# Rhodium-Catalyzed Regioselective Amidation of Indoles with Sulfonyl Azides via C−H Bond Activation

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***General methods:***

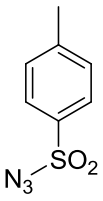
Mass spectra and high-resolution mass spectra were measured on a Finnigan MAT-95 mass spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were determined on Bruker AM-300, Bruker AM-400, Bruker AM-500 instruments using tetramethylsilane as internal reference. Data are presented as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, m = multiplet), *J* = coupling constant in hertz (Hz). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

***Materials:***

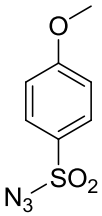
$AgSbF_6$ was purchased from Aldrich and used without further purification. $[Cp^*RhCl_2]_2$ [S1], $[Cp^*Rh(MeCN)_3][SbF_6]_2$ [S2], substrate 1-(Pyrimidin-2-yl)- 1*H*-indole [S3] and benzenesulfonyl azide [S4] were synthesized according to published procedures.

***Experimental Procedures and Characterizations:***

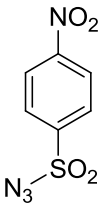
**General Procedure for Preparation of benzenesulfonyl azide**: benzenesulfonyl chloride (10.0 mmol) was dissolved in acetone (20 mL) and water (20 mL). The solution was cooled on ice and $NaN_3$ (10.0 mmol) was added. The reaction was stirred for 2 h. The acetone was removed under vacuum and the remaining water layer was extracted with EtOAc (150 mL), the EtOAc layer was washed with brine, dried on $Na_2SO_4$, filtered and concentrated. The benzenesulfonyl azide was obtained for future use without purification.




**4-methylbenzenesulfonyl azide:** This compound was obtained in 95% yield as a colourless oil. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.8, 2H), 7.40 (d, *J* = 7.8, 2H), 2.48 (s, 3H). Spectral data matched those previously reported.[S4]

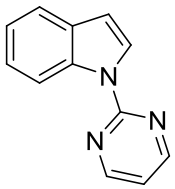


**4-methoxybenzenesulfonyl azide:** This compound was obtained in 98% yield as a colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.7, 2H), 7.05 (d, *J* = 8.7, 2H), 3.91 (s, 3H). Spectral data matched those previously reported.[S4]



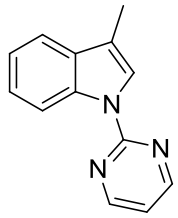
**4-nitrobenzenesulfonyl azide:** This compound was obtained in 98% yield as a light yellow solid. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.7, 1H), 8.17 (d, *J* = 8.7, 1H). Spectral data matched those previously reported.[S4]

**General Procedure for Preparation of substrate 1-(Pyrimidin-2-yl)-1*H*-indole moiety** [S3]: NaH (60% dispersion in mineral oil, 11.0 mmol) was added in portions at 0 ℃ to astirred solution of indole (10.0 mmol) in DMF (25 mL). After stirring for 30 min at 0 ℃, 2-chloropyrimidine (12.0 mmol) was added and the mixture was stirred at 130 ℃ for 24 h. Then, the reaction mixture was cooled to ambient temperature, poured into H2O (300 mL) and extracted with EtOAc (250 mL). The organic phase was dried over Na2SO4. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (cyclohexane/EtOAc: 10/1) to give product.

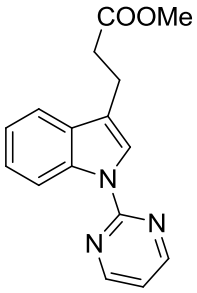


**1-(Pyrimidin-2-yl)-1*H*-indole (1f).** This compound was obtained in 85% yield as a white solid. M. p. = 86−88 °C. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 3.7 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.35

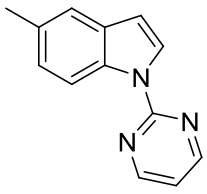
(dd, *J* = 9.0, 6.5 Hz, 1H), 7.25 (t, *J* = 6.1 Hz, 1H), 7.04 (m, 1H), 6.71 (d, *J* = 3.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 157.8, 135.4, 131.4, 125.9, 123.7, 122.2, 120.9, 116.3, 116.1, 107.0. Spectral data matched those previously reported.[S3]



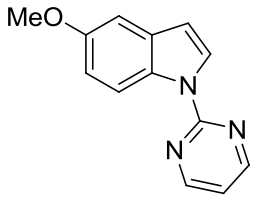
**3-methyl-1-(pyrimidin-2-yl)-1H-indole (1g).** This compound was obtained in 79% yield as a white solid. M. p. = 76−78 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.78 (d, *J* = 8.2 Hz, 1H), 8.66 (d, *J* = 4.8 Hz, 2H), 8.04 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 4.8 Hz, 1H), 2.37 (d, *J* = 1.3 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 173.6, 158.1, 157.6, 135.7, 130.8, 123.9, 122.6, 121.9, 119.1, 118.6, 116.4, 115.8, 51.7, 34.0, 20.5. Spectral data matched those previously reported.[S3]



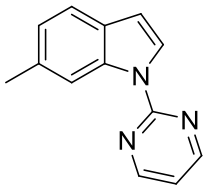

**methyl 3-(1-(pyrimidin-2-yl)-1H-indol-3-yl)propanoate (1h).** This compound was obtained in 81% yield as a white solid. M. p. = 72−74 °C. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.3, 1H), 8.67 (d, *J* = 4.8, 2H), 8.08 (s, 1H), 7.59 (d, *J* = 7.8, 1H), 7.35 (t, *J* = 7.7, 1H), 7.26 (t, *J* = 7.4, 1H), 7.01 (t, *J* = 4.8, 1H), 3.71 (s, 3H), 3.13 (t, *J* = 7.8, 2H), 2.80 (t, *J* = 7.8, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.58, 158.08, 157.59, 135.69, 130.85, 123.89, 122.61, 121.89, 119.12, 118.65, 116.37, 115.80, 51.72, 33.96, 20.54. HRMS (EI) calcd. for $C_{16}H_{15}N_3O_2$ $[M]^+$ : 281.1164. Found: 281.1162.



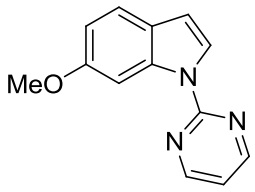
**5-methyl-1-(pyrimidin-2-yl)-1H-indole (1i).** This compound was obtained in 76% yield as a white solid. M. p. = 86−88 °C. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.69-8.65 (m, 3H), 8.22 (d, *J* = 3.6, 1H), 7.41 (s, 1H), 7.16 (d, *J* = 8.4, 1H), 7.02 (t, *J* = 4.8, 1H), 6.62 (d, *J* = 3.4, 1H), 2.47 (s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$): δ 167.4, 157.8, 157.1, 137.5, 130.6, 126.8, 124.5, 123.5, 122.8, 116.4, 115.5, 107.1, 51.8. HRMS (EI) calcd. for $C_{13}H_{11}N_3$ $[M]^+$ : 209.0953. Found: 209.09458.




**5-methoxy-1-(pyrimidin-2-yl)-1H-indole (1j).** This compound was obtained in 83% yield as a white solid. M. p. = 110−112 °C. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.75 – 8.63 (m, 3H), 8.25 (d, *J* = 3.6, 1H), 7.10 (d, *J* = 2.5, 1H), 7.04 – 6.92 (m, 2H), 6.63 (d, *J* = 3.6, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 157.6, 1556, 132.15, 130.3, 126.4, 117.1, 115.9, 112.6, 106.8, 103.2, 55.7. Spectral data matched those previously reported.[S3]

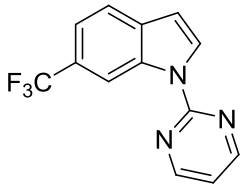



**6-methyl-1-(pyrimidin-2-yl)-1H-indole (1k).** This compound was obtained in 78% yield as a white solid. M. p. = 120−122 °C. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.8, 2H), 8.64 (s, 1H), 8.21 (d, *J* = 3.6, 1H), 7.51 (d, *J* = 7.8, 1H), 7.08 (d, *J* = 7.8, 1H), 7.03 (t, *J* = 4.8, 1H), 6.66 (d, *J* = 3.6, 1H), 2.55 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 167.4, 157.8, 157.1, 137.5, 130.6, 126.8, 124.5, 123.5, 122.8, 116.4, 115.5, 107.1, 51.6. HRMS (EI) calcd. for $C_{13}H_{11}N_3$ $[M]^+$ : 209.0953. Found: 209.09459.

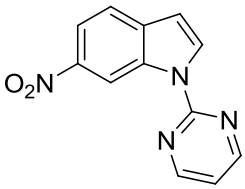



**6-methoxy-1-(pyrimidin-2-yl)-1H-indole (1l).** This compound was obtained in 70% yield as a white solid. M. p. = 78−80 °C. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, *J* =

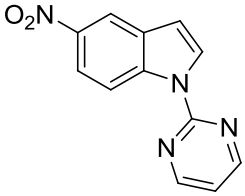
4.8, 2H), 8.45 (d, *J* = 2.4, 1H), 8.17 (d, *J* = 3.6, 1H), 7.49 (d, *J* = 8.4, 1H), 7.03 (t, *J* = 4.8, 1H), 6.90 (dd, *J* = 8.4, 2.4, 1H), 6.63 (dd, *J* = 4.2, 0.6, 1H), 3.93 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 157.8, 157.4, 136.3, 125.4, 124.8, 121.1, 116.0, 111.1, 106.8, 101.1, 55.8. HRMS (EI) calcd. for $C_{13}H_{11}N_3O$ $[M]^+$ : 225.0902. Found: 225.0899.



**1-(pyrimidin-2-yl)-6-(trifluoromethyl)-1H-indole (1m).** This compound was obtained in 78% yield as a white solid. M. p. = 98−100 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 9.16 (s, 1H), 8.74 (d, *J* = 4.8, 2H), 8.42 (d, *J* = 3.6, 1H), 7.70 (d, *J* = 8.4, 1H), 7.48 (d, *J* = 8.8, 1H), 7.11 (t, *J* = 4.8, 1H), 6.75 (d, *J* = 3.6, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.3, 157.5, 134.4, 133.8, 129.3, 128.3, 126.6, 125.6 (q, *J* = 31.7), 125.2 (q, *J* = 272.2), 123.9, 121.2, 121.0, 11878 (q, *J* = 3.6), 116.8, 114.0 (q, *J* = 4.5), 106.6. HRMS (EI) calcd. for $C_{13}H_8F_3N_3$ $[M]^+$ : 263.0670. Found: 263.0666.

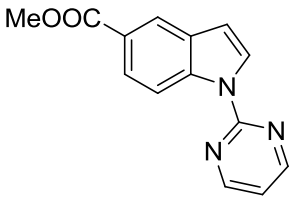


**6-nitro-1-(pyrimidin-2-yl)-1H-indole (1n).** This compound was obtained in 80% yield as a light yellow solid. M. p. = 179−181 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 9.77 (d, *J* = 2.1, 1H), 8.79 (d, *J* = 4.8, 2H), 8.55 (d, *J* = 3.6, 1H), 8.14 (dd, *J* = 8.7, 2.1, 1H), 7.68 (d, *J* = 8.7, 1H), 7.18 (t, *J* = 4.8, 1H), 6.79 (d, *J* = 3.6, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.4, 157.1, 144.5, 136.1, 134.0, 131.0, 120.6, 117.5, 117.3, 113.1, 106.7. HRMS (EI) calcd. for $C_{12}H_8N_4O_2$ $[M]^+$ : 240.0647. Found: 240.0653.

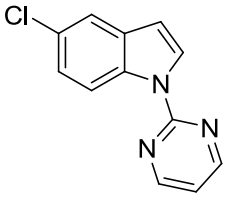


**5-nitro-1-(pyrimidin-2-yl)-1H-indole (1o).** This compound was obtained in 80% yield as a light yellow solid. M. p. = 244−246 ℃. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.92

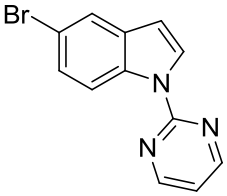
(d, *J* = 9.3, 1H), 8.77 (d, *J* = 4.8, 2H), 8.55 (s, 1H), 8.44 (d, *J* = 3.9, 1H), 8.22 (d, *J* = 9.3, 1H), 7.18 (t, *J* = 4.8, 1H), 6.84 (d, *J* = 3.6, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.4, 157.2, 143.3, 138.39, 131.0, 128.9, 118.9, 117.4, 117.2, 116.4, 107.7. HRMS (EI) calcd. for $C_{12}H_8N_3O_2$ $[M]^+$ : 240.0647. Found: 240.0650.




**methyl 1-(pyrimidin-2-yl)-1H-indole-5-carboxylate (1p).** This compound was obtained in 80% yield as a white solid. M. p. = 120−122 ℃. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.84 (d, *J* = 8.7, 1H), 8.73 (d, *J* = 4.8, 2H), 8.42 – 8.27 (m, 2H), 8.03 (dd, *J* = 8.7, 1.5, 1H), 7.10 (t, *J* = 4.8, 1H), 6.77 (dd, *J* = 3.6, 0.6, 1H), 3.95 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.4, 157.8, 157.1, 137.5, 130.6, 126.8, 124.5, 123.5, 122.8, 116.4, 115.5, 107.1, 51.6. HRMS (EI) calcd. for $C_{14}H_{11}N_3O_2$ $[M]^+$ : 253.0851. Found: 253.0847.

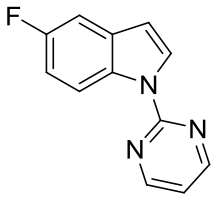



**5-chloro-1-(pyrimidin-2-yl)-1H-indole (1q).** This compound was obtained in 89% yield as a white solid. M. p. = 110−112 ℃. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.76 (dd, *J* = 9.1, 4.8, 1H), 8.71 – 8.64 (m, 2H), 8.31 (d, *J* = 3.6, 1H), 7.27 (dd, *J* = 8.8, 2.8, 1H), 7.10-7.03 (m, 2H), 6.65 (d, *J* = 3.6, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.2, 133.8, 132.5, 127.7, 127.1, 123.7, 120.3, 117.3, 116.4, 106.2. HRMS (EI) calcd. for $C_{12}H_8ClN_3$ $[M]^+$ : 229.0407. Found: 229.0403.

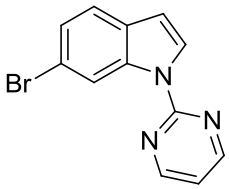



**5-bromo-1-(pyrimidin-2-yl)-1H-indole (1r).** This compound was obtained in 83% yield as a white solid. M. p. = 120−122 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.73 – 8.63 (m, 3H), 8.28 (d, *J* = 3.4, 1H), 7.75 (s, 1H), 7.42 (d, *J* = 9.0, 1H), 7.08 (t, *J* = 4.8,

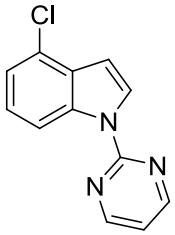
1H), 6.63 (d, *J* = 3.5, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 157.5, 134.1, 133.1, 127.0, 126.4, 123.3, 117.8, 116.4, 115.4, 106.1. HRMS (EI) calcd. for $C_{12}H_8BrN_3$ $[M]^+$ : 272.9902. Found: 272.9904.




**5-fluoro-1-(pyrimidin-2-yl)-1H-indole (1s).** This compound was obtained in 76% yield as a white solid. M. p. = 112−114 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.76 (dd, *J* = 9.1, 4.8, 1H), 8.71 – 8.64 (m, 2H), 8.31 (d, *J* = 3.6, 1H), 7.27 (dd, *J* = 8.8, 2.8, 1H), 7.10-7.03 (m, 2H), 6.65 (d, *J* = 3.6, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.89 (d, *J* = 265.9 Hz), 158.13, 157.8, 131.86, 127.35, 117.24 (d, *J* = 9.0), 116.29, 111.36 (d, *J* = 24.8), 106.62 (d, *J* = 4.1), 106.03 (d, *J* = 23.5). HRMS (EI) calcd. for $C_{12}H_8FN_3$ $[M]^+$ : 213.0702. Found: 213.0699.

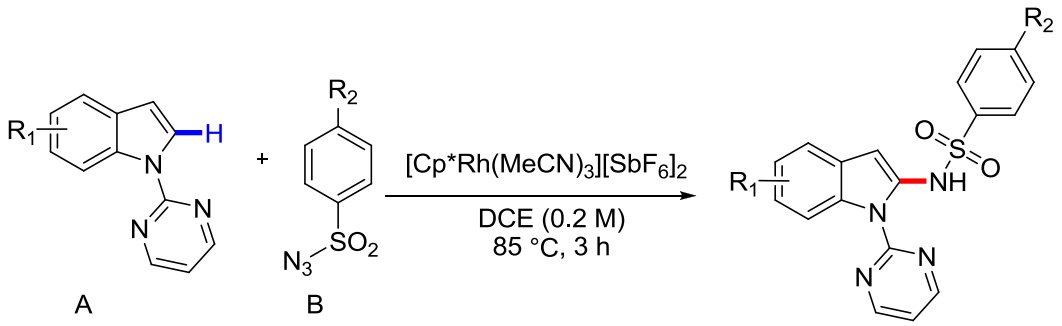



**6-bromo-1-(pyrimidin-2-yl)-1H-indole (1t).** This compound was obtained in 80% yield as a white solid. M. p. = 130−132 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.72 (d, *J* = 4.8, 2H), 8.25 (d, *J* = 3.9, 1H), 7.47 (d, *J* = 8.4, 1H), 7.35 (d, *J* = 8.4, 1H), 7.09 (t, *J* = 4.2, 1H), 6.66 (d, *J* = 3.0, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 167.4, 157.8, 157.1, 137.5, 130.6, 126.8, 124.5, 123.5, 122.8, 116.4, 115.5, 107.1, 51.6. HRMS (EI) calcd. for $C_{12}H_8BrN_3$ $[M]^+$ : 272.9902. Found: 272.9907.

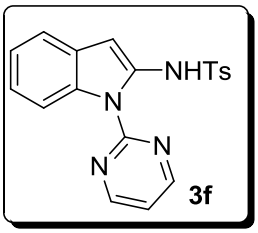



**4-chloro-1-(pyrimidin-2-yl)-1H-indole (1u).** This compound was obtained in 76% yield as a white solid. M. p. = 118−120 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.75 – 8.64 (m, 3H), 8.31 (d, *J* = 3.7, 1H), 7.28 – 7.21 (m, 2H), 7.05 (td, *J* = 4.8, 1.2, 1H),

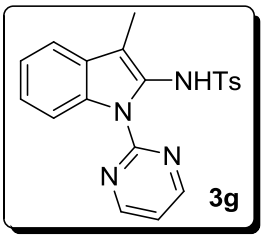
6.82 (d, $J$ = 3.6, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.2, 157.6, 136.1, 130.0, 126.4, 125.9, 124.2, 121.9, 116.6, 114.9, 105.0. HRMS (EI) calcd. for $C_{12}H_8ClN_3$ $[M]^+$ : 229.0407. Found: 229.0404.



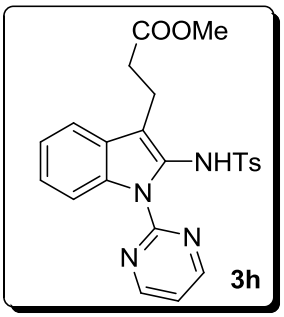

**General Procedure for Preparation of substrate N-(1-(pyrimidin-2-yl)-1H-indol-2-yl)benzenesulfonamide moiety**: The mixture of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8 mg, 0.01 mmol)，substrate **A** (0.2 mmol), **B** (0.26 mmol, 1.3 equiv) and $H_2O$ (36 mg, 2 mmol)were dissolved in DCE (1 mL) and refluxed for 5 h. The resulting mixture was cooled to room temperature, silica gel column directly to give product.



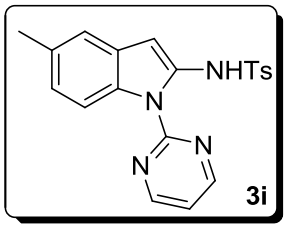

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 86% as a white solid (M. p. = 152−154 ℃). IR (film): 3048, 2917, 1583, 1427, 1344, 1172, 1091, 802, 684, 543 $cm^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): δ 11.07 (s, 1H), 8.68 (d, $J$ = 4.8, 2H), 8.48 (dd, $J$ = 6.3, 3.3, 1H), 7.61 (d, $J$ = 8.1, 2H), 7.48 (dd, $J$ = 6.0, 3.0, 1H), 7.23 – 7.16 (m, 2H), 7.11 – 7.06 (m, 3H), 6.64 (s, 1H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.1, 152.7, 138.9, 131.1, 128.6, 128.5, 124.5, 123.6, 122.1, 118.1, 118.0, 115.0, 111.4, 110.8, 92.6, 16.5. HRMS (EI) calcd. for $C_{19}H_{16}N_4O_2S$ $[M]^+$ : 364.0994. Found: 364.0989.



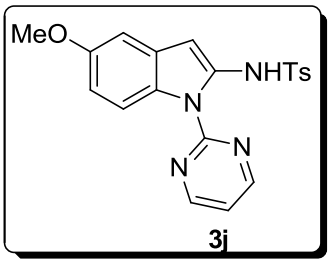

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 86% as a white solid (M. p. = 195−197 ℃). IR (film): 3049, 2915, 1563, 1428, 1346, 1169, 1090, 814, 746, 681, 550 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.49 (d, *J* = 4.8, 2H), 8.27 – 8.23 (m, 1H), 7.64 – 7.52 (m, 1H), 7.34 – 7.16 (m, 4H), 6.94 (t, *J* = 4.8, 1H), 6.85 (d, *J* = 8.7, 2H), 2.47 (s, 3H), 2.22 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 157.51, 157.16, 143.54, 135.87, 134.01, 129.15, 128.92, 127.16, 126.87, 124.61, 122.53, 119.30, 115.98, 115.59, 114.66, 21.49, 9.26. HRMS (EI) calcd. for $C_{20}H_{18}N_4O_2S$ $[M]^+$ : 378.1150. Found: 378.1155.



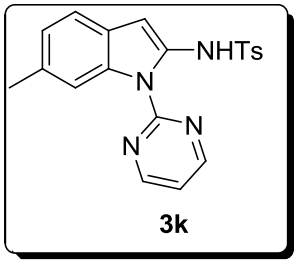

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 81% as a white solid (M. p. = 132−134 ℃). IR (film): 3049, 2923, 1732, 1558, 1443, 1339, 1156, 1092, 826, 741, 667, 542 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.49 (d, *J* = 4.8, 2H), 8.28 – 8.13 (m, 1H), 7.69 – 7.52 (m, 1H), 7.34 – 7.22 (m, 2H), 7.19 (d, *J* = 8.1, 2H), 6.96 (t, *J* = 4.8, 1H), 6.84 (d, *J* = 8.1, 2H), 3.71 (s, 3H), 3.33 (d, *J* = 8.1, 2H), 2.89 (d, *J* = 8.1, 2H), 2.22 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 173.8, 157.5, 157.0, 143.6, 135.7, 134.1, 129.1, 127.6, 127.3, 126.8, 124.6, 122.6, 119.3, 117.8, 116.2, 114.7, 51.6, 33.5, 21.4, 19.6. HRMS (EI) calcd. for $C_{23}H_{22}N_4O_4S$ $[M]^+$ : 450.1362. Found: 450.1366.




Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 86% as a white solid (M. p. = 138−140 ℃). $^{1}$H NMR (300 MHz, $CDCl_3$): δ 11.12 (br s, 1H), 8.64 (d, *J* = 4.8, 2H), 8.35 (d, *J* = 8.4, 1H), 7.60 (d, *J* = 8.1, 2H), 7.26 (d, *J* = 2.1, 1H), 7.12 – 6.93 (m, 4H), 6.57 (s, 1H), 2.41 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 157.6, 143.8, 136.2, 133.6, 132.6, 131.8, 129.5, 128.8, 127.1, 124.3, 120.0, 116.2, 115.6, 97.5, 21.4, 21.3. HRMS (EI) calcd. for $C_{20}H_{18}N_4O_2S$ $[M]^+$ : 378.1150. Found: 378.1154.

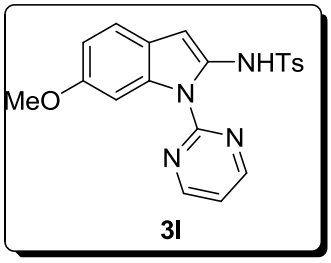



Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 77% as a white solid (M. p. = 146−148 °C). IR (film): 2937, 2832, 1585, 1452, 1342, 1157, 1093, 956, 789, 653, 540 $cm^{-1}$. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 11.23 (s, 1H), 8.63 (ddd, *J* = 4.9, 1.4, 0.7, 2H), 8.39 (d, *J* = 9.0, 1H), 7.62 (d, *J* = 8.4, 2H), 7.10 – 7.03 (m, 3H), 6.95 (d, *J* = 2.7, 1H), 6.79 (dd, *J* = 9.0, 2.7, 1H), 6.56 (s, 1H), 3.84 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 158.1, 158.0, 157.7, 156.1, 144.0, 136.1, 134.2, 129.6, 128.2, 127.2, 117.0, 116.2, 111.4, 102.7, 97.2, 55.7, 21.6. HRMS (EI) calcd. for $C_{20}H_{18}N_4O_3S$ $[M]^+$ : 394.1100. Found: 394.1104.



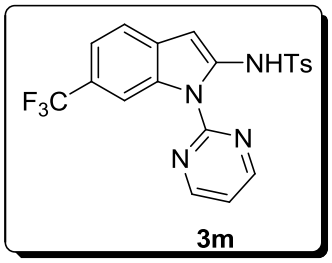

**3k**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 90% as a white solid (M. p. = 188−190 °C). IR (film): 2921, 2852, 1585, 1463, 1427, 1338, 1159, 1087, 912, 817, 659, 553 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 10.87 (s, 1H), 8.65 (d, *J* = 4.8, 2H), 8.27 (s, 1H), 7.56 (d, *J* = 8.1, 2H), 7.37 (d, *J* = 7.8, 1H), 7.08 – 7.02 (m, 4H), 6.62 (s, 1H), 2.45 (s, 3H), 2.26 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 157.8, 157.6, 143.7, 136.0, 133.9, 132.9, 132.6, 129.4, 127.0, 126.0, 124.4, 119.6, 116.2, 115.7, 98.4, 22.0, 21.4. HRMS (EI) calcd. for $C_{20}H_{18}N_4O_2S$ $[M]^+$ : 378.1150. Found: 378.1155.



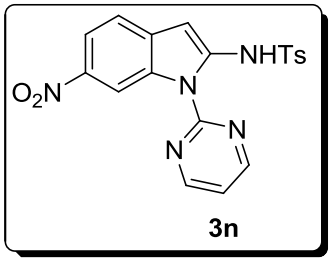

**3l**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane: EtOAc (2:1) in a 83% as a white solid (M. p. = 143−145 ℃). IR (film): 2990, 2940, 1585, 1427, 1342, 1160, 1087, 903, 796, 661, 557 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 10.69 (br s, 1H), 8.64 (d, *J* = 4.8, 2H), 8.09 (d, *J* = 2.4, 1H), 7.52 (d, *J* = 8.4, 2H), 7.37 (d, *J* = 8.4, 1H), 7.13 – 6.99 (m, 3H), 6.85 (dd, *J* = 8.4, 2.4, 1H), 6.60 (d, *J* = 0.6, 1H), 3.84 (s, 3H), 2.26 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.0, 157.7, 157.0, 143.8, 136.2, 134.7, 132.1, 129.5, 127.1, 122.4, 120.6, 116.4, 111.2, 101.3, 99.2, 55.9, 21.6. HRMS (EI) calcd. for $C_{20}H_{18}N_4O_3S$ $[M]^+$ : 394.1100. Found: 394.1094.



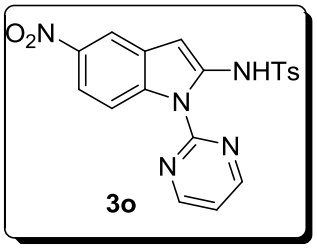

**3m**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 75% as a white solid (M. p. = 256−258 °C). IR (film): 2967, 2927, 1583, 1500, 1326, 1159, 1087, 896, 802, 660, 563 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.37 (s, 1H), 8.86 (s, 1H), 8.76 (d, *J* = 4.8, 2H), 7.67 (d, *J* = 7.2, 2H), 7.54 (d, *J* = 8.1, 1H), 7.44 (d, *J* = 8.4, 1H), 7.20 (t, *J* = 4.8, 1H), 7.13 (d, *J* = 7.8, 2H), 6.64 (s, 1H), 2.31 (s, 3H). $^{13}C$ NM (125 MHz, $CDCl_3$): δ 158.0, 157.9, 144.6, 143.3, 139.3, 135.8, 134.4, 131.8, 129.8, 127.2, 119.0, 119.0, 117.5, 113.1, 94.4, 21.5. HRMS (EI) calcd. for $C_{20}H_{15}F_3N_4O_2S$ $[M]^+$ : 432.0868. Found: 432.0866.



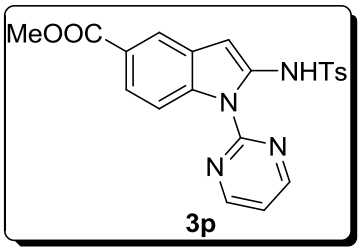

**3n**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 79% as a light yellow solid (M. p. = 299−301 °C). IR (film): 3138, 2924, 1577, 1511, 1461, 1423, 1330, 1155, 1087, 789, 659, 543 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.72 (s, 1H), 9.54 (d, *J* = 2.1, 1H), 8.83 (d, *J* = 4.8, 2H), 8.12 (dd, *J* = 8.7, 2.1, 1H), 7.75 (d, *J* = 8.4, 2H), 7.48 (d, *J* = 8.7, 1H), 7.29 – 7.26 (m, 1H), 7.19 (d, *J* = 8.1, 2H), 6.63 (s, 1H), 2.34 (s, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 158.0, 157.9, 144.2, 136.3, 135.9, 132.5, 131.4, 129.6, 127.1, 119.9, 119.8, 117.0, 113.6, 113.6, 95.7, 21.5. HRMS (EI) calcd. for $C_{19}H_{15}N_5O_4S$ $[M]^+$ : 409.0845. Found: 409.0844.



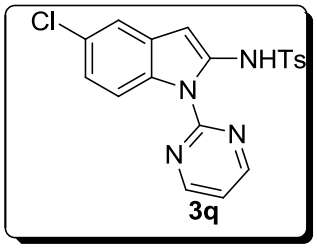

**3o**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 84% as a light yellow solid (M. p. = 206−208 °C). IR (film): 3142, 2968, 2924, 1598, 1512, 1423, 1355, 1184, 1088, 904, 838, 667, 551 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.24 (s, 1H), 8.78 (d, *J* = 4.8, 2H), 8.60 (d, *J* = 9.3, 1H), 8.32 (d, *J* = 2.4, 1H), 8.03 (dd, *J* = 9.3, 2.4, 1H), 7.68 (d, *J* = 8.4, 2H), 7.26 (t, *J* = 4.8, 1H), 7.15 (d, *J* = 8.4, 2H), 6.66 (s, 1H), 2.32 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 158.0, 157.7, 144.4, 143.9, 136.7, 136.5, 135.9, 129.7, 128.7, 127.2, 117.9, 117.6, 116.1, 115.6, 96.1, 21.5. HRMS (EI) calcd. for $C_{19}H_{15}N_5O_4S$ $[M]^+$ : 409.0845. Found: 409.0850.

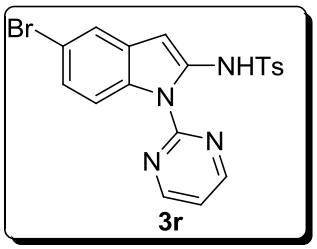



**3p**

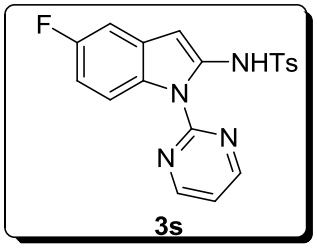
Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 87% as a white solid (M. p. = 186−188 °C). IR (film): 2986, 2923, 1719, 1604, 1585, 1423, 1344, 1165, 1089, 946, 815, 661, 546 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.08 (br s, 1H), 8.71 (d, *J* = 4.8, 2H), 8.50 (d, *J* = 8.7, 1H), 8.17 (s, 1H), 7.87 (d, *J* = 9.0, 1H), 7.62 (d, *J* = 7.8, 2H), 7.16 (t, *J* = 4.8, 1H), 7.08 (d, *J* = 7.8, 2H), 6.65 (s, 1H), 3.92 (s, 3H), 2.28 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 167.5, 157.8, 144.1, 136.1, 135.8, 134.8, 129.6, 128.3, 127.1, 124.9, 124.2, 121.9, 117.0, 115.5, 97.2, 52.0, 21.5. HRMS (EI) calcd. for $C_{21}H_{18}N_4O_4S$ $[M]^+$ : 422.1049. Found: 422.1045.




Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 83% as a white solid (M. p. = 184−186 °C). IR (film): 2970, 2927, 1578, 1461, 1419, 1341, 1148, 1094, 917, 803, 680, 555 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.24 (s, 1H), 8.68 (d, *J* = 4.8, 2H), 8.42 (d, *J* = 8.7, 1H), 7.64 (d, *J* = 8.4, 2H), 7.41 (d, *J* = 2.1, 1H), 7.18 – 7.02 (m, 4H), 6.53 (s, 1H), 2.29 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 157.9, 157.7, 144.1, 136.0, 135.0, 131.8, 130.0, 129.6, 128.6, 127.1, 122.8, 119.3, 117.1, 116.7, 95.9, 21.5. HRMS (EI) calcd. for $C_{19}H_{15}ClN_4O_2S$ $[M]^+$ : 398.0604. Found: 398.0608.

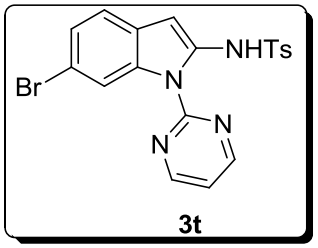



Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 83% as a white solid (M. p. = 193−195 °C). IR (film): 2923, 2871, 1583, 1448, 1425, 1336, 1162, 1091, 956, 788, 678, 563 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.23 (s, 1H), 8.70 (d, *J* = 4.7, 2H), 8.39 (d, *J* = 8.8, 1H), 7.63 (d, *J* = 8.1, 2H), 7.58 (s, 1H), 7.28 – 7.25 (m, 2H), 7.16 – 7.09 (m, 3H), 6.53 (s, 1H), 2.30 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 157.8, 157.7, 144.1, 135.8, 134.8, 132.1, 130.4, 129.5, 127.1, 125.4, 122.3, 117.4, 116.7, 116.3, 95.6, 21.4. HRMS (EI) calcd. for $C_{19}H_{15}BrN_4O_2S$ $[M]^+$ : 442.0099. Found: 442.0096.



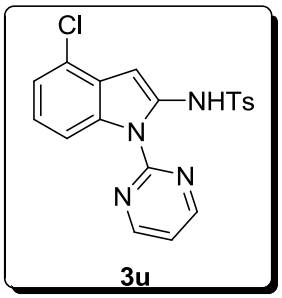

**3s**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 81% as a white solid (M. p. = 166−168 °C). IR (film): 2969, 2923, 1572, 1500, 1458, 1338, 1081, 886, 793, 669, 560 $cm^{-1}$.$^1$H NMR (300 MHz, $CDCl_3$): δ 11.29 (s, 1H), 8.67 (dd, *J* = 4.8, 0.7, 2H), 8.45 (dd, *J* = 9.3, 4.8, 1H), 7.64 (d, *J* = 8.1, 2H), 7.18 – 7.04 (m, 4H), 6.88 (td, *J* = 9.3, 2.7, 1H), 6.55 (s, 1H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.5 (d, *J* = 239.1), 157.9, 157.7, 144.1, 136.1, 135.2, 129.8, 129.6 (d, *J* = 5.9), 129.6, 127.1, 117.1 (d, *J* = 8.9), 116.6, 110.22 (d, *J* = 24.4), 105.3 (d, *J* = 24.1), 96.3 (d, *J* = 3.8), 21.5. HRMS (EI) calcd. for $C_{19}H_{15}FN_4O_2S$ $[M]^+$ : 382.0900. Found: 382.0894.



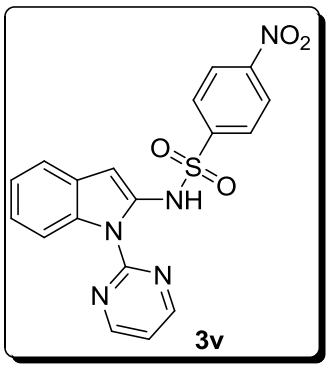

**3t**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 74% as a white solid (M. p. = 215−217 °C). IR (film): 3126, 2956, 1594, 1500, 1427, 1340, 1164, 1087, ,890, 820, 667, 563 $cm^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): δ 11.07 (s, 1H), 8.69 (d, *J* = 4.8, 3H), 7.60 (d, *J* = 8.4, 2H), 7.36 – 7.27 (m, 2H), 7.15 – 7.04 (m, 3H), 6.58 (s, 1H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 157.9, 144.2, 136.0, 134.2, 134.2, 129.7, 127.6, 127.2, 126.3, 121.1, 119.0, 116.9, 116.3, 97.2, 21.6. HRMS (EI) calcd. for $C_{19}H_{15}$ $BrN_4O_2S$ $[M]^+$ : 442.0099. Found: 442.0093.



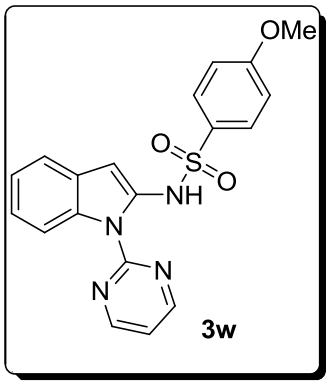

**3u**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 79% as a white solid (M. p. = 210−212 °C). IR (film): 3140, 2937, 1585, 1452, 1342, 1160, 1088, ,886, 811, 665, 542 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.16 (s, 1H), 8.70 (d, *J* = 4.8, 2H), 8.40 (d, *J* = 7.8, 1H), 7.66 (d, *J* = 7.8, 2H), 7.23 – 7.03 (m, 5H), 6.73 (s, 1H), 2.30 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 157.9, 157.8, 144.1, 136.1, 134.4, 134.1, 129.6, 127.5, 127.2, 125.0, 123.4, 122.9, 116.8, 114.4, 95.0, 21.5. HRMS (EI) calcd. for $C_{19}H_{15}ClN_4O_2S$ $[M]^+$ : 398.0604. Found: 398.0610.



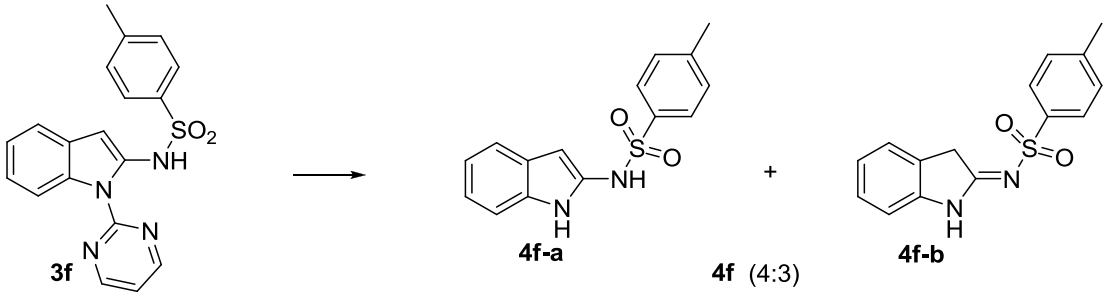

**3v**

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 74% as a yellow solid (M. p. = 168−170 °C). IR (film): 3143, 2963, 2924, 1617, 1452, 1429, 1329, 1150, 1088, 775, 659, 539 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.32 (s, 1H), 8.69 (d, *J* = 4.8, 2H), 8.47 (s, 1H), 8.12 (d , *J* = 7.2, 2H), 7.90 (d, *J* = 8.4, 2H), 7.50 (s, 1H), 7.25 – 7.13 (m, 3H), 6.71 (s, 1H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 157.9, 157.8, 150.2, 144.8, 133.6, 132.2, 128.3, 128.1, 124.1, 123.6, 123.4, 120.2, 116.6, 116.0, 98.5. HRMS (EI) calcd. for $C_{18}H_{13}N_5O_4S$ $[M]^+$ : 395.0688. Found: 395.0691.



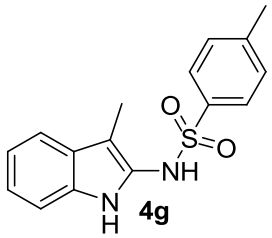

Following general procedure, the indicated compound was purified by flash column chromatography on silica gel using cyclohexane:EtOAc (2:1) in a 82% as a yellow solid (M. p. = 122−124 ℃). IR (film): 2938, 2832, 1585, 1486, 1342, 1160, 1084, 884, 659, 561 $cm^{-1}$. $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 11.04 (br s, 1H), 8.66 (d, *J* = 4.8, 2H), 8.48 (dd, *J* = 6.0, 3.3, 1H), 7.65 (d, *J* = 8.7, 2H), 7.48 (dd, *J* = 6.3, 3.0, 1H), 7.24 – 7.14 (m, 2H), 7.08 (t, *J* = 4.8, 1H), 6.73 (d, *J* = 9.0, 2H), 6.64 (s, 1H), 3.73 (s, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 163.1, 158.0, 157.7, 133.6, 133.6, 130.5, 129.2, 128.6, 123.0, 123.0, 119.9, 116.4, 115.8, 114.1, 97.6, 55.5. HRMS (EI) calcd. for $C_{19}H_{16}N_4O_3S$ $[M]^+$ : 380.0943. Found: 380.0942.

***Deprotection of 3f and 3g***




Under Ar, **3f** (36mg) was dissolved in dry DMSO 1 mL, 20% EtONa in EtOH (50 μL) was added, the mixture was stirred at 100 ℃ for 10 min, then cooled, extracted with EtOAc, washed with water. The organic phase was dried over $Na_2SO_4$. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (DCM/MeOH : 100/1) to give product **4f** (15mg yeild 50%) two dynamic isomers (4:3) as a white solid (M. p. = 210 − 212 ℃). IR (film): 3091, 2923, 1591, 1300, 1145, 1087, 854, 773, 669, 545 $cm^{-1}$. $^{1}H$ NMR (**4f-a**,

300 MHz, DMSO): δ 10.86 (s, 1H), 10.58 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.17 (m, 4H), 6.99 – 6.92 (m, 1H), 6.91 – 6.84 (m, 1H), 5.70 (d, *J* = 1.5 Hz, 1H), 2.32 (s, 3H). $^{1}$H NMR (**4f-b**, 300 MHz, DMSO): δ 11.57 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.17 (m, 4H), 7.03 (t, *J* = 7.0 Hz, 2H), 5.70 (d, *J* = 1.5 Hz, 1H), 4.08 (s, 2H), 2.35 (s, 3H). $^{13}$C NMR (**4f-a** and **4f-b**, 100 MHz, DMSO): δ 143.78, 142.88, 140.09, 137.13, 134.16, 132.59, 130.13, 129.93, 128.27, 127.49, 127.22, 126.65, 125.03, 123.28, 120.97, 119.68, 119.61, 111.65, 111.28, 92.38, 55.43, 37.39, 21.48. HRMS (EI) calcd. for $C_{15}H_{14}N_2O_2S$ $[M]^+$ : 286.0776. Found: 287.0768.




**4g**

Following procedure of **4f**, to give product **4g** (yeild 73%) as a light yellow viscous liquid. IR (film): 3062, 2925, 1618, 1471, 1278, 1203, 1083, 924, 868, 777, 678, 551 $cm^{-1}$. $^{1}$H NMR (300 MHz, DMSO): δ 11.07 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.21 (m, 5H), 7.10 – 7.02 (m, 1H), 6.15 (s, 1H), 2.36 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (125 MHz, DMSO): δ 171.45, 142.78, 140.79, 139.06, 133.50, 129.46, 129.23, 126.20, 123.52, 123.18, 112.29, 77.77, 25.66, 21.00. HRMS (EI) calcd. for $C_{15}H_{13}FN_2O_2S$ $[M]^+$ : 300.0932. Found: 300.0927.

Reference:

S1: K. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, *Org. Lett.* 2004, 6, 2785.

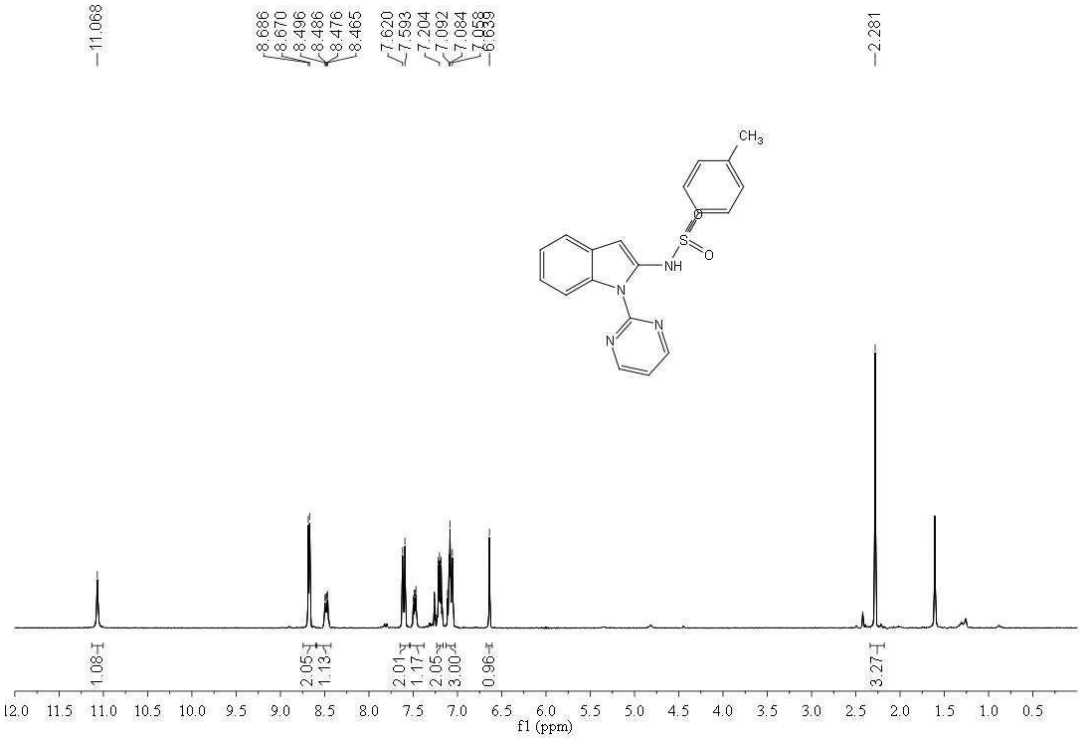
S2: Yang Li, Bi-Jie Li, Wen-Hua Wang, Wei-Ping Huang, Xi-Sha Zhang, Kang Chen, and Zhang-Jie Shi, *Angew. Chem. Int. Ed.* 2011, 50, 2115.

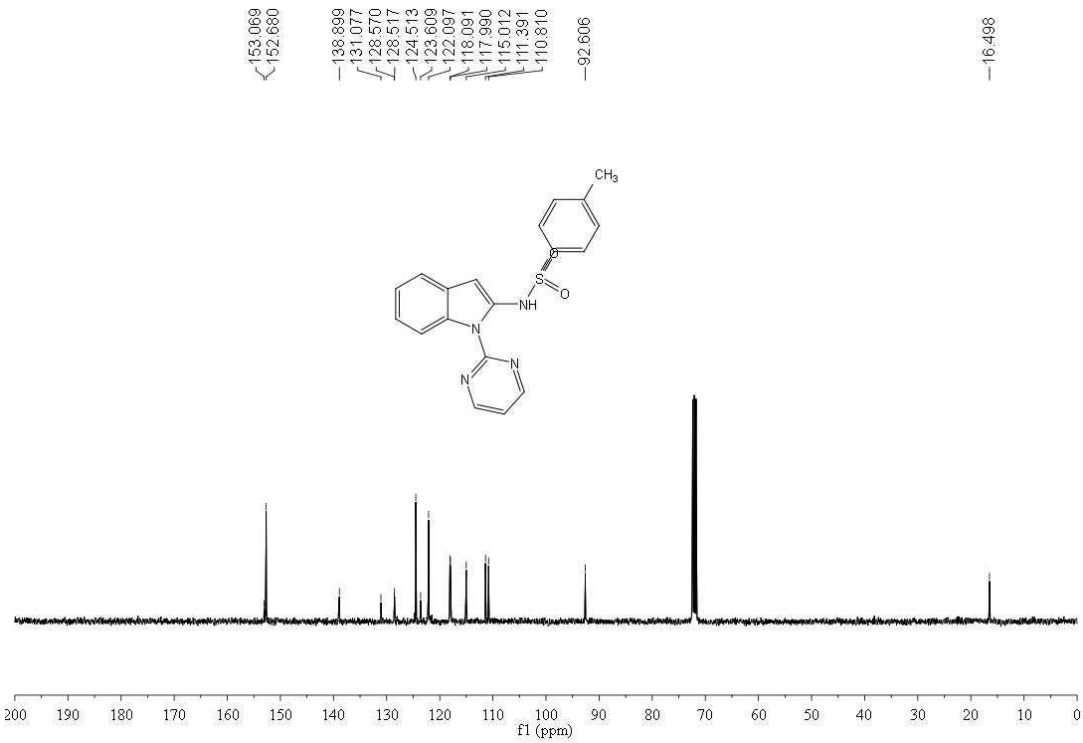
S3: Lutz Ackermann, Alexander V. Lygin, *Org. Lett.* 2011, 13, 3332.

S4: Joshua V. Ruppel, Jess E. Jones, Chelsea A. Huff, Rajesh M. Kamble, Ying Chen, and X. Peter Zhang, *Org. Lett.* 2008, 10, 1995.

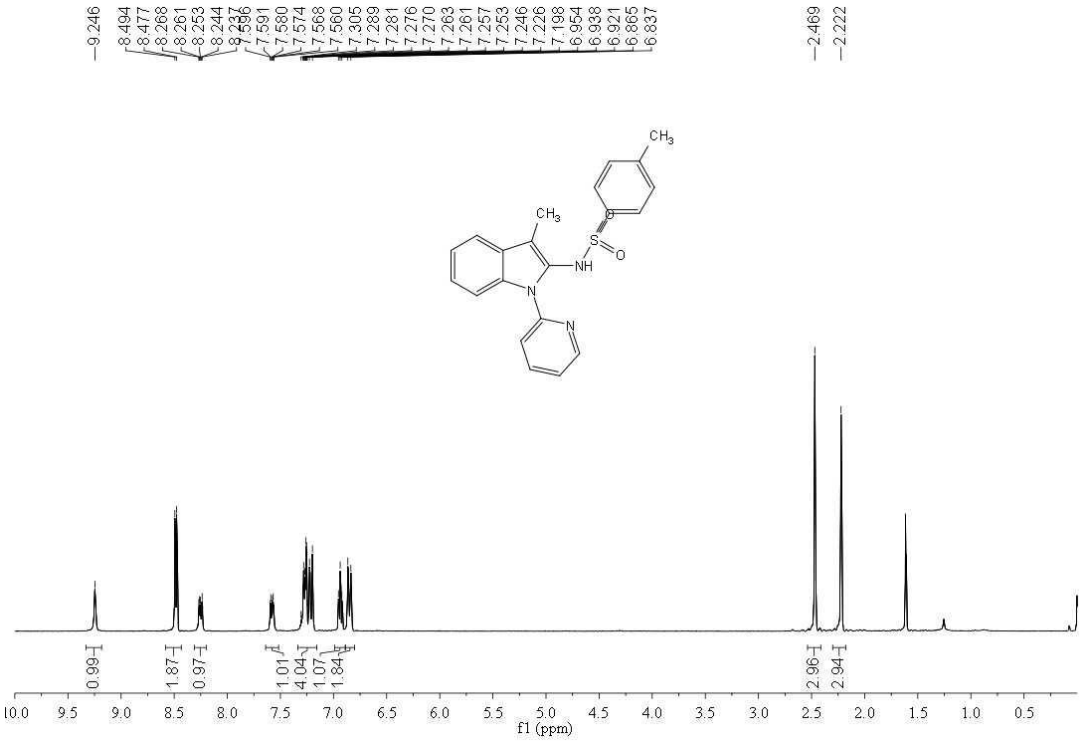
$^{1}H$ and $^{13}C$ NMR Spectra of Compounds

**Compound 3f**



## Compound 3g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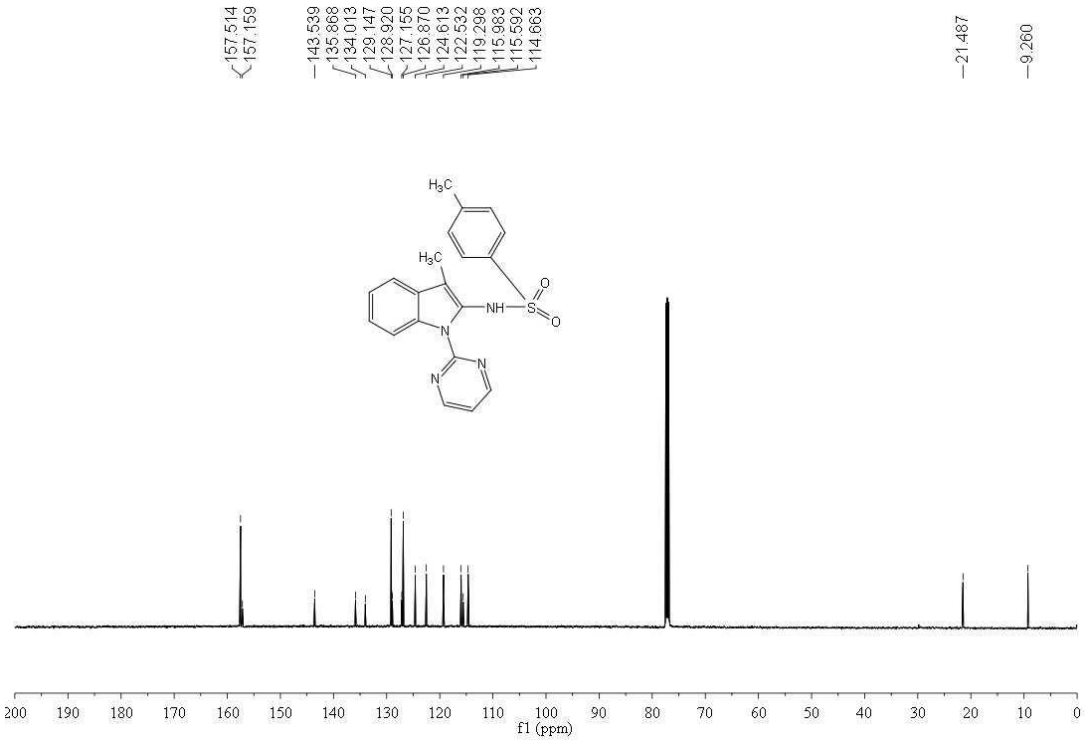
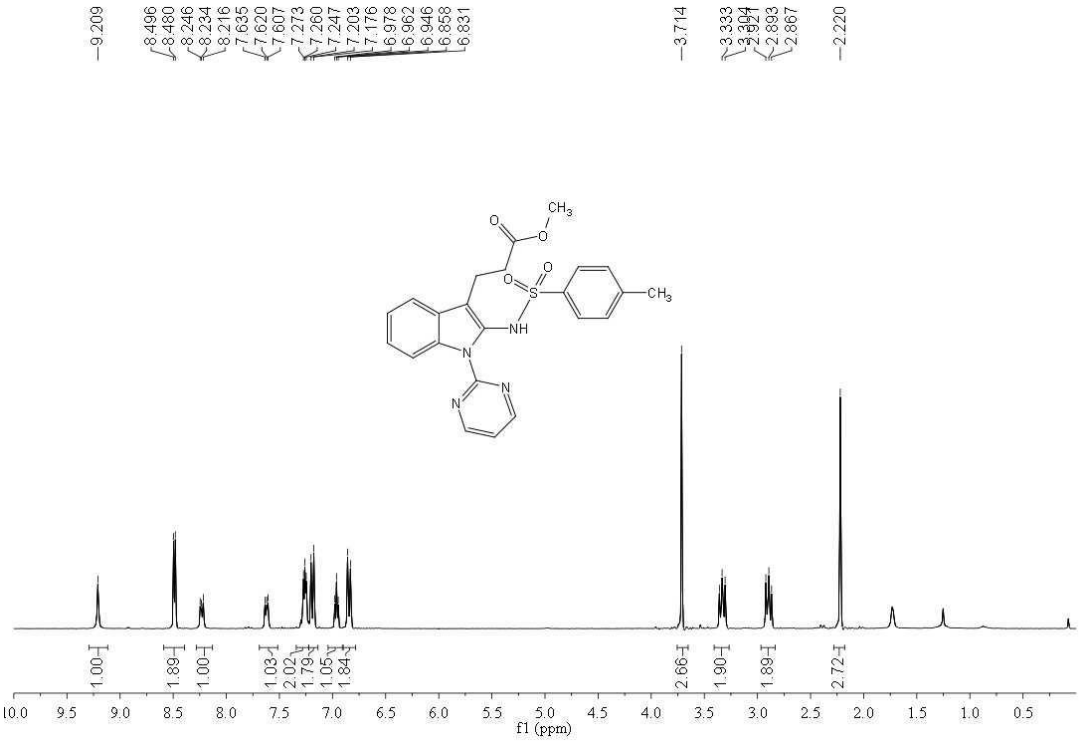
8.477
8.268
8.261
8.253
8.244
8.237
7.596
7.591
7.580
7.574
7.568
7.560
7.305
7.289
7.281
7.276
7.270
7.263
7.261
7.257
7.253
7.246
7.226
7.198
6.954
6.938
6.921
6.865
6.837
2.469
2.222
CH3
CH3
O
S
O
NH
N
N
0.99
1.87
0.97
1.01
4.04
1.07
1.84
2.96
2.94
f1 (ppm)


157.514
157.159
143.539
135.868
134.013
129.147
128.920
127.155
126.870
124.613
122.532
119.298
115.983
115.592
114.663
21.487
9.260
H3C
H3C
NH
S
O
O
N
N
N
f1 (ppm)

## Compound 3h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8.496
8.480
8.246
8.234
8.216
7.635
7.620
7.607
7.273
7.260
7.247
7.203
7.176
6.978
6.962
6.946
6.858
6.831
3.714
3.333
3.304
2.893
2.867
2.220
1.00
1.89
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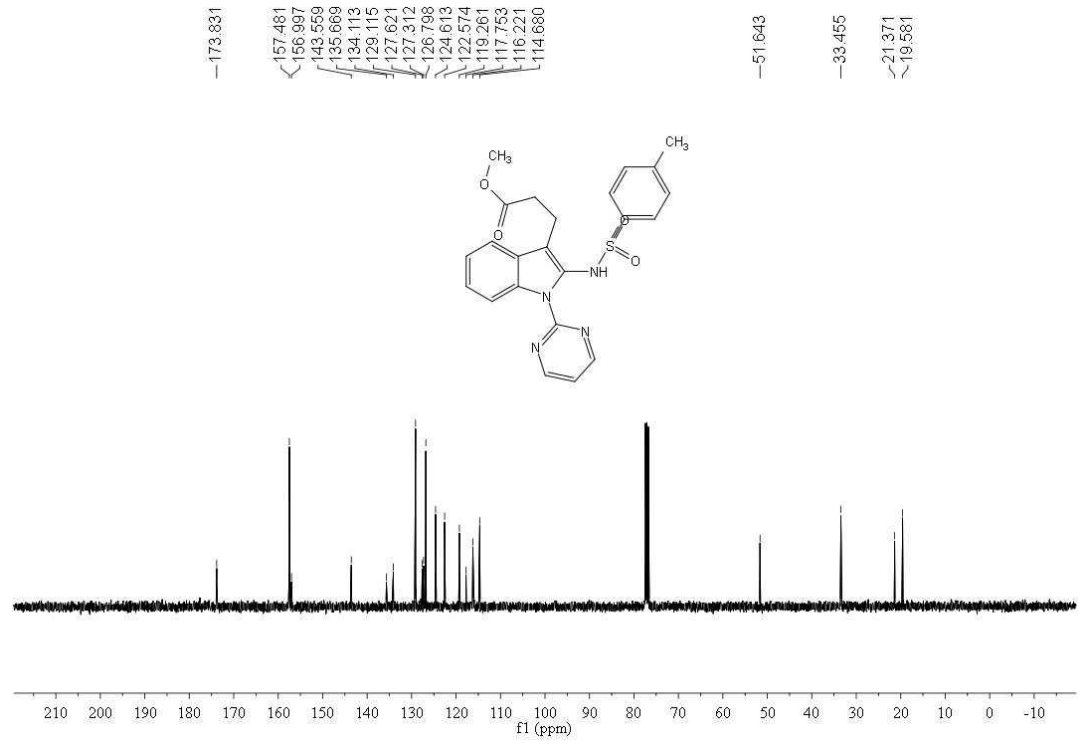
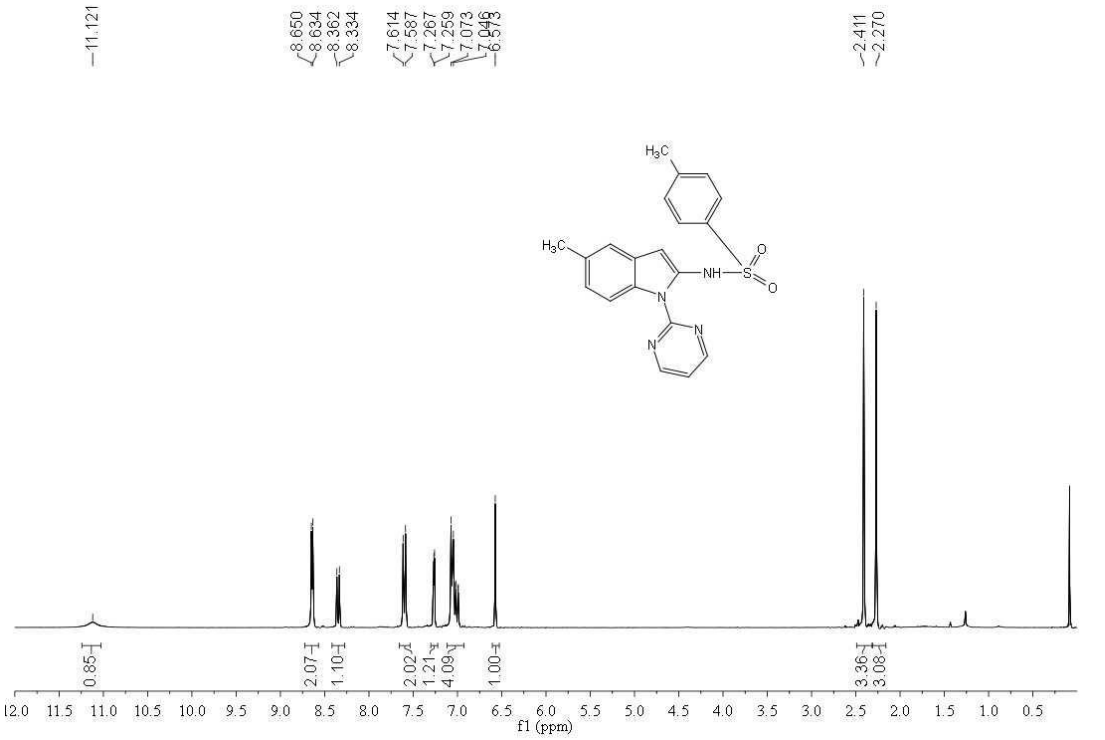
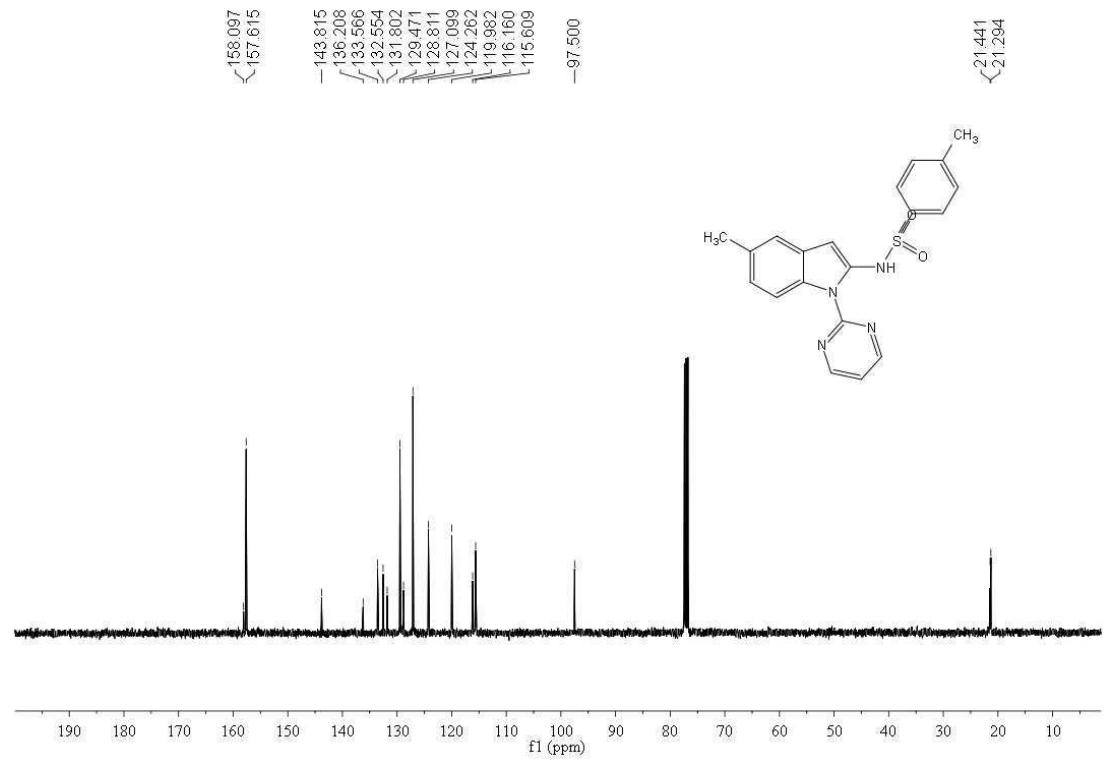
1.05
1.84
2.66
1.90
1.89
2.72
f1 (ppm)

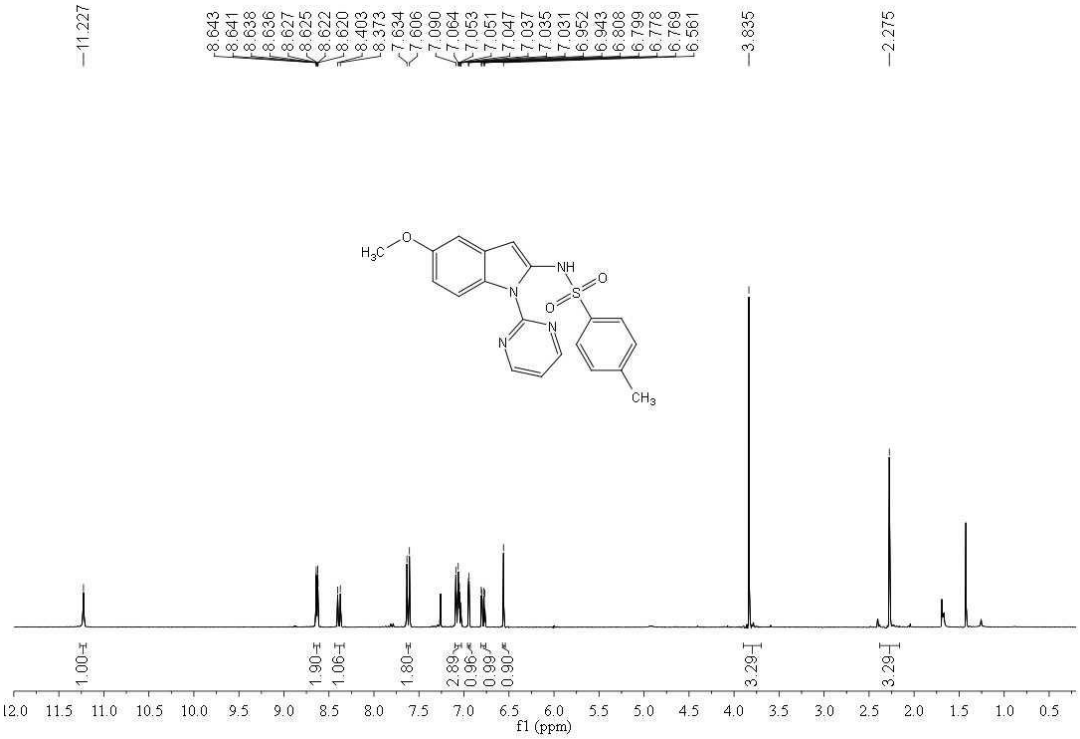

173.831
157.481
156.997
143.559
135.669
134.113
129.115
127.621
127.312
126.798
124.613
122.574
119.261
117.753
116.221
114.680
51.643
33.455
21.371
19.581
f1 (ppm)

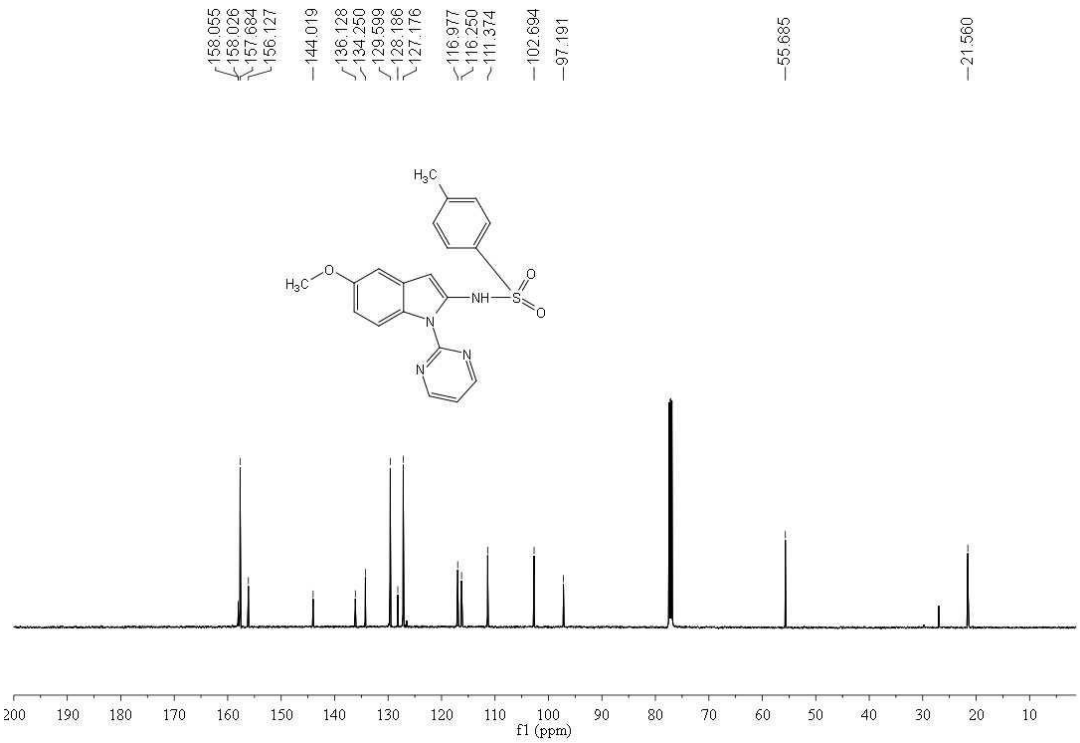
## Compound 3i


11.121
8.650
8.634
8.362
8.334
7.614
7.587
7.267
7.259
7.073
7.046
6.573
2.411
2.270
0.85
2.07
1.10
2.02
1.21
4.09
1.00
3.36
3.08
f1 (ppm)

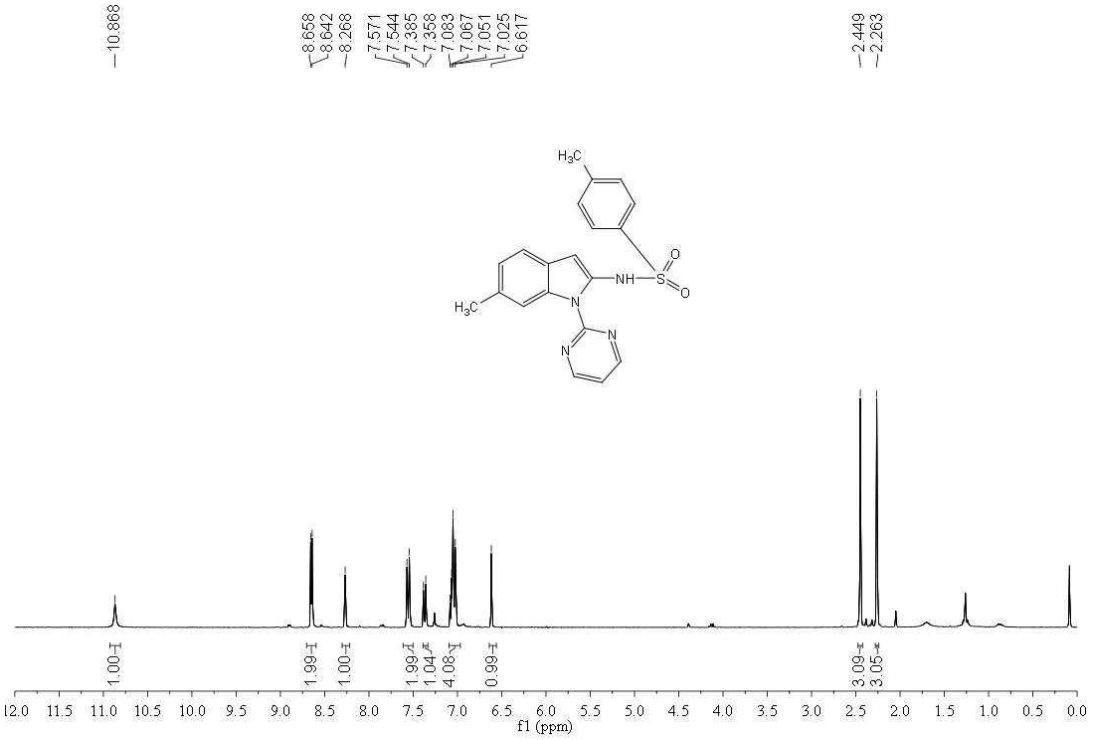

158.097
157.615
143.815
136.208
133.566
132.554
131.802
129.471
128.811
127.099
124.262
119.982
116.160
115.609
97.500
21.441
21.294
f1 (ppm)

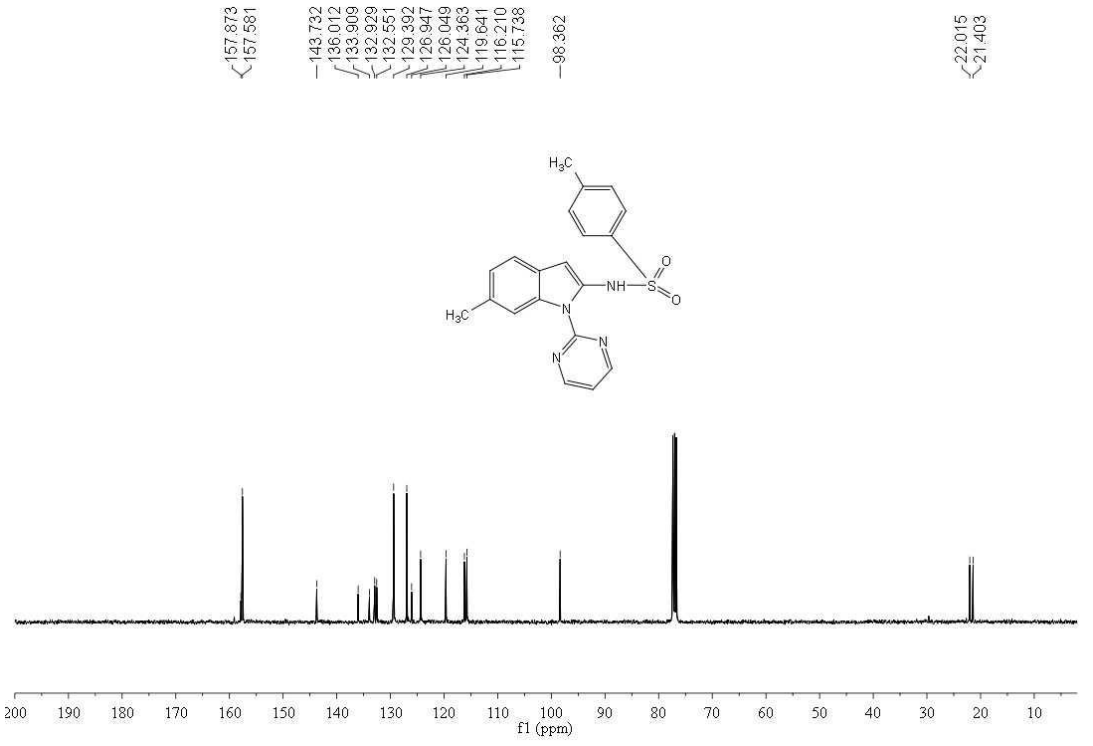
## Compound 3j


11.227
8.643
8.641
8.638
8.636
8.627
8.625
8.622
8.620
8.403
8.373
7.634
7.606
7.090
7.064
7.053
7.051
7.047
7.037
7.035
7.031
6.952
6.943
6.808
6.799
6.778
6.769
6.561
3.835
2.275
1.00
1.90
1.06
1.80
2.89
0.96
0.99
0.90
3.29
3.29
f1 (ppm)

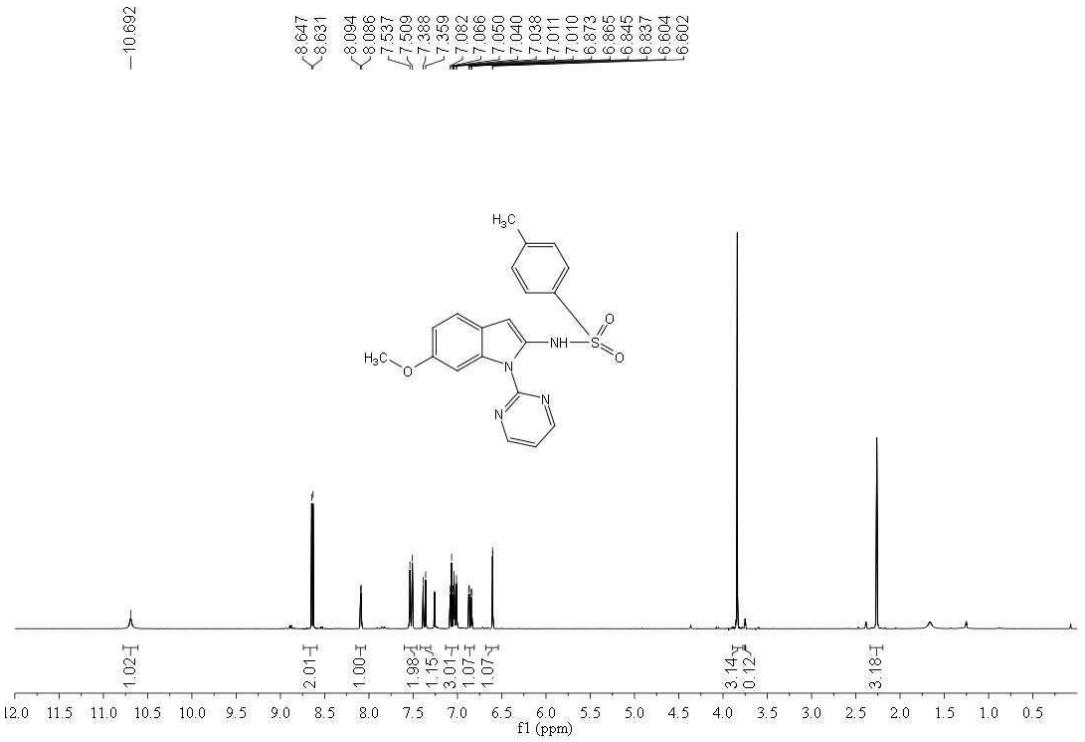

158.055
158.026
157.684
156.127
144.019
136.128
134.250
129.599
128.186
127.176
116.977
116.250
111.374
102.694
97.191
55.685
21.560
f1 (ppm)

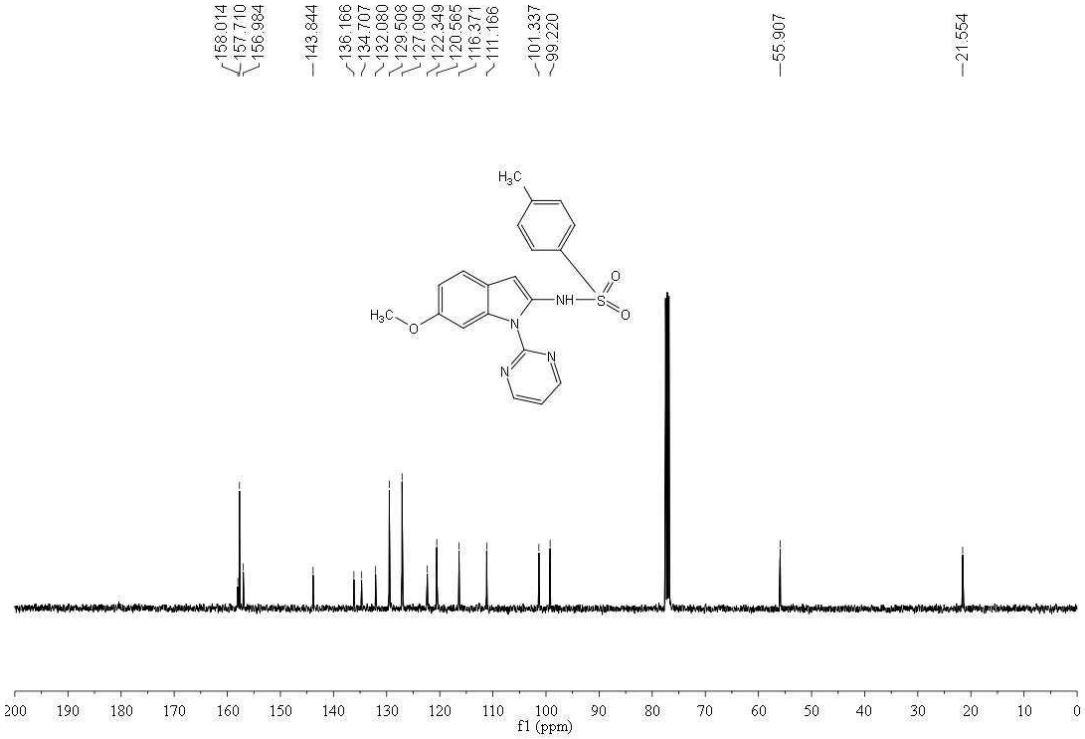
## Compound 3k



## Compound 3l


10.692
8.647
8.631
8.094
8.086
7.537
7.509
7.388
7.359
7.082
7.066
7.050
7.040
7.038
7.011
7.010
6.873
6.865
6.845
6.837
6.604
6.602
1.02
2.01
1.00
1.98
1.15
3.01
1.07
1.07
3.14
0.12
3.18
f1 (ppm)


158.014
157.710
156.984
143.844
136.166
134.707
132.080
129.508
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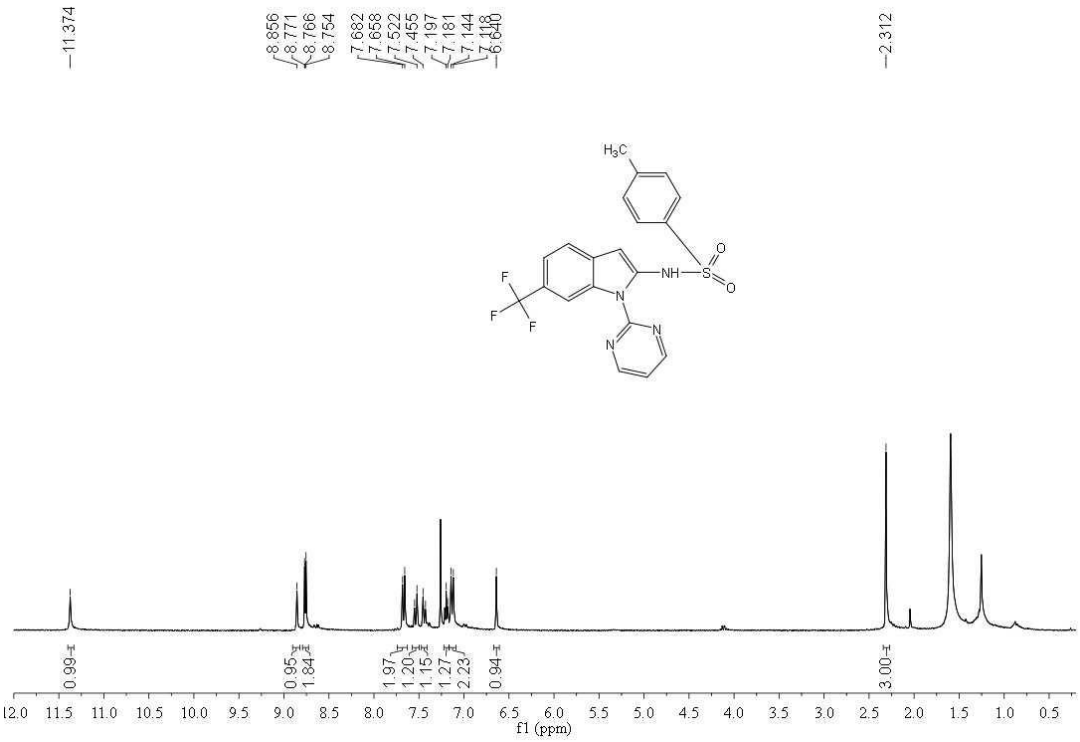
122.349
120.565
116.371
111.166
101.337
99.220
55.907
21.554
f1 (ppm)

## Compound 3m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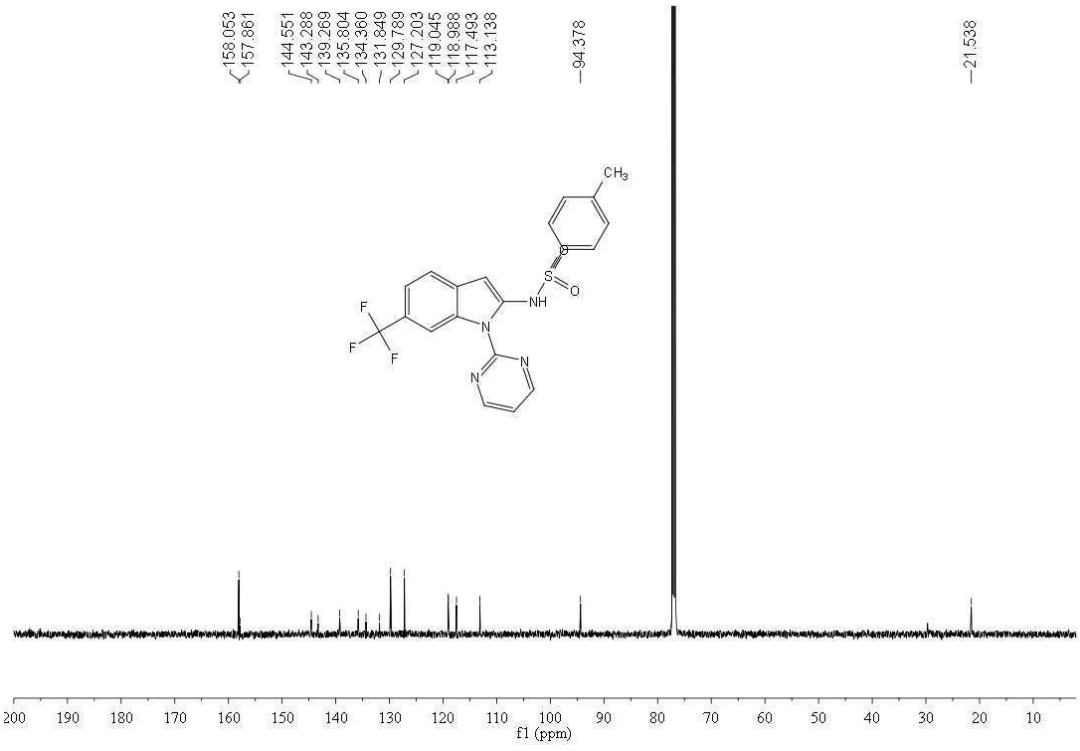
8.771
8.766
8.754
7.682
7.658
7.522
7.455
7.197
7.181
7.144
7.118
6.640
2.312
H3C
NH
S
O
O
F
F
F
N
N
N
0.99
0.95
1.84
1.97
1.20
1.15
1.27
2.23
0.94
3.00
f1 (ppm)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157.861
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143.288
139.269
135.804
134.360
131.849
129.789
127.203
119.045
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117.493
113.138
94.378
21.538
CH3
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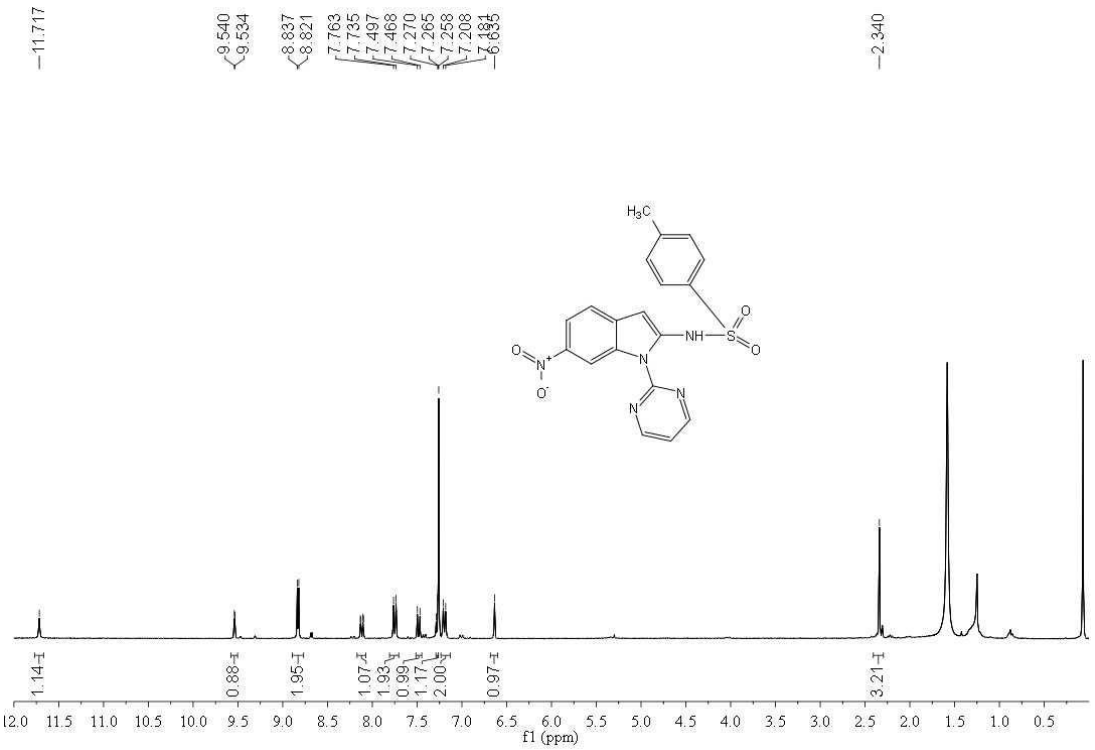
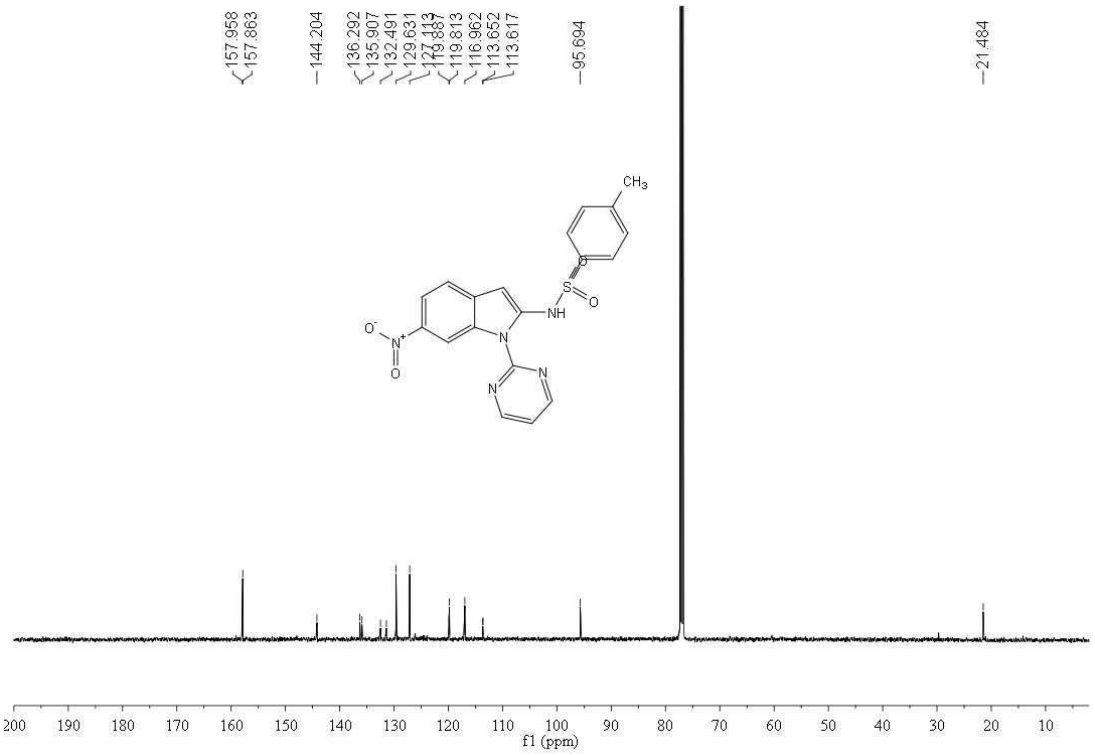
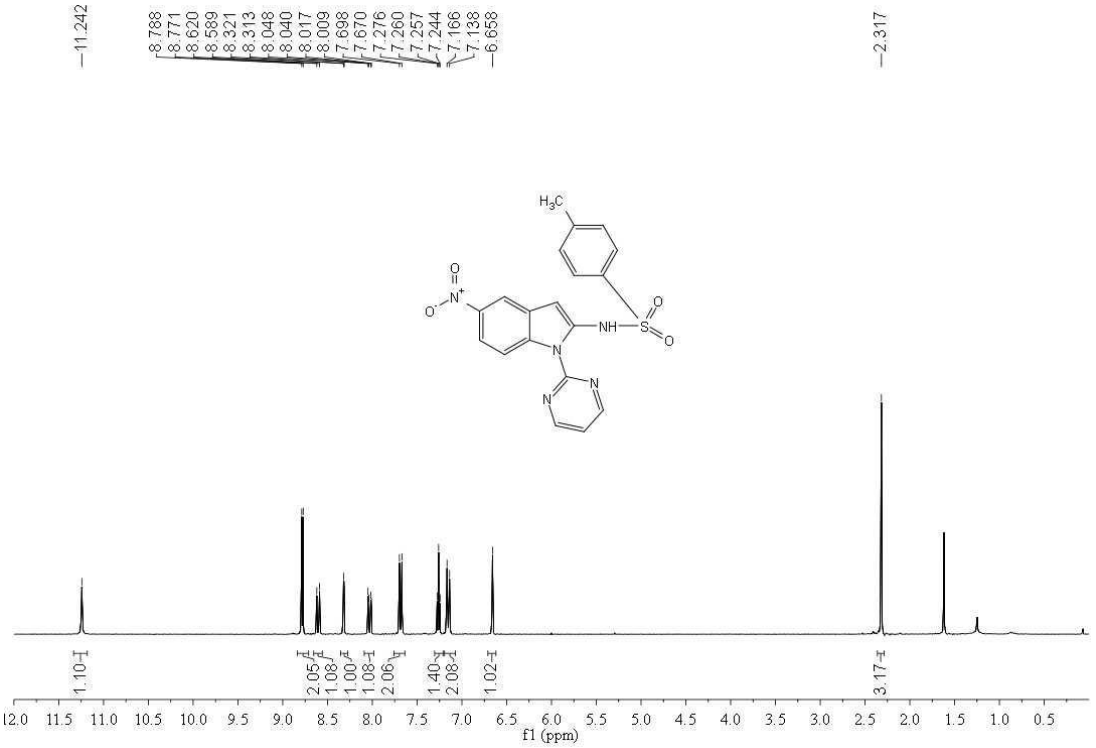
S
O
NH
F
F
F
N
N
N
f1 (ppm)

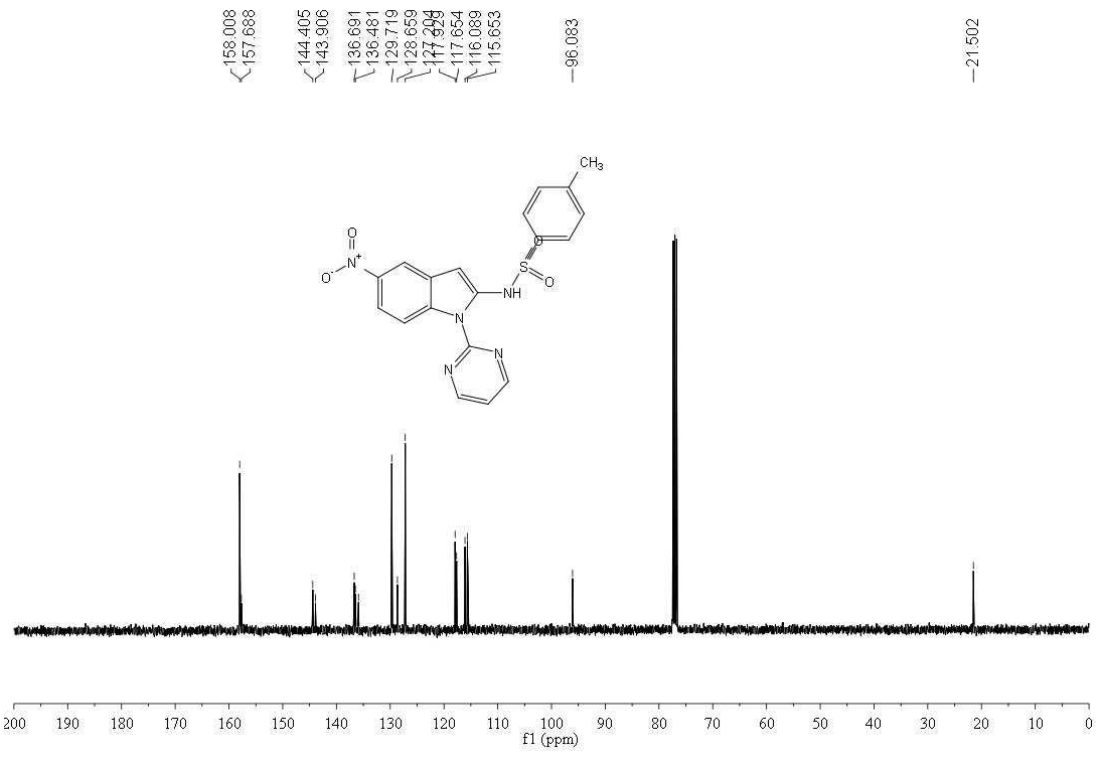
## Compound 3n



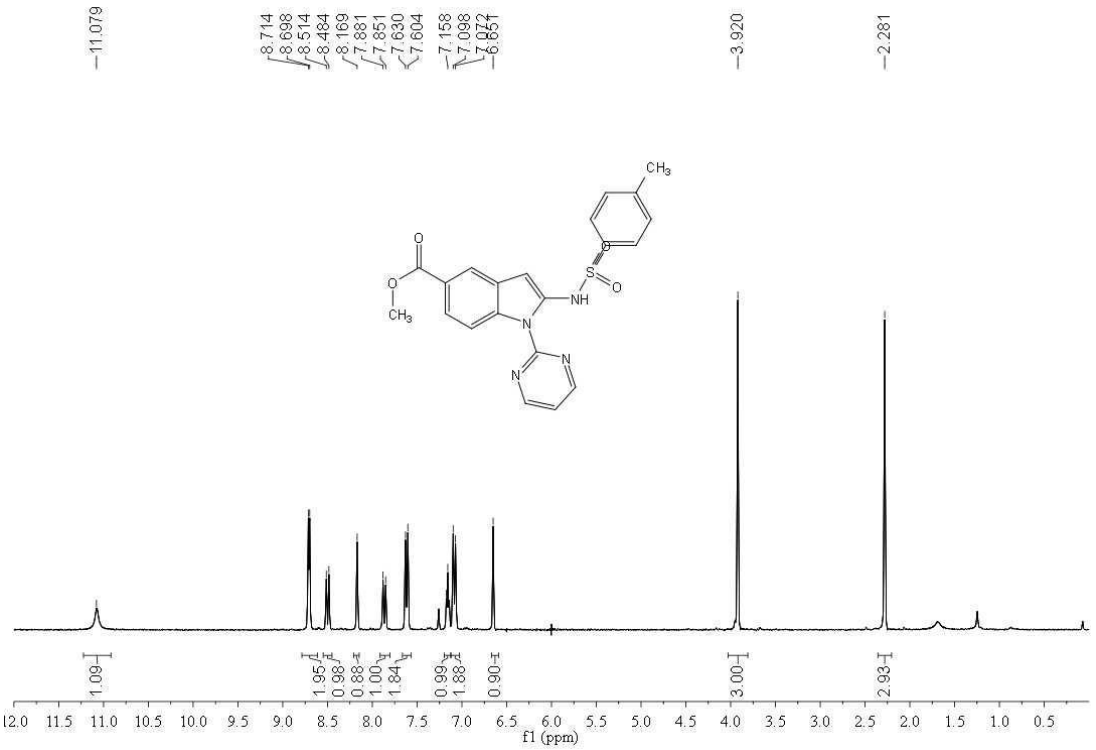



## Compound 3o



## Compound 3p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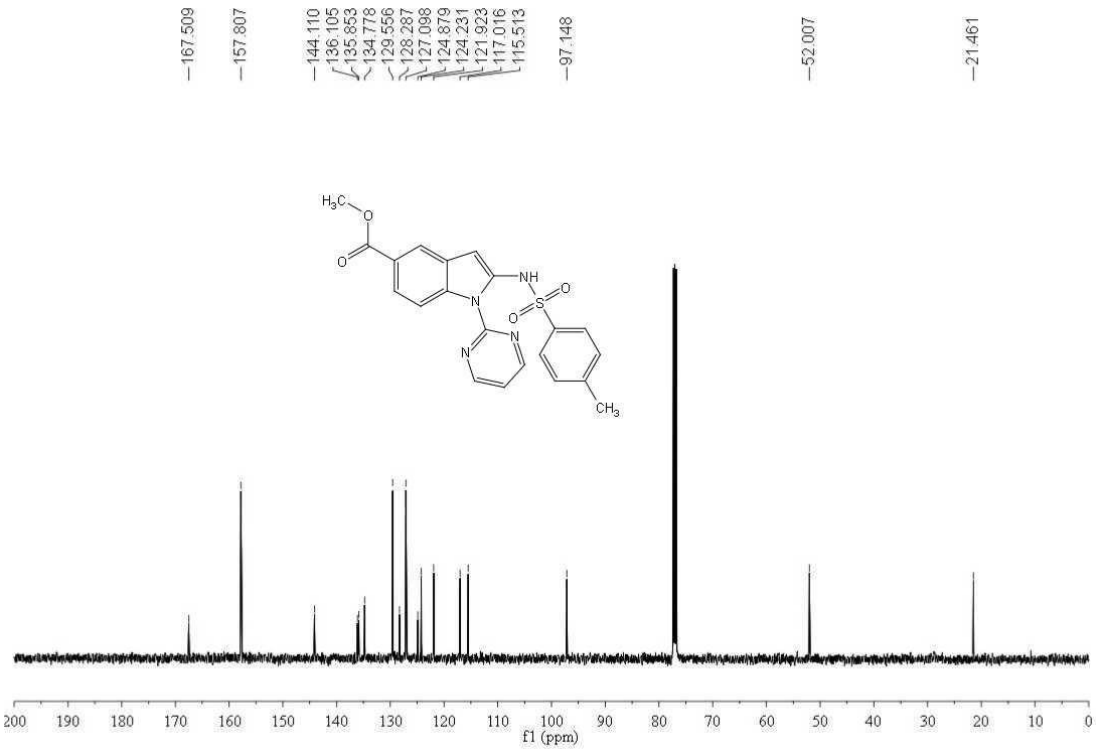
8.514
8.484
8.169
7.881
7.851
7.630
7.604
7.158
7.098
7.072
6.651
3.920
2.281
1.09
1.95
0.98
0.88
1.00
1.84
0.99
1.88
0.90
3.00
2.93
f1 (ppm)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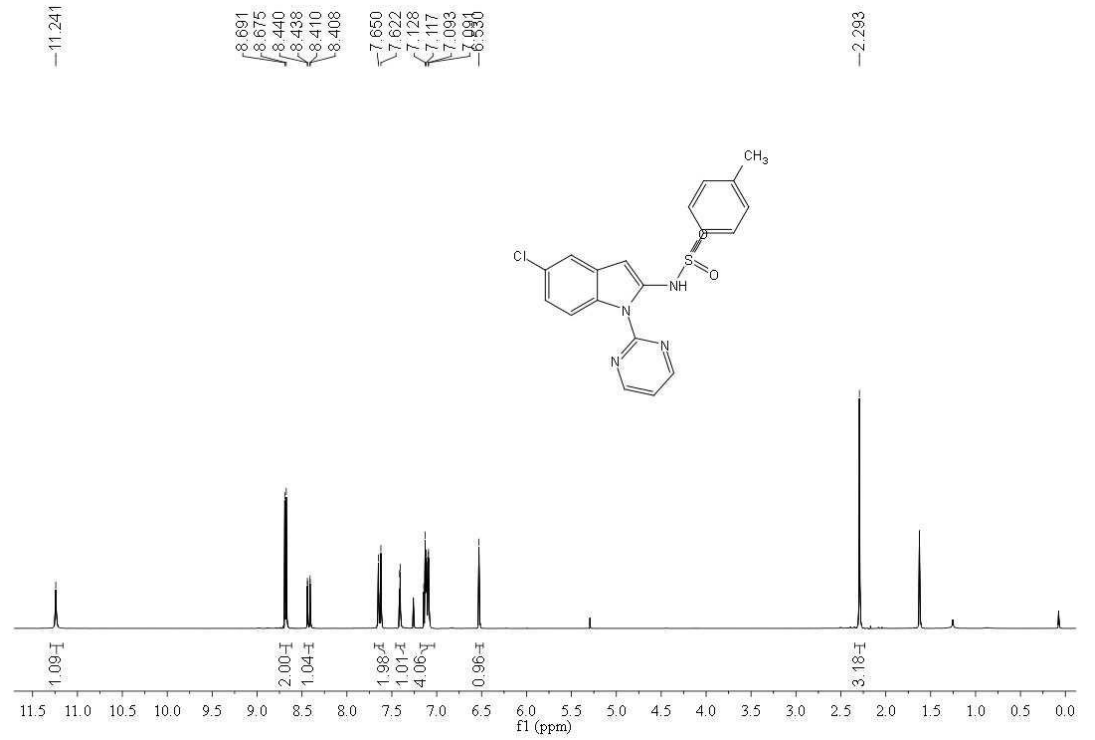
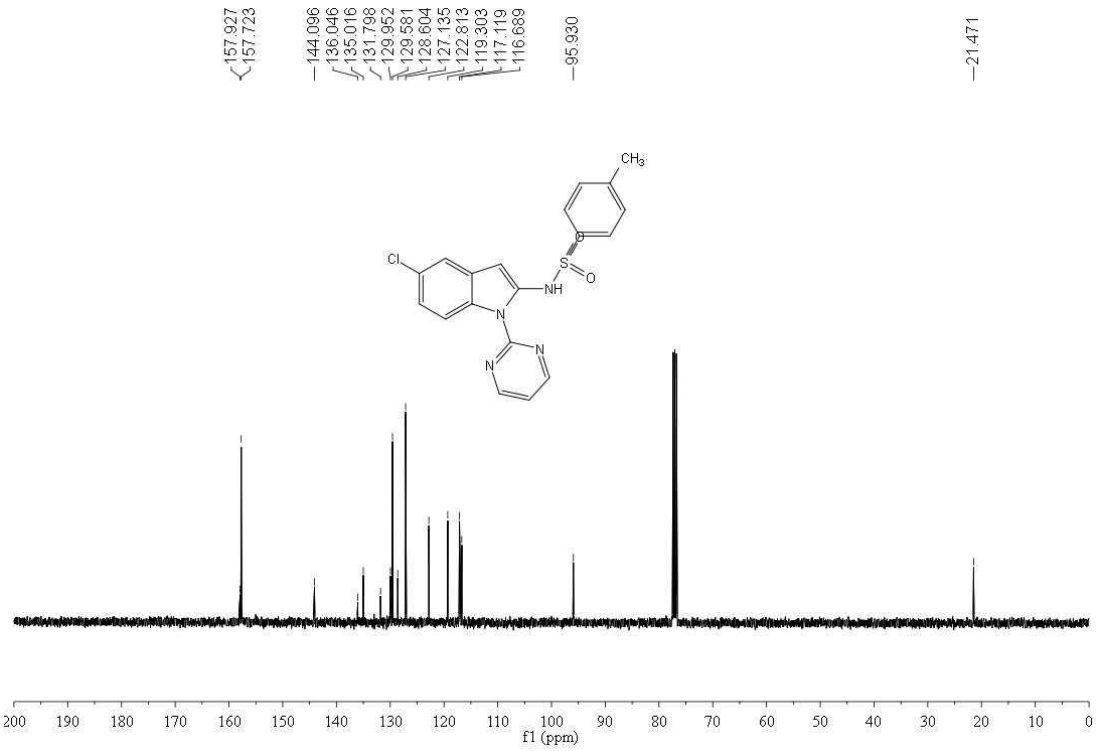
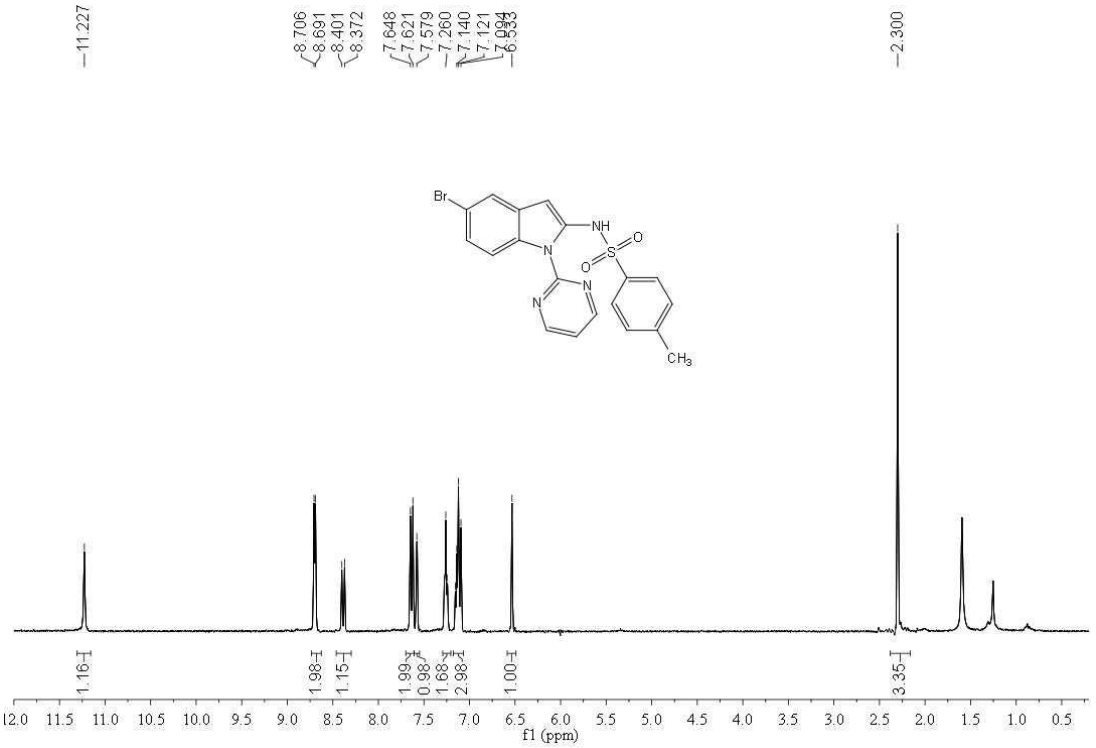
135.853
134.778
129.556
128.287
127.098
124.879
124.231
121.923
117.016
115.513
97.148
52.007
21.461
f1 (ppm)

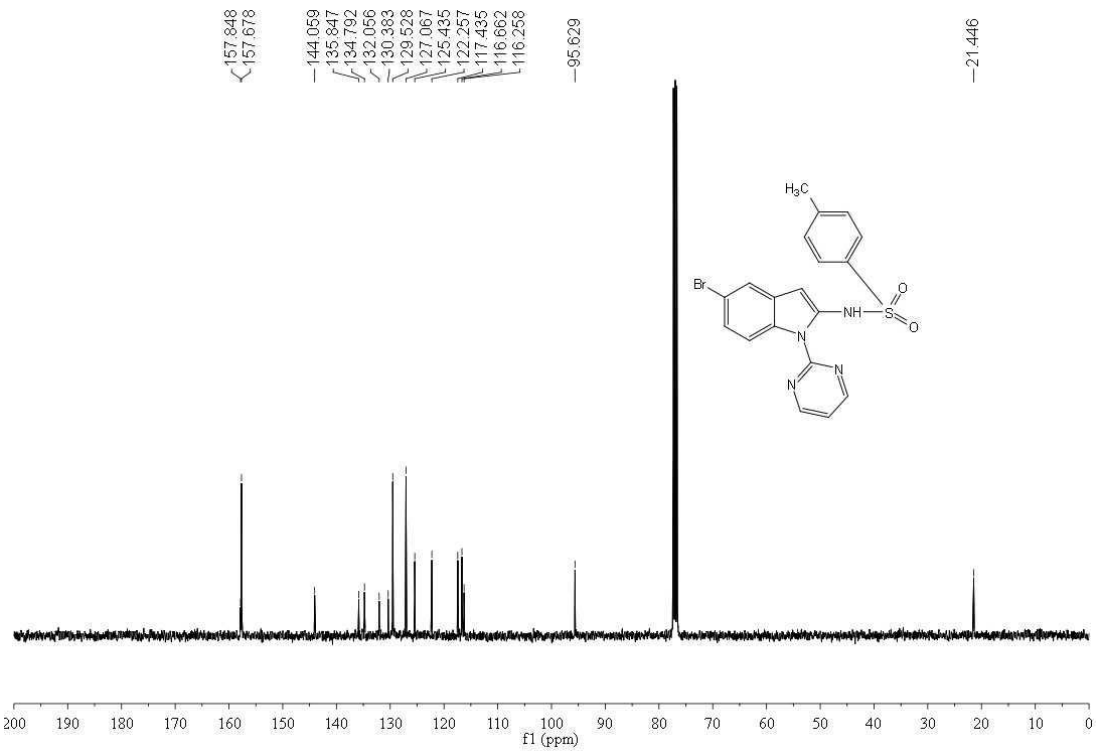
## Compound 3q



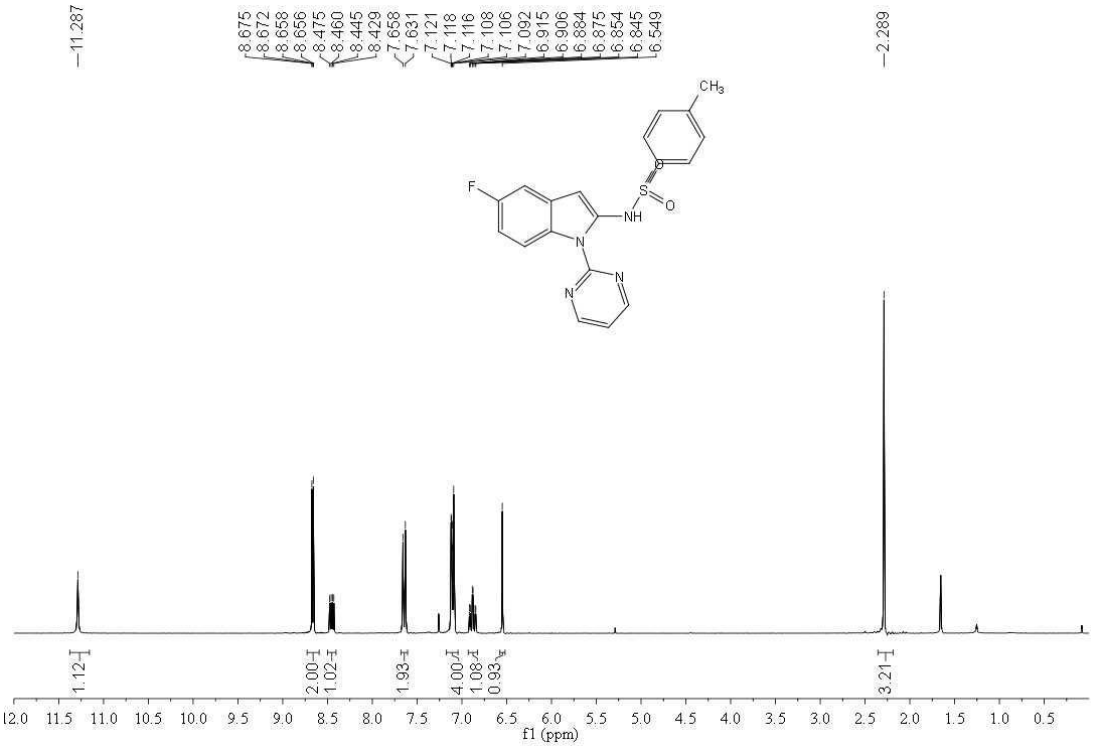



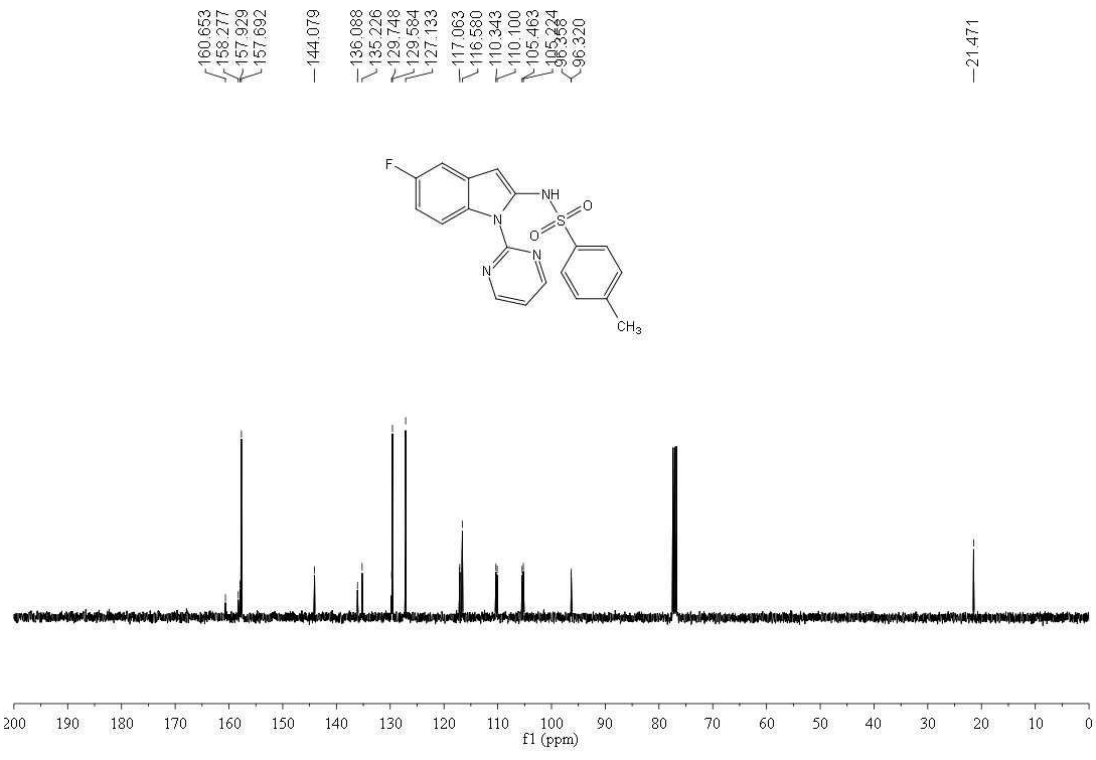
## Compound 3r



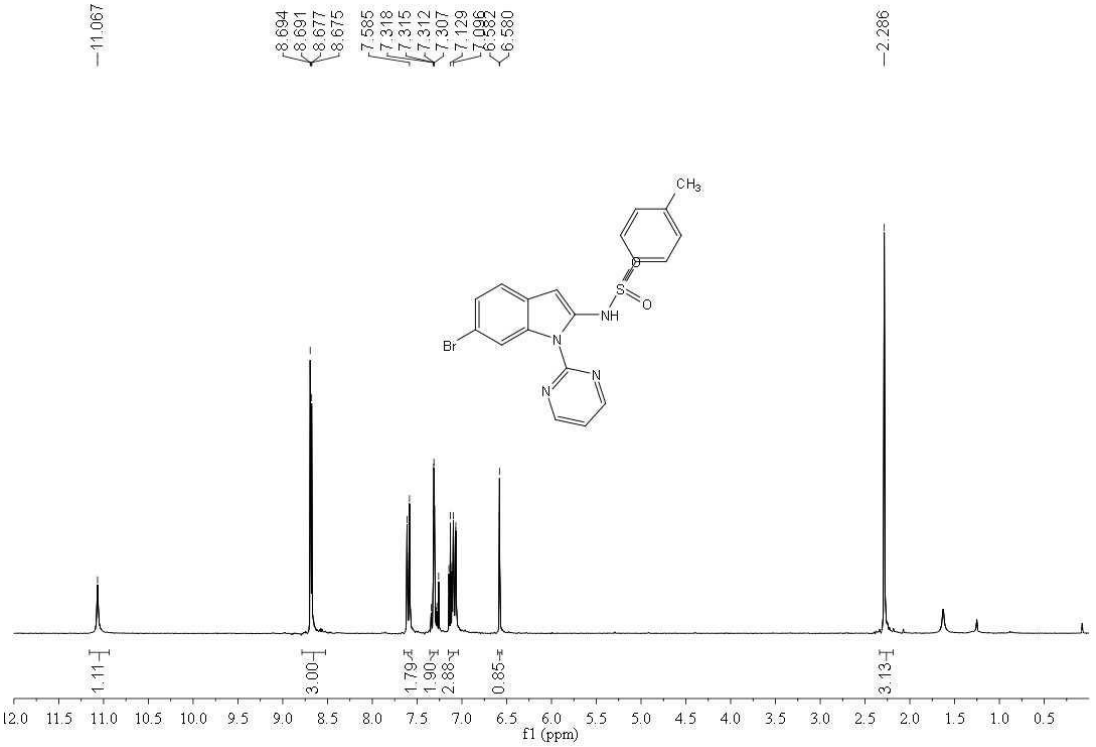



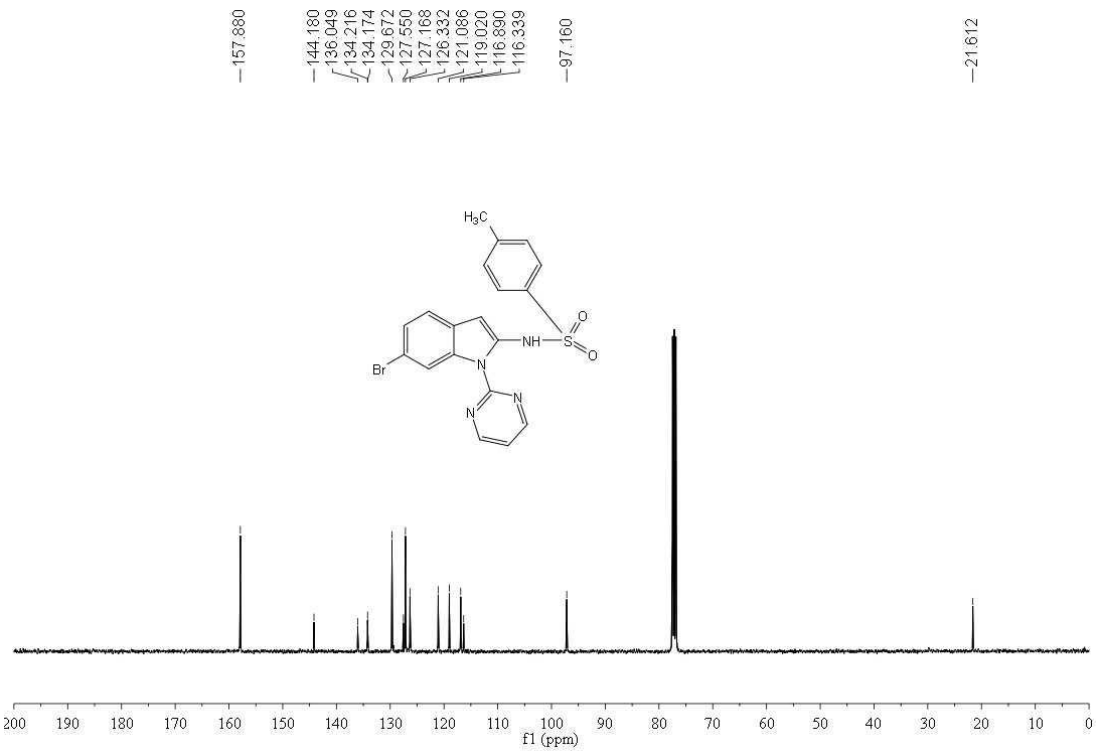
## Compound 3s



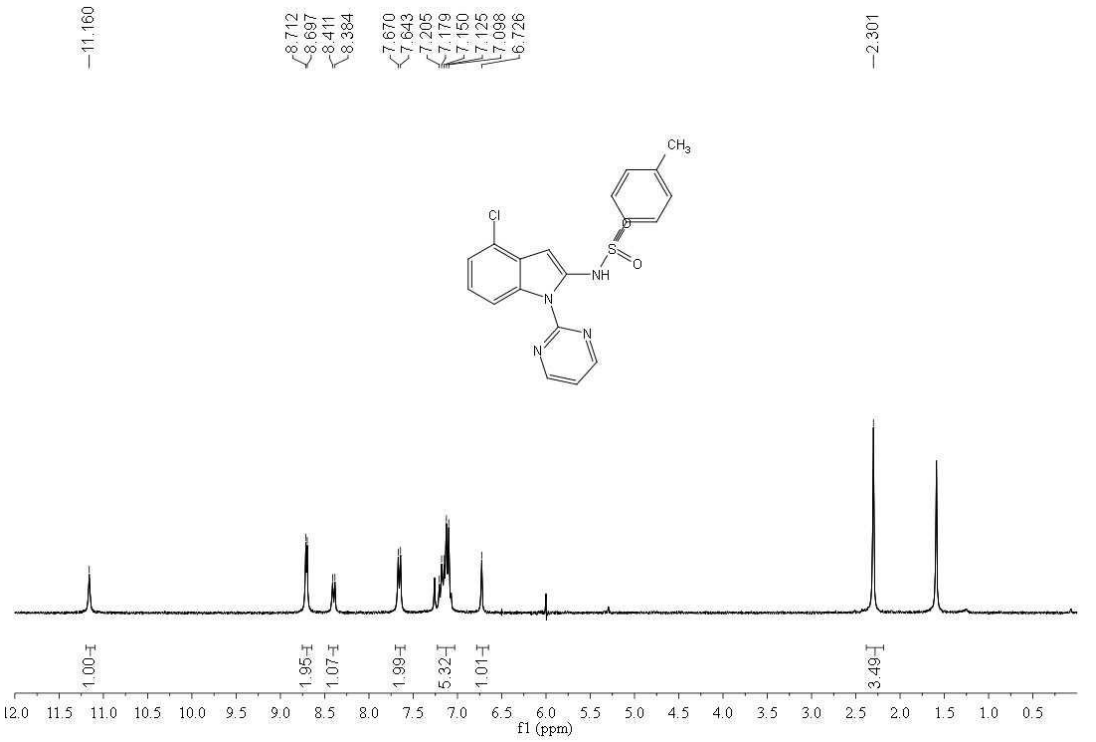



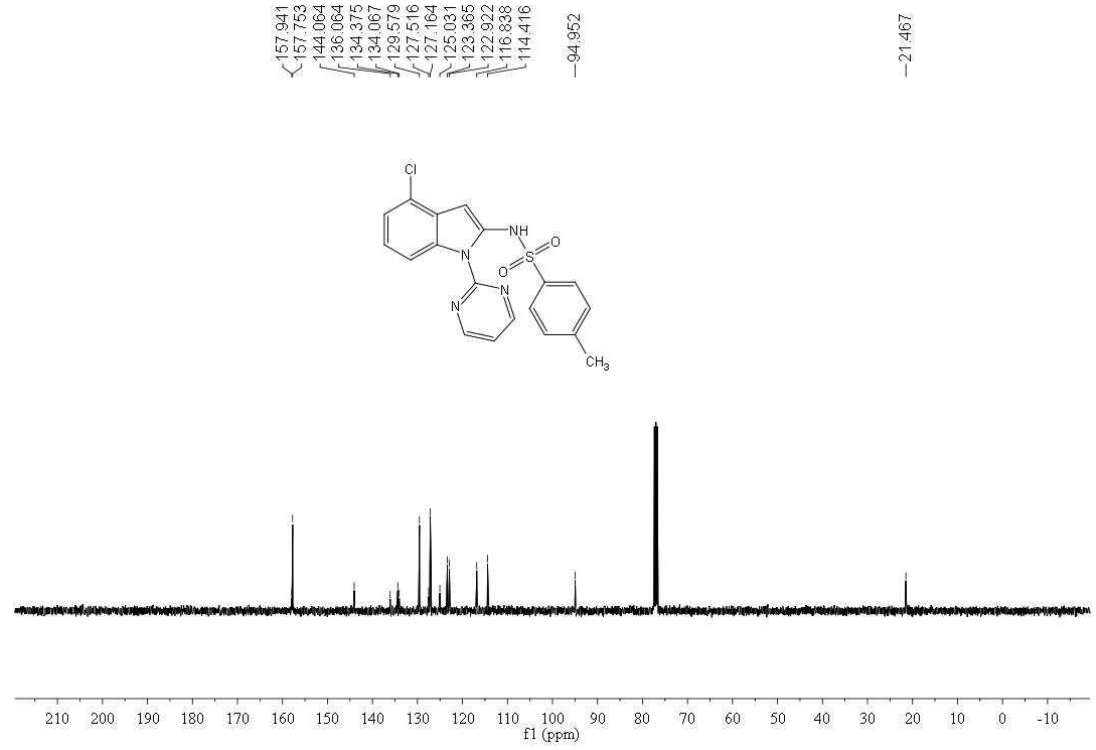
## Compound 3t



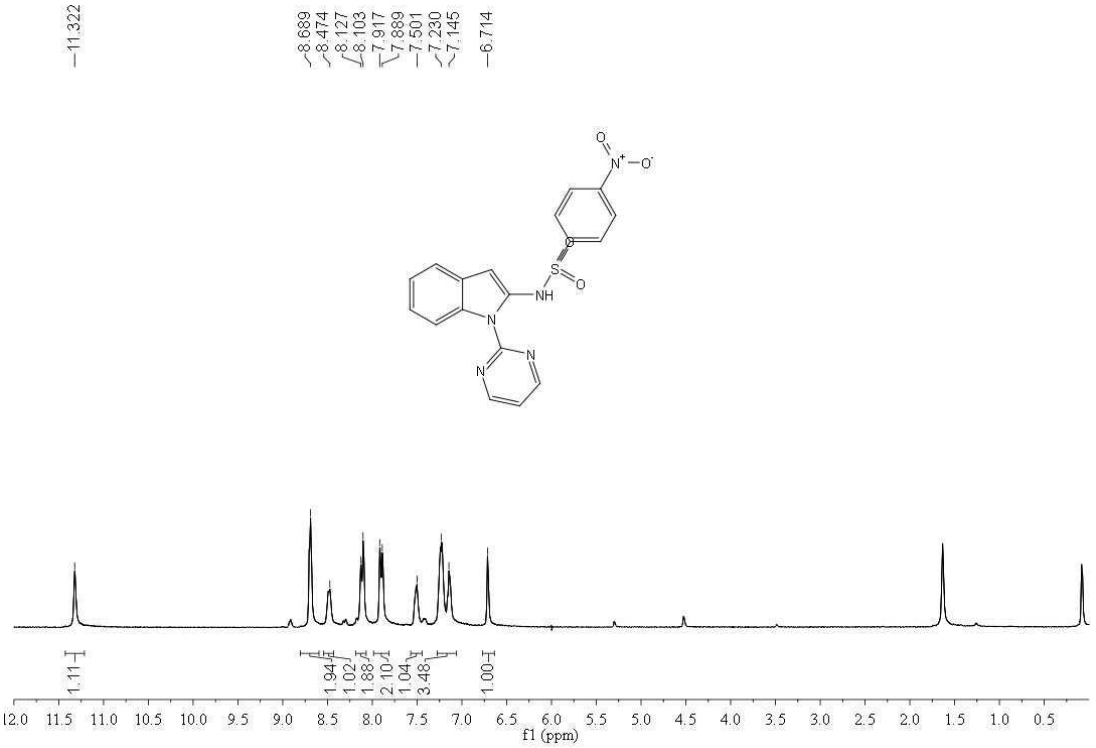



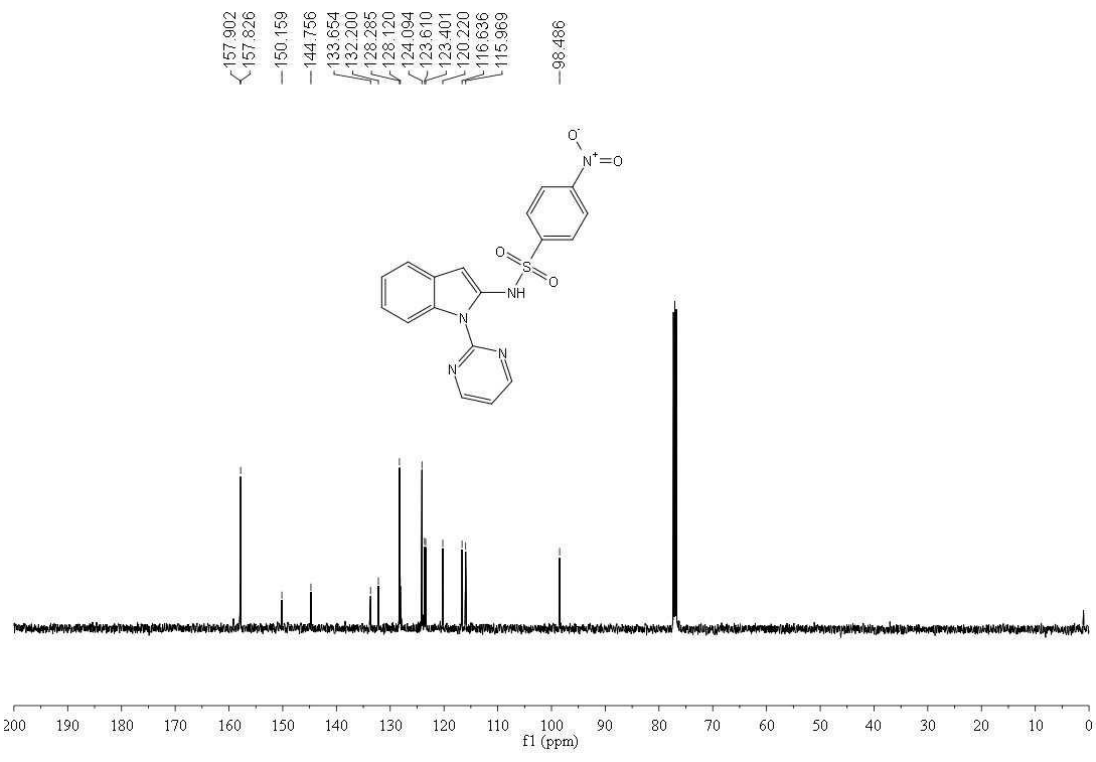
## Compound 3u



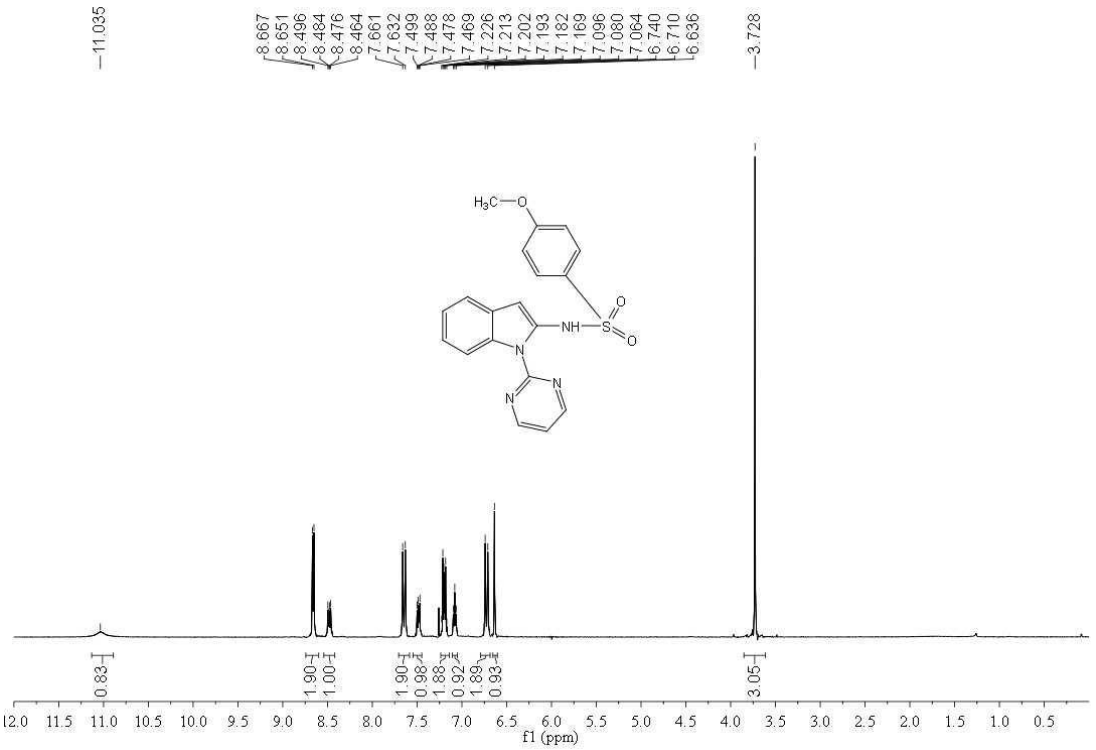



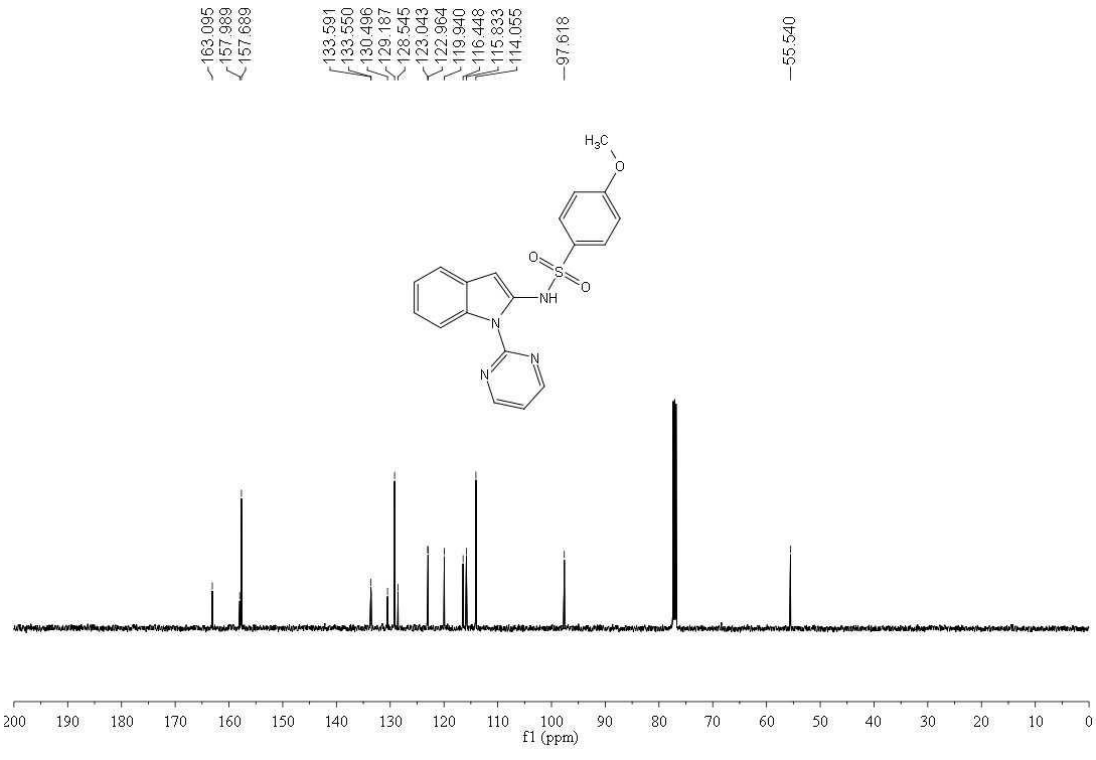
## Compound 3v


11.322
8.689
8.474
8.127
8.103
7.917
7.889
7.501
7.230
7.145
6.714
1.11
1.94
1.02
1.88
2.10
1.04
3.48
1.00
f1 (ppm)

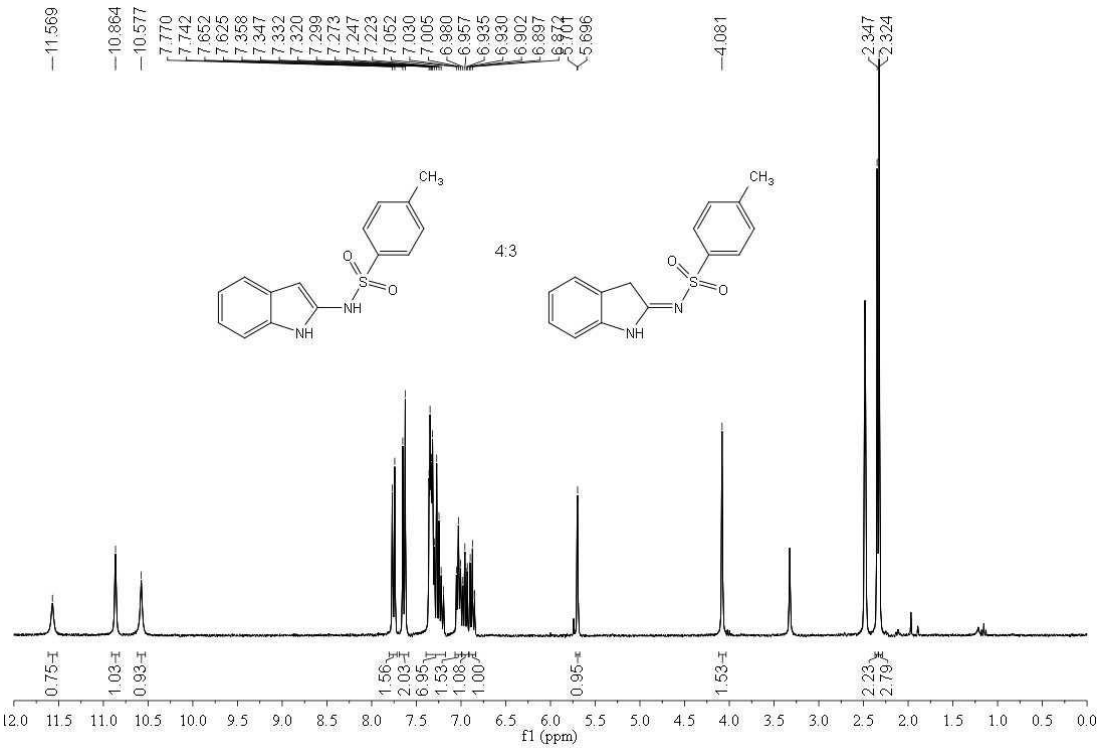

157.902
157.826
150.159
144.756
133.654
132.200
128.285
128.120
124.094
123.610
123.401
120.220
116.636
115.969
98.486
f1 (ppm)

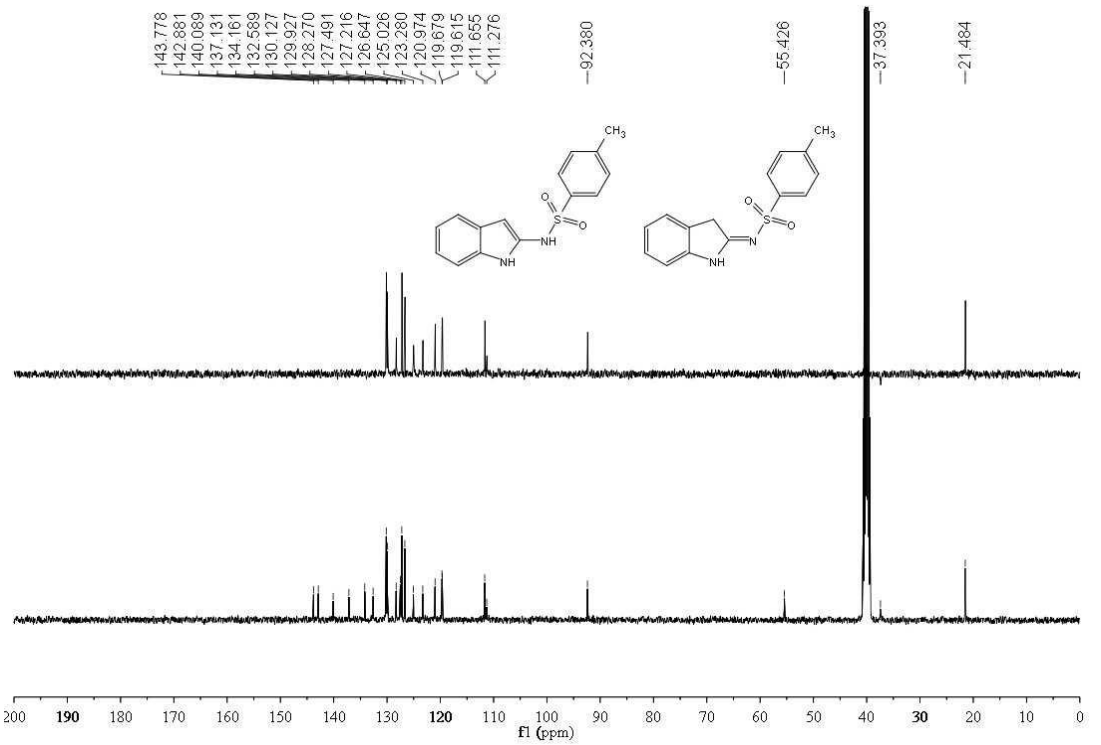
## Compound 3w


11.035
8.667
8.651
8.496
8.484
8.476
8.464
7.661
7.632
7.499
7.488
7.478
7.469
7.226
7.213
7.202
7.193
7.182
7.169
7.096
7.080
7.064
6.740
6.710
6.636
3.728
H3C
O
NH
S
O
O
N
N
N
0.83
1.90
1.00
1.90
0.98
1.88
0.92
1.89
0.93
3.05
f1 (ppm)

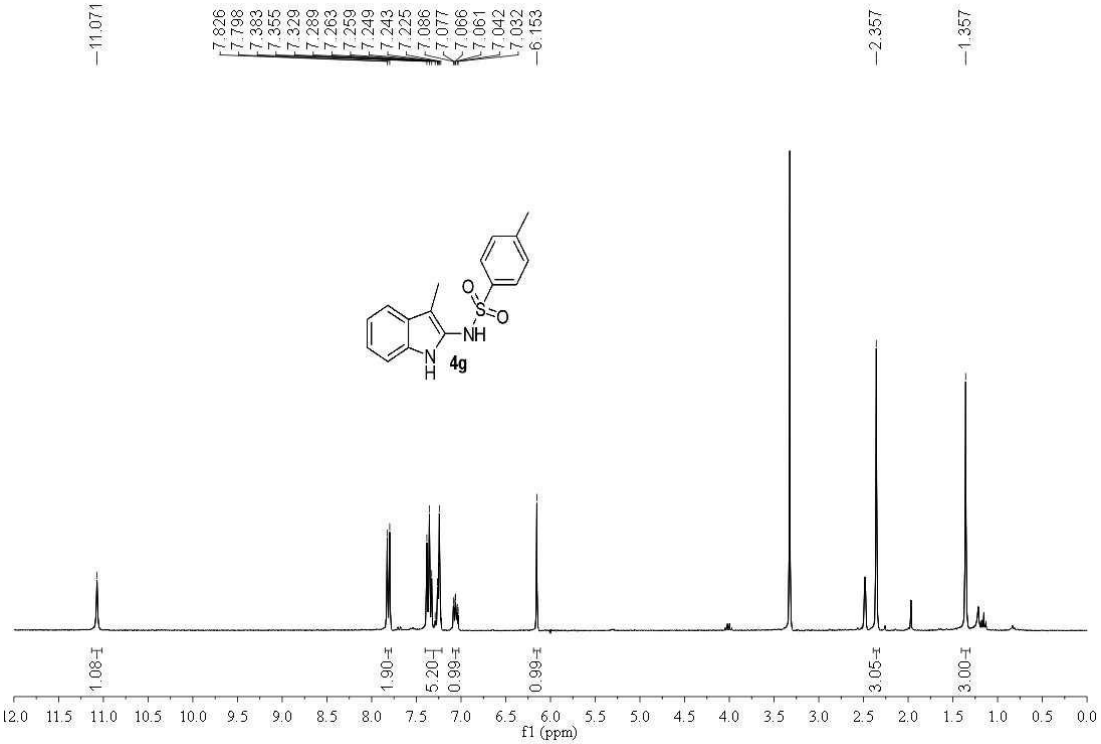

163.095
157.989
157.689
133.591
133.550
130.496
129.187
128.545
123.043
122.964
119.940
116.448
115.833
114.055
97.618
55.540
H3C
O
O
S
O
NH
N
N
N
f1 (ppm)

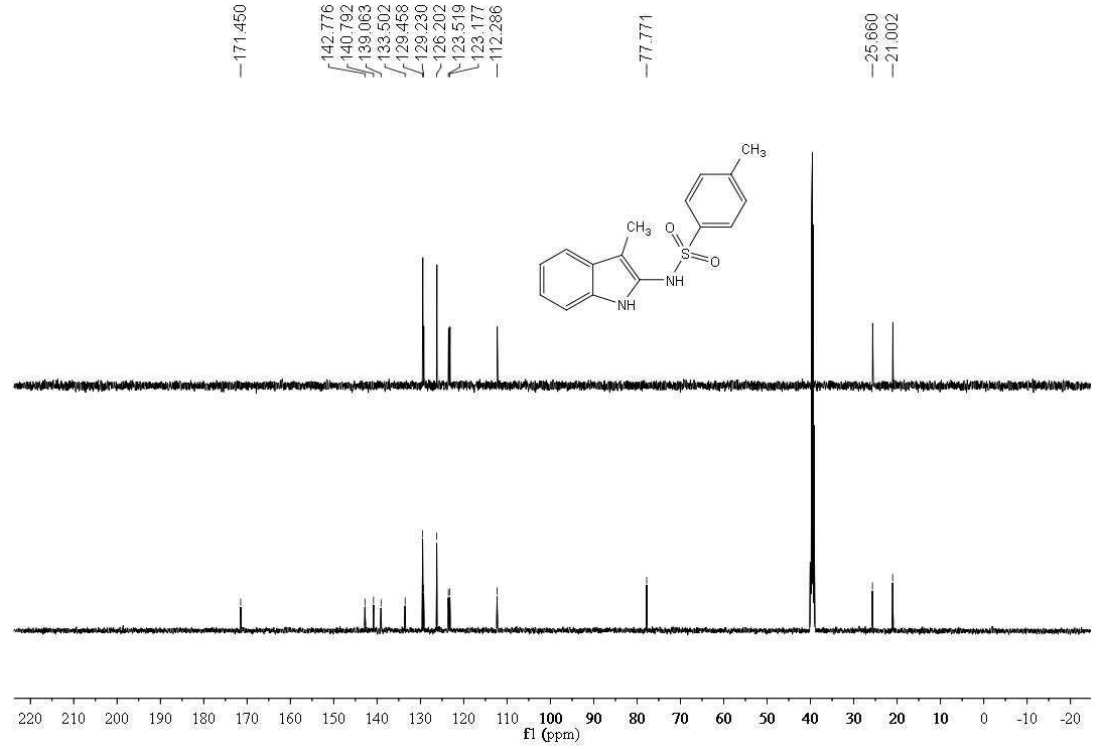
Compound **4f**


11.569
10.864
10.577
7.770
7.742
7.652
7.625
7.358
7.347
7.332
7.320
7.299
7.273
7.247
7.223
7.052
7.030
7.005
6.980
6.957
6.935
6.930
6.902
6.897
6.872
5.701
5.696
4.081
2.347
2.324
4:3
0.75
1.03
0.93
1.56
2.03
6.95
1.53
1.08
1.00
0.95
1.53
2.23
2.79
f1 (ppm)


143.778
142.881
140.089
137.131
134.161
132.589
130.127
129.927
128.270
127.491
127.216
126.647
125.026
123.280
120.974
119.679
119.615
111.655
111.276
92.380
55.426
37.393
21.484
f1 (ppm)

Compound **4g**


11.071
7.826
7.798
7.383
7.355
7.329
7.289
7.263
7.259
7.249
7.243
7.225
7.086
7.077
7.066
7.061
7.042
7.032
6.153
2.357
1.357
4g
1.08
1.90
5.20
0.99
0.99
3.05
3.00
f1 (ppm)


171.450
142.776
140.792
139.063
133.502
129.458
129.230
126.202
123.519
123.177
112.286
77.771
25.660
21.002
f1 (ppm)