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Facile, One-Pot Reductive Alkylations in Aqueous Micellar Media: A Chemo-enzymatic Approach

Krithika Ganesh, [a,b] Ganesh Sambasivam,*[a] and Karthikeyan. S*[b]

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General information

The reactions were carried out in commercial solvents without degassing them prior to the reactions. All the reagents were commercially available and were used as received without further purification. The aryl allyl acetates were prepared according to the procedures available in the literature. The compounds were purified by flash chromatography using Biotage Selekt autocolumn on a pre-packed pre-packed 25-gram KP-Sil BiotageϴSNAP. All the compounds were characterized by HRMS, ^{1}HNMR and ^{13}CNMR. Melting points were measured with a Polmon AUTO-MELT MP98 apparatus and are uncorrected. Thin layer chromatography (TLC) was done using Silica Gel 60 F_{254} plates (0.25 mm thick), purchased from Merck. LC-MS data was recorded on an Agilent Technologies 1200 LC system coupled with Agilent Technologies 5975C mass spectrometer using HP-column (4.6 mm × 50 mm, 5µ) purchased from Agilent Technologies. HPLC analyses were carried out in Shimadzu Prominence systems using Chiralpak IG 250mm*4.6mm, 5µ columns. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ or DMSO-d6 using 300 MHz and 400 MHz Bruker NMR spectrometer. All the chemical shift values reported in the 1H NMR spectra are in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.26 ppm) or the central peak of DMSO-d^6 (2.50 ppm).

The data are reported as follows:

Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet), integration, and coupling constant in Hertz (Hz). Chemical shifts in ^{13}C NMR spectra are reported in ppm on the δ scale from the central peak of residual $CDCl_3$ (77.16 ppm) or the central peak of DMSO- d^6 (39.52 ppm).

Procedure for synthesis of aryl allylacetates:

All the manipulations were carried out in oven-dried glassware under air. To a sealed tube containing aryl boronic acid in DMSO: AcOH (10V, 1:1), $Pd(OAc)_2$ (5 mol%) and 1,4-benzoquinone (2.5 mmol), 40 mmol (20 Equiv) of vinyl acetate was added. The reaction mixture was heated 60 ℃ for 12 h. The completion of the reaction was monitored by TLC.

On Completion of the reaction, the reaction mixture was quenched by a saturated solution of sodium bicarbonate (2 mL) and extracted with ethyl acetate (2 * 5 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

General Procedure for Selective Mono- ethylation

To a solution of 250mg of the aniline/ nitro substrate (2.25mmol) in 2 wt% Triton- x- 100 (10 mL) taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 2.25 mmol (1 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

General Procedure for Selective di- ethylation

To a solution of 250mg of the aniline/ nitro substrate (2.25mmol) in 2 wt% Triton- x- 100 (10 mL) taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 4.5 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

General Procedure for Selective isopropenylation

To a solution of 250mg of the aniline/ nitro substrate (2.25mmol) in 2 wt% Triton- x- 100 (10 mL) taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 4.5 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 50 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

General Procedure for Selective N- alkylations and arylations:

To a solution of **6** (2.25mmol) in 2 wt% Triton- x- 100 (10 mL) taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 2.5 mmol (1.1 equiv) **7** and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

Scale-up reaction

To a solution of 2g of **1**(18.01 mmol) in 2 wt% Triton- x- 100 (80 mL) taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 36.02 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 100 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

E- factor studies

1st Cycle:

To a solution of 2g of **1** (18.01 mmol) in 2 wt% Triton- x- 100 (80 mL) taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 36.02 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

Yield: 2.1g, 85%

2nd Cycle:

To a solution of 2g of **1** (18.01 mmol) in 2 wt% Triton- x- 100 (80 mL) taken from the previous reaction mixture taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 36.02 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

Yield: 2.0g, 81%

3rd Cycle:

To a solution of 2g of **1** (18.01 mmol) in 2 wt% Triton- x- 100 (80 mL) taken from the previous reaction mixture taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 36.02 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

Yield: 1.8g, 75%

4^{th} Cycle:

To a solution of 2g of **1** (18.01 mmol) in 2 wt% Triton- x- 100 (80 mL) taken from the previous reaction mixture taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 36.02 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

Yield: 1.6g, 65%

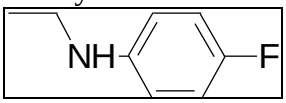
5^{th} Cycle:

To a solution of 2g of **1** (18.01 mmol) in 2 wt% Triton- x- 100 (80 mL) taken from the previous reaction mixture taken in an autoclave vessel, 5 wt% of 10% Pd/ C, 36.02 mmol (2 equiv) vinyl acetate and 10 wt% Novozym- 435 beads were added. The reaction mixture was hydrogenated under a 2 Kg/ Cm^2 hydrogen pressure at 25 ℃ for 12 h. The progress of the reaction was monitored by TLC.

On completion of the reaction, the reaction mixture was filtered through a celite bed and the crude product was extracted using ethyl acetate (2 * 20 mL). The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure at 45 ℃. The crude product was then purified using a flash column using silica gel (230-400 mesh).

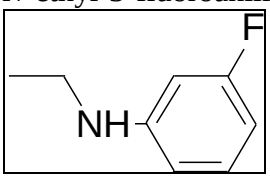
Yield: 0.14g, 58%

N-ethyl-4-fluoroaniline (**3a, 5a**)



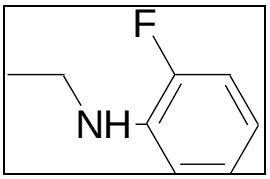
Yellow Liquid; (Yield = **3a**-85%, **5a**-80%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9-6.8 (m, 2H), 6.5 (m, 2H), 3.4 (s, 1H), 3.1 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.0 and 154.7 (d, $^{1}J_{C\text{-}F}$ = 236 Hz), 144.9, 115.7 and 115.7 (d, $^{2}J_{C\text{-}F}$ = 22 Hz) , 113.6 and 113.6 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 39.2, 14.9. HRMS (ESI) m/z calcd for $(C_8H_{10}FN)^+$ $(M+H)^+$ 140.0831, found 140.0831.

N-ethyl-3-fluoroaniline (**3b, 5b**)



Yellow Liquid; (Yield = **3b**-82%, **5b**-82%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11- 7.05 (m, 1H), 6.39-6.36 (m, 2H), 6.3 (d, J = 4Hz, 1H), 3.7 (s, 1H), 3. 1(d, J = 8Hz, 2H), 1.2 (t, J = 8Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9 and 162.7 (d, $^{1}J_{C\text{-}F}$ = 240 Hz), 130.4 and 130.3 (d, $^{3}J_{C\text{-}F}$ = 10.5 Hz), 108.7, 103.6, 99.5 and 99.1 (d, $^{2}J_{C\text{-}F}$ = 25.5 Hz), 38.5, 14.8. HRMS (ESI) m/z calcd for $(C_8H_{10}FN)^+$ $(M+H)^+$ 140.0831, found 140.0831.

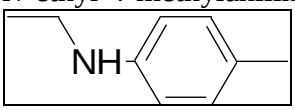
N-ethyl-2-fluoroaniline (**3c, 5c**)



Yellow Liquid; (Yield = **3c**- 75%, **5c**-73%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28- 6.95 (m, 2H), 6.76-6.71 (m, 1H), 6.70-6.66 (m, 1H), 3.8 (s, 1H), 3.2 (q, J = 8 Hz, 2H), 1.29 (t, J = 4 Hz, 3H).

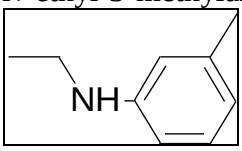
^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2 and 150.0 (d, $^1J_{C\text{-}F}$ = 240 Hz), 137.1 and 136.9(d, $^2J_{C\text{-}F}$ = 15 Hz), 124.7 and 124.6 (d, $^3J_{C\text{-}F}$ = 7 Hz), 116.5 and 116.4 (d, $^4J_{C\text{-}F}$ = 7 Hz), 114.5 and 114.2 (d, $^3J_{C\text{-}F}$ = 18 Hz),112.1, 38.2, 14.9. HRMS (ESI) m/z calcd for $(C_8H_{10}FN)^+$ $(M+H)^+$ 140.0831, found 140.0831.

N-ethyl-4-methylaniline (**3d, 5d**)



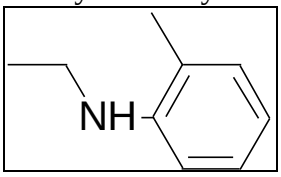
Yellow Liquid; (Yield = **3d**- 77%, **5d**-74%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9 (d, *J* = 8 Hz, 2H), 6.5 (d, *J* = 4 Hz, 2H), 3.4 (s, 1H), 3.14 (q, *J* = 8 Hz, 2H), 2.2 (s, 3H), 1.23 (t, *J* = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):146.3, 129.8, 126.5, 113.1, 38.9, 20.5,15.0. HRMS (ESI) m/z calcd for $(C_9H_{13}N)^+$ $(M+H)^+$ 136.1082, found 136.1082.

N-ethyl-3-methylaniline (**3e, 5e**)



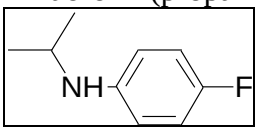
Yellow liquid; (Yield = **3e**- 71%, **5e**-70%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (t, *J* = 8 Hz, 1H), 6.5 (d, *J* = 0.4 Hz, 1H), 6.5 (s, 2H), 3.5 (s, 1H), 3.1 (q, *J* = 4 Hz, 2H), 2.2 (s, 3H), 1.2 (t, *J* = 4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6, 139.1, 129.2, 118.3, 113.7, 110.0, 38.63, 21.8, 15.0. HRMS (ESI) m/z calcd for $(C_9H_{13}N)^+$ $(M+H)^+$ 136.1082, found 136.1082.

N-ethyl-2-methylaniline (**3f, 5f**)



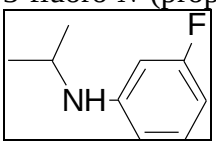
Yellow liquid; (Yield = **3f**- 63%, **5f**-60%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (t, *J* = 1.2 Hz, 1H), 7.0 (d, , *J* = 8 Hz, 2H), 3.4 (s, 1H), 3.2 (q, *J* = 8 Hz, 2H), 2.1 (s, 3H), (t, *J* = 4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.5, 130.1, 127.2, 121.8, 116.8, 109.8, 38.5, 17.5, 15.1. HRMS (ESI) m/z calcd for $(C_9H_{13}N)^+$ $(M+H)^+$ 136.1082, found 136.1082.

4-fluoro-*N*-(propan-2-yl)aniline (**3g, 5g**)



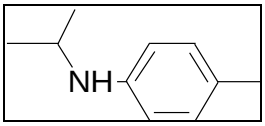
Yellow liquid; (Yield = **3g**- 78%, **5g**- 75%),^{1}H NMR (400 MHz, $CDCl_3$): δ 6.8 (t, *J* = 2.4 Hz, 2H), 6.54-6.49 (m, 2H), 3.58-3.52 (m, 1H), 1.7 (d, *J* = 8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8 and 154.5(d, $^{1}J_{C\text{-}F}$ = 230 Hz), 143.9, 115.8 and 115.6 (d, $^{3}J_{C\text{-}F}$ = 20 Hz), 114.3 and 114.2(d, $^{2}J_{C\text{-}F}$ = 40 Hz) , 45.0, 23.0. HRMS (ESI) m/z calcd for $(C_9H_{12}FN)^+$ $(M+H)^+$ 154.0987, found 154.0987.

3-fluoro-*N*-(propan-2-yl)aniline (**3h, 5h**)



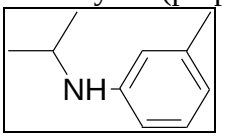
Yellow Liquid; (Yield = **3h**- 65%, **5h**- 60%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (q, *J* = 2 Hz, 1H), 6.36- 6.24 (m, 3H), 3.62- 3.54 (m, 1H), 1.2 (d, *J* = 8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9 and 162.8 (d, $^{1}J_{C\text{-}F}$ = 232 Hz) , 130.4, 109.1, 103.5, 103.4 and103.2 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 99.7 and 99.5 (d, $^{1}J_{C\text{-}F}$ = 16 Hz), 44.4, 23.0.HRMS (ESI) m/z calcd for $(C_9H_{12}FN)^+$ $(M+H)^+$ 154.0987, found 154.0987.

4-methyl-*N*-(propan-2-yl)aniline **(3i, 5i**)



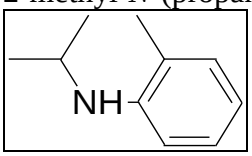
Yellow liquid; (Yield = **3i**- 70%, **5i**- 68%), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.0 (d, , *J* = 9 Hz, 2H), 6.5 (d, *J* = 9 Hz, 2H), 3.66-3.57 (m, 1H), 3.4 (s, 1H), 2.2 (s, 3H), 1.21 (d, , *J* = 6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 130.0, 124.9, 112.7, 44.6, 20.2, 12.7. HRMS (ESI) m/z calcd for $(C_{10}H_{15}N)^+$ $(M+H)^+$ 150.1238, found 150.1240.

3-methyl-*N*-(propan-2-yl)aniline (**3j, 5j**)



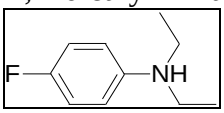
Yellow liquid; (Yield = **3j**- 68%, **5j**- 65%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (t, *J* = 8 Hz, 1H), 6.5 (d, *J* = 0.8 Hz, 1H), 6.4 (s, 2H), 3.65-3.58 (m, 1H), 2.2 (s, 3H), 1.2 (d, *J* = 8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 139.1, 129.2, 118.0, 114.1, 110.5, 44.3, 23.2, 21.8. HRMS (ESI) m/z calcd for $(C_{10}H_{15}N)^+$ $(M+H)^+$ 150.1238, found 150.1240.

2-methyl-*N*-(propan-2-yl)aniline (**3k, 5k**)



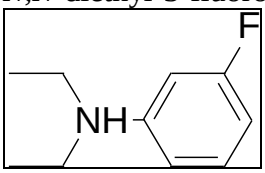
Yellow liquid; (Yield = **3k**- 59%, **5k**- 56%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (t, *J* = 7 Hz, 2H), 7.0 (d, *J* = 0.8 Hz, 2H), 3.71-3.64 (m, 1H), 3.3 (s, 1H), 2.1 (s, 3H), 1.2 (d, *J* = 4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 130.3, 127.2, 121.8, 116.4, 110.3, 44.1, 23.3, 17.7. HRMS (ESI) m/z calcd for $(C_{10}H_{15}N)^+$ $(M+H)^+$ 150.1238, found 150.1240.

N,*N*-diethyl-4-fluoroaniline (**3l, 5l**)



Yellow liquid; (Yield = **3l**- 79%, **5l**- 75%),^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9 (t, *J* = 4 Hz, 2H), 6.6 (m, 2H), 3.3 (q, *J* = 4 Hz, 4H), 1.12 (t, *J* = 8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7 and 153.6 (d, $^{1}J_{C\text{-}F}$ = 232 Hz), 144.8, 115.7 and 115.5(d, $^{2}J_{C\text{-}F}$ = 15 Hz), 113.8, 113.7 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 45.0, 12.5. HRMS (ESI) m/z calcd for $(C_{10}H_{15}FN)^+$ $(M+H)^+$ 169.1222, found 169.1222.

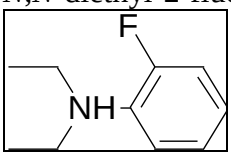
N,*N*-diethyl-3-fluoroaniline (**3m, 5m**)



Yellow liquid; (Yield = **3m**- 68%, **5m**- 66%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (q, *J* = 8 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.3 (m, 2H), 3.3 (q, *J* = 8 Hz, 4H), 1.1 (t, 4 Hz, 6H). ^{13}C NMR (100

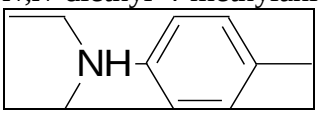
MHz, $CDCl_3$): δ 165.7 and 163.3(d, $^1J_{C\text{-}F}$ = 240 Hz), 149.6 and 149.5(d, $^3J_{C\text{-}F}$ = 10 Hz), 130.3 and 130.2(d, $^3J_{C\text{-}F}$ = 10 Hz), 107.3, 107.2, 101.8 and 101.5(d, $^2J_{C\text{-}F}$ = 30 Hz), 98.6 and 98.4(d, $^3J_{C\text{-}F}$ = 20 Hz), 44.5, 12.5. HRMS (ESI) m/z calcd for $(C_{10}H_{15}FN)^+$ $(M+H)^+$ 169.1222, found 169.1222.

N,*N*-diethyl-2-fluoroaniline (**3n, 5n**)



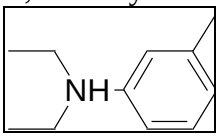
Yellow liquid; (Yield = **3n**- 60%, **5n**- 60%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02- 6.83 (m, 4H), 3.2 (q, *J* = 8 Hz, 4H), 1.08 (t, *J* = 8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 and 155.0 (d, $^1J_{C\text{-}F}$ = 100 Hz), 138.3 and 138.2 (d, $^3J_{C\text{-}F}$ = 10 Hz) , 124.1 and 124.0 (d, $^3J_{C\text{-}F}$ = 10 Hz), 121.3, 116.4 and 116.2 (d, $^2J_{C\text{-}F}$ = 20 Hz), 46.3, 12.5. HRMS (ESI) m/z calcd for $(C_{10}H_{15}FN)^+$ $(M+H)^+$ 169.1222, found 169.1222.

N,*N*-diethyl-4-methylaniline (**3o, 5o**)



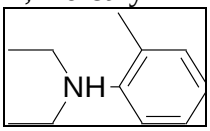
Yellow liquid; (Yield = **3o**- 75%, **5o**- 74%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (d, *J* = 8 Hz, 4H), 6.6 (d, *J* = 8 Hz, 4H), 3.3 (q, *J* = 8 Hz, 4H), 2.2 (s, 3H), 1.2 (t, *J* = 4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 129.8, 126.1, 113.5, 48.5, 29.8, 29.3,21.5, 20.4. HRMS (ESI) m/z calcd for $(C_{11}H_{18}N)^+$ $(M+H)^+$ 165.1473, found 165.1474.

N,*N*-diethyl-3-methylaniline (**3p, 5p**)



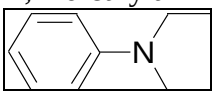
Yellow liquid; (Yield = **3p**- 67%, **5p**- 65%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (t, *J* = 4 Hz, 1H), 6.53-6.46 (m, 3H), 3.3 (q, *J* = 8 Hz, 4H), 2.3 (s, 3H), 1.2 (t, *J* = 4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 139.0, 129.2, 116.4, 112.7, 109.2, 44.4, 22.1, 12.7. HRMS (ESI) m/z calcd for $(C_{11}H_{18}N)^+$ $(M+H)^+$ 165.1473, found 165.1474.

N,*N*-diethyl-2-methylaniline (**3q, 5q**)



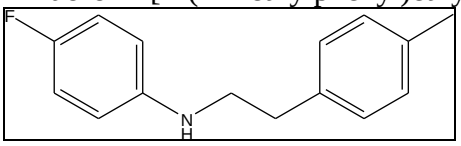
Yellow liquid; (Yield = **3q**- 56%, **5q**- 54%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26- 7.14 (m, 2H), 7.12-7.12 (m, 1H), 7.07- 6.95 (m, 1H), 3.0 (q, *J* = 8 Hz, 4H), 2.3 (s, 3H), 1.0 (t, *J* = 8 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 135.5, 130.9, 126.1, 123.3, 122.3, 47.7, 18.4, 12.7. HRMS (ESI) m/z calcd for $(C_{11}H_{18}N)^+$ $(M+H)^+$ 165.1473, found 165.1474.

N,*N*-diethylaniline (**3r**, **5r**)



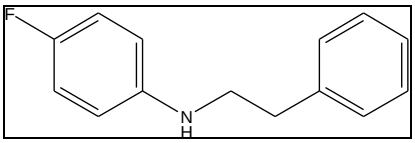
Yellow liquid; (Yield = **3r**- 56%, **5r**- 53%),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26- 7.18 (m, 2H), 6.72-6.62 (m, 2H), 3.4 (q, *J* = 4 Hz, 8H), 1.2 (t, *J* = 8Hz, 6H) .^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 128.7, 114.9, 111.4, 43.8, 12.0. HRMS (ESI) m/z calcd for $(C_{10}H_{15}N)^+$ $(M+H)^+$ 150.1238, found 150.1238.

4-fluoro-*N*-[2-(4-methylphenyl)ethyl]aniline (**8a**)



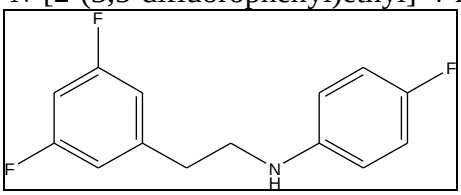
Yellow liquid; (Yield = 50%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (s, 4H), 6.8 (t, *J* = 2 Hz, 2H), 6.55-6.52 (m, 2H), 3.3 (t, *J* = 8 Hz, 2H), 2.8 (t, *J* = 4 Hz, 2H), 2.3 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5 and 154.4 (d, $^{1}J_{C\text{-}F}$ = 232 Hz), 114.5, 139.3, 128.9 and 128.7(d, $^{2}J_{C\text{-}F}$ = 15 Hz), 126.6, 115.9, 155.6, 113.9 and 113.8 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 65.0, 45.8, 35.2. HRMS (ESI) m/z calcd for $(C_{15}H_{16}FN)^+$ $(M+H)^+$ 230.1300, found 230.1300.

4-fluoro-*N*-(2-phenylethyl)aniline (**8b**)



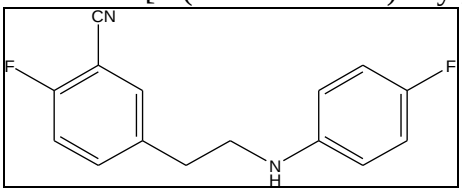
Yellow liquid; (Yield = 57%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 2H), 7.23-7.20 (m, 3H), 6.9 (t, *J* = 4 Hz, 2H), 6.89-6.55 (m, 2H), 3.8 (s, 1H), 3.3 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 and 154.8(d, $^{1}J_{C\text{-}F}$ = 230 Hz), 144.5 and 144.5 (d, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 129.4, 128.7, 115.9 and 115.7 (d, $^{2}J_{C\text{-}F}$ = 20 Hz) , 113.9 and 113.9(d, $^{3}J_{C\text{-}F}$ = 7 Hz), 45.8, 35.0. HRMS (ESI) m/z calcd for $(C_{14}H_{14}FN)^{+}$ $(M+H)^{+}$ 216.1144, found 216.1145.

N-[2-(3,5-difluorophenyl)ethyl]-4-fluoroaniline (**8c**)



Yellow liquid; (Yield = 45%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9 (t, *J* = 8 Hz, 2H), 6.75-6.72 (m, 3H), 6.56-6.53 (m, 2H), 3.3 (t, *J* = 8 Hz, 2H), 2.9 ((t, *J* = 8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9 and 161.7 (d, $^{1}J_{C\text{-}F}$ = 240 Hz), 164.8 and 161.5, (d, $^{1}J_{C\text{-}F}$ = 240 Hz), 147.7, 143.5 and 143.5(d, $^{3}J_{C\text{-}F}$ = 7.5 Hz) 139.3, 111.8, 111.7, 111.6, 111.5,102.0, (t, $^{2}J_{C\text{-}F}$ = 30 Hz), 44.7, 35.5,. HRMS (ESI) m/z calcd for $(C_{15}H_{12}F_2N_2)^{+}$ $(M+H)^{+}$ 259.1036, found 259.1036.

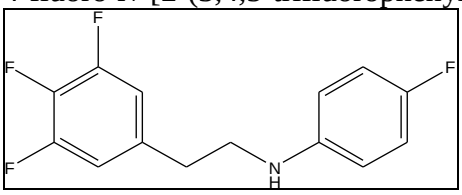
2-fluoro-5-[2-(4-fluoroanilino)ethyl]benzonitrile (**8d**)



Brown liquid; (Yield = 45%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46- 7.27 (m, 2H), 7.2 (s, 1H), 7.1 (t, *J* = 8 Hz, 2H), 6.89- 6.52 (m, 2H), 2.2 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.8 and 160.3(d, $^{1}J_{C\text{-}F}$ = 262 Hz), 157.8 and 154.6(d, $^{1}J_{C\text{-}F}$ = 240 Hz), 143.8, 136.6, 135.6, 135.5 and 133.4(d, $^{3}J_{C\text{-}F}$ = 8 Hz), 116.8 and 116.6(d, $^{2}J_{C\text{-}F}$ = 15 Hz), 116.1,115.8,

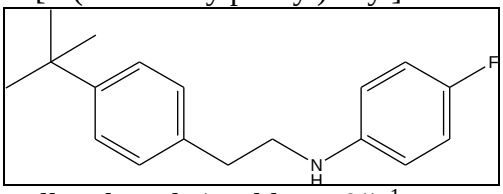
114.0 and 113.9 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 101.7 and 101.5 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 45.5, 34.5. HRMS (ESI) m/z calcd for $(C_{15}H_{12}F_2N_2)^+$ $(M+H)^+$ 259.1002, found 259.1002.

4-fluoro-*N*-[2-(3,4,5-trifluorophenyl)ethyl]aniline (**8e**)



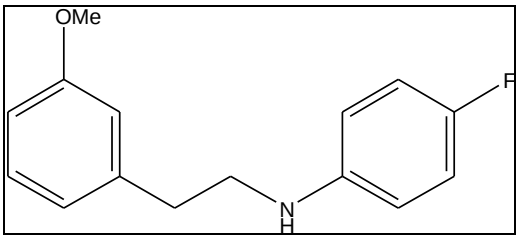
Yellow solid; (Yield = 50%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9 (t, *J* = 4 Hz, 1H), 6.93-6.79 (m, 1H), 6.56-6.51 (m, 1H), 3.3 (t, *J* = 4 Hz, 1H), 2.8 (t, *J* = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3 and 154.9(d, $^{1}J_{C\text{-}F}$ = 240 Hz), 152.6 and 150.0 (d, $^{1}J_{C\text{-}F}$ = 260 Hz), 139.8 and 137.3 (d, $^{1}J_{C\text{-}F}$ = 250 Hz), 143.9 and 143.9 (d, $^{4}J_{C\text{-}F}$ = 1.6 Hz), 139.8, 137.3, 135.7, 135.7, 135.6, 135.6 and 135.5(d, $^{3}J_{C\text{-}F}$ = 10 Hz), 116.0 and 115.8(d, $^{2}J_{C\text{-}F}$ = 20 Hz), 113.9, 113.9, 112.8 and 112.6(d, $^{2}J_{C\text{-}F}$ = 20 Hz), 45.3, 34.9.HRMS (ESI) m/z calcd for $(C_{14}H_{11}F_4N)^+$ $(M+H)^+$ 270.0861, found 270.0862. mp- 38.3- 56.5 ℃

N-[2-(4-*tert*-butylphenyl)ethyl]-4-fluoroaniline **(8f**)



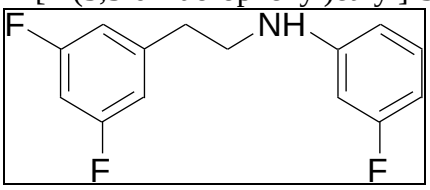
Yellow liquid; (Yield = 54%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.21 (m, 3H), 7.2 (s, 1H), 7.0 (t, *J* = 4 Hz, 1H), 6.91-6.87 (m, 2H), 6.56- 6.52 (m, 2H), 3.3 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 4 Hz, 2H), 1.3 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 and 154.8(d, $^{1}J_{C\text{-}F}$ = 230 Hz), 151.6, 144.5, 144.5, 138.9, 126.0 and 125.8(d, $^{3}J_{C\text{-}F}$ = 12 Hz) , 123.6, 115.9 and 115.6 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 114.0, 113 , 45.9, 35.8, 34.7, 31.5. HRMS (ESI) m/z calcd for $(C_{17}H_{19}FN)^+$ $(M+H)^+$ 257.1535, found 257.1535.

4-fluoro-*N*-[2-(3-methoxyphenyl)ethyl]aniline (**8g**)



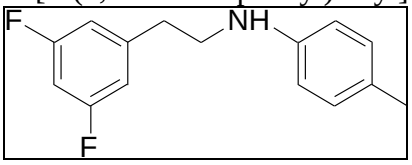
Brown liquid; (Yield = 42%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (d, *J* = 2.4 Hz, 2H), 6.91- 6.83 (m, 4H), 6.56- 6.51 (m, 2H), 4.8 (s, 3H), 3.3 (t, *J* = 8 Hz, 2H), 2.8 (t, *J* = 8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 157.5 and 154.4(d, $^{1}J_{C\text{-}F}$ = 232 Hz), 144.5, 131.2, 129.9 ,129.9, 129.8, 115.9 and 115.6(d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 114.1 and 114.0 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 113.9, 55.4, 46.0, 34.6. HRMS (ESI) m/z calcd for $(C_{15}H_{16}FNO)^{+}$ $(M+H)^{+}$ 246.1249, found 246.1250.

N-[2-(3,5-difluorophenyl)ethyl]-3-fluoroaniline (**8h**)



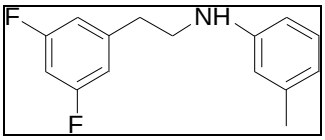
Yellow liquid; (Yield = 42%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (q, *J* = 4 Hz, 1H), 6.76-6.66 (m, 3H), 6.43-6.33 (m, 3H), 3.4 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9 and 162.7(d, $^{1}J_{C\text{-}F}$ = 240 Hz), 165.0 and 161.7 (d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 164.8 and 161.5 (d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 149.6 and 149.5 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 143.0 and 142.9 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 130.6 and 130.5(d, $^{3}J_{C\text{-}F}$ = 8 Hz), 111.8 and 111.5(d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 108.9, 104.4 and 104.1(d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 102.2, 101.8, 99.8 and 99.5(d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 44.5, 35.3. HRMS (ESI) m/z calcd for $(C_{14}H_{12}F_3N)^{+}$ $(M+H)^{+}$ 252.0955 found 252.0955.

N-[2-(3,5-difluorophenyl)ethyl]-4-methylaniline (**8i**)



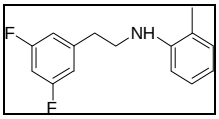
Yellow liquid; (Yield = 42%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (d, *J* = 8 Hz, 2H), 6.76- 6.66 (m, 3H), 6.5 (d, *J* = 4 Hz, 2H), 3.4 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 4 Hz, 2H), 2.2 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9 and 161.7 (d, $^{1}J_{C\text{-}F}$ = 240 Hz), 145.4, 143.5(t, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 130.0, 127.2, 113.4, 111.8 and 111.6 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 102.0(t, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 45.0, 35.5, 20.5.HRMS (ESI) m/z calcd for $(C_{15}H_{15}F_2N)^+$ $(M+H)^+$ 248.1026 found 248.1026.

N-[2-(3,5-difluorophenyl)ethyl]-3-methylaniline (**8j**)



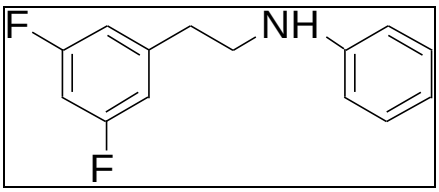
Yellow liquid; (Yield = 38%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.1 (t, *J* = 4 Hz, 1H), 6.7 (d, *J* = 4 Hz, 2H), 6.7 (t, *J* = 4 Hz, 1H), 6.6 (d, *J* = 4 Hz, 1H), 6.4 (s, 2H), 3.4 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 8 Hz, 2H), 2.3 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5 and 160.2(d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 146.3, 141.9 (t, $^{3}J_{C\text{-}F}$ = 15 Hz), 137.8, 127.9, 117.4, 112.5, 110.4 and 110.1(d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 110.3 and 110.0(d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 100.9 (t, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 43.2, 34.0, 20.3. HRMS (ESI) m/z calcd for $(C_{15}H_{15}F_2N)^+$ $(M+H)^+$ 248.1026 found 248.1026.

N-[2-(3,5-difluorophenyl)ethyl]-2-methylaniline (**8k**)



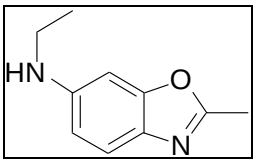
Yellow liquid; (Yield = 35%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.2 (t, *J* = 4 Hz, 1H), 7.1 (d, *J* = 4 Hz, 1H), 6.7 (d, *J* = 4 Hz, 2H), 6.6 (q, *J* = 4 Hz, 3H), 3.4 (t, *J* = 8 Hz, 2H), 2.9 (t, 4 Hz, 2H), 2.0 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0 and 161.7(d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 145.5, 143.5(t, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 130.4, 127.3, 122.2, 117.4, 111.8 and 111.6 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 109.9, 102.0 (t, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 44.5, 35.8,s 17.4.HRMS (ESI) m/z calcd for $(C_{15}H_{15}F_2N)^+$ $(M+H)^+$ 248.1026 found 248.1026.

N-[2-(3,5-difluorophenyl)ethyl]aniline (**8l**)



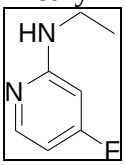
Yellow liquid; (Yield = 48%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.18 (m, 2H), 6.76- 6.64 (m, 4H), 6.6 (d, *J* = 8 Hz, 2H), 3.4 (t, *J* = 8 Hz, 2H), 2.9 (t, *J* = 8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.8 and 161.4 (d, $^{1}J_{C\text{-}F}$ = 255 Hz), 147.5, 143.3, (t, ^{3}J = 7.5 Hz), 129.4, 117.8, 113.0, 111.7 and 111.5 (d, $^{1}J_{C\text{-}F}$ = 22.5 Hz), 101.9 (t, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 44.5, 35.3.HRMS (ESI) m/z calcd for $(C_{14}H_{13}F_2N)^+$ $(M+H)^+$ 234.1050 found 234.1051.

N-ethyl-2-methyl-1,3-benzoxazol-6-amine (**10a**)



Brown solid; (Yield = 50%, 120mg) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4 (d, *J* = 8 Hz, 1H), 6.7 (s, 1H), 6.6 (d, *J* = 8 Hz, 1H), 3.2 (q, *J* = 8 Hz, 2H), 2.6 (s, 3H), 1.3 (t, *J* = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 152.7, 146.8, 132.7, 119.4, 112.3, 93.2, 39.0, 14.8, 14.5. HRMS (ESI) m/z calcd for $(C_{10}H_{12}N_2O)^+$ $(M+H)^+$ 176.0950 found 176.0950. mp- 45.6- 63.3 °C

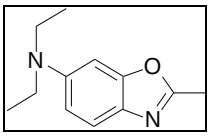
N-ethyl-4-fluoropyridin-2-amine (**10b**)



Yellow solid; (Yield = 45%, 110mg) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 1H), 6.34-6.30 (m, 1H), 6.04-6.01 (m, 1H), 4.7 (s, 1H), 3.2 (m, 2H), 1.2 (t, *J* = 8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.1 and 168.7 (d, $^{1}J_{C\text{-}F}$ = 255 Hz), 161.4 and 161.3 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 150.7 and 150.6

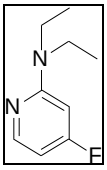
(d, $^{1}J_{C\text{-}F}$ = 7.5Hz), 101.6 and 101.3 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 92.6 and 92.3 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 37.1, 29.8, 14.8. HRMS (ESI) m/z calcd for $(C_7H_9FN_2)^+$ $(M+H)^+$ 141.0783 found 141.0784.

N,*N*-diethyl-2-methyl-1,3-benzoxazol-6-amine (**10c**)



Brown liquid; (Yield = 40%, 115mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4 (d, *J* = 8 Hz, 1H), 6.27-6.24 (m,1H), 6.12- 6.06 (m, 1H), 3.4 (q, *J* = 4 Hz, 4H), 2.5 (s, 3H), 1.1 (t, *J* = 8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.1, 168.7, 161.4, 161.3, 150.7, 150.6, 101.6, 101.3, 92.6, 92.3, 37.1, 29.8, 14.8. HRMS (ESI) m/z calcd for $(C_{12}H_{16}N_2O)^+$ $(M+H)^+$ 205.1296 found 205.1296.

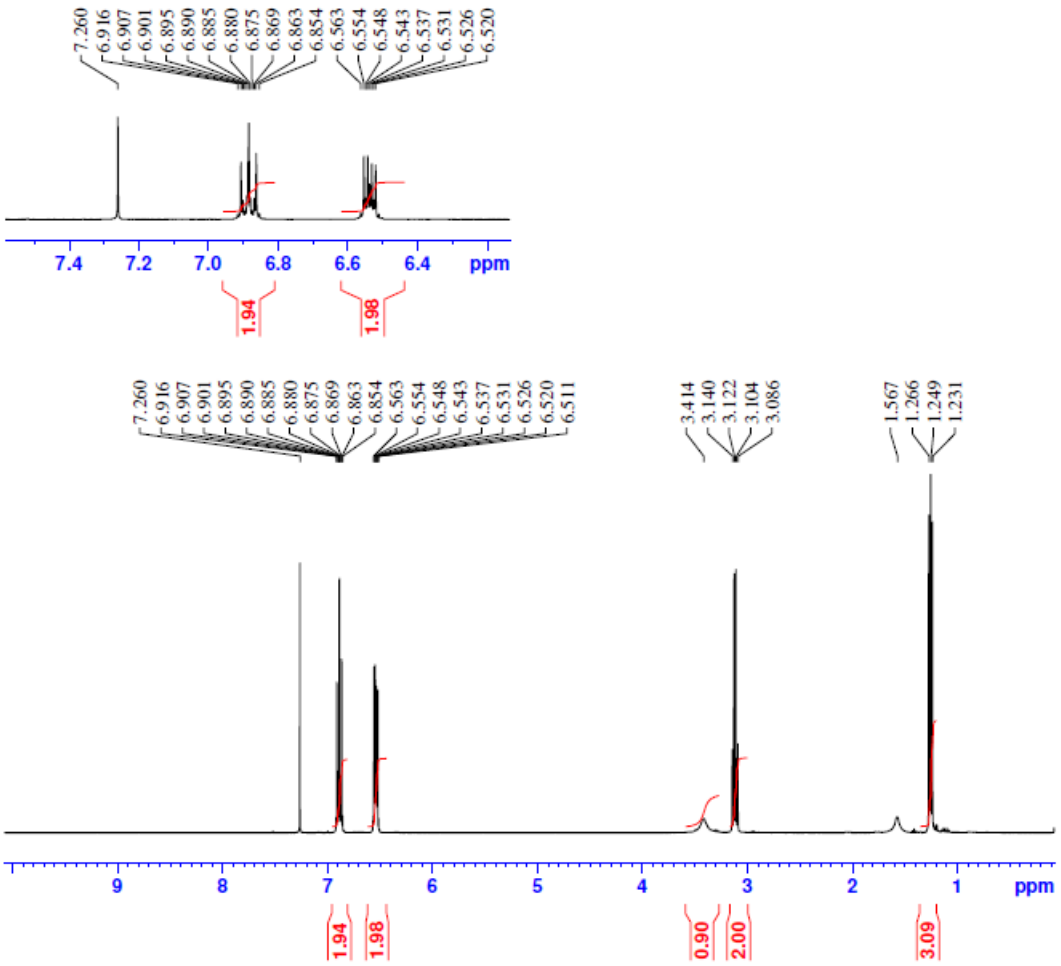
N,*N*-diethyl-4-fluoropyridin-2-amine (**10d**)



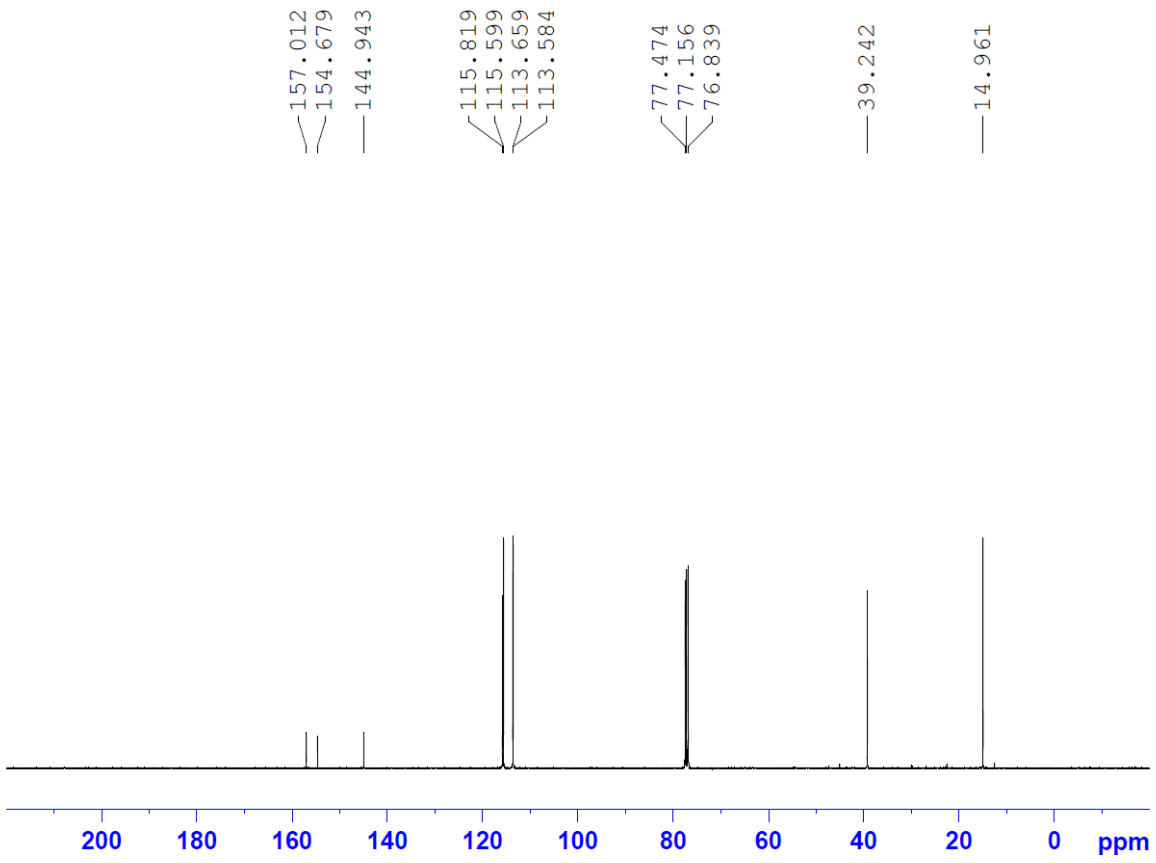
Yellow liquid; (Yield = 20%, 60mg).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.05 (m, 1H), 6.2 (t, *J* = 4 Hz, 1H), 6.1 (dd, *J* = 4 Hz, 1H), 3.5 (q, *J* = 8 Hz, 4H), 1.3 (t, *J* = 4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 176.9, 172.7 and 169.3 (d, $^{1}J_{C\text{-}F}$ = 255 Hz), 160.9 and 160.7(d, $^{3}J_{C\text{-}F}$ = 15 Hz), 148.0 and 147.9 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 101.1 and 100.9 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 92.4, 92.1, 72.6, 71.6, 70.5, 70.2, 37.1, 21.9, 14.1. HRMS (ESI) m/z calcd for $(C_{12}H_{16}FN_2)^+$ $(M+H)^+$ 169.0196 found 169.0196.

N-ethyl-4-fluoroaniline (**3a, 5a**)

^{1}H NMR

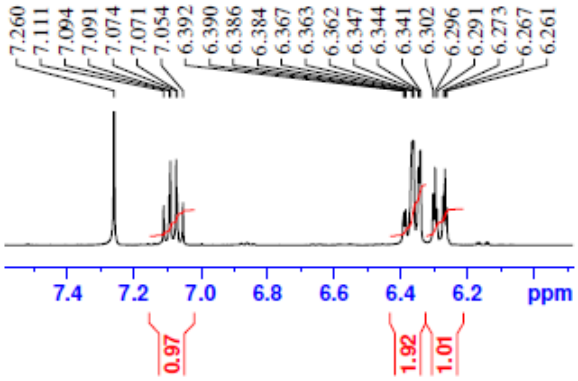

7.260
6.916
6.907
6.901
6.895
6.890
6.885
6.880
6.875
6.869
6.863
6.854
6.563
6.554
6.548
6.543
6.537
6.531
6.526
6.520
7.4
7.2
7.0
6.8
6.6
6.4
ppm
1.94
1.98
7.260
6.916
6.907
6.901
6.895
6.890
6.885
6.880
6.875
6.869
6.863
6.854
6.563
6.554
6.548
6.543
6.537
6.531
6.526
6.520
6.511
3.414
3.140
3.122
3.104
3.086
1.567
1.266
1.249
1.231
9
8
7
6
5
4
3
2
1
ppm
1.94
1.98
0.90
2.00
3.09

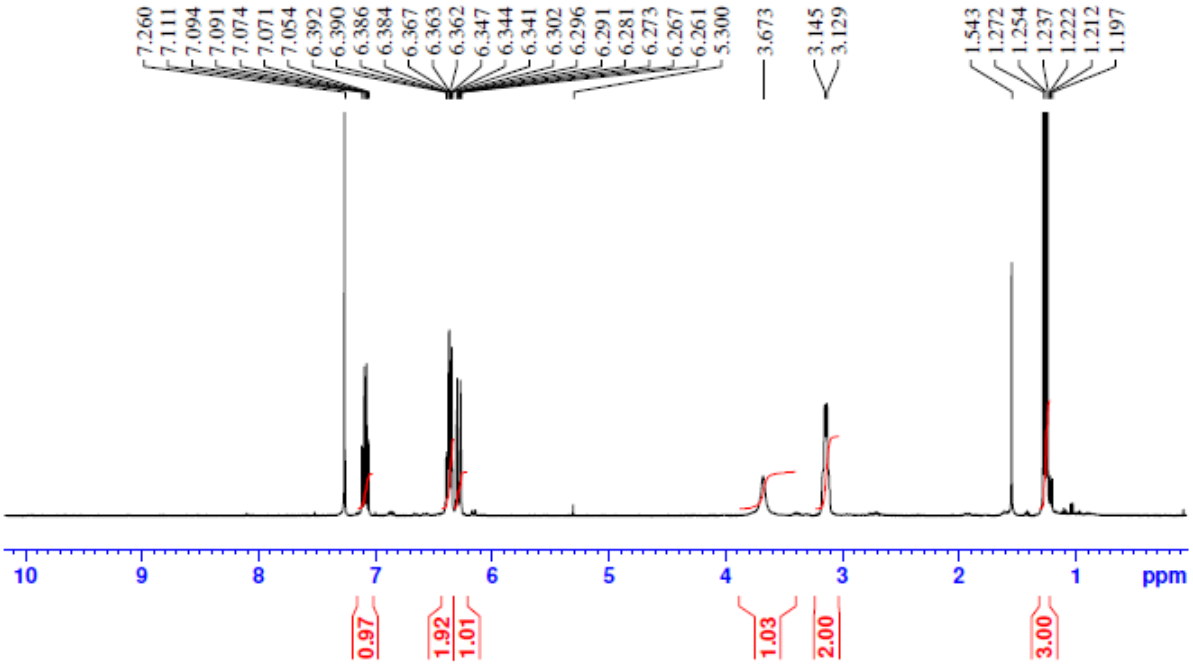
^{13}C NMR



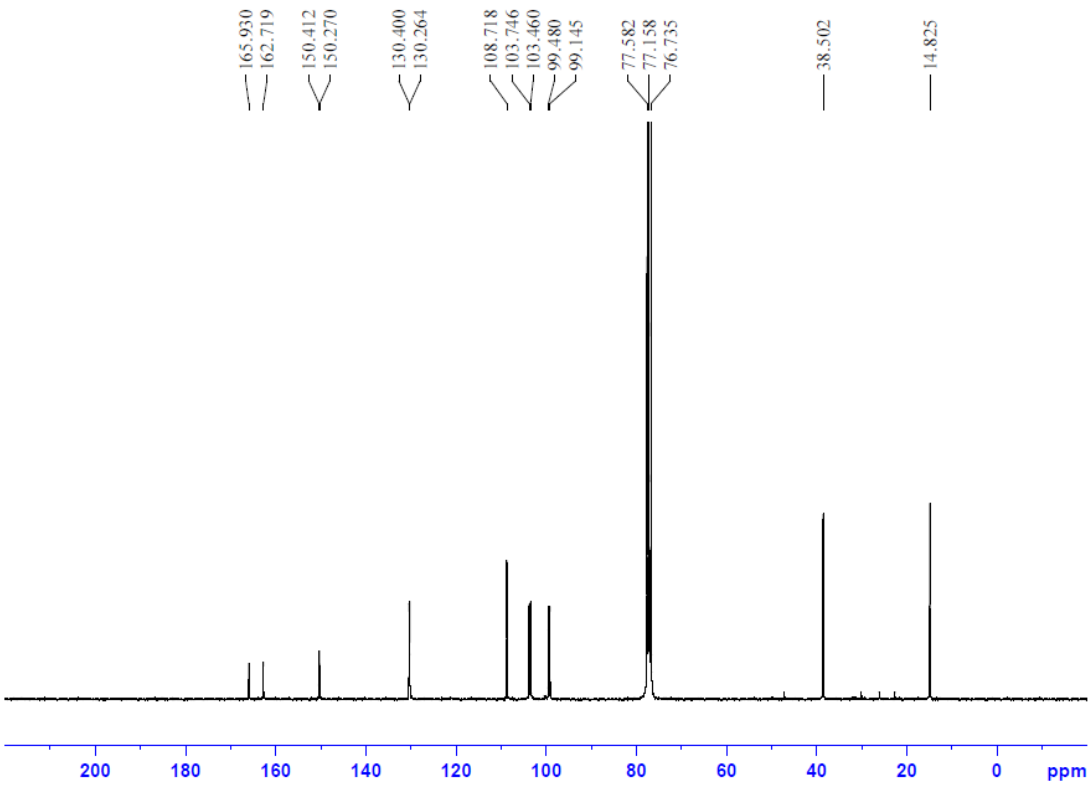
N-ethyl-3-fluoroaniline (**3b, 5b**)

^{1}H NMR


7.260
7.111
7.094
7.091
7.074
7.071
7.054
6.392
6.390
6.386
6.384
6.367
6.363
6.362
6.347
6.344
6.341
6.302
6.296
6.291
6.273
6.267
6.261
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm
0.97
1.92
1.01

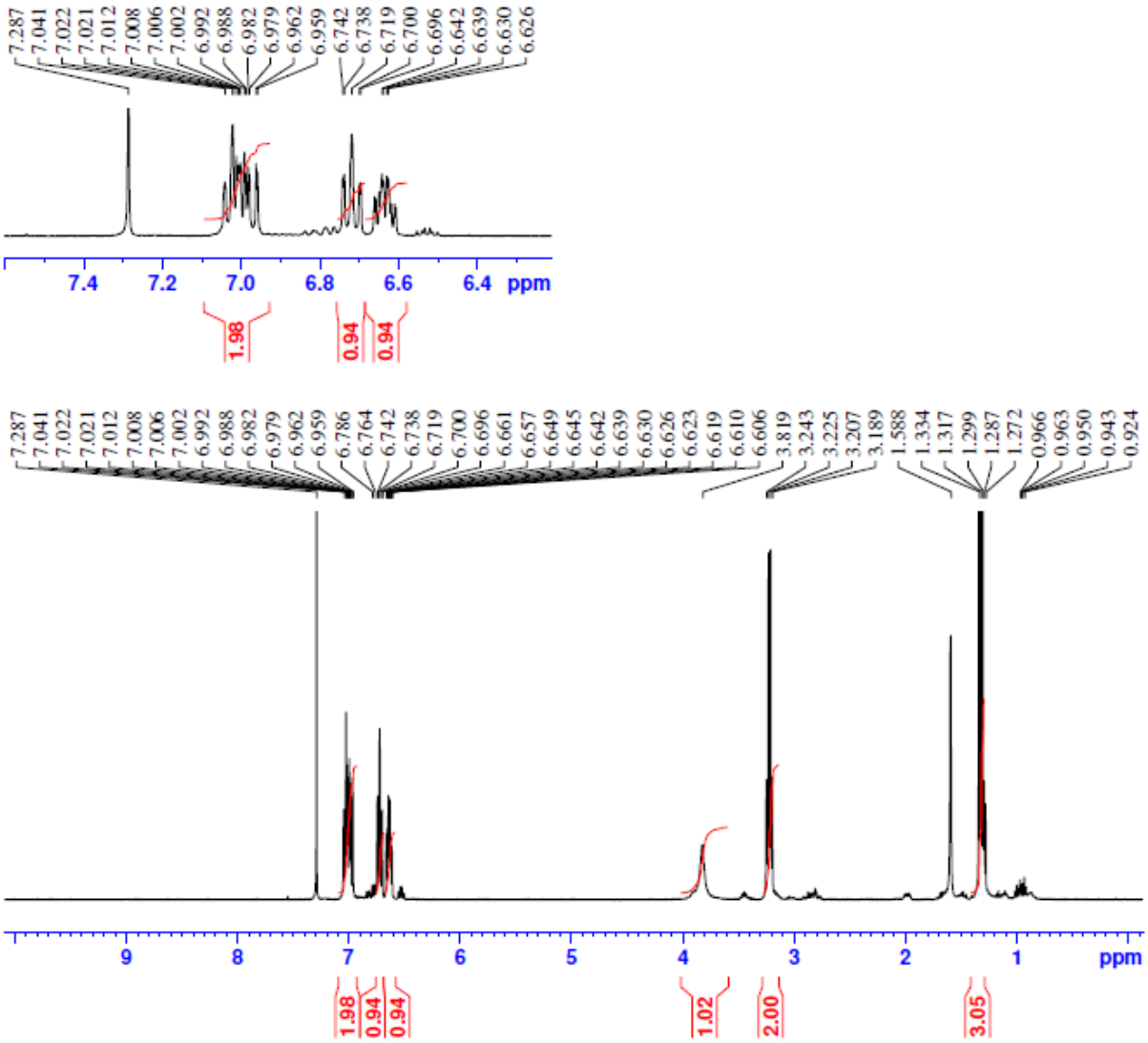

7.260
7.111
7.094
7.091
7.074
7.071
7.054
6.392
6.390
6.386
6.384
6.367
6.363
6.362
6.347
6.344
6.341
6.302
6.296
6.291
6.281
6.273
6.267
6.261
5.300
3.673
3.145
3.129
1.543
1.272
1.254
1.237
1.222
1.212
1.197
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.92
1.01
1.03
2.00
3.00

^{13}C NMR

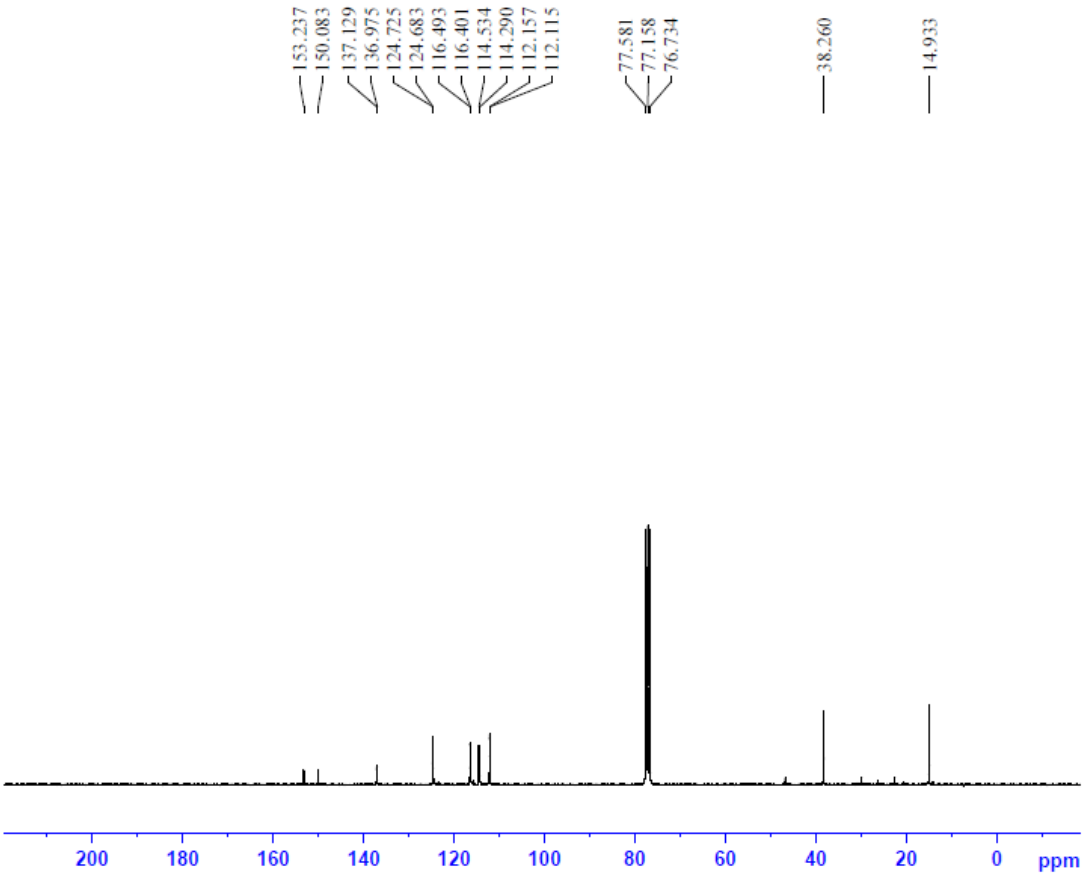


N-ethyl-2-fluoroaniline (**3c, 5c**)

^{1}H NMR

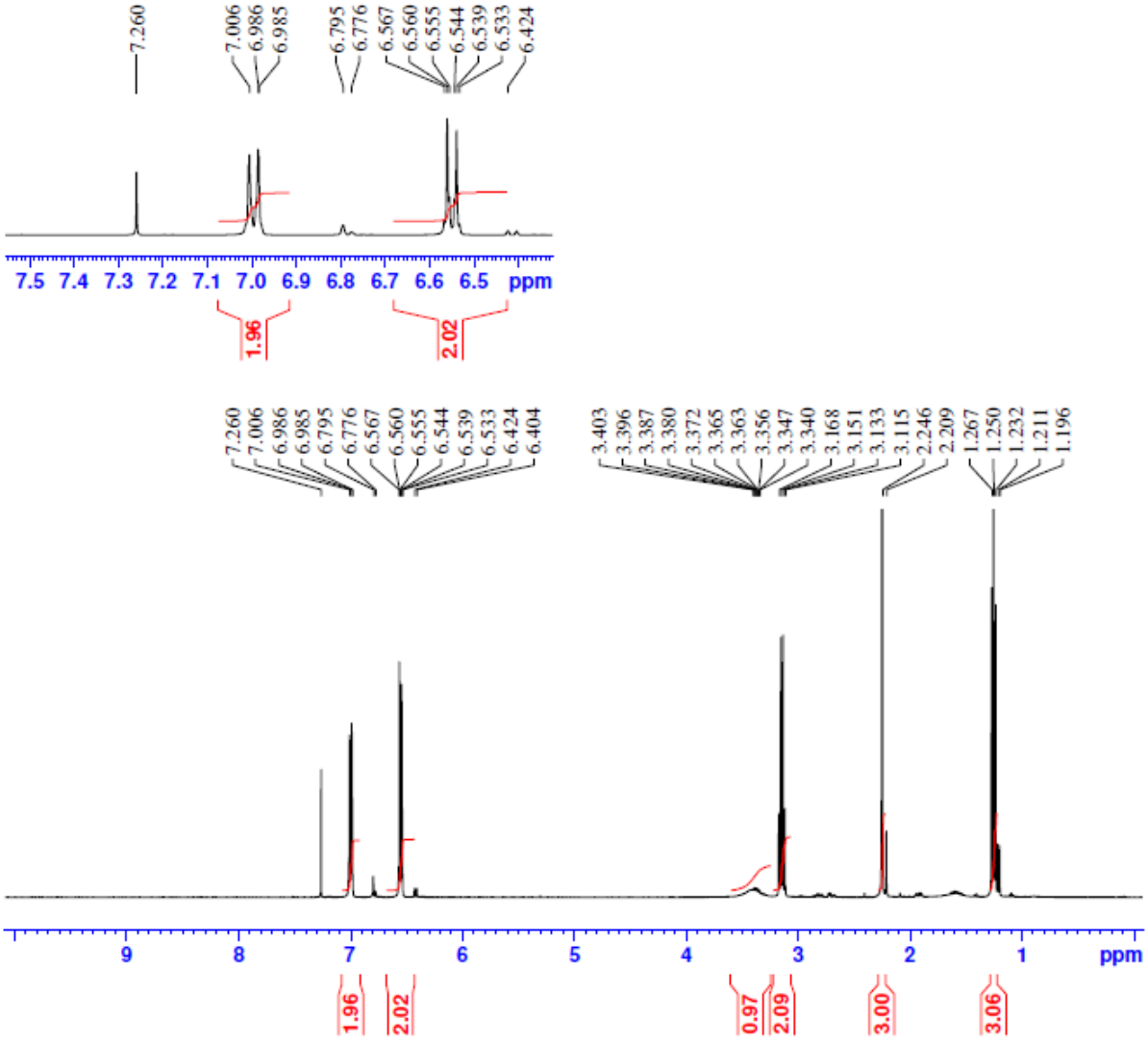

7.287
7.041
7.022
7.021
7.012
7.008
7.006
7.002
6.992
6.988
6.982
6.979
6.962
6.959
6.742
6.738
6.719
6.700
6.696
6.642
6.639
6.630
6.626
7.4
7.2
7.0
6.8
6.6
6.4
ppm
1.98
0.94
0.94
7.287
7.041
7.022
7.021
7.012
7.008
7.006
7.002
6.992
6.988
6.982
6.979
6.962
6.959
6.786
6.764
6.742
6.738
6.719
6.700
6.696
6.661
6.657
6.649
6.645
6.642
6.639
6.630
6.626
6.623
6.619
6.610
6.606
3.819
3.243
3.225
3.207
3.189
1.588
1.334
1.317
1.299
1.287
1.272
0.966
0.963
0.950
0.943
0.924
9
8
7
6
5
4
3
2
1
ppm
1.98
0.94
0.94
1.02
2.00
3.05

^{13}C NMR

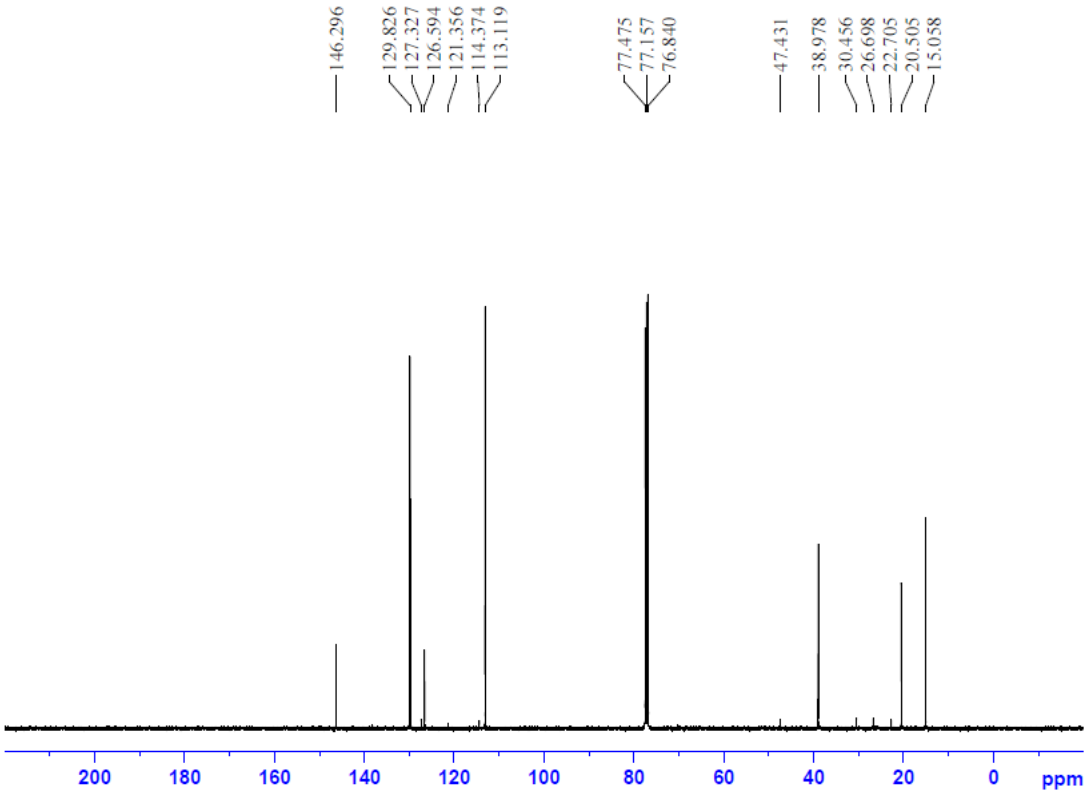


N-ethyl-4-methylaniline (**3d, 5d**)

^{1}H NMR

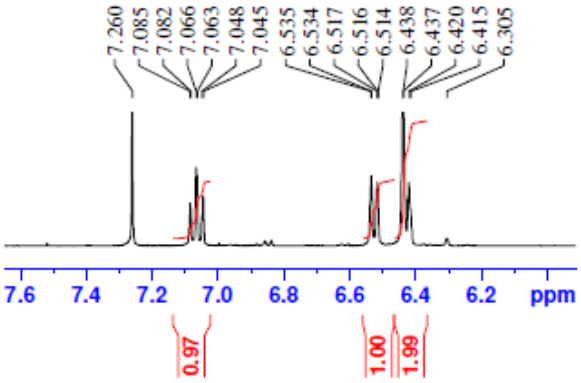

7.260
7.006
6.986
6.985
6.795
6.776
6.567
6.560
6.555
6.544
6.539
6.533
6.424
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm
1.96
2.02
7.260
7.006
6.986
6.985
6.795
6.776
6.567
6.560
6.555
6.544
6.539
6.533
6.424
6.404
3.403
3.396
3.387
3.380
3.372
3.365
3.363
3.356
3.347
3.340
3.168
3.151
3.133
3.115
2.246
2.209
1.267
1.250
1.232
1.211
1.196
9 8 7 6 5 4 3 2 1 ppm
1.96
2.02
0.97
2.09
3.00
3.06

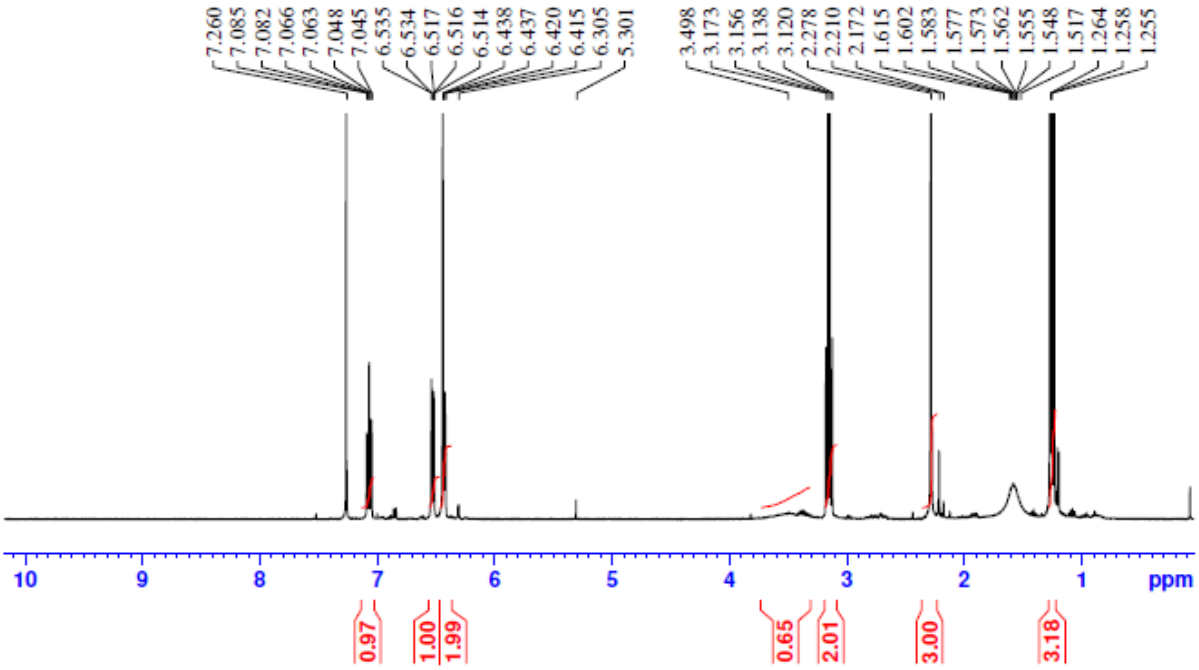
^{13}C NMR



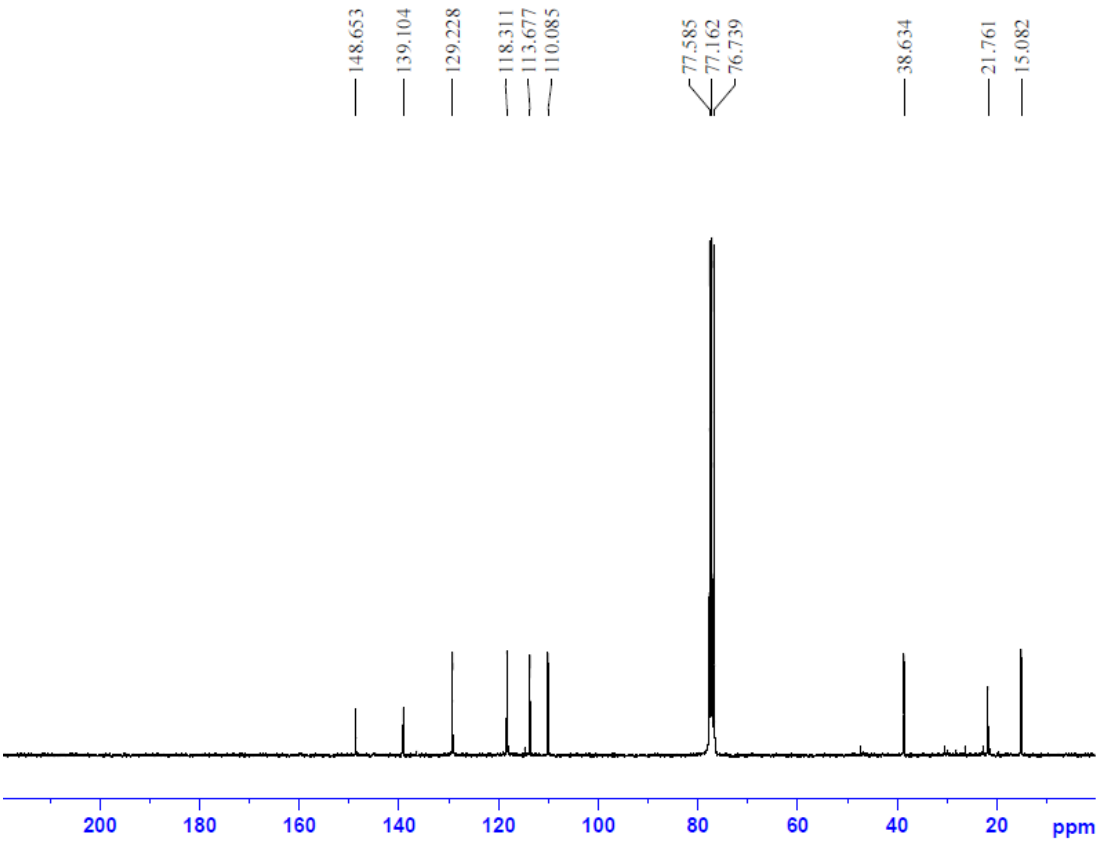
N-ethyl-3-methylaniline (**3e, 5e**)

^{1}H NMR


7.260
7.085
7.082
7.066
7.063
7.048
7.045
6.535
6.534
6.517
6.516
6.514
6.438
6.437
6.420
6.415
6.305
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm
0.97
1.00
1.99

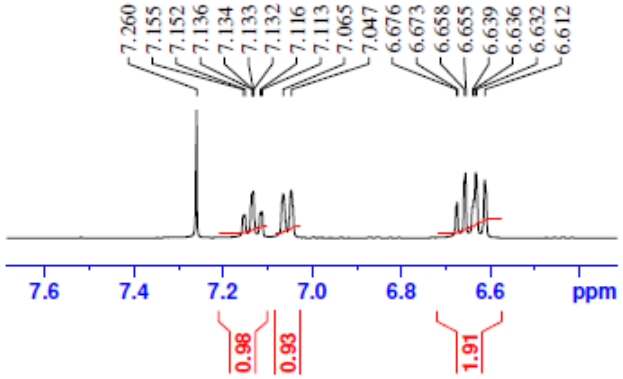

7.260
7.085
7.082
7.066
7.063
7.048
7.045
6.535
6.534
6.517
6.516
6.514
6.438
6.437
6.420
6.415
6.305
5.301
3.498
3.173
3.156
3.138
3.120
2.278
2.210
2.172
1.615
1.602
1.583
1.577
1.573
1.562
1.555
1.548
1.517
1.264
1.258
1.255
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.00
1.99
0.65
2.01
3.00
3.18

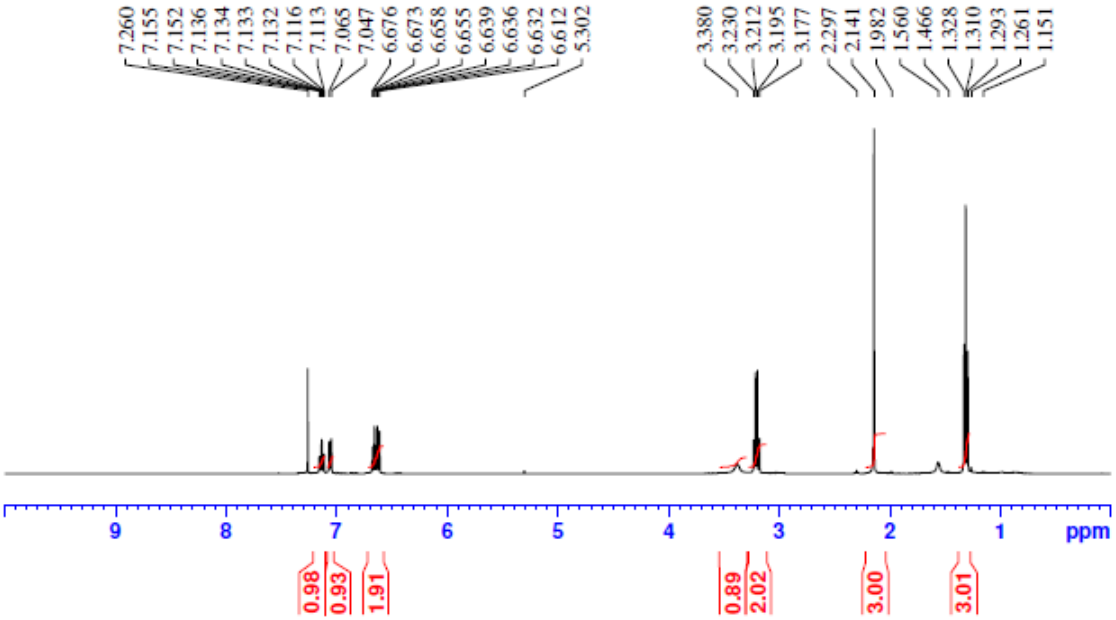
^{13}C NMR



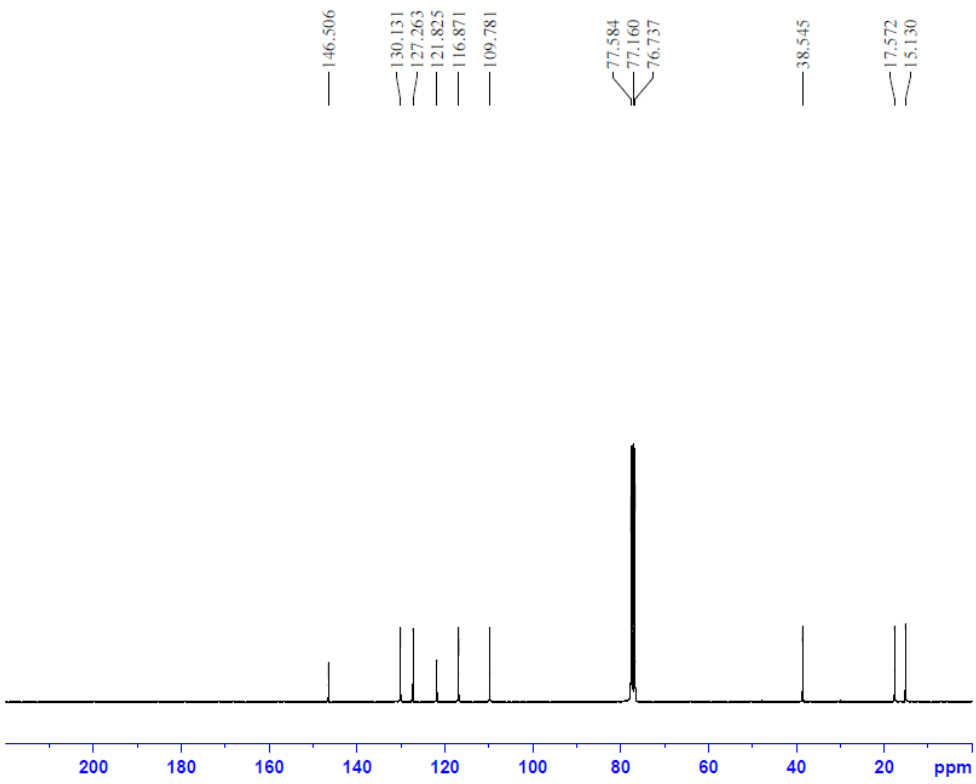
N-ethyl-2-methylaniline (**3f, 5f**)

^{1}H NMR


7.260
7.155
7.152
7.136
7.134
7.133
7.132
7.116
7.113
7.065
7.047
6.676
6.673
6.658
6.655
6.639
6.636
6.632
6.612
7.6
7.4
7.2
7.0
6.8
6.6
ppm
0.98
0.93
1.91

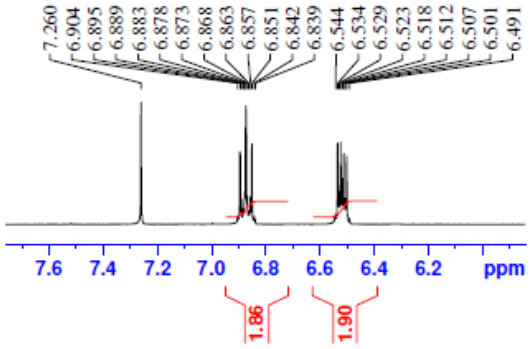

7.260
7.155
7.152
7.136
7.134
7.133
7.132
7.116
7.113
7.065
7.047
6.676
6.673
6.658
6.655
6.639
6.636
6.632
6.612
5.302
3.380
3.230
3.212
3.195
3.177
2.297
2.141
1.982
1.560
1.466
1.328
1.310
1.293
1.261
1.151
9
8
7
6
5
4
3
2
1
ppm
0.98
0.93
1.91
0.89
2.02
3.00
3.01

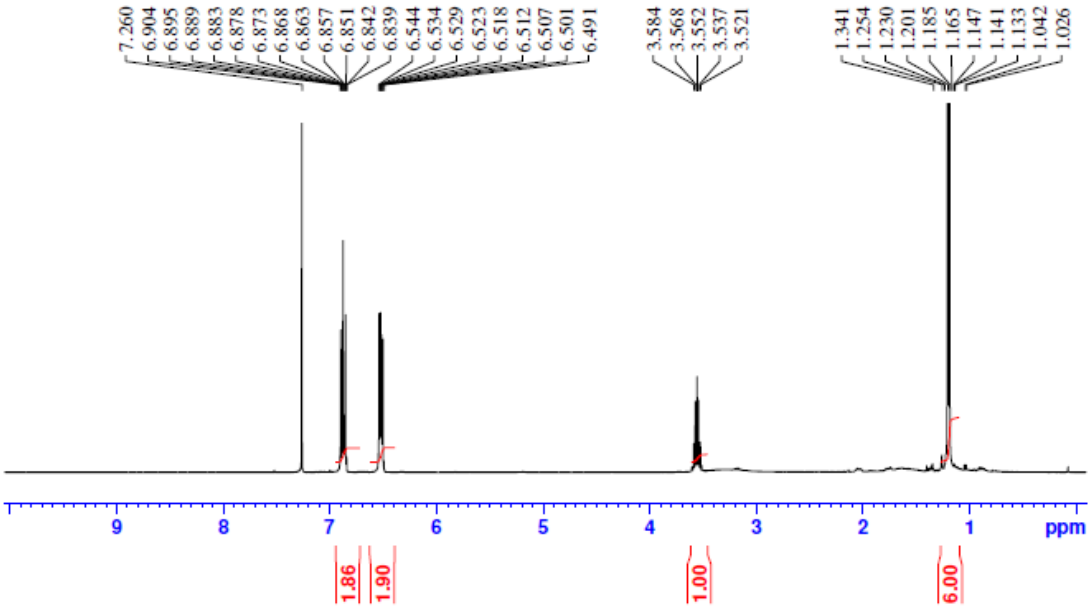
^{13}C NMR



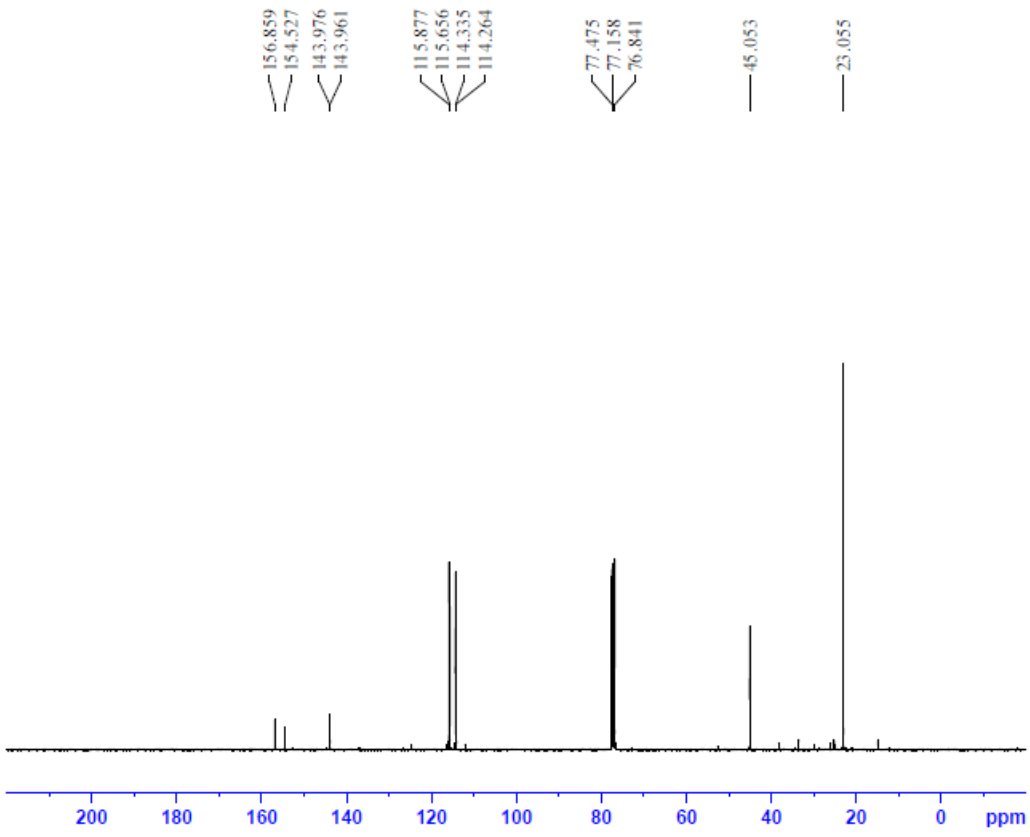
4-fluoro-*N*-(propan-2-yl)aniline (**3g, 5g**)

^{1}H NMR


7.260
6.904
6.895
6.889
6.883
6.878
6.873
6.868
6.863
6.857
6.851
6.842
6.839
6.544
6.534
6.529
6.523
6.518
6.512
6.507
6.501
6.491
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm
1.86
1.90

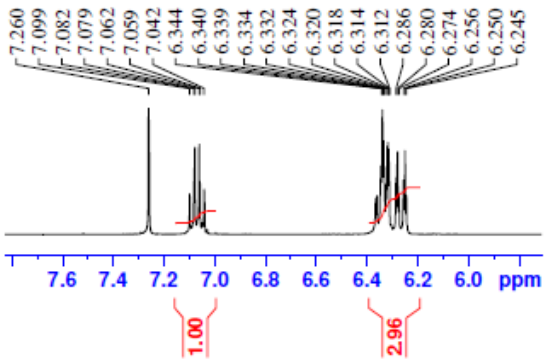

7.260
6.904
6.895
6.889
6.883
6.878
6.873
6.868
6.863
6.857
6.851
6.842
6.839
6.544
6.534
6.529
6.523
6.518
6.512
6.507
6.501
6.491
3.584
3.568
3.552
3.537
3.521
1.341
1.254
1.230
1.201
1.185
1.165
1.147
1.141
1.133
1.042
1.026
9
8
7
6
5
4
3
2
1
ppm
1.86
1.90
1.00
6.00

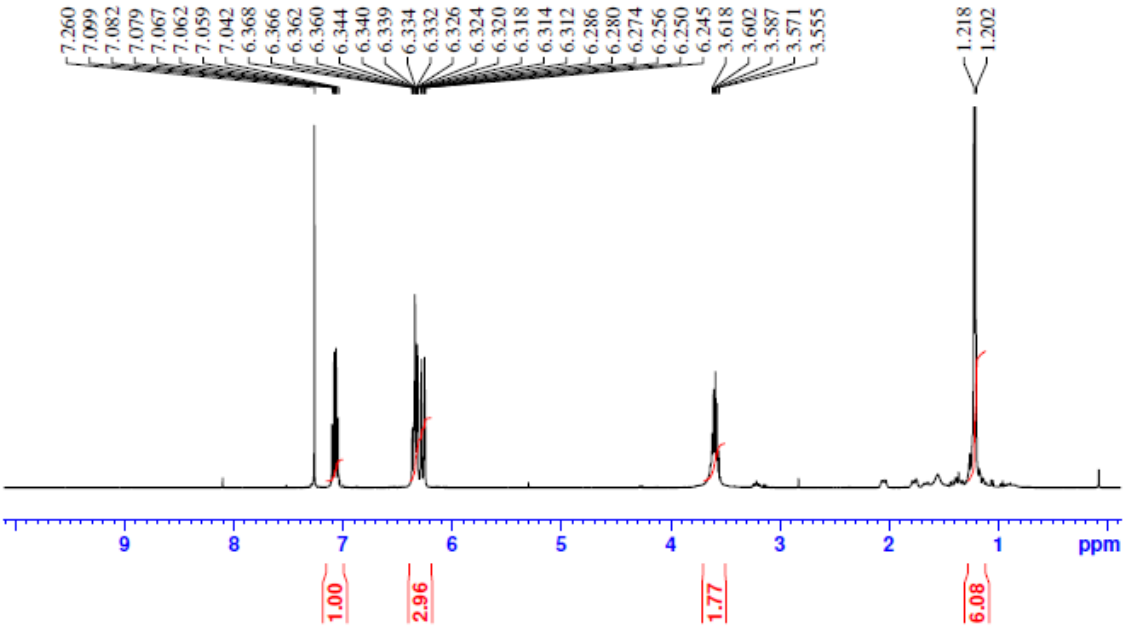
^{13}C NMR



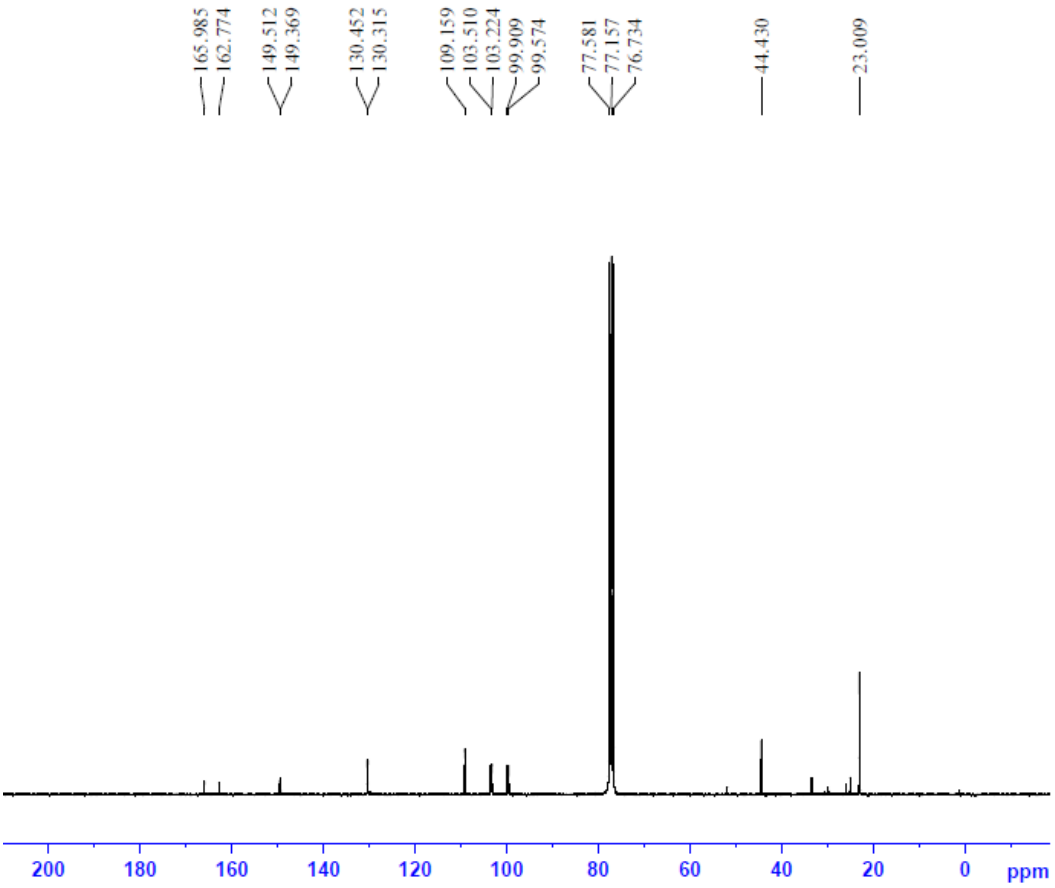
3-fluoro-*N*-(propan-2-yl)aniline (**3h, 5h**)

^{1}H NMR

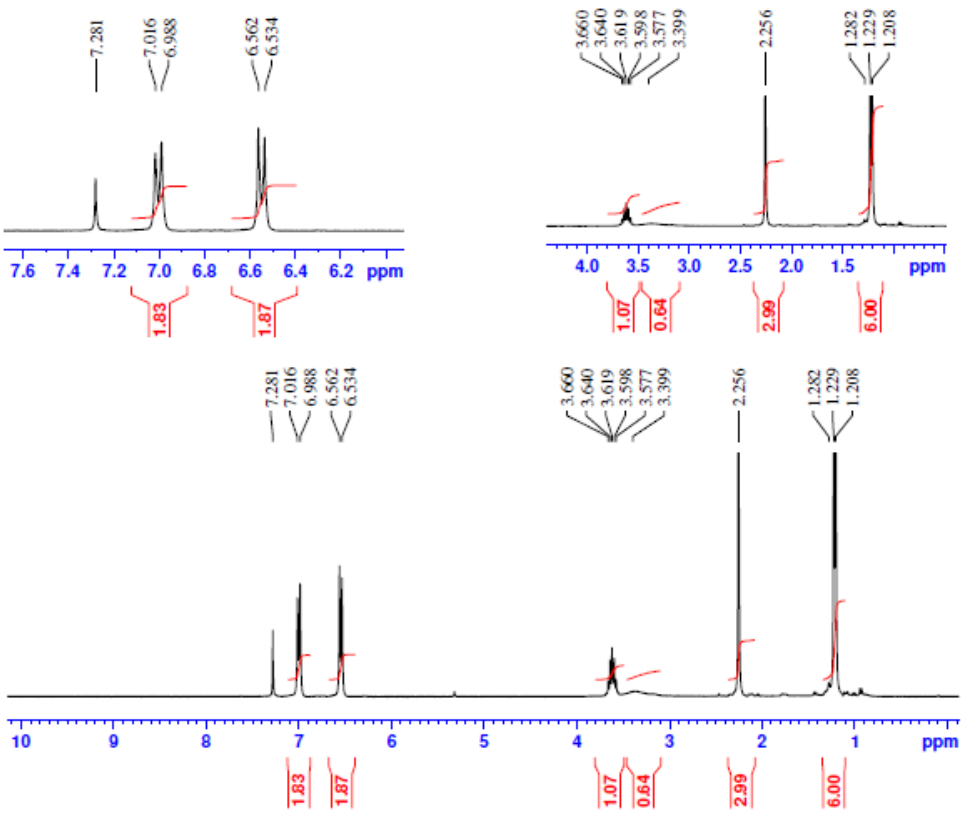

7.260
7.099
7.082
7.079
7.062
7.059
7.042
6.344
6.340
6.339
6.334
6.332
6.324
6.320
6.318
6.314
6.312
6.286
6.280
6.274
6.256
6.250
6.245
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 ppm
1.00
2.96


7.260
7.099
7.082
7.079
7.067
7.062
7.059
7.042
6.368
6.366
6.362
6.360
6.344
6.340
6.339
6.334
6.332
6.326
6.324
6.320
6.318
6.314
6.312
6.286
6.280
6.274
6.256
6.250
6.245
3.618
3.602
3.587
3.571
3.555
1.218
1.202
9 8 7 6 5 4 3 2 1 ppm
1.00
2.96
1.77
6.08

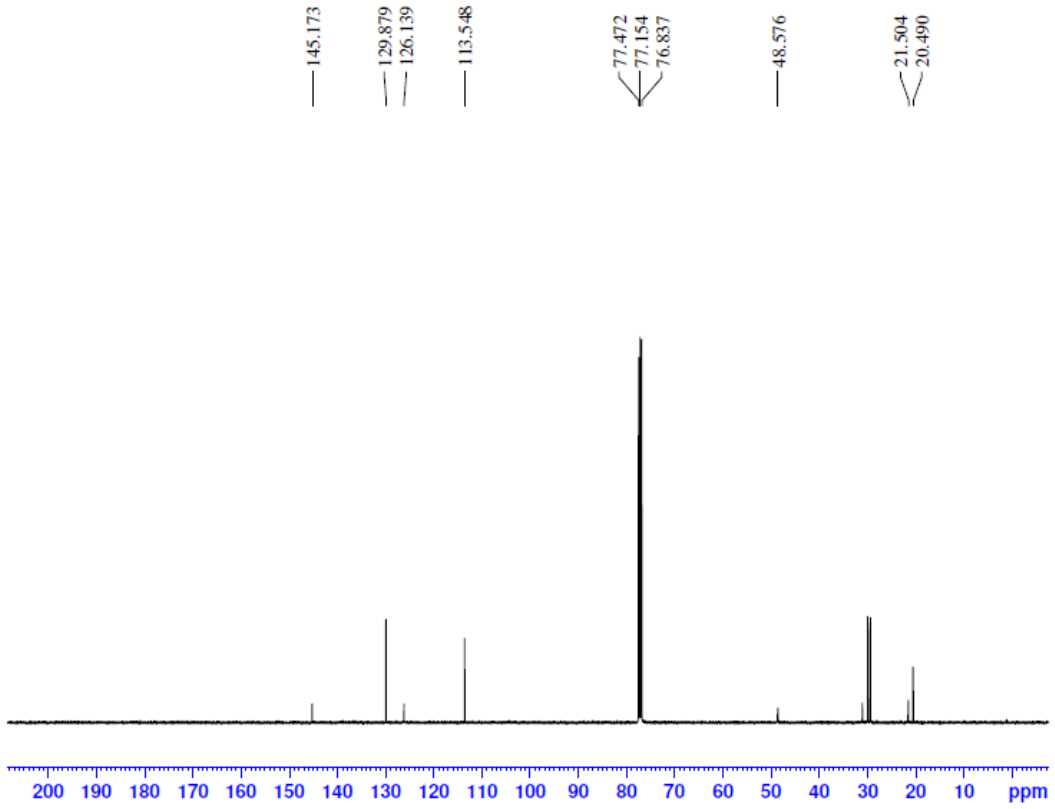
^{13}C NMR



4-methyl-*N*-(propan-2-yl)aniline **(3i, 5i)**
^{1}H NMR

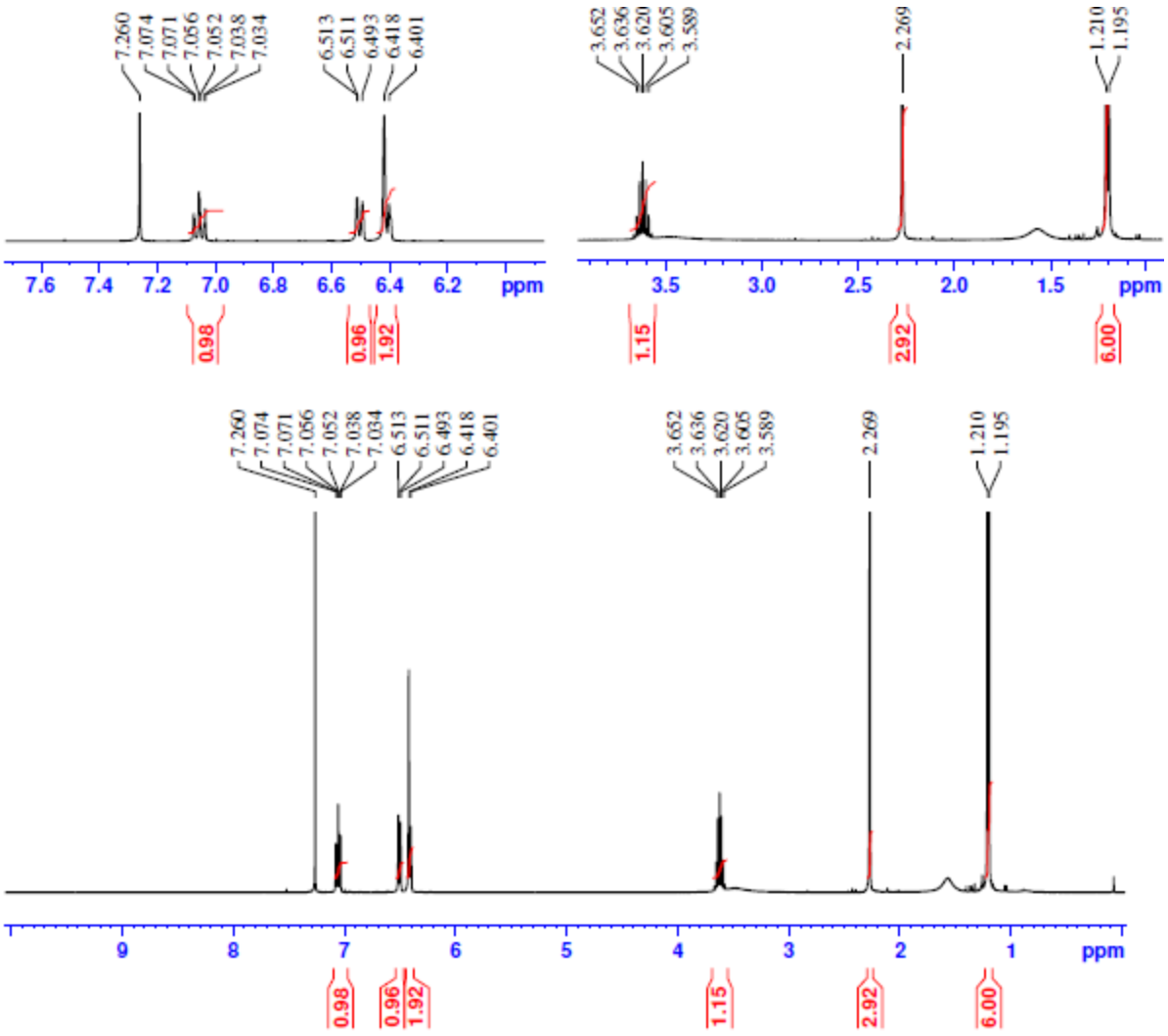

7.281
7.016
6.988
6.562
6.534
3.660
3.640
3.619
3.598
3.577
3.399
2.256
1.282
1.229
1.208
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm
4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.83
1.87
1.07
0.64
2.99
6.00
10 9 8 7 6 5 4 3 2 1 ppm

^{13}C NMR

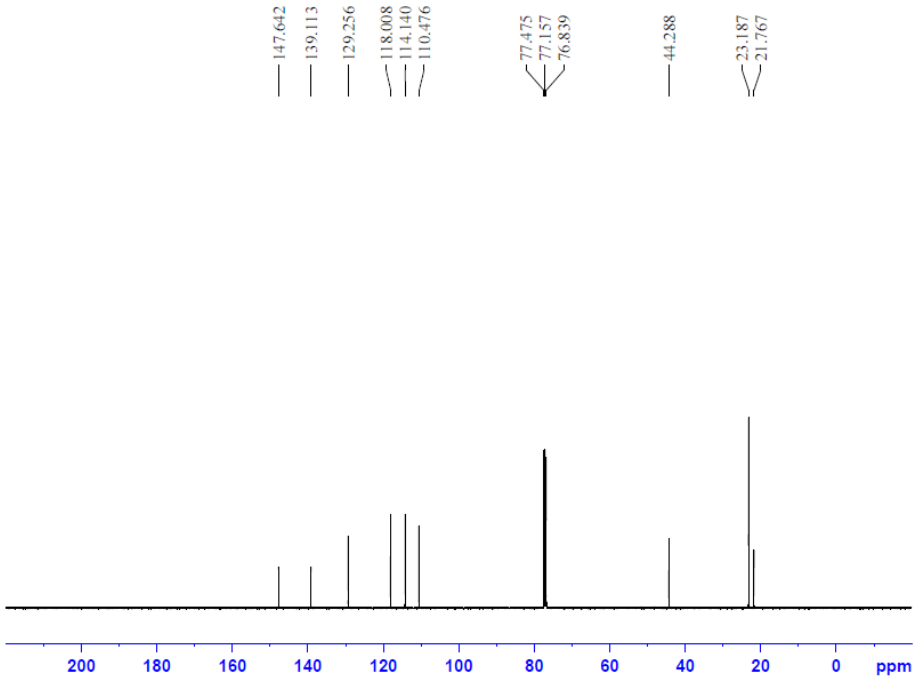


3-methyl-*N*-(propan-2-yl)aniline (**3j, 5j**)

^{1}H NMR


7.260
7.074
7.071
7.056
7.052
7.038
7.034
6.513
6.511
6.493
6.418
6.401
3.652
3.636
3.620
3.605
3.589
2.269
1.210
1.195
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm
3.5 3.0 2.5 2.0 1.5 ppm
0.98
0.96
1.92
1.15
2.92
6.00
9 8 7 6 5 4 3 2 1 ppm

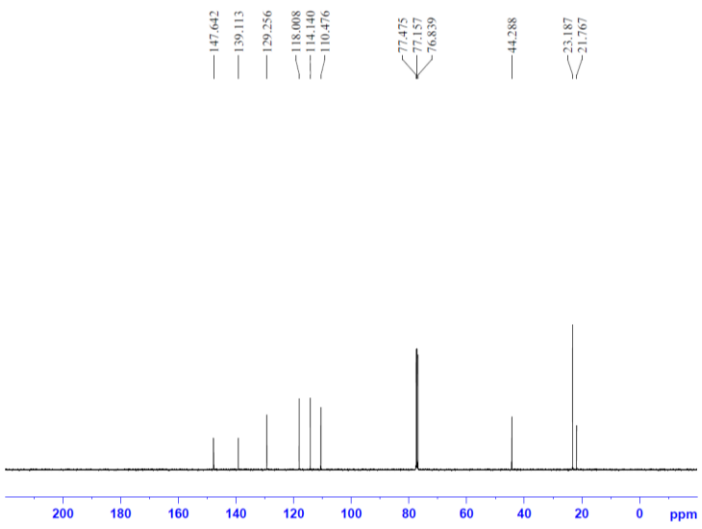
^{13}C NMR



2-methyl-*N*-(propan-2-yl)aniline (**3k, 5k**)

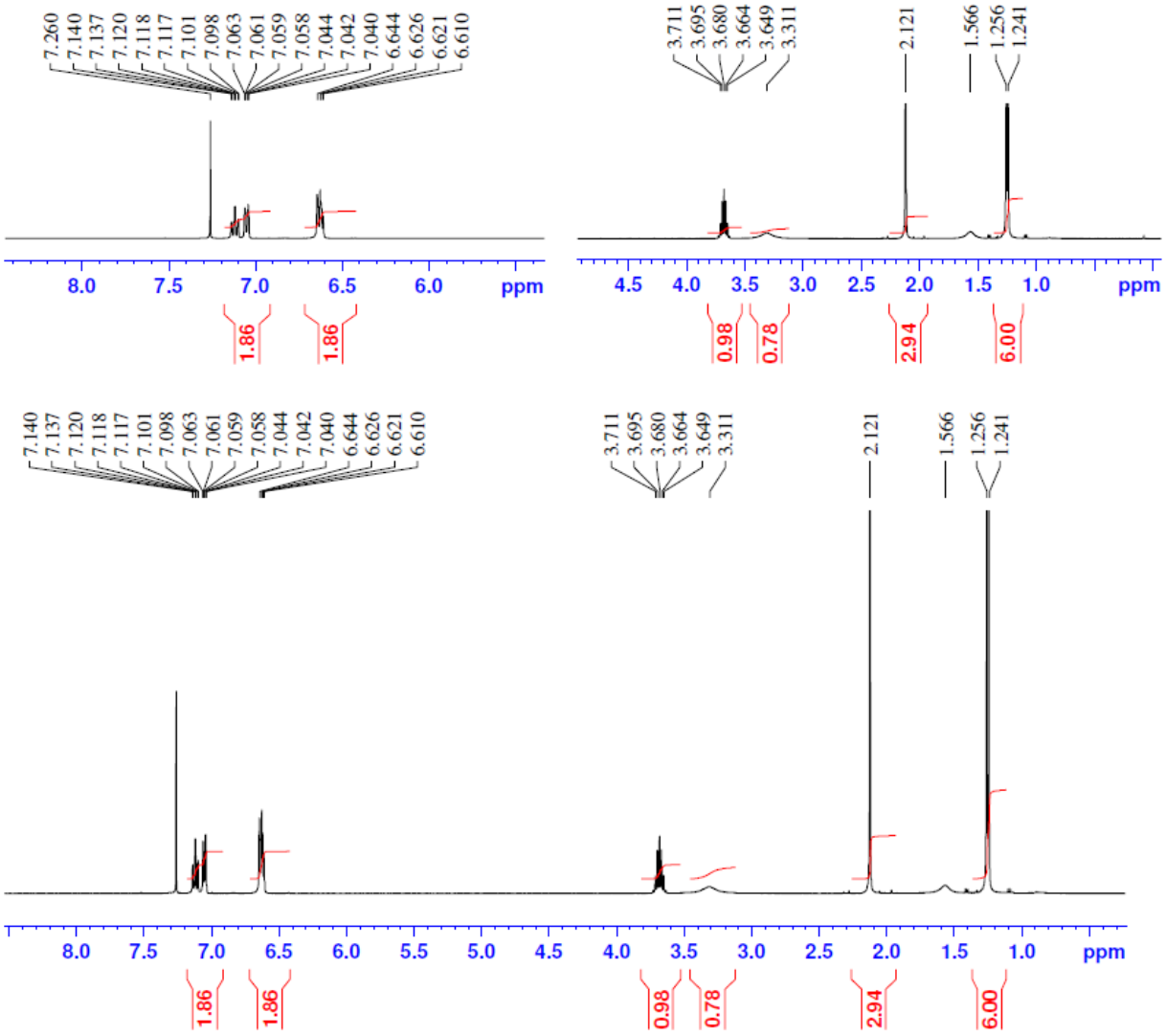
^{1}H NMR

^{13}C NMR

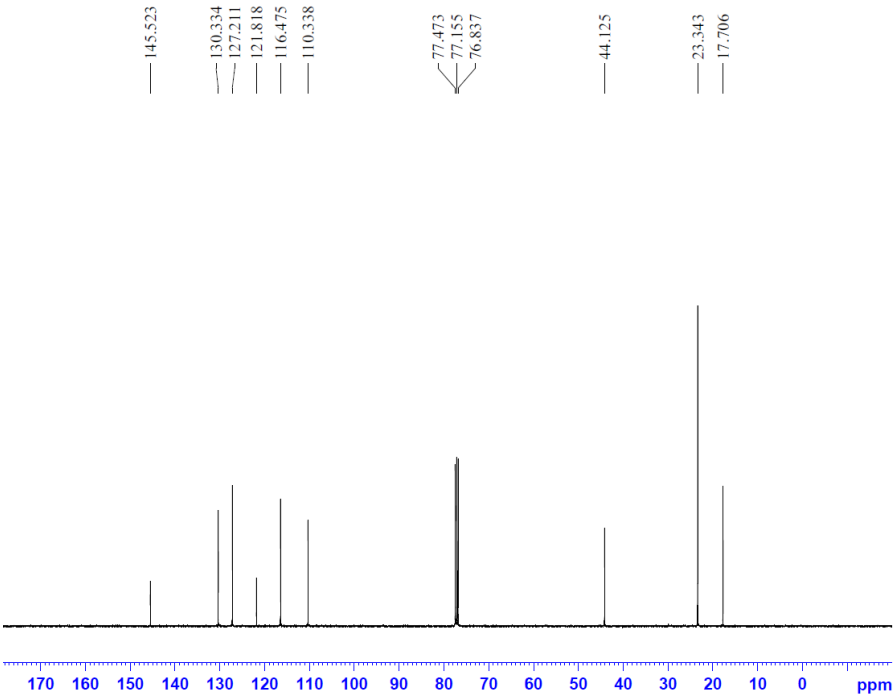


2-methyl-*N*-(propan-2-yl)aniline (**3k, 5k**)

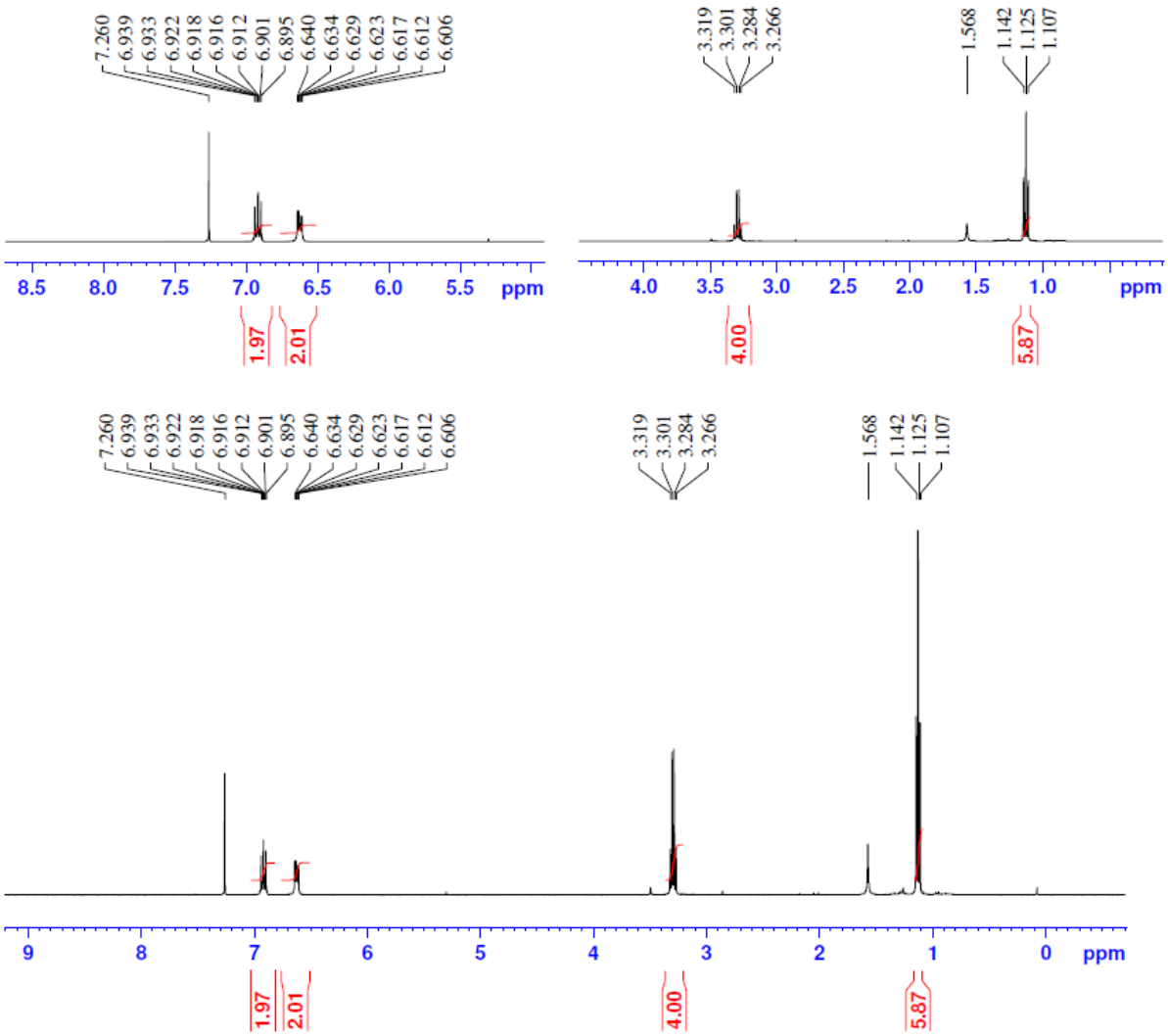
^{1}H NMR


7.260
7.140
7.137
7.120
7.118
7.117
7.101
7.098
7.063
7.061
7.059
7.058
7.044
7.042
7.040
6.644
6.626
6.621
6.610
3.711
3.695
3.680
3.664
3.649
3.311
2.121
1.566
1.256
1.241
8.0
7.5
7.0
6.5
6.0
ppm
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.86
1.86
0.98
0.78
2.94
6.00

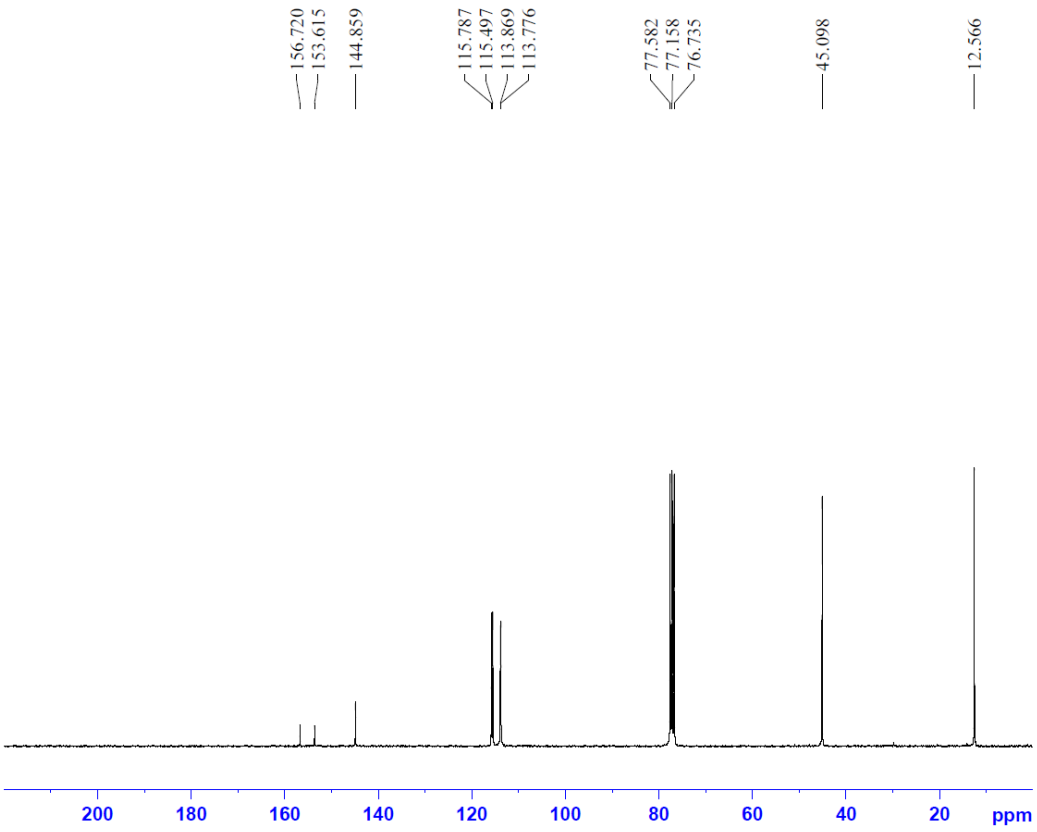
^{13}C NMR



N,*N*-diethyl-4-fluoroaniline (**3l, 5l**)
^{1}H NMR

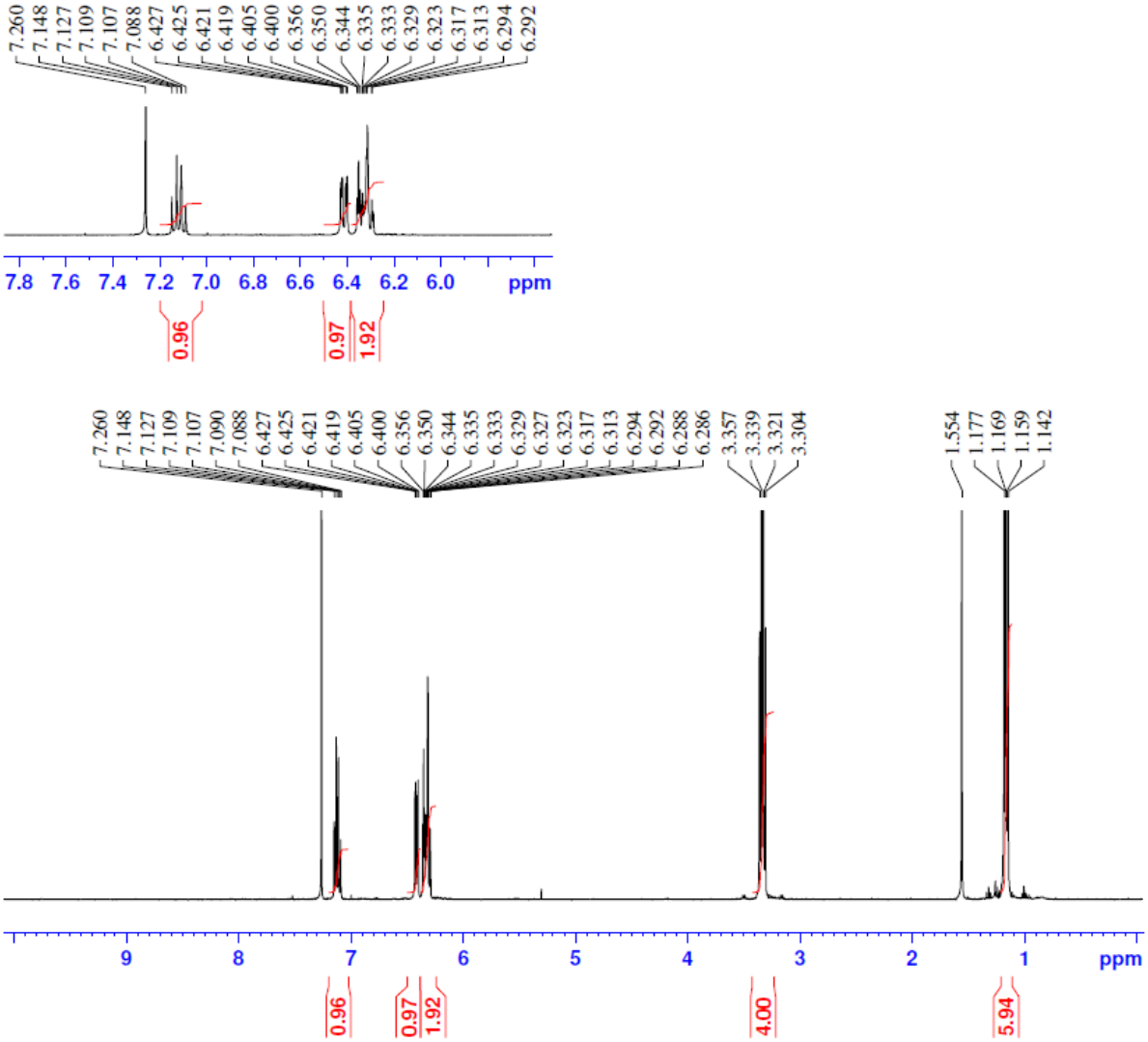

7.260
6.939
6.933
6.922
6.918
6.916
6.912
6.901
6.895
6.640
6.634
6.629
6.623
6.617
6.612
6.606
3.319
3.301
3.284
3.266
1.568
1.142
1.125
1.107
8.5
8.0
7.5
7.0
6.5
6.0
5.5
ppm
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.97
2.01
4.00
5.87
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

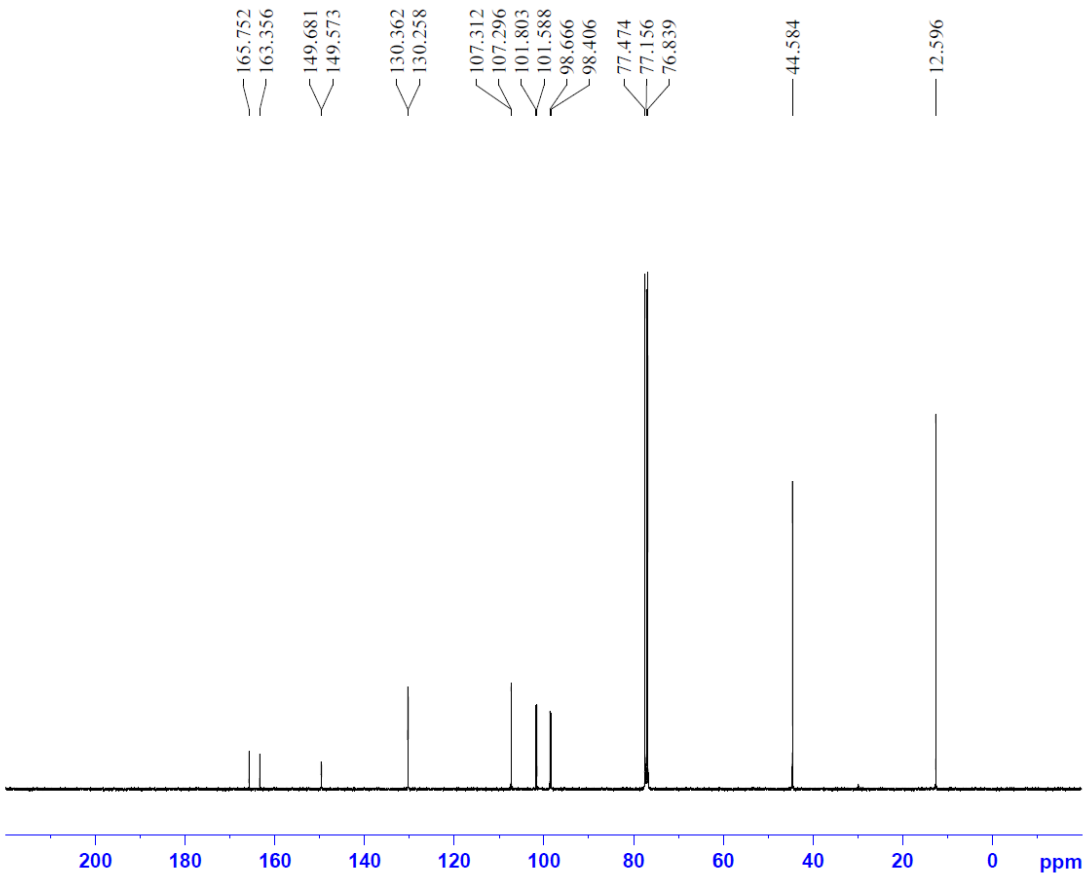


N,*N*-diethyl-3-fluoroaniline (**3m, 5m**)

^{1}H NMR

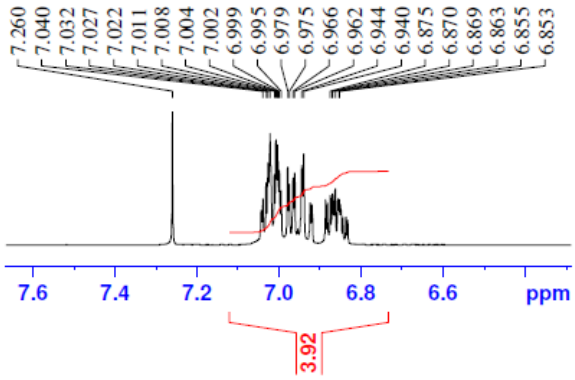

7.260
7.148
7.127
7.109
7.107
7.088
6.427
6.425
6.421
6.419
6.405
6.400
6.356
6.350
6.344
6.335
6.333
6.329
6.323
6.317
6.313
6.294
6.292
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 ppm
0.96
0.97
1.92
7.260
7.148
7.127
7.109
7.107
7.090
7.088
6.427
6.425
6.421
6.419
6.405
6.400
6.356
6.350
6.344
6.335
6.333
6.329
6.327
6.323
6.317
6.313
6.294
6.292
6.288
6.286
3.357
3.339
3.321
3.304
1.554
1.177
1.169
1.159
1.142
9 8 7 6 5 4 3 2 1 ppm
0.96
0.97
1.92
4.00
5.94

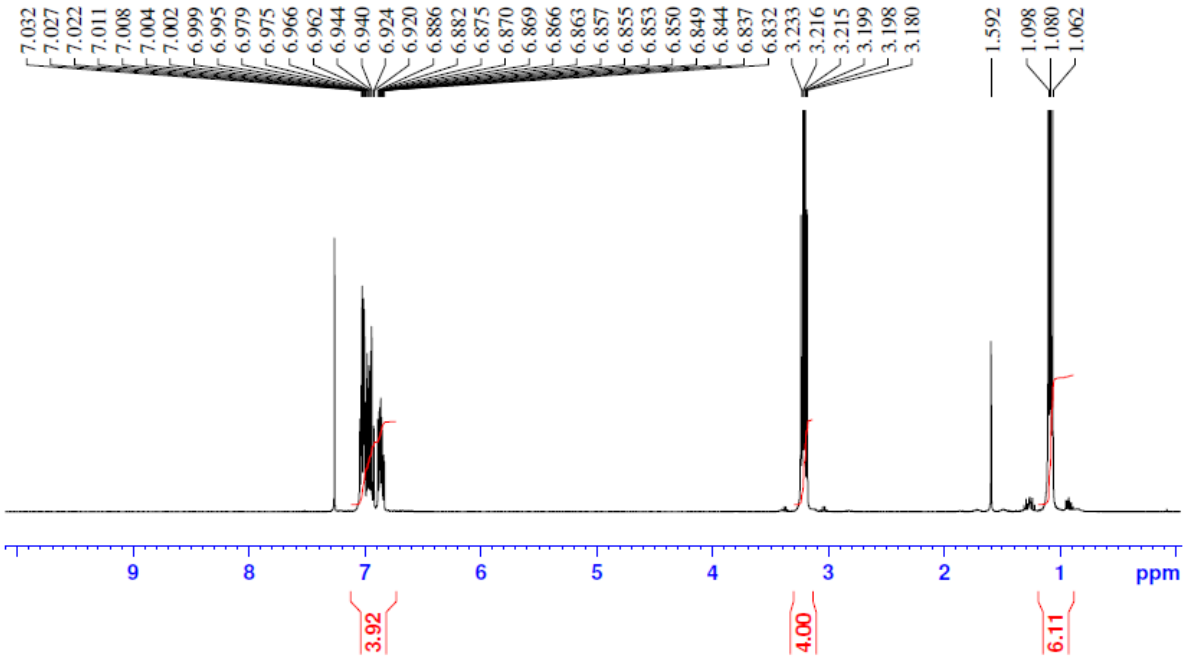
^{13}C NMR



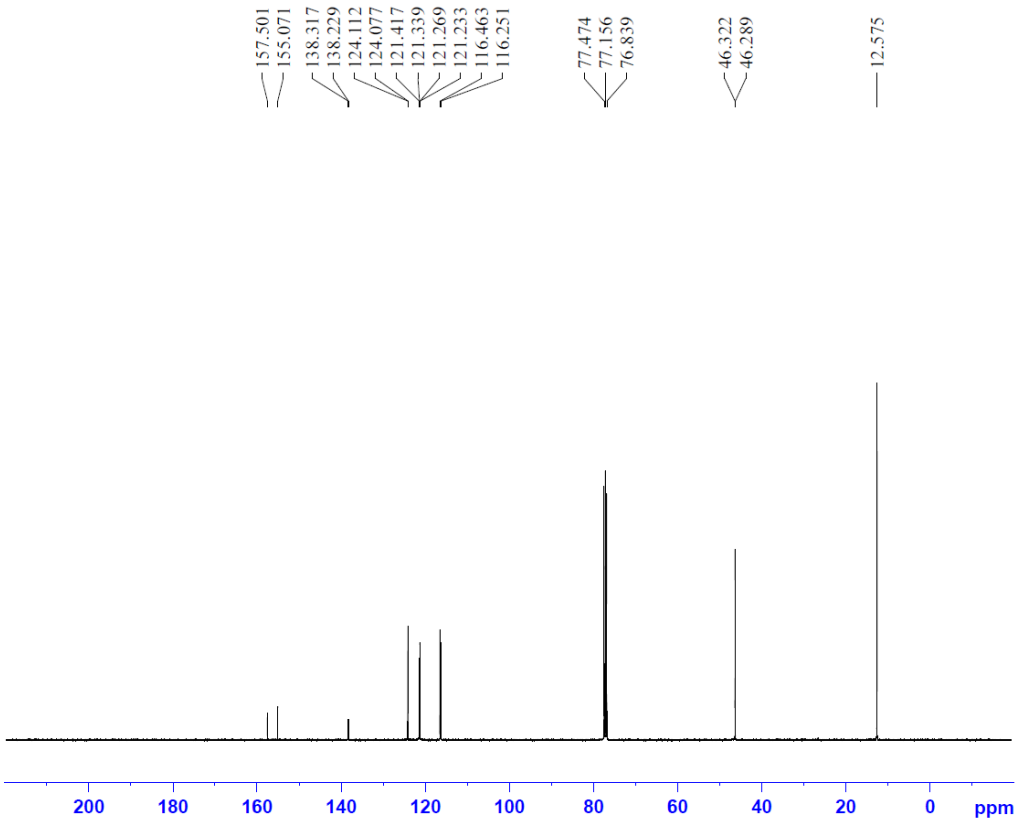
N,*N*-diethyl-2-fluoroaniline (**3n, 5n**)

^{1}H NMR


7.260
7.040
7.032
7.027
7.022
7.011
7.008
7.004
7.002
6.999
6.995
6.979
6.975
6.966
6.962
6.944
6.940
6.875
6.870
6.869
6.863
6.855
6.853
7.6
7.4
7.2
7.0
6.8
6.6
ppm
3.92

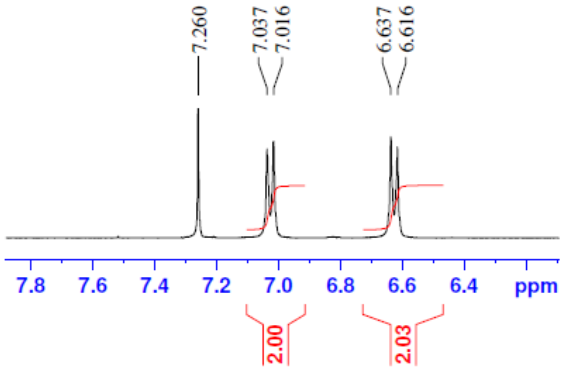

7.032
7.027
7.022
7.011
7.008
7.004
7.002
6.999
6.995
6.979
6.975
6.966
6.962
6.944
6.940
6.924
6.920
6.886
6.882
6.875
6.870
6.869
6.866
6.863
6.857
6.855
6.853
6.850
6.849
6.844
6.837
6.832
3.233
3.216
3.215
3.199
3.198
3.180
1.592
1.098
1.080
1.062
9
8
7
6
5
4
3
2
1
ppm
3.92
4.00
6.11

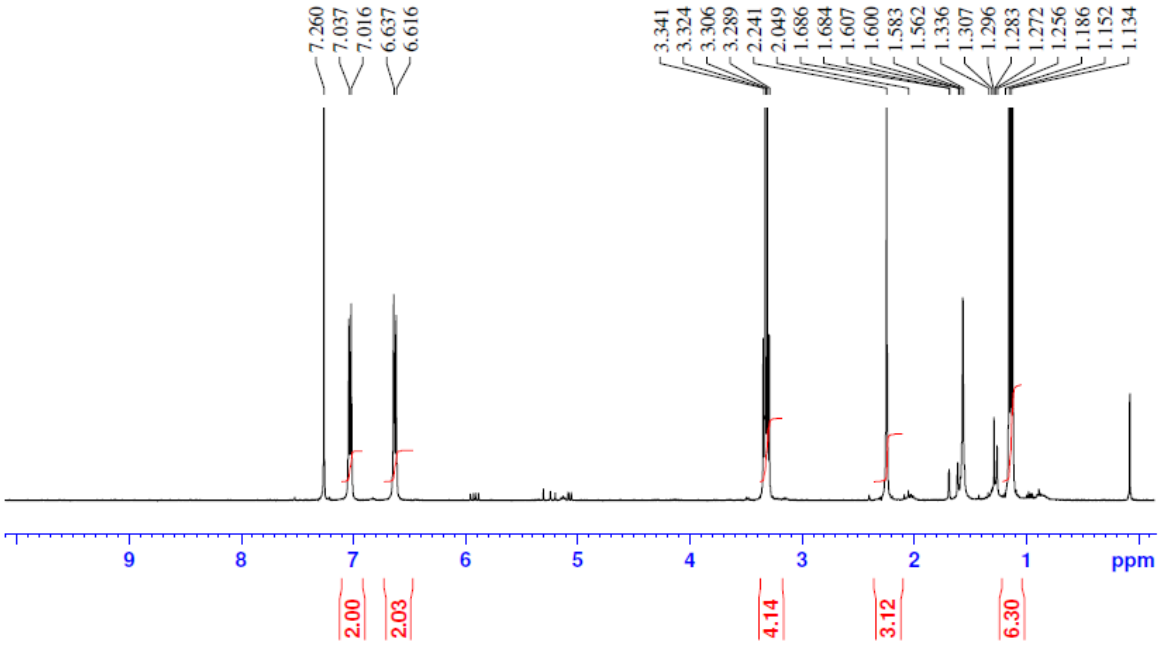
^{13}C NMR



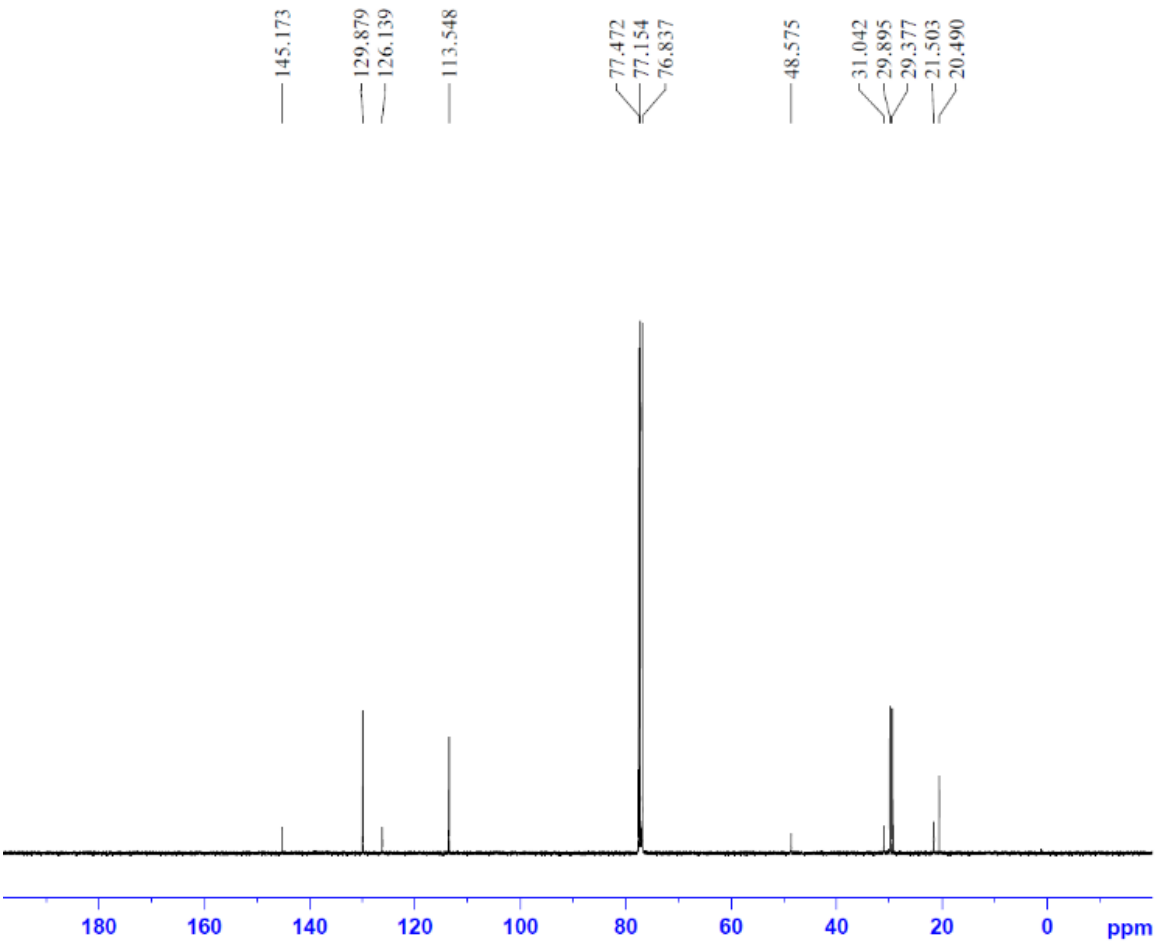
N,*N*-diethyl-4-methylaniline (**3o, 5o**)

^{1}H NMR


7.260
7.037
7.016
6.637
6.616
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
2.00
2.03

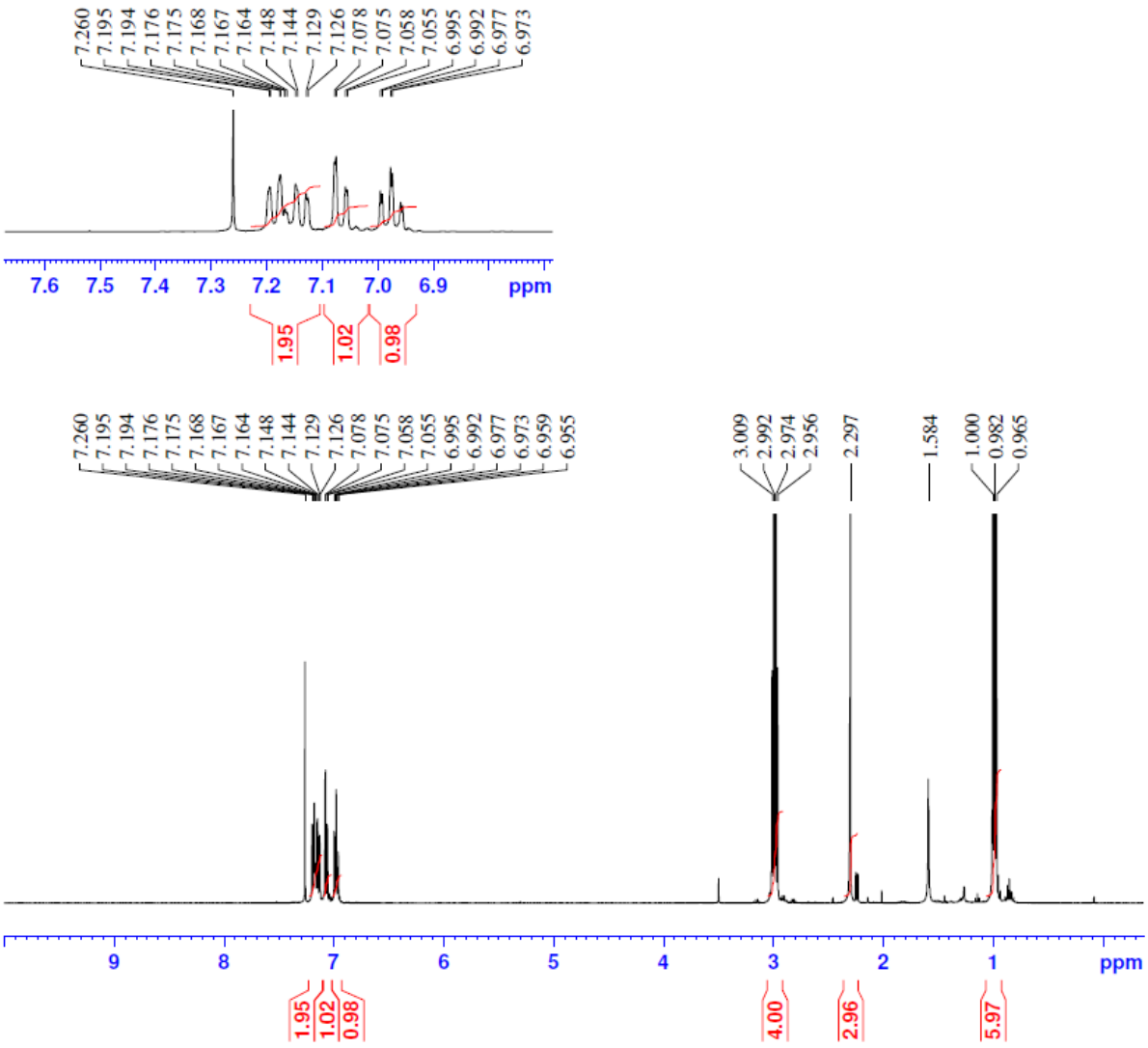

7.260
7.037
7.016
6.637
6.616
3.341
3.324
3.306
3.289
2.241
2.049
1.686
1.684
1.607
1.600
1.583
1.562
1.336
1.307
1.296
1.283
1.272
1.256
1.186
1.152
1.134
9
8
7
6
5
4
3
2
1
ppm
2.00
2.03
4.14
3.12
6.30

^{13}C NMR

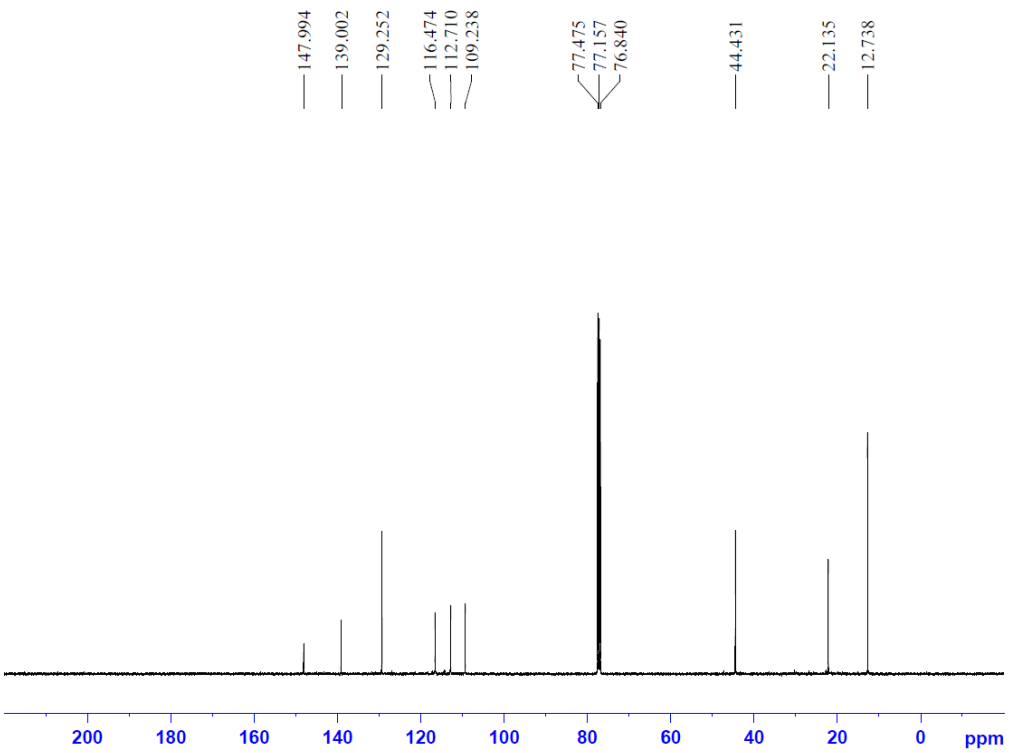


N,*N*-diethyl-3-methylaniline (**3p, 5p**)

^{1}H NMR

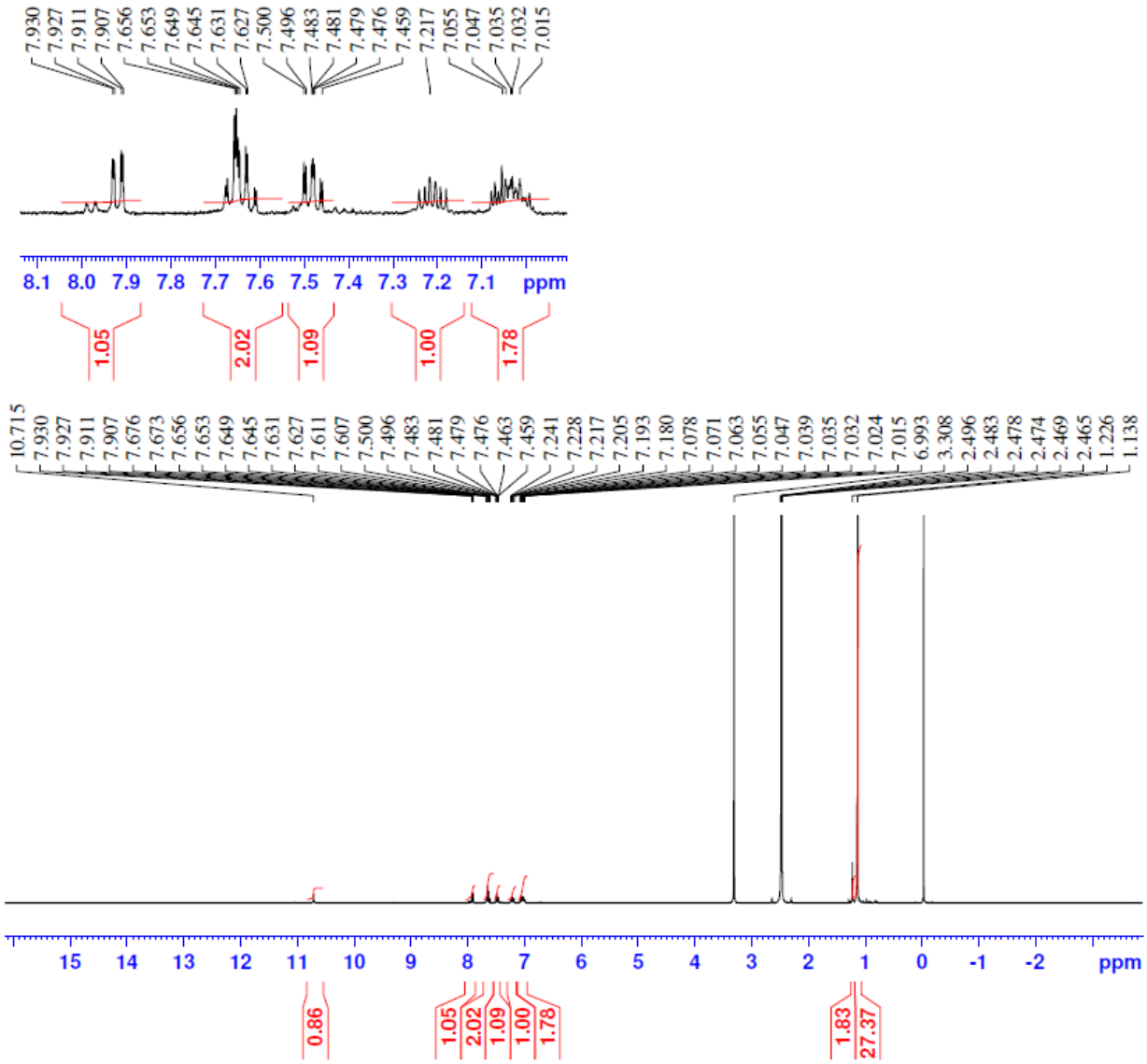

7.260
7.195
7.194
7.176
7.175
7.168
7.167
7.164
7.148
7.144
7.129
7.126
7.078
7.075
7.058
7.055
6.995
6.992
6.977
6.973
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm
1.95
1.02
0.98
6.959
6.955
3.009
2.992
2.974
2.956
2.297
1.584
1.000
0.982
0.965
9
8
7
6
5
4
3
2
1
4.00
2.96
5.97

^{13}C NMR

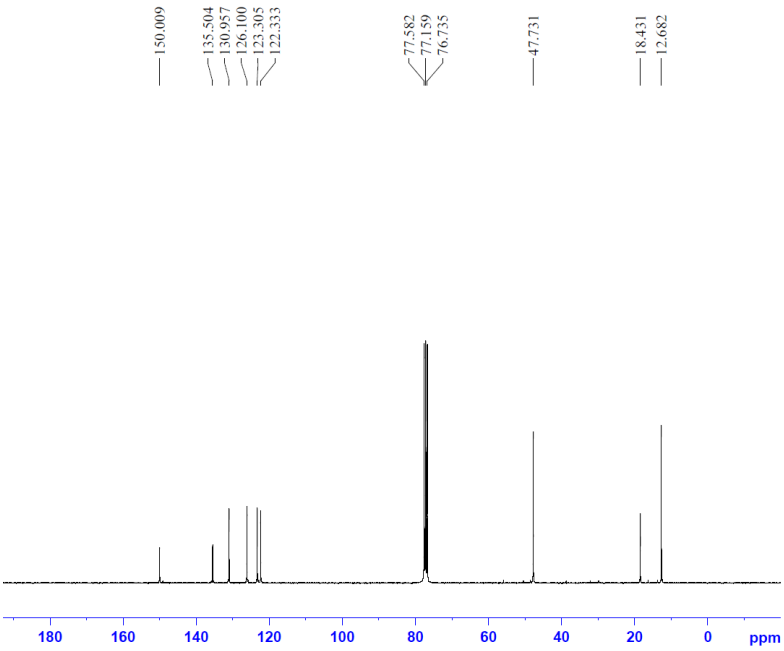


N,*N*-diethyl-2-methylaniline (**3q, 5q**)

^{1}H NMR

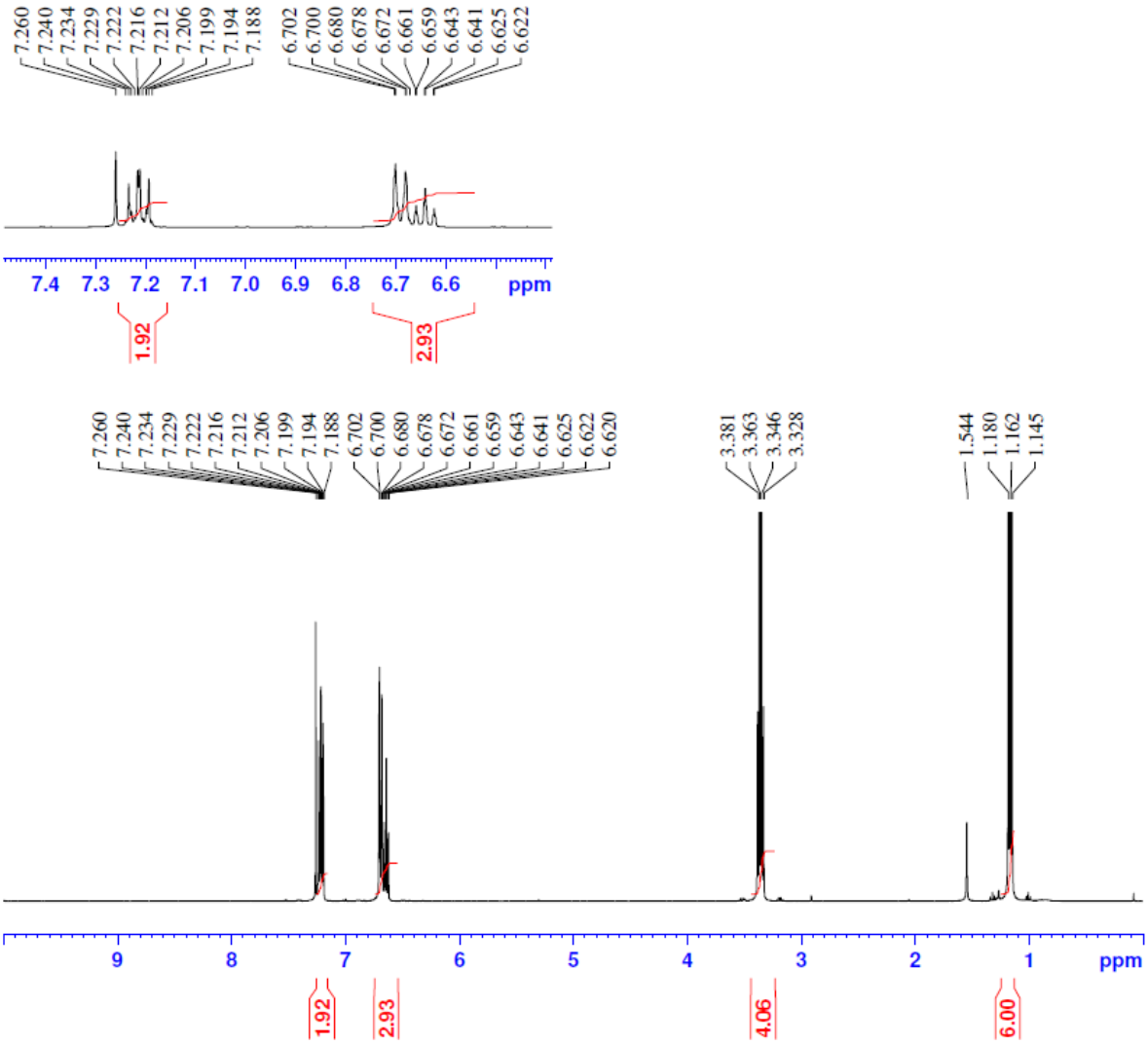

7.930
7.927
7.911
7.907
7.656
7.653
7.649
7.645
7.631
7.627
7.500
7.496
7.483
7.481
7.479
7.476
7.459
7.217
7.055
7.047
7.035
7.032
7.015
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
1.05
2.02
1.09
1.00
1.78
10.715
7.930
7.927
7.911
7.907
7.676
7.673
7.656
7.653
7.649
7.645
7.631
7.627
7.611
7.607
7.500
7.496
7.483
7.481
7.479
7.476
7.463
7.459
7.241
7.228
7.217
7.205
7.193
7.180
7.078
7.071
7.063
7.055
7.047
7.039
7.035
7.032
7.024
7.015
6.993
3.308
2.496
2.483
2.478
2.474
2.469
2.465
1.226
1.138
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
0.86
1.05
2.02
1.09
1.00
1.78
1.83
27.37

^{13}C NMR

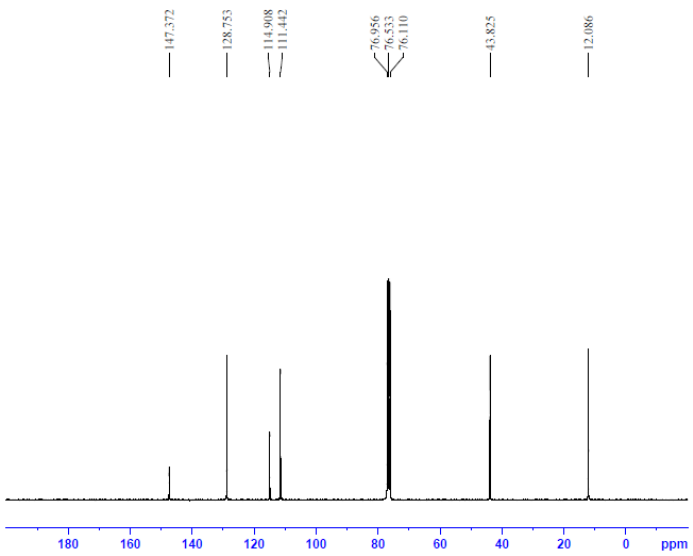


N,*N*-diethylaniline (**3r**, **5r**)

^{1}H NMR

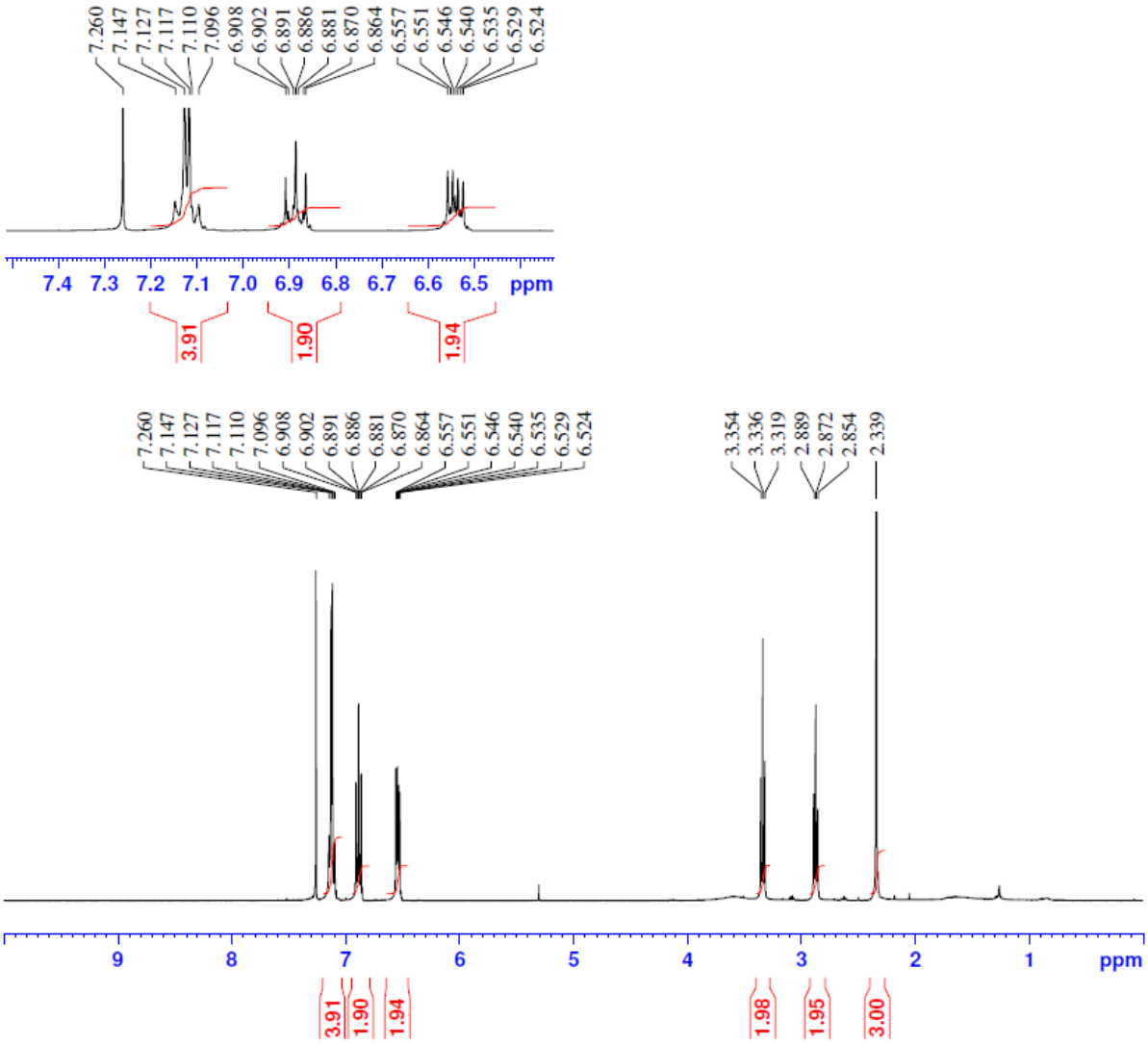

7.260
7.240
7.234
7.229
7.222
7.216
7.212
7.206
7.199
7.194
7.188
6.702
6.700
6.680
6.678
6.672
6.661
6.659
6.643
6.641
6.625
6.622
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 ppm
1.92
2.93
7.260
7.240
7.234
7.229
7.222
7.216
7.212
7.206
7.199
7.194
7.188
6.702
6.700
6.680
6.678
6.672
6.661
6.659
6.643
6.641
6.625
6.622
6.620
3.381
3.363
3.346
3.328
1.544
1.180
1.162
1.145
9 8 7 6 5 4 3 2 1 ppm
1.92
2.93
4.06
6.00

^{13}C NMR

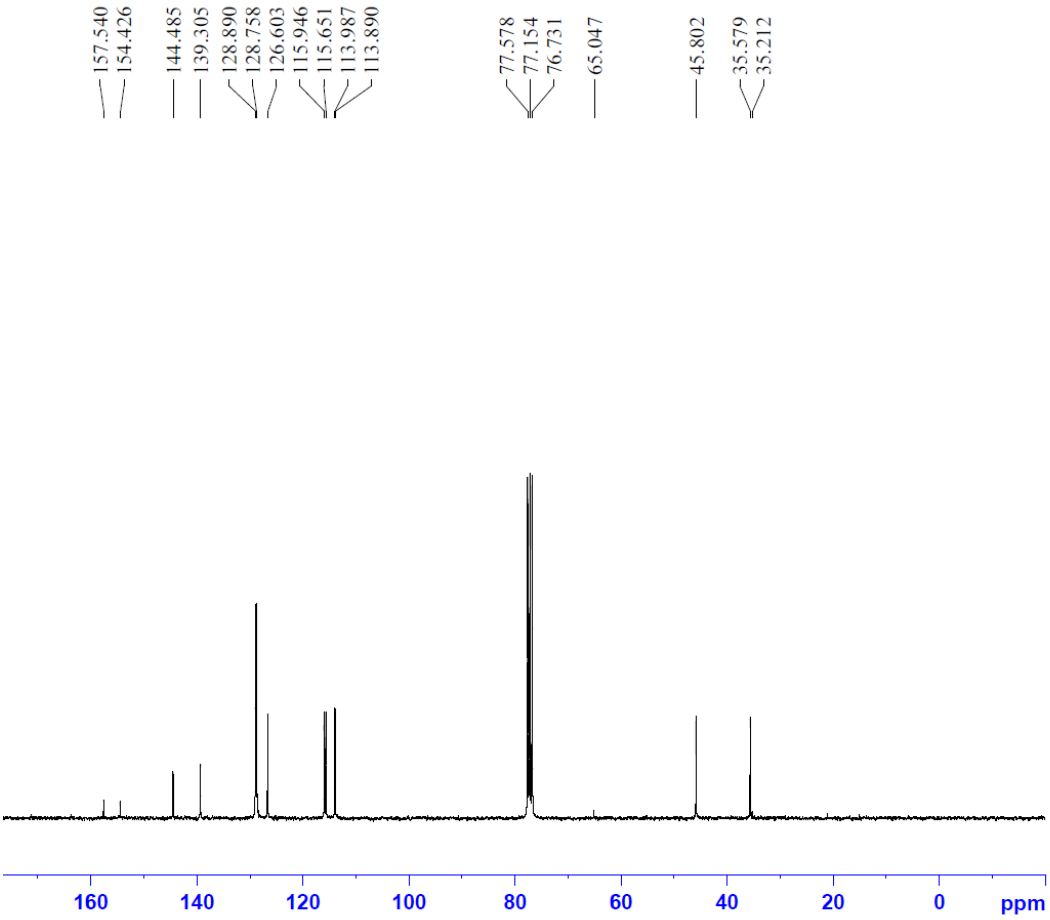


4-fluoro-*N*-[2-(4-methylphenyl)ethyl]aniline (**8a**)

^{1}H NMR

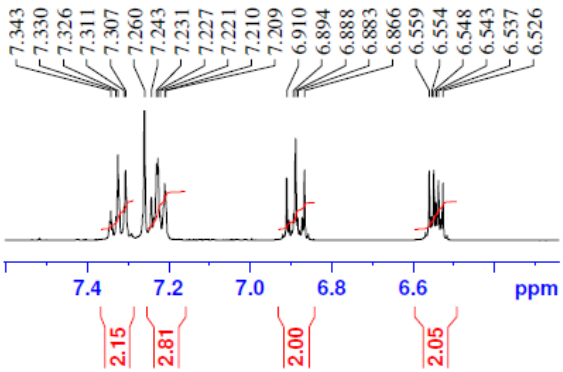

7.260
7.147
7.127
7.117
7.110
7.096
6.908
6.902
6.891
6.886
6.881
6.870
6.864
6.557
6.551
6.546
6.540
6.535
6.529
6.524
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm
3.91
1.90
1.94
3.354
3.336
3.319
2.889
2.872
2.854
2.339
9 8 7 6 5 4 3 2 1 ppm
3.91
1.90
1.94
1.98
1.95
3.00

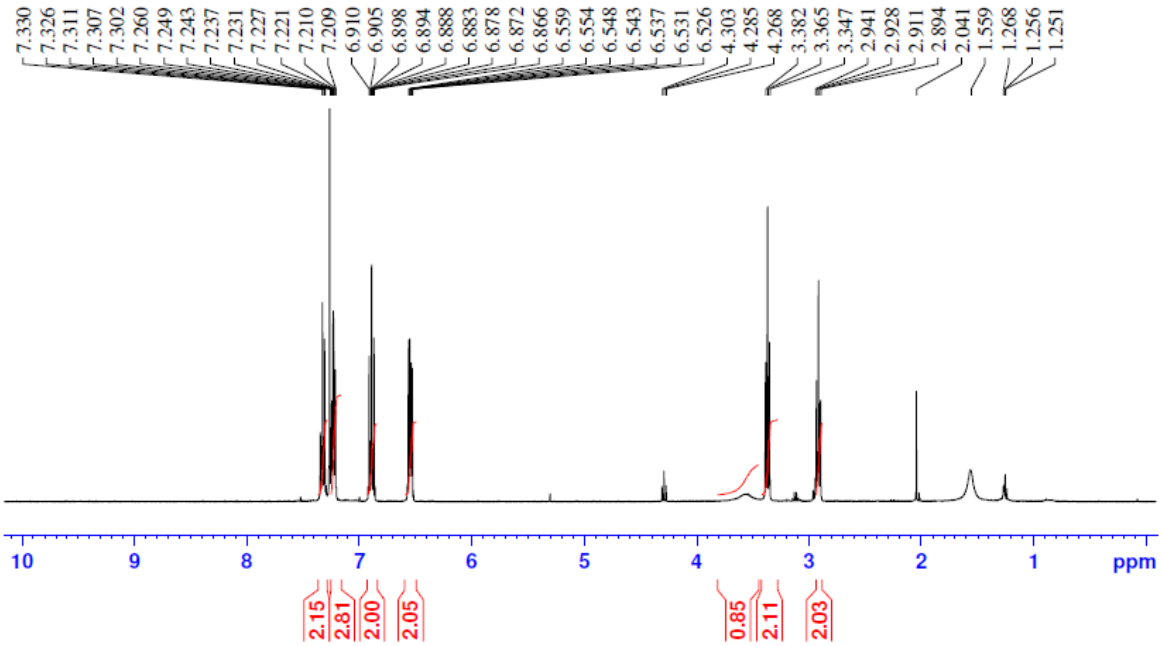
^{13}C NMR



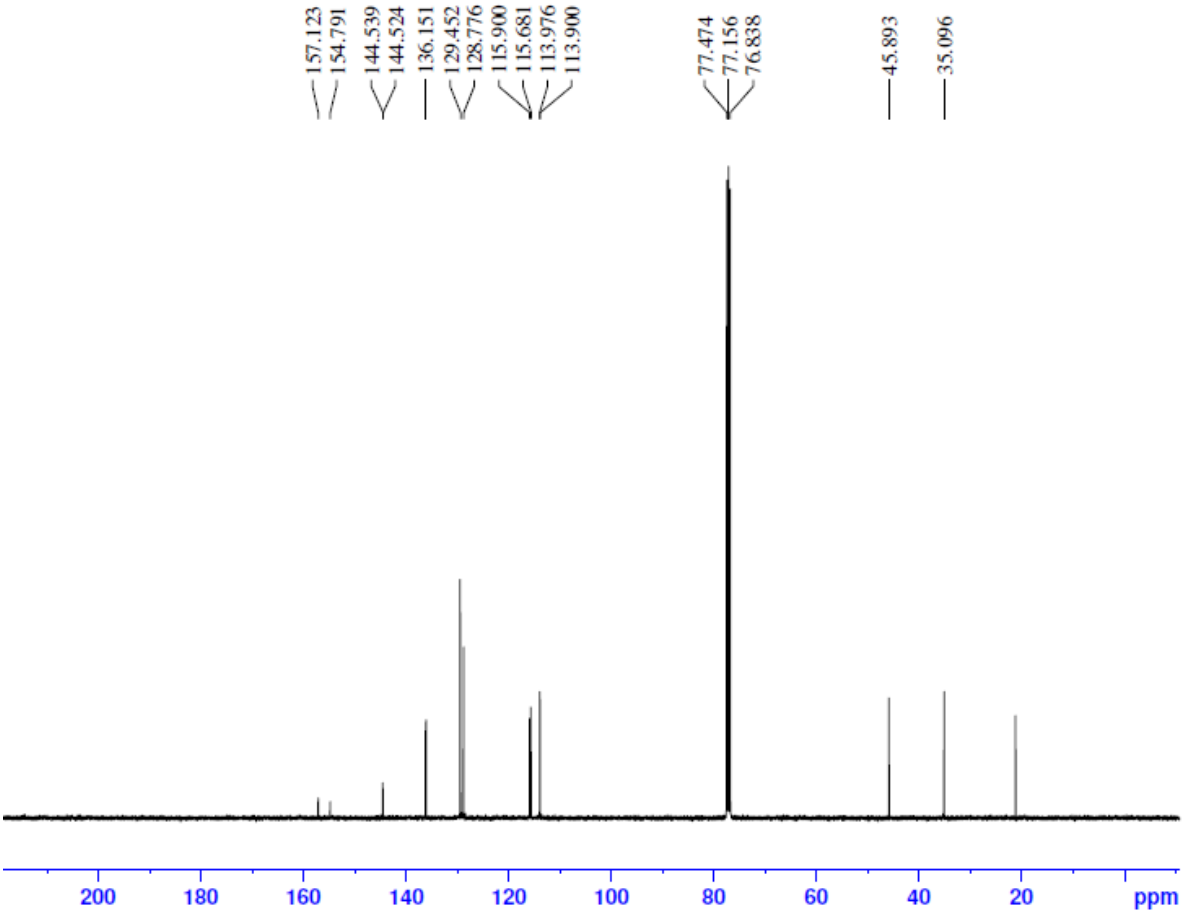
4-fluoro-*N*-(2-phenylethyl)aniline (**8b**)

^{1}H NMR


7.343
7.330
7.326
7.311
7.307
7.260
7.243
7.231
7.227
7.221
7.210
7.209
6.910
6.894
6.888
6.883
6.866
6.559
6.554
6.548
6.543
6.537
6.526
7.4
7.2
7.0
6.8
6.6
ppm
2.15
2.81
2.00
2.05

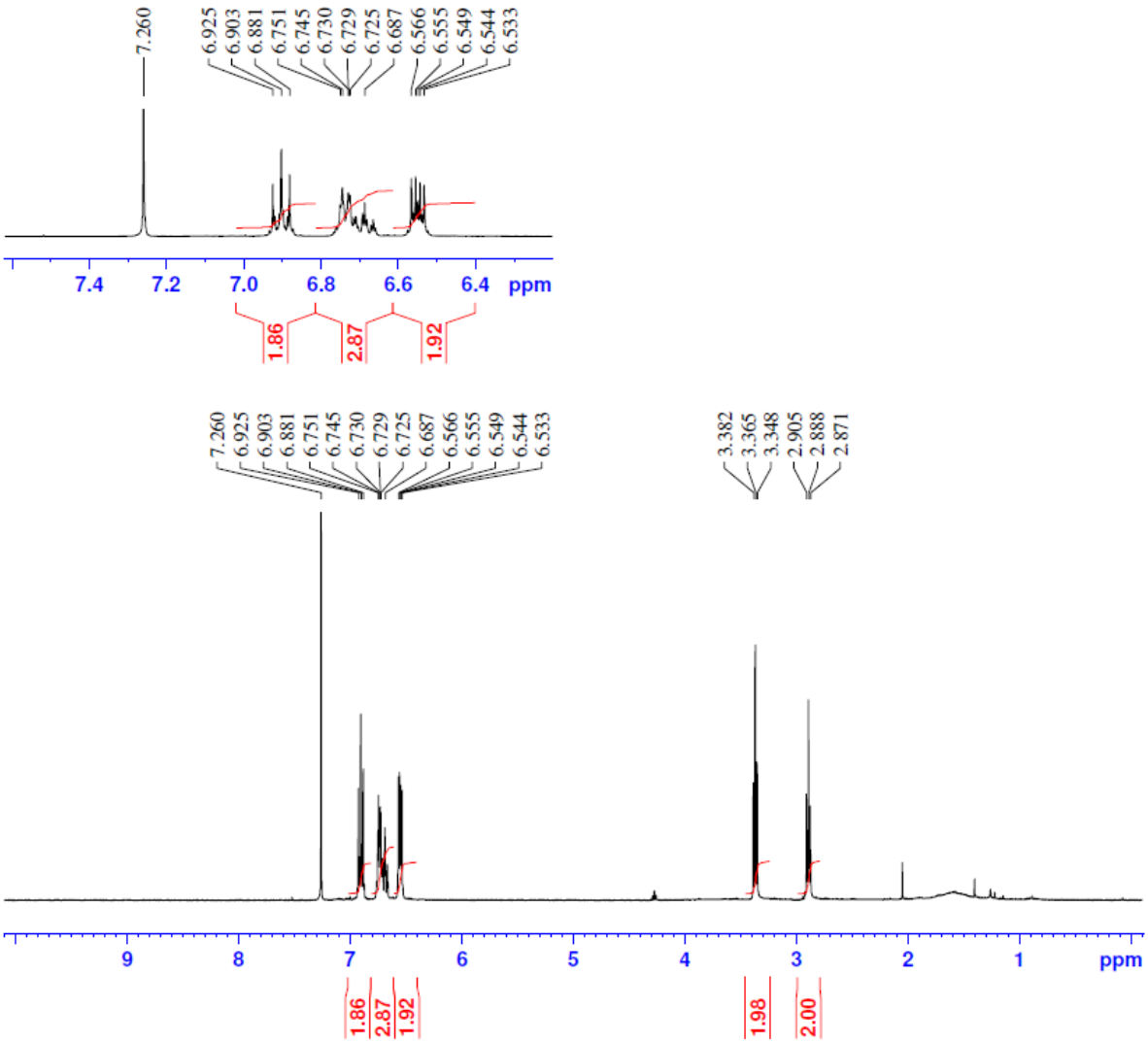

7.330
7.326
7.311
7.307
7.302
7.260
7.249
7.243
7.237
7.231
7.227
7.221
7.210
7.209
6.910
6.905
6.898
6.894
6.888
6.883
6.878
6.872
6.866
6.559
6.554
6.548
6.543
6.537
6.531
6.526
4.303
4.285
4.268
3.382
3.365
3.347
2.941
2.928
2.911
2.894
2.041
1.559
1.268
1.256
1.251
10
9
8
7
6
5
4
3
2
1
ppm
2.15
2.81
2.00
2.05
0.85
2.11
2.03

^{13}C NMR

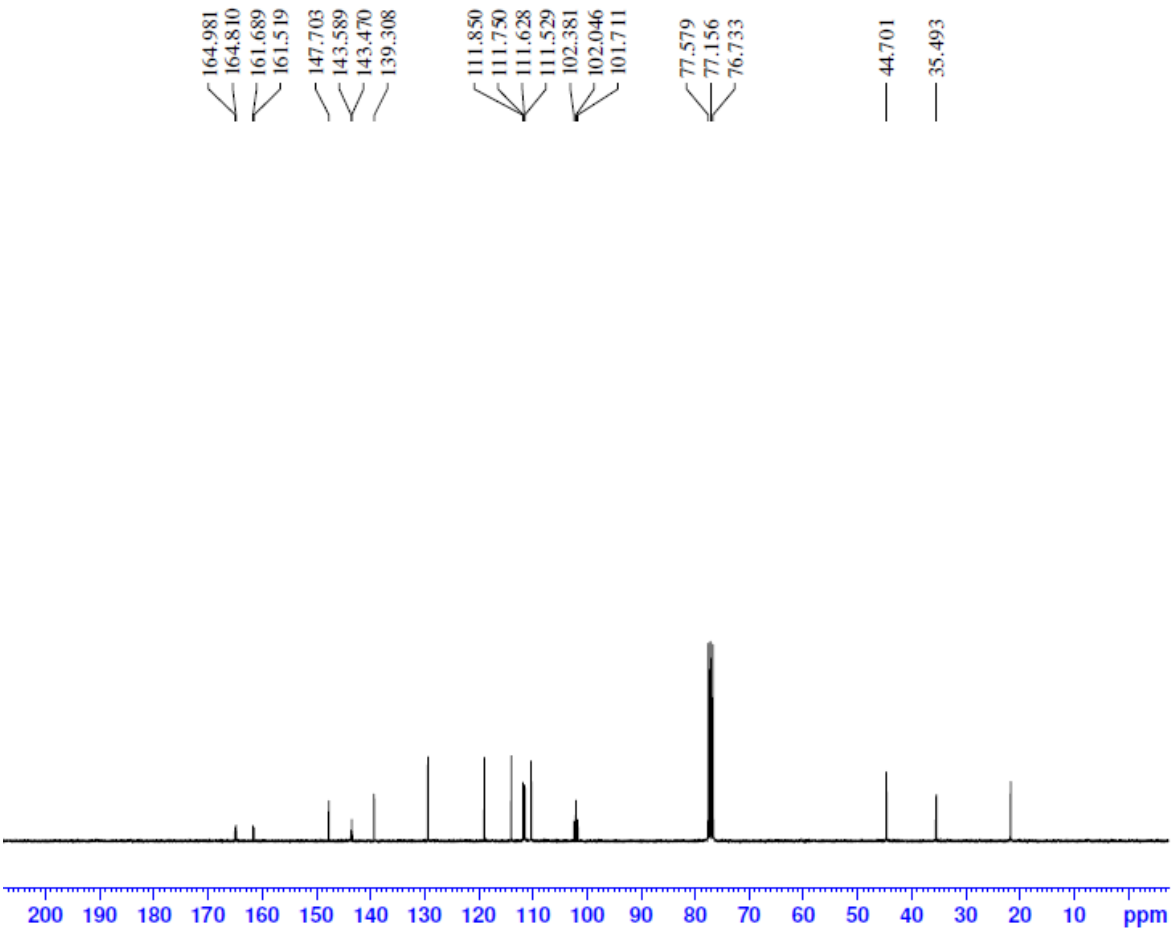


N-[2-(3,5-difluorophenyl)ethyl]-4-fluoroaniline (**8c**)

^{1}H NMR

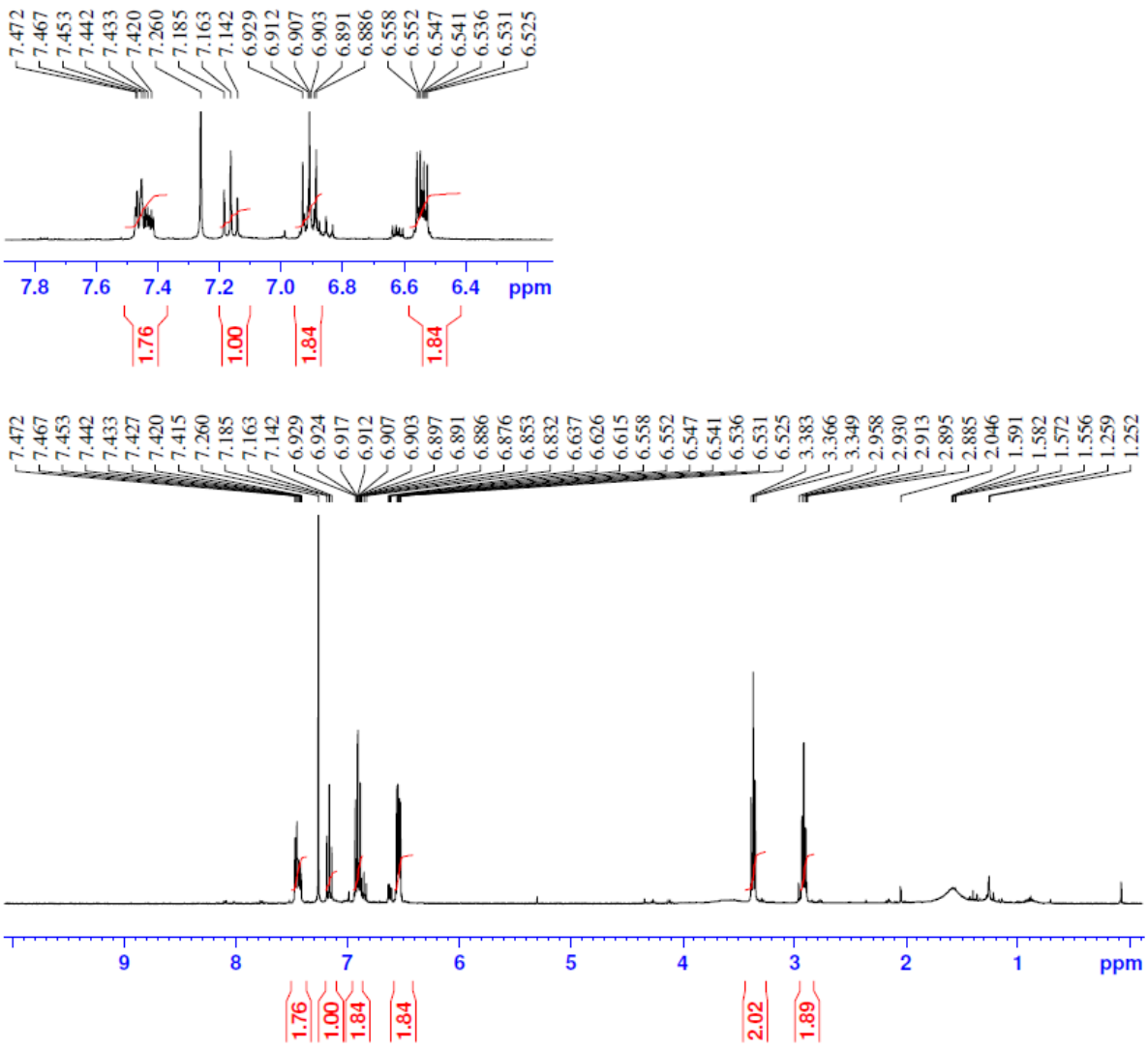

7.260
6.925
6.903
6.881
6.751
6.745
6.730
6.729
6.725
6.687
6.566
6.555
6.549
6.544
6.533
7.4
7.2
7.0
6.8
6.6
6.4
ppm
1.86
2.87
1.92
7.260
6.925
6.903
6.881
6.751
6.745
6.730
6.729
6.725
6.687
6.566
6.555
6.549
6.544
6.533
3.382
3.365
3.348
2.905
2.888
2.871
9
8
7
6
5
4
3
2
1
ppm
1.86
2.87
1.92
1.98
2.00

^{13}C NMR

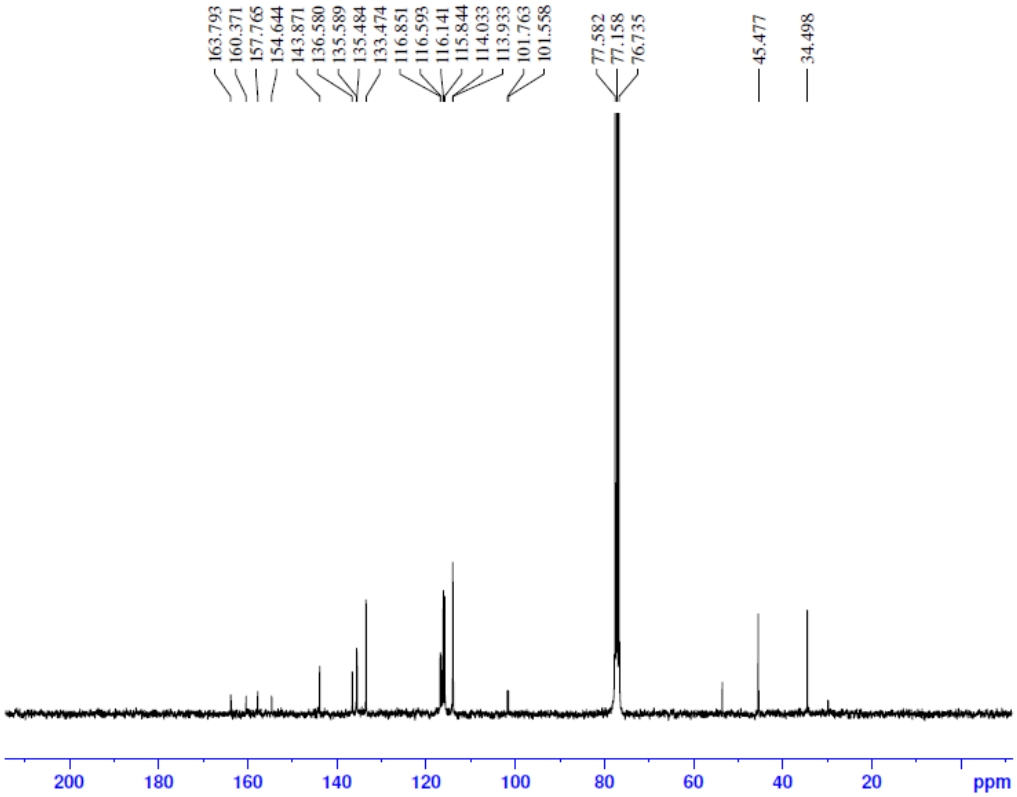


2-fluoro-5-[2-(4-fluoroanilino)ethyl]benzonitrile (**8d**)

^{1}H NMR

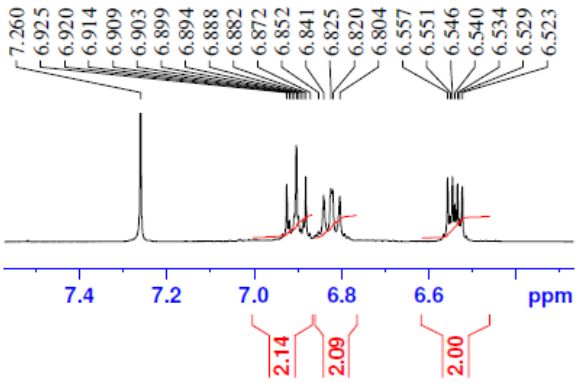

7.472
7.467
7.453
7.442
7.433
7.420
7.260
7.185
7.163
7.142
6.929
6.912
6.907
6.903
6.891
6.886
6.558
6.552
6.547
6.541
6.536
6.531
6.525
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
1.76
1.00
1.84
1.84
7.472
7.467
7.453
7.442
7.433
7.427
7.420
7.415
7.260
7.185
7.163
7.142
6.929
6.924
6.917
6.912
6.907
6.903
6.897
6.891
6.886
6.876
6.853
6.832
6.637
6.626
6.615
6.558
6.552
6.547
6.541
6.536
6.531
6.525
3.383
3.366
3.349
2.958
2.930
2.913
2.895
2.885
2.046
1.591
1.582
1.572
1.556
1.259
1.252
9
8
7
6
5
4
3
2
1
ppm
1.76
1.00
1.84
1.84
2.02
1.89

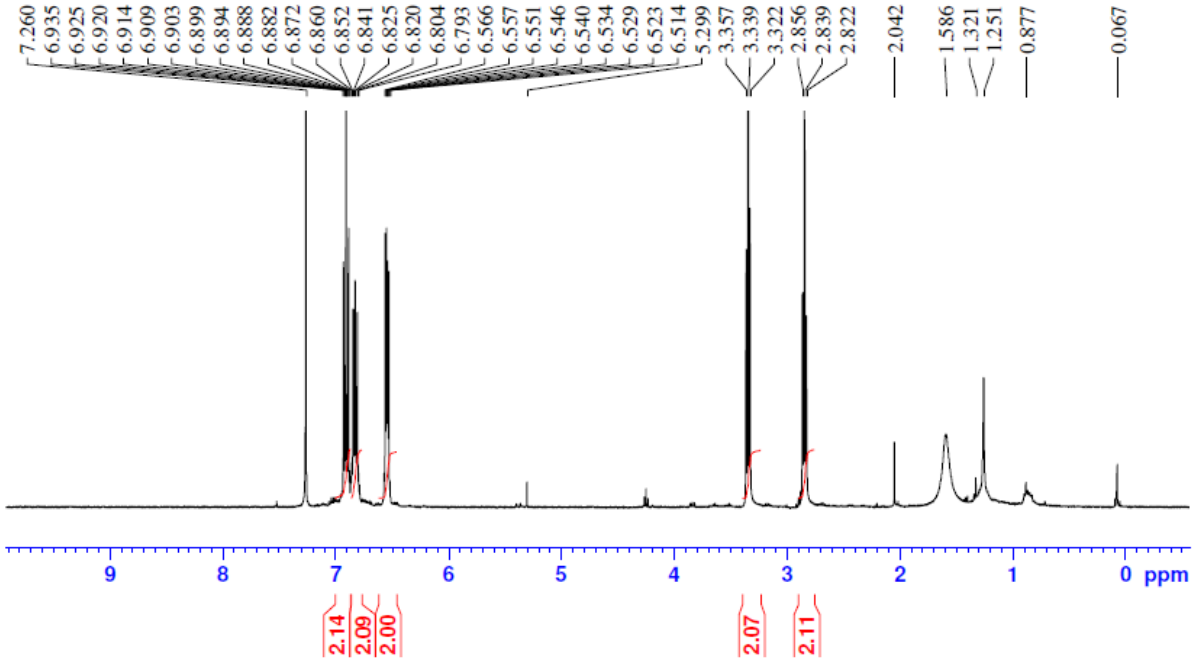
^{13}C NMR



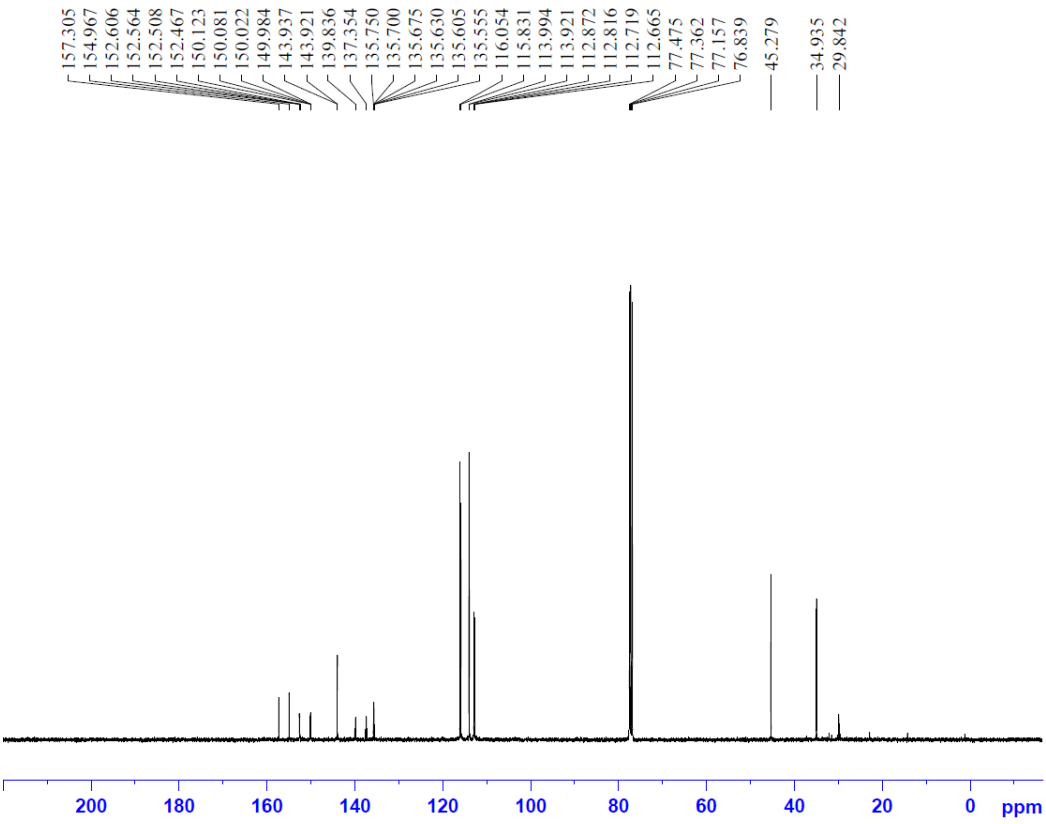
4-fluoro-*N*-[2-(3,4,5-trifluorophenyl)ethyl]aniline (**8e**)

^{1}H NMR


7.260
6.925
6.920
6.914
6.909
6.903
6.899
6.894
6.888
6.882
6.872
6.852
6.841
6.825
6.820
6.804
6.557
6.551
6.546
6.540
6.534
6.529
6.523
7.4
7.2
7.0
6.8
6.6
ppm
2.14
2.09
2.00

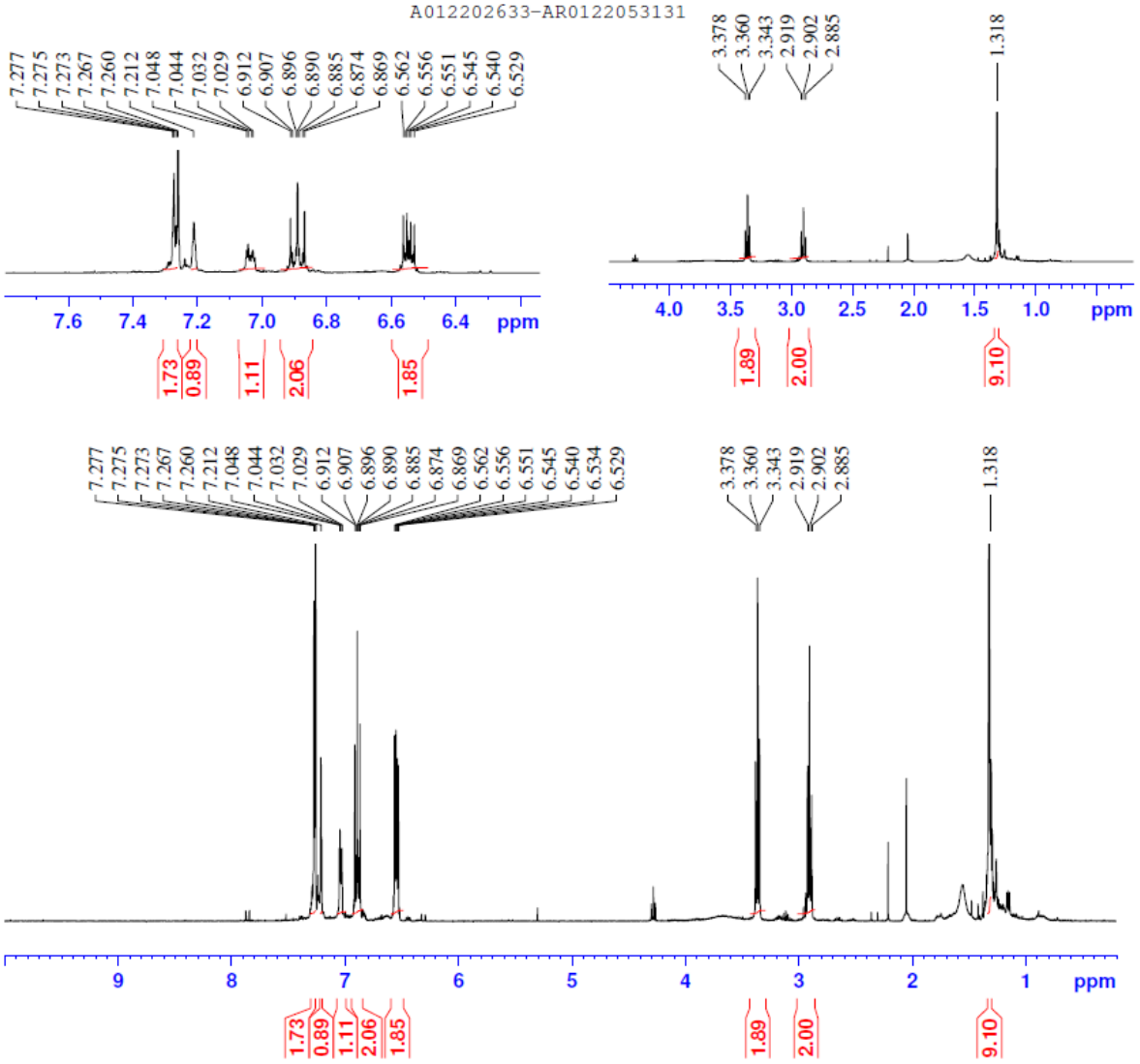

7.260
6.935
6.925
6.920
6.914
6.909
6.903
6.899
6.894
6.888
6.882
6.872
6.860
6.852
6.841
6.825
6.820
6.804
6.793
6.566
6.557
6.551
6.546
6.540
6.534
6.529
6.523
6.514
5.299
3.357
3.339
3.322
2.856
2.839
2.822
2.042
1.586
1.321
1.251
0.877
0.067
9
8
7
6
5
4
3
2
1
0 ppm
2.14
2.09
2.00
2.07
2.11

^{13}C NMR



N-[2-(4-*tert*-butylphenyl)ethyl]-4-fluoroaniline **(8f)**

^{1}H NMR


A012202633-AR0122053131
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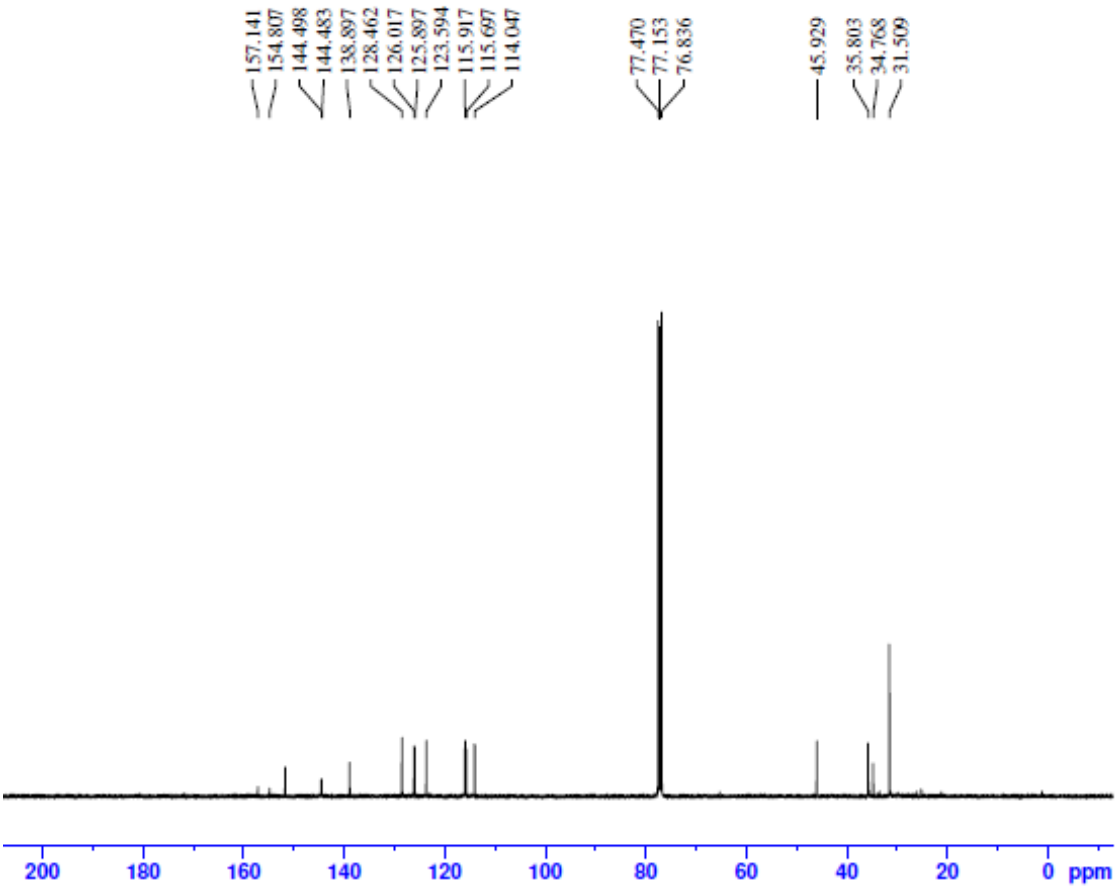
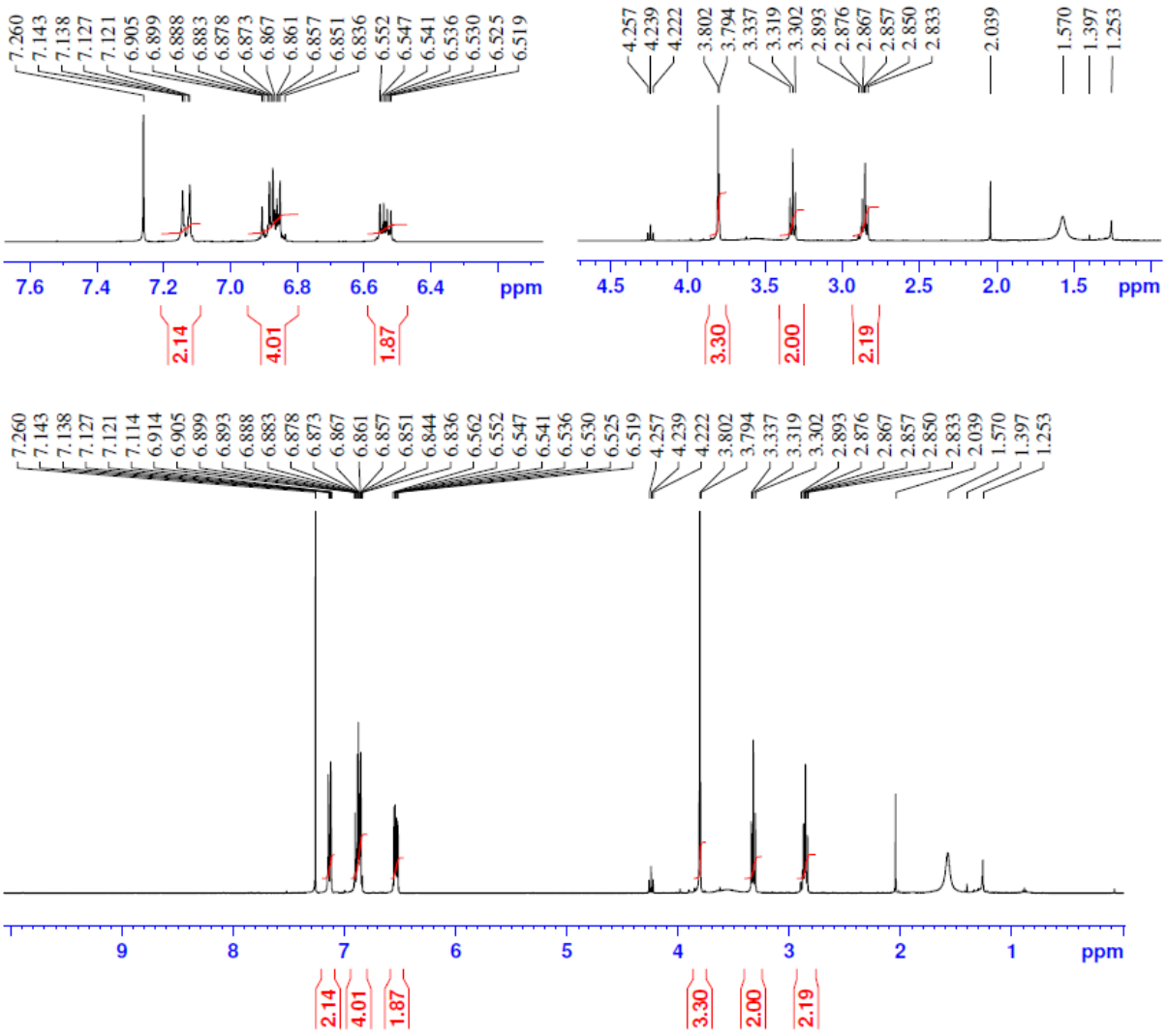
7.275
7.273
7.267
7.260
7.212
7.048
7.044
7.032
7.029
6.912
6.907
6.896
6.890
6.885
6.874
6.869
6.562
6.556
6.551
6.545
6.540
6.529
3.378
3.360
3.343
2.919
2.902
2.885
1.318
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.73
0.89
1.11
2.06
1.85
1.89
2.00
9.10
9
8
7
6
5
4
3
2
1
ppm

^{13}C NMR



4-fluoro-*N*-[2-(3-methoxyphenyl)ethyl]aniline (**8g**)

^{1}H NMR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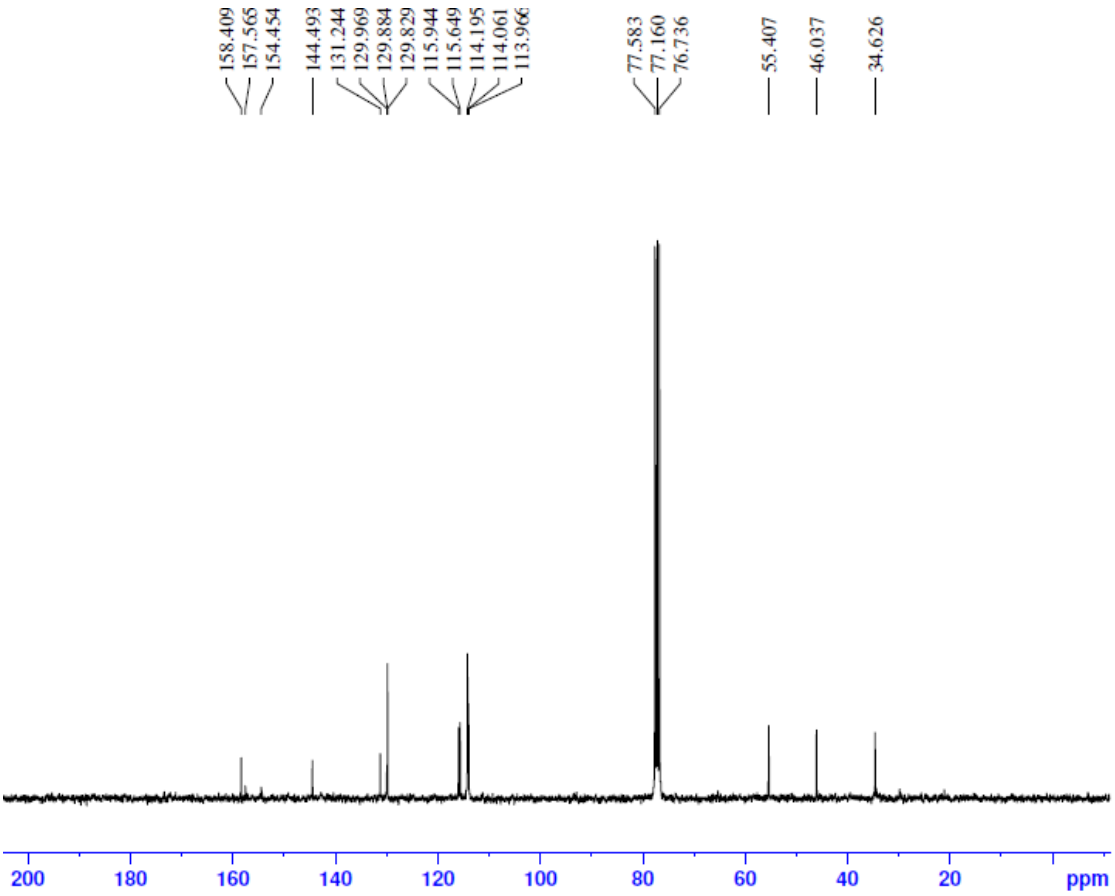
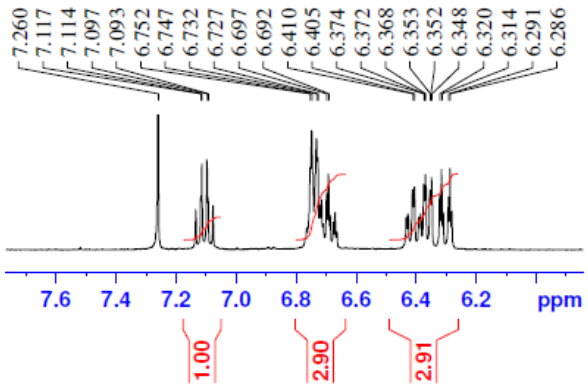
7.143
7.138
7.127
7.121
6.905
6.899
6.888
6.883
6.878
6.873
6.867
6.861
6.857
6.851
6.836
6.552
6.547
6.541
6.536
6.530
6.525
6.519
4.257
4.239
4.222
3.802
3.794
3.337
3.319
3.302
2.893
2.876
2.867
2.857
2.850
2.833
2.039
1.570
1.397
1.253
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.14
4.01
1.87
3.30
2.00
2.19
7.260
7.143
7.138
7.127
7.121
7.114
6.914
6.905
6.899
6.893
6.888
6.883
6.878
6.873
6.867
6.861
6.857
6.851
6.844
6.836
6.562
6.552
6.547
6.541
6.536
6.530
6.525
6.519
4.257
4.239
4.222
3.802
3.794
3.337
3.319
3.302
2.893
2.876
2.867
2.857
2.850
2.833
2.039
1.570
1.397
1.253
9
8
7
6
5
4
3
2
1
ppm
2.14
4.01
1.87
3.30
2.00
2.19

^{13}C NMR



N-[2-(3,5-difluorophenyl)ethyl]-3-fluoroaniline (**8h**)

^{1}H NMR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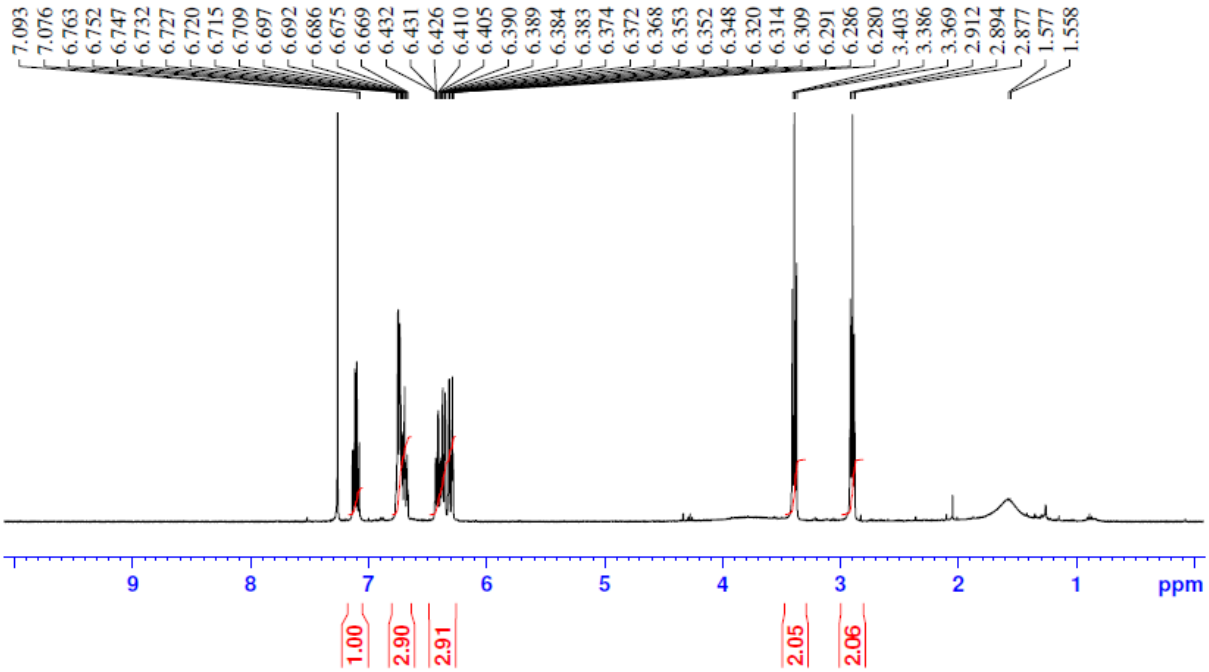
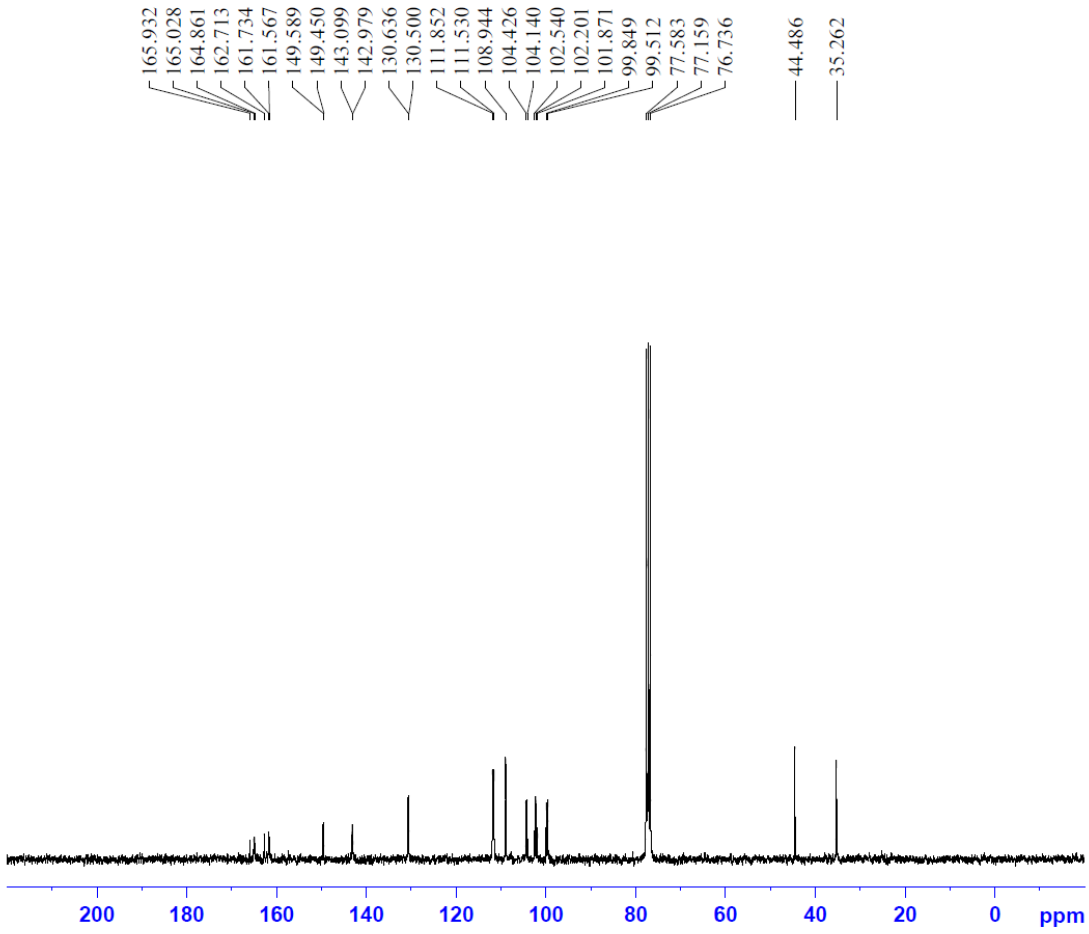
7.117
7.114
7.097
7.093
6.752
6.747
6.732
6.727
6.697
6.692
6.410
6.405
6.374
6.372
6.368
6.353
6.352
6.348
6.320
6.314
6.291
6.286
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm
1.00
2.90
2.91

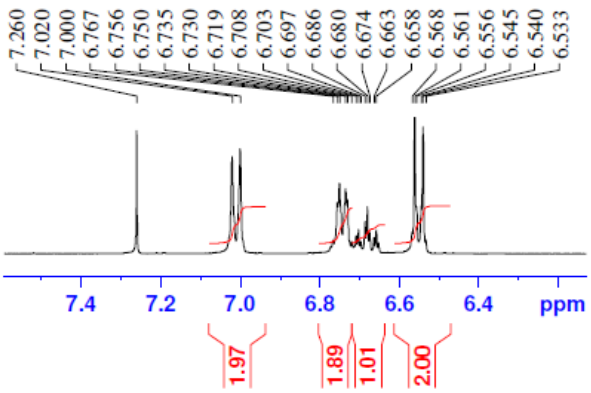

7.093
7.076
6.763
6.752
6.747
6.732
6.727
6.720
6.715
6.709
6.697
6.692
6.686
6.675
6.669
6.432
6.431
6.426
6.410
6.405
6.390
6.389
6.384
6.383
6.374
6.372
6.368
6.353
6.352
6.348
6.320
6.314
6.309
6.291
6.286
6.280
3.403
3.386
3.369
2.912
2.894
2.877
1.577
1.558
9
8
7
6
5
4
3
2
1
ppm
1.00
2.90
2.91
2.05
2.06

^{13}C NMR



N-[2-(3,5-difluorophenyl)ethyl]-4-methylaniline (**8i**)

^{1}H NMR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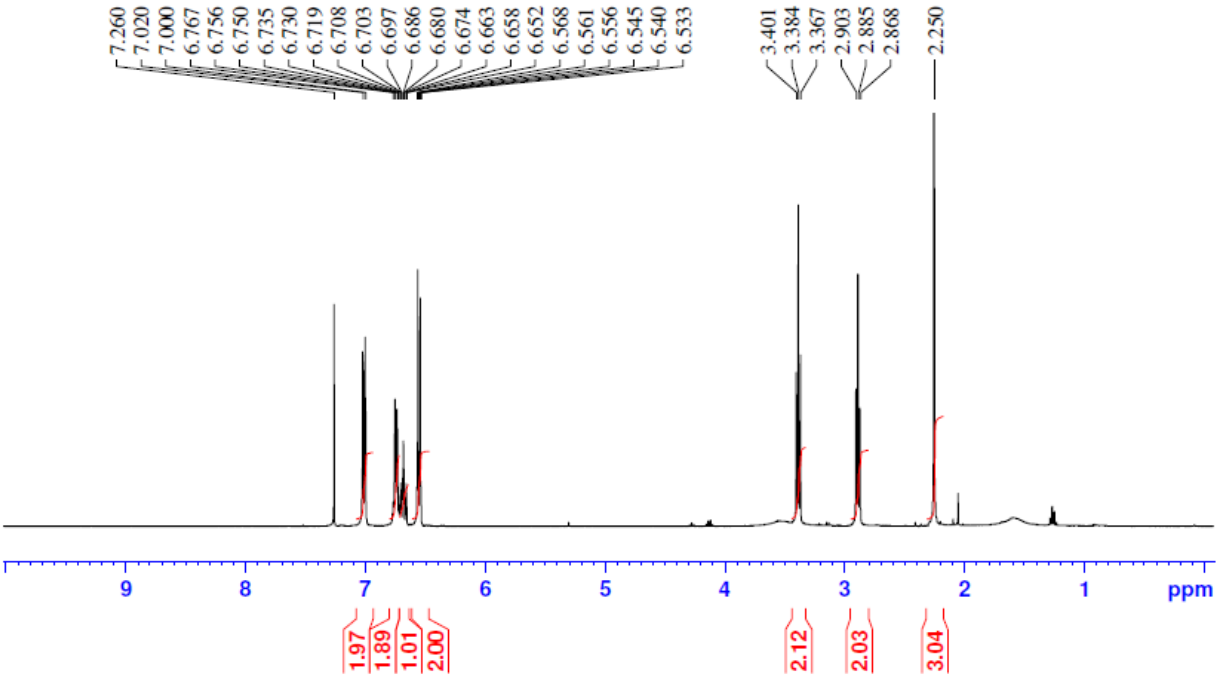
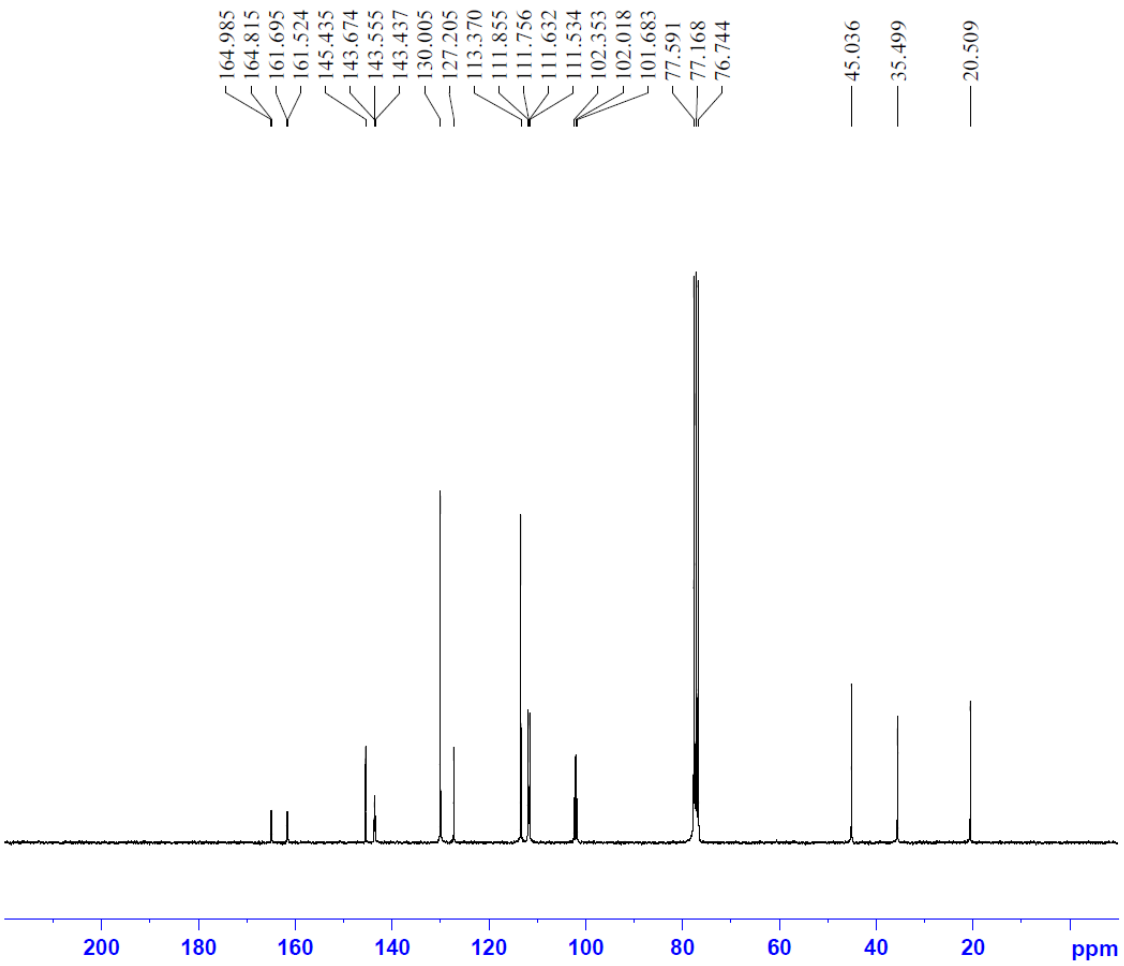
7.020
7.000
6.767
6.756
6.750
6.735
6.730
6.719
6.708
6.703
6.697
6.686
6.680
6.674
6.663
6.658
6.568
6.561
6.556
6.545
6.540
6.533
7.4
7.2
7.0
6.8
6.6
6.4
ppm
1.97
1.89
1.01
2.00

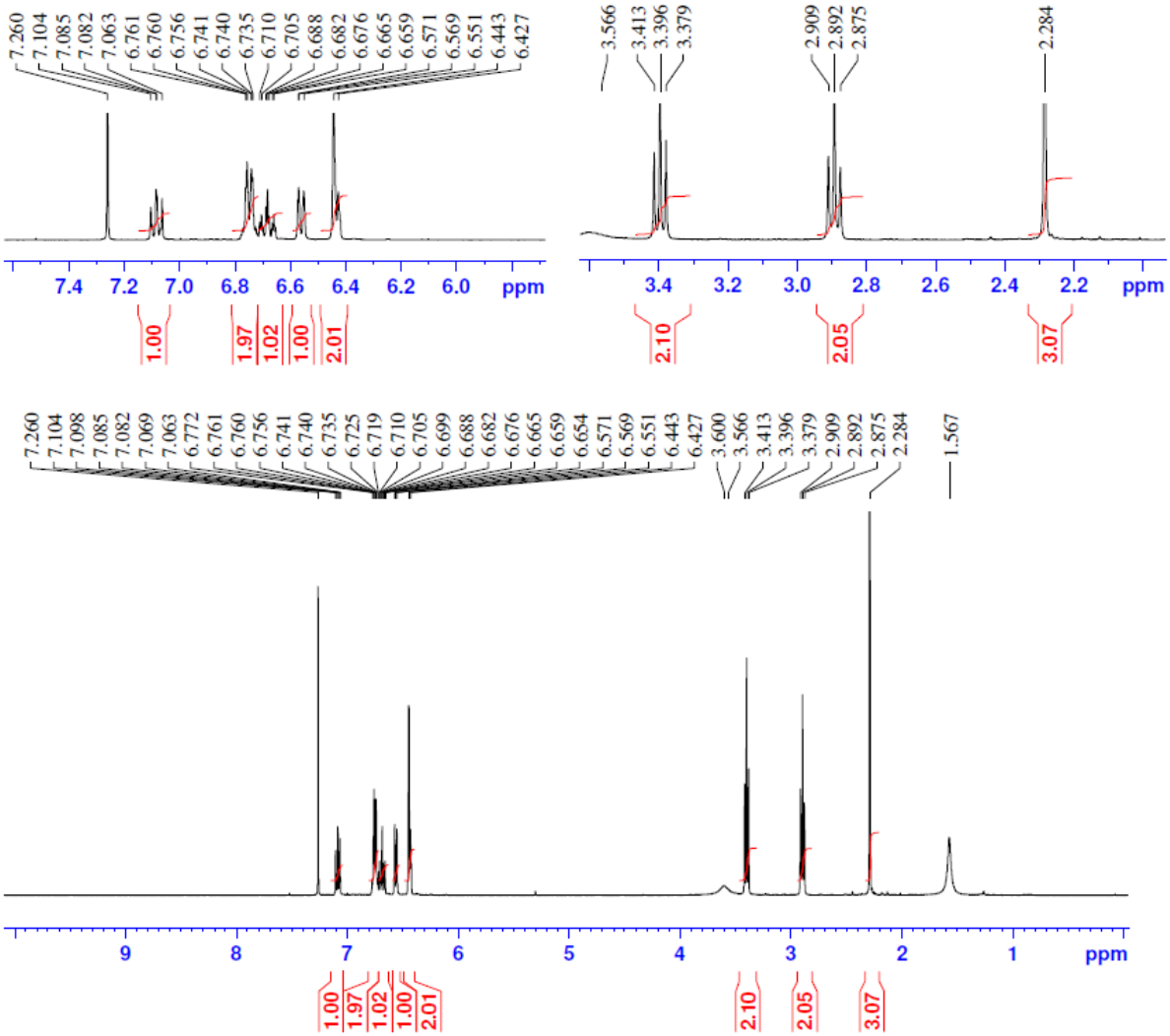

7.260
7.020
7.000
6.767
6.756
6.750
6.735
6.730
6.719
6.708
6.703
6.697
6.686
6.680
6.674
6.663
6.658
6.652
6.568
6.561
6.556
6.545
6.540
6.533
3.401
3.384
3.367
2.903
2.885
2.868
2.250
9
8
7
6
5
4
3
2
1
ppm
1.97
1.89
1.01
2.00
2.12
2.03
3.04

^{13}C NMR



N-[2-(3,5-difluorophenyl)ethyl]-3-methylaniline (**8j**)

^{1}H NMR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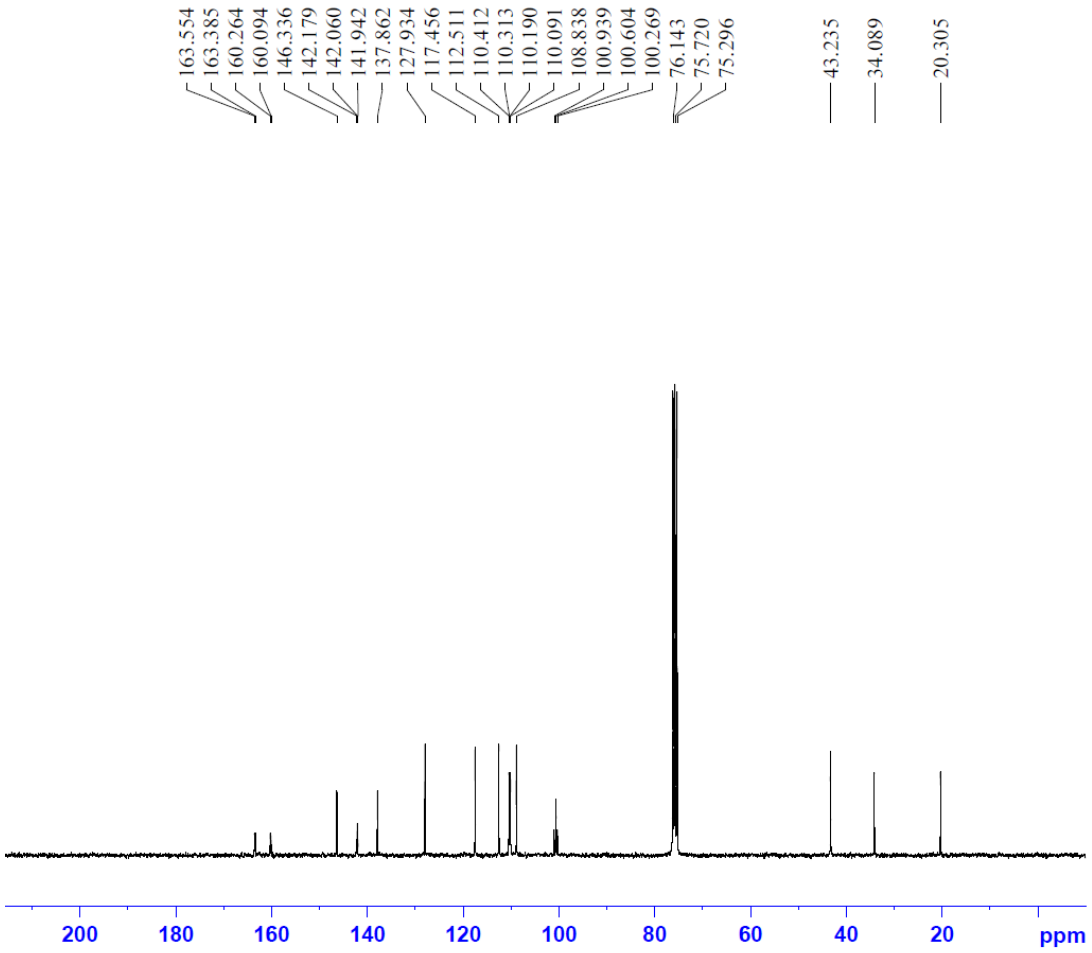
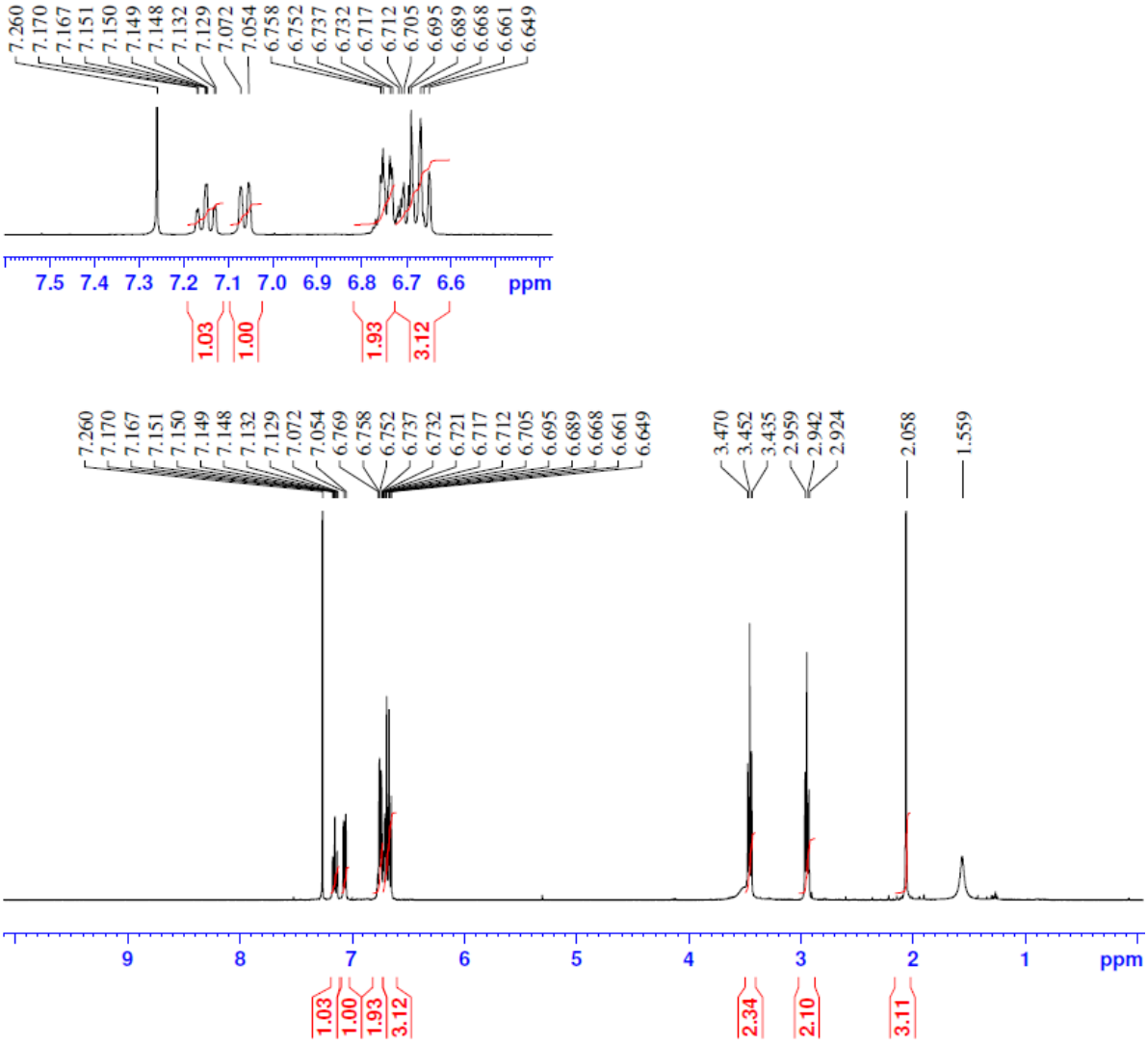
7.085
7.082
7.063
6.761
6.760
6.756
6.741
6.740
6.735
6.710
6.705
6.688
6.682
6.676
6.665
6.659
6.571
6.569
6.551
6.443
6.427
3.566
3.413
3.396
3.379
2.909
2.892
2.875
2.284
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 ppm
3.4 3.2 3.0 2.8 2.6 2.4 2.2 ppm
1.00
1.97
1.02
1.00
2.01
2.10
2.05
3.07
7.260
7.104
7.098
7.085
7.082
7.069
7.063
6.772
6.761
6.760
6.756
6.741
6.740
6.735
6.725
6.719
6.710
6.705
6.699
6.688
6.682
6.676
6.665
6.659
6.654
6.571
6.569
6.551
6.443
6.427
3.600
3.566
3.413
3.396
3.379
2.909
2.892
2.875
2.284
1.567
9 8 7 6 5 4 3 2 1 ppm
1.00
1.97
1.02
1.00
2.01
2.10
2.05
3.07

^{13}C NMR



N-[2-(3,5-difluorophenyl)ethyl]-2-methylaniline (**8k**)

^{1}H NMR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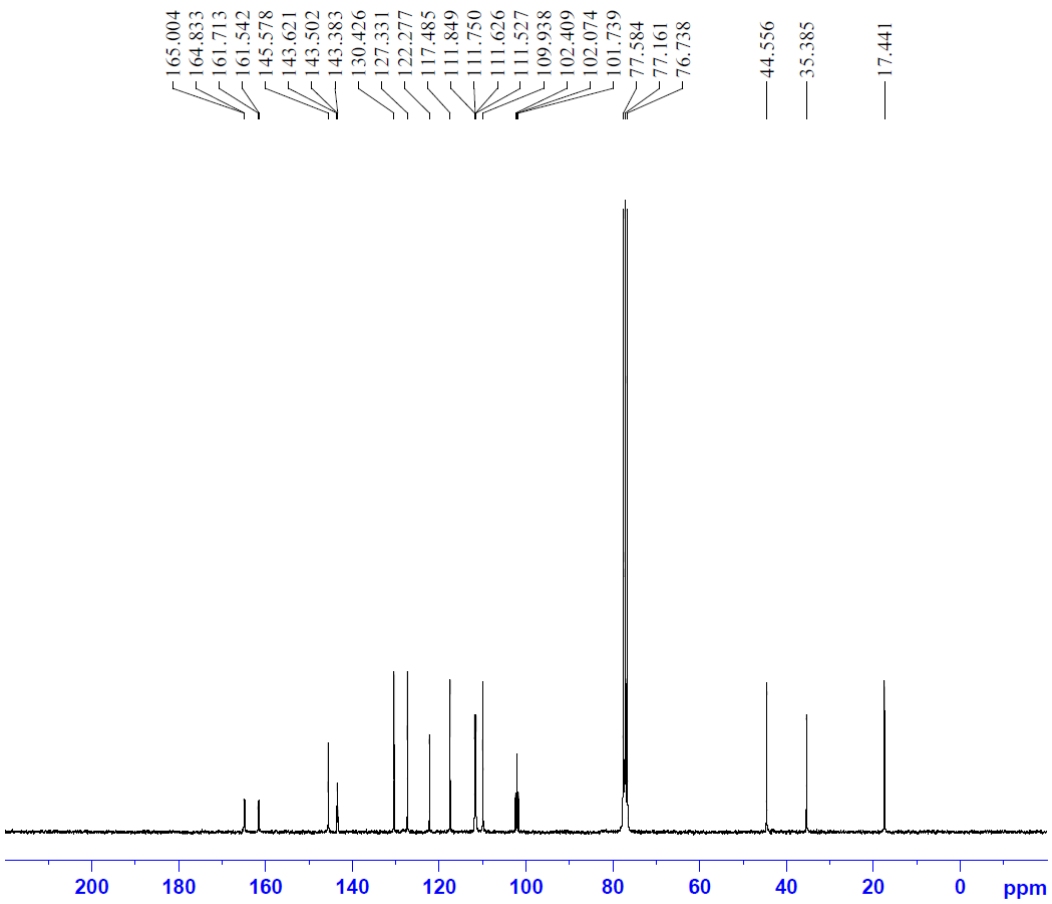
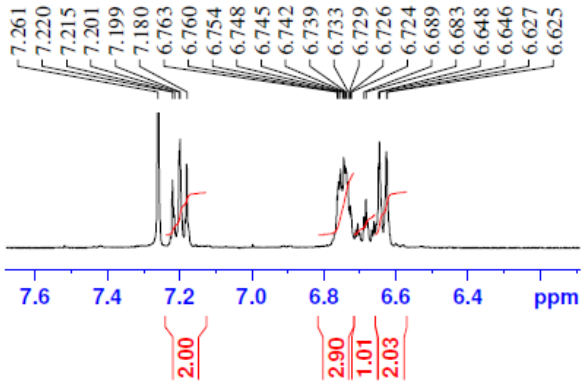
7.170
7.167
7.151
7.150
7.149
7.148
7.132
7.129
7.072
7.054
6.758
6.752
6.737
6.732
6.717
6.712
6.705
6.695
6.689
6.668
6.661
6.649
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 ppm
1.03
1.00
1.93
3.12
7.260
7.170
7.167
7.151
7.150
7.149
7.148
7.132
7.129
7.072
7.054
6.769
6.758
6.752
6.737
6.732
6.721
6.717
6.712
6.705
6.695
6.689
6.668
6.661
6.649
3.470
3.452
3.435
2.959
2.942
2.924
2.058
1.559
9 8 7 6 5 4 3 2 1 ppm
1.03
1.00
1.93
3.12
2.34
2.10
3.11

^{13}C NMR



N-[2-(3,5-difluorophenyl)ethyl]aniline (**8l**)

^{1}H NMR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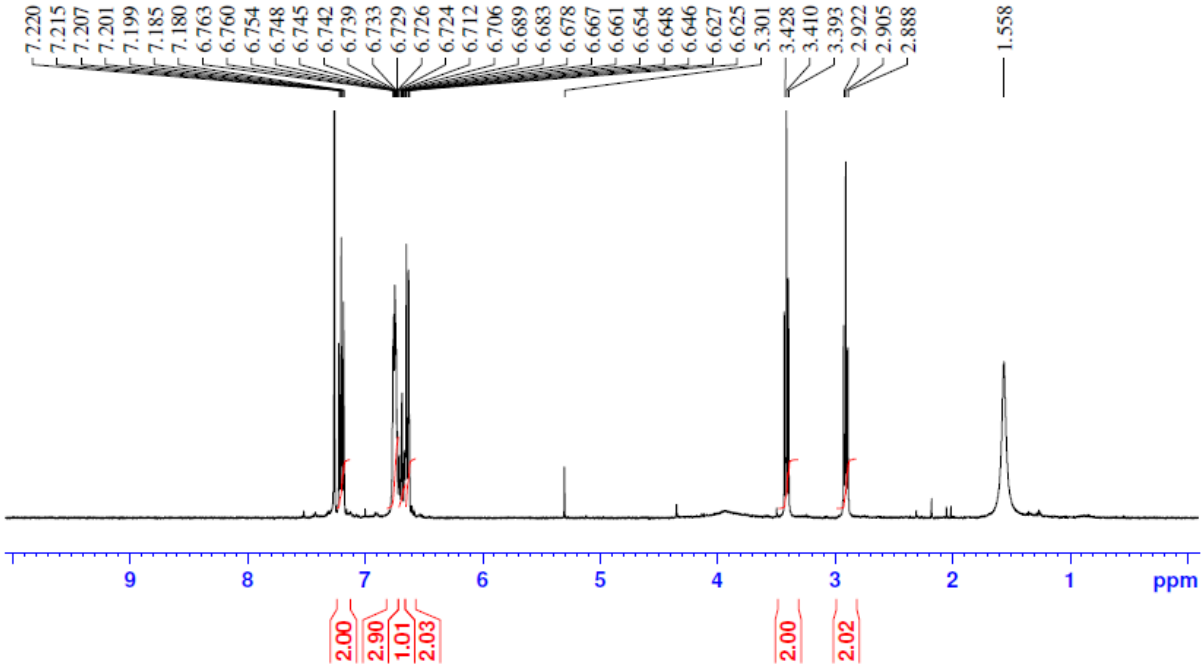
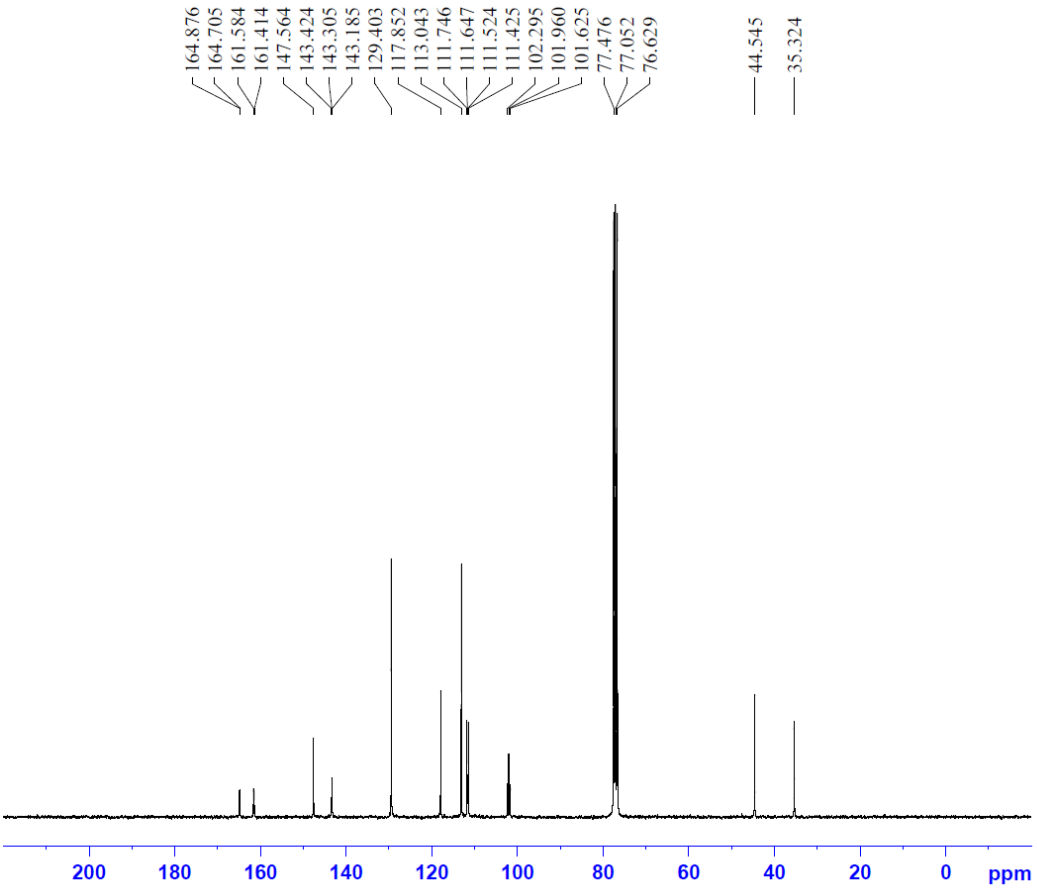
7.220
7.215
7.201
7.199
7.180
6.763
6.760
6.754
6.748
6.745
6.742
6.739
6.733
6.729
6.726
6.724
6.689
6.683
6.648
6.646
6.627
6.625
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
2.00
2.90
1.01
2.03

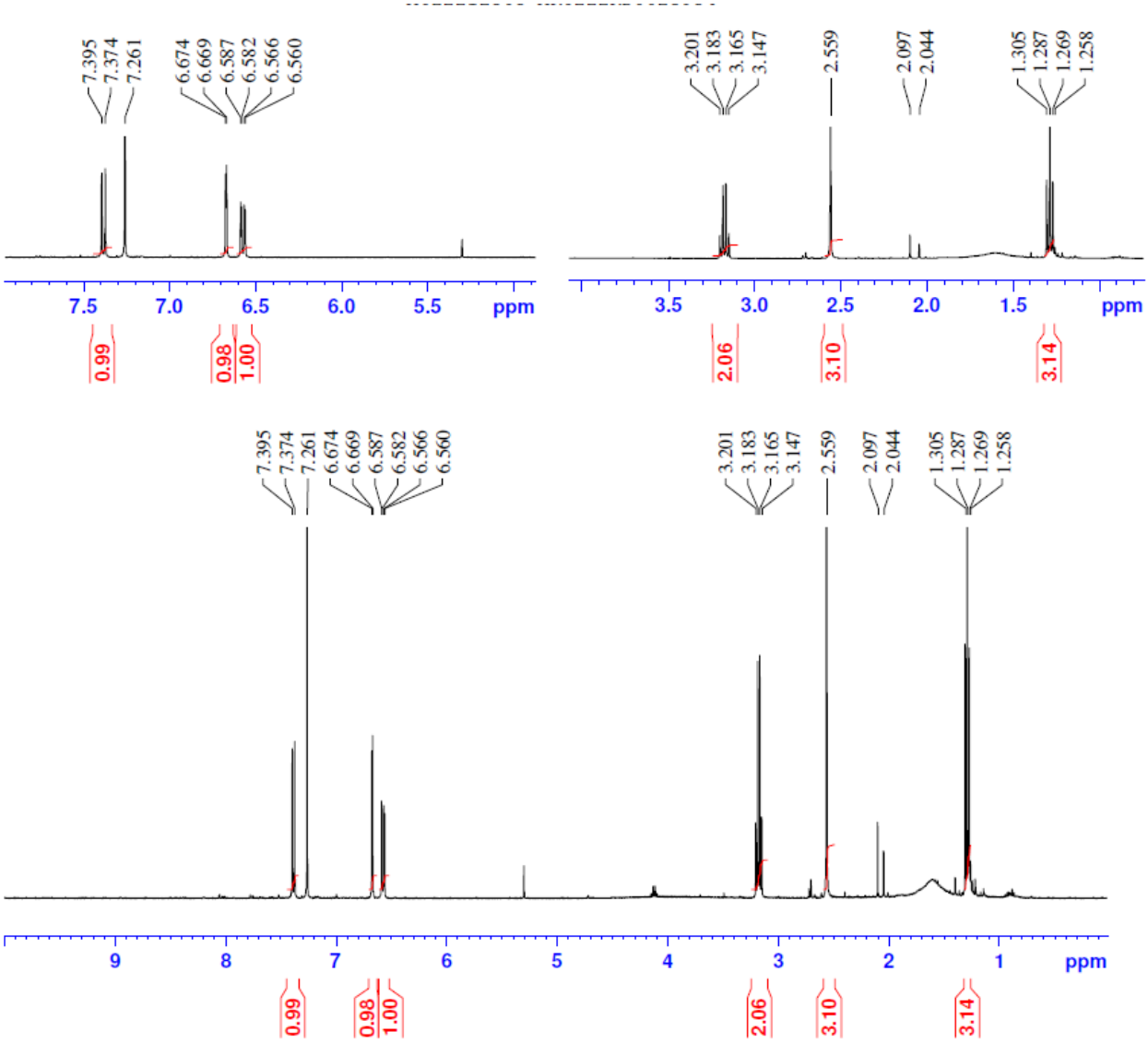

7.220
7.215
7.207
7.201
7.199
7.185
7.180
6.763
6.760
6.754
6.748
6.745
6.742
6.739
6.733
6.729
6.726
6.724
6.712
6.706
6.689
6.683
6.678
6.667
6.661
6.654
6.648
6.646
6.627
6.625
5.301
3.428
3.410
3.393
2.922
2.905
2.888
1.558
9
8
7
6
5
4
3
2
1
ppm
2.00
2.90
1.01
2.03
2.00
2.02

^{13}C NMR



N-ethyl-2-methyl-1,3-benzoxazol-6-amine (**10a**)

^{1}H NMR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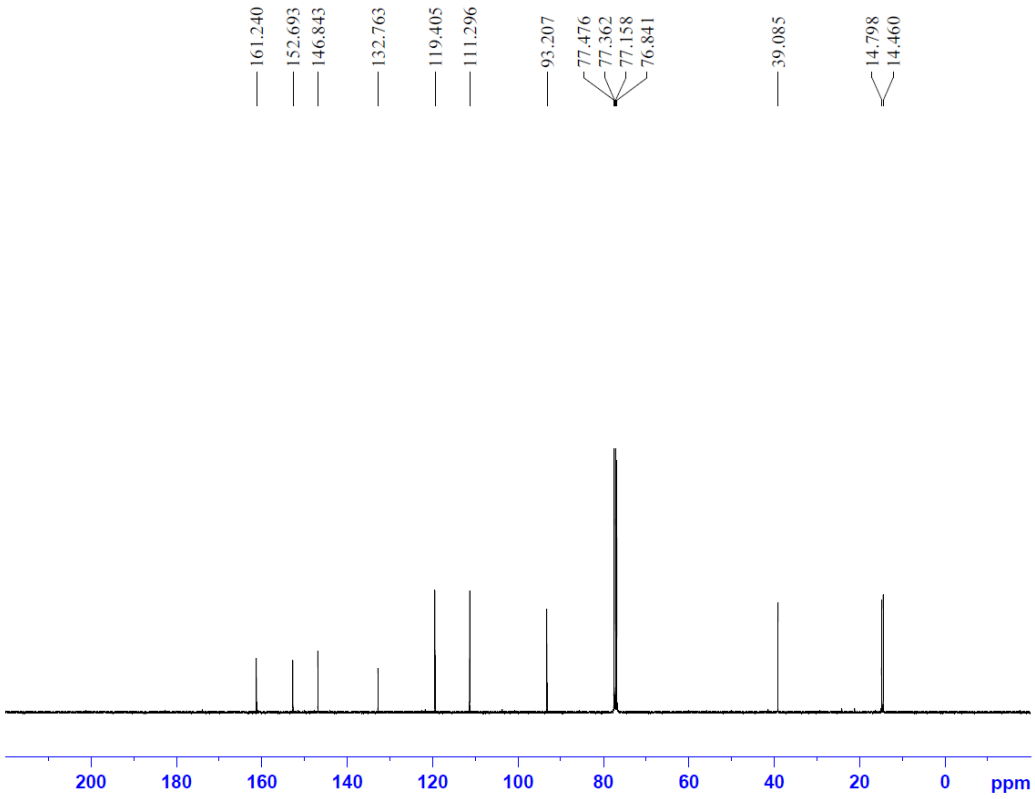
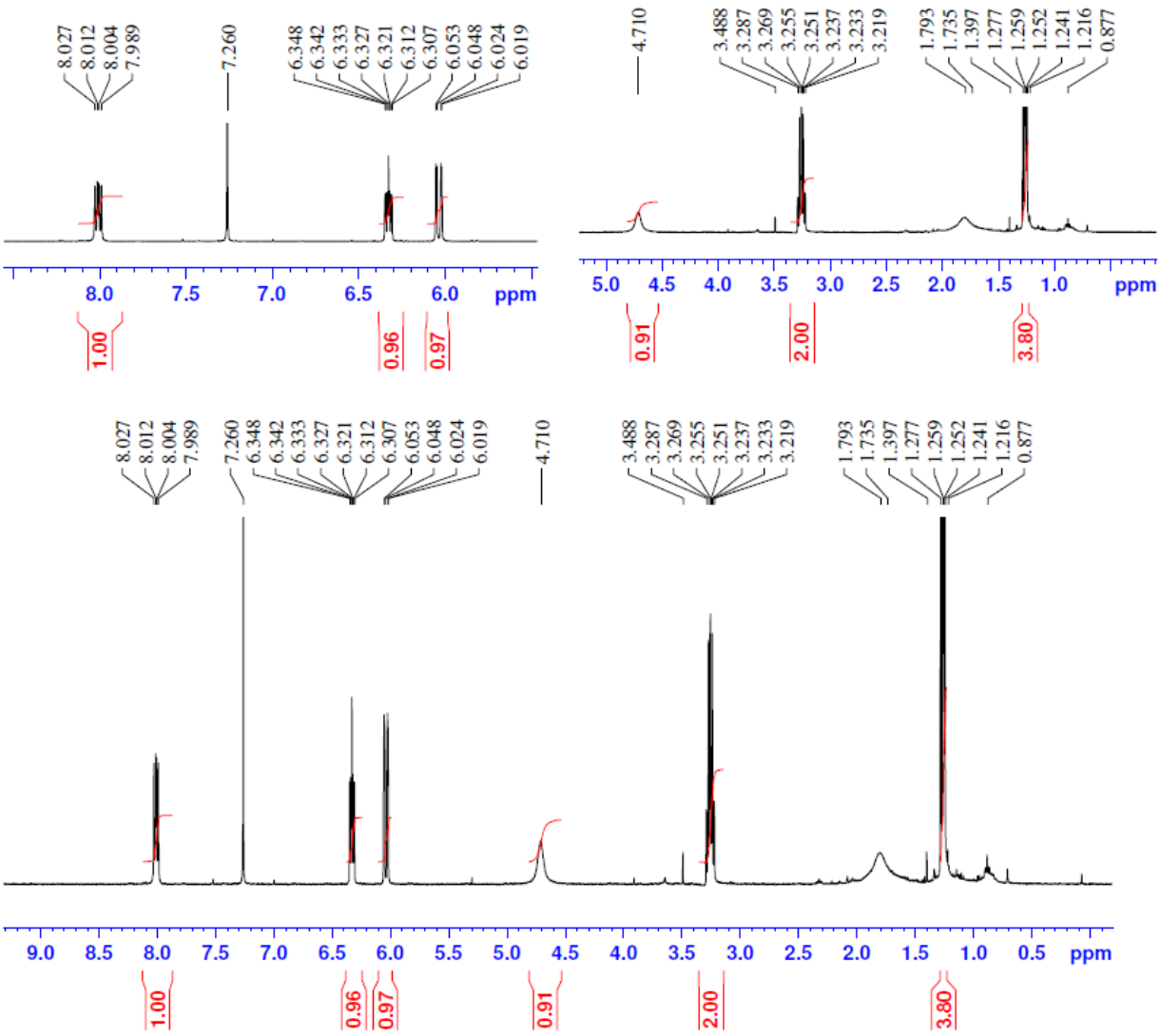
7.374
7.261
6.674
6.669
6.587
6.582
6.566
6.560
3.201
3.183
3.165
3.147
2.559
2.097
2.044
1.305
1.287
1.269
1.258
ppm
0.99
0.98
1.00
2.06
3.10
3.14

^{13}C NMR

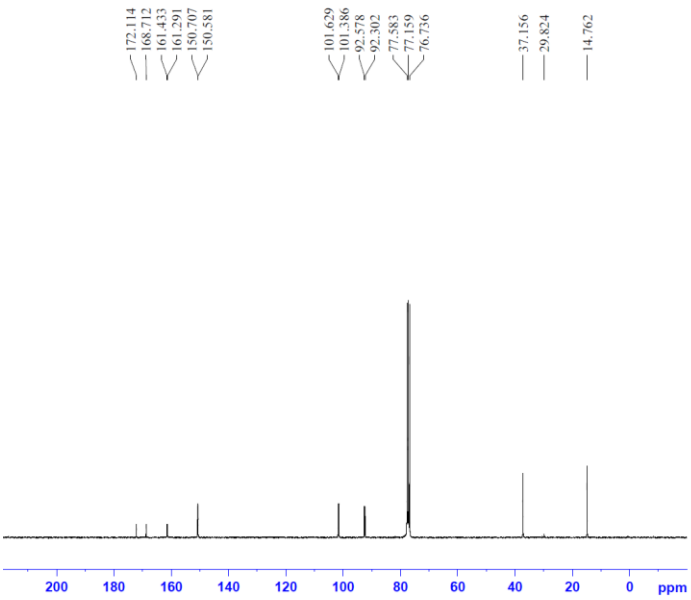


N-ethyl-4-fluoropyridin-2-amine (**10b**)

^{1}H NMR

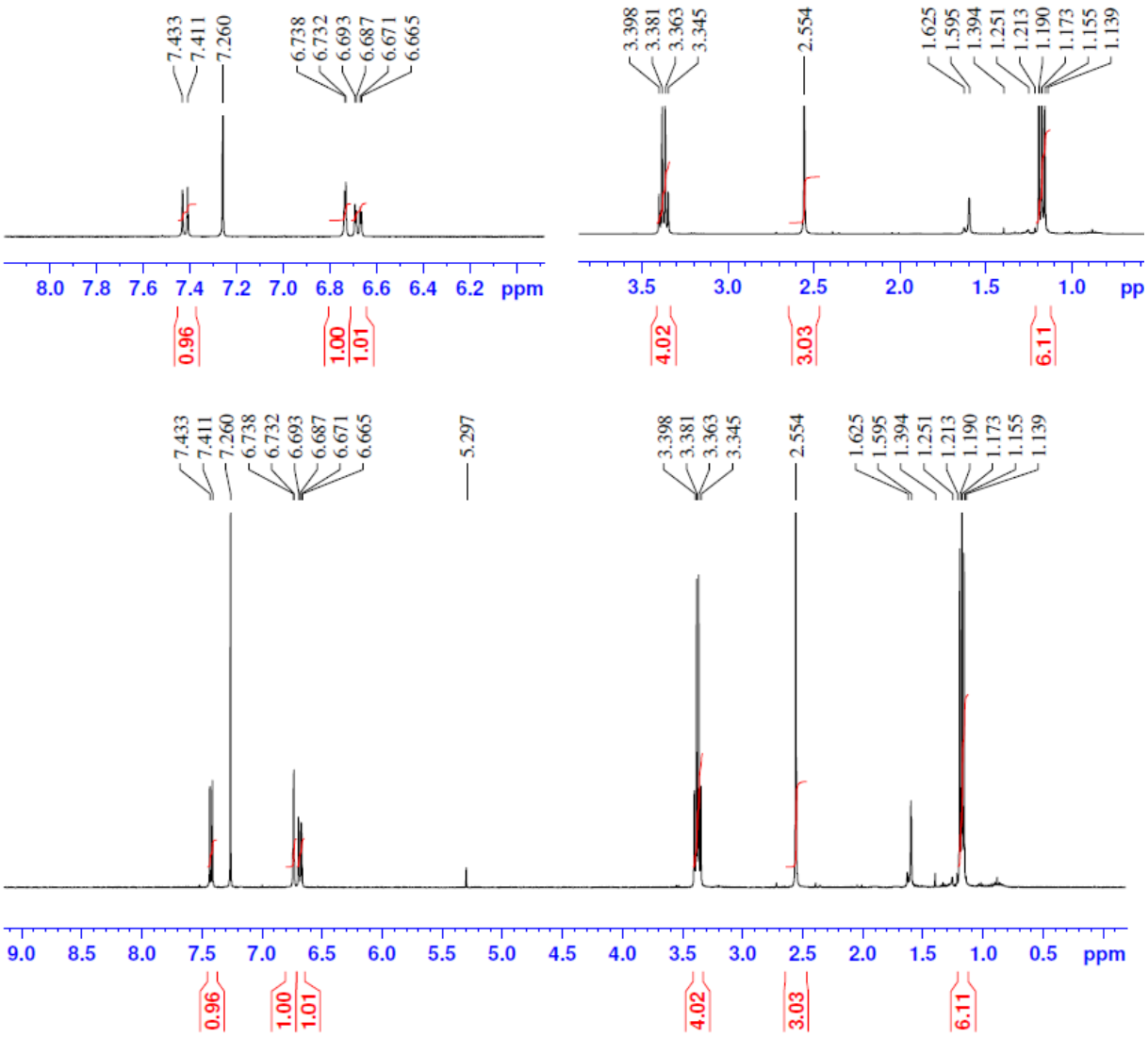

8.027
8.012
8.004
7.989
7.260
6.348
6.342
6.333
6.327
6.321
6.312
6.307
6.053
6.048
6.024
6.019
4.710
3.488
3.287
3.269
3.255
3.251
3.237
3.233
3.219
1.793
1.735
1.397
1.277
1.259
1.252
1.241
1.216
0.877
ppm
1.00
0.96
0.97
0.91
2.00
3.80

^{13}C NMR

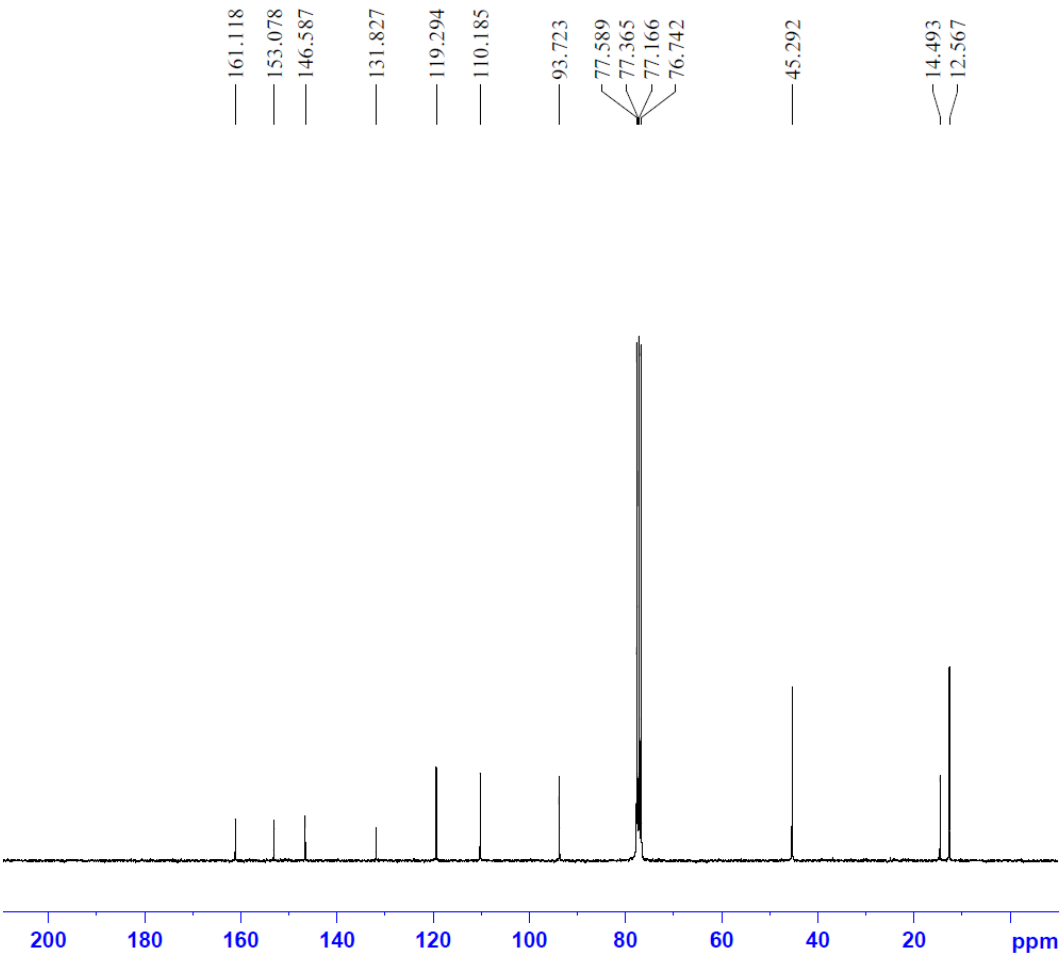


N,*N*-diethyl-2-methyl-1,3-benzoxazol-6-amine (**10c**)

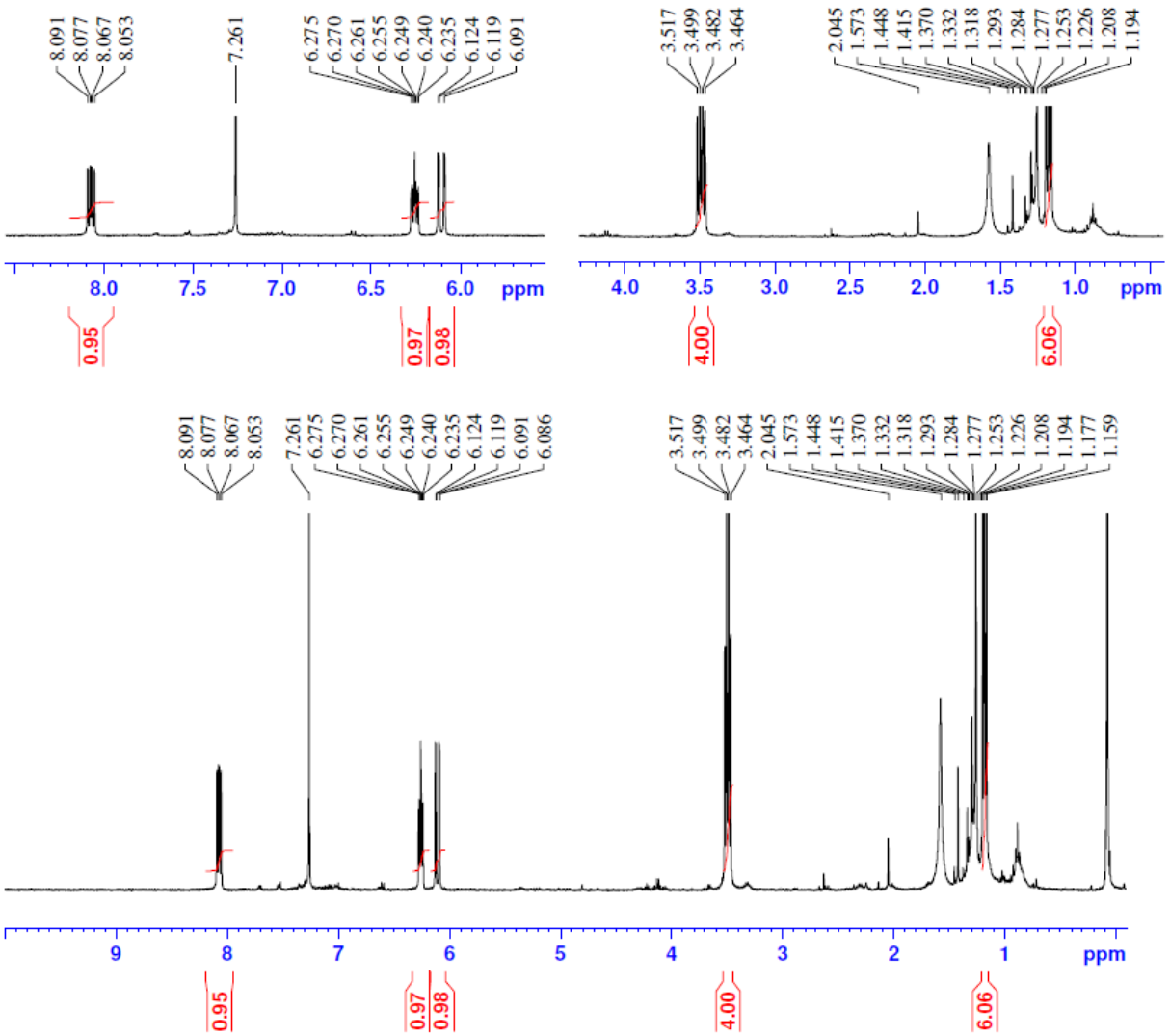
^{1}H NMR


7.433
7.411
7.260
6.738
6.732
6.693
6.687
6.671
6.665
3.398
3.381
3.363
3.345
2.554
1.625
1.595
1.394
1.251
1.213
1.190
1.173
1.155
1.139
5.297
ppm
0.96
1.00
1.01
4.02
3.03
6.11

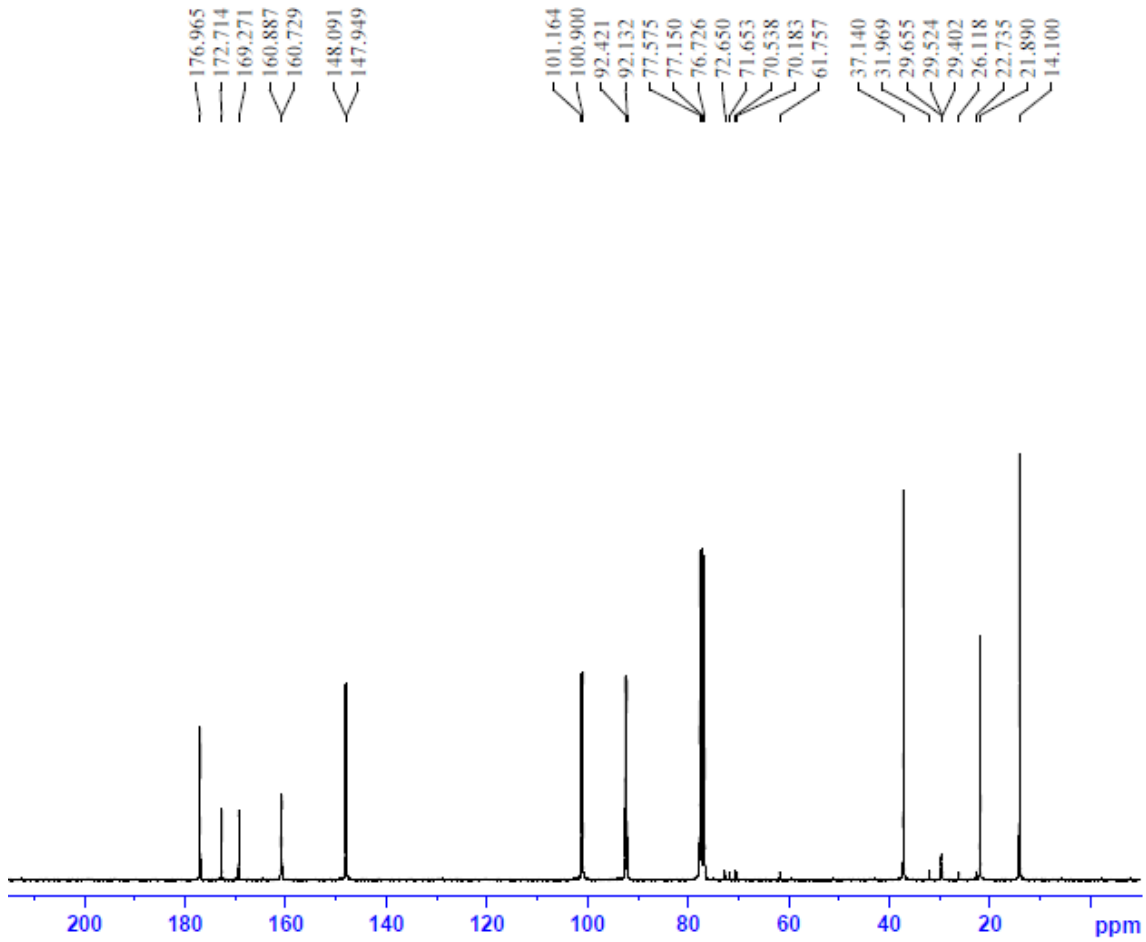
^{13}C NMR



N,*N*-diethyl-4-fluoropyridin-2-amine (**10d**)
^{1}H NMR


8.091
8.077
8.067
8.053
7.261
6.275
6.270
6.261
6.255
6.249
6.240
6.235
6.124
6.119
6.091
3.517
3.499
3.482
3.464
2.045
1.573
1.448
1.415
1.370
1.332
1.318
1.293
1.284
1.277
1.253
1.226
1.208
1.194
8.0
7.5
7.0
6.5
6.0
ppm
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.95
0.97
0.98
4.00
6.06
8.091
8.077
8.067
8.053
7.261
6.275
6.270
6.261
6.255
6.249
6.240
6.235
6.124
6.119
6.091
6.086
3.517
3.499
3.482
3.464
2.045
1.573
1.448
1.415
1.370
1.332
1.318
1.293
1.284
1.277
1.253
1.226
1.208
1.194
1.177
1.159
9
8
7
6
5
4
3
2
1
ppm
0.95
0.97
0.98
4.00
6.06

^{13}C NMR


176.965
172.714
169.271
160.887
160.729
148.091
147.949
101.164
100.900
92.421
92.132
77.575
77.150
76.726
72.650
71.653
70.538
70.183
61.757
37.140
31.969
29.655
29.524
29.402
26.118
22.735
21.890
14.100
200
180
160
140
120
100
80
60
40
20
ppm

Reference:

L. Meng, C. Liu, W. Zhang, C. Zhou and A. Lei, *Chem. Commun*., 2014, **50**, 1110.