Electronic Supplementary Material (ESI) for New Journal of Chemistry.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-Promoted Reduction of Azides to Amines under Metal-Free Conditions

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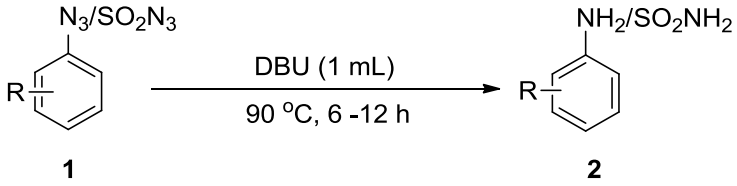
General Considerations

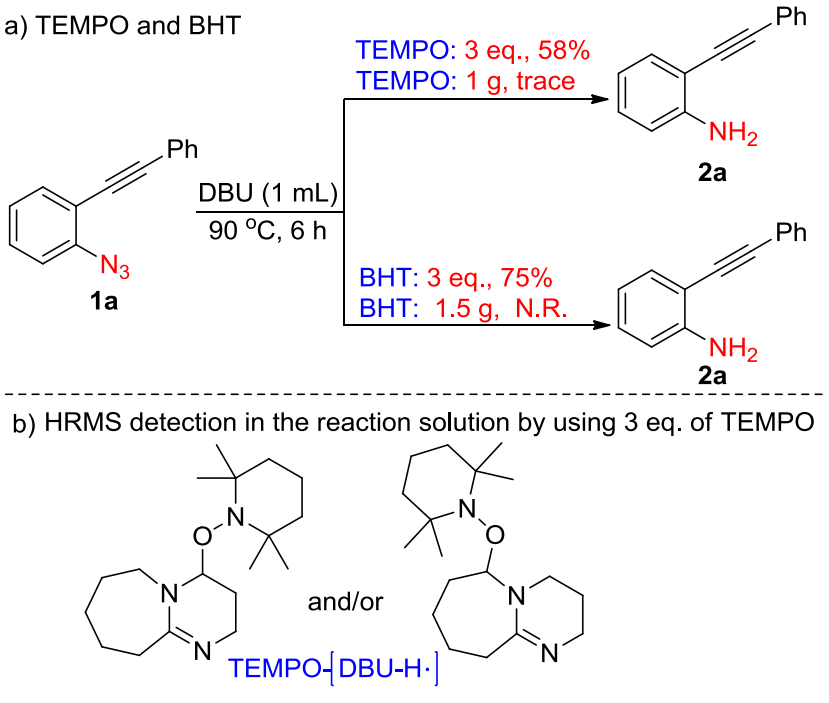
Unless specified, all reactions were carried out in oven-dried glassware with magnetic stirring. All reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (Ethyl acetate: Petrol ether as eluant). ^{1}H and ^{13}C spectra was measured on 400 MHz spectrometers. HRMS was performed on Waters Xevo G2-XS Tof. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). Organic azides[1-3] were prepared according to the published procedures.

General experimental procedure for the reduction of azides 1 to amines 2.



To a 10 mL of flask was added azide **1** (0.1 mmol, 1 equiv) and DBU (1 mL). The reaction mixture was stirred at 90 ℃, until the azide disappeared monitored by TLC (about 6 h for most of **1**). Upon cooling to room temperature, water (10 mL) was added, and the mixture was extracted with ethyl acetate (2 x 20 mL). The organic layers were combined, dried over anhydrous $NaSO_4$, and filtered. On completion, the reaction mixture was directly subjected to purification by flash column chromatography on silica gel to give the desired **2**. (eluent: petrol ether: ethyl acetate = 20:1)

Radical control experiments.

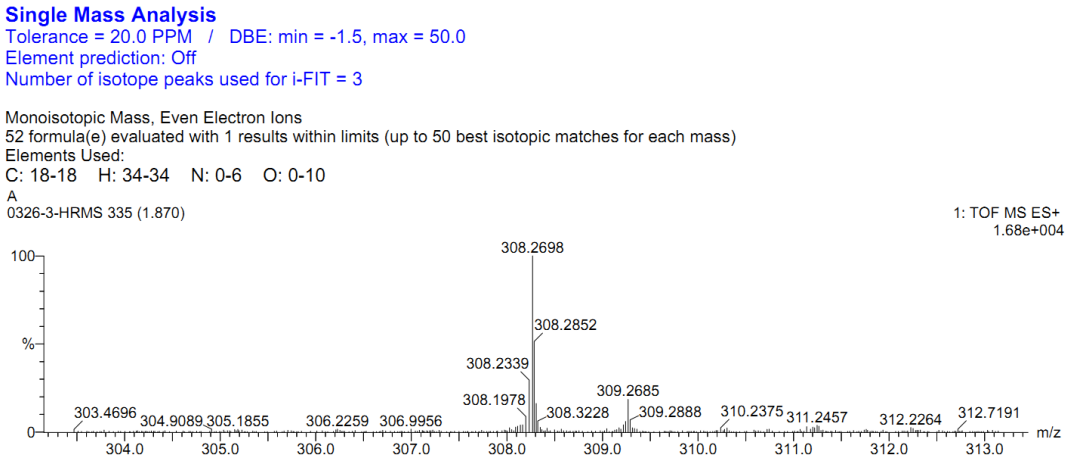


HRMS(ESI) cacl. for $C_{18}H_{34}N_3O$ $[M+H]^+$ 308.2702, found: 308.2698

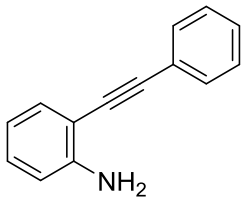
To a 10 mL of test tube was added 1-azido-2-(phenylethynyl)benzene **1a** (0.1 mmol, 1 equiv.), 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (3eq. or 1 g) and DBU (1 mL). Next, the reaction mixture was stirred at 90 ℃ for 6 h. After cooling to room

temperature, it was found that a trace amount of reduced 2-(phenylethynyl)aniline **2a** was detected and most of the starting material **1a** was left. Furthermore, to a 10 mL of test tube was added 1-azido-2-(phenylethynyl)benzene **1a** (0.1 mmol, 1 equiv.), butylated hydroxytoluene (BHT) (3eq. or 1.5 g) and DBU (1 mL). Next, the reaction mixture was stirred at 90 ℃ for 6 h. After cooling to room temperature, it was found that no 2-(phenylethynyl)aniline **2a** was detected and most of the starting material **1a** was left.

We repeated the reaction by employing 3 equiv. of TEMPO to trap the radical [DBU-H ·]. After 6 hours, the reaction solution was then directly sent to check HRMS and the desired compound TEMPO-[DBU-H ·] was successfully found (HRMS(ESI) cacl. for $C_{18}H_{34}N_3O$ $[M+H]^+$ 308.2702, found: 308.2698). We have added this trapping experiment in the revised manuscript. Please check the HRMS detail below:

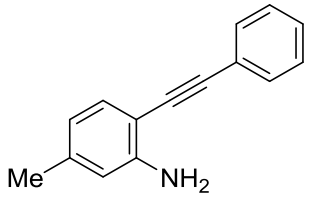


2-Phenylethynylaniline (2a):



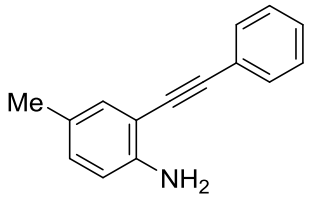
Known compound[4]; isolated yield = 90%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.19 (s, 2 H), 6.51-6.55 (m, 2 H), 7.03-7.07 (m, 1 H), 7.25-7.29 (m, 4 H), 7.43-7.44 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.8, 132.2, 131.5, 129.8, 128.4, 128.3, 123.4, 118.0, 114.4, 108.0, 94.7, 85.9.

5-Methyl-2-(phenylethynyl)aniline (2b):



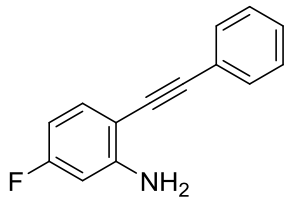
Known compound[4]; isolated yield = 81%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =2.26 (s, 3 H), 4.20 (s, 2 H), 6.53-6.55 (m, 2 H), 7.24 (s, 1 H), 7.31-7.33 (m, 3 H), 7.49-7.51 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.7, 140.1, 132.0, 131.4, 128.4, 128.0, 123.6, 119.2, 115.0, 105.2, 94.1, 86.2, 21.7.

4-Methyl-2-(phenylethynyl)aniline (2c):



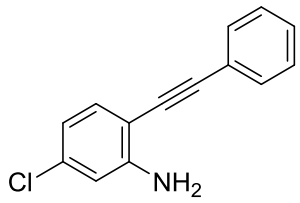
Known compound[5]; isolated yield = 90%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =2.25 (s, 3 H), 4.15 (s, 2 H), 6.65-6.66 (d, *J*= 5.2 Hz, 1 H), 6.96-6.97 (d, *J*= 4.8 Hz, 1 H), 7,21 (s, 1 H), 7.35-7.36 (d, *J*= 4.8 Hz, 3 H), 7.52-7.53 (d, *J*= 4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =145.5, 132.3, 131.5, 130.6, 128.4, 128.2, 127.3, 123.5, 114.6, 108.0, 94.5, 86.2, 20.3.

5-Fluoro-2-(phenylethynyl)aniline (2d):



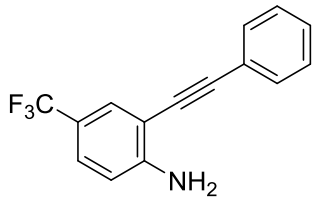
Known compound[6]; isolated yield = 83%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.39 (s, 2 H), 6.41-6.43 (d, *J*= 9.2 Hz, 2 H), 6.96-6.97 (d, *J*= 4.8 Hz, 1 H), 7.30-7.35 (m, 4 H), 7.50-7.52 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =163.8 (d, *J*= 245.5 Hz), 149.5 (d, *J*= 11.6 Hz), 133.7 (d, *J*= 10.4 Hz,), 131.5, 128.4, 128.3, 123.2, 105.3 (d, *J*= 22.4 Hz), 104.1, 101.7 (d, *J*= 25.4 Hz), 94.3 (d, *J*= 1.4 Hz), 85.0.

5-Chloro-2-(phenylethynyl)aniline (2e):



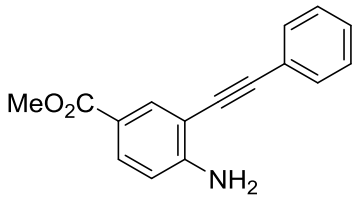
Known compound[7]; isolated yield = 90%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.33 (s, 2 H), 6.67-6.71 (m, 2 H), 7.28 (s, 1 H), 7.34-7.35 (m, 3 H), 7.50-7.52 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =148.7, 135.3, 133.1, 131.5, 128.5, 123.0, 118.2, 114.1, 106.5, 95.4, 84.9.

2-(Phenylethynyl)-4-(trifluoromethyl)aniline (2f):



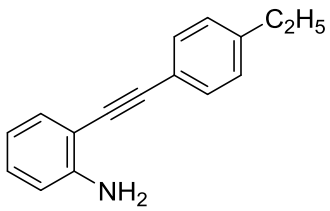
Known compound[6]; isolated yield = 52%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.59 (s, 2 H), 6.74-6.75 (d, *J*= 5.6 Hz, 1 H), 7.35-7.37 (m, 4 H), 7.53-7.54 (m, 2 H), 7.63 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =150.3, 131.7, 129.7 (d, *J*= 2.9 Hz), 128.7, 128.5, 126.7 (d, *J*= 2.2 Hz), 124.4 ,122.7, 120.0 (d, *J*= 10.9 Hz), 113.7, 107.7, 95.8, 84.5.

Methyl 4-amino-3-(phenylethynyl)benzoate (2g):



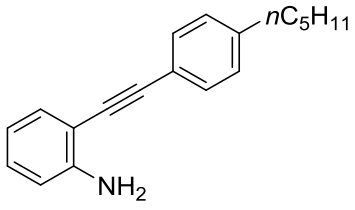
Known compound[8]; isolated yield = 90%; brown solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =3.86 (s, 2 H), 4.71 (s, 2 H), 6.69-6.71 (d, *J*= 8.4 Hz, 1 H), 7.35-7.36 (m, 3 H), 7.51-7.53 (m, 2 H), 7.80-7.82 (d, *J*= 8.4 Hz, 1 H), 8.09 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =166.7, 151.5, 134.5, 131.5, 131.5, 128.5, 128.5, 122.9, 119.5, 113.3, 107.2, 95.1, 84.8, 51.8.

2-((4-Ethylphenyl)ethynyl)aniline (2h):



Known compound[9]; isolated yield = 81%; brown solid; 1H NMR($CDCl_3$, 400 MHz): δ =1.30 (s, 3 H), 2.69-2.71 (d, *J*= 7.6 Hz, 2 H), 4.31 (s, 2 H), 6.75-6.77 (d, *J*= 7.6 Hz, 2 H), 7.15-7.19 (m, 1 H), 7.21-7.23 (d, *J*= 8.0 Hz, 2 H), 7.39-7.41 (d, *J*= 7.6 Hz, 1 H), 7.48-7.50 (d, *J*= 7.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.8, 144.7, 132.1, 131.5, 129.6, 128.0, 120.5, 118.0, 114.3, 108.2, 94.9, 85.2, 28.9, 15.4.

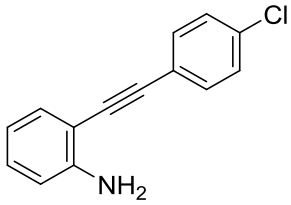
2-((4-Pentylphenyl)ethynyl)aniline (2i):



Known compound[10]; isolated yield = 88%; brown liquid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =0.92 (m, 3 H), 1.35-1.37 (m, 4 H), 1.64-1.65 (m, 2 H), 2.63-2.64 (m, 2 H), 4.26 (s, 2 H), 6.72-6.74 (m, 2 H), 7.14-7.18 (m, 3 H), 7.37-7.38 (m, 1 H), 7.45-7.46 (m, 2 H).

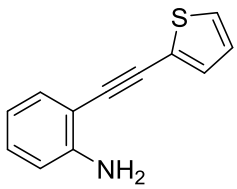
^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.8, 143.5, 132.1, 131.4, 129.6, 128.6, 120.5, 118.0, 114.4, 108.3, 95.0, 85.2, 35.9, 31.5, 31.0, 22.6, 14.1.

2-((4-Chlorophenyl)ethynyl)aniline (2j):



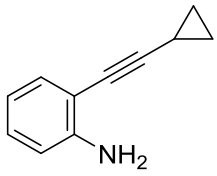
Known compound[5]; isolated yield = 83%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.26 (s, 2 H), 6.72-6.73 (m, 2 H), 7.14-7.17 (m, 1 H), 7.32-7.36 (dd, *J*=5.6 Hz, *J*=5.2 Hz, 3 H), 7.44-7.45 (d, *J*= 5.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.8, 134.2, 132.7, 132.2, 130.0, 128.8, 121.9, 118.1, 114.5, 107.6, 93.6, 87.0.

2-(Thiophen-2-ylethynyl)aniline (2k):



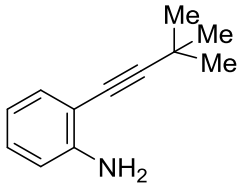
Known compound[5]; isolated yield = 74%; yellow solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.26 (s, 2 H), 6.72-6.73 (m, 2 H), 7.13-7.15 (m, 1 H), 7.20-7.21 (m, 1 H), 7.30-7.31 (m, 1 H), 7.35-7.46 (d, *J*= 4.8 Hz, 1 H), 7.51 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.8, 132.2, 129.9, 129.7, 128.4, 125.5, 122.3, 118.0, 114.4, 107.9, 89.7, 85.4.

2-(Cyclopropylethynyl)aniline (2l):



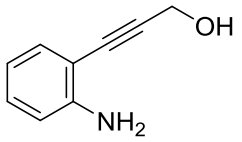
Known compound[11]; isolated yield = 78%; black liquid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =0.78-0.83 (m, 2 H), 0.86-0.91 (m, 2 H), 1.46-1.53 (m, 1 H), 4.13 (s, 2 H), 6.62-6.67 (m, 2 H), 7.04-7.08 (m, 1 H), 7.20-7.23 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.9, 132.2, 128.9, 117.9, 114.2, 108.8, 98.8, 77.4, 77.0, 76.7, 72.1, 8. 9, 0.4.

2-(3,3-Dimethyl-1-butynyl)aniline (2m):



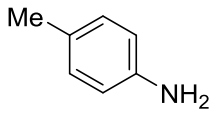
Known compound[11]; isolated yield = 75%; black liquid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =1.34 (s, 9 H), 4.13 (s, 2 H), 6.63-6.68 (m, 2 H), 7.04-7.08 (t, *J*= 7.6 Hz, 1 H), 7.21-7.23 (d, *J*= 7.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ =147.4, 131.9, 128.8, 117.9, 114.1, 108.9, 104.2, 75.4, 31.3, 28.3.

2-(2-(Hydroxymethyl)ethynyl)aniline (2n):



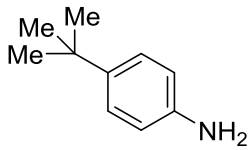
Known compound[12]; isolated yield = 49%; black liquid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =1.70 (m, 1 H), 4.25 (s, 2 H), 4.53 (s, 2 H), 6.65-6.69 (m, 2 H), 7.10-7.14 (m, 1 H), 7.26-7.27 (m, 1 H).^{13}C NMR ($CDCl_3$, 100 MHz) δ =148.0, 132.4, 130.0, 118.0, 114.4, 107.2, 92.7, 82.4, 51.7.

***p*-Toluidine (2o):**



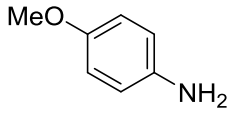
Known compound[13]; isolated yield = 90%; brown solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =2.24 (s, 3 H), 3.54 (s, 2 H), 6.62 (s, 2 H), 6.98 (s, 2 H).

4-(Tert-butyl)aniline (2p):



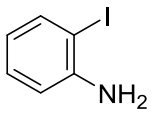
Known compound[14]; isolated yield = 53%; brown liquid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =1.33 (s, 9 H), 3.57 (s, 2 H), 6.68-6.70 (d, *J*= 7.6 Hz, 2 H), 7.22-7.24 (d, *J*= 7.6 Hz, 2 H).

4-Methoxy-aniline (2q):



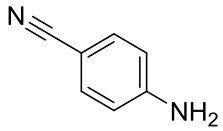
Known compound[13]; isolated yield = 49%; brown solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =3.34 (s, 2 H), 3.74 (s, 3 H), 6.63-6.65 (m, 2 H), 6.73-6.76 (m, 2 H).

2-Iodoaniline (2r):



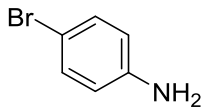
Known compound[15]; isolated yield = 80%; white solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.11 (s, 2 H), 6.48-6.52 (m, 2 H), 6.62-6.64 (d, *J*= 8.8 Hz, 2 H)

4-Aminobenzonitrile (2s):



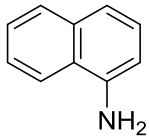
Known compound[13]; isolated yield = 69%; white solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.20 (s, 2 H), 6.62-6.64 (d, *J*= 8.8 Hz, 2 H), 7.38-7.40 (d, *J*= 8.8 Hz, 2 H).

4-Bromoaniline (2t):



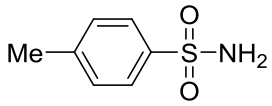
Known compound[13]; isolated yield = 65%; brown solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =3.67 (s, 2 H), 6.56-6.58 (d, *J*= 7.6 Hz, 2 H), 7.23-7.25 (d, *J*= 7.6 Hz, 2 H).

Naphthalene-1-amine (2u):



Known compound[13]; isolated yield = 64%; brown liquid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =4.15 (s, 2 H), 6.78-6.80 (m, 1 H), 7.28-7.35 (m, 2 H), 7.46-7.49 (m, 2 H), 7.81-7.83 (m, 2 H).

Toluene-4-sulfonamide (2v):



Known compound[16]; isolated yield = 69%; white solid; ^{1}H NMR($CDCl_3$, 400 MHz): δ =2.42 (s, 2 H), 4.96 (s, 2 H), 7.29-7.31 (d, *J*= 8 Hz, 2 H), 7.79-7.81 (d, *J*= 8 Hz, 2 H).

Figure 1. ^{1}H NMR and ^{13}C NMR Spectra of

2-Phenylethynylaniline (**2a**)

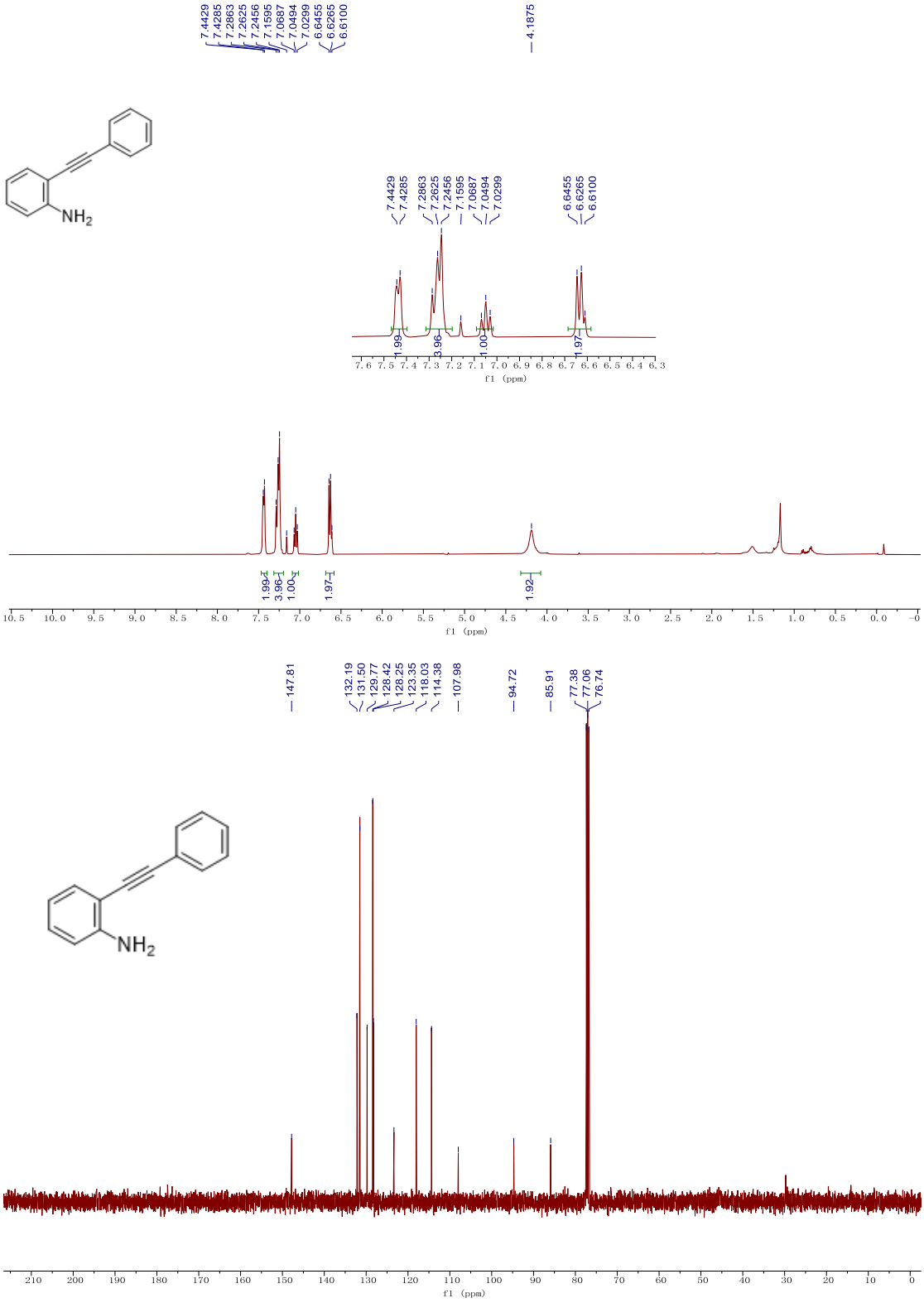
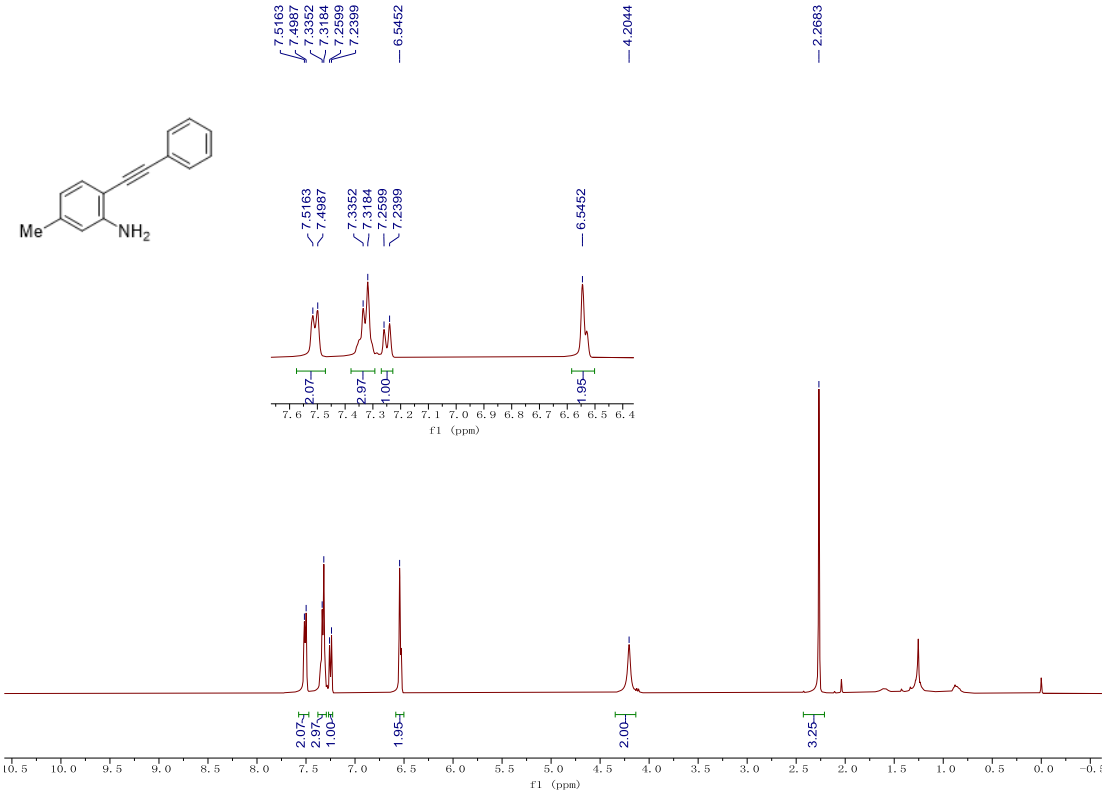


Figure 2. ^{1}H NMR and ^{13}C NMR Spectra of

5-Methyl-2-(phenylethynyl)aniline (**2b**)



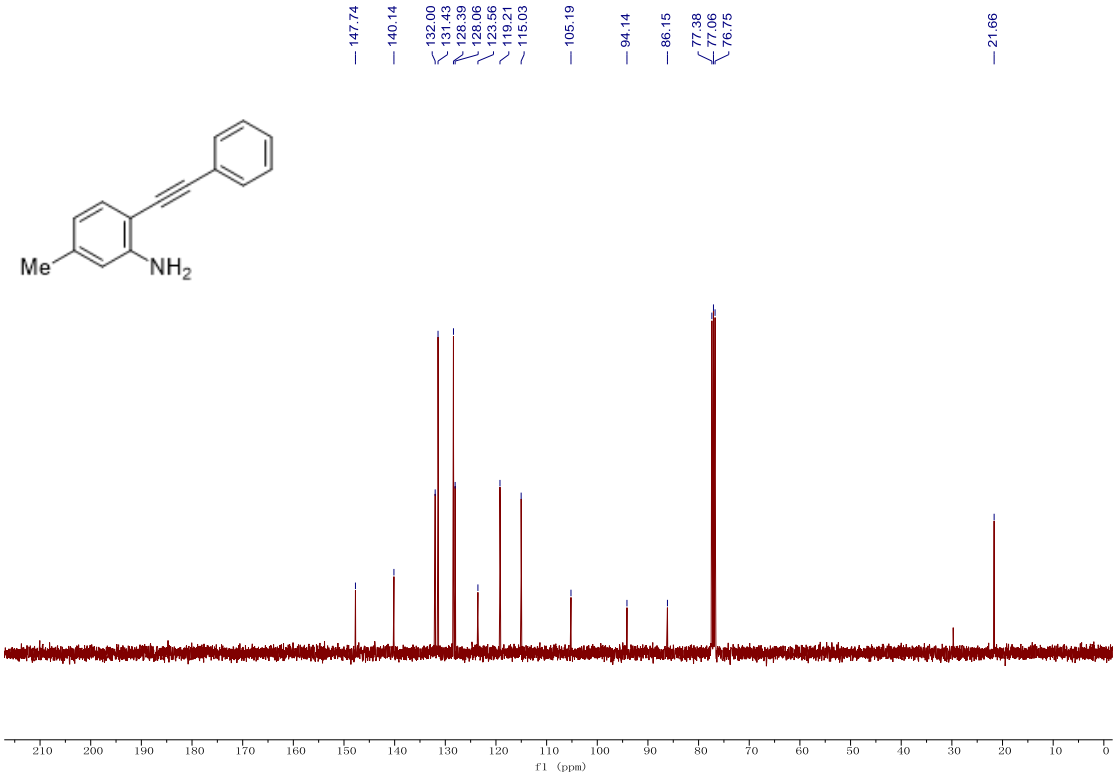


Figure 3. ^{1}H NMR and ^{13}C NMR Spectra of

4-Methyl-2-(phenylethynyl)aniline (**2c**)

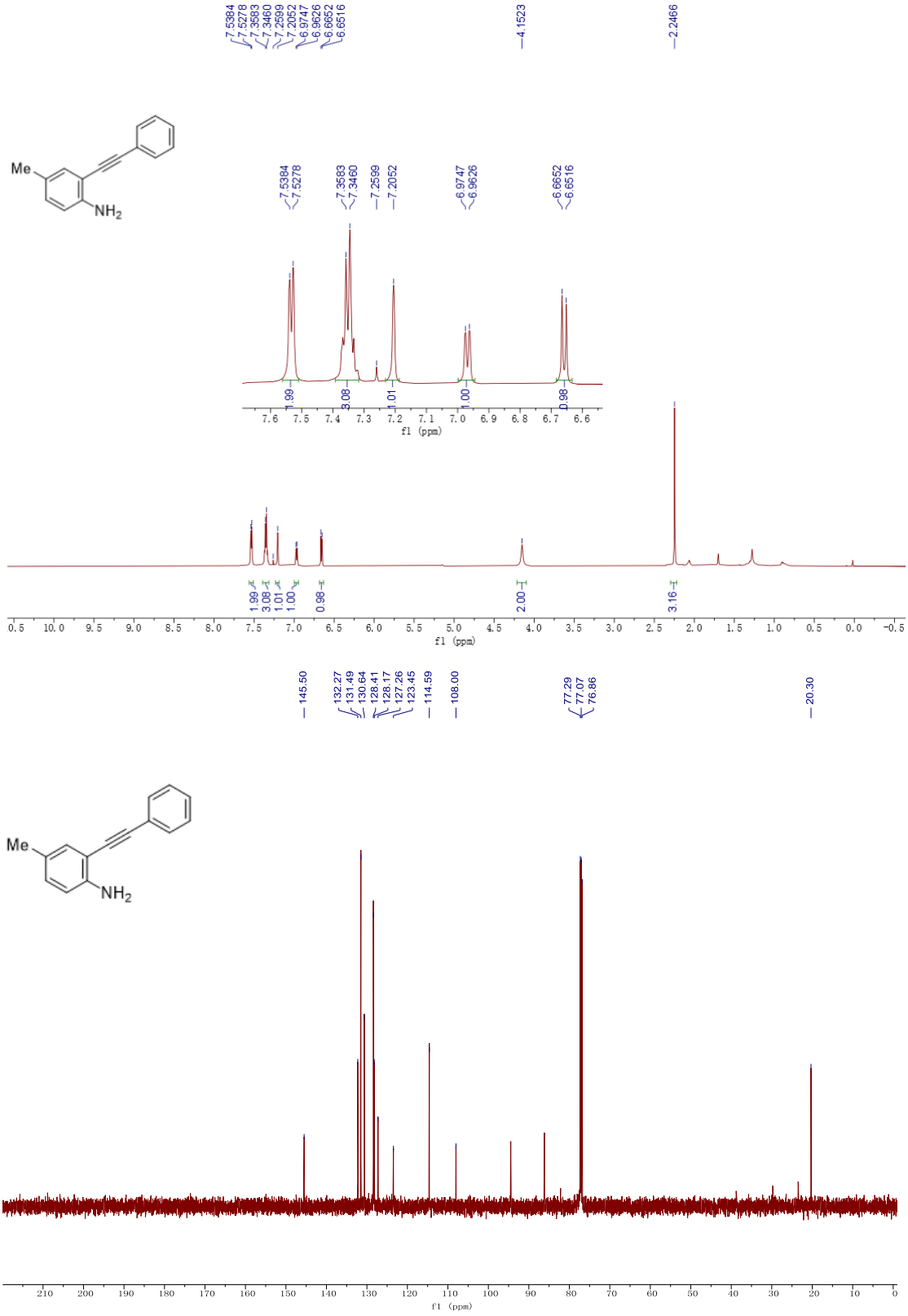


Figure 4. ^{1}H NMR and ^{13}C NMR Spectra of

5-Fluoro-2-(phenylethynyl)aniline (2d)

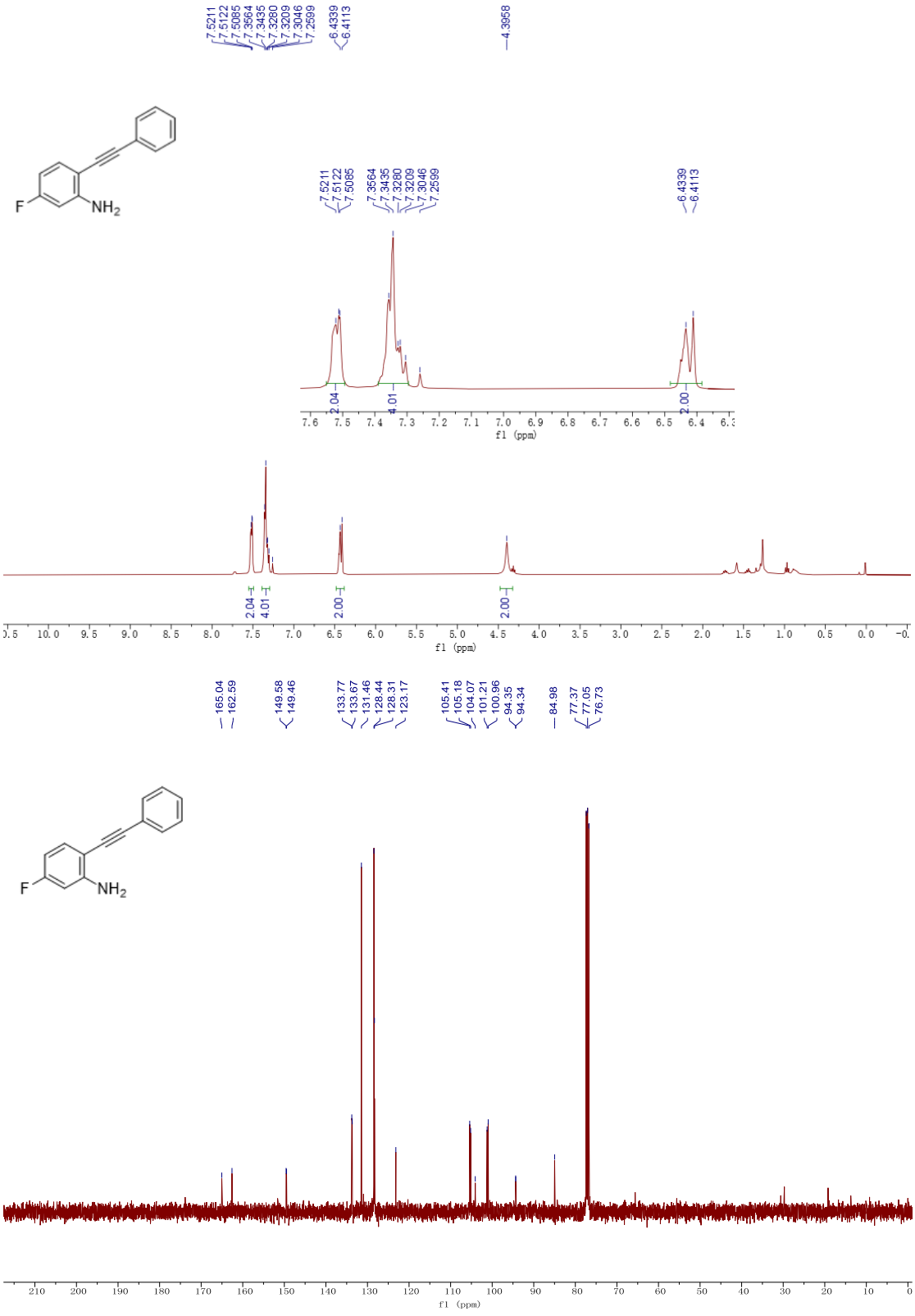


Figure 5. ^{1}H NMR and ^{13}C NMR Spectra of

5-Chloro-2-(phenylethynyl)aniline (**2e**)

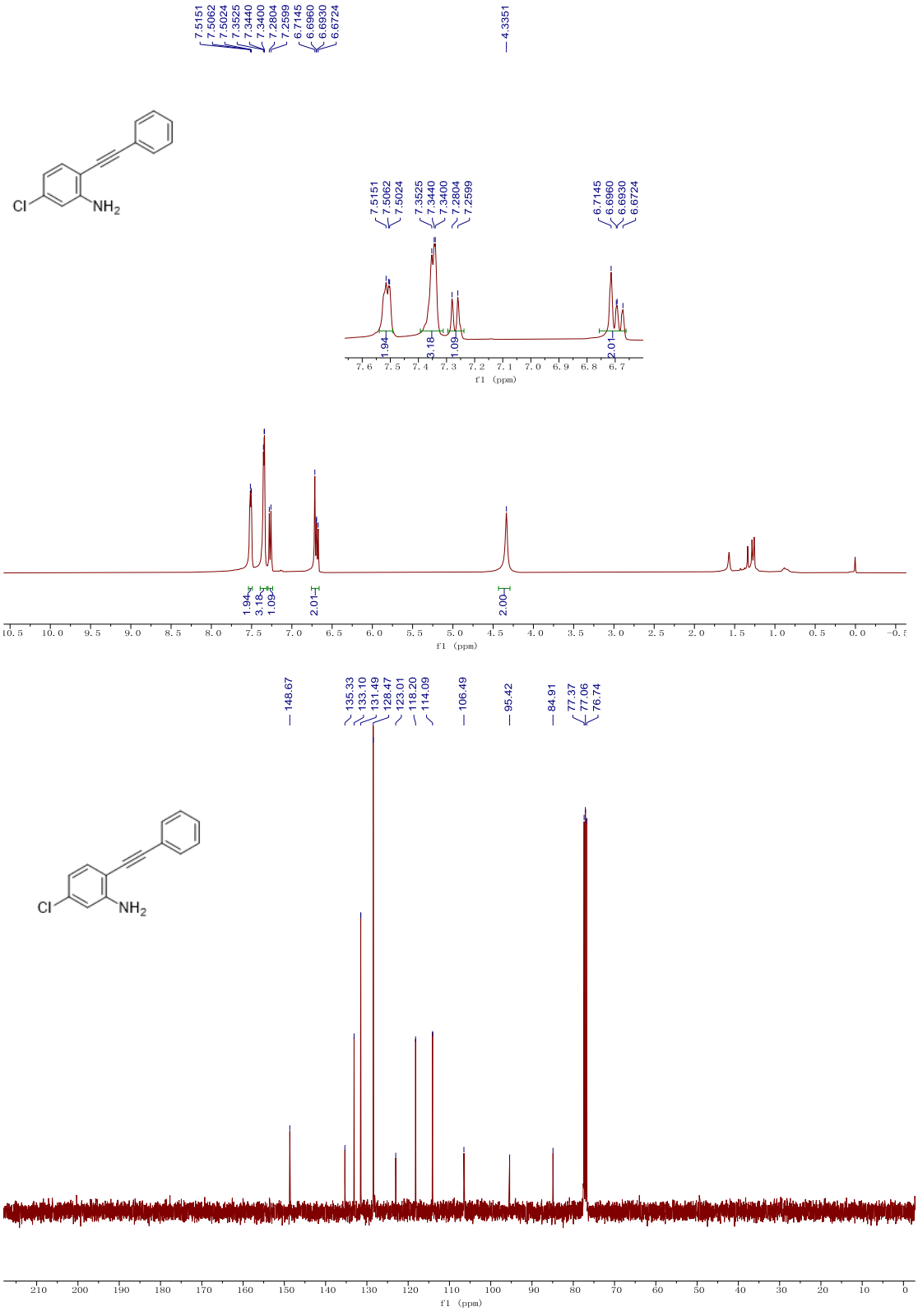


Figure 6. ^{1}H NMR and ^{13}C NMR Spectra of

2-(Phenylethynyl)-4-(trifluoromethyl)aniline (**2f**)

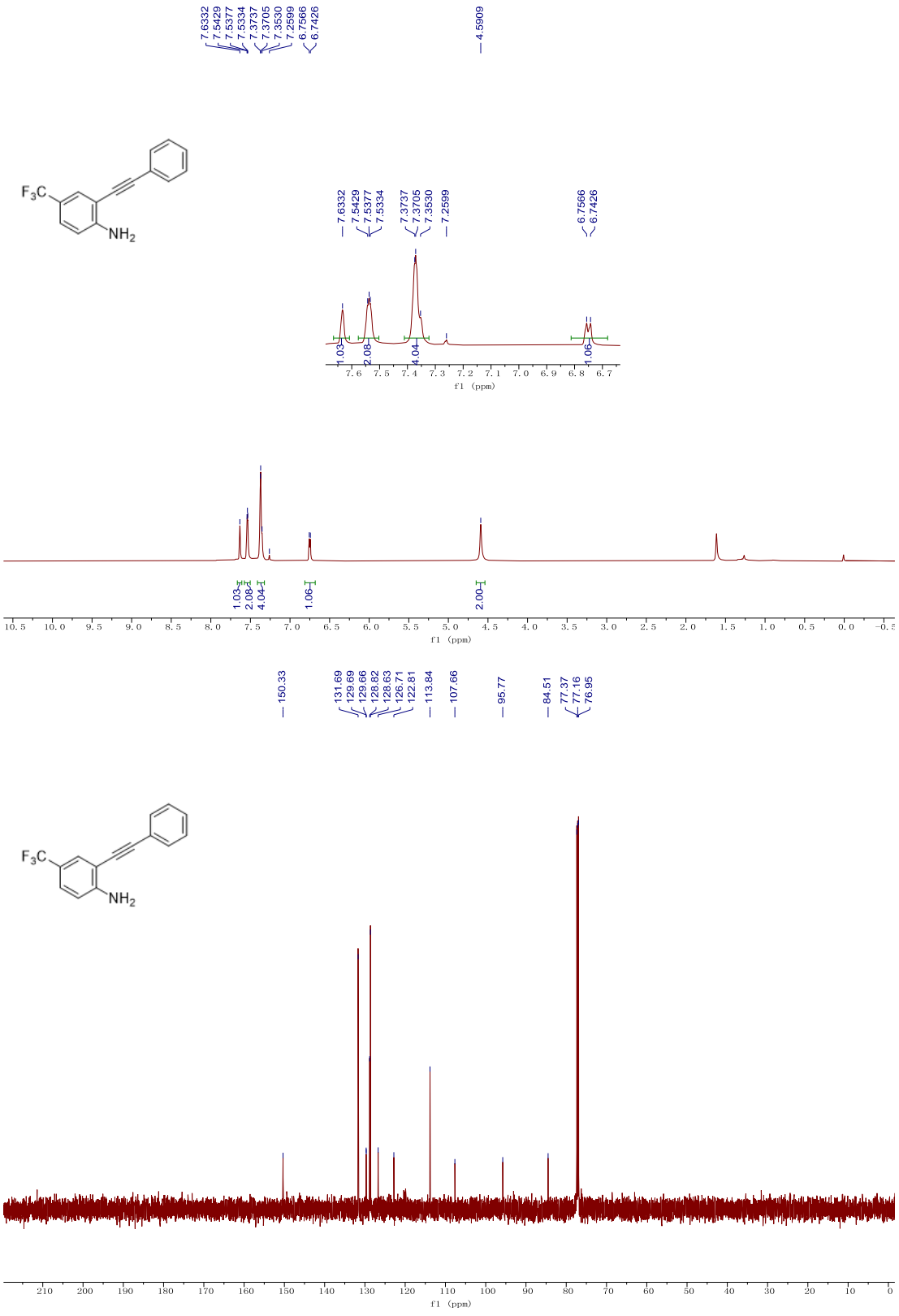


Figure 7. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 4-amino-3-(phenylethynyl)benzoate (2g)

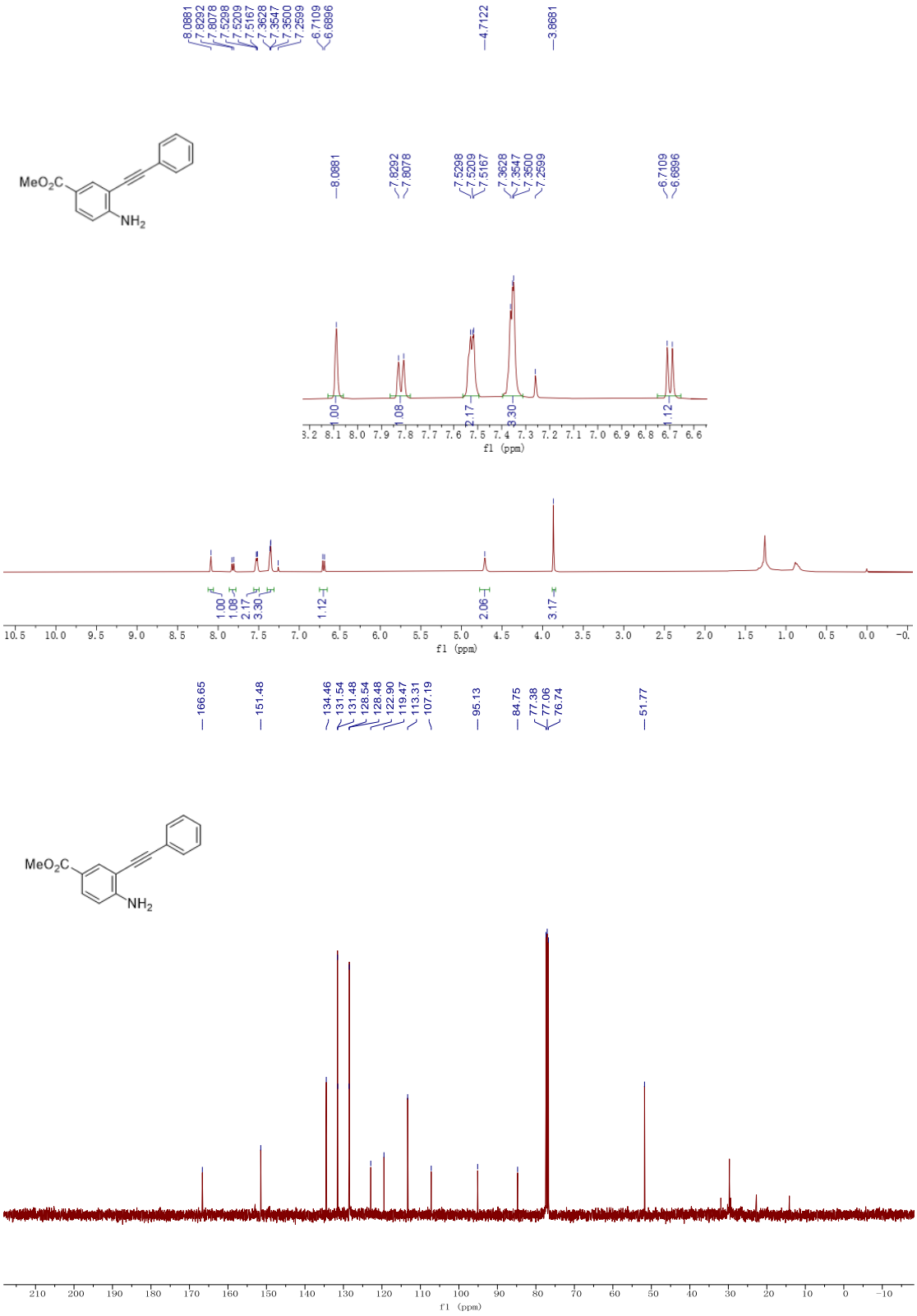


Figure 8. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-((4-ethylphenyl)ethynyl)aniline (**2h**)

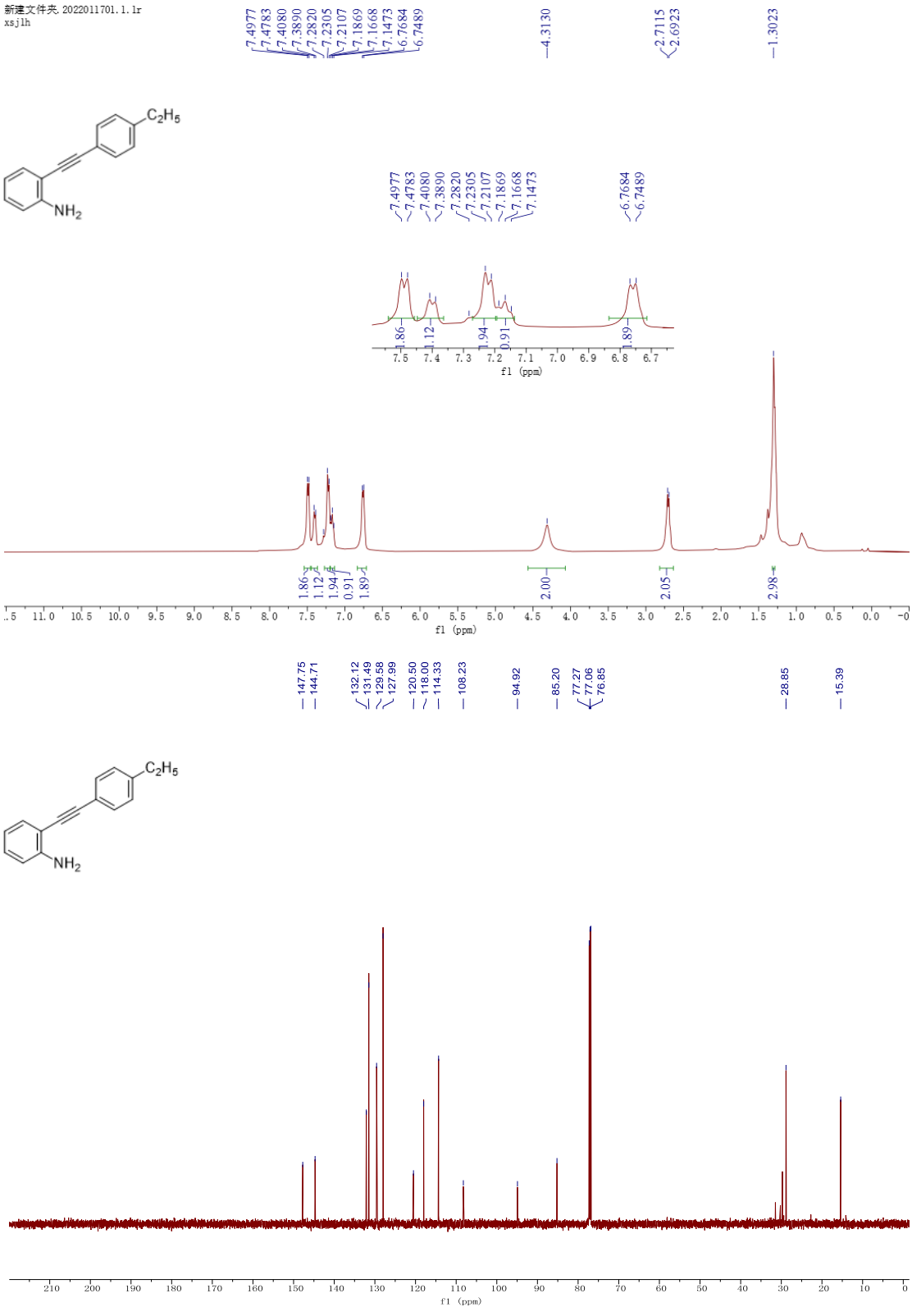


Figure 9. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-((4-pentylphenyl)ethynyl)aniline (**2i**)

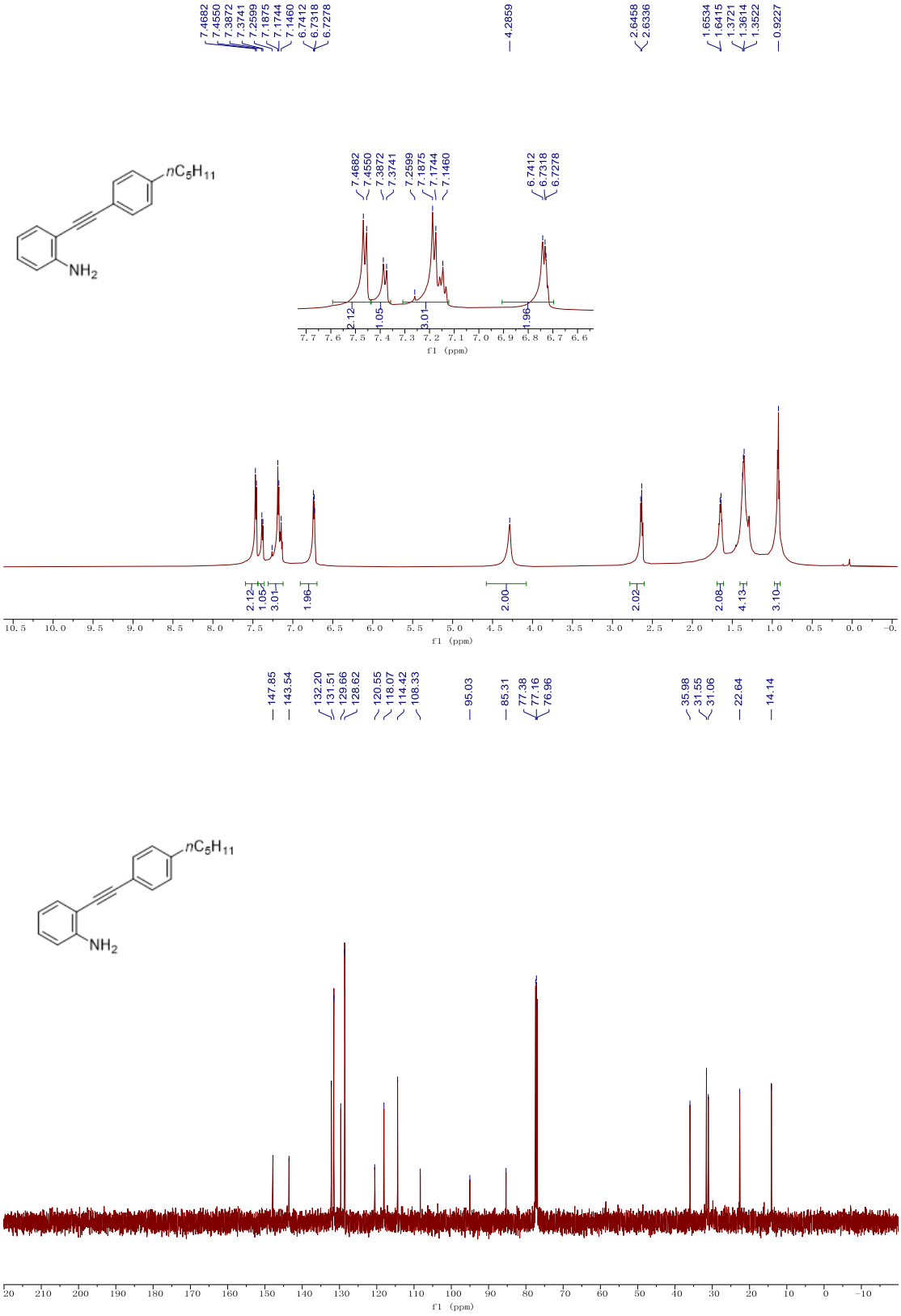


Figure 10. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-((4-chlorophenyl)ethynyl)aniline (2j)

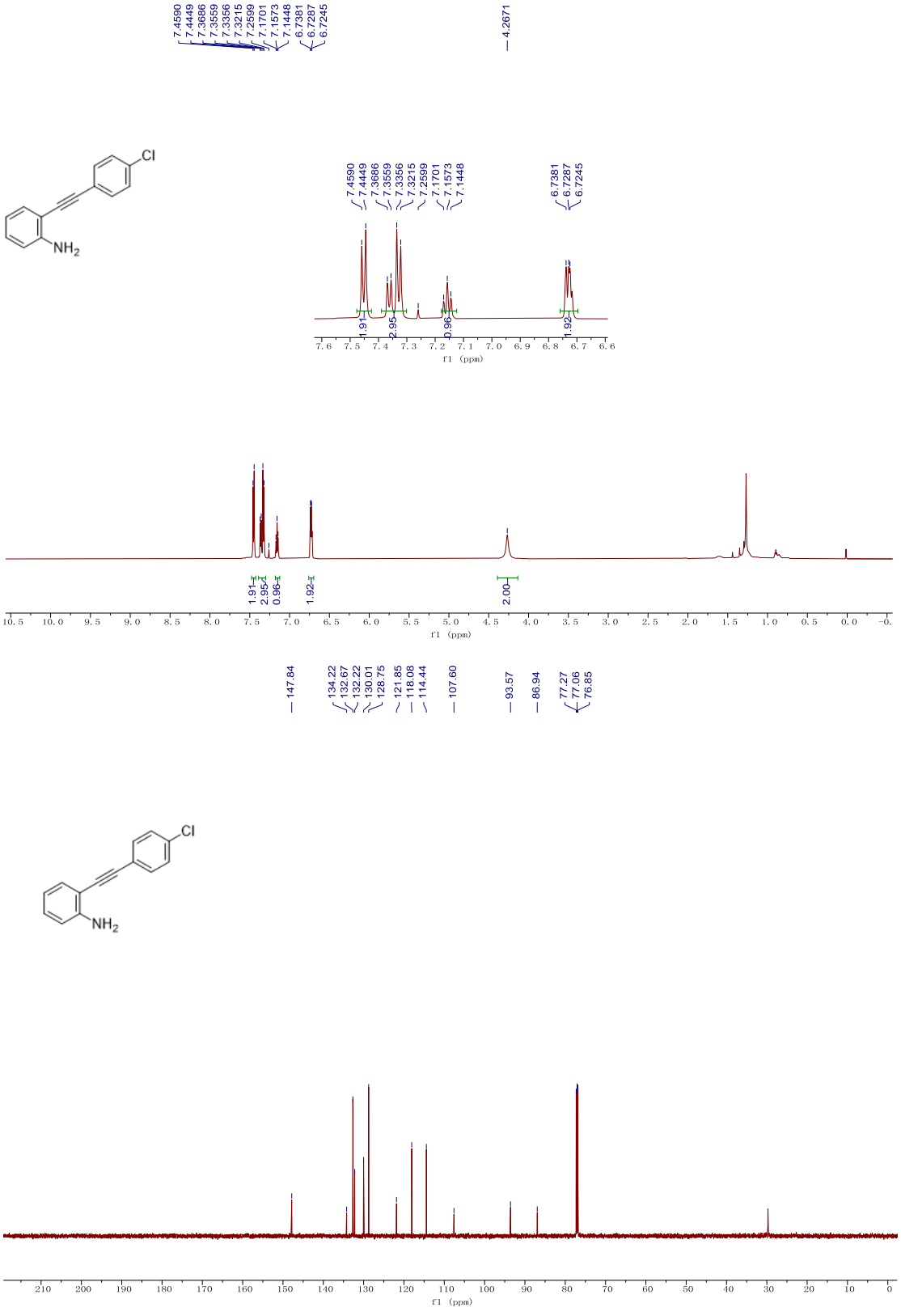


Figure 11. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-(Thiophen-2-ylethynyl)aniline (**2k**)

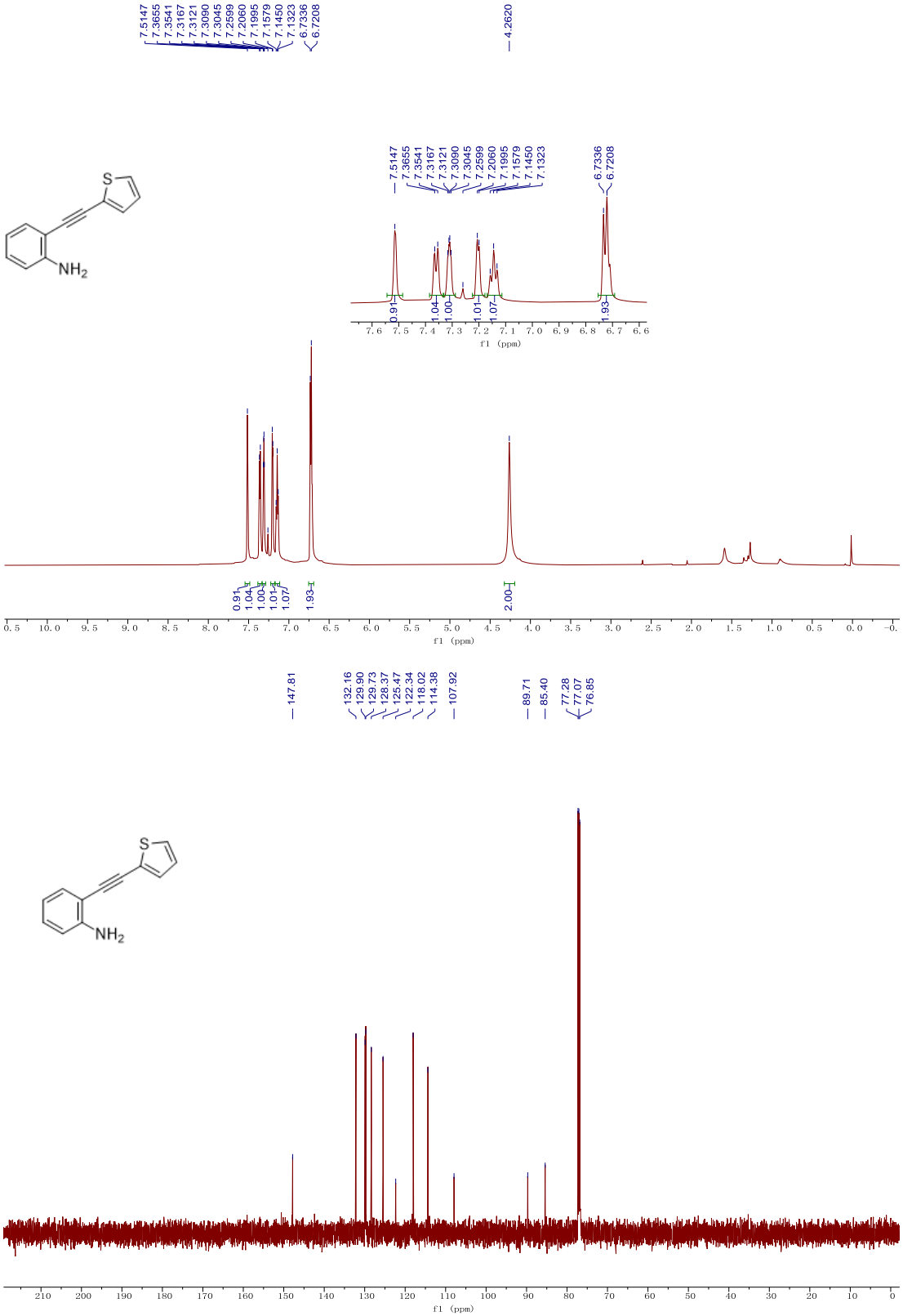


Figure 12. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-(cyclopropylethynyl)aniline (2l)

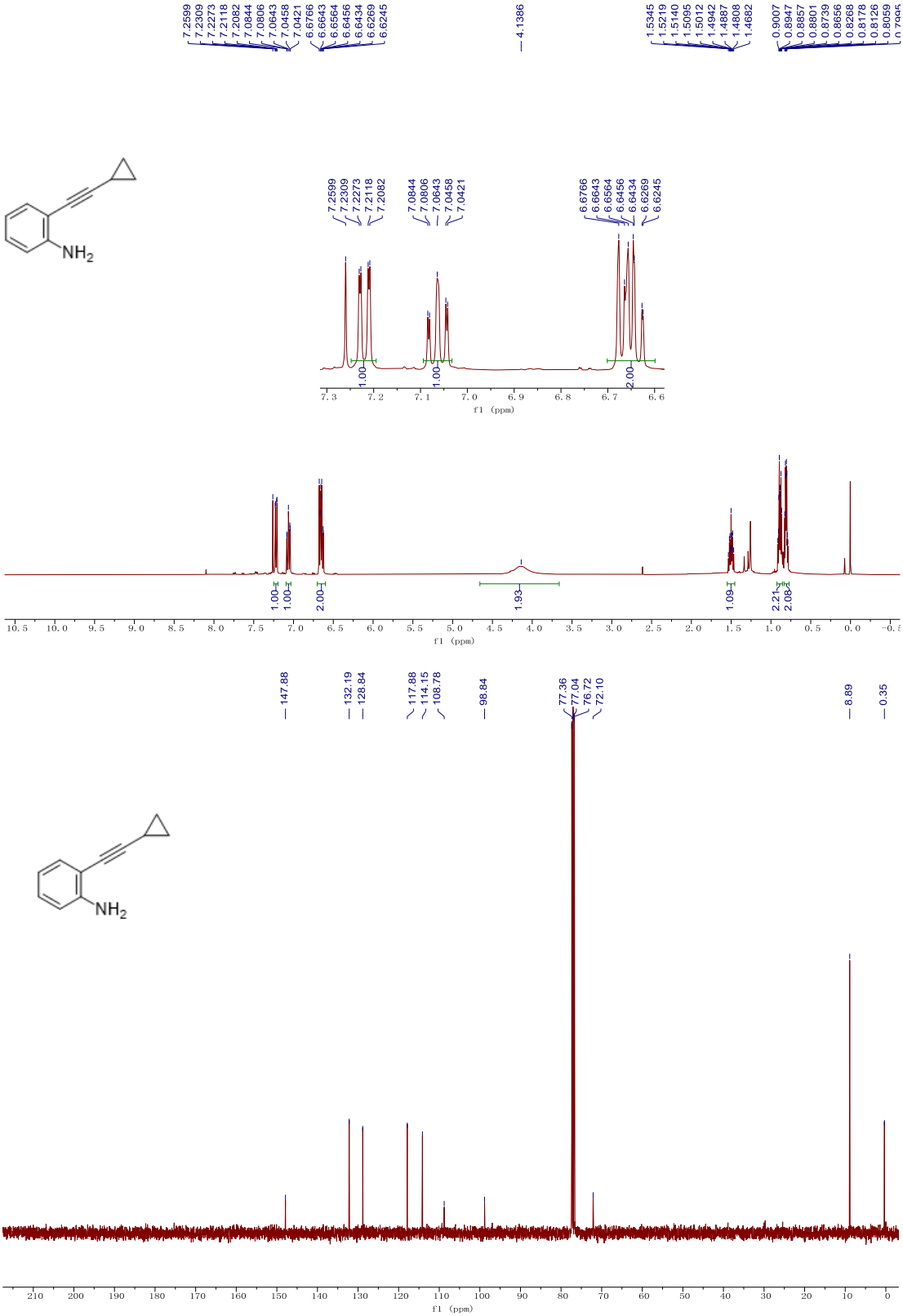


Figure 13. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-(3,3-dimethyl-1-butynyl)aniline (2m)

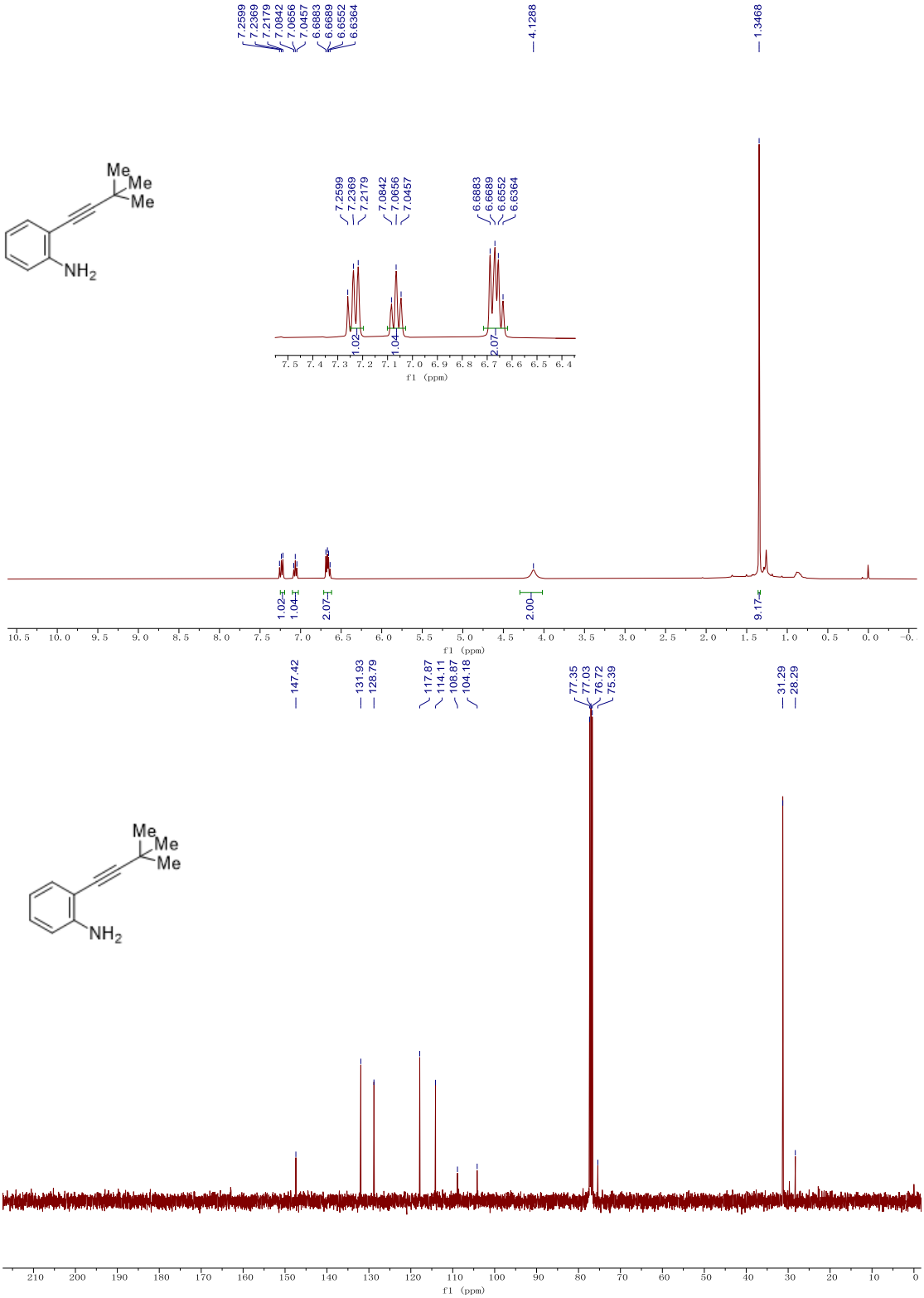
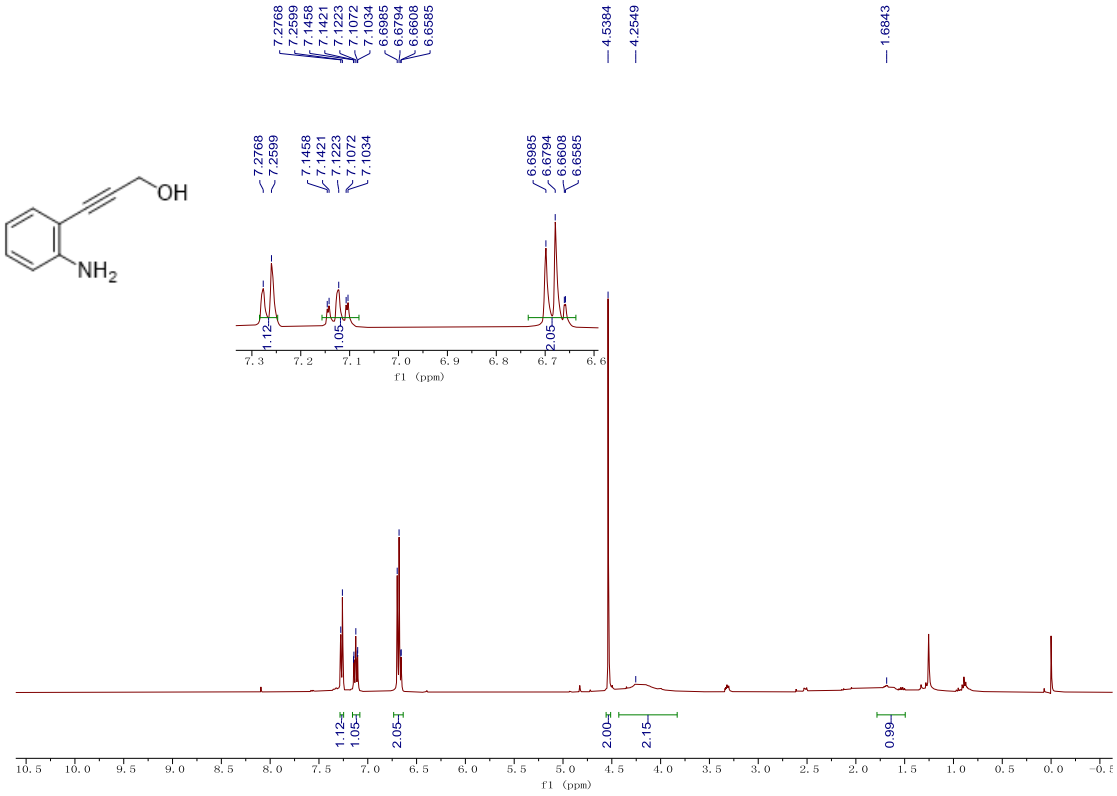


Figure 14. ^{1}H NMR and ^{13}C NMR Spectra of

Methyl 2-(2-(hydroxymethyl)ethynyl)aniline (**2n**)



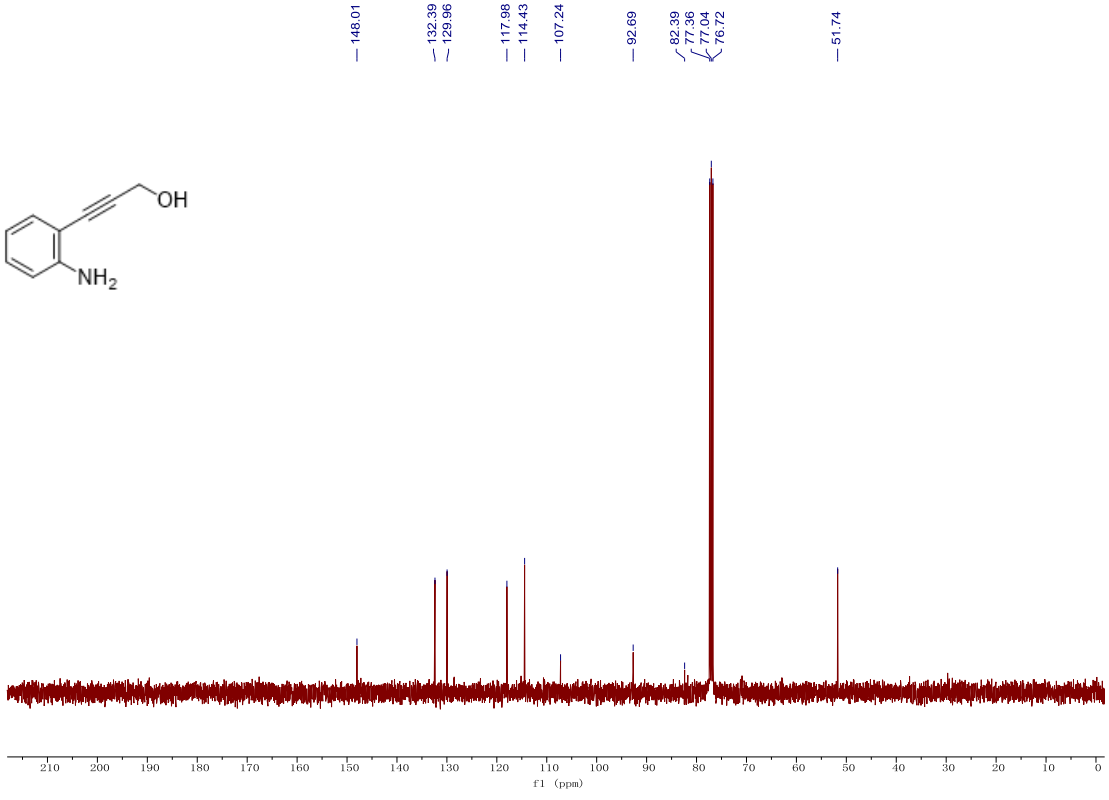


Figure 15. ^{1}H NMR Spectra of

Methyl p-toluidine (**2o**)

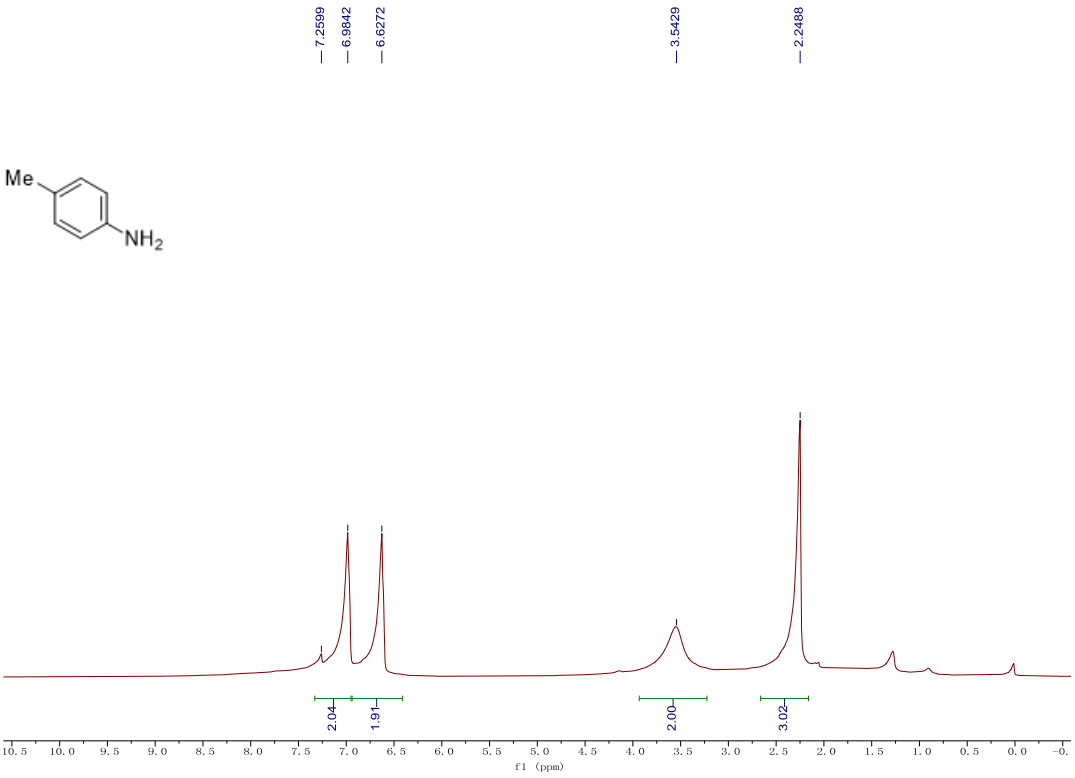


Figure 16. ^{1}H NMR Spectra of

Methyl 4-(tert-butyl)aniline (**2p**)

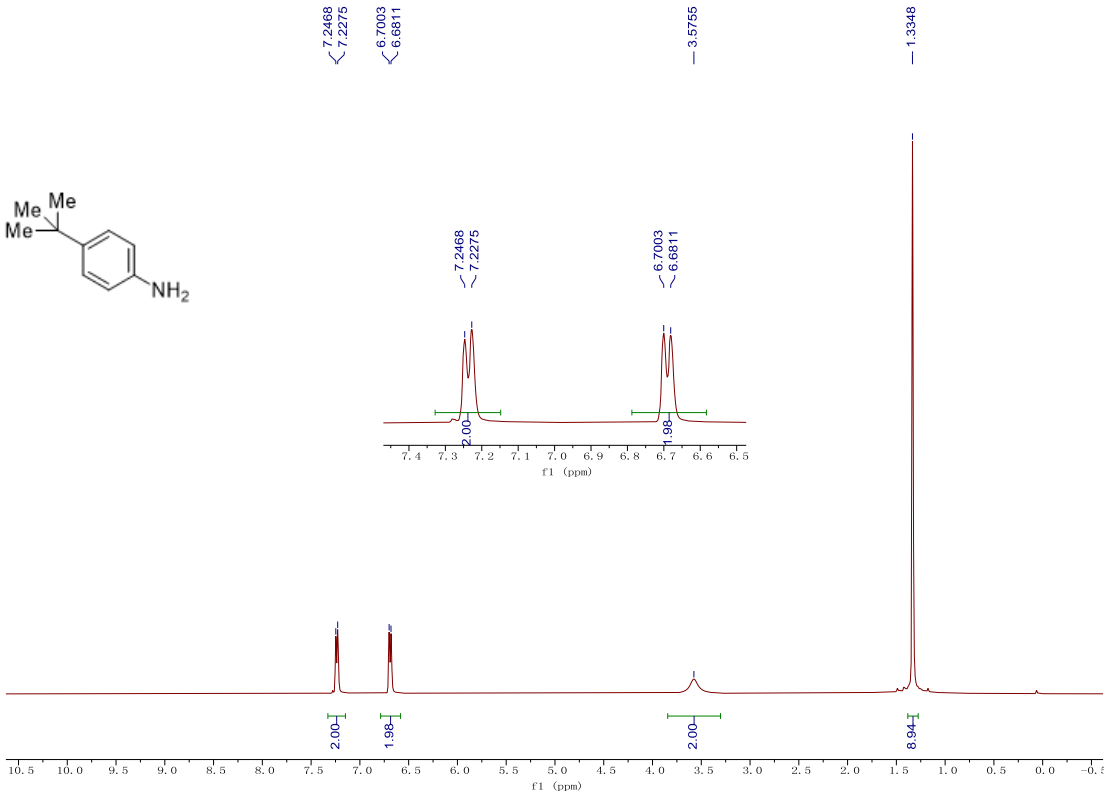


Figure 17. ^{1}H NMR Spectra of

Methyl 4-methoxy-aniline (2q)

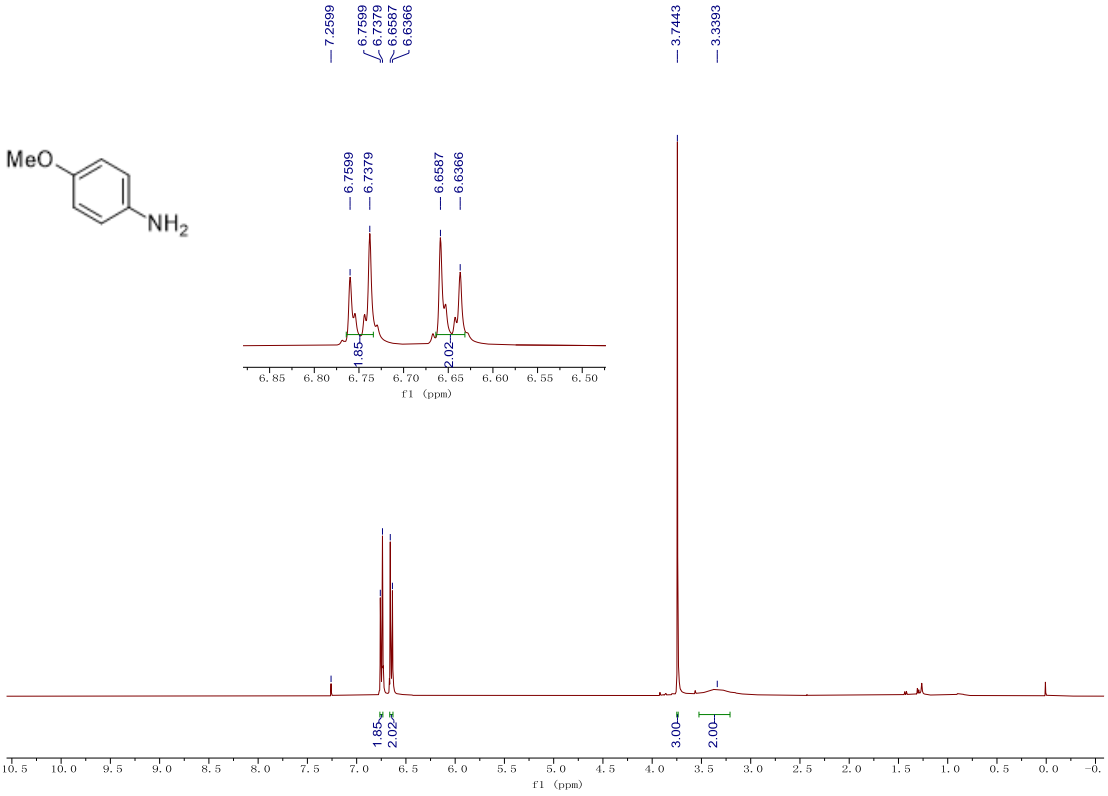


Figure 18. ^{1}H NMR Spectra of

Methyl 1,4-phenylenediamine (2r)

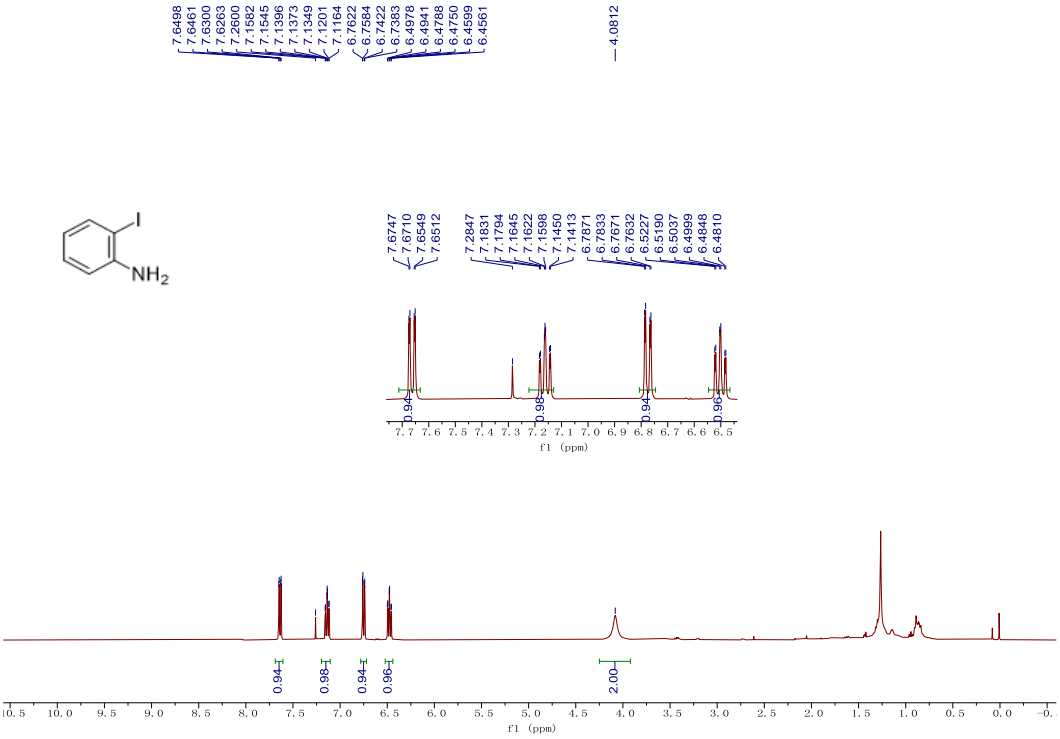


Figure 19. ^{1}H NMR Spectra of

Methyl 4-Aminobenzonitrile (**2s**)

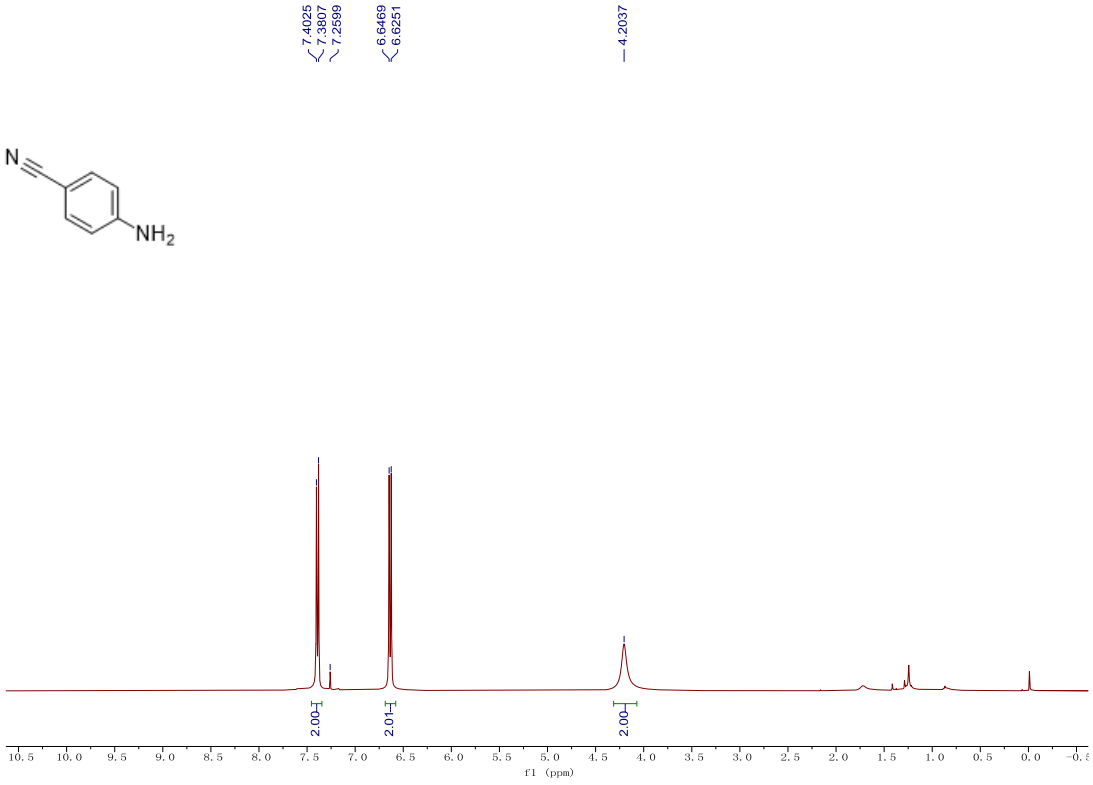


Figure 20. ^{1}H NMR Spectra of

Methyl 4-Bromoaniline (**2t**)

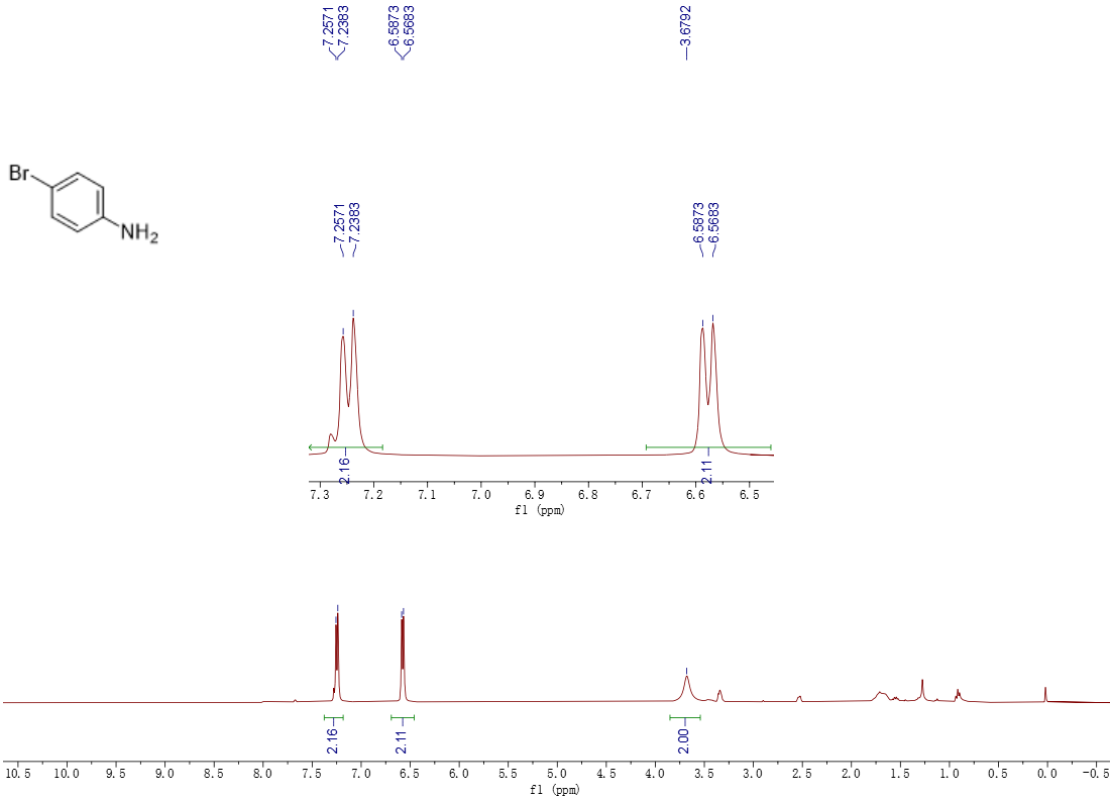


Figure 21. ^{1}H NMR Spectra of

Methyl Naphthalene-1-amine (**2u**)

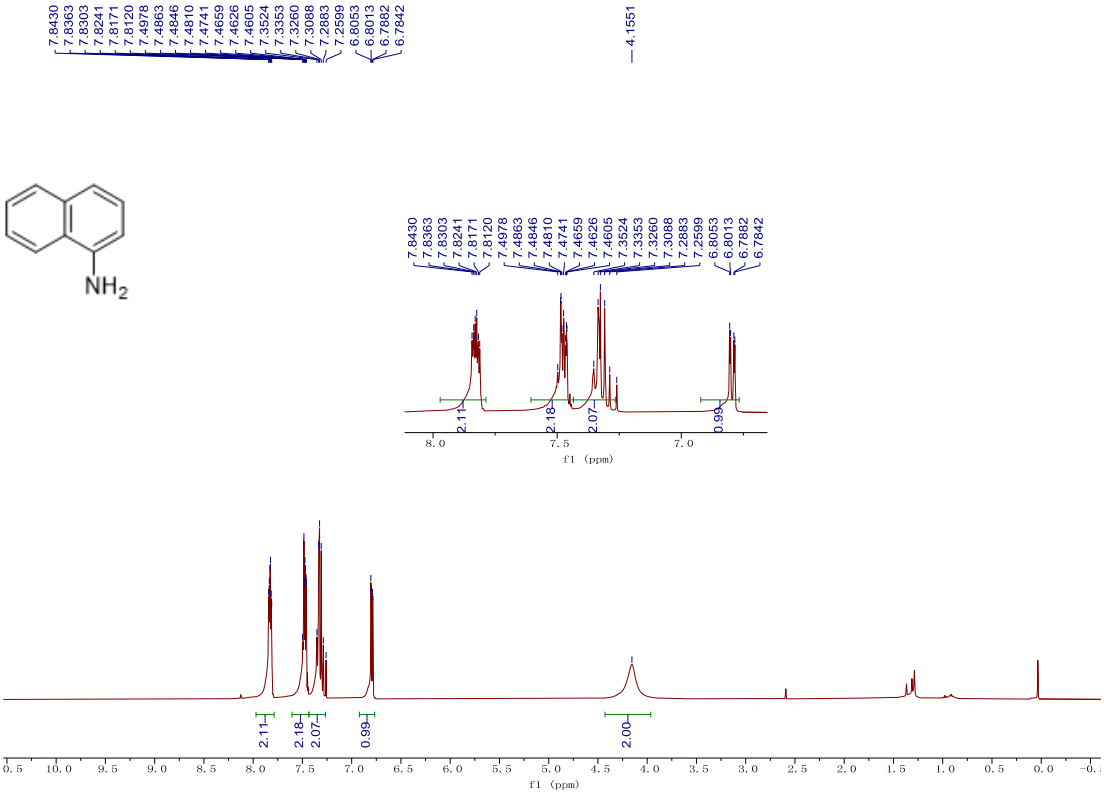
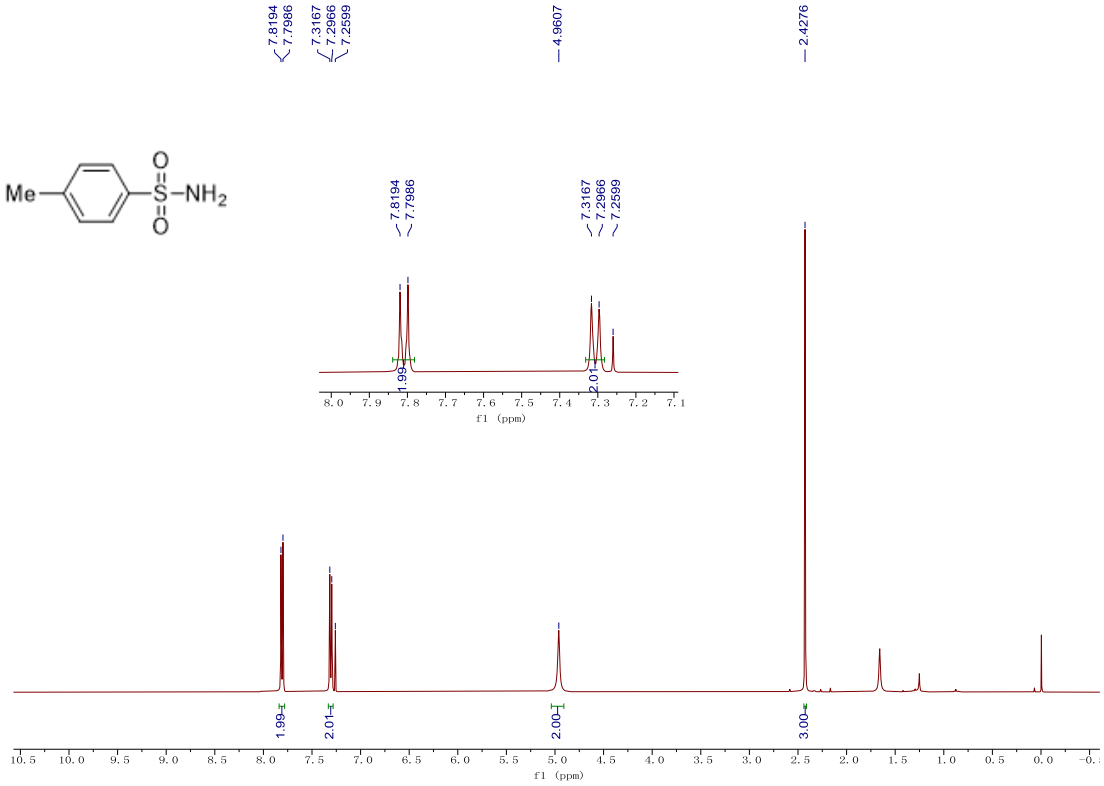


Figure 22. ^{1}H NMR Spectra of

Toluene-4-sulfonamide (**2v**)



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