

Nickel-Catalyzed Highly Efficient Chemoselective Reduction of Azoarenes to Hydrazoarenes in Water

Dawei Gong,^{*,[a]} Qixuan Li,^[a] Yufei Li,^[a] Qinghua Yang,^[a] Caiyu Gao,^[a] Jiku Wang,^{*,[a]} and Lina Zhao ^{*,[a]}

^a Key Laboratory of Preparation and Application of Environmental Friendly Materials, Ministry of Education, College of Chemistry, Jilin Normal University, Changchun, 130103, P.R. of China

Email: dawei.gong@jlnu.edu.cn

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1. General Procedure

General Procedure for Transfer Hydrogenation of Azoarenes. Ni complexes **1a-1e** were prepared as previously described.^[1-2] A solution of Ni-catalyst, azoarenes (27.3 mg, 0.15 mmol, 1.0 equiv.), NH_3BH_3 (1.5-2.0 equiv.), H_2O (0.5 mL) and THF (0.05 mL) were reacting under an N_2 atmosphere at 60 °C for 20 min. Then the solution was quenched saturated K_2CO_3 until the mixture became colourless. The mixture was extracted with EtOAc (3 mL x 3) and reduced in vacuo to give the hydrazoarenes products.

Transfer Hydrogenation of Azoarenes with NH_3BH_3 in THF. A solution of **1a** (5 mol%, 2.3 mg), azoarenes (27.3 mg, 0.15 mmol, 1.0 equiv.), NH_3BH_3 (7.0 mg, 0.22 mmol, 1.5 equiv.) and THF (0.5 mL) were reacting under an N_2 atmosphere at 60 °C for 20 min. After cooling to RT, the mixture was reduced in vacuo. No product was observed by TLC and ^1H NMR.

Transfer Hydrogenation of Azoarenes with ND_3BH_3 . A solution of **1a** (5 mol%, 2.3 mg), azoarenes (27.3 mg, 0.15 mmol, 1.0 equiv.), ND_3BH_3 (7.0 mg, 0.22 mmol, 1.5 equiv.), H_2O (0.5 mL) and THF (0.05 mL) were reacting under an N_2 atmosphere at 60 °C for 20 min. After cooling to RT, the mixture was extracted with EtOAc (3 mL x 3) and reduced in vacuo to give the hydrazoarenes products.

Transfer Hydrogenation of Azoarenes in D_2O . A solution of **1a** (5 mol%, 2.3 mg), azoarenes (27.3 mg, 0.15 mmol, 1.0 equiv.), NH_3BH_3 (7.0 mg, 0.22 mmol, 1.5 equiv.) and D_2O (0.5 mL) were reacting under an N_2 atmosphere at 100 °C for 20 min. After cooling to RT, the mixture was extracted with EtOAc (3 mL x 3) and reduced in vacuo to give the hydrazoarenes products. The product was identified by ^1H NMR. **3a-d1**: ^1H NMR (400 MHz, CDCl_3 , ppm): 7.25-7.21 (m, 4H), 6.88-6.83 (m, 6H), 5.62 (s, 1.03 H).

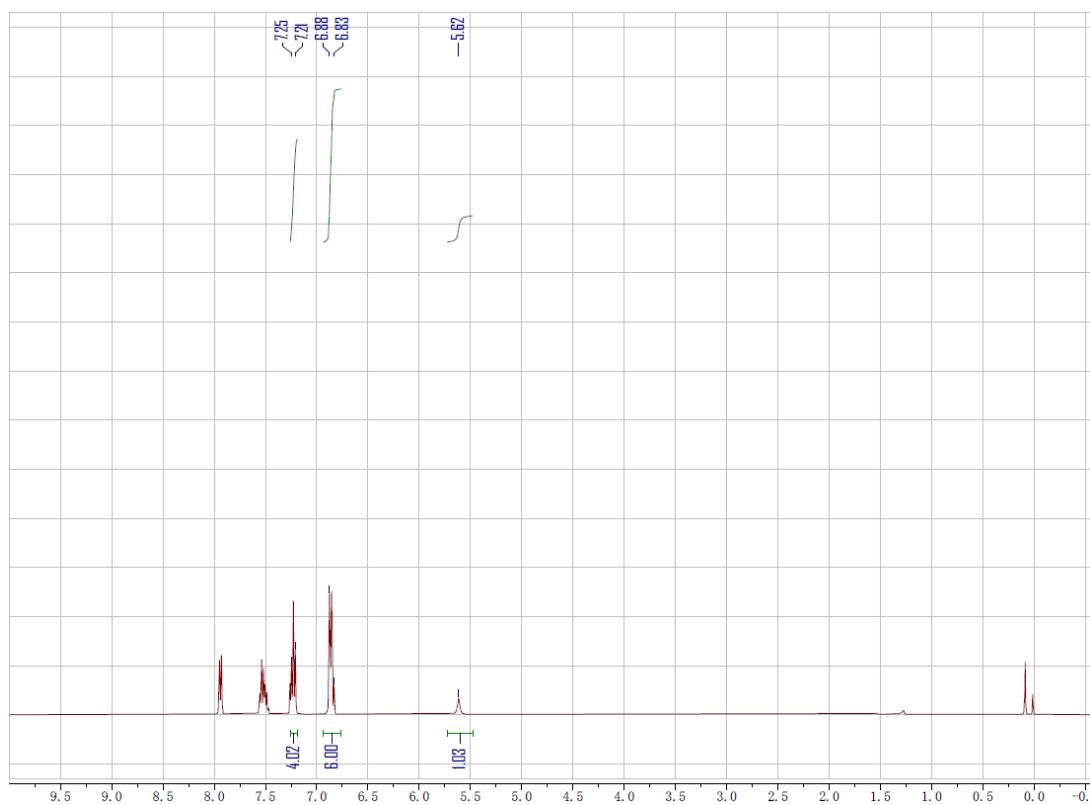
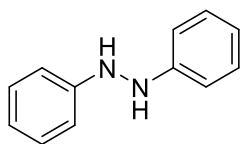
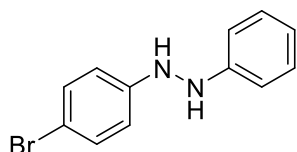


Figure S1. ¹H NMR Spectrum of **3a-d1**

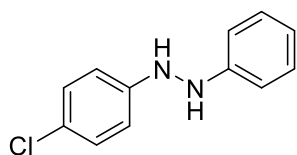
2. NMR data



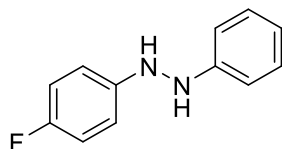
1,2-diphenylhydrazine (3a)^[3]: White powder (26.3mg, 95%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.29-7.25 (m, 4H), 6.91-6.87 (m, 6H), 5.64 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.8, 129.4, 119.9, 112.3.



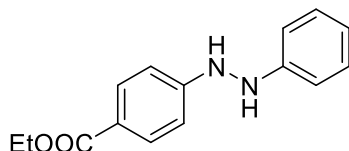
1-(4-bromophenyl)-2-phenylhydrazine (3b)^[3]: White powder (37.9mg, 96%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.34-7.32 (m, 2H), 7.28-7.24 (m, 2H), 6.91-6.83 (m, 3H), 6.79-6.77 (m, 2H), 5.65 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.3, 147.9, 132.1, 129.4, 120.2, 113.9, 112.3, 111.5.



1-(4-chlorophenyl)-2-phenylhydrazine (3c)^[3]: White powder (30.2 mg, 92%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.28-7.18 (m, 4H), 6.91-6.81 (m, 5H), 5.65 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.4, 147.4, 129.4, 129.2, 124.4, 120.2, 113.5, 112.3.

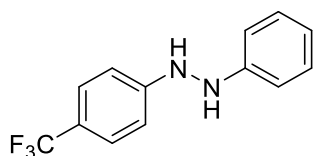


1-(4-fluorophenyl)-2-phenylhydrazine (3d)^[3]: White powder (26.7 mg, 88%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.28-7.24 (m, 2H), 6.97-6.93 (m, 2H), 6.90-6.82 (m, 5H), 5.65 (s, 1H), 5.57 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 158.3, 155.9, 148.7, 145.0, 129.4, 120.0, 115.9, 115.7, 113.4, 112.3.

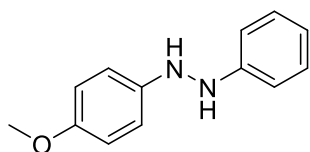


ethyl 4-(2-phenylhydrazineyl)benzoate (3e)^[4]: White powder (34.2 mg, 89%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.95-7.93 (m, 2H), 7.28-7.23 (m, 2H), 6.91-6.83 (m, 5H), 5.98 (s, 1H), 5.75 (s, 1H), 4.37-4.32 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 166.6, 152.7,

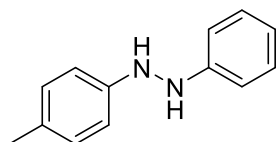
148.0, 131.5, 129.4, 121.4, 120.4, 112.4, 111.1, 60.4, 14.4.



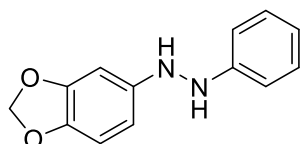
1-phenyl-2-(4-(trifluoromethyl)phenyl)hydrazine (3f)^[3]: White powder (35.2 mg, 93%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.50-7.48 (m, 2H), 7.29-7.25 (m, 2H), 6.94-6.84 (m, 5H), 5.88 (s, 1H), 5.71 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 151.5, 148.0, 129.5, 126.85, 126.81, 126.77, 126.73, 120.4, 112.3, 111.5.



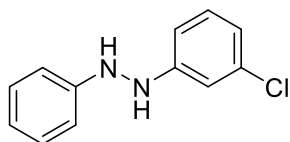
1-(4-methoxyphenyl)-2-phenylhydrazine (3g)^[5]: White powder (29.2 mg, 91%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.28-7.17 (m, 2H), 6.89-6.86 (m, 2H), 6.83-6.81 (m, 3H), 6.79-6.77 (m, 1H), 6.73-6.68 (m, 1H), 5.63 (s, 1H), 5.48 (s, 1H), 3.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 153.7, 149.1, 142.7, 129.3, 119.7, 116.5, 115.1, 114.8, 113.7, 112.3, 55.7.



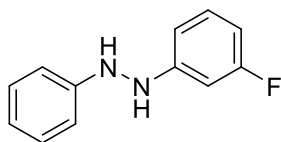
1-phenyl-2-(p-tolyl)hydrazine (3h)^[4]: White powder (26.8 mg, 90%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.28-7.23 (m, 2H), 7.07-7.06 (m, 2H), 6.90-6.85 (m, 3H), 6.81-6.79 (m, 2H), 5.62 (s, 1H), 5.56 (s, 1H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 149.0, 146.5, 129.8, 129.3, 129.2, 119.8, 112.5, 112.3, 20.5.



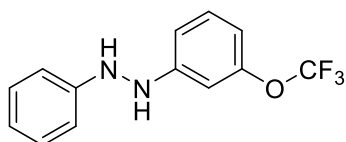
1-(benzo[d][1,3]dioxol-5-yl)-2-phenylhydrazine (3i): Colorless oil (30.8 mg, 90%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.28-7.23 (m, 2H), 6.88-6.85 (m, 3H), 6.71-6.69 (m, 1H), 6.52 (s, 1H), 6.33-6.31 (m, 1H), 5.90 (s, 2H), 5.62 (s, 1H), 5.49 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.9, 148.5, 144.5, 141.3, 129.3, 119.9, 112.3, 108.6, 106.8, 104.1, 100.7, 98.1, 95.4.



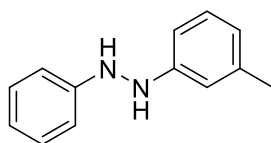
1-(3-chlorophenyl)-2-phenylhydrazine (3j)^[4]: White powder (28.5 mg, 87%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.29-7.25 (m, 2H), 7.18-7.14 (m, 1H), 6.92-6.82 (m, 5H), 6.76-6.74 (m, 1H), 5.65 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 150.2, 148.3, 135.2, 130.4, 129.4, 120.2, 119.8, 112.3, 112.2, 110.4.



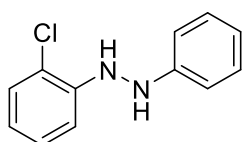
1-(3-fluorophenyl)-2-phenylhydrazine (3k)^[3]: White powder (27.3 mg, 90%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.29-7.25 (m, 2H), 7.21-7.15 (m, 1H), 6.92-6.85 (m, 3H), 6.65-6.62 (m, 2H), 6.57-6.53 (m, 1H), 5.71 (s, 1H), 5.66 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 165.3, 162.9, 150.9, 150.8, 148.3, 130.6, 129.4, 120.2, 112.3, 107.8, 106.4, 99.6.



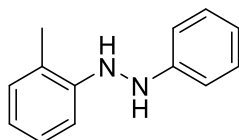
1-phenyl-2-(3-(trifluoromethoxy)phenyl)hydrazine(3l)^[4]: Colorless oil (37.8 mg, 94%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.28-7.20 (m, 3H), 6.91-6.85 (m, 3H), 6.80-6.76 (m, 2H), 6.71-6.68 (m, 1H), 5.75 (s, 1H), 5.68 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 150.5, 148.2, 130.4, 129.4, 121.7, 120.3, 119.1, 112.3, 111.6, 110.3, 104.8.



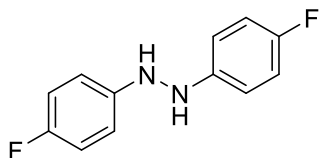
1-phenyl-2-(m-tolyl)hydrazine (3m)^[4]: White powder (26.5 mg, 89%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.27-7.23 (m, 2H), 7.15-7.11 (m, 1H), 6.90-6.85 (m, 3H), 6.82-6.68 (m, 3H), 5.63 (s, 1H), 5.60 (s, 1H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.98, 148.94, 139.3, 129.3, 129.2, 120.8, 119.8, 112.9, 112.3, 109.4, 21.6.



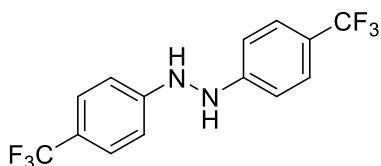
1-(2-chlorophenyl)-2-phenylhydrazine (3n)^[3]: Colorless oil (31.2 mg, 95%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.32-7.30 (m, 1H), 7.29-7.24 (m, 2H), 7.17-7.13 (m, 1H), 7.07-7.05 (m, 1H), 6.90-6.77 (m, 4H), 6.22 (s, 1H), 5.68 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.2, 144.3, 129.4, 129.3, 127.9, 120.2, 119.8, 117.7, 113.0, 112.3.



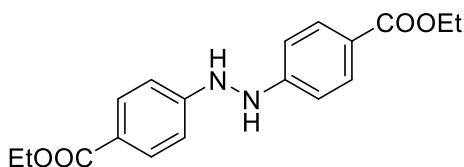
1-phenyl-2-(o-tolyl)hydrazine (3o)^[4]: Colorless oil (26.8 mg, 90%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.26-7.23 (m, 2H), 7.14-7.10 (m, 2H), 6.98-6.95 (m, 1H), 6.89-6.78 (m, 4H), 5.62 (s, 1H), 5.59 (s, 1H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.8, 146.2, 130.4, 129.3, 129.0, 127.2, 119.9, 119.4, 112.3, 111.1, 17.1.



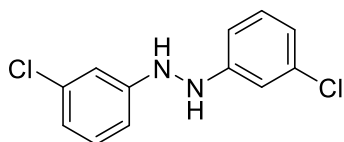
1,2-bis(4-fluorophenyl)hydrazine (3p)^[3]: White powder (28.7 mg, 87%). ¹H NMR (400 MHz, CDCl₃, ppm): 6.96-6.93 (m, 4H), 6.83-6.80 (m, 4H), 5.58 (s, 2H) ¹³C NMR (100 MHz, CDCl₃, ppm): 158.3, 156.0, 144.9, 144.8, 116.0, 115.7, 113.4, 113.3.



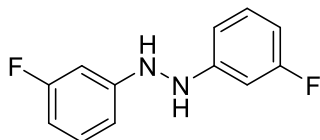
1,2-bis(4-(trifluoromethyl)phenyl)hydrazine (3q)^[4]: White powder (45.6 mg, 95%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.51-7.49 (m, 4H), 6.91-6.89 (m, 4H), 5.98 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 150.7, 126.95, 126.91, 126.87, 126.84, 125.9, 123.2, 122.2, 121.9, 111.6.



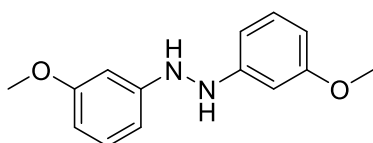
diethyl 4,4'-(hydrazine-1,2-diyl)dibenzoate (3r)^[4]: White powder (43.3 mg, 88%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.93-7.90 (m, 4H), 6.82-6.80 (m, 4H), 6.22 (s, 2H), 4.35-4.30 (m, 4H), 1.37 (t, *J* = 8.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 166.6, 152.0, 131.5, 121.8, 111.2, 60.5, 14.4.



1,2-bis(3-chlorophenyl)hydrazine (3s)^[4]: White powder (34.9 mg, 92%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.18-7.14 (m, 2H), 6.87-6.84 (m, 4H), 6.73-6.71 (m, 2H), 5.69 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 149.6, 135.3, 130.5, 120.1, 112.2, 110.4.

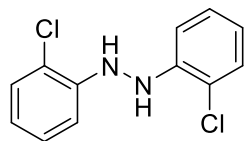


1,2-bis(3-fluorophenyl)hydrazine (3t)^[4]: White powder (28.1 mg, 85%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.22-7.16 (m, 2H), 6.63-6.54 (m, 6H), 5.74 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 165.3, 162.8, 150.4, 150.3, 130.7, 130.6, 107.85, 107.83, 106.8, 106.6, 99.6, 99.4.



1,2-bis(3-methoxyphenyl)hydrazine (3u)^[4]: White powder (33.3 mg, 91 %). ¹H NMR (400 MHz,

CDCl₃, ppm): 7.17-7.13 (m, 2H) 6.48-6.41 (m, 6H), 5.63 (s, 2H), 3.78 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 160.9, 150.4, 130.2, 105.1, 105.0, 98.3, 55.1.



1,2-bis(2-chlorophenyl)hydrazine(3v)^[3]: White powder (36.1 mg, 95%). ¹H NMR (400 MHz, CDCl₃, ppm): 7.34-7.28 (m, 2H), 7.17-7.14 (m, 2H), 6.99-6.97 (m, 2H), 6.83-6.80 (m, 2H), 6.24 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 143.8, 129.4, 128.0, 120.2, 117.9, 112.9.

References

- (1) P.-P. Xu, J.-Y. Liao, J.-J. Zhang, W.-M. Shi, C. Liang, G.-F. Su and D.-L. Mo, *Org. Lett.*, 2021, **23**, 7482–7486.
- (2) T. Hu, M. Jaber, G. Tran, D. Bouyssi, N. Monteiro and A. Amgoune, *Chemistry A European J*, 2023, **29**, e202301636.
- (3) M. K. Sahoo, G. Sivakumar, S. Jadhav, S. Shaikh and E. Balaraman, *Org. Biomol. Chem.*, 2021, **19**, 5289–5293.
- (4) D. Gong, D. Kong, Y. Li, C. Gao and L. Zhao, *Org. Lett.*, 2023, **25**, 4198–4202.
- (5) L. Wang, A. Ishida, Y. Hashidoko and M. Hashimoto, *Angew. Chem. Int. Ed.*, 2017, **129**, 888-891.

3. NMR Spectra



Figure S2. ¹H NMR Spectrum of **3a**

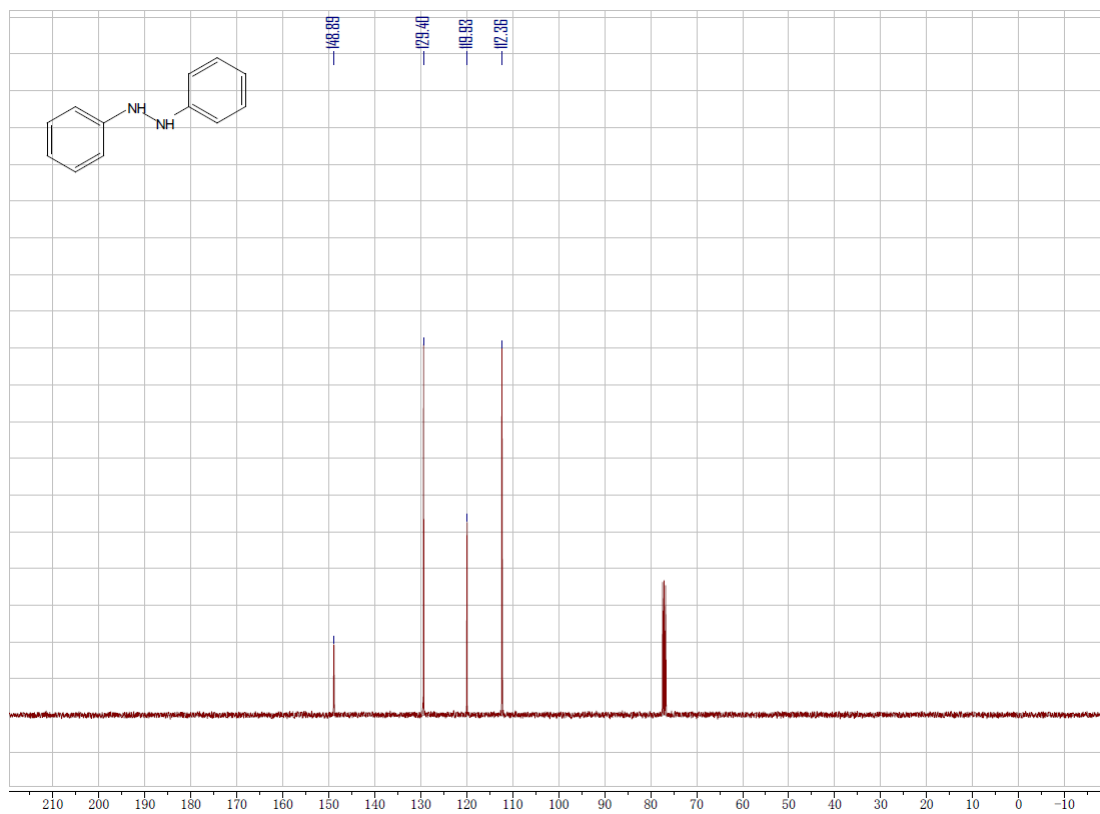


Figure S3. ¹³C NMR Spectrum of **3a**

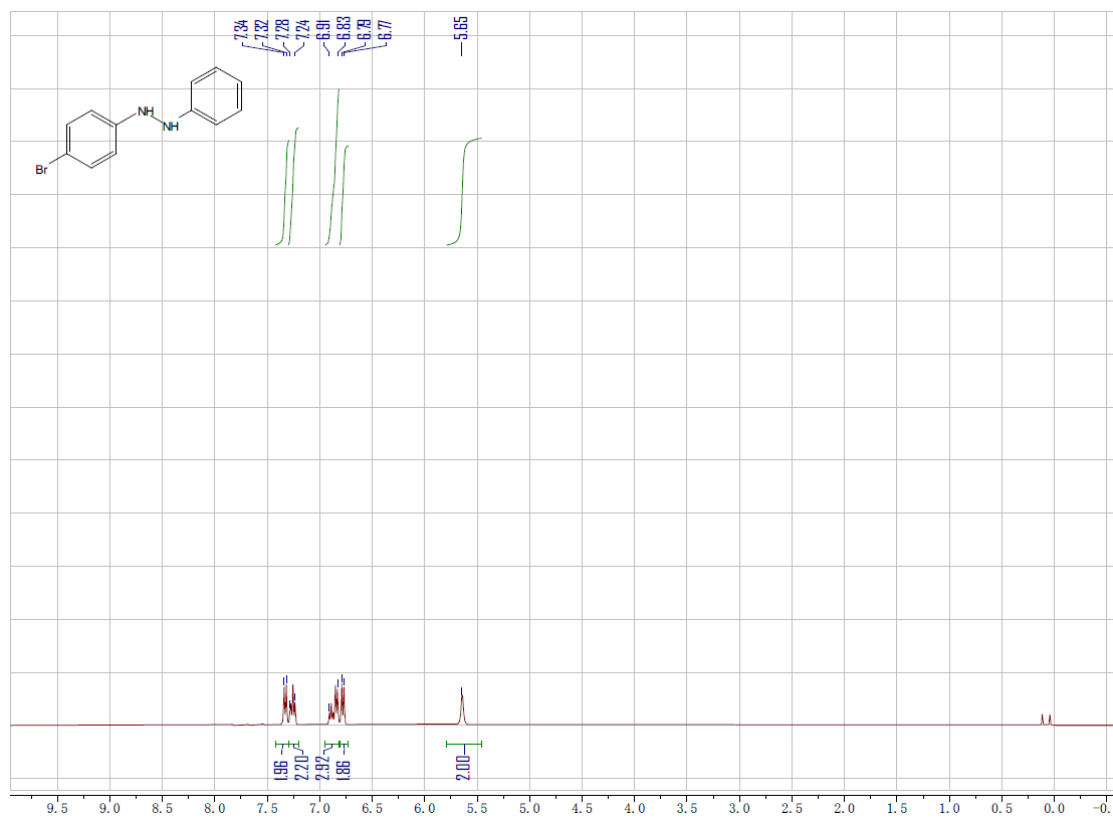


Figure S4. ¹H NMR Spectrum of **3b**

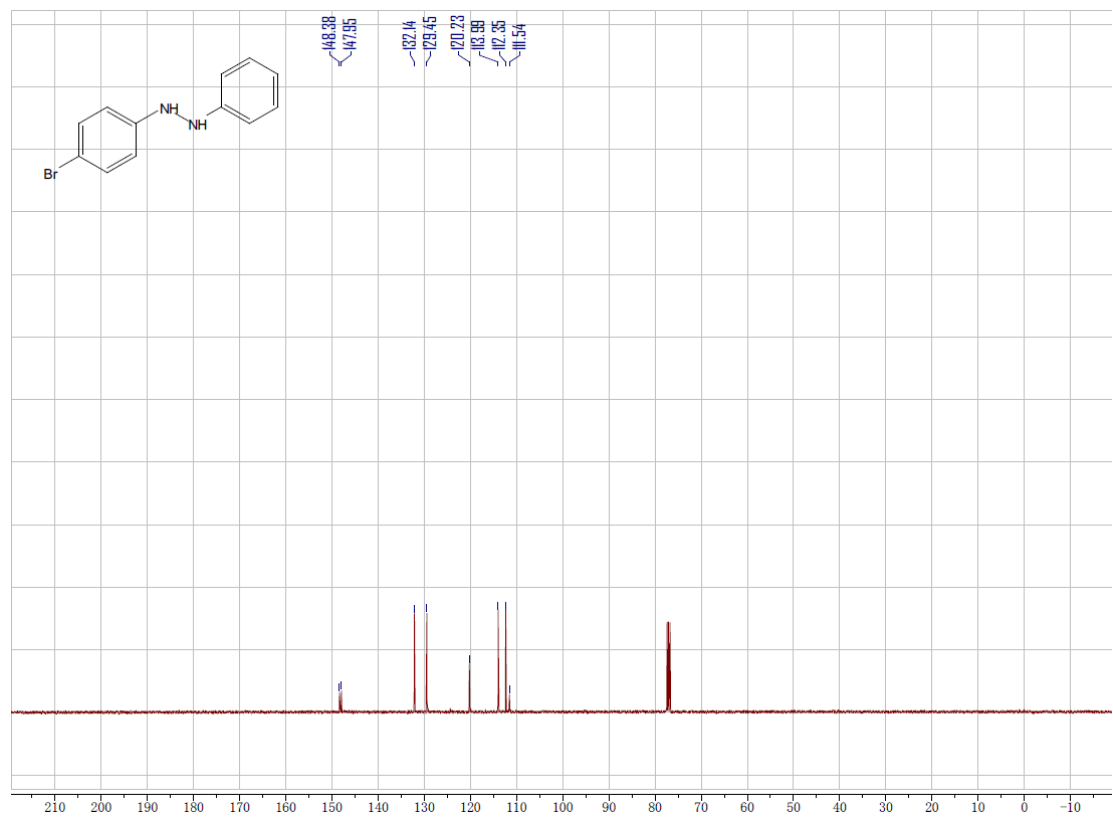


Figure S5. ¹³C NMR Spectrum of **3b**

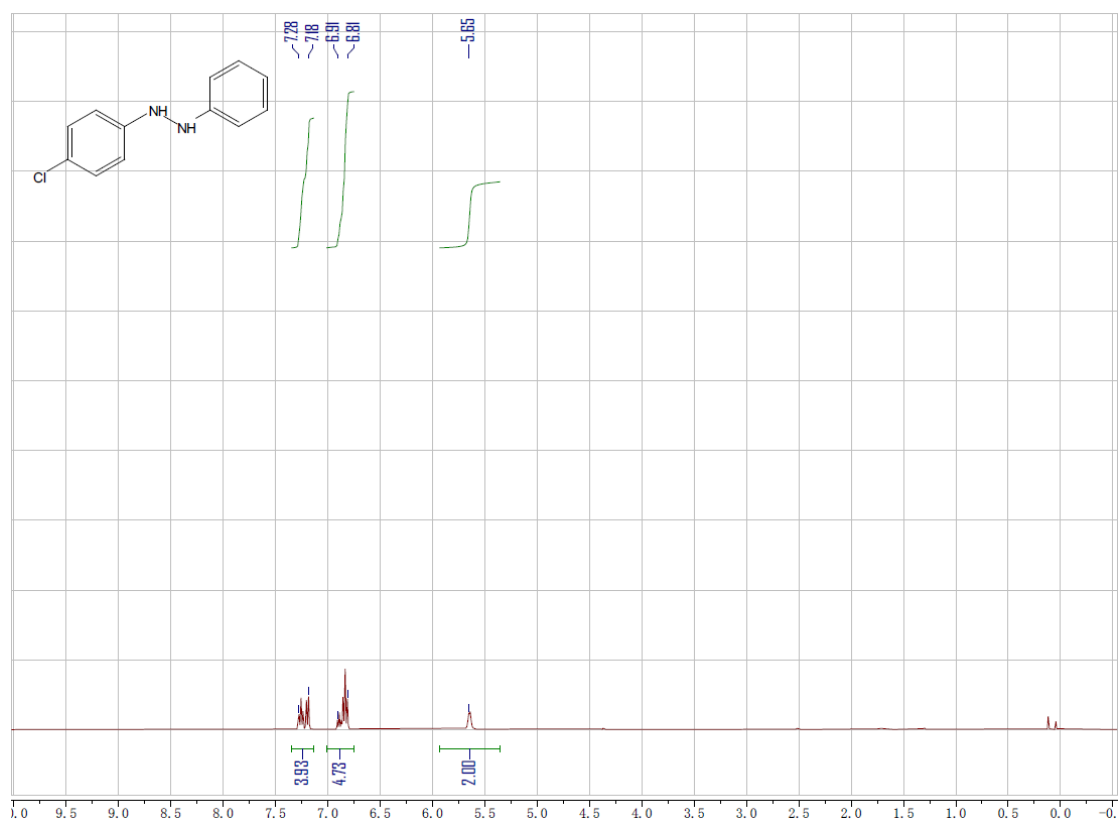


Figure S6. ¹H NMR Spectrum of 3c

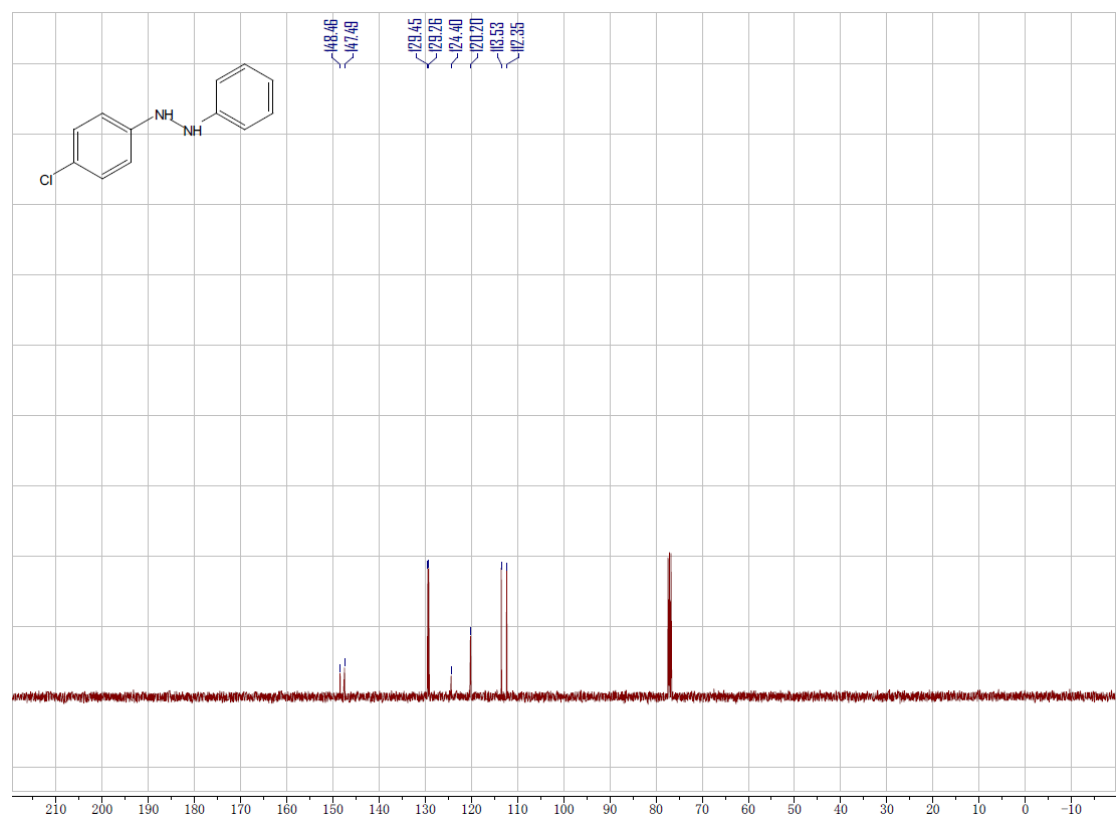


Figure S7. ¹³C NMR Spectrum of 3c

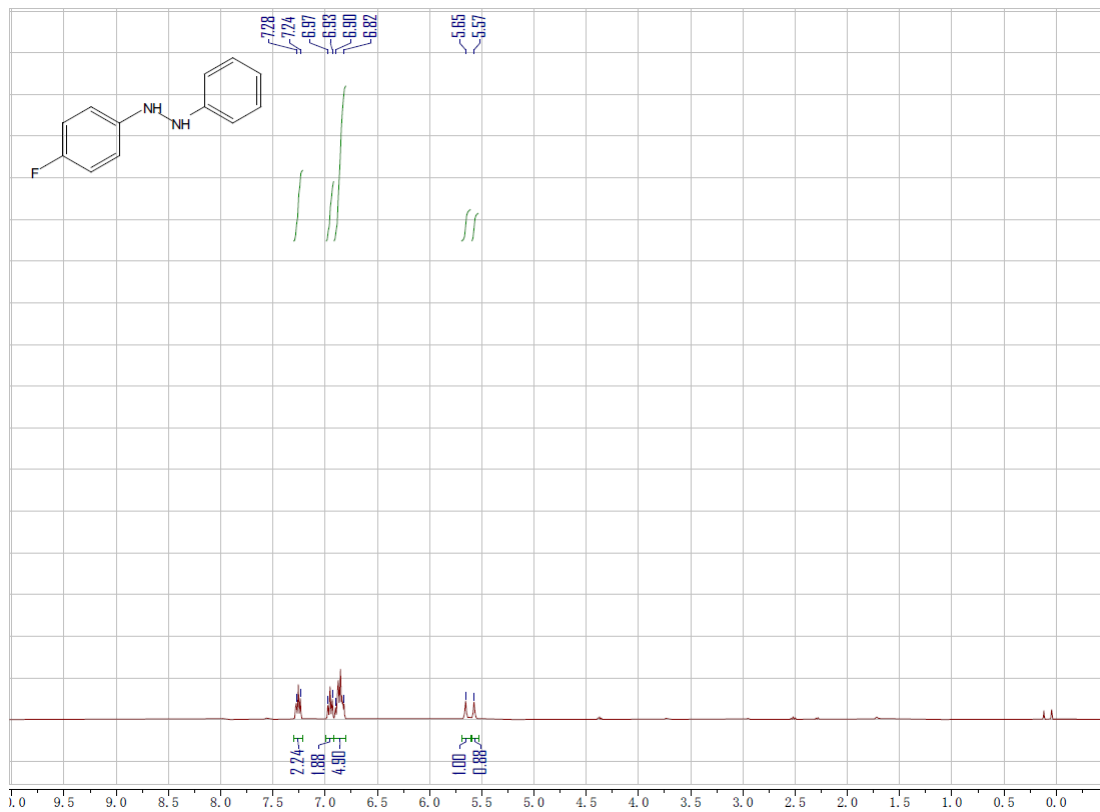


Figure S8. ¹H NMR Spectrum of **3d**

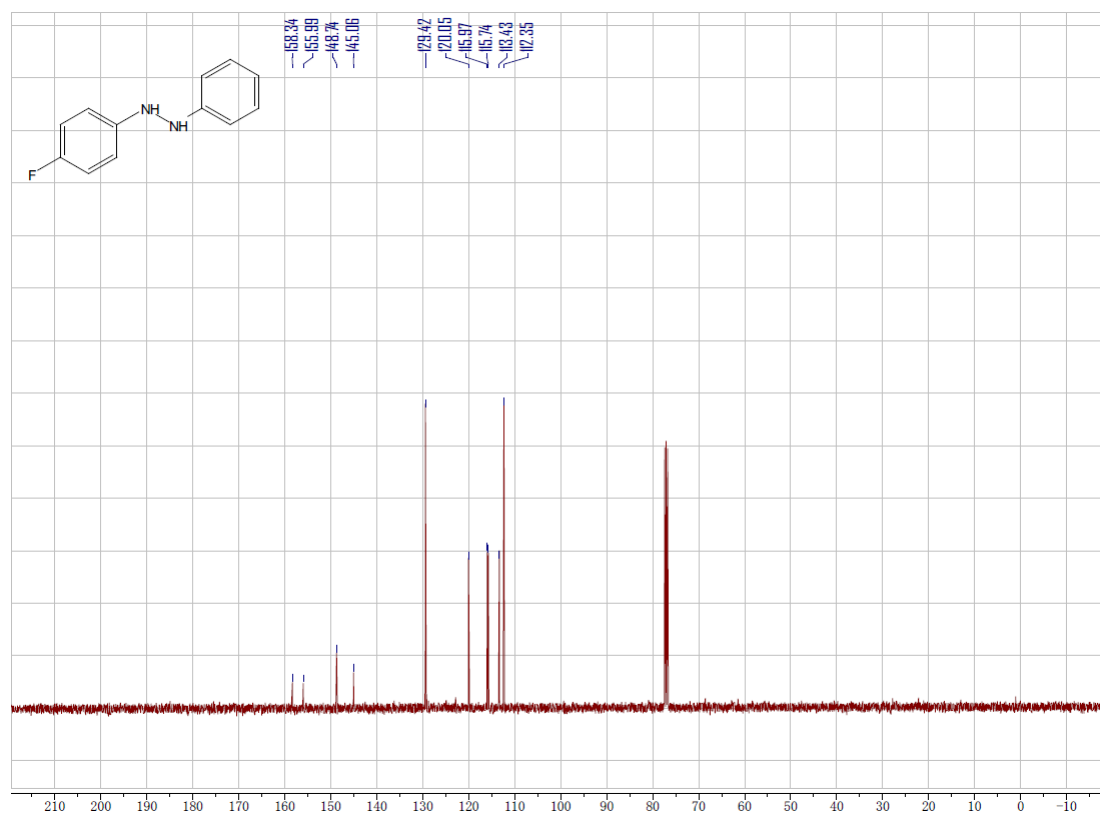


Figure S9. ¹³C NMR Spectrum of **3d**

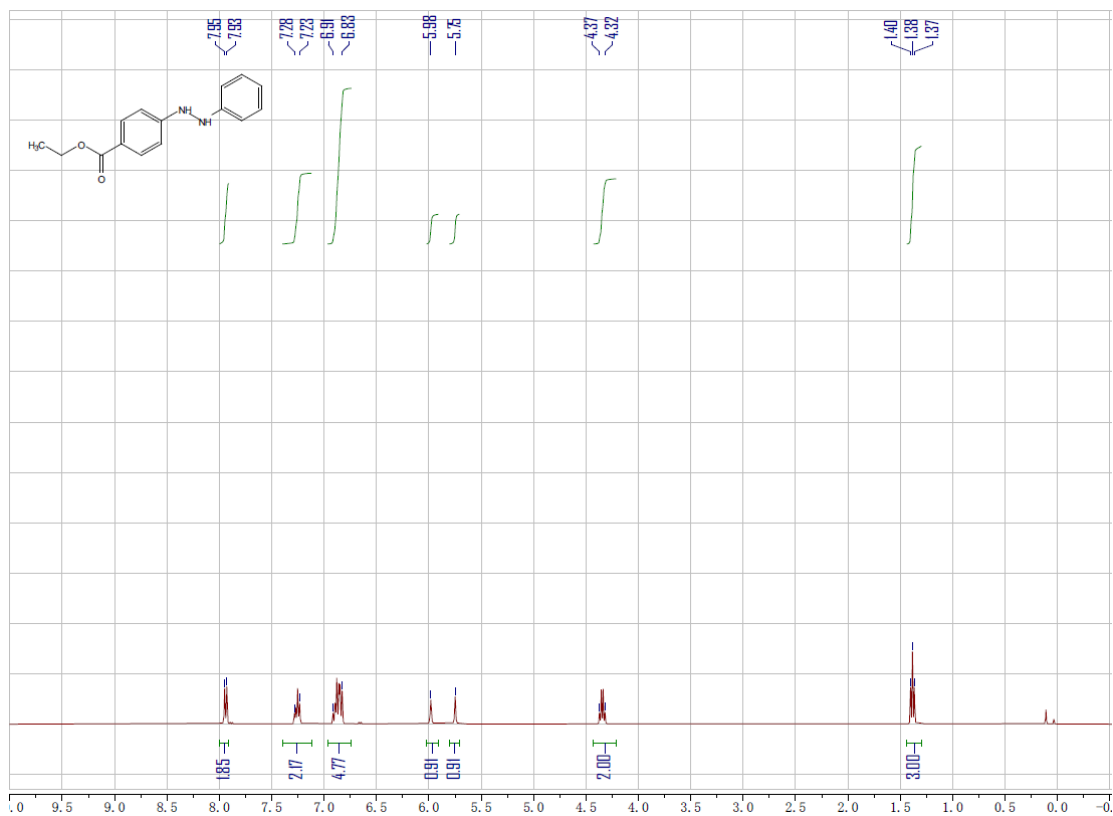


Figure S10. ¹H NMR Spectrum of **3e**

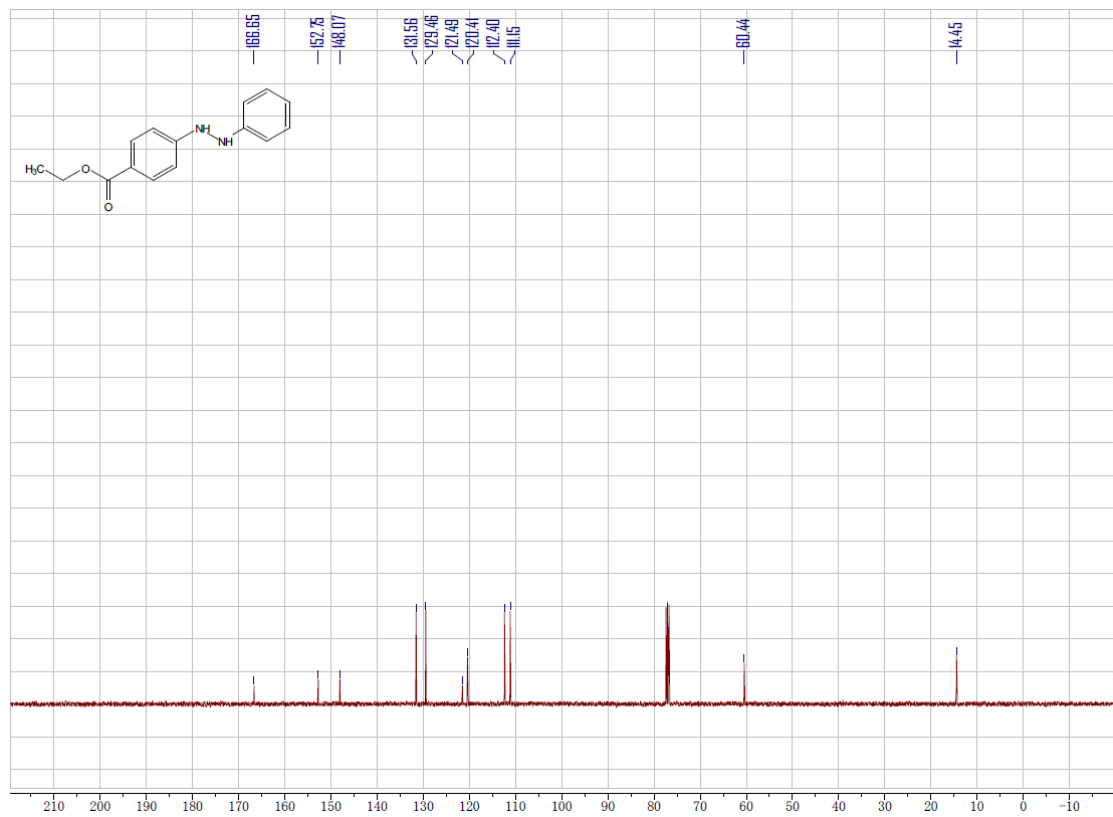


Figure S11. ¹³C NMR Spectrum of **3e**

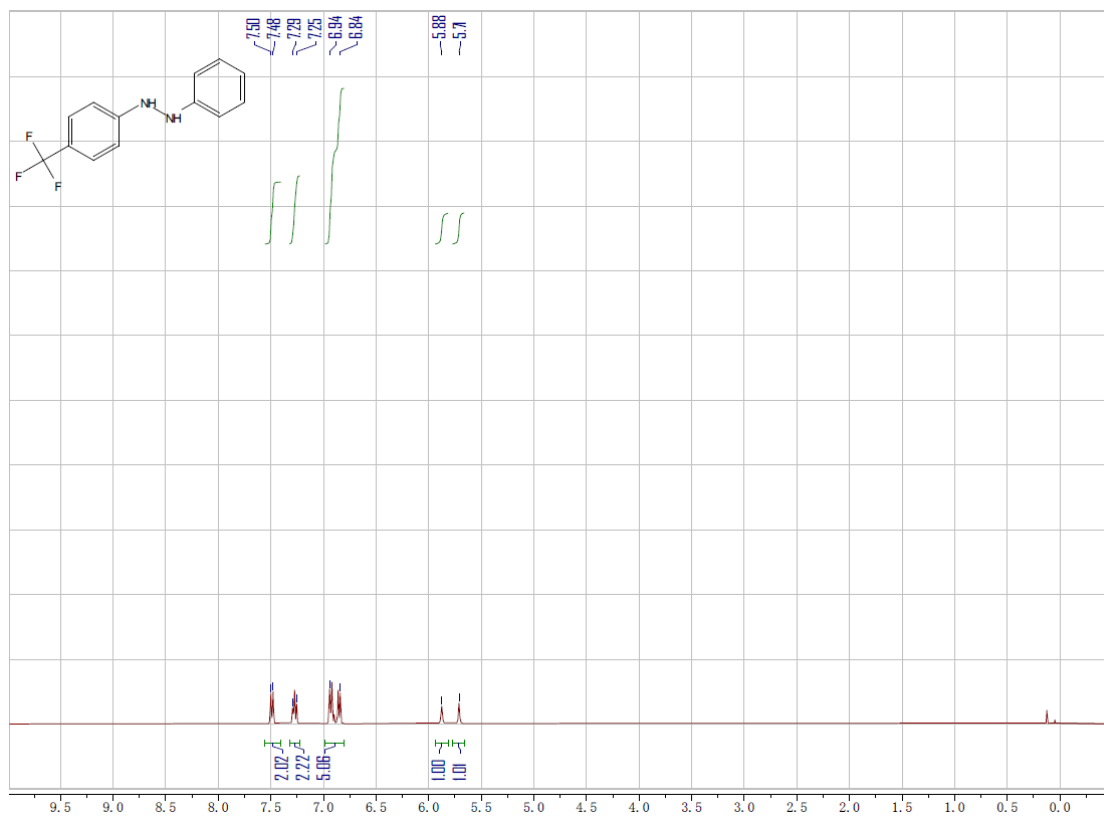


Figure S12. ^1H NMR Spectrum of **3f**

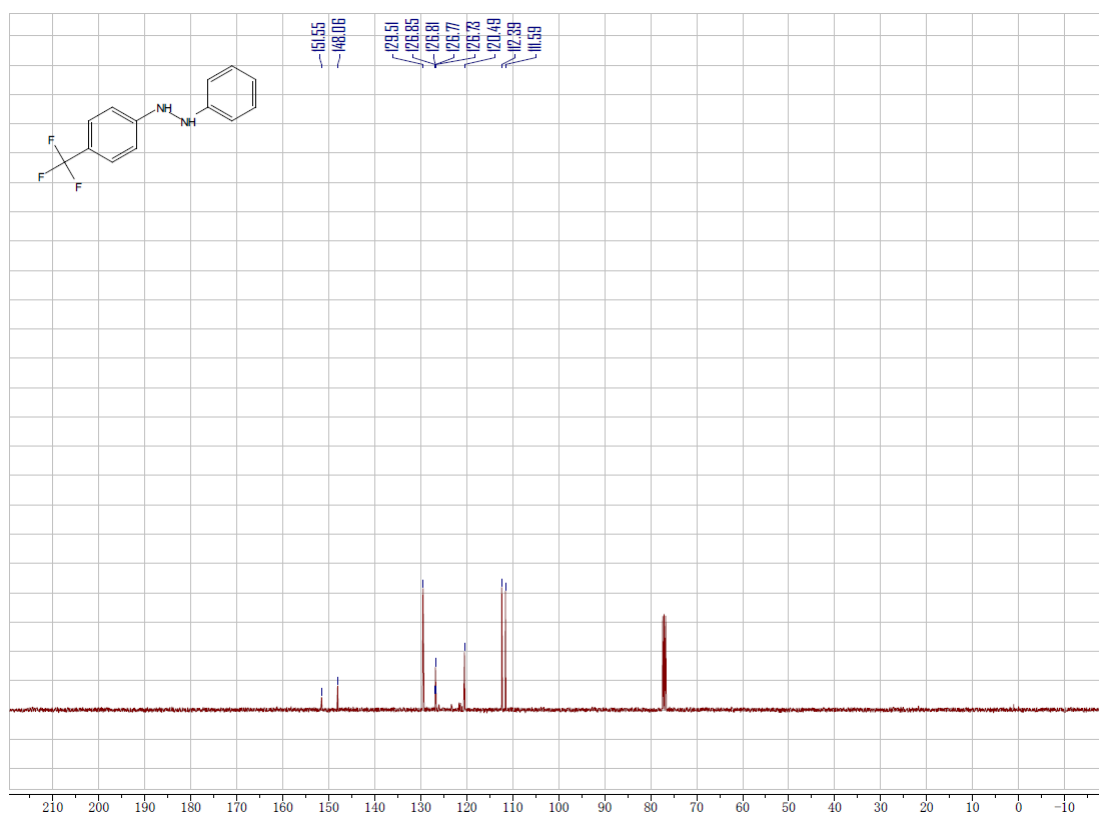


Figure S13. ^{13}C NMR Spectrum of **3f**



Figure S14. ¹H NMR Spectrum of **3g**

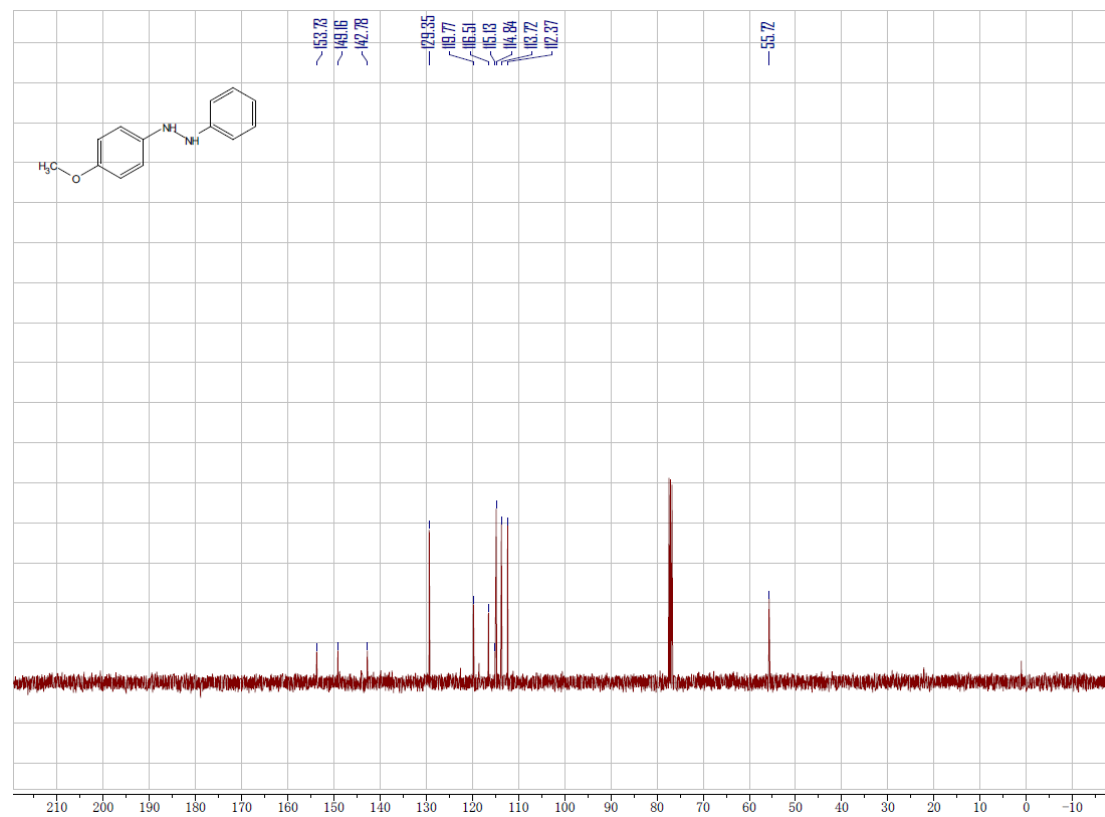


Figure S15. ¹³C NMR Spectrum of **3g**

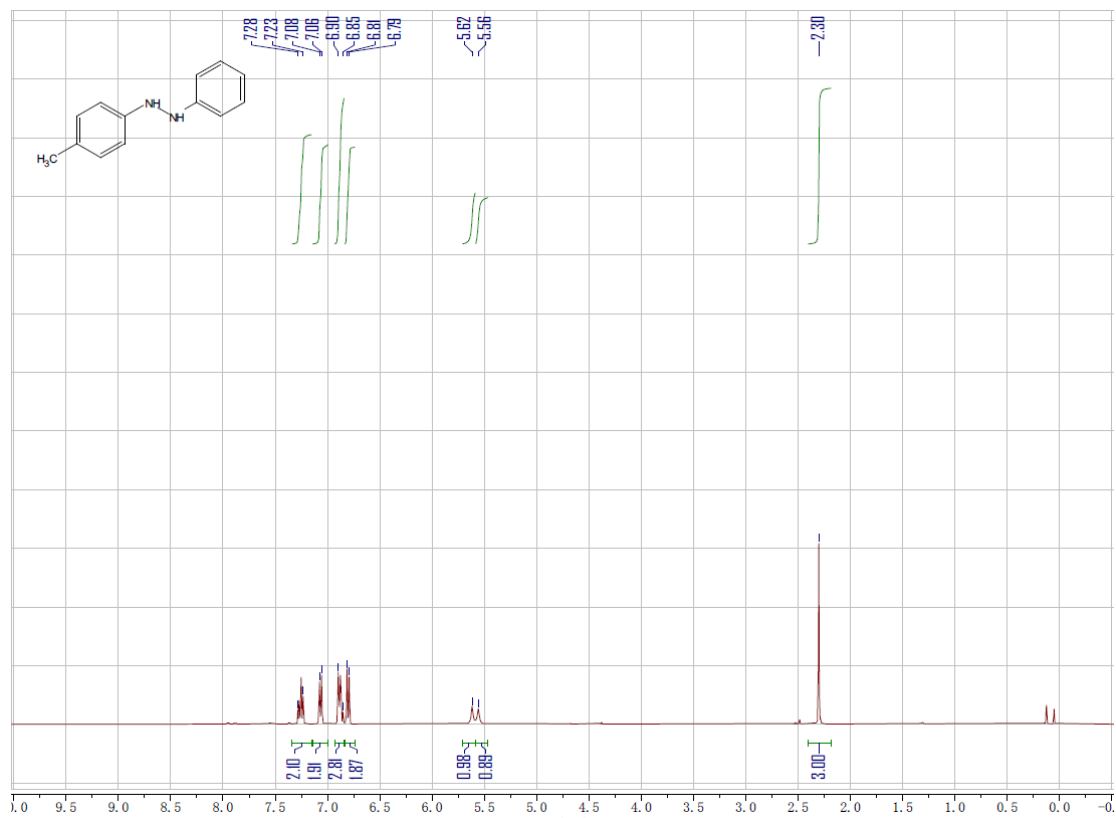


Figure S16. ^1H NMR Spectrum of **3h**

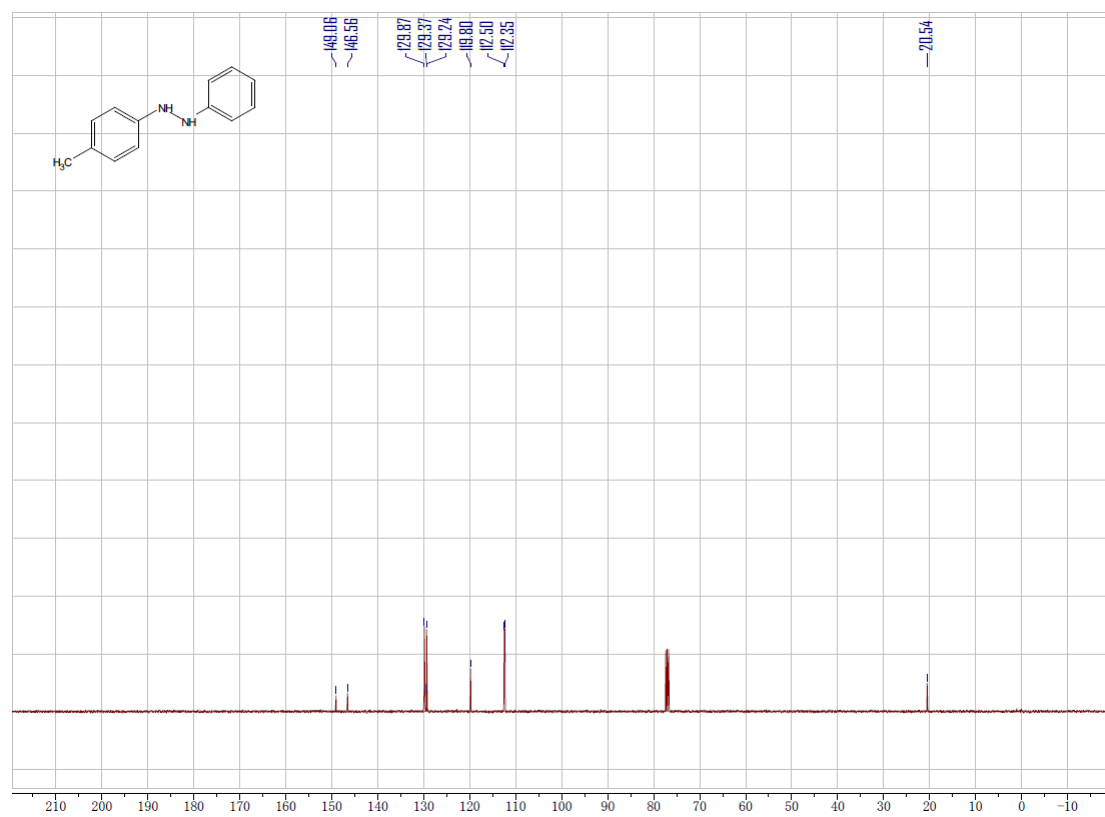


Figure S17. ^{13}C NMR Spectrum of **3h**

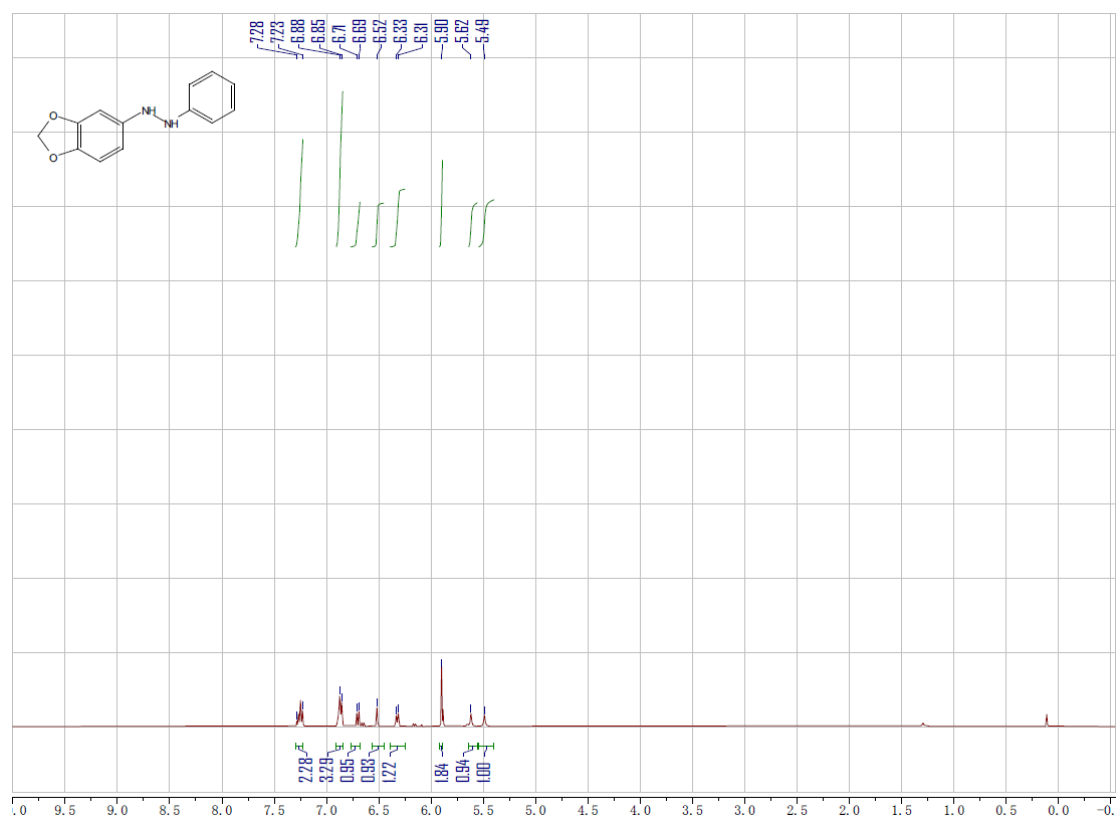


Figure S18. ^1H NMR Spectrum of **3i**

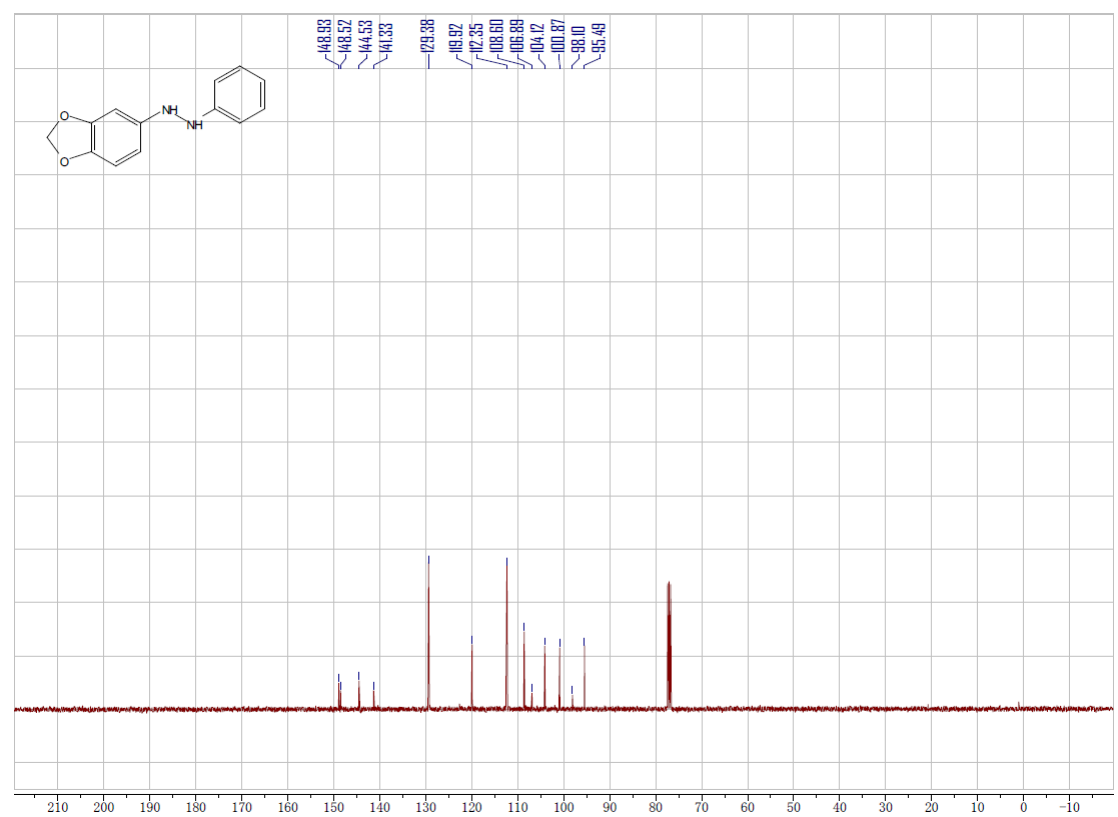


Figure S19. ^{13}C NMR Spectrum of **3i**

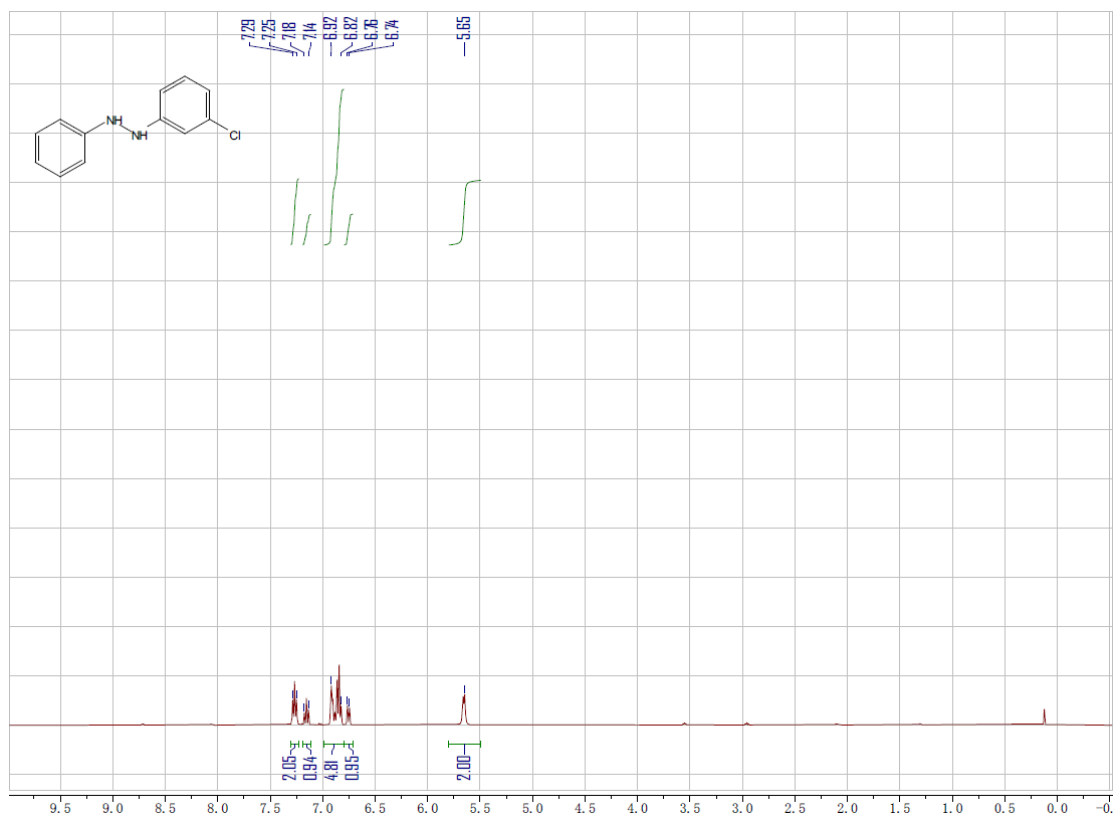


Figure S20. ¹H NMR Spectrum of **3j**

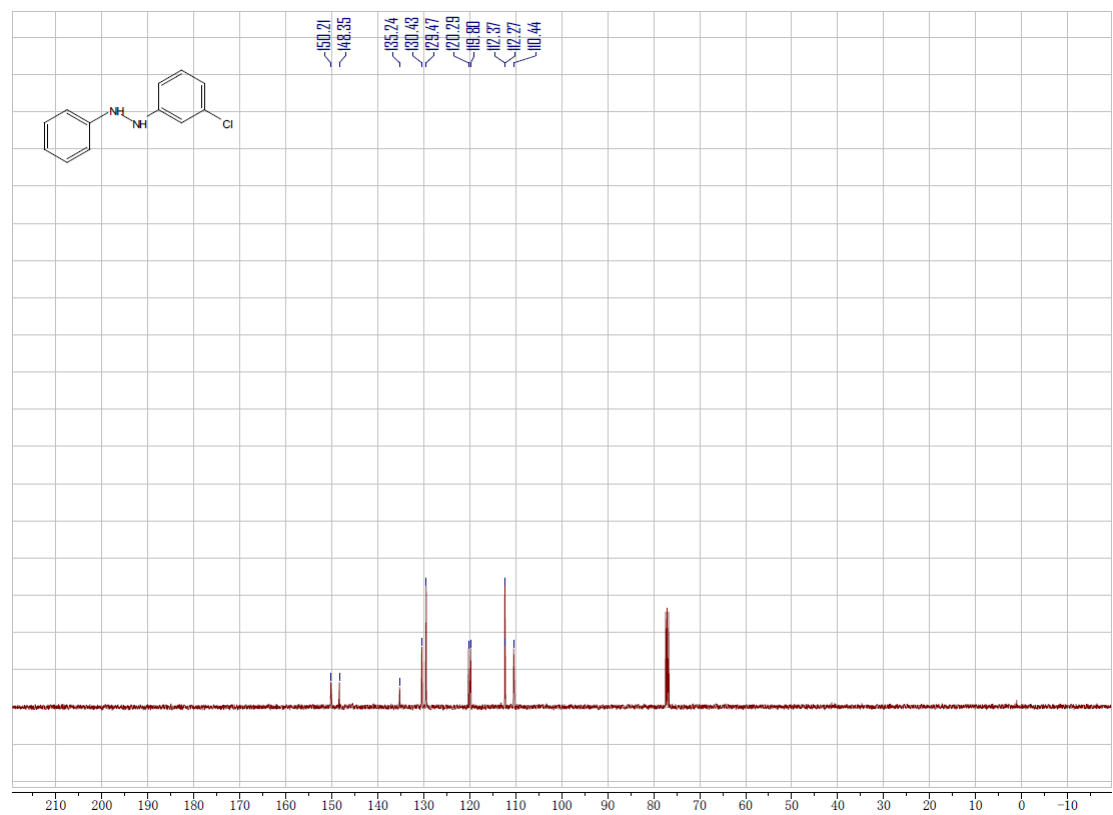


Figure S21. ¹³C NMR Spectrum of **3j**

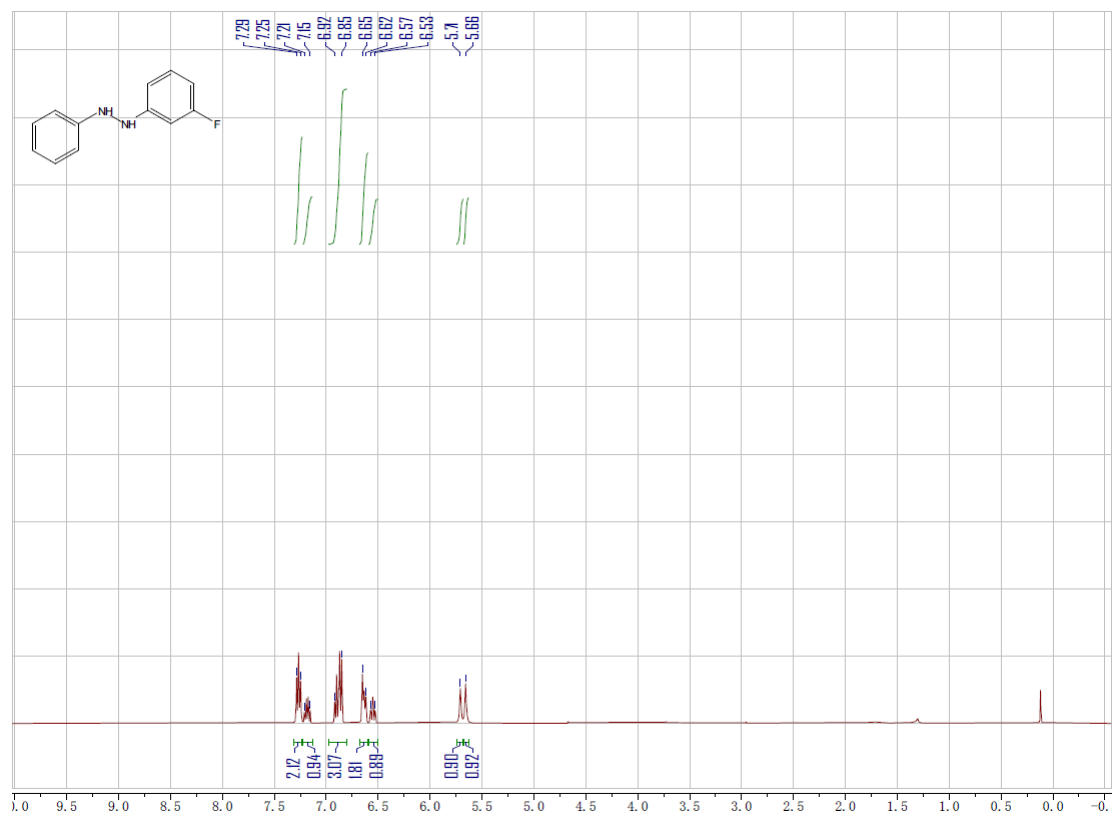


Figure S22. ¹H NMR Spectrum of **3k**

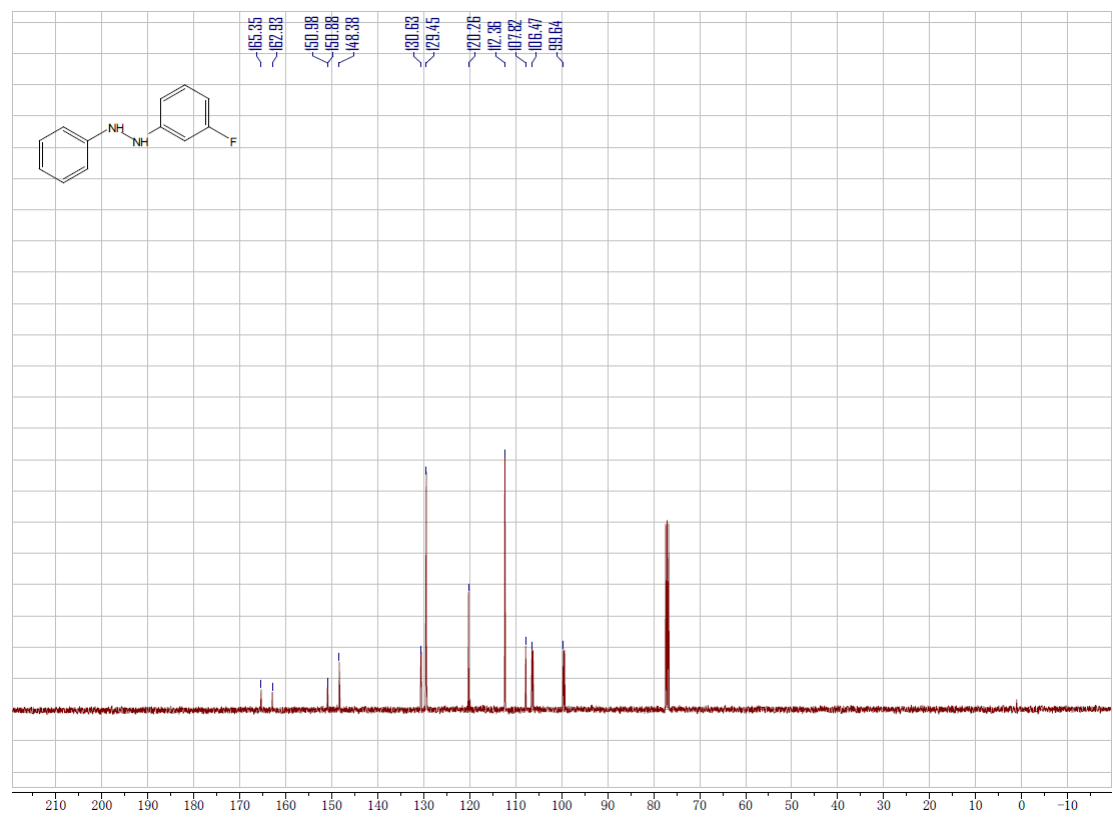


Figure S23. ¹³C NMR Spectrum of **3k**



Figure S24. ¹H NMR Spectrum of **31**

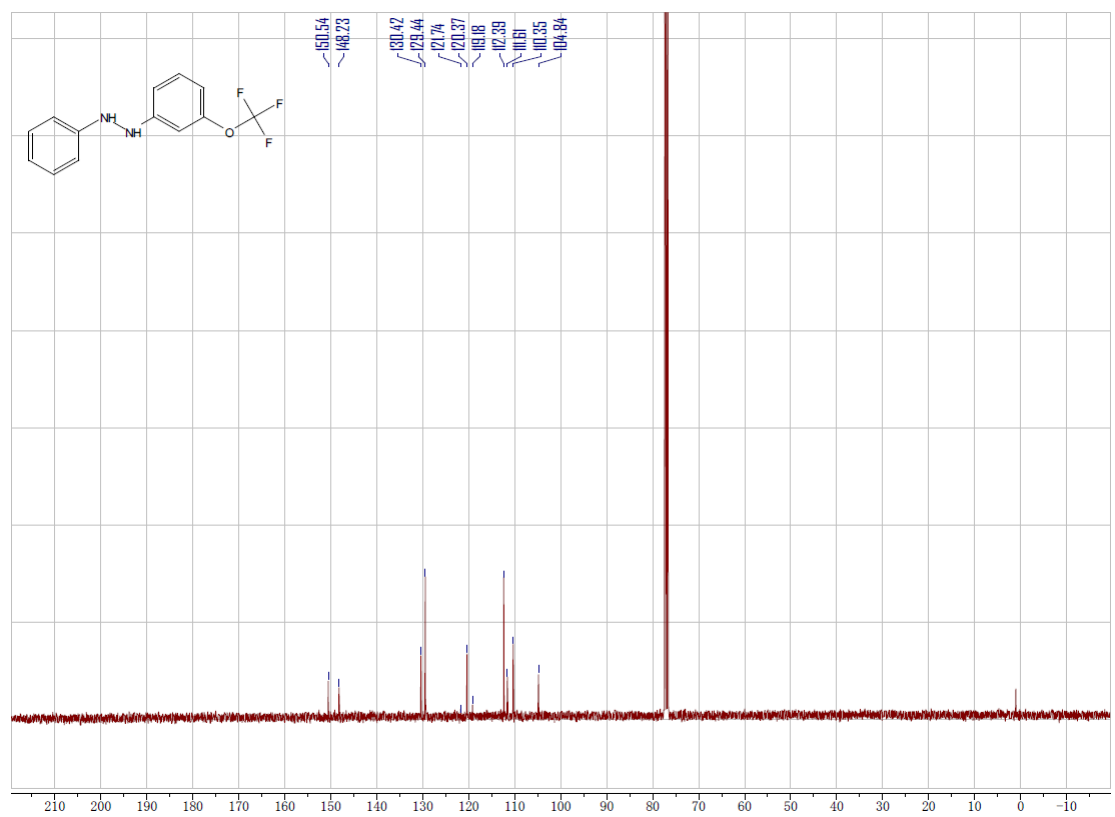


Figure S25. ¹³C NMR Spectrum of **31**

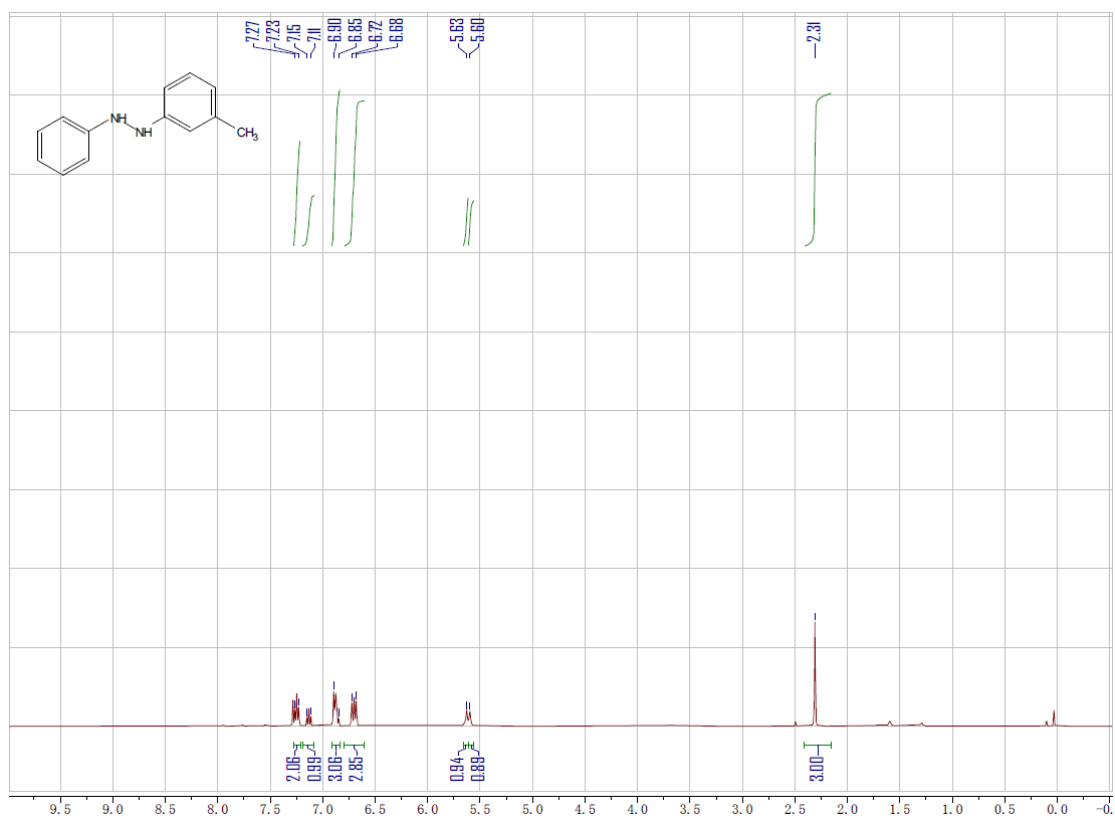


Figure S26. ^1H NMR Spectrum of **3m**

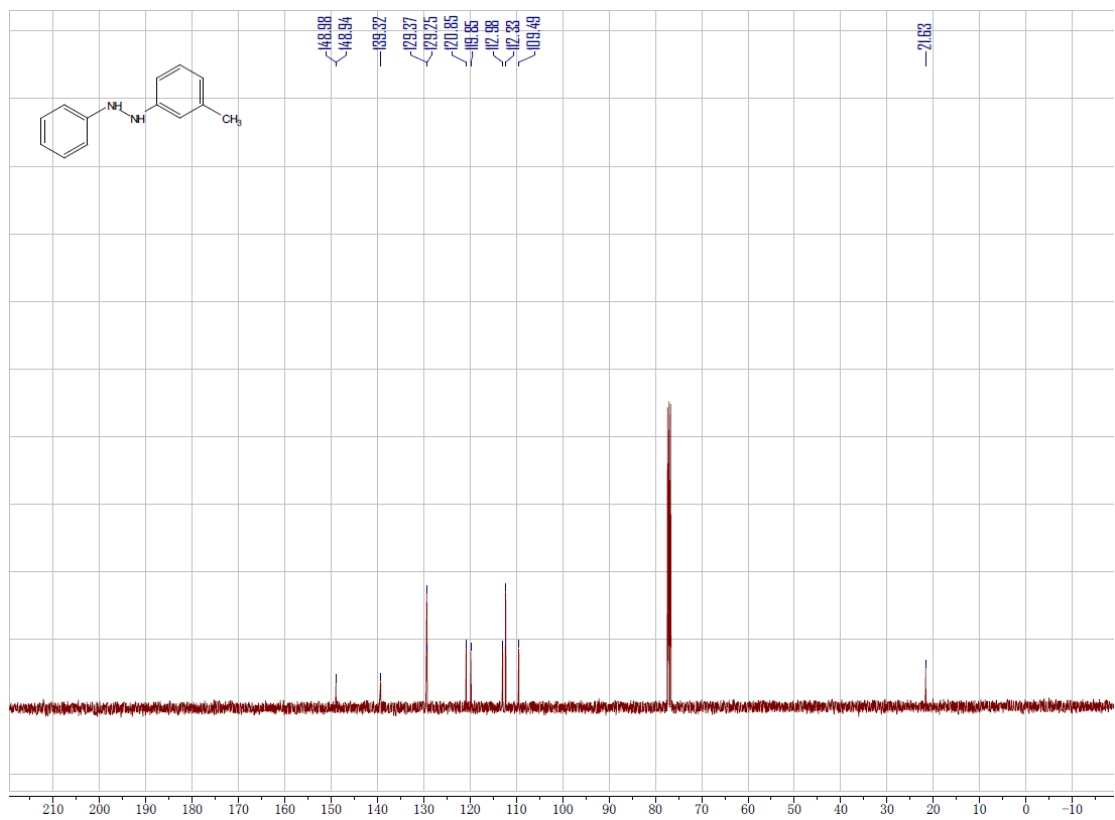


Figure S27. ^{13}C NMR Spectrum of **3m**

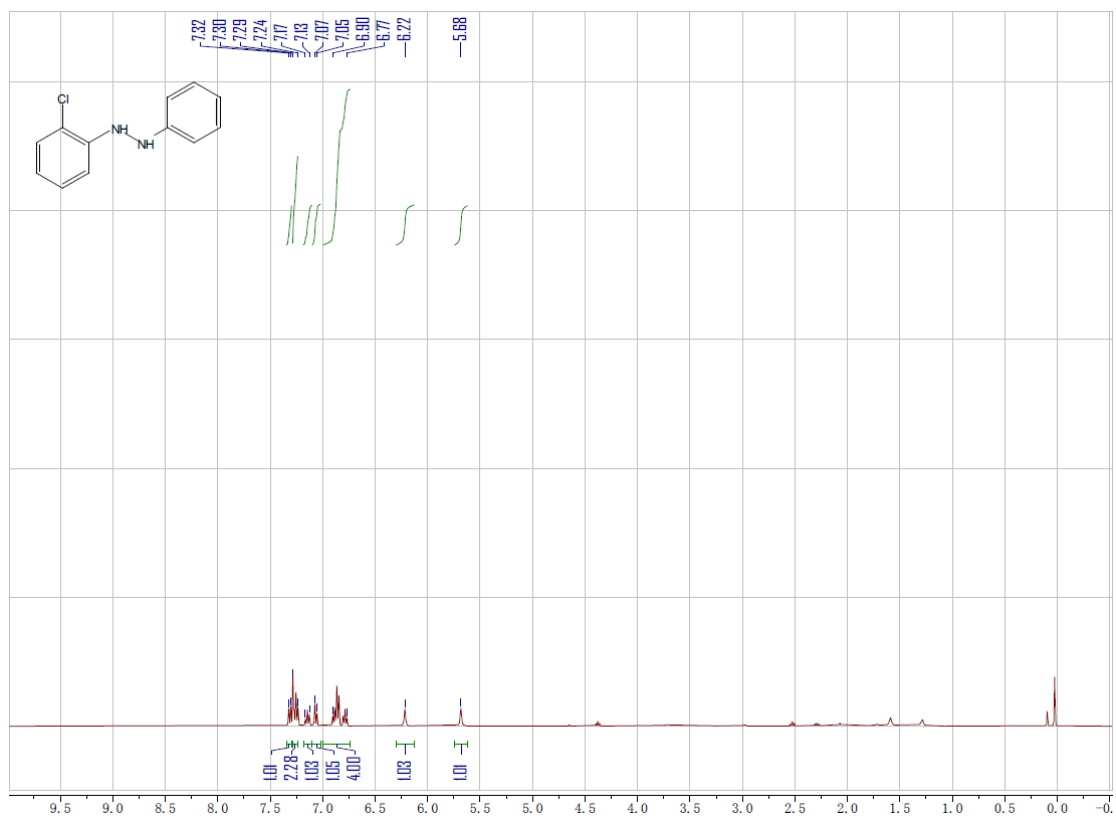


Figure S28. ^1H NMR Spectrum of **3n**

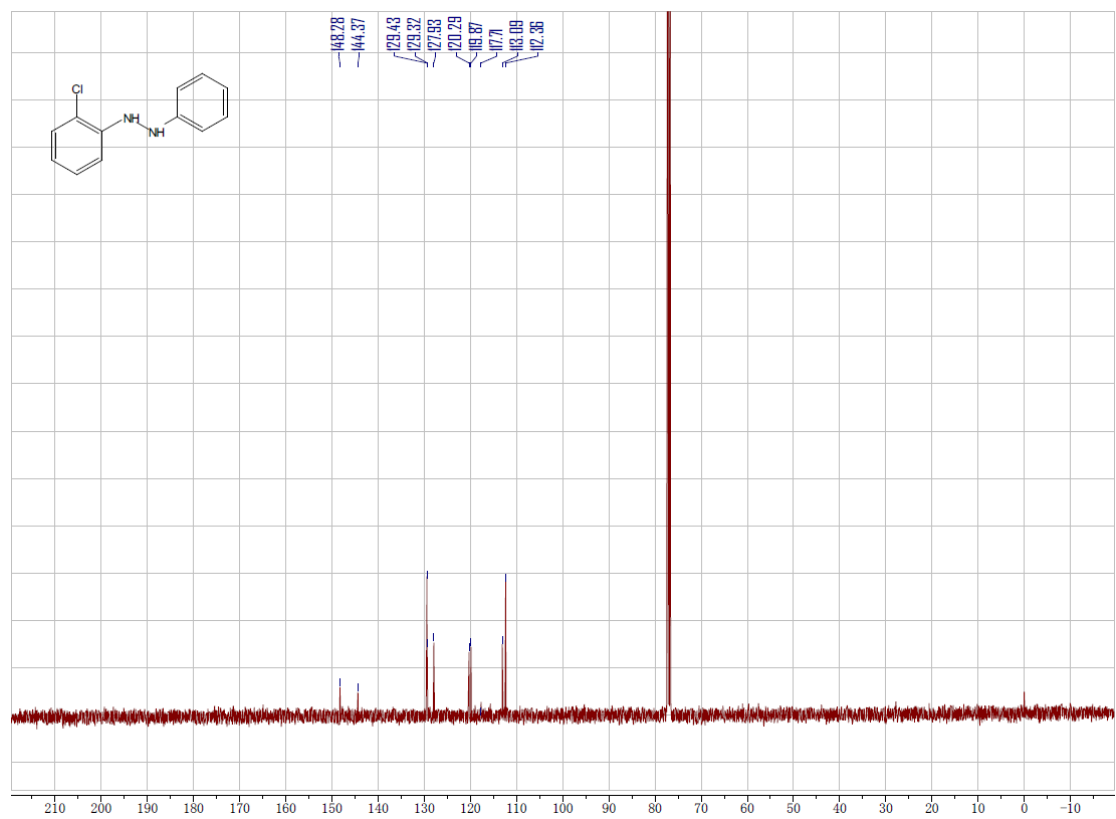


Figure S29. ^{13}C NMR Spectrum of **3n**

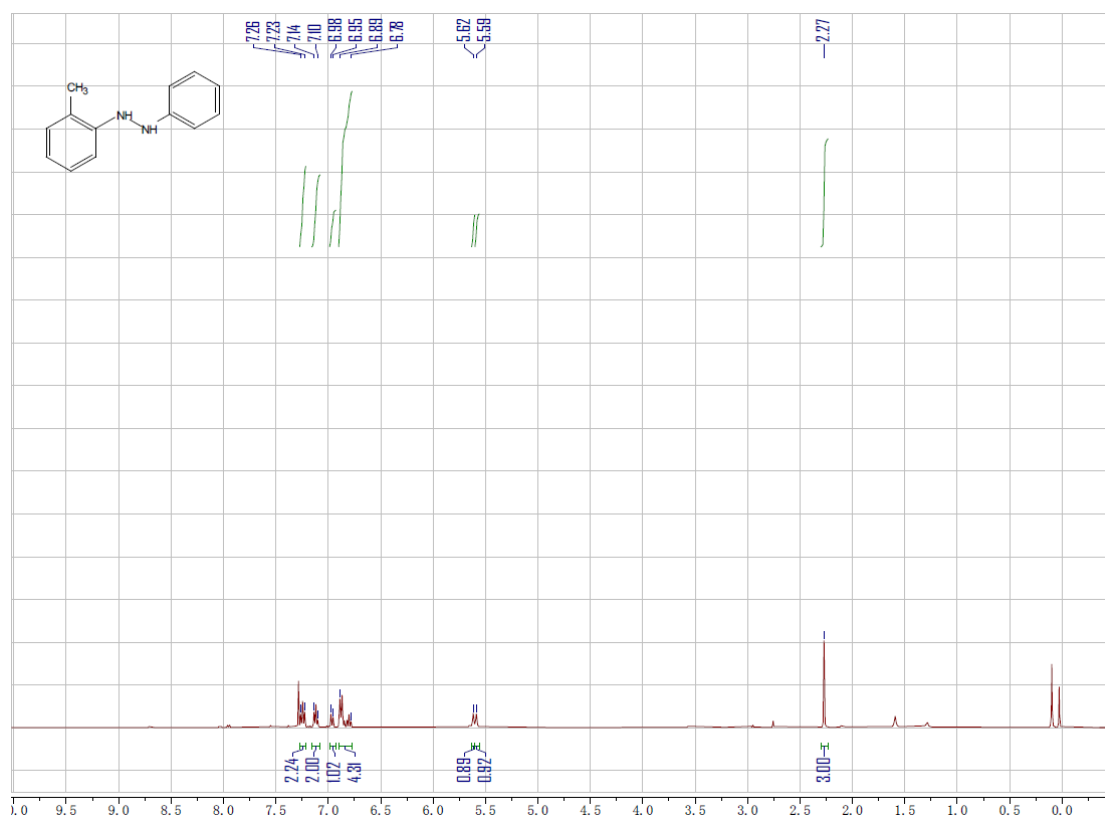


Figure S30. ^1H NMR Spectrum of **3o**

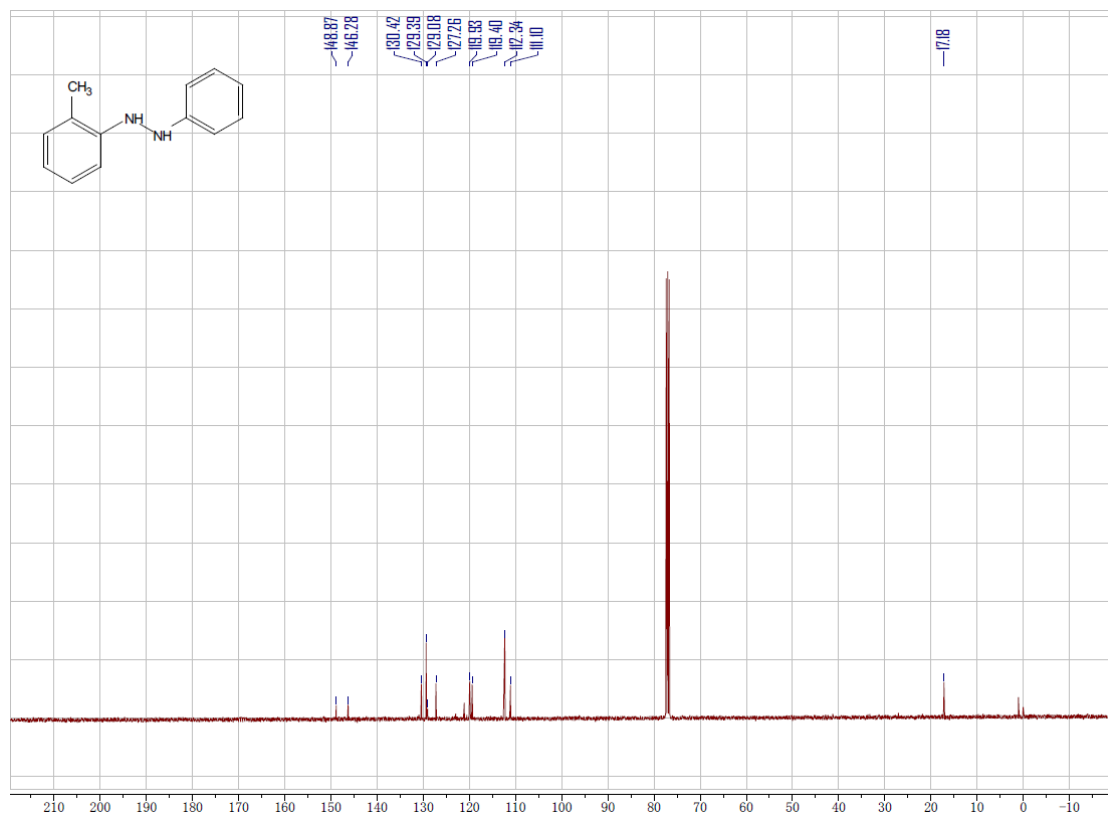


Figure S31. ^{13}C NMR Spectrum of **3o**

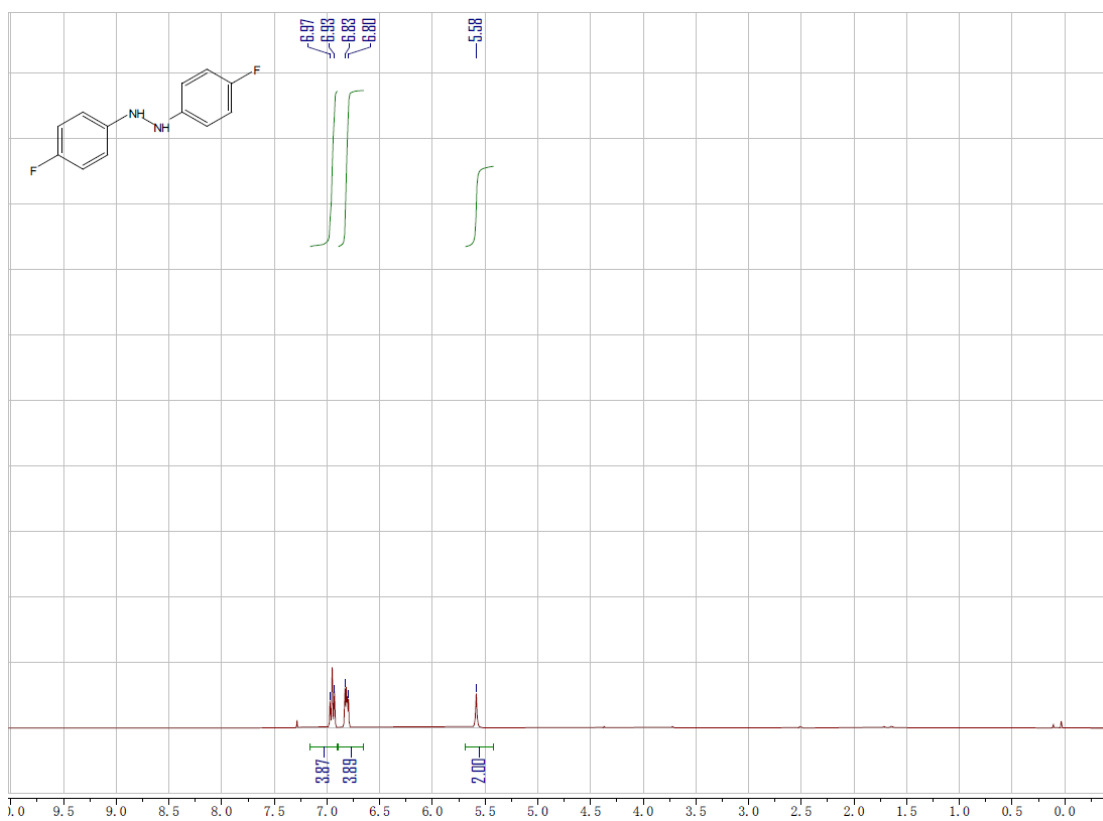


Figure S32. ^1H NMR Spectrum of **3p**

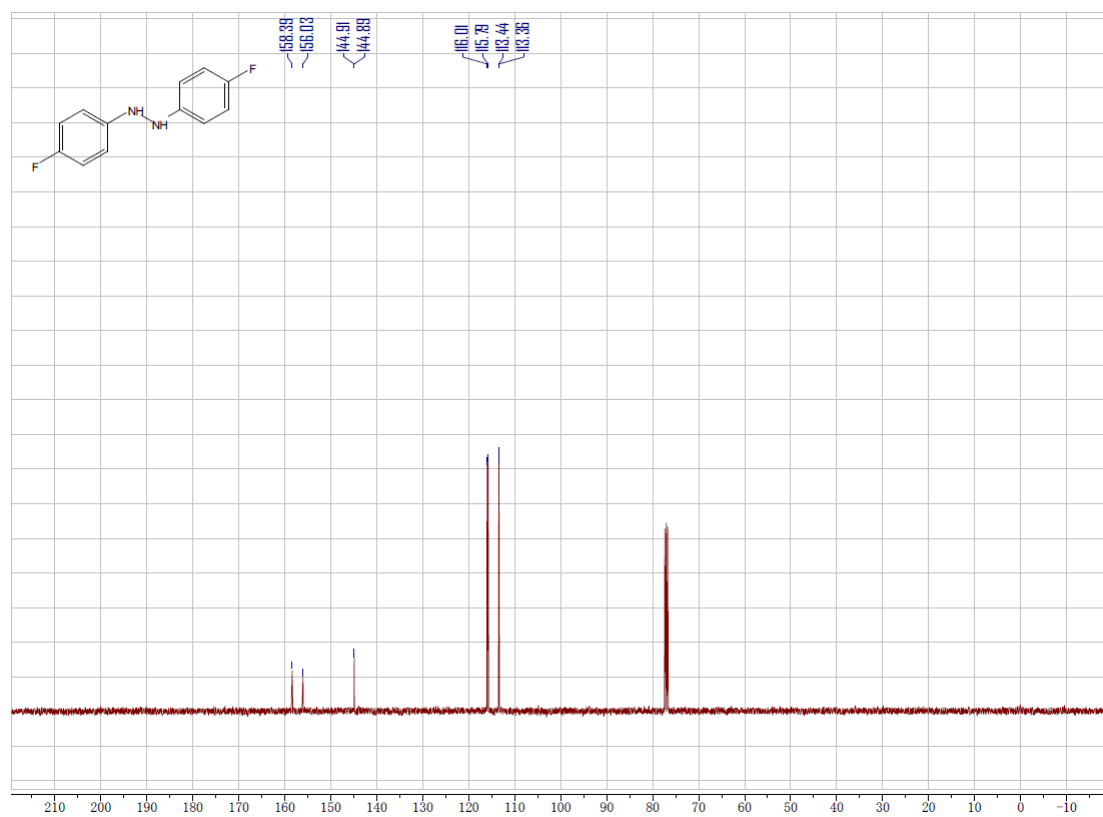


Figure S33. ^{13}C NMR Spectrum of **3p**

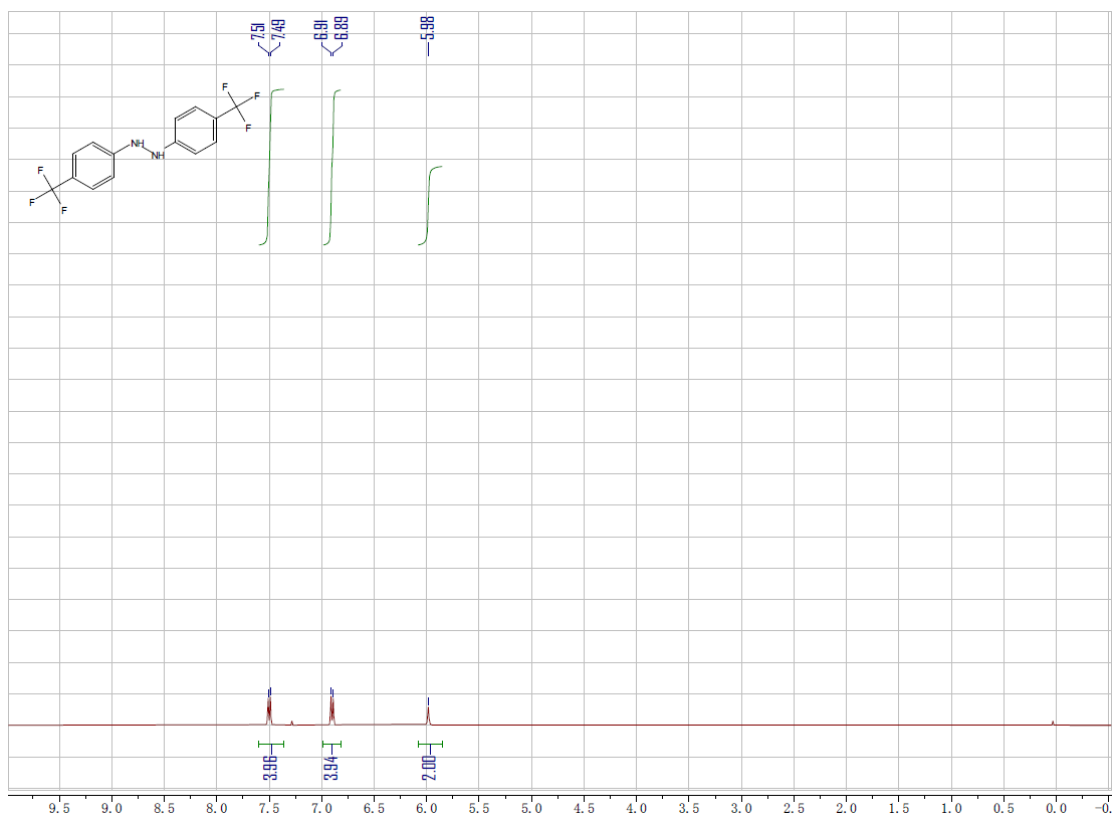


Figure S34. ^1H NMR Spectrum of **3q**

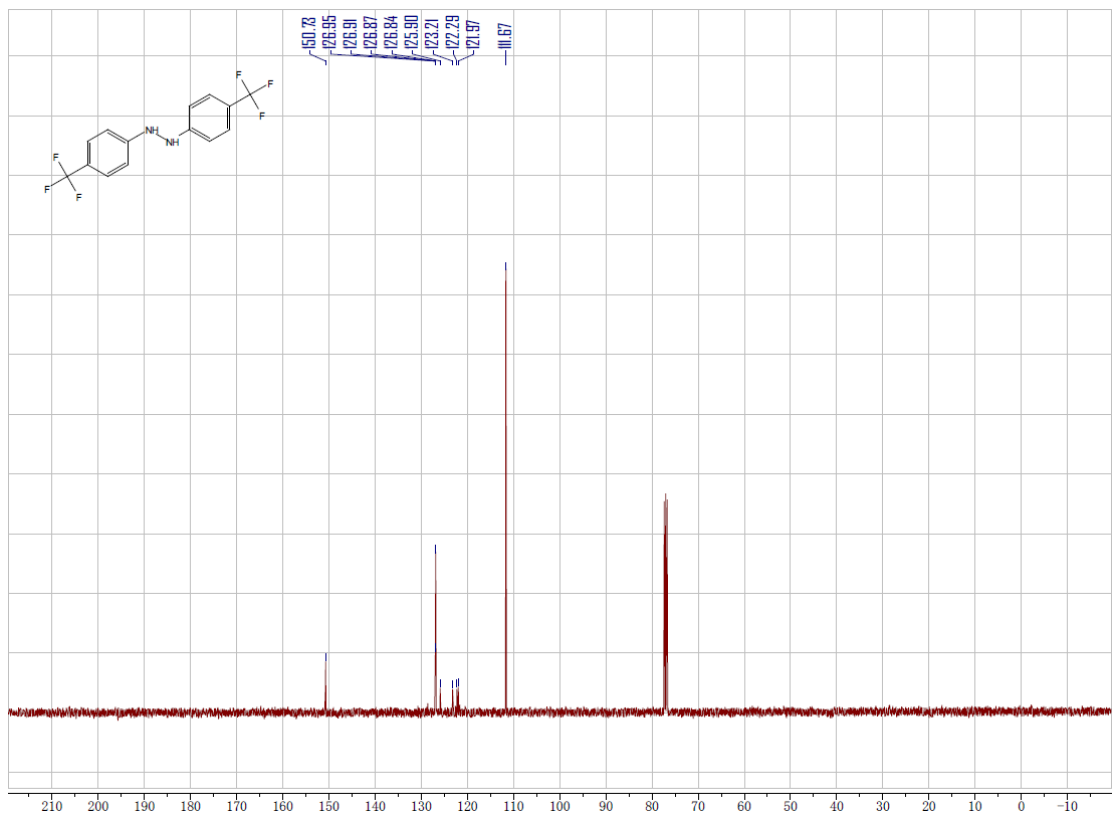


Figure S35. ^{13}C NMR Spectrum of **3q**

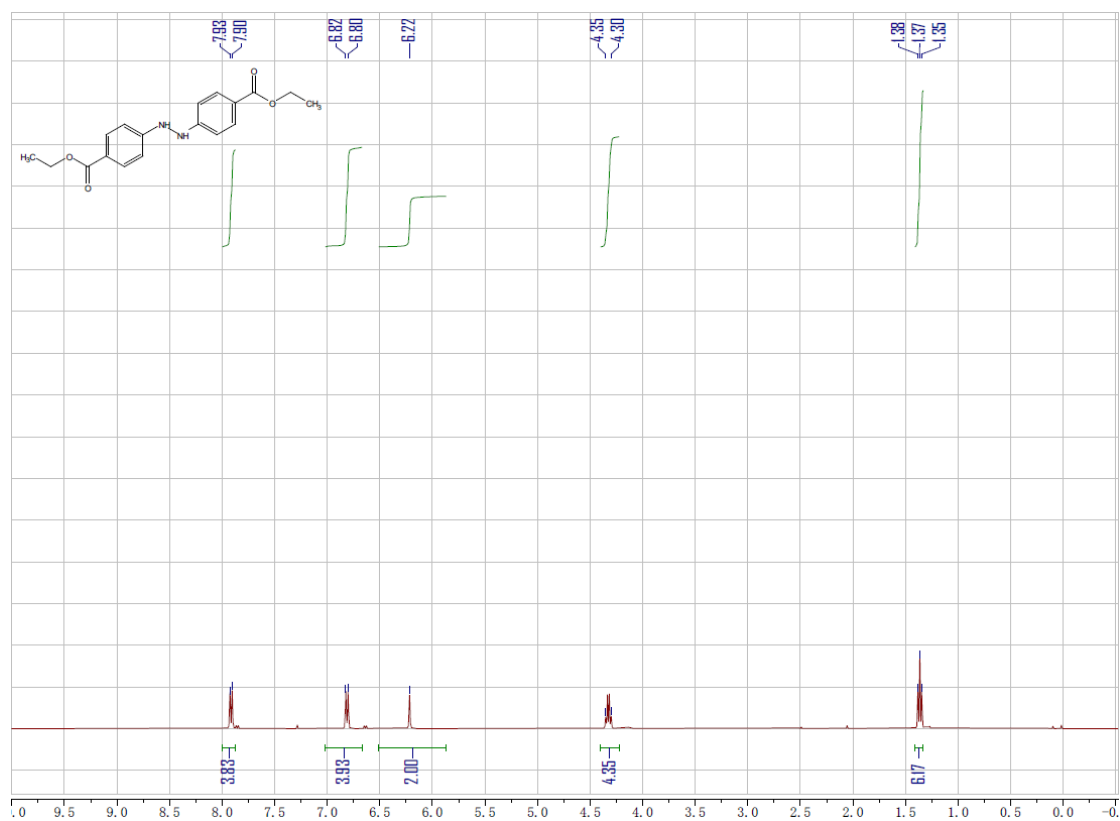


Figure S36. ^1H NMR Spectrum of **3r**

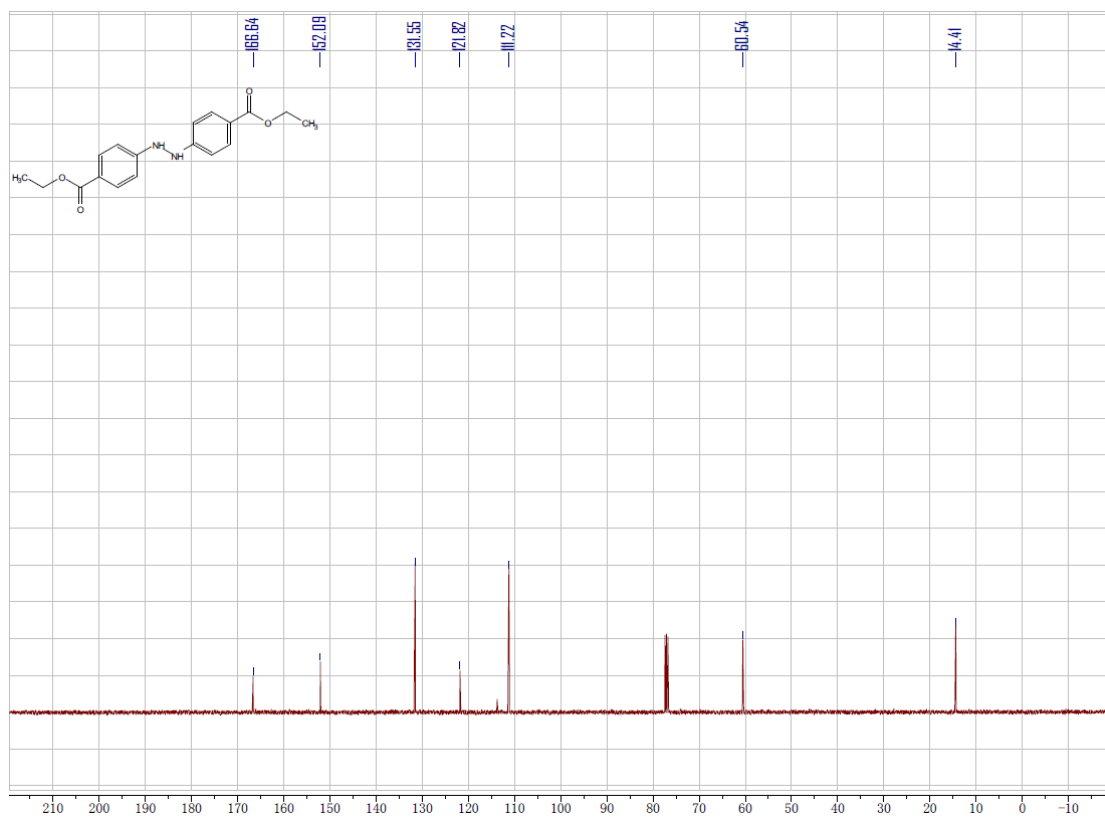


Figure S37. ^{13}C NMR Spectrum of **3r**

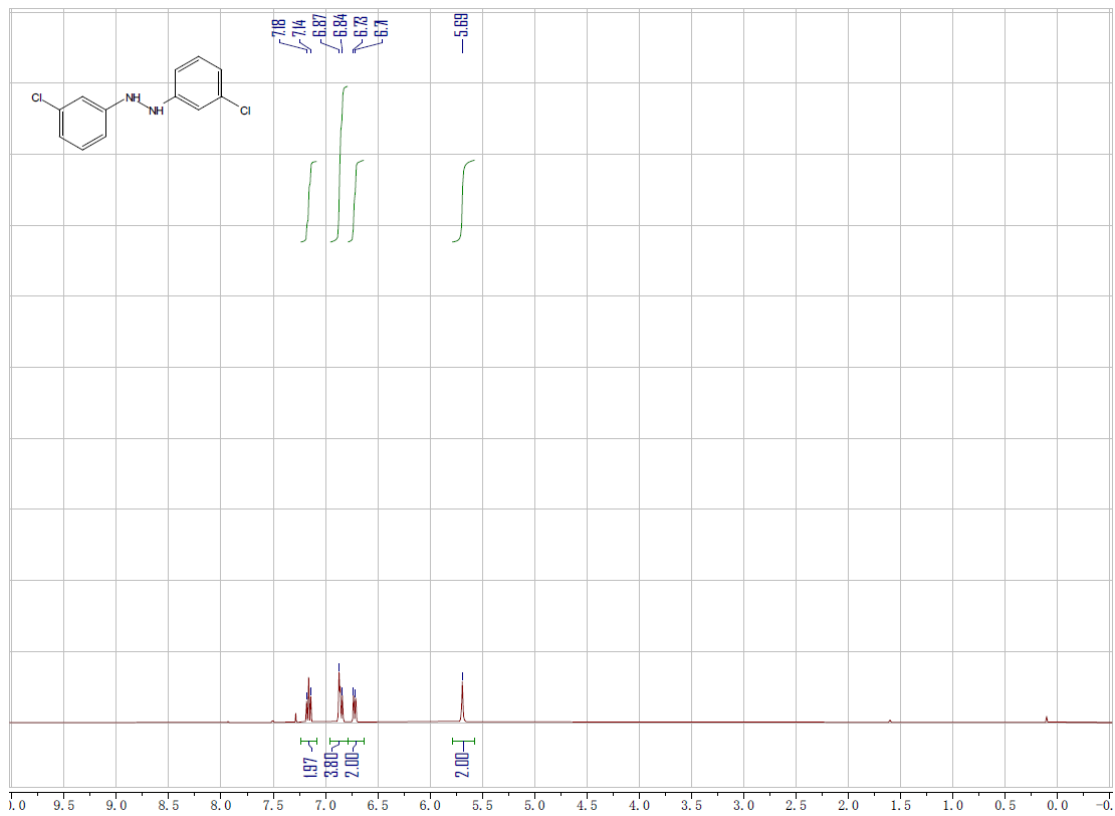


Figure S38. ^1H NMR Spectrum of **3s**

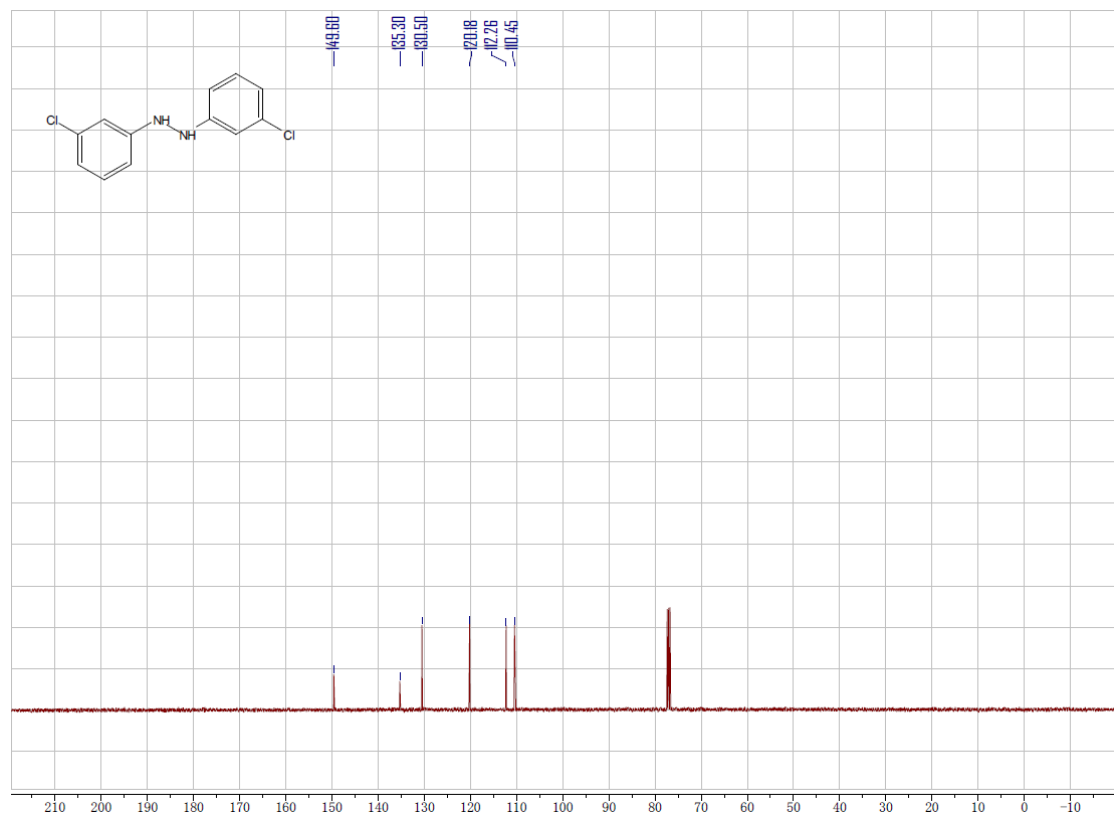


Figure S39. ^{13}C NMR Spectrum of **3s**

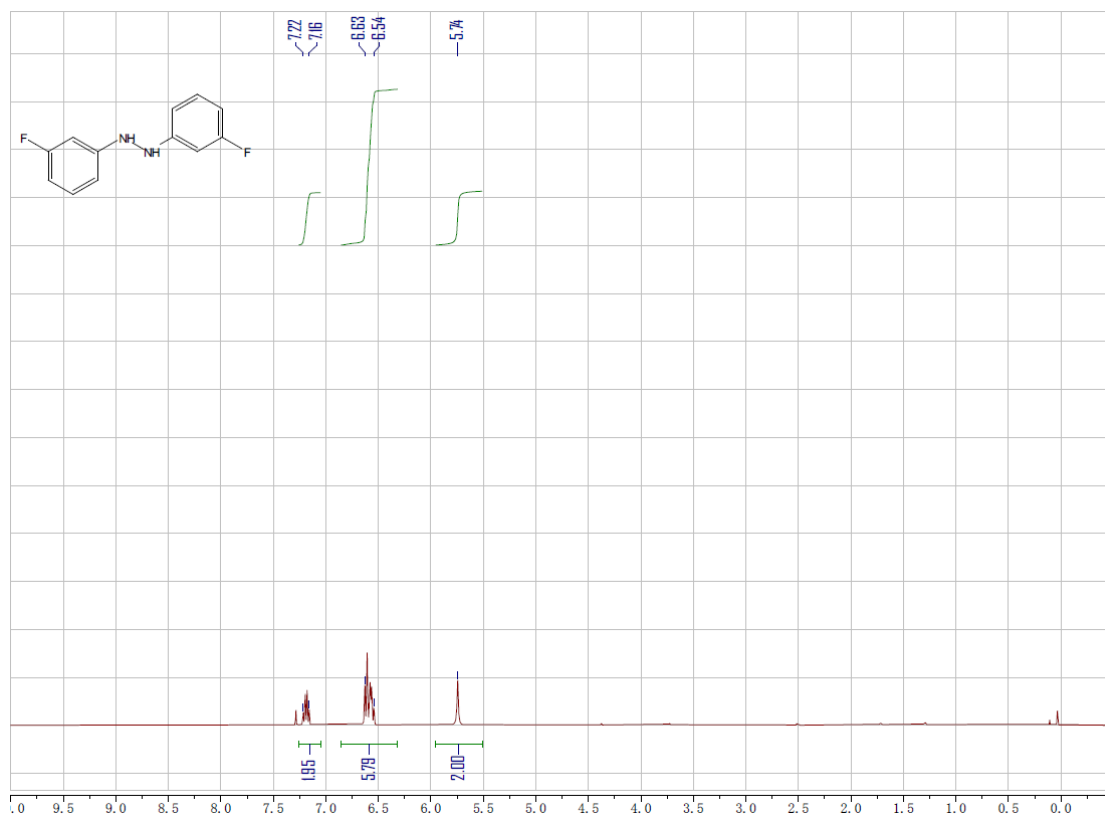


Figure S40. ^1H NMR Spectrum of **3t**

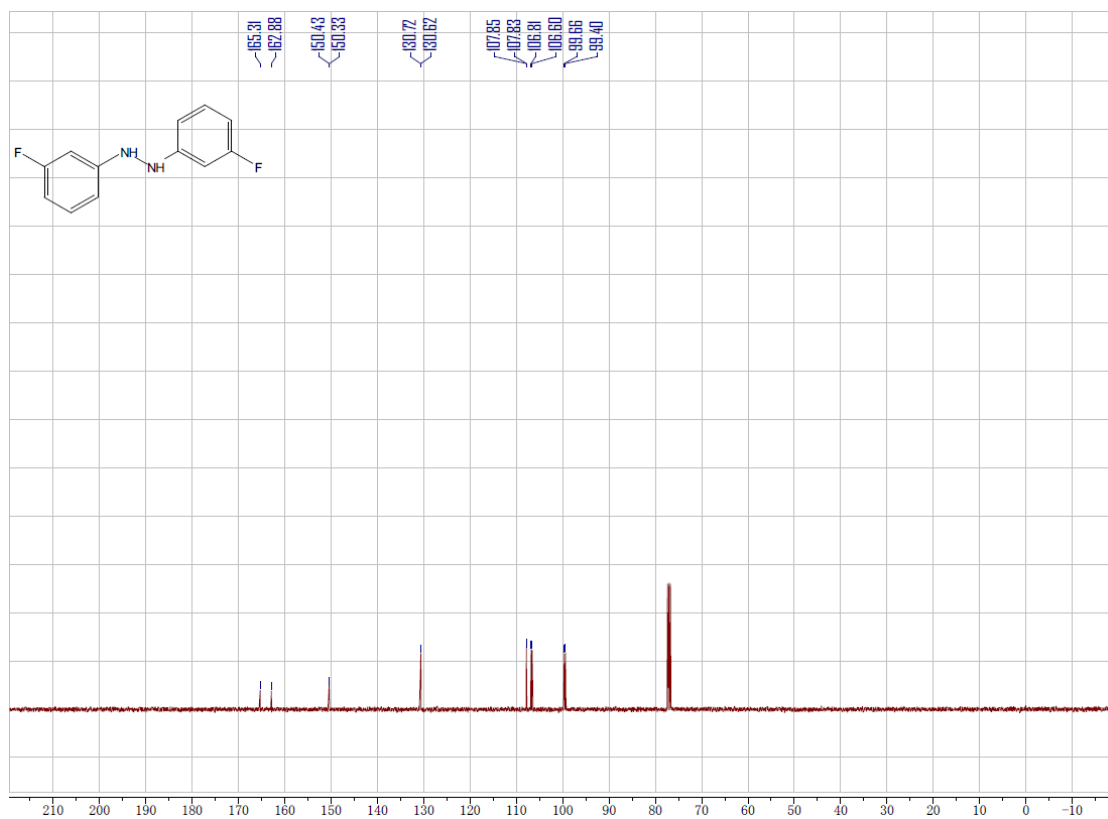


Figure S41. ^{13}C NMR Spectrum of **3t**

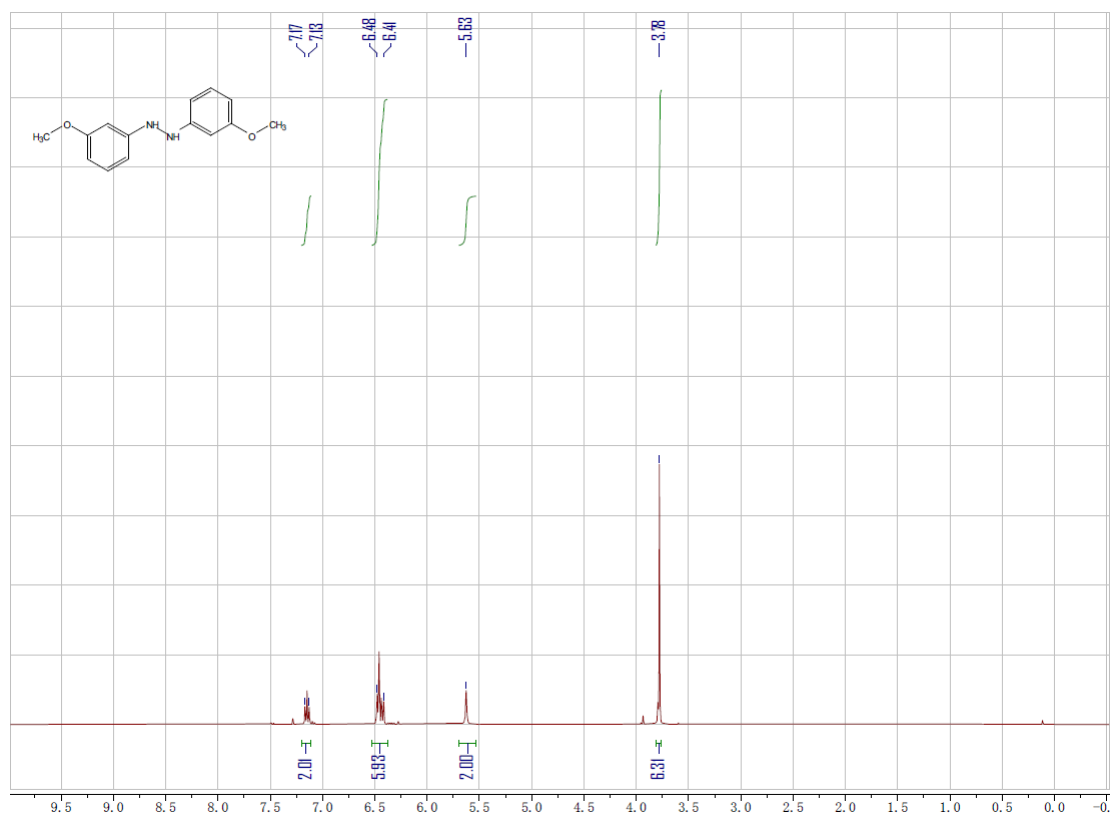


Figure S42. ^1H NMR Spectrum of **3u**

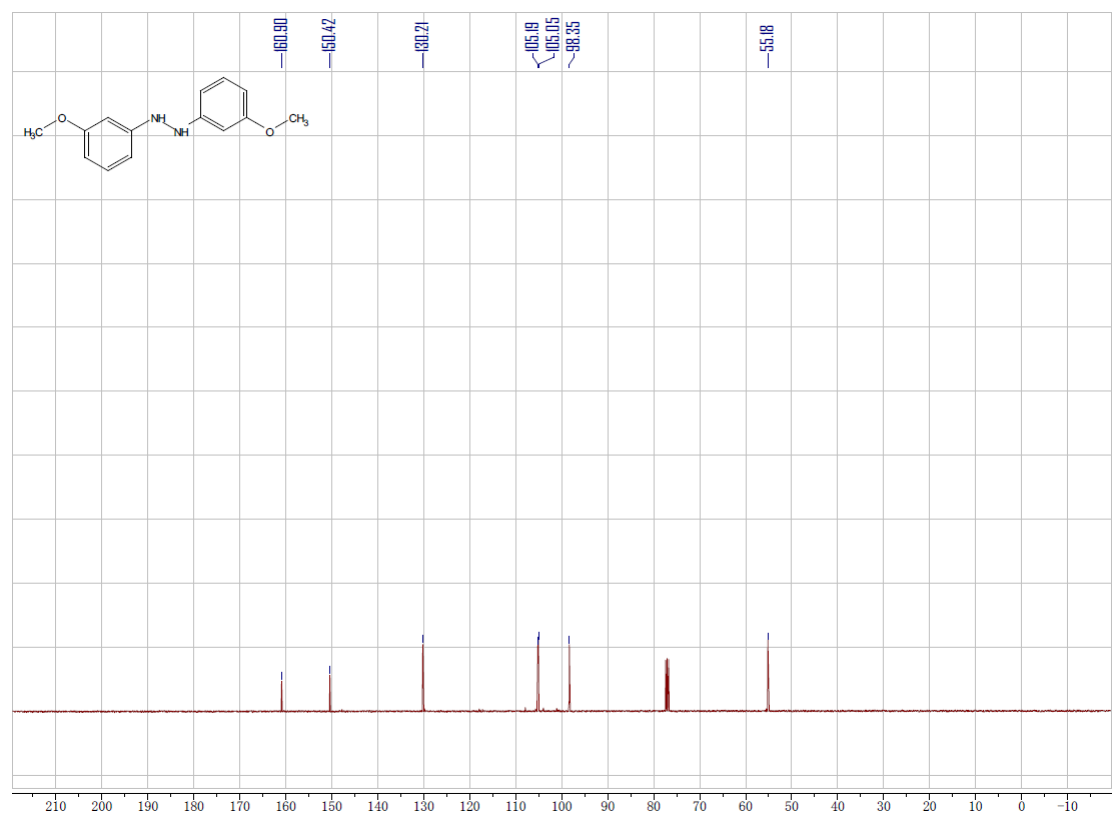


Figure S43. ^{13}C NMR Spectrum of **3u**

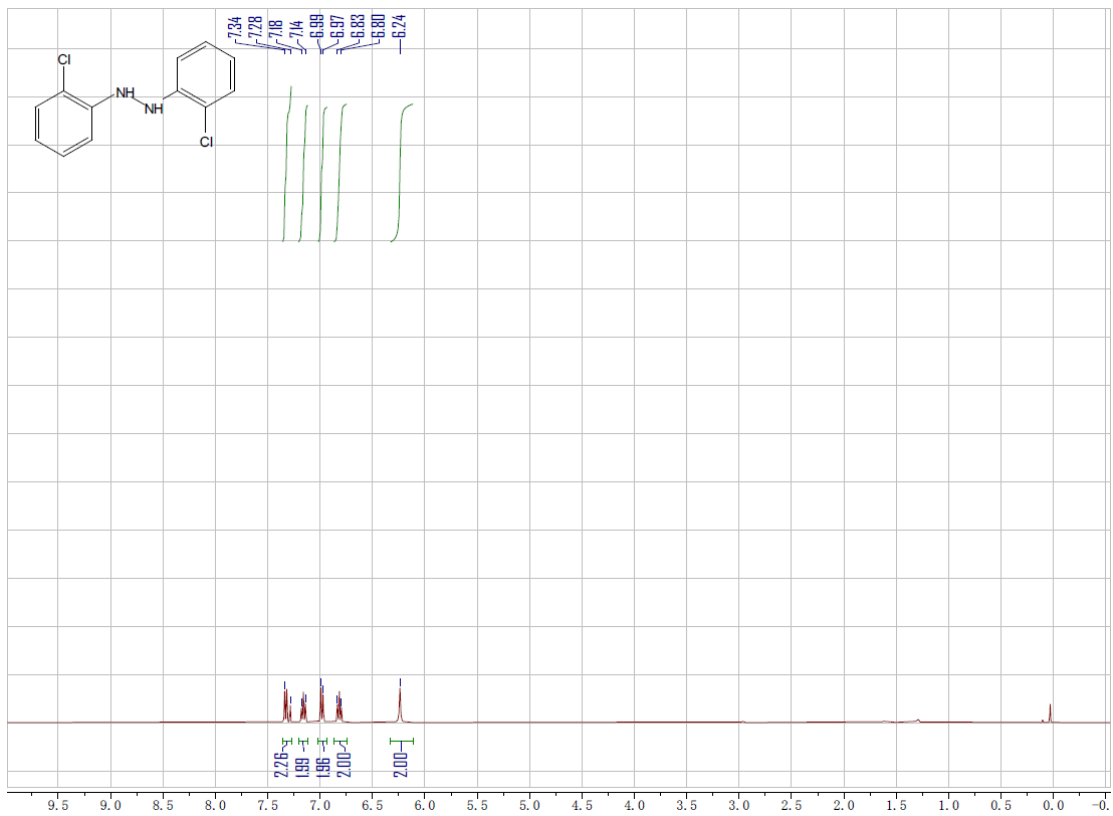


Figure S44. ¹H NMR Spectrum of **3v**

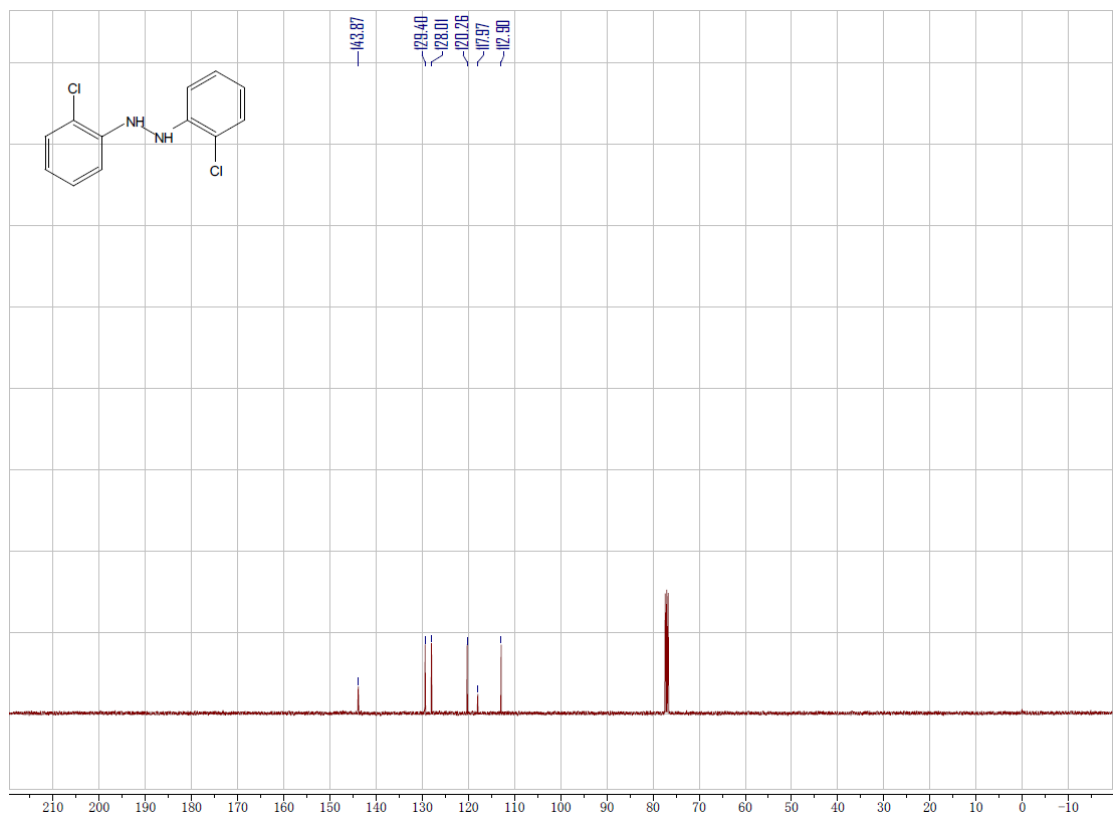


Figure S45. ¹³C NMR Spectrum of **3v**