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On the edge of the steric repulsion and reactivity of bulky anilines; a case study of a chloro(imino)phosphine synthesis

Jan Vrána*, Maksim A. Samsonov, Vlastimil Němec and Aleš Růžička

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Materials and Methods

Elemental analysis
Elemental analyses were performed on an LECO-CHNS-932 analyzer.

NMR spectroscopy
^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer or Bruker Ultrashield 400 MHz, using 5 mm tuneable broad-band probe. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were related to the residual signals of the solvent (C_6D_6: $\delta(^{1}H)$ = 7.16 ppm and $\delta(^{13}C)$ = 128.39 ppm).

Characterization of prepared compounds

Deprotonation of Ar*-NH_2

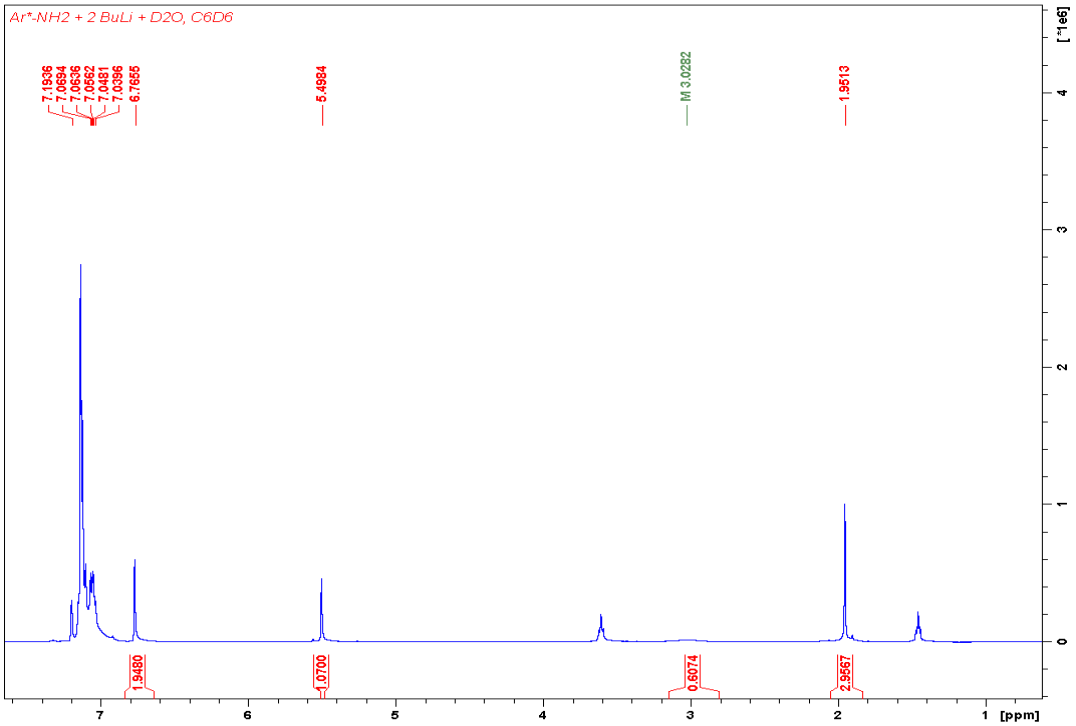


Figure S1. ^{1}H NMR spectrum of the deuterated Ar*-NH_2.

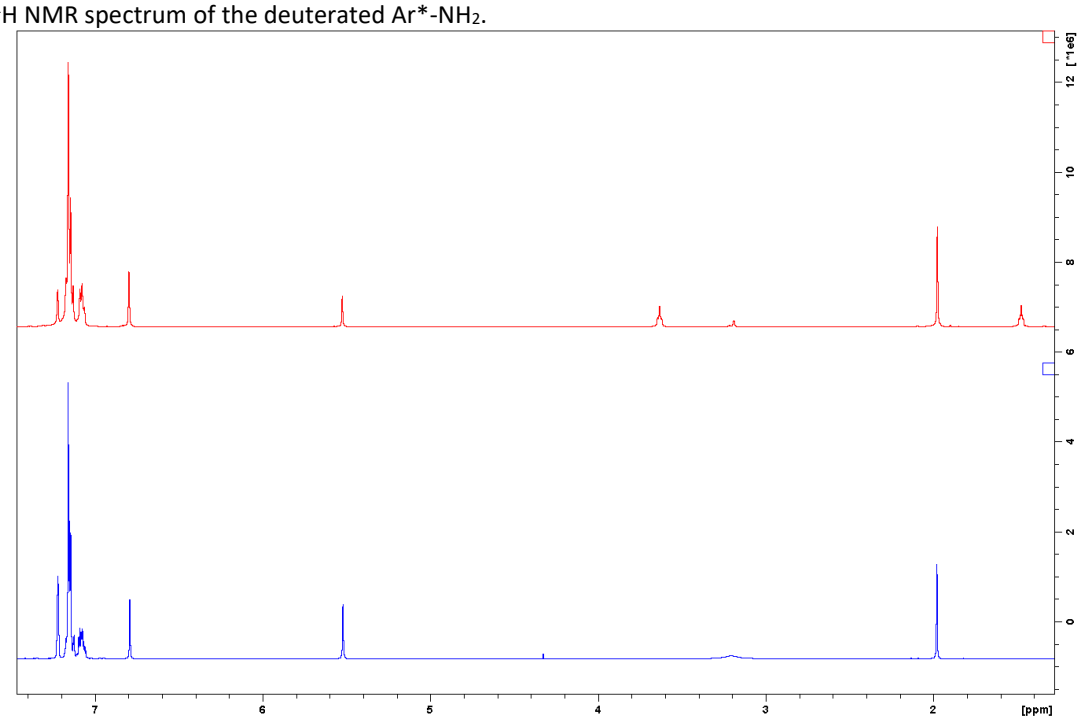


Figure S2. ^{1}H NMR spectrum of the parent (bellow) and deuterated (above) Ar*-NH_2.

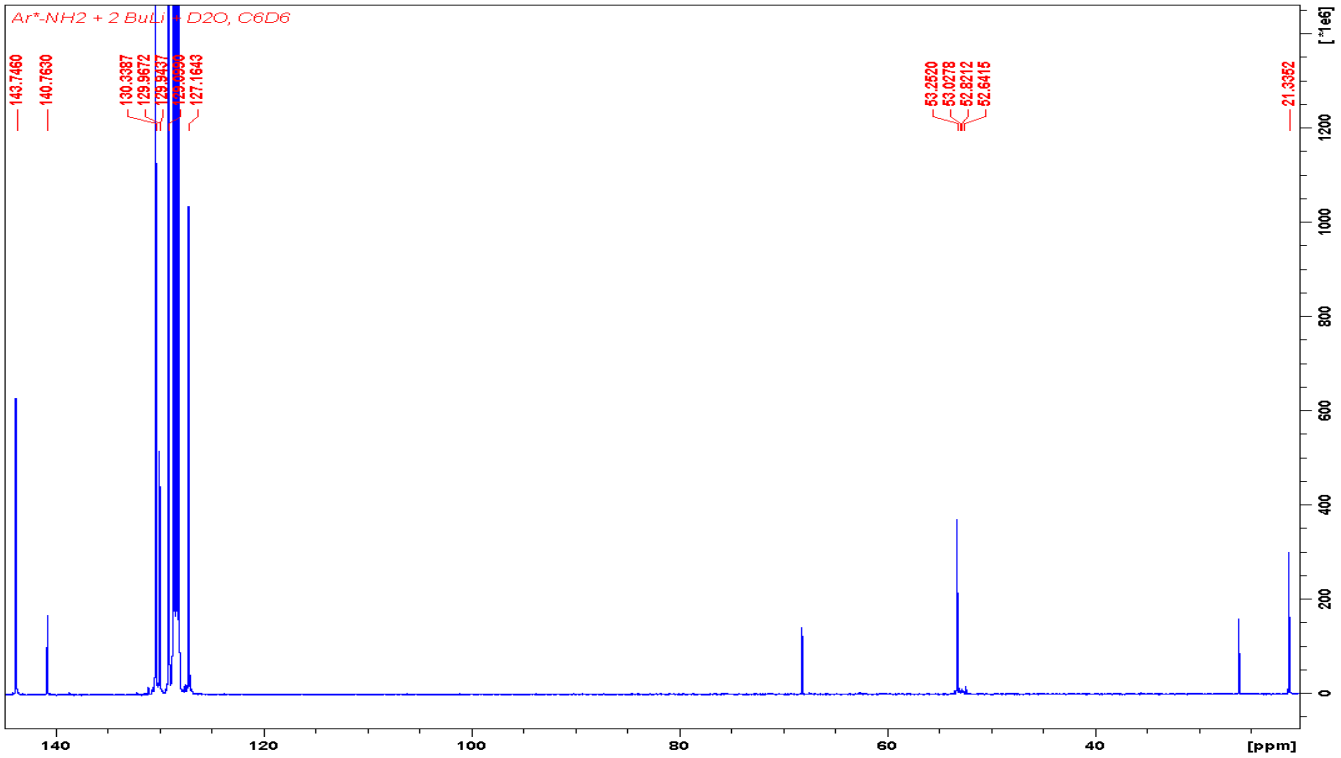


Figure S3. ^{13}C NMR spectrum of the deuterated Ar*-NH_2.

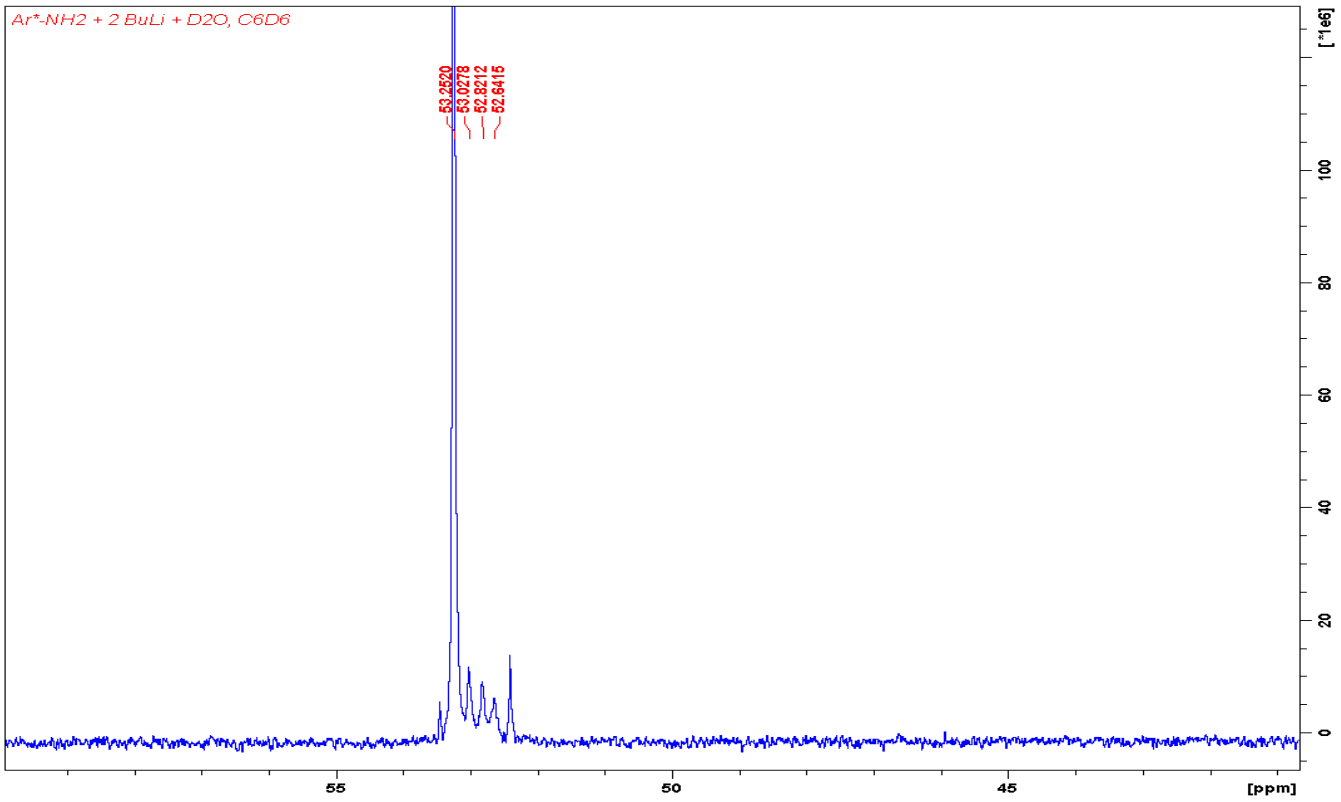


Figure S4. ^{13}C NMR spectrum of the deuterated Ar*-NH_2.

Spectroscopic characterization of Ar*-N(SiMe$_3$)$_2$ (1)

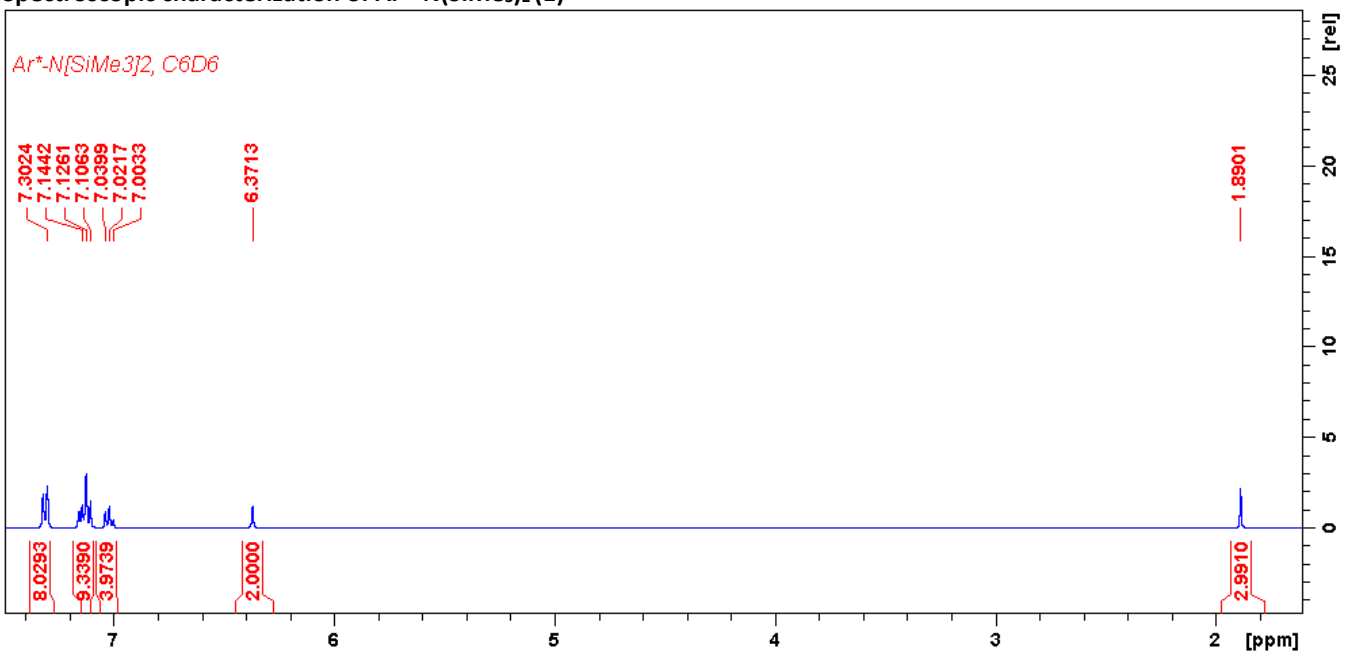


Figure S5. ^{1}H NMR spectrum of Ar*-N(SiMe$_3$)$_2$.

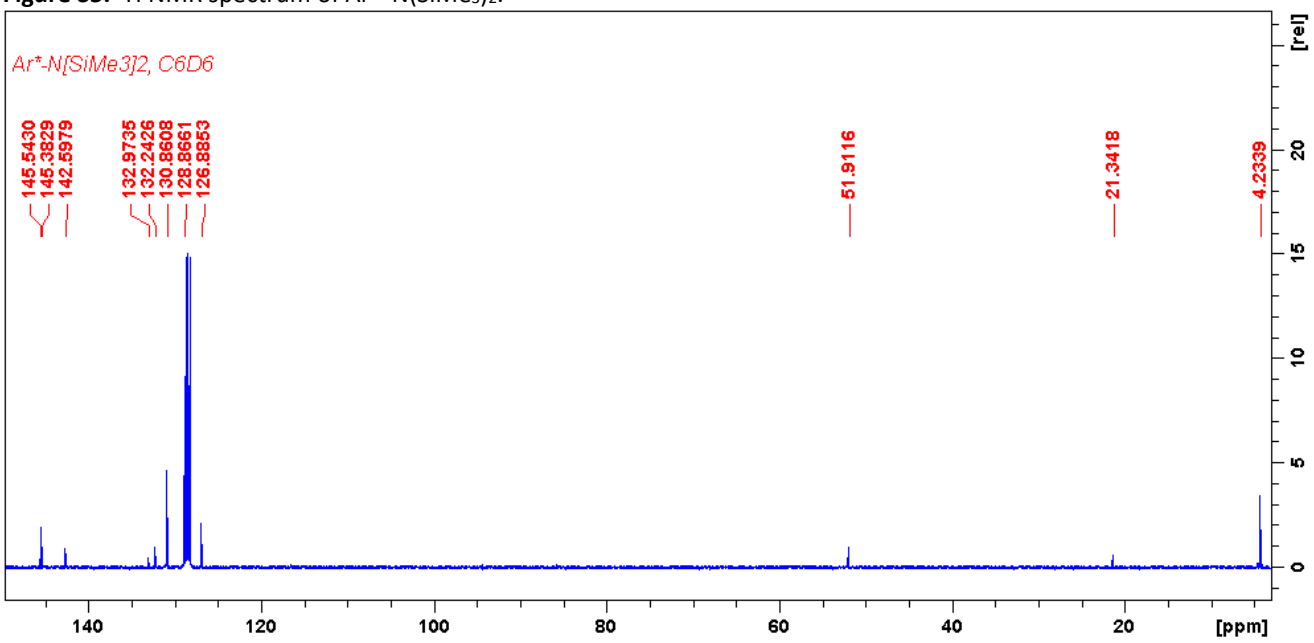


Figure S6. ^{13}C{^{1}H} NMR spectrum of Ar*-N(SiMe$_3$)$_2$.

Spectroscopic characterization of Ar*-N(CH$_2$Ph)$_2$ (2)

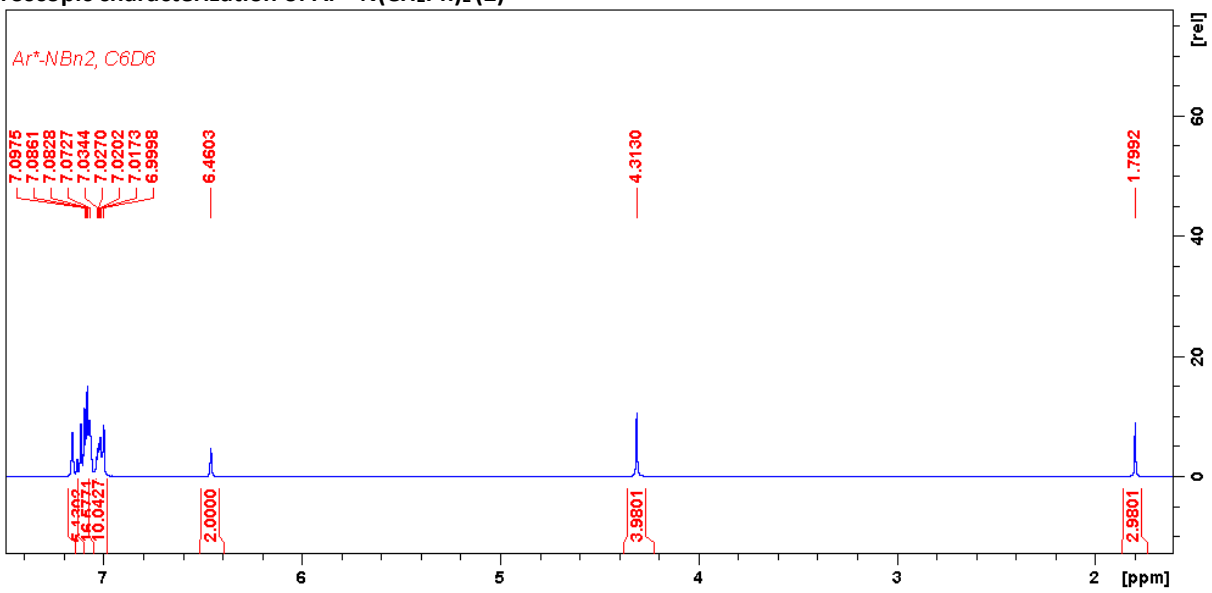


Figure S7. ^{1}H NMR spectrum of Ar*-N(CH$_2$Ph)$_2$.

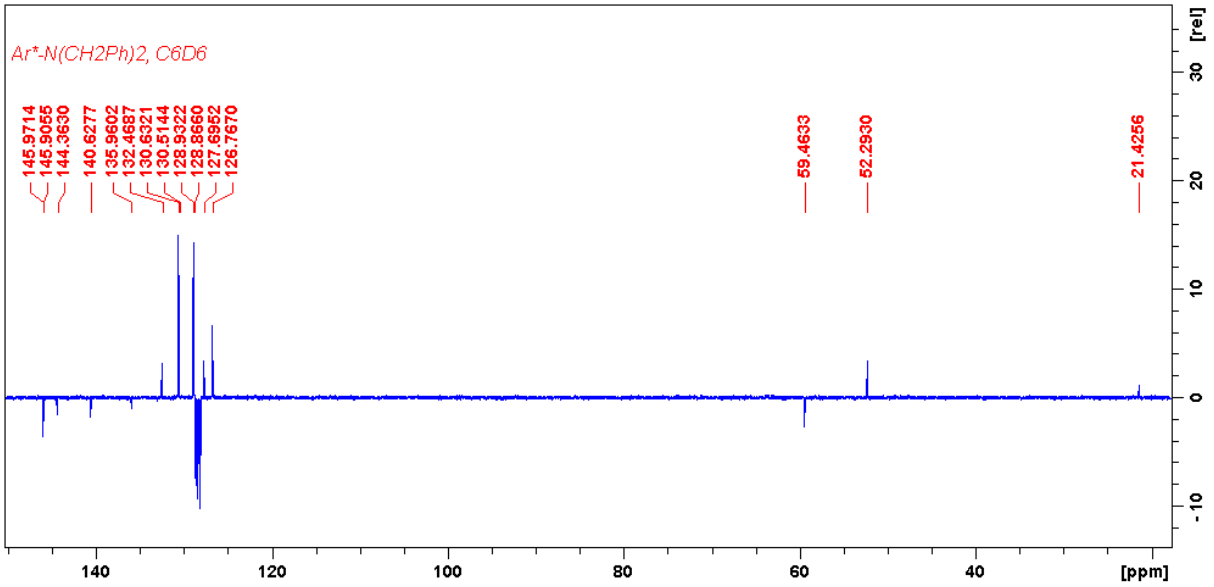


Figure S8. ^{13}C{^{1}H} APT NMR spectrum of Ar*-N(CH$_2$Ph)$_2$.

Spectroscopic characterization of Ar*-NCO (3)

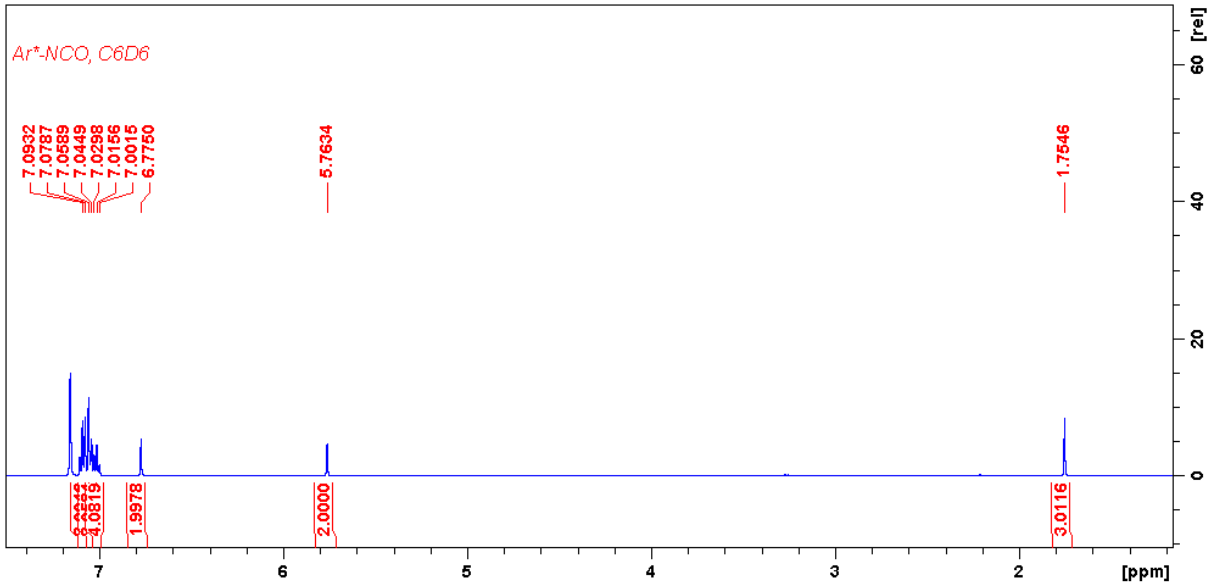


Figure S9. ^{1}H NMR spectrum of Ar*-NCO.

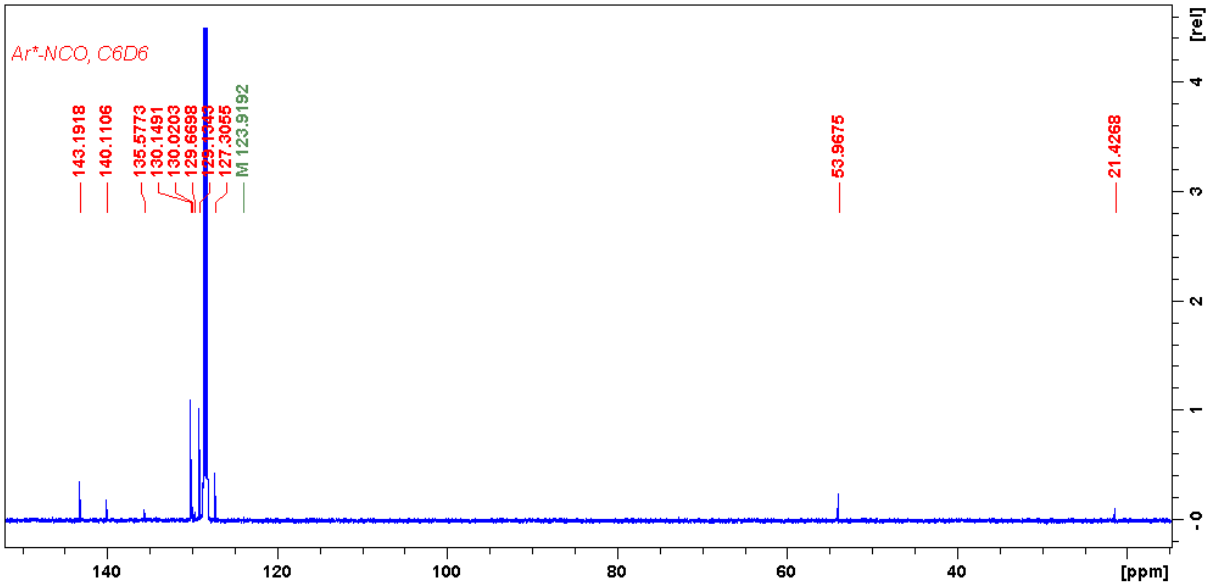


Figure S10. ^{13}C{^{1}H} NMR spectrum of Ar*-NCO.

Spectroscopic characterization of Ar*-N(CO)$_2$C$_6$H$_4$ (4)

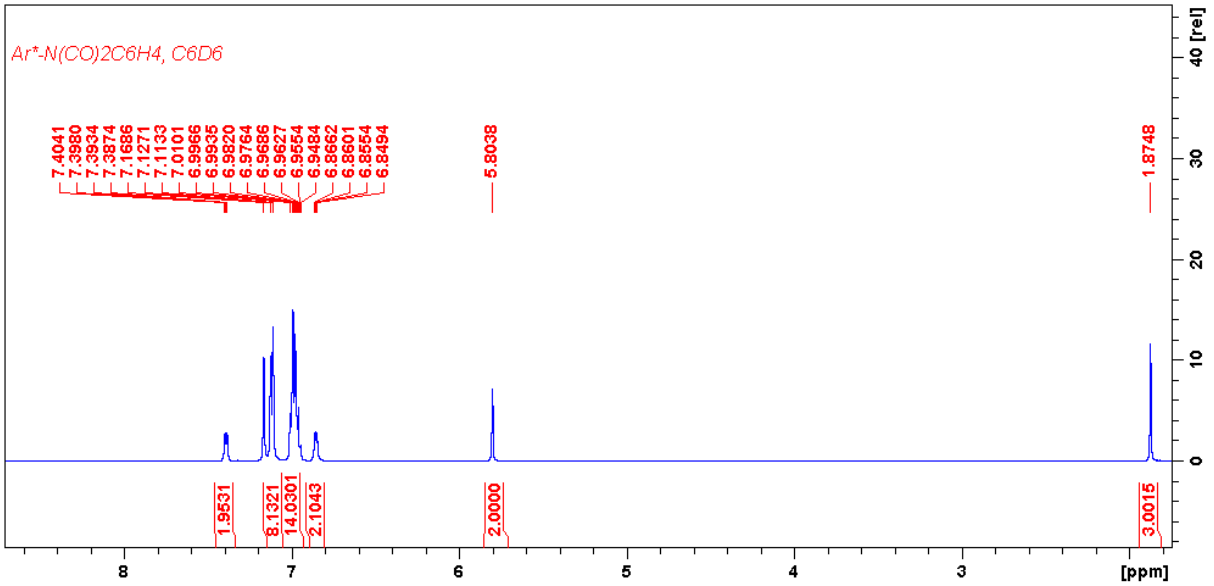


Figure S11. ^{1}H NMR spectrum of Ar*-N(CO)$_2$C$_6$H$_4$.

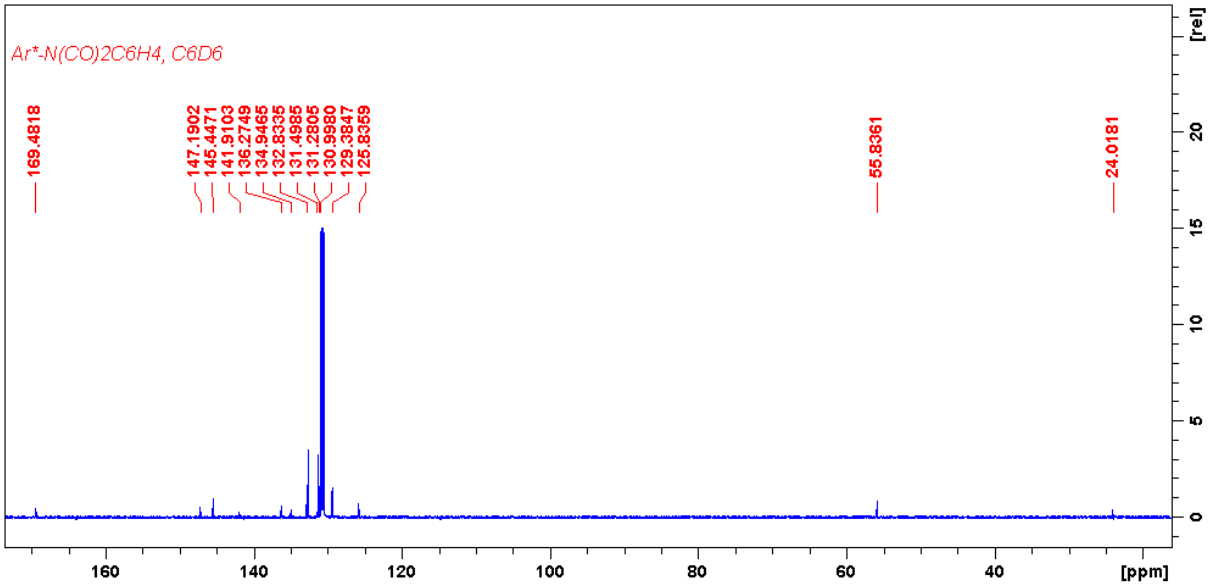


Figure S12. ^{13}C{^{1}H} NMR spectrum of Ar*-N(CO)$_2$C$_6$H$_4$.

Spectroscopic characterization of Ar*-N=CHPh (5)

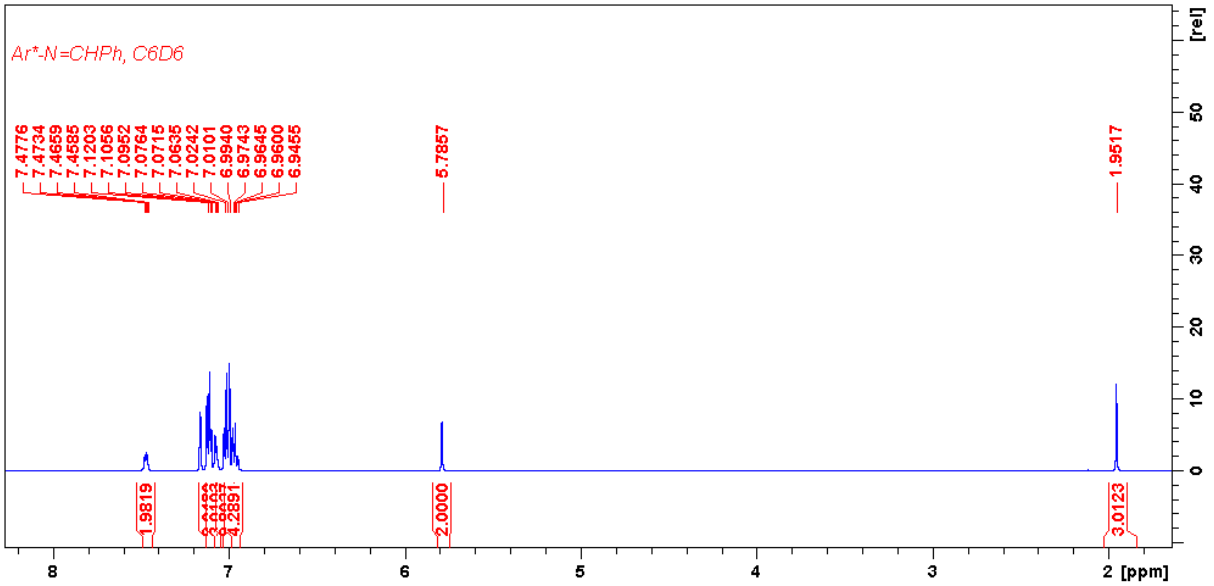


Figure S13. ^{1}H NMR spectrum of Ar*-N=CHPh.

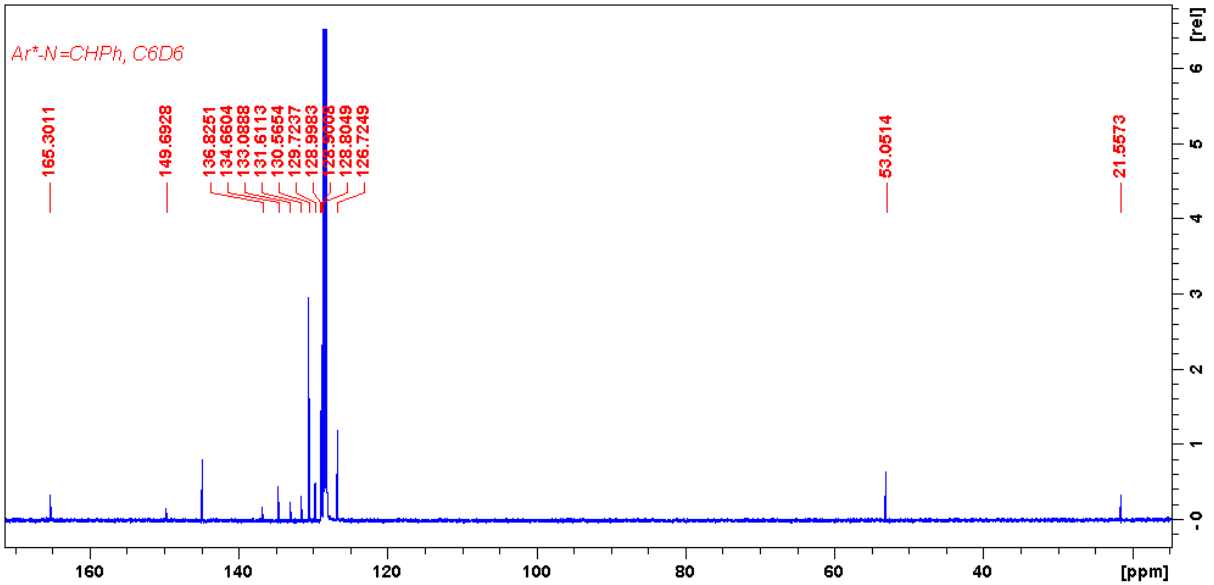


Figure S14. ^{13}C{^{1}H} NMR spectrum of Ar*-N=CHPh.

Spectroscopic characterization of Ar*-N=C(CH$_3$)Ph (6)

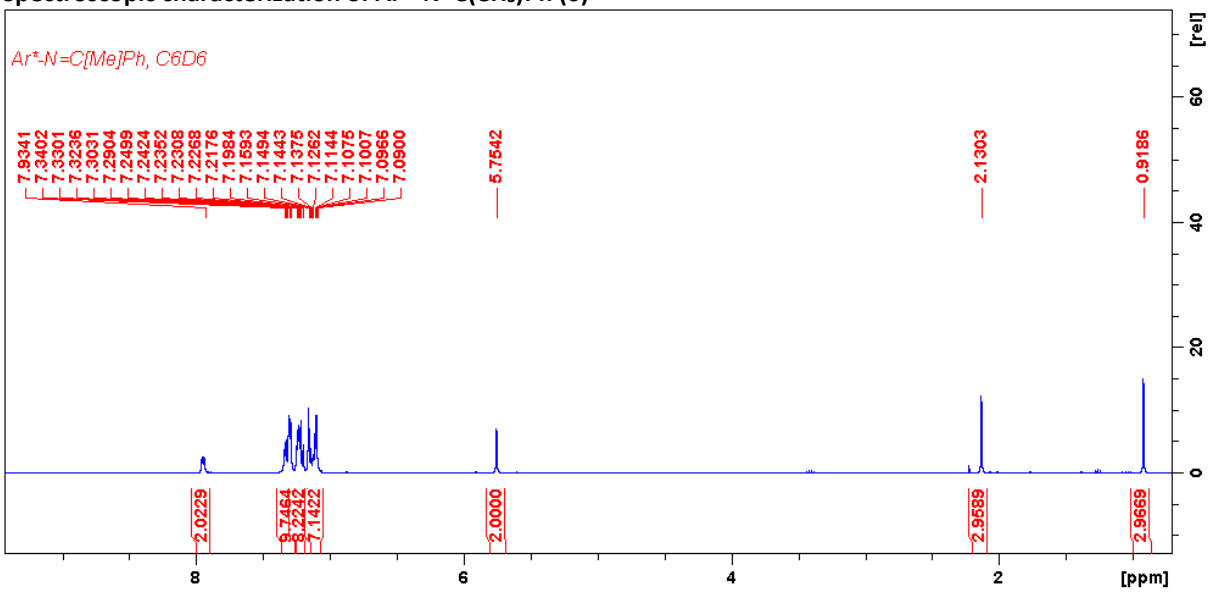


Figure S15. ^{1}H NMR spectrum of Ar*-N=C(CH$_3$)Ph.

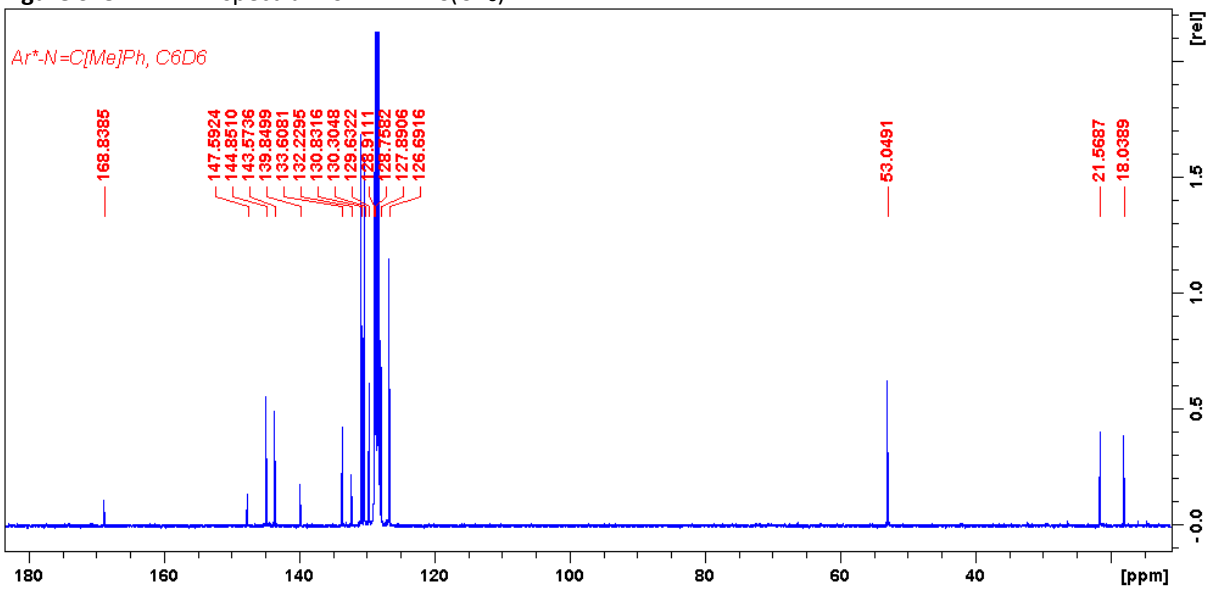


Figure S16. ^{13}C{^{1}H} NMR spectrum of Ar*-N=C(CH$_3$)Ph.

Spectroscopic characterization of Ar^{Bn}-N(H)CH(Bu)Ph (7)

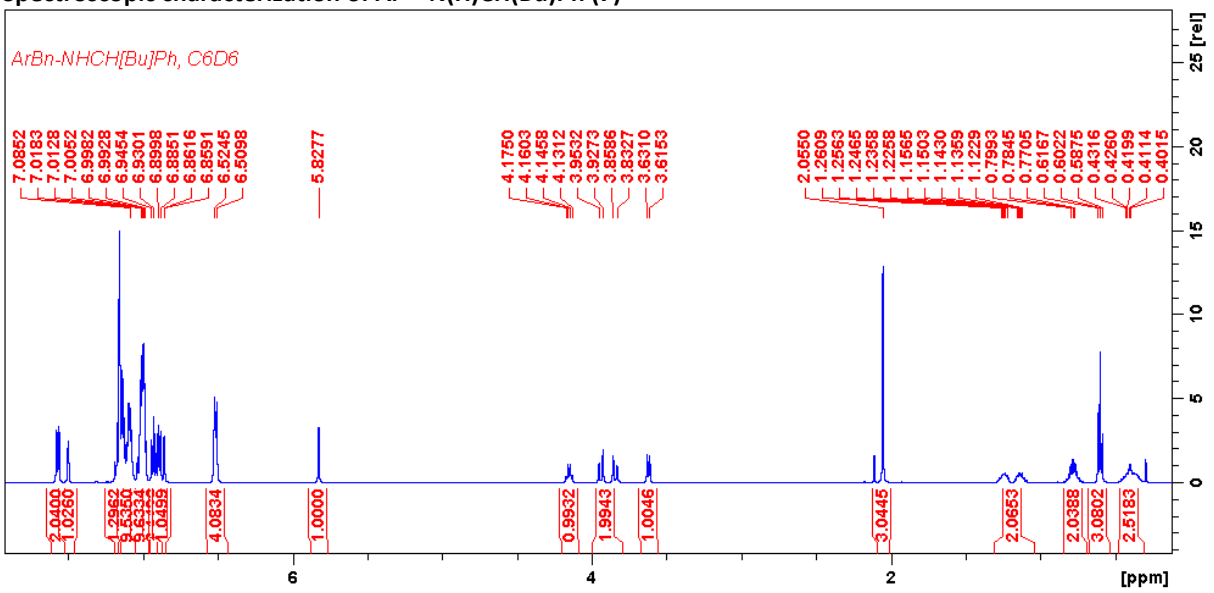


Figure S17. ^{1}H NMR spectrum of Ar^{Bn}-N(H)CH(Bu)Ph.

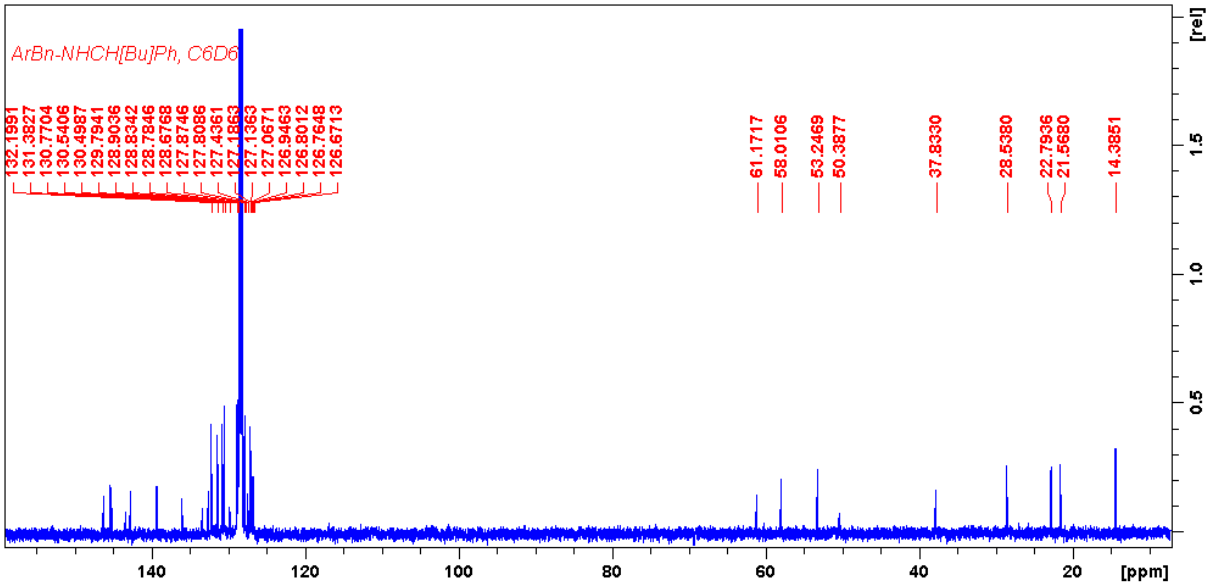


Figure S18. ^{13}C{^{1}H} NMR spectrum of Ar^{Bn}-N(H)CH(Bu)Ph.

Spectroscopic characterization of Ar^{Bn}-NH_2 (8)

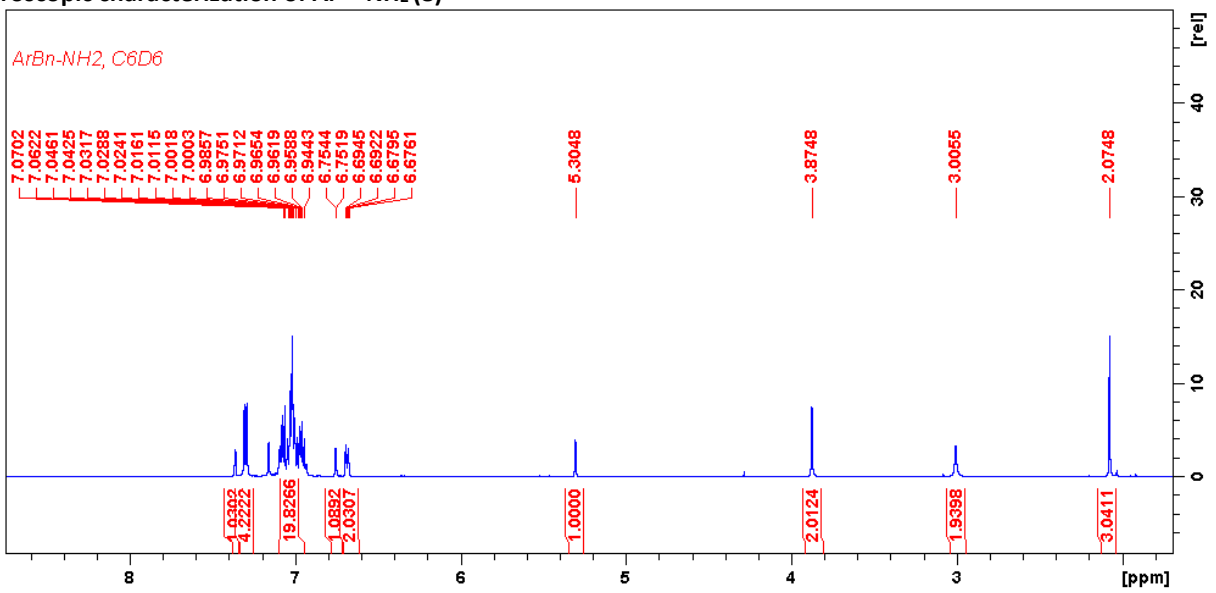


Figure S19. ^{1}H NMR spectrum of Ar^{Bn}-NH_2.

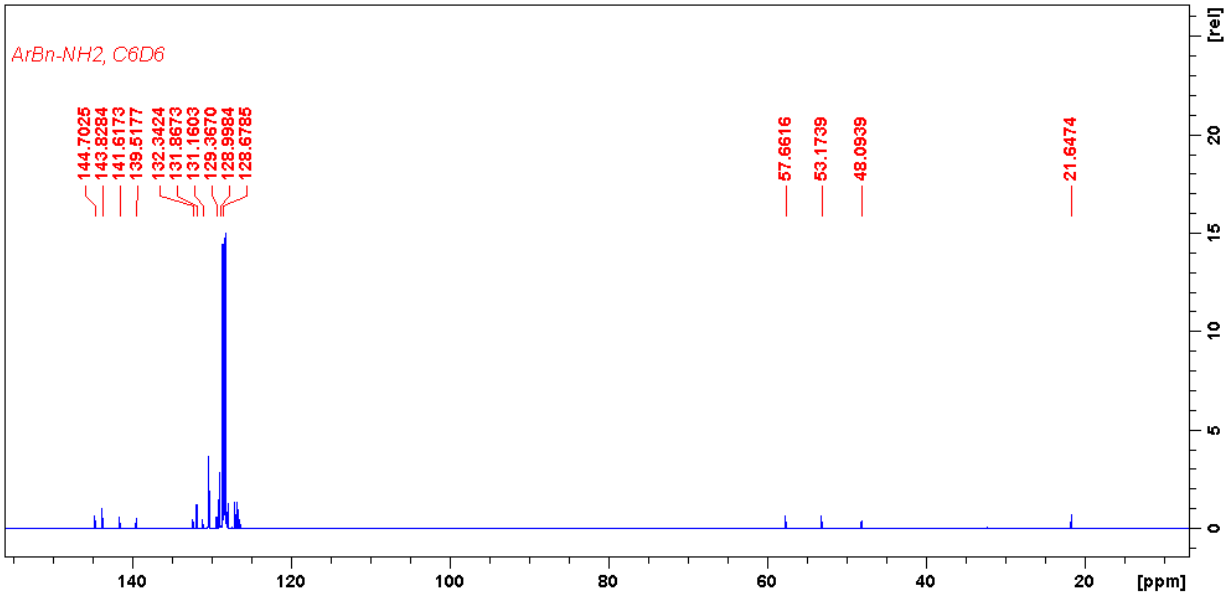


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of Ar^{Bn}-NH_2.

Spectroscopic characterization of [ClP(μ-N-Ar*)]$_2$ (9)

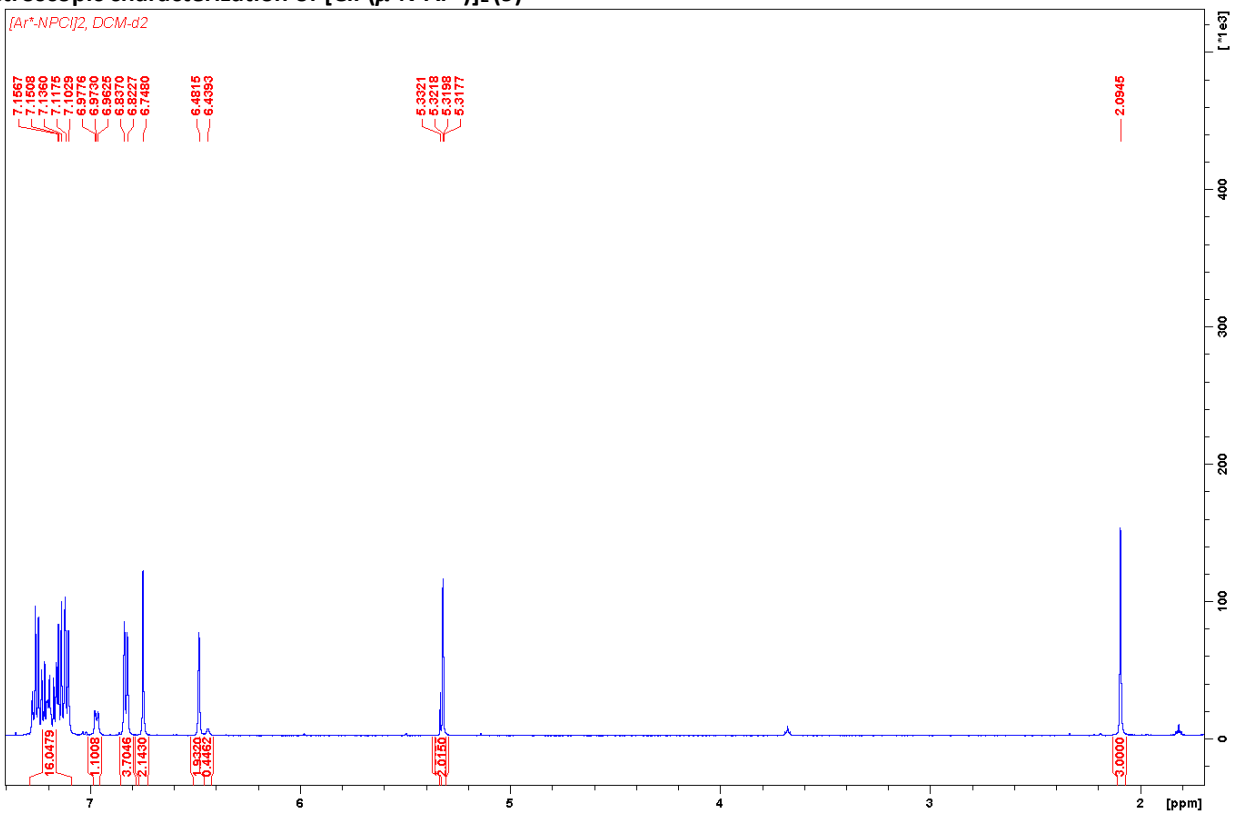


Figure S21. ^{1}H NMR spectrum of [ClP(μ-N-Ar*)]$_2$.

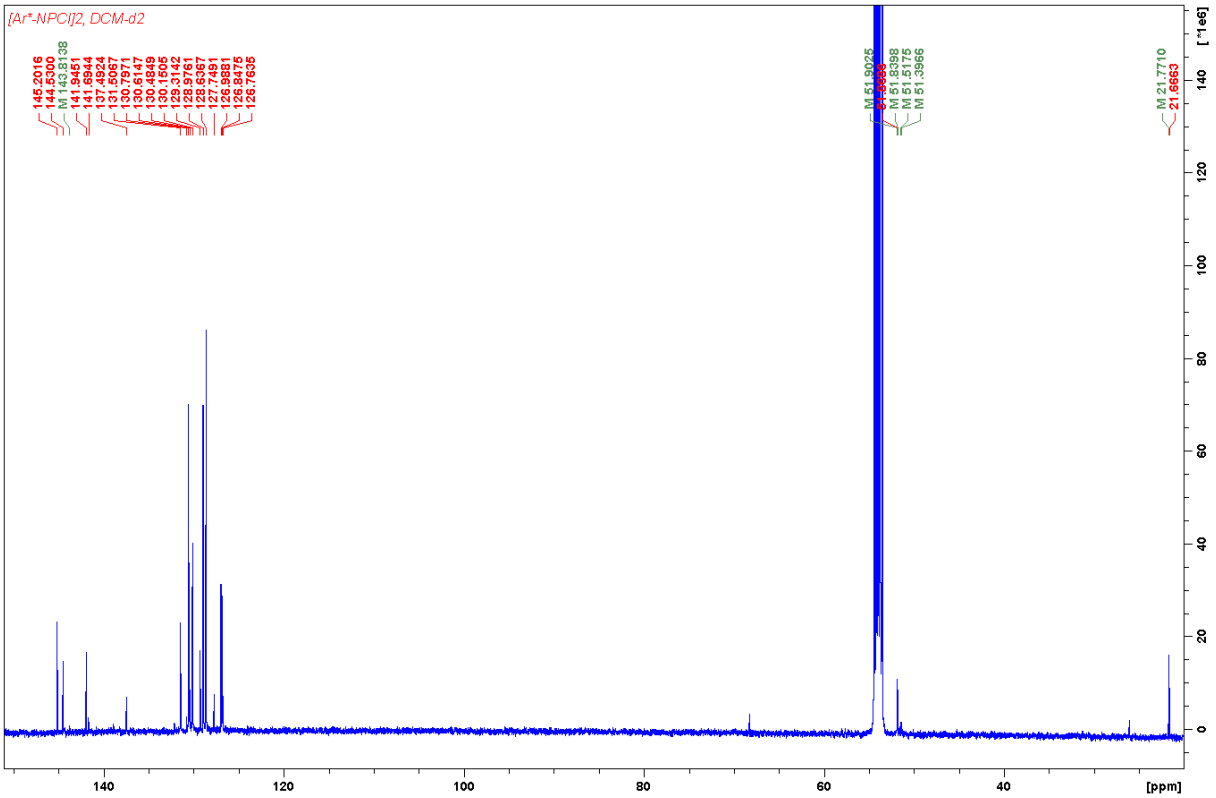


Figure S22. ^{13}C{^{1}H} NMR spectrum of [ClP(μ-N-Ar*)]$_2$.

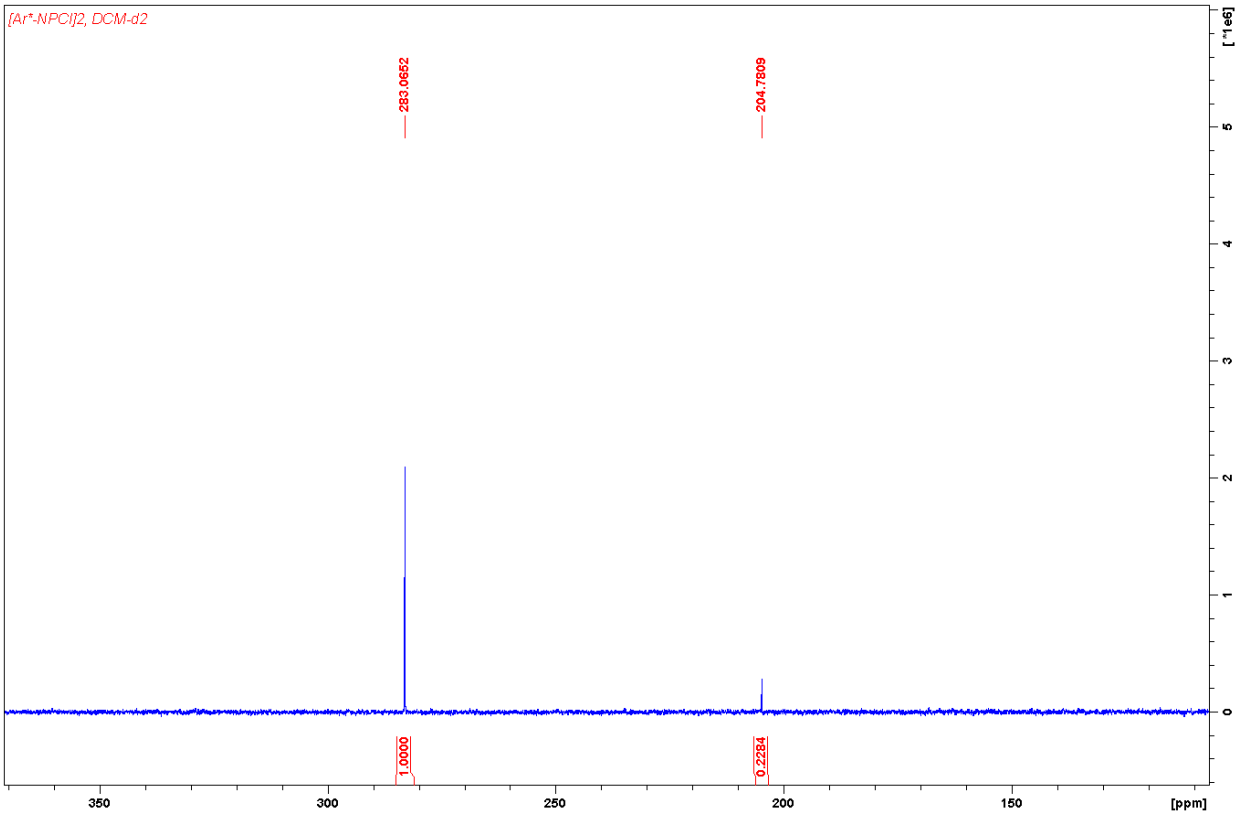


Figure S23. ^{31}P NMR spectrum of [ClP(μ-N-Ar*)]$_2$.

Spectroscopic characterization of Ar^{Bn}-N=PCl (10)

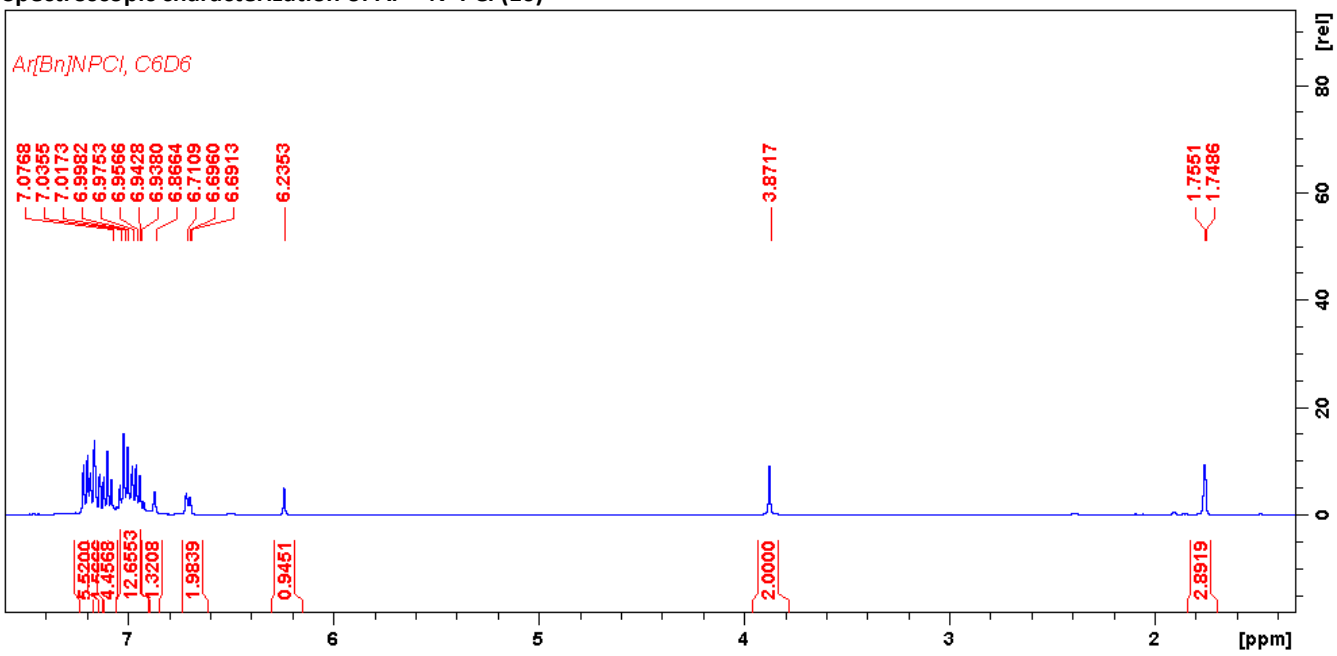


Figure S24. ^{1}H NMR spectrum of Ar^{Bn}-N=PCl.

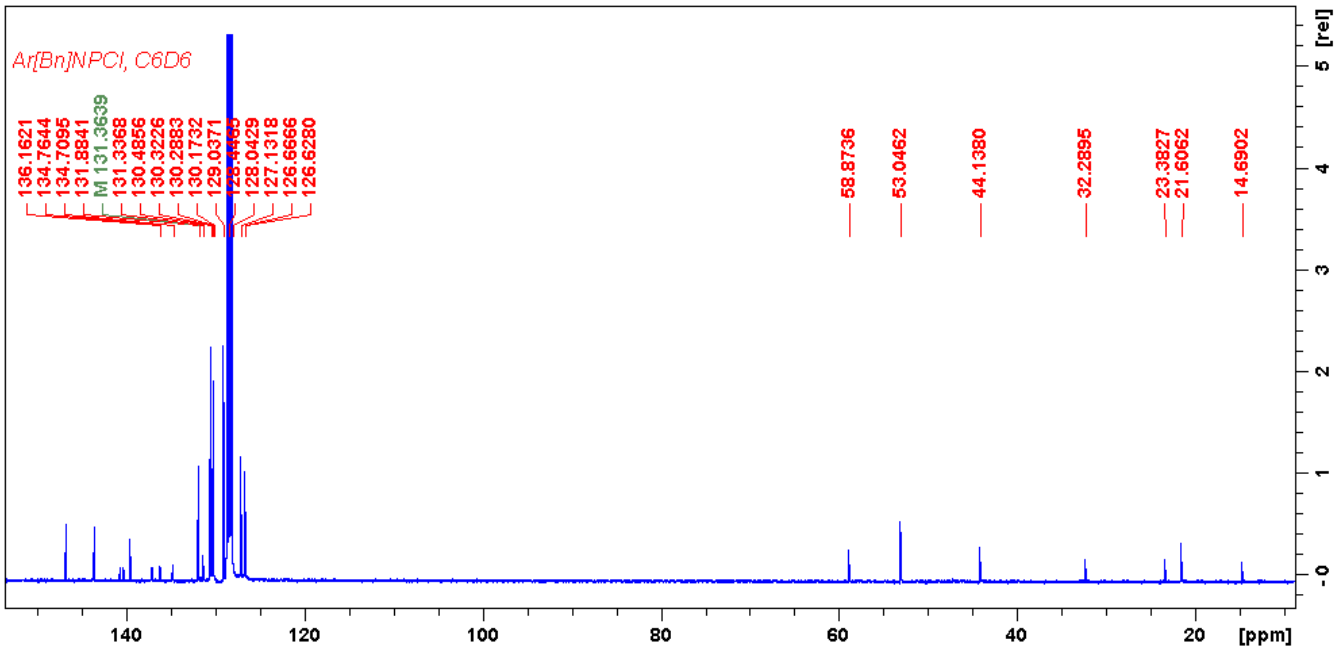


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of Ar^{Bn}-N=PCl.

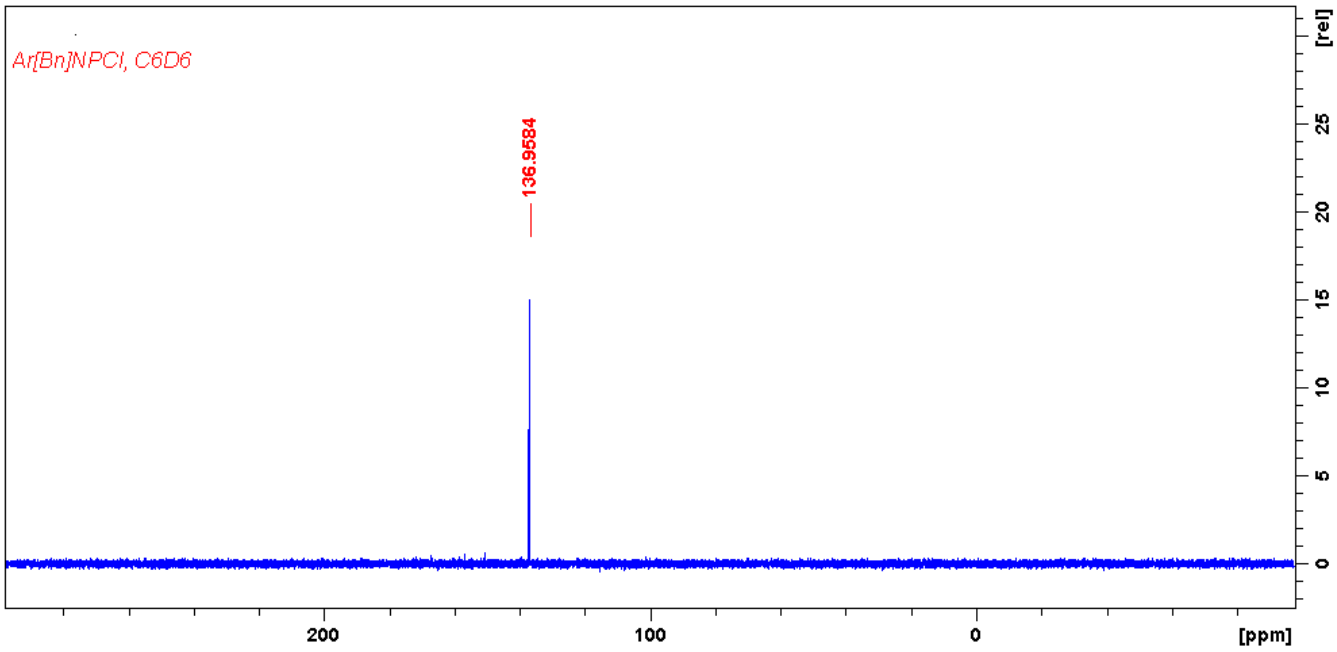


Figure S26. ^{31}P NMR spectrum of Ar^{Bn}-N=PCl.

Crystallographic section

Table S1: Experimental details for **1**

Crystal data	
Chemical formula	$C_{39}H_{45}NSi_2$
M_r	583.94
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	9.3294 (5), 10.4494 (6), 18.6129 (10)
α, β, γ (°)	78.955 (2), 84.572 (2), 69.270 (2)
V (Å^3)	1664.89 (16)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	1.16
Crystal size (mm)	0.56 × 0.12 × 0.10
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.352, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18789, 6207, 5223
R_{int}	0.087
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.619
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.134, 0.372, 1.12
No. of reflections	6207
No. of parameters	387
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 28.5468P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.01, −0.55

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S2: Experimental details for **2**

Crystal data	
Chemical formula	$C_{47}H_{41}N$
M_r	619.81
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	13.6239 (5), 16.2204 (6), 18.3295 (8)
α, β, γ (°)	111.979 (2), 96.405 (2), 104.882 (2)
V (Å^3)	3531.4 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.48 × 0.26 × 0.23
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.699, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	122452, 17644, 11544
R_{int}	0.090
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.061, 0.145, 1.04
No. of reflections	17644
No. of parameters	867
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.36

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S3: Experimental details for **3**

Crystal data	
Chemical formula	$C_{34}H_{27}NO$
M_r	465.56
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	5.4624 (11), 13.410 (3), 17.986 (4)
α, β, γ (°)	102.708 (11), 97.662 (12), 98.134 (11)
V (Å^3)	1253.6 (5)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.21 × 0.19 × 0.11
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.559, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18008, 4859, 3271
R_{int}	0.110
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.109, 0.295, 1.05
No. of reflections	4859
No. of parameters	327
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.37

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S4: Experimental details for **4**

Crystal data	
Chemical formula	$C_{41}H_{31}NO_2$
M_r	569.67
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	12.1041 (5), 16.6818 (5), 15.3349 (5)
β (°)	91.605 (1)
V (Å^3)	3095.18 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.59 × 0.29 × 0.24
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.696, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	74613, 7574, 5581
R_{int}	0.074
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.664
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.123, 1.04
No. of reflections	7574
No. of parameters	398
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.23

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S5: Experimental details for **5**

Crystal data	
Chemical formula	$C_{40}H_{33}N$
M_r	527.67
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	12.7282 (11), 16.8510 (12), 13.9530 (11)
β (°)	98.367 (3)
V (Å^3)	2960.8 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.55 × 0.55 × 0.33
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan
T_{min}, T_{max}	0.671, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	65778, 8205, 5672
R_{int}	0.102
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.072, 0.139, 1.08
No. of reflections	8205
No. of parameters	371
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.29

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S6: Experimental details for **6**

Crystal data	
Chemical formula	$C_{41}H_{35}N$
M_r	541.70
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	12.889 (3), 16.963 (4), 13.963 (4)
β (°)	98.517 (9)
V (Å^3)	3019.3 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.31 × 0.16 × 0.10
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.690, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46616, 6975, 4208
R_{int}	0.135
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.129, 1.04
No. of reflections	6975
No. of parameters	381
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.27

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S7: Experimental details for **7**

Crystal data	
Chemical formula	$C_{51}H_{49}N{\cdot}0.5(C_7H_8)$
M_r	721.98
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	13.6590 (9), 14.2712 (8), 21.5396 (14)
α, β, γ (°)	88.277 (2), 79.673 (2), 85.386 (2)
V (Å^3)	4116.8 (4)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.50 × 0.15 × 0.12
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.668, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	79331, 16064, 11189
R_{int}	0.079
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.056, 0.150, 1.01
No. of reflections	16064
No. of parameters	1013
No. of restraints	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.28

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S8: Experimental details for **8**

Crystal data	
Chemical formula	$C_{40}H_{35}N$
M_r	529.69
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	10.9439 (10), 11.4579 (10), 12.4427 (11)
α, β, γ (°)	73.734 (3), 75.085 (3), 77.426 (3)
V (Å^3)	1429.4 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.41 × 0.15 × 0.14
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.494, 0.958
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11417, 4199, 3297
R_{int}	0.084
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.119, 0.302, 1.12
No. of reflections	4199
No. of parameters	371
No. of restraints	349
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.57

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S9: Experimental details for **10**

Crystal data	
Chemical formula	$C_{40}H_{33}ClNP$
M_r	594.09
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	8.622 (2), 19.654 (2), 18.335 (2)
β (°)	94.724 (9)
V (Å^3)	3096.5 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.41 × 0.18 × 0.07
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.645, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	72188, 7109, 4960
R_{int}	0.117
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.151, 1.07
No. of reflections	7109
No. of parameters	389
No. of restraints	342
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.54

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Quantum-Chemical Section

Buried Volume was calculated by SambVca with default parameters, nitrogen atom was chosen as the centre of the sphere with radii = 3.5 Å (all anilines except $Ar^{Bn}NH_2$ (**8**) were calculated by us previously[S1] and are added here for comparison) and 6.0 Å.[S2-5] Spatial orientation of the anilines is depicted in figure S32.

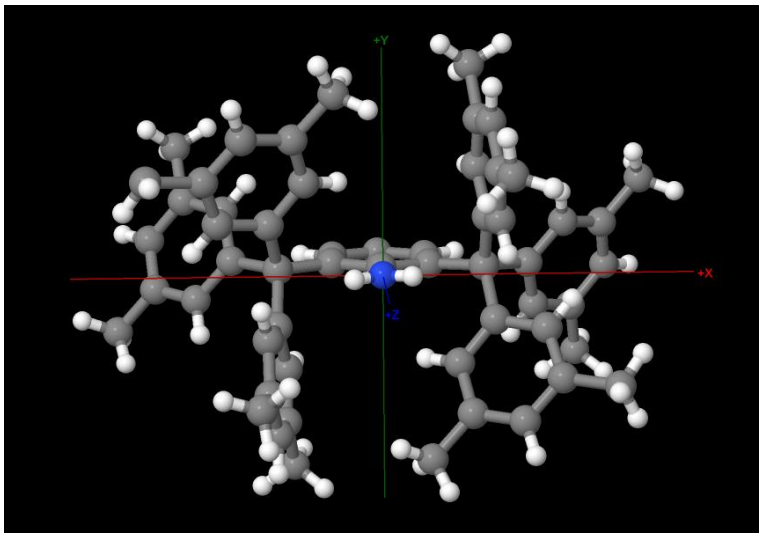
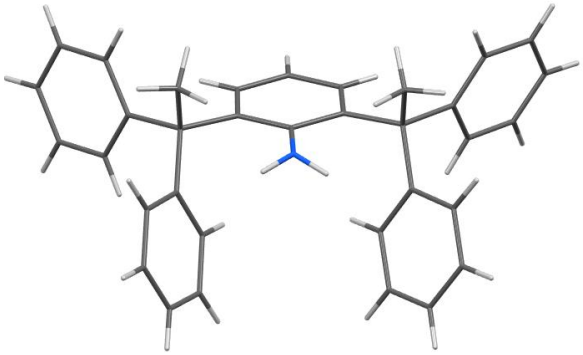


Figure S27. Spatial orientation of the bulky anilines chosen for the calculation of the buried volume.

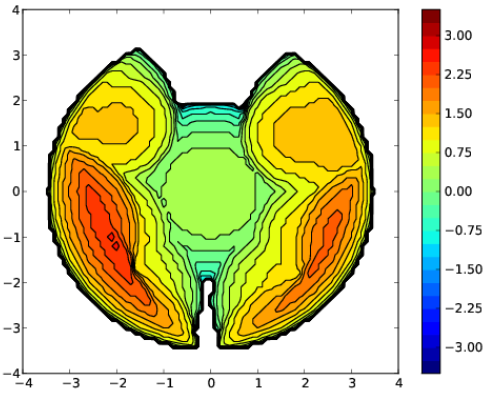
Structure/ Buried volumes

%V_Bur(3.5 Å) = 64.4; %V_Bur(6.0 Å) = 43.7

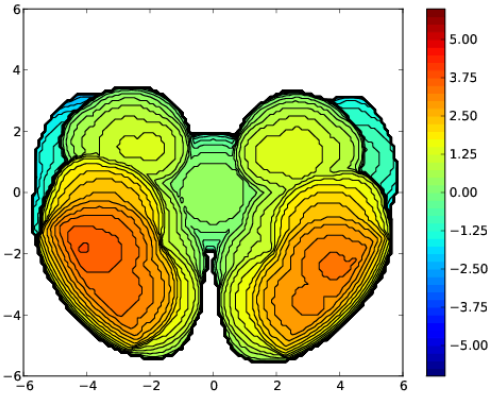


Steric Maps

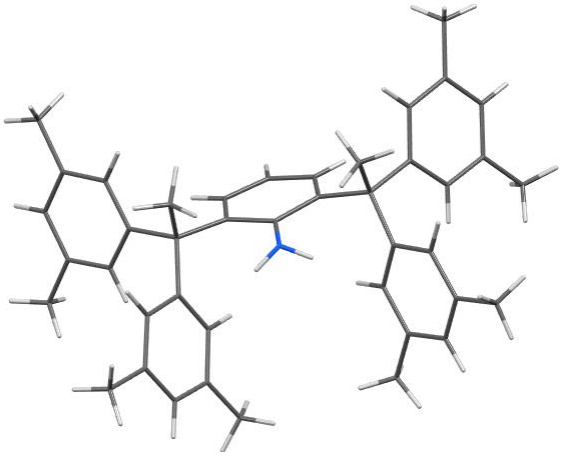
3.5 Å



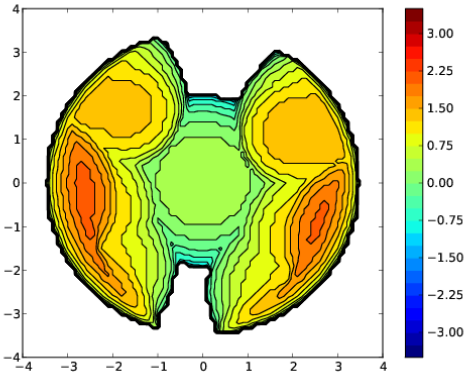
6.0 Å



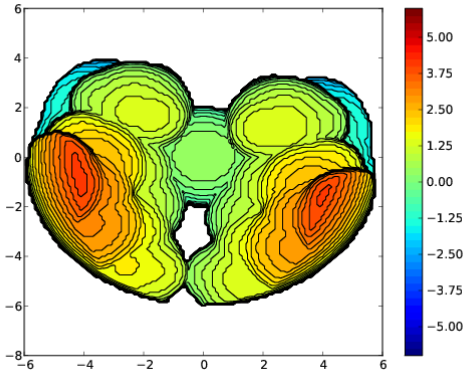
%V_Bur(3.5 Å) = 62.6; %V_Bur(6.0 Å) = 46.1



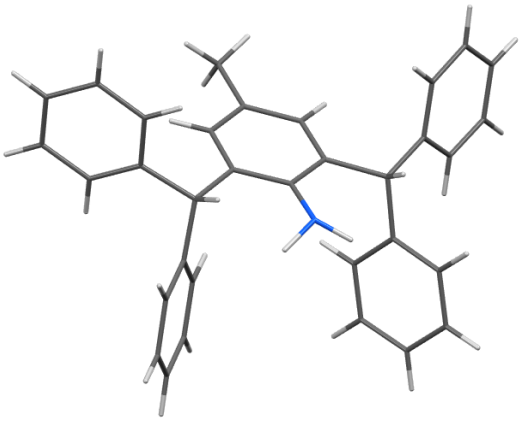
3.5 Å



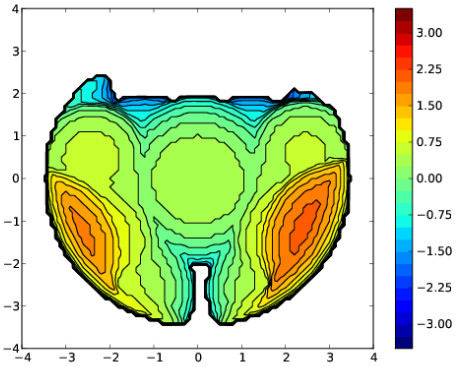
6.0 Å



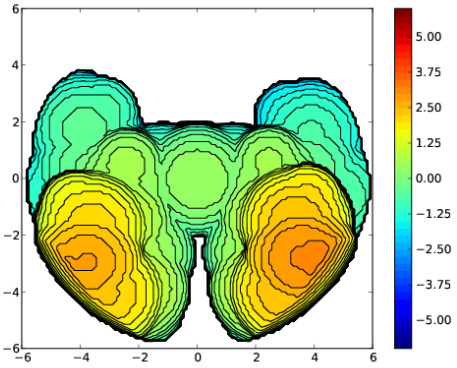
%V_Bur(3.5 Å) = 51.7; %V_Bur(6.0 Å) = 39.7



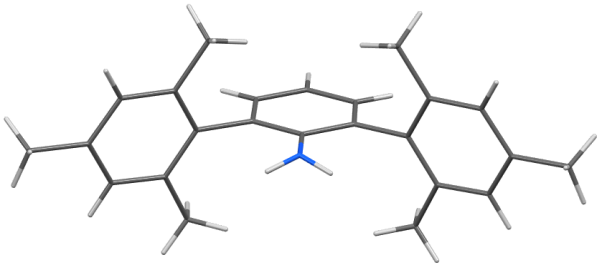
3.5 Å



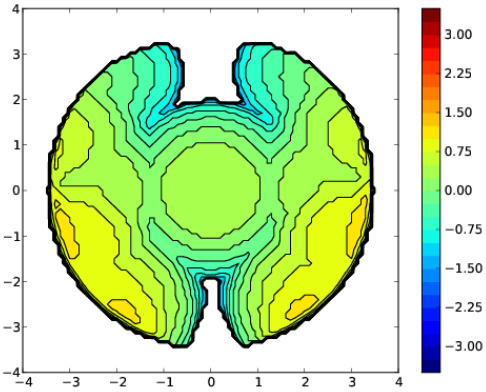
6.0 Å



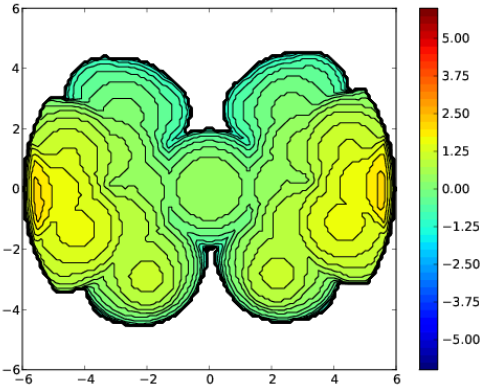
%V_Bur(3.5 Å) = 52.8; %V_Bur(6.0 Å) = 36.3



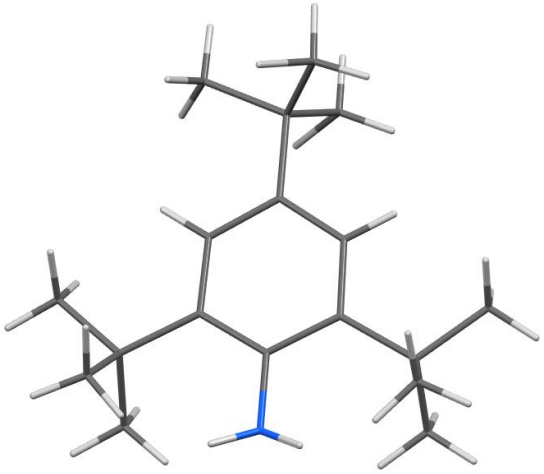
3.5 Å



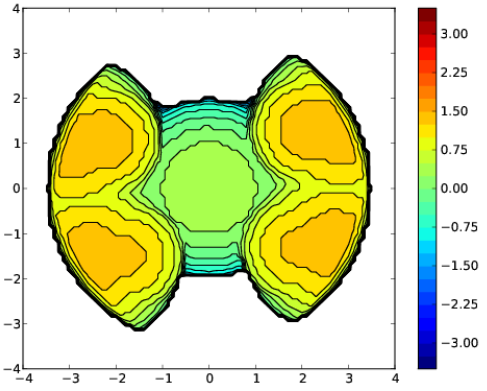
6.0 Å



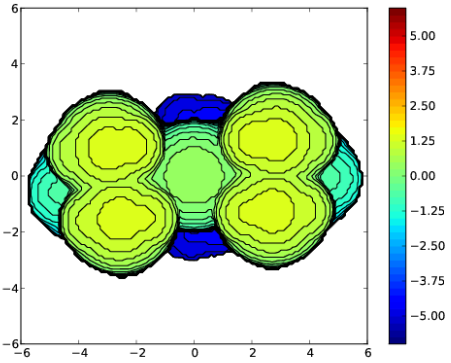
%V_Bur(3.5 Å) = 54.9; %V_Bur(6.0 Å) = 28.5



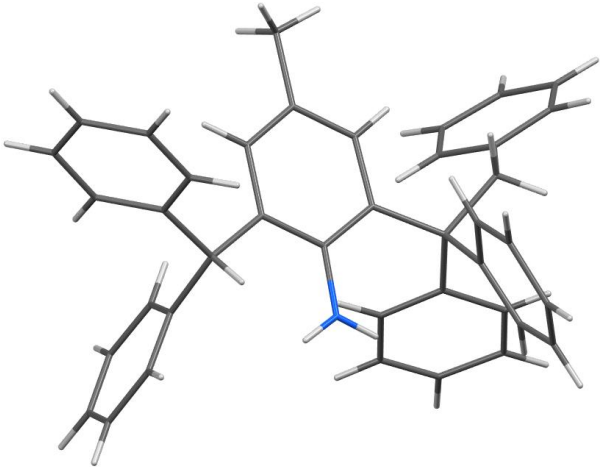
3.5 Å



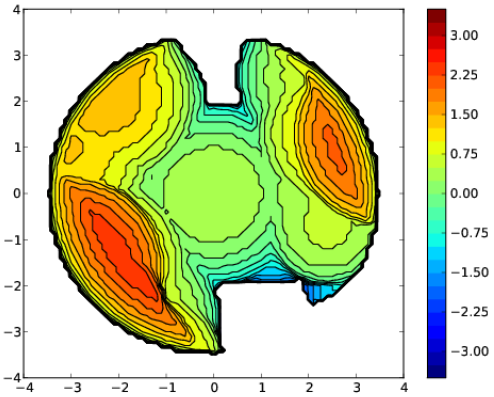
6.0 Å



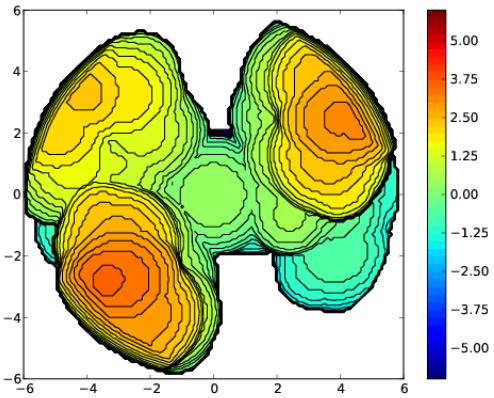
%V_Bur(3.5 Å) = 60.0; %V_Bur(6.0 Å) = 46.9



3.5 Å



6.0 Å



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