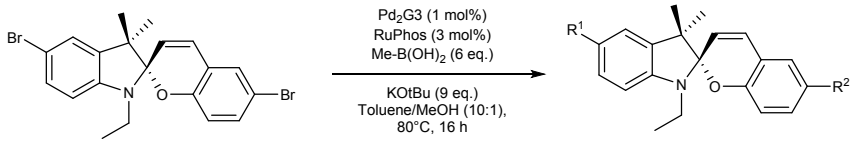


Figure 15: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **12**.

Suzuki-Miyaura coupling with boronic acids

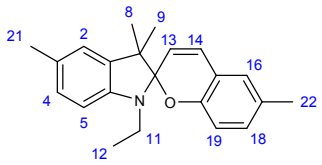


1

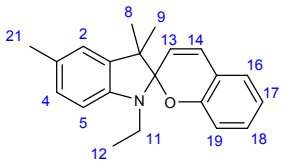
$C_{20}H_{19}Br_2NO$
449,19

$R^1 = R^2 =$ Me:	7%	**13**
R^1 = Me, R^2 = H:	24%	**14**
R^1 = H, R^2 = Me:	19%	**15**
$R^1 = R^2$ = H:	50%	**12**

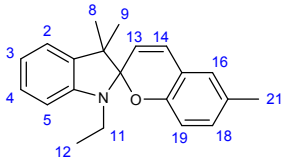
Under N_2 atmosphere a small Schlenk tube was loaded with 50.0 mg (111 µmol) of **1**, 112 mg (1.00 µmol) KOtBu, 0.82 mg (1.11 µmol) Pd_2G3 and 1.56 mg (3.33 µmol) of RuPhos. 90.9 mg (500 µmol) of 3-Butenyl-Bpin were dissolved in 0.5 ml of dry toluene and 0.05 ml of dry MeOH. This solution was purged with N_2 then added to the reaction mixture, which was stirred at 80 °C for 16 h. The addition of 1.0 ml aqueous sat. NH_4Cl solution finished the reaction. The organic phase was separated, the aqueous layer was extracted two times with 2 ml of diethyl ether. All combined organic phases were dried with $MgSO_4$ and the volatiles were removed under reduced pressure. Suzuki-Miyaura couplings with boronic esters did not yield the desired dialkylated spiropyran as the main product. This is mainly due to a competing debromination reaction, leading to mixtures of monoalkylated or entirely debrominated SP, which were found to be hard to separate. Nevertheless, through purifying by HPLC (MeOH : aq. KH_2PO_4 (5.0 mM) 9 : 1) and comparison of obtained ^{1}H NMR signals with the fully characterised compound **4a** we could determine the different products and therefore their approx. ratios.



compound 13: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.129 (s, 3 H, 8-H), 1.139 (dd, AB*X*$_3$ signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H), 1.270 (s, 3 H, 9-H), 2.238 (s, 3 H, 22-H), 2.304 (s, 3 H, 21-H), 3.05-3.38 (m, *AB*X$_3$ signal, 2 H, 11-H), 5.639 (d, $^{3}J_{13,14}$ = 10.2 Hz, 1 H, 13-H), 6.434 (d, $^{3}J_{5,4}$ = 7.8 Hz, 1 H, 5-H), 6.580 (d, $^{3}J_{19,18}$ = 8.2 Hz, 1 H, 19-H), 6.759 (d, $^{3}J_{14,13}$ = 10.2 Hz, 1 H, 14-H), 6.838 (d, $^{4}J_{16,18}$ = 2.0 Hz, 1 H, 16-H), 6.869 (d, $^{4}J_{2,4}$ = 1.9 Hz, 1 H, 2-H), 6.91-6.97 (m, 1 H, 18-H), 7.143 (dd, $^{3}J_{4,5}$ = 7.8 Hz, $^{4}J_{4,2}$ = 1.4 Hz, 1 H, 4-H).



compound 14: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.139 (s, 3 H, 8-H / 9-H), 1.146 (dd, AB*X*$_3$ signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H,), 1.279 (s, 3 H, 9-H / 8-H), 2.310 (s, 3 H, 21-H), 3.08-3.40 (m, *AB*X$_3$ signal, 2 H, 11-H), 5.658 (d, $^{3}J_{13,14}$ = 10.3 Hz, 1 H, 13-H), 6.443 (d, ^{3}J = 7.8 Hz, 1 H, 5-H), 6.677 (d, ^{3}J = 8.2 Hz, 1 H, $H_{arom.}$), 6.75-6.91 (m, 3 H, $H_{arom.}$ / $H_{olef.}$), 6.951 (d, ^{3}J = 8.2 Hz, 1 H, $H_{arom.}$), 7.149 (dd, $^{3}J_{4,5}$ = 7.8 Hz, $^{4}J_{4,2}$ = 1.4 Hz, 1 H, 4-H).



compound 15: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.136 (s, 3 H, 8-H / 9-H), 1.153 (dd, AB*X*$_3$ signal: $^{3}J_{12,11A}$ = 7.1 Hz, $^{3}J_{12,11B}$ = 7.1 Hz, 3 H, 12-H,), 1.285 (s, 3 H, 9-H / 8-H), 2.241 (s, 3 H, 21-H), 3.08-3.40 (m, *AB*X$_3$ signal, 2 H, 11-H), 5.646 (d, $^{3}J_{13,14}$ = 10.3 Hz, 1 H, 13-H), 6.527 (d, ^{3}J = 7.8 Hz, 1 H, $H_{arom.}$), 6.580 (d, ^{3}J = 8.1 Hz, 1 H, 19-H), 6.75-6.91 (m, 3 H, $H_{arom.}$ / $H_{olefin.}$), 6.838 (d, ^{4}J = 2.0 Hz, 1 H, 16-H), 7.03-7.08 (m, 1 H, 18-H), 7.143 (ddd, ^{3}J = 7.7 Hz, ^{3}J = 7.7 Hz, ^{5}J = 1.3 Hz, 1 H, $H_{arom.}$).

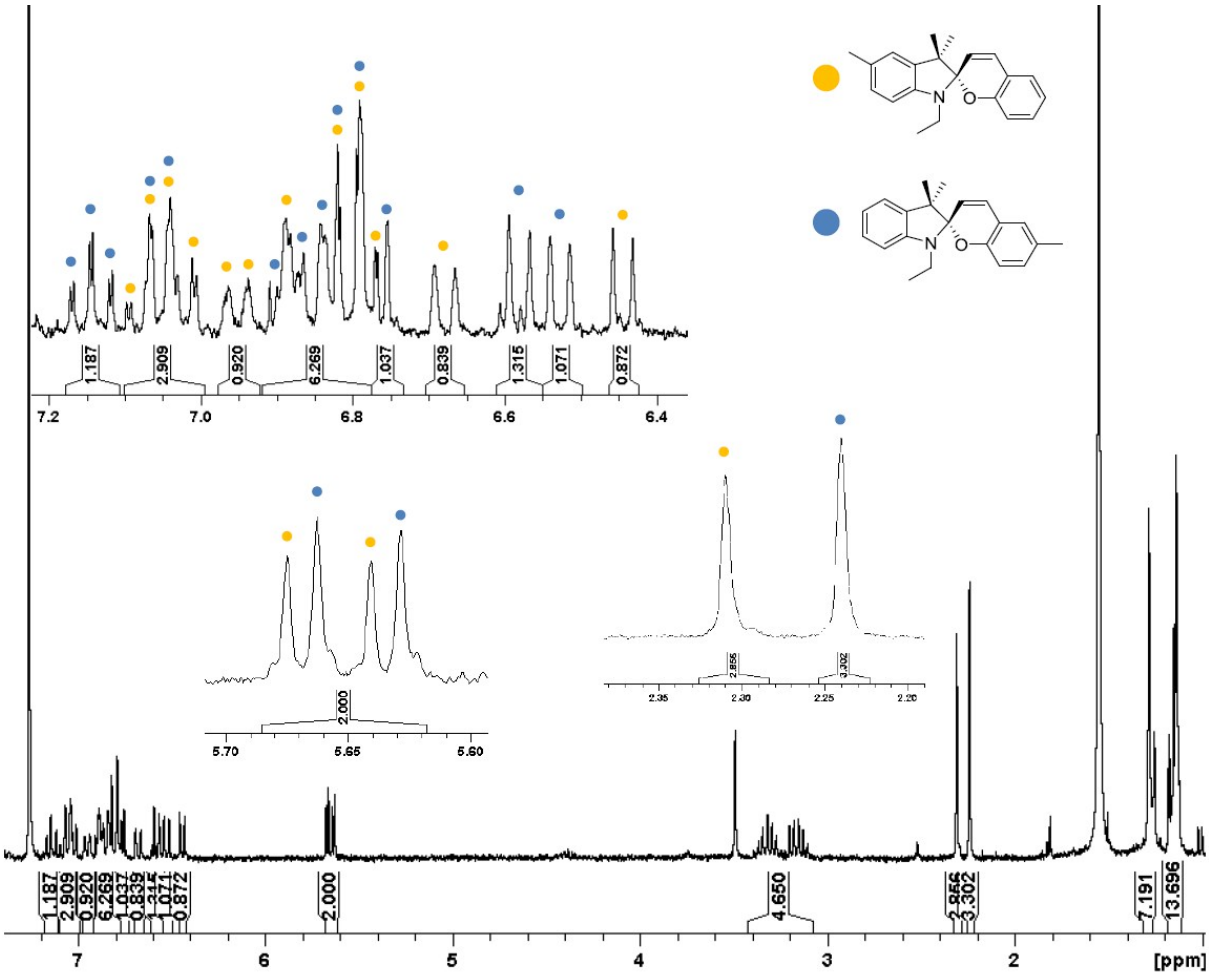


Figure 16: ^{1}H NMR (300 MHz, $CDCl_3$) of compound **14** (yellow dot) and **15** (blue dot).

^{1}H NMR of alkylated SP and MCH^{+}

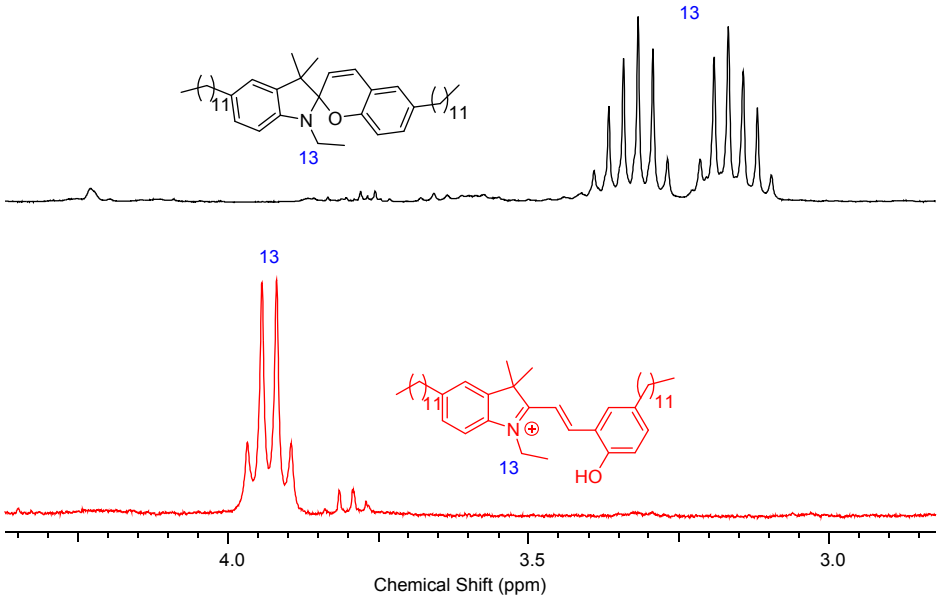


Figure 17: Comparison of the methylene group's ^{1}H NMR Signals from alkylated spiropyran **3a** in $CDCl_3$ (top) and in its protonated merocyanine form in $CDCl_3$ with trifluoroacedic acid as an additive (bottom).

^{13}C NMR of P(octylSP) 6

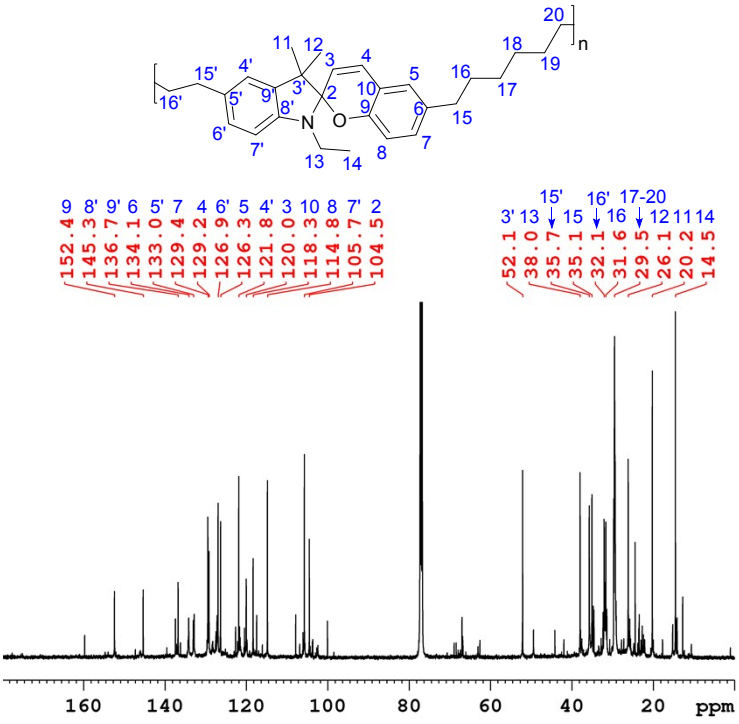


Figure 18: ^{13}C NMR (75 MHz, $CDCl_3$) of the P(octylSP) **6** with the peak assignment.

^{11}B NMRs of the hydroboration reaction

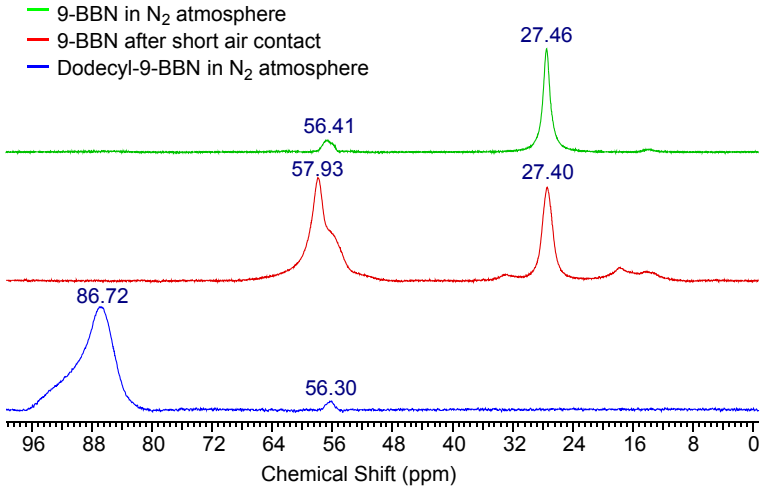


Figure 19: ^{11}B NMR (96.2 MHz, $CDCl_3$) under N_2 atmosphere of the 9-BBN reactant (top), of 9-BBN after short contact with air (middle) and of the dodecyl-9-BBN product (bottom). After 4 h of hydroboration no residual 9-BBN is in the product NMR visible anymore, the impurity signal at 56.3 ppm might arise from quenched 9-BBN after air contact (whether before, during the reaction or while loading the NMR tube).

Infrared spectroscopy of alkylated SP

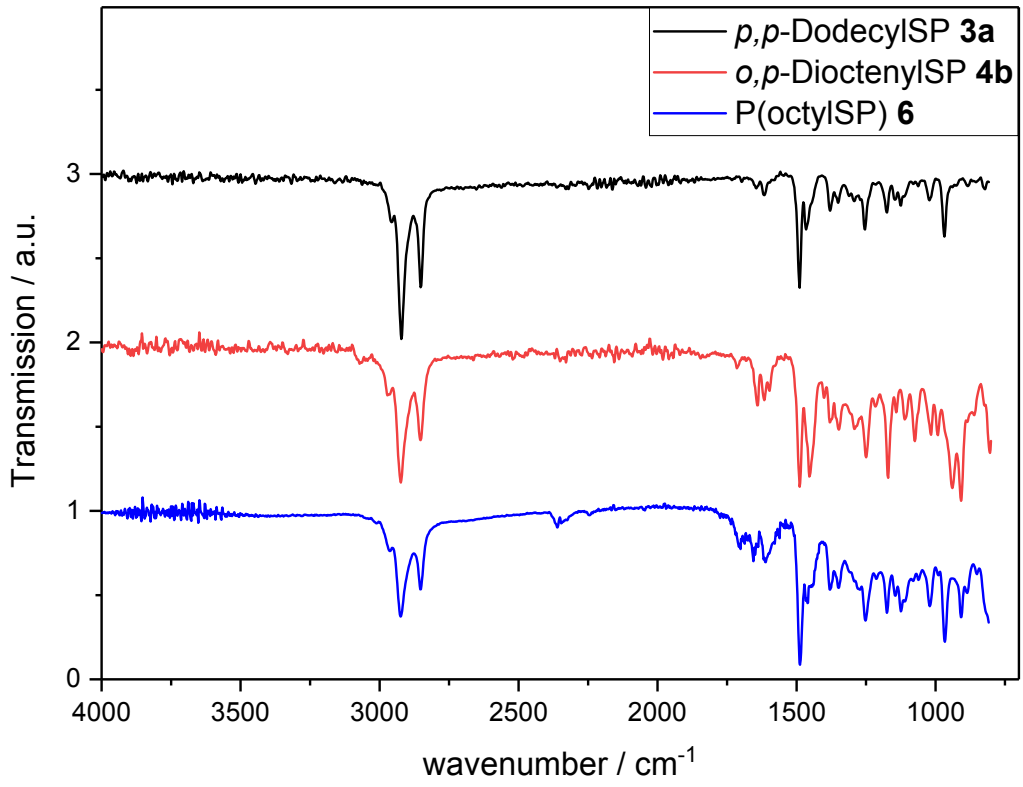


Figure 20: Infrared spectra of alkylated Spiropyrans: *p,p*-DidodecylSP **3a** (top), *o,p*-DioctenylSP **4b** (middle) and P(octylSP) (bottom). Measured on the ATR-IR FTS-165 from BioRad.

Thermogravimetrical analysis of 4b

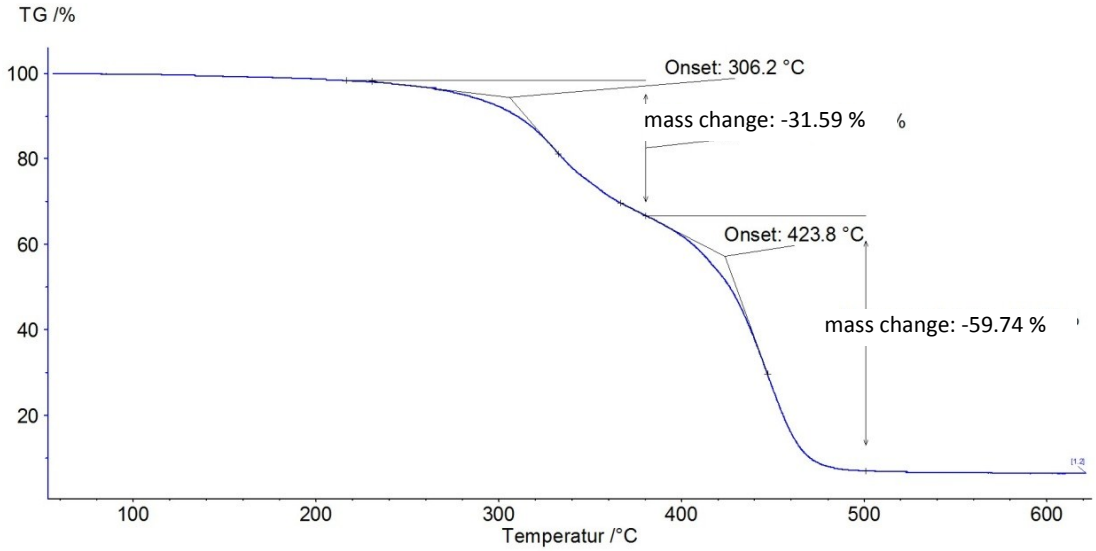


Figure 21: Thermogravimetrical analysis of compound **4b** under N_2 atmosphere at a constant heating rate of 10 K/min, measured in a Netzsch STA 409 machine.

References

1 O. Brügner, T. Reichenbach, M. Sommer and M. Walter, *J. Phys. Chem. A*, 2017, **121**, 2683–2687.