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Diarylamines with switchable intramolecular H-bonding: a new approach to molecular logic gates

Oleg A. Levitskiy, Yuri K. Grishin and Tatiana V. Magdesieva

Contents

1. General information

All solvents were dried and purified according to the standard procedures. Other reagents are commercially available and were used as received.

^{1}H (400 MHz), ^{13}C (101 MHz) NMR spectra were recorded using an Aglient 400-MR spectrometer in $CDCl_3$. Chemical shifts were referenced to a residual non-deuterated solvent. High-resolution mass spectra were recorded with AB Sciex TripleTOF 5600+ instrument using electrospray ionization (DuoSpray ESI). IR spectra were recorded using a Nicolet iS5 (Thermo Scientific) Fourier transform spectrophotometer using an internal reflectance attachment with diamond optical element; attenuated total reflection (ATR, iD7) with 45° angle of incidence. Resolution was 4 cm^{-1}, the number of scans was 20.

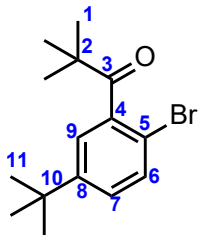
Voltammetric experiments were performed with Biologic BP-300 potentiostat. Voltrammetric measurements were performed at a stationary Pt disk electrode (r = 0.8 mm) or at a rotating Pt disc electrode (r = 2.5 mm, Autolab Rotating Ring Disc Electrode (RRDE) system); a Pt wire counter electrode and Ag/Ag^{+} (0.01 M $AgNO_3$ in MeCN) reference electrode were used. The standard potential of Fc^{+}/Fc couple was taken as 475 mV vs Ag/AgCl, KCl(sat.) under the applied conditions. Ohmic drops corrections were performed using Manual IR Compensation procedure implemented in Biologic software. All solutions were thoroughly deaerated by passing an argon flow through the solution prior to the CV experiments and above the solution during the measurements. The supporting electrolyte in all experiments was 0.1 M Bu_4NBF_4 (Aldrich, purity >99%), which has been recrystallized from water and dried by gentle heating under reduced pressure (0.05 Torr) prior to use. Acetonitrile (Aldrich spectroscopic quality, <0.02% water content) was distilled over P_2O_5 and stored under argon.

Quantum-chemical calculations were carried out using PBEh-3c [*J. Chem. Phys.* **2015**; 143 : 054107] approach, including gCP [*J. Chem. Phys.* **2012**; 136 : 154101] and D3BJ [*J. Chem. Phys.* **2010**;132:154104; *J. Comput. Chem.* **2011**; 32:1456–65] corrections implemented in ORCA 5.0.4 quantum chemistry package. A threshold of $1{\cdot}10^{-8}$ Hartree was used for SCF convergence; thresholds of $1{\cdot}10^{-6}$ Hartree and $3{\cdot}10^{-5}$ Hartree $Bohr^{-1}$ on energy and RMS gradient, respectively, were employed in optimization procedures. SMD solvation model [*J. Phys. Chem. B* **2009**, *113* (18), 6378] with acetonitrile as the solvent was applied.

2. Synthesis of 1-(2-bromo-5-*tert*-butylphenyl)-2,2-dimethylpropan-1-one

A two-necked round-bottom flask with a stir bar and septum connected to a Schlenk line was charged with 1-bromo-4-*tert*-butyl-2-iodobenzene (9.23 g, 0.028 mol) and filled with argon; abs THF (85 mL) was added *via* cannula. The solution was cooled to –90 °C and 2M $Pr^{i}MgCl$ in THF soln (16 mL, 0.032 mol) was added with stirring; the solution was stirred for 2.5 h maintaining the temperature of the cooling bath in the range –80 to –70 °C. Then CuCl (1.91 g, 0.019 mol) was added under an argon counterflow and the temperature was gradually raised to –40 °C over 1 h. Pivaloyl chloride (3.86 g, 0.032 mol) was added under stirring at –40 °C. The cooling bath was removed, and after the temperature achieved 20 °C, the solution was heated to 50 °C (5 min). The mixture was diluted with sat. aq NaCl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried (K_2CO_3), filtered and concentrated under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and passed through a short pad of Silica-gel (2.5 cm x 2 cm, EtOAc as an eluent). After evaporation, the residue was recrystallized from methanol yielding 4.66 g of a targeted ketone as a white crystalline solid. Additional amount of the product (0.89 g) was collected from the mother liquor

by flash chromatography on Silica-gel (the admixture was eluted first with hexane; the targeted ketone was then eluted with CH_2Cl_2). The total yield of the product was 5.55 g (67%).



^{1}H NMR ($CDCl_3$, δ, ppm): 1.28 (s, 9H, *H-1*); 1.29 (s, 9H, *H-11*); 7.10 (d, 1H, ^4J = 2.4 Hz, *H-9*); 7.24 (dd, 1H, ^4J = 2.4 Hz, ^3J = 8.6 Hz, *H-7*); 7.46 (d, 1H, ^3J = 8.6 Hz, *H-6*) (signal assignment was made based on HMBC and HSQC 2D NMR spectra).

^{13}C NMR ($CDCl_3$, δ, ppm): 212.54 (*C-3*), 150.16 (*C-8*), 142.11 (*C-4*), 132.61 (*C-6*), 127.25 (*C-7*), 123.28 (*C-9*), 114.60 (*C-5*), 45.09 (*C-2*), 34.73 (*C-10*), 31.23 (*C-11*), 27.28 (*C-1*) (signal assignment was made based on HMBC and HSQC 2D NMR spectra).

ESI-HRMS: m/z 297.0854 ($[M+H]^+$, 297.0854 calcd. for $C_{15}H_{22}BrO^+$).

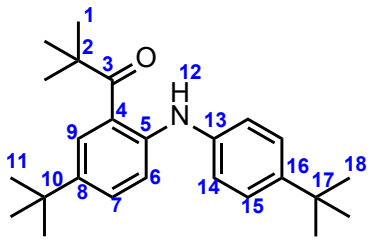
3. Synthesis of amines 1 and 2

General procedure:

A two-necked round-bottom flask with a stir bar and septum connected to a Schlenk line was charged consequently with 1-(2-bromo-5-(tert-butyl)phenyl)-2,2-dimethylpropan-1-one (100 mg, 0.34 mmol), $Pd_2(dba)_3$ (9.4 mg, 8.2 µmol, 4.8 mol% of Pd) , 1,1'-bis(diphenylphosphino)ferrocene (dppf, 11 mg, 0.02 mmol), sodium *tert*-butoxide (33 mg, 0.34 mmol) and a solution of an arylamine (0.34 mmol) in absolute toluene (3.5 ml). The mixture was refluxed under argon for 13 h. The mixture was quenched with brine and extracted with ethyl acetate (3x2 ml). The combined organic fractions were dried over Na_2SO_4. The solvent was removed under reduced pressure. Flash chromatography on Silica-gel yields the targeted product.

*amine **1** (1-(5-(tert-butyl)-2-((4-(tert-butyl)phenyl)amino)phenyl)-2,2-dimethylpropan-1-one):*

Hexane / CH_2Cl_2 4:1 was used as an eluent. The product was obtained as a yellow oil (122 mg, 98%).



^{1}H NMR ($CDCl_3$, δ, ppm): 1.33 (s, 18H, *H-11,18*); 1.41 (s, 9H, *H-1*); 7.08-7.13 (m, 2H, *H-14,14'*); 7.29-7.34 (m, 4H, *H-15,15',6,7*); 7.80 (dd, 1H, ^4J = 1.8 Hz, ^5J = 0.9 Hz, *H-9*); 8.88 (s, 1H, *H-12*) (signal assignment was made based on HMBC and HSQC 2D NMR spectra).

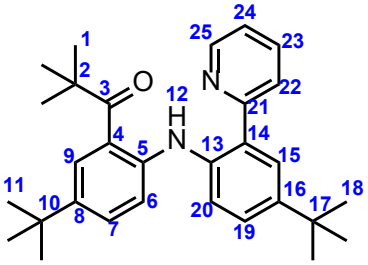
^{1}H NMR (DMSO-d6, δ, ppm): 1.20 (s, 9H, *tBu*); 1.24 (s, 9H, *tBu*); 1.27 (s, 9H, *tBu*); 6.92-6.97 (m, 2H, *H-14,14'*); 6.18 (d, 1H, ^3J = 8.6 Hz, *H-6*); 7.20-7.24 (m, 2H, *H-15,15'*); 7.31 (d, 1H, ^4J = 2.4 Hz, *H-9*); 7.34 (dd, 1H, ^3J = 8.6 Hz, ^4J = 2.4 Hz, *H-7*); 7.89 (s, 1H, *H-12*)

^{13}C NMR ($CDCl_3$, δ, ppm): 210.98 (*C-3*), 145.28 (*C-16*), 143.42 (*C-5*), 139.48 (*C-8*), 139.23 (*C-13*), 129.50 (*C-7*), 126.53 (*C-9*), 126.19 (*C-15*), 122.00 (*C-4*), 120.51 (*C-14*), 116.41 (*C-6*), 44.97 (*C-2*), 34.39 (*C-17*), 34.19 (*C-10*), 31.60 (*C-18*), 31.49 (*C-11*), 28.93 (*C-1*). (signal assignment was made based on HMBC and HSQC 2D NMR spectra).

ESI-HRMS: m/z 366.2798 ($[M+H]^+$, 366.2797 calcd. for $C_{25}H_{36}NO^+$).

amine 2 (1-(5-(tert-butyl)-2-((4-(tert-butyl)-2-(pyridin-2-yl)phenyl)amino)phenyl)-2,2-dimethylpropan-1-one):

Hexane / CH_2Cl_2 1:2 was used as an eluent. The product was obtained as a yellow powder (143 mg, 95%).



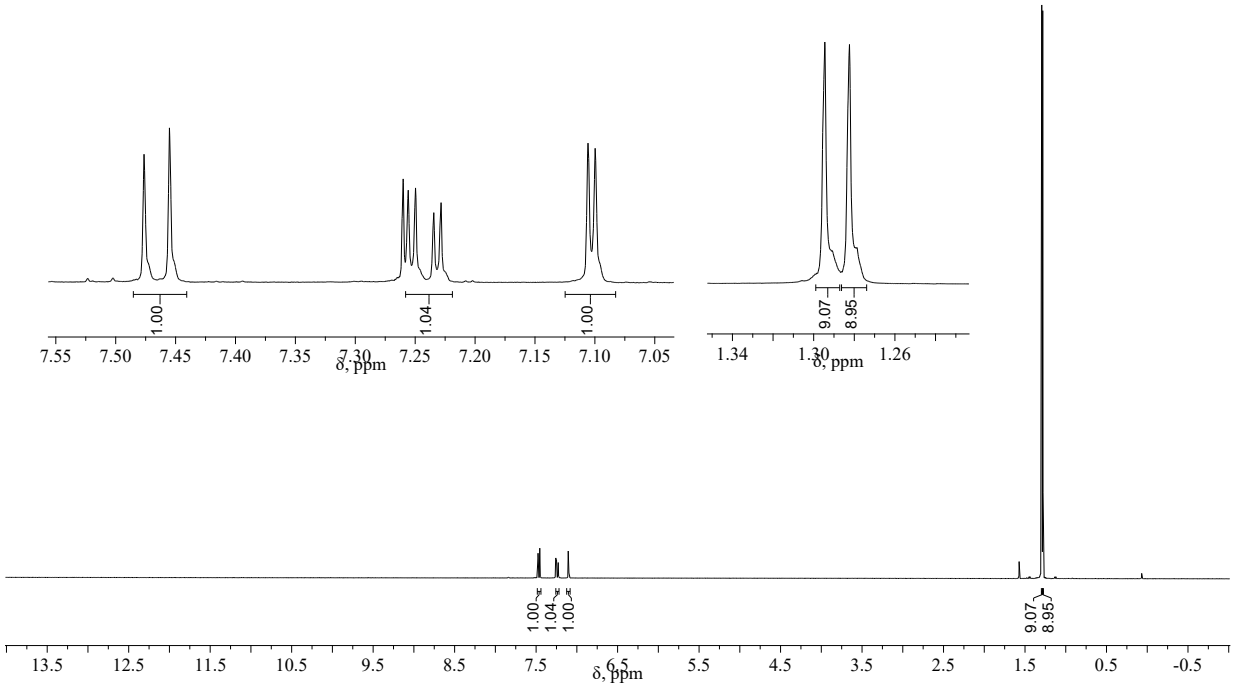
^{1}H NMR ($CDCl_3$, δ, ppm): 1.30 (s, 9H, *H-11*); 1.34 (s, 9H, *H-1*); 1.37 (s, 9H, *H-18*); 7.19 (ddd, 1H, ^{3}J =7.4 Hz, ^{3}J = 4.9 Hz, ^{4}J = 1.2 Hz, *H-24*); 7.23 (dd, 1H, ^{3}J = 8.6 Hz, ^{4}J = 2.4 Hz, *H-7*); 7.26 (d, 1H, ^{4}J = 2.4 Hz, *H-9*); 7.30 (dd, 1H, ^{3}J = 8.6 Hz, ^{4}J = 2.4 Hz, *H-19*); 7.36 (d, 1H, ^{3}J = 8.6 Hz, *H-6*); 7.43 (d, 1H, ^{3}J = 8.6 Hz, *H-20*); 7.62 (d, 1H, ^{4}J = 2.4 Hz, *H-15*); 7.68 (ddd, 1H, ^{3}J = 8.1 Hz, ^{4}J = 1.2 Hz, ^{5}J = 1.0 Hz, *H-22*); 7.75 (ddd, 1H, ^{3}J = 8.1 Hz, ^{3}J = 7.4 Hz, ^{4}J = 1.9 Hz, *H-23*); 8.73 (ddd, 1H, ^{3}J = 4.9 Hz, ^{4}J = 1.9 Hz, ^{5}J = 1.0 Hz, *H-25*), 10.49 (s, 1H, *H-12*) (signal assignment was made based on COSY, HMBC and HSQC 2D NMR spectra).

^{1}H NMR (DMSO-d6, δ, ppm): 1.22 (s, 9H, *tBu*), 1.26 (s, 9H, *tBu*), 1.32 (s, 9H, *tBu*), 7.23 (d, ^{4}J = 2.2 Hz, 1H, *H-9*), 7.26 (d, ^{3}J = 8.6 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.37 (ddd, ^{3}J = 7.2, ^{3}J = 4.9, ^{4}J = 1.3 Hz, 1H, *H-24*), 7.65 (dd, ^{4}J = 1.8, ^{5}J = 0.8 Hz, 1H, *H-15*), 7.89 (ddd, ^{3}J = 8.2, ^{4}J = 1.3 Hz, ^{5}J = 0.9 Hz, 1H, *H-22*), 7.94 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 7.2 Hz, ^{4}J = 1.9 Hz, 1H, *H-23*), 8.60 (ddd, ^{3}J = 4.9 Hz, ^{4}J = 1.9, ^{5}J = 0.9 Hz, 1H, *H-25*), 10.49 (s, 1H, *H-12*).

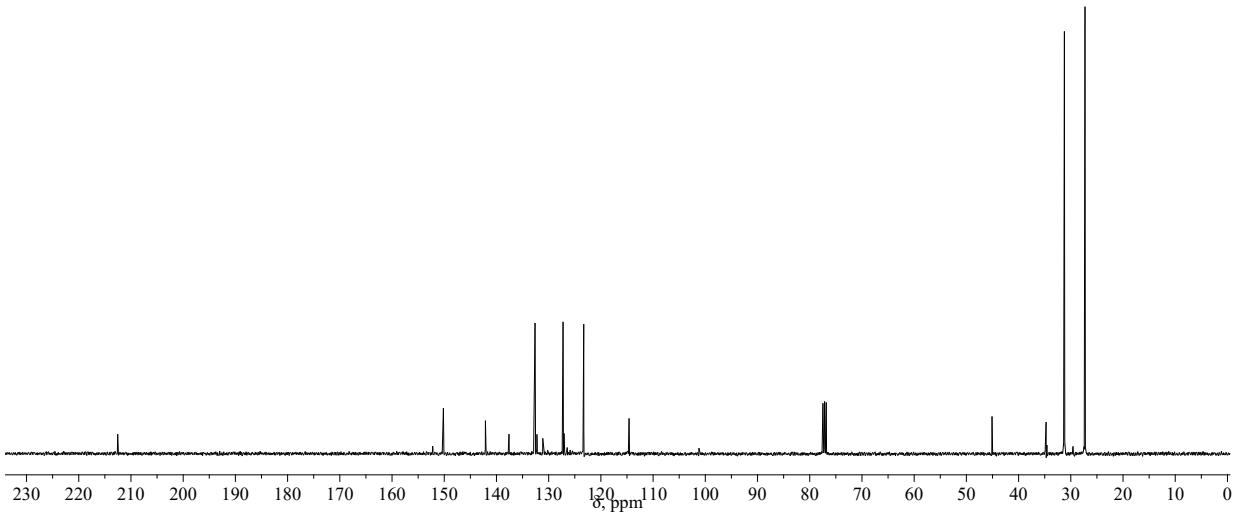
^{13}C NMR ($CDCl_3$, δ, ppm): 214.19 (*C-3*), 158.95 (*C-21*), 148.04 (*C-25*), 142.52 (*C-16*), 142.10 (*C-8*), 139.75 (*C-13*), 138.34 (*C-5*), 136.88 (*C-23*), 130.51 (*C-4*), 126.73 (*C-7*), 126.63 (*C-19*), 126.56 (*C-15*), 125.80 (*C-14*), 123.68 (*C-9*), 122.31 (*C-22*), 121.25 (*C-24*), 118.15 (*C-6*), 117.57 (*C-20*), 45.21 (*C-2*), 34.33 (*C-17*), 34.26 (*C-10*), 31.62 (*C-18*), 31.51 (*C-11*), 27.67 (*C-1*).

ESI-HRMS: m/z 443.3062 ($[M+H]^+$, 443.3062 calcd. for $C_{30}H_{39}N_2O^+$).

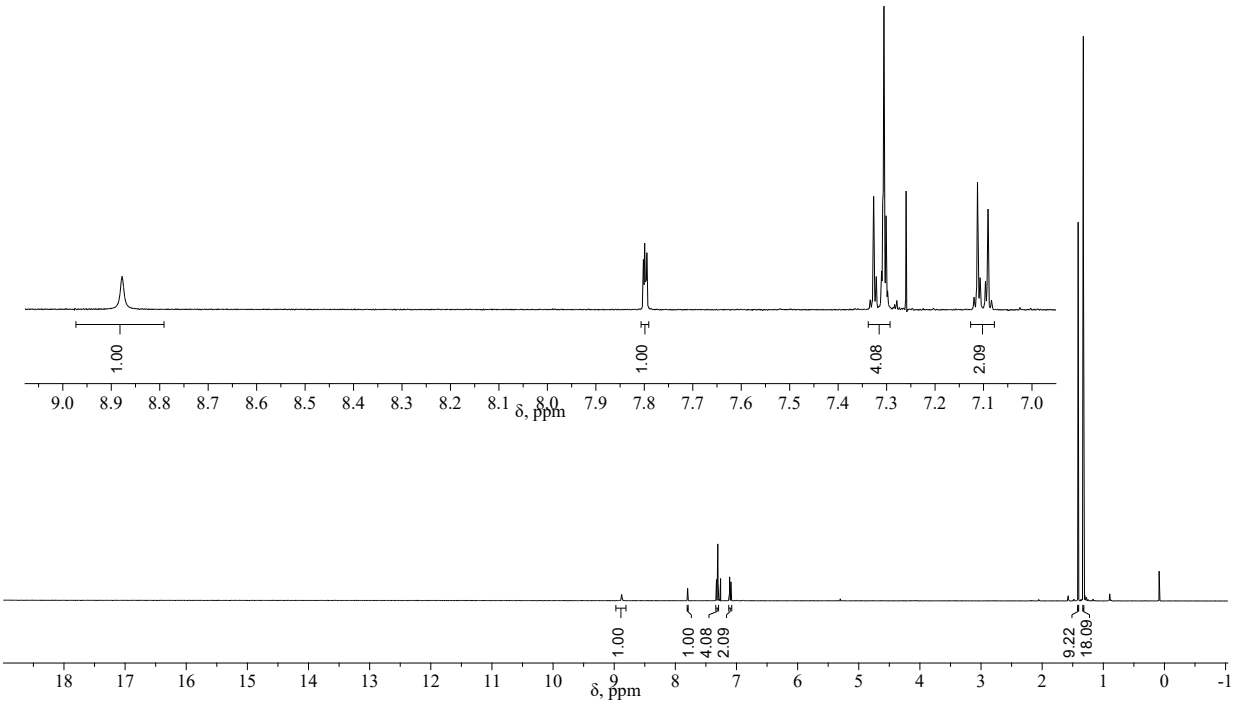
4. ^{1}H NMR spectrum of 1-(2-bromo-5-*tert*-butylphenyl)-2,2-dimethylpropan-1-one in $CDCl_3$



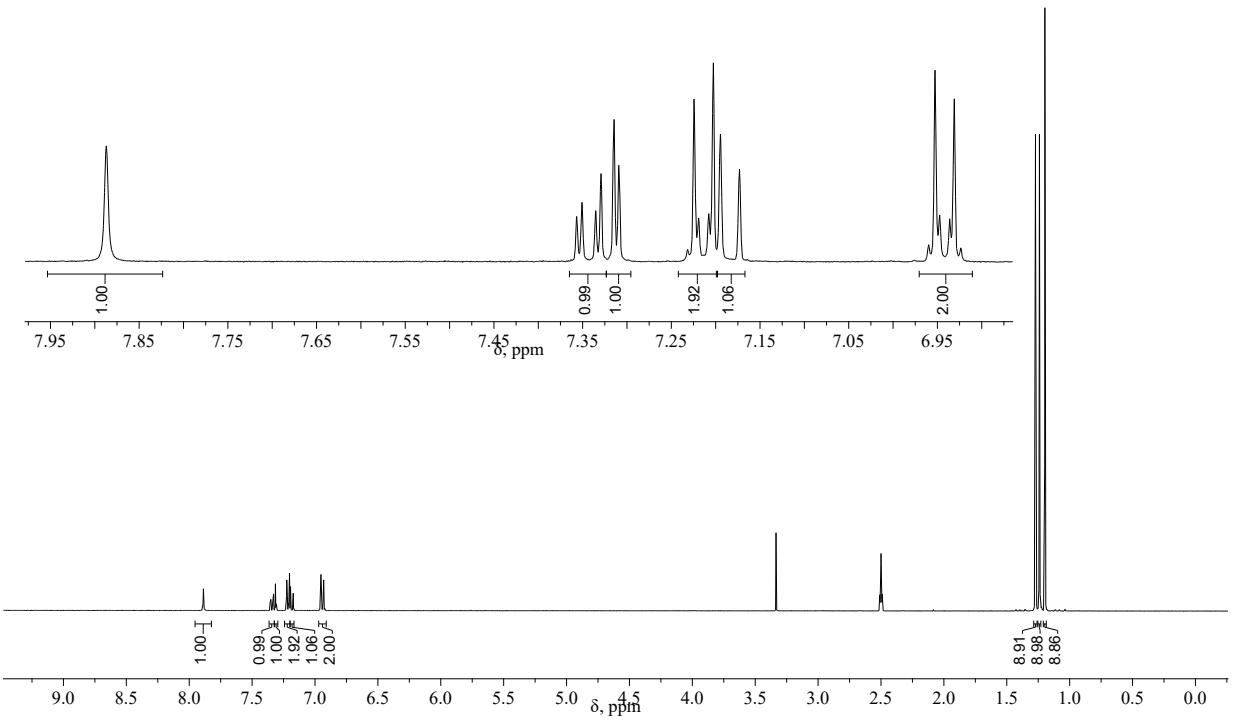
5. ^{13}C NMR spectrum of 1-(2-bromo-5-*tert*-butylphenyl)-2,2-dimethylpropan-1-one in $CDCl_3$



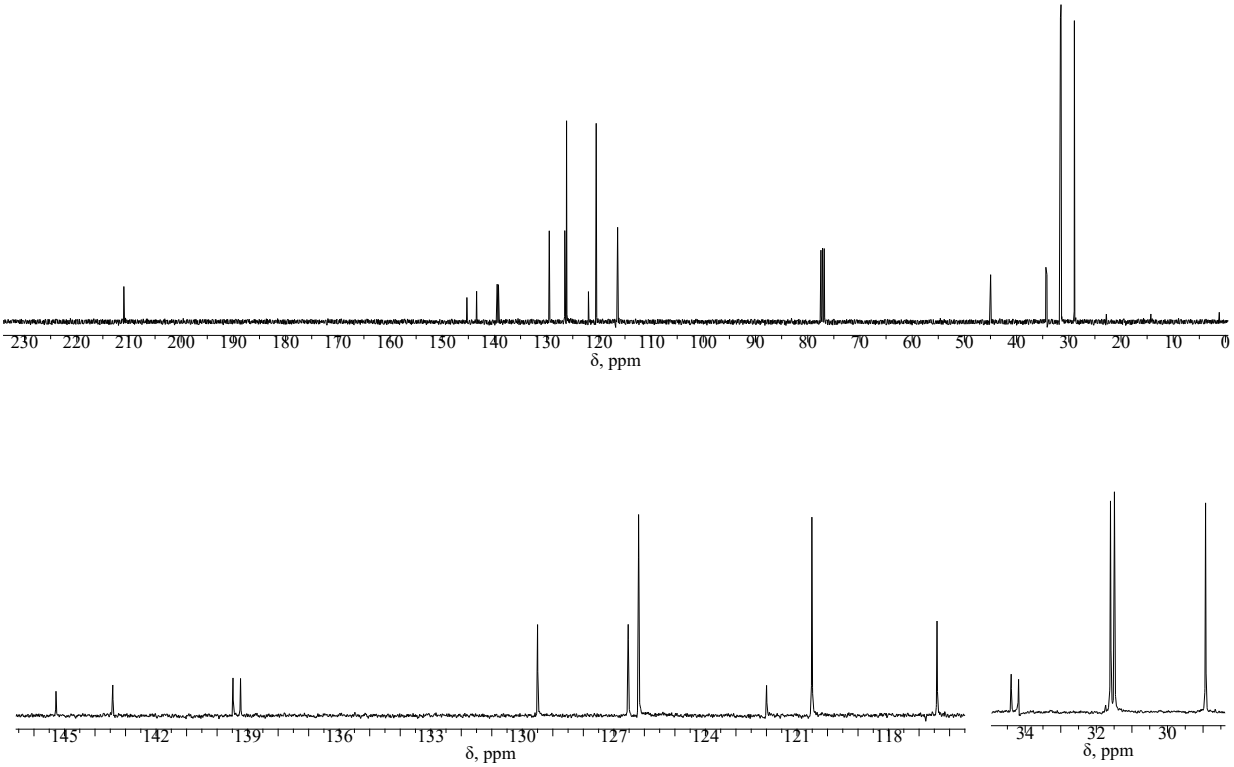
6. ^{1}H NMR spectrum of amine **1** in $CDCl_3$



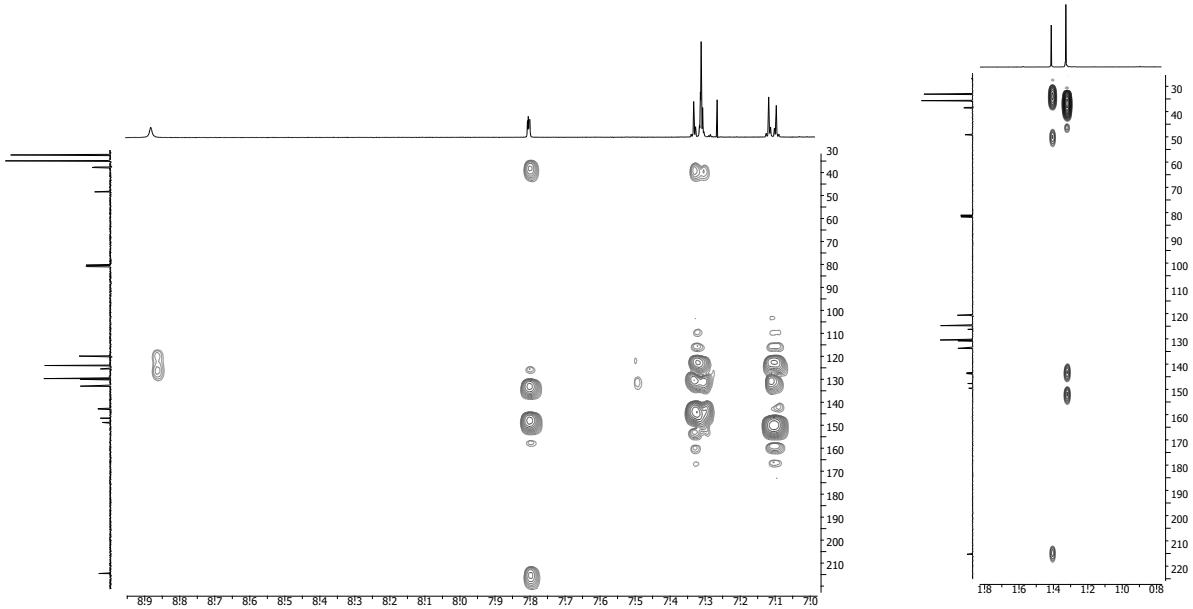
7. ^{1}H NMR spectrum of amine **1** in DMSO-d_6



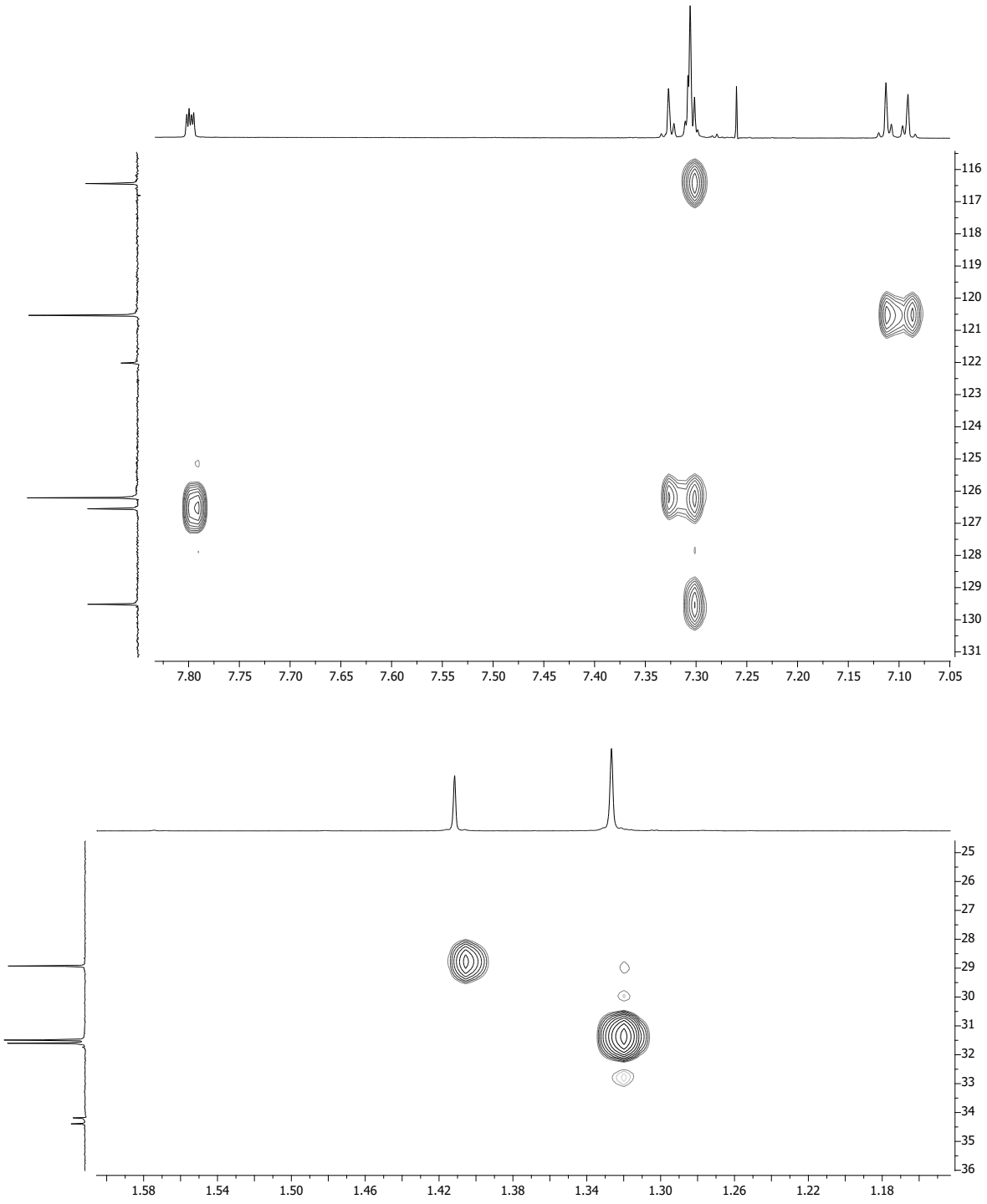
8. ^{13}C NMR spectrum of amine **1** in $CDCl_3$



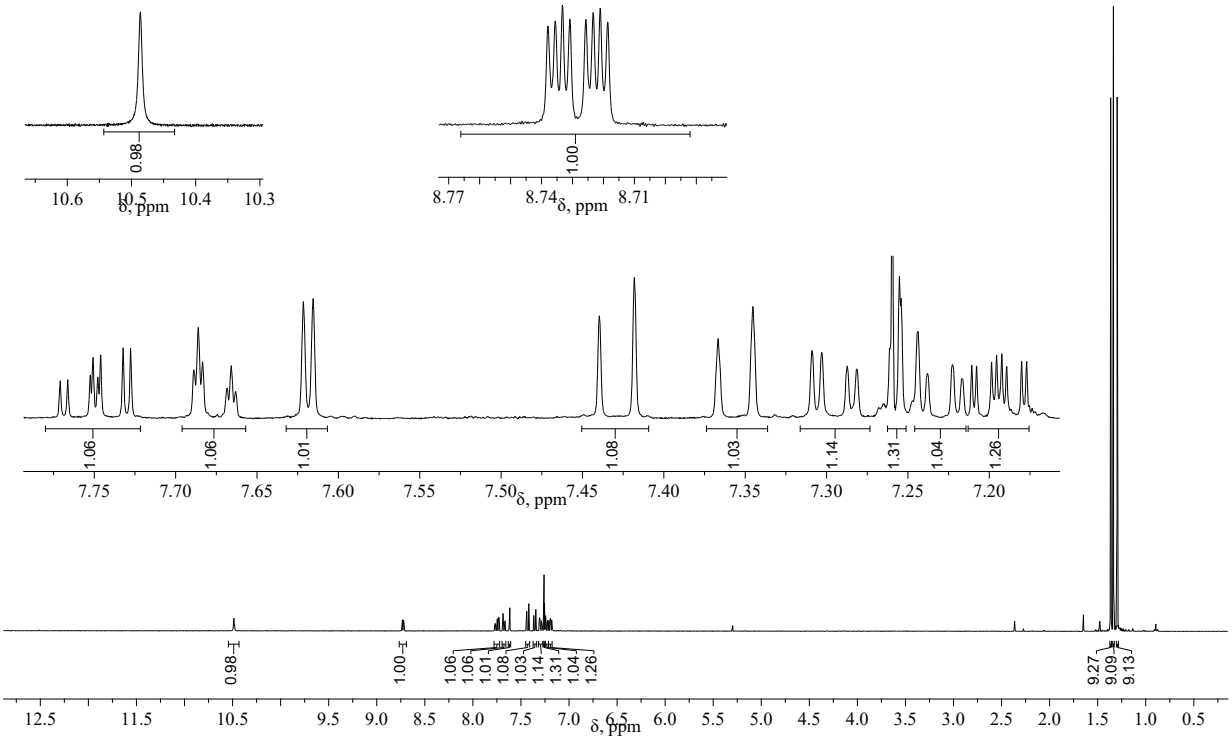
9. HMBC spectrum of amine **1** in $CDCl_3$



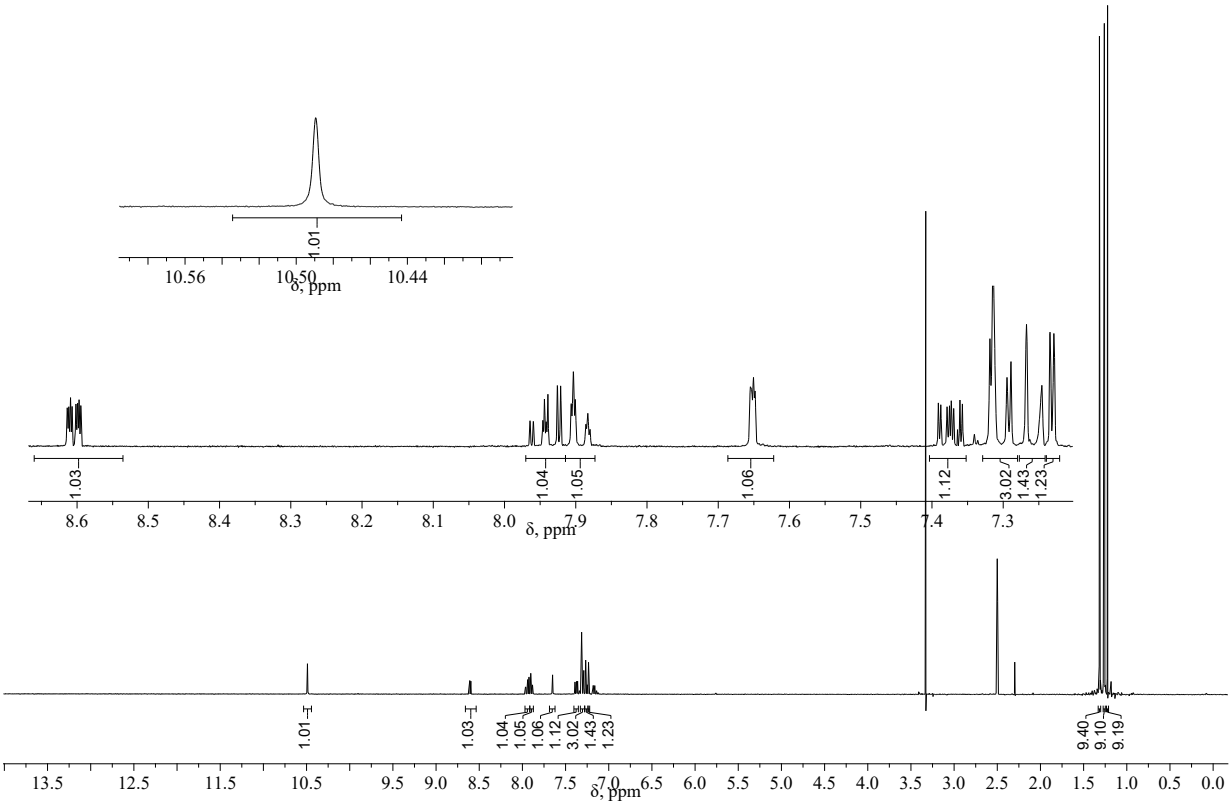
10. HSQC spectrum of amine **1** in $CDCl_3$



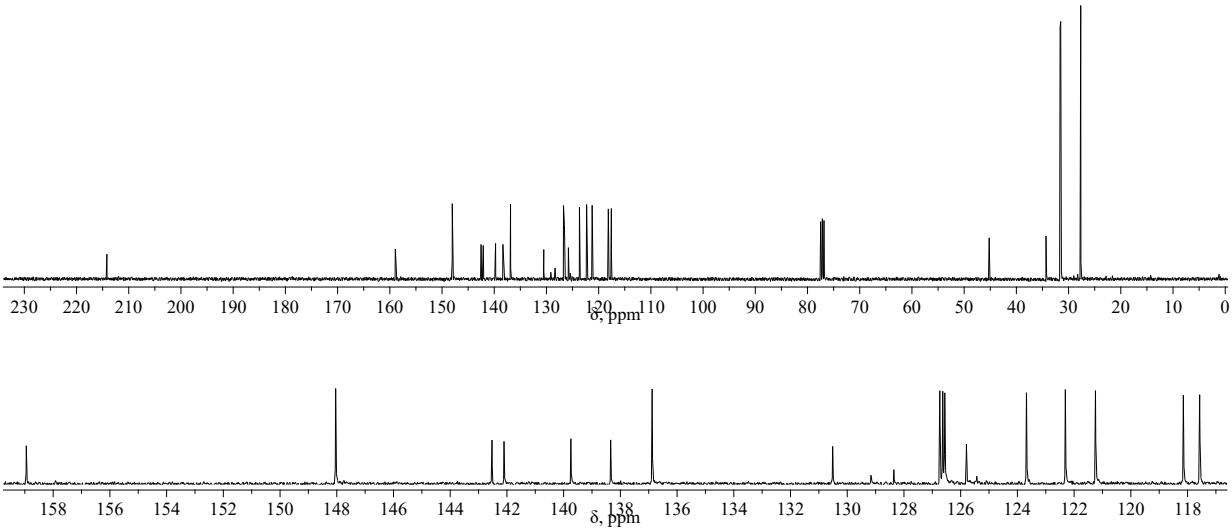
11. ^{1}H NMR spectrum of amine **2** in $CDCl_3$



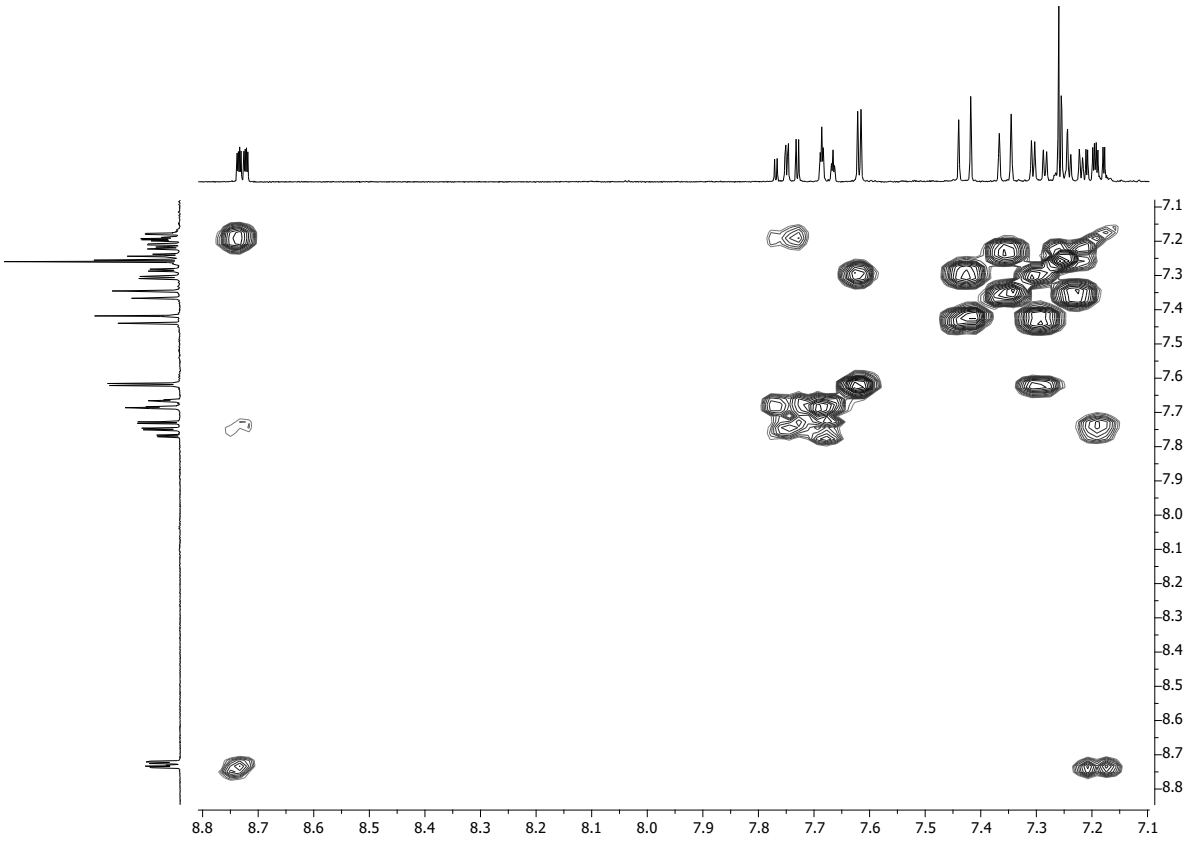
12. ^{1}H NMR spectrum of amine **2** in DMSO-d_6



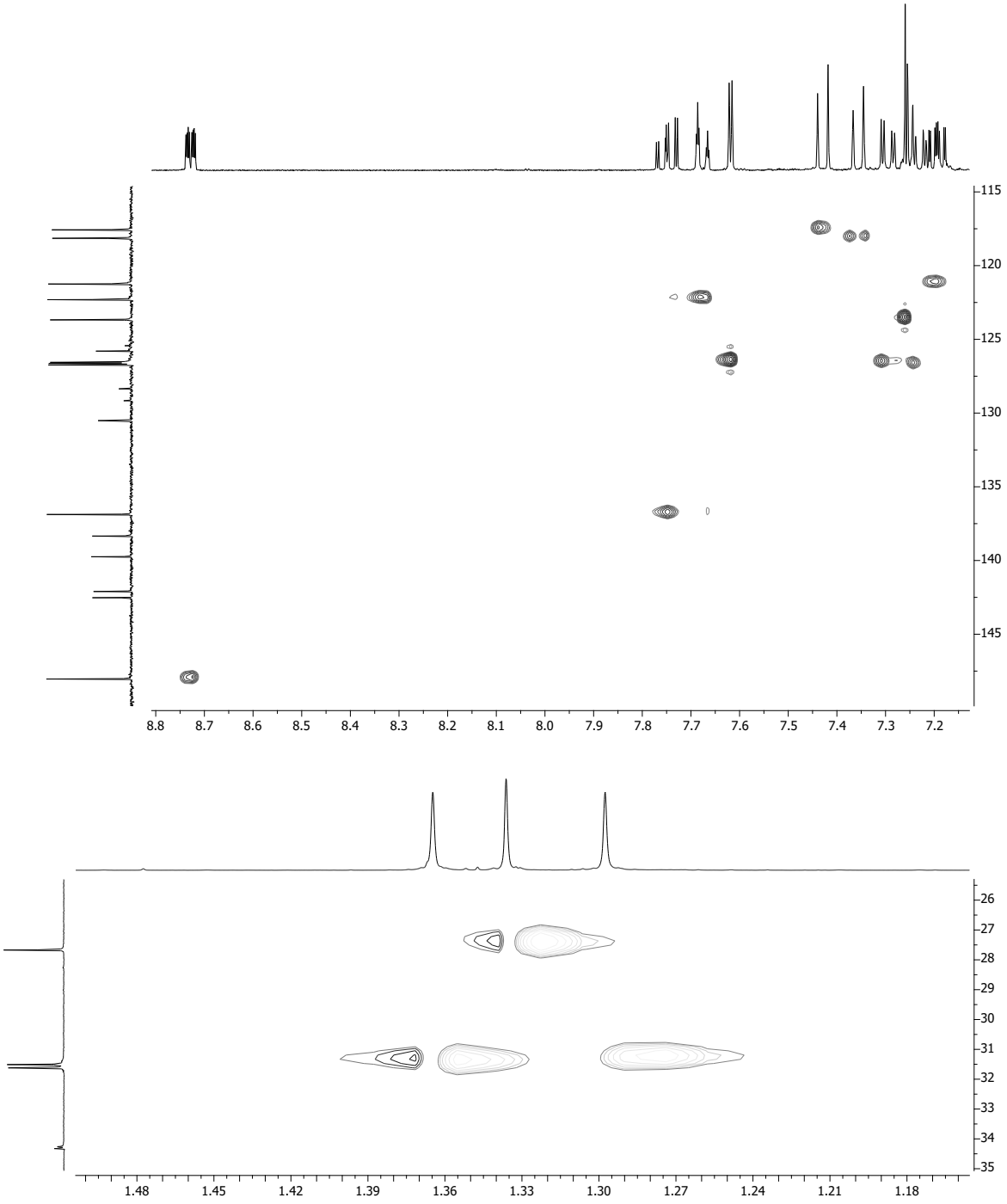
13. ^{13}C NMR spectrum of amine **2** in $CDCl_3$



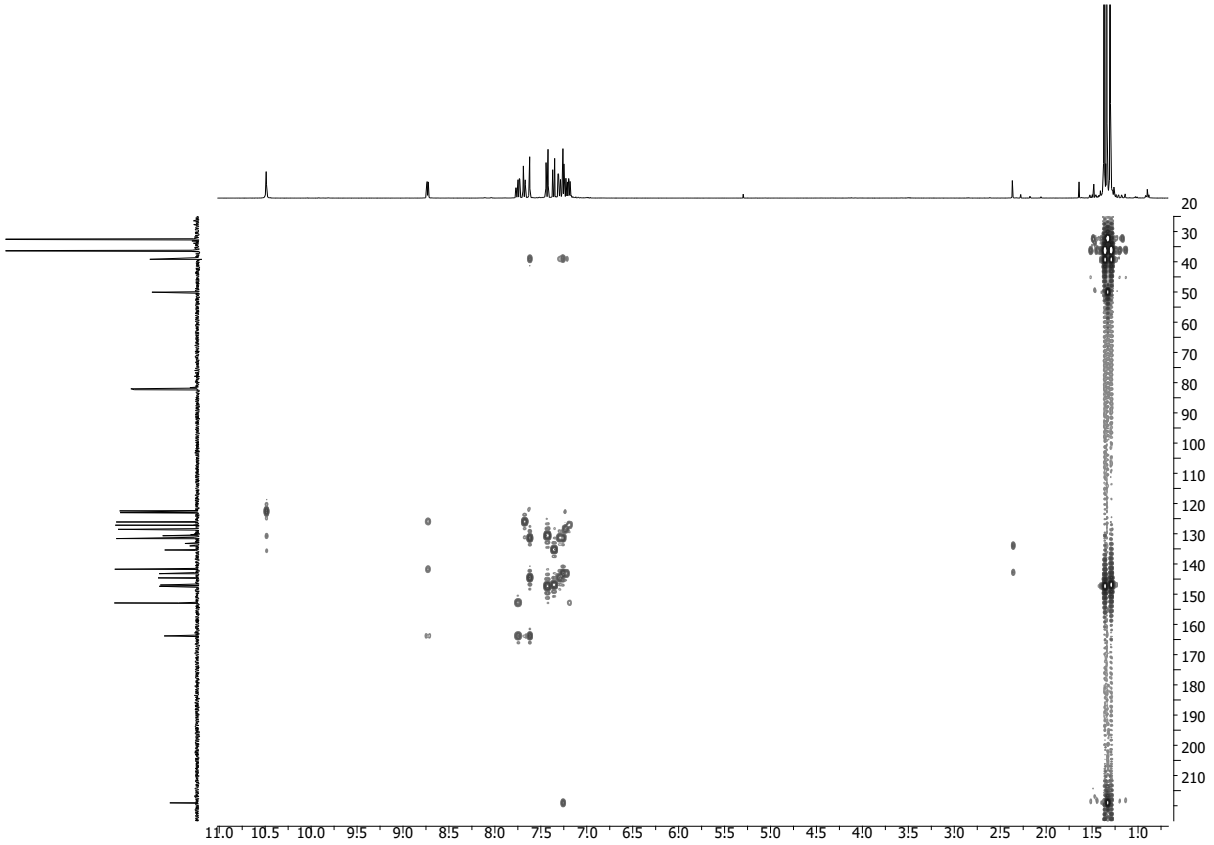
14. COSY spectrum of amine **2** in $CDCl_3$

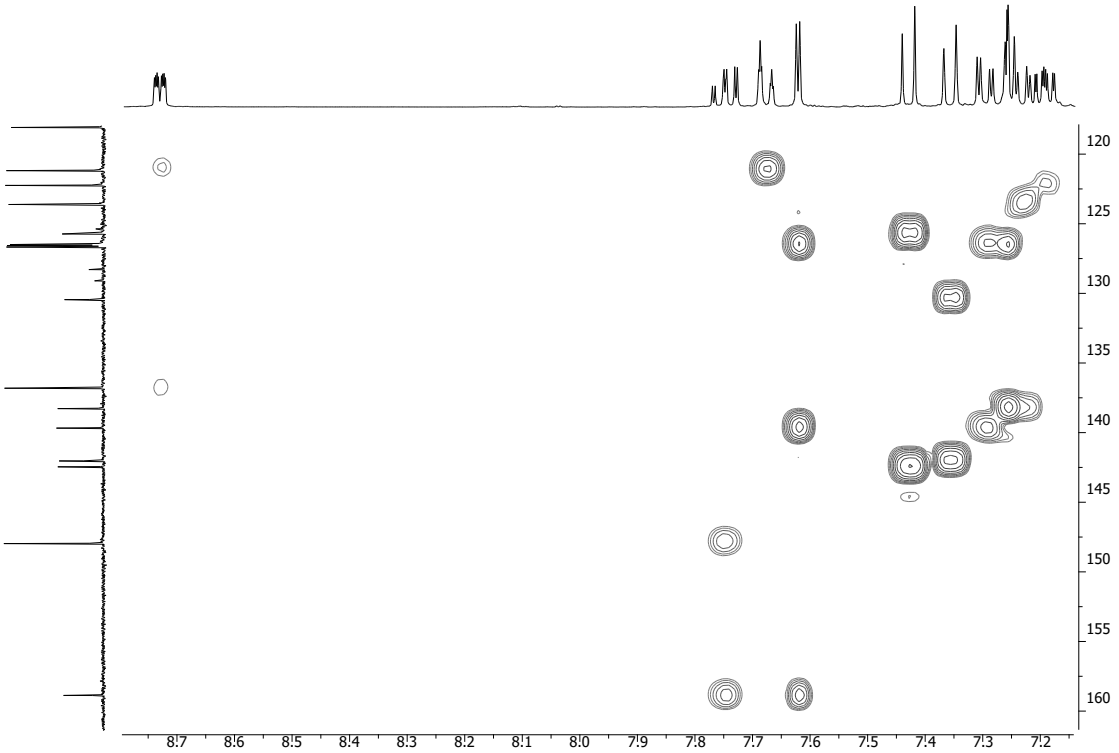


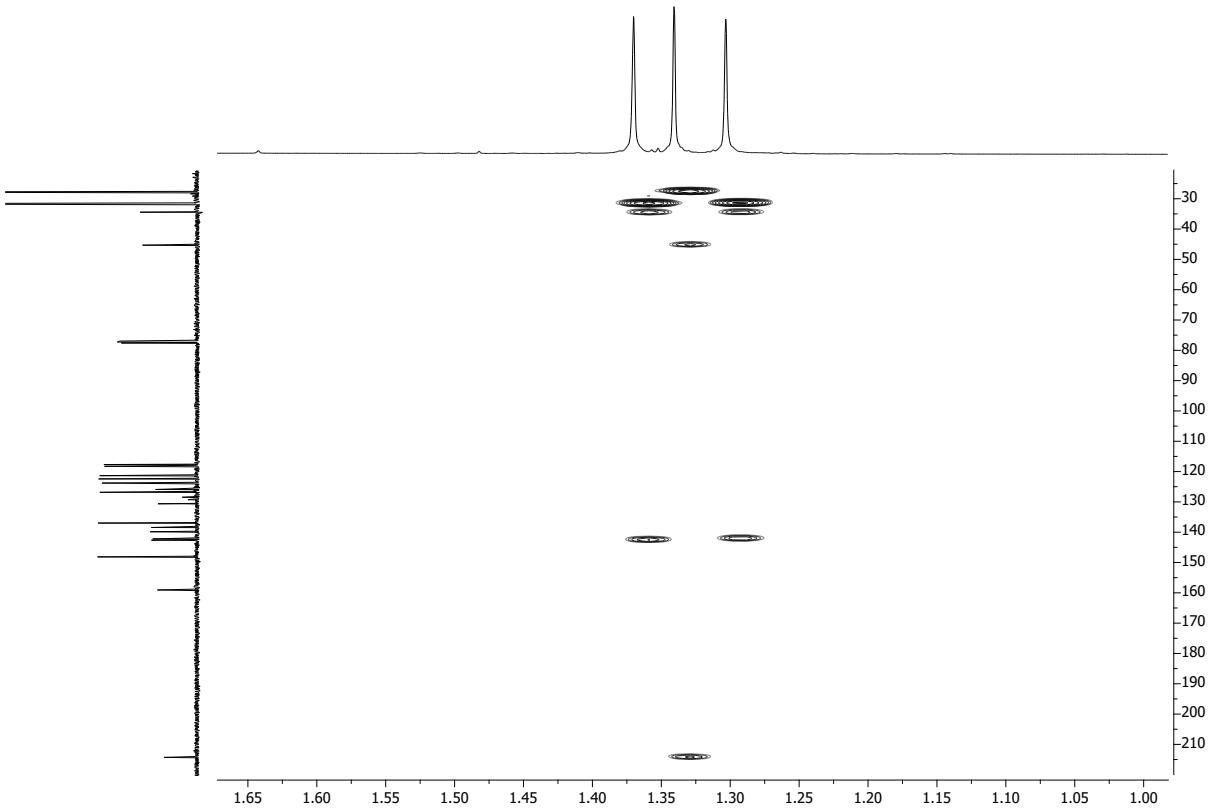
15. HSQC spectrum of amine **2** in $CDCl_3$



16. HMBC spectrum of amine **2** in $CDCl_3$

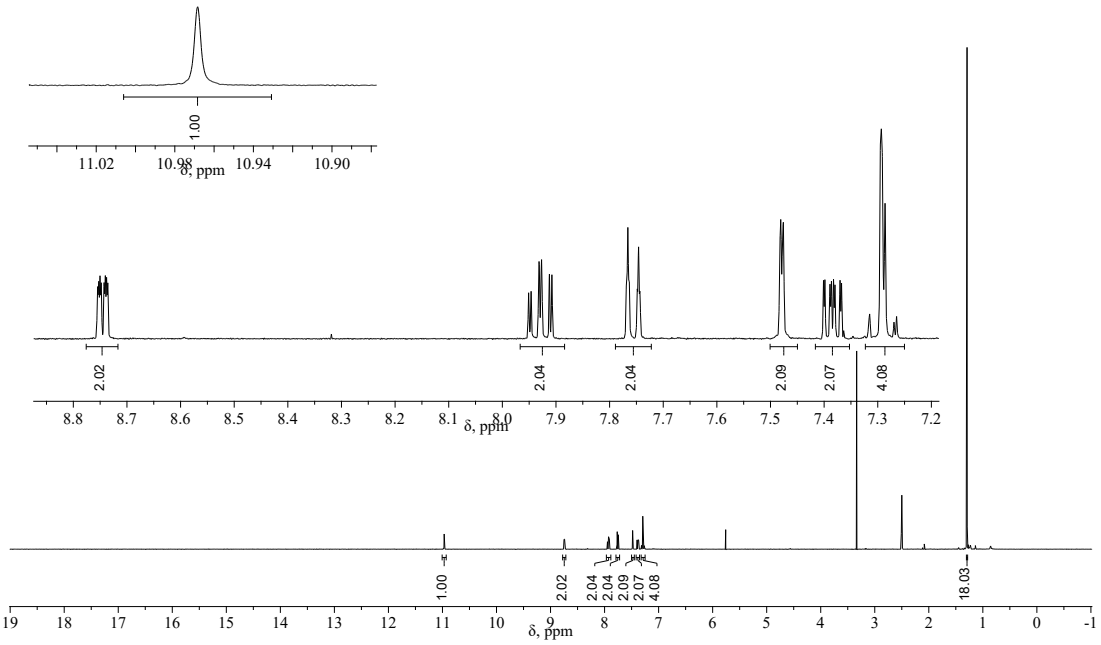




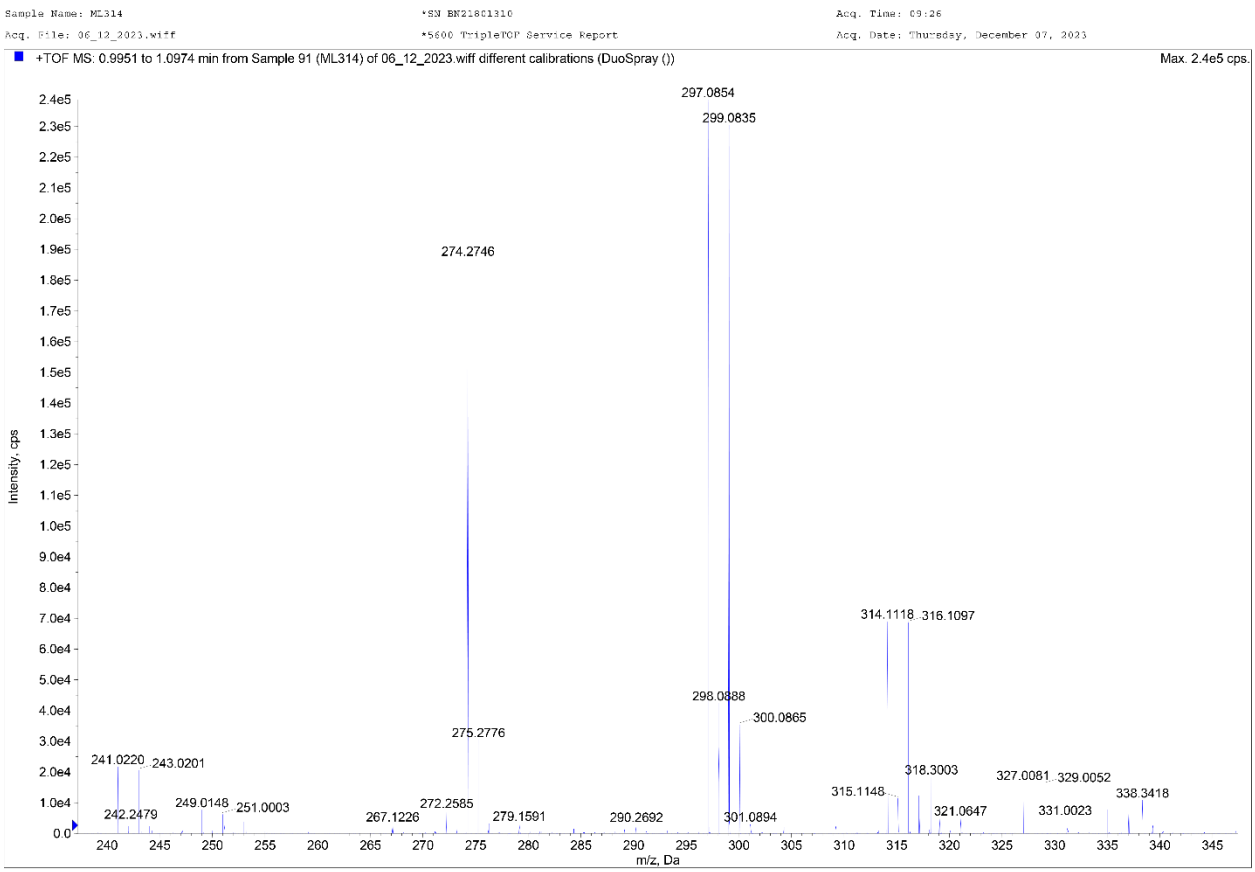


17. ^{1}H NMR spectrum of amine **3** (bis(4-(tert-butyl)-2-(pyridin-2-yl)phenyl)amine) in DMSO-d_6

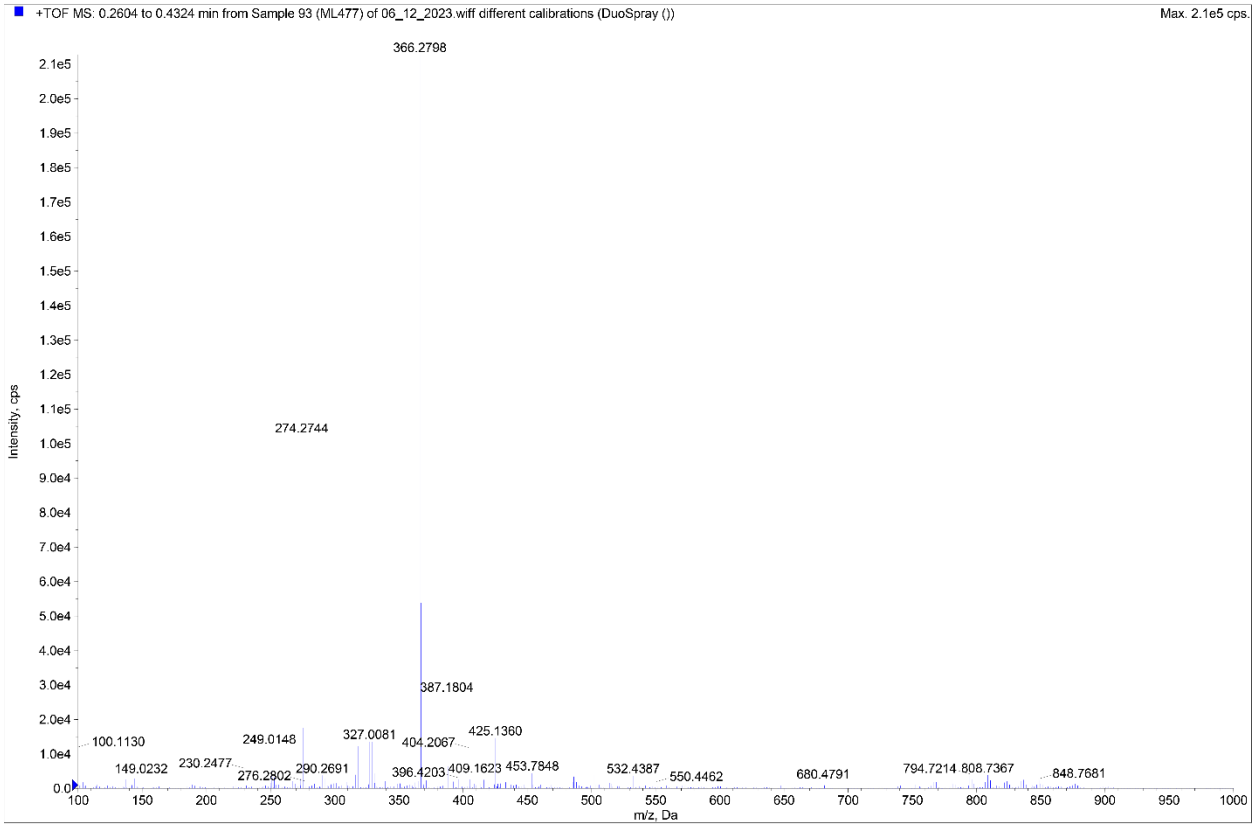
^{1}H NMR (DMSO-d_6, δ, ppm): 1.29 (s, 9H), 7.33 – 7.26 (m, 2H), 7.38 (ddd, ^{3}J = 7.5, ^{3}J = 4.9, ^{4}J = 1.1 Hz, 1H), 7.48 (d, ^{4}J = 1.9 Hz, 1H), 7.76 (ddd, ^{3}J = 8.1, ^{4}J = 1.1 Hz, ^{5}J = 0.9 Hz, 1H), 7.93 (ddd, ^{3}J = 8.1, ^{3}J = 7.5, ^{4}J = 1.8 Hz, 1H), 8.75 (ddd, ^{3}J = 4.9, ^{4}J = 1.8, ^{5}J = 0.9 Hz, 1H), 10.97 (s, 1H, *NH*),



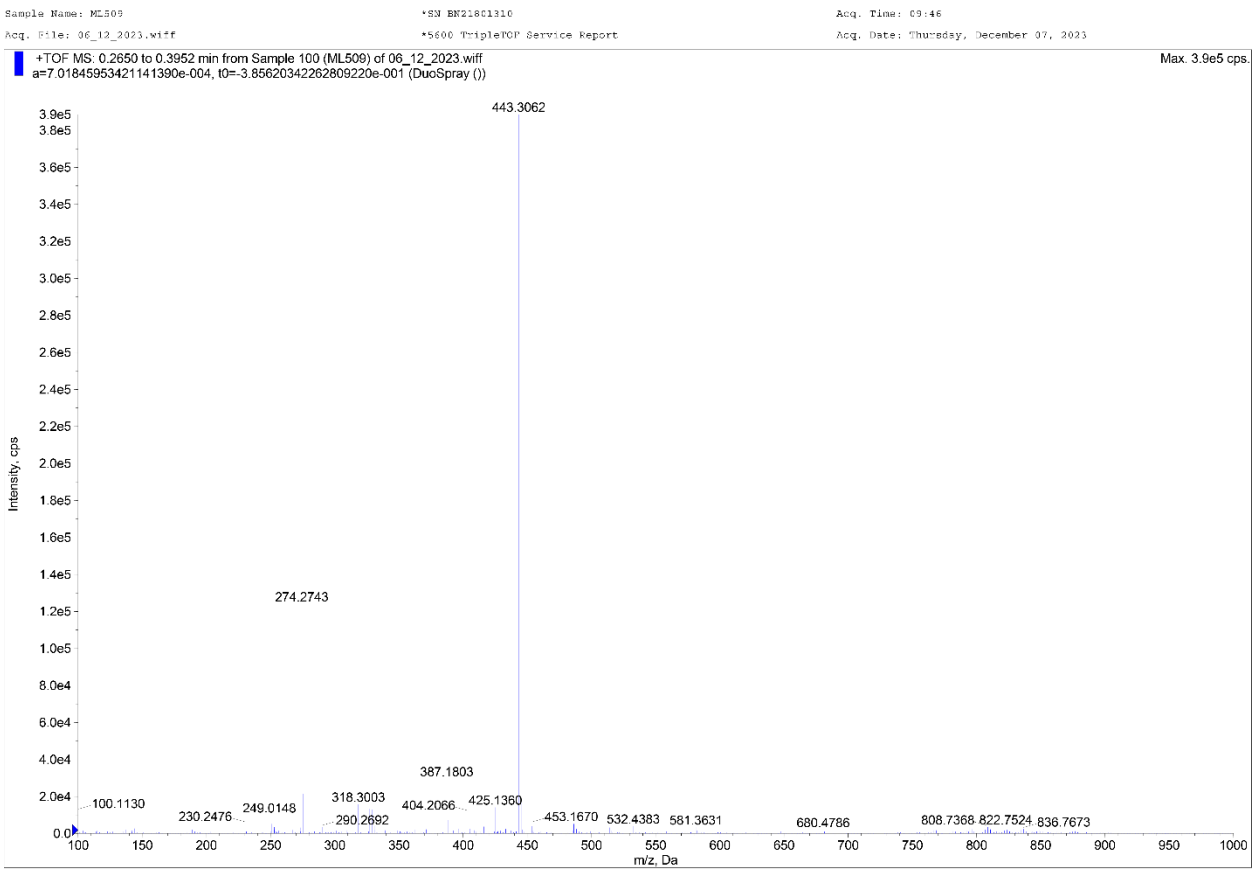
18. ESI-HRMS of 1-(2-bromo-5-*tert*-butylphenyl)-2,2-dimethylpropan-1-one



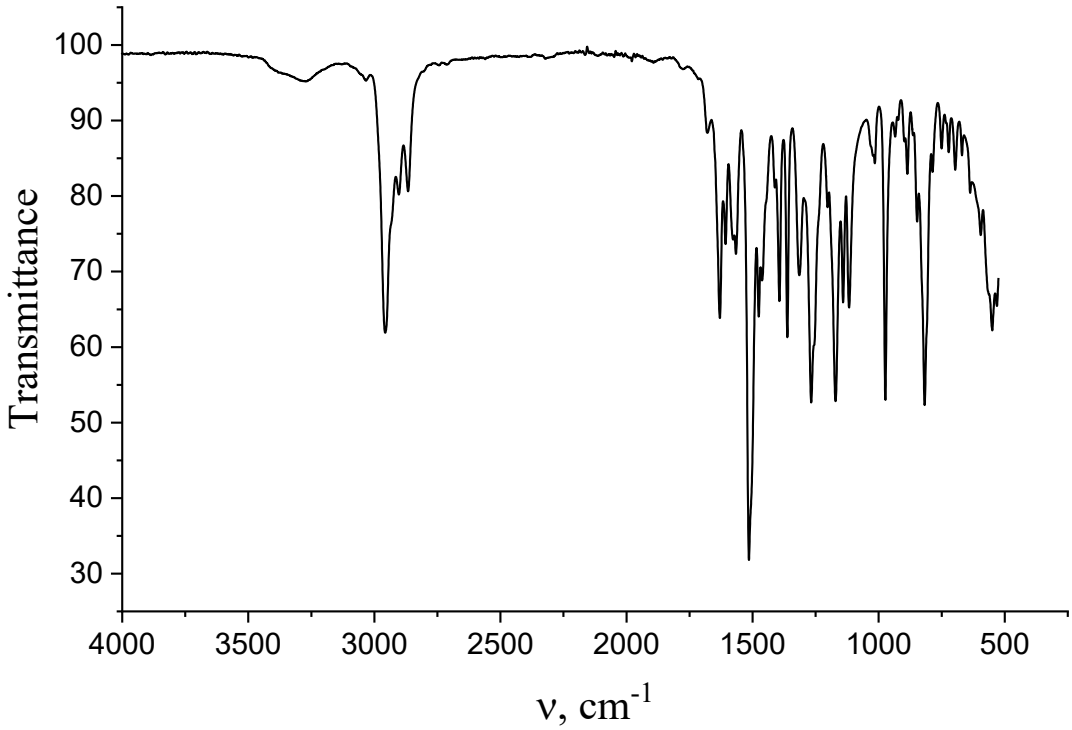
19. ESI-HRMS of amine **1**



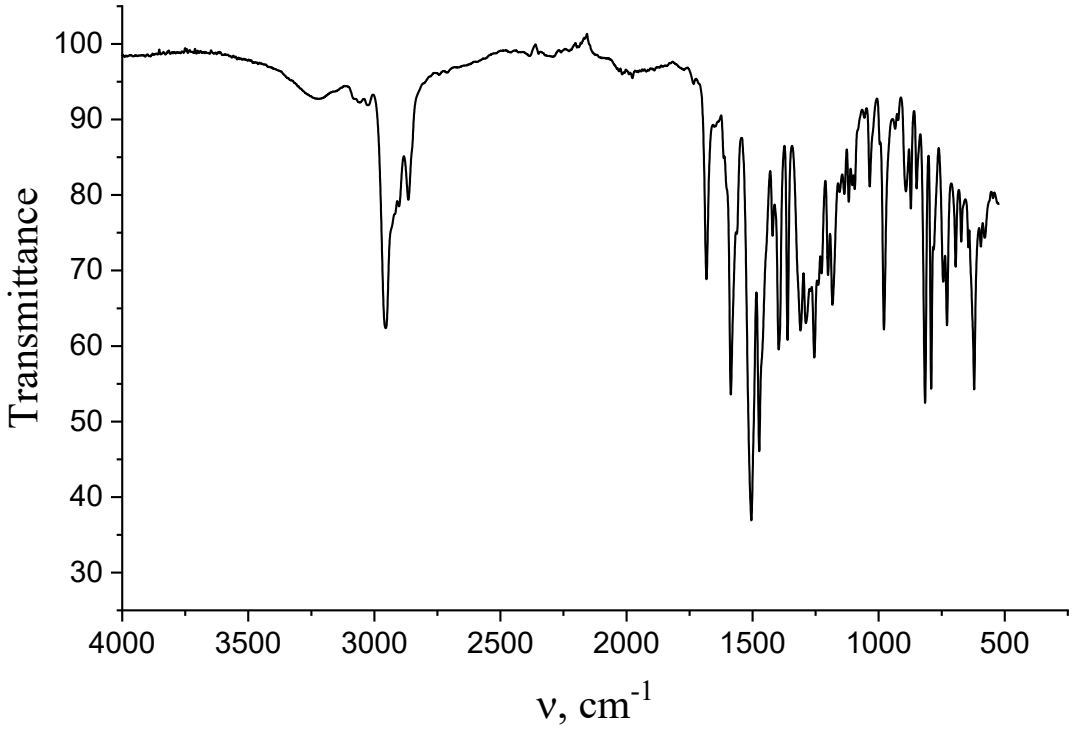
20. ESI-HRMS of amine **2**



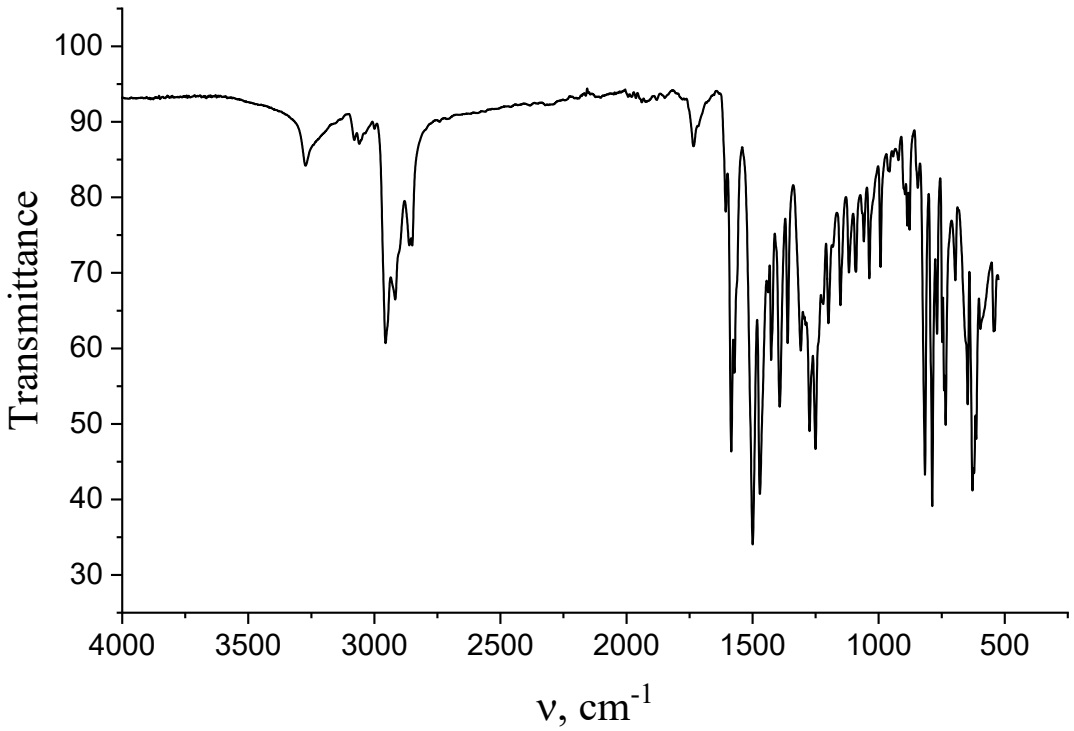
21. IR spectrum of amine **1**



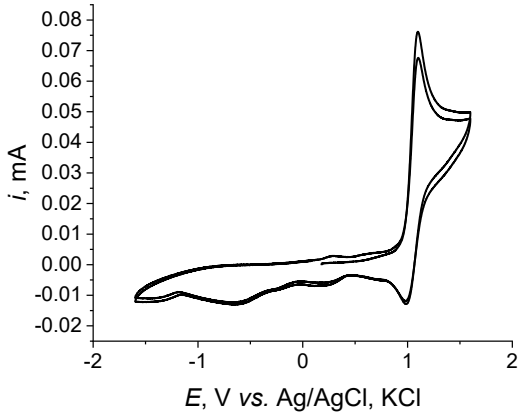
22. IR spectrum of amine **2**



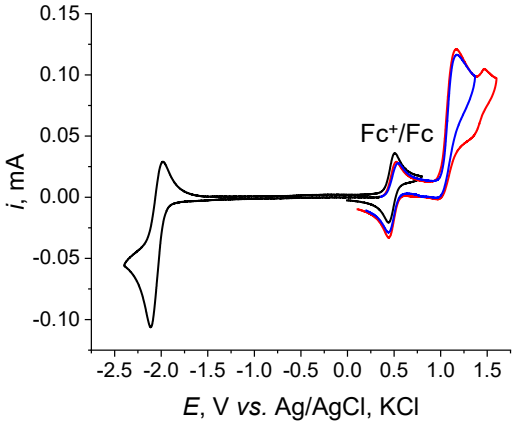
23. IR spectrum of amine **3**



24. Cyclic voltammograms of amine **1**

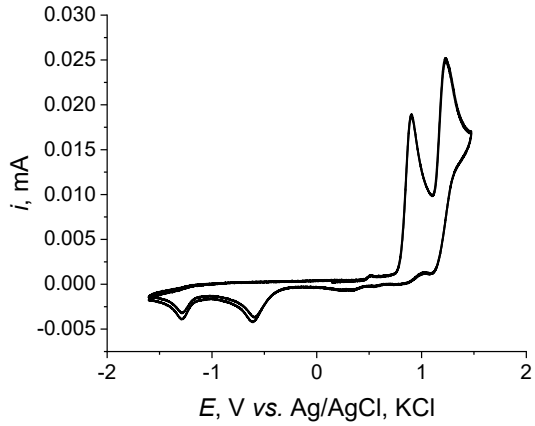


CV at Pt electrode, 1 V/s

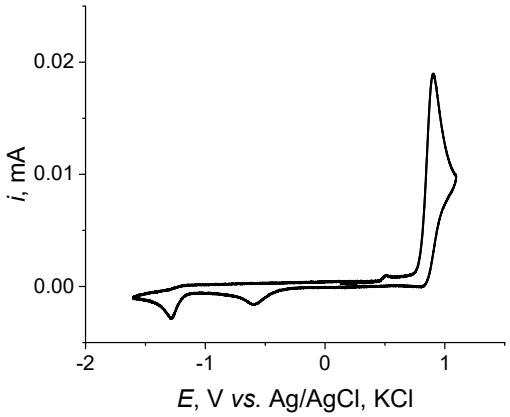


CV at GC electrode, 0.1 V/s, ferrocene added as an internal standard

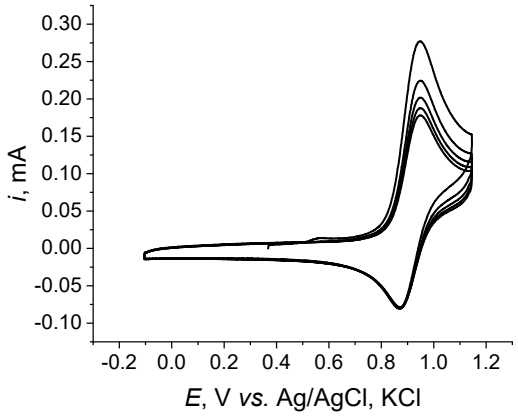
25. Cyclic voltammograms of amine **2**



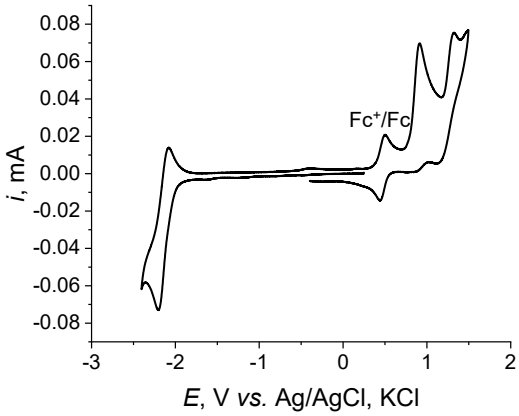
CV at Pt electrode, 0.1 V/s.



CV at Pt electrode, 0.1 V/s.

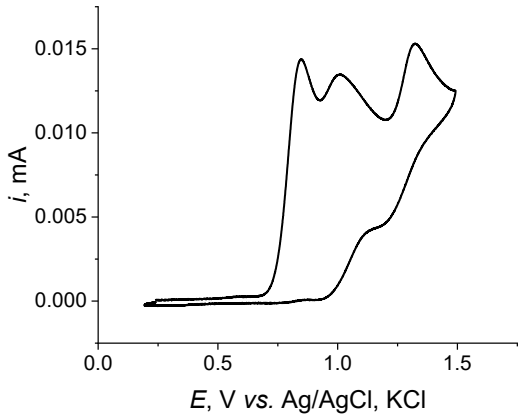


CV at Pt electrode, 20 V/s

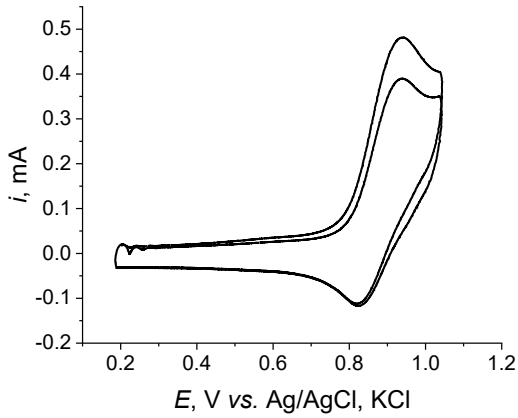


CV at glassy carbon electrode, 20 V/s ferrocene added as an internal standard

26. Cyclic voltammograms of amine **3**



CV at Pt electrode, 0.1 V/s.



CV at Pt electrode, 100 V/s.

27. Cartesian coordinates and electronic energies for optimized structure of amine **3**

PBEh-3c, SMD solvation model, acetonitrile as a solvent			E_e = -1324.493343746329 Hartree
Element	x, Å	y, Å	z, Å
C	-3.563977000000	0.596713000000	-0.222341000000
C	-3.820962000000	-0.761694000000	-0.319576000000
C	-2.706056000000	-1.604601000000	-0.302916000000
C	-1.421948000000	-1.110009000000	-0.210845000000
C	-1.166453000000	0.264982000000	-0.111826000000
C	-2.276711000000	1.133962000000	-0.105545000000
N	0.125270000000	0.751488000000	-0.043238000000
C	1.243241000000	0.045022000000	0.373052000000
C	2.491148000000	0.196584000000	-0.259340000000
C	1.166014000000	-0.835197000000	1.460014000000
C	2.264636000000	-1.547778000000	1.893351000000
C	3.515125000000	-1.411917000000	1.282211000000
C	3.591221000000	-0.523509000000	0.221704000000
C	-2.142080000000	2.600509000000	0.015073000000
C	-3.072134000000	3.353015000000	0.737946000000
N	-1.108845000000	3.183071000000	-0.593728000000
C	-0.973255000000	4.500680000000	-0.529800000000
C	-1.861949000000	5.324645000000	0.139701000000
C	-2.931318000000	4.728072000000	0.792436000000
C	-5.224718000000	-1.341255000000	-0.453154000000
C	-6.296934000000	-0.253071000000	-0.480637000000
C	-5.506498000000	-2.265736000000	0.737807000000
C	-5.325844000000	-2.148120000000	-1.753889000000
H	-4.389997000000	1.294697000000	-0.251764000000
H	-2.832839000000	-2.677508000000	-0.386493000000
H	-0.594218000000	-1.806303000000	-0.233974000000
H	0.224977000000	-0.952961000000	1.981933000000
H	2.142277000000	-2.211936000000	2.740506000000

C	4.711264000000	-2.207567000000	1.791979000000
H	4.542755000000	-0.360920000000	-0.266411000000
H	-3.884583000000	2.869264000000	1.262993000000
H	-1.712167000000	6.395299000000	0.157264000000
H	-3.642725000000	5.325737000000	1.347566000000
H	-6.168649000000	0.429725000000	-1.322978000000
H	-7.283474000000	-0.709342000000	-0.579834000000
H	-6.304481000000	0.340082000000	0.435936000000
H	-4.795649000000	-3.092101000000	0.792965000000
H	-5.457111000000	-1.720018000000	1.682274000000
H	-6.505994000000	-2.699278000000	0.656980000000
H	-5.138687000000	-1.518715000000	-2.626175000000
H	-4.614865000000	-2.975848000000	-1.782452000000
H	-6.325499000000	-2.575324000000	-1.860821000000
C	2.688478000000	1.079832000000	-1.427124000000
H	0.287858000000	1.663662000000	-0.456255000000
H	-0.113339000000	4.919799000000	-1.040392000000
C	3.540433000000	0.712211000000	-2.471827000000
N	2.027542000000	2.237414000000	-1.447888000000
C	2.192976000000	3.060615000000	-2.474461000000
C	3.716764000000	1.579763000000	-3.534947000000
H	4.044102000000	-0.244790000000	-2.461928000000
H	4.372475000000	1.311532000000	-4.353180000000
C	3.033397000000	2.787516000000	-3.540834000000
H	3.139351000000	3.494772000000	-4.351824000000
H	1.628949000000	3.986170000000	-2.442952000000
C	5.976729000000	-1.933198000000	0.980829000000
C	4.986220000000	-1.837051000000	3.254892000000
C	4.399013000000	-3.706328000000	1.700209000000
H	6.800366000000	-2.534191000000	1.370244000000
H	5.854834000000	-2.193955000000	-0.072369000000
H	6.285559000000	-0.887321000000	1.035904000000
H	5.238098000000	-4.294208000000	2.079378000000
H	3.519667000000	-3.980817000000	2.285061000000
H	4.220558000000	-4.012216000000	0.667258000000
H	5.837448000000	-2.404468000000	3.638045000000
H	5.221728000000	-0.775741000000	3.357077000000
H	4.133482000000	-2.051853000000	3.901134000000