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Supporting Information

Rational Design of Azothiophenes—Substitution Effects on the Switching Properties

Andreas H. Heindl[a, b] and Hermann A. Wegner*[a, b]

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Andreas H. Heindl, Hermann A. Wegner[1]

Address: [1]Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen (Germany) and Center for Materials Research (LaMa), Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen (Germany)

Email: Hermann A. Wegner – hermann.a.wegner@org.chemie.uni-giessen.de

* Corresponding author

Supporting Information

General Information

Chemicals were used as purchased from Sigma-Aldrich, Acros Organics, Alfa Aesar or TCI Europe. Anhydrous solvents were purchased from Acros Organics. Technical grade solvents for workup and purification were distilled prior to use. Air and/or water-sensitive reactions were carried out under Schlenk-conditions or in a nitrogen-filled glovebox. Solids were dried under high vacuum (oil pump, ca 10^{-3} mbar) at room temperature (rt), 50 °C or 60 °C if necessary. Flash column chromatography and column chromatography was carried out with Silica 60 M (0.04 – 0.063 mm) from Macherey Nagel GmbH & Co. KG. Thin layer chromatography was performed on Polygram® SIL G/UV_{254} from Macherey Nagel GmbH & Co. KG. NMR spectra were measured on a Bruker Avance II 200 MHz, Avance II 400 MHz or Avance III 400 MHz HD spectrometer at rt, if not stated otherwise. Chemical shifts are reported in parts per million (ppm) relative to the solvent peak, coupling constants (*J*) are reported in Hertz (Hz). Deuterated solvents were obtained from Deutero GmbH (Kastellaun, Germany) or Euriso-Top GmbH. For all azobenzenes, the thermodynamically more stable (*E*)-isomer is reported if not stated otherwise. ESI-MS spectra were recorded on a Bruker Daltonics Micro TOF. Melting points were measured on a Krüss M5000 capillary melting point meter with a heating rate of 1 °C min^{-1}. GC-MS monitoring of quenched reaction aliquots was carried out on a HP 5890 gas chromatograph with a HP 5971 mass detector.

Irradiation Experiments

Irradiation of the NMR or UV/Vis samples was conducted in an in-house built box using high power LEDs by Lumitronix or Nichia, purchased from leds.de. After the given irradiation times, the samples were immediately placed and measured in the corresponding spectrometer.

Table S1: LEDs used for all irradiation experiments with their specifications.

λ_{max} / nm	$\Delta\lambda_{FWHM}$ / nm	Luminous Flux / mW	Product name
365	9	780	NCSU276AT-U365
385	10	900	NCSU276AT-U385
405	12	950	NCSU276AT-U405
425 - 430	14	675	LHUV-0425-0650
448	20	520	LXML-PR01-0500
305	+10/–5	300	LEUVA77N50KU00, 4 in 1

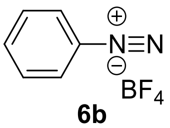
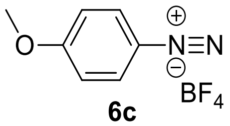
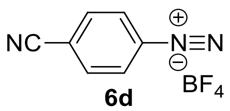
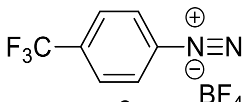
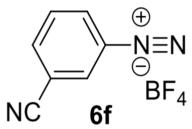
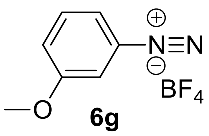
Figure S1: In-house built LED irradiation box for UV/Vis cuvettes as well as NMR tubes.

Synthesis of Starting Materials

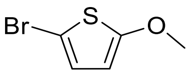
General procedure for the synthesis of aryldiazonium tetrafluoroborates[1]

To an ice-cooled suspension of the corresponding aniline (20 mmol, 1.0 eq.) in water (8.0 mL), 50% aq. HBF_4 (7.5 mL, 60 mmol, 3.0 eq.) was added dropwise. Then, $NaNO_2$ (1.4 g, 20 mmol, 1.0 eq.) in water (4.0 mL) was added dropwise and the reaction mixture was stirred at 0 °C for 45 min. Afterwards, the precipitate was filtered off, washed with excess Et_2O and was dried in vacuum to obtain the corresponding aryldiazonium tetrafluoroborates (77 – 99% yield). The diazoniumsalts were directly used without further purification and were stored in a nitrogen-filled glovebox under exclusion of light at –20 °C. Under these conditions, the diazonium salts were found to be stable for at least one year. Note that 3-methoxybenzenediazonium tetrafluoroborate (**6g**) could not be handled in solution ($CHCl_3$, MeOH, DMSO, Acetone) due to azo coupling with itself.

Table S2: Yields of the prepared aryldiazonium tetrafluoroborates.

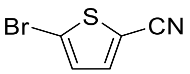
Compound	Yield / %
 **6b**	77
 **6c**	88
 **6d**	84
 **6e**	82
 **6f**	86
 **6g**	99

5-Bromo-2-methoxythiophene (5b)



2-Methoxythiophene (1.01 g, 8.57 mmol, 1.00 eq.) was dissolved in CCl_4 (2 mL) and the solution was cooled to 0 °C. NBS (1.4 g, 7.7 mmol, 0.89 eq.) was added in one portion and the suspension was heated to reflux for 10 min. After cooling to rt, the mixture was treated with sat. aq. Na_2CO_3 (2 mL) and was diluted with DCM (5 mL). After phase separation, the aqueous phase was extracted with DCM (3 x 5 mL) and the combined organic phases were dried over $MgSO_4$, filtered and the solvents were evaporated under reduced pressure. The obtained brown oil was purified by column chromatography (SiO_2, cycohexane/EtOAc; 50:1) to yield the product as a slightly yellow oil (1.07 g, 65%), which was stored at –20 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 4.0 Hz, 1H), 5.97 (d, *J* = 4.0 Hz, 1H), 3.85 (s, 3H). The product was used without further purification.

5-Bromo-2-cyanothiophene (5c)



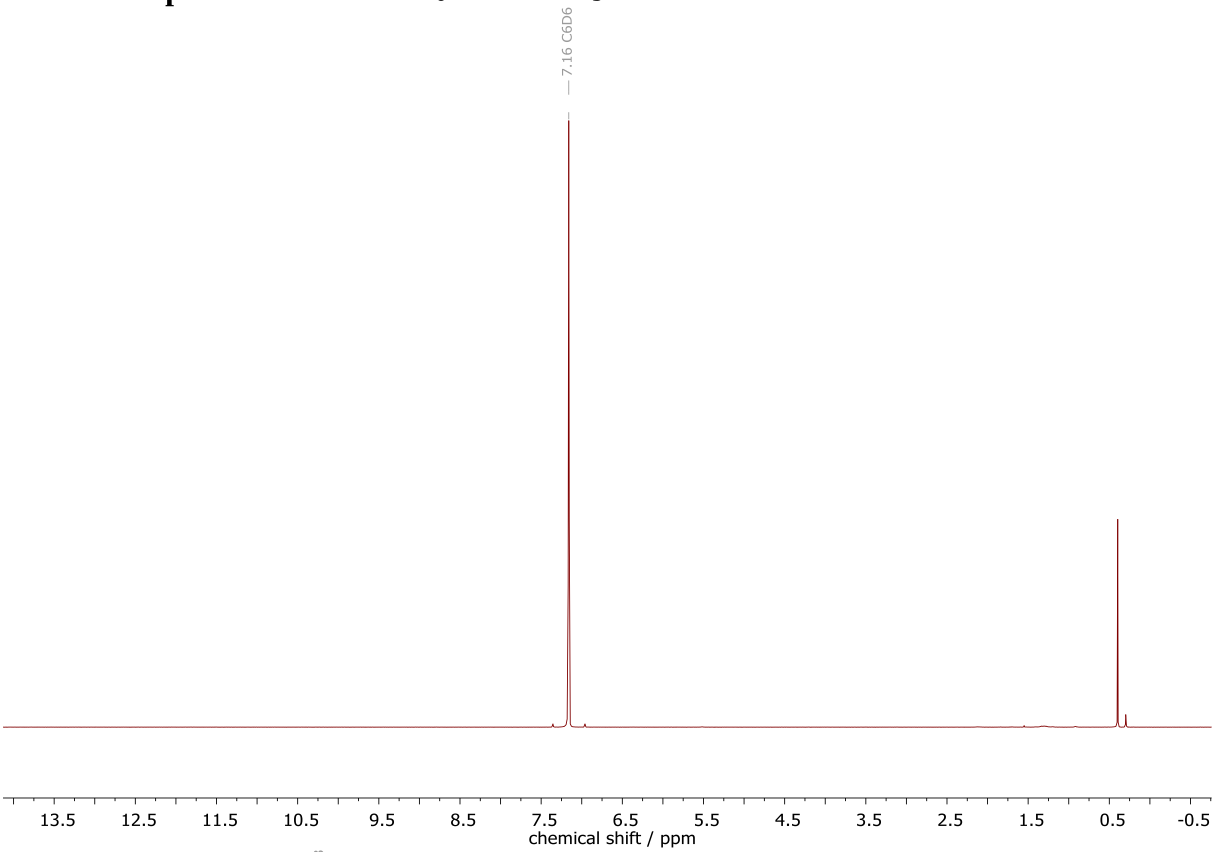
To a solution of 2-thiophenecarbonitrile (1.9 mL, 20 mmol, 1.0 eq.) in a mixture of acetic acid (1.1 mL, 19 mmol, 0.95 eq.) and acetic anhydride (7.6 mL, 80 mmol, 4.0 eq.) was added NBS (3.60 g, 20.0 mmol, 1.00 eq.) and bromine (1.0 mL, 20 mmol, 1.0 eq.) and the reaction mixture was stirred at rt for 2.5 h. After the addition of ice-water (20 mL) and sat. aq. $NaHSO_3$ solution (20 mL), the mixture was extracted with DCM (3 x 25 mL) and the combined organic phases were washed with sat. aq. $NaHCO_3$ (3 x 45 mL), dried over $MgSO_4$ and filtered. After solvent evaporation, a red oil was obtained, which was purified by flash column chromatography (SiO_2, cyclohex/EtOAc; 25:1) to yield a yellow oil (2.54 g, 67%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 4.0 Hz, 1H). The product was used without further purification.

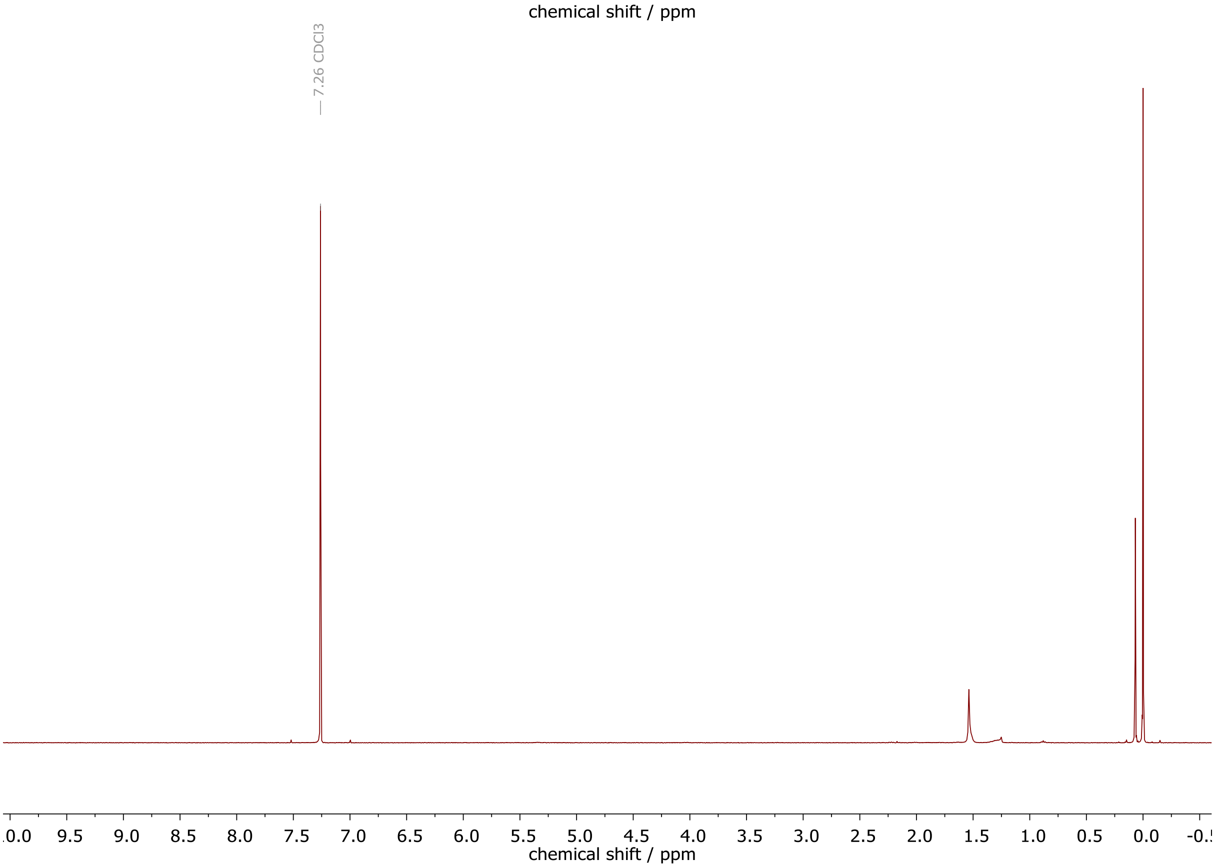
Preparation of 1 molar $ZnBr_2$-solution

For the preparation of the zincthiophenyl reagents, a $ZnBr_2$-solution in dry THF (1 mol/L) was prepared and used according to the literature.[2] The solution was stored and handled in a Schlenk flask in a nitrogen-filled glovebox.

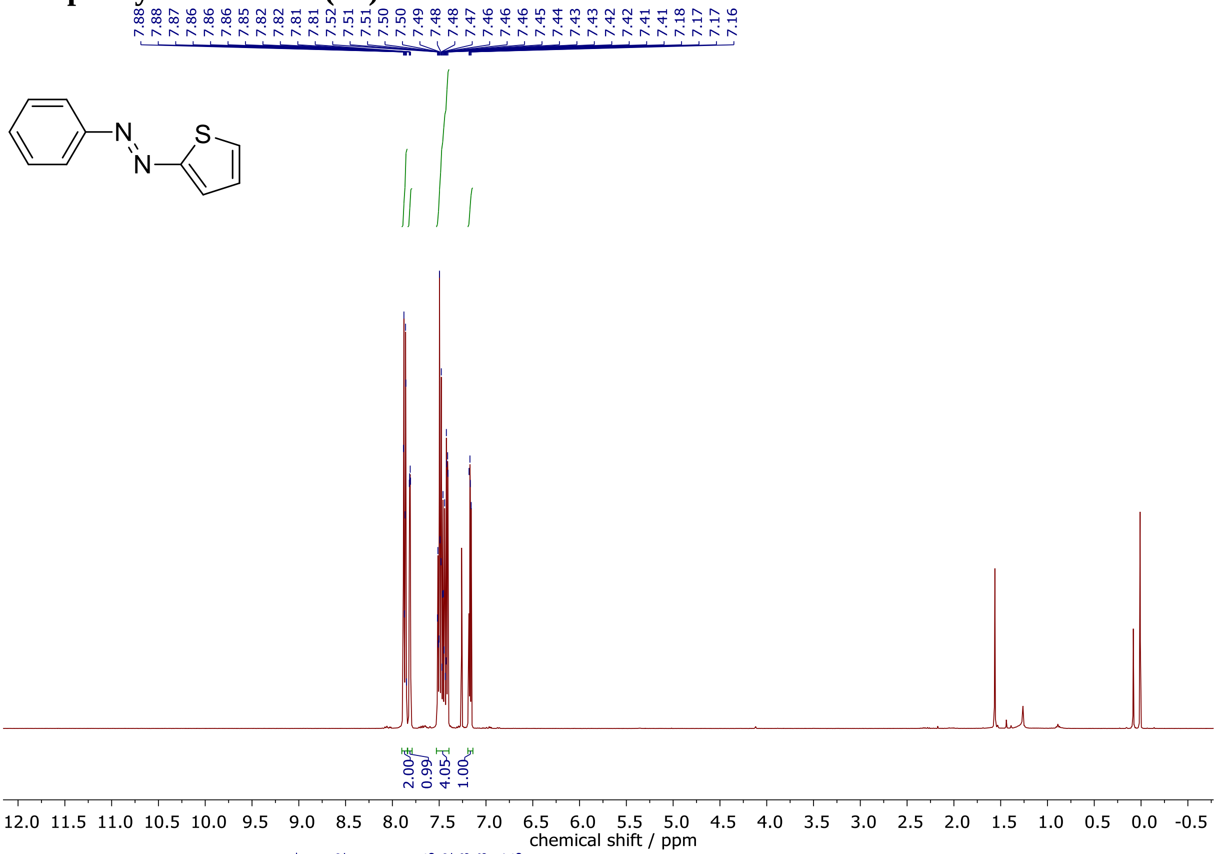
^{1}H-, ^{13}C{^{1}H}- and ^{19}F{^{1}H}{^{13}C}-NMR Spectra

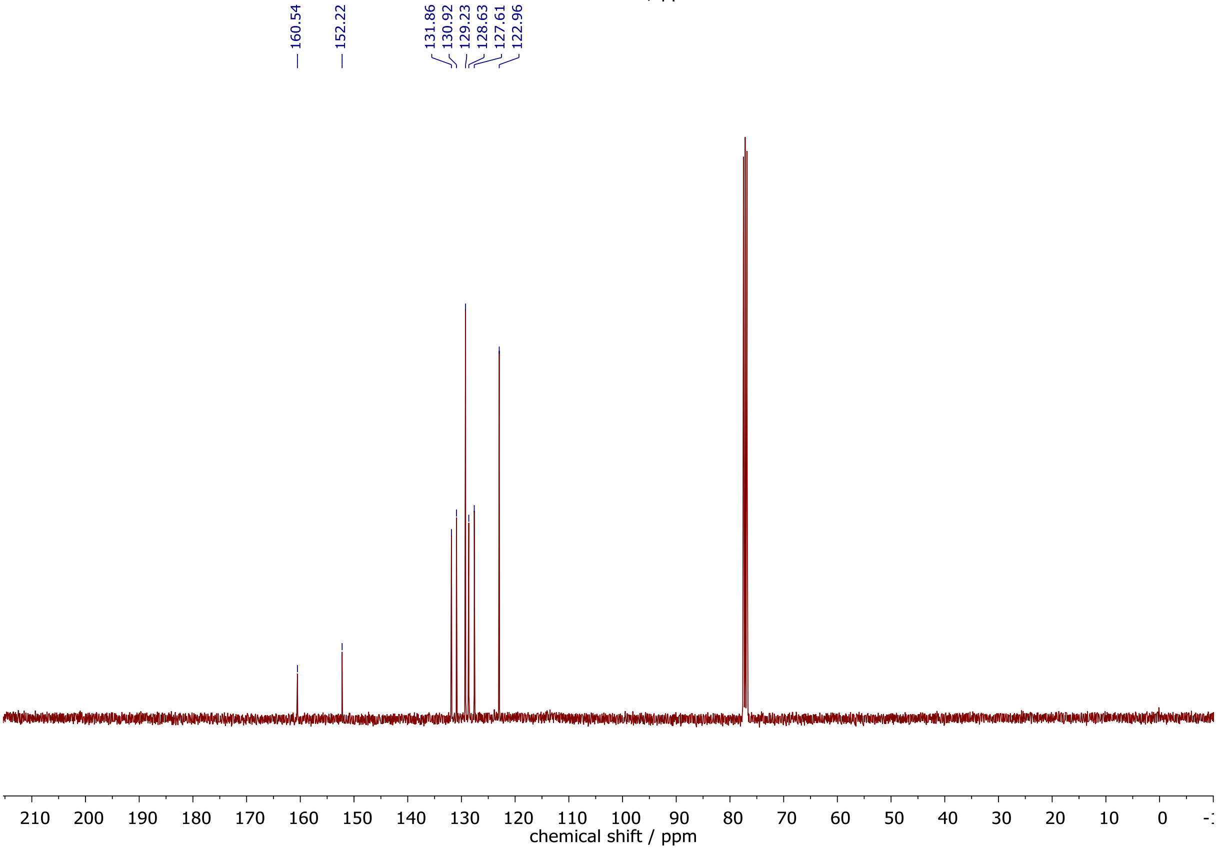
Reference Spectra of Benzene-d_6 and $CDCl_3$



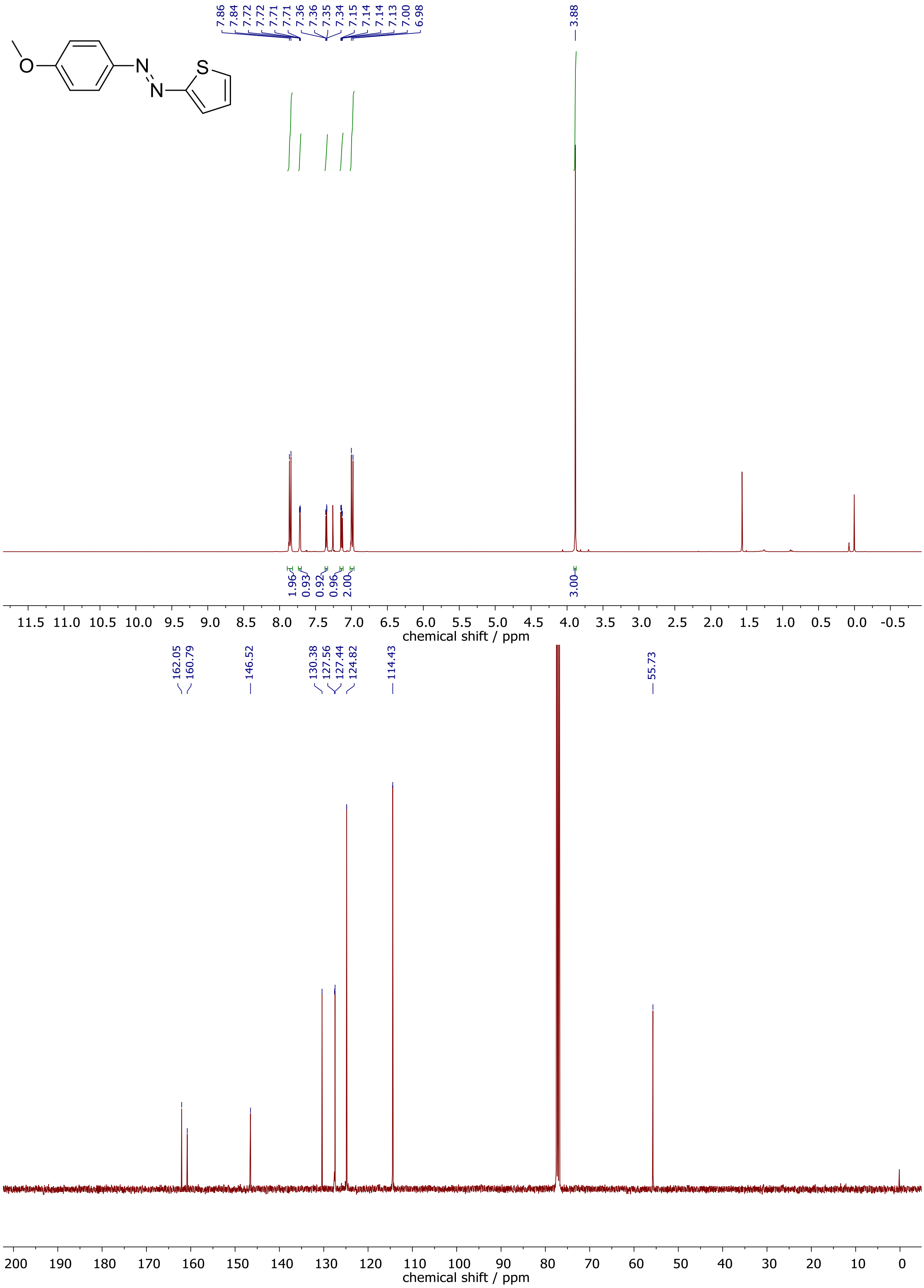


Thiophenylazobenzene (4b)

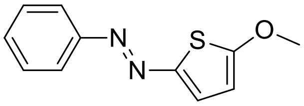


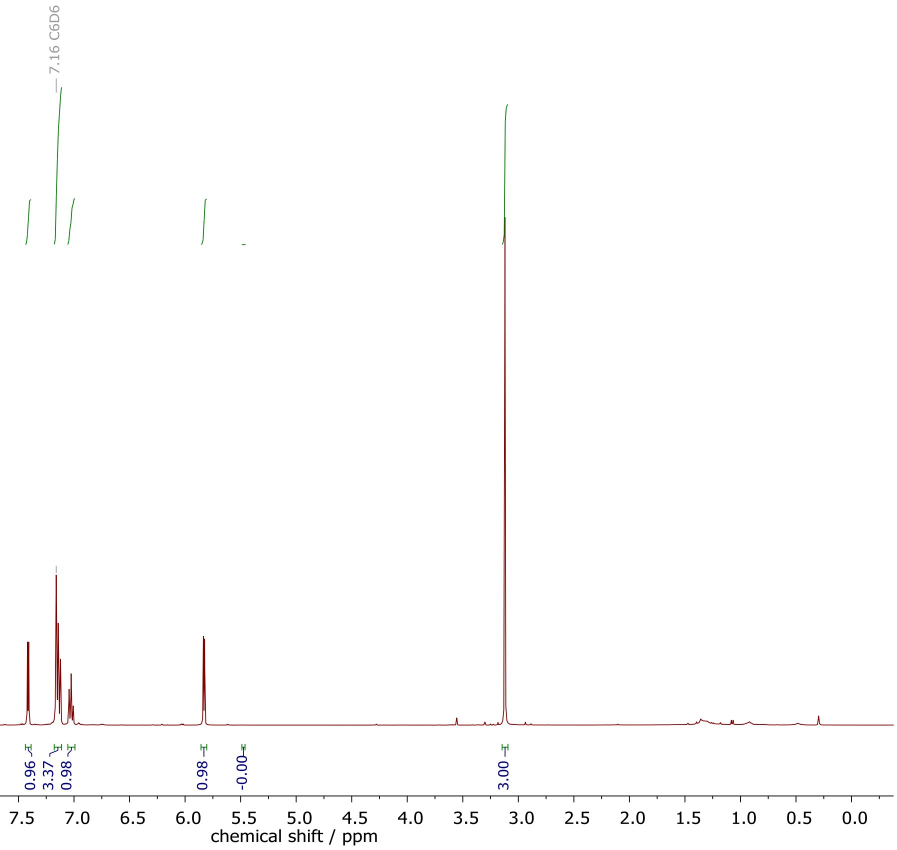


4-Methoxyphenylazothiophene (4c)

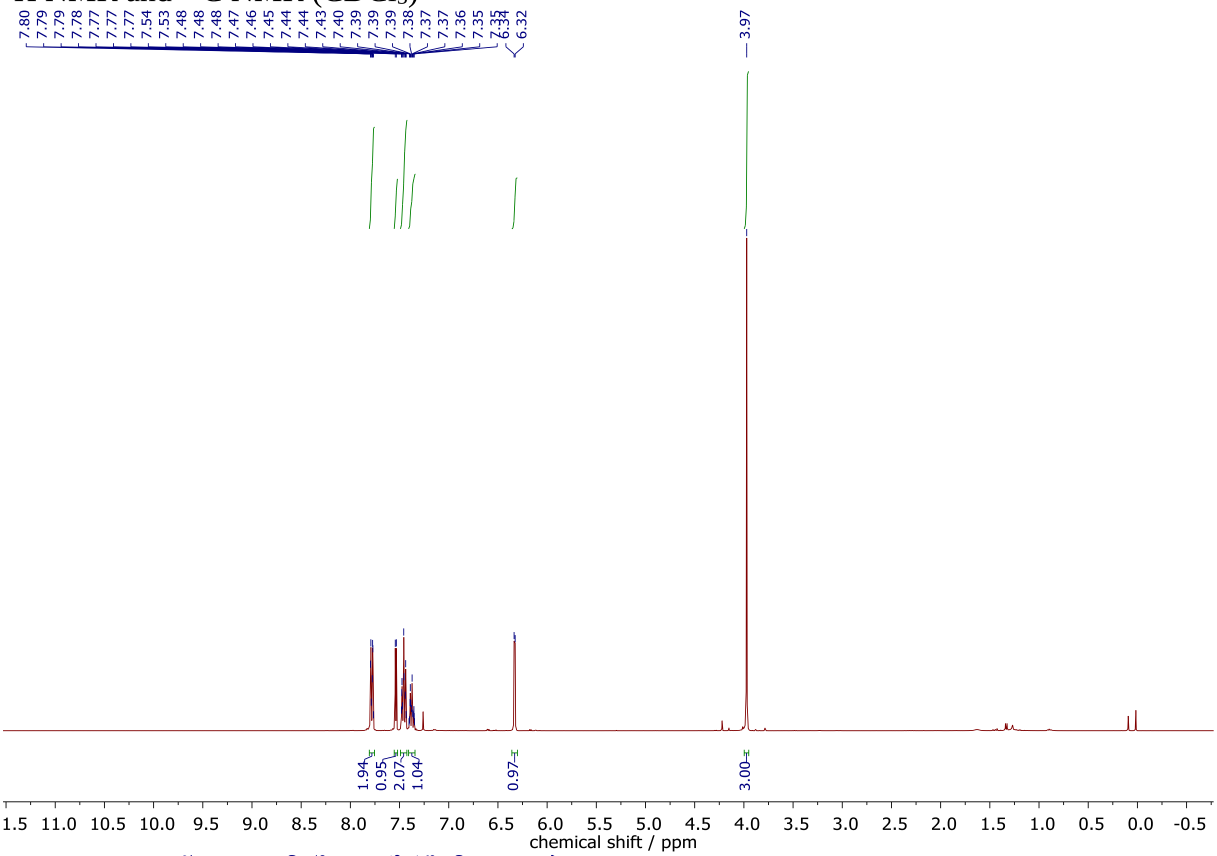


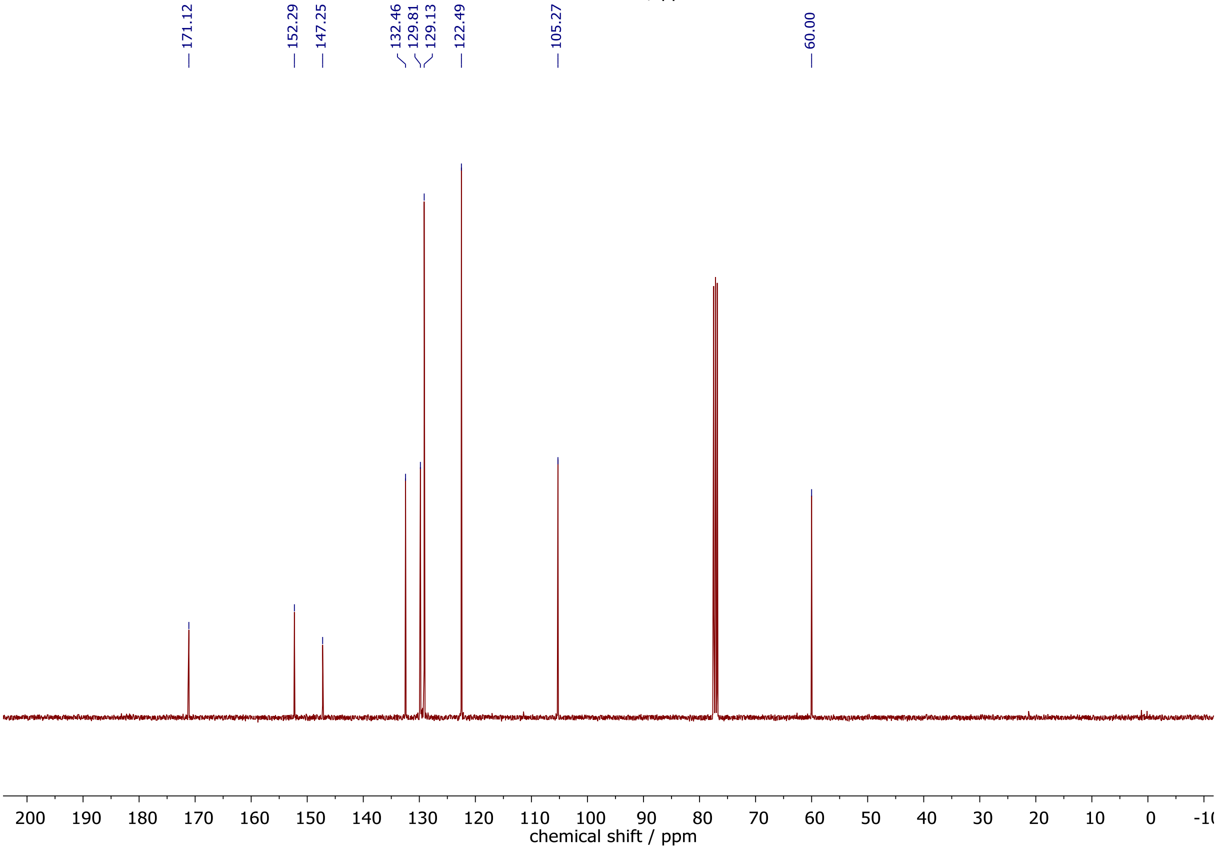
5-Methoxythiophenylazobenzene (4h)
^{1}H NMR (Benzene-d_6)



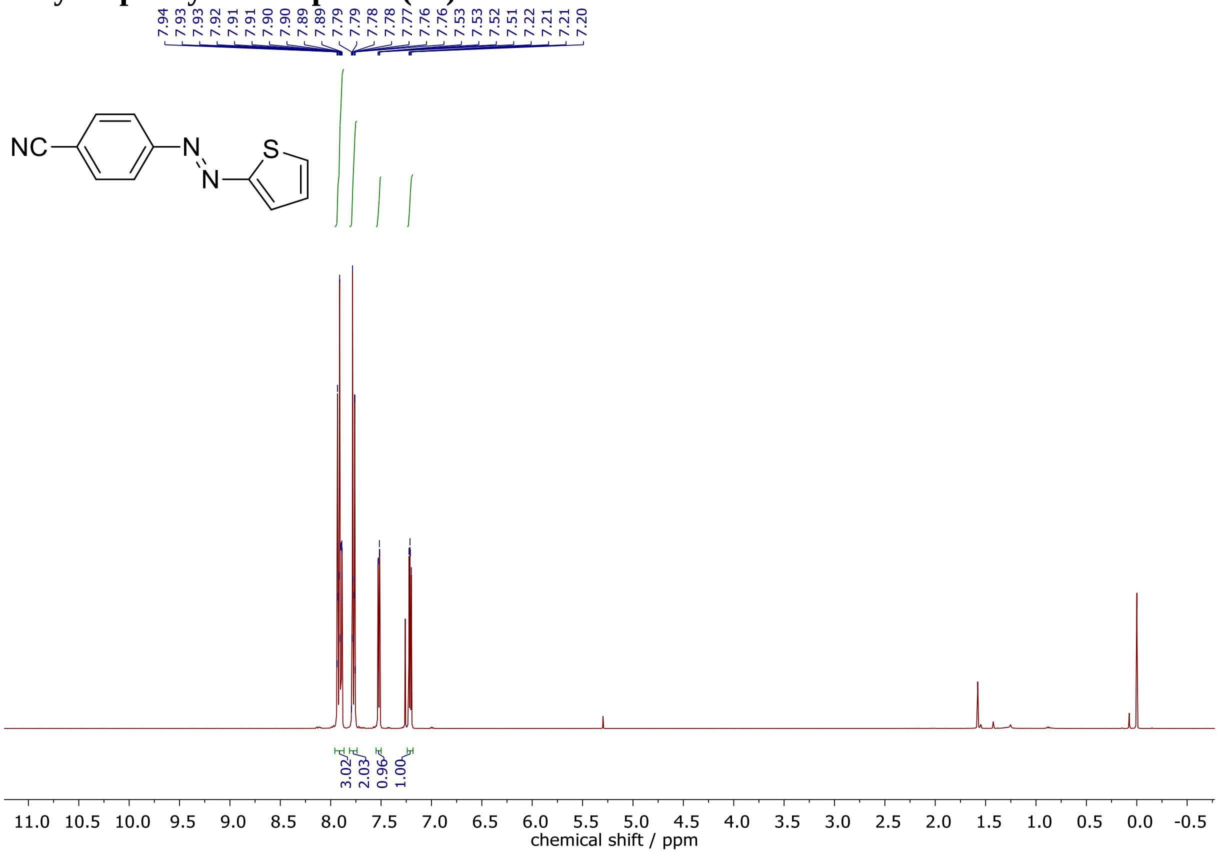


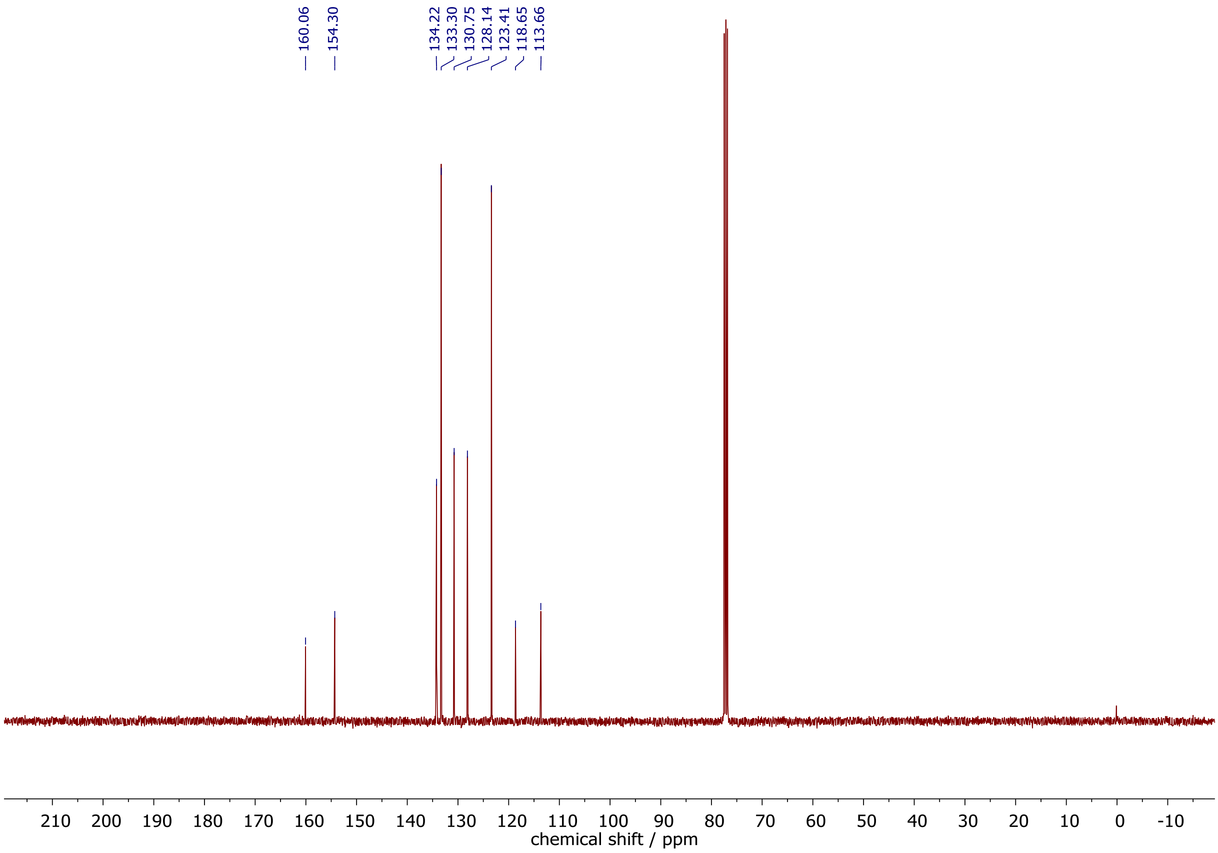
1H NMR and 13C NMR ($CDCl_3$)



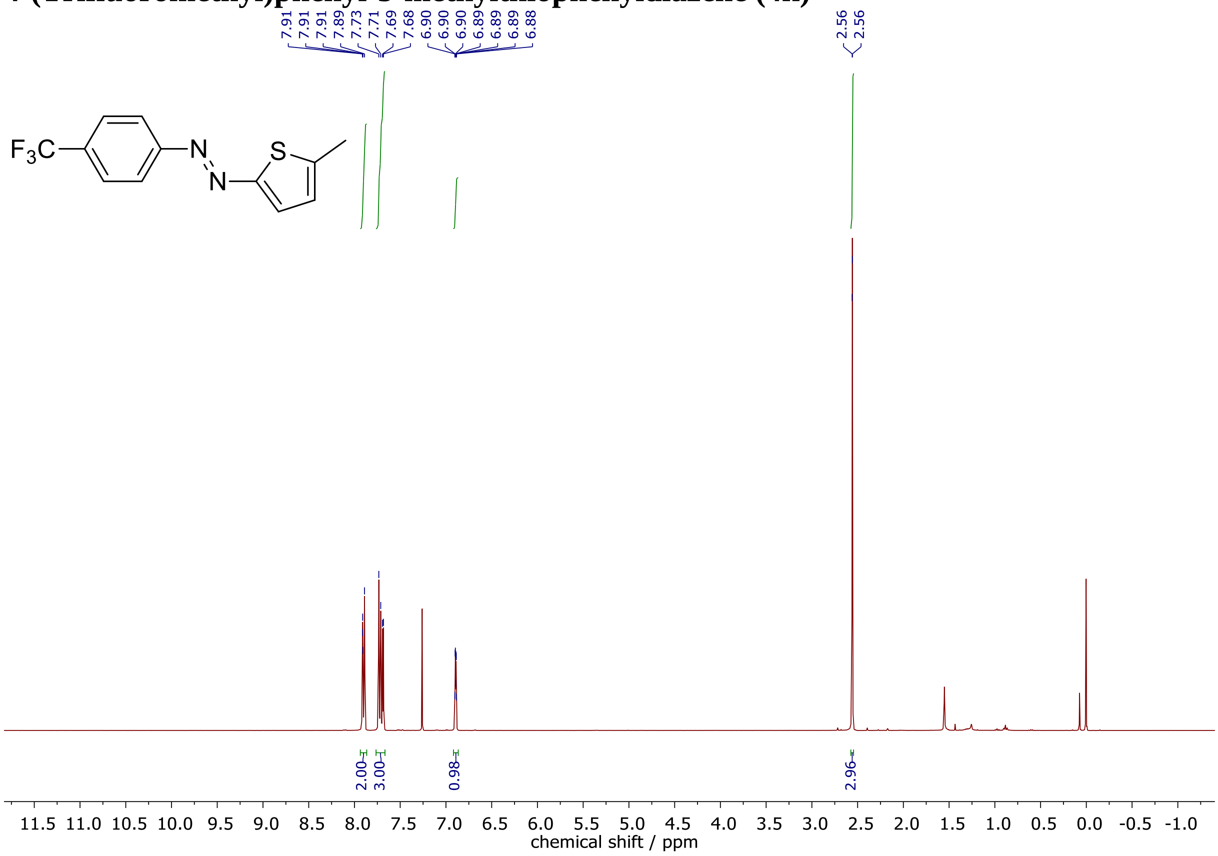


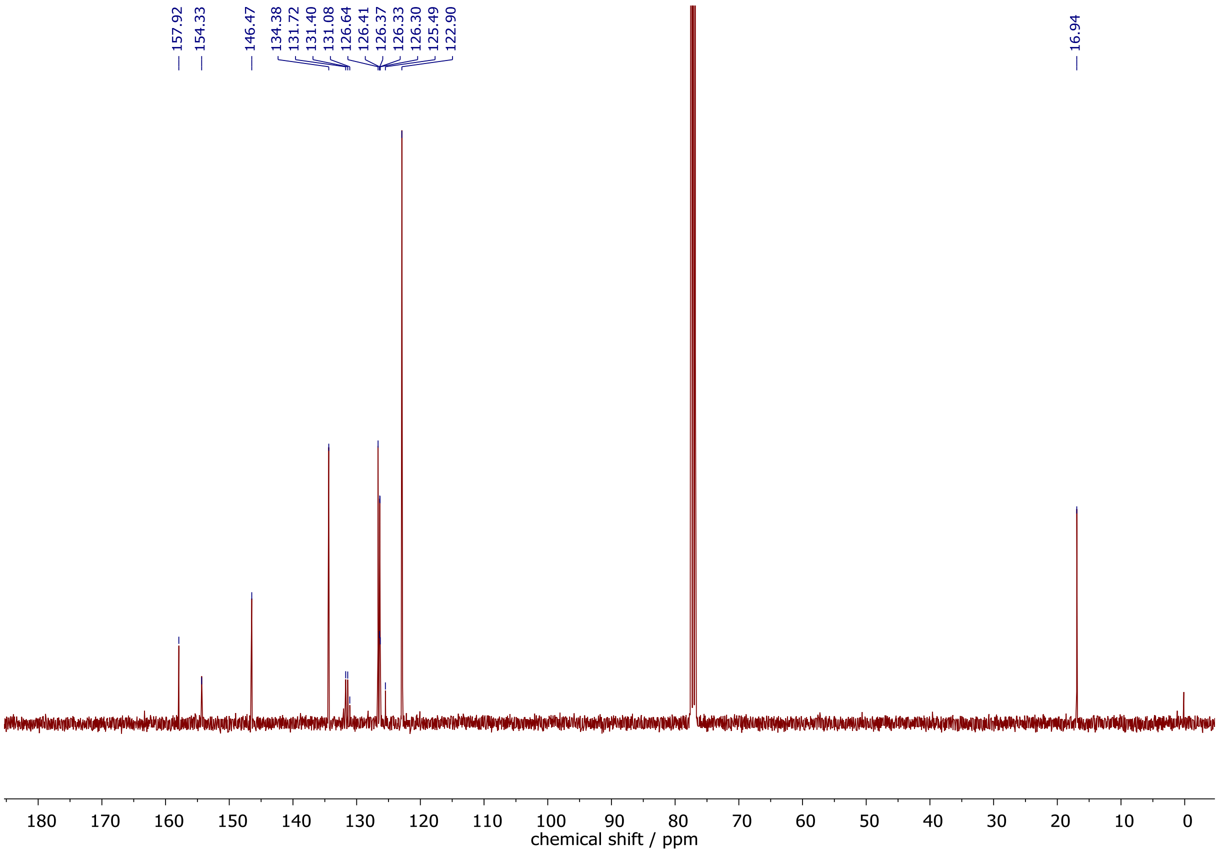
4-Cyanophenylazothiophene (4d)

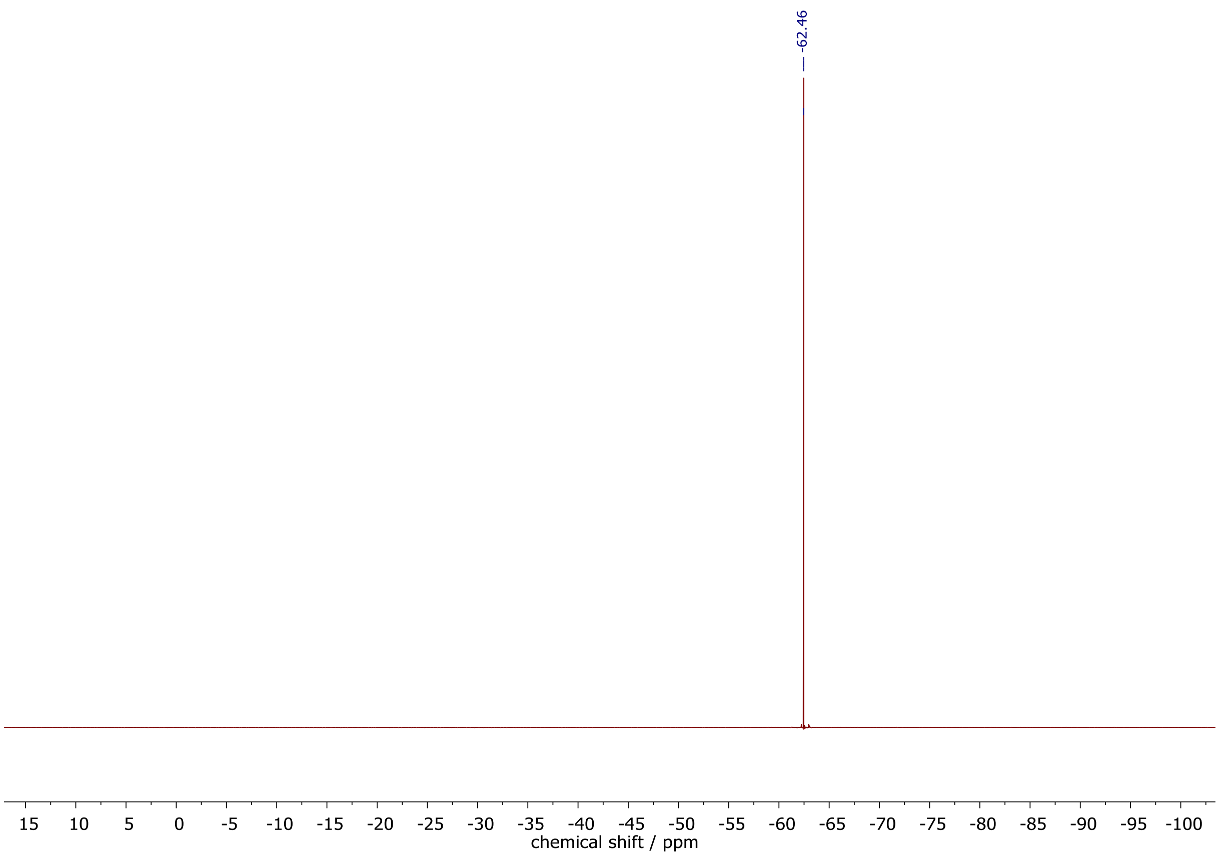




4-(Trifluoromethyl)phenyl-5-methylthiophenyldiazene (4k)



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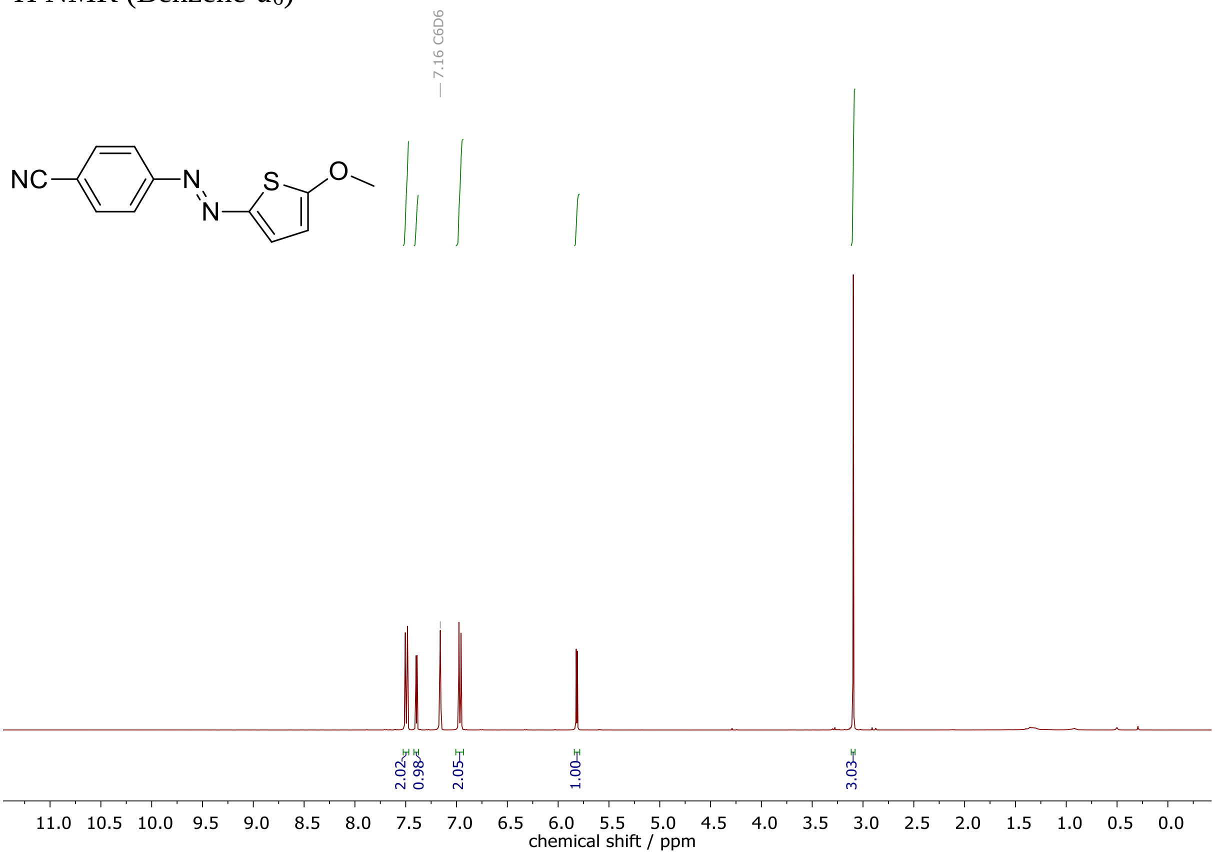
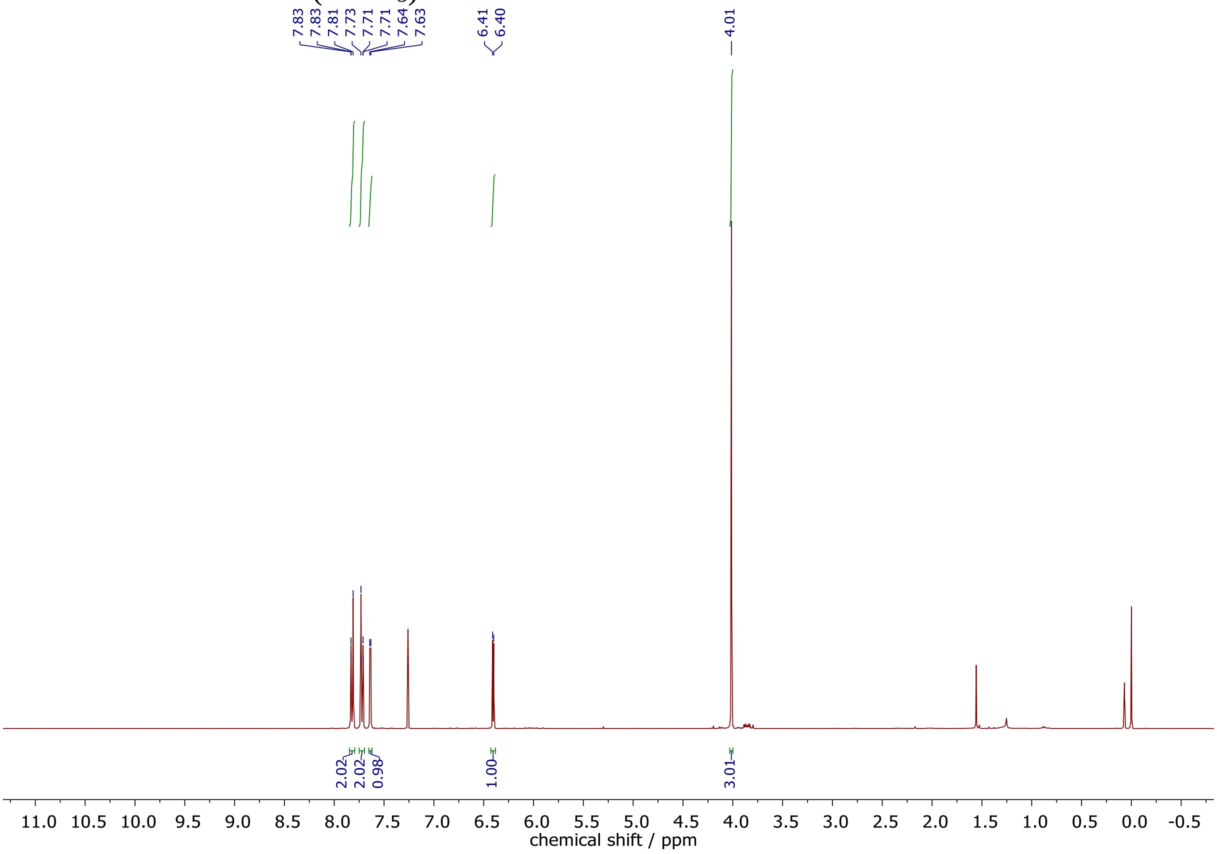
chemical shift / ppm

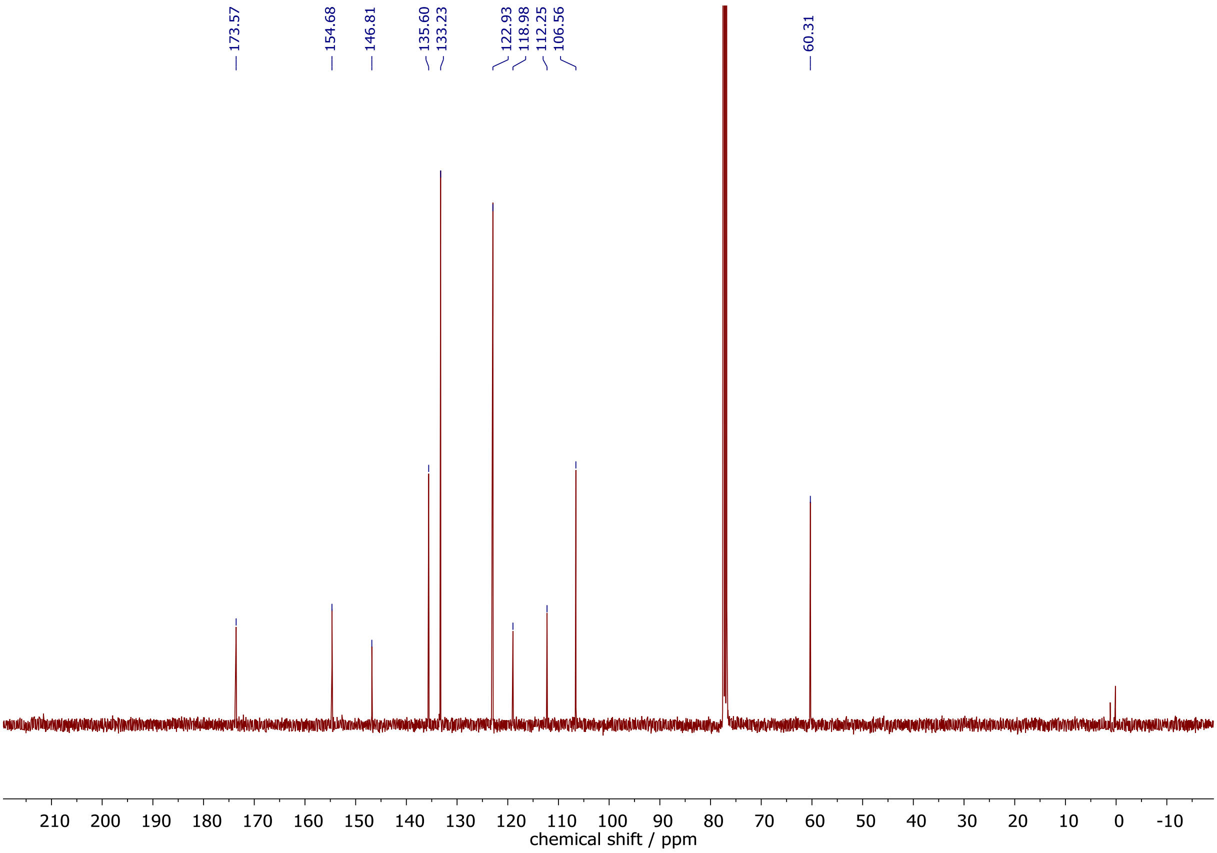
4-Cyanophenyl-5-methoxythiophenyldiazene (4i)

^{1}H NMR (Benzene-d_6)

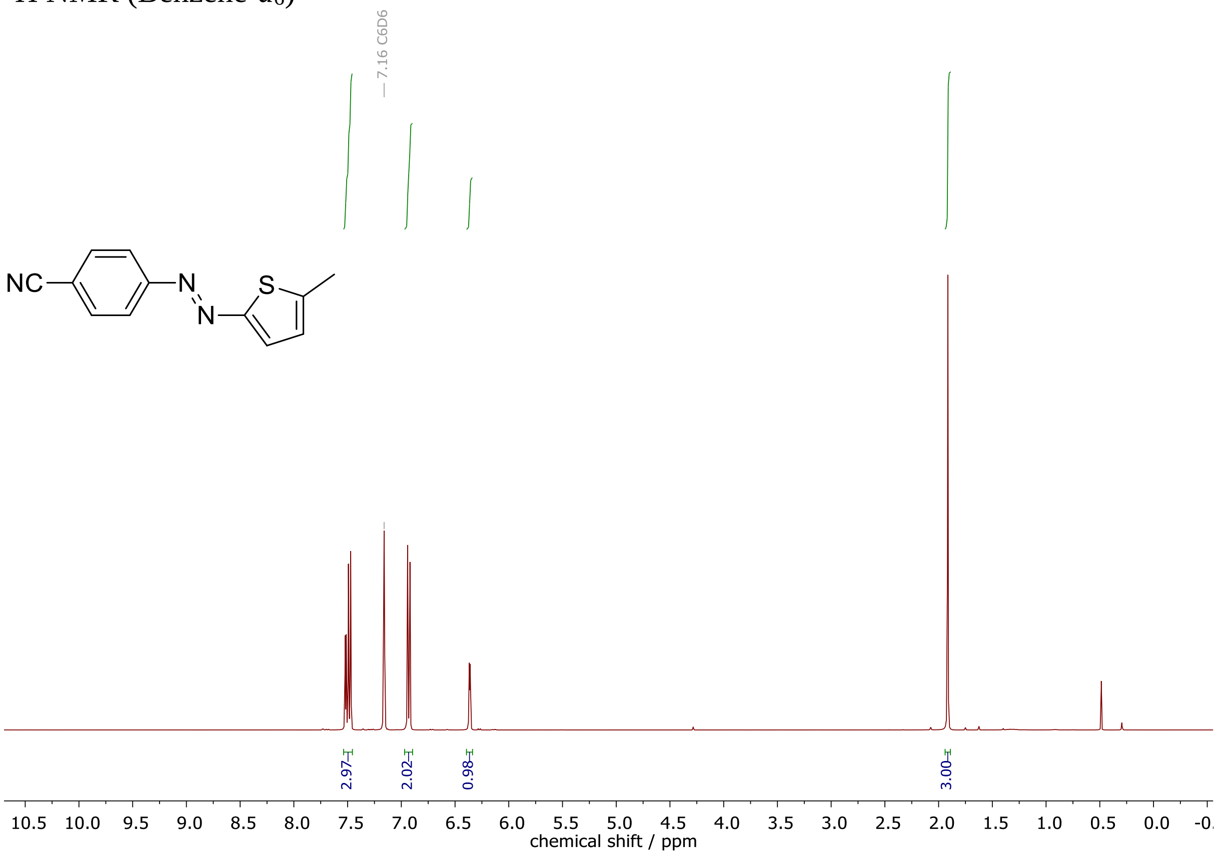


^{1}H NMR and ^{13}C NMR ($CDCl_3$)

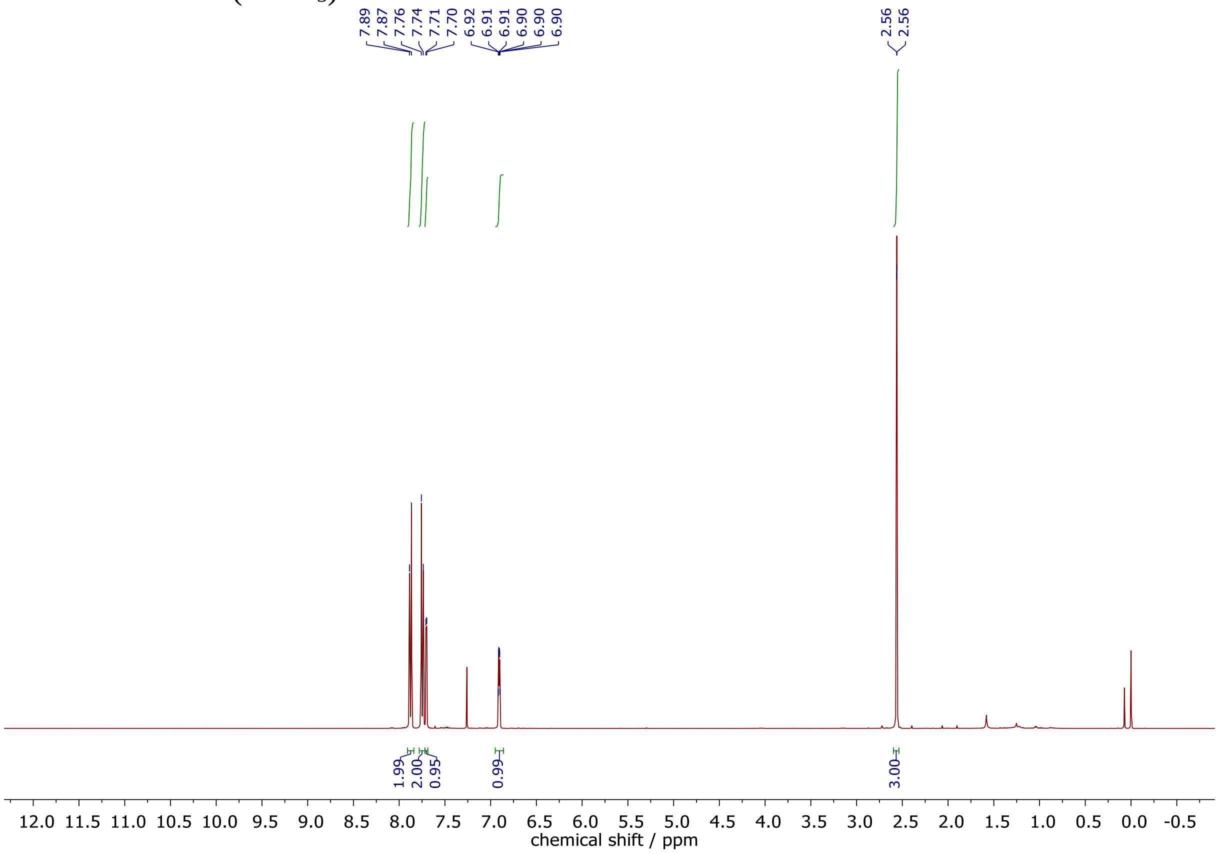


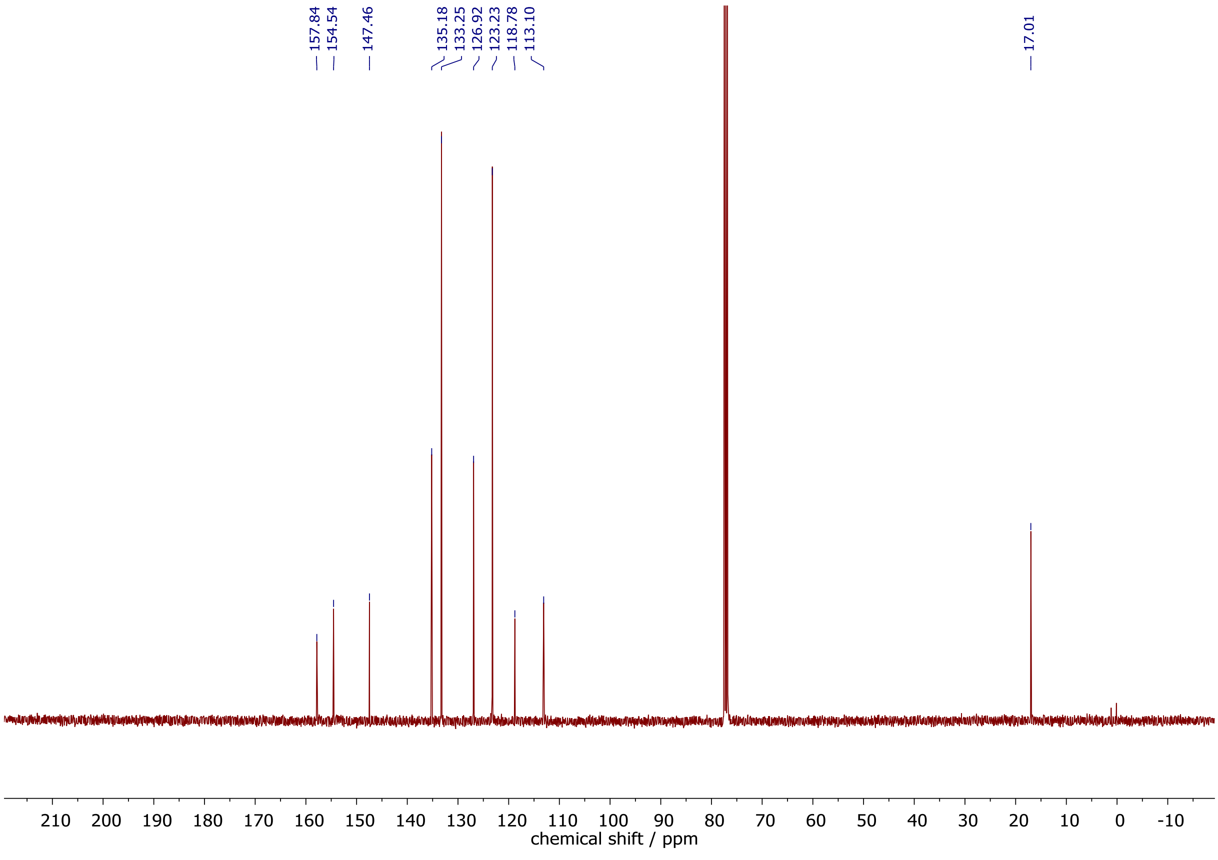


4-Cyanophenyl-5-methylthiophenyldiazene (4j)
[1]H NMR (Benzene-d_6)

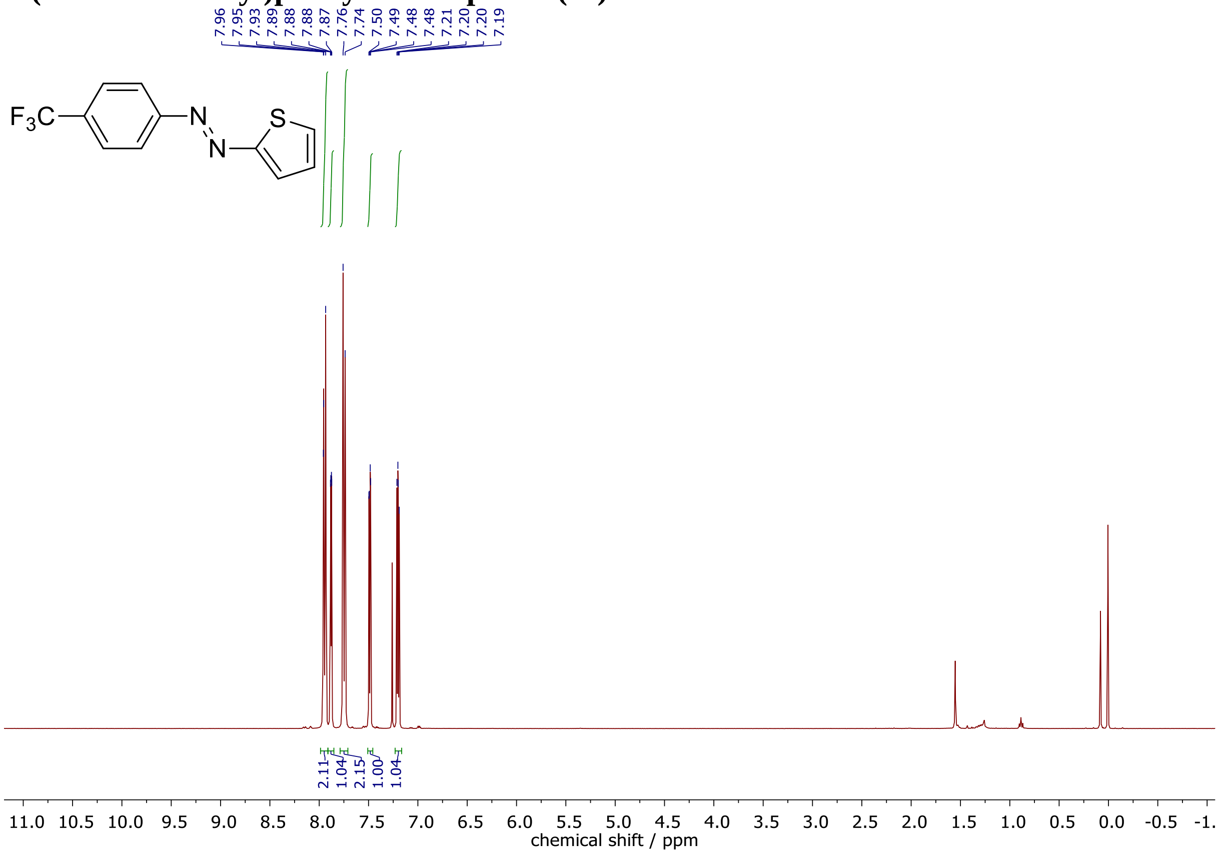


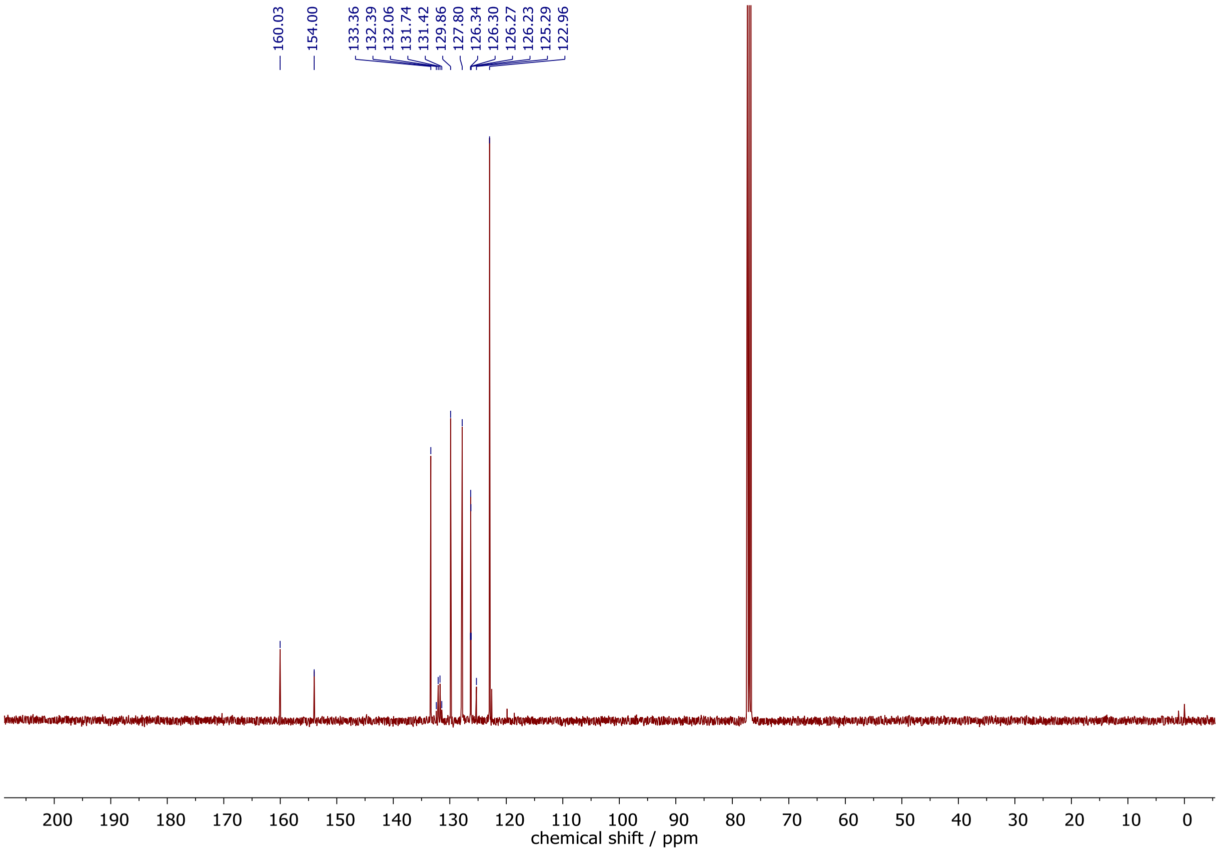
^{1}H and ^{13}C NMR ($CDCl_3$)

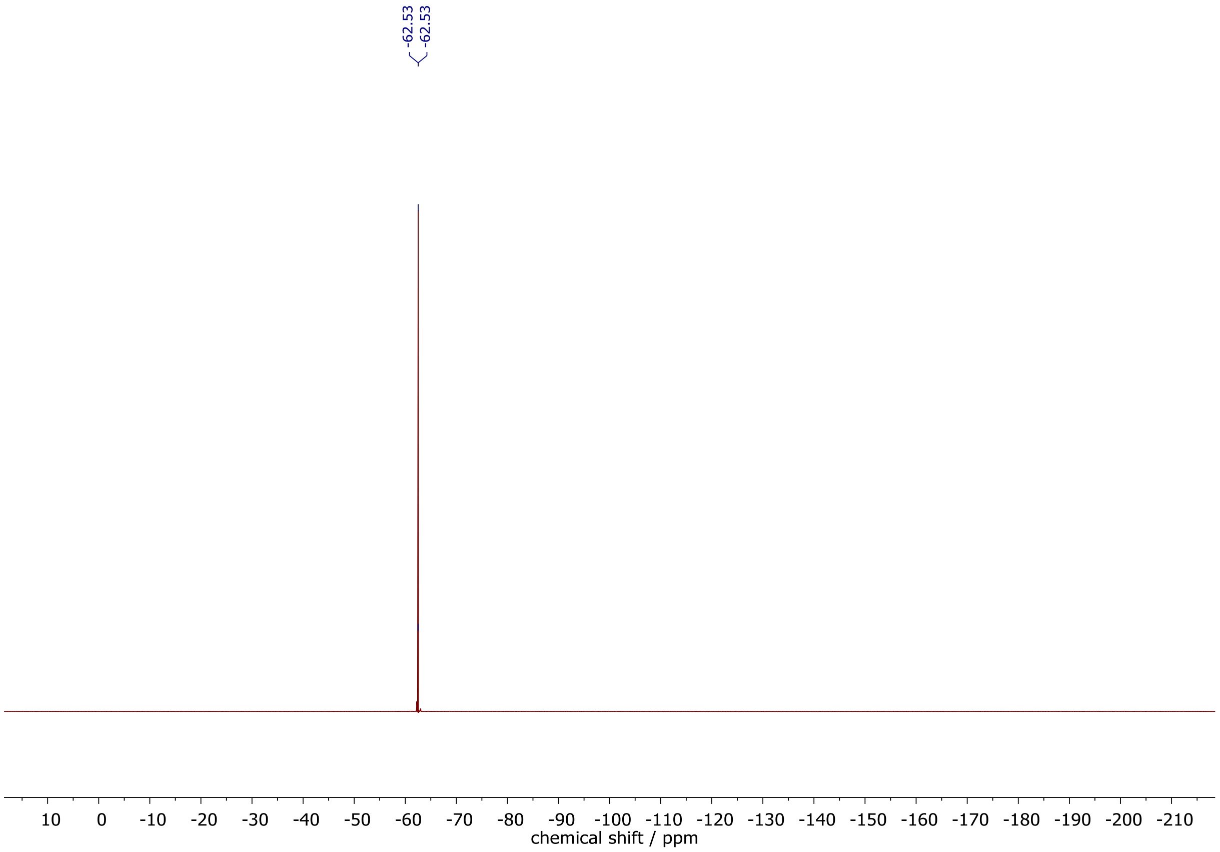




4-(Trifluoromethyl)phenylazothiophene (4e)



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-140
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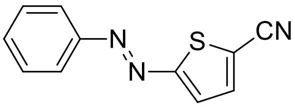
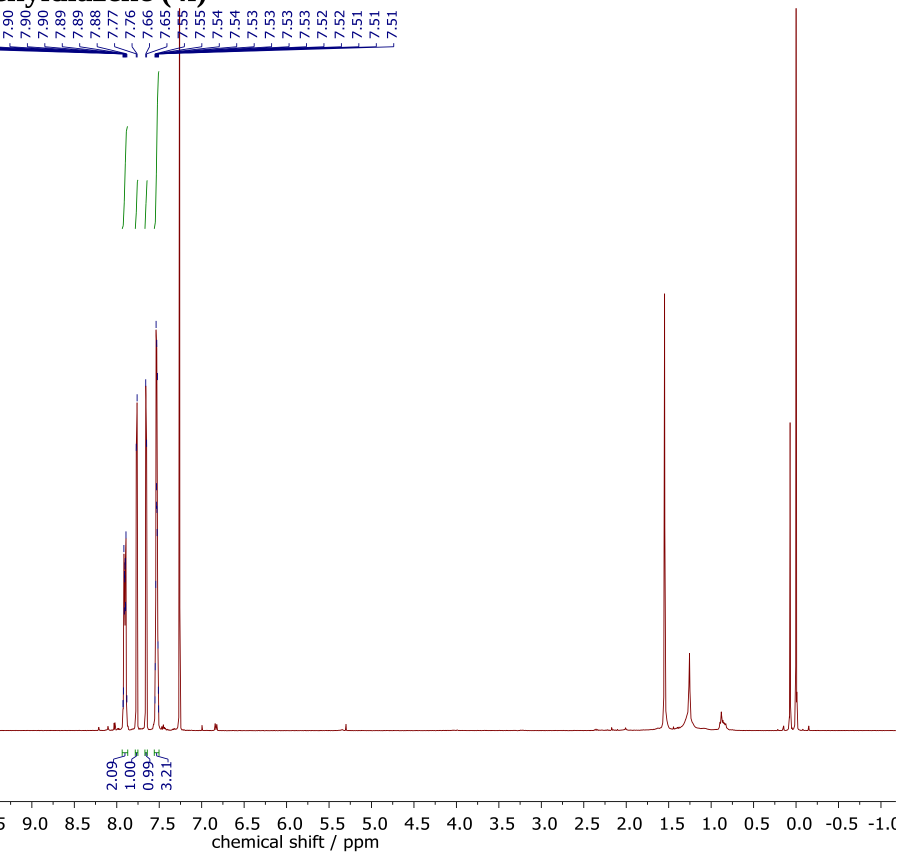
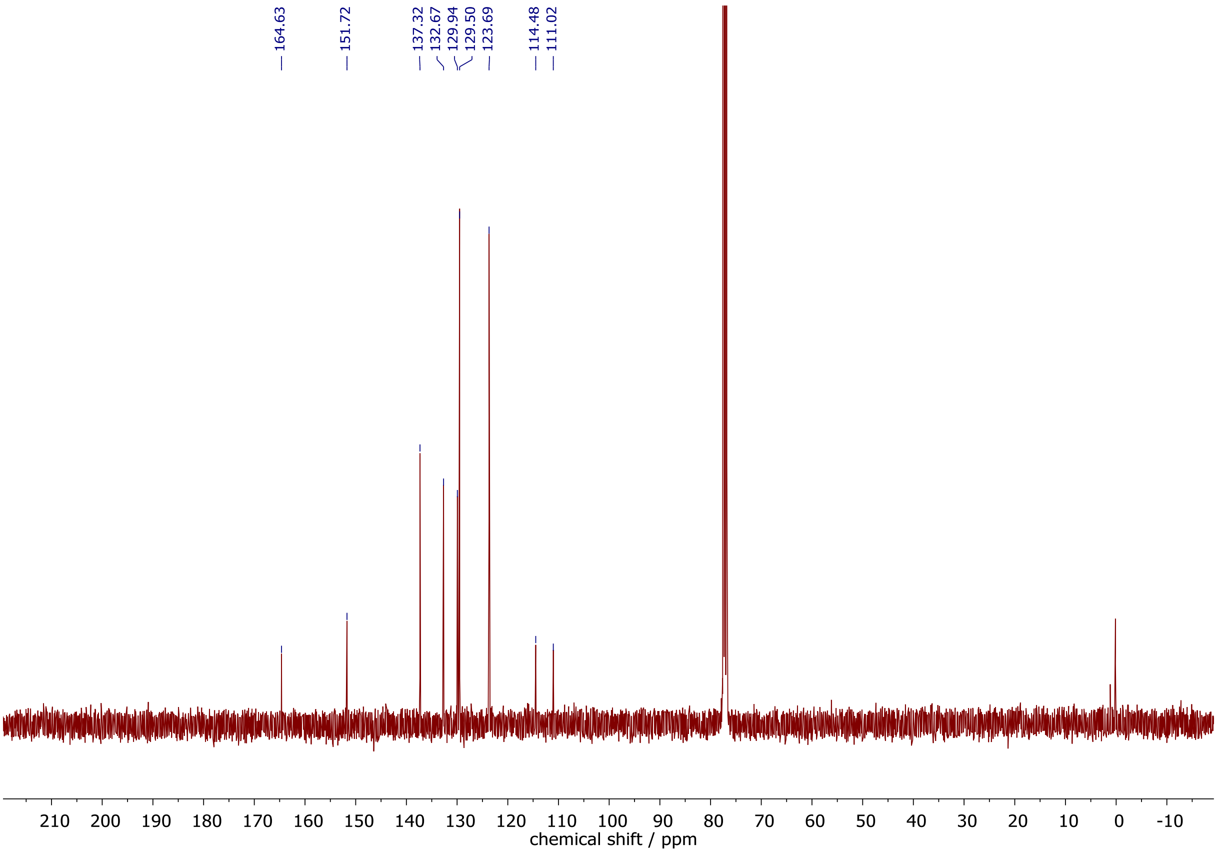
-160
-170
-180
-190
-200
-210
chemical shift / ppm

5-Cyanothiophenyl-phenyldiazene (4l)

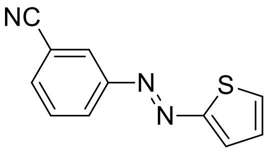


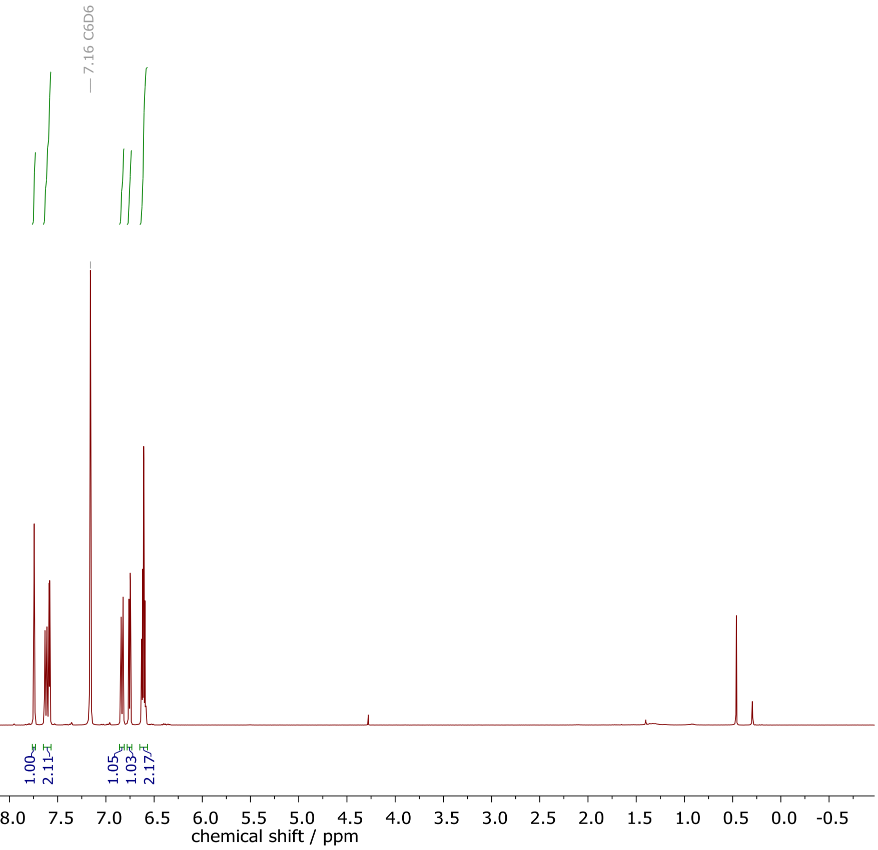




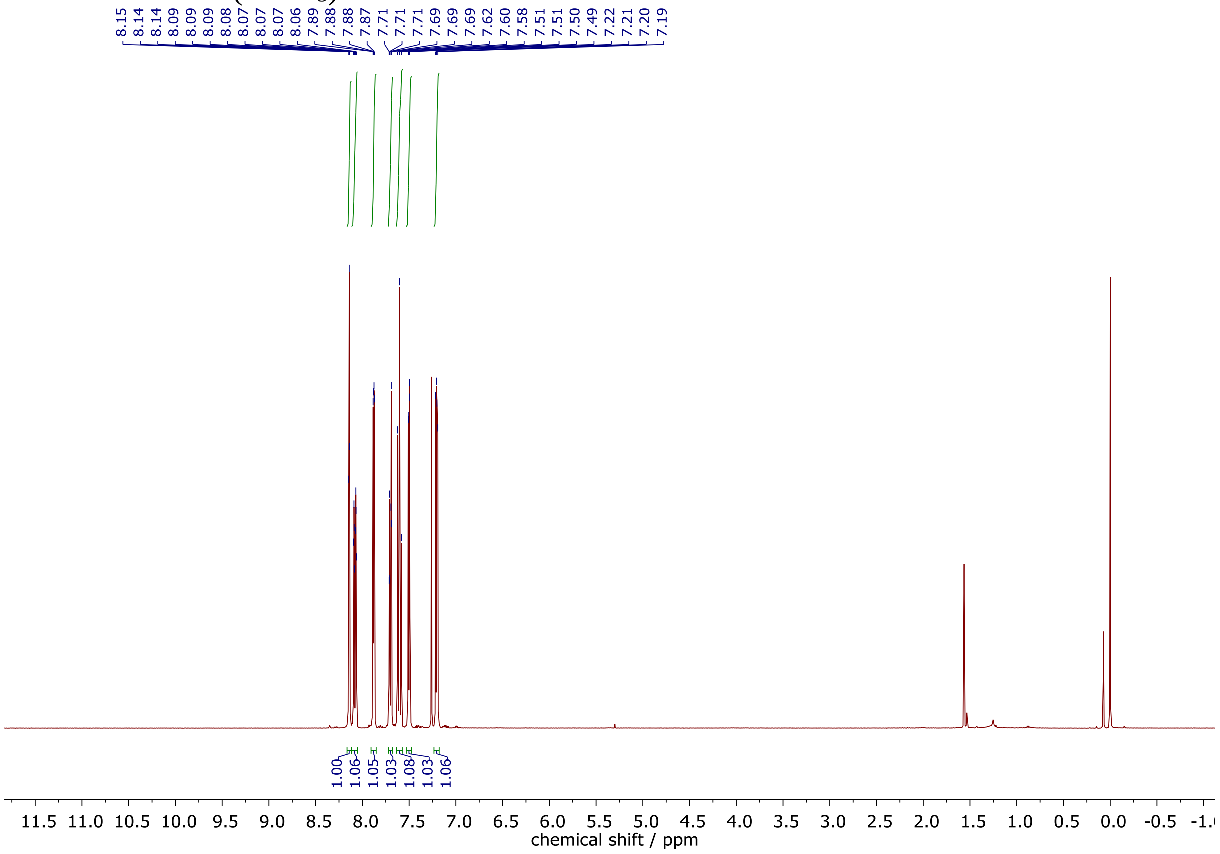
3-Cyanophenylazothiophene (4g)

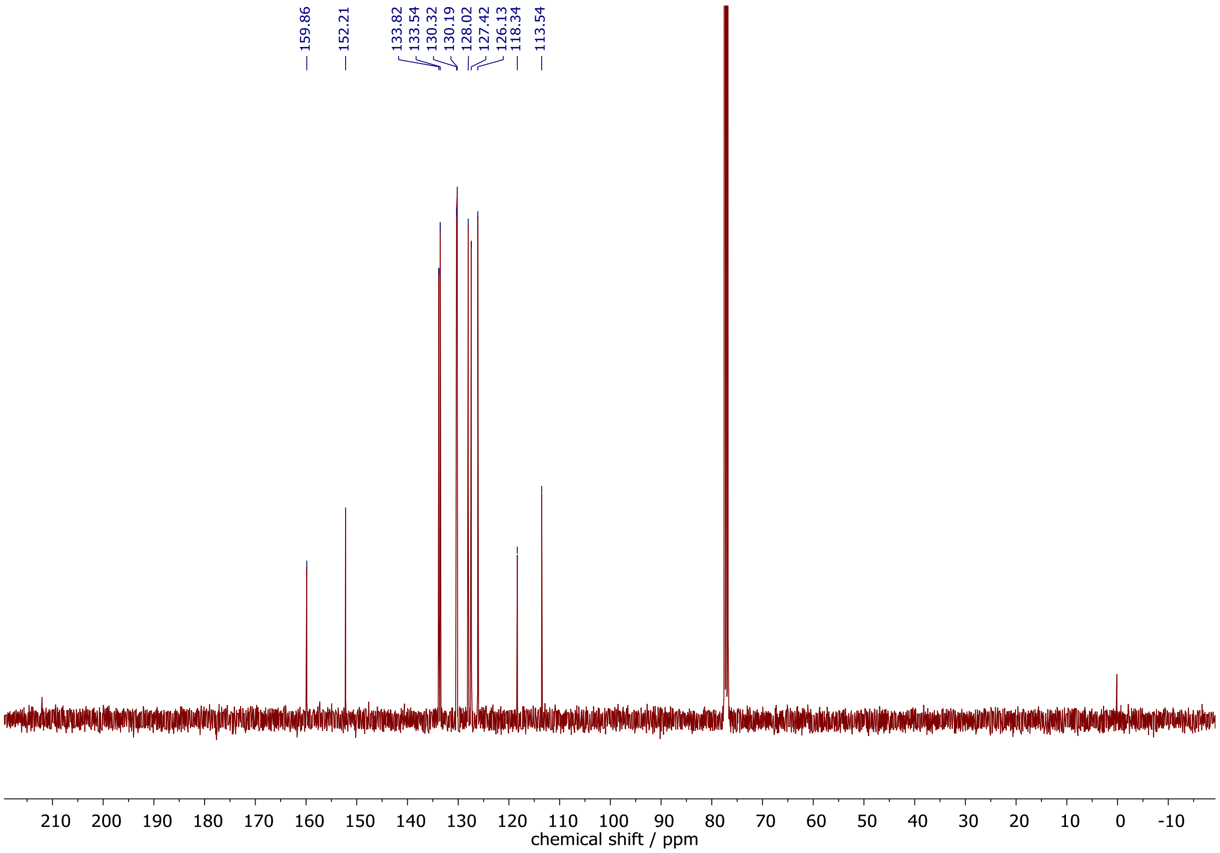
^{1}H NMR (Benzene-d_6)



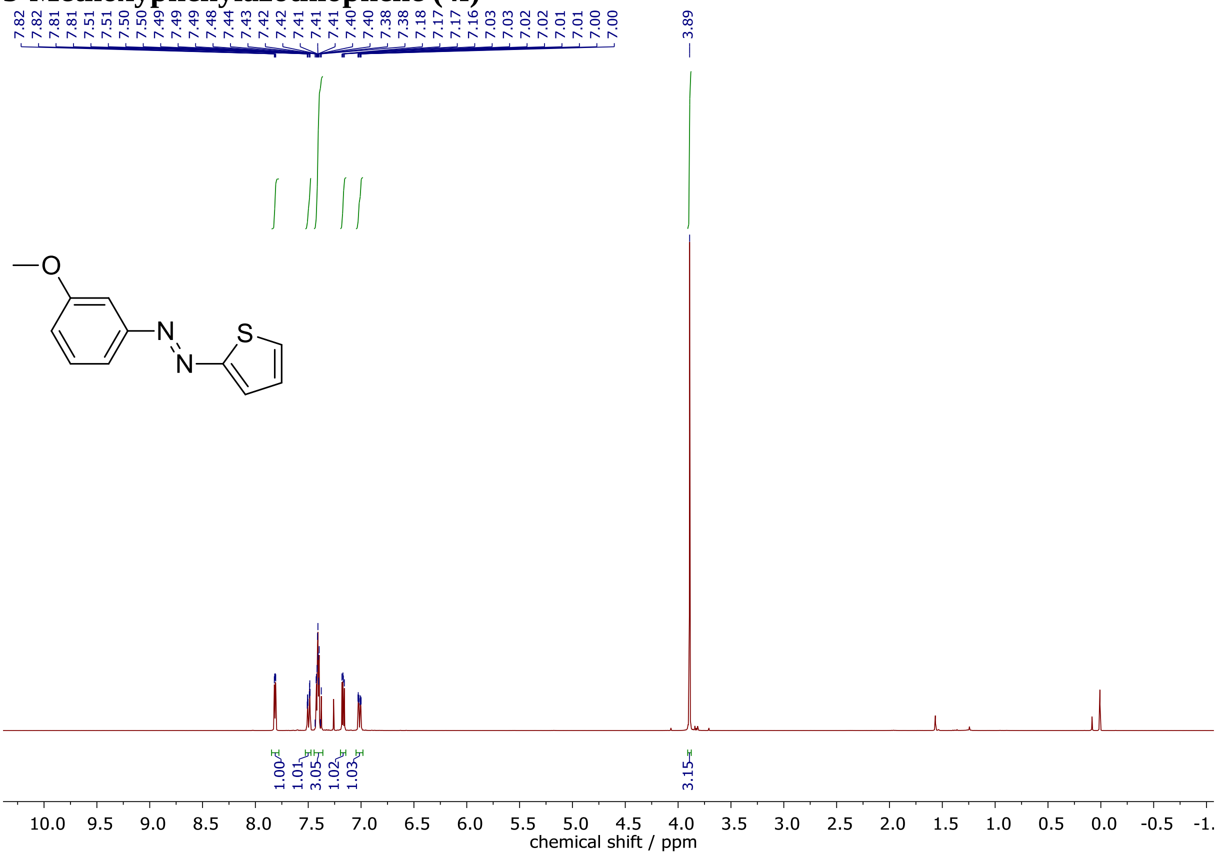


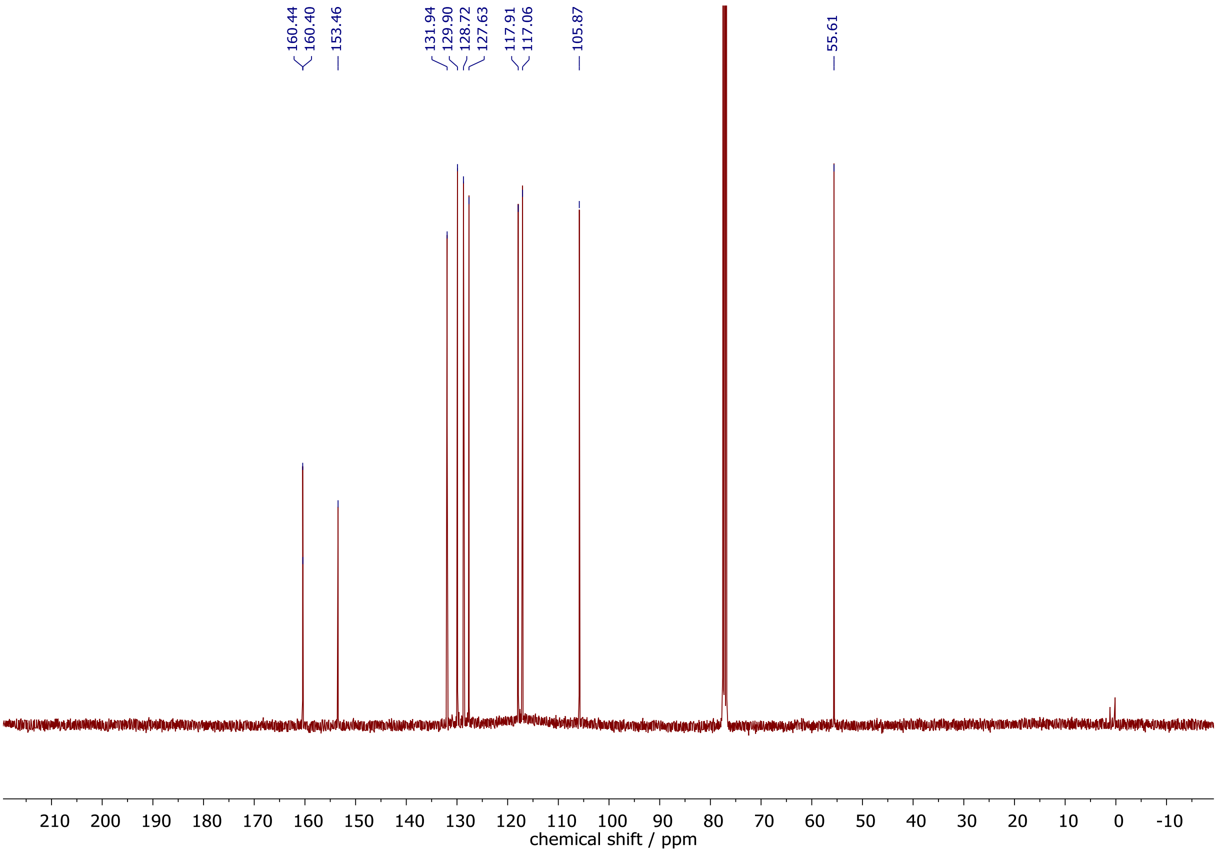
^{1}H and ^{13}C NMR ($CDCl_3$)





3-Methoxyphenylazothiophene (4f)





UV/Vis Spectroscopy

All samples were measured in acetonitrile for UV-Vis spectroscopy, purchased from Merck (Uvasol® quality). Photoisomerization as well as kinetic experiments were carried out in concentrations of $5 \cdot 10^{-5}$ mol/L (**4g**: $7 \cdot 10^{-5}$ mol/L). All solutions were freshly prepared from stock solutions ($c_{\text{stock}} = 5 \cdot 10^{-4}$ mol/L) prior to every UV/Vis experiment. The measurements were carried out with a SPECORD® 200 PLUS spectrophotometer equipped with two automatic eight-fold cell changers and a Peltier element thermostat system (0.1 °C accuracy) by Analytik Jena. The system was operated with the ASpect UV software by Analytik Jena. The sample solutions were measured in QS High Precision Cells made of Quartz Suprasil® with a light path of 10 mm by Hellma Analytics.

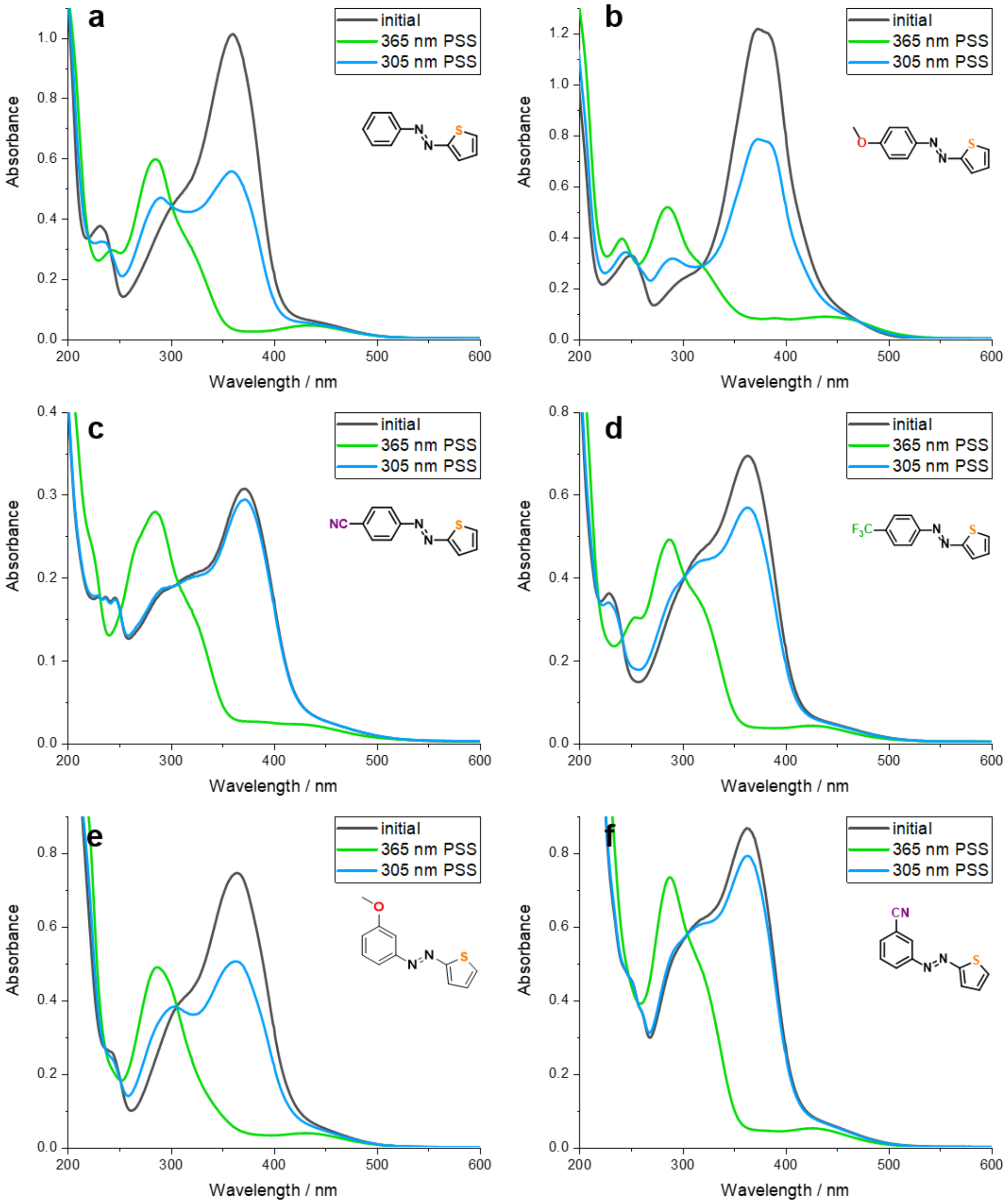


Figure S2: UV-Vis spectra of arylazothiophenes in their initial states and PSS_Z as well as PSS_E (acetonitrile, 25 °C).

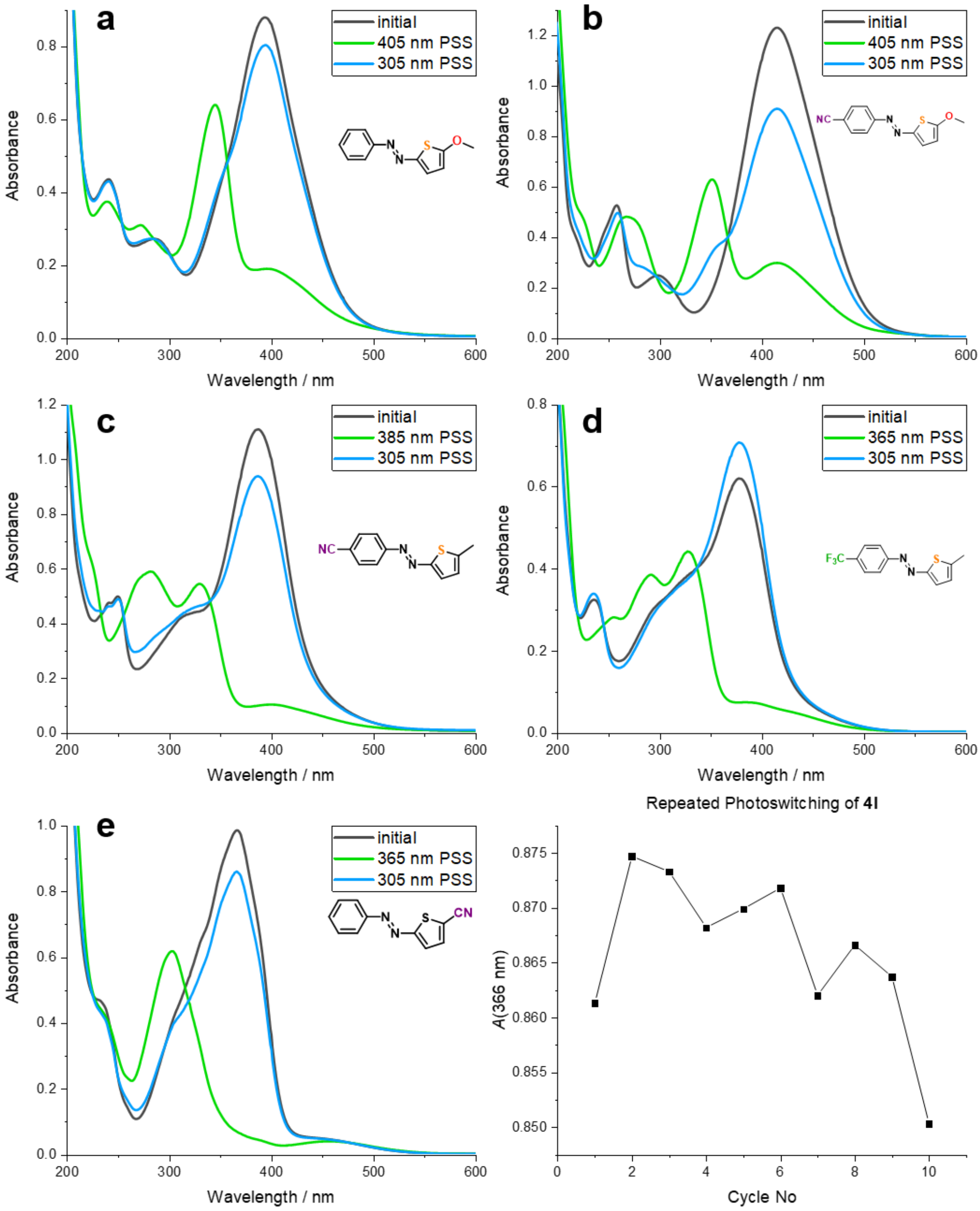


Figure S3: UV-Vis spectra of arylazothiophenes in their initial states and PSS_Z as well as PSS_E (acetonitrile, 25 °C). Compound **4l** showed slight signs of photodegradation after repeating the photoisomerization.

Kinetic Measurements

All samples were irradiated at the corresponding wavelengths for 1 min prior to the kinetic measurements. Spectra were recorded from 190 – 600 nm with a scan speed of 20 nm/s. The thermal isomerizations were monitored in 15 min intervals (10 °C and 15 °C) for 24 h and in 10 min intervals (20 °C and 25 °C) for 18 h. All compounds were measured three-fold at each temperature at concentrations of $5 \cdot 10^{-5}$ mol/L (**4g**: $7 \cdot 10^{-5}$ mol/L) in acetonitrile. For data analysis, Origin Pro 2016G by Origin Lab Corporation was used. The absorbances A at the maximum wavelengths were plotted against the time t elapsed after the start of the measurements. Rate constants k and half-lives $t_{1/2}$ were determined after fitting the data with an Exponential Decay Function (ExpDec1, Origin) according to the literature.[3]

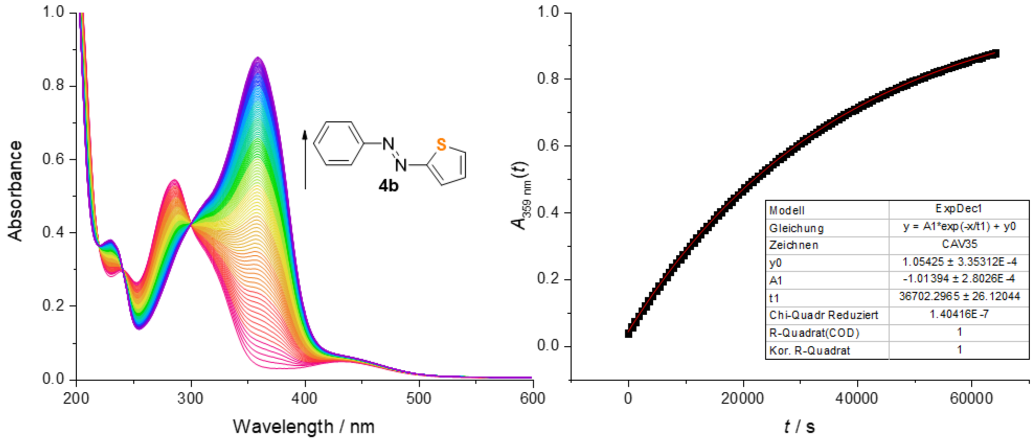


Figure S4: Left: reaction spectrum of the thermal isomerization of **4b** at 20 °C. Right: absorbance at 359 nm vs t and exponential fit of the data.

Table S3: k-values of azothiophenes **4** at 10 – 25 °C in acetonitrile.

		k / 10^{-5} s^{-1}			
ϑ / °C		10	15	20	25
4b	run 1	0.70	1.41	2.72	5.52
	run 2	0.70	1.37	2.70	5.36
	run 3	0.85	1.49	2.76	5.52
	Mean	0.75	1.43	2.73	5.47
	Δ	0.08	0.06	0.03	0.10
4c	run 1	11.2	20.6	38	72
	run 2	10.1	20.1	41	70
	run 3	11.1	19.9	38	73
	Mean	10.8	20.2	39	72

	Δ	0.6	0.4	1	2
	run 1	1.9	3.4	6.7	13.1
	run 2	1.7	3.7	6.7	13.3
4h	run 3	1.8	3.4	7.0	13.3
	Mean	1.8	3.5	6.8	13.3
	Δ	0.1	0.2	0.2	0.1
	run 1	0.72	1.5	2.98	5.95
	run 2	0.74	1.8	3.14	5.77
4d	run 3	0.77	1.5	2.99	5.92
	Mean	0.75	1.6	3.04	5.88
	Δ	0.03	0.2	0.09	0.10
	run 1	0.61	1.4	2.43	4.71
	run 2	0.59	1.2	2.43	4.79
4k	run 3	0.67	1.3	2.37	4.80
	Mean	0.63	1.3	2.41	4.77
	Δ	0.04	0.1	0.04	0.05
	run 1	38.3	70	117	200
	run 2	38.6	68	127	197
4i	run 3	37.6	69	118	205
	Mean	38.2	69	121	201
	Δ	0.5	1	6	4
	run 1	1.31	2.8	5.2	10.4
	run 2	1.29	2.8	5.5	10.4
4j	run 3	1.31	3.0	5.7	10.5
	Mean	1.30	2.9	5.5	10.5
	Δ	0.01	0.1	0.2	0.1
	run 1	0.37	0.60	1.35	2.37
	run 2	0.28	0.60	1.32	2.34
4e	run 3	0.30	0.55	1.35	2.39
	Mean	0.32	0.58	1.34	2.37
	Δ	0.04	0.03	0.02	0.02
	run 1	0.27	0.50	1.08	2.05
	run 2	0.32	0.52	1.11	2.06
4g	run 3	0.32	0.50	1.08	2.16
	Mean	0.30	0.51	1.09	2.09
	Δ	0.03	0.01	0.02	0.06
4l	run 1	6.7	15	26	48.9
	run 2	7.0	14	29	49.9

	run 3	6.8	16	28	49.6
	Mean	6.8	15	27	49.5
	Δ	0.1	1	1	0.5
	run 1	0.62	1.28	2.8	5.31
	run 2	0.69	1.29	2.9	5.27
4f	run 3	0.76	1.24	2.6	5.25
	Mean	0.69	1.27	2.8	5.28
	Δ	0.07	0.03	0.1	0.03

Table S4: Half-lives of azothiophenes **4** at 10 – 25 °C in acetonitrile.

		$t_{1/2}$ / h			
ϑ / °C		10	15	20	25
	run 1	28	13.6	7.08	3.49
	run 2	27	14.0	7.13	3.60
4b	run 3	23	12.9	6.96	3.49
	Mean	26	13.5	7.06	3.52
	Δ	3	0.5	0.09	0.06
	run 1	1.7	0.93	0.50	0.27
	run 2	1.9	0.96	0.47	0.28
4c	run 3	1.7	0.97	0.51	0.26
	Mean	1.8	0.95	0.49	0.27
	Δ	0.1	0.02	0.02	0.01
	run 1	10.1	5.7	2.87	1.46
	run 2	10.1	5.2	2.86	1.45
4h	run 3	10.4	5.6	2.76	1.46
	Mean	10.2	5.5	2.83	1.46
	Δ	0.2	0.3	0.06	0.01
	run 1	26.6	13	6.5	3.24
	run 2	26.1	11	6.1	3.34
4d	run 3	24.9	13	6.4	3.25
	Mean	25.9	12	6.3	3.28
	Δ	0.9	1	0.2	0.05
	run 1	32	14	7.9	4.09
	run 2	32	16	7.9	4.02
4k	run 3	29	15	8.1	4.01
	Mean	31	15	8.0	4.04
	Δ	2	1	0.1	0.04
4i	run 1	0.50	0.277	0.17	0.096

	run 2	0.50	0.285	0.15	0.098
	run 3	0.51	0.281	0.16	0.094
	Mean	0.50	0.281	0.16	0.096
	Δ	0.01	0.004	0.01	0.002
4j	run 1	14.72	6.8	3.7	1.85
	run 2	14.88	6.8	3.5	1.84
	run 3	14.73	6.4	3.4	1.83
	Mean	14.78	6.7	3.5	1.84
	Δ	0.09	0.2	0.1	0.01
4e	run 1	52	32	14.3	8.14
	run 2	68	32	14.5	8.21
	run 3	64	35	14.2	8.05
	Mean	61	33	14.3	8.13
	Δ	8	2	0.2	0.08
4g	run 1	73	38.4	17.9	9.4
	run 2	60	37.3	17.4	9.3
	run 3	60	38.4	17.8	8.9
	Mean	64	38.0	17.7	9.2
	Δ	7	0.6	0.2	0.3
4l	run 1	2.86	1.3	0.74	0.394
	run 2	2.75	1.4	0.67	0.386
	run 3	2.84	1.2	0.70	0.388
	Mean	2.82	1.3	0.70	0.389
	Δ	0.06	0.1	0.04	0.004
4f	run 1	31	15.0	7.0	3.63
	run 2	28	14.9	6.7	3.65
	run 3	25	15.6	7.3	3.67
	Mean	28	15.2	7.0	3.65
	Δ	3	0.4	0.3	0.02

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by an Eyring-Polanyi plot. The natural logarithm of k divided by the absolute temperature were plotted against T^{-1} for every experimental run to obtain $\Delta H^{\ddagger}$ from the slope and $\Delta S^{\ddagger}$ from the y-intercept according to

$$m = \frac{-\Delta H^{\ddagger}}{R}$$

and

$$y_{x=0} = \ln\left(\frac{k_{\mathrm{B}}}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$$

with the molar gas constant R, the Boltzmann-constant k_{B}, and the Planck-constant h.

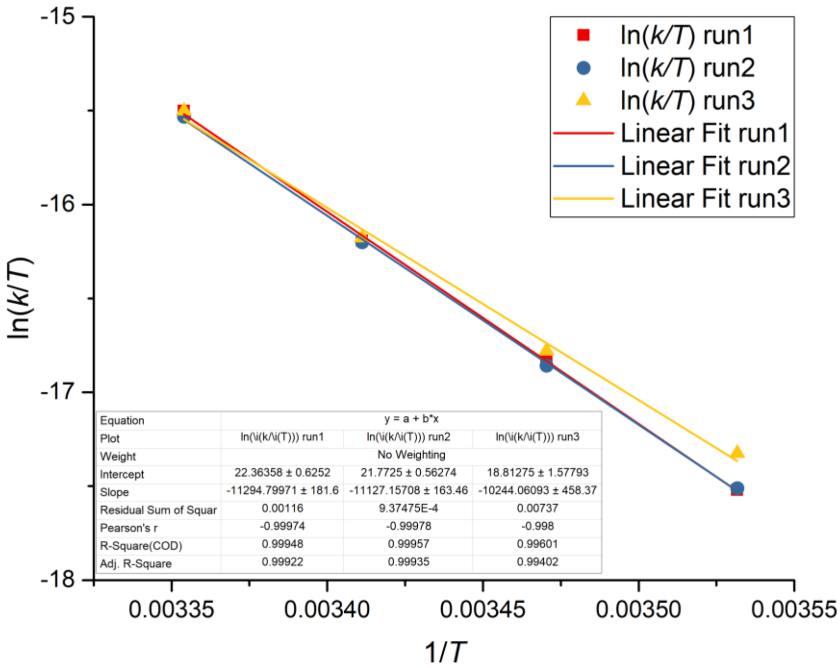


Figure S5: Eyring-Polanyi plot of azothiophene **4b**.

Finally, $\Delta G^{\ddagger}$ was calculated at 298.15 K according to the Gibbs-Helmholtz equation.

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\,\Delta S^{\ddagger}$$

The average values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ from all three runs were calculated and are given in Table S5.

Table S5: Half-lives, rate constants (both 20 °C) and $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$ values for azothiophenes **4a-l**.

Compound	$t_{1/2,20\,°C}$ / h	$k_{20\,°C}$ / 10^{-5} s^{-1}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ / kcal mol^{-1}
4a[a]	1.92	10.0	20.4	–7.2	22.5
4b	7.06	2.73	22 ± 1	–5 ± 4	23.27 ± 0.01
4c	0.494	39.0	20.7 ± 0.5	–3 ± 2	21.73 ± 0.01
4d	6.35	3.04	22.4 ± 0.5	–3 ± 2	23.21 ± 0.01
4e	14.3	1.34	23 ± 1	–4 ± 5	23.73 ± 0.01
4f	6.99	2.76	23 ± 1	–3 ± 4	23.28 ± 0.02
4g	17.7	1.09	22 ± 1	–8 ± 3	23.84 ± 0.01
4h	2.83	6.80	21.6 ± 0.4	–4 ± 1	22.74 ± 0.01
4i	0.160	121	18.0 ± 0.3	–10.4 ± 0.9	21.11 ± 0.01
4j	3.53	5.46	22.5 ± 0.1	–1.1 ± 0.5	22.86 ± 0.01
4k	7.99	2.41	22.0 ± 0.9	–5 ± 3	23.34 ± 0.01
4l	0.704	27.4	21.4 ± 0.2	–1.7 ± 0.8	21.93 ± 0.01

[a] Taken from ref. [4]

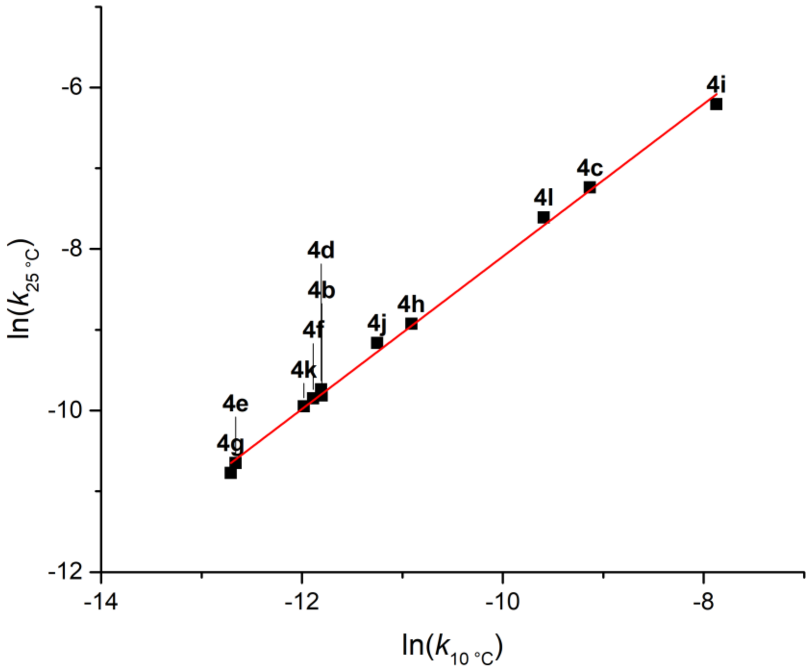


Figure S6: The Exner-plot of the natural logarithm of *k* at 25 °C vs the natural logarithm of *k* at 10 °C showed a linear relationship, which indicates that all azothiophenes isomerize according to the same mechanism in the experimental temperature range.

Determination of PSS compositions by HPLC

The PSS isomer concentrations were determined with a Shimadzu LCMS-2020 system using a 150 x 4 mm Eurospher 100-5 C18 column with acetonitrile/water (90:10) as isocratic eluent (1.5 mL/min). Detection was carried out using a Shimadzu SPD-M20A diode array detector at the previously determined isosbestic wavelengths (see Figure S2, Figure S3). The change from pure acetonitrile to acetonitrile/water (90:10) in the separation had only negligible effect on the isosbestic wavelengths, as show in Figure S7. Irradiation of the samples was carried out in 2 mL glass vials for 3 min (1 min at 305 nm) at the corresponding wavelength in 100% acetonitrile, from which aliquots of 10 µL ($5 \cdot 10^{-4}$ mol/L) or 50 µL ($5 \cdot 10^{-5}$ mol/L) were injected for analysis. For all determined isomer ratios, an error of ±1% is assumed.

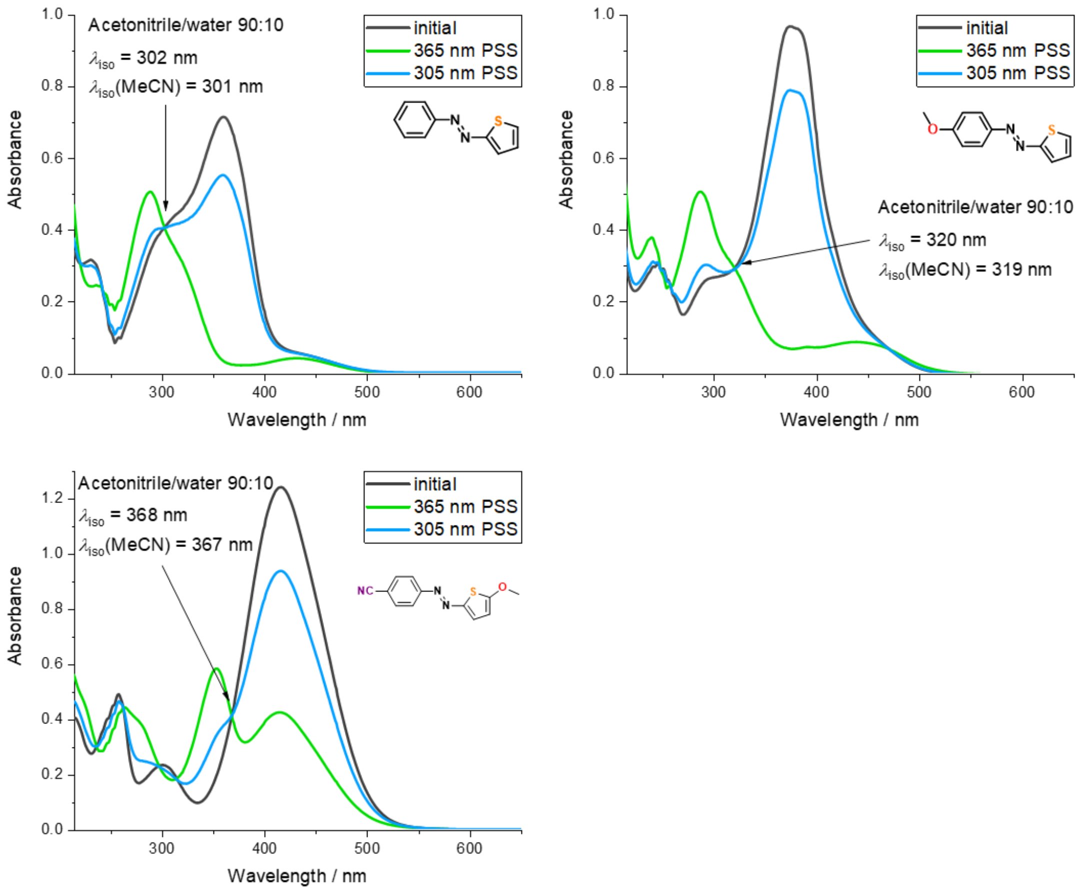
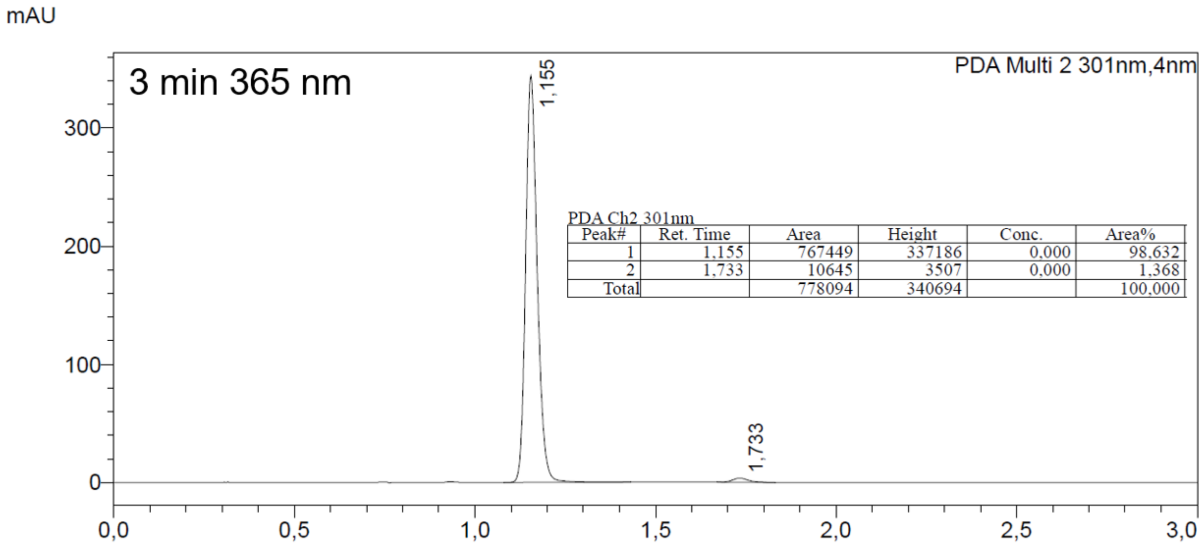
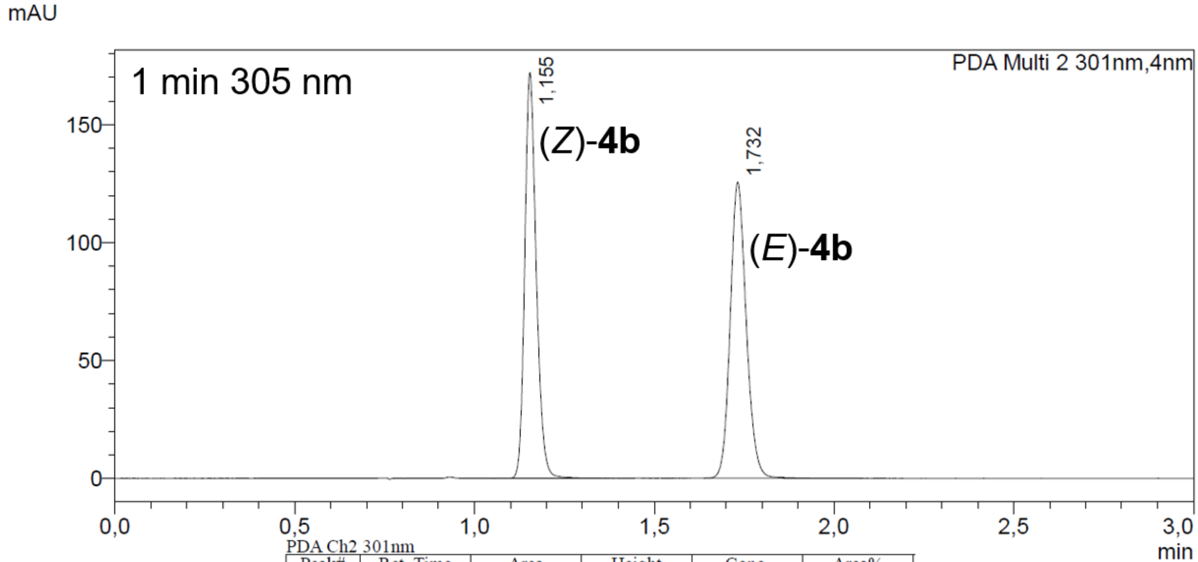


Figure S7: UV-Vis spectra of compounds **4b**,**c**,**i** in acetonitrile/water, 90:10. The isosbestic points shifted to +1 nm compared to pure MeCN, which had no impact on the intregration and obtained isomer ratios at the PSSs.



PDA Ch2 301nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	1,155	767449	337186	0,000	98,632
2	1,733	10645	3507	0,000	1,368
Total		778094	340694		100,000



PDA Ch2 301nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	1,155	382984	167223	0,000	49,590
2	1,732	389318	124539	0,000	50,410
Total		772302	291762		100,000

Figure S8: Chromatograms of the PSSs of azothiophene **4b**, detected at the isosbestic wavelength of 301 nm. Top: after irradiation at 365 nm for 3 min, bottom: after irradiation at 305 nm for 1 min.

Computations

All computations were performed using the Gaussian16[5] and ORCA 4.2[6] program packages. Geometry optimizations were performed on the PBE0-D3(BJ)[7] and TPSSh[8] levels of theory, using the def2-TZVP[9] basis set. Geometries were visualized using CYLView.[10] High level single point corrections were computed at the DLPNO-CCSD(T)[11] level with tight PNO cutoff using the def2-TZVP basis set. All T_1 diagnostic values were found < 0.02, verifying the validity of the single-reference-based electron correlation method.[12] Thermal energies were obtained from DFT frequency computations on every optimized geometry. Additionally, solvation energies were obtained using the SMD model[13] at the same DFT level of theory. Ground-state geometries were verified by the absence of imaginary frequencies, and transition states were identified by showing one imaginary frequency. Furthermore, transition states were confirmed by IRC computations using the LQA algorithm[14] on the corresponding DFT level with the def2-TZVP basis set.

Conformational analysis of (*E*)-4b

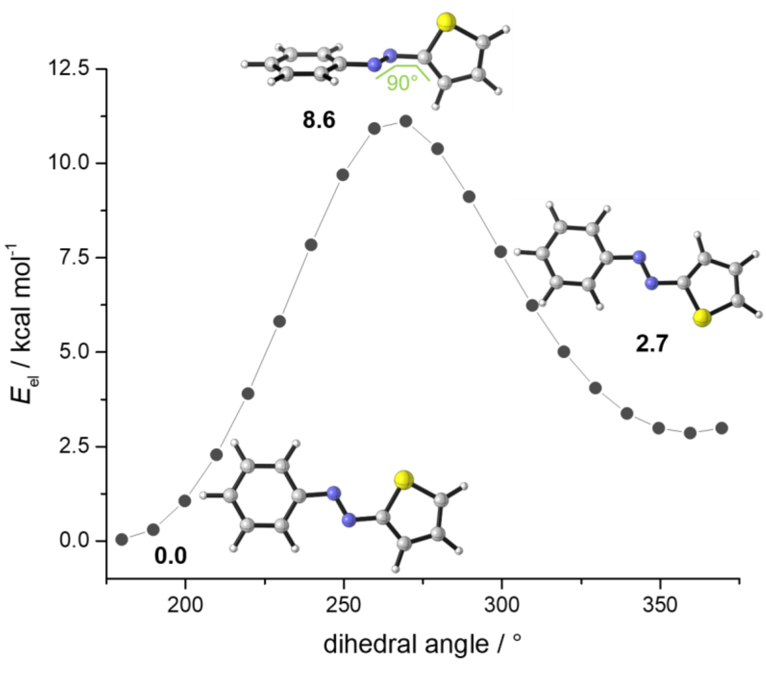


Figure S9: Rotational energy profile of the NNC$_{2\text{-thiophene}}$C$_{3\text{-thiophene}}$ dihedral angle from (*E*)-*cis* to (*E*)-*trans*-**4b** at PBE0-D3(BJ)/def2-TZVP. Bold numbers are DLPNO-CCSD(T)/def2-TZVP energies of the corresponding structures.

Conformational analysis of (*Z*)-4b

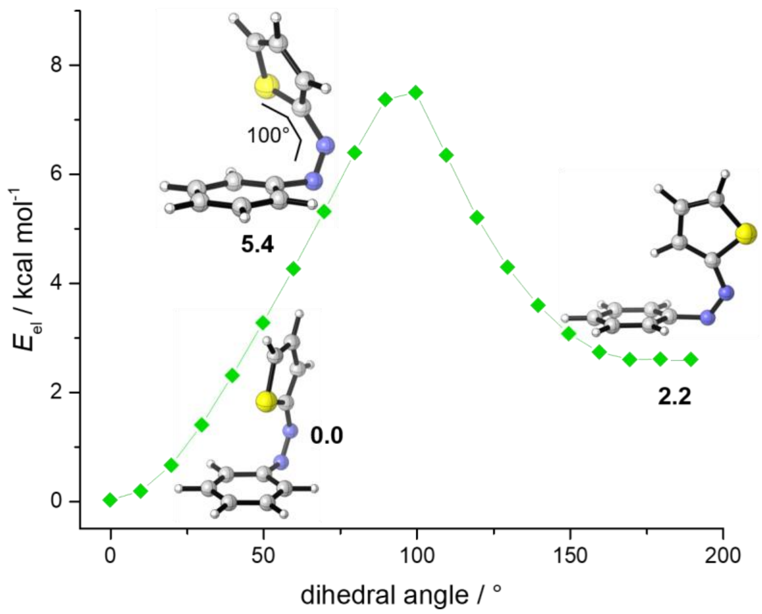


Figure S10: Rotational energy profile of the NNCS dihedral angle from (*Z*)-T-shaped to (*Z*)-twist-**4b** at PBE0-D3(BJ)/def2-TZVP. Bold numbers are DLPNO-CCSD(T)/def2-TZVP energies of the corresponding structures.

Transition states on the S_0 isomerization pathway

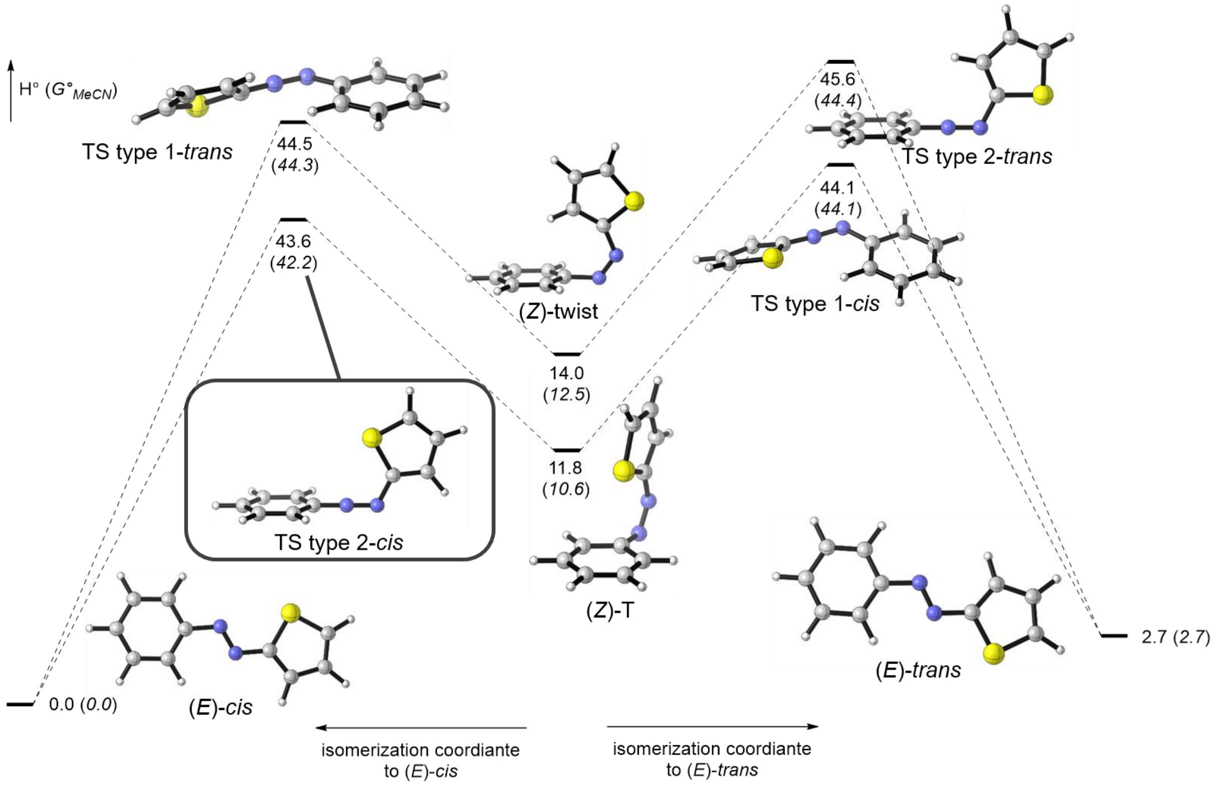


Figure S11: Relative energy landscape of the singlet (*Z*)⟶(*E*) isomerization pathway of azothiophene **4b** on DLPNO-CCSD(T)/def2-TZVP//PBE0-D3(BJ)/def2-TZVP level of theory. The lowest-lying TS was found to be the type 2-*cis* transition state.

Relative energies on the S_0 and T_1 pathways

Table S6: Relative energies of all geometries involved on the minimum energy pathway of the thermal isomerization of azothiophene **4b**.

Structure	DLPNO-CCSD(T)/def2-TZVP//PBE0(D3BJ)-def2-TZVP		TPSSh/def2-TZVP	
	$\Delta H°$ / kcal mol^{-1}	$\Delta G°_{MeCN}$ / kcal mol^{-1}	$\Delta H°$ / kcal mol^{-1}	$\Delta G°_{MeCN}$ / kcal mol^{-1}
E-*cis*	0.0	0.0	0.0	0.0
TS	43.6	42.2	38.7	37.0
Z-T	11.8	10.6	14.5	12.9
T_1 NNCS-*cis*	-	-	25.7	24.4
T_1 TS	-	-	37.0	36.5
T_1 NNCS-*trans*	-	-	27.4	24.5

Coordinates of PBE0-D3(BJ)/def2-TZVP geometries

(*E*)-*cis*

H	-1.67704211	-0.91739285	0.94774598
H	-4.06071146	-1.60115098	0.82709982
C	-2.17058072	-1.05325532	-0.00582937
H	2.17255245	0.18187236	1.94700954
C	-3.49579278	-1.43333279	-0.08283385
C	2.55355584	0.29748494	0.94166756
H	4.6434045	0.89526917	1.32185724
N	-0.09814156	-0.45064471	-1.22280025
C	3.86650176	0.67661039	0.6021483
C	-1.44711255	-0.83827678	-1.18090595
C	-4.1109329	-1.60237066	-1.32001543
C	1.76749905	0.07857392	-0.16333924
N	0.45126643	-0.29972149	-0.11138742
C	-2.06282932	-1.00748048	-2.41791698
C	4.05156198	0.73810378	-0.75143558
C	-3.39238082	-1.38885551	-2.48667511
S	2.64834191	0.34059505	-1.63433211
H	-1.47528938	-0.83326554	-3.31155072
H	-3.86856489	-1.51966641	-3.4512637
H	-5.15167284	-1.90092336	-1.37020415
H	4.9578948	1.00161045	-1.27652969

E(el) / Hartree		-893.017139	
E(el) SMD / Hartree		-893.031172	
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree		-892.1454101	
Thermal corrections / Hartree			
ZPVE	0.158131	E(therm):	0.168512
H(corr)	0.169456	G(corr):	0.120327
Imaginary frequencies	0		

***(E)*-trans**

H	1.07902517	-1.63410294	9.407E-07
H	3.50277627	-2.17139697	6.696E-07
C	1.82408044	-0.84917807	1.151E-07
H	-2.07999399	2.53480523	-1.3927E-06
C	3.17423984	-1.13825871	-4.6E-08
C	-2.66757007	1.62804516	-4.99E-07
H	-4.71876545	2.42868198	-5.172E-07
N	0.06133452	0.89577362	-7.342E-07
C	-4.07062995	1.56241069	-2.37E-08
C	1.40538469	0.48320006	-8.036E-07
C	4.11589759	-0.11304864	-1.1147E-06
C	-2.09075447	0.37748898	3.259E-07
N	-0.7733801	-0.03339311	2.536E-07
C	2.34777653	1.50771114	-1.8722E-06
C	-4.54167687	0.27371905	1.1433E-06
C	3.70037336	1.2098541	-2.0328E-06
S	-3.28287132	-0.86353426	1.6846E-06
H	1.99262671	2.53146324	-2.5637E-06
H	4.43093974	2.01024277	-2.8643E-06
H	5.17355966	-0.35008548	-1.2315E-06
H	-5.57046363	-0.05272981	1.7038E-06

E(el) / Hartree	-893.01263
E(el) SMD / Hartree	-893.026334
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree	-892.1411172

Thermal corrections / Hartree

ZPVE:	0.157992	E(therm):	0.168437
H(corr):	0.169381	G(corr):	0.119979
Imaginary frequencies	0		

(Z)-T

H	-0.69227127	-1.76532324	-2.13739307
H	-2.57419501	-0.1539141	-2.14085905
S	1.36146761	0.33077925	-1.1172E-06
C	-1.10760137	-1.39826248	-1.20620431
C	-2.16033323	-0.49826083	-1.20011232
C	2.85022274	1.14994402	-2.6854E-06
N	1.6567934	-2.50731121	3.1267E-06
N	0.45589404	-2.81708935	3.8402E-06
C	2.16568317	-1.21629339	1.0943E-06
C	-0.56738145	-1.83183045	2.6546E-06
C	-2.68510753	-0.04017159	5.786E-07
C	3.92578461	0.30345377	-1.5895E-06
C	3.53258047	-1.04370128	5.543E-07
C	-1.10760052	-1.39825867	1.20620864
C	-2.16033239	-0.49825706	1.20011455
H	4.95315915	0.64035323	-2.3074E-06
H	4.19919245	-1.89515342	1.7145E-06
H	-0.69226975	-1.76531649	2.13739826
H	-2.57419352	-0.15390736	2.14086049
H	2.8647813	2.2304805	-4.3495E-06
H	-3.51008085	0.66210801	-2.373E-07

E(el) / Hartree		-892.996767	
E(el) SMD / Hartree		-893.012816	
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree		-892.1262461	
Thermal corrections / Hartree			
ZPVE:	0.157736	E(therm):	0.168113
H(corr):	0.169057	G(corr):	0.120031
Imaginary frequencies	0		

(*Z*)-twisted

H	1.48373317	1.58250194	-2.20500221
H	3.40497567	0.01963043	-2.07848308
S	-3.27926624	0.69024421	0.31414429
C	1.80100202	1.17094011	-1.25409871
C	2.87483361	0.2979571	-1.17488105
C	-3.26042528	-0.99950286	0.25704752
N	-1.14373198	2.10673555	-0.08975341
N	0.04630889	2.44921552	-0.17525057
C	-1.58328852	0.78547132	0.00732979
C	1.10748036	1.51116156	-0.0993579
C	3.2768185	-0.21117142	0.05180873
C	-2.00801148	-1.48966352	-0.0112016
C	-1.04312689	-0.47786588	-0.15283049
C	1.52021177	1.02525051	1.1369021
C	2.60344461	0.16572849	1.20617976
H	-1.78815939	-2.54531485	-0.09901508
H	-0.00476166	-0.67157662	-0.36969194
H	0.98376474	1.31887386	2.03153021
H	2.92297553	-0.21458512	2.16967863
H	4.12178407	-0.88665399	0.11048517
H	-4.16512251	-1.56426208	0.42459508

E(el) / Hartree		-892.992653	
E(el) SMD / Hartree		-893.008277	
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree		-892.1228054	
Thermal corrections / Hartree			
ZPVE:	0.157845	E(therm):	0.168243
H(corr):	0.169187	G(corr):	0.11917
Imaginary frequencies	0		

TS type 1-*cis*

C	3.73324417	-0.27280475	-0.15502925
C	2.48833072	-0.88098939	-0.27822659
C	1.33221115	-0.13510945	-0.14717656
C	3.81919911	1.08958891	0.09527277
H	2.4238533	-1.94471581	-0.47704902
H	0.3585694	-0.60002094	-0.2474814
N	0.29920919	2.09706799	0.24652732
C	2.66462908	1.84291175	0.22222754
C	1.42053016	1.23225599	0.1079526
H	4.78875514	1.56451166	0.18986825
H	2.69684721	2.90952642	0.41203216
N	-0.8130873	1.56686013	0.18294733
C	-1.98912934	1.06157647	0.17038481
C	-3.1852901	1.61544489	-0.2918479
H	-3.22045513	2.63888343	-0.63960722
S	-2.32896446	-0.6636086	0.63980459
C	-4.27476457	0.74479236	-0.25220956
C	-3.97389642	-0.4806979	0.29580456
H	-5.2776816	1.02595889	-0.54394882
H	4.63595027	-0.86392159	-0.25673044
H	-4.68483318	-1.24352059	0.57940789

E(el) / Hartree	-892.953515
E(el) SMD / Hartree	-892.967681
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree	-892.0725992

Thermal corrections / Hartree

ZPVE:	0.155666	E(therm):	0.165994
H(corr):	0.166938	G(corr):	0.117948
Imaginary frequencies	1	–383.226 cm^{-1}	

TS type 1-*trans*

C	-0.48653219	-4.6024917	2.75709975
C	0.82380215	-4.19354661	2.55221553
C	1.08359793	-2.91993585	2.07537756
C	-1.53803876	-3.73373649	2.48442316
H	1.64340581	-4.87066617	2.76262925
H	2.09435876	-2.57203882	1.89624953
N	0.406595	-0.76967026	1.30973025
C	-1.2842877	-2.45814651	2.01615507
C	0.032028	-2.04919158	1.81349193
H	-2.56064848	-4.05819436	2.64038736
H	-2.09519677	-1.77479561	1.79479297
N	-0.50728736	0.03357033	1.11690377
C	-1.49319738	0.83365395	0.92720417
C	-2.65204113	1.02730108	1.68545807
H	-2.88697609	0.39059634	2.52767946
S	-1.43446392	2.11329657	-0.3411101
C	-3.43147152	2.10683529	1.26254822
C	-2.93884369	2.72407489	0.13754979
H	-4.37278697	2.38166452	1.71925173
H	-0.69198536	-5.60008983	3.12750881
H	-3.45189102	3.45934818	-0.4652298

E(el) / Hartree	-892.95261		
E(el) SMD / Hartree	-892.96747		
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree	-892.0719886		
Thermal corrections / Hartree			
ZPVE:	0.155772	E(therm):	0.16604
H(corr):	0.166984	G(corr):	0.118244
Imaginary frequencies	1	–386.732 cm^{-1}	

TS type 2-*cis*

H	1.33721419	-3.64099154	2.46243908
H	0.45905305	-4.47506048	4.59712208
C	0.49352209	-3.1557991	2.93578848
H	2.06032021	0.05913766	-1.98206977
C	-0.01173054	-3.61336131	4.1362125
C	2.35818536	0.34817851	-0.98343667
H	3.91553829	1.85937808	-1.39124178
N	0.36075983	-1.59004708	1.15441402
C	3.34260541	1.30342621	-0.66178557
C	-0.10066668	-2.03779613	2.31154867
C	-1.09391361	-3.00160172	4.75483943
C	1.79023772	-0.2029347	0.13469275
N	0.78636657	-1.17705632	0.09495058
C	-1.20029517	-1.41025087	2.93578452
C	3.49572318	1.4520103	0.6892337
C	-1.67284862	-1.90151109	4.13620855
S	2.45882224	0.44584059	1.59193139
H	-1.65989311	-0.55234941	2.46243209
H	-2.52000034	-1.40502395	4.59711501
H	-1.47726113	-3.37358624	5.69589667
H	4.17758863	2.11367016	1.20298025

E(el) / Hartree	-892.952367		
E(el) SMD / Hartree	-892.967976		
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree	-892.0735000		
Thermal corrections / Hartree			
ZPVE:	0.155649	E(therm):	0.166099
H(corr):	0.167043	G(corr):	0.117209
Imaginary frequencies	1	–457.549 cm^{-1}	

TS type 2-*trans*

H	-2.11907474	0.6568949	0.80863276
H	-3.80910547	2.34469745	1.37153803
C	-2.11861133	1.61988543	0.31468243
H	1.60502658	1.7908499	0.88441624
C	-3.06311992	2.57914544	0.61971983
C	2.21395558	0.9882132	0.48992311
H	4.02311649	1.157517	1.73666592
N	-0.22635958	0.9902628	-0.97353019
C	3.50132434	0.64606008	0.93894279
C	-1.1369661	1.89477395	-0.6636903
C	-3.07775411	3.81792231	-0.00774388
C	1.7986258	0.17144076	-0.53303374
N	0.59716197	0.15048059	-1.27437162
C	-1.14603309	3.15380096	-1.30492362
C	4.03305147	-0.41594352	0.25244141
C	-2.10985027	4.08260969	-0.96774377
S	2.97838826	-1.00480318	-0.93858624
H	-0.3983797	3.37071253	-2.05678932
H	-2.09944636	5.04111578	-1.47553183
H	-3.82608338	4.55791377	0.2437209
H	4.99890281	-0.87628347	0.3964588

E(el) / Hartree	-892.948998
E(el) SMD / Hartree	-892.964278
E(el) DLPNO-CCSD(T)/def2-TZVP / Hartree	-892.0703463

Thermal corrections / Hartree

ZPVE:	0.15557	E(therm):	0.166045
H(corr):	0.166989	G(corr):	0.117244
Imaginary frequencies	1	–434.271 cm^{-1}	

Coordiantes of TPSSh/def2-TZVP geometries

Singlet (*E*)-*cis*

H	1.63658661	2.02702329	4.4149E-06
H	4.11289996	2.25348145	6.8706E-06
C	2.27575741	1.153496	2.3584E-06
H	-2.49647583	2.45759648	2.3059E-06
C	3.65617301	1.26988892	3.7035E-06
C	-2.74594609	1.40537052	-7.917E-07
H	-4.95337198	1.47628242	-2.2193E-06
N	0.30084399	-0.36374764	-3.444E-06
C	-4.05358039	0.87594573	-3.2203E-06
C	1.68966097	-0.12071138	-1.7374E-06
C	4.46402071	0.1300888	1.0066E-06
C	-1.77604602	0.42404557	-2.7942E-06
N	-0.42537828	0.66957371	-1.1178E-06
C	2.49914687	-1.26082007	-4.4199E-06
C	-4.05892568	-0.49620555	-7.0308E-06
C	3.88264359	-1.13446487	-3.0498E-06
S	-2.48476521	-1.1734288	-7.7464E-06
H	2.01928293	-2.23249764	-7.5617E-06
H	4.50682444	-2.02068284	-5.1427E-06
H	5.54336672	0.23198706	2.0841E-06
H	-4.92033074	-1.14777416	-9.4681E-06

E(el) / Hartree		-893.769867	
E(el) SMD / Hartree		-893.783378	
Thermal corrections / Hartree			
ZPVE:	0.156246	E(therm):	0.166763
H(corr):	0.167707	G(corr):	0.118335
Imaginary frequencies	0		

Singlet (*Z*)-T

H	1.37672557	0.82627011	-2.14330012
H	3.12002238	-0.93665202	-2.14521625
S	-0.9960683	-1.00269216	-1.9725E-06
C	1.75370153	0.42355822	-1.21036924
C	2.73433635	-0.56157304	-1.20380967
C	-2.59384378	-1.60821896	-3.3708E-06
N	-0.89921947	1.86366908	2.2704E-06
N	0.34230011	2.01255156	2.8695E-06
C	-1.58364642	0.65212376	3.448E-07
C	1.24807916	0.90383679	1.7305E-06
C	3.22455806	-1.0607706	-8.93E-08
C	-3.54301894	-0.6161643	-2.1457E-06
C	-2.96668256	0.66692624	-4.51E-08
C	1.75370016	0.4235546	1.21037183
C	2.73433501	-0.56157663	1.20381043
H	-4.60752246	-0.8071302	-2.7452E-06
H	-3.51245608	1.60051369	1.1709E-06
H	1.37672314	0.82626369	2.1433035
H	3.12001999	-0.9366584	2.14521633
H	-2.75873744	-2.67617244	-5.0291E-06
H	3.99294401	-1.82497698	-7.978E-07

E(el) / Hartree	-893.74632		
E(el) SMD / Hartree	-893.761844		
Thermal corrections / Hartree			
ZPVE:	0.155679	E(therm):	0.16627
H(corr):	0.167214	G(corr):	0.117422
Imaginary frequencies	0		

Singlet TS type 2-*cis*

H	-1.72156636	0.42831277	-2.15755576
H	-3.99458051	-0.50535875	-2.14374
C	-2.22264723	0.21974933	-1.22105796
H	3.45922168	2.09296483	3.1154E-06
C	-3.50411816	-0.30537492	-1.19678565
C	3.19740377	1.04364381	1.4614E-06
H	5.18765472	0.08277587	-7.14E-08
N	-0.33331718	1.02140211	1.4928E-06
C	4.11200314	-0.03135017	-2.398E-07
C	-1.55589496	0.49383207	7.202E-07
C	-4.16433429	-0.57656707	-8.36E-07
C	1.8895775	0.61611707	8.057E-07
N	0.79426433	1.496586	2.2121E-06
C	-2.22264699	0.2197452	1.2210586
C	3.48178397	-1.25029384	-2.1475E-06
C	-3.50411793	-0.30537894	1.19678477
S	1.77461267	-1.12236725	-1.9255E-06
H	-1.72156594	0.42830547	2.15755702
H	-3.99458011	-0.50536595	2.14373854
H	-5.16607473	-0.98671182	-1.4317E-06
H	3.94163961	-2.22760482	-3.6889E-06

E(el) / Hartree	-893.705796		
E(el) SMD / Hartree	-893.720821		
Thermal corrections / Hartree			
ZPVE:	0.153639	E(therm):	0.16429
H(corr):	0.165234	G(corr):	0.114694
Imaginary frequencies	1	–463.921 cm^{-1}	

Triplet NNCS-*cis*

H	1.21277431	1.78083107	-0.11308001
H	3.43660594	2.04712604	-1.17557839
C	1.94316979	0.98194271	-0.07744577
H	-2.68118674	2.15930235	1.2951481
C	3.18821322	1.123975	-0.66357801
C	-2.70188047	1.31269218	0.62333735
H	-4.66992073	1.55214439	-0.31641497
N	0.41166749	-0.44741726	1.20289935
C	-3.75321297	0.98266987	-0.23789123
C	1.61751243	-0.21709962	0.59832458
C	4.12761983	0.09148965	-0.59936799
C	-1.62768898	0.40892165	0.5393644
N	-0.4999525	0.48519118	1.22852329
C	2.57704215	-1.25163776	0.66945279
C	-3.51714022	-0.15891109	-0.9754875
C	3.81271689	-1.09454807	0.06986977
S	-1.98250901	-0.85931526	-0.63805985
H	2.31427198	-2.16108546	1.19632066
H	4.54180939	-1.89503569	0.12353819
H	5.10002033	0.21307121	-1.06209647
H	-4.17754512	-0.62986008	-1.68781529

E(el) / Hartree	-893.72679		
E(el) SMD / Hartree	-893.740833		
Thermal corrections / Hartree			
ZPVE:	0.153834	E(therm):	0.16459
H(corr):	0.165534	G(corr):	0.114665
Imaginary frequencies	0		

Triplet NNCS-*trans*

H	-1.02771044	-1.56952006	-0.06547252
H	-3.16305059	-2.11506345	1.06787945
C	-1.83800848	-0.85150036	-0.03608224
H	1.24997499	1.7795901	0.63551588
C	-3.03513026	-1.14976788	0.5904665
C	1.94063815	1.02141849	0.29421174
H	3.69730148	1.44267026	1.5427335
N	-0.51929357	0.78523371	-1.30470852
C	3.24609091	0.83873382	0.76615119
C	-1.6686099	0.40269786	-0.66717872
C	-4.07938204	-0.22174604	0.61046192
C	1.60274943	0.10487373	-0.71680032
N	0.48115163	-0.04509323	-1.41554537
C	-2.7334654	1.33088607	-0.65335699
C	3.91295116	-0.19463896	0.14231428
C	-3.9193188	1.01789583	-0.01497232
S	2.95427548	-0.96333524	-1.0556132
H	-2.59149739	2.28392211	-1.14881532
H	-4.73007337	1.73753983	-0.00447799
H	-5.01296715	-0.4655355	1.10384513
H	4.91866815	-0.53839709	0.32945093

E(el) / Hartree	-893.724133		
E(el) SMD / Hartree	-893.740833		
Thermal corrections / Hartree			
ZPVE:	0.153901	E(therm):	0.164639
H(corr):	0.165583	G(corr):	0.114758
Imaginary frequencies	0		

Triplet TS

C	4.56721854	0.44759993	0.38543623
C	4.19046934	-0.64510419	-0.3995774
C	2.85457126	-0.9096645	-0.64566877
C	3.58297646	1.2770661	0.92378935
H	4.94886348	-1.29527947	-0.82134326
H	2.55180304	-1.75496241	-1.25212029
N	0.55114988	-0.38581963	-0.3855043
C	2.23993435	1.03032111	0.68809201
C	1.85889671	-0.07298228	-0.10407078
H	3.86789211	2.12663133	1.53519657
H	1.47001326	1.66936936	1.10412457
N	-0.41891738	0.30710577	0.06923604
C	-1.73639864	0.35074319	-0.05127274
C	-2.50617404	1.05267435	-0.98030369
H	-2.05036397	1.60612844	-1.78982227
S	-2.80067264	-0.41445236	1.14621022
C	-3.8853347	0.95474204	-0.74468678
C	-4.19061493	0.20068319	0.36718594
H	-4.63909412	1.42017101	-1.36562321
H	5.61477772	0.64889857	0.57549468
H	-5.17309973	-0.02098354	0.75675086

E(el) / Hartree	-893.707912		
E(el) SMD / Hartree	-893.721457		
Thermal corrections / Hartree			
ZPVE:	0.153405	E(therm):	0.163774
H(corr):	0.164718	G(corr):	0.114542
Imaginary frequencies	1	–197.087 cm^{-1}	

References

[1] M. J. Hansen, M. M. Lerch, W. Szymanski, B. L. Feringa, *Angew. Chem. Int. Ed.* **2016**, *55*, 13514–13518.

[2] B. Haag, Z. Peng, P. Knochel, *Org. Lett.* **2009**, *11*, 4270–4273.

[3] L. Schweighauser, M. A. Strauss, S. Bellotto, H. A. Wegner, *Angew. Chem. Int. Ed.* **2015**, *54*, 13436–13439.

[4] C. Slavov, C. Yang, A. H. Heindl, H. A. Wegner, A. Dreuw, J. Wachtveitl, *Angew. Chem. Int. Ed.* **2020**, *59*, 380–387.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji et al., *Gaussian 16 Rev. A.03*, Wallingford, CT, **2016**.

[6] a) F. Neese, *WIREs Comput Mol Sci* **2012**, *2*, 73–78; b) F. Neese, *WIREs Comput Mol Sci* **2018**, *8*, 33.

[7] a) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868; c) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; d) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[8] a) V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, *J. Chem. Phys.* **2003**, *119*, 12129–12137; b) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.

[9] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[10] C. Y. Legault, *CYLview*, Université de Sherbrooke, **2009**.

[11] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.* **2013**, *139*, 134101.

[12] T. J. Lee, P. R. Taylor, *Int. J. Quantum Chem.* **1989**, *36*, 199–207.

[13] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[14] a) M. Page, C. Doubleday, J. W. McIver, *J. Chem. Phys.* **1990**, *93*, 5634–5642; b) M. Page, J. W. McIver, *J. Chem. Phys.* **1988**, *88*, 922–935.