Supporting Information

A reusable $FeCl_3 \cdot 6H_2O$/cationic 2,2′-bipyridyl catalytic system for reduction of nitroarenes in water

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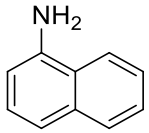
[†] These authors contributed equally to this work.

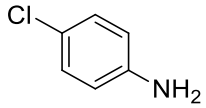
Table of Contents:

^{1}H and ^{13}C NMR spectral data for the reduction products



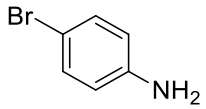
Naphthalen-1-amine (2a)[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2H), 7.46–7.43 (m, 2H), 7.31–7.27 (m, 2H), 6.79–6.76 (m, 1H), 4.12 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 134.4, 128.5, 126.3, 125.8, 124.8, 123.6, 120.8, 119.0, 109.7.



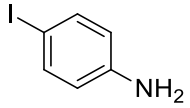
4-Chloroaniline (2b)[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 3.63 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 129.1, 123.1, 116.2.



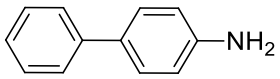
4-Bromoaniline (2c)[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 3.65 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 132.0, 116.7, 110.2.



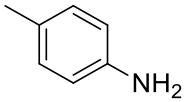
4-Iodoaniline (2d)[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.7 Hz, 2H), 6.44 (d, J = 8.7 Hz, 2H), 3.67 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 137.9, 117.3, 79.3.



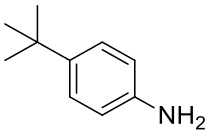
[1,1'-Biphenyl]-4-amine (2e)[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.47–7.32 (m, 4H), 7.24–7.19 (m, 1H), 6.71 (d, J = 8.6 Hz, 2H), 3.67 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 141.1, 131.6, 128.6, 128.0, 126.4, 126.2, 115.4.



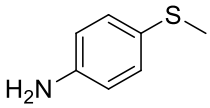
***p*-Toluidine (2f)**[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, J = 8.2 Hz, 2H), 6.59 (d, J = 8.2 Hz, 2H), 3.51 (br, 2H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 129.7, 127.7, 115.2, 20.4.



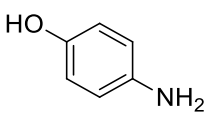
4-(*tert*-Butyl)aniline (2g)[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H), 3.53 (br, 2H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 141.4, 126.0, 114.9, 33.9, 31.5.



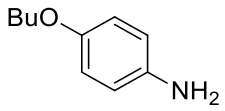
4-(Methylthio)aniline (2h)[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.6 Hz, 2H), 3.64 (br, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 131.0, 125.8, 115.7, 18.8.



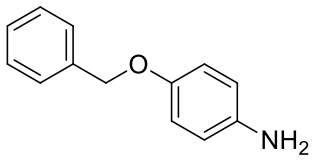
4-Aminophenol (2i)[5]

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.32 (s, 1H), 6.45 (d, J = 8.9 Hz, 2H), 6.39 (d, J = 8.9 Hz, 2H), 4.38 (br, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.2, 140.7, 115.5, 115.2.



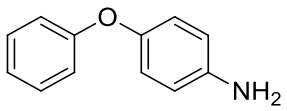
4-Butoxyaniline (2j)[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 3.87 (t, J = 6.5 Hz, 2H), 3.17 (br, 2H), 1.75–1.66 (m, 2H), 1.52–1.42 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 139.8, 116.4, 115.7, 68.4, 31.5, 19.2, 13.8.



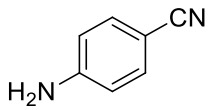
4-(Benzyloxy)aniline (2k)[9]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5H), 6.80 (d, J = 8.9 Hz, 2H), 6.62 (d, J = 8.9 Hz, 2H), 4.97 (s, 2H), 3.40 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 140.2, 137.5, 128.5, 127.8, 127.5, 116.4, 116.1, 70.8.



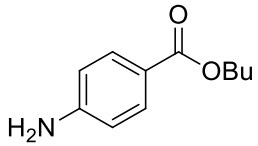
4-Phenoxyaniline (2l)[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.21 (m, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.7 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 3.54 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 148.6, 142.6, 129.5, 122.0, 121.1, 117.2, 116.2.



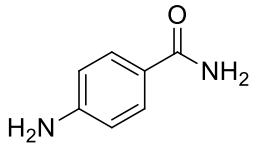
4-Aminobenzonitrile (2m)[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2H), 6.62 (d, J = 8.6 Hz, 2H), 4.13 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 133.8, 120.1, 114.4, 100.1.



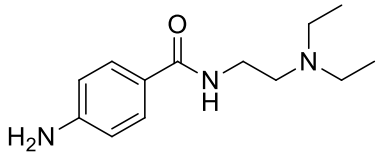
Butyl 4-aminobenzoate (2n)[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 4.24 (t, J = 6.6 Hz, 2H), 4.01 (br, 2H), 1.75–1.66 (m, 2H), 1.51–1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 150.7, 131.5, 120.0, 113.7, 64.2, 30.8, 19.3, 13.8.



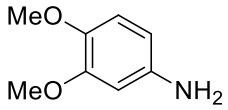
4-Aminobenzamide (2o)[10]

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.56 (d, J = 8.6 Hz, 2H), 7.50 (br, 1H), 6.80 (br, 1H), 6.50 (d, J = 8.6 Hz, 2H), 5.57 (br, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.1, 151.7, 129.2, 120.9, 112.5.



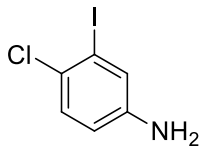
Procainamide (2p)[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 8.6 Hz, 2H), 6.79 (br, 1H), 6.62 (d, J = 8.6 Hz, 2H), 3.96 (br, 2H), 3.45–3.39 (m, 2H), 2.61–2.57 (m, 2H), 2.56–2.49 (m, 4H), 1.00 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 149.4, 128.5, 124.2, 114.1, 51.4, 46.7, 37.1, 11.9.



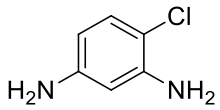
3,4-Dimethoxyaniline (2q)[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.68 (d, J = 8.4 Hz, 1H), 6.29 (d, J = 2.6 Hz, 1H), 6.21 (dd, J = 8.4, 2.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.11 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 142.1, 140.5, 112.9, 106.3, 100.6, 56.5, 55.7.



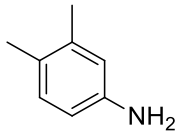
4-Chloro-3-iodoaniline (2r)[14]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–7.13 (m, 2H), 6.57 (dd, J = 8.6, 2.7 Hz, 1H), 3.64 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 129.3, 127.3, 125.8, 116.2, 98.3.



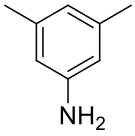
4-Chlorobenzene-1,3-diamine (2s)[15]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (d, J = 8.3 Hz, 1H), 6.07–6.02 (m, 2H), 3.87 (br, 2H), 3.58 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 143.4, 129.8, 109.2, 106.7, 102.2.



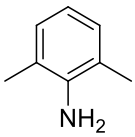
3,4-Dimethylaniline (2t)[16]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (d, J = 7.8 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.44 (dd, J = 7.9, 2.4 H, 1H), 3.46 (br, 2H), 2.16 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 137.3, 130.2, 126.5, 116.8, 112.6, 19.8, 18.7.



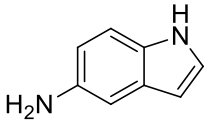
3,5-Dimethylaniline (2u)[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 1H), 6.33 (s, 2H), 3.54 (br, 2H), 2.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 139.0, 120.5, 113.1, 21.3.



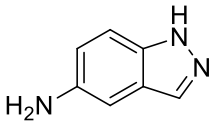
2,6-Dimethylaniline (2v)[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (d, J = 7.5 Hz, 2H), 6.63 (t, J = 7.5 Hz, 1H), 3.56 (br, 2H), 2.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 128.2, 121.6, 117.9, 17.6.



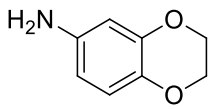
1*H*-indol-5-amine (2w)[19]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (br, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.11 (t, J = 2.8 Hz, 1H), 6.93 (d, J = 2.1 Hz, 1H), 6.65 (dd, J = 8.5, 2.2 Hz, 1H), 6.36 (s, 1H), 3.49 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 130.6, 128.7, 124.7, 112.9, 111.5, 105.5, 101.5.



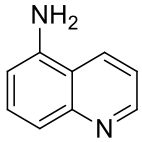
1*H*-indazol-5-amine (2x)[2]

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.55 (br, 1H), 7.70 (s, 1H), 7.22 (d, J = 8.7 Hz, 1H), 6.77–6.73 (m, 2H), 4.74 (br, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.3, 134.5, 131.5, 123.9, 118.1, 110.2, 100.4.



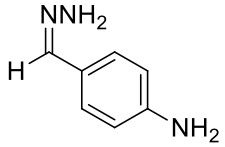
1,4-Benzodioxan-6-amine (2y)[20]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, J = 8.4 Hz, 1H), 6.22 (d, J = 2.6 Hz, 1H), 6.18 (dd, J = 8.4, 2.6 Hz, 1H), 4.22–4.19 (m, 2H), 4.17–4.14 (m, 2H), 3.36 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 140.7, 136.4, 117.5, 108.6, 104.1, 64.6, 64.1.



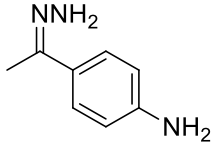
Quinolin-5-amine (2z)[21]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (dd, J = 4.1, 1.4 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.53–7.48 (m, 2H), 7.33–7.32 (m, 1H), 6.79 (dd, J = 7.3, 0.9 Hz, 1H), 4.20 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.0, 142.3, 130.0, 129.5, 120.0, 119.5, 118.6, 109.9.



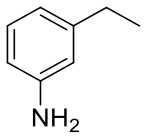
4-(hydrazonomethyl)aniline(4a)[22]

^{1}H NMR (300 MHz, Acetone-d_6) δ 8.44 (s, 1H), 7.57 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 8.6 Hz, 2H), 5.21 (br, 2H), 2.88 (s, 2H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 160.9, 152.3, 130.7, 124.1, 114.8.



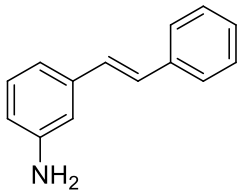
4-(1-hydrazonoethyl)aniline (4b)[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.6 Hz, 2H), 3.84 (br, 2H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 158.0, 147.8, 129.0, 127.9, 114.4, 14.5.



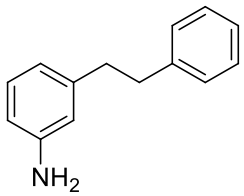
3-Ethylaniline (4c′)[23]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.54–6.53 (m, 2H), 3.60 (br, 2H), 2.60–2.52 (m, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 145.5, 129.2, 118.2, 114.7, 112.5, 28.8, 15.5.



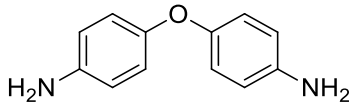
(*E*)-3-Styrylaniline (4d)[24]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.36–7.31 (m, 2H), 7.26–7.21 (m, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.03 (d, J = 2.9 Hz, 2H), 6.93–6.90 (m, 1H), 6.84–6.83 (m, 1H), 6.61–6.57 (m, 1H), 3.67 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 138.2, 137.2, 129.5, 128.7, 128.6, 128.4, 127.4, 126.4, 117.2, 114.6, 112.8.



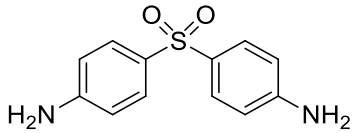
3-Phenethylaniline (4d′)[25]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.24–7.21 (m, 3H), 7.13–7.08 (m, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.56–6.54 (m, 2H), 3.60 (br, 2H), 2.96–2.90 (m, 2H), 2.88–2.82 (m, 2H); 13C NMR (75 MHz, CDCl3) δ 146.3, 143.0, 141.9, 129.2, 128.4, 128.3, 125.8, 118.7, 115.2, 112.7, 37.9, 37.7.



4,4'-Oxydianiline (6a)[24]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, J = 8.8 Hz, 4H), 6.62 (d, J = 8.8 Hz, 4H), 3.49 (br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 141.7, 119.5, 116.2.



4,4'-Sulfonyldianiline / 4,4'-*Dapsone* (6b)[26]

^{1}H NMR (300 MHz, Acetone-d_6) δ 7.55 (d, J = 8.7 Hz, 4H), 6.70 (d, J = 8.7 Hz, 4H), 5.43 (br, 4H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 153.4, 131.2, 129.8, 114.2.

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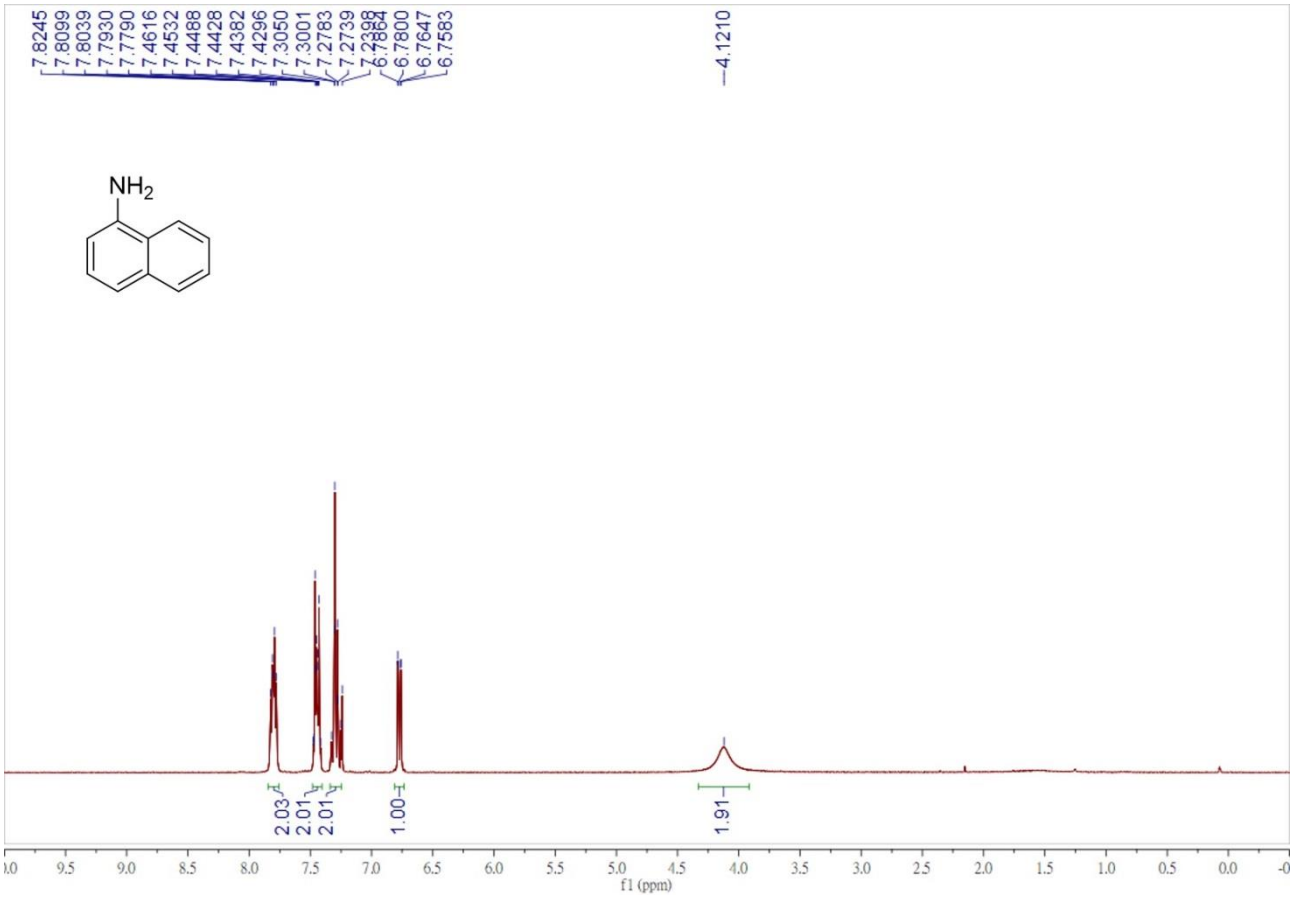
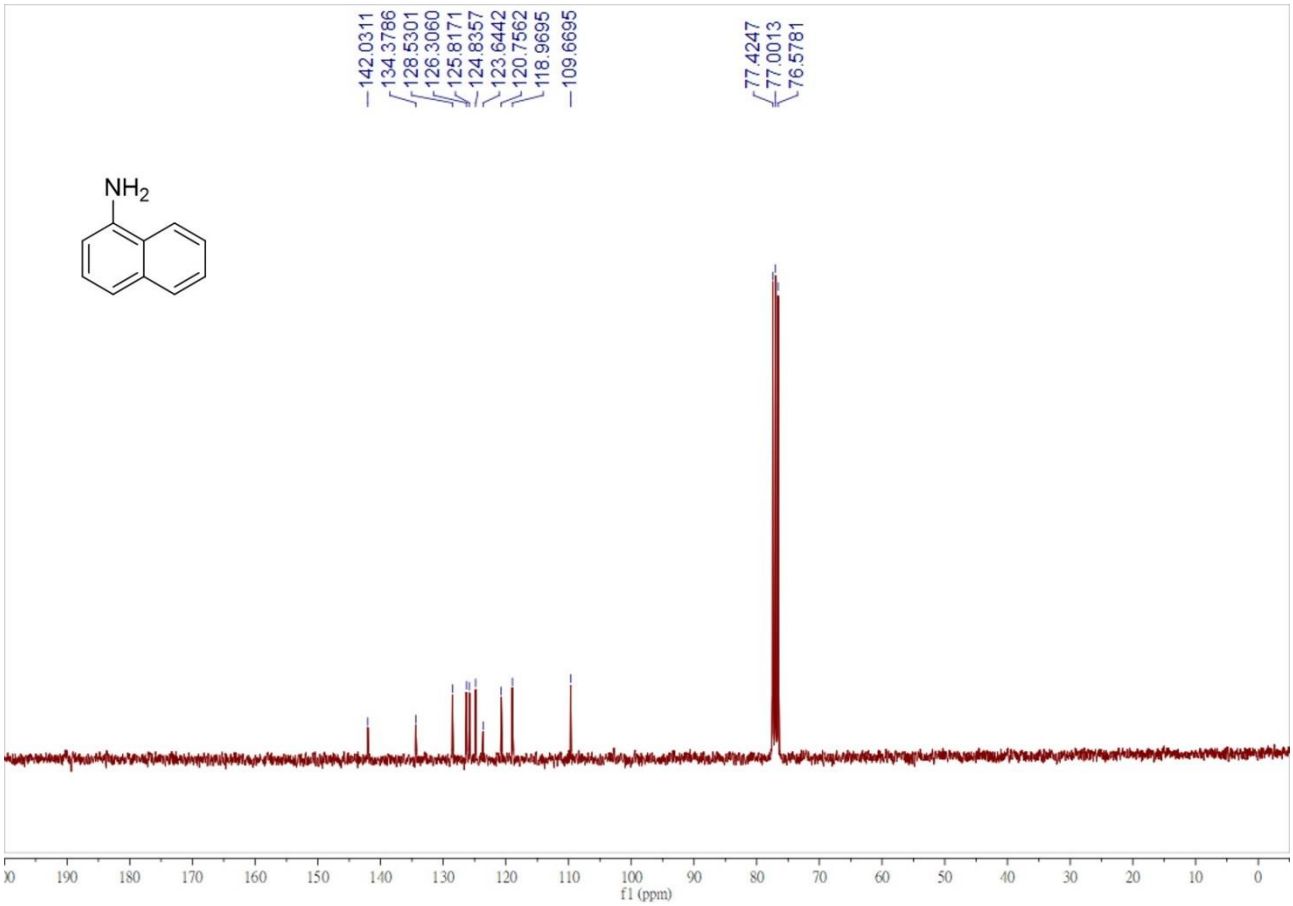
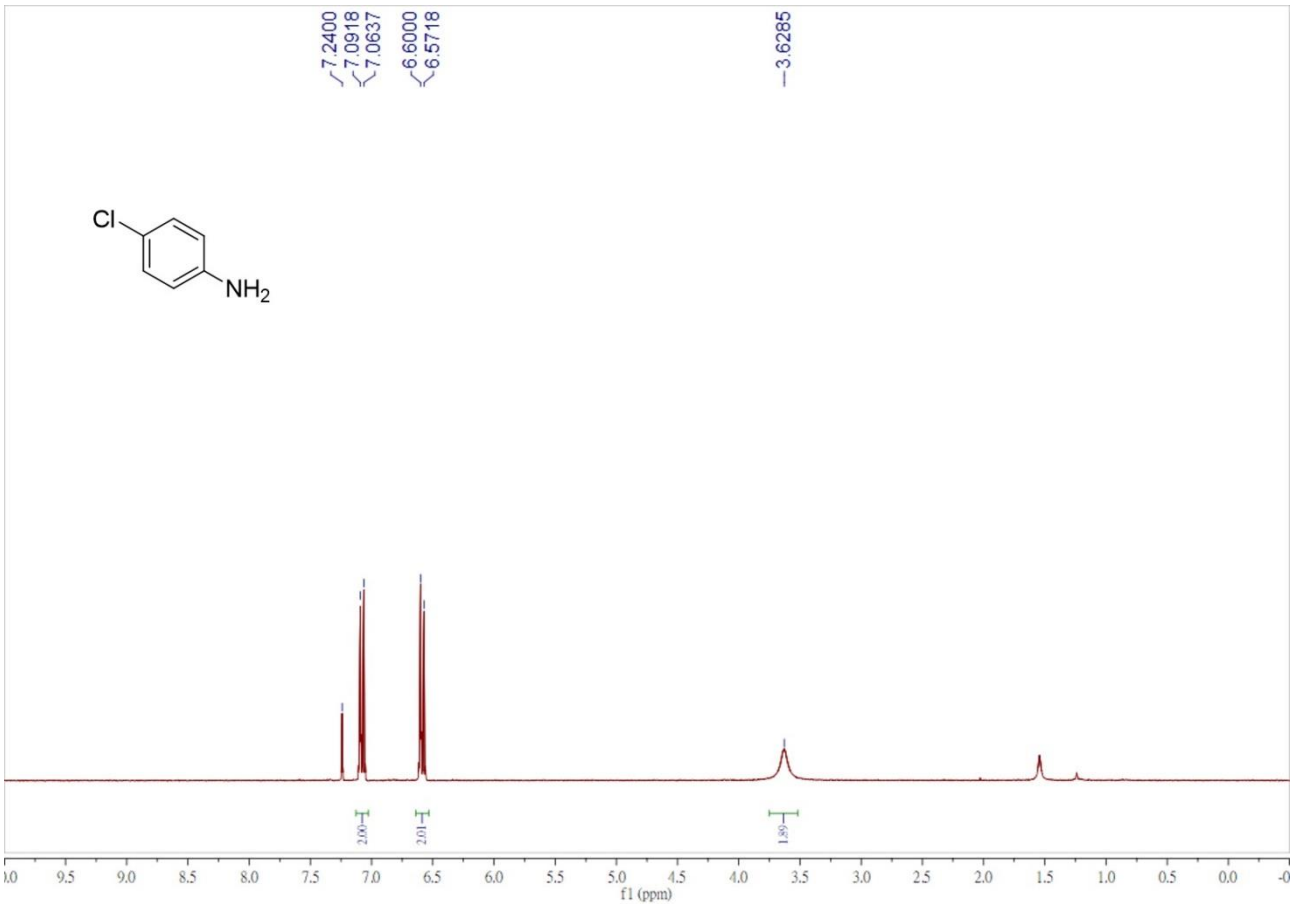
Copies of ^{1}H and ^{13}C NMR spectra for all reduction products

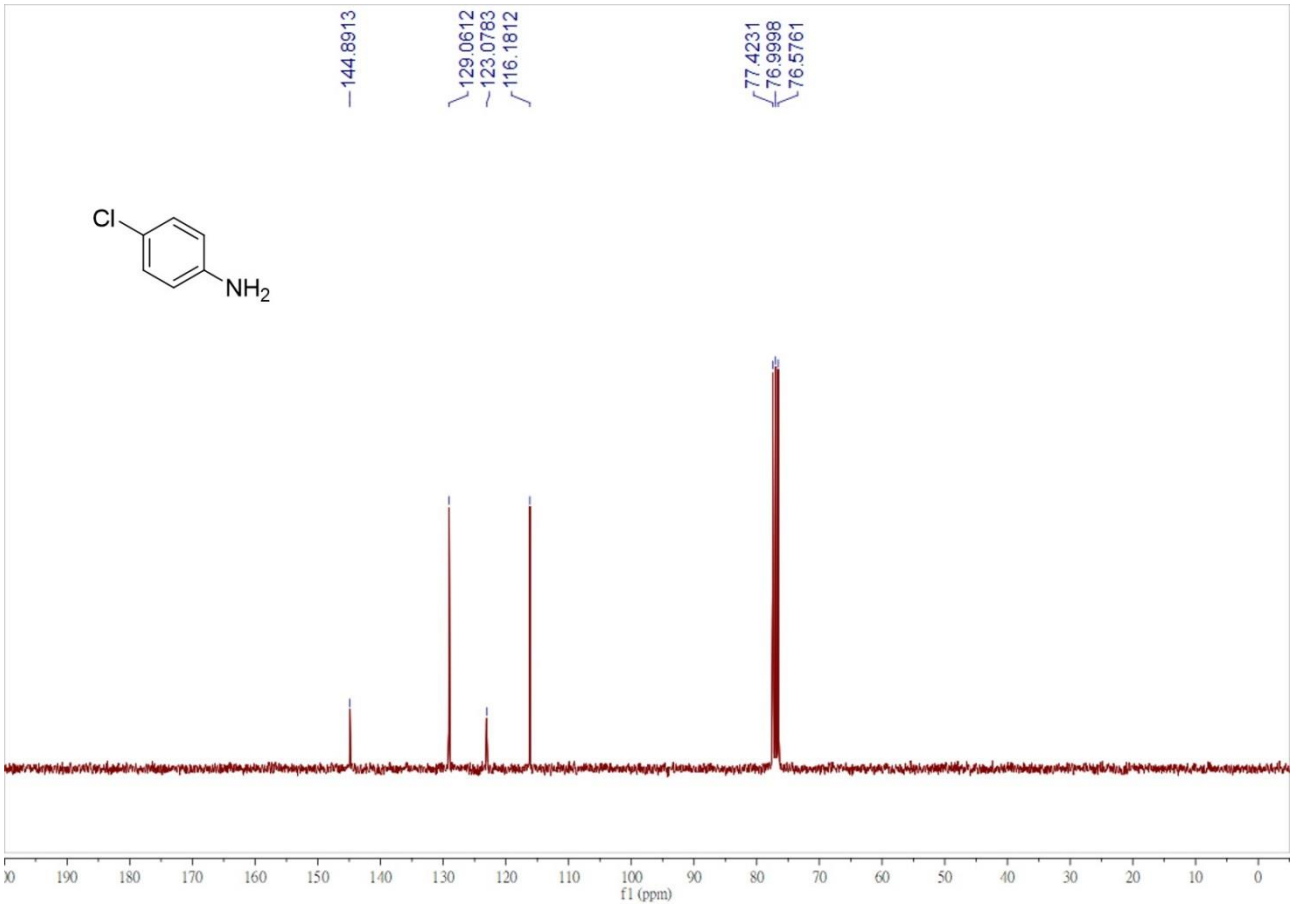
^{1}H and ^{13}C NMR spectra of compound **2a**



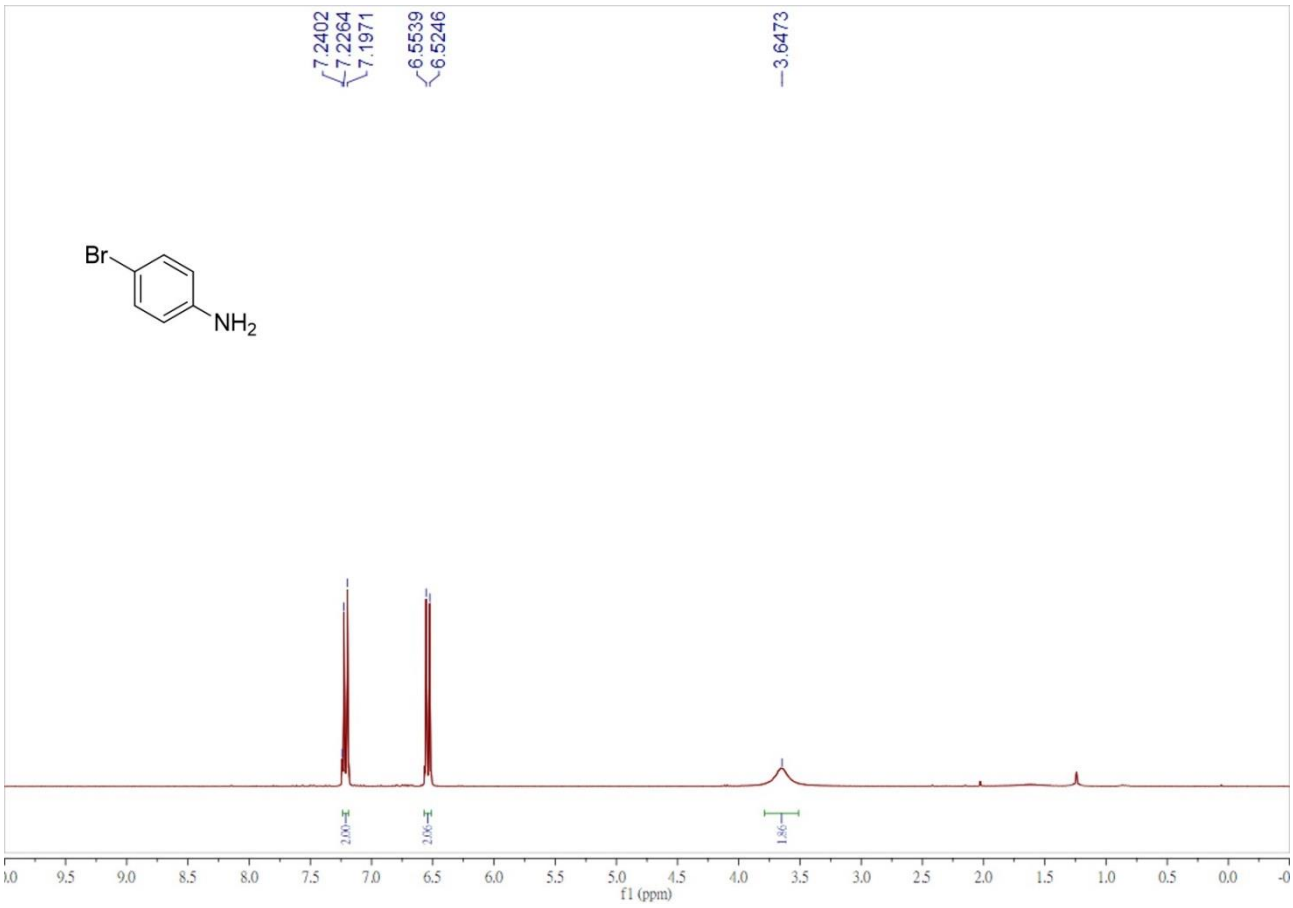


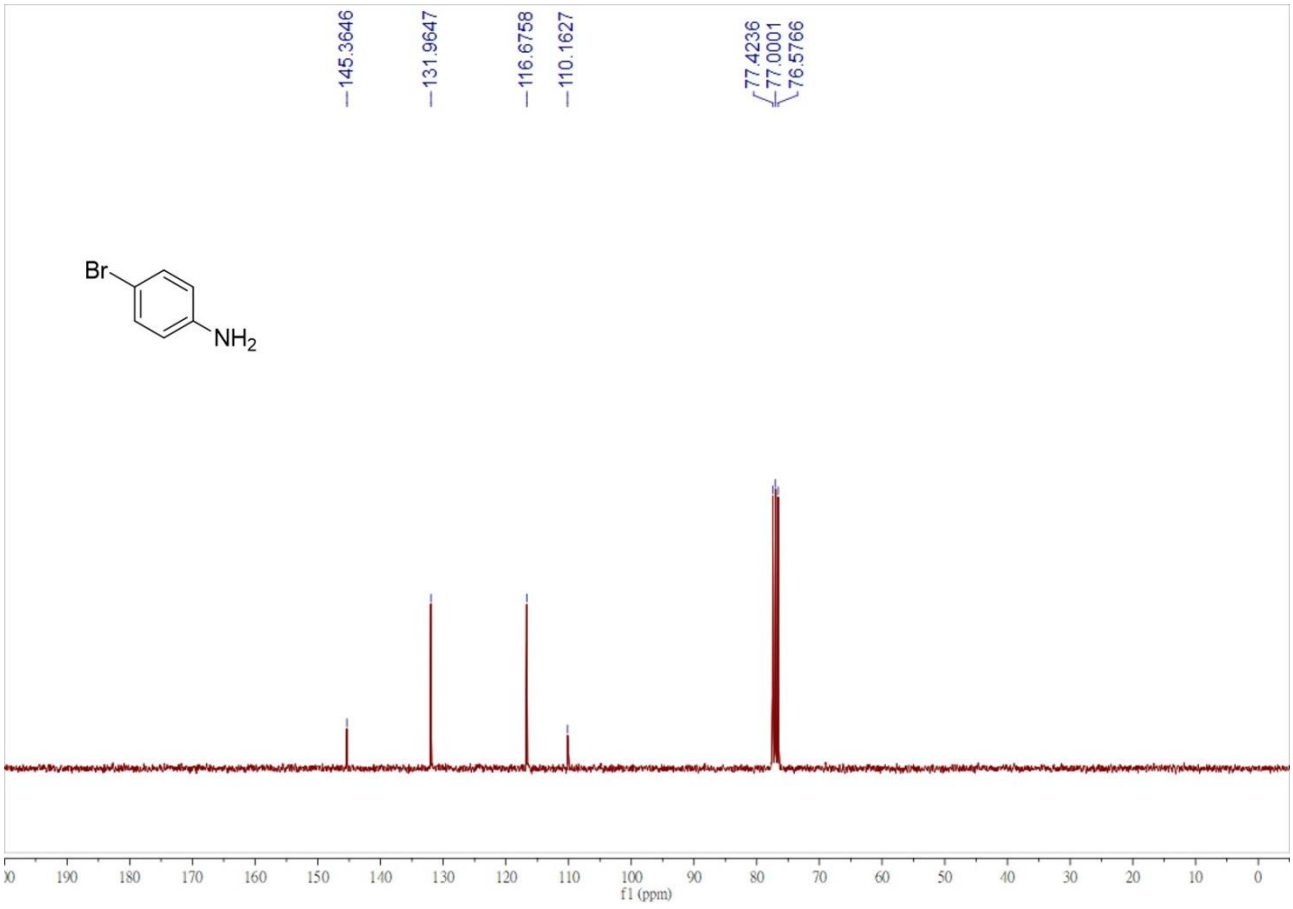
^{1}H and ^{13}C NMR spectra of compound **2b**





^{1}H and ^{13}C NMR spectra of compound **2c**





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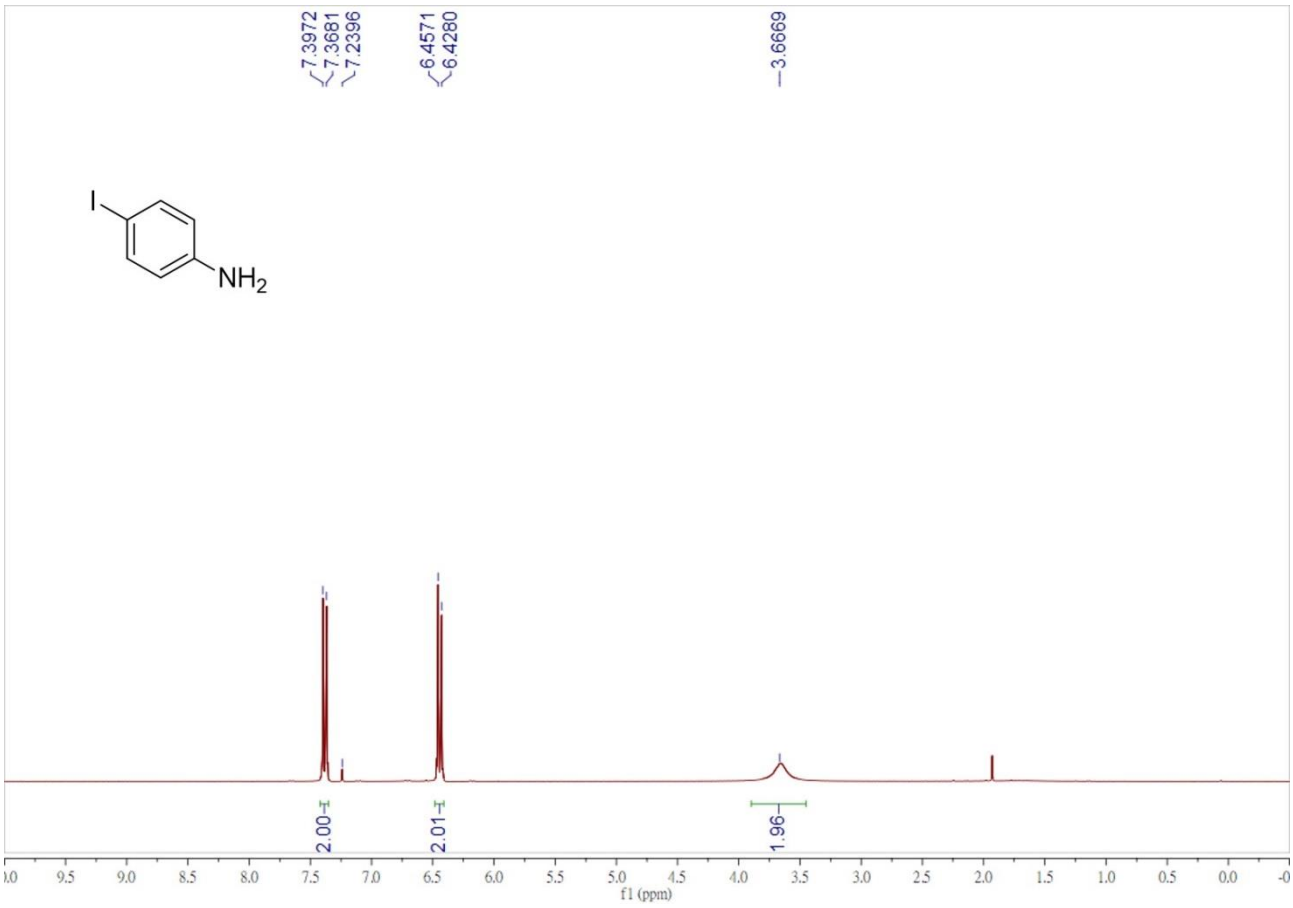
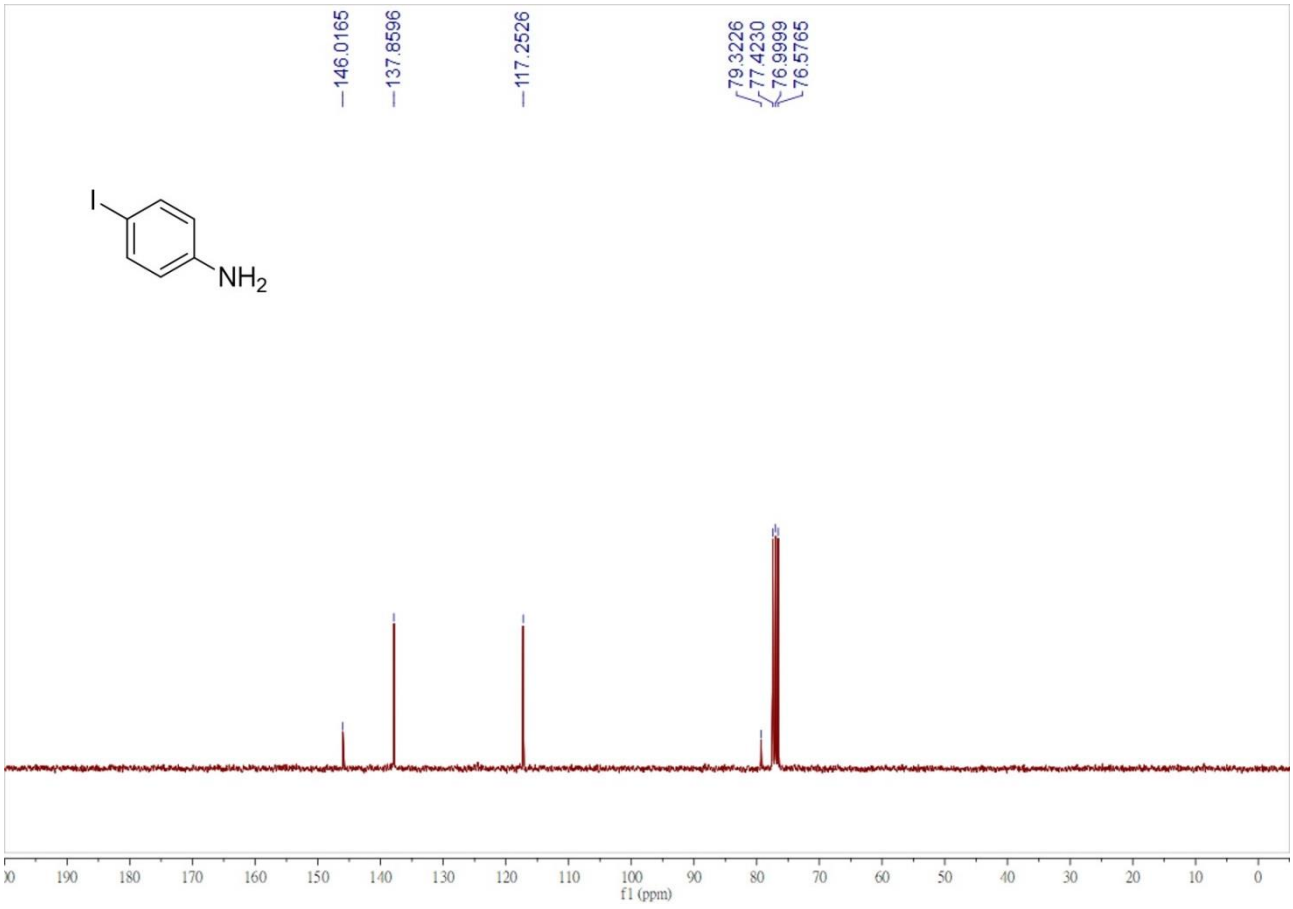
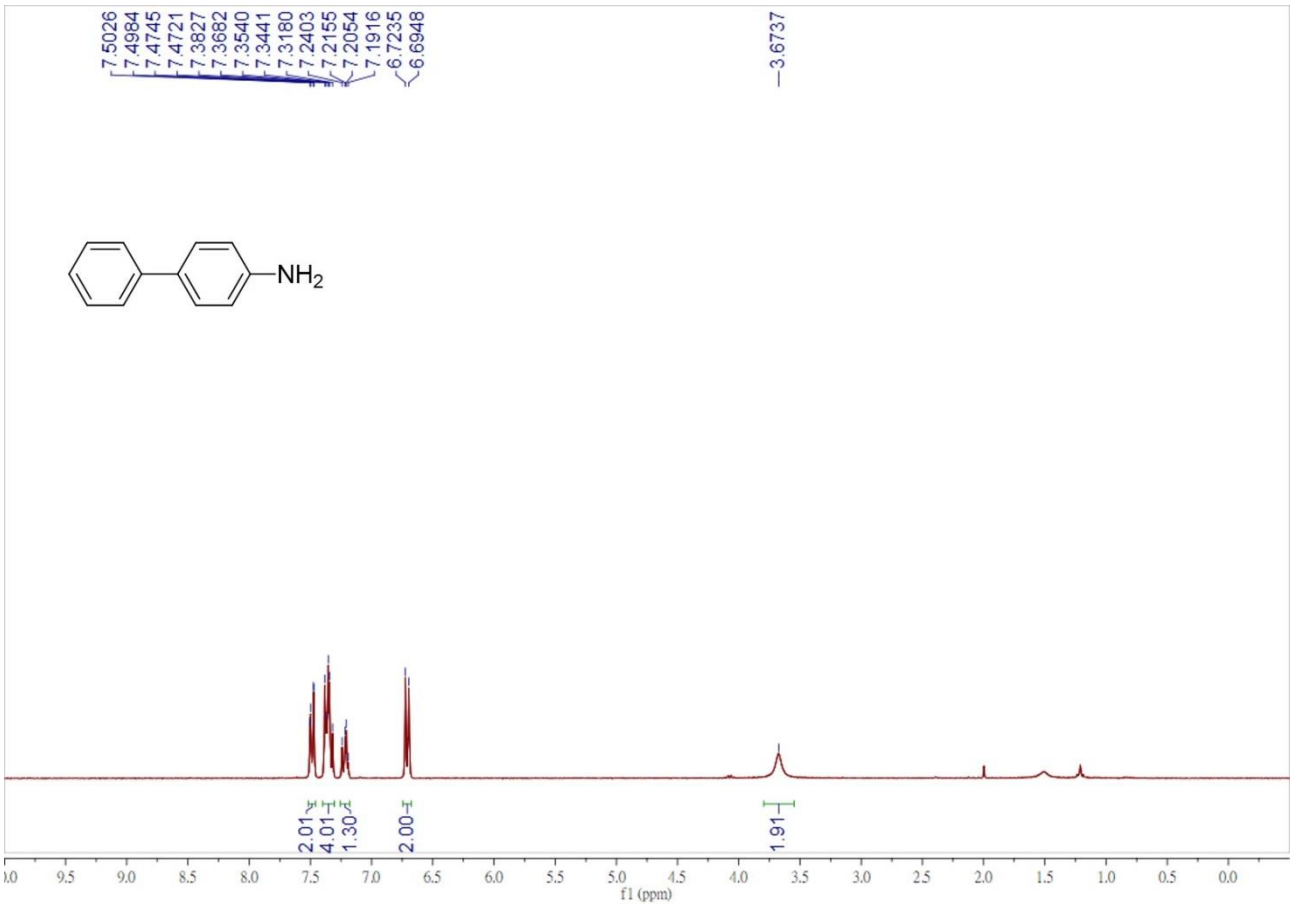
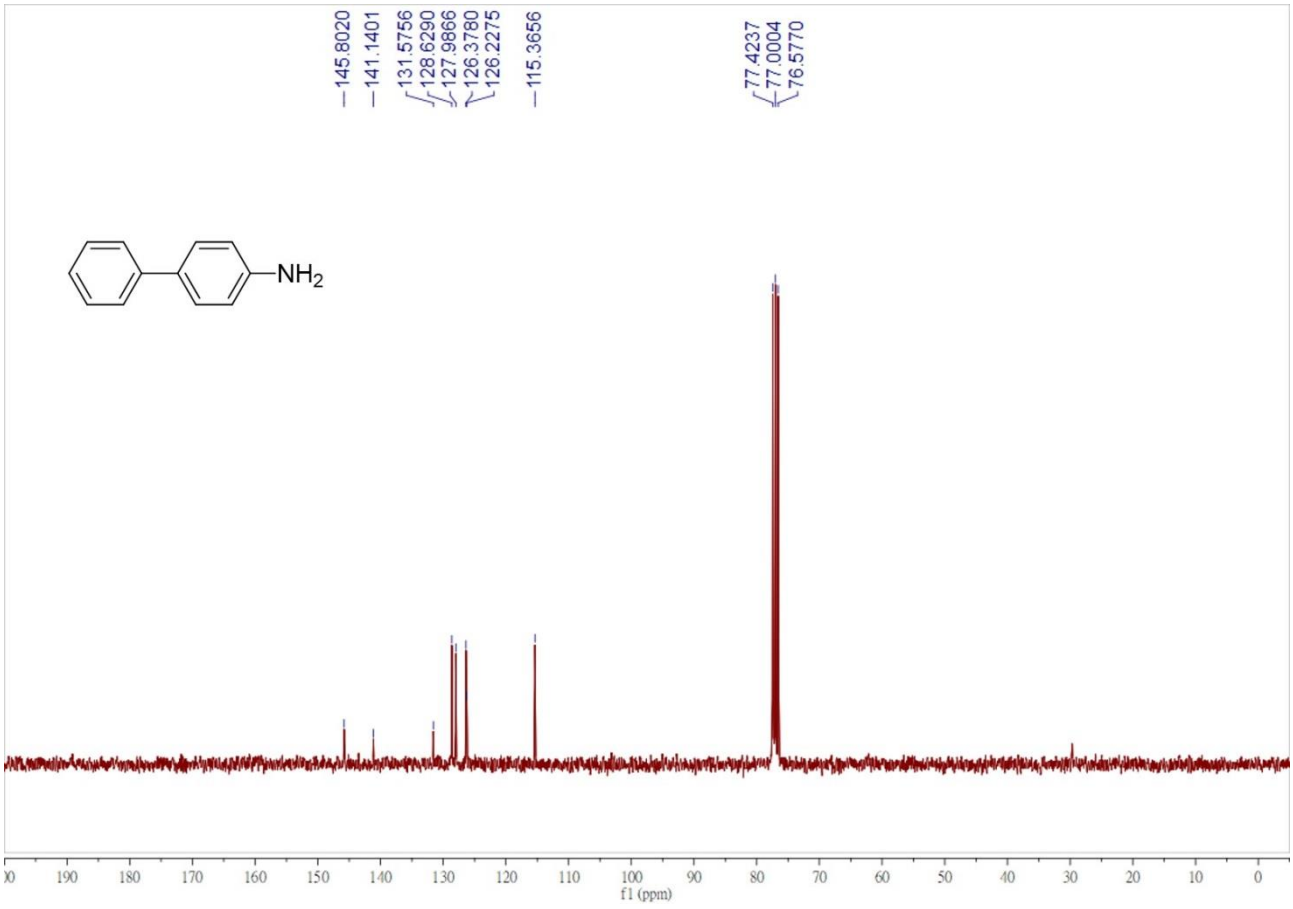


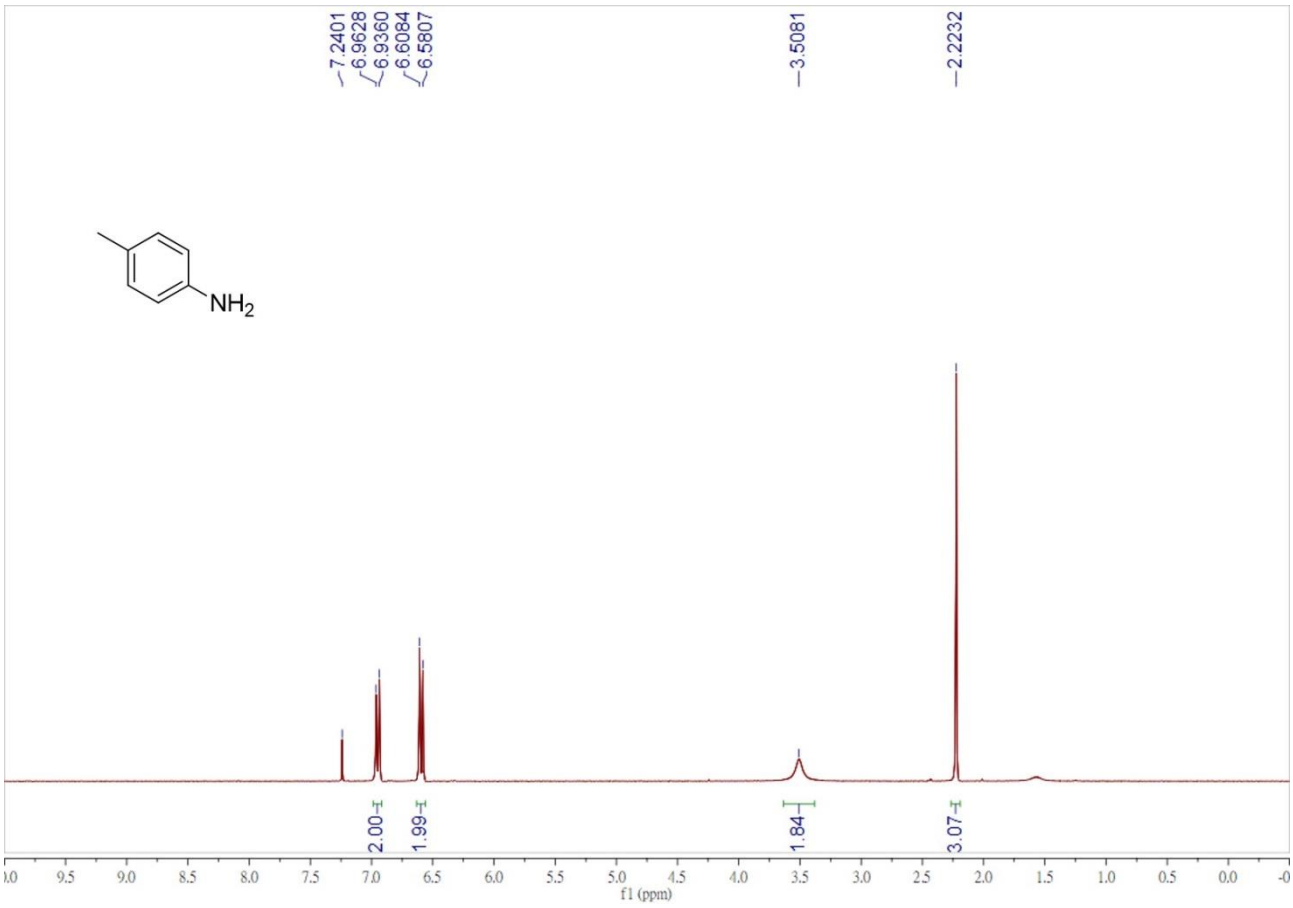


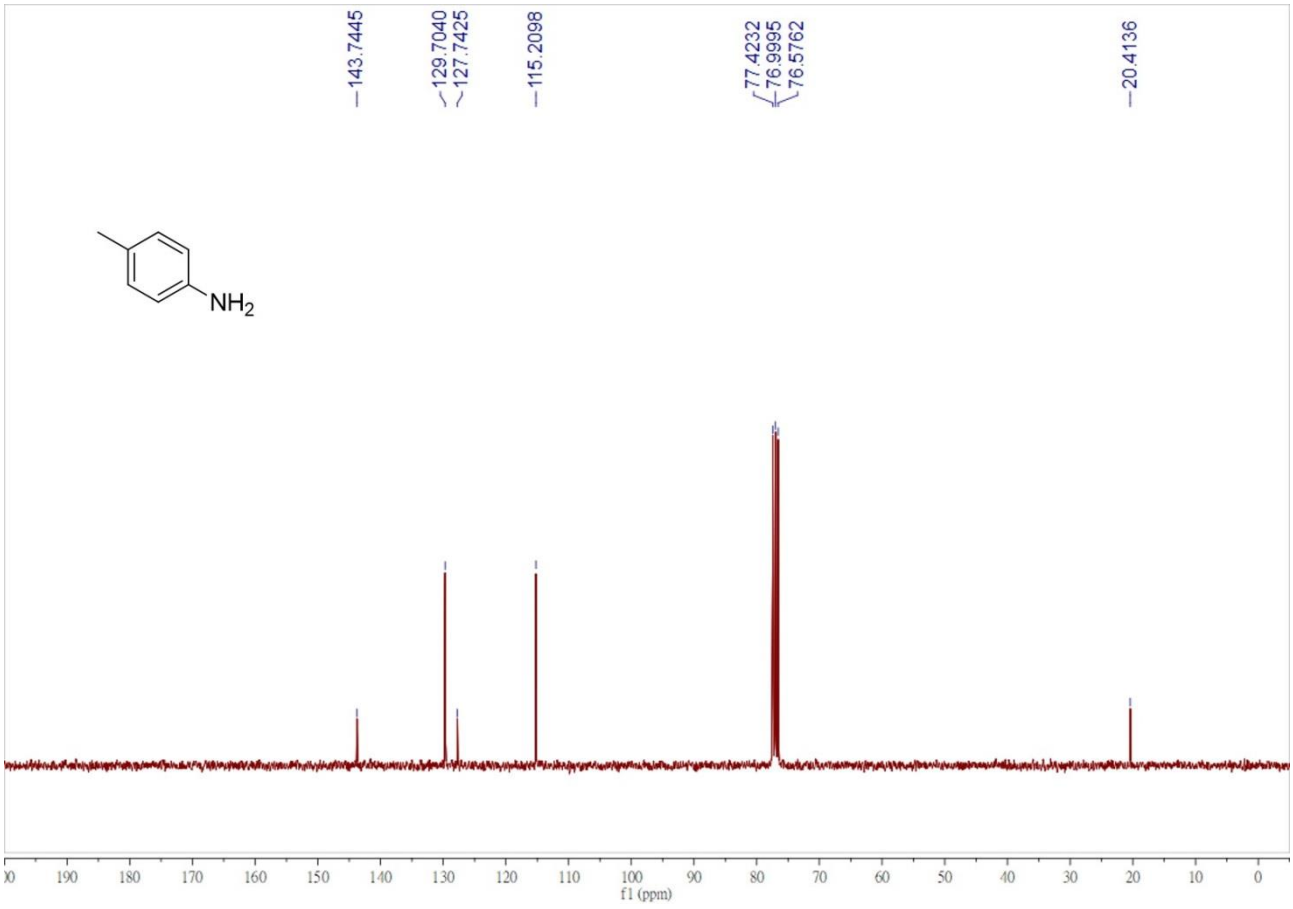
^{1}H and ^{13}C NMR spectra of compound **2e**



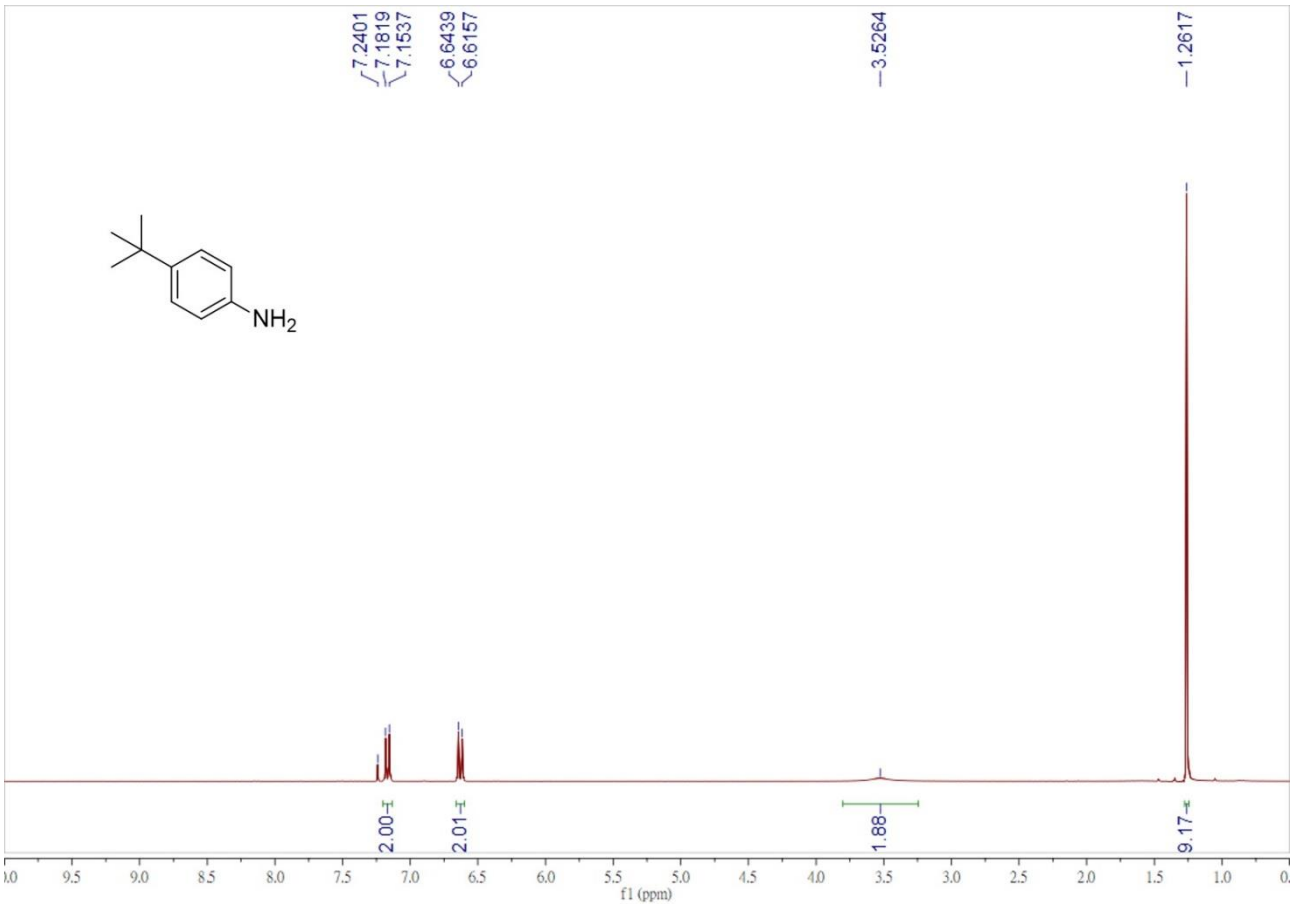


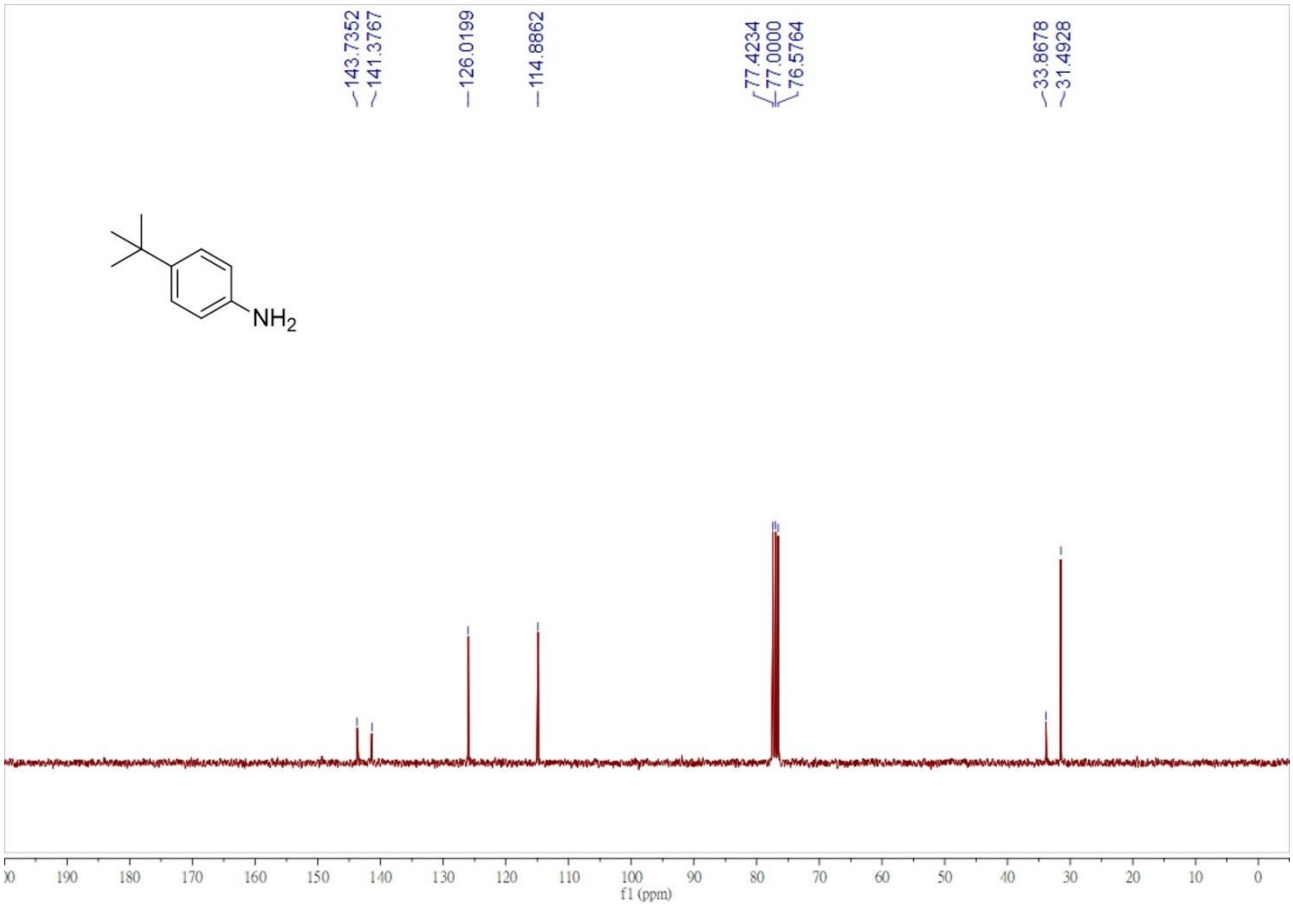
^{1}H and ^{13}C NMR spectra of compound **2f**



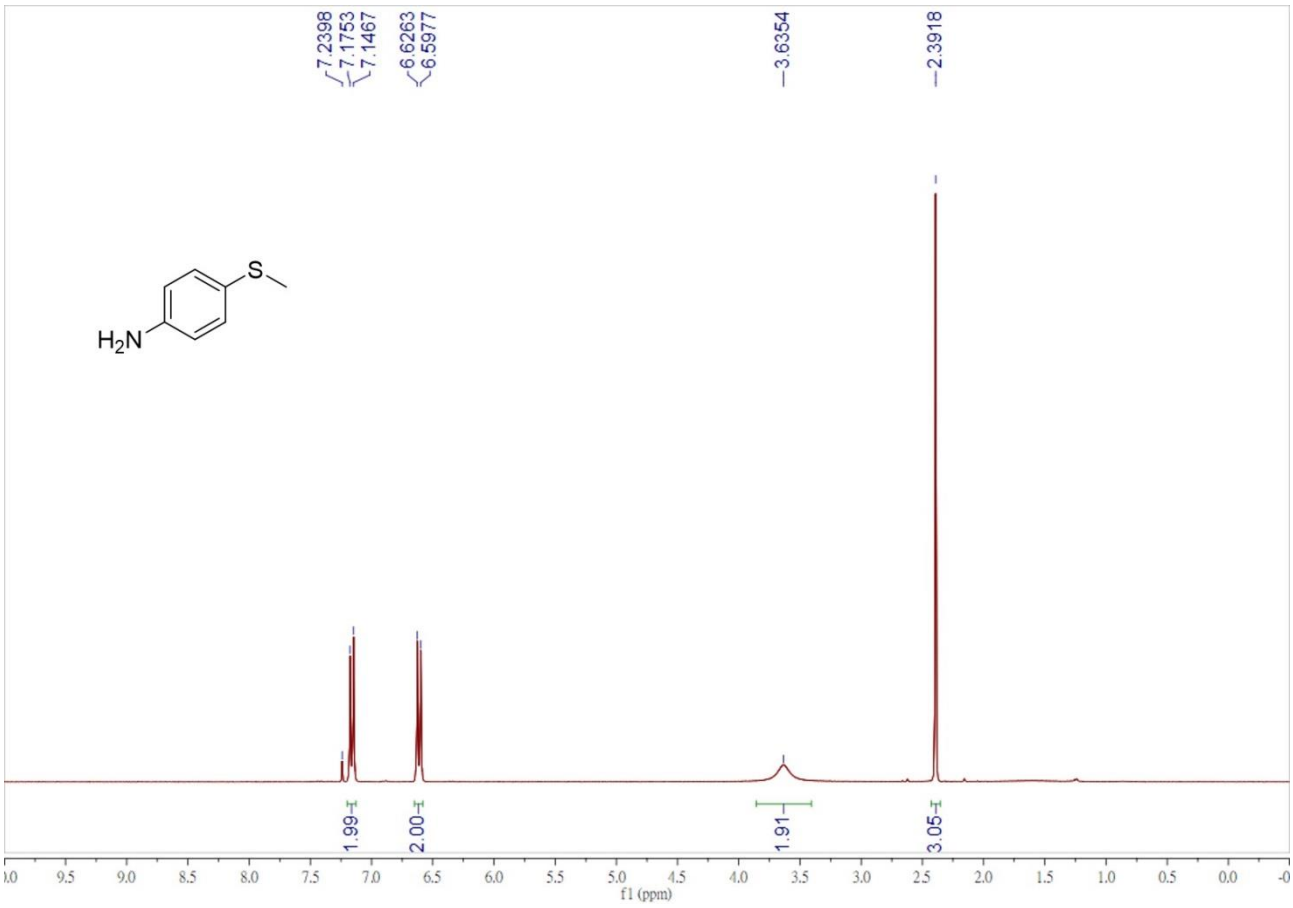


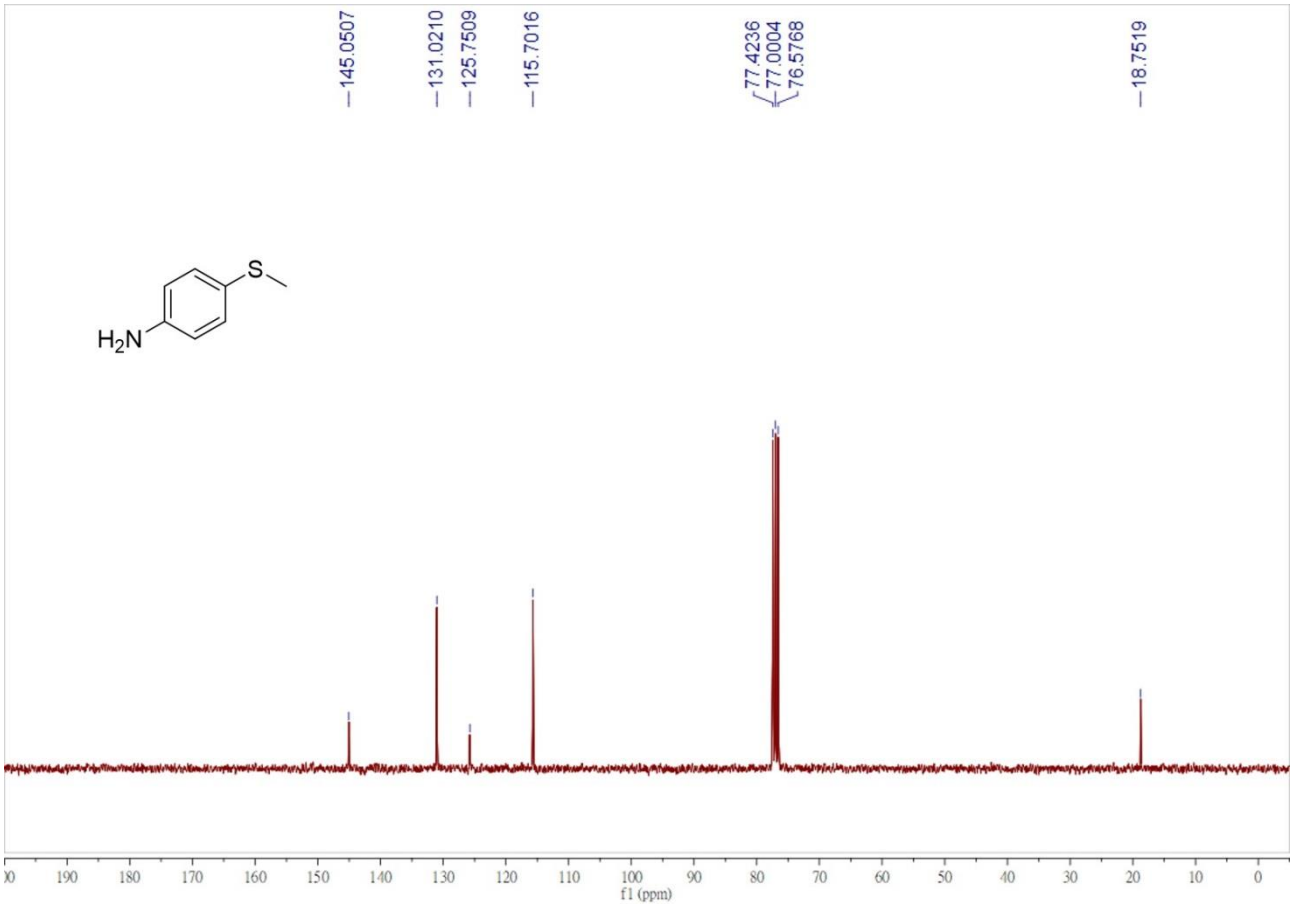
^{1}H and ^{13}C NMR spectra of compound **2g**



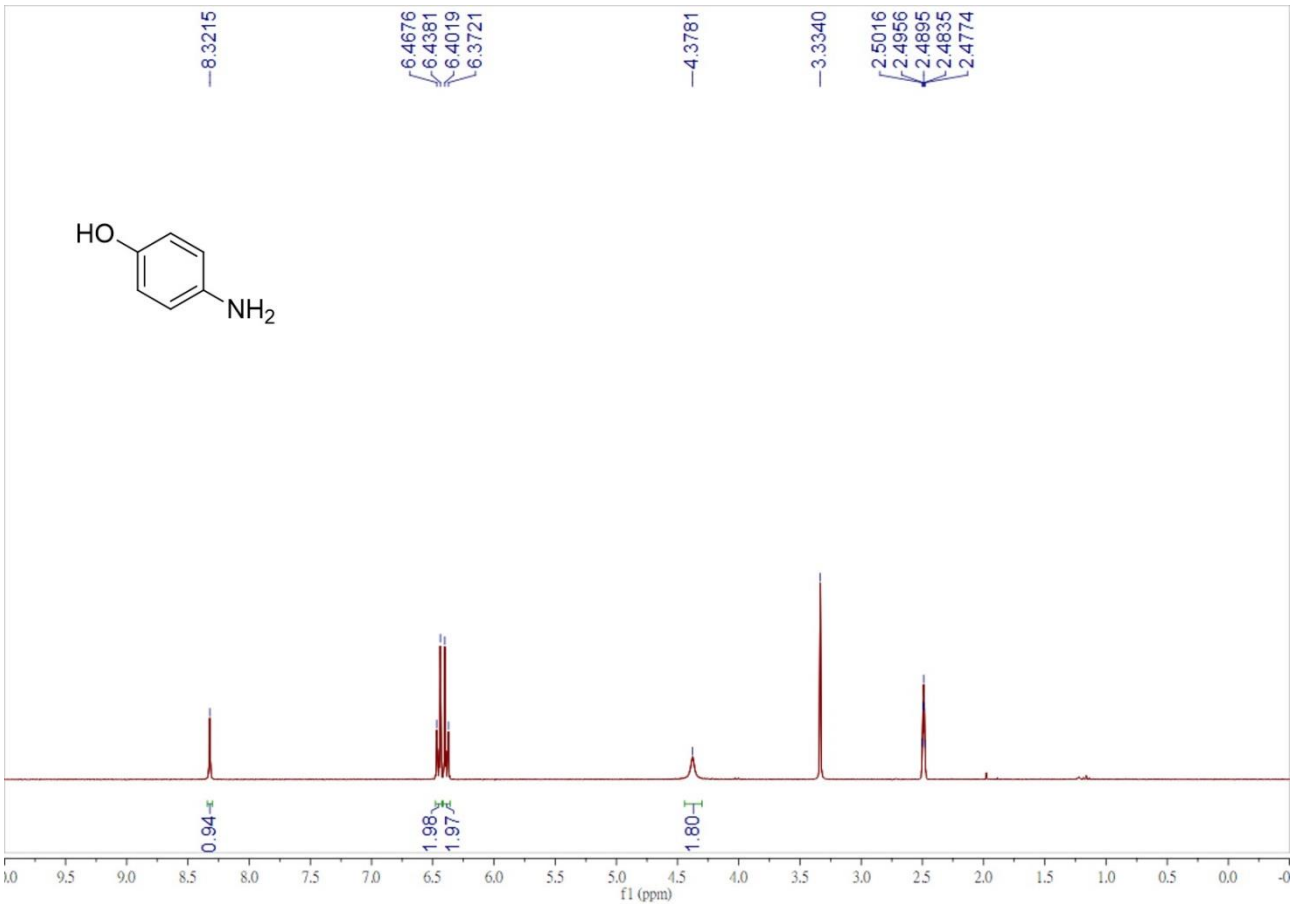


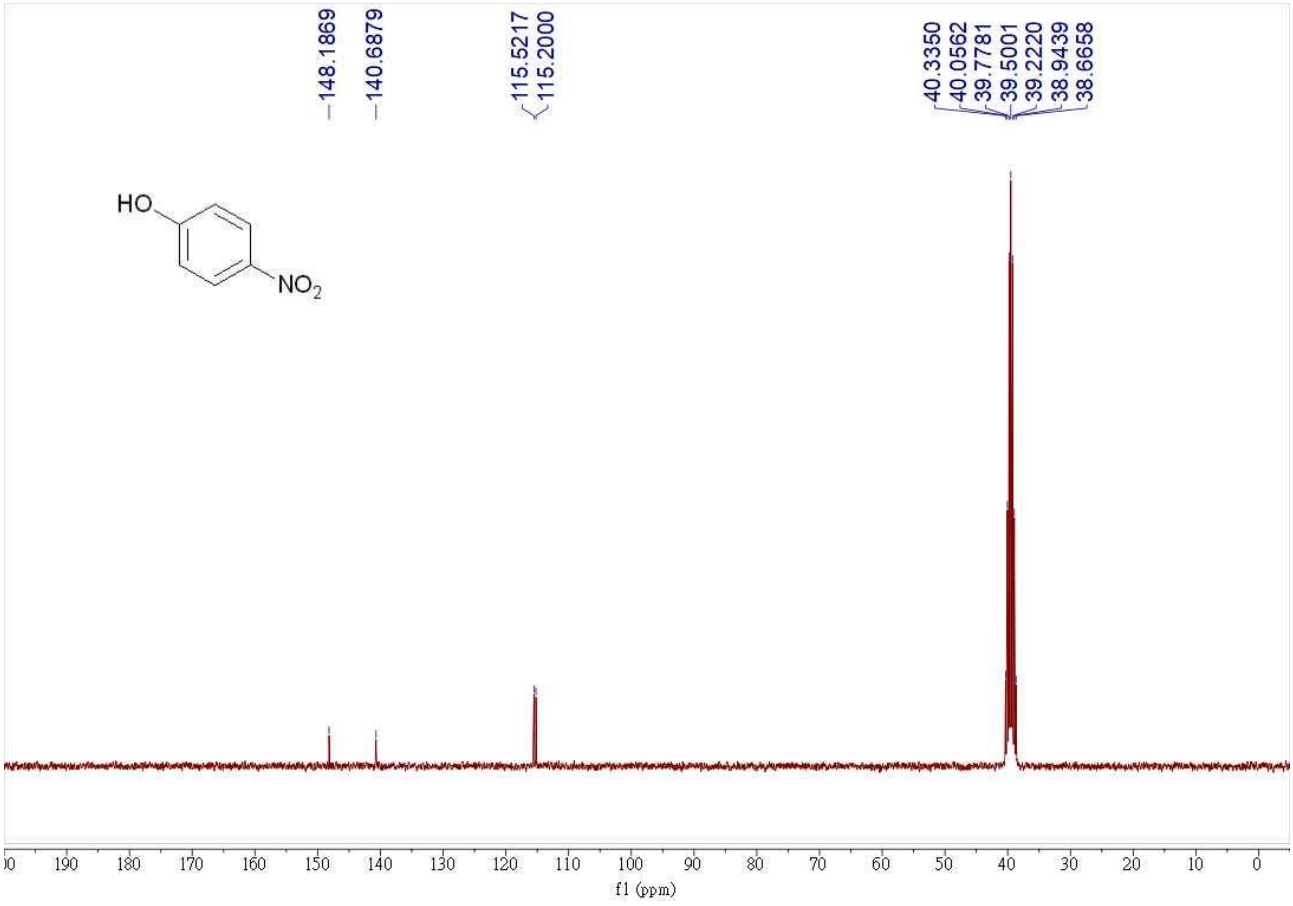
^{1}H and ^{13}C NMR spectra of compound **2h**



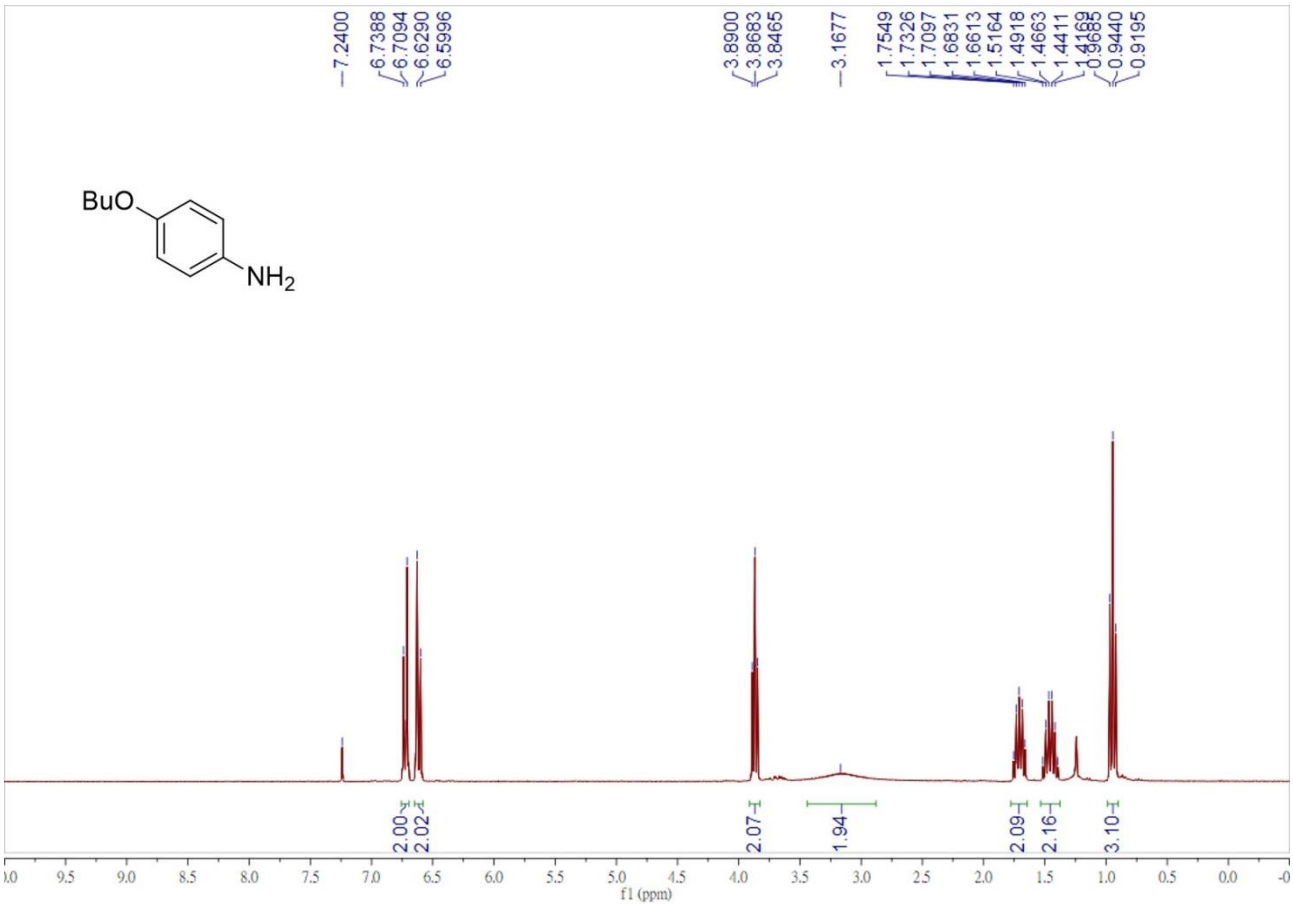


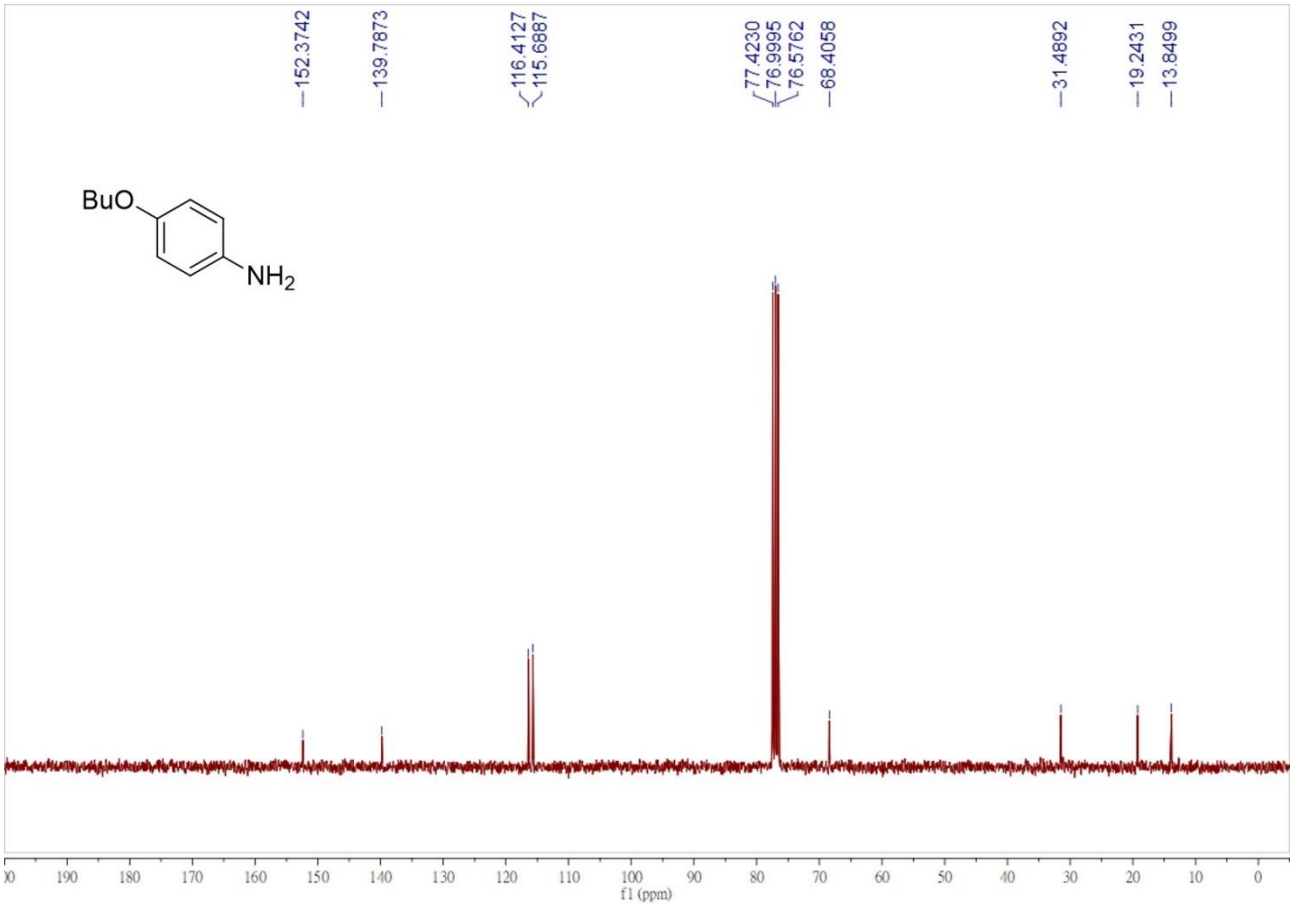
^{1}H and ^{13}C NMR spectra of compound **2i**



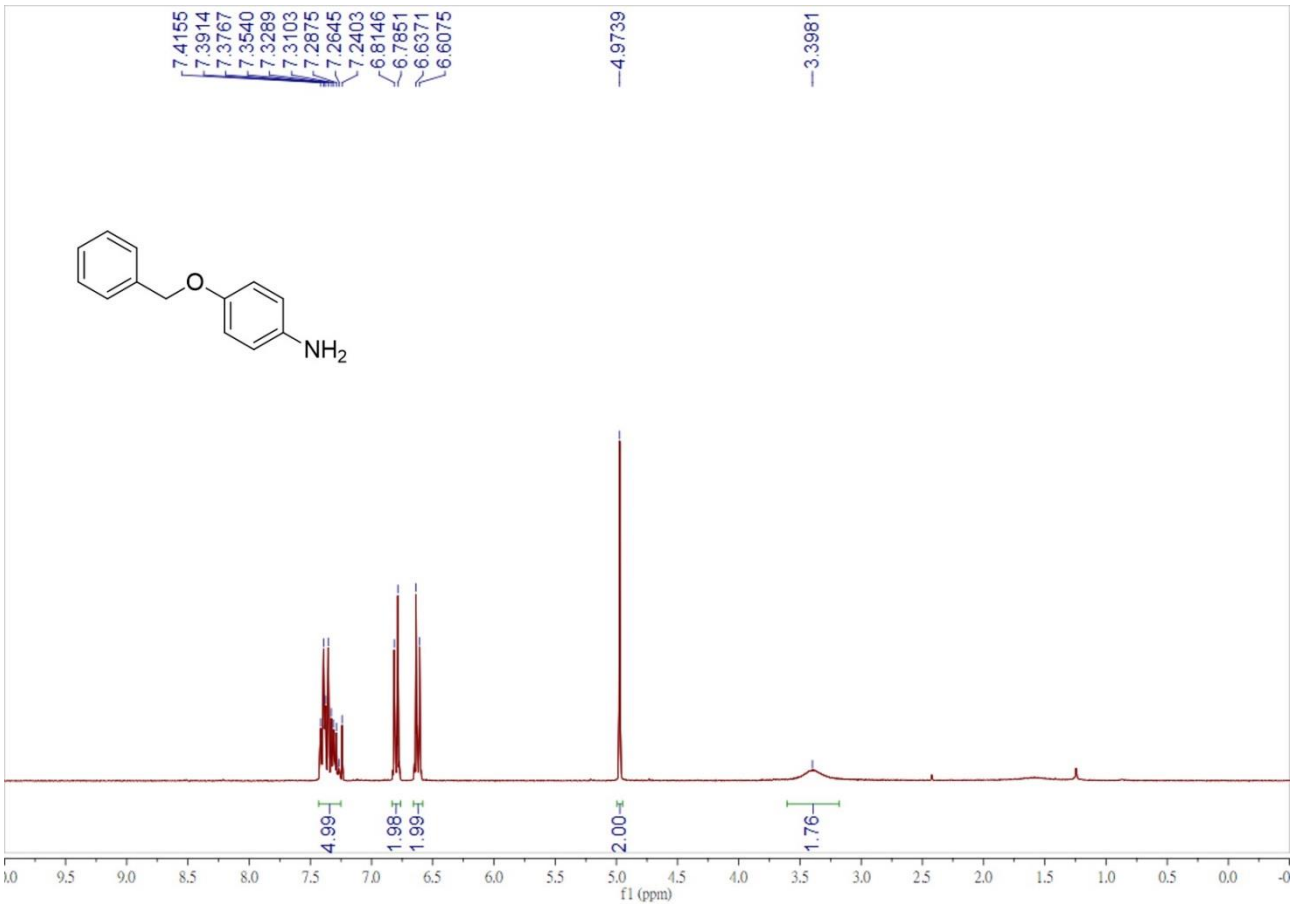


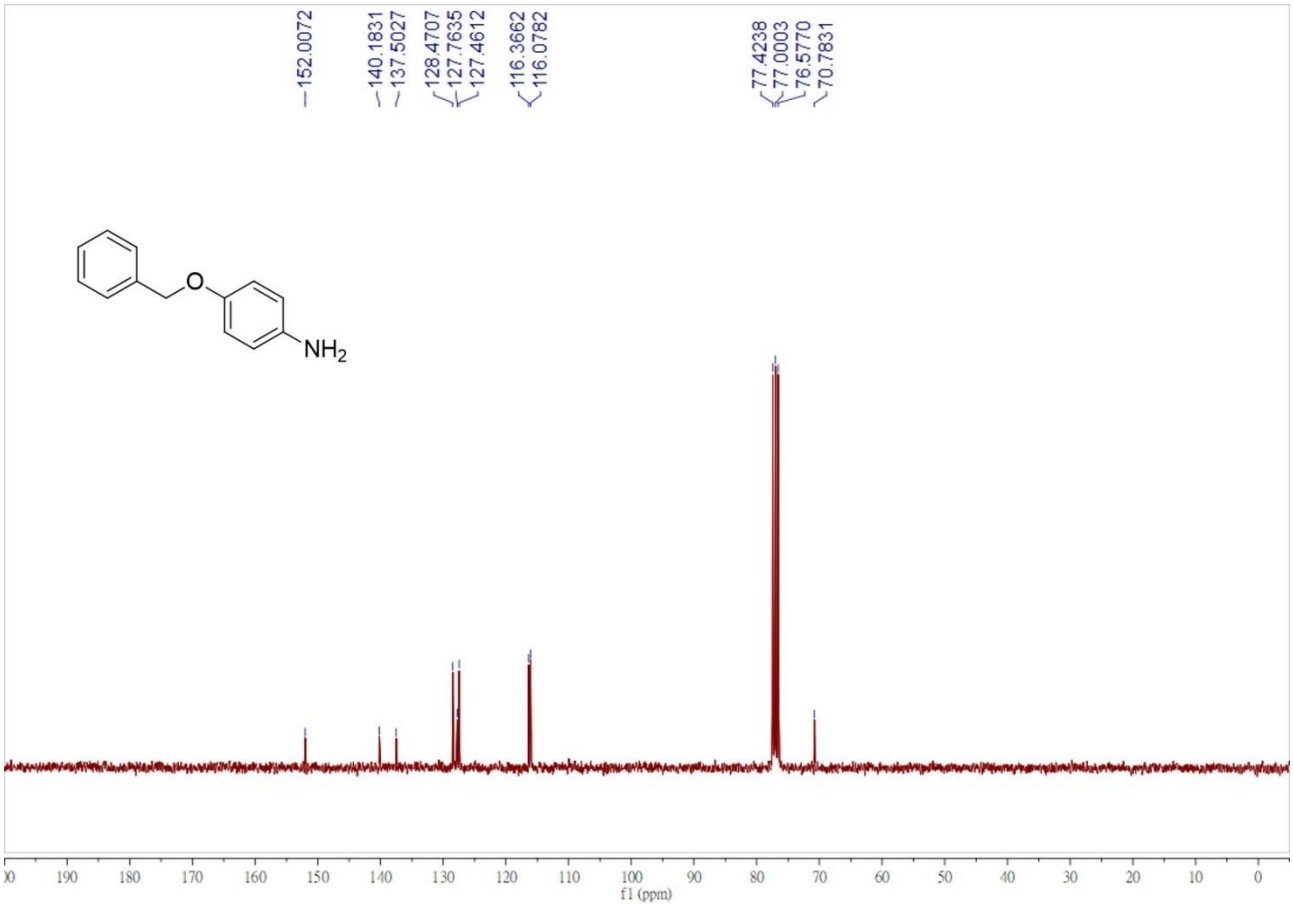
^{1}H and ^{13}C NMR spectra of compound **2j**



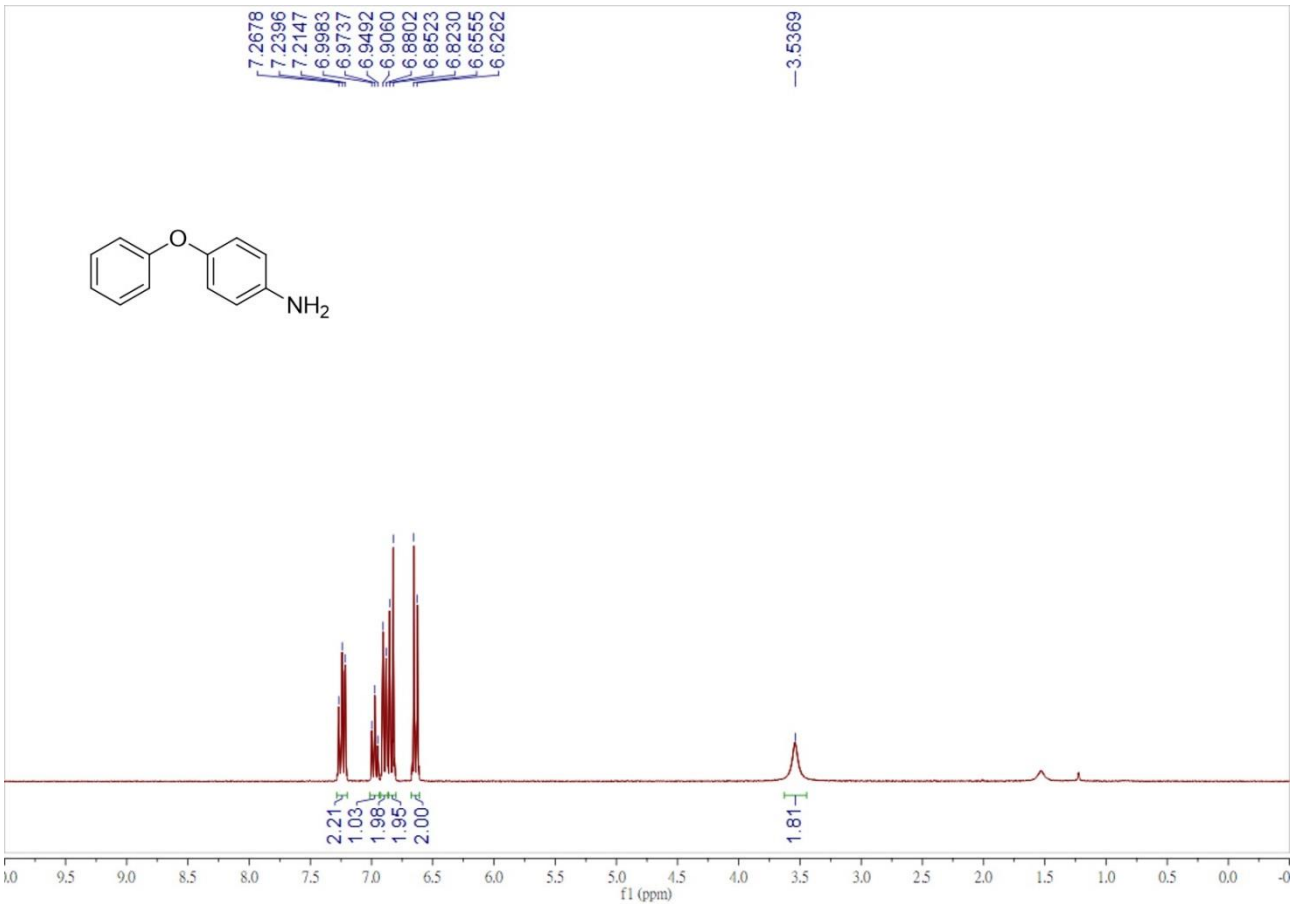


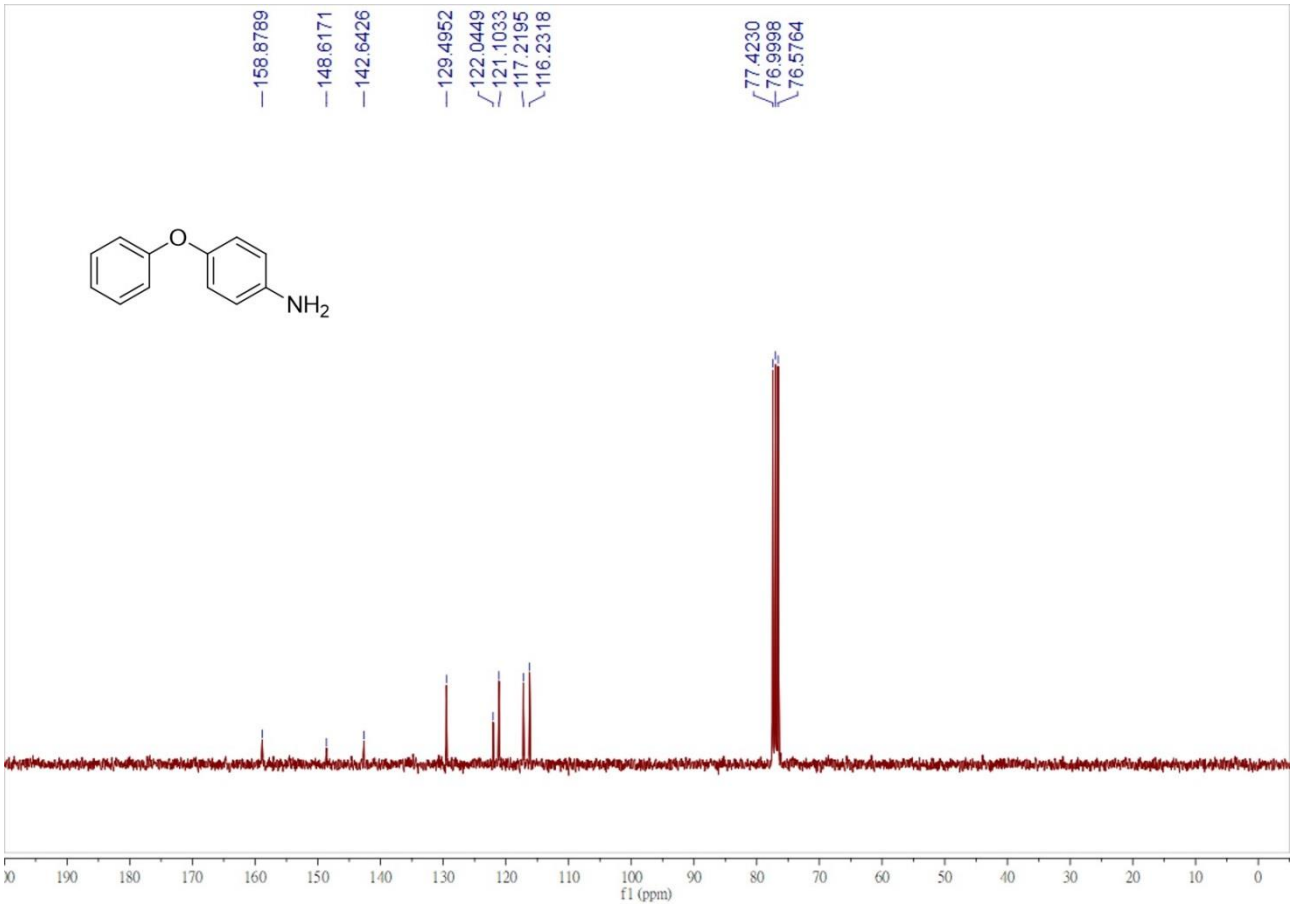
^{1}H and ^{13}C NMR spectra of compound **2k**



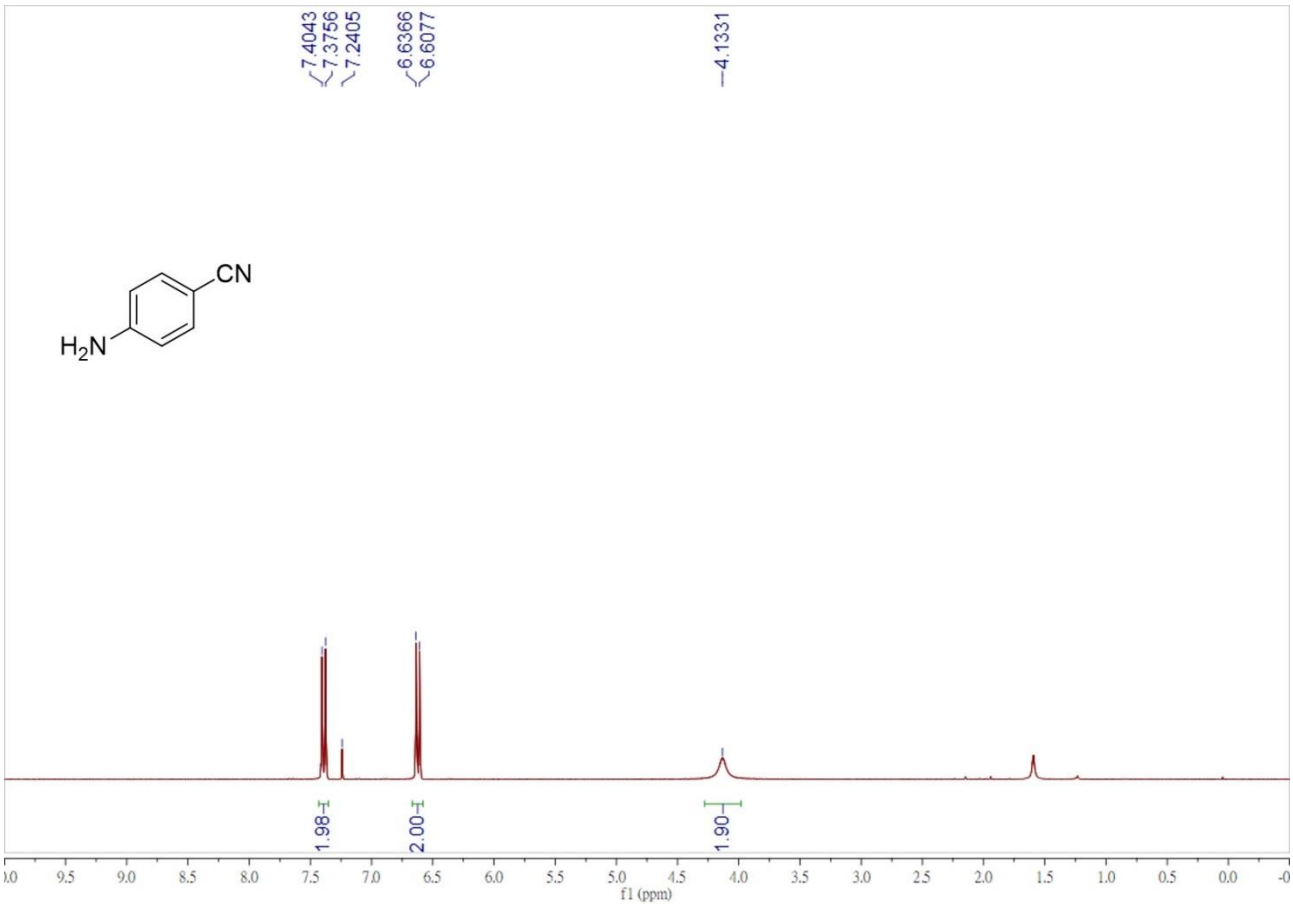


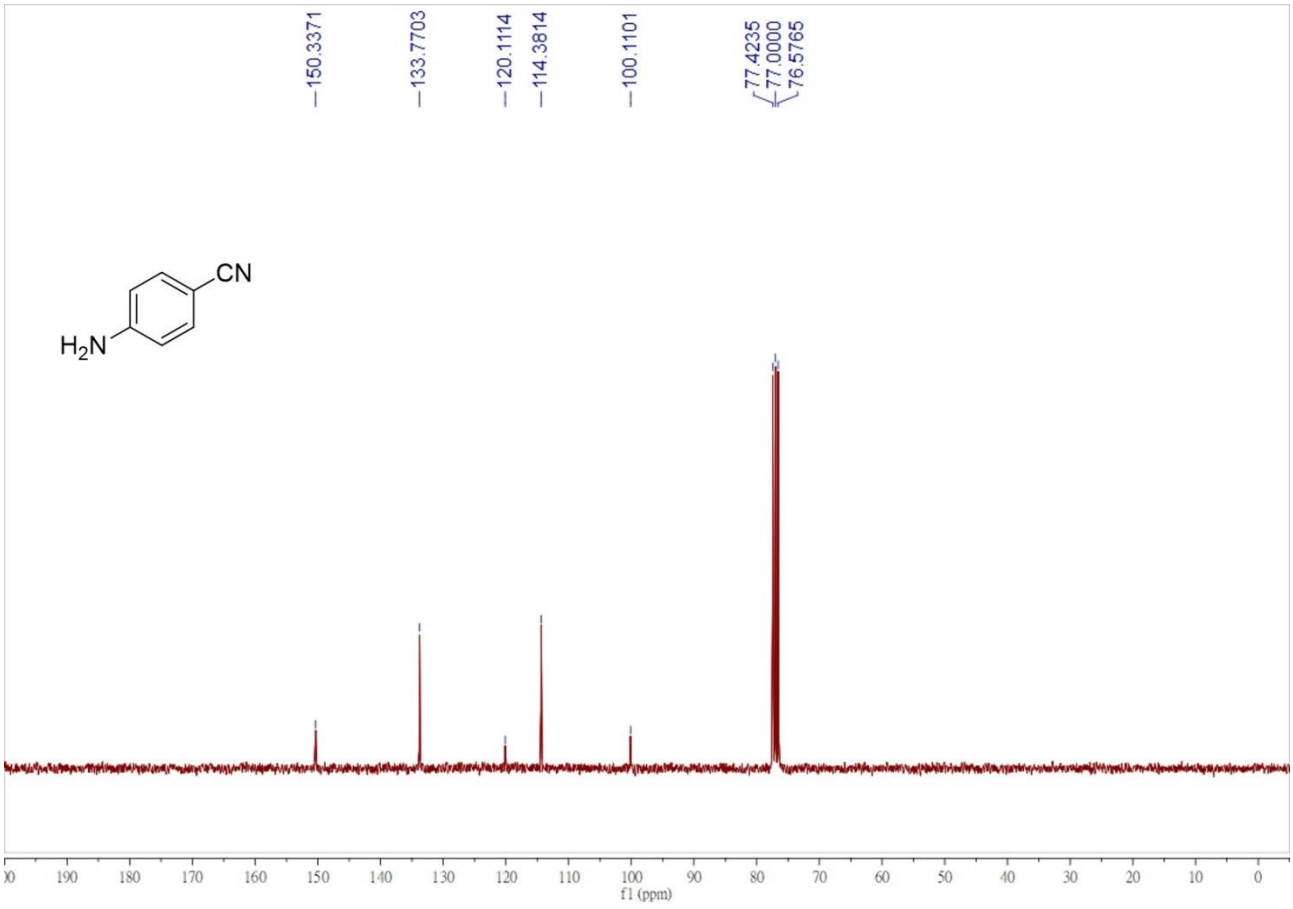
^{1}H and ^{13}C NMR spectra of compound **2l**



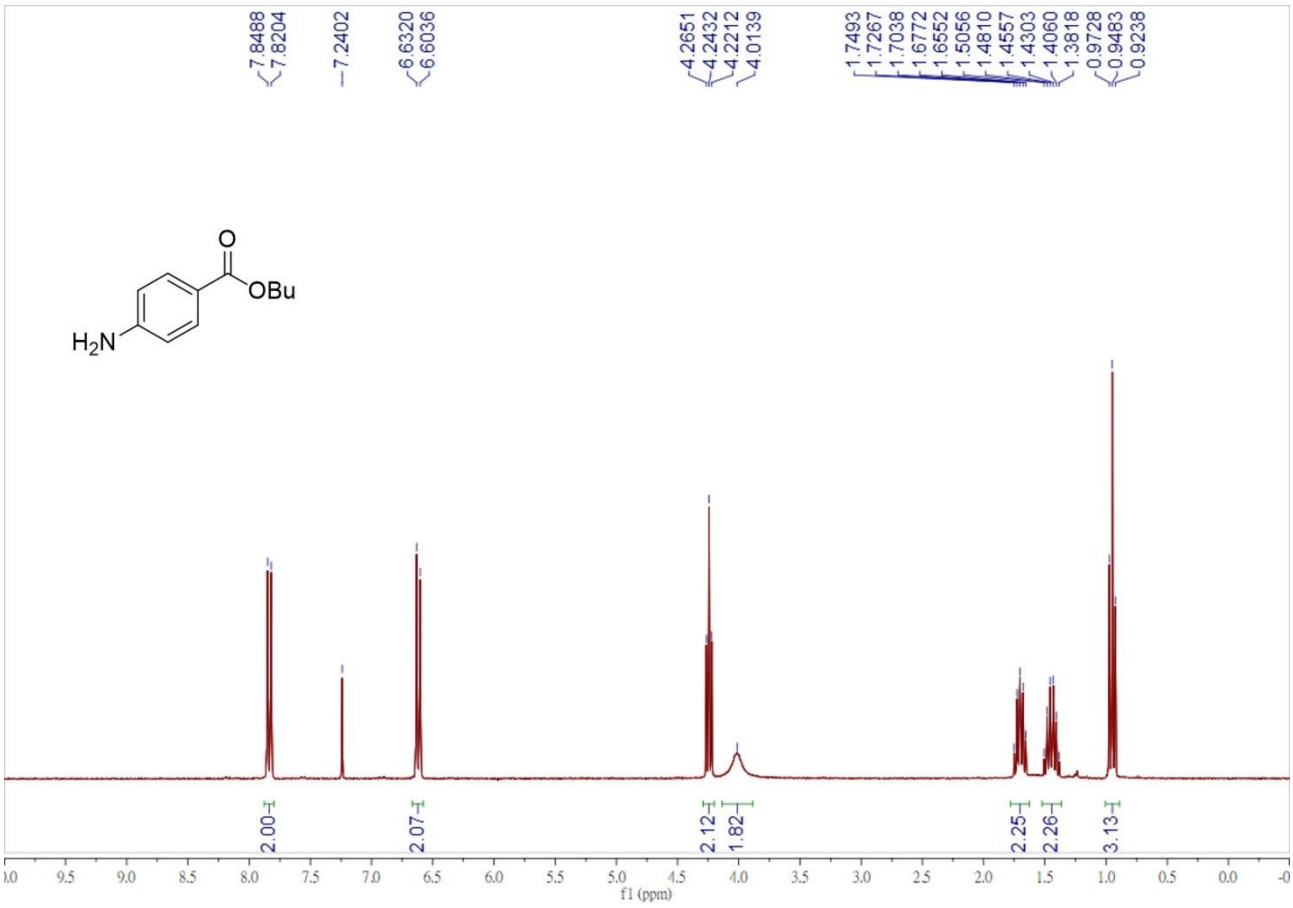


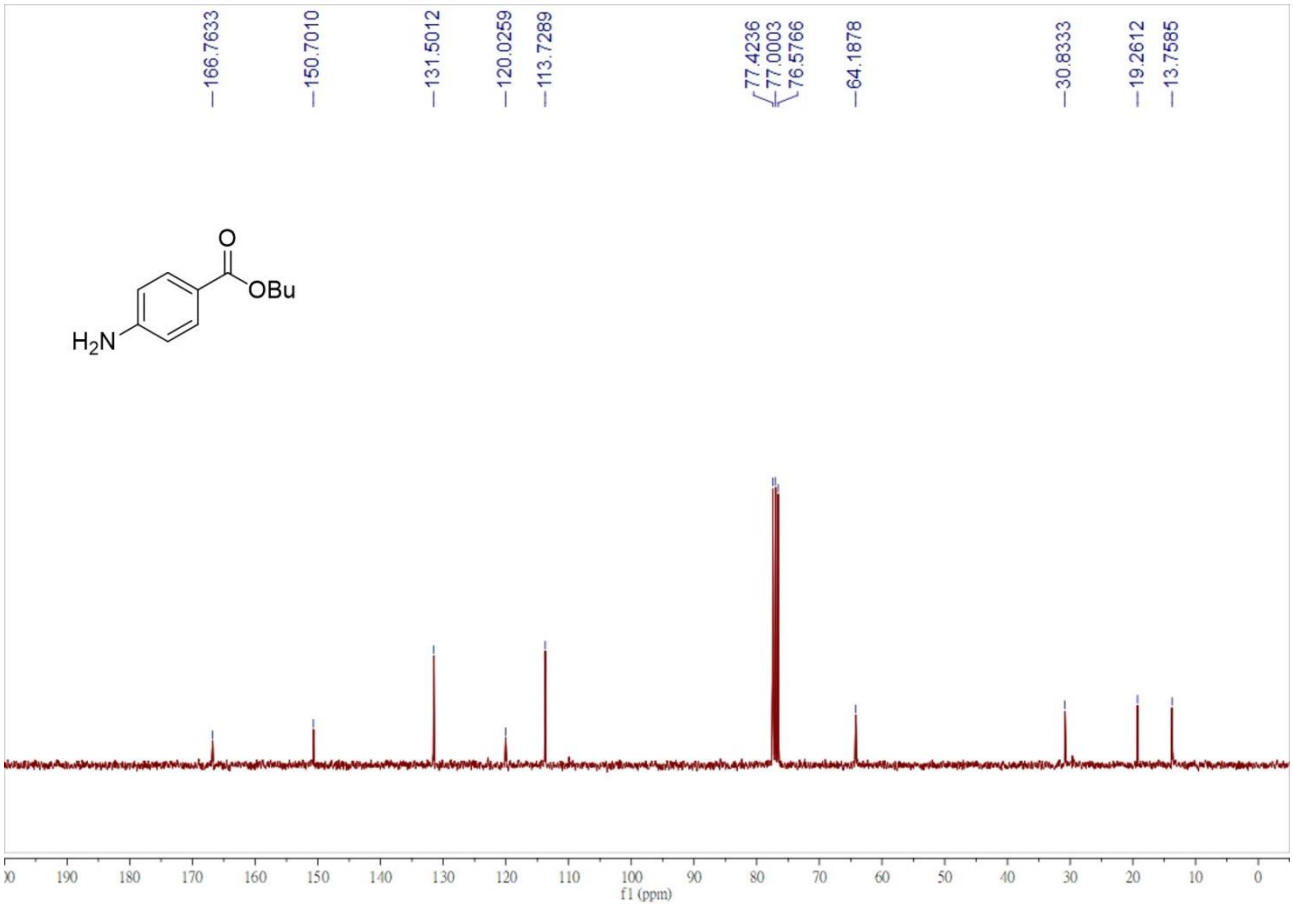
^{1}H and ^{13}C NMR spectra of compound **2m**



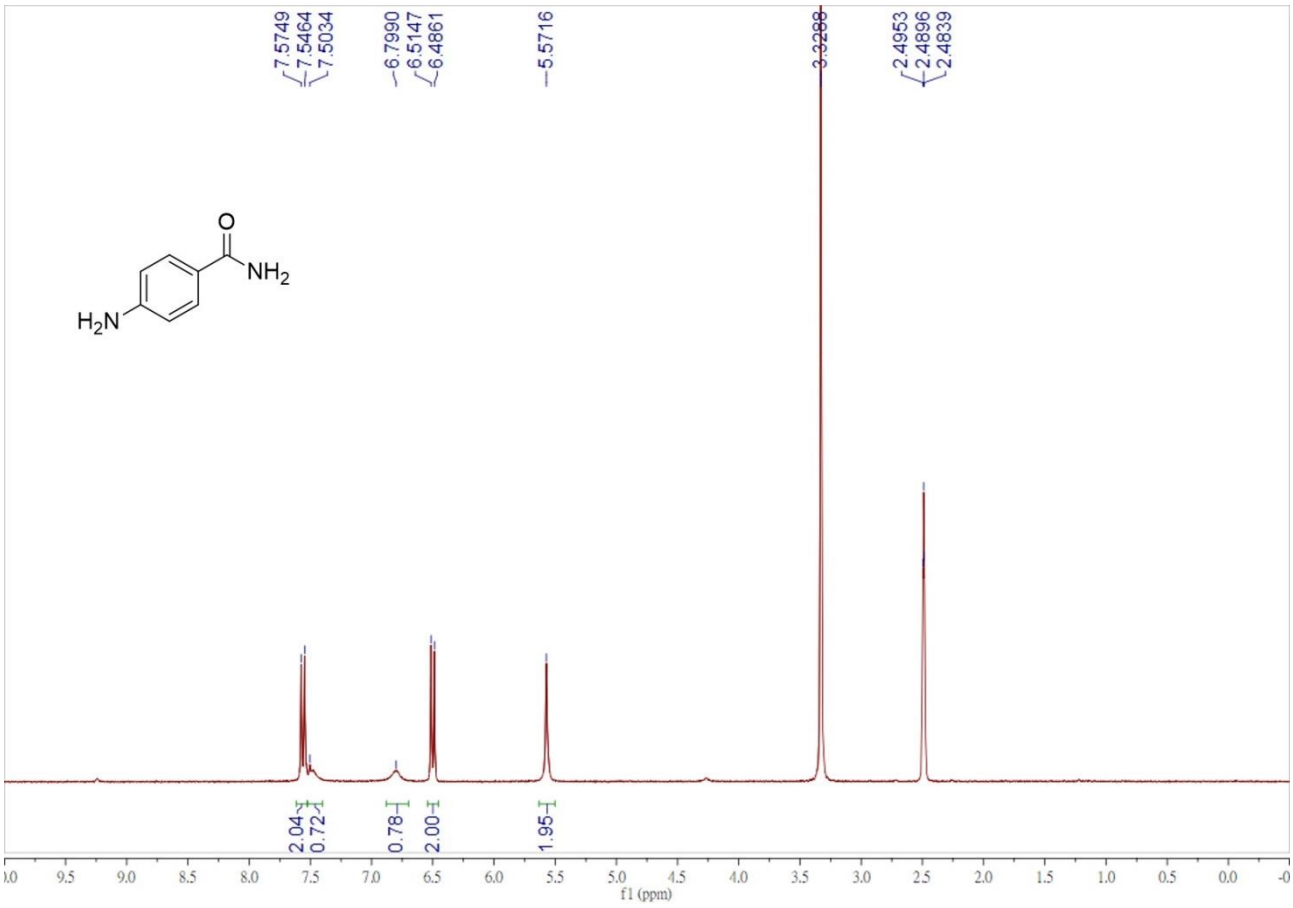


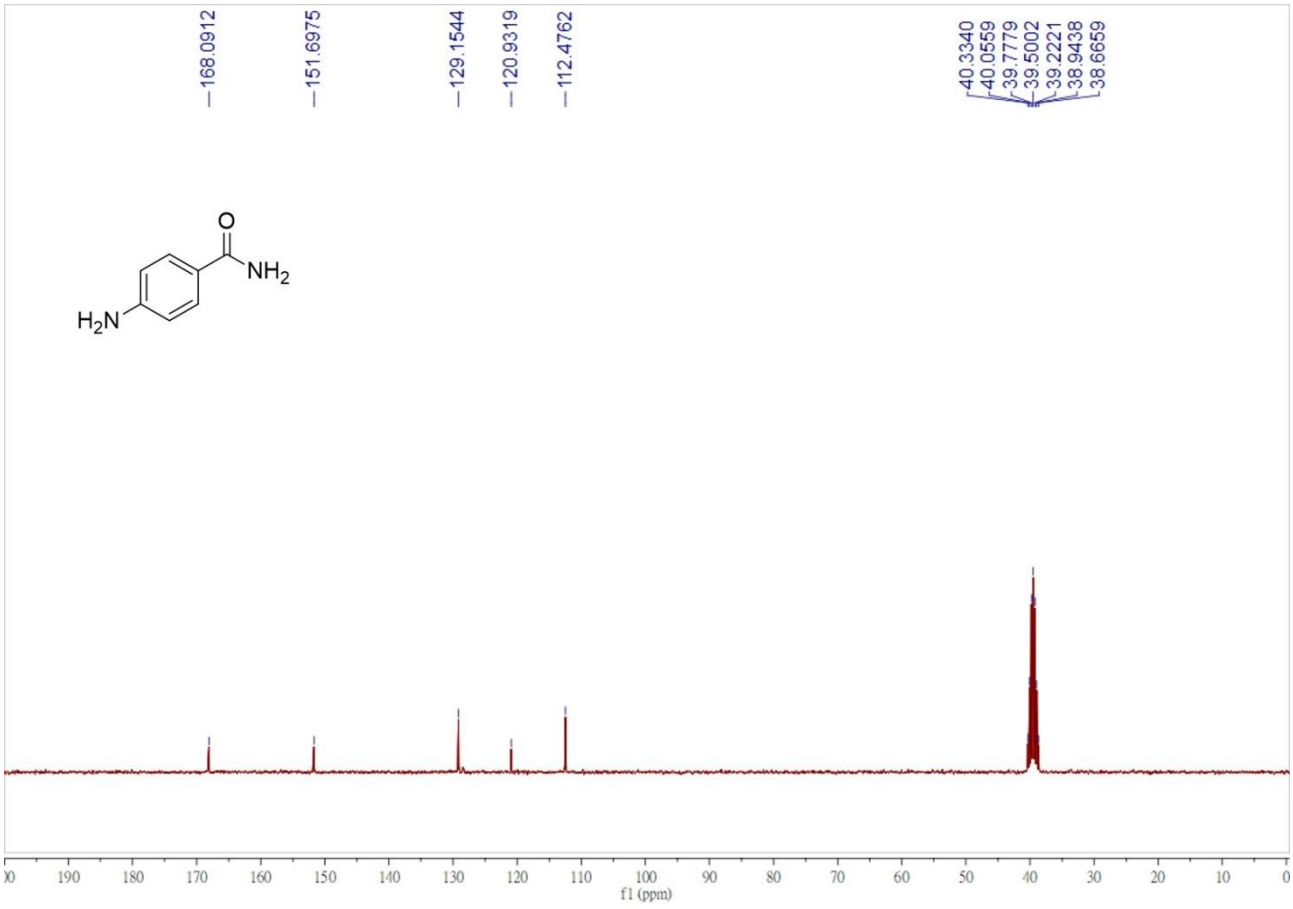
^{1}H and ^{13}C NMR spectra of compound **2n**



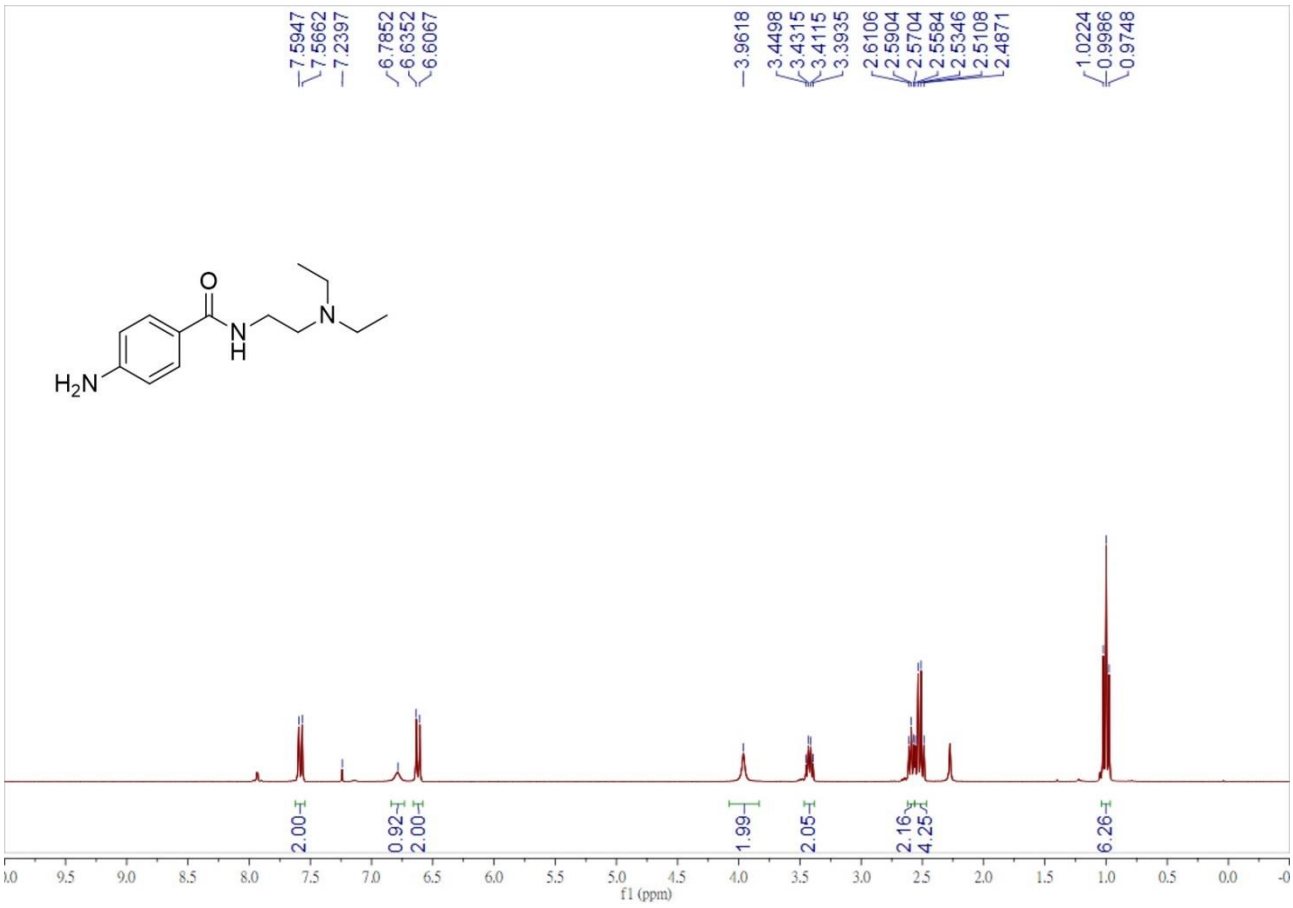


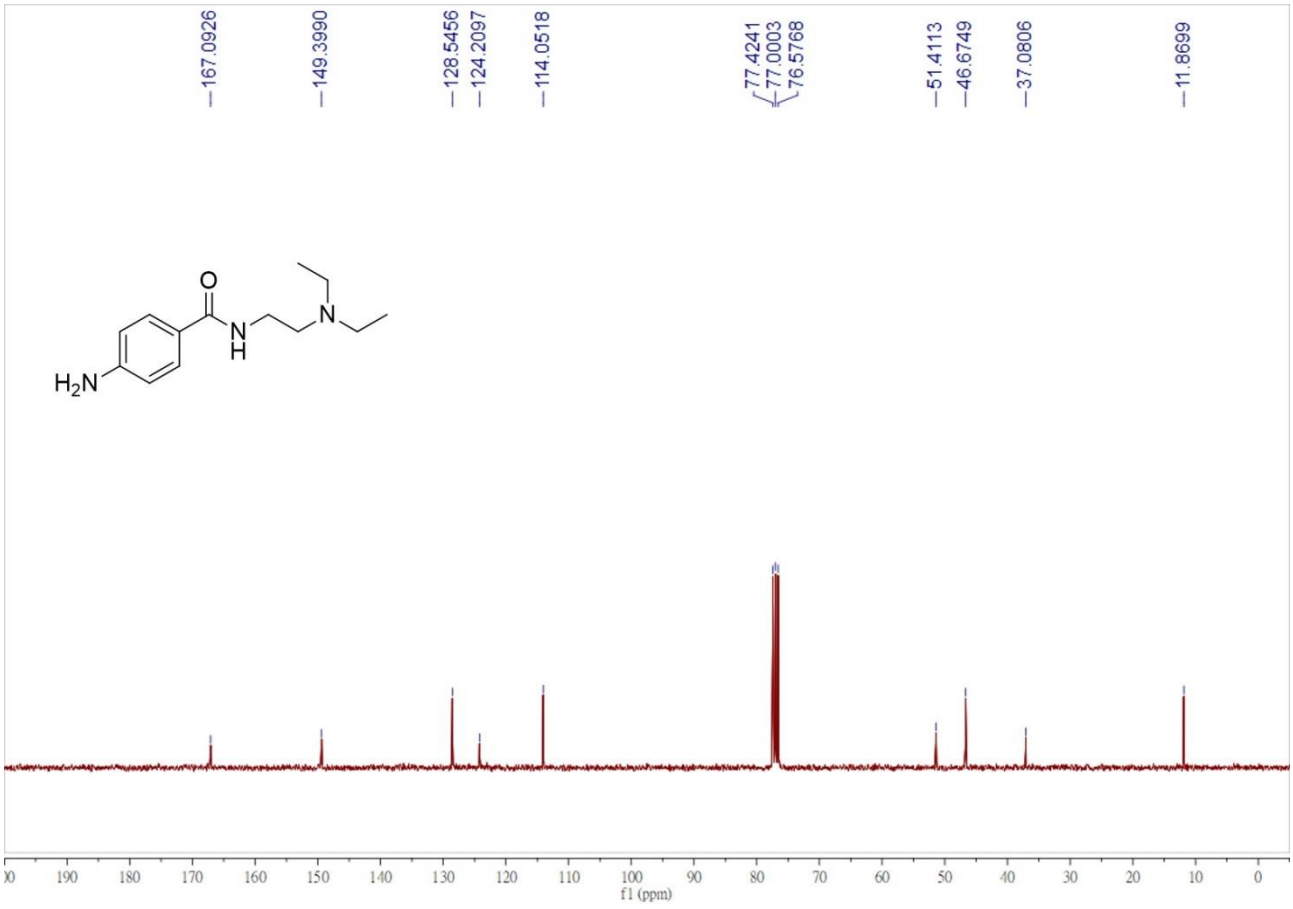
^{1}H and ^{13}C NMR spectra of compound **2o**



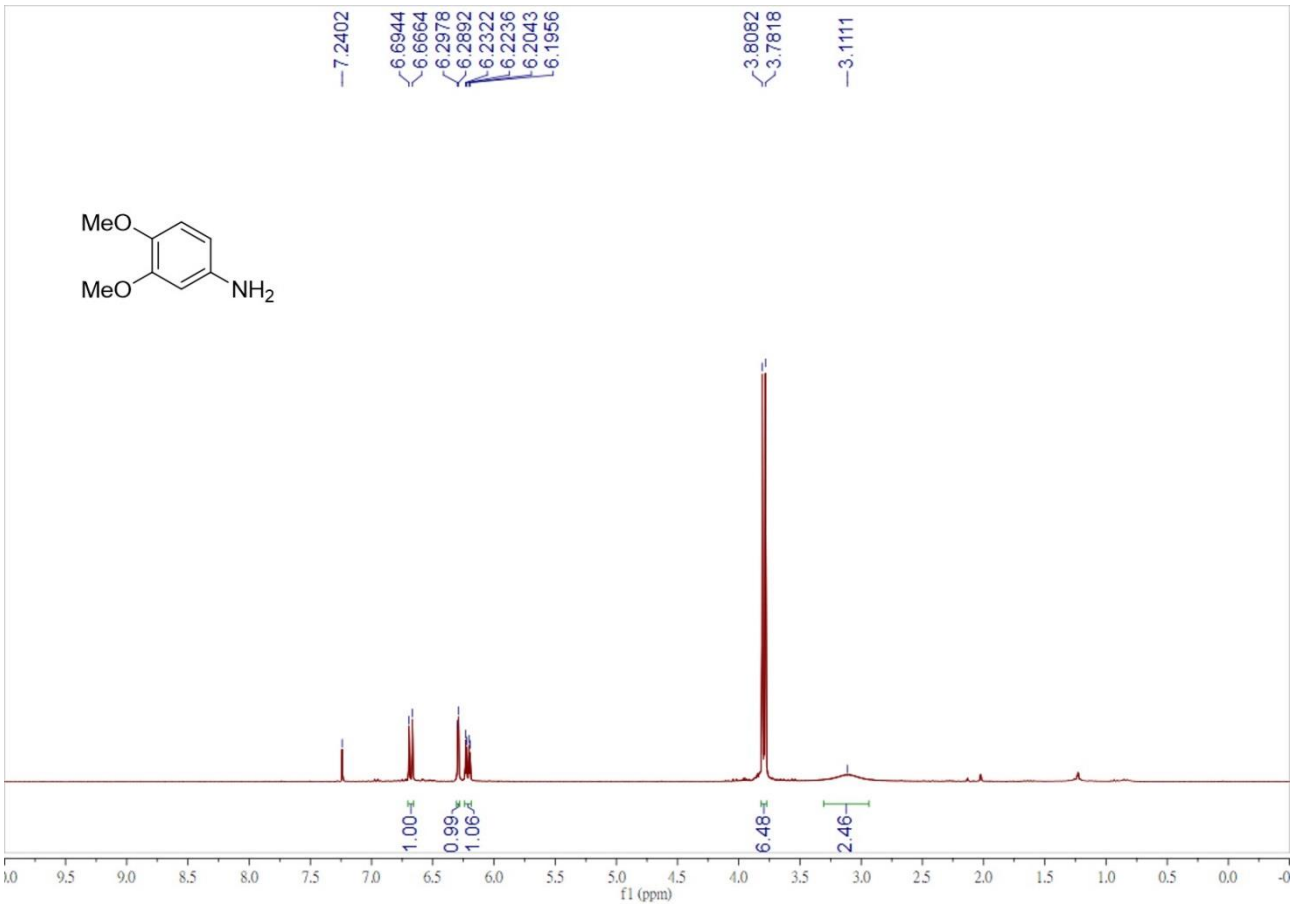


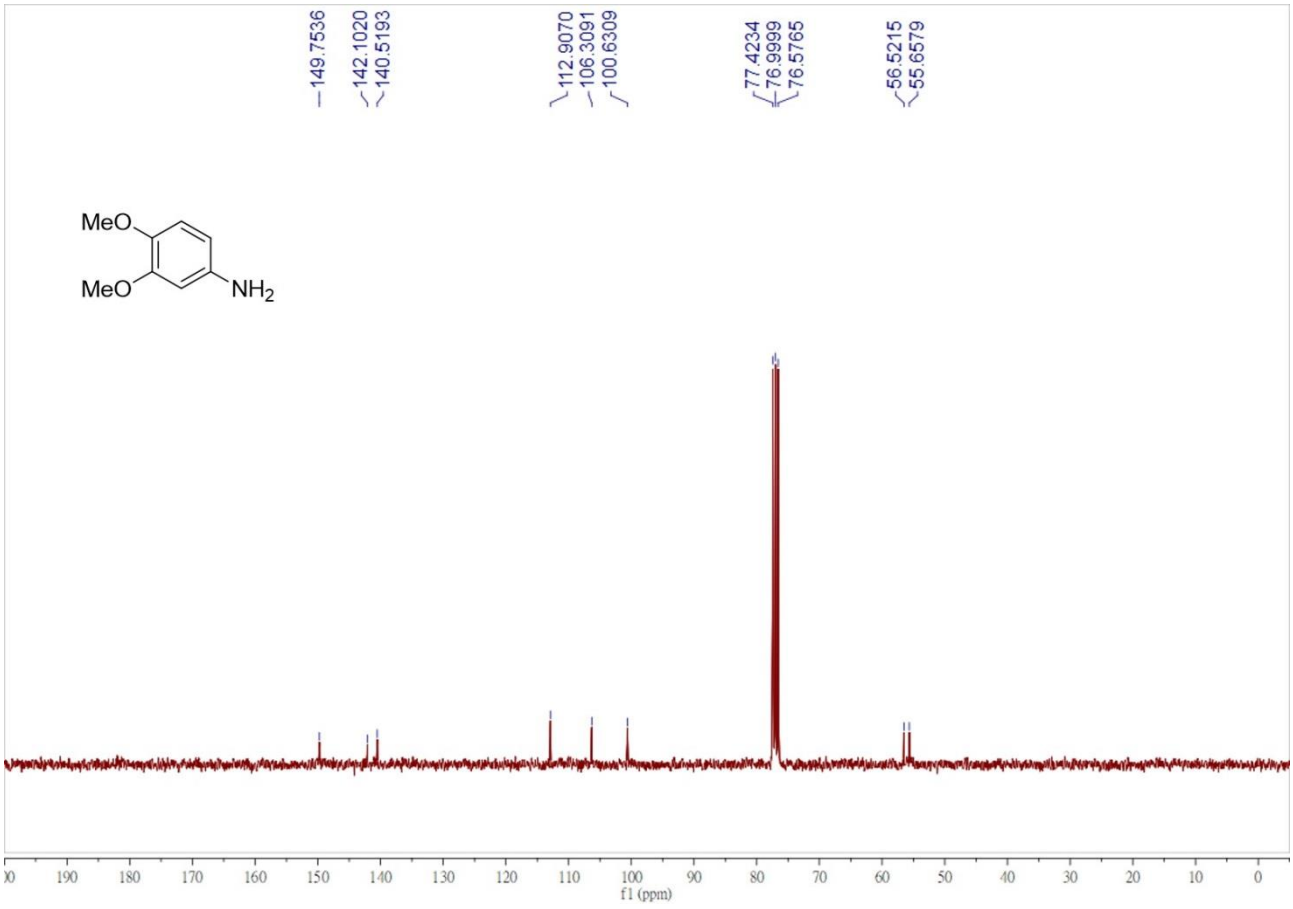
^{1}H and ^{13}C NMR spectra of compound **2p**



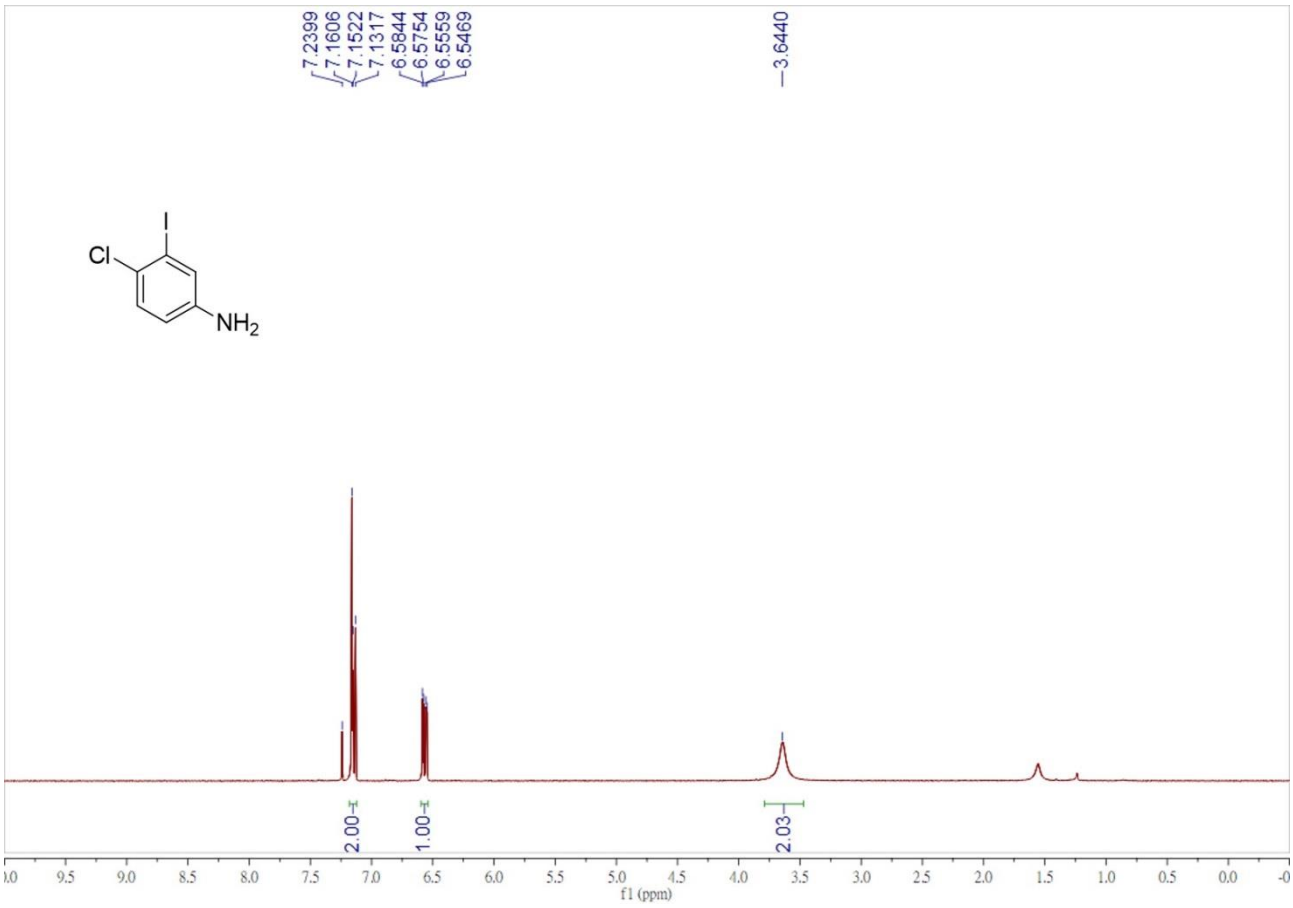


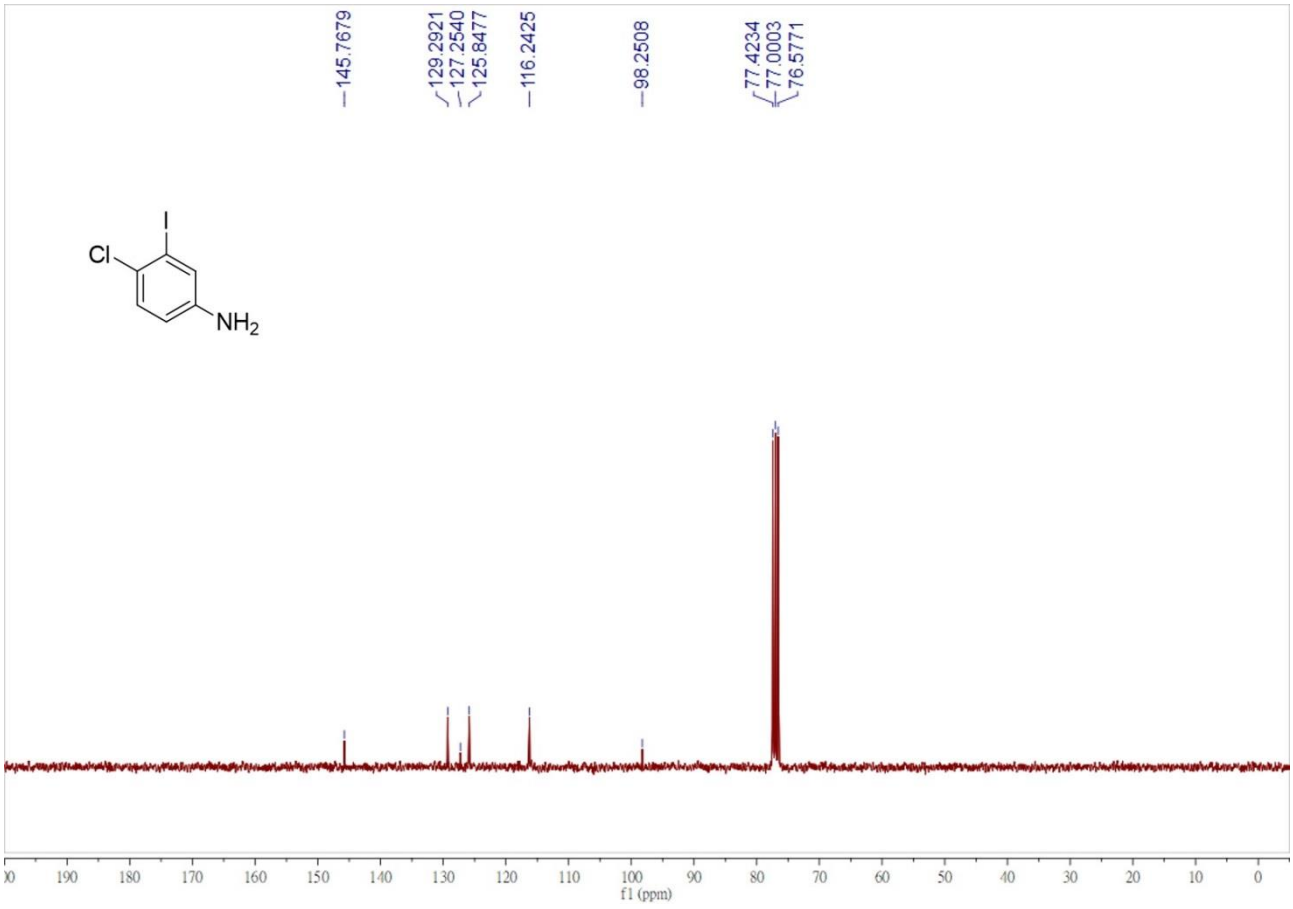
^{1}H and ^{13}C NMR spectra of compound **2q**



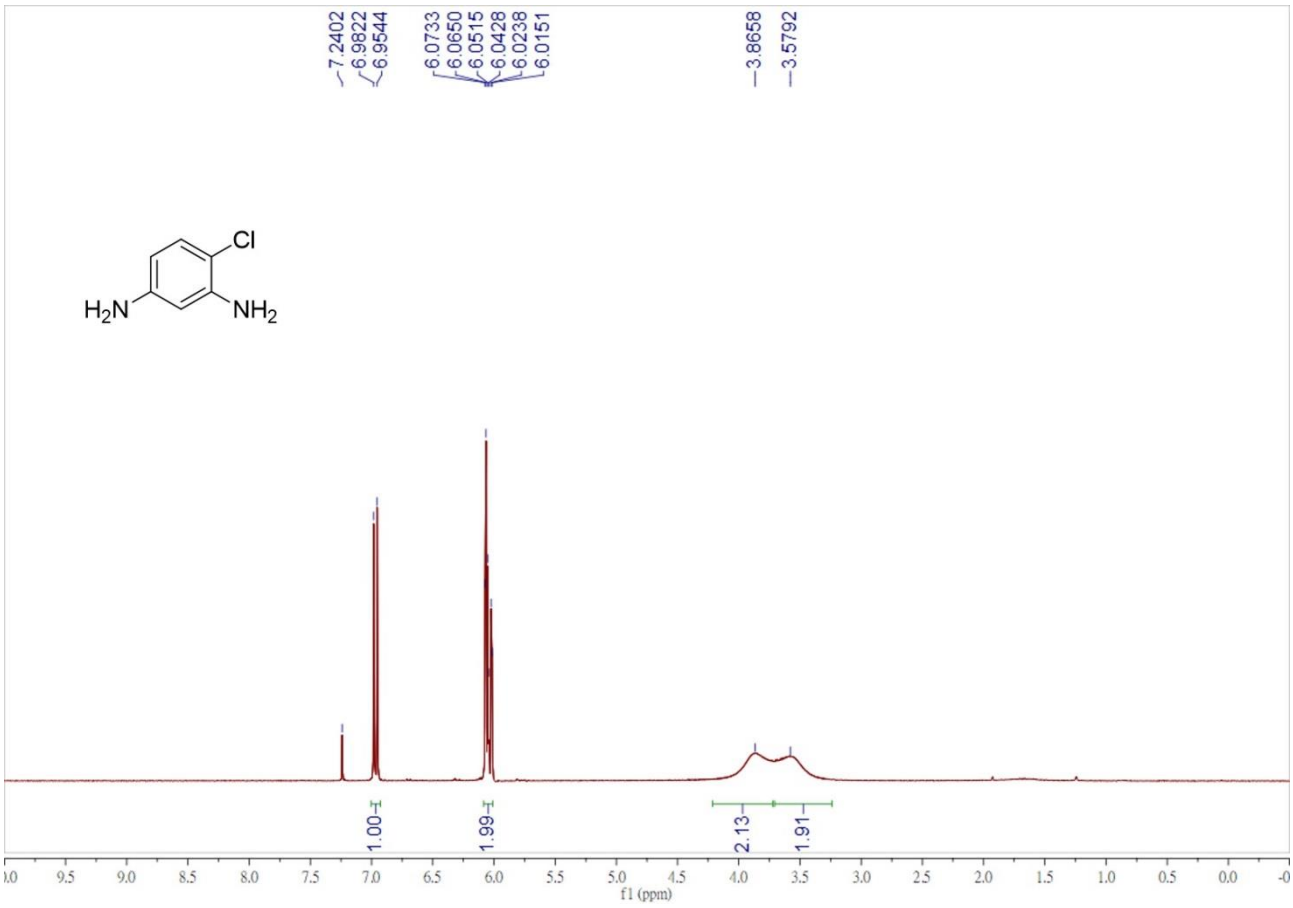


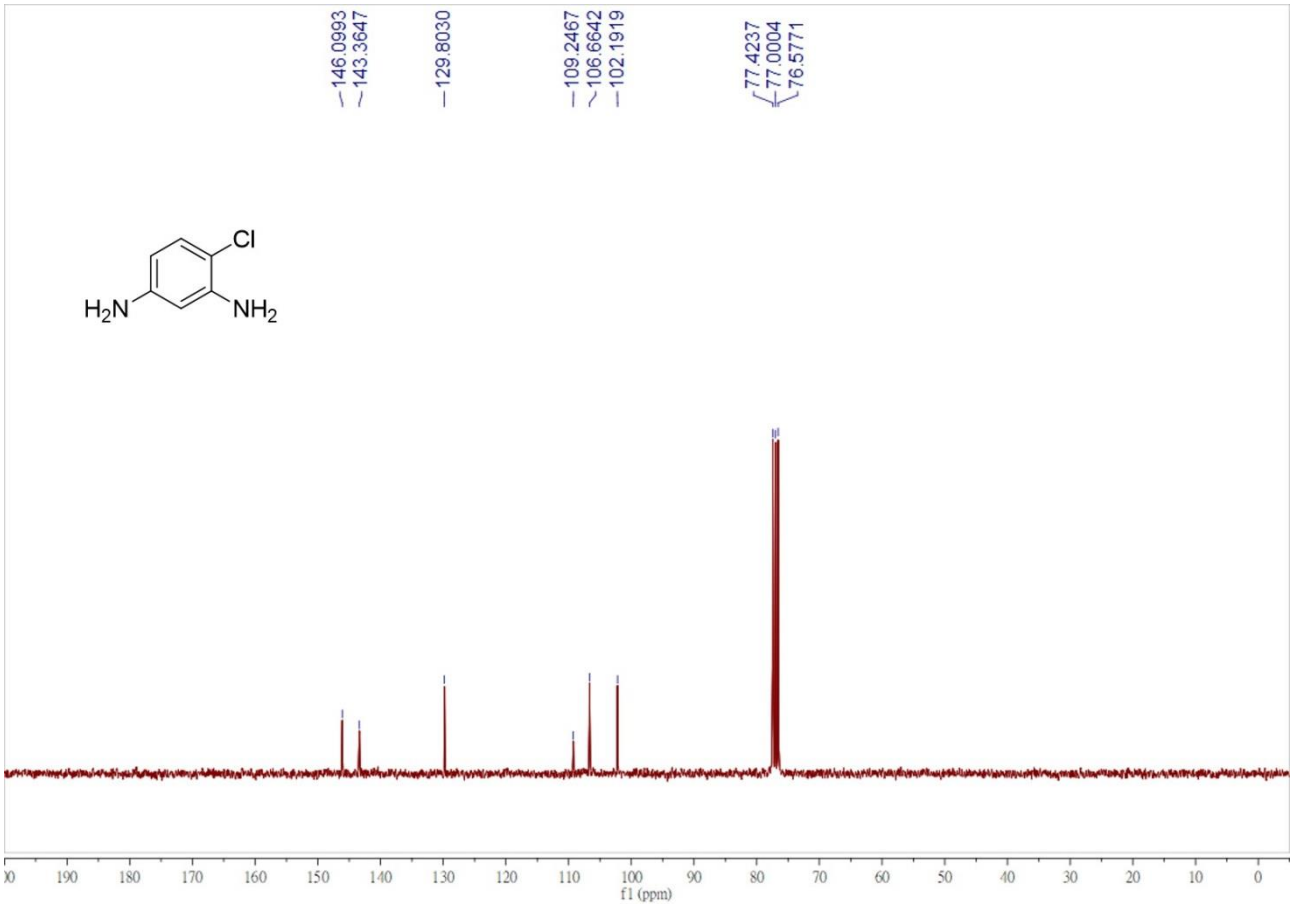
^{1}H and ^{13}C NMR spectra of compound **2r**



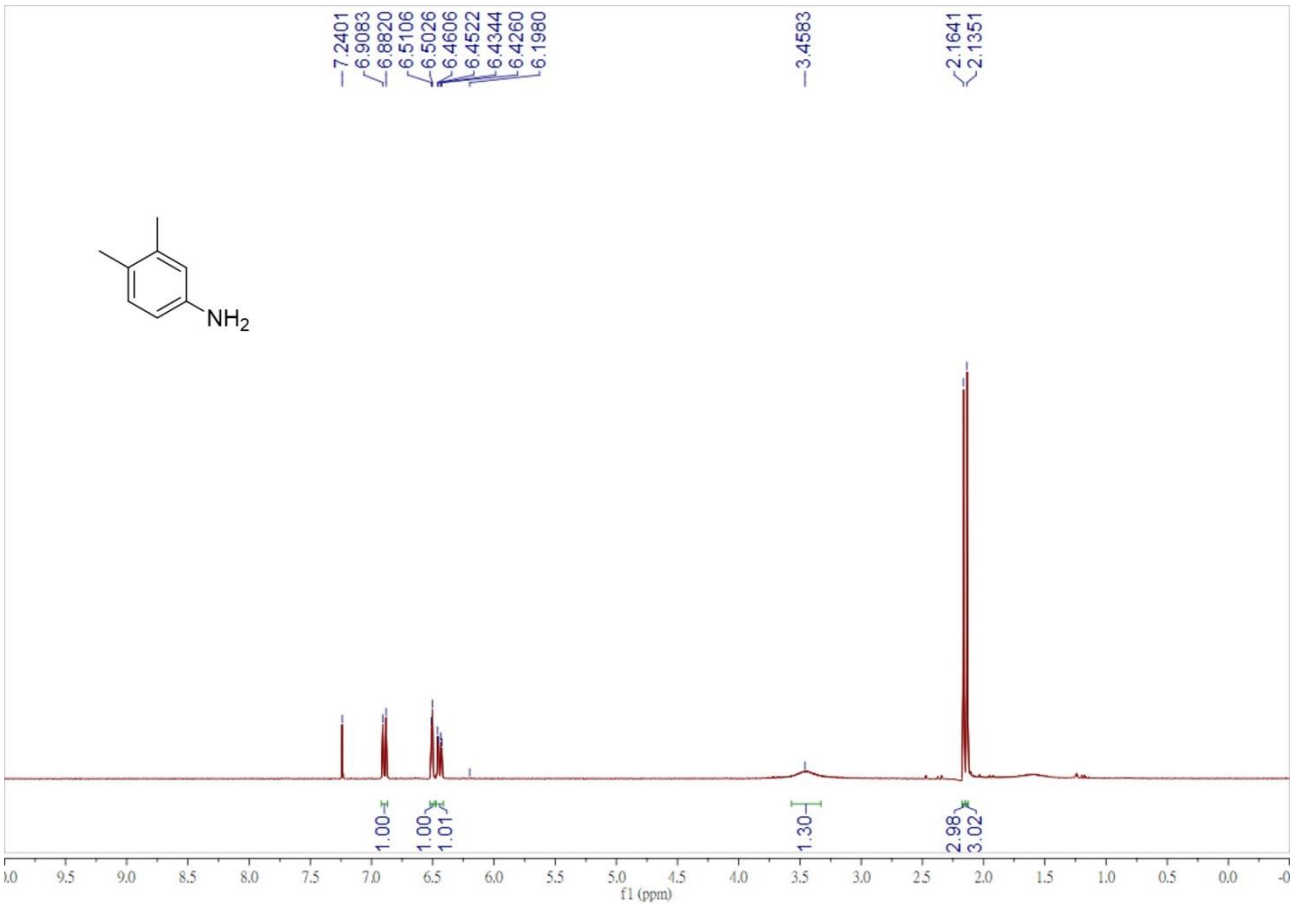


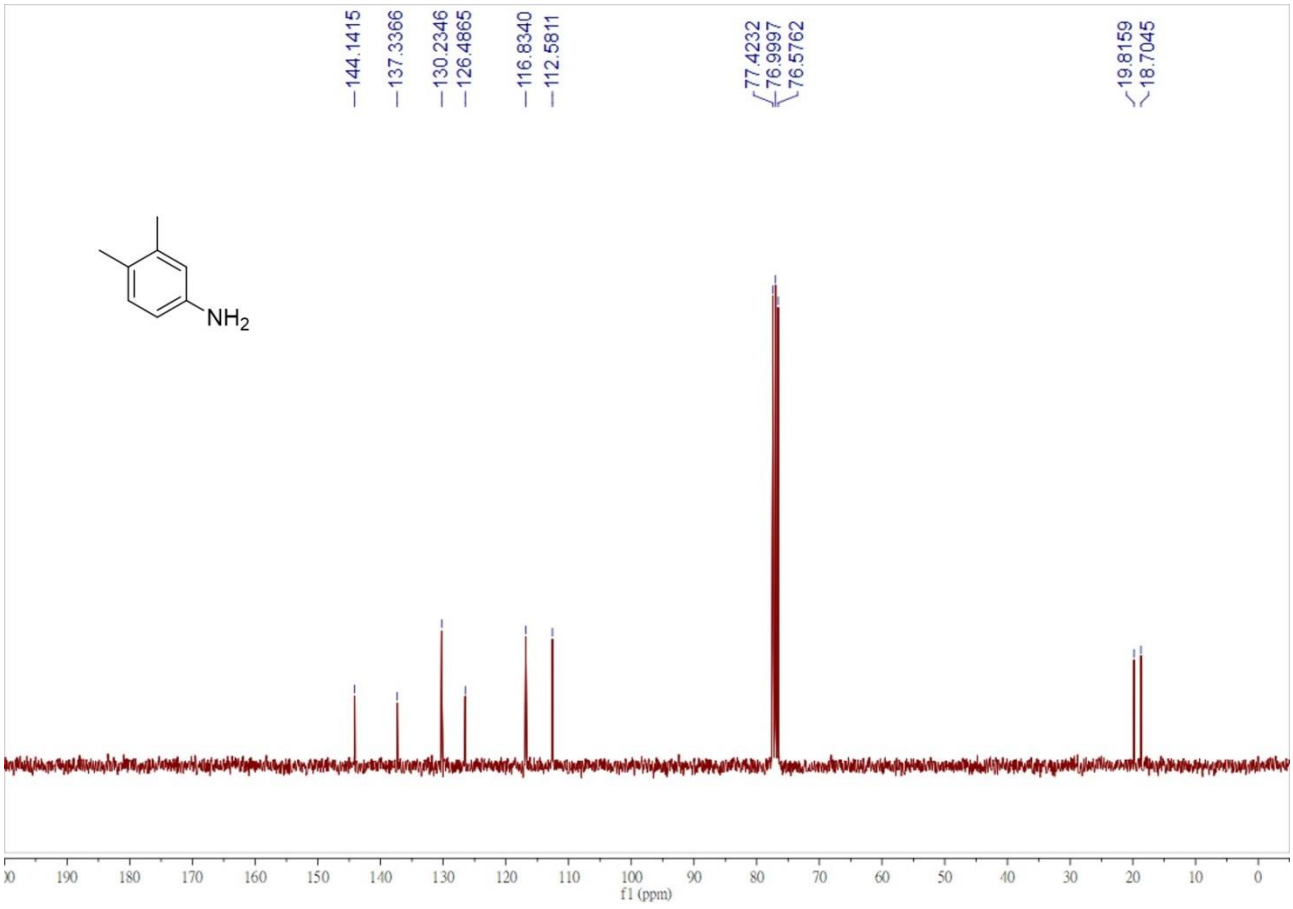
^{1}H and ^{13}C NMR spectra of compound **2s**



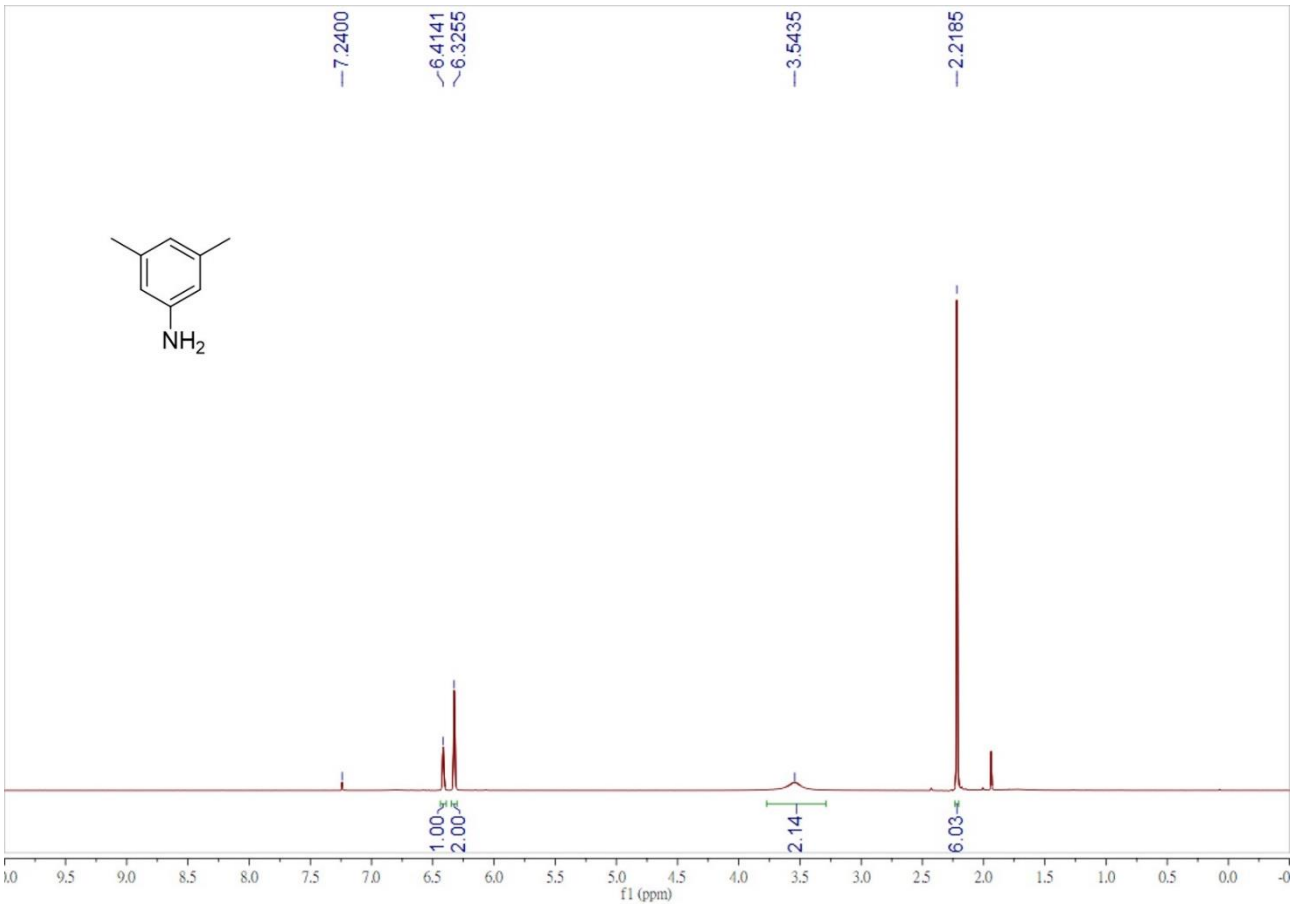


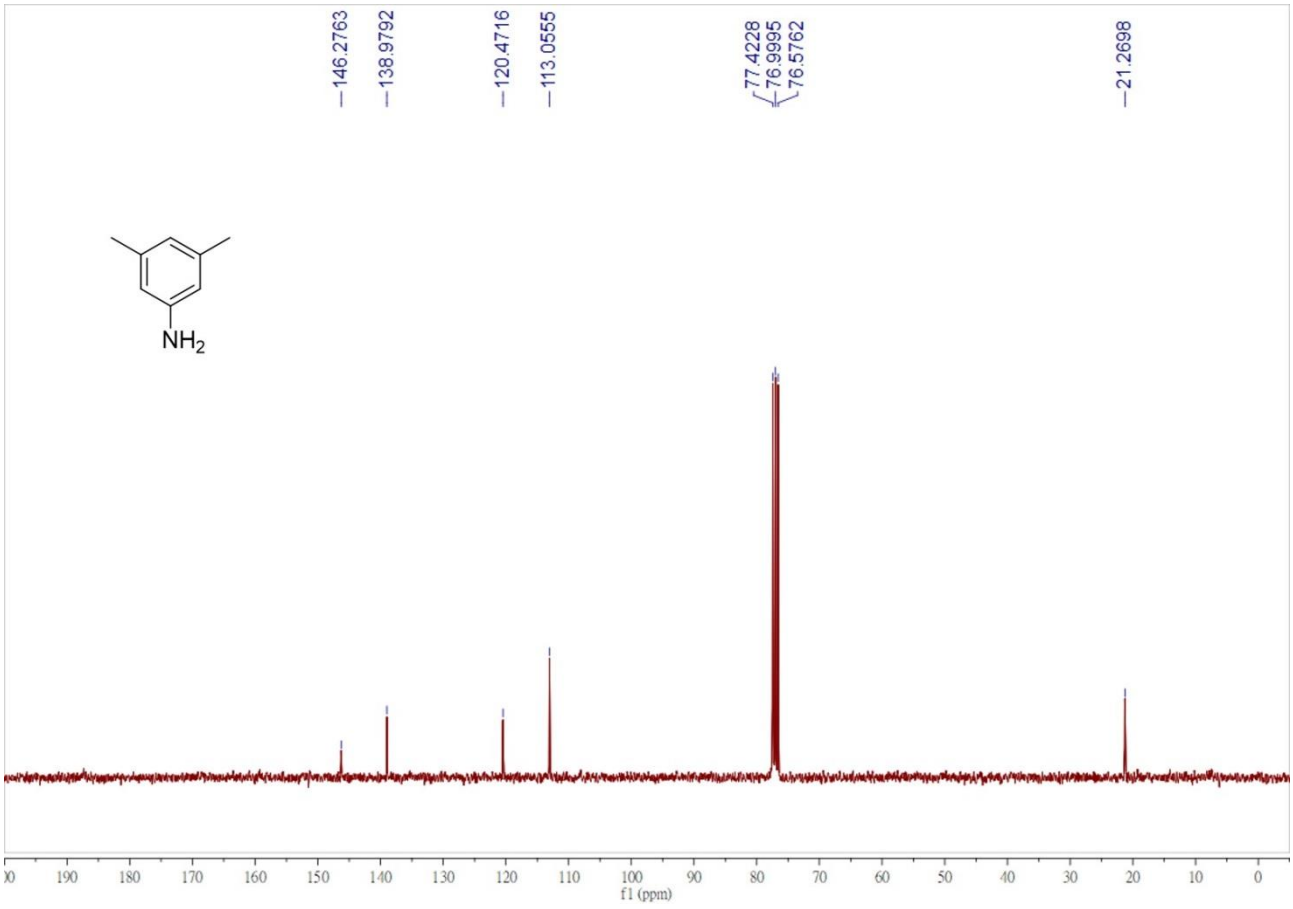
^{1}H and ^{13}C NMR spectra of compound **2t**



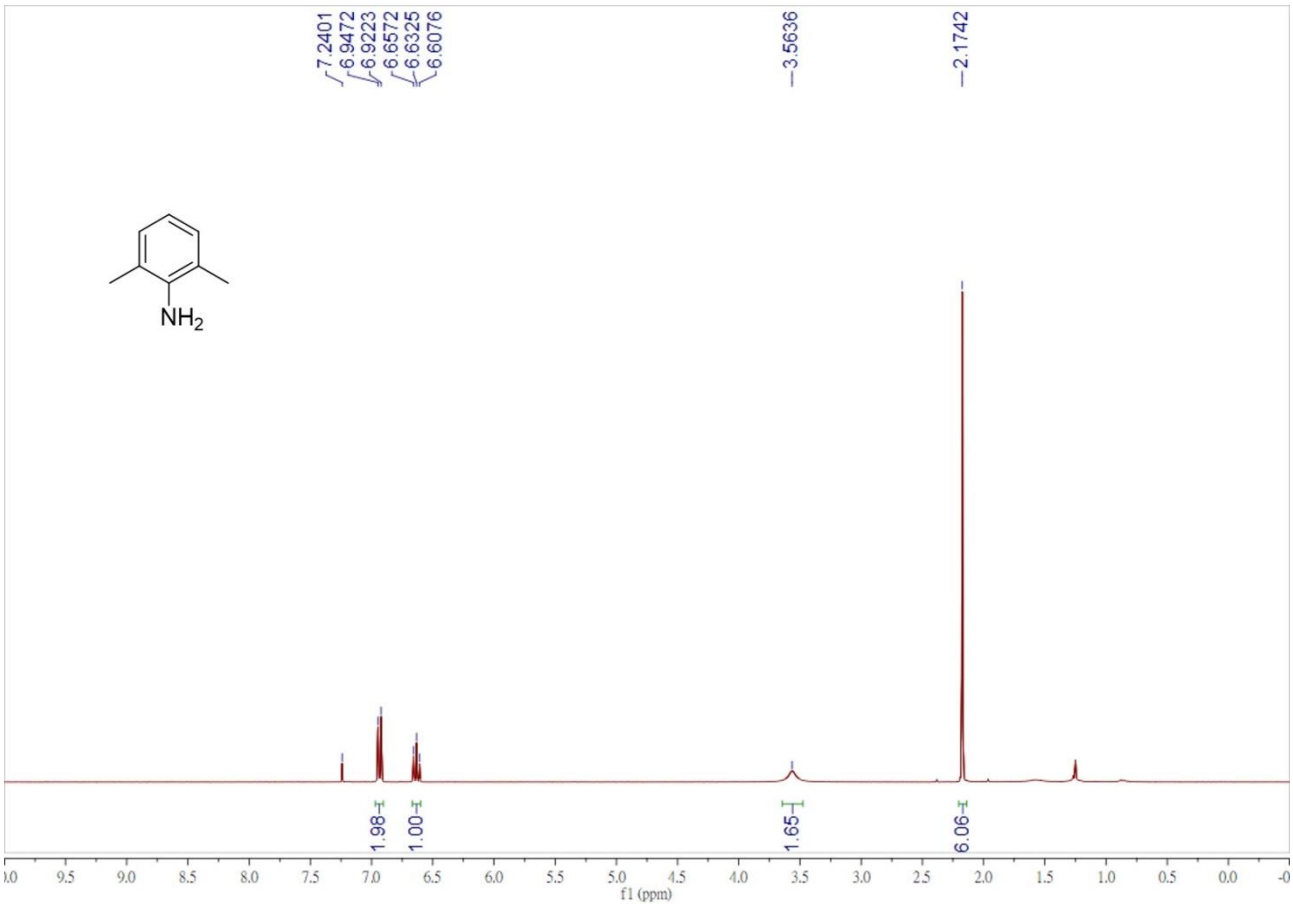


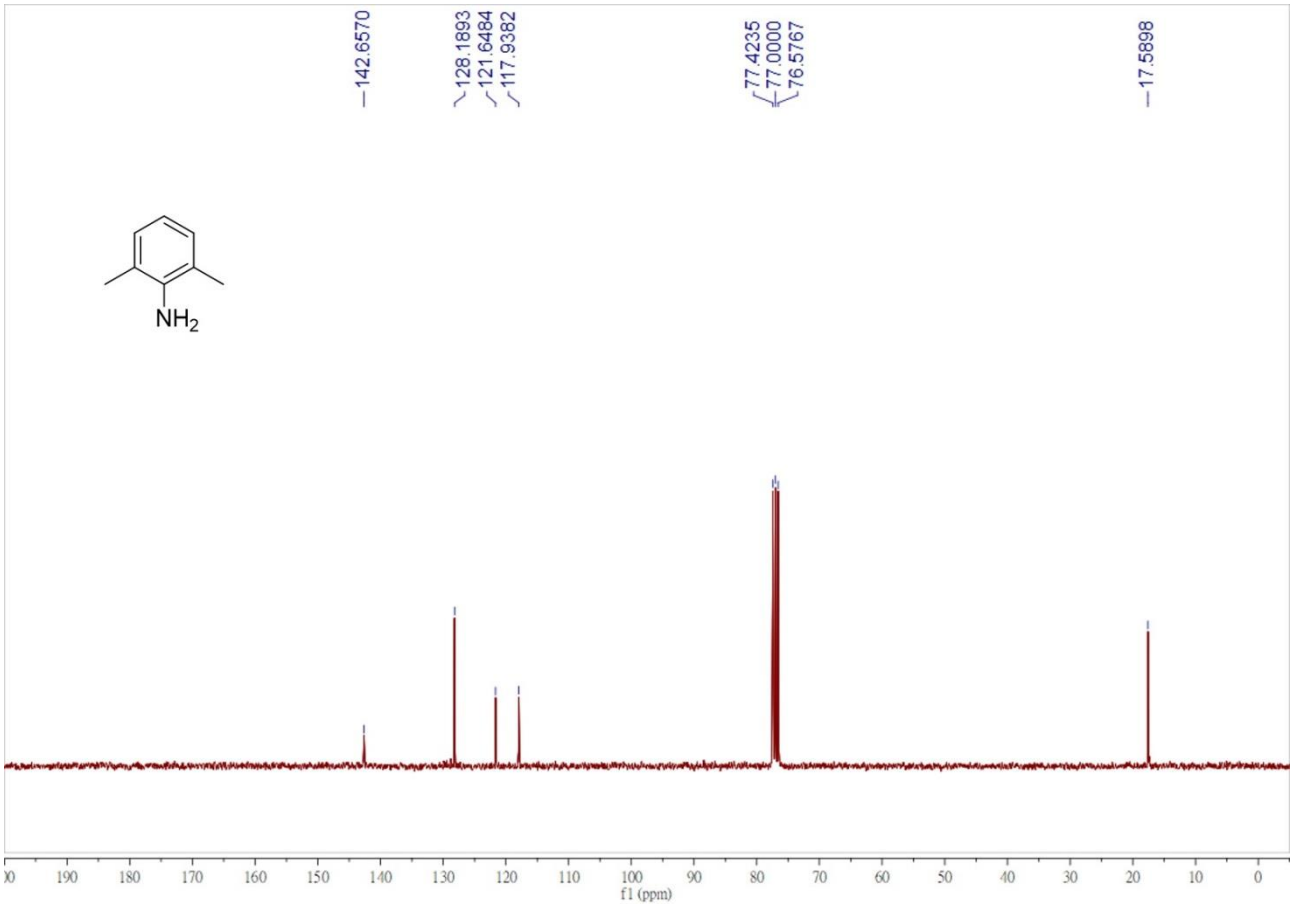
^{1}H and ^{13}C NMR spectra of compound **2u**



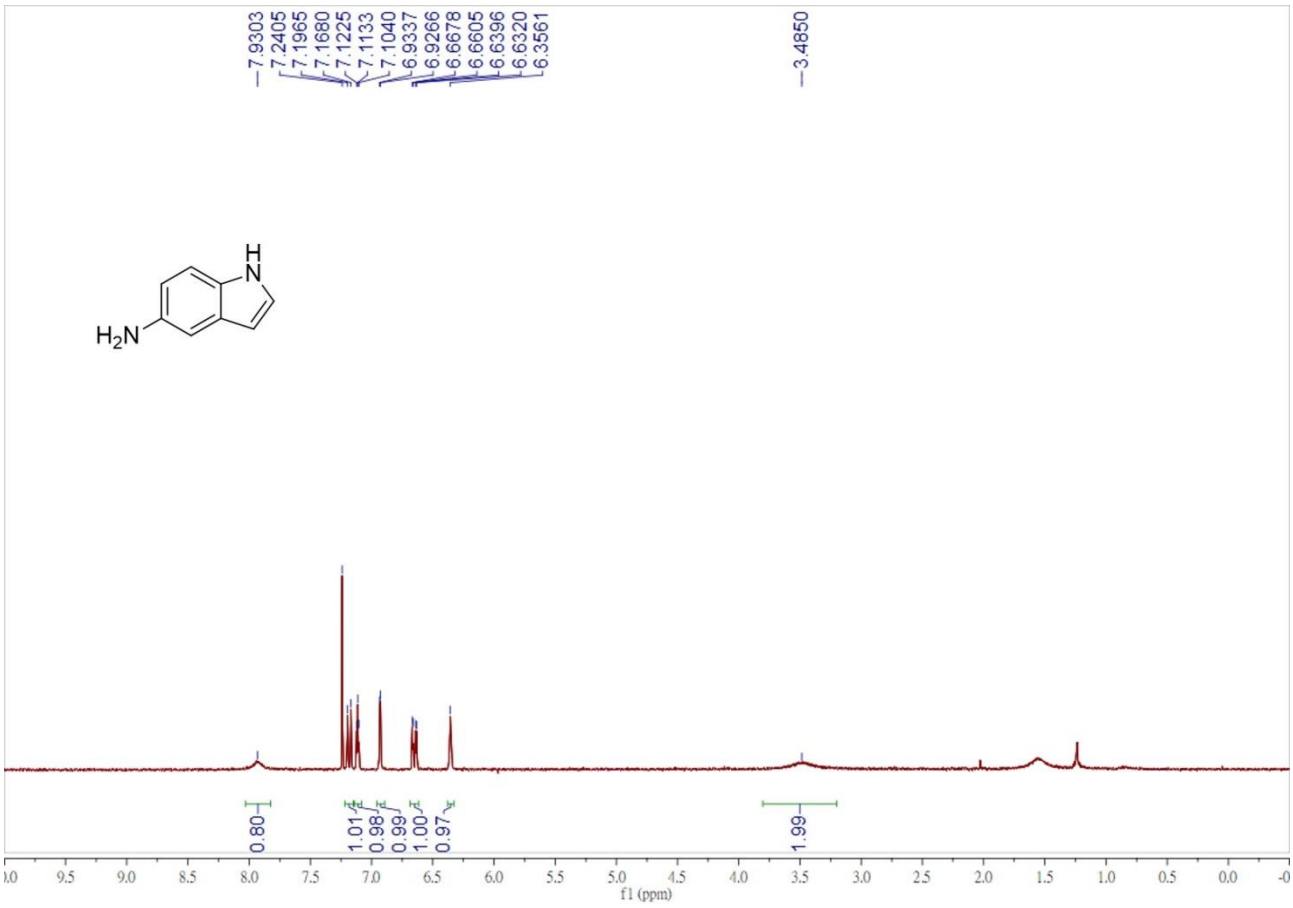


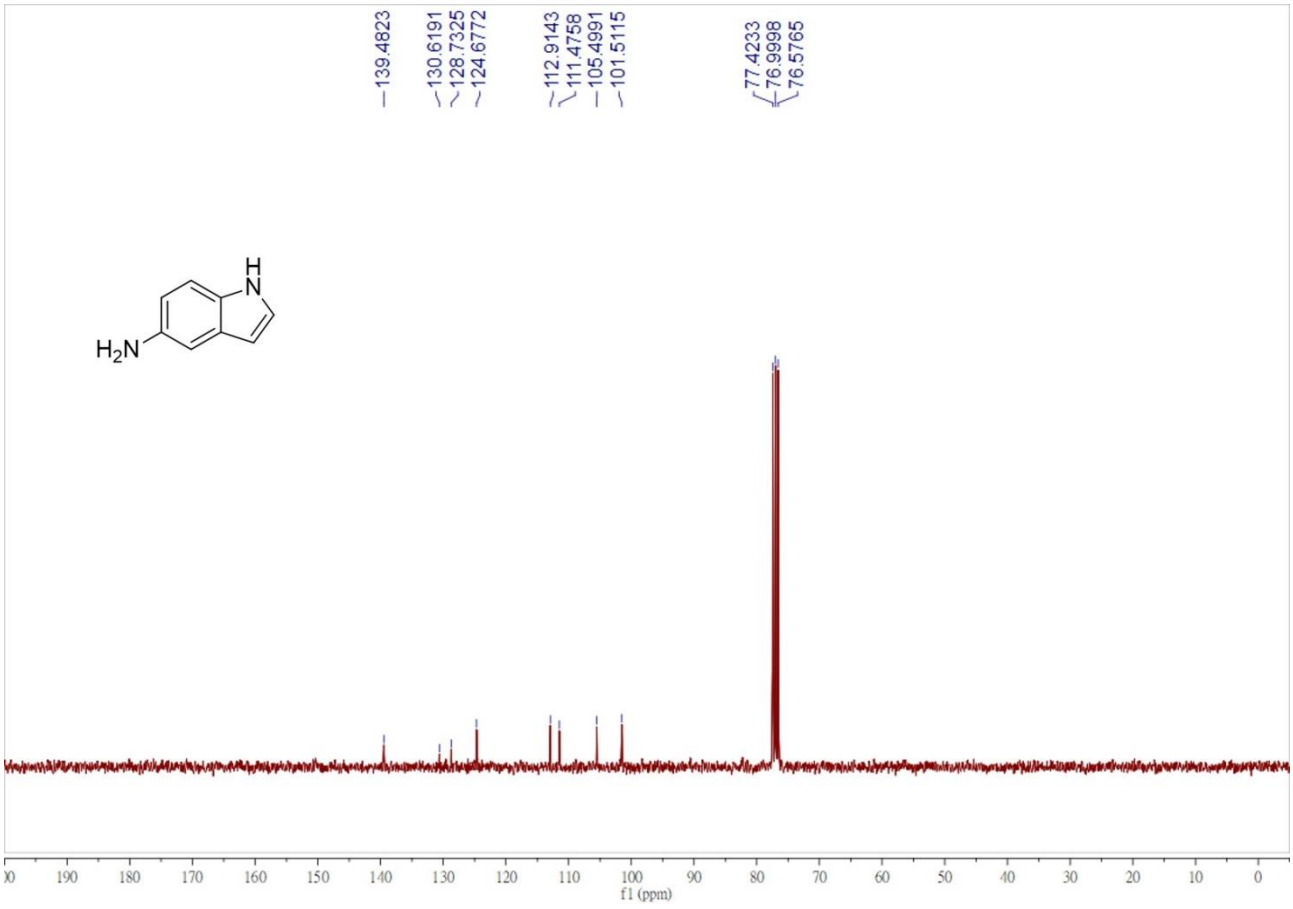
^{1}H and ^{13}C NMR spectra of compound **2v**



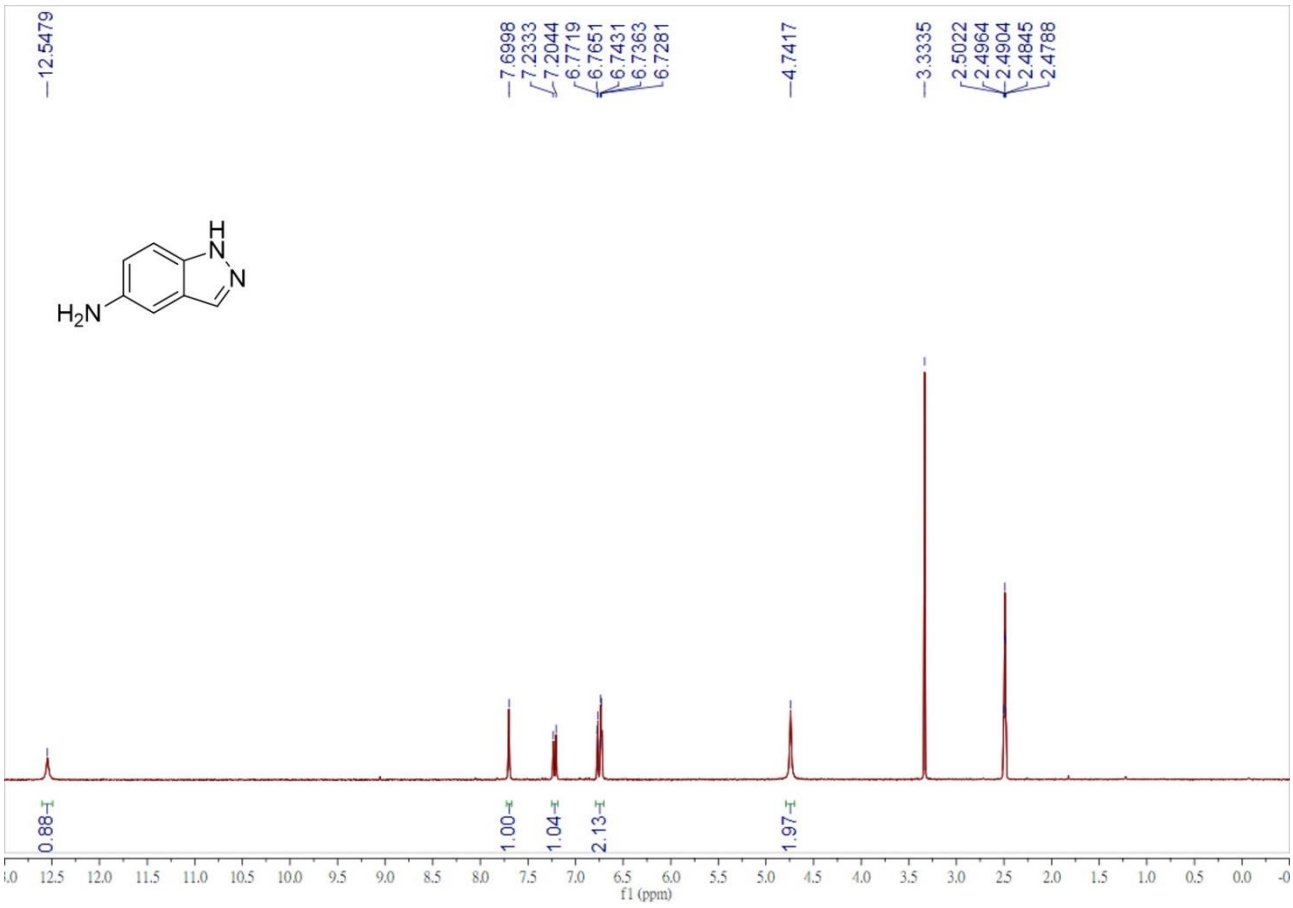


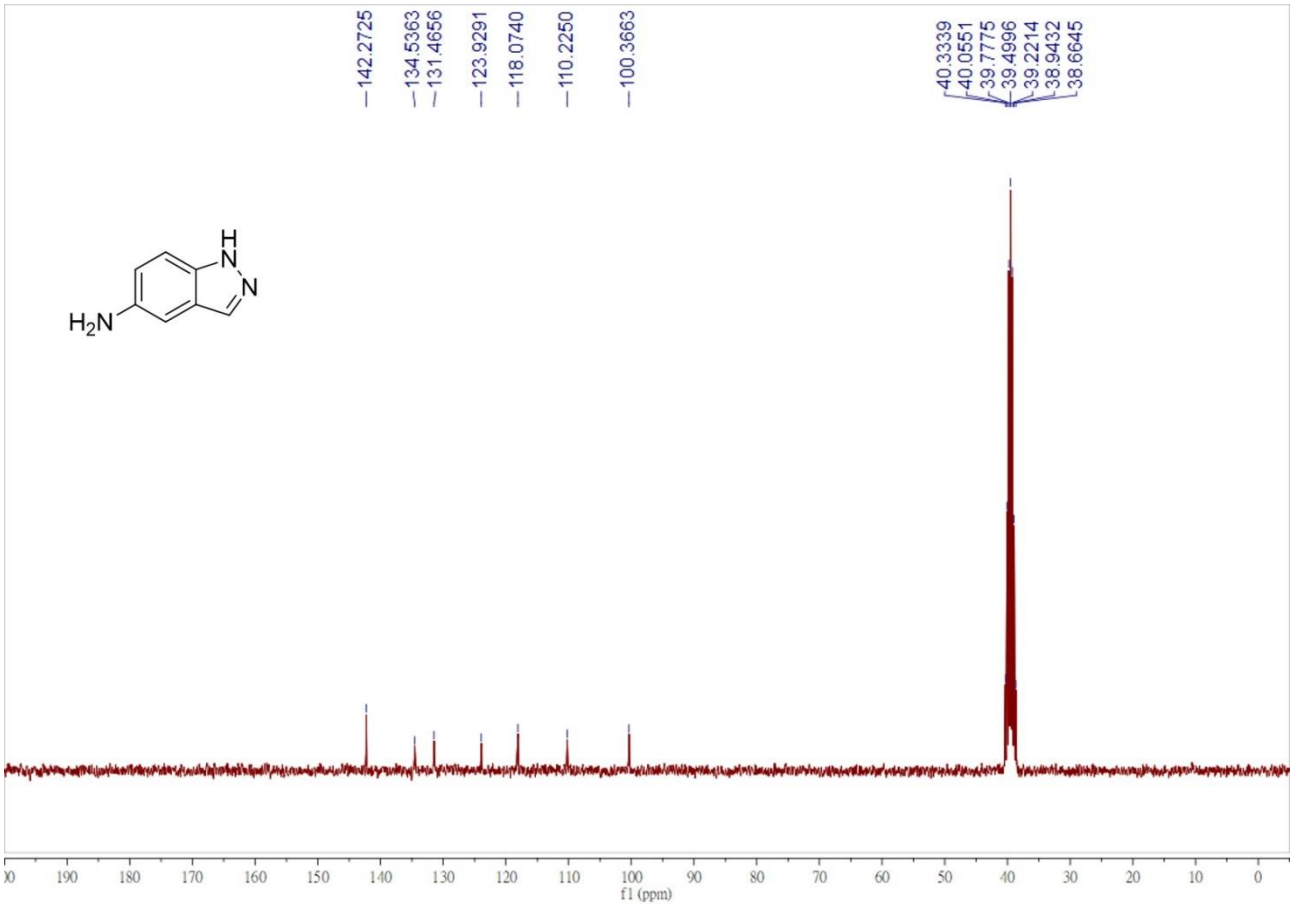
^{1}H and ^{13}C NMR spectra of compound **2w**



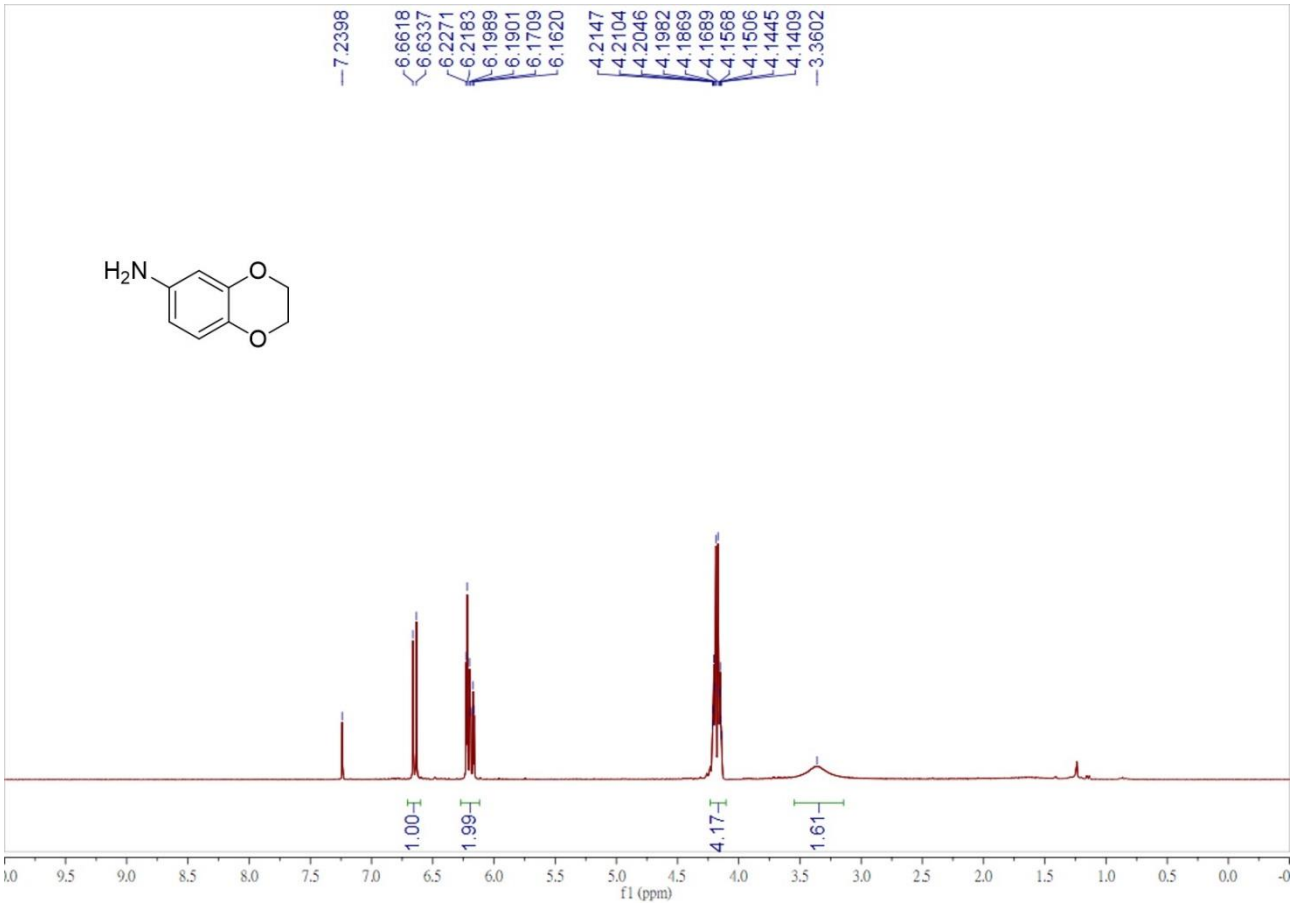


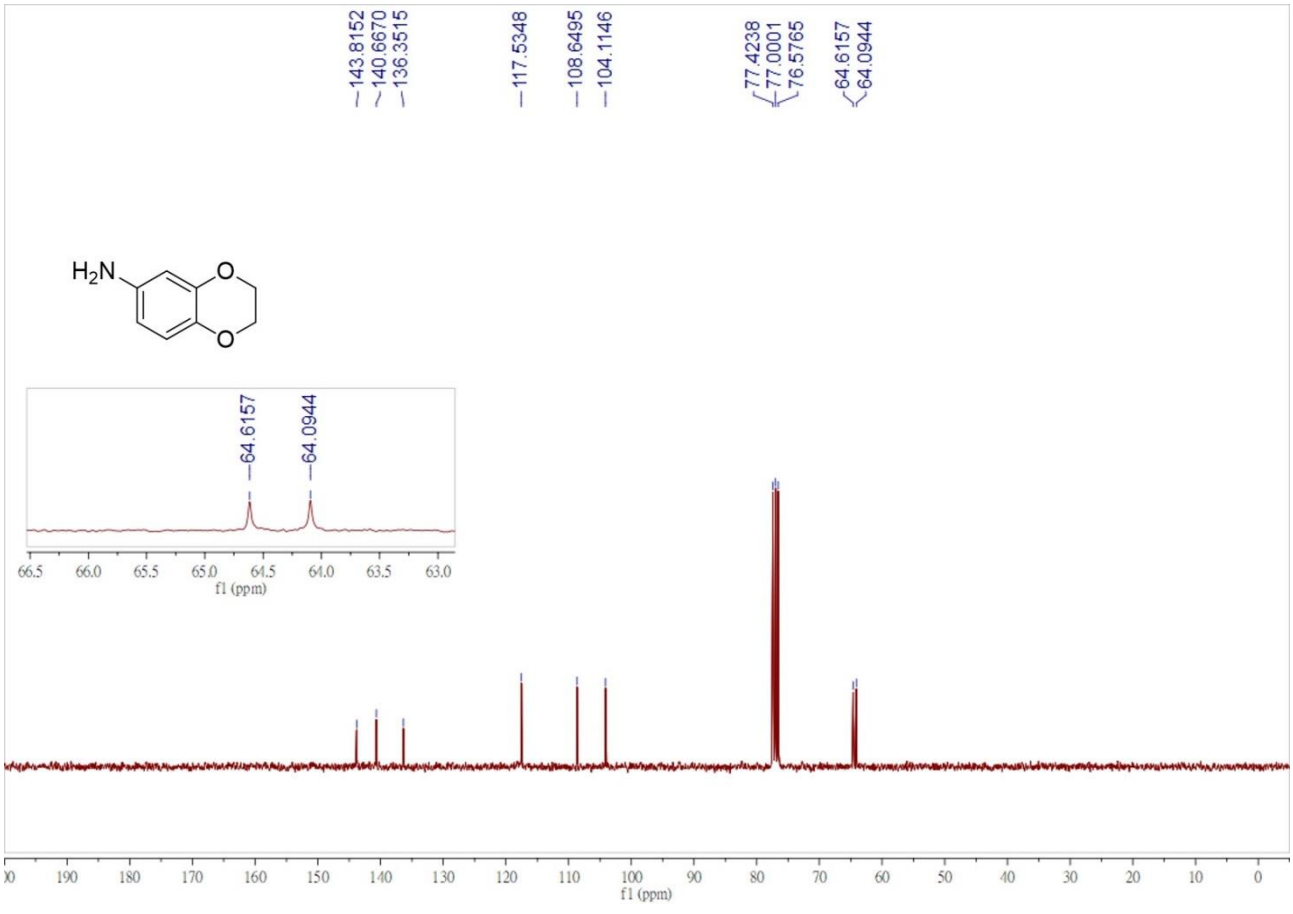
^{1}H and ^{13}C NMR spectra of compound **2x**



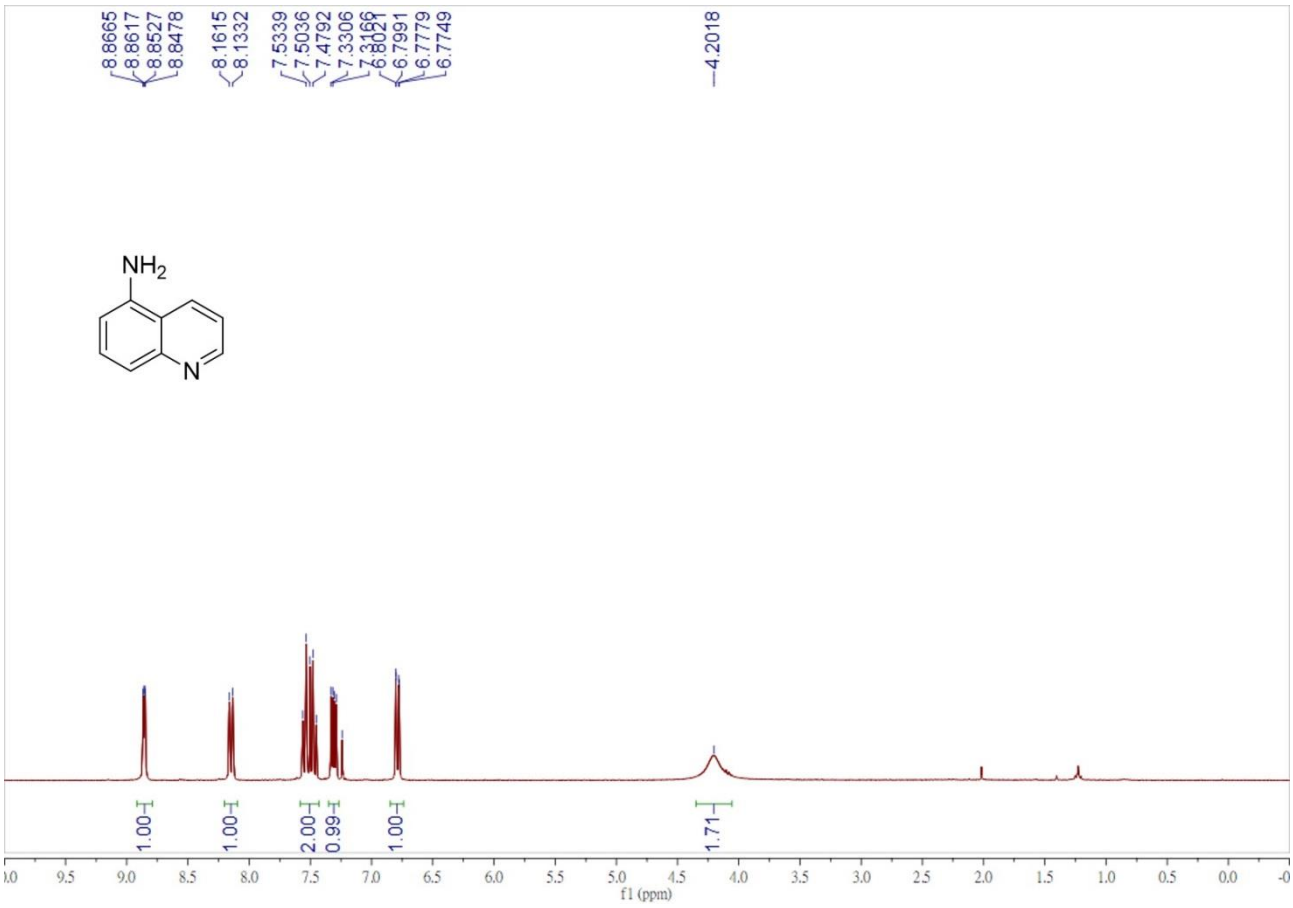


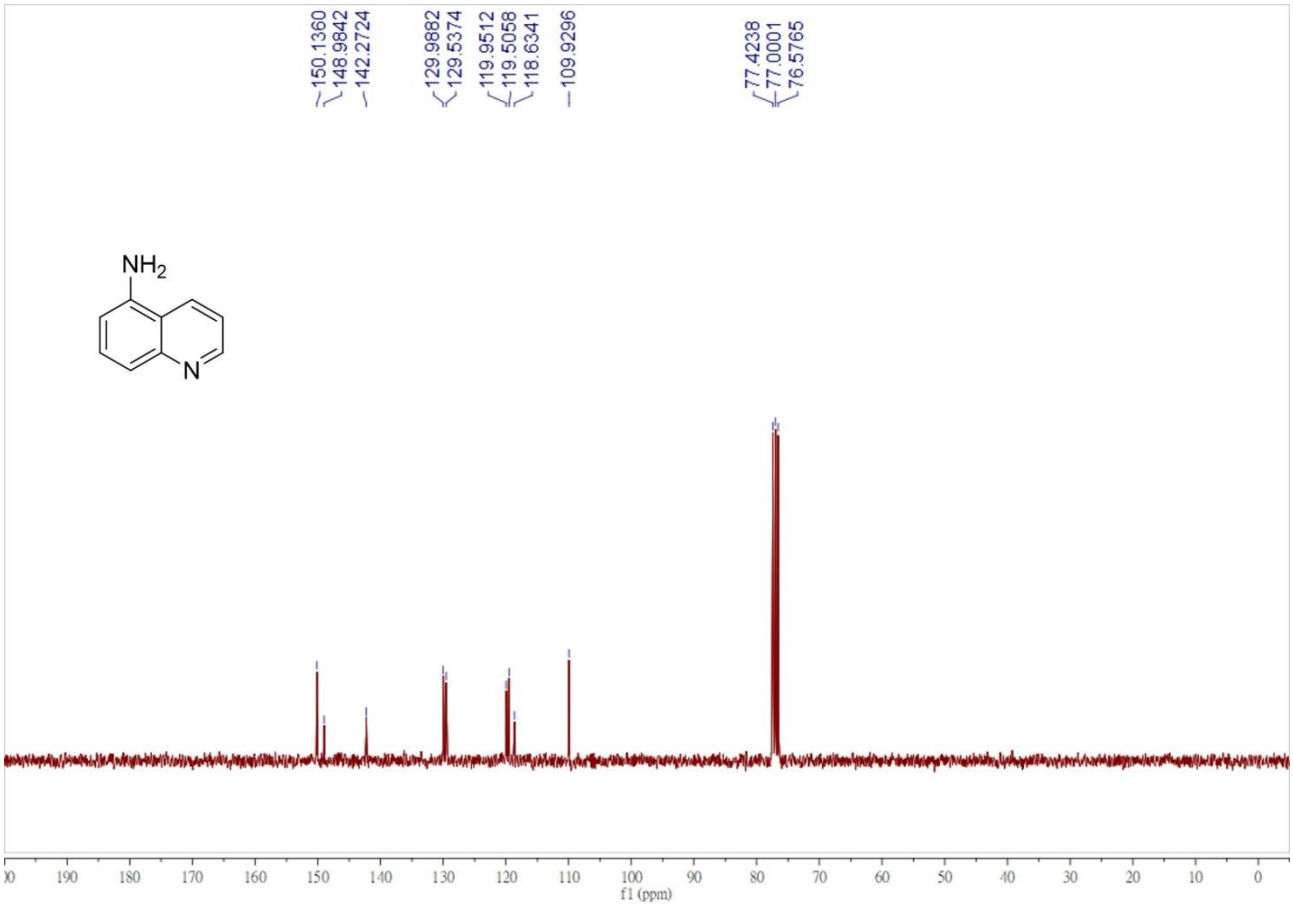
^{1}H and ^{13}C NMR spectra of compound **2y**



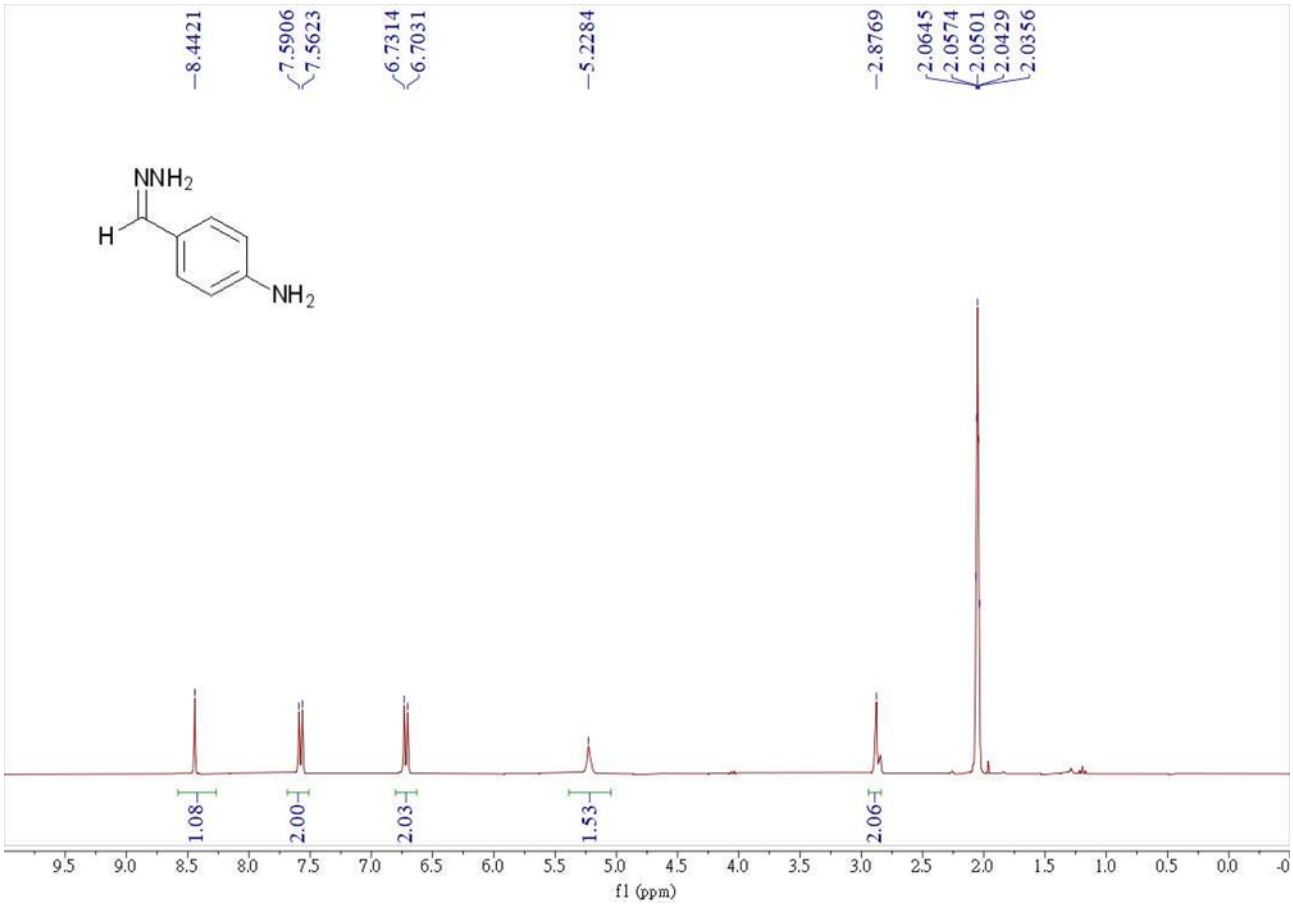


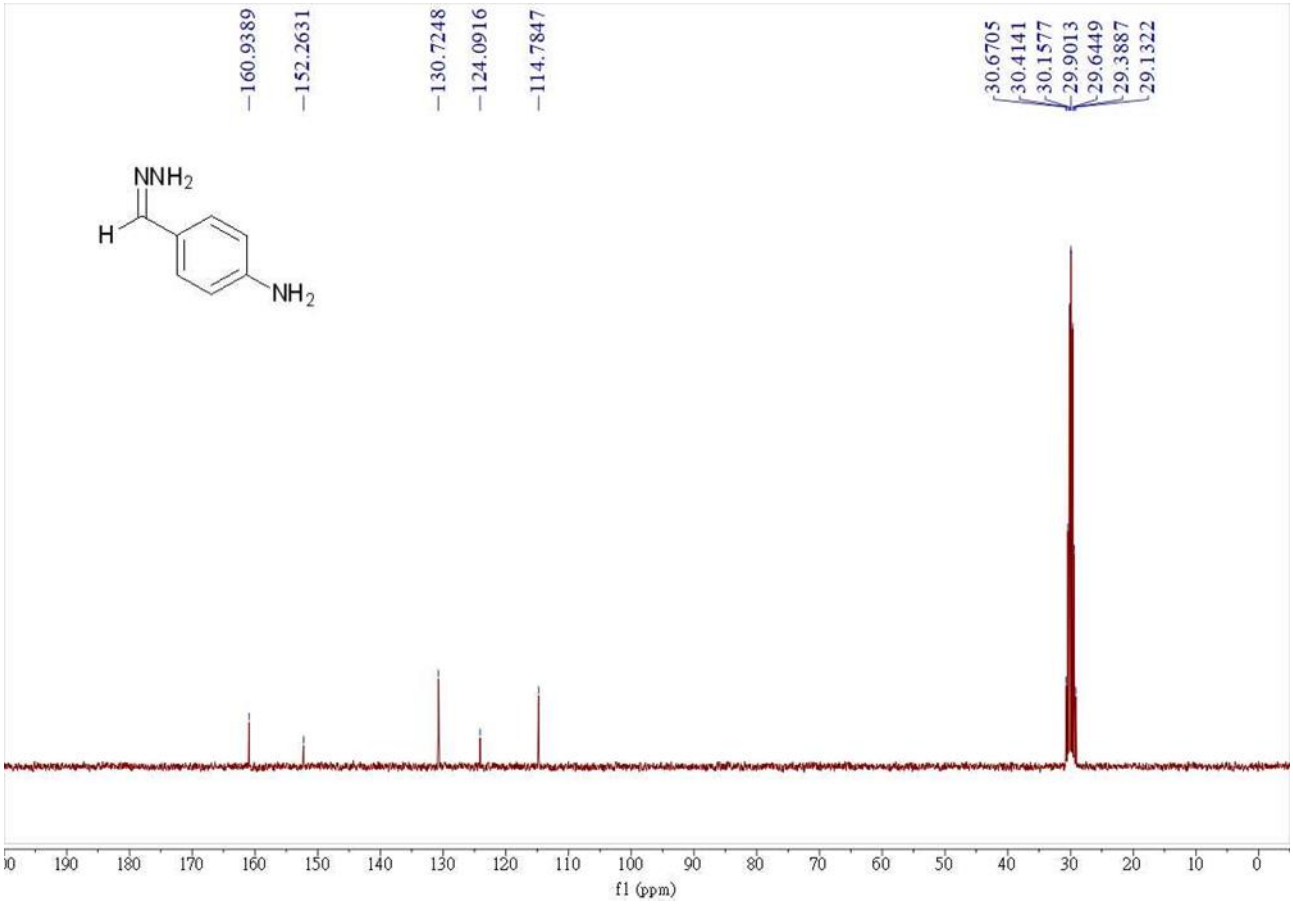
^{1}H and ^{13}C NMR spectra of compound **2z**



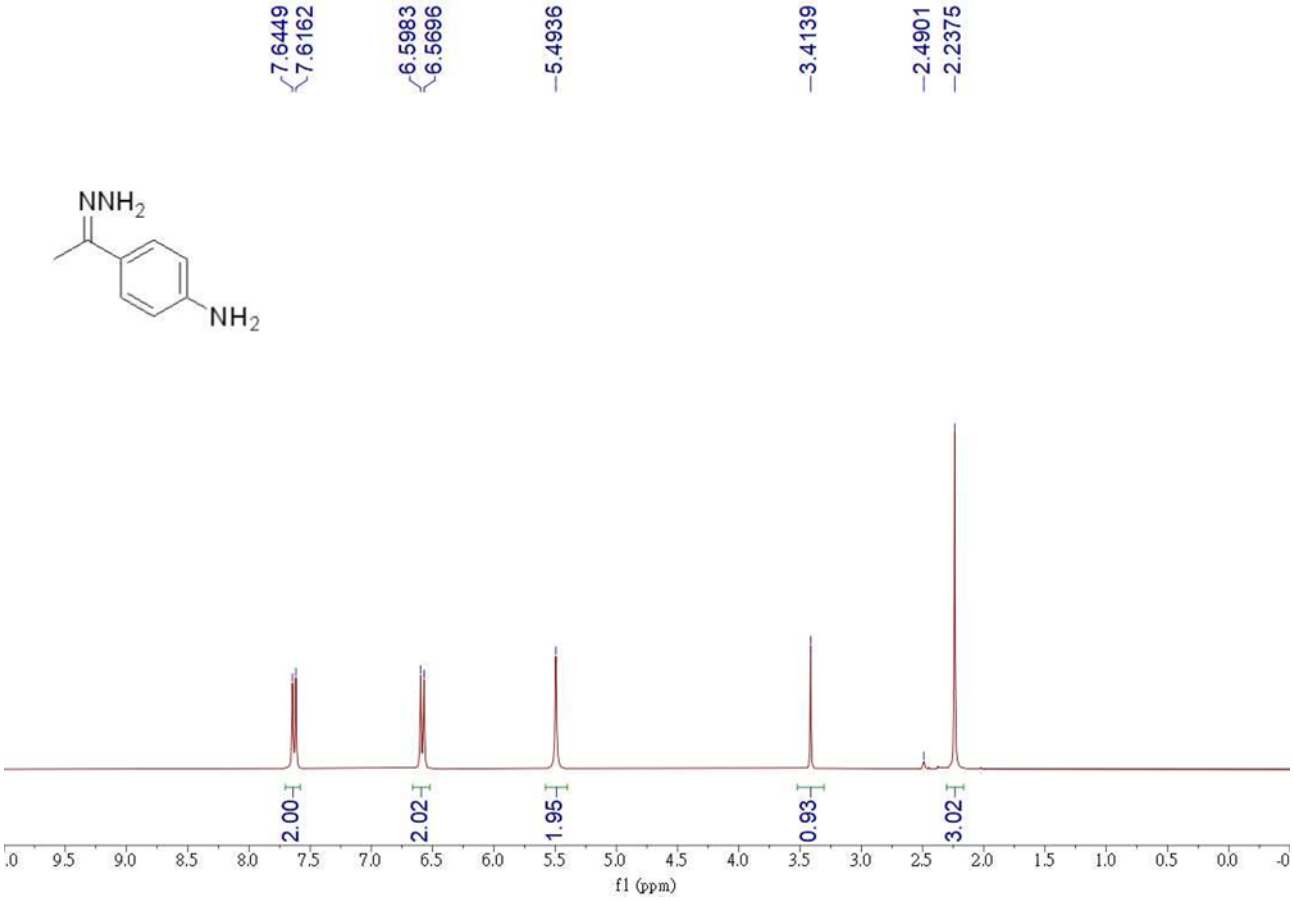


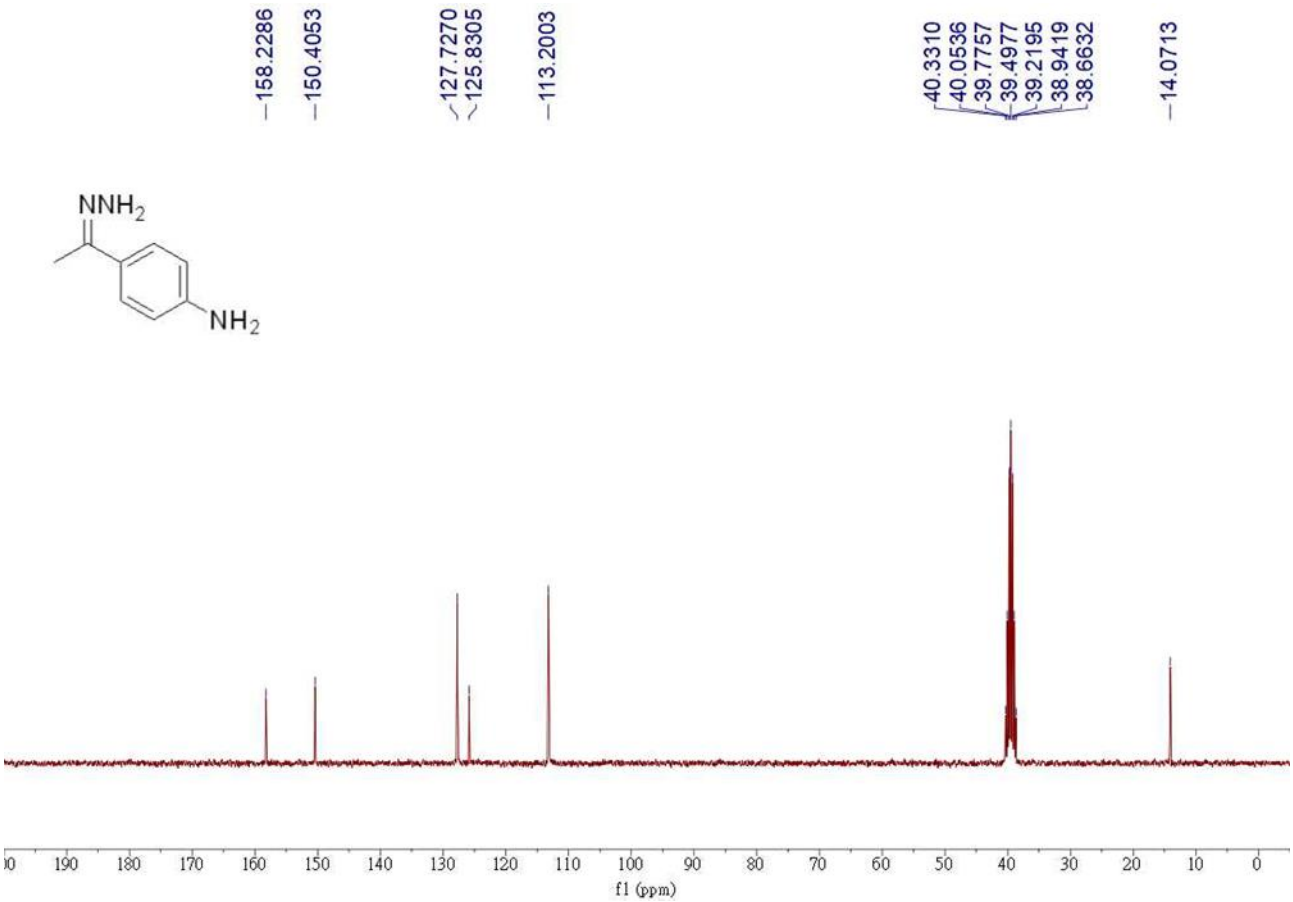
^{1}H and ^{13}C NMR spectra of compound **4a**



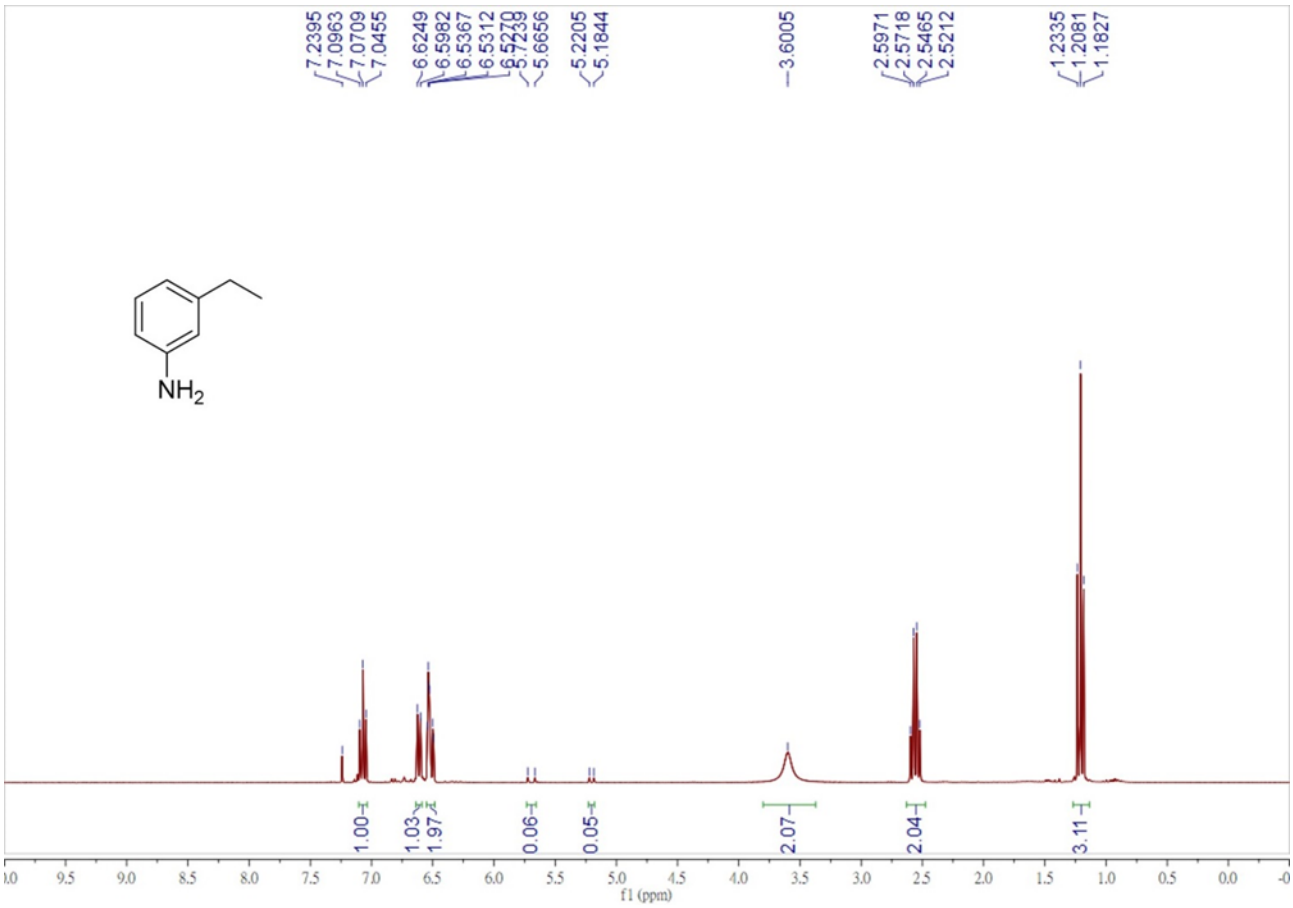


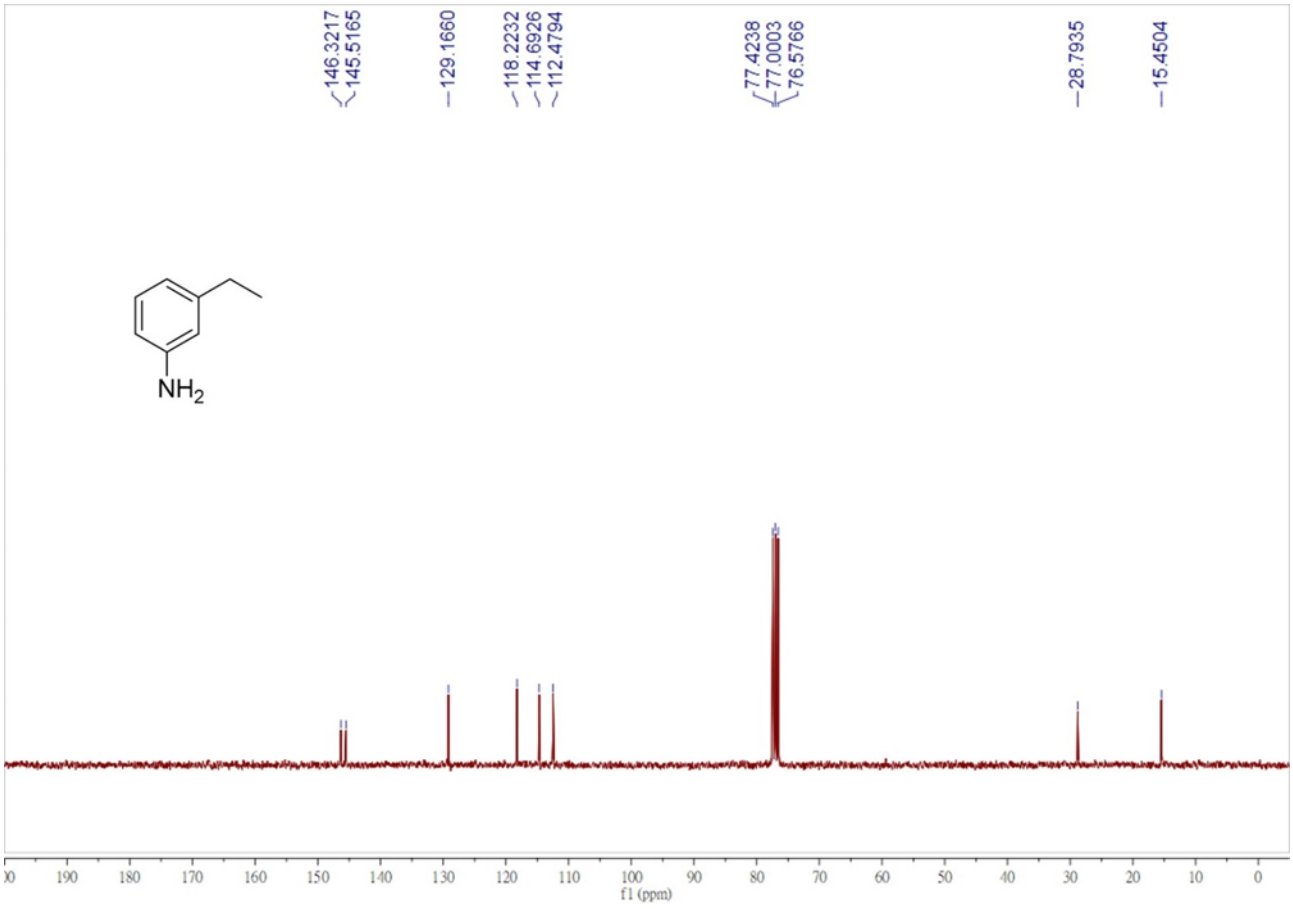
^{1}H and ^{13}C NMR spectra of compound **4b**



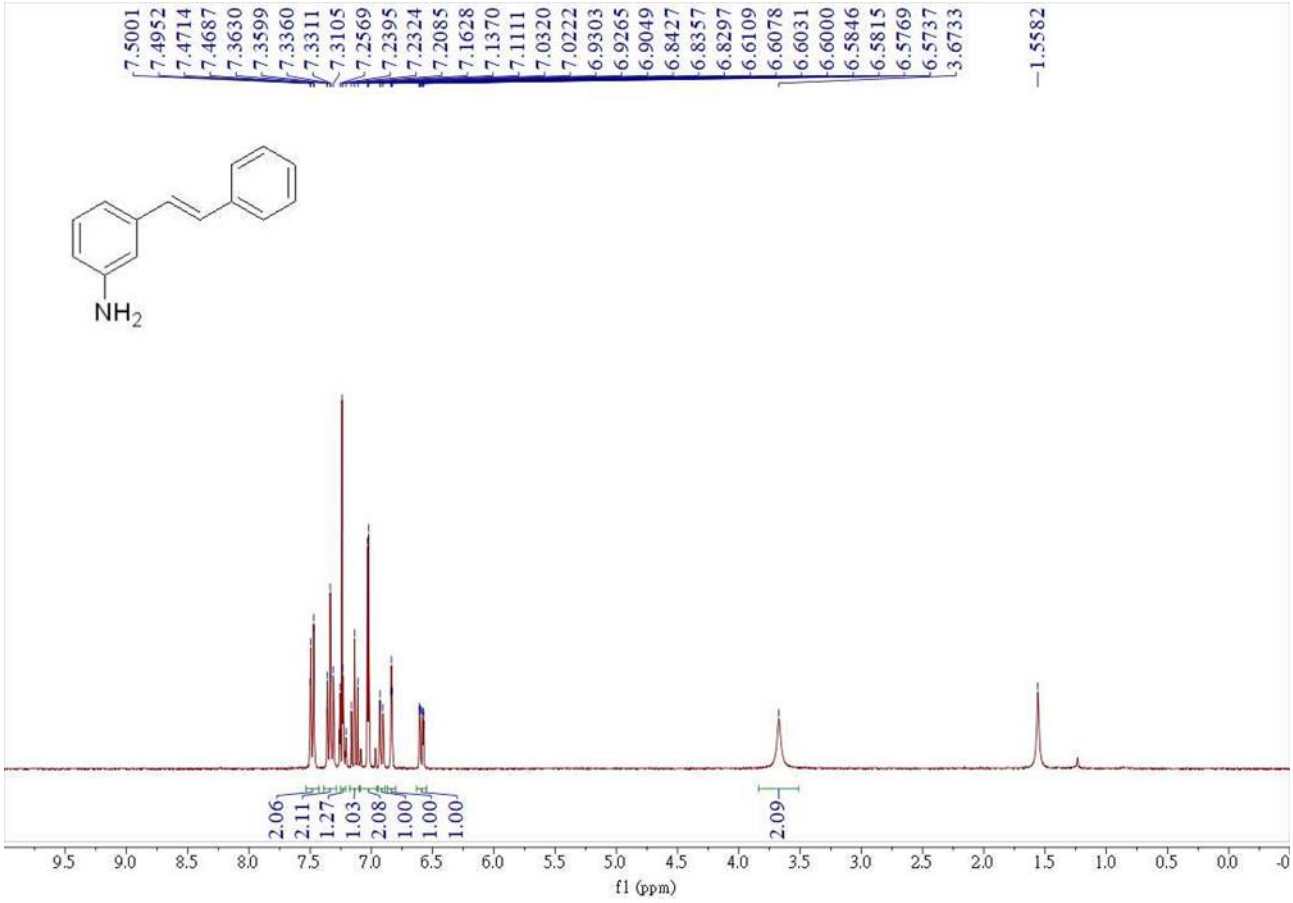


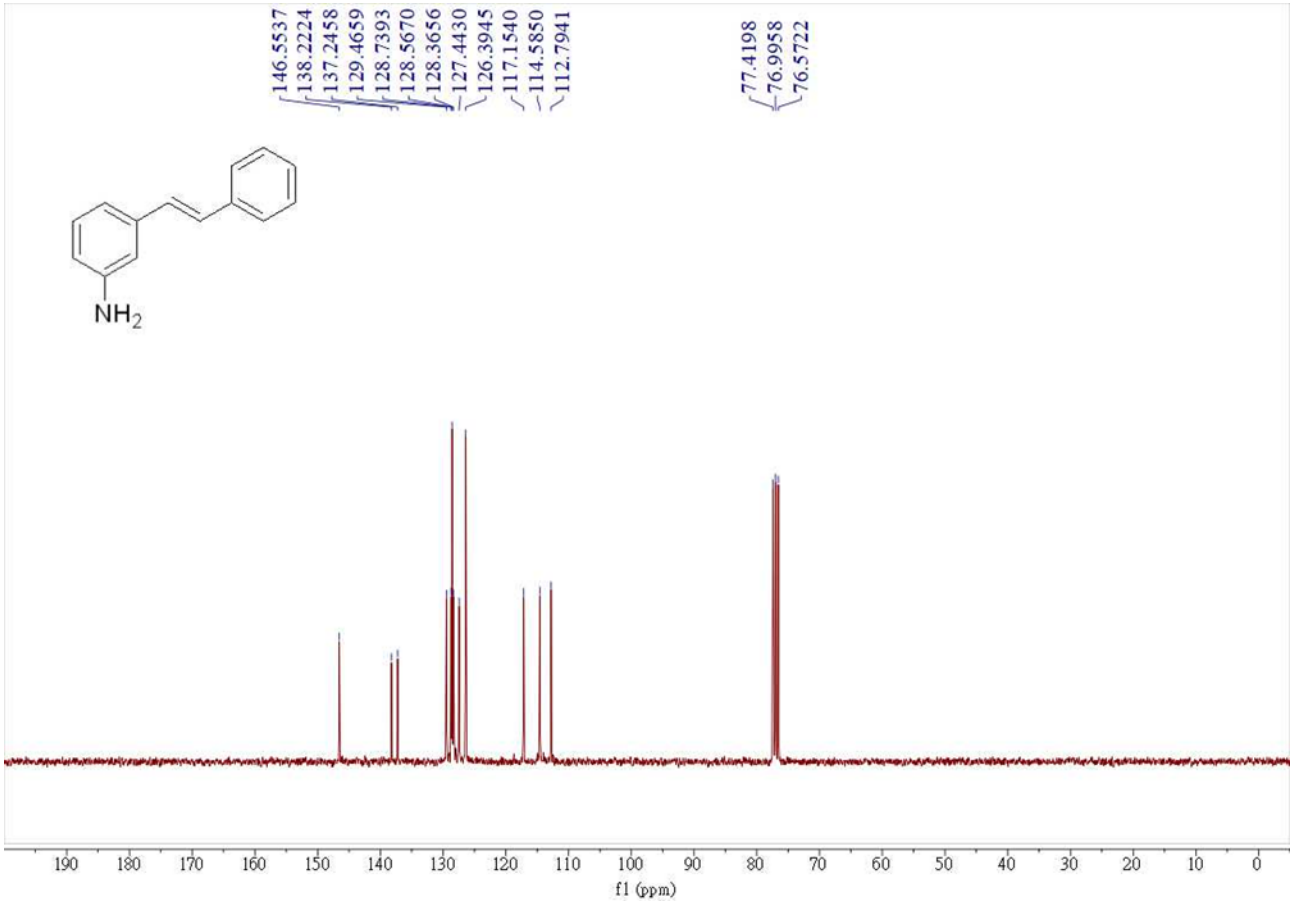
^{1}H and ^{13}C NMR spectra of compound **4c′**



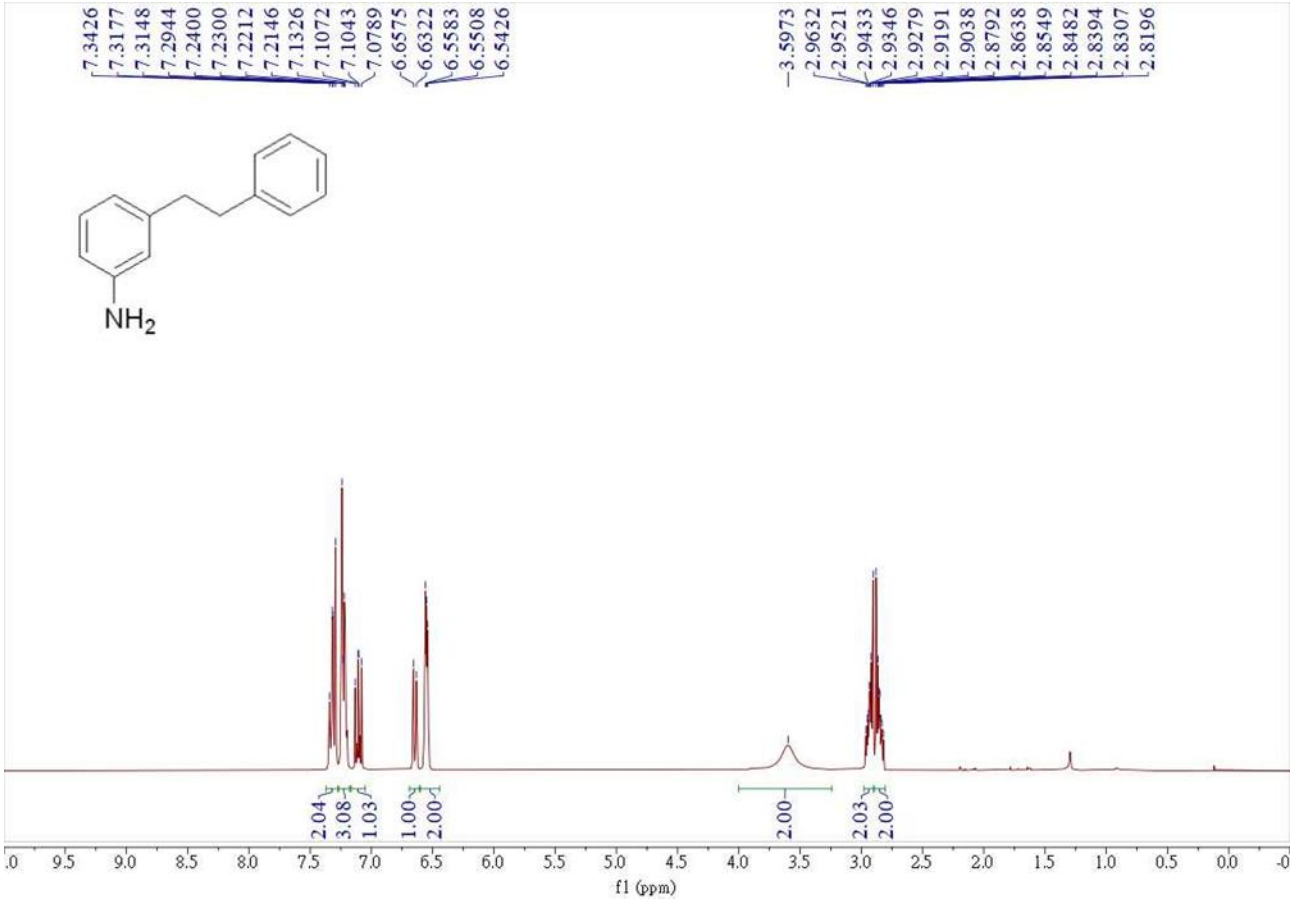


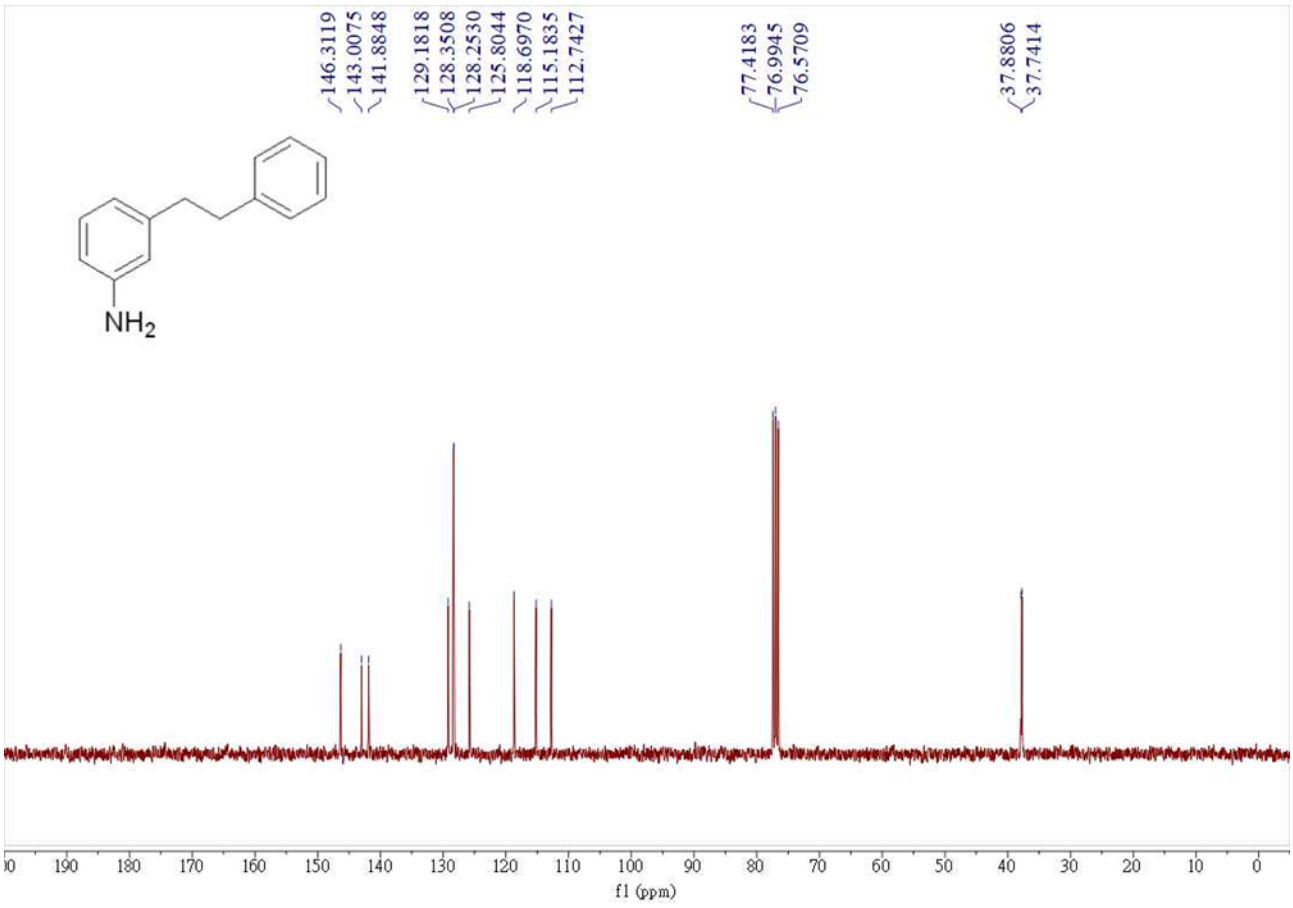
^{1}H NMR spectrum of compound **4d**



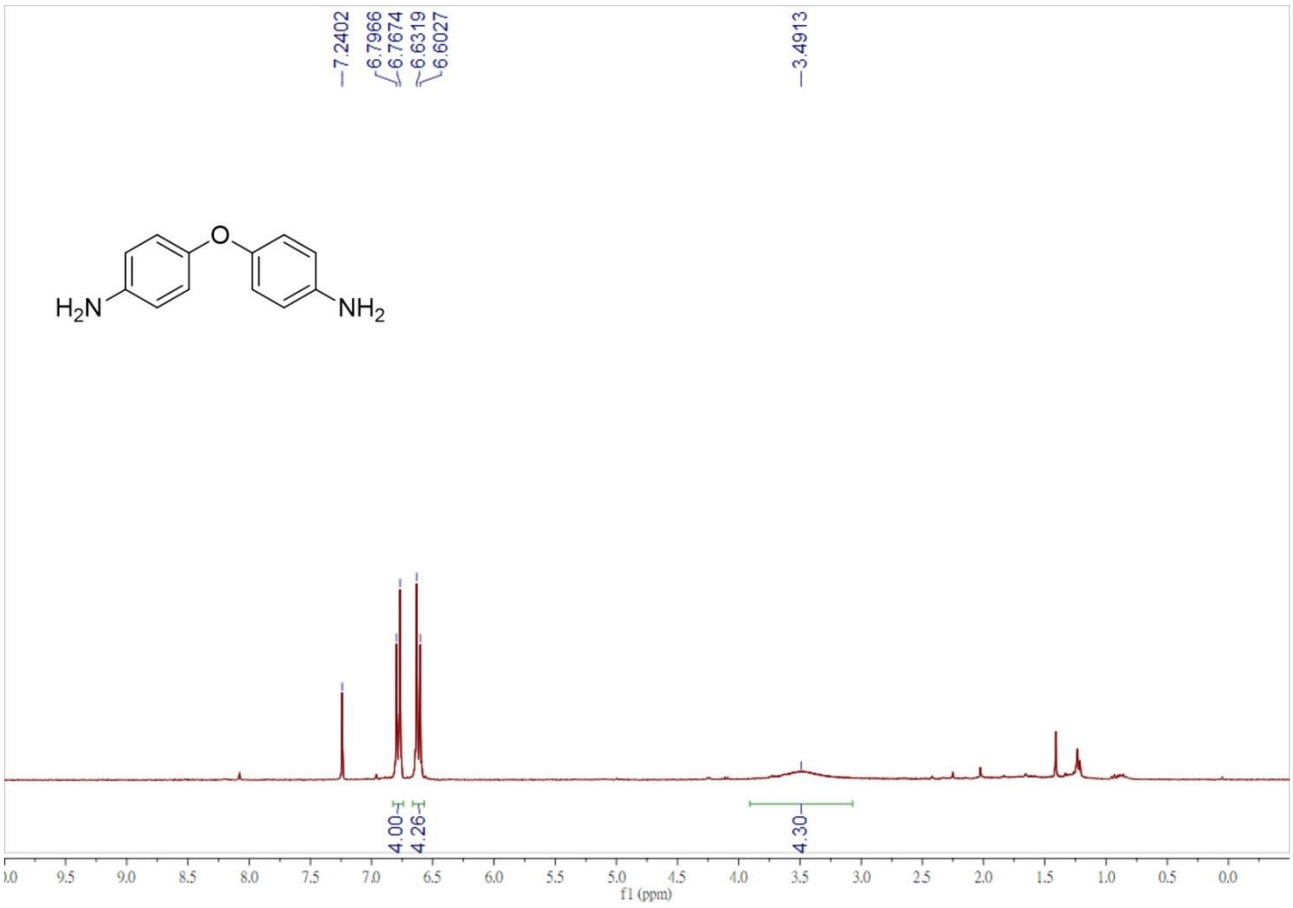


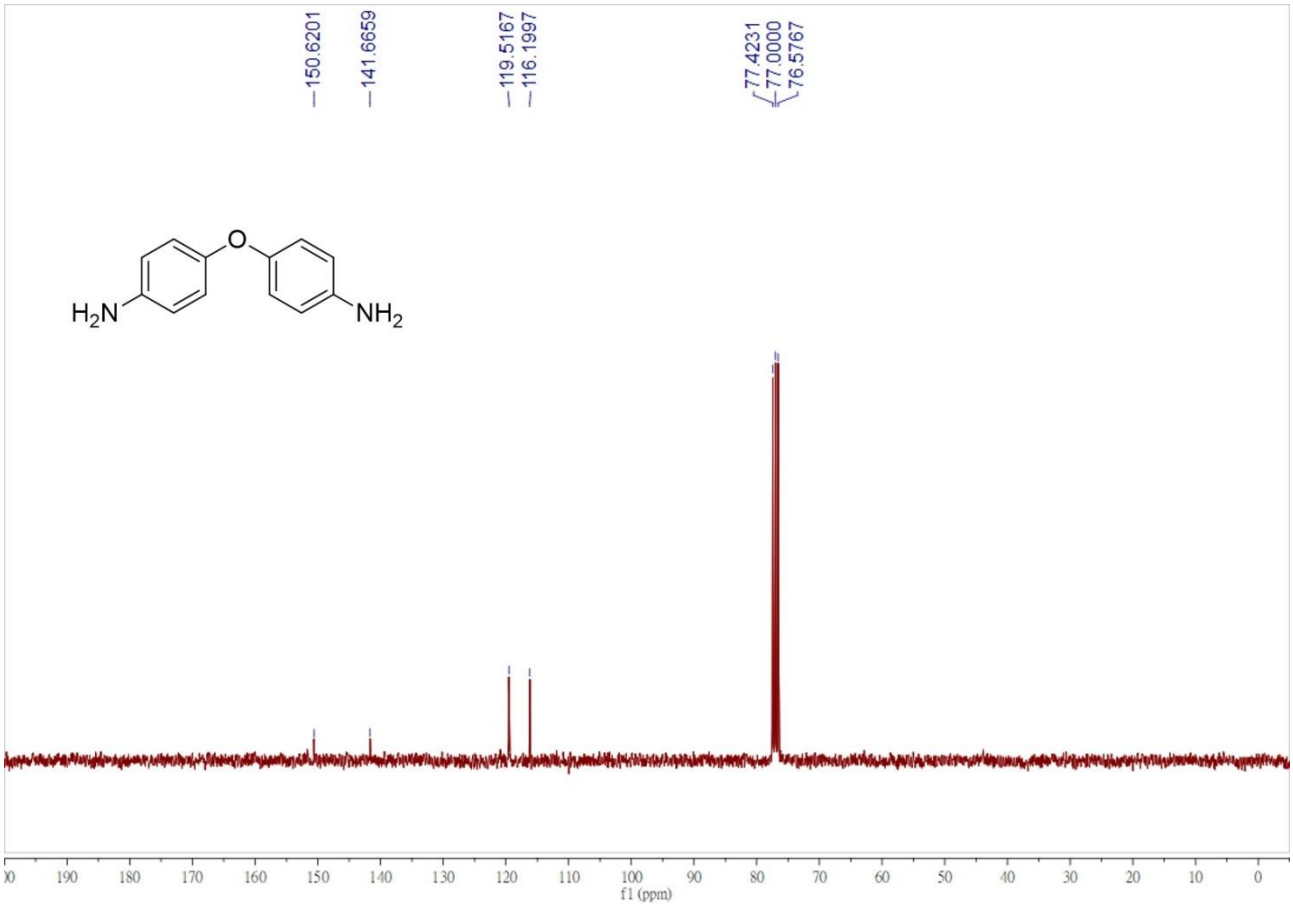
^{1}H NMR spectrum of compound **4d′**





^{1}H and ^{13}C NMR spectra of compound **6a**





^{1}H and ^{13}C NMR spectra of compound **6b**