Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Hydrogenation and *N*-alkylation of anilines and imines via transfer hydrogenation with homogeneous nickel compounds

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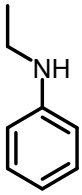
1 Analytical Data

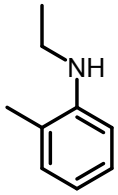


2a

***N*-Ethylaniline**[1,2]

Prepared following the general procedure, the crude product was analyzed directly by NMR spectroscopy, which corresponds to product **2a**, brown oil, yield (GC-MS: 100%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.15-7.02 (*m*, 2H), 6.62 (*p*, *J*=6.7Hz, 1H), 6.53 (*d*, *J*=7.8Hz, 2H), 3.08 (*q*, *J*=7.1Hz, 2H), 1.17 (*t*, *J*=7.1Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 148.4, 129.2, 117.3, 112.8, 38.5, 14.9; **IR** (cm^{-1}) ν 3399, 3050, 3021, 2967, 2929, 2871, 1600, 1503, 1353, 1257, 745, 691, 507; **EI-MS** (m/z) 121, 106 (100%), 91, 77.

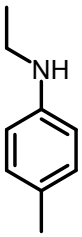


2b

***N*-Ethyl-2-methylaniline**[2]

Prepared according to general procedure, the crude product was analyzed directly by NMR spectroscopy, which corresponds to product **2b**, brown oil, yield (GC-MS: 100%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.05 (*td, J_1*=7.5Hz*, J_2*=1.6Hz, 1H), 6.97 (*d*, *J*= 7.7Hz, 1H), 6.58 (*d, J*=7.4Hz, 1H), 6.54 (*d, J*=8.0Hz, 1H), 3.3 (br), 3.12 (*q, J*= 7.1Hz, 2H), 2.06 (*s*, 3H), 1.22 (*t, J*=7.1 Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm): 146.4, 130.0, 127.2, 116.8, 109.7, 38.4, 17.5, 15.0; **IR** (cm^{-1}) ν 3424, 3016, 2967, 2929, 2872, 1605, 1585, 1511, 1377, 1258, 742, 440; **EI-MS** (m/z) 135, 120 (100%), 106, 91, 77.



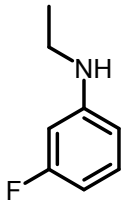
2d

***N*-Ethyl-4-methylaniline**[2]

Following the general procedure, the crude product was analyzed directly by NMR spectroscopy, which corresponds to product **2d**, brown oil, yield (GC-MS: 100%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.94-6.91 (*m*, 1H), 6.91-6.88 (*m*, 1H), 6.49-6.46 (*m*, 1H), 6.46-6.43 (*m*, 1H), 3.05 (*q, J*= 7.1Hz, 2H), 2.16 (*s*, 3H), 1.16 (*t,*

J=7.1 Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 146.3, 129.7, 126.4, 113.0, 38.9, 20.4, 15.0; **IR** (cm^{-1}) ν 3397, 3015, 2966, 2920, 2868, 1617, 1518, 1377, 1275, 802, 507; **EI-MS** (m/z) 135, 120 (100%), 106, 91, 77.

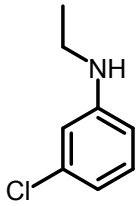


2e

_N_-Ethyl-2-fluoroaniline[5]

m-Fluoroaniline (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the crude product was purified through column chromatography over silica gel 70/230 (12.0 g) and hexane/THF (95/5) as eluent to give *N*-monoalkyl product **2e**, brown oil, yield (GC-MS: 100%, isolated product: 93%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.09 (*q, J*=7.2Hz, 1H), 6.43-6.32 (*m*, 2H), 6.28 (*dd, J_1*=11.7Hz, *J_2*= 2.2Hz, 1H), 3.45 (*br*, 1H), 3.13 (*q, J*=7.2Hz, 2H), 1.25 (*t, J*=7.2 Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 130.2 (*d, J_{CF}*=10.1Hz), 108.6, 103.6, 103.3, 99.4, 99.0, 38.4, 14.7; **IR** (cm^{-1}) ν 3403, 3290, 3059, 2967, 2934, 2874, 1619, 1589, 1511, 1366, 1258, 814, 747, 454; **EI-MS** (m/z) 139, 124, 109, 95, 75.

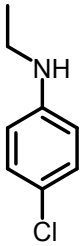


2g

3-Chloro-_N_-ethylaniline[5]

m-Chloroaniline (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the crude product was purified through column chromatography over silica gel 70/230 (12.0 g) and hexane/THF (95/5) as eluent to give *N*-monoalkyl product **2g**, brown oil, yield (GC-MS: 74%, isolated product: 58%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.98 (*t, J*=8.0Hz, 1H), 6.57 (*ddd*, *J*= 7.8Hz, 2.0Hz, 0.9 Hz, 1H), 6.49 (*t, J*=2.2Hz, 1H), 6.38 (*ddd, J*=8.2Hz, 2.3Hz, 0.9Hz, 1H), 3.56 (*br*., 1H), 3.05 (*q, J*= 7.1Hz, 2H), 1.17 (*t, J*=7.1 Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 149.7, 130.3, 117.1, 112.3, 111.2, 38.4, 14.8; **IR** (cm^{-1}) ν 3410, 3026, 2968, 2927, 2872, 1599, 1497, 1292, 1279, 878, 810, 732, 504; **EI-MS** (m/z) 155, 140(100%), 118, 105, 99, 77.

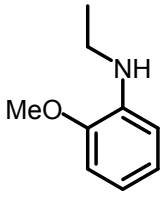


2h

4-Chloro-_N_-ethylaniline[2]

p-Chloroaniline (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the crude product was purified through column chromatography over silica gel 70/230 (12.0 g) and hexane/THF (95/5) as eluent to give *N*-monoalkyl product **2h**, brown oil, yield (GC-MS: 55%, isolated product: 51%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.05 (*d, J*=8.8Hz, 2H), 6.44 (*d*, *J*= 8.8Hz, 2H), 3.04 (*q, J*=7.1Hz, 2H), 1.17 (*t, J*=7.1 Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 129.0, 125.6, 113.8, 38.6, 14.7; **IR** (cm^{-1}) ν 3411, 2969, 2928, 2872, 1569, 1500, 1379, 1276, 816, 439; **EI-MS** (m/z) 155, 140(100%), 118, 105, 91, 77.

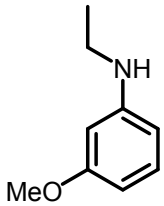


2i

***N*-Ethyl-2-methoxyaniline**[2]

o-Methoxyaniline (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the crude product was analyzed directly by NMR spectroscopy, which corresponds to product **2i**, brown oil, yield (GC-MS: 100%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.80 (*td*, *J*=7.6Hz, *J*=1.5Hz, 1H), 6.69 (*dd*, *J*=7.9Hz, *J*=1.4Hz, 1H), 6.59 (*dd*, *J*=7.5Hz, *J*=1.5Hz, 1H), 6.56-6.49 (*m*, 1H),4.0 (*br.*, 1H), 3.76 (*s*, 3H), 3.09 (*q*, *J*=7.2Hz, 2H), 1.21 (*t*, *J*=7.2Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 146.8, 138.5, 121.3, 116.3, 109.8, 109.3, 55.4, 38.2, 14.9; **IR** (cm^{-1}) ν 3419, 3064, 2965, 2935, 2871, 2834, 1600, 1511, 1453, 1248, 1218, 729, 506; **EI-MS** (m/z) 151, 136(100%), 120, 108, 77.



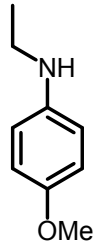
2j

***N*-Ethyl-3-methoxyaniline**[6]

m-Methoxyaniline (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the crude product was analyzed directly by NMR spectroscopy, which corresponds to product **2j**, brown oil, yield (GC-MS: 100%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.00 (*t, J*=8.1Hz, 1H), 6.22-6.13 (*m*, 2H), 6.09 (*t, J*=2.3Hz, 1H), 3.7 (*s*, 3H), 3.07 (*q, J*=7.2Hz, 2H), 1.17 (*t, J*=7.1 Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 149.9, 129.9, 106.0, 102.3, 98.7, 55.1, 38.5, 14.9 ;)

; **IR** (cm^{-1}) ν 3397, 2966, 2933, 2872, 2834, 1610, 1588, 1453, 1207, 1159, 988, 885, 815, 753, 686, 455; **EI-MS** (m/z) 151, 136(100%), 121, 108, 77.

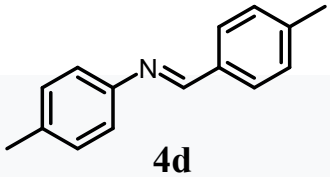


2k

***N*-Ethyl-4-methoxyaniline**[2]

p-Methoxyaniline (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the crude product was analyzed directly by NMR spectroscopy, which corresponds to product **2k**, brown oil, yield (GC-MS: 100%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.78-6.64 (*m*, 2H), 6.57-6.44 (*m*, 2H), 3.67 (*s*, 3H), 3.03 (*q*, *J*=7.1Hz, 2H), 1.16 (*t*, *J*=7.1Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 142.8, 114.9, 114.1, 55.8, 39.4, 15.0; **IR** (cm^{-1}) ν 3382, 2965, 2902, 2831, 1509, 1230, 1033, 815, 516; **EI-MS** (m/z) 151, 136(100%), 108.

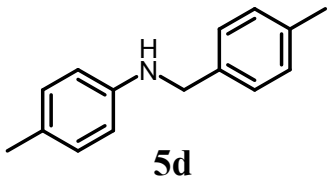


4d

***N*,1-di-p-tolylmethanimine**[7]

p-Toluidine (1.0 mmol) and *p*-Tolualdehyde were reacted in Ethanol drops and stirred manually with a glass rod for 10 minutes (getting a pearly white solid), the crude product was washed with cold ethanol, later it was solubilized in ethanol (25ºC) and crystallized by evaporation at room temperature obtaining translucent white crystal, isolated yield 97%.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.35 (*s*, 1H), 7.70 (*d*, *J*=8.2Hz, 2H), 7.19 (*d*, *J*=7.9Hz, 2H), 7.14-7.00 (*m*, 4H), 2.33 (*s*, 3H), 2.29 (*s*, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 159.6, 149.7, 141.7, 135.6, 133.8, 129.7, 129.5, 128.7, 120.8, 21.6, 21.0; **IR** (cm^{-1}) ν 3049, 3015, 2917, 2887, 1627, 1543, 850, 825, 532; **EI-MS** (m/z) 208 (100%), 194, 118, 91, 77.



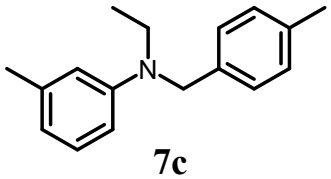
5d

4-Methyl-*N*-(4-methylbenzyl)aniline[8]

N-di-*p*-tolymethanimine **4** (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure, the

crude product was purified via preparative thin layer chromatography and hexane/THF (95/5) as eluent to give amine **7c**, brown oil, yield (GC-MS: 96% **7c**, isolated product **7c**: 73%)

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.18 (*d*, *J*=7.8Hz, 2H), 7.06 (*d*, *J*=7.9Hz, 2H), 6.95-6.84 (*m*, 2H), 6.51-6.46 (*m*, 3H), 4.18 (*s*, 2H), 2.26 (*s*, 3H), 2.16 (*s*, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 129.7, 129.3, 129.2, 127.5, 127.7, 113.0, 112.5, 48.4, 38.9, 21.1, 20.4; **IR** (cm^{-1}) ν 3409, 3331, 3016, 2928, 2854, 1603, 1511, 1489, 1176, 799, 766, 690, 477, 440; **EI-MS** (m/z) 211, 196, 105(100%), 91, 77.

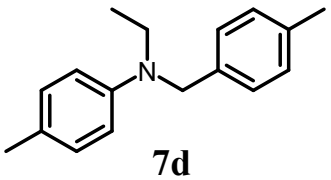


7c

***N*-Ethyl-3-methyl-*N*-(4-methylbenzyl)aniline**

m-Toluidine (1.2 mmol) and *p*-Tolualdehyde (1 mmol) were reacted in dry Ethanol (5.0 mL) according to general procedure for *N*-alkylation of imines, the crude product was purified via preparative thin layer chromatography and hexane/THF (95/5) as eluent to give amine **7c**, brown oil, yield (GC-MS: 95% **7c**, and 5% **5c**, isolated product **7c**: 83%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.12-6.86 (*m*, 5H), 6.58-6.30 (*m*, 3H), 4.38 (*s*, 2H), 3.35 (*q*, *J*=7.0Hz, 2H), 2.24 (s, 3H), 2.19 (*s*, 3H), 1.10 (*t*, *J*=7.0Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 148.7, 138.9, 136.3, 129.2, 129.1, 126.6, 125.6, 117.0, 112.8, 109.4, 53.6, 44.9, 30.4, 21.1, 12,1; **IR** (cm-1) ν 2963, 2921, 2869, 1600, 1496, 1257,1073, 1011, 863, 790, 690, 477; **EI-MS** (m/z) 239, 205, 105(100%), 77.



7d

***N*-Ethyl-4-methyl-*N*-(4-methylbenzyl)aniline**[8]

N-di-*p*-tolymethanimine **4** (1.0 mmol) was reacted in dry Ethanol (5.0 mL) according to general procedure for *N*-alkylation of imines, the crude product was purified via preparative thin layer chromatography and hexane/THF (95/5) as eluent to give amine **7d**, brown oil, yield (GC-MS: 98%, isolated product: 86%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.11-6.98 (*m*, 4H), 6.95-6.86 (*m*, 2H), 6.55 (*d*, *J*=8.6Hz, 2H), 4.37 (*s*, 2H), 3.35, (*q*, *J*=7.0Hz, 2H), 2.25 (*s*, 3H), 2.15 (*s*, 3H), 1.10 (*t*, *J*=7.0Hz, 3H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) δ (ppm) 129.7, 129.2, 126.6, 125.5, 112.5, 53.9, 45.1, 30.3, 29.4, 12.1; **IR** (cm^{-1}) ν 2961, 2919, 2866, 1617, 1516, 795, 512, 478; **EI-MS** (m/z) 239, 205, 105(100%), 91, 77.

2 References

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3 Spectra and Chromatograms

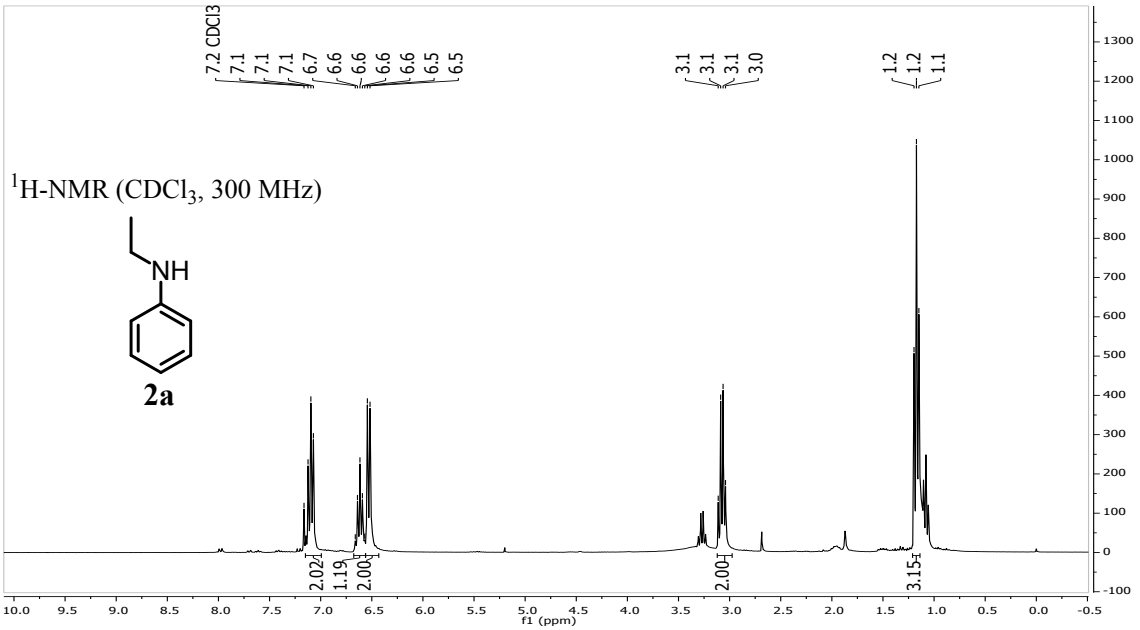

Figure S1. ^{1}H-NMR spectrum of *N*-ethylaniline **2a** in $CDCl_3$.

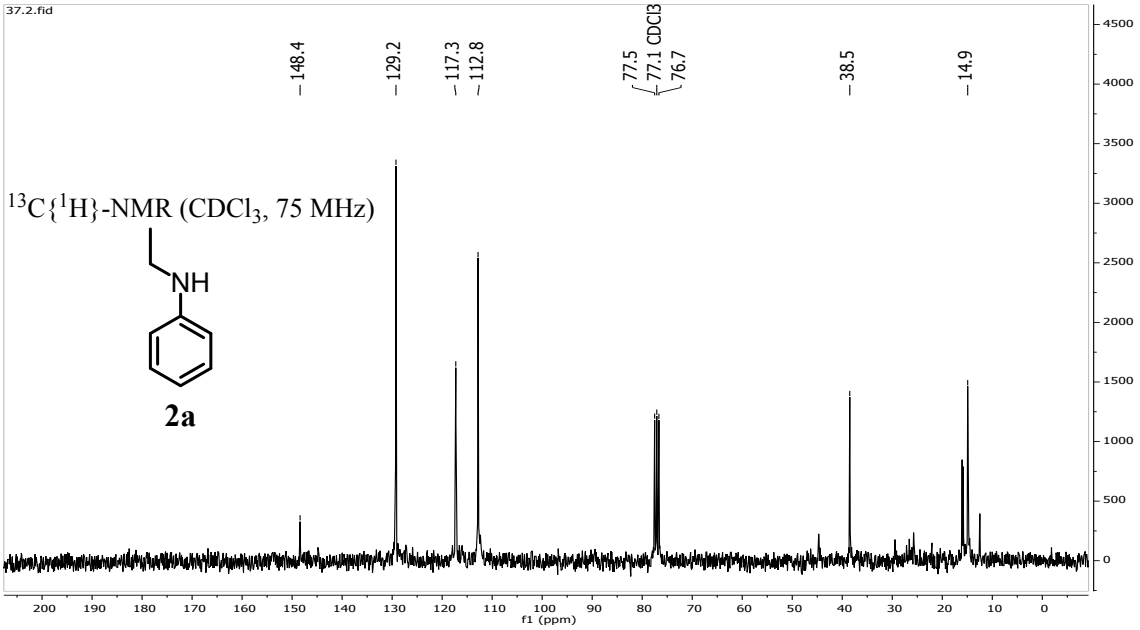

Figure S2. ^{13}C{^{1}H}-NMR spectrum of *N*-ethylaniline **2a** in $CDCl_3$.

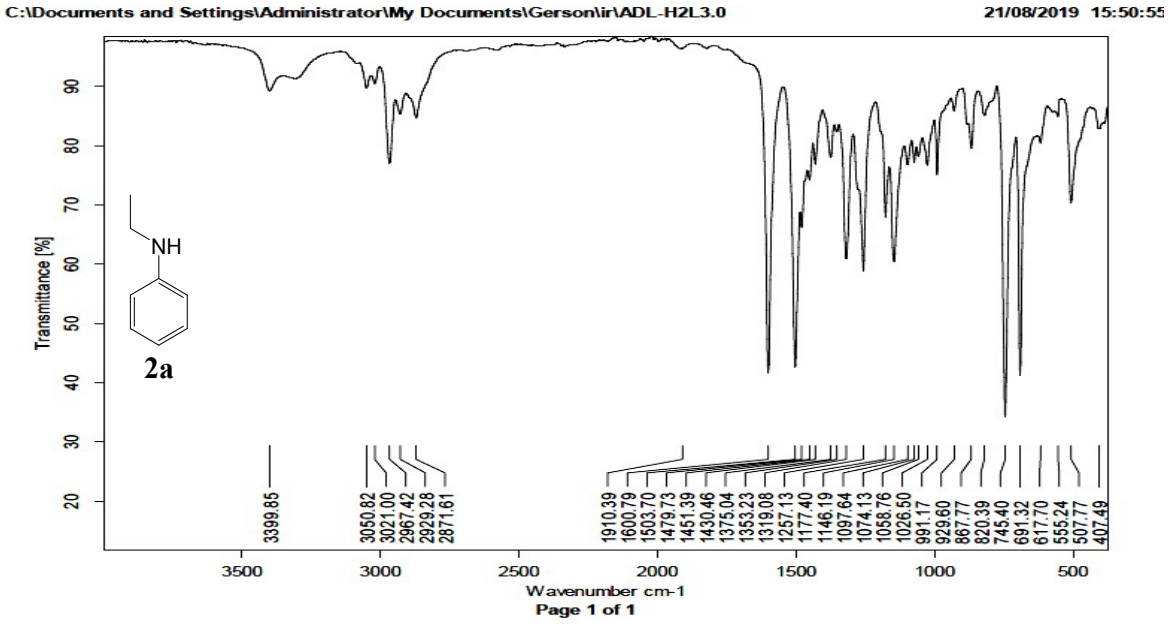

Figure S3. FT-IR spectrum of *N*-ethylaniline **2a**.

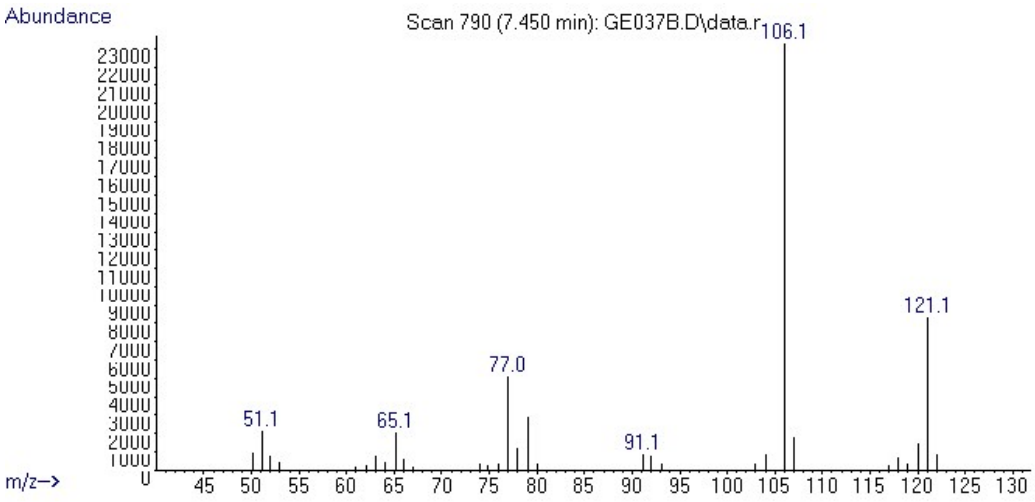

Figure S4. Mass spectrum of *N*-ethylaniline **2a**.

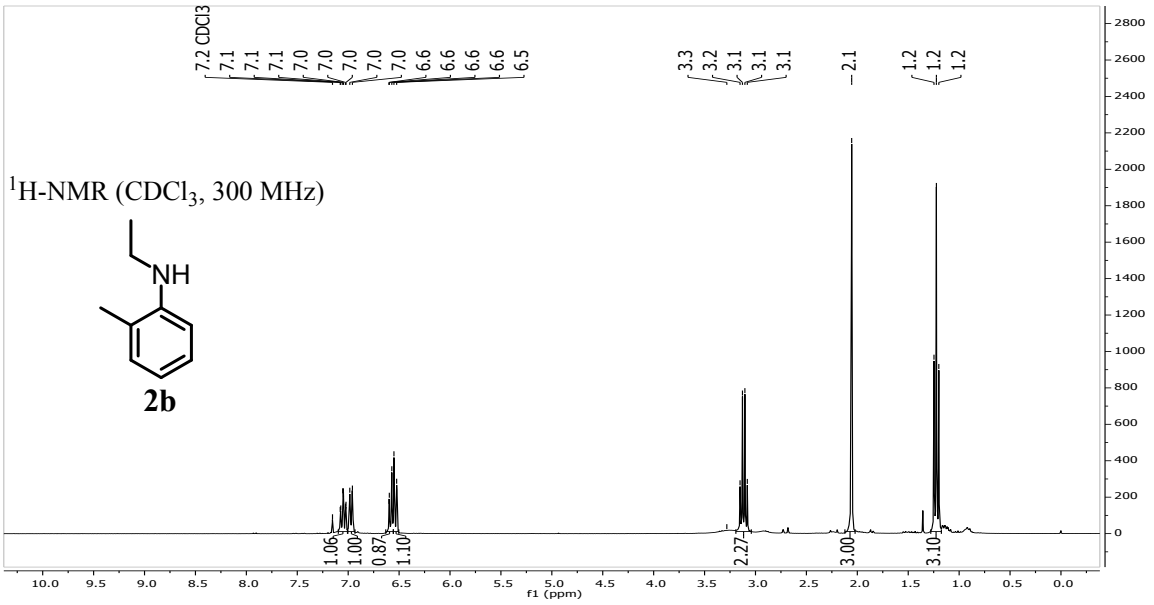

Figure S5. ^{1}H-NMR spectrum of *N*-Ethyl-2-methylaniline **2b** in $CDCl_3$.

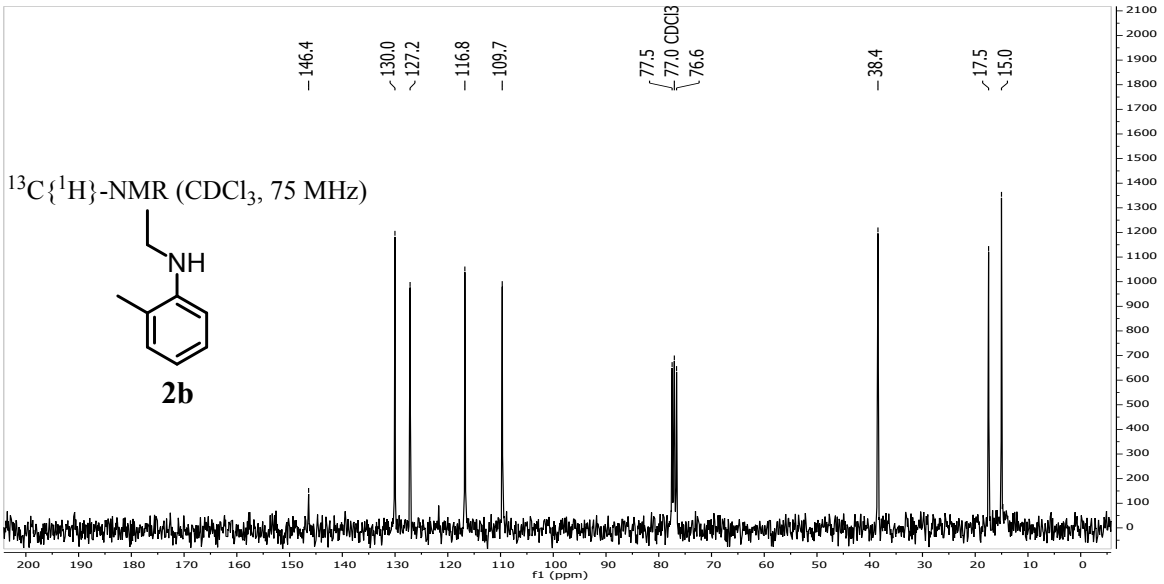

Figure S6. ^{13}C{^{1}H}-NMR spectrum of *N*-Ethyl-2-methylaniline **2b** in $CDCl_3$.

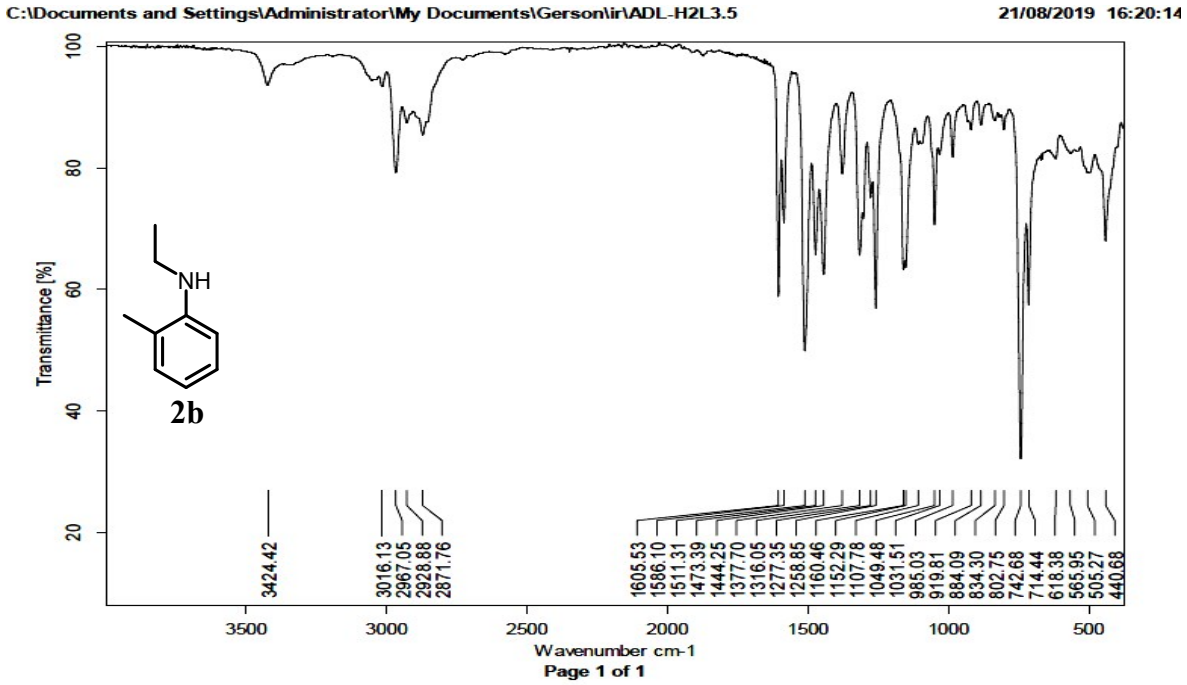

Figure S7. FT-IR spectrum of *N*-Ethyl-2-methylaniline **2b**.

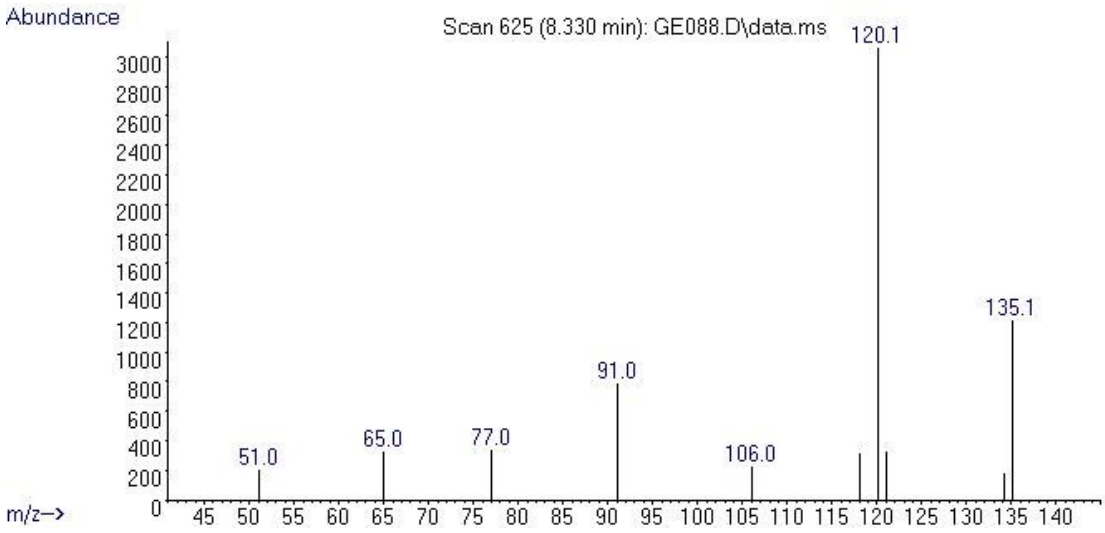

Figure S8. Mass spectrum of *N*-Ethyl-2-methylaniline **2b**.

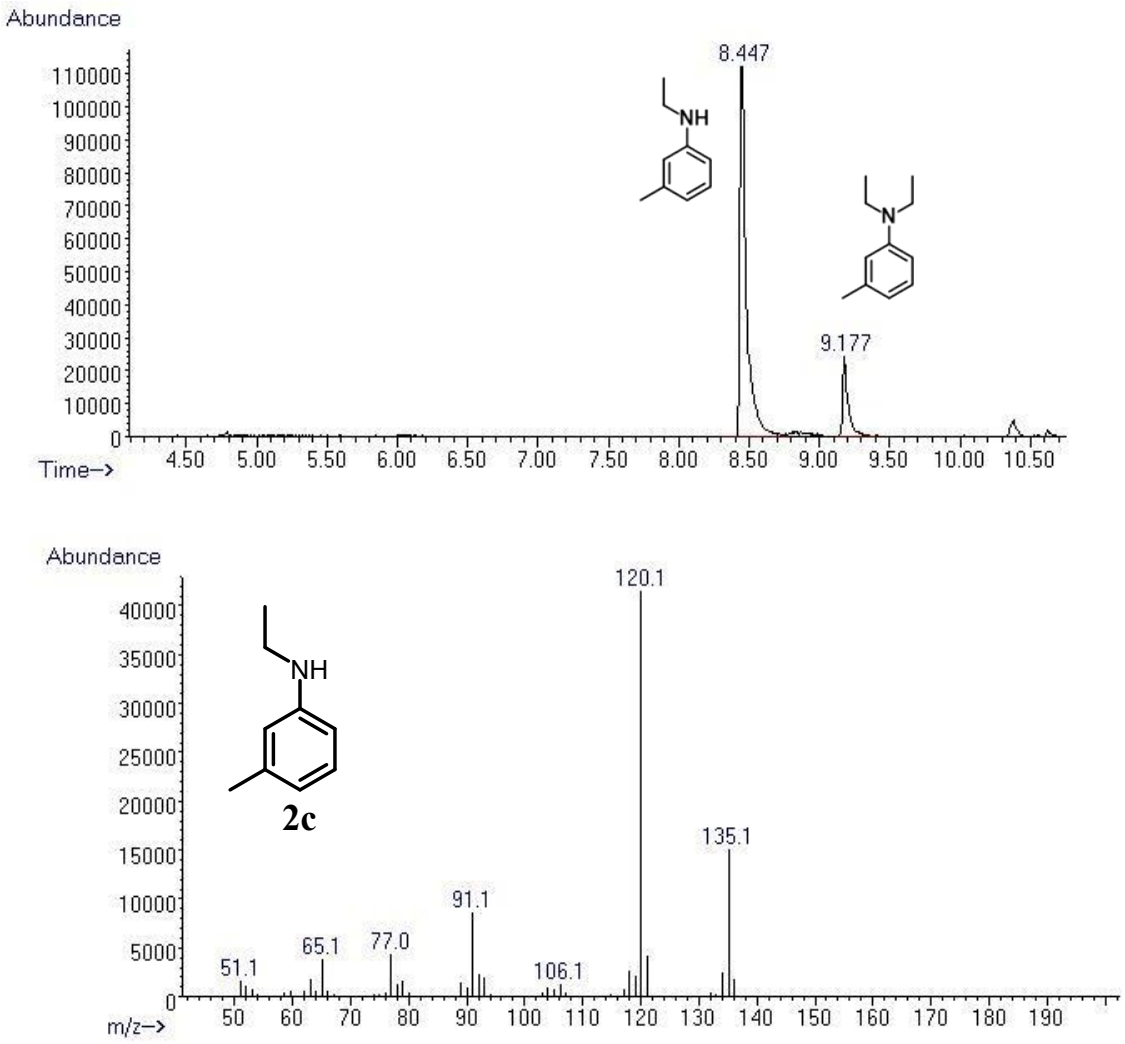

Figure S9. Chromatogram and mass spectrum of *N*-Ethyl-3-methylaniline **2c**.

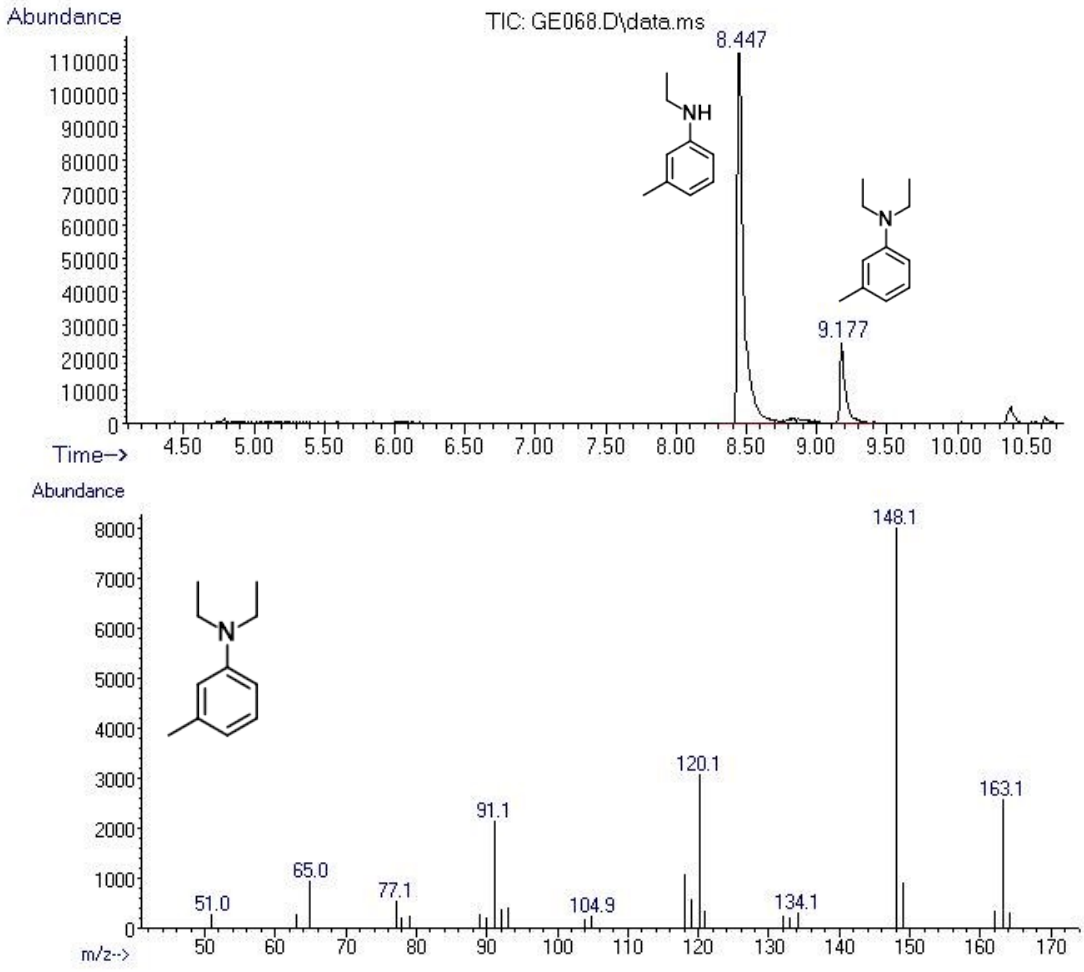

Figure S10. Chromatogram and mass spectrum of *N, N*-diethyl-3-methylaniline **3c**.

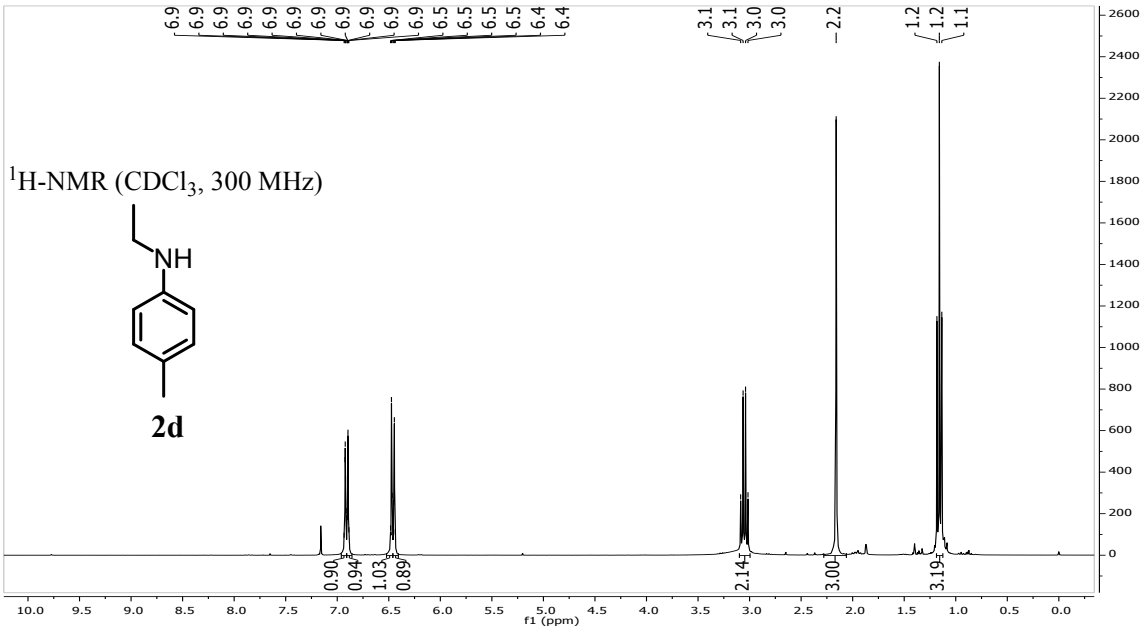

Figure S11. ^{1}H-NMR spectrum of *N*-Ethyl-4-methylaniline **2d** in $CDCl_3$.

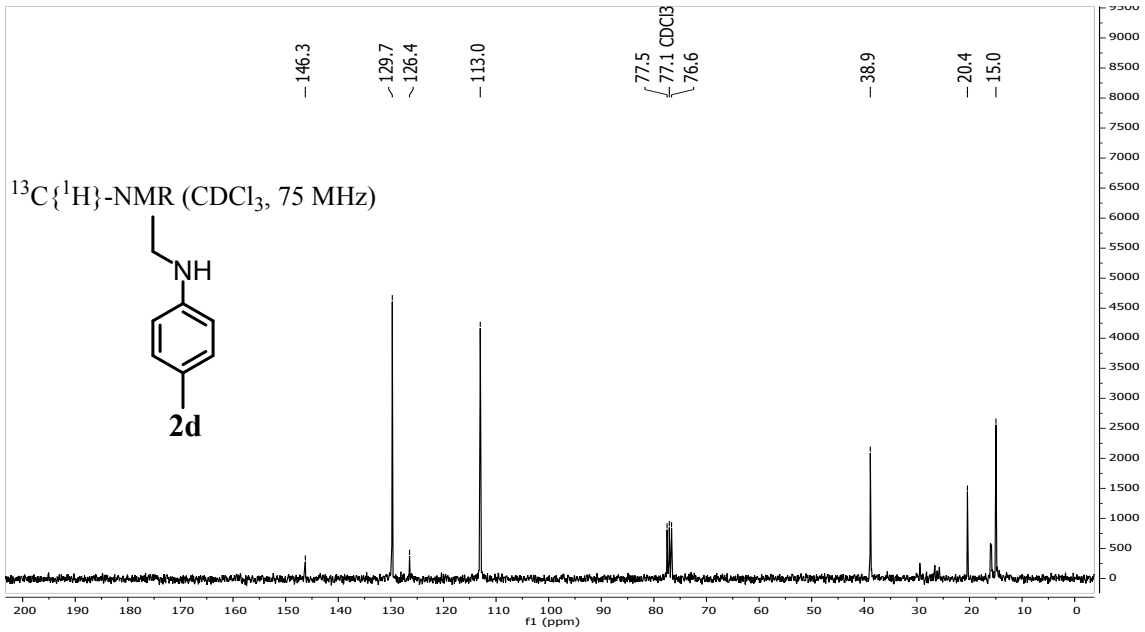

Figure S12. ^{13}C{^{1}H}-NMR spectrum of *N*-Ethyl-4-methylaniline **2d** in $CDCl_3$.

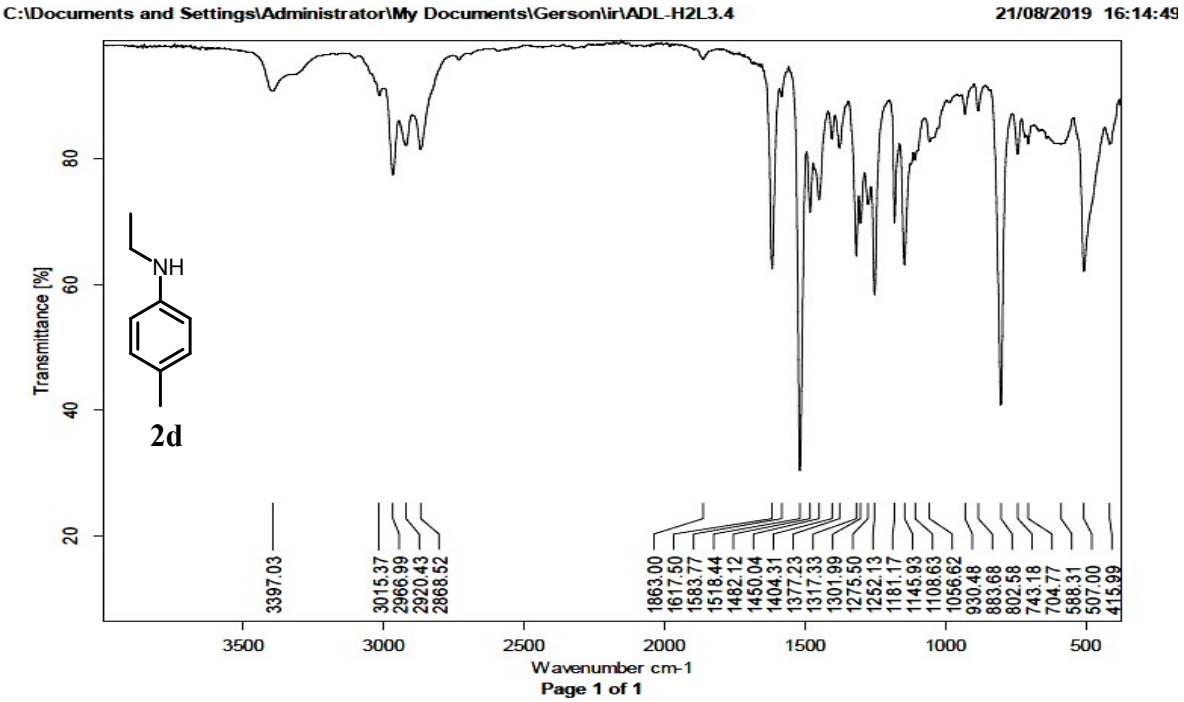

Figure S13. FT-IR spectrum of *N*-Ethyl-4-methylaniline **2d**.

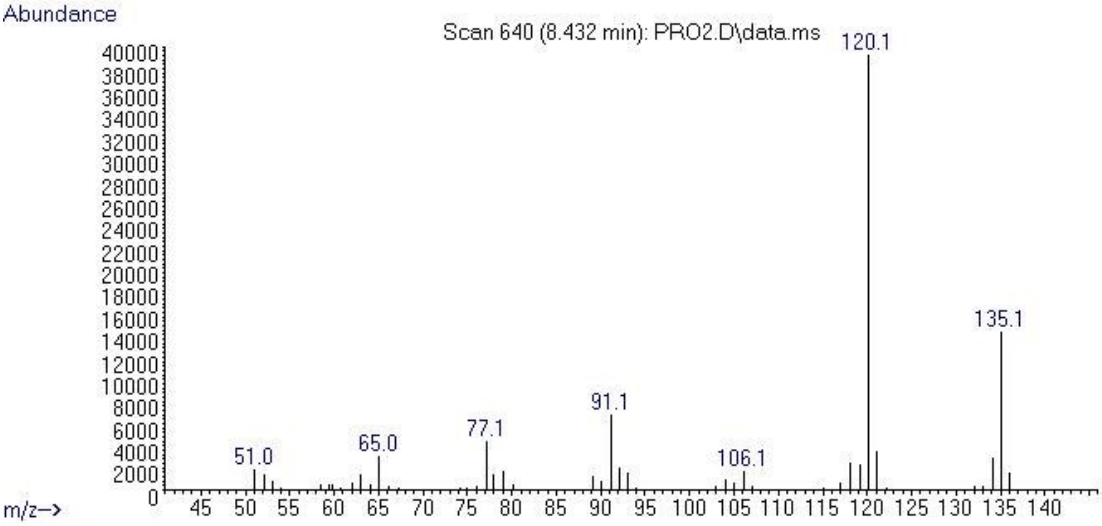

Figure S14. Mass spectrum of *N*-Ethyl-4-methylaniline **2d**.

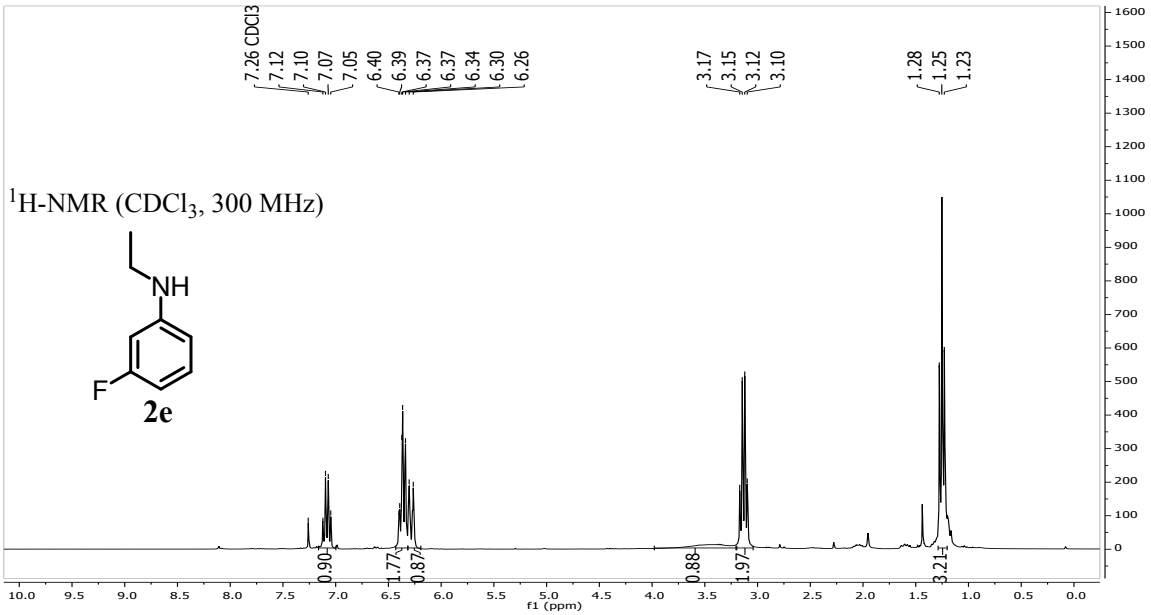

Figure S15. ^{1}H-NMR spectrum of *N*-Ethyl-3-fluoroaniline **2e** in $CDCl_3$.

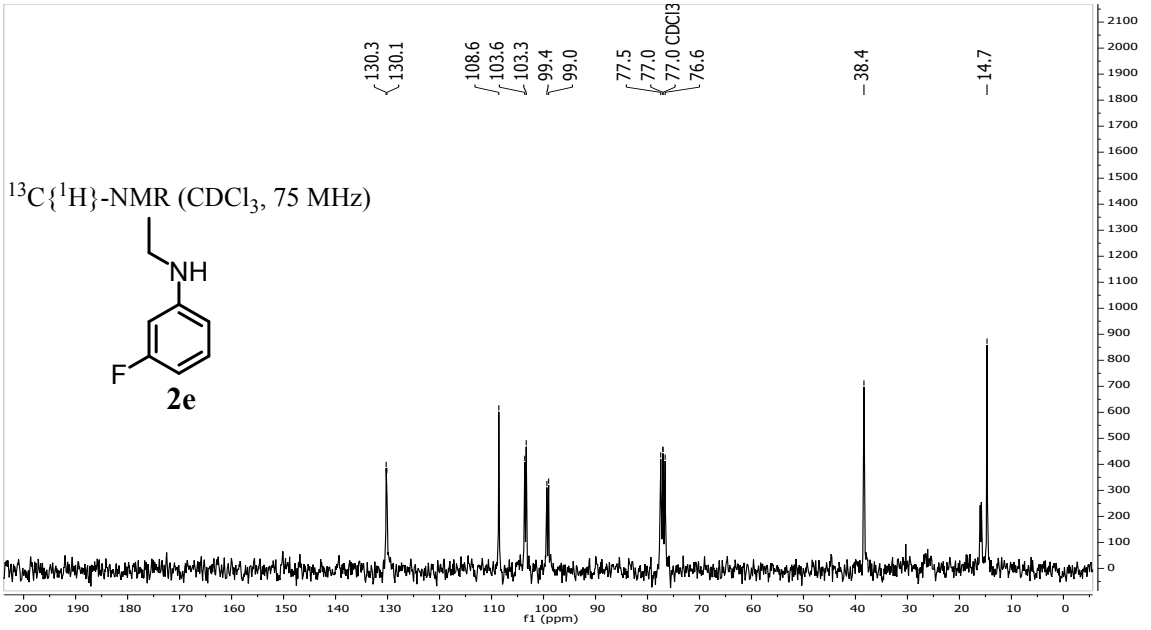

Figure S16. ^{13}C{^{1}H}-NMR spectrum of *N*-Ethyl-3-fluoroaniline **2e** in $CDCl_3$.

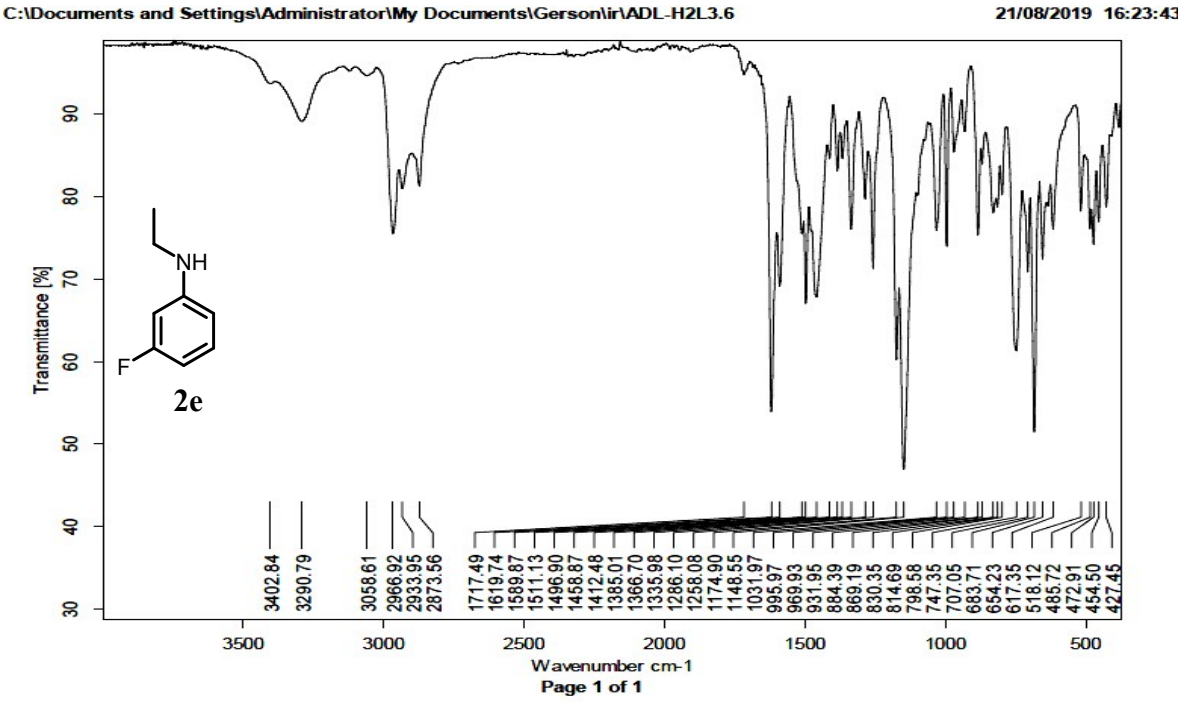

Figure S17. FT-IR spectrum of *N*-Ethyl-3-fluoroaniline **2e**.

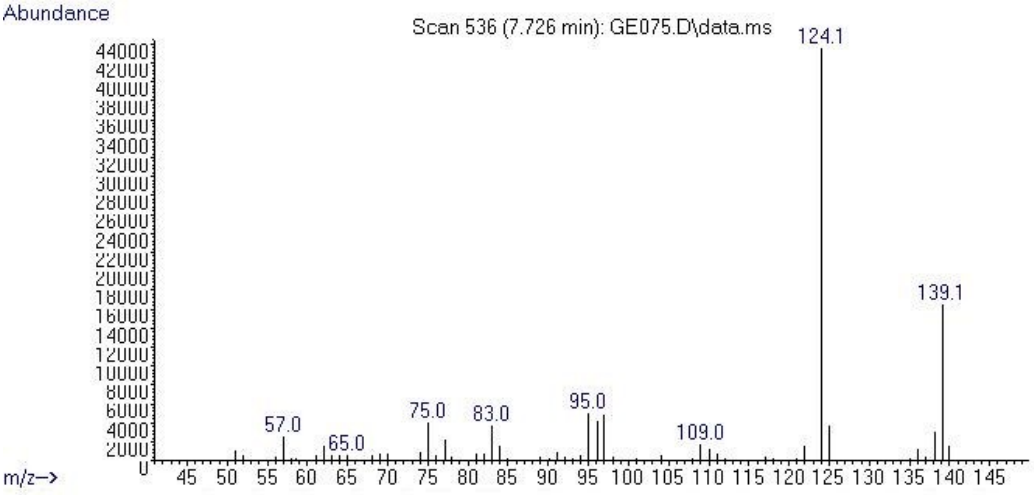

Figure S18. Mass spectrum of *N*-Ethyl-3-fluoroaniline **2e**.

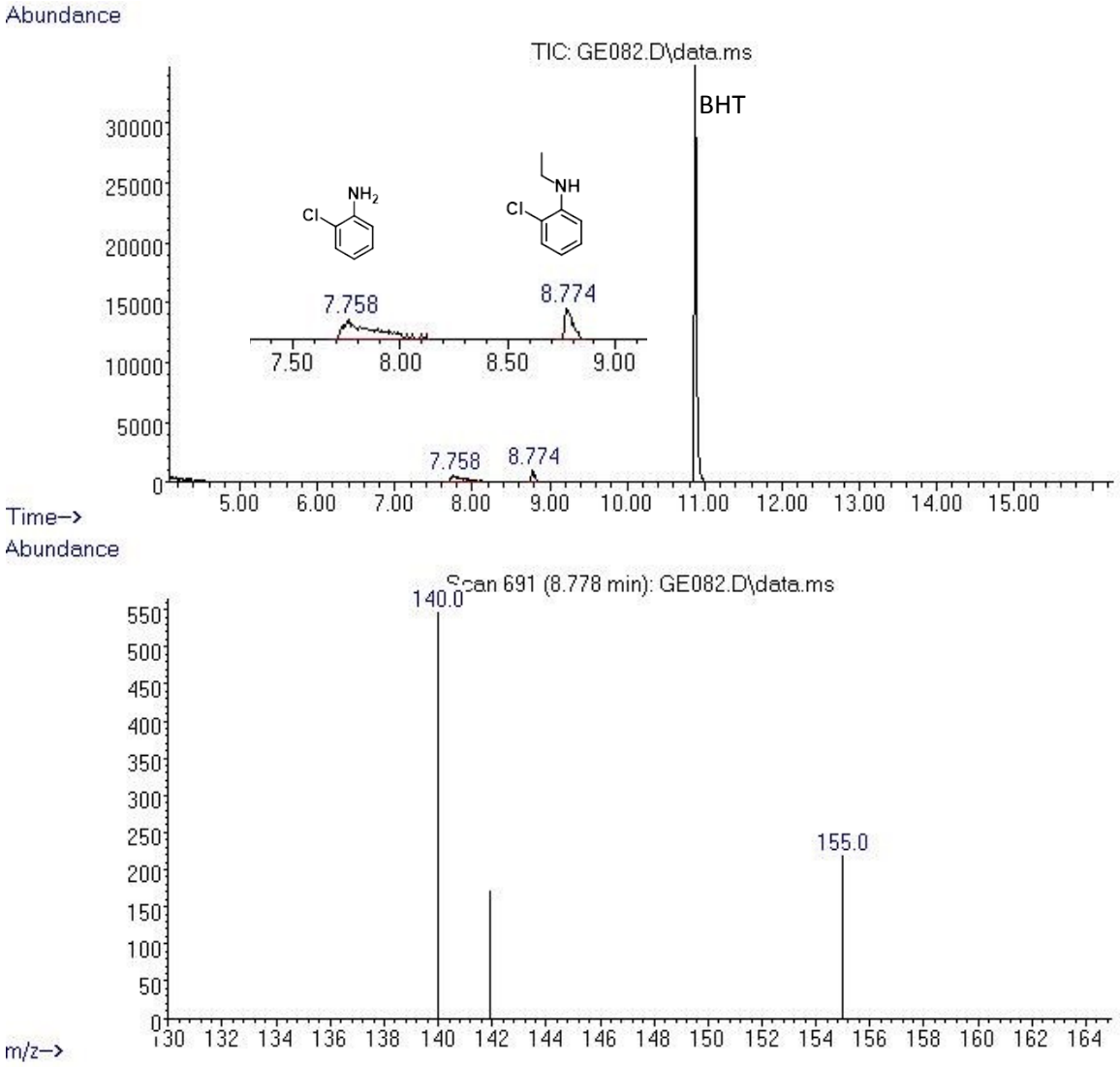

Figure S19. Chromatogram and mass spectrum of 2-chloro-*N*-ethylaniline **2f**.

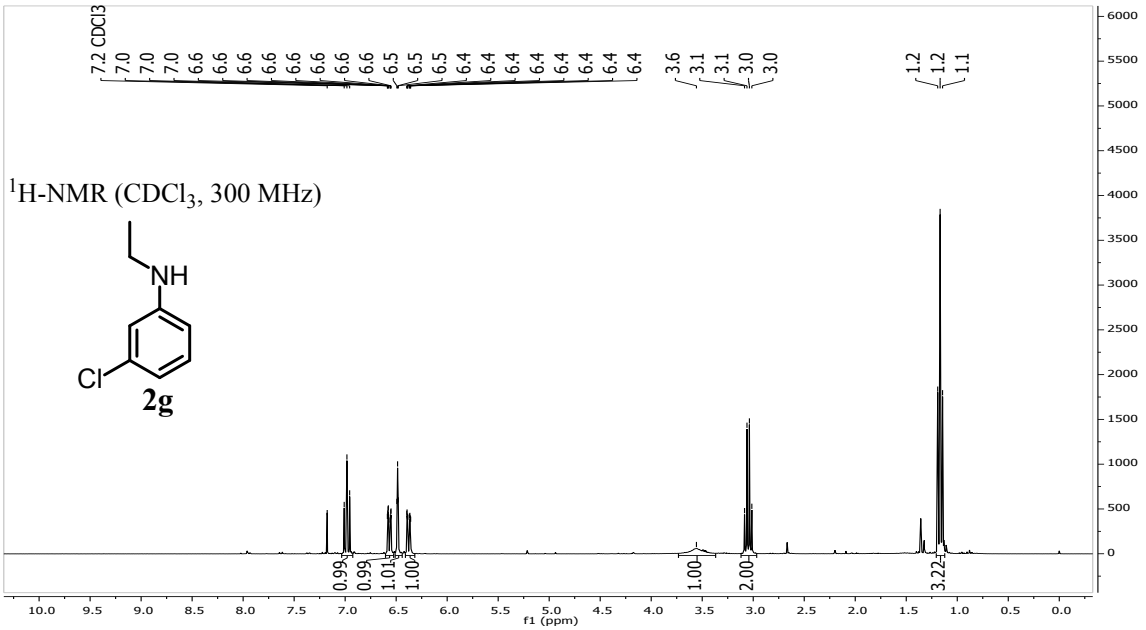

Figure S20. ^{1}H-NMR spectrum of 3-chloro-*N*-ethylaniline **2g** in $CDCl_3$.

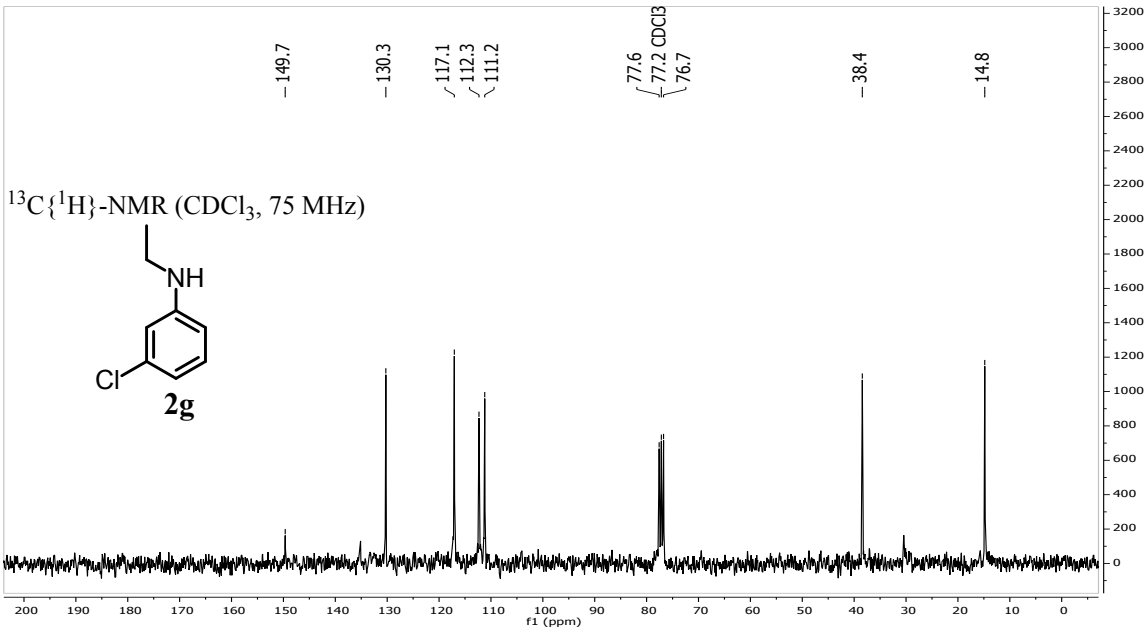

Figure S21. ^{13}C{^{1}H}-NMR spectrum of 3-chloro-*N*-ethylaniline **2g** in $CDCl_3$.

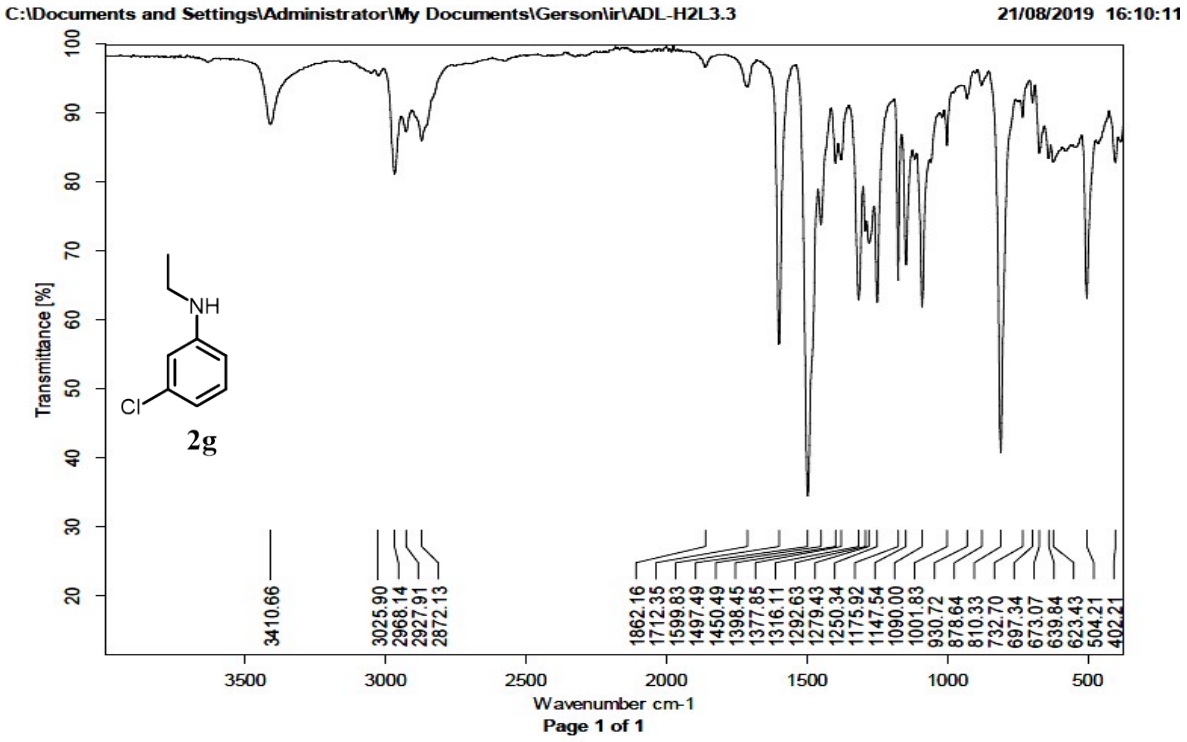

Figure S22. FT-IR spectrum of 3-chloro-*N*-ethylaniline **2g**.

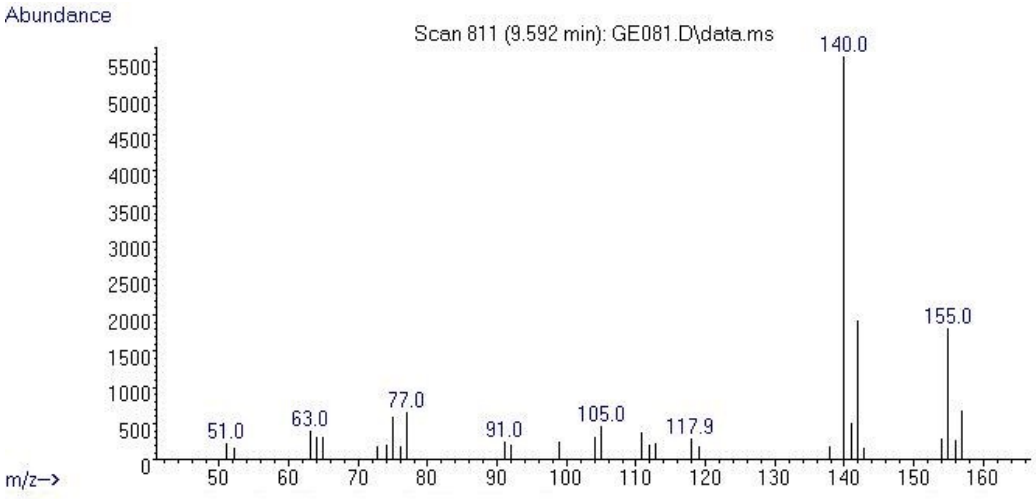

Figure S23. Mass spectrum of 3-chloro-*N*-ethylaniline **2g**.

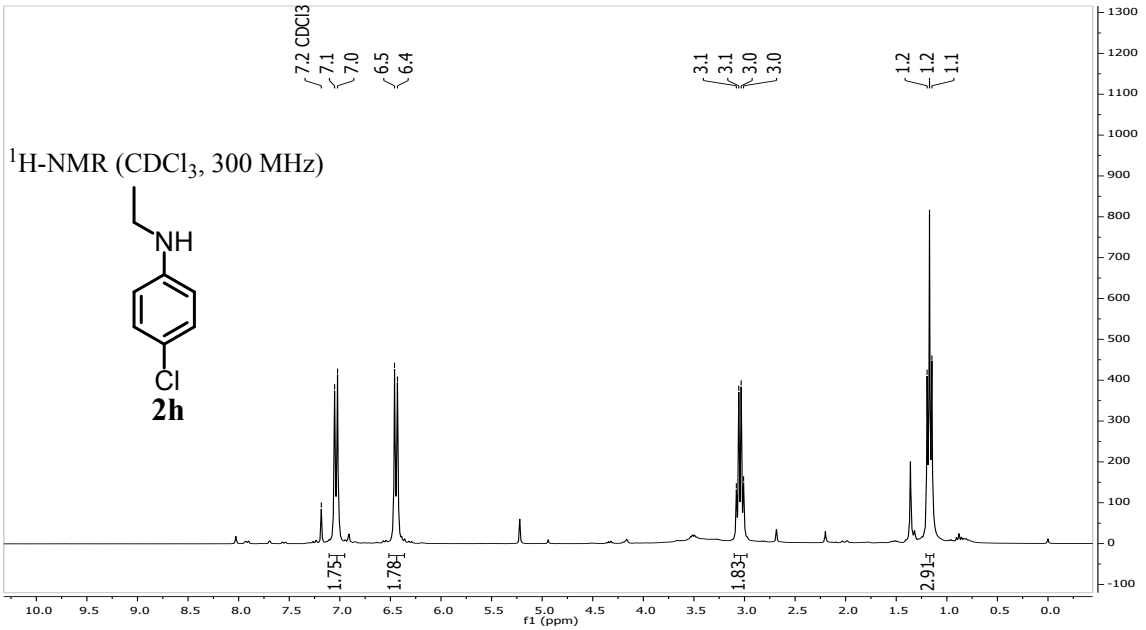

Figure S24. ^{1}H-NMR spectrum of 4-Chloro-*N*-ethylaniline **2h** in $CDCl_3$.

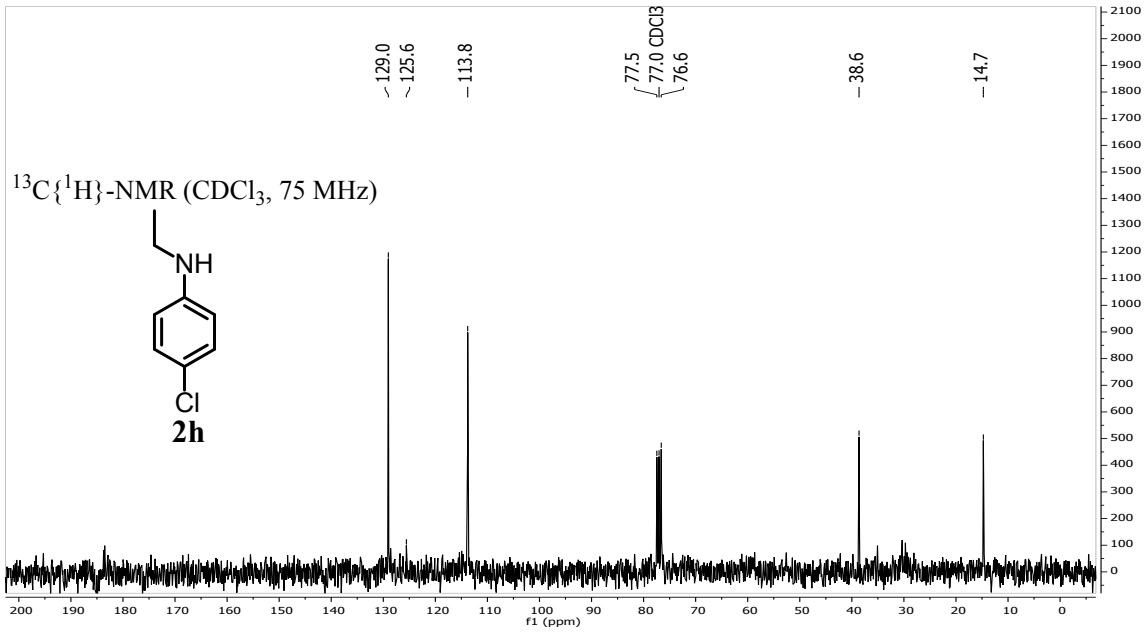

Figure S25. ^{13}C{^{1}H}-NMR spectrum of 4-Chloro-*N*-ethylaniline **2h** in $CDCl_3$.

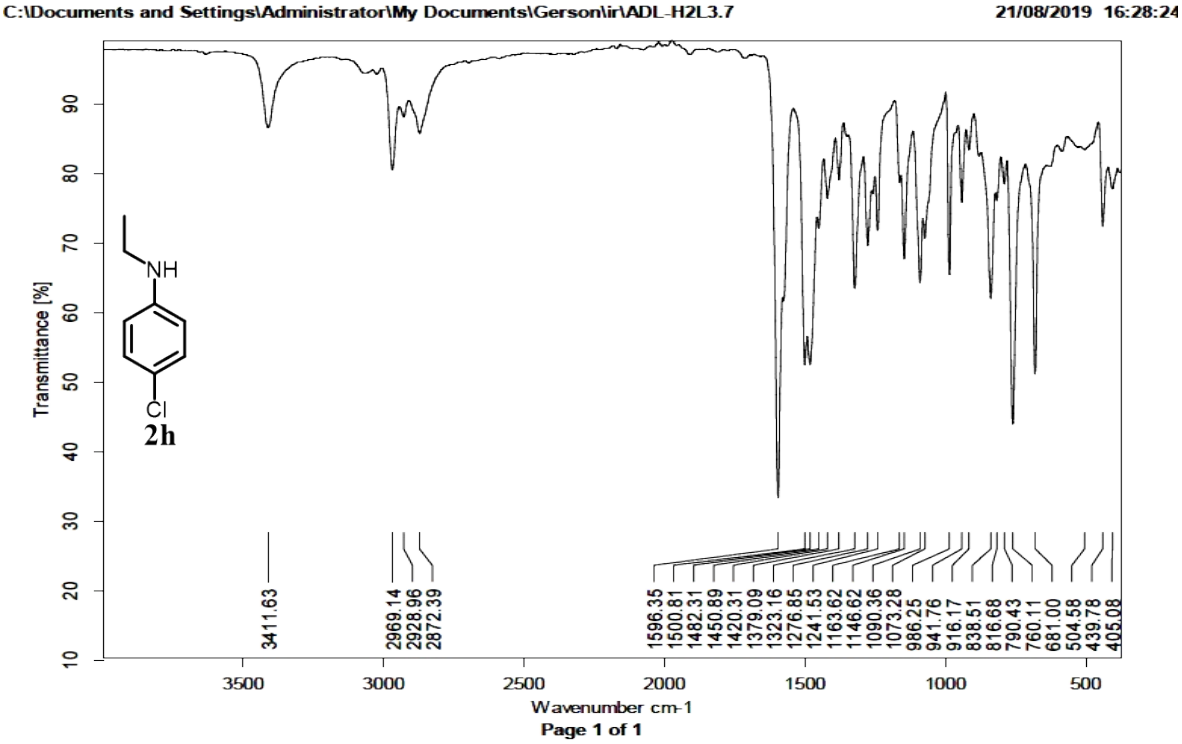

Figure S26. FT-IR spectrum of 4-Chloro-*N*-ethylaniline **2h**.

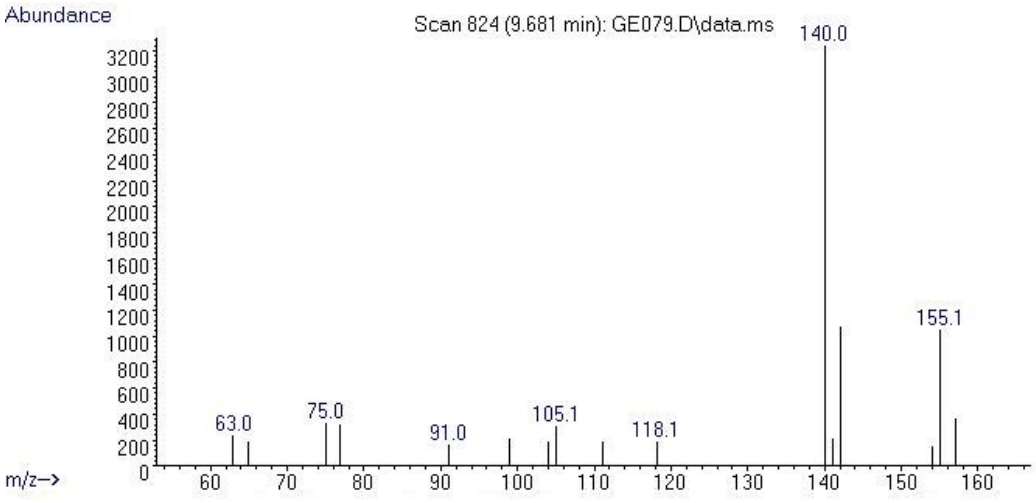

Figure S27. Mass spectrum of 4-Chloro-*N*-ethylaniline **2h**.

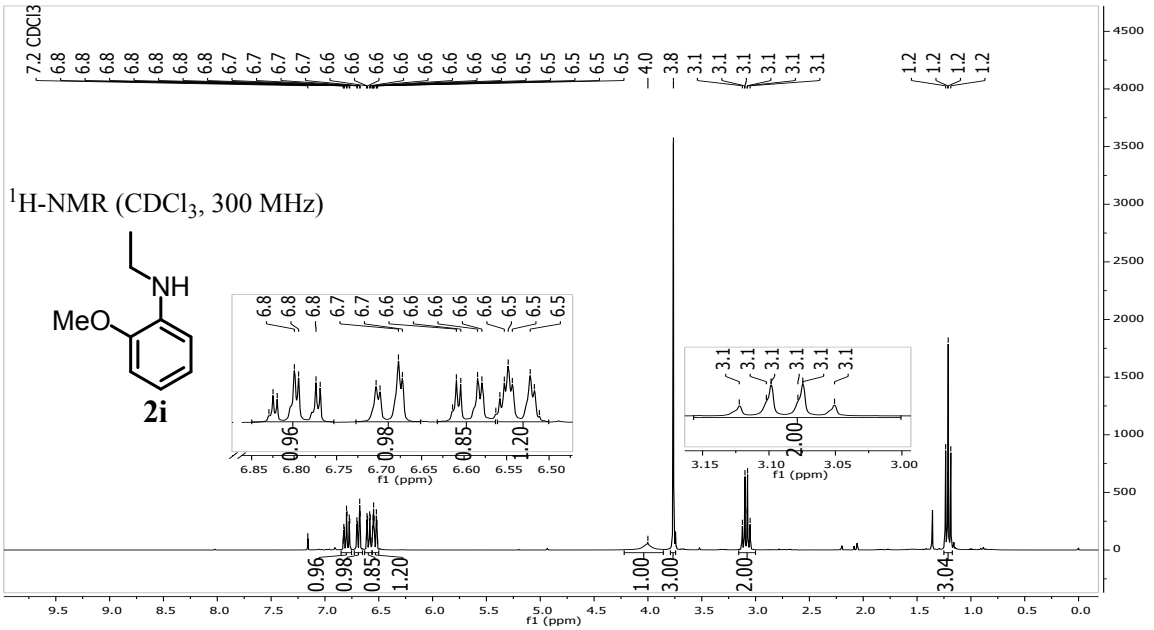

Figure S28. ^{1}H-NMR spectrum of *N*-Ethyl-2-methoxyaniline **2i** in $CDCl_3$.

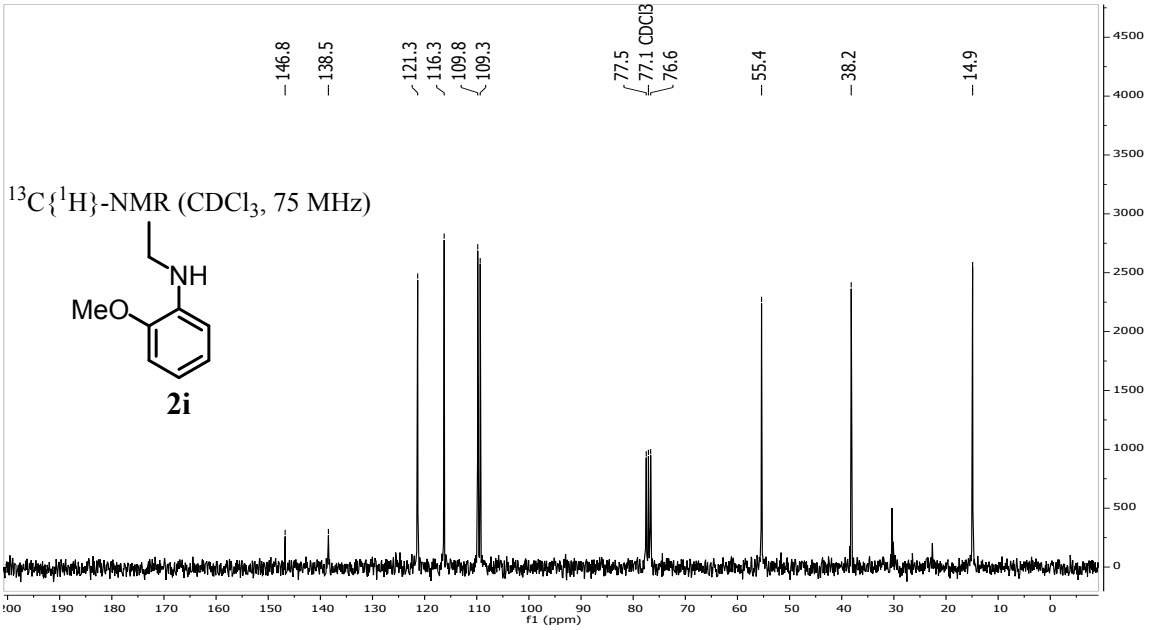

Figure S29. ^{13}C{^{1}H}-NMR spectrum of *N*-Ethyl-2-methoxyaniline **2i** in $CDCl_3$.

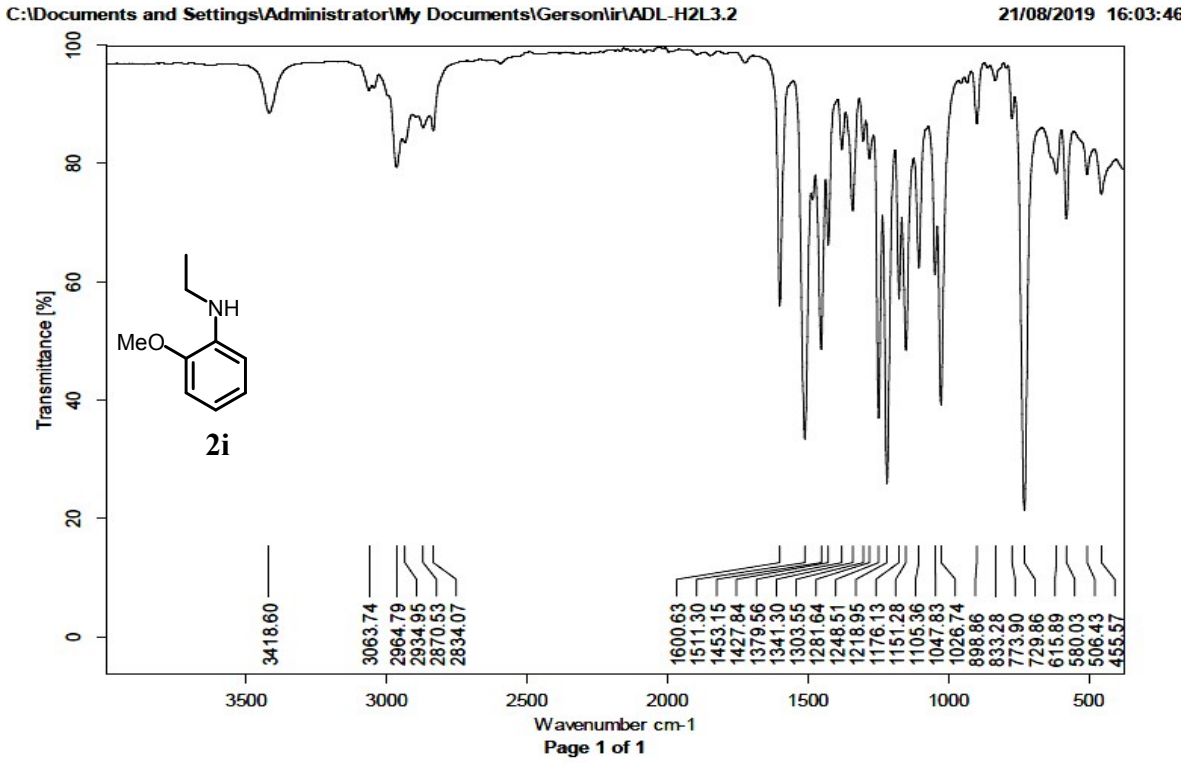

Figure S30. FT-IR spectrum of *N*-Ethyl-2-methoxyaniline **2i**.

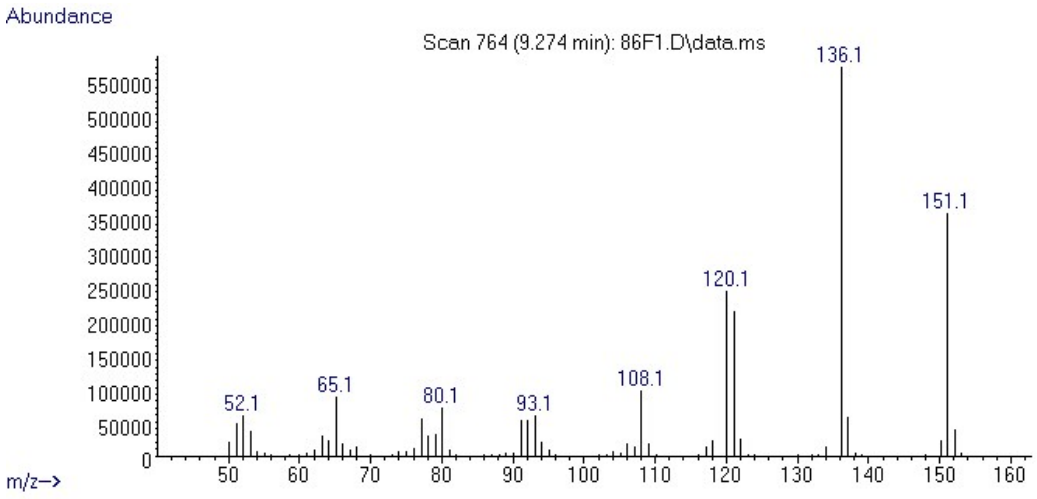

Figure S31. Mass spectrum of *N*-Ethyl-2-methoxyaniline **2i**.

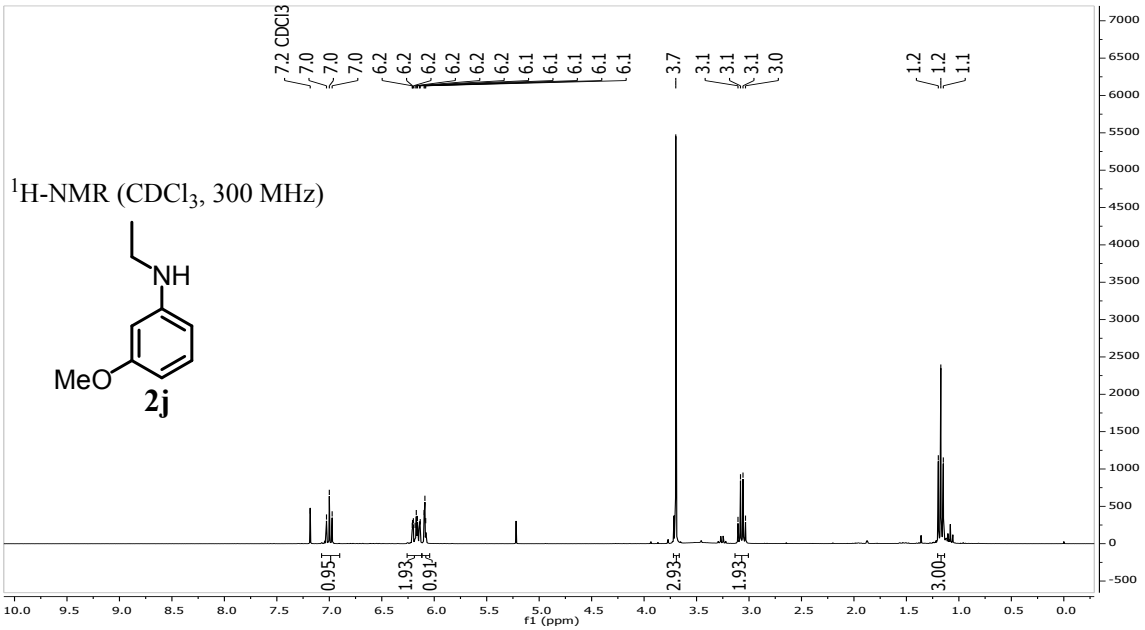

Figure S32. ^{1}H-NMR spectrum of *N*-Ethyl-3-methoxyaniline **2j** in $CDCl_3$.

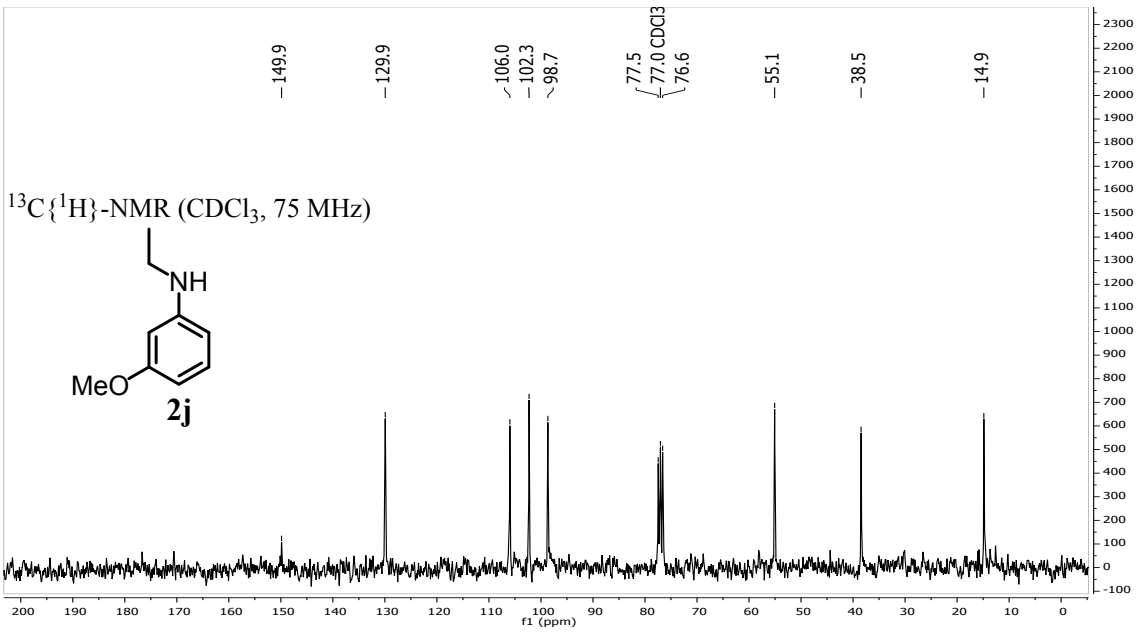

Figure S33. ^{13}C{^{1}H}-NMR spectrum of *N*-Ethyl-3-methoxyaniline **2j** in $CDCl_3$.

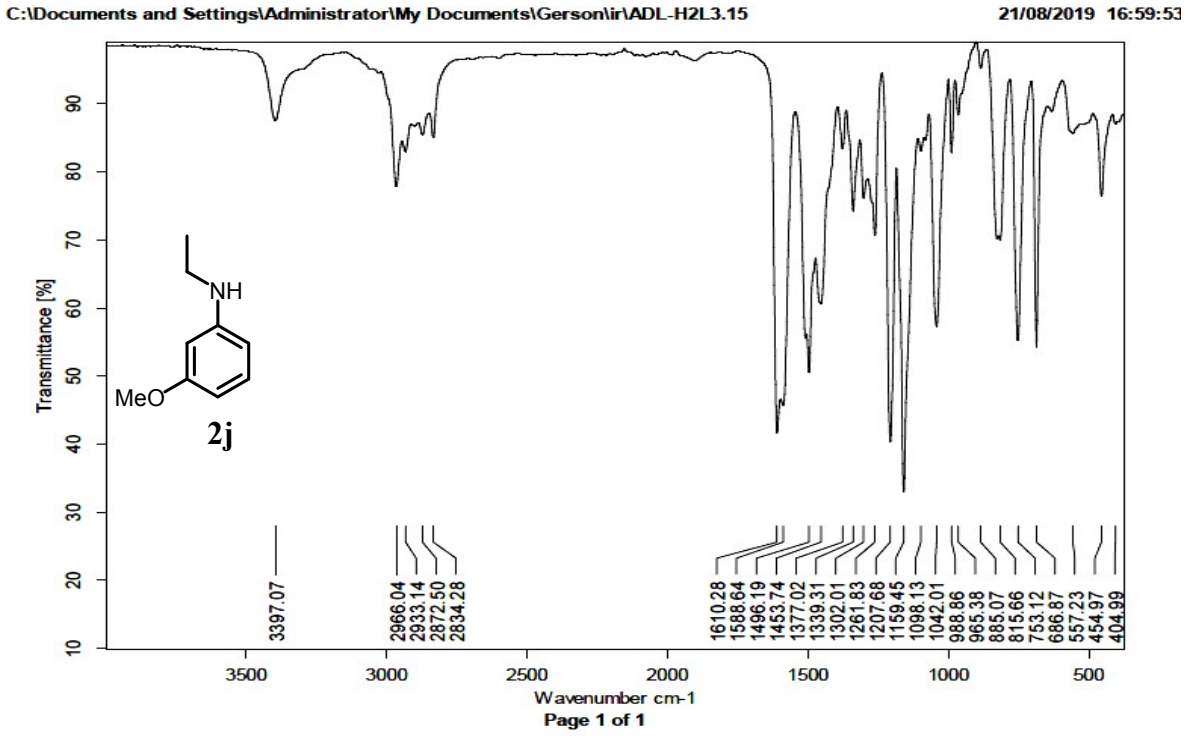

Figure S34. FT-IR spectrum of *N*-Ethyl-3-methoxyaniline **2j**.

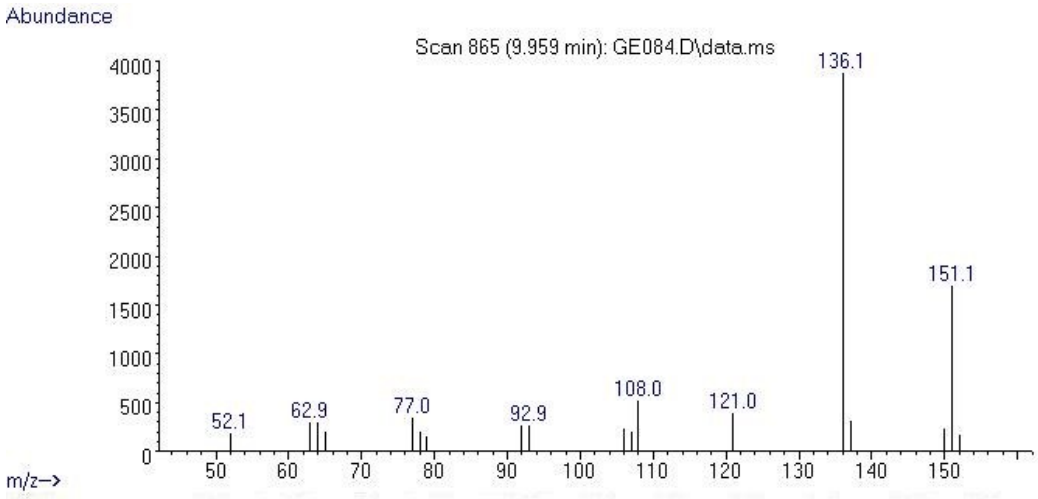

Figure S35. Mass spectrum of *N*-Ethyl-3-methoxyaniline **2j**.

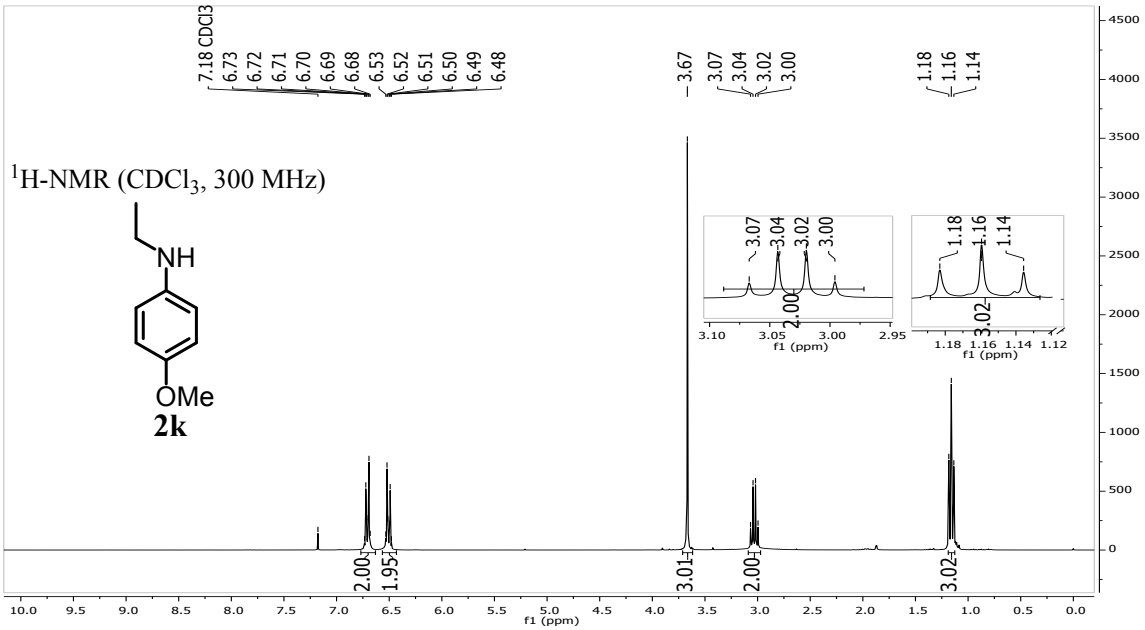

Figure S36. ^{1}H-NMR spectrum of *N*-Ethyl-4-methoxyaniline **2k** in $CDCl_3$.

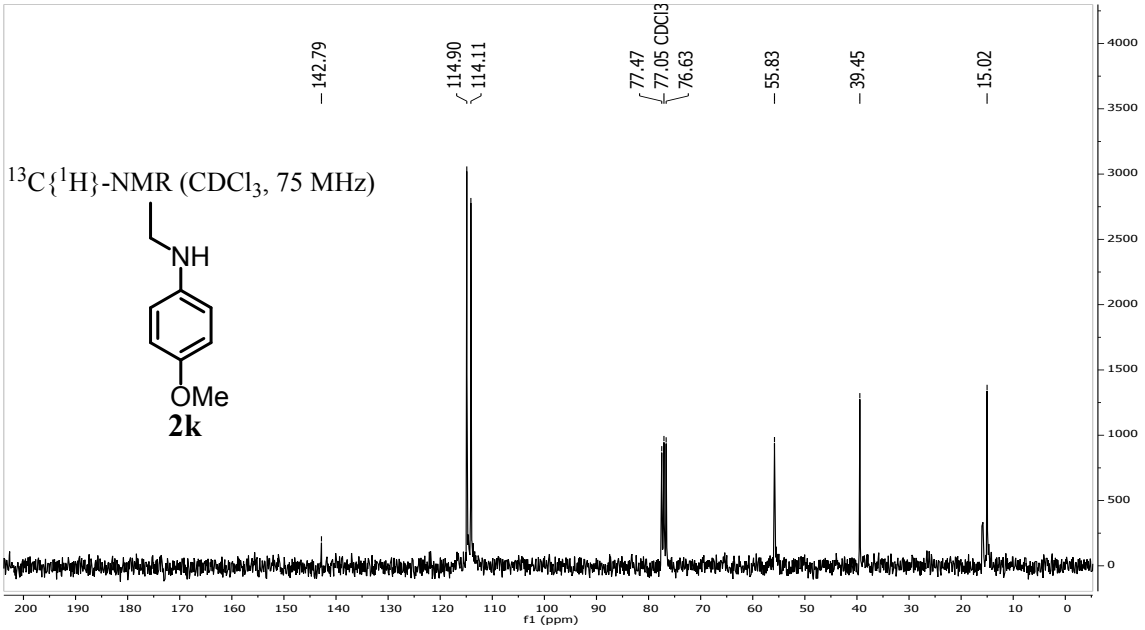

Figure S37. ^{13}C{^{1}H}-NMR spectrum of *N*-Ethyl-4-methoxyaniline **2k** in $CDCl_3$.

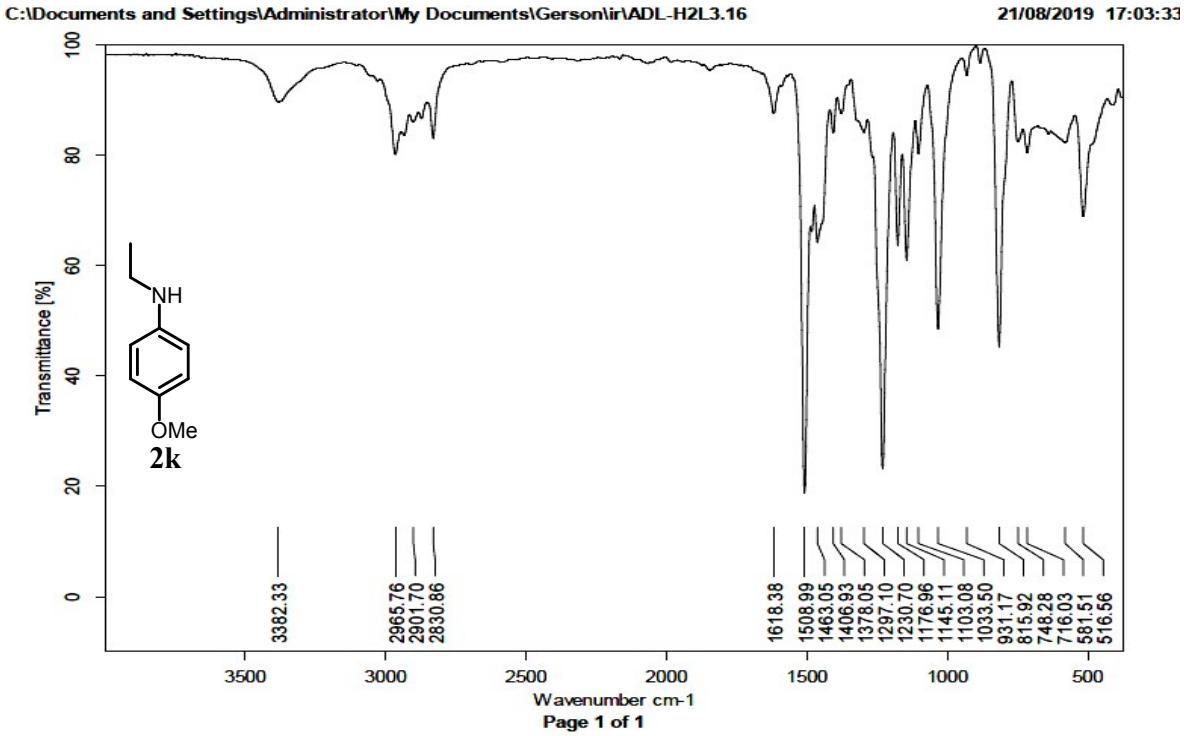

Figure S38. FT-IR spectrum of *N*-Ethyl-4-methoxyaniline **2k**.

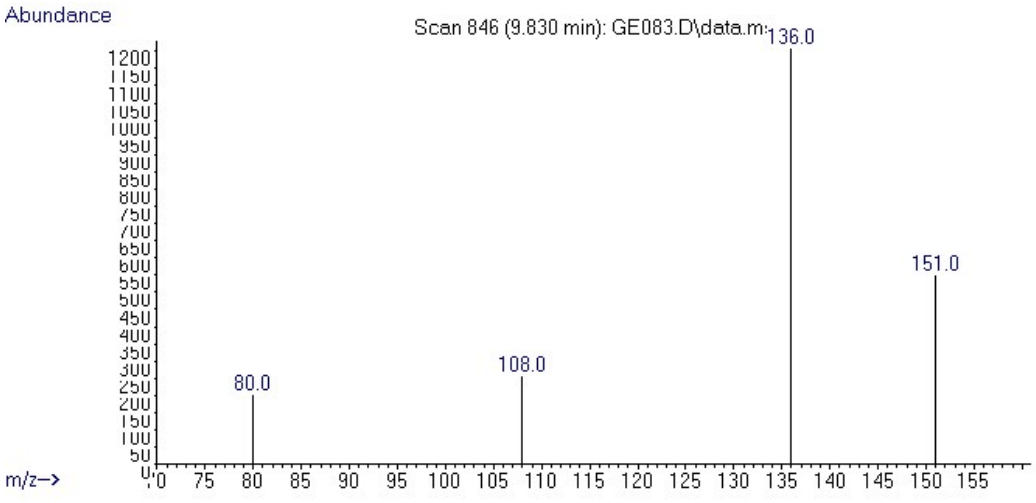

Figure S39. Mass spectrum of *N*-Ethyl-4-methoxyaniline **2k**.

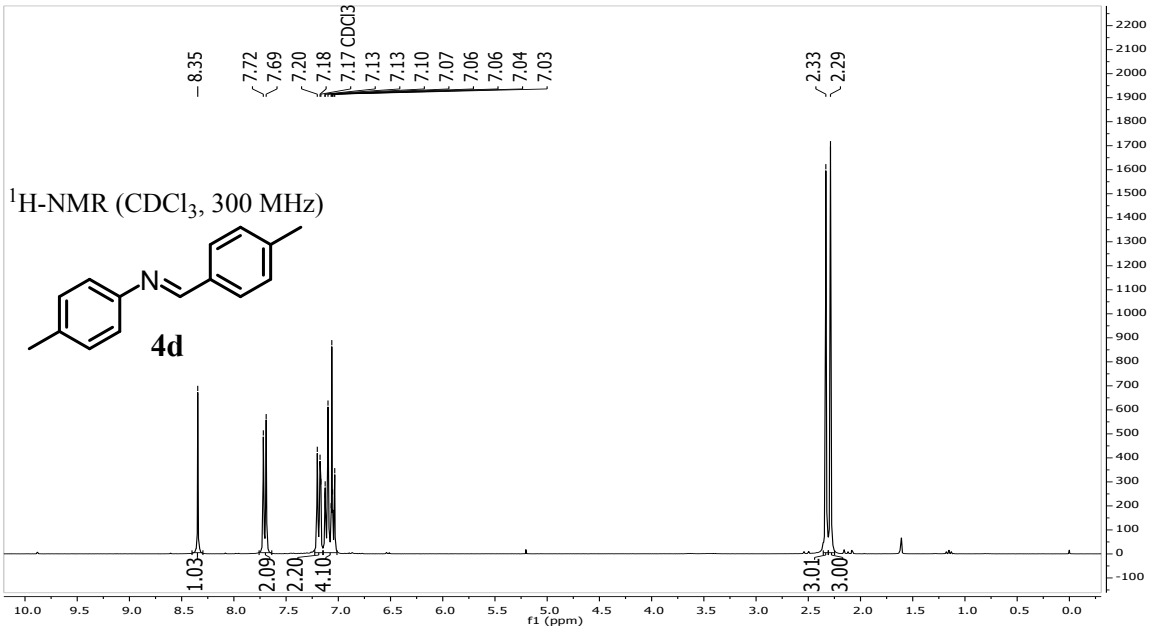

Figure S40. ^{1}H-NMR spectrum of *N*-di-*p*-tolylmethanimine **4d** in $CDCl_3$.

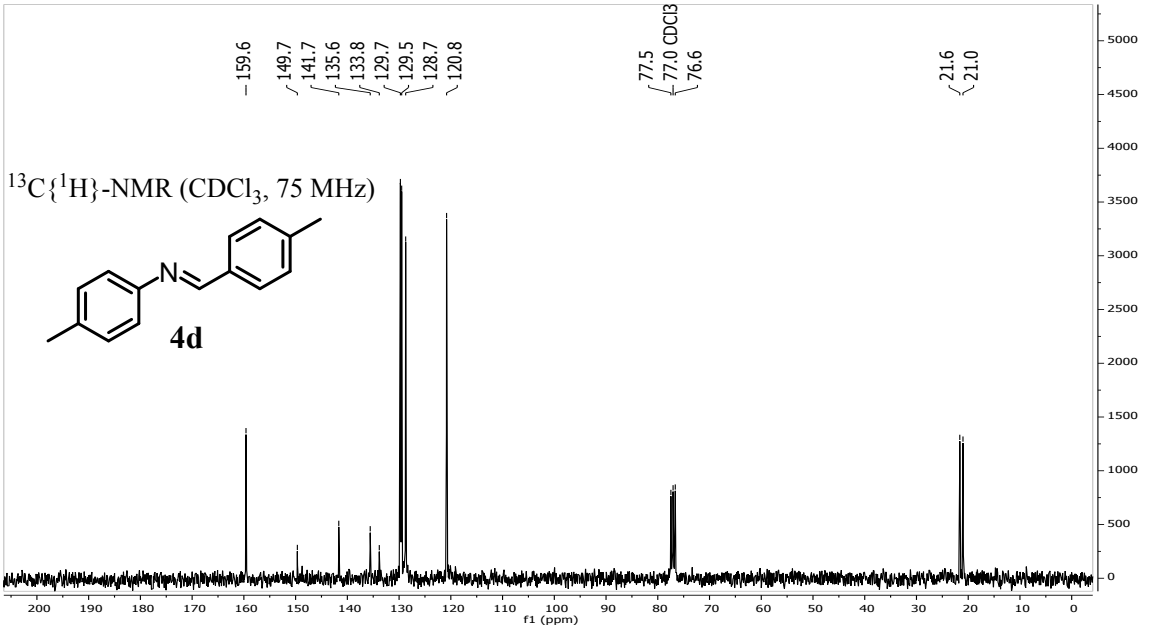

Figure S41. ^{13}C{^{1}H}-NMR spectrum of *N*-di-*p*-tolylmethanimine **4d** in $CDCl_3$.

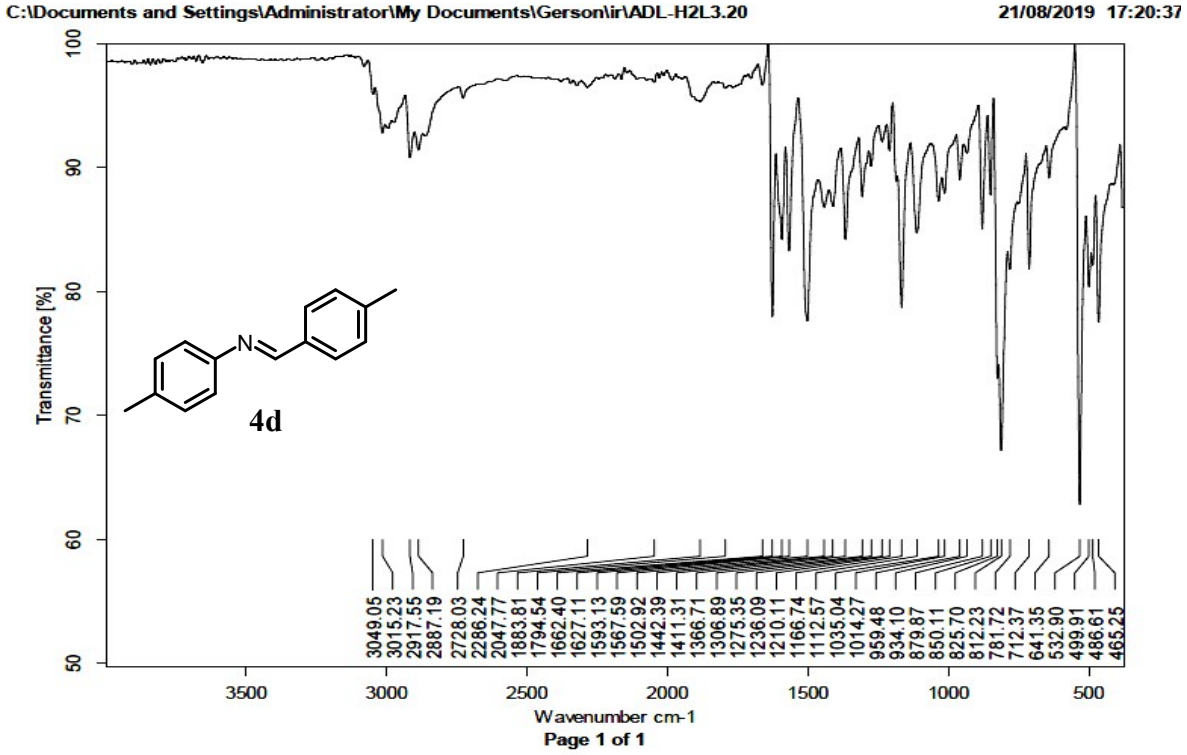

Figure S42. FT-IR spectrum of *N*-di-*p*-tolylmethanimine **4d**.

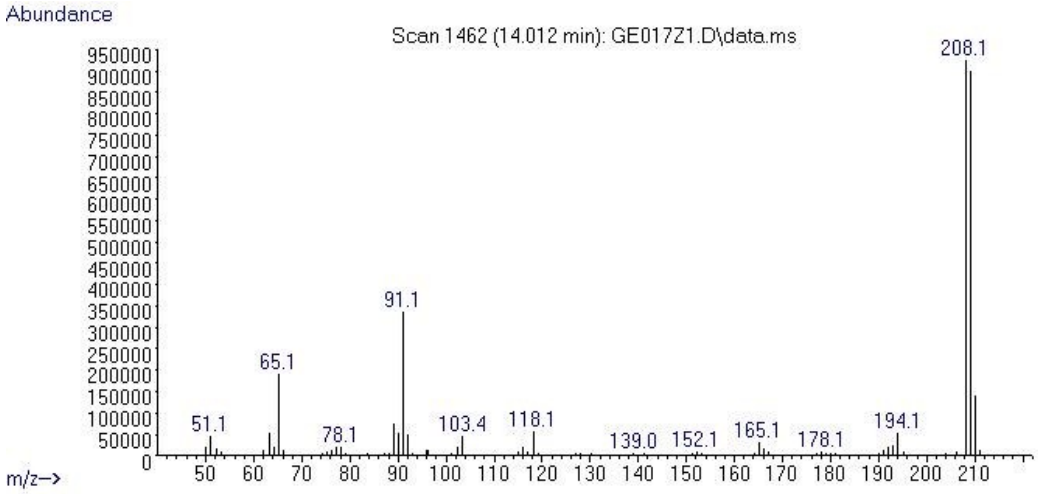

Figure S43. Mass spectrum of *N*-di-*p*-tolylmethanimine **4d**.

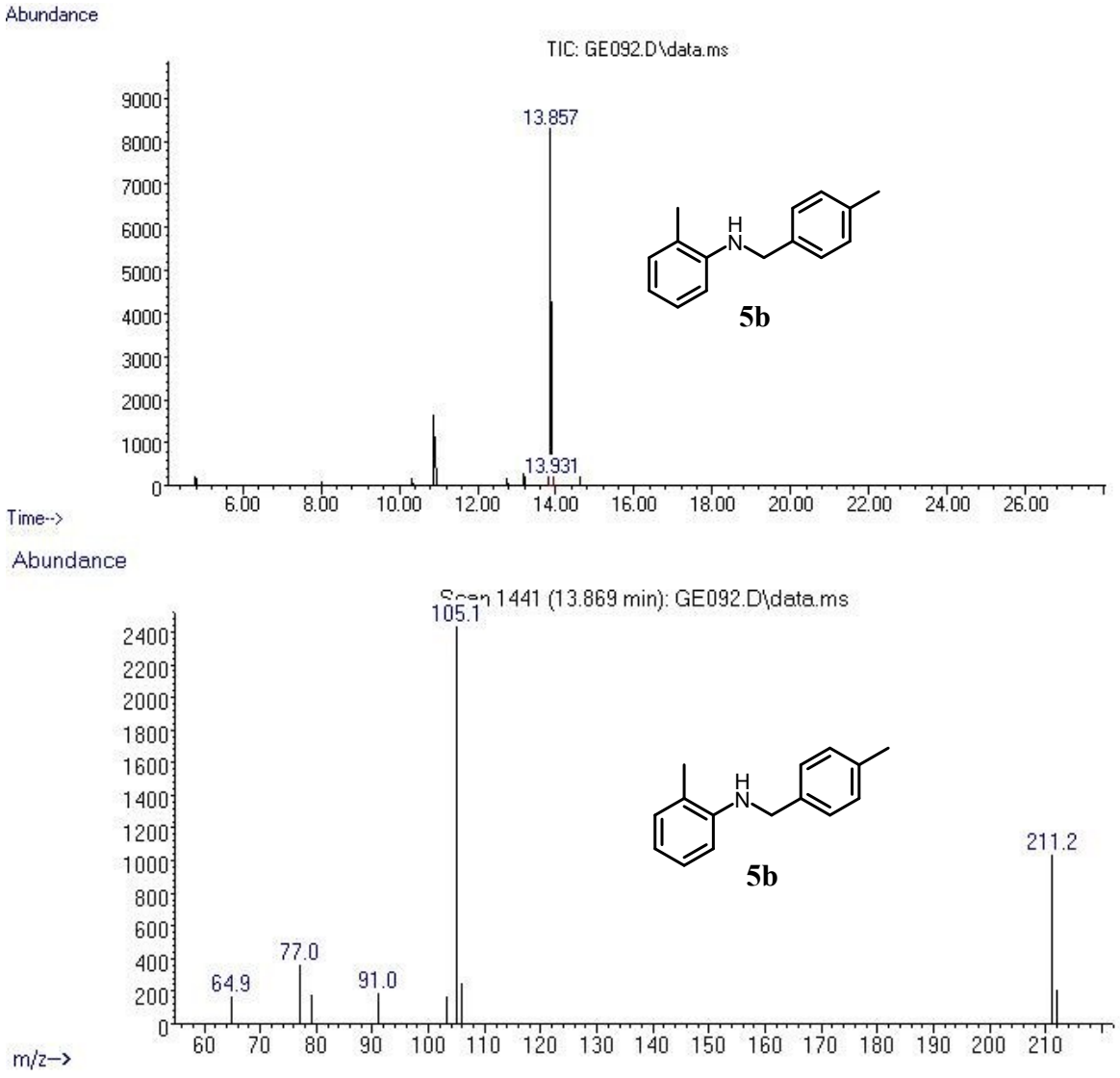

Figure S44. Chromatogram and mass spectrum of 2-Methyl-*N*-(4-methylbenzyl)aniline **5b**.

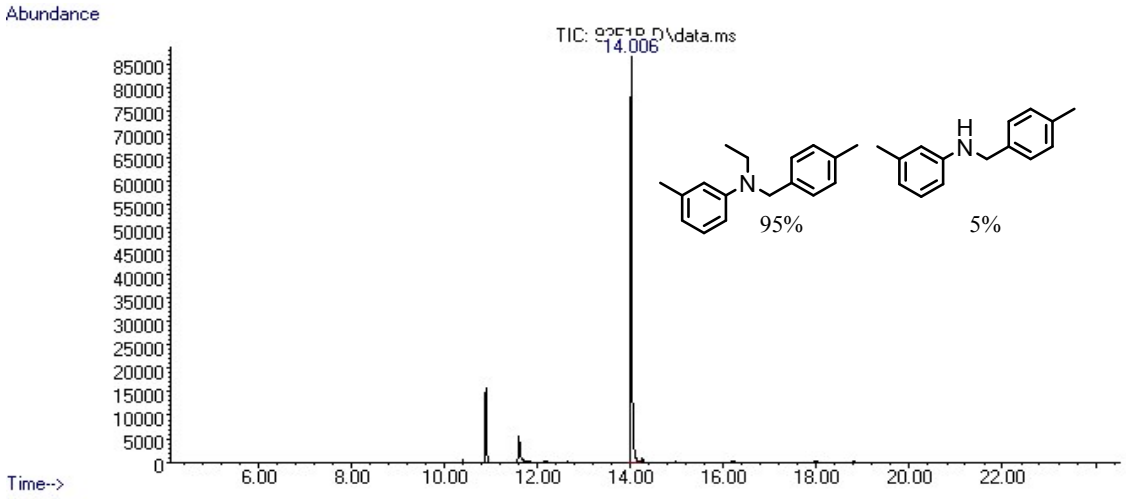

Figure S45. Chromatogram of *N*-ethyl-3-methyl-*N*-(4-methylbenzyl)aniline **7d** and 3-Methyl-*N*-(4-methylbenzyl)aniline **5c**.

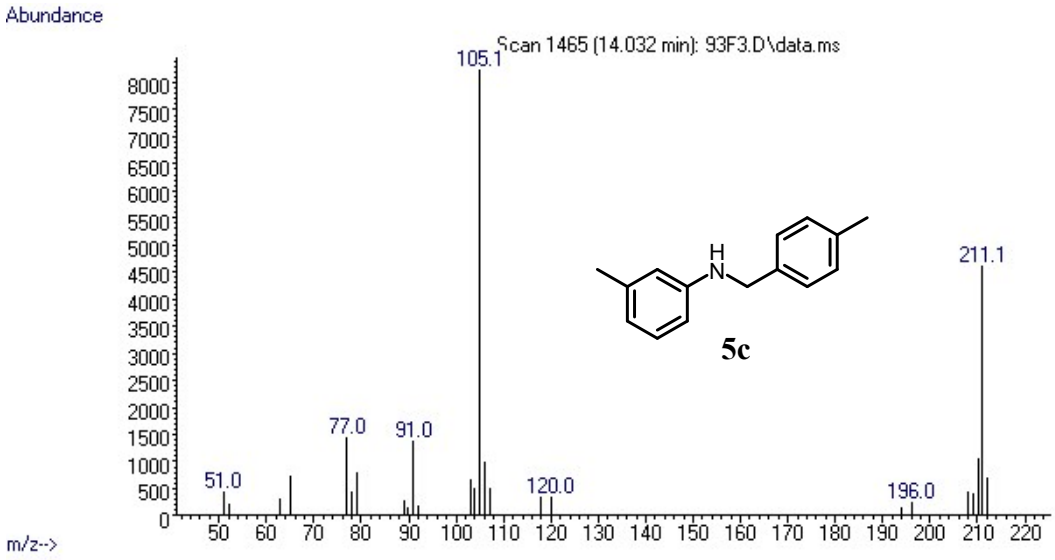

Figure S46. Mass spectrum of 3-Methyl-*N*-(4-methylbenzyl)aniline **5c** (5%).

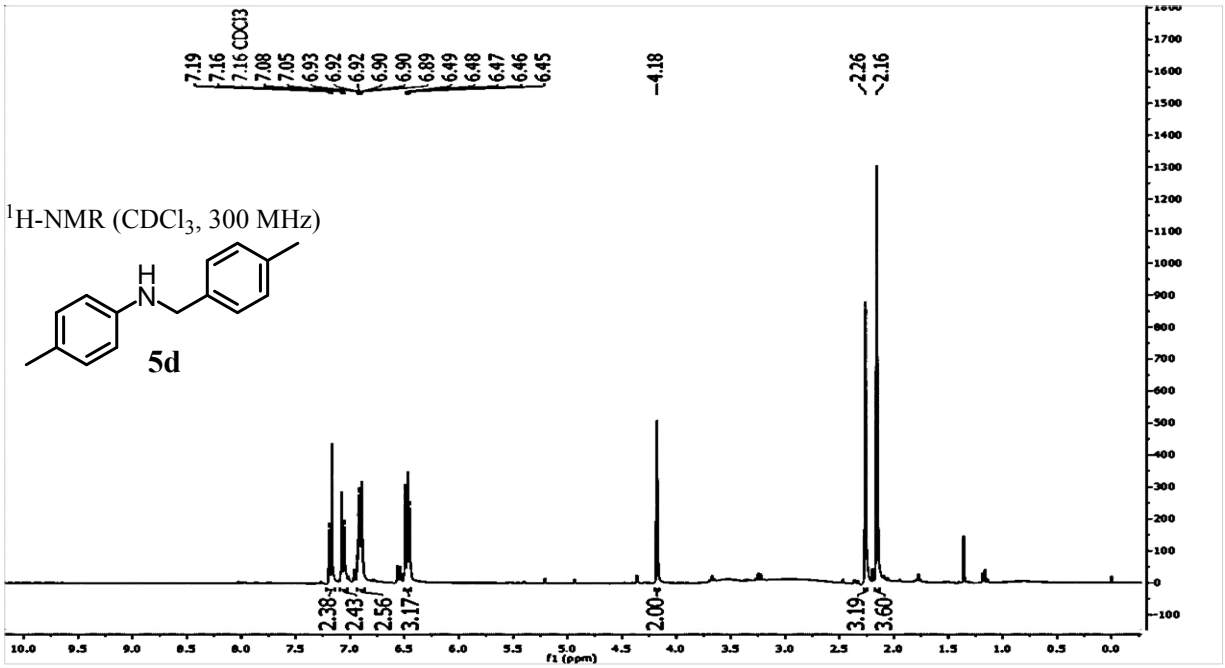

Figure S47. ^{1}H-NMR spectrum of 4-Methyl-*N*-(4-methylbenzyl)aniline **5d** in $CDCl_3$.

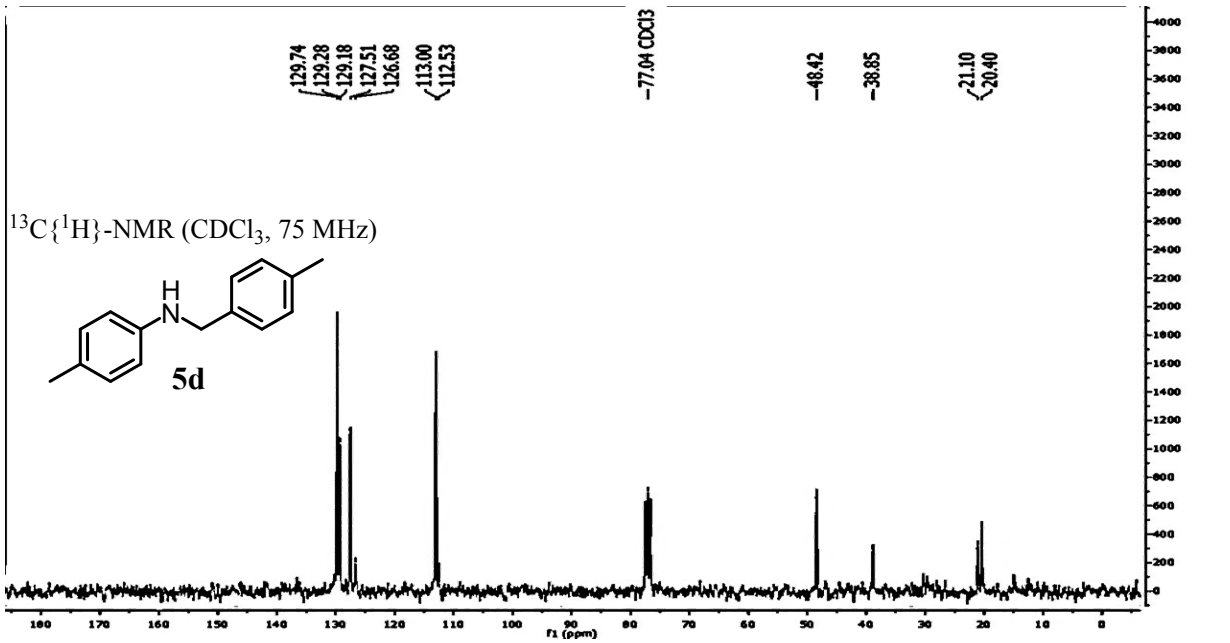

Figure S48. ^{13}C{^{1}H}-NMR spectrum of 4-Methyl-*N*-(4-methylbenzyl)aniline **5d** in $CDCl_3$.

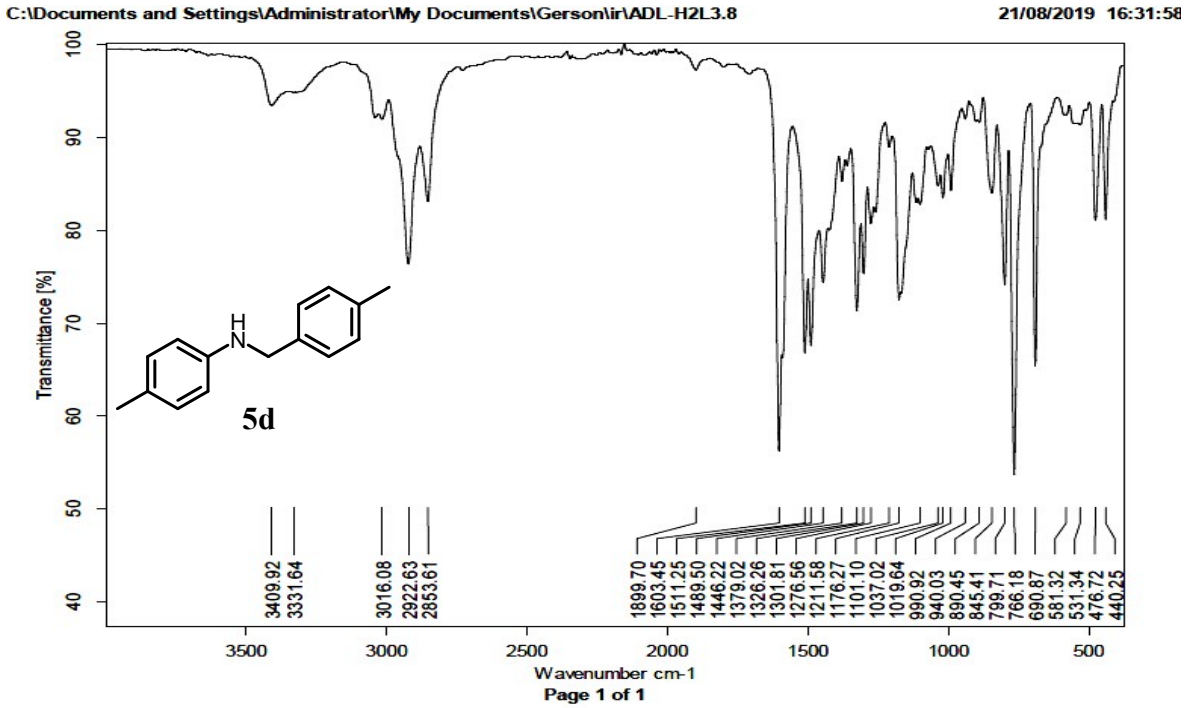

Figure S49. FT-IR spectrum of 4-Methyl-*N*-(4-methylbenzyl)aniline **5d**.

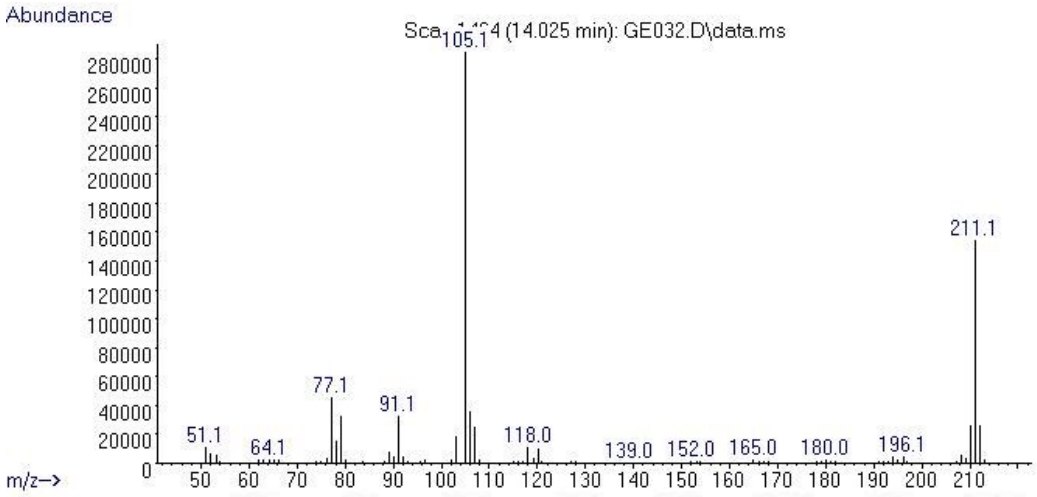

Figure S50. Mass spectrum of 4-Methyl-*N*-(4-methylbenzyl)aniline **5d**.

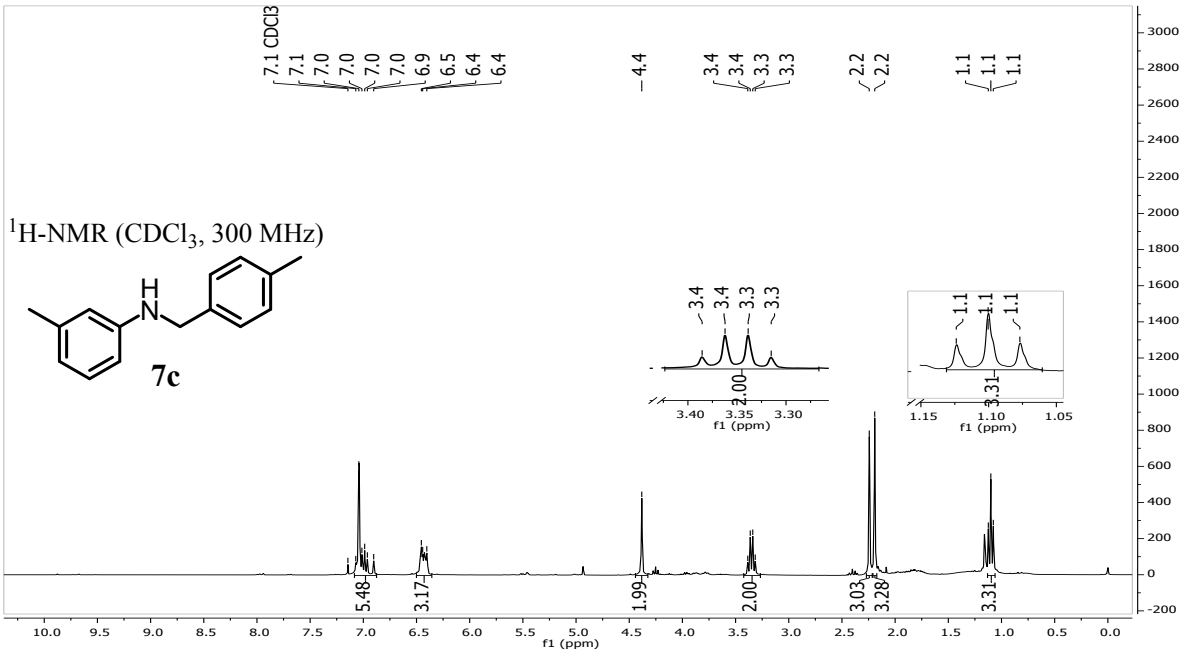

Figure S51. ^{1}H-NMR spectrum of *N*-ethyl-3-methyl-*N*-(4-methylbenzyl)aniline **7c** in $CDCl_3$.

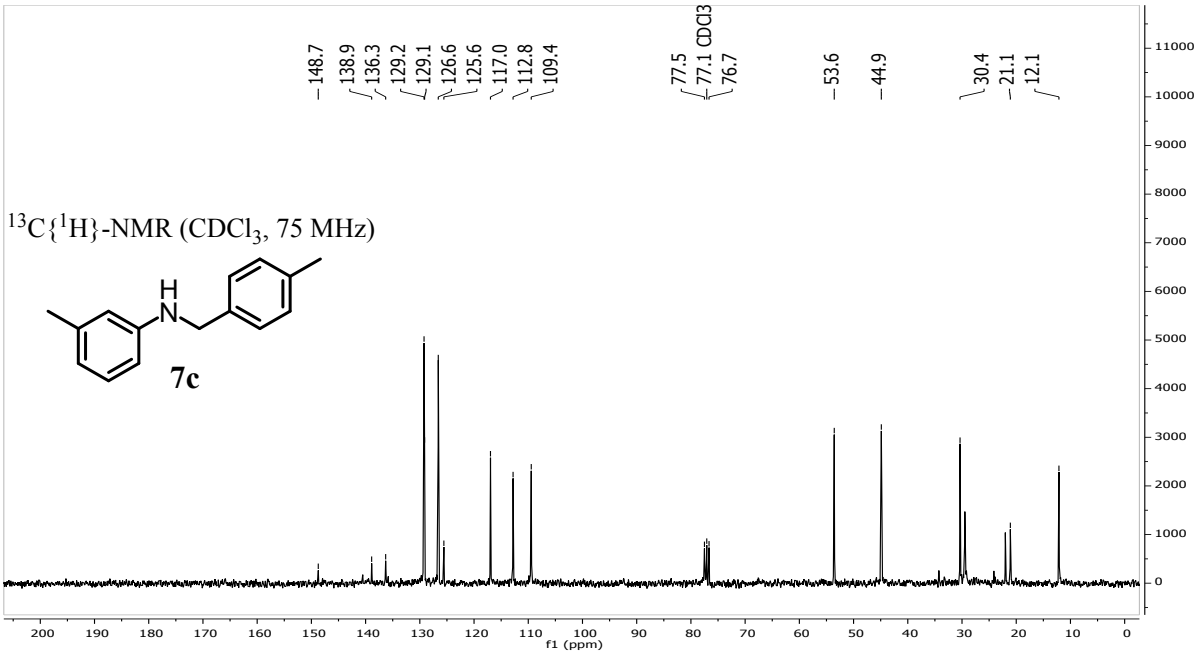

Figure S52. ^{13}C{^{1}H}-NMR spectrum of *N*-ethyl-3-methyl-*N*-(4-methylbenzyl)aniline **7c** in $CDCl_3$.

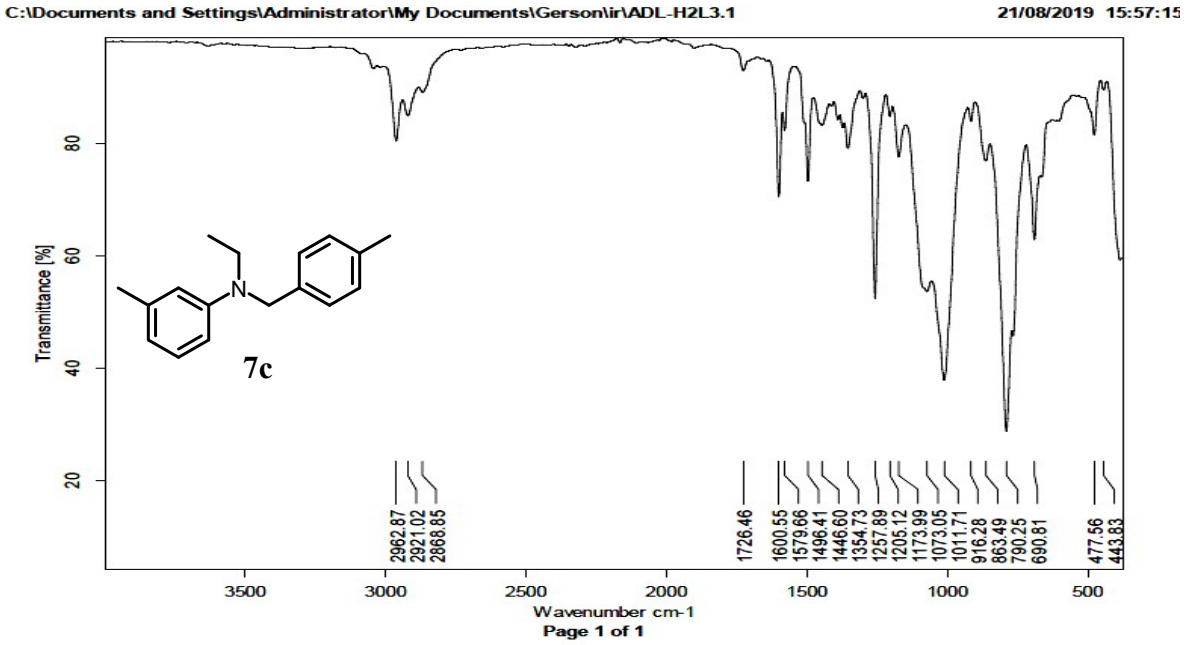

Figure S53. FT-IR spectrum of *N*-ethyl-3-methyl-*N*-(4-methylbenzyl)aniline **7c**.

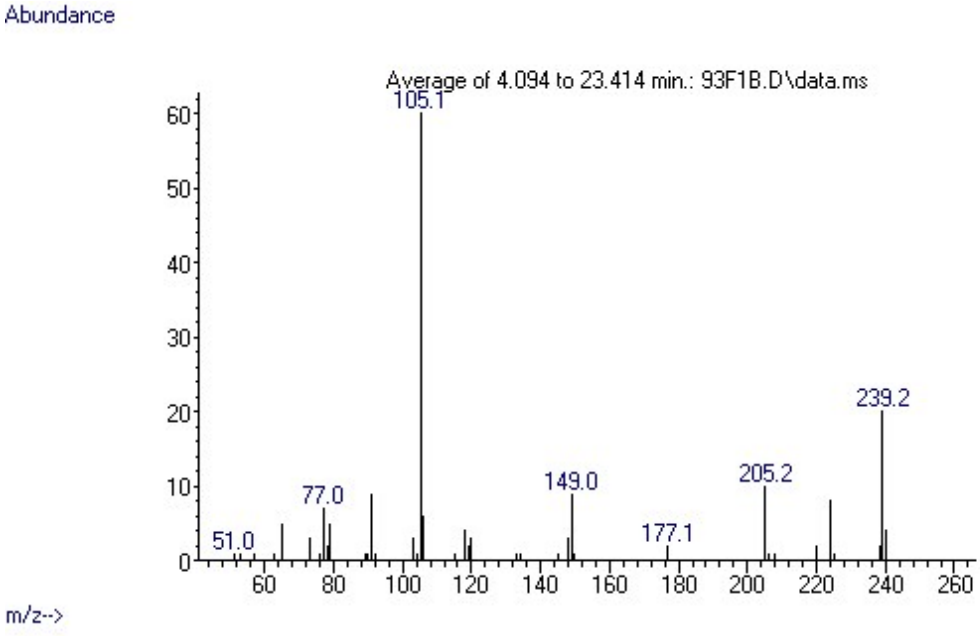

Figure S54. Mass spectrum of *N*-ethyl-3-methyl-*N*-(4-methylbenzyl)aniline **7c**.

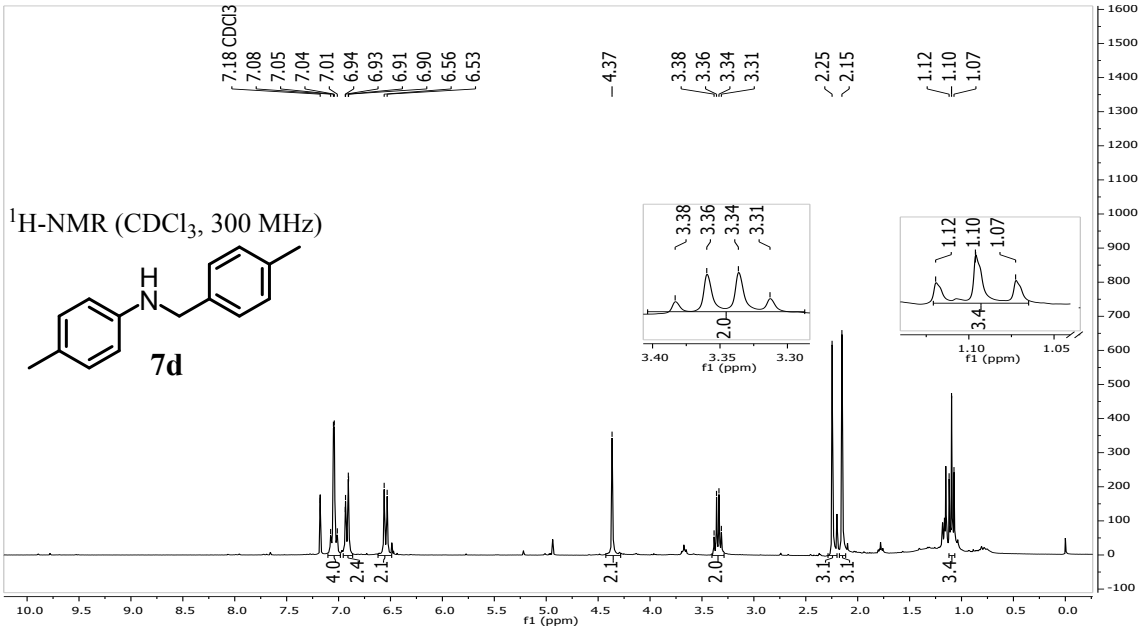

Figure S55. ^{1}H-NMR spectrum of *N*-ethyl-4-methyl-*N*-(4-methylbenzyl)aniline **7d** in $CDCl_3$.

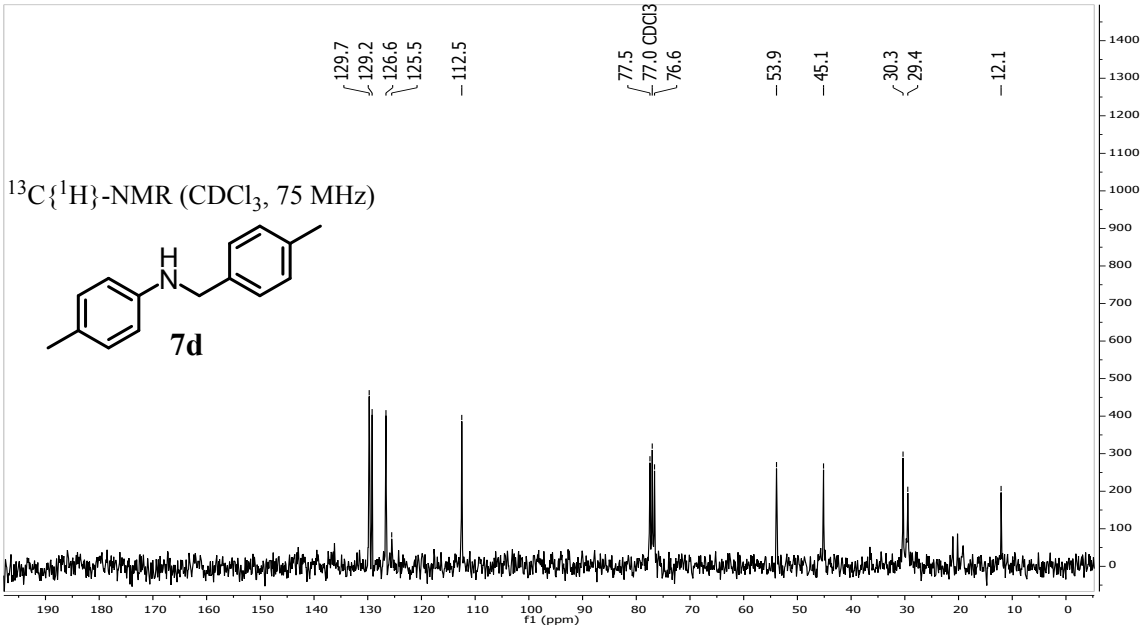

Figure S56. ^{13}C{^{1}H}-NMR spectrum of *N*-ethyl-4-methyl-*N*-(4-methylbenzyl)aniline **7d** in $CDCl_3$.

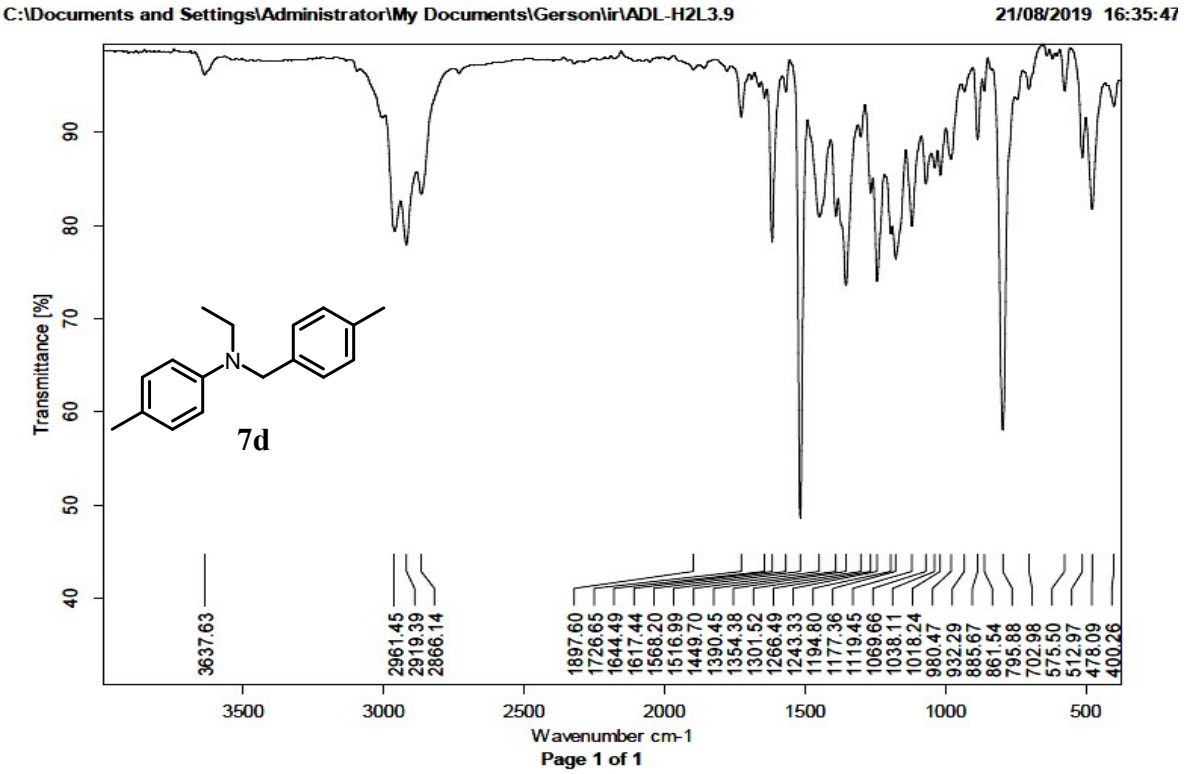

Figure S57. FT-IR spectrum of *N*-ethyl-4-methyl-*N*-(4-methylbenzyl)aniline **7d**.

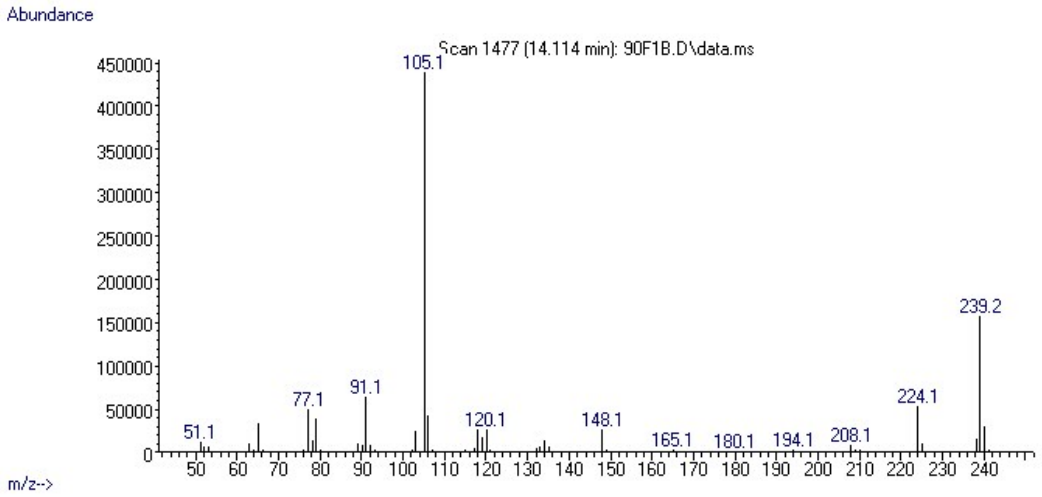

Figure S58. Mass spectrum of *N*-ethyl-4-methyl-*N*-(4-methylbenzyl)aniline **7d**.

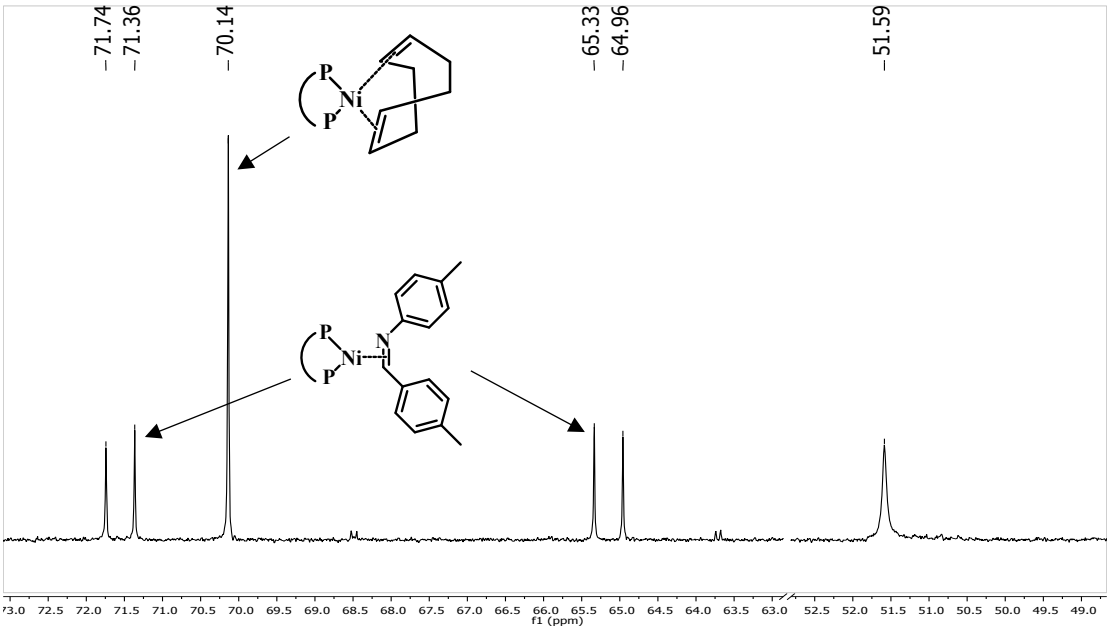

Figure S59. $^{31}P\{^{1}H\}$-NMR spectrum of [(dippe)Ni(η^2-C, N)-PhHC=NPh], dippe and $[Ni(COD)_2]$ mixture in THF-d^8.

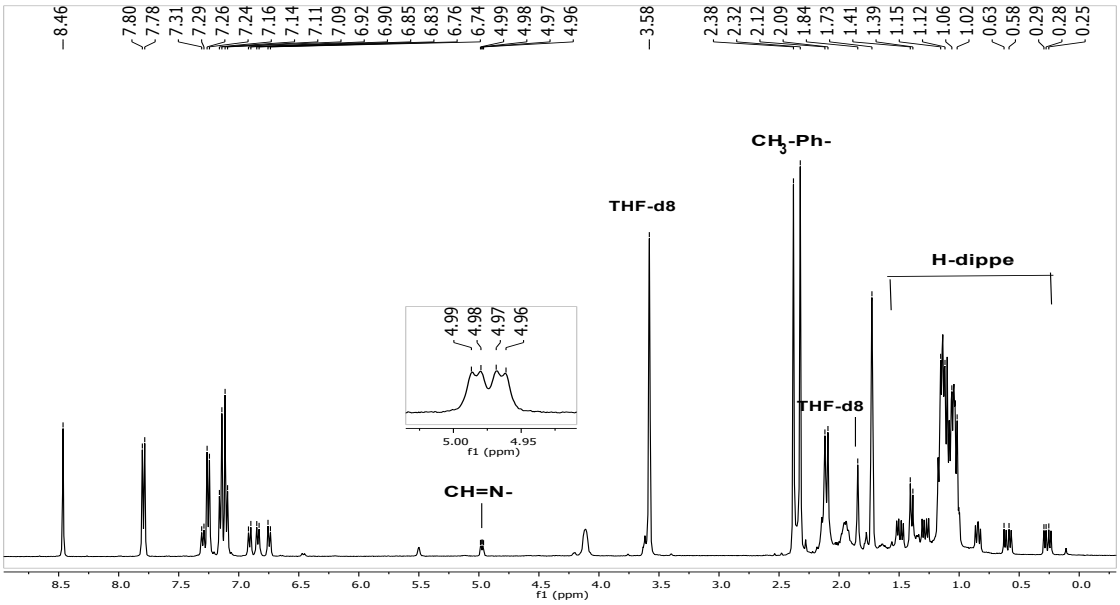

Figure S60. ^{1}H-NMR spectrum of [(dippe)Ni(η^2-C, N)-PhHC=NPh], dippe and $[Ni(COD)_2]$ mixture in THF-d^8.