Organometallics - Full Paper

Probing Donor - Acceptor Interactions in *Peri*-Substituted Diphenylphosphinoacenaphthylelement Dichlorides of Group 13 and 15 Elements

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Supporting Information

Contents

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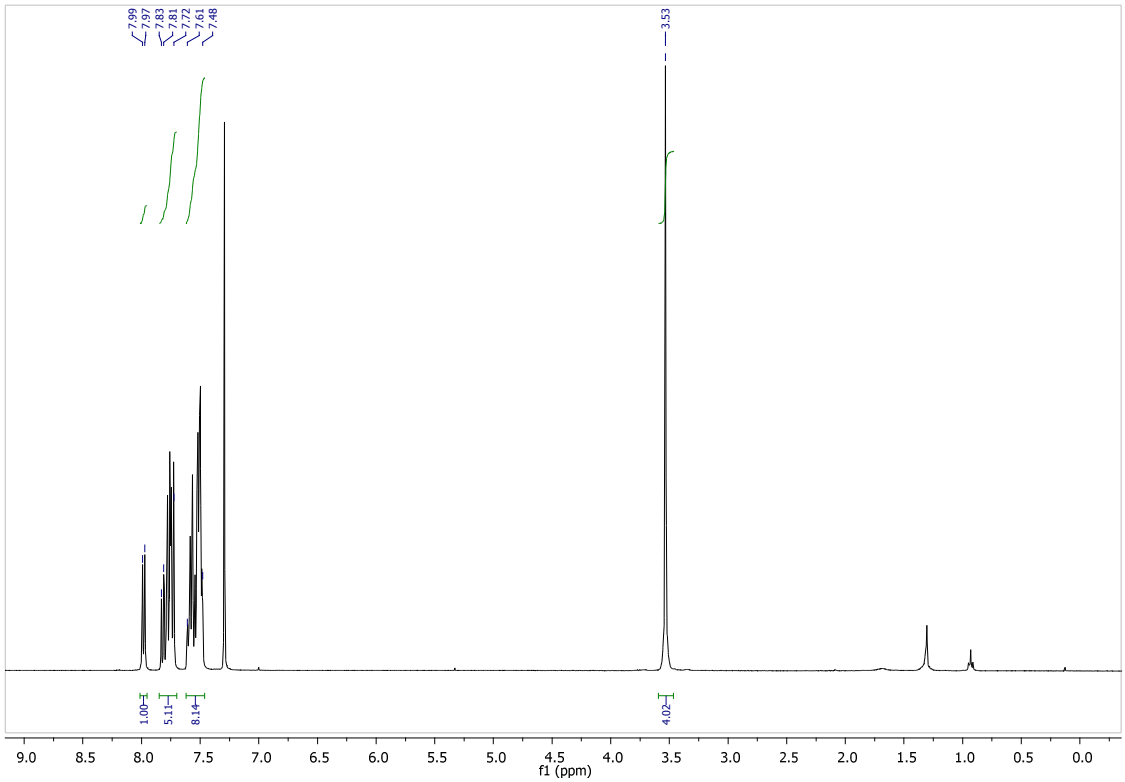

Figure S1. ^{1}H-NMR of **1** ($CDCl_3$).

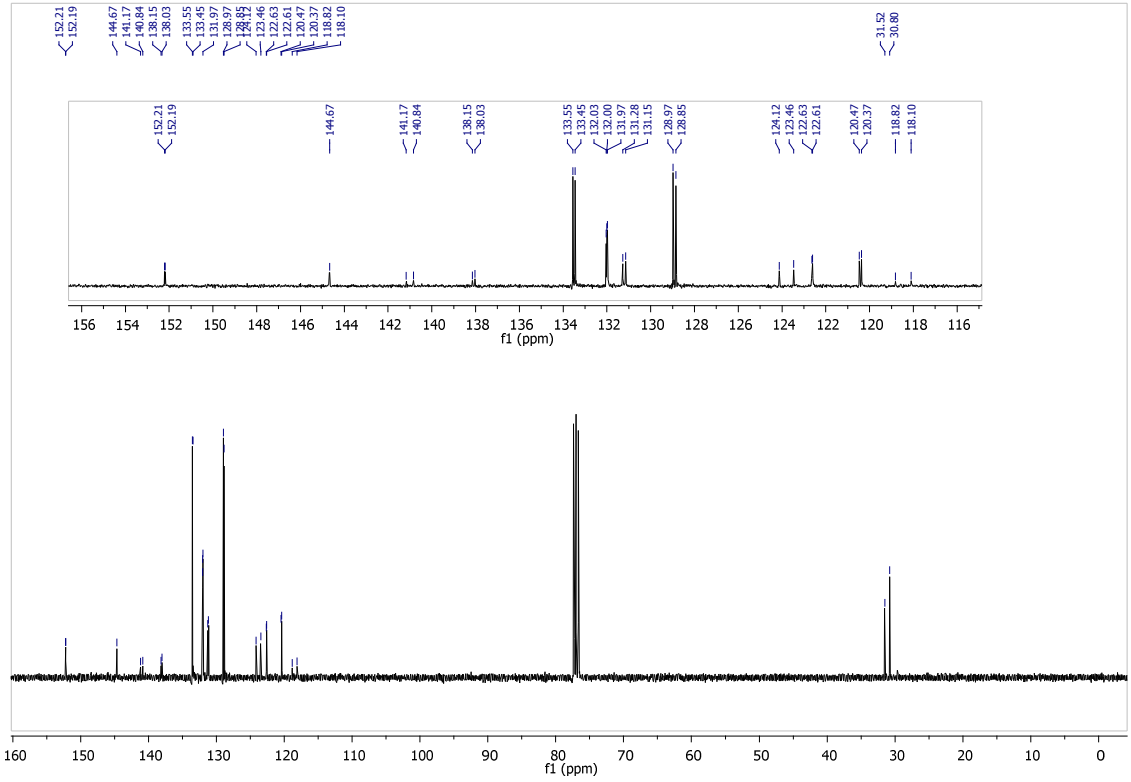

Figure S2. ^{13}C{^{1}H}-NMR of **1** ($CDCl_3$).

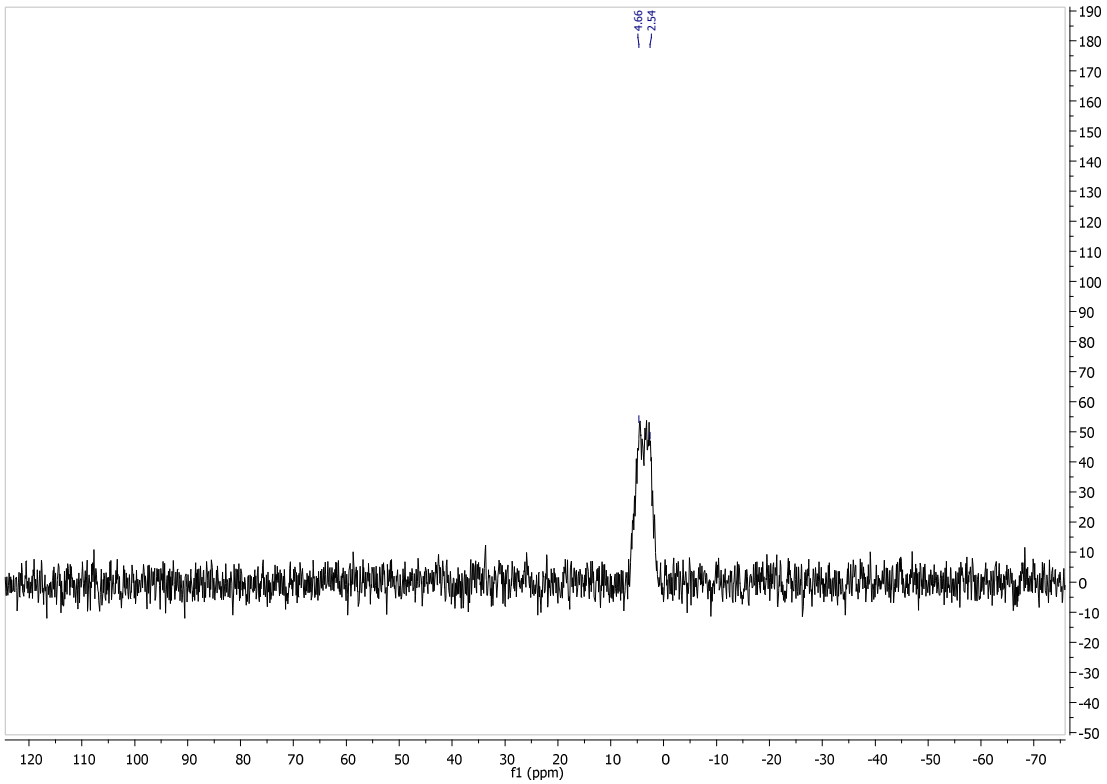

Figure S3. $^{31}P\{^{1}H\}$-NMR of **1** ($CDCl_3$).

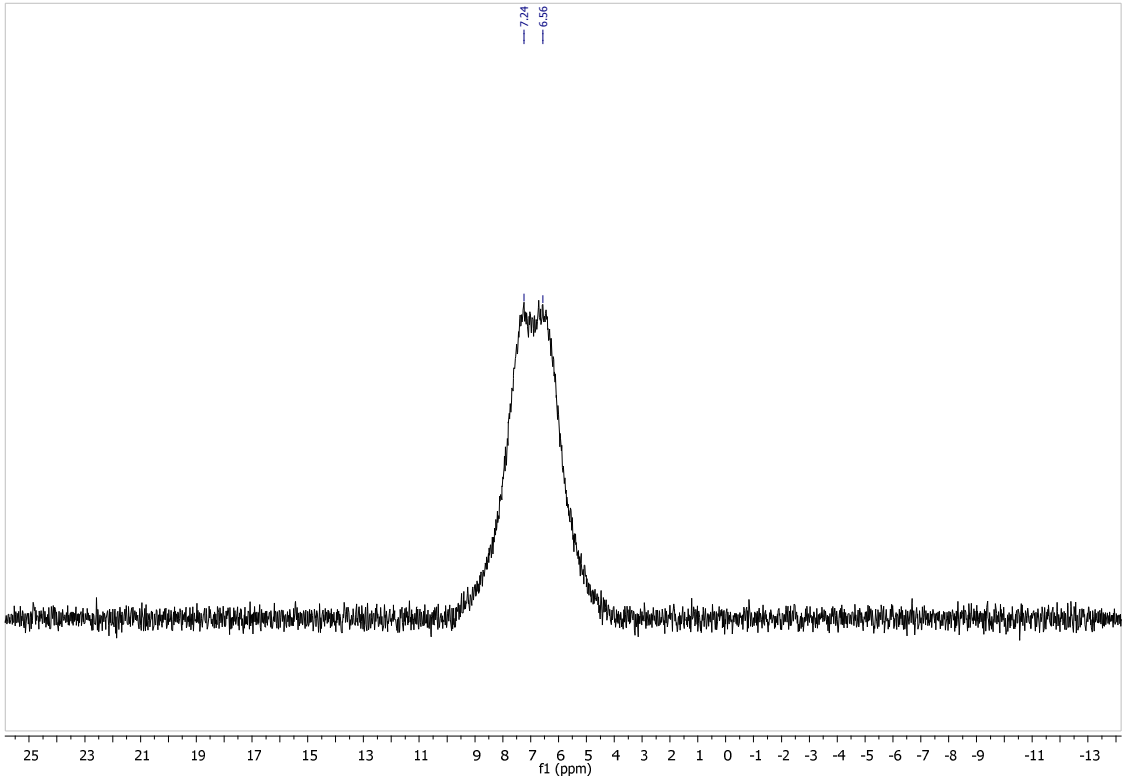

Figure S4. $^{11}B\{^{1}H\}$-NMR of **1** ($CDCl_3$).

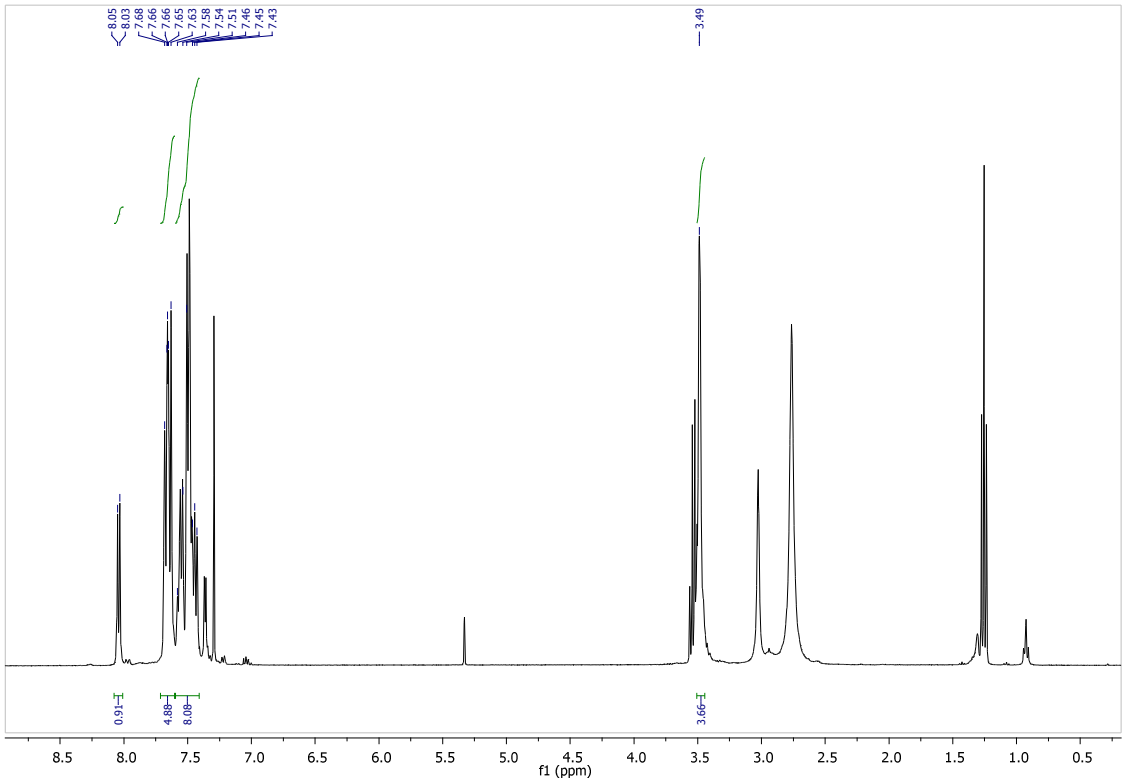

Figure S5. ^{1}H-NMR of **2** ($CDCl_3$).

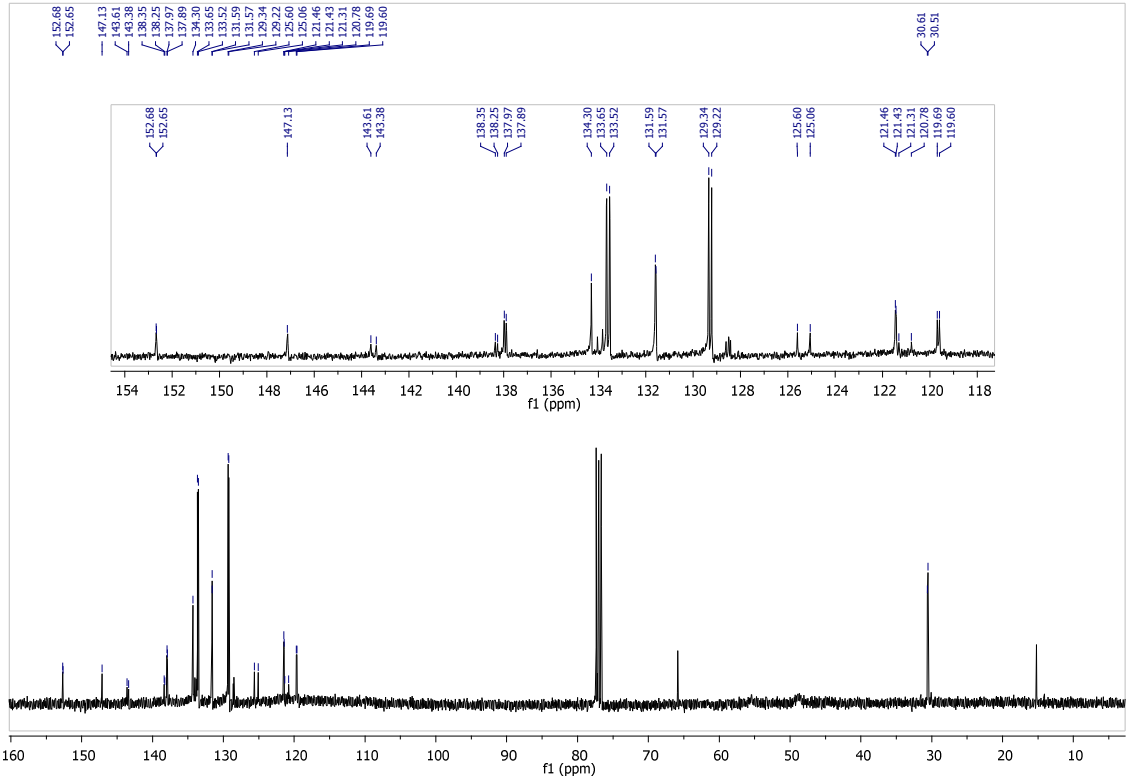

Figure S6. ^{13}C{^{1}H}-NMR of **2** ($CDCl_3$).

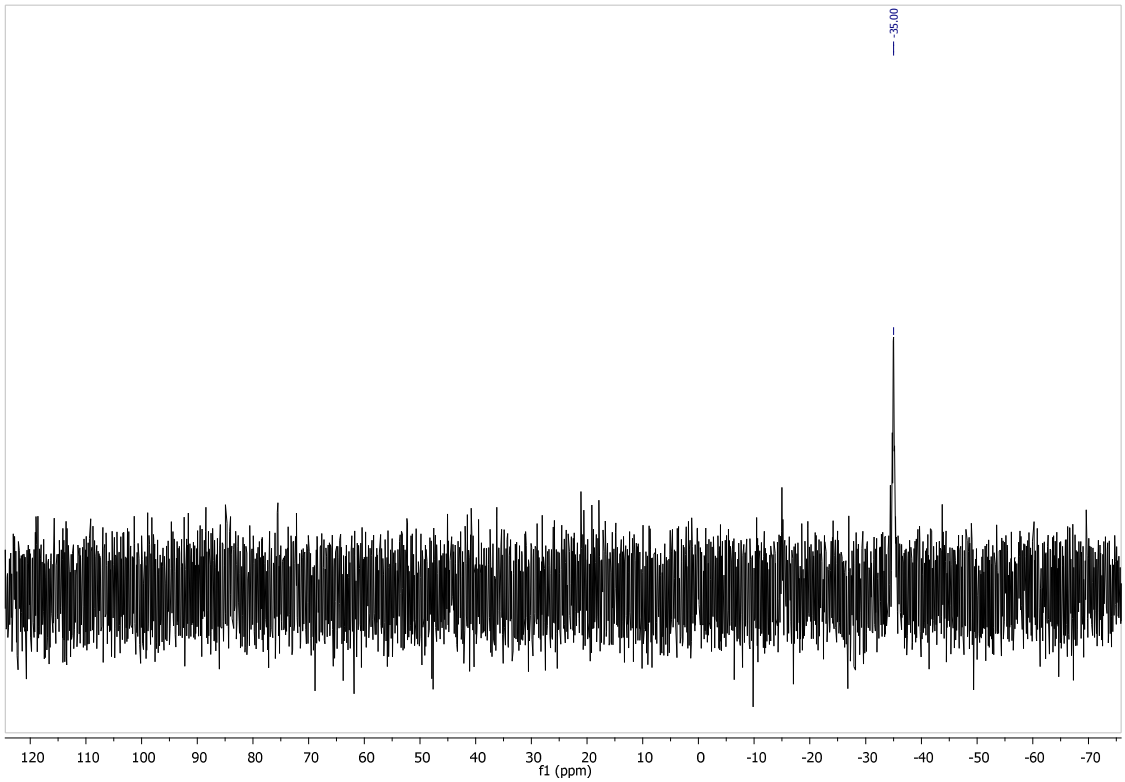

Figure S7. $^{31}P\{^{1}H\}$-NMR of **2** ($CDCl_3$).

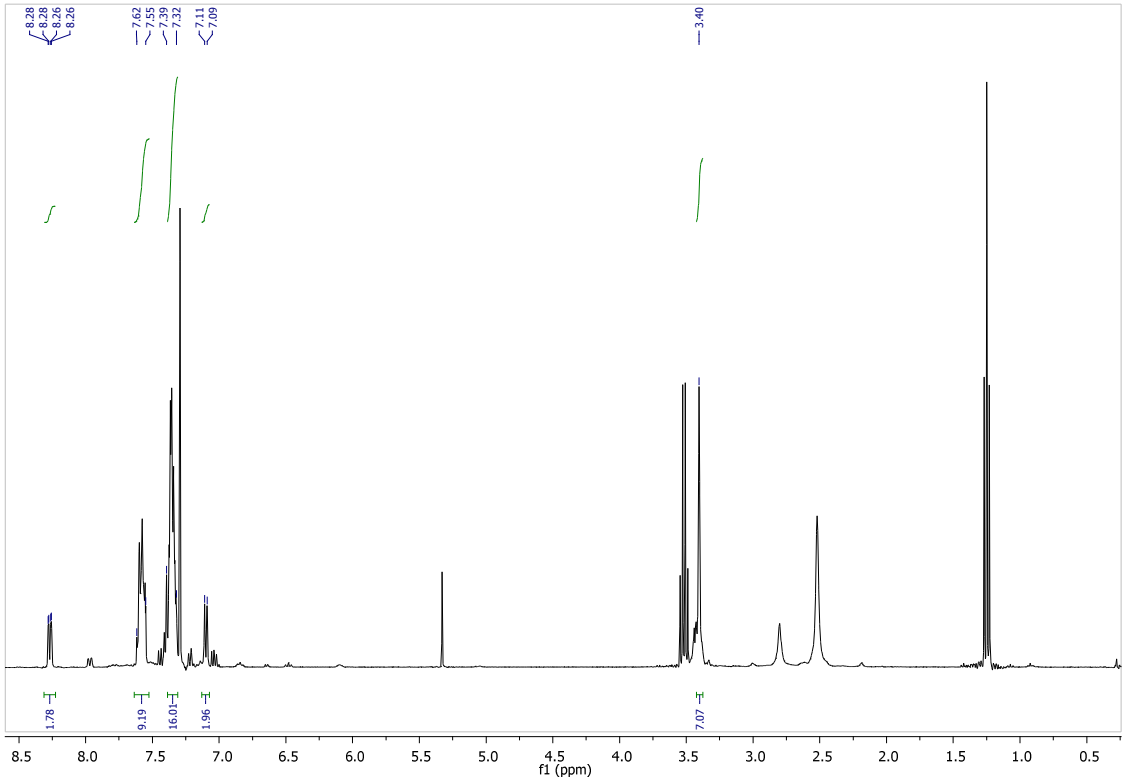

Figure S8. ^{1}H-NMR of **2a** ($CDCl_3$).

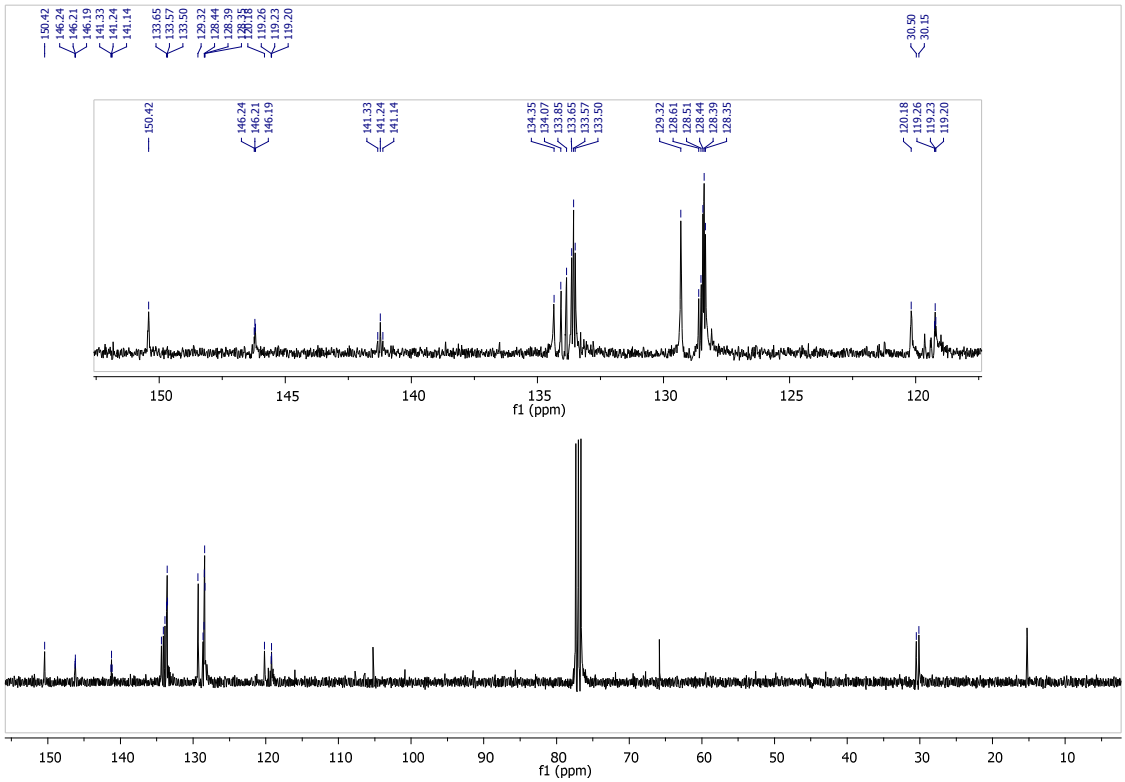

Figure S9. $^{13}C\{^{1}H\}$-NMR of **2a** ($CDCl_3$).

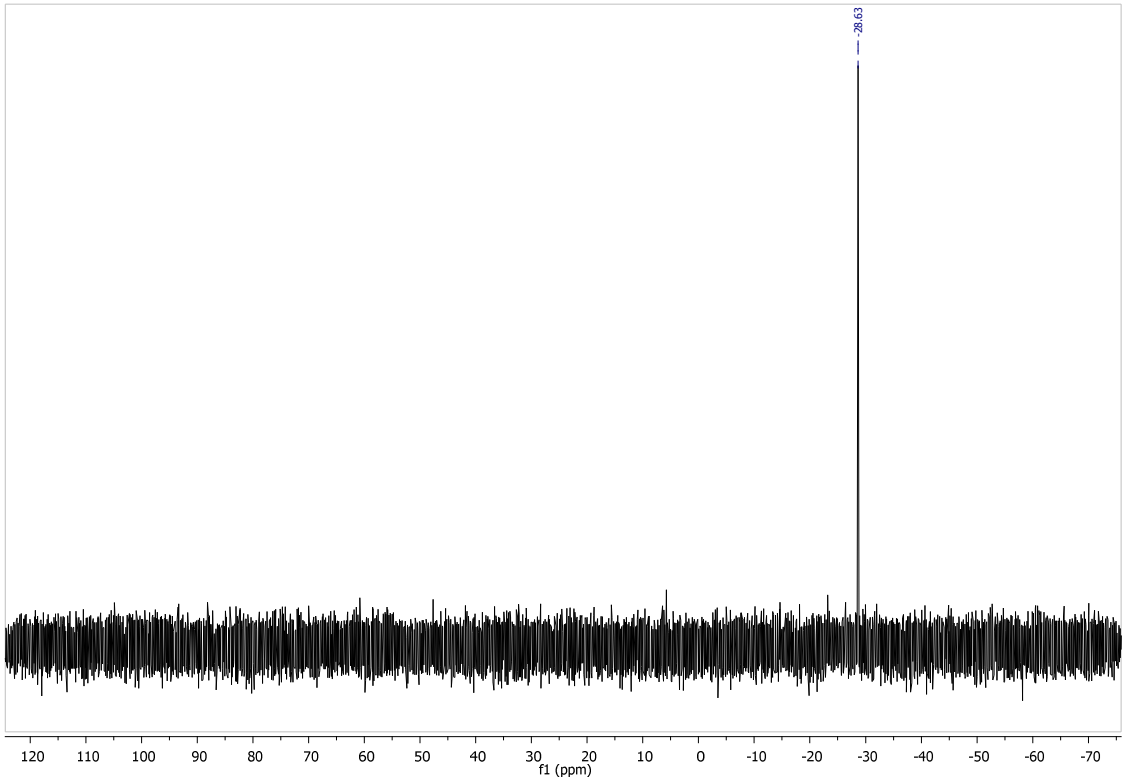

Figure S10. $^{31}P\{^{1}H\}$-NMR of **2a** ($CDCl_3$).

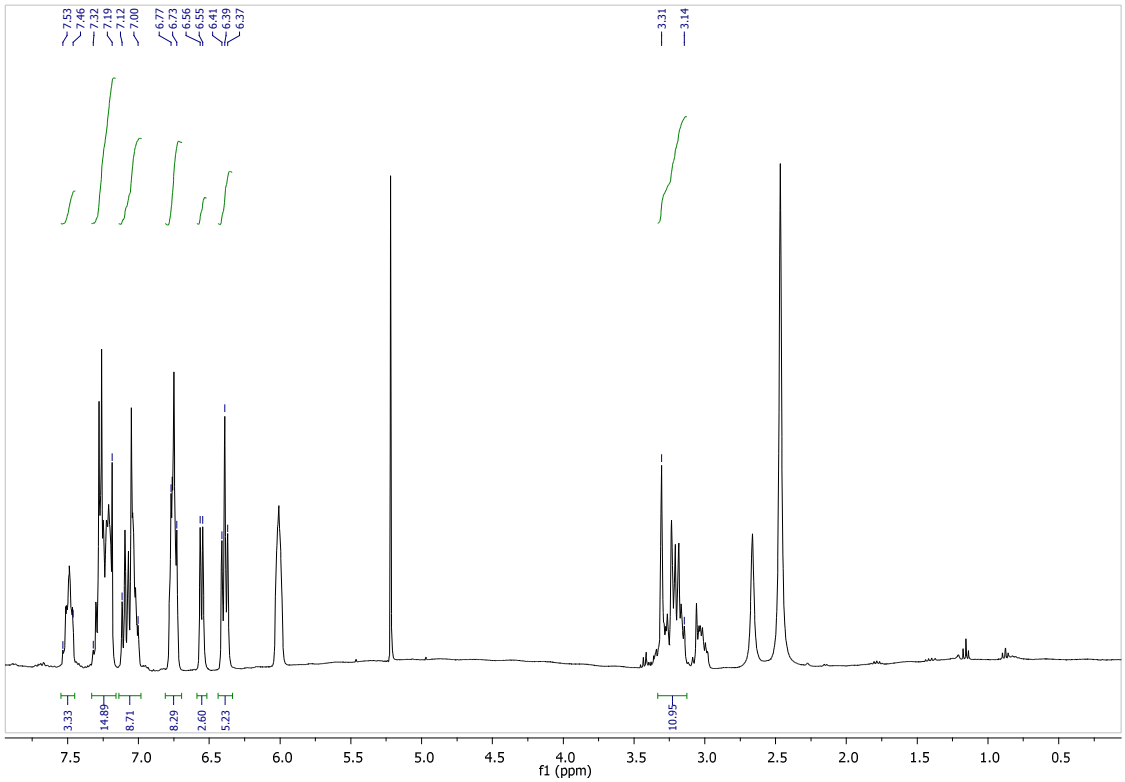

Figure S11. ^{1}H-NMR of **2b** ($CDCl_3$).

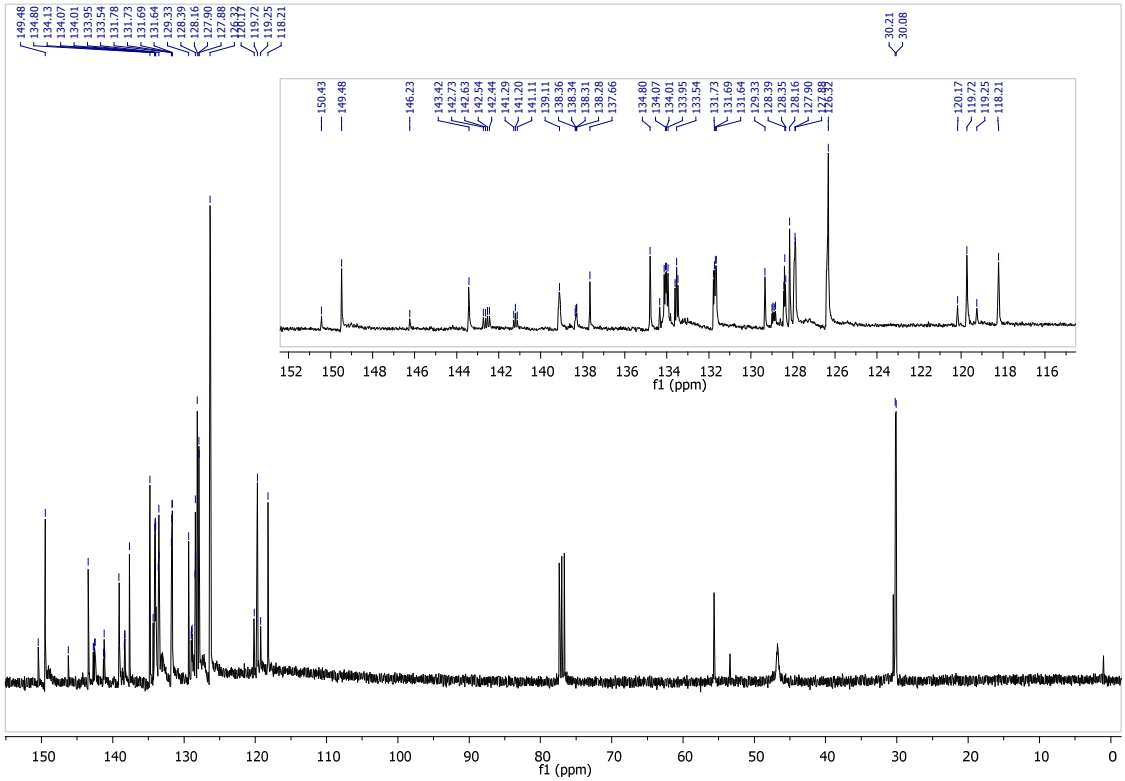

Figure S12. ^{13}C{^{1}H}-NMR of **2b** ($CDCl_3$).

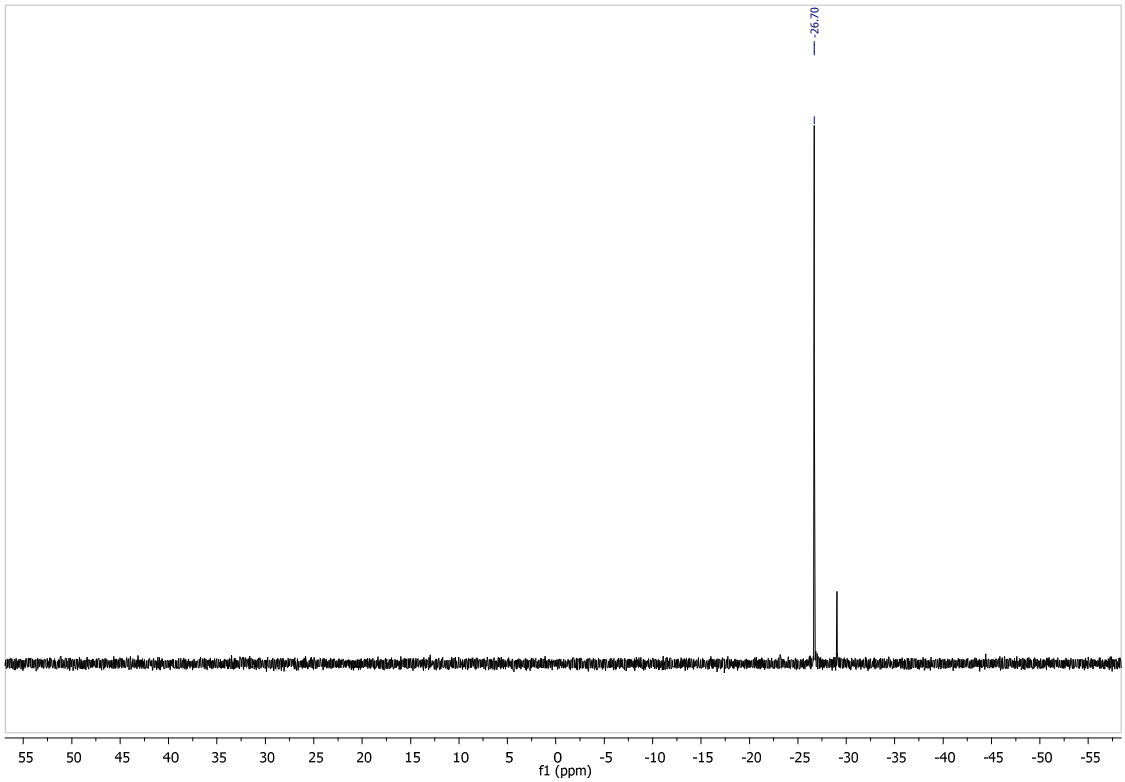

Figure S13. $^{31}P\{^{1}H\}$-NMR of **2b** ($CDCl_3$).

NMR Spectra of $RGaCl_2$ (3)

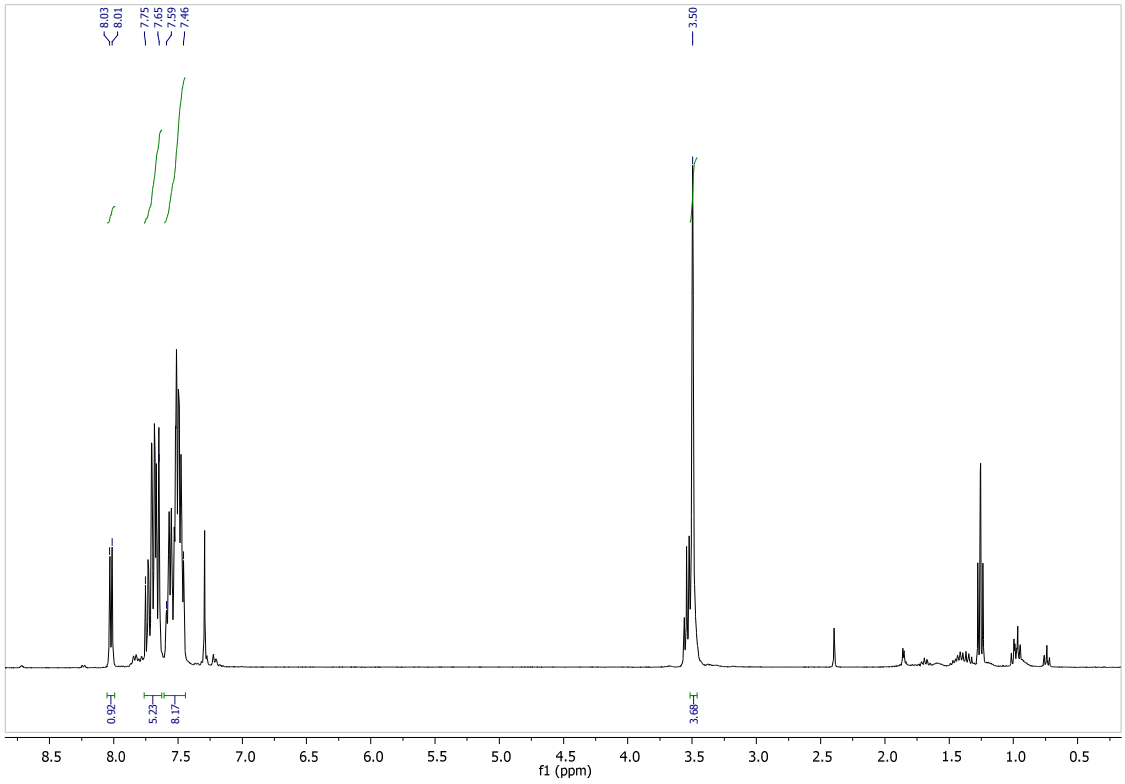

Figure S14. ^{1}H-NMR of **3** ($CDCl_3$).

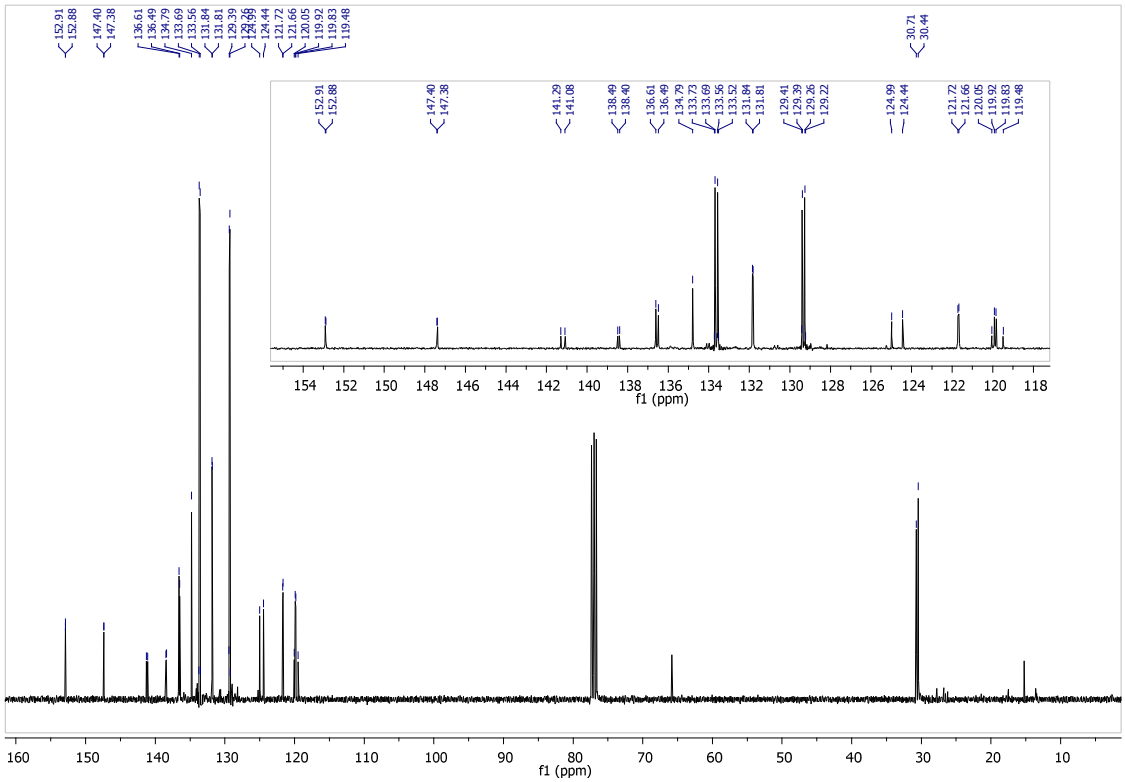

Figure S15. $^{13}C\{^{1}H\}$-NMR of **3** ($CDCl_3$).

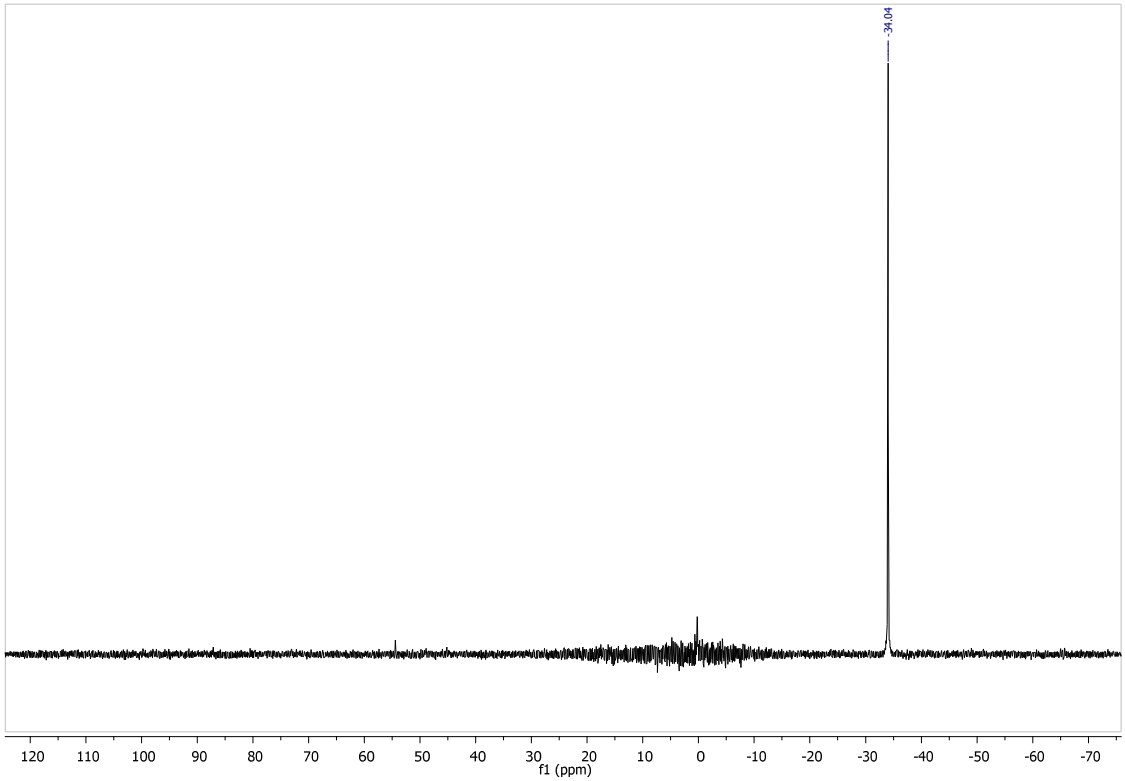

Figure S16. $^{31}P\{^{1}H\}$-NMR of **3** ($CDCl_3$).

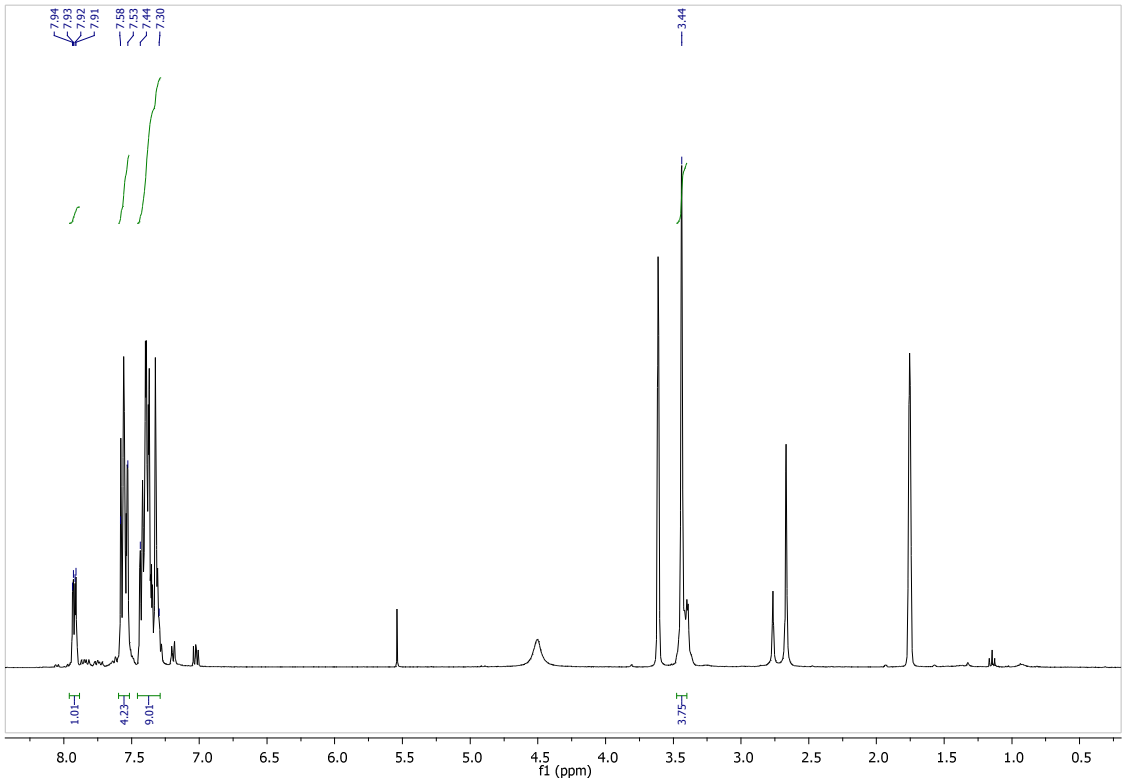

Figure S17. ^{1}H-NMR of **4** (d_8-THF).

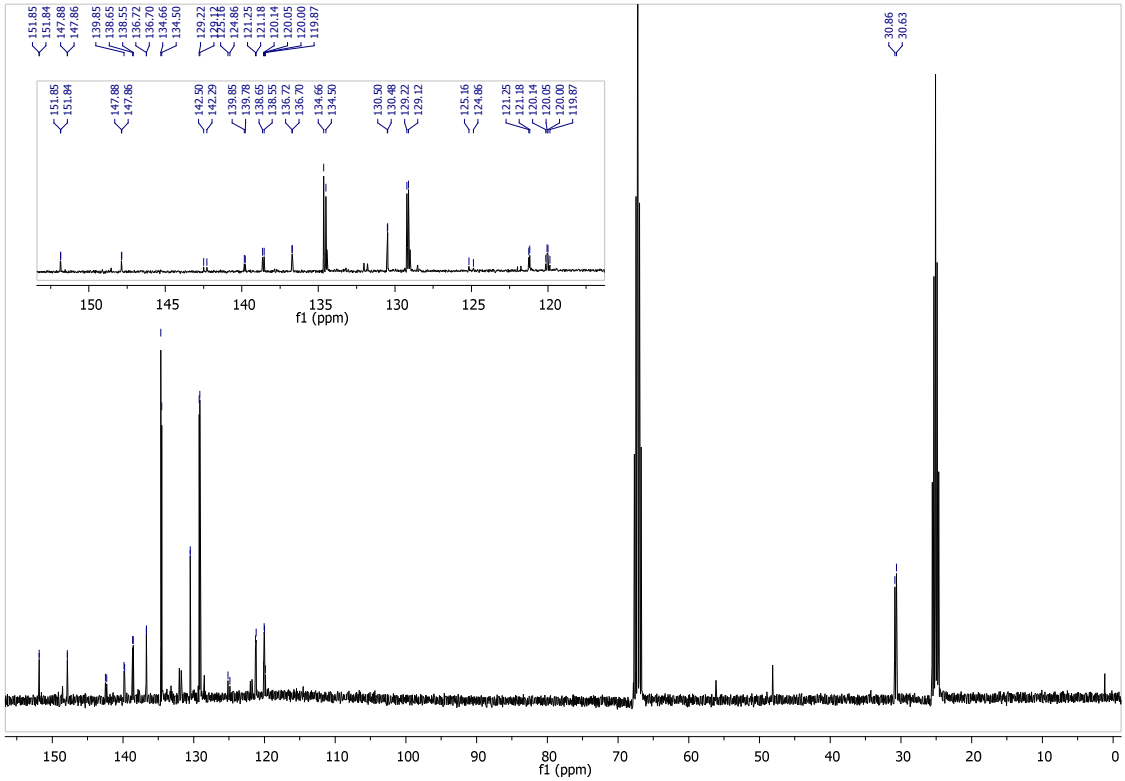

Figure S18. ^{13}C{^{1}H}-NMR of **4** (d_8-THF).

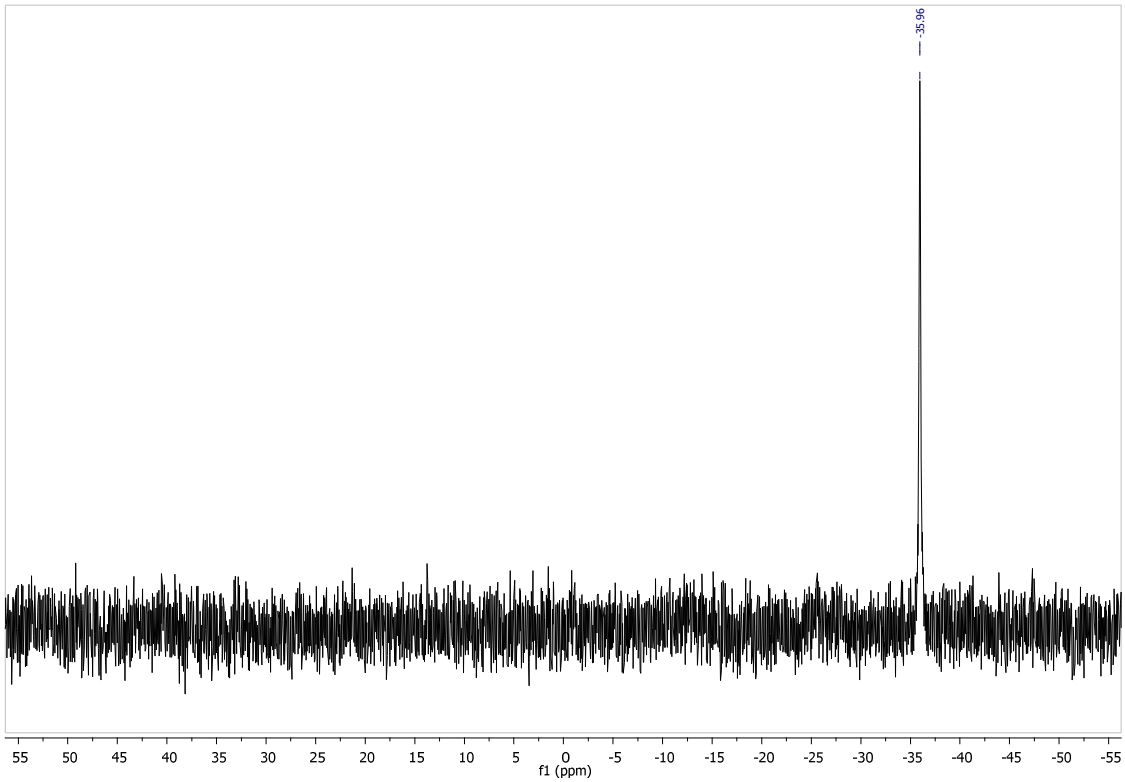

Figure S19. $^{31}P\{^{1}H\}$-NMR of **4** (d_8-THF).

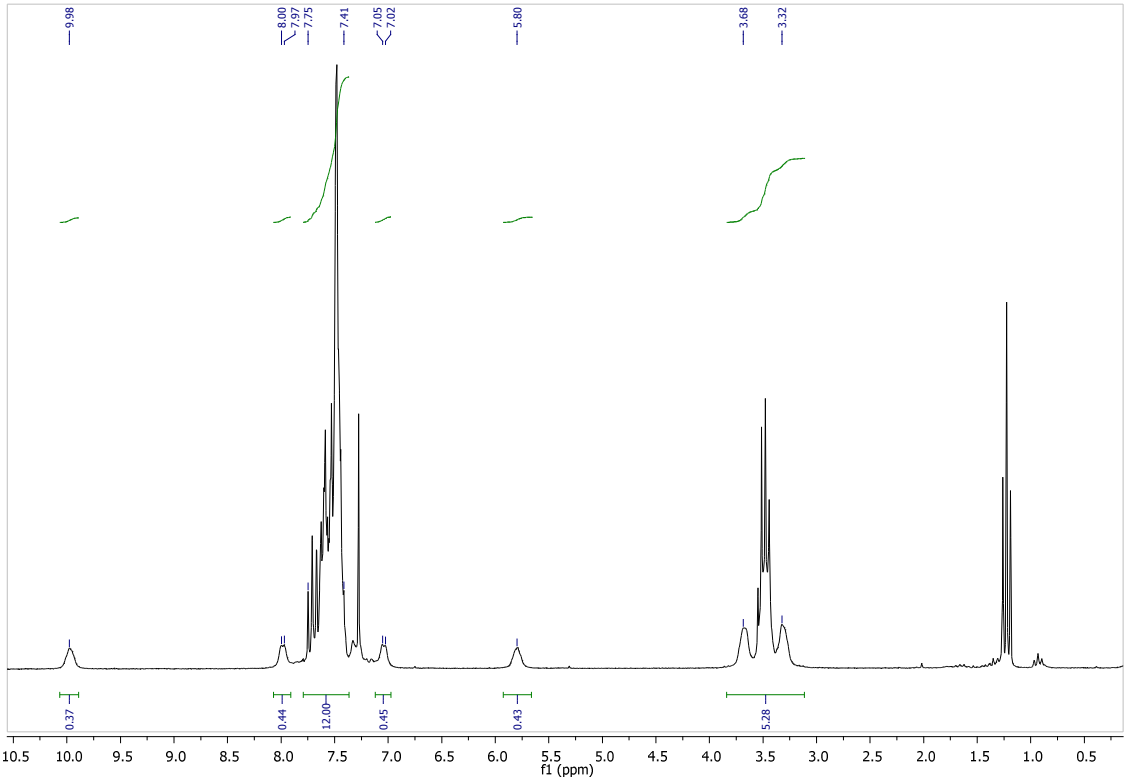

Figure S20. ^{1}H-NMR of **5** ($CDCl_3$).

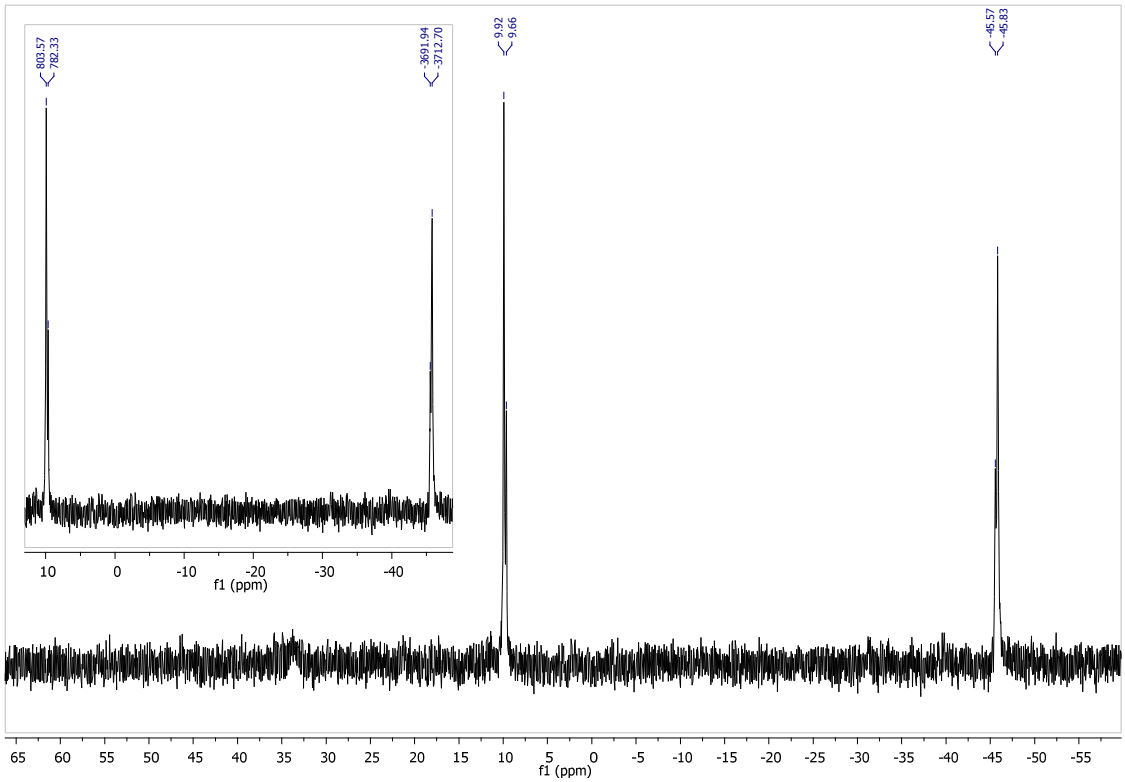

Figure S21. $^{31}P\{^{1}H\}$-NMR of **5** ($CDCl_3$).

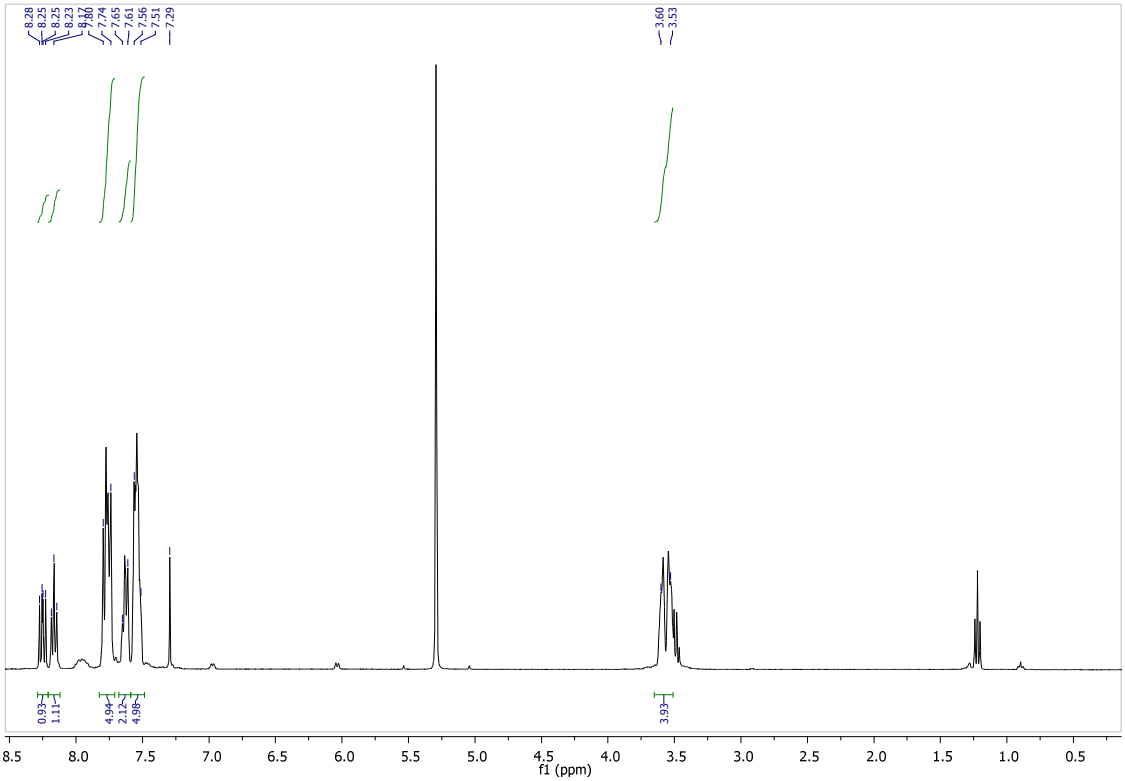

Figure S22. ^{1}H-NMR of **6** ($CDCl_3$).

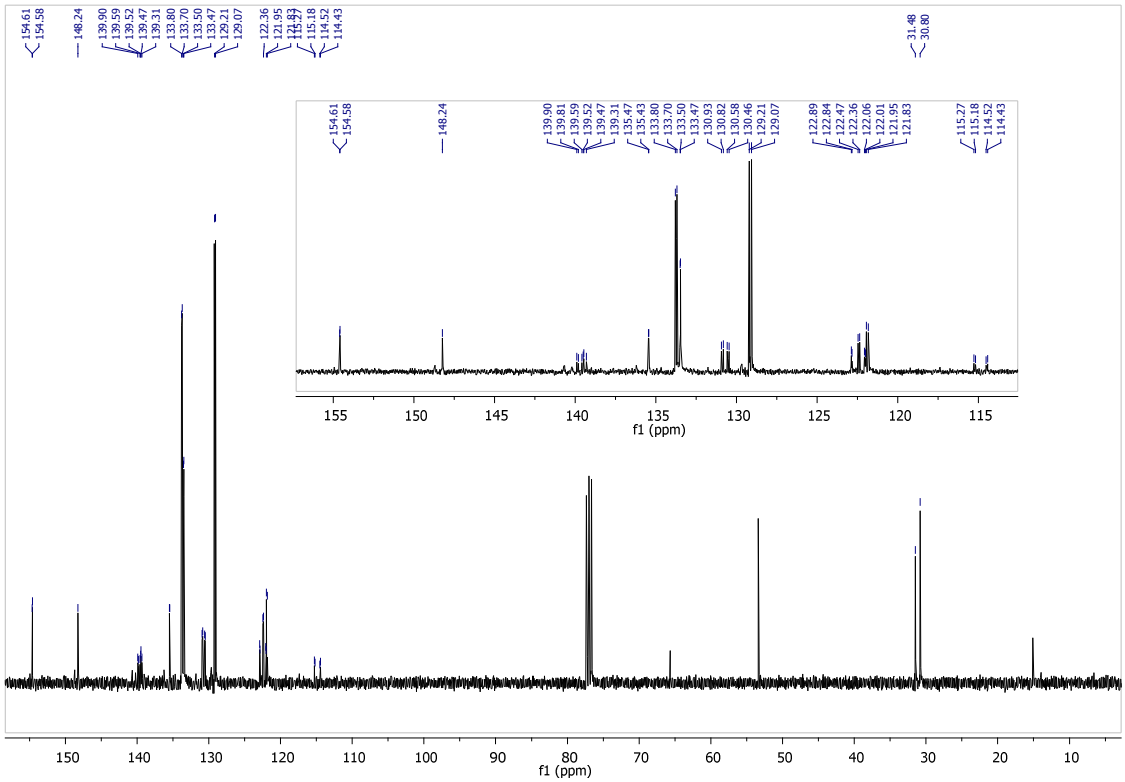

Figure S23. $^{13}C\{^{1}H\}$-NMR of **6** ($CDCl_3$).

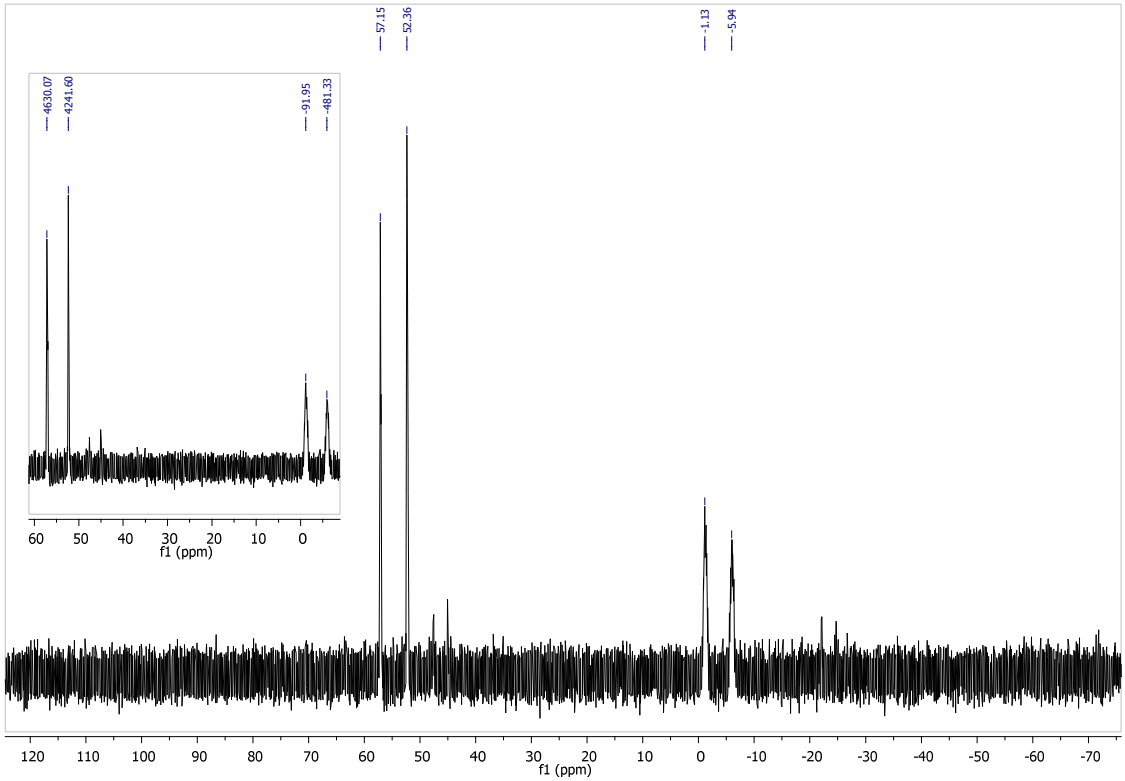

Figure S24. $^{31}P\{^{1}H\}$-NMR of **6** ($CDCl_3$).

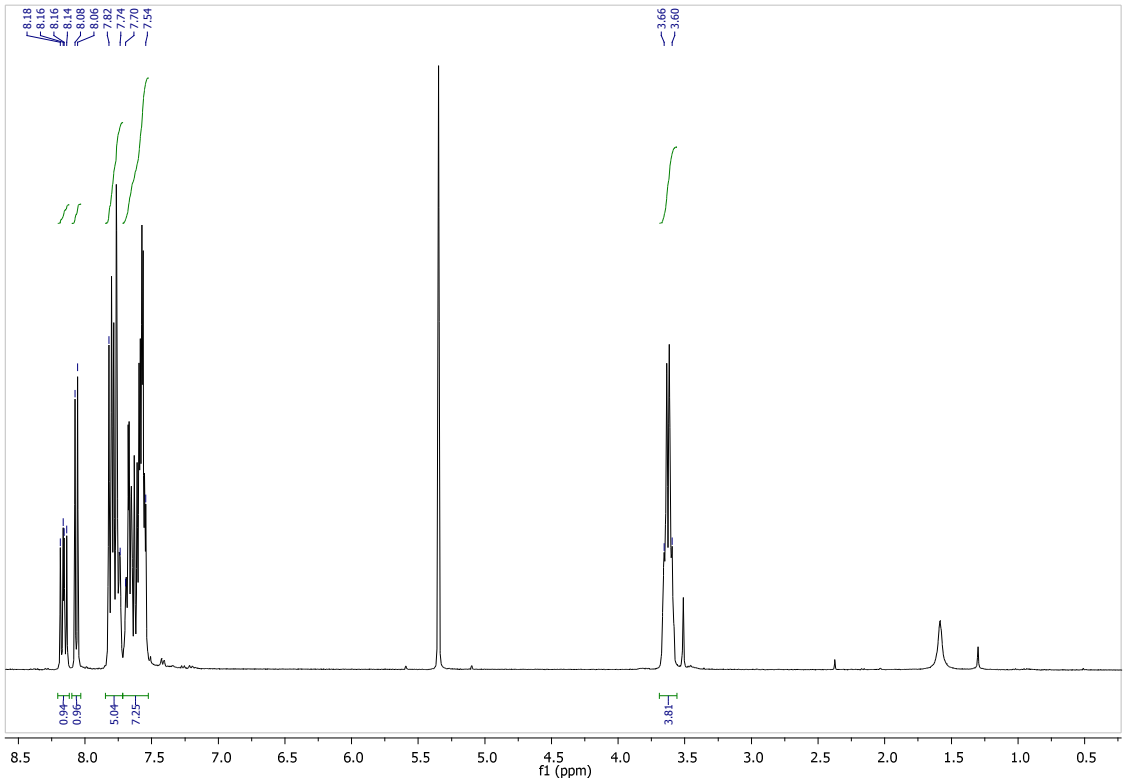

Figure S25. ^{1}H-NMR of **7** (CD_2Cl_2).

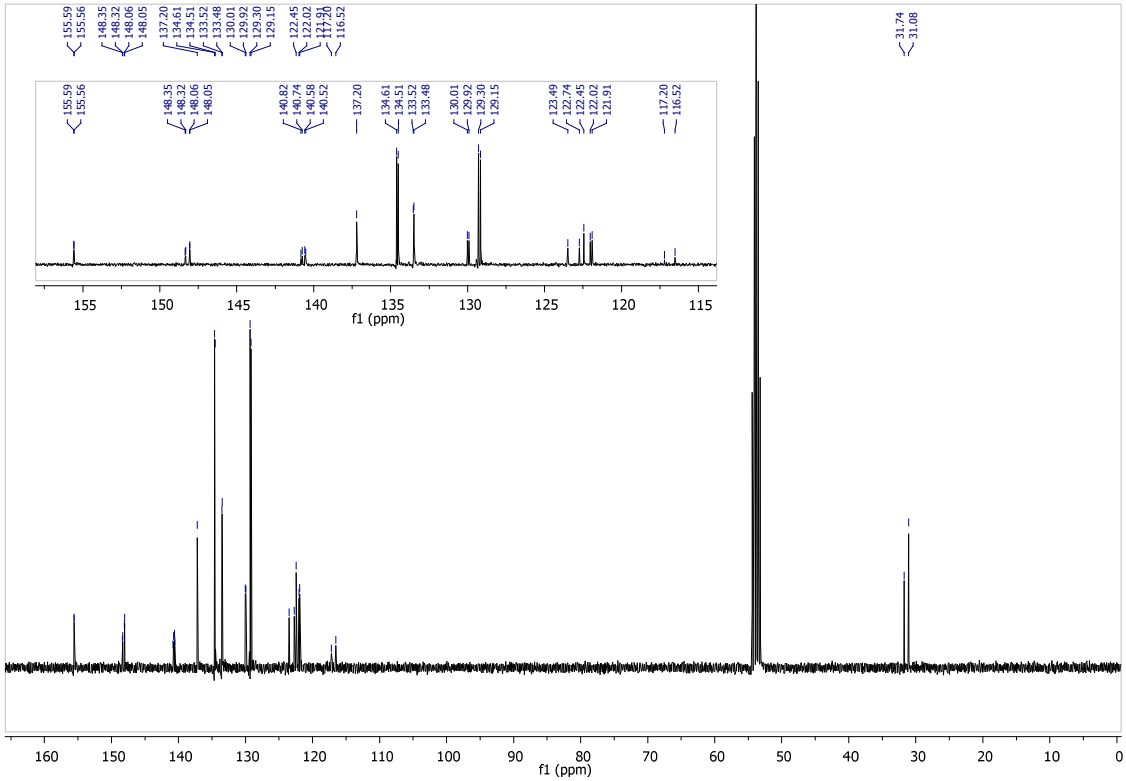

Figure S26. ^{13}C{^{1}H}-NMR of **7** (CD_2Cl_2).

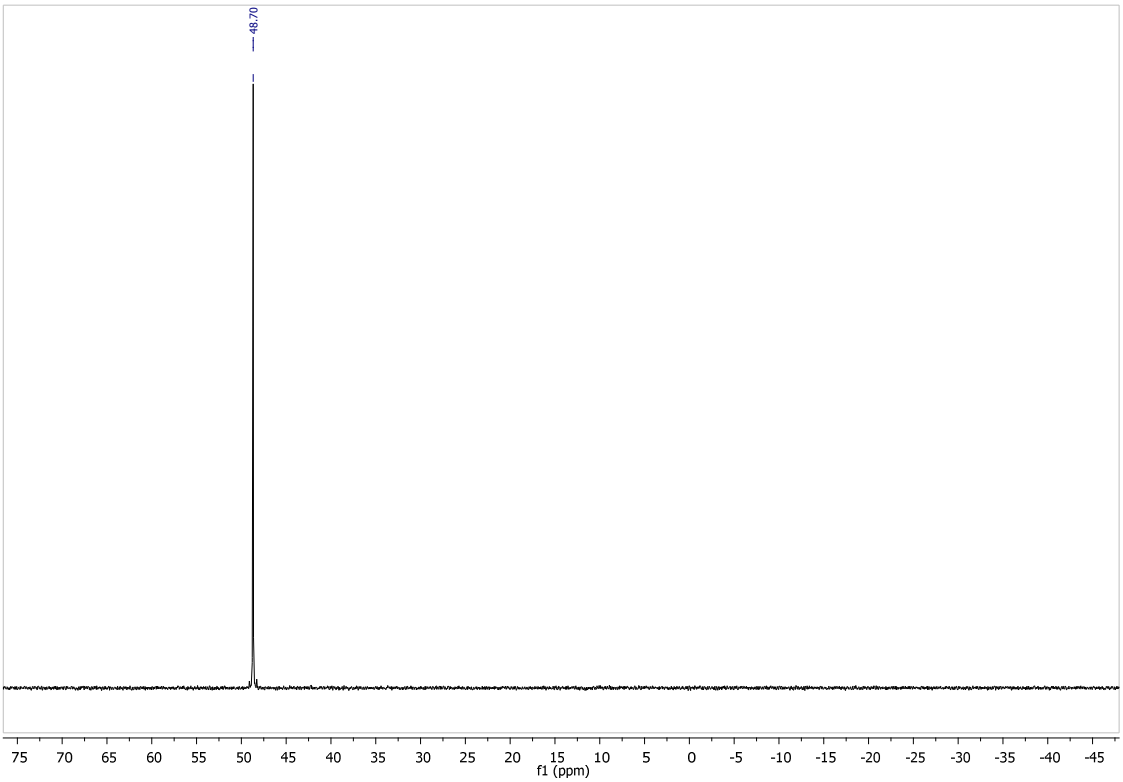

Figure S27. $^{31}P\{^{1}H\}$-NMR of **7** (CD_2Cl_2).

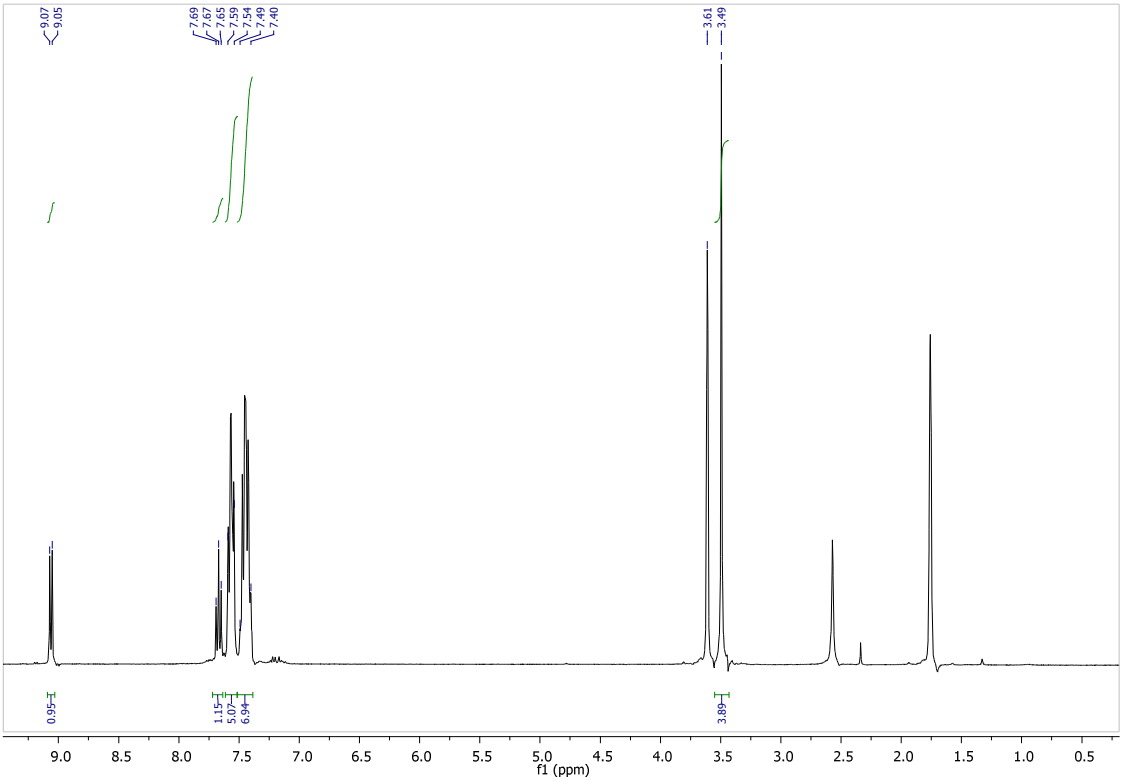

Figure S28. ^{1}H-NMR of **8** (d_8-THF).

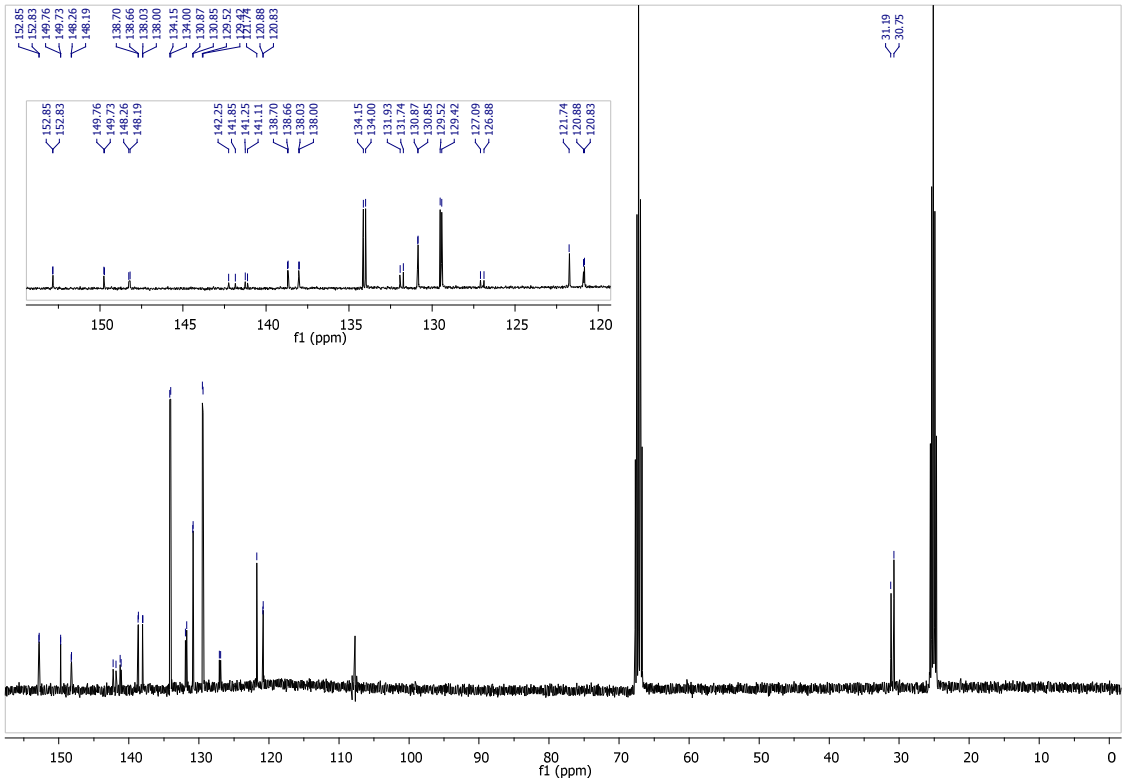

Figure S29. $^{13}C\{^{1}H\}$-NMR of **8** (d_8-THF).

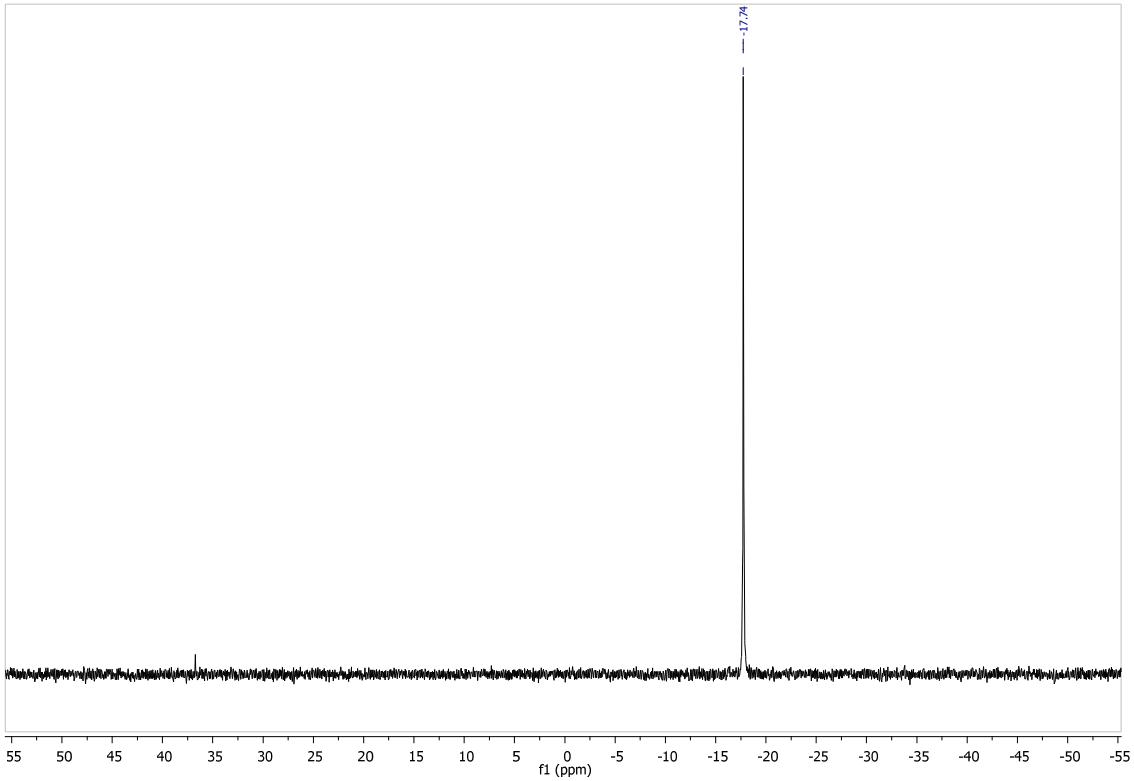

Figure S30. $^{31}P\{^{1}H\}$-NMR of **8** (d_8-THF).

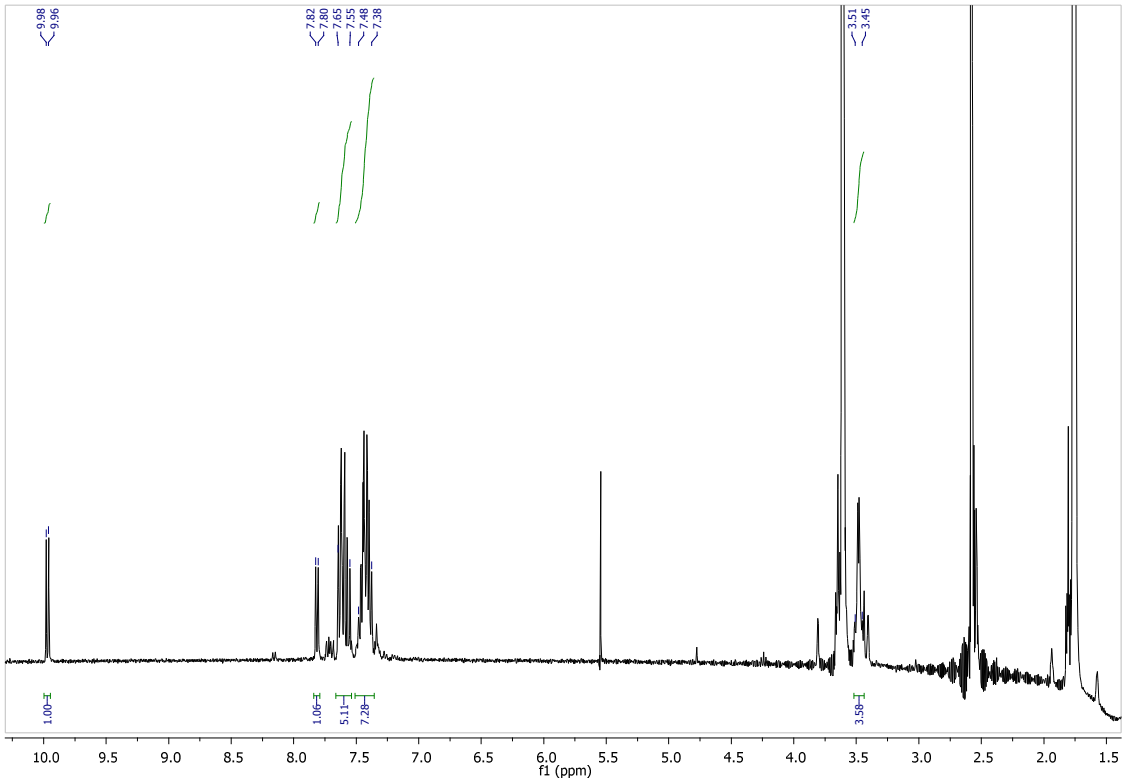

Figure S31. ^{1}H-NMR of **9** (d_8-THF).

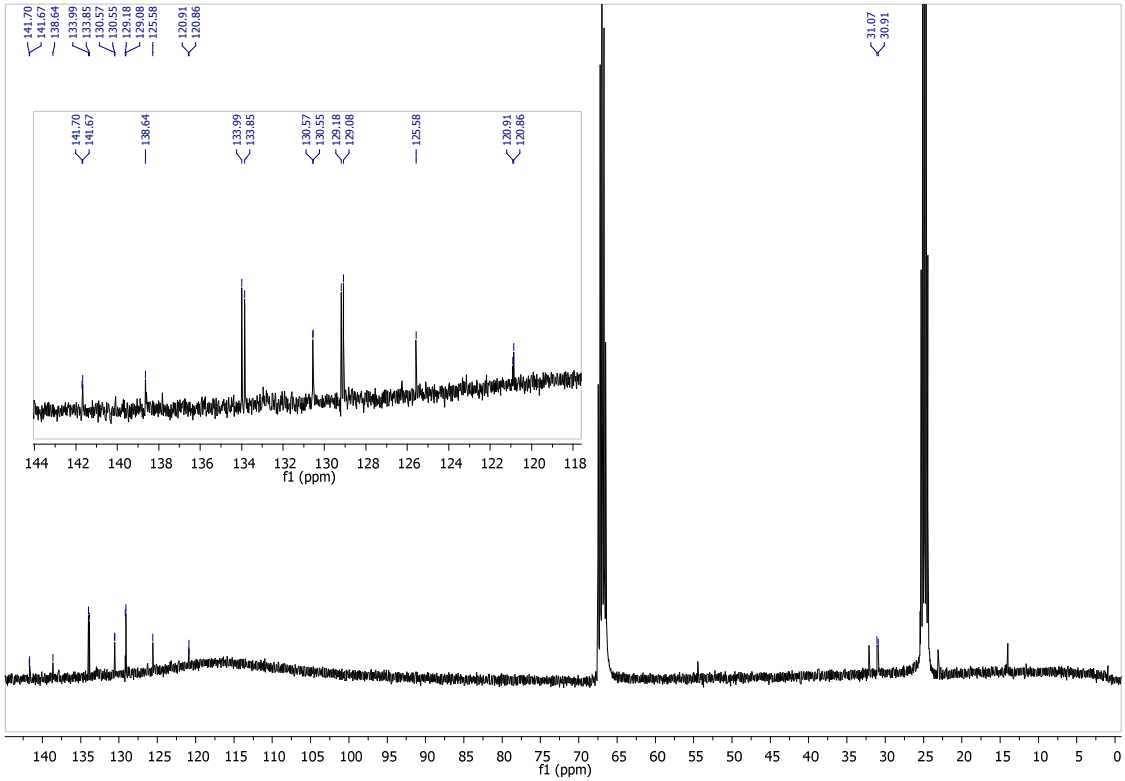

Figure S32. ^{13}C{^{1}H}-NMR of **9** (d_8-THF).

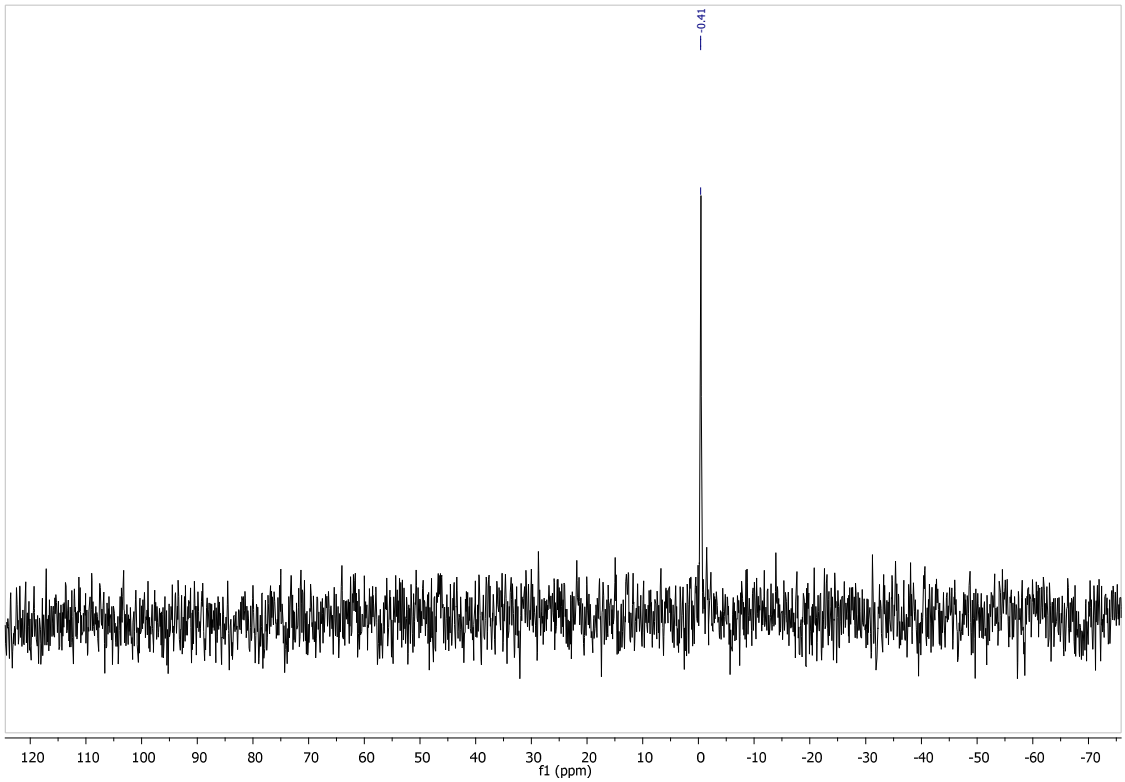

Figure S33. $^{31}P\{^{1}H\}$-NMR of **9** (d_8-THF).

Synthesis of (6-(diphenylphosphino)acenaphth-5-yl)dibutylstannyl chloride [6-(Ph_2P)-5-Ace]$SnBu_2Cl$. *n*-Butyllithium (1.20 mmol, 2.5 M in *n*-hexane) and N,N,N′,N′-tetramethyl-ethylenediamine (0.14 g, 1.20 mmol) were added at –78°C to a suspension of 5-bromo-6-diphenylphosphinoacenaphthene (0.50 g, 1.20 mmol) in diethyl ether (5 ml) and stirred for 2 h at this temperature. The suspension was allowed to warm up to r.t., stirred for 1 h and dibutyltin dichloride (0.36 g, 1.20 mmol) was added. The reaction mixture was stirred at r.t. overnight. After aqueous workup the organic solvent was removed by rotary evaporation yielding [6-(Ph_2P)-5-Ace]$SnBu_2Cl$ as yellowish oil (0.52 g, 0.86 mmol, 72%).

^{1}H-NMR ($CDCl_3$): δ = 8.71 (d, $^3J(^1H\text{-}^1H)$ = 7.0 Hz, $^3J(^{119/117}Sn\text{-}^1H)$ = 64.6 Hz, 1H, H-4), 7.55-7.27 (m, 13H), 3.47 (m, 4H, H-1,2), 1.71-1.37 (m, 8H, CH_2-*β/γ*), 1.19-1.08 (m, 4H, CH_2-*α*), 0.71 ppm (t, $^3J(^1H\text{-}^1H)$ = 7.2 Hz, 6H, CH_3). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ = 151.5 (s, C_c or C_d), 148.0 (s, C_d or C_c), 142.2 (d, $^2J(^{31}P\text{-}^{13}C)$ = 30.0 Hz, C_a), 140.6 (d, $^2J(^{31}P\text{-}^{13}C)$ = 5.6 Hz, C_7), 137.2 (s, C_4), 132.5 (d, $^2J(^{31}P\text{-}^{13}C)$ = 14.2 Hz, C_o), 129.5 (s, C_p), 128.8 (d, $^3J(^{31}P\text{-}^{13}C)$ = 8.0, C_m), 124.8 (d, $^1J(^{31}P\text{-}^{13}C)$ = 17.0 Hz, C_i or C_6), 121.1 (d, $^5J(^{31}P\text{-}^{13}C)$ = 2.5 Hz, $^3J(^{119/117}Sn\text{-}^{13}C)$ = 60.8 Hz,C_3), 119.8 (d, $^3J(^{31}P\text{-}^{13}C)$ = 4.0 Hz, C_8), 30.5 (s, C_1 or C_2), 30.4 (s, C_2 or C_1), 28.5 (s, $^2J(^{119/117}Sn\text{-}^{13}C)$ = 32.6 Hz, C_β), 26.6 (s, $^3J(^{119/117}Sn\text{-}^{13}C)$ = 106.9/101.0 Hz, C_γ), 22.5 (d, $J(^{31}P\text{-}^{13}C)$ = 24.6 Hz, $^1J(^{119/117}Sn\text{-}^{13}C)$ = 525.5 Hz, C_α), 13.4 ppm (s, CH_3). **^{31}P{^{1}H}-NMR ($CDCl_3$):** δ = –30.6 ppm (s, $J(^{119/117}Sn\text{-}^{31}P)$ = 580.6/554.8 Hz). **^{119}Sn{^{1}H}-NMR ($CDCl_3$):** δ = –84.5 ppm (d, $J(^{31}P\text{-}^{119}Sn)$ = 583.7 Hz).

Table S1. Crystal data and structure refinement of **1** - **8**.

	1·CH_2Cl_2	**2**	**3**
Formula	$C_{25}H_{20}BCl_4P$	$C_{24}H_{18}AlCl_2P$	$C_{24}H_{18}Cl_2GaP$
Formula weight, g mol^{-1}	503.99	435.23	477.97
Crystal system	monoclinic	triclinic	triclinic
Crystal size, mm	0.8 × 0.6 × 0.4	0.2 × 0.2 × 0.1	0.6 × 0.4 × 0.2
Space group	$P2_1/n$	P-1	P-1
a, Å	10.188(1)	8.5571(2)	8.585(2)
b, Å	15.934(2)	9.5960(3)	9.585(2)
c, Å	14.790(1)	14.2689(4)	14.360(3)
α, °	90	98.927(2)	99.31(2)
β, °	97.96(1)	97.929(2)	97.45(2)
γ, °	90	111.229(1)	111.18(2)
V, $Å^3$	2377.8(4)	1054.69(5)	1064.3(4)
Z	4	2	2
ρ_{calcd}, Mg m^{-3}	1.408	1.370	1.491
μ (Mo $K\alpha$), mm^{-1}	0.577	0.433	1.626
F(000)	1032	448	484
θ range, deg	2.56 to 27.52	0.985 to 35.06	2.71 to 25.00
Index ranges	$-9 \le h \le 13$	$-13 \le h \le 13$	$-10 \le h \le 10$
	$-20 \le h \le 20$	$-15 \le h \le 15$	$-11 \le h \le 11$
	$-19 \le h \le 19$	$-23 \le h \le 23$	$0 \le h \le 7$
No. of reflns collected	12719	48401	3711
Completeness to θ_{max}	99.9%	98.5%	99.2%
No. indep. Reflns	5473	9200	3711
No. obsd reflns with ($I>2\sigma(I)$)	4370	6750	2807
No. refined params	288	253	253
GooF (F^2)	1.034	1.021	1.002
R_1 (F) ($I > 2\sigma(I)$)	0.0405	0.0419	0.0502
wR_2 (F^2) (all data)	0.1091	0.1051	0.1255
Largest diff peak/hole, e $Å^{-3}$	0.370 / –0.521	0.673 / –0.403	0.672 / –0.746
CCDC number	1027170	1027171	1027174

Table S1. cont.

	4	**5**·toluene
Formula	$C_{24}H_{18}Cl_2InP$	$C_{31}H_{26}Cl_2PTl$
Formula weight, g mol^{-1}	523.07	704.76
Crystal system	monoclinic	monoclinic
Crystal size, mm	0.2 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Space group	$P2_1/n$	$P2_1/c$
a, Å	10.3718(4)	11.3829(3)
b, Å	15.6718(5)	19.2451(6)
c, Å	13.5877(5)	12.1133(4)
α, °	90	90
β, °	101.9000(10)	94.8590(10)
γ, °	90	90
V, Å^3	2161.14(13)	2644.06(14)
Z	4	4
ρ_{calcd}, Mg m^{-3}	1.608	1.770
μ (Mo $K\alpha$), mm^{-1}	1.422	6.390
F(000)	1040	1368
θ range, deg	2.39 to 30.05	2.58 to 36.41
Index ranges	–14 ≤ h ≤ 14	–18 ≤ h ≤ 18
	–21 ≤ h ≤ 22	0 ≤ h ≤ 32
	–19 ≤ h ≤ 19	0 ≤ h ≤ 20
No. of reflns collected	103271	12859
Completeness to θ_{max}	99.8%	99.7%
No. indep. Reflns	6324	12859
No. obsd reflns with ($I>2\sigma(I)$)	5381	11333
No. refined params	253	312
GooF (F^2)	1.094	1.118
R_1 (F) ($I > 2\sigma(I)$)	0.0262	0.0370
wR_2 (F^2) (all data)	0.0581	0.0820
Largest diff peak/hole, e Å^{-3}	0.891 / –0.477	1.797 / –1.935
CCDC number	1027175	1027176

Table S1. cont.

	6·CH_2Cl_2	**7**	**8**
Formula	$C_{25}H_{20}Cl_4P_2$	$C_{24}H_{18}AsCl_2P$	$C_{24}H_{18}Cl_2PSb$
Formula weight, g mol^{-1}	524.15	483.17	530.00
Crystal system	monoclinic	monoclinic	monoclinic
Crystal size, mm	0.4 × 0.4 × 0.3	0.1 × 0.1 × 0.1	0.8 × 0.6 × 0.4
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	10.149(2)	10.063(1)	12.497(3)
b, Å	17.806(4)	13.766(2)	9.194(3)
c, Å	14.673(3)	14.613(2)	19.193(4)
α, °	90	90	90
β, °	102.06(3)	91.380(4)	106.22(1)
γ, °	90	90	90
V, $Å^3$	2593.0(9)	2023.7(5)	2118(1)
Z	4	4	4
ρ_{calcd}, Mg m^{-3}	1.343	1.586	1.663
μ (Mo $K\alpha$), mm^{-1}	0.591	2.031	1.638
F(000)	1072	976	1048
θ range, deg	2.11 to 26.11	2.68 to 27.00	2.54 to 27.50
Index ranges	$-12 \le h \le 12$	$-11 \le h \le 11$	$-14 \le h \le 17$
	$0 \le h \le 21$	$-16 \le h \le 16$	$-20 \le h \le 14$
	$0 \le h \le 18$	$-17 \le h \le 16$	$-22 \le h \le 22$
No. of reflns collected	5052	19982	4823
Completeness to θ_{max}	97.7%	99.7%	99.1%
No. indep. Reflns	5052	3576	4823
No. obsd reflns with ($I>2\sigma(I)$)	4119	2458	4297
No. refined params	280	233	253
GooF (F^2)	1.098	1.101	1.092
R_1 (F) ($I > 2\sigma(I)$)	0.0409	0.0700	0.0304
wR_2 (F^2) (all data)	0.1355	0.1597	0.0729
Largest diff peak/hole, e $Å^{-3}$	0.473 / –0.538	1.270 / –0.605	0.843 / –0.624
CCDC number	1027177	1027178	1027179

Table S1. cont.

	9
Formula	$C_{24}H_{18}BiCl_2P$
Formula weight, g mol^{-1}	617.23
Crystal system	monoclinic
Crystal size, mm	0.1 × 0.1 × 0.1
Space group	$P2_1/n$
a, Å	10.3721(4)
b, Å	11.1934(4)
c, Å	18.9618(7)
α, °	90
β, °	103.955(1)
γ, °	90
V, Å^3	2136.5(1)
Z	4
ρ_{calcd}, Mg m^{-3}	1.919
μ (Mo $K\alpha$), mm^{-1}	8.585
F(000)	1176
θ range, deg	2.53 to 32.60
Index ranges	–15 ≤ h ≤ 15
	–16 ≤ h ≤ 16
	–28 ≤ h ≤ 28
No. of reflns collected	120385
Completeness to θ_{max}	99.8%
No. indep. Reflns	7785
No. obsd reflns with ($I>2\sigma(I)$)	6438
No. refined params	253
GooF (F^2)	1.127
R_1 (F) ($I > 2\sigma(I)$)	0.0313
wR_2 (F^2) (all data)	0.0551
Largest diff peak/hole, e Å^{-3}	1.440 / –1.107
CCDC number	1027180

Table S1. cont.

	2a	**2b**·2 CH_2Cl_2
Formula	$C_{48}H_{36}AlClP_2$	$C_{74}H_{58}AlCl_4P_3$
Formula weight, g mol^{-1}	737.14	1208.89
Crystal system	monoclinic	triclinic
Crystal size, mm	0.2 × 0.2 × 0.2	0.5 × 0.4 × 0.3
Space group	$P2_1/c$	P-1
a, Å	16.8250(5)	11.740(2)
b, Å	10.6263(3)	14.237(3)
c, Å	20.6240(7)	19.069(4)
α, °	90	89.79(3)
β, °	96.717(1)	78.96(3)
γ, °	90	86.29(3)
V, $Å^3$	3662.0(2)	3122(1)
Z	4	2
ρ_{calcd}, Mg m^{-3}	1.337	1.286
μ (Mo $K\alpha$), mm^{-1}	0.251	0.324
F(000)	1536	1256
θ range, deg	2.42 to 27.14	2.19 to 26.00
Index ranges	$-21 \le h \le 21$	$-12 \le h \le 12$
	$-13 \le h \le 13$	$-22 \le h \le 22$
	$-26 \le h \le 26$	$-31 \le h \le 33$
No. of reflns collected	44772	41224
Completeness to θ_{max}	99.7%	91.1%
No. indep. Reflns	8100	11259
No. obsd reflns with ($I>2\sigma(I)$)	6880	8033
No. refined params	469	775
GooF (F^2)	1.129	1.012
R_1 (F) ($I > 2\sigma(I)$)	0.0414	0.0613
wR_2 (F^2) (all data)	0.1016	0.1879
Largest diff peak/hole, e $Å^{-3}$	0.421 / –0.374	0.548 / –0.623
CCDC number	1027172	1027173

Table S2. Selected bond parameters [Å, °] of **2a**.

	2a		**2a**
Bond Lengths and Angles		***Out-of-Plane Displacement****	
Al(1)-Cl(1)	2.1657(7)	P(1)	0.1461(4)
Al(1)-C(10)	2.006(3)	P(2)	0.1523(5)
Al(1)-C(40)	2.006(2)	Al(1)	0.3981(5)
C(10)-Al(1)-Cl(1)	113.95(6)	Al(1)	0.0786(5)
C(40)-Al(1)-Cl(1)	111.34(6)	***Central Acenaphthene Ring Torsion Angles***	
C(10)-Al(1)-C(40)	134.70(7)	C:(13)-(14)-(19)-(18)	–176.4(3)
peri Region Distances		C:(43)-(44)-(49)-(48)	–173.0(3)
P(1)···Al(1)	2.7405(7)	C:(15)-(14)-(19)-(10)	–174.2(3)
P(2)···Al(1)	2.6934(7)	C:(45)-(44)-(49)-(40)	–179.3(2)
peri Region Bond Angles			
Al(1)-C(10)-C(19)	122.8(2)		
Al(1)-C(40)-C(49)	122.3(2)		
C(10)-C(19)-C(18)	125.5(2)		
C(40)-C(49)-C(48)	125.6(2)		
P(1)-C(18)-C(19)	115.8(2)		
P(2)-C(48)-C(49)	115.6(2)		
Σ of bay angles	364.1(6)		
	363.5(6)		
Splay angle[a]	4.1(6)		
	3.5(6)		
C(20)-P(1)-C(30)	105.1(2)		
C(50)-P(2)-C(60)	106.5(2)		

[a] Splay angle: Σ of the three bay region angles - 360.

[*] Compound **2a** shows a transoid out-of- plane displacement.

Table S3. Selected bond parameters [Å, °] of **2b**.

	2b		**2b**
Bond Lengths and Angles		***Out-of-Plane Displacement****	
Al(1)-C(10)	2.019(3)	P(1)	0.2346(9)
Al(1)-C(40)	2.011(3)	P(2)	0.2509(8)
Al(1)-C(70)	2.010(3)	P(3)	0.1353(8)
C(10)-Al(1)-C(40)	108.9(2)	Al(1)	0.304(2)
C(10)-Al(1)-C(70)	108.7(2)	Al(2)	0.099(1)
C(40)-Al(1)-C(70)	107.8(2)	Al(3)	0.2332(9)
peri Region Distances		***Central Acenaphthene Ring Torsion Angles***	
P(1)···Al(1)	2.831(2)	C:(13)-(14)-(19)-(18)	177.8(4)
P(2)···Al(1)	2.909(2)	C:(43)-(44)-(49)-(48)	–176.7(4)
P(3)···Al(1)	2.943(2)	C:(73)-(74)-(79)-(78)	179.9(4)
peri Region Bond Angles		C:(15)-(14)-(19)-(10)	177.2(4)
Al(1)-C(10)-C(19)	125.1(2)	C:(45)-(44)-(49)-(40)	–178.2(4)
Al(1)-C(40)-C(49)	126.1(2)	C:(75)-(74)-(79)-(70)	174.9(4)
Al(1)-C(70)-C(79)	127.0(2)		
C(10)-C(19)-C(18)	125.3(3)		
C(40)-C(49)-C(48)	126.3(3)		
C(70)-C(79)-C(78)	125.9(3)		
P(1)-C(18)-C(19)	116.0(2)		
P(2)-C(48)-C(49)	117.0(2)		
P(3)-C(78(-C(79)	117.5(2)		
Σ of bay angles	366.4(7)		
	369.4(7)		
	370.4(7)		
Splay angle[a]	6.4(7)		
	9.4(7)		
	10.4(7)		
C(20)-P(1)-C(30)	103.9(2)		
C(50)-P(2)-C(60)	103.3(2)		
C(80)-P(3)-C(90)	101.8(2)		

[a] Splay angle: Σ of the three bay region angles - 360.

[*] Compound **2b** shows a transoid out-of- plane displacement.

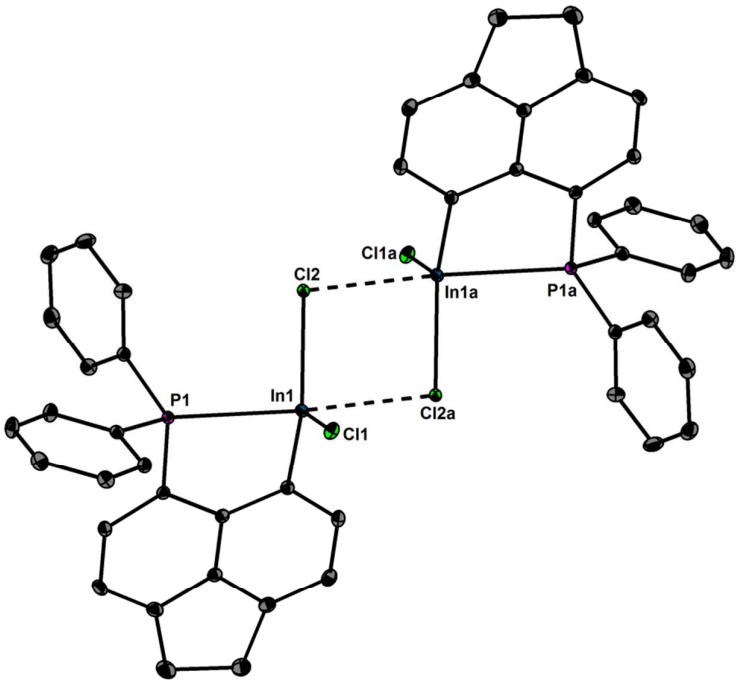

Figure S34. Crystal structure of **4** showing the intermolecular association

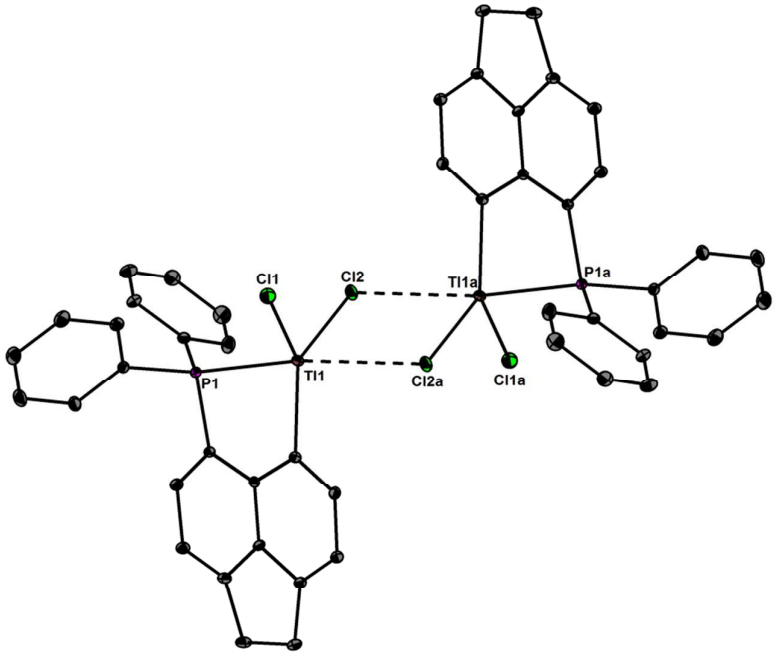

Figure S35. Crystal structure of **5** showing the intermolecular association

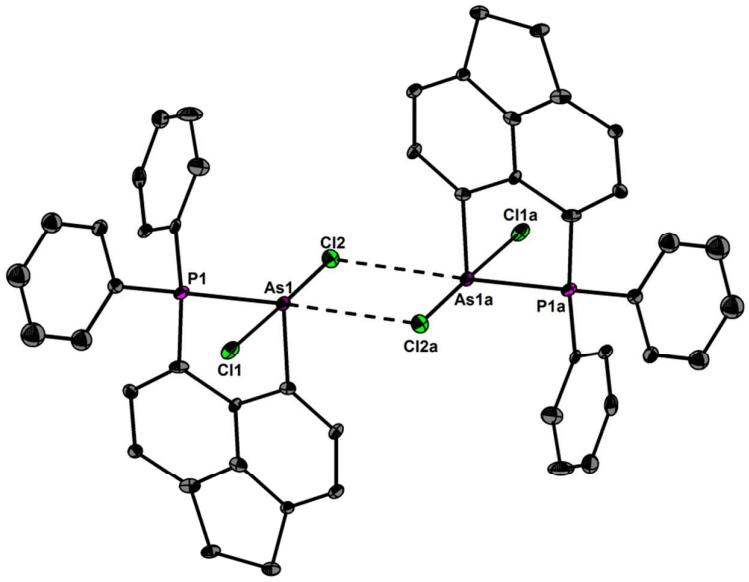

Figure S36. Crystal structure of **7** showing the intermolecular association

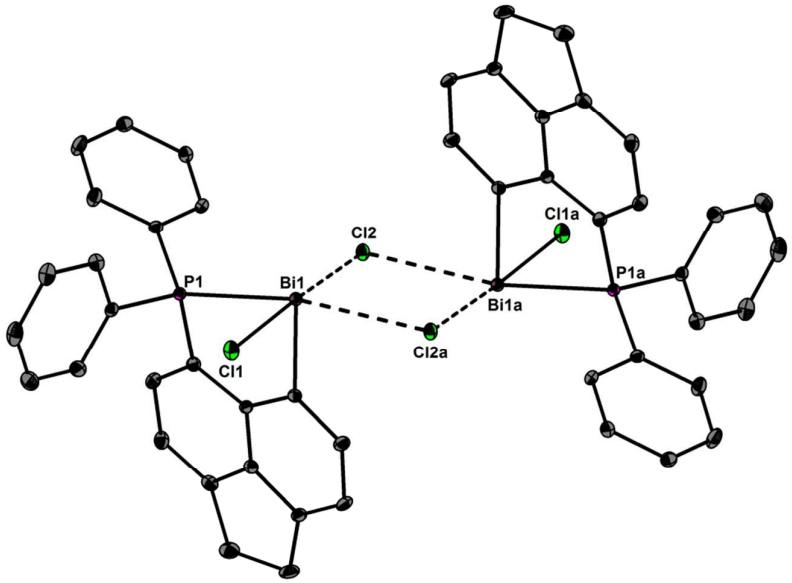

Figure S37. Crystal structure of **9** showing the intermolecular association

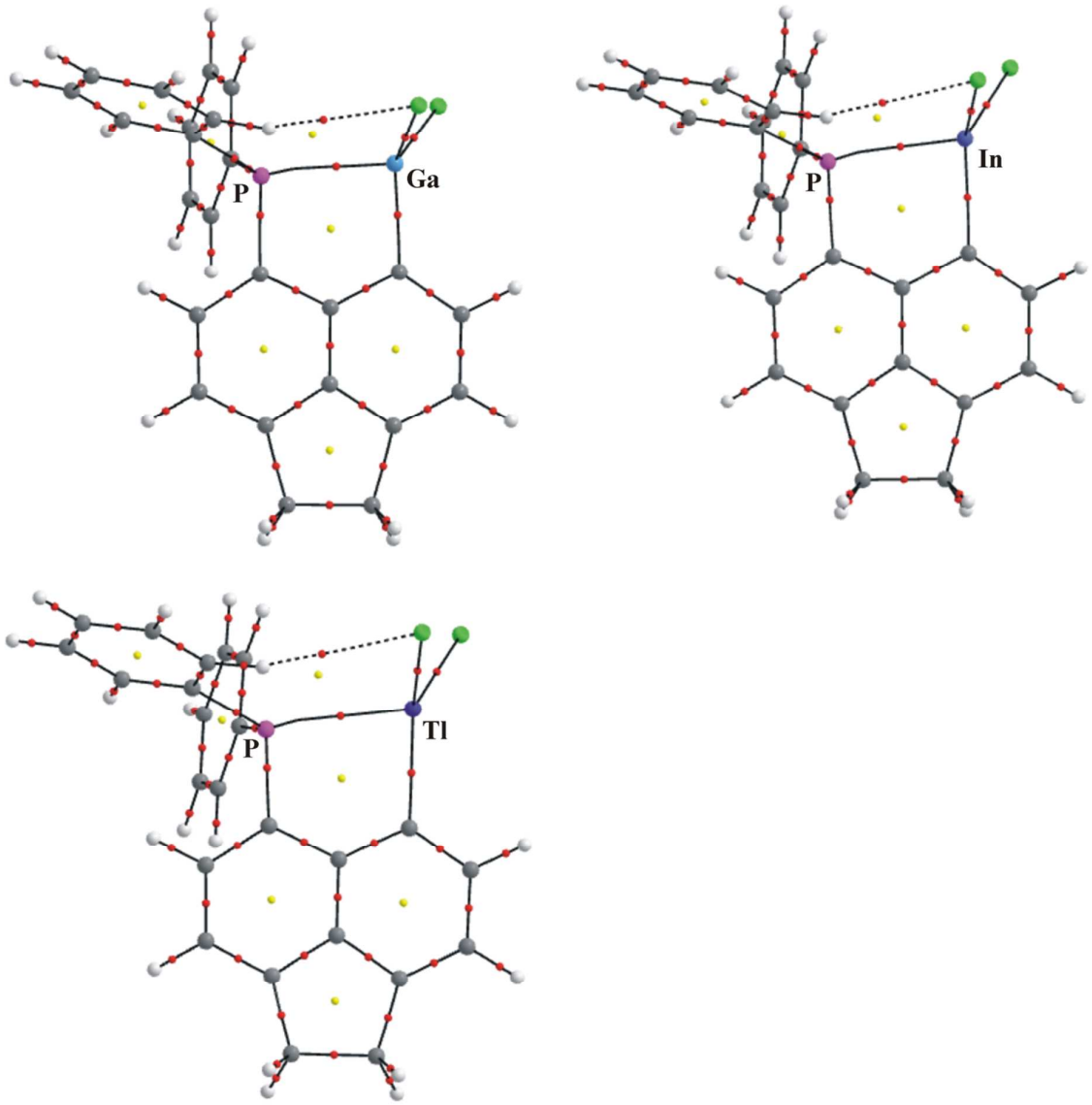

Figure S38. AIM bond paths of **3A**, **4A** and **5A**. Bond critical points are given as red dots.

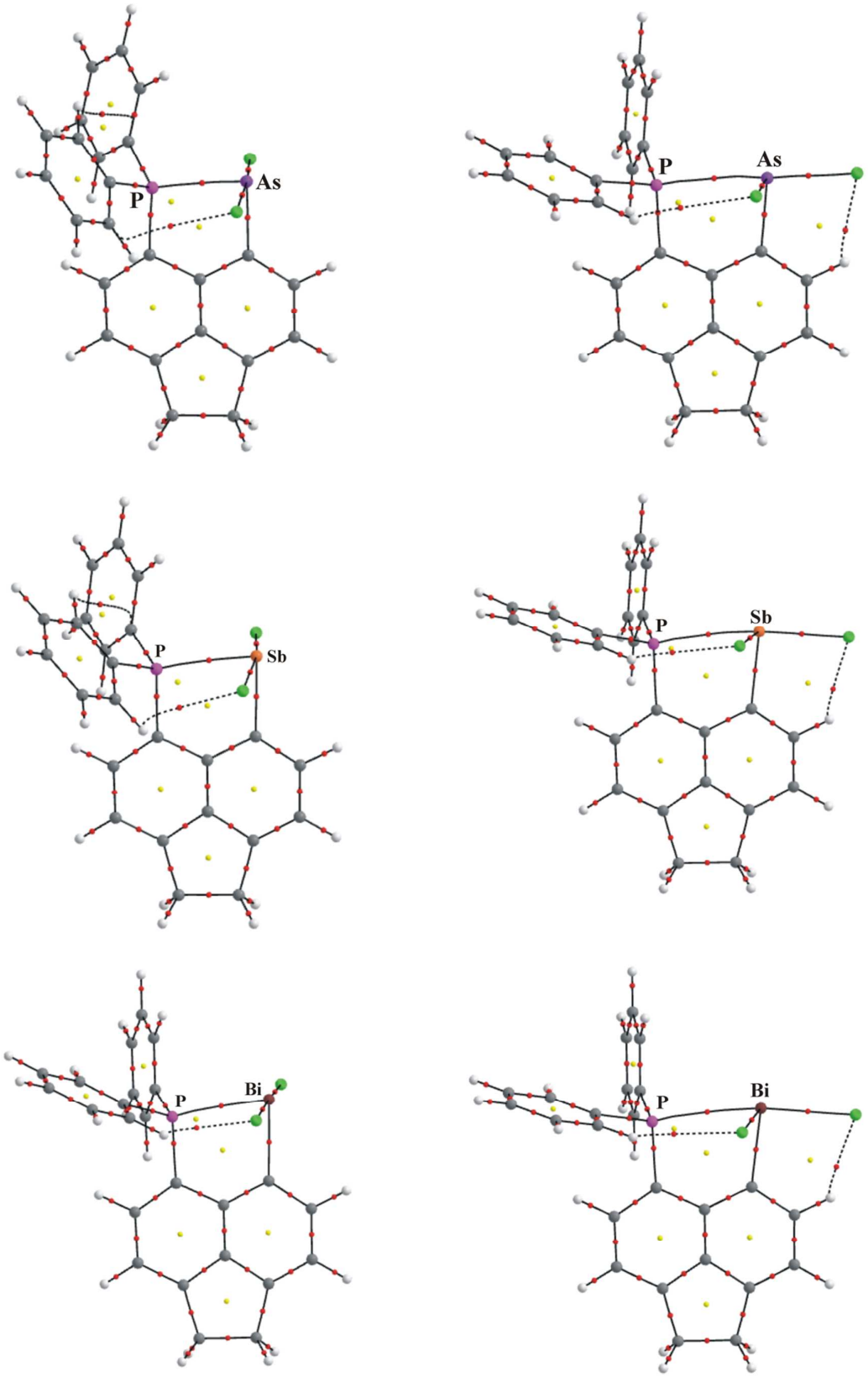

Figure S39. AIM bond paths of **7B – 9B** (left) and **7C – 9C** (right). Bond critical points are given as red dots.

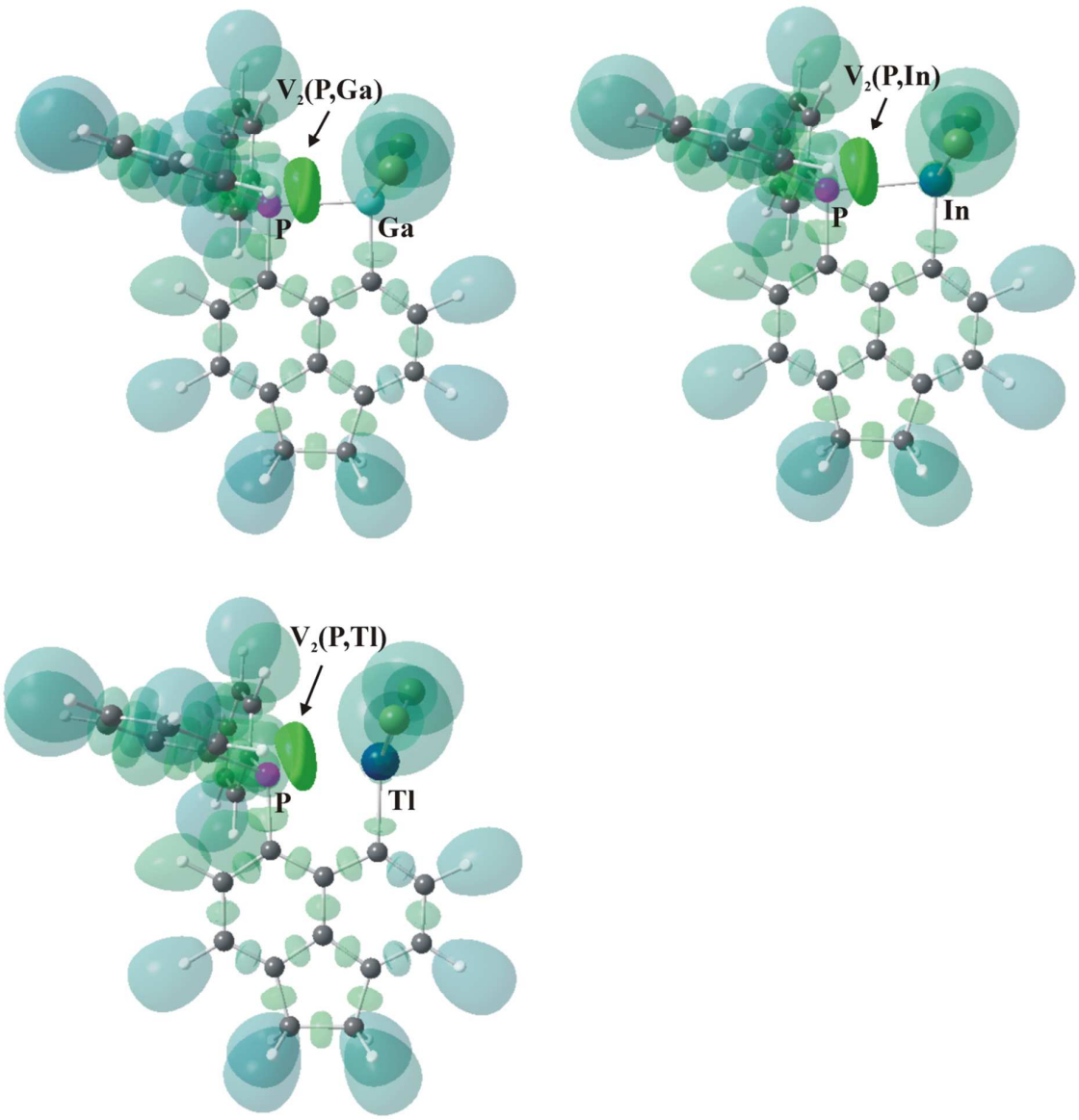

Figure S40. Isosurface representation of the localization domains of the ELI-D (an iso-value of Y = 1.40) of **3A**, **4A** and **5A.**

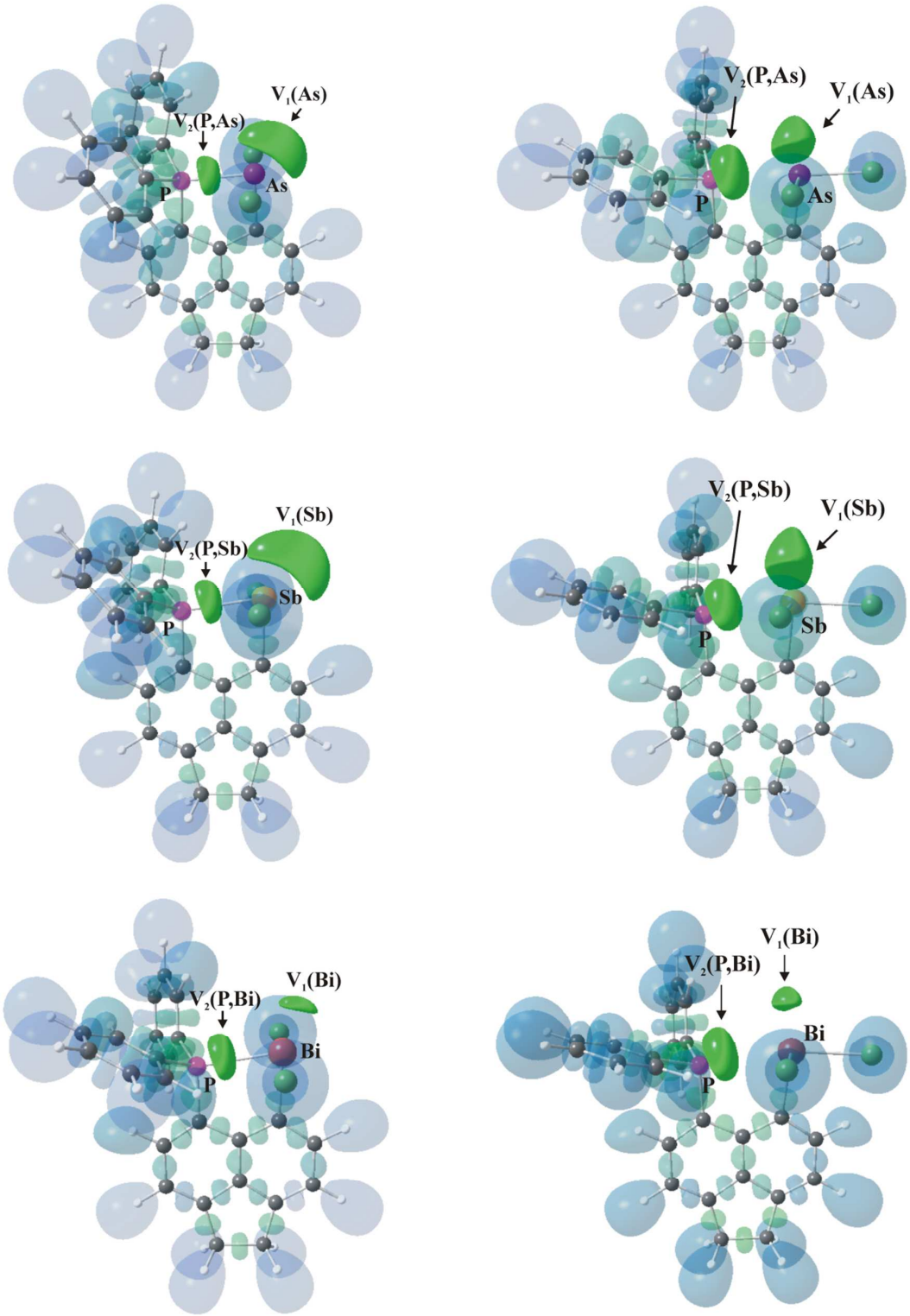

Figure S41. Isosurface representation of the localization domains of the ELI-D (an iso-value of Y = 1.40) of **7B** - **9B** (left) and **7C** - **9C** (right).

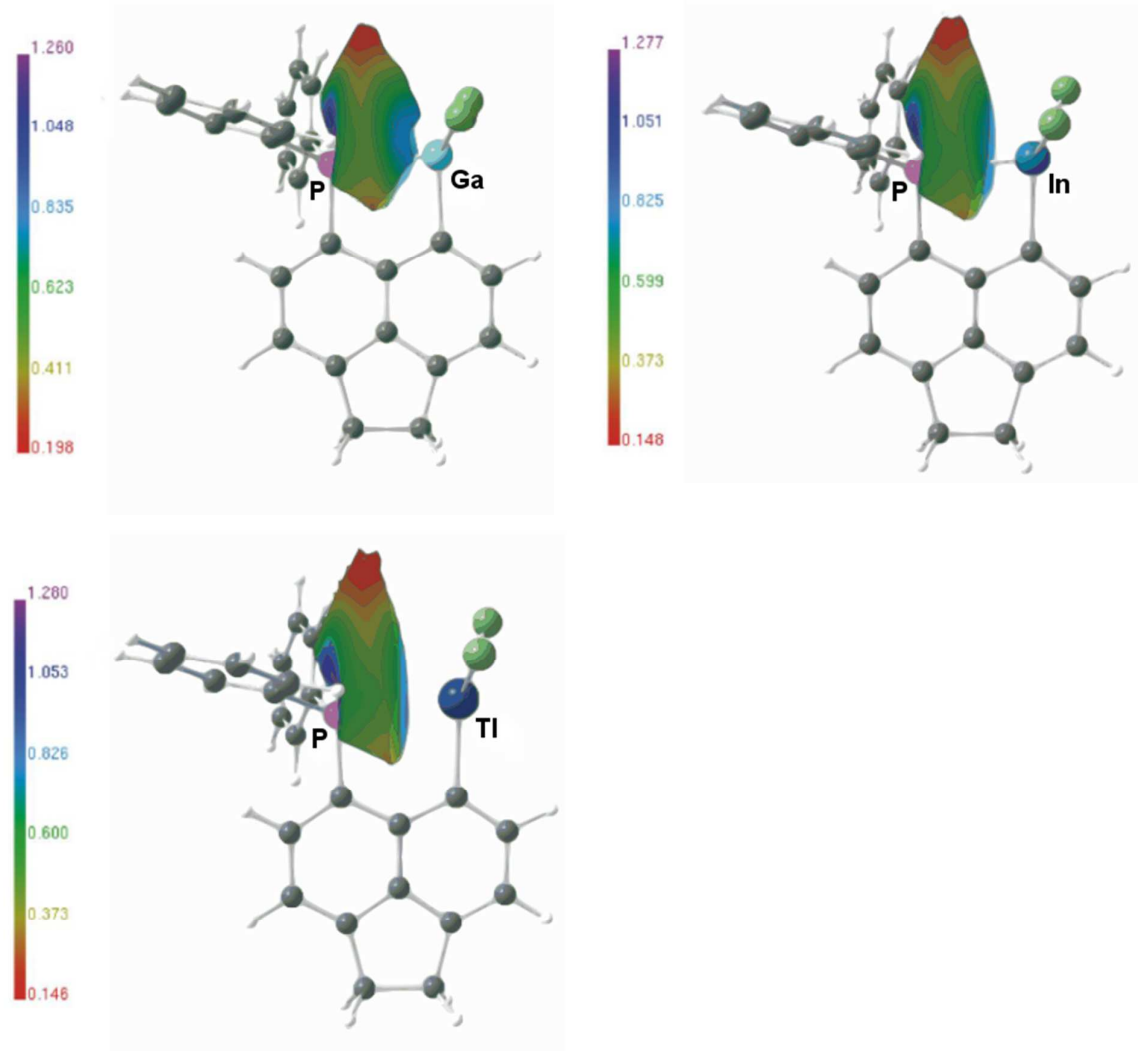

Figure S42. ELI-D distribution mapped on bonding V_2(P,E)-basins of **3A**, **4A** and **5A**. All structures are MOLISO representations.

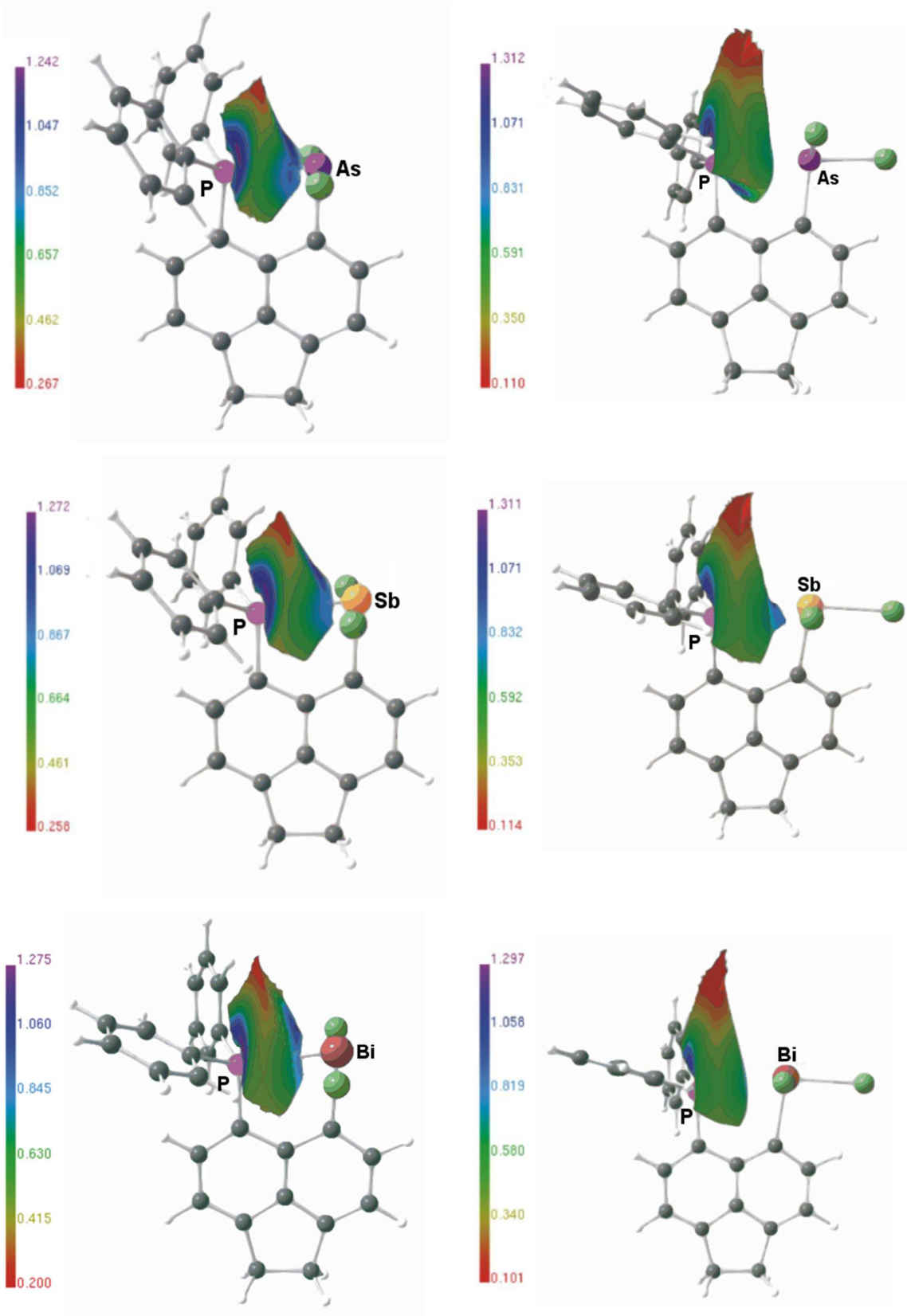

Figure S43. ELI-D distribution mapped on bonding V_2(P,E)-basins of **7B – 9B** (left) and **7C – 9C** (right).

Table S4. Calculated bond lengths (in Å) and angles (in deg) of **1** - **5**

	1A (E = B)	**2A** (E = Al)	**3A** (E = Ga)	**4A** (E =In)	**5A** (E = Tl)
bond lengths					
E1–P1	2.0804	2.4788	2.4703	2.6550	2.7407
E1–C10	1.6019	1.9716	1.9780	2.1602	2.1829
E1–Cl1	1.8495	2.1386	2.1891	2.3763	2.4561
E1–Cl2	1.8453	2.1297	2.1777	2.3618	2.4265
C18–P1	1.7979	1.8093	1.8094	1.8142	1.8174
C20–P1	1.8170	1.8182	1.8163	1.8165	1.8169
C30–P1	1.8106	1.8194	1.8167	1.8188	1.8191
C10–C11	1.3827	1.3857	1.3817	1.3809	1.3767
C10–C19	1.4123	1.4250	1.4210	1.4224	1.4185
C18–C19	1.4168	1.4289	1.4286	1.4328	1.4327
C17–C18	1.3811	1.3823	1.3824	1.3831	1.3831
C14–C19	1.3953	1.4056	1.4055	1.4094	1.4107
bond angles					
P1–E1–C10	97.87	86.62	87.41	82.36	81.13
P1–E1–Cl1	109.80	109.05	109.83	107.94	105.53
P1–E1–Cl2	108.87	109.01	108.22	109.65	108.52
C10–E1–Cl1	113.85	115.94	116.78	118.19	119.31
C10–E1–Cl2	113.89	119.45	120.11	123.54	129.51
Cl1–E1–Cl2	111.60	112.88	111.13	109.99	105.85
E1–P1–C18	95.57	94.88	94.55	94.74	93.73
E1–P1–C20	119.95	124.69	124.50	124.87	126.18
E1–P1–C30	114.41	113.29	113.16	113.29	113.62
C18–P1–C20	108.42	107.79	107.97	107.53	106.94
C18–P1–C30	110.93	108.29	108.45	107.87	107.27
C20–P1–C30	106.87	106.33	106.65	106.73	106.73
C18–C19–C10	122.78	125.90	126.28	127.50	128.40
E1–C10–C19	115.43	116.01	115.22	115.77	116.36
P1–C18–C19	108.27	115.21	115.72	118.16	118.88

Table S5. Calculated bond lengths (in Å) and angles (in deg) of **6**

	6B[#]	**6B$_{pcm}$**[#]	**6C**
bond lengths			
P2–P1	2.2831	2.2886	2.8913
P2–C10	1.8431	1.8356	1.8465
P2–Cl1	2.3227	2.2998	2.0894
P2–Cl2	2.3701	2.4857	2.1220
C18–P1	1.7969	1.7933	1.8287
C20–P1	1.8130	1.8089	1.8366
C30–P1	1.8073	1.8030	1.8304
C10–C11	1.3773	1.3797	1.3838
C10–C19	1.4100	1.4113	1.4337
C18–C19	1.4132	1.4141	1.4291
C17–C18	1.3832	1.3850	1.3847
C14–C19	1.3952	1.3950	1.4129
bond angles			
P1–P2–C10	88.79	89.01	83.86
P1–P2–Cl1	90.28	92.81	94.95
P1–P2–Cl2	85.82	86.43	165.51
C10–P2–Cl1	89.86	92.51	100.44
C10–P2–Cl2	86.16	85.95	100.30
Cl1–P2–Cl2	174.49	178.29	97.90
P2–P1–C18	97.97	97.62	85.72
P2–P1–C20	118.57	116.48	157.01
P2–P1–C30	111.98	111.29	94.41
C18–P1–C20	108.01	108.62	102.99
C18–P1–C30	114.33	115.65	105.23
C20–P1–C30	106.11	107.27	103.50
C18–C19–C10	124.35	124.62	128.77
P2–C10–C19	117.50	117.14	120.37
P1–C18–C19	111.20	111.16	119.33

[#] Structure type resembling the experimentally observed structure most

Table S6. Calculated bond lengths (in Å) and angles (in deg) of **7**

	7B[#]	**7B$_{pcm}$**[#]	**7C**
bond lengths			
As1–P1	2.4103	2.4091	2.8377
As1–C10	1.9625	1.9552	1.9922
As1–Cl1	2.4372	2.4533	2.2218
As1–Cl2	2.4460	2.5105	2.2887
C18–P1	1.7974	1.7938	1.8107
C20–P1	1.8118	1.8084	1.8251
C30–P1	1.8076	1.8054	1.8250
C10–C11	1.3758	1.3782	1.3811
C10–C19	1.4103	1.4116	1.4313
C18–C19	1.4157	1.4167	1.4249
C17–C18	1.3838	1.3854	1.3837
C14–C19	1.3990	1.3988	1.4115
bond angles			
P1–As1–C10	85.57	85.90	80.12
P1–As1–Cl1	89.27	90.82	88.48
P1–As1–Cl2	86.34	88.07	176.47
C10–As1–Cl1	88.77	90.47	97.48
C10–As1–Cl2	86.48	86.80	98.15
Cl1–As1–Cl2	173.77	177.12	94.81
As1–P1–C18	97.87	97.65	92.23
As1–P1–C20	119.14	117.04	139.59
As1–P1–C30	111.42	110.94	104.00
C18–P1–C20	108.23	108.99	105.40
C18–P1–C30	112.99	114.01	106.08
C20–P1–C30	107.08	108.10	105.43
C18–C19–C10	125.43	125.65	128.44
As1–C10–C19	117.72	117.30	122.14
P1–C18–C19	113.37	113.33	116.95

[#] Structure type resembling the experimentally observed structure most

Table S7. Calculated bond lengths (in Å) and angles (in deg) of **8** and **9**

	8B (E =Sb)	**8C**[#] (E = Sb)	**9B**[#] (E = Bi)	**9C** (E = Bi)
bond lengths				
E1–P1	2.6262	2.9237	2.7315	3.0049
E1–C10	2.1595	2.1885	2.2564	2.2824
E1–Cl1	2.5719	2.3966	2.6697	2.4890
E1–Cl2	2.5595	2.4616	2.6375	2.5562
C18–P1	1.8029	1.8096	1.8046	1.8141
C20–P1	1.8152	1.8229	1.8164	1.8227
C30–P1	1.8120	1.8254	1.8104	1.8269
C10–C11	1.3772	1.3816	1.3770	1.3800
C10–C19	1.4151	1.4284	1.4154	1.4264
C18–C19	1.4208	1.4259	1.4223	1.4267
C17–C18	1.3842	1.3835	1.3838	1.3835
C14–C19	1.4044	1.4112	1.4069	1.4123
bond angles				
P1–E1–C10	80.41	75.23	77.69	73.14
P1–E1–Cl1	86.01	86.12	91.78	87.80
P1–E1–Cl2	85.00	169.80	87.11	167.12
C10–E1–Cl1	87.18	95.84	87.87	94.54
C10–E1–Cl2	86.45	94.85	88.51	94.22
Cl1–E1–Cl2	169.74	92.64	176.36	95.82
E1–P1–C18	97.79	95.56	98.10	95.89
E1–P1–C20	120.90	135.29	122.50	133.55
E1–P1–C30	111.88	105.02	110.46	106.94
C18–P1–C20	107.68	106.23	107.90	106.06
C18–P1–C30	111.20	106.25	110.02	105.92
C20–P1–C30	106.94	105.52	107.18	105.55
C18–C19–C10	126.75	128.29	127.32	128.60
E1–C10–C19	118.46	123.27	119.13	123.57
P1–C18–C19	116.50	117.05	117.49	117.83

[#] Structure type resembling the experimentally observed structure most

Table S8. Calculated bond topological parameters [(a)] for the E-Cl and E-C bonds of **1** - **9** (E = B, Al, Ga, In, Tl, P, As, Sb, Bi).

	bond	d	ρ_{bcp}	$\nabla^2\rho_{bcp}$	d_1	d_2	ε	G/ρ_{bcp}	H/ρ_{bcp}
1A	Cl1–B1	1.8495	0.84	–1.1	1.299	0.551	0.08	0.84	–0.93
2A	Cl1–Al1	2.1386	0.47	6.3	1.336	0.803	0.02	1.22	–0.28
3A	Cl1–Ga1	2.1891	0.61	4.2	1.229	0.960	0.01	0.91	–0.43
4A	Cl1–In1	2.3763	0.52	4.7	1.241	1.135	0.01	0.91	–0.28
5A	Cl1–Tl1	2.4561	0.51	4.1	1.231	1.225	0.01	0.83	–0.27
6B[#]	Cl1–P2	2.3227	0.54	0.1	1.293	1.031	0.04	0.42	–0.40
6C	Cl1–P2	2.0894	0.82	–3.6	1.243	0.847	0.10	0.42	–0.72
7B[#]	Cl1–As1	2.4372	0.46	1.4	1.310	1.128	0.02	0.52	–0.32
7C	Cl1–As1	2.2218	0.70	0.4	1.218	1.004	0.06	0.56	–0.52
8B	Cl1–Sb1	2.5719	0.40	2.0	1.347	1.225	0.01	0.61	–0.27
8C[#]	Cl1–Sb1	2.3966	0.56	2.5	1.268	1.129	0.05	0.68	–0.37
9B[#]	Cl1–Bi1	2.6697	0.36	2.5	1.348	1.321	0.01	0.67	–0.20
9C	Cl1–Bi1	2.4890	0.52	3.0	1.263	1.226	0.03	0.70	–0.30
1A	Cl2–B1	1.8453	0.85	–1.1	1.296	0.549	0.07	0.84	–0.93
2A	Cl2–Al1	2.1297	0.48	6.3	1.329	0.800	0.03	1.23	–0.28
3A	Cl2–Ga1	2.1777	0.63	4.4	1.222	0.9561	0.01	0.92	–0.43
4A	Cl2–In1	2.3618	0.54	4.9	1.232	1.130	0.01	0.92	–0.29
5A	Cl2–Tl1	2.4265	0.55	4.2	1.214	1.213	0.02	0.82	–0.28
6B[#]	Cl2–P2	2.3701	0.49	0.5	1.311	1.060	0.03	0.43	–0.36
6C	Cl2–P2	2.1220	0.78	–2.9	1.242	0.880	0.09	0.40	–0.66
7B[#]	Cl2–As1	2.4460	0.45	1.4	1.315	1.132	0.02	0.52	–0.31
7C	Cl2–As1	2.2887	0.62	0.9	1.242	1.046	0.04	0.54	–0.44
8B	Cl2–Sb1	2.5595	0.41	2.0	1.342	1.218	0.01	0.62	–0.28
8C[#]	Cl2–Sb1	2.4616	0.50	2.2	1.295	1.167	0.02	0.65	–0.34
9B[#]	Cl2–Bi1	2.6375	0.39	2.6	1.333	1.304	0.02	0.69	–0.21
9C	Cl2–Bi1	2.5562	0.45	2.8	1.293	1.263	0.02	0.70	–0.26
1A	C10–B1	1.6019	1.20	–6.9	1.070	0.532	0.01	0.67	–1.07
2A	C10–Al1	1.9716	0.58	6.1	1.188	0.783	0.02	1.11	–0.37
3A	C10–Ga1	1.9780	0.77	3.5	1.044	0.934	0.03	0.80	–0.48
4A	C10–In1	2.1602	0.67	3.8	1.053	1.107	0.05	0.78	–0.37
5A	C10–Tl1	2.1829	0.71	2.9	1.003	1.180	0.08	0.68	–0.39
6B[#]	C10–P2	1.8431	1.10	–8.3	1.071	0.773	0.06	0.41	–0.94
6C	C10–P2	1.8465	1.10	–8.4	1.073	0.773	0.07	0.41	–0.94
7B[#]	C10–As1	1.9625	0.96	–2.8	1.004	0.958	0.02	0.45	–0.65
7C	C10–As1	1.9922	0.92	–2.6	1.015	0.977	0.08	0.42	–0.62
8B	C10–Sb1	2.1595	0.75	1.0	1.070	1.090	0.01	0.57	–0.49
8C[#]	C10–Sb1	2.1885	0.72	0.7	1.083	1.105	0.07	0.54	–0.47
9B[#]	C10–Bi1	2.2564	0.69	1.5	1.067	1.189	0.01	0.57	–0.41
9C	C10–Bi1	2.2824	0.66	1.4	1.079	1.203	0.07	0.54	–0.40

[(a)] electron density ρ_{bcp} in eÅ^{-3} and its corresponding Laplacian $\nabla^2\rho_{bcp}$ in eÅ^{-5}, d_1 and d_2 – distances from bond critical point to nucleus, ε - the bond ellipticity, G/ρ_{bcp} and H/ρ_{bcp} – kinetic and total energy density over ρ_{bcp} ratios in he^{-1}

[#] Structure type resembling the experimentally observed structure most

Table S9. Calculated topological[(a)] and integrated[(b)] bond descriptors for the Cl–E and C10–E-bonds of **1** - **9** (E = B, Al, Ga, In, Tl, P, As, Sb, Bi).

	bond	$V_{001}{}^{ELI}$	ELI_{pop}	ELI_{max}	Δ_{ELI}	*RJI* [e]	*RJI* [%]
1A	Cl1–B1	2.49	1.46	1.61	0.02	1.24	85
2A	Cl1–Al1	3.95	1.44	1.55	0.04	1.31	91
3A	Cl1–Ga1						
4A	Cl1–In1						
5A	Cl1–Tl1						
6B[#]	Cl1–P2						
6C	Cl1–P2	2.03	1.22	1.46	0.07	0.82	67
7B[#]	Cl1–As1						
7C	Cl1–As1	1.85	1.03	1.44	0.08	0.59	57
8B	Cl1–Sb1						
8C[#]	Cl1–Sb1						
9B[#]	Cl1–Bi1						
9C	Cl1–Bi1						
1A	Cl2–B1	2.50	1.46	1.61	0.02	1.25	85
2A	Cl2–Al1	4.01	1.45	1.55	0.03	1.31	91
3A	Cl2–Ga1						
4A	Cl2–In1						
5A	Cl2–Tl1						
6B[#]	Cl2–P2						
6C	Cl2–P2	1.86	1.11	1.45	0.15	0.73	66
7B[#]	Cl2–As1						
7C	Cl2–As1	1.23	0.72	1.44	0.25	0.37	51
8B	Cl2–Sb1						
8C[#]	Cl2–Sb1						
9B[#]	Cl2–Bi1						
9C	Cl2–Bi1						
1A	C10–B1	5.04	2.22	2.13	0.05	1.88	85
2A	C10–Al1	10.84	2.37	2.07	0.09	2.18	92
3A	C10–Ga1	10.81	2.48	1.79	0.09	1.80	72
4A	C10–In1	12.01	2.26	1.73	0.10	1.73	77
5A	C10–Tl1	7.93	1.86	1.60	0.08	1.44	77
6B[#]	C10–P2	4.35	2.15	1.90	0.02	1.59	74
6C	C10–P2	5.28	2.24	1.88	0.07	1.63	73
7B[#]	C10–As1	4.96	2.19	1.78	0.02	1.43	65
7C	C10–As1	6.22	2.30	1.75	0.05	1.48	65
8B	C10–Sb1	6.24	2.18	1.76	0.01	1.57	72
8C[#]	C10–Sb1	8.25	2.30	1.74	0.04	1.65	72
9B[#]	C10–Bi1	6.52	2.03	1.71	0.02	1.56	77
9C	C10–Bi1	8.49	2.11	1.69	0.04	1.63	77

[(a)] ELI_{max} – ELI-D value at the attractor position, Δ_{ELI} – the distance in Å of the attractor position perpendicular to the atom-atom axis;

[(b)] $V_{001}{}^{ELI}$ – is the volume of the ELI-D basin in $Å^3$ cut at 0.001au, ELI_{pop} – the electron population within the ELI-D basin in *e,* and *RJI* – the Raub-Jansen index in *e* and %

Table S10. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**1A**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
C	-0.677311	0.205402	-0.908922
C	-1.763685	-0.049708	-0.035944
C	-1.590230	-0.350063	1.333086
C	-2.739173	-0.574234	2.069008
C	-4.043327	-0.505899	1.512232
C	-4.203559	-0.197042	0.182665
C	-3.048542	0.030043	-0.574143
C	-3.300543	0.363193	-1.910020
C	-2.233206	0.630658	-2.738614
C	-0.915694	0.550715	-2.224788
C	-5.399768	-0.021771	-0.724934
C	-4.797516	0.361865	-2.114896
H	-2.649225	-0.808227	3.125377
H	-4.897692	-0.692607	2.155590
H	-2.376617	0.907017	-3.778004
H	-0.085977	0.776202	-2.887122
H	-5.990842	-0.939934	-0.789031
H	-6.074312	0.755772	-0.355452
H	-5.090971	-0.350875	-2.890938
H	-5.150059	1.342552	-2.447351
P	0.848994	0.035819	0.026101
C	1.853497	-1.326340	-0.617154
C	1.505772	-2.028378	-1.768032
C	2.297106	-3.082268	-2.205173
C	3.433781	-3.441523	-1.495554
C	3.777280	-2.752021	-0.339358
C	2.988838	-1.702754	0.104200
H	0.611319	-1.760097	-2.317953
H	2.019733	-3.625255	-3.101896
H	4.049080	-4.266328	-1.837973
H	4.655863	-3.040215	0.226777
H	3.250253	-1.183846	1.019872
C	1.823398	1.554896	-0.184838
C	3.061647	1.559632	-0.824673
C	3.756219	2.750393	-0.988892
C	3.220861	3.940553	-0.518820
C	1.985330	3.940904	0.116347
C	1.287702	2.755955	0.285897
H	3.485956	0.635617	-1.198578
H	4.718902	2.744563	-1.488102
H	3.766077	4.869351	-0.646376
H	1.563803	4.867967	0.488454
H	0.330460	2.762728	0.792940
B	-0.073356	-0.361794	1.848041
Cl	0.495937	-2.007548	2.458527
Cl	0.317172	0.984257	3.054765

Table S11. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**2A**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
C	-0.664740	-0.904270	0.128547
C	-1.820200	-0.074447	-0.005665
C	-1.820547	1.308014	-0.351435
C	-3.054603	1.935591	-0.410654
C	-4.288664	1.286275	-0.160191
C	-4.287479	-0.050628	0.140682
C	-3.052820	-0.714566	0.210065
C	-3.190089	-2.080355	0.500806
C	-2.062703	-2.861261	0.580532
C	-0.802174	-2.253835	0.394353
C	-5.389121	-1.042238	0.426055
C	-4.657040	-2.397732	0.654137
H	-3.098448	2.988657	-0.676187
H	-5.212218	1.852994	-0.227218
H	-2.116822	-3.925392	0.784952
H	0.086050	-2.874484	0.462413
H	-5.969869	-0.749016	1.305397
H	-6.096368	-1.103016	-0.405874
H	-4.870942	-2.811197	1.643944
H	-4.973392	-3.153232	-0.070859
P	0.921060	-0.052669	-0.055028
C	1.692047	0.078952	1.587707
C	1.166244	-0.539869	2.718988
C	1.788134	-0.382504	3.950832
C	2.934563	0.390718	4.060155
C	3.457793	1.017708	2.935945
C	2.836706	0.870462	1.706401
H	0.266580	-1.139122	2.640664
H	1.370714	-0.865044	4.827742
H	3.416693	0.514241	5.023678
H	4.344847	1.635544	3.018987
H	3.237428	1.382864	0.838163
C	2.011295	-1.116579	-1.047643
C	2.979312	-1.931525	-0.462164
C	3.769890	-2.751961	-1.255129
C	3.600668	-2.763429	-2.632551
C	2.641373	-1.948339	-3.219771
C	1.850674	-1.123773	-2.434463
H	3.122158	-1.921778	0.612441
H	4.521546	-3.382381	-0.792810
H	4.221409	-3.402985	-3.250459
H	2.513106	-1.945609	-4.296441
H	1.117761	-0.474356	-2.900550
Al	-0.073081	2.076370	-0.844476
Cl	0.725895	3.682784	0.303072
Cl	0.298976	2.285928	-2.939990

Table S12. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**3A**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
C	-0.670839	-1.073286	0.001673
C	-1.824692	-0.231012	0.006084
C	-1.831149	1.186783	-0.088410
C	-3.054564	1.828145	-0.055352
C	-4.291743	1.147283	0.061150
C	-4.294494	-0.221457	0.126622
C	-3.061821	-0.892399	0.093621
C	-3.204660	-2.287302	0.141939
C	-2.079094	-3.073655	0.098204
C	-0.815957	-2.447708	0.030456
C	-5.400497	-1.243851	0.226041
C	-4.673539	-2.620893	0.221120
H	-3.087294	2.911060	-0.131457
H	-5.213758	1.719788	0.081945
H	-2.136600	-4.156881	0.115944
H	0.069450	-3.075073	-0.002084
H	-5.987386	-1.105394	1.138591
H	-6.101246	-1.157214	-0.608980
H	-4.899382	-3.201493	1.120151
H	-4.982103	-3.236071	-0.629090
P	0.924272	-0.219812	-0.031449
C	1.715346	-0.416315	1.592076
C	1.126938	-1.132436	2.631145
C	1.758165	-1.212624	3.865590
C	2.975766	-0.580335	4.069010
C	3.561704	0.144093	3.037903
C	2.932729	0.234270	1.807314
H	0.173238	-1.623928	2.479115
H	1.292552	-1.770573	4.670491
H	3.465807	-0.642486	5.034410
H	4.505611	0.653252	3.196834
H	3.385430	0.820285	1.014380
C	1.988519	-1.067212	-1.234909
C	2.893781	-2.054692	-0.846704
C	3.660260	-2.707475	-1.801607
C	3.529453	-2.378893	-3.144119
C	2.634191	-1.390964	-3.532898
C	1.867100	-0.731694	-2.584386
H	3.005956	-2.308120	0.201433
H	4.363350	-3.473742	-1.493968
H	4.131900	-2.888538	-3.888091
H	2.538234	-1.122666	-4.579015
H	1.186010	0.054855	-2.891128
Ga	-0.059619	2.021046	-0.367851
Cl	0.766896	3.360677	1.137070
Cl	0.387746	2.732821	-2.389056

Table S13. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**4A**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the effective-core potential for In (ECP28MDF at the cc-pVTZ) in accordance with B. Metz, H. Stoll, M. Dolg, (2000). *J. Chem. Phys*. **113**, 2563.

atom	X	Y	Z
C	-0.719246	-1.194366	-0.126220
C	-1.866812	-0.345359	-0.002385
C	-1.887914	1.073783	0.091639
C	-3.109119	1.705084	0.222144
C	-4.344591	1.014673	0.263465
C	-4.342822	-0.348763	0.140644
C	-3.110052	-1.009181	0.003370
C	-3.265439	-2.397001	-0.144056
C	-2.149485	-3.178296	-0.309239
C	-0.883703	-2.557565	-0.292468
C	-5.452849	-1.369999	0.109741
C	-4.734451	-2.733054	-0.102528
H	-3.144772	2.788544	0.286327
H	-5.266613	1.576958	0.372117
H	-2.216440	-4.252326	-0.446614
H	-0.004105	-3.181579	-0.416406
H	-6.024425	-1.360614	1.042296
H	-6.165499	-1.160829	-0.692762
H	-4.956807	-3.439184	0.702524
H	-5.051537	-3.214778	-1.031971
P	0.924188	-0.431910	-0.029903
C	1.641292	-0.853759	1.587468
C	1.039397	-1.738443	2.479444
C	1.628789	-1.992965	3.711066
C	2.817574	-1.368419	4.058968
C	3.416572	-0.477560	3.176815
C	2.829179	-0.214124	1.950278
H	0.107272	-2.224725	2.216417
H	1.152506	-2.680731	4.401148
H	3.273486	-1.566566	5.022747
H	4.336694	0.026229	3.450519
H	3.290071	0.502105	1.277998
C	1.968916	-1.223207	-1.287663
C	2.819533	-2.285300	-0.982577
C	3.580168	-2.874359	-1.982944
C	3.498629	-2.406918	-3.287495
C	2.660458	-1.342096	-3.592399
C	1.900729	-0.745534	-2.597863
H	2.895317	-2.646695	0.036914
H	4.240622	-3.699553	-1.739989
H	4.096561	-2.866875	-4.066622
H	2.605437	-0.963899	-4.607015
H	1.268096	0.103061	-2.838013
In	0.017567	2.060147	-0.158438
Cl	1.041872	3.365499	1.522361
Cl	0.560011	2.926809	-2.303586

Table S14. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**5A**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the effective-core potential for Tl (ECP60MDF at the cc-pVTZ) in accordance with B. Metz, M. Schweizer, H. Stoll, M. Dolg, W. Liu (2000). *Theor. Chem. Acc.* 104, 22.

atom	X	Y	Z
C	0.723201	1.421105	-0.149747
C	1.868807	0.574634	0.004524
C	1.909100	-0.836028	0.148219
C	3.116828	-1.479241	0.300221
C	4.352131	-0.788443	0.321137
C	4.349418	0.569579	0.150924
C	3.118467	1.228891	-0.011961
C	3.281373	2.609826	-0.210485
C	2.169893	3.388693	-0.407350
C	0.901386	2.775297	-0.367653
C	5.463131	1.584673	0.085987
C	4.751403	2.941150	-0.179355
H	3.143235	-2.559620	0.396400
H	5.272792	-1.348069	0.450181
H	2.242151	4.456331	-0.585600
H	0.026031	3.399750	-0.515805
H	6.030688	1.606963	1.020691
H	6.177736	1.342074	-0.705127
H	4.975674	3.676822	0.598128
H	5.071453	3.385163	-1.126340
P	-0.934342	0.685800	-0.028109
C	-1.628184	1.181064	1.578931
C	-1.006872	2.084162	2.439031
C	-1.582365	2.385849	3.666574
C	-2.777691	1.790986	4.043098
C	-3.396535	0.881972	3.193742
C	-2.822331	0.570659	1.972125
H	-0.070076	2.548996	2.154866
H	-1.090444	3.087782	4.331053
H	-3.222881	2.026267	5.003529
H	-4.321706	0.400576	3.489892
H	-3.297167	-0.161450	1.327111
C	-1.958217	1.474327	-1.305300
C	-2.781038	2.567239	-1.034006
C	-3.530942	3.140625	-2.051509
C	-3.466566	2.626893	-3.339640
C	-2.657535	1.530720	-3.610376
C	-1.909565	0.948976	-2.598237
H	-2.843908	2.964641	-0.027023
H	-4.169905	3.989780	-1.834850
H	-4.056371	3.074642	-4.131990
H	-2.617743	1.115563	-4.611182
H	-1.302989	0.073800	-2.809430
Tl	0.008538	-1.887274	-0.070953
Cl	-1.231947	-3.189892	1.557637
Cl	-0.623748	-2.783016	-2.268756

Table S15. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**6C**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
C	0.092441	0.946949	0.259769
C	1.474314	0.600934	0.145277
C	2.058166	-0.614288	-0.342328
C	3.435110	-0.697216	-0.452310
C	4.313995	0.335459	-0.079893
C	3.785392	1.487959	0.435389
C	2.388459	1.604544	0.536952
C	2.014717	2.860448	1.047986
C	0.683884	3.157106	1.169248
C	-0.254294	2.191744	0.757353
C	4.433543	2.751392	0.936840
C	3.250681	3.667093	1.350450
H	3.867732	-1.616016	-0.829438
H	5.383291	0.193986	-0.195907
H	0.339842	4.113595	1.548620
H	-1.306730	2.449196	0.812938
H	5.100676	2.545163	1.778717
H	5.050138	3.212429	0.160017
H	3.297141	3.933181	2.410437
H	3.254146	4.609118	0.794891
P	-1.174815	-0.198338	-0.393341
C	-1.876174	-1.029545	1.078978
C	-1.572984	-0.681343	2.393413
C	-2.116759	-1.394589	3.454804
C	-2.972765	-2.459636	3.215339
C	-3.277325	-2.818391	1.907741
C	-2.724787	-2.115519	0.848574
H	-0.905561	0.149813	2.591594
H	-1.868635	-1.114732	4.473141
H	-3.395961	-3.015806	4.044701
H	-3.937021	-3.656918	1.712570
H	-2.948501	-2.415329	-0.170814
C	-2.518734	0.933913	-0.927327
C	-3.693170	1.154916	-0.208958
C	-4.675301	2.000892	-0.710094
C	-4.495920	2.636878	-1.930142
C	-3.331258	2.417576	-2.656113
C	-2.355881	1.565226	-2.163651
H	-3.844132	0.664518	0.746174
H	-5.584207	2.163564	-0.140458
H	-5.264101	3.296364	-2.319039
H	-3.187866	2.903424	-3.615285
H	-1.457856	1.381533	-2.745578
P	0.996829	-2.082520	-0.699288
Cl	2.412848	-3.643372	-0.451303
Cl	0.980405	-2.038935	-2.788204

Table S16. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**7C**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
C	0.029406	1.202632	0.008777
C	1.399684	0.816920	0.071188
C	1.957833	-0.499141	0.000636
C	3.328765	-0.640683	0.090057
C	4.220242	0.442841	0.238408
C	3.712705	1.711435	0.285449
C	2.319983	1.879628	0.197396
C	1.957946	3.237202	0.224390
C	0.633358	3.577356	0.124499
C	-0.315336	2.542653	0.020059
C	4.370817	3.060854	0.411783
C	3.201100	4.080572	0.345878
H	3.750434	-1.636837	0.034043
H	5.285636	0.246966	0.299578
H	0.304435	4.611215	0.124088
H	-1.364510	2.809024	-0.059308
H	4.922365	3.142181	1.352924
H	5.098055	3.224974	-0.388086
H	3.164121	4.715376	1.235752
H	3.301928	4.754304	-0.509945
P	-1.194235	-0.128424	-0.090118
C	-1.895578	-0.296052	1.586427
C	-1.617022	0.575537	2.637688
C	-2.151255	0.347714	3.899469
C	-2.971229	-0.748568	4.124562
C	-3.249498	-1.626964	3.084477
C	-2.706552	-1.409074	1.827954
H	-0.977909	1.435368	2.472671
H	-1.924464	1.032597	4.709461
H	-3.387093	-0.924361	5.110575
H	-3.880744	-2.492052	3.255545
H	-2.911519	-2.111585	1.025830
C	-2.548480	0.533699	-1.118951
C	-3.782503	0.932324	-0.606984
C	-4.773088	1.404090	-1.459023
C	-4.542000	1.482671	-2.824839
C	-3.316052	1.081052	-3.341929
C	-2.327609	0.601538	-2.497459
H	-3.973282	0.875337	0.458657
H	-5.729133	1.713064	-1.050086
H	-5.317612	1.850478	-3.487632
H	-3.132431	1.130870	-4.409639
H	-1.379690	0.268905	-2.907450
As	0.820997	-2.123506	-0.194111
Cl	2.486444	-3.692692	-0.148902
Cl	0.652274	-2.094672	-2.409275

Table S17. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**8C**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the effective-core potential for Sb (ECP28MDF at the cc-pVTZ) in accordance with B. Metz, H. Stoll, M. Dolg, (2000). *J. Chem. Phys*. **113**, 2563.

atom	X	Y	Z
C	-0.128351	1.374274	-0.153390
C	1.266269	1.119628	-0.000595
C	1.925664	-0.139287	0.143340
C	3.298215	-0.150829	0.300597
C	4.094489	1.016191	0.314526
C	3.487537	2.229602	0.143738
C	2.091158	2.264584	-0.015036
C	1.620152	3.573651	-0.212263
C	0.277410	3.779297	-0.402228
C	-0.581754	2.664460	-0.363023
C	4.029958	3.634057	0.074546
C	2.786558	4.528088	-0.188113
H	3.803187	-1.105598	0.398730
H	5.168285	0.923531	0.440578
H	-0.133120	4.768453	-0.575464
H	-1.645714	2.826598	-0.503887
H	4.531910	3.908245	1.006949
H	4.775471	3.733428	-0.719110
H	2.660851	5.288666	0.587749
H	2.870878	5.065969	-1.136849
P	-1.242235	-0.046881	-0.033763
C	-1.944645	-0.005051	1.650612
C	-1.729051	1.034164	2.553870
C	-2.254308	0.966876	3.838081
C	-3.001357	-0.133945	4.232020
C	-3.216353	-1.177647	3.340293
C	-2.683103	-1.118840	2.062362
H	-1.147242	1.898367	2.254497
H	-2.077696	1.780853	4.532834
H	-3.409827	-0.183666	5.235360
H	-3.791458	-2.045205	3.644628
H	-2.841909	-1.945943	1.376989
C	-2.637694	0.304024	-1.152861
C	-3.889706	0.718167	-0.700072
C	-4.914419	0.959792	-1.605747
C	-4.698489	0.790843	-2.966049
C	-3.453950	0.373585	-3.422121
C	-2.429217	0.124202	-2.522900
H	-4.066728	0.851909	0.361001
H	-5.884678	1.282819	-1.244081
H	-5.500761	0.978813	-3.671177
H	-3.282215	0.231490	-4.483415
H	-1.465113	-0.220790	-2.881132
Sb	0.876272	-2.058725	0.078332
Cl	2.928311	-3.418384	0.084882
Cl	0.688716	-2.153326	-2.309013

Table S18. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**9C**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the effective-core potential for Bi (ECP60MDF at the cc-pVTZ) in accordance with B. Metz, H. Stoll, M. Dolg, (2000). *J. Chem. Phys*. **113**, 2563

atom	X	Y	Z
C	-0.560204	1.526162	-0.166364
C	0.857081	1.571983	-0.009137
C	1.768885	0.488557	0.162448
C	3.112306	0.762987	0.318543
C	3.645786	2.071964	0.310346
C	2.796949	3.126001	0.113985
C	1.424586	2.864746	-0.046324
C	0.691295	4.041980	-0.271885
C	-0.663847	3.958185	-0.465457
C	-1.271229	2.689378	-0.401618
C	3.033669	4.611208	0.013983
C	1.632426	5.219529	-0.269834
H	3.805245	-0.064652	0.433765
H	4.714442	2.210899	0.437986
H	-1.271619	4.835529	-0.659949
H	-2.345178	2.623682	-0.544036
H	3.462201	5.004859	0.940274
H	3.746065	4.847371	-0.781150
H	1.346543	5.955112	0.487343
H	1.607355	5.740203	-1.231492
P	-1.376903	-0.086985	-0.018640
C	-2.094724	-0.133478	1.660736
C	-2.017269	0.928798	2.559485
C	-2.530422	0.799627	3.844064
C	-3.127952	-0.386877	4.243460
C	-3.205049	-1.453664	3.355963
C	-2.683201	-1.331853	2.078019
H	-1.553895	1.860072	2.254949
H	-2.462498	1.633407	4.534433
H	-3.527806	-0.484601	5.246700
H	-3.664656	-2.386562	3.663468
H	-2.736646	-2.174672	1.395139
C	-2.799711	-0.037807	-1.156886
C	-4.104168	0.219942	-0.736682
C	-5.141767	0.245701	-1.659258
C	-4.886447	0.015039	-3.003735
C	-3.589294	-0.247938	-3.426615
C	-2.550100	-0.281770	-2.509797
H	-4.313213	0.398379	0.312116
H	-6.153203	0.447955	-1.323655
H	-5.698770	0.034434	-3.722028
H	-3.385522	-0.437781	-4.474655
H	-1.541267	-0.505765	-2.841090
Bi	1.152620	-1.706884	0.065147
Cl	3.544636	-2.583440	0.275670
Cl	1.074945	-1.779624	-2.421573

Table S19. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**6B**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
P	0.913689	0.015978	0.063133
Cl	-0.072434	1.931757	2.516023
P	0.007315	-0.356389	2.125236
Cl	0.004550	-2.647620	1.519114
C	-1.737394	-0.135330	-0.040954
C	-1.667598	-0.279583	1.359932
C	-2.996369	-0.103085	-0.641397
C	-4.194247	-0.215734	0.079119
C	-2.842944	-0.379147	2.070897
H	-2.806329	-0.483169	3.150058
C	-0.791552	0.208113	-2.241910
H	0.066822	0.369127	-2.885464
C	-0.613089	0.011940	-0.884340
C	0.996543	2.744595	-0.440827
H	-0.083844	2.696010	-0.403166
C	-2.079470	0.226894	-2.823290
H	-2.171724	0.377277	-3.893576
C	1.758154	1.591171	-0.241065
C	2.083906	-1.279153	-0.405266
C	3.150225	1.671136	-0.276635
H	3.754942	0.783505	-0.139470
C	3.084761	-1.635462	0.499393
H	3.114791	-1.188850	1.487565
C	2.021643	-1.898035	-1.649145
H	1.226697	-1.655240	-2.343400
C	2.965097	-2.856037	-1.992301
H	2.907823	-3.341770	-2.959933
C	-4.113893	-0.352284	1.441821
H	-5.002980	-0.437610	2.057900
C	3.968127	-3.199451	-1.097768
H	4.700195	-3.952815	-1.366682
C	-3.184885	0.067132	-2.017857
C	3.770598	2.890036	-0.506573
H	4.853172	2.942888	-0.533294
C	4.024663	-2.590730	0.149526
H	4.793384	-2.871962	0.860230
C	1.623347	3.956459	-0.678072
H	1.024487	4.847108	-0.830584
C	-4.668312	0.050379	-2.295155
H	-4.929946	-0.761407	-2.979935
H	-4.990939	0.977481	-2.777363
C	-5.341892	-0.136688	-0.899778
H	-6.010278	0.696536	-0.665515
H	-5.953270	-1.043006	-0.871770
C	3.009423	4.032488	-0.708068
H	3.496889	4.984014	-0.890193

Table S20. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**7B**) optimized at the B3PW91/6-311+G(2df,p) level of theory.

atom	X	Y	Z
C	4.612927	0.313390	2.529708
H	4.848365	-0.430392	3.296322
H	4.925796	1.281190	2.931757
C	5.325696	-0.006598	1.180315
H	6.009037	0.796174	0.889938
H	5.928117	-0.916338	1.253956
C	0.599825	0.164576	1.012752
C	0.746282	0.482004	2.351664
H	-0.130318	0.700165	2.952862
C	2.016179	0.549961	2.964651
H	2.081880	0.799454	4.018210
C	3.139183	0.309713	2.206412
C	2.986617	0.014719	0.845869
C	4.207414	-0.167682	0.178608
C	4.175620	-0.425190	-1.167606
H	5.085129	-0.569474	-1.741401
C	2.925862	-0.498392	-1.833436
H	2.927277	-0.695959	-2.900378
C	1.729673	-0.327676	-1.175569
C	1.743118	-0.064041	0.209795
C	-2.034944	-1.244484	0.683450
C	-1.833516	-1.867862	1.910376
H	-0.986952	-1.596928	2.529183
C	-2.703642	-2.863418	2.331047
H	-2.538270	-3.351383	3.284994
C	-3.770654	-3.242086	1.529754
H	-4.444681	-4.025452	1.858133
C	-3.964751	-2.631823	0.297202
H	-4.782976	-2.941712	-0.342800
C	-3.098009	-1.639753	-0.129892
H	-3.236030	-1.191623	-1.108311
C	-1.830426	1.636711	0.321845
C	-1.102389	2.828831	0.326917
H	-0.029589	2.811285	0.188405
C	-1.756993	4.037883	0.495884
H	-1.185198	4.958813	0.495505
C	-3.136063	4.071120	0.652387
H	-3.644863	5.020246	0.780808
C	-3.863295	2.889137	0.646435
H	-4.939769	2.909078	0.774228
C	-3.215907	1.673671	0.483657
H	-3.791975	0.756993	0.498366
P	-0.944276	0.072469	0.097314
Cl	0.121478	1.934274	-2.548114
Cl	-0.050976	-2.786631	-1.340367
As	-0.015643	-0.450527	-2.064505

Table S21. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**8B**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the effective-core potential for Sb (ECP28MDF at the cc-pVTZ) in accordance with B. Metz, H. Stoll, M. Dolg, (2000). *J. Chem. Phys*. **113**, 2563.

atom	X	Y	Z
C	4.497944	1.405098	2.533608
H	4.681068	1.017267	3.539765
H	4.791777	2.458505	2.550507
C	5.287064	0.605907	1.455398
H	5.999823	1.243827	0.925680
H	5.868804	-0.203932	1.904644
C	0.578555	0.632718	0.962875
C	0.658576	1.431139	2.090762
H	-0.251179	1.838543	2.519888
C	1.889581	1.748981	2.700229
H	1.899163	2.379244	3.582958
C	3.047580	1.254264	2.149565
C	2.968406	0.466478	0.992200
C	4.230418	0.067569	0.522161
C	4.291099	-0.675634	-0.626380
H	5.236588	-1.009357	-1.041315
C	3.087295	-1.006967	-1.296145
H	3.166181	-1.585865	-2.211424
C	1.846697	-0.623362	-0.837524
C	1.761965	0.135182	0.354132
C	-1.973401	-0.886622	1.238915
C	-1.676193	-1.070533	2.585667
H	-0.814352	-0.584206	3.025767
C	-2.472273	-1.898667	3.364221
H	-2.231171	-2.042865	4.411443
C	-3.562602	-2.547801	2.804074
H	-4.178710	-3.199239	3.413891
C	-3.853310	-2.379145	1.456567
H	-4.690006	-2.902927	1.008544
C	-3.058550	-1.558569	0.673603
H	-3.274203	-1.457802	-0.385052
C	-1.929763	1.717871	-0.068840
C	-1.273200	2.849141	-0.559371
H	-0.218186	2.806206	-0.795667
C	-1.978111	4.025082	-0.759953
H	-1.461399	4.896552	-1.145593
C	-3.336320	4.084763	-0.478684
H	-3.884198	5.006930	-0.638770
C	-3.991867	2.963259	0.009734
H	-5.050980	3.005613	0.238243
C	-3.294568	1.782071	0.215236
H	-3.814454	0.918599	0.611209
P	-0.980030	0.189837	0.172190
Cl	0.200680	1.181482	-3.020553
Cl	-0.111749	-3.164350	-0.348958
Sb	0.018508	-1.114847	-1.876631

Table S22. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**9B**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the effective-core potential for Bi (ECP60MDF at the cc-pVTZ) in accordance with B. Metz, H. Stoll, M. Dolg, (2000). *J. Chem. Phys*. **113**, 2563.

atom	X	Y	Z
Bi	0.064700	-1.942531	-0.506202
Cl	-0.156381	-2.448316	2.072833
Cl	0.415434	-1.324531	-3.079587
P	-1.021710	0.507295	0.021918
C	5.197997	1.966360	0.694762
H	5.924366	2.045072	-0.118738
H	5.770864	1.766333	1.604677
C	4.349575	3.263835	0.830265
H	4.492443	3.741649	1.803713
H	4.626148	4.007528	0.077498
C	1.888646	-0.696709	-0.045383
C	3.155194	-1.236956	-0.050121
H	3.289933	-2.295335	-0.253099
C	4.320745	-0.469705	0.193070
H	5.289974	-0.957380	0.175493
C	4.192889	0.872782	0.429803
C	2.904247	1.431867	0.431112
C	2.920714	2.817771	0.649753
C	1.733175	3.508427	0.647934
H	1.694549	4.582333	0.795225
C	0.535806	2.793959	0.442289
H	-0.400120	3.343644	0.435408
C	0.516244	1.424335	0.245938
C	1.731567	0.686315	0.211405
C	-2.036742	1.405993	-1.186911
C	-1.586394	1.486240	-2.506957
H	-0.678850	0.974039	-2.807530
C	-2.319166	2.200568	-3.441574
H	-1.967401	2.251951	-4.465775
C	-3.496513	2.838168	-3.072433
H	-4.066022	3.395726	-3.808018
C	-3.945494	2.759277	-1.761598
H	-4.863032	3.256847	-1.467484
C	-3.221697	2.044399	-0.817677
H	-3.578597	1.991043	0.203636
C	-1.950827	0.466156	1.575164
C	-1.497920	1.109890	2.722767
H	-0.570561	1.669327	2.702915
C	-2.228195	1.021833	3.899830
H	-1.867239	1.520800	4.792120
C	-3.405189	0.289911	3.938392
H	-3.969087	0.216756	4.861674
C	-3.853745	-0.364693	2.797947
H	-4.763905	-0.952813	2.828553
C	-3.127713	-0.284030	1.622087
H	-3.475074	-0.814461	0.741319

Table S23. Final Cartesian coordinates (x, y, z in Å) for the structure of (**6B$_{pcm}$**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the solvent=acetonitrile modelled as a polarizable continuum (pcm).

atom	X	Y	Z
P	0.914634	0.010438	0.002857
Cl	0.058715	1.924908	2.580487
P	0.041702	-0.322361	2.092073
Cl	-0.025510	-2.738027	1.509898
C	-1.734949	-0.144597	-0.037922
C	-1.642586	-0.234386	1.367475
C	-3.006262	-0.123490	-0.611872
C	-4.190977	-0.187354	0.137342
C	-2.805117	-0.291659	2.108227
H	-2.748712	-0.359512	3.189810
C	-0.834658	0.079475	-2.274585
H	0.007261	0.197009	-2.947628
C	-0.626888	-0.049989	-0.911399
C	0.903386	2.715115	-0.607130
H	-0.173031	2.613703	-0.667432
C	-2.134249	0.083106	-2.827311
H	-2.246762	0.178024	-3.901375
C	1.701387	1.611437	-0.296793
C	2.119633	-1.264355	-0.413846
C	3.087241	1.757604	-0.224257
H	3.721964	0.910146	0.001524
C	3.128570	-1.564325	0.503184
H	3.154072	-1.084241	1.475406
C	2.079424	-1.913603	-1.645079
H	1.289582	-1.704832	-2.355574
C	3.053142	-2.851147	-1.960454
H	3.017353	-3.357033	-2.918394
C	-4.087953	-0.268816	1.504953
H	-4.965869	-0.316050	2.140034
C	4.062936	-3.141854	-1.053213
H	4.820894	-3.875580	-1.303161
C	-3.224851	-0.018805	-1.991679
C	3.665644	2.995965	-0.459909
H	4.743037	3.101441	-0.406251
C	4.098216	-2.500059	0.178886
H	4.878443	-2.732938	0.894186
C	1.489990	3.947331	-0.847649
H	0.865553	4.798218	-1.094422
C	-4.712177	-0.029895	-2.235093
H	-4.996523	-0.873425	-2.869863
H	-5.031798	0.873910	-2.760239
C	-5.356410	-0.133420	-0.819342
H	-5.999896	0.724852	-0.609196
H	-5.985061	-1.022982	-0.728995
C	2.869855	4.090319	-0.772111
H	3.325890	5.055558	-0.961475

Table S24. Final Cartesian coordinates (x, y, z in Å) for the gas-phase structure of (**7B$_{pcm}$**) optimized at the B3PW91/6-311+G(2df,p) level of theory with the solvent=acetonitrile modelled as a polarizable continuum (pcm).

atom	X	Y	Z
C	4.665070	0.206025	2.471913
H	4.921142	-0.576273	3.191391
H	4.977528	1.152769	2.920135
C	5.348802	-0.033063	1.092964
H	6.016190	0.791012	0.828069
H	5.960895	-0.938720	1.101041
C	0.618912	0.102157	1.040028
C	0.795720	0.349304	2.391734
H	-0.064354	0.527801	3.027491
C	2.078181	0.394241	2.977752
H	2.164582	0.584862	4.041432
C	3.186635	0.207003	2.182809
C	3.003550	-0.016091	0.811105
C	4.211715	-0.152503	0.109024
C	4.155848	-0.343174	-1.249625
H	5.054323	-0.449162	-1.847803
C	2.892887	-0.399588	-1.890752
H	2.873176	-0.549504	-2.965524
C	1.709036	-0.273718	-1.196345
C	1.746354	-0.074907	0.200717
C	-2.055415	-1.253026	0.688542
C	-1.882497	-1.885015	1.917571
H	-1.051614	-1.624971	2.561179
C	-2.774534	-2.870058	2.317733
H	-2.635015	-3.360598	3.274146
C	-3.834775	-3.227914	1.496269
H	-4.528467	-3.999116	1.811496
C	-4.001571	-2.606418	0.264564
H	-4.820080	-2.892597	-0.385698
C	-3.113238	-1.624487	-0.144331
H	-3.239712	-1.163902	-1.118021
C	-1.786816	1.643763	0.380125
C	-1.024289	2.796846	0.580560
H	0.056776	2.741997	0.601818
C	-1.653080	4.018456	0.762121
H	-1.056062	4.908389	0.924622
C	-3.039445	4.101068	0.734641
H	-3.528276	5.058280	0.877167
C	-3.799920	2.956910	0.530521
H	-4.882084	3.015791	0.514803
C	-3.179591	1.728971	0.355440
H	-3.786261	0.843446	0.214673
P	-0.940066	0.061991	0.153653
Cl	0.002734	1.995409	-2.560138
Cl	-0.016632	-2.833066	-1.416348
As	-0.051534	-0.400845	-2.037195