Supporting Information

for

Meta-metallation of *N*,*N*-dimethylaniline: contrasting direct sodium-mediated zincation with indirect sodiation-dialkylzinc co-complexation

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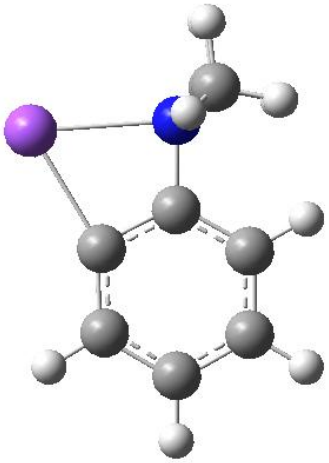
Computational details and NMR spectra for compounds 3, 4, 5 and 6

DFT calculations were carried out using the Gaussian G03 computational package [1]. The B3LYP density functionals [2,3] were used along with the 6-311G(d,p) basis set [4,5]. After the geometry optimisation of each molecule, a frequency analysis was carried out. The resulting calculated zero-point energy was added to the electronic energy and this is the energy value quoted below.

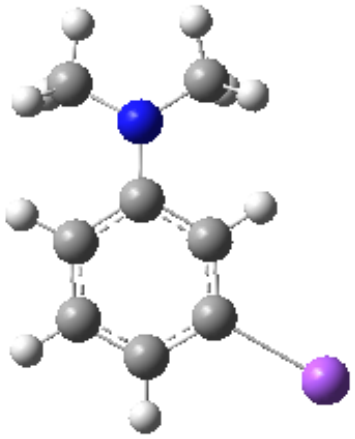
***o*-NaC$_6$H$_4$-NMe$_2$**



Principal bond lengths (Å) and angles (°)

Na-N	2.289 Å	C-Na-N	63.0°
Na-C	2.439 Å	Na-N-C	85.6°
Na-C$_i$	2.758 Å	N-C-C	117.8°
C$_i$-N	1.487 Å	C-C-Na	93.6°

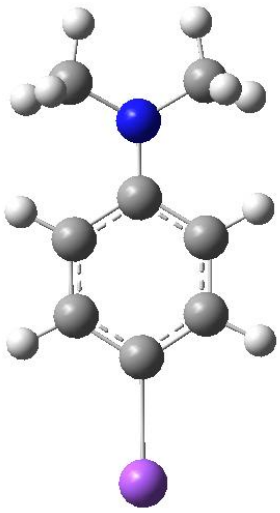
***m*-NaC$_6$H$_4$-NMe$_2$**



Principal bond lengths (Å) and angles (°)

Na-C	2.301 Å
Na-C-C	122.8 ° 120.5 °

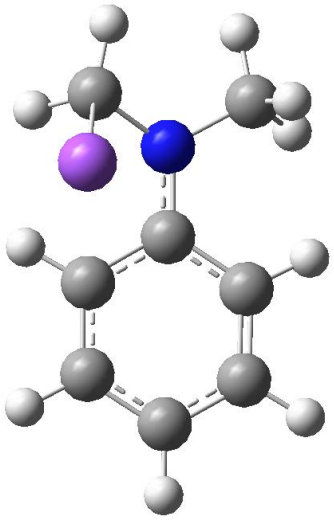
***p*-NaC$_6$H$_4$-NMe$_2$**



Principal bond lengths (Å) and angles (°)

Na-C	2.301 Å
Na-C-C	123.0 °

C_6H_5-N(Me)CH_2Na



Principal bond lengths (Å) and angles (°)

Na-C	2.387 Å	N-C_i	1.371 Å
Na..C_i	3.023 Å	N-C_{Me}	1.469 Å 1.451Å
Na..C_o	2.862 Å		
Na..N	2.959 Å		

Energies/au

***o*-NaC_6H_4-NMe_2**	-527.821237
***m*-NaC_6H_4-NMe_2**	-527.807529
***p*-NaC_6H_4-NMe_2**	-527.807352
C_6H_5-N(Me)CH_2Na	-527.818668

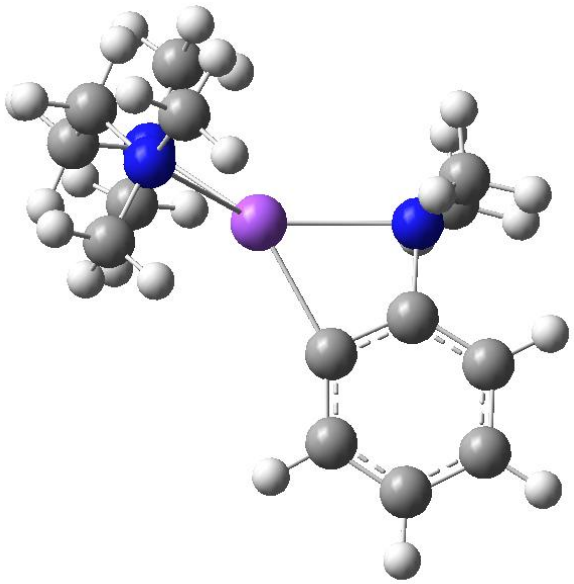
Relative energies/kcal mol^{-1}

ortho:*meta*:*para*:*methyl* 0.00:8.60:8.71:1.61

[*o*-NaC_6H_4-NMe_2(TMEDA)]

Principal bond lengths (Å) and angles (°)

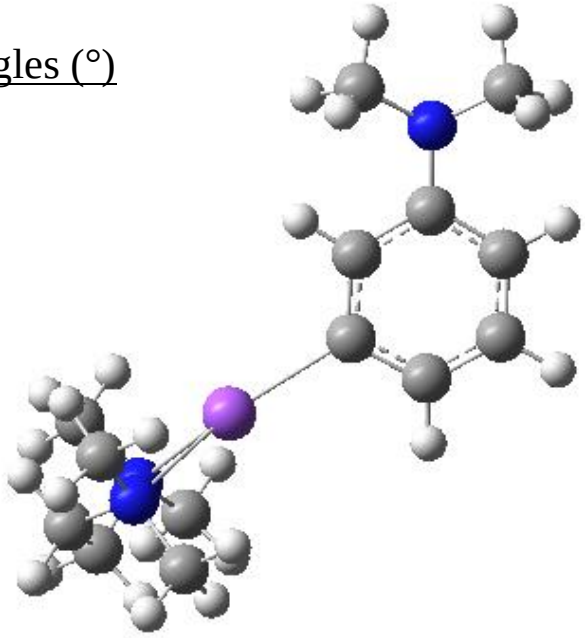
Na-N_{tm}	2.521 Å 2.533 Å
Na-N	2.501 Å
Na-C	2.357 Å
C_i-N	1.488 Å
N_{tm}-Na-N_{tm}	74.5 °
C-Na-N	61.1 °
Na-N-C	86.8 °
N-C-C	117.5 °
C-C-Na	94.6 °



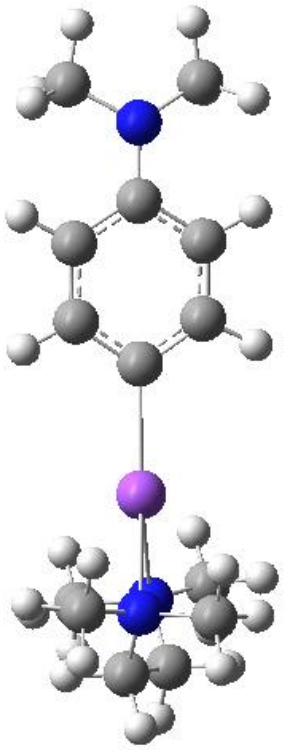
[*m*-NaC_6H_4-NMe_2(TMEDA)]

Principal bond lengths (Å) and angles (°)

Na-C	2.356 Å
Na-N	2.513 Å 2.517 Å
Na-C-C	119.5 ° 125.4 °
N-Na-N	74.7 °



[*p*-NaC_6H_4-NMe_2(TMEDA)]

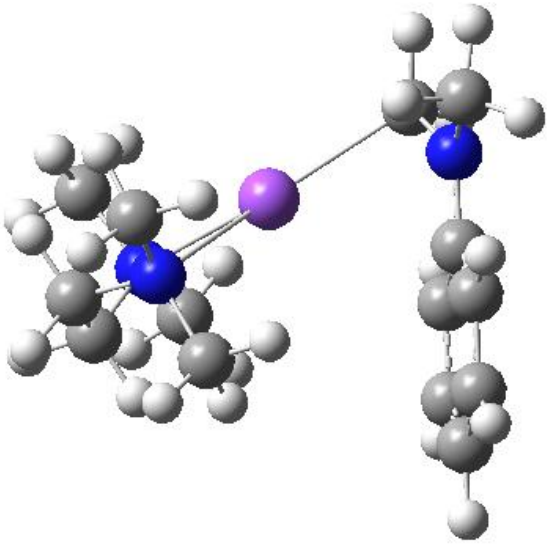


Principal bond lengths (Å) and angles (°)

Na-C	2.351 Å
Na-N	2.518 Å 2.517 Å
Na-C-C	123.8 ° 123.7 °
N-Na-N	74.6 °

[{C_6H_5-N(Me)CH_2Na}(TMEDA)]

Principal bond lengths (Å) and angles (°)



Na-C	2.424 Å
Na..C_i	3.118 Å
Na..C_o	2.963 Å
N-C_{Me}	1.489 Å 1.448 Å
Na-N	2.518 Å 2.527 Å
N-Na-N	74.8 °

Energies/au

[*o*-NaC_6H_4-NMe_2(TMEDA)]	-875.471777
[*m*-NaC_6H_4-NMe_2(TMEDA)]	-875.460731
[*p*-NaC_6H_4-NMe_2(TMEDA)]	-875.460371
[{C_6H_5-N(Me)CH_2Na}(TMEDA)]	-875.469626

Relative energies kcal mol^{-1}

ortho:*meta*:*para*:methyl 0.00:6.93:7.15:1.35

Energies of the reactions

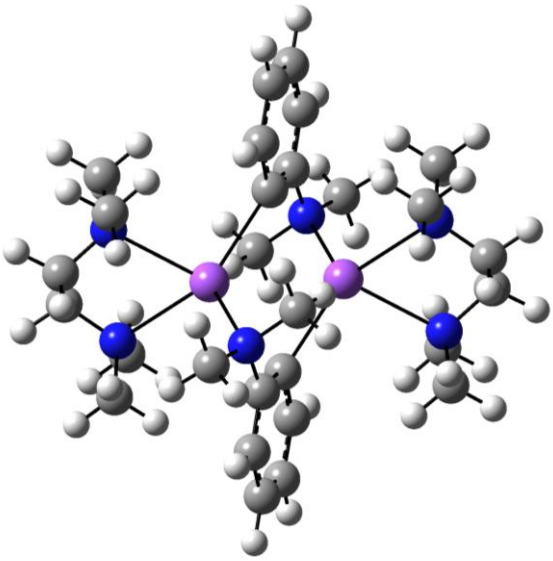
TMEDA·BuNa + C_6H_5-NMe_2 → BuH + TMEDA·NaC_6H_4-NMe_2

[*o*-NaC_6H_4-NMe_2(TMEDA)]	ΔE = -12.74 kcal mol^{-1}
[*m*-NaC_6H_4-NMe_2(TMEDA)]	ΔE = -5.81 kcal mol^{-1}
[*p*-NaC_6H_4-NMe_2(TMEDA)]	ΔE = -5.59 kcal mol^{-1}
[{C_6H_5-N(Me)CH_2Na}(TMEDA)]	ΔE = -11.39 kcal mol^{-1}

[*o*-NaC_6H_4-NMe_2(TMEDA)]$_2$

Principal bond lengths (Å) and angles (°)

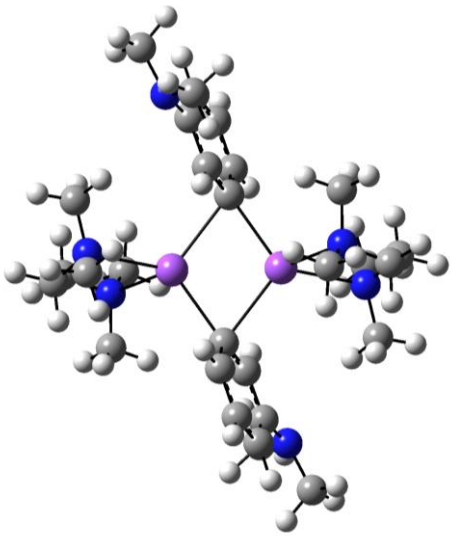
Na-N_{tm}	2.604 Å 2.674 Å
Na-N	2.662 Å
Na-C	2.594 Å 2.605 Å
C_i-N	1.461 Å
N_{tm}-Na-N_{tm}	70.6 °
C-Na-N	55.6 °
Na-N-C	85.3 °
N-C-C	117.0 °
C-C-Na	88.8 °
C-Na-C	105.3 °
Na-C-Na	74.7 °



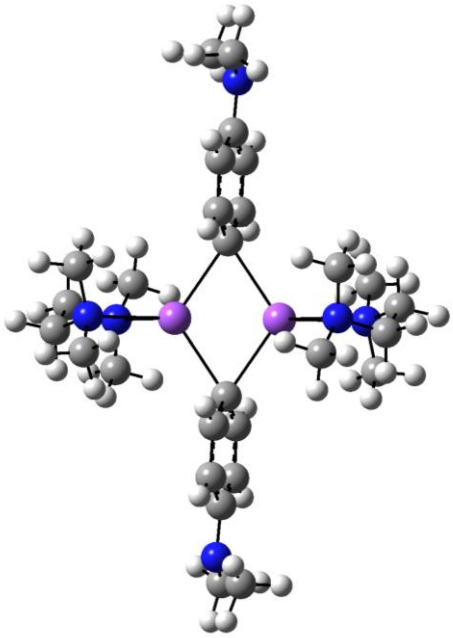
[*m*-NaC_6H_4-NMe_2(TMEDA)]$_2$

Principal bond lengths (Å) and angles (°)

Na-C	2.571 Å 2.532 Å
Na-N	2.546 Å 2.546 Å
Na-C-Na	72.1 °
C-Na-C	107.9 °
N-Na-N	74.7 °



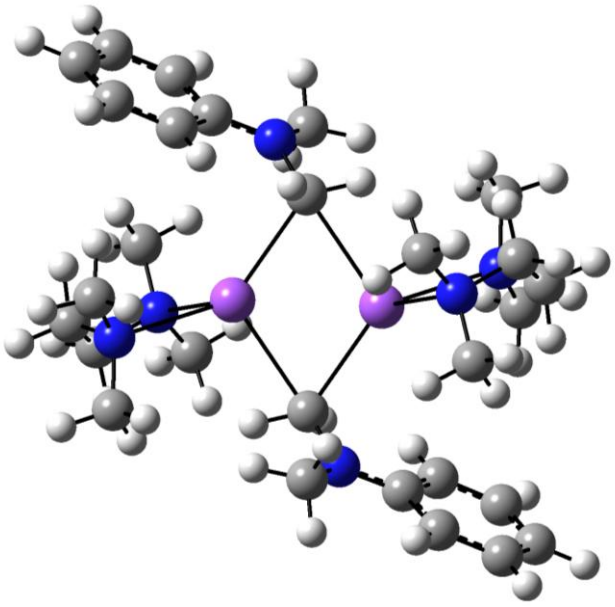
[*p*-NaC$_6$H$_4$-NMe$_2$(TMEDA)]$_2$



Principal bond lengths (Å) and angles (°)

Na-C	2.551 Å 2.548 Å
Na-N	2.545 Å 2.544 Å
Na-C-Na	69.1 °
C-Na-C	110.9 °
N-Na-N	74.7 °

[{C$_6$H$_5$-N(Me)CH$_2$Na}(TMEDA)]$_2$



Principal bond lengths (Å) and angles (°)

Na-C	2.598 Å 2.563 Å
Na..C$_i$	3.632 Å
Na..C$_o$	4.320 Å
N-C$_{Me}$	1.496 Å 1.459 Å
Na-N	2.581 Å 2.587 Å
N-Na-N	73.5 °
Na-C-Na	74.1 °
C-Na-C	105.9 °

Energies/au

[*o*-NaC_6H_4-NMe_2(TMEDA)]$_2$	-1750.978739
[*m*-NaC_6H_4-NMe_2(TMEDA)]$_2$	-1750.971326
[*p*-NaC_6H_4-NMe_2(TMEDA)]$_2$	-1750.969999
[{C_6H_5-N(Me)CH_2Na}(TMEDA)]$_2$	-1750.965031

Relative energies/kcal mol^{-1}

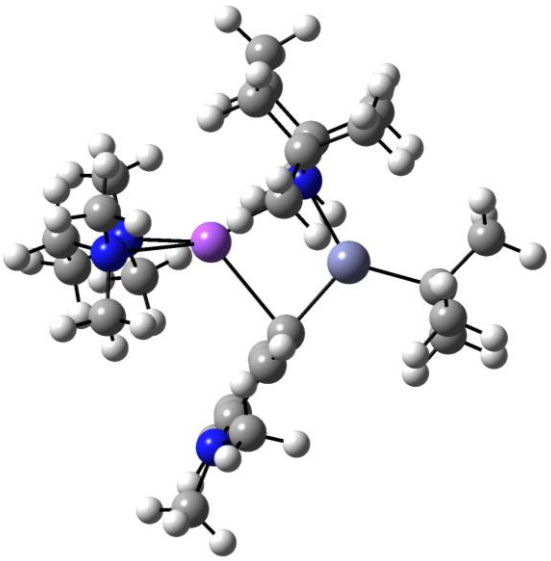
ortho:*meta*:*para*:methyl 0.00:4.65:5.48:8.60

Energies of the reactions

2 TMEDA·BuNa + 2 C_6H_5-NMe_2 → 2 BuH + [TMEDA·NaC_6H_4-NMe_2]$_2$

[*o*-NaC_6H_4-NMe_2(TMEDA)]$_2$	ΔE = -47.55 kcal mol^{-1}
[*m*-NaC_6H_4-NMe_2(TMEDA)]$_2$	ΔE = -42.90 kcal mol^{-1}
[*p*-NaC_6H_4-NMe_2(TMEDA)]$_2$	ΔE = -42.07 kcal mol^{-1}
[{C_6H_5-N(Me)CH_2Na}(TMEDA)]$_2$	ΔE = -38.95 kcal mol^{-1}

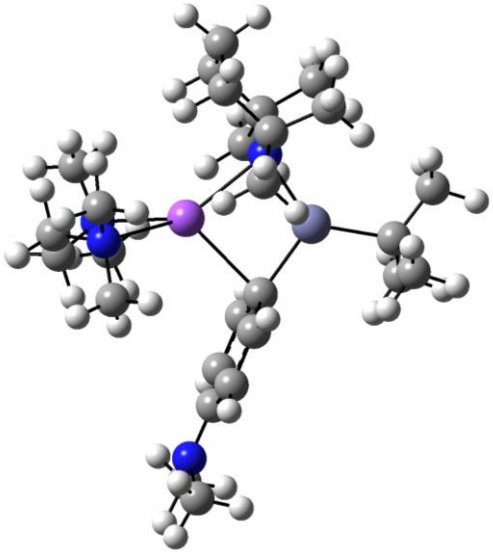
[(TMEDA)Na(μ-TMP)(μ-*m*-C_6H_4-NMe_2)Zn(*t*Bu)]



Principal bond lengths (Å)

Na-C	2.594
Na…C	3.070 3.212
Na-N_{TMP}	2.454
Na-N_{TMEDA}	2.602 2.606
Zn-C_{br}	2.084
Zn-C_{ter}	2.040
Zn-N	2.054

[(TMEDA)Na(μ-TMP)(μ-*p*-C_6H_4-NMe_2)Zn(*t*Bu)]

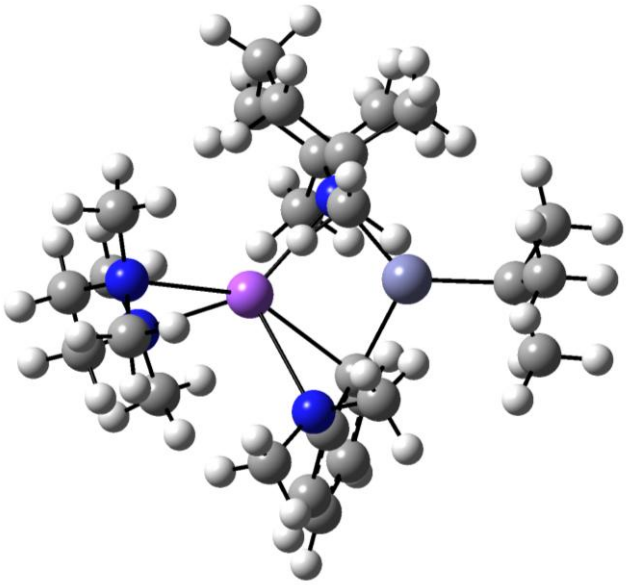


Principal bond lengths (Å)

Na-C	2.596
Na…C	3.178 3.239
Na-N_{TMP}	2.445
Na-N_{TMEDA}	2.599 2.591
Zn-C_{br}	2.083
Zn-C_{ter}	2.042
Zn-N	2.055

[(TMEDA)Na(μ-TMP)(μ-*o*-C_6H_4-NMe_2)Zn(*t*Bu)]

Principal bond lengths (Å)



Na-C	2.747
Na…C	2.937
Na-N	2.780
Na-N_{TMP}	2.497
Na-N_{TMEDA}	2.651 2.807
Zn-C_{br}	2.107
Zn-C_{ter}	2.055
Zn-N	2.048

Energies/au

[(TMEDA)Na(μ-TMP)(μ-*m*-C_6H_4-NMe_2)Zn(*t*Bu)]	-3221.012984
[(TMEDA)Na(μ-TMP)(μ-*p*-C_6H_4-NMe_2)Zn(*t*Bu)]	-3221.011929
[(TMEDA)Na(μ-TMP)(μ-*o*-C_6H_4-NMe_2)Zn(*t*Bu)]	-3221.006092
[(TMEDA)Na(μ-TMP)(μ-C_6H_5-$N(CH_2)Me$)Zn(*t*Bu)]	-3220.998630

Relative energies/kcal mol^{-1}

meta:*para*:*ortho*:methyl 0.00:0.66:4.32:9.01

Energies of the reactions

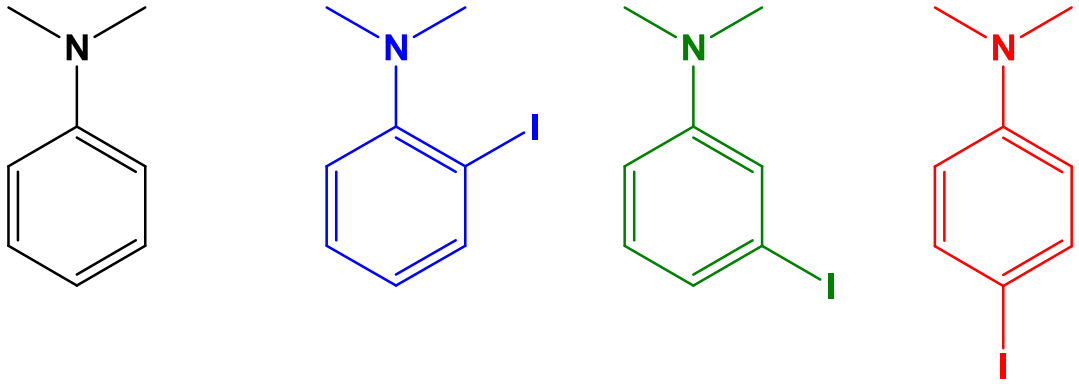
[(TMEDA)Na(μ-TMP)(μ-*t*Bu)Zn(*t*Bu)] + C_6H_5-NMe_2 →

BuH + [(TMEDA)Na(μ-TMP)(μ-C_6H_4-NMe_2)Zn(*t*Bu)]

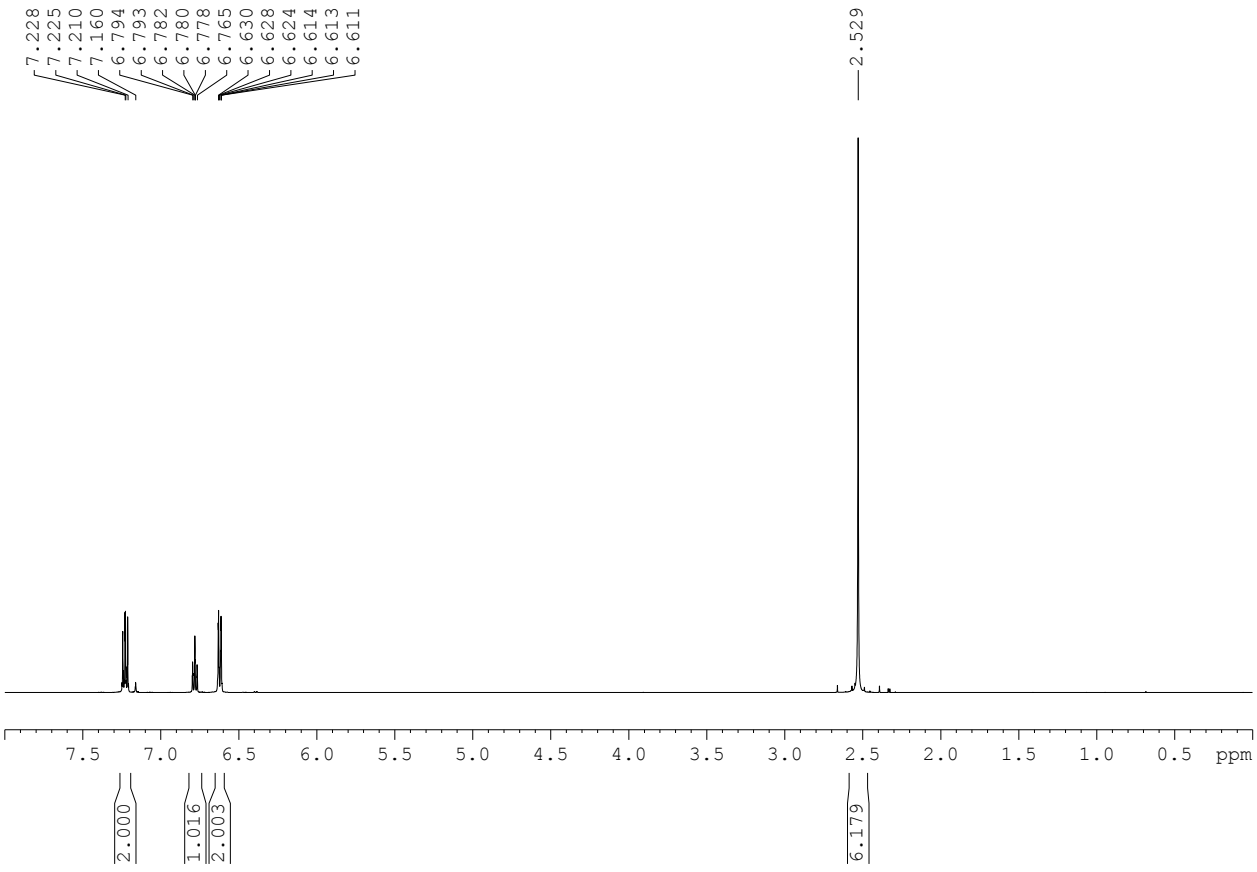
[(TMEDA)Na(μ-TMP)(μ-*m*-C_6H_4-NMe_2)Zn(*t*Bu)]	ΔE =-21.46 kcal mol^{-1}
[(TMEDA)Na(μ-TMP)(μ-*p*-C_6H_4-NMe_2)Zn(*t*Bu)]	ΔE=-20.80 kcal mol^{-1}
[(TMEDA)Na(μ-TMP)(μ-*o*-C_6H_4-NMe_2)Zn(*t*Bu)]	ΔE=-17.13 kcal mol^{-1}
[(TMEDA)Na(μ-TMP)(μ-C_6H_5-$N(CH_2)Me$)Zn(*t*Bu)]	ΔE=-12.45 kcal mol^{-1}

NMR spectroscopic analysis

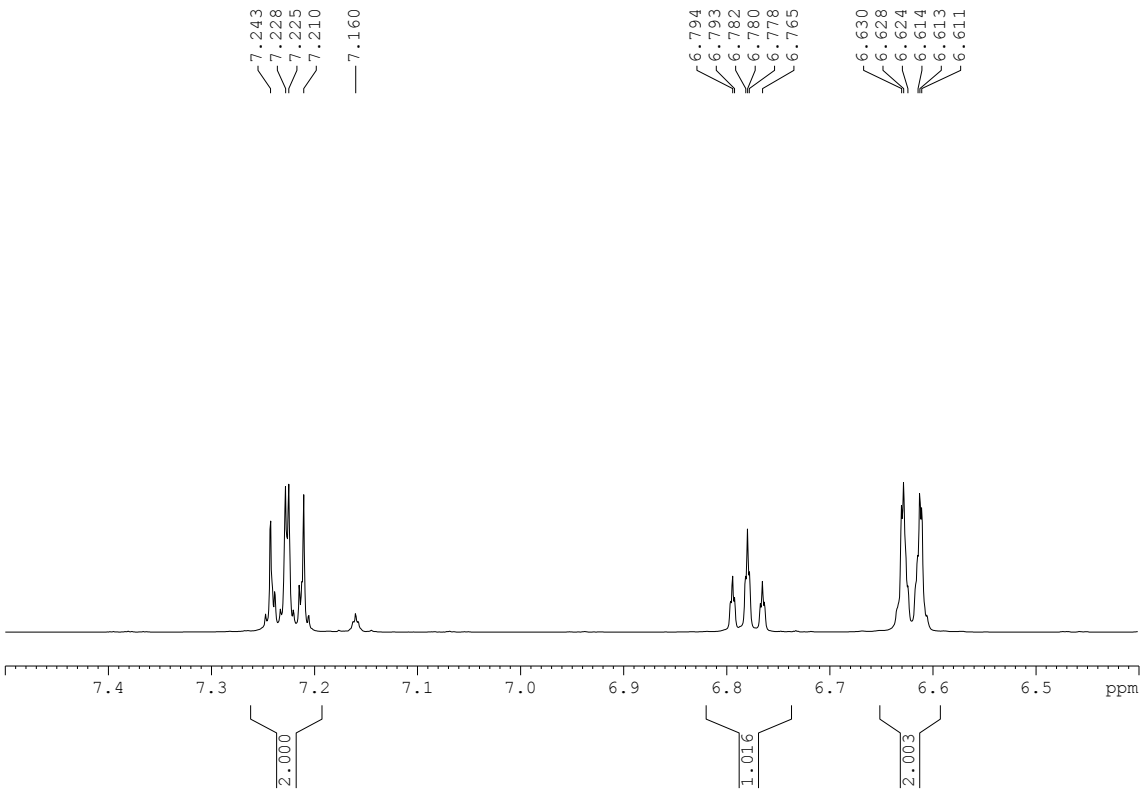
- Key



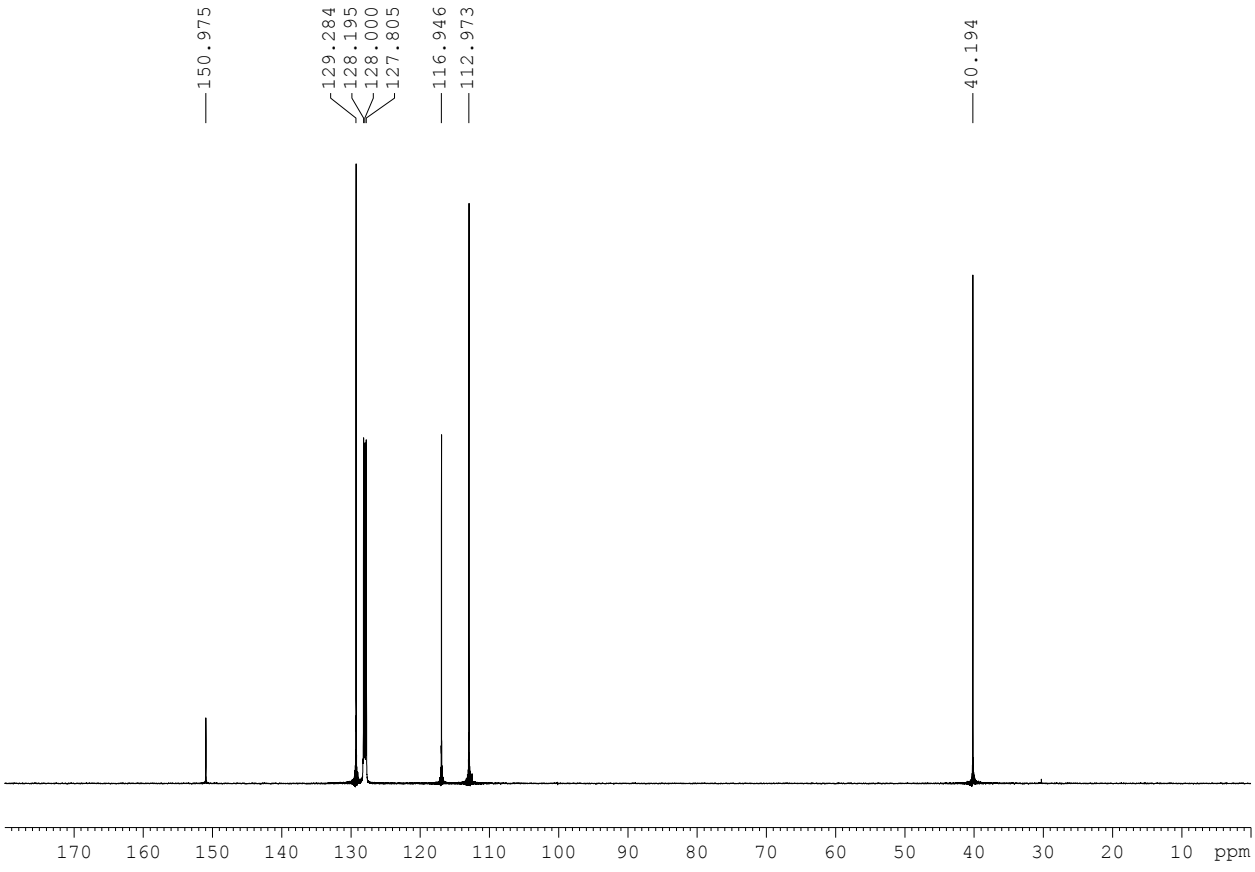
N*,*N*-dimethylaniline** ***ortho ***meta*** ***para***



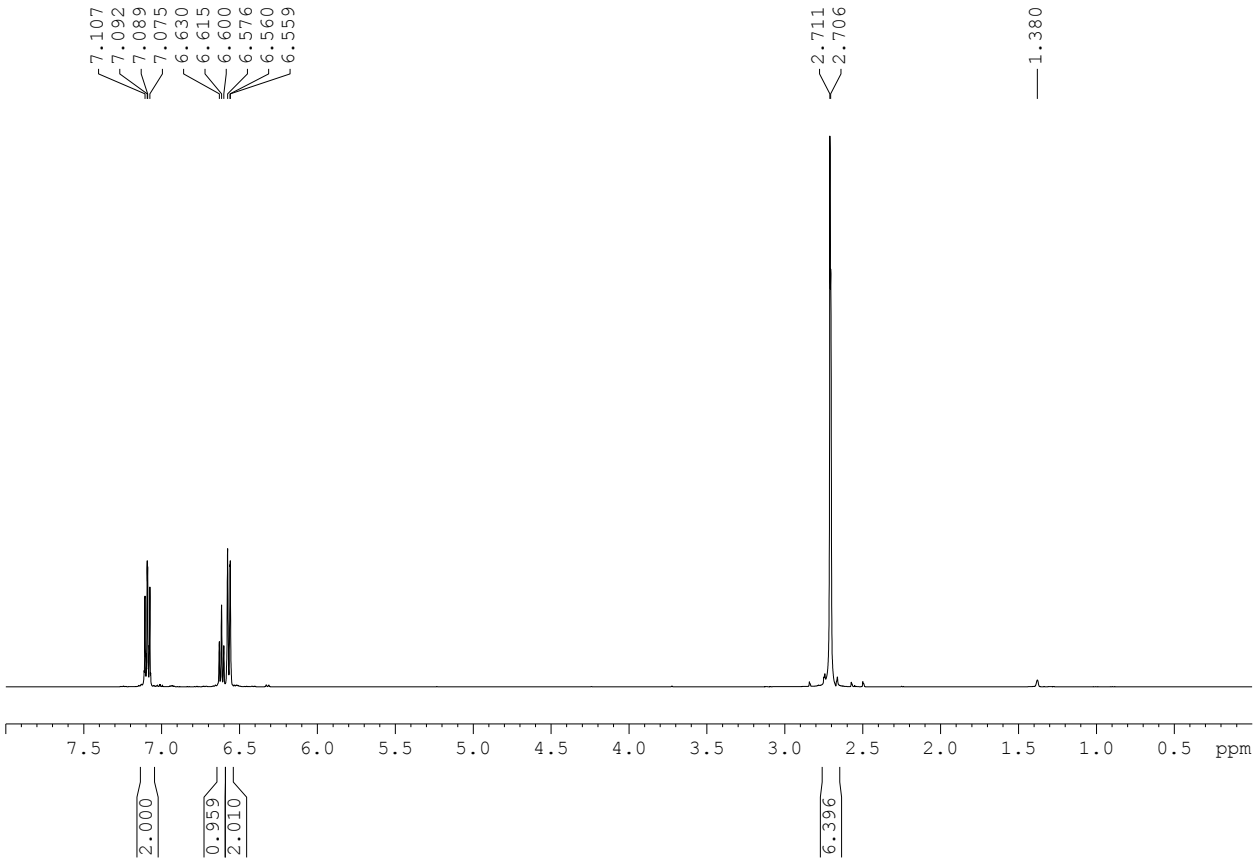
Spectrum 1. ^{1}H NMR (400.13 MHz, 300 K) spectrum of *N*,*N*-dimethylaniline in C_6D_6 solution.



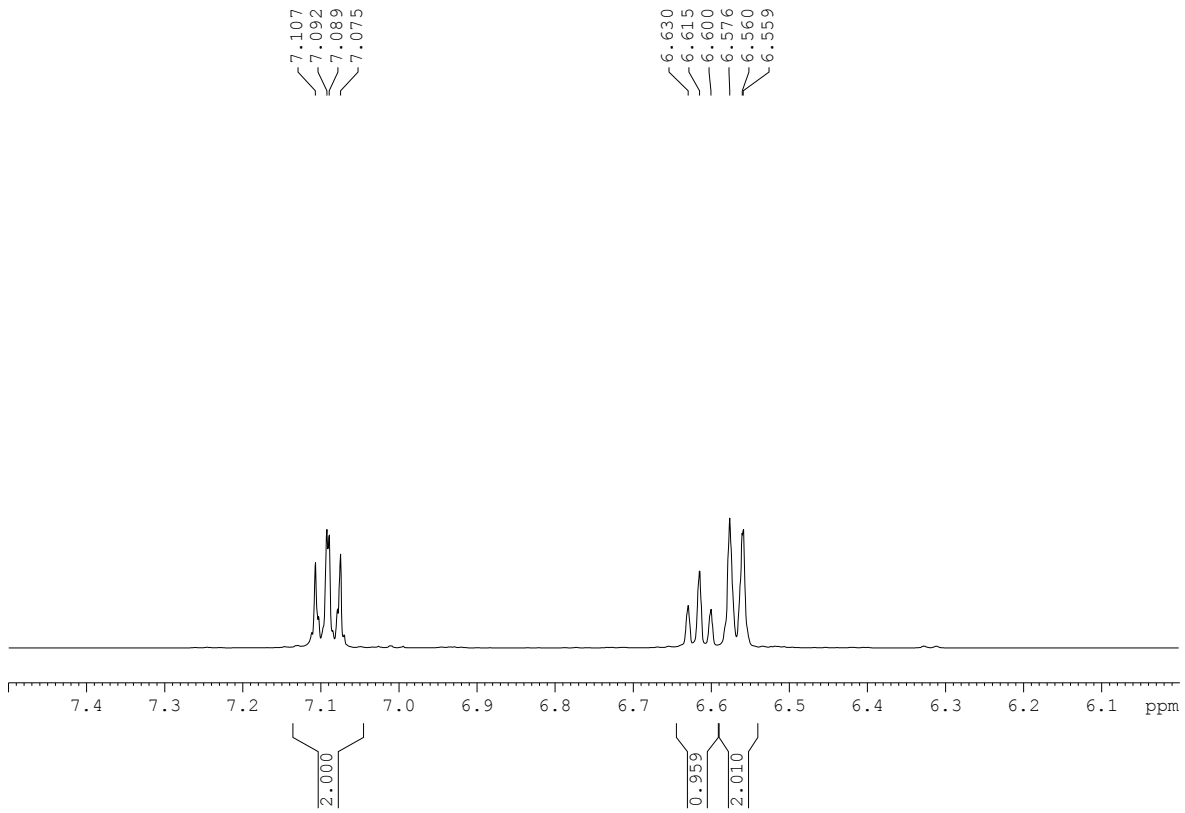
Spectrum 2. Aromatic region of ^{1}H NMR spectrum of *N*,*N*-dimethylaniline in C_6D_6 solution.



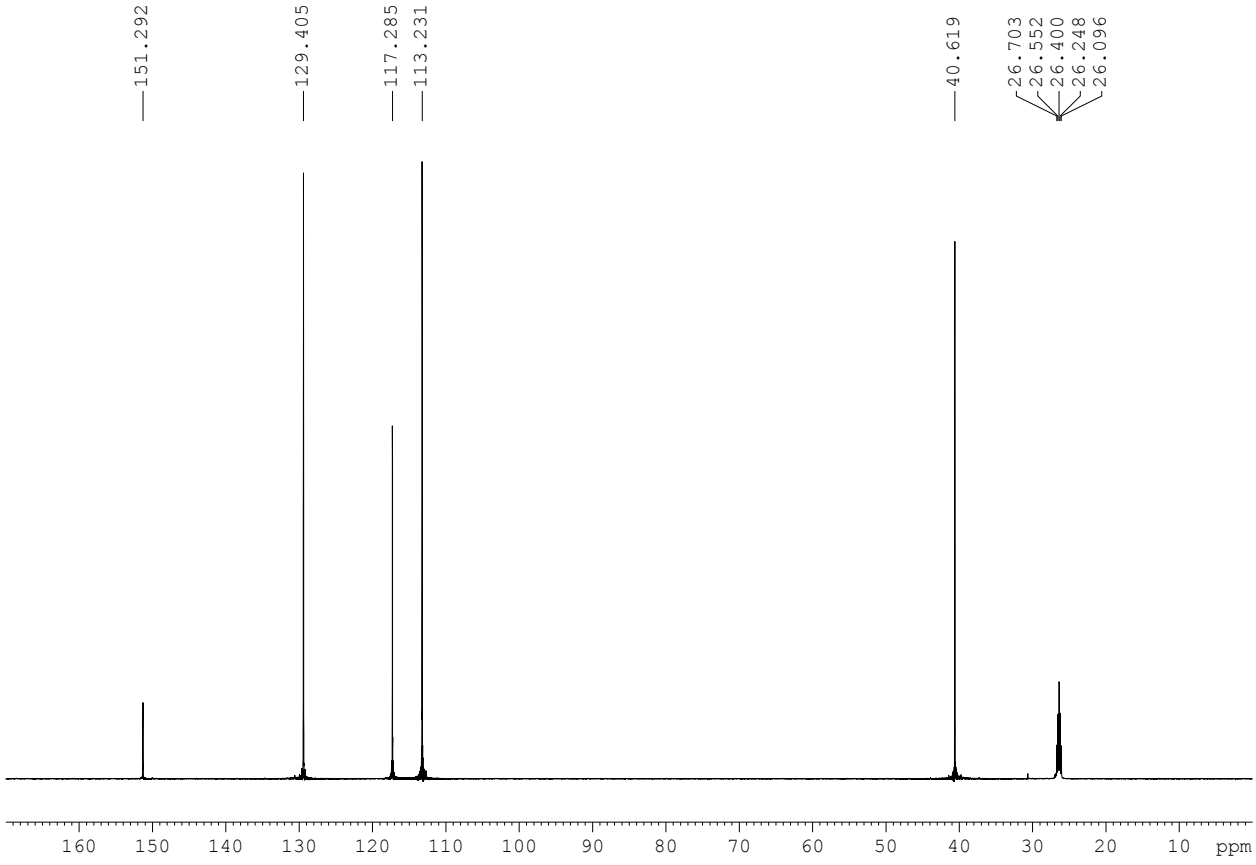
Spectrum 3. ^{13}C {^{1}H} NMR (100.62 MHz, 300 K) spectrum of *N*,*N*-dimethylaniline in C_6D_6 solution.



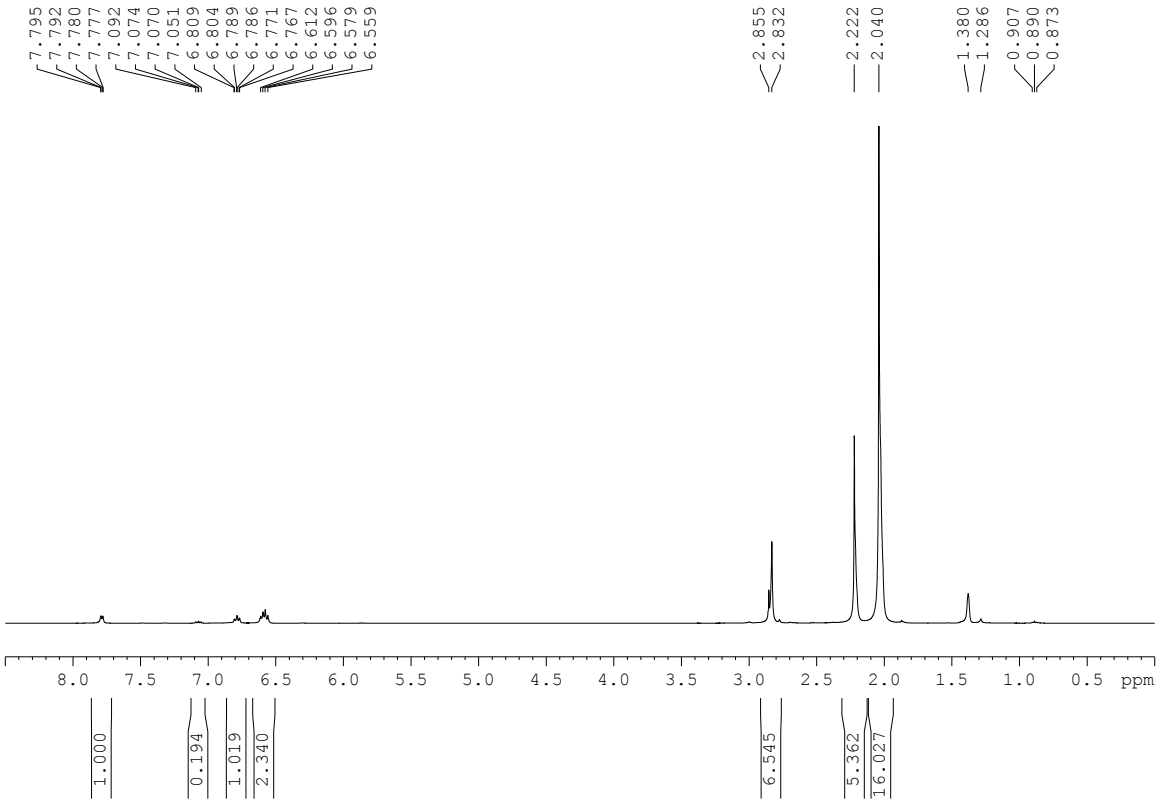
Spectrum 4. ^{1}H NMR (400.13 MHz, 300 K) spectrum of *N*,*N*-dimethylaniline in C_6D_{12} solution.



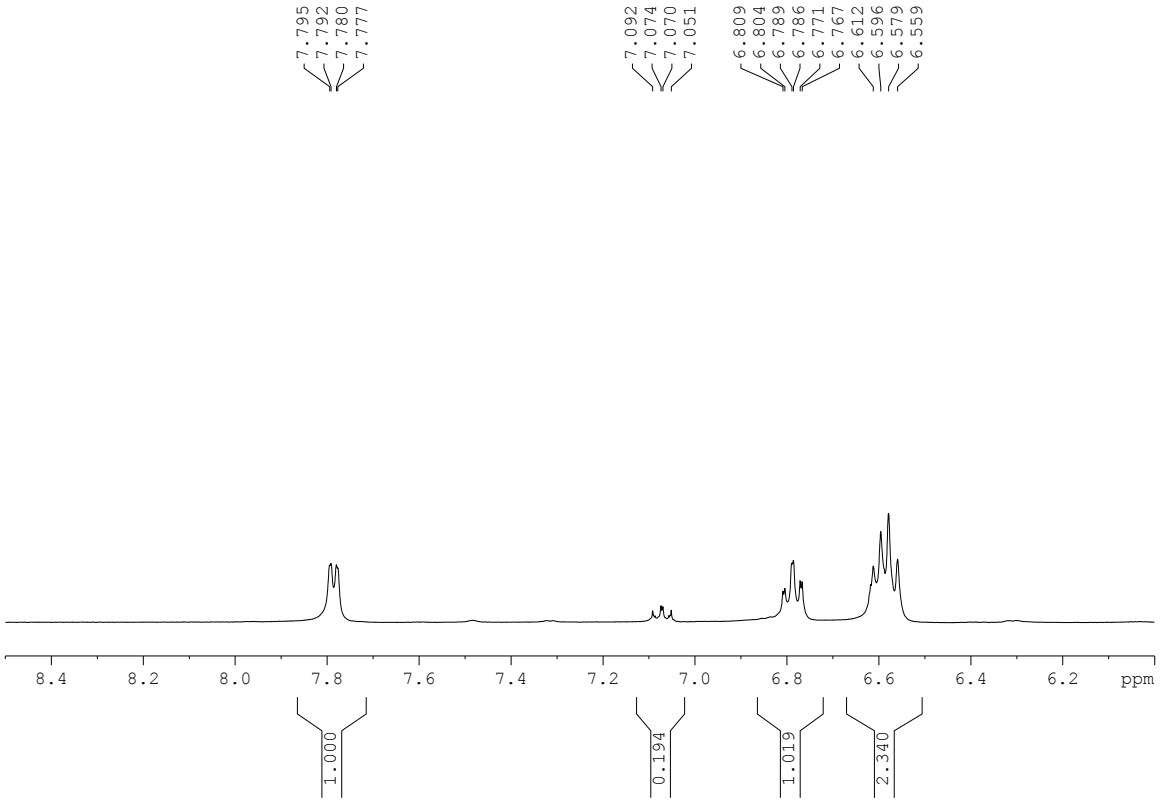
Spectrum 5. Aromatic region of ^{1}H NMR spectrum of *N*,*N*-dimethylaniline in C_6D_{12} solution.



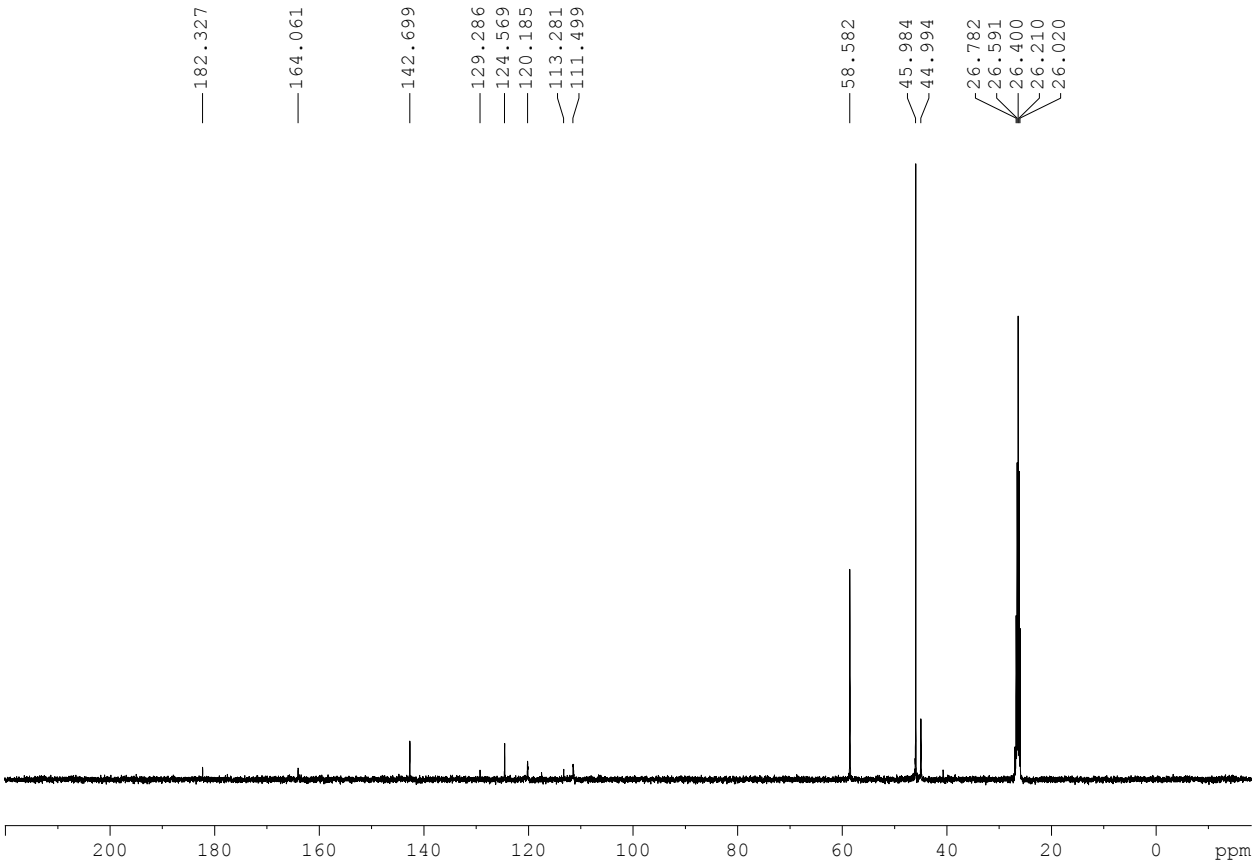
Spectrum 6. ^{13}C {^{1}H} NMR (100.62 MHz, 300 K) spectrum of *N*,*N*-dimethylaniline in C_6D_{12} solution.



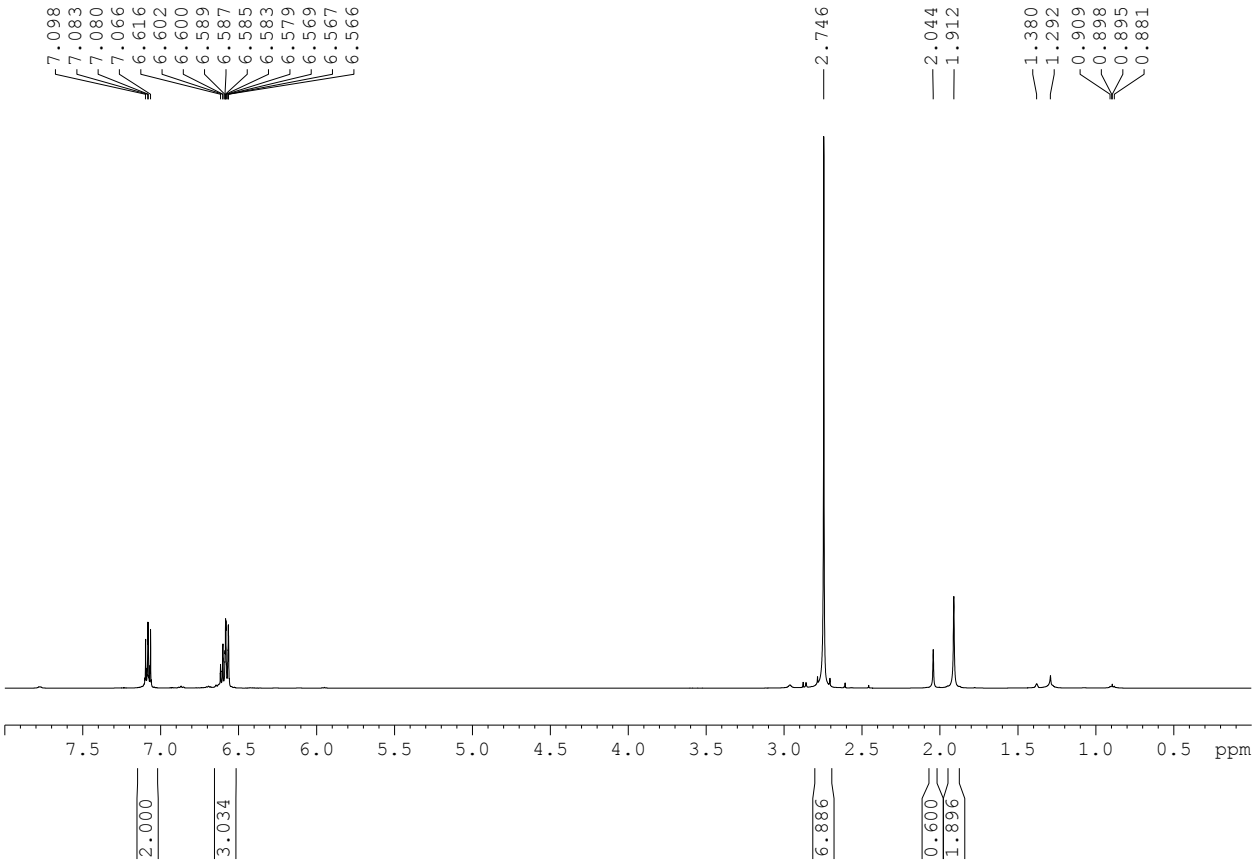
Spectrum 7. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **3** in C_6D_{12} solution.



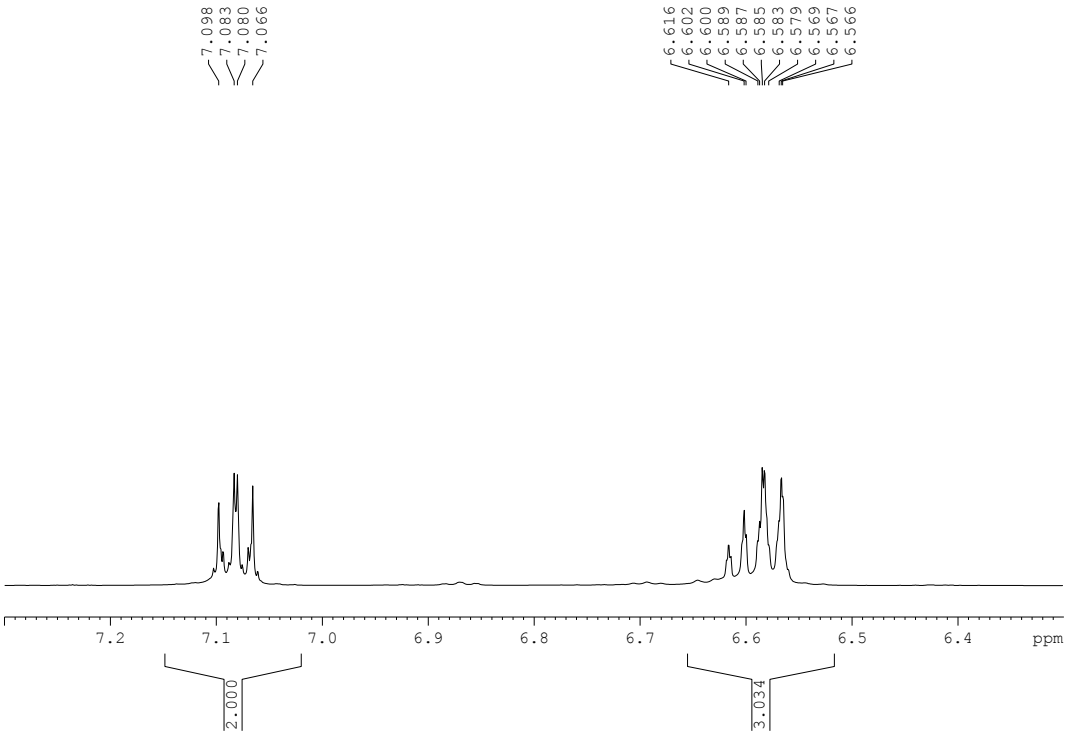
Spectrum 8. Aromatic region of ^{1}H NMR spectrum of **3** in C_6D_{12} solution.



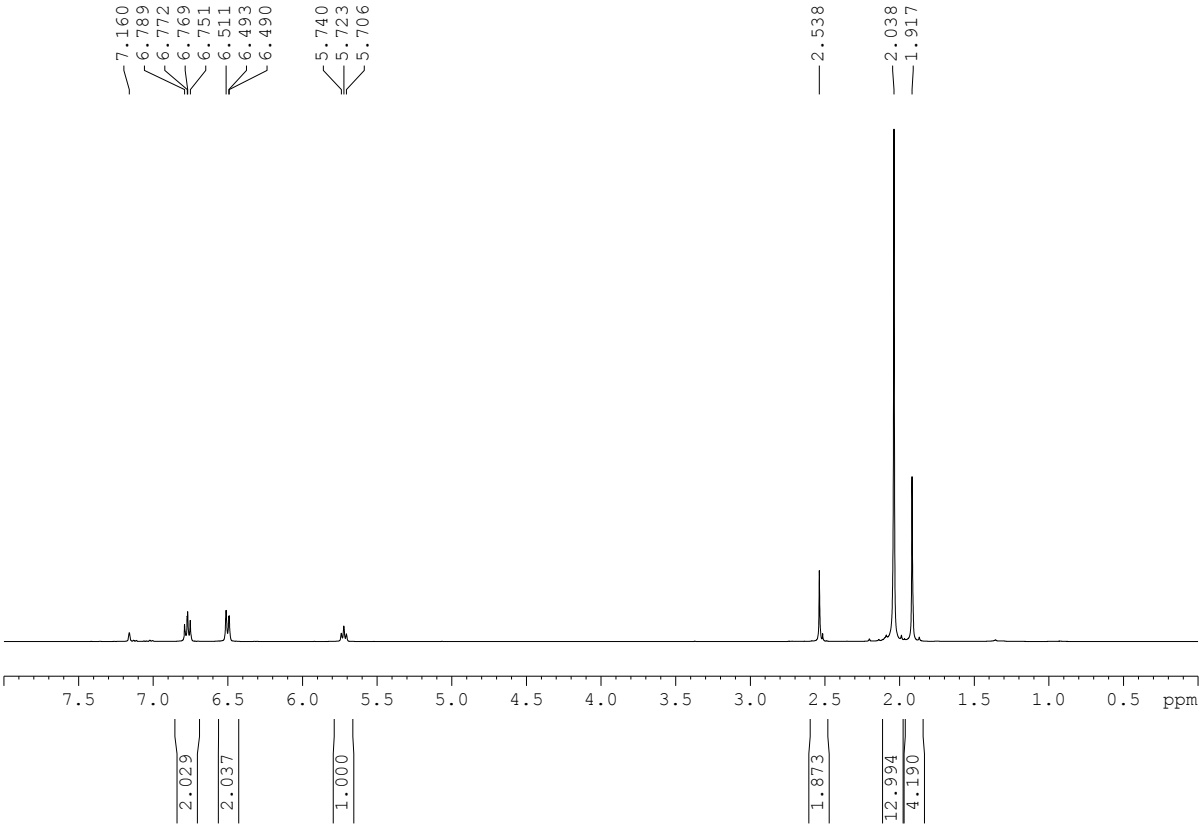
Spectrum 9. ^{13}C {^{1}H} NMR (100.62 MHz, 300 K) spectrum of **3** in C_6D_{12} solution.



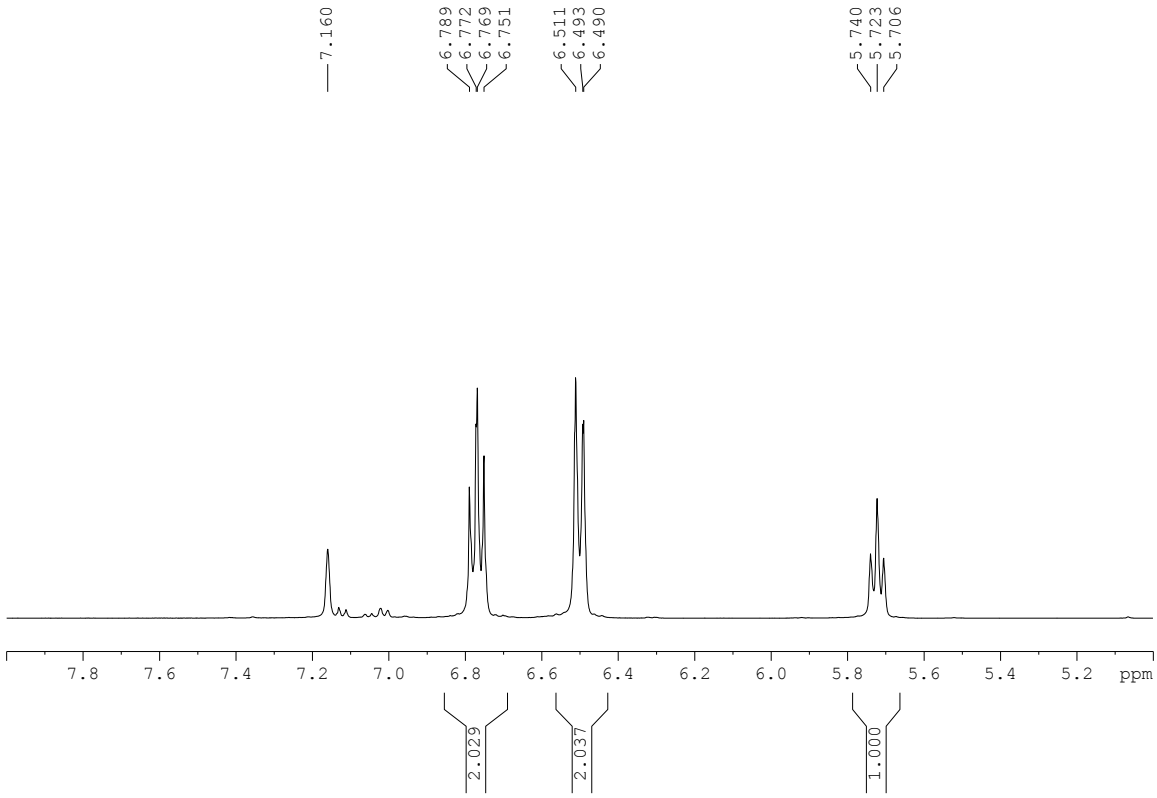
Spectrum 10. ^{1}H NMR (400.13 MHz, 300 K) spectrum of mother liquor following isolation of **3** in C_6D_{12} solution.



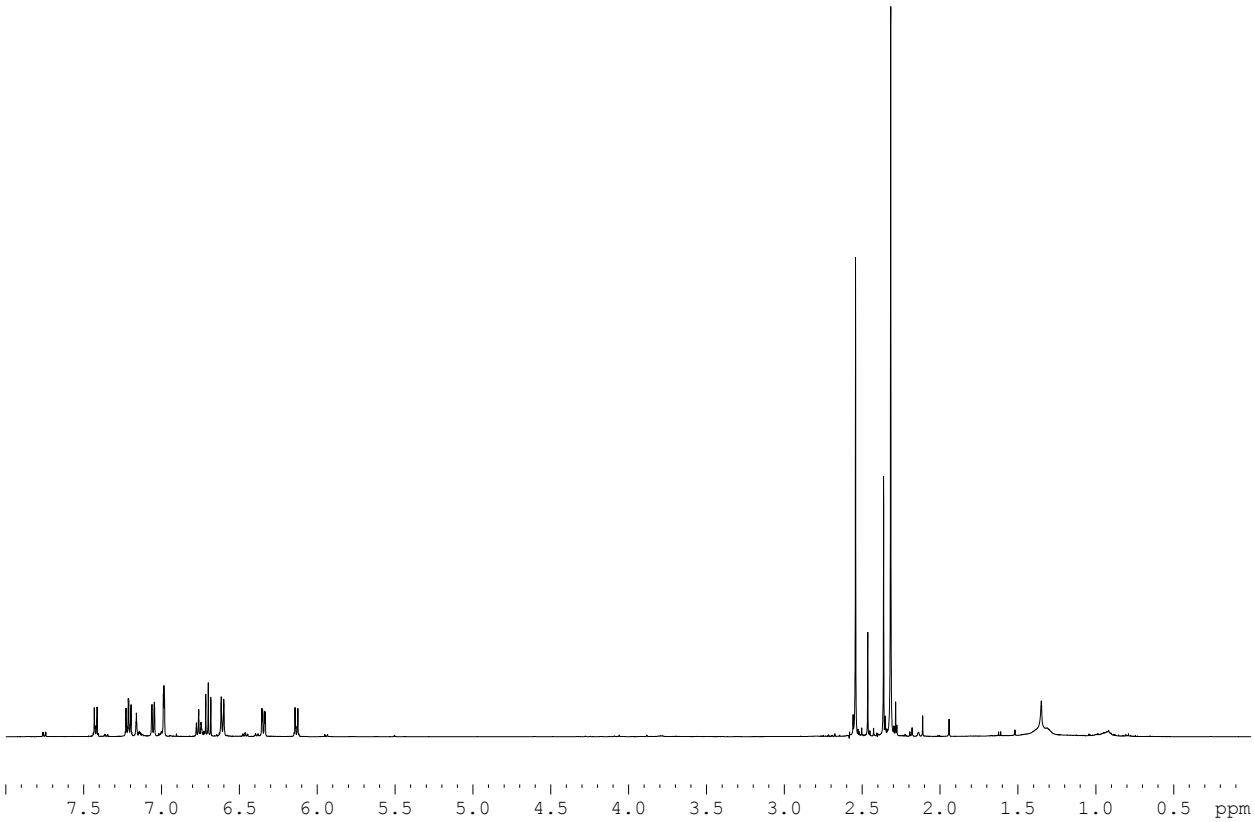
Spectrum 11. Aromatic region of ^{1}H NMR spectrum of mother liquor following isolation of **3** in C_6D_{12} solution.



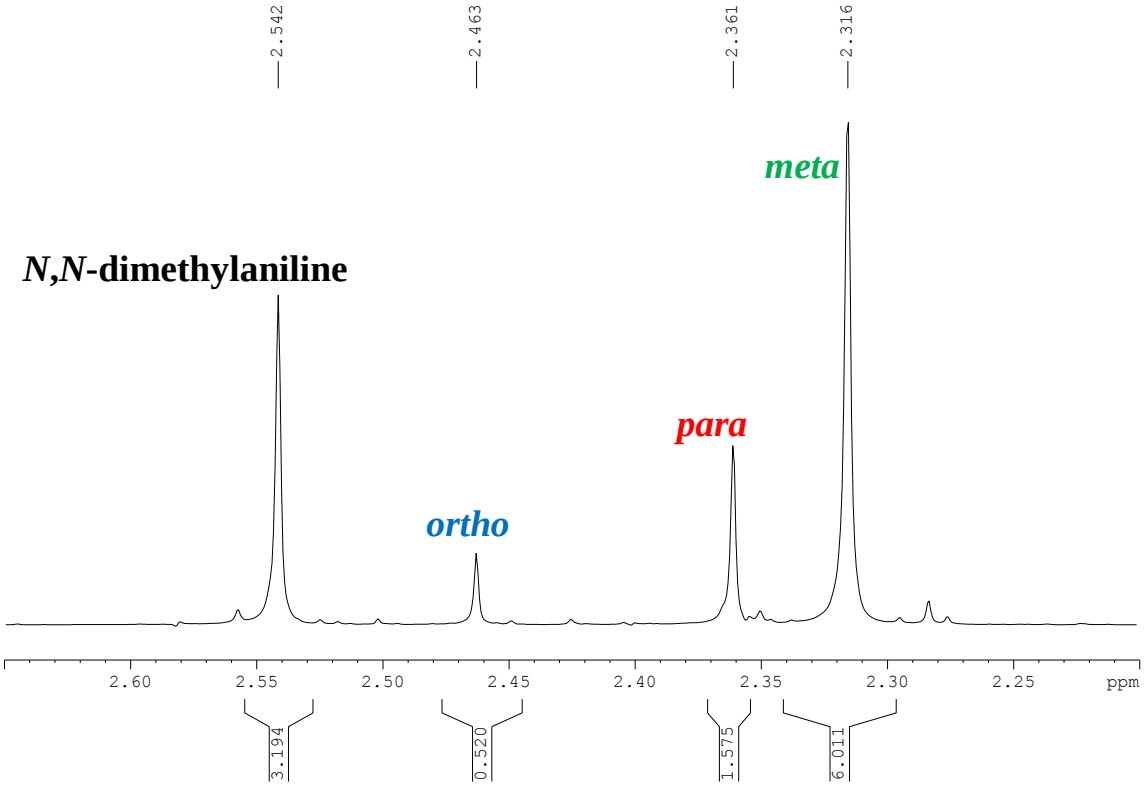
Spectrum 12. ^{1}H NMR (400.13 MHz, 300 K) spectrum from the reaction of **3** with toluene in C_6D_6 solution.



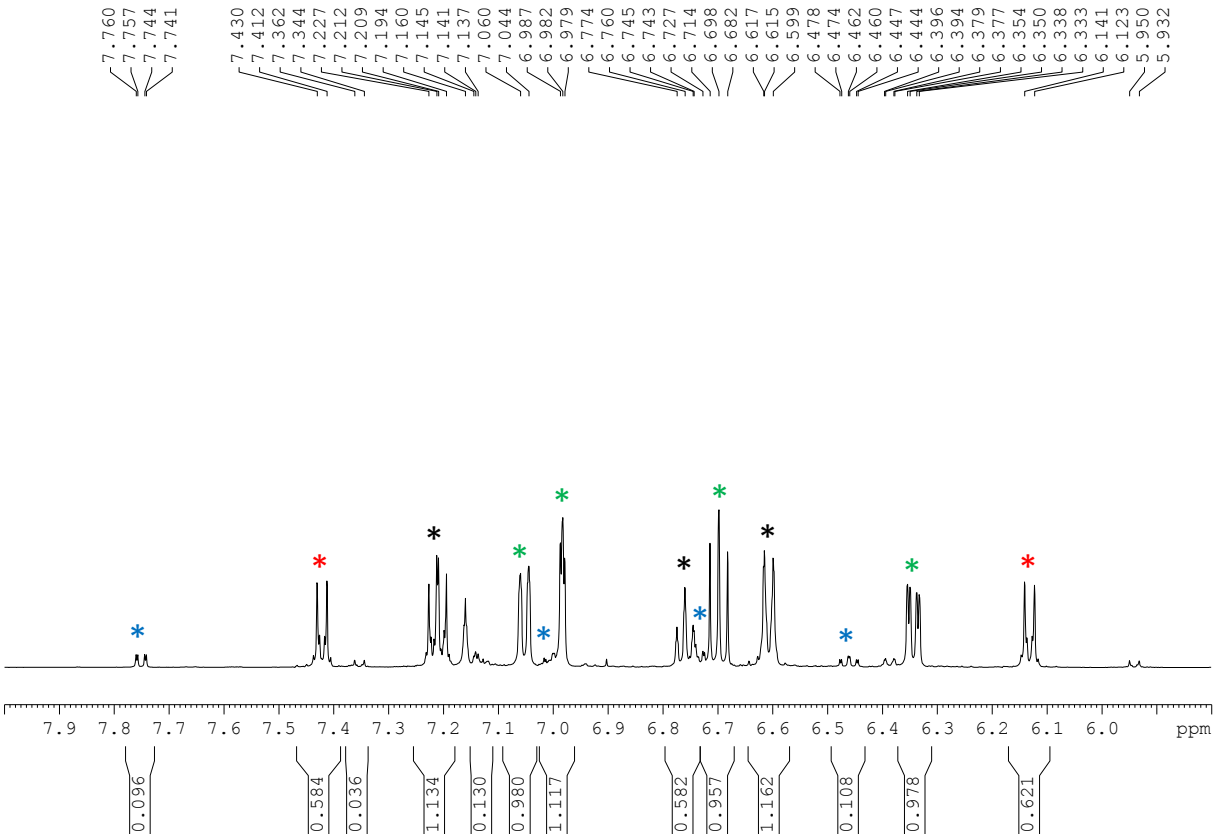
Spectrum 13. Aromatic region of ^{1}H NMR spectrum from the reaction of **3** with toluene in C_6D_6 solution.



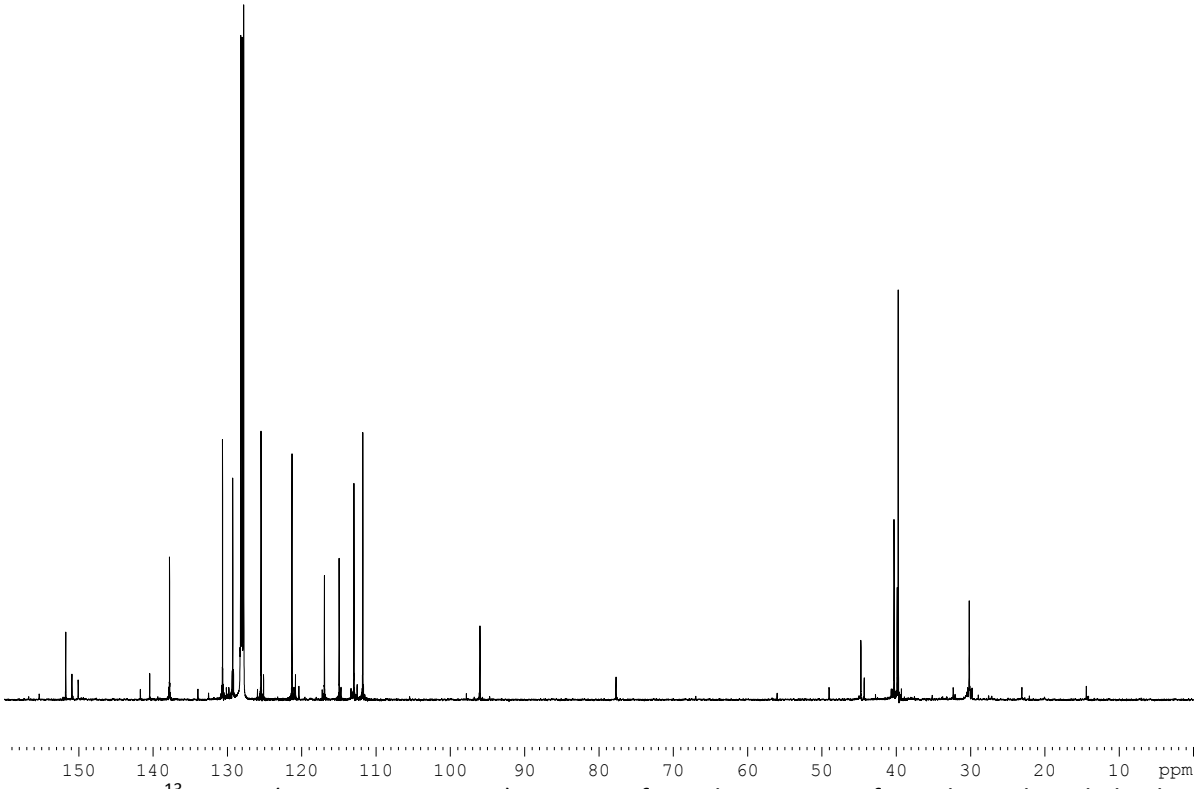
Spectrum 14. ^{1}H NMR (400.13 MHz, 300 K) spectrum from the reaction of **1** and *N*,*N*-dimethylaniline with iodine in C_6D_6 solution.



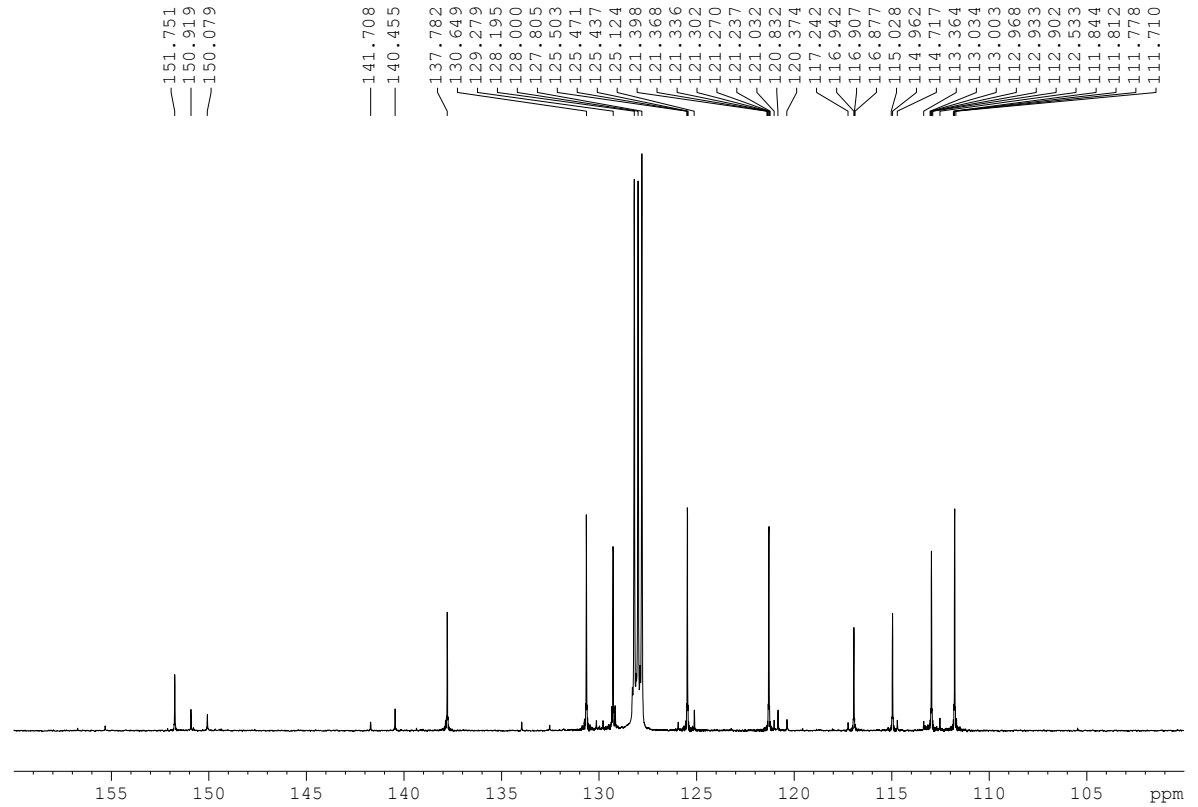
Spectrum 15. Aliphatic region of ^{1}H NMR spectrum from the reaction of **1** and *N*,*N*-dimethylaniline with iodine in C_6D_6 solution.



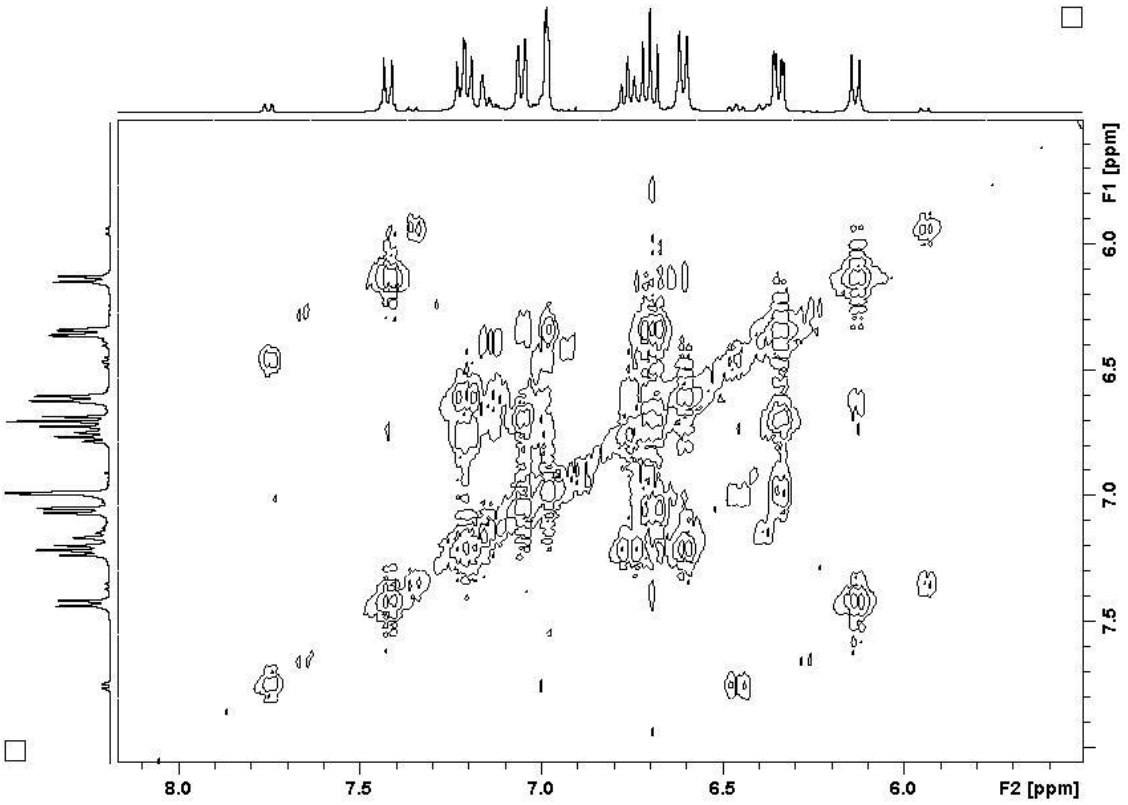
Spectrum 16. Aromatic region of ^{1}H NMR spectrum from the reaction of **1** and *N*,*N*-dimethylaniline with iodine in C_6D_6 solution.



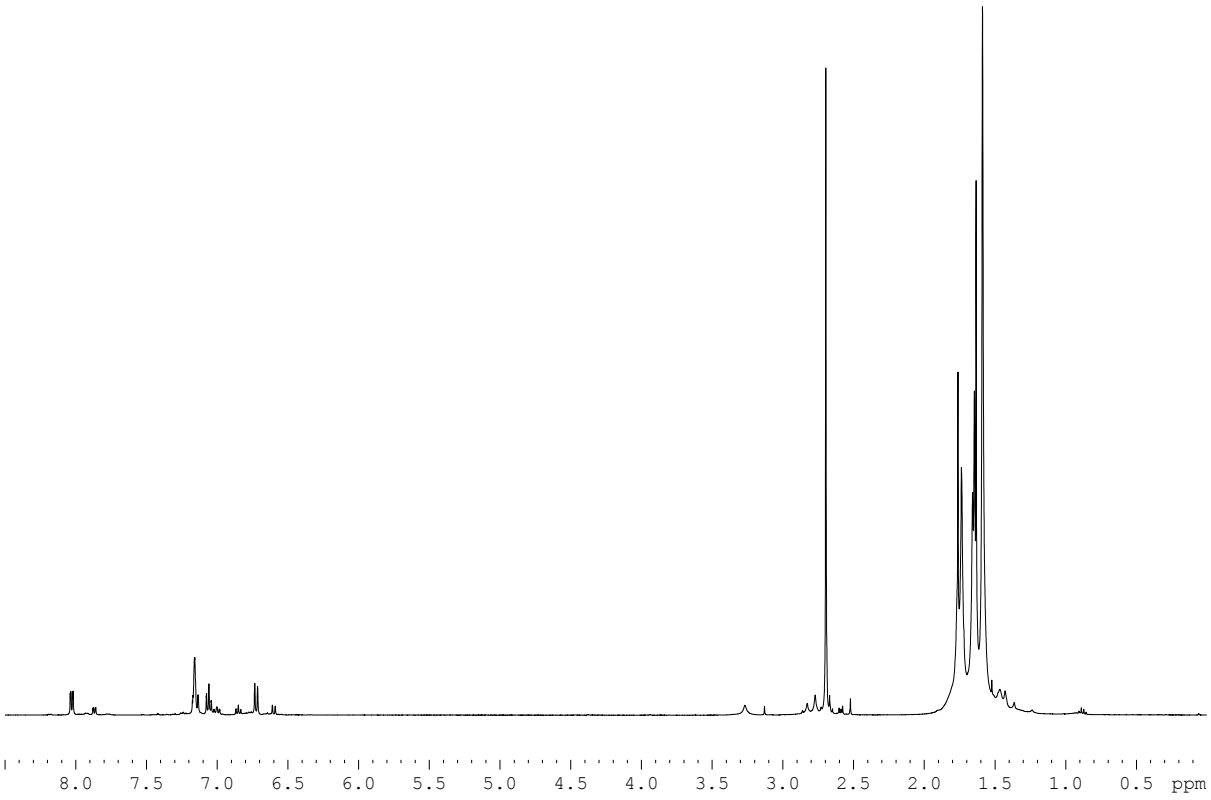
Spectrum 17. ^{13}C NMR (100.62 MHz, 300 K) spectrum from the reaction of **1** and *N*,*N*-dimethylaniline with iodine in C_6D_6 solution.



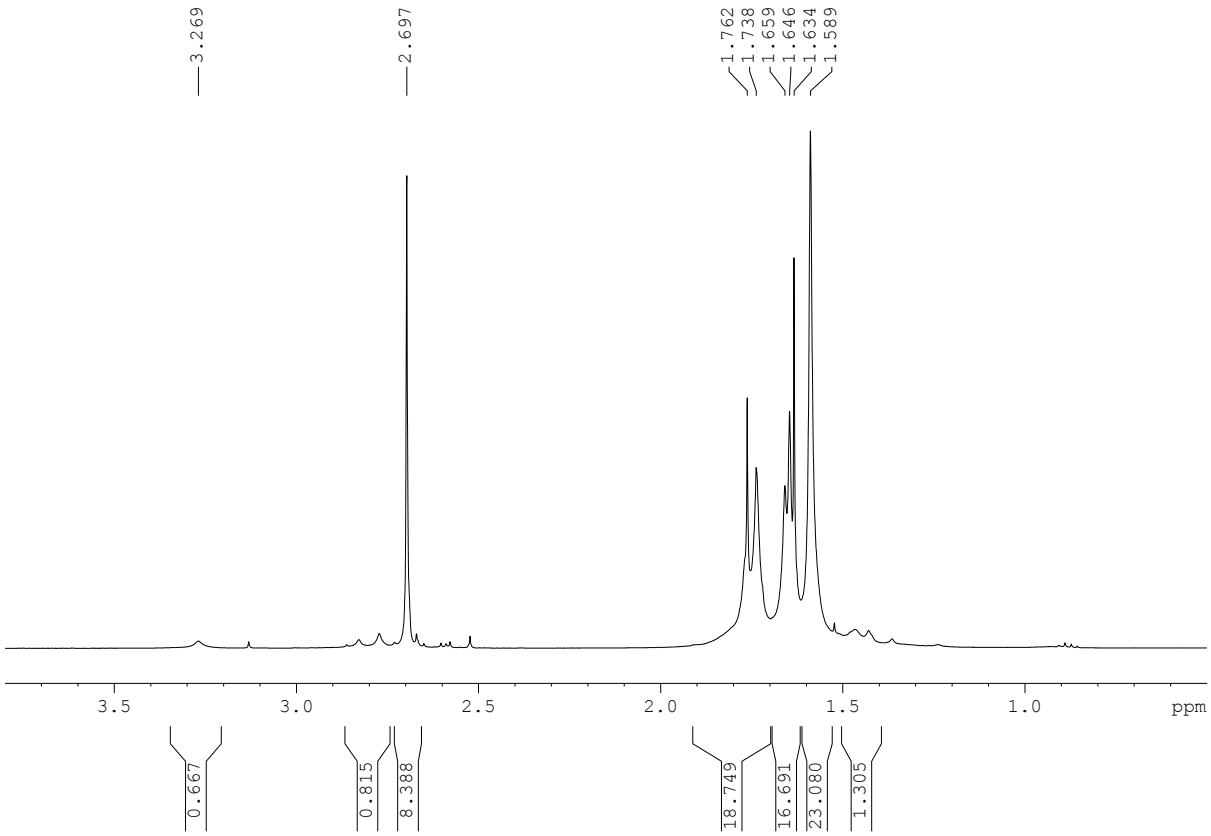
Spectrum 18. Aromatic region of ^{13}C NMR spectrum from the reaction of **1** and *N*,*N*-dimethylaniline with iodine in C_6D_6 solution.



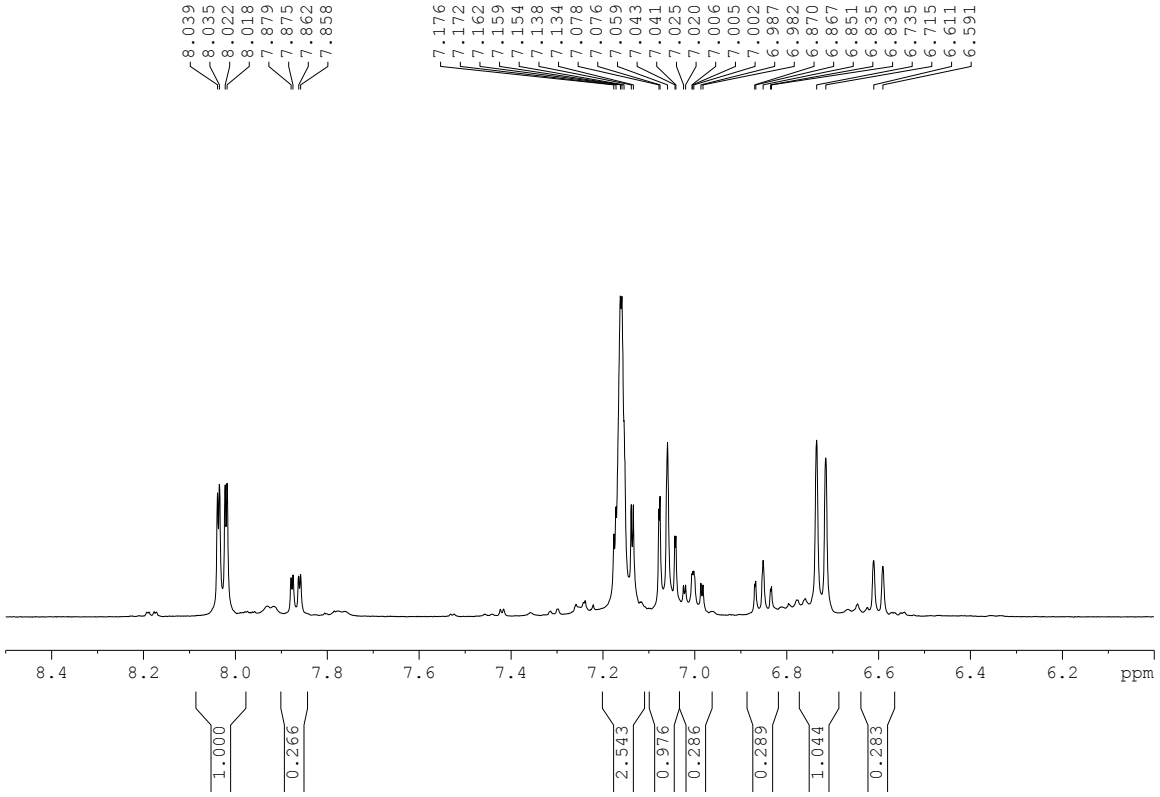
Spectrum 19. Aromatic region of ^{1}H-^{1}H COSY NMR spectrum from the reaction of **1** and *N*,*N*-dimethylaniline with iodine in C_6D_6 solution.



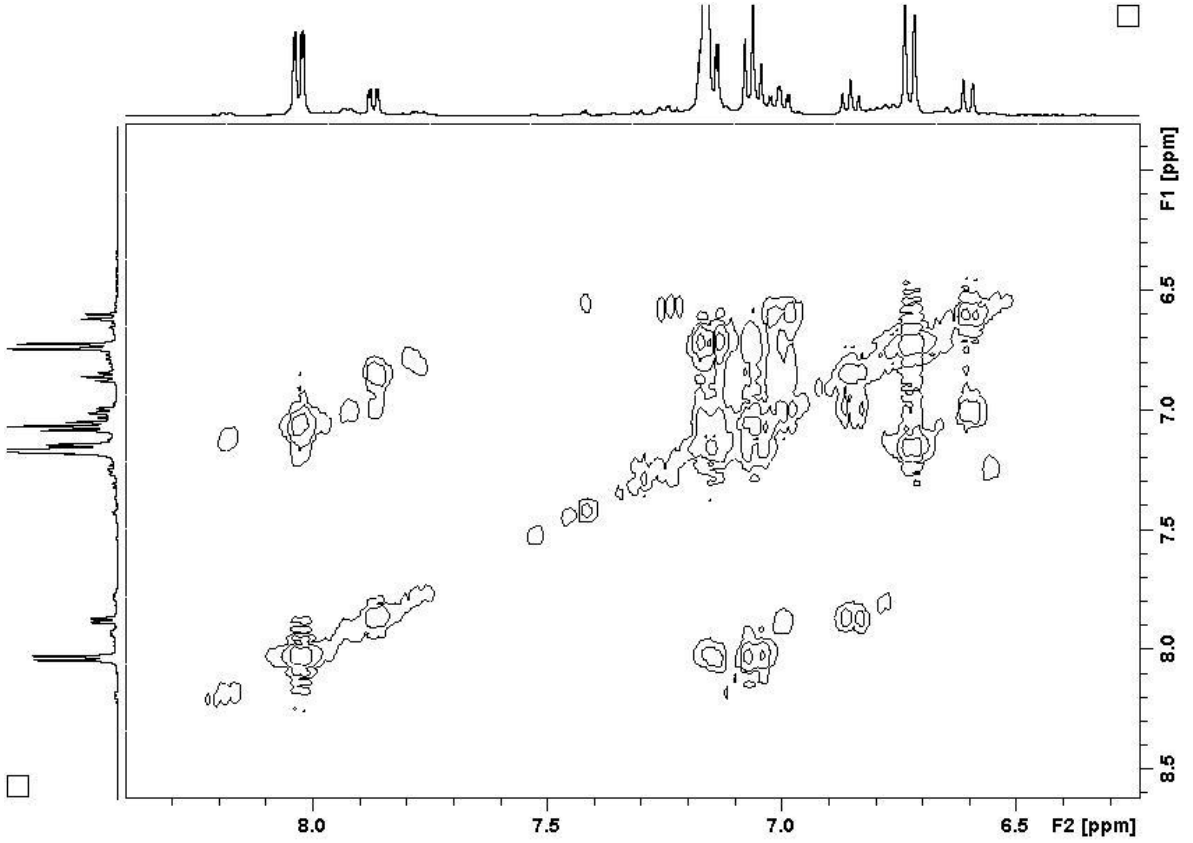
Spectrum 20. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **4** and **5** in C_6D_6 solution.



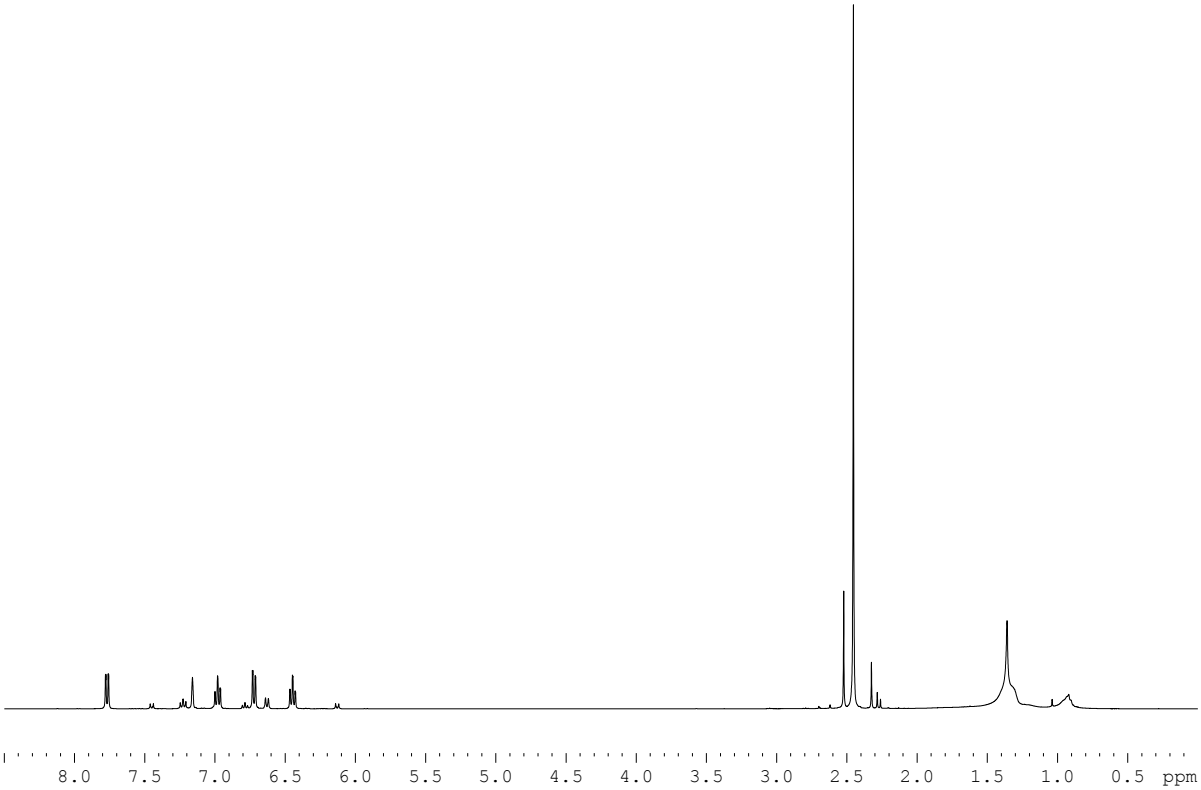
Spectrum 21. Aliphatic region of ^{1}H NMR spectrum of **4** and **5** in C_6D_6 solution.



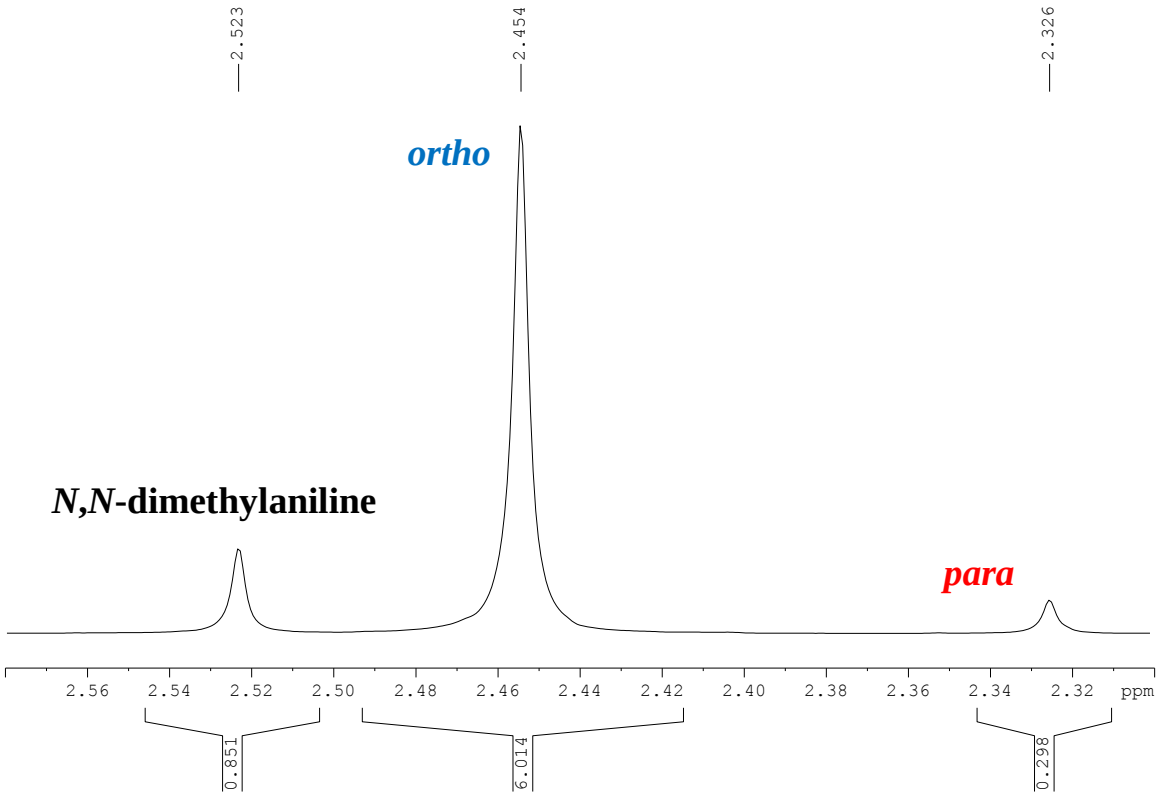
Spectrum 22. Aromatic region of ^{1}H NMR spectrum of **4** and **5** in C_6D_6 solution.



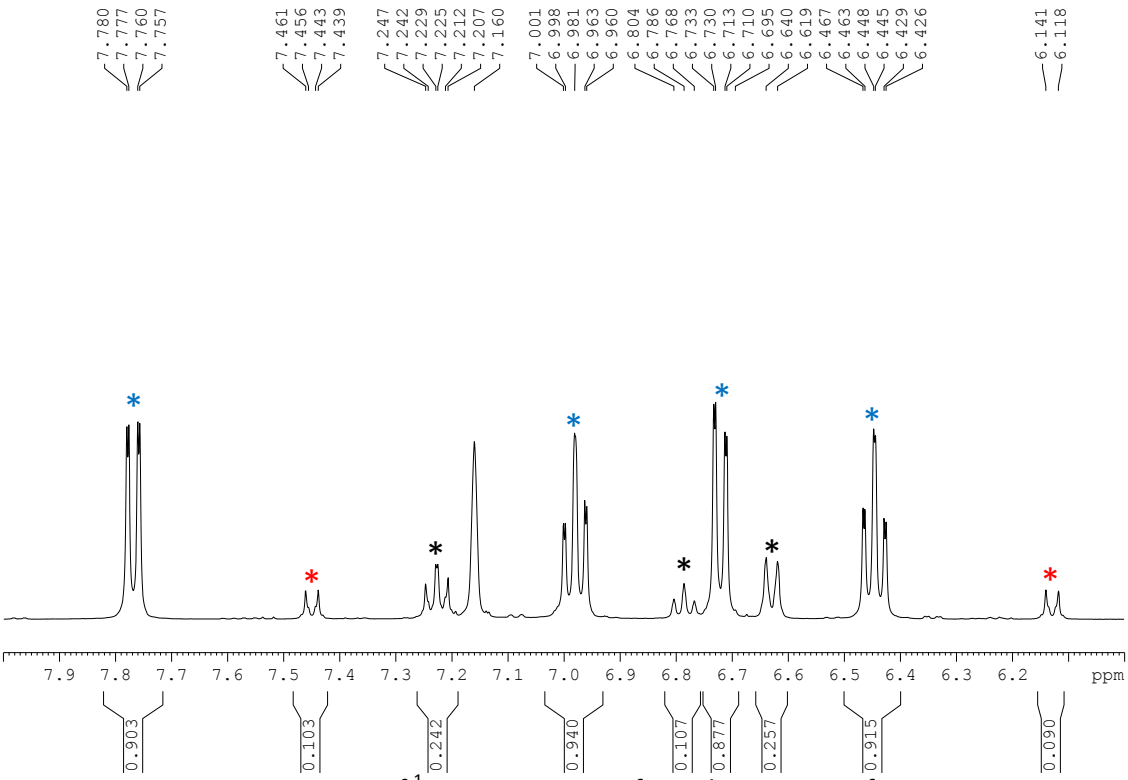
Spectrum 23. Aromatic region of ^{1}H-^{1}H COSY NMR spectrum of **4** and **5** in C_6D_6 solution.



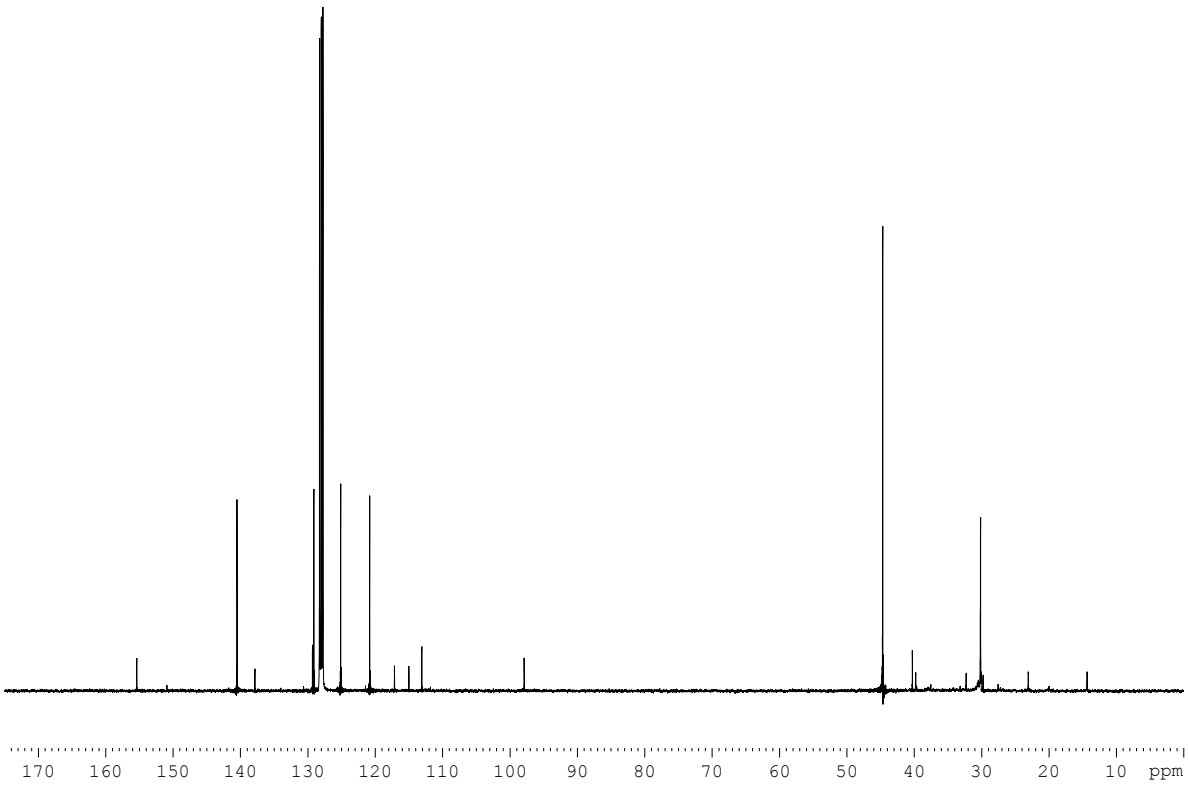
Spectrum 24. ^{1}H NMR (400.13 MHz, 300 K) spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline and *t*Bu_2Zn with iodine in C_6D_6 solution.



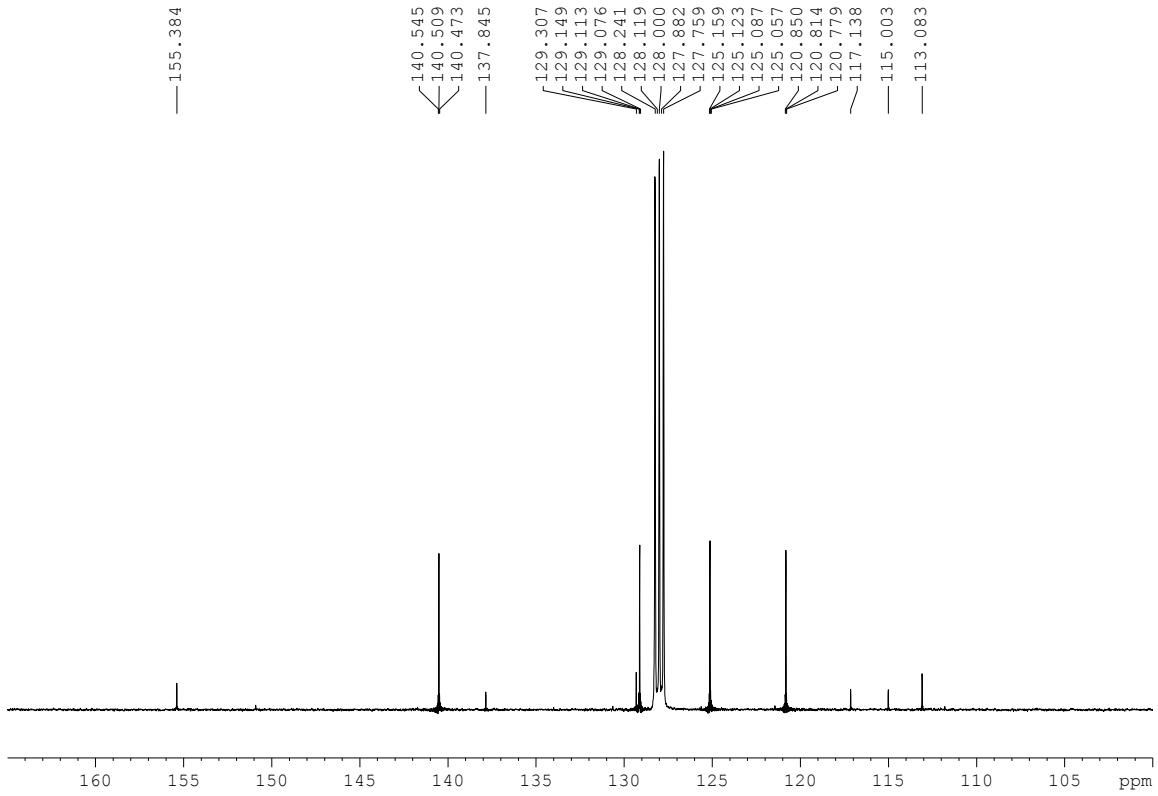
Spectrum 25. Aliphatic region of ^{1}H NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline and *t*Bu_2Zn with iodine in C_6D_6 solution.



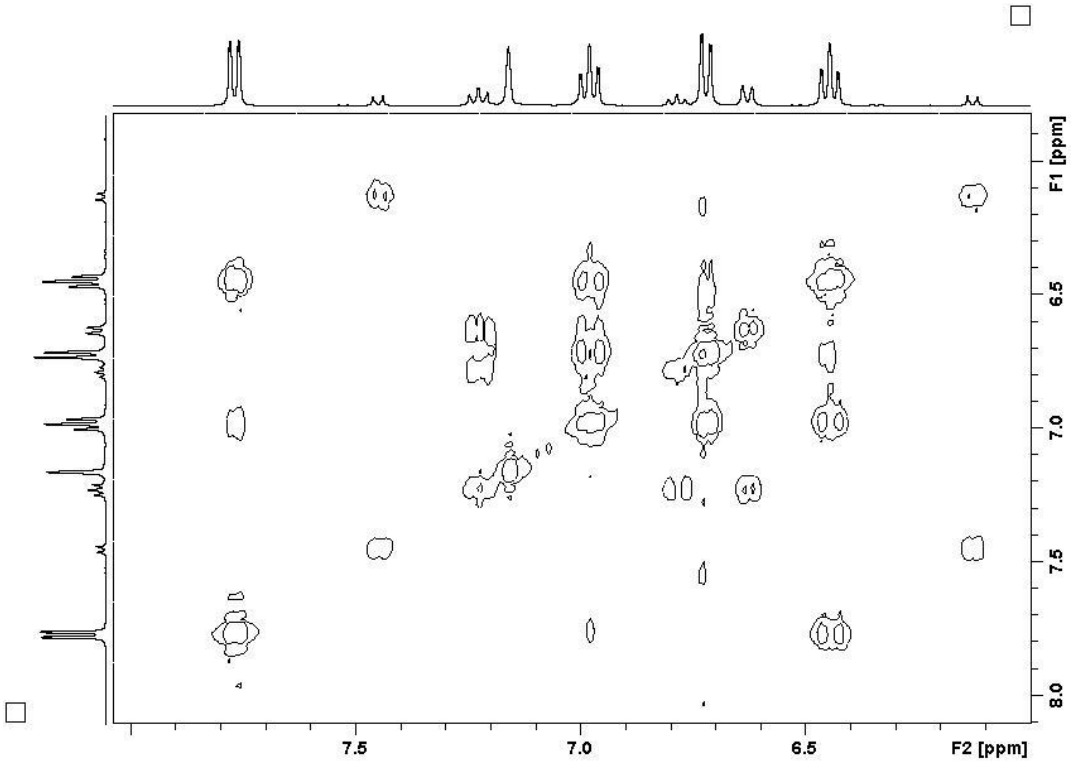
Spectrum 26. Aromatic region of ^{1}H NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline and *t*Bu_2Zn with iodine in C_6D_6 solution.



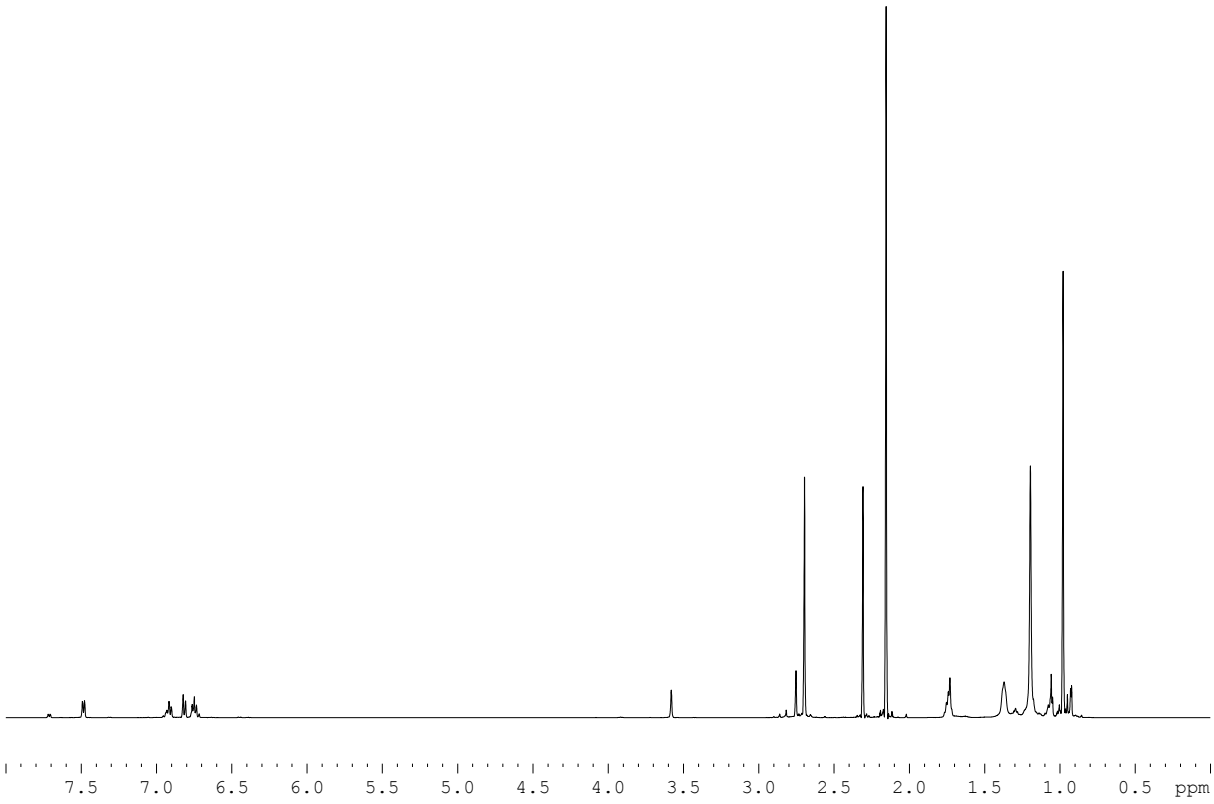
Spectrum 27. ^{13}C NMR (100.62 MHz, 300 K)spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline and *t*Bu_2Zn with iodine in C_6D_6 solution.



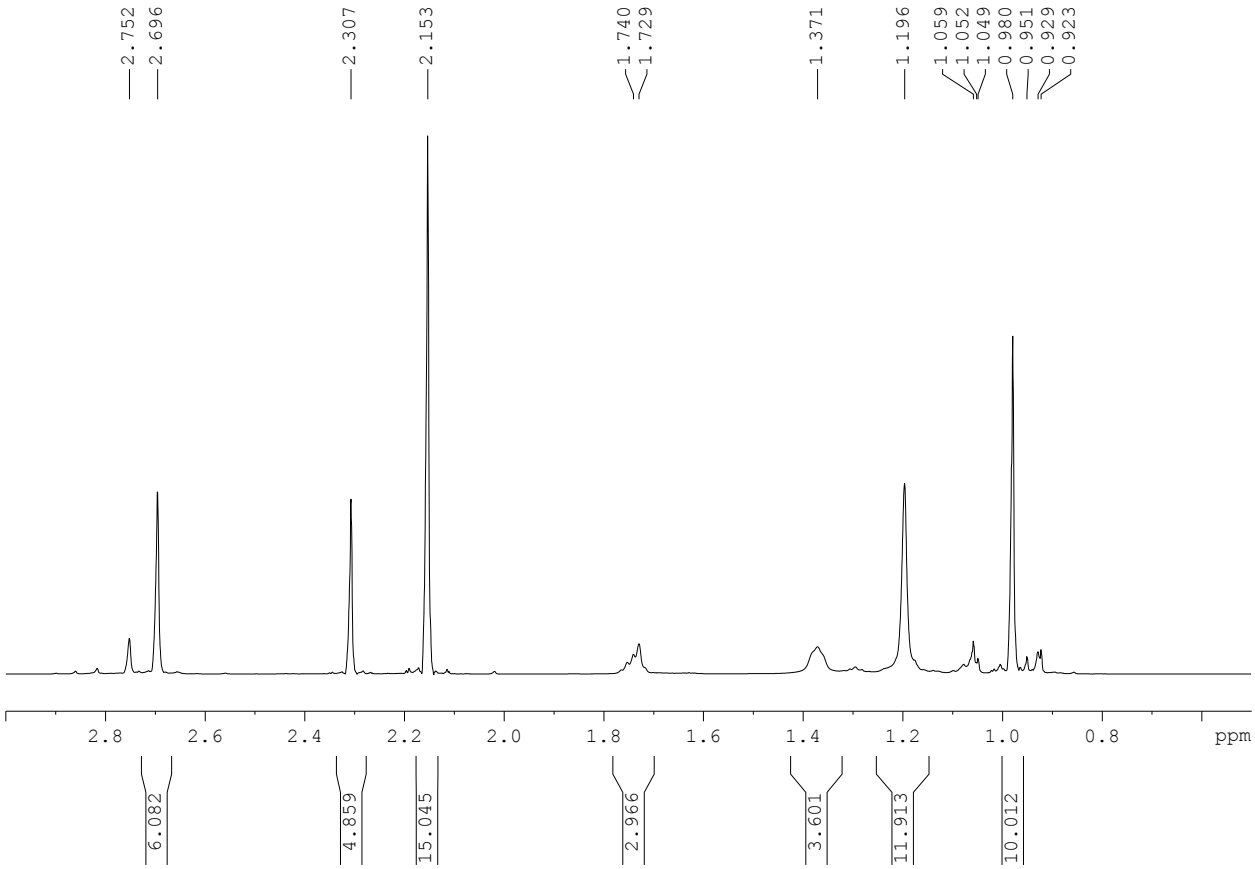
Spectrum 28. Aromatic region of ^{13}C NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline and *t*Bu_2Zn with iodine in C_6D_6 solution.



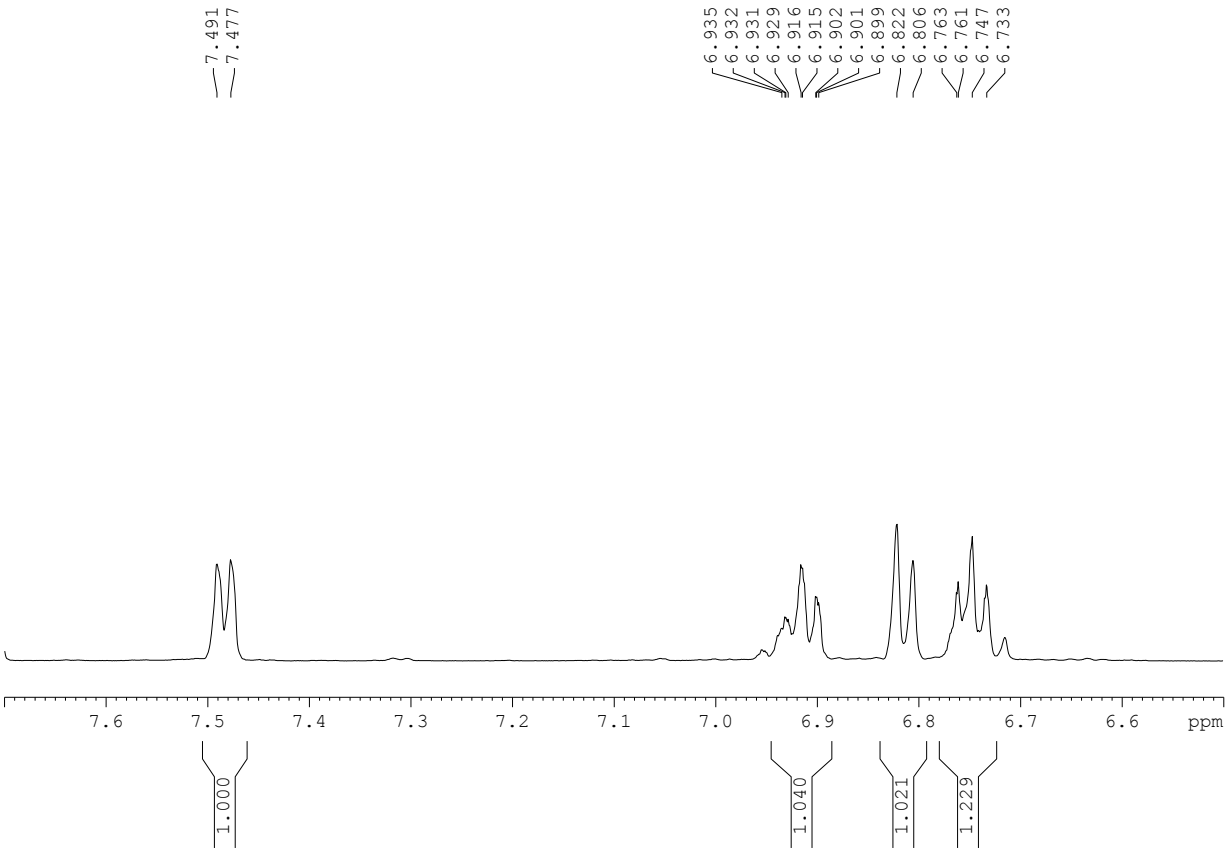
Spectrum 29. Aromatic region of ^{1}H-^{1}H COSY NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline and *t*Bu_2Zn with iodine in C_6D_6 solution.



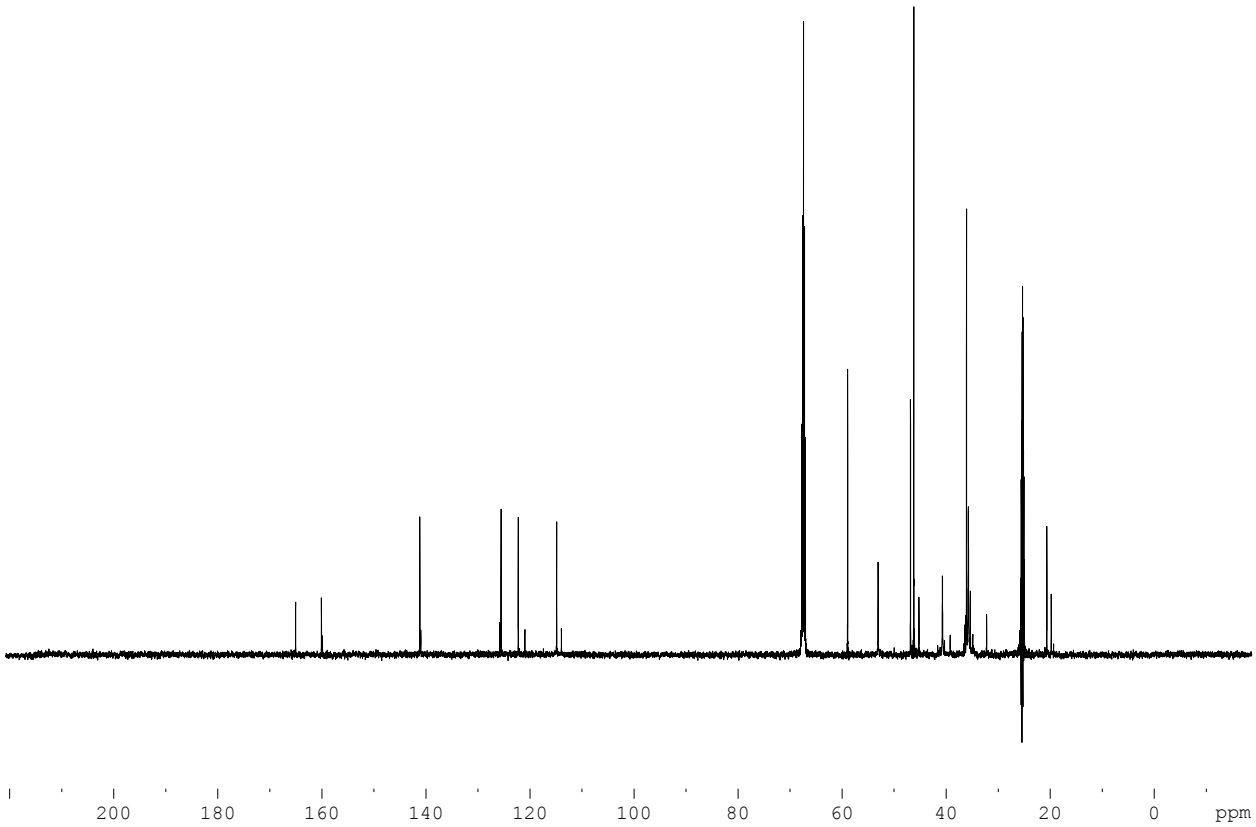
Spectrum 30. ^{1}H NMR (400.13 MHz, 300 K) spectrum of **6** in d_8-THF solution.



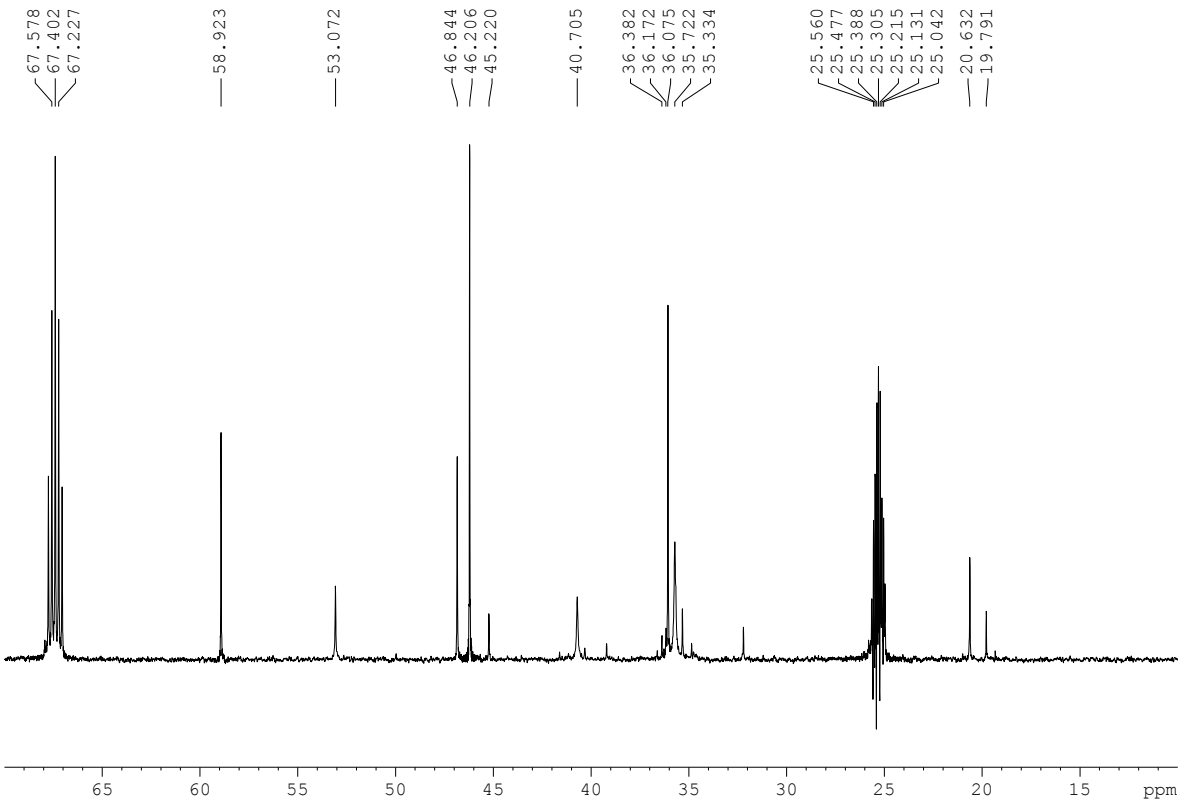
Spectrum 31. Aliphatic region of ^{1}H NMR spectrum of **6** in d_8-THF solution.



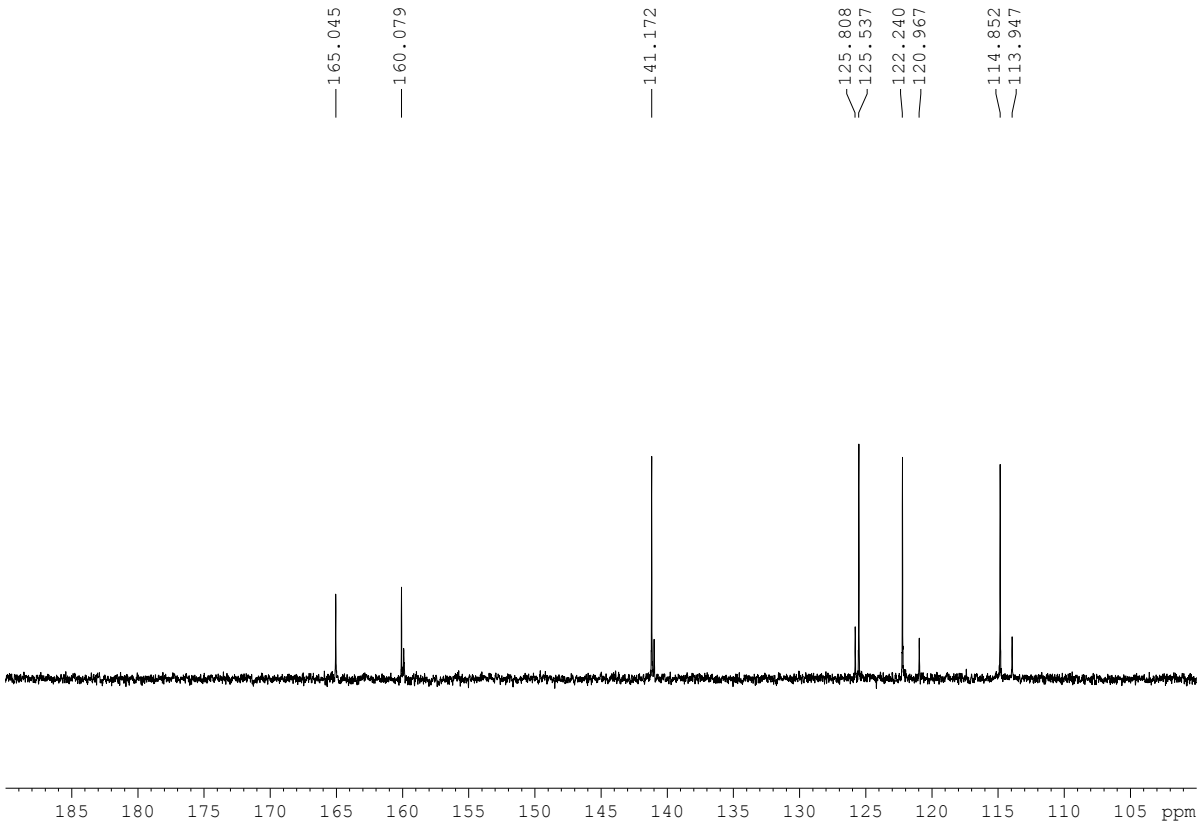
Spectrum 32. Aromatic region of ^{1}H NMR spectrum of **6** in d_8-THF solution.



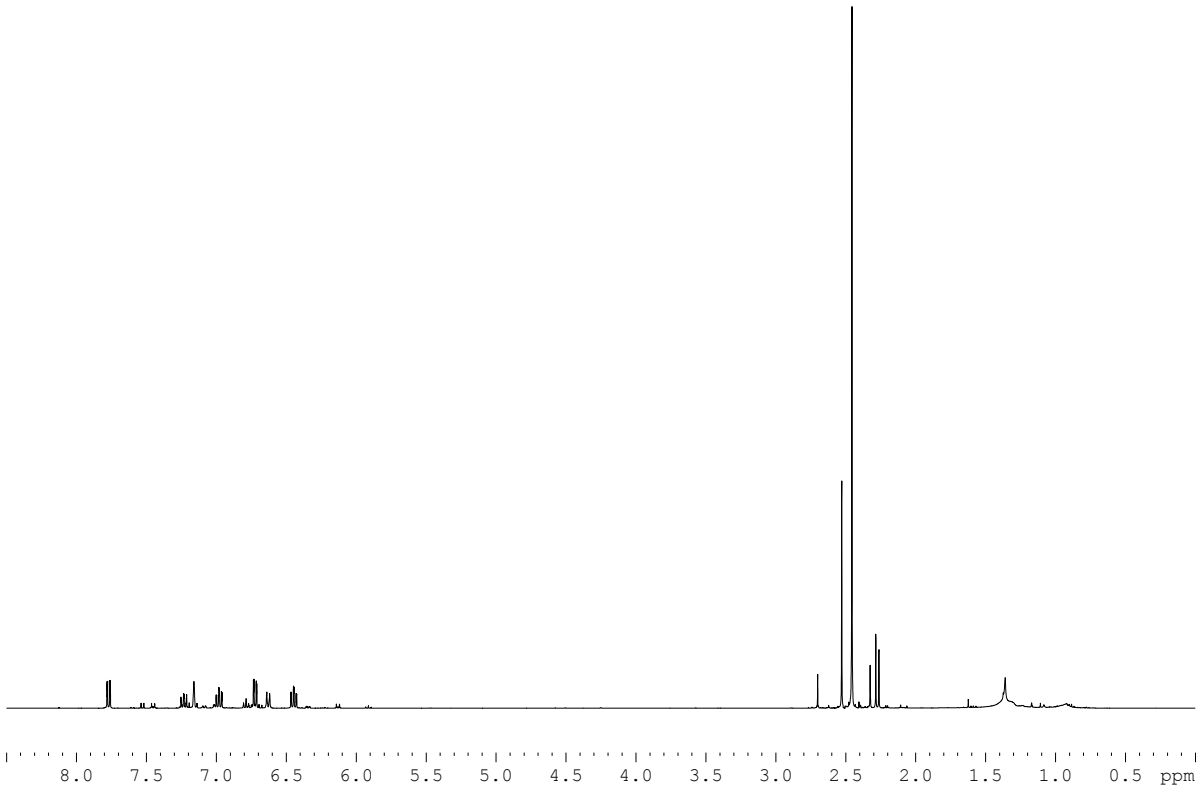
Spectrum 33. ^{13}C NMR (100.62 MHz, 300 K) spectrum of **6** in d_8-THF solution.



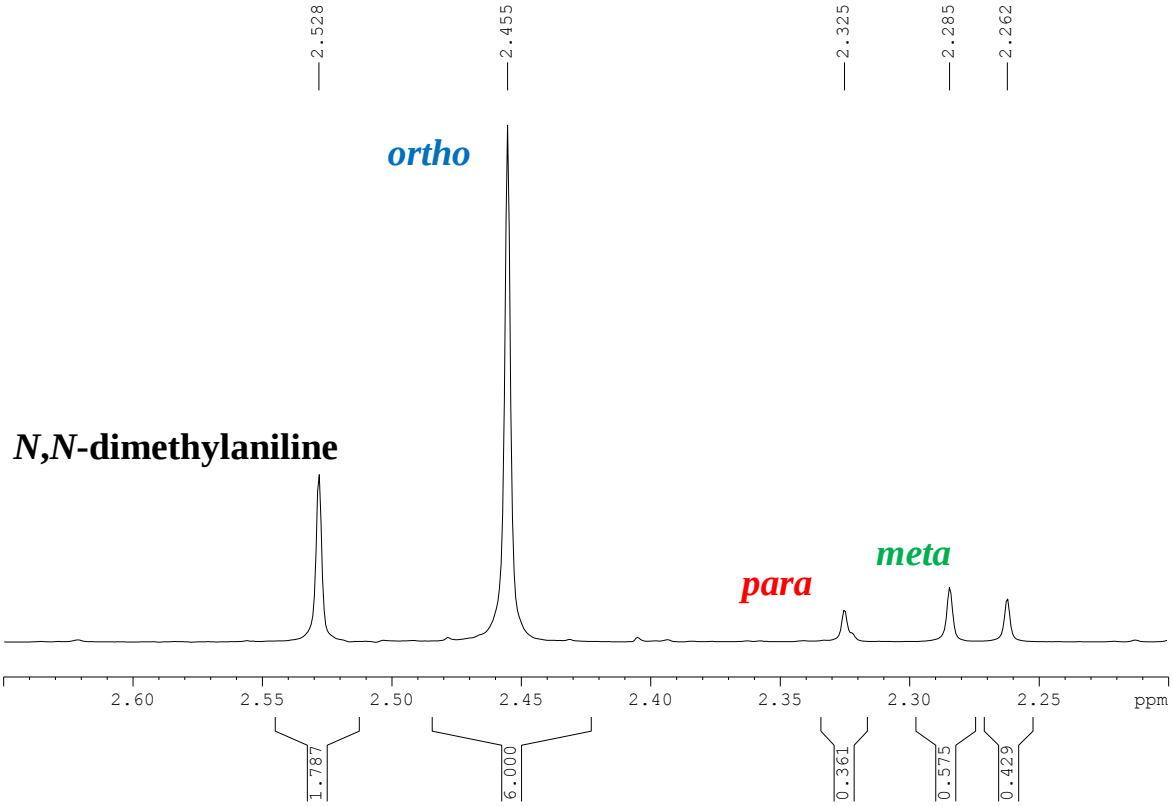
Spectrum 34. Aliphatic region of ^{13}C NMR spectrum of **6** in d_8-THF solution.



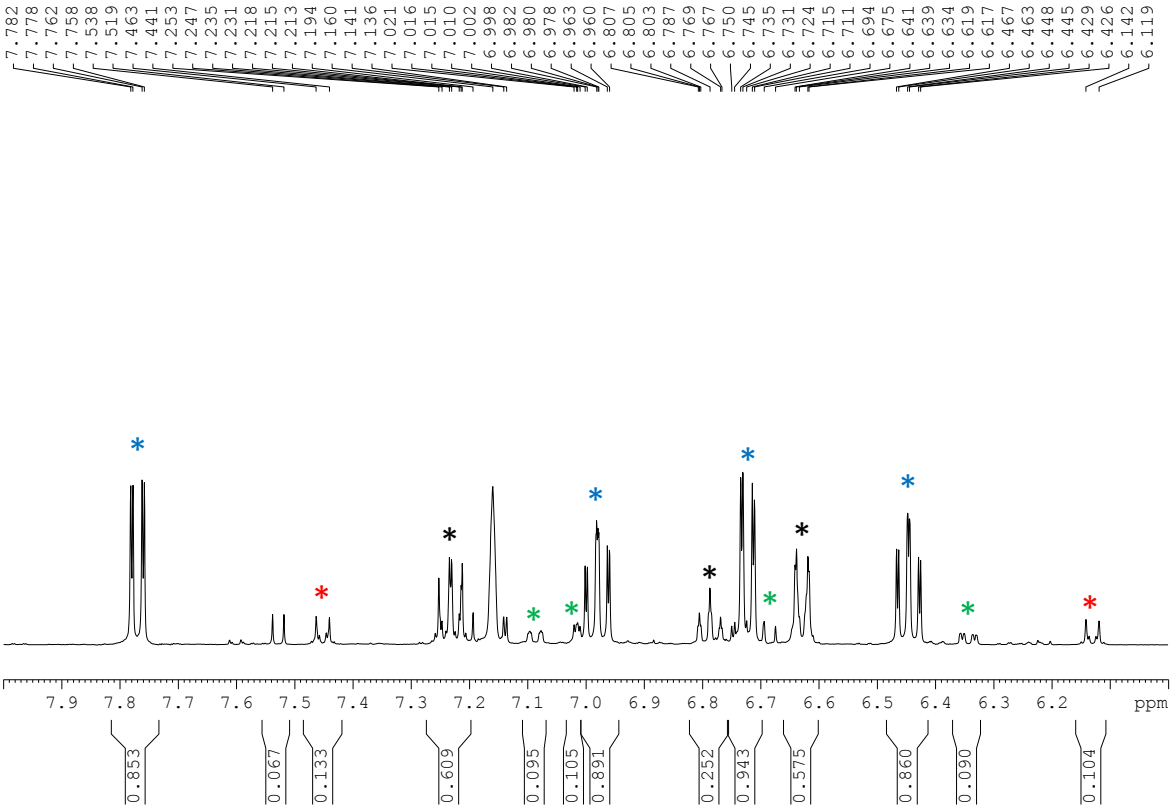
Spectrum 35. Aromatic region of ^{13}C NMR spectrum of **6** in d_8-THF solution.



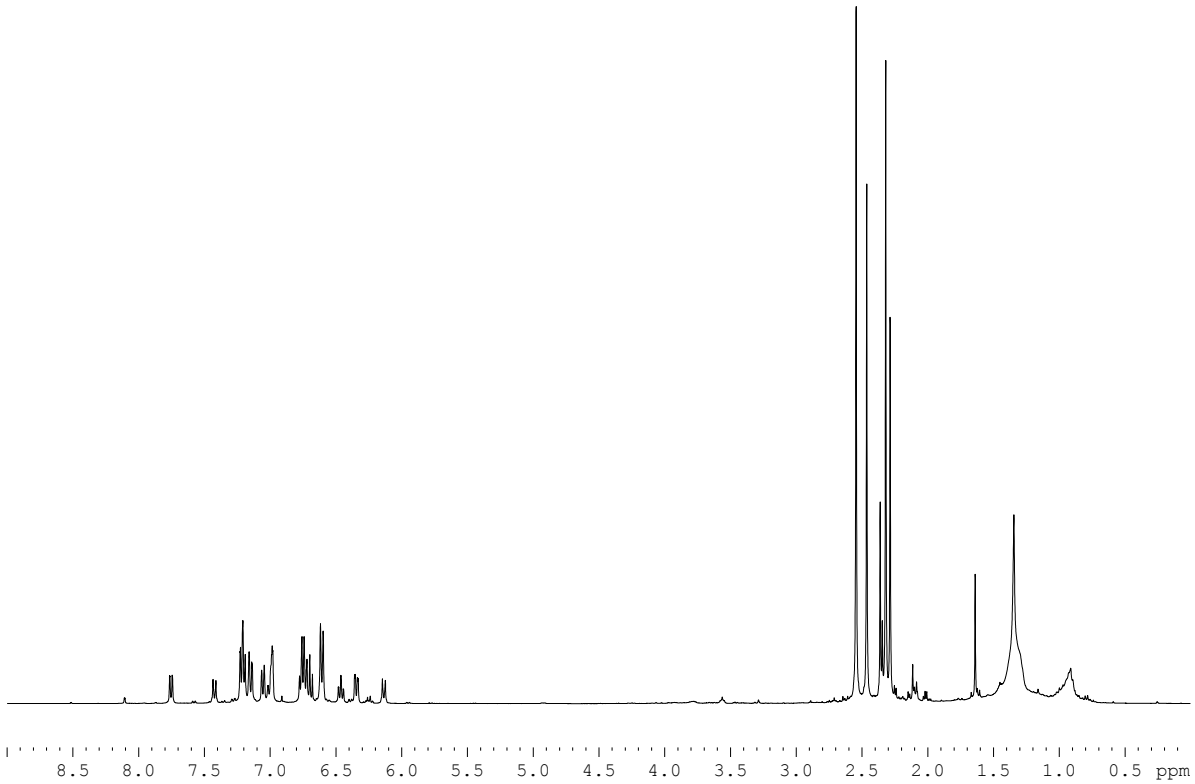
Spectrum 36. ^1H NMR (400.13 MHz, 300 K) from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu_2Zn and TMP(H) with iodine in C_6D_6 solution.



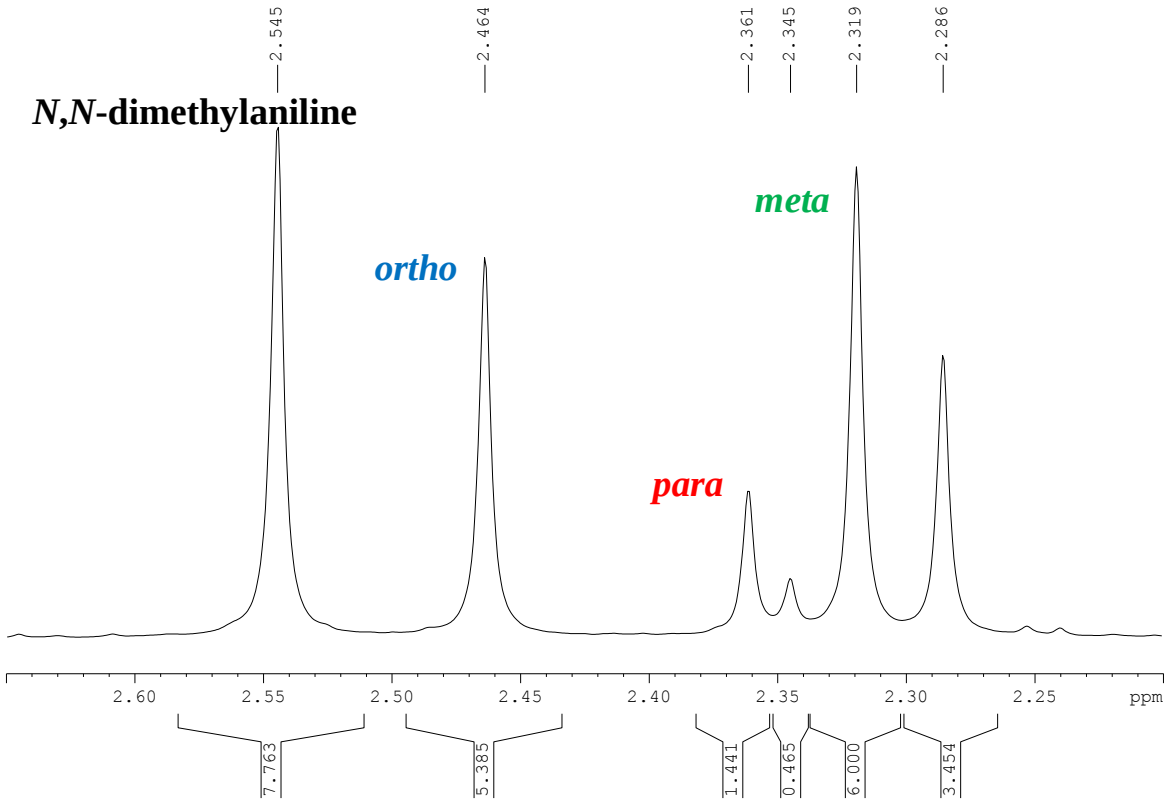
Spectrum 37. Aliphatic region of ^{1}H NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu$_2$Zn and TMP(H) with iodine in C_6D_6 solution.



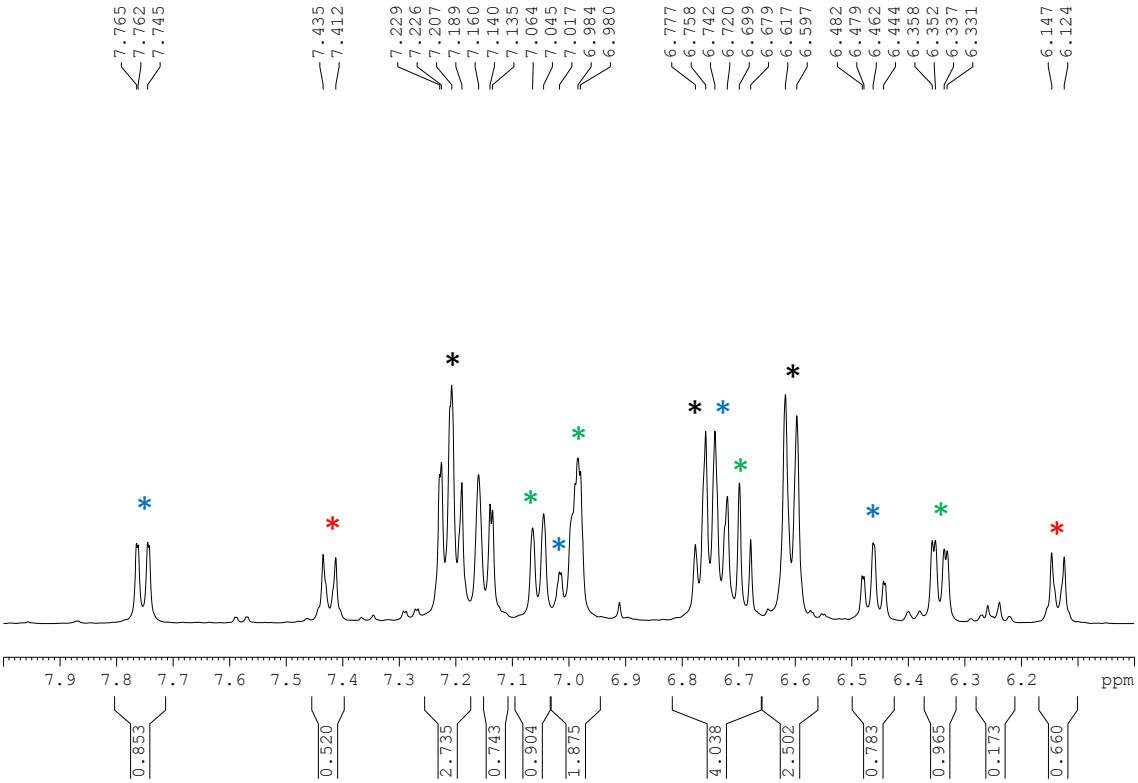
Spectrum 38. Aromatic region of ^{1}H NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu$_2$Zn and TMP(H) with iodine in C_6D_6 solution.



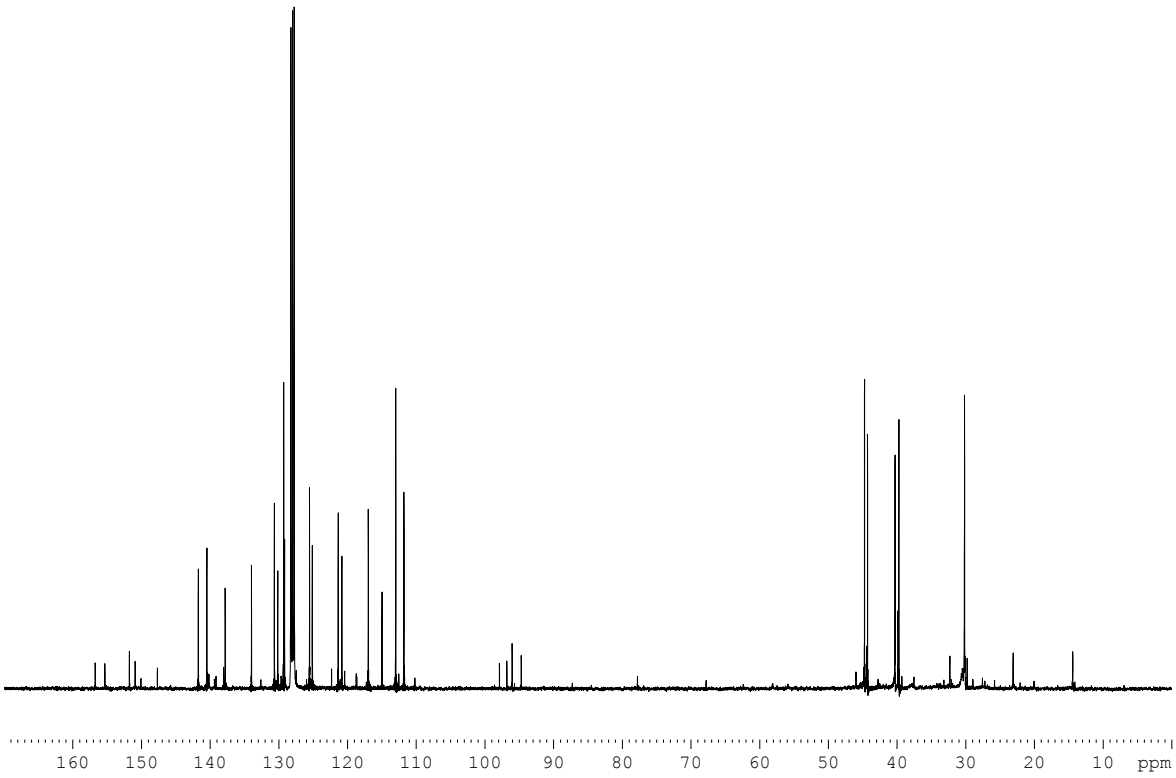
Spectrum 39. ^{1}H NMR (400.13 MHz, 300 K) spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu_2Zn and TMP(H) with iodine following an overnight reflux in C_6D_6 solution.



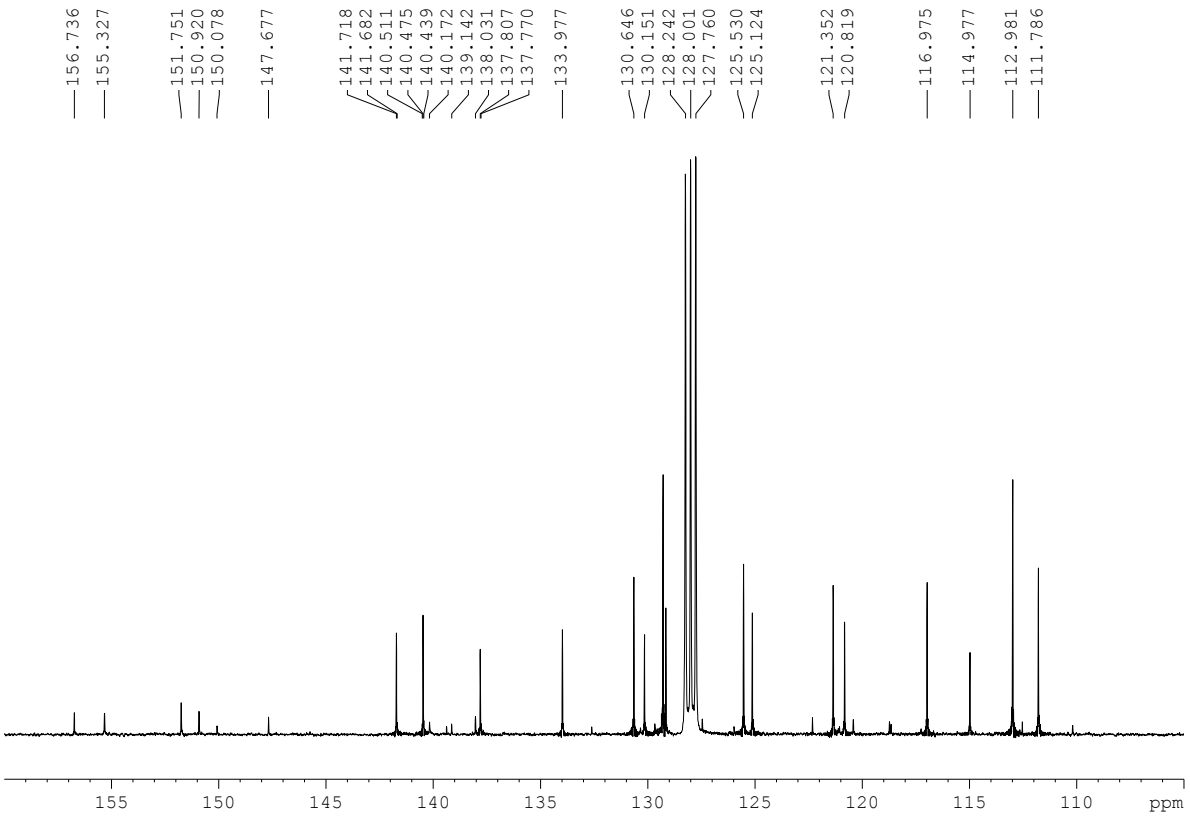
Spectrum 40. Aliphatic region of ^{1}H NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu_2Zn and TMP(H) with iodine following an overnight reflux in C_6D_6 solution.



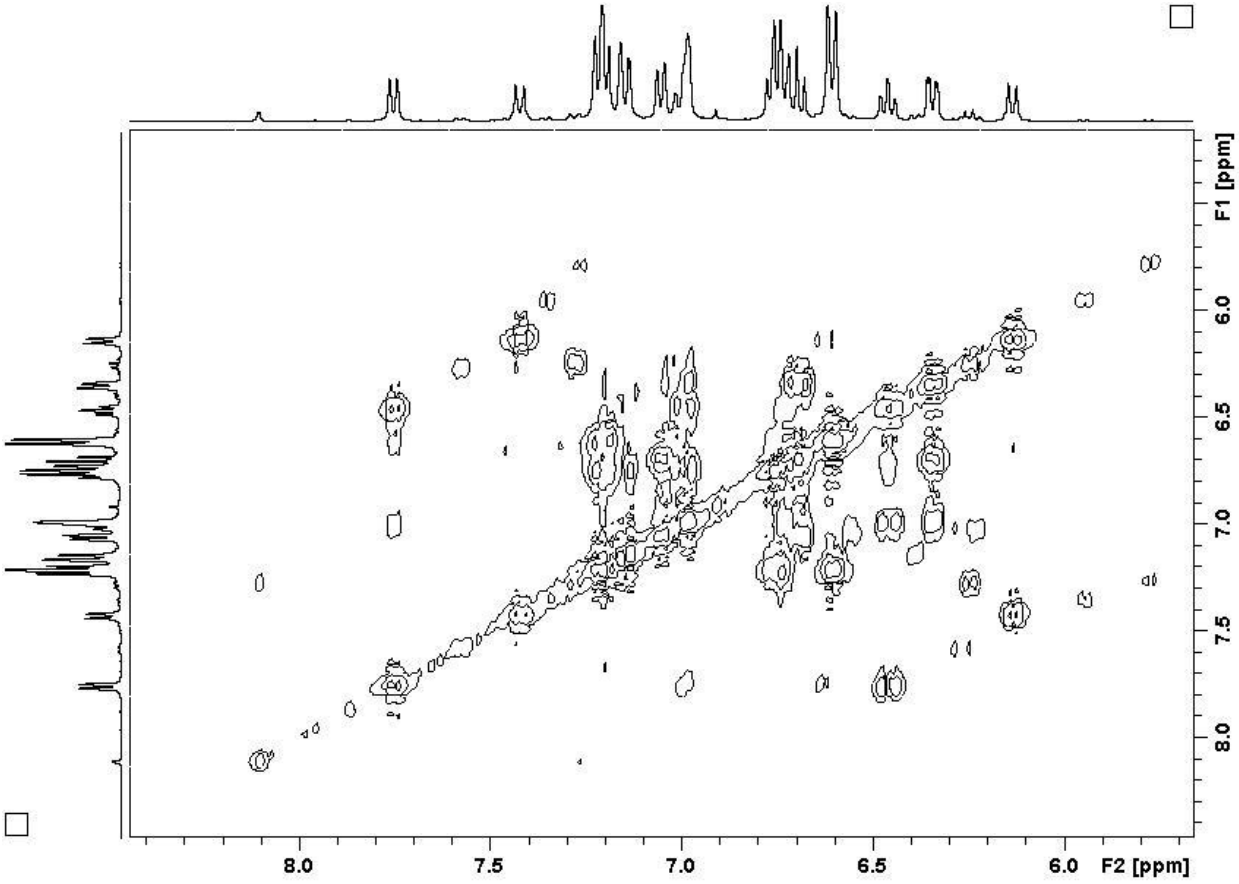
Spectrum 41. Aromatic region of ^{1}H NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu$_2$Zn and TMP(H) with iodine following an overnight reflux in C_6D_6 solution.



Spectrum 42. ^{13}C NMR (100.62 MHz, 300 K) spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu$_2$Zn and TMP(H) with iodine following an overnight reflux in C_6D_6 solution.



Spectrum 43. Aromatic region of ^{13}C NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu_2Zn and TMP(H) with iodine following an overnight reflux in C_6D_6 solution.



Spectrum 44. Aromatic region of ^{1}H-^{1}H COSY NMR spectrum from the reaction of BuNa·TMEDA, *N*,*N*-dimethylaniline, *t*Bu_2Zn and TMP(H) with iodine following an overnight reflux in C_6D_6 solution.

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