Supporting Information

Iodine catalyzed diamination of styrene in water with the oxidation of H_2O_2

Liyan Liu,‡ Qi Sun,‡ Zicong Yan, Xinping Liang, Zhenggen Zha, Yu Yang* and Zhiyong Wang*

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry & Center for Excellence in Molecular Synthesis of Chinese Acade my of Sciences, Collaborative Innovation Center of Suzhou Nano Science and Technology & School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, 230026, Anhui, Hefei, P. R. China.

E-mail: zwang3@ustc.edu.cn.

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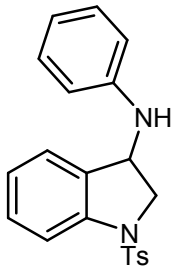
1. General Information

Unless otherwise indicated, all commercial reagents were used without additional purification. All Substances were synthesized according to the previous literature.[1] ^{1}H NMR and ^{13}C NMR were recorded on a Bruker-400 MHz Spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), and $CDCl_3$ (77 ppm for ^{13}C), respectively. HRMS (ESI) were recorded on a Water ^{TM} Q-TOF Premier Mass Spectrometer.

2. General Procedure for Diamination

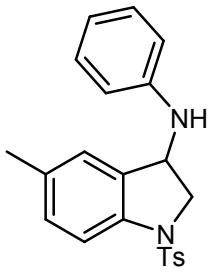
To a 5 mL tube was added 2-aminostyreen **1** (0.2 mmol), aniline **2** (0.3 mmol, 1.5 equiv), H_2O_2 (0.6 mmol, 30% in water), TMDAI (20% mol) and water (1 mL). The mixture was stirred at 45 °C for 12 hours, and extracted with DCM (1 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel to give the product **3**.

3. Characterization Data for the Products



_N_-phenyl-1-tosylindolin-3-amine (3a)

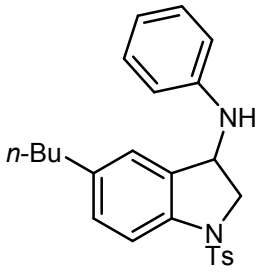
White solid. m.p. 135-136 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.21 - 7.13 (m, 4H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 2H), 4.85 (dd, *J* = 7.4, 3.5 Hz, 1H), 4.10 (dd, *J* = 11.6, 7.3 Hz, 1H), 3.83 (dd, *J* = 11.7, 3.5 Hz, 1H), 3.32 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.1, 142.0, 133.6, 132.2, 129.9, 129.7, 129.3, 127.2, 125.5, 124.3, 118.4, 115.8, 113.1, 56.6, 53.1, 21.5. HRMS (ESI) m/z calcd for $C_{21}H_{20}N_2NaO_2S$ $[M+Na]^+$ 387.1143, found 387.1140.



5-methyl-_N_-phenyl-1-tosylindolin-3-amine (3b)

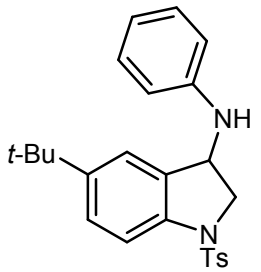
Red solid. m.p. 141 - 143 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.3 Hz, 1H), 7.59 - 7.54 (m, 2H), 7.21 - 7.12 (m, 5H), 7.05 (s, 1H), 6.79 - 6.70 (m, 1H), 6.47 - 6.35 (m, 2H), 4.78 (dd, *J* = 7.3, 3.4 Hz, 1H), 4.09 (dd, *J* = 11.8, 7.2 Hz, 1H), 3.80 (dd, *J* = 11.8, 3.5 Hz, 1H), 3.19 (s, 1H), 2.38 (s,

3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 144.0, 139.7, 134.2, 133.6, 132.5, 130.5, 129.6, 129.3, 127.3, 125.9, 118.3, 115.9, 113.1, 56.8, 53.2, 21.5, 20.9. HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2NaO_2S$ $[M+Na]^+$ 401.1300, found 401.1297.



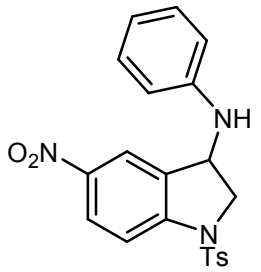
5-butyl-*N*-phenyl-1-tosylindolin-3-amine (3c)

Yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.21 - 7.12 (m, 5H), 7.06 (s, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 2H), 4.79 (s, 1H), 4.10 (dd, *J* = 11.7, 7.2 Hz, 1H), 3.80 (dd, *J* = 11.7, 3.4 Hz, 1H), 3.21 (s, 1H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 1.50 - 1.58 (m, 2H), 1.29 - 1.35(m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 144.0, 139.8, 139.4, 133.7, 132.3, 129.9, 129.6, 129.3, 127.3, 125.2, 118.3, 115.8, 113.1, 56.8, 53.2, 35.0, 33.6, 22.2, 21.5, 13.9. HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2NaO_2S$ $[M+Na]^+$ 443.1769, found 443.1767.



5-(tert-butyl)-*N*-phenyl-1-tosylindolin-3-amine (3d)

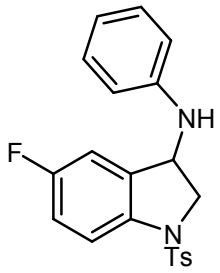
Gray oil. m.p. 136 - 137 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 3H), 7.36 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.22 - 7.14 (m, 4H), 6.79 - 6.73 (m, 1H), 6.49 - 6.41 (m, 2H), 4.84 (dd, *J* = 7.2, 3.5 Hz, 1H), 4.09 (dd, *J* = 11.5, 7.2 Hz, 1H), 3.80 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.32 (s, 1H), 2.39 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 145.7, 144.0, 139.5, 133.8, 131.8, 129.7, 129.3, 127.3, 127.0, 122.2, 118.3, 115.2, 113.2, 56.8, 53.4, 34.5, 31.4, 21.5. HRMS (ESI) m/z calcd for $C_{25}H_{28}N_2NaO_2S$ $[M+Na]^+$ 443.1769, found 443.1770.



5-nitro-*N*-phenyl-1-tosylindolin-3-amine (3e)

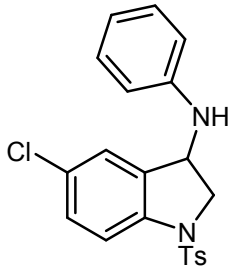
Yellow solid. m.p. 148 - 150 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.13 (d, *J* = 2.3 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.71 - 7.64 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 - 7.15 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.53 - 6.47 (m, 2H), 5.03 (dd, *J* = 7.9, 4.2 Hz, 1H), 4.25 (dd, *J* = 11.3, 7.8 Hz, 1H), 3.90 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.61 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 145.2, 145.0, 143.9, 133.3, 133.0, 130.1, 129.5, 127.1,

126.4, 121.7, 119.1, 114.2, 113.3, 57.2, 52.3, 21.6. HRMS (ESI) m/z calcd for $C_{21}H_{20}N_3O_4S$ $[M+H]^+$ 410.1175, found 410.1175.



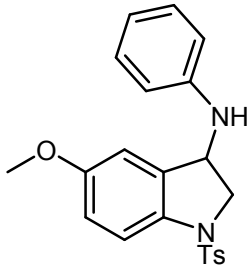
5-fluoro-*N*-phenyl-1-tosylindolin-3-amine (3f)

Red solid. m.p. 133 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 8.9, 4.5 Hz, 1H), 7.59 - 7.53 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.19 - 7.14 (m, 2H), 7.04 (td, *J* = 8.8, 2.7 Hz, 1H), 6.97 - 6.91 (m, 1H), 6.77 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.43 - 6.35 (m, 2H), 4.80 (dd, *J* = 7.6, 3.7 Hz, 1H), 4.15 (dd, *J* = 12.0, 7.4 Hz, 1H), 3.83 (dd, *J* = 11.9, 3.7 Hz, 1H), 3.15 (br, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, *J* = 244.0 Hz), 145.3, 144.3, 138.0 (d, *J* = 2.2 Hz), 134.4 (d, *J* = 7.9 Hz), 133.4, 129.8, 129.4, 127.3, 118.7, 117.4 (d, *J* = 8.3 Hz), 116.7 (d, *J* = 23.7 Hz), 113.2, 112.5 (d, *J* = 24.1 Hz), 57.0, 53.1 (d, *J* = 1.8 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.7. HRMS (ESI) m/z calcd for $C_{21}H_{19}FN_2NaO_2S$ $[M+Na]^+$ 405.1049, found 405.1045.



5-chloro-*N*-phenyl-1-tosylindolin-3-amine (3g)

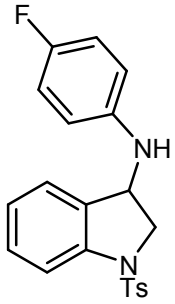
Gray solid. m.p. 154 - 155 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.60 - 7.55 (m, 2H), 7.29 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.24 - 7.20 (m, 3H), 7.19 - 7.14 (m, 2H), 6.75 - 6.79 (m, 1H), 6.44 - 6.37 (m, 2H), 4.82 (dd, *J* = 7.5, 3.8 Hz, 1H), 4.12 (dd, *J* = 11.7, 7.5 Hz, 1H), 3.81 (dd, *J* = 11.7, 3.8 Hz, 1H), 3.25 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 144.4, 140.7, 134.1, 133.3, 129.9, 129.8, 129.4, 129.4, 127.2, 125.6, 118.6, 116.9, 113.2, 56.8, 52.9, 21.5. HRMS (ESI) m/z calcd for $C_{21}H_{20}ClN_2O_2S$ $[M+H]^+$ 399.0934, found 399.0925.



5-methoxy-*N*-phenyl-1-tosylindolin-3-amine (3h)

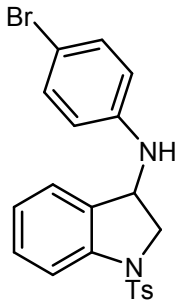
Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.20 - 7.14 (m, 4H), 6.89 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.74 (d, *J* = 7.4, 1H), 6.70 - 6.66 (m, 1H), 6.40 - 6.33 (m, 2H), 4.74 (dd, *J* = 7.2, 3.5 Hz, 1H), 4.11 (dd, *J* = 12.1, 7.2 Hz, 1H), 3.80 (dd, *J* = 12.1, 3.5 Hz, 1H), 3.75 (s, 3H), 3.09 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.0, 135.3, 134.1, 133.5, 129.7, 129.3, 127.3, 118.4, 117.6, 115.6, 115.1,

113.1, 110.4, 57.0, 55.6, 53.5, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2NaO_3S$ $[M+Na]^+$ 417.1249, found 417.1248.



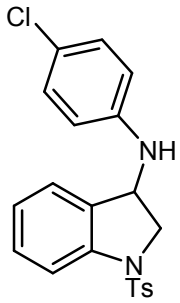
***N*-(4-fluorophenyl)-1-tosylindolin-3-amine (3i)**

Red solid. m.p. 125 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.36 (m, 1H), 7.26 - 7.23 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (dd, *J* = 9.7, 7.7 Hz, 2H), 6.39 - 6.31 (m, 2H), 4.79 (dd, *J* = 7.3, 3.4 Hz, 1H), 4.07 (dd, *J* = 11.7, 7.3 Hz, 1H), 3.81 (dd, *J* = 11.6, 3.4 Hz, 1H), 3.19 (br, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (d, *J* = 235.1 Hz), 144.2, 141.9, 141.9, 133.6, 132.0, 129.9, 129.7, 127.2, 125.5, 124.3, 115.9 (d, *J* = 22.3 Hz), 115.8, 114.1 (d, *J* = 7.3 Hz), 56.3, 53.7, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.5. HRMS (ESI) m/z calcd for $C_{21}H_{20}FN_2O_2S$ $[M+H]^+$ 383.1230, found 383.1230.



***N*-(4-bromophenyl)-1-tosylindolin-3-amine (3j)**

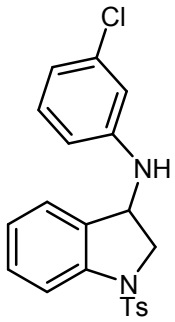
Red solid. m.p. 144 - 146 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.27 – 7.16 (m, 5H), 7.06 (td, *J* = 7.6, 2.1 Hz, 1H), 6.32 – 6.23 (m, 2H), 4.79 (s 1H), 4.04 – 4.09 (m, 1H), 3.78 - 3.82 (m, 1H), 3.32 (s, 1H), 2.38 (d, *J* = 2.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 144.2, 141.9, 133.6, 132.0, 131.8, 130.0, 129.7, 127.2, 125.5, 124.4, 115.8, 114.6, 109.9, 56.2, 53.1, 21.5. HRMS (ESI) m/z calcd for $C_{21}H_{19}BrN_2O_2SNa$ $[M+Na]^+$ 465.0248, found 465.0211.



***N*-(4-chlorophenyl)-1-tosylindolin-3-amine (3k)**

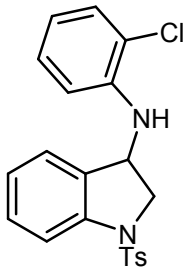
Red solid. 133 - 134 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 - 6.96 (m, 3H), 6.33 (d, *J* = 8.4 Hz, 2H), 4.79 (dd, *J* = 7.4, 3.3 Hz, 1H), 4.06 (dd, *J* = 11.7, 7.3 Hz, 1H), 3.80 (dd, *J* = 11.6, 3.4 Hz, 1H), 3.31 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 144.1, 142.0, 133.6, 131.8, 130.0, 129.7, 129.2, 127.2, 125.5, 124.4, 122.9, 115.9, 114.2, 56.2, 53.2, 21.5.

HRMS (ESI) m/z calcd for $C_{21}H_{20}ClN_2O_2S$ $[M+H]^+$ 399.0934, found 399.0922.



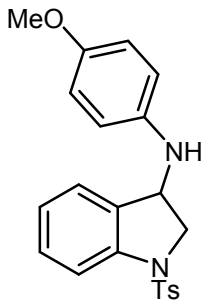
***N*-(3-chlorophenyl)-1-tosylindolin-3-amine (3l)**

Yellow solid. m.p. 125 - 127 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 - 7.05 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.31 (s, 1H), 6.28 (d, *J* = 8.2 Hz, 1H), 4.77 (dd, *J* = 7.1, 3.0 Hz, 1H), 4.07 (dd, *J* = 11.8, 7.1 Hz, 1H), 3.82 (dd, *J* = 11.8, 2.8 Hz, 1H), 3.26 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 144.3, 142.0, 135.0, 133.6, 131.8, 130.3, 130.1, 129.8, 127.2, 125.5, 124.5, 118.2, 116.2, 113.1, 111.1, 56.3, 53.0, 21.5. HRMS (ESI) m/z calcd for $C_{21}H_{20}ClN_2O_2S$ $[M+H]^+$ 399.0934, found 399.0930.



***N*-(2-chlorophenyl)-1-tosylindolin-3-amine (3m)**

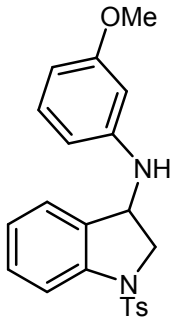
Red solid. m.p. 141 - 143 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.39 - 7.33 (m, 1H), 7.27 - 7.23 (m, 2H), 7.18 - 7.12 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 4.88 (td, *J* = 7.3, 3.8 Hz, 1H), 4.19 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.05 (d, *J* = 7.4 Hz, 1H), 3.82 (dd, *J* = 11.6, 3.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.1, 141.8, 133.6, 131.6, 130.2, 129.8, 129.6, 127.9, 127.2, 125.5, 124.5, 119.5, 118.4, 115.7, 111.4, 56.8, 53.1, 21.7. HRMS (ESI) m/z calcd for $C_{21}H_{19}ClN_2O_2SNa$ $[M+Na]^+$ 421.0753, found 421.0739.



***N*-(4-methoxyphenyl)-1-tosylindolin-3-amine (3n)**

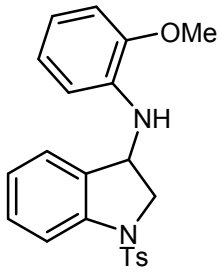
Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.63 - 7.57 (m, 2H), 7.34 - 7.30 (m, 1H), 7.23 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 - 6.73 (m, 2H), 6.43 - 6.35 (m, 2H), 4.79 (dd, *J* = 7.4, 3.5 Hz, 1H), 4.07 (dd, *J* = 11.6, 7.4 Hz, 1H), 3.81 (dd, *J* = 11.6, 3.5 Hz, 1H), 3.75 (s, 3H), 3.03 (br, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 144.1, 141.8, 139.6, 133.6, 132.4, 129.7, 129.6, 127.2, 125.5, 124.2, 115.7, 114.8, 114.7, 56.4, 55.6, 54.0, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{23}N_2O_3S$ $[M+H]^+$ 395.1429, found

395.1423.



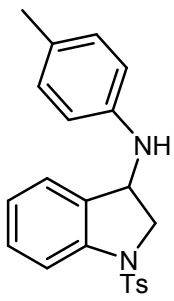
***N*-(3-methoxyphenyl)-1-tosylindolin-3-amine (3o)**

Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.62 - 7.57 (m, 2H), 7.37 - 7.28 (m, 1H), 7.26 - 7.24 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.12 - 7.01 (m, 2H), 6.32 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.03 (dd, *J* = 8.1, 1.5 Hz, 1H), 5.98 - 5.99 (m, 1H), 4.82 (dd, *J* = 7.4, 3.4 Hz, 1H), 4.08 (dd, *J* = 11.7, 7.3 Hz, 1H), 3.83 (dd, *J* = 11.7, 3.5 Hz, 1H), 3.75 (s, 3H), 3.31 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 147.0, 144.1, 141.9, 133.6, 132.1, 130.1, 129.9, 129.7, 127.2, 125.5, 124.3, 115.8, 106.1, 103.1, 99.4, 56.6, 55.0, 53.1, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2NaO_3S$ $[M+Na]^+$ 417.1249, found 417.1251.



***N*-(2-methoxyphenyl)-1-tosylindolin-3-amine (3p)**

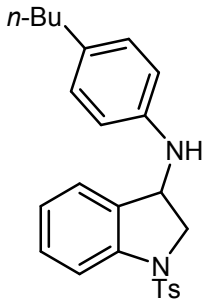
Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.32 (td, *J* = 7.8, 1.3 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (td, *J* = 7.4, 1.8 Hz, 1H), 6.78 - 6.75 (m, 1H), 6.75 - 6.70 (m, 1H), 6.54 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.92 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.15 (dd, *J* = 11.1, 7.7 Hz, 1H), 3.83 (s, 1H), 3.80 (dd, *J* = 11.1, 4.4 Hz, 1H), 3.74 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 144.1, 141.9, 135.7, 133.6, 132.1, 129.6, 127.2, 125.5, 124.0, 121.1, 117.5, 115.0, 115.0, 110.0, 109.7, 56.8, 55.2, 52.8, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2NaO_3S$ $[M+Na]^+$ 417.1249, found 417.1243.



***N*-(p-tolyl)-1-tosylindolin-3-amine (3q)**

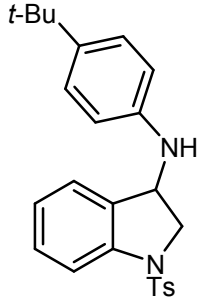
Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.54 - 7.50 (m, 2H), 7.28 - 7.23 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.92 - 6.88 (m, 2H), 6.26 (d, *J* = 8.4 Hz, 2H), 4.75 (dd, *J* = 7.5, 3.5 Hz, 1H), 4.02 (dd, *J* = 11.6, 7.4 Hz, 1H), 3.74 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.04 (br, 1H), 2.31 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.3, 141.9, 133.7, 132.4, 129.9, 129.8, 129.7, 127.6, 127.2, 125.5, 124.3, 115.8, 113.4, 56.6, 53.4, 21.5, 20.3. HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2NaO_2S$ $[M+Na]^+$ 401.1300, found

401.1293.



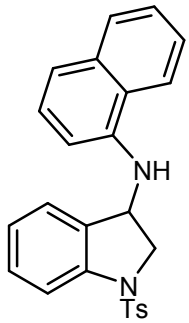
***N*-(4-butylphenyl)-1-tosylindolin-3-amine (3r)**

Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.63 - 7.57 (m, 2H), 7.36 - 7.30 (m, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 - 6.96 (m, 2H), 6.40 - 6.32 (m, 2H), 4.83 (dd, *J* = 7.5, 3.6 Hz, 1H), 4.10 (dd, *J* = 11.6, 7.3 Hz, 1H), 3.82 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.16 (s, 1H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 1.60 - 1.50 (m, 2H), 1.39 - 1.30 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.5, 141.9, 133.7, 132.9, 132.4, 129.8, 129.7, 129.2, 127.2, 125.5, 124.3, 115.8, 113.2, 56.7, 53.4, 34.6, 33.9, 22.3, 21.5, 14.0. HRMS (ESI) m/z calcd for $C_{25}H_{29}N_2O_2S$ $[M+H]^+$ 421.1950, found 421.1949.



***N*-(4-(tert-butyl)phenyl)-1-tosylindolin-3-amine (3s)**

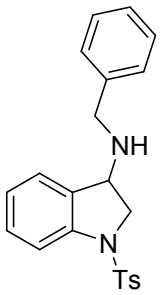
Red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.64 - 7.59 (m, 2H), 7.36 - 7.30 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.22 - 7.18 (m, 4H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.42 - 6.37 (m, 2H), 4.85 (dd, *J* = 7.7, 3.7 Hz, 1H), 4.12 (dd, *J* = 11.5, 7.4 Hz, 1H), 3.82 (dd, *J* = 11.5, 3.8 Hz, 1H), 3.23 (s, 1H), 2.39 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.3, 141.9, 141.2, 133.7, 132.4, 129.8, 129.7, 127.3, 126.1, 125.5, 124.2, 115.7, 112.9, 56.8, 53.3, 33.9, 31.5, 21.5. HRMS (ESI) m/z calcd for $C_{25}H_{29}N_2O_2S$ $[M+H]^+$ 421.1950, found 421.1937.



***N*-(naphthalen-1-yl)-1-tosylindolin-3-amine (3t)**

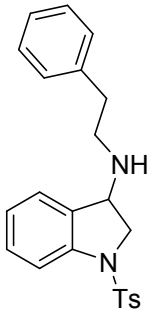
Red solid. m.p.118 - 119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.47 - 7.41 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.35 - 7.28 (m, 4H), 7.24 (d, *J* = 4.8 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 7.3 Hz, 1H), 4.97 (dd, *J* = 7.2, 2.9 Hz, 1H), 4.25 (dd, *J* = 11.9, 7.2 Hz, 1H), 4.01 (dd, *J* = 12.0, 2.3 Hz, 1H), 3.91 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 141.3, 139.8, 133.3, 132.7, 131.2, 129.1, 128.7, 127.7, 126.1, 125.3, 124.9, 124.7, 123.7, 123.5, 122.2, 118.8, 117.6, 115.1, 104.0, 55.6, 52.4, 20.5. HRMS

(ESI) m/z calcd for $C_{25}H_{22}N_2NaO_2S$ $[M+Na]^+$ 437.1300, found 437.1312.



***N*-benzyl-1-tosylindolin-3-amine (3u)**

Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.25 (m, 4H), 7.22 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.05 (td, *J* = 7.5, 0.8 Hz, 1H), 4.15 (dd, *J* = 7.6, 3.7 Hz, 1H), 3.92 (dd, *J* = 11.5, 7.7 Hz, 1H), 3.82 (dd, *J* = 11.6, 3.8 Hz, 1H), 3.64 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 141.7, 139.4, 133.7, 133.4, 129.6, 129.3, 128.3, 127.9, 127.1, 127.1, 125.4, 123.9, 115.5, 57.3, 55.9, 50.5, 21.4. HRMS (ESI) m/z calcd for $C_{22}H_{23}N_2O_2S$ $[M+H]^+$ 379.1475, found 379.1478.

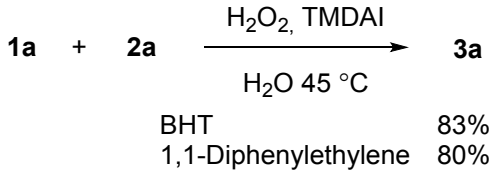


***N*-phenethyl-1-tosylindolin-3-amine (3v)**

Colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.62 (m, 3H), 7.32 – 7.10 (m, 9H), 7.00 (td, *J* = 7.5, 1.0 Hz, 1H), 4.16 (dd, *J* = 7.9, 4.1 Hz, 1H), 3.90 (dd, *J* = 11.3, 7.9 Hz, 1H), 3.73 (dd, *J* = 11.3, 4.1 Hz, 1H), 2.79 – 2.68 (m, 2H), 2.68 – 2.58 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.7, 139.5, 133.7, 133.1, 129.6, 129.2, 128.5, 128.4, 127.2, 126.2, 125.3, 123.8, 115.1, 57.7, 55.9, 47.6, 36.4, 21.5. HRMS (ESI) m/z calcd for $C_{23}H_{25}N_2O_2S$ $[M+H]^+$ 393.1631, found 393.1642.

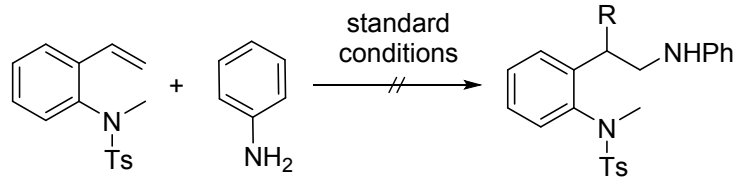
4. Mechanistic Studies

4.1. Radial Trapping Experiments



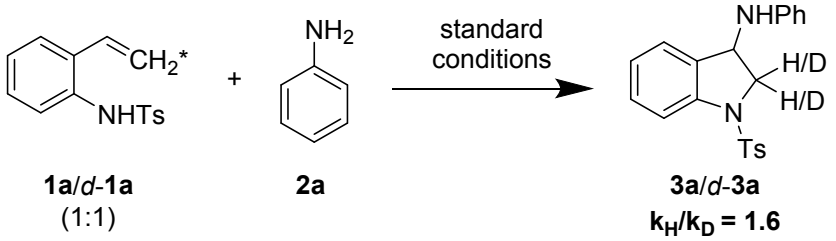
To a 5 mL tube was added **1a** (0.2 mmol), **2a** (0.3 mmol), H_2O_2 (0.6 mmol, 30% in water), TMDAI (20% mol), radial scavenger (BHT or 1,1-Diphenyethylene, 0.6 mmol) and water (1 mL). The mixture was stirred at 45 °C for 12 hours, and extracted with DCM (1 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel to give the product 3.

4.2 Effect of *N*-Substituents



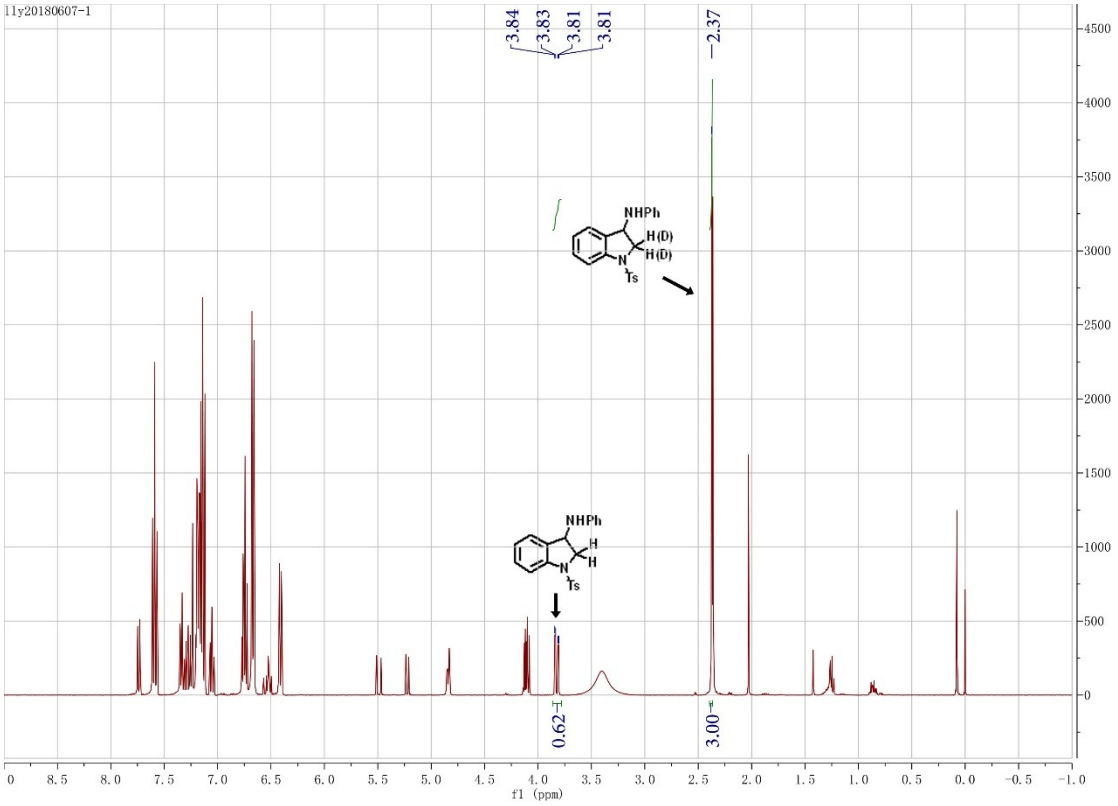
Standard conditions: **4** (0.2 mmol), aniline (0.3 mmol), H_2O_2 (0.6 mmol, 30% in water), TMDAI (20% mol) inwater (1 mL) at 45 °C for 12 hours.

4.3 kinetics Isotope Effect (KIE)



Substrate **1a** (0.1 mmol, 27.3 mg), d-**1a** (0.1 mmol, 27.5 mmol), aniline (0.3 mmol), TMDAI (20 mol%, 0.04 mmol), H_2O_2 (30% aq, 3eq, 0.6 mmol) and H_2O (1mL) were added to a 5 mL tube. The mixture was stirred at 45 °C for 30 min and then extracted with DCM (3 × 1 mL), the combined organic layers were dried over Na_2SO_4, filtered and evaporated under vaccum. The residue was analyzed by ^{1}H NMR without futher purification. The ^{1}H NMR analysis showed that the ratio of **3a**

to *d*-**3a** was 1.6 :1 when compared with the standard ^{1}H NMR spectrum of 3a, in which the integration of the peak at 3.82 ppm was 0.62 instead of 1.

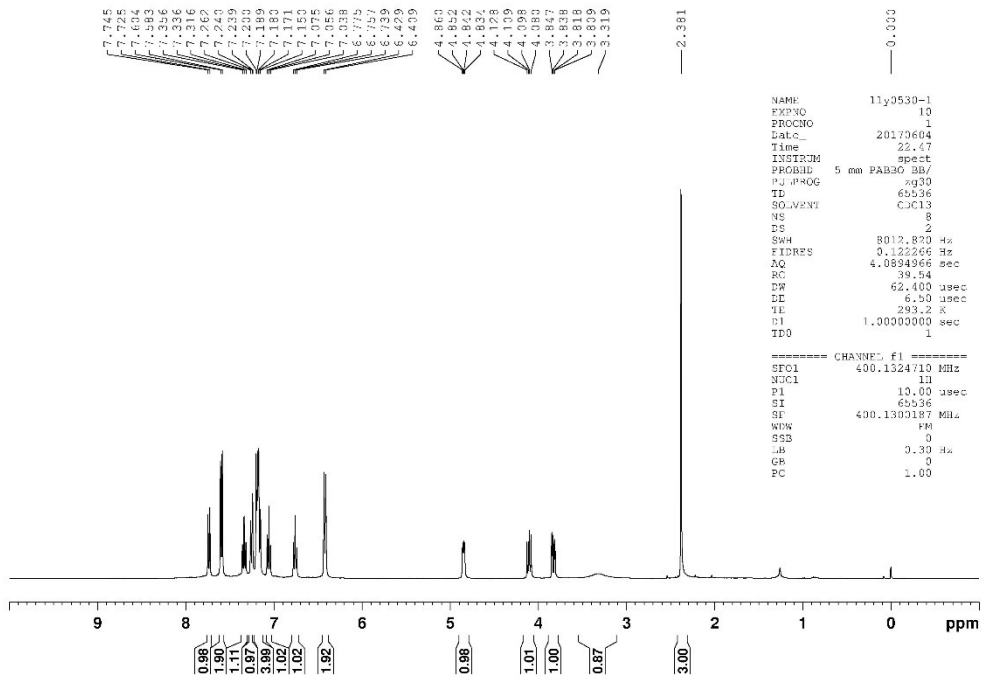


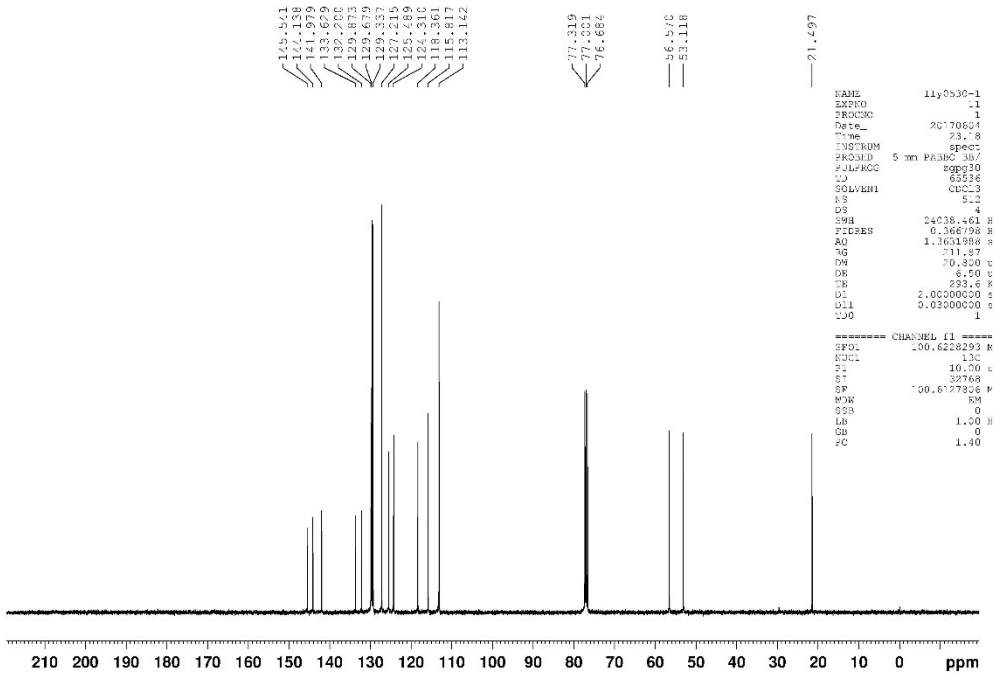
5. References

1. *Green Chem.*, **2017**, *19*, 2076-2079.

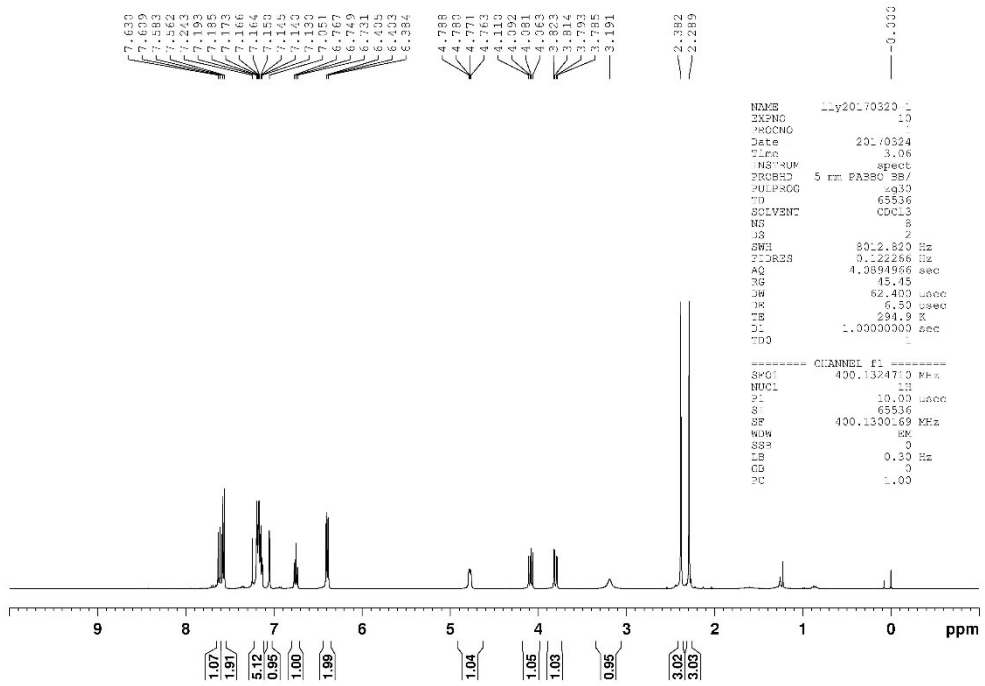
6. NMR spectra of products

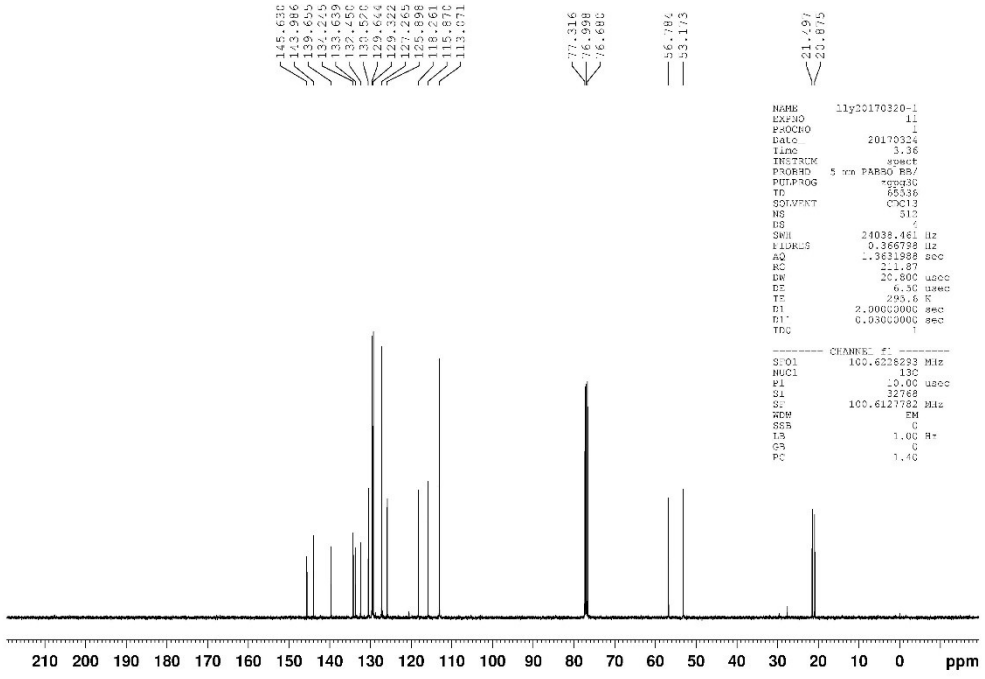
N-phenyl-1-tosylindolin-3-amine (3a)



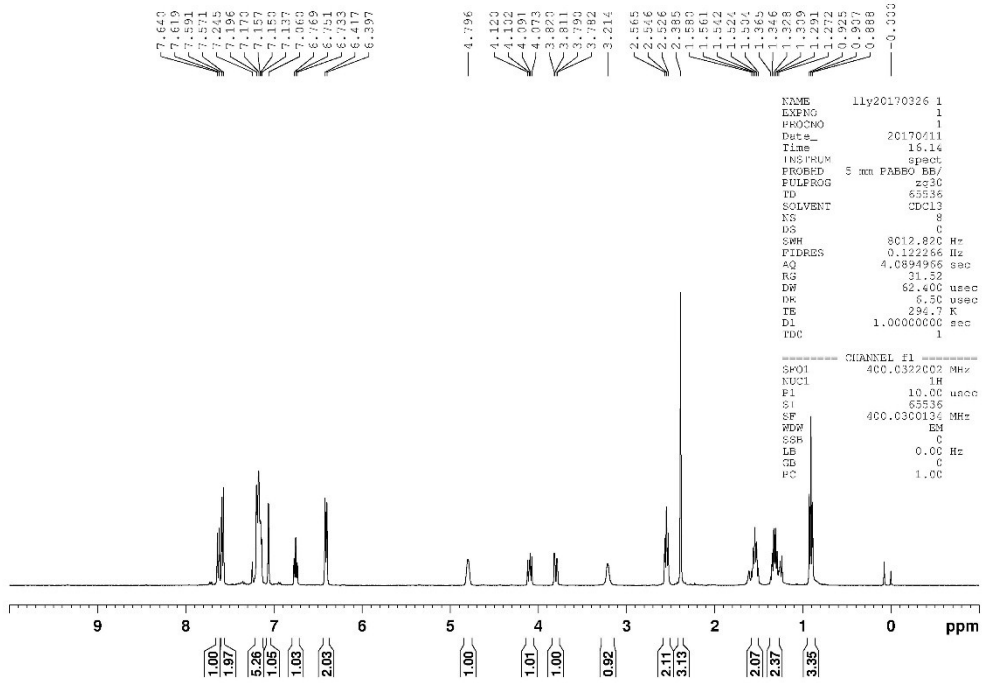


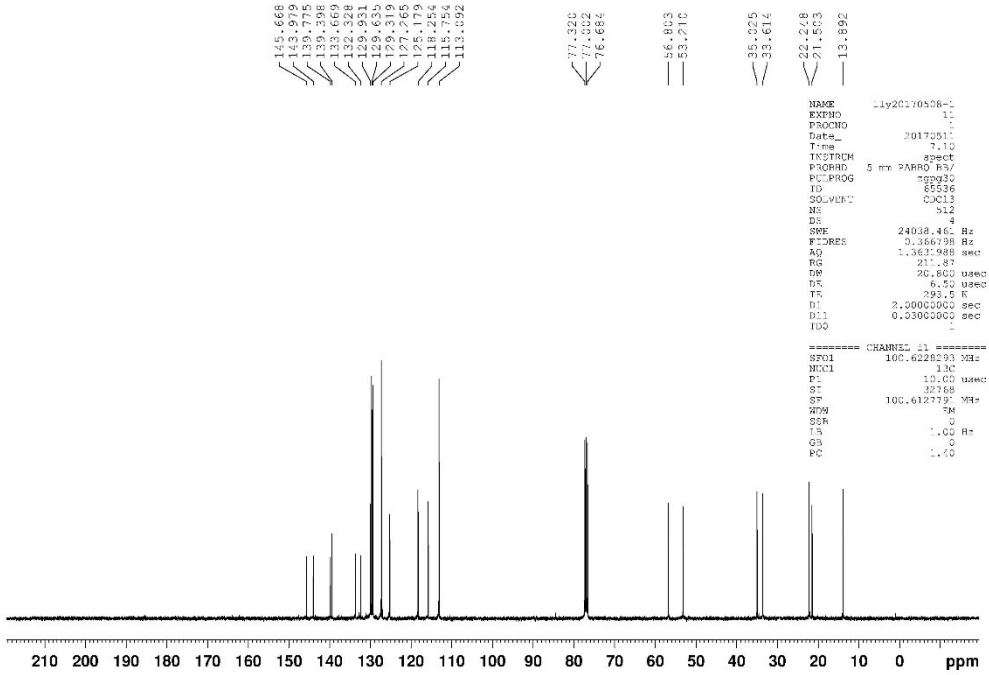
5-methyl-*N*-phenyl-1-tosylindolin-3-amine (3b)



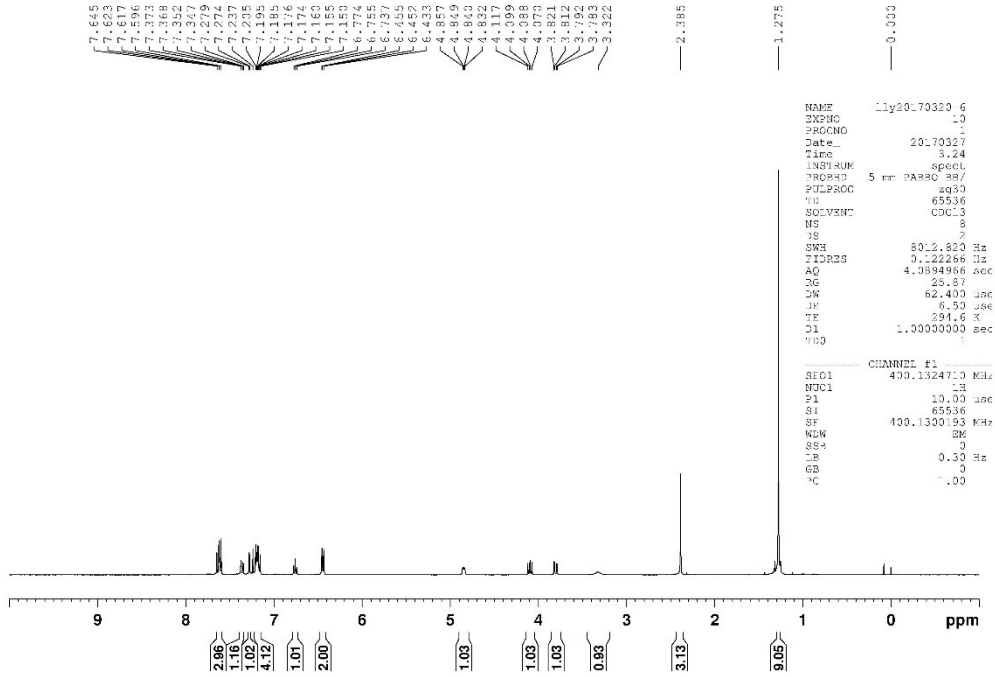


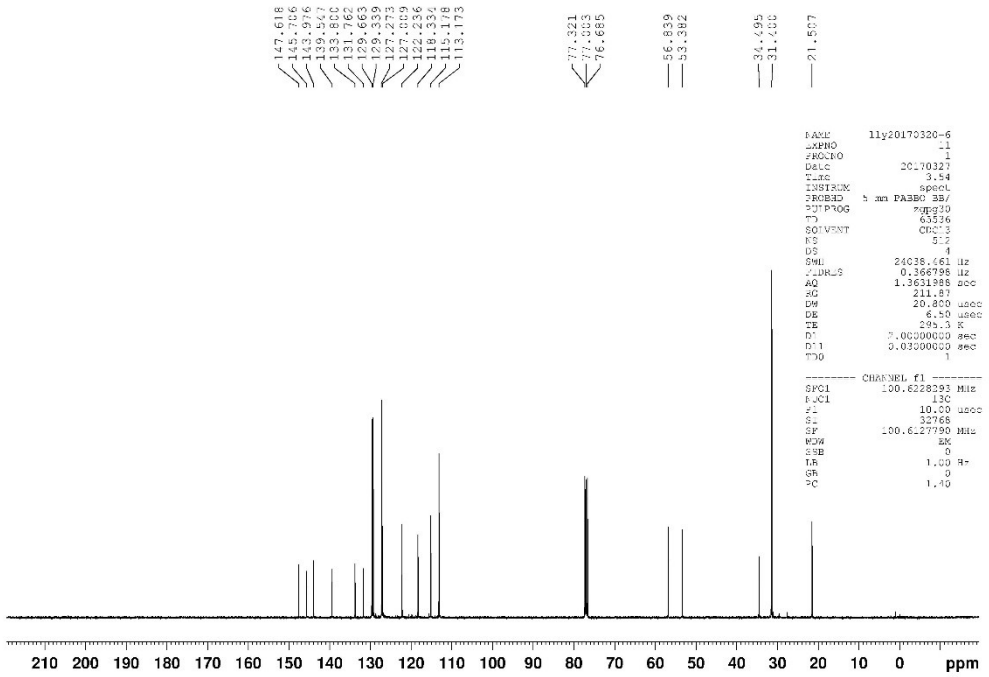
5-butyl-*N*-phenyl-1-tosylindolin-3-amine (3c)



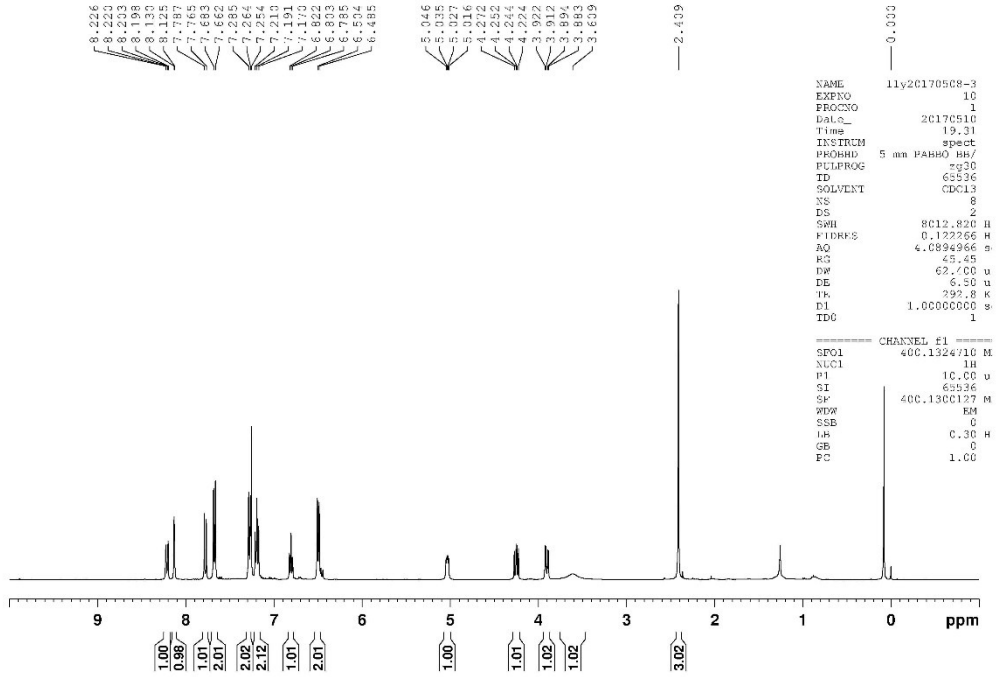


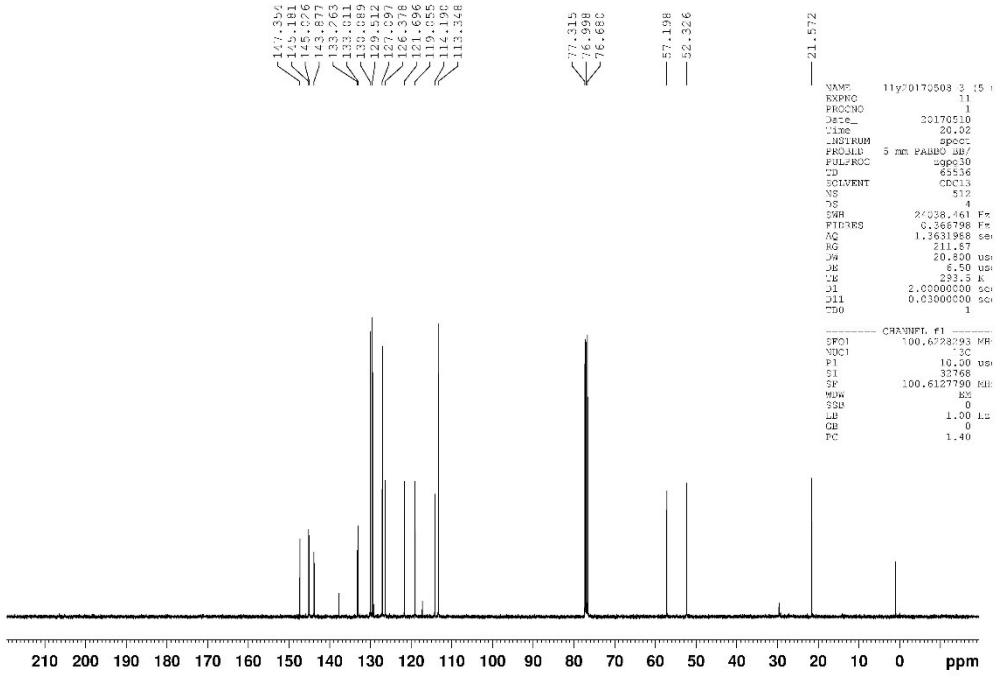
5-(tert-butyl)-*N*-phenyl-1-tosylindolin-3-amine (3d)



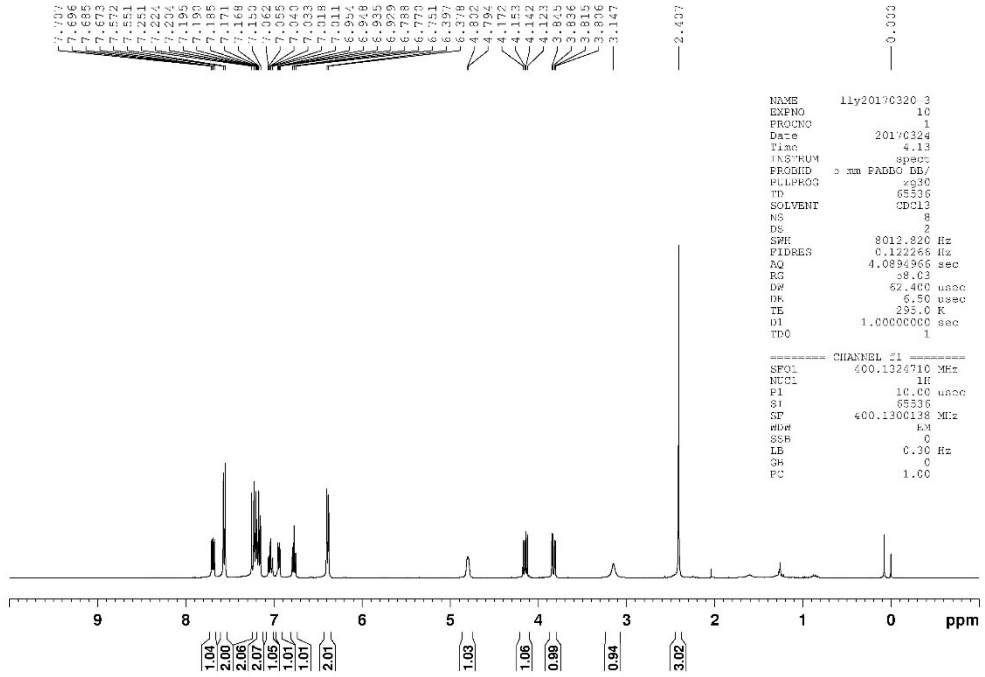


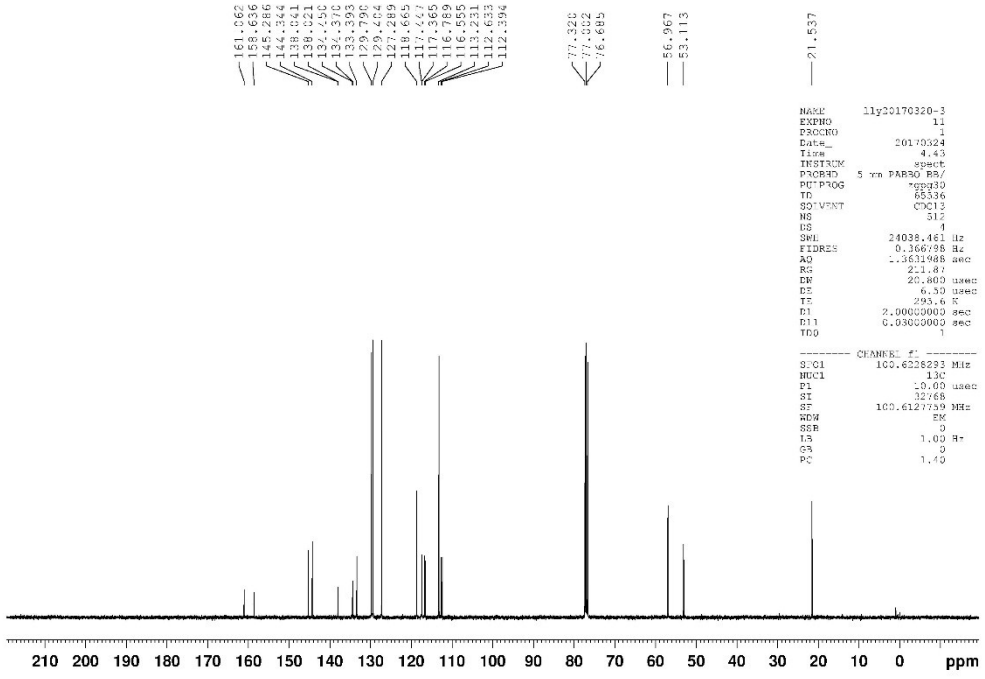
5-nitro-*N*-phenyl-1-tosylindolin-3-amine (3e)

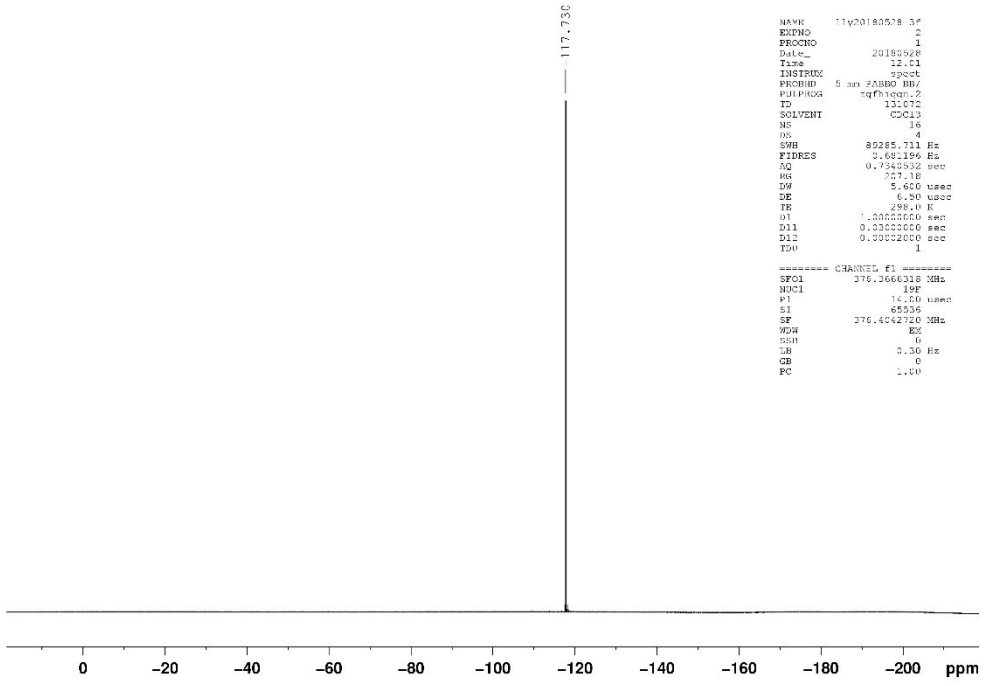




5-fluoro-*N*-phenyl-1-tosylindolin-3-amine (3f)



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LB 0.30 Hz
GB 0
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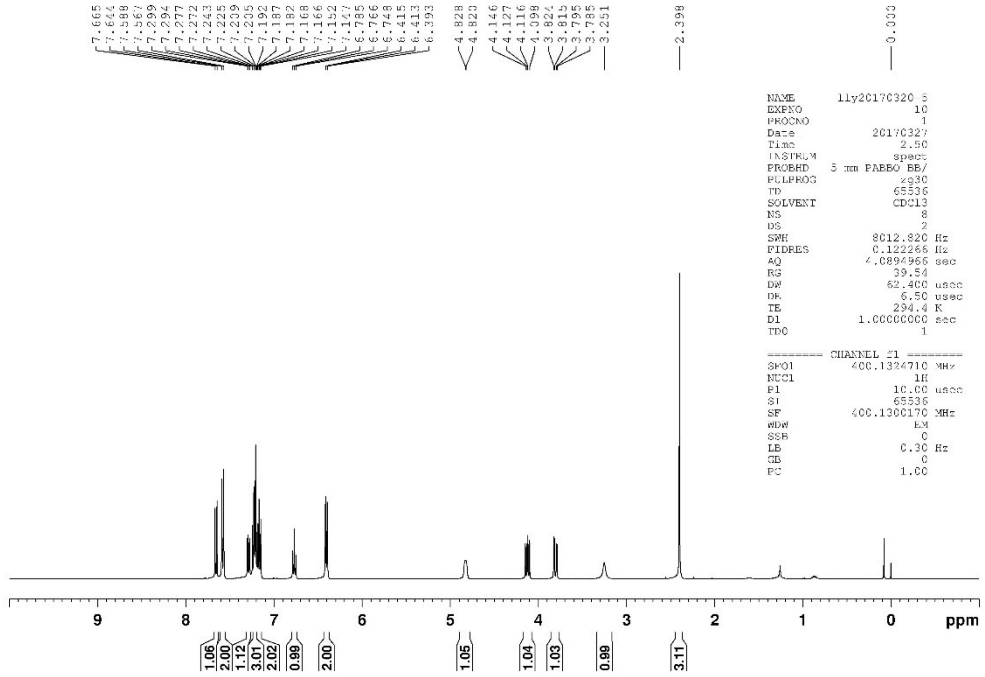
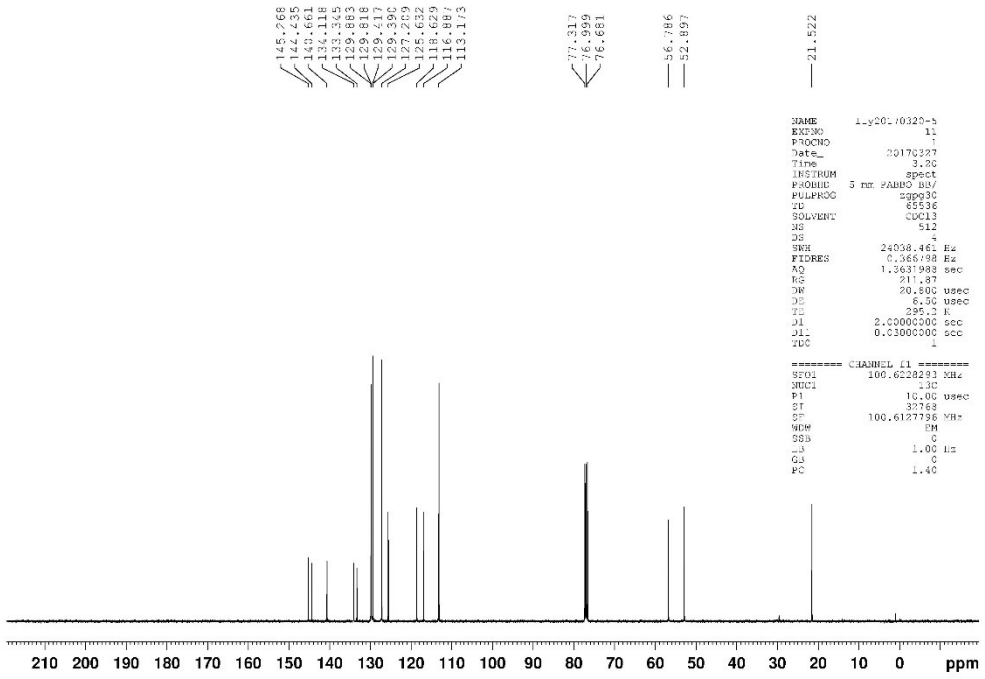
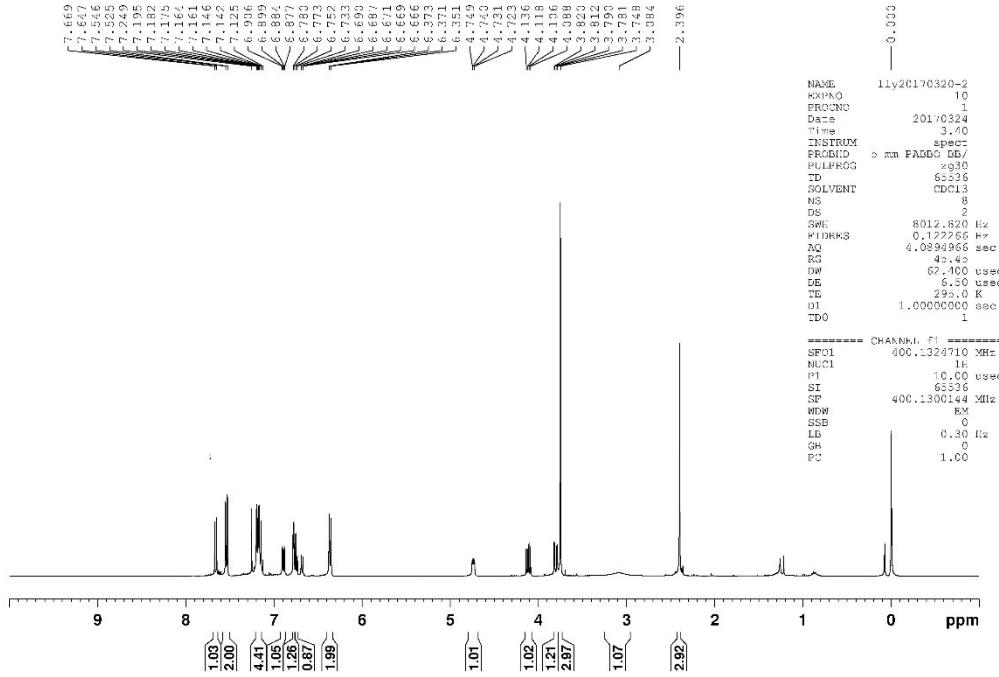
ppm

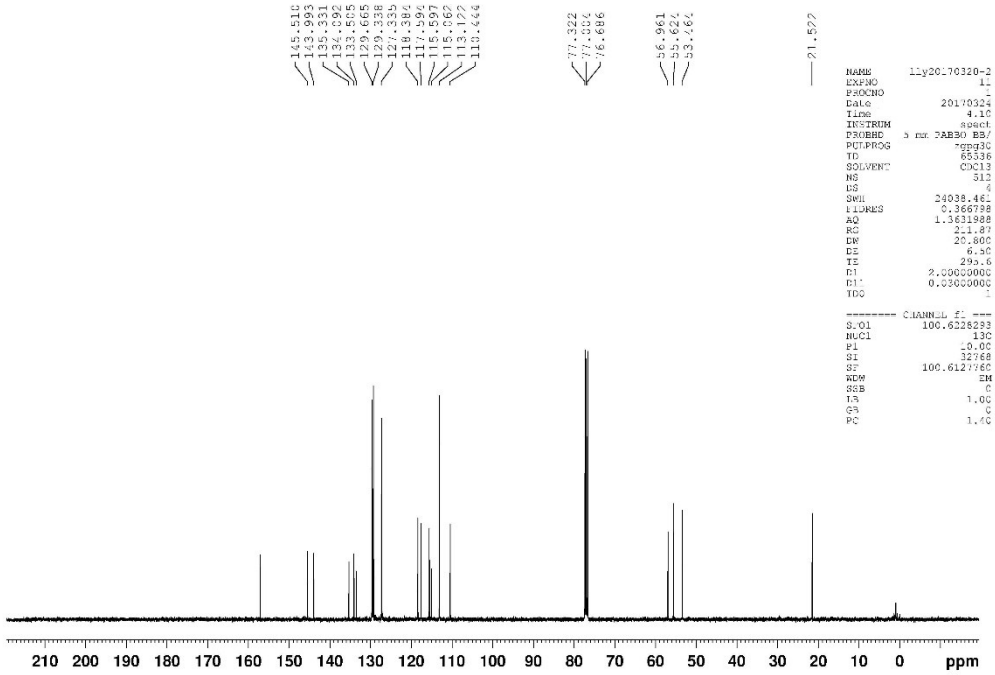
5-chloro-*N*-phenyl-1-tosylindolin-3-amine (3g)



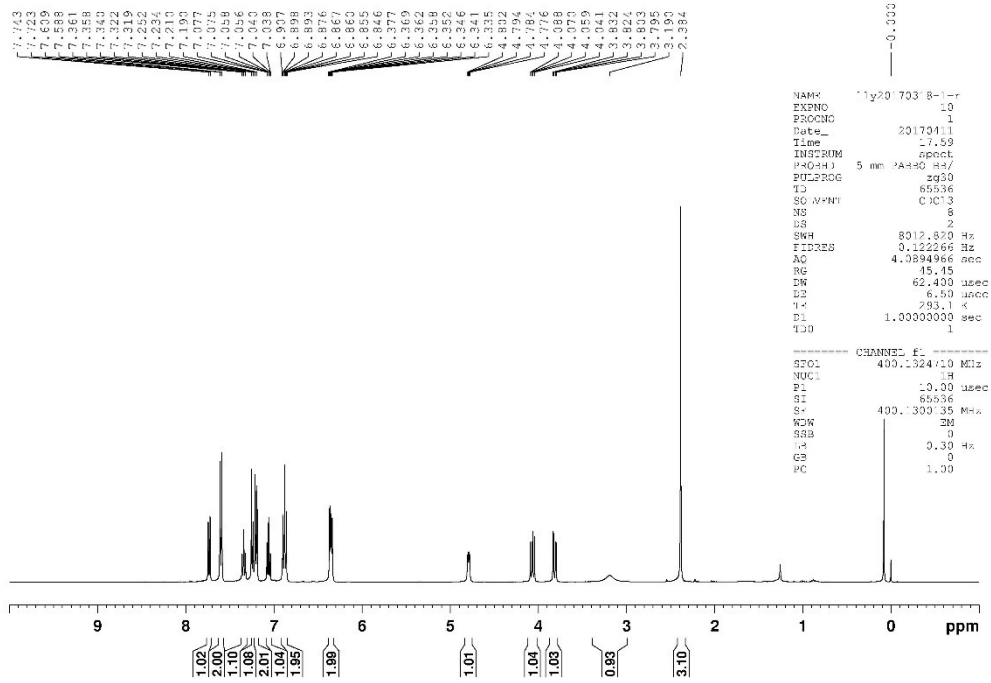


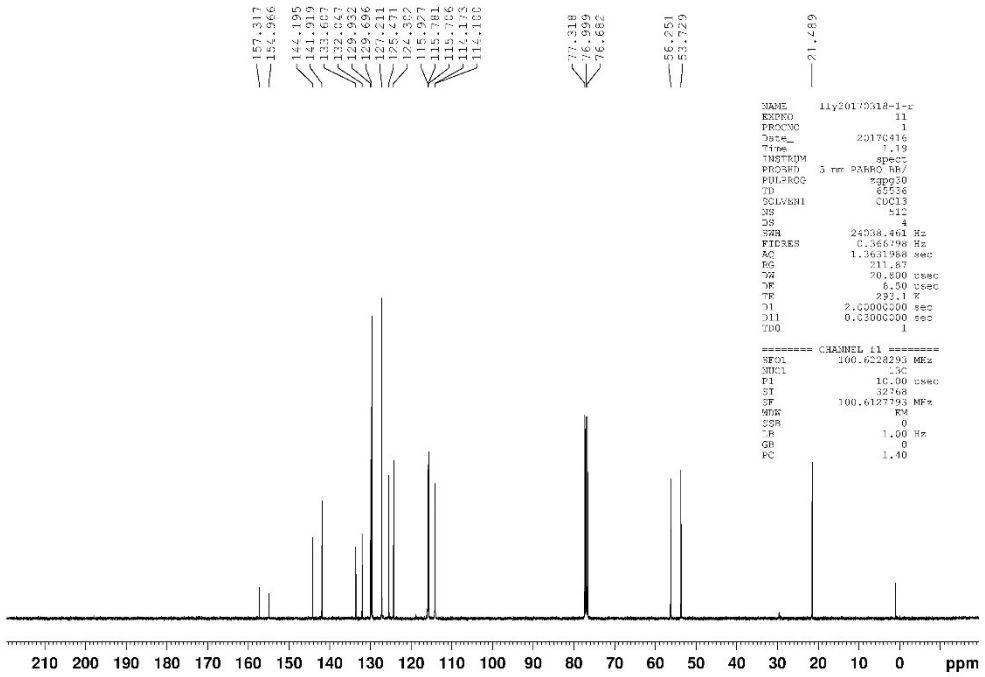
5-methoxy-*N*-phenyl-1-tosylindolin-3-amine (3h)

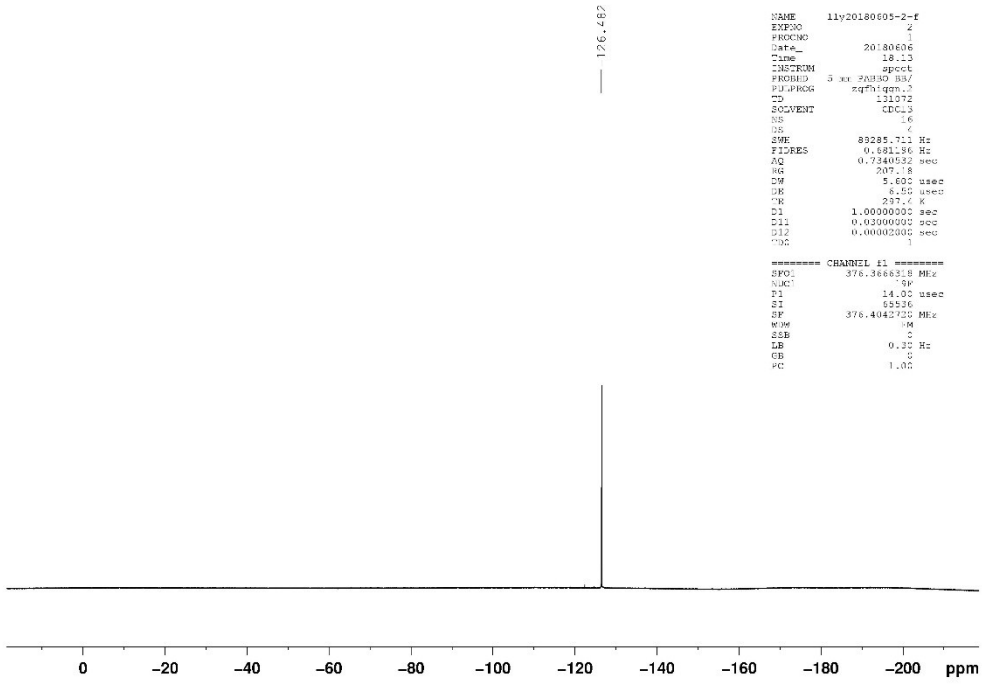




N-(4-fluorophenyl)-1-tosylindolin-3-amine (3i)



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PROCNO 1
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Time 18.13
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TD 131072
SOLVENT CDCl3
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DS 2
SWH 88285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 207.18
DW 5.600 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.3666318 MHz
NUC1 19F
P1 14.00 usec
SI 65536
SF 376.4042720 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0
-20
-40
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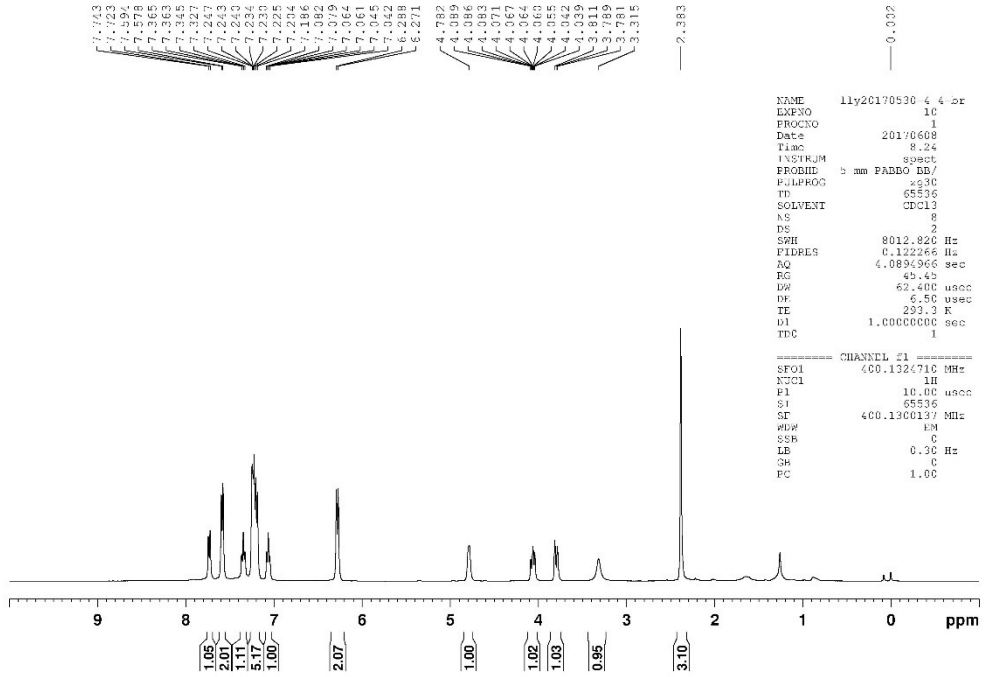
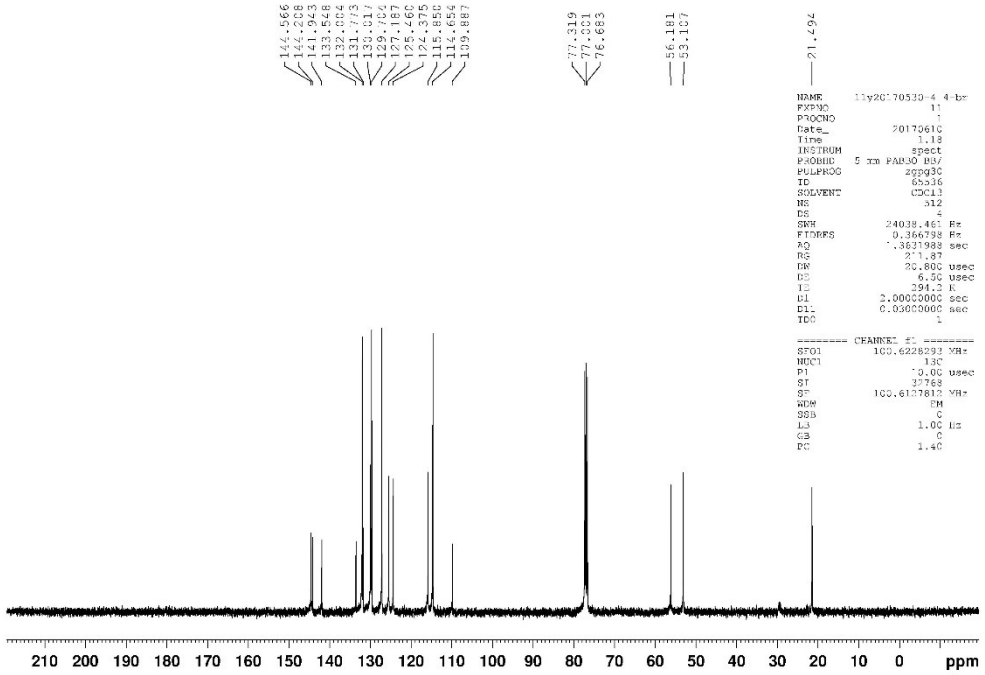
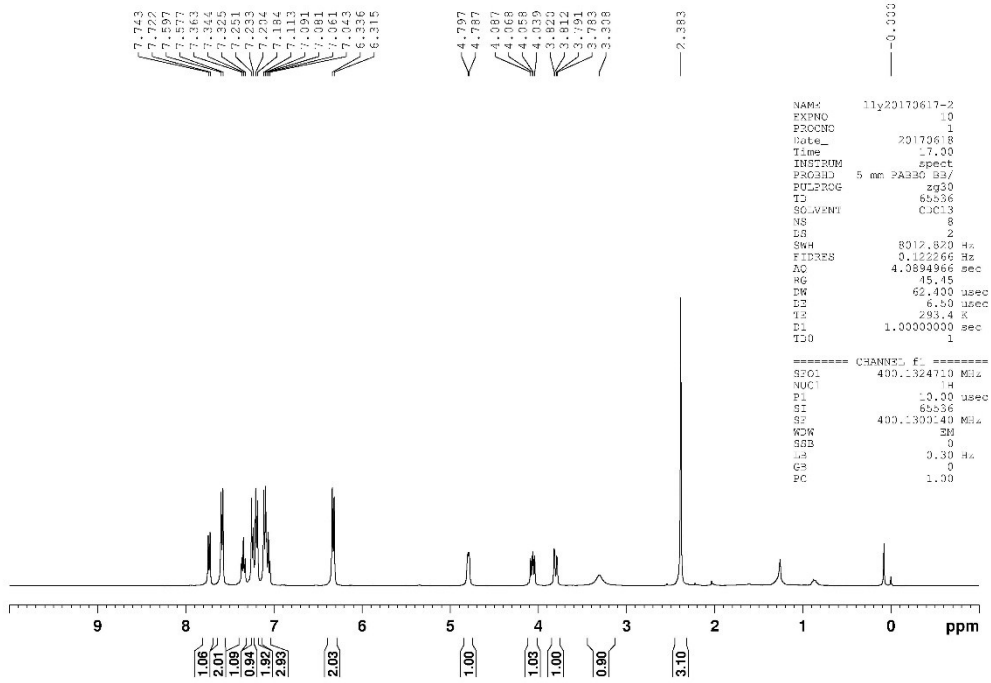
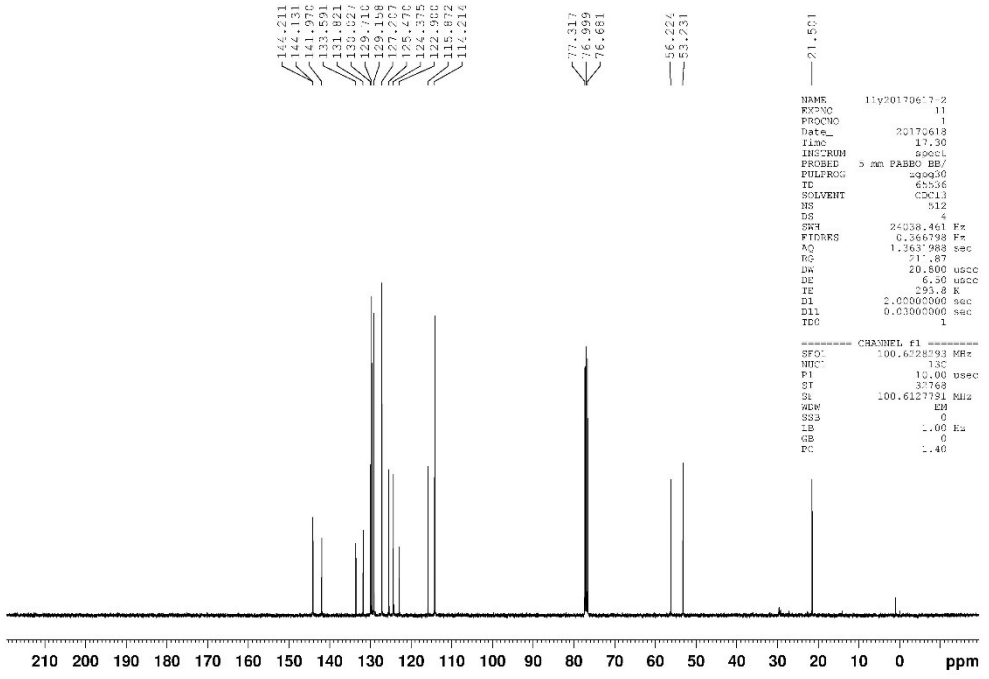
***N*-(4-bromophenyl)-1-tosylindolin-3-amine (3j)**



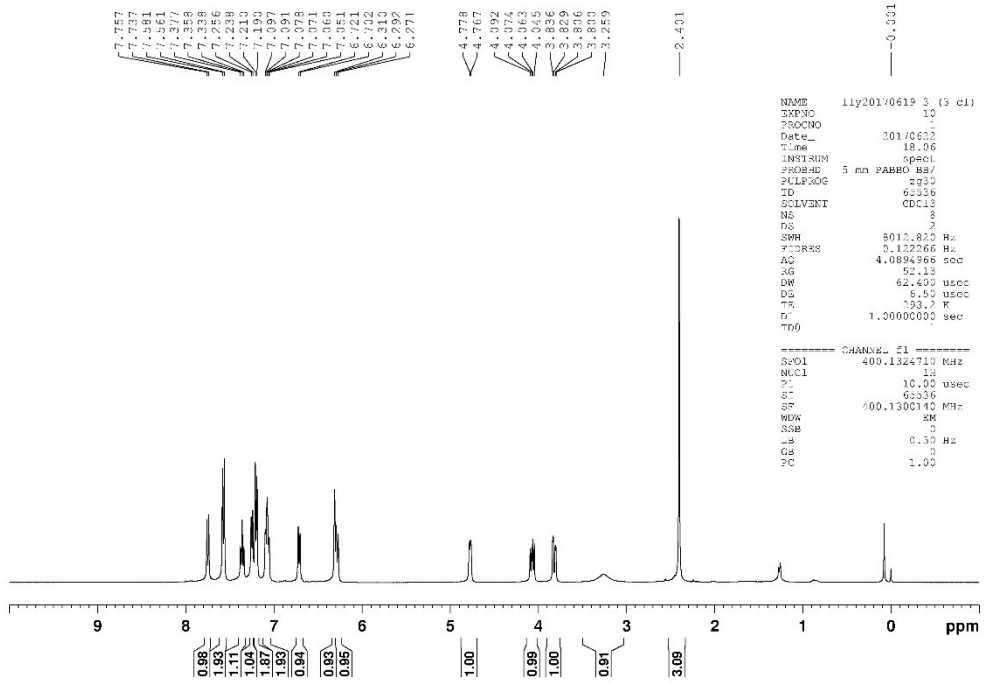


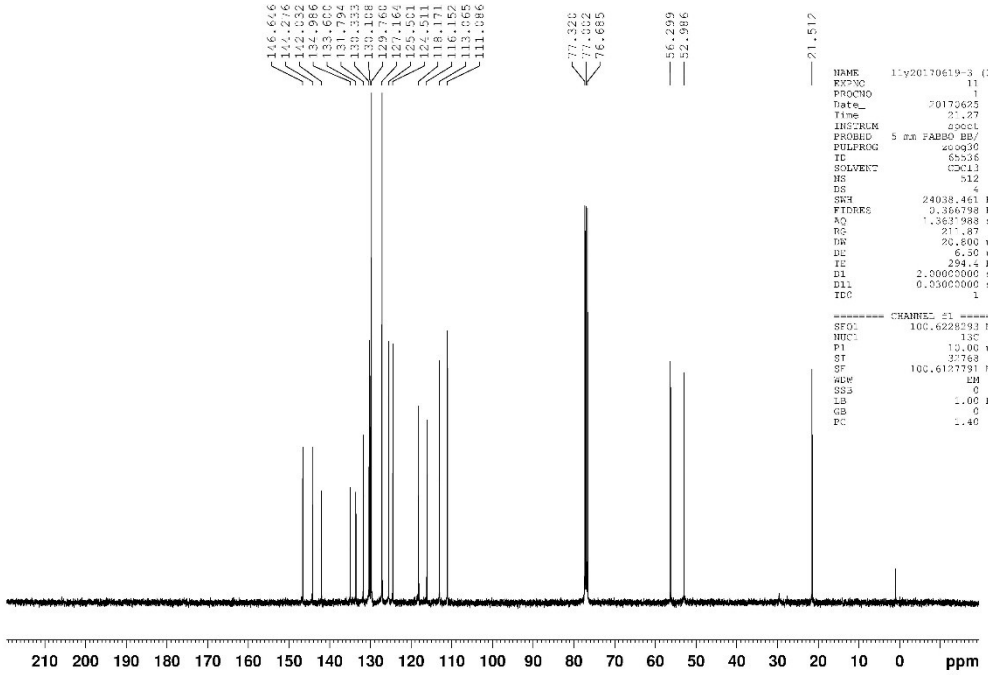
***N*-(4-chlorophenyl)-1-tosylindolin-3-amine (3k)**



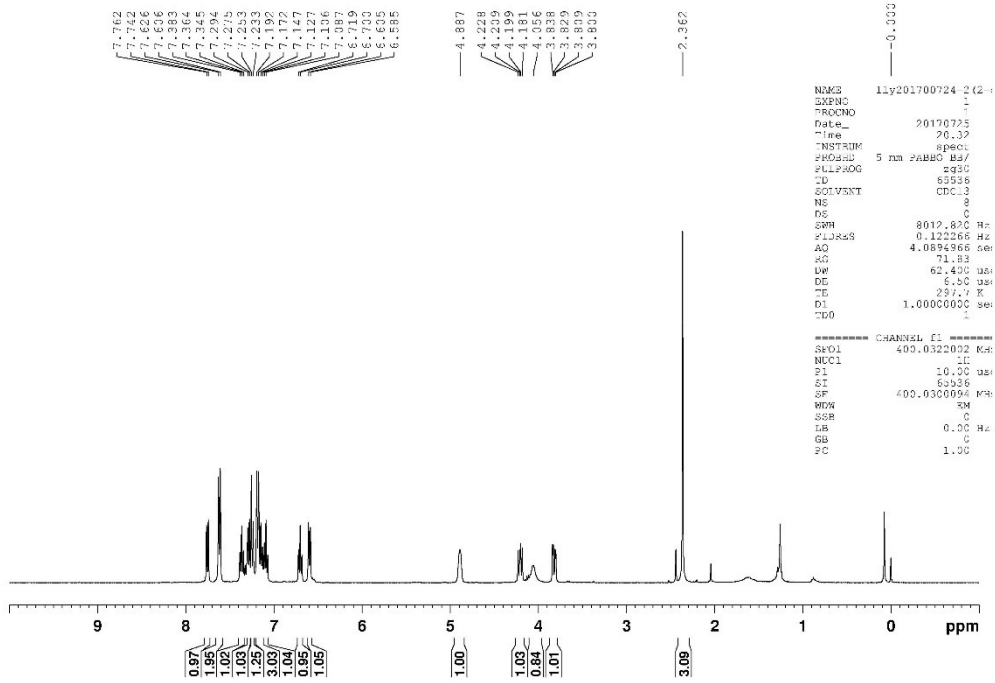


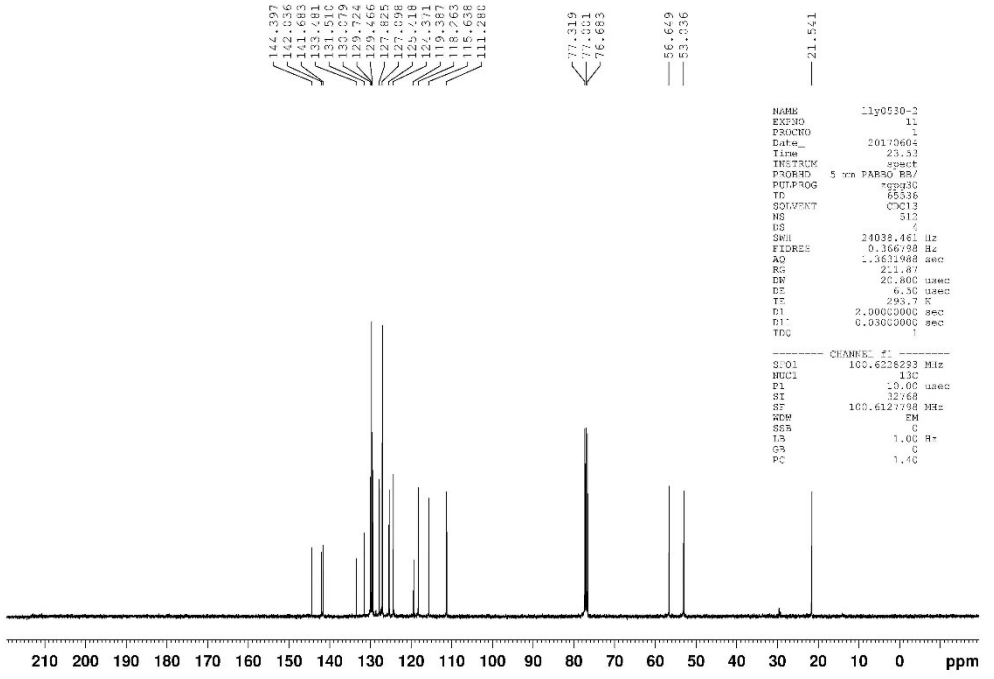
***N*-(3-chlorophenyl)-1-tosylindolin-3-amine (3l)**





***N*-(2-chlorophenyl)-1-tosylindolin-3-amine (3m)**





N-(4-methoxyphenyl)-1-tosylindolin-3-amine (3n)

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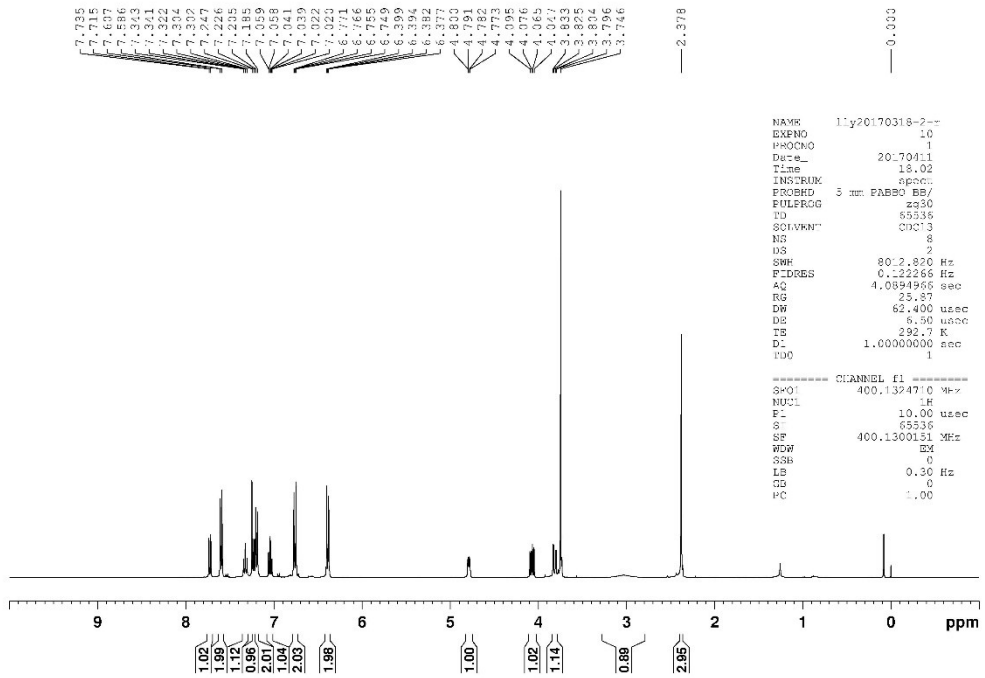
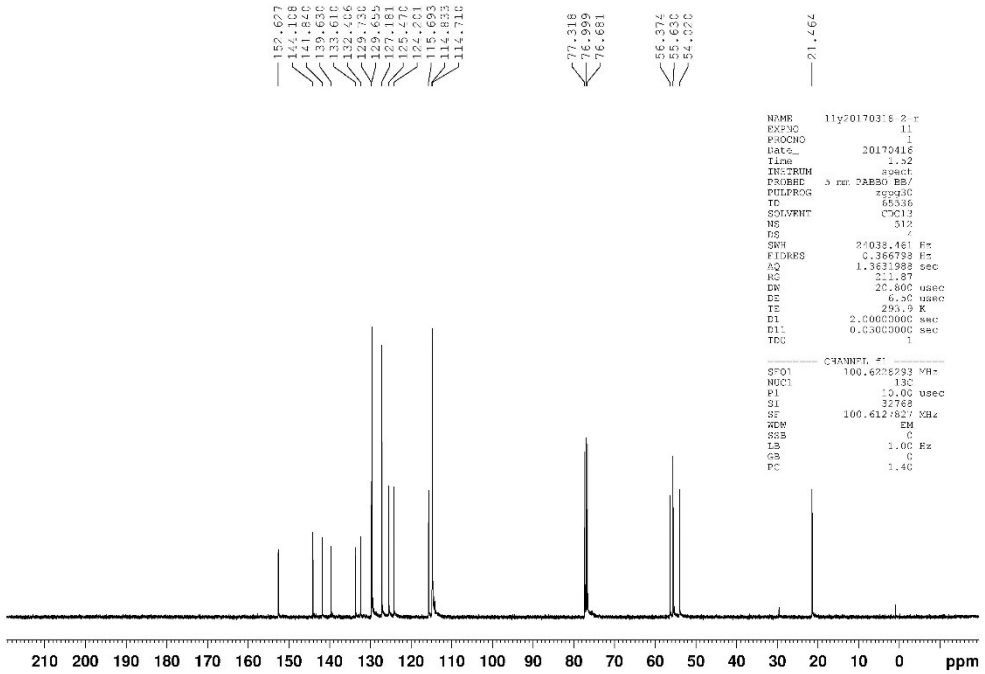
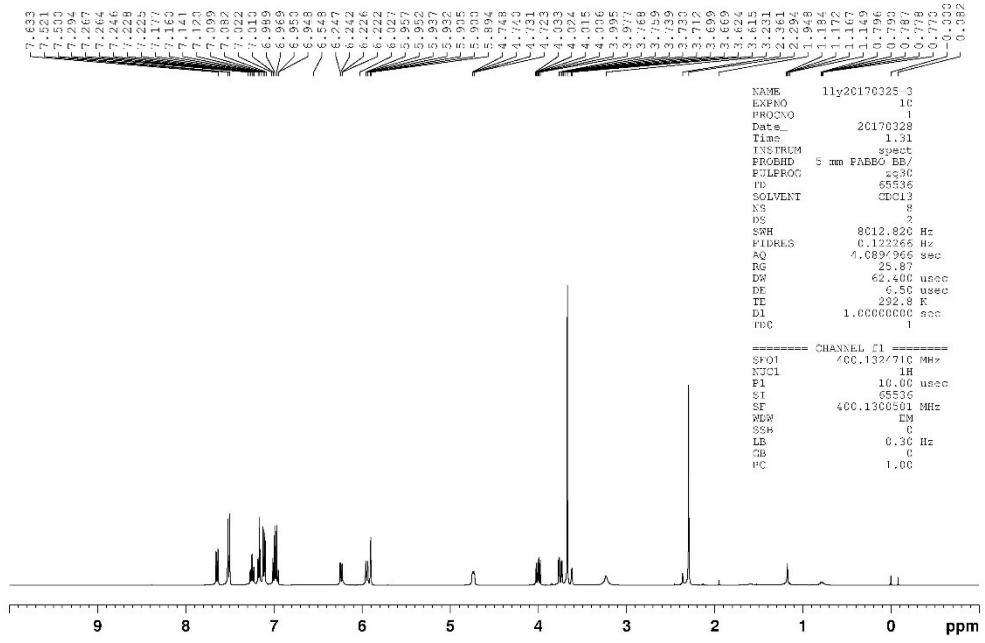
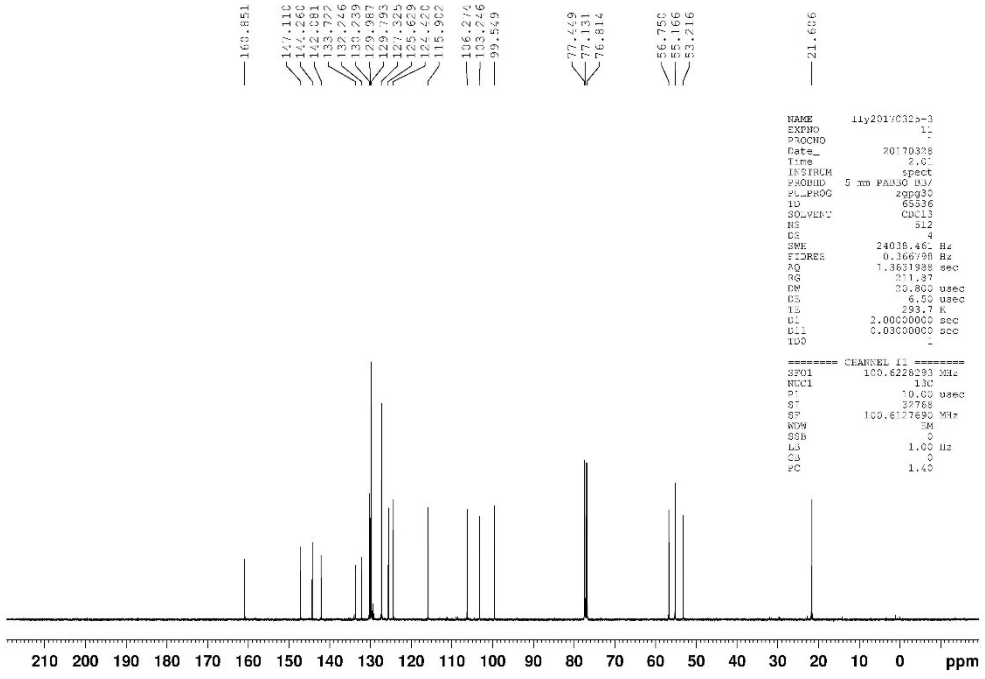


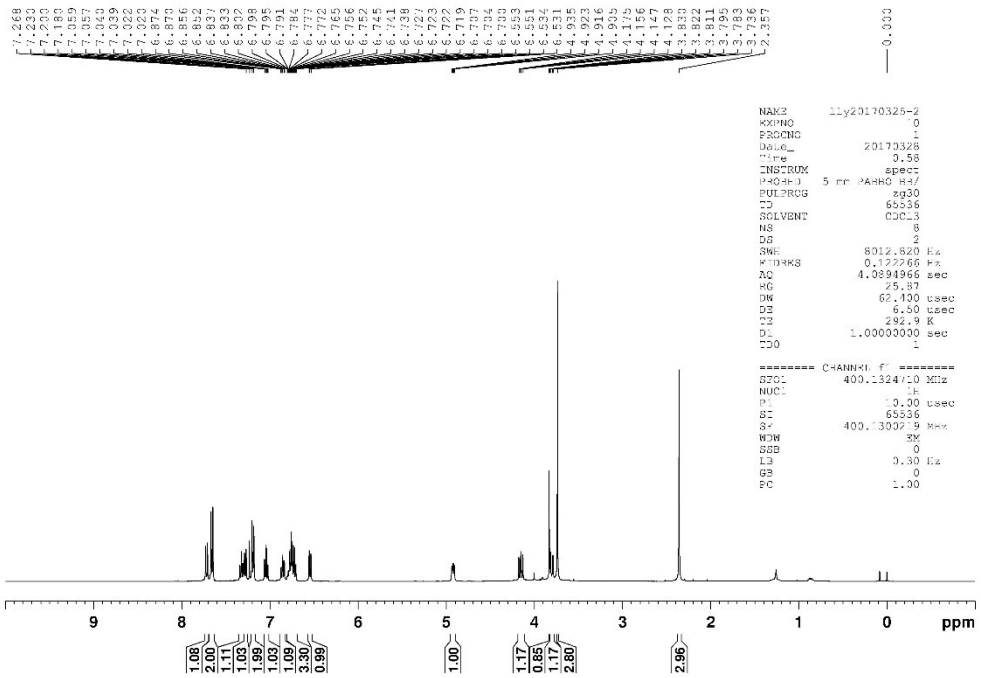


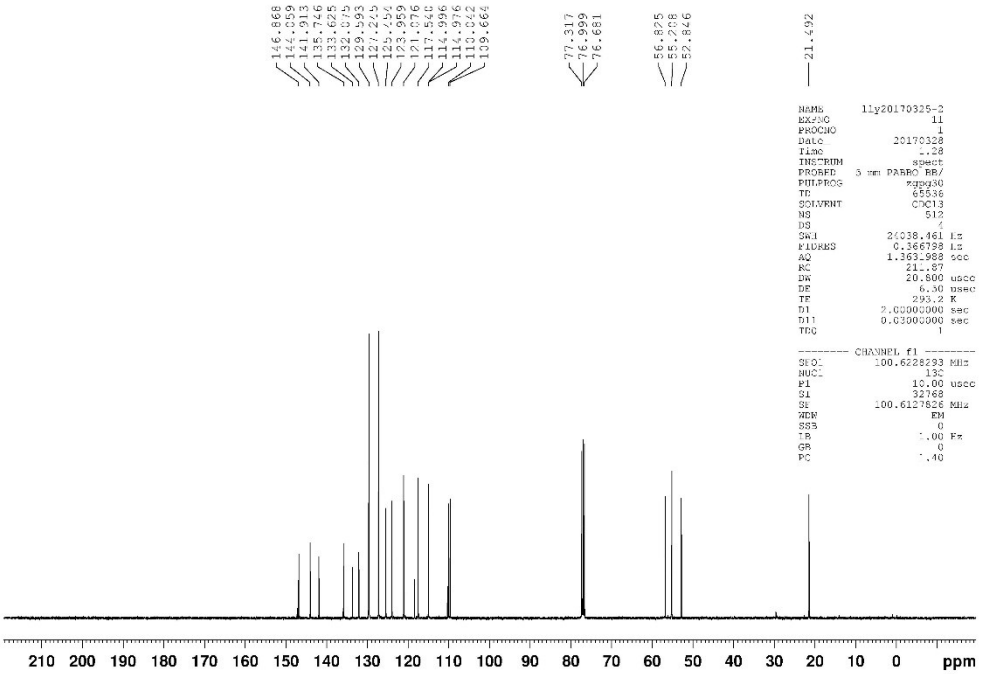
***N*-(3-methoxyphenyl)-1-tosylindolin-3-amine (3o)**



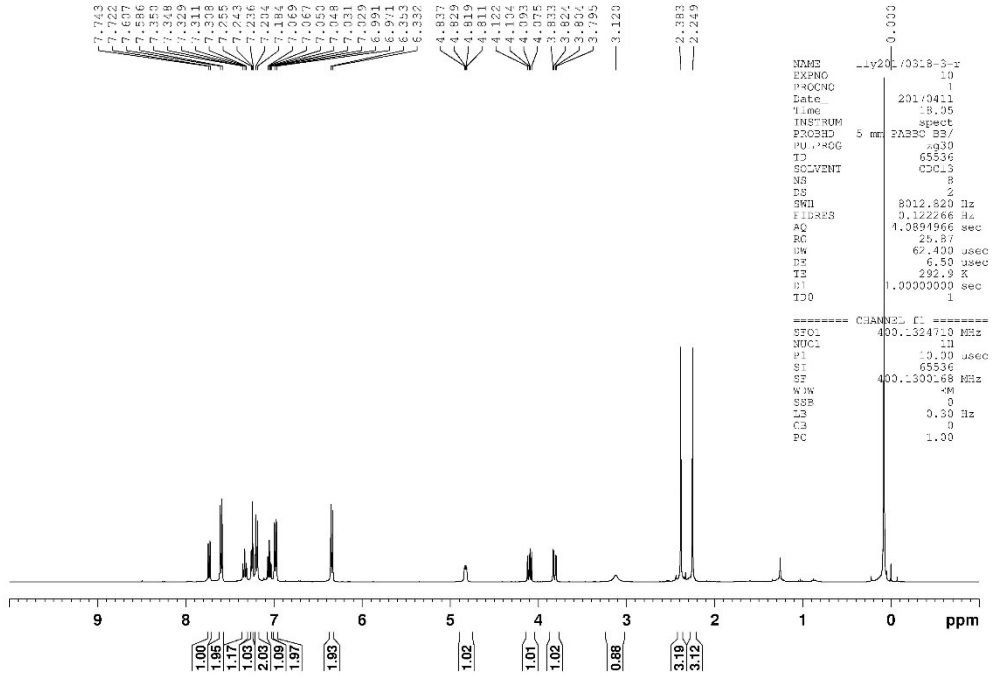


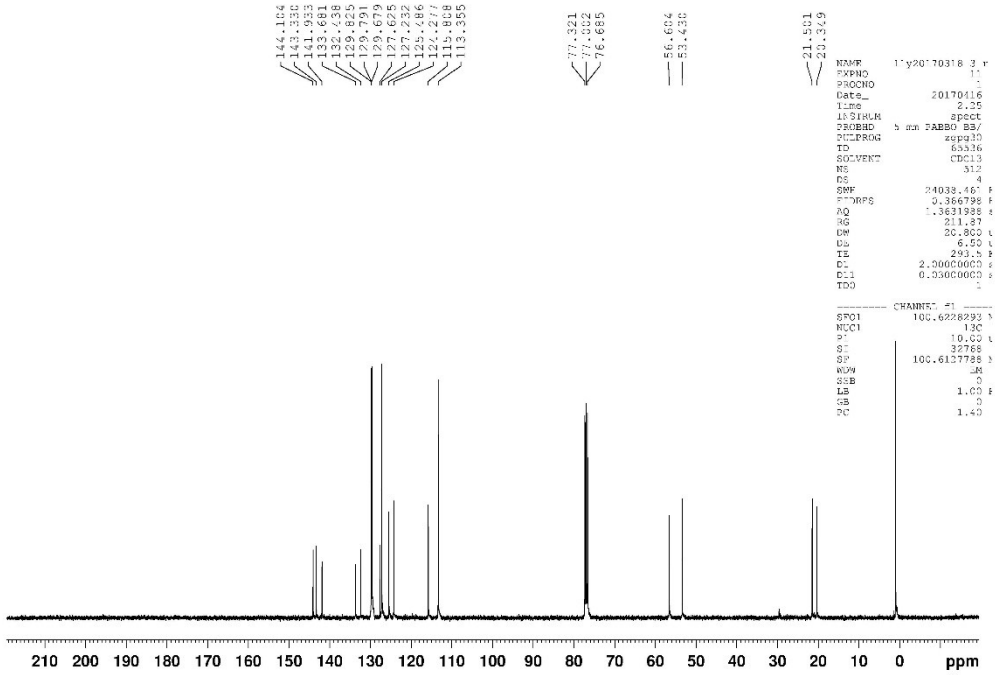
***N*-(2-methoxyphenyl)-1-tosylindolin-3-amine (3p)**



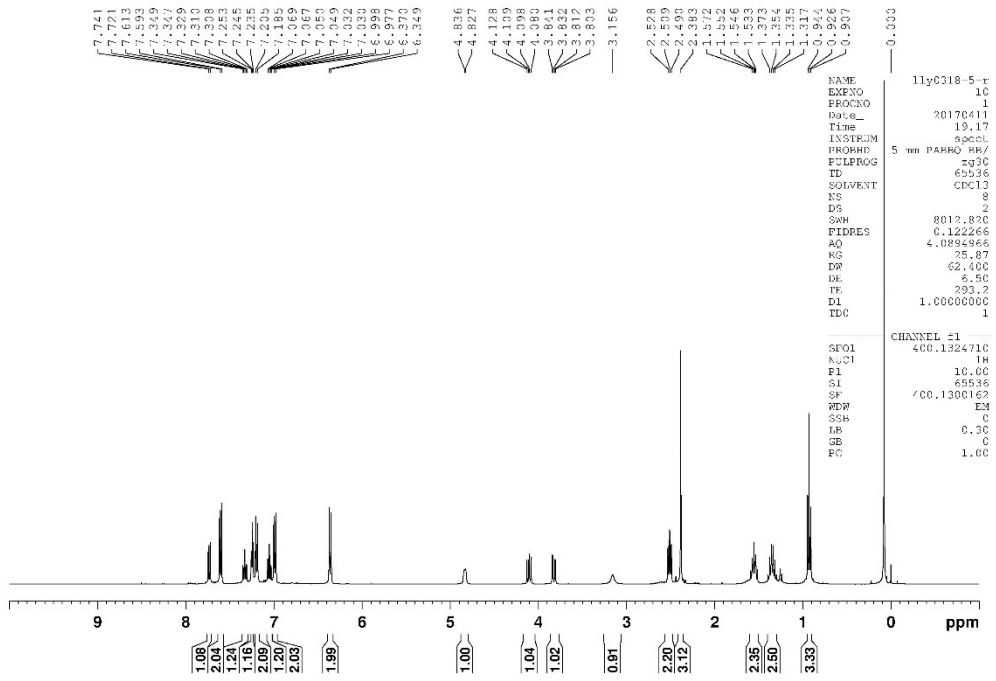


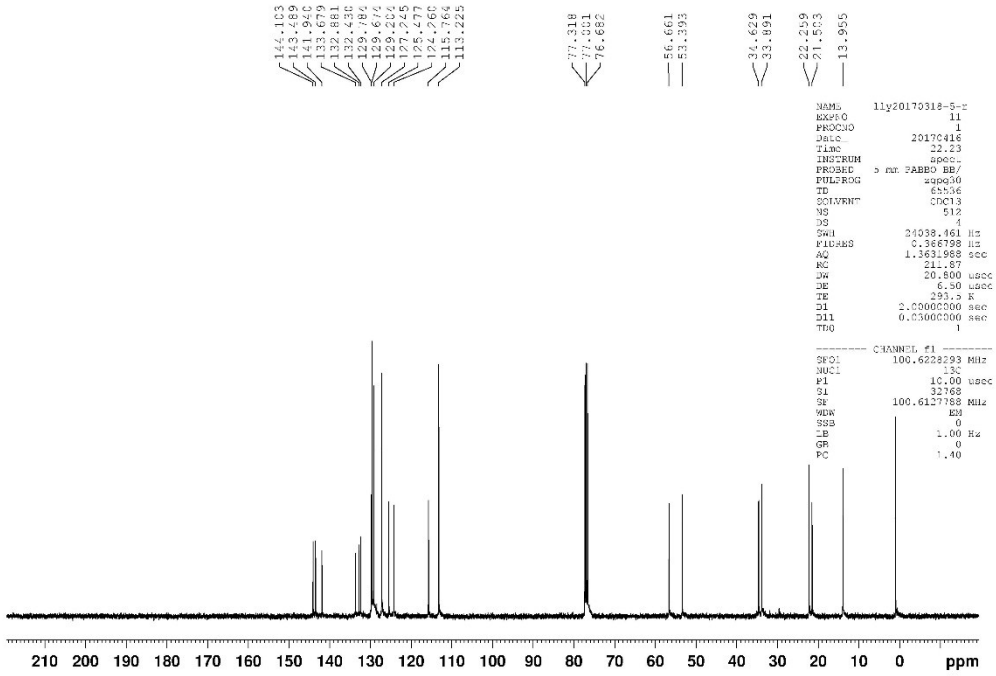
***N*-(p-tolyl)-1-tosylindolin-3-amine (3q)**



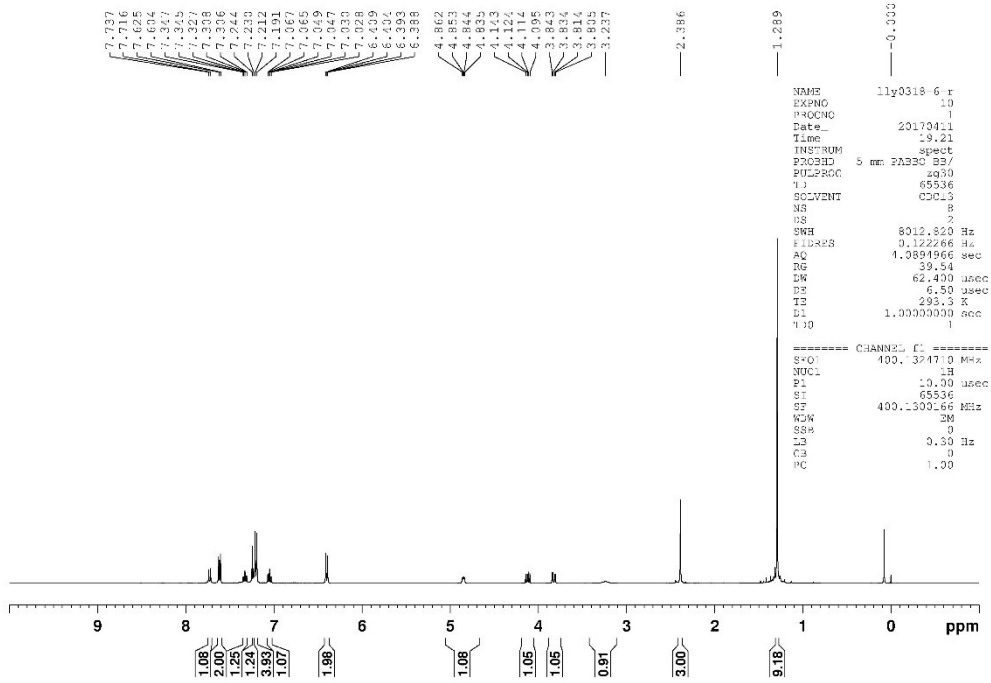


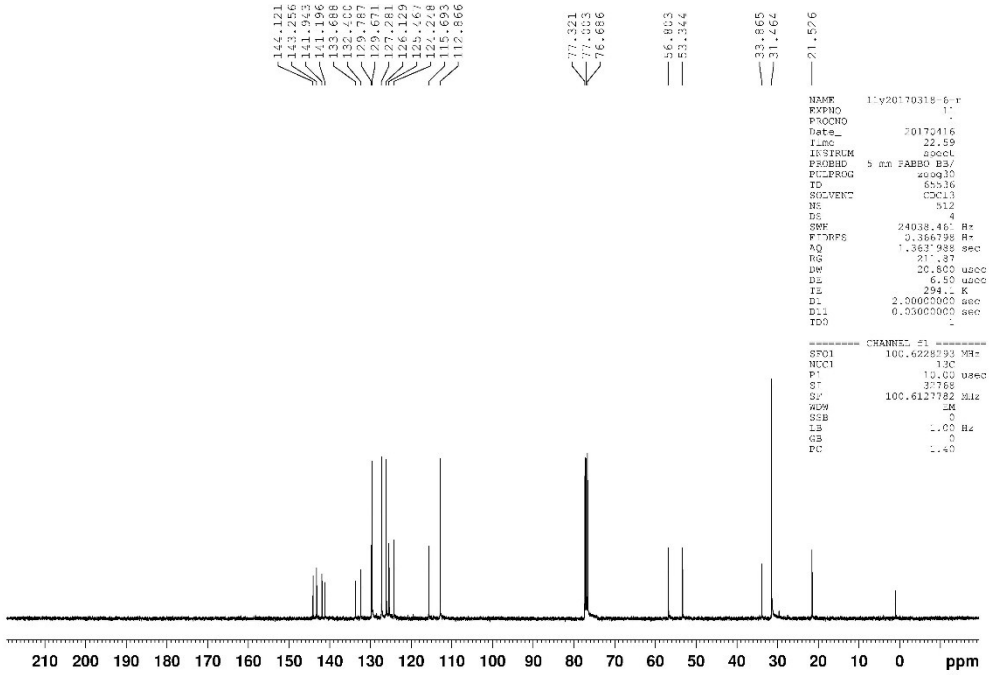
***N*-(4-butylphenyl)-1-tosylindolin-3-amine (3r)**



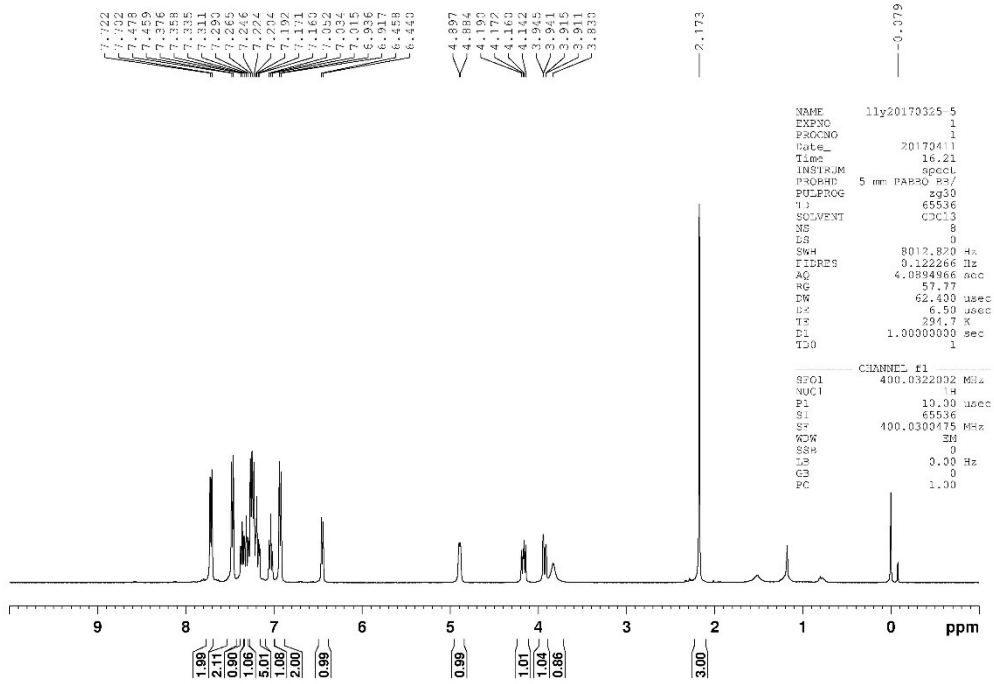


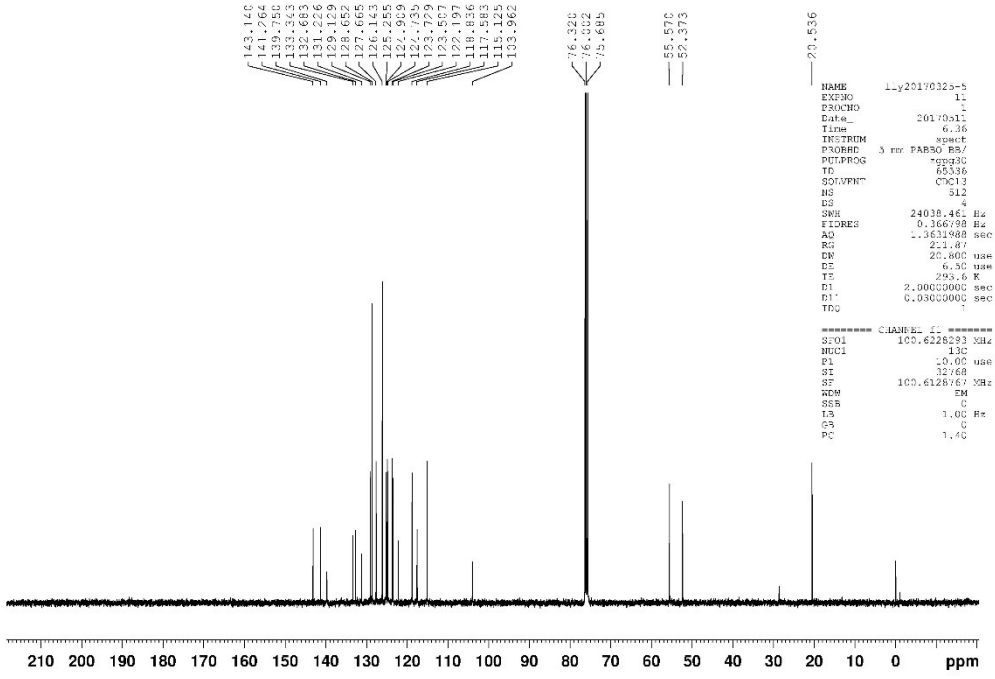
***N*-(4-(tert-butyl)phenyl)-1-tosylindolin-3-amine (3s)**



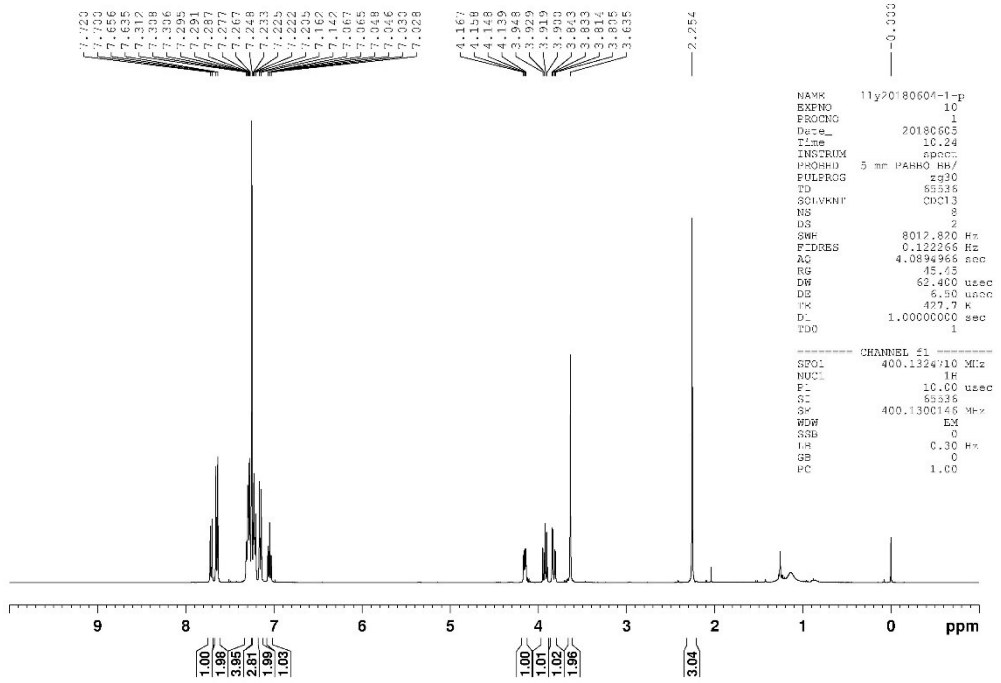


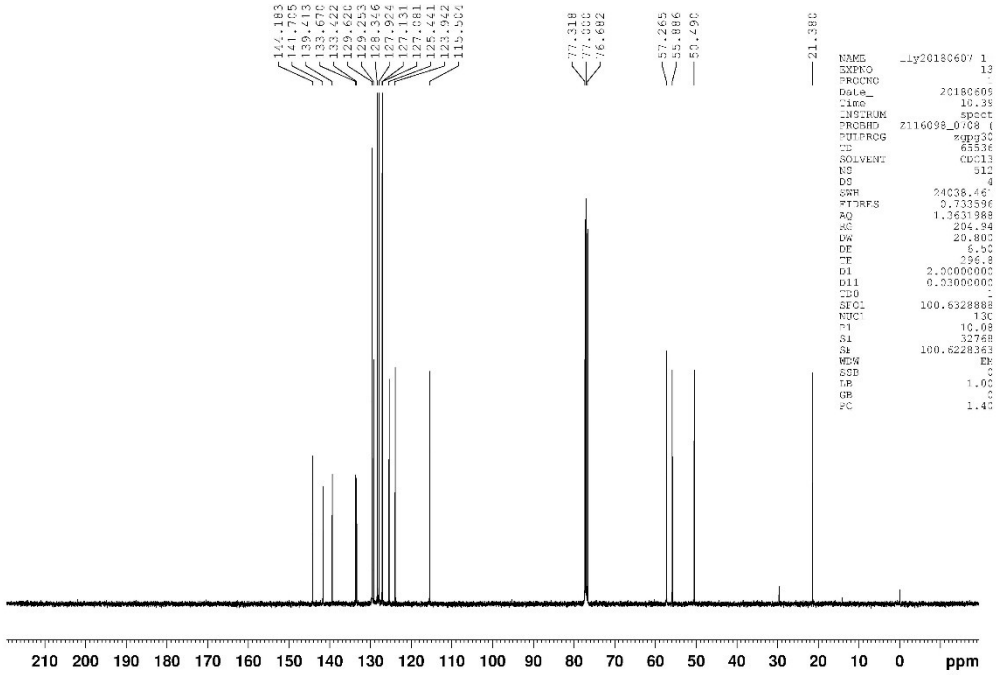
***N*-(naphthalen-1-yl)-1-tosylindolin-3-amine (3t)**





***N*-benzyl-1-tosylindolin-3-amine (3u)**





***N*-phenethyl-1-tosylindolin-3-amine (3v)**