Supporting Information

Spiroconjugated Donor−σ−Acceptor Charge-Transfer Dyes: Effect of the π-Subsystems on the Optoelectronic Properties

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1. Single-Crystal X-Ray Analysis

1.1 Growing singles crystals by solvent layering

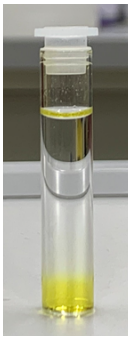


Figure S1: A solution of the spirocompound **7** in CH_2Cl_2 was layered with *n*-hexane. The crystals were grown at 268 K.

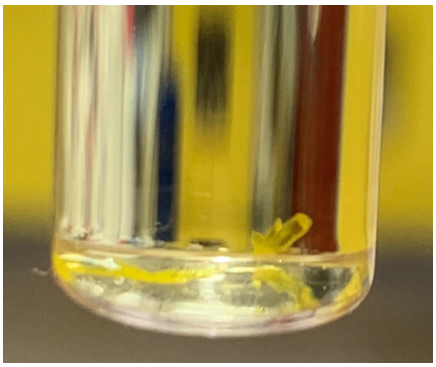
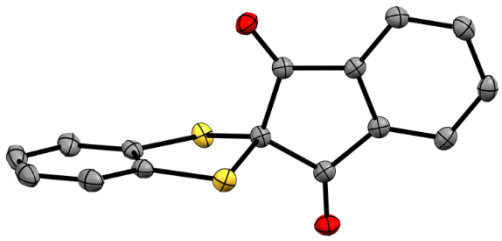


Figure S2: Single-crystals of **7**.

Figure S3: A shock-cooled single-crystal of **7** mounted on a holder in perfluoroether oil.

1.2 Single-crystal structure and packing of 7

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single yellow block-shaped crystals of **7** were recrystallised from a mixture of $CHCl_3$ and methanol by solvent layering. A suitable crystal 0.45×0.30×0.10 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{15}H_8O_2S_2$, M_r = 284.33, monoclinic, $P2_1/n$ (No. 14), a = 9.424(9) Å, b = 9.680(9) Å, c = 13.829(10) Å, β = 94.214(6)°, $\alpha = \gamma = 90°$, V = 1258.2(18) Å³, T = 100(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.415, 22528 reflections measured, 2875 unique (R_{int} = 0.0422) which were used in all calculations. The final wR_2 was 0.0947 (all data) and R_1 was 0.0339 (I > 2(I)).

Compound	**7**
CCDC	1859605
Formula	$C_{15}H_8O_2S_2$
$D_{calc.}$/ g cm^{-3}	1.501
μ/mm^{-1}	0.415
Formula Weight	284.33
Colour	yellow
Shape	block
Size/mm³	0.45×0.30×0.10
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	9.424(9)
b/Å	9.680(9)
c/Å	13.829(10)
α/°	90
β/°	94.214(6)
γ/°	90
V/Å³	1258.2(18)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.531
Θ_{max}/°	27.481
Measured Refl.	22528
Independent Refl.	2875
Reflections with I > 2(I)	2621
R_{int}	0.0422
Parameters	172
Restraints	0
Largest Peak	0.470
Deepest Hole	-0.289
GooF	1.064
wR_2 (all data)	0.0947
wR_2	0.0919
R_1 (all data)	0.0371
R_1	0.0339

A yellow block-shaped crystal with dimensions 0.45×0.30×0.10 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100(2) K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 27.481° (0.77 Å).

The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 9978 reflections, 44% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 100.00 % out to 27.481° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1360 before and 0.0558 after correction. The Ratio of minimum to maximum transmission is 0.7882. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.415 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.588 and 0.746.

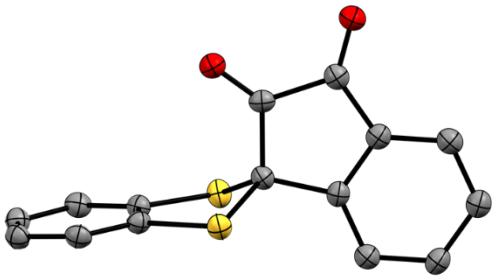
The structure was solved and the space group $P2_1/n$ (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1360 before and 0.0558 after correction. The Ratio of minimum to maximum transmission is 0.7882. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

1.3 Single-crystal structure and packing of 8

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single brown block-shaped crystals of **8** were recrystallised from a mixture of CH_2Cl_2 and cyclohexane by solvent layering. A suitable crystal 0.31×0.23×0.20 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Rigaku Spider diffractometer. The crystal was kept at a steady T = 100 K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{15}H_8O_2S_2$, M_r = 284.33, orthorhombic, *Pnma* (No. 62), a = 15.3775(11) Å, b = 7.2583(6) Å, c = 11.0501(9) Å, $\alpha = \beta = \gamma = 90°$, V = 1233.35(17) Å³, T = 100 K, Z = 4, Z' = 0.5, μ(MoK$_\alpha$) = 0.424, 15119 reflections measured, 1525 unique (R_{int} = 0.0610) which were used in all calculations. The final wR_2 was 0.1243 (all data) and R_1 was 0.0475 (I > 2(I)).

Compound	**8**
CCDC	1874678
Formula	$C_{15}H_8O_2S_2$
$D_{calc.}$/ g cm^{-3}	1.531
μ/mm^{-1}	0.424
Formula Weight	284.33
Colour	brown
Shape	block
Size/mm³	0.31×0.23×0.20
T/K	100
Crystal System	orthorhombic
Space Group	*Pnma*
a/Å	15.3775(11)
b/Å	7.2583(6)
c/Å	11.0501(9)
α/°	90
β/°	90
γ/°	90
V/Å³	1233.35(17)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.228
Θ_{max}/°	27.474
Measured Refl.	15119
Independent Refl.	1525
Reflections with I > 2(I)	1375
R_{int}	0.0610
Parameters	103
Restraints	0
Largest Peak	0.489
Deepest Hole	-0.393
GooF	1.131
wR_2 (all data)	0.1243
wR_2	0.1193
R_1 (all data)	0.0560
R_1	0.0475

A brown block-shaped crystal with dimensions 0.31×0.23×0.20 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Rigaku Spider diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100 K.

Data were measured using ω and ϕ scans using MoK_α radiation. The maximum resolution that was achieved was Θ = 27.474° (0.77 Å).

The diffraction pattern was indexed and the unit cell was refined on 1088 reflections, 7% of the observed reflections.

Data reduction, scaling and absorption corrections were performed. The final completeness is 99.80 % out to 27.474° in Θ. A empirical absorption correction was performed using Empirical Absorption Correction March 2001 T Higashi. The absorption coefficient μ of this material is 0.424 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.668 and 1.000.

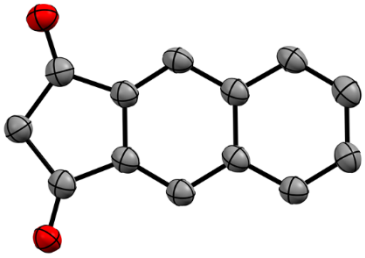
The structure was solved and the space group *Pnma* (# 62) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: Empirical Absorption Correction March 2001 T Higashi

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

1.4 Single-crystal structure and packing of 13

Crystal Data and Experimental



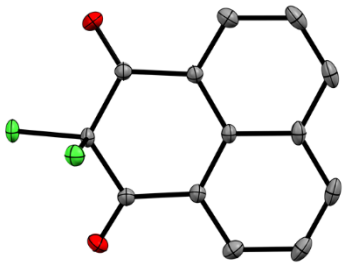
(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single colourless block-shaped crystals of **13** were recrystallised from a mixture of $CHCl_3$ and methanol by solvent layering. The data for **13** were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used CuK_α radiation (λ = 1.54184 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS-2016/2 was applied. The structure were solved by direct methods using SHELXT 2014/5 (Sheldrick, 2014) and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1964046 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Compound	**13**
CCDC number	1964046
Empirical formula	$C_{13}H_8O_2$
Formula weight	196.19
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	9.559(13)
b [Å]	5.316(5)
c [Å]	17.355(16)
α [Å]	90
β [Å]	92.38(12)
γ [Å]	90
Volume [Å^3]	881.1(17)
Z	4
ρ_{calc} [g/cm^3]	1.479
μ [mm^{-1}]	0.809
F(000)	408
Crystal size [mm^3]	0.16×0.06×0.03
Crystal colour	colourless
Crystal shape	block
Radiation	CuK_α (λ=1.54184)
2Θ range [°]	10.20 to 147.47
Index ranges	-11 ≤ h ≤ 11 -6 ≤ k ≤ 5 -21 ≤ l ≤ 21
Reflections collected	21945
Independent reflections	1726 R_{int} = 0.1011 R_{sigma} = 0.0417
Completeness to θ = 67.684°	99.10
Data / Restraints / Parameters	1726/0/136
Goodness-of-fit on F^2	1.455
Final *R* indexes [I≥2σ(I)]	R_1 = 0.0779 wR_2 = 0.1968
Final *R* indexes [all data]	R_1 = 0.1021 wR_2 = 0.2149
Largest peak/hole [eÅ^3]	0.27/-0.36

1.5 Single-crystal structure and packing of 14

Crystal Data and Experimental



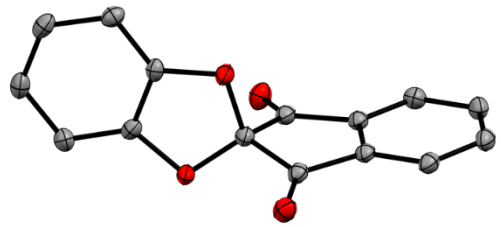
(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single colourless block-shaped crystals of **14** were recrystallised from a mixture of $CHCl_3$ and methanol by solvent layering. The data for **14** were collected from a shock-cooled single crystal at 100(2) K on a Bruker APEX2 QUAZAR three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker APEXII detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS-2016/2 was applied. The structure were solved by direct methods using SHELXT 2014/5 (Sheldrick, 2014) and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1964067 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Compound	**14**
CCDC number	1964067
Empirical formula	$C_{13}H_6Cl_2O_2$
Formula weight	265.08
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$C2/m$ (12)
a [Å]	13.357(10)
b [Å]	12.364(9)
c [Å]	7.308(5)
α [Å]	90
β [Å]	118.676(16)
γ [Å]	90
Volume [Å^3]	1058.8(13)
Z	4
ρ_{calc} [g/cm^3]	1.663
μ [mm^{-1}]	0.595
F(000)	1072
Crystal size [mm^3]	0.140×0.100×0.080
Crystal colour	yellow
Crystal shape	block
Radiation	MoK_α (λ=0.71073)
2Θ range [°]	4.79 to 60.17
Index ranges	-18 ≤ h ≤ 18 -17 ≤ k ≤ 17 -10 ≤ l ≤ 10
Reflections collected	12615
Independent reflections	1541 R_{int} = 0.0355 R_{sigma} = 0.0221
Completeness to θ = 25.242°	100.00
Data / Restraints / Parameters	1541/0/85
Goodness-of-fit on F^2	0.865
Final *R* indexes [I≥2σ(I)]	R_1 = 0.0260 wR_2 = 0.0992
Final *R* indexes [all data]	R_1 = 0.0292 wR_2 = 0.1040
Largest peak/hole [eÅ^3]	0.47/-0.23

1.6 Single-crystal structure and packing of 21

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single yellow block-shaped crystals of **21** were recrystallised from a mixture of $CHCl_3$ and *n*-hexane by solvent layering. A suitable crystal 0.16×0.13×0.11 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 100 K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{15}H_8O_4$, M_r = 252.21, monoclinic, $P2_1/n$ (No. 14), a = 9.217(11) Å, b = 12.573(9) Å, c = 9.542(8) Å, β = 99.09(5)°, $\alpha = \gamma = 90°$, V = 1091.9(18) Å³, T = 100 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.113, 12122 reflections measured, 2497 unique (R_{int} = 0.0207) which were used in all calculations. The final wR_2 was 0.0901 (all data) and R_1 was 0.0363 (I > 2(I)).

Compound	**21**
CCDC	1864464
Formula	$C_{15}H_8O_4$
$D_{calc.}$/ g cm^{-3}	1.534
μ/mm^{-1}	0.113
Formula Weight	252.21
Colour	yellow
Shape	block
Size/mm³	0.16×0.13×0.11
T/K	100
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	9.217(11)
b/Å	12.573(9)
c/Å	9.542(8)
α/°	90
β/°	99.09(5)
γ/°	90
V/Å³	1091.9(18)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.701
Θ_{max}/°	27.482
Measured Refl.	12122
Independent Refl.	2497
Reflections with I > 2(I)	2215
R_{int}	0.0207
Parameters	172
Restraints	0
Largest Peak	0.302
Deepest Hole	-0.268
GooF	1.045
wR_2 (all data)	0.0901
wR_2	0.0870
R_1 (all data)	0.0409
R_1	0.0363

A yellow block-shaped crystal with dimensions 0.16×0.13×0.11 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100 K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 27.482° (0.77 Å).

The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 6594 reflections, 54% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 99.80 % out to 27.482° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1123 before and 0.0342 after correction. The Ratio of minimum to maximum transmission is 0.9450. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.113 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.705 and 0.746.

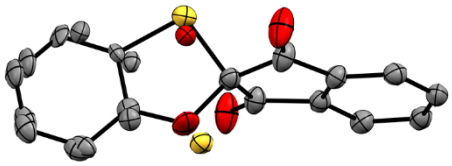
The structure was solved and the space group $P2_1/n$ (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1123 before and 0.0342 after correction. The Ratio of minimum to maximum transmission is 0.9450. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

1.7 Single-crystal structure and packing of 23

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single yellow plate-shaped crystals of **23** were recrystallised from $CDCl_3$ by slow evaporation. A suitable crystal 0.30×0.11×0.03 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 109(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{15}H_8O_3S$, M_r = 268.27, monoclinic, $P2_1/n$ (No. 14), a = 9.457(3) Å, b = 9.423(4) Å, c = 13.368(5) Å, β = 90.586(16)°, $\alpha = \gamma = 90°$, V = 1191.1(8) Å³, T = 109(2) K, Z = 4, Z' = 1, μ(MoK_α) = 0.271, 9330 reflections measured, 2752 unique (R_{int} = 0.0302) which were used in all calculations. The final wR_2 was 0.1227 (all data) and R_1 was 0.0562 (I > 2(I)).

Compound	**23**
CCDC	1874255
Formula	$C_{15}H_8O_3S$
$D_{calc.}$/ g cm^{-3}	1.496
μ/mm^{-1}	0.271
Formula Weight	268.27
Colour	yellow
Shape	plate
Size/mm³	0.30×0.11×0.03
T/K	109(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	9.457(3)
b/Å	9.423(4)
c/Å	13.368(5)
α/°	90
β/°	90.586(16)
γ/°	90
V/Å³	1191.1(8)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK_α
Θ_{min}/°	2.626
Θ_{max}/°	27.551
Measured Refl.	9330
Independent Refl.	2752
Reflections with I > 2(I)	2257
R_{int}	0.0302
Parameters	227
Restraints	424
Largest Peak	0.519
Deepest Hole	-0.367
GooF	1.128
wR_2 (all data)	0.1227
wR_2	0.1179
R_1 (all data)	0.0716
R_1	0.0562

A yellow plate-shaped crystal with dimensions 0.30×0.11×0.03 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 109(2) K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 27.551° (0.77 Å).

The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 3436 reflections, 37% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 99.80 % out to 27.551° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1259 before and 0.0500 after correction. The Ratio of minimum to maximum transmission is 0.9233. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.271 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.688 and 0.746.

The structure was solved and the space group $P2_1/n$ (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1259 before and 0.0500 after correction. The Ratio of minimum to maximum transmission is 0.9233. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

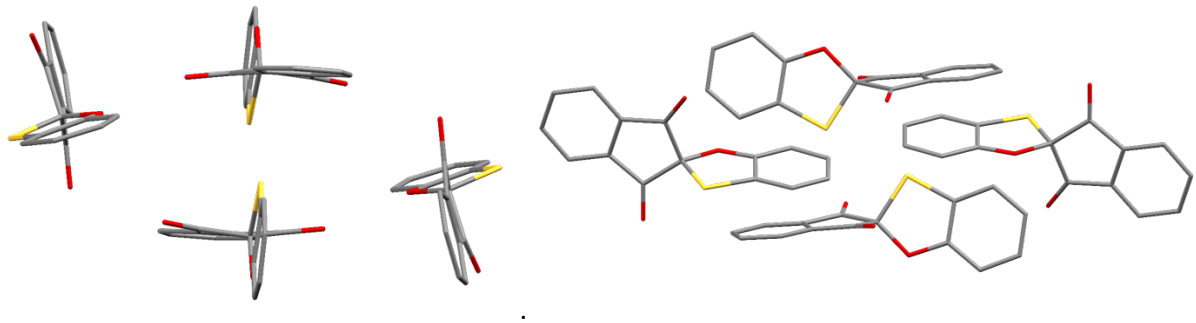
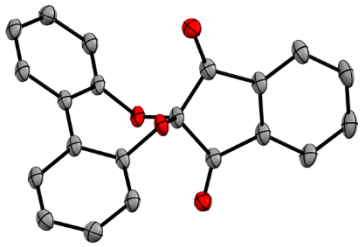


Figure S4: Packing model of **23**.

1.8 Single-crystal structure and packing of 25

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single yellow block-shaped crystals of **25** were recrystallised from a mixture of $CHCl_3$ and cyclohexane by solvent layering. A suitable crystal 0.20×0.14×0.07 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{42}H_{24}O_8$, M_r = 656.61, monoclinic, $P2_1/n$ (No. 14), a = 11.825(15) Å, b = 17.04(3) Å, c = 16.23(2) Å, β = 109.86(3)°, $\alpha = \gamma = 90°$, V = 3076(8) Å³, T = 100(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.099, 59170 reflections measured, 7087 unique (R_{int} = 0.0797) which were used in all calculations. The final wR_2 was 0.1830 (all data) and R_1 was 0.0684 (I > 2(I)).

Compound	**25**
CCDC	1864468
Formula	$C_{42}H_{24}O_8$
$D_{calc.}$/ g cm^{-3}	1.418
μ/mm^{-1}	0.099
Formula Weight	656.61
Colour	yellow
Shape	block
Size/mm³	0.20×0.14×0.07
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	11.825(15)
b/Å	17.04(3)
c/Å	16.23(2)
α/°	90
β/°	109.86(3)
γ/°	90
V/Å³	3076(8)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.791
Θ_{max}/°	27.618
Measured Refl.	59170
Independent Refl.	7087
Reflections with I > 2(I)	5273
R_{int}	0.0797
Parameters	451
Restraints	0
Largest Peak	0.614
Deepest Hole	-0.399
GooF	1.090
wR_2 (all data)	0.1830
wR_2	0.1686
R_1 (all data)	0.0914
R_1	0.0684

A yellow block-shaped crystal with dimensions 0.20×0.14×0.07 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100(2) K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 27.618° (0.77 Å).

The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 9915 reflections, 17% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 100.00 % out to 27.618° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1627 before and 0.0847 after correction. The Ratio of minimum to maximum transmission is 0.6467. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.099 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.482 and 0.746.

The structure was solved and the space group $P2_1/n$ (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1627 before and 0.0847 after correction. The Ratio of minimum to maximum transmission is 0.6467. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

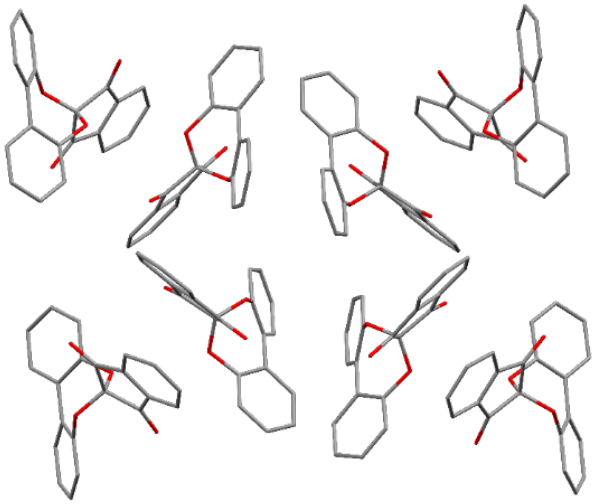
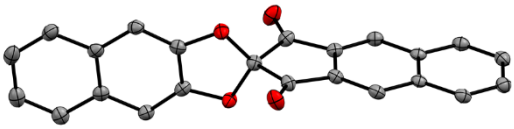


Figure S5: Packing of **25**.

1.9 Single-crystal structure and packing of 26

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single yellow block-shaped crystals of **26** were obtained by the vapor diffusion DMSO/H_2O at ambient temperature. A suitable crystal 0.33×0.10×0.08 mm³ was selected with perfluorpolyether on a Mitegen Loop on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 100.01 K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{23}H_{12}O_4$, M_r = 352.33, orthorhombic, $Pna2_1$ (No. 33), a = 17.395(8) Å, b = 9.112(4) Å, c = 10.203(3) Å, α = β = γ = 90°, V = 1617.2(11) Å³, T = 100.01 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.099, 36026 reflections measured, 4166 unique (R_{int} = 0.0381) which were used in all calculations. The final wR_2 was 0.0944 (all data) and R_1 was 0.0342 (I > 2(I)).

Compound	**26**
CCDC	1912192
Formula	$C_{23}H_{12}O_4$
$D_{calc.}$/ g cm^{-3}	1.447
μ/mm^{-1}	0.099
Formula Weight	352.33
Colour	yellow
Shape	block
Size/mm³	0.33×0.10×0.08
T/K	100.01
Crystal System	orthorhombic
Flack Parameter	-0.6(4)
Hooft Parameter	-0.3(2)
Space Group	$Pna2_1$
a/Å	17.395(8)
b/Å	9.112(4)
c/Å	10.203(3)
α/°	90
β/°	90
γ/°	90
V/Å³	1617.2(11)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.342
Θ_{max}/°	28.704
Measured Refl.	36026
Independent Refl.	4166
Reflections with I > 2(I)	3953
R_{int}	0.0381
Parameters	244
Restraints	1
Largest Peak	0.298
Deepest Hole	-0.177
GooF	1.085
wR_2 (all data)	0.0944
wR_2	0.0925
R_1 (all data)	0.0364
R_1	0.0342

A yellow block-shaped crystal with dimensions 0.33×0.10×0.08 mm^3 was selected and fixed with perfluorpolyether on a Mitegen Loop. Data were collected using an Bruker SMART APEX2 area detector diffractometer operating at T = 100.01 K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program Bruker APEX3 software The maximum resolution that was achieved was Θ = 28.704° (0.74 Å).

The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program Bruker APEX3 software and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 9866 reflections, 27% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 100.00 % out to 28.704° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1307 before and 0.0507 after correction. The Ratio of minimum to maximum transmission is 0.8728. The $\lambda/2$ correction factor is not present. The absorption coefficient μ of this material is 0.099 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.651 and 0.746.

The structure was solved and the space group $Pna2_1$ (# 33) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

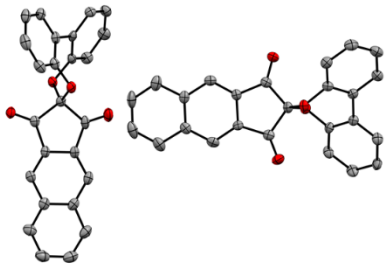
_exptl_absorpt_process_details: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1307 before and 0.0507 after correction. The Ratio of minimum to maximum transmission is 0.8728. The $\lambda/2$ correction factor is Not present.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

The Flack parameter was refined to -0.6(4). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.3(2). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

1.10 Single-crystal structure and packing of 27

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single colourless block-shaped crystals of **27** were recrystallised from a mixture of $CHCl_3$ and methanol by solvent layering. A suitable crystal 0.20×0.17×0.10 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{25}H_{14}O_4$, M_r = 378.36, orthorhombic, $P2_12_12_1$ (No. 19), a = 13.845(5) Å, b = 13.921(5) Å, c = 18.938(7) Å, $\alpha = \beta = \gamma = 90^\circ$, V = 3650(2) Å³, T = 100(2) K, Z = 8, Z' = 2, μ(MoK$_\alpha$) = 0.093, 74657 reflections measured, 7595 unique (R_{int} = 0.0809) which were used in all calculations. The final wR_2 was 0.0839 (all data) and R_1 was 0.0404 (I > 2(I)).

Compound	**27**
CCDC	1900045
Formula	$C_{25}H_{14}O_4$
$D_{calc.}$/ g cm^{-3}	1.377
μ/mm^{-1}	0.093
Formula Weight	378.36
Colour	colourless
Shape	block
Size/mm³	0.20×0.17×0.10
T/K	100(2)
Crystal System	orthorhombic
Flack Parameter	0.6(4)
Hooft Parameter	1.0(5)
Space Group	$P2_12_12_1$
a/Å	13.845(5)
b/Å	13.921(5)
c/Å	18.938(7)
α/°	90
β/°	90
γ/°	90
V/Å³	3650(2)
Z	8
Z'	2
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.075
Θ_{max}/°	26.570
Measured Refl.	74657
Independent Refl.	7595
Reflections with I > 2(I)	6776
R_{int}	0.0809
Parameters	524
Restraints	0
Largest Peak	0.170
Deepest Hole	-0.175
GooF	1.074
wR_2 (all data)	0.0839
wR_2	0.0794
R_1 (all data)	0.0506
R_1	0.0404

A colourless block-shaped crystal with dimensions 0.20×0.17×0.10 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100(2) K. Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 26.570° (0.79 Å). The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 9959 reflections, 13% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 100.00 % out to 26.570° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.0773 before and 0.0683 after correction. The Ratio of minimum to maximum transmission is 0.9188. The $\lambda/2$ correction factor is Not present. The absorption coefficient μ of this material is 0.093 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.685 and 0.745. The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. *_refine_special_details*: Refined as a 2-component twin. *_exptl_absorpt_process_details*: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.0773 before and 0.0683 after correction. The Ratio of minimum to maximum transmission is 0.9188. The $\lambda/2$ correction factor is Not present. The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

The Flack parameter was refined to 0.6(4). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 1.0(5). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

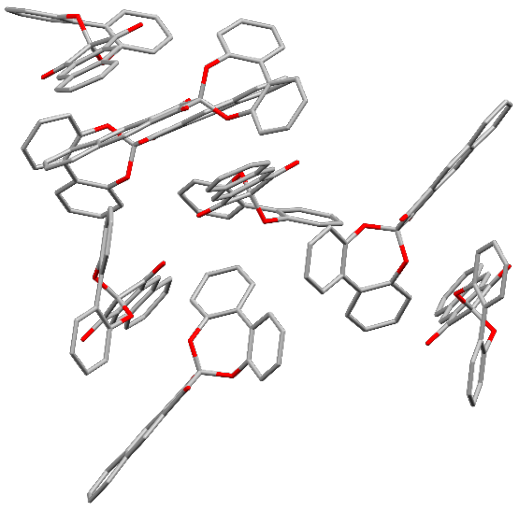
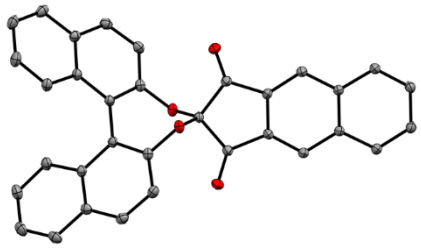


Figure S6: Packing model of **27**.

1.11 Single-crystal structure and packing of 29

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single colourless block-shaped crystals of **29** were recrystallised from a mixture of $CHCl_3$ and methanol by solvent layering. The data for **29** were collected from a shock-cooled single crystal at 100(2) K on a Bruker APEX2 QUAZAR three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker APEXII detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS-2016/2 was applied. The structure were solved by direct methods using SHELXT 2014/5 (Sheldrick, 2014) and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1964127 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Compound	**29**
CCDC number	1964127
Empirical formula	$C_{33}H_{18}O_4$
Formula weight	478.47
Temperature [K]	100(2)
Crystal system	orthorhombic
Space group (number)	$C222_1$ (20)
a [Å]	8.351(4)
b [Å]	21.414(6)
c [Å]	13.480(4)
α [Å]	90
β [Å]	90
γ [Å]	90
Volume [Å^3]	2410.7(15)
Z	4
ρ_{calc} [g/cm^3]	1.318
μ [mm^{-1}]	0.086
F(000)	992
Crystal size [mm^3]	0.10×0.08×0.05
Crystal colour	yellow
Crystal shape	block
Radiation	MoK_α (λ=0.71073)
2Θ range [°]	3.80 to 61.92
Index ranges	-11 ≤ h ≤ 12 -30 ≤ k ≤ 30 -19 ≤ l ≤ 19
Reflections collected	39656
Independent reflections	3683 R_{int} = 0.0253 R_{sigma} = 0.0141
Completeness to θ = 25.242°	99.50
Data / Restraints / Parameters	3683/0/168
Goodness-of-fit on F^2	1.071
Final *R* indexes [I≥2σ(I)]	R_1 = 0.0362 wR_2 = 0.1175
Final *R* indexes [all data]	R_1 = 0.0375 wR_2 = 0.1194
Largest peak/hole [eÅ^3]	0.41/-0.23
Flack X parameter	0.01(17)

A colourless block-shaped crystal with dimensions 0.10×0.08×0.05 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100 K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 33.185° (0.65 Å).

The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 3683 reflections.

Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 100.00 % out to 33.185° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1407 before and 0.0485 after correction. The Ratio of minimum to maximum transmission is 0.9321. The $\lambda/2$ correction factor is not present. The absorption coefficient μ of this material is 0.291 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.696 and 0.747.

The structure was solved and the space group $C222_1$ *(20)* determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

The Flack parameter was refined to 0.01(17). A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

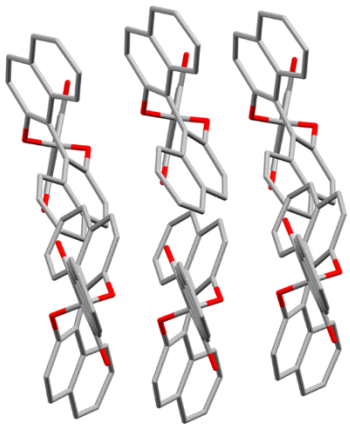
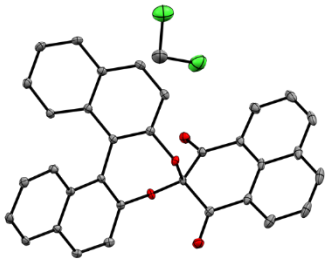


Figure S7: Packing of **29**.

1.12 Single-crystal structure and packing of 32

Crystal Data and Experimental



(displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity)

Experimental. Single colourless block-shaped crystals of **32** were recrystallised from CH_2Cl_2 by slow evaporation. A suitable crystal 0.25×0.14×0.08 mm³ was selected and mounted on a MITIGEN holder in perfluoroether oil on an Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 100 K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{34}H_{20}Cl_2O_4$, M_r = 563.40, orthorhombic, $P2_12_12_1$ (No. 19), a = 5.3479(8) Å, b = 17.257(3) Å, c = 28.107(4) Å, $\alpha = \beta = \gamma = 90°$, V = 2593.9(6) Å³, T = 100 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.291, 34844 reflections measured, 8789 unique (R_{int} = 0.0333) which were used in all calculations. The final wR_2 was 0.1312 (all data) and R_1 was 0.0496 (I > 2(I)).

Compound	**32**
CCDC	1886536
Formula	$C_{34}H_{20}Cl_2O_4$
$D_{calc.}$/g cm^{-3}	1.443
μ/mm^{-1}	0.291
Formula Weight	563.40
Colour	colourless
Shape	block
Size/mm³	0.25×0.14×0.08
T/K	100
Crystal System	orthorhombic
Flack Parameter	0.025(17)
Hooft Parameter	0.008(17)
Space Group	$P2_12_12_1$
a/Å	5.3479(8)
b/Å	17.257(3)
c/Å	28.107(4)
α/°	90
β/°	90
γ/°	90
V/Å³	2593.9(6)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.385
Θ_{max}/°	33.185
Measured Refl.	34844
Independent Refl.	8789
Reflections with I > 2(I)	7572
R_{int}	0.0333
Parameters	361
Restraints	0
Largest Peak	0.412
Deepest Hole	-0.715
GooF	1.039
wR_2 (all data)	0.1312
wR_2	0.1251
R_1 (all data)	0.0612
R_1	0.0496

A colourless block-shaped crystal with dimensions 0.25×0.14×0.08 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using an Bruker SMART APEX2 area detector diffractometer equipped with an Oxford Cryosystems 800 low-temperature device operating at T = 100 K.

Data were measured using ω and ϕ scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) The maximum resolution that was achieved was Θ = 33.185° (0.65 Å).
The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 9869 reflections, 28% of the observed reflections.
Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 100.00 % out to 33.185° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1407 before and 0.0485 after correction. The Ratio of minimum to maximum transmission is 0.9321. The $\lambda/2$ correction factor is Not present.. The absorption coefficient μ of this material is 0.291 mm^{-1} at this wavelength (λ = 0.711 Å) and the minimum and maximum transmissions are 0.696 and 0.747.
The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.
_exptl_absorpt_process_details: **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.1407 before and 0.0485 after correction. The Ratio of minimum to maximum transmission is 0.9321. The $\lambda/2$ correction factor is Not present.
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.
The Flack parameter was refined to 0.025(17). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.008(17). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

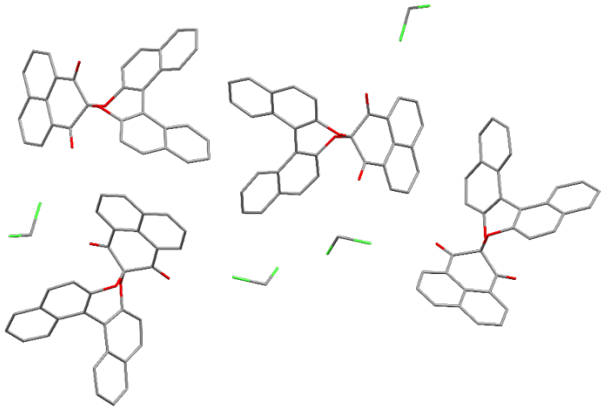


Figure S8: Packing model of **32**.

2. Cyclic Voltammograms

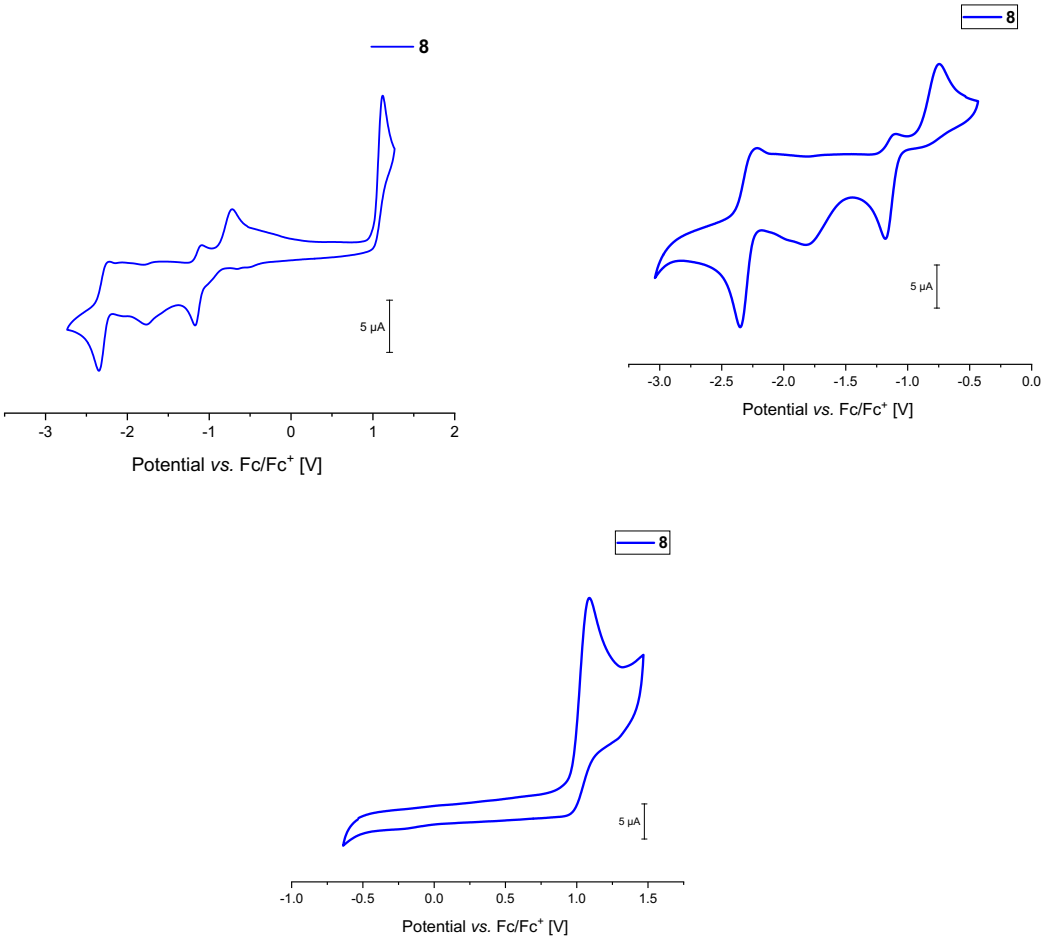


Figure S9: Cyclic voltammograms of **8** in acetonitrile at 100 mV/s scan rate using a glassy carbon electrode.

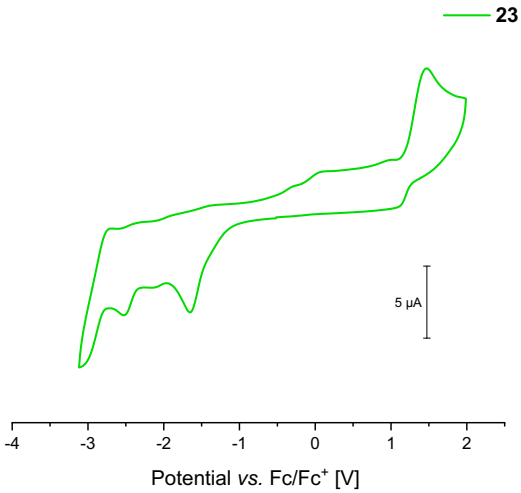


Figure S10: Cyclic voltammogram of **23** in acetonitrile at 100 mV/s scan rate using a glassy carbon electrode.

3. Optical Properties

a) b)

Figure S11: a) Solutions of spiro compounds **8** (left) and **7** (right) in CH_2Cl_2; b) Solution of **4** in CH_2Cl_2.

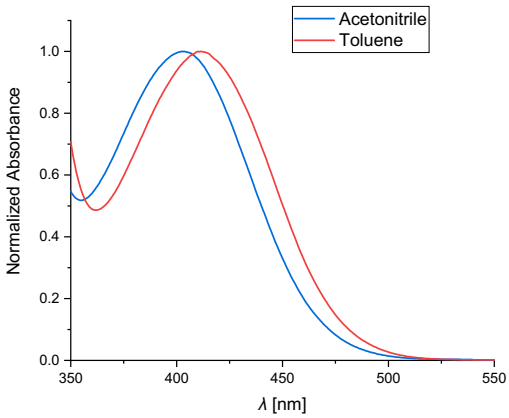


Figure S12: Absorption spectra of **7** in solvents of different polarity**.**

4. Thermal Measurements

4.1 Thermogravimetric Analyses

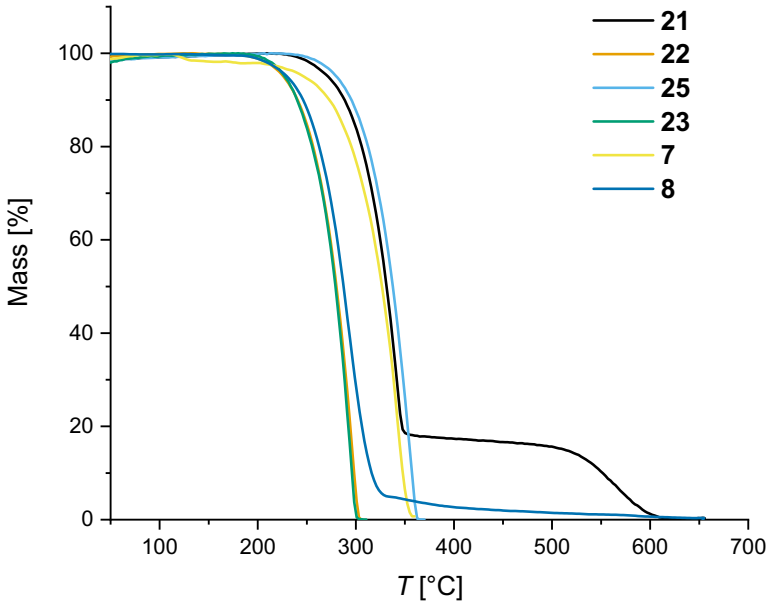


Figure S13: TGA measurements under inert N_2 atmosphere at a heating rate of 10 K·min^{-1}.

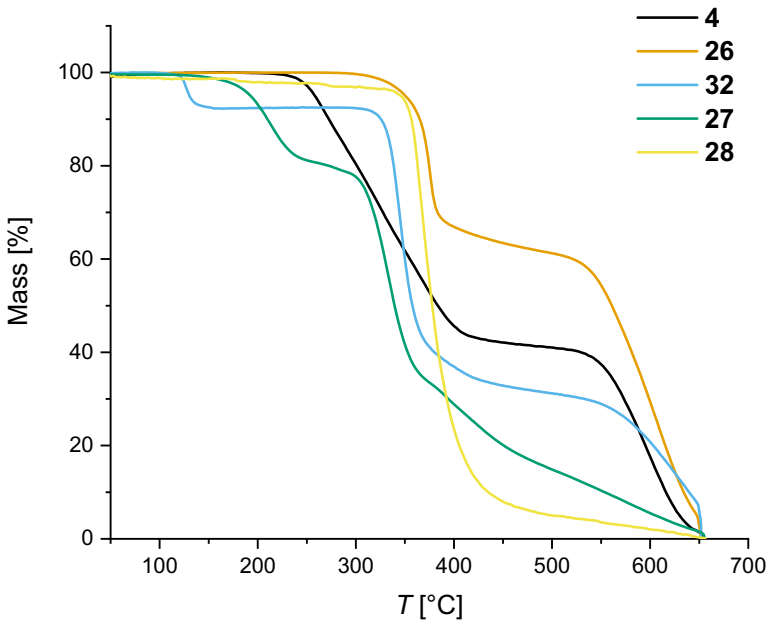


Figure S14: TGA measurements under inert N_2 atmosphere at a heating rate of 10 K·min^{-1}.

4.2 Differential Scanning Calorimetry

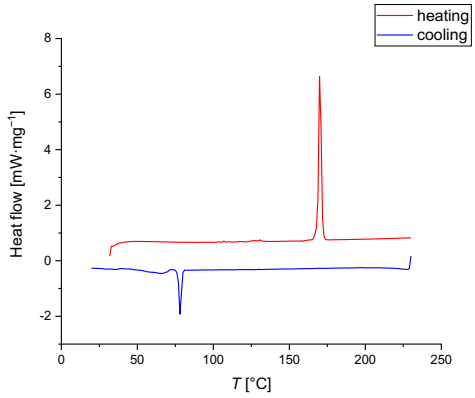


Figure S15: DSC of **7** at a heating rate of 10 K·min^{-1}.

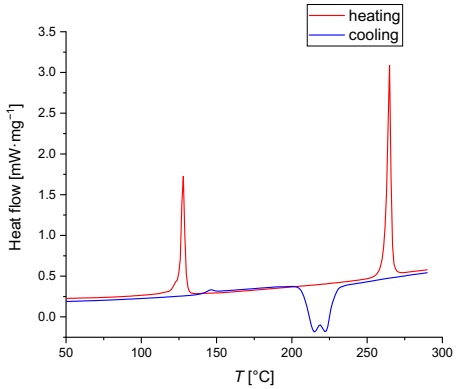


Figure S16: DSC of **32** at a heating rate of 10 K·min^{-1}.

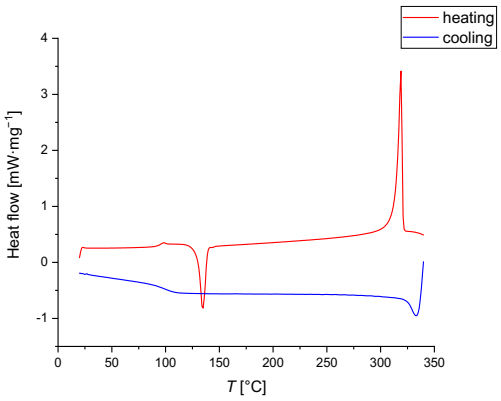


Figure S17: DSC of **30** at a heating rate of 10 K·min^{-1}.

5. DFT Calculations

DFT calculations were performed with either the TURBOMOLE v7.3 program package.[4] The resolution-of-identity[5] (RI, RIJDX for SP) approximation for the Coulomb integrals was used in all DFT calculations employing matching auxiliary basis set def2-XVP/J.[6] Furthermore, the D3 dispersion correction scheme[7] with the Becke-Johnson damping function was applied.[8] Using the TURBOMOLE v7.3 program package, the geometries of all molecules were optimized without symmetry restrictions with the PBEh-3c[9]-D3/def2-mSVP composite scheme followed by harmonic vibrational frequency analysis to confirm minima as stationary points. Vertical excitation energies were calculated using TDDFT applying the B3LYP[9] functional with the def2-TZVP basis set.[10]

5.1 Frontier Molecular Orbitals

Table S1: Frontier molecular orbitals of **7** (top) and **8** (bottom) (B3LYP-D3/def2-TZVP).

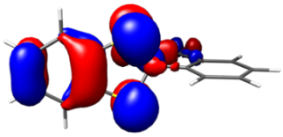
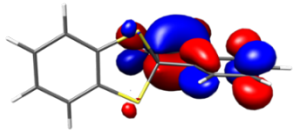
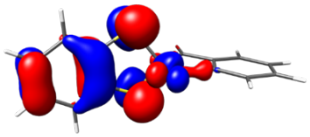
HOMO	LUMO
	
	

Table S2: Frontier molecular orbitals of **4** (top) and **21** (bottom) (B3LYP-D3/def2-TZVP).

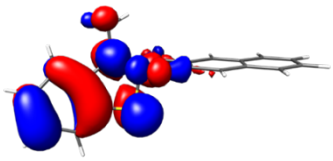
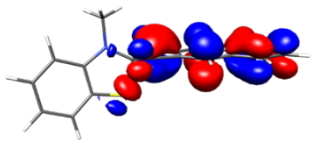
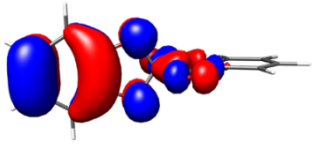
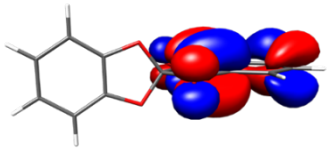
HOMO	LUMO
	
	

Table S3: Frontier molecular orbitals of **22** (top) and **25** (bottom) (B3LYP-D3/def2-TZVP).

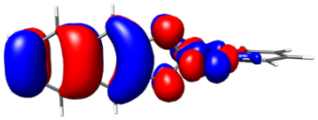
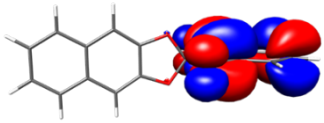
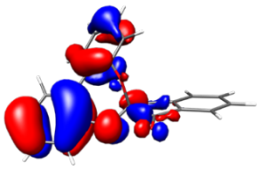
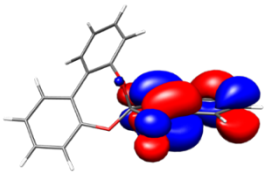
HOMO	LUMO
	
	

Table S4: Frontier molecular orbitals of **23** (top) and **30** (bottom) (B3LYP-D3/def2-TZVP).

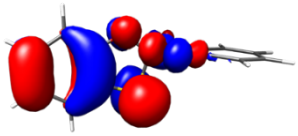
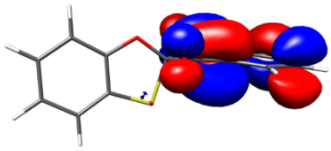
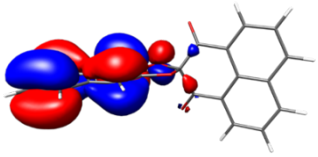
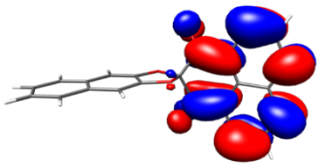
HOMO	LUMO
	
	

Table S5: Frontier molecular orbitals of **32** (top) and **31** (bottom) (B3LYP-D3/def2-TZVP).

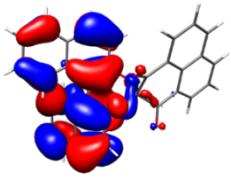
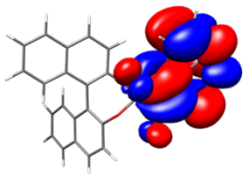
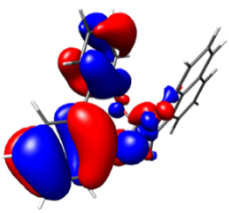
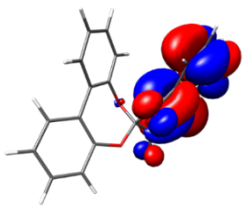
HOMO	LUMO
	
	

Table S6: Frontier molecular orbitals of **26** (top) and **27** (bottom) (B3LYP-D3/def2-TZVP).

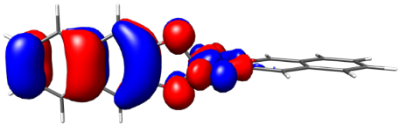
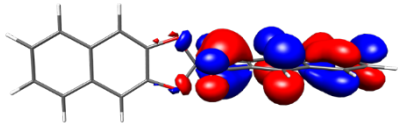
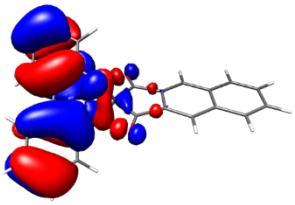
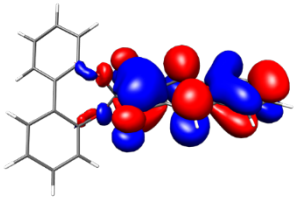
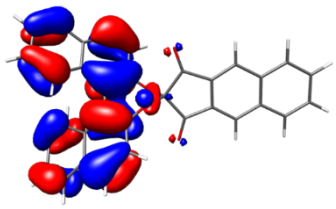
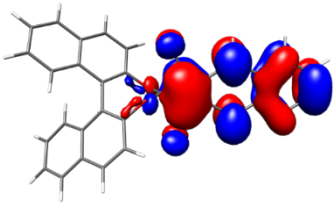
HOMO	LUMO
	
	

Table S7: Frontier molecular orbitals of **29** (B3LYP-D3/def2-TZVP).

HOMO	LUMO
	

5.2 TDDFT Calculations

5.2.1 Charge Transfer Transitions

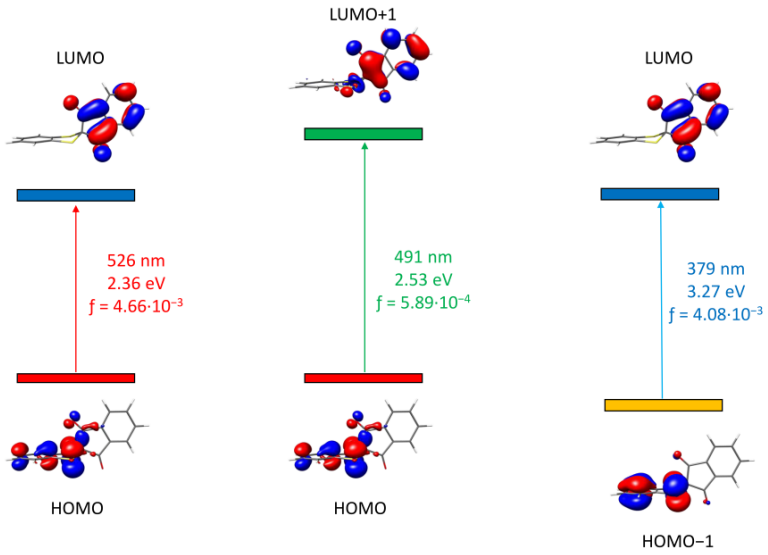


Figure S18: Calculated intramolecular charge transfer transition of **7** (B3LYP-D3/def2-TZVP).

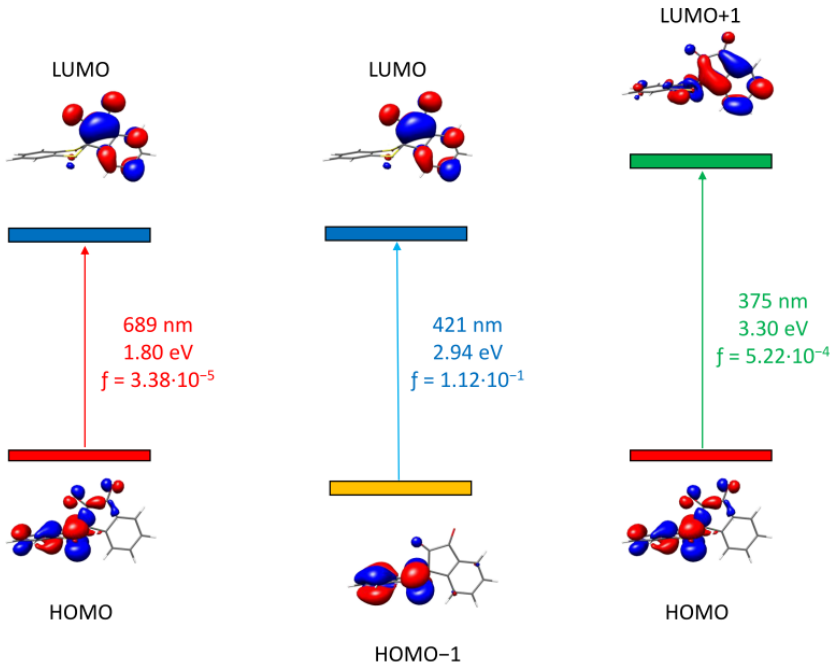


Figure S19: Calculated intramolecular charge transfer transition of **8** (B3LYP-D3/def2-TZVP).

5.2.2 Calculated Bandgaps

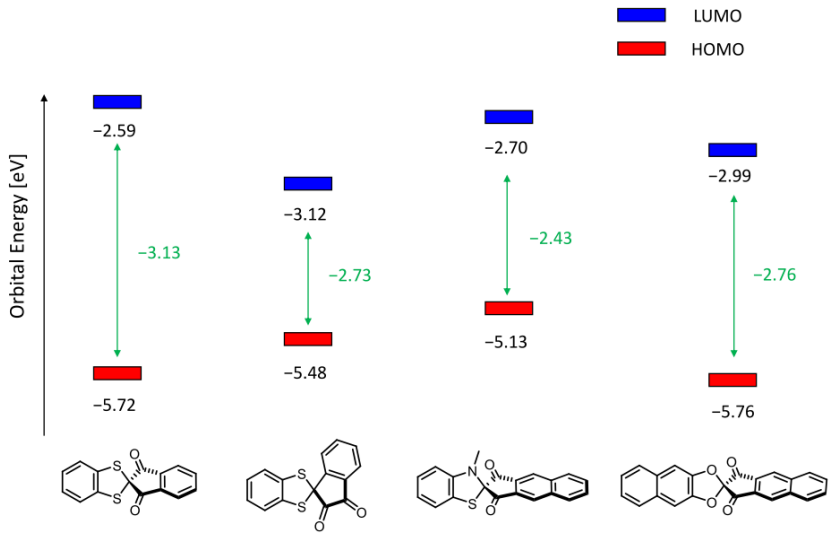


Figure S20: Calculated HOMO energy levels (red), LUMO energy levels (blue) and band gaps (green) in eV (B3LYP-D3/def2-TZVP).

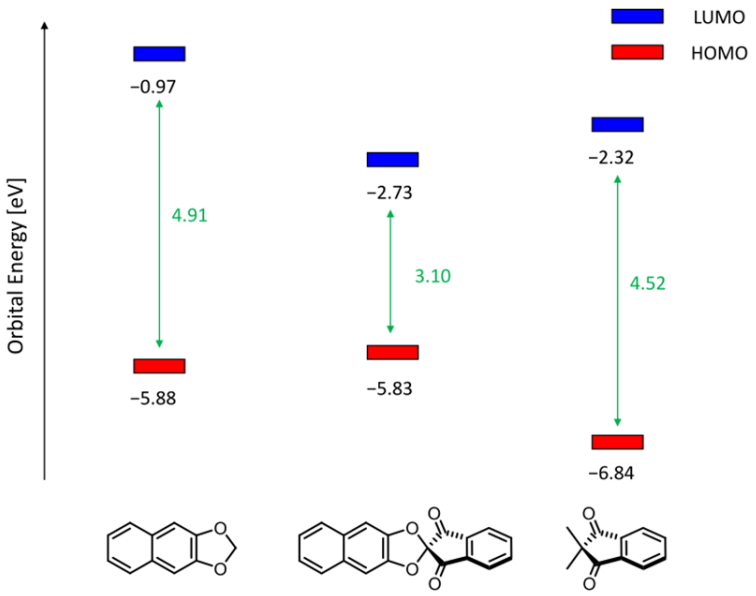


Figure S21: Calculated HOMO energy levels (red), LUMO energy levels (blue) and band gaps (green) in eV (B3LYP-D3/def2-TZVP).

Table S8: Calculated Photophysical Properties.

Compound	E_{HOMO} [eV]	E_{LUMO} [eV]	E_g [eV]	S_1 [eV]	T_1 [eV]	ΔE_{ST} [eV]	Oscillator strength $S_0 \rightarrow S_1$
4	−5.13	−2.70	2.43	1.75	1.64	0.11	$4.93 \cdot 10^{-03}$
7	−5.84	−3.12	2.73	1.80	1.49	0.31	$3.38 \cdot 10^{-05}$
8	−5.72	−2.59	3.13	2.36	2.22	0.14	$4.67 \cdot 10^{-04}$
21	−5.71	−2.67	3.03	2.21	2.05	0.17	$1.30 \cdot 10^{-05}$
22	−5.84	−2.73	3.10	2.33	2.15	0.18	$2.82 \cdot 10^{-06}$
25	−6.04	−2.49	3.55	2.82	2.58	0.24	$5.38 \cdot 10^{-03}$
23	−5.74	−2.56	3.19	2.40	2.22	0.18	$5.59 \cdot 10^{-03}$
30	−5.86	−2.69	3.17	2.61	2.42	0.19	$8.79 \cdot 10^{-03}$
32	−5.71	−2.49	3.22	2.76	2.47	0.28	$2.23 \cdot 10^{-03}$
31	−6.00	−2.50	3.50	2.88	2.47	0.41	$6.10 \cdot 10^{-04}$
26	−5.76	−2.99	2.76	2.07	1.94	0.13	$4.69 \cdot 10^{-07}$
27	−6.16	−2.75	3.41	2.74	2.36	0.38	$2.12 \cdot 10^{-02}$

5.2.3 Calculated Absorption Spectra

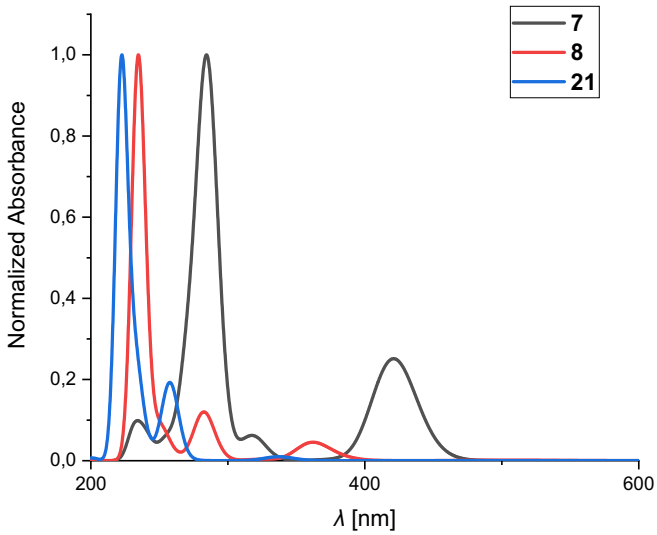


Figure S22: Calculated absorption spectra of **7**, **8**, and **21** (B3LYP-D3/def2-TZVP).

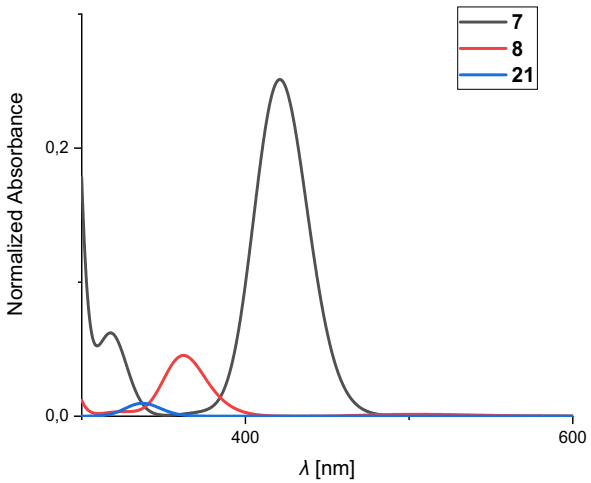


Figure S23: Calculated absorption spectra of **7**, **8**, and **21** (B3LYP-D3/def2-TZVP).

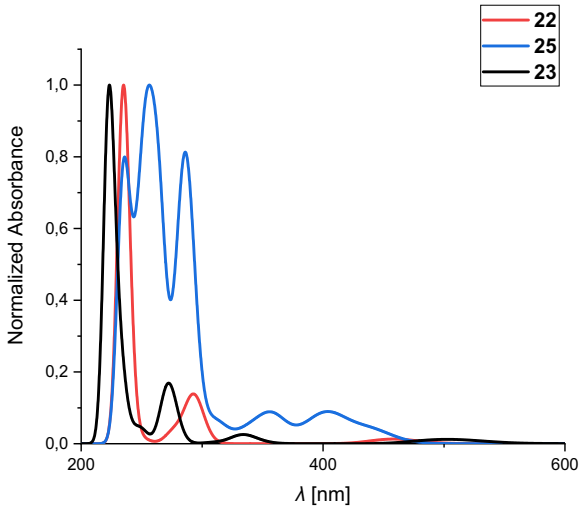


Figure S24: Calculated absorption spectra of **22**, **25**, and **23** (B3LYP-D3/def2-TZVP).

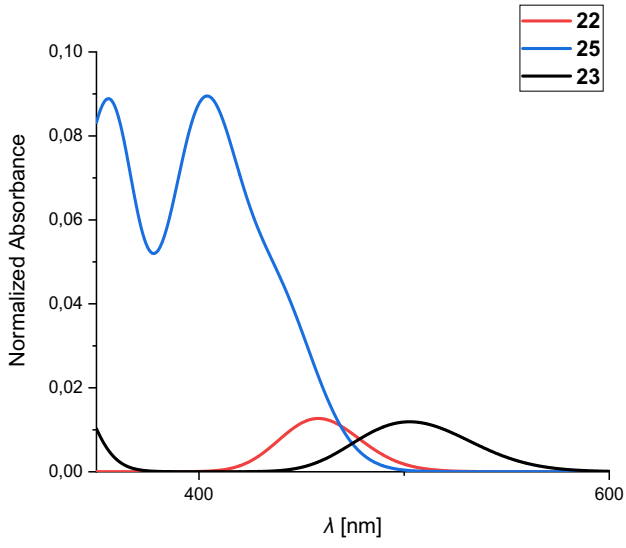


Figure S25: Calculated absorption spectra of **22**, **25**, and **23** (B3LYP-D3/def2-TZVP).

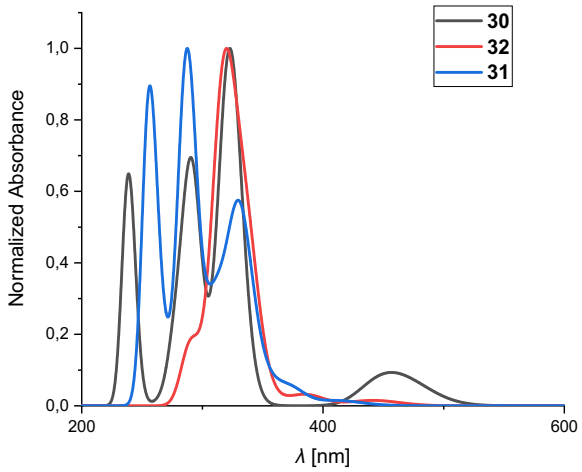


Figure S26: Calculated absorption spectra of **30**, **32**, and **31** (B3LYP-D3/def2-TZVP).

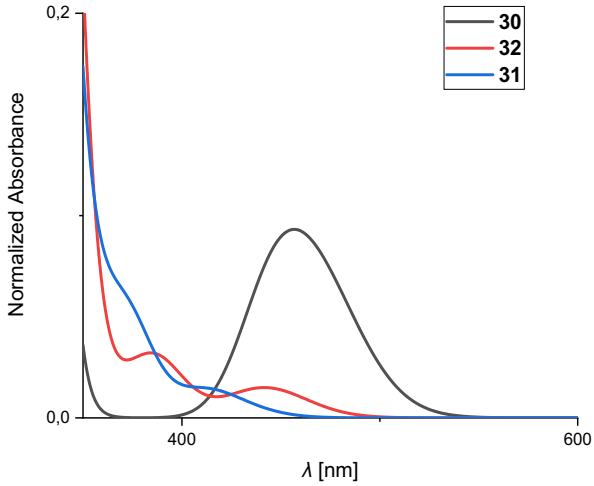


Figure S27: Calculated absorption spectra of **30**, **32**, and **31** (B3LYP-D3/def2-TZVP).

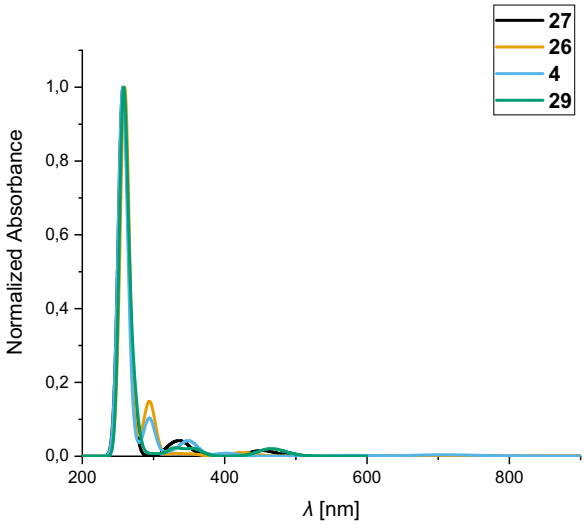


Figure S28: Calculated absorption spectra of **27**, **26**, **4** and **29** (B3LYP-D3/def2-TZVP).

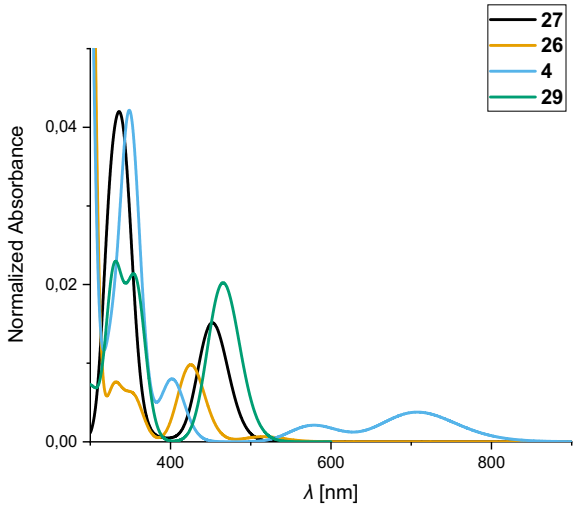


Figure S29: Calculated absorption spectra of **27**, **26**, **4** and **29** (B3LYP-D3/def2-TZVP).

5.2.4 Calculated Circular Dichroism Spectra

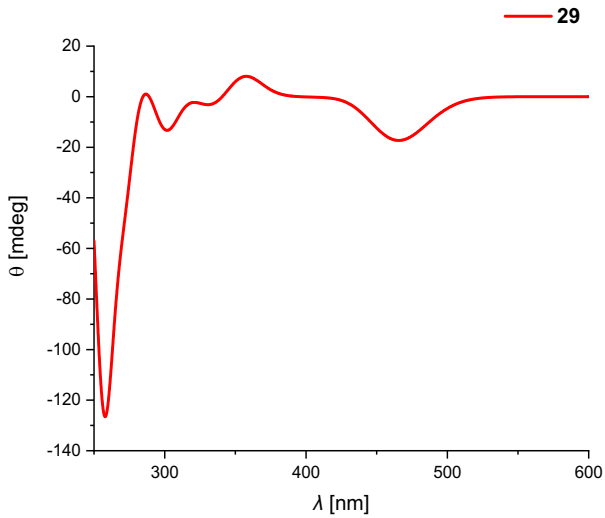


Figure S30: Calculated circular dichroism spectrum of **29** (B3LYP-D3/def2-TZVP).

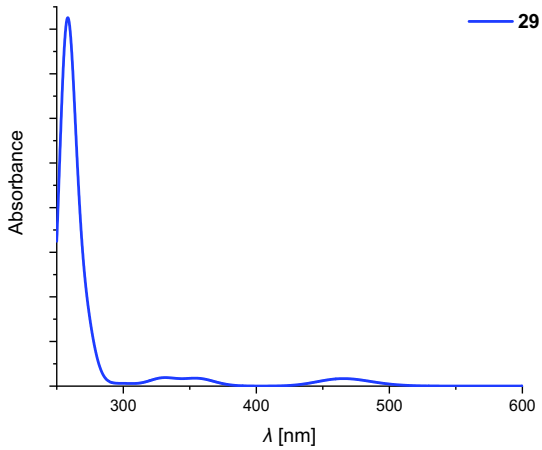


Figure S31: Calculated absorption spectrum of **29** (B3LYP-D3/def2-TZVP).

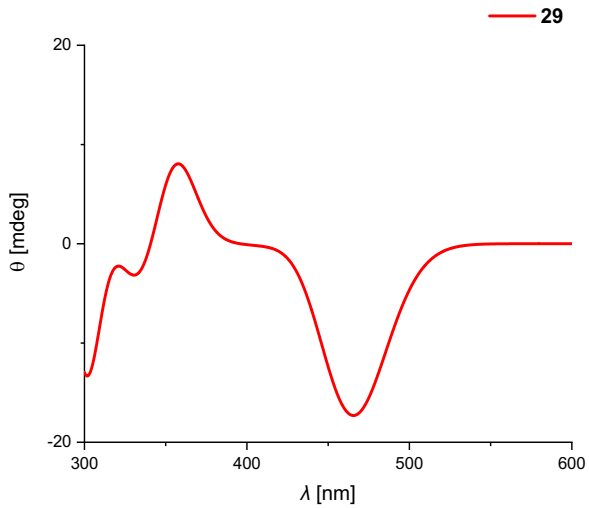


Figure S32: Calculated circular dichroism spectrum of **29** (B3LYP-D3/def2-TZVP).

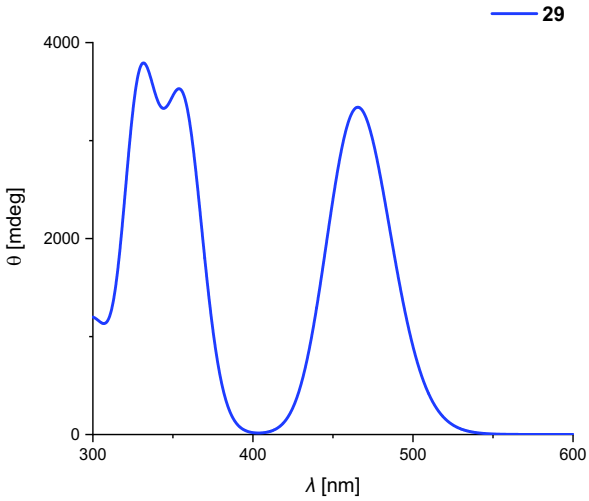


Figure S33: Calculated absorption spectrum of **29** (B3LYP-D3/def2-TZVP).

5.3 Total Energies and Zero-Point Vibrational Energies

Table S9: Total Energies and Zero-Point Vibrational Energies (B3LYP-D3/def2-TZVP).

Compound	Total Energy [hartrees]	Zero-Point Vibrational Energy [hartrees]
4	−1373.1946904400	0.2882897
8	−1523.0868647840	0.1949222
7	−1523.0953571740	0.1952106
21	−877.1899304018	0.2013141
22	−1030.8096112940	0.2496693
25	−1108.2093358380	0.2852229
23	−1200.1428123670	0.1983521
30	−1184.4326368030	0.2985921
32	−1569.0673952810	0.4309591
31	−1261.8347526790	0.3341390
26	−1261.8314975000	0.2979319
27	−1184.4272581100	0.3335377
29	−1569.0617225000	0.4303727

5.4 Cartesian Coordinates of the Calculated Structures

The Cartesian coordinates are listed in angstrom.

Table S10: Coordinates of the calculated structure of **4** (PBEh-3c/def2-mSVP).

	x	y	z				
N	-2.2473462	1.0950535	-0.1267133	C	-1.0879732	0.3029143	-0.3550185
C	-3.4011485	0.3505741	0.0184787	C	-0.2820923	-0.1244361	0.8809792
C	-3.2941471	-0.9532957	-0.4713270	O	-0.2421853	1.6107178	-2.2367381
S	-1.6903676	-1.2583873	-1.1277521	O	-0.7258149	-0.3179938	1.9780756
C	-2.1008289	2.3707494	0.5262083	H	-2.9098392	3.0350259	0.2228354
C	-4.6033828	0.7751430	0.5594244	H	-1.1746436	2.8455115	0.2083452
C	-5.6843679	-0.1034797	0.5781027	H	-2.0990732	2.2939454	1.6177741
C	-5.5726037	-1.3882009	0.0789104	H	-4.7093719	1.7699014	0.9704333
C	-4.3586908	-1.8243884	-0.4506647	H	-6.6226448	0.2291863	1.0014605
C	3.6244764	-0.0403064	-0.7688969	H	-6.4184117	-2.0609535	0.1058300
C	3.4779699	-0.6467929	0.5148868	H	-4.2553401	-2.8317855	-0.8315790
C	4.6257037	-1.1622942	1.1599887	H	4.5151473	-1.6228595	2.1336162
C	5.8541132	-1.0840146	0.5689434	H	6.7240979	-1.4825980	1.0732260
C	5.9987377	-0.4853218	-0.6997541	H	6.9780635	-0.4305610	-1.1557212
C	4.9116672	0.0228510	-1.3510105	H	5.0225154	0.4822538	-2.3251703
C	2.4940416	0.4876010	-1.4282867	H	2.5970588	0.9583359	-2.3984625
C	1.2731928	0.3924340	-0.8228621	H	2.0839477	-1.1664868	2.0951537
C	1.1281876	-0.2089312	0.4459254				
C	2.2030699	-0.7164718	1.1170716				

Table S11: Coordinates of the calculated structure of **8** (PBEh-3c/def2-mSVP).

	x	y	z		x	y	z
S	-0.0214690	-0.6486699	1.4689882	C	1.1494852	2.6740160	0.0007740
O	2.5551120	0.6884422	-0.0020562	C	-2.4676503	3.7830217	0.0004462
C	0.6808920	-2.0620724	0.6965145	H	-3.1020005	4.6590959	0.0011284
C	1.1703353	-3.1505841	1.3948759	C	-3.0485869	2.5130774	0.0001340
H	1.1897566	-3.1427436	2.4766333	H	-4.1269244	2.4243944	0.0005515
O	1.9666578	3.5494965	0.0033480	C	-2.2711737	1.3662856	-0.0004536
C	1.6468319	-4.2514164	0.6928061	H	-2.7232448	0.3833612	-0.0005691
H	2.0327023	-5.1030579	1.2361836	C	-0.8935018	1.5088961	-0.0006414
C	0.1296129	0.4119012	-0.0011163	S	-0.0218909	-0.6495307	-1.4704955
C	1.4650558	1.1644876	-0.0011277	C	0.6809478	-2.0624525	-0.6974108
C	-1.0932287	3.9235703	-0.0000269	C	1.1703517	-3.1515611	-1.3949128
H	-0.6244033	4.8987261	-0.0000823	H	1.1897846	-3.1444709	-2.4766832
C	-0.3132672	2.7733678	-0.0001805	C	1.6466340	-4.2519183	-0.6919628
				H	2.0331816	-5.1036621	-1.2346646

Table S12: Coordinates of the calculated structure of **7** (PBEh-3c/def2-mSVP).

	x	y	z		x	y	z
S	-0.1689884	1.8982281	-0.8563658	C	-1.2897180	-1.2865065	2.9697346
S	1.5551044	-0.4815977	-0.9255561	H	-2.1213318	-1.8839818	2.6213850
O	2.0669284	1.7253451	1.4362917	C	-0.5365316	-0.5351612	2.0810845
O	-1.5813570	-0.8835180	-0.0454744	C	-0.7136852	-0.3975231	0.6198118
C	0.4256032	0.4938392	0.1133090	C	0.7328445	-0.0789592	-2.4247156
C	1.1603091	0.9473119	1.3874958	C	0.9021941	-0.7857946	-3.6013660
C	0.5298898	0.2385648	2.5177483	H	1.5216763	-1.6725805	-3.6229612
C	0.8817829	0.2881482	3.8584845	C	0.2613631	-0.3495107	-4.7546839
H	1.7128467	0.8955916	4.1906780	H	0.3892159	-0.9011133	-5.6759687
C	0.1340275	-0.4637342	4.7486385	C	-0.5490613	0.7732134	-4.7224340
H	0.3805103	-0.4503931	5.8019289	H	-1.0570347	1.1020897	-5.6186747
C	-0.9400406	-1.2423188	4.3089700	C	-0.7304419	1.4753880	-3.5370674
H	-1.5056384	-1.8166420	5.0305982	H	-1.3780806	2.3416108	-3.5092504
				C	-0.0823865	1.0500042	-2.3916407

Table S13: Coordinates of the calculated structure of **21** (PBEh-3c/def2-mSVP).

	x	y	z		x	y	z
O	1.4687752	0.0887844	0.2507781	C	-2.2688739	-0.0273646	-4.0204723
C	0.0736003	0.0808684	0.1104362	H	-2.7343126	0.3302846	-4.9292428
O	-0.5031050	0.3467756	1.3607135	C	-1.6654637	0.8710801	-3.1581164
C	-0.4172210	-1.2743374	-0.4467129	H	-1.6465435	1.9314588	-3.3708661
O	-0.2561968	-2.3353408	0.0833805	C	-1.0804788	0.3700443	-2.0039650
C	-1.0998369	-0.9933828	-1.7221620	C	-0.3832789	1.1160250	-0.9411671
C	-1.7046009	-1.8950377	-2.5860900	C	0.5262140	0.4433755	2.2471393
H	-1.7157034	-2.9528312	-2.3603234	C	0.4730593	0.6630054	3.5982058
O	-0.1909209	2.2952184	-0.8749098	H	-0.4664580	0.7850413	4.1181361
C	-2.2882319	-1.3963414	-3.7374192	C	1.6993122	0.7199631	4.2698162
H	-2.7682967	-2.0722907	-4.4324288	H	1.7053066	0.8900968	5.3375132
				C	2.8974256	0.5622840	3.5955180

H	3.8288578	0.6104039	4.1424075	H	3.8634364	0.2160037	1.6811797
C	2.9316697	0.3397796	2.2144634	C	1.7218656	0.2864336	1.5741884

Table S14: Coordinates of the calculated structure of **22** (PBEh-3c/def2-mSVP).

	x	y	z	C	0.4733256	-0.9724442	-2.2933601
C	-3.1404240	3.9796940	2.9994322	O	-0.7629058	0.4728591	-0.7595080
C	-3.9139088	2.8545307	3.3000119	O	0.5205366	0.0799199	1.0761790
C	-3.5742204	1.6044680	2.8133308	C	3.4878946	-2.9777453	-1.3402962
C	-2.4418093	1.5037030	2.0180609	C	3.7840005	-3.5894164	-2.5292511
C	-1.6709077	2.6242452	1.7191467	C	2.9918608	-3.3465838	-3.6628684
C	-2.0106919	3.8780438	2.2067454	C	1.9201034	-2.4977894	-3.5831916
C	-1.8780816	0.2968451	1.3885706	H	-3.4334896	4.9427291	3.3957075
C	-0.6210930	0.7417823	0.6082820	H	-4.7903380	2.9679394	3.9239968
C	-0.5266705	2.2619843	0.8643476	H	-4.1678689	0.7295508	3.0415352
O	-2.2875271	-0.8261012	1.4488635	H	-1.4072149	4.7441571	1.9708762
O	0.3285638	2.9794629	0.4339912	H	2.6897009	-1.6468629	0.8900401
C	0.2239489	-0.3974558	-1.0963176	H	-0.1424609	-0.7798429	-3.1613484
C	1.0158520	-0.6398442	0.0364063	H	4.0994113	-3.1651794	-0.4660833
C	2.0848930	-1.4657665	0.0119242	H	4.6292759	-4.2612087	-2.5965937
C	2.3918984	-2.0991858	-1.2265024	H	3.2297756	-3.8315007	-4.6002080
C	1.5896807	-1.8536309	-2.3741003	H	1.3088905	-2.3113569	-4.4578191

Table S15: Coordinates of the calculated structure of **25** (PBEh-3c/def2-mSVP).

C	-4.6598836	0.3285467	1.2384193	C	2.9669941	-1.9123611	-2.6963495
C	-3.4013536	0.5391913	1.7579989	C	4.0672769	-1.1414727	-3.0321493
C	-2.2227304	0.2438991	1.0568493	C	4.1077048	0.2238222	-2.7371854
C	-2.3772848	-0.3320827	-0.2115825	C	3.0481034	0.8480368	-2.1009638
C	-3.6490336	-0.5427722	-0.7427124	O	0.1998783	-2.9600635	-1.8507943
C	-4.7828514	-0.2111582	-0.0344105	O	0.3174701	1.6173477	-0.9265813
C	-0.8326126	1.6033274	2.6292570	H	-5.5352883	0.5695613	1.8253728
C	0.3358372	1.8437957	3.3295262	H	-3.3167362	0.9253346	2.7646243
C	1.4455665	1.0361989	3.1305596	H	-3.7229297	-0.9839990	-1.7277197
C	1.3841943	0.0154941	2.1979761	H	-5.7577089	-0.3893188	-0.4679118
C	0.2069216	-0.2077837	1.5053088	H	-1.6756268	2.2644014	2.7772856
C	-0.9399792	0.5497204	1.7180979	H	0.3803202	2.6685372	4.0277652
O	0.1969868	-1.2056034	0.5674521	H	2.3603498	1.2132354	3.6797615
O	-1.3959113	-0.7380606	-1.0590161	H	2.2408651	-0.6151702	1.9988410
C	-0.0655304	-0.7982377	-0.7398252	H	2.9252431	-2.9677276	-2.9298270
C	0.6292632	-1.8711071	-1.6119084	H	4.9089753	-1.5979432	-3.5357634
C	0.6995505	0.4963471	-1.1039029	H	4.9803108	0.7989275	-3.0169824
C	1.9126223	-1.2875067	-2.0482572	H	3.0675841	1.9060025	-1.8764677
C	1.9534423	0.0706414	-1.7547849				

Table S16: Coordinates of the calculated structure of **23** (PBEh-3c/def2-mSVP).

	x	y	z	C	-0.5313938	2.5837293	2.7624178
C	-2.9257750	2.5078548	2.4088049	C	-0.3868986	1.7550126	1.6603556
C	-1.8148226	2.9510056	3.1307474	C	-1.4937291	1.3140723	0.9411809

C	-2.7783106	1.6878865	1.3022889	C	1.3796970	-1.0154995	-1.6506295
C	0.8606700	1.2405012	1.0592486	C	1.0830416	-2.0698000	-0.7970018
C	0.4264181	0.2031300	0.0173264	O	1.1885240	0.2255853	-1.1360256
C	-1.0614887	0.4921989	-0.2096963	H	-3.9148747	2.8170069	2.7195691
O	1.9857213	1.5516533	1.3170870	H	-1.9639867	3.5941210	3.9877903
O	-1.7180745	0.1298829	-1.1423570	H	0.3340093	2.9284510	3.3122355
S	0.5451969	-1.4828864	0.7679239	H	-3.6331770	1.3480343	0.7333638
C	1.2701643	-3.3760429	-1.2014857	H	1.0394306	-4.1996898	-0.5398259
C	1.7615399	-3.6115543	-2.4821933	H	1.9102619	-4.6291525	-2.8159093
C	2.0552261	-2.5539815	-3.3276843	H	2.4316936	-2.7486731	-4.3225483
C	1.8647967	-1.2368613	-2.9197264	H	2.0861401	-0.4059845	-3.5752567

Table S17: Coordinates of the calculated structure of **30** (PBEh-3c/def2-mSVP).

	x	y	z	C	1.5501563	3.7222713	-0.8836752
C	-3.5350200	-2.1664371	0.0509325	C	0.7071835	3.3674862	0.2076143
C	-3.7949691	-3.5429806	0.0012315	C	2.7284406	3.1406607	-2.9361997
C	-2.8880612	-4.4279019	0.5164728	C	3.2168062	4.4166113	-3.0276999
C	-1.6866943	-3.9775682	1.1049453	C	2.8828946	5.3701808	-2.0522655
C	-1.4108576	-2.5875308	1.1417331	C	2.0682703	5.0274185	-1.0064012
C	-2.3673441	-1.6907414	0.5968739	O	-0.5567851	1.5153971	1.1724784
C	-0.7585354	-4.8809292	1.6663742	O	-0.0154673	-0.0352149	-0.4114105
C	0.3887107	-4.4331879	2.2616317	H	-4.2537133	-1.4641704	-0.3501674
C	0.6562301	-3.0583091	2.3187582	H	-4.7139023	-3.8996966	-0.4430689
C	-0.2128007	-2.1499813	1.7648110	H	-3.0860824	-5.4922625	0.4842383
C	-2.1269184	-0.2350770	0.6269170	H	-0.9724502	-5.9418628	1.6241133
C	0.1013413	-0.7105239	1.8405185	H	1.0900672	-5.1346534	2.6919120
C	-0.6644737	0.1734485	0.8443437	H	1.5587998	-2.7004462	2.7961823
O	-2.9738204	0.5928546	0.4365085	H	1.6357919	0.6873174	-2.5223918
O	0.9405369	-0.2389685	2.5572261	H	0.4462667	4.0948216	0.9642259
C	0.2553804	2.0946235	0.2551894	H	2.9860404	2.4053170	-3.6887706
C	0.5886647	1.1417840	-0.7211643	H	3.8609752	4.6920654	-3.8520612
C	1.3847801	1.4286165	-1.7757508	H	3.2708949	6.3771675	-2.1285544
C	1.8882164	2.7571396	-1.8714669	H	1.8114476	5.7632622	-0.2541836

Table S18: Coordinates of the calculated structure of **32** (PBEh-3c/def2-mSVP).

	x	y	z	C	-2.8032861	-0.5898382	-0.2314966
C	-4.3069730	-0.1608903	-2.1396481	C	-1.0329934	-2.3903678	-0.4843439
C	-4.7336859	-0.3958969	-3.4555593	C	-1.3474260	-0.9865553	0.0665634
C	-4.1014097	-1.3346081	-4.2235868	O	-3.5004038	-0.0885377	0.6069525
C	-3.0176791	-2.0814528	-3.7120140	O	-0.4029025	-3.1970798	0.1382975
C	-2.5695542	-1.8302052	-2.3923076	C	-1.6417458	0.6676194	3.0119667
C	-3.2392389	-0.8479826	-1.6188734	C	-0.7707370	0.2225936	2.0029315
C	-2.3746531	-3.0778368	-4.4783812	C	0.3701167	0.9105065	1.6646822
C	-1.3475705	-3.8139824	-3.9545436	C	0.5967015	2.1880250	2.2593253
C	-0.9189902	-3.5851882	-2.6380467	C	-0.2748826	2.6385236	3.2843050
C	-1.5039569	-2.6081035	-1.8714462	C	-1.3765632	1.8369531	3.6583488

C	1.6370198	3.0516309	1.8425731	H	-5.5655430	0.1662226	-3.8571486
C	1.8269529	4.2663262	2.4410174	H	-4.4323190	-1.5216982	-5.2377797
C	0.9892411	4.6890914	3.4894051	H	-2.7132971	-3.2577930	-5.4913296
C	-0.0427232	3.8914083	3.8942275	H	-0.8665810	-4.5784555	-4.5491982
O	-1.0458307	-0.9779085	1.4062782	H	-0.1154661	-4.1755947	-2.2175704
C	0.7455225	-0.1195158	-0.5202507	H	-2.5078558	0.0708527	3.2586822
C	1.5322176	-0.6134371	-1.5727330	H	-2.0350335	2.1821489	4.4456907
C	2.8841466	-0.6952003	-1.4115509	H	2.2818358	2.7560851	1.0270799
C	3.4871281	-0.3417973	-0.1844754	H	2.6252214	4.9116334	2.0989627
C	2.6809951	0.1503620	0.8758858	H	1.1550320	5.6491632	3.9596748
C	1.2815736	0.3208335	0.6639336	H	-0.7091820	4.2163231	4.6840018
C	4.8782720	-0.4935552	0.0138676	H	1.0553214	-0.9098035	-2.4978812
C	5.4502120	-0.2046026	1.2192675	H	3.5069437	-1.0606819	-2.2184731
C	4.6460588	0.2381635	2.2864223	H	5.4843045	-0.8574974	-0.8069033
C	3.3004693	0.4110349	2.1208601	H	6.5151816	-0.3299005	1.3623958
O	-0.6141117	-0.0561225	-0.6971793	H	5.0960752	0.4362520	3.2501191
H	-4.8119226	0.5755140	-1.5286058	H	2.6979745	0.7348228	2.9576086

Table S19: Coordinates of the calculated structure of **31** (PBEh-3c/def2-mSVP).

	x	y	z	O	-0.3388418	1.8007709	1.6040656
C	-4.0665419	-0.1720002	-0.7039156	C	0.9182153	0.6045783	-0.9415233
C	-4.6199035	-1.2415866	-1.4254225	C	0.9878282	-0.2871847	-2.0000827
C	-3.9315500	-2.4171017	-1.5463108	C	2.2049321	-0.8417142	-2.3500383
C	-2.6624276	-2.5787610	-0.9480869	C	3.3341134	-0.5258163	-1.6076183
C	-2.0941187	-1.4948332	-0.2358645	C	3.2473323	0.3704837	-0.5585839
C	-2.8243908	-0.2830111	-0.1317697	C	2.0416547	0.9924083	-0.2159085
C	-1.9487299	-3.7943483	-1.0312531	O	-0.3149181	1.0886341	-0.5999371
C	-0.7374384	-3.9441628	-0.4125105	H	-4.6144989	0.7555837	-0.6040282
C	-0.1857026	-2.8822294	0.3194022	H	-5.5936956	-1.1312440	-1.8823784
C	-0.8385862	-1.6780589	0.3963617	H	-4.3588271	-3.2450351	-2.0986726
C	-2.2565623	0.8612643	0.6156027	H	-2.3805840	-4.6161339	-1.5892761
C	-0.2458834	-0.5652490	1.1649444	H	-0.2035311	-4.8820073	-0.4809206
C	-0.7164544	0.8338836	0.7204045	H	0.7693150	-2.9992002	0.8140379
O	-2.9062907	1.7676362	1.0501620	H	0.1342634	3.5401522	3.2316558
O	0.5380835	-0.7084354	2.0616516	H	4.0022939	2.6334424	0.3686411
C	1.0039975	3.3385192	2.6207687	H	4.1783804	4.3493694	2.0831450
C	0.9008901	2.3494826	1.6432580	H	2.2218858	4.8132163	3.5623086
C	1.9988854	2.0355802	0.8293156	H	0.0802167	-0.5424910	-2.5312655
C	3.1585159	2.8021138	1.0234070	H	2.2656299	-1.5363263	-3.1767807
C	3.2617141	3.7848787	1.9830432	H	4.2862403	-0.9821755	-1.8424626
C	2.1703819	4.0480872	2.7994464	H	4.1347072	0.5790208	0.0229882

Table S20: Coordinates of the calculated structure of **26** (PBEh-3c/def2-mSVP).

	x	y	z	C	3.3318636	-0.5012778	-1.4114530
C	2.2488719	-0.0585736	0.7014713	C	4.5634853	-0.5948900	-0.7018308
C	2.2200403	-0.2379286	-0.6900973	C	4.5927065	-0.4130431	0.7077616

C	3.3905251	-0.1361027	1.4200501	C	-0.6986457	1.4016049	-0.1371643
C	5.7703213	-0.8702914	-1.3753806	C	0.1477918	0.1168682	0.0155610
C	6.9552467	-0.9635204	-0.6950702	C	-0.8879292	-1.0201519	0.1784549
C	6.9841464	-0.7838006	0.6971560	O	-0.6144083	-2.1753799	0.3353727
C	5.8274705	-0.5148071	1.3793084	O	-0.2496789	2.5027549	-0.2743939
O	0.9871206	0.1956367	1.1337307	H	3.3003363	-0.6380205	-2.4838470
O	0.9406207	-0.0948475	-1.1210958	H	3.4034617	0.0037296	2.4924113
C	-7.0145017	-0.0317870	0.0647444	H	5.7484588	-1.0092925	-2.4494114
C	-6.9055429	1.3631419	-0.1166361	H	7.8712418	-1.1761920	-1.2299760
C	-5.6785642	1.9558114	-0.1968005	H	7.9223423	-0.8584212	1.2306256
C	-4.4960061	1.1859443	-0.0998602	H	5.8501910	-0.3766452	2.4534410
C	-4.6063680	-0.2260610	0.0837607	H	-7.9938774	-0.4866442	0.1266613
C	-5.8942140	-0.8054543	0.1622295	H	-7.8025871	1.9627739	-0.1919447
C	-3.2223508	1.7850718	-0.1805790	H	-5.5953815	3.0262676	-0.3359325
C	-2.1116390	0.9940897	-0.0808665	H	-5.9780907	-1.8758644	0.3014077
C	-2.2209762	-0.4020430	0.1008438	H	-3.1293587	2.8553140	-0.3194262
C	-3.4410460	-1.0131940	0.1834694	H	-3.5150763	-2.0847751	0.3233045

Table S21: Coordinates of the calculated structure of **27** (PBEh-3c/def2-mSVP).

	x	y	z	C	0.6798448	0.7312470	1.6968342
C	-0.6918049	1.1430734	-3.4457136	C	1.7097769	0.6462269	0.7387042
C	-1.2196667	0.3042270	-2.4806240	C	2.9917573	1.0122744	1.0394703
C	-1.9582610	-0.8267689	-2.8236178	C	-0.6021495	0.2913560	1.1184363
C	-2.1441934	-1.0995655	-4.1765732	C	-0.3228988	-0.1442269	-0.3393442
C	-1.6204331	-0.2679742	-5.1516903	C	1.1889838	0.1187697	-0.5347691
C	-0.8972584	0.8576645	-4.7854016	O	1.7954421	-0.0539379	-1.5536974
O	-1.1008965	0.6552265	-1.1590499	O	-1.6677606	0.2408119	1.6639851
C	-1.8051667	-1.9650251	-0.6224689	H	-0.1304217	2.0166828	-3.1432185
C	-2.3083256	-2.7906178	0.3669556	H	-2.6923793	-1.9875844	-4.4647275
C	-3.5677030	-3.3475300	0.2170631	H	-1.7730720	-0.5006250	-6.1968569
C	-4.3186946	-3.0688520	-0.9153911	H	-0.4832351	1.5101318	-5.5422719
C	-3.8038868	-2.2416288	-1.8990766	H	-1.7095306	-2.9982350	1.2434529
C	-2.5364185	-1.6784263	-1.7738087	H	-3.9650014	-3.9911167	0.9903197
O	-0.5164686	-1.5058764	-0.5121654	H	-5.3071116	-3.4925197	-1.0308764
C	4.8517210	2.3296734	3.9652988	H	-4.3990806	-2.0108276	-2.7734504
C	3.8199298	2.4186836	4.9232396	H	5.8568295	2.6249699	4.2346646
C	2.5453836	2.0504219	4.6017311	H	4.0445452	2.7813883	5.9172150
C	2.2346746	1.5732704	3.3070171	H	1.7537027	2.1188487	5.3371538
C	3.2788461	1.4840414	2.3371690	H	5.3793842	1.8062920	1.9707518
C	4.5873335	1.8744731	2.7058017	H	0.1235967	1.2535164	3.6904051
C	0.9227649	1.1872835	2.9621229	H	3.7773022	0.9407840	0.2970015

Table S22: Coordinates of the calculated structure of **29** (PBEh-3c/def2-mSVP).

	x	y	z	C	0.2041357	-0.6751785	8.0454748
O	-1.1369089	-0.2640379	0.1570443	H	0.3590217	-1.1857163	8.9864136
O	0.6604843	-2.2746472	1.5109301	C	0.4031263	-1.3365425	6.8680436

H	0.7159631	-2.3730861	6.8683106	H	-1.6598173	2.0143601	-5.9802944
C	0.2051091	-0.6838602	5.6289824	C	-0.8105062	1.3366253	-4.1582167
C	0.4033808	-1.3562392	4.4052593	H	-1.3538111	0.4026872	-4.1839479
H	0.7137311	-2.3940383	4.3950672				
C	0.1987407	-0.6759815	3.2376141				
C	0.3523533	-1.1700885	1.8581243				
C	0.0000000	0.0000000	0.9092583				
C	-0.9792589	-1.1111721	-0.9109018				
C	-0.2697470	-0.6874428	-2.0074865				
C	-0.0541772	-1.6112443	-3.0724572				
C	-0.6958512	-2.8767860	-3.0319173				
C	-0.5069857	-3.7863127	-4.0966735				
H	-1.0135153	-4.7431160	-4.0591544				
C	0.3102582	-3.4782389	-5.1461425				
H	0.4523584	-4.1841761	-5.9535291				
C	-1.6091297	-2.3644232	-0.8589573				
H	-2.1827707	-2.6324770	0.0177688				
C	-1.4919239	-3.2165028	-1.9159112				
H	-1.9828884	-4.1813345	-1.8931805				
C	0.9869083	-2.2443979	-5.1648919				
H	1.6598173	-2.0143601	-5.9802944				
C	0.8105062	-1.3366253	-4.1582167				
H	1.3538111	-0.4026872	-4.1839479				
O	1.1369089	0.2640379	0.1570443				
O	-0.6604843	2.2746472	1.5109301				
C	-0.2041357	0.6751785	8.0454748				
H	-0.3590217	1.1857163	8.9864136				
C	-0.4031263	1.3365425	6.8680436				
H	-0.7159631	2.3730861	6.8683106				
C	-0.2051091	0.6838602	5.6289824				
C	-0.4033808	1.3562392	4.4052593				
H	-0.7137311	2.3940383	4.3950672				
C	-0.1987407	0.6759815	3.2376141				
C	-0.3523533	1.1700885	1.8581243				
C	0.9792589	1.1111721	-0.9109018				
C	0.2697470	0.6874428	-2.0074865				
C	0.0541772	1.6112443	-3.0724572				
C	0.6958512	2.8767860	-3.0319173				
C	0.5069857	3.7863127	-4.0966735				
H	1.0135153	4.7431160	-4.0591544				
C	-0.3102582	3.4782389	-5.1461425				
H	-0.4523584	4.1841761	-5.9535291				
C	1.6091297	2.3644232	-0.8589573				
H	2.1827707	2.6324770	0.0177688				
C	1.4919239	3.2165028	-1.9159112				
H	1.9828884	4.1813345	-1.8931805				
C	-0.9869083	2.2443979	-5.1648919				

6. NMR-Spectra

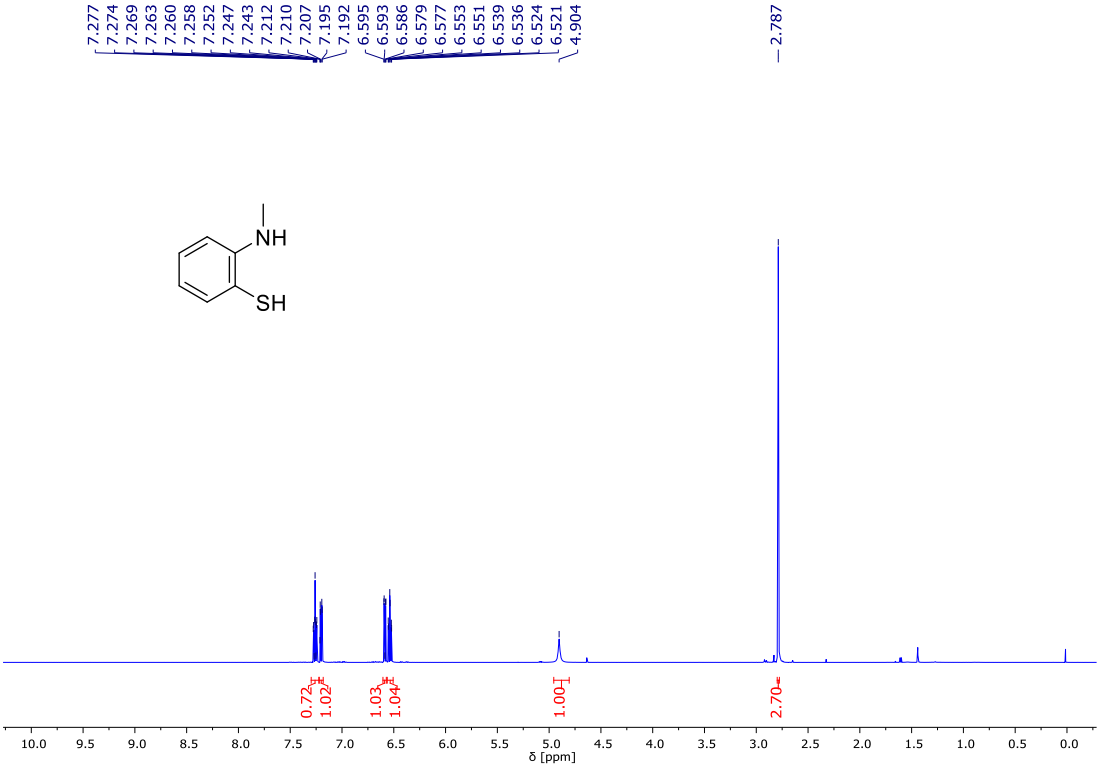


Figure S34: ^{1}H NMR-spectrum of **2** in $CDCl_3$ (500 MHz).

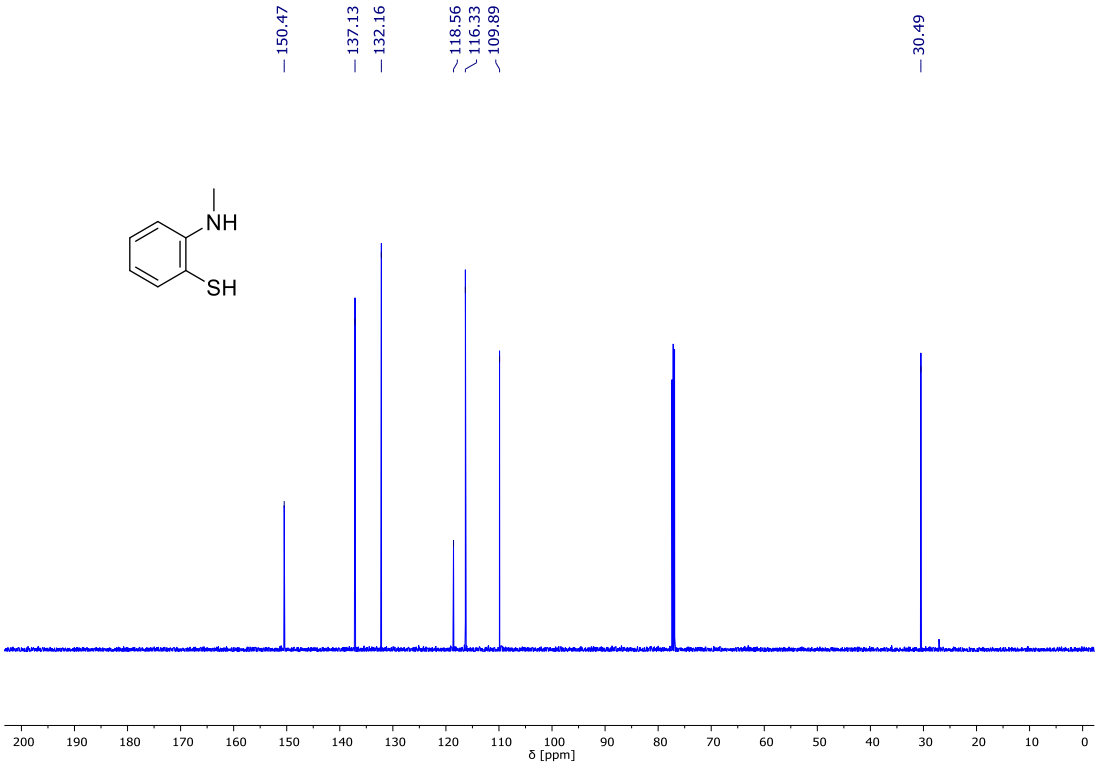


Figure S35: ^{13}C NMR-spectrum of **2** in $CDCl_3$ (125 MHz).

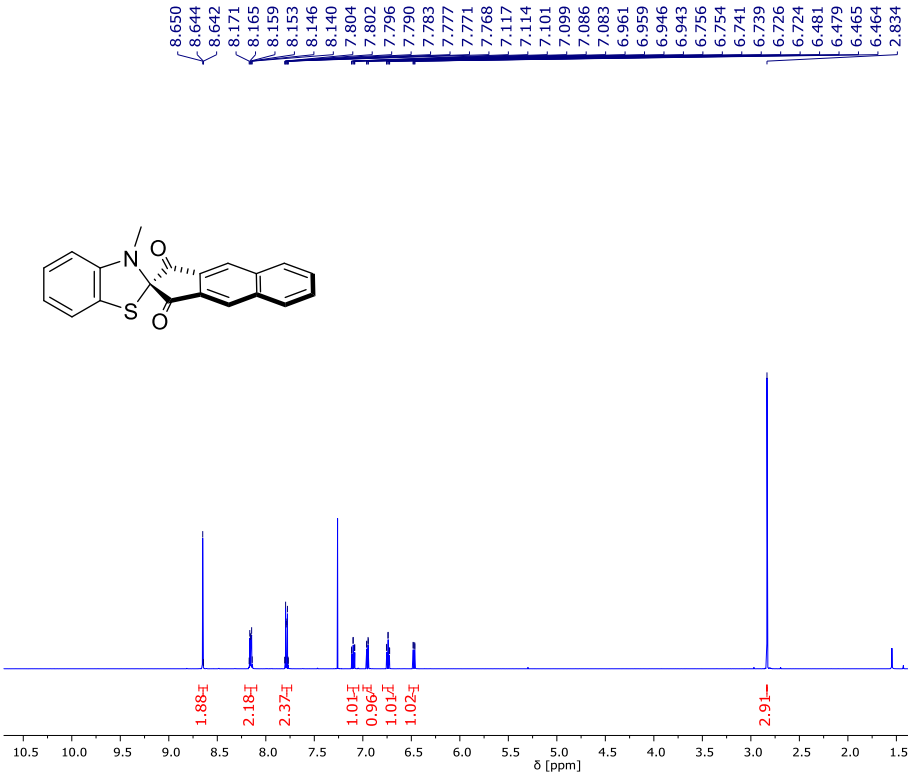


Figure S36: ^{1}H NMR-spectrum of **4** in $CDCl_3$ (500 MHz).

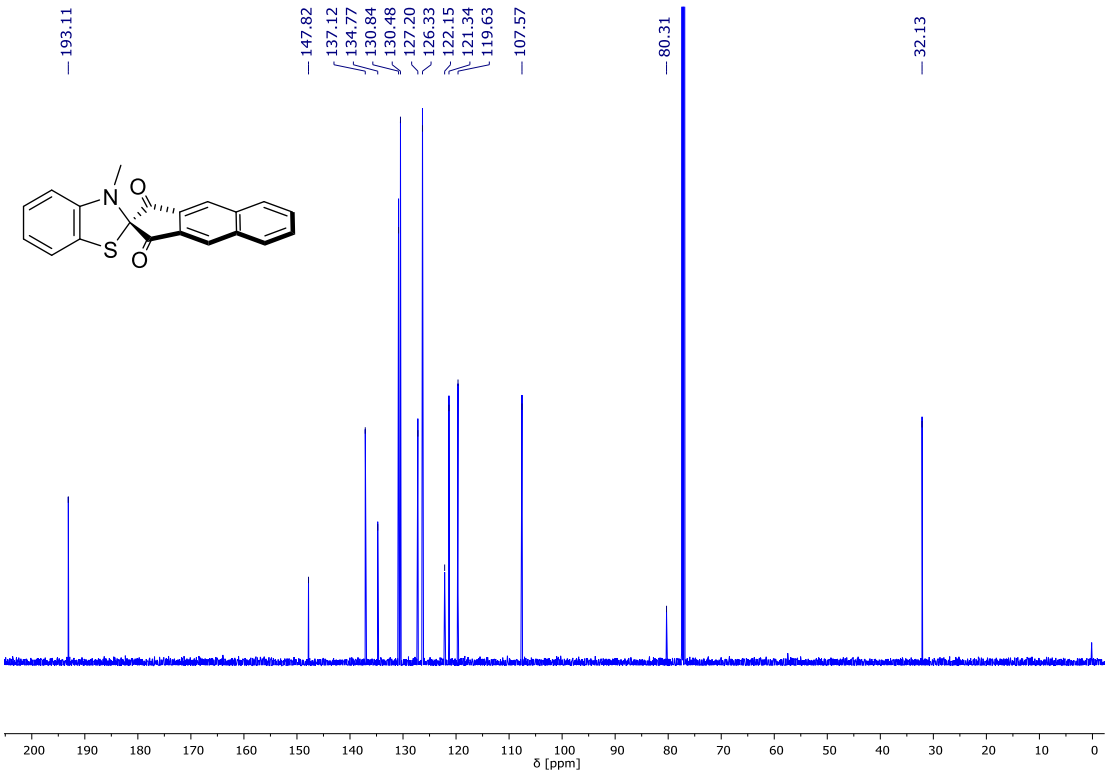


Figure S37: ^{13}C NMR-spectrum of **4** in $CDCl_3$ (125 MHz).

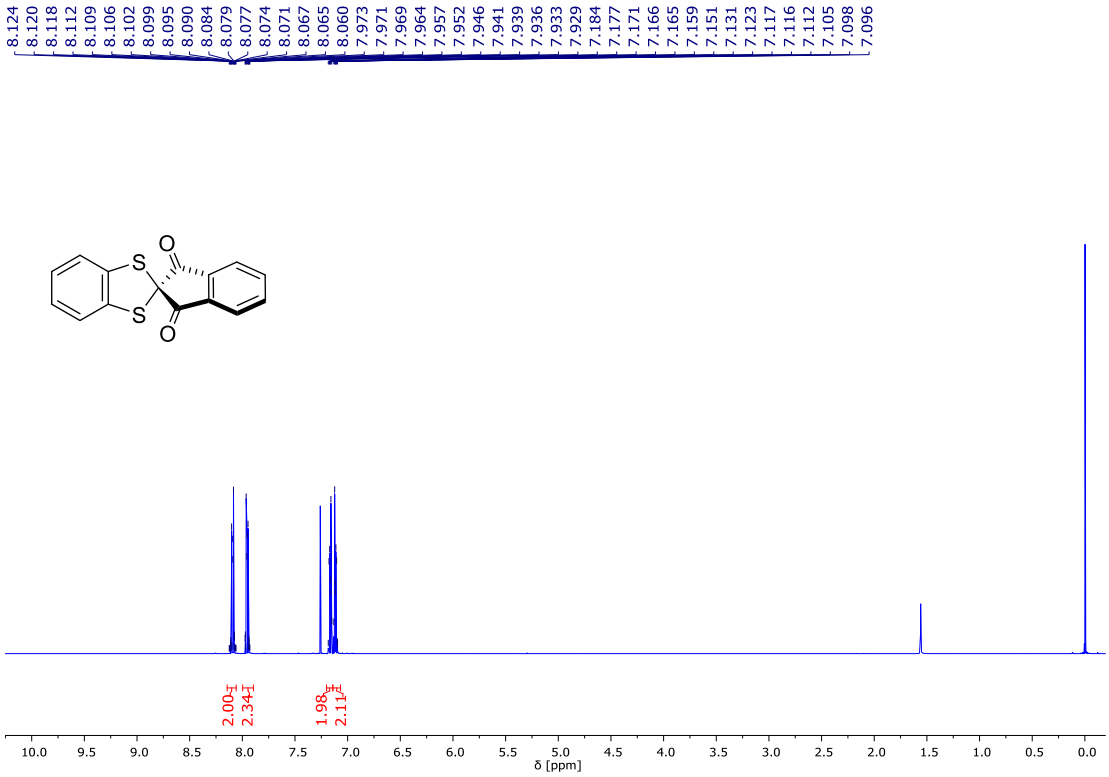


Figure S38: ^{1}H NMR-spectrum of **7** in $CDCl_3$ (500 MHz).

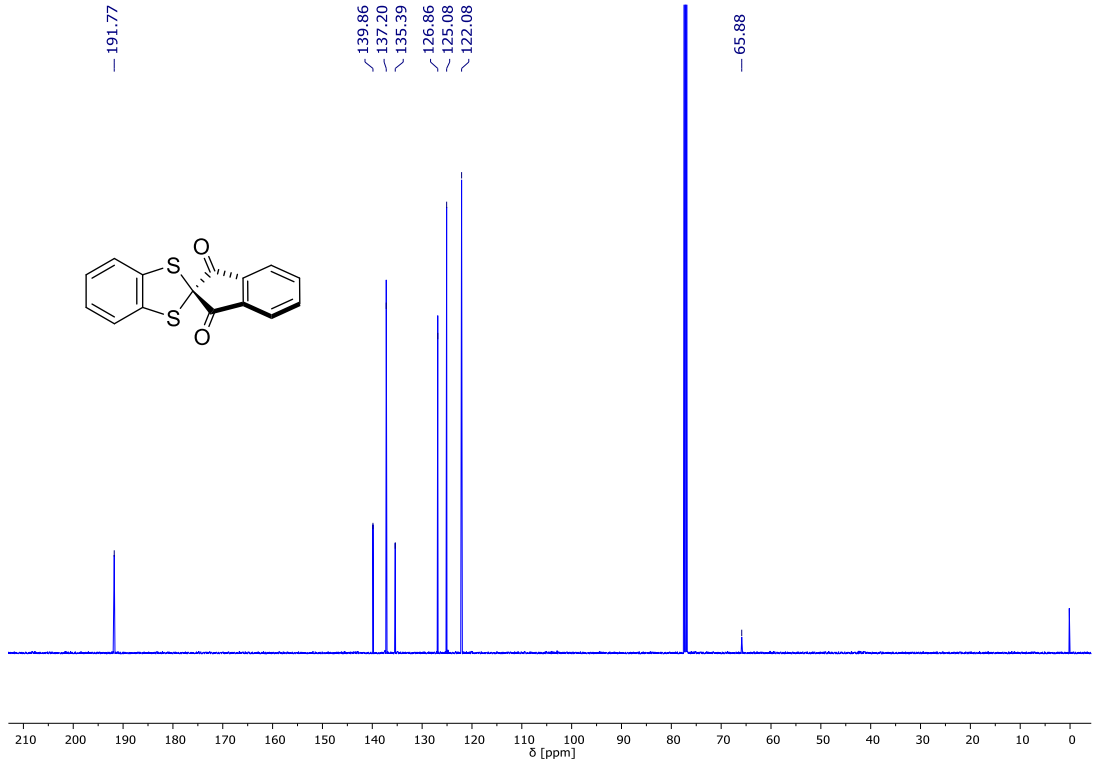


Figure S39: ^{13}C NMR-spectrum of **7** in $CDCl_3$ (125 MHz).

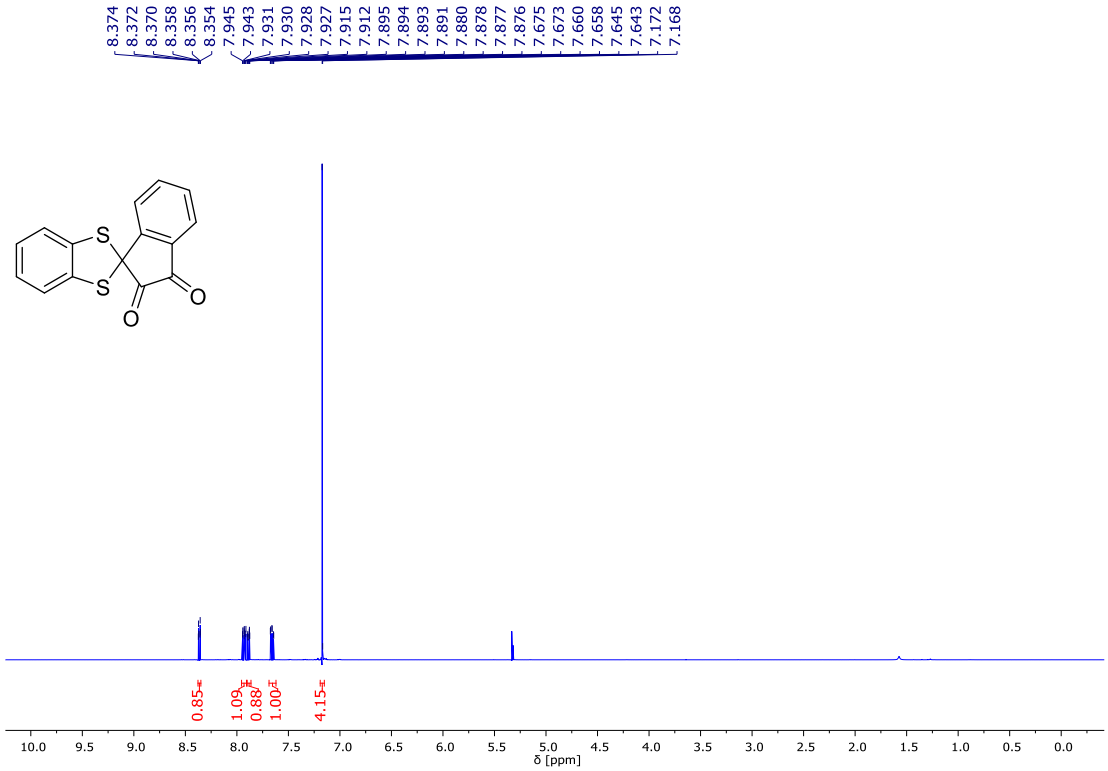


Figure S40: ^{1}H NMR-spectrum of **8** in CD_2Cl_2 (400 MHz).

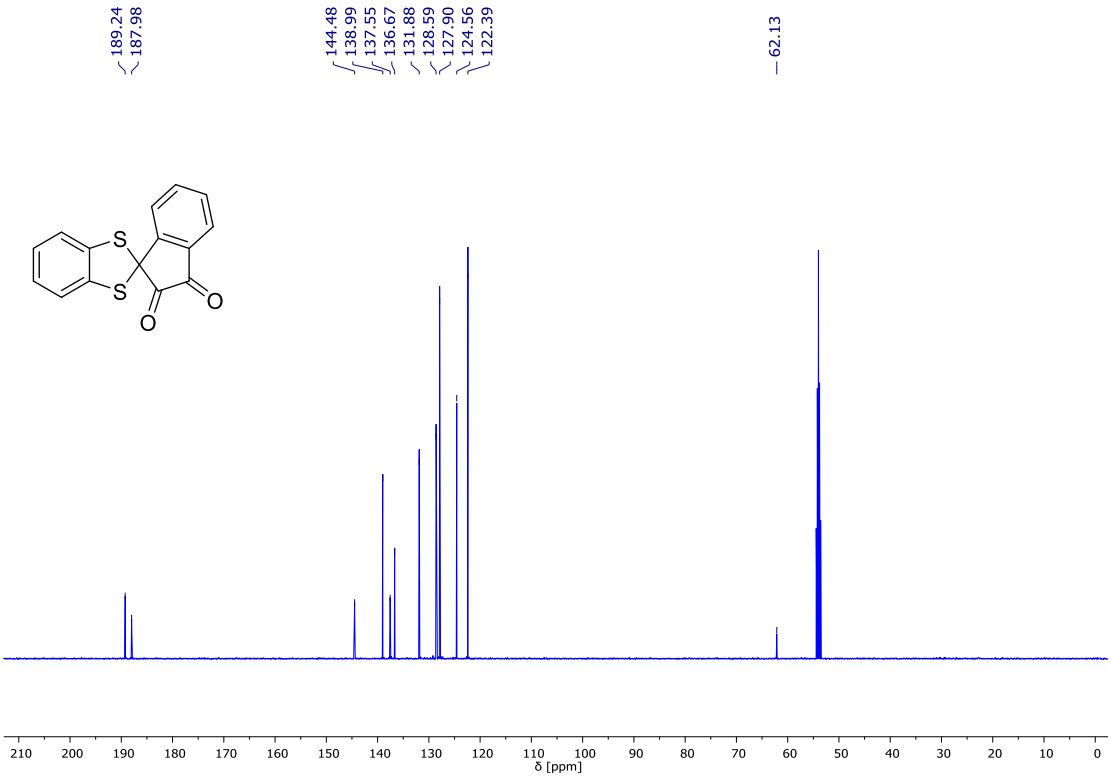


Figure S41: ^{13}C NMR-spectrum of **8** in CD_2Cl_2 (101 MHz).

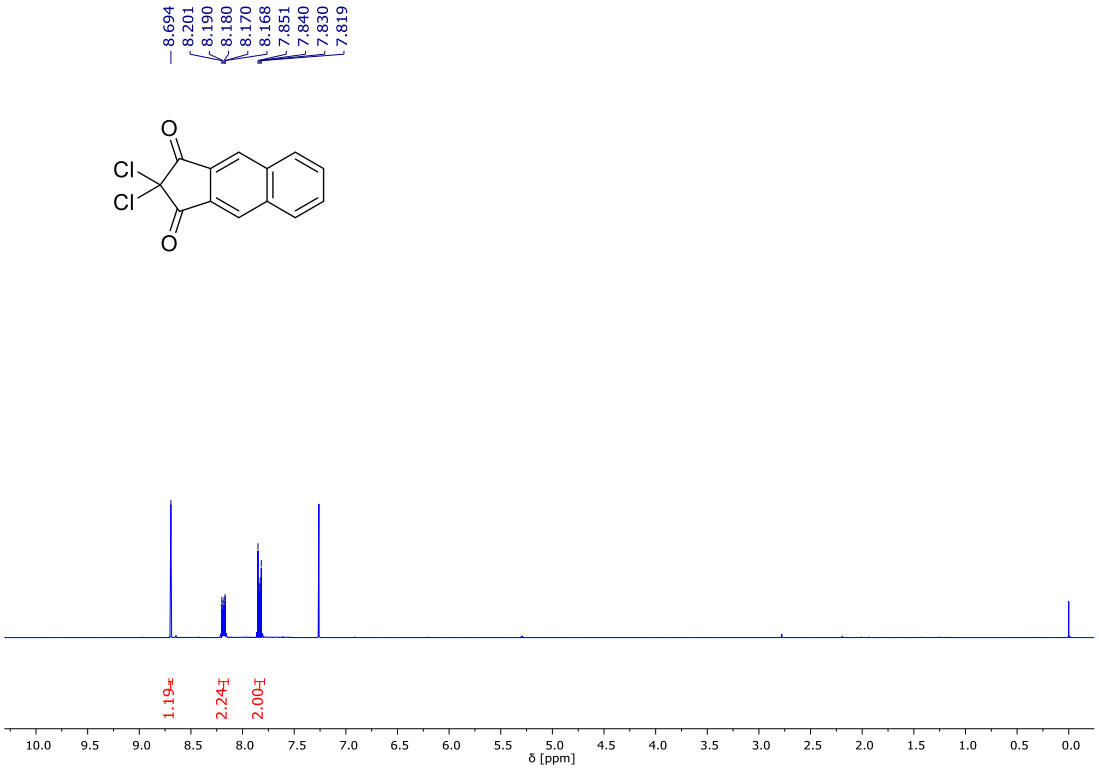


Figure S42: ^{1}H NMR-spectrum of **10** in $CDCl_3$ (500 MHz).

Figure S43: ^{13}C NMR-spectrum of **10** in $CDCl_3$ (125 MHz).

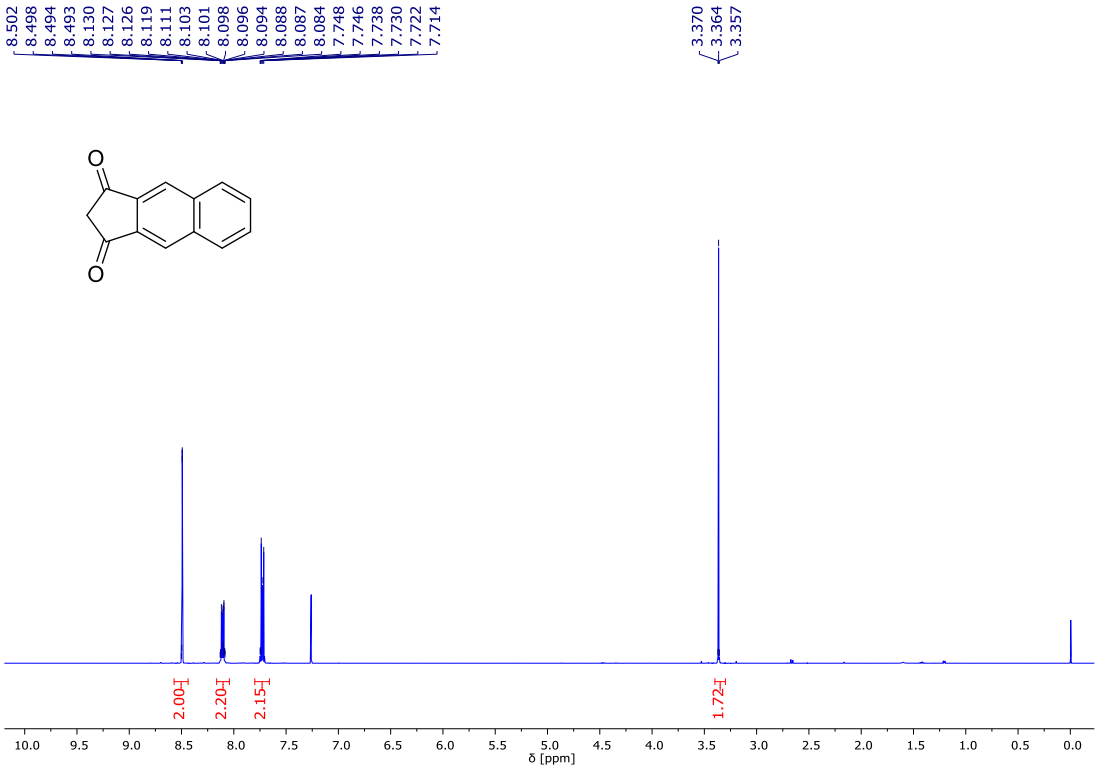


Figure S44: ^{1}H NMR-spectrum of **13** in $CDCl_3$ (500 MHz).

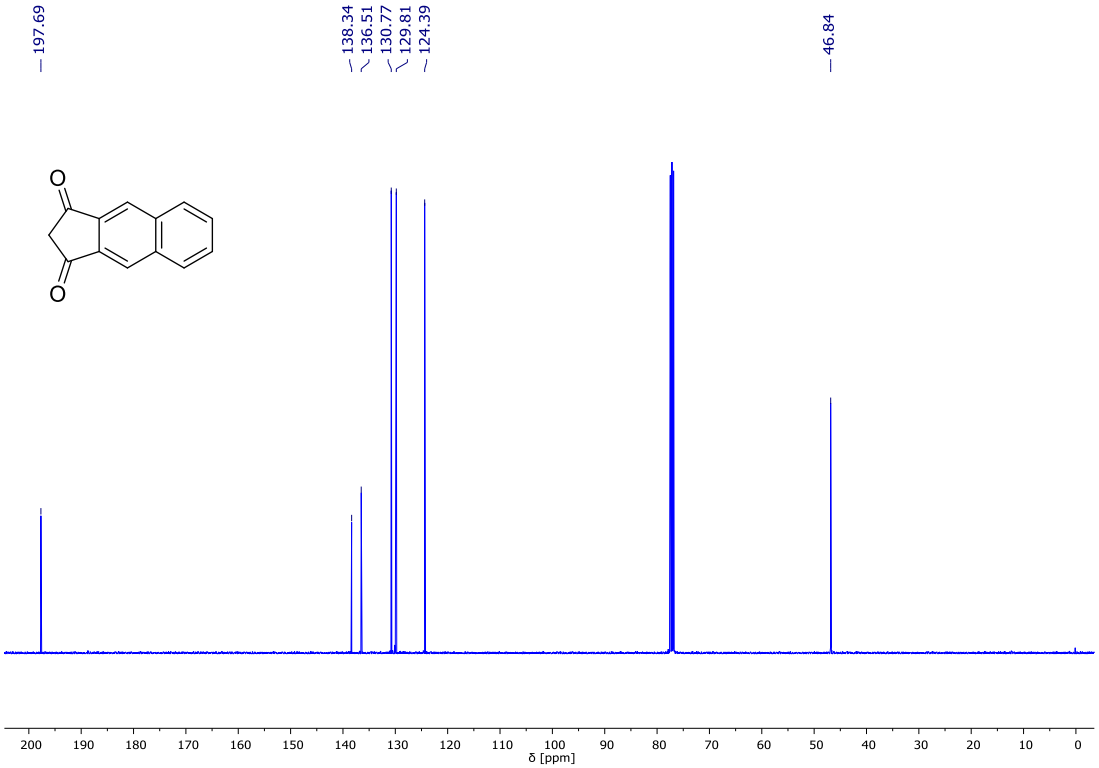


Figure S45: ^{13}C NMR-spectrum of **13** in $CDCl_3$ (125 MHz).

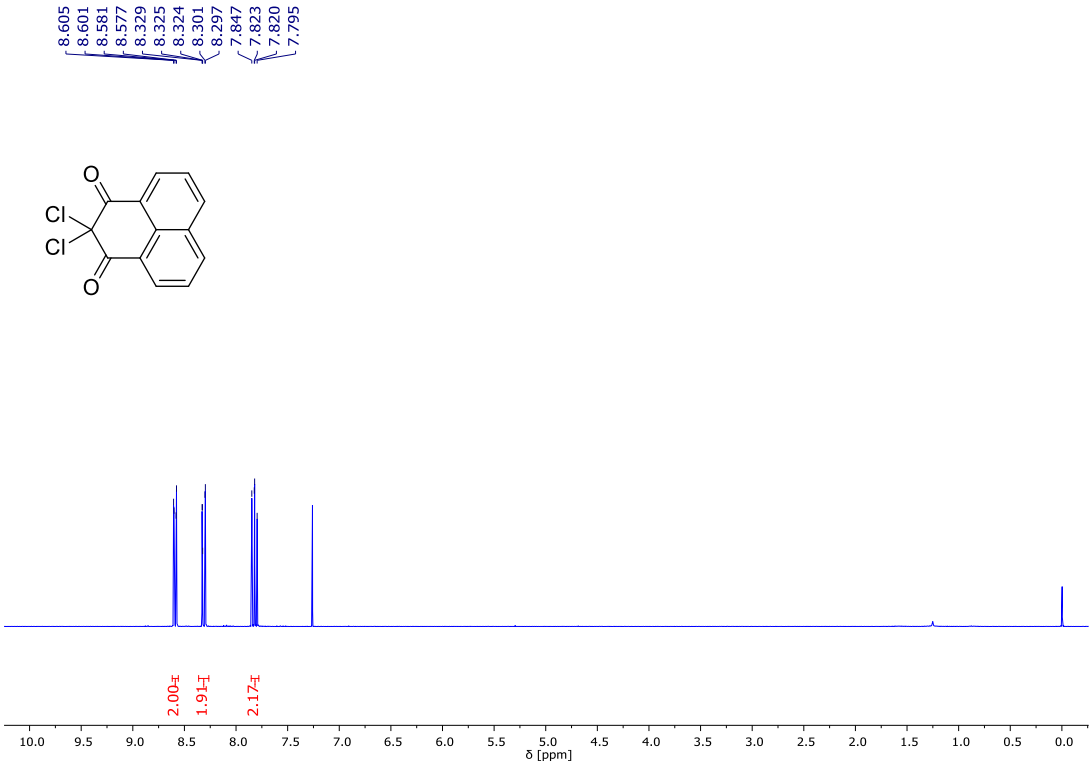


Figure S46: ^{1}H NMR-spectrum of **14** in $CDCl_3$ (500 MHz).

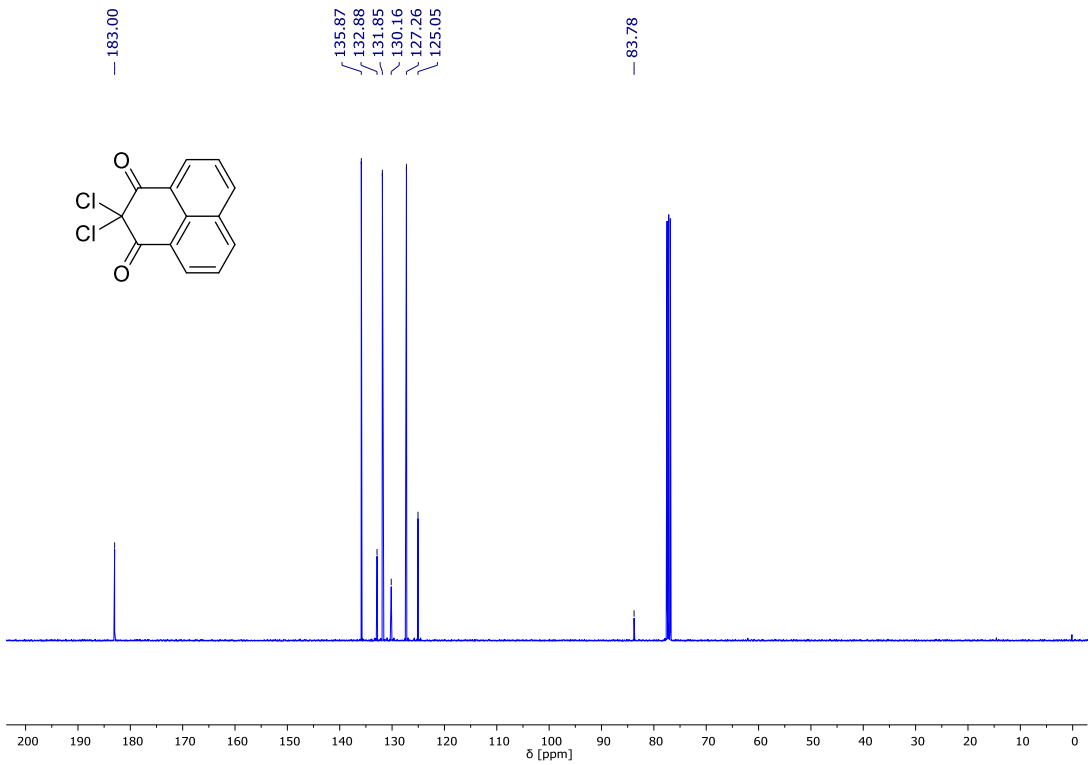


Figure S47: ^{13}C NMR-spectrum of **14** in $CDCl_3$ (101 MHz).

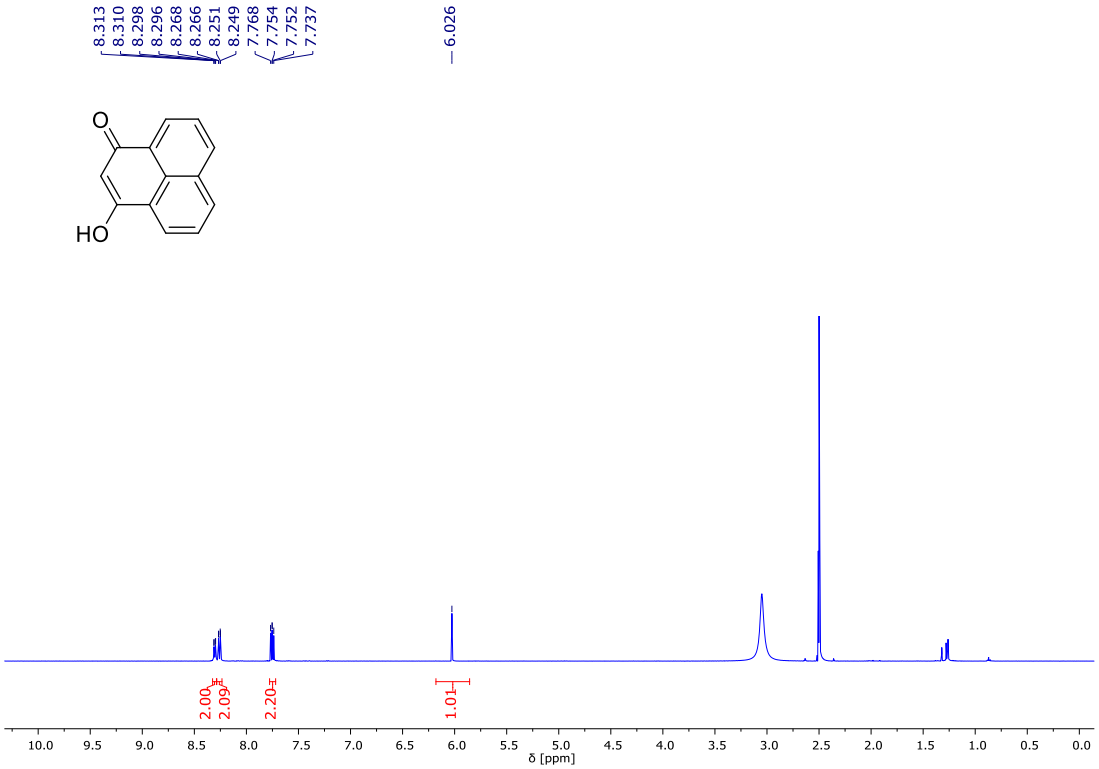


Figure S48: ^{1}H NMR-spectrum of **15** in DMSO-d_6 (400 MHz).

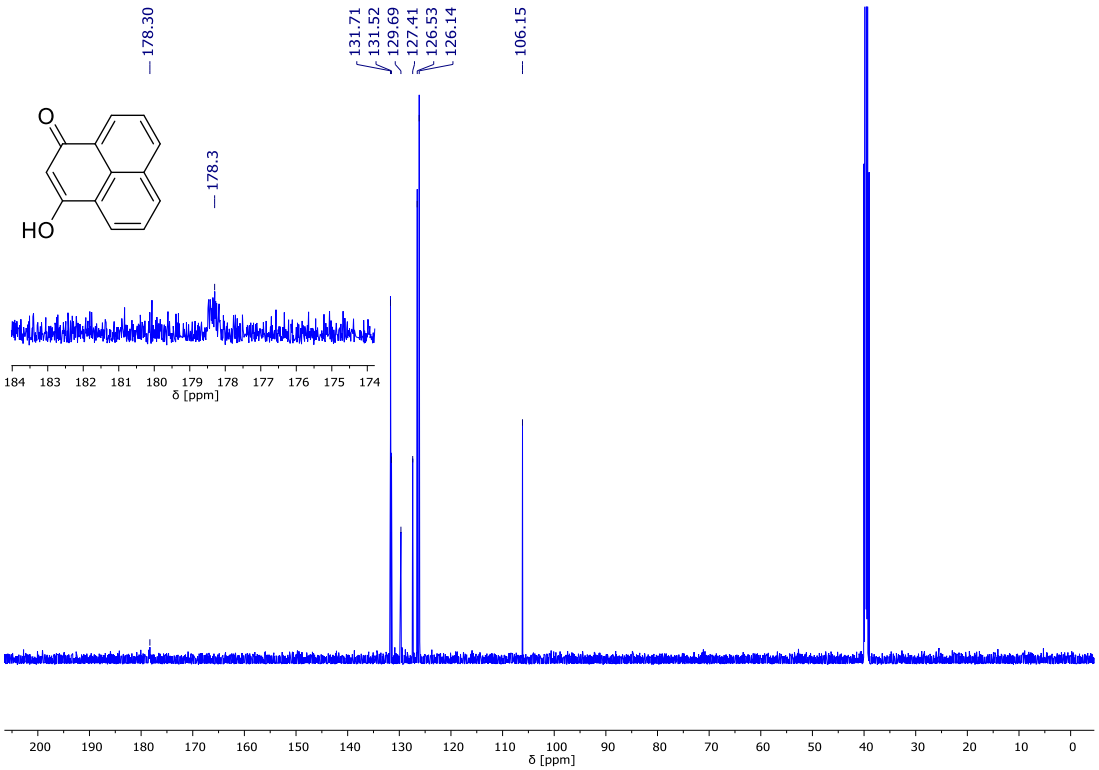


Figure S49: ^{13}C NMR-spectrum of **15** in DMSO-d_6 (101 MHz).

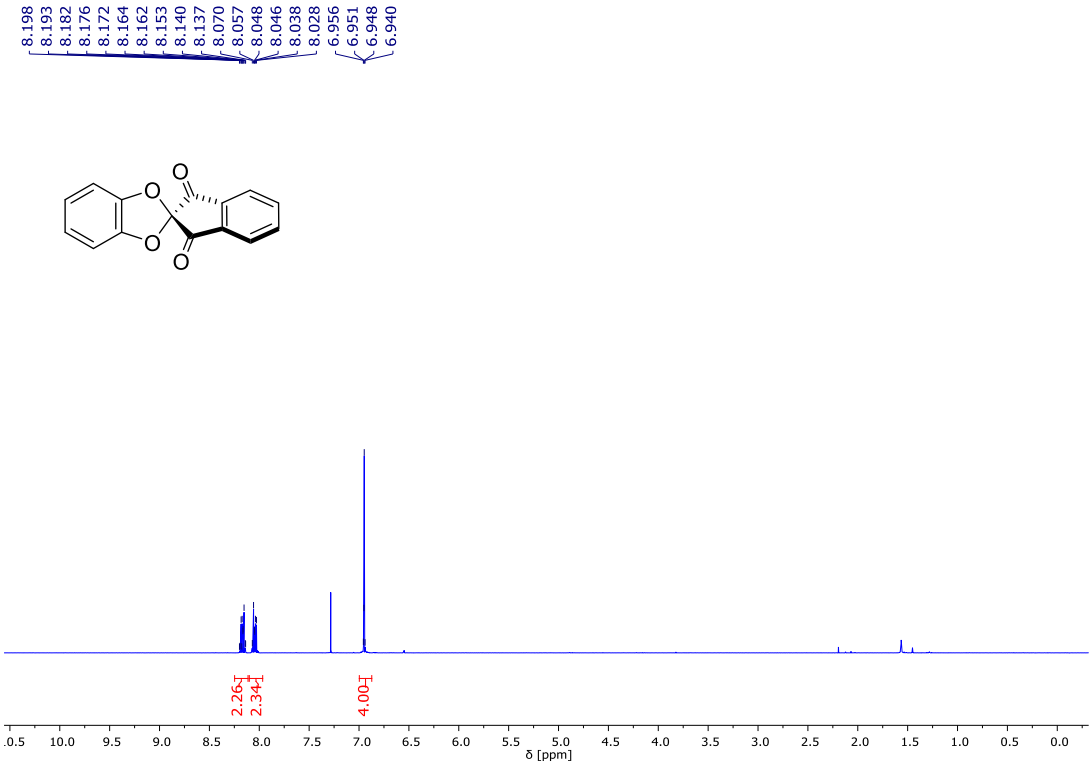


Figure S50: ^{1}H NMR-spectrum of **21** in $CDCl_3$ (500 MHz).

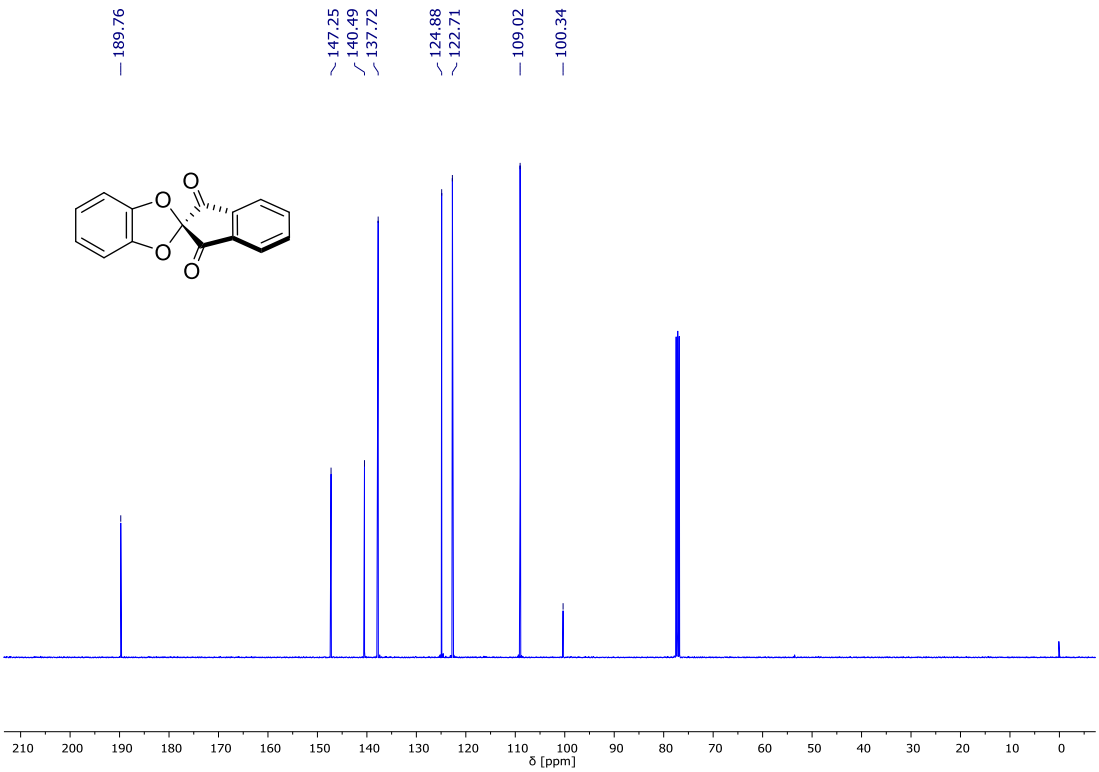


Figure S51: ^{13}C NMR-spectrum of **21** in $CDCl_3$ (125 MHz).

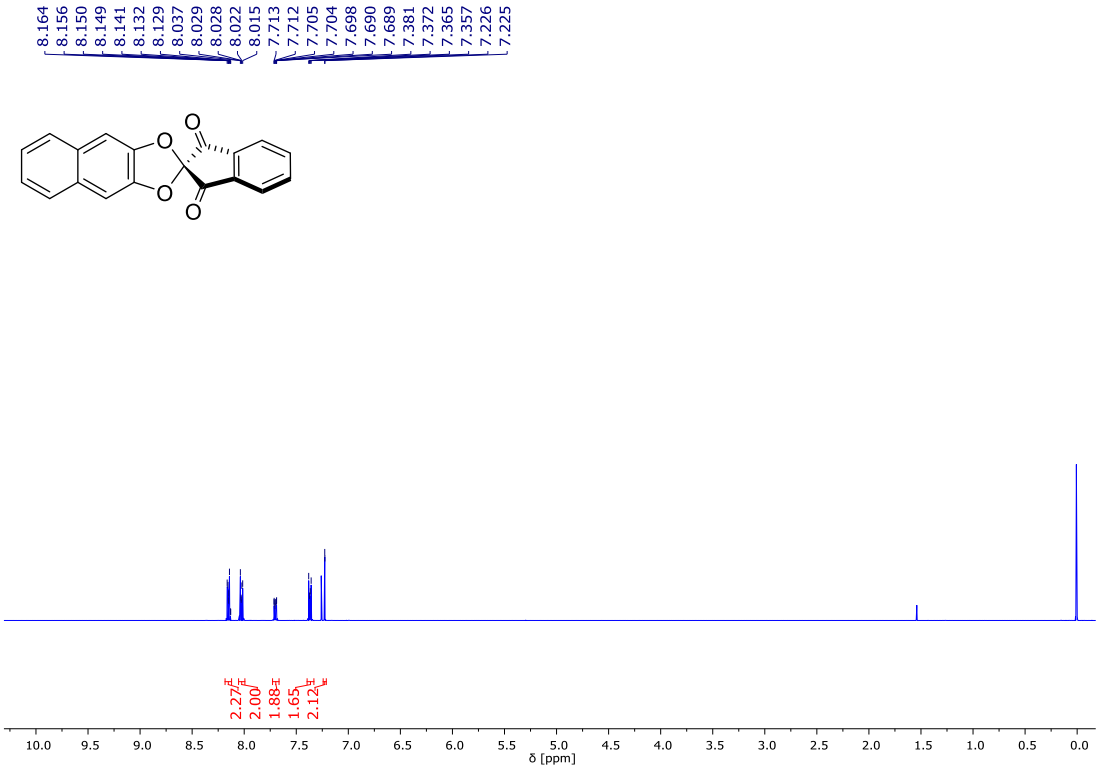


Figure S52: ^{1}H NMR-spectrum of **22** in $CDCl_3$ (500 MHz).

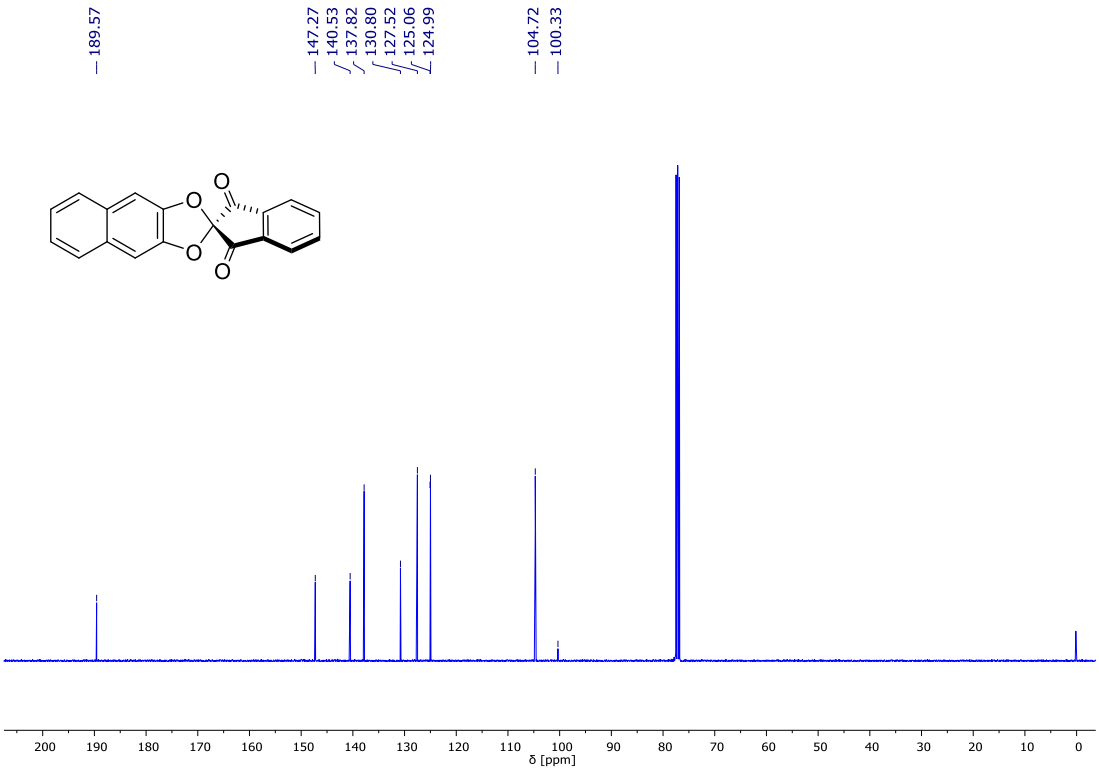


Figure S53: ^{13}C NMR-spectrum of **22** in $CDCl_3$ (101 MHz).

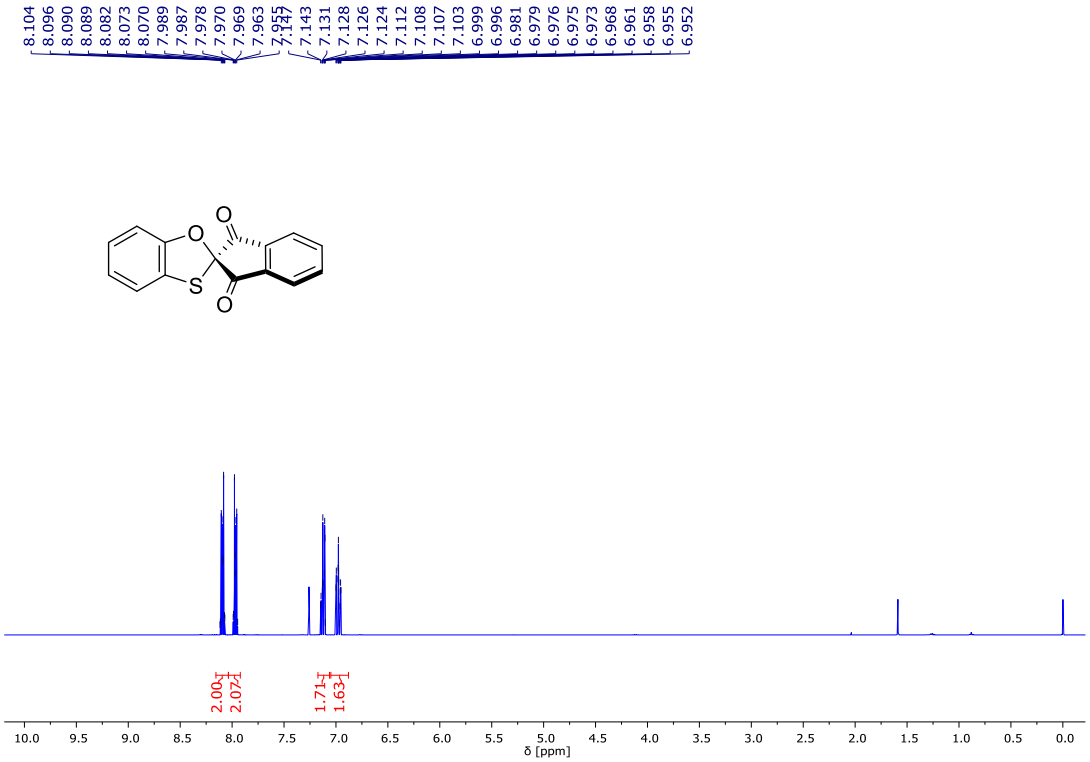


Figure S54: ^{1}H NMR-spectrum of **23** in $CDCl_3$ (500 MHz).

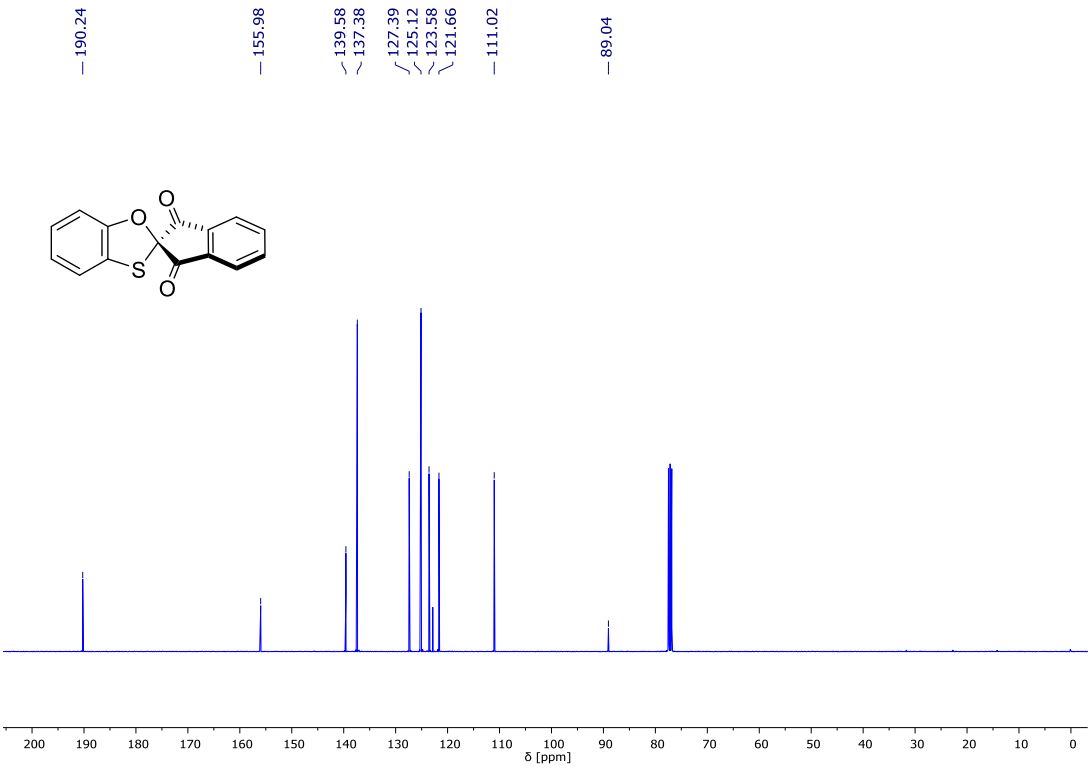


Figure S55: ^{13}C NMR-spectrum of **23** in $CDCl_3$ (101 MHz).

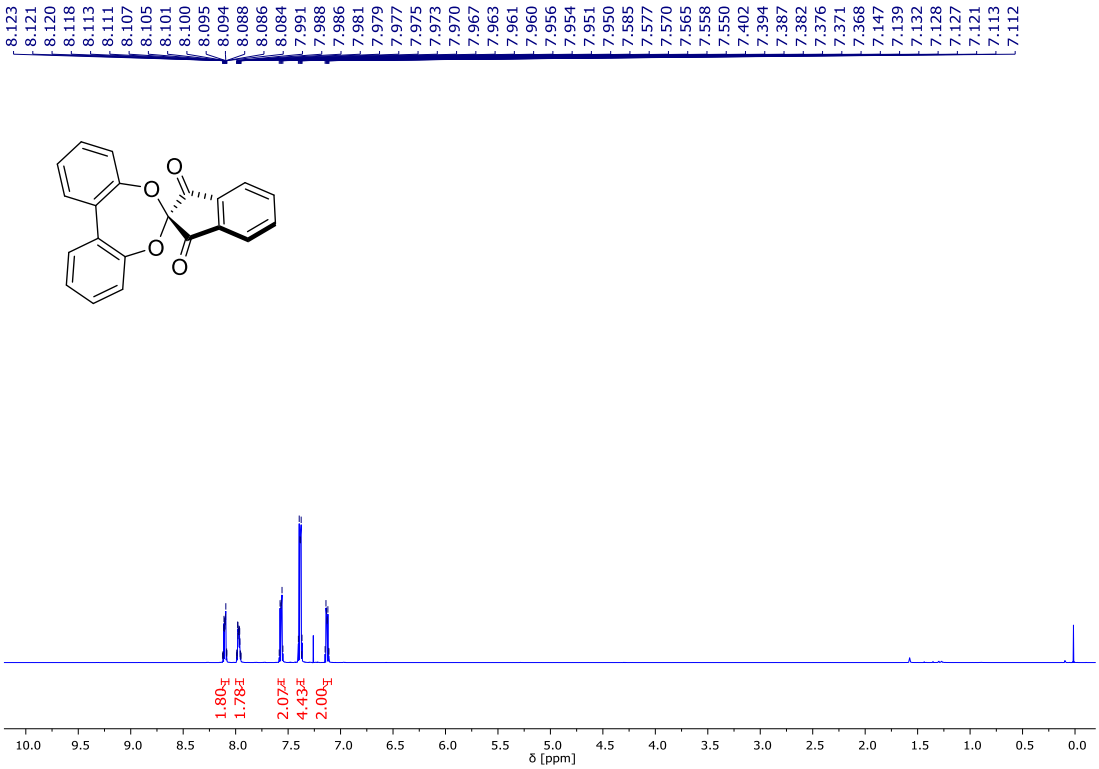


Figure S56: ^{1}H NMR-spectrum of **25** in $CDCl_3$ (500 MHz).

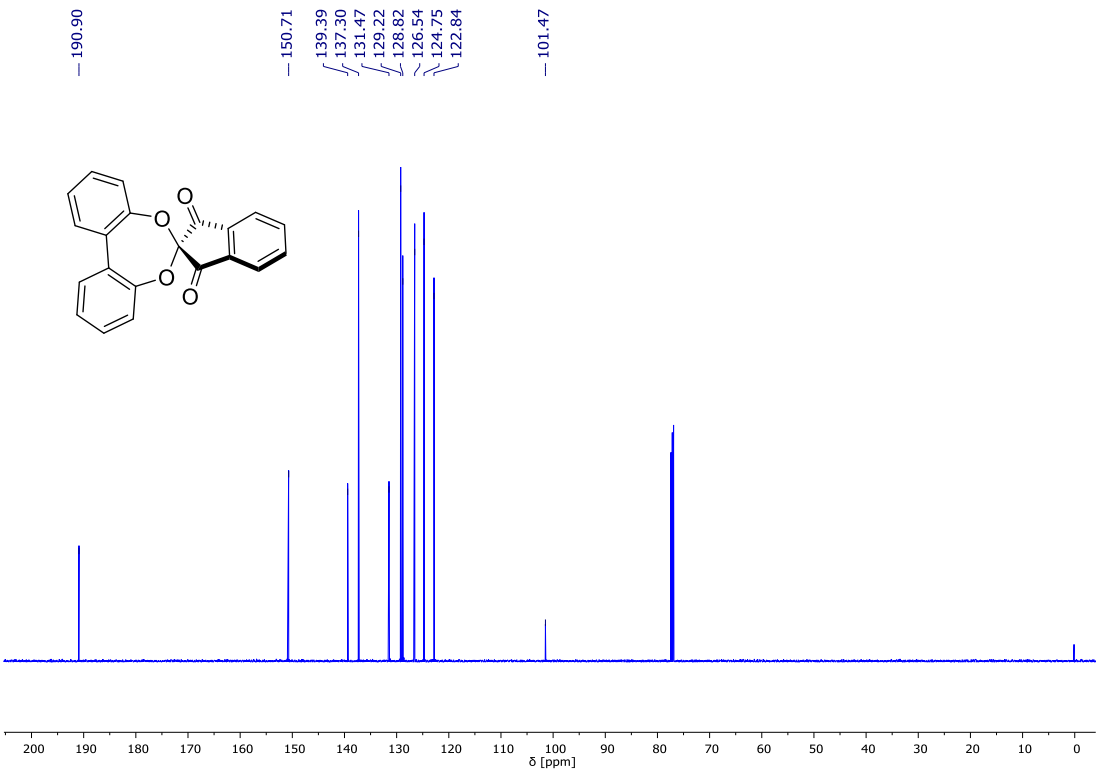


Figure S57: ^{13}C NMR-spectrum of **25** in $CDCl_3$ (101 MHz).

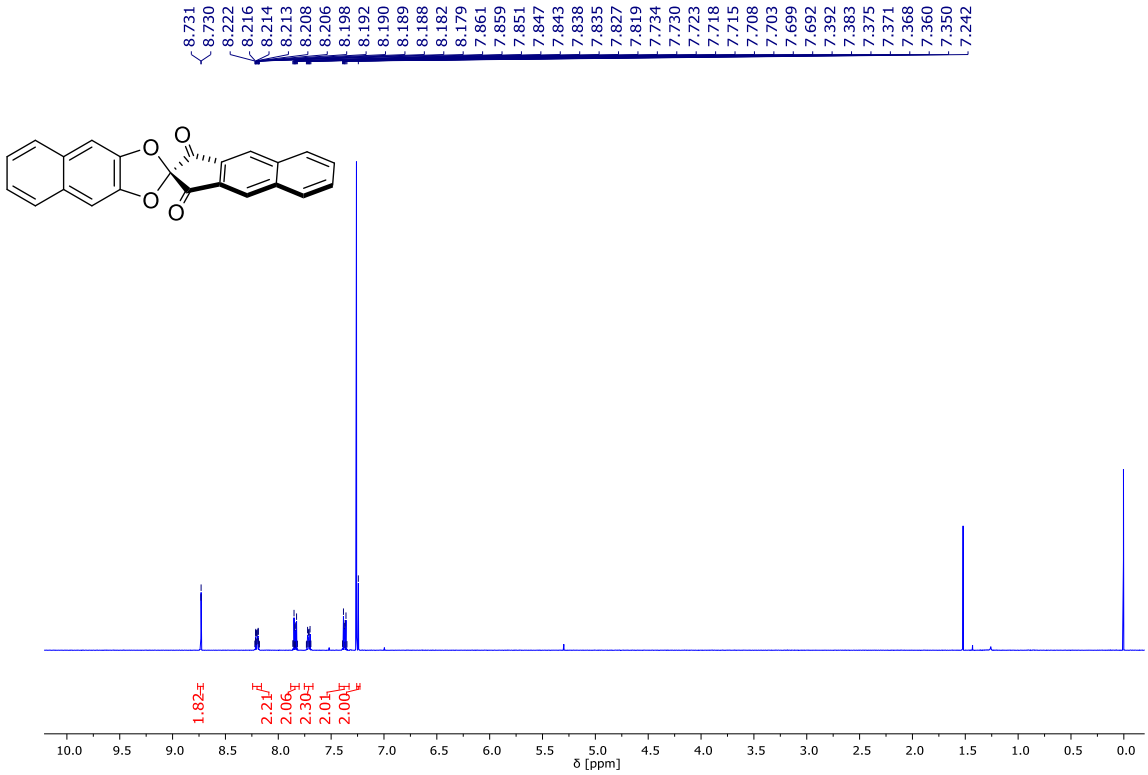


Figure S58: ^{1}H NMR-spectrum of **26** in $CDCl_3$ (500 MHz).

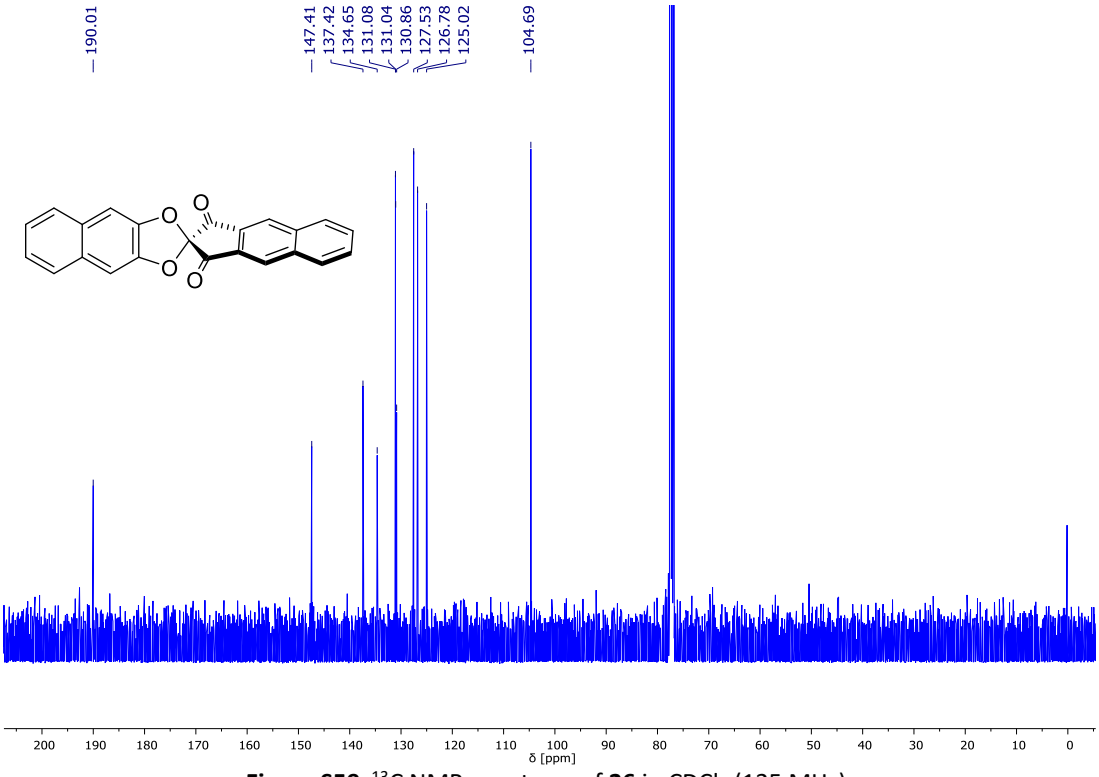


Figure S59: ^{13}C NMR-spectrum of **26** in $CDCl_3$ (125 MHz).

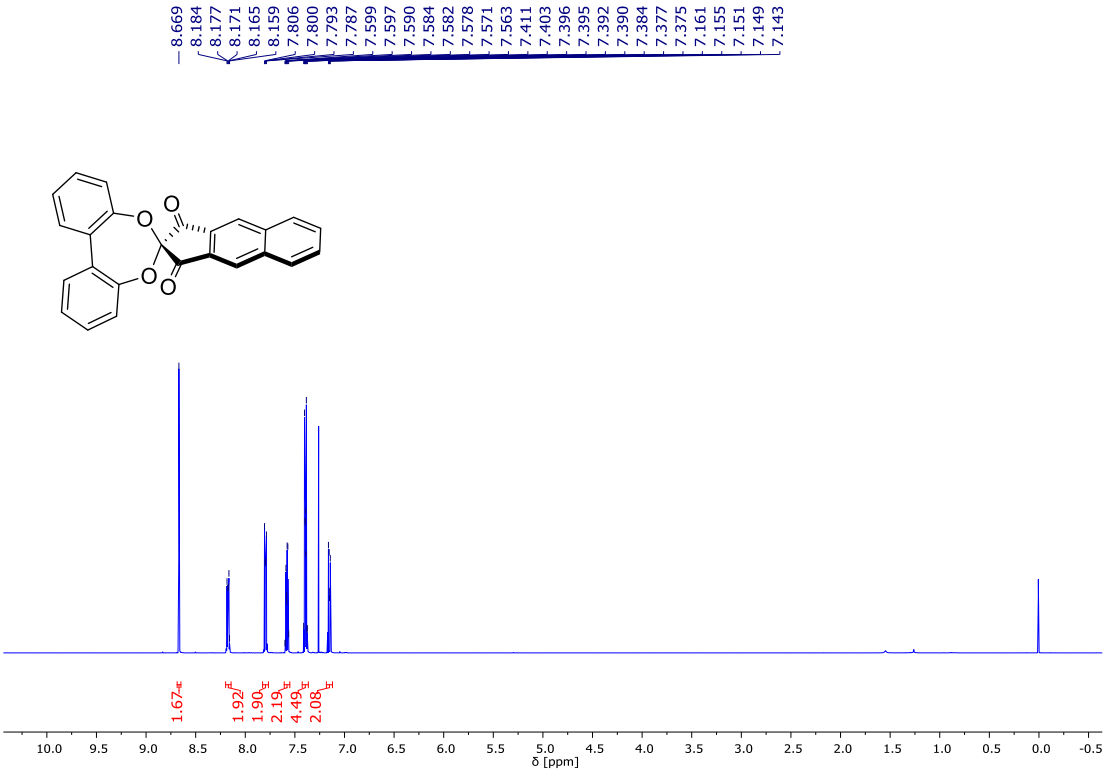


Figure S60: ^{1}H NMR-spectrum of **27** in $CDCl_3$ (500 MHz).

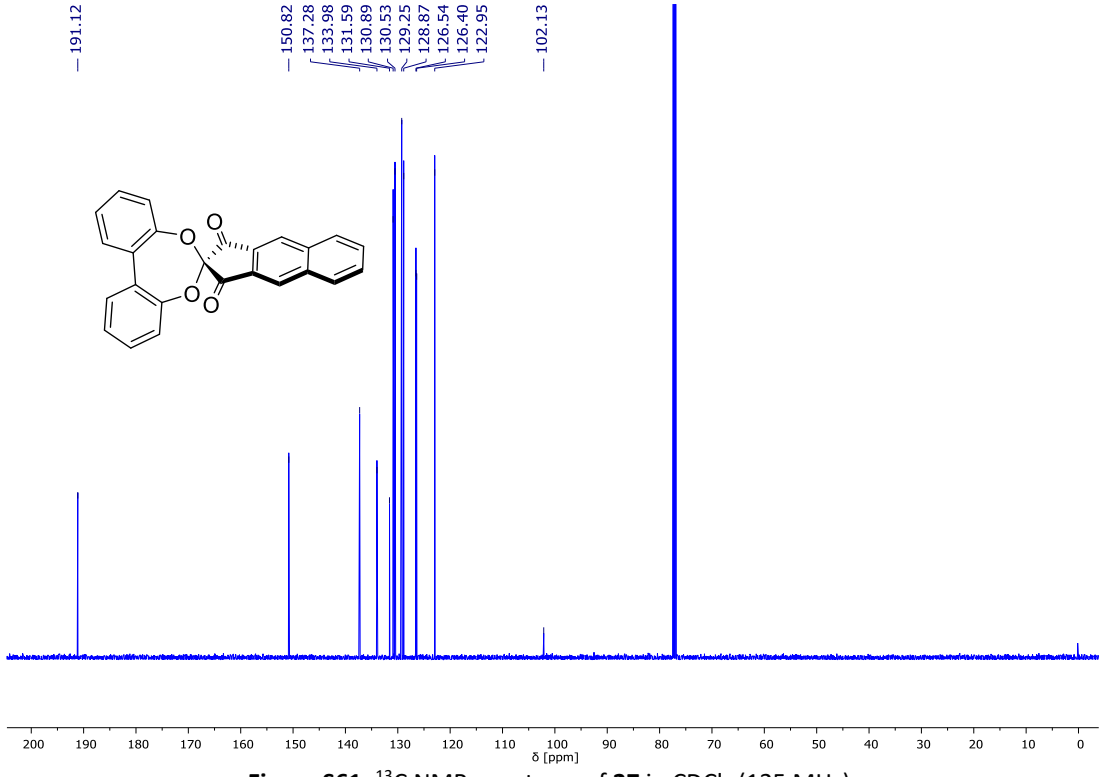


Figure S61: ^{13}C NMR-spectrum of **27** in $CDCl_3$ (125 MHz).

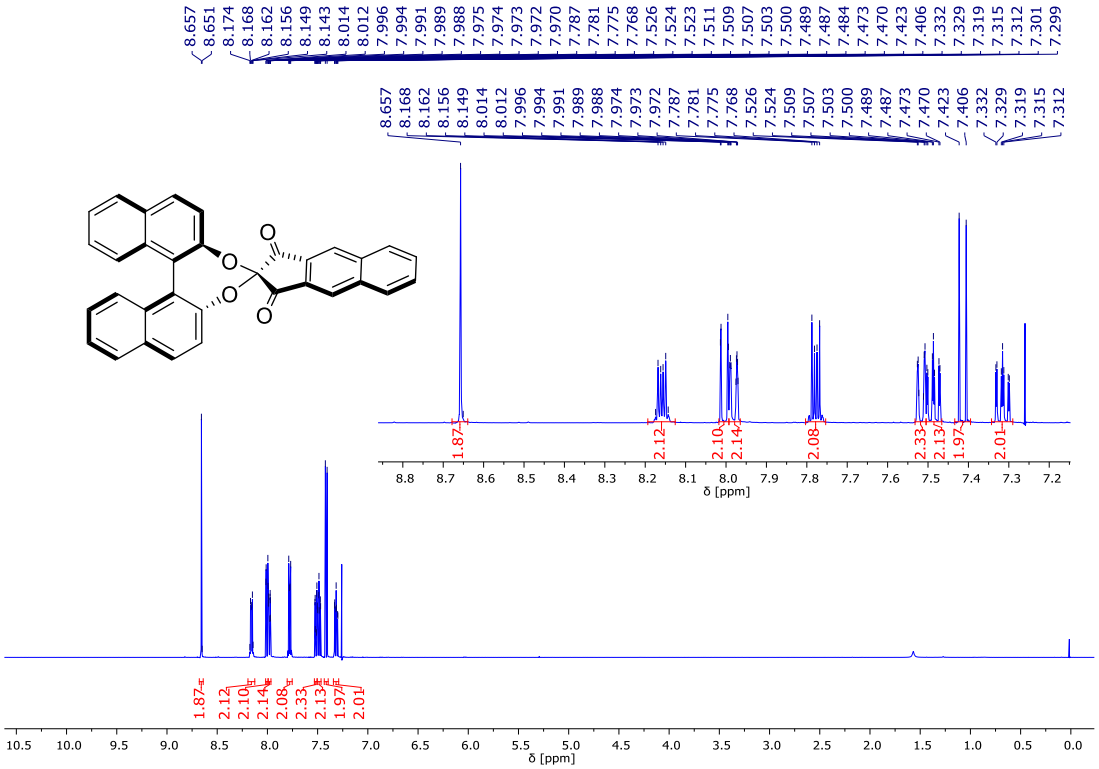


Figure S62: ^{1}H NMR-spectrum of **28** in $CDCl_3$ (500 MHz).

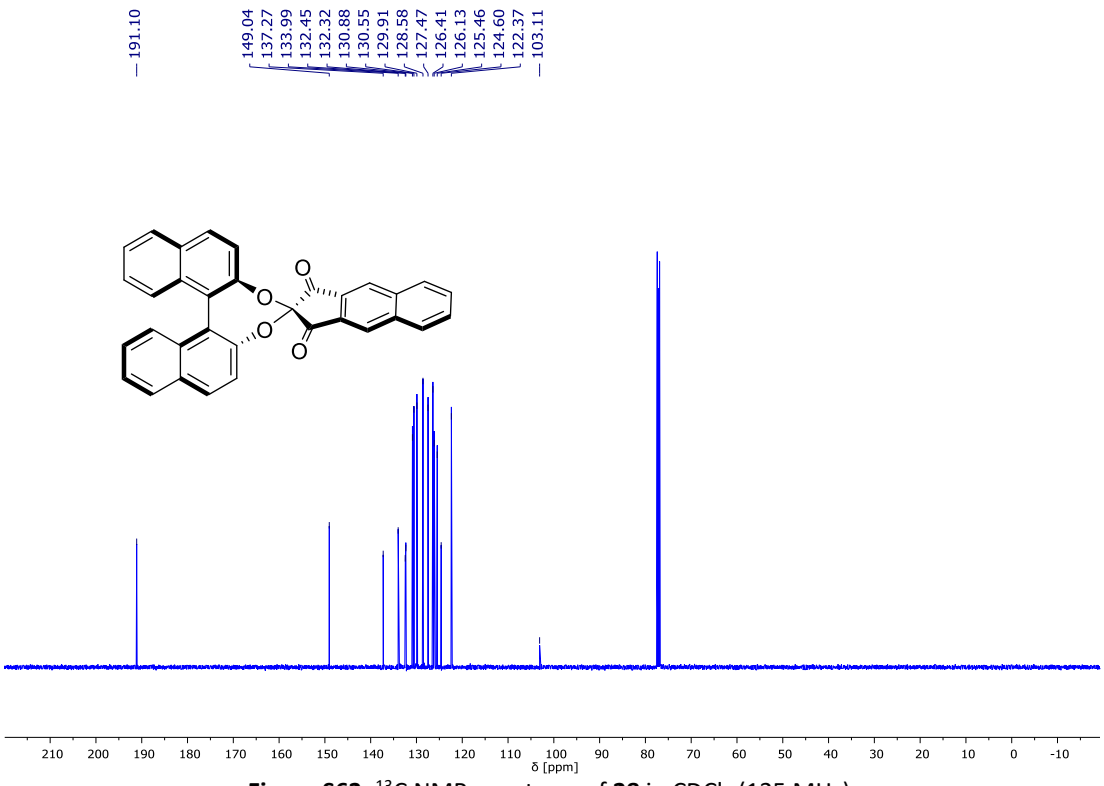


Figure S63: ^{13}C NMR-spectrum of **28** in $CDCl_3$ (125 MHz).

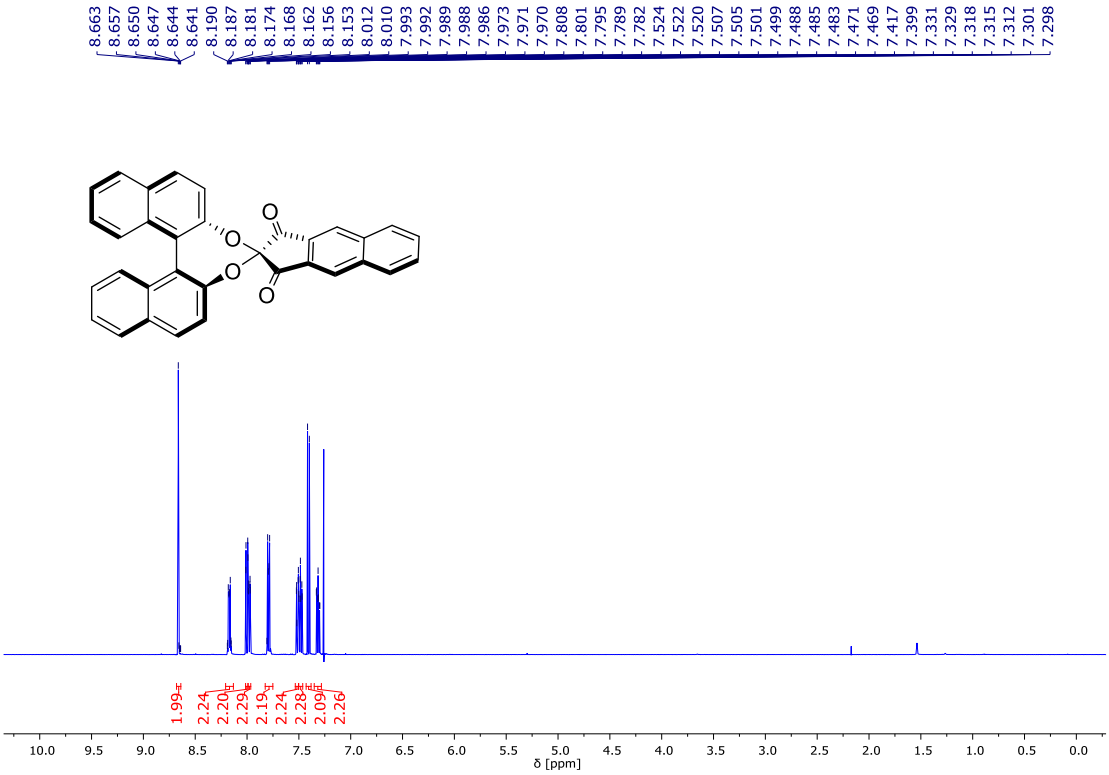


Figure S64: ^{1}H NMR-spectrum of **29** in $CDCl_3$ (500 MHz).

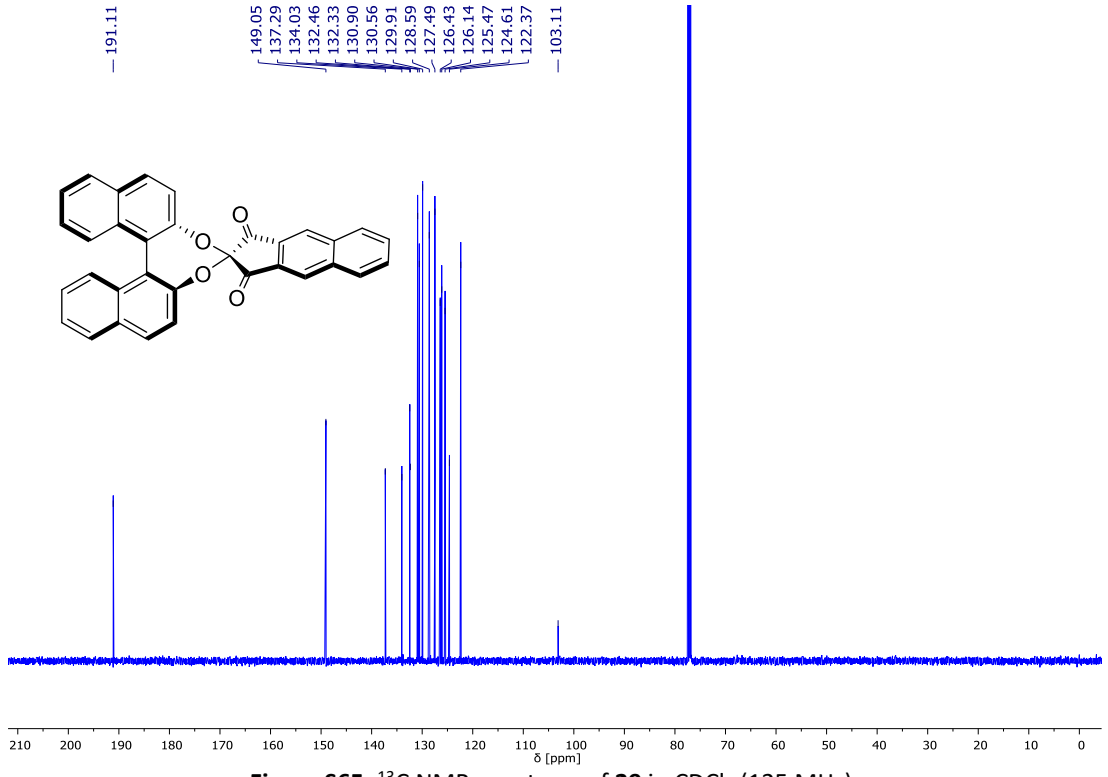


Figure S65: ^{13}C NMR-spectrum of **29** in $CDCl_3$ (125 MHz).

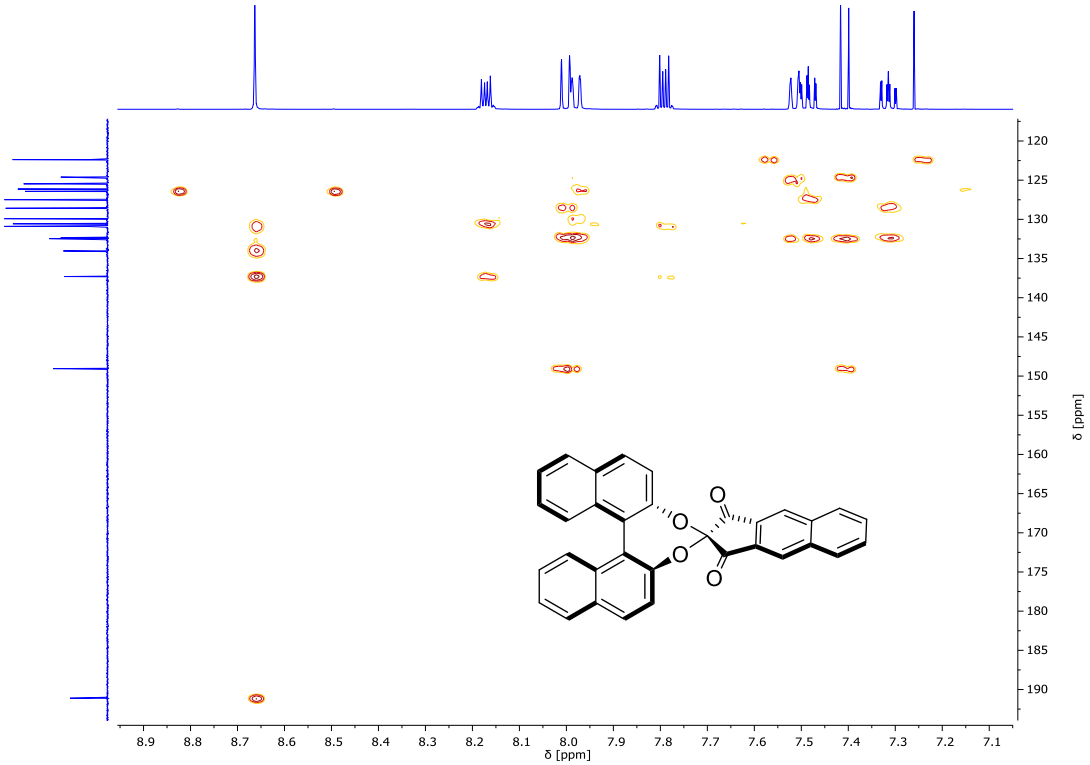


Figure S66: HMBC-spectrum of **29** in $CDCl_3$ (500/125 MHz).

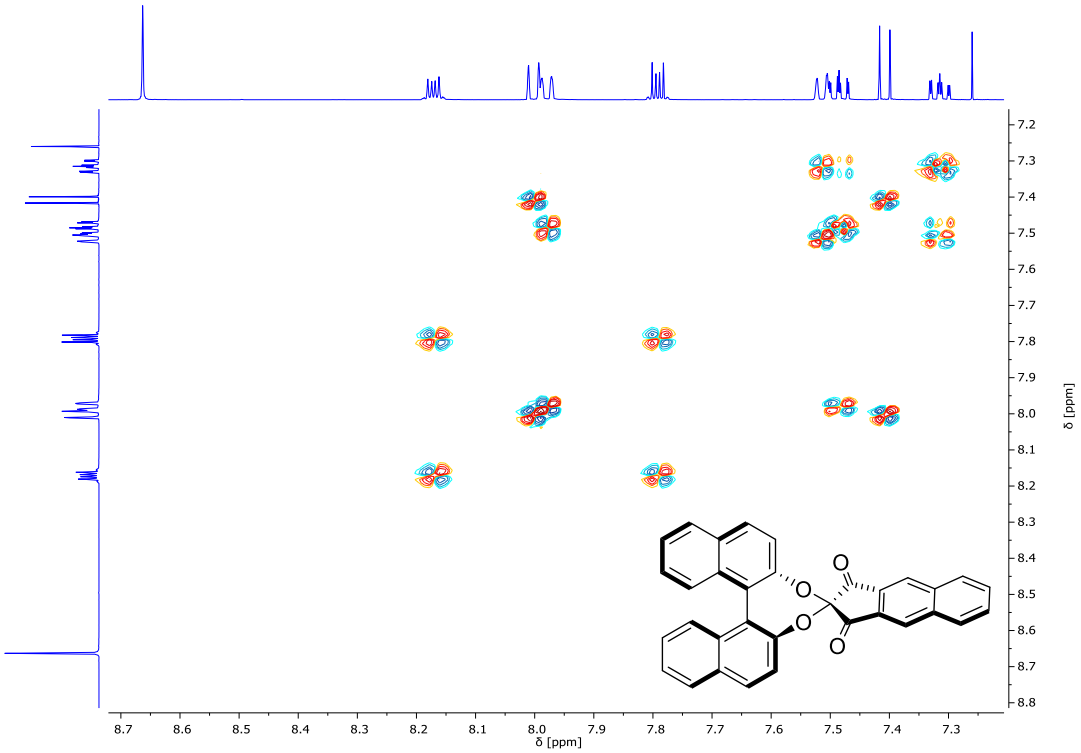


Figure S67: DQF-COSY-spectrum of **29** in $CDCl_3$ (500 MHz).

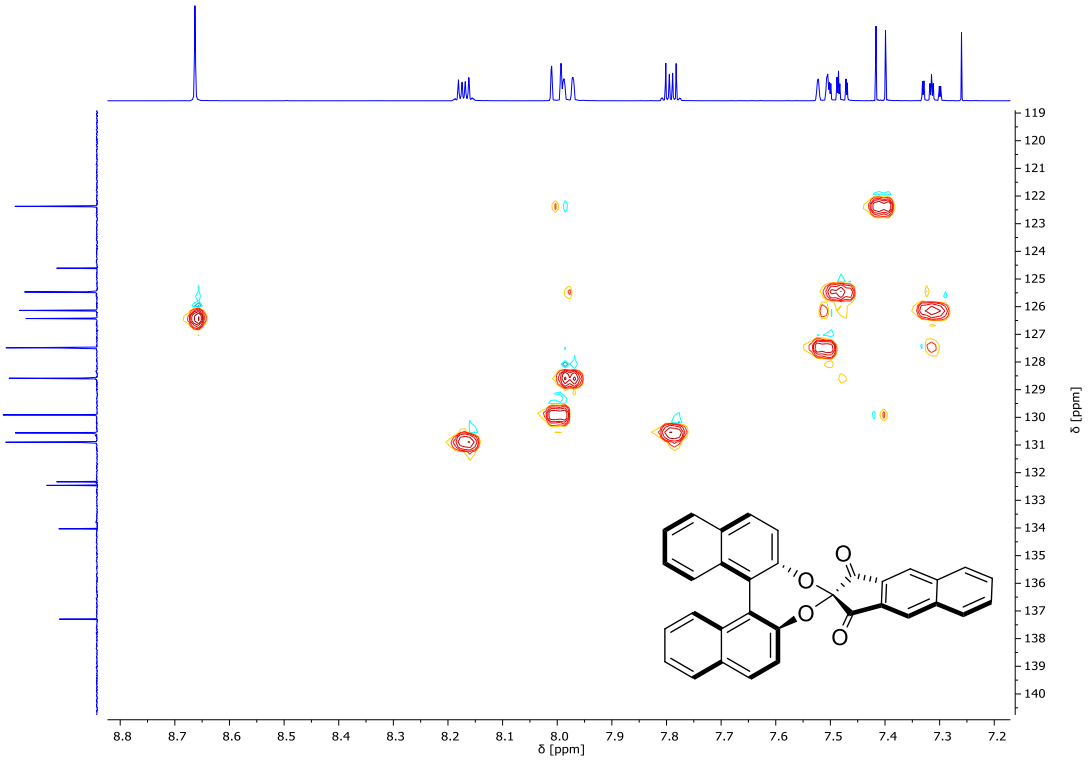


Figure S68: HSQC-spectrum of **29** in $CDCl_3$ (500/125 MHz).

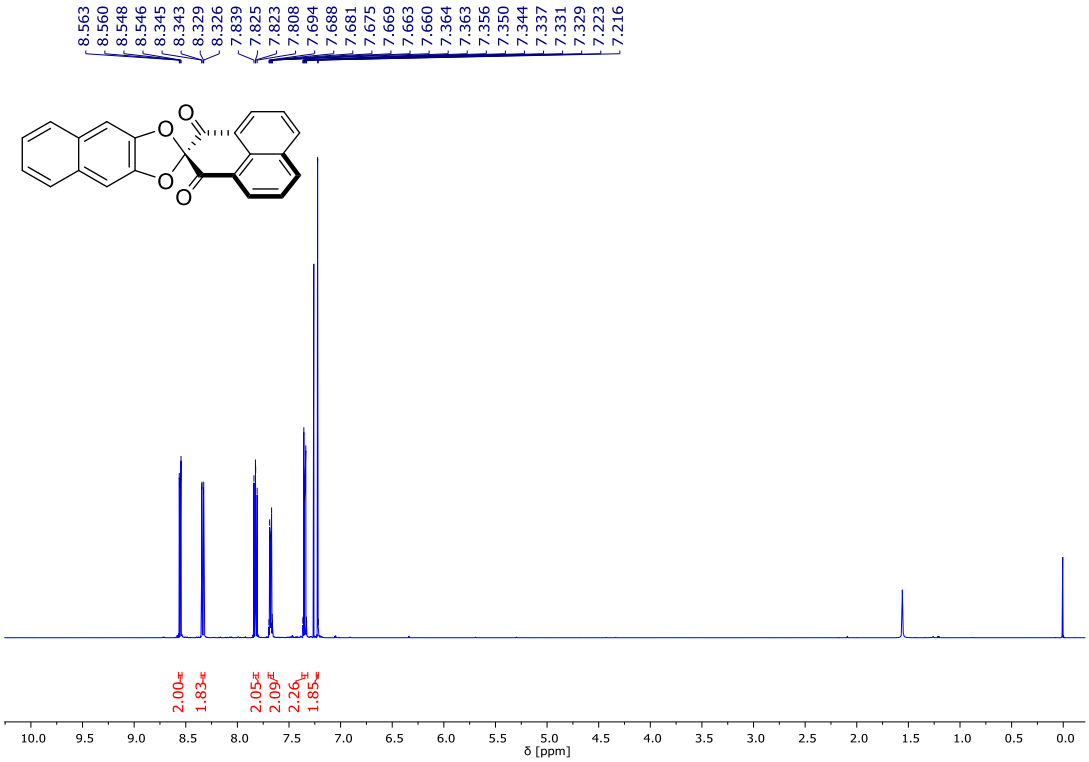


Figure S69: ^{1}H NMR-spectrum of **30** in $CDCl_3$ (500 MHz).

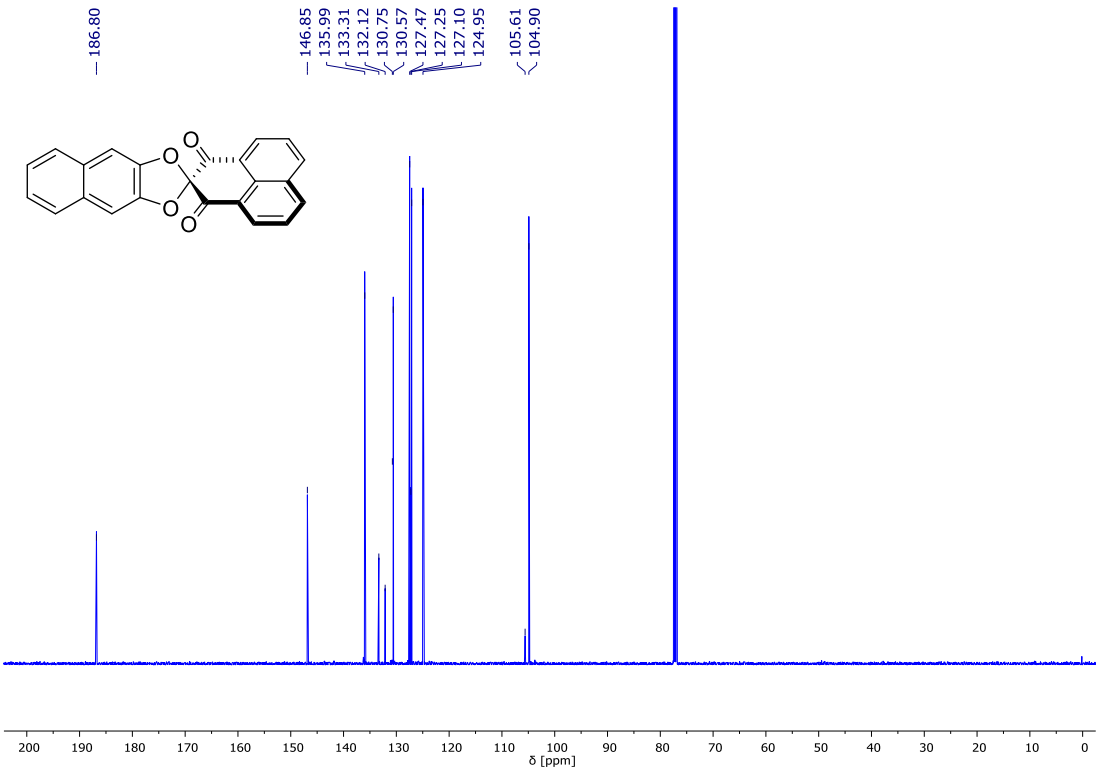


Figure S70: ^{13}C NMR-spectrum of **30** in $CDCl_3$ (101 MHz).

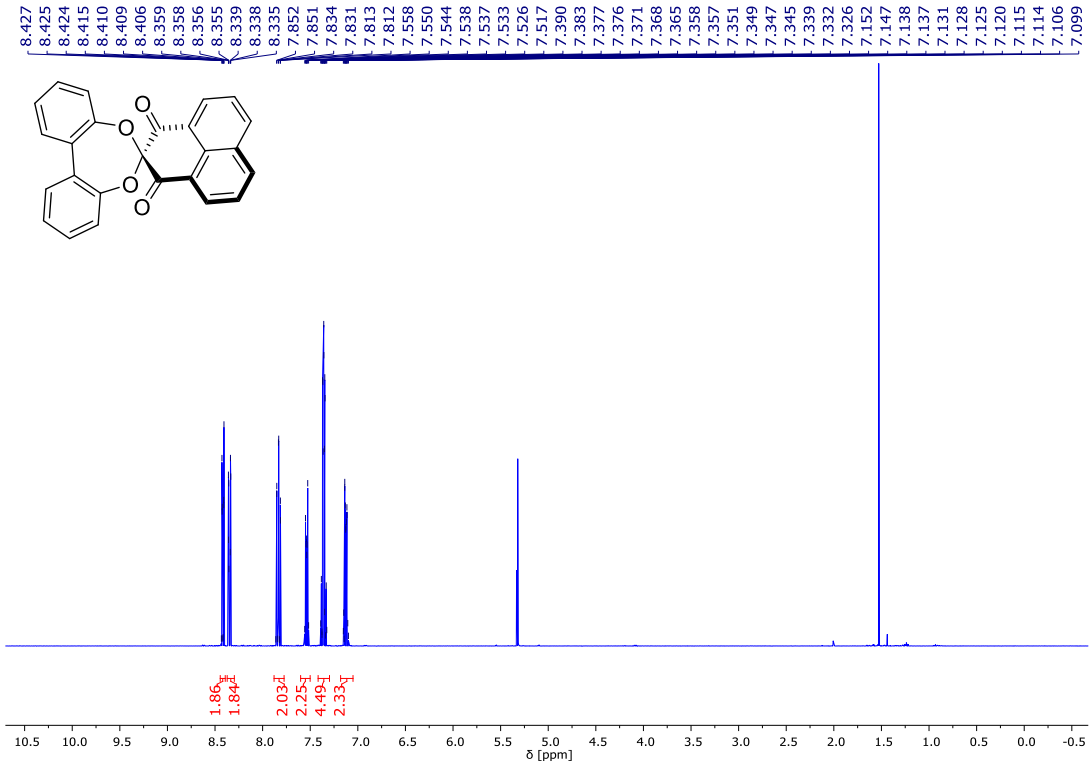


Figure S71: ^{1}H NMR-spectrum of **31** in CD_2Cl_2 (400 MHz).

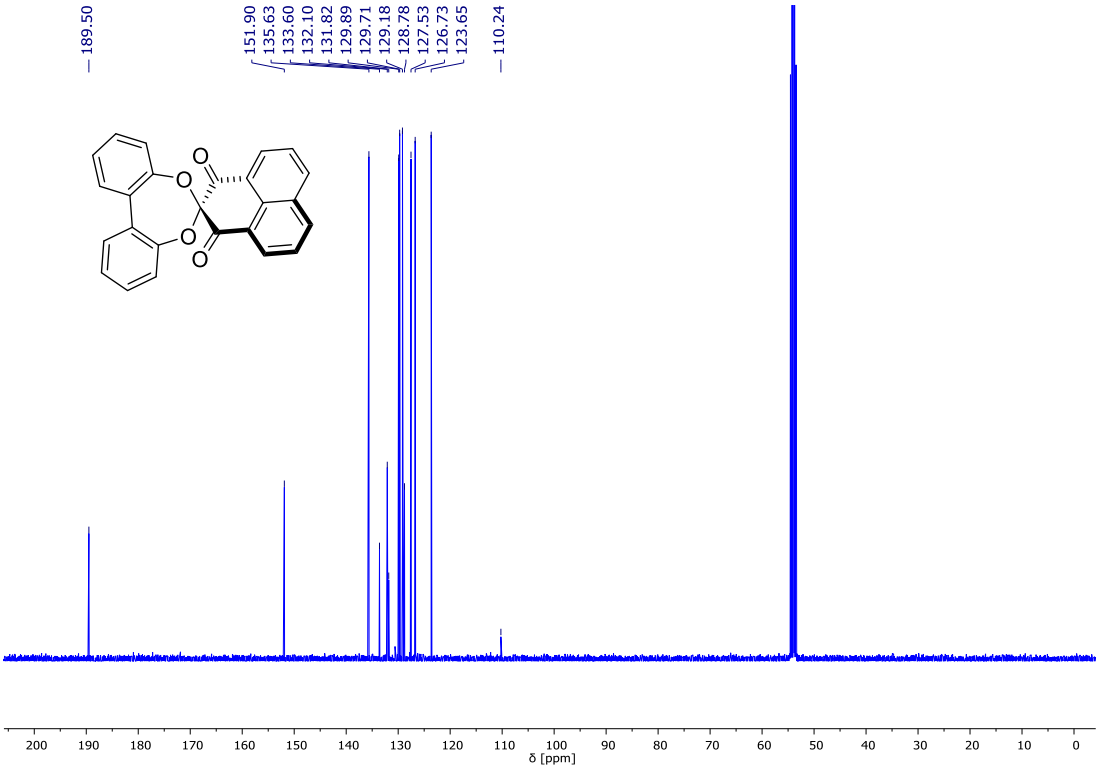


Figure S72: ^{13}C NMR-spectrum of **31** in CD_2Cl_2 (101 MHz).

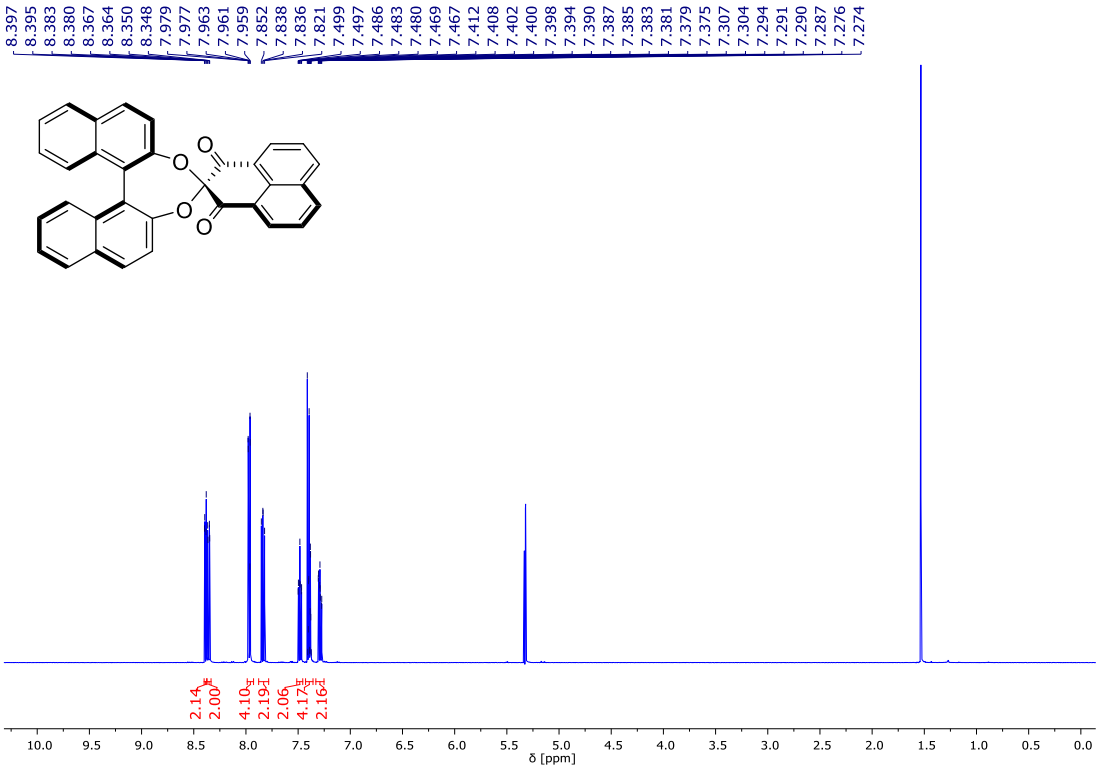


Figure S73: ^{1}H NMR-spectrum of **32** in CD_2Cl_2 (400 MHz).

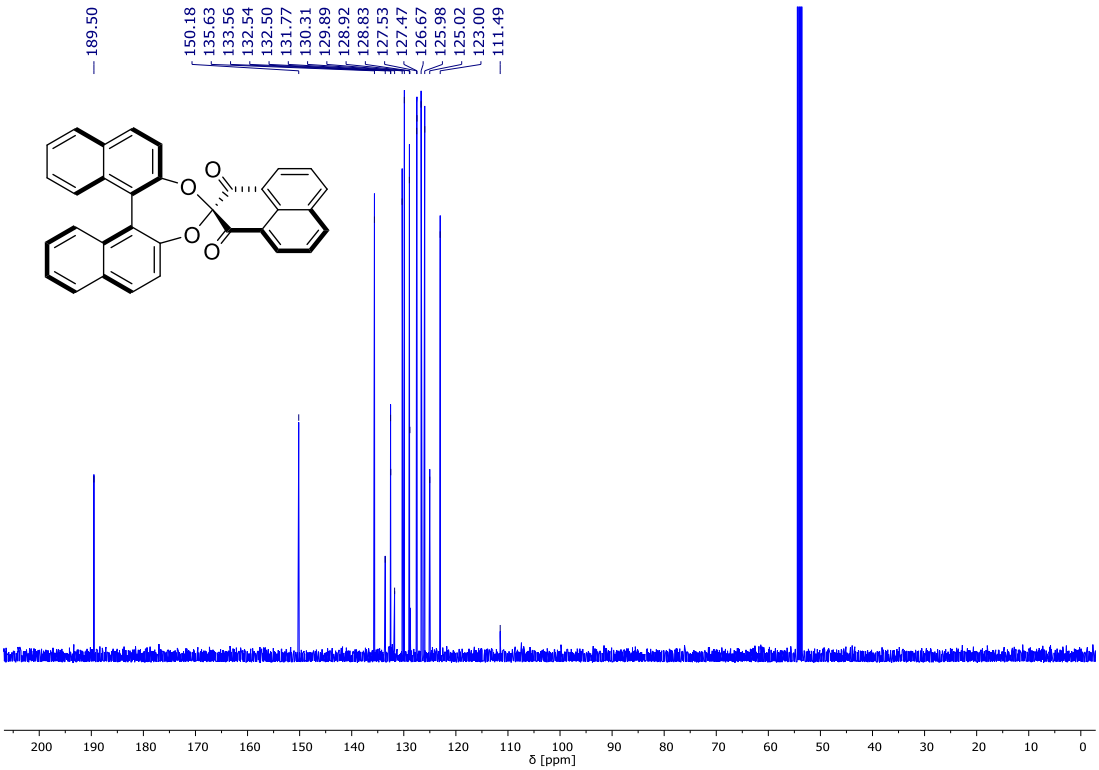


Figure S74: ^{13}C NMR-spectrum of **32** in CD_2Cl_2 (101 MHz).

7. References

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