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Access to most sterically crowded anilines via non-catalysed C-C coupling reactions

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Materials and Methods

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube technique. Solvents were dried using a Pure Solv–Innovative Technology equipment under argon gas atmosphere. Deuterated benzene was obtained from Euriso-Top GmbH. Dimethyl-2-amino*iso*phtalate was prepared according to the published procedure.[1] Phenylmagnesium bromide (1M solution in THF, Sigma Aldrich), Methylmagnesium bromide (3.4M solution in 2-methyltetrahydrofuran, Sigma Aldrich), magnesium (Sigma Aldrich), 1-bromo-4-*tert*-butylbenzene (Sigma Aldrich), 1-bromo-3,5-dimethylbenzene (Sigma Aldrich) and triethyl orthoformate (Sigma Aldrich) were used as purchased.

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).

sc-XRD
Full-sets of diffraction data for **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b** and **4c** were collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Cu (Cu/Kα radiation; λ = 1.54178 Å) or Mo (Mo/Kα radiation; λ = 0.71073 Å) microfocus X-ray (IμS) sources, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection.
The frames were integrated with the Bruker SAINT software package using a narrowframe algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2014/7 software implemented in APEX3 v2016.5-0 (Bruker AXS) system.[S1]
Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors Hiso(H) = 1.2 Ueq (pivot atom) or of 1.5 Ueq (methyl). H atoms in methyl, methylene, methine, vinylidene moieties and hydrogen S6 atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98, 0.93 and 0.93 Å and 0.88 Å for N-H and 0.82 Å for O-H bonds.
Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ (methyl). H atoms in methyl, methylene, vinylidene moieties and hydrogen atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.93 and 0.93Å and 0.88 Å for N-H bonds. Minor disorders of the solvents were treated by standard methods.
$R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | |F_o| - |F_c| | / \sum |F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

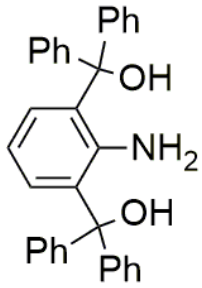
Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1956669-1956677. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Syntheses and Characterization

General procedure for synthesis of 1-NH_2-2,6-[C(OH)Ar_2]$_2$-C_6H_3 (1a-c)

This synthetic procedure was performed under argon atmosphere. Solution of ArMgBr (8 eq) in THF was added to the stirring solution of dimethyl-2-amino*iso*phtalate (1 eq) in THF at 0 °C. The reaction mixture was slowly heated to room temperature and stirred for two hours. The reaction was carefully quenched by saturated solution of NH_4Cl, the organic phase was separated, dried with $MgSO_4$ and filtered. The yellow solution was dried *in vacuo* and the solid residue was washed with small amount of acetone giving **1a-c** in the form of white powder.

1-NH_2-2,6-[C(OH)Ph_2]$_2$-C_6H_3 (1a):



Dimethyl-2-amino*iso*phtalate (15.53 g, 74.2 mmol); phenylmagnesium bromide (593.8 mL, 1M solution in THF, 593.8 mmol). Yield 30.57 g, 90 %. **Mp** 199 °C. **Anal. Calc**. for $C_{32}H_{27}NO_2$ (457.56): C 84.0, H 6.0, N 3.1; found C 83.8, H 5.9, N 3.0. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 3.95 (s broad, 2H, N*H*$_2$), 5.35 (s broad, 2H, O*H*), 6.39 (t, ^3J(^{1}H-^{1}H) = 7.8 Hz, 1H, *p*-C_6H_3), 6.66 (d, ^3J(^{1}H-^{1}H) = 7.8 Hz, 2H, *m*-C_6H_3), 7.01 (t, ^3J(^{1}H-^{1}H) = 7.3 Hz, 4H, *p*-C_6H_5), 7.07 (t, ^3J(^{1}H-^{1}H) = 7.9 Hz, 8H, *m*-C_6H_5), 7.29 (d, ^3J(^{1}H-^{1}H) = 7.5 Hz, 8H, *o*-C_6H_5) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 83.3 (s, *C*OH), 119.0 (s, *p*-C_6H_3), 127.8 (s, *p*-C_6H_5), 128.6 (s, *m*-C_6H_5, *o*-C_6H_5), 130.7 (s, *m*-C_6H_3), 136.6 (s, *o*-C_6H_3), 144.7 (s, *ipso*-C_6H_3), 147.0 (s, *ipso*-C_6H_5) ppm.

Spectroscopic characterization of 2,6-[C(OH)Ph_2]$_2$-C_6H_3 (1a):

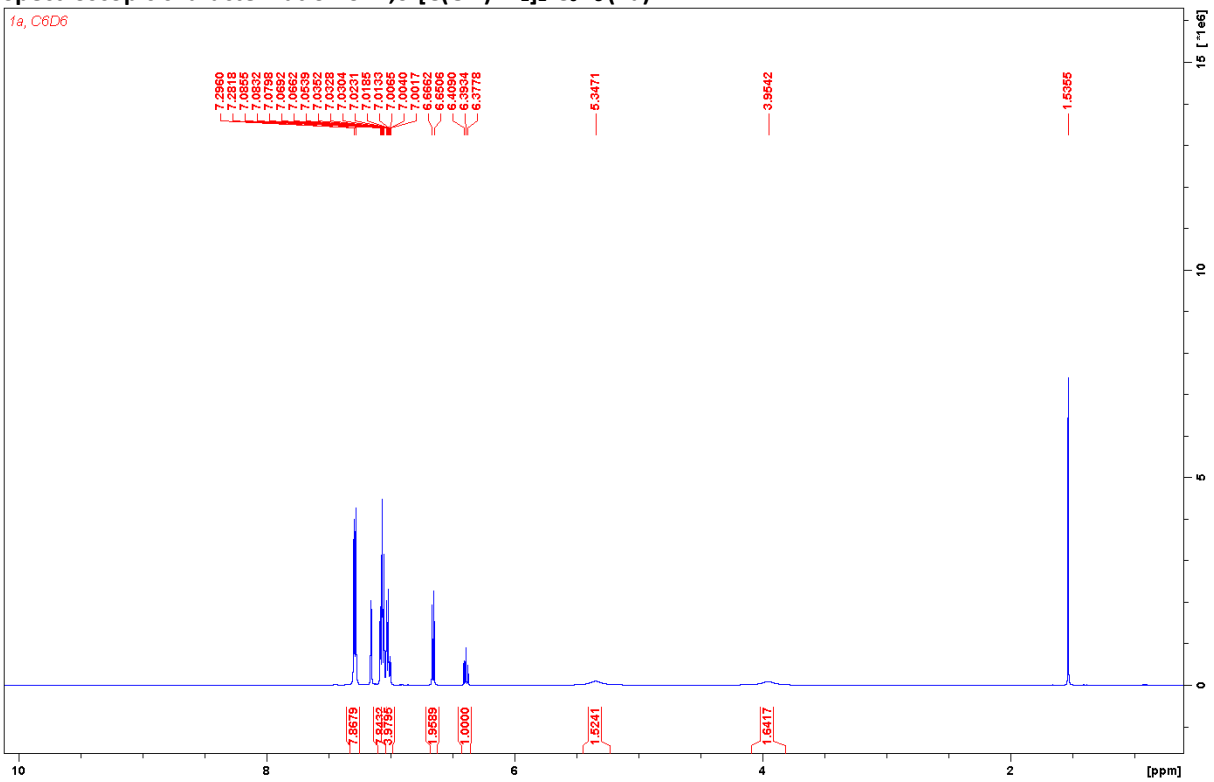


Figure S1. ^{1}H NMR spectrum of **1a**.

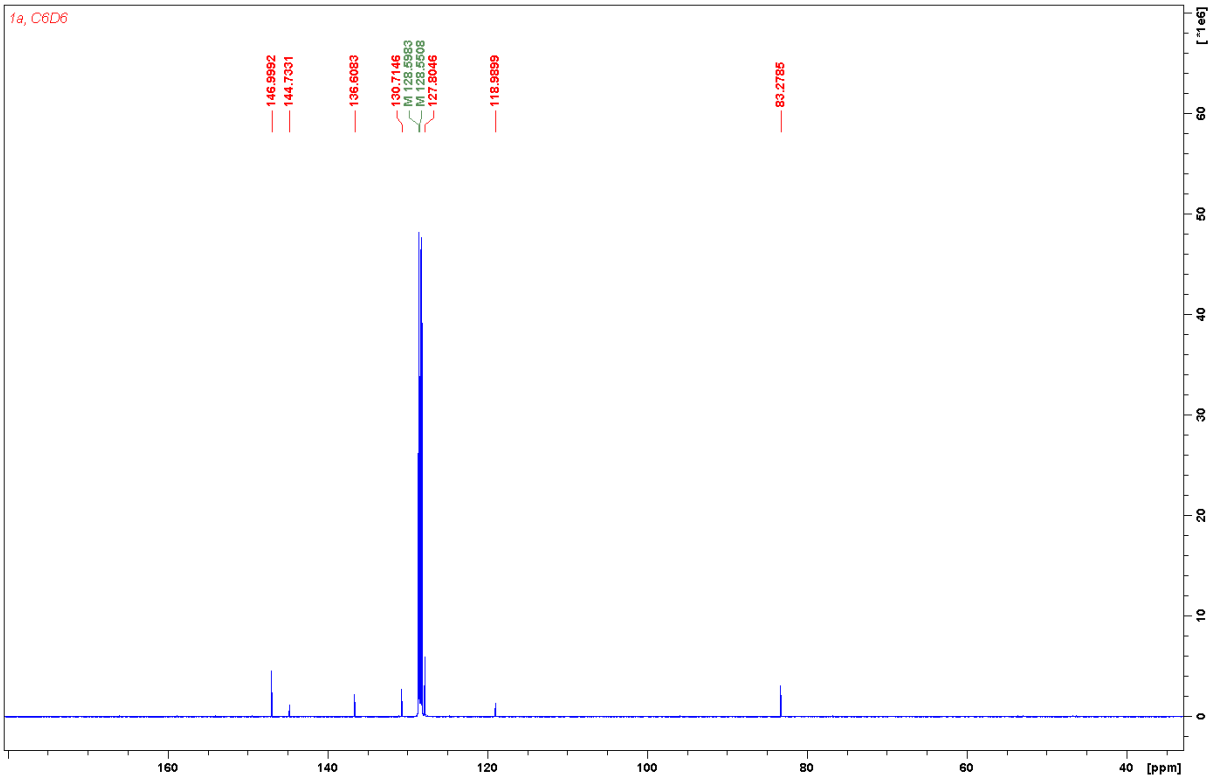


Figure S2. ^{13}C NMR spectrum of **1a**.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(OH)Ph_2]$_2$-C_6H_3 (1a):

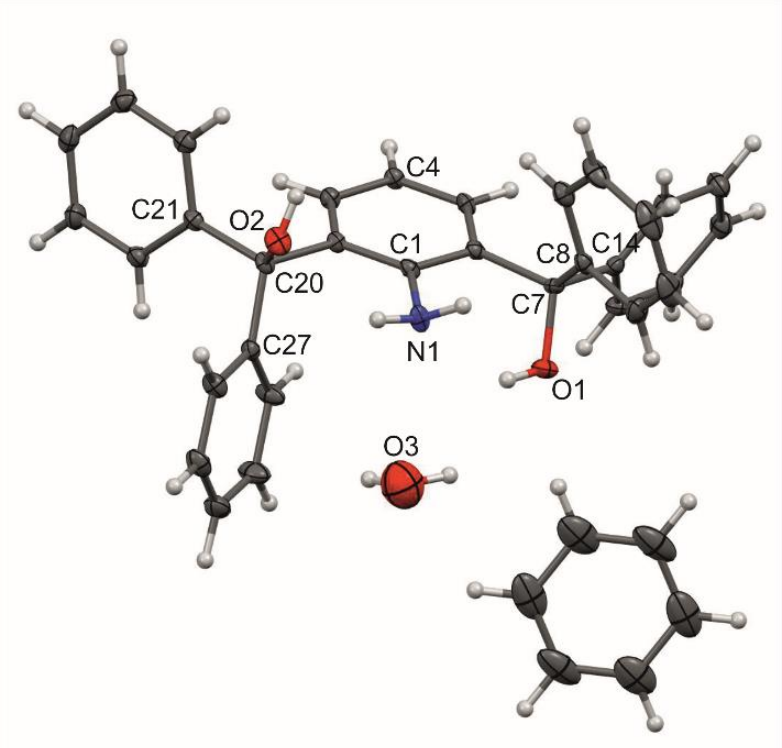


Figure S3. The molecular structure of **1a**·0.25H_2O·0.5C_6H_6, ORTEP diagram, 35% probability level, selected interatomic distances [Å] and bond angles[°]: O1 N1 2.830(5), O2 N1 2.891(5), C7 C20 5.106(5), C1 N1 1.407(4), C1 C2 C7 O1 57.7(4), C1 C6 C20 O2 53.8(4).

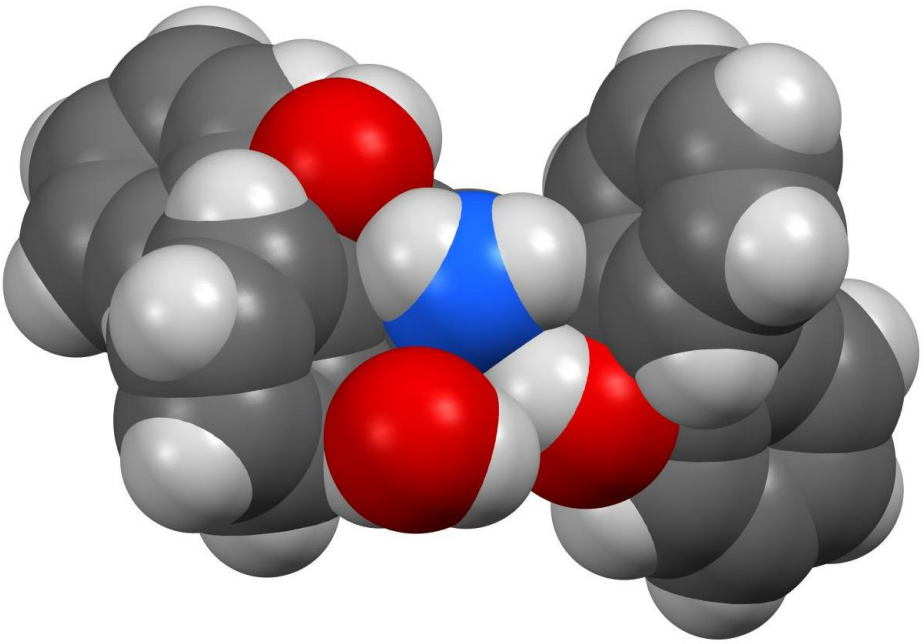


Figure S4. The molecular structure of **1a**, space filling model.

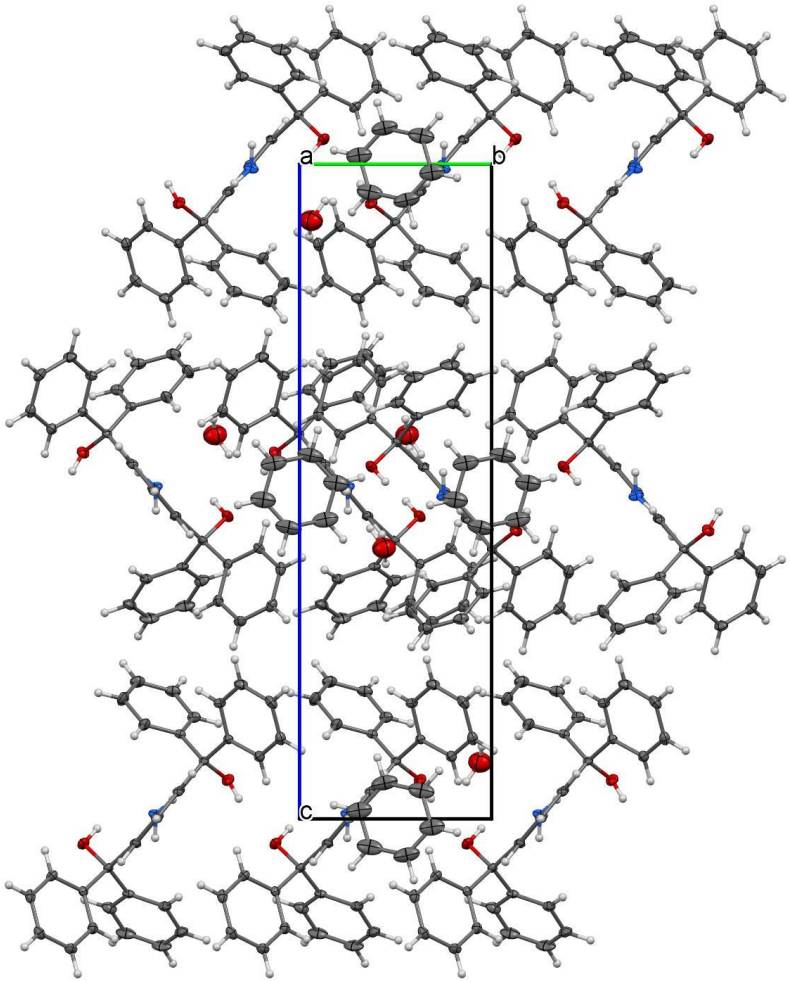
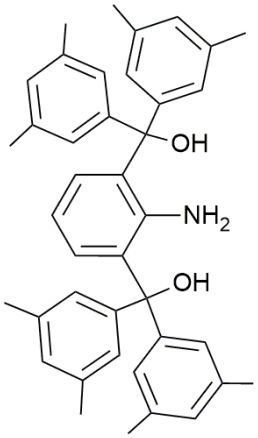


Figure S5. The crystal packing model of **1a**.

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

Chemical formula	$C_{35}H_{30.50}NO_{2.25}$
M_r	505.10
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	16.515 (4), 6.8442 (13), 24.238 (4)
β (°)	105.844 (6)
V (Å^3)	2635.6 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.31 × 0.20 × 0.19
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.796, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31014, 5468, 3313
R_{int}	0.179
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.079, 0.201, 1.03
No. of reflections	5468
No. of parameters	373
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.26

1-NH_2-2,6-[C(OH)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (1b):



Dimethyl-2-amino*iso*phtalate (14.77 g, 70.6 mmol); 1-bromo-3,5-dimethylbenzene (76.75 mL, 564.9 mmol); magnesium (15.10 g, 621.3 mmol). Yield 36.61 g, 91 %. **Mp** 155 °C. **Anal. Calc**. for $C_{40}H_{43}NO_2$ (569.77): C 84.3, H 7.6, N 2.5; found C 84.5, H 7.7, N 2.4. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.08 (s, 24H, CH_3), 4.74 (s broad, 4H, NH_2 + OH), 6.50 (t, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 1H, *p*-C_6H_3), 6.72 (s, 4H, *p*-$C_6H_3^{Me}$), 6.89 (d, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 2H, *m*-C_6H_3), 7.19 (s, 8H, *o*-$C_6H_3^{Me}$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 21.6 (s, CH_3), 83.0 (s, *C*OH), 118.6 (s, *p*-C_6H_3), 126.1 (s, *o*-$C_6H_3^{Me}$), 129.3 (s, *p*-$C_6H_3^{Me}$), 130.4 (s, *m*-C_6H_3), 136.7 (s, *o*-C_6H_3), 137.6 (s, *m*-$C_6H_3^{Me}$), 144.5 (s, *ipso*-C_6H_3), 147.1 (s, *ipso*-$C_6H_3^{Me}$) ppm.

Spectroscopic characterization of 2,6-[C(OH)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (1b):

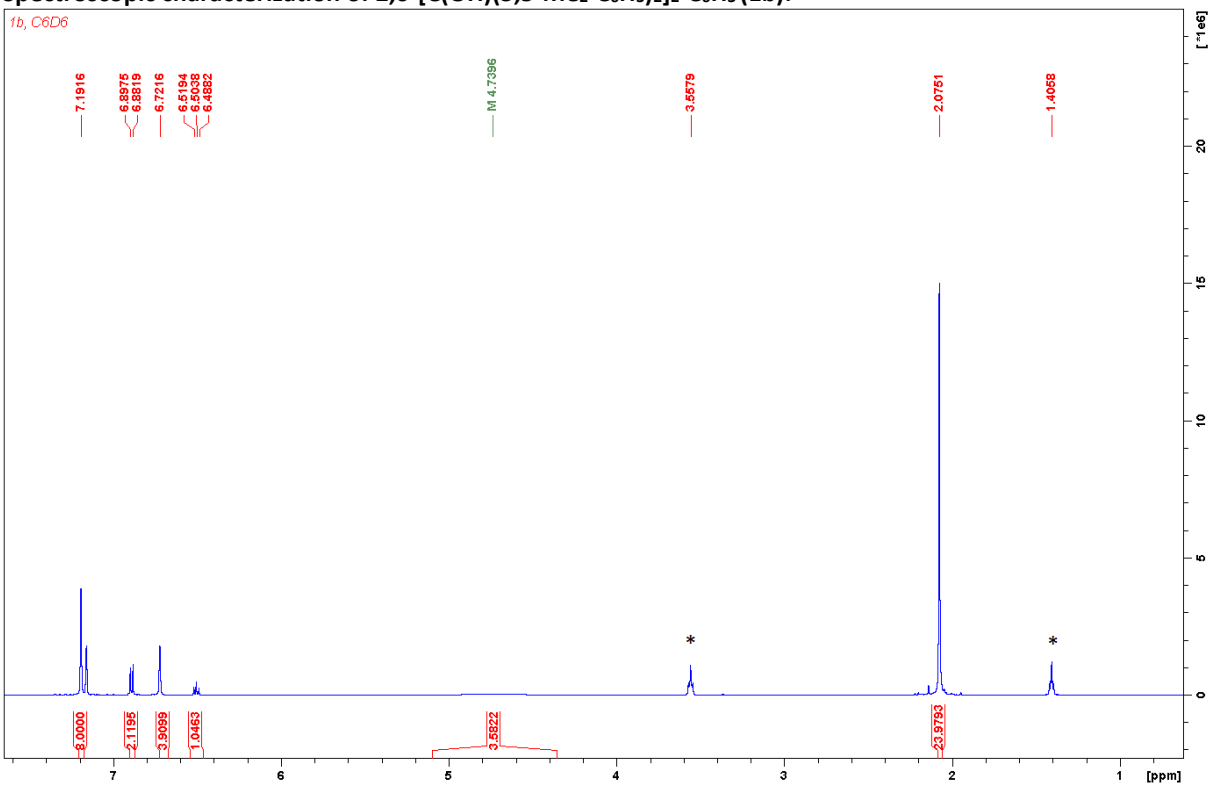


Figure S6. ^{1}H NMR spectrum of **1b**. Residual THF marked by *.

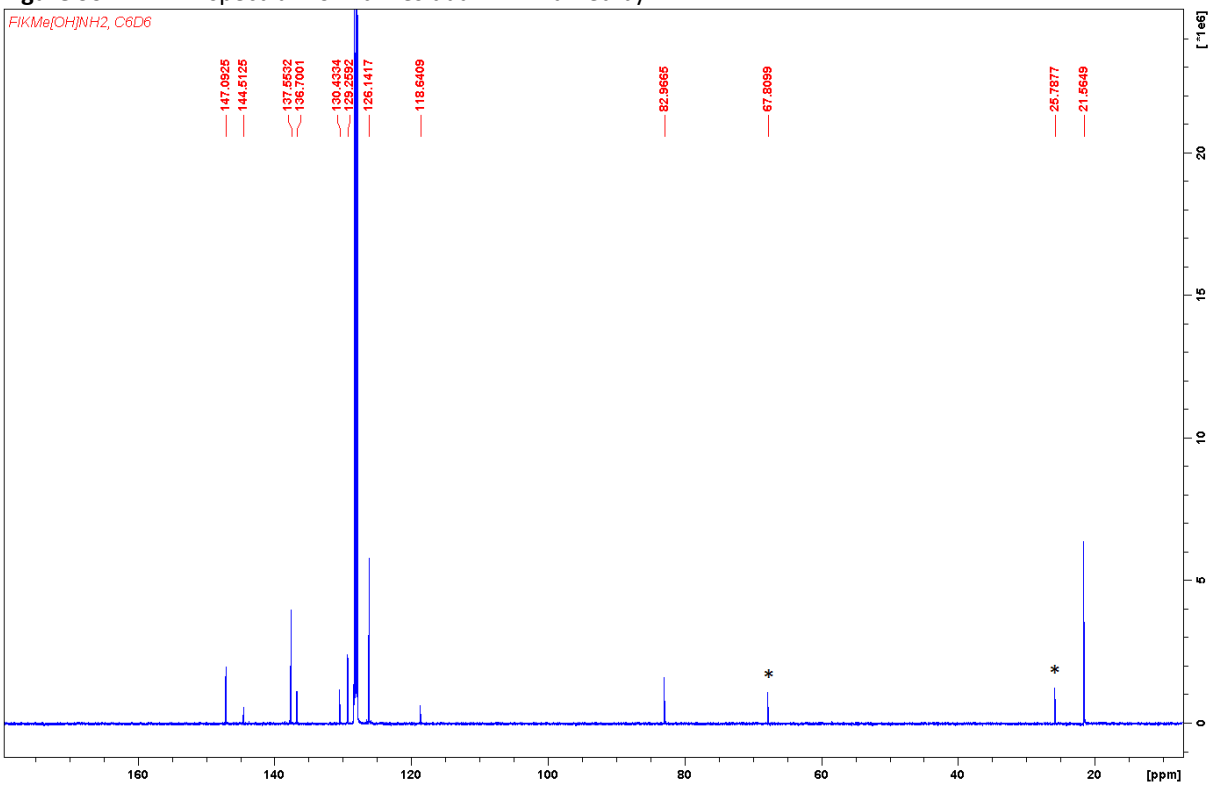


Figure S7. ^{13}C NMR spectrum of **1b**. Residual THF marked by *.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(OH)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (1b):

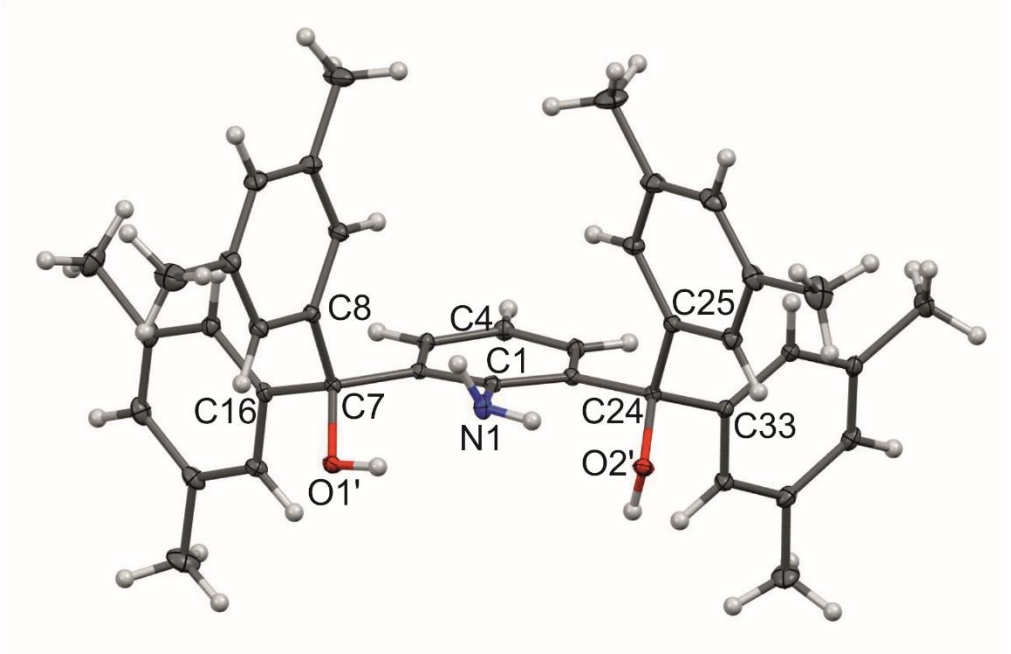


Figure S8. The molecular structure of **1b**, ORTEP diagram, 40% probability level. Selected interatomic distances [Å] and bond angles[°]: [°]: O1' N1 2.696(1), O2' N1 2.764(1), C7 C24 5.123(2), C1 N1 1.422(2), C1 C2 C7 O1' 47.6(1), C1 C6 C24 O2' 41.9(1).

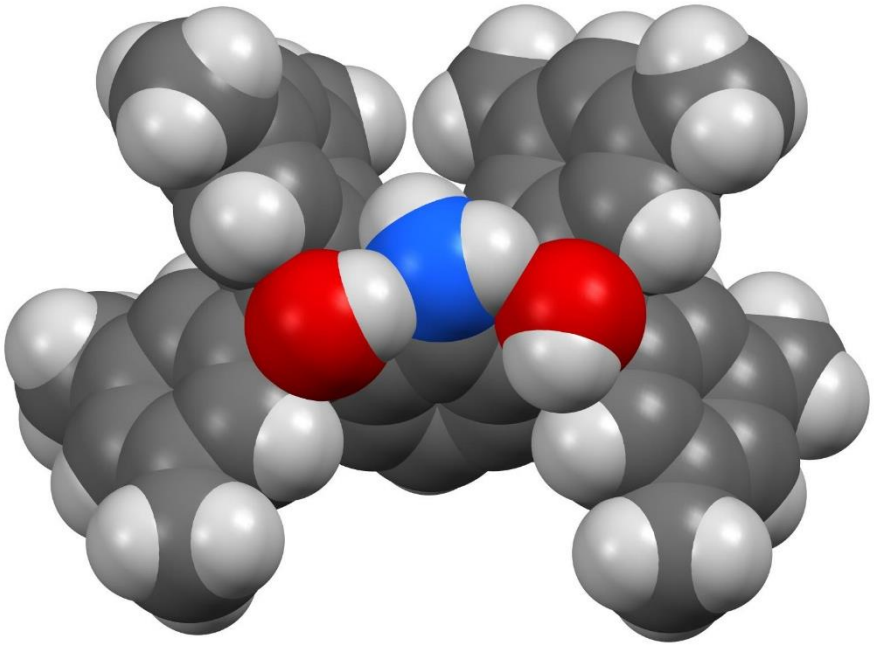


Figure S9. The molecular structure of **1b**, space filling model.

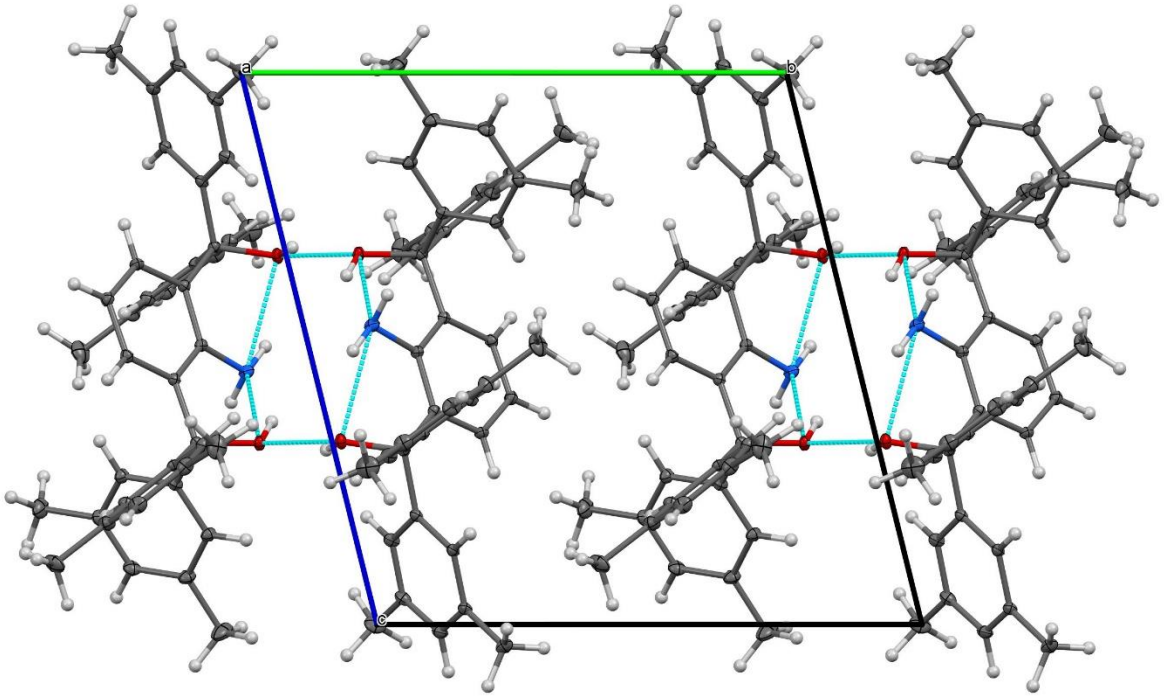
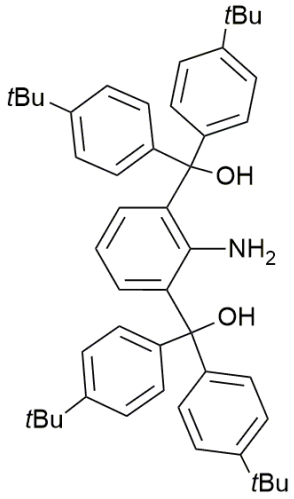


Figure S10. The crystal packing model of **1b**.

Table S2. Crystal data and structure refinement for **1b**.

Crystal data	
Chemical formula	$C_{40}H_{43}NO_2$
M_r	569.75
Crystal system, space group	Triclinic, *P*1
Temperature (K)	150
a, *b*, *c* (Å)	10.3051 (4), 12.5154 (6), 13.8322 (6)
α, β, γ (°)	73.950 (2), 68.779 (2), 80.981 (2)
V (Å^3)	1594.98 (12)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.51 × 0.39 × 0.21
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.722, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	65626, 11316, 8469
R_{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.787
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.160, 1.03
No. of reflections	11316
No. of parameters	412
No. of restraints	357
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.33

1-NH$_2$-2,6-[C(OH)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (1c):



Dimethyl-2-amino*iso*phtalate (13.61 g, 65.1 mmol); 1-bromo-4-*tert*-butylbenzene (90.27 mL, 520.6 mmol); magnesium (13.92 g, 572.6 mmol). Yield 39.04 g, 88 %. **Mp** 283 °C. **Anal. Calc**. for $C_{48}H_{59}NO_2$ (681.99): C 84.5, H 8.7, N 2.1; found C 84.3, H 8.9, N 2.0. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.22 (s, 36H, C(C*H*$_3$)$_3$), 4.03 (s broad, 2H, N*H*$_2$), 5.13 (s broad, 2H, O*H*), 6.40 (t, ^3J(^{1}H-^{1}H) = 7.8 Hz, 1H, *p*-C$_6$*H*$_3$), 6.82 (d, ^3J(^{1}H-^{1}H) = 7.8 Hz, 2H, *m*-C$_6$*H*$_3$), 7.21 (d, ^3J(^{1}H-^{1}H) = 8.3 Hz, 8H, *m*-C$_6$*H*$_4$), 7.36 (d, ^3J(^{1}H-^{1}H) = 8.3 Hz, 8H, *o*-C$_6$*H*$_4$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 31.8 (s, C(*C*H$_3$)$_3$), 34.8 (s, *C*(CH$_3$)$_3$), 83.1 (s, *C*OH), 118.9 (s, *p*-*C*$_6$H$_3$), 125.5 (s, *m*-*C*$_6$H$_4$), 128.5 (s, *o*-*C*$_6$H$_4$), 130.7 (s, *m*-*C*$_6$H$_3$), 136.7 (s, *o*-*C*$_6$H$_3$), 144.5 (s, *ipso*-*C*$_6$H$_4$), 145.0 (s, *ipso*-*C*$_6$H$_3$), 150.2 (s, *p*-*C*$_6$H$_4$) ppm.

Spectroscopic characterization of 2,6-[C(OH)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (1c):

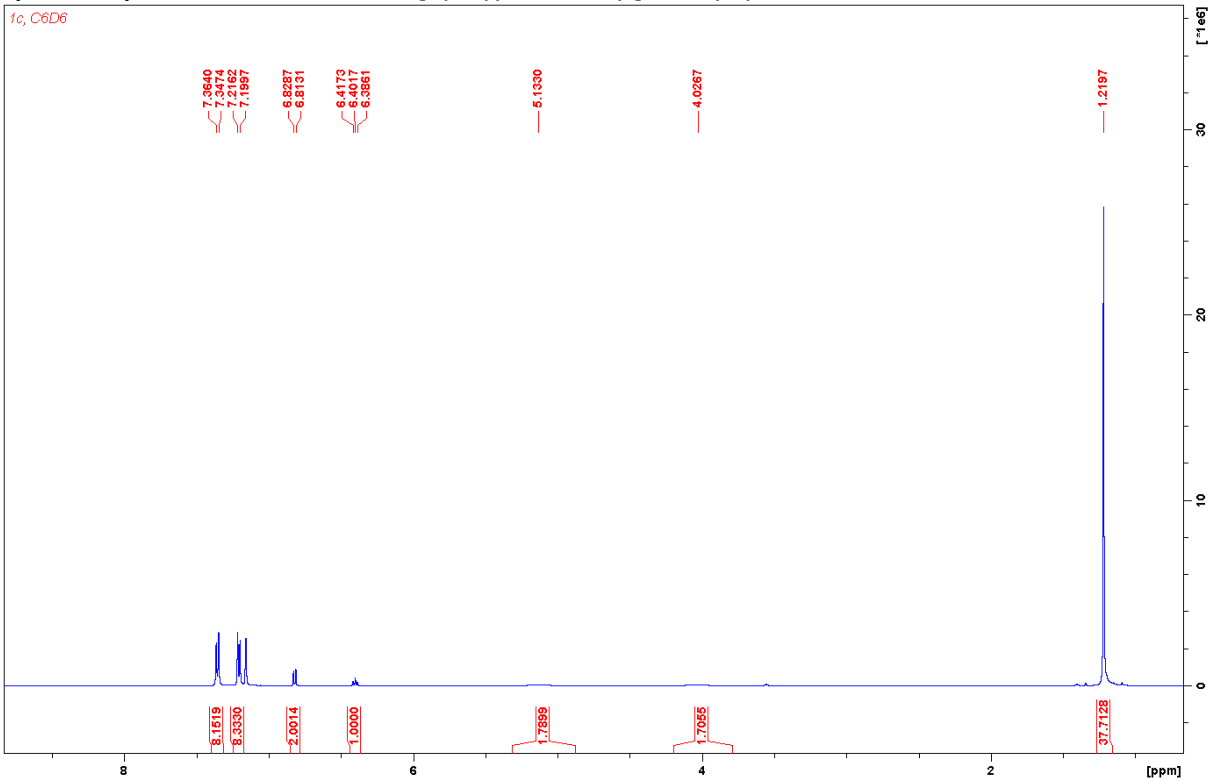


Figure S5. ^{1}H NMR spectrum of **1c**.

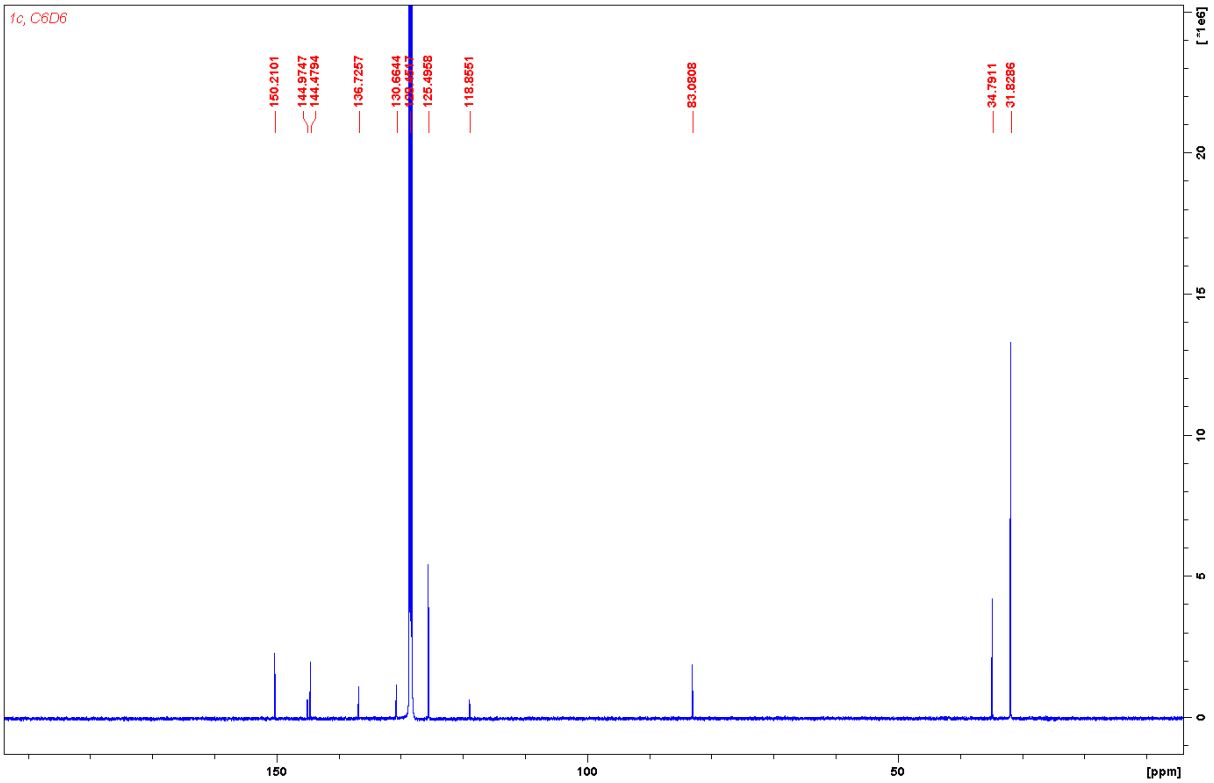
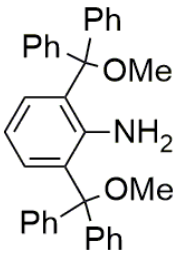


Figure S6. ^{13}C NMR spectrum of **1c**.

General procedure for synthesis of 1-NH_2-2,6-[C(OMe)Ar_2]$_2$-C_6H_3 (2a-c)

Sulfuric acid was added dropwise to the solution of triethyl orthoformate (10 eq) and 2,6-[C(OH)Ar_2]$_2$-C_6H_3 (**1a-c**, 1 eq) in dichloromethane/methanol (1:1) while stirring. The resulting reaction mixture was stirred for two days and then neutralized with saturated solution of sodium bicarbonate. The organic layer was separated and dried with $MgSO_4$. The volatiles were removed *in vacuo* and the solid residue was washed with small amount of acetone yielding **2a-c** in the form of white powder.

1-NH_2-2,6-[C(OMe)Ph_2]$_2$-C_6H_3 (2a):



2,6-[C(OH)Ph_2]$_2$-C_6H_3 (**1a**) (20.53 g, 44.9 mmol); $HC(OEt)_3$ (74.6 mL, 448.7 mmol); H_2SO_4 (3.74 mL, 96%, 67.3 mmol); DCM/MeOH (500 mL). Yield 18.52 g, 85 %. **Mp** 226 °C. **Anal. Calc**. for $C_{34}H_{31}NO_2$ (485.62): C 84.1, H 6.4, N 2.9; found C 84.3, H 6.3, N 2.9. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 3.15 (s, 6H, OCH_3), 4.88 (s, 2H, NH_2), 6.51 (t, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 1H, *p*-C_6H_3), 6.98 (t, $^3J(^1H\text{-}^1H)$ = 7.4 Hz, 4H, *p*-C_6H_5), 7.10 (t, $^3J(^1H\text{-}^1H)$ = 7.5 Hz, 8H, *m*-C_6H_5), 7.40 (d, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 2H, *m*-C_6H_3), 7.48 (d, $^3J(^1H\text{-}^1H)$ = 7.3 Hz, 8H, *o*-C_6H_5) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 53.1 (s, OCH_3), 89.0 (s, $COCH_3$), 114.2 (s, *p*-C_6H_3), 123.9 (s, *o*-C_6H_3), 127.2 (s, *p*-C_6H_5), 128.1 (s, *o*-C_6H_5), 128.5 (s, *m*-C_6H_5), 133.1 (s, *m*-C_6H_3), 145.3 (s, *ipso*-C_6H_5), 147.7 (s, *ipso*-C_6H_3) ppm.

Spectroscopic characterization of 2,6-[C(OMe)Ph$_2$]$_2$-C$_6$H$_3$ (2a):

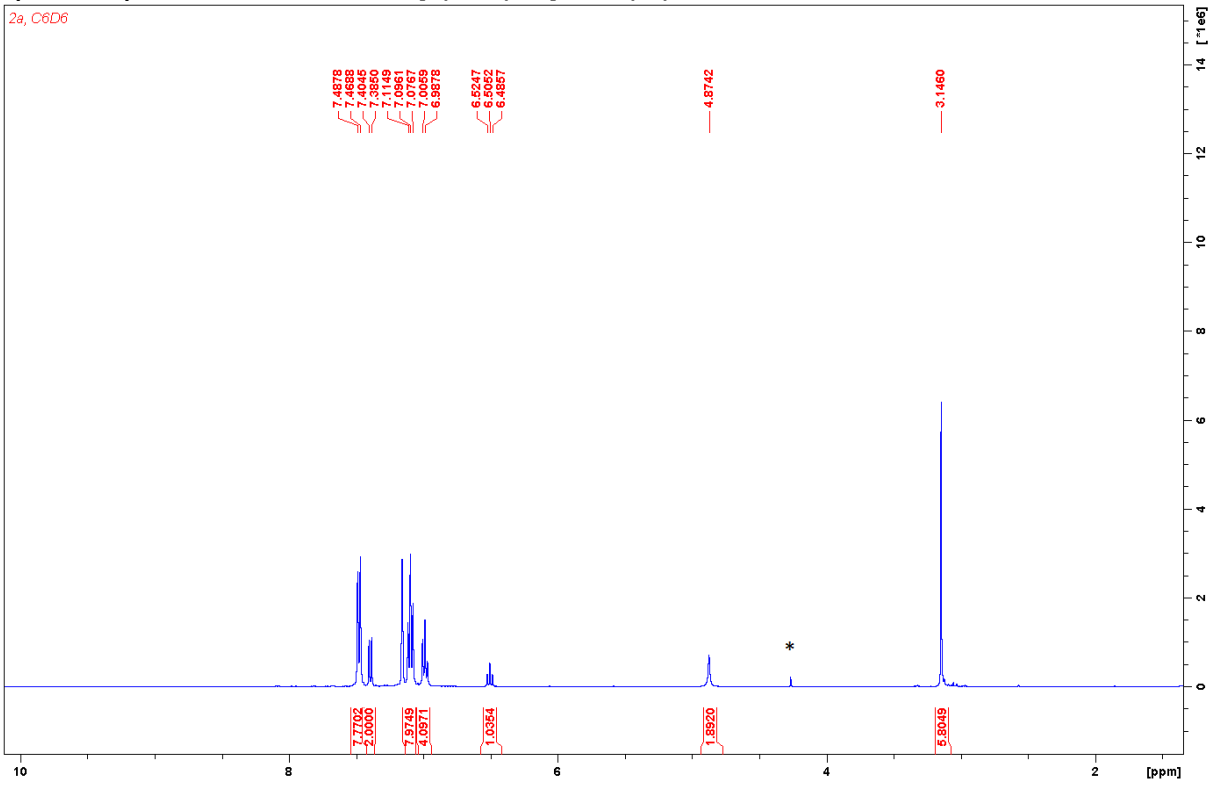


Figure S7. ^{1}H NMR spectrum of **2a**. Residual dichloromethane marked by *.

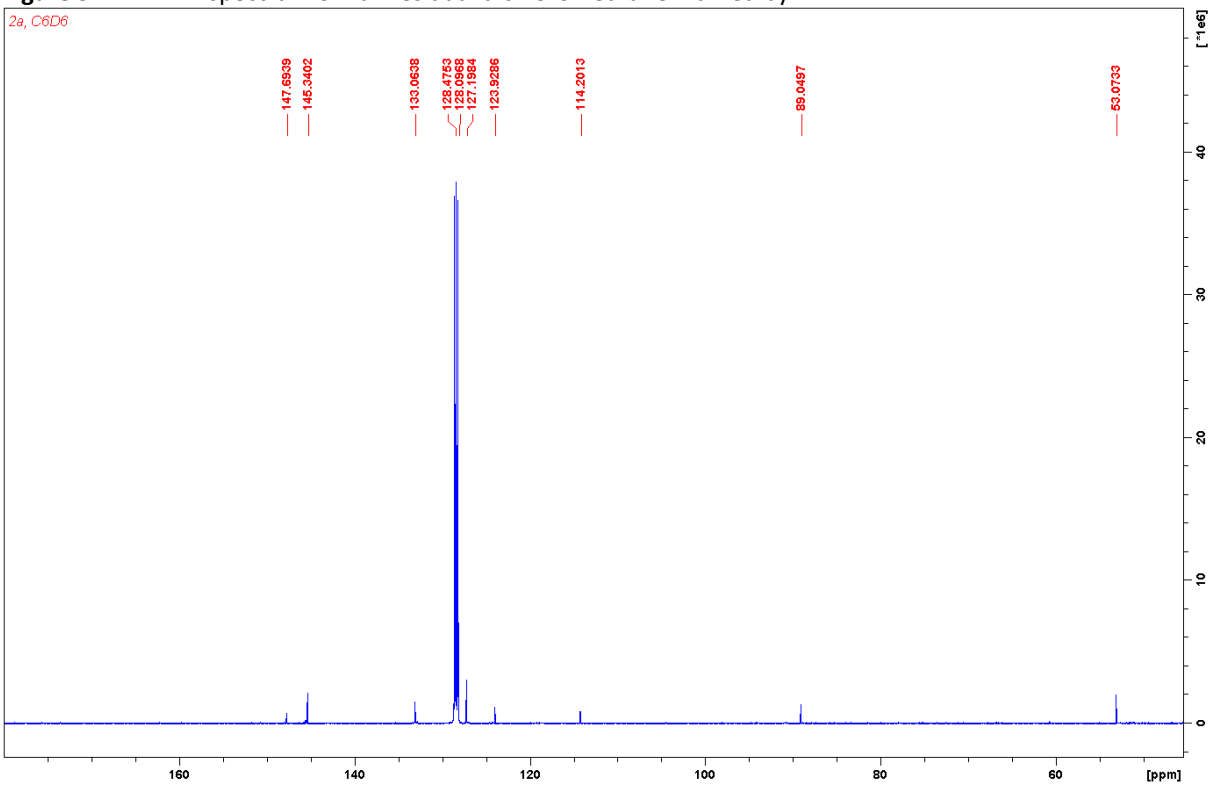


Figure S8. ^{13}C NMR spectrum of **2a**.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[$C(OMe)Ph_2$]$_2$-C_6H_3 (2a):

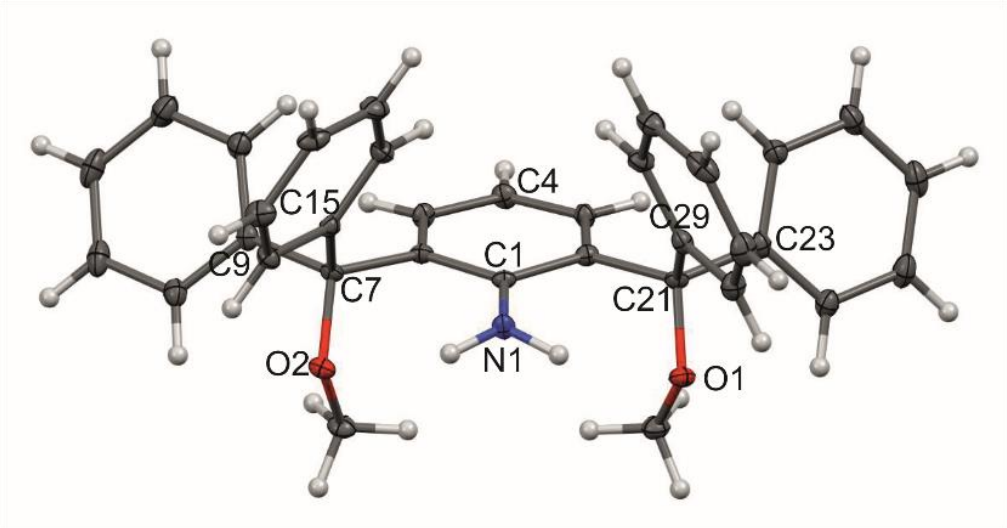


Figure S31. The molecular structure of **2a**, ORTEP diagram, 40% probability level, selected interatomic distances [Å] and bond angles[°]: O1 N1 2.907(4), O2 N1 2.866(4), C7 C21 5.097(4), C1 N1 1.373(4), C1 C2 C21 O1 60.4(4), C1 C6 C7 O2 59.1(4).

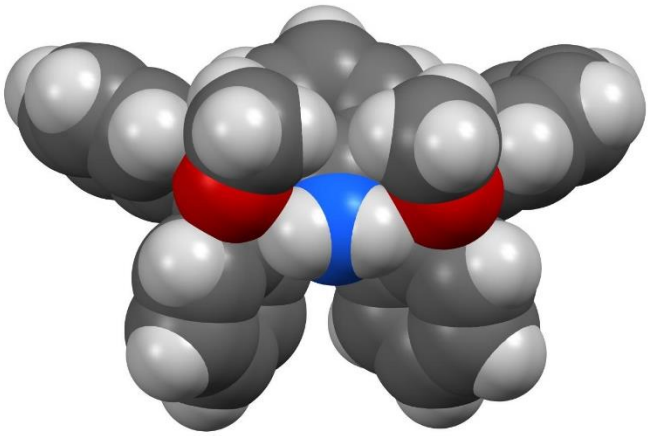


Figure S32. The molecular structure of **2a**, space filling model.

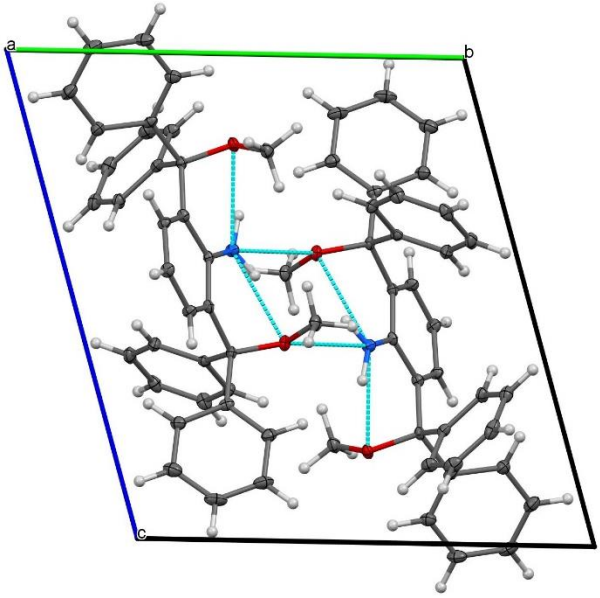
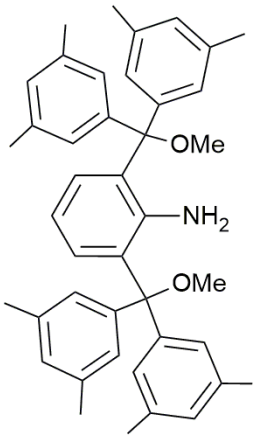


Figure S33. The crystal packing model of **2a**.

Table S3. Crystal data and structure refinement for **2a**.

Crystal data	
Chemical formula	$C_{34}H_{31}NO_2$
M_r	485.60
Crystal system, space group	Triclinic, *P*1
Temperature (K)	150
a, *b*, *c* (Å)	8.7448 (8), 12.2039 (12), 13.7109 (12)
α, β, γ (°)	71.125 (4), 73.114 (4), 76.737 (4)
V (Å^3)	1309.9 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.58 × 0.47 × 0.45
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.557, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	43758, 5102, 3978
R_{int}	0.108
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.076, 0.247, 1.08
No. of reflections	5102
No. of parameters	344
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.52, −0.34

1-NH$_2$-2,6-[C(OMe)(3,5-Me$_2$-C$_6$H$_3$)$_2$]$_2$-C$_6$H$_3$ (2b):



2,6-[C(OH)(3,5-Me$_2$-C$_6$H$_3$)$_2$]$_2$-C$_6$H$_3$ (**1b**) (16.91 g, 29.7 mmol); HC(OEt)$_3$ (49.4 mL, 296.8 mmol); H_2SO_4 (2.47 mL, 96%, 44.5 mmol); DCM/MeOH (400 mL). Yield 14.73 g, 83 %. **Mp** 185 °C. **Anal. Calc**. for $C_{42}H_{47}NO_2$ (597.83): C 84.4, H 7.9, N 2.3; found C 84.3, H 8.0, N 2.2. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.09 (s, 24H, Ar-CH_3), 3.37 (s, 6H, OCH_3), 4.93 (s, 2H, NH_2), 6.65 (t, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 1H, *p*-C$_6H_3$), 6.67 (s, 4H, *p*-C$_6H_3^{Me}$), 7.36 (s, 8H, *o*-C$_6H_3^{Me}$), 7.65 (d, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 2H, *m*-C$_6H_3$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 22.0 (s, Ar-*C*H$_3$), 53.1 (s, O*C*H$_3$), 89.1 (s, *C*OCH$_3$), 114.4 (s, *p*-*C*$_6$H$_3$), 124.4 (s, *o*-*C*$_6$H$_3$), 126.0 (s, *o*-*C*$_6H_3^{Me}$), 129.0 (s, *p*-*C*$_6H_3^{Me}$), 133.3 (s, *m*-*C*$_6$H$_3$), 137.7, (s, *m*-*C*$_6H_3^{Me}$), 145.8 (s, *ipso*-*C*$_6H_3^{Me}$), 147.9 (s, *ipso*-*C*$_6$H$_3$) ppm.

Spectroscopic characterization of 2,6-[C(OMe)(3,5-Me$_2$-C$_6$H$_3$)$_2$]$_2$-C$_6$H$_3$ (2b):

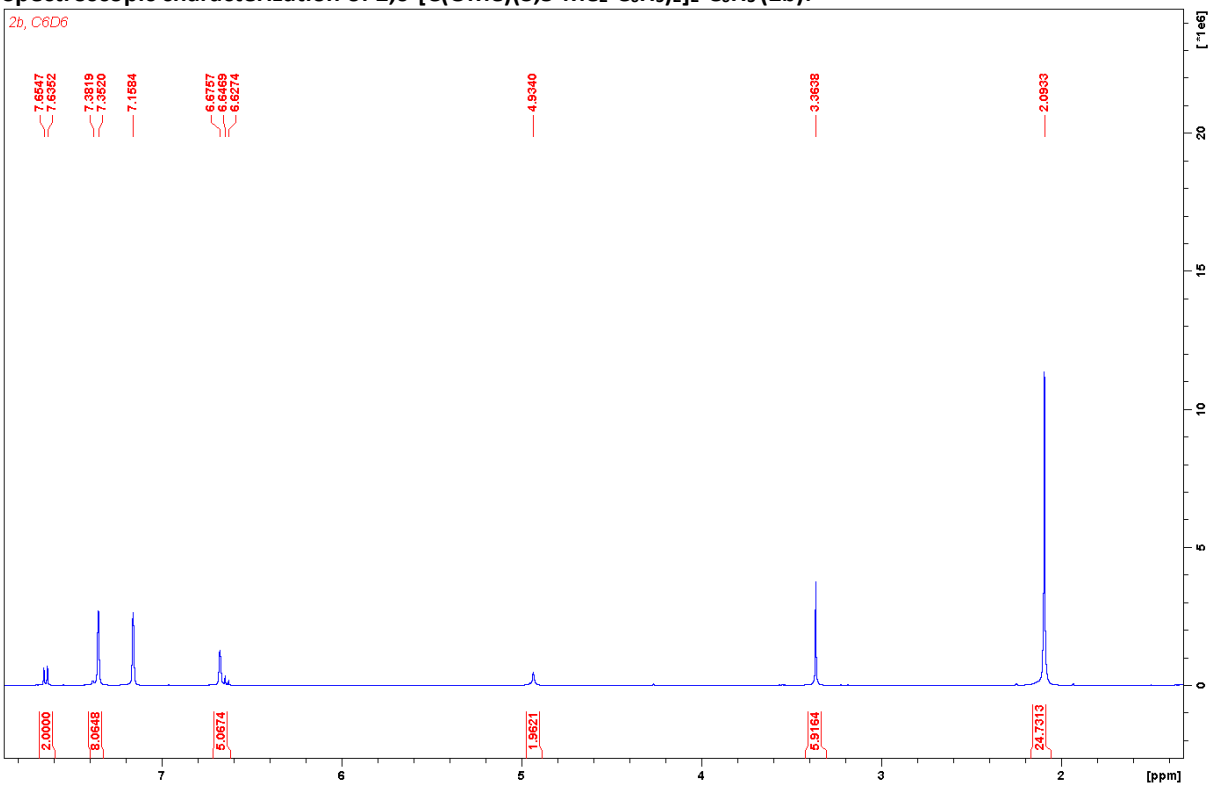


Figure S9. ^{1}H NMR spectrum of **2b**.

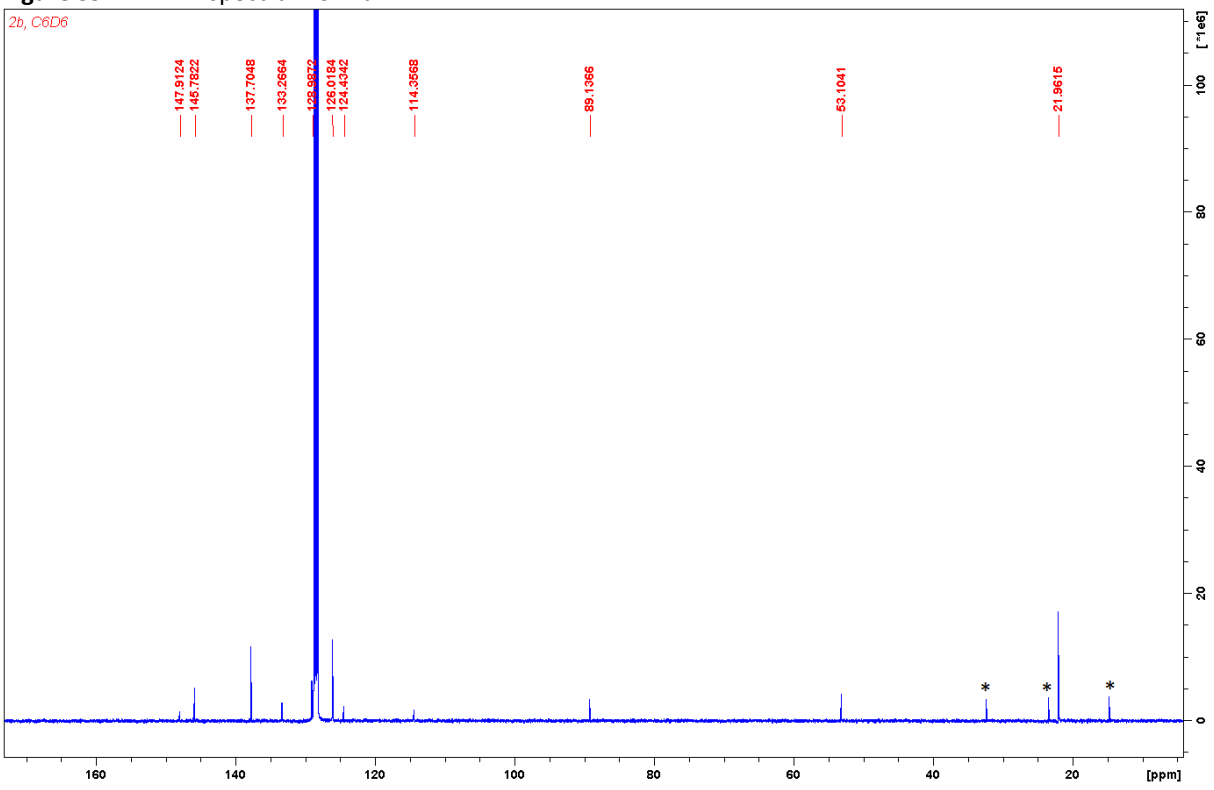


Figure S10. ^{13}C NMR spectrum of **2b**. Residual hexane marked by *.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(OMe)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (2b):

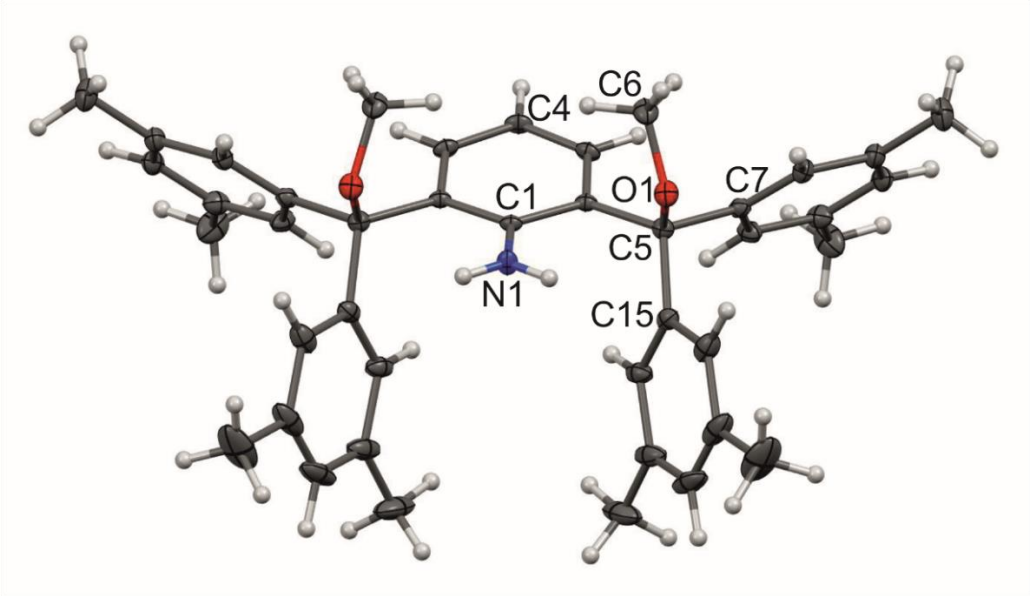


Figure S34. The molecular structure of **2b**·CH_2Cl_2, ORTEP diagram, 40% probability level, dichloromethane solvate is omitted for clarity. Selected interatomic distances [Å] and bond angles[°]: O1 N1 2.917(2), C5 C5*i* 5.110(3), C1 N1 1.370(3), C1 C2 C5 O1 61.3(2).

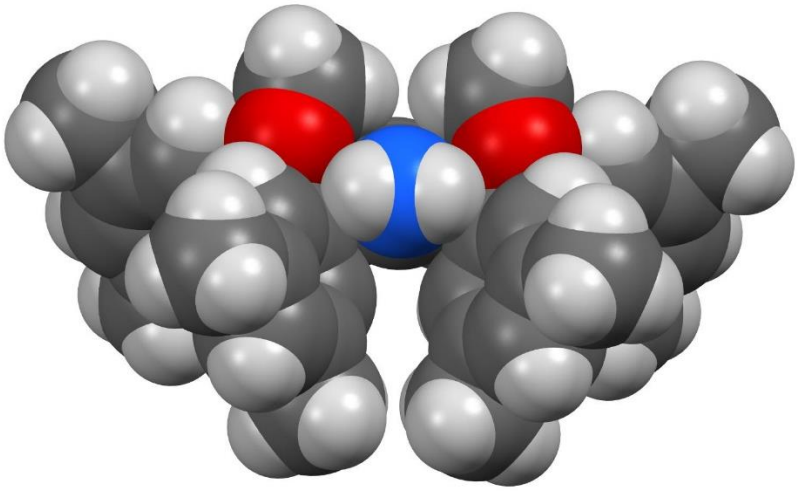


Figure S35. The molecular structure of **2b**, space filling model, dichloromethane solvate is omitted for clarity.

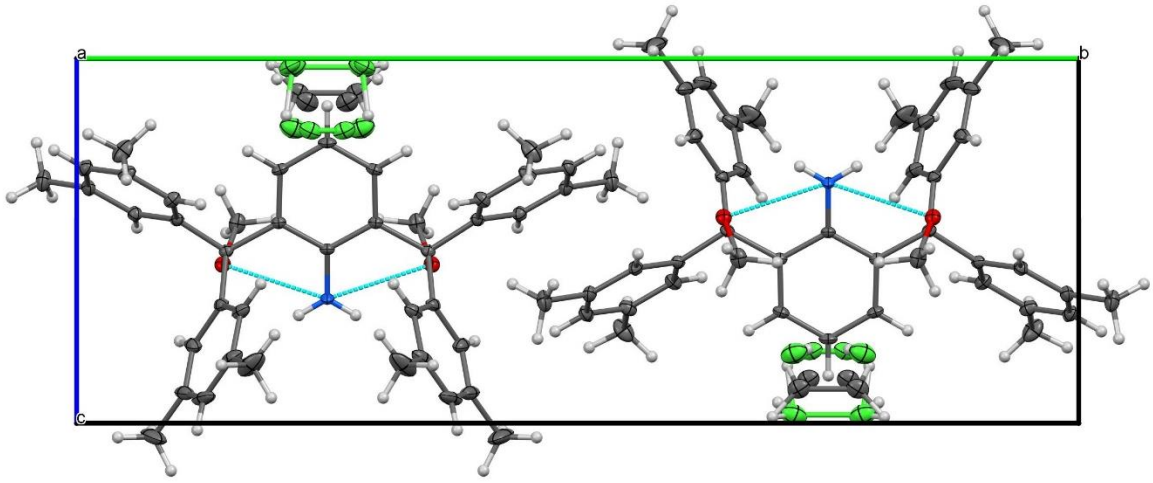
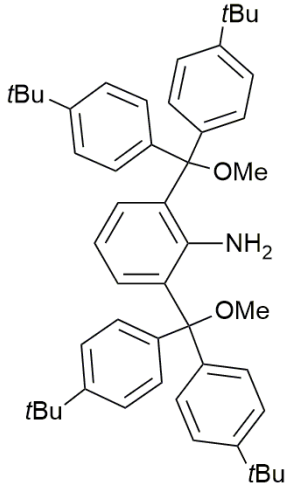


Figure S36. The crystal packing model of **2b** - dichloromethane solvate.

Table S4. Crystal data and structure refinement for **2b**.

Crystal data	
Chemical formula	$C_{43}H_{49}Cl_2NO_2$
M_r	682.73
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	150
a, b, c (Å)	8.0461 (4), 25.3743 (11), 9.3223 (5)
β (°)	98.680 (2)
V (Å^3)	1881.48 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	1.51 × 0.81 × 0.55
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.756, 0.862
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	45673, 4789, 3812
R_{int}	0.075
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.168, 1.07
No. of reflections	4789
No. of parameters	257
No. of restraints	40
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.33

1-NH$_2$-2,6-[C(OMe)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (2c):



2,6-[C(OH)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (**1c**) (14.43 g, 21.2 mmol); HC(OEt)$_3$ (35.2 mL, 211.6 mmol); H_2SO_4 (1.76 mL, 96%, 31.7 mmol); DCM/MeOH (300 mL). Yield 12.17 g, 81 %. **Mp** 232 °C. **Anal. Calc**. for $C_{50}H_{63}NO_2$ (710.04): C 84.6, H 8.9, N 2.0; found C 84.8, H 8.9, N 1.9. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.18 (s, 36H, C(C*H*$_3$)$_3$), 3.28 (s, 6H, OC*H*$_3$), 5.05 (s, 2H, N*H*$_2$), 6.53 (t, ^3J(^{1}H-^{1}H) = 7.8 Hz, 1H, *p*-C$_6$*H*$_3$), 7.25 (d, ^3J(^{1}H-^{1}H) = 8.6 Hz, 8H, *m*-C$_6$*H*$_4$), 7.53 (d, ^3J(^{1}H-^{1}H) = 7.8 Hz, 2H, *m*-C$_6$*H*$_3$), 7.57 (d, ^3J(^{1}H-^{1}H) = 8.3 Hz, 8H, *o*-C$_6$*H*$_4$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 31.8 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 53.2 (s, O*C*H$_3$), 89.1 (s, *C*OCH$_3$), 114.0 (s, *p*-*C*$_6$H$_3$), 124.2 (s, *o*-*C*$_6$H$_3$), 125.4 (s, *m*-*C*$_6$H$_4$), 128.1 (s, *o*-*C*$_6$H$_4$), 133.2 (s, *m*-*C*$_6$H$_3$), 142.7 (s, *ipso*-*C*$_6$H$_4$), 148.0 (s, *ipso*-*C*$_6$H$_3$), 149.6 (s, *p*-*C*$_6$H$_4$) ppm.

Spectroscopic characterization of 2,6-[C(OMe)(4-*t*Bu-C_6H_4)$_2$]$_2$-C_6H_3 (2c):

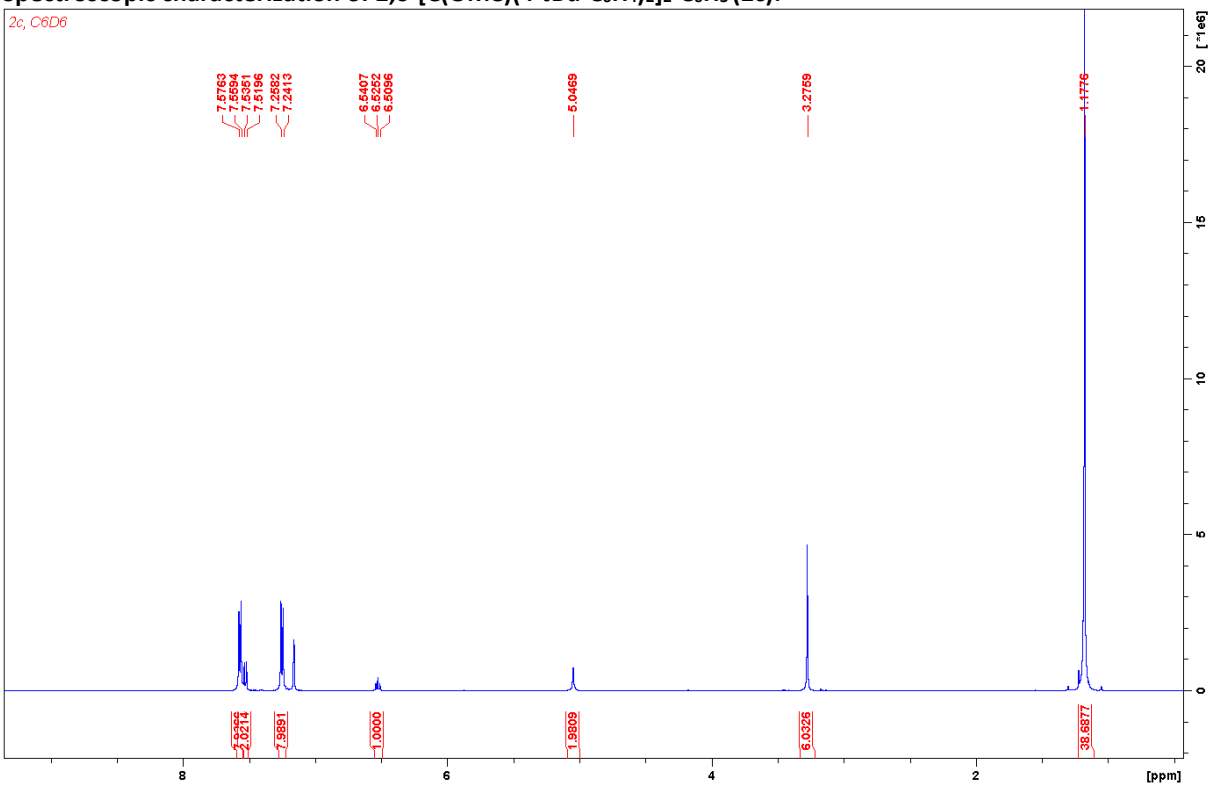


Figure S11. ^{1}H NMR spectrum of **2c**.

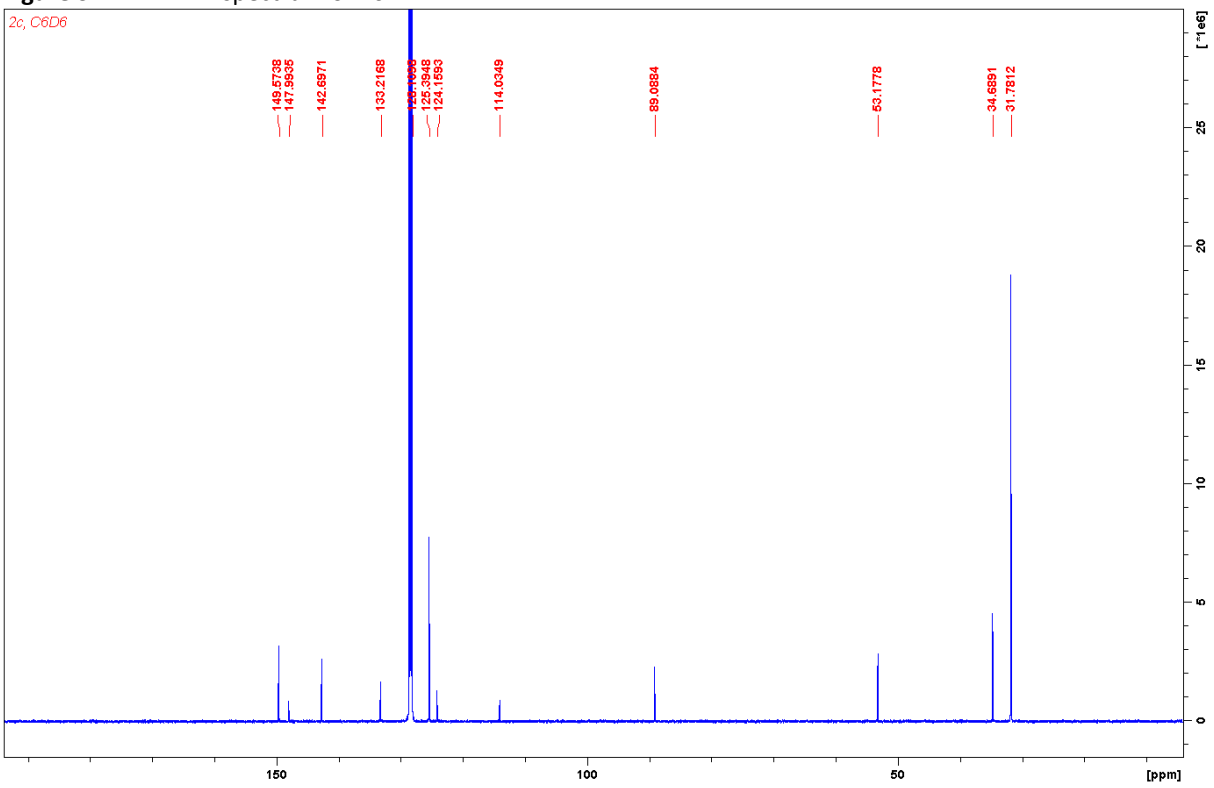
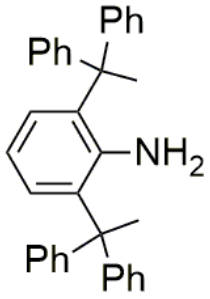


Figure S12. ^{13}C NMR spectrum of **2c**.

General procedure for synthesis of 1-NH_2-2,6-[C(Me)Ar$_2$]$_2$-C_6H_3 (3a-c) and 1-NH_2-2,6-(CAr_3)$_2$-C_6H_3 (4a-c)

This synthetic procedure was performed under argon atmosphere. Solution of the Grignard reagent (4 eq) in THF was added to the stirring solution of 2,6-[C(OMe)Ar$_2$]$_2$-C_6H_3 (**2a-c**, 1 eq) in THF at 0 °C. The reaction mixture was slowly heated to room temperature and stirred overnight. The reaction was carefully quenched by saturated solution of NH_4Cl, the organic phase was separated, dried with $MgSO_4$ and filtered. The orange solution was dried *in vacuo* and the solid residue was washed with small amount of acetone giving **3/4a-c** in the form of white powder.

1-NH_2-2,6-[C(Me)Ph_2]$_2$-C_6H_3 (3a):



2,6-[C(OMe)Ph_2]$_2$-C_6H_3 (**2a**) (12.53 g, 25.8 mmol); Methylmagnesium bromide (30.4 mL, 3.4M solution in 2-methyltetrahydrofuran, 103.2 mmol). Yield 8.78 g, 75 %. **Mp** 197 °C. **Anal. Calc**. for $C_{34}H_{31}N$ (453.62): C 90.0, H 6.9, N 3.1; found C 89.9, H 7.0, N 3.1. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.15 (s, 6H, CH_3), 3.13 (s, 2H, NH_2), 6.58 (t, ^3J(^{1}H-^{1}H) = 7.8 Hz, 1H, *p*-C_6H_3), 6.94 (d, ^3J(^{1}H-^{1}H) = 7.9 Hz, 2H, *m*-C_6H_3), 7.01 (t, ^3J(^{1}H-^{1}H) = 7.2 Hz, 4H, *p*-C_6H_5), 7.08 (t, ^3J(^{1}H-^{1}H) = 7.9 Hz, 8H, *m*-C_6H_5), 7.21 (d, ^3J(^{1}H-^{1}H) = 7.5 Hz, 8H, *o*-C_6H_5) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 28.3 (s, CH_3), 52.8 (s, CCH_3), 117.7 (s, *p*-C_6H_3), 126.8 (s, *p*-C_6H_5), 128.8 (s, *m*-C_6H_5), 129.3 (s, *o*-C_6H_5), 129.5 (s, *m*-C_6H_3), 134.5 (s, *o*-C_6H_3), 144.2 (s, *ipso*-C_6H_3), 147.8 (s, *ipso*-C_6H_5) ppm.

Spectroscopic characterization of 2,6-[C(Me)Ph_2]$_2$-C_6H_3 (3a):

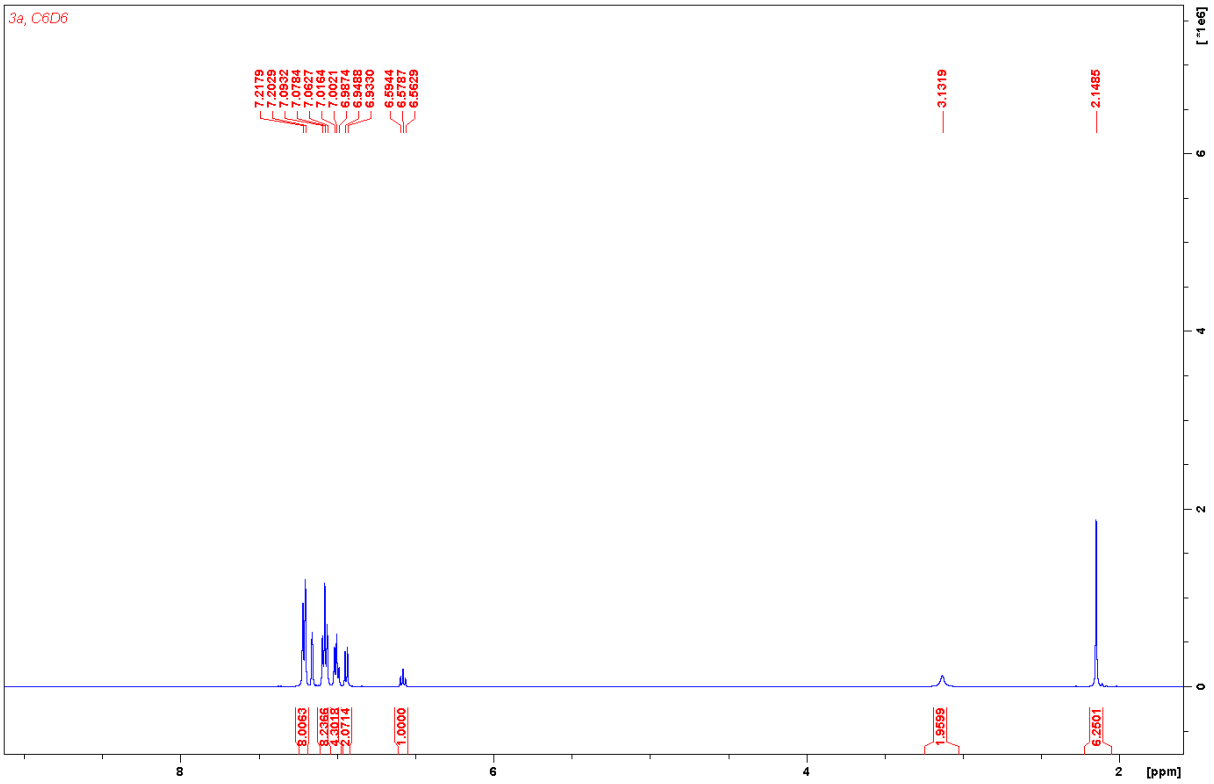


Figure S13. ^{1}H NMR spectrum of **3a**.

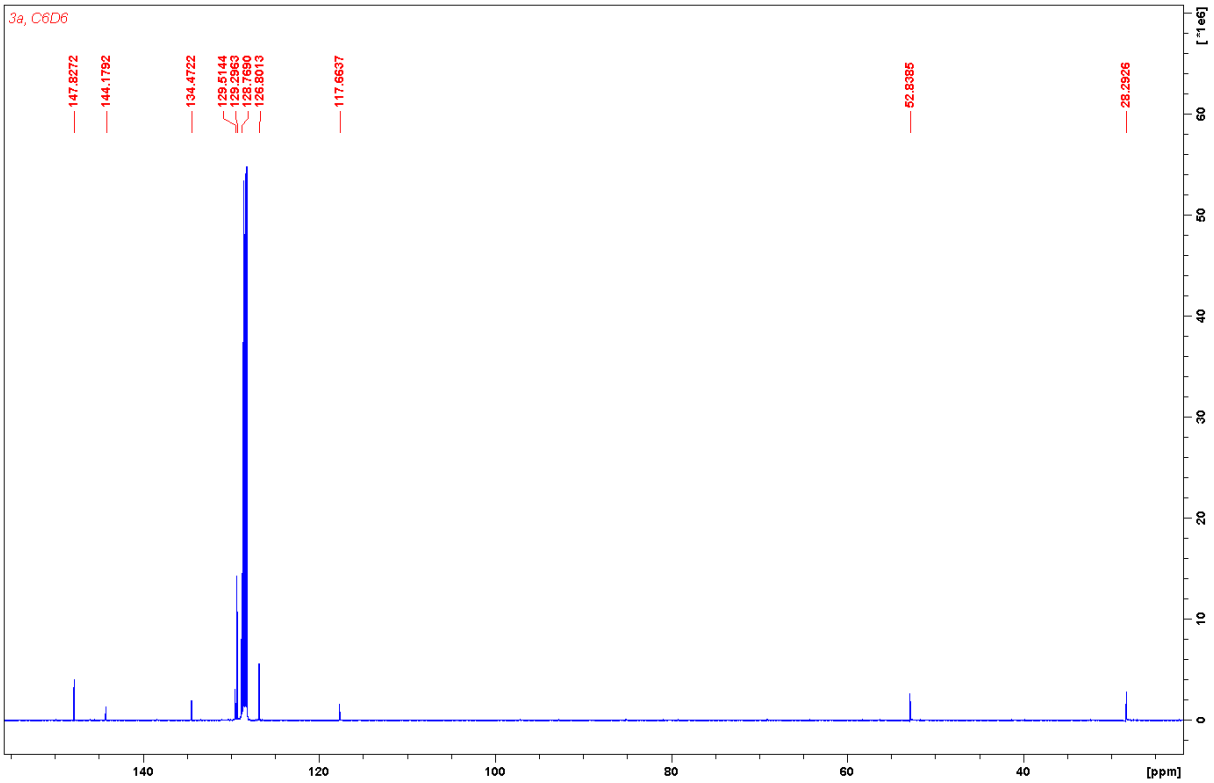


Figure S14. ^{13}C NMR spectrum of **3a**.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(Me)Ph_2]$_2$-C_6H_3 (3a):

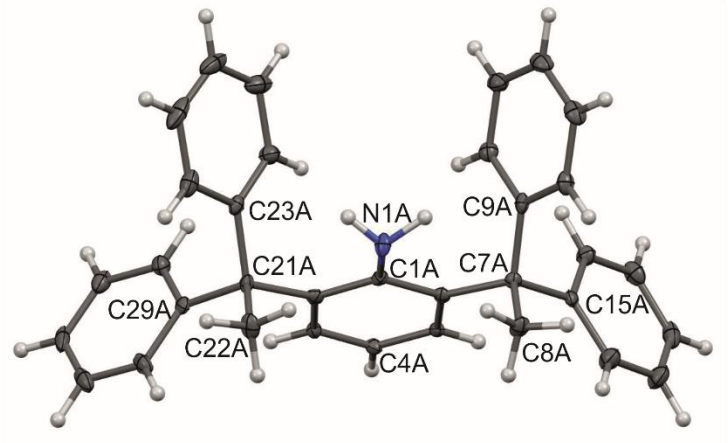


Figure S37. The molecular structure of **3a**, the second independent molecule is omitted for clarity, ORTEP diagram, 40% probability level, selected interatomic distances [Å] and bond angles[°], parameters for the second independent molecule are given in parentheses: C8A N1A 3.082(6) (3.087(6)), C22A N1A 3.018(6) (2.995(6)), C7A C21A 5.159(5) (5.176(5)), C1A N1A 1.412(5) (1.411(5)), C1A C6A C7A C8A 65.7(7) (65.1(5)), C1A C2A C21A C22A 62.0(5) (60.7(5)).

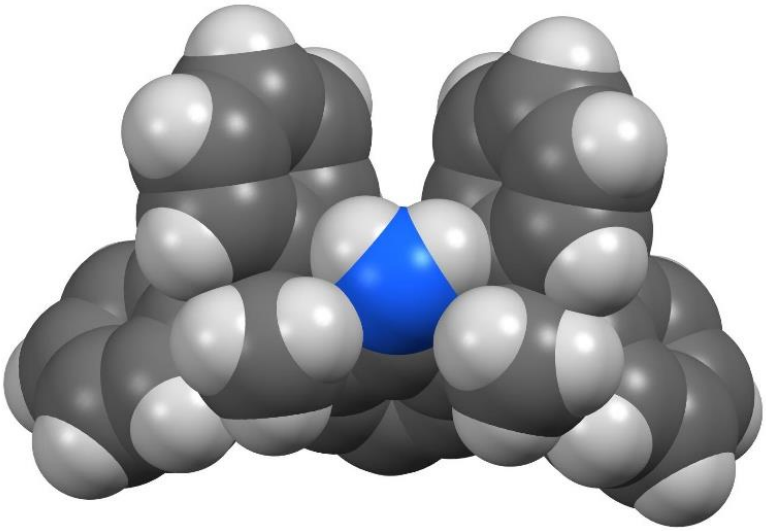


Figure S38. The molecular structure of **3a**, space filling model.

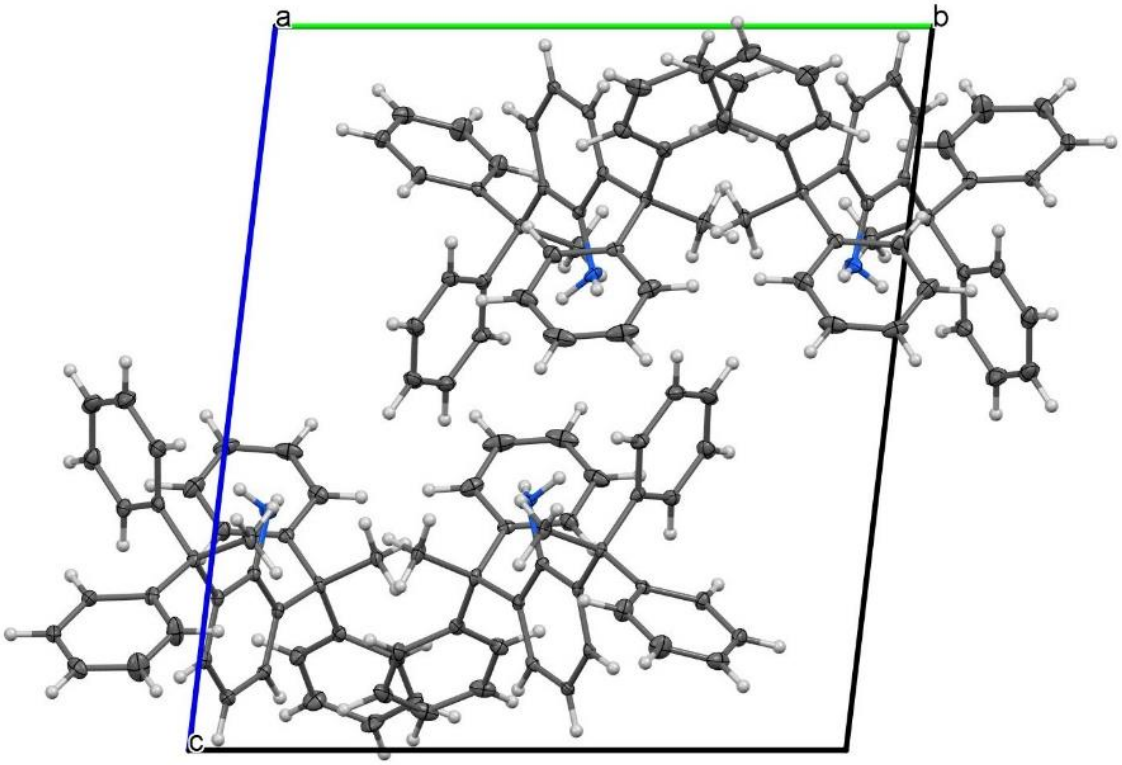
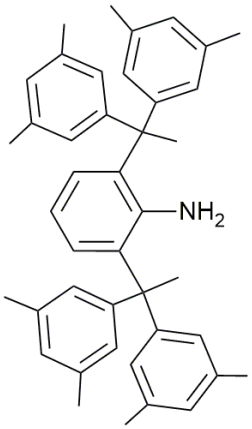


Figure S39. The crystal packing model of **3a**.

Table S5. Crystal data and structure refinement for **3a**.

Crystal data	
Chemical formula	$C_{34}H_{31}N$
M_r	453.60
Crystal system, space group	Triclinic, *P*1
Temperature (K)	150
a, *b*, *c* (Å)	10.694 (1), 14.5078 (15), 16.6117 (17)
α, β, γ (°)	96.571 (5), 104.496 (5), 90.146 (5)
V (Å^3)	2477.5 (4)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.33 × 0.32 × 0.19
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.619, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44031, 9480, 6874
R_{int}	0.107
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.099, 0.284, 1.03
No. of reflections	9480
No. of parameters	652
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.39

1-NH$_2$-2,6-[C(Me)(3,5-Me$_2$-C$_6$H$_3$)$_2$]$_2$-C$_6$H$_3$ (3b):



2,6-[C(OMe)(3,5-Me$_2$-C$_6$H$_3$)$_2$]$_2$-C$_6$H$_3$ (**2b**) (13.43 g, 22.5 mmol); Methylmagnesium bromide (26.4 mL, 3.4M solution in 2-methyltetrahydrofuran, 89.9 mmol). Yield 10.04 g, 79 %. **Mp** 226 °C. **Anal. Calc**. for $C_{42}H_{47}N$ (565.83): C 89.1, H 8.4, N 2.5; found C 89.3, H 8.3, N 2.4. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.09 (s, 24H, Ar-CH_3), 2.38 (s, 6H, CCH_3), 3.51 (s, 2H, NH_2), 6.61 (t, $^3J(^1H\text{-}^1H)$ = 7.9 Hz, 1H, *p*-C$_6$H$_3$), 6.70 (s, 4H, *p*-C$_6$H$_3^{Me}$), 7.06 (d, $^3J(^1H\text{-}^1H)$ = 7.8 Hz, 2H, *m*-C$_6$H$_3$), 7.10 (s, 8H, *o*-C$_6$H$_3^{Me}$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 22.0 (s, Ar-*C*H$_3$), 28.1 (s, C*C*H$_3$), 52.9 (s, *C*CH$_3$), 117.6 (s, *p*-C$_6$H$_3$), 127.4 (s, *o*-C$_6$H$_3^{Me}$), 128.6 (s, *p*-C$_6$H$_3^{Me}$), 129.8 (s, *m*-C$_6$H$_3$), 135.1 (s, *o*-C$_6$H$_3$), 137.9 (s, *m*-C$_6$H$_3^{Me}$), 144.6, (s, *ipso*-C$_6$H$_3$), 148.4 (s, *ipso*-C$_6$H$_3^{Me}$) ppm.

Spectroscopic characterization of 2,6-[C(Me)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (3b):

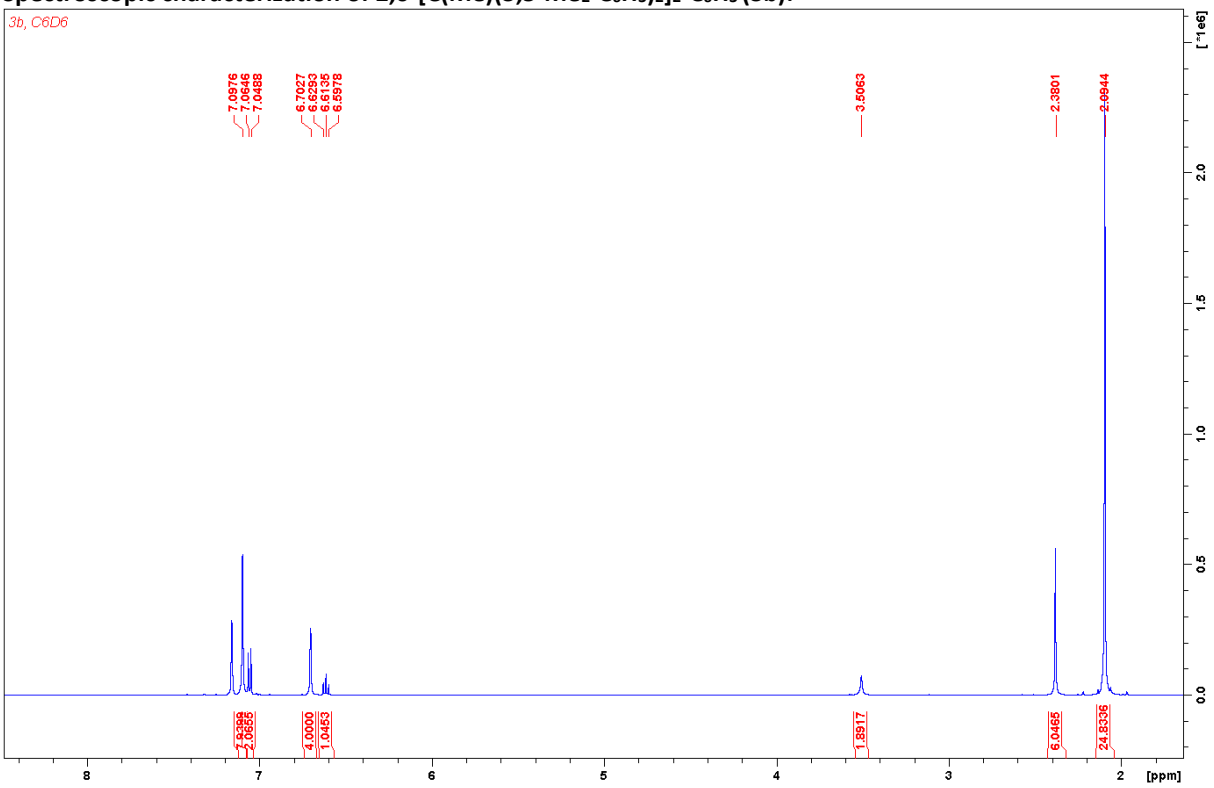


Figure S15. ^{1}H NMR spectrum of **3b**.

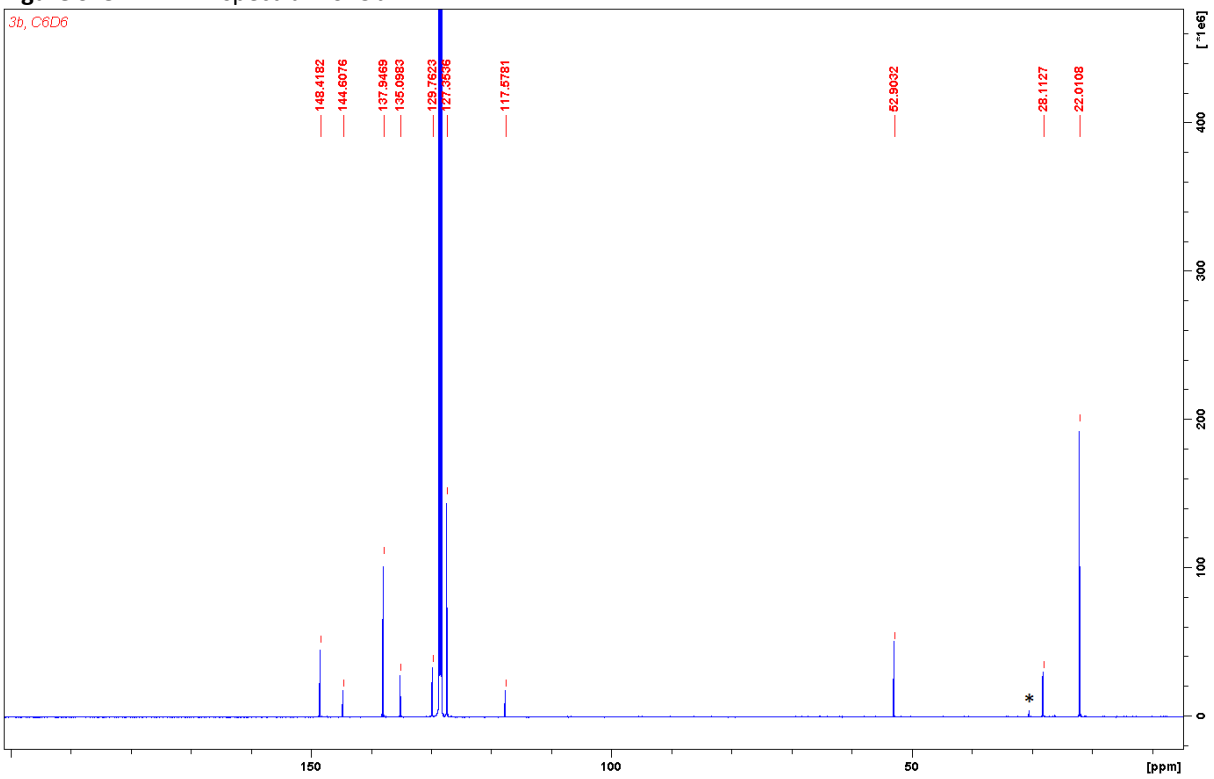


Figure S16. ^{13}C NMR spectrum of **3b**. Residual acetone marked by *.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(Me)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (3b):

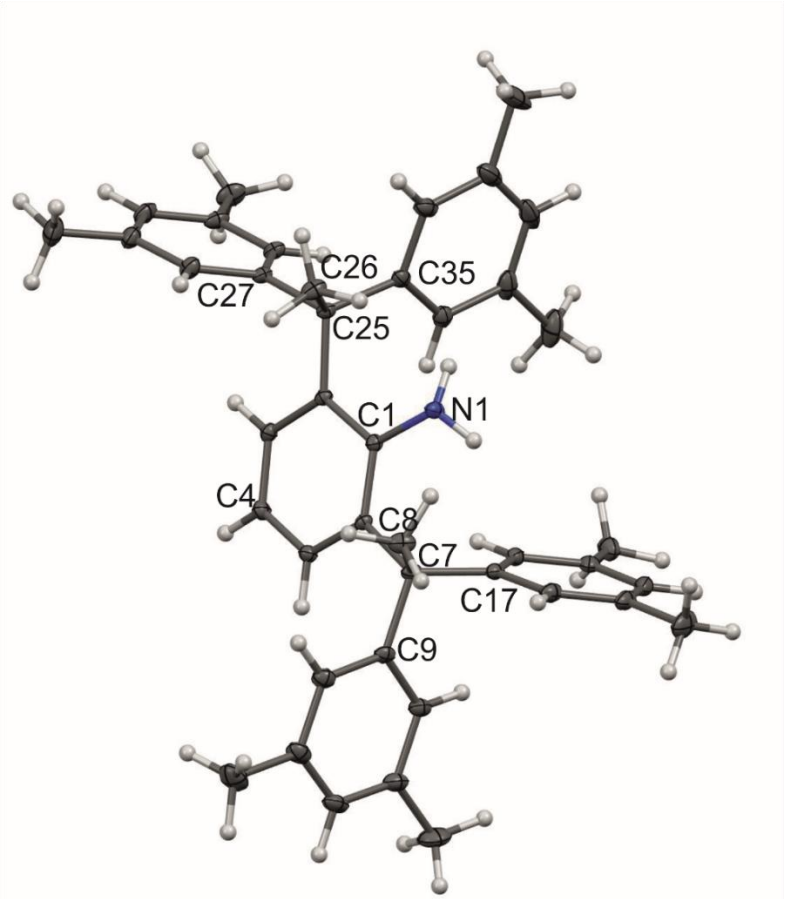


Figure S40. The molecular structure of **3b**, ORTEP diagram, 40% probability level. Selected interatomic distances [Å] and bond angles[°]: C8 N1 3.003(2), C26 N1 3.018(2), C7 C25 5.155(2), C1 N1 1.405(1), C1 C6 C7 C8 57.2(1), C1 C2 C25 C26 58.8(1).

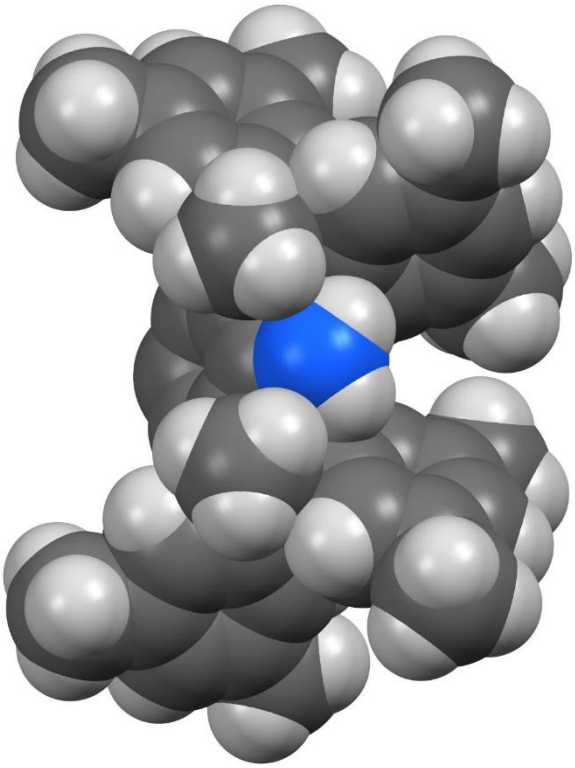


Figure S41. The molecular structure of **3b**, space filling model.

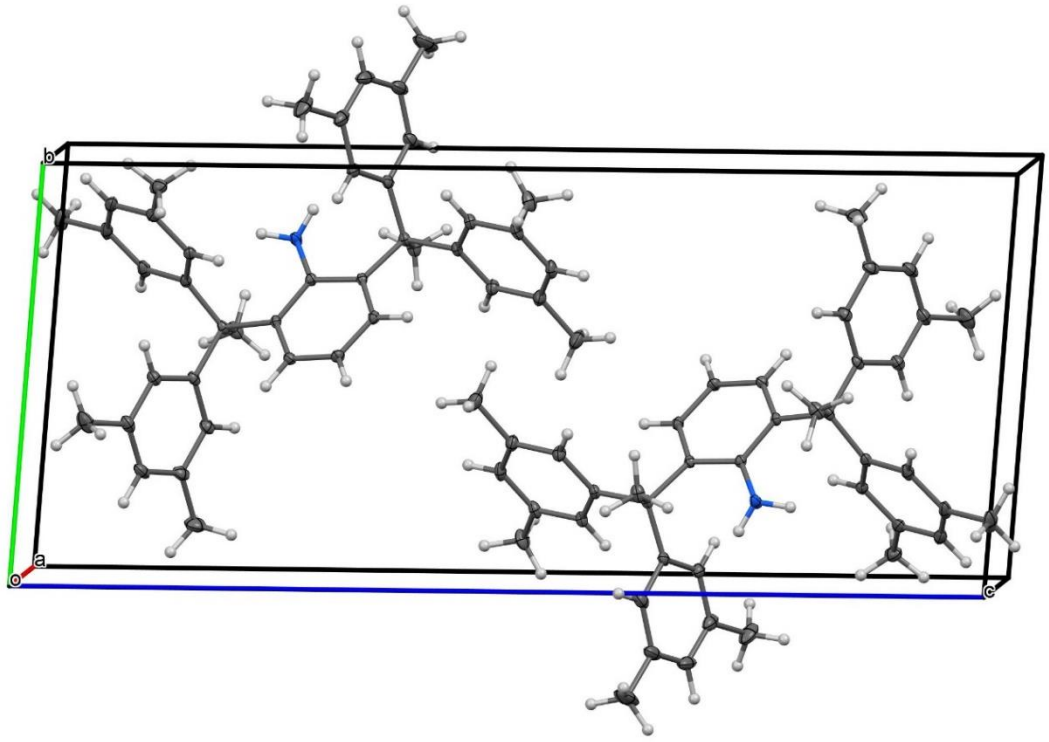
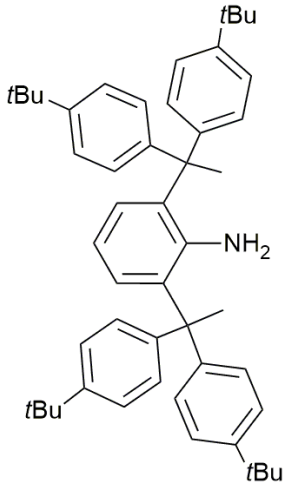


Figure S42. Figure S21c: The crystal packing model of **3b**.

Table S6. Crystal data and structure refinement for **3b**.

Crystal data	
Chemical formula	$C_{42}H_{47}N$
M_r	565.80
Crystal system, space group	Triclinic, *P*1
Temperature (K)	150
a, *b*, *c* (Å)	6.3152 (2), 10.7638 (3), 24.7246 (8)
α, β, γ (°)	85.9667 (13), 87.0612 (15), 88.1823 (14)
V (Å^3)	1673.63 (9)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.06
Crystal size (mm)	0.51 × 0.37 × 0.25
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.815, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	53939, 8344, 7123
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.138, 1.02
No. of reflections	8344
No. of parameters	406
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.24

1-NH$_2$-2,6-[C(Me)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (3c):



2,6-[C(OMe)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (**2c**) (14.19 g, 20.0 mmol); Methylmagnesium bromide (23.5 mL, 3.4M solution in 2-methyltetrahydrofuran, 79.9 mmol). Yield 10.84 g, 80 %. **Mp** 224 °C. **Anal. Calc**. for $C_{50}H_{63}N$ (678.04): C 88.6, H 9.4, N 2.0; found C 88.6, H 9.3, N 2.1. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.23 (s, 36H, C(C*H*$_3$)$_3$), 2.27 (s, 6H, CC*H*$_3$), 3.27 (s, 2H, N*H*$_2$), 6.58 (t, $^3J(^1H\text{-}^1H)$ = 7.9 Hz, 1H, *p*-C$_6$*H*$_3$), 7.06 (d, $^3J(^1H\text{-}^1H)$ = 7.9 Hz, 2H, *m*-C$_6$*H*$_3$), 7.21 (d, $^3J(^1H\text{-}^1H)$ = 8.6 Hz, 8H, *m*-C$_6$*H*$_4$), 7.28 (d, $^3J(^1H\text{-}^1H)$ = 8.3 Hz, 8H, *o*-C$_6$*H*$_4$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 28.0 (s, CCH$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 52.2 (s, *C*CH$_3$), 117.5 (s, *p*-*C*$_6$H$_3$), 125.6 (s, *m*-*C*$_6$H$_4$), 129.2 (s, *o*-*C*$_6$H$_4$), 129.6 (s, *m*-*C*$_6$H$_3$), 134.7 (s, *o*-*C*$_6$H$_3$), 144.4 (s, *ipso*-*C*$_6$H$_3$), 145.2 (s, *ipso*-*C*$_6$H$_4$), 149.1 (s, *p*-*C*$_6$H$_4$) ppm.

Spectroscopic characterization of 2,6-[C(Me)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (3c):

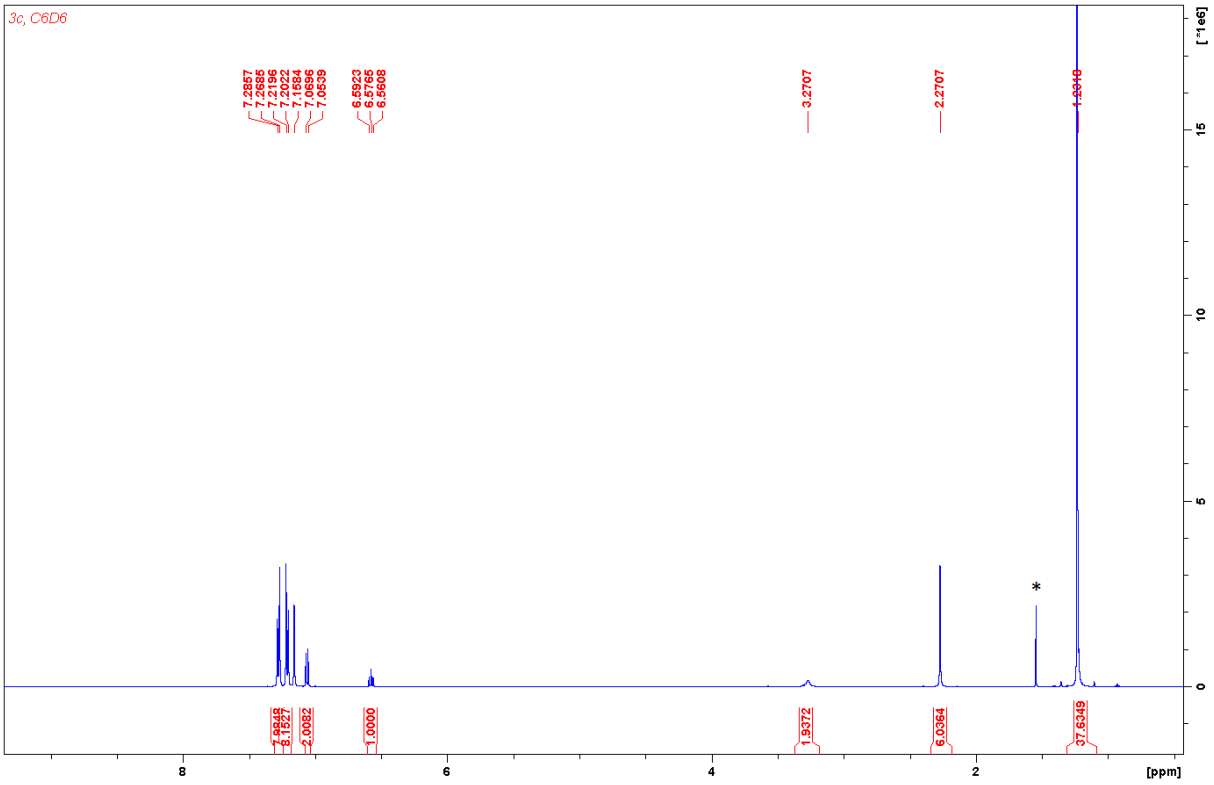


Figure S17. ^{1}H NMR spectrum of **3c**. Residual acetone marked by *.

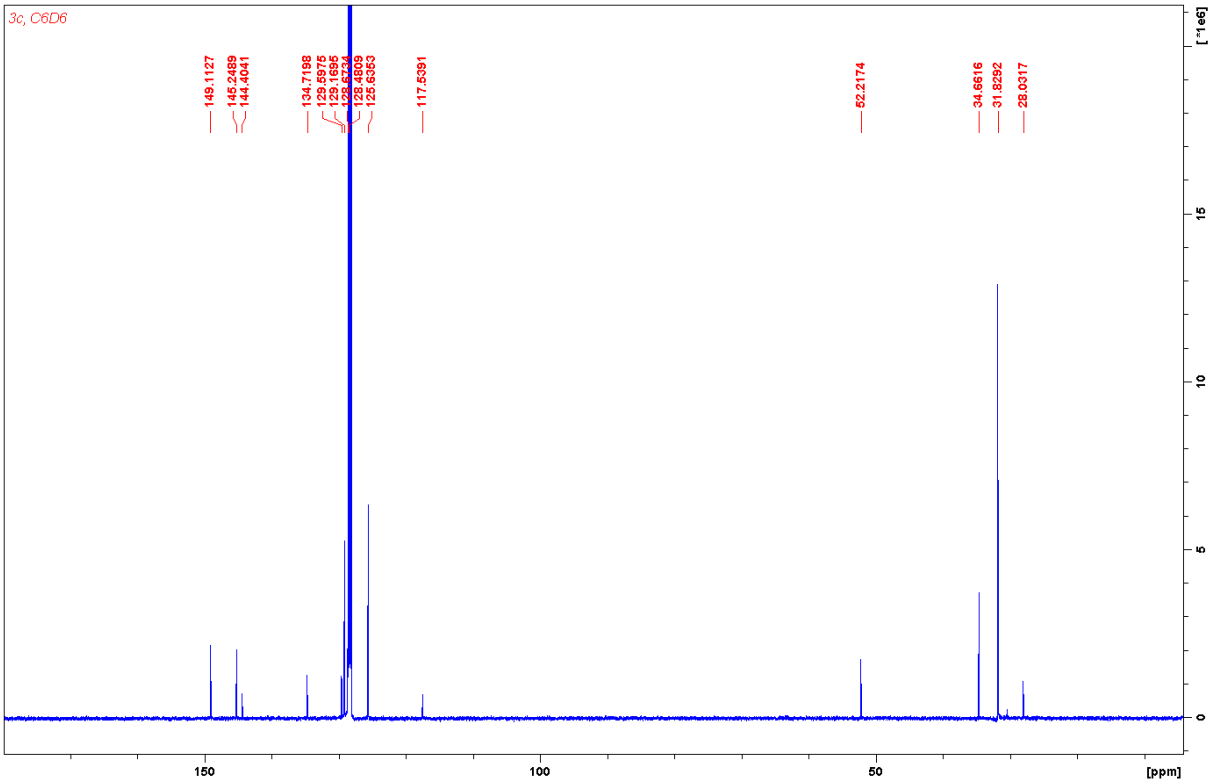
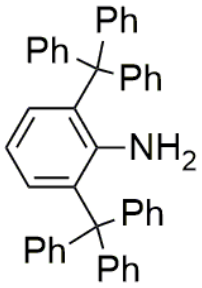


Figure S18. ^{13}C NMR spectrum of **3c**.

1-NH$_2$-2,6-(CPh$_3$)$_2$-C$_6$H$_3$ (4a):



2,6-[C(OMe)Ph$_2$]$_2$-C$_6$H$_3$ (**2a**) (2.77 g, 5.7 mmol); Phenylmagnesium bromide (22.8 mL, 1M solution in THF, 22.8 mmol). Yield 2.97 g, 90 %. **Mp** > 320 °C. **Anal. Calc**. for C$_{44}$H$_{35}$N (577.76): C 91.5, H 6.1, N 2.4; found C 91.4, H 6.3, N 2.3. **^{1}H NMR** (25 °C, CDCl$_3$, 500 MHz): δ = 6.55 (t, ^3J(^{1}H-^{1}H) = 7.9 Hz, 1H, *p*-C$_6$*H*$_3$), 6.94 (d, ^3J(^{1}H-^{1}H) = 8.0 Hz, 2H, *m*-C$_6$*H*$_3$), 7.07 (m, 12H, *o*-C$_6$*H*$_5$), 7.13 (m, 12H, *m*-C$_6$*H*$_5$), 7.16 (m, 6H, *p*-C$_6$*H*$_5$) ppm. **^{13}C{^{1}H} NMR** (25 °C, CDCl$_3$, 125.76 Hz): δ = 63.9 (s, *C*Ph$_3$), 115.5 (s, *p*-C$_6$H$_3$), 126.3 (s, *m*-C$_6$H$_5$), 127.5 (s, *p*-C$_6$H$_5$), 130.4 (s, *m*-C$_6$H$_3$), 131.5 (s, *o*-C$_6$H$_5$), 132.9 (s, *o*-C$_6$H$_3$), 144.1 (s, *ipso*-C$_6$H$_3$), 144.8 (s, *ipso*-C$_6$H$_5$) ppm.

Spectroscopic characterization of 2,6-$(CPh_3)_2$-C_6H_3 (4a):

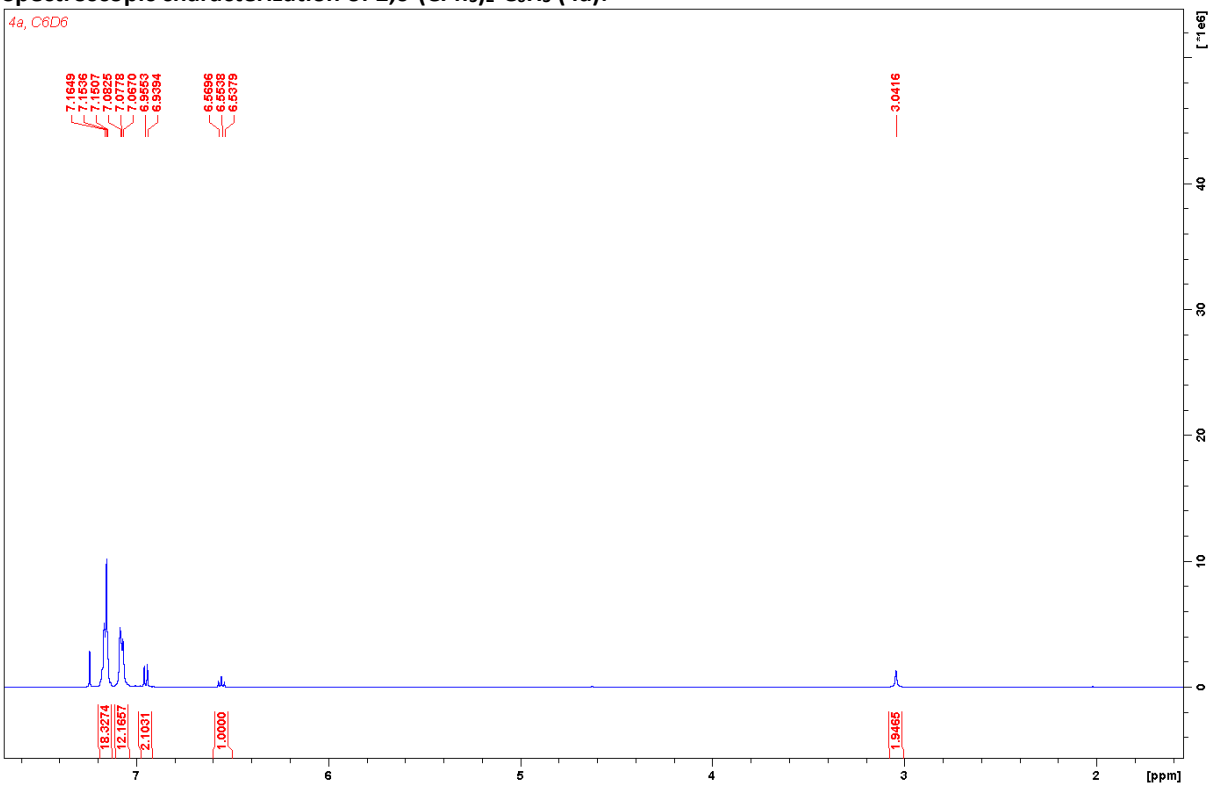


Figure S19. ^{1}H NMR spectrum of **4a**.

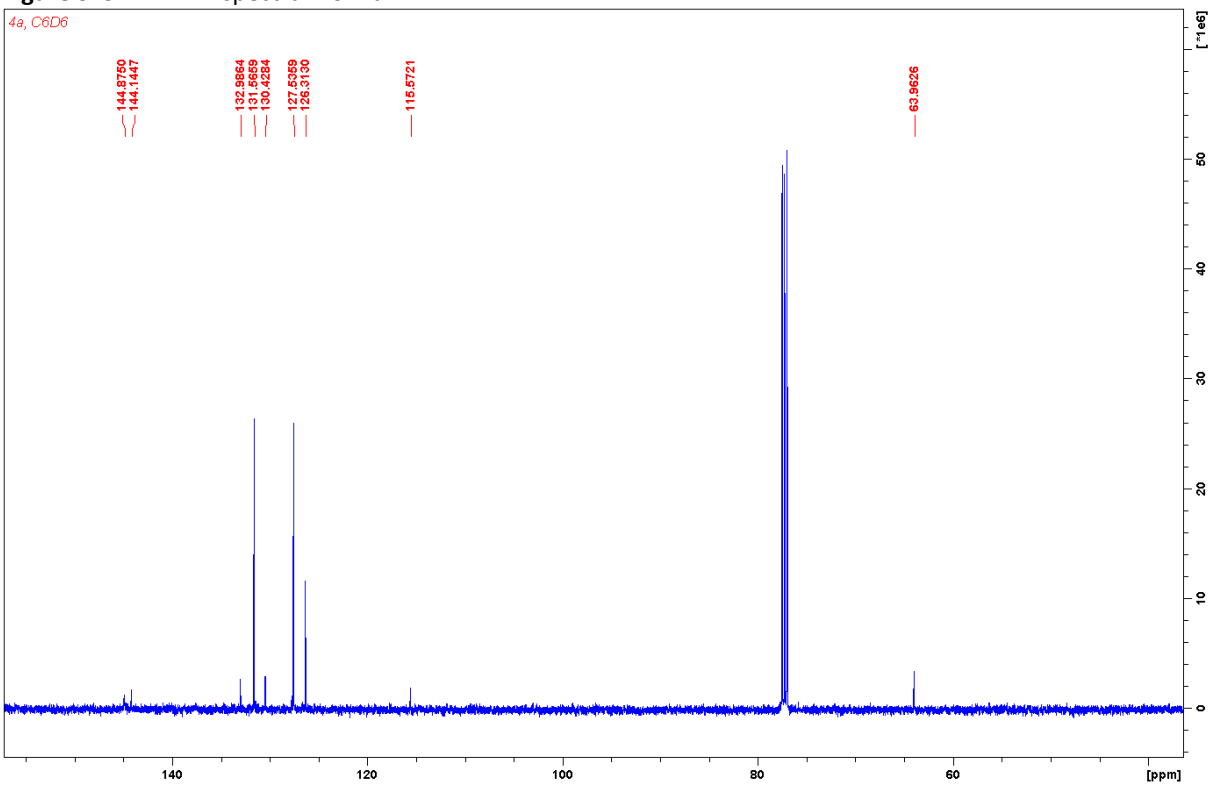


Figure S20. ^{13}C NMR spectrum of **4a**.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-$(CPh_3)_2$-C_6H_3 (4a):

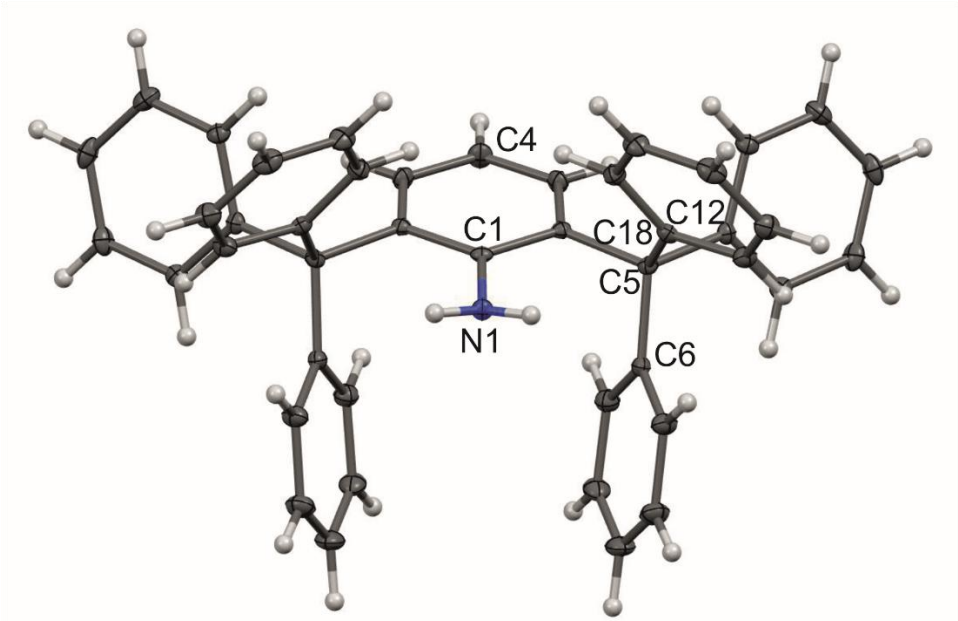


Figure S43. The molecular structure of **4a**·CH_2Cl_2, ORTEP diagram, 50% probability level, dichloromethane solvate molecule is omitted for clarity. Selected interatomic distances [Å]: C1 N1 1.392(3), C5 C5*i* 5.148(4).

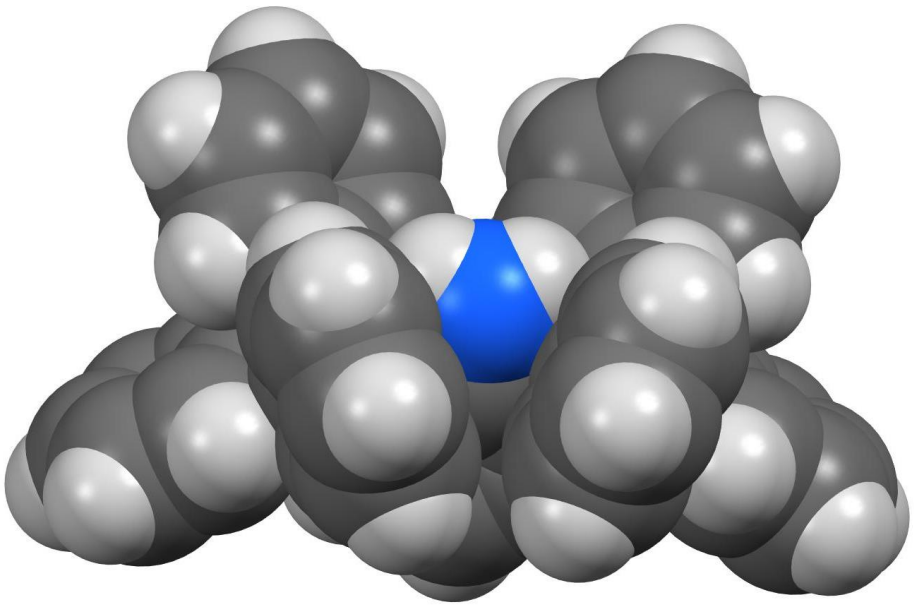


Figure S44. The molecular structure of **4a**, space filling model.

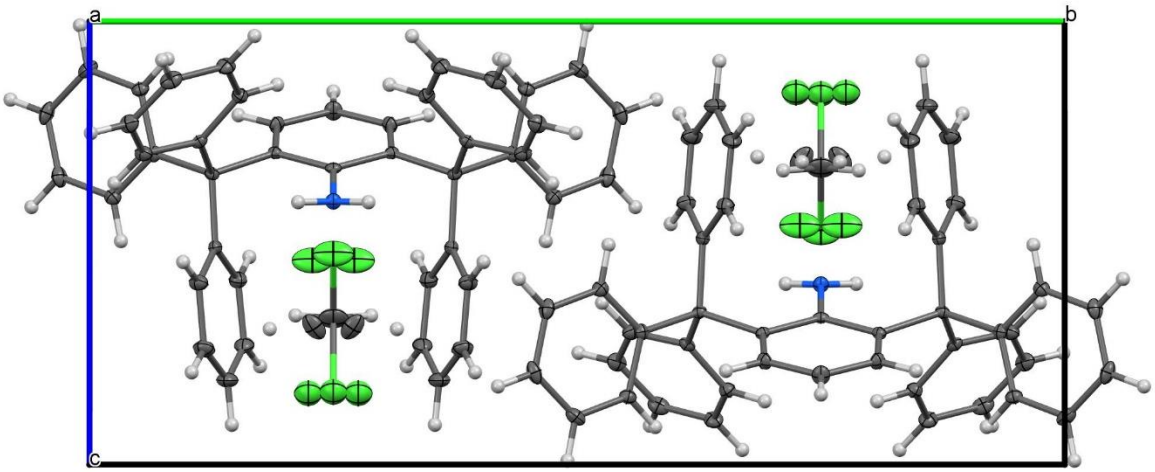
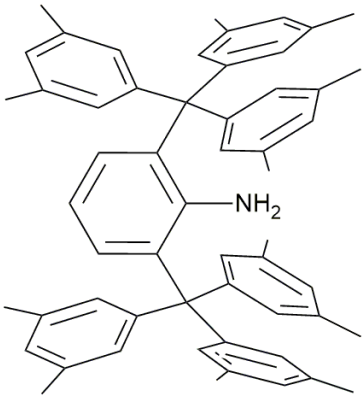


Figure S45. The crystal packing model of **4a** dichloromethane solvate.

Table S7. Crystal data and structure refinement for **4a**.

Crystal data	
Chemical formula	$C_{45}H_{37}Cl_2N$
M_r	662.65
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	150
a, b, c (Å)	8.7550 (4), 20.6545 (11), 9.7582 (5)
β (°)	106.074 (2)
V (Å^3)	1695.59 (15)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.23
Crystal size (mm)	0.38 × 0.16 × 0.16
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.789, 0.837
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23655, 3424, 2765
R_{int}	0.078
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.143, 1.05
No. of reflections	3424
No. of parameters	245
No. of restraints	28
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.81, −1.13

1-NH_2-2,6-[C(3,5-Me_2-C_6H_3)$_3$]$_2$-C_6H_3 (4b):



2,6-[C(OMe)(3,5-Me_2-C_6H_3)$_2$]$_2$-C_6H_3 (**2b**) (2.98 g, 5.0 mmol); 1-bromo-3,5-dimethylbenzene (2.71 mL, 19.9 mmol); magnesium (0.53 g, 21.9 mmol). Yield 3.16 g, 85 %. **Mp** > 320 °C. **Anal. Calc**. for $C_{56}H_{59}N$ (746.07): C 90.1, H 8.0, N 1.9; found C 90.0, H 8.2, N 1.8. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 2.03 (s, 36H, CH_3), 3.93 (s, 2H, NH_2), 6.67 (s, 6H, *p*-$C_6H_3^{Me}$), 6.83 (t, $^3J(^1H\text{-}^1H)$ = 8.0 Hz, 1H, *p*-C_6H_3), 7.17 (s, 12H, *o*-$C_6H_3^{Me}$), 7.74 (d, $^3J(^1H\text{-}^1H)$ = 8.0 Hz, 2H, *m*-C_6H_3) ppm. **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 22.0 (s, CH_3), 64.8 (s, CAr_3), 116.3 (s, *p*-C_6H_3), 128.5 (s, *p*-$C_6H_3^{Me}$), 130.3 (s, *o*-$C_6H_3^{Me}$), 131.4 (s, *m*-C_6H_3), 133.6 (s, *o*-C_6H_3), 137.0 (s, *m*-$C_6H_3^{Me}$), 145.2, (s, *ipso*-C_6H_3), 145.9 (s, *ipso*-$C_6H_3^{Me}$) ppm.

Spectroscopic characterization of 2,6-[C(3,5-Me_2-C_6H_3)$_3$]$_2$-C_6H_3 (4b):

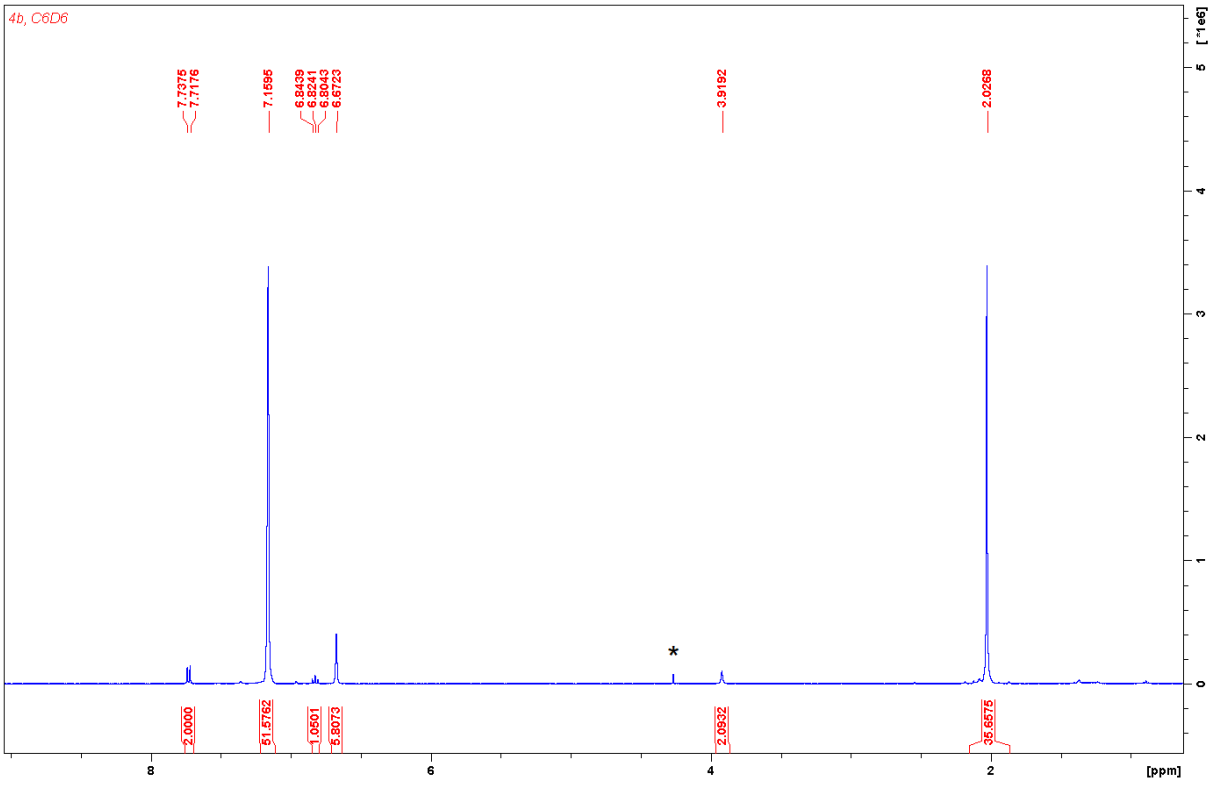


Figure S21. ^{1}H NMR spectrum of **4b**. Residual dichloromethane marked by *.

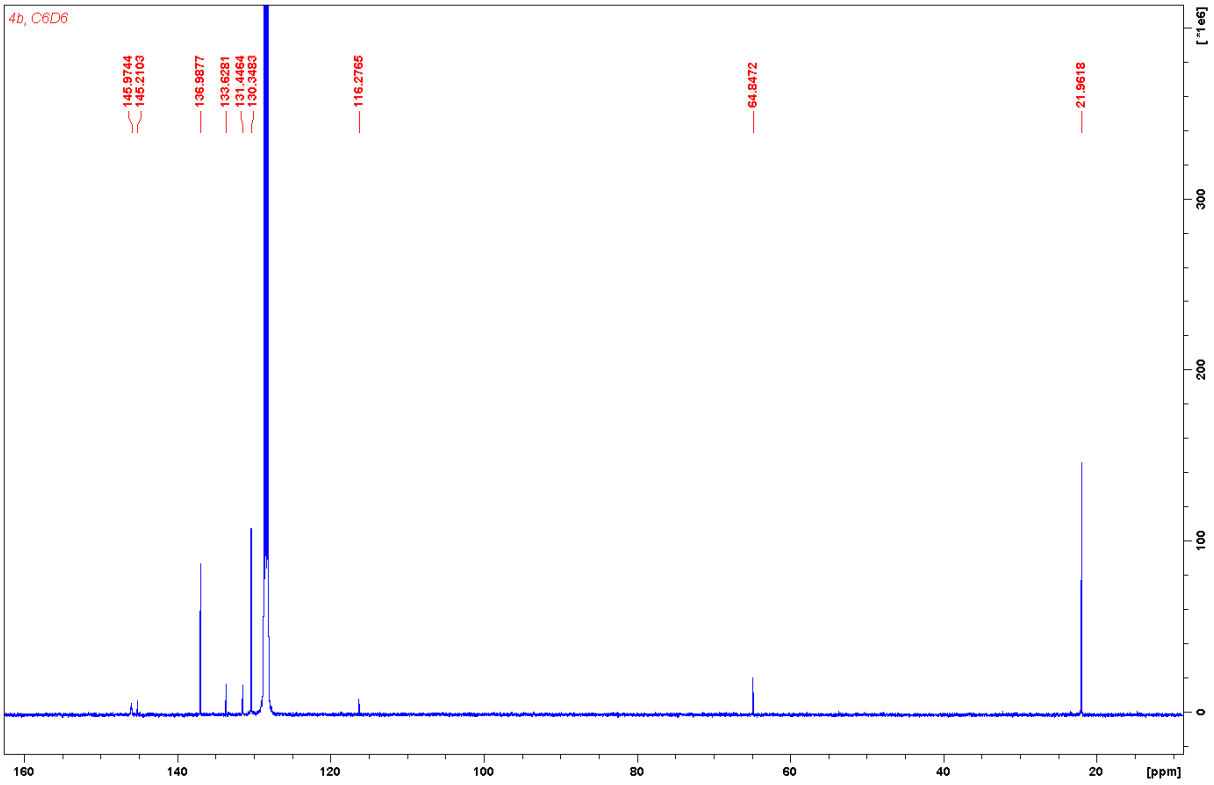


Figure S22. ^{13}C NMR spectrum of **4b**.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(3,5-Me_2-C_6H_3)$_3$]$_2$-C_6H_3 (4b):

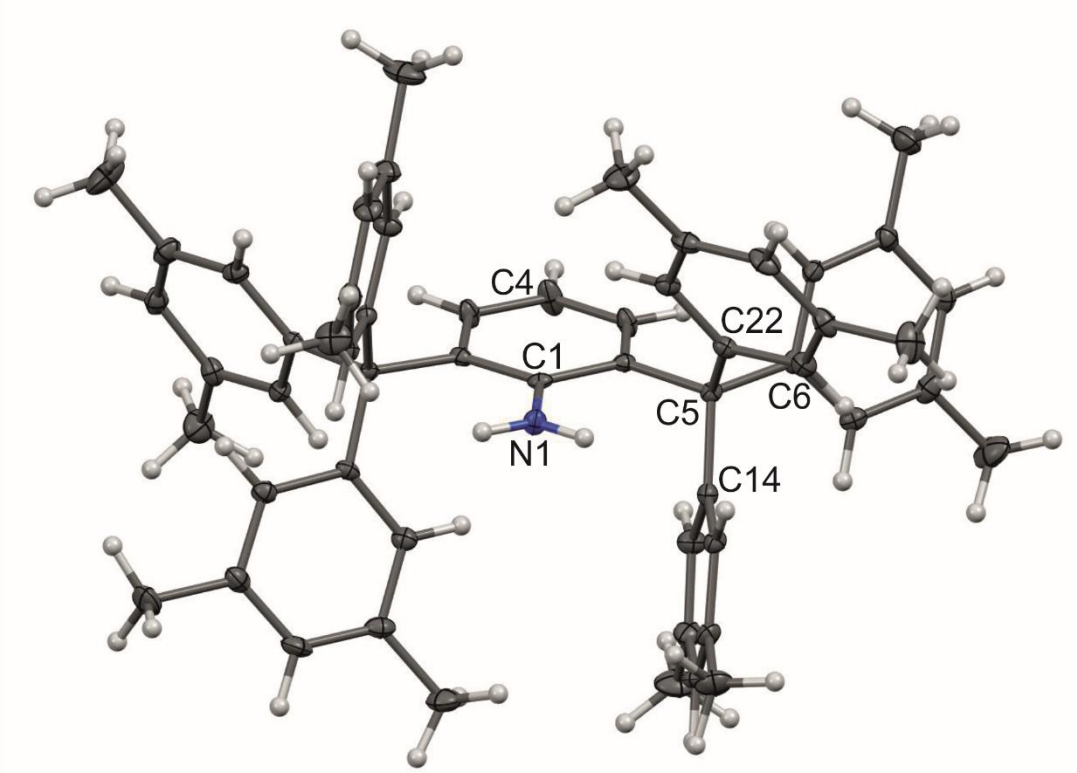


Figure S46. The molecular structure of **4b**, ORTEP diagram, 40% probability level. Selected interatomic distances [Å] and bond angles[°]: C5 N1 2.929(3), C5 C5*i* 5.193(5), C1 N1 1.377(5).

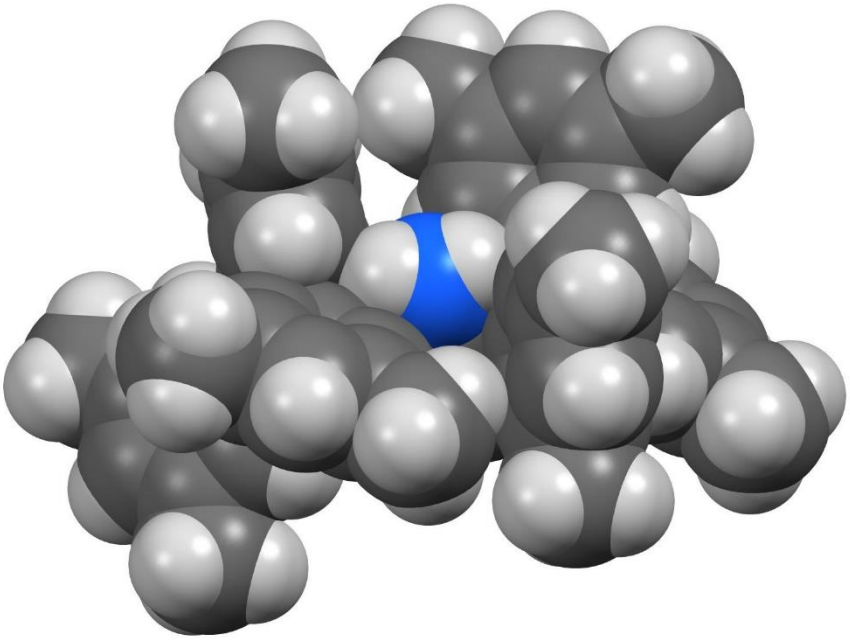


Figure S47. The molecular structure of **4b**, space filling model.

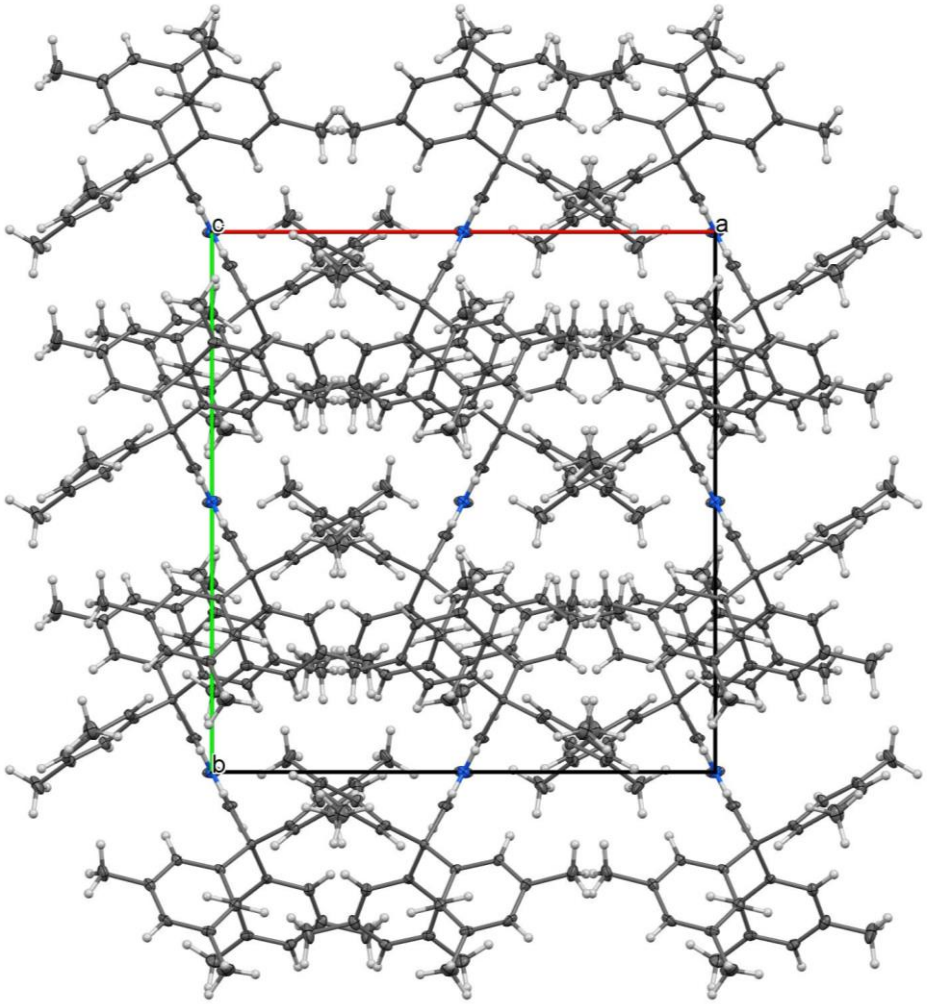
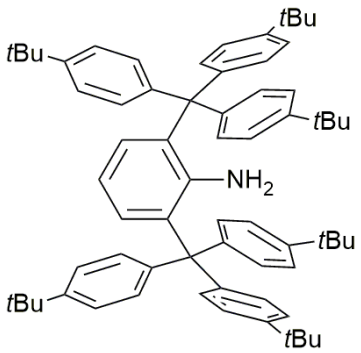


Figure S48. The crystal packing model of **4b**.

Table S8. Crystal data and structure refinement for **4b**.

Crystal data	
Chemical formula	$C_{56}H_{59}N$
M_r	746.04
Crystal system, space group	Orthorhombic, *Aba*2
Temperature (K)	150
a, *b*, *c* (Å)	15.828 (6), 16.995 (6), 16.819 (10)
V (Å^3)	4524 (4)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.06
Crystal size (mm)	0.52 × 0.40 × 0.30
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.836, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19658, 5150, 4089
R_{int}	0.070
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.122, 1.04
No. of reflections	5150
No. of parameters	269
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.24
Absolute structure	Flack x determined using 1538 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). The Flack parameter was deleted because the value (-4.0(10)) does not match the valid range

1-NH$_2$-2,6-[C(4-*t*Bu-C$_6$H$_4$)$_3$]$_2$-C$_6$H$_3$ (4c):



2,6-[C(OMe)(4-*t*Bu-C$_6$H$_4$)$_2$]$_2$-C$_6$H$_3$ (**2c**) (2,62 g, 3.7 mmol); 1-bromo-4-*tert*-butylbenzene (2.56 mL, 14.8 mmol); magnesium (0.39 g, 16.2 mmol). Yield 2.77 g, 82 %. **Mp** > 320 °C. **Anal. Calc**. for $C_{68}H_{83}N$ (914.39): C 89.3, H 9.2, N 1.5; found C 89.1, H 9.4, N 1.5. **^{1}H NMR** (25 °C, C_6D_6, 500 MHz): δ = 1.30 (s, 54H, C(C*H*$_3$)$_3$), 3.27 (s, 2H, N*H*$_2$), 6.64 (t, $^3J(^1H\text{-}^1H)$ = 8.0 Hz, 1H, *p*-C$_6$*H*$_3$), 7.18 (d, $^3J(^1H\text{-}^1H)$ = 8.5 Hz, 12H, *m*-C$_6$*H*$_4$), 7.34 (d, $^3J(^1H\text{-}^1H)$ = 8.5 Hz, 12H, *o*-C$_6$*H*$_4$), 7.49 (d, $^3J(^1H\text{-}^1H)$ = 8.0 Hz, 2H, *m*-C$_6$*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 125.76 Hz): δ = 31.9 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 63.6 (s, *C*Ar$_3$), 116.0 (s, *p*-*C*$_6$H$_3$), 124.9 (s, *m*-*C*$_6$H$_4$), 131.2 (s, *m*-*C*$_6$H$_3$), 132.1 (s, *o*-*C*$_6$H$_4$), 133.6 (s, *o*-*C*$_6$H$_3$), 143.4 (s, *ipso*-*C*$_6$H$_4$), 144.8 (s, *ipso*-*C*$_6$H$_3$), 149.0 (s, *p*-*C*$_6$H$_4$) ppm.

Spectroscopic characterization of 2,6-[C(4-*t*Bu-C_6H_4)$_3$]$_2$-C_6H_3 (4c):

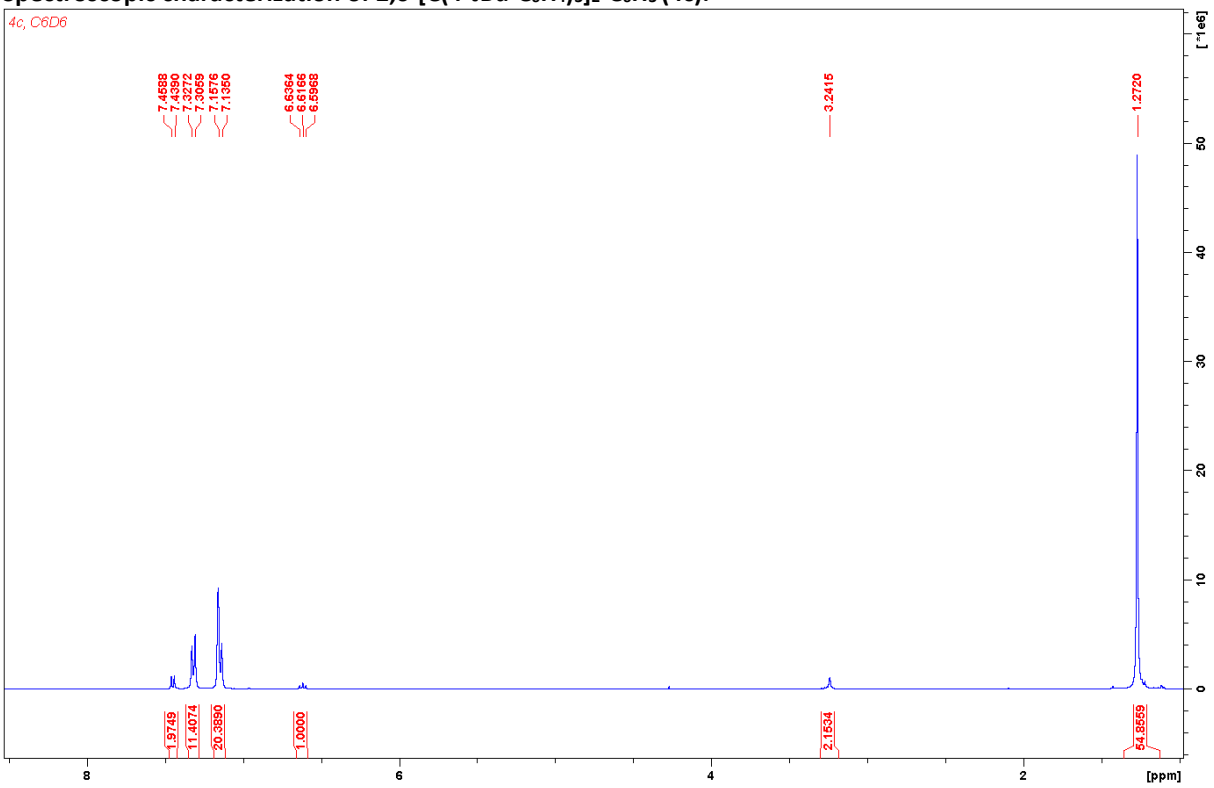


Figure S23. ^{1}H NMR spectrum of **4c**.

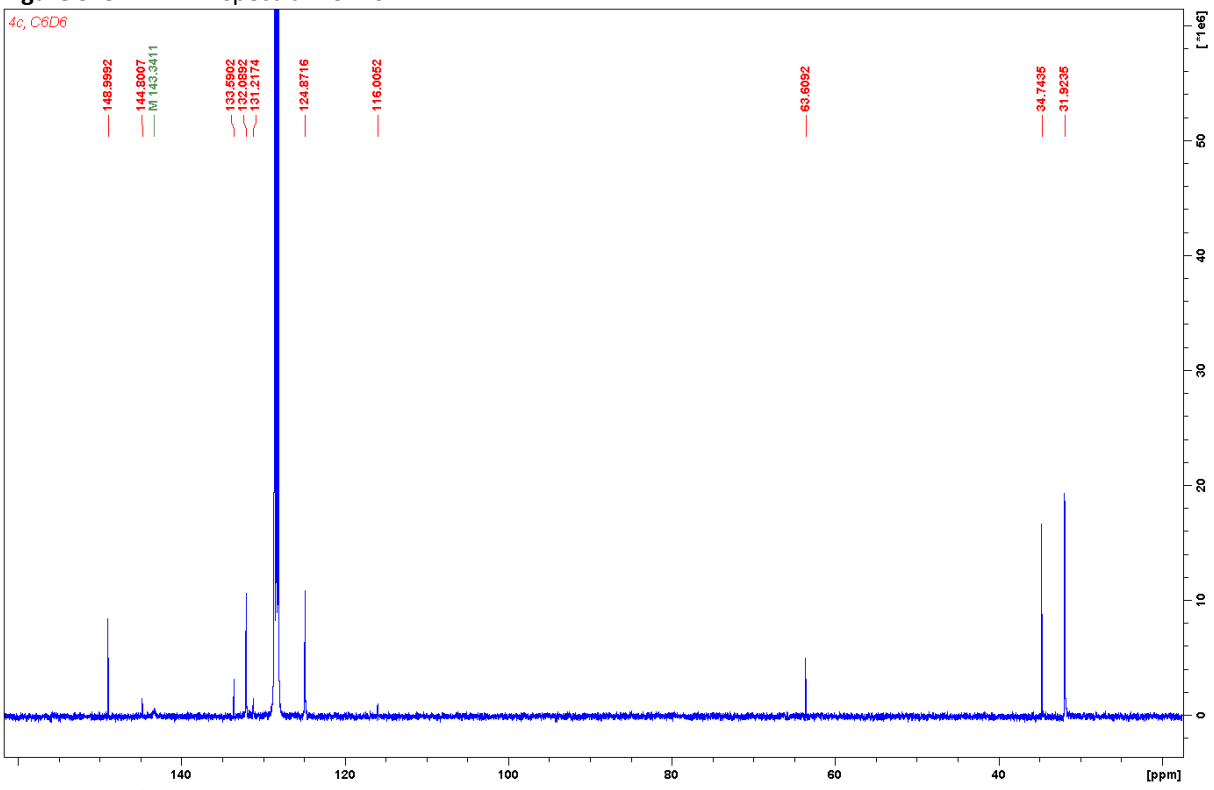


Figure S24. ^{13}C NMR spectrum of **4c**.

X-Ray Single-Crystal Structure Analysis of 1-NH_2-2,6-[C(4-*t*Bu-C_6H_4)$_3$]$_2$-C_6H_3 (4c):

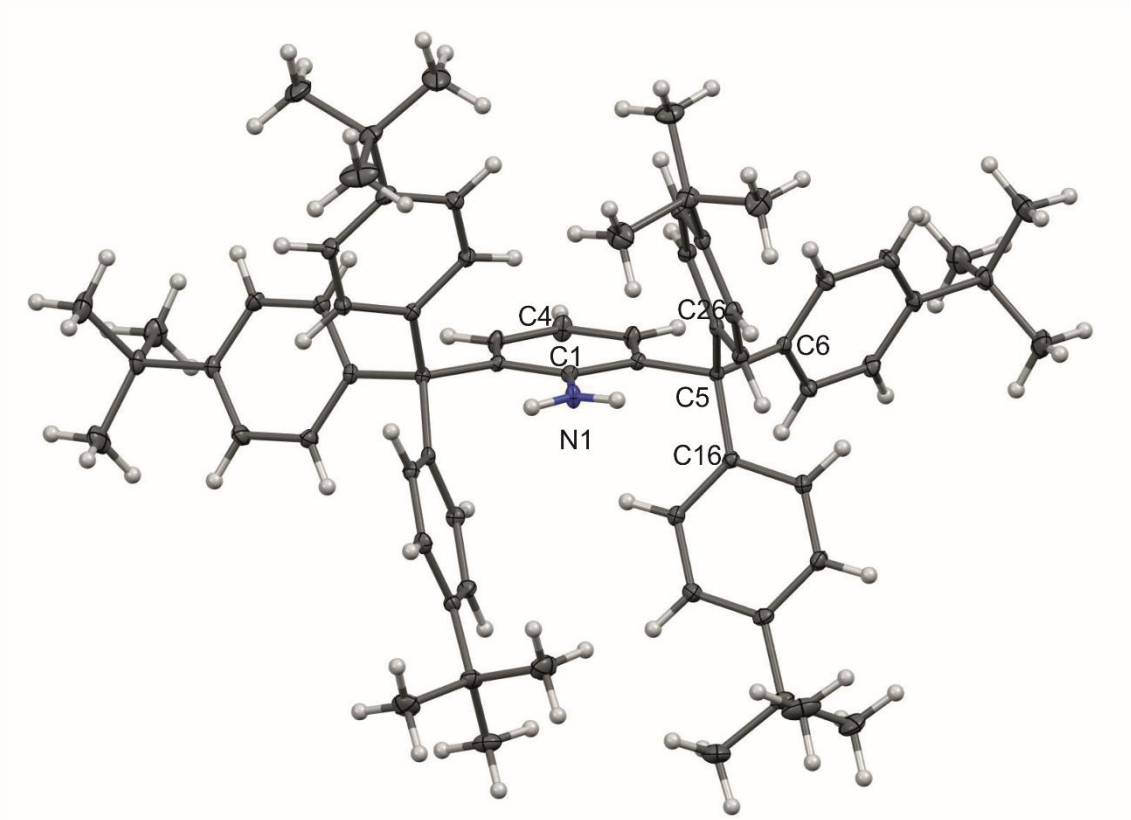


Figure S49. The molecular structure of **4c**, ORTEP diagram, 40% probability level. Selected interatomic distances [Å] and bond angles[°]: C5 N1 2.905(1), C5 C5*i* 5.174(2), C1 N1 1.384(2).

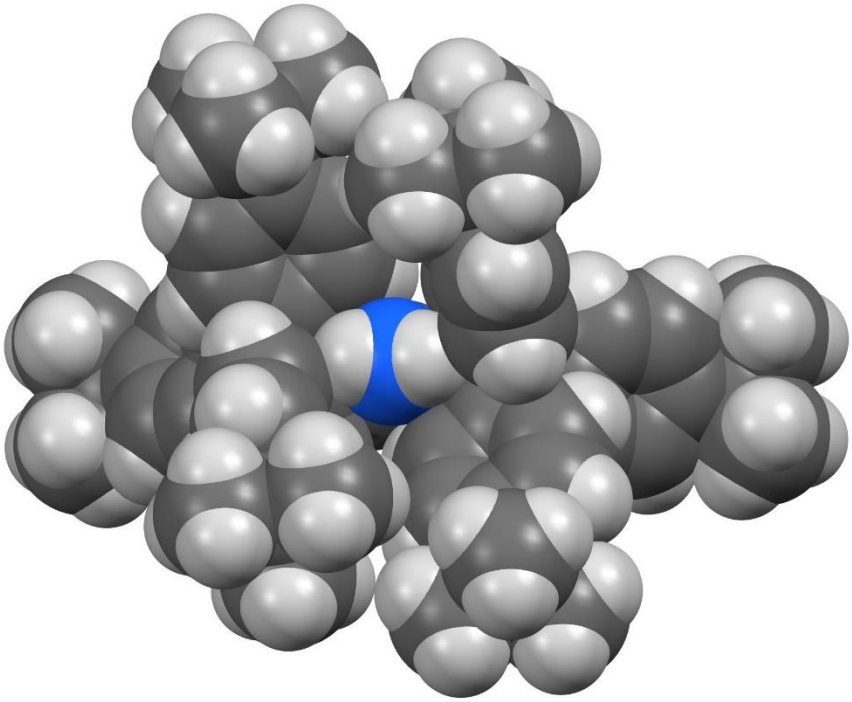


Figure S50. The molecular structure of **4c**, space filling model.

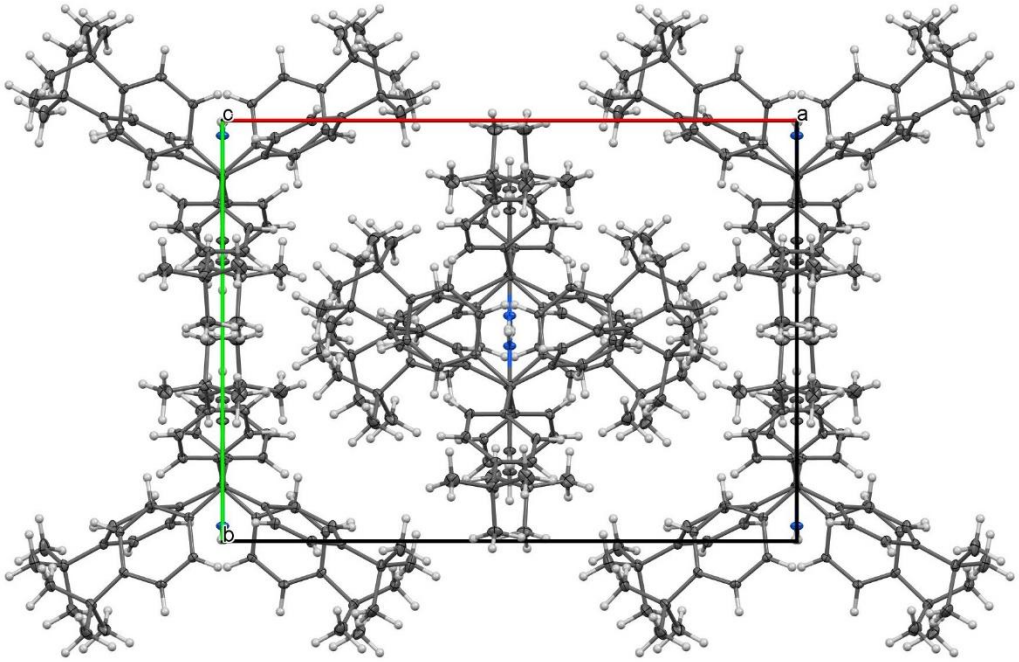


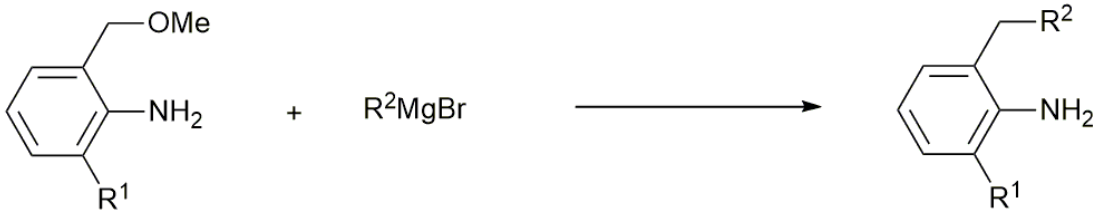
Figure S51. The crystal packing model of **4c**.

Table S9. Crystal data and structure refinement for **4c**.

Crystal data	
Chemical formula	$C_{68}H_{83}N$
M_r	914.35
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	19.1224 (7), 13.9671 (5), 20.7356 (7)
β (°)	93.252 (1)
V (Å^3)	5529.2 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.06
Crystal size (mm)	0.28 × 0.23 × 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}	0.714, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	65521, 6349, 5359
R_{int}	0.054
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.130, 1.03
No. of reflections	6349
No. of parameters	326
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.22

Results and discussion

Similar alkylation as it was described in the synthesis of compounds **3a-c** and **4a-c** was performed only in the case of 2-methoxymethyl-6-methylaniline and of 2-methoxymethylaniline, which were alkylated by vinyl- and allylmagnesium bromides.



R_1 = H, Me

R_2 = -CH=CH_2, -CH_2-CH=CH_2

Scheme S1. Alkylation described in the literature.[S2]

Quantum-Chemical Section

Computational Details

Buried Volume was calculated by SambVca with default parameters, nitrogen atom was chosen as the center of the sphere with radii = 3.5 Å.[S3-6] Spatial orientation of the anilines is depicted in figure S52.

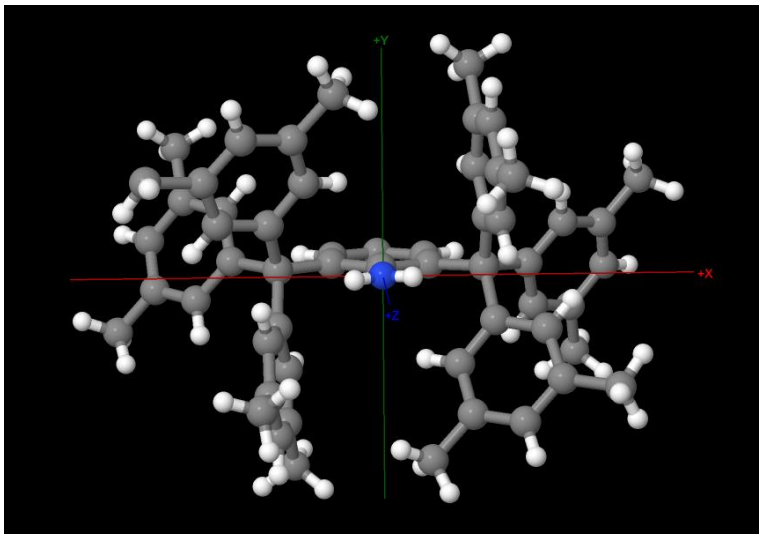
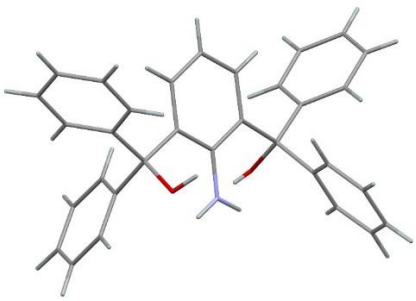
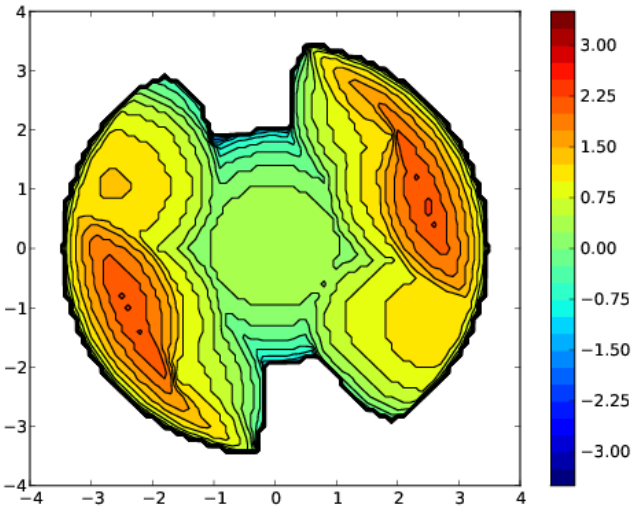


Figure S52. Spatial orientation of the bulky anilines chosen for the calculation of the buried volume.

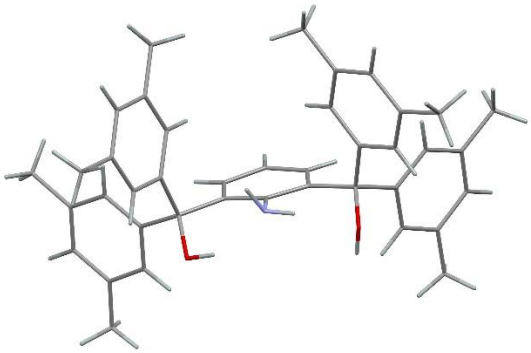
Buried volumes and steric maps

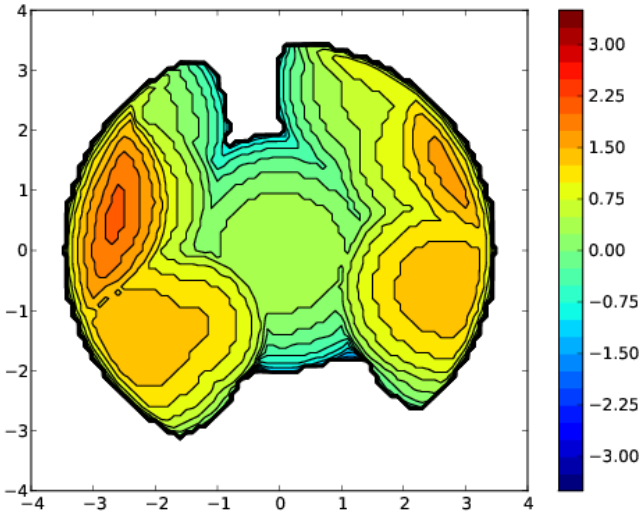
Name / Structure	Steric Maps
1a; %V_Bur = 60.7	



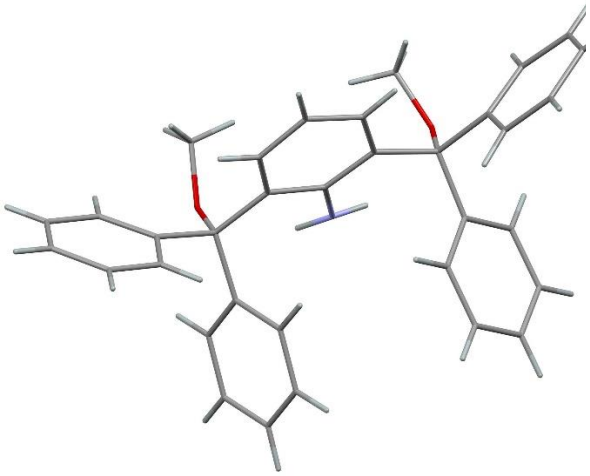


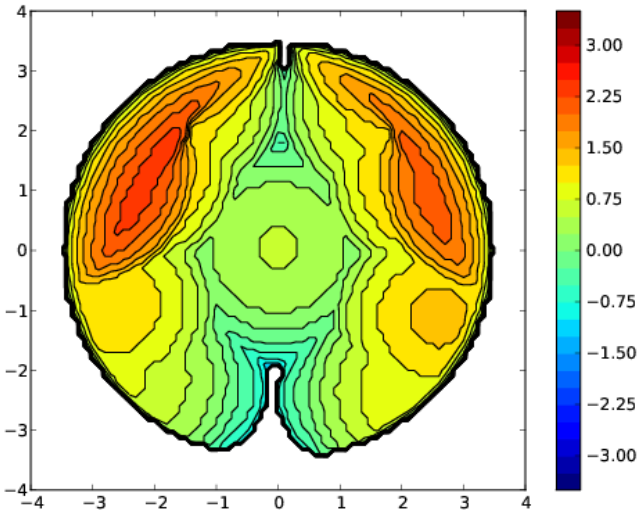
1b; %V_Bur = 57.2



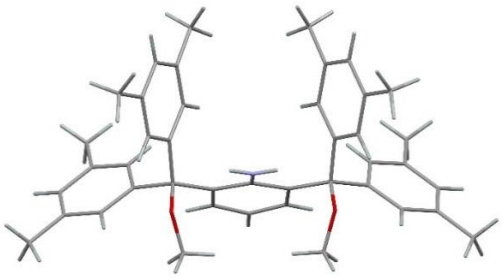


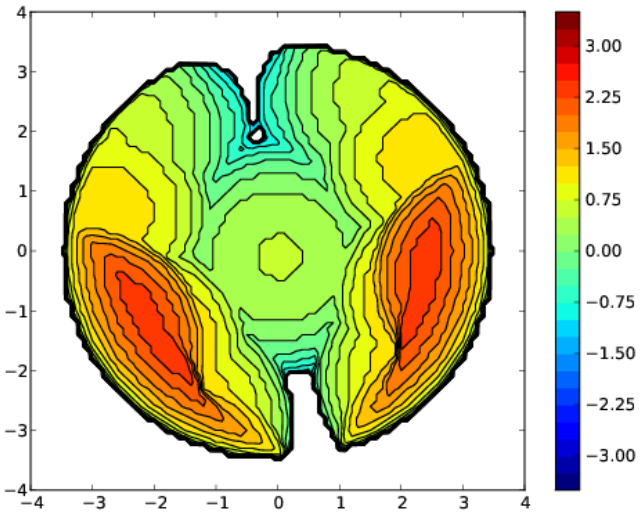
2a; %V_Bur = 67.2



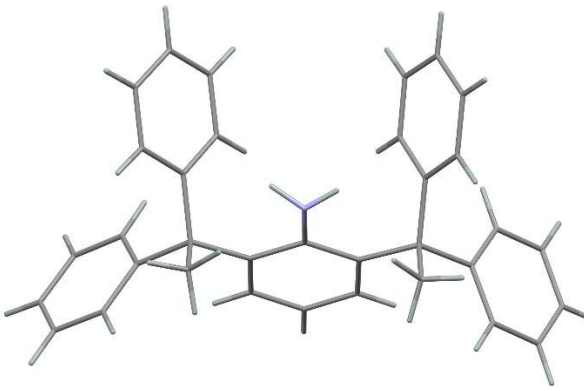


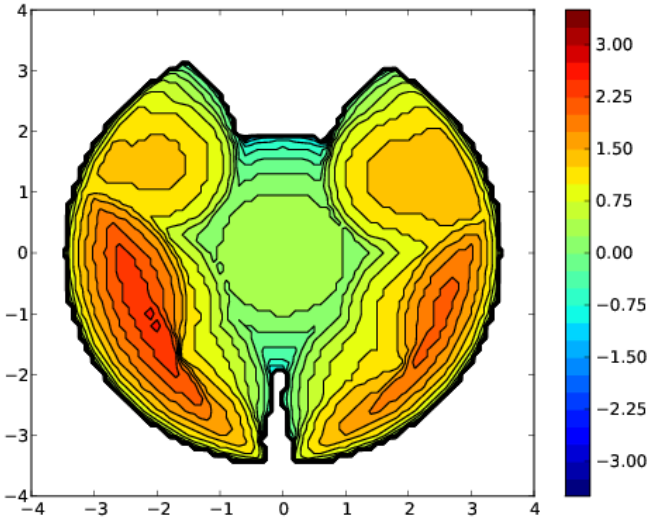
2b; %V_Bur = 66.1



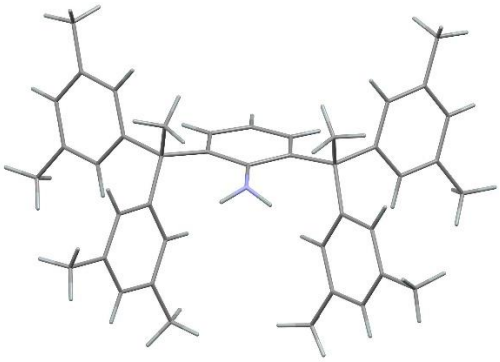


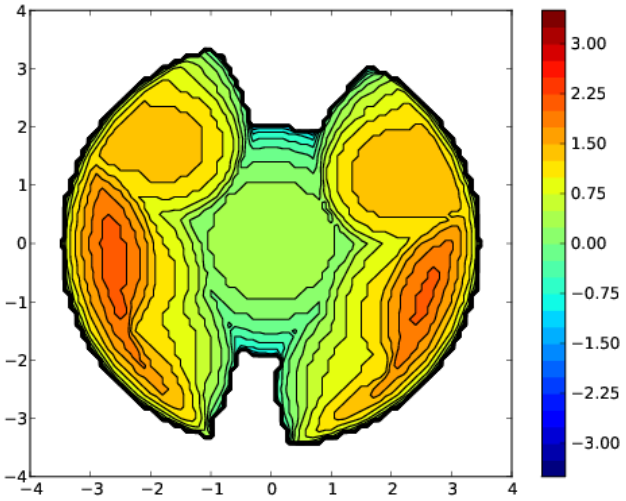
3a; %V_Bur = 64.4



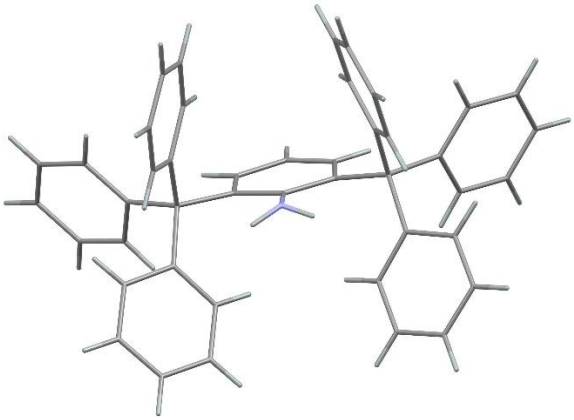


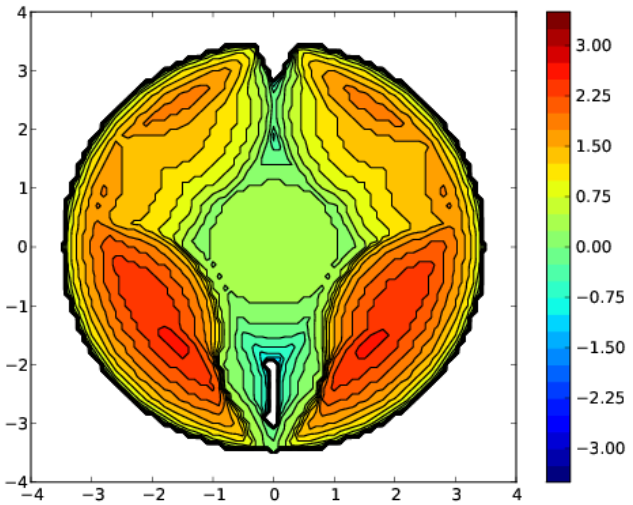
3b; %V_Bur = 62.6



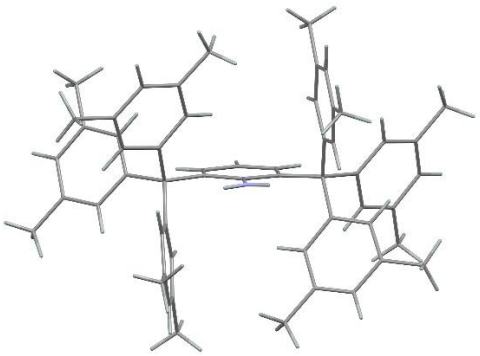


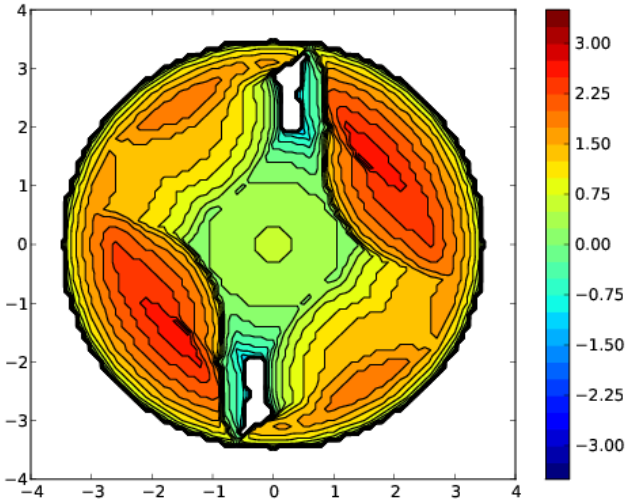
4a; %V_Bur = 73.6



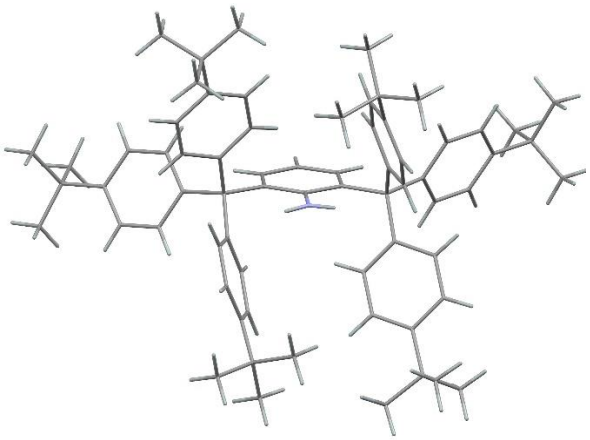


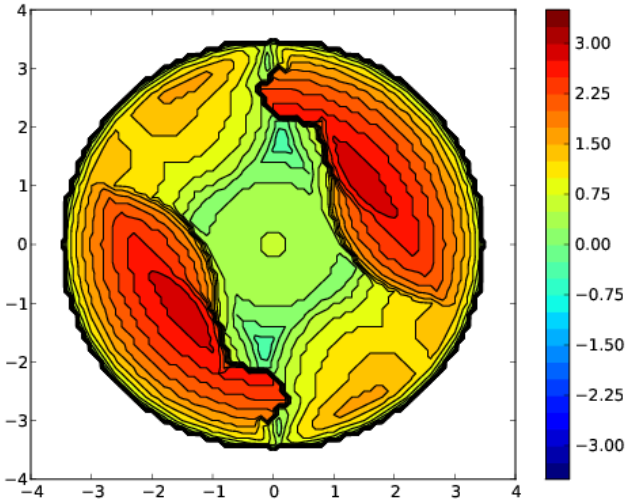
4b; %V_Bur = 73.0





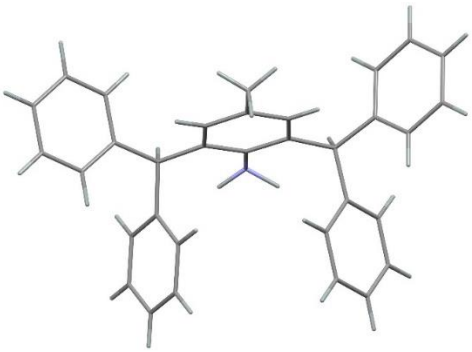
4c; %V_Bur = 76.9

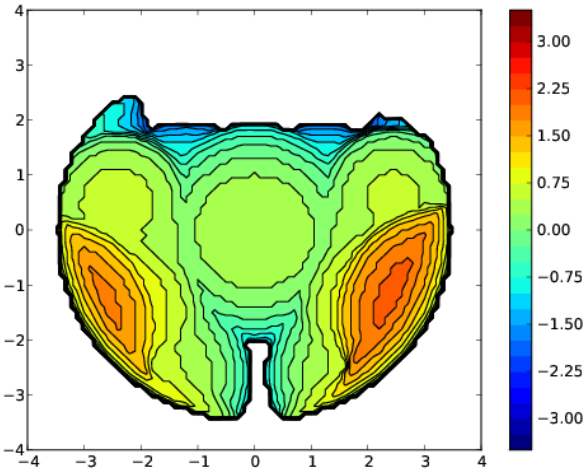




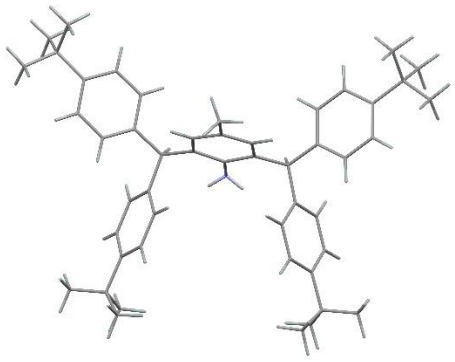
The following buried volumes were calculated for comparison with the prepared anilines. The XRD data were taken from the CCDC.[7]

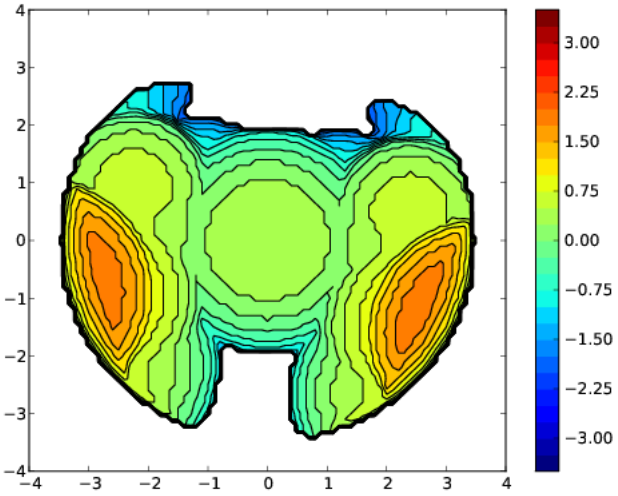
1-NH_2-2,6-$[C(H)Ph_2]_2$-C_6H_3
%V_Bur = 51.7



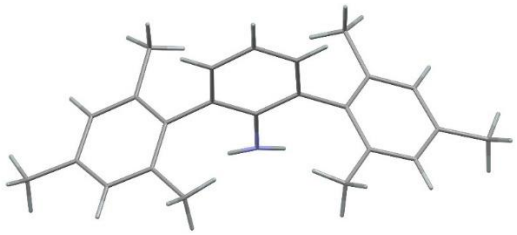


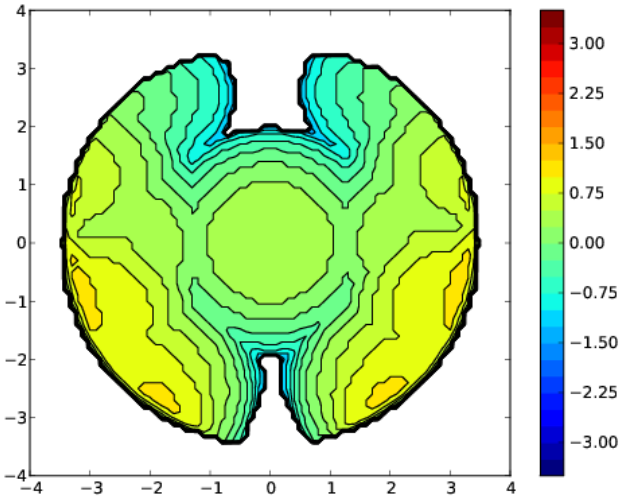
1-NH_2-2,6-[C(H)(4-*t*Bu-C_6H_4)$_2$]$_2$-C_6H_3 %V_Bur = 50.1



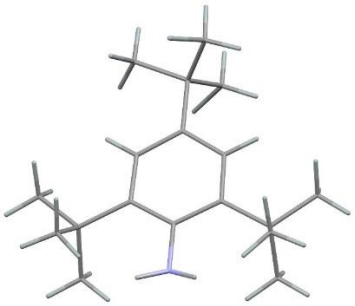


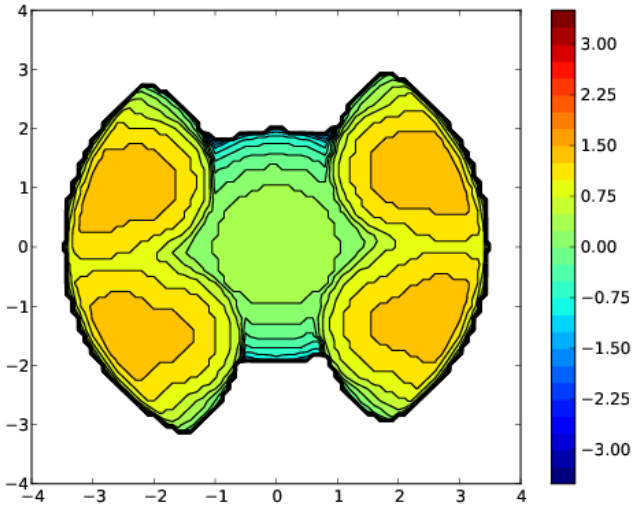
1-NH_2-2,6-(2,4,6-Me_3-C_6H_2)$_2$-C_6H_3 %V_Bur = 52.8





1-NH_2-2,4,6-*t*Bu_3-C_6H_3; %V_Bur = 54.9





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