Electronic Supplementary Material (ESI) for Chemical Communications

Iodine-mediated Regioselective C2-Amination of Indoles and Consice Total Synthesis of (±)-Folicanthine

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Table of Contents

General Remarks

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 400 MHz in $CDCl_3$. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All compounds were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Room temperature is 20–25°C. Commercially available reagents and solvents were used without further purification.

Experimental Section

General Procedure A: Starting materials 1a−1r were prepared by methylation, benzylation, or allylation of the corresponding indoles according to the literature procedure.[1] Starting materials 2a−2r were prepared by tosylation of the corresponding anilines according to the literature procedure[2]

A mixture of indole derivative (0.5 mmol) **1**, Cs_2CO_3 (325 mg, 1 mmol), *N*-tosylbenzenamine derivative (1.0 mmol) **2**, I_2 (254 mg, 1mmol) and acetonitrile (CH_3CN) (2.5 mL) was stirred at room temperature under air for 3 h. The reaction was quenched with a saturation solution of $Na_2S_2O_3$ (5 mL) and then extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The remains was purified the mixture of petroleum ether and ethyl acetate as eluent to afford of the corresponding product **3** 42-90% yields.

Characterization Data of 3a-3r

1-methyl-N-p-tolyl-N-tosyl-1H-indol-2-amine ***3a***: Compound **3a** was isolated in 84% yield as a white solid following the general procedure A. Reaction time: 3h. mp: 141-145□; 1H NMR (400 MHz, CDCl3, TMS) δ 7.55 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8 Hz, 1H), 7.22-7.28 (m, 6H), 7.07-7.11 (m, 3H), 6.12 (s, 1H), 3.76 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H); 13C NMR (100 MHz, CDCl3, TMS) δ 144.0, 137.7, 137.6, 135.4, 134.9, 134.7, 129.7, 129.3, 128.4, 127.7, 125.8, 122.5, 120.9, 119.8, 109.8, 99.4, 29.0, 21.6, 21.0; HRMS (ESI): calc for $C_{23}H_{22}N_2O_2S$ $[M+1]^+$: 391.1475 found: 391.1471; IR (neat, cm-1): 3413 , 2924, 1383, 1357, 1165, 667.

1-methyl-N-phenyl-N-tosyl-1H-indol-2-amine ***3b:*** Compound **3b** was isolated in 55% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 177-180℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.7.36-7.40 (m, 2H), 7.21-7.32 (m, 7H), 7.06-7.10 (m, 1H), 6.15 (s, 1H), 3.75 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.1, 140.2, 135.5, 135.0, 134.4, 129.4, 129.1, 128.4, 125.8, 122.6, 120.9, 119.9, 109.8, 99.7, 29.0, 21.6; HRMS (ESI): calc for $C_{22}H_{20}N_2O_2S$ $[M+1]^+$: 377.1318 found: 377.1310 IR (neat,

cm^{-1}): 3394 , 2924, 1358, 1166, 752, 665, 565.

1-methyl-N-(3,4-dimethylphenyl)-N-tosyl-1H-indol-2-amine **3c**: Compound **3c** was isolated in 45% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 174-178℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.16-7.27 (m, 5H), 7.05-7.08 (m, 3H), 6.12 (s, 1H), 3.75 (s, 3H), 2.43 (s, 3H,), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.9, 137.9, 137.5, 136.4, 135.7, 134.9, 134.8, 130.1, 129.3, 128.9, 128.4, 125.8, 125.0, 122.5, 120.8, 119.8, 109.7, 99.5, 29.0, 21.6, 19.8, 19.3; HRMS (ESI): calc for $C_{24}H_{24}N_2O_2S$ $[M+1]^+$: 405.1631 found: 405.1635; IR (neat, cm^{-1}): 3404 , 2923, 1384, 1357, 1166, 753, 667.

1-methyl-N-tosyl-N-(4-(trifluoromethoxy)phenyl)-1H-indol-2-amine ***3d*:** Compound **3d** was isolated in 63% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 158-162℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.41-7.45 (m, 2H), 7.12-7.41 (m, 7H), 6.62 (s, 1H), 3.89 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.0, 148.0, 144.5, 138.7, 135.1, 135.0, 133.9, 129.5, 128.8, 128.3, 125.7, 122.9, 121.4, 121.0, 120.1, 109.9; HRMS (ESI): calc for $C_{23}H_{19}N_2O_3F_3S$ $[M+1]^+$:461.1141 found: 461.1146 IR (neat, cm^{-1}): 2927, 1503, 1361, 1263, 1167, 667.

N-(4-chlorophenyl)-1-methyl-N-tosyl-1H-indol-2-amine **3e***:* Compound **3e** was isolated in 67% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 155-158℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50-7.55, (m, 3H), 7.31-7.34 (m, 2H), 7.23-7.28 (m, 6H), 7.08-7.10 (m, 1H), 6.12 (s, 1H), 3.72 (s, 3H), 3.2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.4, 138.7, 135.1, 134.9, 133.9, 133.3, 129.5, 129.2, 128.7, 128.3, 125.7, 122.8, 120.9, 120.0, 29.0, 21.6; HRMS (ESI): calc for $C_{22}H_{19}N_2O_2SCl$ $[M+1]^+$: 411.0929 found: 411.0934; IR (neat, cm^{-1}): 3398 , 2924, 1487, 1359, 1166, 1091, 754, 666.

1, 5-dimethyl-N-p-tolyl-N-tosyl-1H-indol-2-amine **3f*:*** Compound **3f** was isolated in 45% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 78-80℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.22-7.29 (m, 5H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.02 (s,

1H), 3.73 (s, 3H), 2.45 (s, 3H,), 2.40 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.0, 137.7, 137.6, 135.5, 134.6, 133.3, 129.7, 129.3, 129.0, 128.4, 127.6, 125.9, 124.2, 120.4, 109.5, 98.9, 29.0, 21.6, 21.4, 21.0; HRMS (ESI): calc for $C_{24}H_{24}N_2O_2S$ $[M+1]^+$: 405.1631 found: 405.1638 IR (neat, cm^{-1}): 3403 , 2922, 1380, 1356, 1163, 671, 548.

1, 7-dimethyl-N-p-tolyl-N-tosyl-1H-indol-2-amine ***3g***: Compound **3g** was isolated in 42% yield as a white solid following the general procedure **A**. Reaction time: 3h. Mp: 117-120℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, J = 8.4Hz, 2H), 7.25-7.34 (m, 5H), 7.11 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 6.8 Hz, 2H), 6.07 (s, 1H), 4.01 (s, 3H), 2.73 (s, 3H) 2.46 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.0, 137.7, 137.6, 135.5, 134.8, 133.9, 129.7, 129.3, 128.4, 127.6, 126.5, 125.4, 121.5, 119.8, 118.9, 100.0, 31.9, 21.6, 21.0, 20.1; HRMS (ESI): calc for $C_{24}H_{24}N_2O_2S$ $[M+1]^+$: 405.1631 found: 405.1637 IR (neat, cm^{-1}): 3403 , 2919, 2360, 1382, 1164, 666.

5-bromo-1-methyl-N-p-tolyl-N-tosyl-1H-indol-2-amine ***3h:*** Compound **3h** was isolated in 45% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 140-142℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, J = 1.6 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.11-7.32 (m, 8H), 6.05 (s, 1H), 3.75 (s, 3H), 2.47 (s, 3H) 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.0, 137.0, 135.1, 128.4, 127.7, 122.4, 121.0, 120.4, 120.2, 120.1, 119.6, 109.6, 109.4, 107.4, 101.4, 33.0, 31.0; HRMS (ESI): calc for $C_{23}H_{21}N_2O_2SBr$ $[M+1]^+$: 469.0580 found: 469.0574 IR (neat, cm^{-1}): 3395 , 2923, 1384, 1358, 1165, 668.

1, 4-dimethyl-N-p-tolyl-N-tosyl-1H-indol-2-amine Compound ***3i:*** Compound **3i**

was isolated in 57% yield as a colorless liquid following the general procedure **A**. Reaction time: 3h. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8 Hz, 4H), 7.09-7.13 (m, 4H), 6.88 (d, J = 8.0, 1H), 6.13 (s, 1H), 3.74 (s, 3H), 2.44 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.0, 137.7, 137.6, 135.5, 134.7, 134.1, 130.3, 129.7, 129.3, 128.5, 127.6, 125.8, 122.7, 120.0, 107.4, 98.0, 29.2, 21.6, 21.0, 18.6; HRMS (ESI): calc for $C_{24}H_{24}N_2O_2S$ $[M+1]^+$: 405.1631

found: 405.1636 IR (neat, cm^{-1}): 2922 , 1504, 1357, 1166, 761, 665, 596,550.

N-(4-chlorophenyl)-1,3-dimethyl-N-tosyl-1H-indol-2-amine ***3j:*** Compound **3j** was isolated in 88% yield as a white solid following the general procedure **A**. Reaction time: 3h. Mp: 153-157℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.20-7.27 (m, 8H), 7.08-7.12 (m, 1H), 3.67, (s, 3H), 2.41 (s, 3H), 1.83 (s, 3H,); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.4, 139.8, 136.9, 135.0, 131.6, 130.4, 129.7, 129.2, 127.9, 126.5, 125.5, 123.1, 119.4, 119.2, 109.6, 109.0,29.5, 21.5, 8.9 ; HRMS (ESI): calc for $C_{23}H_{21}N_2O_2SCl$ $[M+1]^+$: 425.1085 found: 425.1090 IR (neat, cm^{-1}): 3397 , 2921, 1595, 1359, 1166, 1092, 910, 736, 669, 576, 545.

1,3-dimethyl-N-tosyl-N-(4-(trifluoromethoxy)phenyl)-1H-indol-2-amine ***3k:*** Compound **3k** was isolated in 87% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 132-136℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8 Hz, 1H), 7.28-7.35 (m, 6H), 7.12 (t, 3H), 3.69 (s, 3H), 2.44 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 146.8, 144.5, 139.8, 136.9, 135.1, 130.4, 129.8, 127.9, 126.5, 125.6, 123.2, 121.6, 119.5, 119.3, 109.7, 109.1, 29.7, 29.5, 21.6, 8.9; HRMS (ESI): calc for $C_{24}H_{21}N_2O_3F_3S$ $[M+1]^+$: 475.1298 found: 475.1284 IR (neat, cm^{-1}): 3410 , 2923, 1502, 1360, 1261, 1165, 670, 575, 545.

N-(2-methoxyphenyl)-1, 3-dimethyl-N-tosyl-1H-indol-2-amine ***3l:*** Compound **3l** was isolated in 78% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 127-129℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.20-7.27 (m, 5H), 7.06-7.10 (m, 1H), 6.84-6.88 (m, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 2.42 (s, 3H) , 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 155.8, 143.6, 137.9, 135.0, 131.2, 129.5, 129.2, 128.2, 126.6, 122.6, 120.4, 119.2, 118.8, 112.3, 109.5, 108.8, 55.1, 30.0, 29.7, 21.6, 9.1; HRMS (ESI): calc for $C_{24}H_{24}N_2O_3S$ $[M+1]^+$: 421.1580 found: 421.1587 IR (neat, cm^{-1}): 3400 , 2923, 1595, 1496, 1354, 1164, 749, 667.

1, 3-dimethyl-N-(3, 4-dimethylphenyl)-N-tosyl-1H-indol-2-amine ***3m:*** Compound

3m was isolated in 73% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 172-173℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.23-7.29 (m, 4H), 7.01-7.12 (m, 4H), 3.72 (s, 3H), 2.44 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.9, 138.9, 137.7, 137.6, 135.2, 135.0, 131.3, 130.2, 129.6, 128.0, 126.6, 126.5, 122.8, 122.7, 119.3, 119.0, 109.5, 108.729.7, 29.6, 21.6, 20.0, 19.2, 9.0; HRMS (ESI): calc for $C_{25}H_{26}N_2O_2S$ $[M+1]^+$: 419.1788 found: 419.1778 IR (neat, cm^{-1}): 3398 , 2921, 1560, 1354, 1165, 745, 671.

1, 3-dimethyl-N-p-tolyl-N-tosyl-1H-indol-2-amine ***3n:*** Compound **3n** was isolated in 90% yield as a colorless liquid following the general procedure **A**. Reaction time: 3h. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.20-7.27 (m, 6H), 7.06-7.09 (m, 3H), 3.70 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.0, 138.7, 137.5, 136.4, 135.0, 131.2 129.8, 129.6, 127.9, 126.6, 125.1, 122.8, 119.3, 119.1, 109.5, 108.7; HRMS (ESI): calc for $C_{24}H_{24}N_2O_2S$ $[M+1]^+$: 405.1631 found: 405.1636 IR (neat, cm^{-1}): 3418 , 2920, 1379, 1355, 1164, 769, 670, 547.

3o: Compound **3o** was isolated in 56% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 148-152℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61-7.63 (dd, *J* = 2.0 Hz, 2H), 7.50-7.52 (dd, *J* = 2.0 Hz, 3H), 7.21-7.29 (m, 4H), 7.07-7.08 (m, 1H), 6.81-6.83 (dd, *J* = 2.4 Hz, 2H), 6.10 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 159.2, 137.2, 134.9, 134.6, 132.5, 132.0, 129.9, 129.5, 128.3, 125.7, 122.8, 120.9, 120.0, 114.4, 109.8, 99.1, 55.4, 29.0; HRMS (ESI): calc for $C_{22}H_{19}N_2O_3SBr$ $[M+1]^+$: 471.0373 found: 471.0386 IR (neat, cm^{-1}): 3414 , 2925, 1506, 1385, 1363,1167, 770, 746.

3p: Compound **3p** was isolated in 62% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 147-150℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (s, 4H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.23-7.31 (m, 4H), 7.08-7.12 (m, 1H), 6.81-6.84 (m, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 158.6, 139.4, 135.0, 133.5, 132.3, 131.1, 129.4, 128.2, 128.0, 126.5,

123.1, 119.4, 119.2, 114.5, 109.6, 108.4, 55.4, 29.7, 29.6, 9.2; HRMS (ESI): calc for $C_{23}H_{21}N_2O_3SBr$ $[M+1]^+$: 485.0529 found: 485.0538 IR (neat, cm^{-1}): 3396 , 2925, 1506, 1385, 1163, 741, 553.

N-(4-(4-methoxyphenoxy)phenyl)-1,3-dimethyl-N-tosyl-1H-indol-2-amine ***3q:*** Compound **3q** was isolated in 45% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 161-163℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.23-7.29 (m, 6H), 7.08-7.10 (m, 1H), 6.93-6.95 (m, 2H), 6.83-6.87 (m, 4H), 3.78 (s, 3H), 3.73 (s, 3H), 2.44 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 157.3, 156.2, 149.4, 144.1, 137.5, 135.4, 135.0, 131.3, 129.7, 127.9, 127.5, 126.6, 122.9, 121.1, 119.3, 119.1, 117.7, 114.9, 109.6, 108.6, 55.6, 29.6, 21.6, 9.0; HRMS (ESI): calc for $C_{30}H_{28}N_2O_4S$ $[M+1]^+$: 513.1843 found: 513.1849 IR (neat, cm^{-1}): 3398 , 2922, 1496, 1356, 1225, 1164, 772.

1-allyl-5-methoxy-N-p-tolyl-N-tosyl-1H-indol-2-amine ***3r:*** Compound **3r** was isolated in 42% yield as a white solid following the general procedure **A**. Reaction time: 3h. mp: 135-137℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.22-7.28 (m, 4H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.85-6.88 (dd , *J* = 2.4 Hz, 1H), 6.07 (s, 1H), 5.73-5.80 (m, 1H), 5.01-5.04 (dd, *J* = 1.2 Hz, 1H), 4.92-4.97 (dd, *J* = 1.2 Hz, 1H), 4.83 (d, *J* = 5.2 Hz, 2H), 3.79 (s, 3H), 2.44 (s, *3*H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 154.2, 144.0, 137.6, 137.5, 135.3, 134.5, 133.3, 129.6, 129.3, 128.5, 127.8, 126.2, 116.8, 113.0, 111.4, 102.4, 99.4, 55.7, 45.2, 29.6, 21.6, 21.0; HRMS (ESI): calc for $C_{26}H_{26}N_2O_3S$ $[M+1]^+$: 447.1737 found: 447.1745 IR (neat, cm^{-1}): 3403, 2924, 1480, 1358, 1167, 669.

General Procedure B:A mixture of indole derivative (10 mmol) **4**, Cs_2CO_3 (20 mmol), I_2 (20 mmol) and acetonitrile (25 mL) was stirred at room temperature under air for 1 h. The reaction was quenched with a saturation solution of $Na_2S_2O_3$ (25 mL) and then extracted with ethyl acetate (3×50 mL). The combined organic phases were washed with brine (150 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography using

mixture of petrolium ether and ethyl acetate as eluent to afford of the corresponding product **5** as a white solid.

To a solution of naphthalene (641 mg, 5.0 mmol) in THF (10 mL) was added metal sodium (115 mg, 5.0 mmol) at room temperature. The mixture was stirred at room temperature for 2 h to yield a deep-blue sodium-naphthalenide solution (0.5 M). The fresh-prepared sodium-naphthalenide solution was added slowly to a solution of **5** (122 mg, 0.19 mmol) in THF (5 ml) at −78 °C until the color of reaction mixture maintained unchanged blue (about 5 mL, 10 equiv was used). After being stirred at −78 °C for 30 min, saturated aqueous NH_4Cl solution (2 mL) was added. The resulting mixture was warmed to room temperature and diluted with EtOAc (50 mL), washed with brine (20 mL × 3), dried over sodium sulfate and concentrated. The crude residue was purified by column chromatography (10% EtOAc/petroleum to 25% MeOH/CH_2Cl_2) to afford crude secondary amine as a colorless foam. The crude amine was used immediately.

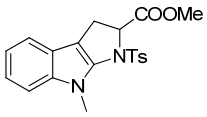
Formalin (37%, 5.5 μL, 0.0734 mmol, 5.2 equiv) followed by solid sodium triacetoxyborohydride (15.6 mg, 0.0734 mmol, 5.2 equiv) were added to a solution of **6** (5.0 mg, 0.0145 mmol, 1 equiv) in acetonitrile (700 μL) at 23 °C and placed under an argon atmosphere. After 30 min, a solution of methanol (5:95) in dichloromethane saturated with ammonia was added slowly. After 5 min, the resulting slurry was concentrated under reduced pressure and the residue was purified by flash column chromatography (1% methanol in dichloromethane saturated with ammonia) to afford (±)-folicanthine **1** as a white solid (100 %). All spectral data were in agreement with the literature.

1,2,3,3a,8,8a-hexahydro-3a-(1,2,3,3a,8,8a-hexahydro-8-methyl-1-tosylpyrrolo[2,3-b]indol-3a-yl)-8-methyl-1-tosylpyrrolo[2,3-b]indole **5**: Compound **5** was isolated in 90% yield as a white solid following the general procedure **B**. Reaction time: 1h. mp: 149-152℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36 (d, J = 8.0 Hz, 4H), 7.21-7.27 (m, 6H), 6.86 (d, J = 7.6 Hz, 2H), 6.65 (t, J = 4.8 Hz, 2H), 6.50 (d, J = 7.6 Hz, 2H), 5.05 (s, 2H), 3.21-3.25 (m, 2H), 2.99 (s, 6H), 2.74-2.76 (m, 2H), 2.44 (s, 6H)

1.79-1.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 151.6, 142.9, 136.1, 129.9, 129.5, 127.7, 127.2, 124.6, 117.7, 106.9, 87.23, 60.4, 47.4, 32.6, 31.5, 21.5; HRMS (ESI): calc for $C_{36}H_{38}N_4O_4S_2$ $[M+1]^+$: 655.2407 found: 655.2401 IR (neat, cm^{-1}): 3398 , 2951, 1602, 1491, 1342, 1157, 1012, 752, 660.

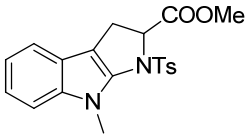
1,2,3,3a,8,8a-hexahydro-3a-(1,2,3,3a,8,8a-hexahydro-8-methylpyrrolo[2,3-b]indol-3a-yl)-8-methylpyrrolo[2,3-b]indole ***6*** Compound **6** was isolated in 56% yield as a white solid, Mp: 186-188℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.17 (d, J = 7.2 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 6.57 (t, J = 7.2 Hz, 2H), 6.29 (d, J = 8.0, 2H), 4.38 (s, 2H), 2.98-3.00 (m, 2H), 2.80 (s, 6H), 2.42-2.49 (m, 4H), 2.12-2.16 (m, 2H), 1.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 152.6, 131.4, 128.5, 124.2, 116.1, 104.8, 87.5, 62.1, 45.8, 38.7, 31.1; HRMS (ESI): calc for $C_{22}H_{26}N_4$ $[M+1]^+$: 347.2230 found: 347.2236 IR (neat, cm^{-1}): 3395 , 2925, 1603, 1494, 1383, 748.

1,2,3,3a,8,8a-hexahydro-3a-(1,2,3,3a,8,8a-hexahydro-1,8-dimethylpyrrolo[2,3-b]indol-3a-yl)-1,8-dimethylpyrrolo[2,3-b]indole ***1*** Compound **1** was isolated in 99% yield as a white solid, Mp: 164-167℃; 1H NMR (400 MHz, $CDCl_3$, TMS) δ 6.91-6.99 (m, 4H), 6.48-6.51 (t, 2H), 6.26 (d, J = 7.6 Hz, 2H), 4.39 (s, 2H), 2.99 (s, 6H), 2.64 (s, 2H), 2.40-2.47 (m, 10H), 1.94-1.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 152.8, 132.7, 128.0, 123.6, 116.6, 105.8, 91.9, 62.6, 52.6, 37.8, 35.4, 35.2; HRMS (ESI): calc for $C_{24}H_{30}N_4$ $[M+1]^+$: 375.2543 found: 375.2547 IR (neat, cm^{-1}): 3397 , 2912, 2787, 1602, 1492, 1381, 1155, 1022, 741.

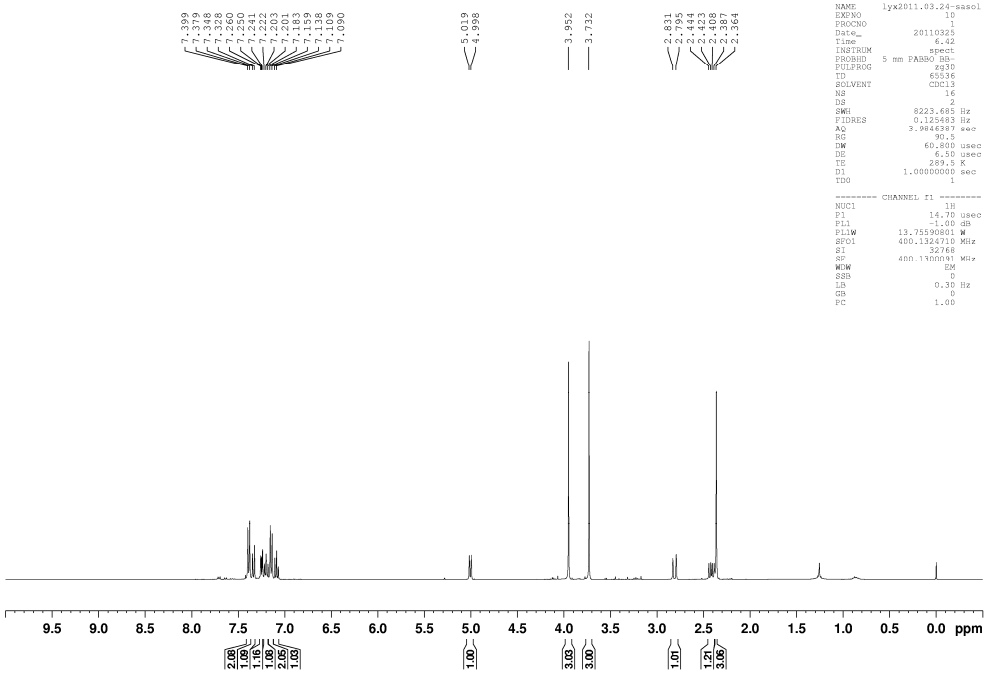


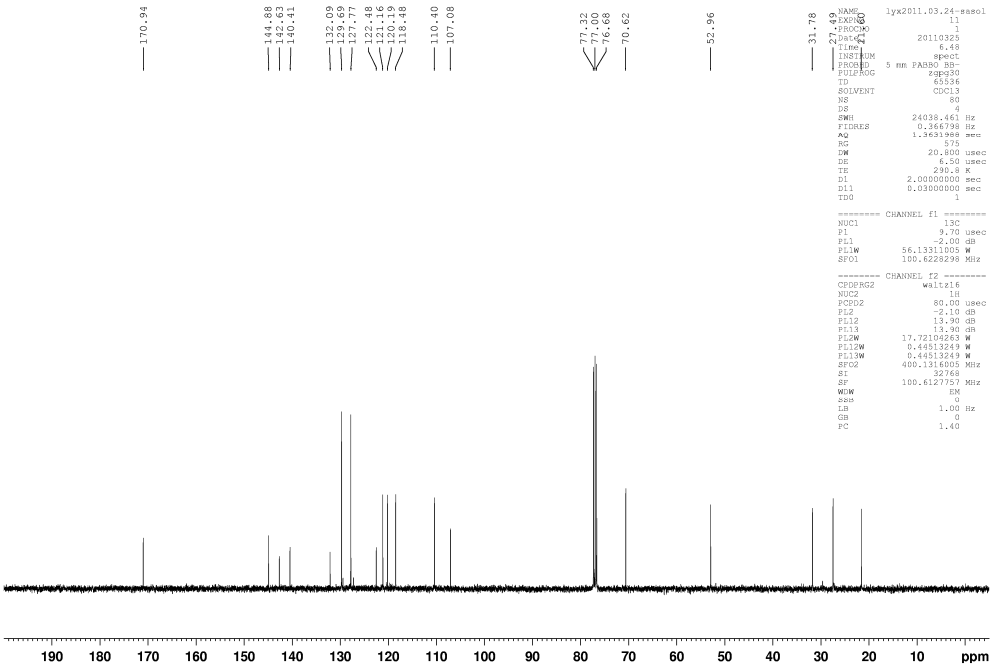
A

Compound **A** was isolated in 61% yield as a white solid 1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40-7.38 (d, J = 8 Hz, 2H), 7.35-7.33 (d, J = 8 Hz,1H), 7.26-7.24 (t, J = 4 Hz, 1H), 7.22-7.20 (m, 1H), 7.18-7.09 (m,3H), 5.02-5.00(d, J = 8.4 Hz,1H), 3.95 (s, 1H), 3.73 (s, 1H), 2.83-2.80 (d, J = 14.4 Hz, 1H), 2.44-2.39 (q, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.9, 144.9, 142.6, 140.4, 132.1, 129.7, 127.8, 122.5, 121.2, 120.2, 118.5, 110.4, 107.1, 70.6, 53.0, 31.8, 27.5, 21.6; HRMS (ESI): calc for $C_{20}H_{20}N_2O_4S$ $[M+1]^+$: 385.1217 found: 385.1223 .

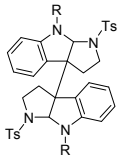


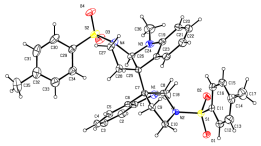
A





Crystallographic data of 6





checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: c2c

Bond precision: C-C = 0.0067 A Wavelength=0.71073

Cell: a=31.563(7) b=12.194(3) c=19.897(4)
alpha=90 beta=102.099(3) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	7488(3)	7488(3)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C36 H38 N4 O4 S2	?
Sum formula	C36 H38 N4 O4 S2	C36 H38 N4 O4 S2
Mr	654.84	654.82
Dx,g cm-3	1.162	1.162
Z	8	8
Mu (mm-1)	0.183	0.183
F000	2768.0	2768.0
F000'	2771.04	
h,k,lmax	38,14,24	37,14,24
Nref	6990	6776
Tmin,Tmax	0.955,0.961	0.956,0.961
Tmin'	0.955	

Correction method= MULTI-SCAN

Data completeness= 0.969 Theta(max)= 25.500

R(reflections)= 0.0653(3339) wR2(reflections)= 0.2020(6776)

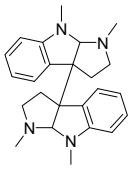
S = 0.976 Npar= 419

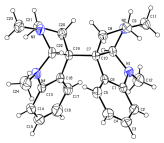
The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT026_ALERT_3_C Ratio Observed / Unique Reflections too Low .... 49 Perc.
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low 0.97
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.68
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.44 Ratio

Crystallographic data of 7





checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: c2c

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=28.442(8) b=16.060(5) c=13.506(4)
alpha=90 beta=90.289(3) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	6169(3)	6169(3)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C24 H30 N4	?
Sum formula	C24 H30 N4	C36 H45 N6
Mr	374.52	561.78
Dx,g cm-3	1.210	1.210
Z	12	8
Mu (mm-1)	0.073	0.073
F000	2424.0	2424.0
F000'	2424.74	
h,k,lmax	34,19,16	34,19,16
Nref	5748	5714
Tmin,Tmax	0.982,0.984	0.982,0.984
Tmin'	0.982	

Correction method= MULTI-SCAN

Data completeness= 0.994 Theta(max)= 25.490

R(reflections)= 0.0526(3055) wR2(reflections)= 0.1406(5714)

S = 1.006 Npar= 385

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
PLAT045_ALERT_1_C Calculated and Reported Z Differ by ..... 1.50 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for N5 -- C33 .. 7.00 su

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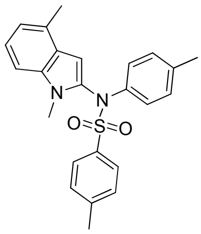
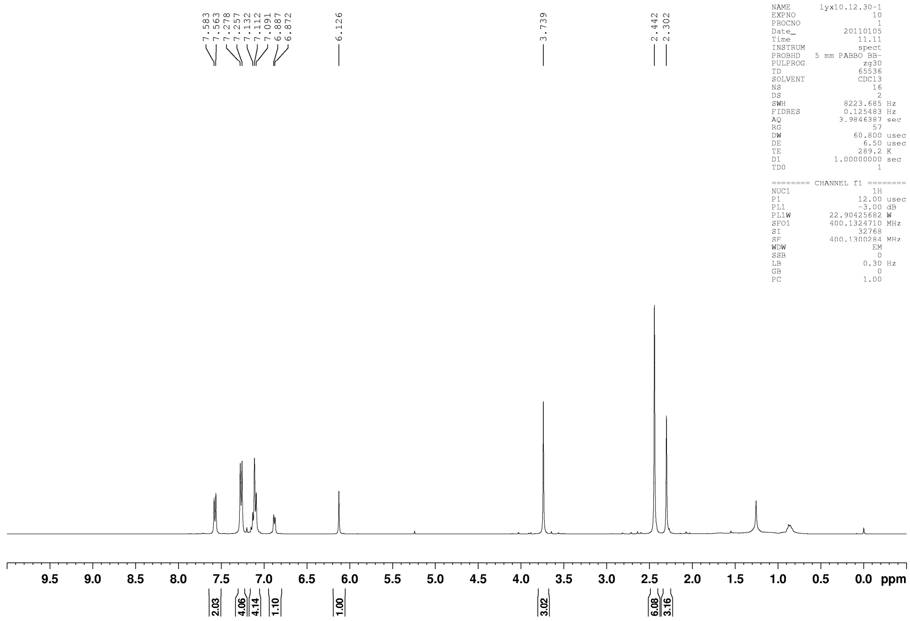
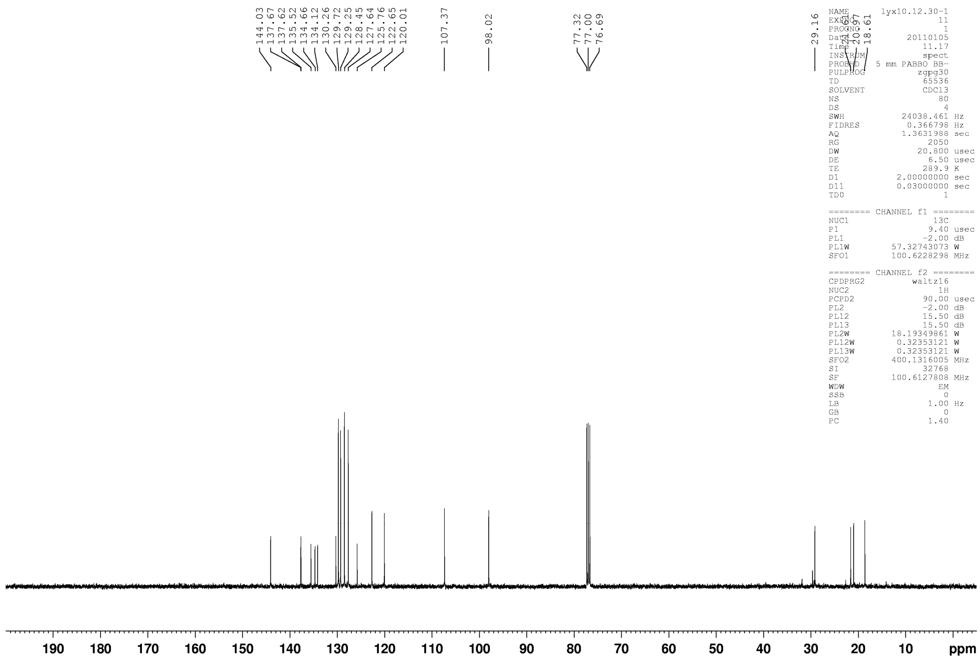
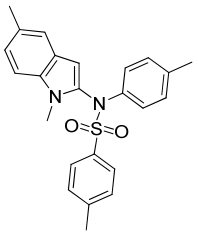
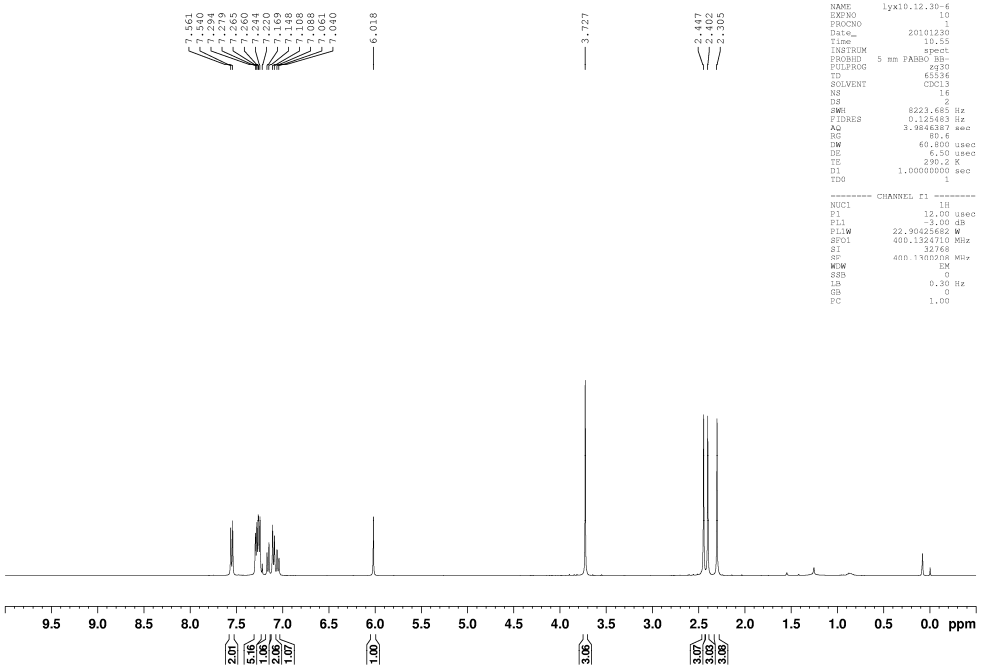
Electronic Supplementary Material (ESI) for Chemical Communications

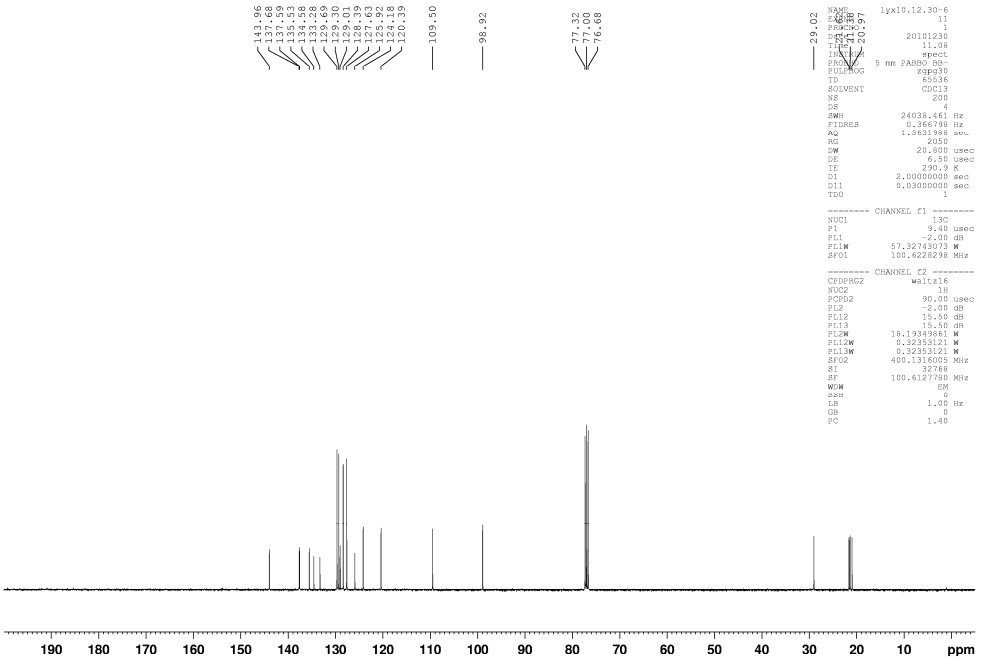


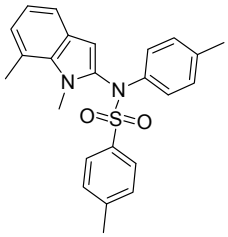


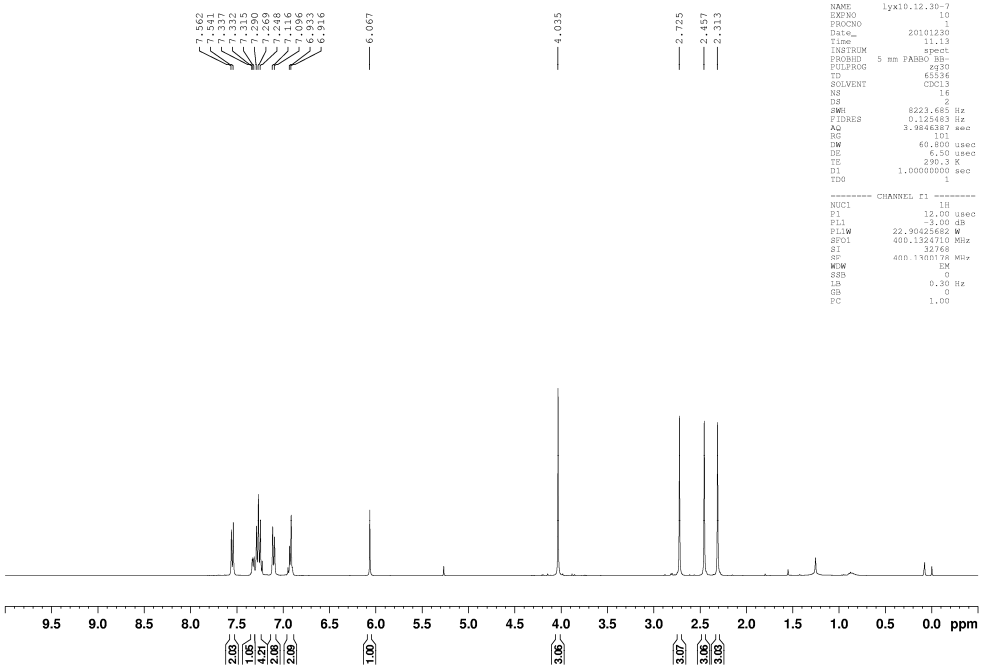


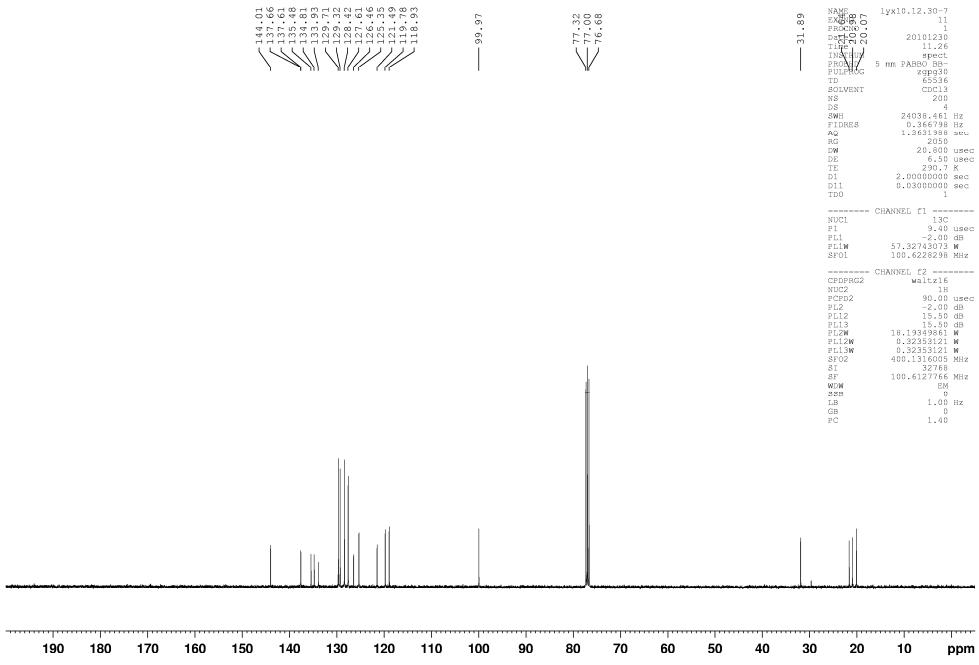


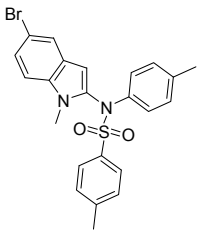


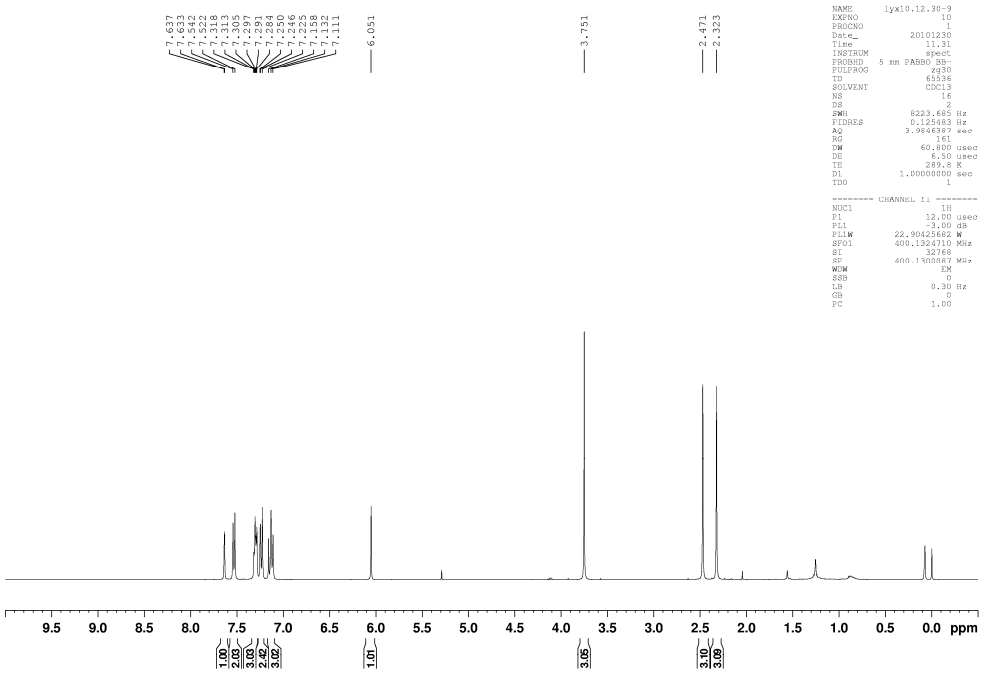


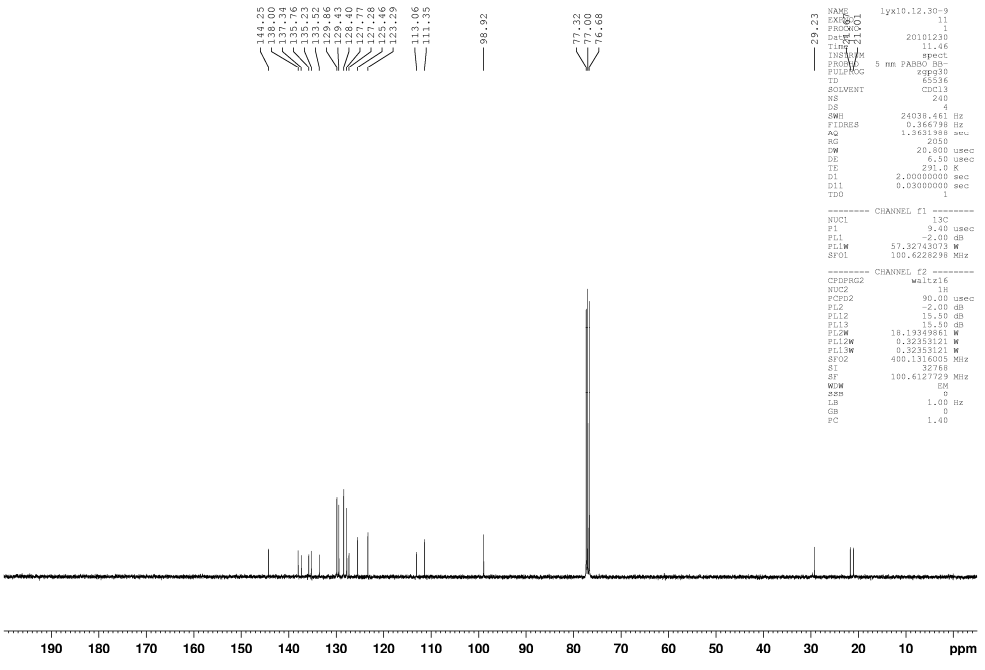


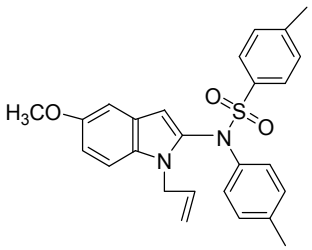


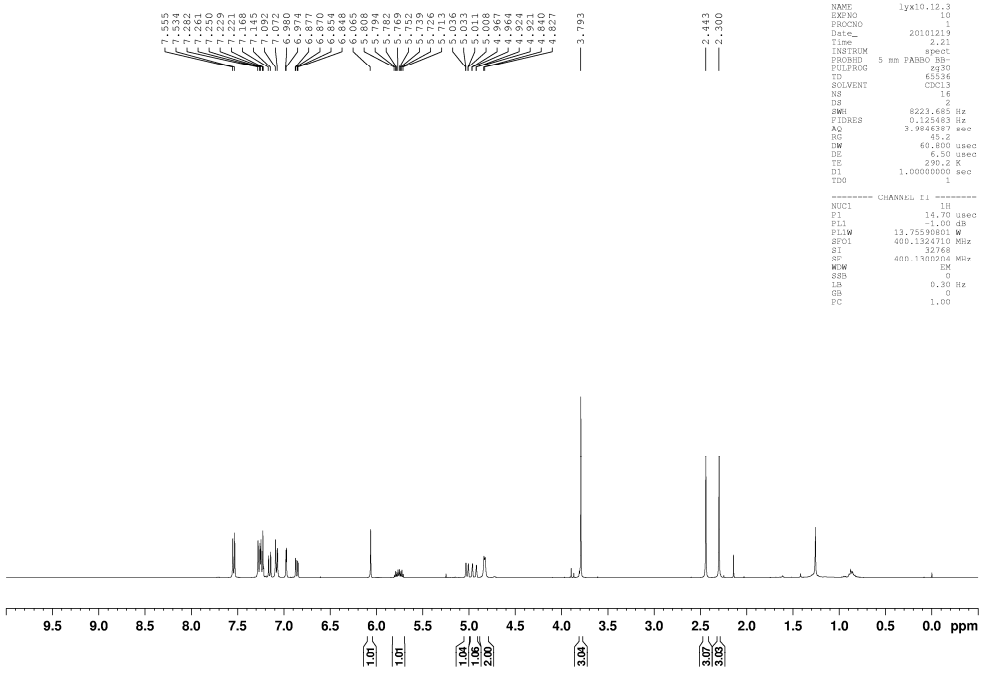


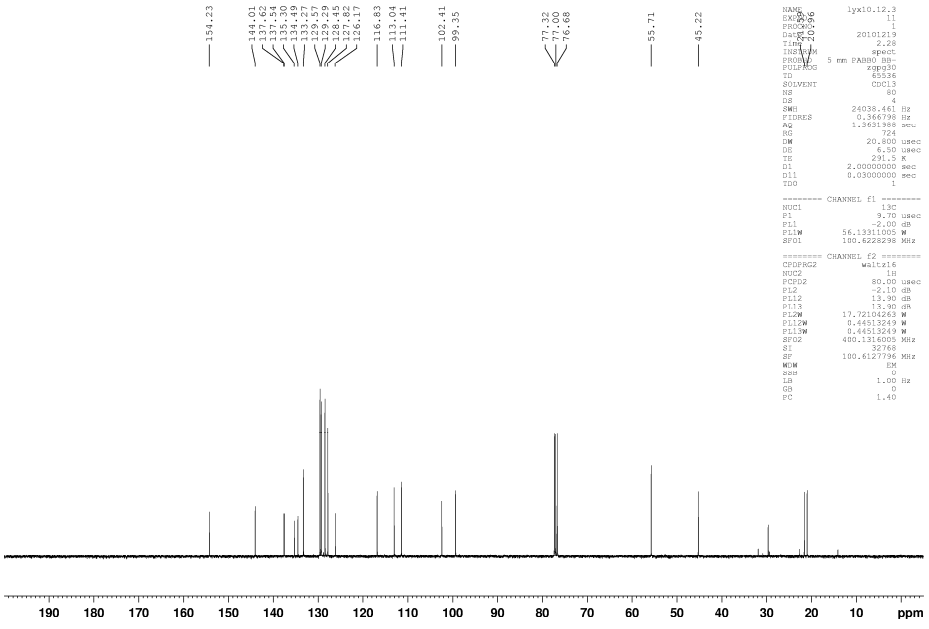


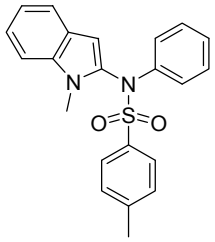


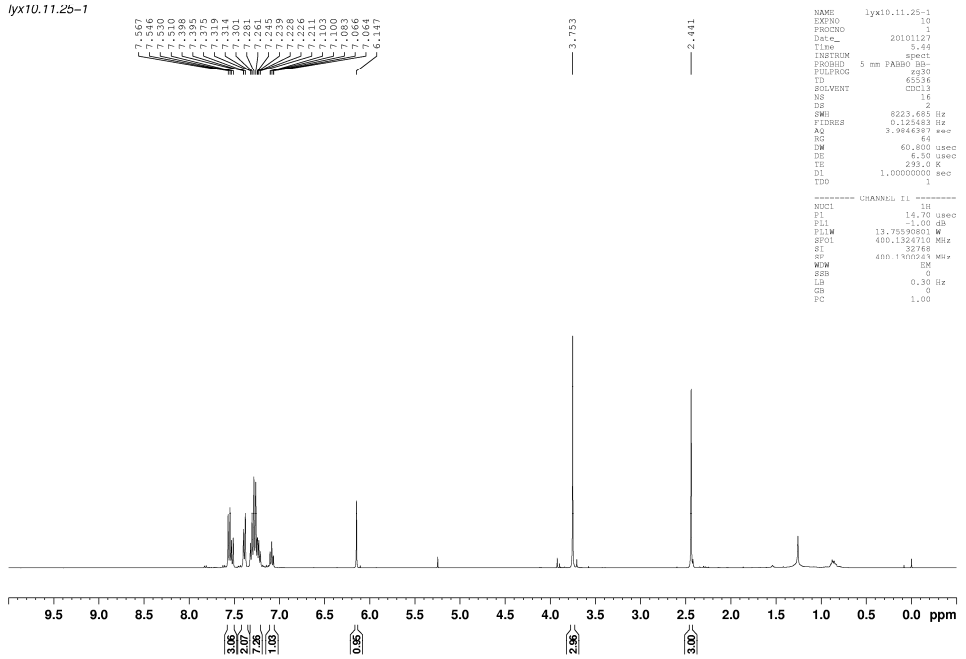


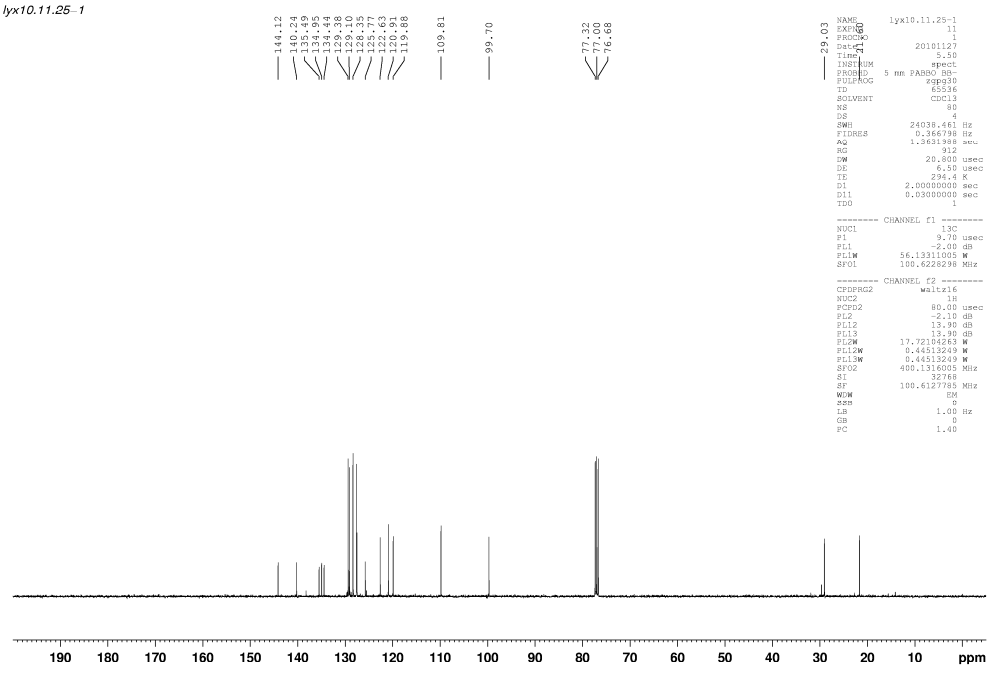


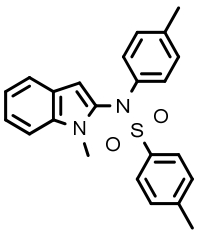


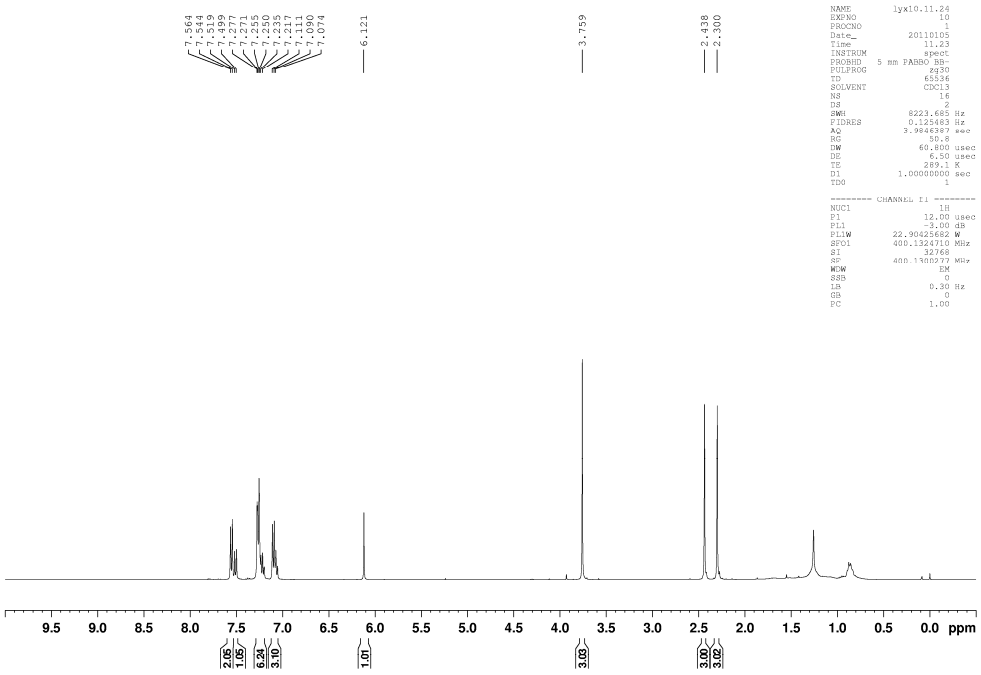


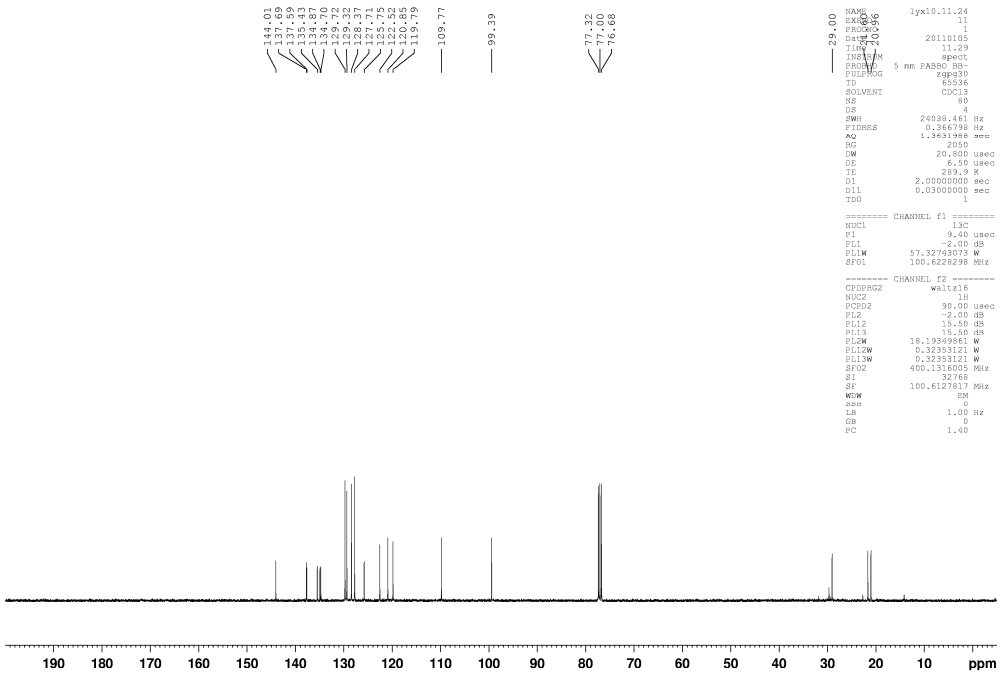


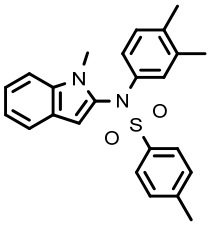


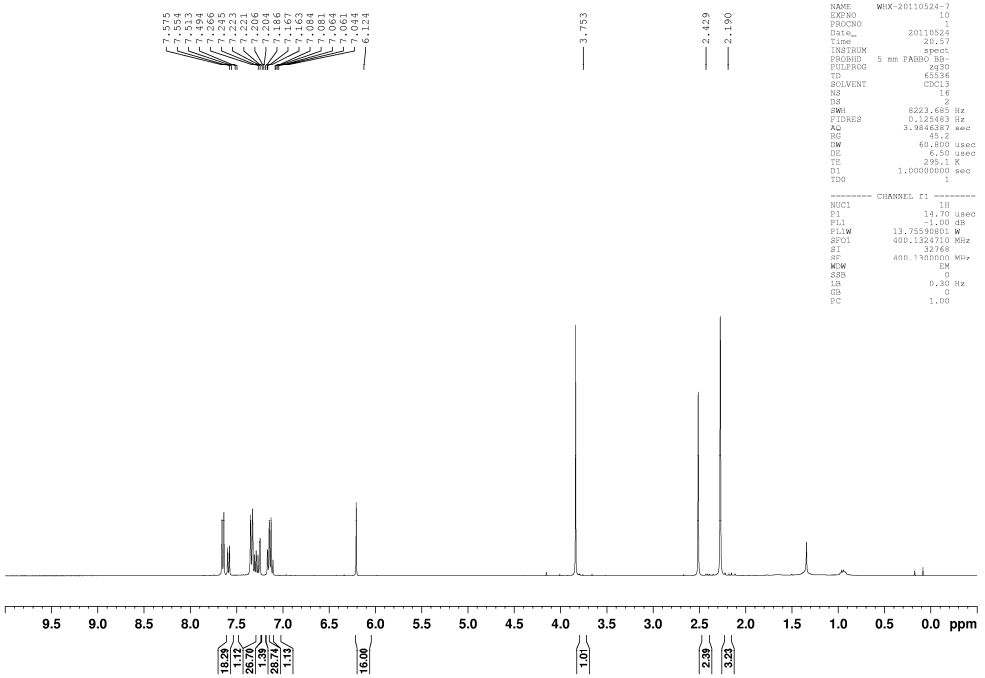


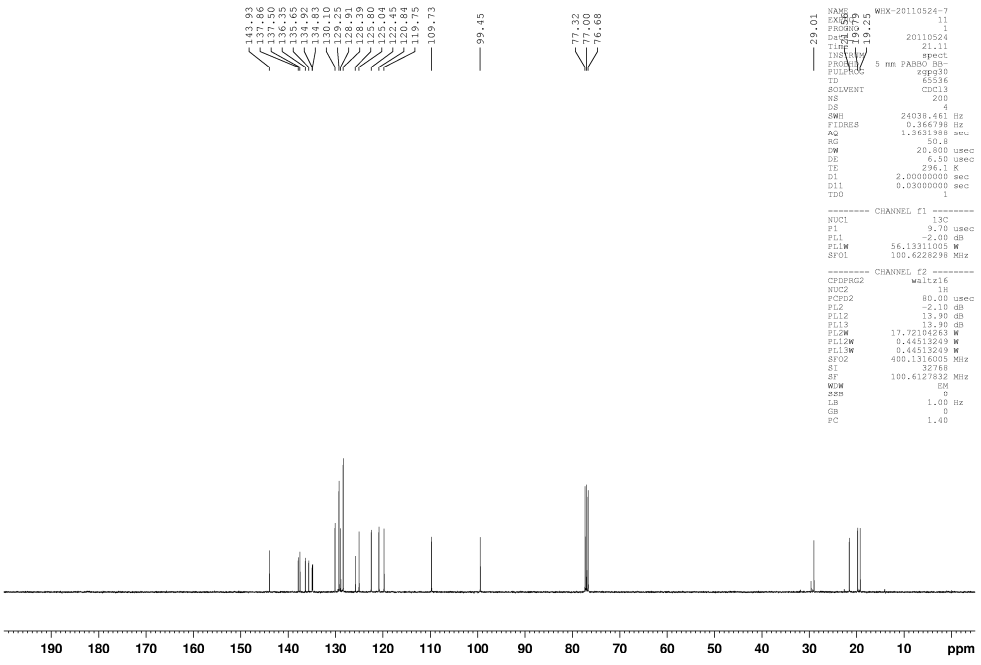


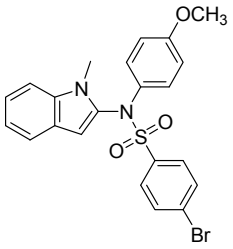


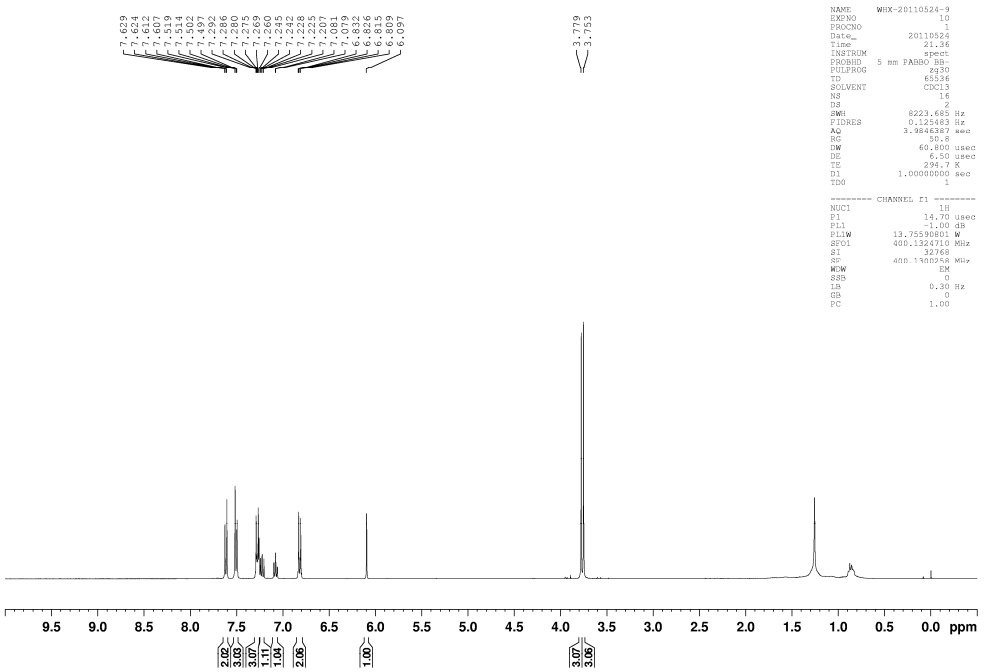


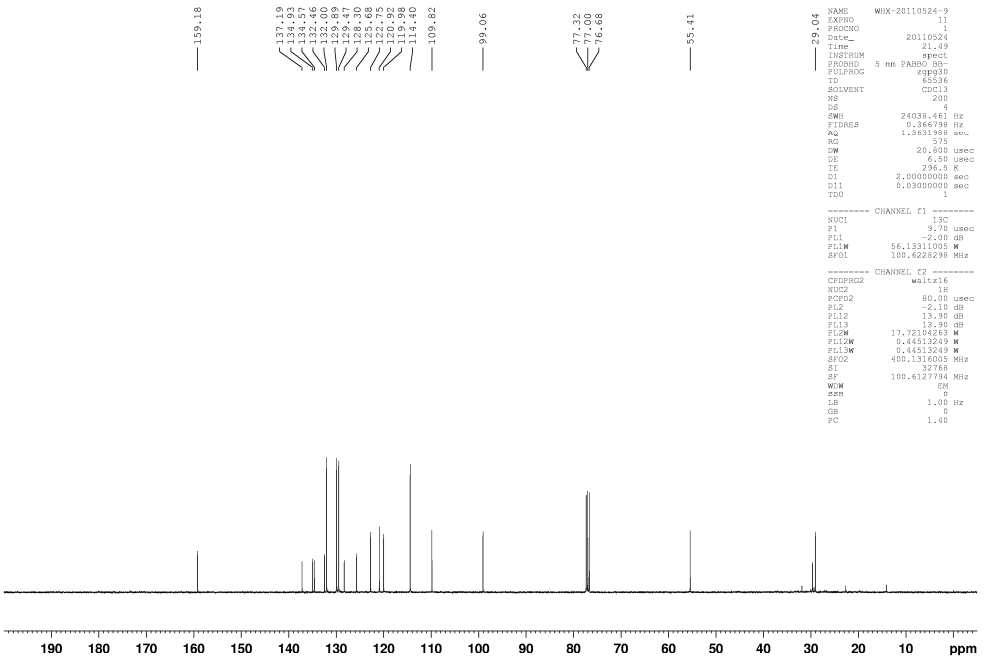


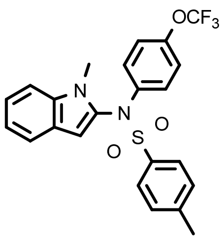








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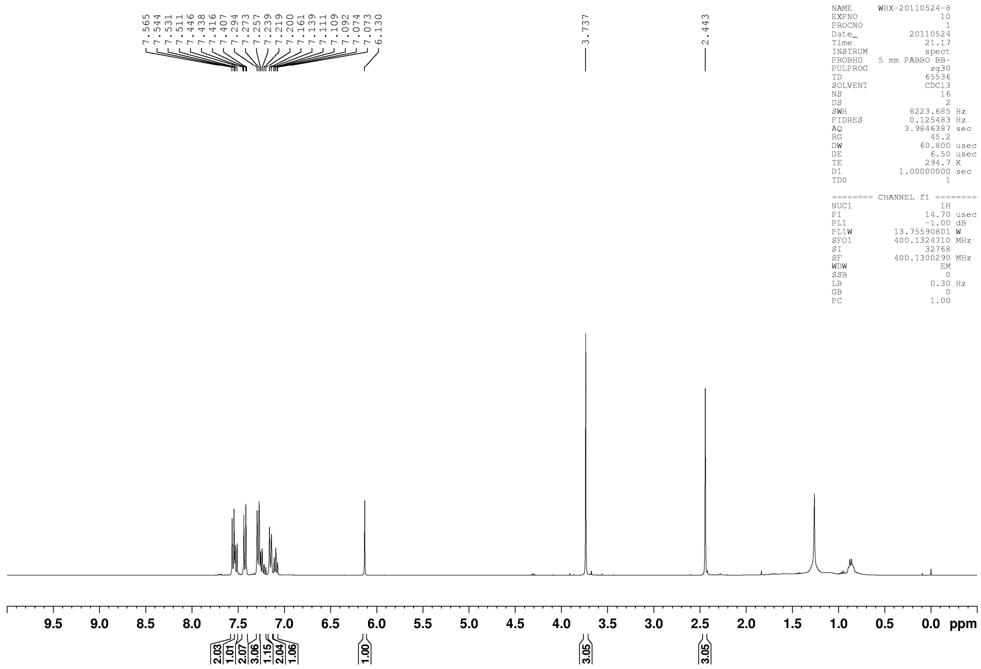

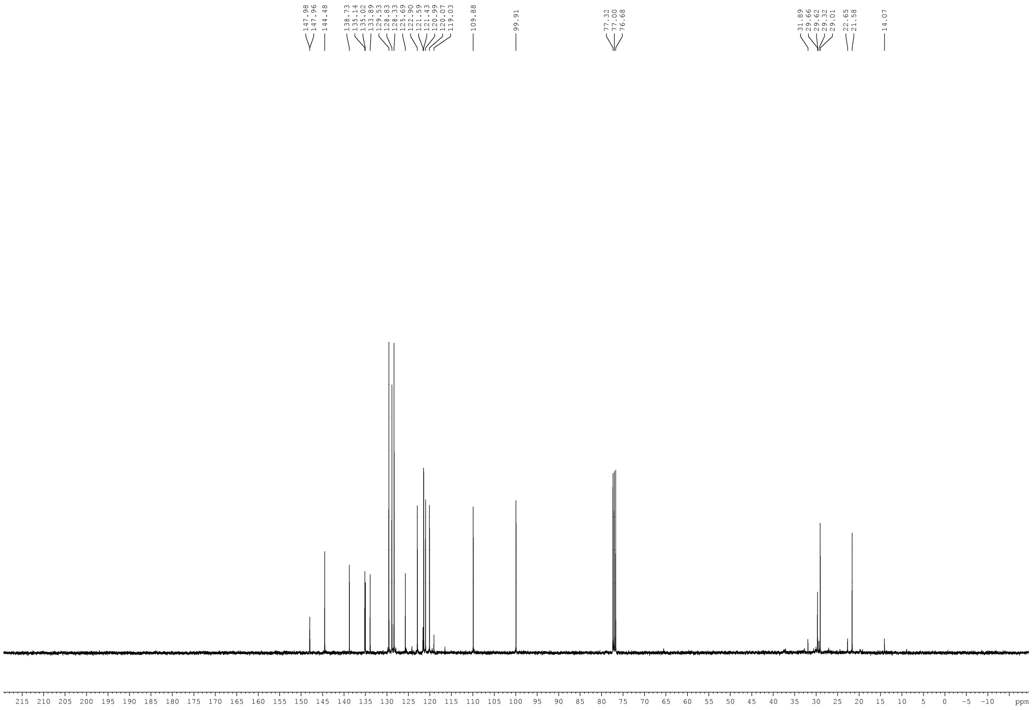

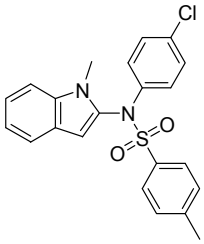

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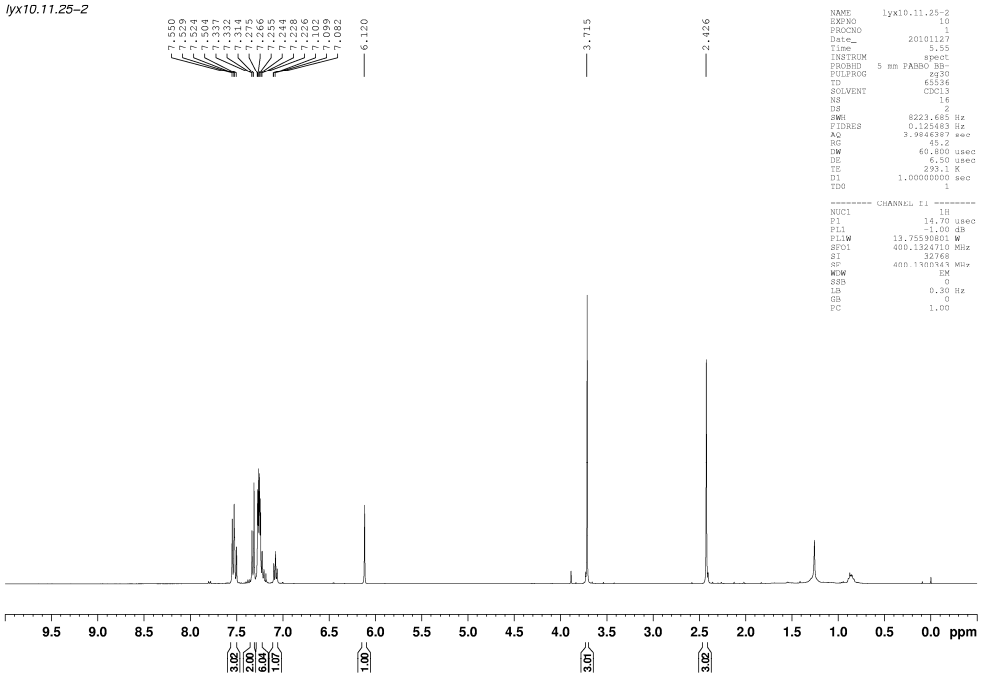

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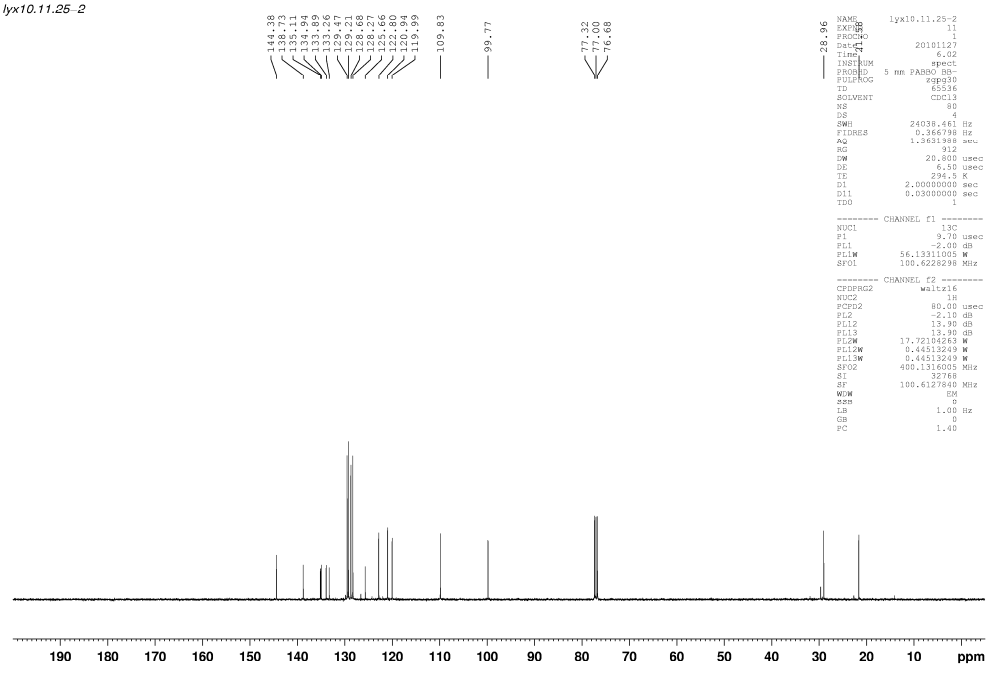

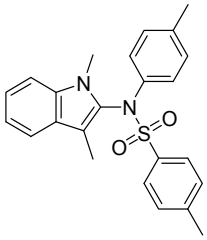

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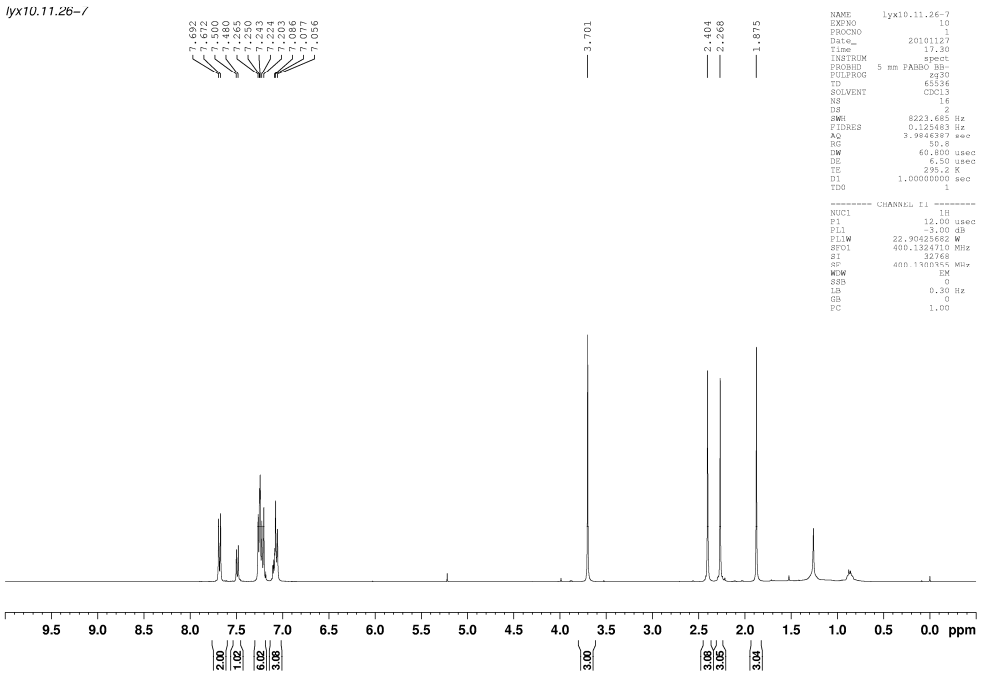

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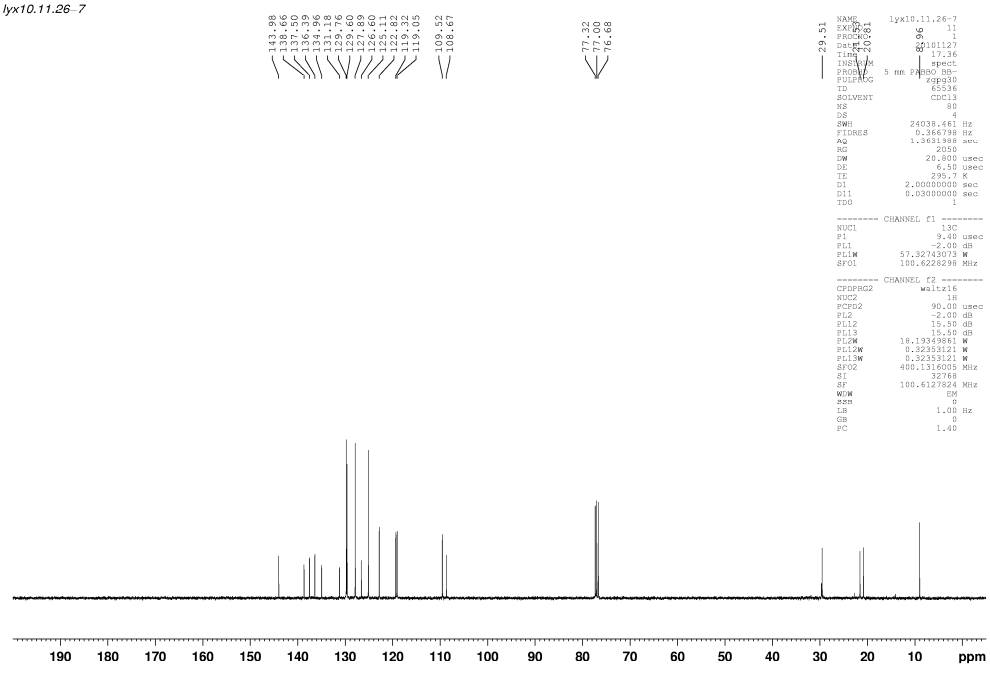

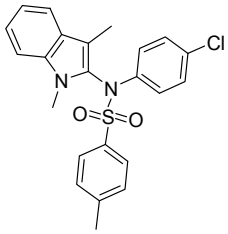

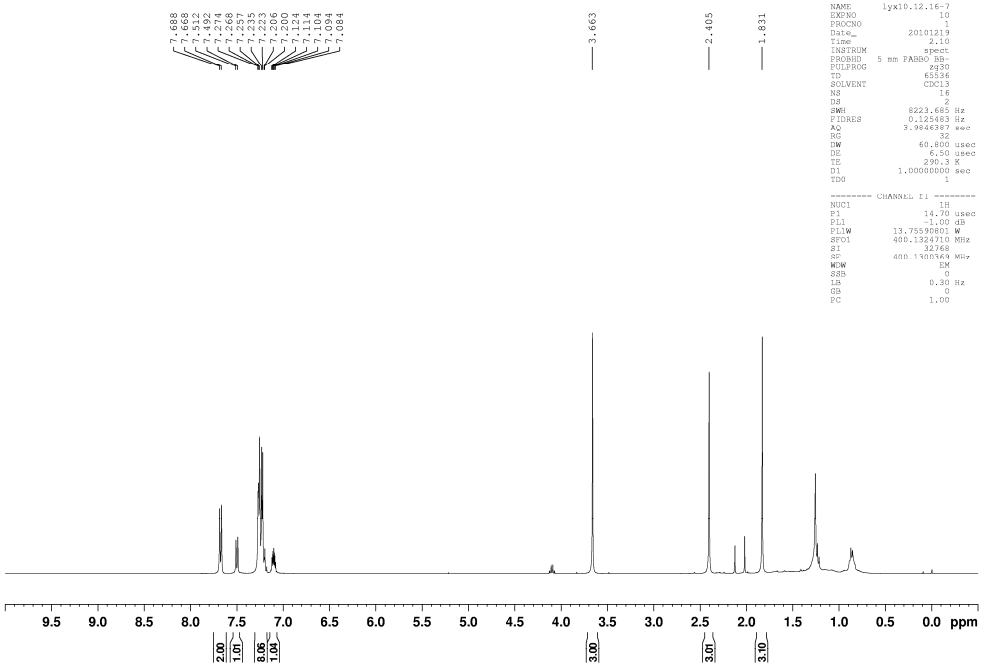

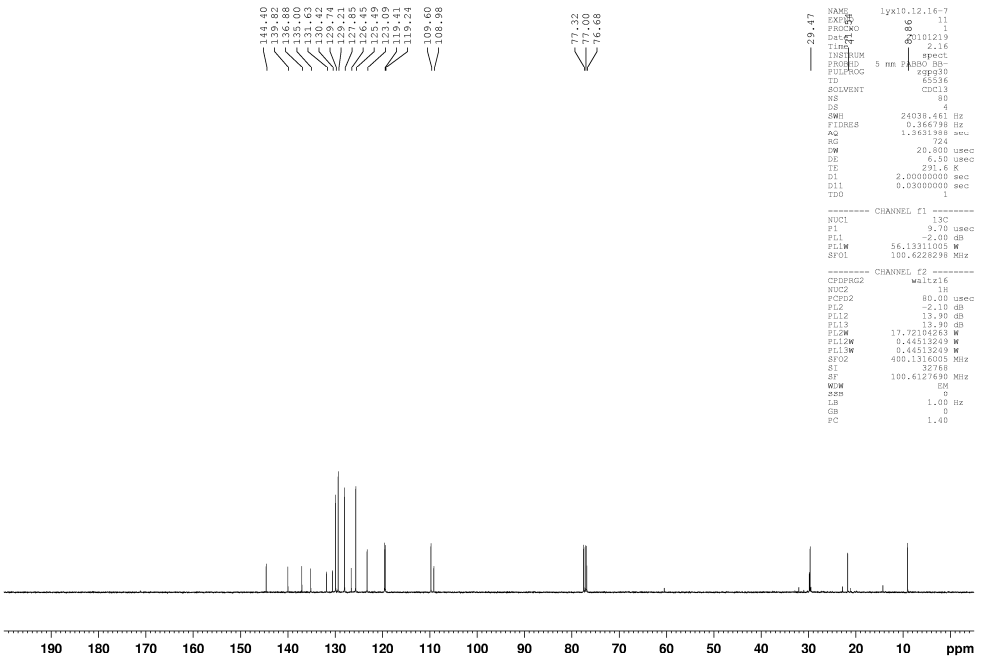

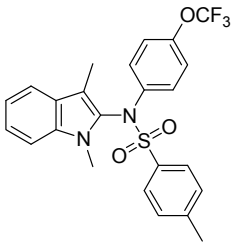

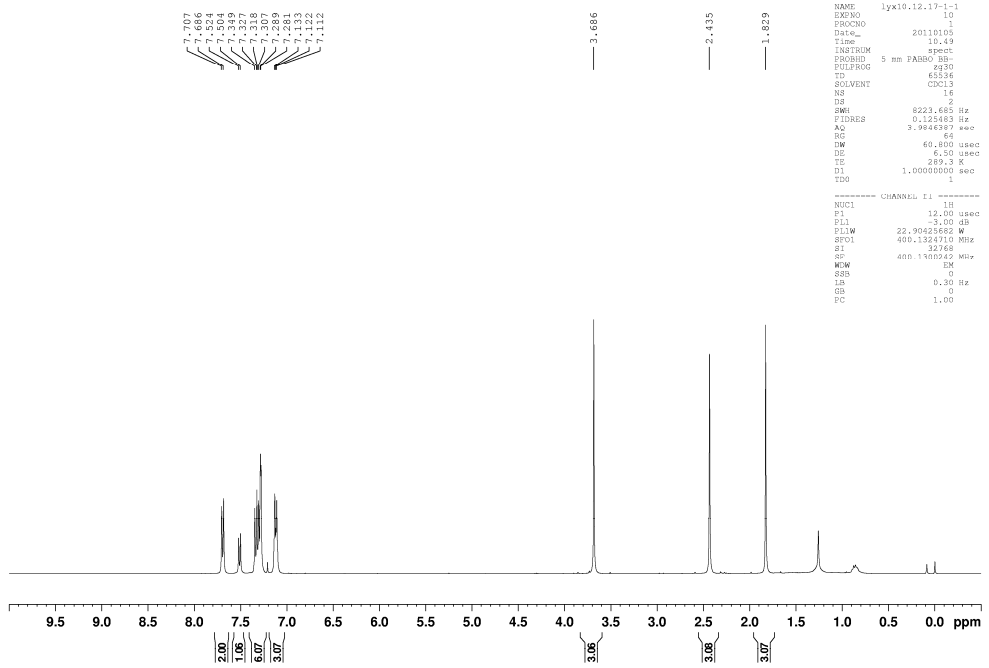

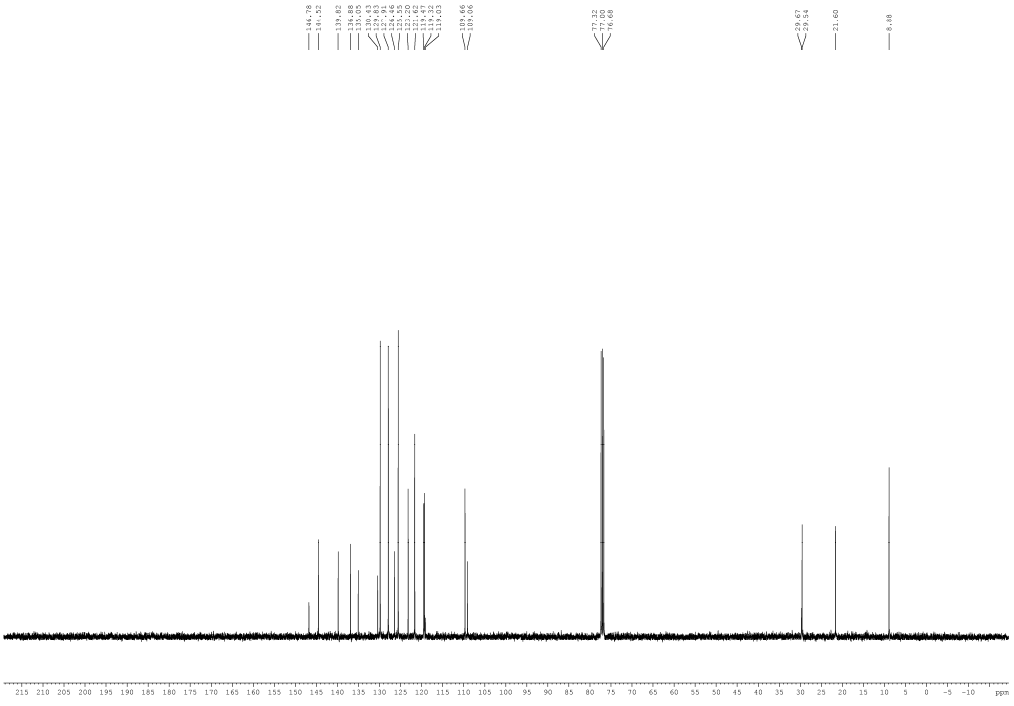

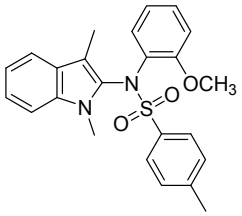

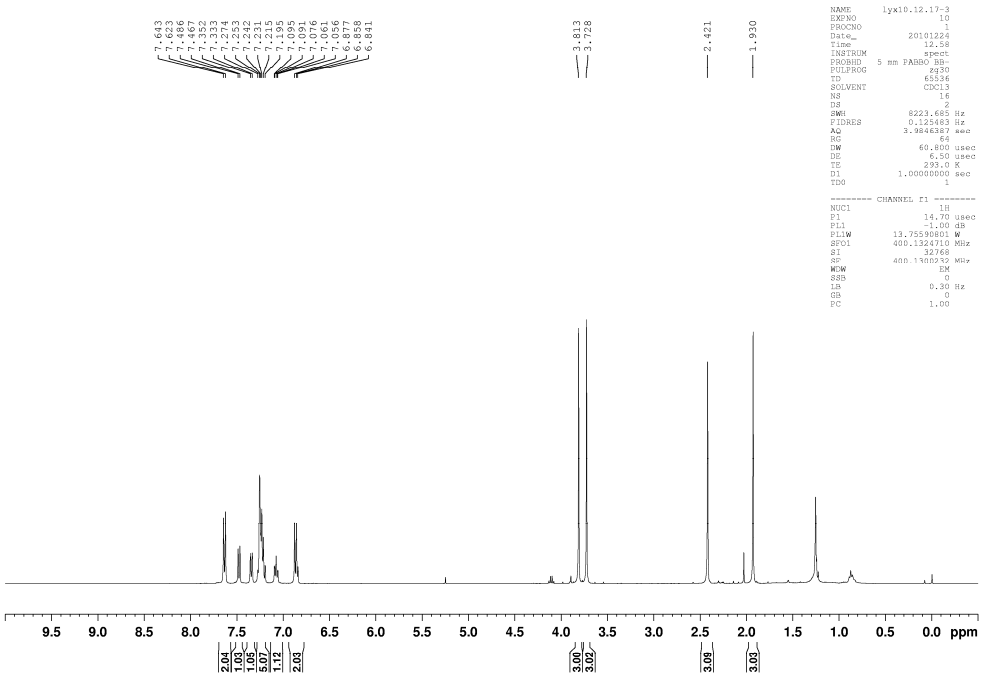

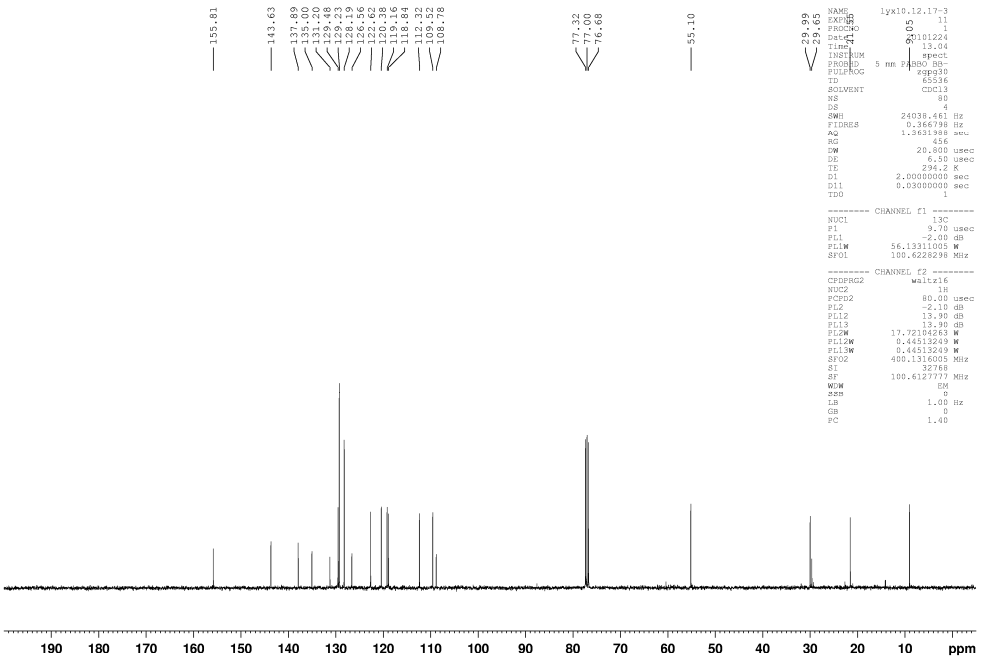

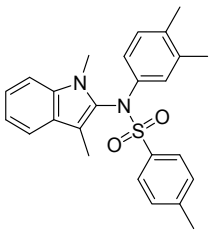

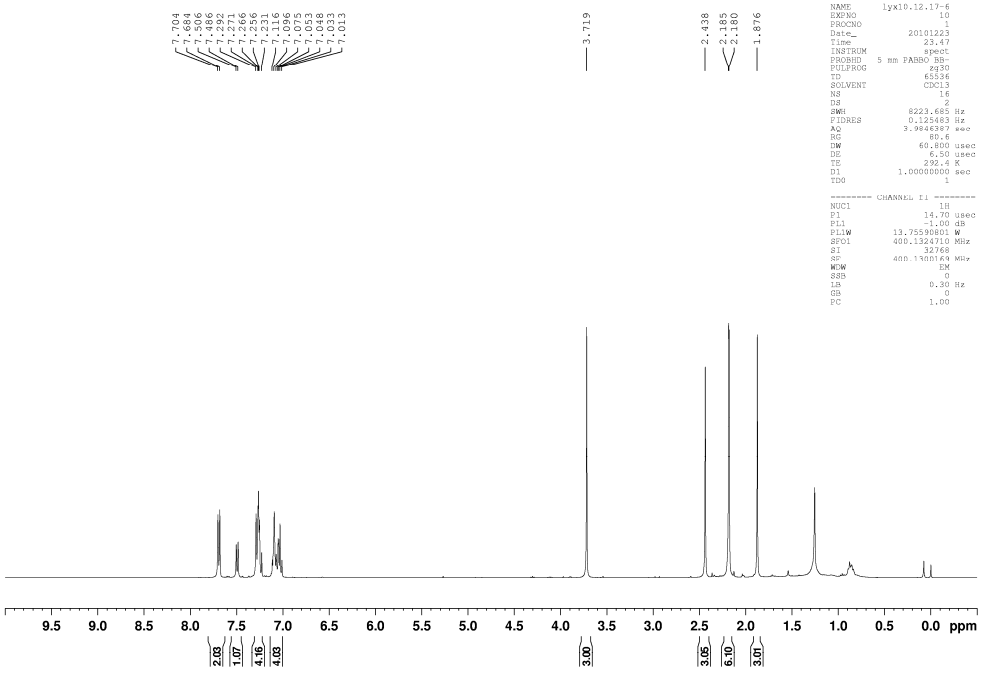

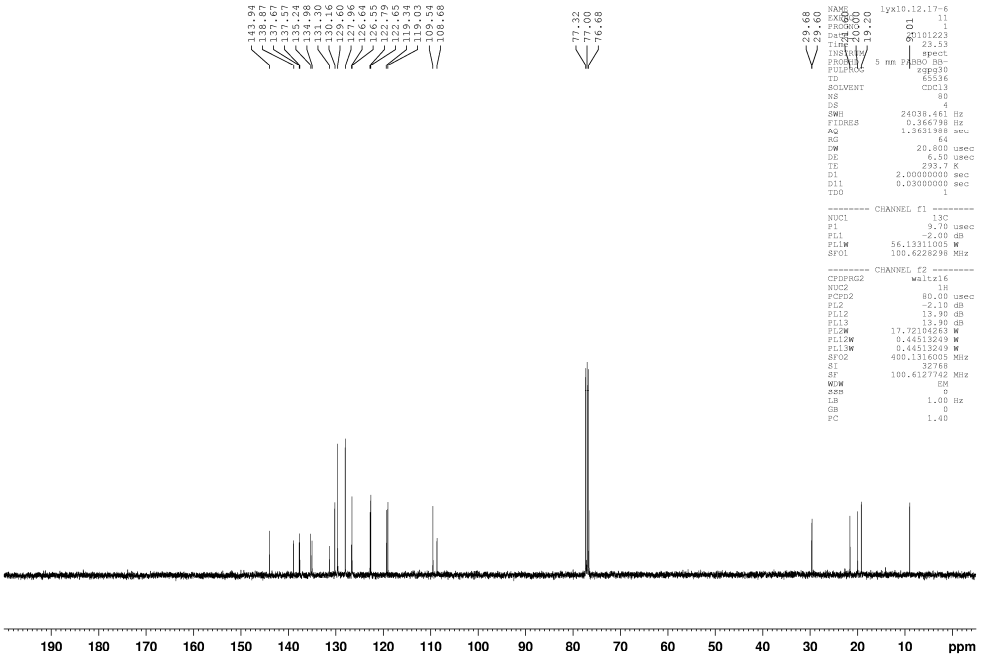

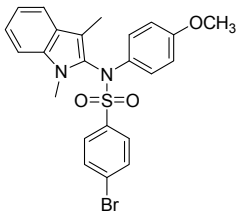

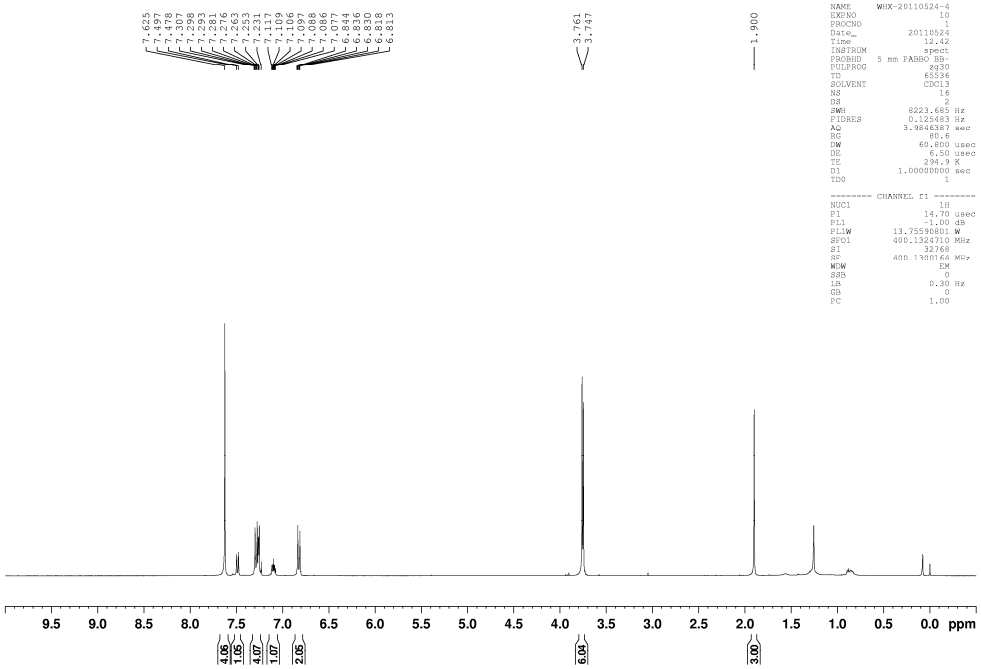

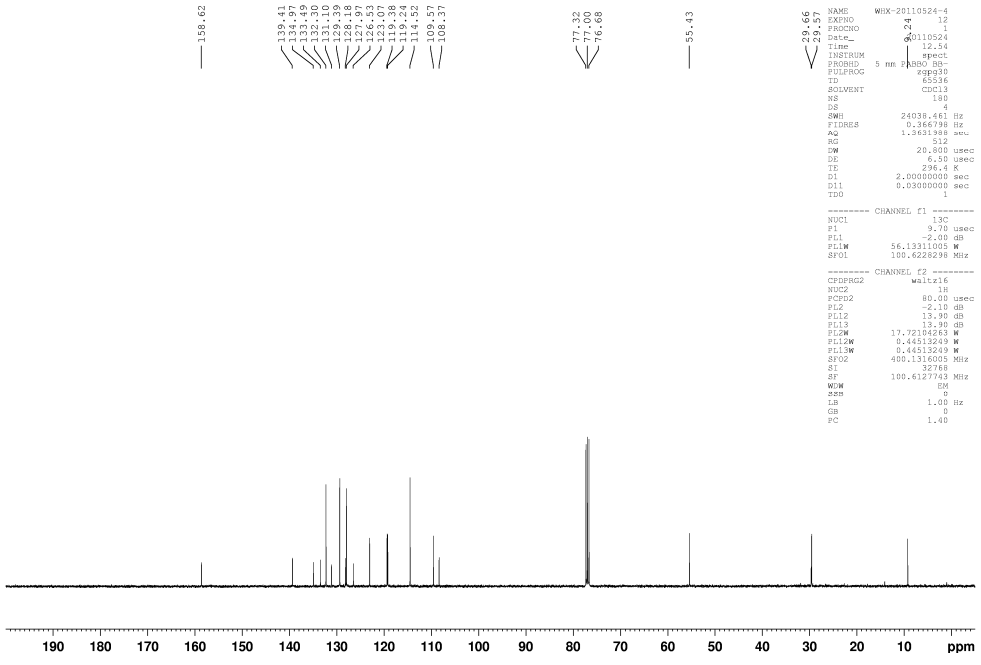

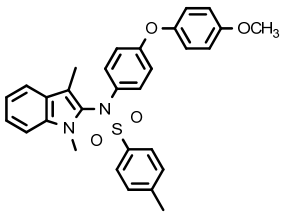

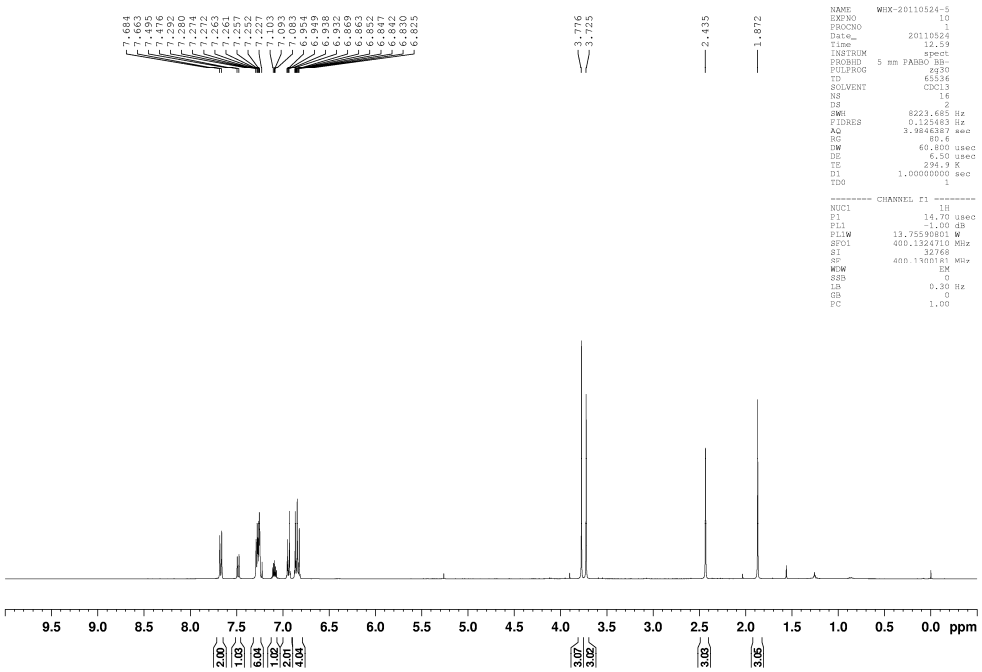

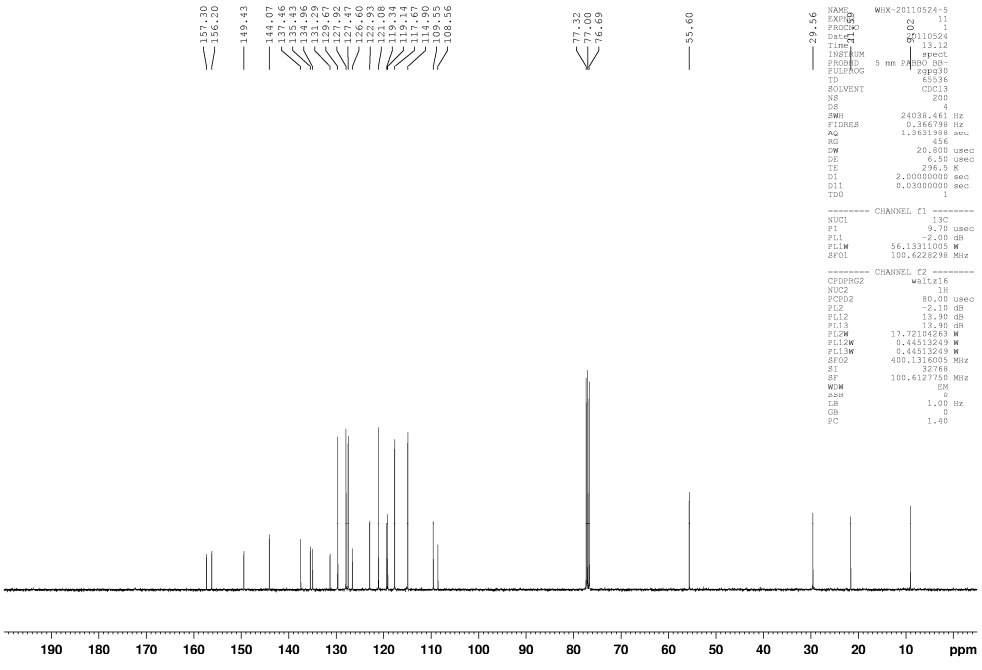

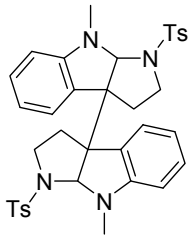

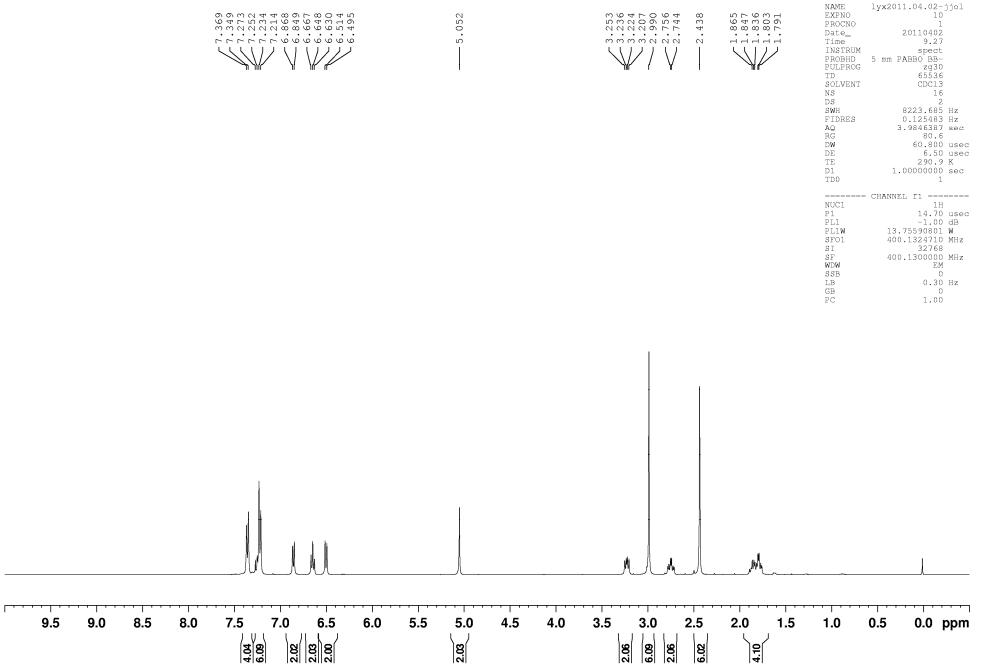

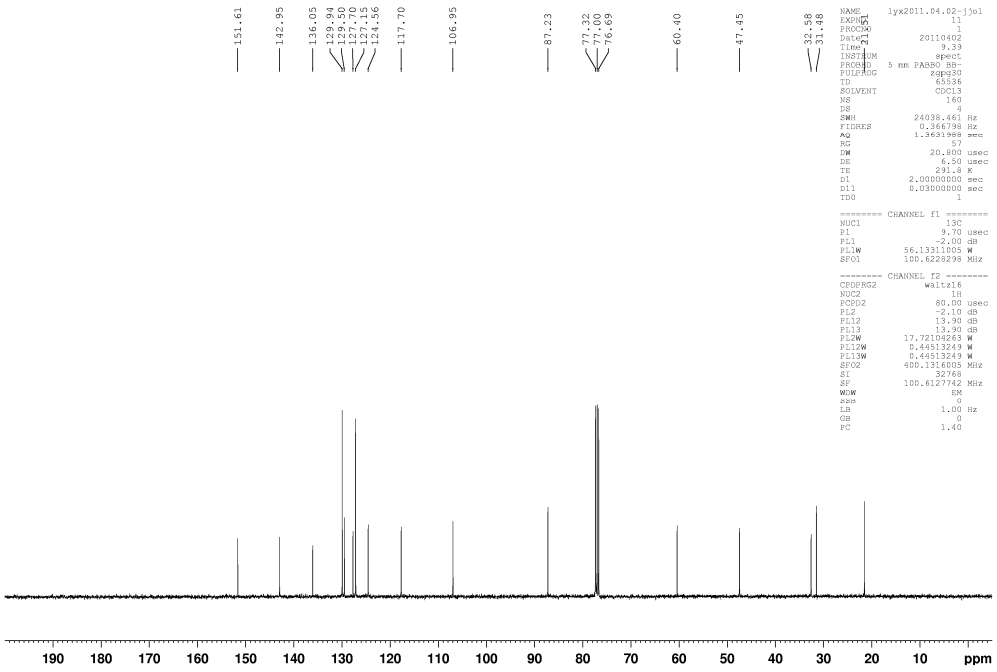

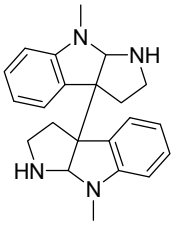

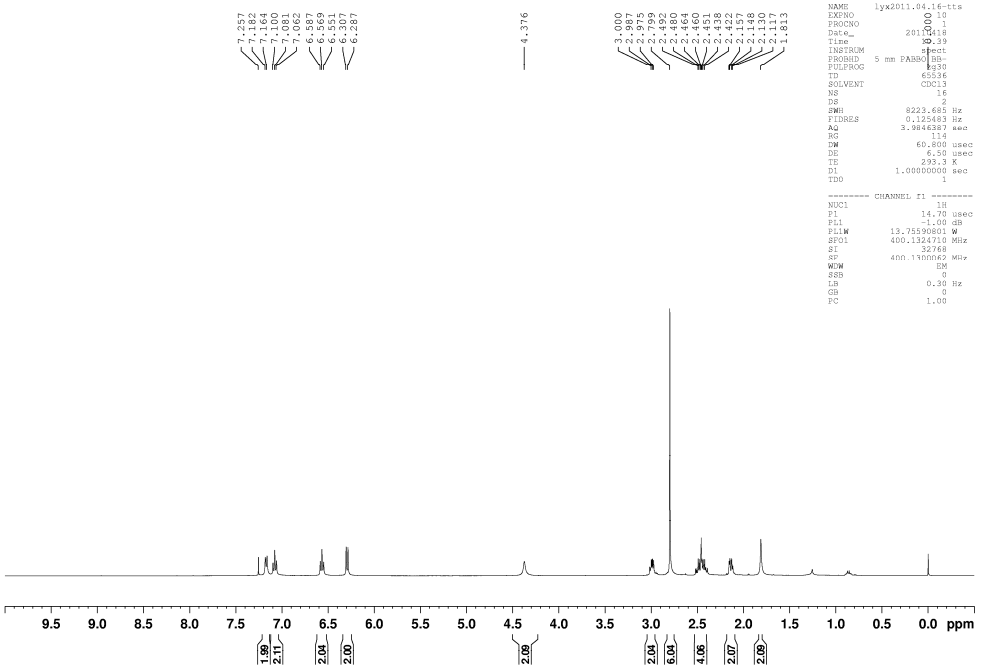

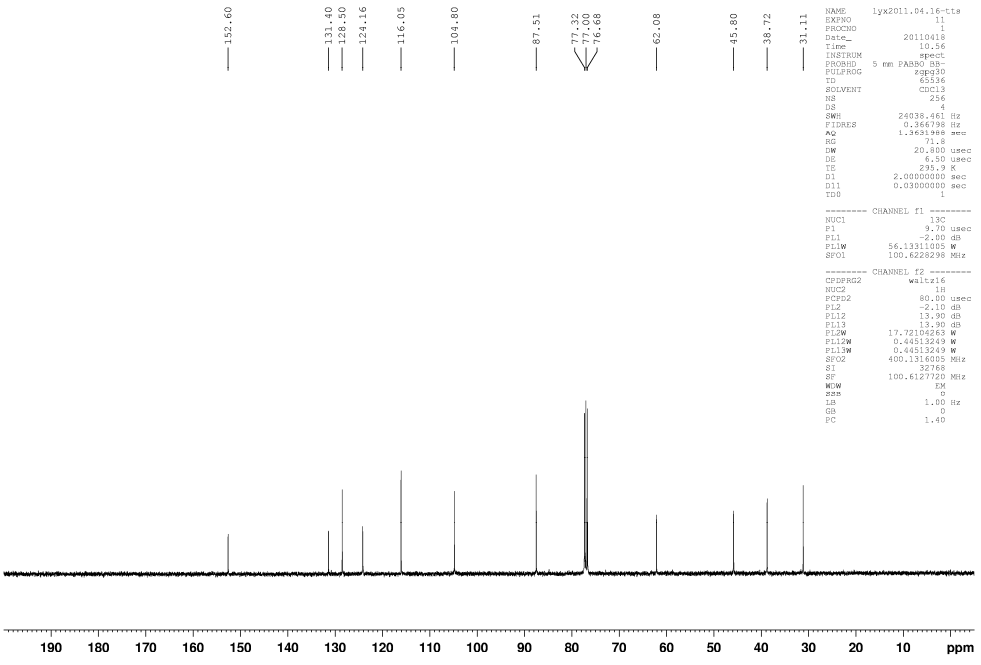

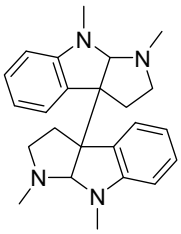

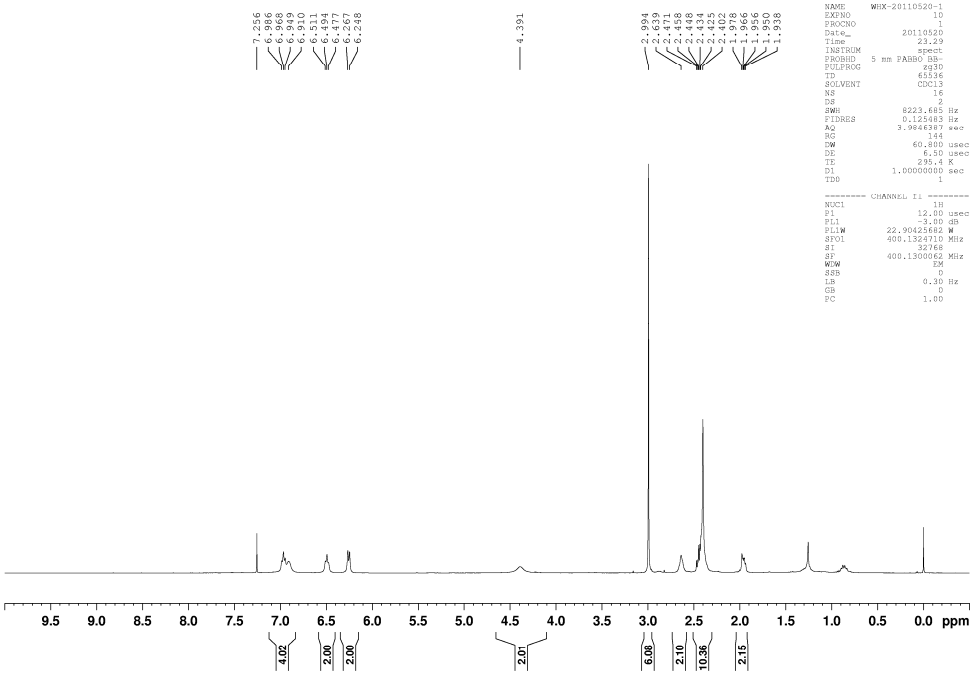

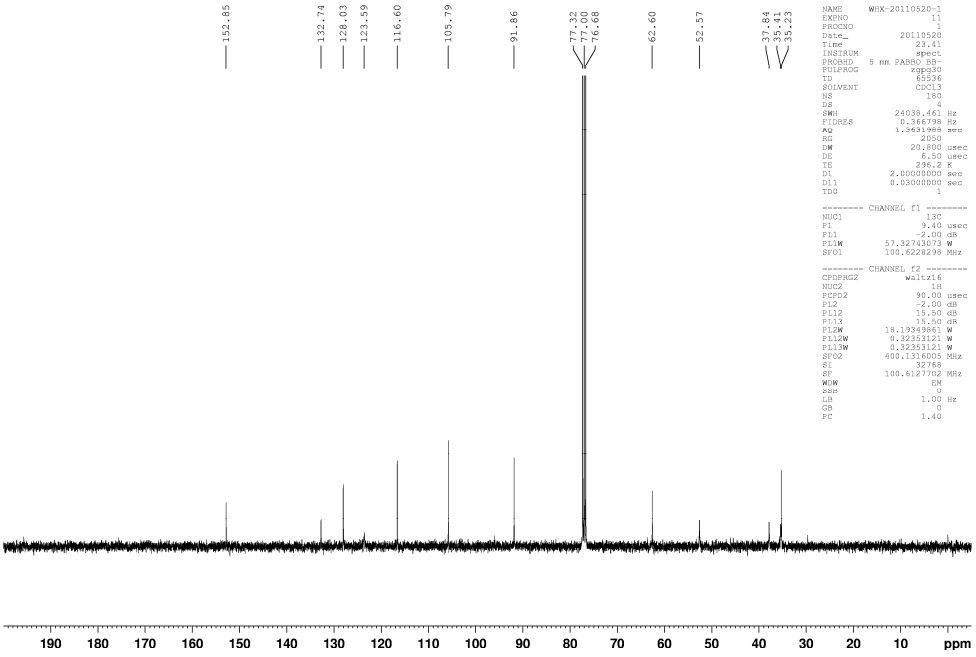

(1) C. A. Merlic; Y. You; D. M. Mclnnes; A. L. Zechman; M. M. Miller; Q. Deng, *Tetrahedron* 2001, 57, 5199−5212.
(2) K. K. Park, J. J. Lee, J. Ryu, *Tetrahedron, 2003, 59, 7651-7659.*