Supporting Information

for

Reactivity Studies of [(thf)$_2$Mg{μ-C(CH$_3$)$_2$C$_2$H$_4$C(CH$_3$)$_2$}]$_2$: Scrambling Reactions and Diverse Reactions with Dichlorophenylphosphane

Reinald Fischer, Helmar Görls, and Matthias Westerhausen*

Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena,
Humboldtstrasse 8, D-07743 Jena, Germany,
e-mail: m.we@uni-jena.de, fax: +49 3641 94813

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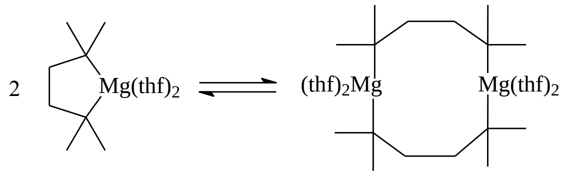
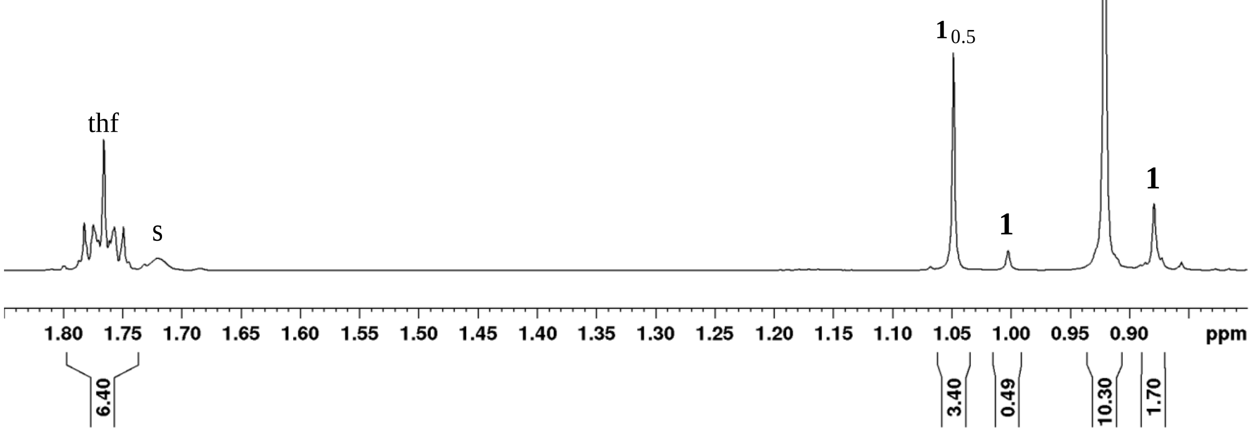
NMR Spectra



1$_{0.5}$ **1**



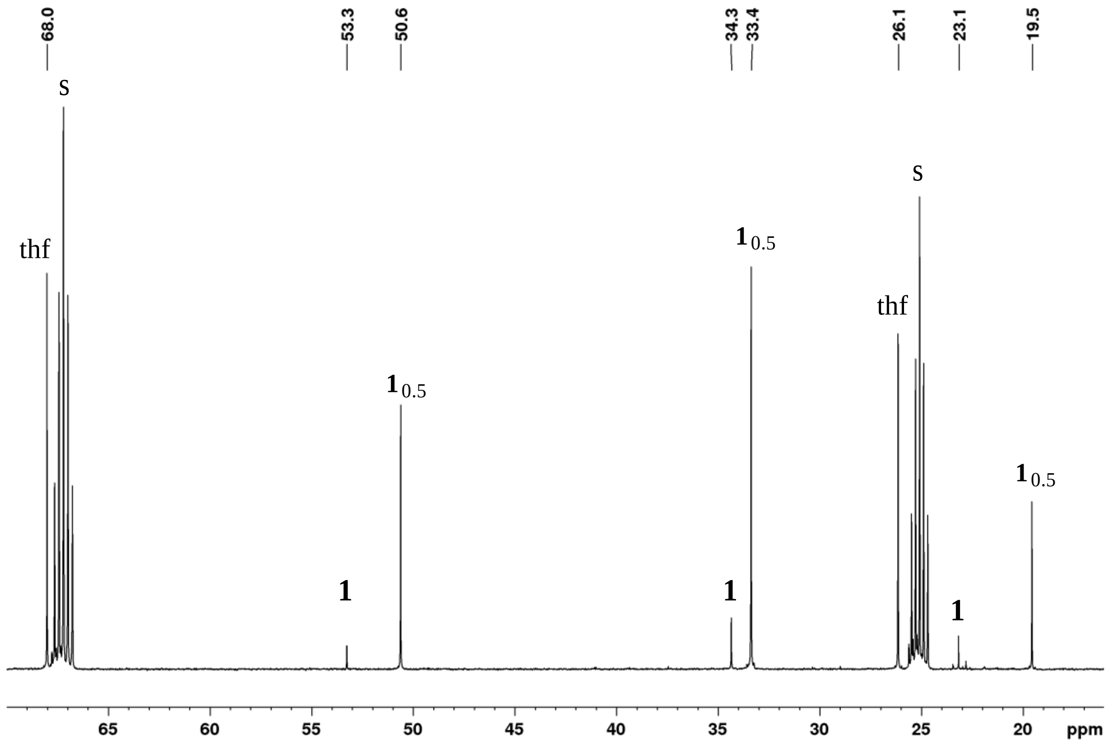


Figure S1. ^{1}H NMR (top) and ^{13}C{^{1}H} NMR spectrum (bottom) of **1**, measured at 600 MHz and at 150.9 MHz, respectively, in [D$_8$]THF (s = (residual) signal of [D$_8$]THF).

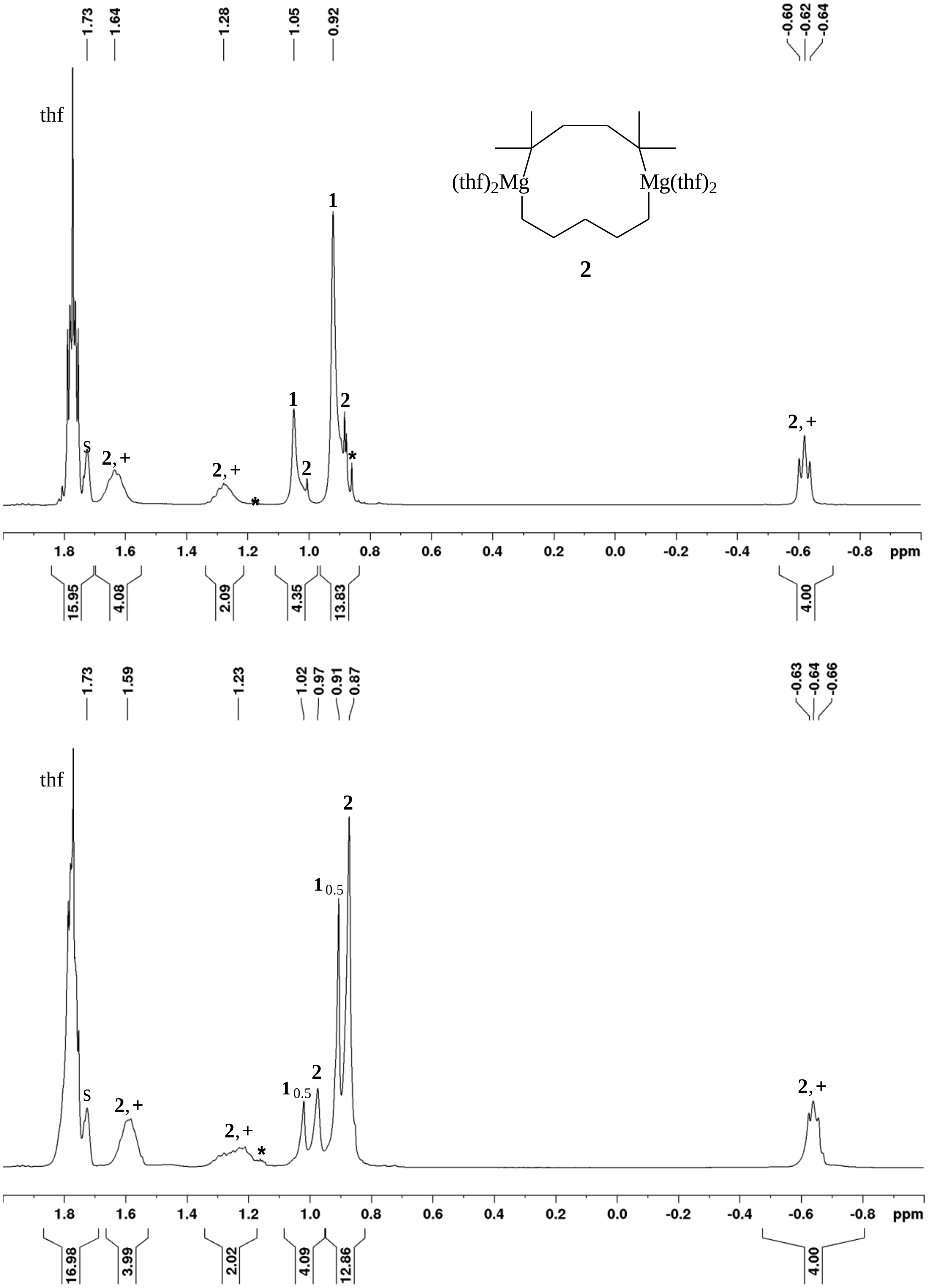


Figure S2. ^{1}H NMR spectrum of **2** at 20 °C (top) and at -40 °C (bottom) measured at 400 MHz in [D$_8$]THF (**1** = signals of [{(thf)$_2$Mg{μ-C(CH$_3$)$_2$(CH$_2$)$_2$(CH$_3$)$_2$C}}$_2$], + = signals of [{(thf)$_2$Mg{μ-CH$_2$)$_5$}}$_2$], * = signals of hydrolysis product, s = (residual) signal of [D$_8$]THF).

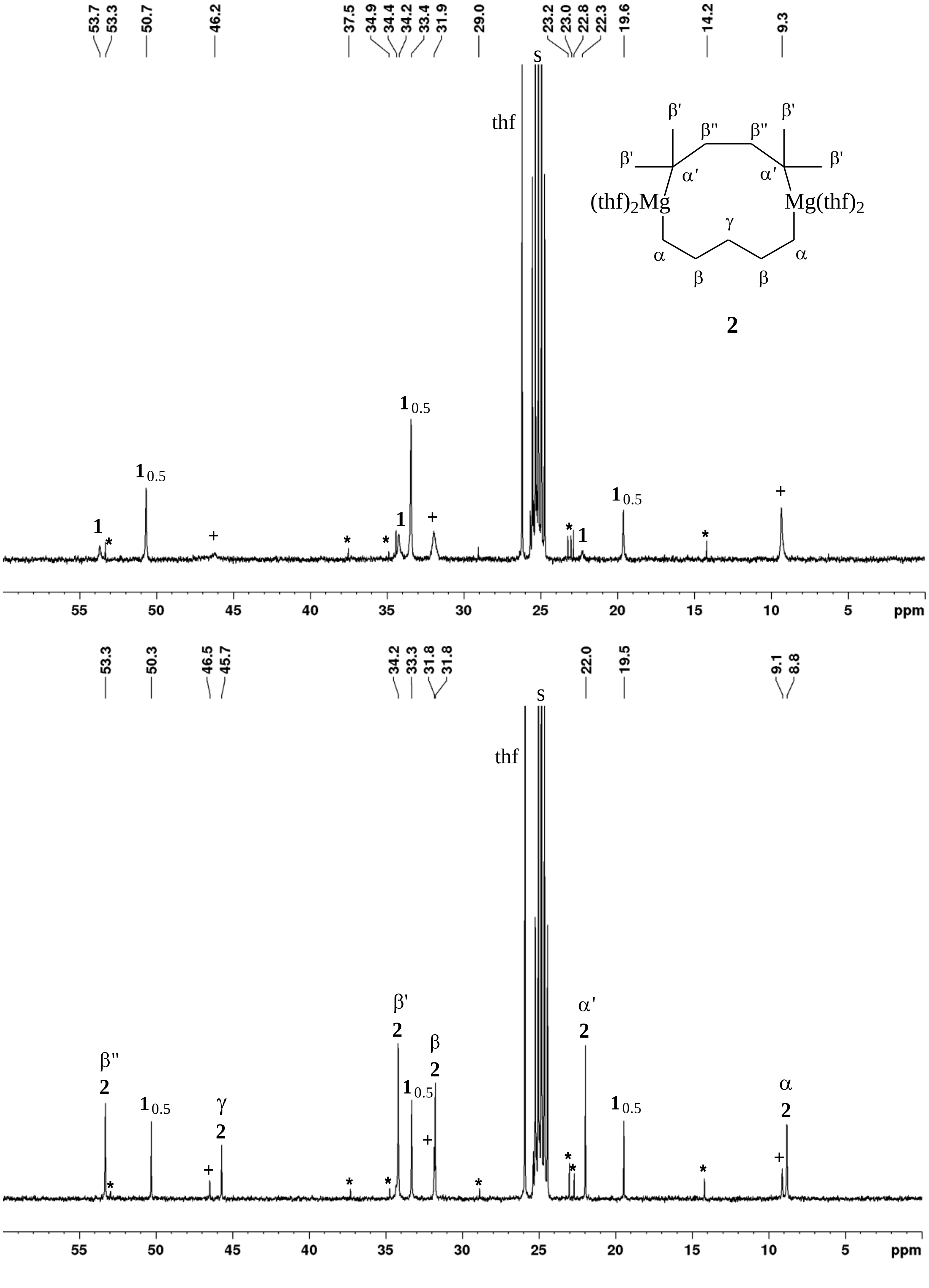


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **2** at 20 °C (top) and at -40 °C (bottom) measured at 400.1 MHz in [D$_8$]THF (**1** = signals of dinuclear [{(thf)$_2$Mg{μ-C(CH$_3$)$_2$(CH$_2$)$_2$(CH$_3$)$_2$C}}$_2$], **1**$_{0.5}$ = signals of mononuclear isomer of **1**, + = signals of [{(thf)$_2$Mg{μ-CH$_2$)$_5$}}$_2$], * = signals of hydrolysis product, s = signal of [D$_8$]THF).

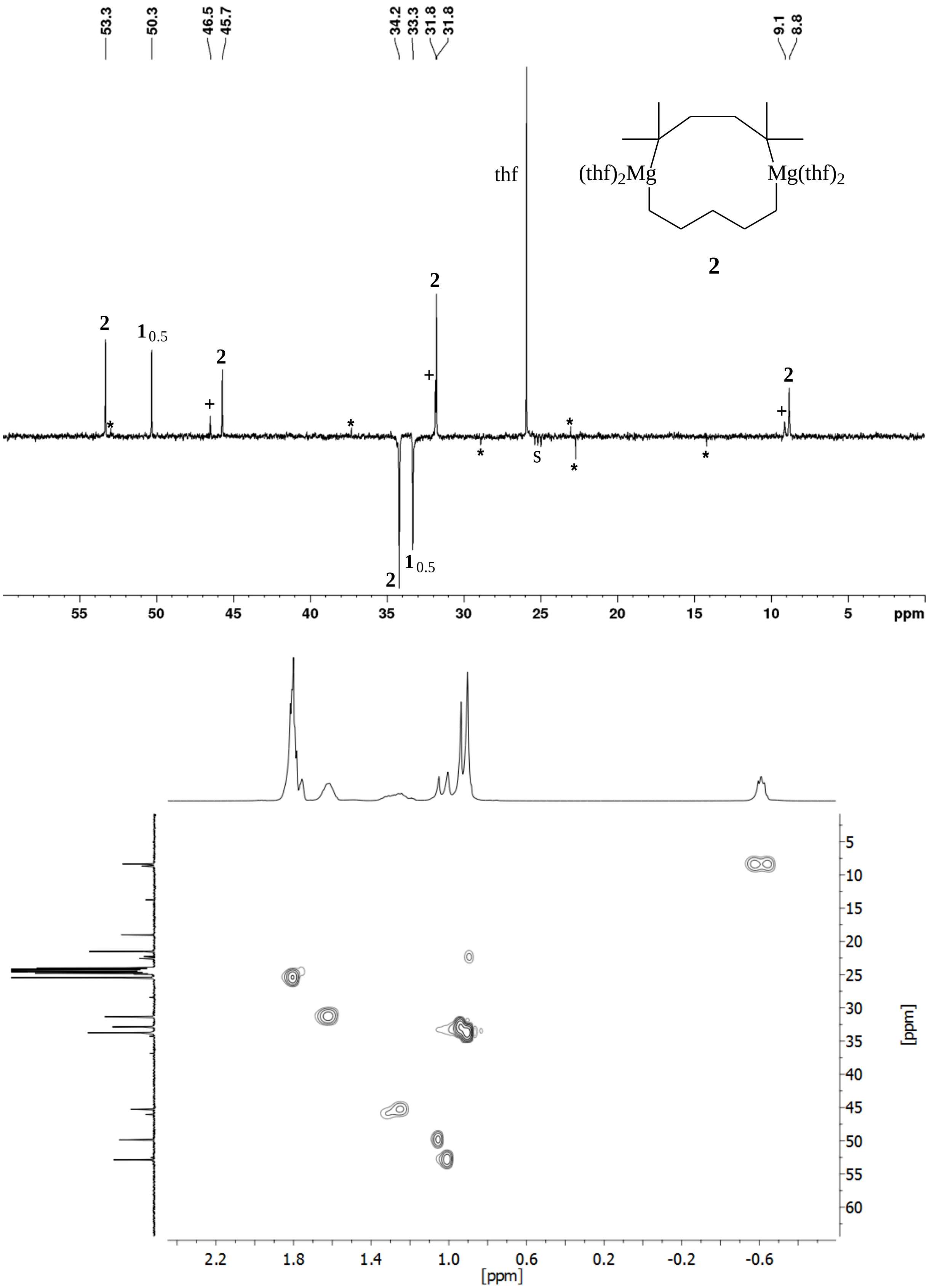


Figure S4. DEPT (top) and HSQC spectrum (bottom) of **2** at -40 °C measured in [D$_8$]THF at 150.9 MHz and 400.1 MHz, respectively. (**1**$_{0.5}$ = mononuclear complex of **1**, + = [{(thf)$_2$Mg{μ-CH$_2$)$_5$}}$_2$], * = hydrolysis product, s = [D$_8$]THF).

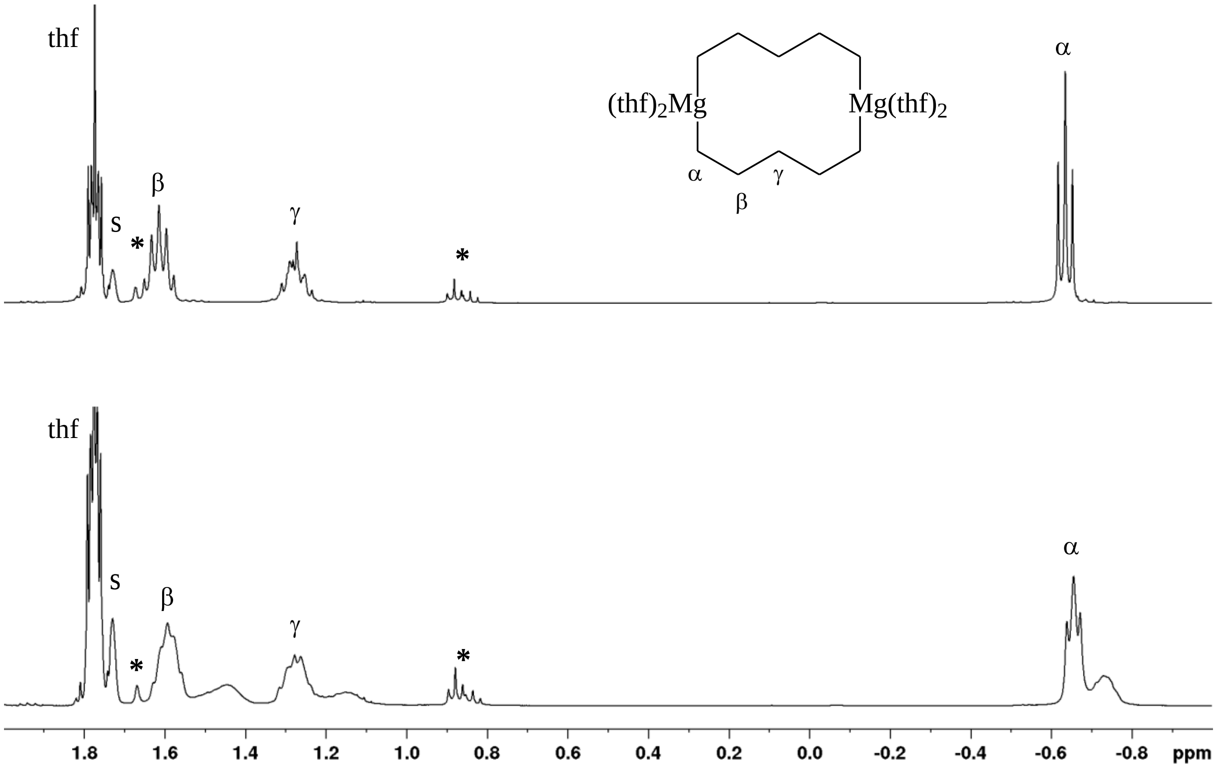


Figure S5. ^{1}H NMR spectrum of [{(thf)$_2$Mg{μ-CH$_2$)$_5$}}$_2$] at 20 °C (top) and -40 °C (bottom), measured at 400 MHz in [D$_8$]THF (* = hydrolysis product, s = (residual) signal of [D$_8$]THF).

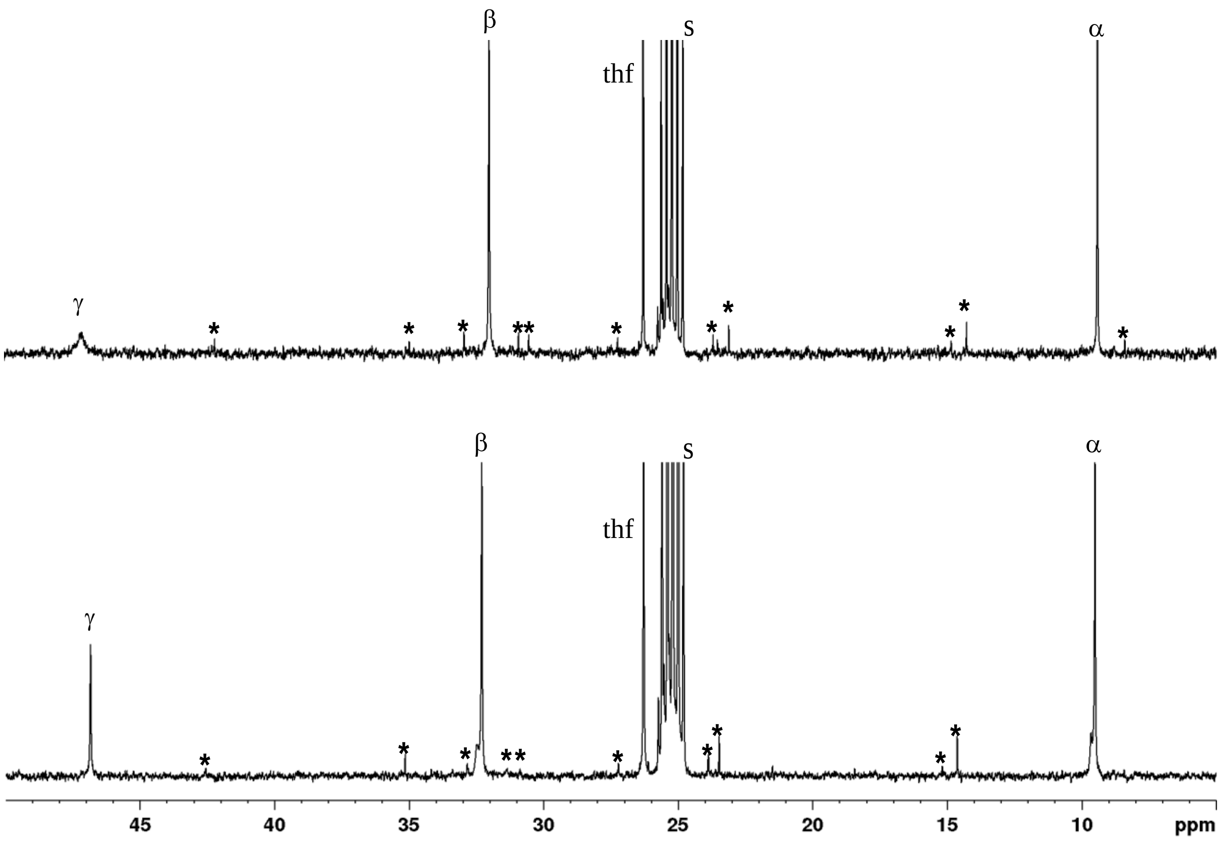


Figure S6. Temperature dependent $^{13}C\{^{1}H\}$ NMR spectrum of [{(thf)$_2$Mg{μ-CH$_2$)$_5$}}$_2$] at 20 °C (top) and -40 °C (bottom), measured at 100.6 MHz in [D$_8$]THF (* = hydrolysis product, s = (residual) signal of [D$_8$]THF).

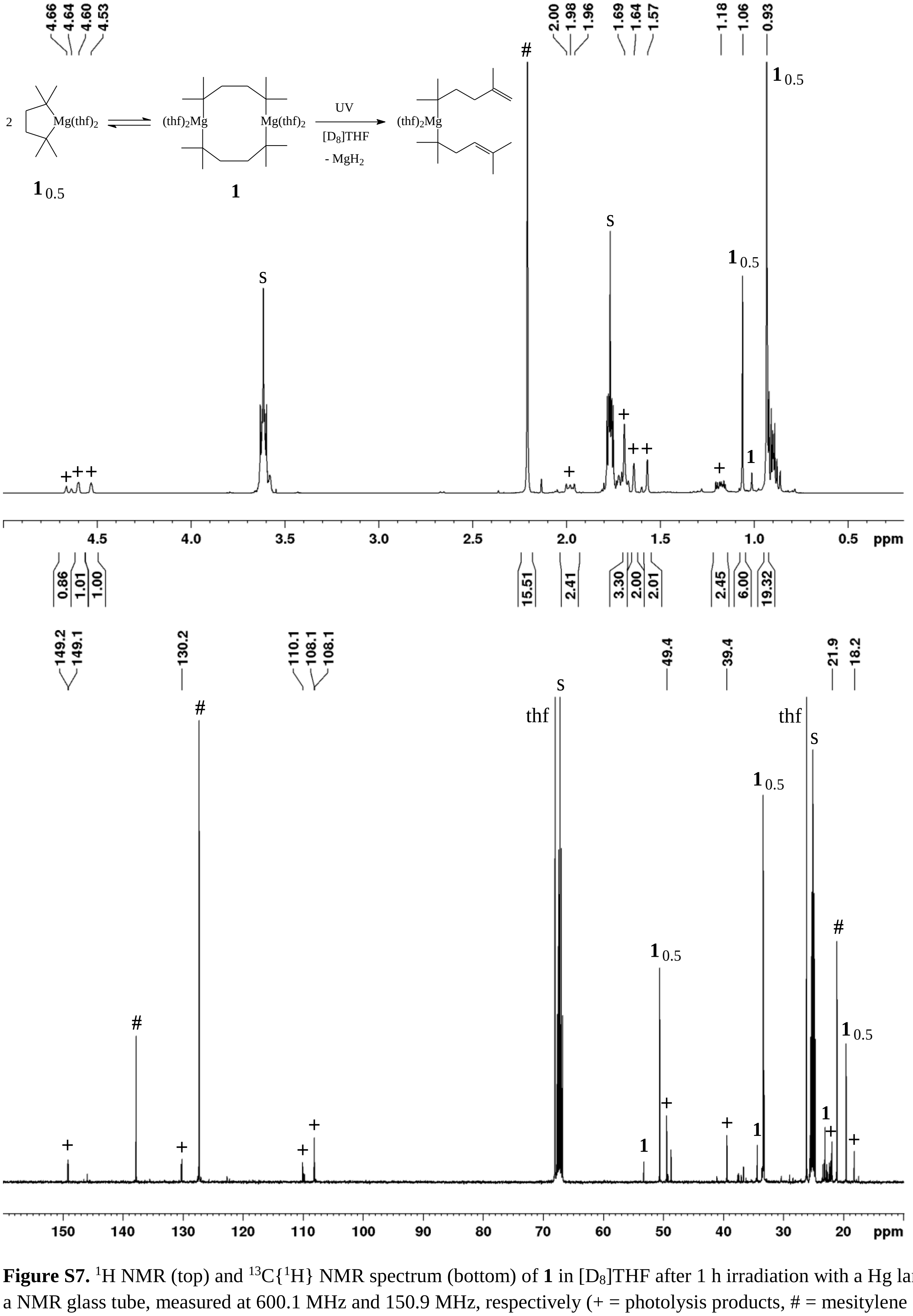


Figure S7. ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectrum (bottom) of **1** in [D$_8$]THF after 1 h irradiation with a Hg lamp in a NMR glass tube, measured at 600.1 MHz and 150.9 MHz, respectively (+ = photolysis products, # = mesitylene as internal standard, s = (residual) signal of [D$_8$]THF).

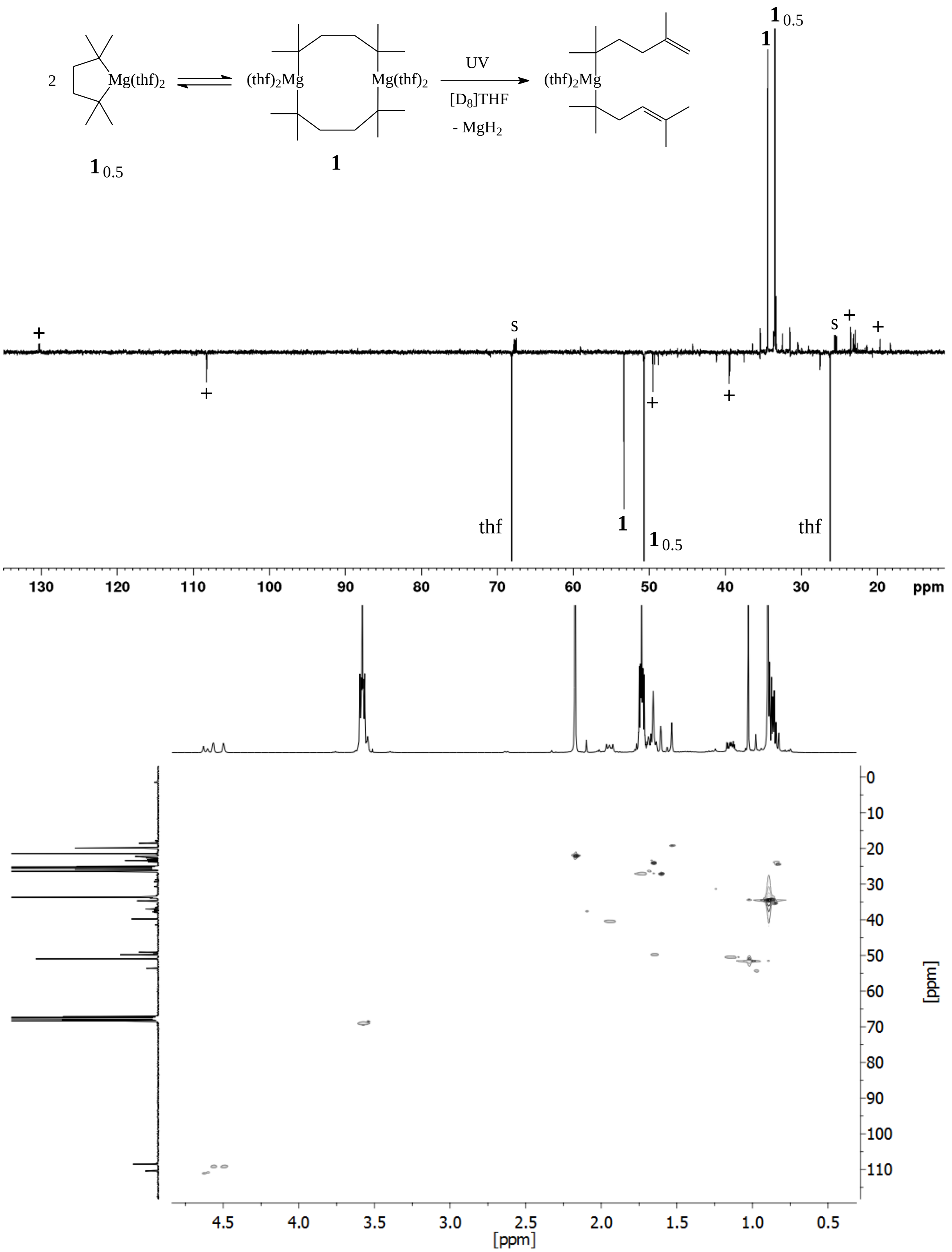


Figure S8. DEPT (top) and HSQC spectrum (bottom) of **1** in [D_8]THF after 1 h irradiation with a Hg lamp in a NMR glass tube, measured at 150.9 MHz and 400.1 MHz and, respectively (+ = signals of photolysis products, s = residual signal of [D_8]THF).

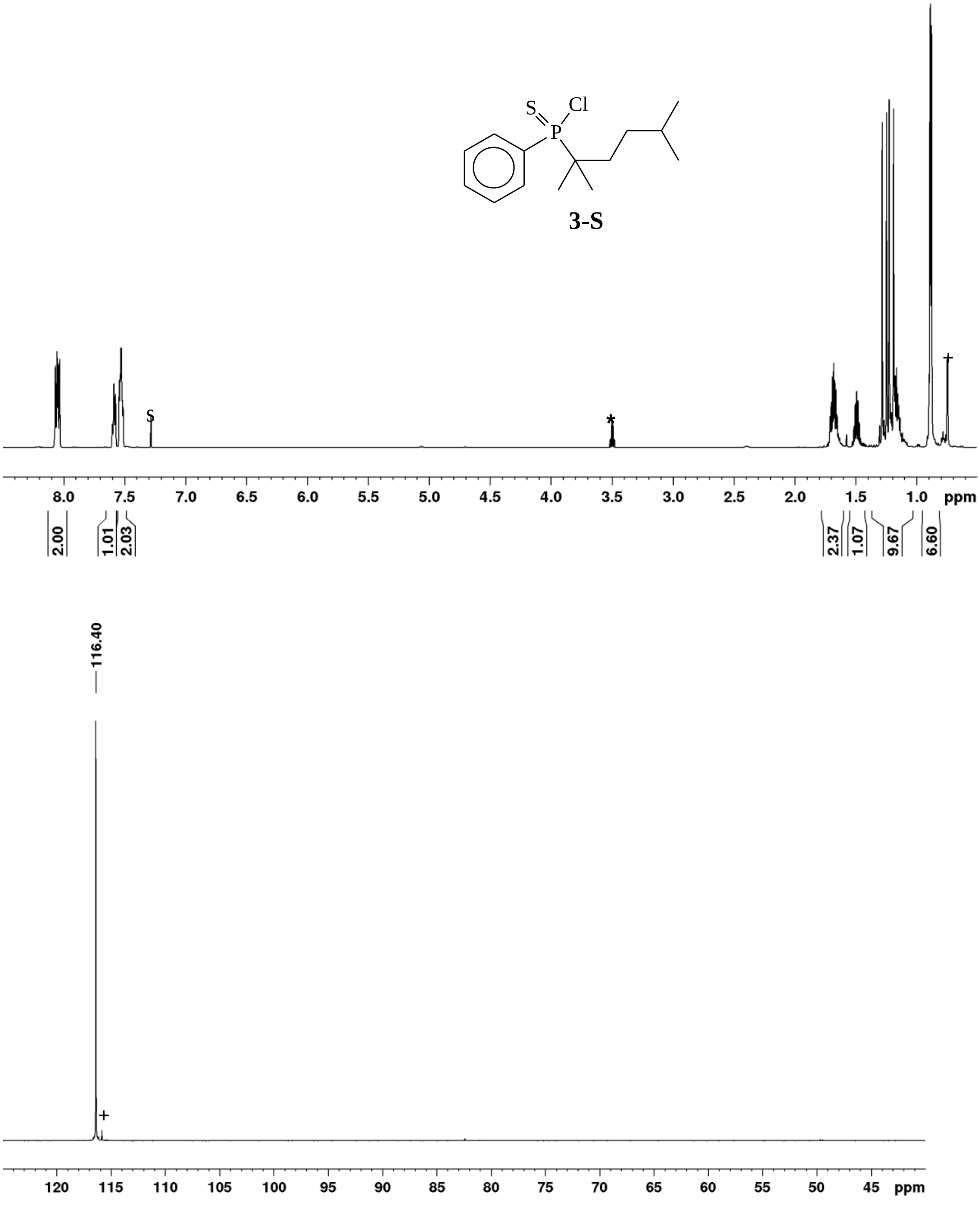


Figure S9. ^{1}H NMR (top) and $^{31}P\{^{1}H\}$ NMR spectrum (bottom) of [PhP(S)(Cl){C(CH_3)$_2$(CH_2)$_2$(CH_3)$_2$CH}] (**3-S**), measured at 600 MHz and at 162.0 MHz, respectively, in $CDCl_3$ (* = residual signal of diethyl ether, + = [{PhP(S)(Cl)}$_2${C(CH_3)$_2$(CH_2)$_2$(CH_3)$_2$C}] (**5-S$_2$**), s = residual signal of $CDCl_3$).

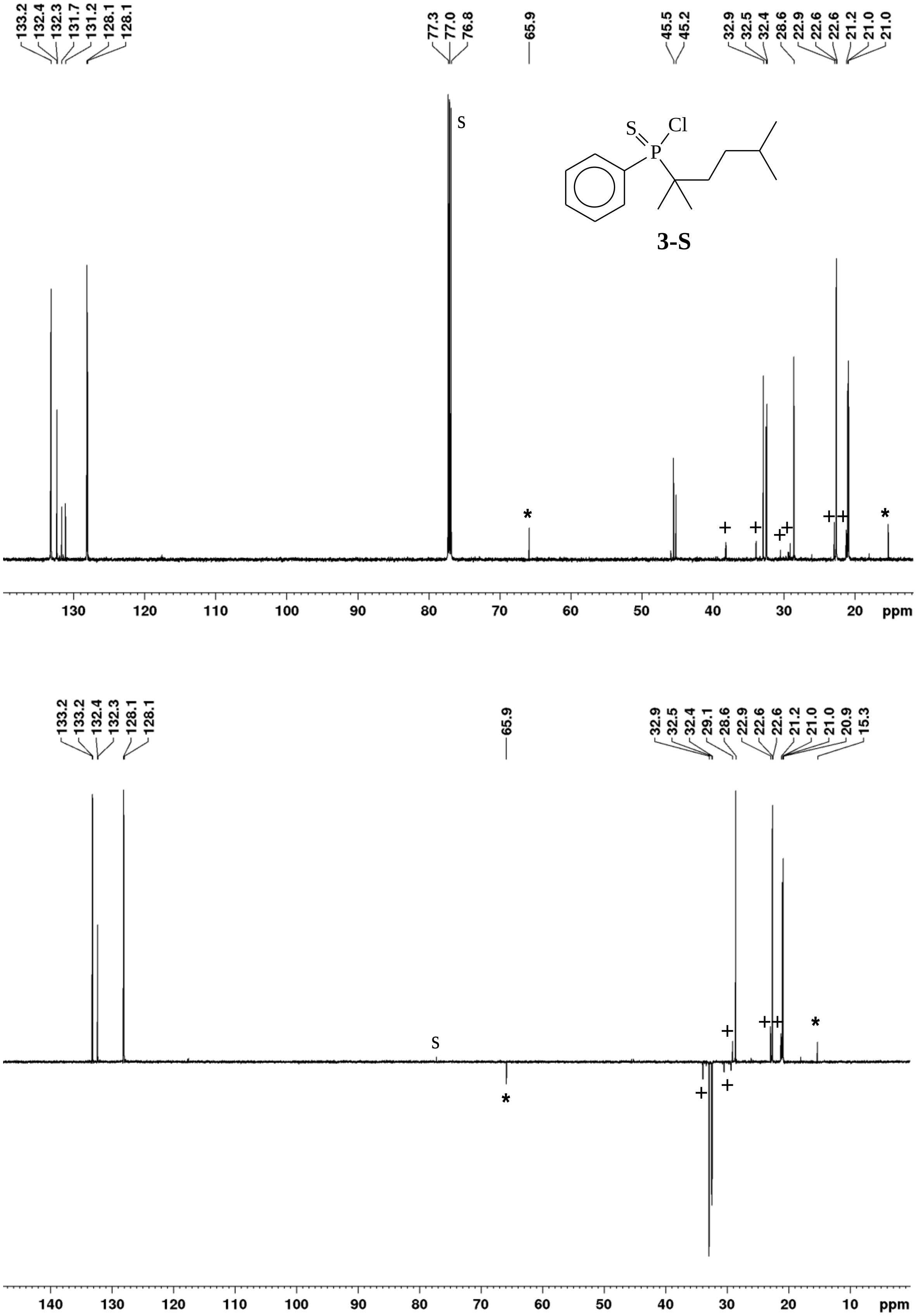


Figure S10. $^{13}C\{^{1}H\}$ NMR (top) and DEPT spectrum (bottom) of **3-S**, measured at 150.9 MHz, in $CDCl_3$ (* = residual signal of diethyl ether, + = $[\{PhP(S)(Cl)\}_2\{C(CH_3)_2(CH_2)_2(CH_3)_2C\}]$ (5-**S**$_2$), s = residual signal of $CDCl_3$).

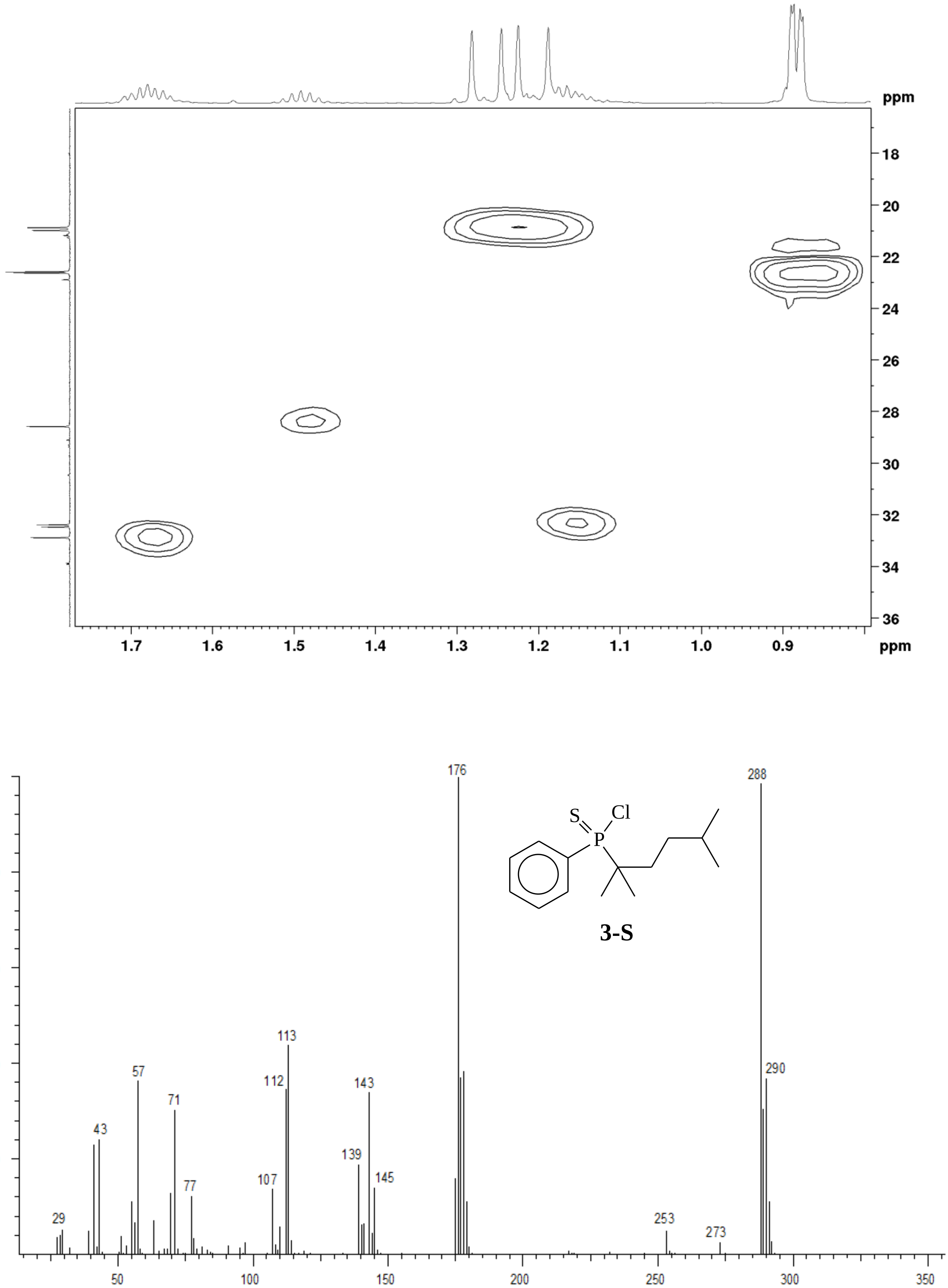


Figure S11. Detail of HSQC spectrum, measured in $CDCl_3$ (top), and mass spectrum (bottom) of **3-S**.

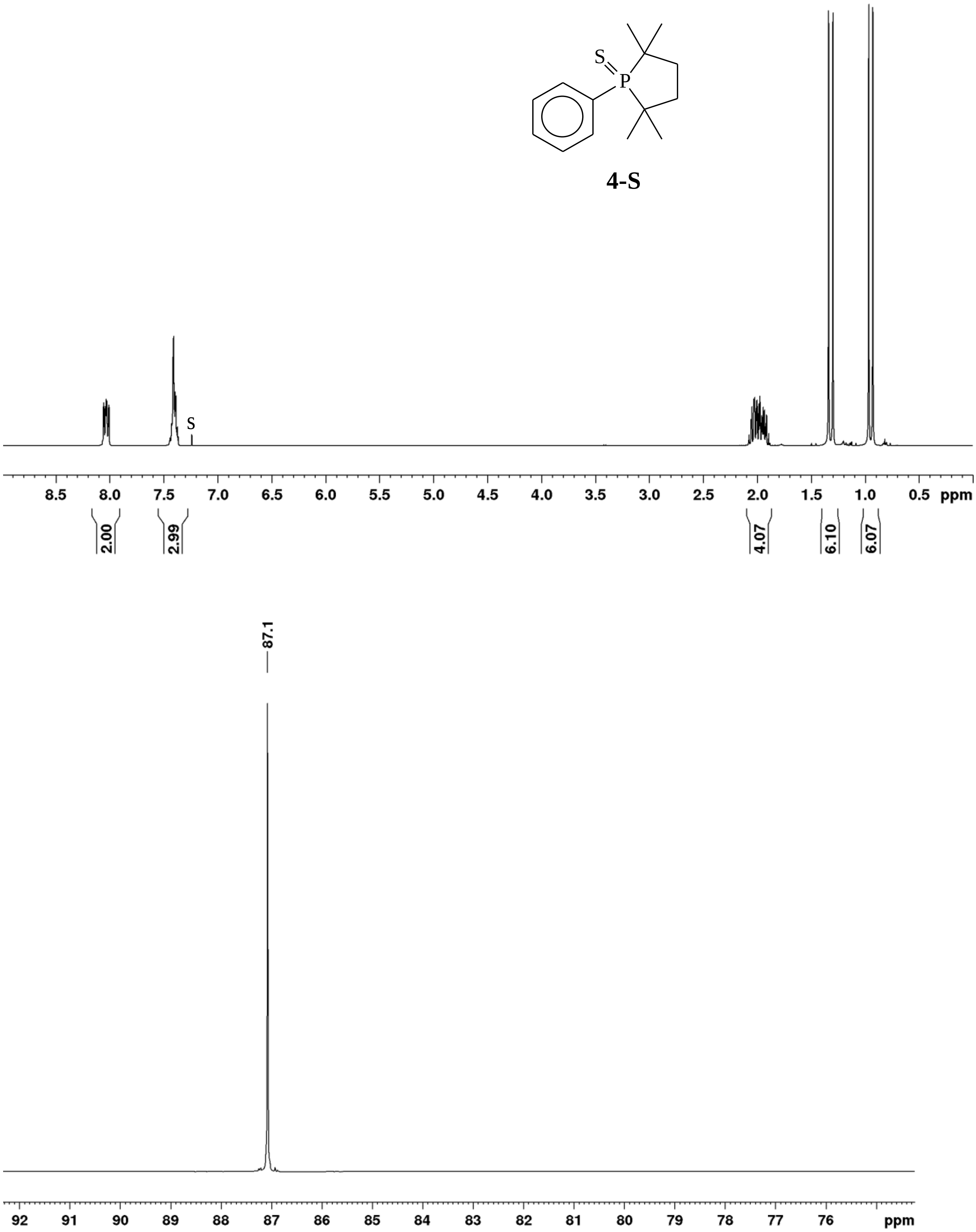
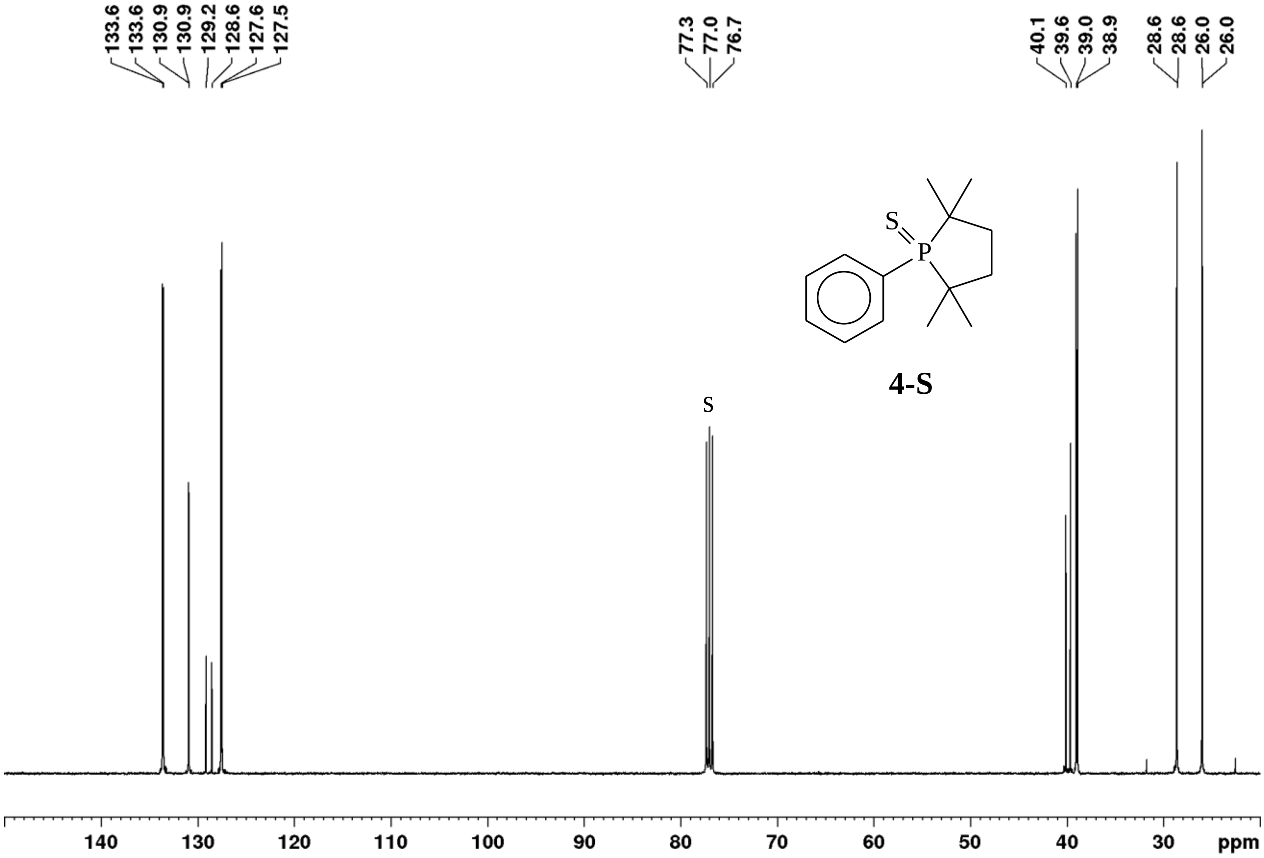


Figure S12. ^{1}H NMR (top) and $^{31}P\{^{1}H\}$ NMR spectrum (bottom) of **4-S**, measured at 400.1 MHz, and at 162.0 MHz, respectively, in $CDCl_3$.



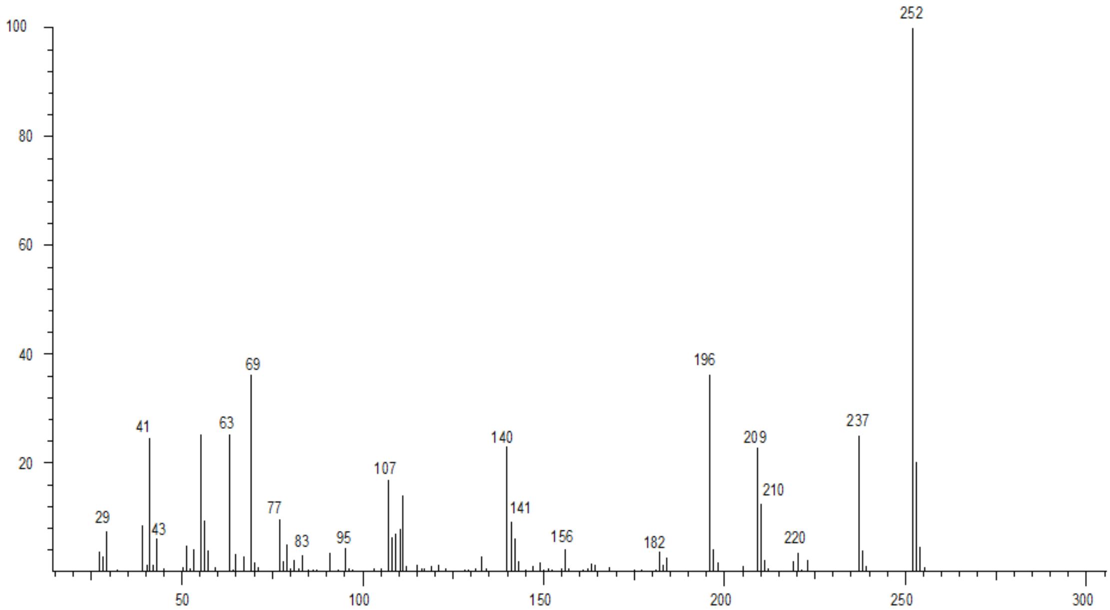


Figure S13. $^{13}C\{^1H\}$ NMR spectrum (top) measured at 100.6 MHz in $CDCl_3$ and mass spectrum (bottom) of **4-S** (s = signal of $CDCl_3$).

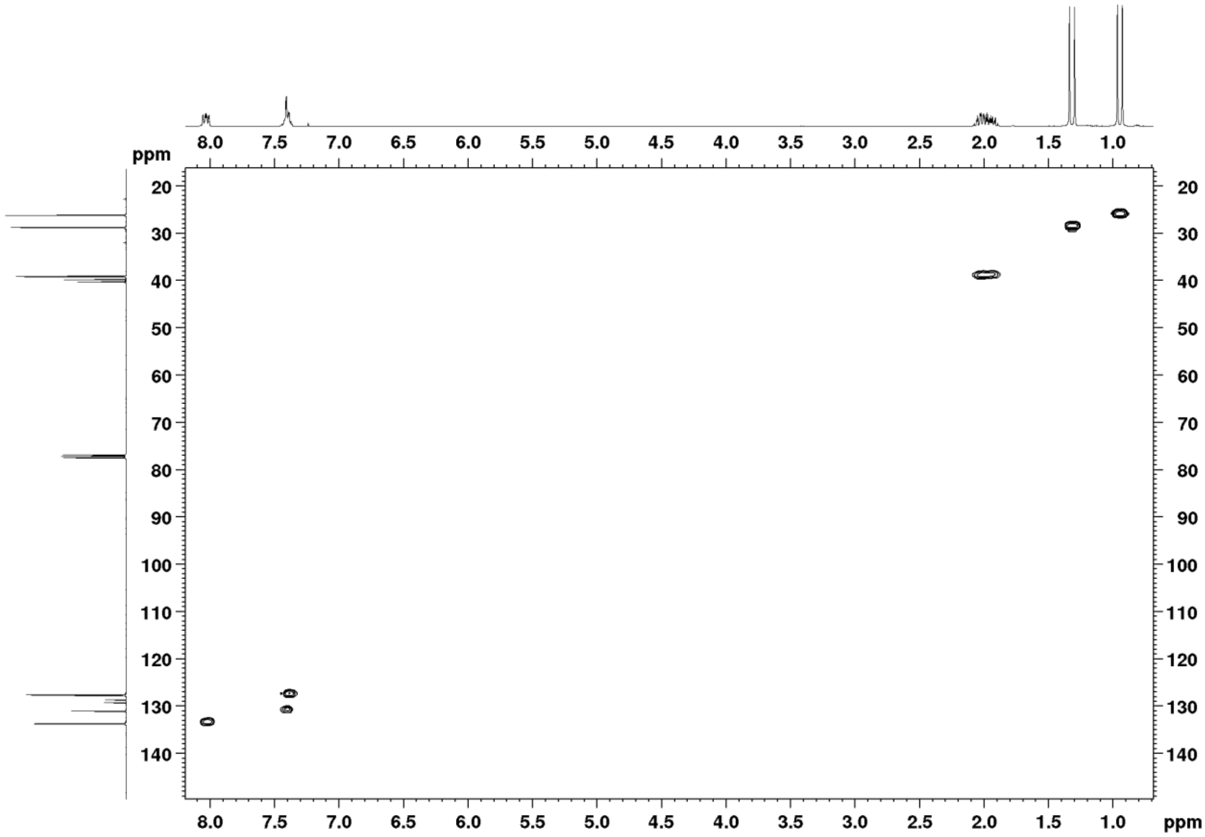


Figure S14. HSQC spectrum of **4-S**, measured at 400.1 MHz, in $CDCl_3$.

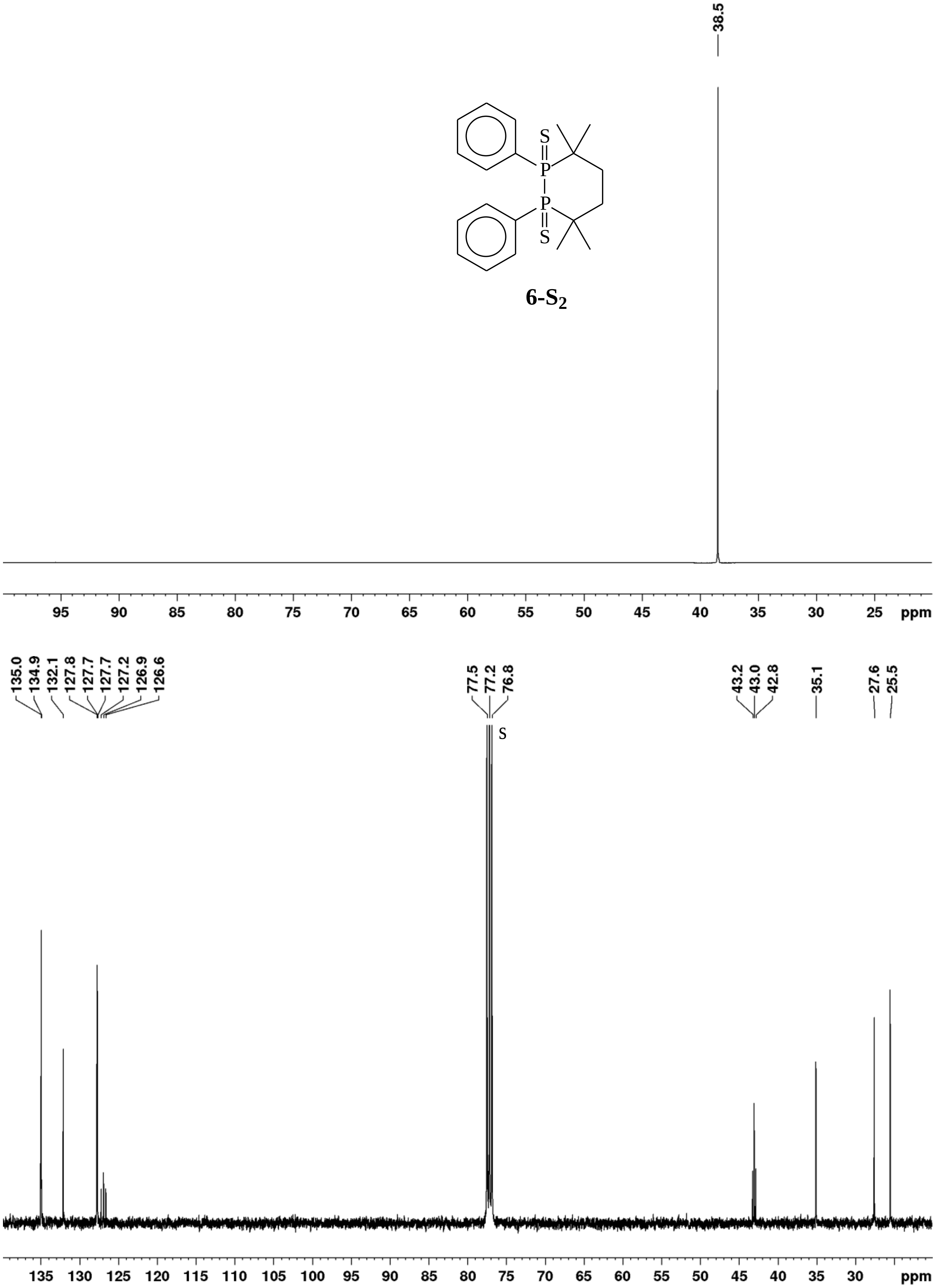
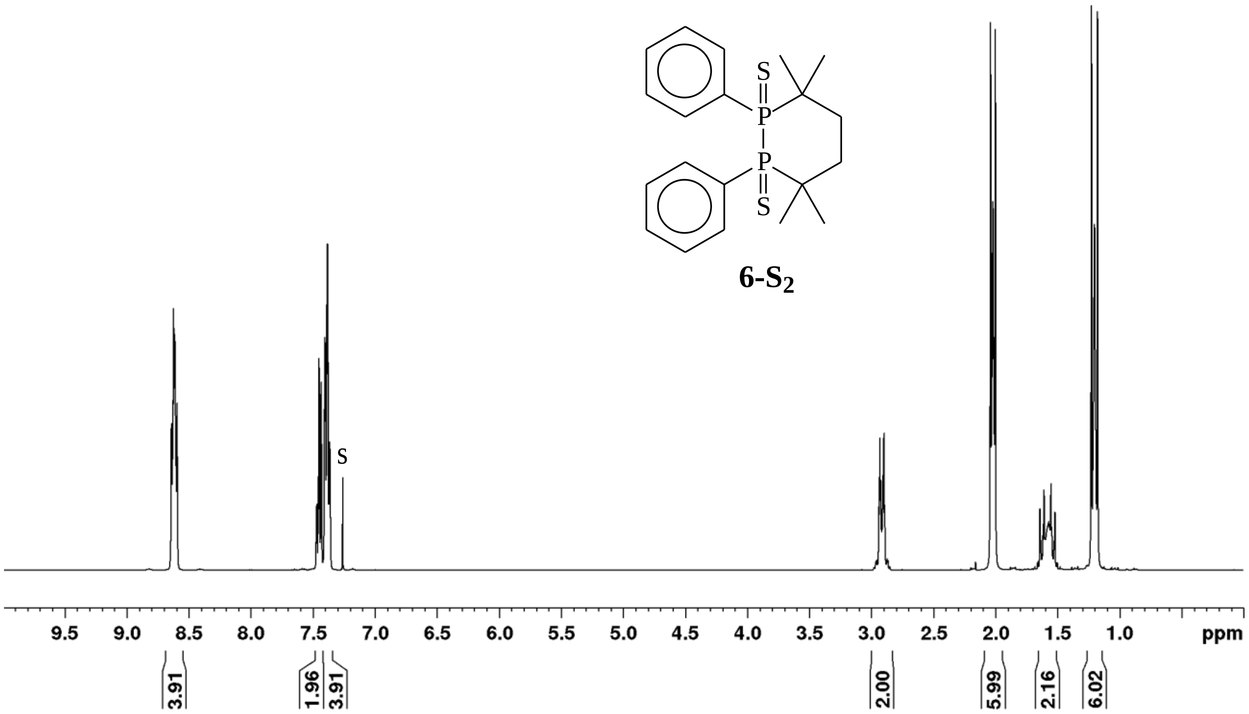


Figure S15. $^{31}P\{^{1}H\}$ NMR and $^{13}C\{^{1}H\}$ NMR spectrum of **6-S$_2$**, measured at 162.0 MHz and 100.6 MHz, respectively, in $CDCl_3$ (s = signal of $CDCl_3$).



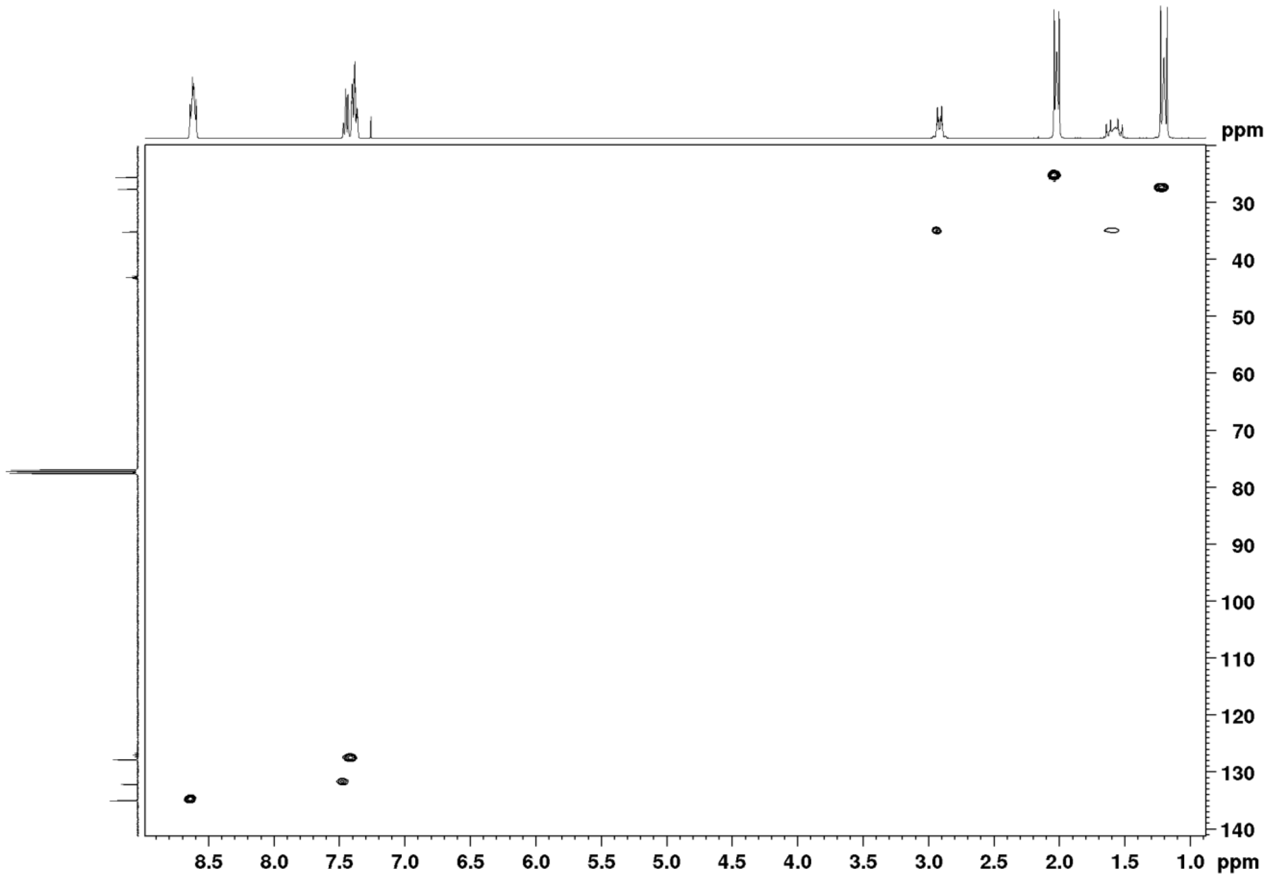
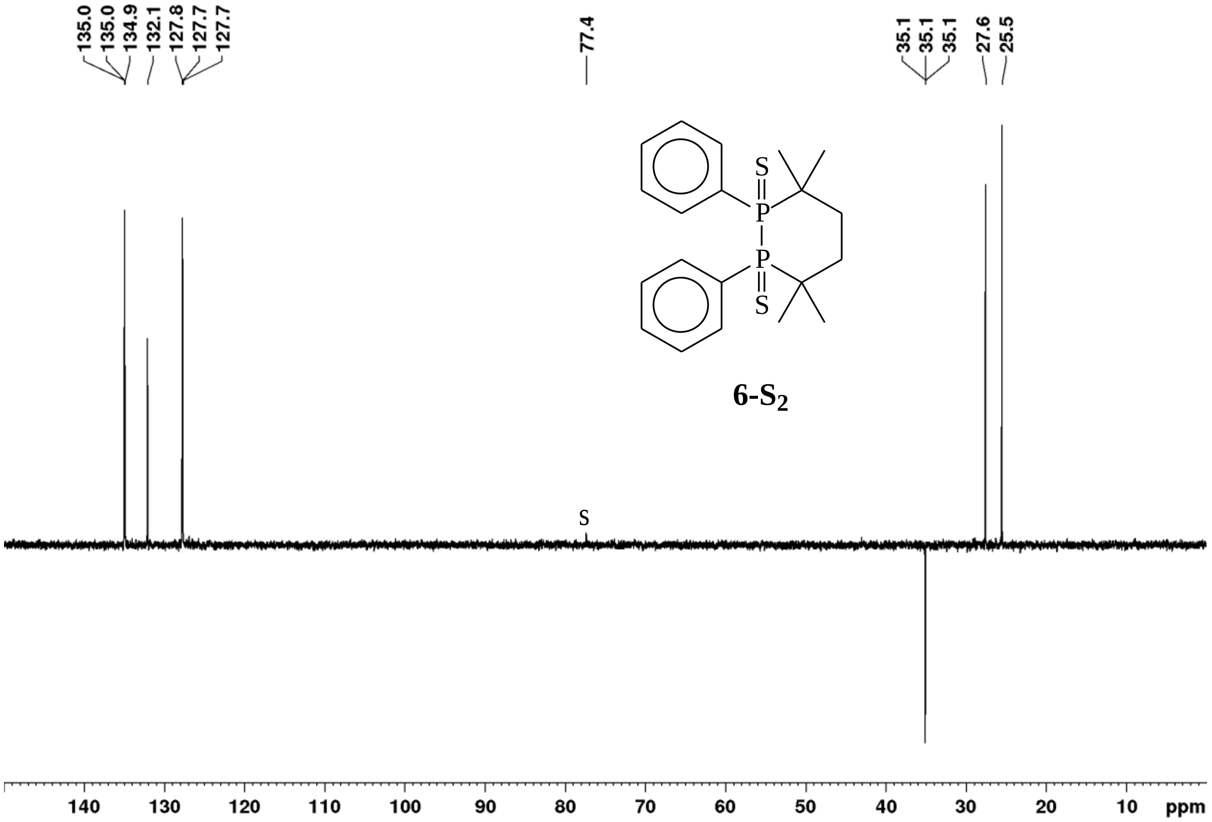


Figure S16. [1]H NMR and HSQC spectrum of **6-S₂**, measured at 400.1 MHz, in $CDCl_3$ (s = signal of $CDCl_3$).



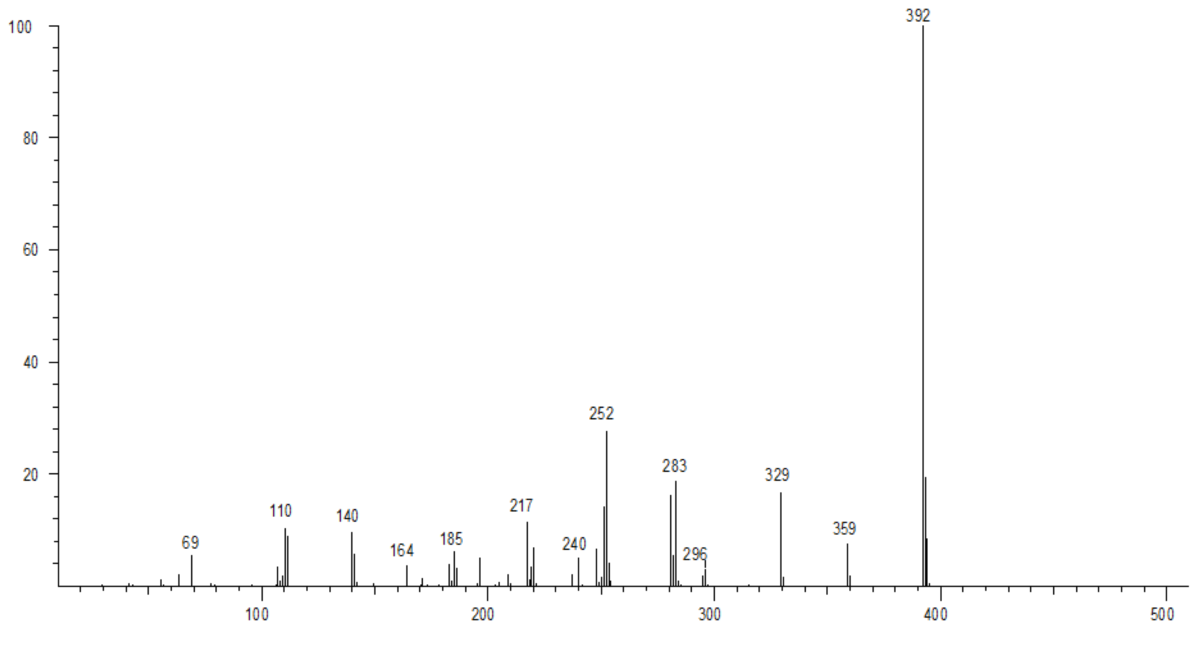


Figure S17. DEPT spectrum (top), measured at 100.6 MHz, in $CDCl_3$ (s = (residual) signal of $CHCl_3$) and mass spectrum (bottom) of **6-S$_2$**.

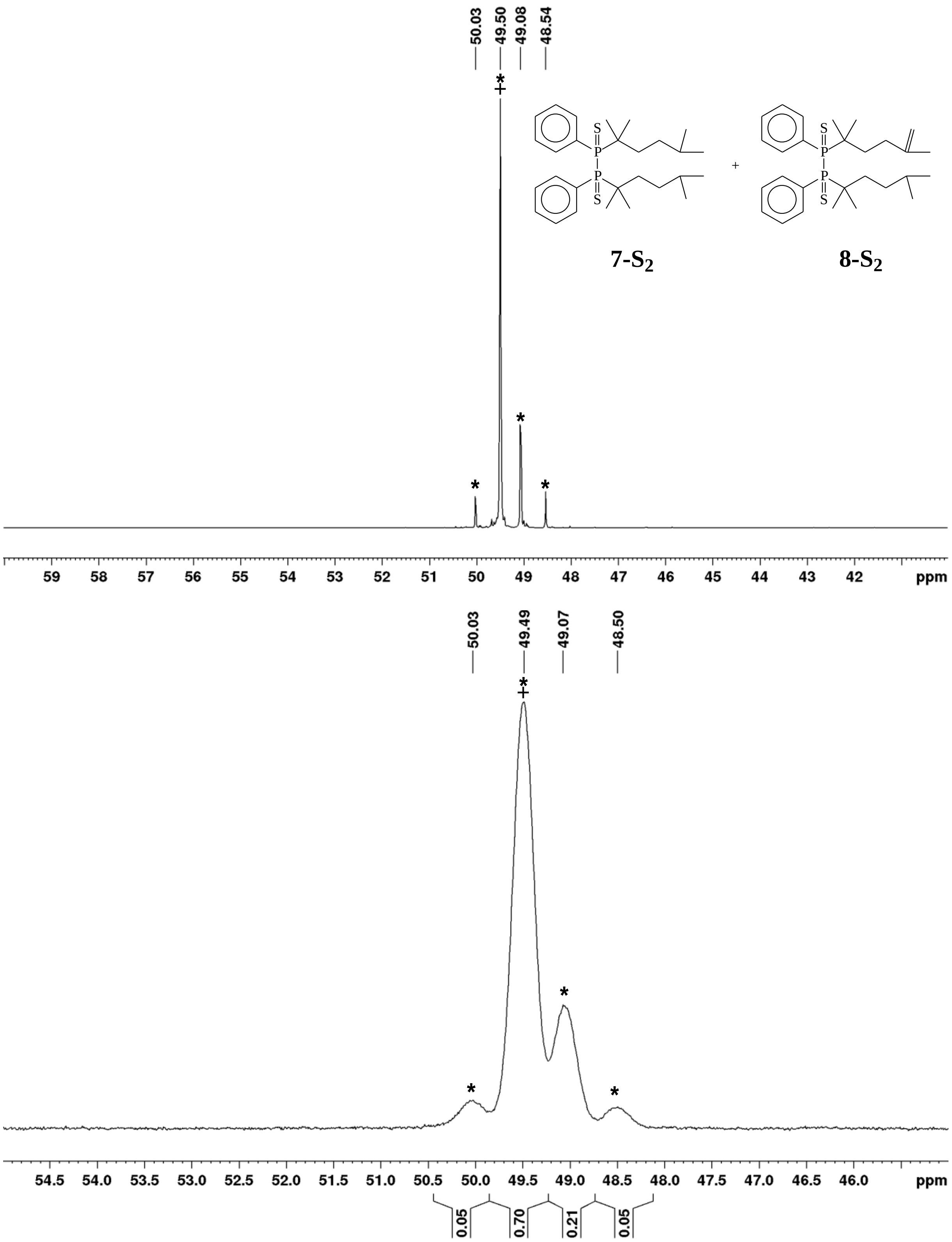


Figure S18. $^{31}P\{^{1}H\}$ NMR (top) and ^{31}P NMR spectrum (bottom) of a 1:1 mixture of **7-S$_2$** (+) and **8-S$_2$** (*), measured at 202.5 MHz, in $CDCl_3$ at 50 °C.

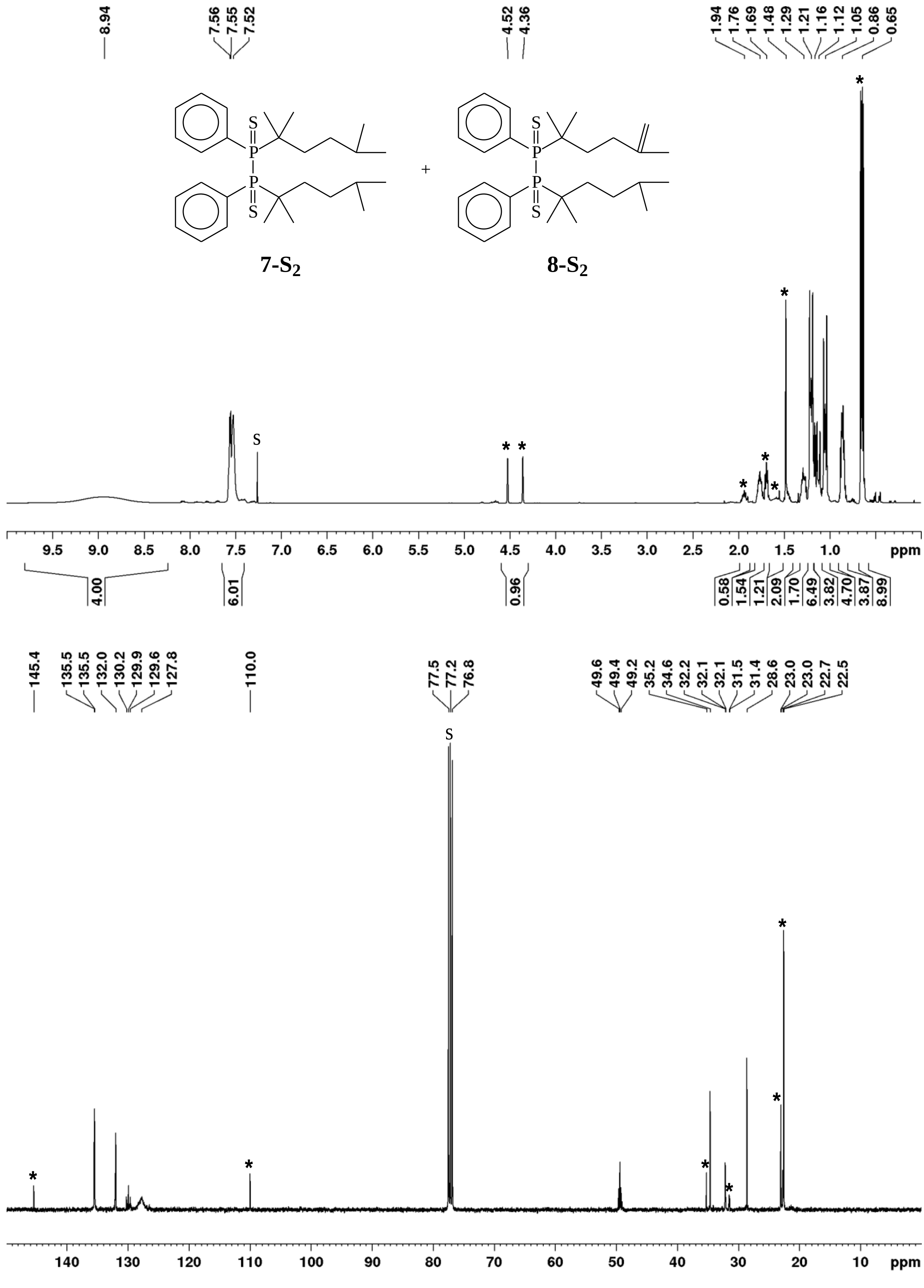


Figure S19. ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR spectrum (bottom) of a 1:1 mixture of **7-S₂** and **8-S₂**, measured at 600.1 MHz and at 150.9 MHz, in $CDCl_3$ at 50 °C (s = (residual) signal of $CDCl_3$, * = additional signals of **8-S₂**).

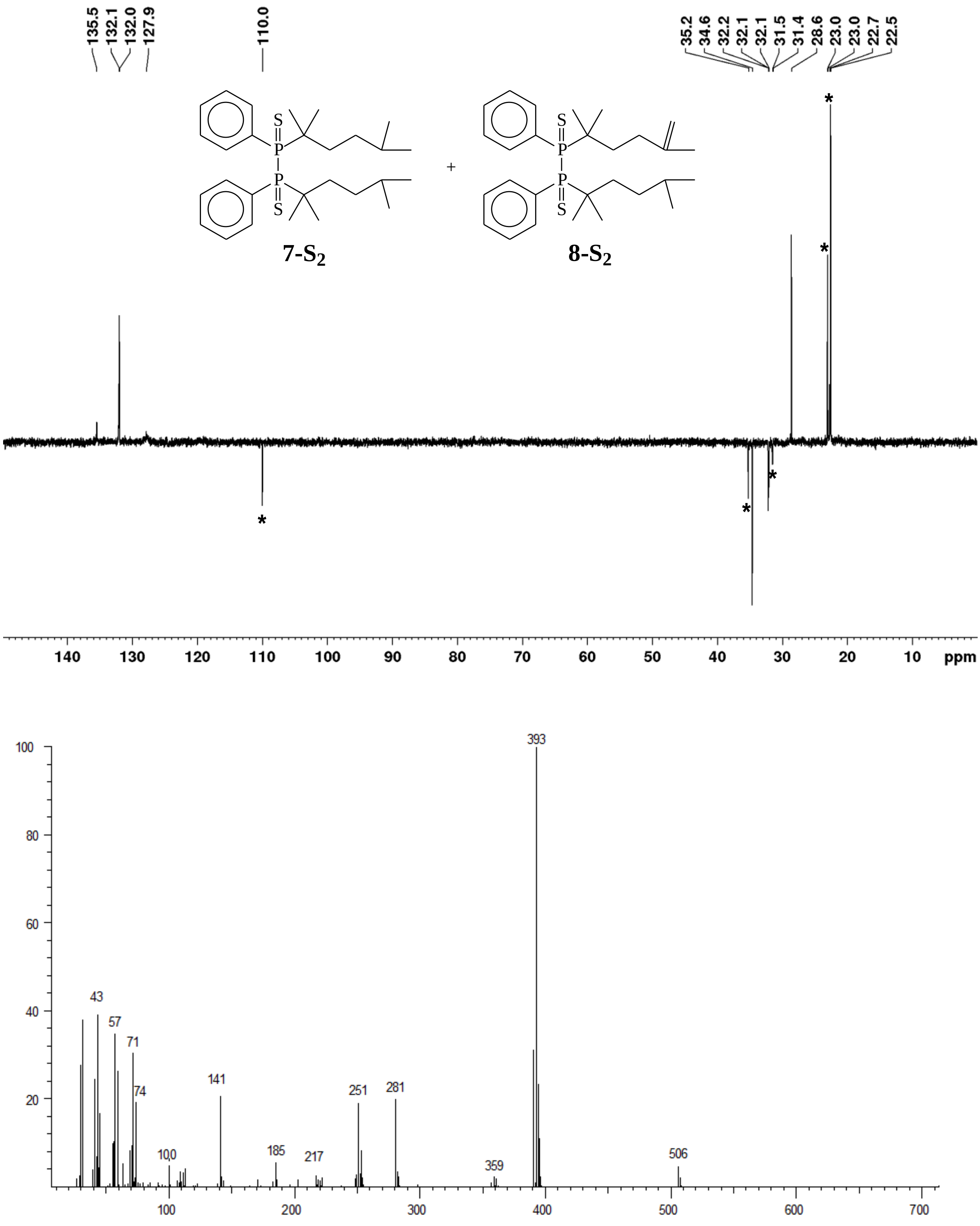
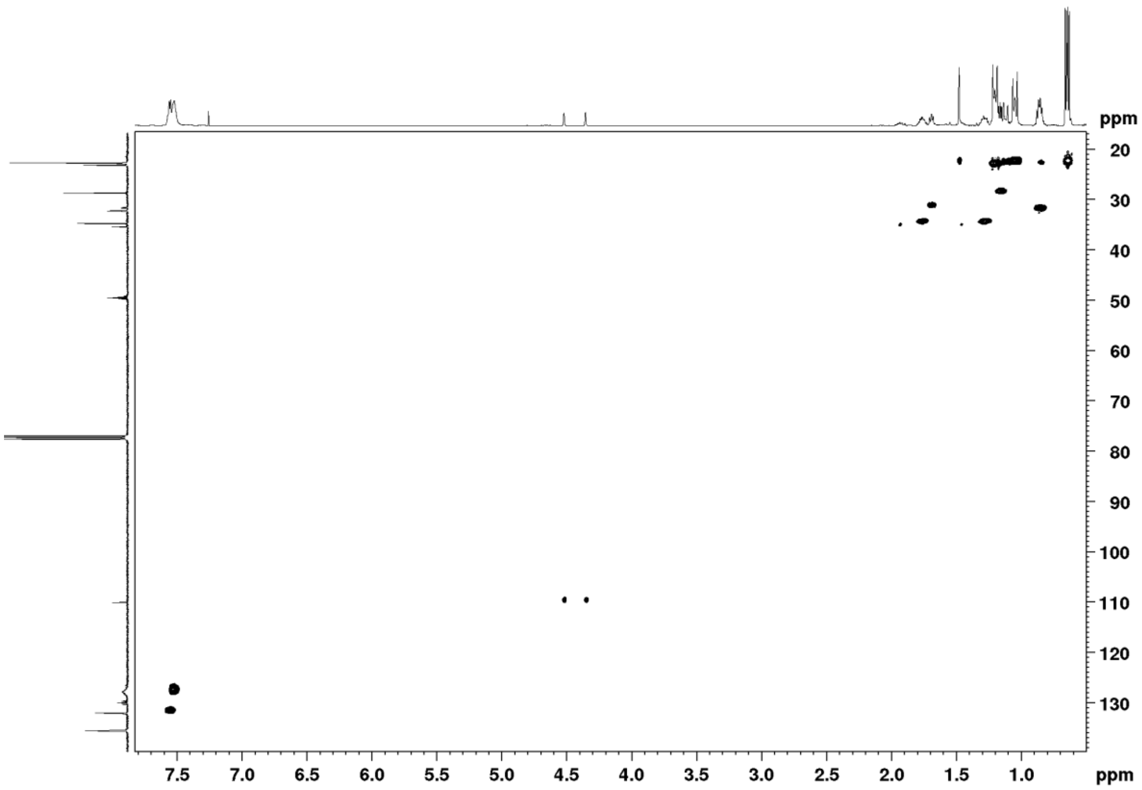


Figure S20. DEPT spectrum (top) measured at 100.6 MHz in $CDCl_3$ and mass spectrum (bottom) of a 1:1 mixture of **7-S$_2$** and **8-S$_2$** (* = additional signals of **8-S$_2$**).



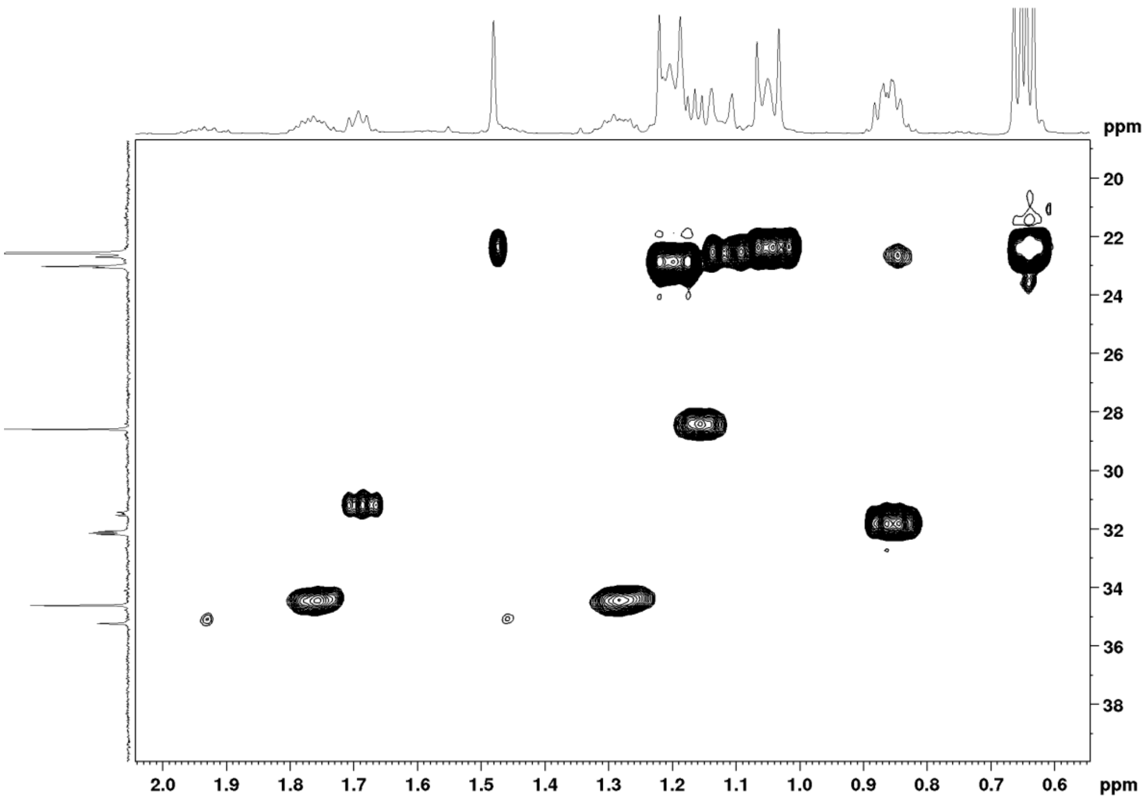


Figure S21. HSQC spectrum (top) and detail of the HSQC spectrum (bottom) of a 1:1 mixture of **7-S_2** and **8-S_2** measured at 600.1 MHz, in $CDCl_3$ at 50 °C.

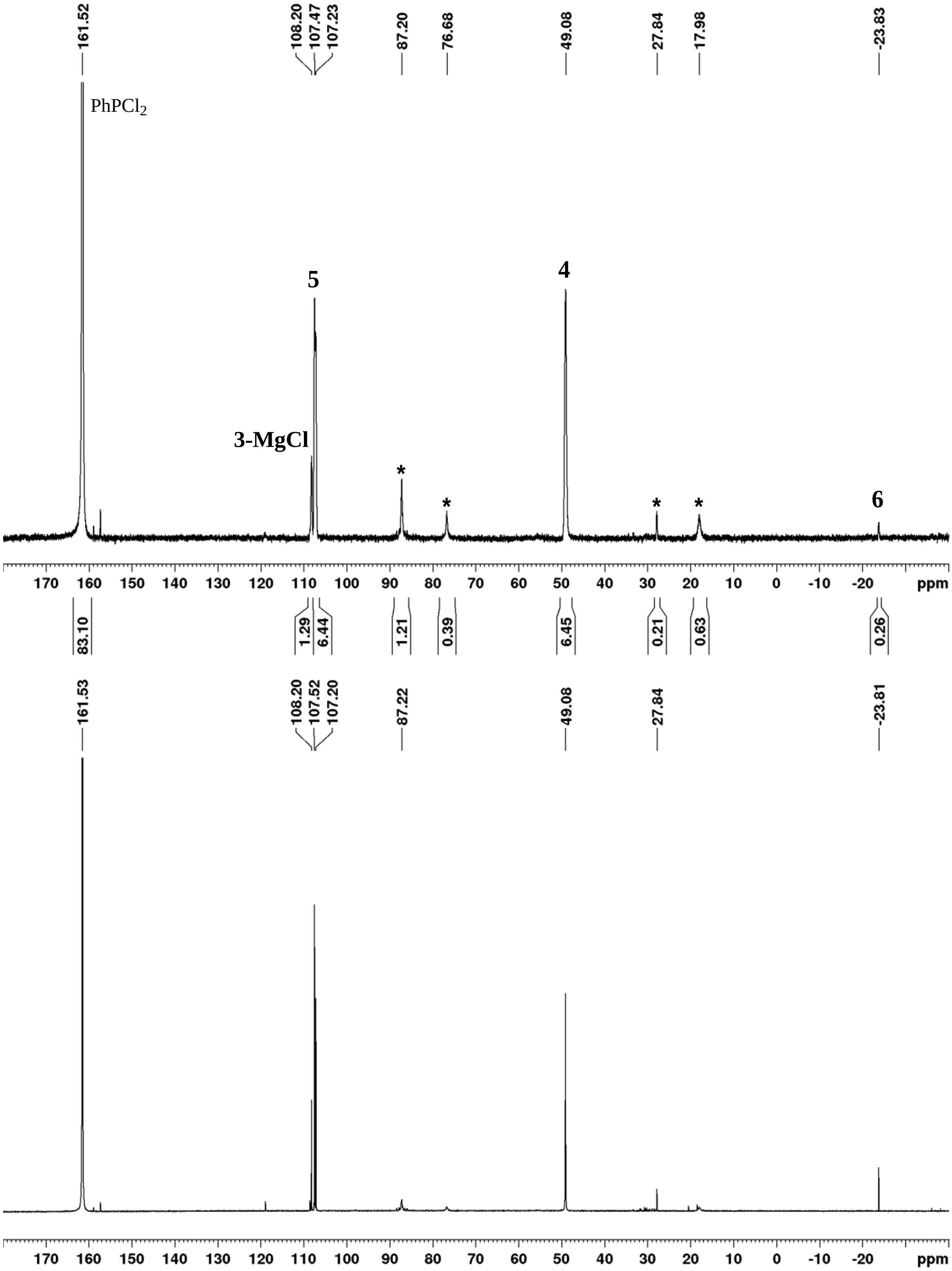


Figure S22. ^{31}P NMR (top) and $^{31}P\{^1H\}$ NMR spectrum (bottom) of the reaction mixture of a 0.27 M solution of **1** in THF and dichlorophenylphosphane (molar ratio 1:10) at -50 °C containing 25 % of C_6D_6, measured at 162.0 MHz (* = signals of unknown side products).

Table S1: Crystal data and refinement details for the X-ray structure determinations of the compounds **2 -7-S_2.**

Compound	**2**	**3-S**	**4-S**	**6-S_2**	**7-S_2**
formula	$C_{29}H_{58}Mg_2O_4$	$C_{14}H_{22}ClPS$	$C_{14}H_{21}PS$	$C_{20}H_{26}P_2S_2$	$C_{28}H_{42}P_2S_2$
fw (g·mol^{-1})	519.37	288.80	252.34	392.47	504.68
T (°C)	-140(2)	-130(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	P 2_1	P c a 2_1	P 2_1 2_1 2_1	P 2_1/n	P $\bar{1}$
a/ Å	14.8611(4)	11.8438(3)	8.28330(10)	16.4073(3)	8.0198(7)
b/ Å	13.4710(2)	11.9540(3)	12.1905(2)	8.0918(2)	9.2558(8)
c/ Å	15.9249(4)	10.7610(3)	14.0260(2)	16.7052(3)	11.4204(9)
α/°	90	90	90	90	111.061(5)
β/°	93.810(1)	90	90	114.488(1)	93.960(5)
γ/°	90	90	90	90	112.432(5)
V/Å^3	3181.02(13)	1523.55(7)	1416.31(4)	2018.36(7)	710.04(10)
Z	4	4	4	4	1
ρ (g·cm^{-3})	1.084	1.259	1.183	1.292	1.180
μ (cm^{-1})	1.04	4.71	3.15	4.22	3.14
measured data	42435	11118	17739	15150	7212
data with I > 2σ(I)	11206	3101	3125	4230	2520
unique data (R_{int})	14013/0.0433	3469/0.0632	3255/0.0293	4601/0.0350	3231/0.0503
wR_2 (all data, on F^2)[a)]	0.1240	0.0884	0.0730	0.1092	0.1920
R_1 ($I > 2\sigma(I)$) [a)]	0.0536	0.0385	0.0312	0.0453	0.0698
s [b)]	1.067	1.104	1.097	1.119	1.072
Res. dens./e·Å^{-3}	0.323/-0.224	0.304/-0.207	0.400/-0.312	1.165/-0.412	0.582/-0.448
Flack-parameter	0.07(19)	-0.11(8)	-0.01(9)	-	-
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min}/_{max}$	0.6750/0.7456	0.5967/0.7456	0.7144/0.7456	0.7053/0.7456	0.5684/0.7456
CCDC No.	1504993	1504994	1504995	1504996	1504997

[a)] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$;

$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$;

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.