Supporting information

Synthesis of P-stereogenic diarylphosphinic amides by directed lithiation: transformation into tertiary phosphine oxides via aryne chemistry and complexation behaviour toward zinc(II)

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Contents

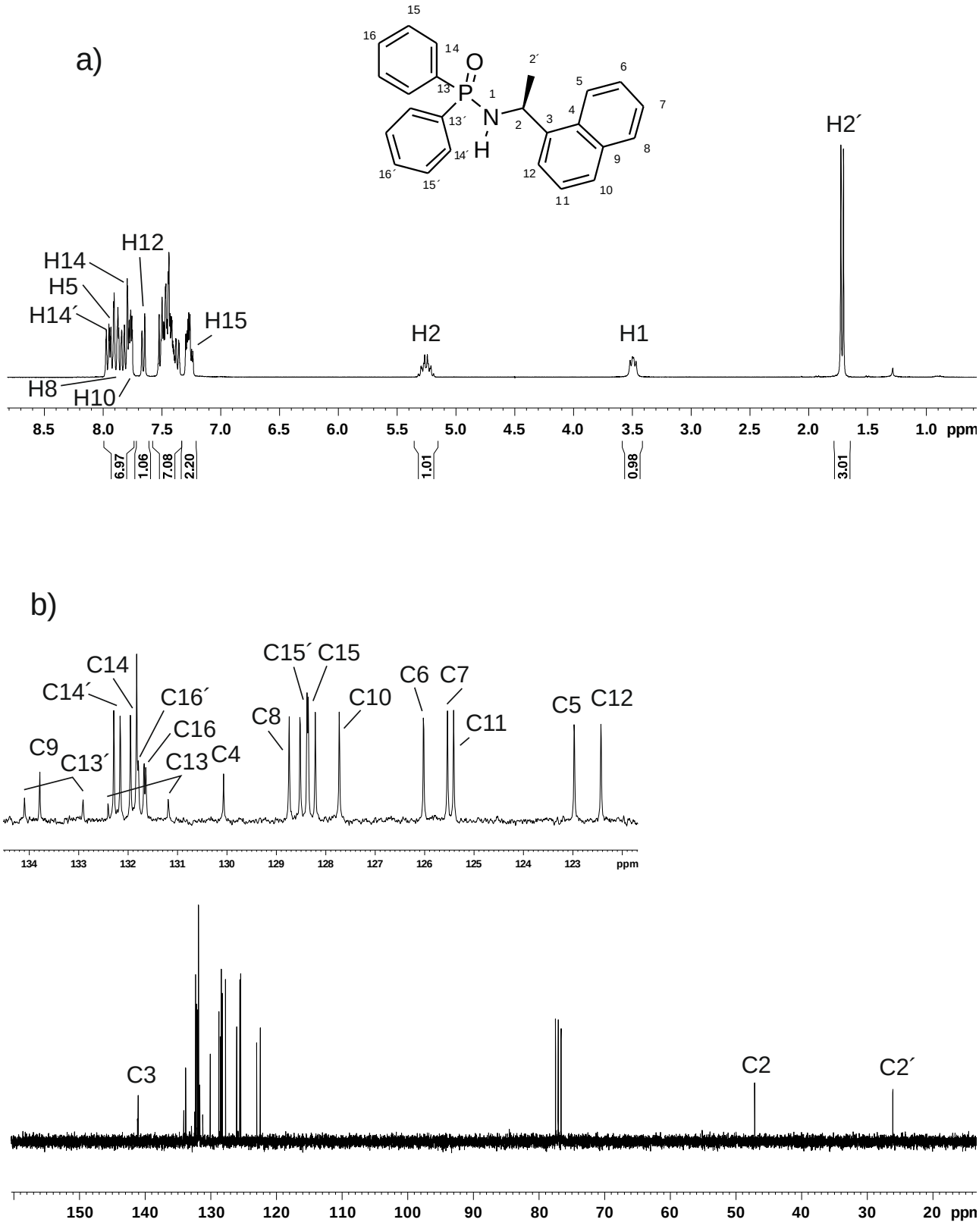


Figure S1. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **7c**

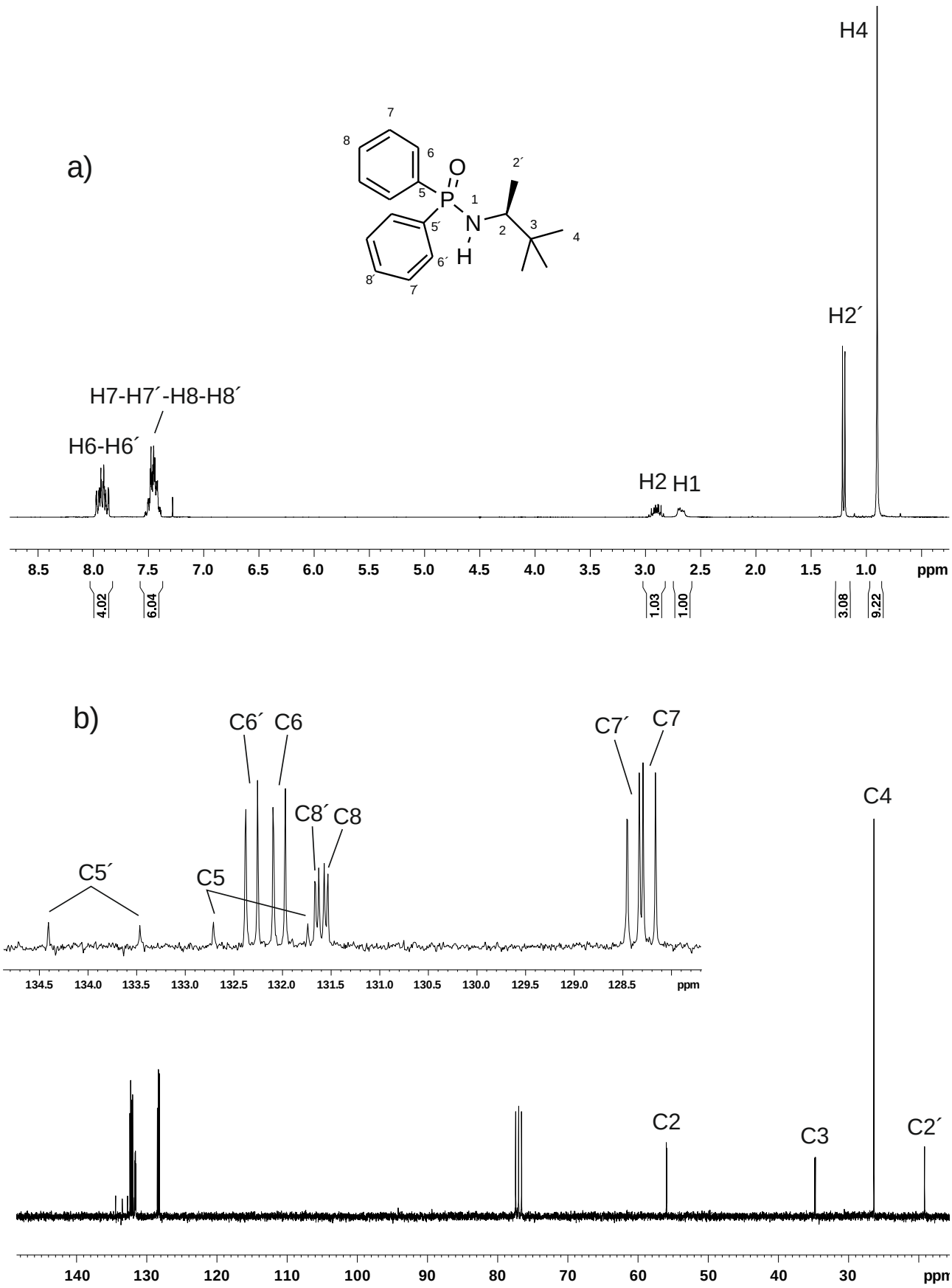


Figure S2. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **7d**

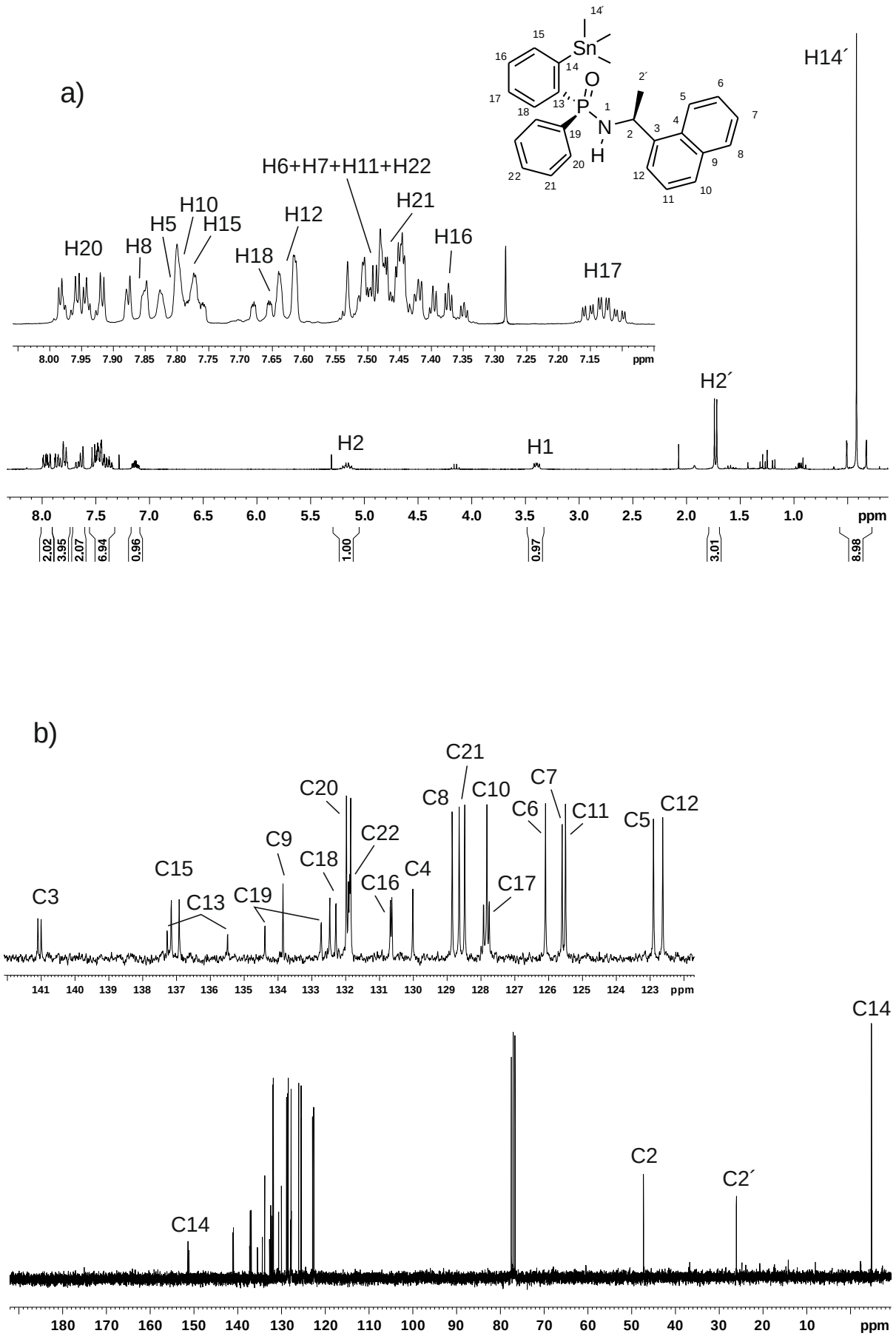
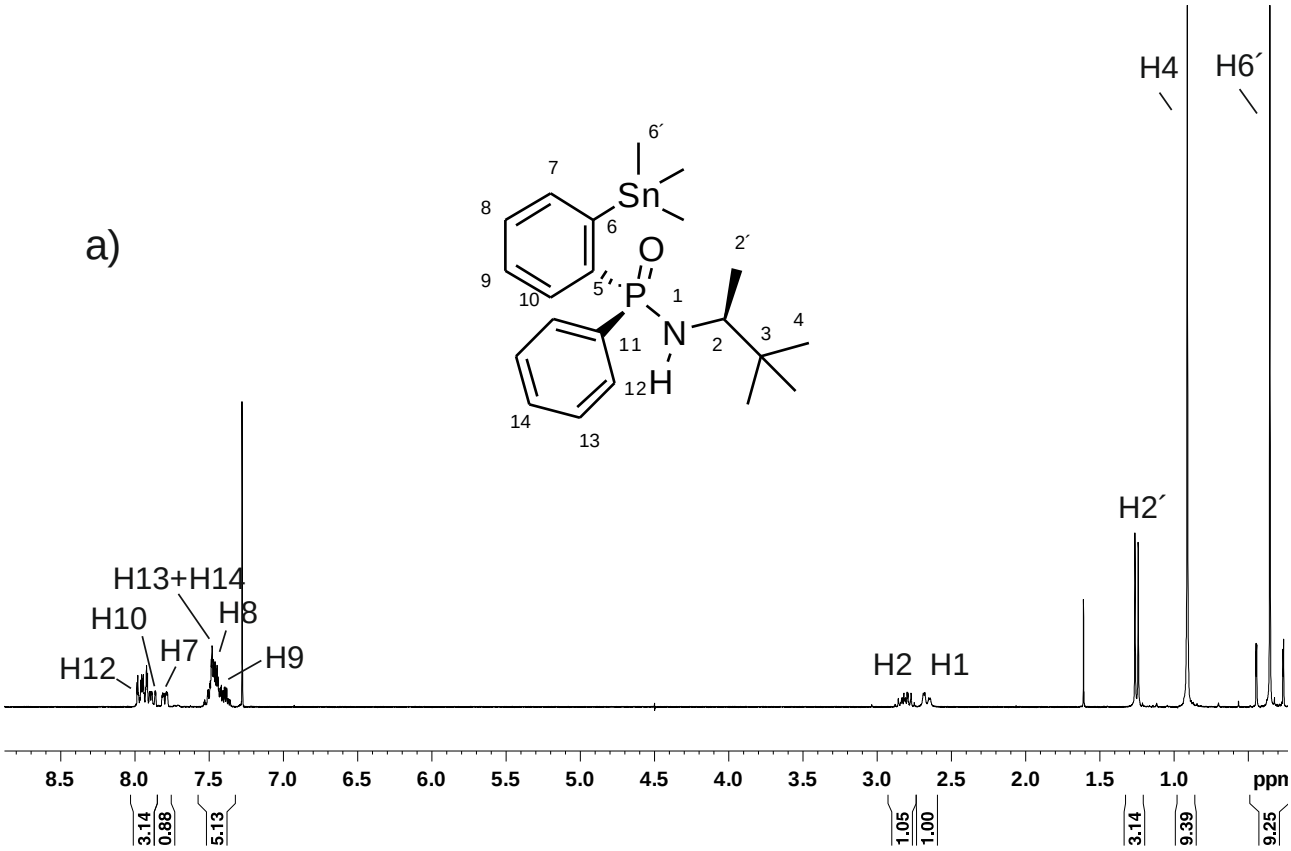


Figure S3. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **18 or 18´**



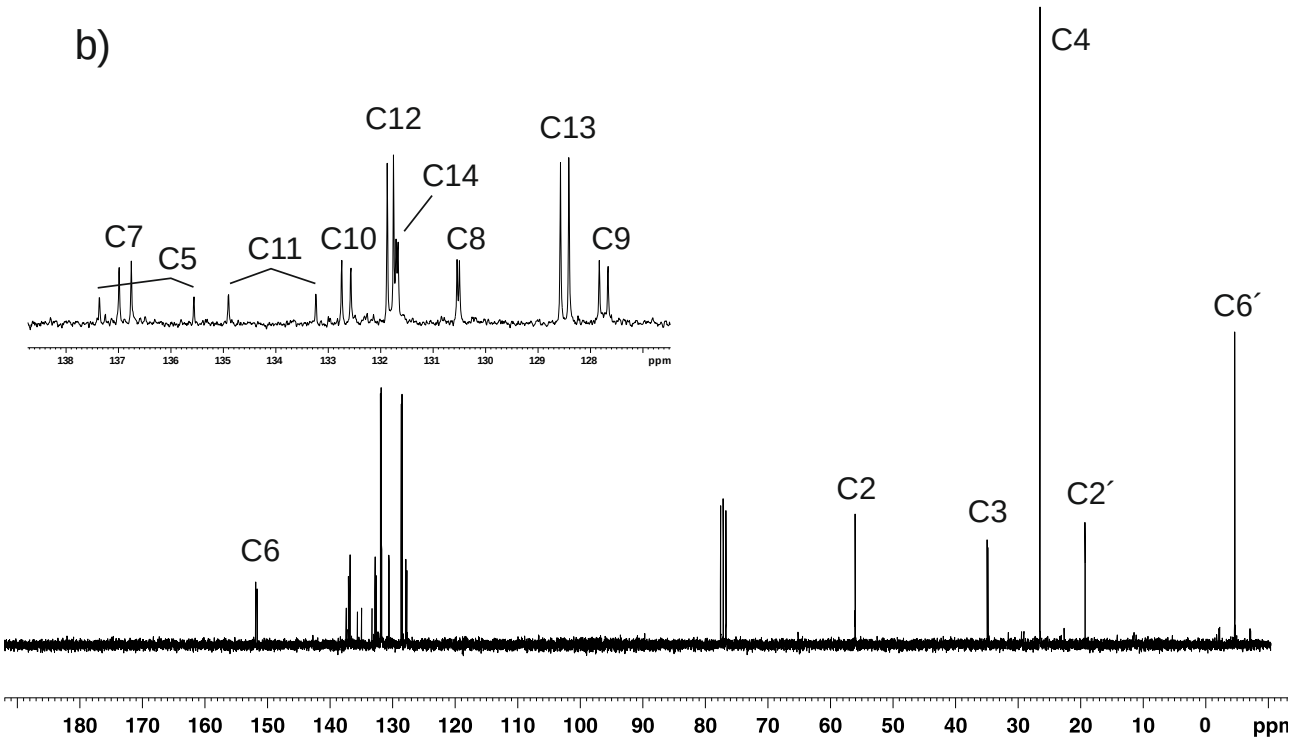


Figure S4. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound (S_P,S_C)-**19**

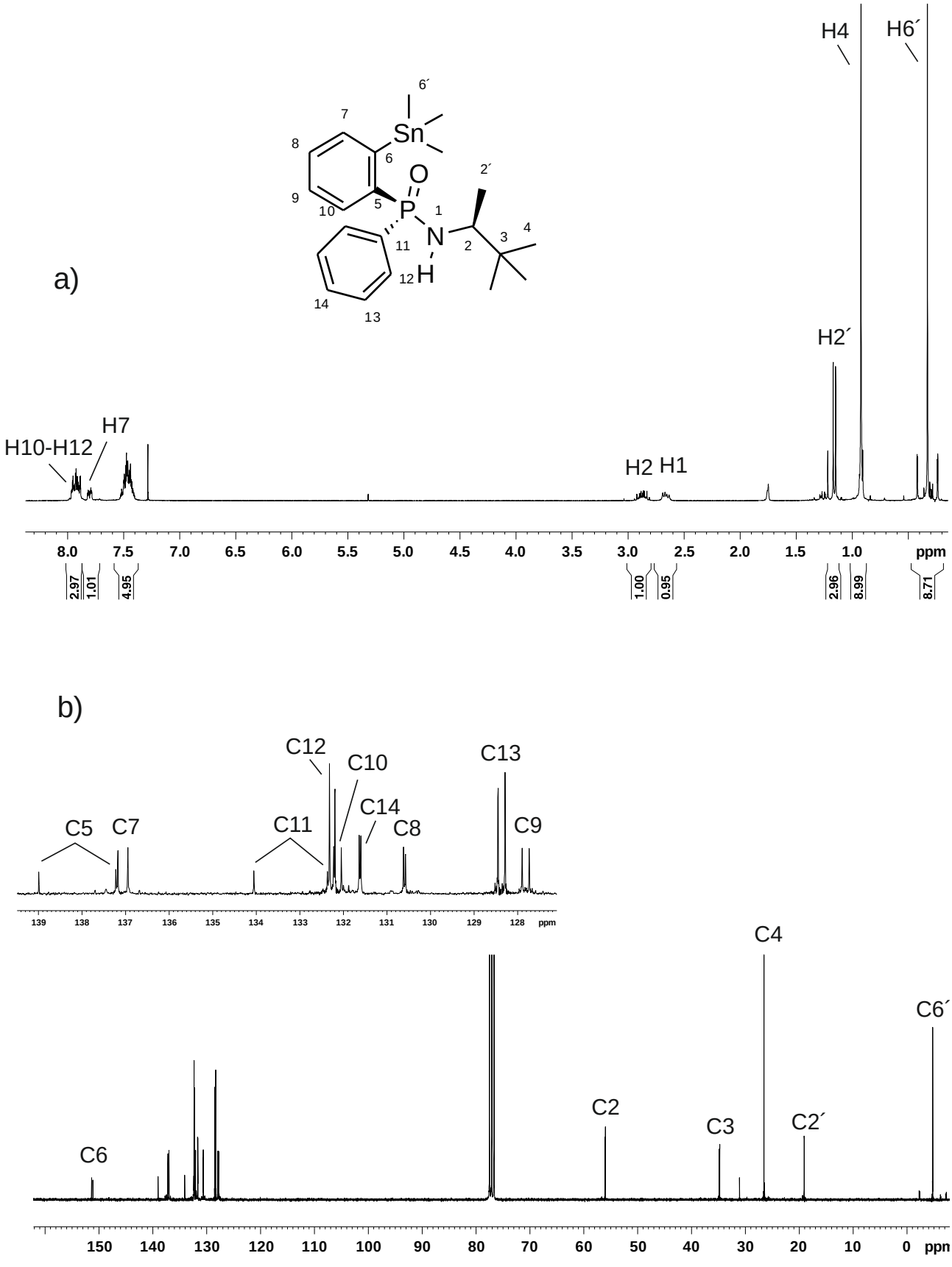


Figure S5. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound (R_P,S_C)-**19´**

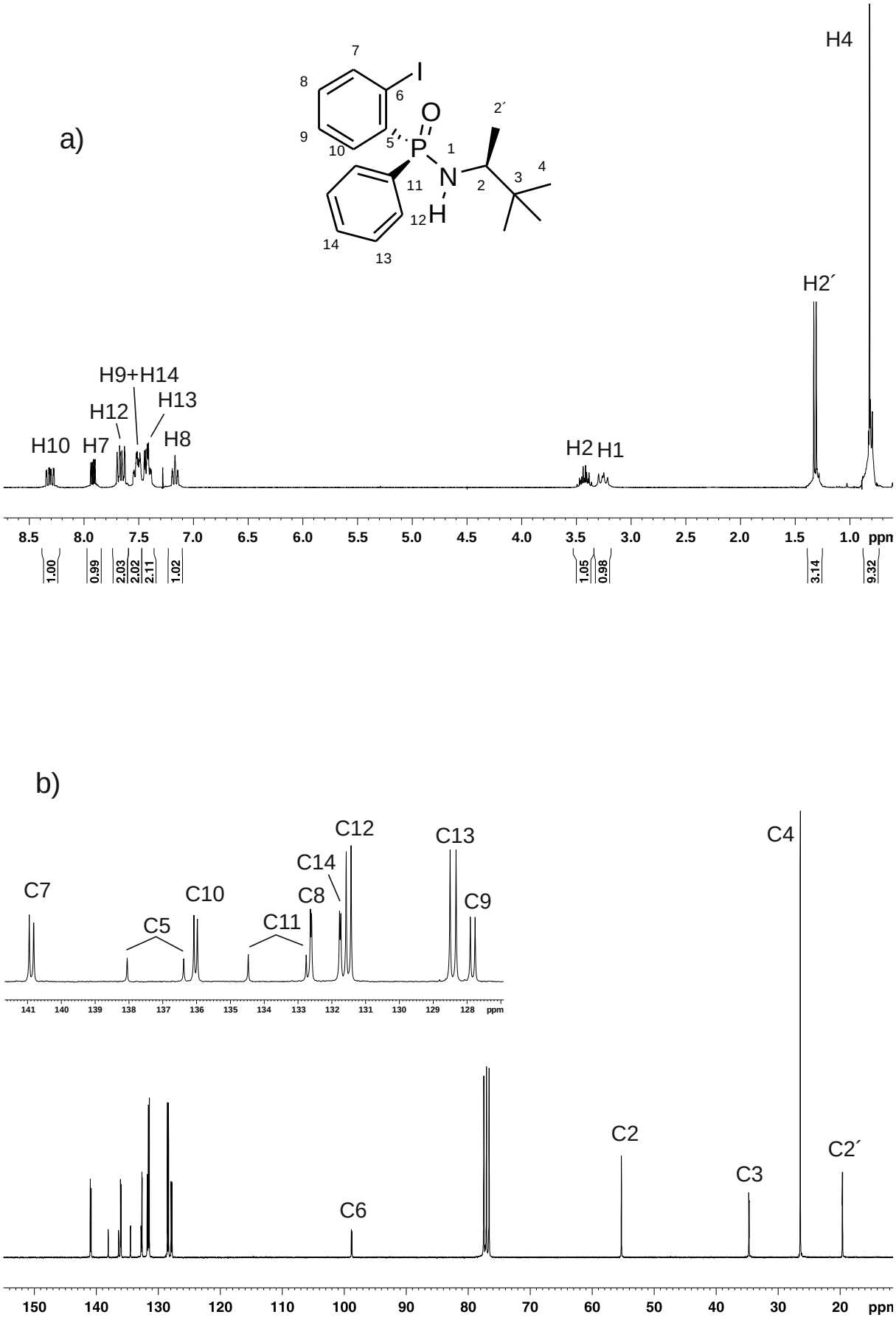
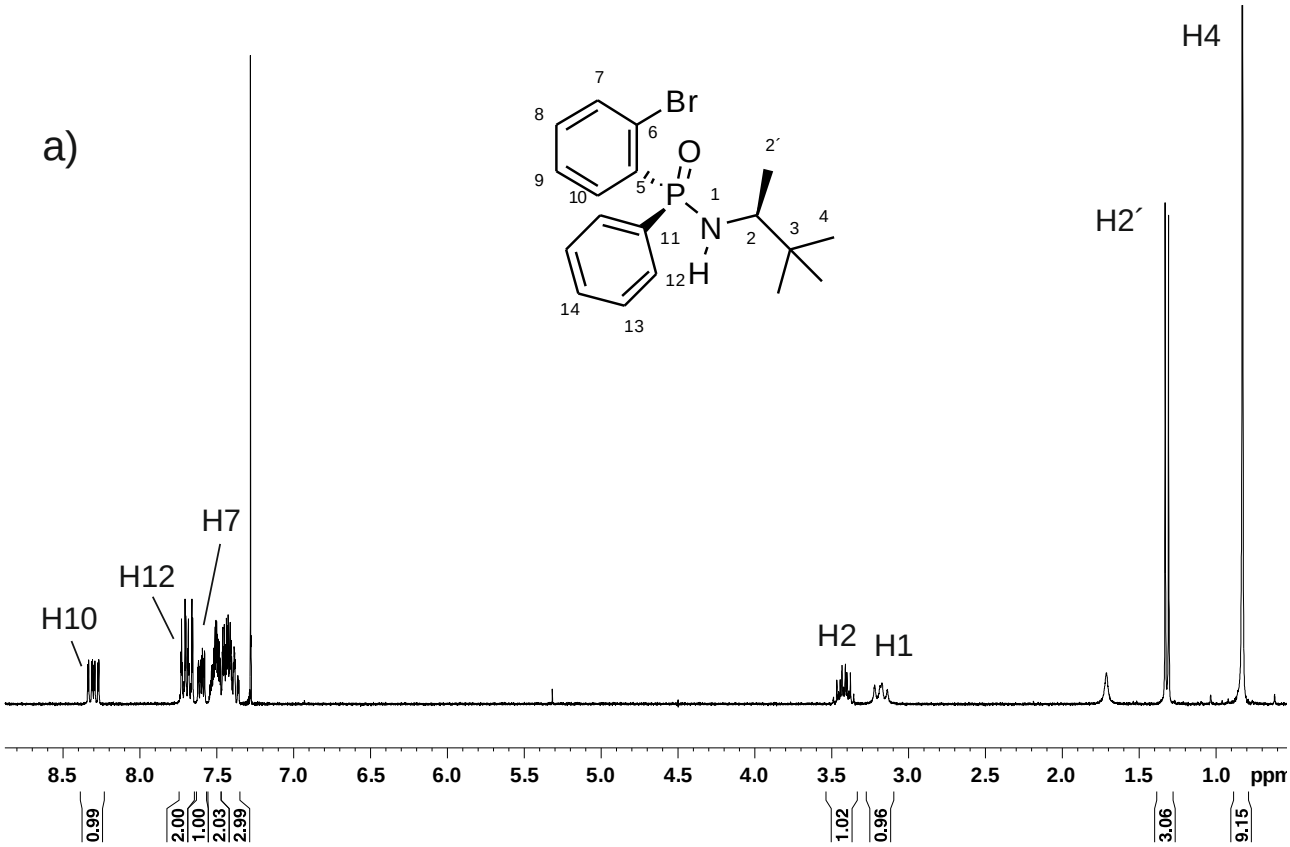


Figure S6. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **20**



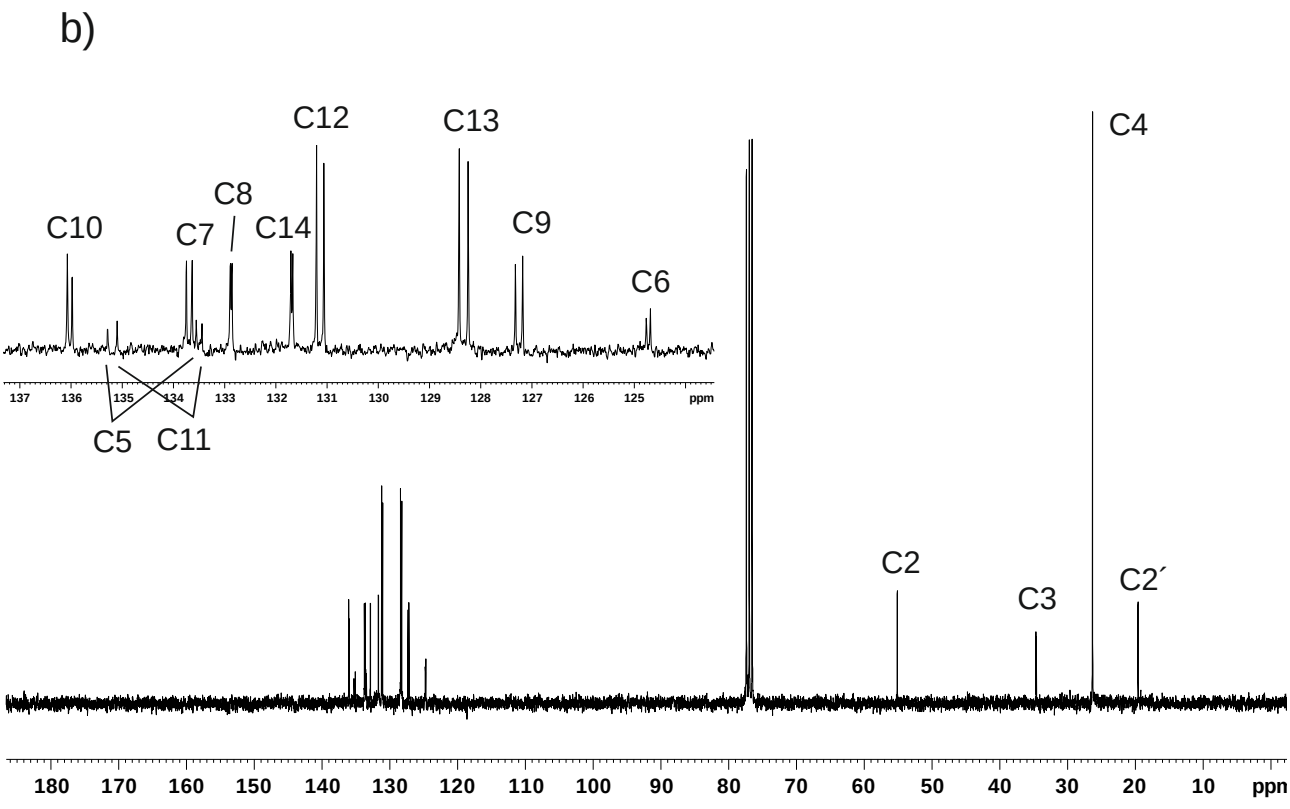


Figure S7. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **21**

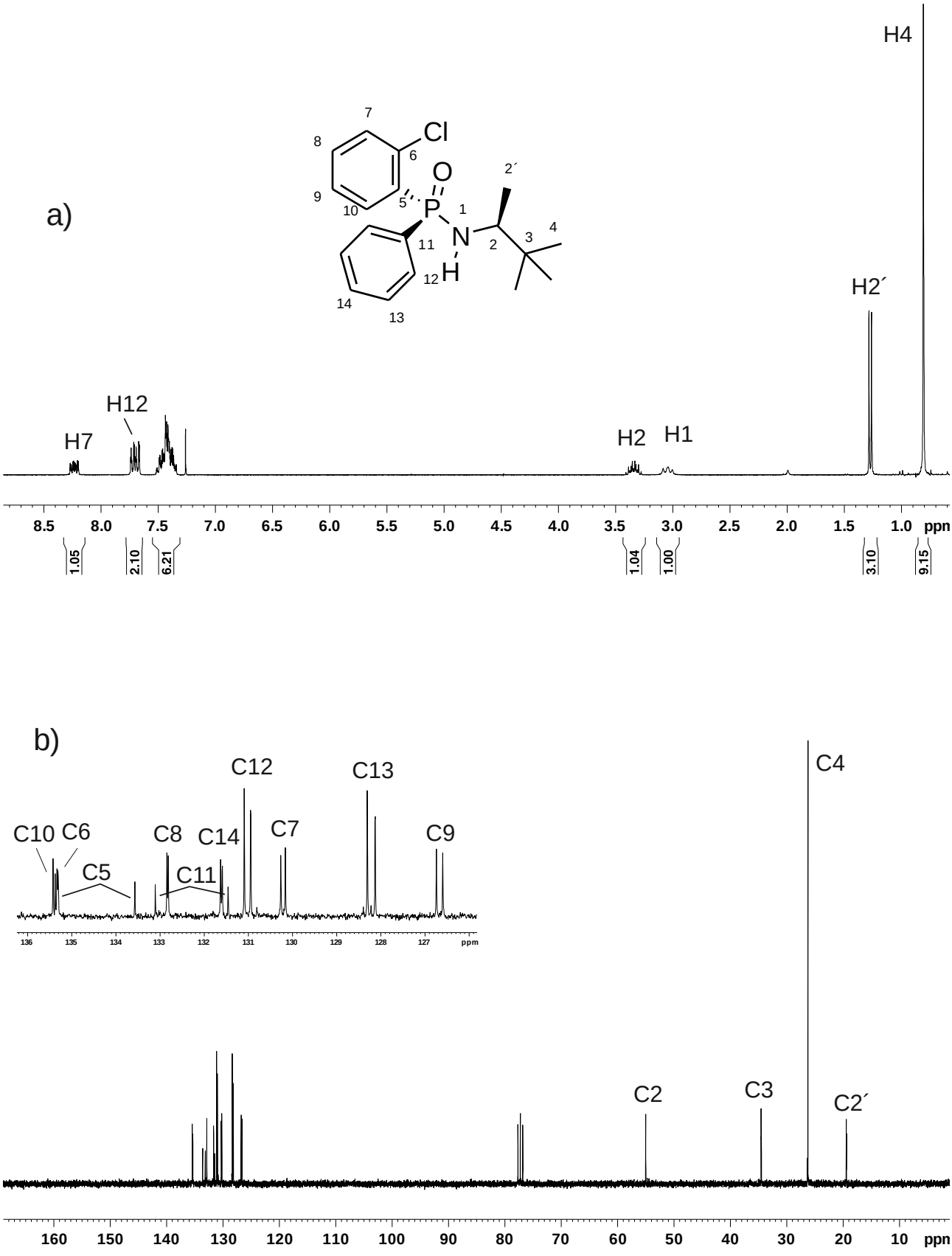


Figure S8. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **22**

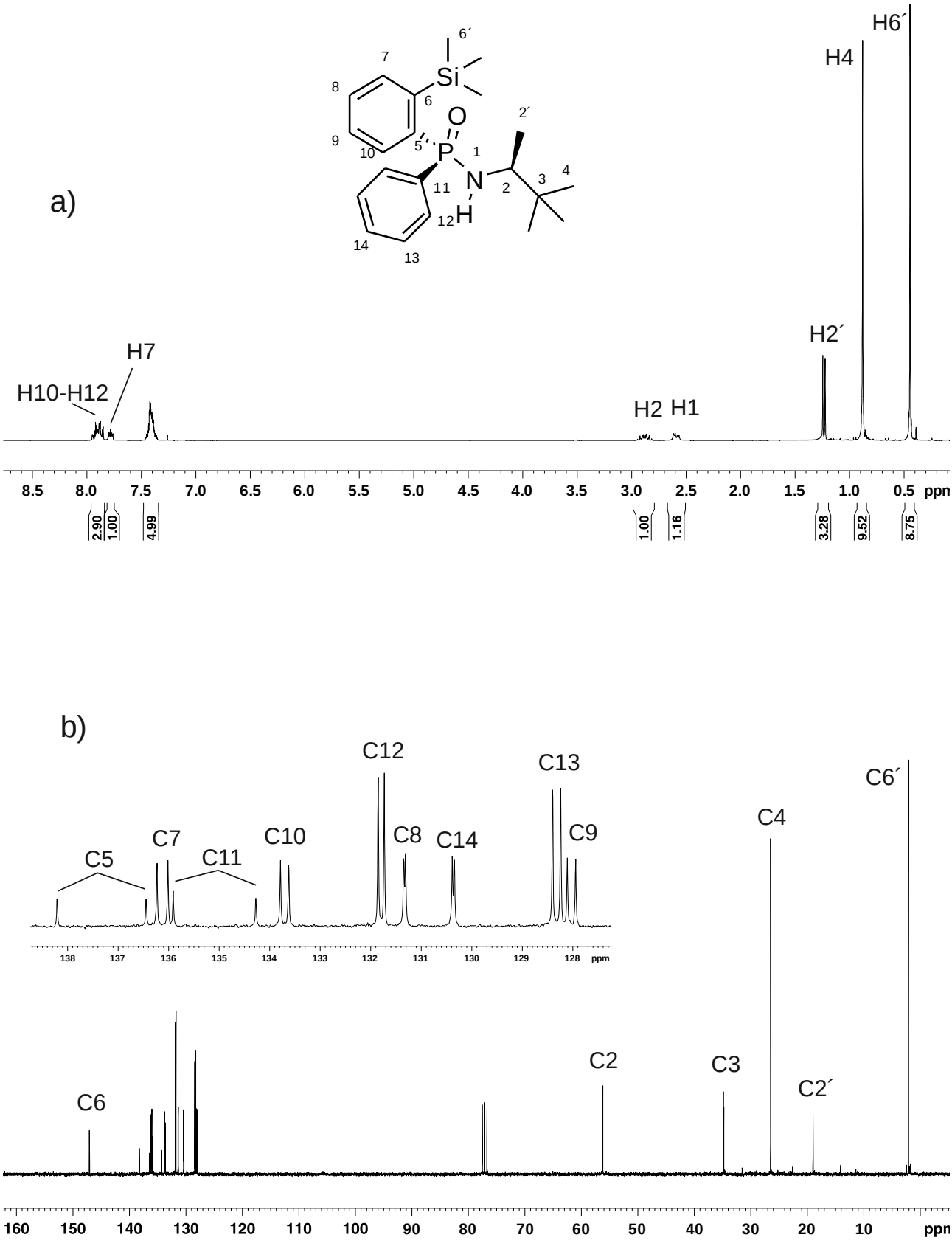


Figure S9. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **23**

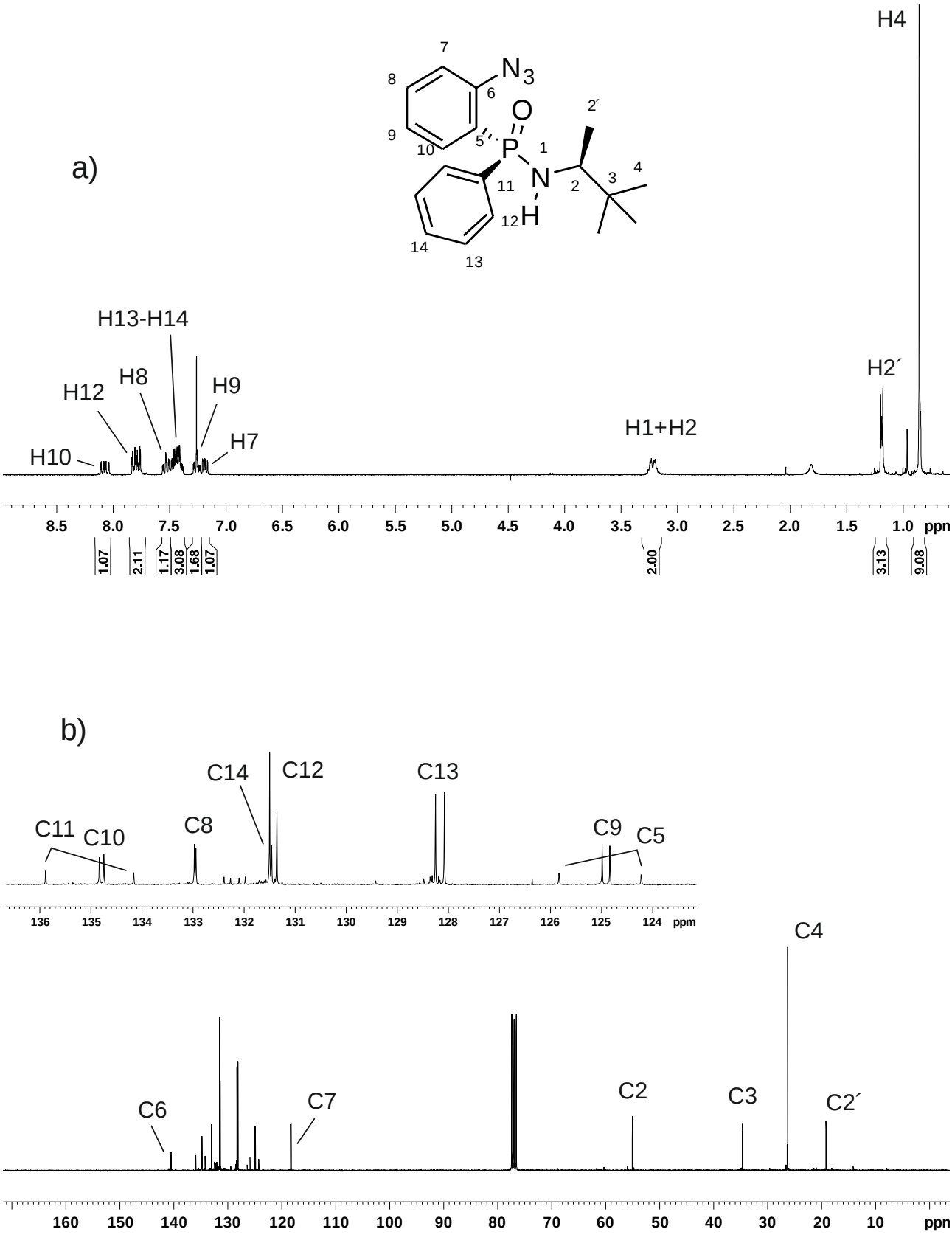


Figure S10. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **24**

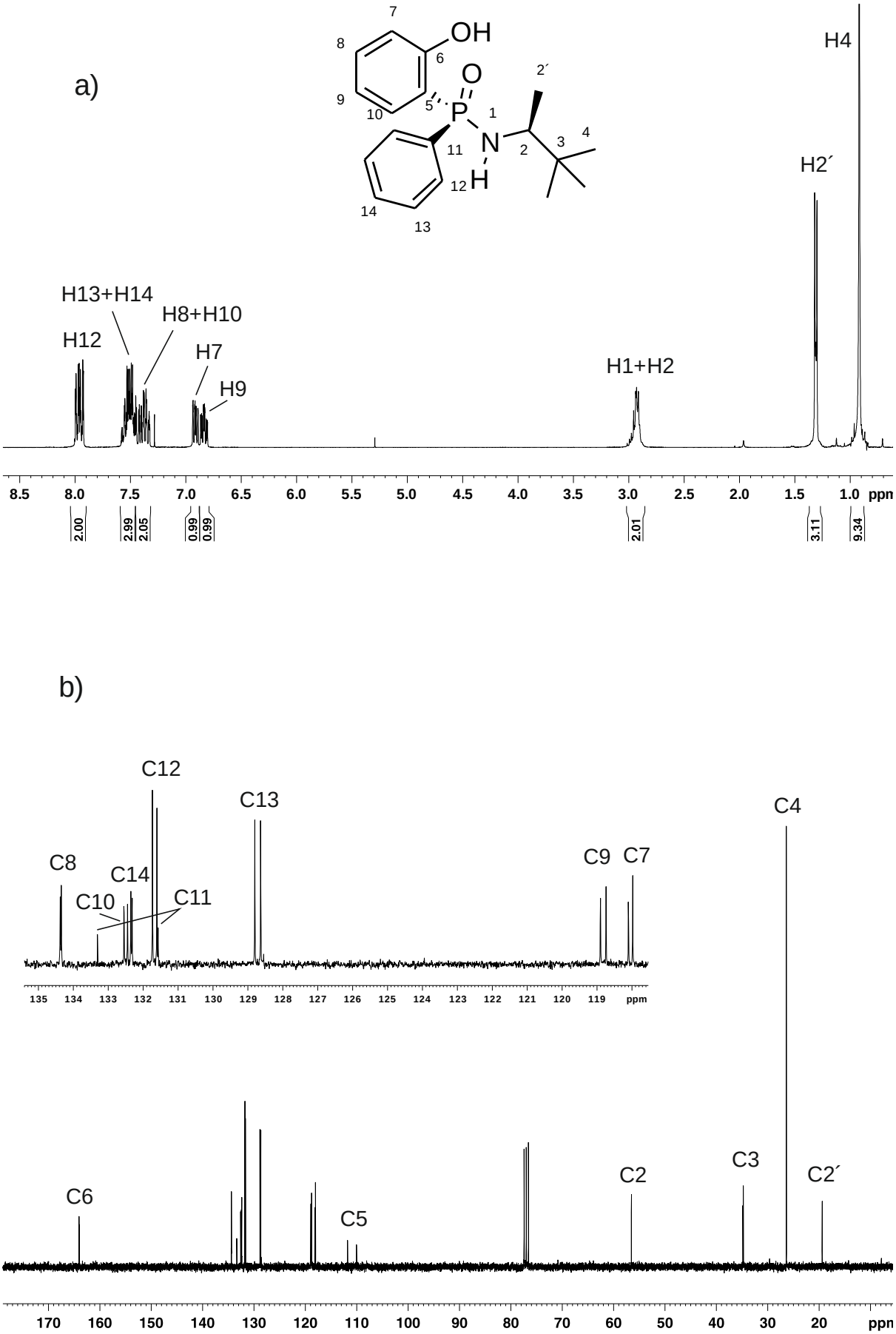


Figure S11. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **25**

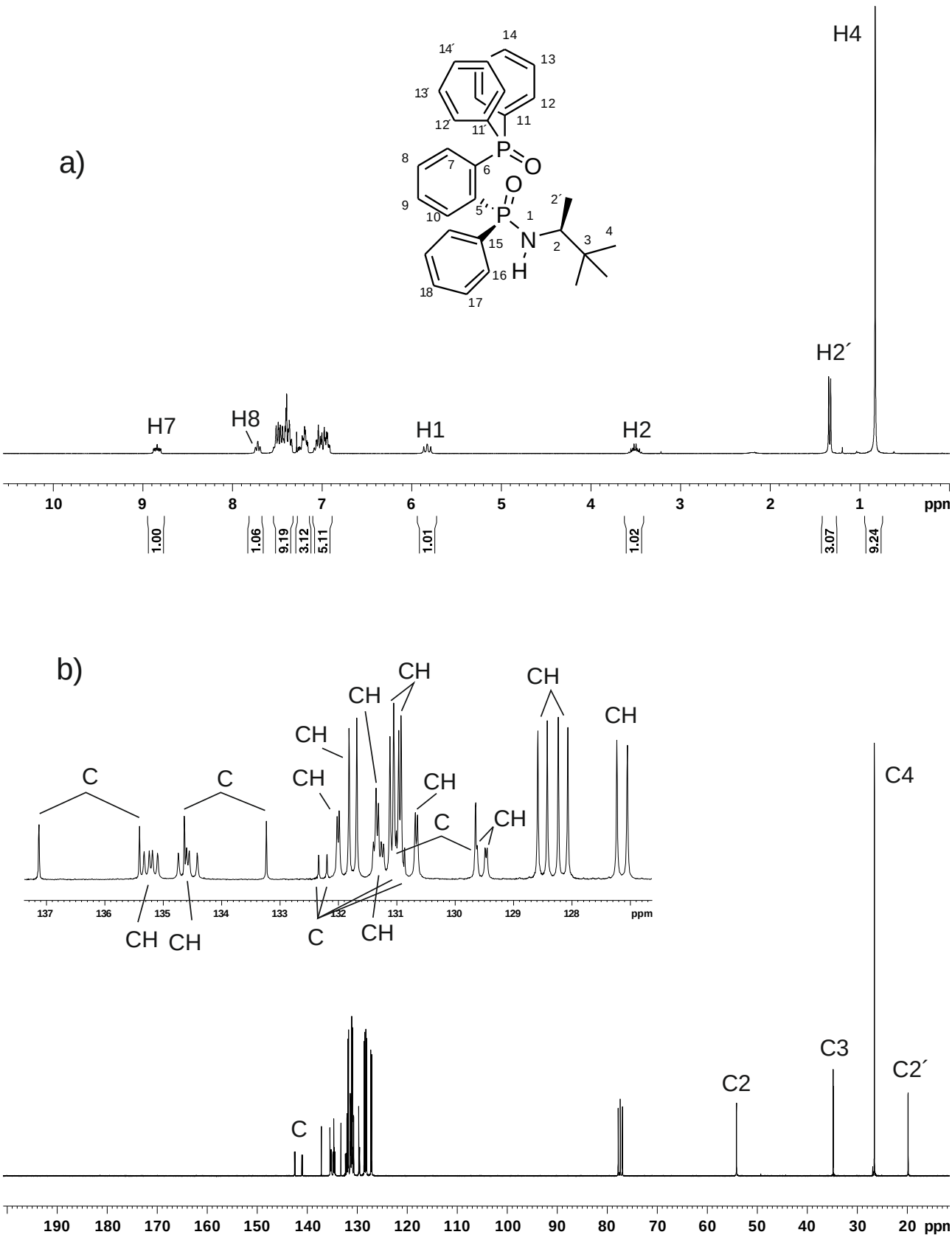


Figure S12. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **26**

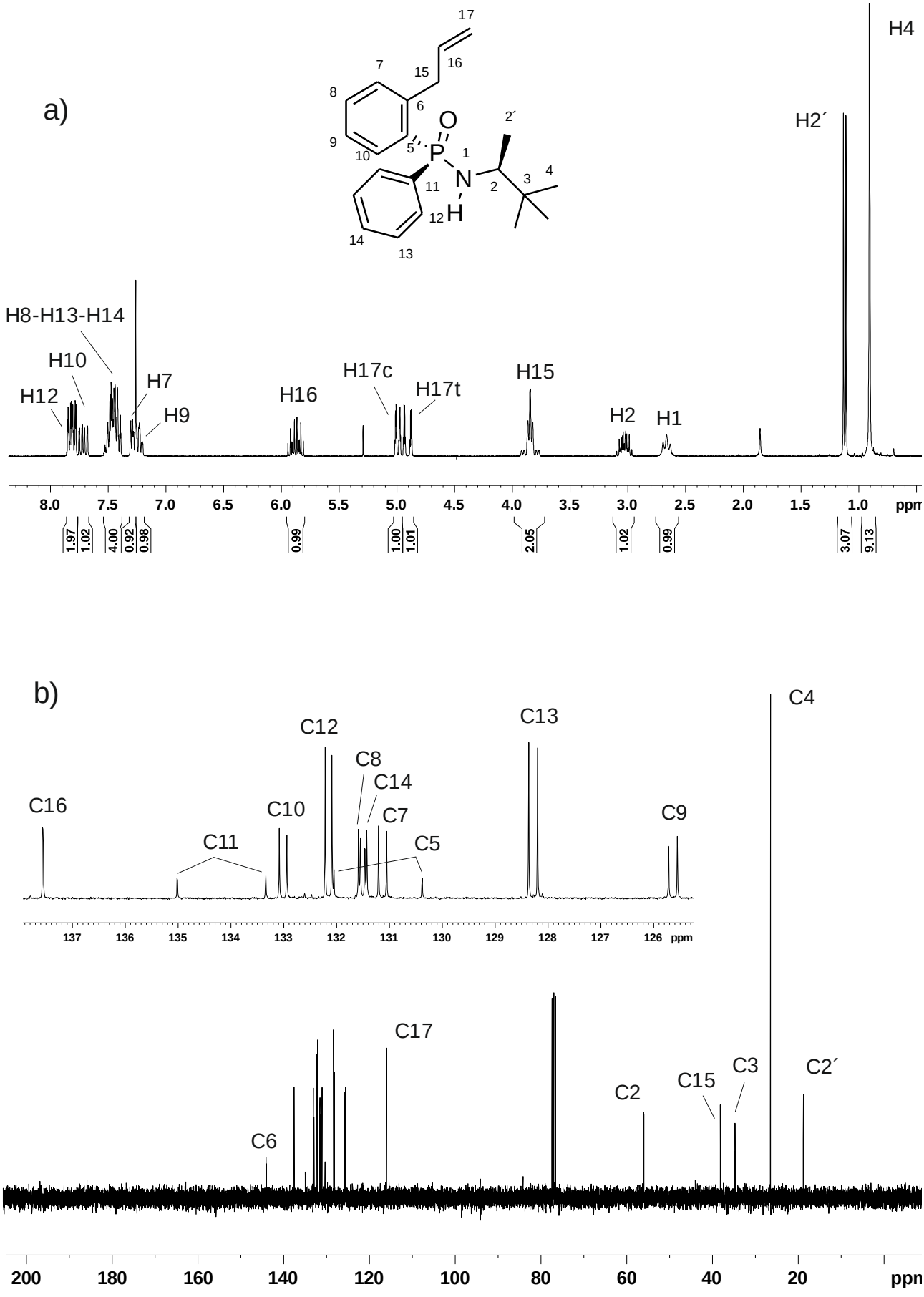


Figure S13. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **27**

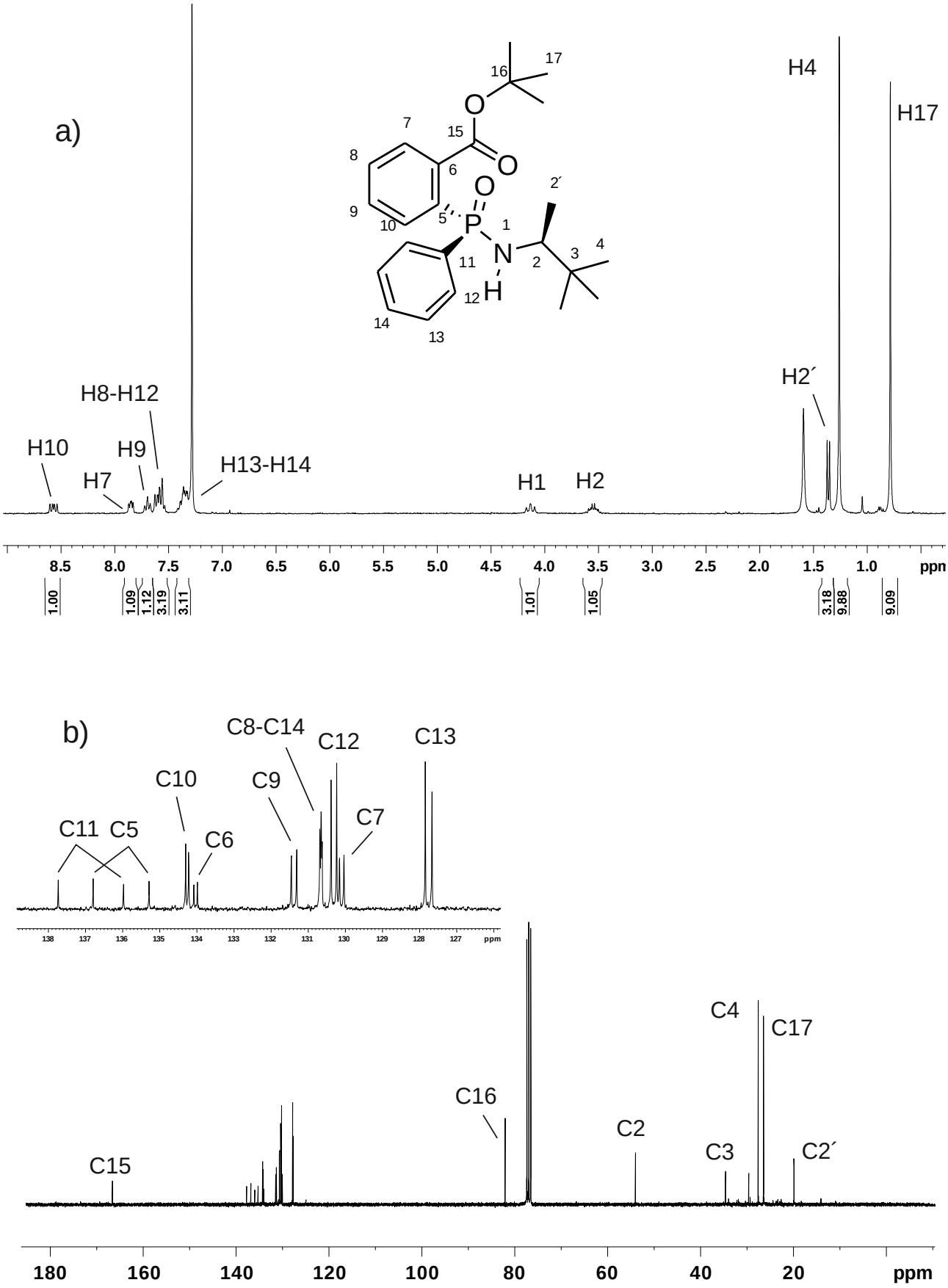


Figure S14. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **28**

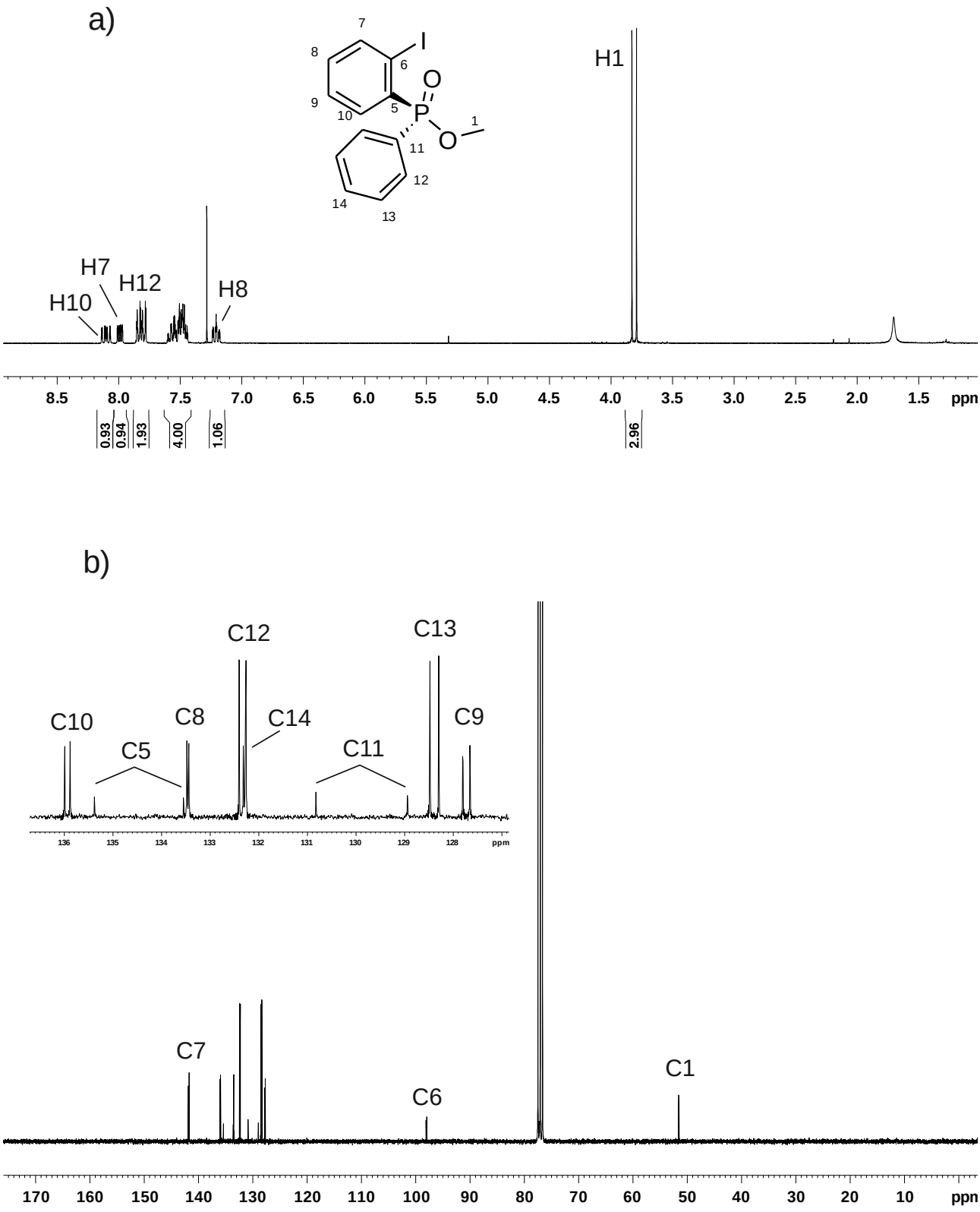


Figure S15. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **29**

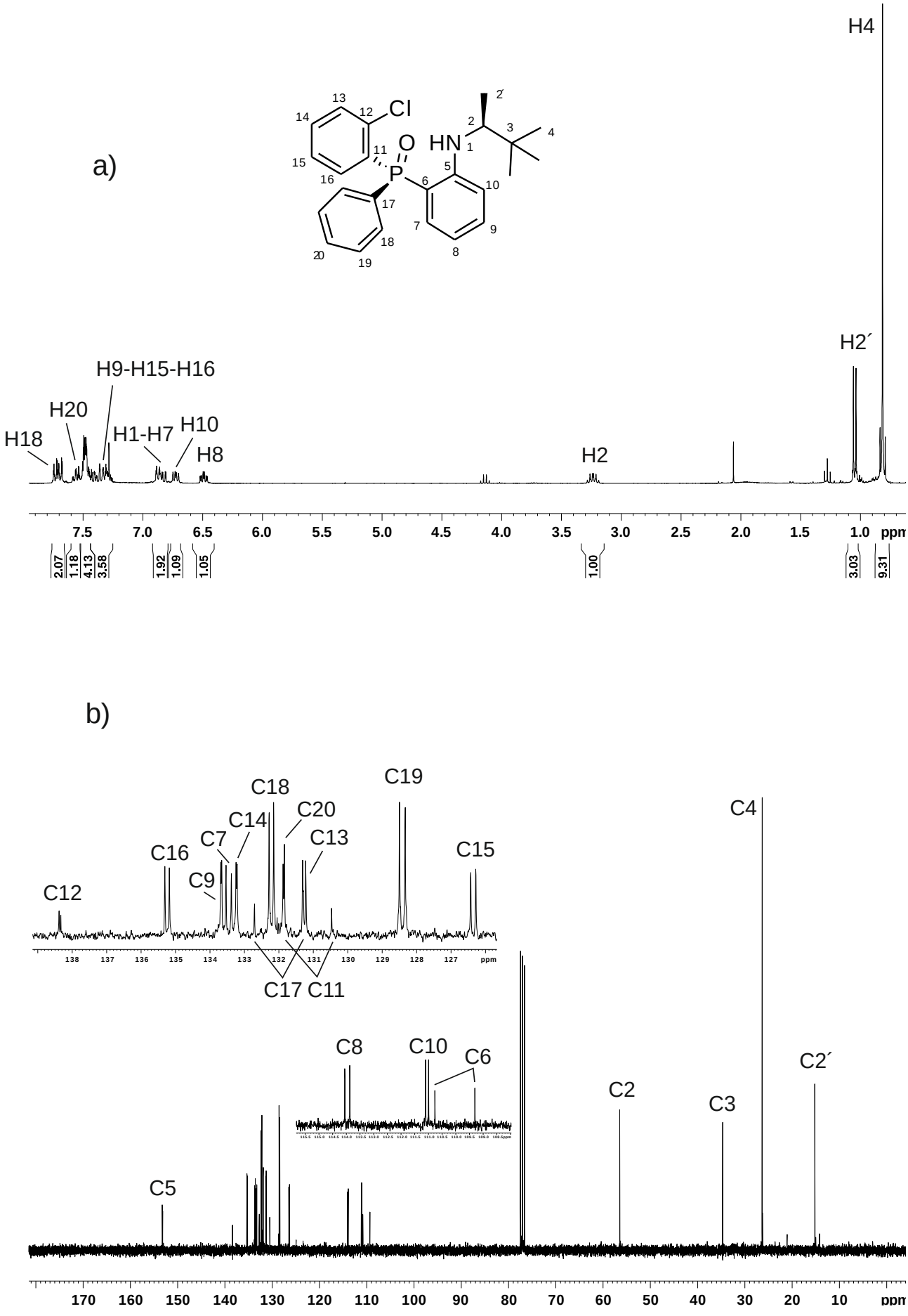


Figure S16. (a) ^{1}H (300.13 MHz) and (b) ^{13}C (75.47 MHz) NMR spectra of compound **32**

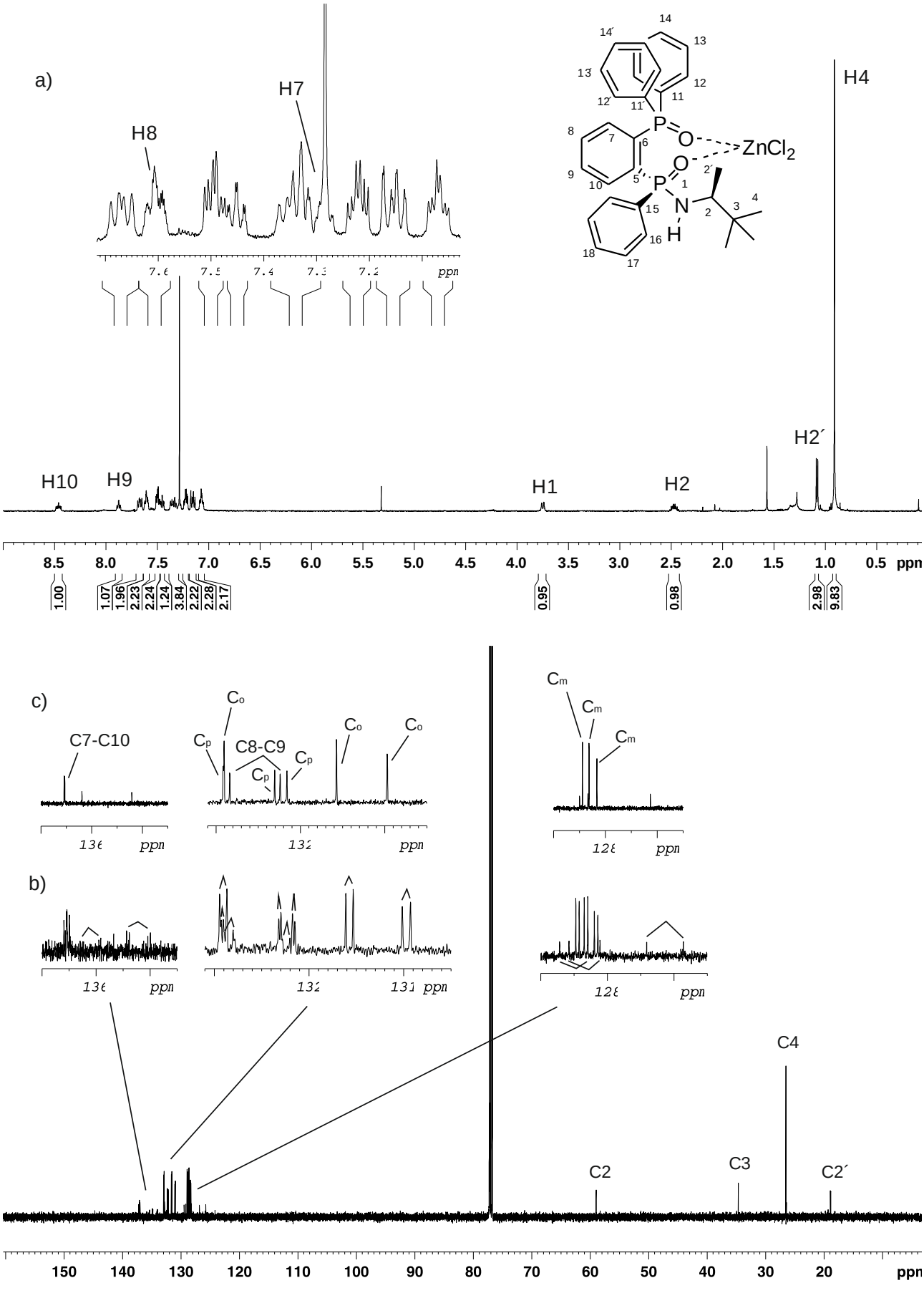


Figure S17. (a) ^{1}H (500.13 MHz), (b) ^{13}C and (c) $^{13}C\{^{31}P\}$ (125.76 MHz) NMR spectra of complex **34**.

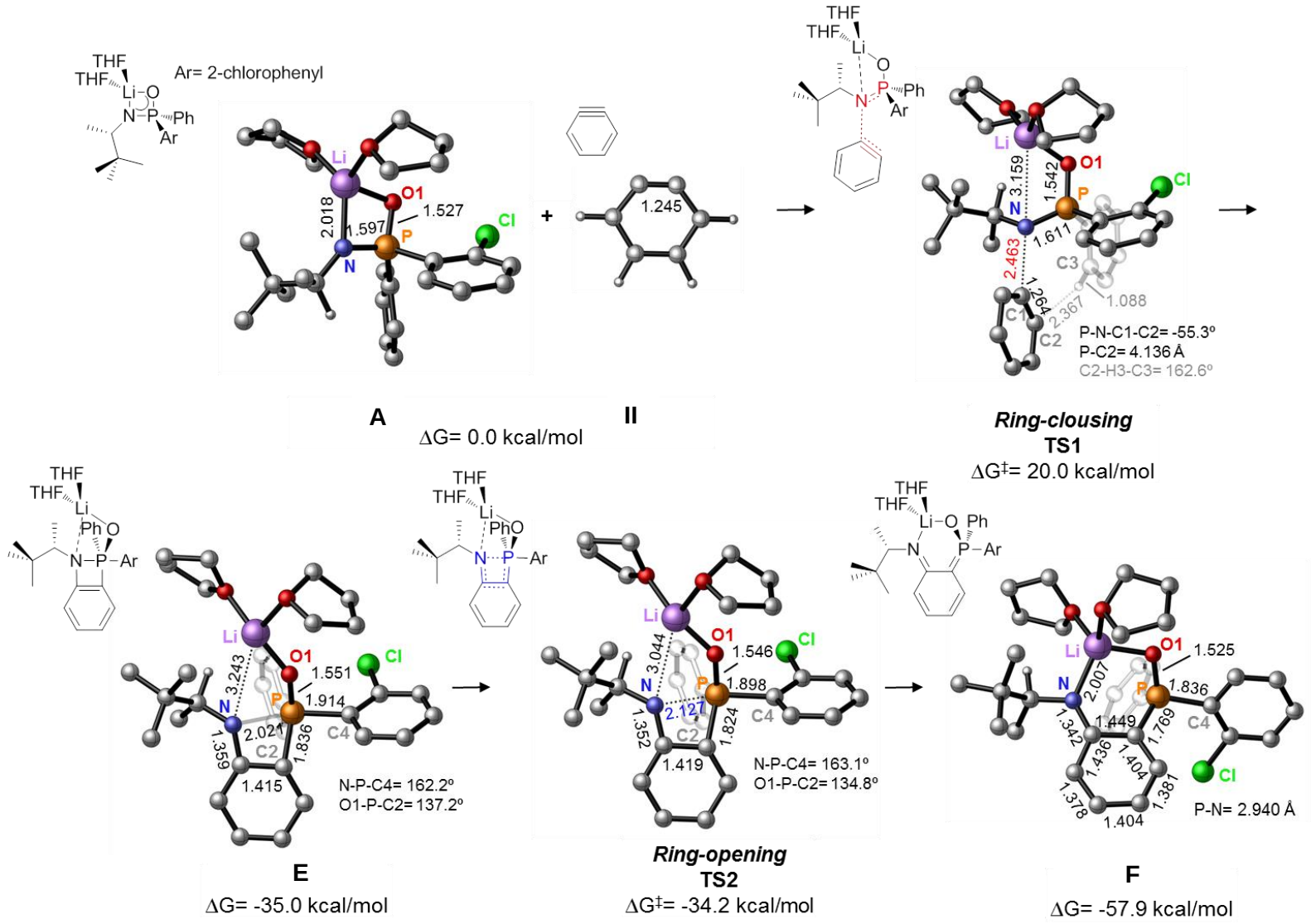


Figure S18. Computed structures for the reaction between **A** and benzyne **II**.

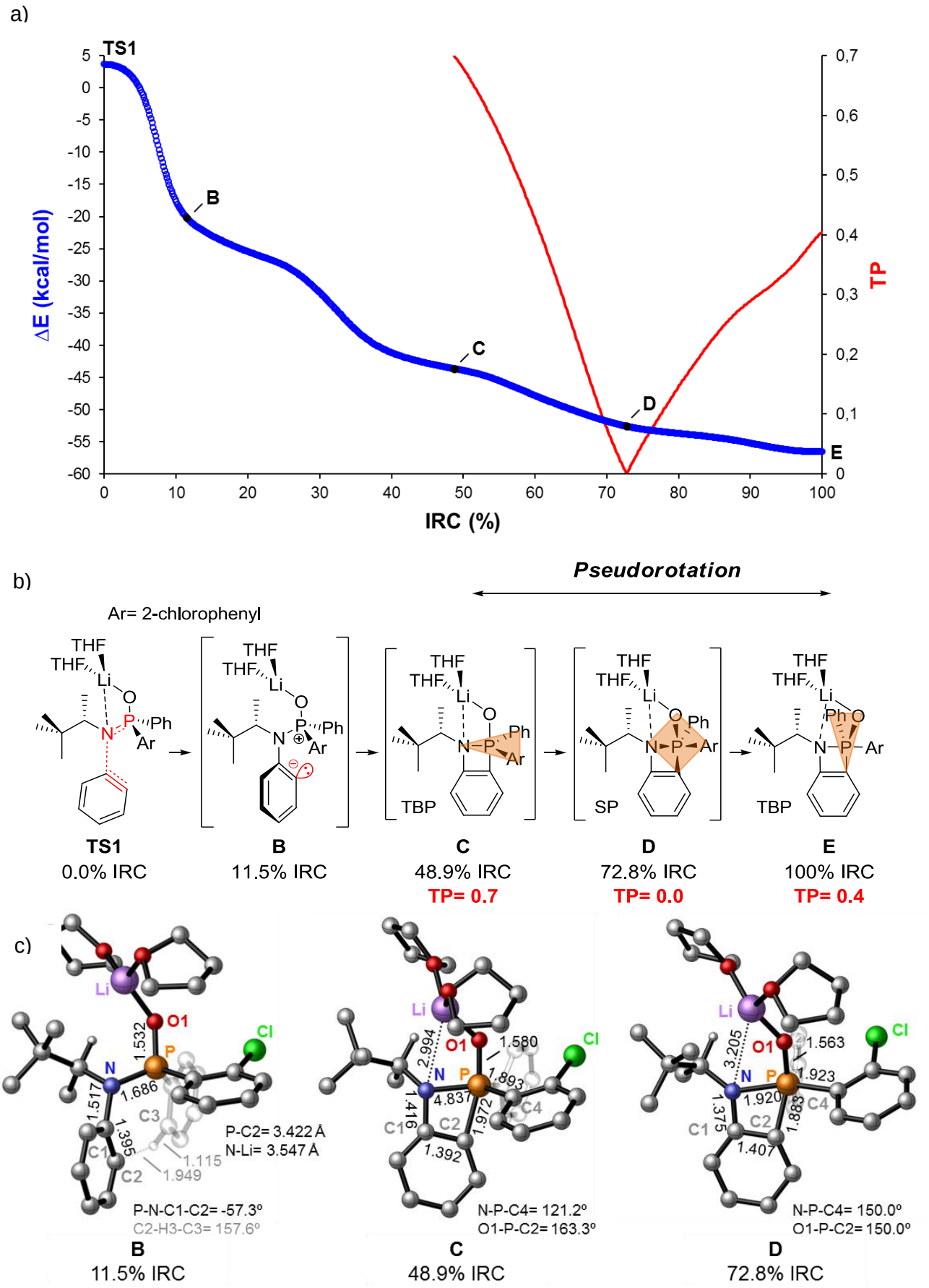


Figure S19. (a) Graph of relative energy ΔE (blue) and TP (red) along the IRC for the transformation of **TS1** into intermediate **E**. (b) Key structures found along the IRC. (c) Computed structures of species **B**, **C** and **D** including selected geometrical parameters.

Table S1. The Cartesian coordinates (Å), SCF energies, enthalpies at 333 K, and Gibbs free energies at 333 K for the optimized structures.

A

M06-2X SCF energy in gas phase:	-2102.63267278	a.u.
M06-2X enthalpy in gas phase :	-2101.97811800	a.u.
M06-2X free energy in gas phase:	-2102.10430900	a.u.
M06-2X SCF energy in solution:	-2103.07697341	a.u.
M06-2X enthalpy in solution:	-2102.42241863	a.u.
M06-2X free energy in solution:	-2102.54860963	a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	1.10002700	-1.50157900	-0.00509000
O	-0.11446600	-0.63339400	-1.26106800
P	-0.49391100	0.34328100	-0.15059800
C	-2.25357500	0.04507700	0.33966000
C	-0.56838000	2.05103300	-0.77526100
C	-3.31561300	-0.06895800	-0.56450100
C	-2.55424500	-0.08606000	1.69866100
C	-1.17138400	3.07333900	-0.03831500
C	0.06568300	2.35038500	-1.98257800
C	-4.61293600	-0.34134400	-0.13915300
C	-3.84736300	-0.34201200	2.14626600
H	-1.73871400	0.00767500	2.40820900
C	-1.11721300	4.38869800	-0.49232600
H	-1.69196500	2.84054600	0.88856900
C	0.11833500	3.66456200	-2.43698200
H	0.50441800	1.53832200	-2.55696500
C	-4.87687200	-0.48000200	1.22046500
H	-5.40512700	-0.43595800	-0.87406600
H	-4.04760000	-0.43792400	3.20869800
C	-0.46680600	4.68447900	-1.68851000
H	-1.58568700	5.18161400	0.08288200
H	0.60954300	3.89559000	-3.37757200
H	-5.88981500	-0.68961200	1.54996800
H	-0.42551300	5.70997200	-2.04329100
N	0.50685100	0.10013500	1.07010600
C	0.88573100	0.93587000	2.19260300
H	0.20856500	1.80377500	2.30444400
C	0.78895700	0.10656800	3.48194600
H	-0.22245800	-0.28792500	3.61003500
H	1.03483700	0.68512100	4.37667900
H	1.46003400	-0.75741200	3.42527500
C	2.31271100	1.55617300	2.01732800
C	3.36726800	0.46774800	1.79234600
H	3.11933300	-0.11631500	0.89922700
H	3.44605000	-0.21632500	2.64458500
H	4.35365800	0.92459400	1.64324400
C	2.32194900	2.48792500	0.80275300
H	2.09572000	1.93679100	-0.11381900
H	3.30783700	2.95406700	0.68858700
H	1.57696600	3.28696700	0.90101000
C	2.68861300	2.38158900	3.25604700
H	1.88798800	3.08443900	3.51813300
H	3.59385500	2.96720000	3.06029600
H	2.88834100	1.75195800	4.12835000
O	2.71400700	-1.77194900	-0.98666200
C	3.96177500	-2.32925100	-0.55284500
C	2.92852600	-0.76149000	-1.99027900
C	5.03935200	-1.42697300	-1.14902000
H	4.03559300	-3.35441800	-0.93381900
H	3.96823200	-2.35550500	0.54075200
C	4.36998700	-0.96004700	-2.44485300
H	2.78032600	0.22330100	-1.52835100
H	2.17450500	-0.89790700	-2.76673800
H	5.22175400	-0.57170100	-0.48990600
H	5.98342300	-1.95269600	-1.30728700
H	4.80737100	-0.04682200	-2.85373100
H	4.42613300	-1.74427700	-3.20726900
O	0.31936100	-3.22092900	0.40329400
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C	-0.74841000	-3.19399500	1.36952000
C	-1.63532500	-3.42428600	-0.86684200
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H	0.43142300	-3.38493300	-1.63034500
C	-2.04526800	-3.52468900	0.60927100
H	-0.75130600	-2.19116400	1.80621600
H	-0.52939000	-3.92663600	2.15348800
H	-1.71707700	-2.39652500	-1.22946600
H	-2.21773200	-4.08505900	-1.51349100
H	-2.85359100	-2.83358500	0.86397300
H	-2.37709300	-4.54001400	0.84791800
Cl	-3.06312200	0.13464800	-2.27987200

II

M06-2X SCF energy in gas phase:	-230.80521790	a.u.
M06-2X enthalpy in gas phase :	-230.72238800	a.u.
M06-2X free energy in gas phase:	-230.76005300	a.u.
M06-2X SCF energy in solution:	-230.87481087	a.u.
M06-2X enthalpy in solution:	-230.79198097	a.u.
M06-2X free energy in solution:	-230.82964597	a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.46080500	-0.13246700	-0.00001000
C	-0.62234600	-1.23245600	0.00000600
C	0.62244200	-1.23246500	0.00000700
C	1.46079900	-0.13238200	-0.00001000
C	0.70287800	1.05274600	0.00000200
C	-0.70294700	1.05270600	0.00000300
H	-2.54474800	-0.13327500	-0.00000500
H	2.54474400	-0.13310800	-0.00000800
H	1.22432100	2.00617700	0.00001400
H	-1.22444600	2.00610600	0.00001000

TS1

Ring-closing

M06-2X SCF energy in gas phase:	-2333.43213250	a.u.
M06-2X enthalpy in gas phase :	-2332.69339400	a.u.
M06-2X free energy in gas phase:	-2332.83342500	a.u.
M06-2X SCF energy in solution:	-2333.94506493	a.u.
M06-2X enthalpy	-2333.20632643	a.u.

in solution:

M06-2X free energy
in solution: -2333.34635743 a.u.

Imaginary frequency: -88.7995 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
P	-0.25387900	0.38241500	0.50324700
C	-0.57670400	0.25604600	2.29776000
C	-1.68798300	-0.44879900	2.76653500
C	0.32613700	0.80720700	3.21104100
C	-1.89635400	-0.59115100	4.13584300
H	-2.37470500	-0.91288900	2.06100500
C	0.12262400	0.65390000	4.57965100
C	-0.99108600	-0.04371100	5.04255600
H	-2.76193100	-1.14021500	4.49421600
H	0.82703300	1.08474100	5.28533400
H	-1.15259600	-0.16159200	6.11023000
C	-1.55061500	1.48564800	-0.18674800
C	-2.27074800	1.06264700	-1.30905400
C	-1.80392000	2.78188500	0.27858600
C	-3.22392600	1.86829600	-1.92161800
H	-2.05602200	0.07568200	-1.69476000
C	-2.75144200	3.60580100	-0.32517700
C	-3.46899200	3.14444000	-1.42316600
H	-3.77248400	1.49659600	-2.78119900
H	-2.91742000	4.60077300	0.07332600
H	-4.21134800	3.78684100	-1.88664500
O	1.09859000	1.11593600	0.39345800
N	-0.38822300	-1.01131700	-0.29299300
C	-2.59042800	-2.09281900	-0.51175200
C	-3.32625400	-2.38700900	0.47243000
C	-2.74904400	-2.23290900	-1.87124100
C	-4.56964000	-2.97878800	0.21789900
C	-3.98908400	-2.82425900	-2.15500300
H	-2.03612600	-1.95078000	-2.63895400
C	-4.87978700	-3.18800300	-1.13134300
H	-5.27445100	-3.26843400	0.99435400
H	-4.26065800	-3.00562800	-3.19138800
H	-5.83010600	-3.64297100	-1.39915700
C	0.69262300	-1.97194800	-0.01216800
H	1.60900000	-1.42690400	0.30135800
Cl	-0.93284400	3.46161100	1.63268400
H	1.17149500	1.37477100	2.83205500
Li	2.26936200	0.59916700	-0.86124600
O	2.20113200	1.73685500	-2.38814200
C	0.86220500	1.72534100	-2.94084300
C	2.51375000	3.05996800	-1.91347600
C	0.31361500	3.14468800	-2.77480800
H	0.92729200	1.40244500	-3.98358400
H	0.27535400	0.99253300	-2.37600200
C	1.16536600	3.70405500	-1.63115300
H	3.14771200	2.95203700	-1.02777300
H	3.07327600	3.59145000	-2.69341100
H	-0.75518100	3.14177000	-2.54557700
H	0.47204000	3.72554900	-3.68953500
H	0.79384900	3.34876800	-0.66623800
H	1.21300900	4.79537500	-1.62480800
O	3.91092500	0.08415100	-0.08674500
C	3.93214500	-0.05034600	1.34128500
C	5.11387000	-0.49977800	-0.59547400
C	4.49693200	-1.44773800	1.56061500
H	4.58867400	0.72408700	1.76116900
H	2.90997300	0.10206900	1.69225200
C	5.53096000	-1.58318100	0.42397500
H	4.88997100	-0.89259600	-1.59021300
H	5.87613600	0.28238400	-0.68744100
H	3.69722100	-2.18579300	1.44795600
H	4.93956800	-1.56792500	2.55147600
H	5.51603800	-2.58230300	-0.01704600
H	6.54420100	-1.39332500	0.78635300
C	0.32898700	-2.90795100	1.14888900
H	0.23737900	-2.33848000	2.07761800
H	-0.63708100	-3.38279400	0.95813500
H	1.08170000	-3.68991700	1.30376700
C	1.15549100	-2.76518600	-1.28062200
C	0.25281200	-3.96684500	-1.58424400
H	-0.79717500	-3.68015000	-1.65807700
H	0.55003300	-4.43119300	-2.53208400
H	0.33550400	-4.72897500	-0.80290600
C	2.58157900	-3.28703000	-1.05047900
H	2.92421400	-3.86544100	-1.91648000
H	3.27666600	-2.45130100	-0.90399900
H	2.64520000	-3.93820600	-0.17175600
C	1.19522500	-1.83937800	-2.49817300
H	1.89888000	-1.00453300	-2.34805800
H	1.54440000	-2.38281300	-3.38398500
H	0.21242300	-1.40870200	-2.70089000

[B]

Electronic energy from IRC: -2333.47011051 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	-0.42747000	0.22716300	0.46881100
C	-0.61190800	0.13462300	2.27299900
C	-1.68612600	-0.56850400	2.82334000
C	0.33818000	0.74180600	3.10465400
C	-1.81307800	-0.64664100	4.20734400
H	-2.35024900	-1.14916900	2.14153500
C	0.20489000	0.64660900	4.48624000
C	-0.87650800	-0.04243000	5.03807900
H	-2.64566700	-1.19959700	4.63298700
H	0.93965600	1.11451400	5.13481000
H	-0.97764400	-0.11068200	6.11794800
C	-1.62460500	1.41492900	-0.23460300
C	-2.33214700	1.05826100	-1.38797900
C	-1.80380600	2.72107500	0.24641100
C	-3.23539300	1.92144200	-1.99430200
H	-2.19270100	0.07258300	-1.80427800
C	-2.70769300	3.59564700	-0.35138600
C	-3.43865600	3.18887300	-1.46187000
H	-3.78345300	1.59198300	-2.87055000
H	-2.82931600	4.59034400	0.06298000
H	-4.15296800	3.87109000	-1.91189400
O	0.97656300	0.77638700	0.19508200
N	-0.67130900	-1.24727000	-0.31064600
C	-2.02869900	-1.89221700	-0.51660700
C	-2.85687000	-2.18150000	0.56746500
C	-2.37842300	-2.16041800	-1.85552800
C	-4.08194600	-2.79596500	0.20262500
C	-3.60096500	-2.75377400	-2.14997000
H	-1.71407100	-1.90296700	-2.68003500
C	-4.46545900	-3.08502800	-1.10275300
H	-4.78855700	-3.06052700	0.99390200
H	-3.87044100	-2.95459700	-3.18353200
H	-5.42431700	-3.55434100	-1.31740200
C	0.49819800	-2.15513100	-0.04953400
H	1.31520800	-1.49369900	0.27317600
Cl	-0.88985800	3.36381000	1.59077700
H	1.15904300	1.30217500	2.66496200
Li	2.33048000	0.53381500	-0.93960600
O	2.24468700	1.69815000	-2.42959000
C	0.90668500	1.69269700	-2.98871800
C	2.55852400	3.02043900	-1.95310100
C	0.35968900	3.11050500	-2.80834600

H	0.97523400	1.37833400	-4.03327800
H	0.31576600	0.95978200	-2.42945900
C	1.20838500	3.65260500	-1.65441800
H	3.20752500	2.91223200	-1.07808500
H	3.10441600	3.55975100	-2.73679800
H	-0.70999400	3.10630900	-2.58341400
H	0.52324100	3.70355800	-3.71398700
H	0.83384800	3.27794200	-0.69695100
H	1.24939000	4.74351300	-1.62383100
O	3.94366500	0.02603200	-0.11648200
C	3.95701900	-0.10517100	1.31268900
C	5.15453600	-0.55336500	-0.61835500
C	4.54036600	-1.49341800	1.54575600
H	4.59673300	0.68124400	1.73514200
H	2.92952700	0.02773000	1.65750900
C	5.56361100	-1.64014400	0.39920300
H	4.93850200	-0.94249800	-1.61621800
H	5.91402800	0.23225500	-0.69990600
H	3.74915200	-2.24321000	1.45974000
H	4.99621400	-1.58973200	2.53300100
H	5.52835600	-2.63852500	-0.04214800
H	6.58287700	-1.46660400	0.75178200
C	0.22054400	-3.10973300	1.11331000
H	0.06983800	-2.54114600	2.03449700
H	-0.69038700	-3.68604300	0.94038400
H	1.05986200	-3.79607300	1.26637800
C	1.07529700	-2.85949300	-1.31819600
C	0.29370700	-4.12168400	-1.70440100
H	-0.76049300	-3.91932600	-1.89619800
H	0.73163700	-4.56834800	-2.60484700
H	0.35130600	-4.86667300	-0.90458700
C	2.52592500	-3.27853100	-1.01891700
H	2.96727700	-3.75575300	-1.90147300
H	3.13636300	-2.40185900	-0.76738500
H	2.59335300	-3.99133800	-0.19102100
C	1.14745900	-1.88429500	-2.49825100
H	1.84951300	-1.06108300	-2.29079400
H	1.53106800	-2.39427700	-3.38907800
H	0.18104500	-1.44028700	-2.73468200

[C]

Electronic energy from IRC: -2333.50755578 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	-0.82261700	-0.00539900	0.43690500
C	-0.87016100	-0.11390500	2.29445200
C	-1.85948400	-0.79642900	3.00920300
C	0.16984500	0.48885600	3.01798000
C	-1.81168900	-0.87441100	4.40124500
H	-2.66985800	-1.28243800	2.47931400
C	0.21898100	0.41413100	4.40531100
C	-0.77462000	-0.27033600	5.10324000
H	-2.59077200	-1.41094200	4.93460500
H	1.02822100	0.89836200	4.94467000
H	-0.74094100	-0.32906000	6.18738900
C	-1.73810800	1.45716300	-0.34068500
C	-2.41690200	1.22894600	-1.55081000
C	-1.79747100	2.76021800	0.15985500
C	-3.12767600	2.22586100	-2.20858000
H	-2.40275500	0.22908700	-1.97701000
C	-2.53071300	3.76925800	-0.46841800
C	-3.20137000	3.50183900	-1.65422500
H	-3.63724300	1.99991900	-3.14001600
H	-2.56881400	4.75378100	-0.01442100
H	-3.77367400	4.28612100	-2.13965800
O	0.61129100	0.64271200	0.29268600
N	-0.40627400	-1.49984500	-0.54708400
C	-1.72814600	-2.00270200	-0.61582800
C	-2.44967500	-1.07777200	0.13399700
C	-2.36142700	-2.99815400	-1.35591200
C	-3.83158800	-1.12731900	0.17794200
C	-3.75878300	-3.06690200	-1.26995700
H	-1.83335700	-3.67628100	-2.01462600
C	-4.48992900	-2.15778100	-0.51063100
H	-4.40639100	-0.38290800	0.72611400
H	-4.28095100	-3.83986500	-1.82720200
H	-5.57226500	-2.23727500	-0.47090400
C	0.78113900	-2.31623200	-0.27260500
H	1.52629100	-1.58105100	0.06316600
Cl	-0.97705300	3.21929300	1.63643500
H	0.91788100	1.04238100	2.46232600
Li	1.89820300	0.38599000	-0.86096700
O	2.14851800	1.48861200	-2.39361500
C	0.85093200	1.64326300	-3.02251900
C	2.56948200	2.76061000	-1.86688500
C	0.41529700	3.08857800	-2.76131100
H	0.95392700	1.40453200	-4.08472000
H	0.17055800	0.92219100	-2.55510900
C	1.27022400	3.48535200	-1.55408800
H	3.19902800	2.55831200	-0.99557100
H	3.16181200	3.28451900	-2.62829300
H	-0.65582600	3.16106300	-2.56493200
H	0.65622500	3.72122800	-3.62235400
H	0.84094500	3.07715800	-0.63300600
H	1.39762600	4.56546600	-1.45179000
O	3.59252700	0.13117200	-0.05212100
C	3.61292000	-0.10263700	1.36008600
C	4.91752600	-0.08693800	-0.53586800
C	4.49438900	-1.33917300	1.51065800
H	4.05154600	0.77274400	1.85906600
H	2.57612900	-0.22366400	1.67956300
C	5.51871500	-1.18978700	0.36257500
H	4.84087100	-0.35968200	-1.59101400
H	5.48348700	0.84970500	-0.45271100
H	3.88858800	-2.23879500	1.37151600
H	4.96529700	-1.39408000	2.49412600
H	5.64195500	-2.12838000	-0.18260200
H	6.50092100	-0.88860500	0.73380600
C	0.53684600	-3.26883900	0.90367300
H	0.27678400	-2.69282400	1.79717600
H	-0.29560200	-3.94609100	0.68721100
H	1.42086800	-3.87514200	1.12943900
C	1.42181300	-3.02493900	-1.51387700
C	0.89600100	-4.44891100	-1.74129900
H	-0.19035100	-4.49263900	-1.81439400
H	1.31181800	-4.85328200	-2.67088400
H	1.19624800	-5.11594200	-0.92709600
C	2.93437900	-3.14138600	-1.27203600
H	3.42098600	-3.64934200	-2.11236800
H	3.38685000	-2.15011700	-1.16240400
H	3.15323200	-3.71714300	-0.36509200
C	1.19795100	-2.18088000	-2.77078900
H	1.61376800	-1.17002300	-2.65431400
H	1.69951600	-2.63920100	-3.63087200
H	0.13328600	-2.07115300	-2.99576600

[D]

Electronic energy from IRC: -2333.52181147 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	-0.98350200	0.02613900	0.17062300
C	-0.99975200	-0.13059600	2.00462900
C	-1.98785800	-0.81002600	2.72418200
C	0.10358200	0.37778600	2.69832900

C	-1.86481000	-0.98160900	4.10250000
H	-2.85358400	-1.21640600	2.21178900
C	0.22766800	0.20579000	4.07349300
C	-0.75849400	-0.47908900	4.78059900
H	-2.64096100	-1.51210200	4.64600000
H	1.08844000	0.61519500	4.59512000
H	-0.66792100	-0.61408700	5.85442600
C	-1.91879600	1.62339800	-0.34976000
C	-2.62385200	1.53458300	-1.56250800
C	-1.82941300	2.91124000	0.18945700
C	-3.21955700	2.63132800	-2.18096200
H	-2.71103300	0.56165800	-2.03826500
C	-2.42887900	4.02483000	-0.39669500
C	-3.13143300	3.88612900	-1.58873700
H	-3.75204400	2.50081000	-3.11827600
H	-2.33686500	4.99170400	0.08686600
H	-3.59747900	4.75349700	-2.04599000
O	0.38761300	0.67021000	-0.21585900
N	-0.37363100	-1.74987900	-0.23113800
C	-1.64725800	-2.26404000	-0.28774000
C	-2.43405000	-1.09835800	-0.25048800
C	-2.26569500	-3.51791300	-0.33144200
C	-3.81013900	-1.12854900	-0.27563900
C	-3.66708100	-3.54177100	-0.36755500
H	-1.70590800	-4.44596400	-0.34940400
C	-4.44035100	-2.38495300	-0.34189400
H	-4.39582000	-0.21288100	-0.23373700
H	-4.16520800	-4.50682600	-0.41570200
H	-5.52279200	-2.45319200	-0.37174400
C	0.89150300	-2.42023100	-0.06475500
H	1.59048400	-1.62385100	0.23728000
Cl	-0.93284200	3.22678900	1.66456600
H	0.84593700	0.93973400	2.14001200
Li	1.91478400	0.35952600	-0.99502900
O	2.22028700	1.62206500	-2.39781900
C	0.96150700	1.83374500	-3.08607600
C	2.62497900	2.85173100	-1.77189700
C	0.52167000	3.26478200	-2.75912600
H	1.12266700	1.66142200	-4.15369500
H	0.24798700	1.10400900	-2.69374900
C	1.32239000	3.58563400	-1.49336200
H	3.19661300	2.58838400	-0.87638800
H	3.27347400	3.40825600	-2.46126700
H	-0.55728400	3.32880700	-2.59935100
H	0.79739900	3.94731800	-3.57004800
H	0.83466600	3.14287700	-0.61999300
H	1.46400400	4.65688700	-1.33260900
O	3.53064400	0.03416400	-0.03716000
C	3.58320000	-0.13939600	1.38212500
C	4.84217000	-0.19994200	-0.55900900
C	4.50421800	-1.33856400	1.56690600
H	3.99654800	0.76885300	1.84213200
H	2.56125400	-0.29333100	1.73307200
C	5.53677000	-1.15588400	0.43581700
H	4.72259900	-0.61838800	-1.56147000
H	5.37085900	0.75710500	-0.63808400
H	3.93230000	-2.26080800	1.42841000
H	4.96177000	-1.36498100	2.55783400
H	5.79648100	-2.10806000	-0.03195400
H	6.45927700	-0.70824300	0.81323700
C	0.86448700	-3.43131600	1.08870900
H	0.48427800	-2.92850500	1.98391400
H	0.20291700	-4.27683700	0.87794800
H	1.86008900	-3.82899100	1.31157400
C	1.46312400	-2.98046400	-1.40995900
C	0.57233000	-4.08206100	-1.99105400
H	-0.41827400	-3.69550600	-2.24792600
H	1.02602900	-4.48882500	-2.90244500
H	0.44796900	-4.91239100	-1.28776700
C	2.87805800	-3.53066600	-1.19796100
H	3.33380200	-3.78817400	-2.16140700
H	3.51429700	-2.77565400	-0.71742600
H	2.88443400	-4.43216000	-0.57729800
C	1.55135500	-1.83795000	-2.43177500
H	2.41779200	-1.18975800	-2.22734400
H	1.71035400	-2.22798500	-3.44377600
H	0.63094300	-1.24416400	-2.43137900

E

M06-2X SCF energy in gas phase:	-2333.52812597	a.u.
M06-2X enthalpy in gas phase :	-2332.78706300	a.u.
M06-2X free energy in gas phase:	-2332.92449400	a.u.
M06-2X SCF energy in solution:	-2334.03762846	a.u.
M06-2X enthalpy in solution:	-2333.29656549	a.u.
M06-2X free energy in solution:	-2333.43399649	a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	1.06917700	0.46786500	-0.17288300
C	0.71712200	0.78474600	1.58959800
C	1.31018300	1.83415400	2.29377300
C	-0.25134800	0.00058600	2.22104800
C	0.92550400	2.10125800	3.60631700
H	2.06484800	2.44941400	1.81175000
C	-0.64052300	0.27175600	3.52855000
C	-0.05347400	1.32743100	4.22427200
H	1.39247600	2.91898500	4.14705700
H	-1.39290800	-0.34648800	4.01167400
H	-0.35248500	1.54022800	5.24616300
C	2.73248500	-0.47765400	-0.20124400
C	3.39755200	-0.40547300	-1.43986200
C	3.27735800	-1.38320300	0.71242500
C	4.52572400	-1.15855400	-1.74349600
H	3.00112200	0.26672200	-2.19729100
C	4.41109800	-2.14948800	0.43698200
C	5.04033300	-2.03777600	-0.79516100
H	4.99717400	-1.06129900	-2.71675600
H	4.78612400	-2.82937800	1.19463300
H	5.92147300	-2.63479900	-1.00865600
O	0.29172000	-0.75145900	-0.73360400
N	-0.43388700	1.73266200	-0.64945000
C	0.46947400	2.72436800	-0.86883500
C	1.71832500	2.06164000	-0.81213900
C	0.44690300	4.11291200	-1.09122300
C	2.92463700	2.71349800	-0.98322700
C	1.66995400	4.75967700	-1.27610100
H	-0.47990200	4.67380000	-1.13759300
C	2.89630800	4.09302200	-1.22820100
H	3.86955200	2.18094100	-0.91170400
H	1.66417600	5.83128200	-1.46086700
H	3.82044700	4.64270300	-1.37070400
C	-1.80027900	1.83659900	-0.20768700
H	-1.99970100	0.87593900	0.30301700
Cl	2.56371500	-1.65916400	2.29702400
H	-0.67507200	-0.84982600	1.68893500
Li	-1.35758300	-1.37374300	-0.76502800
O	-1.10397100	-3.11239000	-1.59094500
C	0.00242400	-3.06412600	-2.51801100
C	-0.77012800	-4.08917100	-0.59616100
C	1.24974000	-3.53845100	-1.74665300

H	-0.23504600	-3.72024500	-3.36293400
H	0.08590700	-2.03195100	-2.86015200
C	0.71714700	-3.87526300	-0.34281700
H	-1.40974100	-3.90438800	0.27107900
H	-0.97891400	-5.09218300	-0.99414700
H	2.00964700	-2.75627000	-1.69831000
H	1.68276500	-4.42034400	-2.22716500
H	0.85898000	-3.01784500	0.31987600
H	1.19699700	-4.75158600	0.09915300
O	-2.89792200	-1.79540700	0.34901300
C	-3.45426600	-1.25601900	1.56112400
C	-3.89933400	-2.60505000	-0.28017200
C	-4.98733600	-1.34358100	1.41284700
H	-3.08914800	-1.84817300	2.40793400
H	-3.08515600	-0.23312400	1.66623800
C	-5.19031200	-1.84187000	-0.02718300
H	-3.62131200	-2.71769900	-1.32999300
H	-3.91641900	-3.59689100	0.19340300
H	-5.46951500	-0.37982900	1.58959100
H	-5.39937500	-2.06020900	2.12817100
H	-5.26166200	-1.00033200	-0.72355300
H	-6.07980700	-2.46480300	-0.14124400
C	-2.02872400	2.92932600	0.84546500
H	-1.25683300	2.85069700	1.61739200
H	-1.97237900	3.93437700	0.41601000
H	-3.00548700	2.82353500	1.32816000
C	-2.81163700	1.86748200	-1.39558600
C	-2.55761000	3.06748500	-2.31055000
H	-1.54893000	3.02678600	-2.73298300
H	-3.27795500	3.07585400	-3.13698800
H	-2.66763400	4.01387600	-1.76939800
C	-4.24850900	1.91648900	-0.86479000
H	-4.96607700	1.73417400	-1.67390500
H	-4.40474400	1.14639900	-0.09542100
H	-4.48747600	2.88771900	-0.42060600
C	-2.63188700	0.57909600	-2.21068000
H	-3.03214500	-0.27930300	-1.64938700
H	-3.18695000	0.62328400	-3.15460200
H	-1.56981800	0.41963200	-2.43224400

TS2

Ring-opening

M06-2X SCF energy in gas phase:	-2333.52786064	a.u.
M06-2X enthalpy in gas phase :	-2332.78774600	a.u.
M06-2X free energy in gas phase:	-2332.92323900	a.u.
M06-2X SCF energy in solution:	-2334.03741823	a.u.
M06-2X enthalpy in solution:	-2333.29730359	a.u.
M06-2X free energy in solution:	-2333.43279659	a.u.
Imaginary frequency:	-37.3311	cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
P	1.13539400	0.38689600	-0.14921800
C	0.76250500	0.83741500	1.57671000
C	1.35004400	1.94027200	2.19817500
C	-0.20135100	0.09585800	2.26351200
C	0.96260000	2.30350100	3.48672700
H	2.09932400	2.52284000	1.66914700
C	-0.59323300	0.46354800	3.54615700
C	-0.01259100	1.57258400	4.16031400
H	1.42338900	3.16303600	3.96420100
H	-1.34313100	-0.11997000	4.07431500
H	-0.31445100	1.86055800	5.16274100
C	2.82095900	-0.48426200	-0.12792000
C	3.49735300	-0.46441500	-1.36175200
C	3.38743600	-1.30368500	0.85180300
C	4.67102900	-1.17171900	-1.59402800
H	3.07613500	0.12793900	-2.17024400
C	4.57067100	-2.01492000	0.64908500
C	5.21910600	-1.94635400	-0.57606700
H	5.15278900	-1.11840100	-2.56548900
H	4.96523400	-2.62385600	1.45548500
H	6.13861000	-2.50164200	-0.73260300
O	0.36974100	-0.86767900	-0.62910000
N	-0.50851300	1.62453300	-0.68727100
C	0.39149600	2.58567500	-0.99527600
C	1.65810500	1.95031900	-0.92966900
C	0.35150300	3.96302000	-1.30444300
C	2.84889200	2.61479800	-1.17391700
C	1.55391800	4.61509200	-1.56393200
H	-0.58403400	4.50783400	-1.35901900
C	2.79429100	3.97162200	-1.50733300
H	3.80598700	2.10813800	-1.08476700
H	1.52408800	5.67295300	-1.81464100
H	3.70593900	4.52434500	-1.70633700
C	-1.85560500	1.79773800	-0.20972200
H	-2.06559400	0.87660600	0.36856600
Cl	2.63185200	-1.54219700	2.41974000
H	-0.61844000	-0.79357500	1.79410300
Li	-1.35259200	-1.30027000	-0.67928500
O	-1.20442600	-2.98234800	-1.65492900
C	-0.18417200	-2.88707900	-2.66887400
C	-0.82913500	-4.05689300	-0.78462500
C	1.11047000	-3.45336400	-2.05433300
H	-0.51441900	-3.46665300	-3.53865300
H	-0.09949200	-1.83338000	-2.93822200
C	0.68598000	-3.94137000	-0.65647000
H	-1.37170900	-3.92183400	0.15478400
H	-1.12992400	-5.00953100	-1.24323800
H	1.87991200	-2.68357300	-1.97439400
H	1.49462400	-4.27534900	-2.66468100
H	0.93914500	-3.18315600	0.08804200
H	1.14870500	-4.89085900	-0.37754500
O	-2.84163200	-1.80924200	0.50004600
C	-3.36154100	-1.26939400	1.72883900
C	-3.85321100	-2.64010900	-0.08479900
C	-4.89626700	-1.40192400	1.64986400
H	-2.94208700	-1.83735000	2.56691100
H	-3.02080900	-0.23407900	1.80391700
C	-5.14774200	-1.90250500	0.21908400
H	-3.61550600	-2.75136300	-1.14440300
H	-3.83291000	-3.62962100	0.39370100
H	-5.39825500	-0.45365800	1.85320700
H	-5.25404000	-2.13350200	2.37926100
H	-5.26368500	-1.06240800	-0.47311100
H	-6.02860600	-2.54297400	0.14000300
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H	-1.22849900	2.90438000	1.53189800
H	-1.97434300	3.93239300	0.30102800
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C	-2.91418500	1.77960200	-1.35832800
C	-2.69928200	2.93400900	-2.33952300
H	-1.70948800	2.87164600	-2.80216900
H	-3.45399400	2.90292000	-3.13425300
H	-2.78765300	3.90560300	-1.84104700
C	-4.32786800	1.85726900	-0.77109200
H	-5.07965900	1.63792800	-1.53892200
H	-4.45189300	1.12694300	0.04166600
H	-4.54671000	2.84984000	-0.36548200
C	-2.77267700	0.45673700	-2.12370100

H	-3.12902100	-0.38031600	-1.50508800
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H	-1.72501000	0.29784400	-2.40803000

F

M06-2X SCF energy in gas phase:	-2333.57316942	a.u.
M06-2X enthalpy in gas phase :	-2332.83052800	a.u.
M06-2X free energy in gas phase:	-2332.96577400	a.u.
M06-2X SCF energy in solution:	-2334.07796823	a.u.
M06-2X enthalpy in solution:	-2333.33532681	a.u.
M06-2X free energy in solution:	-2333.47057281	a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	-1.39953200	0.18121500	0.00872700
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C	-0.81306200	-2.24631500	1.34154800
C	-1.28832700	-0.31717700	2.71876000
C	-0.57537200	-3.00011500	2.48649300
H	-0.73019300	-2.69421900	0.35393300
C	-1.07256400	-1.07981800	3.86472700
C	-0.70553400	-2.41792800	3.74788200
H	-0.29318200	-4.04475100	2.39584900
H	-1.18067700	-0.62709900	4.84591400
H	-0.52672900	-3.01159400	4.63945200
C	-3.19085500	0.58379800	-0.00593800
C	-3.49719100	1.94860800	-0.05464900
C	-4.25653900	-0.32041900	0.06800400
C	-4.81287100	2.39871000	-0.04491900
H	-2.66972500	2.65096200	-0.08835400
C	-5.57778300	0.11693800	0.08209900
C	-5.85397400	1.47880100	0.02297600
H	-5.02259500	3.46249100	-0.08662300
H	-6.37705700	-0.61375900	0.13945700
H	-6.88598800	1.81506200	0.03338000
O	-0.66253600	1.49320000	0.25657900
N	1.30514400	-0.67205300	-0.76453300
C	0.37151700	-1.18888300	-1.57762900
C	-0.99227800	-0.71261100	-1.46264400
C	0.53720600	-2.20892600	-2.57484500
C	-1.98688800	-1.05450000	-2.39202200
C	-0.46719200	-2.54676000	-3.45627600
H	1.49611800	-2.69279300	-2.68005700
C	-1.73626100	-1.94837100	-3.41440900
H	-2.98009900	-0.62471300	-2.28878600
H	-0.25758000	-3.29951400	-4.21297700
H	-2.50544100	-2.20976000	-4.13177200
C	2.61592800	-1.30045800	-0.57890300
H	2.96515500	-0.87595900	0.37496800
Cl	-3.98640900	-2.04182200	0.14086800
H	-1.54175600	0.73714200	2.80017000
Li	1.18723100	1.12907000	0.11252200
O	1.68757800	2.87091100	-0.64590500
C	1.00271800	2.91216900	-1.90663100
C	1.38702700	4.07503900	0.05242600
C	-0.21742300	3.83506400	-1.72233700
H	1.69303000	3.29627900	-2.66763700
H	0.72860400	1.88288100	-2.15971700
C	-0.06554000	4.39576300	-0.29421700
H	1.55414300	3.88715800	1.11621300
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H	-0.72399000	3.85930800	0.38994800
H	-0.27291100	5.46696700	-0.23439100
O	2.19148800	1.09242800	1.77113500
C	2.11433300	-0.03680900	2.64662200
C	3.34312500	1.83480200	2.14730100
C	3.57332900	-0.42041100	2.96821500
H	1.56793600	0.25498900	3.55156100
H	1.54708800	-0.81295700	2.12504500
C	4.40328400	0.77332800	2.44416000
H	3.59296600	2.50072100	1.31745400
H	3.11638700	2.43520100	3.04072100
H	3.86014000	-1.34853600	2.46694900
H	3.70730400	-0.56754700	4.04255300
H	4.92265500	0.50390400	1.52034800
H	5.14814900	1.12319100	3.16231200
C	2.59152500	-2.82345800	-0.33272600
H	1.65468500	-3.09796700	0.16193700
H	2.68304800	-3.42728300	-1.23964800
H	3.41508200	-3.11284800	0.32826400
C	3.75486700	-0.85009600	-1.55546800
C	3.56698900	-1.28023800	-3.01298600
H	2.64132600	-0.87434200	-3.43110500
H	4.40495000	-0.90730500	-3.61481000
H	3.55085400	-2.37038000	-3.12344100
C	5.08513900	-1.42559500	-1.04783900
H	5.92576800	-0.99368700	-1.60262900
H	5.23556700	-1.20320500	0.01705400
H	5.12968900	-2.51262500	-1.17136500
C	3.83629400	0.67843500	-1.52964900
H	3.90242100	1.05893700	-0.50248200
H	4.71582300	1.03136300	-2.08140500
H	2.94726800	1.11772800	-1.98745700

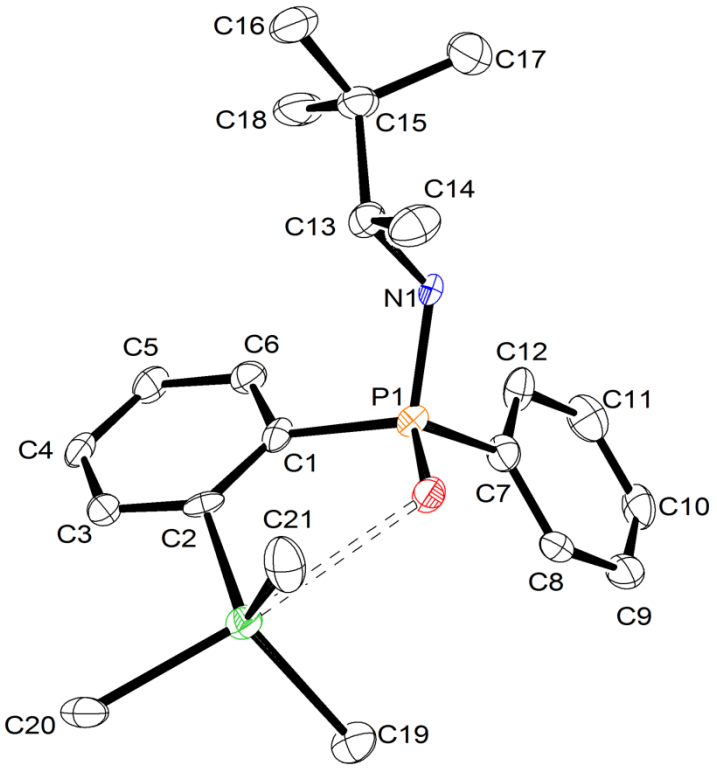

Figure S20. X-ray crystal structure of (S_P)-**19** (thermal ellipsoids shown at 50% probability) including atomic numbering. Hydrogen atoms have been omitted for clarity.

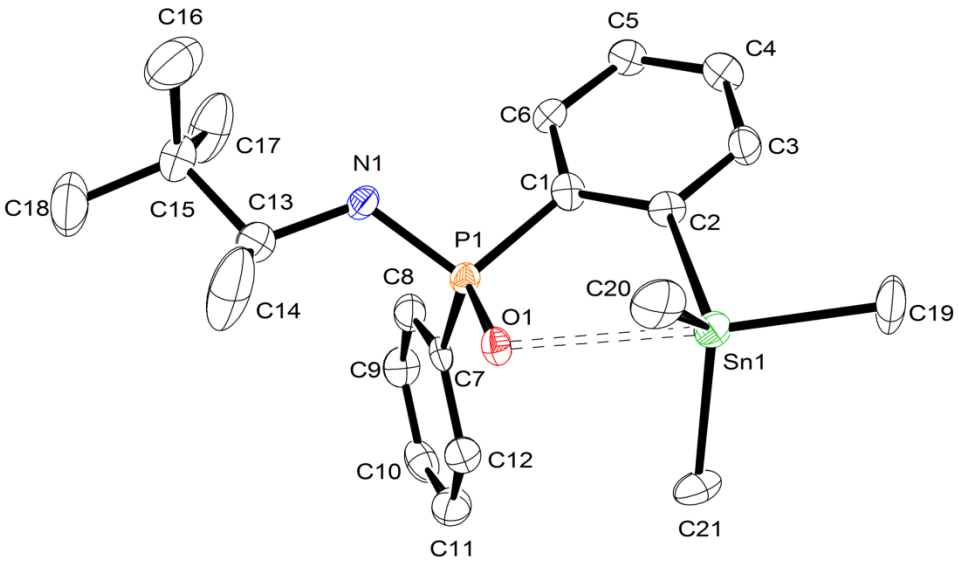

Figure S21. X-ray crystal structure of (R_P)-**19'** (thermal ellipsoids shown at 50% probability) including atomic numbering. Hydrogen atoms have been omitted for clarity.

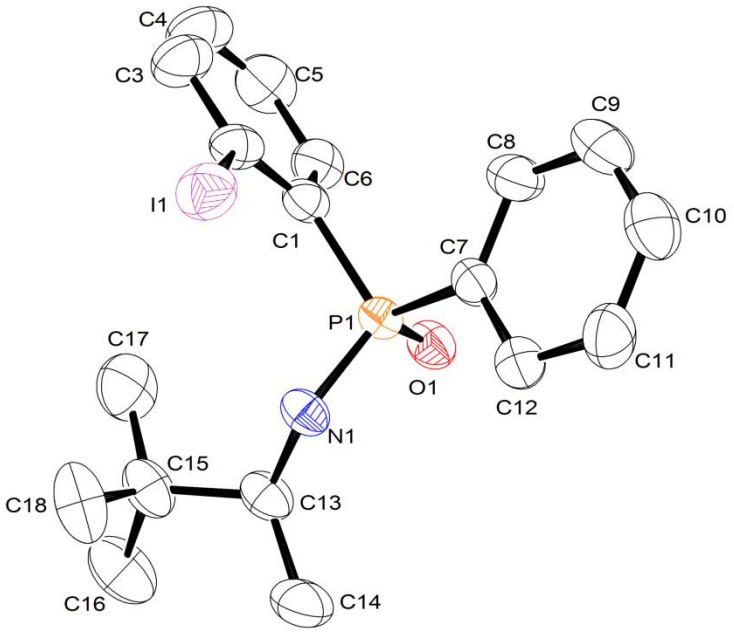

Figure S22. X-ray crystal structure of **20** (thermal ellipsoids shown at 40% probability) including atomic numbering. Hydrogen atoms have been omitted for clarity.

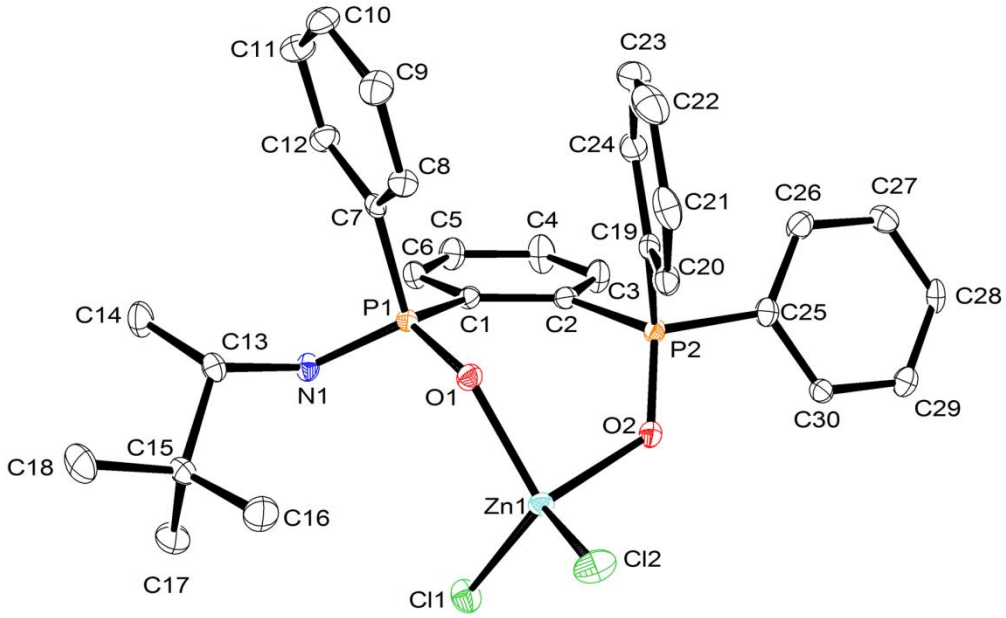

Figure S23. X-ray crystal structure of **34** (thermal ellipsoids shown at 50% probability) including atomic numbering. Protons have been omitted for clarity.

Table S2 Selected crystal data for ligands ligands **19**, **19'**, **20** and complex **34.**

	19	**19'**	**20**	**34**
Empirical formula	$C_{21}H_{32}NOPSn$	$C_{21}H_{32}NOPSn$	$C_{18}H_{23}INOP$	$C_{30}H_{33}Cl_2NO_2P_2Zn$
M	464.16	464.16	427.24	637.80
Crystal system	Orthorhombic	Tetragonal	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P4_32_12$	$P2_12_12_1$	$P2_12_12_1$
Temperature/K	100	100	293	100
a/Å	9.9935(14)	9.3648(2)	10.1337(7)	9.8384(2)
b/Å	14.054(2)	9.3648(2)	10.2928(7)	17.1397(4)
c/Å	15.830(2)	51.2257(12)	18.6620(13)	17.4704(4)
α(°)	90	90	90	90
β(°)	90	90	90	90
γ(°)	90	90	90	90
V/Å ^{3}	2223.2(5)	4492.5(2)	1946.5(2)	2945.99(11)
Z	4	8	4	4
μ/mm^{-1}	1.23	9.77	1.73	4.08
D_{calcd}/g cm^{-3}	1.387	1.372	1.458	1.438
Crystal dimensions/mm	0.40 x 0.22 x 0.14	0.22 x 0.10 x 0.05	0.60 x 0.45 x 0.33	1.13 x 0.95 x 0.26
F(000)	952	1904	856	1320
θ range for data collection/°	2.5-25.1	3.5-59.0	2.8-24.5	3.6-72.2
Refls. measured	9380	13912	9653	17913
Refls. unique	3936	3243	3176	5811
Parameters/restraints	230/0	226/0	203/0	348/0
GOF on F^2	1.06	1.05	1.10	1.07
*R*1 [$I \geq 2\sigma(I)$]	0.045	0.053	0.032	0.029
*wR*2 (all data)	0.094	0.138	0.082	0.069
$\Delta\rho_{max}/\Delta\rho_{min}$/e·Å $^{-3}$	0.83/-1.14	3.12/-0.95	0.73/-0.38	0.32/-0.29

Table S3 Selected bond lengths (Å) and angles (°) for ligands **19**, **19'**, **20** and complex **34.**

19		**19'**	**20**		**34**	
P1-O1	1.492(4)	1.496(4)	P1-O1	1.467(3)	P1-O1	1.502(2)
P1-N1	1.648(5)	1.652(5)	P1-N1	1.629(4)	P1-N1	1.621(2)
P1-C1	1.813(6)	1.813(6)	P1-C1	1.831(4)	P1-C1	1.817(3)
P1-C7	1.813(6)	1.806(6)	P1-C7	1.801(4)	P1-C7	1.798(3)
Sn1-C2	2.175(6)	2.170(6)	I1-C2	2.098(4)	P2-O2	1.506(2)
Sn1-C19	2.149(5)	2.196(8)	O1-P1-N1	113.2(2)	P2-C19	1.793(3)
Sn1-C20	2.167(6)	2.118(7)	O1-P1-C1	107.4(2)	P2-C25	1.807(3)
Sn1-C21	2.143(7)	2.134(6)	O1-P1-C7	113.2(2)	Zn1-O1	1.992(2)
O1-P1-N1	119.9(3)	119.2(2)	C1-P1-C7	105.0(2)	Zn1-O2	2.002(2)
O1-P1-C1	108.5(3)	109.0(3)	P1-N1-C13	124.2(3)	Zn1-Cl1	2.2129(8)
O1-P1-C7	110.6(3)	110.6(2)	O1-P1-C1-C2	176.5(3)	Zn1-Cl2	2.2129(8)
C1-P1-C7	110.8(3)	108.6(3)	N1-P1-C1-C2	52.3(4)	O1-P1-N1	117.9(1)
P1-N1-C13	121.2(4)	123.3(4)			O1-P1-C1	111.6(1)
C2-Sn1-C19	109.4(2)	115.2(2)			O1-P1-C7	107.8(1)
C2-Sn1-C20	102.7(2)	101.6(3)			C1-P1-C7	108.8(1)
C2-Sn1-C21	120.0(3)	115.0(2)			O2-P2-C2	113.6(1)
C19-Sn1-C20	104.8(2)	103.0(3)			O2-P2-C19	113.8(1)
C19-Sn1-C21	115.5(3)	115.5(3)			O2-P2-C25	107.2(1)
O1-P1-C1-C2	1.3(6)	14.7(6)			C19-P2-C25	105.8(1)
N1-P1-C1-C2	-128.0(5)	142.9(5)			Zn1-O1-P1	134.0(1)
P1-C1-C2-Sn1	-8.0(7)	-6.8(7)			Zn1-O2-P2	127.1(1)
					O2-Zn1-O1	90.38(7)
					Cl1-Zn1-Cl2	120.75(3)
					Cl2-Zn1-O2	108.24(6)
					O1-P1-C1-C2	-21.6(3)
					P1-C1-C2-P2	5.4(4)
					O2-P2-C2-C1	64.8(3)
					C1-P1-O1-Zn1	-55.8(2)