Supporting Information

for

Stabilization of bis(chlorogermyliumylidene)s within bifunctional PNNP ligand frameworks and their reactivity studies

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Contents

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CSIR-National Chemical Laboratory,
Pune-411008, Maharashtra,
India

2. Plots of NMR spectra

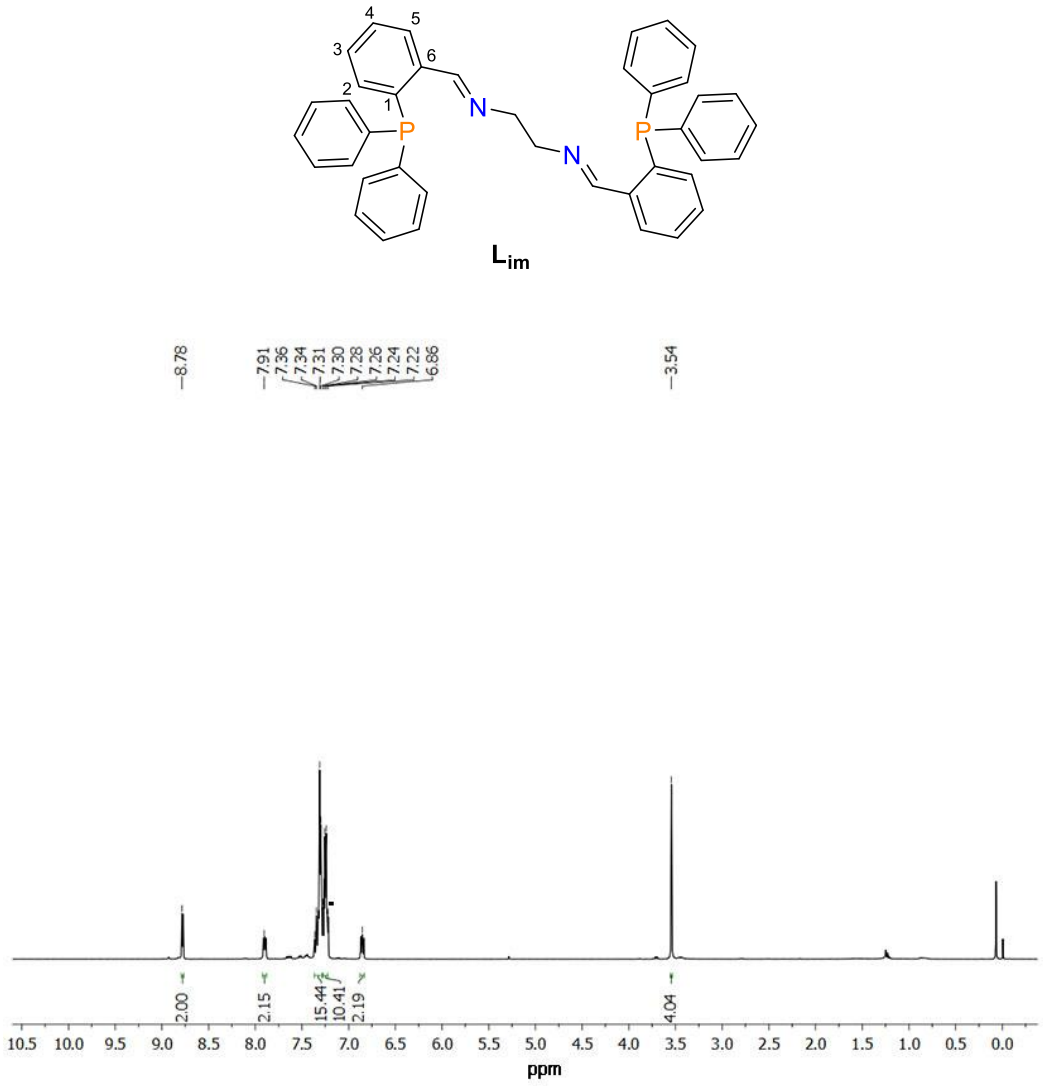


Figure S1. ^{1}H NMR of $\mathbf{L}_{im}$ in $CDCl_3$ (“= residual solvent peak)

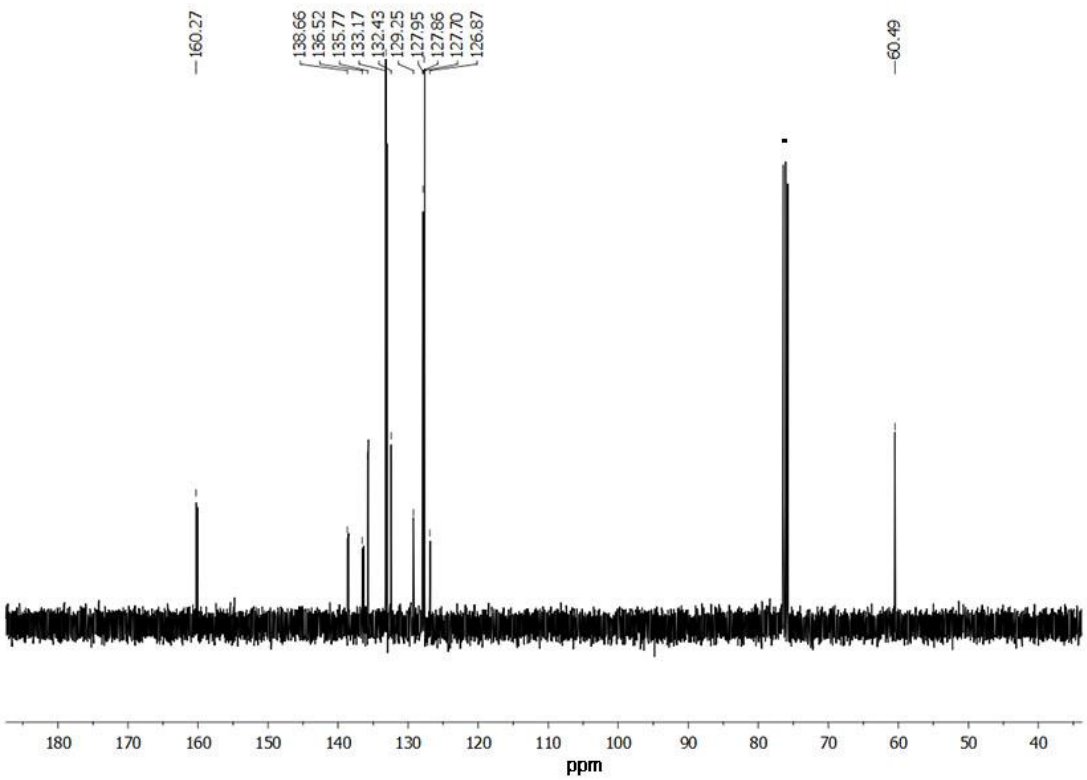


Figure S2. $^{13}C\{^{1}H\}$ NMR of $\mathbf{L}_{im}$ in $CDCl_3$ (“= residual solvent peak)

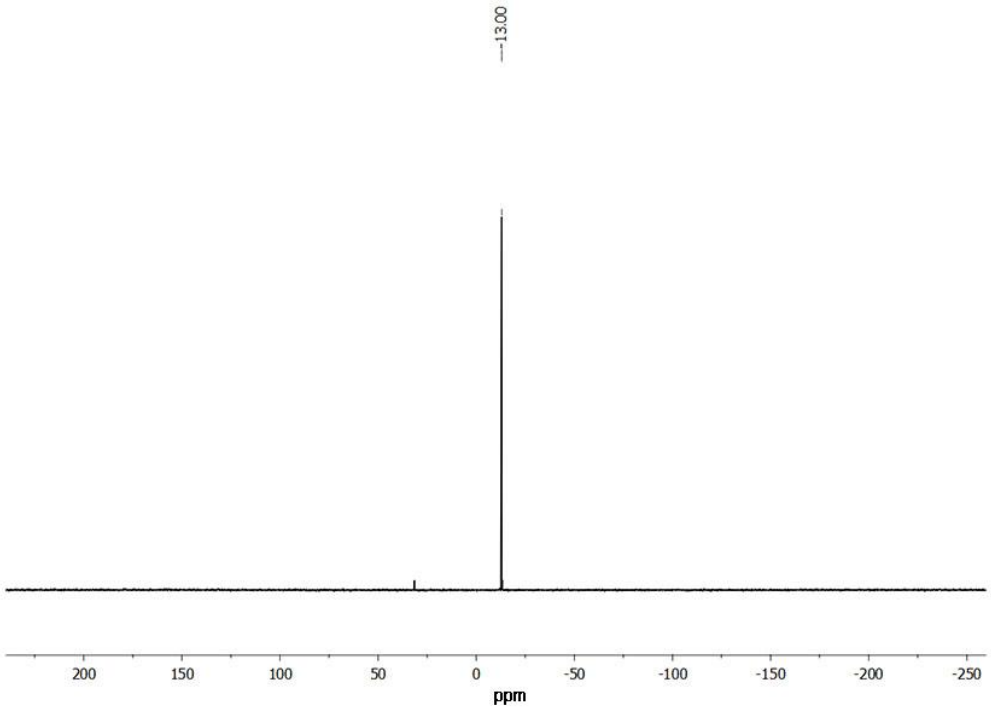


Figure S3. $^{31}P\{^{1}H\}$ NMR of $\mathbf{L}_{im}$ in $CDCl_3$

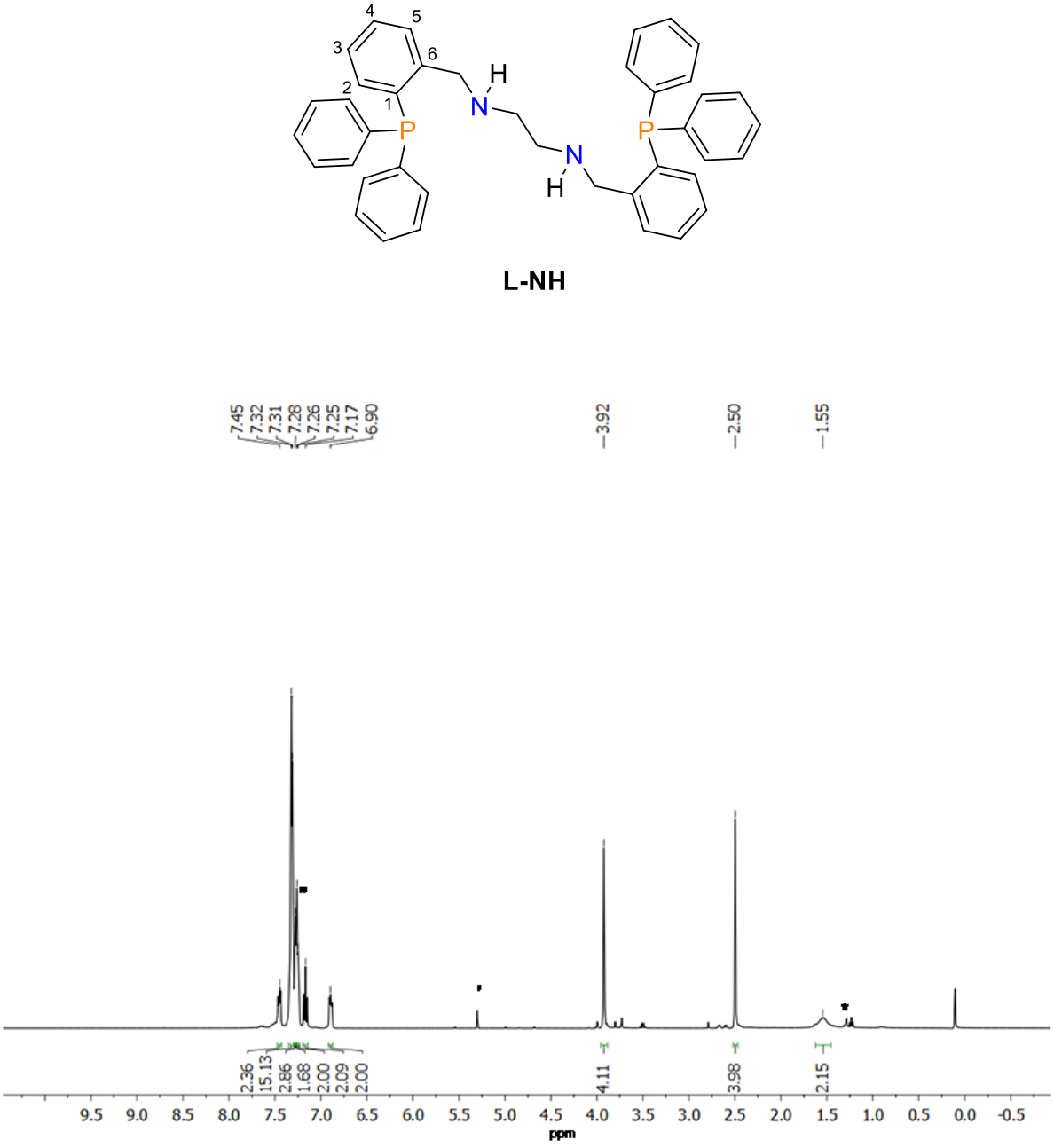


Figure S4. ^{1}H NMR of **L**-NH in $CDCl_3$ (“= residual solvent peak; ‘=DCM; *=impurity)

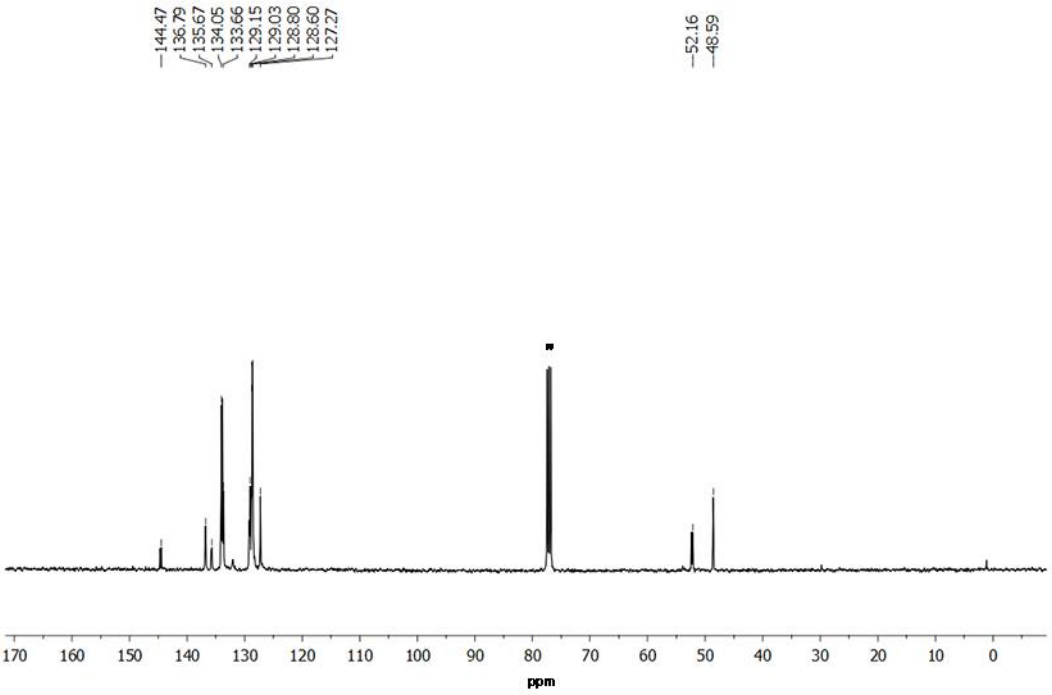


Figure S5. $^{13}C\{^{1}H\}$ NMR of **L**-NH in $CDCl_3$ (“= residual solvent peak)

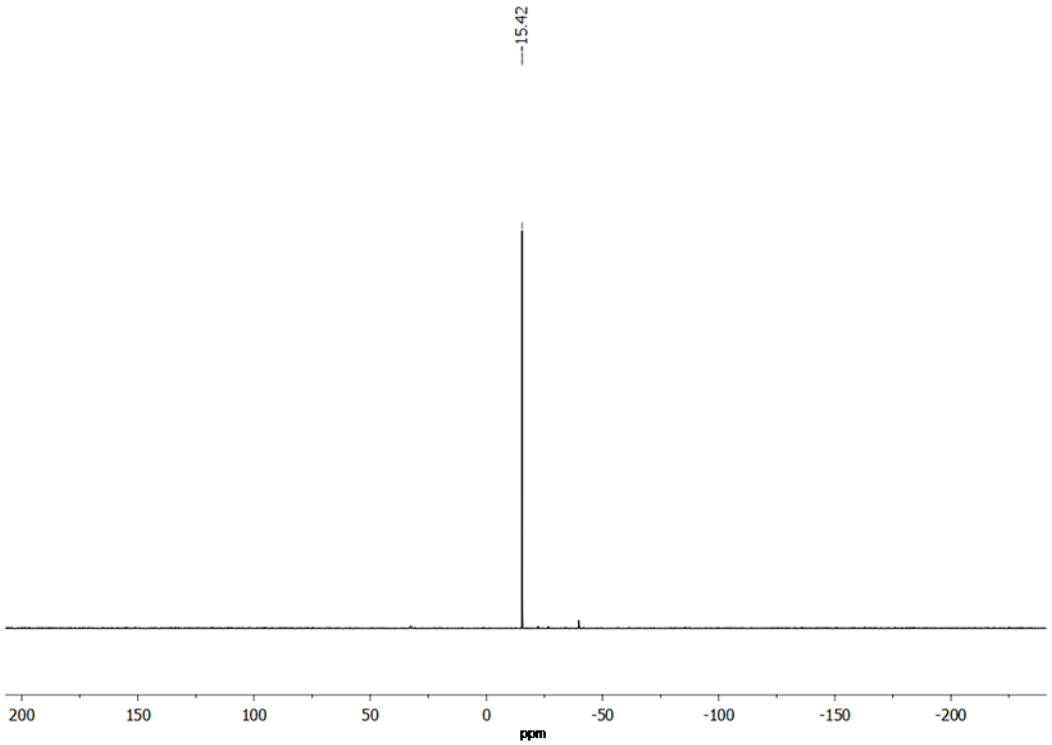


Figure S6. $^{31}P\{^{1}H\}$ NMR of **L**-NH in $CDCl_3$

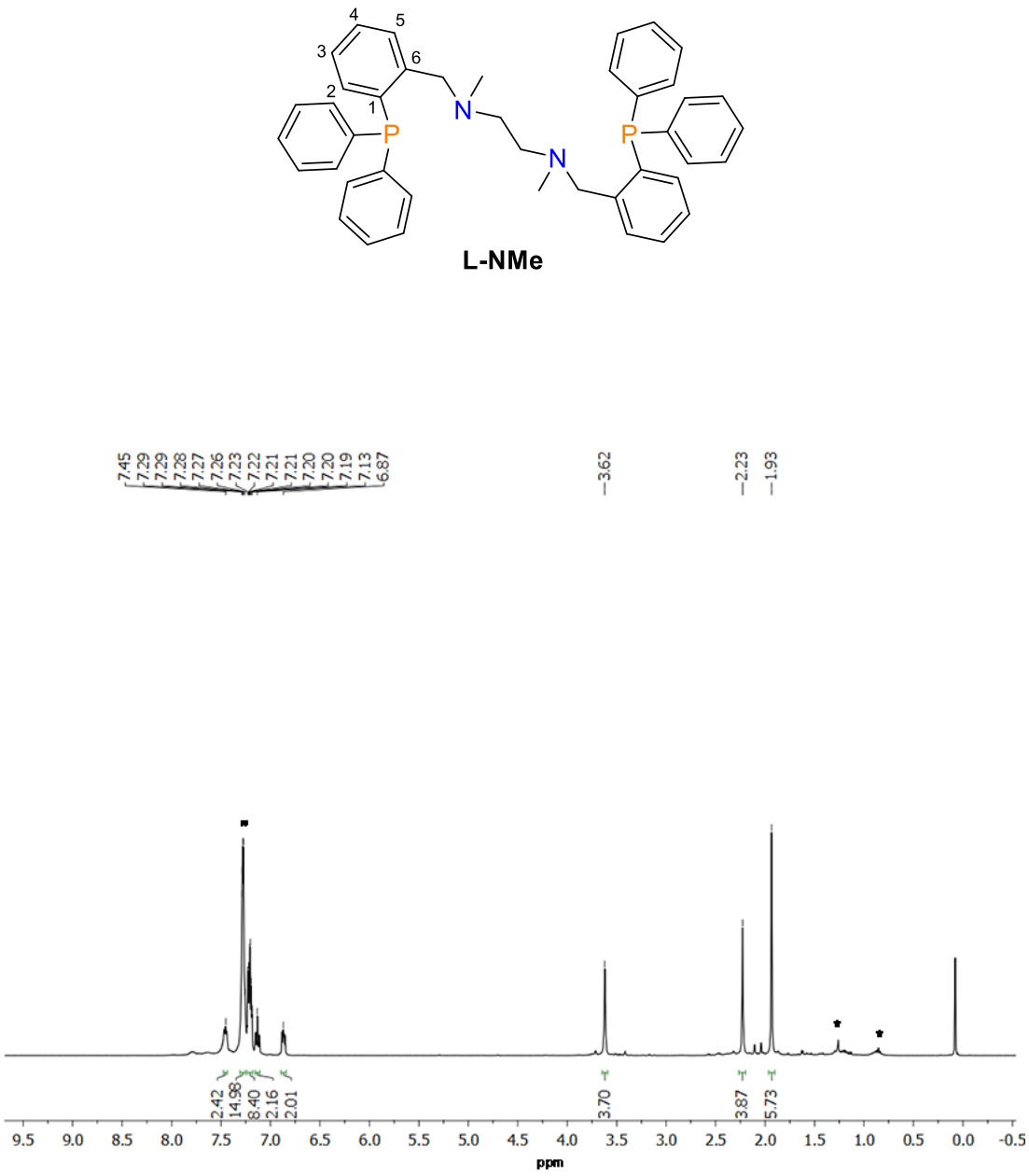


Figure S7. ^{1}H NMR of **L**-NMe in $CDCl_3$ (“= residual solvent peak; *=impurity)

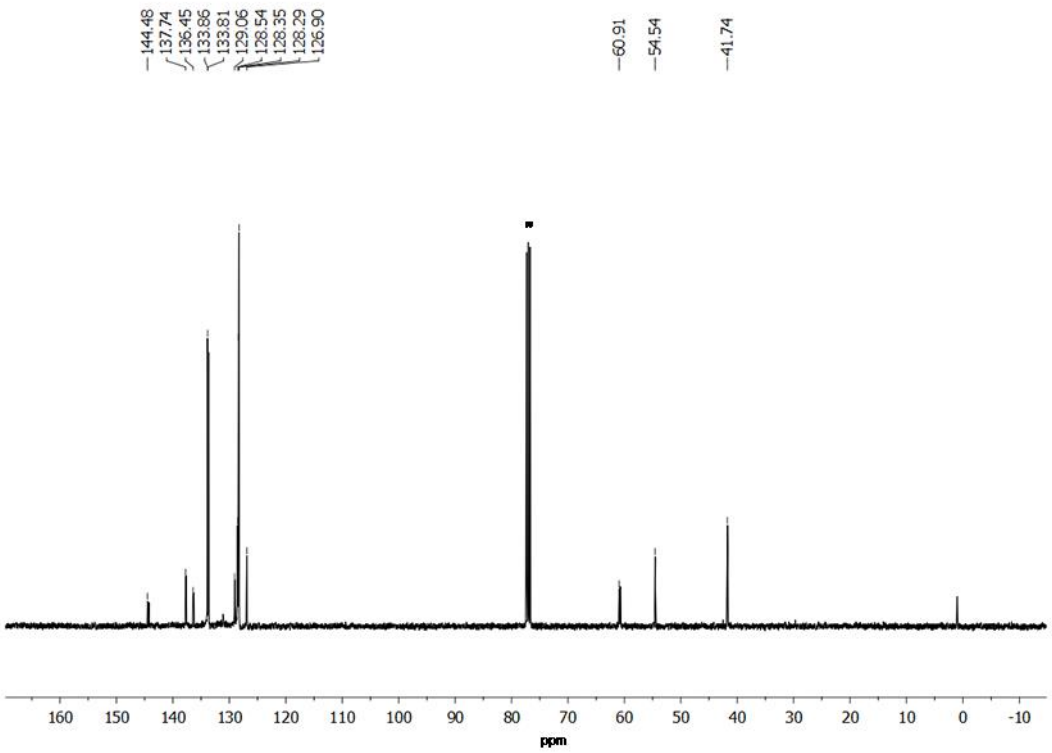


Figure S8. $^{13}C\{^{1}H\}$ NMR of **L**-NMe in $CDCl_3$ (“= residual solvent peak)

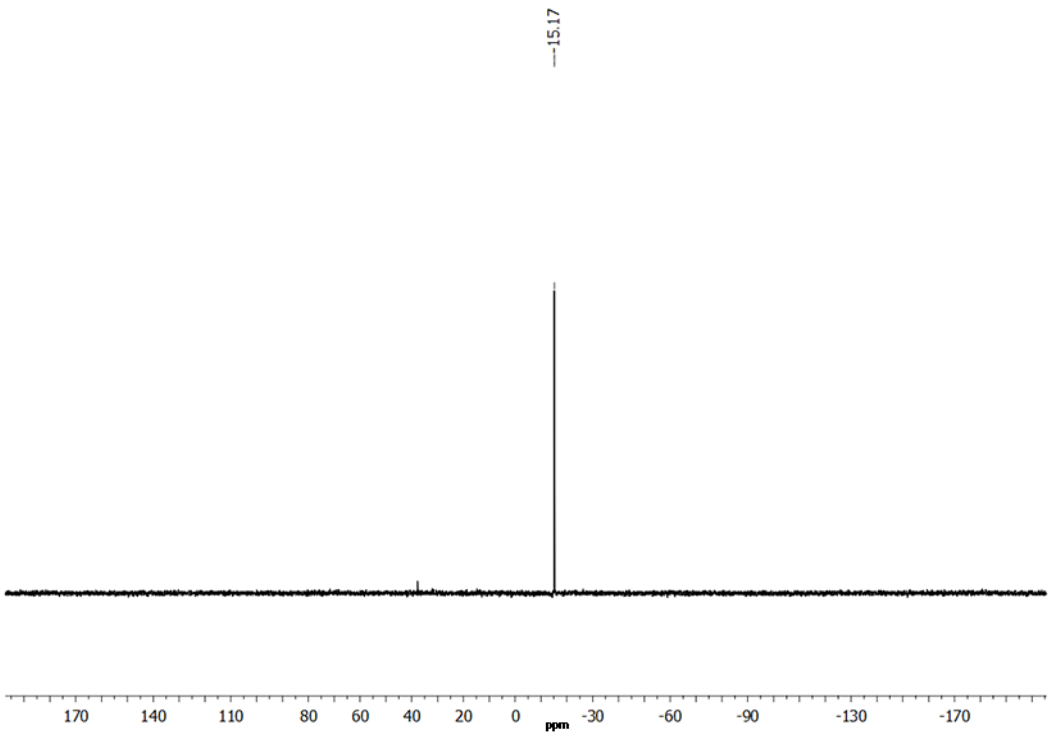


Figure S9. $^{31}P\{^{1}H\}$ NMR of **L**-NMe in $CDCl_3$

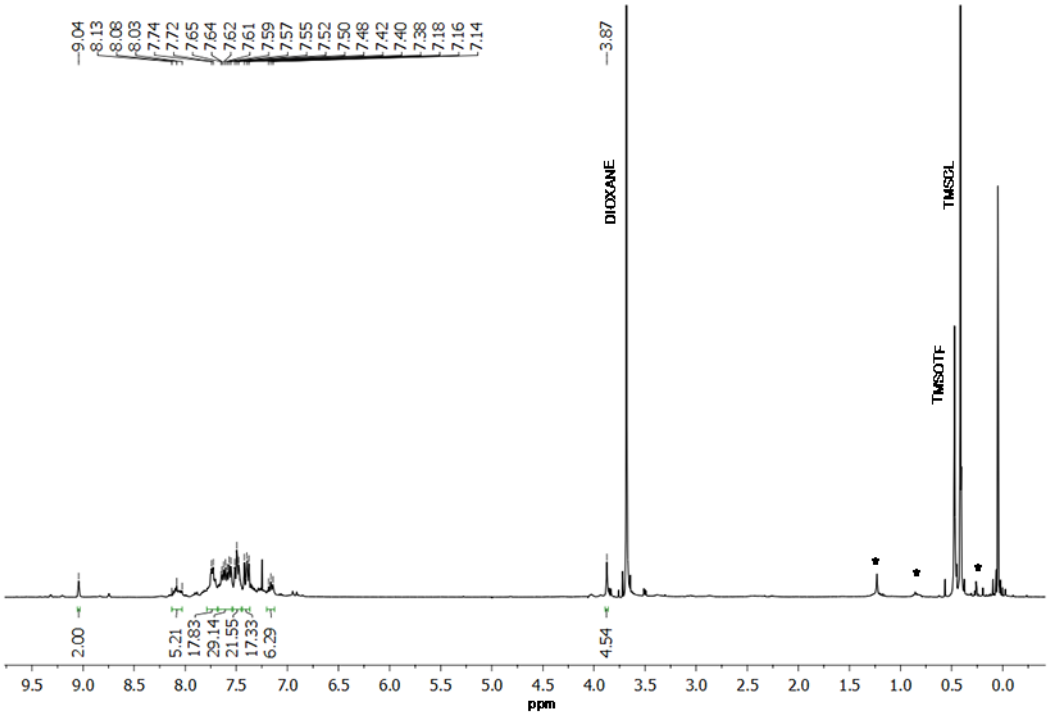


Figure S10. ^{1}H NMR of room temperature *in situ* generated **1** in $CDCl_3$ recorded after 2 hrs (*=impurity)

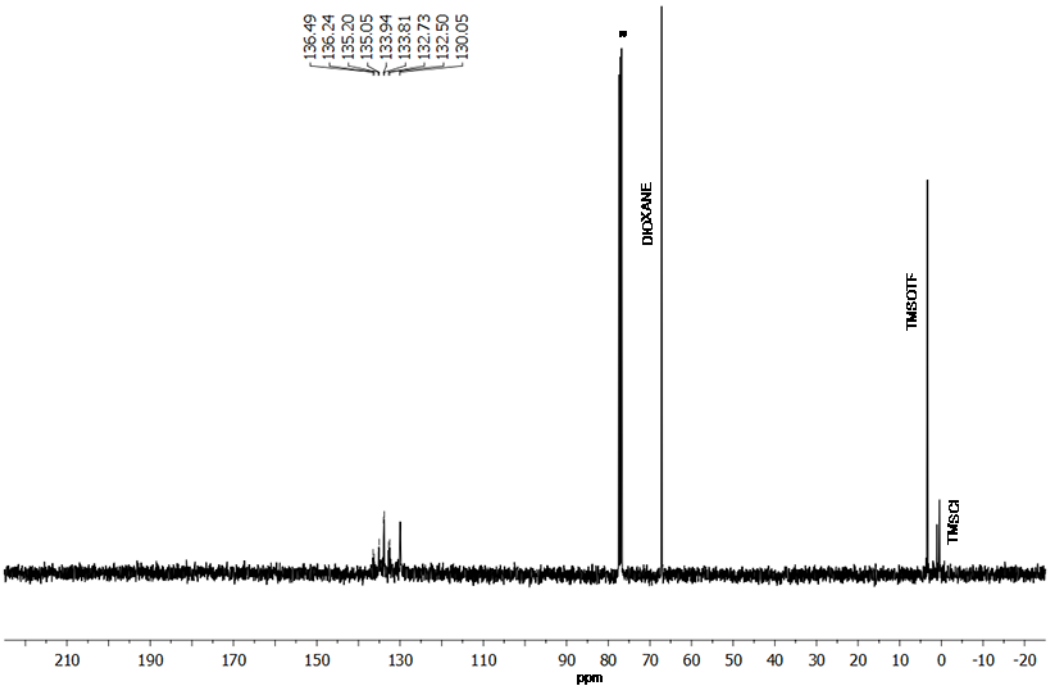


Figure S11. ^{13}C{^{1}H} NMR of room temperature *in situ* generated **1** in $CDCl_3$ recorded after 2 hrs (“= residual solvent peak)

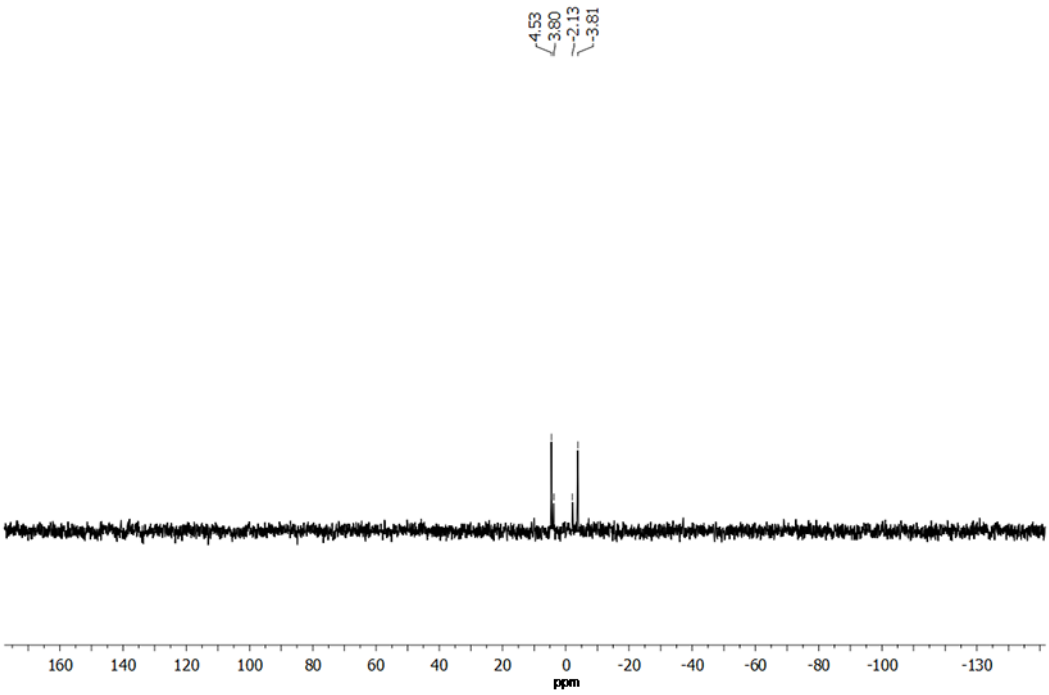


Figure S12. $^{31}P\{^{1}H\}$ NMR of room temperature *in situ* generated **1** in $CDCl_3$ recorded after 2 hrs

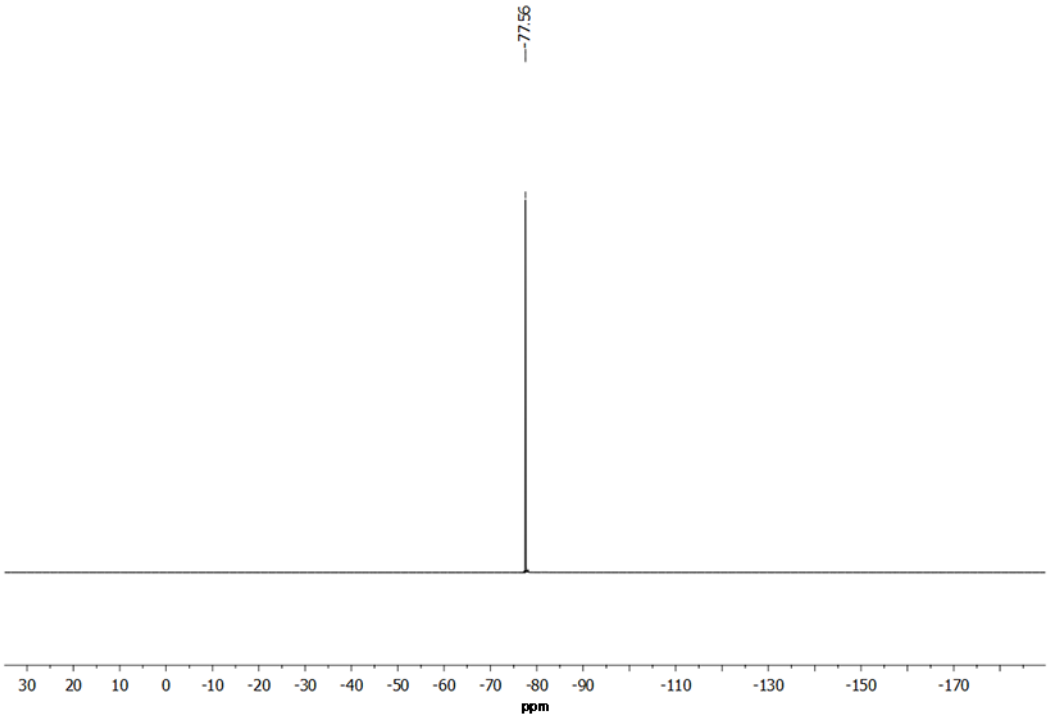


Figure S13. $^{19}F\{^{1}H\}$ NMR of room temperature *in situ* generated **1** in $CDCl_3$ recorded after 2 hrs

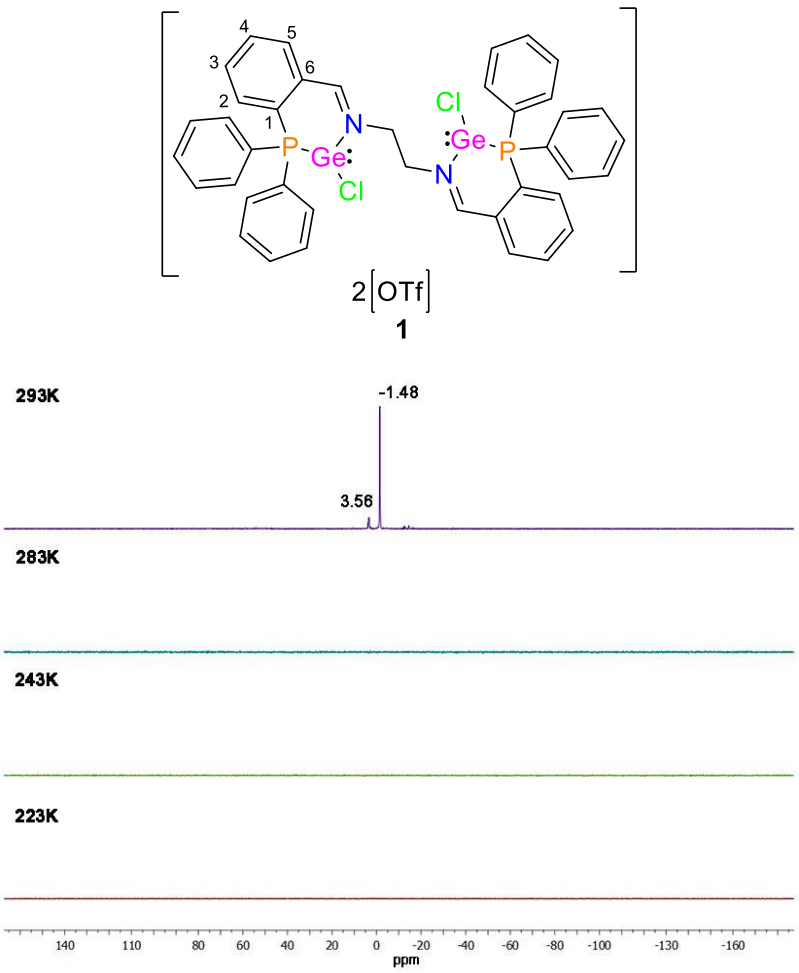


Figure S14. $^{31}P\{^{1}H\}$ VT NMR of *in situ* generated **1** in $CDCl_3$

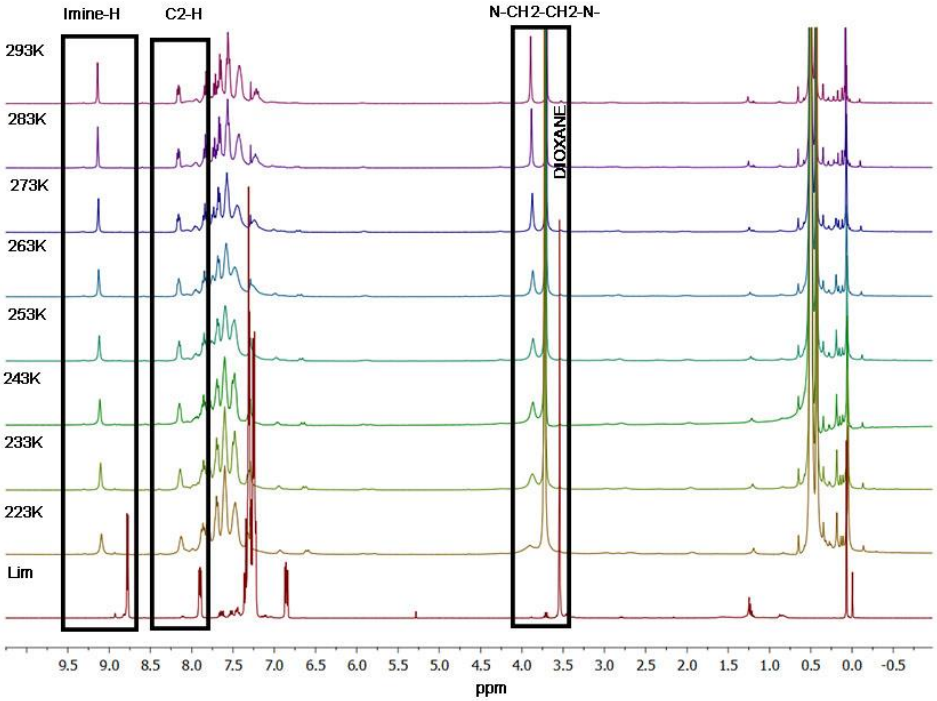


Figure S15. ^{1}H VT NMR of *in situ* generated **1** in $CDCl_3$

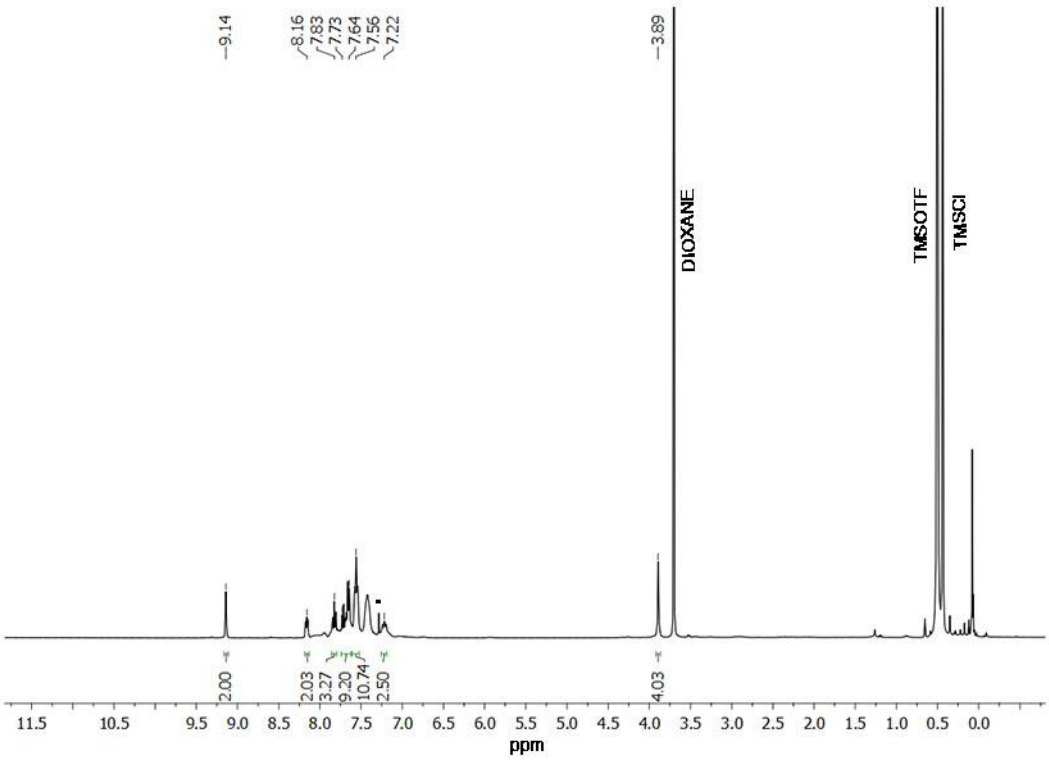


Figure S16. ^{1}H NMR of low temperature *in situ* generated **1** in $CDCl_3$ recorded immediately after thawing to 20 °C (“= residual solvent peak)

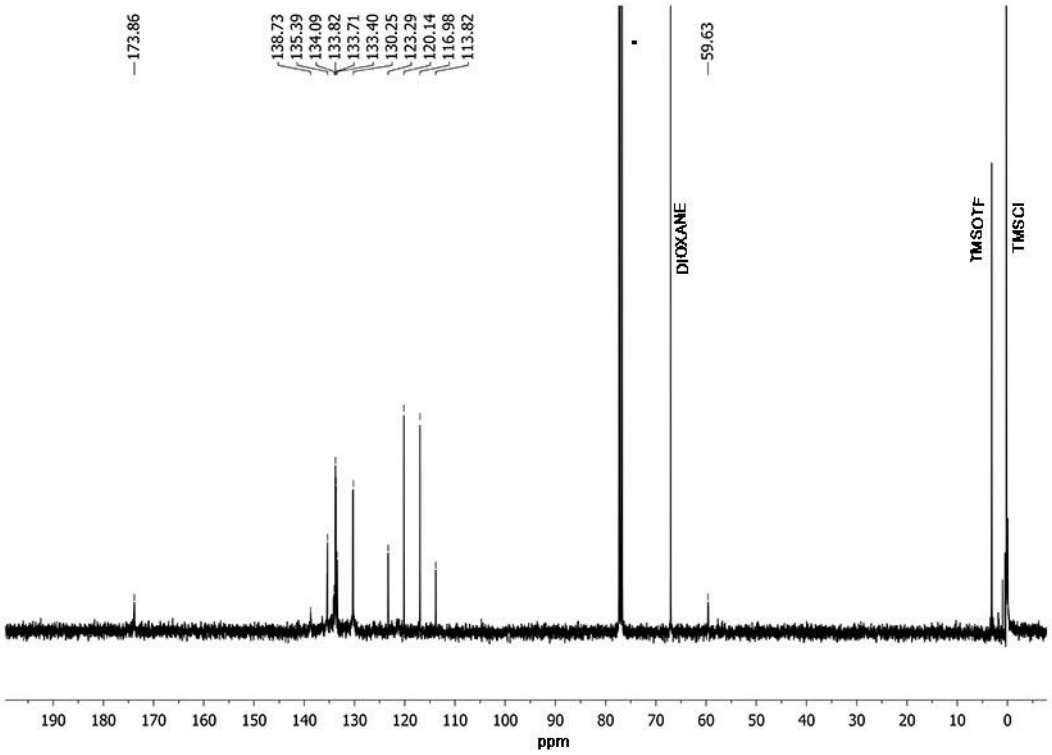


Figure S17. $^{13}C\{^{1}H\}$ NMR of low temperature *in situ* generated **1** in $CDCl_3$ recorded immediately after thawing to 20 °C (“= residual solvent peak)

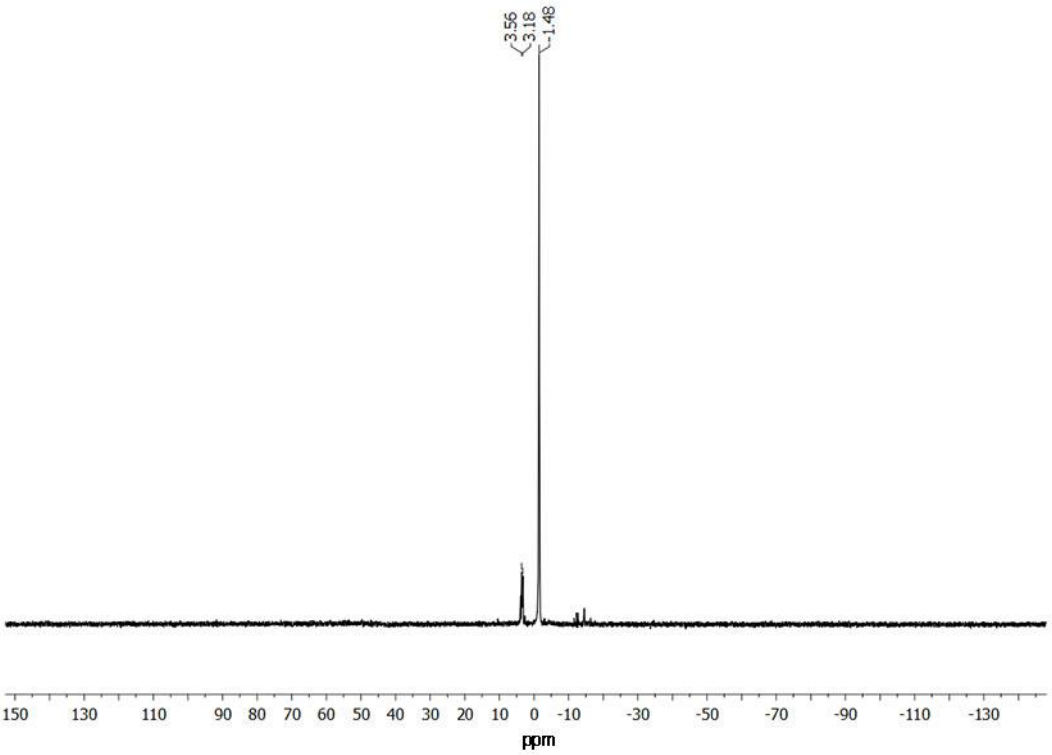


Figure S18. $^{31}P\{^{1}H\}$ NMR of low temperature *in situ* generated **1** in $CDCl_3$ recorded immediately after thawing to 20 °C

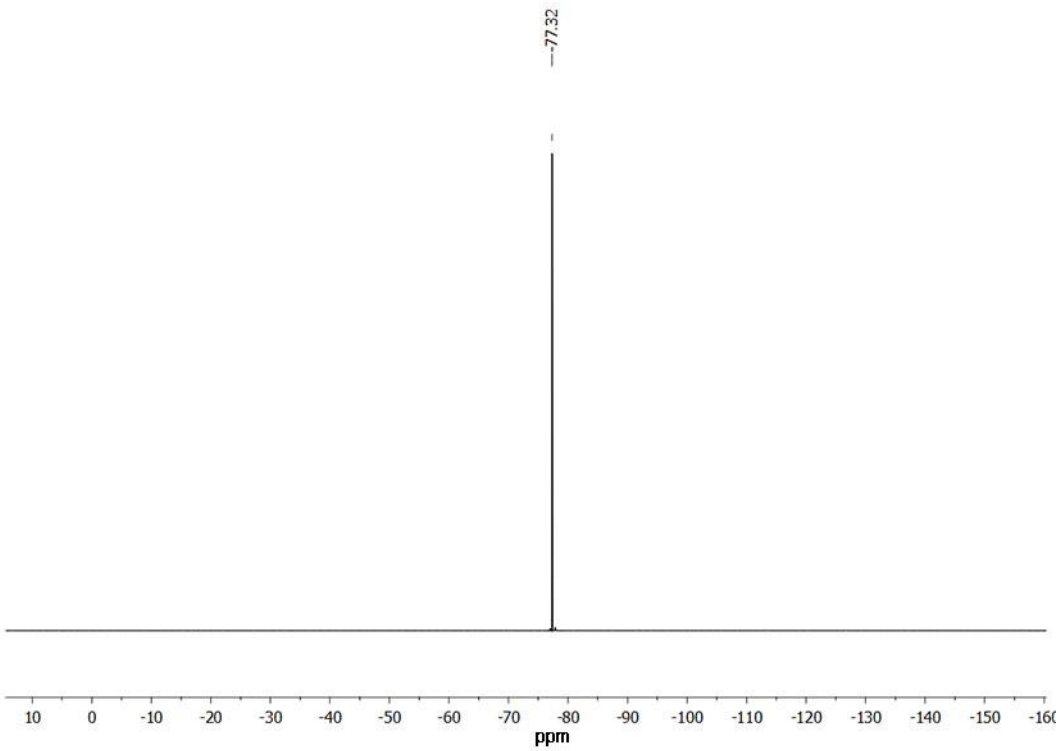
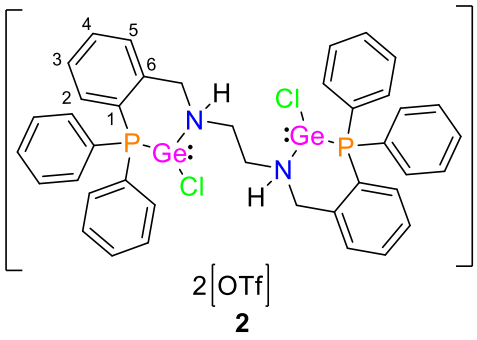


Figure S19. $^{19}F\{^{1}H\}$ NMR of low temperature *in situ* generated **1** in $CDCl_3$ recorded immediately after thawing to 20 °C



2

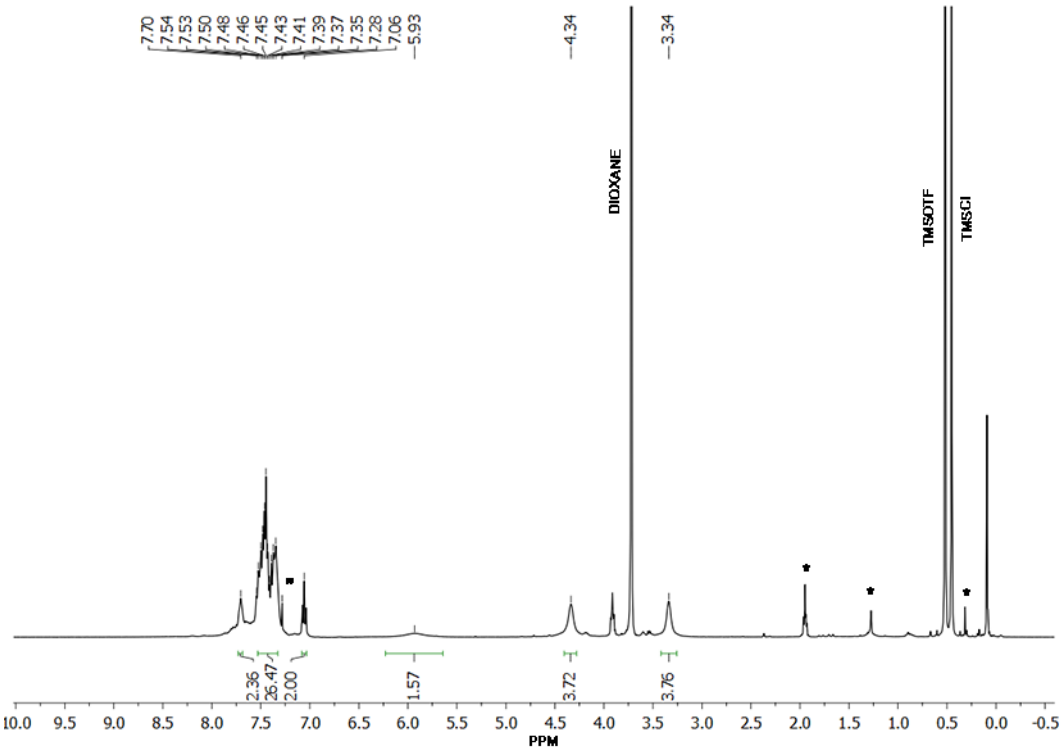


Figure S20. ^{1}H NMR of **2** in $CDCl_3$(“= residual solvent peak ; *=impurity)

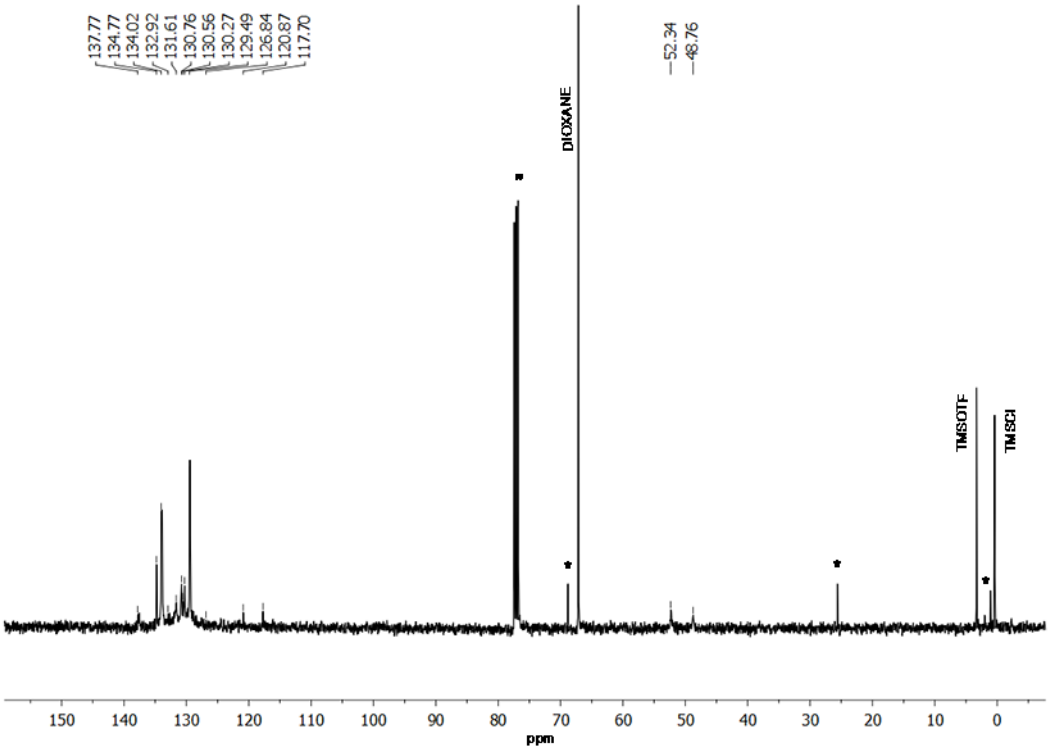


Figure S21. $^{13}C\{^{1}H\}$ NMR of **2** in $CDCl_3$ (“= residual solvent peak; *=impurity)

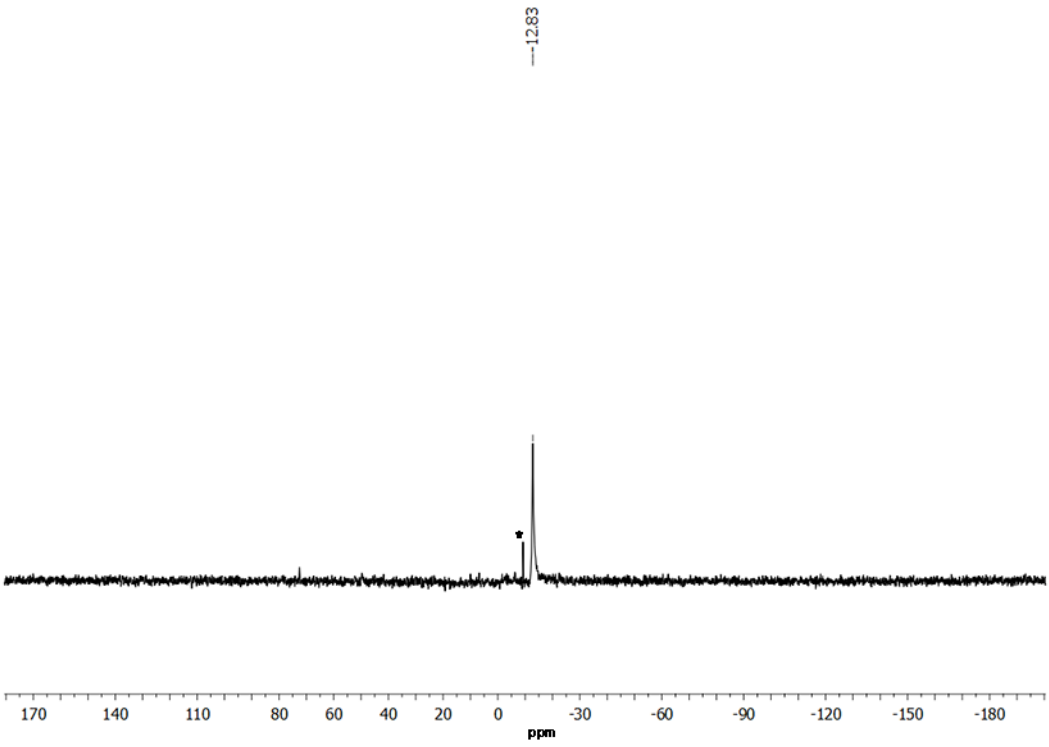


Figure S22. $^{31}P\{^{1}H\}$ NMR of **2** in $CDCl_3$ (*=impurity)

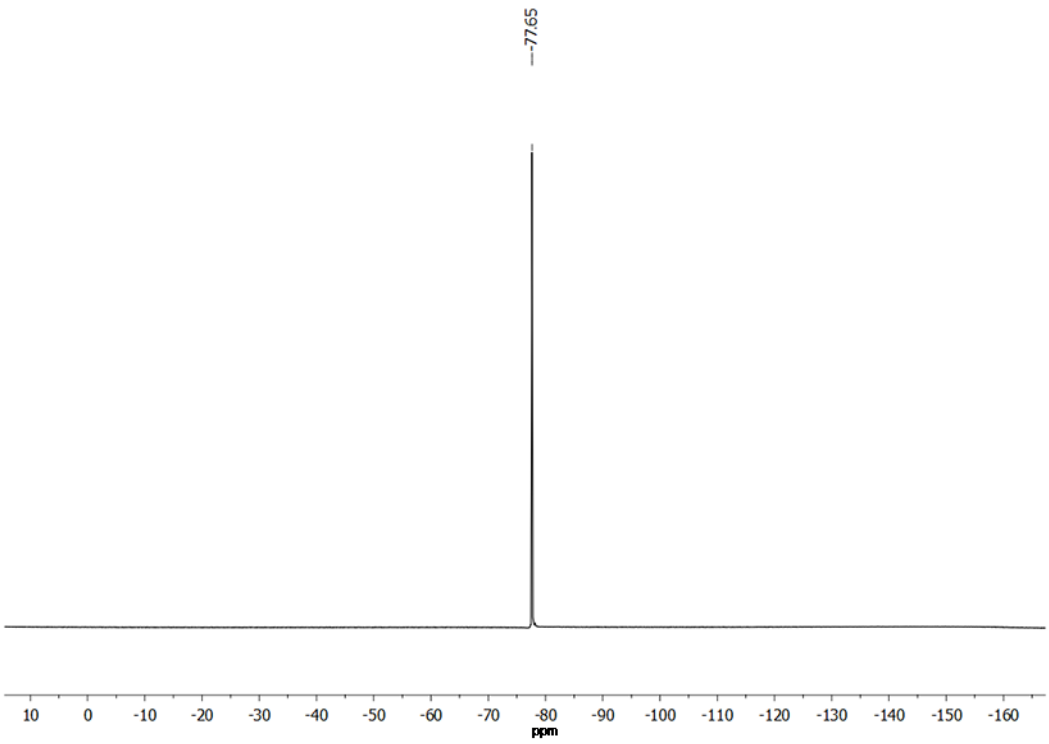


Figure S23. $^{19}F\{^{1}H\}$ NMR of **2** in $CDCl_3$

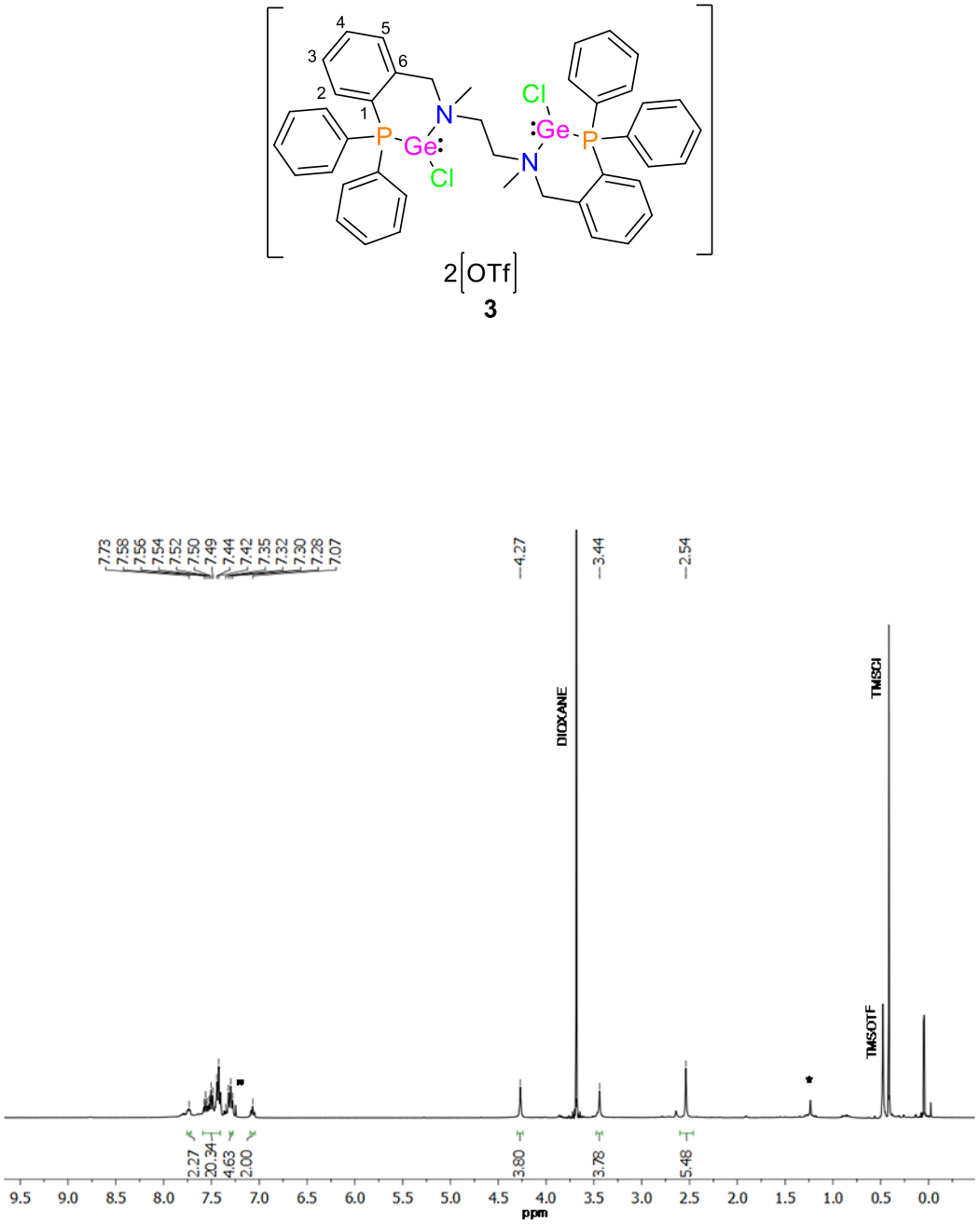


Figure S24. ^{1}H NMR of **3** in $CDCl_3$ (“= residual solvent peak; *=impurity)

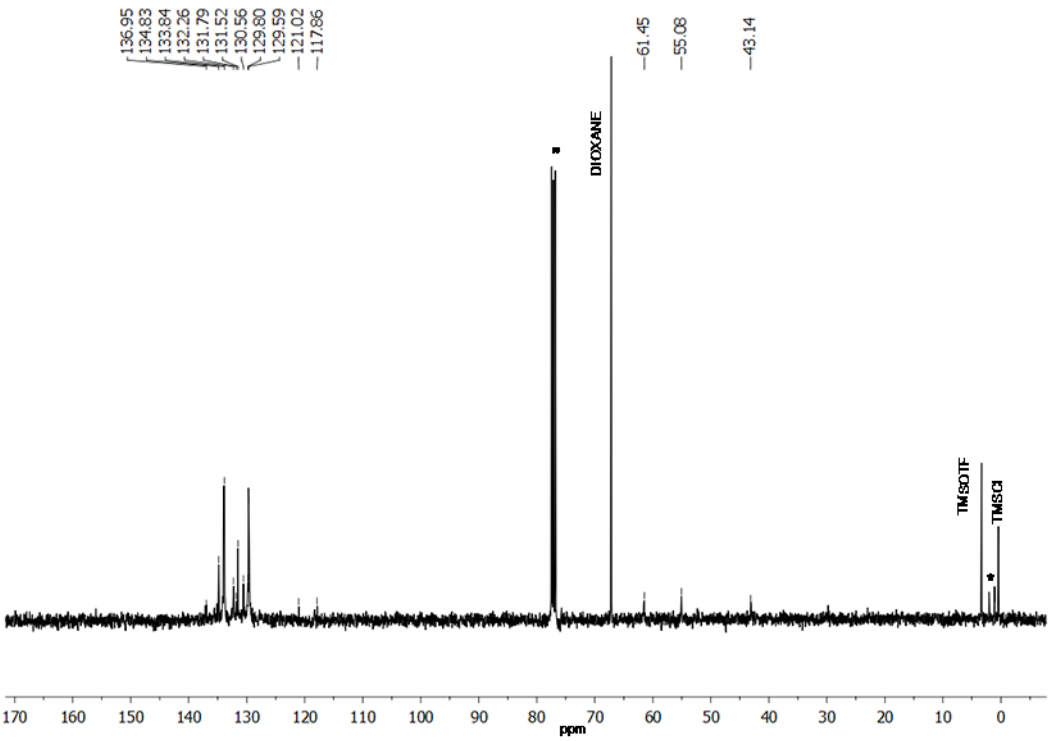


Figure S25. $^{13}C\{^{1}H\}$ NMR of **3** in $CDCl_3$ (“= residual solvent peak; *=impurity)

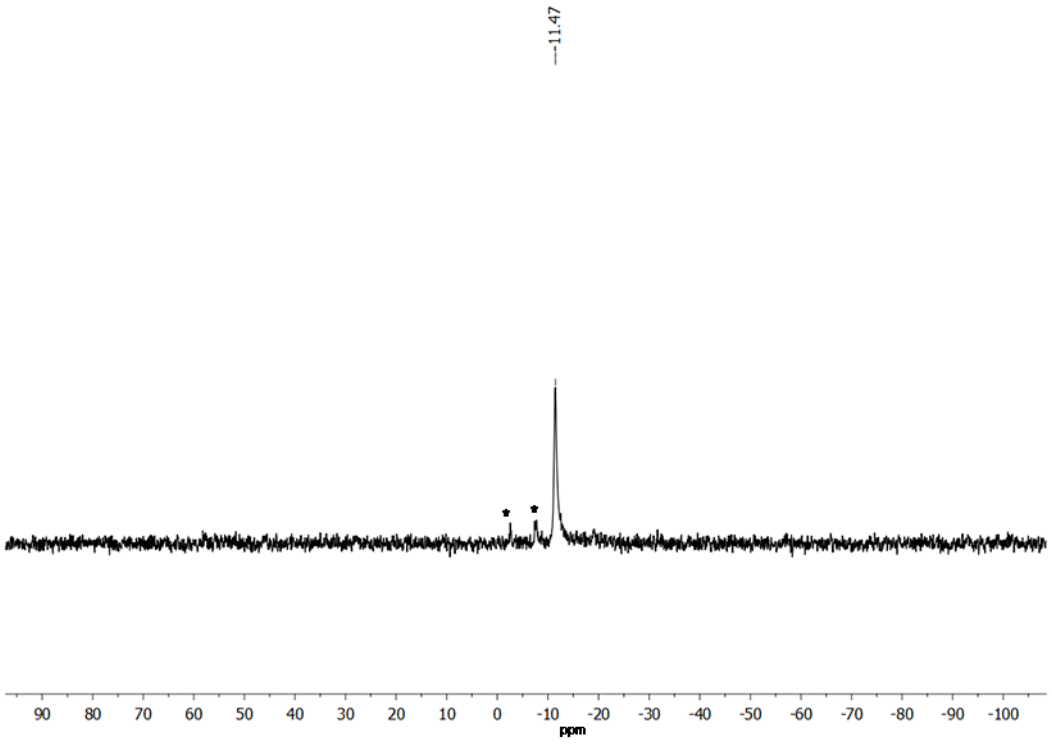


Figure S26. $^{31}P\{^{1}H\}$ NMR of **3** in $CDCl_3$ (*=impurity)

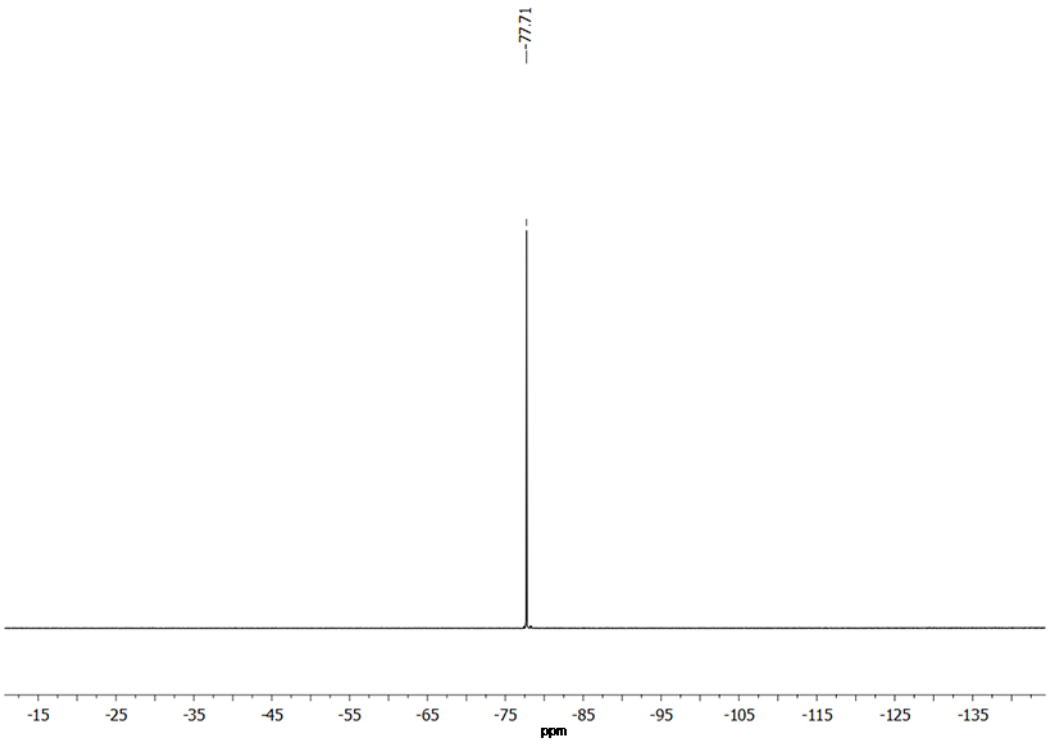


Figure S27. $^{19}F\{^{1}H\}$ NMR of **3** in $CDCl_3$

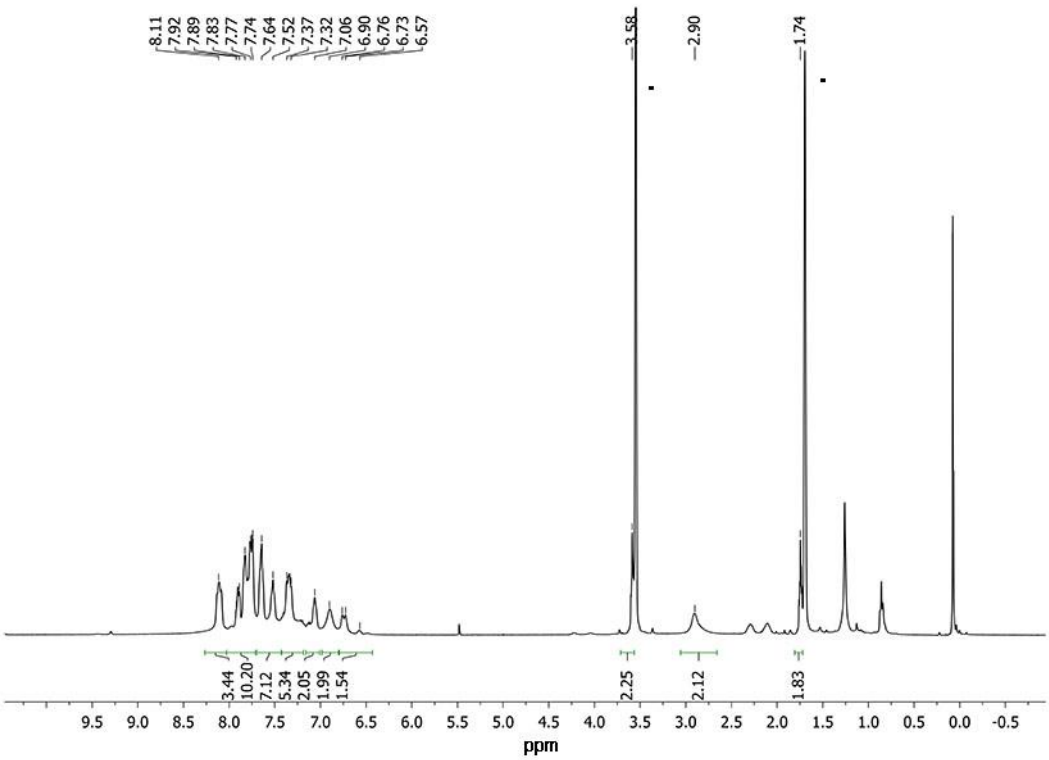


Figure S28. ^{1}H NMR of **4** in THF-d_8 ("= residual solvent peak)

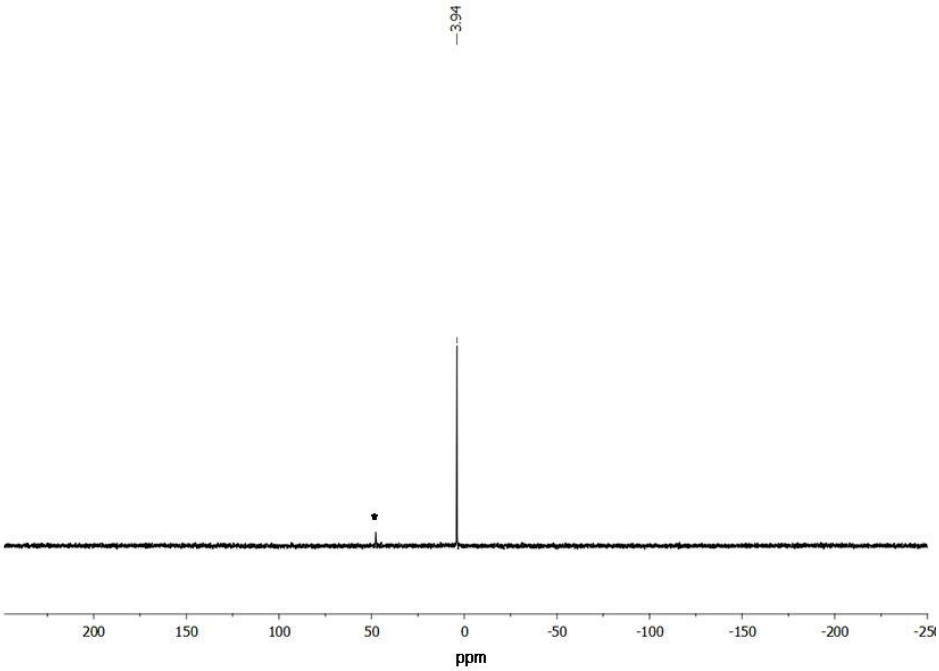


Figure S29. $^{31}P\{^{1}H\}$ NMR of **4** in THF-d_8 (*=impurity)

Reaction of **3** with 4-Dimethylaminopyridine (DMAP) :

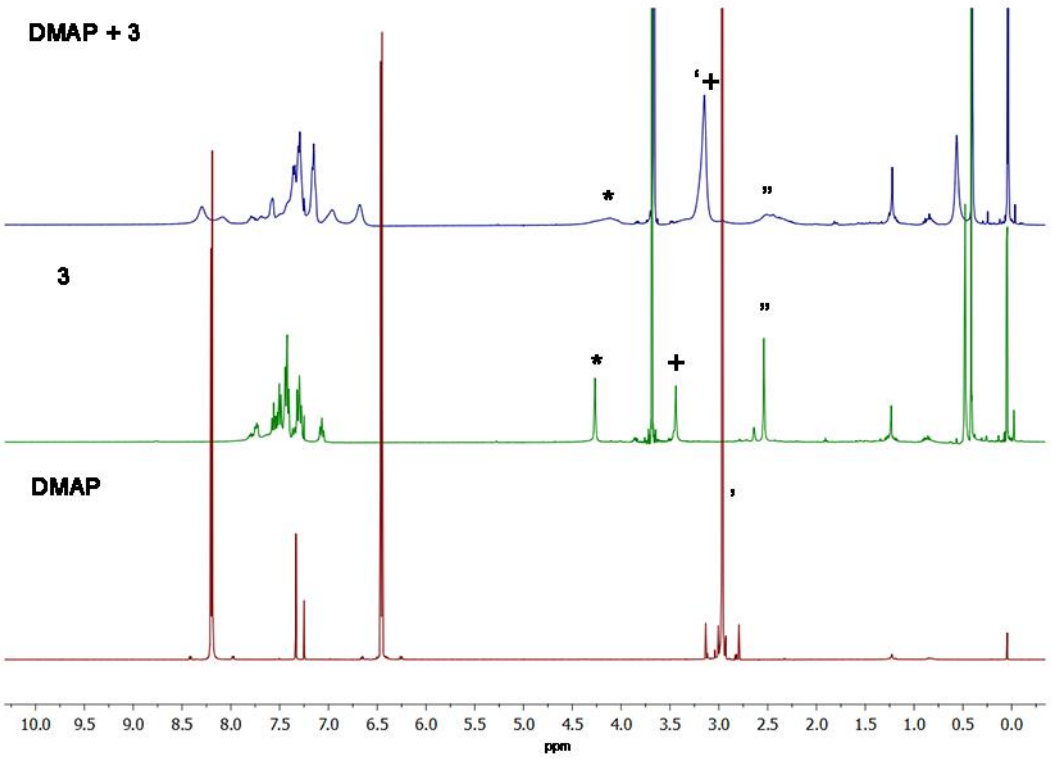


Figure S30. ^{1}H NMR in $CDCl_3$

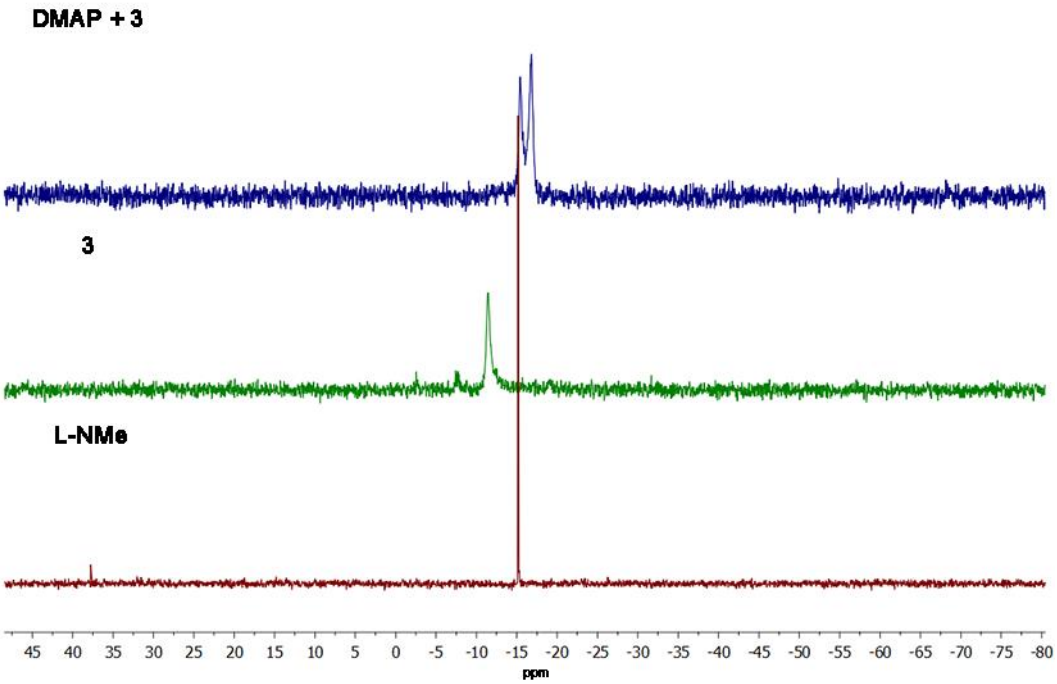


Figure S31. $^{31}P\{^{1}H\}$ NMR in $CDCl_3$

Reaction of **3** with Trimethylphosphine (PMe_3):

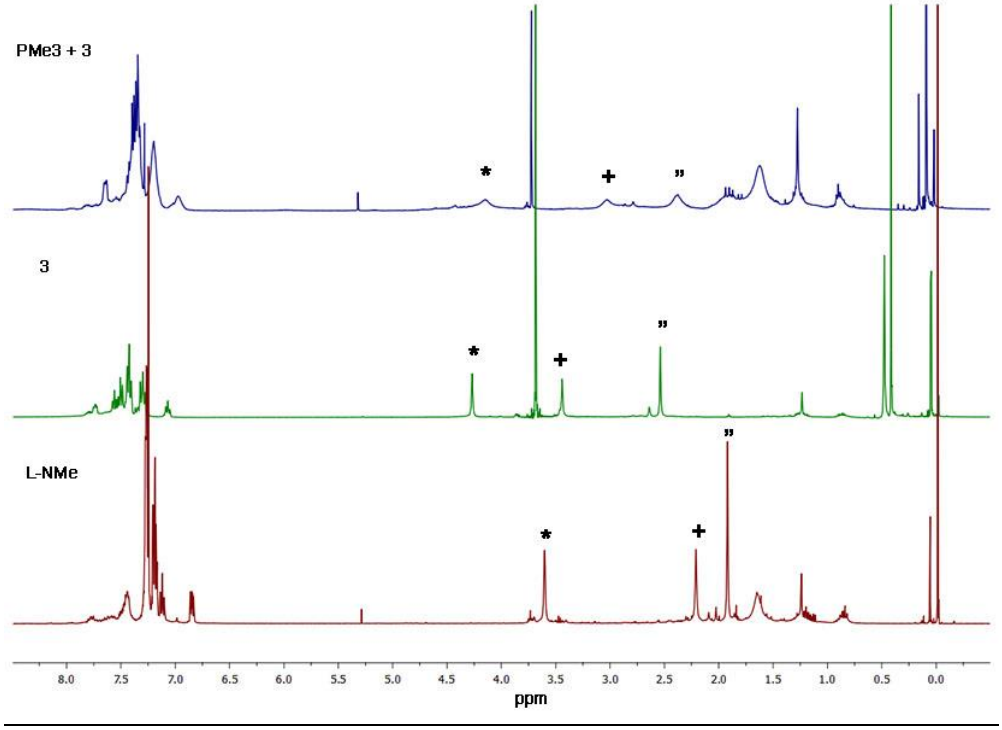


Figure S32. ^{1}H NMR in $CDCl_3$

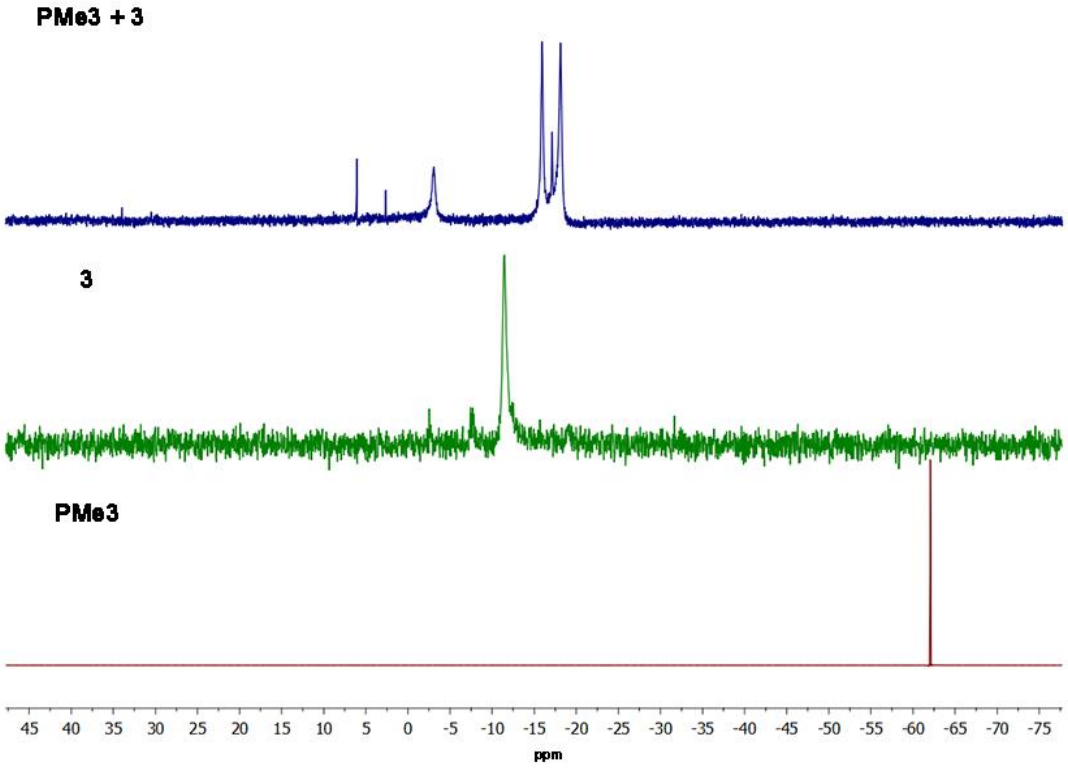


Figure S33. $^{31}P\{^{1}H\}$ NMR in $CDCl_3$

2. DFT calculations

DFT calculations were performed on the dicationic part of the experimental structures **1**-**3** at the B3LYP level of theory (6-31G(d,p) basis set for Ge, Cl, C, N, H) using *Gaussian 09* suite of programs.[S1] Compounds **1'-3'** were optimized at the stationary point with number of imaginary frequency NIMAG = 0.

Coordinates of Optimized structure **1′**

%chk=bisPfreq.chk

%mem=1GB

freq b3lyp/6-31g(d,p)

frequency calculation of optimized bismonocation with P

2 1

Ge	2.74606200	-0.49275100	-1.50398400
Cl	3.24547600	-2.69287000	-1.63898600
P	4.56524500	0.15748400	-0.00524000
N	1.66157200	-0.83710900	0.28892200
C	4.07155500	2.08890000	2.00986000
H	4.39888500	1.35203900	2.73592500
C	4.05618800	1.78213100	0.64054900
C	4.59541900	-1.02075600	1.38696000
C	6.19659900	0.28188300	-0.78203800
C	7.12016800	1.25488200	-0.36197900
H	6.86452700	1.95379000	0.42797600
C	2.04095600	-1.30657400	1.43349600
H	1.25150400	-1.60641100	2.12923900
C	0.22374600	-0.73426000	0.00716200
H	-0.35876700	-1.31326000	0.73284400
H	0.04697600	-1.16505300	-0.98575500
C	8.69764900	0.44584700	-2.00689600
H	9.66995000	0.51120900	-2.48461800
C	3.26400200	4.31693500	1.51901700
H	2.96419600	5.30256800	1.86030300
C	5.81412500	-1.41069000	1.93979300
H	6.73967400	-1.02333600	1.52763100
C	3.24715900	4.01639500	0.15476700
H	2.94055700	4.76867500	-0.56490700

C	7.77845400	-0.51683100	-2.43012200
H	8.03387400	-1.19862300	-3.23455900
C	5.86438200	-2.29565100	3.02515600
H	6.82659300	-2.58532900	3.43484800
C	3.38828800	-1.54651100	1.92904100
C	3.63713400	2.75364000	-0.28848700
H	3.64257800	2.53863900	-1.35435500
C	6.52621900	-0.60413300	-1.82455100
H	5.82024900	-1.35818800	-2.15994300
C	8.36916000	1.32947000	-0.97588400
H	9.08266700	2.08066800	-0.65333300
C	3.67568300	3.35484600	2.44321500
H	3.69861800	3.59136900	3.50213400
C	4.68746000	-2.78855700	3.58187800
H	4.71986400	-3.46499200	4.42897300
C	3.46178600	-2.40494700	3.04276300
H	2.54396100	-2.79300300	3.47502100
P	-4.56608300	-0.15763700	0.00362600
N	-1.66316100	0.84158100	-0.27662600
C	-4.05085600	-2.08924600	-2.00623300
H	-4.37321900	-1.35355800	-2.73571300
C	-4.04879100	-1.78172300	-0.63700900
C	-4.59146300	1.01903500	-1.38997800
C	-6.20131600	-0.28557300	0.77155100
C	-7.12152700	-1.25882600	0.34470200
H	-6.86093100	-1.95585900	-0.44531200
C	-2.03744200	1.30944700	-1.42354000
H	-1.24491500	1.60915500	-2.11584900
C	-0.22650200	0.73893800	0.01112600
H	0.35875900	1.31856800	-0.71184000
H	-0.05366600	1.16897400	1.00504000
C	-8.70847400	-0.45515100	1.98313500
H	-9.68314300	-0.52271100	2.45569500
C	-3.24259000	-4.31512300	-1.50676100
H	-2.93736400	-5.30023600	-1.84473300
C	-5.80803600	1.40600900	-1.94953800
H	-6.73493700	1.01692700	-1.54207300

C	-3.23904600	-4.01383500	-0.14257200
H	-2.93734100	-4.76500400	0.58032600
C	-7.79266900	0.50775100	2.41309600
H	-8.05306500	1.18755800	3.21761700
C	-5.85439500	2.29021400	-3.03568900
H	-6.81503200	2.57760100	-3.45065400
C	-3.38261000	1.54696000	-1.92604400
C	-3.63593500	-2.75173600	0.29637300
H	-3.65137900	-2.53602100	1.36199800
C	-6.53743700	0.59786500	1.81415400
H	-5.83421800	1.35215600	2.15477400
C	-8.37357300	-1.33621900	0.95197400
H	-9.08447800	-2.08761800	0.62418500
C	-3.64797800	-3.35447600	-2.43522900
H	-3.66064600	-3.59162100	-3.49418200
C	-4.67558600	2.78529900	-3.58646400
H	-4.70494000	3.46117400	-4.43411500
C	-3.45197700	2.40453000	-3.04068600
H	-2.53267000	2.79415100	-3.46836600
Ge	-2.75623900	0.49807600	1.51134100
Cl	-3.26082500	2.69729500	1.64063800

Coordinates of Optimized structure **2′**

%chk=bisNHfreq.chk

%mem=1GB

freq b3lyp/6-31g(d,p)

frequency calculation of bisNH with optimized geometry

2 1

Ge	-3.33210300	-0.38189900	-1.53597900
Cl	-3.02988700	-2.55606000	-0.98739200
P	-5.24402200	0.07133000	0.01153200
C	-6.03492600	-1.37857400	0.75673700
C	-6.44501000	0.96730700	-1.02001300
C	-4.65251300	1.20226300	1.31892500

C	-3.36039800	1.05168300	1.87631900
P	5.24400200	-0.07137500	-0.01151400
C	6.03517400	1.37826500	-0.75694800
C	6.44479200	-0.96731500	1.02029100
C	4.65240000	-1.20248200	-1.31871200
C	3.36030000	-1.05189400	-1.87613400
Ge	3.33212900	0.38259700	1.53584300
Cl	3.03011600	2.55658800	0.98653700
C	-3.80282500	2.94546400	3.34177300
H	-3.46887100	3.61337400	4.12896900
C	-2.95675400	1.93367900	2.88484900
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C	-5.49019200	2.23189600	1.77189700
H	-6.47561800	2.35647700	1.33556400
C	-7.81020200	0.64426200	-1.01161600
H	-8.18188800	-0.15450000	-0.37927200
C	-8.69384200	1.35340200	-1.82615400
H	-9.74928500	1.10166600	-1.81788300
C	-8.22419500	2.38035000	-2.64588200
H	-8.91528200	2.92728700	-3.27906300
C	-6.86511000	2.70610600	-2.65520000
H	-6.50120500	3.50577400	-3.29193100
C	-5.97401100	2.00256500	-1.84914000
H	-4.92086700	2.27441400	-1.85814600
C	-6.28964800	-1.45472900	2.13479800
H	-6.01072700	-0.64000700	2.79463800
C	-6.92064700	-2.58381500	2.65712300
H	-7.12295400	-2.64118400	3.72169400
C	-7.29726300	-3.63063400	1.81417900
H	-7.79077800	-4.50534600	2.22541100
C	-7.04090200	-3.55755600	0.44217600
H	-7.33058300	-4.37319100	-0.21201900
C	-6.40367700	-2.43997700	-0.08991400
H	-6.19571400	-2.39418000	-1.15484400
C	2.95658100	-1.93404100	-2.88450200

H	1.96967400	-1.82500200	-3.32586200
C	3.80256700	-2.94598100	-3.34123800
H	3.46855800	-3.61401000	-4.12831000
C	5.07005600	-3.09721400	-2.78216500
H	5.73299600	-3.88255900	-3.12990600
C	5.48999300	-2.23227400	-1.77148900
H	6.47540600	-2.35686400	-1.33512800
C	6.28996800	1.45413000	-2.13501100
H	6.01094600	0.63933200	-2.79471400
C	6.92116400	2.58302400	-2.65751400
H	7.12352500	2.64017000	-3.72208600
C	7.29790300	3.62993700	-1.81474300
H	7.79157100	4.50449900	-2.22611000
C	7.04147000	3.55714900	-0.44273700
H	7.33124600	4.37285900	0.21132000
C	6.40404900	2.43976600	0.08952700
H	6.19603100	2.39419400	1.15445600
C	7.81005900	-0.64458700	1.01177400
H	8.18191300	0.15391300	0.37919700
C	5.97357200	-2.00222400	1.84972700
H	4.92036300	-2.27382200	1.85883700
C	6.86452300	-2.70573600	2.65597400
H	6.50044700	-3.50513300	3.29294800
C	8.22368400	-2.38029800	2.64653300
H	8.91465700	-2.92721000	3.27985900
C	8.69355100	-1.35369500	1.82649800
H	9.74905300	-1.10220400	1.81813500
C	-0.59253300	-0.34610700	-0.34414800
H	-0.64868000	-1.40705100	-0.08721400
H	-0.49115900	-0.29168600	-1.43327300
C	0.59253500	0.34644100	0.34408700
H	0.49112300	0.29209400	1.43321400
H	0.64871900	1.40736900	0.08709100
C	-2.39011100	-0.01204900	1.41128600
H	-2.82315600	-1.01697400	1.39838000
H	-1.53548800	-0.03085000	2.09209600
C	2.39010000	0.01200800	-1.41129100

H	2.82322700	1.01690200	-1.39861400
H	1.53548000	0.03074700	-2.09210900
N	1.91507400	-0.25617300	-0.00263200
H	1.86304600	-1.26791800	0.13911000
N	-1.91508300	0.25645100	0.00266800
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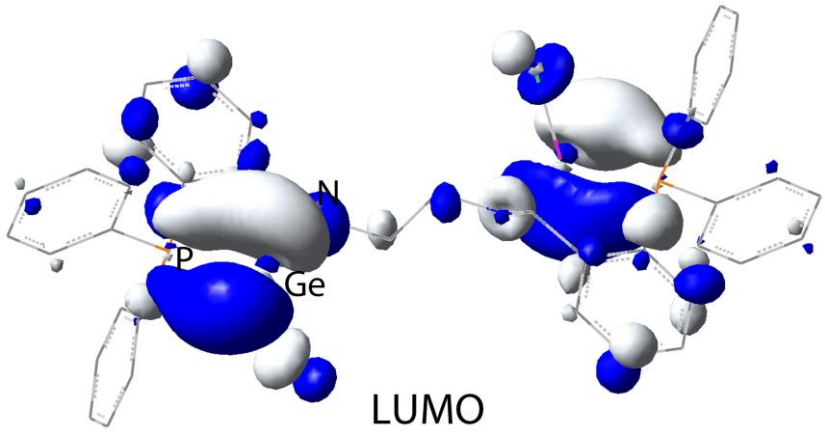
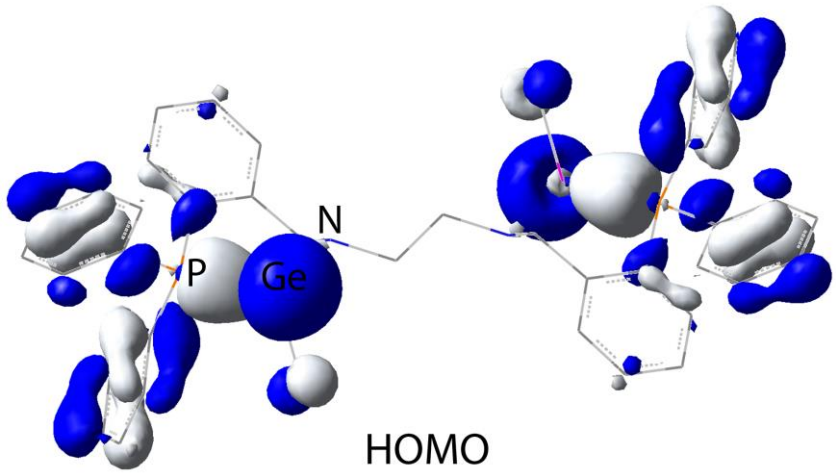
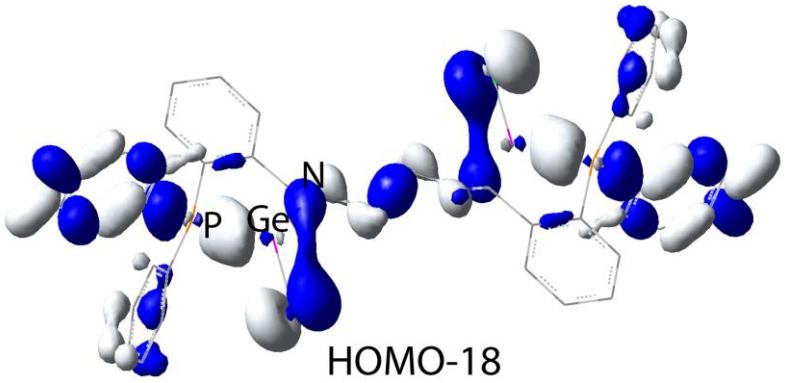
Contour plots of **2′** at 0.03 isovalue







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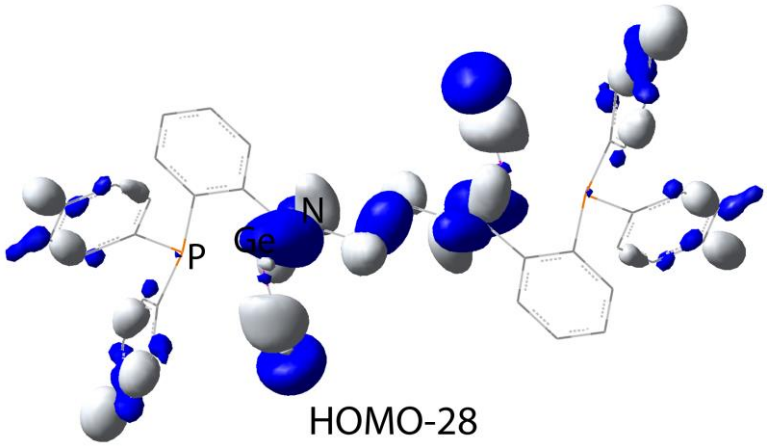

HOMO-28

Coordinates of Optimized structure **3′**

%chk=bisNMefreq.chk

%mem=1GB

freq b3lyp/6-31g(d,p)

frequency calculation of bisNMe optimized geometry

2 1

Ge	3.14493600	0.88479900	-1.70976300
Cl	4.02587900	2.93905800	-1.43714000
P	4.58647600	-0.18304100	0.03114700
N	1.51713300	1.20177900	-0.25046500
C	2.51202100	0.25266500	1.91486300
C	5.15013800	-1.74550000	-0.71555500
C	3.60001300	-0.56398200	1.52450500
C	6.04119600	0.78777000	0.50829500

P	-4.58648000	0.18303800	-0.03116000
N	-1.51713200	-1.20175200	0.25052900
C	-5.15016000	1.74551100	0.71549900
C	-3.59999700	0.56395000	-1.52451300
C	-6.04118800	-0.78779000	-0.50830700
Ge	-3.14495500	-0.88475200	1.70979700
Cl	-4.02587200	-2.93902700	1.43721000
C	-6.89410400	-1.23223900	0.51874800
H	-6.67087900	-1.00662800	1.55774400
C	-8.03131100	-1.96846100	0.20111100
H	-8.69133200	-2.30666300	0.99301000
C	-8.31465700	-2.27937000	-1.13211200
H	-9.20016700	-2.85776800	-1.37508300
C	-7.46192000	-1.85180600	-2.15040100
H	-7.68312100	-2.09419700	-3.18469400
C	-6.32279500	-1.10590900	-1.84506600
H	-5.67030200	-0.77039000	-2.64398600
C	-2.21015900	1.15831500	-3.88495200
H	-1.67866900	1.36826800	-4.80759800
C	-1.83818200	0.06359400	-3.10236000
H	-1.02140300	-0.57191000	-3.43500500
C	-3.26497000	1.97400100	-3.47951200
H	-3.56045300	2.82984200	-4.07743700
C	-3.95256500	1.67698900	-2.30311500
H	-4.77478900	2.31265500	-1.99084100
C	-2.51199500	-0.25270000	-1.91483600
C	-6.43927400	2.24567400	0.46958400
H	-7.12764200	1.69752600	-0.16481600
C	-6.84379900	3.44466700	1.05644100
H	-7.84166600	3.82561300	0.86517000
C	-5.97284800	4.14702300	1.89100100
H	-6.29426100	5.07538800	2.35196400
C	-4.69115100	3.65181100	2.14243000
H	-4.01879800	4.19463100	2.79885600
C	-4.27773400	2.45552200	1.56049200
H	-3.28072800	2.07905700	1.77732100
C	1.83822400	-0.06365400	3.10239000

H	1.02145200	0.57184500	3.43506200
C	2.21020400	-1.15839800	3.88494800
H	1.67872600	-1.36837200	4.80759600
C	3.26500500	-1.97407900	3.47947400
H	3.56049100	-2.82993700	4.07737200
C	3.95258500	-1.67704200	2.30307500
H	4.77480000	-2.31270600	1.99077300
C	6.32282800	1.10585300	1.84505800
H	5.67035000	0.77031200	2.64398100
C	7.46196300	1.85173400	2.15039300
H	7.68318600	2.09409300	3.18468800
C	8.31468100	2.27932500	1.13209800
H	9.20019800	2.85771300	1.37507000
C	8.03130800	1.96845500	-0.20112800
H	8.69131500	2.30667900	-0.99303000
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C	6.43925400	-2.24567400	-0.46967000
H	7.12763300	-1.69754400	0.16473300
C	6.84376500	-3.44465600	-1.05656100
H	7.84163300	-3.82561000	-0.86531200
C	5.97279700	-4.14699200	-1.89112000
H	6.29419700	-5.07535000	-2.35210400
C	4.69109800	-3.65176900	-2.14251800
H	4.01873100	-4.19457400	-2.79894200
C	4.27769600	-2.45548900	-1.56055000
H	3.28068700	-2.07901700	-1.77735400
C	-0.80767000	-2.41783200	0.75000600
H	0.04331600	-2.67146000	0.11220900
H	-0.46262600	-2.23968300	1.77155700
H	-1.50434900	-3.25467000	0.76240700
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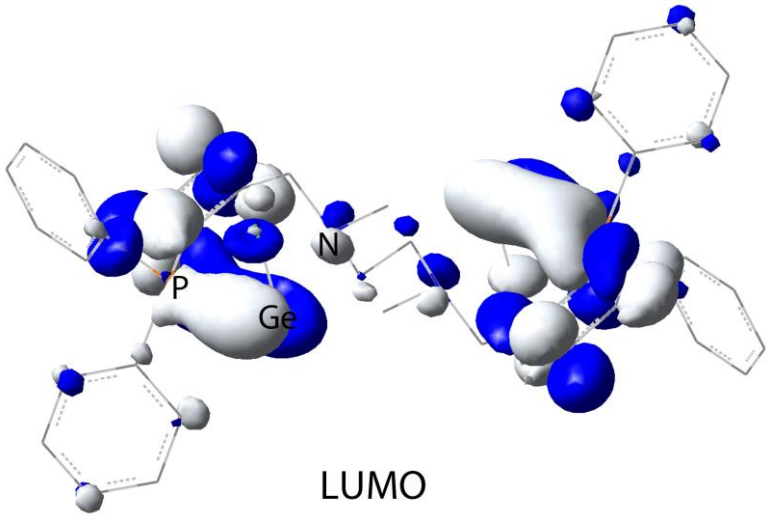
H	0.46260400	2.23975600	-1.77144900
H	-0.04329500	2.67150300	-0.11208000
H	1.50435900	3.25471000	-0.76230100
C	-0.66640000	0.02384500	0.38373200
H	-1.27042300	0.86856100	0.05040000

H	-0.48173800	0.15465600	1.45412700
C	0.66639200	-0.02381000	-0.38368400
H	0.48172500	-0.15460700	-1.45408100
H	1.27040700	-0.86853700	-0.05036500
C	-2.05151100	-1.47212000	-1.14015000
H	-2.85998600	-2.19669600	-0.99711900
H	-1.27158200	-1.97739600	-1.71951100
C	2.05153400	1.47210800	1.14021400
H	1.27161400	1.97737400	1.71959700
H	2.86001000	2.19668400	0.99719000

Contour plots of **3′** at 0.03 isovalue



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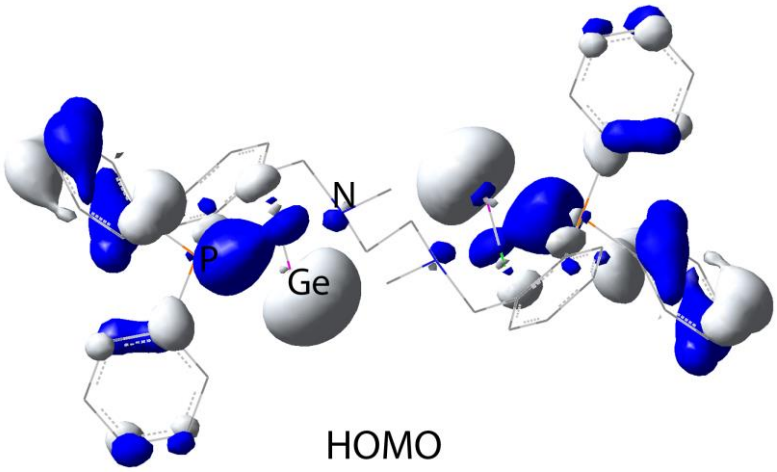

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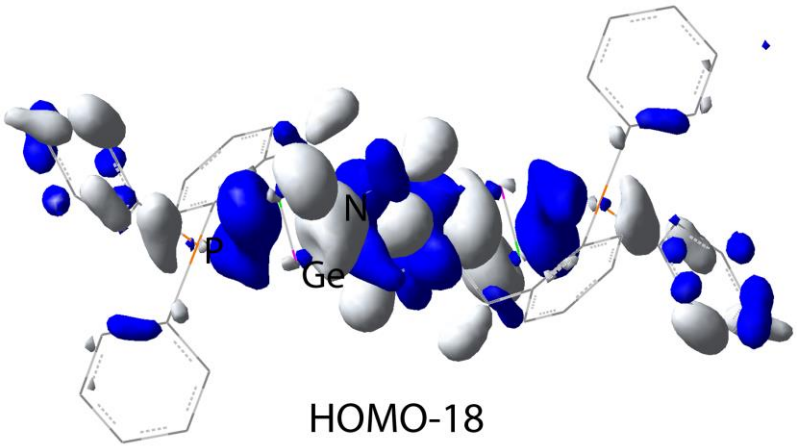
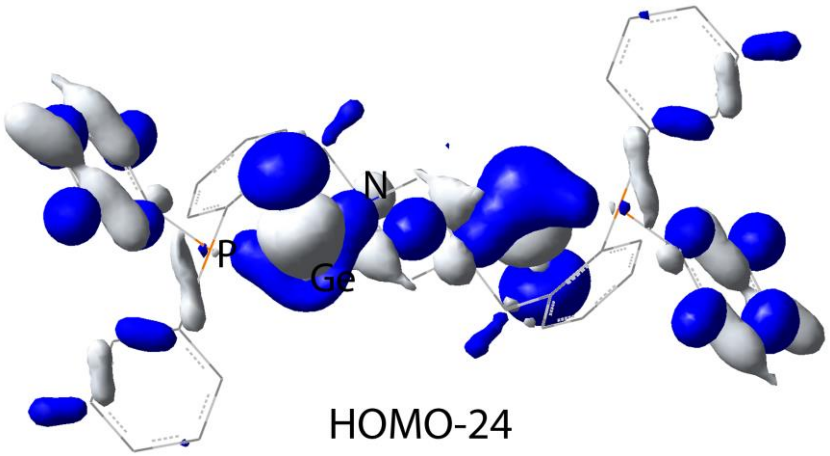


HOMO-18



HOMO-24

3. X-ray Data

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C46 H42 Cl10 F6 Ge2 N2 O6 P2 S2	
Formula weight	1458.55	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0330(10)Å	α= 62.303(3)°.
	b = 12.4374(11) Å	β= 71.710(3)°.
	c = 13.1345(12) Å	γ = 64.929(3)°.
Volume	1430.0 (2) $Å^3$	
Z	1	
Density (calculated)	1.694 Mg/m^3	
Absorption coefficient	7.398 mm^{-1}	
F (000)	730	
Crystal size	0.56 x 0.45 x 0.38 mm^3	
Theta range for data collection	3.84 to 66.87°.	
Index ranges	-13<=h<=13, -14<=k<=14, -15<=l<=15	
Reflections collected	16149	
Independent reflections	5029 [R(int) = 0.0388]	
Completeness to theta = 66.868°	98.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.046 and 0.060	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5029 / 0 / 344	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma (I)]	R1 = 0.0388, wR2 = 0.1026	
R indices (all data)	R1 = 0.0443, wR2 = 0.1055	
Largest diff. peak and hole	0.736 and -0.553 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	C42 H38 Cl2 F6 Ge2 N2 O6 P2 S2	
Formula weight	1122.88	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.9761(12) Å	α= 85.400(6)°.
	b = 13.6739(14) Å	β= 86.134(6)°.
	c = 13.7965(12) Å	γ = 70.497(6)°.
Volume	2297.9(4) $Å^3$	
Z	2	
Density (calculated)	1.623 Mg/m^3	
Absorption coefficient	4.832 mm^{-1}	
F (000)	1132	
Crystal size	0.09 x 0.08 x 0.06 mm^3	
Theta range for data collection	3.21 to 66.59°.	
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=16	
Reflections collected	26902	
Independent reflections	8073 [R(int) = 0.2587]	
Completeness to theta = 66.597°	99.4 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.680 and 0.748	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8073 / 0 / 577	
Goodness-of-fit on F^2	0.999	
Final R indices [I>2sigma (I)]	R1 = 0.0829, wR2 = 0.1585	
R indices (all data)	R1 = 0.1784, wR2 = 0.1965	
Largest diff. peak and hole	1.074 and -1.008 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement for **3**

Empirical formula	C23 H23 Cl3 F3 Ge N O3 P S	
Formula weight	660.39	
Temperature	100 (2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.8139(5) Å	α= 90°.
	b = 17.6150(9) Å	β= 90.808(3)°.
	c = 14.8147(8) Å	γ = 90°.
Volume	2821.7(2) $Å^3$	
Z	4	
Density (calculated)	1.555 Mg/m^3	
Absorption coefficient	5.730 mm^{-1}	
F (000)	1332	
Crystal size	0.33 x 0.21 x 0.10 mm^3	
Theta range for data collection	3.90 to 67.22°.	
Index ranges	-12<=h<=11, -21<=k<=20, -17<=l<=17	
Reflections collected	16690	
Independent reflections	4915 [R (int) = 0.1023]	
Completeness to theta = 66.894°	99.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.271 and 0.564	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4915 / 90 / 353	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma (I)]	R1 = 0.0733, wR2 = 0.1698	
R indices (all data)	R1 = 0.1094, wR2 = 0.1893	
Largest diff. peak and hole	1.714 and -1.402 e.$Å^{-3}$	

Table S4. Crystal data and structure refinement for **4**

Empirical formula	C43 H37 F9 N2 O9 P2 S3	
Formula weight	1054.86	
Temperature	100 (2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.1906(5) Å	α= 90°.
	b = 19.4217(7) Å	β= 101.035(2)°.
	c = 16.8932(6) Å	γ = 90°.
Volume	4596.8(3) $Å^3$	
Z	4	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	2.987 mm^{-1}	
F (000)	2160	
Crystal size	0.09 x 0.06 x 0.05 mm^3	
Theta range for data collection	3.50 to 66.92°.	
Index ranges	-16<=h<=13, -23<=k<=23, -20<=l<=20	
Reflections collected	56035	
Independent reflections	8084 [R (int) = 0.1721]	
Completeness to theta = 66.922°	99.4 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.806 and 0.861	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8084/ 150 / 686	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma (I)]	R1 = 0.1015, wR2 = 0.2399	
R indices (all data)	R1 = 0.1529, wR2 = 0.2693	
Largest diff. peak and hole	0.962 and -0.600 e.$Å^{-3}$	

Table S5. Crystal data and structure refinement for **5**.

Empirical formula	C42 H38 Cl9 F3 Ga2 N2 O3 P2 S	
Formula weight	1228.23	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 10.8764(4) Å	α= 90°.
	b = 37.6034(12) Å	β= 104.849(2)°.
	c = 12.6639(4) Å	γ = 90°.
Volume	5006.4(3) $Å^3$	
Z	4	
Density (calculated)	1.630 Mg/m^3	
Absorption coefficient	7.177 mm^{-1}	
F (000)	2464	
Crystal size	0.56 x 0.48 x 0.32 mm^3	
Theta range for data collection	2.35 to 66.48°.	
Index ranges	-12<=h<=12, -44<=k<=44, -13<=l<=15	
Reflections collected	48512	
Independent reflections	8803[R (int) = 0.0746]	
Completeness to theta = 66.859°	99.1%	
Absorption correction	multi-scan	
Max. and min. transmission	0.045 and 0.101	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8803/ 0 / 578	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma (I)]	R1 = 0.0746, wR2 = 0.1900	
R indices (all data)	R1 = 0.1182, wR2 = 0.2195	
Largest diff. peak and hole	0.758 and -0.702 e.$Å^{-3}$	

References

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