Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Core and Double Bond Functionalisation of Cyclopentadithiophene- Phosphaalkenes

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Supporting information

Experimental details:

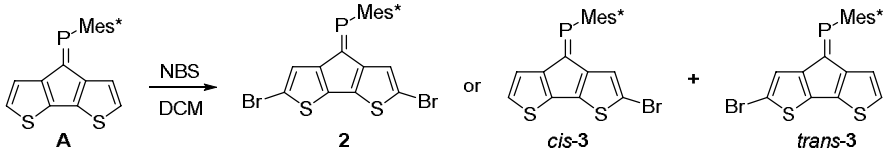
Materials and Measurements: Except where otherwise stated, reagents were purchased from Sigma Aldrich, Fluorochem and VWR and were used without any further purification. All reactions were performed under argon using flame-dried glassware and standard Schlenk techniques. Solvents were dried by distillation THF and diethyl ether were dried over sodium benzophenone, DCM was dried over $CaCl_2$. All solvents were freshly distilled prior to use.

NMR spectra were recorded using a JEOL spectrometer, unless stated otherwise (Frequency of nuclei: ^{1}H 400 MHz; ^{13}C 101 MHz; ^{19}F 376 MHz; ^{31}P 162 MHz). High-resolution mass spectra were measured using FTMS + p APCI or FTMS + p NSI (OrbitrapXL) at the University of Münster, or FTMS +p LDI at the University of Edinburgh. UV/VIS spectra were recorded on a Varian Cary 50 or 50000 diode array spectrophotometers. Cyclic voltammograms were recorded on an AUTOLAB PGSTAT 204 potentiostat with a three-electrode set-up (glassy C working, Pt coil counter, Ag wire reference) in 0.1 M NBu_4PF_6 DCM solution, and are reported using the Fc/Fc^+ couple as an internal pseudo reference.

Table 1: Summary of ^{31}P-NMR data (162 MHz)

compound	^{31}P-NMR shift (ppm)
2	269.3
cis-**3**	262.9
trans-**3**	263.1
cis-**4**	258.1
trans-**4**	257.3
5	265.5
cis-/*trans*-**7**	256.4
9	176.8
10	203.8
11	197.9
12	194
13	157.1
14	-1.3
15	144.2

Synthesis of **2**, and *cis*-**3** and *trans*-**3**.



*Scheme 1: Reaction scheme for the preparation of **2**, and cis- and trans-**3**.*

*Synthesis of **2***

Phosphaalkene **A** (120 mg, 0.27 mmol) and *N*-bromo succinimide (NBS, 110 mg, 2.3 equiv.) were dissolved in 5 ml DCM. The solution was sonicated at room temperature for 30 minutes until all starting materials has been consumed (TLC) and shows full conversion to the target compound based on ^{31}P NMR analysis. Removal of all volatiles followed by chromatographic workup (pentane:DCM gradient) yielded the dibromo derivative **2** in excellent yield (115 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.42 (s, 1H), 4.35 (s, 1H), 1.44 (s, 9H), 1.39 (s, 18H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 162.22 (d, *J* = 43.4 Hz), 154.47, 152.03, 146.27 (d, *J* = 29.9 Hz), 141.17 (d, *J* = 13.5 Hz), 137.36 (d, *J* = 11.6Hz), 135.46 (d, *J* = 18.3 Hz), 134.91 (d, *J* = 55.9 Hz), 126.18, 123.03 (d, *J* = 7.7 Hz), 122.48, 110.73, 109.45, 38.21, 35.30, 33.25 (d, *J* = 6.7 Hz), 31.63 ppm.
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 269.3 ppm.
FTMS+p APCI (*m/z*): $[M]^+$ calc. 609.99466. found 609.99396; $[M+H]^+$ calc. 611.00248 found 611.00029.

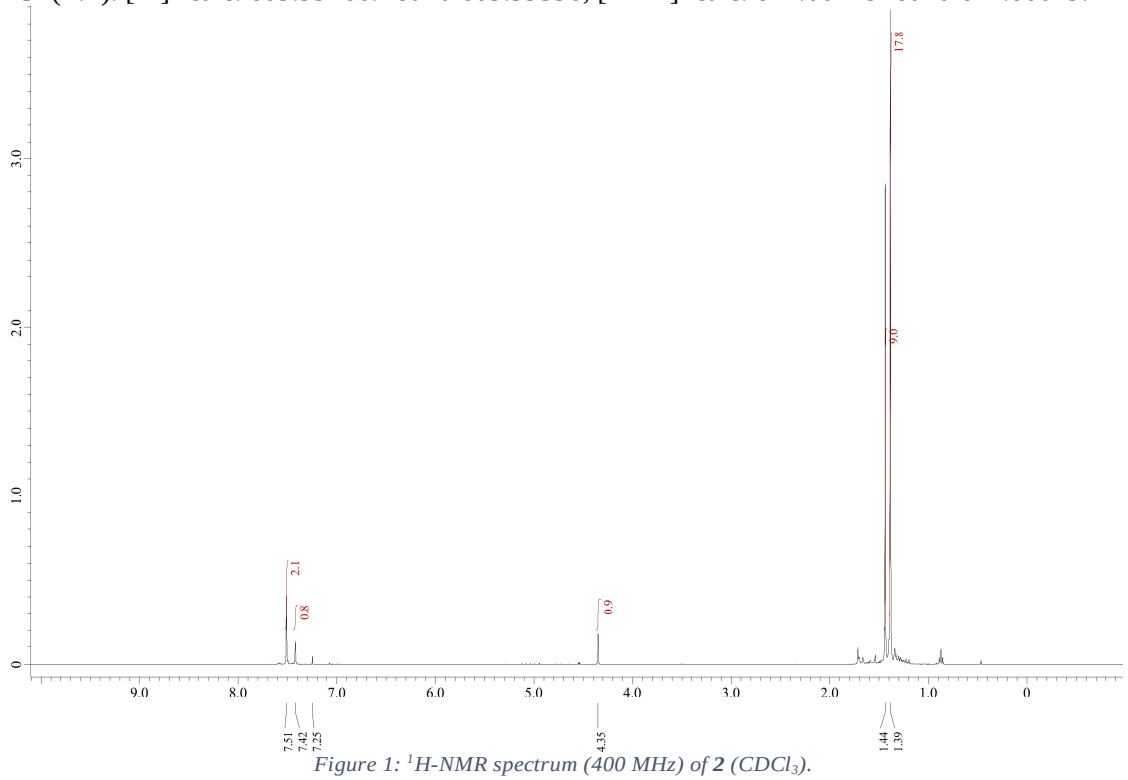


*Figure 1: ^{1}H-NMR spectrum (400 MHz) of **2** ($CDCl_3$).*

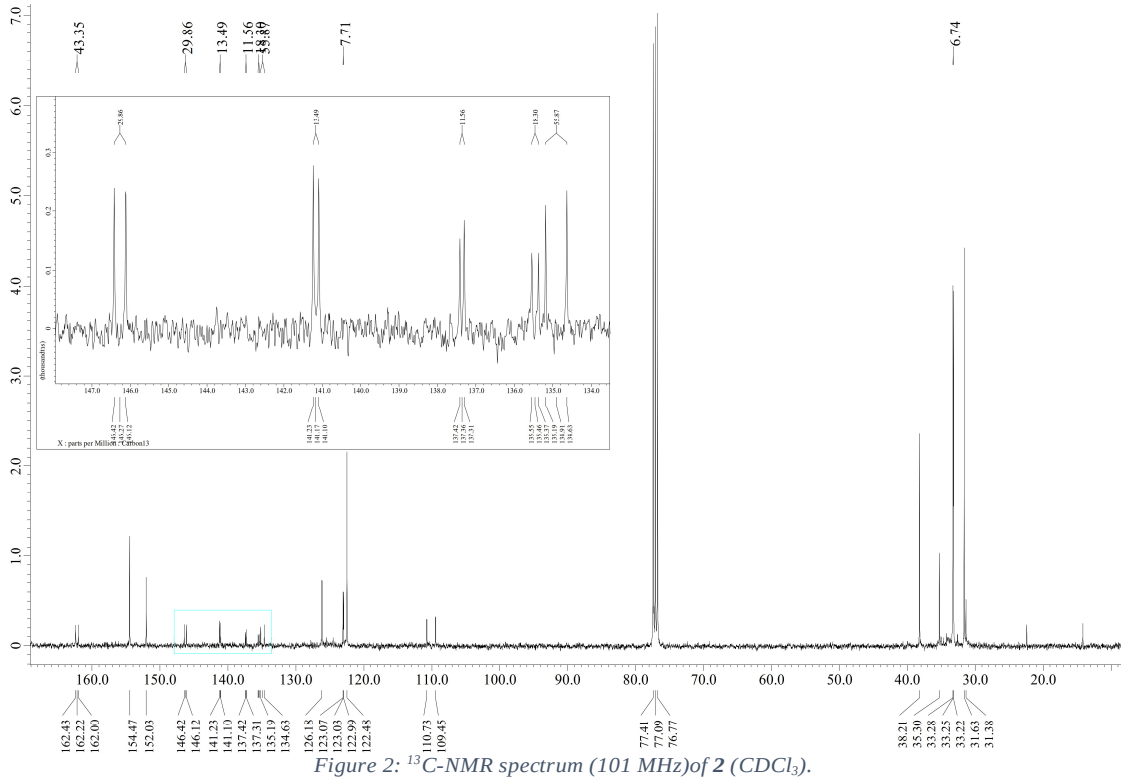


*Figure 2: ^{13}C-NMR spectrum (101 MHz)of **2** ($CDCl_3$).*

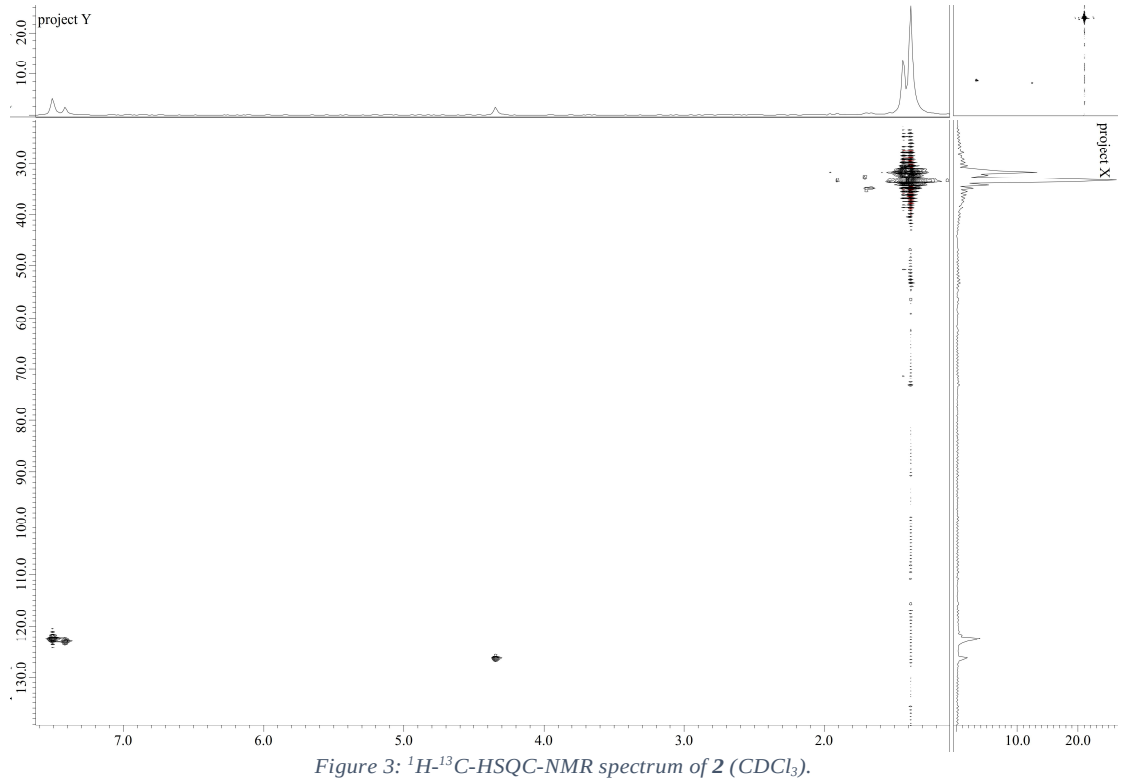


*Figure 3: ^{1}H-^{13}C-HSQC-NMR spectrum of **2** ($CDCl_3$).*

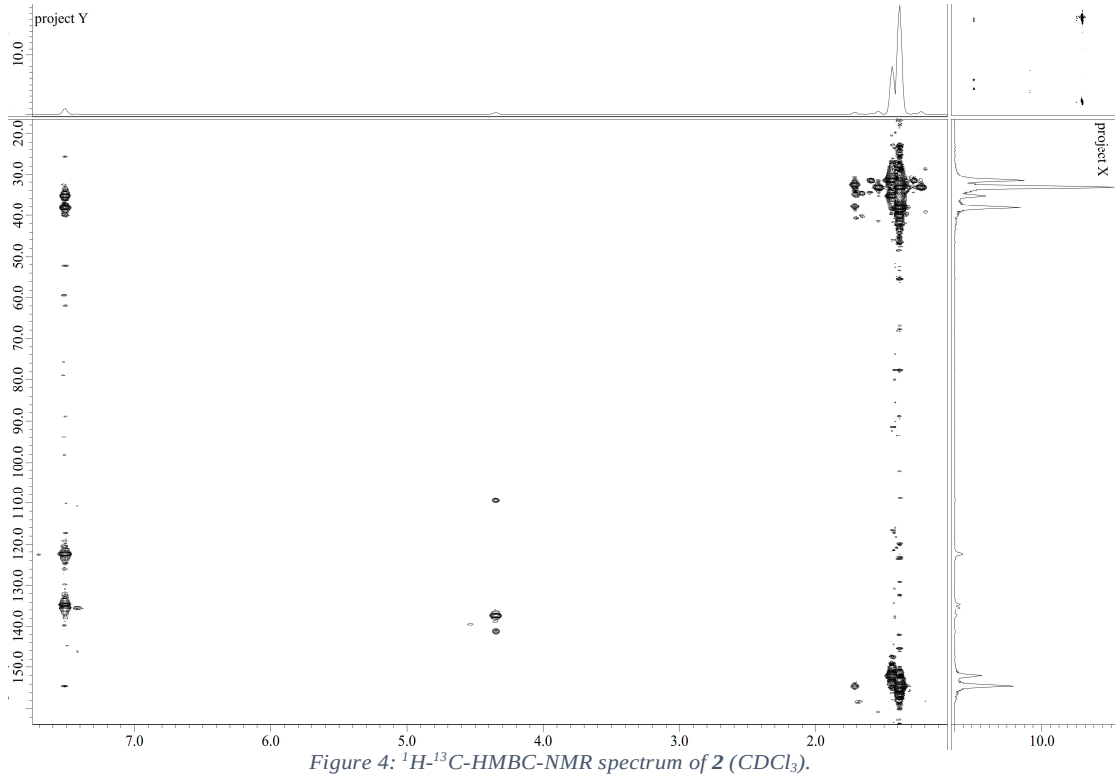


*Figure 4: ^{1}H-^{13}C-HMBC-NMR spectrum of **2** ($CDCl_3$).*

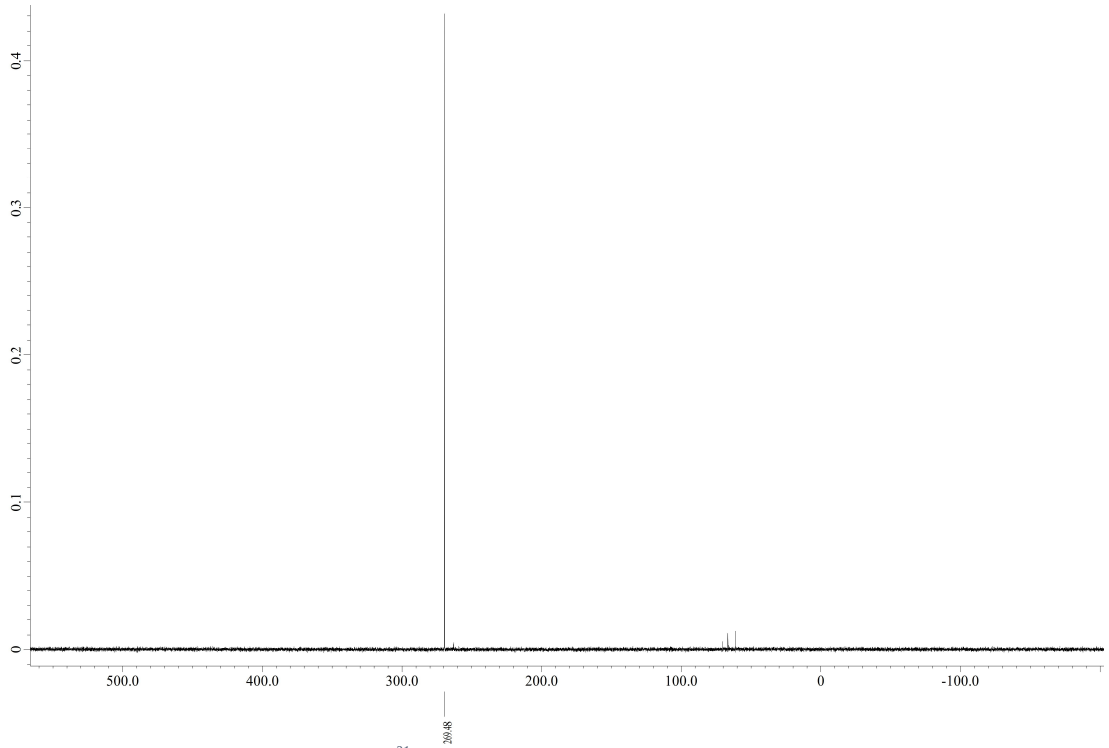


*Figure 5:^{31}P-NMR spectrum (162 MHz)of **2** ($CDCl_3$).*

Synthesis of cis-3 and trans-3.
The synthesis of the monobromo-derivatives *cis*-/*trans*-**3** was attempted using strictly one equivalent of NBS and shortening the reaction times to 5 minutes. NMR and TLC analysis show a statistical mixture of **A**, **2**, and *cis*-/*trans*-**3**. The monosubstituted derivatives could be separated and isolated on a very fast silica column (DCM:pentane) however isomerisation occurs within a couple of hours in solution. (yield not determined, NMR of the crude indicates a statistical mixture of unreacted starting material, **2**, and *cis/trans*-**3**).

cis-**3**:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.41 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.05 (d, *J* = 4.9 Hz, 1H), 4.36 (d, *J* = 1.7 Hz, 1H), 1.45 (s, 9H), 1.41 (s, 18H) ppm.
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 262.9 ppm.
trans-**3**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.43 (d, *J* = 1.5 Hz, 1H), 6.50 (d, *J* = 5.1 Hz), 4.44 (dd, *J* = 5.1, 1.5 Hz, 1H) 1.41 (s, 9H), 1.39 (s, 18H) ppm.
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 263.1 ppm.

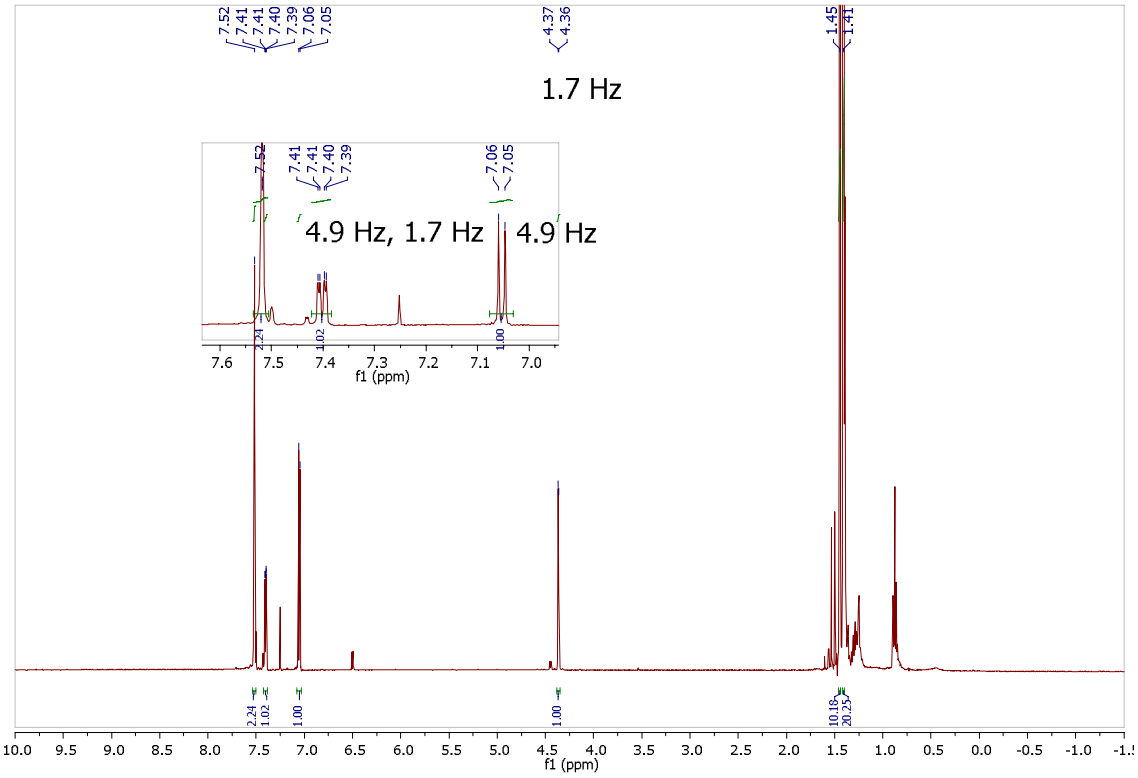


*Figure 6: ^{1}H-NMR spectrum of cis-**3** ($CDCl_3$).*

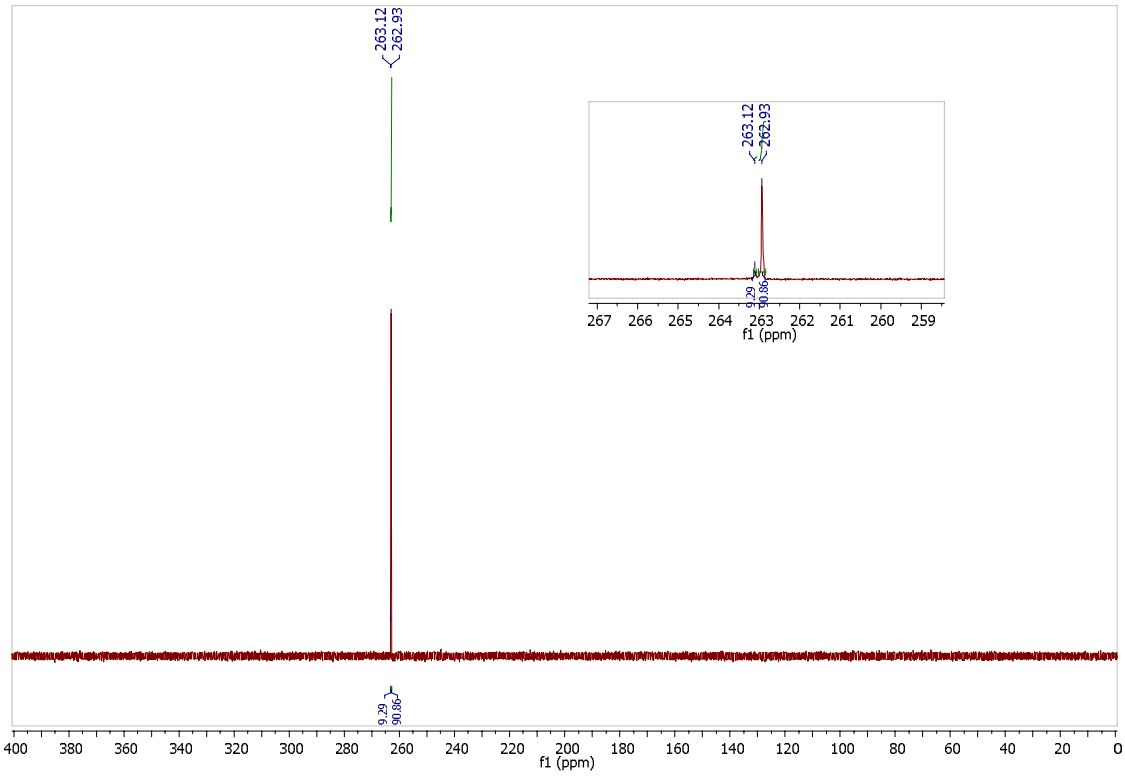


*Figure 7:^{31}P-NMR spectrum (162 MHz) of cis-**3** ($CDCl_3$).*

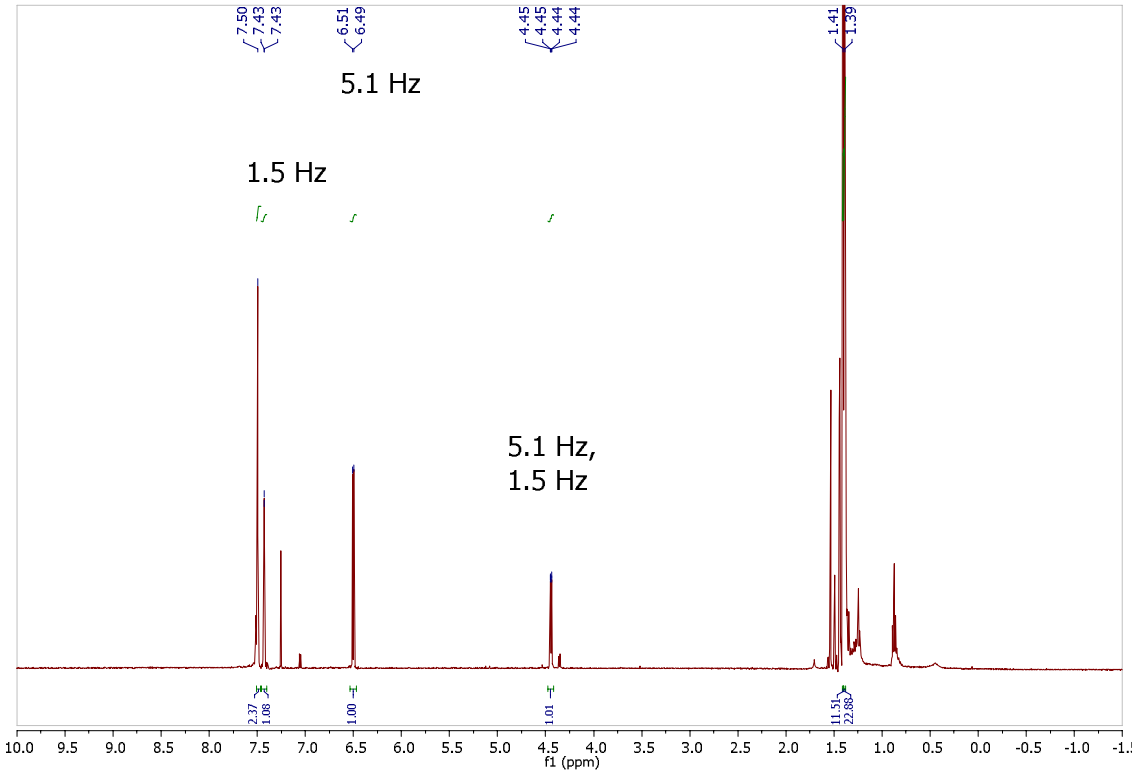


*Figure 8: ^{1}H-NMR spectrum (400 MHz) of trans-**3** ($CDCl_3$).*

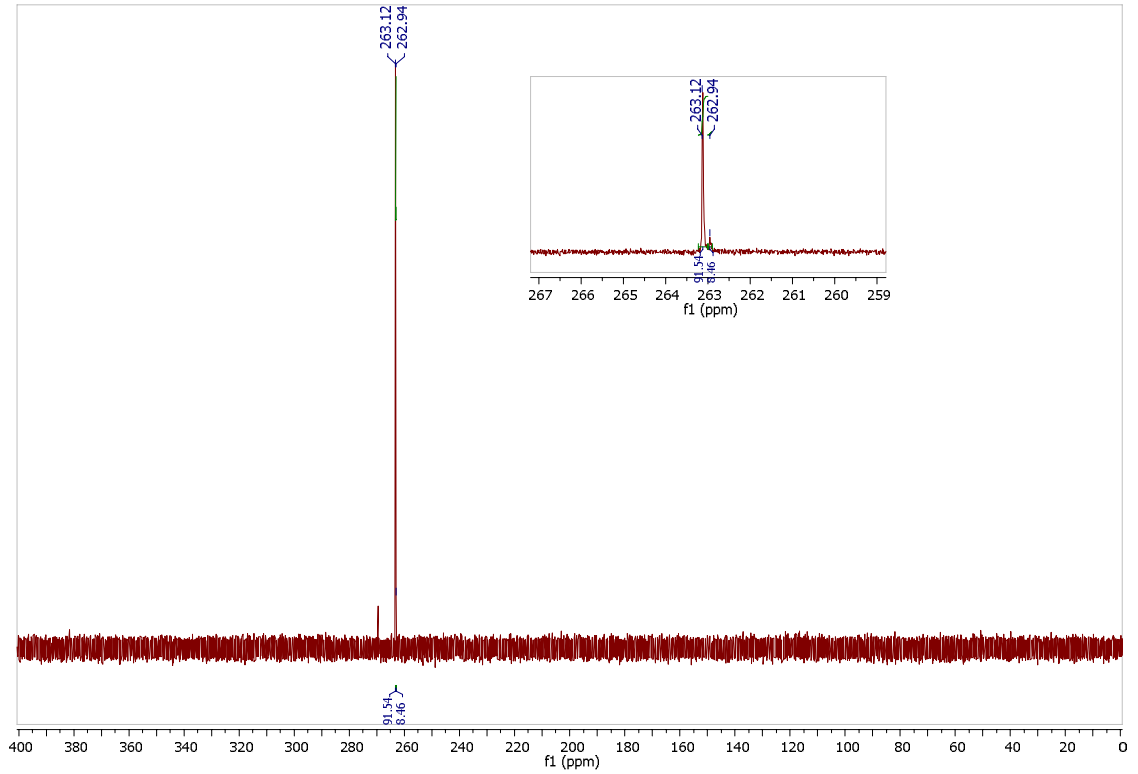


*Figure 9: ^{31}P-NMR spectrum (162 MHz) of trans-**3** ($CDCl_3$).*

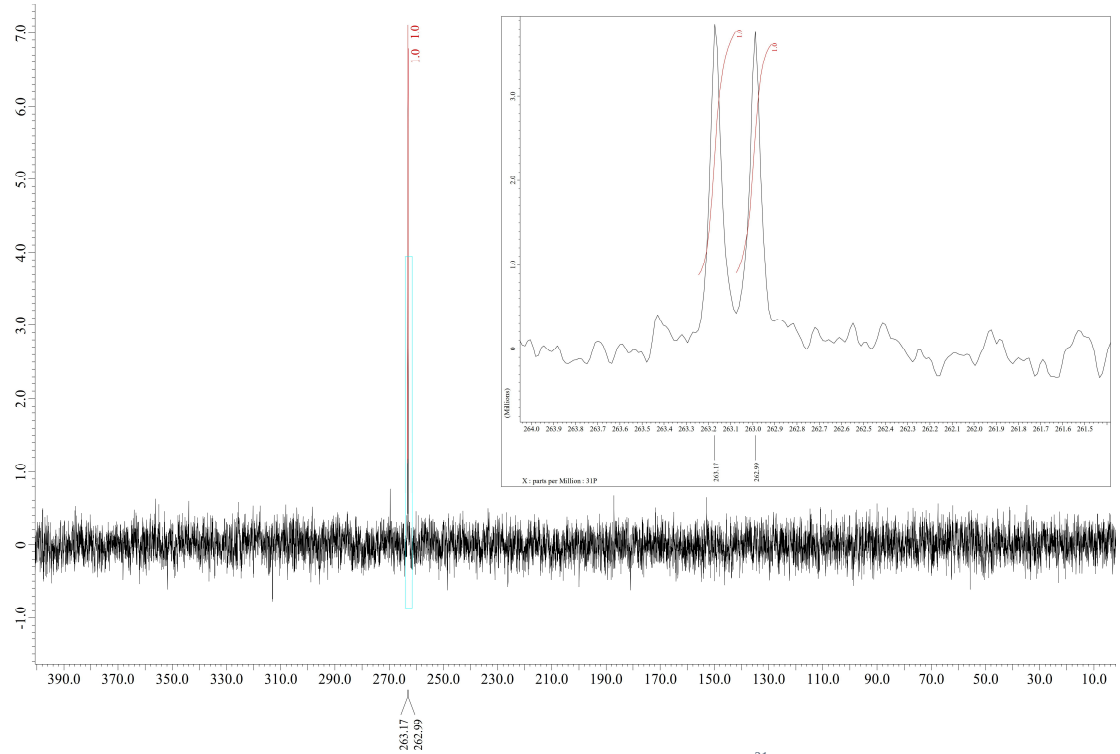
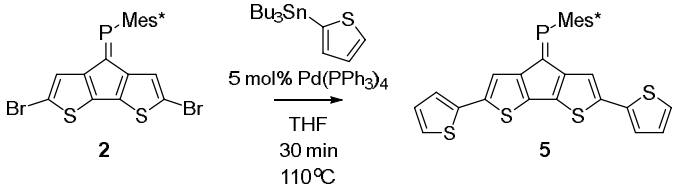


*Figure 10: Thermal isomerization in solution to a 1:1 isomeric mixture of cis-/trans-**3**. ^{31}P-NMR spectrum (162 MHz) of cis-/trans-**3**.*

Synthesis of **5**.



*Scheme 2: Reaction scheme for the preparation of **5**.*

The solution of **2** (40 mg, 0.07 mmol) and 2-tributylstannylthiophene (80 mg, 0.21mmol) in dry THF (15 ml) is deaerated for 15 min. before [$Pd(PPh_3)_4$] (15 mg, 5 mol%) is added. The microwave tube was sealed under argon and placed in the reactor (CEM, Biotage) for 30 min. at 110 °C. Monitoring the reaction by ^{31}P-NMR spectroscopy indicated increased formation of the protodebrominated side product (**3**) and approximately 30% conversion to the desired product **5**. Chromatographic workup (silica, hexane) gave **5** in ca 25% isolated yield (10 mg) as the second fraction.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.50 (s, 1H), 7.18 (d, *J* = 5.1 Hz, 1H), 7.15 (d, *J* = 3.3 Hz, 1H), 7.07 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.90-6.88 (m, 1H), 6.85 (dd, *J* = 3.7, 1.1 Hz, 1H), 4.86-4.91 (1H), 1.42 (s, 18H), 1.41 (s, 9H) ppm.
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ 154.42, 151.66, 149.11 (d, *J* = 30.0 Hz), 144.20 (d, *J* = 15.2 Hz), 138.15 (d, *J* = 13.1 Hz), 137.24, 135.91, 135.05 (d, *J* = 26.14 Hz), 134.45 (d, *J* = 8.5 Hz), 131.93 (d, *J* = 20.0 Hz), 127.90, 127.58, 123.97, 123.55, 122.84 (d, *J* = 18.6 Hz), 122.54, 120.13, 116.72, 116.63, 38.43, 35.32, 33.27(d, *J* = 6.15), 31.63, 29.78 ppm (P=C carbon atom not detected).
^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ 265.5 ppm.
FTMS+p APCI (*m/z*): $[M]^+$ calc. 616.15102. found 616.15093; $[M+H]^+$ calc. 617.15885 found 617.15611.

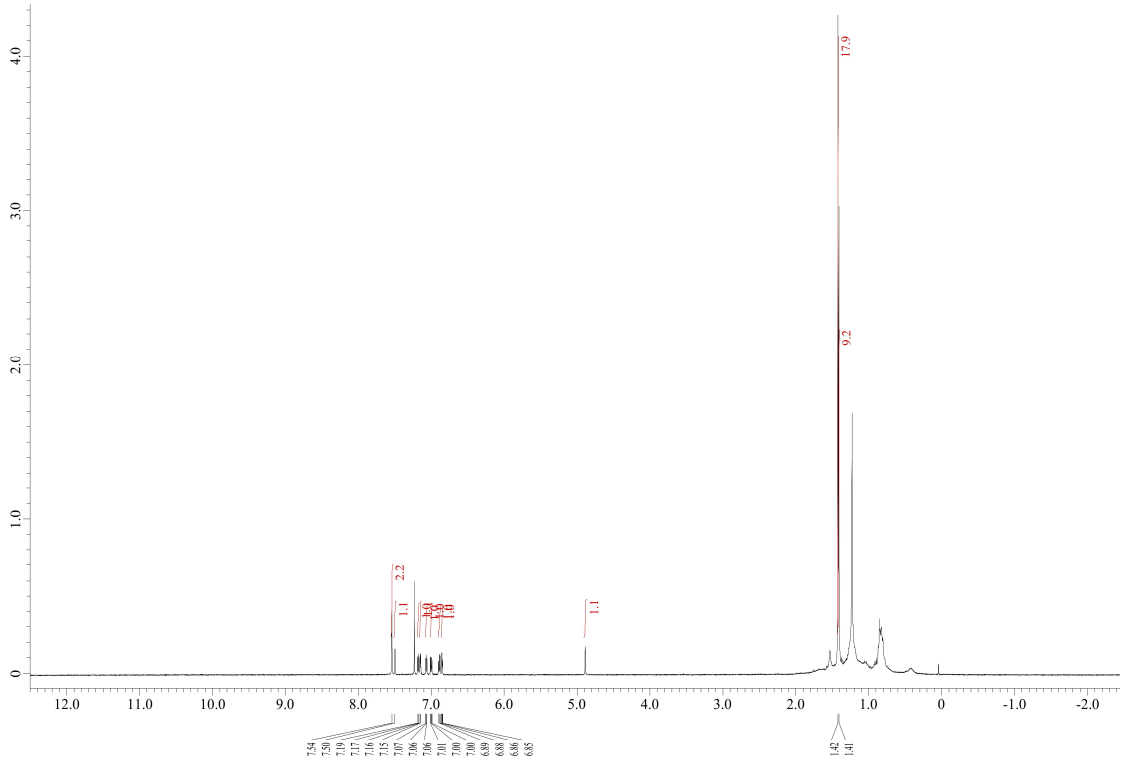


*Figure 11: [1]H NMR spectrum of **5** ($CDCl_3$).*

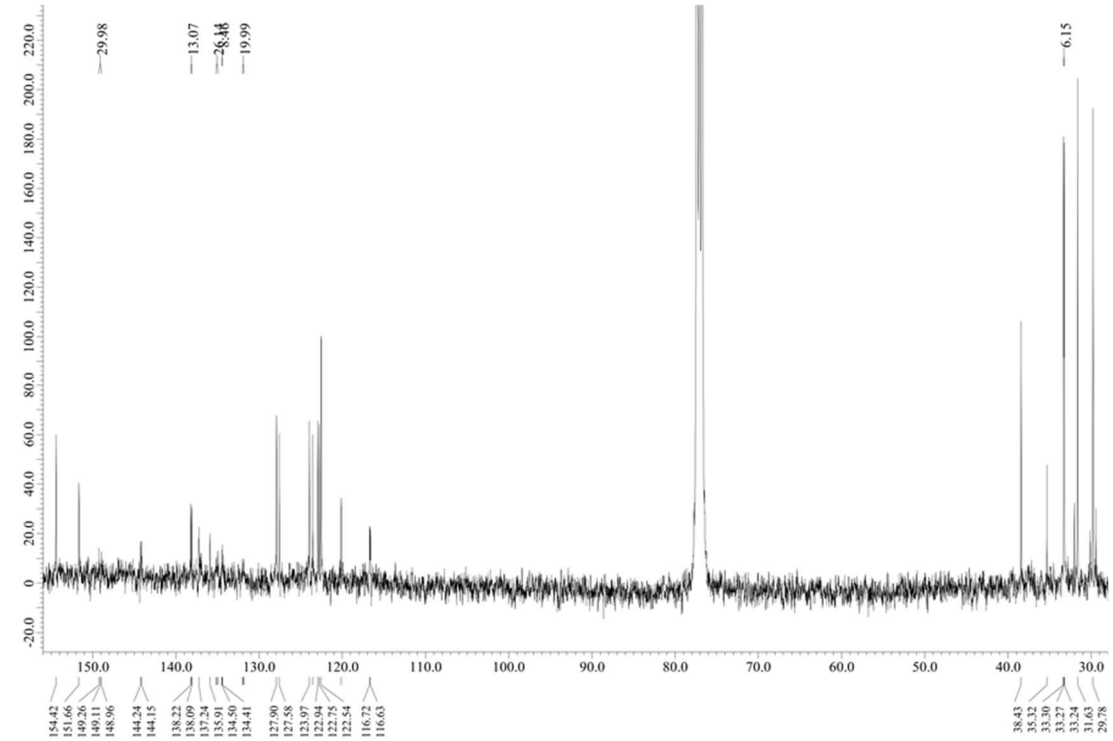


*Figure 12: [13]C NMR spectrum (101 MHz) of **5** ($CDCl_3$).*

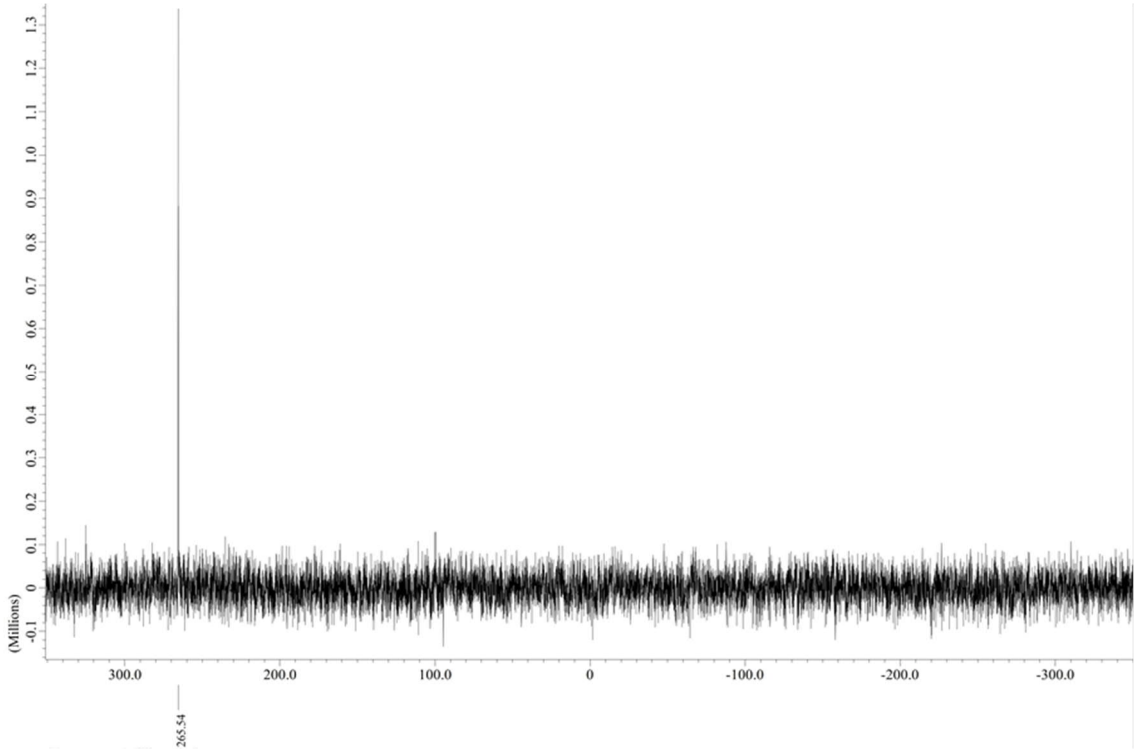
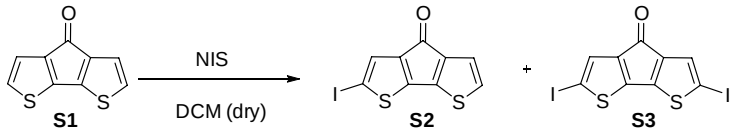


*Figure 13: ^{31}P NMR spectrum (162 MHz) of **5** ($CDCl_3$).*

Synthesis of **S2** and **S3**.



*Scheme 3: Reaction scheme for the preparation of **S2** and **S3**.*

To a solution of ketone **S1** (200 mg, 1.04 mmol) in dry DCM (10 ml) were added 2 equivalents of *N*-iodo succinimide (NIS). The solution was put in an ultrasonic bath for 5 minutes. Chromatographic workup (hexane:ethylacetate gradient) yielded 331 mg (60%) of the monosubstituted derivative **S2**. Increasing the equivalents (>3) and reaction time (30 minutes) gives exclusively di-iodo derivative **S3** in moderated isolated yields (65%).

S2 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.06-7.03 (m, 1H), 6.99-6.96 (m, 1H).
S3 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H).

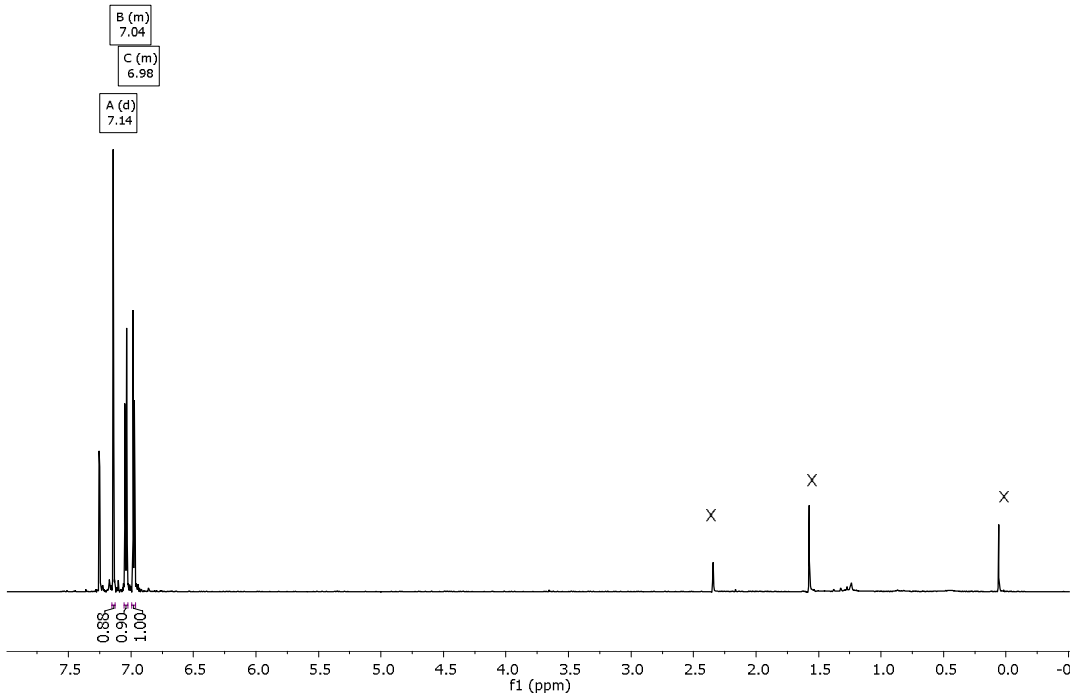


*Figure 14: ^{1}H-NMR spectrum (400 MHz) of **S2** ($CDCl_3$). Resonances denoted by X are impurities.*

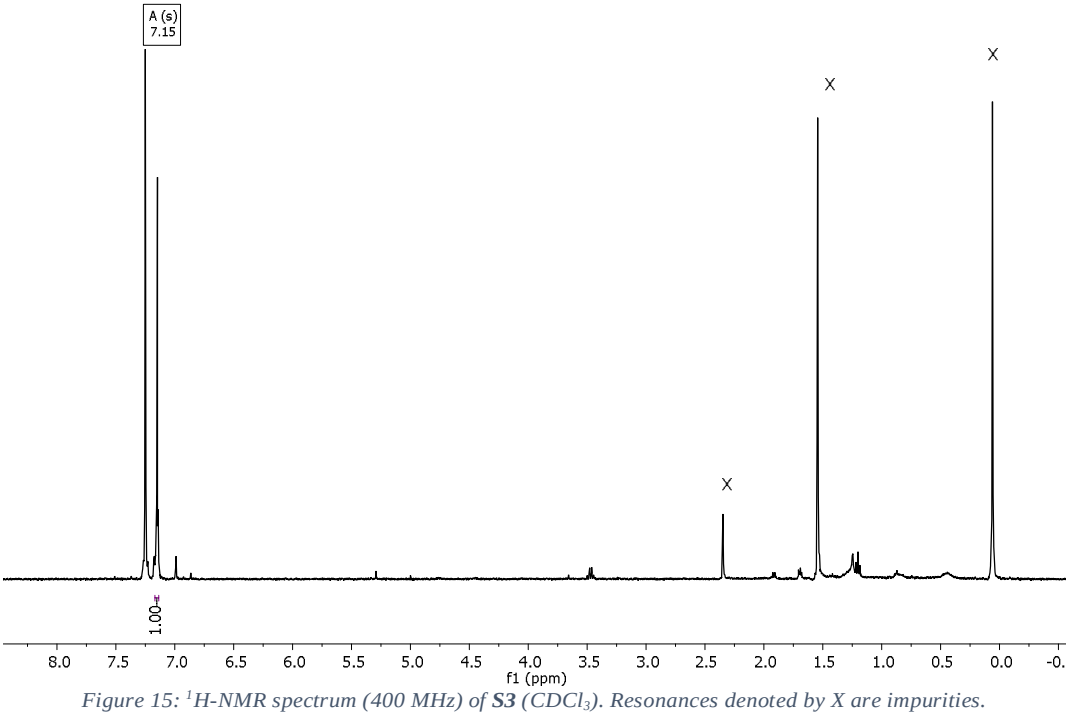
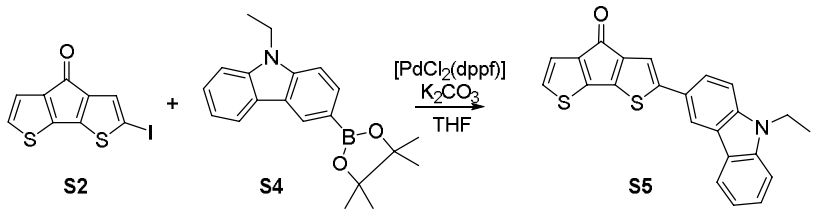


*Figure 15: ^{1}H-NMR spectrum (400 MHz) of **S3** ($CDCl_3$). Resonances denoted by X are impurities.*

Synthesis of **S5**.



*Scheme 4: Reaction scheme for the preparation of **S5**.*

A solution of **S2** (250 mg, 0.69 mmol) and 9-Ethyl-9*H*-carbazole-3-boronic acid pinacol ester (**S4**) (280 mg, 1.1 equiv.) were dissolved in 20 ml of THF (degassed); 1 ml of a 2 M K_2CO_3 solution and 57mg (10 mol%) of [$PdCl_2$(dppf)] were added. The mixture was heated to 70 °C for 20 hours. Chromatographic workup yielded 160 mg (ca. 50%, crude yield) of the coupling product **S5**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.5 Hz, 1H), , 8.11 (d, *J* = 7.7 Hz, 1H), 7.62 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 9.0 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.00 (dd, *J* = 8.2, 4.9 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H)

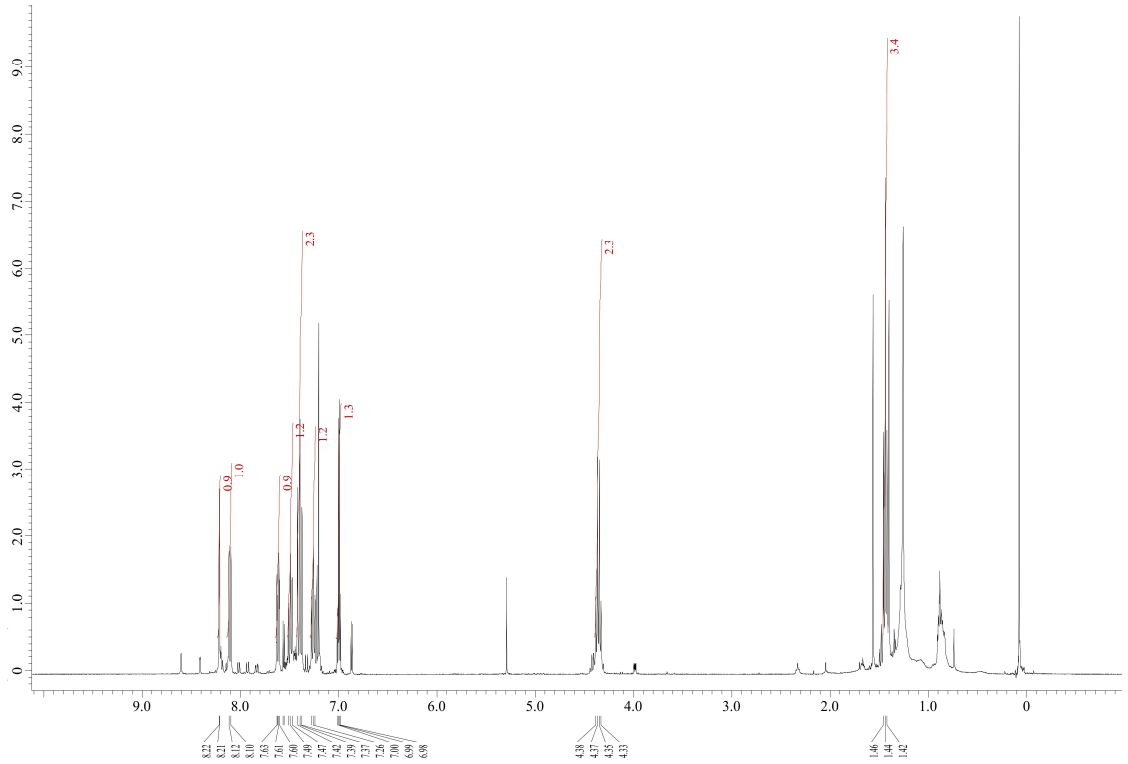
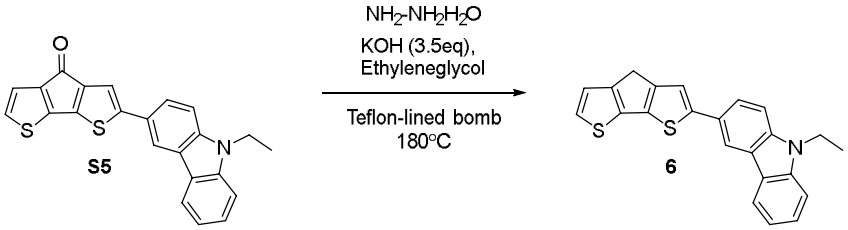


*Figure 16: [1]H-NMR spectrum (400 MHz) of **S5** ($CDCl_3$).*

Synthesis of **6**.



*Scheme 5: Reaction scheme for the preparation of **6**.*

Ketone **6** (152 mg, 0.39 mmol) and KOH (78 mg, 3.5 equiv.) were suspended in ethylene glycol (5 ml) and 5 ml of hydrazine hydrate in a Teflon lined bomb reactor. The reactor was heated for 20 hours to 185 °C. The product was extracted with DCM/water and column chromatographic workup yielded 90 mg (61%) of product **6**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.73 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 (ps.t, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 7.29-7.25 (m, 2H), 7.19 (ps. d. *J* = 5.1 Hz, 2H), 7.11 (d, *J* = 4.8 Hz, 1H), 4.36 (q, *J* = 7.2Hz, 2H) 3.60 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H) ppm.

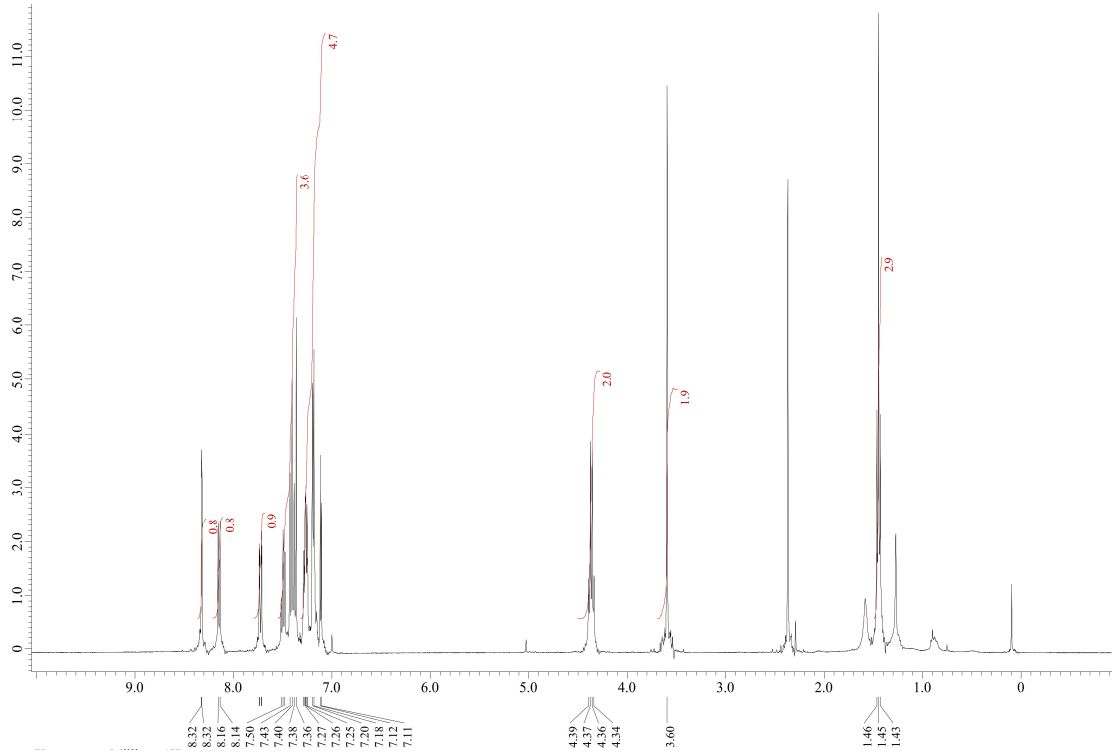
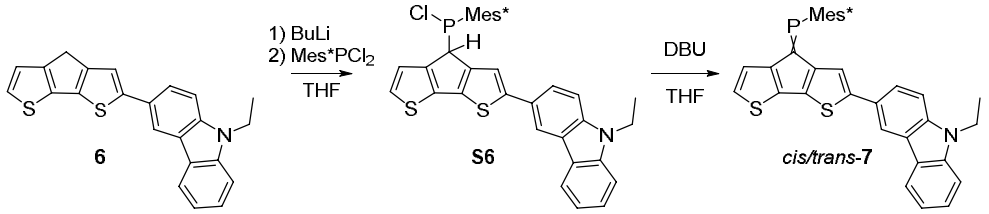


*Figure 17: ^{1}H-NMR spectrum (400 MHz) of **6** ($CDCl_3$).*

Synthesis of *cis/trans*-**7**.



*Scheme 6: Reaction scheme for the preparation of **S5** and cis/trans-**7**.*

A cold solution of **6** (134 mg, 0.36 mmol) in THF was reacted with 1.1 equiv. of *n*-BuLi (0.150 ml, 2.5M) at -78 °C for ca. 30 min. Thereafter a solution of Mes*PCl_2 (ca 0.72 mmol in 20 ml THF) was added at the same temperature and slowly allowed to reach r.t giving **S5**. After 2 hours, DBU (0.4 ml of 1M THF solution) was added and allowed to stir over night. Removal of all volatiles and chromatographic workup gave **7** as mixture of isomers (approx. 1:1) in low isolated yields (25%).
The two isomers crystallized from heptane/DCM as differently shaped and colored crystals suitable for single crystal x-ray diffraction. NMR data was obtained from the isomeric mixture of *cis*/*trans*-**7.**

cis-**7**
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.95 (s, 1H), 7.59 (s, 2H), 7.49-7.37 (m, 3H), 7.25-7.20 (m, 3H, overlapping with solvent signal), 7.06 (d, *J* = 4.9 Hz, 1H), 5.01 (s, 1H) 4.35 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 18H), 1.44 (s, 9H), 1.43 (t, 3H) ppm. This spectrum could be assigned to the *cis* isomer based on the low frequency singlet at 5.01 ppm.
^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ 258.0 ppm.
trans-**7**
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.15 (d, *J*= 7.3 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 1H), 7.52 (s, 2H), 7.49-7.37 (m, 3H), 7.25-7.20 (m, 3H, overlapping with solvent signal), 6.49 (d, *J* = 5.1 Hz, 1H), 4.47 (d, *J* = 5.13 Hz, 1H), 4.39 (q, *J*= 7.1 Hz, 2H), 1.47 (s, 18H), 1.44 (s, 9H), 1.42 (s 3H) ppm. This spectrum could be assigned to the *trans* isomer based on the low frequency doublet at 4.47 ppm, *J* = 5.1 Hz.
^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ 256.4 ppm.
FTMS+p APCI (*m/z*): $[M+Ag]^+$ calc.752.16982 and 754.16982; found 752.17132 and 754.17082.

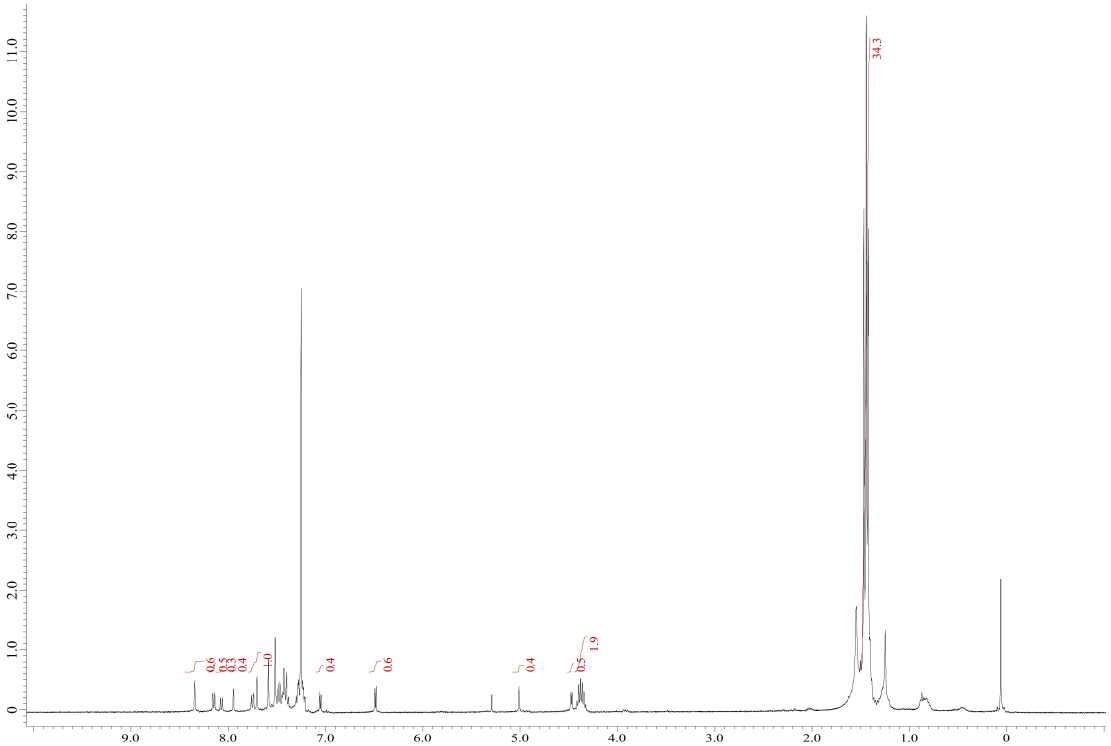


*Figure 18: ^{1}H-NMR spectrum (400 MHz) of trans-**7** and* cis-*7 ($CDCl_3$).*

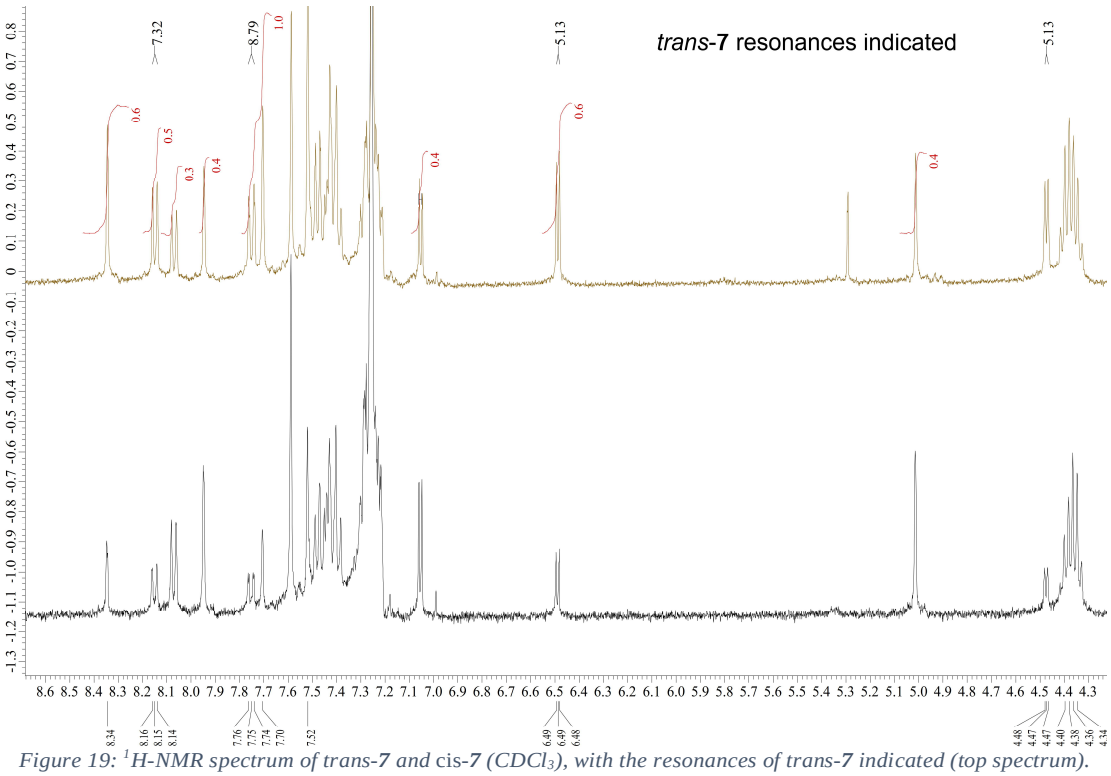


*Figure 19: ^{1}H-NMR spectrum of trans-**7** and* cis-*7 ($CDCl_3$), with the resonances of trans-**7** indicated (top spectrum).*

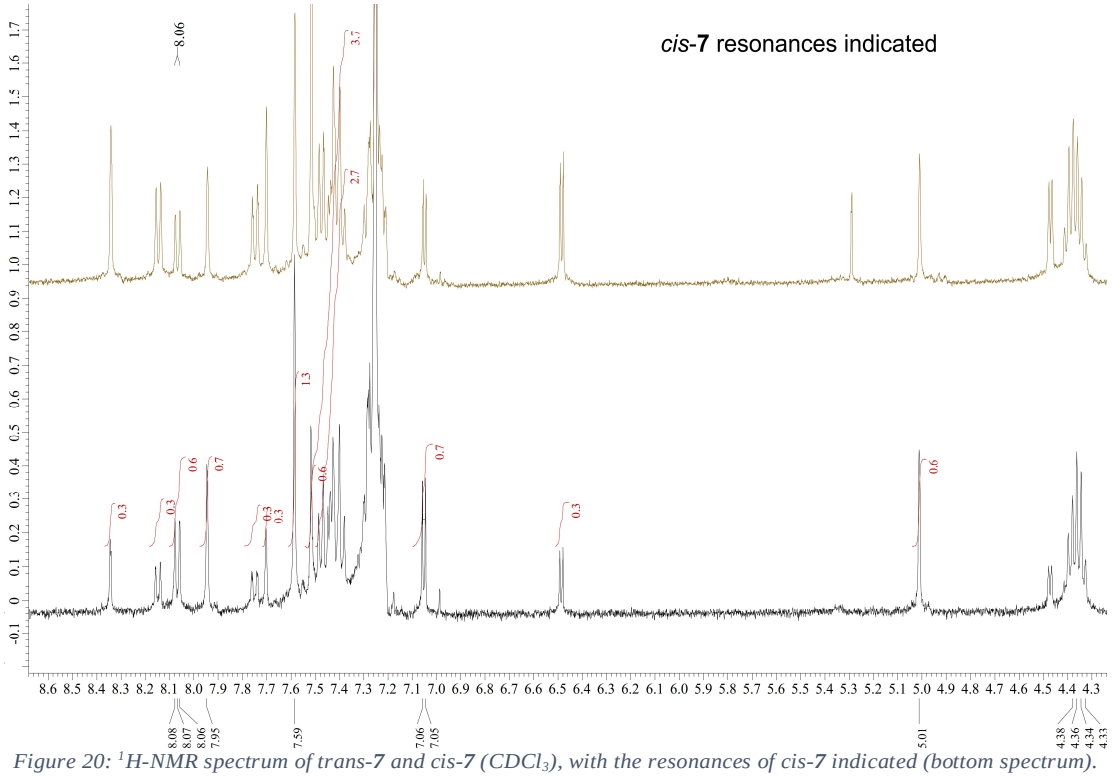


*Figure 20: ^{1}H-NMR spectrum of trans-**7** and cis-**7** ($CDCl_3$), with the resonances of cis-**7** indicated (bottom spectrum).*

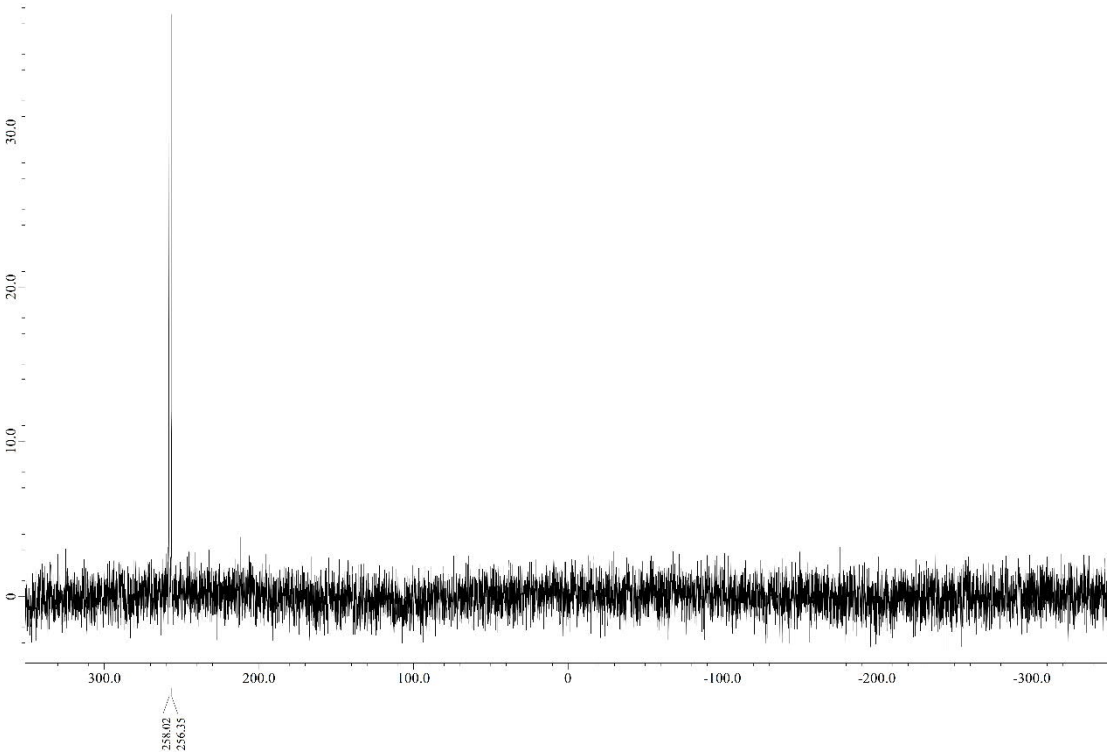


Figure 21: 31P-NMR spectrum (162 MHz) of trans-7 and cis-7 (CDCl3).

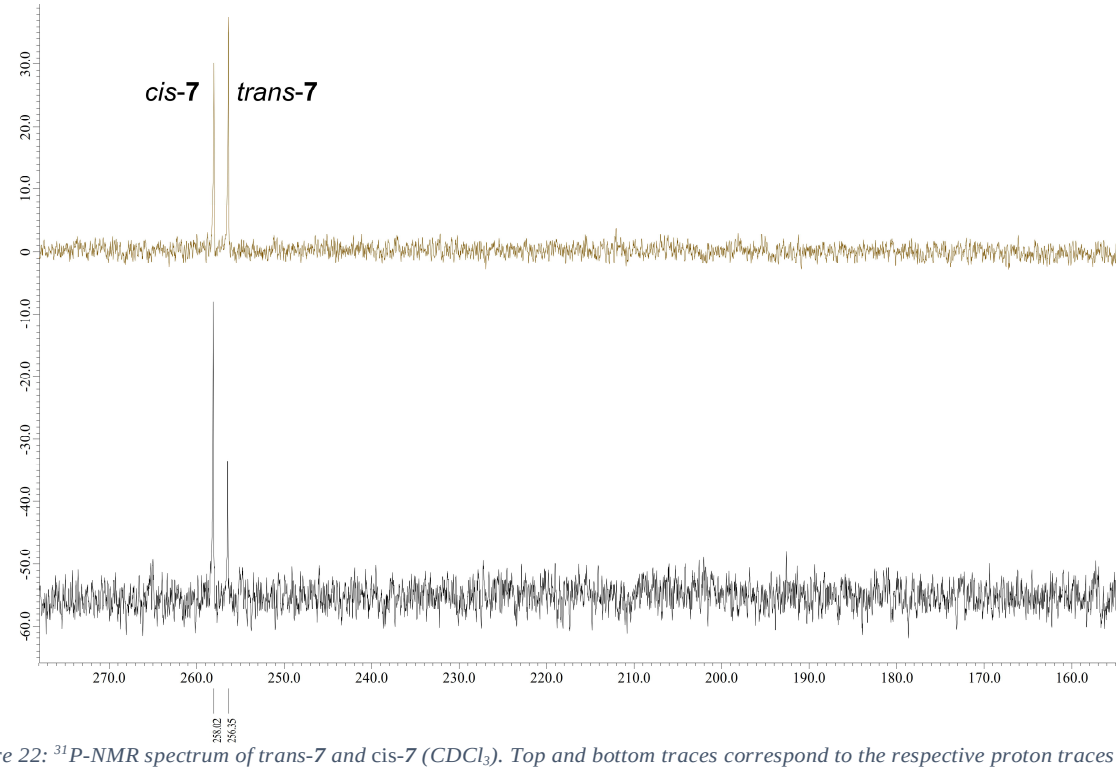
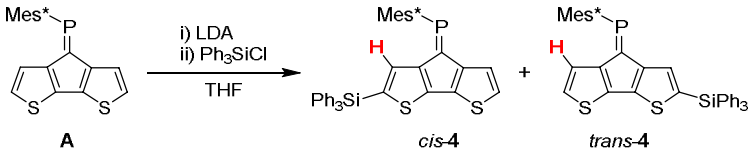


*Figure 22: ^{31}P-NMR spectrum of trans-**7** and* cis-***7*** *($CDCl_3$). Top and bottom traces correspond to the respective proton traces above.*

Synthesis of *cis*-/*trans*-**4**.



*Scheme 7: Reaction scheme for the preparation of cis/trans-**4**.*

Phosphaalkene **A** (100 mg, 0.22 mmol, 5 ml THF) is reacted for 30 min. with freshly prepared LDA (0.12 mmol) at low temperatures (-78 °C), followed by addition of triphenyl chloro silane (ca. 35 mg, 0.11 mmol). The mixture is stirred over night, followed by chromatographic workup (pentane) giving the isomeric mixture of monosilylated product **4** in low crude yields (30 mg). Careful, but fast column chromatography allowed us to obtain small amounts of isomeric pure products as identified bv ^{1}H and ^{31}P NMR analysis. Assignment to *cis*-/and *trans*-**4** is based on the absence and presence of a $^3J_{HH}$ coupling of the low frequency CPDT protons indicated in red: *trans*-**4** 4.43 (d, *J* = 5.1 Hz) and *cis*-**4**: 5.27 (s, 1H), respectively.

cis-**4**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.3 0 (m, 19 H), 7.06 (d, *J* = 4.8 Hz, 1H), 5.27 (s, 1H), 1.47 (27H, meta-tBu groups presumably broadened due to hindered rotation) ppm.
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 258.1 ppm.
trans-**4**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J*= 7.7 Hz, 6H), 7.60 (1H),7.49 – 7.40 (m, 11 H), 6.50 (d, *J* = 5.1 Hz, 1H), 4.43 (d, *J* = 5.1 Hz, 1H), 1.40 (9H), 1.40 (18H) ppm.
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 257.3 ppm.
^{13}C NMR spectra could not be obtained for *cis*- and *trans*-**4** due to slow isomerisation of the P=C bond in solution.

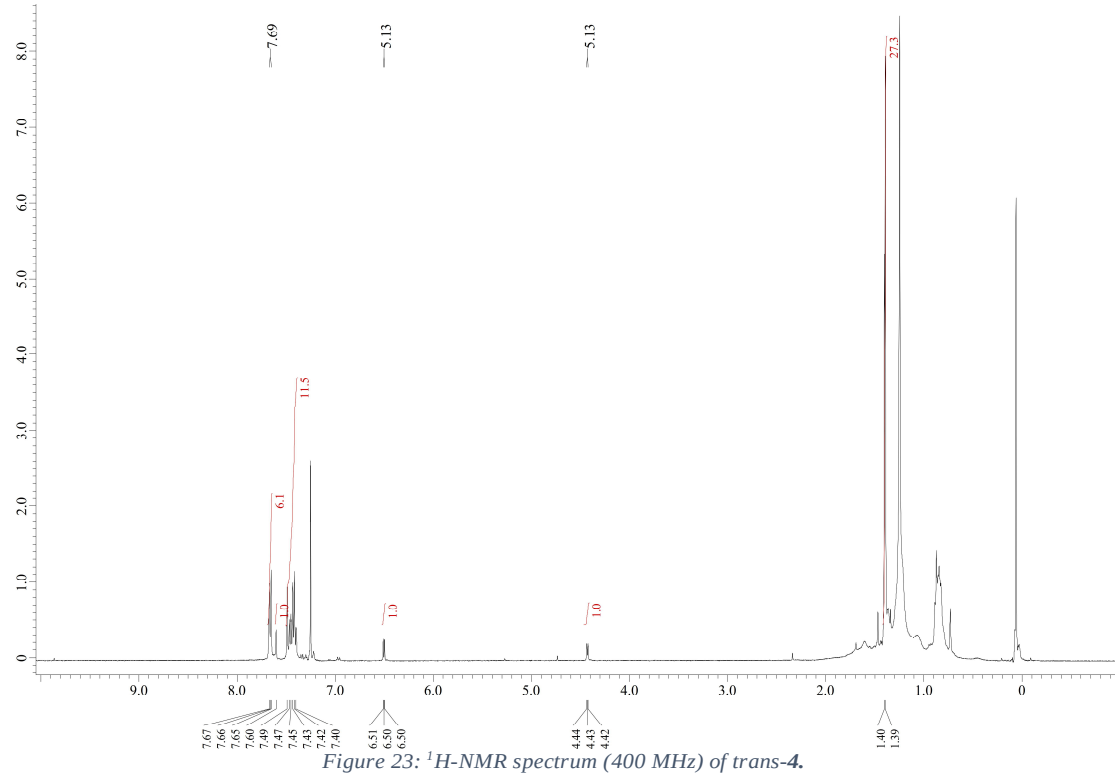


*Figure 23: [1]H-NMR spectrum (400 MHz) of trans-**4**.*

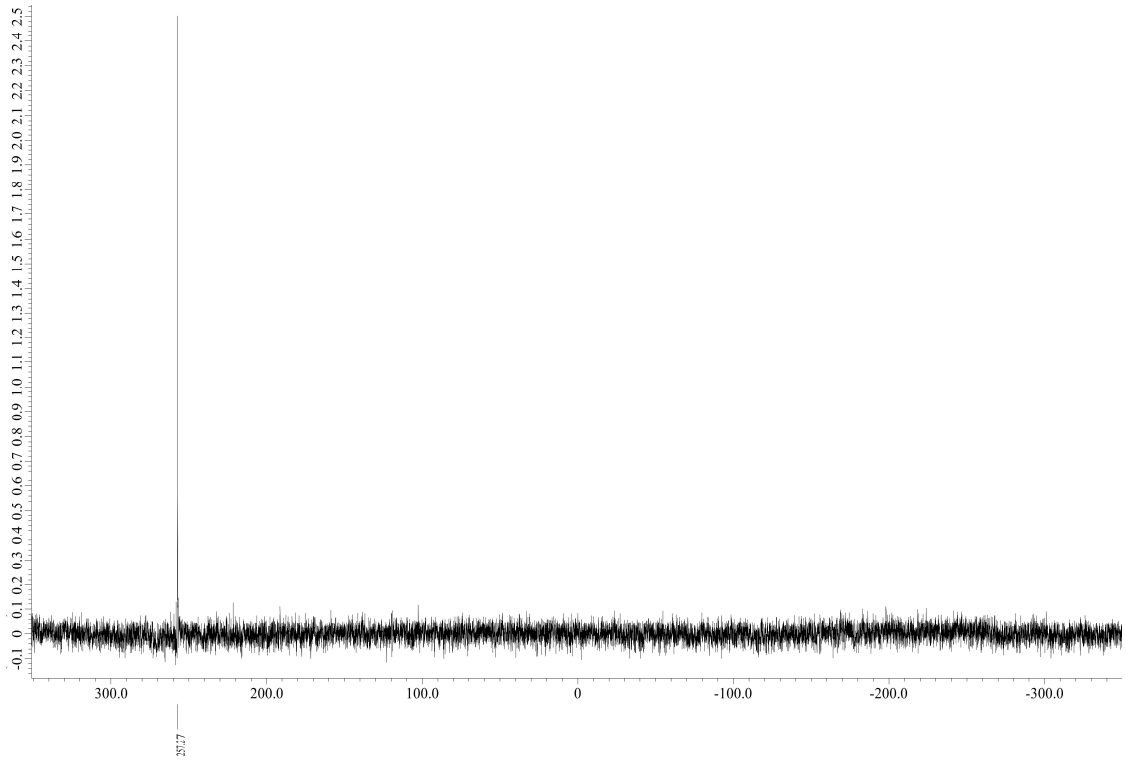


*Figure 24: [31]P-NMR spectrum (162 MHz) of trans-**4**.*

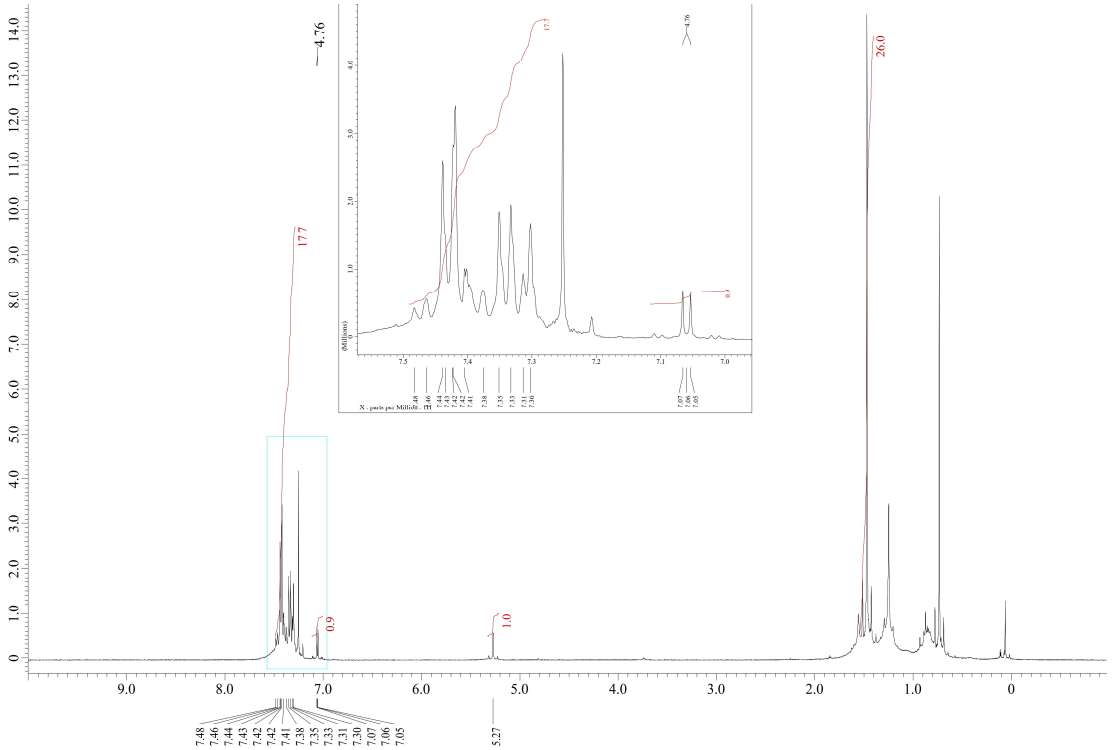


*Figure 25: ^{1}H-NMR spectrum (400 MHz) of cis-**4**.*

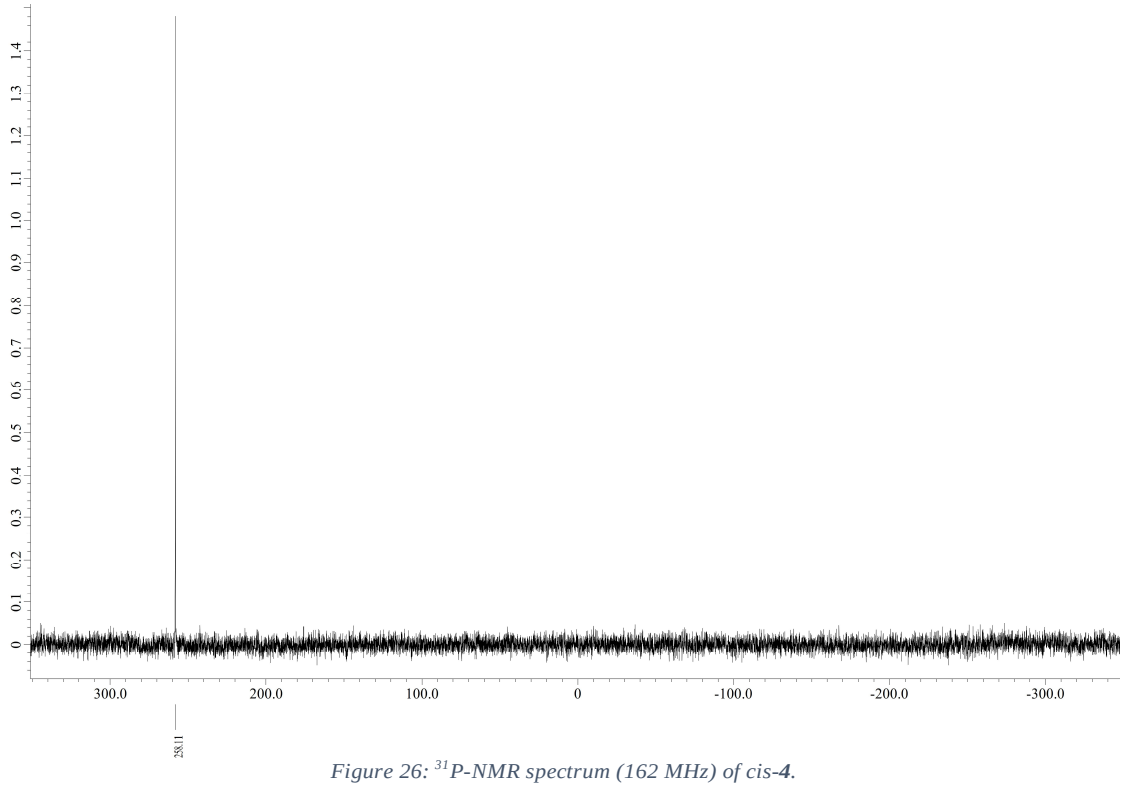
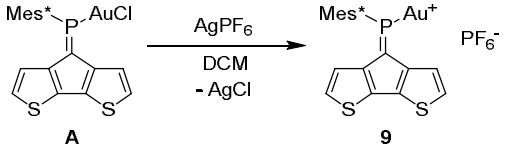


*Figure 26: ^{31}P-NMR spectrum (162 MHz) of cis-**4**.*

Synthesis of **9**.



A **9**

*Scheme 8: Reaction scheme for the preparation of **9**.*

A blue solution of [**A***AuCl] (36 mg, 0.8 mmol) in DCM (0.5 mL) was treated with $AgPF_6$ (20 mg, 0.08 mmol) in CD_2Cl_2. The resulting forest green suspension was filtered into a Young's NMR tube to remove insoluble AgCl. The

NMR data were collected immediately. Decomposition of **9** was evident by NMR spectroscopy in solution after 8 hours, and gold mirror formation occurred within 2-3 days.

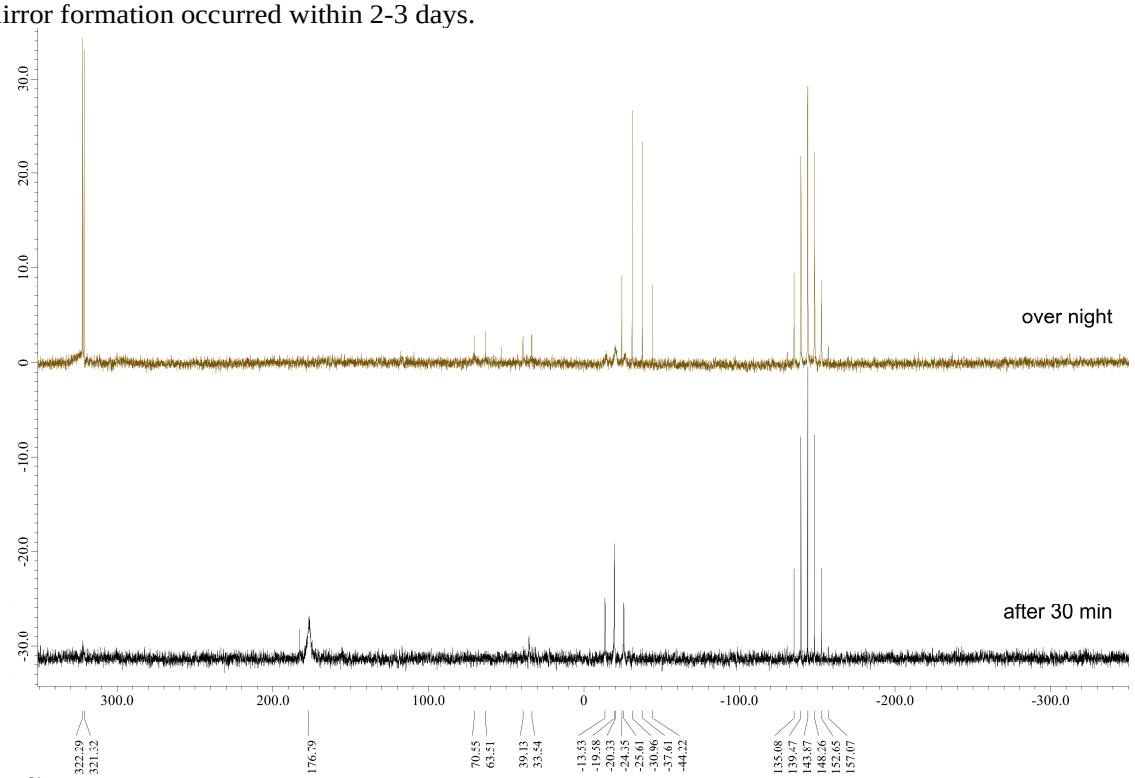


Figure 27: ^{31}P-NMR spectrum (162 MHz) of **9** demonstrating the decomposition of the sample in solution overnight (DCM, Ar atmosphere).

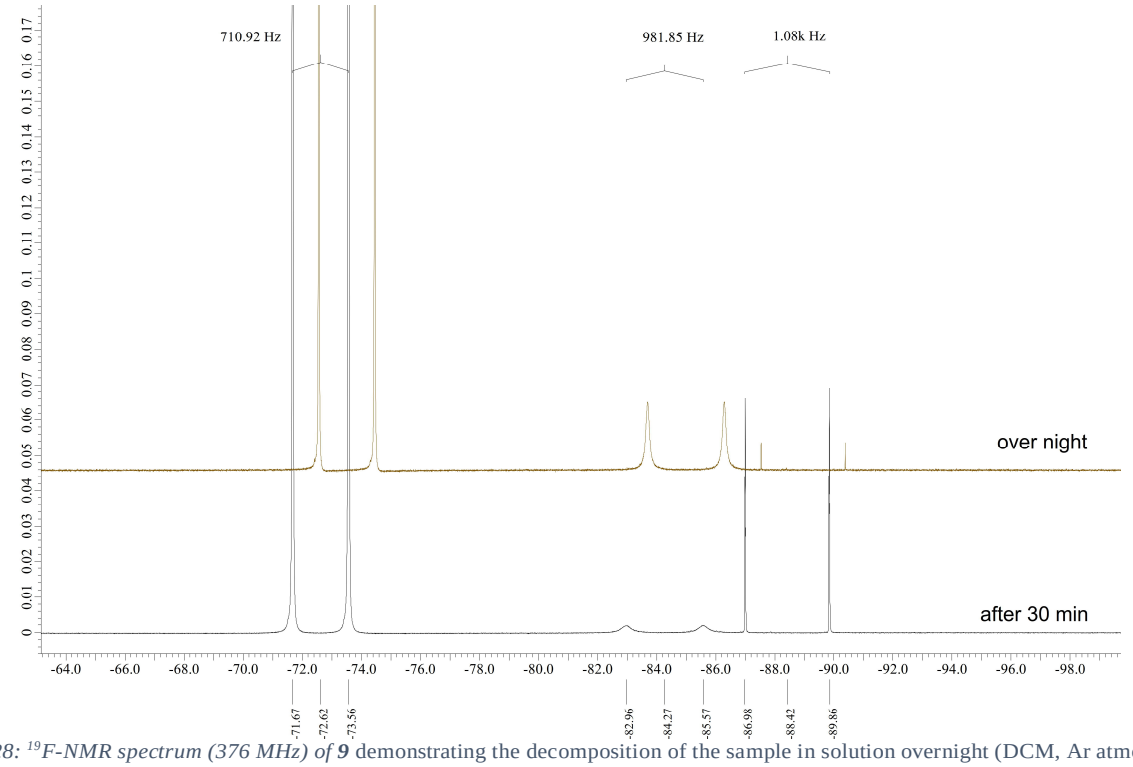
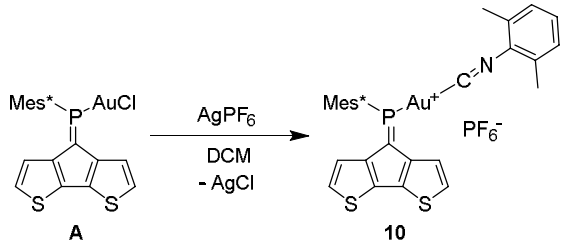


Figure 28: ^{19}F-NMR spectrum (376 MHz) of ***9*** demonstrating the decomposition of the sample in solution overnight (DCM, Ar atmosphere).

Synthesis of **10**.



Scheme 9: Reaction scheme for the preparation of ***10***.

$AgPF_6$ (20 mg, 0.08 mmol) was added to a stirring purple-blue solution containing **A** (34.5 mg, 0.08 mmol), XylNC (10 mg, 0.08 mmol) and [AuCl(tht)] (24 mg, 0.08 mmol) in 0.5 mL CD_2Cl_2. The resulting forest green suspension was filtered in a Young's NMR tube to remove insoluble AgCl. NMR data were collected immediately. Decomposition of the sample could be detected by NMR spectroscopy over the course of a week.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 3.2 Hz, 2H), 7.58 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.42 (*t*, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 5.0 Hz, 1H), 6.60 (d, *J* = 5.0 Hz, 1H), 4.41 (dd, *J* = 5.0, 1.8 Hz, 1H), 2.49 (s, 6H), 1.52 (s, 18H), 1.41 (s, 9H) ppm.
^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2) δ 161.5 (d, *J* = 30.8 Hz), 156.2, 154.9, 150.7 (ps.t, *J* = 27.0 Hz), 145.9 (d, *J* = 15.4 Hz), 144.2 (d, *J* = 12.5 Hz), 140.3 (d, *J* = 18.3 Hz), 139.4 (d, *J* = 21.2 Hz), 137.4, 132.4, 128.7, 126.2 (d, *J* = 2.9 Hz), 125.9, 125.1 (d, *J* = 2.9 Hz), 124.1, 123.1 (d, *J* = 3.4 Hz), 120.1 (d, *J* = 7.7 Hz), 38.7, 36.0, 33.7 (d, *J* = 2.9 Hz), 31.0, 18.5 ppm.
^{19}F-NMR (376 MHz, CD_2Cl_2) δ -72.8 (d, *J* = 711.6 Hz) ppm
^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2) δ 203.8, -143.9 (sept., *J* = 711.6 Hz) ppm.

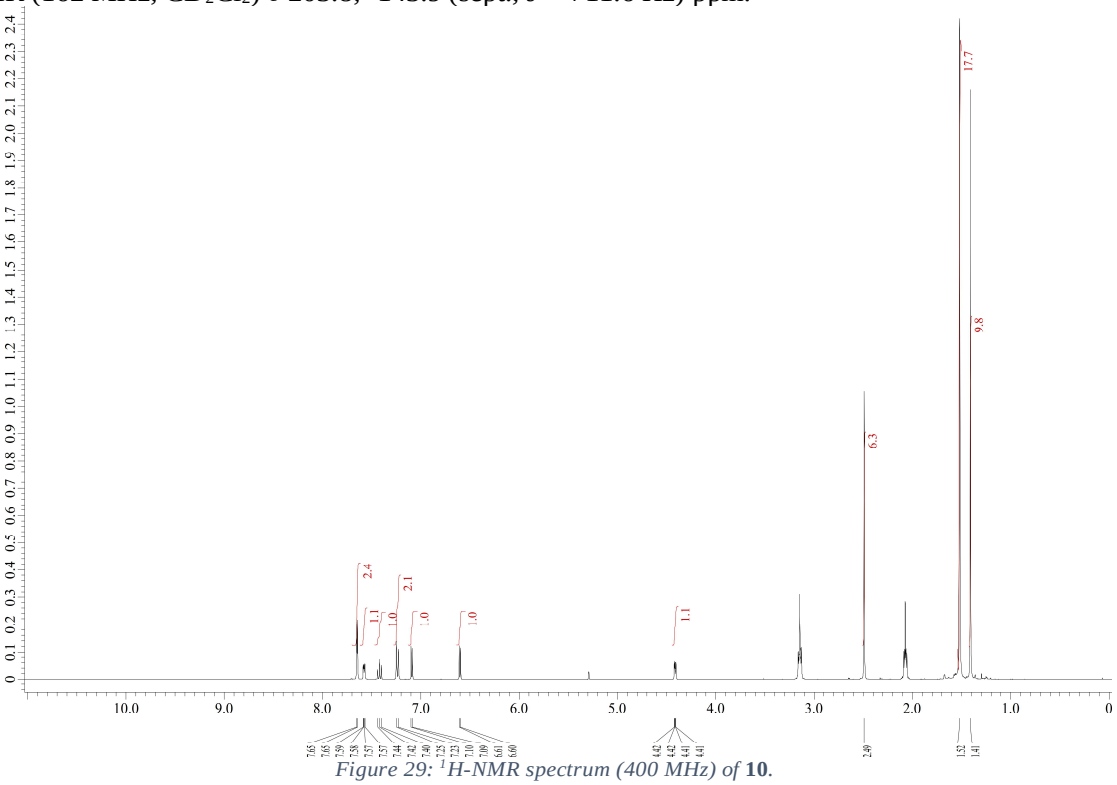


Figure 29: ^{1}H-NMR spectrum (400 MHz) of **10**.

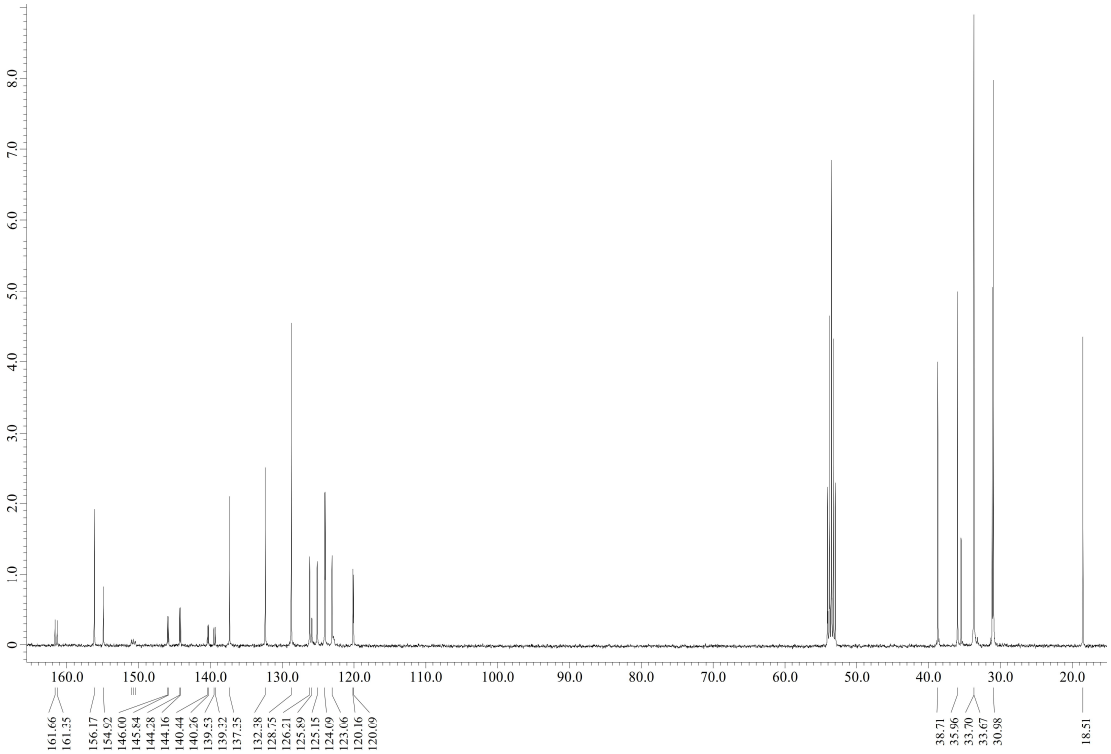


Figure 30: [13]C-NMR spectrum (101 MHz) of **10**.

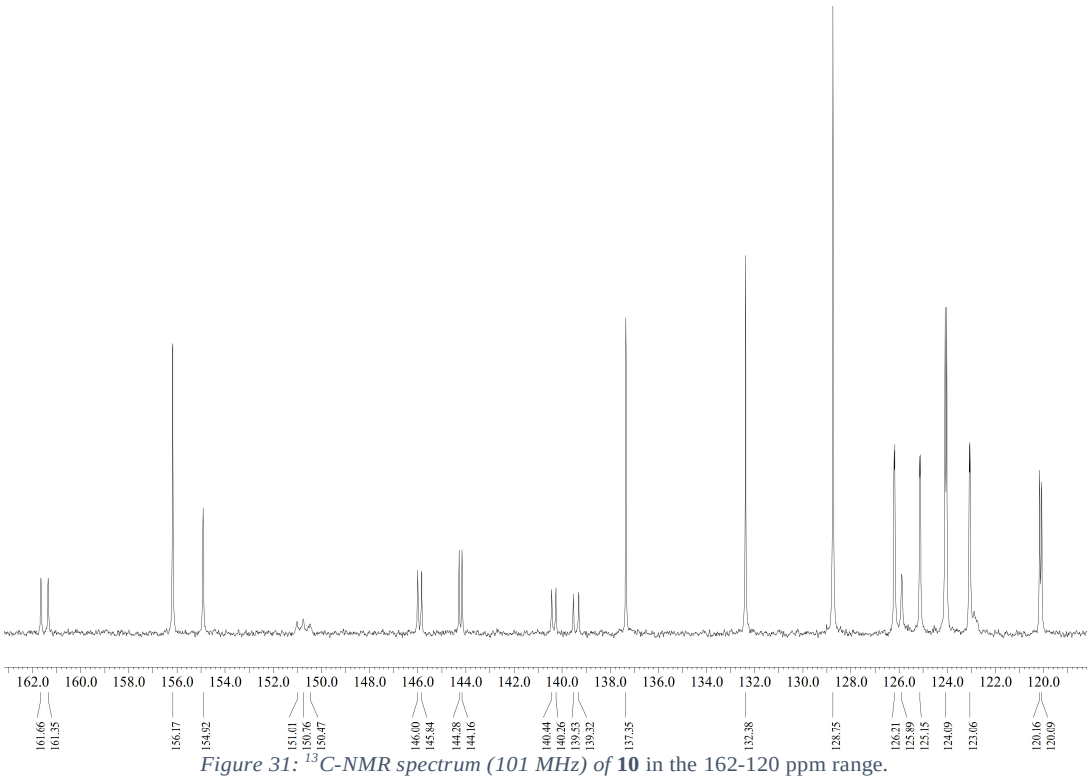


Figure 31: [13]C-NMR spectrum (101 MHz) of **10** in the 162-120 ppm range.

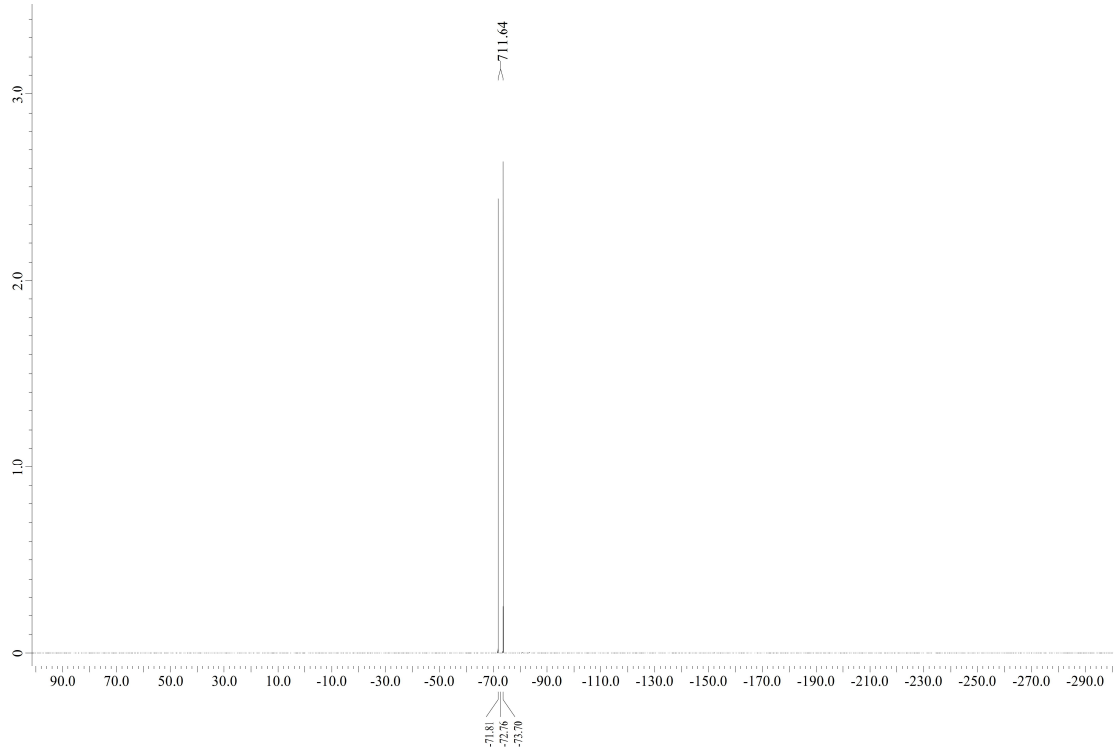


Figure 32: ^{19}F-NMR spectrum (376 MHz) of **10**.

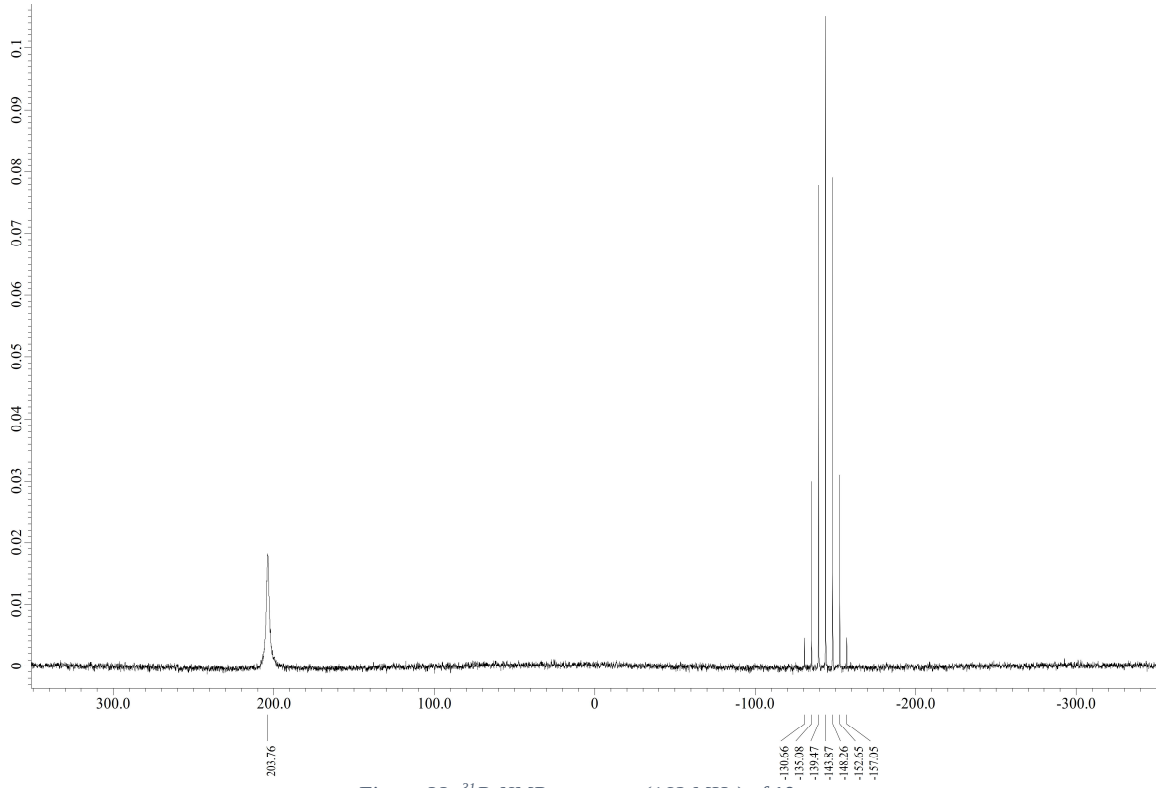
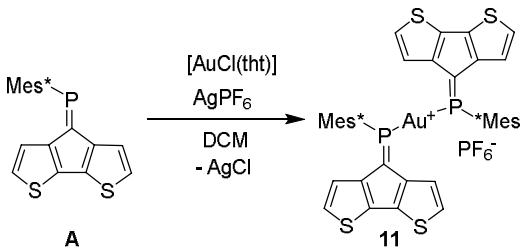


Figure 33: ^{31}P-NMR spectrum (162 MHz) of **10**.

Synthesis of **11.**



Scheme 10: Reaction scheme for the preparation of ***11***.

$AgPF_6$ (8 mg, 0.03 mmol) was added to a stirring purple-blue solution containing **A** (28 mg, 0.06 mmol) and [AuCl(tht)] (10 mg, 0.03 mmol) in 0.5 mL CD_2Cl_2. The resulting forest green suspension was filtered in a Young's NMR tube to remove insoluble AgCl. NMR data were collected immediately. Decomposition of the sample could be detected by NMR spectroscopy over the course of a week.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, J = 3.2 Hz, 2H), 7.58 (d, *J* = 5.0 Hz, 1H), 7.08 (d, *J* = 5.0 Hz, 1H), 6.62 (d, *J* = 5.0 Hz, 1H), 4.40 (d, *J* = 5.0 Hz, 1H), 1.54 (s, 18H), 1.41 (s, 9H) ppm.
^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2) δ 161.3 (d, *J* = 38.5 Hz), 156.4, 155.4, 145.5 (d, *J* = 13.5 Hz), 144.2 (d, *J* = 12.5 Hz), 140.8 (d, *J* = 18.3 Hz), 140.0 (d, *J* = 22.2 Hz), 126.4 (d, *J* = 1.9 Hz), 125.4 (d, *J* = 1.9 Hz), 124.8, 124.3 (d, *J* = 6.7 Hz), 123.0 (d, *J* = 2.9 Hz), 120.0 (d, *J* = 7.7 Hz), 38.8, 35.5, 33.8, 30.9 ppm.
^{19}F-NMR (376 MHz, CD_2Cl_2) δ -73.23 (d, $^1J_{PF}$ = 710 Hz) ppm.
^{31}P-NMR (162 MHz, CD_2Cl_2) δ 197.9, -143.9 (sept., $^1J_{PF}$ = 710 Hz) ppm.

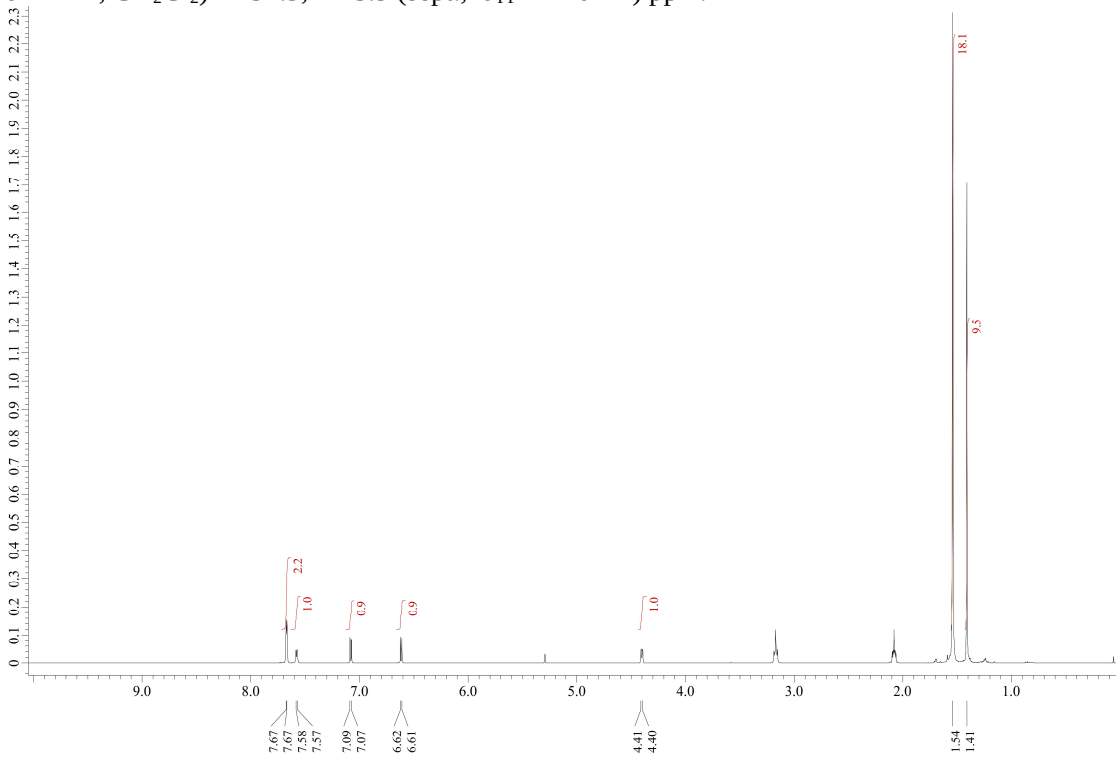


Figure 34: ^{1}H-NMR spectrum (400 MHz) of **11**.

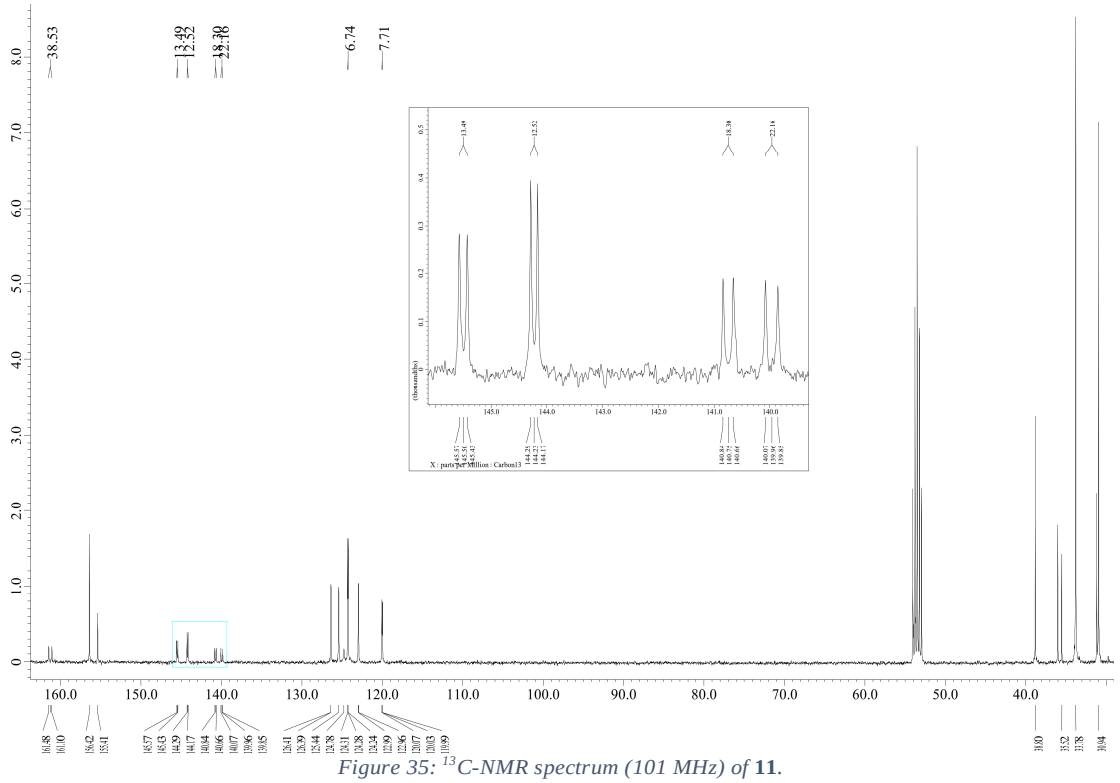


Figure 35: ^{13}C-NMR spectrum (101 MHz) of **11**.

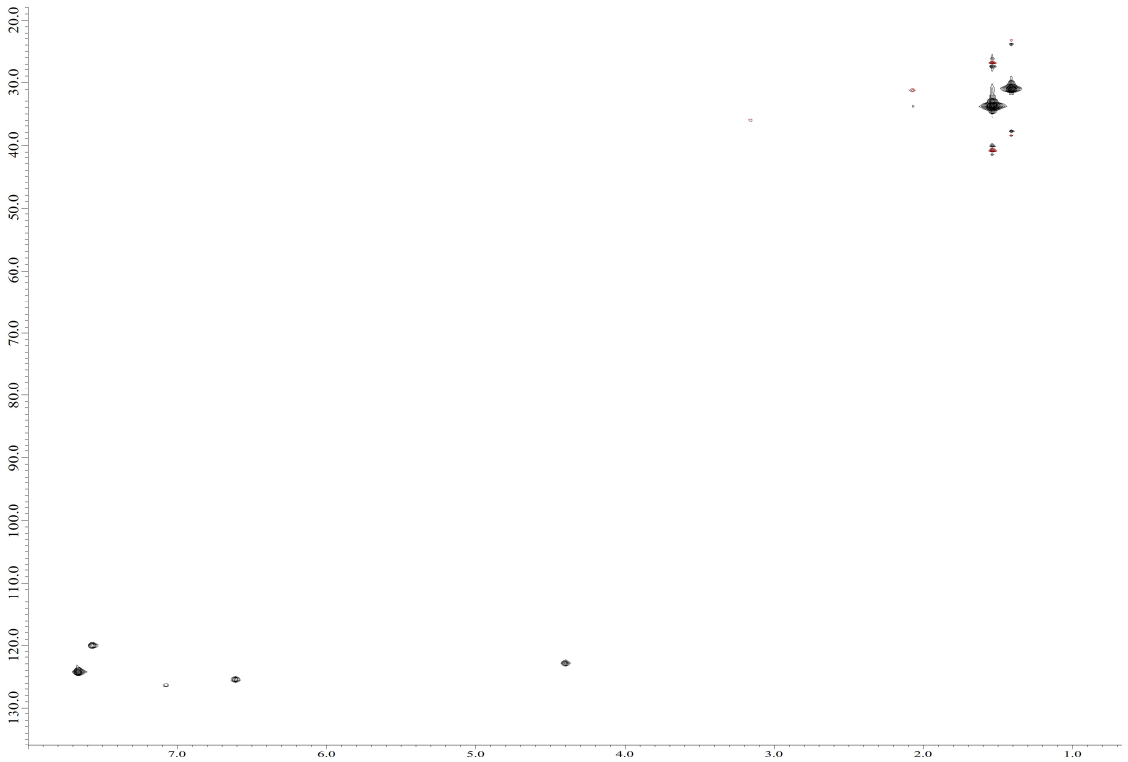


Figure 36: ^{1}H-^{13}C HSQC-NMR spectrum of **11**.

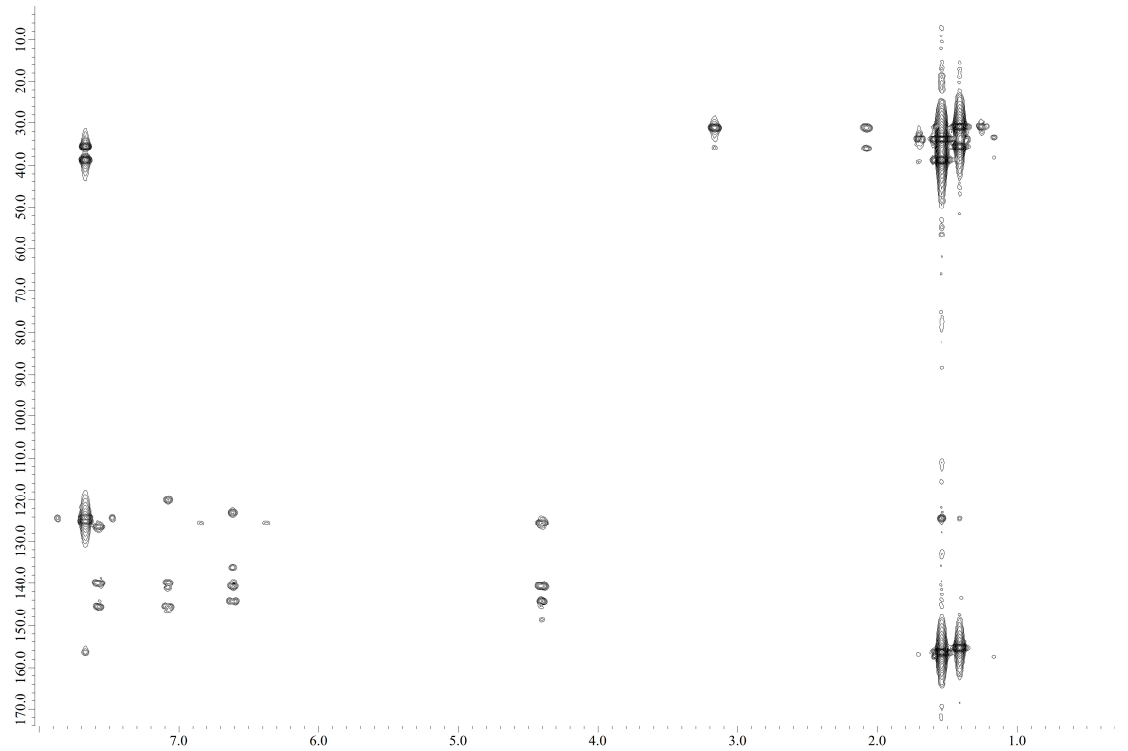


Figure 37: ^{1}H-^{13}C HMBC-NMR spectrum of **11**.

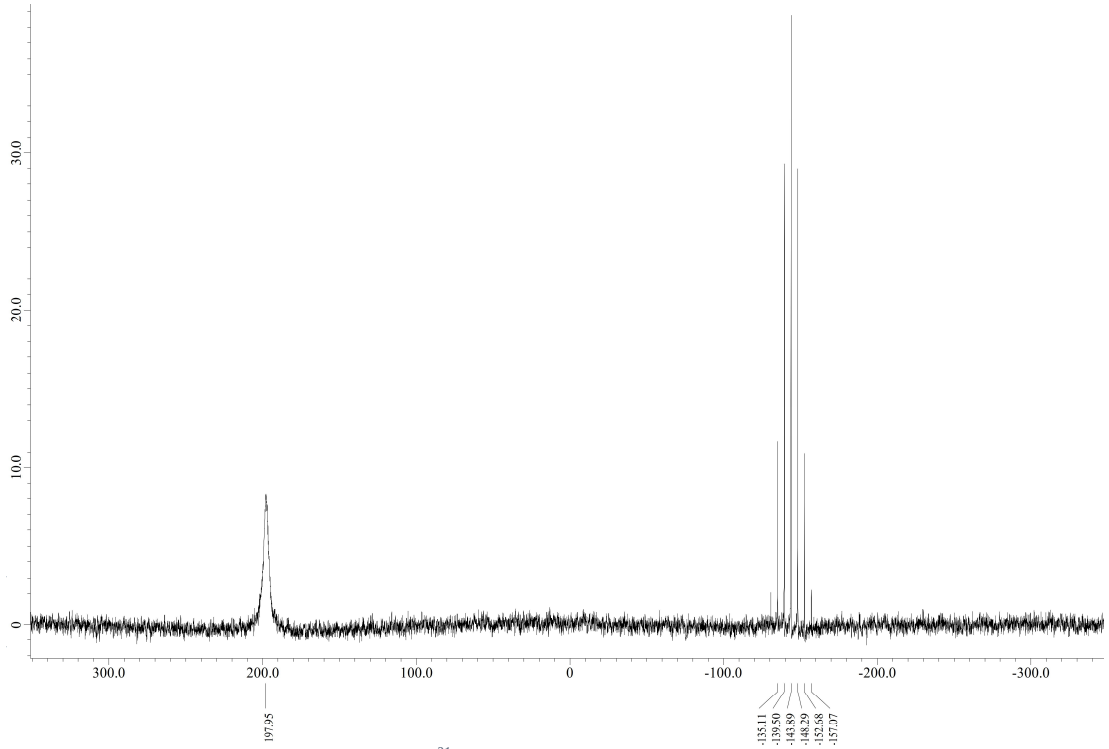


Figure 38: ^{31}P-NMR spectrum (162 MHz) of **11**.

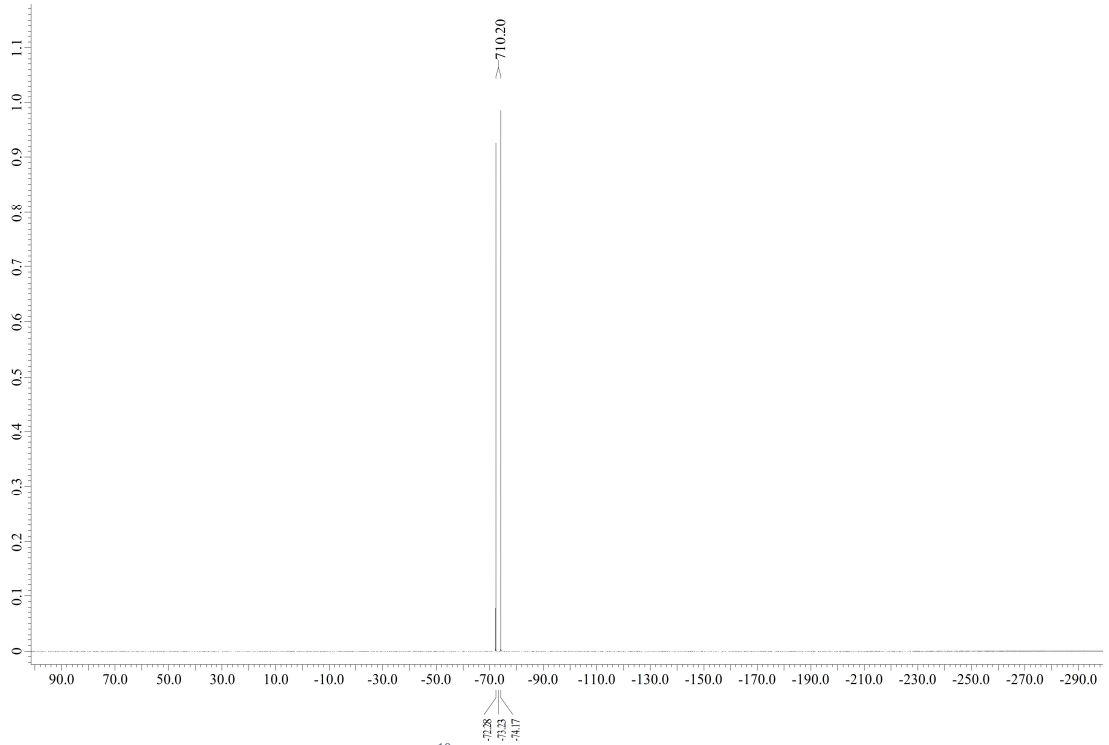
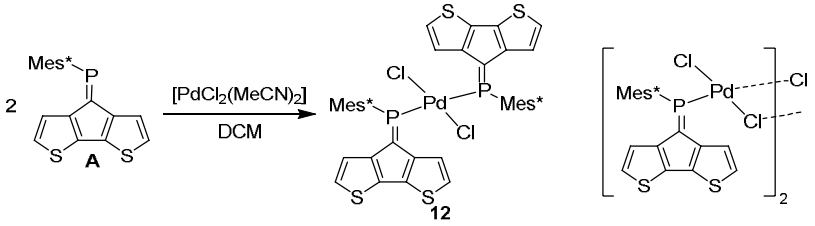


Figure 39: ^{19}F-NMR spectrum (376 MHz) of **11**.

Synthesis of **12.**



Scheme 11: Reaction scheme for the preparation of ***12***.

A dark blue suspension of phosphaalkene **A** (240 mg, 0.053 mmol, 0.5 ml CD_2Cl_2) was added to solid palladium dichloride bis(acetonitrile) (6 mg, 0.023 mmol) to give a green-brown solution. Allowing the reaction solvent to

evaporate at ambient pressure and temperature over 48 hours provided **12** as dark green plates suitable for analysis by single crystal X-ray diffraction.

Analysis of the reaction mixture by ^{31}P NMR spectroscopy shows a new resonance at 194 ppm (δ(**A**) = 258 ppm, Δδ = -64 ppm) and a minor (<20%) resonance at 162 ppm in addition to residual **A**. Dissolution of crystalline **12** followed by ^{31}P NMR analysis similarly gave rise to three signals at 258, 194 and 162 ppm suggesting ligand dissociation in solution. Repeat reactions in which the equivalents of Pd starting material were increased resulted in the peak at 162 ppm to become the major species in solution.

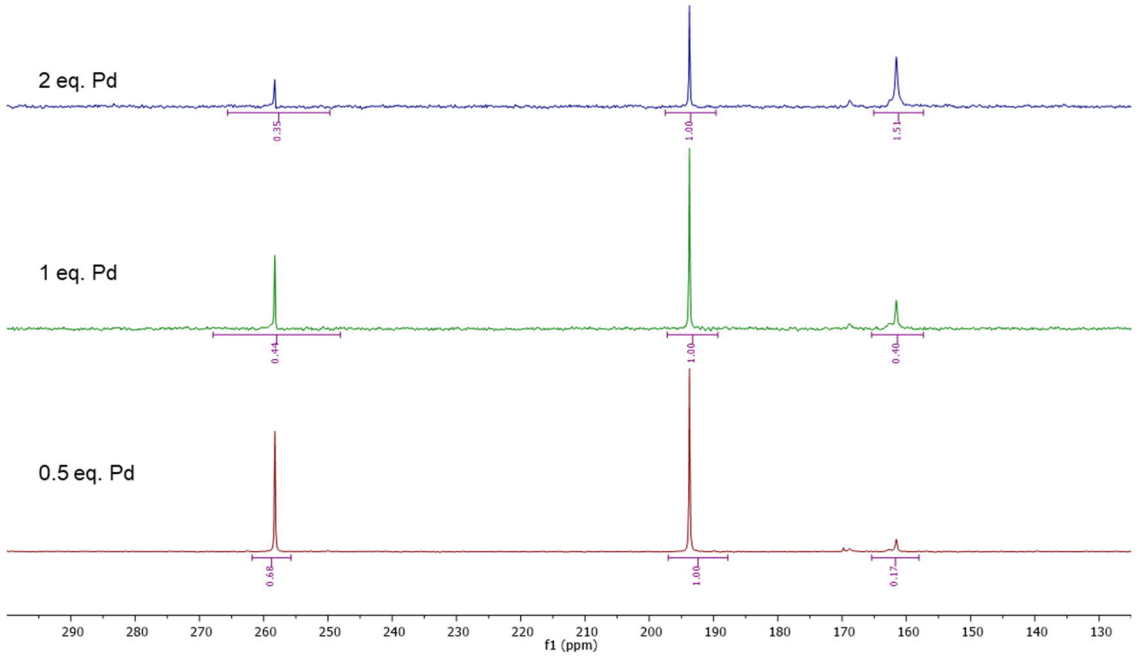
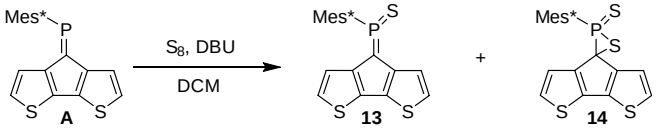


*Figure 40: Stacked ^{31}P-NMR spectra of the reaction of **A** and varying equivalents of [$PdCl_2(MeCN)_2$] in CD_2Cl_2. The resonance at 258 ppm is that of residual **A** which remains unreacted. The signal at 194 ppm is ascribed to **12**.*

Synthesis of **13.**



*Scheme 12: Reaction scheme for the oxidation of **A** with sulfur giving **13** and **14** (minor).*

Elemental sulphur (80 mg, 2.5 mmol) is suspended in a solution of phosphaalkene **A** (150 mg, 0.33 mmol, 15 ml dry DCM). Two drops of DBU are added triggering immediate consumption of starting material **A**. All volatiles are removed under vacuum and the crude is subjected to column chromatography (alumina DCM:pentane). Compound **13** was obtained in very low isolated yields due to partial decomposition on the column (approx. 12 mg, <10 %).

13:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.0, 2.1s Hz, 1H), 7.66 (d, *J* = 5.5 Hz, 2H), 7.09 (d, *J* = 5.0 Hz, 1H), 6.57 (d, *J* = 5.0 Hz, 1H), 4.48 (dd, *J* = 5.0, 1.4 Hz, 1H), 1.59 (s, 18H), 1.40 (s, 9H) ppm.
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ 155.58 (d, *J* = 5.8 Hz) ,145.09 (d, *J* = 5.8 Hz) 143.53 (d, *J* = 6.7 Hz), 135.03 (m), 131.74, 130.4, 129.12, 128.31, 125.29 (d, *J* = 19.3 Hz), 124.34 (d, *J* = 13.5 Hz), 123.92 (d, *J* =2.9 Hz), 122.96 (d, *J* = 20.2 Hz), 120.96, 39.40 (d, *J* = 2.9 Hz), 35.64, 33.93, 31.19 ppm.
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 157.1 ppm.
FTMS+p LDI (*m/z*): $[M+H]^+$ calc. 485.115478 found 485.155460.

14:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 4.6 Hz, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 7.08 (br. s., 1H, overlaps with the residual solvent signal), 6.63 (d, *J* = 5.0 Hz, 1H), 6.14 (d, J = 5.0 Hz), 4.56 (d, *J* = 5.0, 1H), 1.66 (s, 9H), 1.19 (s, 9H), 1.12 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ 158.07 (d, J= 7.7 Hz), ,155.60 (d, *J* = 12.5 Hz), 152.57 (d, J = 4.8 Hz), 150.69 (d, J = 3.9 Hz), 149.98 (s), 139.00 (d, J = 45.3 Hz), 138.94 (d, J = 44.3 Hz), 130.57 (d, J = 80.9 Hz), 125.22 (d, J = 15.4 Hz), 125.05 (s), 123.71 (s), 123.39 (s), 122.29 (d, J = 16.4 Hz), 122.23 (s),47.59 (d, J = 27.9 Hz), 41.21 (d, J = 3.9 Hz), 39.24 (d, J = 2.9 Hz), 34.74 (s), 34.01(s), 32.03 (s), 30.68 (s) ppm.
^{31}P NMR (162 MHz, $CDCl_3$) δ -1.3 ppm.

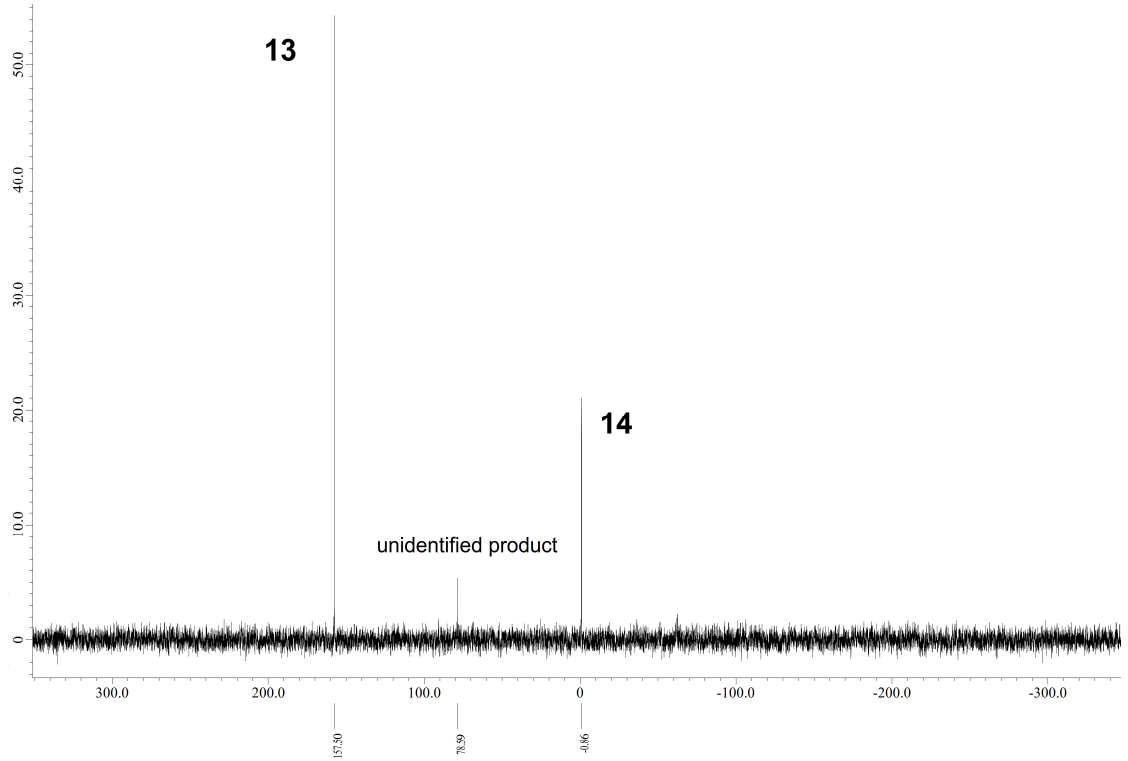


*Figure 41: ^{31}P-NMR spectrum (162 MHz) of the crude reaction mixture containing **13**, **14**, and an unidentified product.*

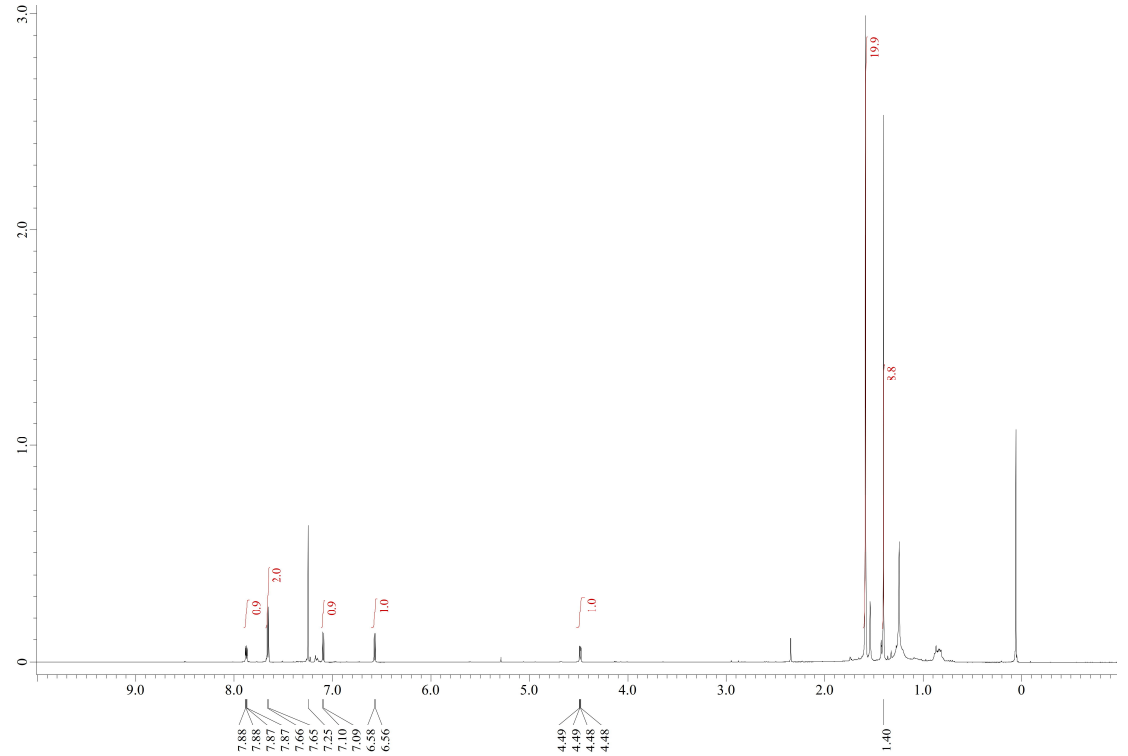


*Figure 42: ^{1}H-NMR spectrum (400 MHz) of **13**.*

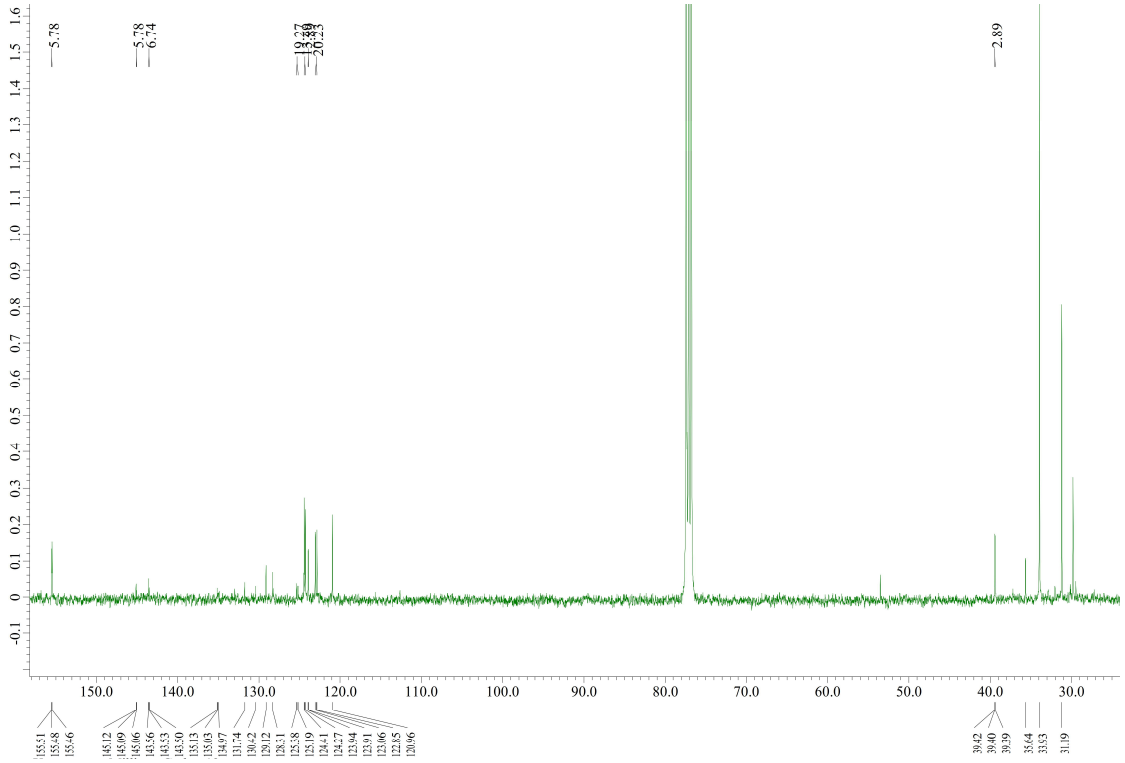


*Figure 43: ^{13}C-NMR spectrum (101 MHz) of **13**.*

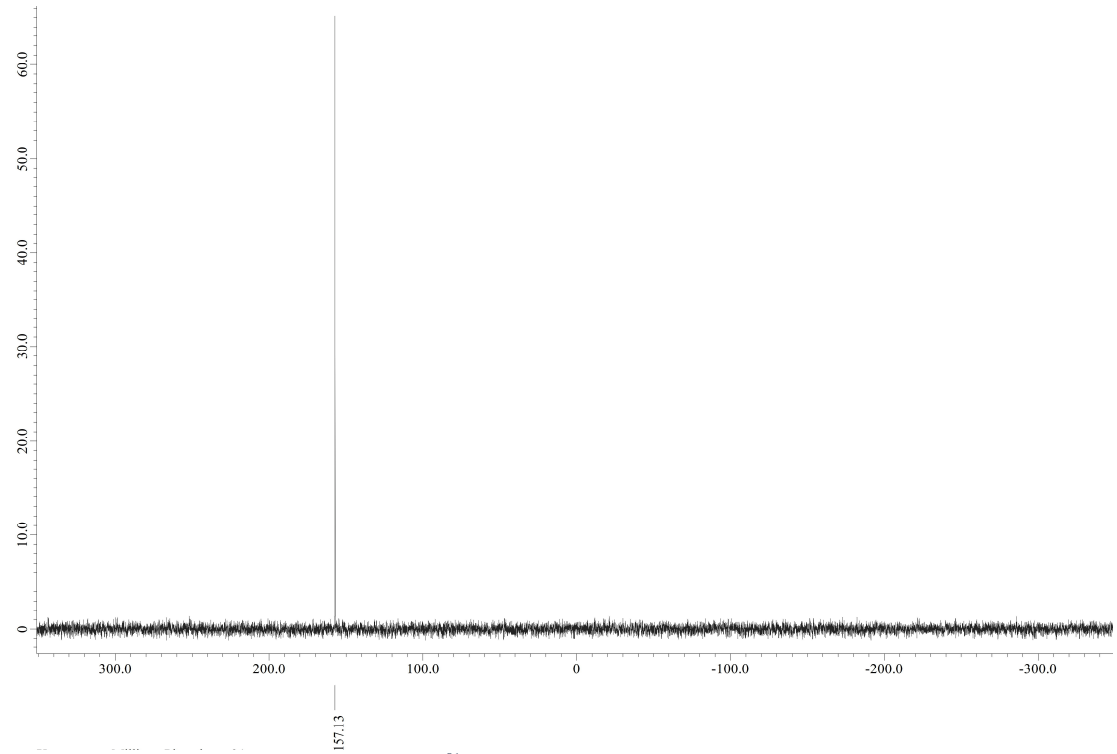


*Figure 44: ^{31}P-NMR spectrum (162 MHz) of **13**.*

The species with the ^{31}P NMR resonance of -0.86 ppm was isolated and tentatively assigned to thiaphosphorane **14** based on 2D NMR analysis.

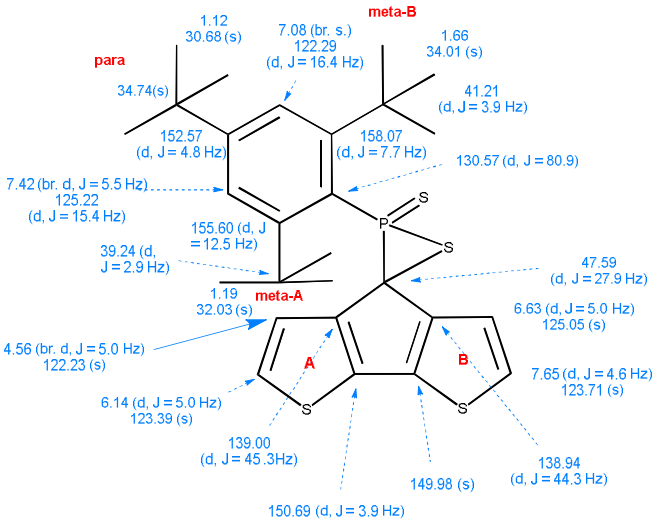


*Figure 45: Schematic representation of **14** indicating the assignment of the proton and carbon resonances, based on 2D correlations experiments.*

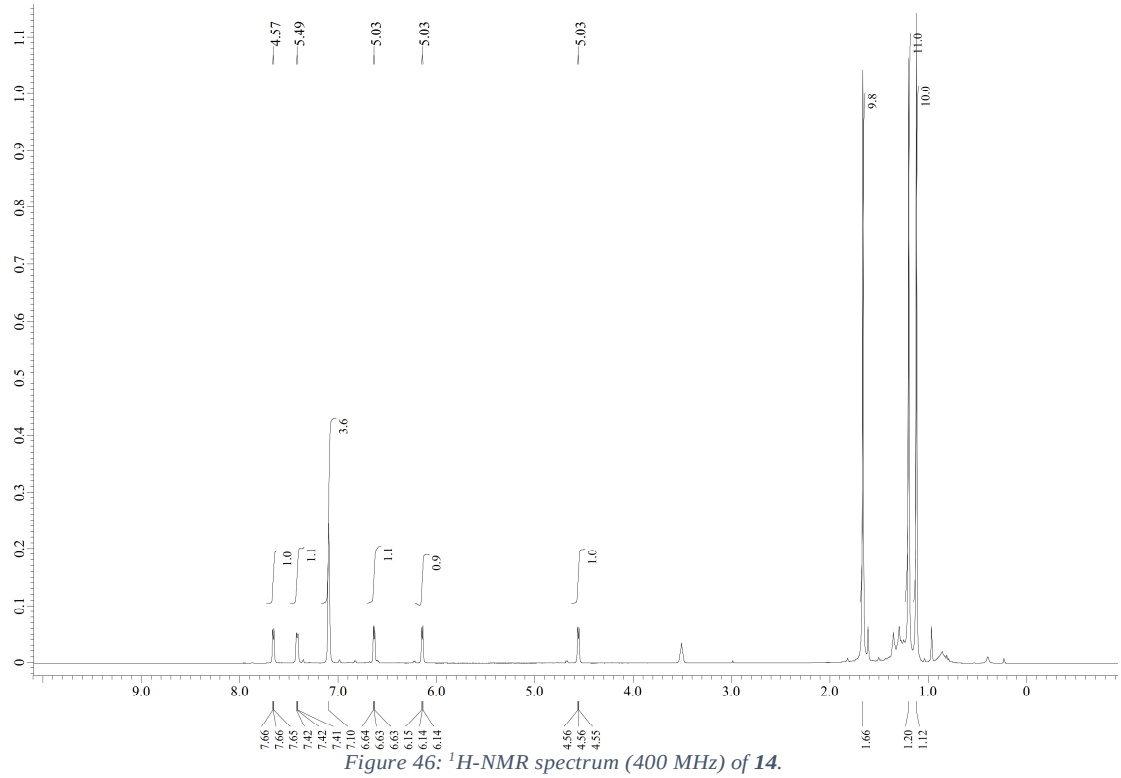


*Figure 46: ^{1}H-NMR spectrum (400 MHz) of **14**.*

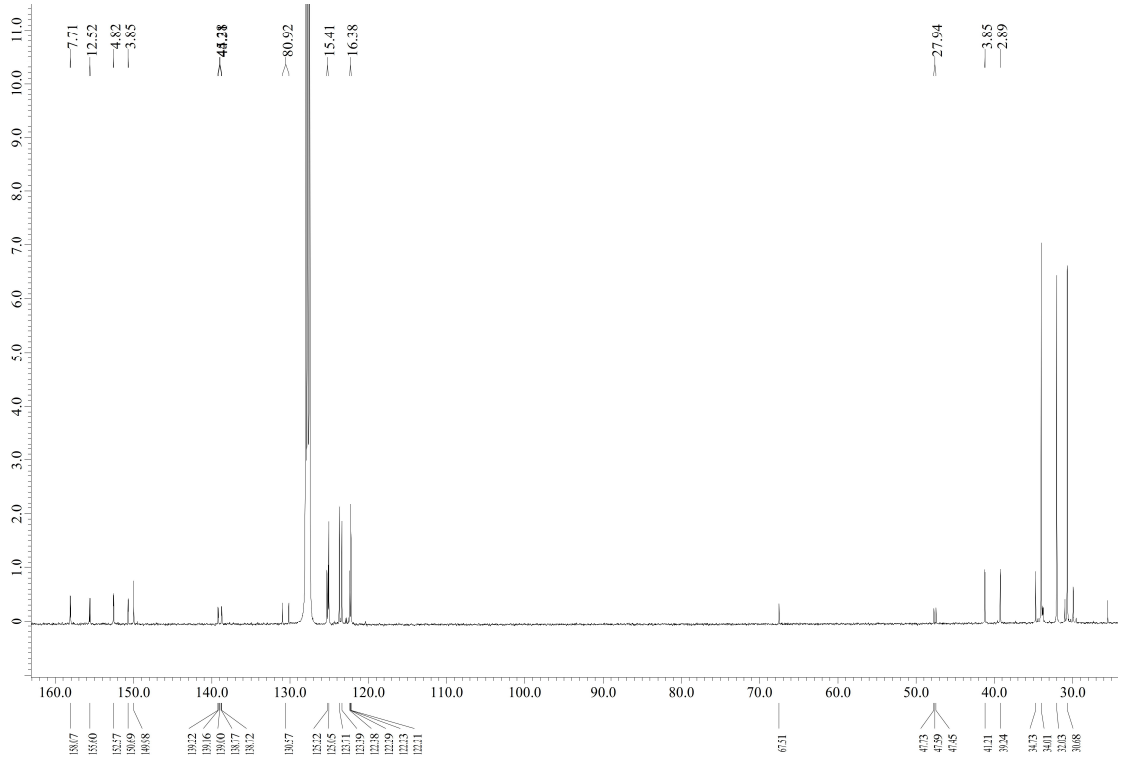


*Figure 47: ^{13}C-NMR spectrum (101 MHz) of **14**.*

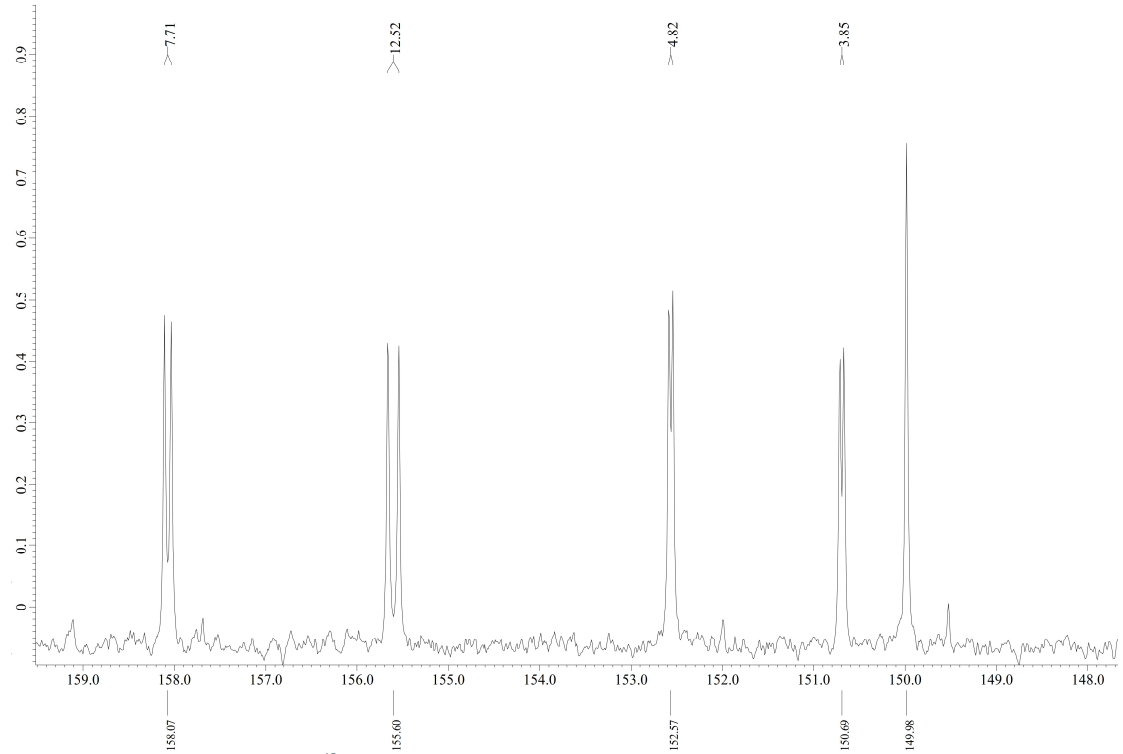


*Figure 48: ^{13}C-NMR spectrum (101 MHz) of **14** in the 160-147 ppm range.*

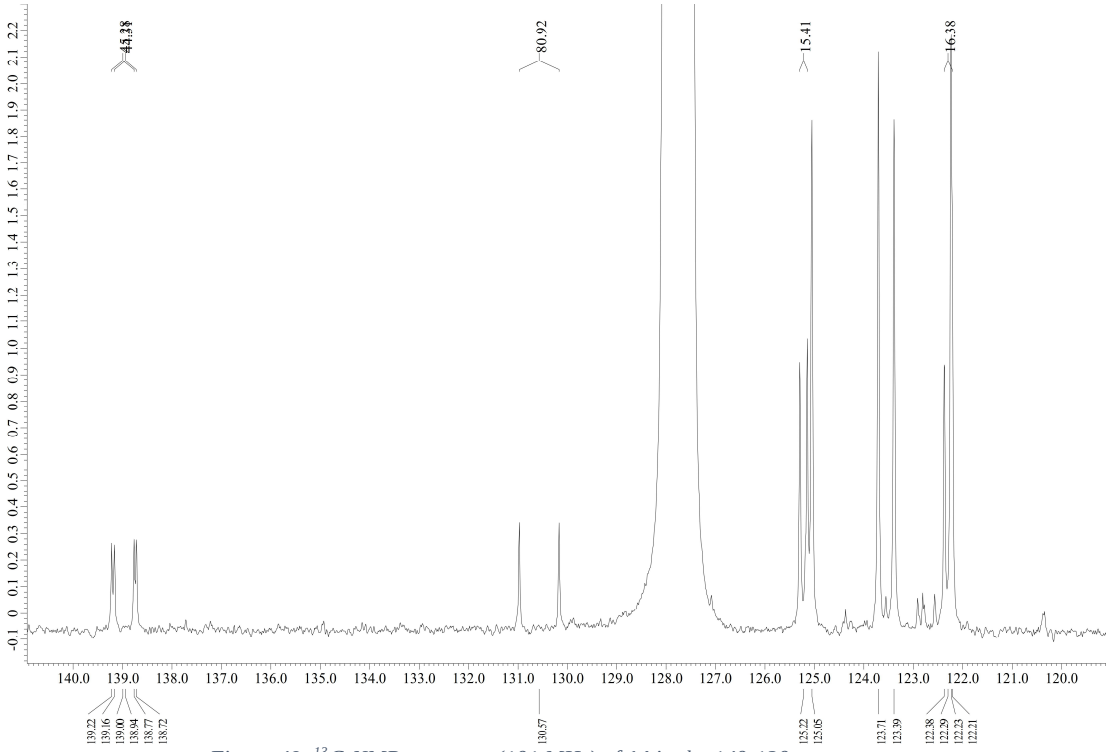


*Figure 49: [13]C-NMR spectrum (101 MHz) of **14** in the 140-120 ppm range.*

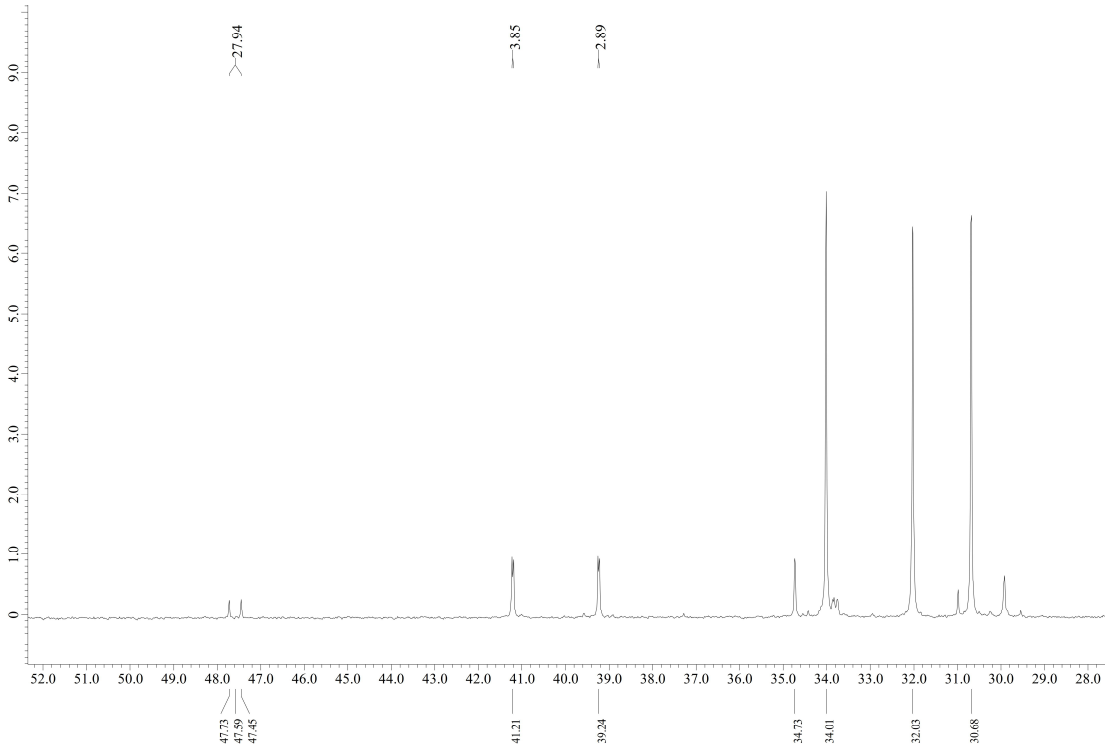


*Figure 50: [13]C-NMR spectrum (101 MHz) of **14** in the 52-28 ppm range.*

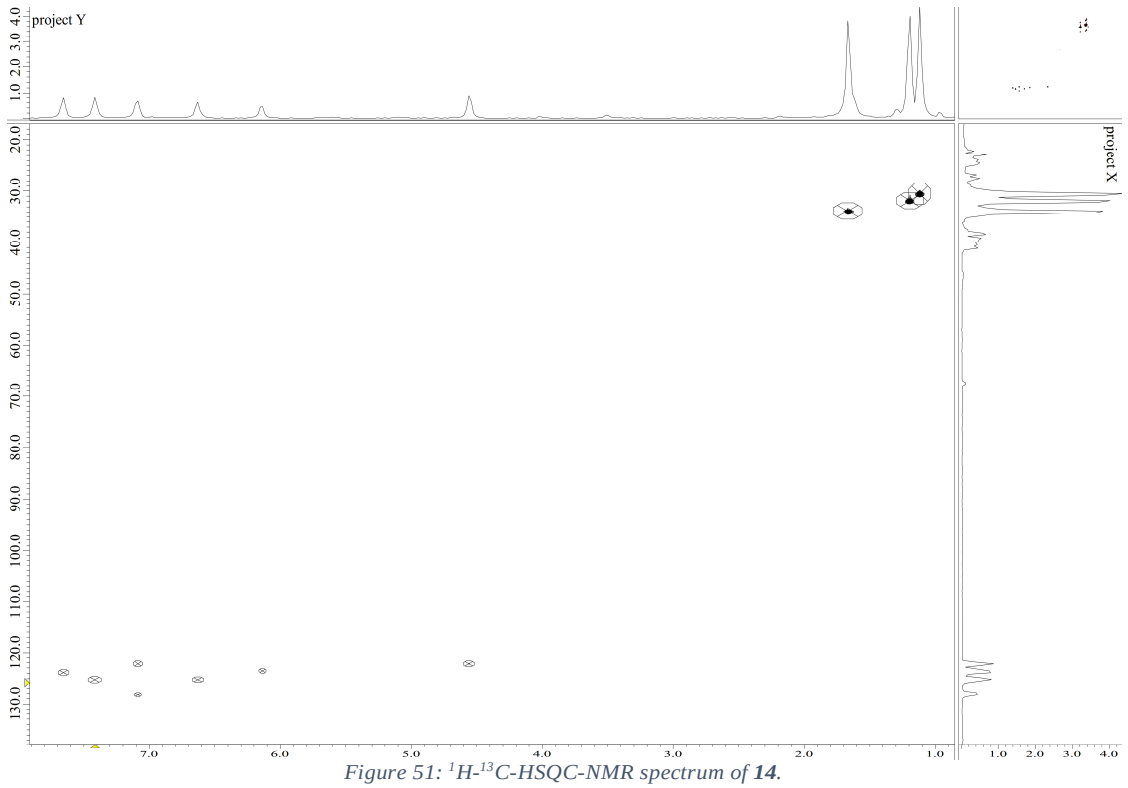


*Figure 51: ^{1}H-^{13}C-HSQC-NMR spectrum of **14**.*

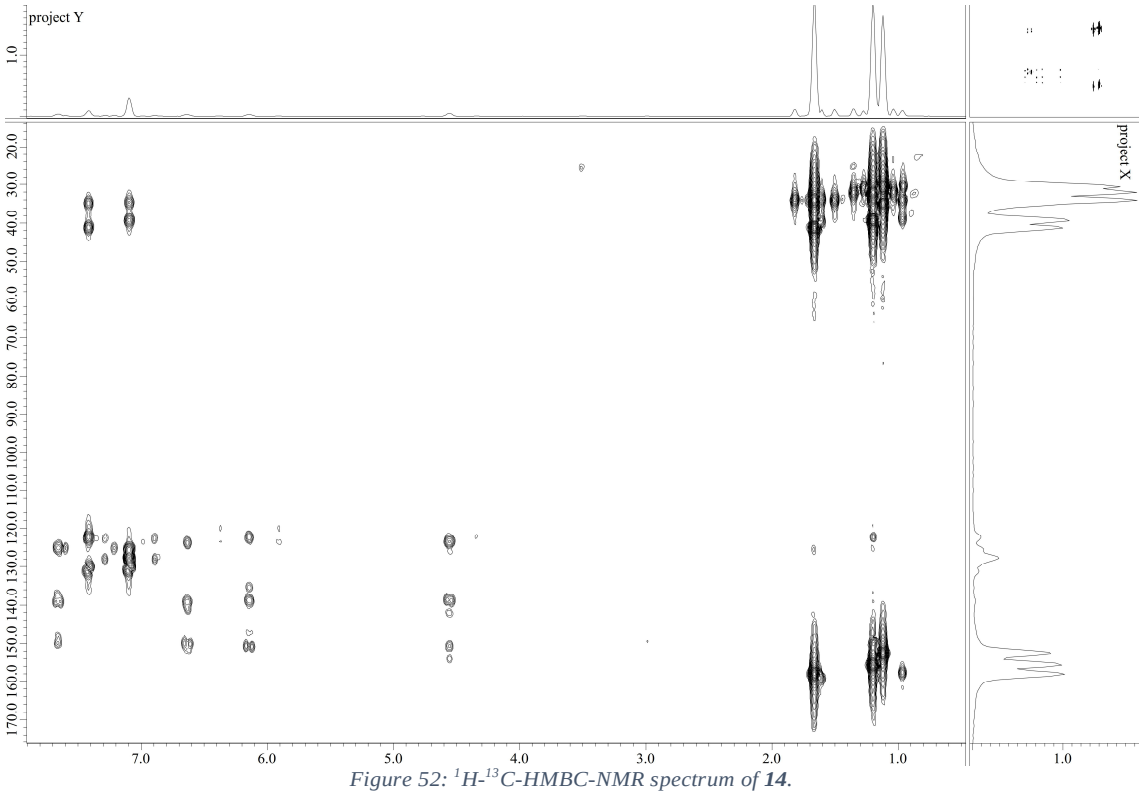


*Figure 52: ^{1}H-^{13}C-HMBC-NMR spectrum of **14**.*

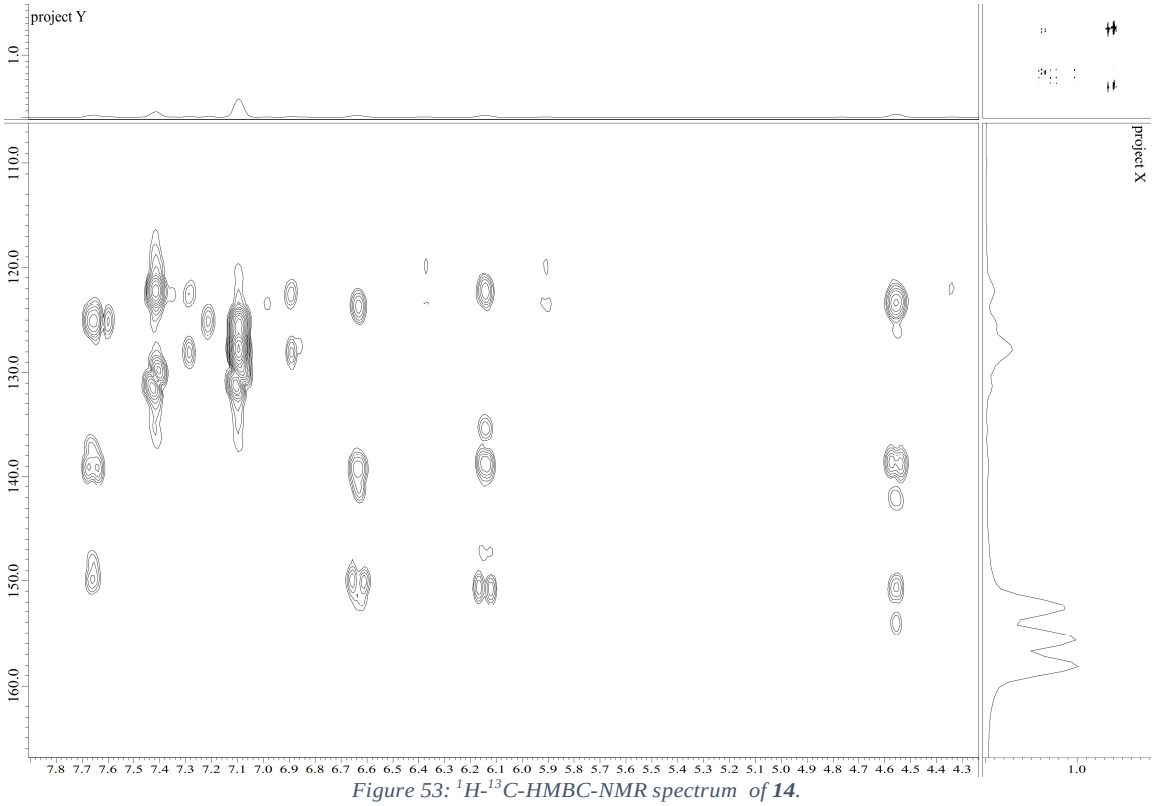


*Figure 53: ^{1}H-^{13}C-HMBC-NMR spectrum of **14**.*

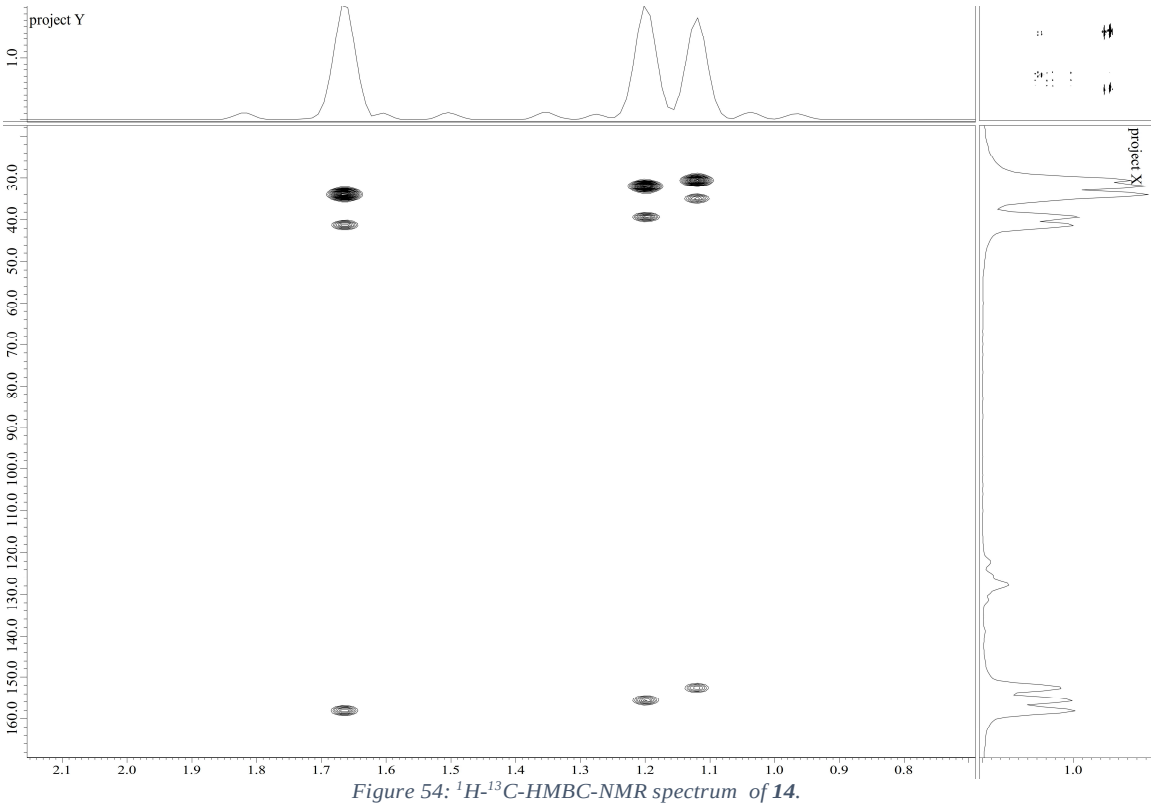


*Figure 54: ^{1}H-^{13}C-HMBC-NMR spectrum of **14**.*

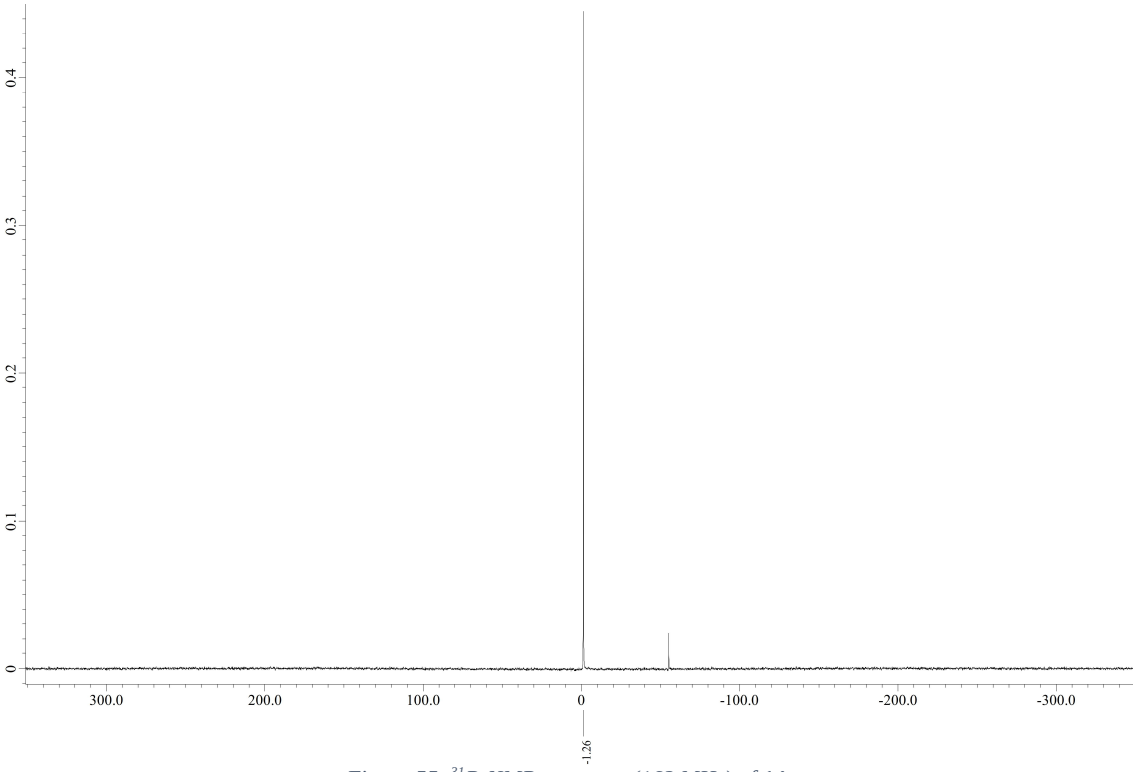
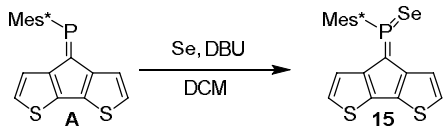


*Figure 55: ^{31}P-NMR spectrum (162 MHz) of **14**.*

Synthesis of **15**.



*Scheme 13: Oxidation of **A** with grey selenium yielding **15**.*

Excess of grey selenium (ca. 150 mg) is suspended in a solution of phosphaalkene **A** (150 mg, 0.33 mmol, 15 ml dry DCM). Two drops of DBU are added triggering the reaction. Reaction is monitored by ^{31}P NMR spectroscopy showing approximate 60% conversion after 4 hours, however no further conversion could be achieved at longer reaction times or at elevated temperatures. All volatiles are removed under vacuum and the crude is subjected to column chromatography (alumina DCM/pentane) yielding **15** in very low yields (ca 18 mg <20%). The low isolated yields are owed to partial decomposition on alumina/DCM.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 5.2, 2.2 Hz, 1H), 7.66 (d, *J* = 5.5 Hz, 2H), 7.08 (d, *J* = 5.0 Hz, 1H), 6.55 (d, *J* = 5.0 Hz, 1H), 4.53 (dd, *J* = 5.1, 1.2 Hz, 1H), 1.61 (s, 18H), 1.40 (s, 9H).
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ 155.80 (D, *J* = 6.0 Hz), 155.32 (d, *J* = 3.4 Hz), 154.40, 151.32, 145.69 (d, *J* = 6.7 Hz), 144.83 (d, *J* = 2.9 Hz), 138.77 (d, *J* = 115.6 Hz), 135.37 (d, *J* = 25 Hz), 133.34, 126.70, 126.10, 124.57, 124.45, 123.93 (d, *J* = 2.9 Hz), 123.21 (d, *J* = 2,9 Hz), 122.62 (d, *J* = 1.9 Hz), 122.36, 121.33, 39.57 (d, *J* = 2.9 Hz), 35.62, 34.21, 31.21. (the ortho and meta positions of the Mes* substituent are not magnetically equivalent on the timescales of ^{13}C experiments).
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 144.2 (7% satellites: $^{1}J_{PSe}$ = 915 Hz) ppm.
FTMS+p LDI (*m/z*): $[M+H]^+$ calc. 533.099963 found 533.099929.

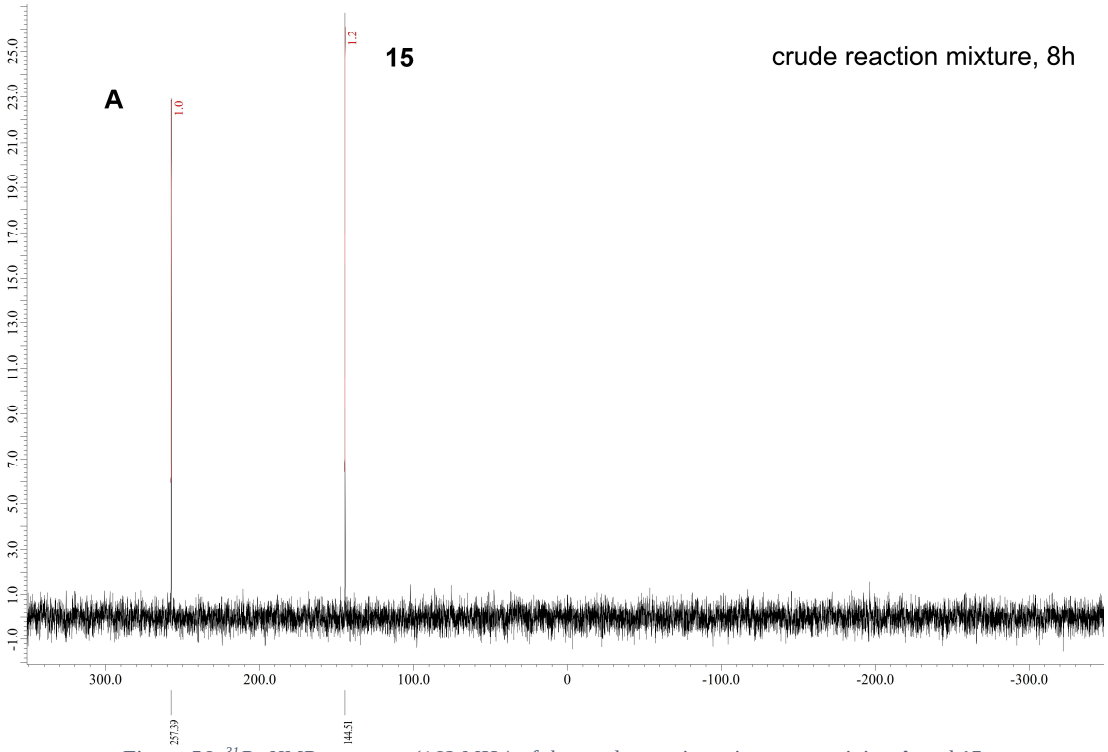


*Figure 56: ^{31}P- NMR spectrum (162 MHz) of the crude reaction mixture containing **A** and **15**.*

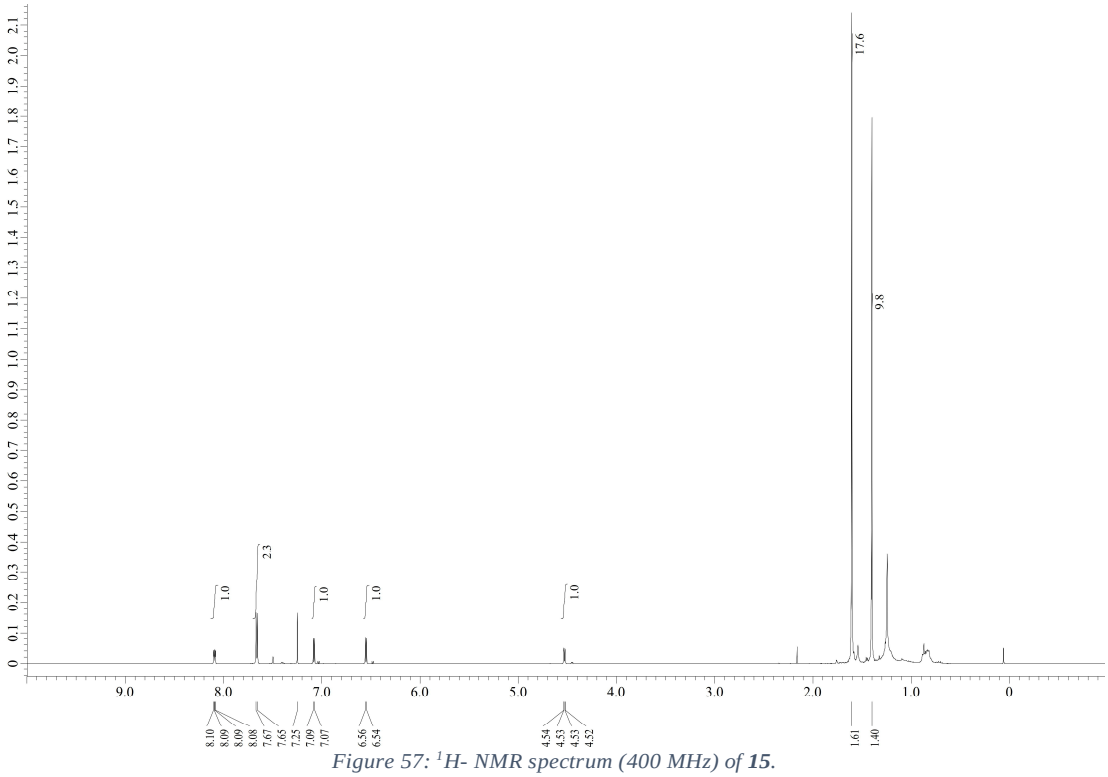


*Figure 57: ^{1}H- NMR spectrum (400 MHz) of **15**.*

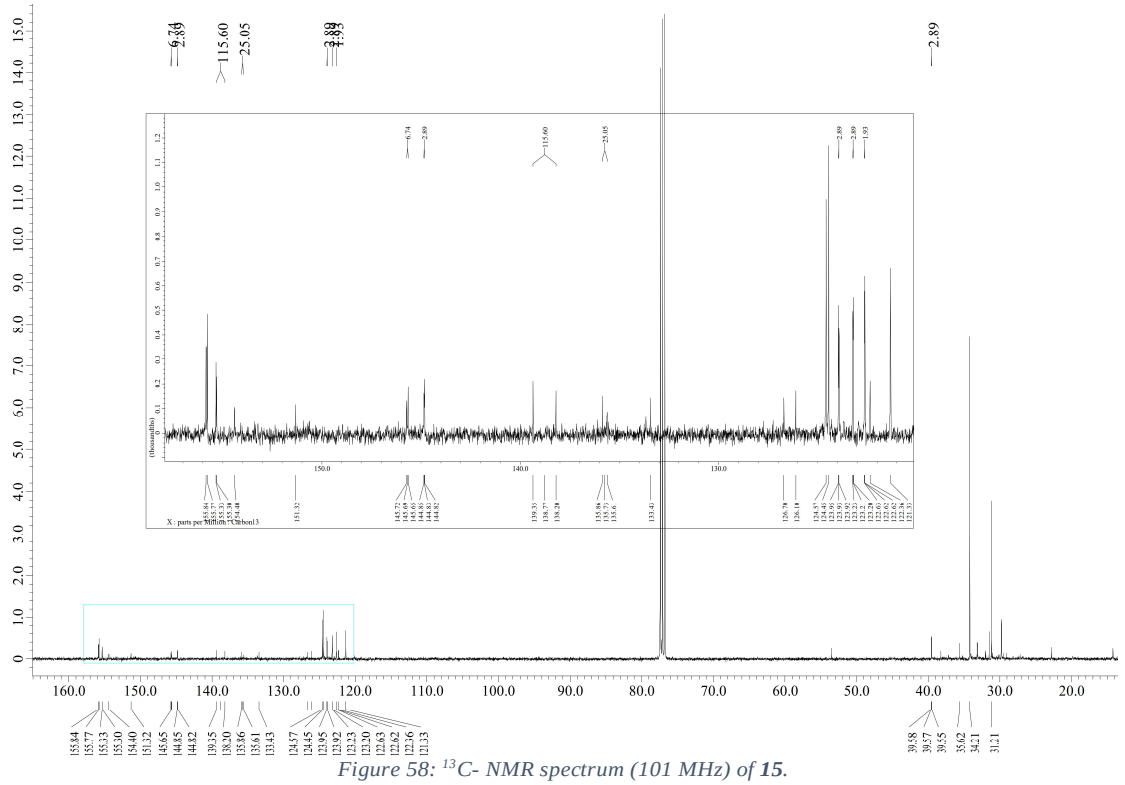


*Figure 58: ^{13}C- NMR spectrum (101 MHz) of **15**.*

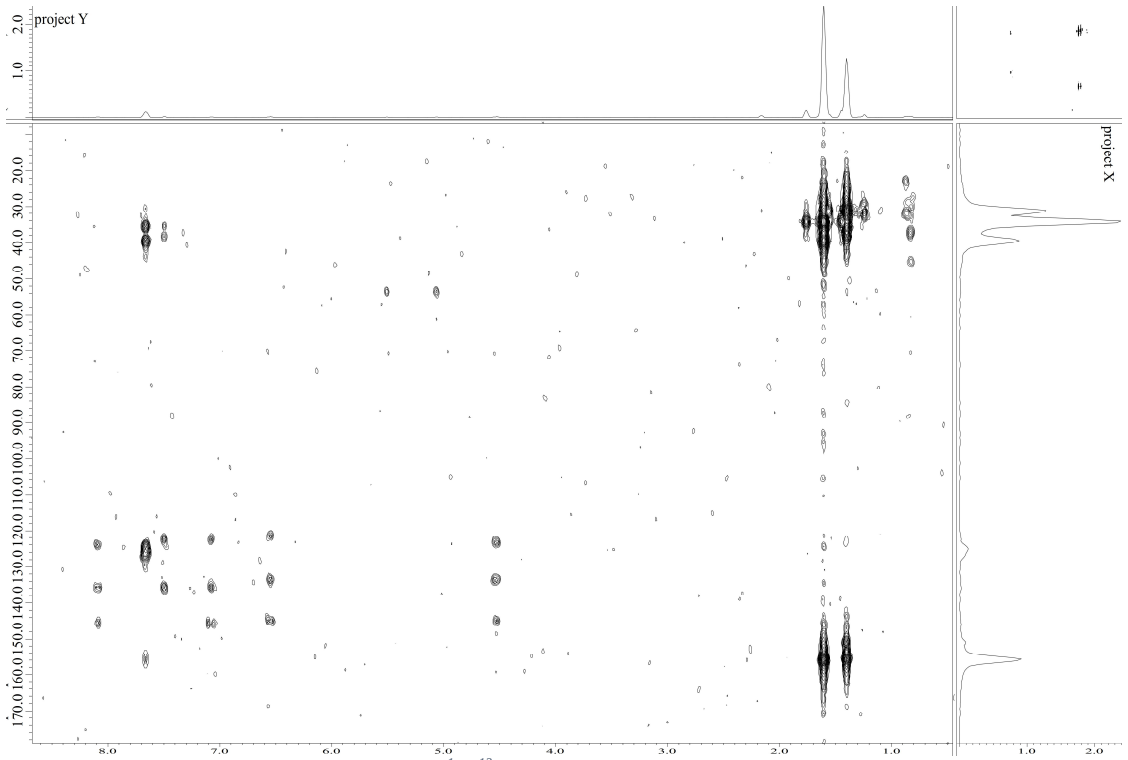


*Figure 59: ^{1}H-^{13}C-HMBC NMR spectrum of **15**.*

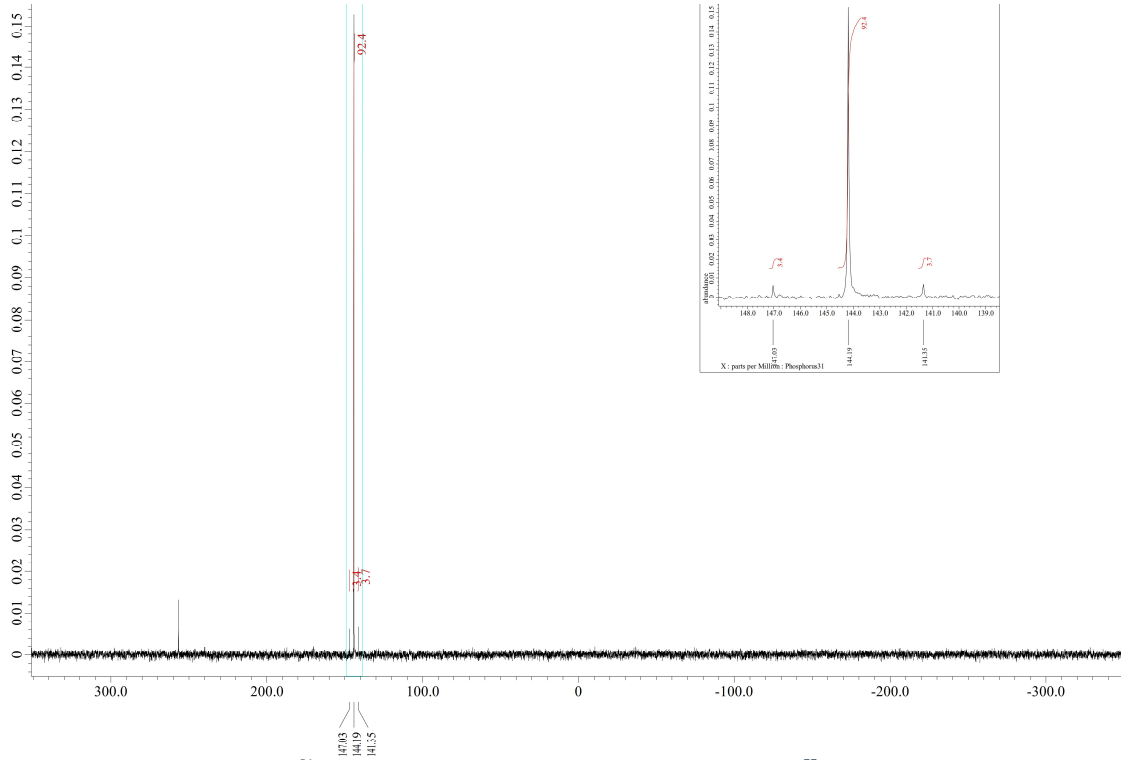


*Figure 60: ^{31}P- NMR spectrum (162 MHz) of **15**, highlighting the ^{77}Se satellites.*

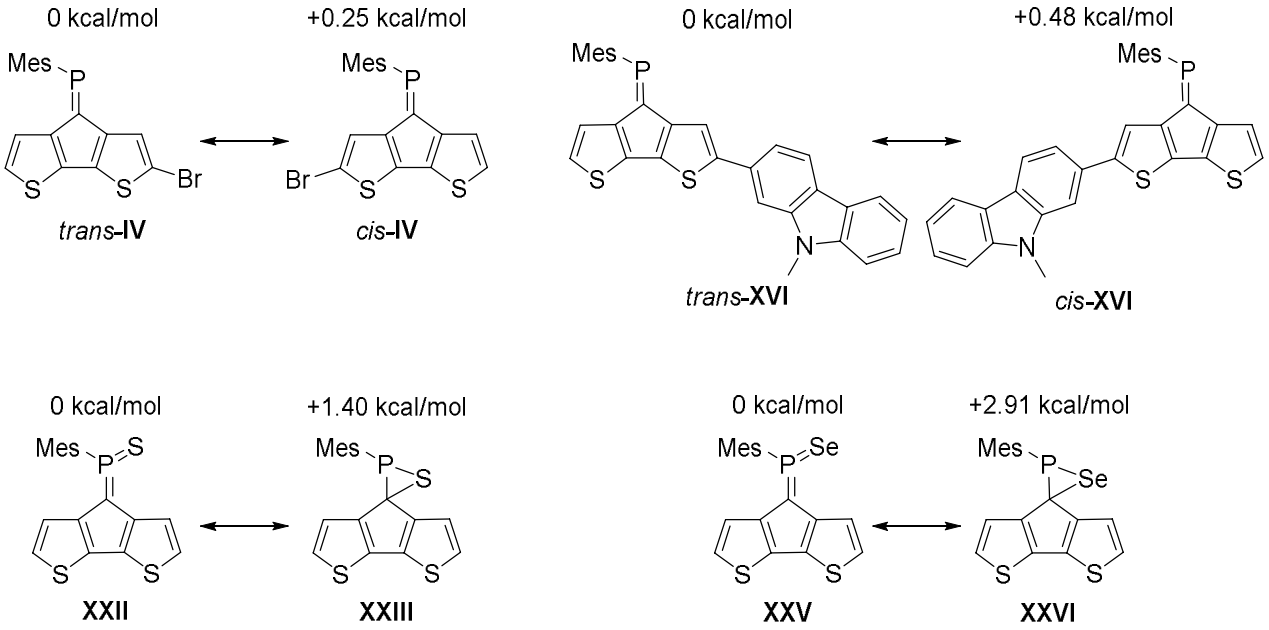
Computational details

Theoretical calculations have been carried out using the Gaussian suite of programs (G09. Rev. D01). The structures are optimized at the DFT cam-B3LYP/6-311G** level of theory using a continuum solvation model (IEF-PCM) for DCM. UV-vis spectra have been simulated at the same level of theory using the TD-DFT approach.

Summary of calculated structures.

Table 2: Calculated energies for structures cis- and trans- ***IV****, cis- and trans-* ***XVI****,* ***XXII****,* ***XXIII****,* ***XXV*** *and* ***XXVI****. (DFT,*

	trans-**IV**	*cis*-**IV**	*trans*-**XVI**	*cis*-**XVI**	**XXII**	**XXIII**	**XXV**	**XXVI**
Zero-point Correction (Hartree/Particle)	0.265723	0.265568	0.462083	0.462185	0.277983	0.278366	0.277373	0.277572
Thermal Correction to								
Energy	0.287178	0.287082	0.493178	0.493195	0.29955	0.299245	0.299211	0.29879
Enthalpy	0.288122	0.288026	0.494122	0.49414	0.300494	0.300189	0.300155	0.299734
Gibbs Free Energy	0.211879	0.211497	0.395795	0.396641	0.224795	0.22722	0.222854	0.225472
SumOf electronic and								
zero-point Energies	-4405.82148	-4405.82165	-2387.39798	-2387.39796	-2230.39705	-2230.39686	-4233.83175	-4233.82952
thermal Energies	-4405.80002	-4405.80014	-2387.36688	-2387.36695	-2230.37548	-2230.37598	-4233.80991	-4233.80831
thermal Enthalpies	-4405.79908	-4405.79919	-2387.36594	-2387.366	-2230.37454	-2230.37504	-4233.80897	-4233.80736
thermal Free Energies	-4405.87532	-4405.87572	-2387.46427	-2387.4635	-2230.45024	-2230.448	-4233.88627	-4233.88162



Scheme 14: Relative energies of isomers trans- and cis- ***IV****, trans- and cis-* ***XVI****,* ***XXII*** *and* ***XXIII****, and* ***XXV*** *and* ***XXVI****.*

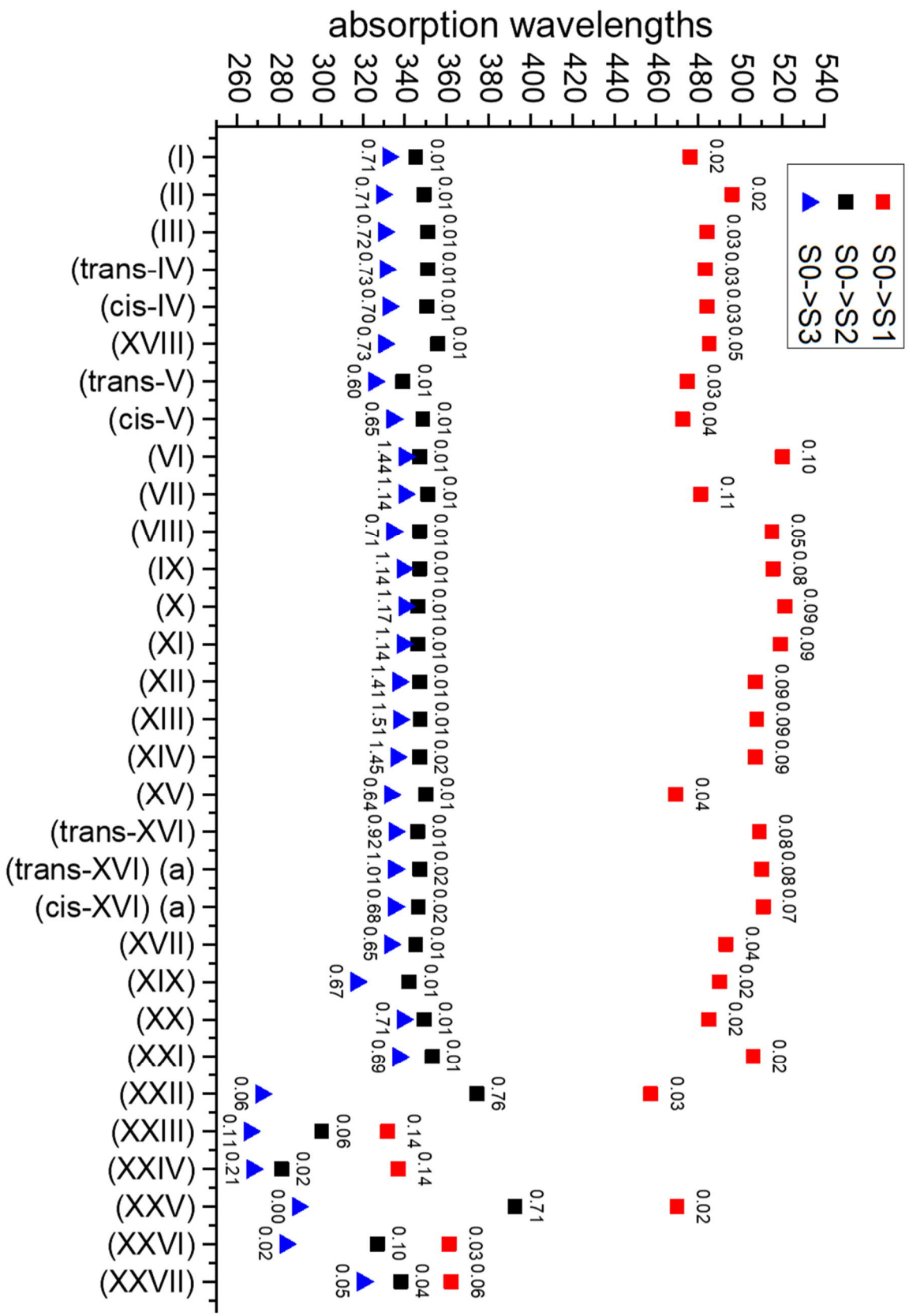


Figure 61: Lowest three allowed transition wavelengths (y-axis) with indicated transition probabilities of the theoretically studied derivatives.

*Table 3: XYZ coordinates for calculated structure **I**.*

	X	Y	Z
S	0	0	0
C	0	0	1.710672
C	1.276786	0	2.238151
C	2.280230	-0.000046	1.227888
C	1.739095	0.000031	-0.019791
C	1.185862	-0.000292	3.709982
C	-0.269041	-0.000512	3.986441
C	-0.957603	-0.000318	2.794537
S	-2.655897	-0.000415	3.024306
C	-2.440102	-0.000692	4.750424
C	-1.130383	-0.000663	5.117164
P	2.334261	-0.000444	4.932646
C	3.947429	0.001017	4.050121
C	4.585590	-1.212355	3.758700
C	5.836078	-1.187934	3.146265
C	6.472531	0.003734	2.826564
C	5.828828	1.197174	3.140659
C	4.581572	1.218913	3.751334
C	3.939020	-2.538289	4.066650
C	3.926710	2.541906	4.054191
C	7.826026	0.014847	2.168953
H	2.251794	0.000035	-0.968679
H	3.344579	-0.000271	1.408559
H	-0.805960	-0.000744	6.148469
H	-3.310938	-0.000844	5.386777
H	6.313989	2.139376	2.905997
H	6.324924	-2.129045	2.916875
H	4.615760	3.366137	3.870015
H	3.041786	2.697481	3.432201
H	3.601477	2.602266	5.096173
H	4.635428	-3.358501	3.892427
H	3.607545	-2.594255	5.106899
H	3.059353	-2.705038	3.440059
H	8.186617	-0.997586	1.985781
H	7.792898	0.540897	1.211908
H	8.560796	0.527617	2.794347

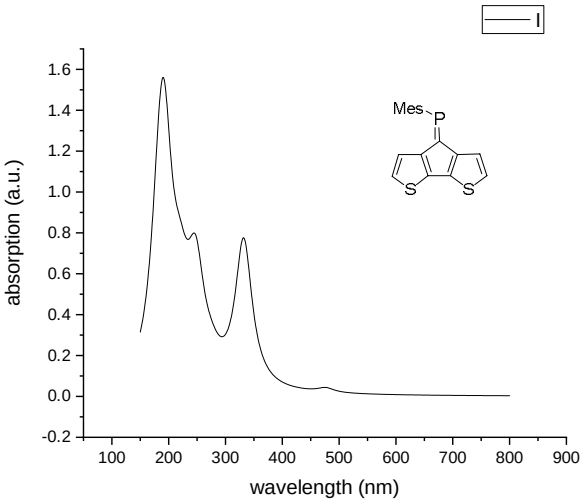


*Figure 62: Calculated UV/vis spectrum of **I**.*

*Table 4: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **I**.*

Excited State 3	Singlet-A	2.6026 eV
476.38 nm	f=0.0218	<S**2>=0.000
	85 -> 86	0.70017
Excited State 6	Singlet-A	3.5848 eV
345.86 nm	f=0.0066	<S**2>=0.000
	79 -> 86	0.22278
	83 -> 86	0.65328
Excited State 8	Singlet-A	3.7353 eV
331.93 nm	f=0.7123	<S**2>=0.000
	84 -> 86	0.70048
Excited State 13	Singlet-A	4.3882 eV
282.54 nm	f=0.0081	<S**2>=0.000
	81 -> 86	0.13474
	82 -> 86	0.68502
Excited State 15	Singlet-A	4.5139 eV
274.67 nm	f=0.0522	<S**2>=0.000
	81 -> 86	0.66971
	82 -> 86	-0.13813
	85 -> 88	0.11920

*Table 5: XYZ coordinates for calculated structure **II**.*

	X	Y	Z
C	0	0	0
C	0	0	1.404126
C	1.213303	0	2.107538
C	2.407016	-0.028421	1.393049
C	2.430021	-0.044007	0.003991
C	1.215337	-0.028304	-0.673565
P	-1.589679	0.111820	2.319852
C	-2.037145	-1.483981	2.576595
C	-1.424468	-2.777605	2.223359
C	-2.232078	-3.797387	2.687757
C	-3.380488	-3.219299	3.348816
C	-3.280188	-1.851272	3.291539
C	-0.265528	-3.266738	1.556455
C	-0.231028	-4.626084	1.536374
S	-1.603660	-5.346041	2.326119
S	-4.800311	-3.753382	4.165400
C	-5.237862	-2.082137	4.417015
C	-4.369547	-1.176574	3.918051
F	-6.371626	-1.828117	5.068875
C	1.251464	-0.001188	3.614041
C	3.731528	-0.043081	-0.751220
C	-1.284935	-0.000838	-0.787347
H	0.520064	-5.268049	1.104132
H	0.503310	-2.651258	1.114301
H	-4.510609	-0.108972	3.999351
H	1.212854	-0.037051	-1.758838
H	3.344371	-0.037450	1.939634
H	-1.087272	0.129876	-1.851200
H	-1.827628	-0.940606	-0.658824
H	-1.954070	0.803038	-0.469105
H	2.270802	0.133299	3.975724
H	0.637863	0.800123	4.034290
H	0.872177	-0.942612	4.019126
H	4.553291	-0.395487	-0.126927
H	3.675924	-0.678015	-1.637114
H	3.981795	0.966444	-1.089192
H	3.675924	-0.678015	-1.637114
H	3.981795	0.966444	-1.089192

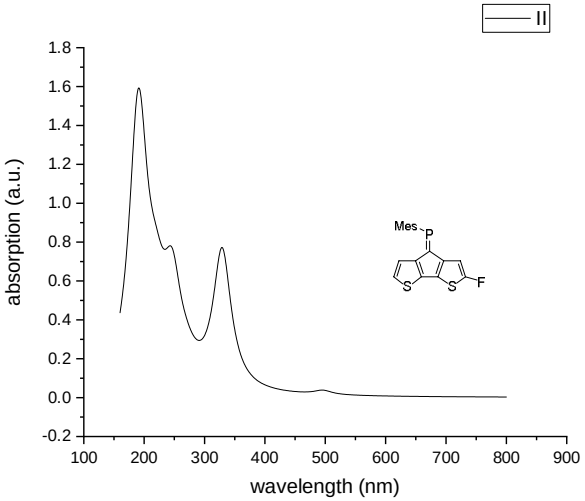


*Figure 63: Calculated UV/vis spectrum of **II**.*

*Table 6: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **II**.*

Excited State 3	Singlet-A	2.4987 eV
496.19 nm	f=0.0213	<S**2>=0.000
	89 -> 90	0.70102
Excited State 6	Singlet-A	3.5448 eV
349.76 nm	f=0.0062	<S**2>=0.000
	83 -> 90	0.22328
	87 -> 90	0.65557
Excited State 8	Singlet-A	3.7672 eV
329.11 nm	f=0.7094	<S**2>=0.000
	88 -> 90	0.70020
Excited State 13	Singlet-A	4.3354 eV
285.98 nm	f=0.0050	<S**2>=0.000
	86 -> 90	0.69955
Excited State 15	Singlet-A	4.5396 eV
273.12 nm	f=0.0066	<S**2>=0.000
	83 -> 90	0.65116
	87 -> 90	-0.21662

*Table 7: XYZ coordinates for calculated structure **III**.*

	X	Y	Z
C	4.608344	1.226061	3.825482
C	3.964127	0.013482	4.113383
C	4.590927	-1.206101	3.813104
C	5.840088	-1.188635	3.203267
C	6.490049	0.001314	2.894663
C	5.857988	1.196841	3.215293
P	2.346371	0.022052	4.983742
C	1.209300	0.009179	3.750833
C	1.310999	-0.004822	2.280842
C	0.039682	-0.017657	1.738197
C	-0.924864	-0.013742	2.811825
C	-0.247291	0.004592	4.012053
C	2.324005	-0.008705	1.280642
C	1.792822	-0.024288	0.028586
S	0.056003	-0.035087	0.027904
S	-2.625164	-0.013085	3.005160
C	-2.424573	0.010417	4.739209
C	-1.118798	0.017849	5.126918
C	-3.605858	-0.010478	5.633551
C	3.927885	-2.526921	4.107519
C	7.855701	-0.007663	2.263221
C	3.964231	2.553367	4.132733
H	2.315351	-0.029903	-0.915025
H	3.386637	0.000048	1.469775
H	-0.815814	0.033087	6.163991
H	6.350567	2.136112	2.985767
H	6.319135	-2.132523	2.963879
H	4.666504	3.371047	3.971236
H	3.093196	2.728318	3.496213
H	3.621191	2.606037	5.169477
H	4.617872	-3.352902	3.935680
H	3.586181	-2.585624	5.144321
H	3.052988	-2.681952	3.471171
H	7.976865	-0.860200	1.593273
H	8.036089	0.905403	1.694529
H	8.634490	-0.078937	3.027797
F	-3.248147	0.158859	6.914498
F	-4.494744	0.956968	5.332429
F	-4.288201	-1.172008	5.565339

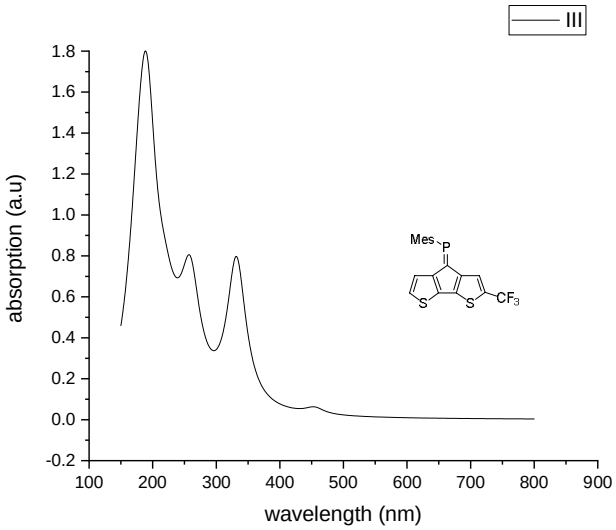


*Figure 64: Calculated UV/vis spectrum of **III**.*

*Table 8: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **III**.*

Excited State 3	Singlet-A	2.7277 eV
454.53 nm	f=0.0320	<S**2>=0.000
	101 ->102	0.69956
Excited State 6	Singlet-A	3.4998 eV
354.26 nm	f=0.0073	<S**2>=0.000
	96 ->102	0.21471
	99 ->102	0.65232
	99 ->103	-0.10520
Excited State 8	Singlet-A	3.7374 eV
331.74 nm	f=0.7214	<S**2>=0.000
	100 ->102	0.69823
Excited State 14	Singlet-A	4.2651 eV
290.70 nm	f=0.0045	<S**2>=0.000
	98 ->102	0.69845
Excited State 15	Singlet-A	4.4995 eV
275.55 nm	f=0.0066	<S**2>=0.000
	96 ->102	0.64913
	96 ->103	-0.11435
	99 ->102	-0.21114

*Table 9: XYZ coordinates for calculated structure trans-**IV**.*

	X	Y	Z
C	-3.759320	-1.212577	4.504682
C	-3.422697	0.002114	3.888566
C	-3.748980	1.219270	4.506994
C	-4.381772	1.197693	5.744718
C	-4.711156	0.005594	6.380272
C	-4.392475	-1.187674	5.742989
P	-2.653152	-0.000210	2.219907
C	-1.003185	0.000068	2.520989
C	0.002934	-0.000148	1.434298
C	1.264012	0.000871	1.983896
C	1.140433	0.001620	3.423660
C	-0.200466	0.001034	3.757141
S	2.501301	0.000912	0.793947
C	1.287786	-0.000412	-0.459817
C	0.014346	-0.000904	0.013370
S	2.157238	0.002681	4.798946
C	0.770422	0.002005	5.846999
C	-0.406725	0.001257	5.165950
Br	1.811613	-0.001091	-2.265019
C	-3.401126	2.542520	3.875331
C	-5.424470	0.009759	7.705078
C	-3.422505	-2.537944	3.871428
H	0.922081	0.002305	6.914833
H	-1.369437	0.000770	5.654238
H	-0.856861	-0.001740	-0.625275
H	-4.625008	2.140006	6.224968
H	-4.644009	-2.128702	6.221313
H	-3.850339	3.366076	4.430204
H	-2.319898	2.700471	3.855867
H	-3.753570	2.602385	2.842187
H	-3.880907	-3.358280	4.423556
H	-3.772738	-2.592610	2.837237
H	-2.342768	-2.706192	3.854583
H	-5.227094	-0.905180	8.265061
H	-5.119459	0.860225	8.316682
H	-6.506332	0.081263	7.561372

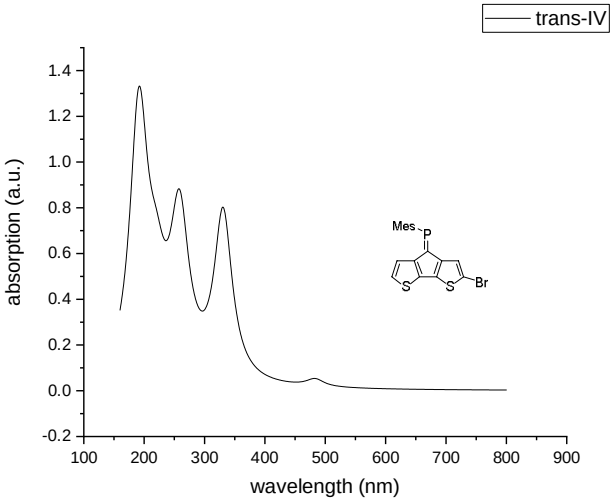


*Figure 65: Calculated UV/vis spectrum of trans-**IV**.*

*Table 10 Contributions to the five lowest energy singlet-singlet excitations for calculated structure trans-**IV**.*

Excited State 3	Singlet-A	2.5662 eV
483.14 nm	f=0.0331	<S**2>=0.000
	102 ->103	0.69841
Excited State 7	Singlet-A	3.5358 eV
350.66 nm	f=0.0062	<S**2>=0.000
	96 ->103	0.22027
	100 ->103	0.65472
Excited State 8	Singlet-A	3.7486 eV
330.74 nm	f=0.7290	<S**2>=0.000
	101 ->103	0.69935
Excited State 13	Singlet-A	4.3172 eV
287.19 nm	f=0.0049	<S**2>=0.000
	99 ->103	0.69883
Excited State 16	Singlet-A	4.5294 eV
273.73 nm	f=0.0065	<S**2>=0.000
	96 ->103	0.65016
	100 ->103	-0.21525

*Table 11: XYZ coordinates for calculated structure cis-**IV**.*

	X	Y	Z
C	-3.757950	-1.211138	4.505125
C	-3.425744	0.004034	3.887304
C	-3.751359	1.220975	4.506752
C	-4.376801	1.198795	5.748181
C	-4.700024	0.006230	6.386040
C	-4.383681	-1.186833	5.747171
P	-2.657282	0.002685	2.217578
C	-1.007621	0.000696	2.520030
C	0.001978	-0.000322	1.437437
C	1.263376	-0.001613	1.989583
C	1.131038	-0.001558	3.428336
C	-0.209001	-0.000246	3.759679
S	2.496571	-0.002732	0.800132
C	1.300695	-0.001493	-0.462251
C	0.027524	-0.000234	0.016451
S	2.152563	-0.002868	4.804054
C	0.750081	-0.001645	5.841206
C	-0.428602	-0.000339	5.166254
H	1.626395	-0.001773	-1.490487
C	-3.410237	2.544514	3.871917
C	-5.405576	0.009386	7.714974
C	-3.424066	-2.536157	3.869505
Br	0.971959	-0.002180	7.708300
H	-1.391198	0.000476	5.653569
H	-0.843879	0.000681	-0.623331
H	-4.618653	2.140707	6.229866
H	-4.630757	-2.127895	6.227674
H	-3.856749	3.367661	4.429540
H	-2.329546	2.704550	3.844214
H	-3.770461	2.602870	2.841369
H	-3.877442	-3.357015	4.424967
H	-3.781979	-2.590942	2.837964
H	-2.344385	-2.703375	3.844433
H	-5.204124	-0.905549	8.273454
H	-5.097995	0.859929	8.325126
H	-6.488319	0.079862	7.577427

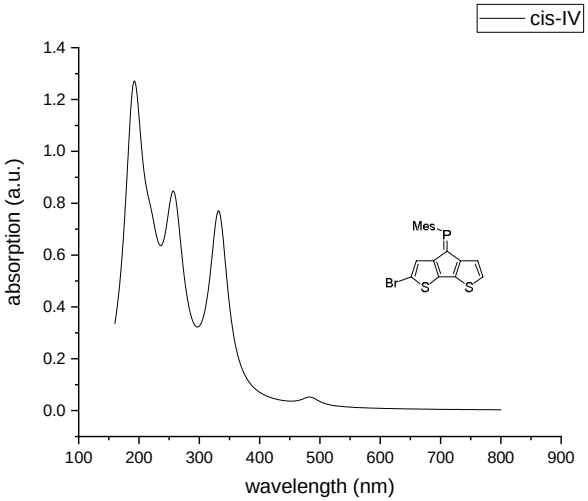


*Figure 66: Calculated UV/vis spectrum of cis-**IV**.*

*Table 12 Contributions to the five lowest energy singlet-singlet excitations for calculated structure cis-**IV**.*

Excited State 3	Singlet-A	2.5612 eV
484.09 nm	f=0.0323	<S**2>=0.000
	102 ->103	0.69767
Excited State 7	Singlet-A	3.5373 eV
350.50 nm	f=0.0061	<S**2>=0.000
	96 ->103	0.21933
	100 ->103	0.65499
Excited State 8	Singlet-A	3.7323 eV
332.19 nm	f=0.7022	<S**2>=0.000
	101 ->103	0.69886
Excited State 13	Singlet-A	4.3184 eV
287.11 nm	f=0.0027	<S**2>=0.000
	99 ->103	0.69887
Excited State 16	Singlet-A	4.5329 eV
273.52 nm	f=0.0064	<S**2>=0.000
	96 ->103	0.64996
	96 ->104	-0.10073
	100 ->103	-0.2145

*Table 13: XYZ coordinates for calculated structure trans-**V**.*

	X	Y	Z
C	-3.644614	2.37982	-1.863736
C	-3.265632	2.017302	-0.568956
C	-2.865747	3.034963	0.304529
C	-2.834684	4.360636	-0.102926
C	-3.211136	4.698096	-1.395741
C	-3.618825	3.705822	-2.274665
Si	-3.250072	0.220245	-0.007328
C	-3.980816	0.125158	1.726171
C	-5.091281	0.906904	2.063798
C	-5.673746	0.825533	3.320548
C	-5.152324	-0.040032	4.271836
C	-4.047466	-0.818680	3.960525
C	-3.469568	-0.735154	2.701236
C	-1.471795	-0.366653	-0.019521
C	-0.344763	0.415205	-0.041191
C	0.856325	-0.333572	-0.000400
C	0.629639	-1.690869	0.048418
S	-1.038587	-2.065319	0.039350
C	1.906828	-2.367230	0.075920
C	2.916963	-1.425129	0.046584
C	2.315175	-0.080075	-0.003727
C	4.210596	-2.017692	0.073332
C	4.140602	-3.374791	0.121615
S	2.506954	-3.967106	0.136081
P	2.958683	1.468203	-0.051855
C	4.779596	1.199095	-0.028726
C	5.468469	1.170003	1.193238
C	6.851140	1.026089	1.186088
C	7.572110	0.922799	0.002879
C	6.872605	0.967787	-1.196380
C	5.490068	1.110900	-1.235012
C	4.739655	1.257598	2.509187
C	4.784709	1.134698	-2.566405
C	9.072064	0.803555	0.020086
C	-4.246223	-0.855247	-1.187911
C	-5.547701	-1.262576	-0.883049
C	-6.290549	-2.021615	-1.776839
C	-5.743677	-2.390608	-2.996868
C	-4.450511	-2.001781	-3.318036
C	-3.711180	-1.244693	-2.420973
H	4.955192	-4.080927	0.149623
H	5.143636	-1.474995	0.057319
H	-0.391271	1.494903	-0.092548
H	7.417524	0.890729	-2.131861
H	7.379411	0.995201	2.133769
H	5.502988	1.188938	-3.384803
H	4.177678	0.237344	-2.709294
H	4.112940	1.992801	-2.651571
H	5.443404	1.352357	3.336457
H	4.066027	2.117858	2.540744
H	4.130579	0.367402	2.684402
H	9.418456	0.271728	0.907671
H	9.439106	0.273212	-0.859900
H	9.539670	1.792339	0.026747
H	-5.503562	1.59978	1.337732
H	-6.532521	1.442209	3.559075
H	-5.603408	-0.103308	5.255225
H	-3.631071	-1.491514	4.701095
H	-2.601136	-1.345549	2.481673
H	-5.986621	-0.991613	0.070557
H	-7.296901	-2.329123	-1.517528
H	-6.321584	-2.985189	-3.694761
H	-4.014928	-2.293702	-4.266492
H	-2.697274	-0.960442	-2.682435
H	-2.582525	2.791271	1.323198
H	-2.520446	5.132025	0.590448
H	-3.19043	5.733471	-1.715221
H	-3.920124	3.963943	-3.283221
H	-3.971753	1.617771	-2.562142

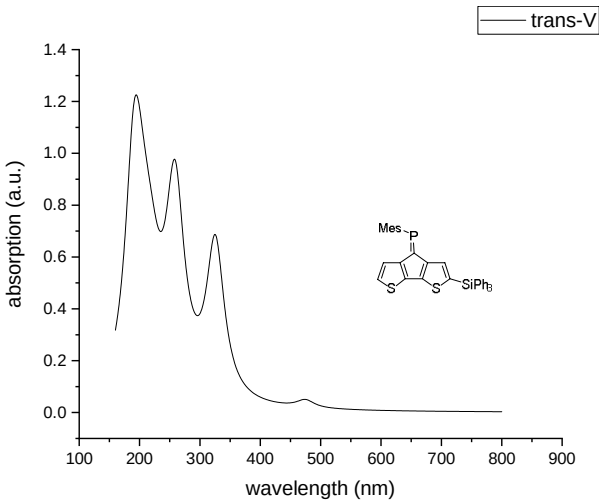


*Figure 67: Calculated UV/vis spectrum of trans-**V**.*

*Table 14 Contributions to the five lowest energy singlet-singlet excitations for calculated structure trans-**V**.*

Excited State 3	Singlet-A	2.6122 eV
474.63 nm	f=0.0302	<S**2>=0.000
	153 ->154	0.69797
Excited State 10	Singlet-A	3.6578 eV
338.96 nm	f=0.0052	<S**2>=0.000
	141 ->154	0.22561
	151 ->154	0.65088
Excited State 12	Singlet-A	3.8102 eV
325.40 nm	f=0.5971	<S**2>=0.000
	152 ->154	0.69729
Excited State 16	Singlet-A	4.4484 eV
278.72 nm	f=0.0154	<S**2>=0.000
	143 ->154	0.19449
	144 ->154	0.22542
	145 ->154	0.33090
	146 ->154	0.16129
	147 ->154	-0.22052
	148 ->154	-0.13257
	150 ->154	0.38091
	153 ->155	-0.16263
	153 ->156	0.12272
Excited State 18	Singlet-A	4.5264 eV
273.91 nm	f=0.0066	<S**2>=0.000
	143 ->154	-0.11806
	144 ->154	-0.13697
	145 ->154	-0.20114
	146 ->154	-0.10991
	147 ->154	0.16037
	148 ->154	0.10865
	150 ->154	0.58701
	153 ->155	0.10650

*Table 15: XYZ coordinates for calculated structure cis-**V**.*

C	3.150673	2.302277	-0.475464
C	2.332952	1.272178	-0.949814
C	1.667163	1.473519	-2.164403
C	1.818125	2.653026	-2.880504
C	2.639456	3.661379	-2.393295
C	3.304452	3.484769	-1.187777
Si	2.180302	-0.356143	-0.017942
C	3.251088	-1.684307	-0.819013
C	3.708800	-1.564095	-2.134450
C	4.462494	-2.568015	-2.728583
C	4.774065	-3.717561	-2.016013
C	4.332597	-3.856859	-0.706834
C	3.582566	-2.848958	-0.116486
C	0.388035	-0.896681	-0.079515
C	-0.731270	-0.103185	-0.049034
C	-1.943306	-0.842187	-0.027584
C	-1.720537	-2.207079	-0.044628
S	-0.058535	-2.591174	-0.090173
C	-2.993720	-2.891090	-0.034827
C	-3.997131	-1.948586	-0.007206
C	-3.397531	-0.594586	-0.000526
C	-5.294154	-2.529845	0.009225
C	-5.234592	-3.888683	-0.006943
S	-3.604373	-4.492599	-0.041489
P	-4.329213	0.799948	0.036863
C	-3.102819	2.169065	0.039082
C	-2.636282	2.689860	1.255129
C	-1.748186	3.760736	1.234038
C	-1.318830	4.334567	0.043742
C	-1.813792	3.819228	-1.149343
C	-2.700755	2.749484	-1.174447
C	-3.053898	2.101067	2.578124
C	-3.186495	2.220421	-2.499340
C	-0.330007	5.468315	0.040643
C	2.718297	-0.139323	1.774162
C	4.073304	-0.160509	2.124129
C	4.480490	0.040468	3.436010
C	3.536092	0.263465	4.429526
C	2.186742	0.283422	4.104836
C	1.784986	0.083767	2.790426
H	-6.052779	-4.591575	-0.001444
H	-6.224672	-1.979935	0.031303
H	-0.675494	0.976027	-0.045407
H	-1.501243	4.262851	-2.08901
H	-1.384681	4.158041	2.176113
H	-2.884047	2.879159	-3.313411
H	-2.778742	1.226811	-2.701630
H	-4.275818	2.132020	-2.525403
H	-2.699621	2.717184	3.404562
H	-4.141111	2.021565	2.660246
H	-2.647799	1.095093	2.710402
H	-0.325125	5.993846	0.996352
H	0.681383	5.093525	-0.139320
H	-0.556063	6.188921	-0.747236
H	3.479763	-0.671841	-2.706188
H	4.808492	-2.451039	-3.748907
H	5.362456	-4.501629	-2.477887
H	4.576265	-4.749782	-0.143181
H	3.258907	-2.971487	0.911660
H	4.825542	-0.344279	1.364273
H	5.535268	0.018878	3.683892
H	3.851606	0.416905	5.454833
H	1.444915	0.451145	4.876887
H	0.726657	0.094368	2.554201
H	1.013355	0.702013	-2.556438
H	1.292339	2.786161	-3.818696
H	2.758232	4.583154	-2.950588
H	3.9435	4.269369	-0.799812
H	3.674583	2.184894	0.466418

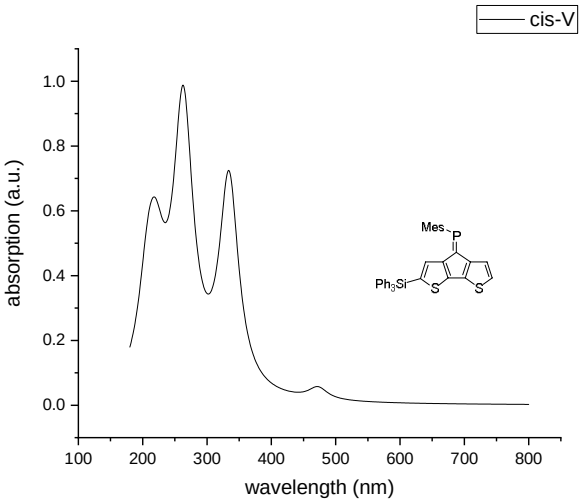


*Figure 68: Calculated UV/vis spectrum of cis-**V**.*

*Table 16 Contributions to the five lowest energy singlet-singlet excitations for calculated structure cis-**V**.*

Excited State 3	Singlet-A	2.6244 eV
472.42 nm	f=0.0372	<S**2>=0.000
	153 ->154	0.69873
Excited State 7	Singlet-A	3.5586 eV
348.41 nm	f=0.0074	<S**2>=0.000
	141 ->154	0.21801
	151 ->154	0.64878
Excited State 11	Singlet-A	3.7121 eV
334.00 nm	f=0.6522	<S**2>=0.000
	152 ->154	0.69764
Excited State 17	Singlet-A	4.3506 eV
284.99 nm	f=0.0057	<S**2>=0.000
	146 ->154	0.10783
	150 ->154	0.67996
Excited State 18	Singlet-A	4.4737 eV
277.14 nm	f=0.0192	<S**2>=0.000
	143 ->154	0.25646
	144 ->154	0.18510
	145 ->154	0.45256
	146 ->154	0.27424
	148 ->154	0.18020
	150 ->154	-0.14669
	153 ->155	0.17220
	153 ->156	-0.10261

*Table 17: XYZ coordinates for calculated structure **VI**.*

	X	Y	Z
C	5.034750	1.521699	-1.009031
C	4.584009	0.838224	0.120147
C	4.438866	1.538111	1.316980
C	4.725006	2.894919	1.381416
C	5.155764	3.569767	0.247651
C	5.310486	2.879711	-0.948272
C	4.292721	-0.622807	0.054382
C	5.462125	-1.535651	-0.017843
C	5.390825	-2.764622	-0.682764
C	6.480913	-3.619951	-0.720915
C	7.673578	-3.263861	-0.104672
C	7.765963	-2.039591	0.543083
C	6.675985	-1.182852	0.579674
C	3.042979	-1.117144	0.075666
C	1.754648	-0.453022	0.048892
S	1.502439	1.274019	-0.185460
C	-0.195960	1.054332	-0.163274
C	-0.560619	-0.261552	0.019388
C	0.555264	-1.118805	0.135686
C	-1.394910	1.851453	-0.268777
C	-2.497825	1.025256	-0.154996
C	-2.038485	-0.362587	0.035326
C	-3.723379	1.742118	-0.254282
C	-3.514885	3.073654	-0.438683
S	-1.827937	3.491098	-0.496765
P	-2.841235	-1.821604	0.236891
C	-4.624475	-1.378315	0.171775
C	-5.310075	-1.416403	-1.052237
C	-6.671655	-1.13399	-1.071902
C	-7.374340	-0.827445	0.087741
C	-6.678848	-0.809578	1.291179
C	-5.317358	-1.085858	1.356528
C	-4.599151	-1.724807	-2.344770
C	-8.854190	-0.558096	0.046330
C	-4.614428	-1.034670	2.688529
H	-4.251362	3.854319	-0.545892
H	-4.707580	1.302885	-0.193304
H	0.504907	-2.191075	0.270017
H	-7.197339	-1.155155	-2.021097
H	-7.210182	-0.574780	2.207862
H	-5.312088	-1.83642	-3.161642
H	-3.901616	-0.927621	-2.613443
H	-4.019381	-2.649054	-2.276123
H	-5.332305	-0.920979	3.500748
H	-4.036940	-1.943917	2.875387
H	-3.916248	-0.195322	2.736377
H	-9.157575	0.115134	0.849289
H	-9.150284	-0.114306	-0.905226
H	-9.419672	-1.486732	0.165286
H	2.938520	-2.197449	0.102692
H	4.479998	-3.043934	-1.197699
H	6.402297	-4.563820	-1.247363
H	8.526725	-3.930572	-0.138874
H	8.692753	-1.747362	1.022507
H	6.763534	-0.230341	1.087061
H	4.095415	1.012931	2.200557
H	4.608639	3.425568	2.318853
H	5.375090	4.629646	0.295856
H	5.649518	3.400597	-1.835783
H	5.161879	0.984128	-1.941545

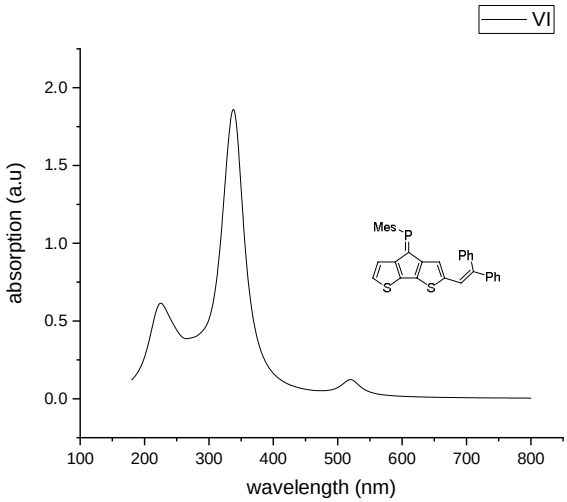


*Figure 69: Calculated UV/vis spectrum of **VI**.*

*Table 18: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **VI**.*

Excited State 3	Singlet-A	2.3834 eV
520.20 nm	f=0.1012	<S**2>=0.000
	129 ->133	-0.16815
	132 ->133	0.67839
Excited State 9	Singlet-A	3.5748 eV
346.83 nm	f=0.0064	<S**2>=0.000
	122 ->133	0.21766
	130 ->133	0.64301
	130 ->134	0.13287
Excited State 11	Singlet-A	3.6455 eV
340.10 nm	f=1.4400	<S**2>=0.000
	129 ->133	0.10149
	131 ->133	0.52461
	132 ->134	-0.43375
Excited State 12	Singlet-A	3.7721 eV
328.69 nm	f=0.5069	<S**2>=0.000
	131 ->133	0.45365
	132 ->134	0.51991
Excited State 16	Singlet-A	4.2973 eV
288.51 nm	f=0.0753	<S**2>=0.000
	123 ->133	-0.15283
	124 ->133	-0.29208
	125 ->133	-0.14812
	127 ->133	-0.25558
	128 ->133	-0.14025
	129 ->133	0.48343
	132 ->133	0.14898

*Table 19: XYZ coordinates for calculated structure **VII**.*

	X	Y	Z
C	0.000000	0	0.000000
C	0.000000	0.000000	1.395787
C	1.220814	0.000000	2.074307
C	2.413383	0.030895	1.365346
C	2.406251	0.060769	-0.022547
C	1.193387	0.043827	-0.701860
N	-1.242876	-0.050003	2.052507
C	-1.416357	0.625773	3.116868
C	-2.658269	0.571057	3.862675
S	-2.854870	1.551194	5.302803
C	-4.435679	0.944982	5.521885
C	-4.797716	0.038309	4.541909
C	-3.778041	-0.174994	3.593923
C	-5.538375	1.092620	6.439162
C	-6.578835	0.280298	6.026118
C	-6.176841	-0.435218	4.802839
C	-7.709432	0.372451	6.885717
C	-7.492743	1.240699	7.910100
S	-5.915744	1.968460	7.860086
P	-6.951362	-1.543377	3.810052
C	-8.606020	-1.766916	4.578162
C	-9.681117	-0.962392	4.170231
C	-10.937302	-1.185279	4.723232
C	-11.159784	-2.189732	5.658311
C	-10.084196	-2.984965	6.036226
C	-8.811189	-2.797101	5.508518
C	-9.496914	0.152688	3.173485
C	-7.679749	-3.679244	5.969466
C	-12.535346	-2.432582	6.217748
H	-8.166919	1.508424	8.708362
H	-8.633668	-0.170302	6.758684
H	-3.830757	-0.836910	2.741435
H	-11.765398	-0.556225	4.412890
H	-10.238630	-3.776376	6.762526
H	-10.459076	0.571466	2.878925
H	-8.891536	0.961267	3.590741
H	-8.990531	-0.193938	2.268737
H	-8.053570	-4.501592	6.579319
H	-7.132859	-4.108652	5.125843
H	-6.957972	-3.117704	6.567920
H	-12.486381	-2.866157	7.217504
H	-13.110678	-1.507246	6.271520
H	-13.092506	-3.128808	5.584466
H	1.235438	-0.053690	3.156230
H	3.354179	0.022741	1.903018
H	3.339240	0.082904	-0.572229
H	1.177926	0.056716	-1.785209
H	-0.951323	-0.025773	-0.516996
H	-0.638946	1.289309	3.511611

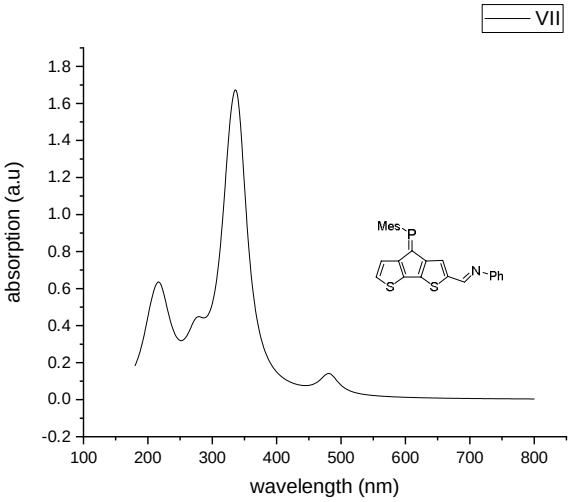


*Figure 70: Calculated UV/vis spectrum of **VII**.*

*Table 20: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **VII**.*

Excited State 3	Singlet-A	2.5756 eV
481.38 nm	f=0.1091	<S**2>=0.000
	109 ->113	-0.14813
	112 ->113	0.67961
Excited State 8	Singlet-A	3.5273 eV
351.49 nm		<S**2>=0.000
	104 ->113	0.21107
	109 ->113	0.10017
	110 ->113	0.63319
	110 ->114	0.1533
Excited State 9	Singlet-A	3.6479 eV
339.88 nm	f=1.1358	<S**2>=0.000
	109 ->113	-0.10826
	111 ->113	0.49262
	112 ->114	0.45981
Excited State 11	Singlet-A	3.7904 eV
327.10 nm	f=0.6824	<S**2>=0.000
	111 ->113	0.4888
	112 ->114	-0.47429
Excited State 16	Singlet-A	4.2634 eV
290.81 nm	f=0.0055	<S**2>=0.000
	103 ->113	-0.12742
	103 ->114	0.16327
	105 ->114	0.22904
	106 ->113	-0.17163
	109 ->113	-0.36006
	109 ->114	0.40923
	112 ->114	-0.16281

*Table 21: XYZ coordinates for calculated structure **VIII**.*

	X	Y	Z
C	-4.689242	1.665856	-0.117599
C	-3.966711	0.980403	0.871660
C	-4.638859	0.167175	1.796370
C	-6.019726	0.031774	1.697205
C	-6.752737	0.689125	0.716335
C	-6.068554	1.502252	-0.180326
P	-2.152025	1.234653	1.021814
C	-1.481410	0.037618	0.056814
C	-0.018892	-0.116224	-0.117183
C	0.228908	-1.164565	-0.973493
C	-1.035462	-1.740906	-1.371527
C	-2.060952	-1.033252	-0.774232
C	1.165446	0.474573	0.393891
C	2.288892	-0.124780	-0.092031
S	1.903718	-1.439371	-1.212186
C	-3.344572	-1.533319	-1.133605
C	-3.253559	-2.592041	-1.982496
S	-1.609341	-3.006795	-2.368980
N	3.620105	0.231863	0.136990
C	4.070874	1.518947	-0.254511
C	5.014095	2.203136	0.513007
C	5.444064	3.464011	0.129193
C	4.932746	4.069941	-1.010868
C	3.984584	3.394880	-1.767712
C	3.558391	2.127854	-1.399868
C	-3.896123	-0.585167	2.870294
C	-8.249792	0.553664	0.647161
C	-4.000343	2.545646	-1.128710
C	4.495374	-0.718823	0.724854
C	5.814987	-0.841806	0.289065
C	6.652284	-1.785890	0.862344
C	6.186414	-2.630656	1.861842
C	4.869972	-2.516786	2.287188
C	4.029370	-1.564677	1.730419
H	-4.054830	-3.170955	-2.413837
H	-4.286430	-1.137469	-0.784816
H	1.207916	1.302432	1.088085
H	-6.535873	-0.605450	2.407946
H	-6.623808	2.025688	-0.952003
H	-4.591461	-1.047203	3.571084
H	-3.274737	-1.375948	2.442561
H	-3.233209	0.072299	3.438934
H	-4.729073	3.097193	-1.722683
H	-3.339561	3.272018	-0.648350
H	-3.385413	1.955706	-1.812998
H	-8.606413	0.618470	-0.381906
H	-8.582253	-0.396352	1.067561
H	-8.736970	1.352608	1.213375
H	5.407951	1.746325	1.411590
H	6.176743	3.981251	0.737312
H	3.575695	3.852645	-2.660680
H	2.821483	1.607767	-1.998085
H	6.182061	-0.197889	-0.499567
H	7.674634	-1.869680	0.513329
H	4.492306	-3.167560	3.066826
H	3.005123	-1.473972	2.069430
H	5.266694	5.057563	-1.303626
H	6.842222	-3.371440	2.302134

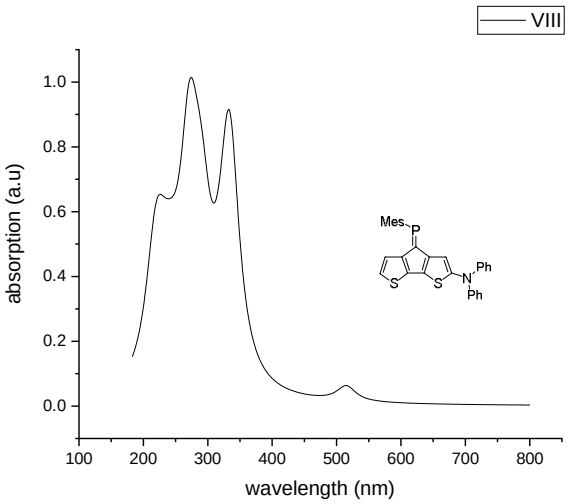


*Figure 71: Calculated UV/vis spectrum of **VIII**.*

*Table 22: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **VIII**.*

ExcitedState 3	Singlet-A	2.4069 eV
515.12 nm	f=0.0471	<S**2>=0.000
	128 ->130	-0.29603
	129 ->130	0.63592
ExcitedState 9	Singlet-A	3.5710 eV
347.20 nm	f=0.0058	<S**2>=0.000
	120 ->130	0.22345
	126 ->130	0.65308
ExcitedState 11	Singlet-A	3.7117 eV
334.03 nm	f=0.7132	<S**2>=0.000
	127 ->130	0.67894
	128 ->130	0.115
ExcitedState 12	Singlet-A	3.8096 eV
325.46 nm	f=0.0859	<S**2>=0.000
	127 ->130	-0.15628
	128 ->130	0.59119
	129 ->130	0.27667
	129 ->131	0.14263
ExcitedState 16	Singlet-A	4.2645 eV
290.74 nm	f=0.3439	<S**2>=0.000
	123 ->130	0.129
	128 ->130	-0.11252
	129 ->131	0.6291
	129 ->138	0.10322

*Table 23: XYZ coordinates for calculated structure **IX**.*

	X	Y	Z
C	6.204272	-1.107629	2.163401
C	6.671677	-0.654630	0.929706
C	7.913661	-1.094516	0.472228
C	8.674150	-1.963310	1.239952
C	8.202770	-2.420111	2.463748
C	6.962512	-1.990258	2.917368
N	5.897197	0.244309	0.152642
C	6.524349	1.350642	-0.474188
C	7.478427	2.102713	0.211423
C	8.100445	3.175872	-0.408104
C	7.770027	3.527154	-1.710398
C	6.814163	2.785287	-2.392060
C	6.201002	1.699638	-1.785654
C	4.508906	0.034636	0.002161
C	3.617811	1.109602	0.010725
C	2.260410	0.902451	-0.150024
C	1.735112	-0.384610	-0.295963
C	2.632283	-1.455276	-0.294522
C	3.993920	-1.252112	-0.160476
C	0.289060	-0.587084	-0.433858
S	-0.337793	-1.927500	-1.382151
C	-1.948950	-1.450449	-1.046417
C	-2.006174	-0.322259	-0.260882
C	-0.723718	0.168863	0.089494
C	-3.424097	0.021189	-0.002707
C	-4.185818	-1.015783	-0.722650
C	-3.297670	-1.880302	-1.334384
S	-4.089634	-3.123303	-2.202967
C	-5.640334	-2.482565	-1.745036
C	-5.542485	-1.371886	-0.966171
P	-3.875794	1.337032	0.934305
C	-5.713791	1.289251	0.936447
C	-6.395371	0.584523	1.941570
C	-7.785145	0.606947	1.956272
C	-8.518077	1.317168	1.011466
C	-7.823228	2.019775	0.034679
C	-6.432784	2.024425	-0.017380
C	-5.655769	-0.217296	2.981270
C	-10.021414	1.349716	1.068729
C	-5.735021	2.789626	-1.112223
H	-6.534114	-2.979372	-2.087883
H	-6.402691	-0.840121	-0.588441
H	-0.543008	1.028784	0.719570
H	-8.309954	0.054045	2.728781
H	-8.377294	2.582052	-0.709908
H	-6.339943	-0.583777	3.746547
H	-5.156584	-1.080758	2.534563
H	-4.884659	0.378117	3.477178
H	-6.444616	3.398999	-1.671812
H	-4.963997	3.453650	-0.712524
H	-5.243165	2.113867	-1.816409
H	-10.450159	1.603391	0.098521
H	-10.427154	0.386575	1.382636
H	-10.365175	2.098568	1.787866
H	1.595657	1.757344	-0.165315
H	4.666302	-2.100157	-0.171721
H	2.262733	-2.468923	-0.395712
H	3.995912	2.116514	0.132174
H	7.731681	1.840909	1.231005
H	8.840353	3.748992	0.137975
H	8.252685	4.370084	-2.189282
H	6.551185	3.043305	-3.411075
H	5.467035	1.116615	-2.327508
H	8.281168	-0.750857	-0.486530
H	9.637534	-2.294641	0.870856
H	8.796034	-3.103861	3.058170
H	6.584937	-2.333073	3.873416
H	5.244008	-0.765466	2.528433

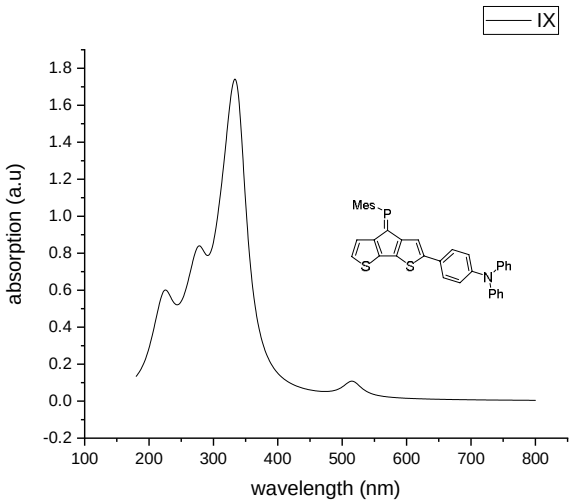


*Figure 72: Calculated UV/vis spectrum of **IX**.*

*Table 24: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **IX**.*

ExcitedState 3	Singlet-A	2.4051 eV
515.51 nm	f=0.0839	<S**2>=0.000
	148 ->150	-0.4227
	149 ->150	0.55488
ExcitedState 9	Singlet-A	3.5759 eV
346.72 nm	f=0.0170	<S**2>=0.000
	138 ->150	0.22111
	146 ->150	0.64511
ExcitedState 11	Singlet-A	3.6742 eV
337.45 nm	f=1.1482	<S**2>=0.000
	147 ->150	0.54536
	148 ->150	0.1683
	149 ->150	0.12946
	149 ->151	0.34509
ExcitedState 13	Singlet-A	3.8071 eV
325.67 nm	f=0.5494	<S**2>=0.000
	147 ->150	0.42719
	148 ->150	-0.25946
	149 ->150	-0.21522
	149 ->151	-0.41679
ExcitedState 16	Singlet-A	3.9956 eV
310.30 nm	f=0.2733	<S**2>=0.000
	142 ->150	-0.1567
	144 ->150	0.10614
	148 ->150	0.40034
	149 ->150	0.33319
	149 ->151	-0.39088

*Table 25: XYZ coordinates for calculated structure **X**.*

	X	Y	Z
C	7.456387	-1.195342	-0.079489
C	6.255241	-0.904722	0.566540
C	5.883032	-1.676327	1.663239
C	6.689349	-2.720948	2.092318
C	7.893599	-3.015311	1.460361
C	8.261645	-2.228129	0.369571
N	5.437782	0.166902	0.116904
C	6.044976	1.418267	-0.170727
C	6.973931	1.970232	0.711068
C	7.581036	3.180595	0.423008
C	7.273916	3.890078	-0.737730
C	6.340137	3.333590	-1.606295
C	5.739163	2.111928	-1.337971
C	7.934205	5.210331	-1.032189
C	8.774554	-4.141548	1.930765
C	4.052350	-0.012983	-0.048888
C	3.157082	1.034058	0.190271
C	1.797770	0.857674	0.013438
C	1.268226	-0.374588	-0.380280
C	2.167450	-1.418929	-0.607810
C	3.530968	-1.242880	-0.458396
C	-0.179307	-0.549327	-0.535472
C	-1.186381	0.106365	0.118509
C	-2.473036	-0.315714	-0.300227
C	-2.425812	-1.293503	-1.266816
S	-0.818384	-1.706430	-1.694417
C	-3.778341	-1.665202	-1.612769
C	-4.658787	-0.913795	-0.857278
C	-3.887808	-0.014321	0.020422
C	-6.018555	-1.223144	-1.143696
C	-6.126533	-2.188512	-2.095703
S	-4.581536	-2.745552	-2.668598
P	-4.327313	1.136366	1.158877
C	-6.165597	1.108969	1.153396
C	-6.875707	1.980068	0.312965
C	-8.265482	1.984747	0.365221
C	-8.970018	1.160239	1.234711
C	-8.246541	0.315792	2.068959
C	-6.856445	0.279145	2.049809
C	-6.168652	2.883839	-0.663938
C	-6.128036	-0.670262	2.965804
C	-10.472730	1.206300	1.296568
H	-7.024635	-2.620118	-2.508423
H	-6.873720	-0.760732	-0.674215
H	-0.999147	0.845410	0.885211
H	-8.777977	-0.334136	2.756687
H	-8.811925	2.652959	-0.292551
H	-6.816009	-1.125364	3.678298
H	-5.647167	-1.473685	2.402263
H	-5.343906	-0.162335	3.533476
H	-6.869771	3.579358	-1.125196
H	-5.384660	3.470190	-0.177551
H	-5.691474	2.308778	-1.461382
H	-10.900901	1.488569	0.333762
H	-10.887692	0.240358	1.587831
H	-10.806981	1.942540	2.033112
H	1.134216	1.697028	0.181812
H	4.200453	-2.070537	-0.652044
H	1.798374	-2.393621	-0.905054
H	3.533577	1.998165	0.505842
H	7.220741	1.442266	1.623900
H	8.301895	3.589282	1.123264
H	6.084422	3.856678	-2.521214
H	5.025883	1.694225	-2.037737
H	7.757842	-0.603910	-0.935270
H	9.192775	-2.434494	-0.147528
H	6.377762	-3.310066	2.947855
H	4.956472	-1.459230	2.180283
H	8.213834	-4.857388	2.532638
H	9.206022	-4.684494	1.086100
H	9.599677	-3.768689	2.542509
H	7.587764	5.623198	-1.980170
H	7.720271	5.942095	-0.249142
H	9.020447	5.105218	-1.088211

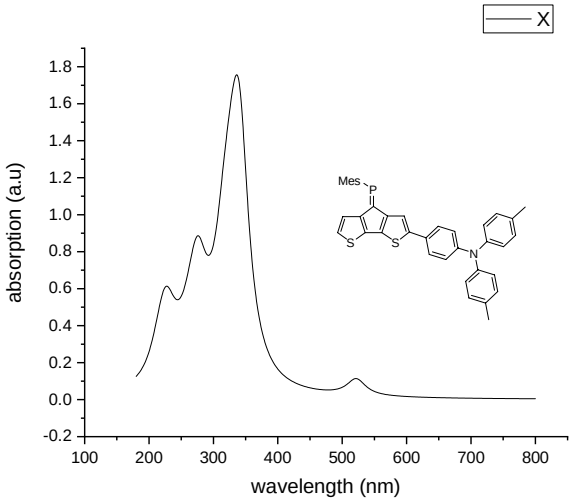


*Figure 73: Calculated UV/vis spectrum of **X**.*

*Table 26: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **X**.*

ExcitedState 3	Singlet-A	2.3763 eV
521.75 nm	f=0.0898	<S**2>=0.000
	156 ->158	-0.43866
	157 ->158	0.54176
ExcitedState 10	Singlet-A	3.5827 eV
346.07 nm	f=0.0066	<S**2>=0.000
	146 ->158	0.22284
	154 ->158	0.65049
ExcitedState 11	Singlet-A	3.6429 eV
340.34 nm	f=1.1731	<S**2>=0.000
	155 ->158	0.43499
	156 ->158	0.25036
	157 ->158	0.20851
	157 ->159	0.40082
ExcitedState 13	Singlet-A	3.7728 eV
328.63 nm	f=0.4335	<S**2>=0.000
	155 ->158	0.54128
	156 ->158	-0.25613
	157 ->158	-0.22889
	157 ->159	-0.26243
ExcitedState 16	Singlet-A	3.9204 eV
316.26 nm	f=0.4418	<S**2>=0.000
	150 ->158	-0.13271
	151 ->158	-0.11183
	156 ->158	-0.34219
	157 ->158	-0.30699
	157 ->159	0.46048

*Table 27: XYZ coordinates for calculated structure **XI**.*

	X	Y	Z
C	-6.853522	0.894737	-1.143377
C	-5.873259	0.707599	-0.167944
C	-5.800277	1.604855	0.887219
C	-6.674181	2.682565	0.974612
C	-7.653963	2.856205	0.002688
C	-7.739195	1.949319	-1.055223
N	-4.961236	-0.385217	-0.259351
C	-5.465065	-1.702427	-0.326365
C	-6.630896	-2.037151	0.351221
C	-7.156922	-3.325052	0.266952
C	-6.510767	-4.301021	-0.484196
C	-5.340220	-3.956199	-1.154139
C	-4.816948	-2.679566	-1.093648
O	-8.302169	-3.530423	0.966815
C	-8.882211	-4.824275	0.942440
O	-8.560974	3.865163	-0.004128
C	-8.518284	4.814454	1.048809
C	-3.576684	-0.125040	-0.233108
C	-2.690838	-0.972550	0.437959
C	-1.336623	-0.698122	0.468269
C	-0.808525	0.431016	-0.164511
C	-1.701307	1.279215	-0.823616
C	-3.057202	1.009306	-0.860311
C	0.632768	0.696375	-0.132635
S	1.236283	2.346799	-0.167313
C	2.855019	1.788353	-0.097368
C	2.931122	0.415839	-0.038282
C	1.657983	-0.206788	-0.060975
C	4.196284	2.325060	-0.087989
C	5.098718	1.280149	-0.023340
C	4.354574	0.007713	0.011020
C	6.448900	1.731170	-0.008470
C	6.528287	3.087885	-0.062001
S	4.967166	3.851804	-0.130872
P	4.829242	-1.599276	0.089378
C	6.666287	-1.533455	0.129742
C	7.338354	-1.501364	1.361127
C	8.729194	-1.507475	1.370918
C	9.471110	-1.557026	0.196585
C	8.785110	-1.603832	-1.011709
C	7.395666	-1.599561	-1.067465
C	6.589014	-1.427708	2.666478
C	6.708001	-1.634147	-2.407974
C	10.974943	-1.595622	0.232524
H	7.413434	3.704062	-0.066369
H	7.317608	1.092060	0.038258
H	1.492939	-1.275323	-0.050865
H	9.246428	-1.472872	2.324329
H	9.346620	-1.645625	-1.939502
H	7.268244	-1.549785	3.510154
H	6.082475	-0.465798	2.778514
H	5.822768	-2.204219	2.736764
H	7.426022	-1.819520	-3.206766
H	5.947289	-2.418054	-2.451423
H	6.205478	-0.687142	-2.619978
H	11.405089	-1.119482	-0.649786
H	11.363831	-1.092783	1.119011
H	11.334691	-2.628232	0.255933
H	-0.679472	-1.357771	1.021826
H	-3.723003	1.679109	-1.388815
H	-1.329537	2.154181	-1.344066
H	-3.071085	-1.845387	0.952224
H	-7.154654	-1.305800	0.951736
H	-4.836321	-4.706934	-1.751498
H	-3.917073	-2.430534	-1.639181
H	-6.918800	0.201566	-1.973112
H	-8.504094	2.101294	-1.806383
H	-6.585750	3.365318	1.807579
H	-5.045839	1.467097	1.652201
H	-6.899881	-5.305661	-0.560456
H	-9.773237	-4.764882	1.562771
H	-9.167132	-5.113596	-0.072848
H	-8.202037	-5.573468	1.357045
H	-9.320123	5.520813	0.848386
H	-8.688392	4.340065	2.019281
H	-7.563159	5.346786	1.065778

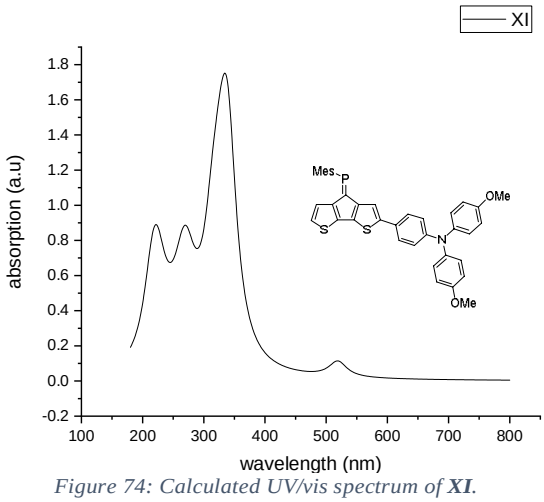


*Figure 74: Calculated UV/vis spectrum of **XI**.*

*Table 28 Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XI**.*

Excited State 3	Singlet-A	2.3887 eV
519.04 nm	f=0.0891	<S**2>=0.000
	164 -> 166	-0.4429
	165 -> 166	0.53729
Excited State 10	Singlet-A	3.5804 eV
346.28 nm	f=0.0061	<S**2>=0.000
	154 -> 166	0.2229
	161 -> 166	0.65067
Excited State 11	Singlet-A	3.6570 eV
339.03 nm	f=1.1369	<S**2>=0.000
	163 -> 166	0.49209
	164 -> 166	0.22571
	165 -> 166	0.19131
	165 -> 167	-0.35765
Excited State 13	Singlet-A	3.7911 eV
327.04 nm	f=0.4715	<S**2>=0.000
	163 -> 166	0.4905
	164 -> 166	-0.27148
	165 -> 166	-0.25061
	165 -> 167	0.31054
Excited State 16	Singlet-A	3.9449 eV
314.29 nm	f=0.4623	<S**2>=0.000
	158 -> 166	-0.13235
	164 -> 166	0.33648
	164 -> 167	-0.11011
	165 -> 166	0.30824
	165 -> 167	0.46304

*Table 29: XYZ coordinates for calculated structure **XII**.*

	X	Y	Z
C	-8.282617	1.464537	1.677315
C	-7.615686	1.684959	0.462877
C	-8.343775	2.029435	-0.686819
C	-9.728737	2.120291	-0.605715
C	-10.411039	1.891971	0.584261
C	-9.669551	1.566276	1.713618
P	-5.779159	1.632336	0.405180
C	-5.417665	0.045871	-0.001919
C	-4.026116	-0.438490	-0.155555
C	-4.045154	-1.773761	-0.488710
C	-5.419881	-2.209167	-0.568734
C	-6.247703	-1.140089	-0.281665
S	-2.470196	-2.420491	-0.674012
C	-1.752735	-0.865221	-0.282157
C	-2.712500	0.078532	-0.036705
C	-7.625844	-1.492209	-0.340072
C	-7.798239	-2.801572	-0.665371
S	-6.294063	-3.639702	-0.909246
C	-0.295461	-0.703764	-0.253683
C	0.554181	-1.764040	0.070483
C	1.926916	-1.592802	0.107126
C	2.510126	-0.354911	-0.170141
C	1.658476	0.703853	-0.495648
C	0.286479	0.533745	-0.543035
C	3.978382	-0.172295	-0.118476
C	4.545235	1.012196	0.356088
C	5.917112	1.179993	0.424253
C	6.778853	0.167099	0.000447
C	6.221720	-1.015963	-0.487922
C	4.848987	-1.181002	-0.536086
N	8.179636	0.330953	0.066928
C	8.768555	1.588233	-0.220411
C	9.789119	2.090260	0.587189
C	10.372513	3.314367	0.297786
C	9.937991	4.063604	-0.787628
C	8.916842	3.569390	-1.588953
C	8.340633	2.338195	-1.316208
C	-7.661556	2.271073	-2.008637
C	-11.907892	2.029094	0.653359
C	-7.534809	1.091008	2.931302
C	9.005694	-0.757933	0.447028
C	8.652454	-1.574659	1.521074
C	9.460751	-2.641112	1.884031
C	10.639347	-2.898578	1.196006
C	10.998144	-2.080721	0.132503
C	10.185881	-1.023055	-0.247224
H	-8.723802	-3.343118	-0.780668
H	-8.448580	-0.818994	-0.152002
H	-2.472692	1.095267	0.242193
H	-10.183161	1.386151	2.652425
H	-10.289876	2.377877	-1.498276
H	-8.201204	1.091918	3.793820
H	-7.093629	0.094622	2.848062
H	-6.717950	1.787801	3.137139
H	-8.369597	2.649393	-2.745874
H	-6.850485	2.998414	-1.917604
H	-7.224404	1.350389	-2.403063
H	-12.378219	1.717186	-0.280431
H	-12.324353	1.43095	1.464818
H	-12.192942	3.069900	0.831361
H	3.903478	1.807777	0.715402
H	6.871286	-1.808264	-0.837154
H	4.447453	-2.103280	-0.938664
H	6.326994	2.100572	0.819392
H	10.124230	1.515702	1.441490
H	11.164831	3.689597	0.934623
H	8.572574	4.139801	-2.443503
H	7.554015	1.951995	-1.952106
H	10.463889	-0.395235	-1.084484
H	11.912285	-2.273123	-0.416528
H	9.172052	-3.266916	2.720177
H	7.741106	-1.370951	2.069056
H	2.077589	1.670615	-0.747217
H	-0.341762	1.366842	-0.833226
H	0.137276	-2.731429	0.324645
H	2.553987	-2.430252	0.387869
H	10.390842	5.022474	-1.007454
H	11.272270	-3.728117	1.486070

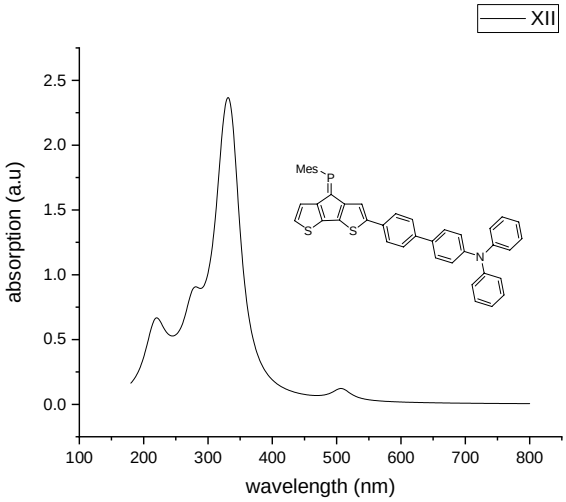


*Figure 75: Calculated UV/vis spectrum of **XII**.*

*Table 30: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XII**.*

Excited State 3	Singlet-A	2.4435 eV
507.40 nm	f=0.0895	<S**2>=0.000
	165 -> 170	0.11944
	168 -> 170	0.54001
	169 -> 170	-0.42616
Excited State 10	Singlet-A	3.5705 eV
347.25 nm	f=0.0096	<S**2>=0.000
	156 -> 170	0.22032
	166 -> 170	0.64774
	166 -> 171	-0.10152
Excited State 12	Singlet-A	3.6836 eV
336.59 nm	f=1.4098	<S**2>=0.000
	167 -> 170	0.58794
	169 -> 171	0.3026
Excited State 14	Singlet-A	3.8235 eV
324.27 nm	f=1.1101	<S**2>=0.000
	167 -> 170	-0.37031
	168 -> 170	0.10334
	168 -> 171	-0.10882
	168 -> 175	0.1684
	169 -> 170	0.17204
	169 -> 171	0.49782
Excited State 17	Singlet-A	4.0924 eV
302.96 nm	f=0.0953	<S**2>=0.000
	161 -> 170	-0.10718
	165 -> 170	0.18552
	168 -> 170	0.33335
	168 -> 171	0.21865
	169 -> 170	0.48108
	169 -> 171	-0.18473

*Table 31: XYZ coordinates for calculated structure **XIII**.*

	X	Y	Z
C	8.896226	-2.046002	-0.598854
C	8.146304	-1.671463	0.527024
C	8.790585	-1.411204	1.745844
C	10.177120	-1.504087	1.809251
C	10.940076	-1.858932	0.703186
C	10.280081	-2.126614	-0.491095
P	6.310845	-1.629445	0.434671
C	5.949497	-0.049988	0.000903
C	4.558597	0.428073	-0.176700
C	4.577935	1.760258	-0.521969
C	5.952300	2.199028	-0.589233
C	6.779608	1.135462	-0.281121
C	3.244930	-0.091589	-0.068482
C	2.285731	0.847438	-0.333116
S	3.003404	2.401119	-0.730518
C	8.157443	1.490531	-0.328736
C	8.330082	2.796617	-0.666811
S	6.826526	3.627968	-0.936451
C	0.828536	0.682837	-0.320335
C	-0.026335	1.739993	0.000171
C	-1.399007	1.566008	0.021924
C	-1.977498	0.328711	-0.268499
C	-1.120209	-0.726747	-0.590291
C	0.252020	-0.554251	-0.621613
C	-3.445850	0.143746	-0.234852
C	-4.017259	-1.048069	0.215721
C	-5.389328	-1.219109	0.265579
C	-6.249415	-0.201387	-0.152634
C	-5.686816	0.990331	-0.614985
C	-4.313915	1.157233	-0.646076
N	-7.648751	-0.363991	-0.101681
C	-8.243831	-1.621055	-0.374233
C	-9.293295	-2.085933	0.416781
C	-9.906914	-3.308102	0.160484
C	-9.439943	-4.083054	-0.898123
C	-8.390261	-3.630636	-1.686280
C	-7.796336	-2.403947	-1.438649
C	-11.060390	-3.772328	1.009860
C	8.019144	-1.004312	2.974854
C	12.436213	-1.985050	0.802670
C	8.238152	-2.330128	-1.924432
C	-8.475680	0.736529	0.252969
C	-9.607040	1.043519	-0.499070
C	-10.418694	2.108705	-0.141477
C	-10.121508	2.910724	0.958229
C	-8.985011	2.596836	1.700111
C	-8.176231	1.522846	1.362943
C	-10.984293	4.090668	1.317169
H	9.255494	3.339283	-0.777947
H	8.979885	0.821681	-0.124530
H	3.004170	-1.106450	0.216456
H	10.673275	-1.293251	2.751041
H	10.858198	-2.407647	-1.365579
H	8.670547	-0.974977	3.848267
H	7.574001	-0.013616	2.853476
H	7.202650	-1.699336	3.187858
H	8.960005	-2.728166	-2.637505
H	7.427743	-3.057183	-1.825404
H	7.805277	-1.423345	-2.35421
H	12.921262	-1.699484	-0.132008
H	12.835007	-1.359536	1.602291
H	12.723742	-3.018084	1.018055
H	-3.379006	-1.848298	0.571077
H	-6.333030	1.787951	-0.958035
H	-3.909885	2.086375	-1.030052
H	-5.801220	-2.146191	0.642666
H	-9.635775	-1.479475	1.247093
H	-8.036033	-4.236576	-2.512077
H	-6.986141	-2.050344	-2.063288
H	-9.852878	0.438924	-1.363453
H	-11.297701	2.326089	-0.738670
H	-8.733772	3.194383	2.569816
H	-7.305497	1.289688	1.963391
H	-1.534689	-1.692806	-0.851967
H	0.885152	-1.384679	-0.908954
H	0.386405	2.706708	0.263591
H	-2.030235	2.400884	0.300949
H	-9.898938	-5.043012	-1.105371
H	-11.150099	-4.859272	0.995627
H	-10.945243	-3.451484	2.046358
H	-12.003827	-3.358551	0.642548
H	-12.026353	3.918378	1.043587
H	-10.942800	4.301032	2.386958
H	-10.653107	4.991936	0.793101

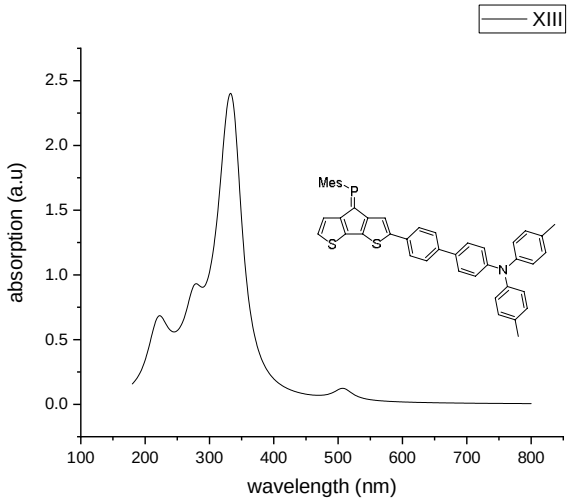


*Figure 76: Calculated UV/vis spectrum of **XIII**.*

*Table 32: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XIII**.*

Excited State 3	Singlet-A	2.4424 eV
507.64 nm	f=0.0901	<S**2>=0.000
	173 -> 178	0.12034
	176 -> 178	0.57436
	177 -> 178	-0.37759
Excited State 10	Singlet-A	3.5716 eV
347.14 nm	f=0.0072	<S**2>=0.000
	164 -> 178	0.22087
	174 -> 178	0.64895
	174 -> 179	-0.10085
Excited State 12	Singlet-A	3.6773 eV
337.16 nm	f=1.5094	<S**2>=0.000
	175 -> 178	0.55914
	176 -> 179	-0.12054
	177 -> 178	0.12687
	177 -> 179	0.3258
Excited State 14	Singlet-A	3.8062 eV
325.74 nm	f=0.9693	<S**2>=0.000
	175 -> 178	-0.41403
	176 -> 178	0.10578
	176 -> 179	-0.11528
	176 -> 182	-0.14143
	177 -> 178	0.20619
	177 -> 179	0.45163
	177 -> 182	-0.1175
Excited State 17	Singlet-A	4.0376 eV
307.07 nm	f=0.1797	<S**2>=0.000
	173 -> 178	0.16244
	176 -> 178	0.29439
	176 -> 179	0.20414
	177 -> 178	0.51051
	177 -> 179	-0.22125

*Table 33: XYZ coordinates for calculated structure **XIV**.*

	X	Y	Z
C	9.242145	-1.281915	1.896214
C	8.612113	-1.649853	0.696839
C	9.374601	-2.126920	-0.379664
C	10.757516	-2.201161	-0.246848
C	11.402776	-1.827848	0.925895
C	10.626523	-1.371959	1.985765
P	6.778046	-1.612135	0.575713
C	6.427169	-0.071116	0.013848
C	5.040266	0.394702	-0.219363
C	5.068609	1.696037	-0.666673
C	6.445180	2.124953	-0.749932
C	7.264872	1.086577	-0.349489
S	3.499202	2.322412	-0.945828
C	2.771260	0.805758	-0.439490
C	3.723550	-0.112204	-0.089798
C	8.644439	1.433105	-0.408088
C	8.825861	2.708250	-0.845166
S	7.328620	3.520001	-1.197076
C	1.313531	0.645422	-0.434776
C	0.457540	1.723945	-0.199937
C	-0.915754	1.554174	-0.184047
C	-1.493703	0.300799	-0.395874
C	-0.635146	-0.775978	-0.632534
C	0.737825	-0.608552	-0.657090
C	-2.962885	0.120571	-0.368581
C	-3.541598	-1.038879	0.151657
C	-4.914481	-1.205911	0.194434
C	-5.767149	-0.217703	-0.301554
C	-5.197566	0.942839	-0.829071
C	-3.824103	1.106644	-0.854308
N	-7.169383	-0.365554	-0.253271
C	-7.785756	-1.619821	-0.448052
C	-8.924298	-1.958620	0.272866
C	-9.559269	-3.181901	0.065353
C	-9.050964	-4.091450	-0.855709
C	-7.906167	-3.744446	-1.567883
C	-7.276504	-2.529170	-1.385206
O	-10.664807	-3.396943	0.823909
C	-11.348785	-4.630823	0.680627
C	8.733174	-2.529099	-1.682654
C	12.896814	-1.946386	1.059947
C	8.455854	-0.764399	3.073011
C	-7.971137	0.766734	0.075970
C	-7.726459	1.497110	1.229603
C	-8.490503	2.614142	1.548136
C	-9.533314	2.997364	0.711378
C	-9.792042	2.258519	-0.444491
C	-9.014234	1.163746	-0.762001
O	-10.344260	4.06313	0.930088
C	-10.123495	4.848946	2.089866
H	9.754528	3.238003	-0.987172
H	9.461898	0.779948	-0.142534
H	3.475303	-1.101539	0.268956
H	11.111590	-1.078343	2.911143
H	11.345491	-2.562185	-1.084480
H	9.095617	-0.657773	3.949007
H	8.015499	0.212129	2.856815
H	7.634350	-1.435760	3.336653
H	9.461787	-2.996799	-2.34473
H	7.915611	-3.238248	-1.528286
H	8.313839	-1.663592	-2.201754
H	13.387333	-1.904030	0.086694
H	13.303350	-1.149782	1.685002
H	13.169147	-2.898030	1.525143
H	-2.909137	-1.814014	0.567717
H	-5.839640	1.718277	-1.226827
H	-3.414236	2.009672	-1.290767
H	-5.332189	-2.105713	0.626874
H	-9.342473	-1.280302	1.004223
H	-7.508947	-4.442019	-2.295923
H	-6.399469	-2.274831	-1.964528
H	-9.213636	0.602882	-1.666909
H	-10.604073	2.572773	-1.088137
H	-8.268312	3.163173	2.452058
H	-6.922015	1.196426	1.889684
H	-1.048593	-1.757092	-0.832471
H	1.372792	-1.457974	-0.877079
H	0.869591	2.705861	0.000937
H	-1.548327	2.407402	0.028327
H	-9.525563	-5.045966	-1.029516
H	-12.184448	-4.592627	1.375249
H	-11.729668	-4.759148	-0.336302
H	-10.703654	-5.475753	0.936936
H	-10.871616	5.637466	2.064777
H	-10.251407	4.258273	3.001215
H	-9.125763	5.296710	2.082930

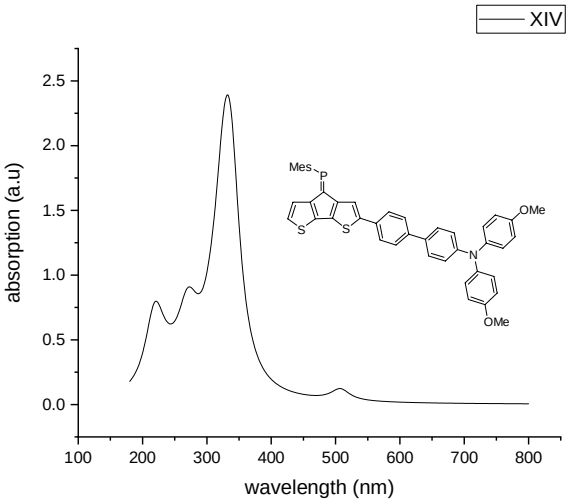


*Figure 77: Calculated UV/vis spectrum of **XIV**.*

*Table 34: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XIV**.*

Excited State 3	Singlet-A	2.4441 eV
507.28 nm	f=0.0895	<S**2>=0.000
	180 -> 186	-0.11105
	184 -> 186	0.58412
	185 -> 186	-0.36047
Excited State 10	Singlet-A	3.5710 eV
347.19 nm	f=0.0157	<S**2>=0.000
	172 -> 186	0.22003
	181 -> 186	0.64384
	181 -> 187	-0.10012
Excited State 12	Singlet-A	3.6806 eV
336.86 nm	f=1.4499	<S**2>=0.000
	183 -> 186	0.56417
	184 -> 187	-0.12956
	185 -> 186	0.12608
	185 -> 187	0.30859
Excited State 14	Singlet-A	3.8113 eV
325.30 nm	f=1.0133	<S**2>=0.000
	183 -> 186	-0.40015
	184 -> 186	0.10473
	184 -> 187	-0.1351
	184 -> 190	-0.13423
	185 -> 186	0.22081
	185 -> 187	0.44994
	185 -> 190	-0.11707
Excited State 18	Singlet-A	4.0335 eV
307.38 nm	f=0.1993	<S**2>=0.000
	180 -> 186	-0.13712
	184 -> 186	0.27845
	184 -> 187	0.21267
	185 -> 186	0.51712
	185 -> 187	-0.22257

Table 35: XYZ coordinates for calculated structure-XV.

	X	Y	Z
C	3.972518	-1.920120	-1.566050
C	4.320133	-0.753573	-0.896803
C	5.621409	-0.222794	-0.948993
C	6.598793	-0.880132	-1.692713
C	6.262696	-2.044558	-2.362342
C	4.962133	-2.556281	-2.297339
N	3.523318	0.073091	-0.104985
C	4.308664	1.128751	0.358077
C	5.613924	0.983859	-0.145008
C	6.581468	1.931586	0.180478
C	6.232033	2.994636	0.995988
C	4.927934	3.120031	1.487015
C	3.947782	2.191963	1.175999
C	2.178983	-0.145664	0.210183
C	1.084678	0.311993	-0.458453
C	-0.122382	-0.109182	0.154181
C	0.088087	-0.879274	1.276980
S	1.748303	-1.112073	1.619798
C	-1.196432	-1.255875	1.822059
C	-2.194276	-0.716155	1.033534
C	-1.577681	0.042672	-0.069399
C	-3.495534	-1.044285	1.509083
C	-3.442317	-1.812737	2.630001
S	-1.815955	-2.157774	3.136733
P	-2.205464	0.925288	-1.350263
C	-4.027341	0.788652	-1.149542
C	-4.727373	-0.238244	-1.801556
C	-6.111524	-0.292657	-1.680336
C	-6.820929	0.648094	-0.942292
C	-6.108974	1.665382	-0.317557
C	-4.724467	1.757798	-0.412312
C	-4.010557	-1.296361	-2.599996
C	-4.005603	2.872945	0.302239
C	-8.321728	0.586582	-0.852640
H	-4.264420	-2.208568	3.205177
H	-4.422381	-0.732475	1.051965
H	1.164645	0.921803	-1.347689
H	-6.645354	2.410809	0.260585
H	-6.650086	-1.092990	-2.177479
H	-4.715026	3.599253	0.698664
H	-3.412976	2.491153	1.137413
H	-3.319140	3.402865	-0.363347
H	-4.721294	-1.922776	-3.138903
H	-3.328214	-0.856609	-3.332220
H	-3.413877	-1.944568	-1.953275
H	-8.679627	-0.443042	-0.896703
H	-8.682855	1.037461	0.072665
H	-8.781111	1.129180	-1.683787
H	6.973844	3.73898	1.257853
H	7.592518	1.838769	-0.198398
H	4.677605	3.960573	2.123064
H	2.937580	2.289830	1.552834
H	7.607156	-0.486789	-1.746471
H	7.012298	-2.566569	-2.944159
H	4.722119	-3.468424	-2.830364
H	2.965066	-2.313570	-1.517985

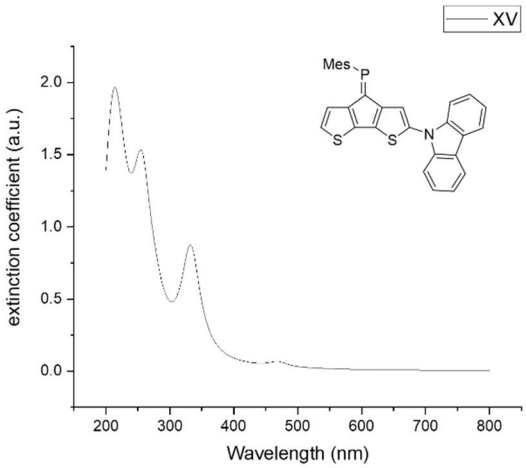


*Figure 78: Calculated UV/vis spectrum of **XV**.*

*Table 36: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XV**.*

Excited State 3	Singlet-A	2.6424 eV
469.21 nm	f=0.0354	<S**2>=0.000
	128 ->129	0.69822
Excited State 7	Singlet-A	3.5422 eV
350.02 nm	f=0.0055	<S**2>=0.000
	120 ->129	0.22029
	124 ->129	0.65428
Excited State 10	Singlet-A	3.7273 eV
332.64 nm	f=0.7538	<S**2>=0.000
	125 ->129	0.69184
Excited State 13	Singlet-A	3.9919 eV
310.59 nm	f=0.0001	<S**2>=0.000
	127 ->129	0.68903
	127 ->131	0.10695
Excited State 20	Singlet-A	4.3255 eV
286.64 nm	f=0.0080	<S**2>=0.000
	123 ->129	0.69616

*Table 37: XYZ coordinates for calculated structure cis-**XVI**.*

	X	Y	Z
C	5.615778	-0.104887	-0.378103
N	4.364594	0.391398	-0.697058
C	3.410858	-0.510523	-0.267290
C	4.053355	-1.625186	0.312658
C	5.472537	-1.364566	0.242316
C	3.281933	-2.675519	0.800830
C	1.904790	-2.600600	0.718601
C	1.265250	-1.485904	0.142702
C	2.026571	-0.432724	-0.360829
C	6.871076	0.460761	-0.589254
C	7.980249	-0.260522	-0.180409
C	7.854068	-1.514002	0.429342
C	6.604809	-2.069829	0.643963
C	-0.199568	-1.410342	0.078460
S	-1.164573	-2.871112	-0.064316
C	-2.607901	-1.954405	-0.083476
C	-2.371090	-0.596784	0.003671
C	-0.988146	-0.292836	0.100067
C	-3.662203	0.116099	-0.011450
C	-4.672315	-0.961891	-0.114728
C	-4.032642	-2.180978	-0.157753
S	-5.132508	-3.488940	-0.284764
C	-6.475231	-2.383002	-0.279959
C	-6.086344	-1.082792	-0.186139
P	-4.077416	1.740218	0.050114
C	-2.464899	2.618700	0.150158
C	-1.810087	3.017728	-1.025262
C	-0.615449	3.723018	-0.925511
C	-0.058641	4.053714	0.304846
C	-0.732203	3.662964	1.456236
C	-1.929547	2.957229	1.402402
C	-2.354689	2.672967	-2.387533
C	-2.603959	2.543739	2.684959
C	1.218757	4.844803	0.387307
C	4.095035	1.681771	-1.289951
H	-7.477345	-2.776172	-0.346955
H	-6.784741	-0.257702	-0.168684
H	-0.582782	0.702043	0.205874
H	-0.107370	4.023795	-1.836097
H	-0.315243	3.914022	2.426169
H	-1.785453	3.174422	-3.170225
H	-2.306819	1.597070	-2.572961
H	-3.401552	2.970244	-2.490897
H	-2.124065	3.013008	3.543692
H	-3.660281	2.825059	2.694618
H	-2.558502	1.460787	2.824714
H	1.775823	4.605786	1.294315
H	1.861639	4.651085	-0.472608
H	1.008666	5.918014	0.404358
H	1.542457	0.415905	-0.825436
H	3.751526	-3.541060	1.253148
H	1.305233	-3.405039	1.126184
H	6.508615	-3.038817	1.119920
H	8.743557	-2.049604	0.737306
H	8.967680	0.158266	-0.334144
H	6.984735	1.432626	-1.052067
H	4.920168	1.963746	-1.942104
H	3.193906	1.625119	-1.899198
H	3.961644	2.457962	-0.531165

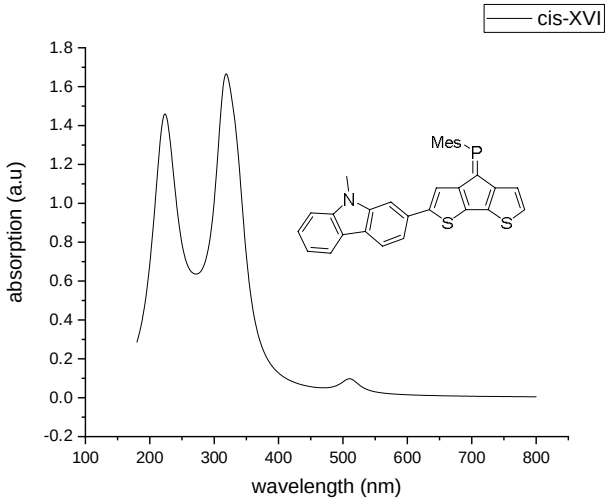


Figure 79: Calculated UV/vis of cis-**XVI**.

*Table 38: Contributions to the five lowest energy singlet-singlet excitations for calculated structure cis-**XVI**.*

Excited State 3	Singlet-A	2.4275 eV
510.75 nm	f=0.0723	<S**2>=0.000
	129 ->133	-0.20486
	130 ->133	-0.10672
	132 ->133	0.66094
Excited State 9	Singlet-A	3.5799 eV
346.34 nm	f=0.0193	<S**2>=0.000
	123 ->133	0.22016
	128 ->133	0.63661
	130 ->133	-0.10926
Excited State 11	Singlet-A	3.7026 eV
334.86 nm	f=0.6783	<S**2>=0.000
	128 ->133	0.12173
	129 ->133	-0.2417
	130 ->133	0.61097
	132 ->134	0.18297
Excited State 12	Singlet-A	3.9197 eV
316.31 nm	f=1.1715	<S**2>=0.000
	129 ->136	0.10039
	130 ->133	-0.21792
	132 ->134	0.62634
Excited State 14	Singlet-A	4.0225 eV
308.23 nm	f=0.0525	<S**2>=0.000
	131 ->133	-0.44614
	131 ->134	0.48925
	131 ->136	0.11877
	132 ->138	0.10661

Table 39: XYZ coordinates for calculated structure trans-**XVI**.

	X	Y	Z
C	-6.891931	-1.329394	-0.228010
N	-5.575815	-1.624411	-0.534580
C	-4.788492	-0.548148	-0.175336
C	-5.609694	0.475442	0.344141
C	-6.963604	-0.027179	0.311474
C	-5.027949	1.671482	0.753650
C	-3.658901	1.828198	0.654348
C	-2.840636	0.803917	0.140131
C	-3.411461	-0.394465	-0.284004
C	-8.033084	-2.112678	-0.385118
C	-9.247401	-1.566459	-0.004803
C	-9.334854	-0.273688	0.524482
C	-8.198060	0.499062	0.685647
C	-1.385095	0.978623	0.057182
S	-0.695506	2.565768	-0.246082
C	0.889845	1.918447	-0.202486
C	0.893465	0.560812	0.022341
C	-0.410151	0.025929	0.172815
C	2.292694	0.075048	0.054021
C	3.102438	1.285024	-0.178507
C	2.256885	2.368221	-0.327537
S	3.106582	3.827294	-0.602826
C	4.624355	2.982015	-0.519335
C	4.473941	1.649523	-0.291646
P	2.680112	-1.536715	0.309532
C	4.517101	-1.583450	0.249753
C	5.260830	-1.435916	1.430771
C	6.646890	-1.532840	1.371671
C	7.314928	-1.783811	0.178599
C	6.558033	-1.941185	-0.976637
C	5.170155	-1.852374	-0.962900
C	4.594132	-1.145278	2.750607
C	4.405094	-2.015327	-2.251012
C	8.813343	-1.917278	0.145058
C	-5.093561	-2.882801	-1.057712
H	5.540285	3.537180	-0.646111
H	5.307339	0.968158	-0.209496
H	-0.631876	-1.011331	0.382727
H	7.219914	-1.409609	2.285043
H	7.060540	-2.139748	-1.917770
H	5.314574	-1.193191	3.567080
H	4.144468	-0.149286	2.756553
H	3.795005	-1.859717	2.965277
H	5.064220	-2.347347	-3.053092
H	3.599982	-2.748319	-2.152597
H	3.945669	-1.073474	-2.561109
H	9.216648	-1.620039	-0.823974
H	9.283609	-1.305218	0.915965
H	9.113086	-2.954305	0.321199
H	-2.790632	-1.175272	-0.702827
H	-5.637171	2.471126	1.158198
H	-3.203231	2.747426	1.000742
H	-8.266889	1.498619	1.099046
H	-10.301491	0.121125	0.811906
H	-10.149259	-2.156341	-0.117532
H	-7.980910	-3.117142	-0.785092
H	-5.864586	-3.340265	-1.675591
H	-4.222189	-2.709372	-1.687936
H	-4.820847	-3.577876	-0.258884

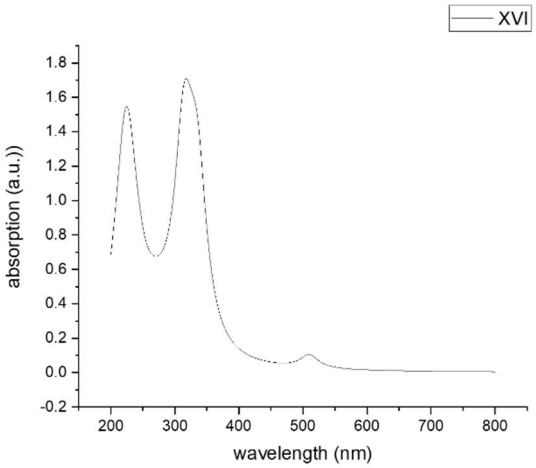


*Figure 80: Calculated UV/vis spectrum of trans-**XVI**.*

*Table 40: Contributions to the five lowest energy singlet-singlet excitations for calculated structure trans-**XVI**.*

Excited State 3	Singlet-A	2.4320 eV
509.81 nm	f=0.0772	<S**2>=0.000
	129 ->133	-0.21654
	132 ->133	0.66261
Excited State 9	Singlet-A	3.5776 eV
346.56 nm	f=0.0068	<S**2>=0.000
	123 ->133	0.22175
	128 ->133	0.64959
Excited State 11	Singlet-A	3.7001 eV
335.09 nm	f=0.9232	<S**2>=0.000
	129 ->133	-0.19783
	130 ->133	0.63805
	132 ->134	0.18726
Excited State 13	Singlet-A	3.9435 eV
314.40 nm	f=1.1217	<S**2>=0.000
	129 ->136	0.10363
	130 ->133	-0.21485
	132 ->134	0.62709
Excited State 14	Singlet-A	4.0256 eV
307.99 nm	f=0.0551	<S**2>=0.000
	131 ->133	-0.44376
	131 ->134	0.49238
	131 ->136	0.12223
Excited State 20	Singlet-A	4.3247 eV
286.69 nm	f=0.0473	<S**2>=0.000
	124 ->133	0.19218
	126 ->133	0.38492
	129 ->133	0.46063
	130 ->133	0.13981
	132 ->133	0.19448

Table 41: XYZ coordinates for calculated structure **XVII**.

	X	Y	Z
C	-6.308949	0.955139	-1.699501
C	-5.158244	1.403975	-1.033376
C	-5.246586	2.458623	-0.111647
C	-6.489391	3.026638	0.146834
C	-7.643893	2.587732	-0.491042
C	-7.531741	1.551631	-1.410982
P	-3.517555	0.686620	-1.451220
C	-3.326633	-0.582936	-0.371590
C	-2.119118	-1.441707	-0.359710
C	-2.247303	-2.389189	0.629340
C	-3.518086	-2.195685	1.291184
C	-4.170558	-1.125990	0.709057
C	-0.898087	-1.556053	-1.076220
C	-0.123196	-2.582257	-0.624397
S	-0.888135	-3.429970	0.701338
C	-5.435464	-0.870570	1.311084
C	-5.700189	-1.744127	2.319141
S	-4.421365	-2.898009	2.562926
C	1.231371	-3.010666	-1.112507
C	2.356187	-2.037054	-0.814355
C	3.376404	-1.843465	-1.740624
C	4.435539	-0.988221	-1.478398
C	4.509937	-0.310941	-0.263392
C	3.493605	-0.503472	0.671694
C	2.430675	-1.346288	0.392237
N	5.594366	0.559565	0.015372
C	6.916760	0.156398	-0.288878
C	7.828043	1.061873	-0.834694
C	9.124236	0.663720	-1.123518
C	9.529803	-0.644209	-0.891810
C	8.622562	-1.550127	-0.358342
C	7.329646	-1.155381	-0.050382
C	-4.033528	2.965588	0.624950
C	-8.972215	3.240514	-0.219633
C	-6.253190	-0.175923	-2.693801
C	5.348933	1.824885	0.600994
C	6.185001	2.318218	1.603913
C	5.942682	3.560152	2.170271
C	4.856176	4.322963	1.762269
C	4.016947	3.830682	0.771427
C	4.262734	2.597439	0.187413
H	-6.575156	-1.791462	2.947960
H	-6.116385	-0.085523	1.018826
H	-0.593239	-0.911646	-1.890209
H	-6.555658	3.835906	0.866900
H	-8.421228	1.195947	-1.920965
H	-4.271838	3.867901	1.188061
H	-3.656882	2.219283	1.328881
H	-3.214988	3.202828	-0.059679
H	-7.210976	-0.293294	-3.200697
H	-5.488268	-0.006212	-3.456211
H	-6.013346	-1.122887	-2.203865
H	-9.795952	2.540833	-0.367556
H	-9.024935	3.623405	0.800526
H	-9.133236	4.085087	-0.895689
H	3.337788	-2.359004	-2.694189
H	3.536882	0.015073	1.621337
H	1.648435	-1.470594	1.131915
H	5.210161	-0.841654	-2.220748
H	7.515976	2.079926	-1.030079
H	9.818171	1.380778	-1.546096
H	8.925372	-2.572776	-0.166462
H	6.632171	-1.864416	0.377188
H	7.026327	1.724039	1.937367
H	6.602743	3.927143	2.947404
H	3.168117	4.416113	0.438215
H	3.610749	2.225884	-0.592933
H	10.541021	-0.953978	-1.124818
H	4.665444	5.289604	2.211744
H	1.182967	-3.171747	-2.192172
H	1.479306	-3.984598	-0.679554

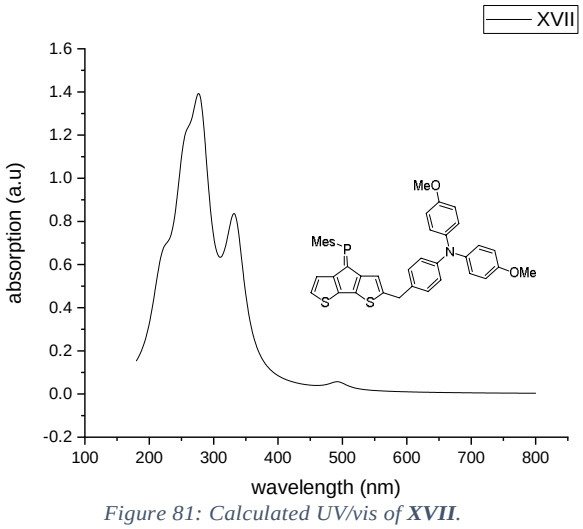


*Figure 81: Calculated UV/vis of **XVII**.*

*Table 42: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XVII**.*

Excited State 3	Singlet-A	2.5154 eV
492.89 nm	f=0.0351	<S**2>=0.000
	152 ->154	0.67025
	153 ->154	-0.2005
Excited State 9	Singlet-A	3.5935 eV
345.03 nm	f=0.0060	<S**2>=0.000
	141 ->154	0.22623
	150 ->154	0.6532
Excited State 11	Singlet-A	3.7212 eV
333.18 nm	f=0.6506	<S**2>=0.000
	151 ->154	0.68028
	153 ->154	-0.15221
Excited State 15	Singlet-A	3.9034 eV
317.63 nm	f=0.0498	<S**2>=0.000
	151 ->154	0.16165
	152 ->154	0.1866
	153 ->154	0.65084
Excited State 19	Singlet-A	4.3237 eV
286.75 nm	f=0.0344	<S**2>=0.000
	152 ->155	0.12576
	153 ->155	0.65881

*Table 43: XYZ coordinates for calculated structure **XVIII**.*

	X	Y	Z
C	-3.760425	-1.212385	4.502843
C	-3.425428	0.002444	3.886138
C	-3.750325	1.219534	4.505425
C	-4.379496	1.197801	5.744949
C	-4.706688	0.005499	6.381285
C	-4.389964	-1.187722	5.742962
P	-2.655329	0.000244	2.217481
C	-1.005825	0.000275	2.520986
C	0.001321	-0.000122	1.435485
C	1.261194	0.000873	1.986759
C	1.136474	0.001818	3.426200
C	-0.204645	0.001325	3.758227
S	2.502615	0.000258	0.800580
C	1.288563	-0.001230	-0.453683
C	0.014610	-0.001296	0.014134
S	2.152281	0.002932	4.802096
C	0.764274	0.002507	5.849068
C	-0.412225	0.001646	5.166814
Br	1.828509	-0.002499	-2.275346
C	-3.403827	2.542684	3.872856
C	-5.416403	0.009212	7.708066
C	-3.424852	-2.537545	3.868525
Br	1.029304	0.003301	7.730492
H	-1.375704	0.001154	5.653743
H	-0.852962	-0.002144	-0.629492
H	-4.621340	2.139949	6.226251
H	-4.639945	-2.128694	6.222205
H	-3.849917	3.366591	4.429717
H	-2.322521	2.699345	3.849131
H	-3.760357	2.603081	2.841144
H	-3.880445	-3.358282	4.422378
H	-3.778912	-2.592580	2.835665
H	-2.345038	-2.704675	3.847714
H	-5.218703	-0.906567	8.266554
H	-5.108998	0.858693	8.319842
H	-6.498568	0.082152	7.567395

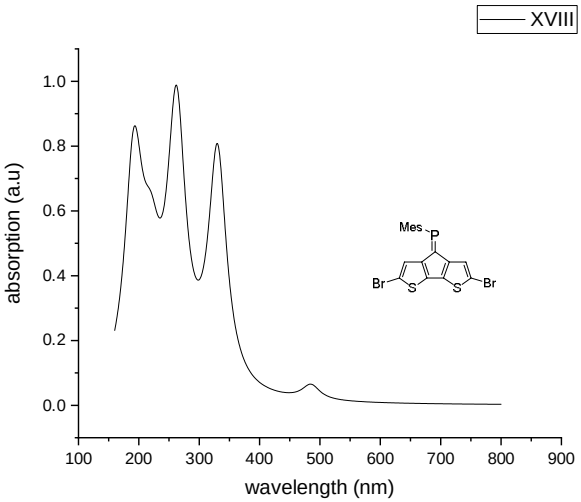


*Figure 82: Calculated UV/vis spectrum of **XVIII**.*

*Table 44: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XVIII**.*

Excited State 3	Singlet-A	2.5561 eV
485.06 nm	f=0.0459	<S**2>=0.000
	119 ->120	0.69774
Excited State 7	Singlet-A	3.4860 eV
355.66 nm	f=0.0057	<S**2>=0.000
	113 ->120	0.21375
	117 ->120	0.65594
Excited State 9	Singlet-A	3.7551 eV
330.18 nm	f=0.7292	<S**2>=0.000
	118 ->120	0.69815
Excited State 13	Singlet-A	4.2394 eV
292.45 nm	f=0.0024	<S**2>=0.000
	116 ->120	0.70021
Excited State 17	Singlet-A	4.4865 eV
276.35 nm	f=0.0066	<S**2>=0.000
	113 ->120	0.65055
	113 ->121	-0.10721
	117 ->120	-0.20936

*Table 45: XYZ coordinates for calculated structure **XIX**.*

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.403413
C	1.214889	0.000000	2.105876
C	2.407638	-0.029521	1.391186
C	2.430141	-0.046128	0.001401
C	1.215677	-0.029531	-0.674790
P	-1.589766	0.116353	2.320554
C	-2.044488	-1.474943	2.582934
C	-1.428801	-2.778537	2.227757
C	-2.227976	-3.811102	2.688847
C	-3.362064	-3.211210	3.343120
C	-3.280253	-1.852593	3.295889
C	-0.268903	-3.258569	1.558565
C	-0.225019	-4.618661	1.533234
S	-1.590025	-5.352263	2.320782
O	-4.461884	-3.635476	3.977771
C	-5.121457	-2.487394	4.358301
C	-4.447869	-1.375477	3.969612
C	1.254469	-0.000672	3.612367
C	3.733525	-0.046026	-0.750619
C	-1.284398	-0.000674	-0.788283
H	0.530426	-5.253056	1.097378
H	0.495665	-2.637128	1.117444
H	-4.760700	-0.359676	4.150055
H	-6.043809	-2.642146	4.890495
H	1.212245	-0.039134	-1.759954
H	3.345331	-0.039111	1.937376
H	-1.086011	0.133115	-1.851674
H	-1.825951	-0.941514	-0.662670
H	-1.955095	0.801045	-0.468072
H	2.274374	0.133098	3.972858
H	0.641574	0.801058	4.032737
H	0.874634	-0.941499	4.018336
H	4.519298	-0.545877	-0.182480
H	3.634986	-0.546002	-1.715185
H	4.068414	0.977089	-0.943907

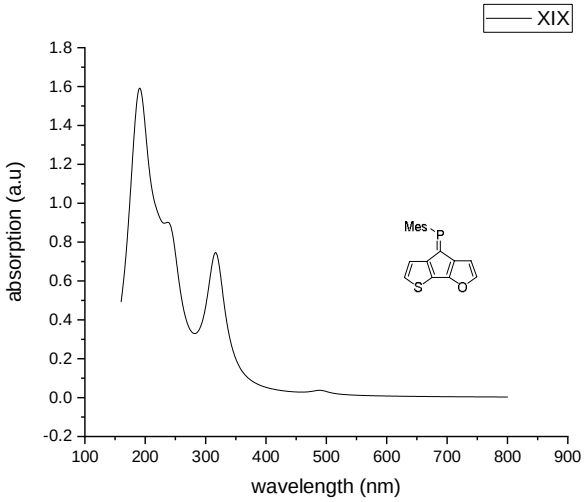


*Figure 83: Calculated UV/vis spectrum of **XIX**.*

*Table 46: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XIX**.*

Excited State 3	Singlet-A	2.5301 eV
490.03 nm	f=0.0206	<S**2>=0.000
	81 -> 82	0.70015
Excited State 7	Singlet-A	3.6231 eV
342.20 nm	f=0.0066	<S**2>=0.000
	76 -> 82	0.2276
	79 -> 82	0.65471
Excited State 8	Singlet-A	3.9131 eV
316.84 nm	f=0.6700	<S**2>=0.000
	80 -> 82	0.69899
Excited State 13	Singlet-A	4.4357 eV
279.51 nm	f=0.0035	<S**2>=0.000
	78 -> 82	0.70241
Excited State 16	Singlet-A	4.6160 eV
268.60 nm	f=0.0072	<S**2>=0.000
	76 -> 82	0.65026
	79 -> 82	-0.22149

*Table 47: XYZ coordinates for calculated structure **XX**.*

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.403444
C	1.214934	0.000000	2.106074
C	2.407607	0.027589	1.391405
C	2.430217	0.042391	0.001577
C	1.215826	0.027604	-0.674675
P	-1.588256	-0.130602	2.319593
C	-2.067589	1.453401	2.596318
C	-3.319332	1.774197	3.318519
C	-3.454540	3.141377	3.396658
C	-2.322225	3.758746	2.743449
C	-1.488716	2.769864	2.262475
S	-4.884120	3.606536	4.221472
C	-5.307684	1.937078	4.465642
C	-4.393394	1.079244	3.938091
Se	-1.683352	5.456858	2.374930
C	-0.234728	4.602057	1.539096
C	-0.323428	3.251045	1.590182
C	1.253882	0.001681	3.612505
C	3.733610	0.038460	-0.750297
C	-1.284545	0.001685	-0.787911
H	-6.219045	1.699637	4.991379
H	0.547239	5.192497	1.087984
H	0.428739	2.608217	1.156164
H	-4.491192	0.004027	3.994406
H	3.345312	0.036573	1.937572
H	1.212477	0.036586	-1.759837
H	2.273711	-0.130915	3.973634
H	0.872930	0.942403	4.017839
H	0.641534	-0.800380	4.033112
H	-1.086573	-0.130825	-1.851535
H	-1.955175	-0.800443	-0.468480
H	-1.826208	0.942359	-0.660999
H	3.636460	0.537865	-1.715293
H	4.520667	0.536628	-0.182459
H	4.065765	-0.985717	-0.942723

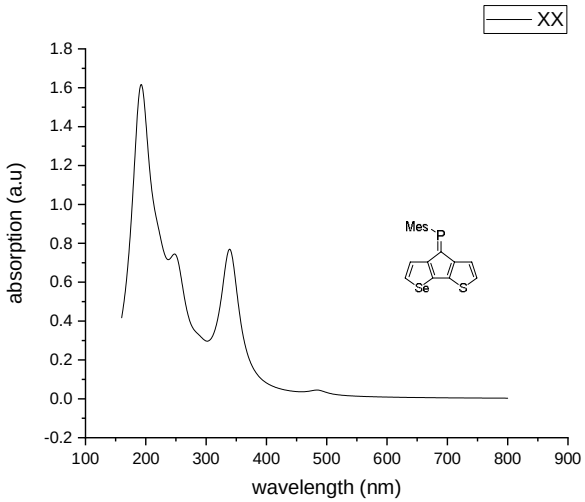


*Figure 84: Calculated UV/vis spectrum of **XX**.*

*Table 48: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XX**.*

Excited State 3	Singlet-A	2.5549 eV	
485.27 nm	f=0.0237	<S**2>=0.000	
	94 -> 95	0.69987	
Excited State 7	Singlet-A	3.5538 eV	
348.87 nm	f=0.0063	<S**2>=0.000	
	88 -> 95	0.22466	
	92 -> 95	0.65365	
Excited State 8	Singlet-A	3.6550 eV	
339.22 nm	f=0.7065	<S**2>=0.000	
	93 -> 95	0.70047	
Excited State 13	Singlet-A	4.2961 eV	
288.60 nm	f=0.0779	<S**2>=0.000	
	90 -> 95	0.60011	
	91 -> 95	-0.34157	
Excited State 15	Singlet-A	4.3884 eV	
282.53 nm	f=0.0073	<S**2>=0.000	
	90 -> 95	0.33867	
	91 -> 95	0.61294	

*Table 49: XYZ coordinates for calculated structure **XXI**.*

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.426403
C	1.259137	0.000000	1.972873
S	2.505302	-0.000444	0.781720
C	1.271755	-0.000075	-0.453638
C	1.146334	0.000715	3.413242
C	-0.190605	0.001135	3.754123
C	-0.997873	0.000426	2.518370
P	-2.646402	0.000563	2.206519
C	-3.442338	0.003499	3.862789
C	-3.791871	-1.209650	4.471491
C	-4.450077	-1.183969	5.698296
C	-4.779292	0.008474	6.328634
C	-4.440172	1.201480	5.696910
C	-3.783526	1.222259	4.473299
C	-3.445979	-2.535654	3.844675
C	-3.427276	2.544235	3.843835
C	-5.492950	0.020731	7.653370
Se	2.251381	0.000497	4.897777
C	0.676897	0.001161	5.922330
C	-0.443306	0.001488	5.160240
F	1.666303	-0.000179	-1.726252
H	0.739609	0.001221	6.999164
H	-1.433325	0.001634	5.592970
H	-0.863413	0.000052	-0.648740
H	-4.696954	2.144058	6.169898
H	-4.713553	-2.124562	6.170601
H	-3.881822	3.369154	4.392319
H	-2.345764	2.700625	3.836075
H	-3.768060	2.602536	2.806662
H	-3.913192	-3.355494	4.390145
H	-3.780071	-2.590720	2.805165
H	-2.366203	-2.704015	3.844596
H	-5.678496	-0.991363	8.013580
H	-4.906149	0.547317	8.409745
H	-6.454478	0.533776	7.575137

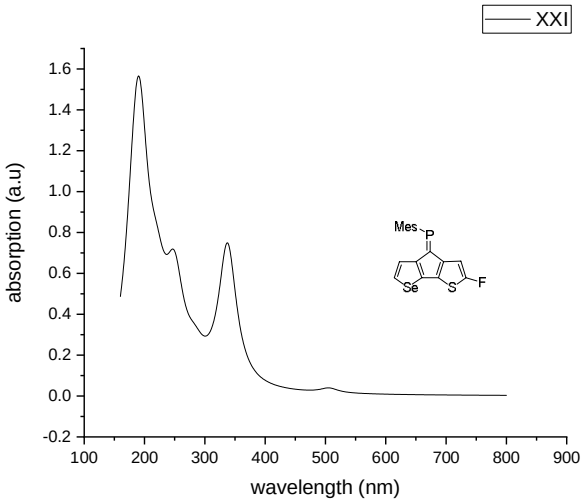


*Figure 85: Calculated UV/vis spectrum of **XXI**.*

*Table 50: Contributions to the five lowest energy singlet-singlet excitations for calculated structure trans **XXI**.*

Excited State 3	Singlet-A	2.4502 eV
506.02 nm	f=0.0230	<S**2>=0.000
	98 -> 99	0.70079
Excited State 6	Singlet-A	3.5096 eV
353.27 nm	f=0.0063	<S**2>=0.000
	92 -> 99	0.22212
	96 -> 99	0.65496
Excited State 8	Singlet-A	3.6730 eV
337.56 nm	f=0.6878	<S**2>=0.000
	97 -> 99	0.69982
Excited State 12	Singlet-A	4.3024 eV
288.17 nm	f=0.0259	<S**2>=0.000
	94 -> 99	-0.21488
	95 -> 99	0.66414
Excited State 14	Singlet-A	4.3933 eV
282.21 nm	f=0.0750	<S**2>=0.000
	94 -> 99	0.65378
	95 -> 99	0.22026

*Table 51: XYZ coordinates for calculated structure **XXII**.*

	X	Y	Z
C	0.406589	-0.062904	-0.000864
C	-0.888687	0.526308	0.000874
C	-0.846265	1.907805	0.004603
S	0.760862	2.504462	0.006026
C	1.385053	0.881329	0.001532
C	-2.293033	0.105149	0.000366
C	-3.076771	1.351069	0.004074
C	-2.194082	2.415285	0.006579
S	-3.001389	3.928249	0.010549
C	-4.543689	3.127343	0.008891
C	-4.437210	1.771844	0.005425
P	-2.871117	-1.451278	-0.004316
C	-4.666670	-1.562009	-0.002810
C	-5.352390	-1.609111	-1.227177
C	-6.738058	-1.691856	-1.197265
C	-7.445466	-1.736919	-0.000362
C	-6.735731	-1.695411	1.195281
C	-5.350005	-1.612694	1.222746
C	-4.630830	-1.553127	-2.547330
C	-4.626035	-1.559744	2.541710
C	-8.943718	-1.857082	0.000930
H	2.453221	0.731947	0.000890
H	-5.443268	3.722312	0.010657
H	-5.294923	1.115750	0.003915
H	0.604577	-1.124292	-0.003755
H	-7.280187	-1.720673	-2.135901
H	-7.276025	-1.727068	2.134884
H	-5.335170	-1.632876	-3.374095
H	-4.083307	-0.614686	-2.662851
H	-3.910556	-2.369093	-2.643571
H	-5.328096	-1.649399	3.369404
H	-3.899774	-2.371077	2.631759
H	-4.085037	-0.618074	2.661664
H	-9.377986	-1.393793	0.887456
H	-9.379690	-1.391596	-0.883604
H	-9.240874	-2.909485	-0.000087
S	-1.777726	-3.056572	-0.010293

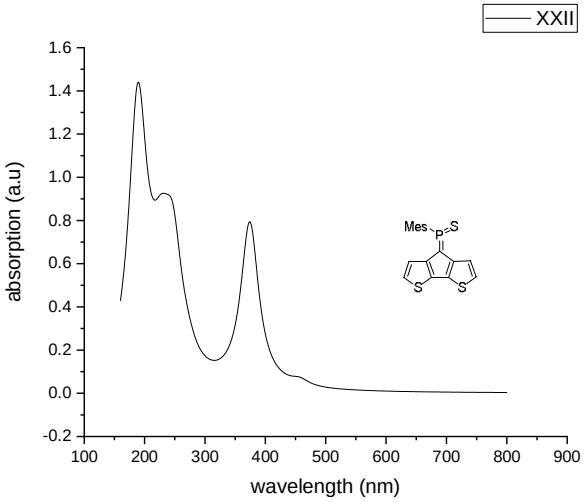


*Figure 86: Calculated UV/vis spectrum of **XXII**.*

*Table 52: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XXII**.*

Excited State 3	Singlet-A	2.7125 eV
457.09 nm	f=0.0277	<S**2>=0.000
	93 -> 94	0.7009
Excited State 4	Singlet-A	3.3133 eV
374.20 nm	f=0.7624	<S**2>=0.000
	92 -> 94	0.69972
Excited State 8	Singlet-A	3.6769 eV
337.20 nm	f=0.0000	<S**2>=0.000
	88 -> 94	0.33337
	91 -> 94	0.60853
Excited State 16	Singlet-A	4.5683 eV
271.40 nm	f=0.0564	<S**2>=0.000
	89 -> 94	0.6249
	90 -> 94	0.27433
	93 -> 96	0.12239
Excited State 18	Singlet-A	4.5806 eV
270.67 nm	f=0.0001	<S**2>=0.000
	88 -> 94	0.60104
	91 -> 94	-0.3304

*Table 53: XYZ coordinates for calculated structure **XXIII**.*

	X	Y	Z
C	-5.479439	-0.748777	0.699575
C	-4.529666	-1.519060	0.003072
C	-4.939262	-2.343954	-1.057763
C	-6.270557	-2.303249	-1.461418
C	-7.210896	-1.500061	-0.829128
C	-6.798011	-0.745897	0.262680
P	-2.826673	-1.573457	0.692556
S	-1.485956	-1.209595	-0.922455
C	-4.004497	-3.289193	-1.768690
C	-8.635734	-1.450898	-1.308539
C	-5.111998	0.065431	1.914690
C	-2.069094	0.075197	0.234020
C	-1.114524	0.702405	1.199779
C	-1.341626	2.054723	1.250640
C	-2.399575	2.388585	0.322030
C	-2.832625	1.242569	-0.300361
S	-0.296061	2.841433	2.361424
C	0.455057	1.324621	2.755738
C	-0.077149	0.277561	2.067825
S	-3.226945	3.781050	-0.242330
C	-4.155708	2.805803	-1.341080
C	-3.841501	1.483844	-1.268382
H	1.254613	1.308902	3.479530
H	-4.884258	3.283166	-1.977249
H	-4.311229	0.725292	-1.877040
H	0.265938	-0.741750	2.177026
H	-6.583389	-2.935821	-2.285639
H	-7.524483	-0.144473	0.799220
H	-4.574059	-4.020050	-2.342457
H	-3.343902	-2.760594	-2.458268
H	-3.369316	-3.837133	-1.069564
H	-6.009716	0.420727	2.419992
H	-4.536694	-0.518664	2.638238
H	-4.511798	0.937364	1.647472
H	-8.770659	-0.641901	-2.032094
H	-8.922019	-2.381608	-1.800044
H	-9.326134	-1.269829	-0.483472

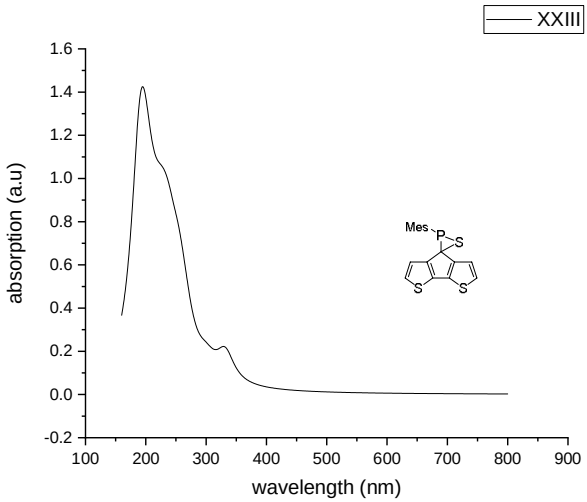


*Figure 87: Calculated UV/vis structure of **XXIII**.*

*Table 54: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XXIII**.*

Excited State 4	Singlet-A	3.7372 eV
331.75 nm f=0.1367 <S**2>=0.000		
	93 -> 94	0.67722
Excited State 7	Singlet-A	4.1295 eV
300.24 nm f=0.0611 <S**2>=0.000		
	88 -> 94	0.11915
	88 -> 95	0.13554
	90 -> 94	-0.1488
	90 -> 95	-0.15496
	91 -> 94	-0.2027
	91 -> 95	-0.22867
	92 -> 94	0.30965
	92 -> 95	0.29091
	93 -> 94	-0.15338
	93 -> 95	0.31911
Excited State 13	Singlet-A	4.6617 eV
265.96 nm f=0.1089 <S**2>=0.000		
	91 -> 94	0.1041
	92 -> 94	-0.40381
	93 -> 95	0.52676
	93 -> 96	-0.10793
Excited State 16	Singlet-A	4.8525 eV
255.51 nm f=0.2245 <S**2>=0.000		
	88 -> 95	-0.11475
	89 -> 94	-0.11964
	90 -> 94	0.18183
	90 -> 95	0.11079
	91 -> 94	0.34267
	91 -> 95	0.18549
	92 -> 94	0.3864
	92 -> 96	-0.11995
	93 -> 95	0.20392
	93 -> 96	-0.15554
Excited State 18	Singlet-A	4.9553 eV
250.20 nm f=0.0809 <S**2>=0.000		
	89 -> 94	0.10938
	90 -> 94	0.14883
	91 -> 94	0.24935
	92 -> 94	-0.12747
	92 -> 95	0.55653
	93 -> 95	-0.12965
	93 -> 96	0.13493

*Table 55: XYZ coordinates for calculated structure **XXIV**.*

	X	Y	Z
C	-3.743794	1.550969	-1.307329
C	-2.768124	1.284919	-0.313284
C	-2.302032	2.418243	0.306541
S	-3.056794	3.833787	-0.294926
C	-4.000261	2.884206	-1.402151
C	-2.064319	0.095503	0.256906
C	-1.106329	0.688450	1.239045
C	-1.281260	2.050533	1.264804
S	-0.221403	2.813206	2.373756
C	0.468521	1.277706	2.799433
C	-0.093309	0.238717	2.122988
P	-2.887364	-1.501944	0.604299
S	-1.503069	-1.241249	-0.925159
C	-4.595736	-1.519817	0.017372
C	-5.530633	-0.697684	0.676206
C	-6.847450	-0.726571	0.242045
C	-7.264427	-1.553888	-0.796242
C	-6.327520	-2.384256	-1.395478
C	-4.993252	-2.398034	-1.002513
C	-5.157204	0.192643	1.832267
C	-4.048429	-3.353050	-1.682790
C	-8.705086	-1.572255	-1.224967
H	1.256315	1.243819	3.535286
H	-4.692328	3.383405	-2.061799
H	-4.231996	0.805755	-1.918413
H	0.206431	-0.790373	2.252562
H	-6.642176	-3.054836	-2.187369
H	-7.572729	-0.090492	0.737693
H	-4.610583	-4.116195	-2.219374
H	-3.411857	-2.837779	-2.405104
H	-3.396870	-3.863210	-0.970900
H	-6.050042	0.636868	2.269768
H	-4.644297	-0.365341	2.618583
H	-4.500656	1.006710	1.519095
H	-9.097392	-0.558924	-1.327514
H	-8.830518	-2.088581	-2.176642
H	-9.320195	-2.085461	-0.481146
S	-2.47104	-2.600141	2.165097

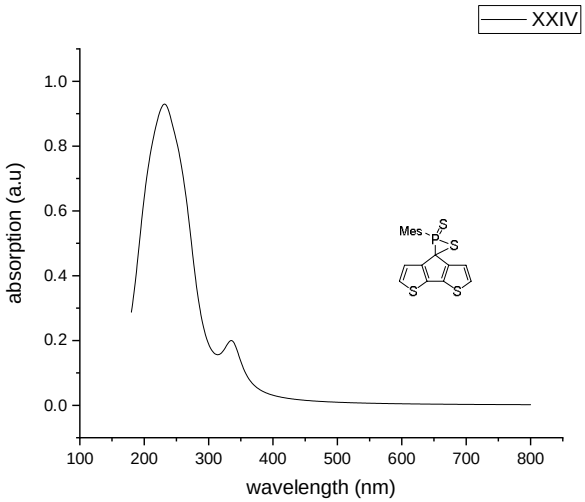


*Figure 88: Calculated UV/vis of (**XXIV**).*

*Table 56: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XXIV**.*

Excited State 3	Singlet-A	3.6823 eV
336.70 nm	f=0.1417	<S**2>=0.000
	101 ->102	0.69362
Excited State 10	Singlet-A	4.4095 eV
281.17 nm	f=0.0244	<S**2>=0.000
	94 ->102	0.17765
	94 ->103	-0.21059
	96 ->102	0.11517
	100 ->102	-0.35362
	100 ->103	0.40985
	101 ->103	-0.27034
Excited State 14	Singlet-A	4.6371 eV
267.38 nm	f=0.2128	<S**2>=0.000
	95 ->103	-0.12006
	99 ->102	0.52587
	99 ->103	-0.39925
	100 ->103	-0.10989
Excited State 16	Singlet-A	4.7566 eV
260.66 nm	f=0.0278	<S**2>=0.000
	96 ->103	0.10653
	100 ->102	-0.2711
	100 ->103	0.15936
	101 ->103	0.58536
Excited State 18	Singlet-A	4.8950 eV
253.29 nm	f=0.2318	<S**2>=0.000
	95 ->103	0.1127
	96 ->102	-0.13158
	99 ->102	0.40503
	99 ->103	0.40183
	99 ->104	0.10496
	99 ->107	0.14295
	100 ->103	0.13371
	100 ->104	0.11134

*Table 57: XYZ coordinates for calculated structure **XXV**.*

	X	Y	Z
C	0.415368	-0.058036	-0.000375
C	-0.882541	0.525387	0.001195
C	-0.845478	1.906946	0.005982
S	0.758216	2.510721	0.008688
C	1.389733	0.890424	0.003211
C	-2.285852	0.098289	-0.000019
C	-3.074226	1.342119	0.004350
C	-2.195582	2.409515	0.007910
S	-3.007498	3.919030	0.012452
C	-4.547159	3.113345	0.009709
C	-4.436176	1.758179	0.005406
P	-2.863232	-1.461716	-0.005733
C	-4.662451	-1.562009	-0.003749
C	-5.349755	-1.609216	-1.227429
C	-6.735742	-1.689162	-1.196948
C	-7.443312	-1.731732	-0.000224
C	-6.732657	-1.690943	1.194639
C	-5.346532	-1.610880	1.221592
C	-4.631499	-1.554087	-2.549280
C	-4.625142	-1.555947	2.541746
C	-8.941816	-1.849529	0.001509
H	2.458577	0.745959	0.002908
H	-5.448639	3.705400	0.011540
H	-5.291729	1.099489	0.003114
H	0.616255	-1.118877	-0.004018
H	-7.277775	-1.718884	-2.135655
H	-7.272177	-1.722174	2.134737
H	-5.333724	-1.674366	-3.373033
H	-4.118680	-0.598480	-2.683281
H	-3.881729	-2.344459	-2.630556
H	-5.323394	-1.691032	3.366591
H	-3.864780	-2.336813	2.615728
H	-4.124692	-0.594496	2.680764
H	-9.374840	-1.388522	0.889850
H	-9.377464	-1.380081	-0.881137
H	-9.241002	-2.901356	-0.003164
Se	-1.70629	-3.205682	-0.012957

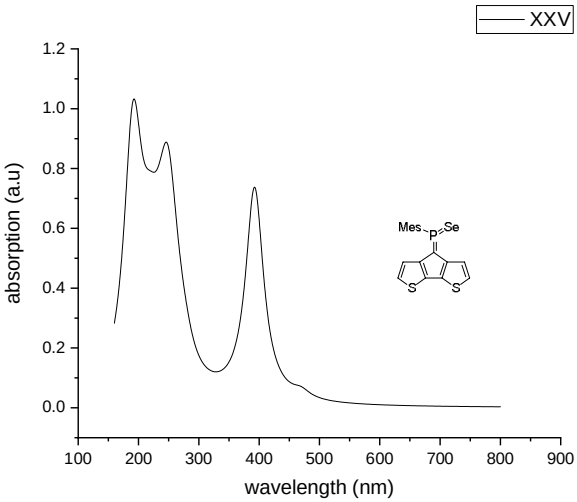


*Figure 89: Calculated UV/vis spectrum of **XXV**.*

*Table 58: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XXV**.*

Excited State 3	Singlet-A	2.6396 eV
469.71 nm	f=0.0237	<S**2>=0.000
	102 ->103	0.70078
Excited State 5	Singlet-A	3.1592 eV
392.45 nm	f=0.7131	<S**2>=0.000
	101 ->103	0.69948
Excited State 6	Singlet-A	3.2418 eV
382.46 nm	f=0.0000	<S**2>=0.000
	97 ->103	-0.15779
	100 ->103	0.67756
	100 ->105	-0.10254
Excited State 14	Singlet-A	4.2921 eV
288.86 nm	f=0.0012	<S**2>=0.000
	96 ->107	0.11153
	101 ->104	0.56563
	101 ->107	0.36557
Excited State 18	Singlet-A	4.4503 eV
278.60 nm	f=0.0003	<S**2>=0.000
	92 ->103	0.10211
	97 ->103	0.6687
	100 ->103	0.15724

*Table 59: XYZ coordinates for calculated structure **XXVI**.*

	X	Y	Z
C	-5.456195	-0.707178	0.683955
C	-4.529785	-1.520795	0.003476
C	-4.969102	-2.368666	-1.027527
C	-6.303115	-2.308990	-1.420024
C	-7.220279	-1.469420	-0.801796
C	-6.778813	-0.688888	0.259378
P	-2.821251	-1.578398	0.682106
Se	-1.357350	-1.286167	-1.031480
C	-4.067225	-3.358100	-1.719730
C	-8.662616	-1.449962	-1.229024
C	-5.063274	0.136142	1.871031
C	-2.066826	0.068442	0.235153
C	-1.129450	0.706534	1.207659
C	-1.330574	2.064692	1.209999
C	-2.357915	2.388352	0.245419
C	-2.799388	1.230100	-0.349297
S	-0.311455	2.865058	2.336042
C	0.391905	1.346129	2.805055
C	-0.135209	0.289094	2.129363
S	-3.152002	3.776742	-0.375265
C	-4.081186	2.782497	-1.457250
C	-3.790515	1.458858	-1.339548
H	1.163664	1.337262	3.558526
H	-4.791473	3.251648	-2.119669
H	-4.263377	0.690600	-1.933421
H	0.183240	-0.732550	2.282490
H	-6.636554	-2.953872	-2.226564
H	-7.485440	-0.051443	0.780647
H	-4.662623	-4.087016	-2.269250
H	-3.397635	-2.865838	-2.427310
H	-3.441458	-3.904404	-1.011279
H	-5.950740	0.504472	2.385064
H	-4.474714	-0.431458	2.597046
H	-4.467382	1.000561	1.571973
H	-9.115950	-0.474100	-1.049743
H	-8.765672	-1.688219	-2.288520
H	-9.241811	-2.189012	-0.668152

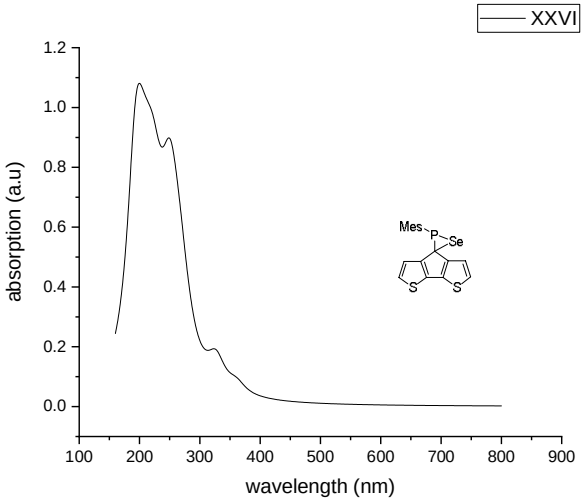


*Figure 90: Calculated UV/vis spectrum of **XXVI**.*

*Table 60: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XXVI**.*

Excited State 4	Singlet-A	3.4346 eV
360.99 nm	f=0.0336	<S**2>=0.000
	100 ->103	-0.2207
	100 ->104	0.12199
	101 ->103	0.26958
	101 ->104	-0.18195
	102 ->103	0.55086
Excited State 6	Singlet-A	3.7931 eV
326.87 nm	f=0.0994	<S**2>=0.000
	97 ->103	0.102
	100 ->103	0.19629
	100 ->104	-0.12505
	101 ->103	-0.36041
	101 ->104	0.18517
	102 ->103	0.40244
	102 ->104	0.29483
Excited State 11	Singlet-A	4.3799 eV
283.08 nm	f=0.0234	<S**2>=0.000
	100 ->103	-0.18303
	101 ->103	0.3011
	101 ->104	0.19586
	101 ->106	0.11049
	102 ->103	-0.11316
	102 ->104	0.50364
Excited State 15	Singlet-A	4.5514 eV
272.41 nm	f=0.1054	<S**2>=0.000
	100 ->103	0.46941
	100 ->104	-0.1829
	101 ->103	0.34245
	101 ->104	-0.22535
	101 ->105	0.1026
Excited State 17	Singlet-A	4.7021 eV
263.68 nm	f=0.1749	<S**2>=0.000
	100 ->103	0.10387
	100 ->104	-0.18626
	101 ->103	0.19725
	101 ->104	0.44775
	102 ->104	-0.34275
	102 ->106	0.12705
	102 ->107	-0.11237

*Table 61: XYZ coordinates for calculated structure **XXVII**.*

	X	Y	Z
C	-3.751258	1.527998	-1.299821
C	-2.774608	1.273322	-0.302712
C	-2.316335	2.414457	0.309553
S	-3.077451	3.821900	-0.303170
C	-4.015035	2.858687	-1.404122
C	-2.061807	0.093828	0.275193
C	-1.118938	0.697396	1.262610
C	-1.299881	2.059615	1.275721
S	-0.256355	2.836917	2.389948
C	0.434187	1.307323	2.837905
C	-0.115026	0.260275	2.164421
P	-2.863163	-1.527485	0.585216
Se	-1.373878	-1.271415	-1.053876
C	-4.581884	-1.535501	0.011051
C	-5.506316	-0.701395	0.672433
C	-6.824603	-0.714215	0.241862
C	-7.255839	-1.534502	-0.795900
C	-6.332252	-2.379829	-1.393511
C	-4.996771	-2.412102	-1.004045
C	-5.127179	0.179433	1.833787
C	-4.076839	-3.393632	-1.680507
C	-8.696882	-1.529443	-1.223775
H	1.213117	1.283180	3.583505
H	-4.709217	3.349100	-2.068121
H	-4.233577	0.776483	-1.907682
H	0.185474	-0.766562	2.308140
H	-6.658439	-3.049621	-2.181425
H	-7.540466	-0.070676	0.741616
H	-4.660405	-4.154692	-2.196986
H	-3.441393	-2.900884	-2.419336
H	-3.424385	-3.902829	-0.969147
H	-6.020308	0.602677	2.291320
H	-4.591439	-0.380479	2.603058
H	-4.490386	1.008918	1.520650
H	-9.058532	-0.510030	-1.371165
H	-8.838220	-2.082111	-2.152529
H	-9.327040	-1.990205	-0.458679
Se	-2.439146	-2.703579	2.288831

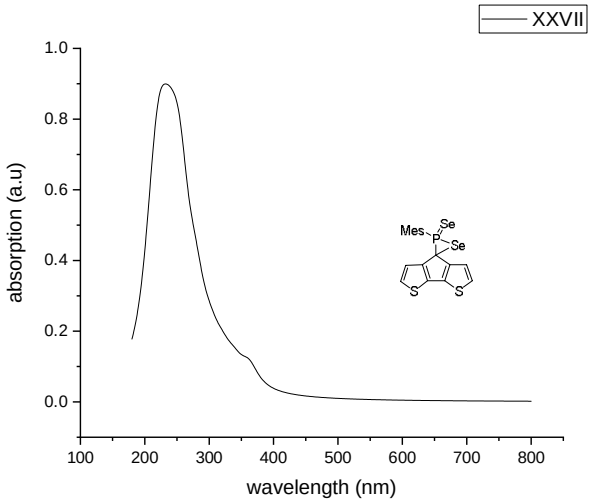


*Figure 91: Calculated UV/vis spectrum of **XXVII**.*

*Table 62: Contributions to the five lowest energy singlet-singlet excitations for calculated structure **XXVII**.*

Excited State 5	Singlet-A	3.4241 eV
362.09 nm	f=0.0569	<S**2>=0.000
	114 ->120	0.14096
	115 ->120	0.10533
	118 ->120	0.18372
	118 ->121	-0.12907
	119 ->120	0.61501
Excited State 8	Singlet-A	3.6679 eV
338.03 nm	f=0.0417	<S**2>=0.000
	112 ->120	-0.15033
	114 ->120	0.14864
	117 ->121	0.10172
	118 ->120	0.43324
	118 ->121	-0.29276
	119 ->120	-0.25283
	119 ->121	-0.24442
Excited State 9	Singlet-A	3.8757 eV
319.90 nm	f=0.0488	<S**2>=0.000
	114 ->120	0.11561
	117 ->120	0.48795
	117 ->121	-0.43113
	118 ->120	0.10082
Excited State 13	Singlet-A	4.1013 eV
302.31 nm	f=0.0625	<S**2>=0.000
	112 ->120	-0.16220
	114 ->120	0.32516
	114 ->121	-0.17581
	115 ->120	0.23079
	115 ->121	-0.10525
	116 ->121	0.10205
	118 ->120	-0.16925
	118 ->121	0.35286
	118 ->122	-0.12629
	119 ->121	-0.17484
Excited State 16	Singlet-A	4.3227 eV
286.82 nm	f=0.0214	<S**2>=0.000
	118 ->120	0.30609
	118 ->121	0.22744
	118 ->122	-0.10404
	118 ->125	0.12642
	119 ->120	-0.15047
	119 ->121	0.50525

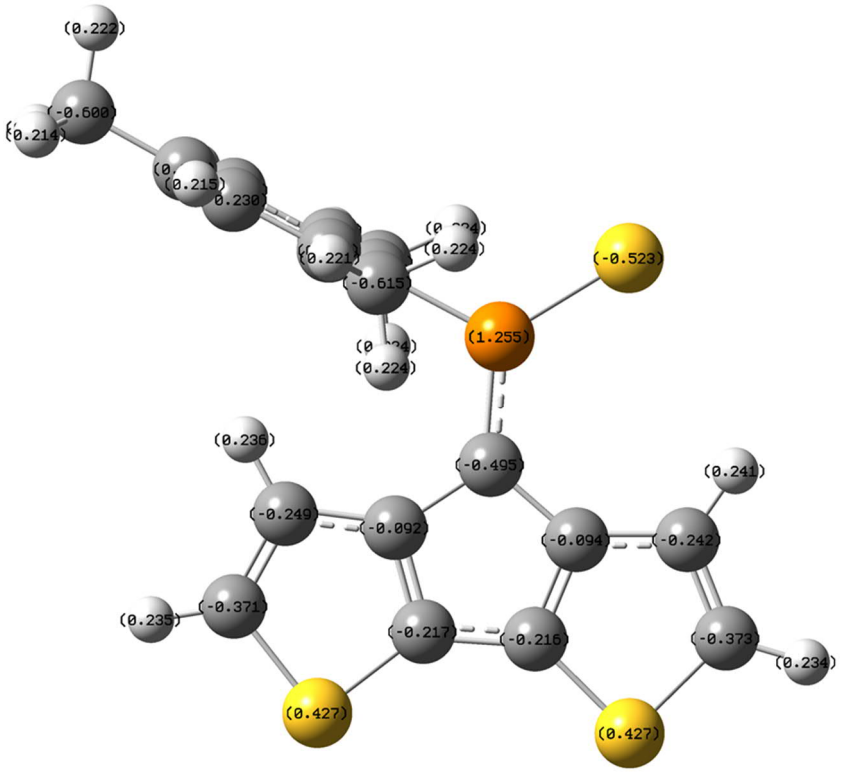


*Figure 92: Calculated NBO charges for model compound **XXII**. Level of theory: cam-B3LYP/6-311G**/PCM(DCM).*

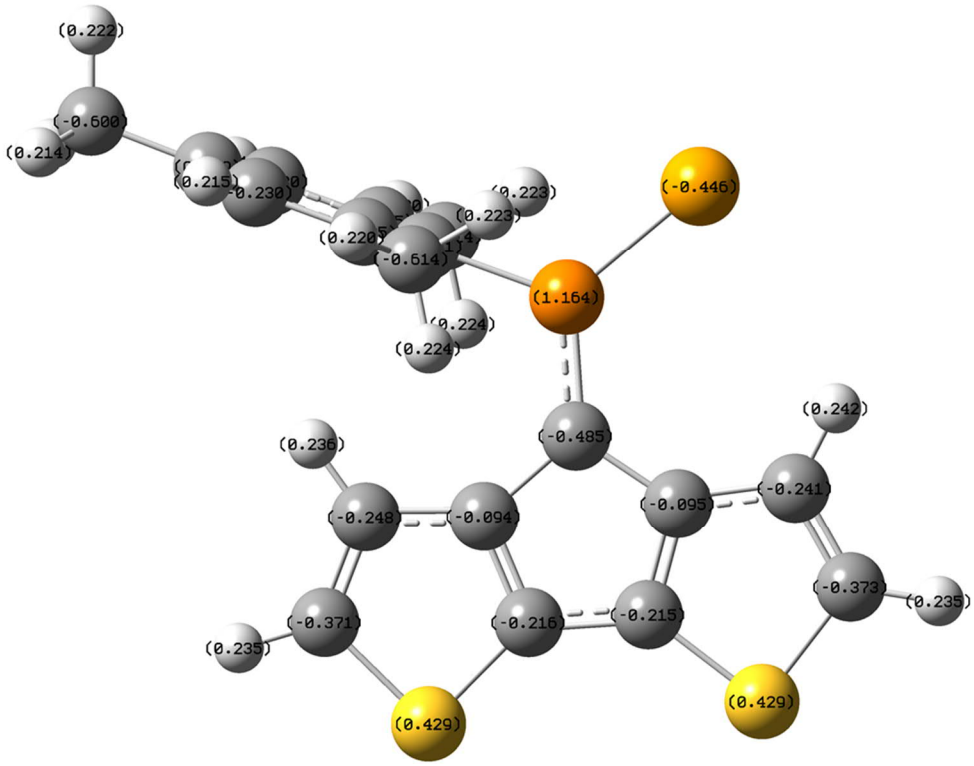


*Figure 93: Calculated NBO charges for model compound **XXV**. Level of theory: cam-B3LYP/6-311G**/PCM(DCM).*

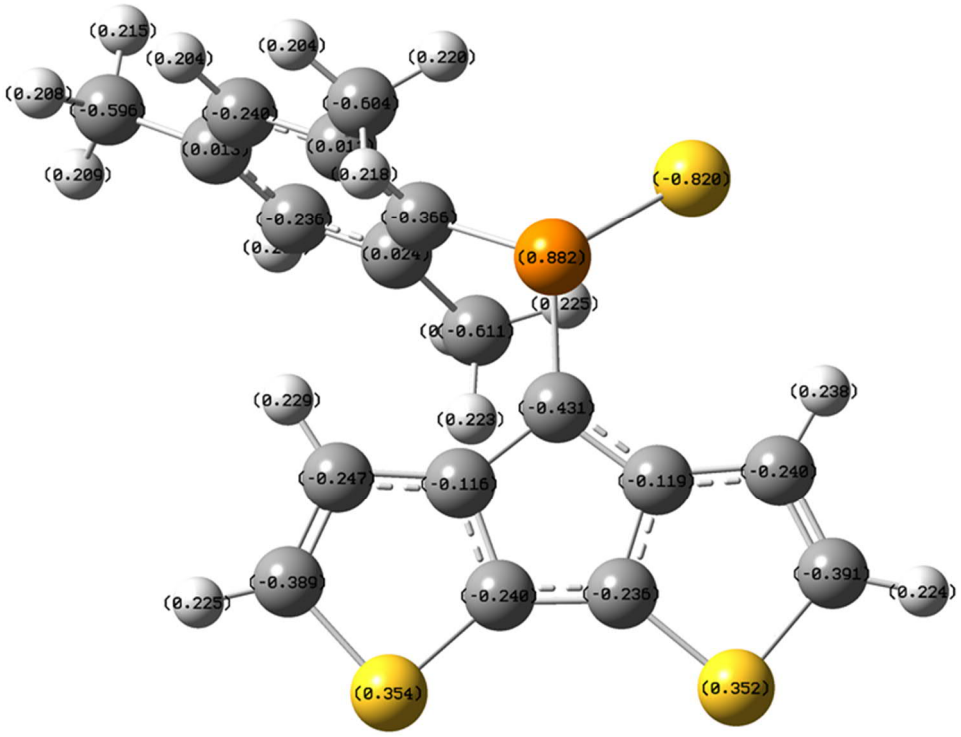


*Figure 94: Calculated NBO charges for model compound **XXII**$^{-}$ (radical anion). Level of theory: cam-B3LYP/6-311G**/PCM(DCM).*

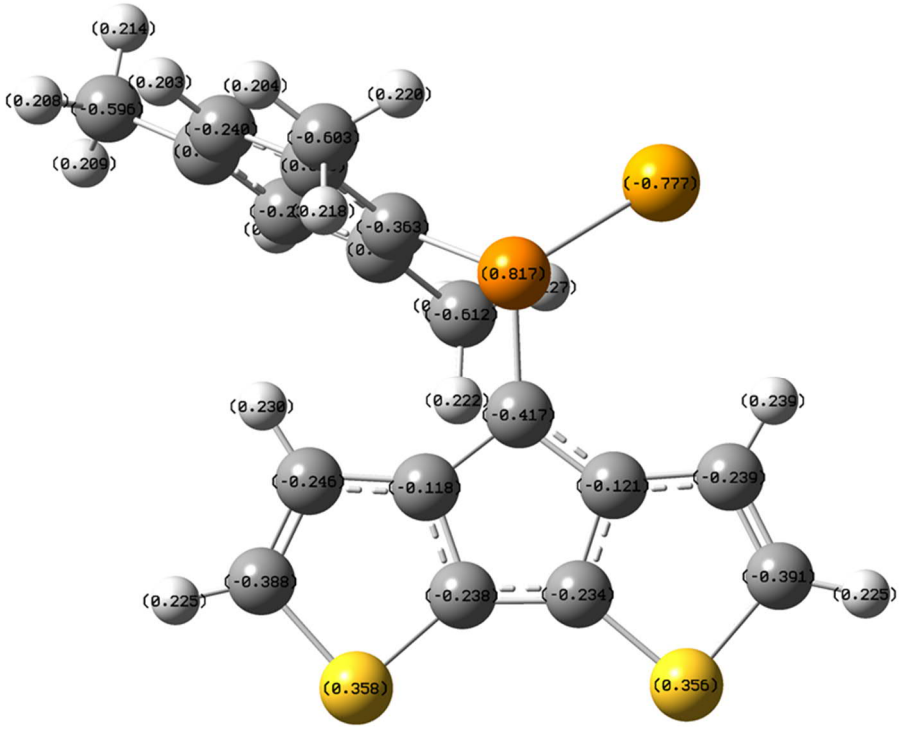


*Figure 95: Calculated NBO charges for model compound **XXV**$^{-}$ (radical anion). Level of theory: cam-B3LYP/6-311G**/PCM(DCM).*

Crystallographic details:

All SC-XRD measurements are performed using graphite-monochromatized Mo Kα radiation using a Bruker D8 APEX-II equipped with a CCD camera. Data reduction was performed with SAINT. Absorption corrections for the area detector were performed using SADABS. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F2 using all data (SHELXT, SHELXS). All non-hydrogen atoms were refined with anisotropic displacement parameters if not stated otherwise. Hydrogen atoms constrained in geometric positions to their parent atoms using OLEX2. Further details of the structure solutions can be found below and are deposited at the CCDC. CCDC 2003575 – 2003582 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

***Table 63**: Crystal data and structure refinement **cis-4**, **trans-3**, **cis-3**, and **8**.*

Compound	***cis*-4**	***trans*-3**	***cis*-3**	**8**
CCDC No.	2003582	2003576	2003575	2003580
Chemical formula	$C_{45}H_{47}PS_2Si$	$C_{41}H_{44}NPS_2$	$C_{41}H_{44}NPS_2$	$C_{55}H_{72}AuCl_3O_2P_2S_4$
M_r	711.00	645.86	645.86	1258.62
Crystal system, space group	Monoclinic $P2_1/c$	Triclinic $P\bar{1}$	Monoclinic $C2/c$	Triclinic $P\bar{1}$
Temperature (K)	150.15	150.15	150.15	170.15
***a*, *b*, *c* (Å)**	11.2582(5) 31.6685(15) 11.3206(5)	9.8171(9) 12.6287(11) 18.4257(16)	37.187(11) 18.843(6) 14.680(5)	14.3023(4) 14.8746(4) 15.9465(4)
***α*, *β*, *γ* (°)**	90 98.667(2) 90	94.130(2) 93.178(2) 108.704(2)	90 97.617(4) 90	67.1250(10) 63.6670(10) 78.5940(10)
***V* (Å^3)**	3990.0(3)	2150.6(3)	10196(6)	2800.01(13)
Z	4	2	8	2
ρ_{calc} g/cm3	1.184	0.997	0.842	1.493
μ (mm^{-1})	0.234	0.185	0.156	3.016
F(000)	1512	688	2752	1284
Crystal size (mm)	0.57 × 0.42 × 0.13	0.1 × 0.04 × 0.02	0.18 × 0.12 × 0.08	0.7 × 0.14 × 0.13
Radiation type (Å)	Mo K_α (λ = 0.71073)			
2Θ range for data collection /°	2.572 to 54	3.42 to 50.496	3.592 to 49.998	3.034 to 53.12
Index ranges	-14 ≤ h ≤ 13 -40 ≤ k ≤ 40 -14 ≤ l ≤ 14	-11 ≤ h ≤ 11 -15 ≤ k ≤ 15 -22 ≤ l ≤ 22	-44 ≤ h ≤ 42 -22 ≤ k ≤ 22 -17 ≤ l ≤ 17	-17 ≤ h ≤ 118 -18 ≤ k ≤ 15 -20 ≤ l ≤ 18
Reflections collected	45526	39217	34437	43292
Independent reflections	8570	7770	8918	11597
R_{int}	0.0438	0.0498	0.0875	0.0653
R_{sigma}	0.0343	0.0405	0.0817	0.0657
Data, restraints, parameters	8570 0 451	7770 0 416	8918 27 447	11597 396 658
Goodness of fit on F^2	1.033	1.03	1.012	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0490 wR_2 = 0.1139	R_1 = 0.0481 wR_2 = 0.1210	R_1 = 0.0643 wR_2 = 0.1685	R_1 = 0.0390 wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0791 wR_2 = 0.1321	R_1 = 0.0700 wR_2 = 0.1333	R_1 = 0.1071 wR_2 = 0.1943	R_1 = 0.0541 wR_2 = 0.0848
Largest diff. peak/hole /eÅ^{-3}	0.26/-0.21	0.27/-0.24	0.34/-0.29	1.12/-1.32

*Table 64: Crystal data and structure refinement **[AuCl*A]**, **10**, and **13**.*

Compound	**[AuCl*A]**	**10**	**13**
CCDC No.	2003577	2003581	2003579
Chemical formula	$C_{27}H_{33}AuClPS_2$	$C_{54}H_{66}Cl_2P_2PdS_4$	$C_{27}H_{33}PS_3$
M_r	685.04	1082.54	484.68
Crystal system, space group	Orthorhombic $P2_12_12_1$	Triclinic $P\bar{1}$	Hexagonal $P6_5$
Temperature (K)	170.15	170.15	180.15
a , *b, c* (Å)	10.8148(10) 15.6701(14) 16.0627(14)	9.3077(8) 10.4351(9) 14.2657(13)	9.1475(4) 9.1475(4) 53.731(3)
***α, β, γ* (°)**	90 90 90	105.983(2) 104.275(2) 94.984(2)	90 90 120
***V* (Å^3)**	2722.1(4)	1272.95(19)	3893.7(4)
Z	4	1	6
ρ_{calc} g/cm3	1.672	1.412	1.24
μ (mm^{-1})	5.728	0.733	0.360
F(000)	1352	564	1548
Crystal size (mm)	0.12 × 0.11 × 0.06	0.2 × 0.08 × 0.06	0.15 × 0.13 × 0.1
Radiation type (Å)		Mo K_α (λ = 0.71073)	
2Θ range for data collection /°	3.632 to 57.644	4.118 to 55.336	4.548 to 57.578
Index ranges	-14 ≤ h ≤ 14 -21 ≤ k ≤ 21 -21 ≤ l ≤ 21	-12 ≤ h ≤ 12 -13 ≤ k ≤ 13 -18 ≤ l ≤ 18	-12 ≤ h ≤ 8 -11 ≤ k ≤ 12 -72 ≤ l ≤ 72
Reflections collected	55400	29100	40809
Independent reflections	7083	5907	6754
R_{int}	0.0843	0.0627	0.096
R_{sigma}	0.0572	0.0532	0.069
Data, restraints, parameters	7083 0 298	5907 0 295	6754 1 289
Goodness of fit on F^2	1.025	1.049	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0319 wR_2 = 0.0532	R_1 = 0.0424 wR_2 = 0.0975	R_1 = 0.0460 wR_2 = 0.0936
Final R indexes [all data]	R_1 = 0.0467 wR_2 = 0.0572	R_1 = 0.0649 wR_2 = 0.1070	R_1 = 0.0619 wR_2 = 0.0999
Largest diff. peak/hole /eÅ^{-3}	0.66/-0.82	0.56/-0.86	0.22/-0.26
Flack parameter	0.002(5)	n.a.	0.06(4)

Electrochemistry

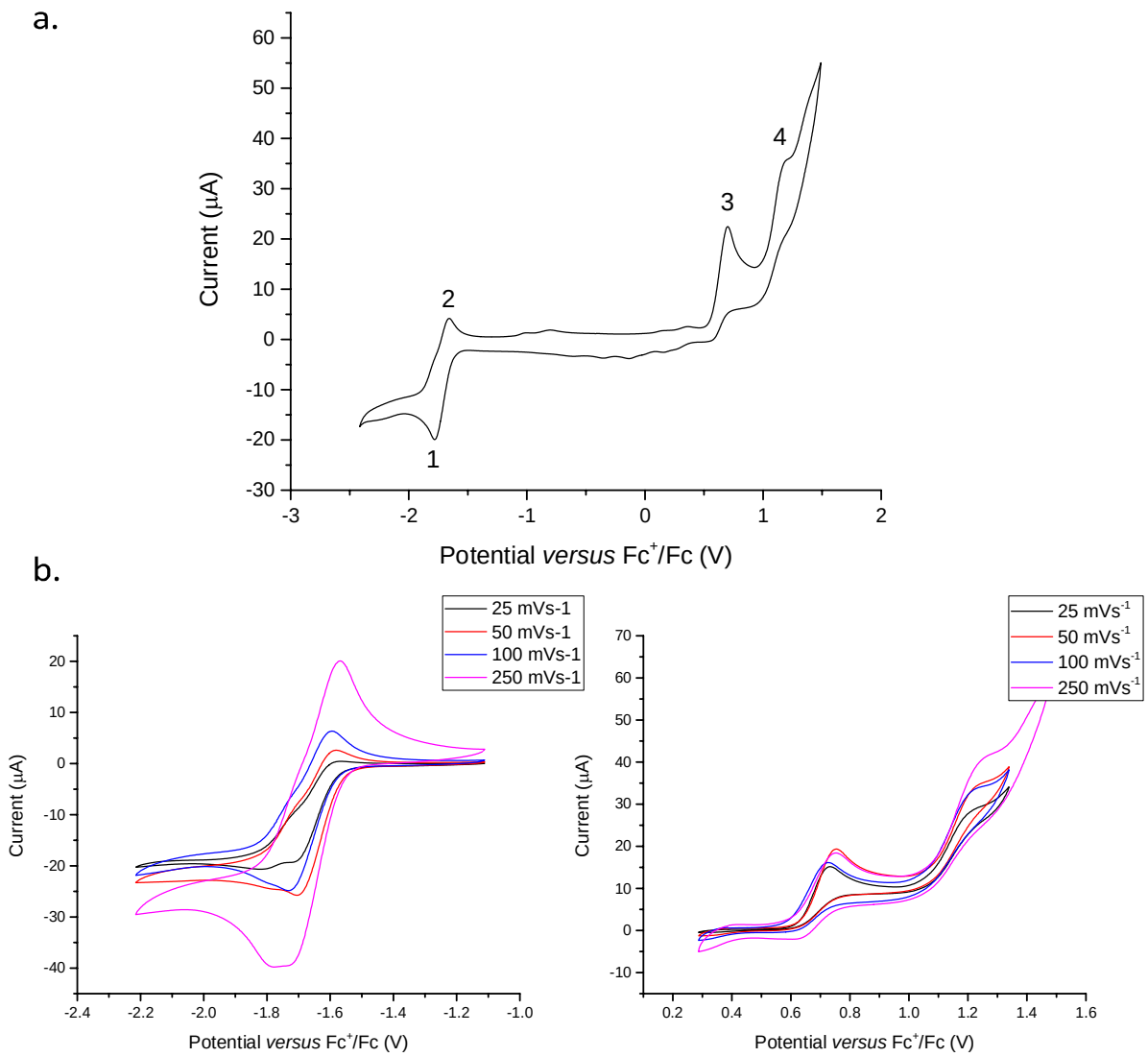


*Figure 96: a. Electrochemical response of **2**. (100 mVs^{-1}). Redox events of interest are numbered 1-4. b. electrochemical response of **2** at variable scan rates. Voltammograms collected in 0.1M NBu_4PF_6/DCM*

*Table 65: Currents and potentials for redox events 1-4 of compound **2** at 100 mVs^{-1} scan rates (0.1M NBu_4PF_6/DCM).*

	1	2	3	4
E_p / V	-1.78	-1.66	0.70	1.21
ΔE / V	0.12		-	-
I / μA	16.65	13.20	-	-
Ipc/Ipa	0.80			

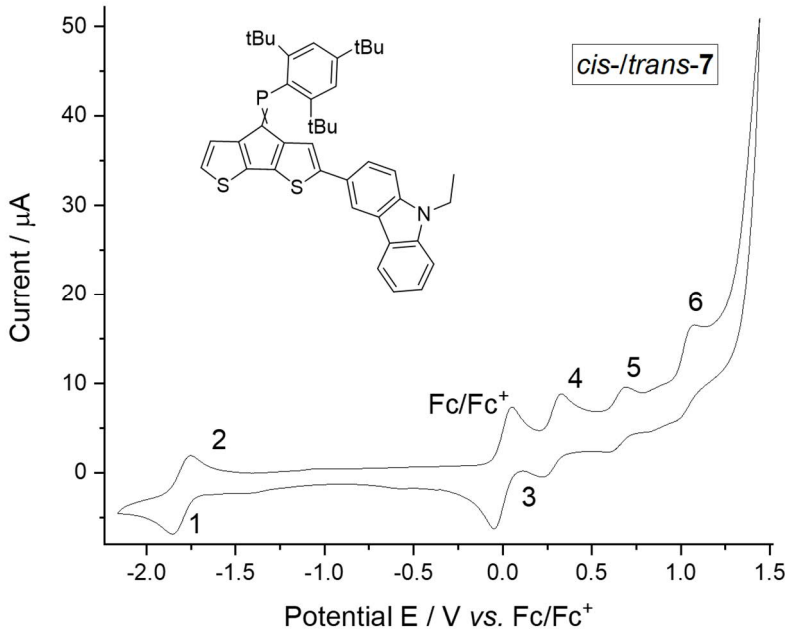


*Figure 97: Electrochemical response of cis-/trans-**7**. (0.1 M NBu_4PF_6/DCM, 100 mVs^{-1}). Ferrocene reference and numbered redox events of interest are shown.*

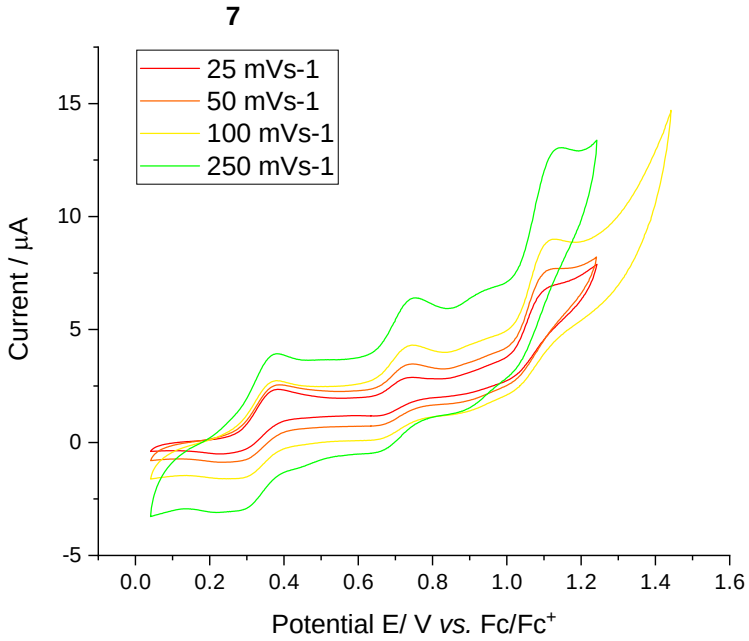


*Figure 98: Scan rate dependent (25 to 250 mV sec^{-1}) cyclic voltammetry of cis-/trans-**7**.*

*Table 66: Currents and potentials for redox events 1-6 of compound **7** at 100 mVs^{-1} scan rates (0.1 M NBu_4PF_6/DCM).*

	1	2	3	4	5	6
E / V	-1.86	-1.75	0.22	0.33	0.69	1.05
ΔE / V	0.11		0.11		-	-
I / µA	3.3	3.2	0.92	3.4	-	-
Ipc/Ipa	0.97		0.27			

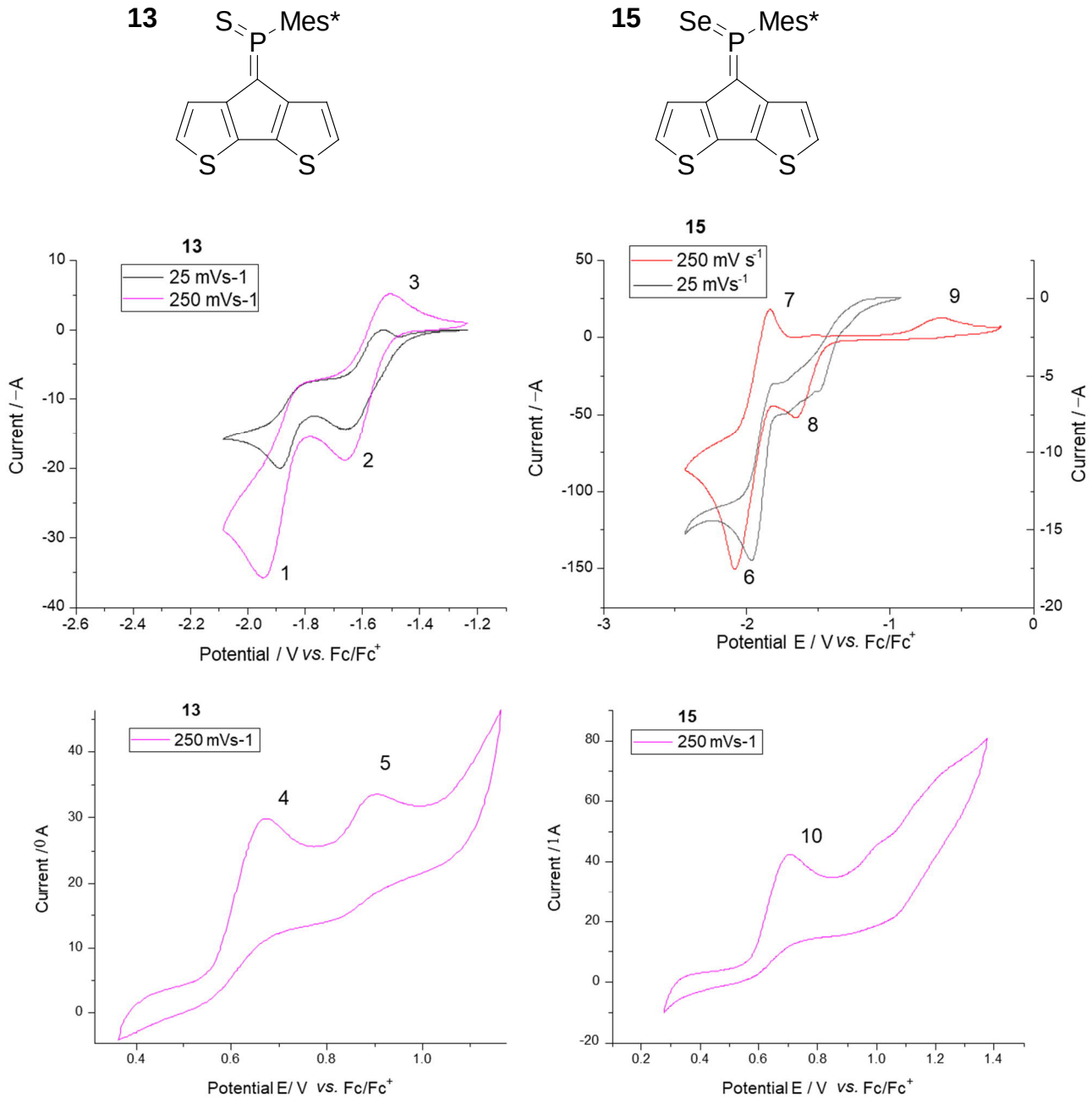


*Figure 99: Oxidative (250 mV sec^{-1}) and reductive (25 and 250 mV sec^{-1}) scans of compounds **13** and **15**. (0.1 M NBu_4PF_6/DCM):*

*Table 67: Currents and potentials for **13** (redox events 1-5) and **15** (redox events 6-9) at 250 mVs^{-1} scan rates (0.1M NBu_4PF_6/DCM).*

	13					**15**				
	1	2	3	4	5	6	7	8	9	10
E / V	-1.94	-1.66	-1.50	0.67	0.90	-2.08	-1.83	-1.66	-0.64	0.71
ΔE / V	-	0.16		-	-	0.25		-		-
I / µA	-	17.5	10.0	-	-	92.0	66.8	-		-
Ipc/Ipa	0.57					0.72				