Supporting Information

Rhodium(III)-Catalyzed Regio- and Stereoselective C-H Allylation of Arenes with Vinyl Benzoxazinanones

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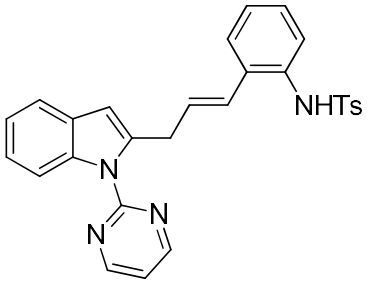
I. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. *N*-(2-pyrimidinyl)-indoles[1], 2-phenylpyridine derivatives[2] and vinyl benzoxazinanones[3] were prepared by literature reports. $[RhCp^*Cl_2]_2$ was prepared from $RhCl_3 \cdot xH_2O$ according to a literature procedure.[4] All reactions were carried out using Schlenk techniques or in a nitrogen-filled glove box. NMR spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Q-TOF analyzer. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

II. Experimental Procedure for the Synthesis of compound 3

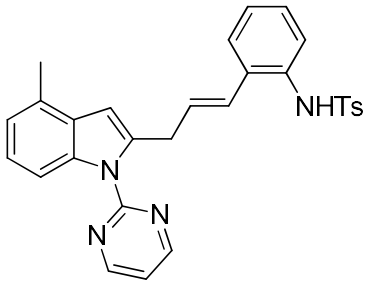
N-(2-pyrimidinyl)-indole **1** (0.2 mmol), vinyl benzoxazinanone **2** (0.24 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (30 mol %), and MeOH (2 mL) were charged into a pressure tube. The reaction mixture was stirred at 45 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product **3**.



3aa, 91%

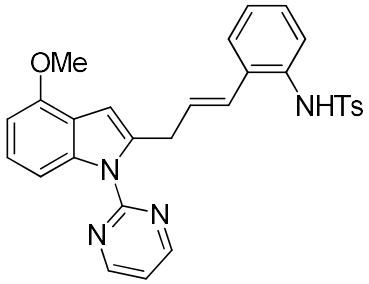
Product **3aa** was obtained as a white solid in 91% yield (87.4 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 4.7 Hz, 2H), 8.18 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.4 Hz,

1H), 7.43 (d, J = 7.9 Hz, 1H), 7.33 – 7.20 (m, 4H), 7.18 – 7.11 (m, 2H), 7.08 (d, J = 7.0 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.73 (s, 1H), 6.67 (d, J = 7.9 Hz, 2H), 6.44 (s, 1H), 5.94 (dt, J = 15.6, 5.1 Hz, 1H), 5.67 (d, J = 15.8 Hz, 1H), 3.92 (d, J = 4.3 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.1, 143.5, 138.0, 137.4, 136.4, 133.4, 133.1, 132.4, 129.4, 129.2, 128.1, 127.3, 126.8, 126.2, 125.6, 125.1, 123.2, 122.0, 120.0, 118.0, 113.6, 107.0, 32.2, 21.5. HRMS: $[M + H]^+$ calculated for $C_{28}H_{25}N_4O_2S$: 481.1698, found 481.1697.



3ba, 84%

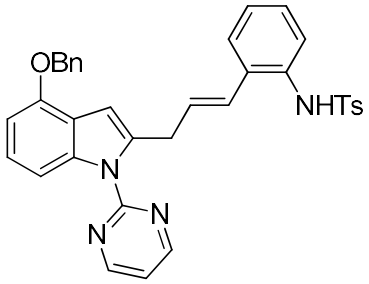
Product **3ba** was obtained as a white solid in 84% yield (83.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 4.8 Hz, 2H), 7.99 (d, J = 8.3 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.09 – 7.01 (m, 3H), 6.72 (s, 1H), 6.61 (d, J = 8.1 Hz, 2H), 6.48 (s, 1H), 5.94 (dt, J = 15.8, 5.2 Hz, 1H), 5.60 (d, J = 15.8 Hz, 1H), 3.93 (dd, J = 5.0, 1.3 Hz, 2H), 2.59 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.3, 143.3, 137.3, 137.2, 136.4, 133.5, 133.4, 132.4, 129.4, 129.3, 128.8, 128.1, 127.4, 126.8, 126.1, 125.5, 125.1, 123.3, 122.4, 118.2, 111.1, 105.4, 32.1, 21.5, 18.8. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1853.



3ca, 87%

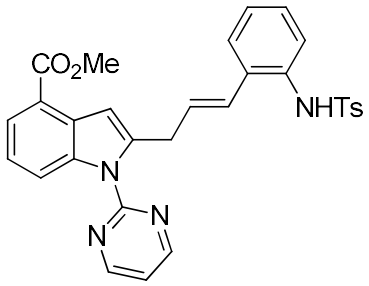
Product **3ca** was obtained as a white solid in 87% yield (88.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 4.8 Hz, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.13 (m, 4H), 7.10 – 7.01 (m, 2H), 6.74 – 6.67 (m, 4H), 6.55 (s, 1H), 5.93 (dt, J = 15.8, 5.2 Hz, 1H), 5.57 (d, J = 15.8 Hz, 1H), 4.01 (s, 3H), 3.89 (d, J = 4.5 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0,

158.3, 152.7, 143.5, 138.8, 136.4, 136.3, 133.5, 133.2, 132.4, 129.5, 128.2, 127.3, 126.8, 126.2, 125.6, 125.3, 124.0, 119.5, 118.2, 106.9, 103.9, 102.2, 55.5, 32.1, 21.5. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_3S$: 511.1804, found 511.1801.



3da, 80%

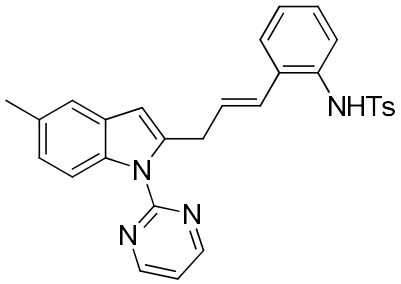
Product **3da** was obtained as a white solid in 80% yield (93.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.51 (d, *J* = 4.9 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.22 (m, 2H), 7.21 – 7.15 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.77 (t, *J* = 4.9 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 2H), 6.38 (s, 1H), 5.67 (dt, *J* = 15.8, 4.0 Hz, 1H), 5.52 (d, *J* = 15.8 Hz, 1H), 4.92 (s, 2H), 3.48 (dd, *J* = 3.7, 2.0 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 157.7, 146.3, 142.9, 137.0, 136.9, 136.6, 134.5, 131.9, 131.7, 130.6, 129.3, 128.9, 128.4, 128.2, 128.1, 128.0, 127.7, 127.1, 126.5, 125.6, 124.8, 121.5, 119.7, 113.5, 104.8, 104.3, 70.6, 29.9, 21.5. HRMS: $[M + H]^+$ calculated for $C_{35}H_{31}N_4O_3S$: 587.2117, found 587.2116.



3ea, 28%

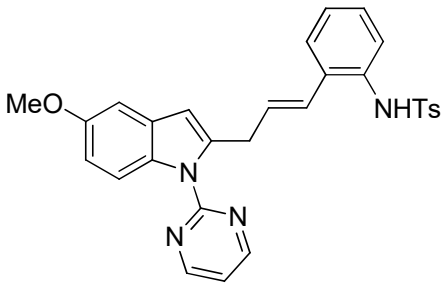
Product **3ea** was obtained as a white solid in 28% yield (30.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.09 – 8.01 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.27 (t, *J* = 4.9 Hz, 1H), 7.20 – 7.12 (m, 4H), 7.11 – 7.03 (m, 2H), 6.69 – 6.61 (m, 3H), 5.94 (dt, *J* = 15.8, 5.1 Hz, 1H), 5.55 (d, *J* = 15.9 Hz, 1H), 4.02 (s, 3H), 3.97 (dd, *J* = 5.0, 1.4 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 159.2, 157.9, 143.6, 140.2, 138.2, 136.4, 133.5, 132.7, 132.2, 129.4, 129.1, 128.3, 127.4, 126.7, 126.3, 125.9, 125.2, 125.1, 122.5, 121.1,

118.7, 118.0, 107.8, 52.0, 32.0, 21.5. HRMS: $[M + H]^+$ calculated for $C_{30}H_{27}N_4O_4S$: 539.1753, found 539.1754.



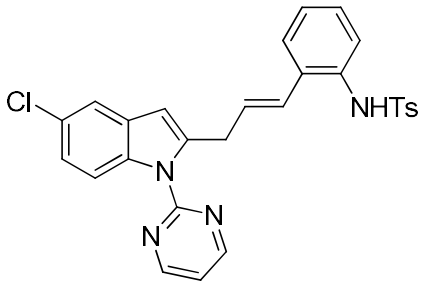
3fa, 82%

Product **3fa** was obtained as a white solid in 82% yield (81.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.11 (m, 3H), 7.10 – 7.01 (m, 2H), 6.69 (d, *J* = 8.1 Hz, 2H), 6.60 (s, 1H), 6.37 (s, 1H), 5.96 (dt, *J* = 15.8, 5.2 Hz, 1H), 5.64 (d, *J* = 15.8 Hz, 1H), 3.93 (d, *J* = 4.5 Hz, 2H), 2.50 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.3, 143.5, 138.0, 136.5, 135.8, 133.9, 133.5, 132.4, 131.4, 129.5, 128.2, 127.5, 126.9, 126.1, 125.5, 124.9, 124.6, 119.9, 117.8, 113.6, 107.0, 32.4, 21.55 (two carbons). HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1856.



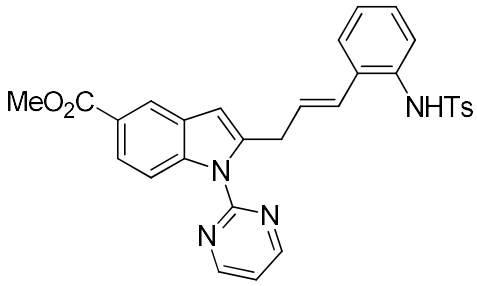
3ga, 88%

Product **3ga** was obtained as a white solid in 88% yield (89.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.3 Hz, 2H), 8.18 (d, *J* = 8.9 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.11 (dd, *J* = 21.8, 14.8 Hz, 6H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 6.38 (s, 1H), 5.98 (d, *J* = 15.6 Hz, 1H), 5.73 (d, *J* = 15.6 Hz, 1H), 3.94 (d, *J* = 3.9 Hz, 2H), 3.89 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.2, 155.7, 143.6, 138.9, 136.4, 133.41, 133.39, 132.4, 132.3, 130.0, 129.5, 128.2, 127.4, 127.0, 126.2, 125.6, 124.9, 117.6, 114.9, 112.1, 107.1, 102.6, 56.0, 32.7, 21.6. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_3S$: 511.1804, found 511.1805.



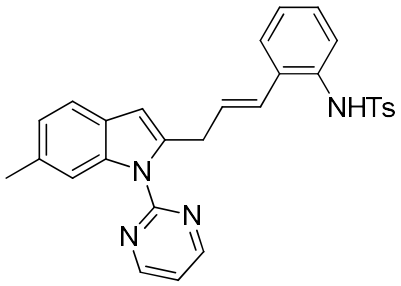
3ha, 69%

Product **3ha** was obtained as a white solid in 69% yield (70.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.7 Hz, 2H), 8.28 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.26 – 7.20 (m, 2H), 7.19 – 7.01 (m, 3H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.55 (s, 1H), 6.42 (s, 1H), 5.99 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.82 (d, *J* = 15.8 Hz, 1H), 3.95 (d, *J* = 5.1 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 157.9, 143.6, 139.8, 136.5, 135.7, 133.4, 132.6, 132.3, 130.3, 129.5, 128.3, 127.6, 127.4, 126.9, 126.3, 126.0, 125.0, 123.2, 119.5, 118.3, 115.0, 106.4, 32.5, 21.6. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}ClN_4O_2S$: 515.1308, found 515.1309.



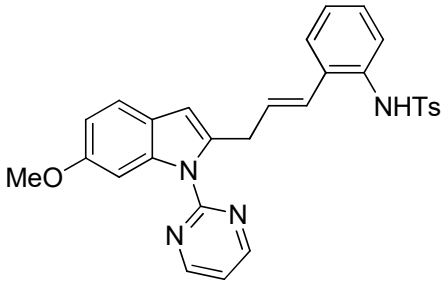
3ia, 44%

Product **3ia** was obtained as a white solid in 44% yield (47.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 1.5 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.99 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.20 – 7.10 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.79 – 6.70 (m, 3H), 6.51 (s, 1H), 5.96 (dt, *J* = 15.8, 5.5 Hz, 1H), 5.77 (d, *J* = 15.8 Hz, 1H), 3.95 (s, 3H), 3.93 (d, *J* = 5.5 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 159.0, 157.8, 143.6, 140.0, 139.8, 136.4, 133.4, 132.3, 132.2, 129.5, 128.8, 128.3, 127.3, 126.8, 126.3, 126.1, 125.2, 124.5, 123.9, 122.6, 118.6, 113.2, 107.3, 52.1, 32.3, 21.5. HRMS: $[M + H]^+$ calculated for $C_{30}H_{27}N_4O_4S$: 539.1753, found 539.1755.



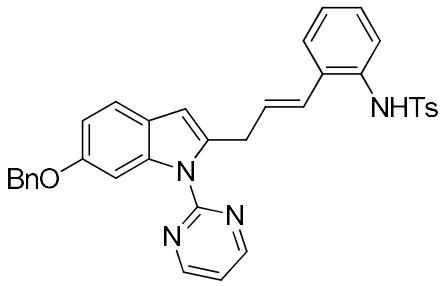
3ja, 86%

Product **3ja** was obtained as a white solid in 86% yield (85.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.8 Hz, 2H), 7.99 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.73 (s, 1H), 6.69 (d, *J* = 8.1 Hz, 2H), 6.38 (s, 1H), 5.93 (dt, *J* = 15.8, 5.3 Hz, 1H), 5.67 (d, *J* = 15.8 Hz, 1H), 3.89 (d, *J* = 4.5 Hz, 2H), 2.51 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.2, 143.5, 137.8, 137.3, 136.4, 133.4, 133.3, 133.0, 132.4, 129.4, 128.1, 127.4, 126.9, 126.9, 126.1, 125.6, 125.0, 123.6, 119.7, 117.9, 113.6, 106.9, 32.3, 22.2, 21.5. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1855.



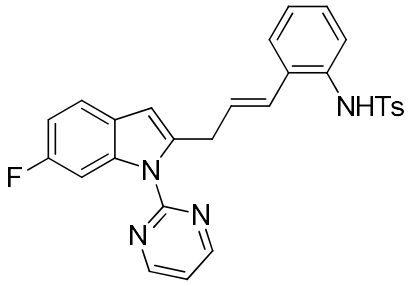
3ka, 91%

Product **3ka** was obtained as a white solid in 91% yield (92.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.8 Hz, 2H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.12 (m, 2H), 7.10 – 7.01 (m, 2H), 6.93 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 3.1 Hz, 1H), 6.38 (s, 1H), 5.93 (dt, *J* = 15.8, 5.3 Hz, 1H), 5.66 (d, *J* = 15.7 Hz, 1H), 3.90 (m, 5H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.3, 157.3, 143.5, 138.3, 136.9, 136.4, 133.5, 132.4, 129.5, 128.1, 127.4, 126.9, 126.1, 125.5, 124.9, 123.3, 120.4, 117.9, 111.2, 107.0, 98.3, 56.0, 32.4, 21.6. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_3S$: 511.1804, found 511.1801.



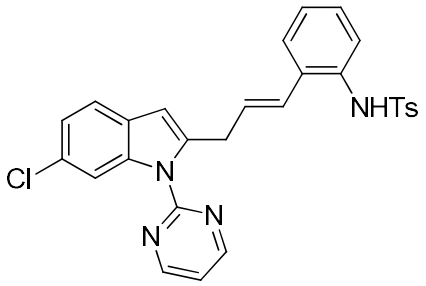
3la, 76%

Product **3la** was obtained as a white solid in 76% yield (89.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 7.92 (s, 1H), 7.52 – 7.41 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.18 – 7.12 (m, 2H), 7.11 – 7.02 (m, 2H), 6.99 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 2H), 6.66 (d, *J* = 5.3 Hz, 1H), 6.37 (s, 1H), 5.93 (dt, *J* = 15.7, 5.3 Hz, 1H), 5.67 (d, *J* = 15.6 Hz, 1H), 5.15 (s, 2H), 3.90 (d, *J* = 4.8 Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.2, 156.4, 143.5, 138.2, 137.6, 137.1, 136.4, 133.5, 133.4, 132.4, 129.5, 128.7, 128.1, 128.0, 127.8, 127.4, 126.9, 126.2, 125.5, 125.0, 123.5, 120.4, 117.9, 111.9, 107.0, 99.9, 71.0, 32.5, 21.5. HRMS: $[M + H]^+$ calculated for $C_{35}H_{31}N_4O_3S$: 587.2117, found 587.2119.



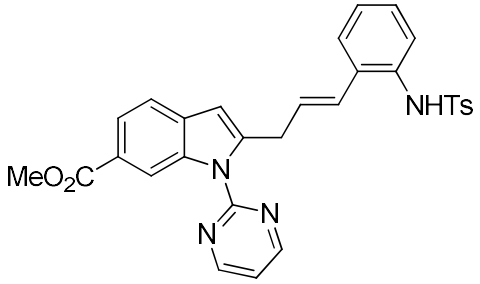
3ma, 71%

Product **3ma** was obtained as a white solid in 71% yield (70.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.02 (dd, *J* = 10.8, 1.9 Hz, 1H), 7.48 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.09 – 6.97 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.58 (s, 1H), 6.41 (s, 1H), 5.99 (dt, *J* = 15.8, 5.5 Hz, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 3.94 (d, *J* = 5.2 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, *J* = 236.4 Hz), 158.8, 158.0, 143.7, 138.9 (d, *J* = 3.7 Hz), 137.4 (d, *J* = 12.7 Hz), 136.5, 133.4, 133.0, 132.4, 129.5, 128.2, 127.4, 127.0, 126.3, 125.8, 125.6, 124.9, 120.4 (d, *J* = 9.8 Hz), 118.1, 113 (d, *J* = 24.2 Hz), 106.8, 101.3(d, *J* = 28.4 Hz), 32.7, 21.6. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}FN_4O_2S$: 499.1604, found 499.1603.



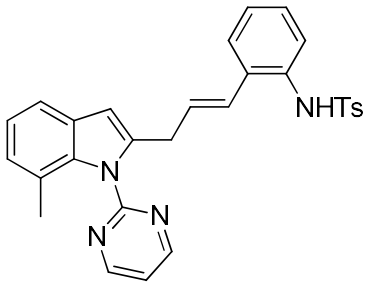
3na, 71%

Product **3na** was obtained as a white solid in 71% yield (73.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.6 Hz, 2H), 8.28 (s, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.27 – 7.19 (m, 2H), 7.18 – 7.10 (m, 2H), 7.08 – 7.01 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.58 (s, 1H), 6.41 (s, 1H), 5.99 (dt, *J* = 15.5, 5.2 Hz, 1H), 5.83 (d, *J* = 15.8 Hz, 1H), 3.94 (d, *J* = 4.8 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 157.9, 143.7, 139.3, 137.6, 136.5, 133.4, 132.8, 132.4, 129.5, 129.0, 128.3, 127.7, 127.4, 127.0, 126.3, 126.0, 124.9, 122.6, 120.7, 118.2, 114.2, 106.8, 32.7, 21.6. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}ClN_4O_2S$: 515.1308, found 515.1306.



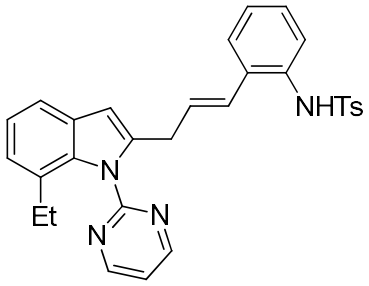
3oa, 55%

Product **3oa** was obtained as a white solid in 55% yield (59.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.8 Hz, 2H), 8.86 (s, 1H), 7.96 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.26 (t, *J* = 4.8 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.62 (s, 1H), 6.49 (s, 1H), 6.00 (dt, *J* = 15.8, 5.6 Hz, 1H), 5.84 (d, *J* = 15.8 Hz, 1H), 3.96 (d, *J* = 5.5 Hz, 2H), 3.94 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.0, 157.8, 143.7, 141.9, 136.7, 136.5, 133.4, 132.9, 132.4, 132.3, 129.5, 128.3, 127.4, 127.0, 126.3, 126.2, 125.1, 124.8, 123.3, 119.7, 118.5, 115.8, 106.8, 52.2, 32.6, 21.6. HRMS: $[M + H]^+$ calculated for $C_{30}H_{27}N_4O_4S$: 539.1753, found 539.1755.



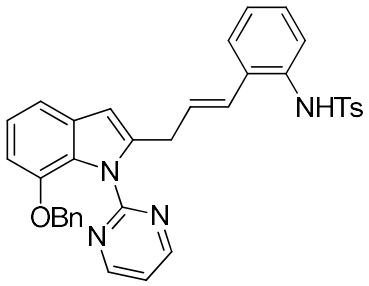
3pa, 78%

Product **3pa** was obtained as a white solid in 78% yield (77.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.9 Hz, 2H), 8.50 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 4.9 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.03 – 6.96 (m, 4H), 6.48 (d, *J* = 8.1 Hz, 2H), 6.44 (s, 1H), 5.69 (dt, *J* = 15.8, 4.1 Hz, 1H), 5.52 (d, *J* = 15.8 Hz, 1H), 3.52 (dd, *J* = 3.9, 2.0 Hz, 2H), 2.16 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 158.8, 143.0, 137.3, 137.2, 136.6, 134.3, 131.8, 131.8, 129.3, 129.2, 128.2, 127.6, 127.2, 126.5, 125.6, 125.6, 124.4, 121.8, 121.4, 120.5, 118.4, 105.0, 30.2, 21.5, 19.6. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1857.



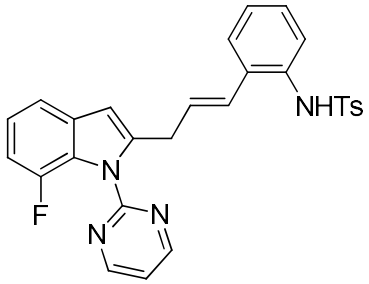
3qa, 71%

Product **3qa** was obtained as a white solid in 71% yield (72.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.9 Hz, 2H), 8.25 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 4.9 Hz, 1H), 7.24 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.21 – 7.12 (m, 2H), 7.05 – 6.97 (m, 4H), 6.52 (d, *J* = 8.1 Hz, 2H), 6.45 (s, 1H), 5.69 (dt, *J* = 15.8, 4.2 Hz, 1H), 5.51 (dt, *J* = 15.8, 1.9 Hz, 1H), 3.53 (dd, *J* = 4.0, 1.9 Hz, 2H), 2.35 (q, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 158.9, 143.1, 137.3, 136.6, 136.6, 134.2, 131.8, 131.7, 129.5, 129.4, 128.2, 128.2, 127.4, 127.2, 126.5, 125.7, 124.5, 123.3, 121.5, 120.5, 118.3, 105.3, 30.4, 25.3, 21.5, 14.1. HRMS: $[M + H]^+$ calculated for $C_{30}H_{29}N_4O_2S$: 509.2011, found 509.2010.



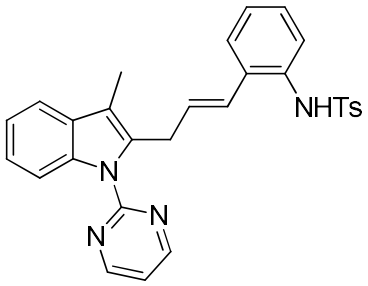
3ra, 59%

Product **3ra** was obtained as a white solid in 59% yield (69.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.51 (d, *J* = 4.9 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.24 (dd, *J* = 4.9, 3.1 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.77 (t, *J* = 4.9 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 2H), 6.38 (s, 1H), 5.67 (dt, *J* = 15.8, 4.0 Hz, 1H), 5.52 (d, *J* = 15.8 Hz, 1H), 4.92 (s, 2H), 3.48 (dd, *J* = 3.7, 2.0 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 157.7, 146.3, 142.9, 137.0, 136.9, 136.6, 134.5, 131.9, 131.7, 130.6, 129.3, 128.9, 128.4, 128.2, 128.1, 128.0, 127.7, 127.1, 126.5, 125.6, 124.8, 121.5, 119.7, 113.5, 104.8, 104.3, 70.6, 29.9, 21.5. HRMS: $[M + H]^+$ calculated for $C_{35}H_{31}N_4O_3S$: 587.2117, found 587.2118.



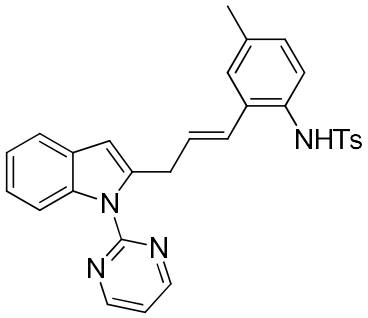
3sa, 66%

Product **3sa** was obtained as a white solid in 66% yield (65.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.8 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 4.8 Hz, 1H), 7.22 – 7.14 (m, 4H), 7.06 – 6.95 (m, 3H), 6.64 (d, *J* = 7.9 Hz, 2H), 6.46 (s, 1H), 5.79 (dt, *J* = 15.8, 4.5 Hz, 1H), 5.54 (d, *J* = 15.9 Hz, 1H), 3.67 (d, *J* = 2.9 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 157.9, 149.9 (d, *J* = 245.9 Hz), 143.3, 138.7, 136.7, 133.9, 132.5 (d, *J* = 4.2 Hz), 131.9, 131.6, 129.3, 128.3, 127.2, 126.9, 126.6, 126.0, 125.5 (d, *J* = 9.3 Hz), 125.0, 121.7 (d, *J* = 6.6 Hz), 120.0, 116.1 (d, *J* = 3.5 Hz), 109.0 (d, *J* = 18.2 Hz), 105.5 (d, *J* = 1.8 Hz), 30.4, 21.5. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}FN_4O_2S$: 499.1604, found 499.1606.



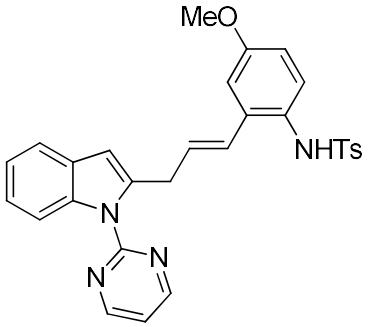
3ta, 85%

Product **3ta** was obtained as a white solid in 85% yield (84.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.18 – 8.10 (m, 1H), 7.61 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.18 – 7.11 (m, 2H), 7.06 – 6.99 (m, 4H), 6.87 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 5.86 (dt, *J* = 15.8, 4.7 Hz, 1H), 5.41 (d, *J* = 15.9 Hz, 1H), 3.87 (dd, *J* = 4.6, 1.7 Hz, 2H), 2.24 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.2, 143.2, 136.7, 136.3, 133.6, 133.4, 132.7, 132.5, 130.2, 129.3, 128.0, 127.3, 126.7, 126.0, 125.2, 125.1, 123.5, 121.7, 118.3, 117.9, 113.8, 113.2, 28.8, 21.5, 8.9. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1855.



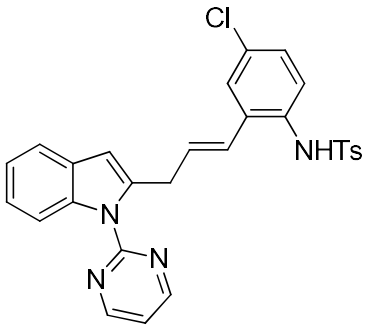
3ab, 91%

Product **3ab** was obtained as a white solid in 91% yield (89.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.21 (m, 5H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.92 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.60 (s, 1H), 6.43 (s, 1H), 5.94 (dt, *J* = 15.8, 5.4 Hz, 1H), 5.67 (d, *J* = 15.8 Hz, 1H), 3.91 (d, *J* = 4.9 Hz, 2H), 2.21 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.2, 143.4, 138.2, 137.4, 136.4, 136.1, 132.5, 132.5, 130.7, 129.4, 129.2, 128.9, 127.7, 126.9, 125.8, 125.6, 123.1, 122.0, 120.0, 118.0, 113.6, 106.9, 32.3, 21.5, 21.0. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1856.



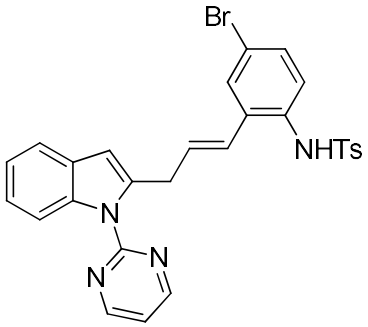
3ac, 88%

Product **3ac** was obtained as a white solid in 88% yield (89.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.32 – 7.19 (m, 5H), 7.16 (dd, *J* = 6.3, 3.0 Hz, 1H), 6.76 – 6.64 (m, 4H), 6.53 (d, *J* = 3.6 Hz, 1H), 6.42 (s, 1H), 5.96 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.68 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 5.0 Hz, 2H), 3.71 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.2, 158.1, 143.4, 138.1, 137.5, 136.4, 134.9, 132.6, 129.4, 129.2, 128.1, 127.0, 126.2, 125.9, 123.2, 122.1, 120.1, 118.0, 113.7, 113.6, 111.8, 107.0, 55.5, 32.3, 21.5. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_3S$: 511.1804, found 511.1803.



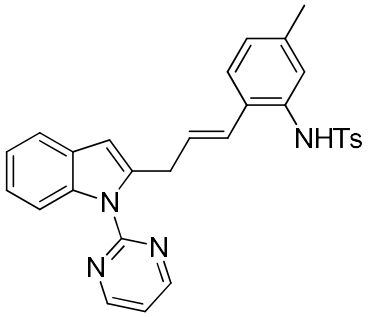
3ad, 84%

Product **3ad** was obtained as a white solid in 84% yield (86.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.33 – 7.17 (m, 5H), 7.13 – 7.04 (m, 2H), 6.77 (s, 1H), 6.67 (d, *J* = 8.1 Hz, 2H), 6.43 (s, 1H), 5.96 (dt, *J* = 15.8, 5.2 Hz, 1H), 5.56 (d, *J* = 15.8 Hz, 1H), 3.91 (d, *J* = 4.6 Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.1, 143.7, 137.5, 137.4, 136.1, 134.4, 134.1, 132.0, 131.7, 129.5, 129.1, 128.0, 127.1, 126.8, 126.6, 124.6, 123.3, 122.1, 120.1, 118.1, 113.6, 107.1, 32.1, 21.5. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}ClN_4O_2S$: 515.1308, found 515.1309.



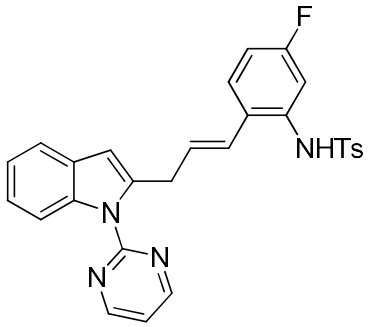
3ae, 83%

Product **3ae** was obtained as a white solid in 83% yield (92.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.33 – 7.16 (m, 8H), 6.79 (s, 1H), 6.66 (d, *J* = 8.1 Hz, 2H), 6.43 (s, 1H), 5.95 (dt, *J* = 15.8, 5.2 Hz, 1H), 5.56 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 4.2 Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.1, 143.7, 137.5, 137.4, 136.1, 134.4, 134.3, 132.6, 131.0, 130.0, 129.5, 129.1, 126.8, 126.7, 124.5, 123.3, 122.1, 120.1, 119.6, 118.1, 113.6, 107.1, 32.1, 21.5. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}BrN_4O_2S$: 559.0803, found 559.0803.



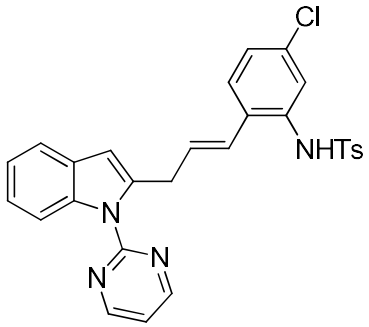
3af, 89%

Product **3af** was obtained as a white solid in 89% yield (87.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.22 (m, 5H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 2H), 6.64 (s, 1H), 6.43 (s, 1H), 5.89 (dt, *J* = 15.8, 5.4 Hz, 1H), 5.60 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 5.0 Hz, 2H), 2.26 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.2, 143.4, 138.2, 138.1, 137.4, 136.5, 133.2, 132.2, 129.5, 129.4, 129.2, 127.1, 127.0, 126.9, 125.7, 125.5, 123.1, 122.0, 120.0, 118.0, 113.6, 106.9, 32.2, 21.5, 21.3. HRMS: $[M + H]^+$ calculated for $C_{29}H_{27}N_4O_2S$: 495.1855, found 495.1857.



3ag, 87%

Product **3ag** was obtained as a white solid in 87% yield (86.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.19 (m, 6H), 7.00 (dd, *J* = 8.5, 6.3 Hz, 1H), 6.86 (s, 1H), 6.73 (td, *J* = 8.3, 2.5 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 2H), 6.46 (s, 1H), 5.89 (dt, *J* = 15.8, 5.1 Hz, 1H), 5.55 (d, *J* = 15.8 Hz, 1H), 3.93 (d, *J* = 4.4 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.0 Hz), 159.0, 158.2, 143.8, 137.7, 137.5, 136.2, 135.0 (d, *J* = 10.8 Hz), 133.7 (d, *J* = 1.2 Hz), 129.6, 129.2, 128.7 (d, *J* = 9.0 Hz), 127.6 (d, *J* = 3.3 Hz), 126.8, 124.8, 123.3, 122.1, 120.1, 118.2, 113.6, 112.8 (d, *J* = 21.4 Hz), 111.1 (d, *J* = 25.1 Hz), 107.1, 32.1, 21.6. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}FN_4O_2S$: 499.1604, found 499.1602.

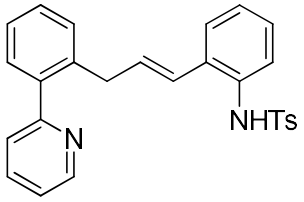


3ah, 87%

Product **3ah** was obtained as a white solid in 87% yield (89.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.50 (s, 1H), 7.35 – 7.18 (m, 5H), 7.03 – 6.95 (m, 2H), 6.81 (s, 1H), 6.67 (d, *J* = 8.1 Hz, 2H), 6.45 (s, 1H), 5.93 (dt, *J* = 15.8, 5.1 Hz, 1H), 5.54 (d, *J* = 15.8 Hz, 1H), 3.92 (d, *J* = 4.6 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.2, 143.8, 137.6, 137.5, 136.2, 134.6, 134.0, 133.6, 130.4, 129.6, 129.1, 128.4, 126.8, 126.1, 124.7, 124.5, 123.3, 122.1, 120.1, 118.2, 113.6, 107.1, 32.1, 21.6. HRMS: $[M + H]^+$ calculated for $C_{28}H_{24}ClN_4O_2S$: 515.1308, found 515.1309.

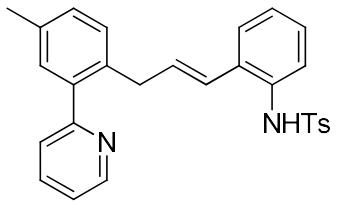
III. Experimental Procedure for the Synthesis of compound 5

Arene **4** (0.2 mmol), vinyl benzoxazinanone **2** (0.24 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (30 mol %), and MeOH (2 mL) were charged into a pressure tube. The reaction mixture was stirred at 45 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product **5**.



5a, 60%

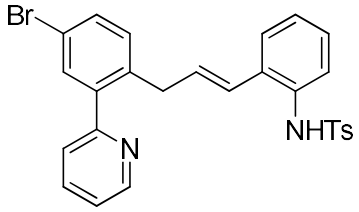
Product **5a** was obtained as a white solid in 60% yield (52.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.7 Hz, 1H), 8.63 (s, 1H), 7.73 (td, *J* = 7.7, 1.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.24 – 7.19 (m, 1H), 7.18 – 7.12 (m, 1H), 7.07 – 6.97 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.77 (dt, *J* = 15.8, 4.9 Hz, 1H), 5.61 (d, *J* = 15.8 Hz, 1H), 3.41 (dd, *J* = 4.8, 1.5 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 149.3, 143.0, 141.6, 137.1, 136.64, 136.62, 134.1, 133.3, 132.3, 130.7, 130.2, 129.4, 128.8, 127.9, 126.98, 126.96, 126.8, 125.8, 124.8, 124.2, 122.5, 37.0, 21.6. HRMS: $[M + H]^+$ calculated for $C_{27}H_{25}N_2O_2S$: 441.1637, found 441.1638.



5b, 84%

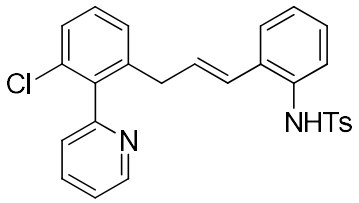
Product **5b** was obtained as a white solid in 84% yield (76.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.6 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.22 (m, 6H), 7.15 (t, *J* = 6.7 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.76 (dt, *J* = 15.7, 4.8 Hz, 1H), 5.60 (d, *J* = 15.8 Hz, 1H), 3.36 (d, *J* = 3.6 Hz, 2H), 2.49 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 149.2, 143.0, 141.4, 137.1, 136.6, 136.4, 134.0, 133.5, 133.4, 132.4, 130.8,

130.6, 129.5, 129.3, 127.8, 126.9, 126.81, 126.78, 125.8, 124.9, 124.1, 122.4, 36.5, 21.7, 21.3. HRMS: $[M + H]^+$ calculated for $C_{28}H_{27}N_2O_2S$: 455.1793, found 455.1791.



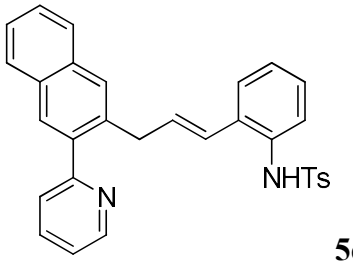
5c, 76%

Product **5c** was obtained as a white solid in 76% yield (78.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 1H), 8.53 (s, 1H), 7.75 (td, *J* = 7.7, 1.5 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.21 – 7.15 (m, 1H), 7.08 – 7.00 (m, 5H), 5.75 (dt, *J* = 15.8, 4.8 Hz, 1H), 5.52 (d, *J* = 15.8 Hz, 1H), 3.33 (dd, *J* = 4.6, 1.5 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 149.5, 143.3, 143.1, 137.1, 136.9, 135.6, 134.1, 132.8, 132.4, 132.3, 131.8, 129.5, 128.0, 127.3, 126.9, 126.7, 125.8, 125.0, 124.0, 122.9, 120.6, 36.4, 21.6. HRMS: $[M + H]^+$ calculated for $C_{27}H_{24}BrN_2O_2S$: 519.0742, found 519.0741.



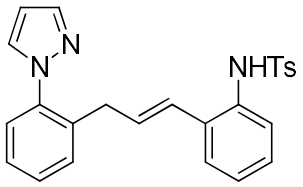
5d, 66%

Product **5d** was obtained as a white solid in 66% yield (62.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.75 (d, *J* = 4.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.28 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.05 – 6.93 (m, 4H), 5.69 (dt, *J* = 15.7, 4.5 Hz, 1H), 5.54 (d, *J* = 15.8 Hz, 1H), 3.20 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 149.5, 142.8, 139.8, 139.1, 137.5, 136.8, 134.4, 134.3, 132.5, 132.2, 129.6, 129.5, 128.9, 128.1, 128.0, 127.9, 126.9, 126.7, 125.6, 124.9, 124.8, 123.1, 37.3, 21.6. HRMS: $[M + H]^+$ calculated for $C_{27}H_{24}ClN_2O_2S$: 475.1247, found 475.1248.



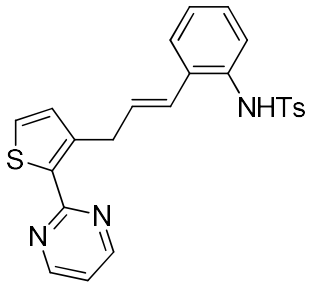
5e, 82%

Product **5e** was obtained as a white solid in 82% yield (80.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.69 (d, *J* = 4.5 Hz, 1H), 8.04 – 7.99 (m, 1H), 7.98 (s, 1H), 7.92 – 7.86 (m, 1H), 7.72 (td, *J* = 7.7, 1.6 Hz, 1H), 7.66 – 7.57 (m, 4H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.20 – 7.13 (m, 1H), 7.03 – 6.95 (m, 4H), 6.11 (d, *J* = 8.0 Hz, 2H), 5.73 (dt, *J* = 15.9, 4.4 Hz, 1H), 5.31 (d, *J* = 15.9 Hz, 1H), 3.51 (d, *J* = 2.2 Hz, 2H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 149.2, 142.5, 140.2, 136.9, 136.6, 134.3, 134.3, 133.9, 133.0, 132.8, 132.6, 129.4, 129.3, 128.8, 128.3, 127.83, 127.76, 127.5, 126.8, 126.6, 126.5, 126.3, 125.8, 125.7, 124.3, 122.6, 37.1, 21.3. HRMS: $[M + H]^+$ calculated for $C_{31}H_{27}N_2O_2S$: 491.1793, found 491.1794.



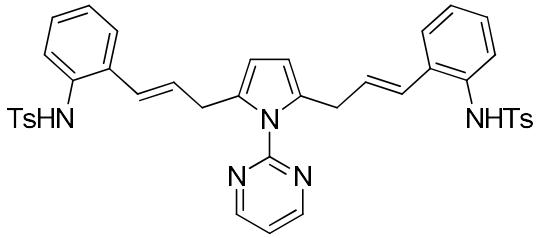
5f, 67%

Product **5f** was obtained as a white solid in 67% yield (57.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 4.5 Hz, 2H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.44 (s, 1H), 5.77 (dt, *J* = 15.6, 5.4 Hz, 1H), 5.64 (d, *J* = 15.8 Hz, 1H), 3.37 (d, *J* = 5.2 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.6, 140.2, 137.0, 135.5, 133.8, 132.2, 132.1, 131.4, 131.1, 129.5, 129.3, 128.0, 127.8, 127.6, 126.99, 126.96, 126.2, 125.9, 124.9, 106.7, 35.5, 21.6. HRMS: $[M + H]^+$ calculated for $C_{25}H_{24}N_3O_2S$: 430.1589, found 430.1589.



5g, 79%

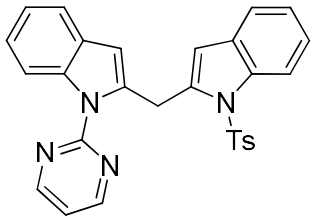
Product **5g** was obtained as a white solid in 79% yield (70.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.9 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 5.7 Hz, 2H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.17 – 7.03 (m, 5H), 6.94 (d, *J* = 5.1 Hz, 1H), 6.67 (s, 1H), 6.18 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.7, 6.2 Hz, 1H), 4.03 (d, *J* = 6.0 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 157.2, 143.8, 142.1, 136.9, 136.5, 134.1, 133.3, 132.6, 131.9, 129.6, 128.5, 128.0, 127.5, 127.2, 126.2, 125.0, 124.3, 118.2, 33.8, 21.6. HRMS: $[M + H]^+$ calculated for $C_{24}H_{22}N_3O_2S_2$: 448.1153, found 448.1154.



5h, 76%

Product **5h** was obtained as a white solid in 76% yield (108.7 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.53 (s, 2H), 8.94 (d, *J* = 4.8 Hz, 2H), 7.56 – 7.45 (m, 5H), 7.37 – 7.26 (m, 6H), 7.17 – 7.07 (m, 4H), 6.94 (d, *J* = 4.2 Hz, 2H), 6.40 (d, *J* = 15.6 Hz, 2H), 6.00 – 5.84 (m, 4H), 3.46 (d, *J* = 6.1 Hz, 4H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.4, 157.4, 143.4, 137.8, 134.5, 133.5, 132.2, 130.0, 129.2, 127.9, 127.8, 127.3, 127.2, 126.7, 126.3, 120.0, 108.3, 31.9, 21.4. HRMS: $[M + H]^+$ calculated for $C_{40}H_{38}N_5O_4S_2$: 716.2365, found 716.2364.

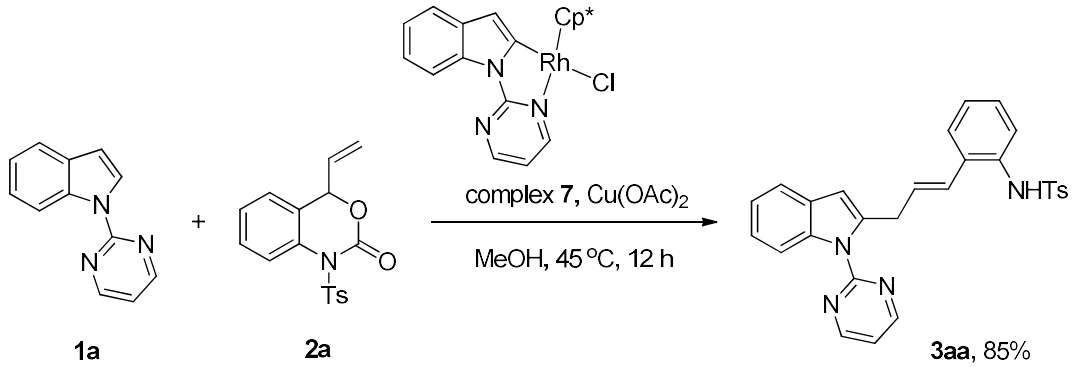
IV. Derivatization



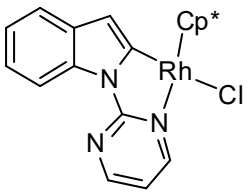
6, 59%

3aa (96 mg, 0.2 mmol), Ag_2CO_3 (1.3 equiv), and DMF (8 mL) were charged into a pressure tube. The reaction mixture was stirred at 150 °C for 2 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product **6** in 59% yield (white solid, 56.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.8 Hz, 2H), 8.38 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.21 – 7.11 (m, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.97 (t, J = 4.8 Hz, 1H), 6.31 (s, 1H), 6.12 (s, 1H), 5.00 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 158.1, 144.8, 139.8, 137.3, 137.13, 137.07, 136.5, 129.8, 129.5, 129.2, 126.6, 124.0, 123.4, 123.2, 122.1, 120.4, 120.2, 117.1, 114.62, 114.57, 109.9, 108.8, 30.0, 21.7. HRMS: $[M + H]^+$ calculated for $C_{28}H_{23}N_4O_2S$: 479.1542, found 479.1543.

V. Mechanism Studies

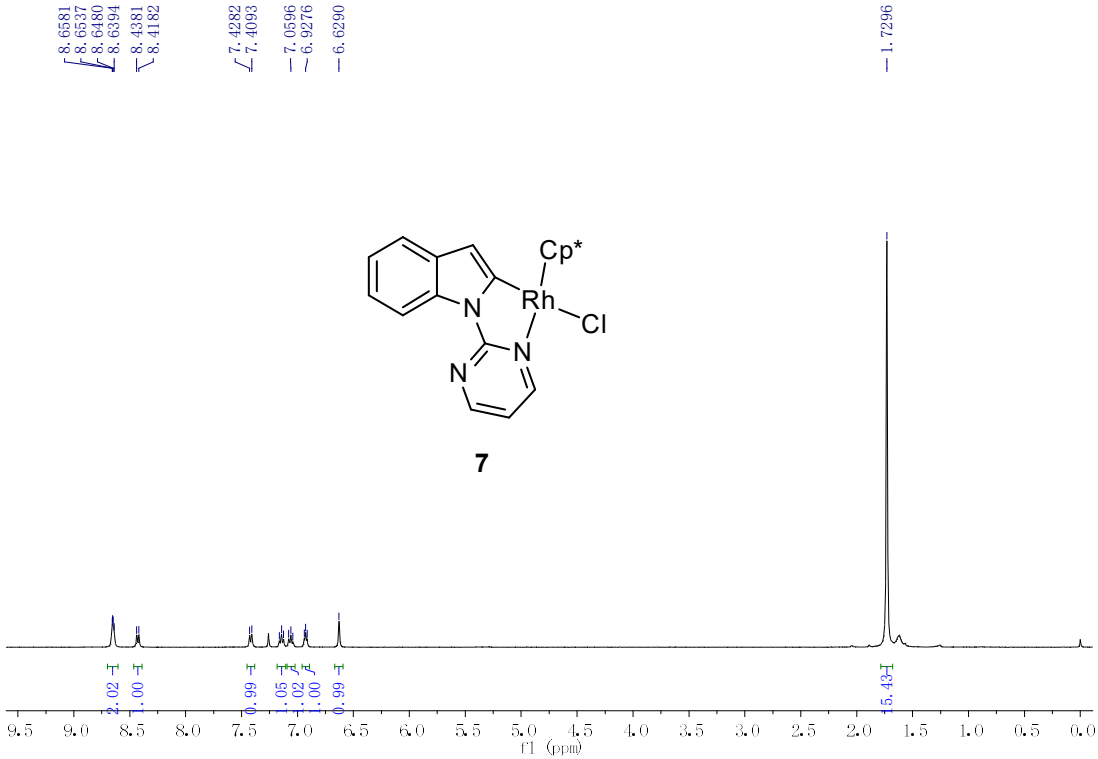


Based on the literature report,[5] complex **7** was synthesized to catalyze the coupling of **1a** (0.2 mol) with **2a** (0.24 mol) under the standard conditions (5 mol % of complex **7**), giving the product **3aa** in 85% yield.



complex **7**[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.9, 2.6 Hz, 2H), 8.43 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 5.0 Hz, 1H), 6.63 (s, 1H), 1.73 (s, 15H).



Reference

(1) Ackermann, L.;Lygin,A. V. *Org. Lett.*, **2011**, *13*, 3332.

(2) a) C. Liu, N. Han, X. Song, J. Qiu, *Eur. J. Org. Chem.* **2010**, *2010*, 5548; b) C. Liu, W. Yang, *Chem. commun.* **2009**, 6267; c) H. Mizuno, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2010**, *133*, 1251.

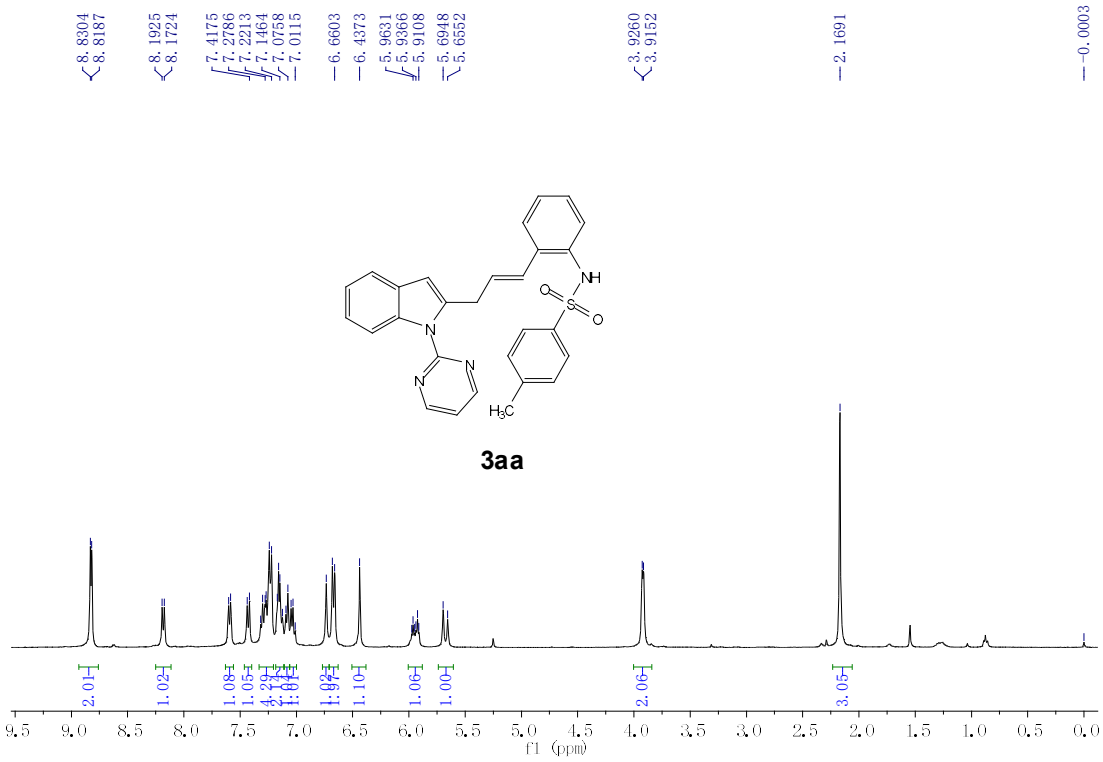
(3) a) Wang, C.; Tunge, J. A. *J. Am. Chem. Soc*. **2008**, *130*, 8118. b) Wang, Q.; Qi, X.; Lu, L.-Q.; Li, T.-R.; Yuan, Z.-G.; Zhang, K.; Li, B.-J.; Lan, Y.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2016**, *55*, 2840.

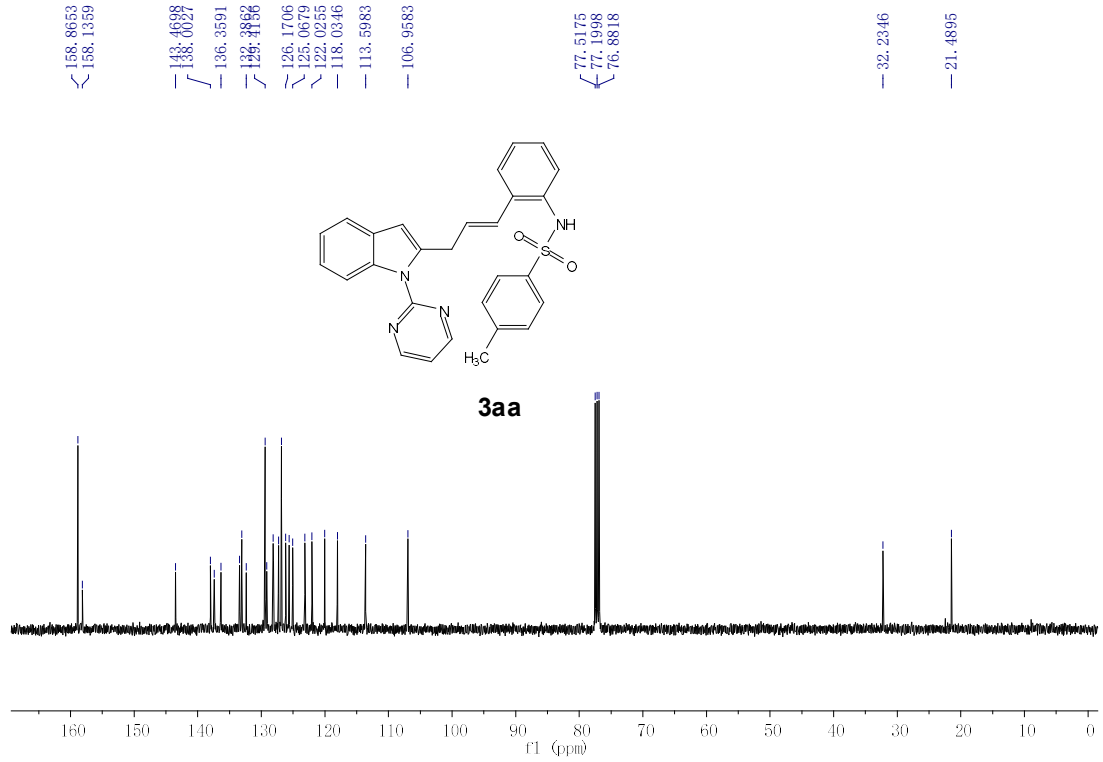
(4) Fujita, K.-i.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2004**, *6*, 2785.

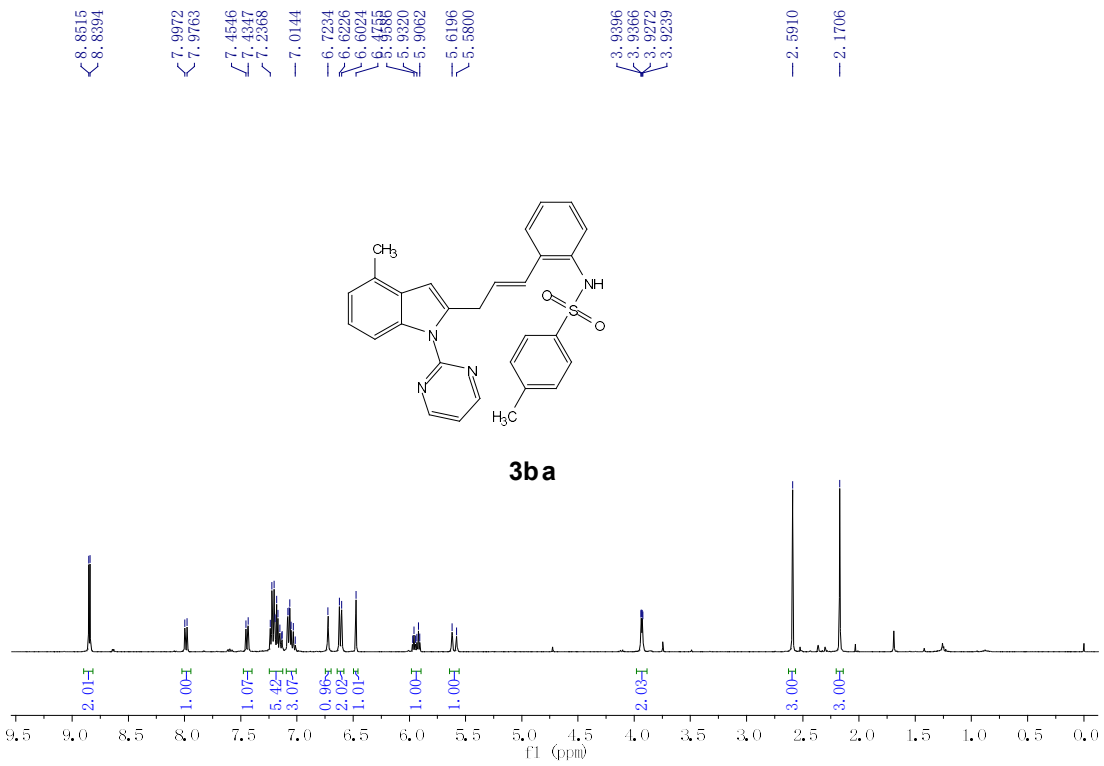
(5) Qin, X.; Liu, H.; Qin, D.; Wu, Q.; You, S.; Zhao, D.; Guo, Q.; Huang, X.; Lan, J.

Chem. Sci. **2013**, *4*, 1964.

VI. ^{1}H and ^{13}C NMR spectra



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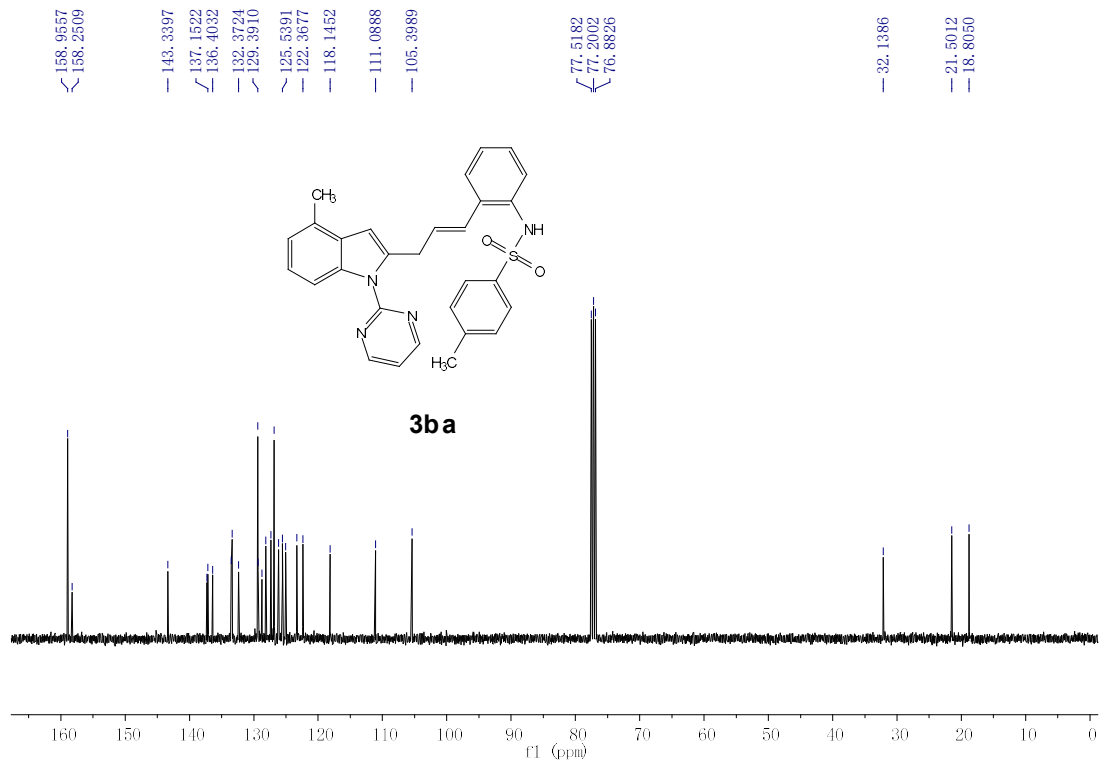
5.6196
5.5800
3.9396
3.9366
3.9272
3.9239
2.5910
2.1706
CH3
NH
O
S
O
N
N
N
H3C
3ba
2.01
1.00
1.07
5.42
3.07
0.96
2.02
1.01
1.00
1.00
2.03
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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105.3989
77.5182
77.2002
76.8826
32.1386
21.5012
18.8050
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N
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N
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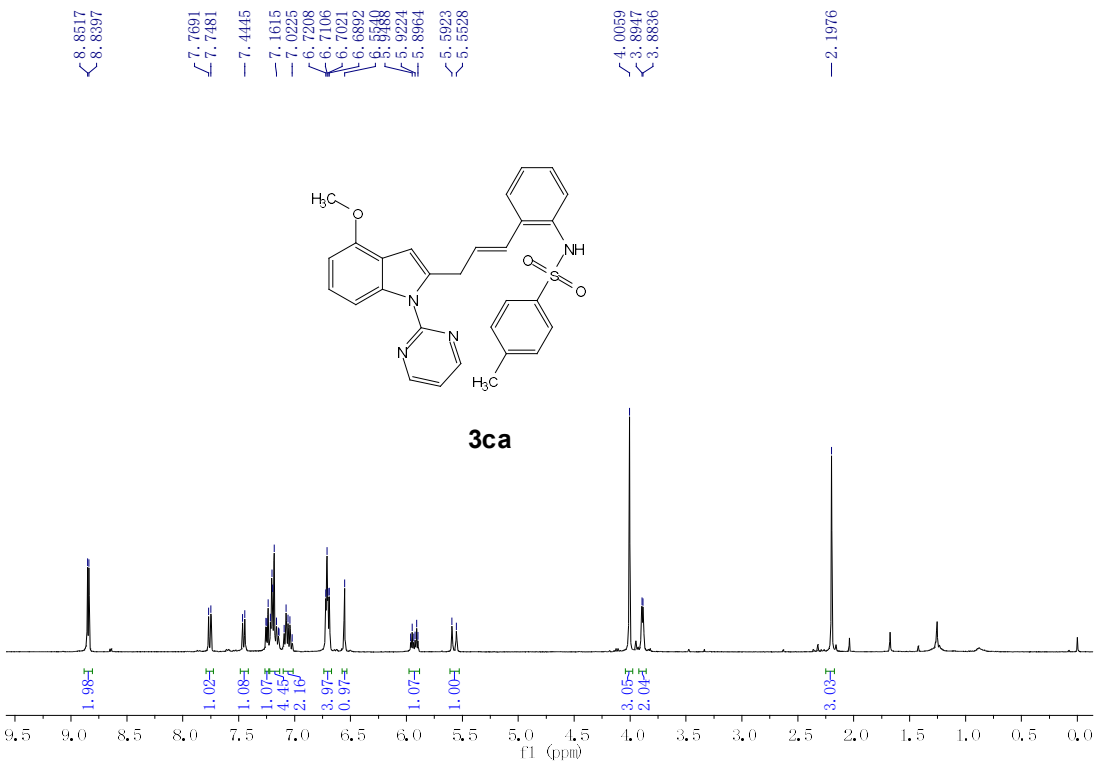
f1 (ppm)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7.0225
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5.5528
4.0059
3.8947
3.8836
2.1976
3ca
1.98
1.02
1.08
1.07
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2.16
3.97
0.97
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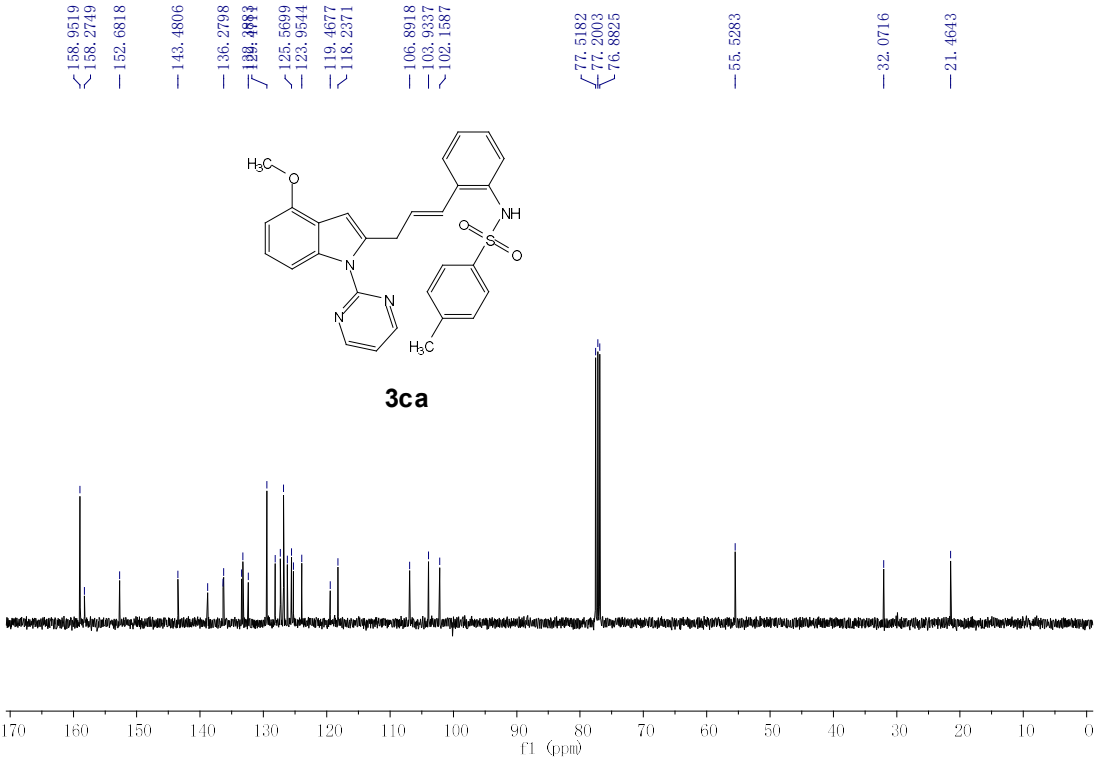
1.00
3.05
2.04
3.03
f1 (ppm)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152.6818
143.4806
136.2798
125.5699
123.9544
119.4677
118.2371
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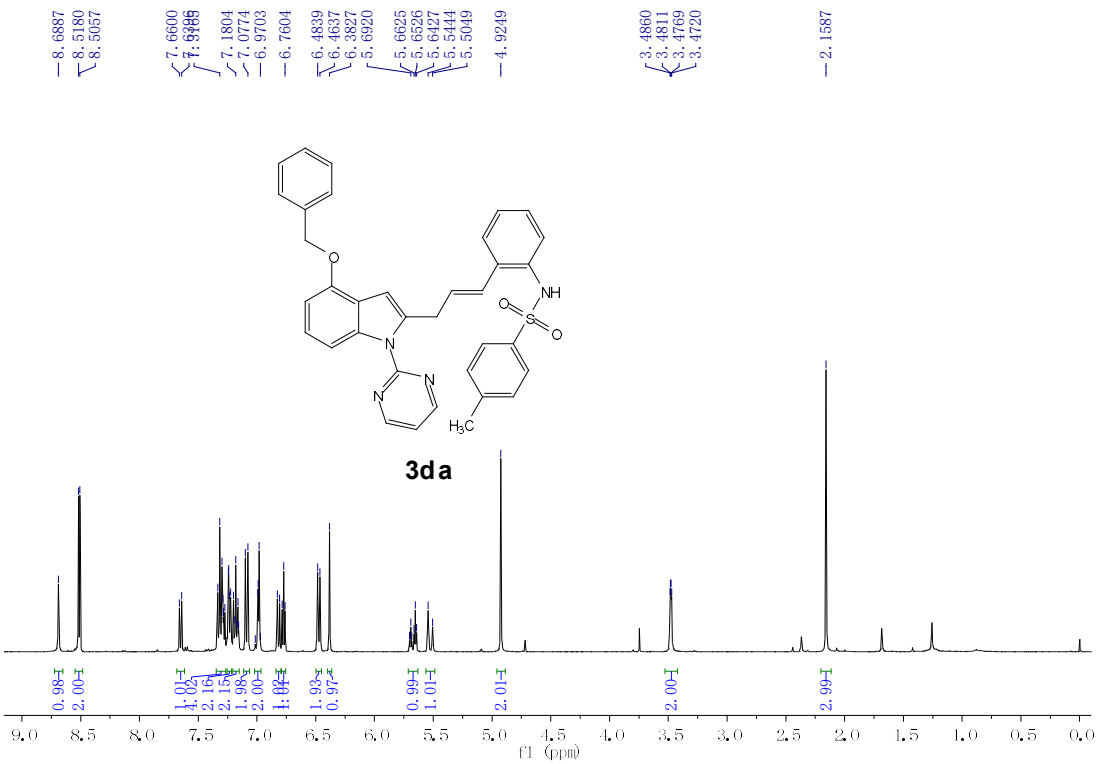
103.9337
102.1587
77.5182
77.2003
76.8825
55.5283
32.0716
21.4643
3ca
f1 (ppm)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6.4839
6.4637
6.3827
5.6920
5.6625
5.6526
5.6427
5.5444
5.5049
4.9249
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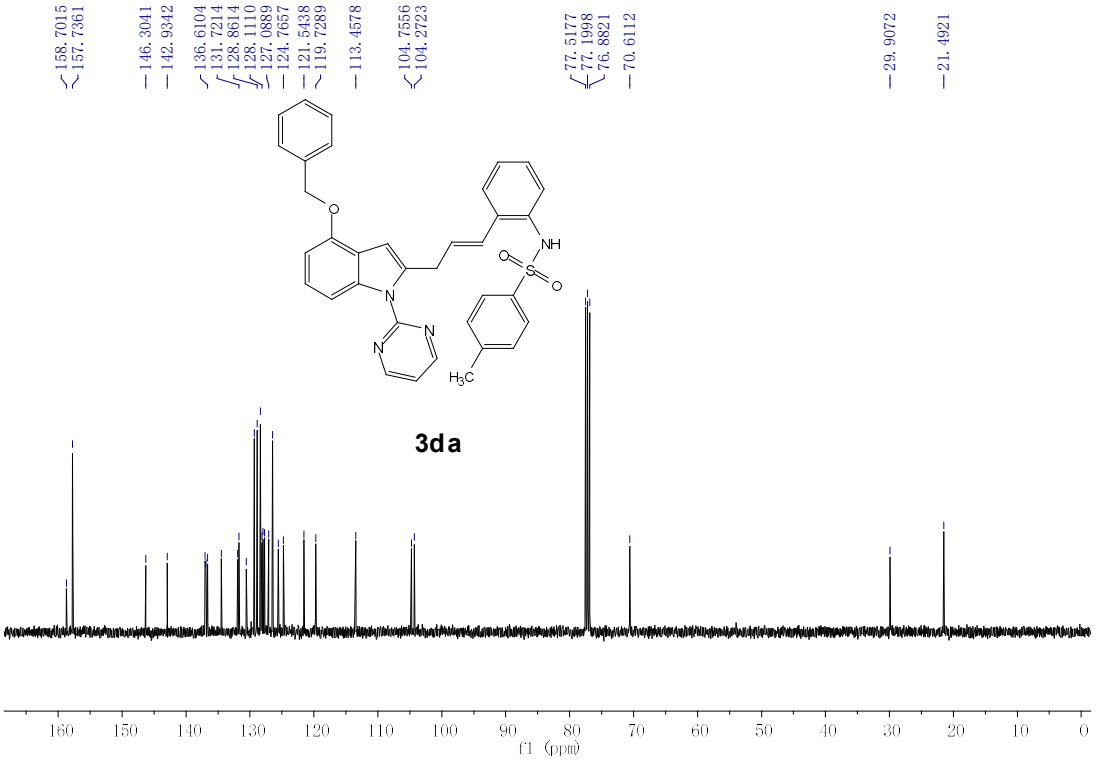
3.4811
3.4769
3.4720
2.1587
NH
O
S
N
H3C
3da
f1 (ppm)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128.8614
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127.0889
124.7657
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119.7289
113.4578
104.7556
104.2723
77.5177
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70.6112
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21.4921
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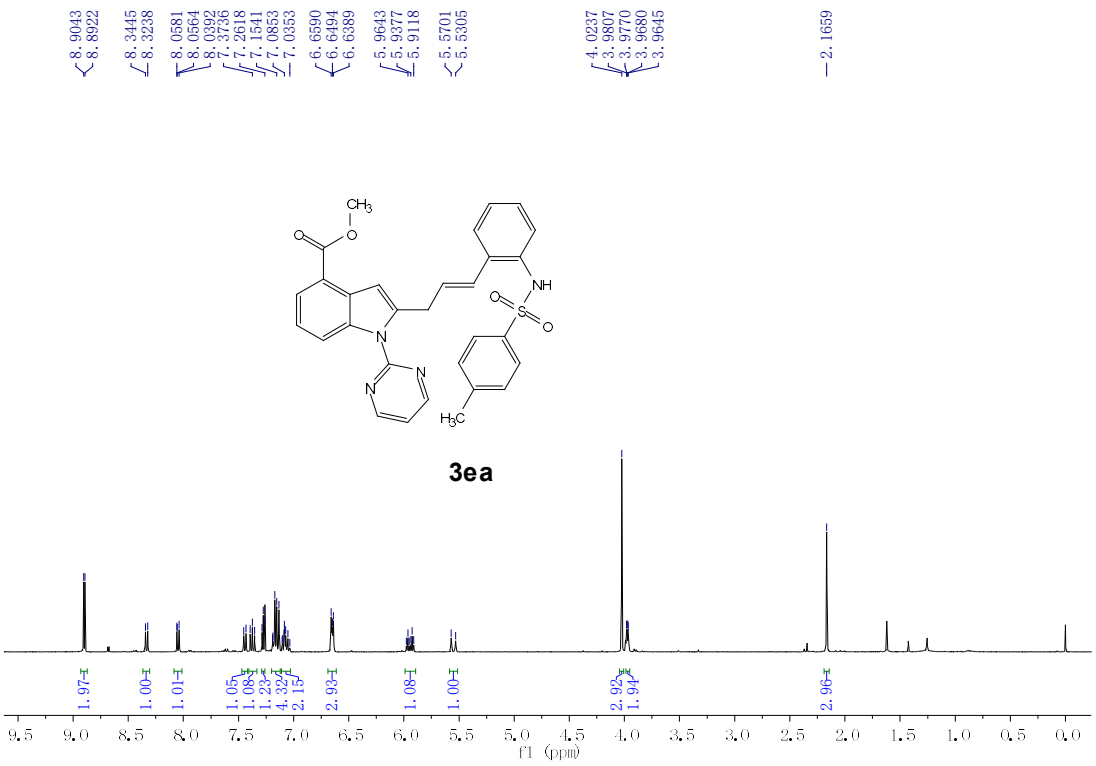
O
S
N
H3C
3da
f1 (ppm)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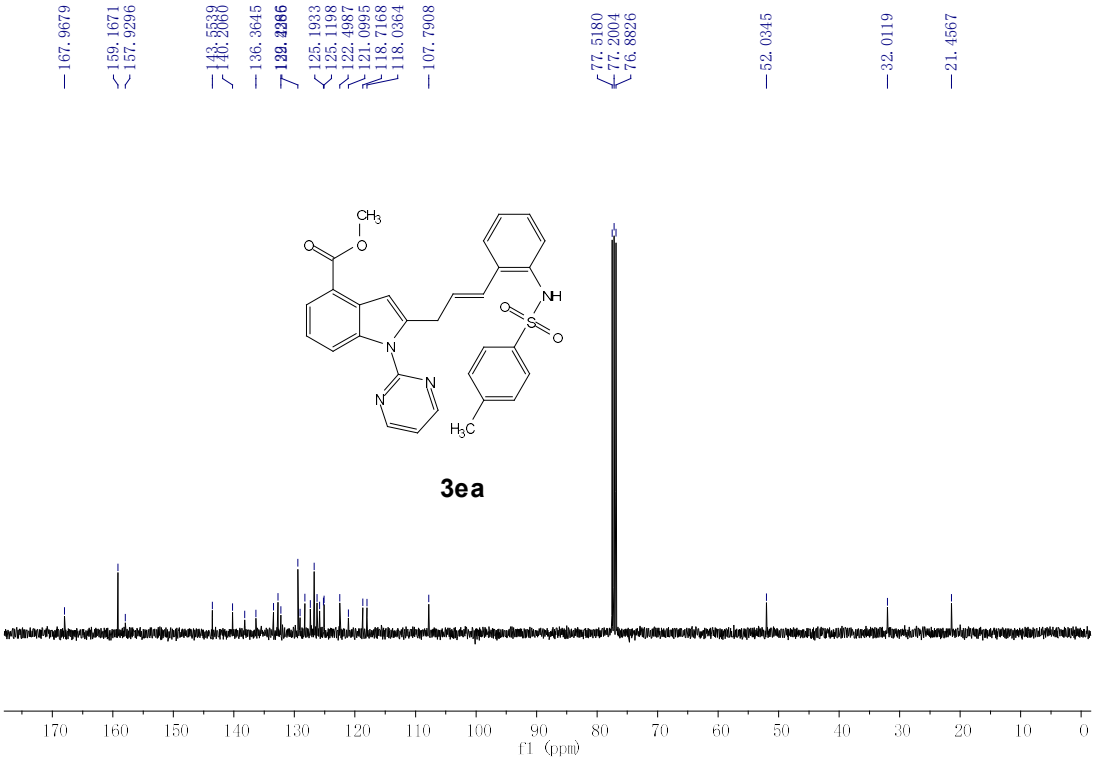
8.0581
8.0564
8.0392
7.3736
7.2618
7.1541
7.0853
7.0353
6.6590
6.6494
6.6389
5.9643
5.9377
5.9118
5.5701
5.5305
4.0237
3.9807
3.9770
3.9680
3.9645
2.1659
CH3
O
O
NH
S
O
O
N
N
N
H3C
3ea
1.97
1.00
1.01
1.05
1.08
1.23
4.32
2.15
2.93
1.08
1.00
2.92
1.94
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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121.0995
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118.0364
107.7908
77.5180
77.2004
76.8826
52.0345
32.0119
21.4567
CH3
O
O
NH
S
O
O
N
N
N
H3C
3ea
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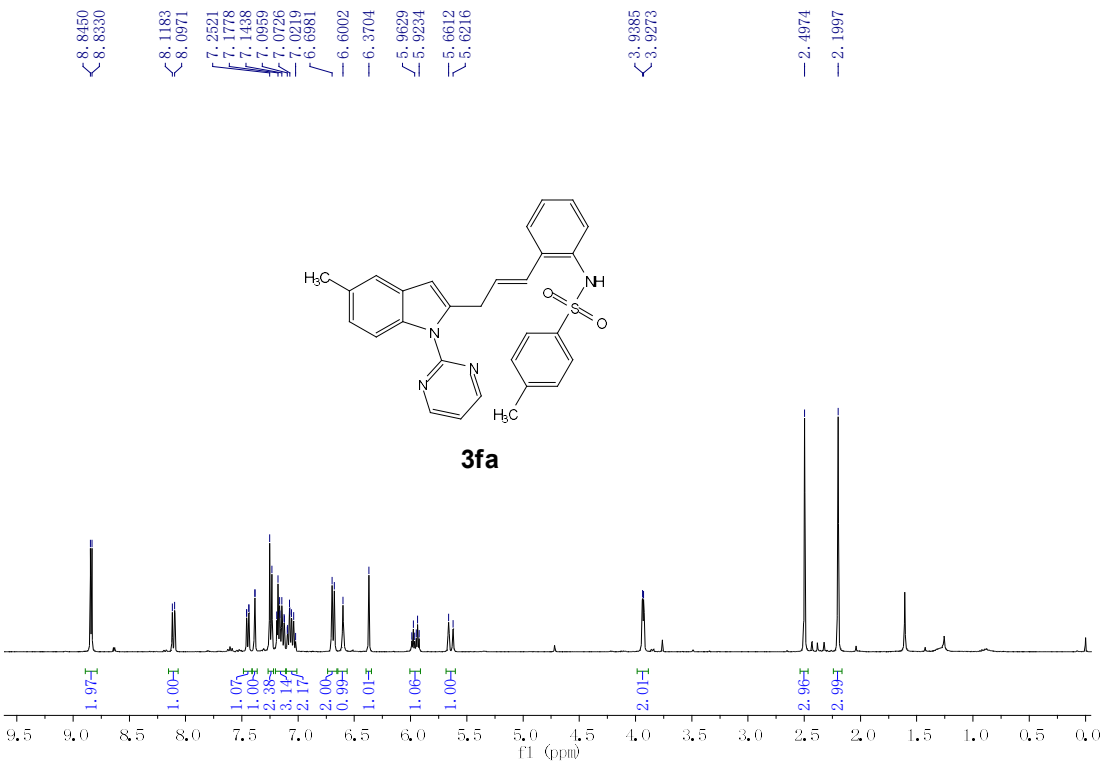
f1 (ppm)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5.9629
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5.6612
5.6216
3.9385
3.9273
2.4974
2.1997
3fa
1.97
1.00
1.07
1.00
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3.14
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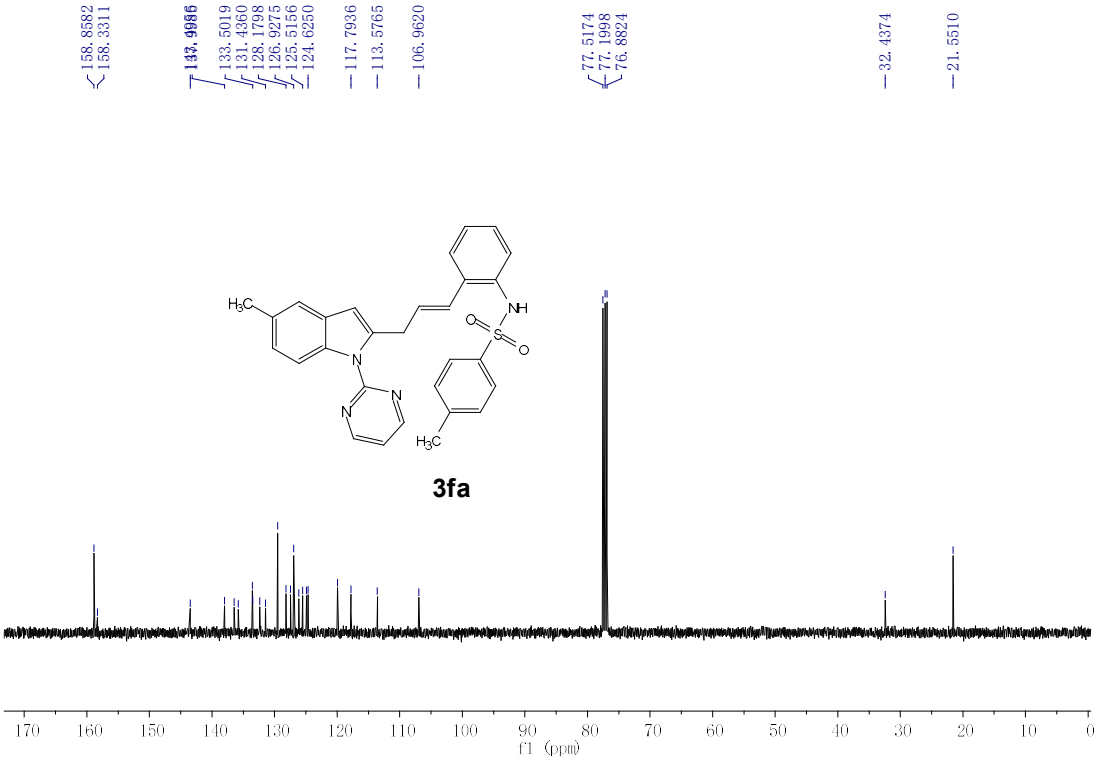
1.01
1.06
1.00
2.01
2.96
2.99
f1 (ppm)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126.9275
125.5156
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77.1998
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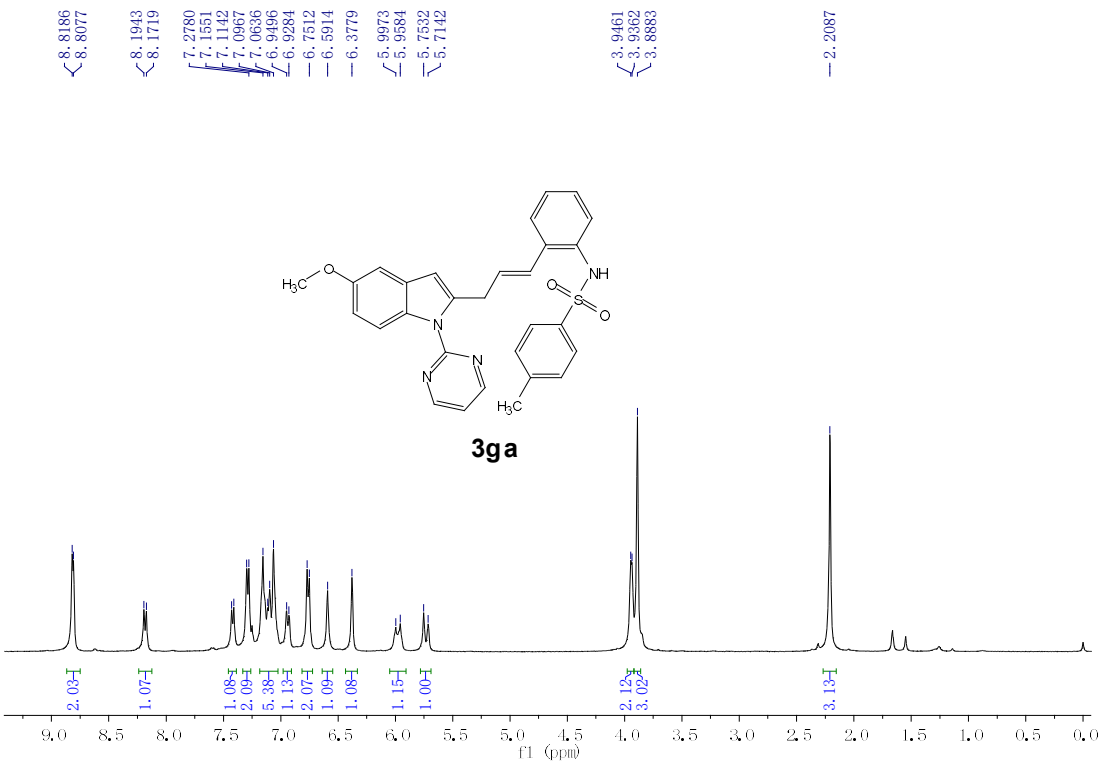
3fa
f1 (ppm)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7.1142
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7.0636
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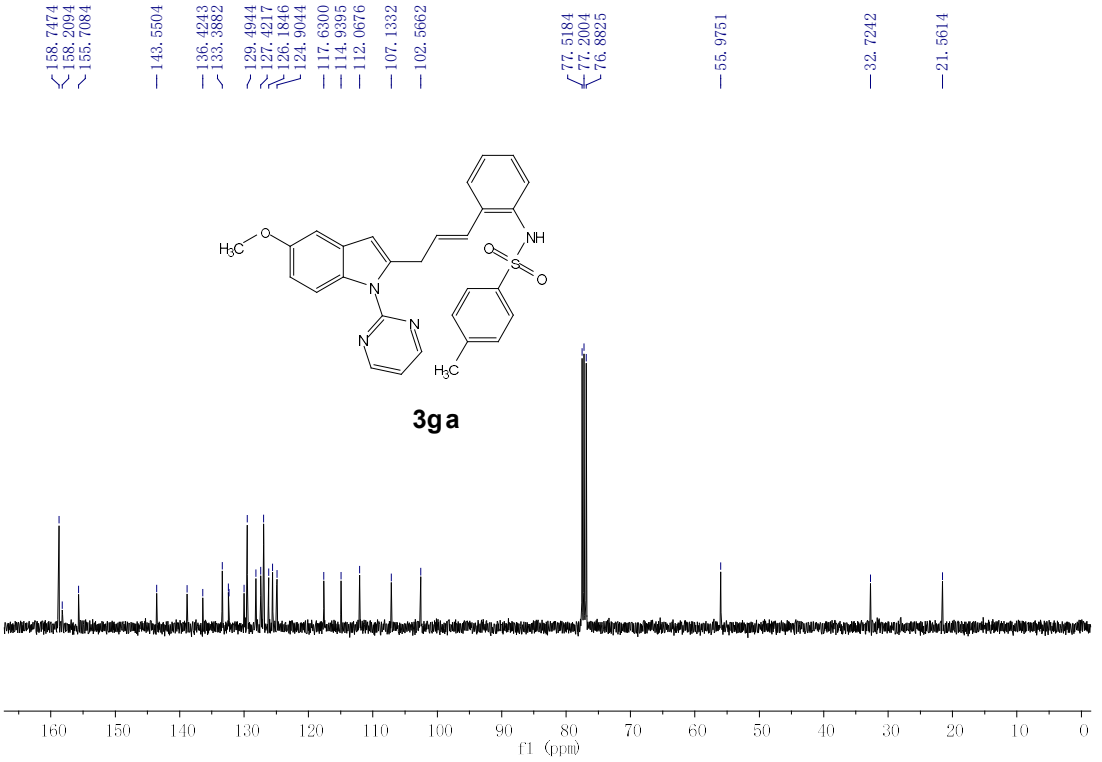
6.9284
6.7512
6.5914
6.3779
5.9973
5.9584
5.7532
5.7142
3.9461
3.9362
3.8883
2.2087
3ga
2.03
1.07
1.08
2.09
5.38
1.13
2.07
1.09
1.08
1.15
1.00
2.12
3.02
3.13
f1 (ppm)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129.4944
127.4217
126.1846
124.9044
117.6300
114.9395
112.0676
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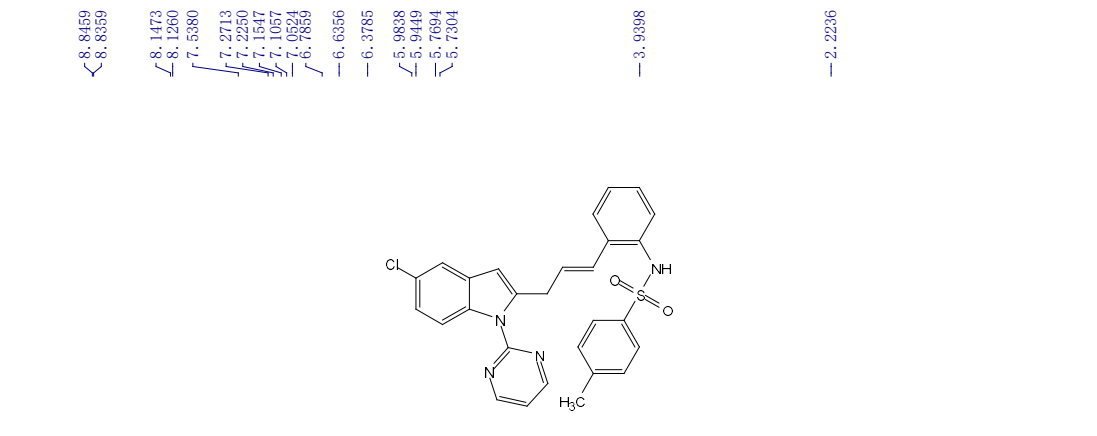
76.8825
55.9751
32.7242
21.5614
3ga
f1 (ppm)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8.1473
8.1260
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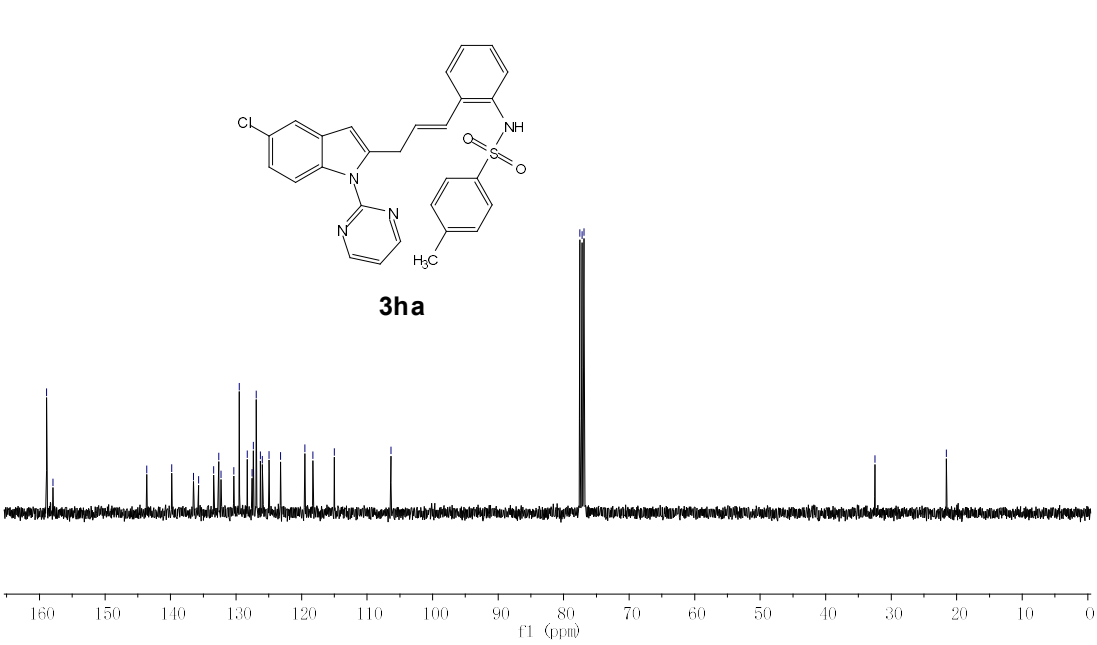
7.2713
7.2250
7.1547
7.1057
7.0524
6.7859
6.6356
6.3785
5.9838
5.9449
5.7694
5.7304
3.9398
2.2236
Cl
NH
O
S
O
N
N
N
H3C
2.09
1.02
1.04
1.08
4.46
2.39
1.14
2.00
1.03
1.10
1.13
1.00
2.08
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ha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127.5512
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123.1798
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114.9744
106.3550
77.5180
77.2004
76.8827
32.4930
21.5631
Cl
NH
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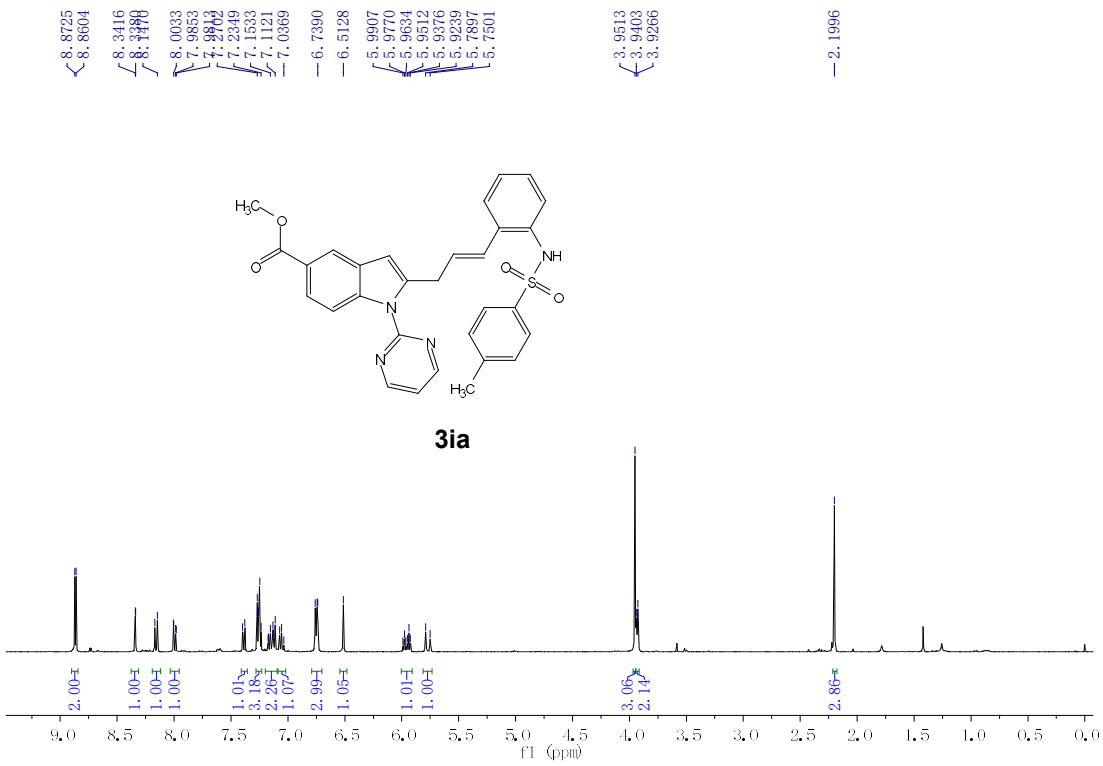
S
O
N
N
N
H3C
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ha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5.9770
5.9634
5.9512
5.9376
5.9239
5.7897
5.7501
3.9513
3.9403
3.9266
2.1996
3ia
2.00
1.00
1.00
1.00
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2.26
1.07
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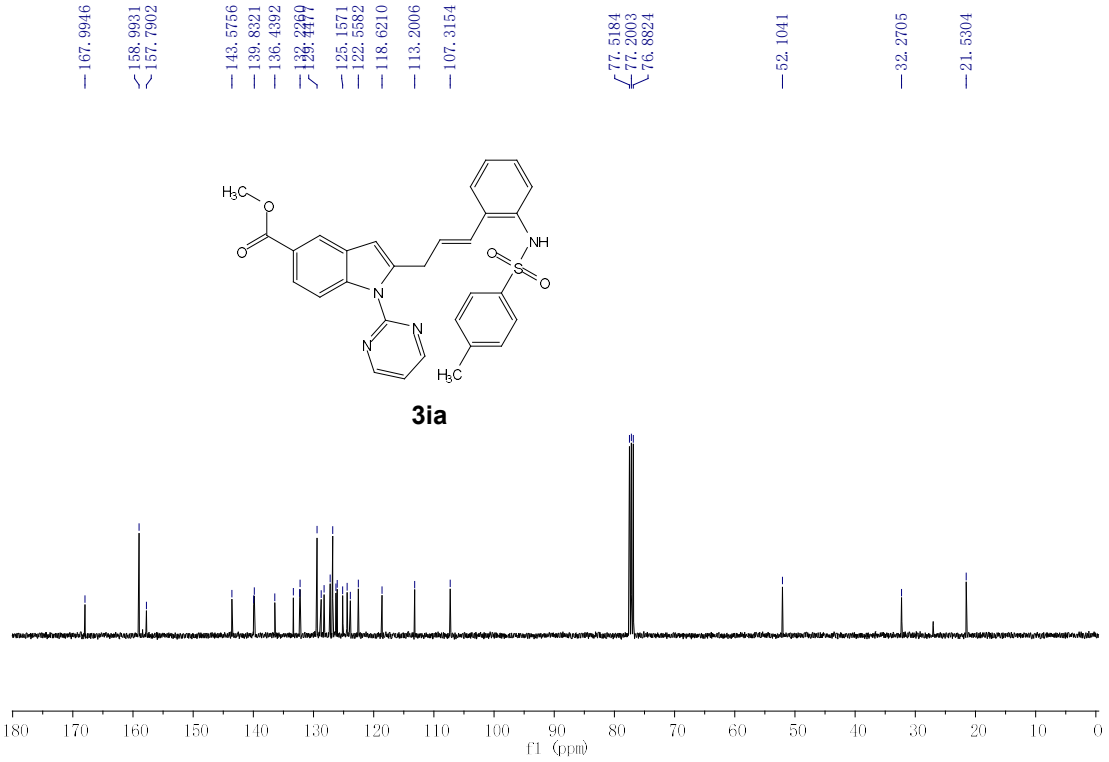
1.05
1.01
1.00
3.06
2.14
2.86
f1 (ppm)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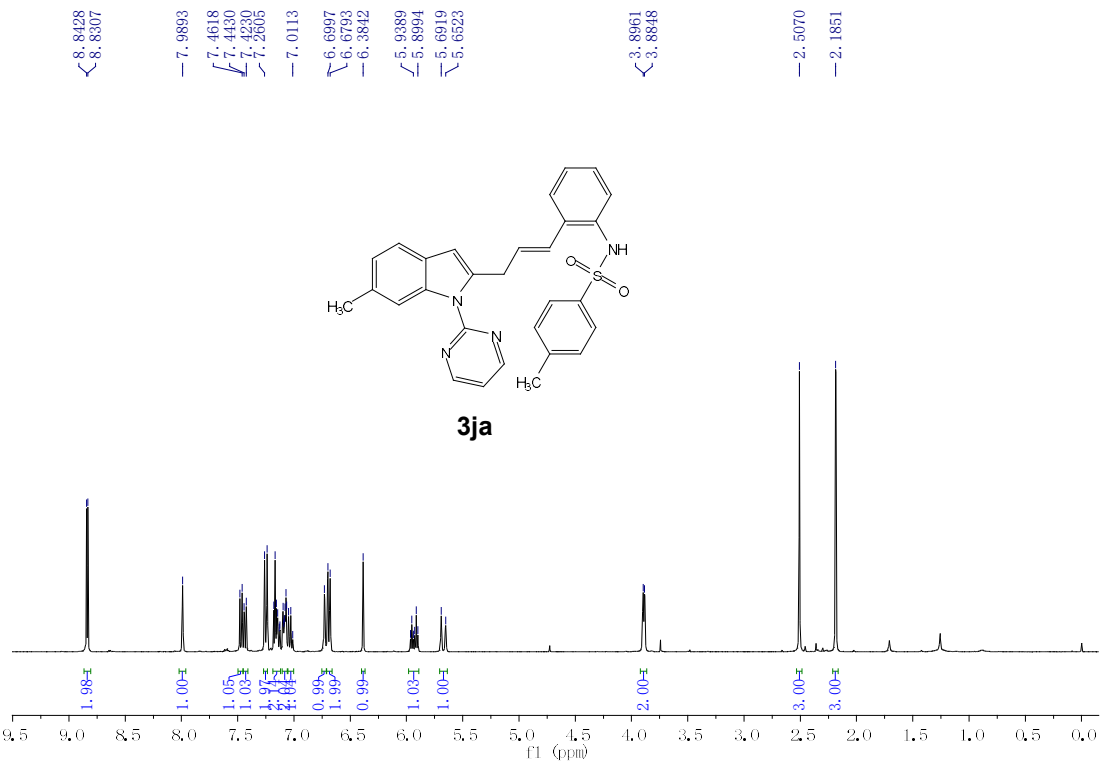
f1 (ppm)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7.2605
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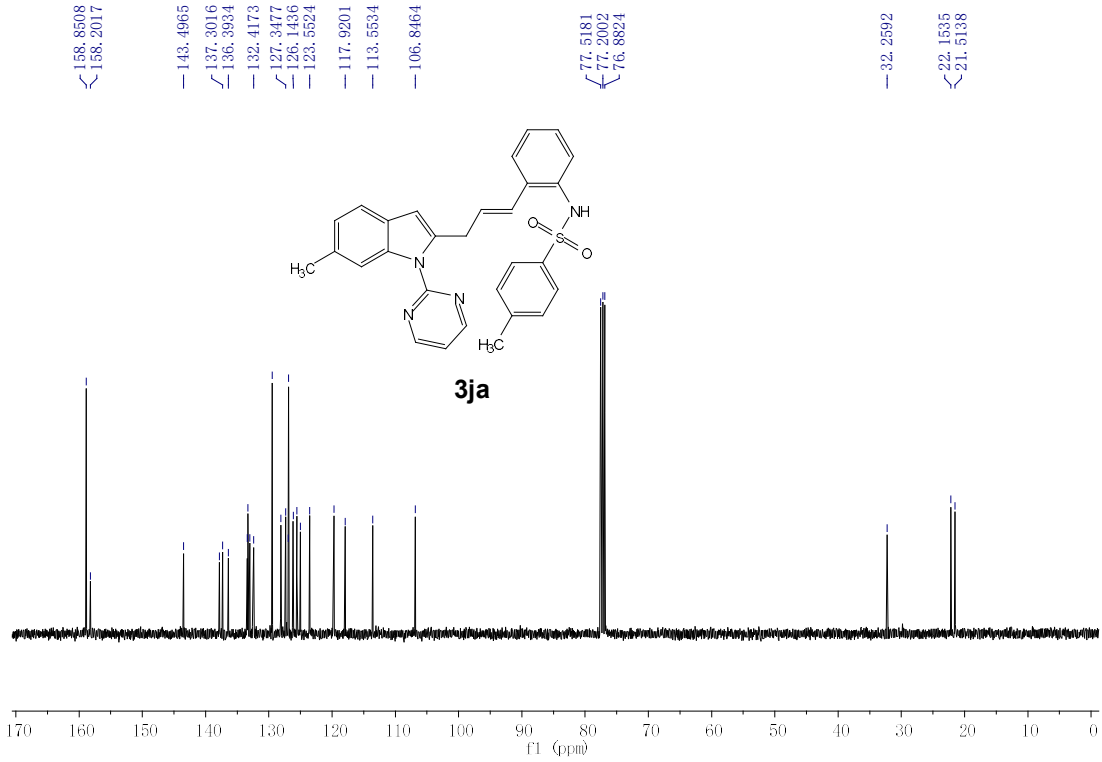
6.3842
5.9389
5.8994
5.6919
5.6523
3.8961
3.8848
2.5070
2.1851
NH
S
O
O
H3C
N
N
N
H3C
3ja
1.98
1.00
1.05
1.03
0.99
1.99
0.99
1.03
1.00
2.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.5181
77.2002
76.8824
32.2592
22.1535
21.5138
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O
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H3C
N
N
N
H3C
3ja
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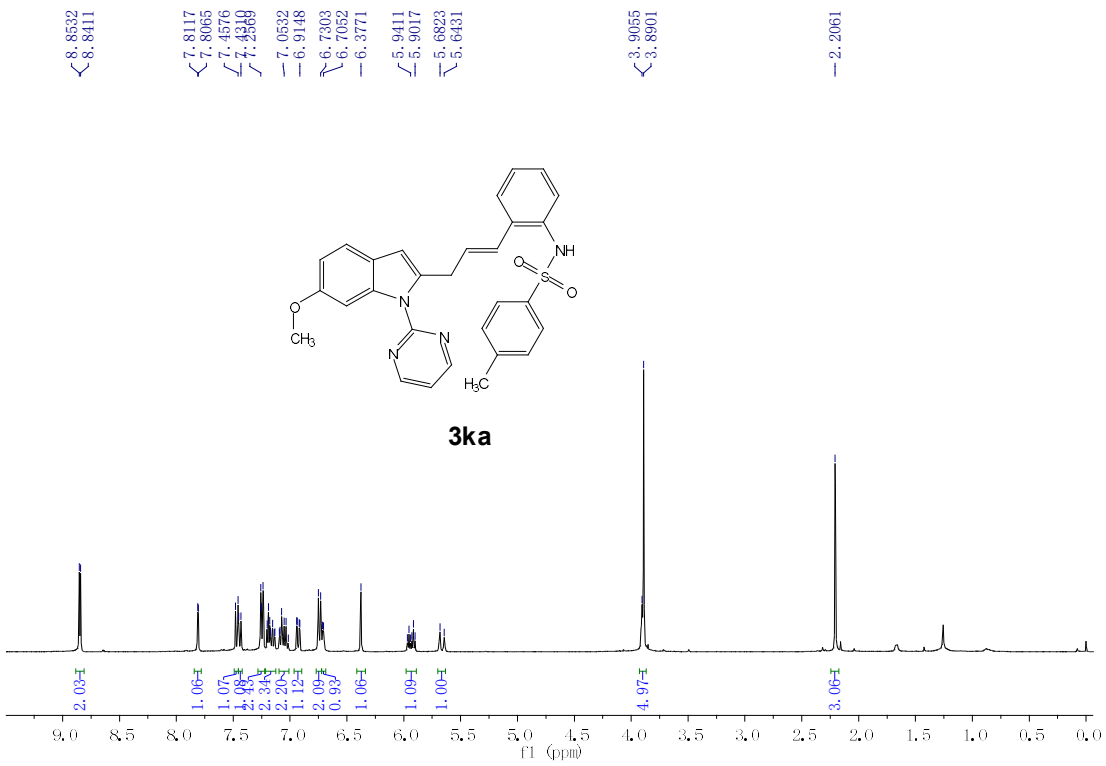
f1 (ppm)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6.3771
5.9411
5.9017
5.6823
5.6431
3.9055
3.8901
2.2061
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S
O
N
N
N
O
CH3
H3C
3ka
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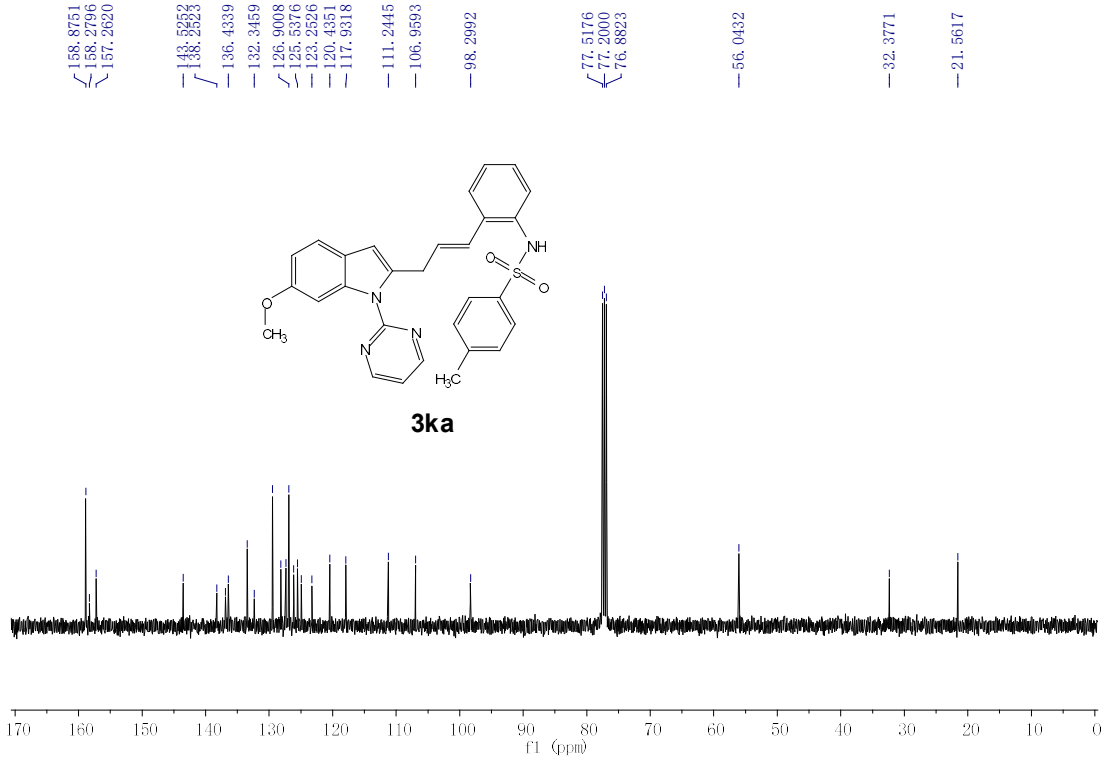
1.06
1.07
1.98
2.43
2.34
2.20
1.12
2.09
0.93
1.06
1.09
1.00
4.97
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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106.9593
98.2992
77.5176
77.2000
76.8823
56.0432
32.3771
21.5617
NH
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N
N
N
O
CH3
H3C
3ka
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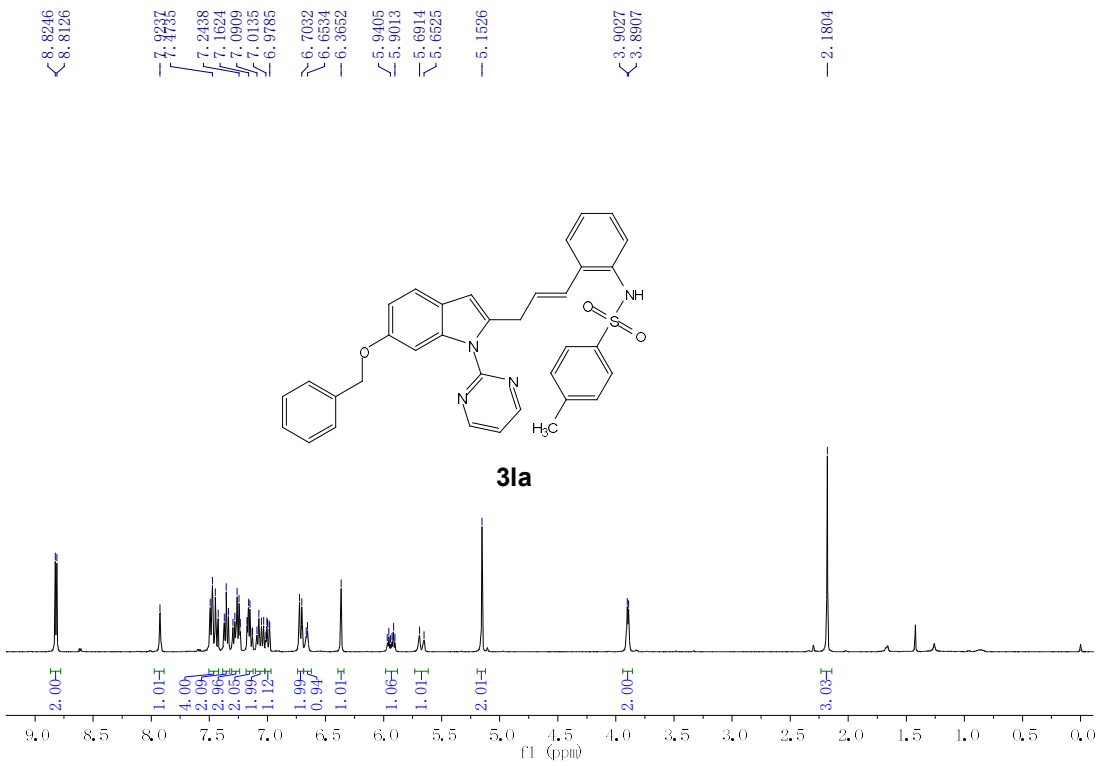
f1 (ppm)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5.9405
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5.6914
5.6525
5.1526
3.9027
3.8907
2.1804
NH
O
S
O
N
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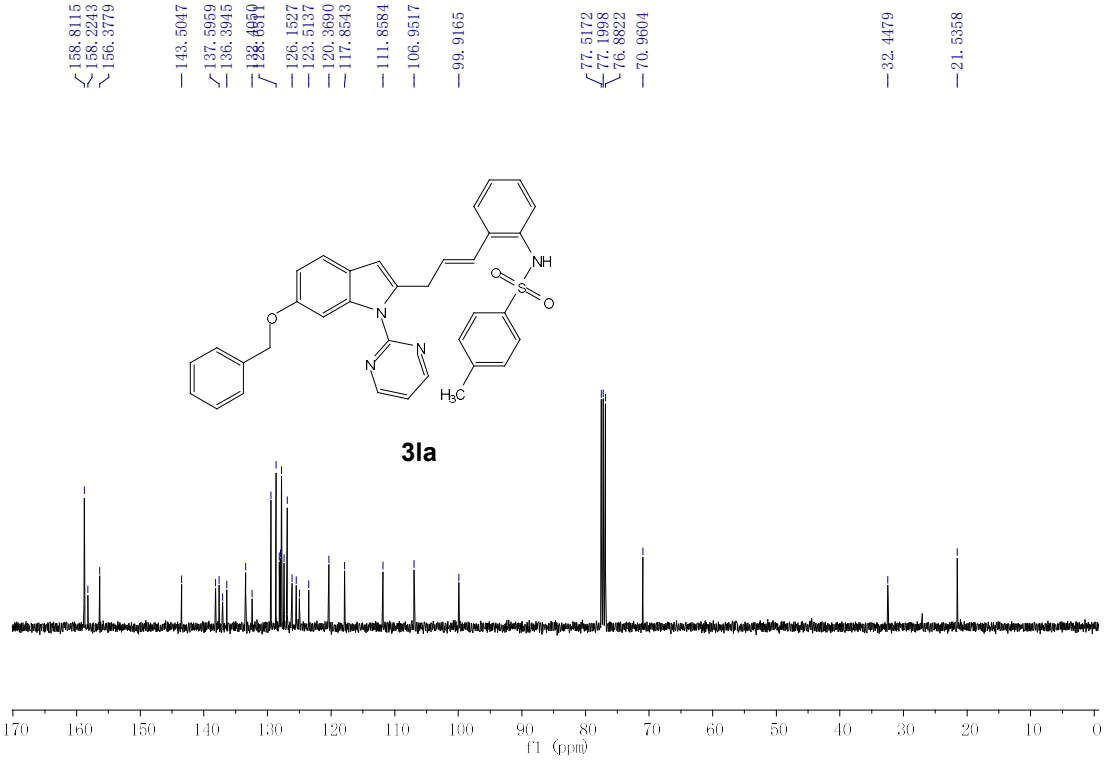
N
O
H3C
3la
2.00
1.01
4.00
2.09
2.96
2.05
1.99
1.12
1.99
0.94
1.01
1.06
1.01
2.01
2.00
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.8822
70.9604
32.4479
21.5358
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N
N
N
O
H3C
3la
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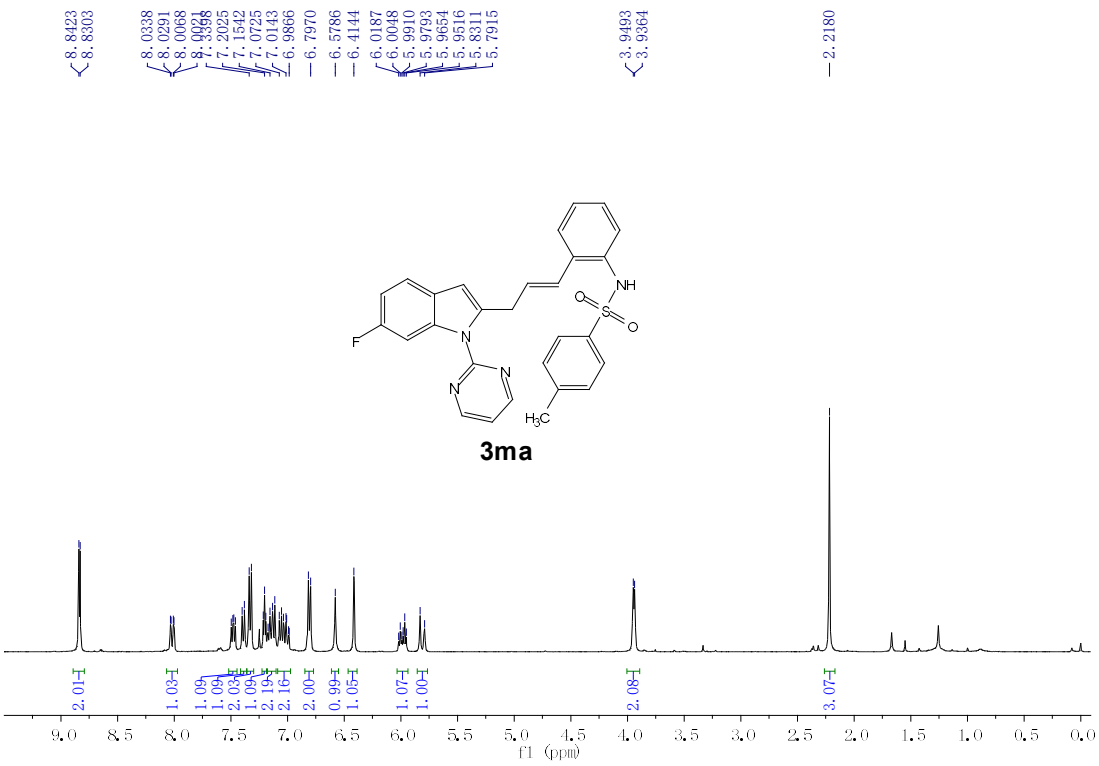
f1 (ppm)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6.5786
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6.0187
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3.9364
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N
N
H3C
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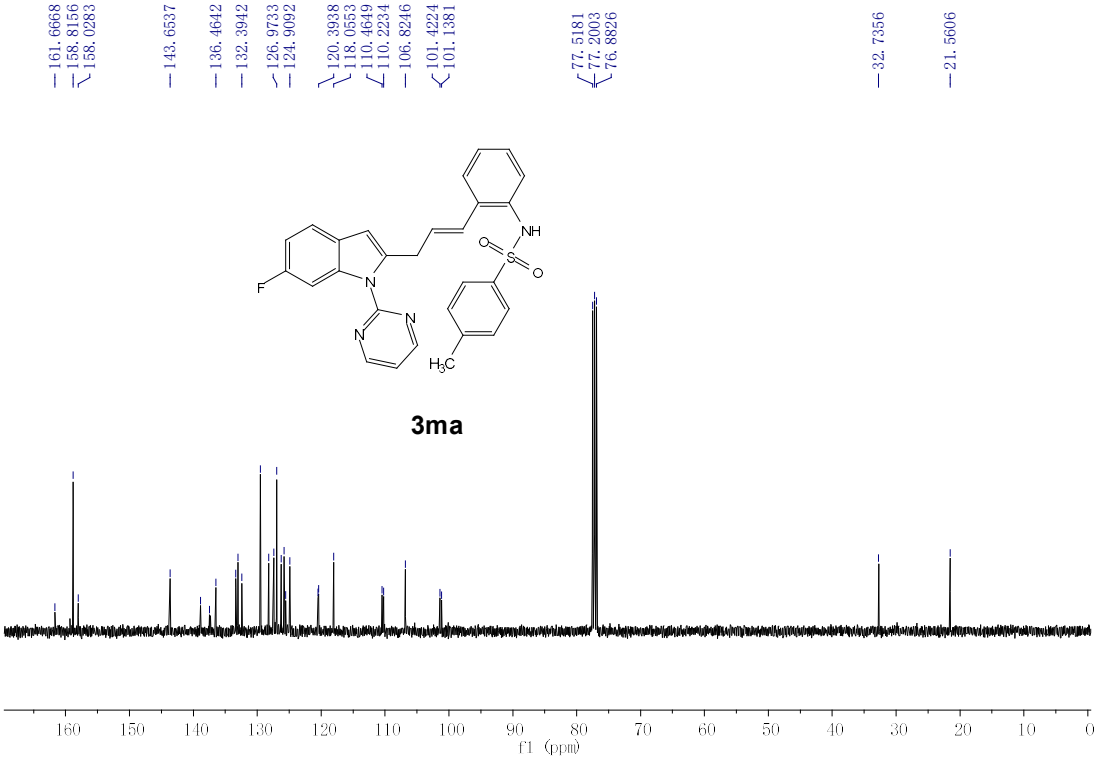
1.03
1.09
1.09
2.03
1.09
2.19
2.16
2.00
0.99
1.05
1.07
1.00
2.08
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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101.4224
101.1381
77.5181
77.2003
76.8826
32.7356
21.5606
NH
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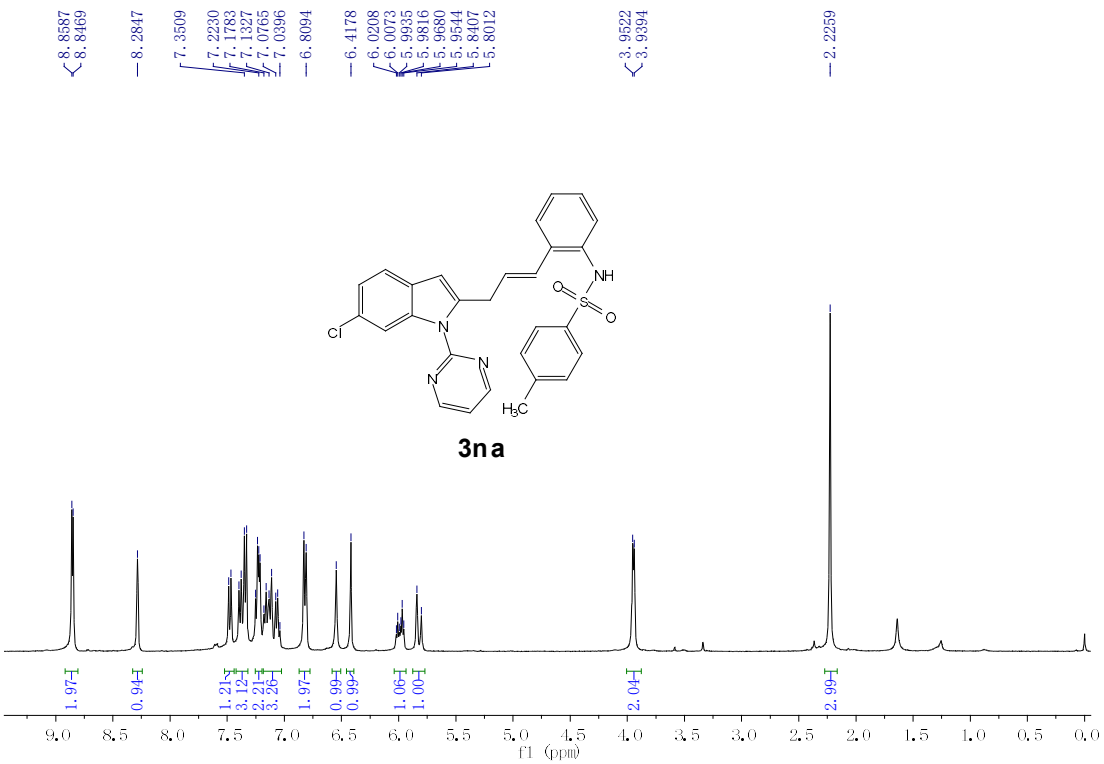
S
O
F
N
N
N
H3C
3ma
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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5.9935
5.9816
5.9680
5.9544
5.8407
5.8012
3.9522
3.9394
2.2259
NH
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S
O
Cl
N
N
N
H3C
3na
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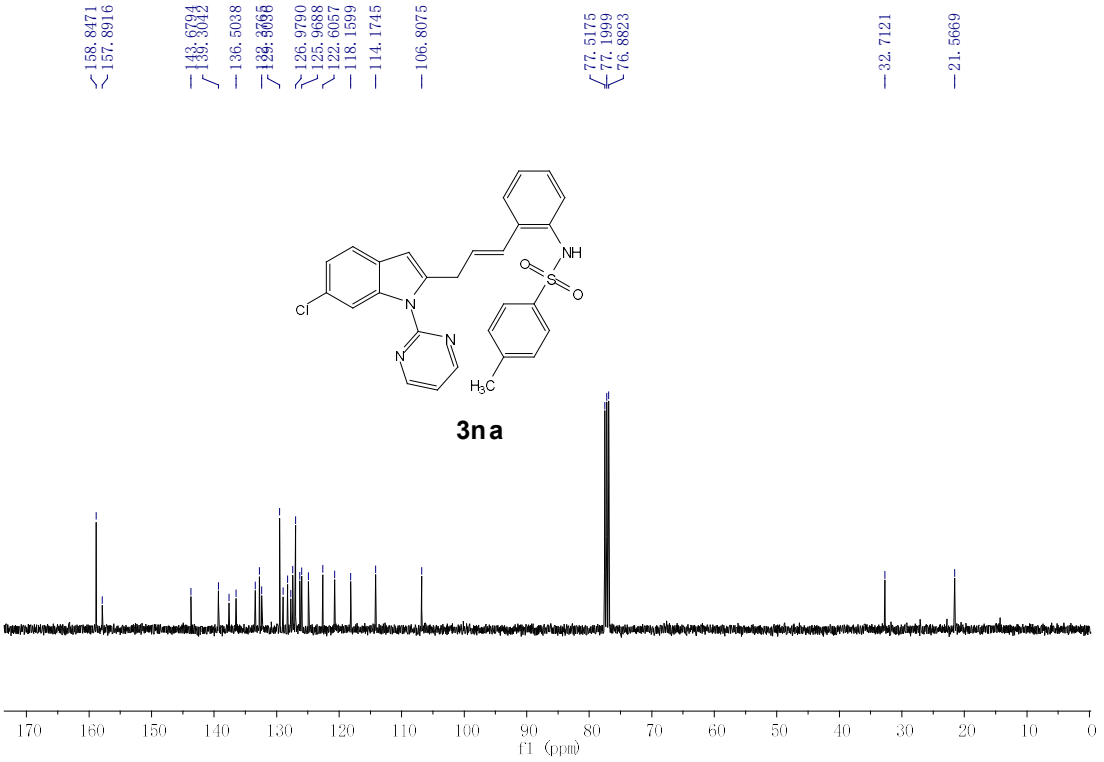
0.94
1.21
3.12
2.21
3.26
1.97
0.99
0.99
1.06
1.00
2.04
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.5175
77.1999
76.8823
32.7121
21.5669
NH
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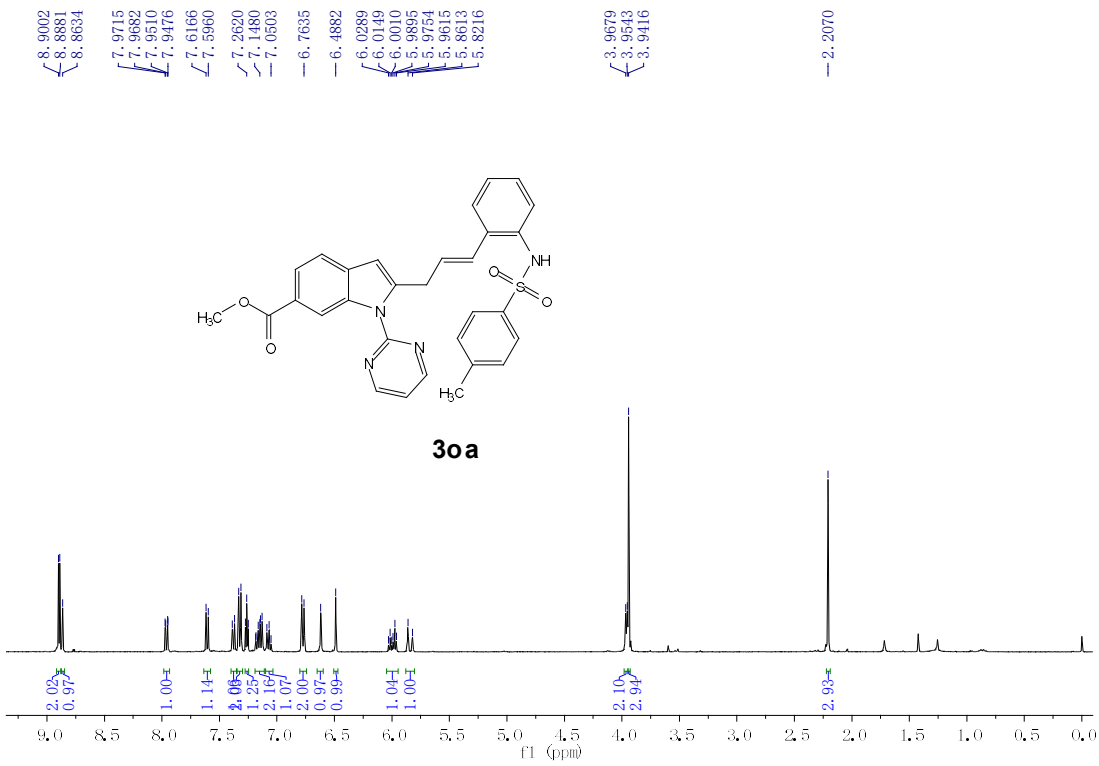
S
O
Cl
N
N
N
H3C
3na
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.9416
2.2070
NH
S
O
O
N
N
N
O
O
H3C
H3C
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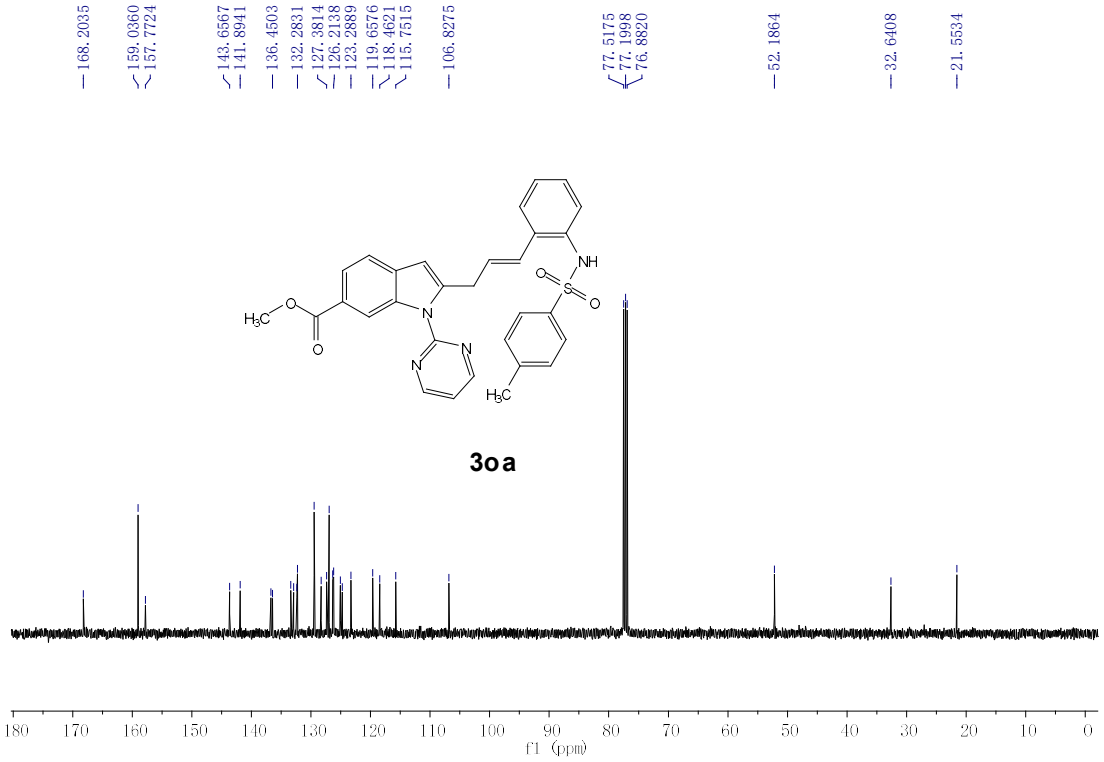
1.25
2.16
1.07
2.00
0.97
0.99
1.04
1.00
2.10
2.94
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.2831
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118.4621
115.7515
106.8275
77.5175
77.1998
76.8820
52.1864
32.6408
21.5534
NH
S
O
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N
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N
O
O
H3C
H3C
3oa
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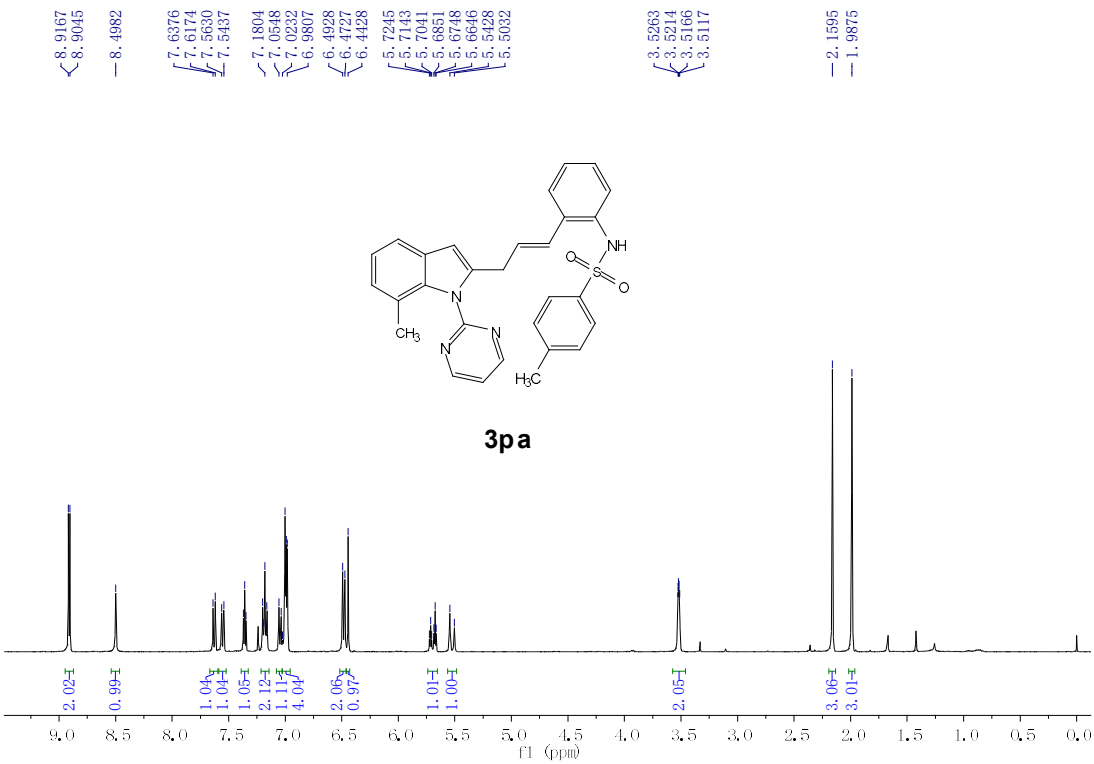
f1 (ppm)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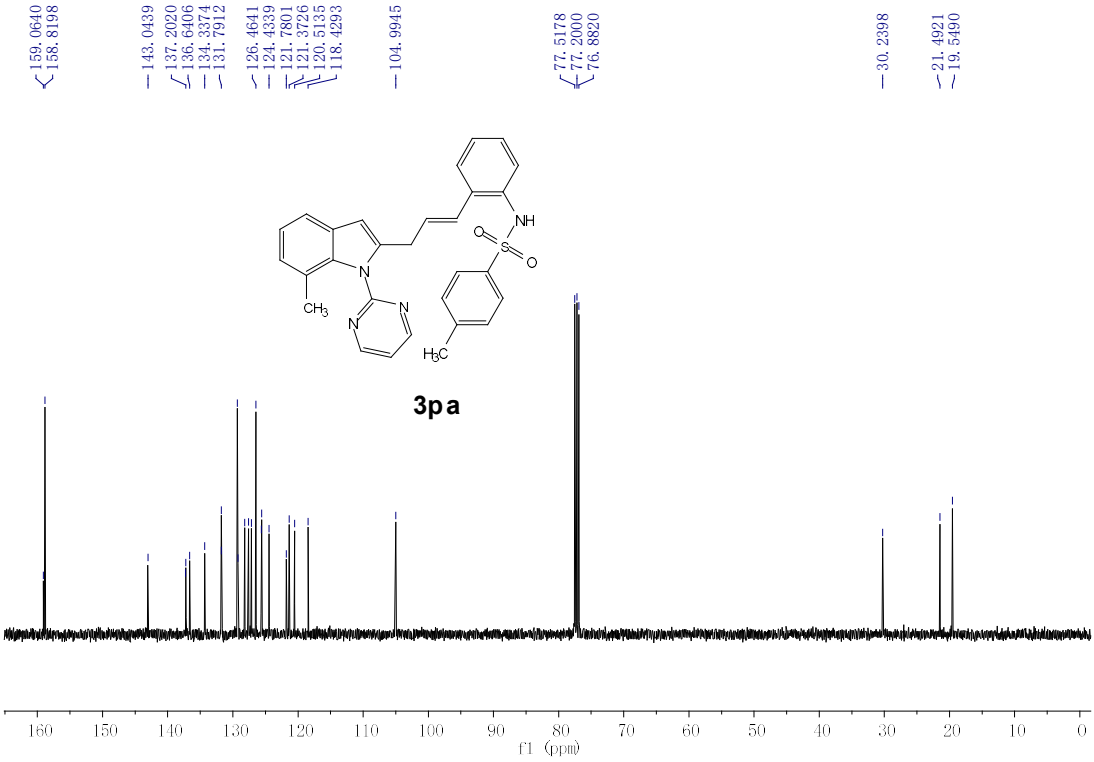
6.9807
6.4928
6.4727
6.4428
5.7245
5.7143
5.7041
5.6851
5.6748
5.6646
5.5428
5.5032
3.5263
3.5214
3.5166
3.5117
2.1595
1.9875
NH
O
S
O
N
N
N
CH3
H3C
3pa
2.02
0.99
1.04
1.04
1.05
2.12
1.11
4.04
2.06
0.97
1.01
1.00
2.05
3.06
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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118.4293
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77.2000
76.8820
30.2398
21.4921
19.5490
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O
N
N
N
CH3
H3C
3pa
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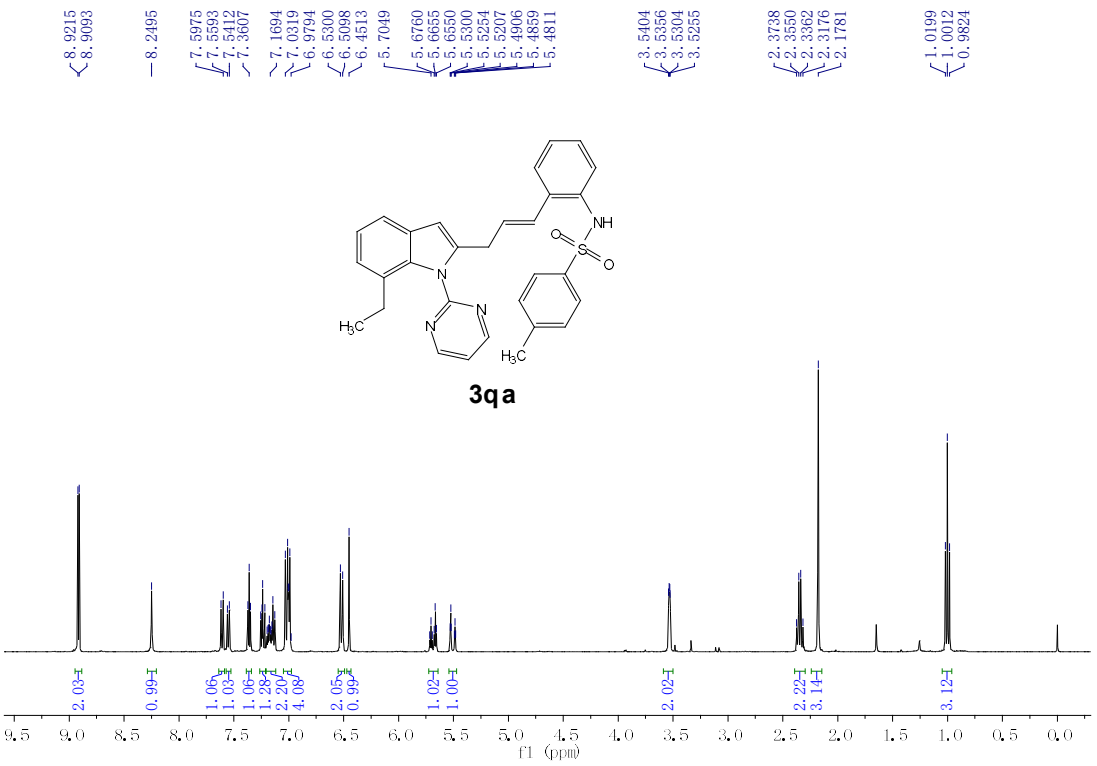
f1 (ppm)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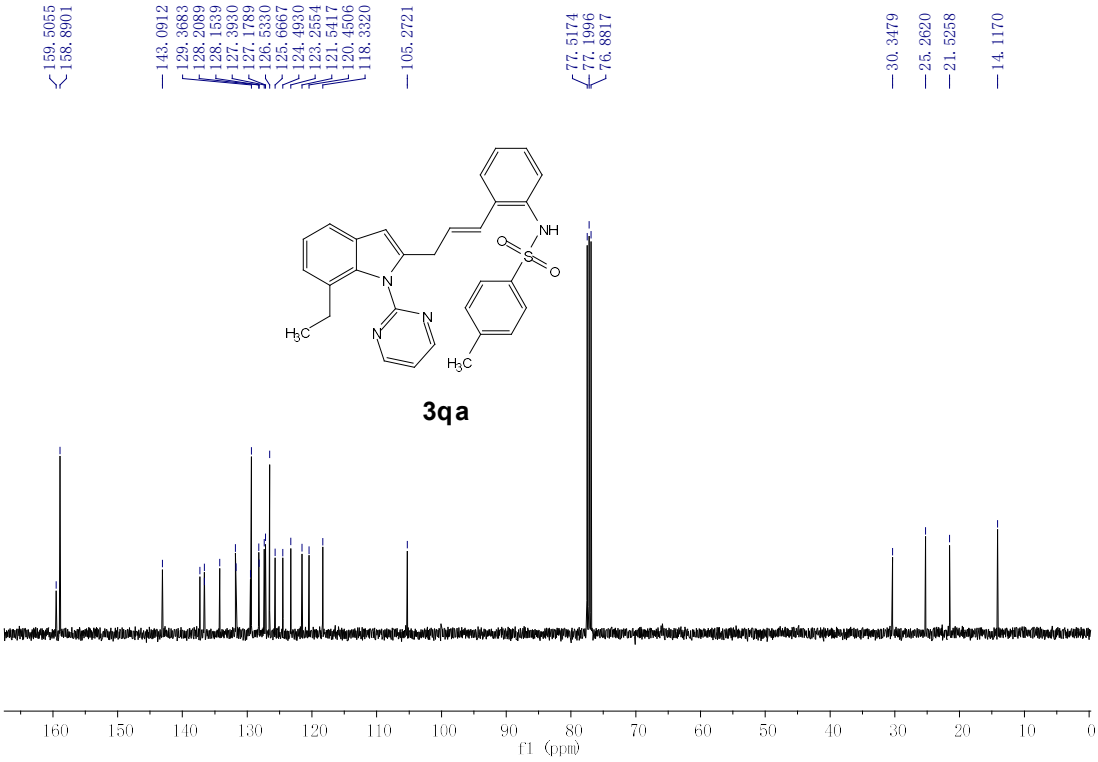
6.5098
6.4513
5.7049
5.6760
5.6655
5.6550
5.5300
5.5254
5.5207
5.4906
5.4859
5.4811
3.5404
3.5356
3.5304
3.5255
2.3738
2.3550
2.3362
2.3176
2.1781
1.0199
1.0012
0.9824
NH
O
S
O
N
N
N
H3C
H3C
3qa
2.03
0.99
1.06
1.03
1.06
1.28
2.20
4.09
2.05
0.99
1.02
1.00
2.02
2.22
3.14
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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121.5417
120.4506
118.3320
105.2721
77.5174
77.1996
76.8817
30.3479
25.2620
21.5258
14.1170
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N
N
N
H3C
H3C
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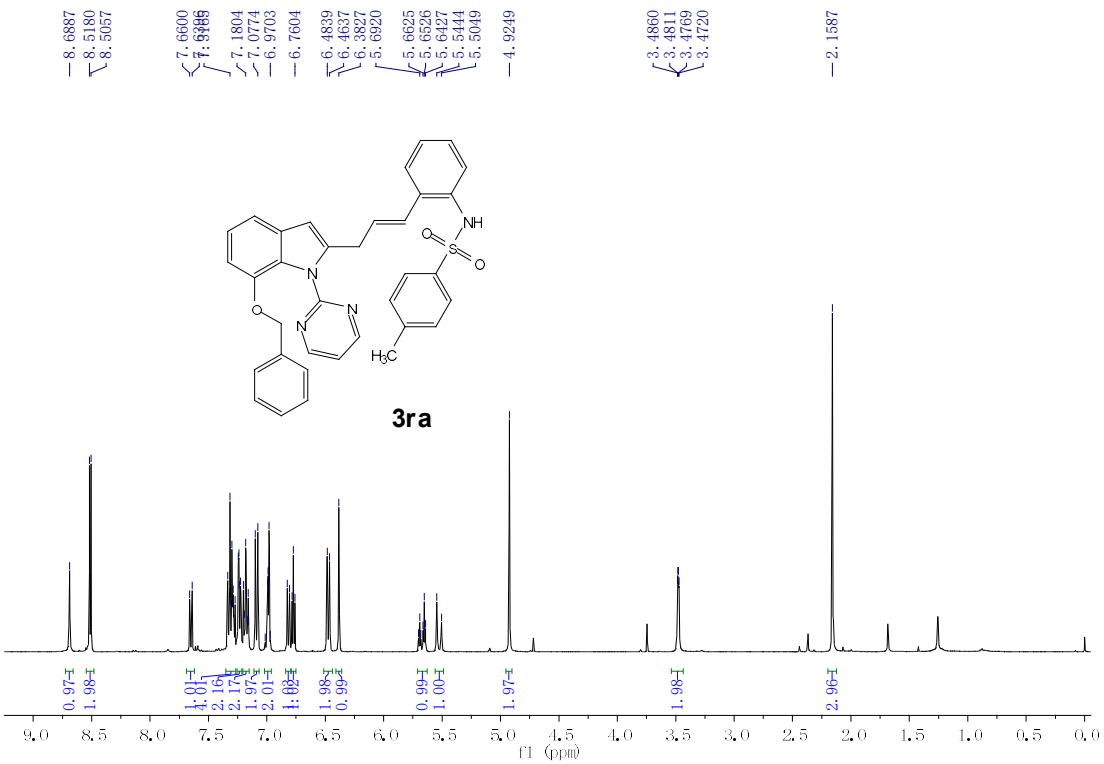
f1 (ppm)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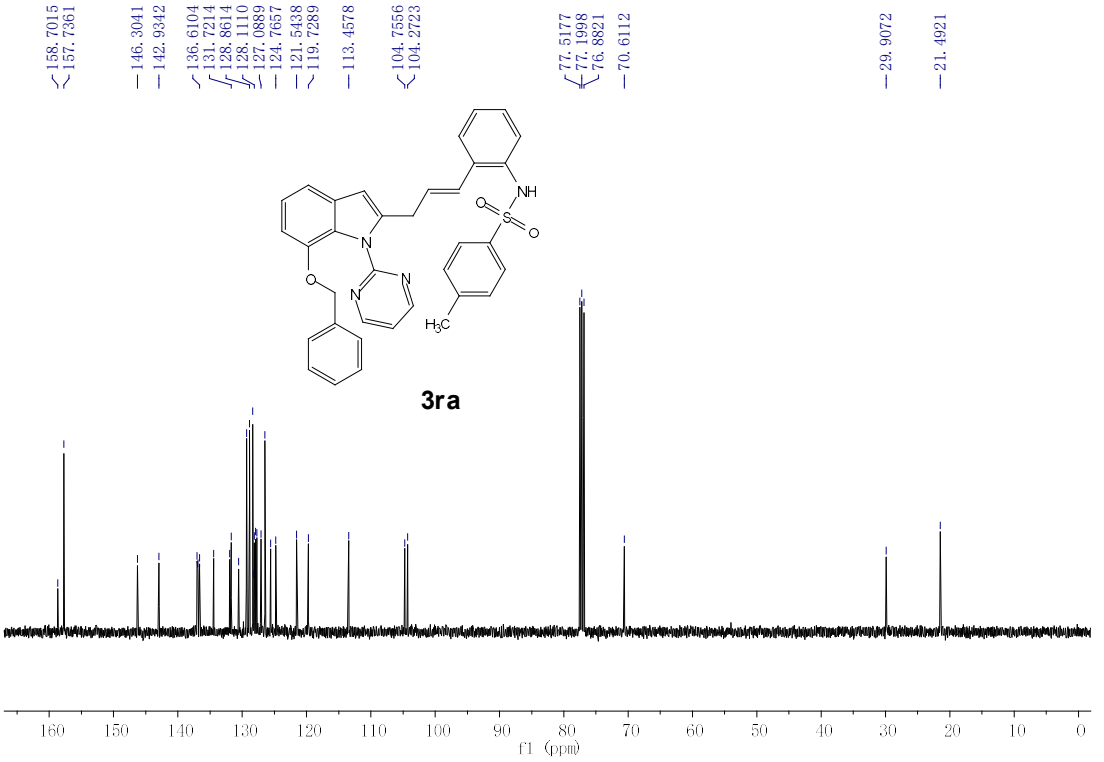
7.1804
7.0774
6.9703
6.7604
6.4839
6.4637
6.3827
5.6920
5.6625
5.6526
5.6427
5.5444
5.5049
4.9249
3.4860
3.4811
3.4769
3.4720
2.1587
NH
S
O
O
N
N
N
O
H3C
3ra
0.97
1.98
1.01
4.01
2.16
2.17
1.97
2.01
1.02
1.02
1.98
0.99
0.99
1.00
1.97
1.98
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.1110
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119.7289
113.4578
104.7556
104.2723
77.5177
77.1998
76.8821
70.6112
29.9072
21.4921
NH
S
O
O
N
N
N
O
H3C
3ra
160
150
140
130
120
110
100
90
80
70
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50
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10
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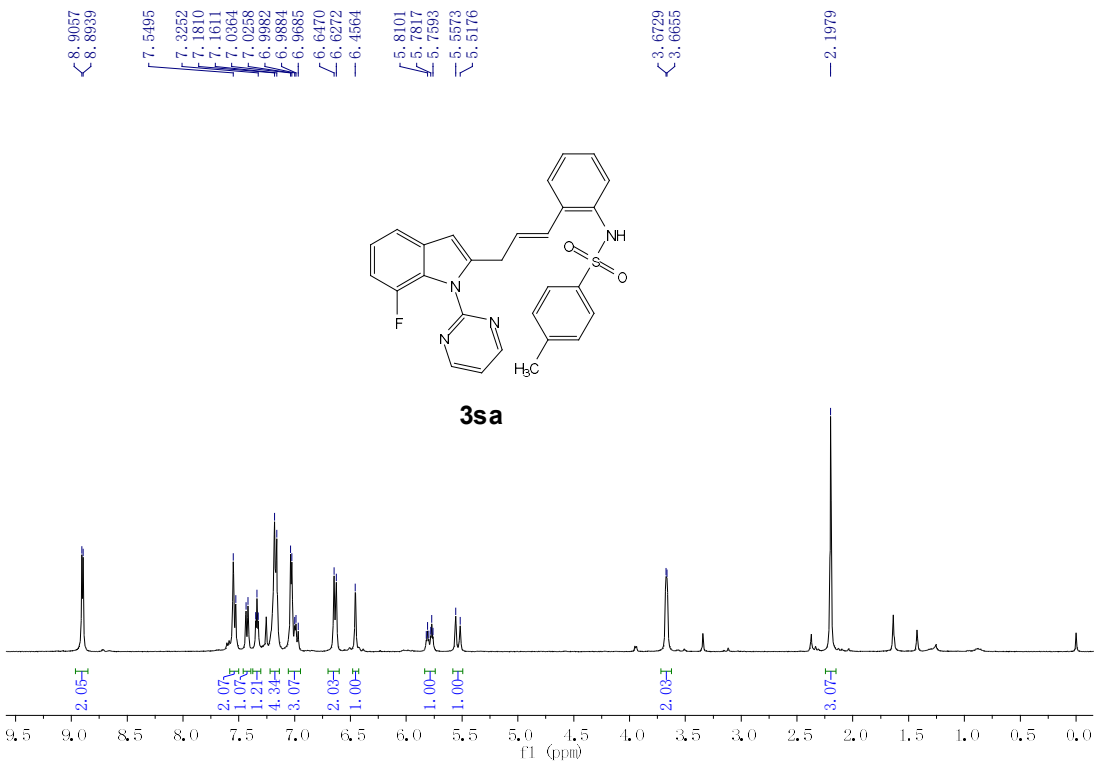
f1 (ppm)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7.1611
7.0364
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6.9982
6.9884
6.9685
6.6470
6.6272
6.4564
5.8101
5.7817
5.7593
5.5573
5.5176
3.6729
3.6655
2.1979
NH
S
O
O
N
N
N
F
H3C
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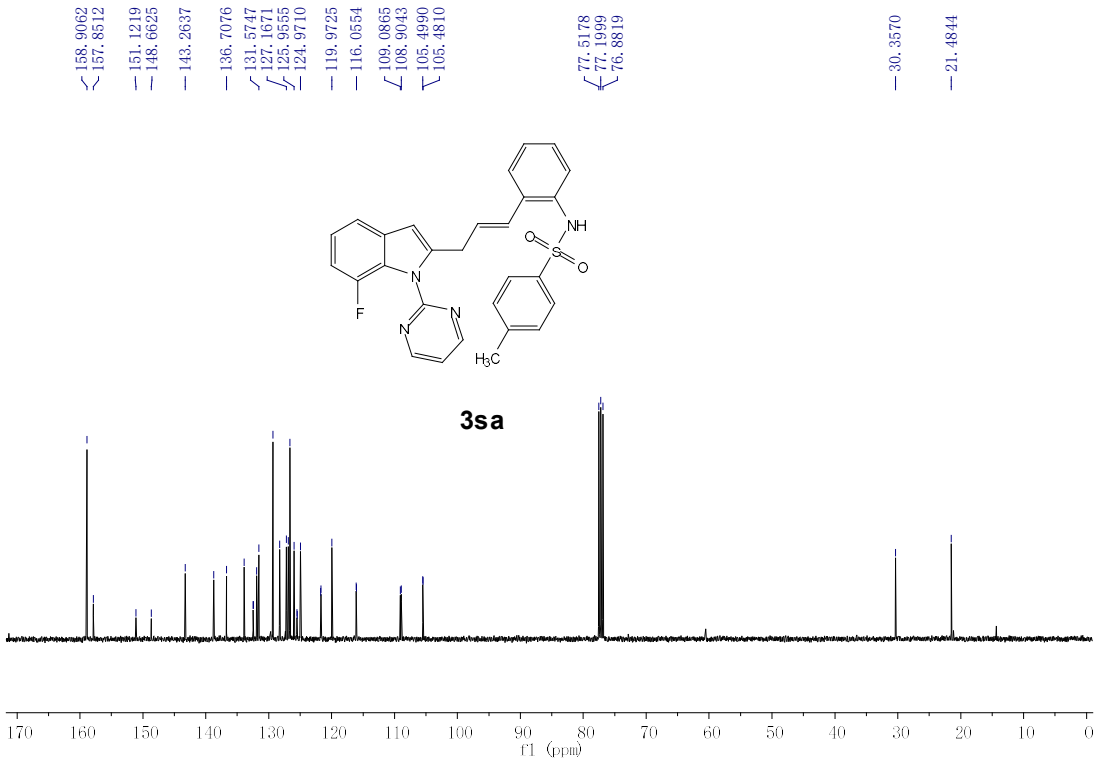
2.07
1.07
1.21
4.34
3.07
2.03
1.00
1.00
1.00
2.03
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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119.9725
116.0554
109.0865
108.9043
105.4990
105.4810
77.5178
77.1999
76.8819
30.3570
21.4844
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S
O
O
N
N
N
F
H3C
3sa
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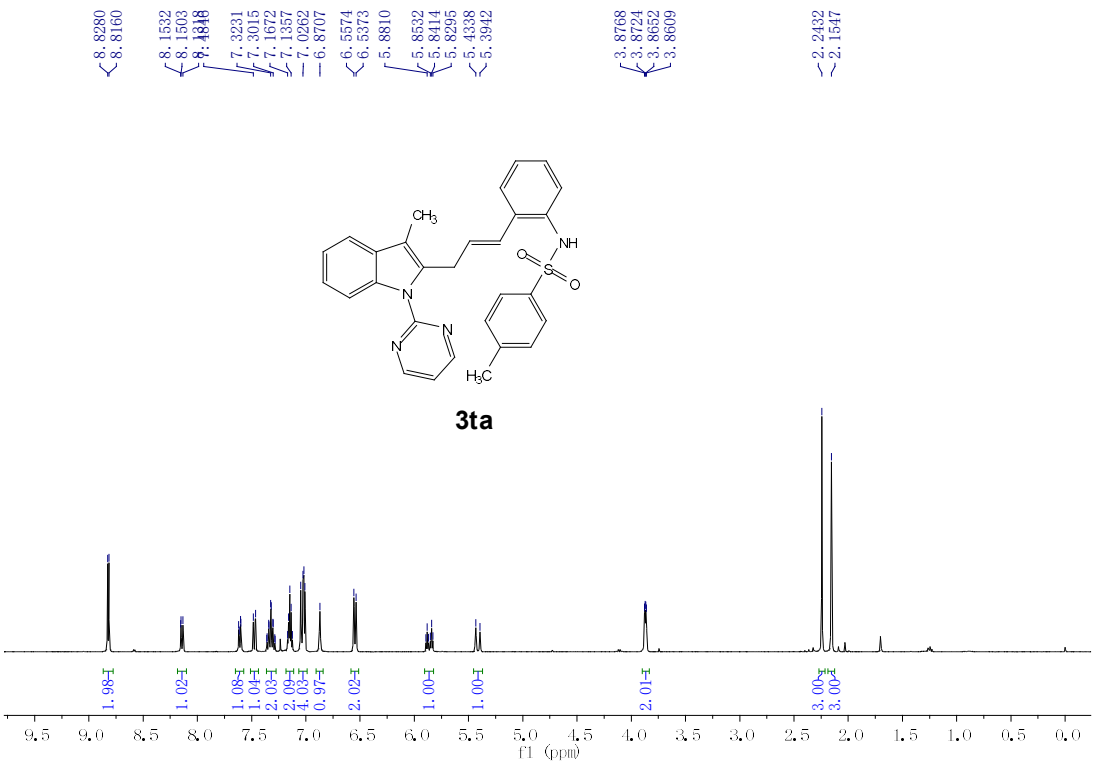
f1 (ppm)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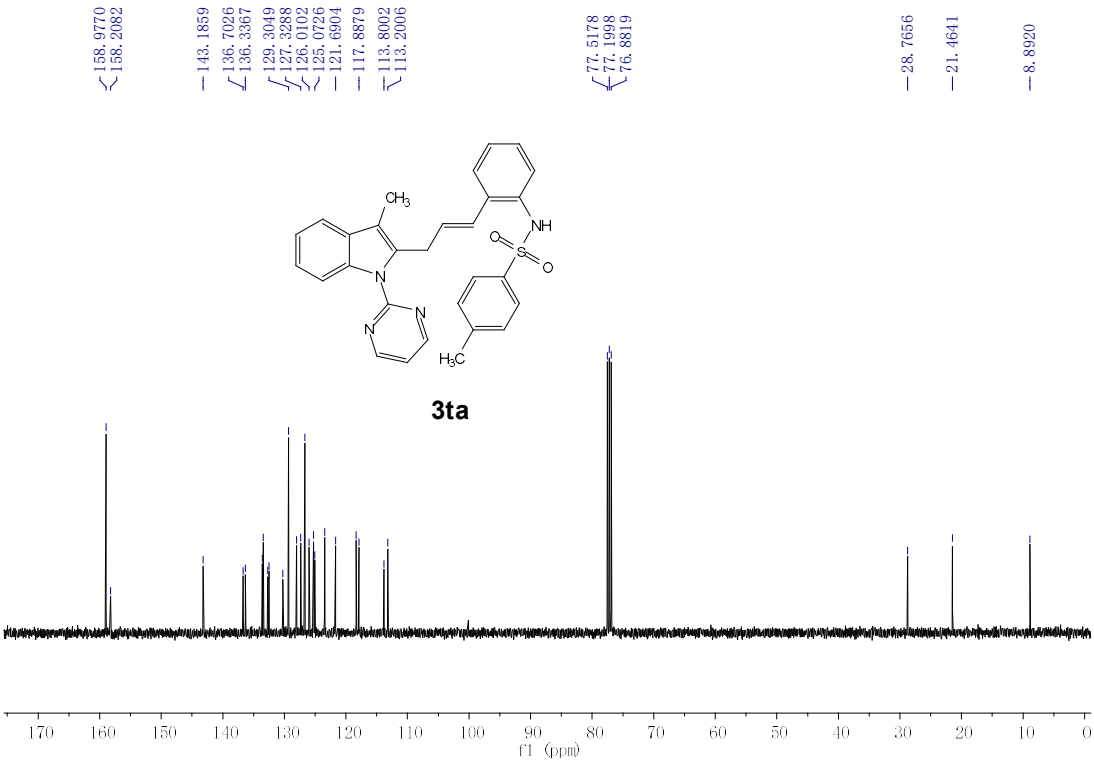
6.5574
6.5373
5.8810
5.8532
5.8414
5.8295
5.4338
5.3942
3.8768
3.8724
3.8652
3.8609
2.2432
2.1547
CH3
NH
O
S
O
N
N
N
H3C
3ta
1.98
1.02
1.08
1.04
2.03
2.09
4.03
0.97
2.02
1.00
1.00
2.01
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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121.6904
117.8879
113.8002
113.2006
77.5178
77.1998
76.8819
28.7656
21.4641
8.8920
CH3
NH
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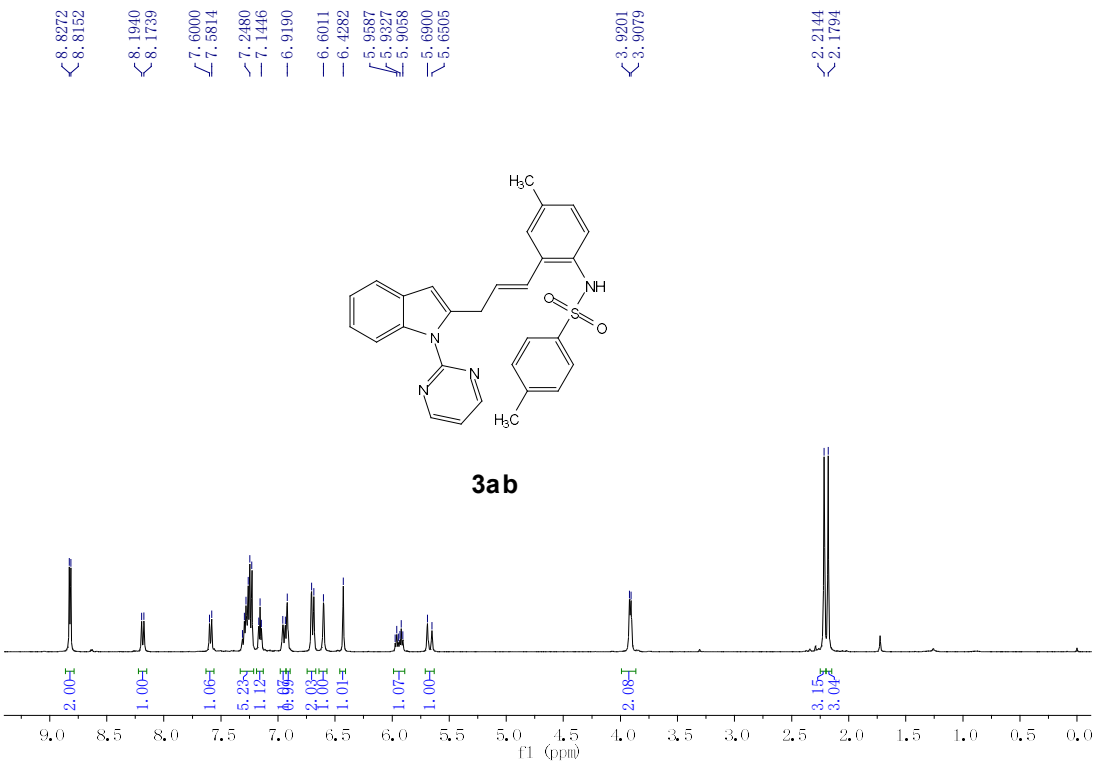
S
O
N
N
N
H3C
3ta
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.2480
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6.9190
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6.4282
5.9587
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2.2144
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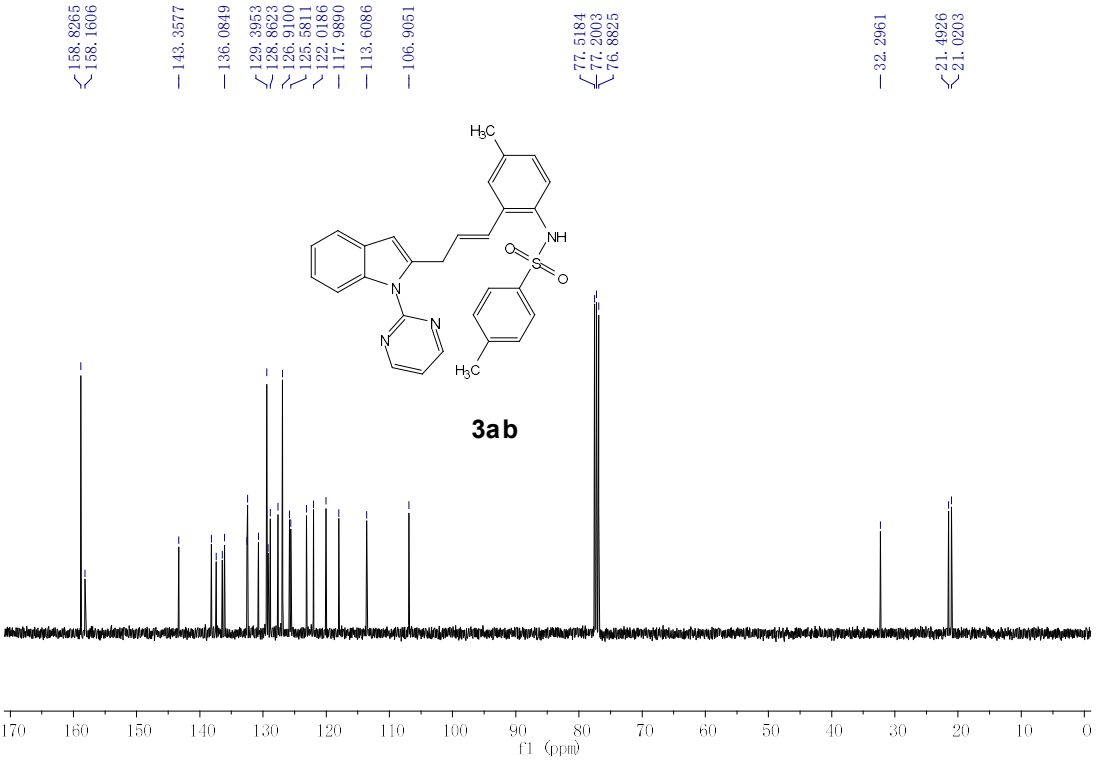
3ab
f1 (ppm)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76.8825
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21.4926
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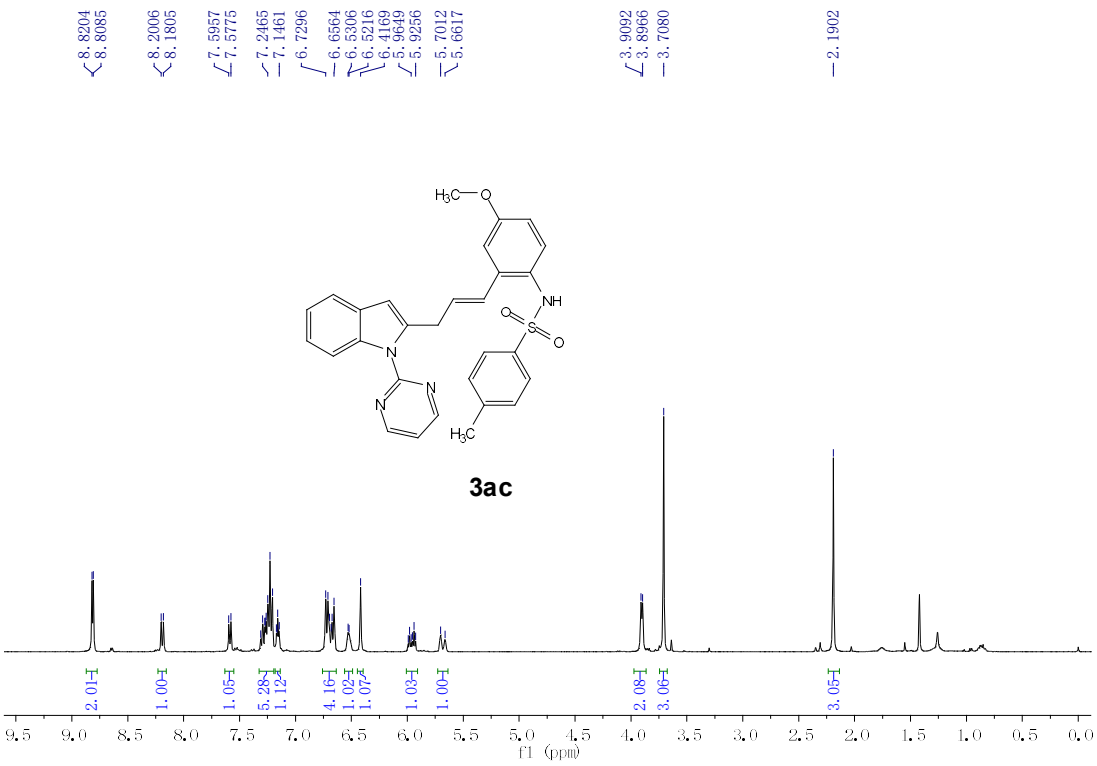
3ab
f1 (ppm)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6.5216
6.4169
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5.7012
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2.01
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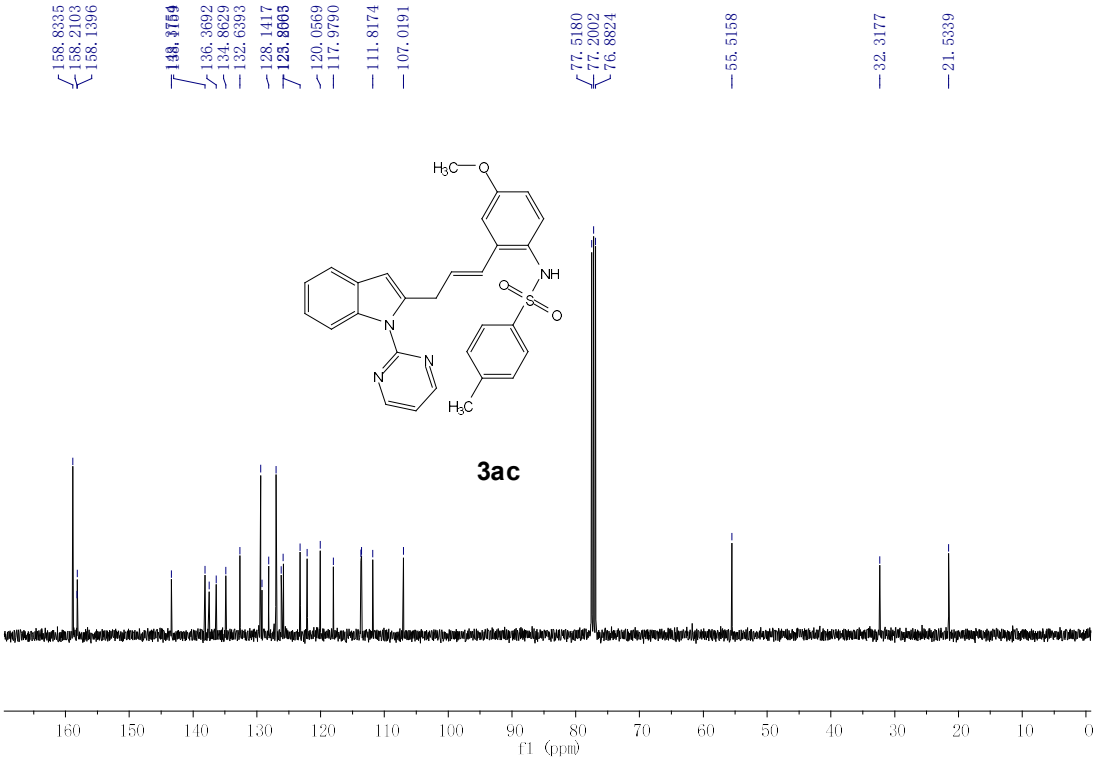
f1 (ppm)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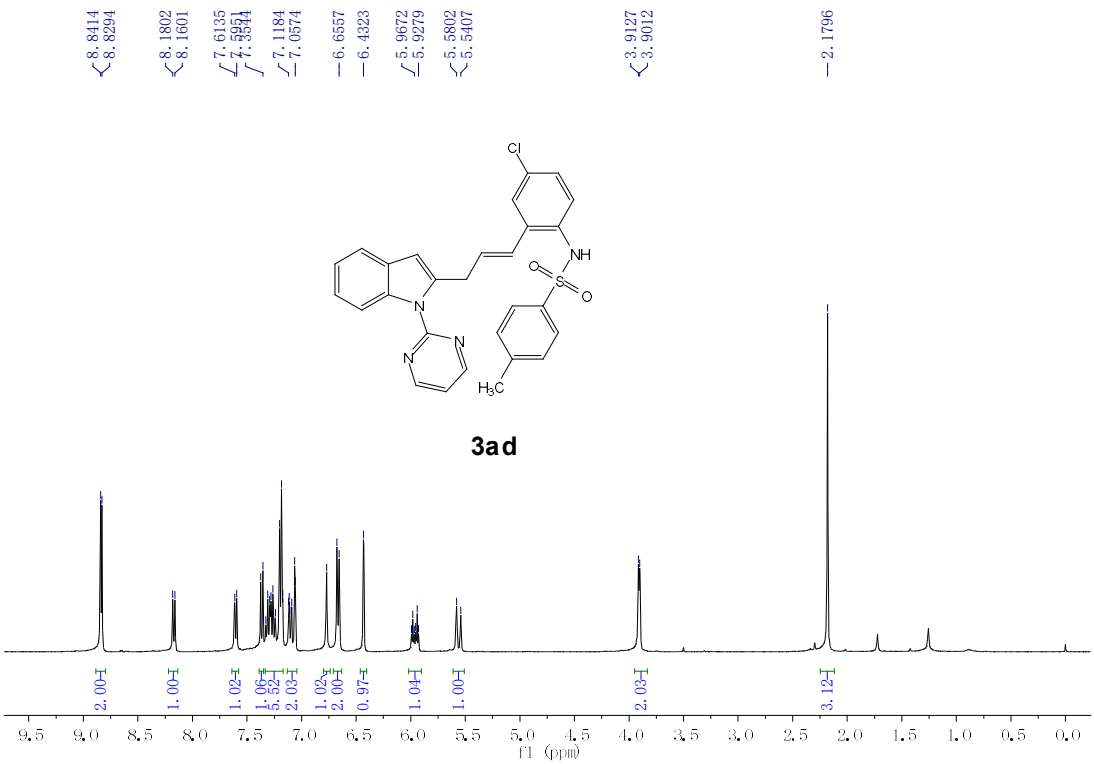
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5.9279
5.5802
5.5407
3.9127
3.9012
2.1796
Cl
NH
S
O
O
N
N
N
H3C
3ad
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1.00
1.02
1.06
5.52
2.03
1.02
2.00
0.97
1.04
1.00
2.03
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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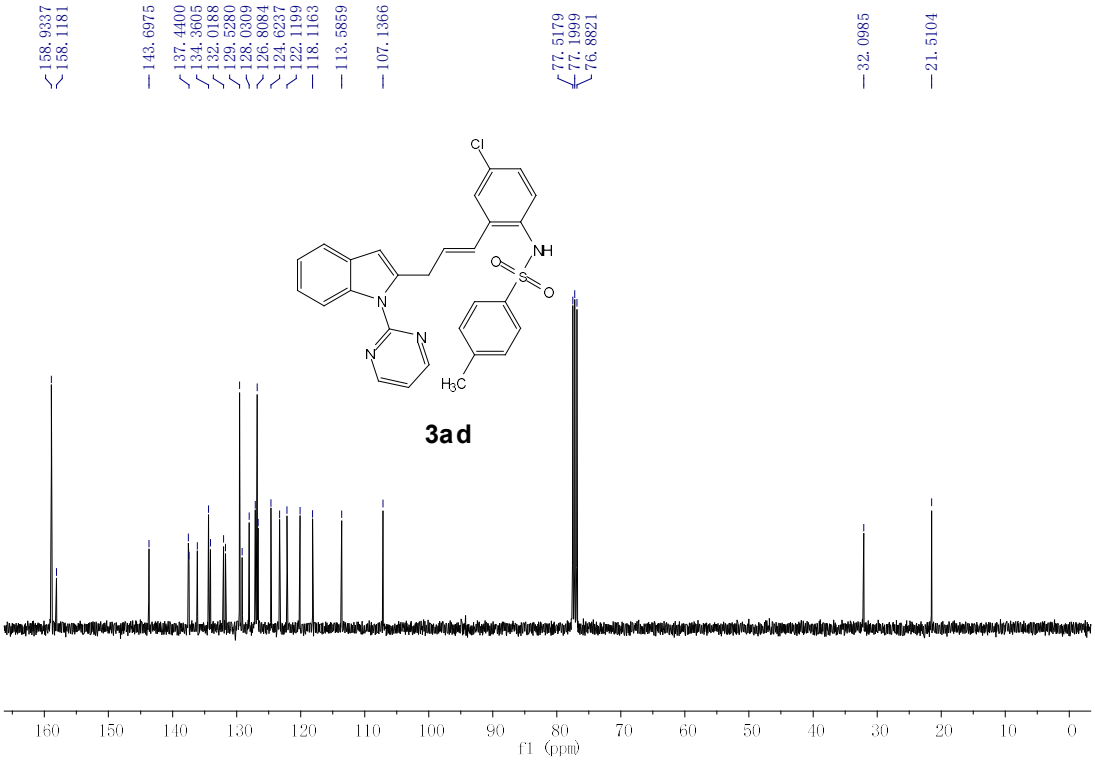
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77.5179
77.1999
76.8821
32.0985
21.5104
Cl
NH
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O
O
N
N
N
H3C
3ad
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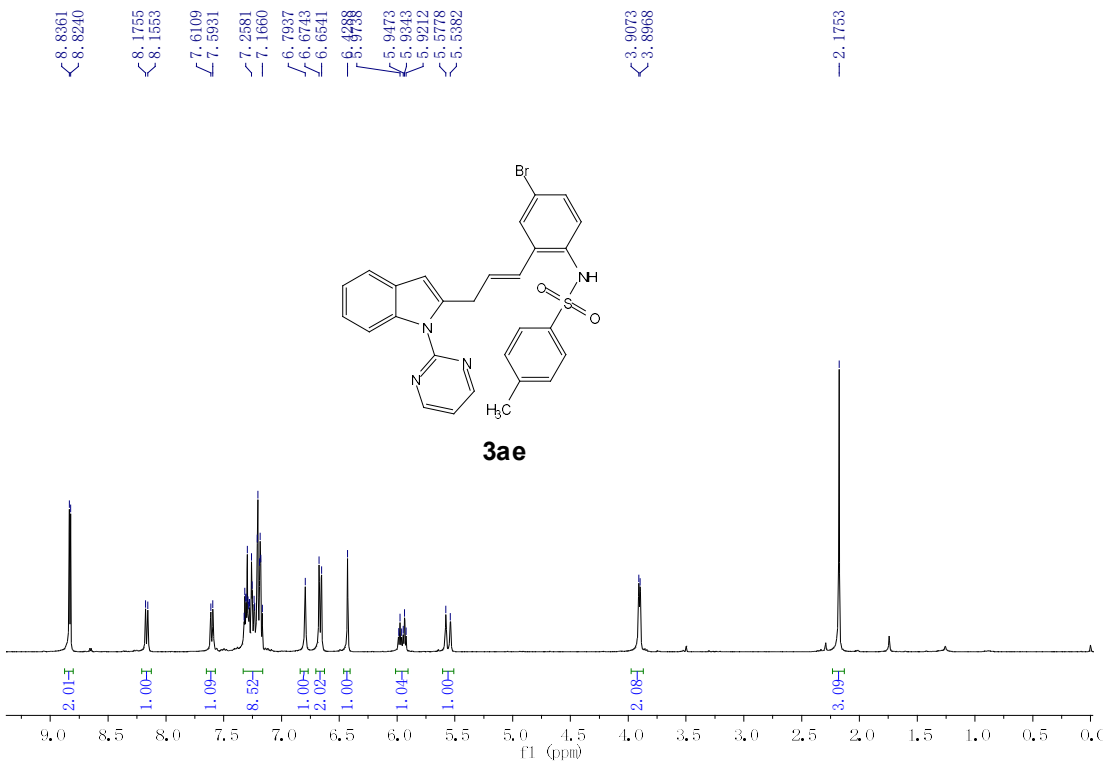
f1 (ppm)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6.4288
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2.1753
Br
NH
S
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O
N
N
N
H3C
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1.00
1.09
8.52
1.00
2.02
1.00
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2.08
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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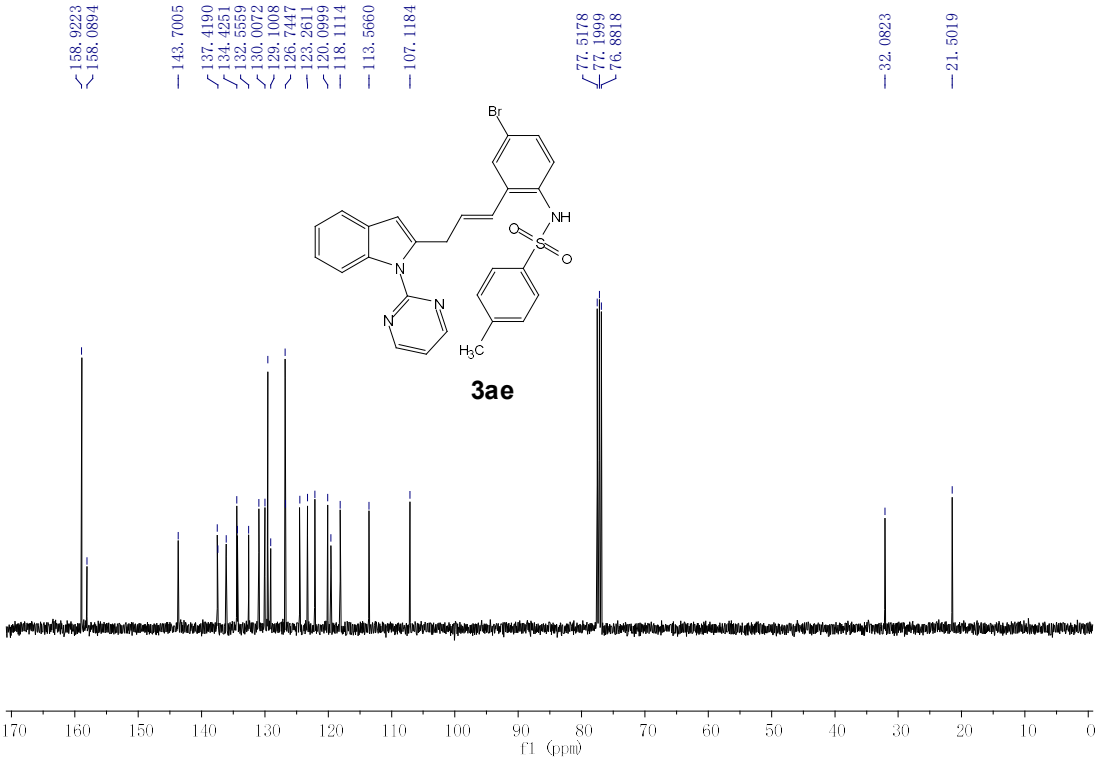
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77.1999
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32.0823
21.5019
Br
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N
N
N
H3C
3ae
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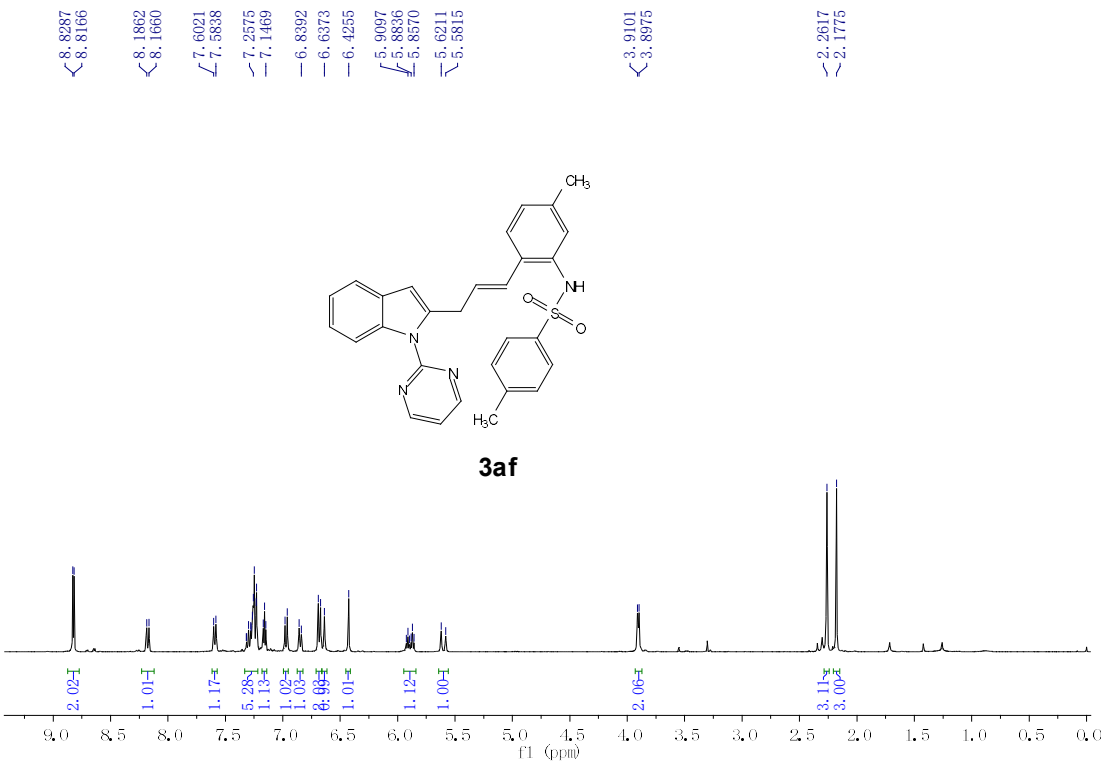
f1 (ppm)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5.8836
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5.6211
5.5815
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3.8975
2.2617
2.1775
CH3
NH
O
S
O
N
N
N
H3C
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1.17
5.28
1.13
1.02
1.03
1.01
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3.11
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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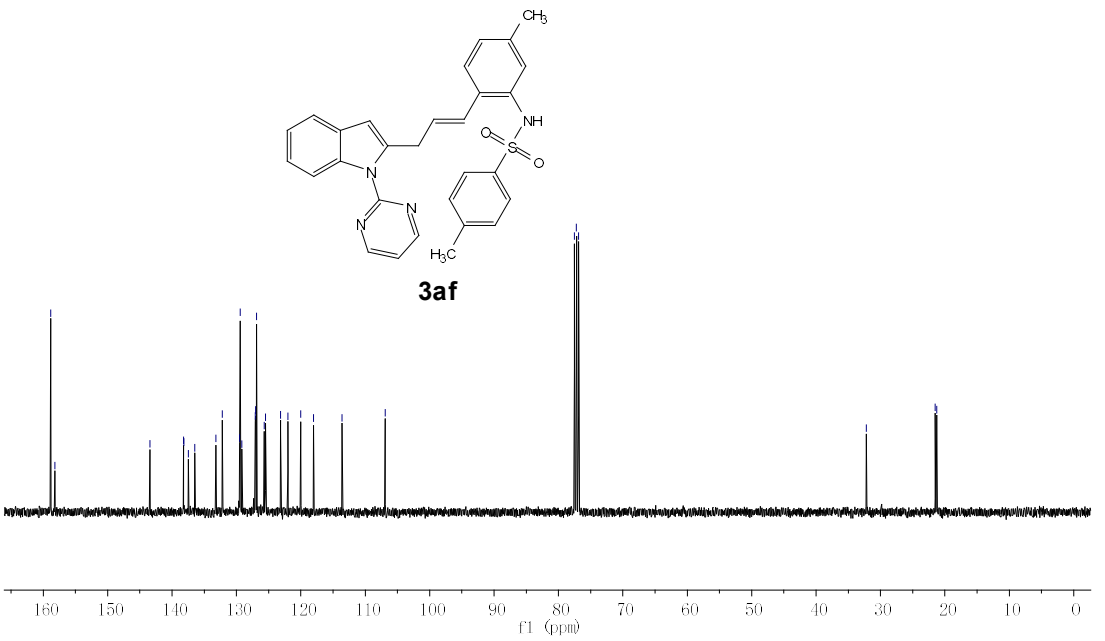
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77.2004
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21.4952
21.2768
CH3
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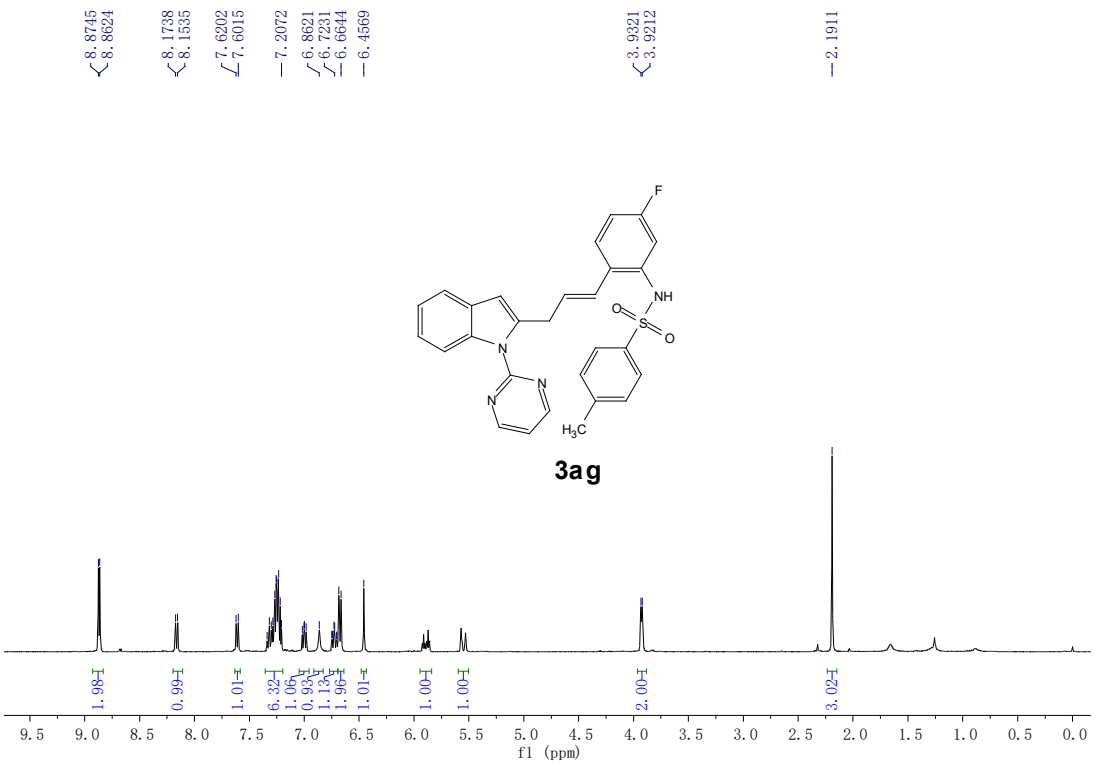
S
O
N
N
N
H3C
3af
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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F
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O
S
O
N
N
N
H3C
3ag
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1.01
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1.06
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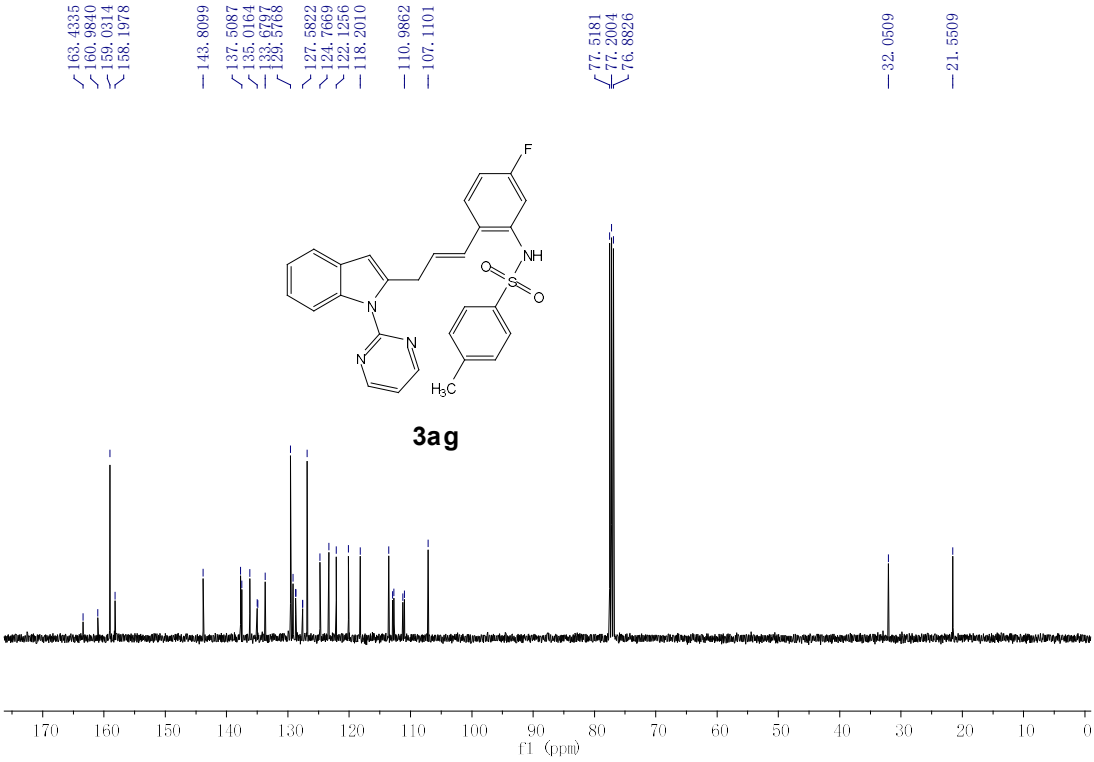
1.13
1.96
1.01
1.00
1.00
2.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.0164
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129.5768
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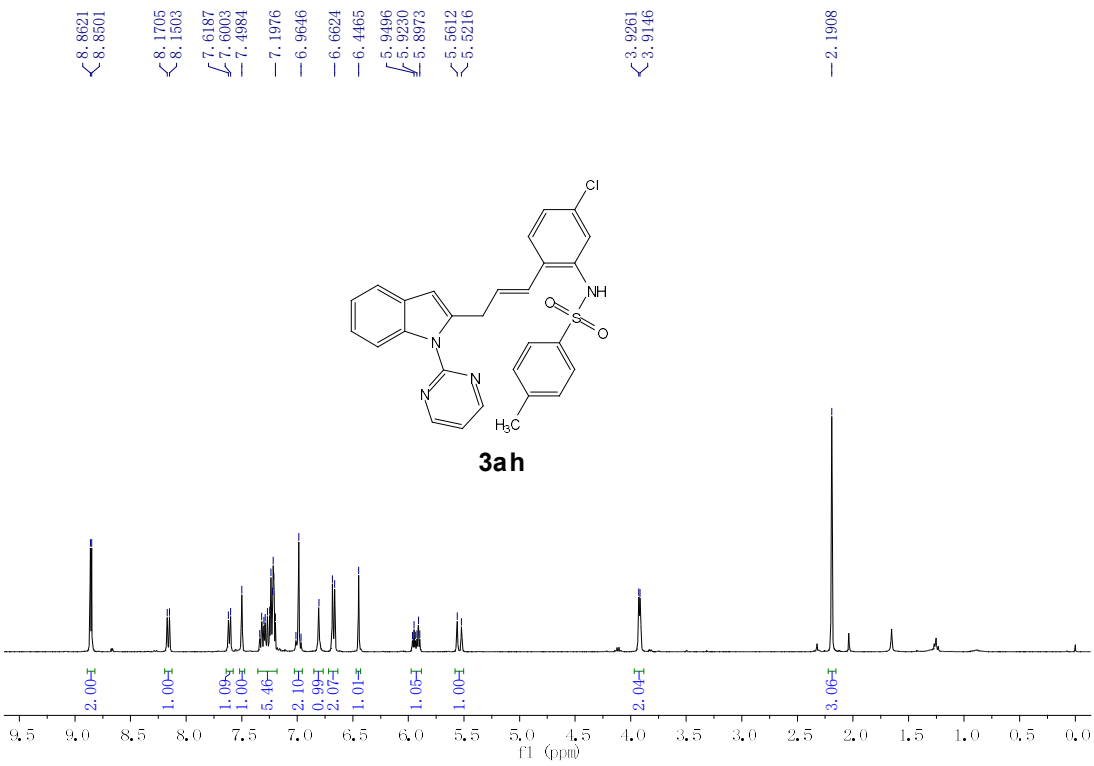
124.7669
122.1256
118.2010
110.9862
107.1101
77.5181
77.2004
76.8826
32.0509
21.5509
F
NH
O
S
O
N
N
N
H3C
3ag
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.4984
7.1976
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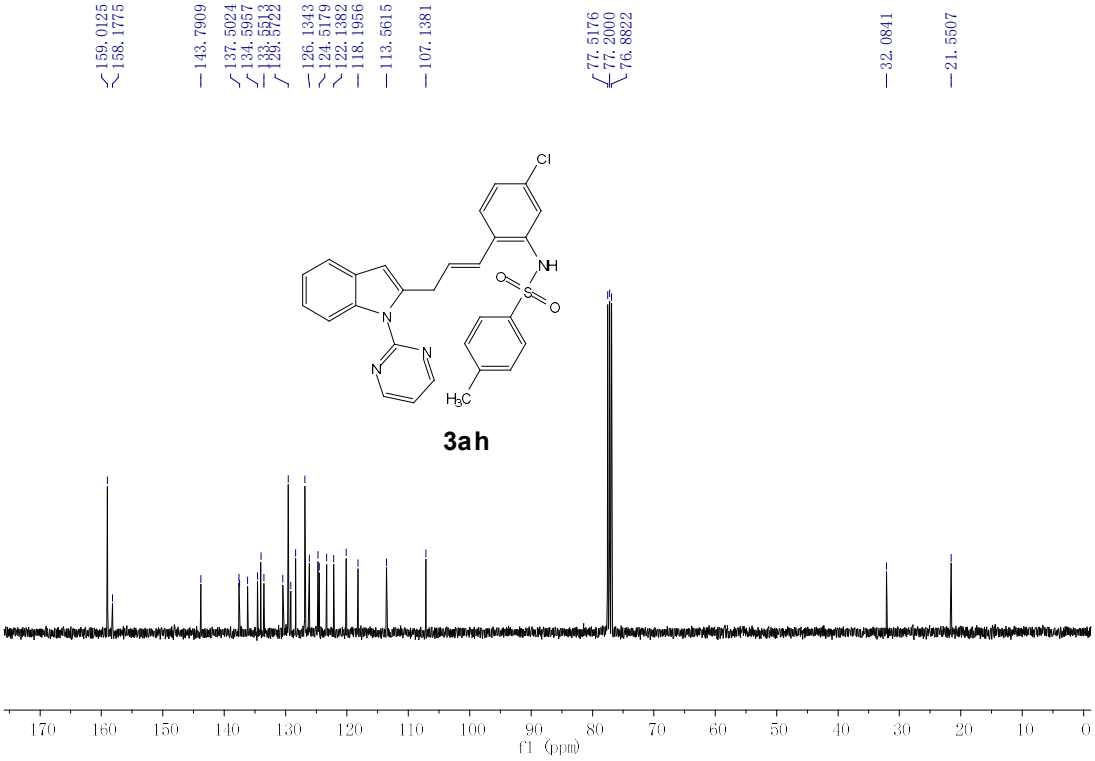
6.4465
5.9496
5.9230
5.8973
5.5612
5.5216
3.9261
3.9146
2.1908
Cl
NH
O
S
O
N
N
N
H3C
3ah
2.00
1.00
1.09
1.00
5.46
2.10
0.99
2.07
1.01
1.05
1.00
2.04
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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118.1956
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77.5176
77.2000
76.8822
32.0841
21.5507
Cl
NH
O
S
O
N
N
N
H3C
3ah
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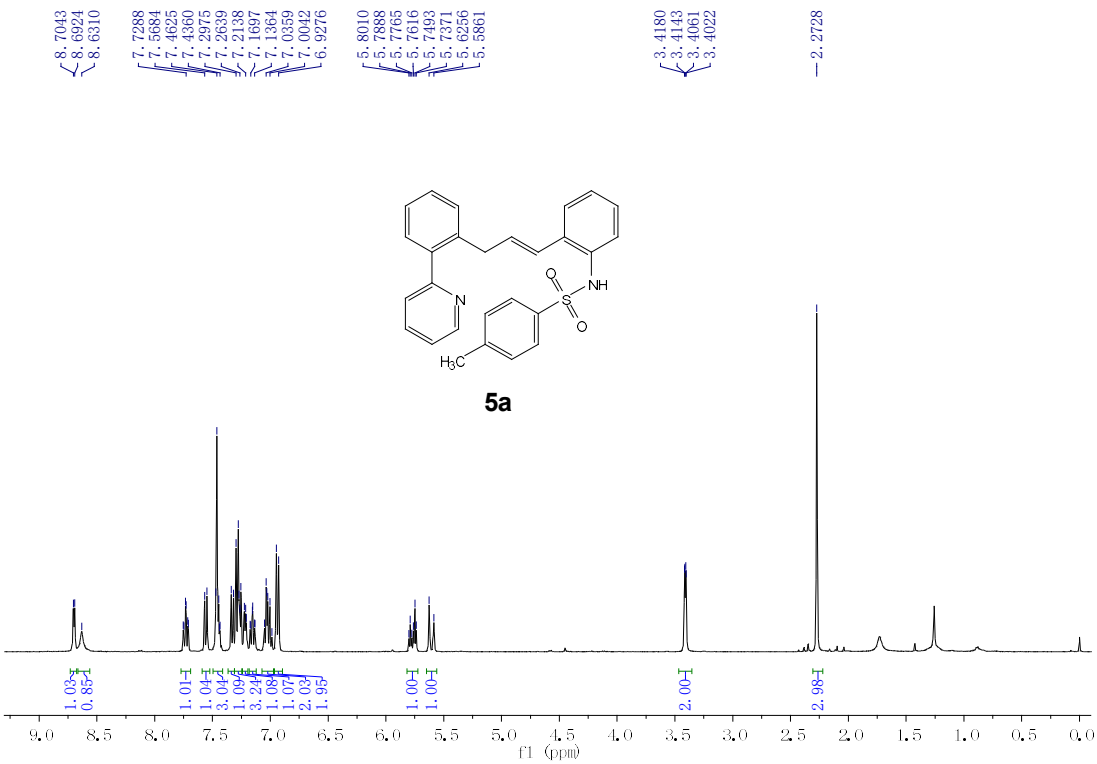
f1 (ppm)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7.4360
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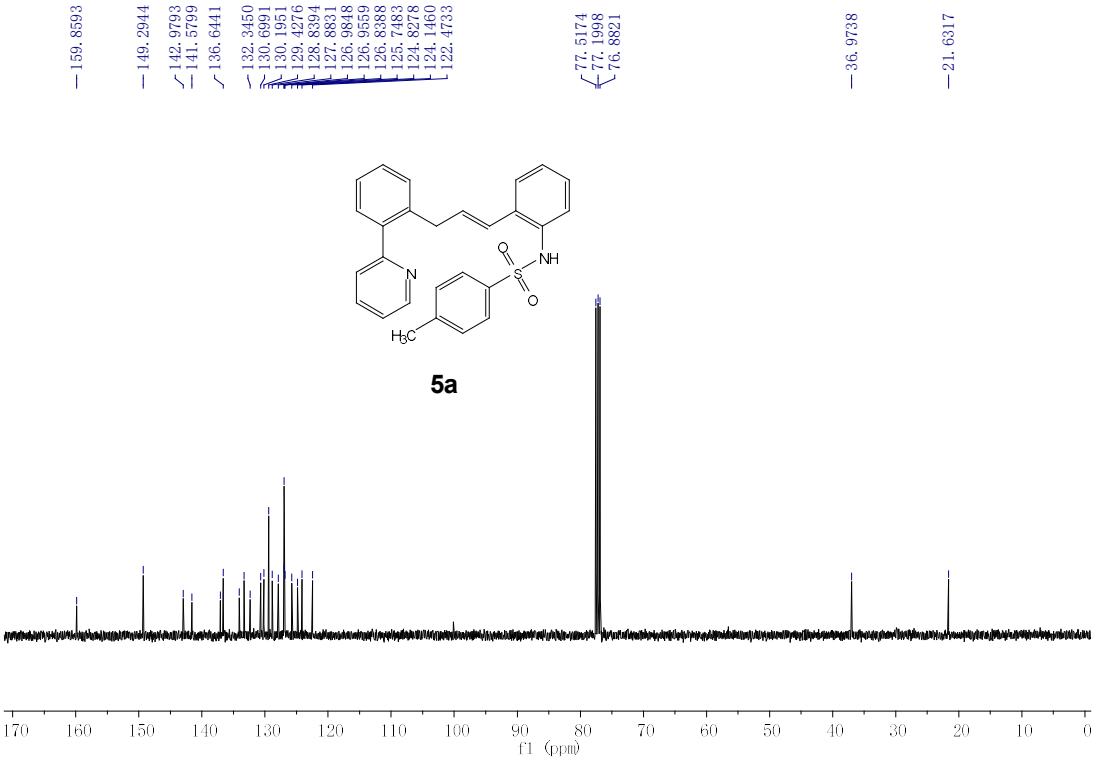
7.1697
7.1364
7.0359
7.0042
6.9276
5.8010
5.7888
5.7765
5.7616
5.7493
5.7371
5.6256
5.5861
3.4180
3.4143
3.4061
3.4022
2.2728
5a
1.03
0.85
1.01
1.04
3.04
1.09
3.24
1.08
1.07
2.03
1.95
1.00
1.00
2.00
2.98
f1 (ppm)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127.8831
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126.9559
126.8388
125.7483
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36.9738
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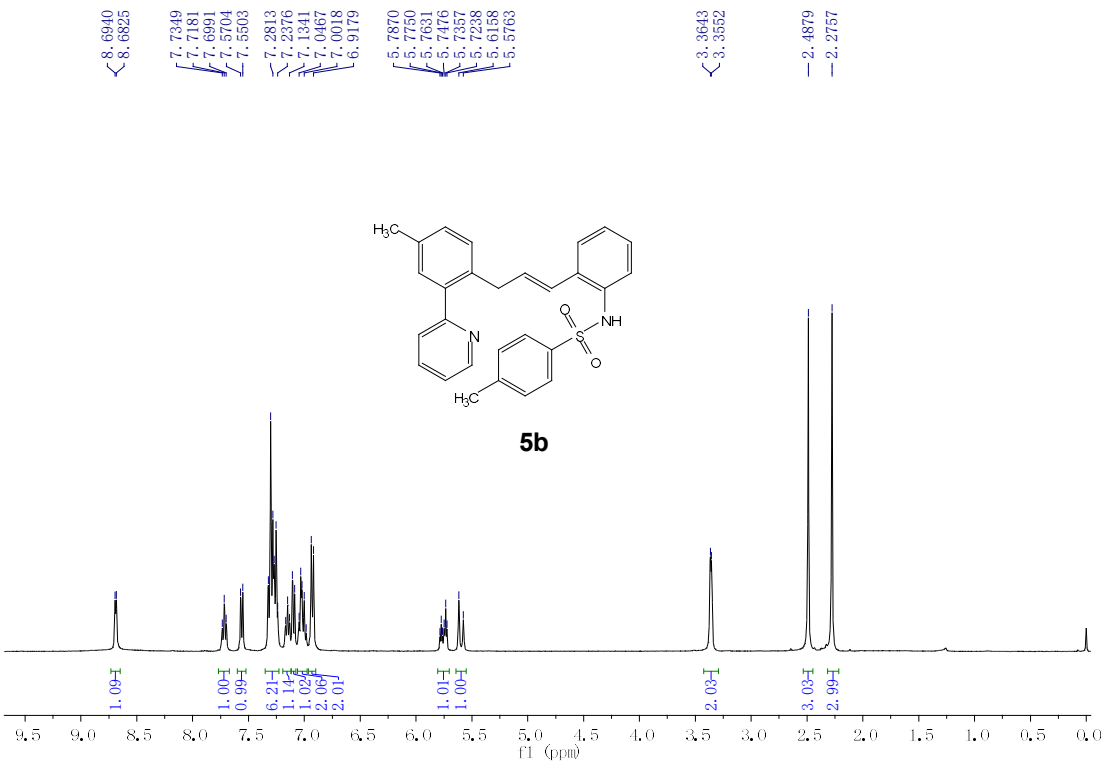
5a
f1 (ppm)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7.5503
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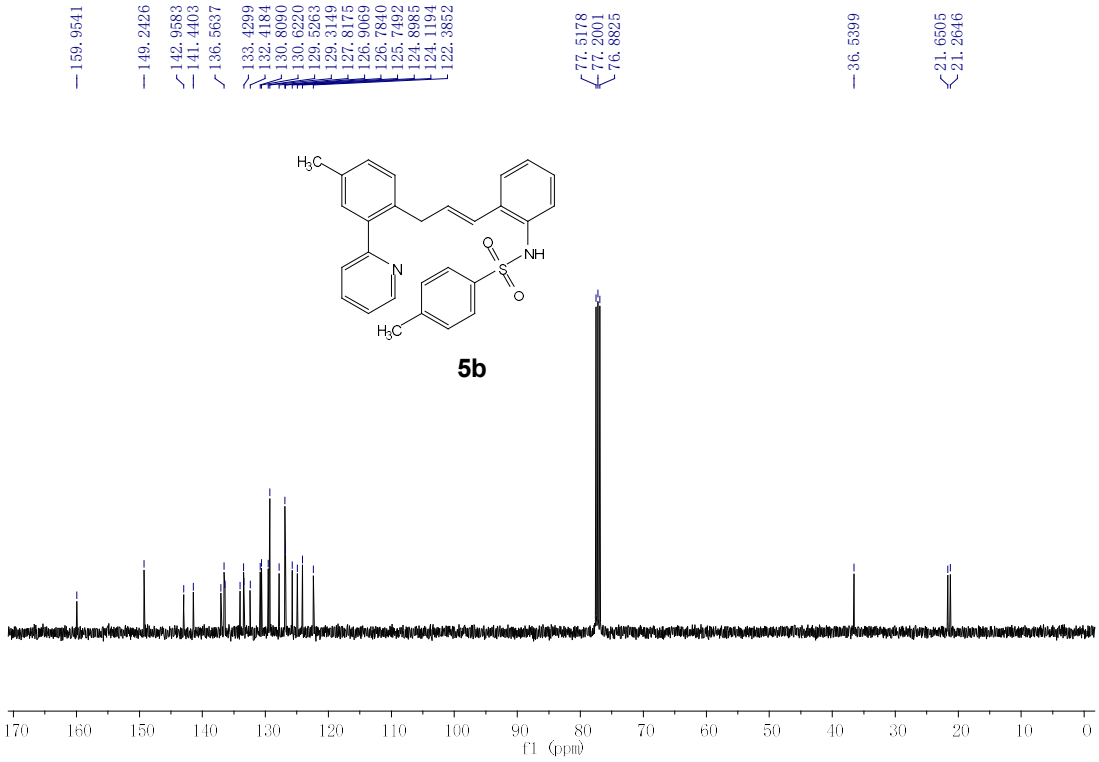
7.0018
6.9179
5.7870
5.7750
5.7631
5.7476
5.7357
5.7238
5.6158
5.5763
3.3643
3.3552
2.4879
2.2757
H3C
N
O
S
NH
O
H3C
5b
1.09
1.00
0.99
6.21
1.14
1.02
2.06
2.01
1.01
1.00
2.03
3.03
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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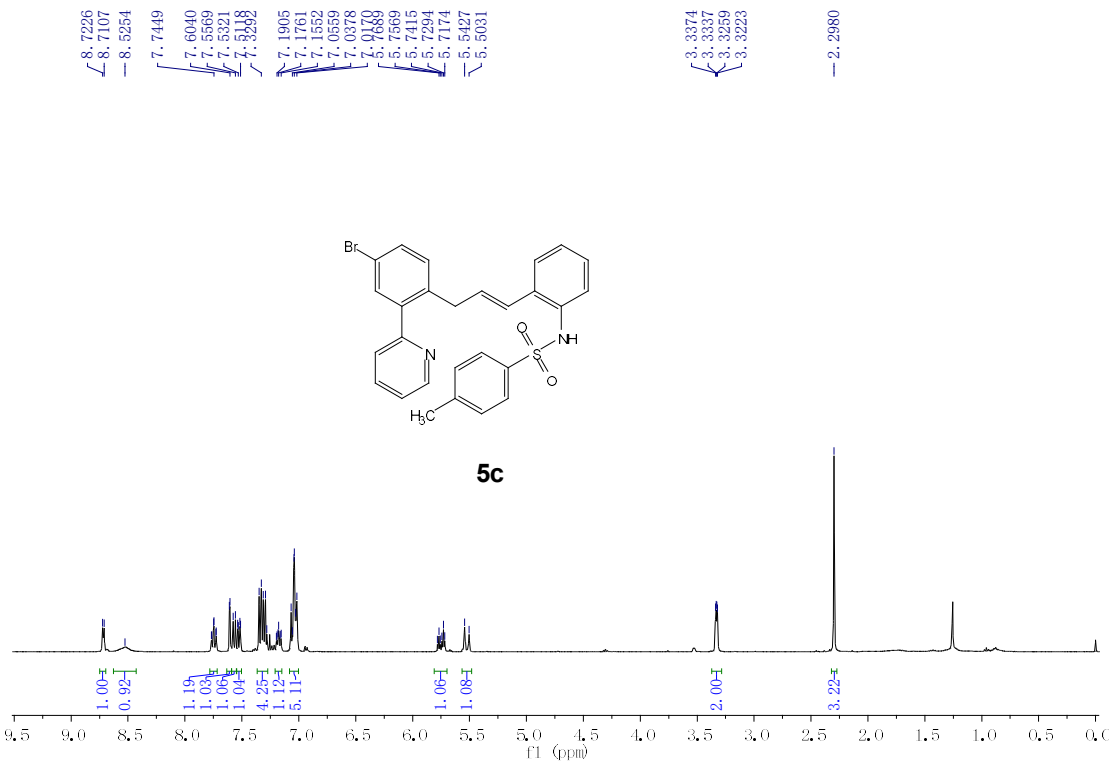
129.3149
127.8175
126.9069
126.7840
125.7492
124.8985
124.1194
122.3852
77.5178
77.2001
76.8825
36.5399
21.6505
21.2646
H3C
N
O
S
NH
O
H3C
5b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.5254
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7.6040
7.5569
7.5321
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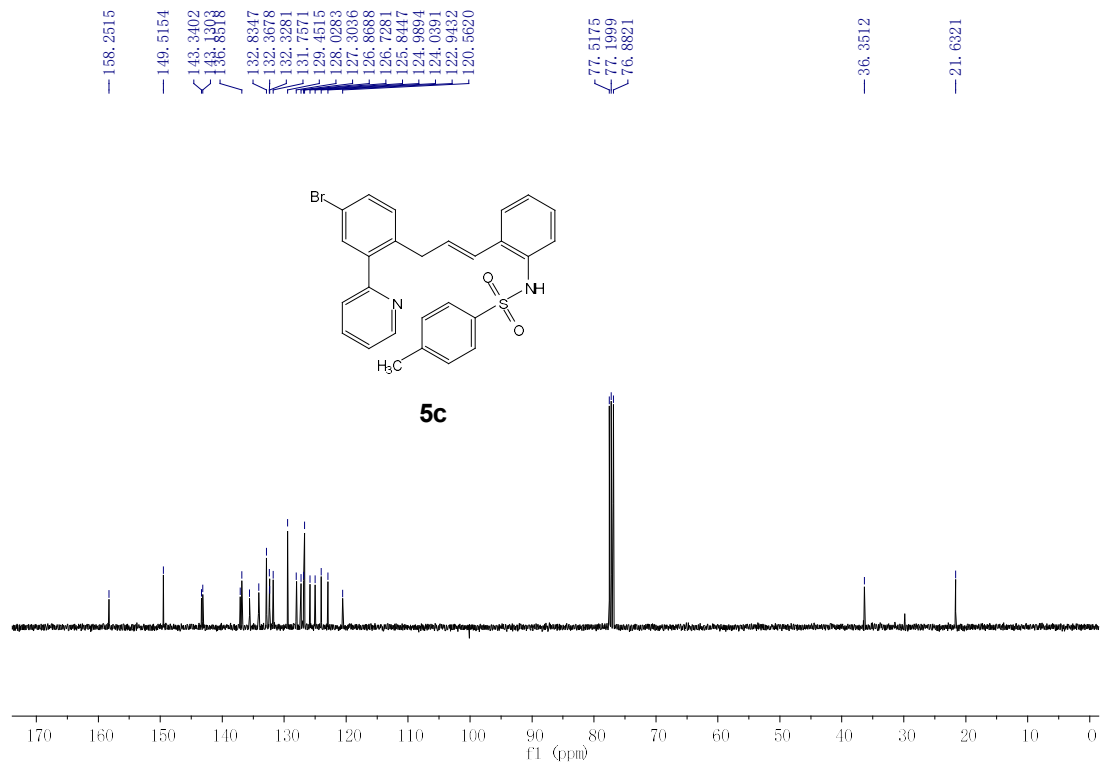
7.1905
7.1761
7.1552
7.0559
7.0378
5.7569
5.7415
5.7294
5.7174
5.5427
5.5031
3.3374
3.3337
3.3259
3.3223
2.2980
Br
N
NH
S
O
O
H3C
5c
1.00
0.92
1.19
1.03
1.06
1.04
4.25
1.12
5.11
1.06
1.08
2.00
3.22
f1 (ppm)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136.8318
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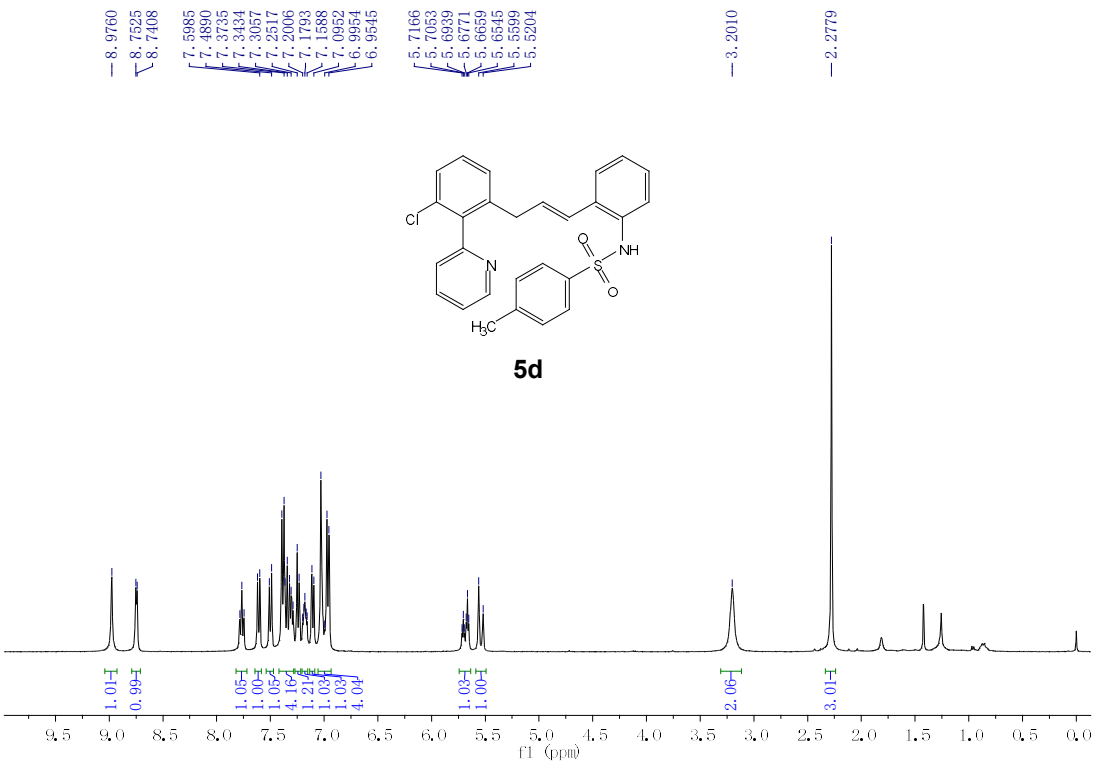
127.3036
126.8688
126.7281
125.8447
124.9894
124.0391
122.9432
120.5620
77.5175
77.1999
76.8821
36.3512
21.6321
Br
N
NH
S
O
O
H3C
5c
f1 (ppm)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7.3434
7.3057
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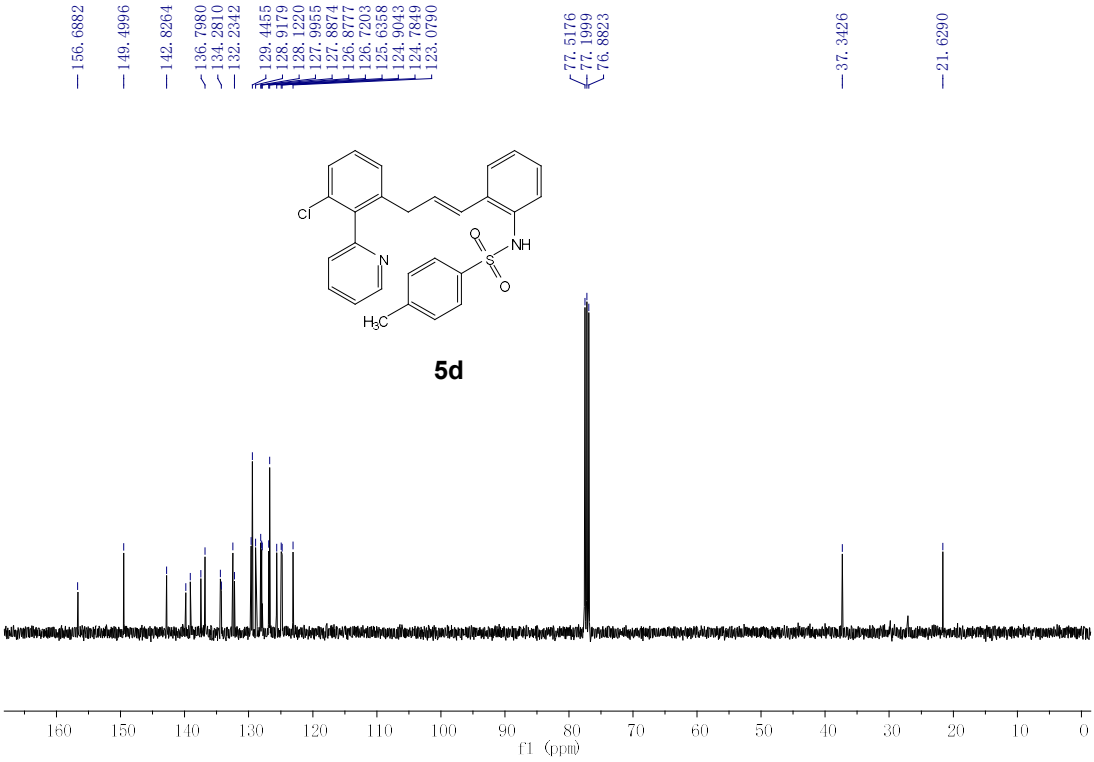
7.1793
7.1588
7.0952
6.9954
6.9545
5.7166
5.7053
5.6939
5.6771
5.6659
5.6545
5.5599
5.5204
3.2010
2.2779
Cl
N
O
NH
S
O
H3C
5d
1.01
0.99
1.05
1.00
1.05
4.16
1.21
1.03
1.03
4.04
1.03
1.00
2.06
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.1220
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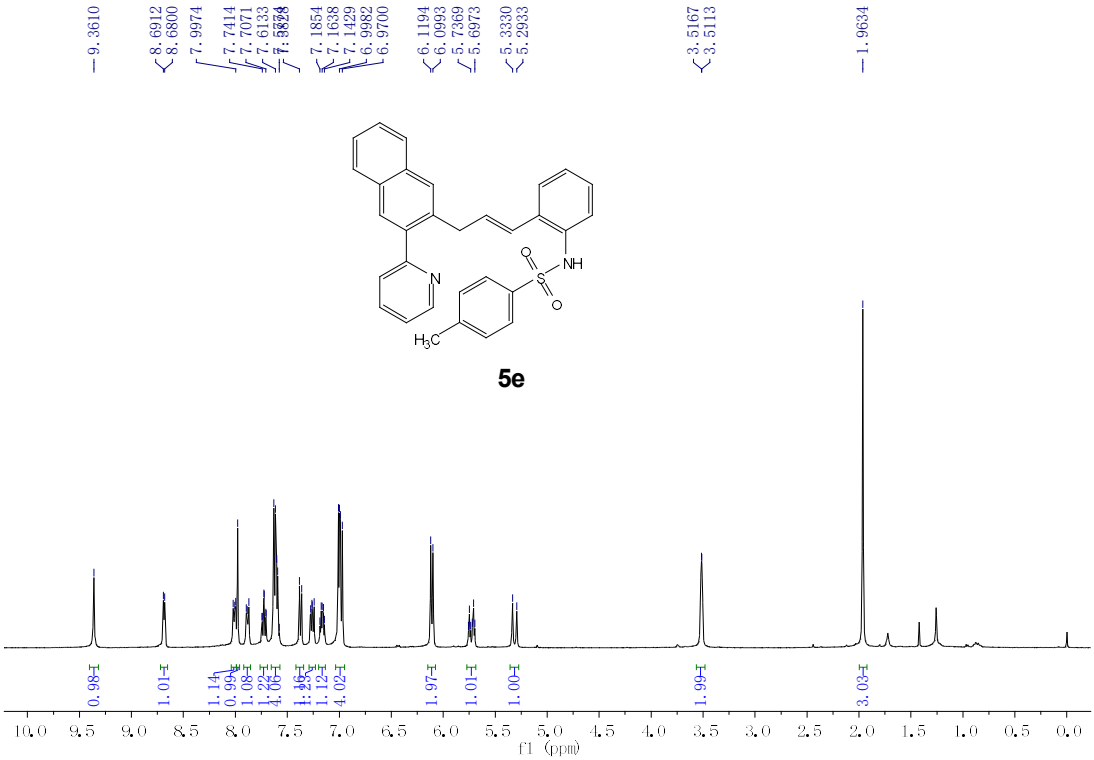
127.8874
126.8777
126.7203
125.6358
124.9043
124.7849
123.0790
77.5176
77.1999
76.8823
37.3426
21.6290
Cl
N
O
NH
S
O
H3C
5d
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.7414
7.7071
7.6133
7.1854
7.1638
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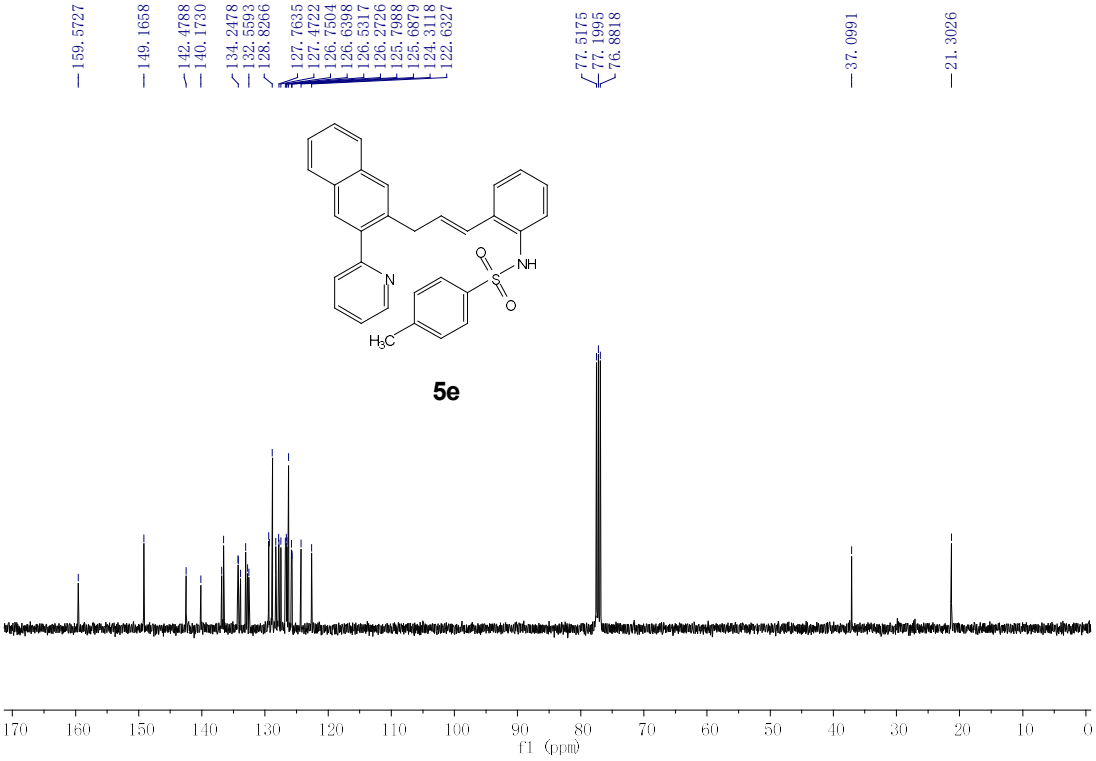
6.9700
6.1194
6.0993
5.7369
5.6973
5.3330
5.2933
3.5167
3.5113
1.9634
0.98
1.01
1.14
0.99
1.08
1.22
4.00
1.12
4.02
1.97
1.01
1.00
1.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
NH
N
H3C
5e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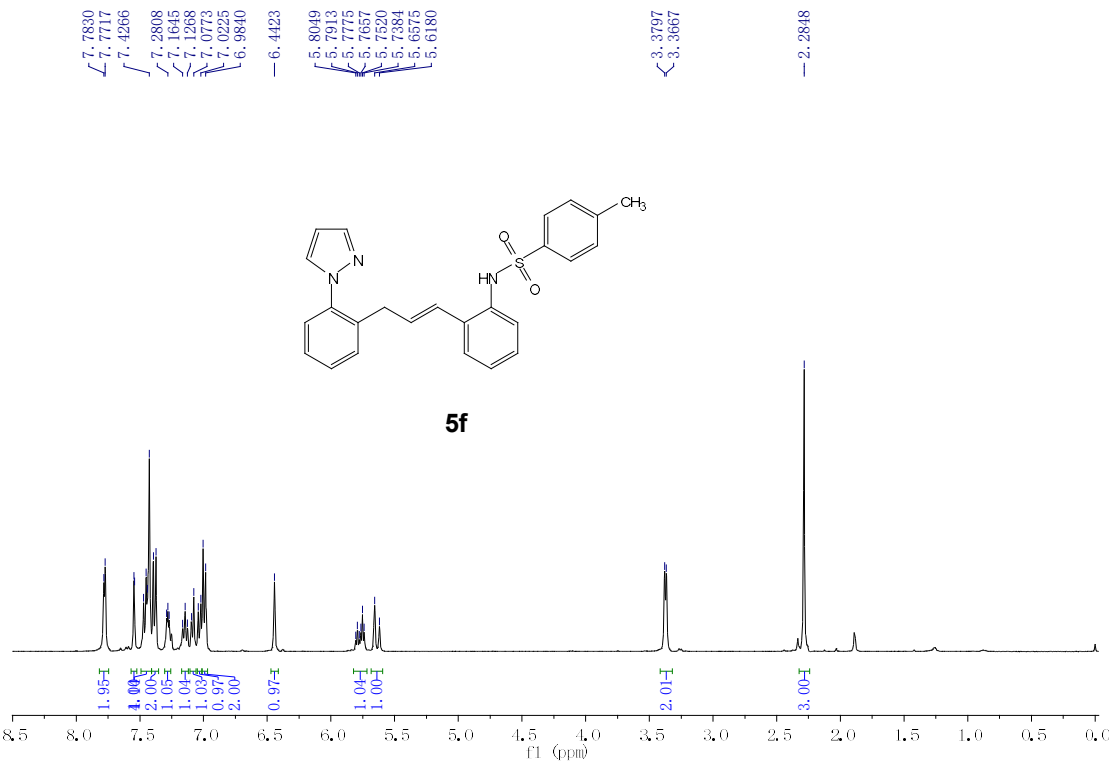
126.2726
125.7988
125.6879
124.3118
122.6327
77.5175
77.1995
76.8818
37.0991
21.3026
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
NH
N
H3C
5e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7.0773
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6.9840
6.4423
5.8049
5.7913
5.7775
5.7657
5.7520
5.7384
5.6575
5.6180
3.3797
3.3667
2.2848
CH3
N
N
HN
S
O
O
5f
1.95
2.00
1.05
1.04
1.03
0.97
2.00
0.97
1.04
1.00
2.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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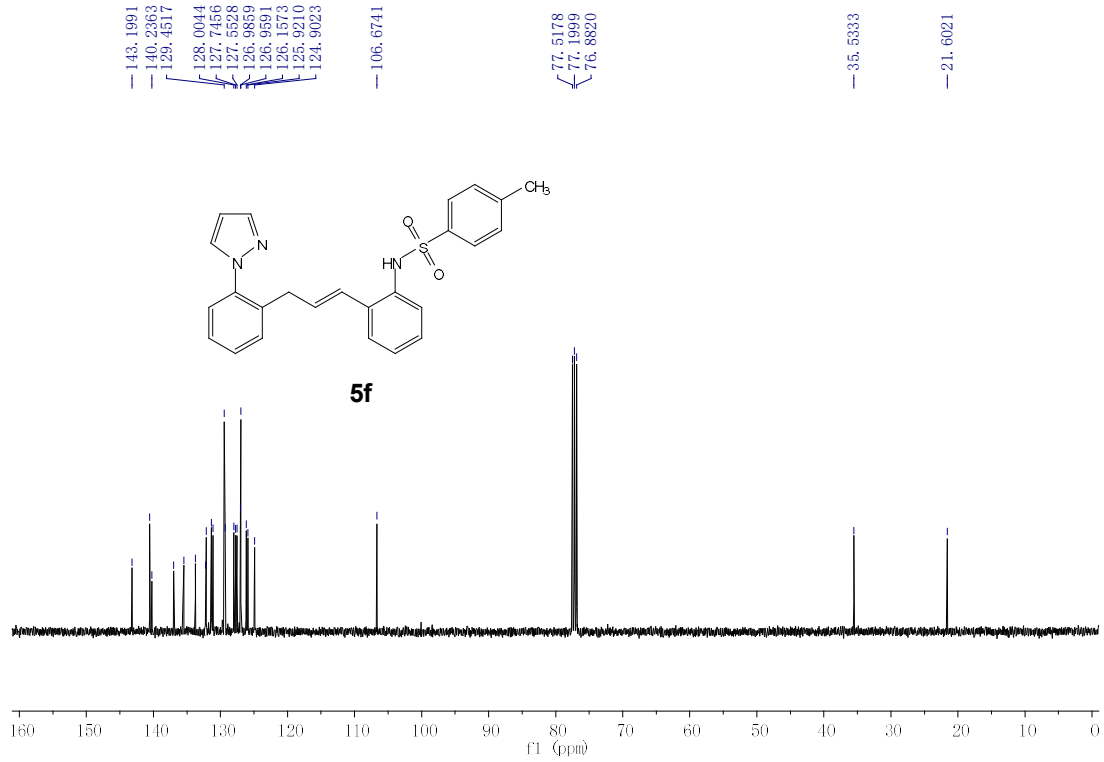
0.0
f1 (ppm)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106.6741
77.5178
77.1999
76.8820
35.5333
21.6021
CH3
N
N
HN
S
O
O
5f
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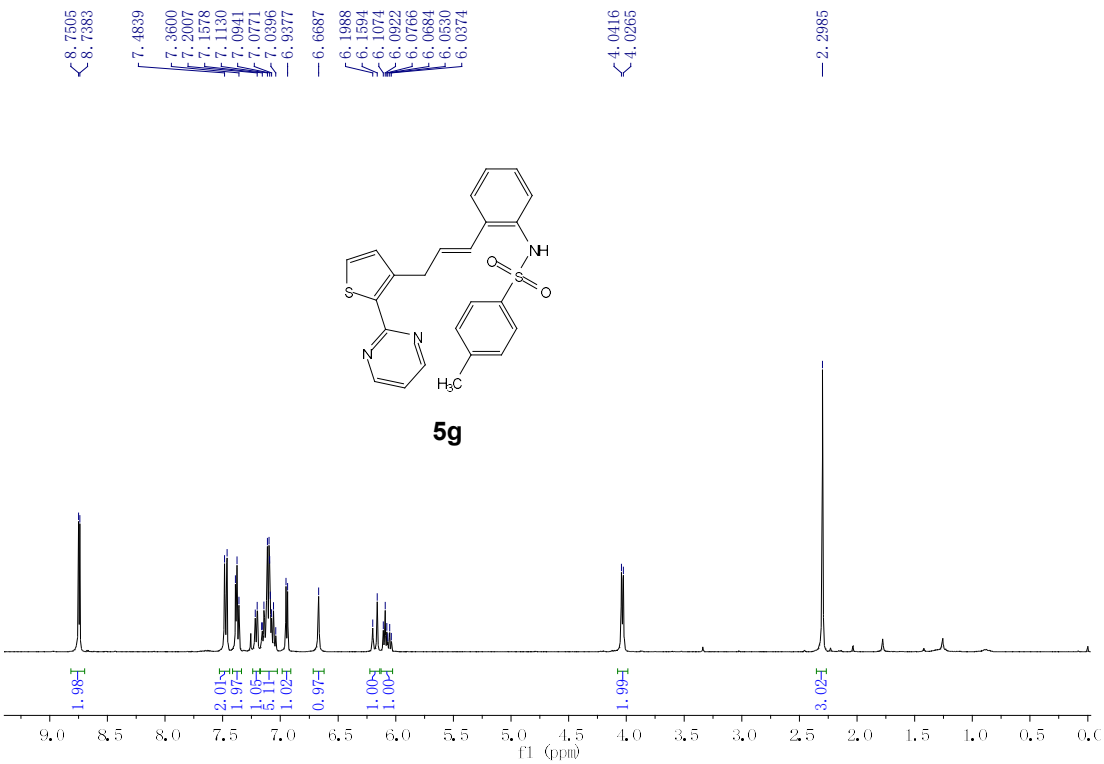
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.0771
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7.9377
6.6687
6.1988
6.1594
6.1074
6.0922
6.0766
6.0684
6.0530
6.0374
4.0416
4.0265
2.2985
NH
S
O
O
S
N
N
H3C
5g
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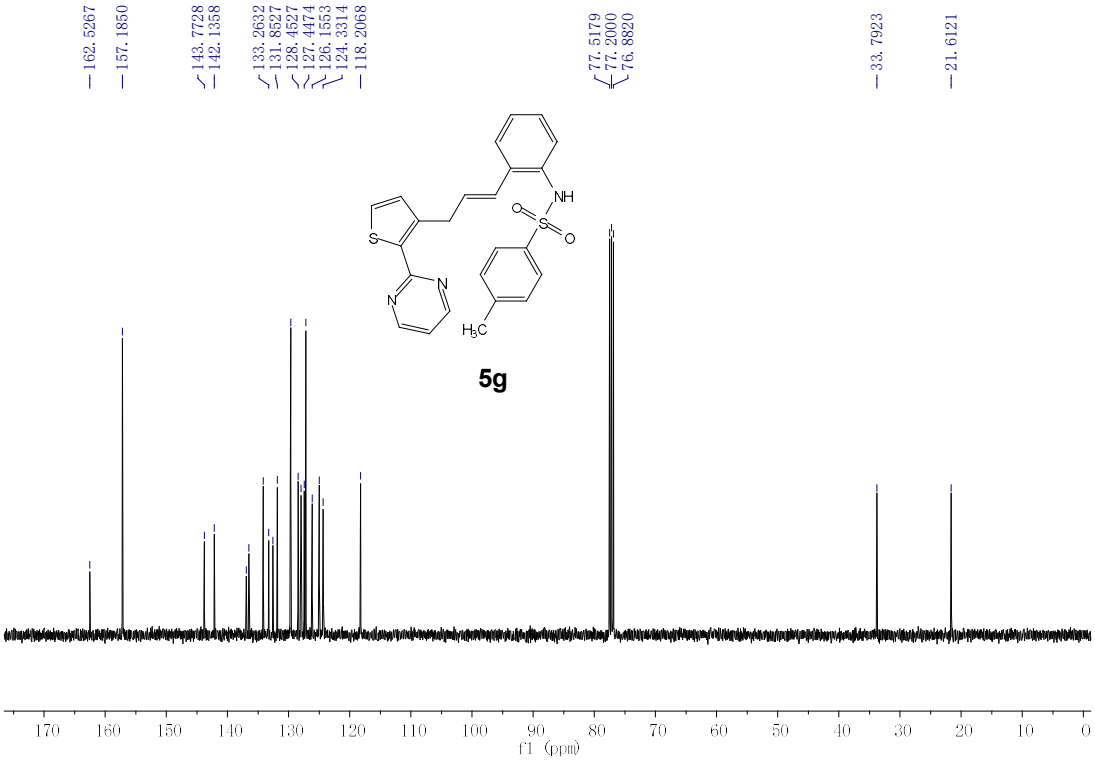
1.97
1.05
5.11
1.02
0.97
1.00
1.00
1.99
3.02
f1 (ppm)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118.2068
77.5179
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33.7923
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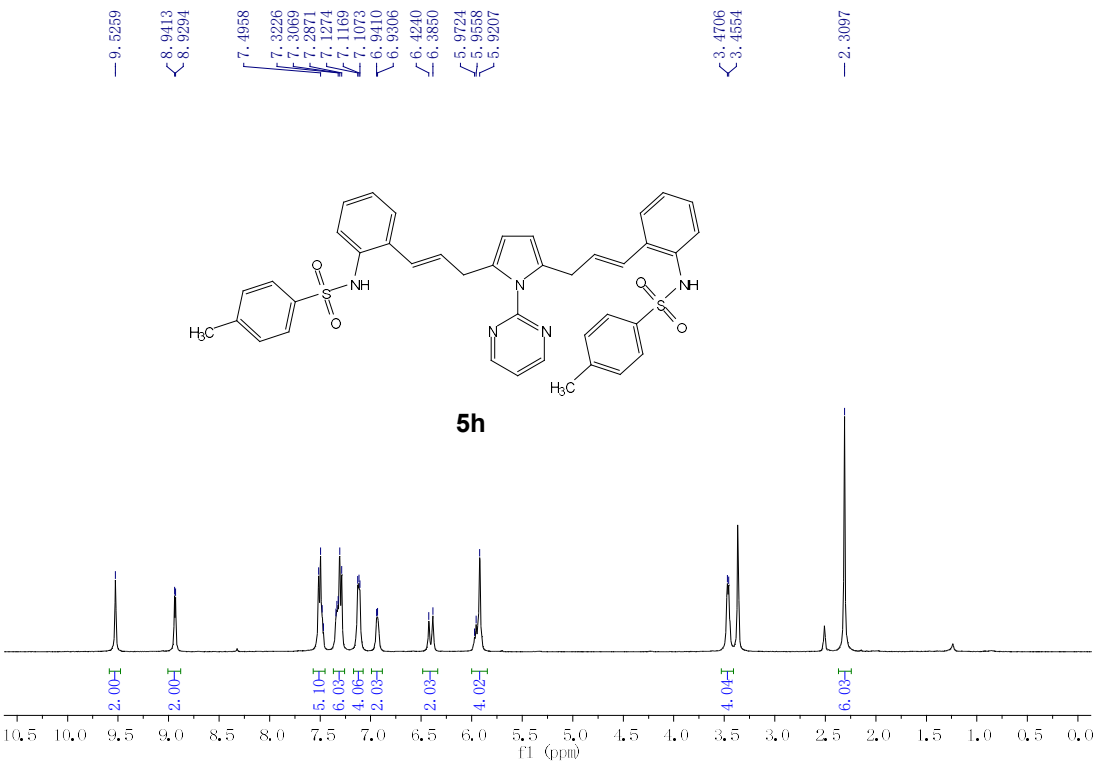
NH
S
O
O
S
N
N
H3C
5g
f1 (ppm)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6.9306
6.4240
6.3850
5.9724
5.9558
5.9207
3.4706
3.4554
2.3097
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5.10
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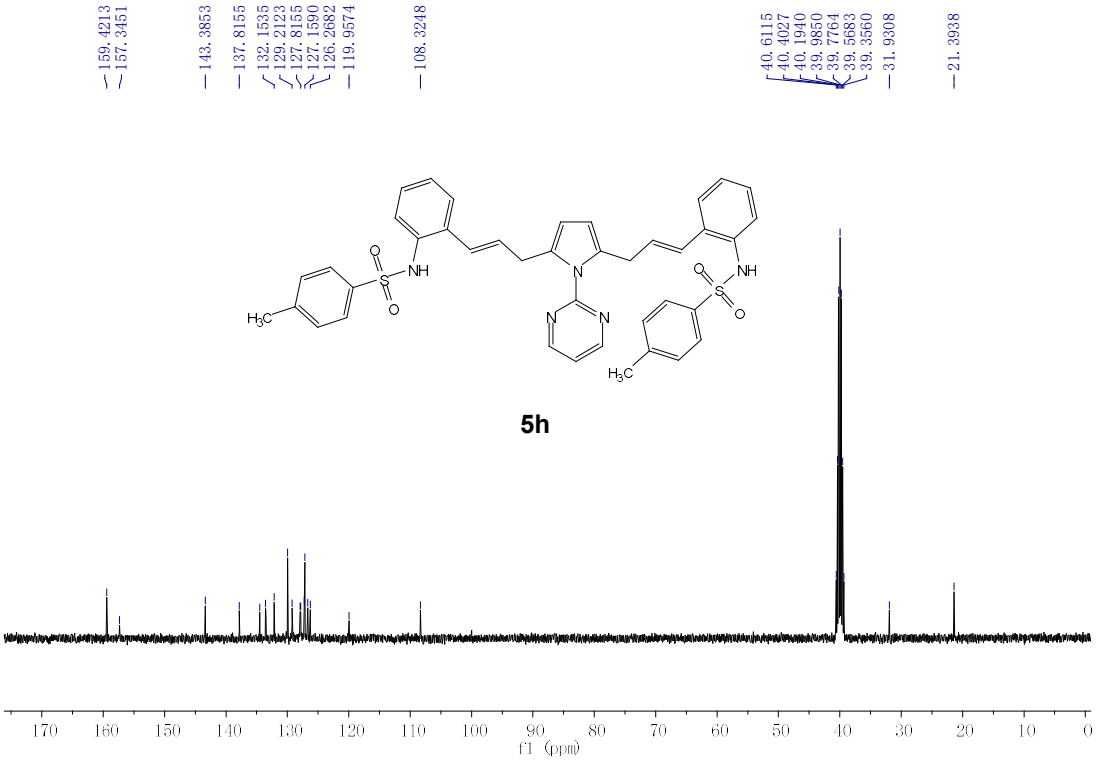
2.03
4.02
4.04
6.03
f1 (ppm)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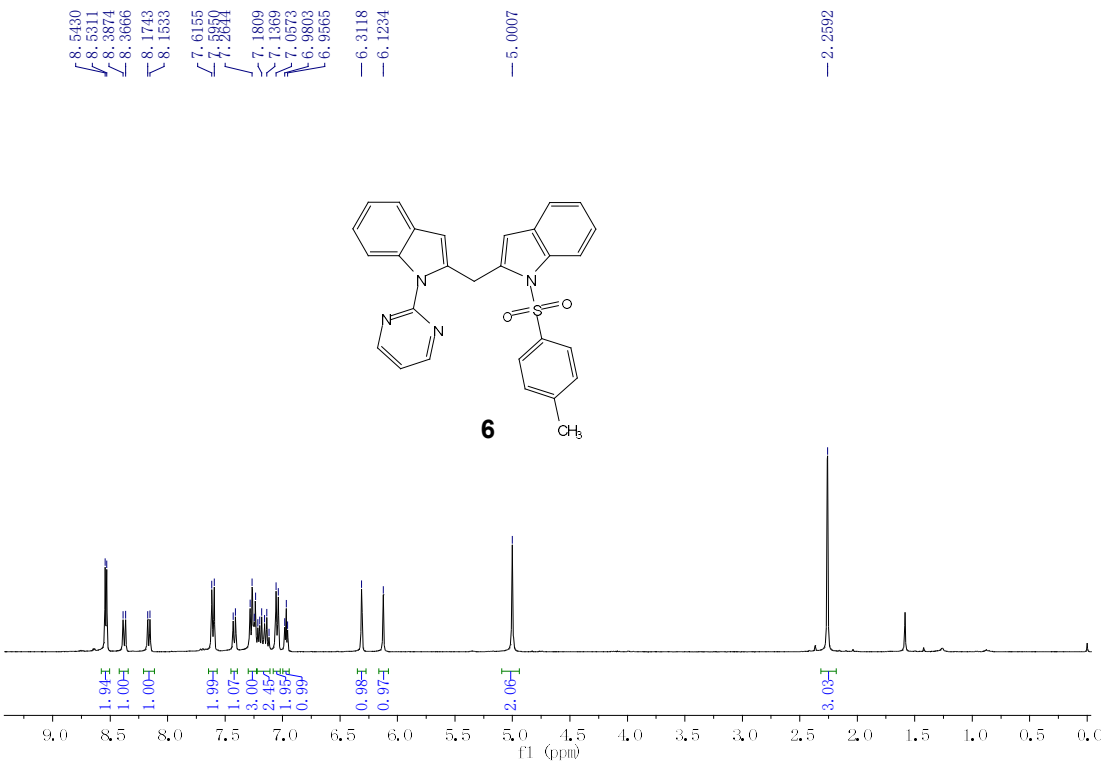
5h
f1 (ppm)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8.1533
7.6155
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7.2644
7.1809
7.1369
7.0573
6.9803
6.9565
6.3118
6.1234
5.0007
2.2592
6
CH3
1.94
1.00
1.00
1.99
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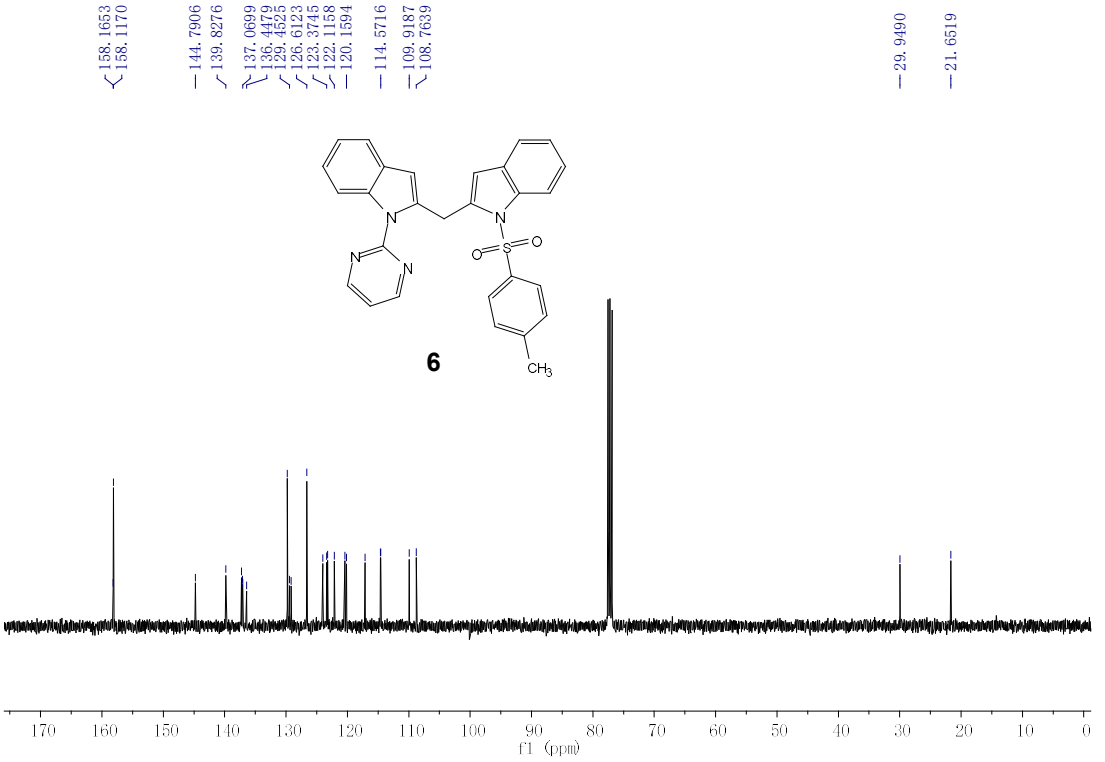
3.00
2.45
1.95
0.99
0.98
0.97
2.06
3.03
f1 (ppm)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114.5716
109.9187
108.7639
29.9490
21.6519
6
CH3
f1 (ppm)