Electronic supporting information

[4+2]-Cycloadditions of a thiazol-based tricyclic 1,4-diphosphinine and a new easy 1,4-diphosphinine protection deprotection strategy

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1 Experimental Procedures and spectra

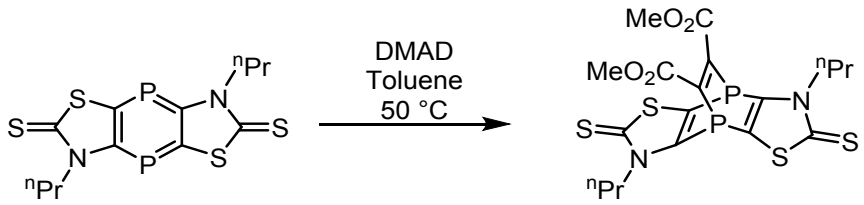
General information

All operations were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Diethyl ether, tetrahydrofuran, and *n*-pentane were dried over sodium wire/benzophenone and further purified by subsequent distillation. The NMR spectra for compound 7a and 7b were recorded on a Bruker AX-300 spectrometer (300.1 MHz for ^{1}H, 75.5 MHz focr ^{13}C, and 121.5 MHz for ^{31}P). While the NMR spectra for the rest of the compounds were recorded on a Bruker Avance III HD Ascend 500 MHz spectrometer (500.1 MHz for ^{1}H, 125.7 MHz for ^{13}C, and 202.4 MHz for ^{31}P). The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus, they are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. IR spectra of all compounds were recorded on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment. UV/vis spectroscopy was performed on a Shimadzu UV-1650PC spectrometer (λ = 190-900 nm) using sealed quartz glass cells (Hellma) of optical path 1 cm at ambient temperature. The X-ray analysis were performed on a Bruker APEX-II CCD or a Bruker X8-KappaApexII type diffractometer at 100(2) K. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97[1] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1941598 (**2**), CCDC-1941597 (**3**) which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

1.1 Synthesis of tricyclic compounds 2 and 3

In a Schlenk tube, reagent (see the table below) was added to a suspension of 1,4-diphosphinine **1** in dry toluene (temperature is given in the table below) and stirred (time is given in the table below). Solvent was removed under reduced pressure ($8 \cdot 10^{-3}$ mbar) and the obtained solid was washed with *n*-pentane ($2 \cdot 2$ mL) and dried *in vacuo* ($8 \cdot 10^{-3}$ mbar). Compound **2** was crystallized via cooling down its toluene solution at -30 °C. Compound 3 was crystallized via slow diffusion of *n*-pentane into a concentrated toluene solution at -30 °C.

1.1.1. 7,8-Bis(methyloxocarbonyl)-[2,3-d:5,6-d']bis(3-^{n}butyl-thiazole-2-thione)-1,4-diphospha-bicyclo[2.2.2]octa-2,5,7-triene (2)

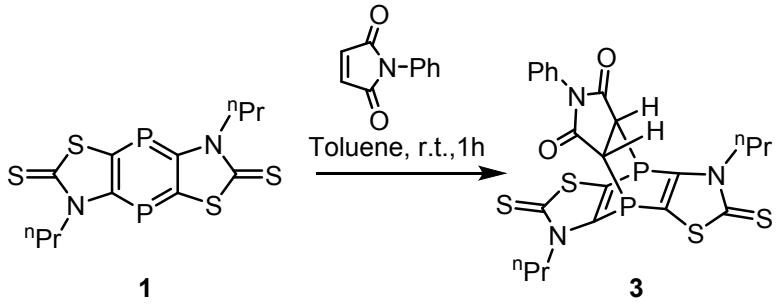


1 **2**

	amount used (g/mL)	**mmol**	**min/°C**
1	0.50 g	1.32	
DMAD	0.17 mL	1.39	
Toluene	20 mL		
Reaction time/temp			45/50

Yield: 0.50 g (0.96 mmol), 73 %, yellow orange solid, m.p, 205°C; ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 1.01 (t, 6H, $^{3}J_{H,H}$ = 7.41 Hz, $CH_2CH_2CH_3$), 1.80 (m, 4H, $CH_2CH_2CH_3$), 3.82 (s, OCH_3), 4.27-4.51 (m, 4H, CH_2-CH_2-CH_3), ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2):δ = 10.9 (s, $CH_2CH_2CH_3$), 22.3 (t, $^{4/5}J_{P,C}$ = 1.62 Hz,N $CH_2CH_2CH_3$), 51.5 (t, $^{3/4}J_{P,C}$ = 4.8 Hz, $CH_2CH_2CH_3$), 53.4 (s, OCH_3), 131.7 (dd, $^{1}J_{P,C}$ = 17.2 Hz, $^{2}J_{P,C}$ = 15.0 Hz, C^5), 157.6 (dd, $^{1}J_{P,C}$ = 15.1 Hz, $^{2}J_{P,C}$ = 14.0 Hz,CCO_2Me), 160.1 (dd, $^{1}J_{P,C}$ = 11.1 Hz, $^{2}J_{P,C}$ = 9.3 Hz,C^4), 165.5 (t, $J_{P,C}$ = 17.1 Hz, CCO_2Me), 189.4 (br, *C*=S), ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ= -75.4 (s); IR (ATR, $\tilde{\nu}$ {cm^{-1}}): $\tilde{\nu}$ = 2953 (w), 1711 (vs), 1572 (m), 1430 (m), 1359 (s), 1332 (m),1253 (vs), 1212 (vs),1141 (vs), 1060 (s),1020 (s), 915 (m), 879 (s), 815 (vs), 744 (m), 653 (s), 618 (s), 468 (s); MS (EI, 70 eV): m/z (%) = 292.0 (100) $[C_6N_2P_2S_4]^+$, 301 (10) $[C_9H_7N_2P_2S_3]^+$, 376.0 (75) $[C_{12}H_{14}N_2P_2S_4]^+$, 518.0 (68) $[M]^+$; HR-MS: found = 517.9777, calc. = 517.9781; Elemental analysis for $C_{18}H_{20}N_2O_4P_2S_4$: Calculated C 41.69 H 3.89 N 5.40 S 24.73, Found C 41.53 H 3.72 N 5.37 S 24.82.

1.1.2. 7,8-(*N*-Phenylmaleimide)-[2,3-d:5,6-d']bis(3-^{n}propyl-thiazole-2-thione)-1,4-diphospha-7,8-dihydro-bicyclo[2.2.2]octa-2,5-diene (3)



1 **3**

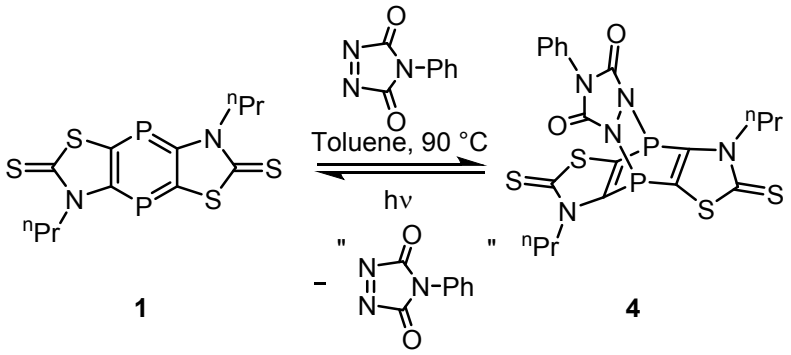
	amount used (g/mL)	mmol	min/°C
1	0.35 g	0.92	
1-phenyl pyrrole-1,5-dione	0.16 g	0.97	
Toluene	15 mL		
Reaction time/temp			120/25

Yield: 0.48 g (0.87 mmol), 94 %, white solid, m.p. 289 °C; ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 1.01 (t, 3H, $^{3}J_{H,H}$ = 7.37 Hz, $CH_2CH_2CH_3$), 1.10 (t, 3H, $^{3}J_{H,H}$ = 7.40 Hz, $CH_2CH_2CH_3$), 1.68-1.83 (m, 2H, $CH_2CH_2CH_3$), 1.84-1.94 (m, 2H, $CH_2CH_2CH_3$), 3.86 (m, 1H, $(CHCO)_2$N-Ph), 3.95 (m, 1H, $(CHCO)_2$ N-C_6H_5), 4.23-4.54 (m, 4H, CH_2-CH_2-CH_3), 6.90-7.00 (m, 2H, N-C_6H_5), 7.44-7.51 (m, 3H, C_6H_5); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2):δ = 11.2 (s, $CH_2CH_2CH_3$), 11.3 (s, $CH_2CH_2CH_3$) 22.3 (d, $^{4}J_{P,C}$ = 3.0 Hz,$CH_2CH_2CH_3$), 22.8 (d, $^{4}J_{P,C}$ = 3.4 Hz,$CH_2CH_2CH_3$), 44.1 (dd, $^{1}J_{P,C}$ = 16.4 Hz, $^{2}J_{P,C}$ = 2.3 Hz, P-*C*H), 44.6 (dd, $^{1}J_{P,C}$ = 16.3 Hz, $^{2}J_{P,C}$ = 2.2 Hz, P-*C*H) 51.6 (d, $^{3}J_{P,C}$ = 10.2 Hz, $CH_2CH_2CH_3$), 125.4 (dd, $^{1}J_{P,C}$ = 29.5 Hz, $^{2}J_{P,C}$ = 5.8 Hz,C^5), 126.8 (s, N-C_6H_5),127.2 (dd, $^{1}J_{P,C}$ = 25.1 Hz, $^{2}J_{P,C}$ = 5.5 Hz,C^5), 128.8 (s, C_6H_5), 129.9 (s, C_6H_5), 131.3 (s, C_6H_5), 151.7 (dd, $^{2}J_{P,C}$ = 21.5 Hz, $^{2}J_{P,C}$ = 3.5 Hz, C^4), 152.5 (dd, $^{2}J_{P,C}$ = 17.1 Hz, $^{2}J_{P,C}$ = 2.3 Hz, C^4), 172.2 (d, $^{2}J_{P,C}$ = 6.5 Hz, $(CHCO)_2$ N-C_6H_5), 172.7 (d, $^{2}J_{P,C}$ = 6.5 Hz, $(CHCO)_2$ N-C_6H_5), 191.0 (d, $^{3}J_{P,C}$ = 2.0 Hz, *C*=S), 191.2 (d, $^{3}J_{P,C}$ = 1.9 Hz, *C*=S); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = -75.7 (d, $^{3}J_{P,P}$ = 28.8 Hz, P), -74.3 (d, $^{3}J_{P,P}$ = 28.8 Hz, P); IR (ATR, $\tilde{\nu}$ {cm^{-1}}): $\tilde{\nu}$ = 2966 (w), 2869 (w), 1769 (m), 1705 (vs), 1491 (w), 1458 (m), 1360 (vs), 1286 (s), 1214 (s), 1140 (s), 1024 (s), 925 (s), 821 (s), 735 (s), 696 (s), 621 (m),735 (s), 696 (s), 621 (m), 541 (m), 452 (s); MS (EI, 70 eV): m/z (%) = 549.1 (10) $[M]^+$, 549.1 (10) $[M]^+$, 376.0 (85) $[C_{12}H_{14}N_2P_2S_4]^+$, 291.9 (100) [M-2^{n}Pr- $C_{10}H_7NO_2]^+$ 173.2 (50) $[C_{10}H_7NO_2]^+$; Elemental analysis for $C_{22}H_{21}N_3O_2P_2S_4$; Calculated C 48.08 H 3.85 N 7.65 S 23.33, Found C 48.20 H 3.89 N 7.50 S 23.14.

1.2 Synthesis of tricyclic compound 4

In a Schlenk tube, 4-phenyl-1,2,4-triazoline-3,5-dione (see the table below) was added to a suspension of 1,4-diphosphinine **1** in dry toluene (temperature is given in the table below) and stirred (time is given in the table below). Solvent was filtered off and the obtained solid was washed with *n*-pentane (3 · 3 mL) and dried *in vacuo* (8 · 10^{-3} mbar).

1.2.1 7,8-(4-Phenyl-1,2,4-triazoline-3,5-dione)-[2,3-d:5,6-d']bis(3-^{n}propylthiazole-2-thione)-1,4-diphospha-7,8-dihydro-bicyclo[2.2.2]octa-2,5-diene (4)



	amount used (g/mL)	mmol	min/°C
1	0.049 g	0.130	
4-Phenyl-1,2,4-triazolinedione	0.024 g	0.136	
Toluene	2 mL		
Reaction time/temp			30/90

Yield: 0.048 g (0.087 mmol), 67 %, light yellow solid; ^{1}H NMR (500.1 MHz, 298.0 K $CDCl_3$): δ = 1.03 (t, 6H, $^{3}J_{H,H}$ = 7.33 Hz, $CH_2CH_2CH_3$), 1.80-1.92 (m, 4H, $CH_2CH_2CH_3$), 4.35-4.43 (m, 2H, $CH_2CH_2CH_3$), 4.45-4.52 (m, 2H, $CH_2CH_2CH_3$), 7.41-7.45 (m, 2H, C_6H_5), 7.46-7.49 (m, 1H, pC_6H_5), 7.49-7.51 (m, 2H, C_6H_5); ^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, $CDCl_3$): δ = 11.4 (s, $CH_2CH_2CH_3$), 22.7 (s, $CH_2CH_2CH_3$), 51.1 (s, $CH_2CH_2CH_3$), 125.7 (s, pC_6H_5), 125.9 (s, C_6H_5), 129.2 (d, $^{2}J_{P,C}$ = 2.42 Hz, N(*CO*)N), 129.5 (C_6H_5), 130.7 (s, *ipso*-C_6H_5), 150.6 (s, P*C*S), 155.2 (s, P*C*N), 189.4 (s, *C*=S); ^{31}P{^{1}H} NMR (202.5 MHz, 298.0 K, CD_2Cl_2): δ = –45.8 (s); ^{31}P NMR (202.5 MHz, 298.0 K, $CDCl_3$): δ [ppm] = –45.8 (s); IR (ATR, $\tilde{\nu}$ {cm^{-1}}): $\tilde{\nu}$ = 1699 (s), 1748 (s), 2873 (w), 2932 (w), 2961 (w); UV7vis (in CH_2Cl_2, λ_{max} {nm} (abs.)): λ_{max} = 317sh (0.95), 327 (1.00), 380sh (0.21), 496 (0.04); MS (EI, 70 eV): m/z (%) = 549.1 (10) $[M]^+$, 549.1 (10) $[M]^+$, 376.0 (85) $[C_{12}H_{14}N_2P_2S_4]^+$, 291.9 (100) [M-2^{n}Pr- $C_{10}H_7NO_2]^+$ 173.2 (50) $[C_{10}H_7NO_2]^+$; Elemental analysis for $C_{22}H_{21}N_3O_2P_2S_4$; Calculated C 48.08 H 3.85 N 7.65 S 23.33, Found C 48.20 H 3.89 N 7.50 S 23.14.

1.3 Photochemical studies on 2

A solution of **2** in dichloromethane was irradiated (240-400 nm) for 1.5 h at ambient temperature. $^{31}P\{^{1}H\}$ NMR spectra of solutions before and after irradiation were measured (see below).

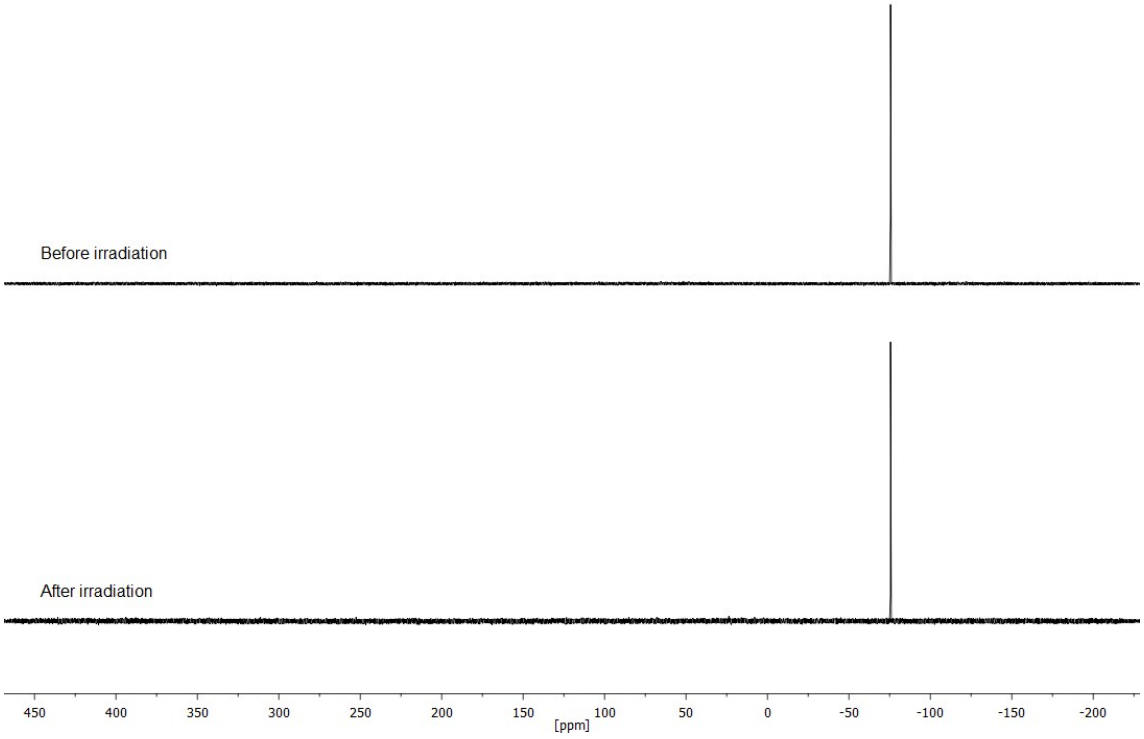


Figure 1 $^{31}P\{^{1}H\}$ NMR spectra (CH_2Cl_2) of **2** before and after the irradiation.

1.4 Photochemical studies on 3

A solution of **3** in dichloromethane was irradiated (240-400 nm) for 1.5 h at ambient temperature. $^{31}P\{^{1}H\}$ NMR spectra of solutions before and after irradiation were measured (see below).

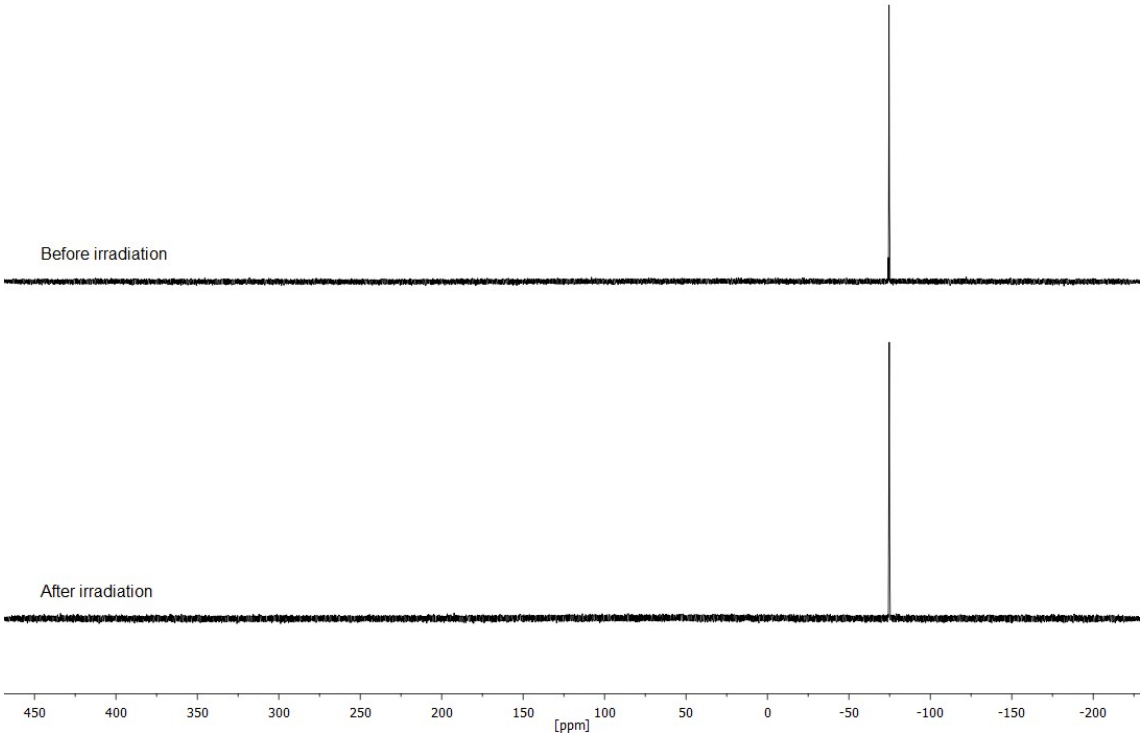


Figure 2 $^{31}P\{^{1}H\}$ NMR spectra (CH_2Cl_2) of **2** before and after the irradiation.

1.5 Photochemical studies on 4

A solution of 80 mg **4** in 24 mL dichloromethane was irradiated (240-400 nm) for 2 h at 10 °C. The dichloromethane was removed under reduced pressure (ca. 10^{-1} mbar) and the residue was splitted into two. To one aliquot 11 mg (0.063 mmol) 4-phenyl-1,2,4-triazoline-3,5-dione was added. After addition of 5 mL toluene to each aliquot the two mixtures were heated to 90 °C for 2 h before filtering off the toluene solution. $^{31}P\{^{1}H\}$ NMR spectra of both residues and both filtered solutions were measured (see below).

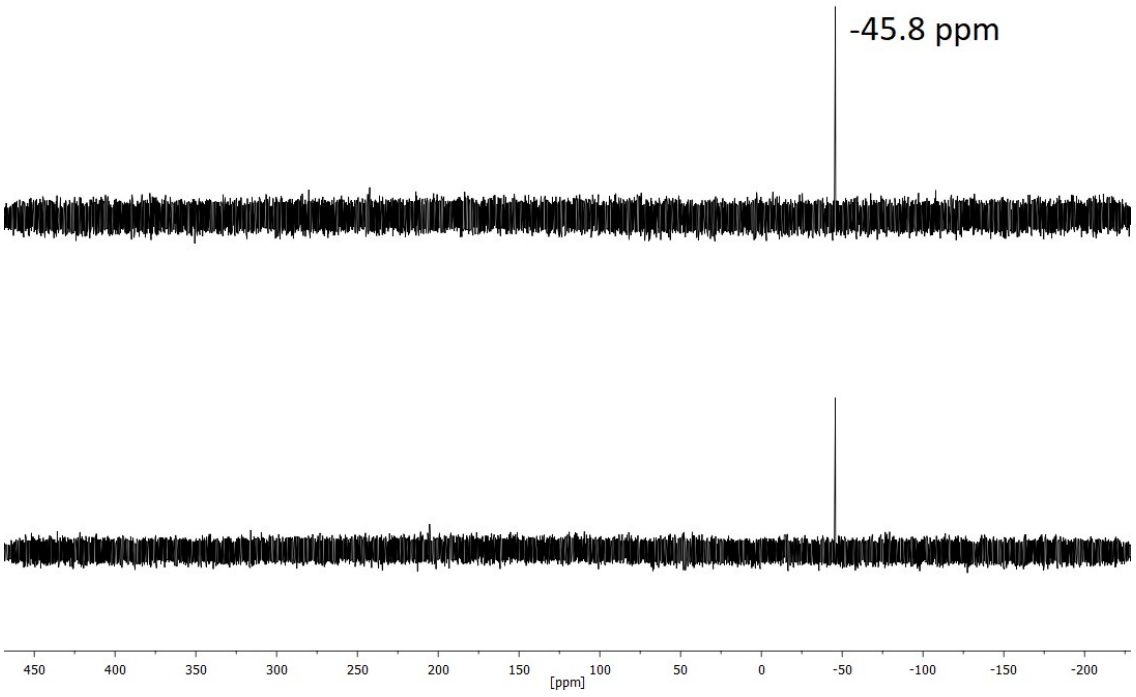


Figure 3 $^{31}P\{^{1}H\}$ NMR spectra of the residues.

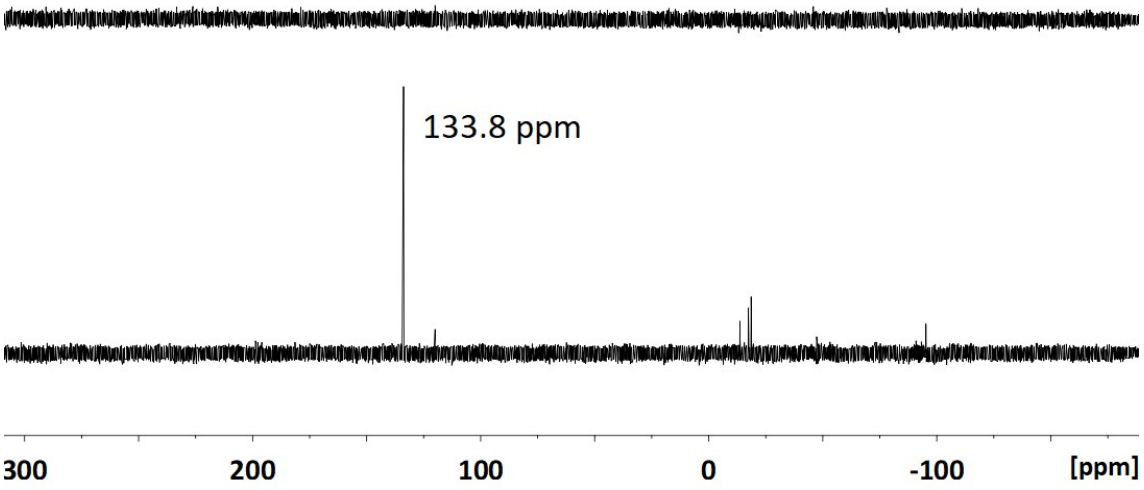
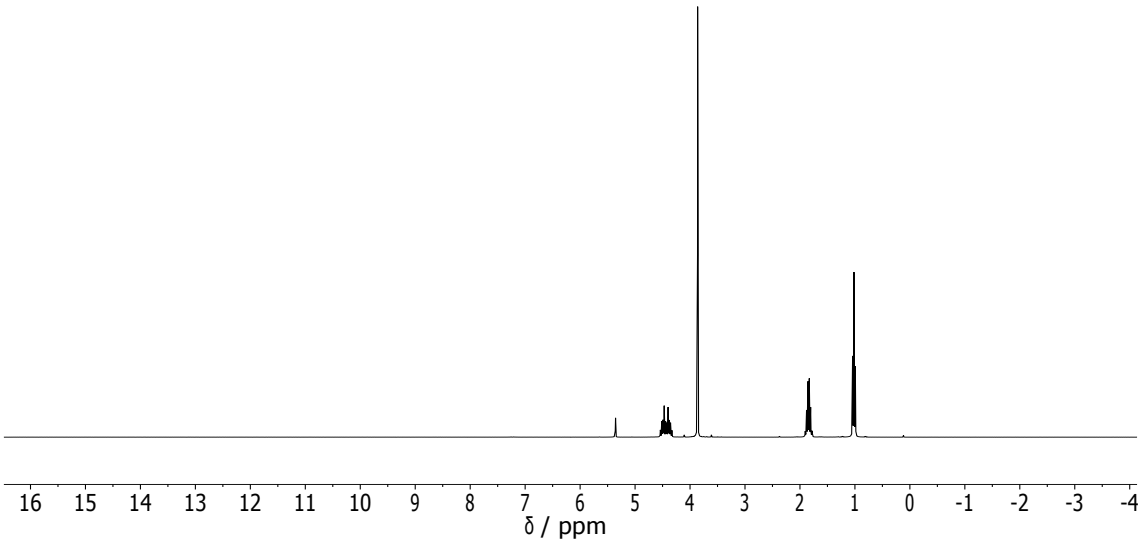


Figure 4 $^{31}P\{^{1}H\}$ NMR spectra of filtered solutions.

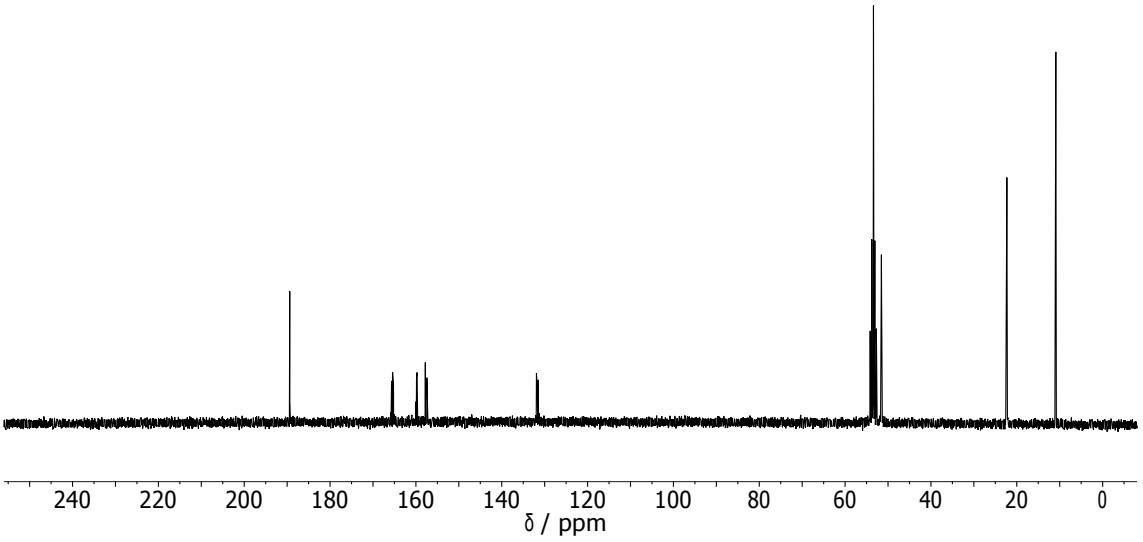
1.6 NMR spectra

Figure 5a-d NMR spectra of 2

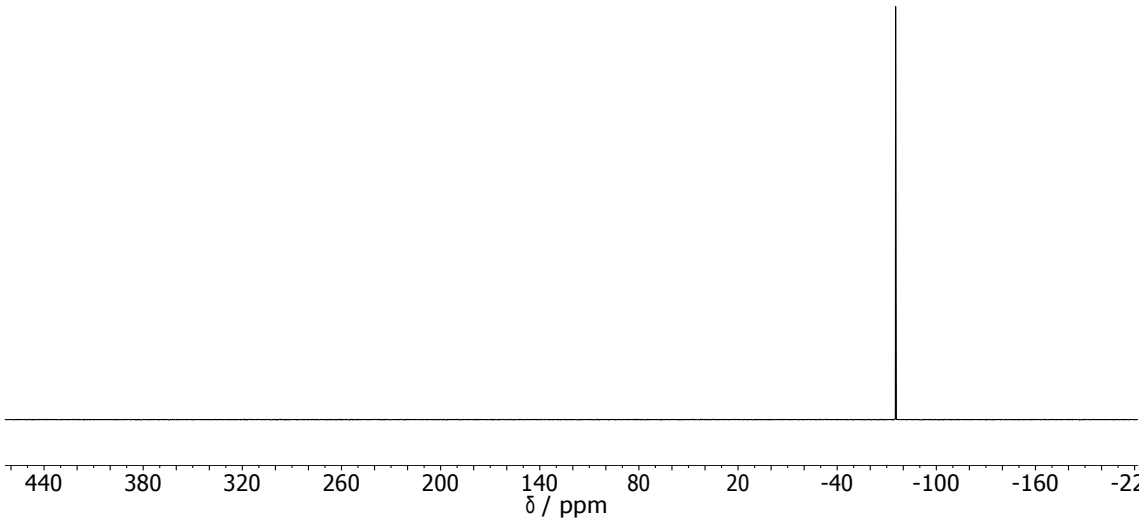
^{1}H NMR spectrum



^{13}C NMR spectrum



$^{31}P\{^{1}H\}$ spectrum



^{31}P NMR spectrum

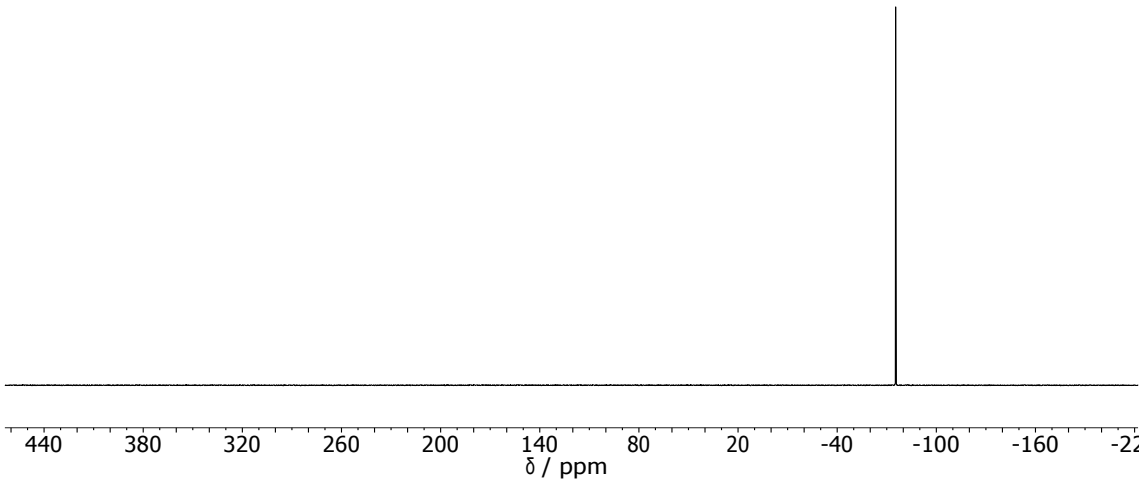
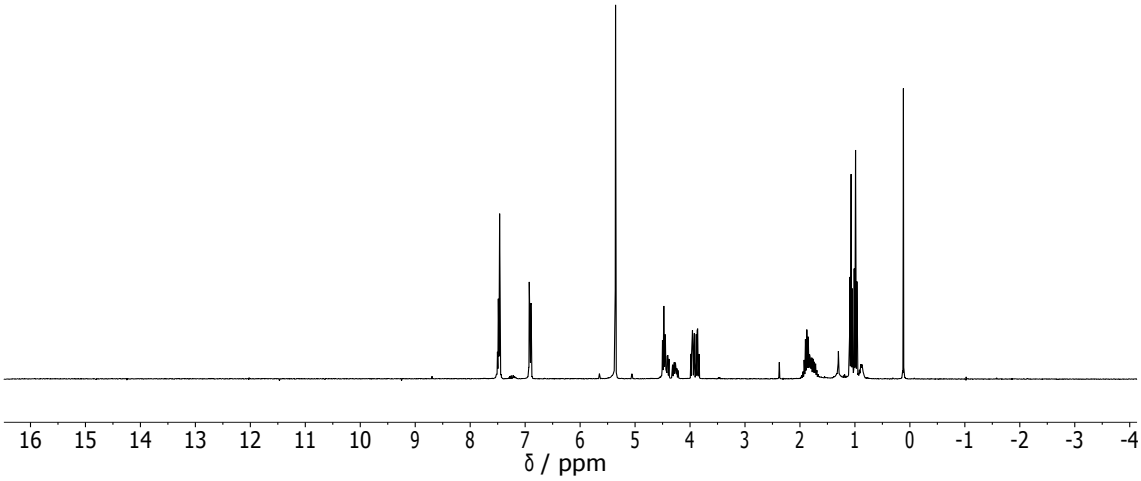
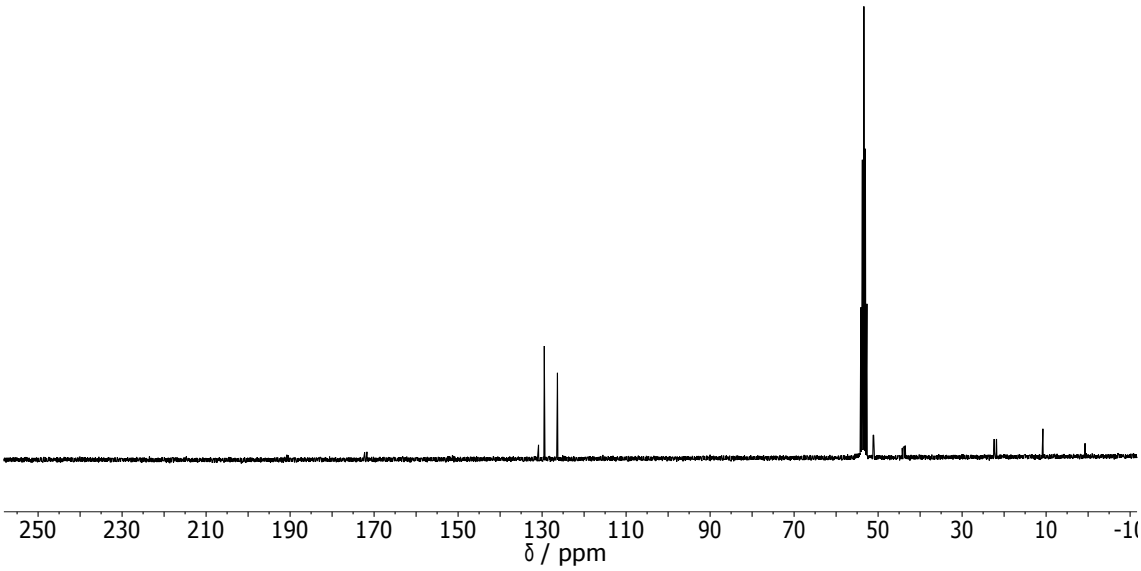


Figure 6a-d NMR spectra of 3

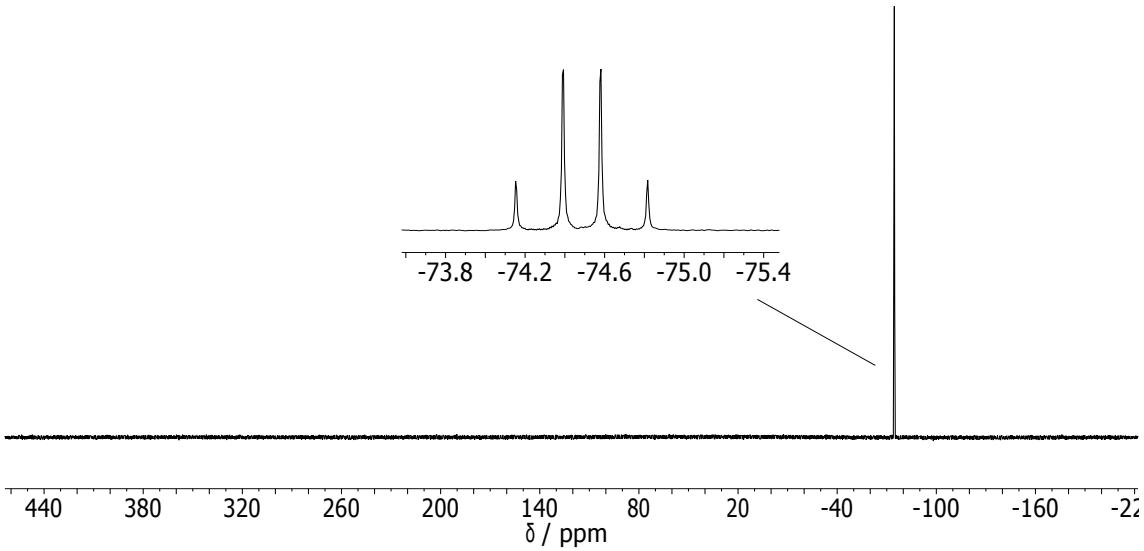
^{1}H NMR spectrum



^{13}C NMR spectrum



$^{31}P\{^{1}H\}$ spectrum



^{31}P NMR spectrum

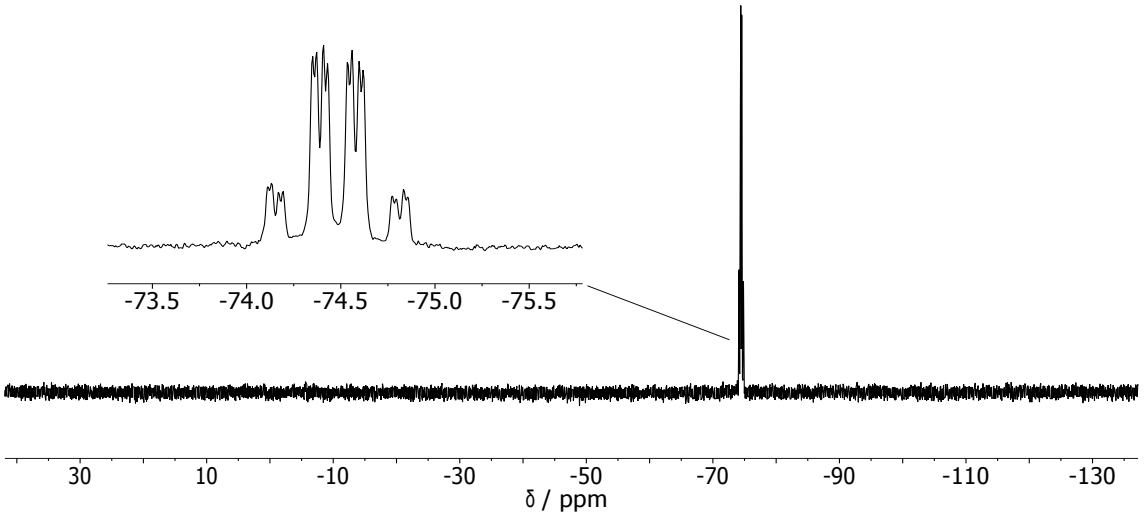
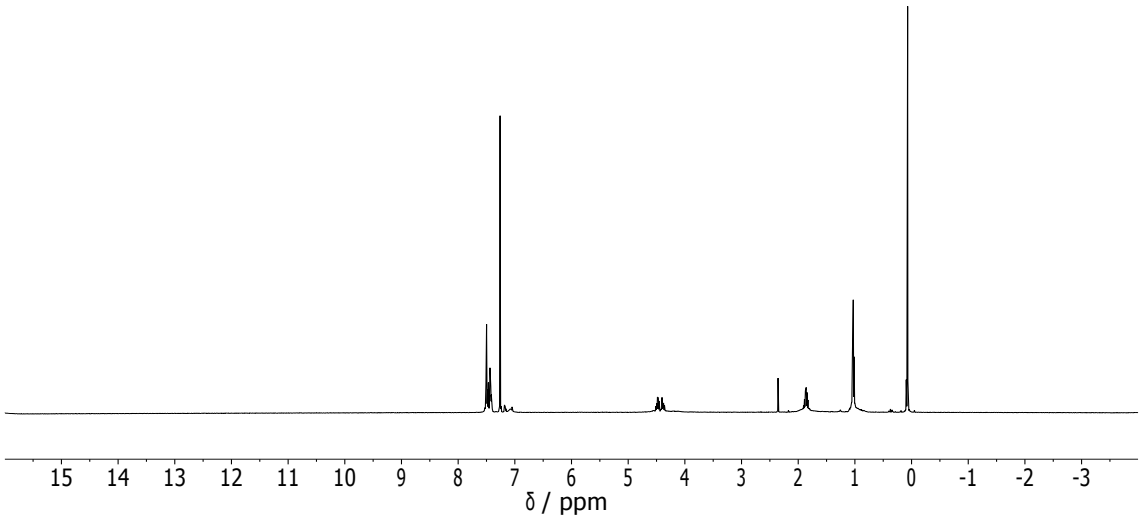
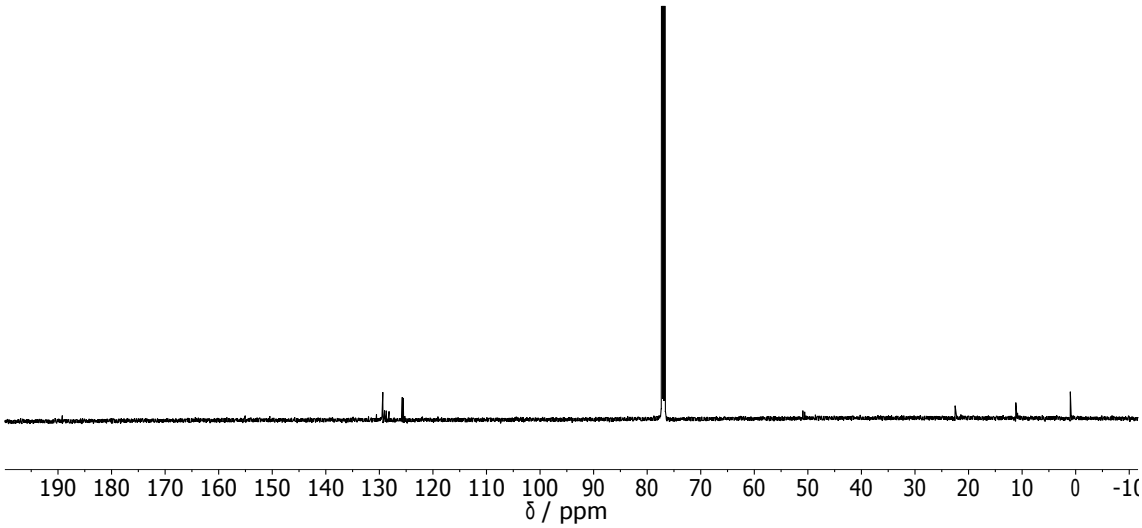


Figure 7a-d NMR spectra of 4

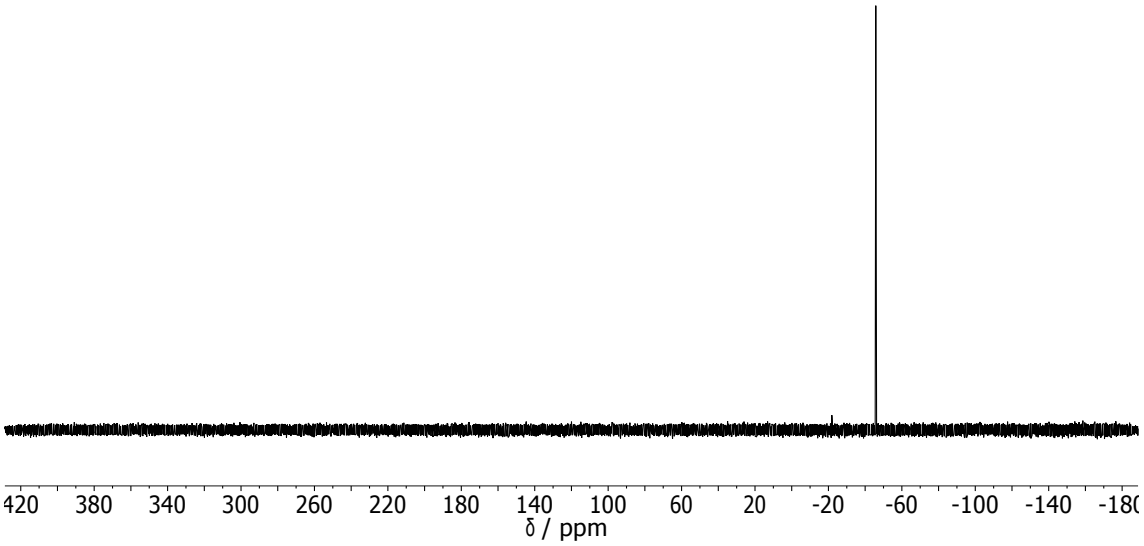
^{1}H NMR spectrum



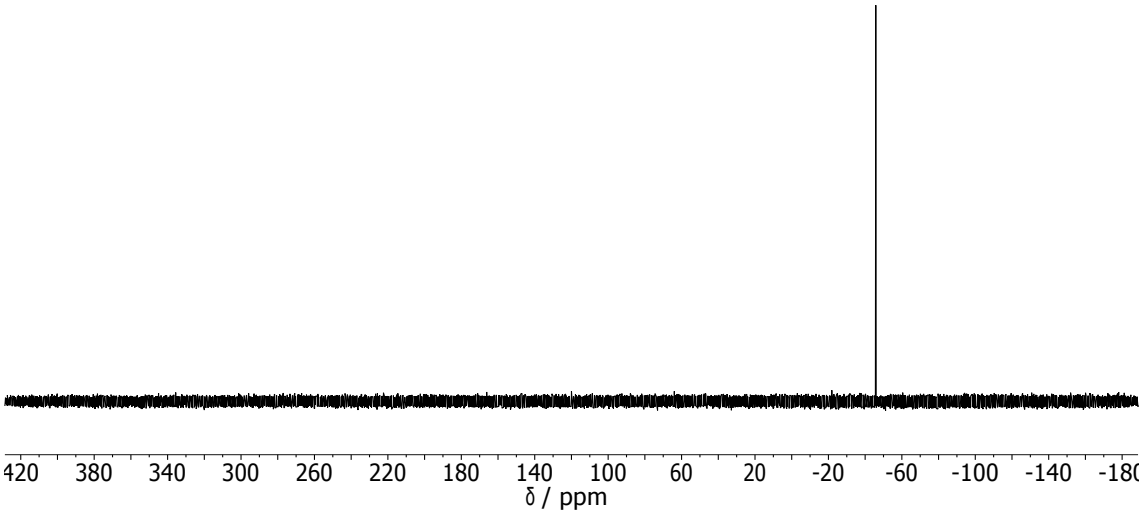
^{13}C NMR spectrum



$^{31}P\{^{1}H\}$ spectrum



^{31}P NMR spectrum



1.7 Simulated ^{31}P NMR spectrum of 3

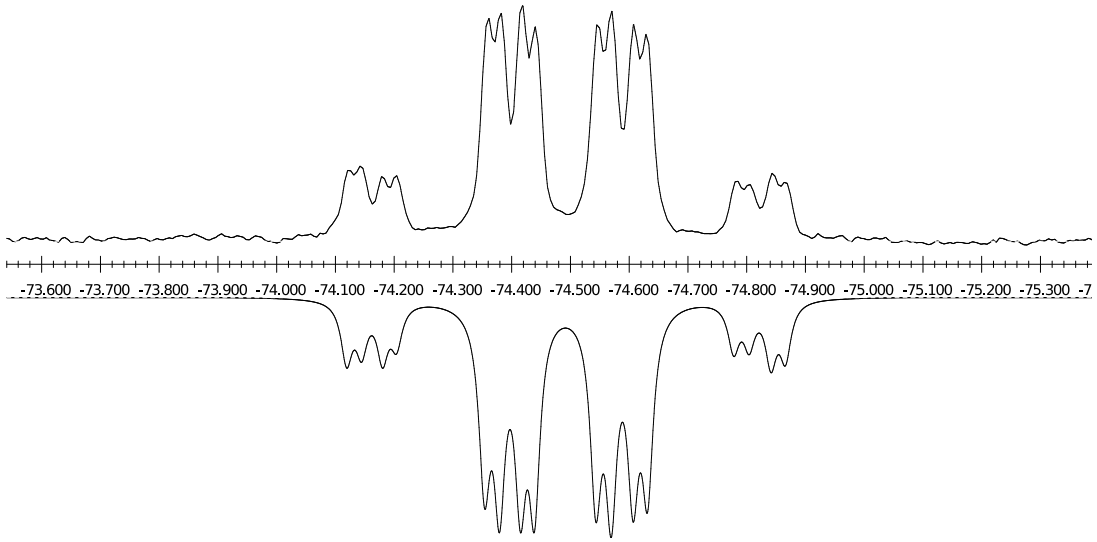


Figure 8: Comparison of experimental (top) and simulated ^{31}P NMR spectrum of **3**.

1.8 UV/vis spectra

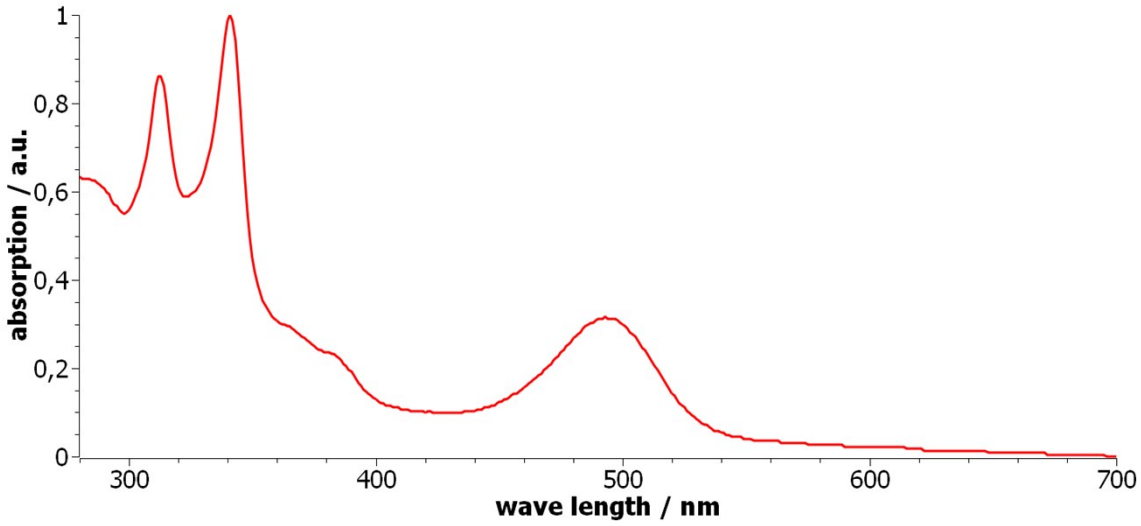


Figure 9 UV/vis spectrum of **1** in recondensed CH_2Cl_2.

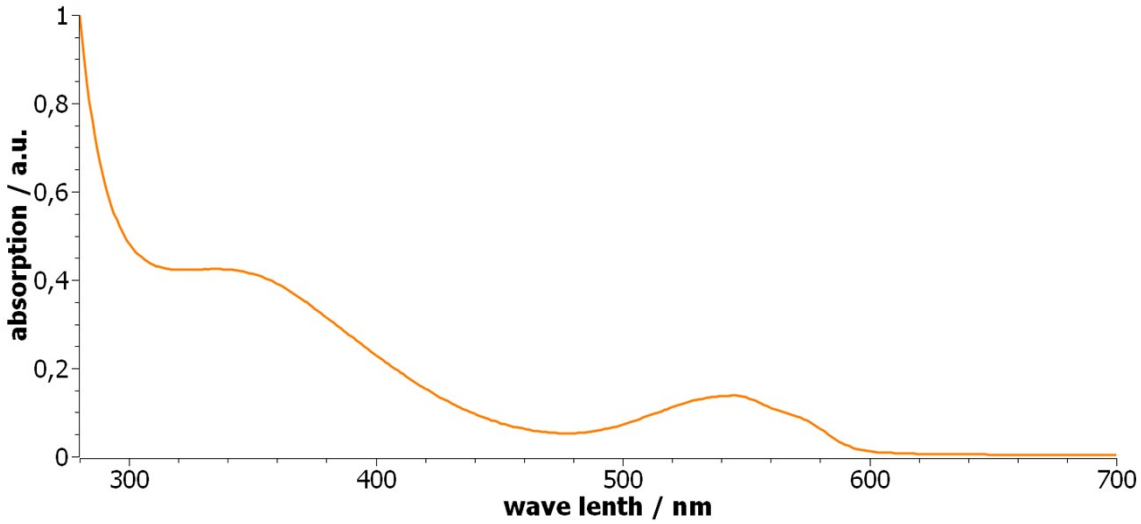


Figure 10 UV/vis spectrum of 4-phenyl-1,2,4-triazoline-3,5-dione in recondensed CH_2Cl_2.

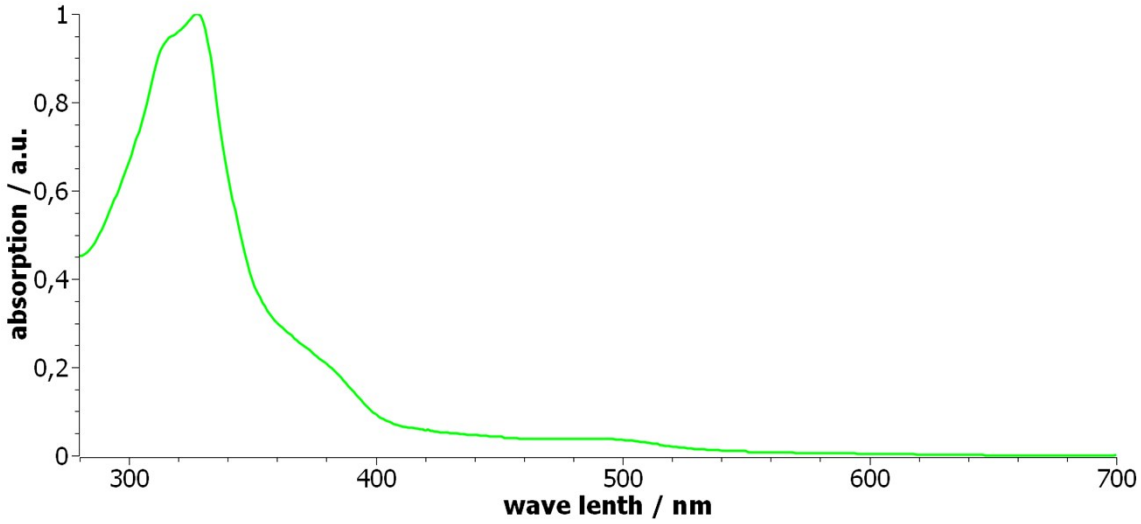


Figure 11 UV/vis spectrum of **4** in recondensed CH_2Cl_2.

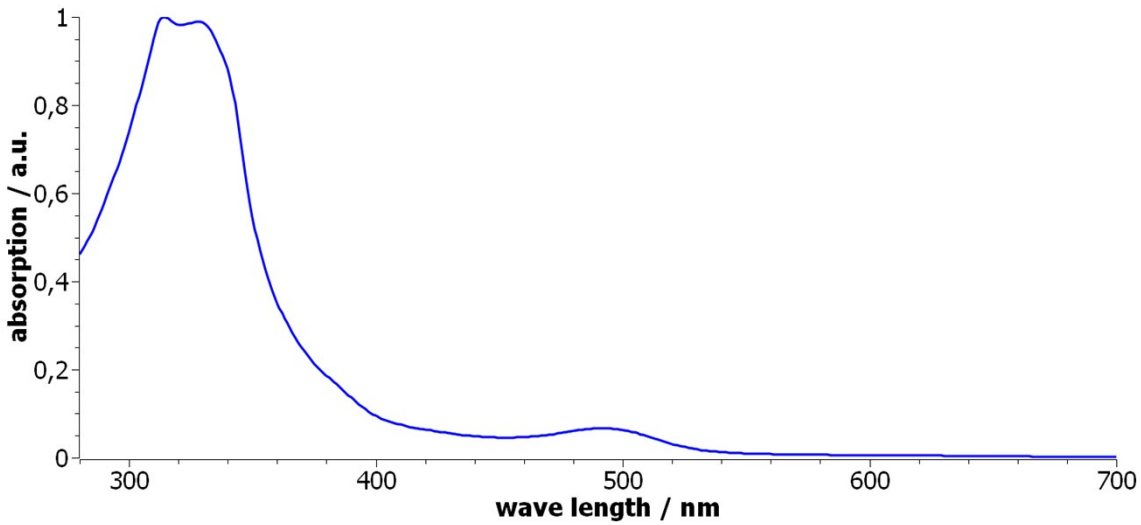


Figure 12 UV/vis spectrum of an irradiated mixture of **4** in recondensed CH_2Cl_2.

2 Crystal structure data

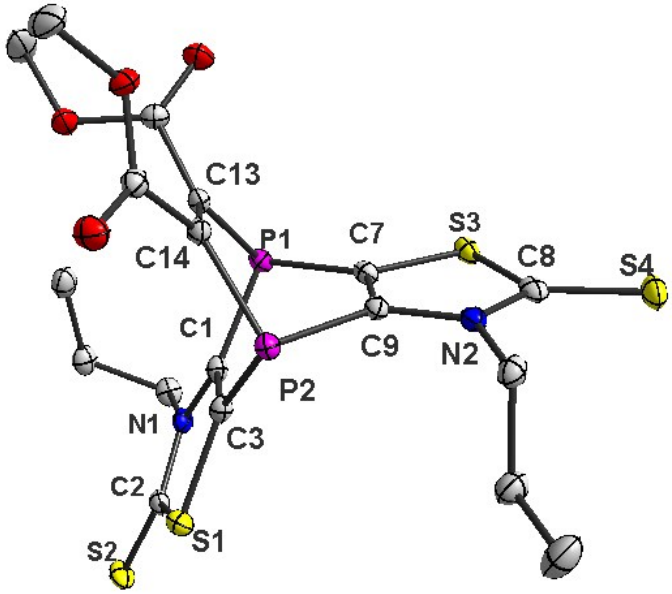


Figure 13 Molecular structure of **2**. Ellipsoids are set to 50 % probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.846(3), P1-C7 1.818(3), C1-C3 1.348(4), P1-C13 1.870(3), C13-C14 1.336(4), C1-P1-C7 95.63(13).

Crystal data for 2: The compound was crystallized by cooling a toluene solution of **2** to –30 °C. Data were collected with a with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite monochromated Mo Kα radiation (λ=0.71073 Å). The structure was solved by Patterson methods (SHELXS-97) and refined by full-matrix least-squares on F2(SHELXL-97). $C_{18}H_{20}N_2O_4P_2S_4$, M = 518.54, crystal dimensions 0.24 × 0.14 × 0.08 mm^3, triclinic, space group P -1, Z=2, a= 10.1125(6) Å, b= 10.1260(6) Å, c= 11.9070(7) Å, α= 77.826(3)°, β= 75.301(3)°, γ= 89.011(3)°, V=1151.99(12) $Å^3$, d_c= 1.495 g cm^{-3}, μ=0.579 mm-1, T=100 K, transmission factors (min./max.) 0.6499/0.7460, empirical absorption correction, 2θmax= 51.034°, no. of unique data 5556, R_{int}= 0.0723, R1 (for I > 2σ(I))=0.0515, wR2 (for all data)= 0.1105, final R= 0.0710, goodness of fit 1.061, ΔF(max./min.)= 0.54/-0.44 e $Å^{-3}$.

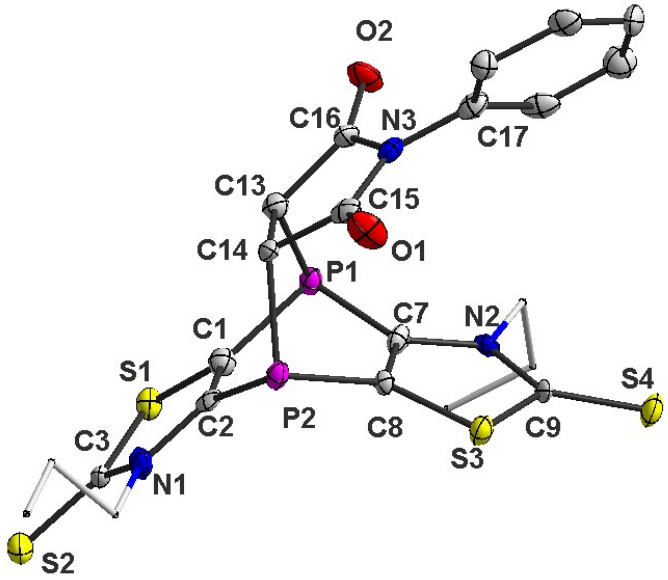


Figure 14 Diamond plot of (reduced) molecular structure of **3** in solid state. Thermal ellipsoids are drawn at a 50 % probability level. Hydrogen atoms have been omitted for clarity.

3 Theoretical Investigations and computational details

All calculations were carried out with the Gaussian 09 program package.[1] Full geometry optimization calculations were performed, followed by calculation of the second derivatives at the optimized structures to establish the nature of the stationary points obtained. The Gibbs free energies were calculated based on the harmonic vibrational frequencies (atmospheric pressure, 298.15 K). **1**, **2**, **3**, **4** and their derivatives were calculated with methyl substituents at the nitrogen atoms (instead of *n*-propyl) to reduce the computational time and they were labeled by the special character ‘.

substrate	**1’**+substrate	Van der Waals complex of **1’**+substrate	TS	product
DMAD	2.0	0.0	17.0	-13.7
1-phenylpyrrole-1,5-dione	5.9	0.0	15.6	-2.6
4-phenyl-1,2,4-triazoline-3,5-dione	5.0	0.0	5.6	-15.6

Table 1 Gibbs free energies (in kcal/mol unit and at B3LYP-D3/6-311+G** level of theory) of the cycloaddition and the corresponding transition states (TS)

Level of theory	**1’**+4-phenyl-1,2,4-triazoline-3,5-dione	Van der Waals complex of **1’**+substrate	product
B3LYP-D3/6-311+G**	5.0	0.0	-15.6
B3LYP-D3/6-311+G** (PCM=toluene)	3.7	0.0	-17.6
ωB97XD/6-311+G**	5.3	0.0	-23.4
BP86/6-311+G**	1.9	0.0	-15.1
M06-2X/6-311+G**	4.6	0.0	-22.5

Table 2. Gibbs free energies (in kcal/mol unit) of the cycloaddition and the corresponding transition state (TS) in the presence of 4-phenyl-1,2,4-triazoline-3,5-dione

XYZ matrix and total energies of the investigated systems

1'

G(B3LYP-D3/6-311+G**)= -2693.620174
E(B3LYP-D3/6-311+G**)= -2693.707670

C	0.012449	0.000000	0.002511
C	0.015389	0.000000	1.407811
N	1.308886	0.000000	1.941337
C	2.350017	0.000000	1.039155
S	1.676368	0.000000	-0.592404
P	-1.379774	0.000000	2.489375
C	-2.692986	0.000000	1.335531
S	-4.356904	0.000000	1.930445
C	-5.030554	0.000000	0.298886
N	-3.989422	0.000000	-0.603295
C	-2.695925	0.000000	-0.069770
P	-1.300763	0.000000	-1.151333
C	-4.219648	0.000000	-2.046814
S	-6.656678	0.000000	-0.002463
C	1.539112	0.000000	3.384855
S	3.976142	0.000000	1.340504
H	-5.291791	0.000000	-2.221814
H	-3.777313	0.891469	-2.496620
H	-3.777313	-0.891469	-2.496620
H	2.611255	0.000000	3.559855
H	1.096777	0.891469	3.834661
H	1.096777	-0.891469	3.834661

G(ωB97XD/6-311+G**)= -2693.323553
E(ωB97XD/6-311+G**)= -2693.413610

S	0.003670	0.000000	-0.001323
C	0.003999	0.000000	1.755436
C	1.322544	0.000000	2.225212
N	2.256315	0.000000	1.188212
C	1.754322	0.000000	-0.085777
P	-1.510238	0.000000	2.600493
C	-0.962158	0.000000	4.261083
N	-1.895915	0.000000	5.298087
C	-1.393906	0.000000	6.572074
S	0.356729	0.000000	6.487620
C	0.356409	0.000000	4.730845
C	-3.325200	0.000000	5.030309
P	1.870628	0.000000	3.885812
S	-2.220418	0.000000	7.995997
C	3.685599	0.000000	1.455996
S	2.580833	0.000000	-1.509694
H	4.210481	0.000000	0.504240

H	3.960475	0.891903	2.023463
H	3.960475	-0.891903	2.023463
H	-3.850075	0.000000	5.982069
H	-3.600077	0.891903	4.462842
H	-3.600077	-0.891902	4.462842

G(M06-2X/6-311+G**)= -2693.245395
E(M06-2X/6-311+G**)=-2693.335263

S	0.000313	0.000000	-0.000132
C	0.000365	0.000000	1.755969
C	1.319765	0.000000	2.226642
N	2.252006	0.000000	1.188249
C	1.752106	0.000000	-0.086286
P	-1.517929	0.000000	2.598673
C	-0.959401	0.000000	4.259625
N	-1.891600	0.000000	5.298030
C	-1.391656	0.000000	6.572550
S	0.360087	0.000000	6.486414
C	0.360065	0.000000	4.730258
C	-3.322873	0.000000	5.027666
P	1.878329	0.000000	3.887621
S	-2.219087	0.000000	7.994281
C	3.683262	0.000000	1.458666
S	2.579546	0.000000	-1.507997
H	4.208661	0.000000	0.508405
H	3.952377	0.891012	2.029002
H	3.952377	-0.891012	2.029002
H	-3.848244	0.000000	5.977946
H	-3.592026	0.891017	4.457358
H	-3.592027	-0.891016	4.457358

G(BP86/6-311+G**)= -2693.775777
E(BP86/6-311+G**)=-2693.858644

C	0.016694	0.000000	-0.006197
C	0.017190	0.000000	1.407776
N	1.311976	0.000000	1.944455
C	2.365592	0.000000	1.039272
S	1.685287	0.000000	-0.600163
P	-1.377557	0.000000	2.505906
C	-2.697234	0.000000	1.344240
S	-4.365823	0.000000	1.938206
C	-5.046131	0.000000	0.298766
N	-3.992513	0.000000	-0.606413
C	-2.697726	0.000000	-0.069732
P	-1.302979	0.000000	-1.167862

C	-4.224319	0.000000	-2.051505
S	-6.674623	0.000000	-0.017347
C	1.543785	0.000000	3.389546
S	3.994086	0.000000	1.355386
H	-5.309564	0.000000	-2.214959
H	-3.778945	0.898673	-2.506694
H	-3.778945	-0.898673	-2.506694
H	2.629030	0.000000	3.552998
H	1.098411	0.898673	3.844736
H	1.098411	-0.898673	3.844736

PCM=toluene
G(B3LYP-D3/6-311+G**)= -2693.620174
E(B3LYP-D3/6-311+G**)= -2693.712914

C	0.010034	-0.000000	0.002694
C	0.014221	0.000000	1.407735
N	1.309330	0.000000	1.940524
C	2.343546	0.000000	1.037957
S	1.674397	-0.000000	-0.591427
P	-1.378980	0.000000	2.490650
C	-2.690570	0.000000	1.335347
S	-4.354934	0.000000	1.929469
C	-5.024083	0.000000	0.300084
N	-3.989867	-0.000000	-0.602482
C	-2.694757	-0.000000	-0.069694
P	-1.301556	-0.000000	-1.152608
C	-4.218778	-0.000000	-2.047956
S	-6.657709	-0.000000	0.001741
C	1.538241	0.000000	3.385997
S	3.977173	0.000000	1.336301
H	-5.289780	-0.000000	-2.226522
H	-3.776238	0.892099	-2.495087
H	-3.776238	-0.892099	-2.495087
H	2.609244	0.000000	3.564564
H	1.095701	0.892099	3.833129
H	1.095701	-0.892099	3.833129

DMAD
G(B3LYP-D3/6-311+G**)= -533.172168
E(B3LYP-D3/6-311+G**)= -533.247813

C	-0.003868	-0.005249	-0.017880
O	-0.002202	-0.012767	1.427619
C	1.208516	0.009282	2.004264
O	2.260971	0.031379	1.414988
C	1.097869	0.003124	3.447200
C	1.083897	-0.006989	4.651187
C	1.055089	0.074192	6.095806

O	0.997208	1.113548	6.705544
O	1.100912	-1.146993	6.648484
C	1.080751	-1.177829	8.093533
H	-1.053139	-0.027140	-0.301226
H	0.480990	0.898159	-0.390413
H	0.521123	-0.881749	-0.400133
H	1.121867	-2.231907	8.356138
H	1.943307	-0.643203	8.493765
H	0.164710	-0.718687	8.467756

1-phenylpyrrole-1,5-dione

G(B3LYP-D3/6-311+G**)= -590.544191
E(B3LYP-D3/6-311+G**)= -590.656443

N	0.097083	-0.007469	-0.225271
C	-0.064169	0.017606	1.174692
C	1.318591	-0.008652	1.754924
C	2.203970	-0.045161	0.761464
C	1.469724	-0.047208	-0.546011
O	1.945011	-0.076030	-1.653450
H	3.283016	-0.073592	0.799630
H	1.479910	0.005904	2.822777
O	-1.109743	0.052175	1.774178
C	-0.968005	0.003833	-1.175336
C	-2.092160	-0.796710	-0.965747
C	-3.131269	-0.775659	-1.892026
C	-3.046497	0.025842	-3.029245
C	-1.916870	0.816207	-3.234582
C	-0.878268	0.815338	-2.307588
H	-2.156841	-1.414800	-0.080840
H	-4.006712	-1.392143	-1.723913
H	-3.855327	0.034501	-3.750686
H	-1.842222	1.441167	-4.116962
H	0.000756	1.424852	-2.466097

4-phenyl-1,2,4-triazoline-3,5-dione

G(B3LYP-D3/6-311+G**)= -622.617826
E(B3LYP-D3/6-311+G**)=-622.705773

C	0.003444	-0.022217	-0.007855
N	0.004581	-0.000048	1.381071
C	1.321512	0.022084	1.822445
N	2.170353	0.012956	0.581967
N	1.449034	-0.013475	-0.419674
C	-1.157709	-0.000010	2.218080
C	-2.250103	0.794900	1.873671
C	-3.378422	0.785658	2.689010

C	-3.409874	0.000071	3.839961
C	-2.308349	-0.785556	4.175008
C	-1.177386	-0.794880	3.363340
O	1.758144	0.038565	2.930091
O	-0.908657	-0.038832	-0.773096
H	-0.318212	-1.399110	3.621610
H	-2.326476	-1.397505	5.068983
H	-4.289222	0.000102	4.473217
H	-4.232009	1.397638	2.422794
H	-2.222668	1.399099	0.976917

G(ωB97XD/6-311+G**)= -622.617826
E(ωB97XD/6-311+G**)= -622.473663

C	-0.002686	-0.002444	0.004804
C	-0.000175	-0.000056	1.393953
C	1.188590	0.002374	2.112687
C	2.393731	-0.004723	1.423558
C	2.406445	0.000028	0.033846
C	1.209343	0.004735	-0.672136
N	-1.243097	-0.000110	2.096396
C	-1.572762	-0.827737	3.154584
N	-2.964494	-0.453784	3.545779
N	-3.372599	0.453675	2.823748
C	-2.319760	0.827421	1.832969
O	-0.936455	-1.671793	3.691191
O	-2.451209	1.671667	1.011243
H	1.171688	-0.000334	3.195234
H	3.324603	-0.009548	1.978009
H	3.349940	0.000060	-0.499373
H	1.214539	0.009592	-1.755607
H	-0.938803	0.000228	-0.539142

G(M06-2X/6-311+G**)= -622.617826
E(M06-2X /6-311+G**)= -622.454004

C	-0.002116	0.053724	0.003407
C	0.001185	-0.000067	1.393174
C	1.190070	-0.053808	2.112913
C	2.395169	-0.059275	1.421689
C	2.409317	0.000037	0.032227
C	1.211692	0.059294	-0.672406
N	-1.242496	-0.000134	2.096039
C	-1.541135	-0.763276	3.211796
N	-2.952290	-0.417652	3.578267
N	-3.394112	0.417609	2.796573
C	-2.352474	0.762903	1.776343
O	-0.874766	-1.539692	3.806692
O	-2.518336	1.539583	0.898829

H	1.170518	-0.100882	3.193749
H	3.325008	-0.106089	1.974739
H	3.352178	0.000078	-0.500628
H	1.217561	0.106146	-1.754268
H	-0.938133	0.100752	-0.537394

G(BP86/6-311+G**)= -622.626139
E(BP86/6-311+G**)= -622.709067

C	-0.002595	0.019532	-0.007458
C	-0.001799	-0.000039	1.394909
C	1.199200	-0.019583	2.118953
C	2.413383	-0.025186	1.422949
C	2.427520	0.000016	0.021919
C	1.219964	0.025190	-0.688641
N	-1.252073	-0.000063	2.101533
C	-1.570867	-0.813902	3.193838
N	-2.990828	-0.447059	3.583373
N	-3.418494	0.446778	2.826698
C	-2.352305	0.813760	1.811244
O	-0.911250	-1.646234	3.758771
O	-2.496094	1.646049	0.954713
H	1.183165	-0.038916	3.209586
H	3.351648	-0.045328	1.982263
H	3.378709	0.000037	-0.515670
H	1.224769	0.045354	-1.780955
H	-0.945214	0.038844	-0.556284

PCM=toluene
G(B3LYP-D3/6-311+G**)= -622.623140
E(B3LYP-D3/6-311+G**)=-622.710887

C	-0.003089	0.005366	0.000107
C	0.000536	-0.000034	1.393583
C	1.192453	-0.005410	2.115471
C	2.401148	-0.011724	1.424010
C	2.413851	0.000013	0.029649
C	1.212754	0.011725	-0.678706
N	-1.247023	-0.000060	2.098673
C	-1.571168	-0.821724	3.166407
N	-2.973656	-0.450091	3.559689
N	-3.389327	0.449839	2.824268
C	-2.329000	0.821529	1.825597
O	-0.927403	-1.663096	3.711990
O	-2.464371	1.662930	0.992703
H	1.173293	-0.012918	3.197253
H	3.332088	-0.021240	1.978059
H	3.357186	0.000033	-0.503496

H	1.218295	0.021259	-1.762029
H	-0.939729	0.012853	-0.541487

Van der waals complex of 1' and DMAD

G(B3LYP-D3/6-311+G**)= -3226.795580
E(B3LYP-D3/6-311+G**)= -3226.976938

C	0.056006	-0.204126	0.164493
C	-0.092252	-0.177467	1.561307
S	1.493120	-0.293184	2.328387
C	2.328567	-0.391617	0.777918
N	1.389910	-0.335123	-0.228604
P	-1.520841	-0.101797	2.565008
C	-2.792408	-0.088858	1.341618
N	-4.133082	-0.108059	1.733020
C	-5.071992	-0.057236	0.726435
S	-4.229508	0.000356	-0.822280
C	-2.640941	-0.044374	-0.054402
C	-4.516847	-0.211437	3.140121
P	-1.210329	-0.075206	-1.057599
S	-6.720402	-0.050591	0.860514
S	3.971016	-0.530402	0.642352
C	1.764284	-0.440682	-1.638061
C	-1.523196	-3.511126	0.115976
C	-1.519261	-3.524951	1.318647
C	-1.416642	-3.558815	2.762969
O	-0.381220	-3.720224	3.358993
C	-1.626765	-3.503380	-1.328654
O	-2.671864	-3.556644	-1.927264
O	-0.412111	-3.432386	-1.901506
C	-0.414116	-3.402659	-3.346599
O	-2.620265	-3.390377	3.338746
C	-2.616714	-3.393136	4.784147
H	1.479796	0.469081	-2.171753
H	2.842313	-0.572236	-1.690925
H	1.262481	-1.303426	-2.080281
H	-5.602400	-0.246387	3.191128
H	-4.095320	-1.125786	3.561985
H	-4.151989	0.656586	3.694051
H	0.634542	-3.397662	-3.634411
H	-0.919993	-4.283334	-3.743318
H	-0.921007	-2.503067	-3.700203

H	-3.660787	-3.299054	5.073294
H	-2.193476	-4.324846	5.160541
H	-2.030277	-2.551551	5.157051

Van der waals complex of 1' and 1-phenylpyrrole-1,5-dione

G(B3LYP-D3/6-311+G**)= -3284.173789
E(B3LYP-D3/6-311+G**)= -3284.393497

C	0.000687	-0.001090	-0.000776
C	0.000966	0.000393	1.396992
C	1.208165	0.000645	2.098998
C	2.410045	0.018644	1.398641
C	2.418477	0.038966	0.006414
C	1.210860	0.025652	-0.687816
N	-1.241135	0.000275	2.107749
C	-2.418637	0.641434	1.681559
C	-3.468634	0.331907	2.703240
C	-2.927006	-0.413449	3.664080
C	-1.489659	-0.670188	3.328662
O	-2.546851	1.322690	0.691009
O	-0.698484	-1.320899	3.963039
C	-1.185344	4.305121	1.015953
N	-0.736620	3.738050	2.290575
C	-1.636045	3.428826	3.312070
C	-1.008623	2.845504	4.427754
S	0.735073	2.788767	4.159748
C	0.594610	3.486950	2.542909
P	-1.658964	2.188933	5.911568
C	-3.379903	2.512001	5.690313
C	-3.996360	3.167752	4.613900
S	-5.743398	3.233949	4.884268
C	-5.623222	2.374280	6.422146
N	-4.297581	2.088153	6.658991
P	-3.349816	3.812063	3.122138
C	-3.865690	1.387510	7.868595
S	-6.937599	2.011206	7.358714
S	1.897358	3.754332	1.566663
H	-1.584377	5.309993	1.174877
H	-0.325322	4.356122	0.353113
H	-1.945888	3.656149	0.580998
H	-3.219945	2.035649	8.465551
H	-4.752038	1.126267	8.441517
H	-3.319301	0.480861	7.598758
H	-0.932325	-0.007151	-0.545019
H	1.204552	0.035359	-1.771635
H	3.357946	0.066590	-0.532971
H	3.342914	0.030932	1.949551

H	1.208819	-0.016425	3.177523
H	-3.378618	-0.823946	4.554604
H	-4.478461	0.699567	2.603207

Van der waals complex of 1' and 4-phenyl-1,2,4-triazoline-3,5-dione

G(B3LYP-D3/6-311+G**)= -3316.245889
E(B3LYP-D3/6-311+G**)= -3316.440159

C	0.609886	0.493197	-0.326122
C	0.937496	0.837048	0.998097
N	2.283548	1.188458	1.142372
C	3.059537	1.146804	0.005372
S	2.046995	0.633939	-1.345546
P	-0.129450	0.858179	2.402206
C	-1.635216	0.353996	1.672447
C	-1.960455	0.008390	0.352980
N	-3.304592	-0.364783	0.211692
C	-4.067800	-0.344812	1.351676
S	-3.067094	0.189878	2.696826
P	-0.892057	-0.027253	-1.049112
S	-5.663662	-0.766471	1.535811
C	-3.853605	-0.773173	-1.083965
C	2.838012	1.579928	2.438214
S	4.667535	1.499947	-0.155011
O	-4.072021	-3.939196	-0.232891
C	-3.589286	-3.731876	0.837906
N	-4.046885	-4.035075	2.106896
C	-3.128097	-3.561785	3.036247
N	-2.015052	-2.944834	2.233975
N	-2.269688	-3.041181	1.029007
C	-5.281679	-4.693274	2.416120
C	-5.304578	-5.661268	3.419051
C	-6.506077	-6.297484	3.718194
C	-7.666203	-5.976165	3.015383
C	-7.625672	-5.009380	2.012120
C	-6.434091	-4.356877	1.708506
O	-3.141448	-3.615388	4.224997
H	3.893768	1.799896	2.300388
H	2.722417	0.763320	3.154437
H	-4.915131	-0.966680	-0.954294
H	2.322595	2.468174	2.810729
H	-3.709189	0.027850	-1.811594
H	-3.360033	-1.685281	-1.422912
H	-6.397177	-3.597451	0.940529
H	-8.525249	-4.753390	1.465005
H	-8.598425	-6.476718	3.249678
H	-6.531492	-7.046779	4.500481

H	-4.401951	-5.902336	3.964400

G(ωB97XD/6-311+G**)= -3315.715950
E(ωB97XD/6-311+G**)= -3315.917049

C	-0.062418	-0.118037	-0.007718
C	0.003051	0.037068	1.381438
N	1.311372	0.080547	1.851285
C	2.301184	-0.021812	0.909692
S	1.561386	-0.185656	-0.669152
P	-1.324106	0.179612	2.514139
C	-2.678753	-0.003814	1.444067
C	-2.742055	-0.224826	0.064324
N	-4.056004	-0.346958	-0.395119
C	-5.042237	-0.180436	0.535092
S	-4.307170	0.088253	2.101292
P	-1.412888	-0.325942	-1.070877
S	-6.676634	-0.226911	0.309276
C	-4.347588	-0.644180	-1.791236
C	1.605604	0.171648	3.273544
S	3.930479	0.000811	1.140464
O	-3.287555	-3.660791	-0.471472
C	-2.617257	-3.525552	0.500170
N	-2.946752	-3.643575	1.834945
C	-1.824603	-3.348520	2.589598
N	-0.737967	-3.055251	1.610242
N	-1.170723	-3.168313	0.462512
C	-4.228065	-4.014370	2.351355
C	-4.303730	-4.906565	3.414207
C	-5.551749	-5.254867	3.912491
C	-6.706872	-4.724457	3.349308
C	-6.614486	-3.838587	2.283076
C	-5.373245	-3.478167	1.779018
O	-1.674803	-3.336094	3.766178
H	2.686453	0.151093	3.393568
H	1.158972	-0.677904	3.795935
H	-5.427829	-0.704760	-1.901713
H	1.209474	1.104941	3.680389
H	-3.959158	0.151414	-2.431147
H	-3.892527	-1.599155	-2.062571
H	-5.306857	-2.792277	0.946338
H	-7.506132	-3.412695	1.838740
H	-7.677843	-5.002684	3.741985
H	-5.618803	-5.947477	4.743035
H	-3.402731	-5.314660	3.853597

G(M06-2X/6-311+G**)= -3315.616594
E(M06-2X /6-311+G**)= -3315.819076

C	-0.051139	-0.025502	0.020296
C	-0.076290	-0.029871	1.421249
N	1.197172	-0.049897	1.976060
C	2.249132	-0.046168	1.097772
S	1.613511	-0.021359	-0.536156
P	-1.473501	-0.007627	2.484661
C	-2.752215	-0.097662	1.310083
C	-2.727584	-0.164594	-0.088218
N	-4.003908	-0.285321	-0.638598
C	-5.046609	-0.314324	0.242091
S	-4.416301	-0.161626	1.871365
P	-1.327675	-0.123947	-1.147406
S	-6.655799	-0.479845	-0.077707
C	-4.193312	-0.475139	-2.072887
C	1.389026	-0.148914	3.418417
S	3.857541	-0.059122	1.436606
O	-3.662191	-3.262274	-0.465300
C	-2.853566	-3.276027	0.404176
N	-2.991138	-3.534762	1.755797
C	-1.754087	-3.350653	2.355433
N	-0.804957	-3.002640	1.251513
N	-1.406013	-2.986858	0.178961
C	-4.197111	-3.934306	2.420900
C	-4.113939	-4.747527	3.548390
C	-5.285095	-5.129016	4.191449
C	-6.522253	-4.711027	3.713679
C	-6.588206	-3.908467	2.580457
C	-5.428233	-3.514314	1.925402
O	-1.425786	-3.459355	3.489202
H	2.456363	-0.204747	3.612855
H	0.892108	-1.050304	3.785313
H	-5.260064	-0.552118	-2.263054
H	0.968949	0.730761	3.910167
H	-3.778500	0.376999	-2.614222
H	-3.694109	-1.396976	-2.378666
H	-5.493913	-2.898929	1.039478
H	-7.544188	-3.575044	2.195632
H	-7.430491	-5.011882	4.221178
H	-5.224005	-5.758938	5.070295
H	-3.153191	-5.070585	3.923634

G(BP86/6-311+G**)= -622.617826
E(BP86/6-311+G**)= -3316.580597

C	4.117259	0.634050	-0.449446
C	4.210310	-0.352580	0.561010
N	5.459147	-0.985951	0.579176
C	6.388499	-0.567285	-0.364719

S	5.643798	0.711958	-1.344147
P	2.973495	-0.838016	1.736007
C	1.662487	0.239448	1.275379
C	1.570437	1.227446	0.269405
N	0.321757	1.864256	0.255966
C	-0.604814	1.421959	1.178199
S	0.128462	0.145982	2.154249
P	2.804389	1.704543	-0.914014
S	-2.173609	1.949845	1.386912
C	-0.004645	2.912614	-0.716704
C	5.773683	-2.042369	1.543738
S	7.935178	-1.118420	-0.594152
O	-3.990928	1.537054	-1.995335
C	-3.489371	0.557451	-1.506482
N	-4.091041	-0.559435	-0.913558
C	-3.096711	-1.488844	-0.594417
N	-1.794195	-0.867119	-1.025385
N	-2.007719	0.269453	-1.505813
C	-5.497926	-0.724546	-0.689680
C	-6.111266	-1.945255	-1.007604
C	-7.484243	-2.097129	-0.781949
C	-8.237457	-1.038933	-0.255945
C	-7.612619	0.176910	0.053111
C	-6.238472	0.340136	-0.155605
O	-3.189775	-2.579834	-0.090595
H	6.806244	-2.363957	1.352867
H	5.084330	-2.891070	1.411212
H	-0.946300	3.378643	-0.399568
H	5.683850	-1.653770	2.570356
H	0.804150	3.658642	-0.735080
H	-0.138904	2.467140	-1.713786
H	-5.744823	1.281885	0.088544
H	-8.194236	1.004898	0.465348
H	-9.309839	-1.161847	-0.086043
H	-7.965411	-3.047848	-1.023639
H	-5.520429	-2.766024	-1.416697

PCM=toluene
G(B3LYP-D3/6-311+G**)= -3316.254187
E(B3LYP-D3/6-311+G**)= -3316.447760

C	0.009820	-0.024080	-0.010970
C	0.021207	-0.002545	1.382052
C	1.216207	0.039521	2.098059
C	2.421467	0.053906	1.400946
C	2.427224	0.038180	0.006595
C	1.222592	0.002179	-0.694627
N	-1.221365	-0.019702	2.096986

C	-2.337403	0.735196	1.791336
N	-3.374155	0.373217	2.815584
N	-2.921358	-0.477110	3.588767
C	-1.508702	-0.814320	3.197050
O	-2.523128	1.530333	0.921388
O	-0.829708	-1.604920	3.773670
N	-5.088972	-1.156162	0.885267
C	-5.970589	-1.228815	1.973841
C	-5.681927	-2.303862	2.827242
S	-4.285751	-3.192832	2.205092
C	-4.110445	-2.112679	0.830038
P	-6.427941	-2.839544	4.313909
C	-7.708403	-1.639009	4.484495
C	-7.999159	-0.563268	3.626841
S	-9.382010	0.337207	4.259849
C	-9.546729	-0.731575	5.649646
N	-8.576326	-1.699574	5.581067
P	-7.243845	-0.022344	2.147778
C	-8.450429	-2.745368	6.598685
S	-10.718213	-0.526162	6.808913
C	-5.210361	-0.103502	-0.128092
S	-2.893430	-2.284418	-0.293113
H	-9.219606	-2.582904	7.348781
H	-7.465068	-2.690510	7.065679
H	-4.449203	-0.272310	-0.884660
H	-8.586847	-3.726920	6.140058
H	-6.200551	-0.147556	-0.584882
H	-5.050152	0.871703	0.333674
H	-0.928552	-0.065776	-0.546008
H	1.222358	-0.012811	-1.777998
H	3.367736	0.053324	-0.531503
H	3.354727	0.081312	1.950592
H	1.203536	0.052005	3.179931

TS of 2’

G(B3LYP-D3/6-311+G**)= -3226.768561
E(B3LYP-D3/6-311+G**)= -3226.953666

N	0.014834	0.071333	-0.023075
C	0.009326	0.072557	1.368647
C	1.277158	0.086530	1.921307
S	2.488204	0.095480	0.643958
C	1.256876	0.065332	-0.625174
P	-1.502127	-0.200395	2.279942
C	-1.008480	0.279452	3.903691
S	-2.208637	0.512456	5.170053
C	-0.979822	0.486857	6.441718

N	0.255295	0.327017	5.846604
C	0.255229	0.201860	4.460508
P	1.732373	-0.286887	3.583793
C	1.483991	0.227903	6.637378
S	-1.325891	0.663119	8.049332
S	1.610829	0.063825	-2.240716
C	-1.221032	0.011768	-0.806613
C	0.564624	-2.565619	3.318467
C	1.611698	-3.370386	3.939607
O	1.669276	-3.145050	5.267341
C	2.657173	-3.917596	5.985617
C	-0.542282	-2.541384	2.755001
C	-1.659808	-3.301860	2.204893
O	-1.702317	-3.193210	0.861997
C	-2.758396	-3.935821	0.212449
O	2.328063	-4.131303	3.339741
O	-2.439087	-3.938120	2.868149
H	2.248451	0.874737	6.204438
H	1.258593	0.546045	7.652457
H	1.834296	-0.806349	6.645551
H	-0.972051	0.214674	-1.845479
H	-1.663095	-0.983169	-0.722130
H	-1.922357	0.761513	-0.437471
H	2.545175	-3.628355	7.028040
H	2.467700	-4.984166	5.860689
H	3.658215	-3.682170	5.620843
H	-2.625191	-3.753116	-0.851376
H	-2.664749	-4.999419	0.433961
H	-3.732813	-3.579657	0.550424

TS of 3’

G(B3LYP-D3/6-311+G**)= -3284.148908
E(B3LYP-D3/6-311+G**)= -3284.372567

N	0.020817	-0.073252	-0.041888
C	0.013519	-0.042169	1.353951
C	1.278747	-0.041672	1.903119
S	2.493929	-0.105458	0.630068
C	1.260924	-0.137311	-0.640342
P	-1.495083	-0.283360	2.291548
C	-0.981724	0.330586	3.870903
C	0.280185	0.275874	4.431946
N	0.290593	0.543447	5.798836
C	-0.935280	0.822713	6.369887
S	-2.164628	0.772973	5.095361
P	1.739560	-0.334296	3.591425
S	-1.278673	1.176449	7.945628

C	1.521031	0.492734	6.598101
S	1.588307	-0.201701	-2.259150
C	-1.187757	-0.035726	-0.870612
C	0.663639	-2.574726	3.467336
C	-0.613544	-2.598672	2.902704
C	-1.597702	-2.860513	3.998781
N	-0.859438	-2.869312	5.208025
C	0.518265	-2.767202	4.945746
C	-1.433047	-3.006565	6.512227
C	-0.782871	-3.773467	7.482708
C	-1.334793	-3.877564	8.756385
C	-2.532180	-3.234516	9.063470
C	-3.183159	-2.487688	8.084132
C	-2.639628	-2.370195	6.809388
O	-2.784496	-3.048394	3.899788
O	1.402887	-2.811805	5.770487
H	1.306484	0.929525	7.570373
H	1.839662	-0.543602	6.721850
H	2.300762	1.066907	6.095370
H	-2.034568	0.259809	-0.254621
H	-1.041791	0.682996	-1.676484
H	-1.373080	-1.016920	-1.311549
H	0.149329	-4.266902	7.250389
H	-0.823265	-4.466045	9.509255
H	-2.955327	-3.316111	10.057903
H	-4.114731	-1.983268	8.311247
H	-3.151173	-1.796641	6.052056
H	-0.840407	-2.941587	1.903973
H	1.558278	-2.926683	2.974173

TS of 4’

G(B3LYP-D3/6-311+G**)= -3316.236937
E(B3LYP-D3/6-311+G**)=-3316.436878

N	-0.025590	-0.002798	-0.013749
C	-0.001454	-0.006692	1.372907
C	1.280937	0.029455	1.894296
S	2.462496	0.101764	0.589953
C	1.204387	0.069655	-0.647213
P	-1.537039	0.122020	2.295799
C	-0.968300	-0.246742	3.914074
C	0.322291	-0.208222	4.435032
N	0.374376	-0.427386	5.807455
C	-0.839930	-0.610491	6.435930
S	-2.120358	-0.538813	5.220758
P	1.769095	0.376685	3.548443

S	-1.133934	-0.870398	8.042891
C	1.642417	-0.465846	6.548344
S	1.514448	0.095787	-2.269544
C	-1.277007	-0.006726	-0.777850
N	0.720947	2.372336	3.530618
C	0.236556	2.679246	4.878914
N	-1.040682	3.171942	4.706365
C	-1.363474	3.126355	3.337630
N	-0.205560	2.566707	2.656529
C	-1.914209	3.606289	5.753630
C	-1.980066	2.874324	6.938529
C	-2.837777	3.294476	7.950381
C	-3.626464	4.430867	7.778084
C	-3.551976	5.153365	6.588035
C	-2.692403	4.749005	5.570053
O	0.880258	2.547174	5.885473
O	-2.347333	3.548937	2.801379
H	-1.037325	-0.228439	-1.815057
H	-1.755507	0.973328	-0.718060
H	1.433095	-0.838923	7.547753
H	-1.945661	-0.770545	-0.379495
H	2.335217	-1.137328	6.039158
H	2.061197	0.538037	6.612758
H	-1.368267	1.994990	7.077261
H	-2.889431	2.723484	8.869764
H	-4.296712	4.751815	8.566989
H	-4.162558	6.037649	6.448032
H	-2.637639	5.298981	4.640721

2’

G(B3LYP-D3/6-311+G**)= -3226.817348
E(B3LYP-D3/6-311+G**)= -3227.006329

S	0.020447	0.024144	-0.024515
C	0.009786	0.018114	1.726712
C	1.272922	0.015395	2.212432
N	2.257902	0.022656	1.233353
C	1.793843	0.029561	-0.067483
P	-1.471552	-0.069008	2.805183
C	-0.824236	-1.492604	3.871000
C	-1.860534	-2.533048	4.169893
O	-1.567558	-3.712951	3.619920
C	-2.468741	-4.796934	3.943778
P	1.582436	-0.032701	4.046034
C	0.421181	-1.498647	4.355793
C	0.925955	-2.630470	5.193041
O	2.259697	-2.759553	5.072002

C	2.861057	-3.830133	5.831622
C	3.698744	0.028172	1.495345
S	2.707623	0.045134	-1.448529
C	0.345482	1.258382	4.465674
C	-0.921172	1.251991	3.989125
N	-1.724254	2.269306	4.487091
C	-1.104169	3.122797	5.377921
S	0.574381	2.584113	5.585897
S	-1.777832	4.431643	6.135159
C	-3.133582	2.470000	4.141576
O	0.237593	-3.339972	5.885757
O	-2.861160	-2.272453	4.790902
H	4.145902	0.919657	1.053473
H	4.155633	-0.849264	1.035973
H	3.863072	0.017796	2.570399
H	-3.740179	2.412522	5.046013
H	-3.263423	3.458706	3.699539
H	-3.440202	1.698863	3.438761
H	3.926465	-3.768749	5.623586
H	2.663701	-3.692260	6.895483
H	2.457496	-4.791570	5.511004
H	-2.106275	-5.650960	3.377133
H	-2.426509	-4.995054	5.015524
H	-3.489128	-4.541902	3.655495

3’

G(B3LYP-D3/6-311+G**)= -3284.177987
E(B3LYP-D3/6-311+G**)=-3284.404670

C	0.068596	0.084621	0.022331
C	0.046909	0.006198	1.413003
C	1.225319	-0.095350	2.146900
C	2.444106	-0.120003	1.473160
C	2.478044	-0.048634	0.081087
C	1.290346	0.053715	-0.642451
N	-1.215356	0.060955	2.092640
C	-1.547821	1.061030	3.017894
C	-3.035172	0.935809	3.324721
C	-3.471596	-0.375580	2.659204
C	-2.261337	-0.831431	1.849335
P	-3.855148	2.562801	2.688759
C	-3.716224	2.135362	0.914846
C	-4.141287	0.957594	0.385263
N	-3.719520	0.741508	-0.921391
C	-2.930066	1.737664	-1.459419
S	-2.745955	3.018323	-0.249793
P	-4.955937	-0.331406	1.437884

C	-6.003481	0.785506	2.425824
C	-5.582042	1.966168	2.944334
N	-6.542740	2.624404	3.705742
C	-7.755741	1.973685	3.817049
S	-7.661383	0.460165	2.897196
S	-9.089258	2.493158	4.648830
C	-6.352023	3.924784	4.353607
S	-2.246575	1.757578	-2.968466
C	-4.024478	-0.458066	-1.707621
O	-0.789843	1.889322	3.452043
O	-2.217931	-1.772151	1.095097
H	-4.476887	-0.162273	-2.654201
H	-3.103308	-1.004519	-1.912595
H	-4.704755	-1.088411	-1.140720
H	-7.101505	4.626375	3.985321
H	-6.481588	3.819439	5.431552
H	-5.352835	4.290977	4.128922
H	1.185566	-0.138641	3.227570
H	3.366120	-0.193135	2.037789
H	3.428872	-0.067465	-0.438856
H	1.308534	0.120551	-1.723681
H	-0.853426	0.175134	-0.535786
H	-3.188234	0.944798	4.404196
H	-3.723268	-1.143149	3.393616

4’

G(B3LYP-D3/6-311+G**)= -3316.270784
E(B3LYP-D3/6-311+G**)= -3316.472876

C	-0.040689	0.102741	-0.018000
C	-0.004624	0.009830	1.372851
C	1.209967	-0.023503	2.057079
C	2.399201	0.042501	1.336936
C	2.376435	0.127731	-0.054339
C	1.156268	0.153984	-0.727319
N	-1.228212	-0.048115	2.113415
C	-1.477089	0.698594	3.273330
N	-2.744684	0.297150	3.715332
N	-3.270497	-0.642136	2.774189
C	-2.341175	-0.816843	1.746046
P	-3.816366	1.385697	4.611690
C	-4.874343	1.861691	3.195639
C	-5.370295	0.944683	2.319978
N	-5.927723	1.497616	1.177154
C	-5.896084	2.879090	1.111500
S	-5.091042	3.486699	2.571784
P	-5.007684	-0.865436	2.554473

C	-5.382024	-0.916472	4.339430
C	-4.890994	-0.000781	5.210904
N	-5.200602	-0.256645	6.537402
C	-5.960986	-1.391683	6.755423
S	-6.264105	-2.168644	5.188217
S	-6.513765	-1.950149	8.209894
C	-4.800606	0.582168	7.670508
S	-6.512456	3.827839	-0.093730
C	-6.555508	0.729306	0.098470
O	-0.759244	1.507793	3.804003
O	-2.483914	-1.499132	0.761820
H	-7.607313	1.007320	0.017817
H	-6.063376	0.961435	-0.846236
H	-6.462008	-0.332551	0.314756
H	-4.230218	-0.016550	8.381207
H	-4.193313	1.408166	7.307053
H	-5.690050	0.961817	8.175083
H	1.220430	-0.081215	3.137095
H	3.344384	0.023884	1.866648
H	3.305141	0.174005	-0.611085
H	1.131438	0.219431	-1.808728
H	-0.989952	0.116117	-0.535256

G(M06-2X/6-311+G**)= -3315.652502
E(M06-2X/6-311+G**)= -3315.858950

C	-0.009009	0.035704	-0.013217
C	0.007779	0.003296	1.377319
C	1.206804	0.010422	2.082990
C	2.404347	0.056517	1.381025
C	2.403453	0.081239	-0.009710
C	1.197536	0.067256	-0.701927
N	-1.224153	-0.036142	2.100001
C	-1.479966	0.717524	3.247580
N	-2.751040	0.326518	3.675481
N	-3.269983	-0.604232	2.744293
C	-2.335042	-0.796747	1.729261
P	-3.801435	1.397679	4.582551
C	-4.877526	1.870224	3.185987
C	-5.371508	0.956050	2.316157
N	-5.973048	1.512434	1.202006
C	-5.976301	2.886085	1.164435
S	-5.153862	3.486829	2.597387
P	-4.987649	-0.845818	2.525895
C	-5.351834	-0.907231	4.308171
C	-4.864565	0.006691	5.175339
N	-5.171086	-0.256438	6.497576
C	-5.921059	-1.389052	6.705699

S	-6.220344	-2.156467	5.152342
S	-6.466347	-1.951143	8.154210
C	-4.780666	0.569957	7.636511
S	-6.646686	3.831881	-0.004882
C	-6.607721	0.758173	0.124392
O	-0.770514	1.524121	3.778519
O	-2.475417	-1.483759	0.756300
H	-7.663581	1.025051	0.072193
H	-6.137602	1.021562	-0.822826
H	-6.492857	-0.305438	0.318090
H	-4.214116	-0.037917	8.341733
H	-4.174931	1.400799	7.283395
H	-5.675813	0.937389	8.138902
H	1.197727	-0.003693	3.164799
H	3.340255	0.069346	1.925793
H	3.340302	0.112003	-0.552369
H	1.190758	0.086150	-1.784742
H	-0.950976	0.020607	-0.544224

G(BP86/6-311+G**)= -3316.422911
E(BP86/6-311+G**)=-3316.614887

S	-0.023920	0.045265	0.009809
C	-0.023740	-0.008781	1.765208
C	1.256963	-0.010157	2.248477
N	2.236177	0.020805	1.262994
C	1.762759	0.038952	-0.049790
P	-1.481446	0.096546	2.864484
C	-0.923080	-1.218688	4.062169
C	0.362963	-1.218245	4.546787
S	0.519245	-2.359180	5.877065
C	-1.190885	-2.856966	5.735106
N	-1.772493	-2.107678	4.711454
P	1.581942	0.067138	4.077178
N	0.508680	1.476385	4.291560
C	0.568854	2.306856	5.430412
N	-0.733283	2.837503	5.575663
C	-1.633710	2.269633	4.644931
N	-0.841658	1.455985	3.814712
C	-1.099248	3.804103	6.571351
C	-2.296286	3.648959	7.286984
C	-2.644946	4.601787	8.251202
C	-1.801956	5.690188	8.511546
C	-0.605325	5.830314	7.795651
C	-0.250582	4.894152	6.817952
O	1.553362	2.522765	6.111411
O	-2.833687	2.448495	4.545572
C	-3.180567	-2.327704	4.359036

S	-1.929297	-4.025289	6.649037
C	3.682432	0.011702	1.513821
S	2.676934	0.043062	-1.431747
H	-3.316272	-3.361864	4.009086
H	-3.807598	-2.178394	5.249296
H	-3.465124	-1.617728	3.572128
H	4.141951	0.887337	1.033481
H	3.855103	0.038756	2.597243
H	4.127404	-0.895133	1.078438
H	0.681761	4.997100	6.261521
H	0.057978	6.675817	7.993541
H	-2.076346	6.427105	9.270349
H	-3.579903	4.485758	8.804759
H	-2.951240	2.802488	7.079387

G(ωB97XD/6-311+G**)= -3315.753168
E(ωB97XD/6-311+G**)=-3315.961136

C	-0.005017	0.206450	0.016733
C	0.011862	0.001307	1.390509
C	1.209033	-0.158631	2.076848
C	2.405225	-0.103731	1.375221
C	2.401574	0.093491	-0.000667
C	1.196840	0.243903	-0.676970
N	-1.217898	-0.041196	2.113775
C	-1.477977	0.724377	3.250194
N	-2.752041	0.343304	3.669799
N	-3.264799	-0.600457	2.745372
C	-2.323825	-0.805027	1.741758
P	-3.812125	1.408024	4.561555
C	-4.888490	1.864801	3.164216
C	-5.374692	0.939974	2.303403
N	-5.986481	1.479201	1.187231
C	-6.007131	2.852813	1.142661
S	-5.185576	3.473276	2.566092
P	-4.976590	-0.851365	2.536475
C	-5.344907	-0.902208	4.315132
C	-4.864020	0.022161	5.172817
N	-5.161901	-0.230677	6.498221
C	-5.901303	-1.368621	6.717091
S	-6.197817	-2.152614	5.172952
S	-6.442094	-1.926586	8.170364
C	-4.777588	0.617876	7.619207
S	-6.695626	3.788577	-0.026374
C	-6.613904	0.703603	0.124376
O	-0.767251	1.533855	3.777889
O	-2.454416	-1.502198	0.773134

H	-7.681279	0.927278	0.089014
H	-6.171490	0.976164	-0.834145
H	-6.458504	-0.356489	0.314949
H	-4.218044	0.028332	8.346045
H	-4.162148	1.437446	7.253453
H	-5.671836	1.009423	8.106460
H	1.202208	-0.310761	3.148754
H	3.342513	-0.219088	1.906583
H	3.337675	0.131859	-0.545605
H	1.189785	0.398285	-1.749515
H	-0.947623	0.321298	-0.502574

PCM=toluene
G(B3LYP-D3/6-311+G**)= -3316.282309
E(B3LYP-D3/6-311+G**)= -3316.484042

S	-0.007818	0.062876	0.038040
C	-0.013428	0.017368	1.786655
C	1.254212	0.003167	2.269098
N	2.233954	0.017878	1.288289
C	1.761466	0.037321	-0.007061
P	-1.476192	0.125154	2.875251
C	-0.934687	-1.198947	4.065787
C	0.335805	-1.205035	4.552880
S	0.487725	-2.367872	5.854229
C	-1.206316	-2.853223	5.690762
N	-1.783265	-2.101833	4.688929
P	1.567175	0.071505	4.096510
N	0.502430	1.466186	4.324577
C	0.561483	2.303689	5.439897
N	-0.723951	2.842292	5.572252
C	-1.613975	2.291702	4.641667
N	-0.839479	1.460408	3.836463
C	-1.089598	3.804385	6.566366
C	-2.220936	3.587990	7.351388
C	-2.571503	4.532046	8.313275
C	-1.789763	5.671825	8.497931
C	-0.655649	5.872777	7.711571
C	-0.304068	4.943166	6.736455
O	1.530315	2.520638	6.127442
O	-2.800460	2.495795	4.538390
C	-3.188375	-2.314308	4.324136
S	-1.940973	-4.035841	6.595559
C	3.678038	-0.008286	1.545491
S	2.669386	0.029828	-1.397316
H	-3.325948	-3.345910	3.998928
H	-3.820510	-2.133543	5.193330
H	-3.456924	-1.631252	3.522000

H	4.143605	0.862022	1.083285
H	3.849804	0.005719	2.618949
H	4.108826	-0.909877	1.109137
H	0.574626	5.089563	6.122170
H	-0.044231	6.756262	7.852111
H	-2.063075	6.400624	9.252052
H	-3.453690	4.371483	8.921683
H	-2.822119	2.701413	7.200703

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