Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

# Cobalt-Catalyzed C8-H Sulfonylation of 1-Naphthylamine Derivatives with Sodium Sulfinates

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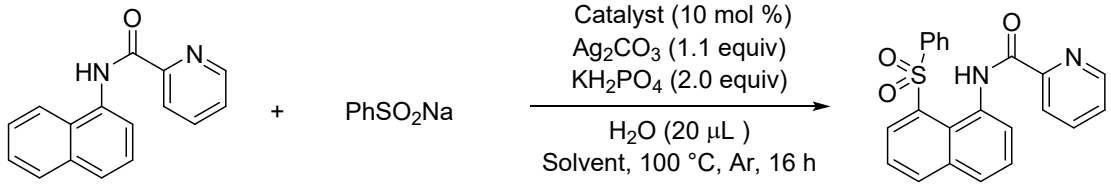
## 1. General Information

$^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on an Agilent Technologies 1290-6540 UHPLC/Accurate-Mass Quadrupole Time-of-Flight LC/MS. All solvents were used with further purification. Dichloromethane, ethyl acetate, and hexane were used for column chromatography. The commercials were obtained from commercial sources and used as-received without further purification unless otherwise noted.

## 2. Optimization of Reaction Conditions

Table S1. Optimization of Solvent and Catalyst[a]



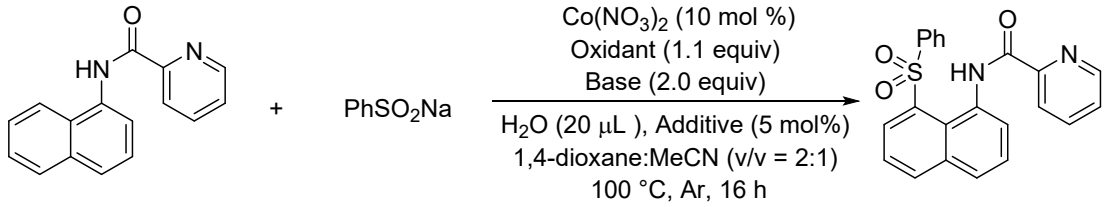

**1a** **2a** **3aa**

| Entry | Catalyst | Solvent | Yield [b] |
|---|---|---|---|
| 1 | $CoCl_2·6H_2O$ | DCE | <5% |
| 2 | $CoCl_2·6H_2O$ | THF | 22% |
| 3 | $CoCl_2·6H_2O$ | DMA | <5% |
| 4 | $CoCl_2·6H_2O$ | DMSO | <5% |
| 5 | $CoCl_2·6H_2O$ | MeCN | 13% |
| 6 | $CoCl_2·6H_2O$ | $CH_3OH$ | <5% |
| 7 | $CoCl_2·6H_2O$ | acetone | 8% |
| 8 | $CoCl_2·6H_2O$ | toluene | <5% |
| 9 | $CoCl_2·6H_2O$ | 1,4-dioxane | 26% |
| 10 | $CoCl_2·6H_2O$ | HFIP | <5% |
| 11 | $CoCl_2·6H_2O$ | 1,4-dioxane/MeCN(v/v = 2:1) | 35% |
| 12 | $NiCl_2·6H_2O$ | 1,4-dioxane/MeCN(v/v = 2:1) | <5% |
| 13 | $FeCl_3$ | 1,4-dioxane/MeCN(v/v = 2:1) | <5% |
| 14 | $Cu(OAc)_2·H_2O$ | 1,4-dioxane/MeCN(v/v = 2:1) | <5% |
| 15 | $Pd(OAc)_2$ | 1,4-dioxane/MeCN(v/v = 2:1) | <5% |
| 16 | $Co(NO_3)_2$ | 1,4-dioxane/MeCN(v/v = 2:1) | 38% |
| 17 | $Co(OAc)_2$ | 1,4-dioxane/MeCN(v/v = 2:1) | <5% |

| | | | |
|---|---|---|---|
| 18 | $Co(acac)_2$ | 1,4-dioxane/MeCN(v/v = 2:1) | 10% |

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv.), catalysts (10 mol %), $KH_2PO_4$ (2.0 equiv.), $Ag_2CO_3$ (1.1 equiv.), $H_2O$ (20 μL) in solvent (1.0 mL) at 100 °C under argon for 16 h. [b] Isolated yield.

Table S2. Optimization of Base, Oxidant and Additive[a]




**1a** **2a** **3aa**

| Entry | Base | Oxidant | Additive | yield [b] |
|---|---|---|---|---|
| 1 | $(NH_4)_2HPO_4$ | $Ag_2CO_3$ | - | 36% |
| 2 | $^t$BuOK | $Ag_2CO_3$ | - | <5% |
| 3 | $Na_2CO_3$ | $Ag_2CO_3$ | - | 38% |
| 4 | $Na_3PO_4$ | $Ag_2CO_3$ | - | 28% |
| 5 | $K_2CO_3$ | $Ag_2CO_3$ | - | 23% |
| 6 | KOAc | $Ag_2CO_3$ | - | 21% |
| 7 | LiF | $Ag_2CO_3$ | - | 23% |
| 8 | NaF | $Ag_2CO_3$ | - | 41% |
| 9 | NaI | $Ag_2CO_3$ | - | 13% |
| 10 | $Cs_2CO_3$ | $Ag_2CO_3$ | - | <5% |
| 11 | PivONa | $Ag_2CO_3$ | - | <5% |
| 12 | DBU | $Ag_2CO_3$ | - | <5% |
| 13 | $NEt_3$ | $Ag_2CO_3$ | - | 24% |
| 14 | Pyridine | $Ag_2CO_3$ | - | 32% |
| 15 | NaF | TBHP | - | <5% |
| 16 | NaF | $I_2$ | - | <5% |
| 17 | NaF | $K_2S_2O_8$ | - | <5% |
| 18 | NaF | BPO | - | <5% |
| 19 | NaF | $MnO_2$ | - | 7% |
| 20 | NaF | $Ag_2O$ | - | <5% |
| 21 | NaF | AgOAc | - | 8% |
| 22 | NaF | $AgNO_2$ | - | 15% |
| 23 | NaF | AgI | - | <5% |
| 24 | NaF | $Ag_2CO_3$ | dppe | 57% |

| | | | | |
|---|---|---|---|---|
| 25 | NaF | $Ag_2CO_3$ | $PPh_3$ | 51% |
| 26 | NaF | $Ag_2CO_3$ | Selectfluor | 62% |
| 27 | NaF | $Ag_2CO_3$ | NFSI | 72% |
| 28[c] | NaF | $Ag_2CO_3$ | NFSI | <5% |
| 29 | NaF | - | NFSI | <5% |
| 30[d] | NaF | $Ag_2CO_3$ | NFSI | 64% |
| 31[e] | NaF | $Ag_2CO_3$ | NFSI | 65% |
| 32[f] | NaF | $Ag_2CO_3$ | NFSI | 52% |
| 33[g] | NaF | $Ag_2CO_3$ | NFSI | 54% |

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (2 equiv.), $Co(NO_3)_2$ (10 mol%), base (2.0 equiv.) and oxidant (1.1 equiv.), additive (5 mol%), $H_2O$ (20 μL) in 1,4-dioxane/MeCN(v/v = 2:1) (1.0 mL) at 100 °C under argon for 16 h. [b] Isolated yield. [c] In the absence of $Co(NO_3)_2$. [d] At an additive loading of 20 mol%. [e] At a catalysis loading of 5 mol%. [f] In the absence of water. [g] Under air.

## 3. Experimental Section

### 3.1. Typical Procedure for the Synthesis of Substrate 1a

A 100 mL two-necked round-bottom flask was equipped with a magnetic stir bar and charged with 1-naphthylamine (20 mmol, 2.86 g), picolinic acid (1.1 equiv., 2.70 g), N,N-dimethyl-4-aminopyridine (DMAP, 0.1 equiv., 0.244 g) in 30 mL anhydrous $CH_2Cl_2$ at 0 °C. After EDCI (4.20 g, 1.1 equiv.) in $CH_2Cl_2$ (20 mL) was added dropwise to the solution under a nitrogen atmosphere, the reaction was then warmed to room temperature, stirred for 12 h and quenched with water (30 mL). The reaction mixture was extracted with $CH_2Cl_2$ (3 × 20 mL), and the combined organic solvent was dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (hexane/ethyl acetate = 3:1) (V/V) to afford the pure product **1a** as a white solid (4.42 g, 89%).

All amides were prepared from the corresponding 1-naphthylamine derivatives and 2-picolinic acid according to the reported procedure.[1]

### 3.2. Typical Procedure for the Product 2a

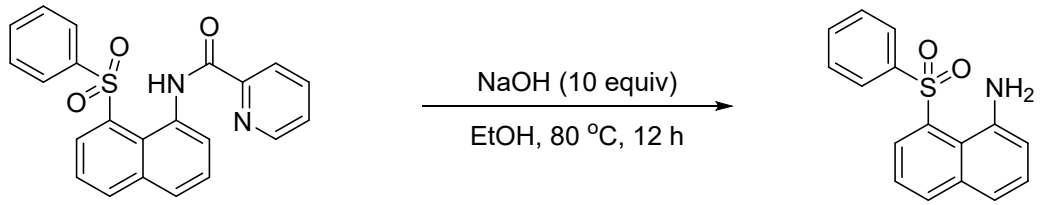
Sodium sulfite (2.50 g, 20 mmol), sodium hydrogen carbonate (1.68 g, 20 mmol), and sulfonyl chlorides (10 mmol) were added to water (10 mL). After stirring at 80 °C for 4 h, water was removed by rotary evaporator. Then, the remaining solid was extracted and recrystallized by ethanol to obtain a white solid as the desired product. Other sodium sulfinates were prepared through a similar route from their corresponding sulfonyl chlorides.[2]

### 3.3. Typical Procedure for the Product 3aa

A Schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (0.1 mmol, 24.8 mg), **2a** (0.2 mmol, 32 mg), $Co(NO_3)_2$ (0.01 mmol, 1.8 mg),

NaF (0.2 mmol, 8 mg), $Ag_2CO_3$ (0.11 mmol, 30 mg), NFSI (0.005 mmol, 1.3 mg), $H_2O$ (20 μL) in 1,4-dioxane/MeCN (v/v = 2:1) (1.0 mL). The resulting mixture was sealed under argon, heated at 100 °C for 16 h, and cooled to room temperature. Upon completion, $CH_2Cl_2$ (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. After the organic material was concentrated in vacuum, the product was purified by column chromatography on silica gel (100–200 mesh) using hexane/EtOAc as an eluent (2:1, V/V) to afford the pure product **3aa**.

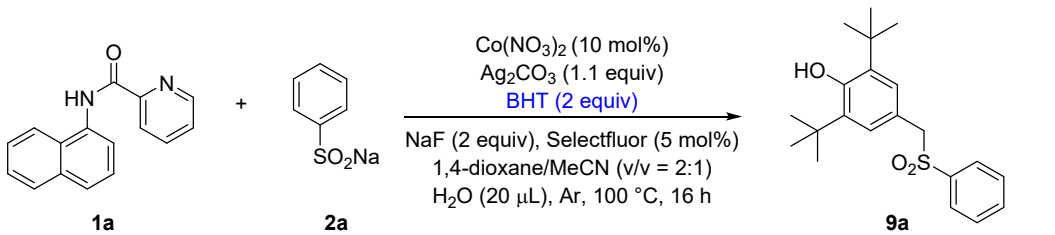
### 3.4. Typical Procedure for the Product 4a




**3aa** **4a** 85%

A mixture of **3aa** (77.6 mg, 0.2 mmol, 1.0 equiv) and NaOH (80 mg, 2 mmol, 10 equiv.) was heated in ethanol (2 mL) for 12 h at 80 °C. After the mixture was cooled to room temperature and diluted with water (3.0 mL), the solution of diluted hydrochloric acid was added until it was acidic. The saturated $NaHCO_3$ solution was then added until the pH value was about 7. The mixture was then extracted with $CH_2Cl_2$ and dried over anhydrous $Na_2SO_4$. After the organic material was concentrated in vacuum, the product was purified by column chromatography on silica gel (100–200 mesh) using hexane/EtOAc as an eluent (2:1, V/V) to afford the pure product **4a**.

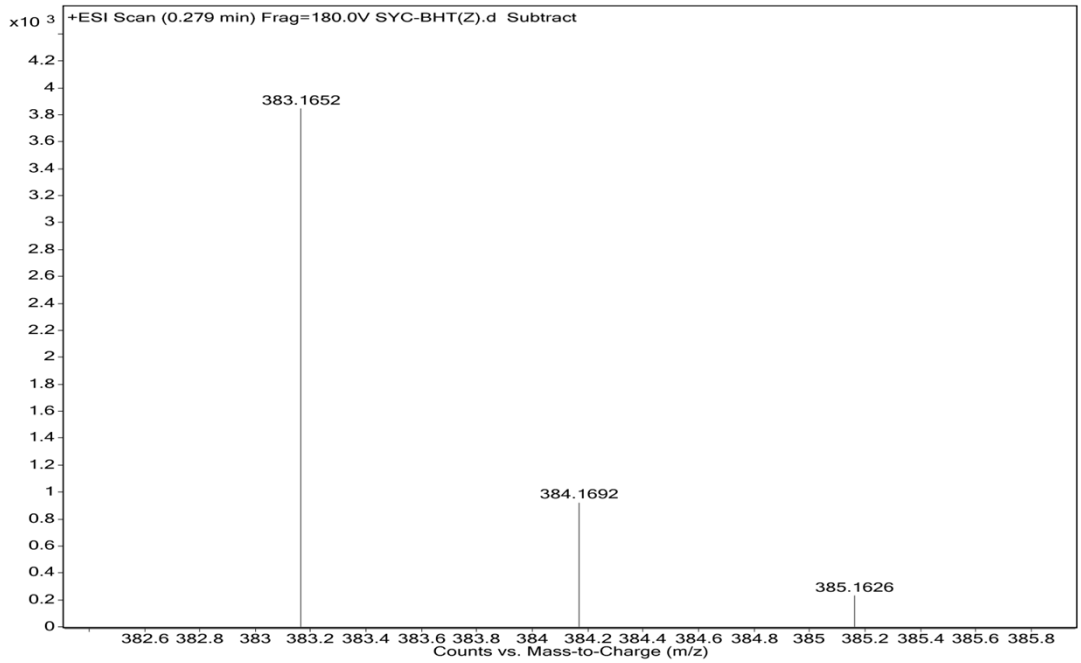
### 3.5. The Experiment of Trapping the Radicals




**1a** **2a** **9a**

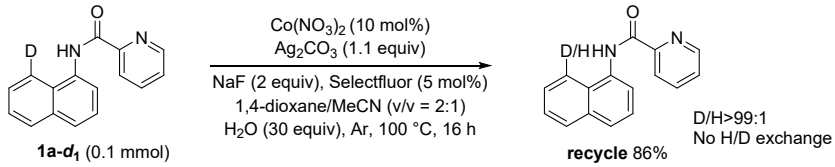
*detected by HR-MS*

HRMS (ESI$^+$): calcd for $C_{21}H_{28}O_3S$ $[M+Na]^+$: 383.1651, Found: 383.1652.



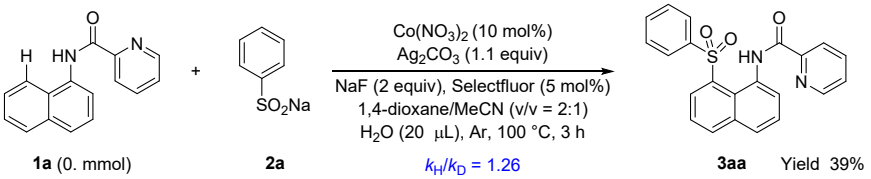

## 3.6. Kinetic Isotope Effect Experiments

(1) H/D exchange reaction

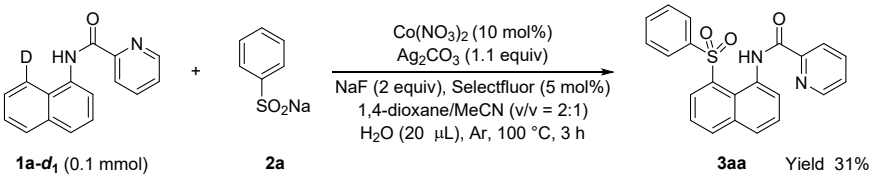



**1a-$d_1$** (0.1 mmol) **recycle** 86%

(2) Parallel reaction

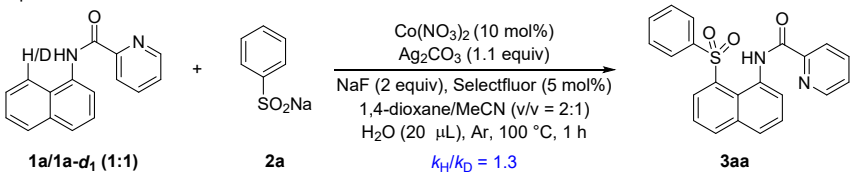



**1a** (0. mmol) **2a** **3aa** Yield 39%




**1a-$d_1$** (0.1 mmol) **2a** **3aa** Yield 31%

(3) Competitive reaction



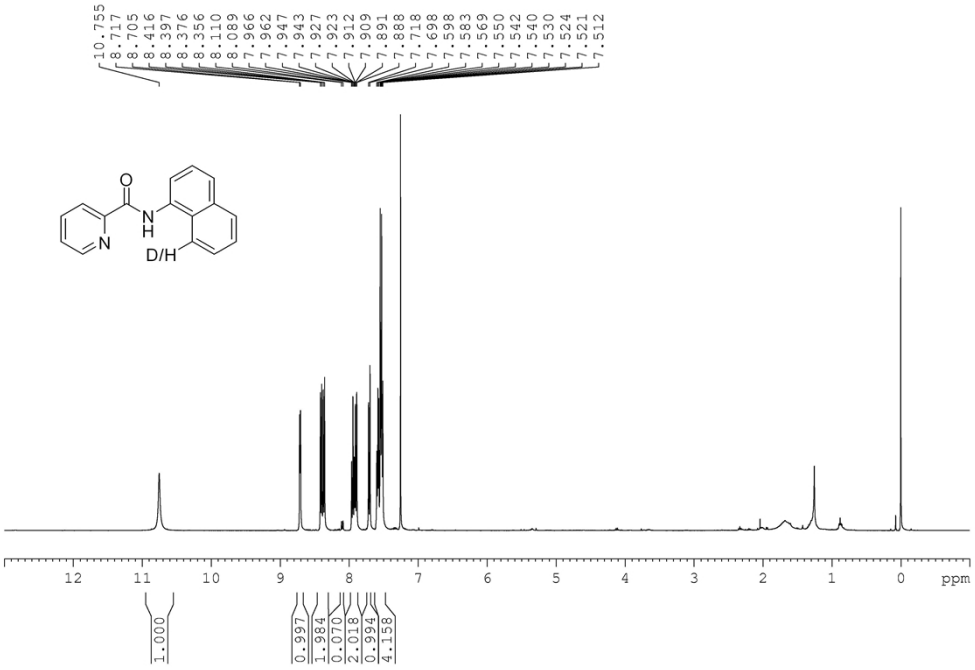

**1a/1a-$d_1$ (1:1)** **2a** **3aa**

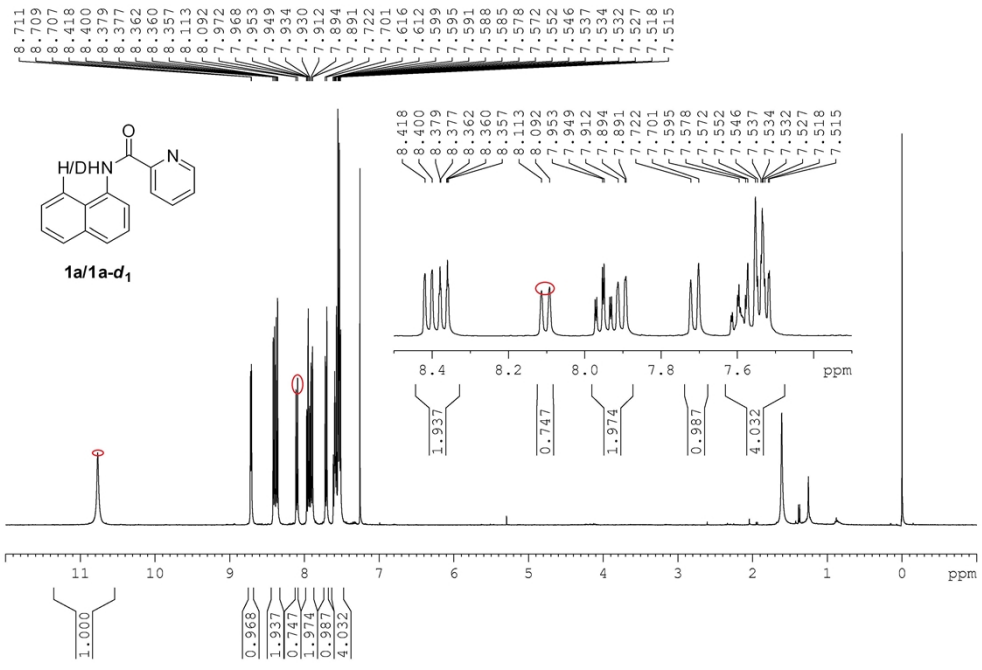
**Deuterium Exchange Experiment**: A Schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a-$d_1$** (0.1 mmol), $Co(NO_3)_2$ (0.01 mmol, 1.8 mg),

NaF (0.2 mmol, 8 mg), $Ag_2CO_3$ (0.11 mmol, 30 mg), NFSI (0.005 mmol, 1.3 mg), $H_2O$ (54 μL, 30 equiv.). in 1,4-dioxane/MeCN (v/v = 2:1) (1.0 mL). The resulting mixture was sealed and heated at 100 °C for 16 h, and cooled to room temperature. Upon completion, the mixture was added into $H_2O$ (20 mL) and extracted with ethyl acetate (10 mL× 3). The organic layer was collected, dried over anhydrous sodium sulfate, and then filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using hexane-EtOAc as an eluent (3:1, V/V). The substrate **1a-*d*$_1$** was successfully recycled (21.3 mg, 86% isolated yield), and its structure was confirmed by $^1$H NMR spectrum, which suggested that the H/D exchange did not occur.

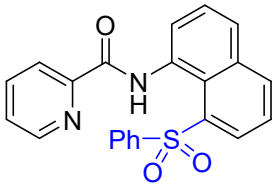
**Parallel Reaction**: A Schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (0.1 mmol) or **1a-*d*$_1$** (0.1 mmol), **2a** (0.2 mmol, 32 mg), $Co(NO_3)_2$ (0.01 mmol, 1.8 mg), NaF (0.2 mmol, 8 mg), $Ag_2CO_3$ (0.11 mmol, 30 mg), NFSI (0.005 mmol, 1.3 mg), $H_2O$ (20 μL) in 1,4-dioxane/MeCN (v/v = 2:1) (1.0 mL). The resulting mixture was sealed under Ar, heated at 100 °C for 3 h and cooled to room temperature. Upon completion, $CH_2Cl_2$ (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. After the organic material was concentrated in vacuum, the product was purified by column chromatography on silica gel (100–200 mesh) using hexane/EtOAc as an eluent (2:1, V/V) to afford the pure product **3aa**, which was analyzed by $^1$H NMR spectrum., respectively. The KIE value was calculated as $k_H/k_D$ = 1.26

**Competitive Reaction**: A Schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (0.05 mmol, 12.4 mg), **1a-*d*$_1$** (0.05 mmol, 12.4 mg), **2a** (0.2 mmol, 32 mg), $Co(NO_3)_2$ (0.01 mmol, 1.8 mg), NaF (0.2 mmol, 8 mg), $Ag_2CO_3$ (0.11 mmol, 30 mg), NFSI (0.005 mmol, 1.3 mg), $H_2O$ (20 μL) in 1,4-dioxane/MeCN (v/v = 2:1) (1.0 mL). The resulting mixture was sealed under Ar, heated at 100 °C for 1 h and cooled to room temperature. Upon completion, $CH_2Cl_2$ (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. After the organic material was concentrated in vacuum, the product was purified by column chromatography on silica gel (100–200 mesh) using hexane/EtOAc as an eluent (2:1, V/V) to afford the pure product **1a/1a-*d*$_1$**, and then analyzed by $^1$H NMR spectrum. The KIE value was calculated as $k_H/k_D$ = 1.3.

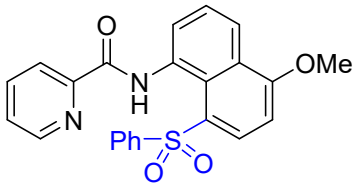


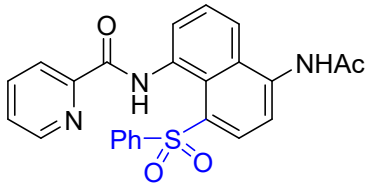

## 4. Characterization Data of the Products



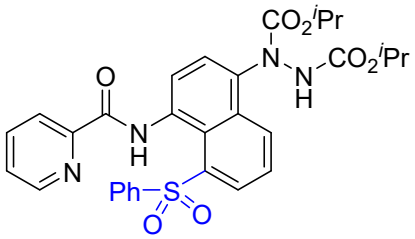
N-(8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3aa**): white solid (72%), mp 230-232 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.10 (s, 1H), 8.77-8.70 (m, 1H), 8.56 (dd, $J_1$ = 7.49 Hz, $J_2$ = 1.27 Hz, 1H), 8.28-8.21 (m, 1H), 8.00-7.93 (m, 1H), 7.81 (d, $J$ = 7.61 Hz, 2H), 7.78-7.73 (m, 1H), 7.70-7.65 (m, 1H), 7.65-7.60 (m 1H), 7.49-7.44 (m, 1H), 7.36-7.32 (m, 2H), 7.24-7.18 (m, 1H), 7.04-6.97 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 150.0, 148.0, 142.8, 136.9, 136.7, 136.3, 133.7, 132.6, 132.1, 131.4, 130.5, 128.7, 128.4, 127.3, 126.2, 126.2, 124.5, 123.9, 122.8; HRMS (ESI$^+$): calcd for $C_{22}H_{16}N_2O_3S$ $[M+H]^+$: 389.0954, Found: 389.0952.



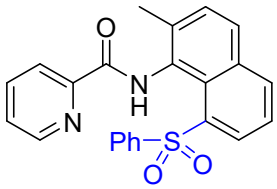
N-(5-methoxy-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3ba**): white solid (67%), mp 213-215 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.08 (s, 1H), 8.75-8.69 (m, 1H), 8.62 (d, $J$ = 8.59 Hz, 1H), 8.50-8.42 (m, 1H), 7.80-7.70 (m, 3H), 7.68-7.60 (m, 1H), 7.48-7.42 (m, 1H), 7.33-7.27 (m, 2H), 7.18-7.11 (m, 1H), 6.98-6.91 (m, 3H), 4.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 161.2, 149.9, 148.0, 143.6, 136.6, 136.1, 131.7, 131.2, 131.0, 128.2, 128.2, 127.6, 126.6, 126.2, 124.1, 123.3, 122.7, 122.2, 102.0, 56.3; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_4S$ $[M+H]^+$: 419.1060, Found: 419.1062.



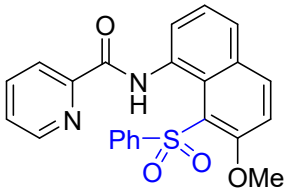
N-(5-acetamino-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3ca**): white solid (62%), mp 259-261 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.05 (s, 1H), 8.73 (d, $J$ =4.38 Hz, 1H), 8.47 (s, 1H), 8.29-8.171 (m, 1H), 8.06 (s, 1H), 7.94-7.84 (m, 2H), 7.84-7.77 (m, 1H), 7.68-7.62 (m, 1H), 7.53-7.42 (m, 4H), 7.34-7.28 (m, 1H), 7.17-7.02 (m, 2H), 2,41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.6, 149.8, 148.2, 142.0, 139.3, 136.9, 133.2, 132.5, 131.8, 130.3, 128.6, 127.1, 126.8, 126.5, 125.5, 122.7, 120.9, 117.8, 43.4, 29.7; HRMS (ESI$^+$): calcd for $C_{24}H_{19}N_3O_4S$ $[M+H]^+$: 446.1169, Found: 446.1167



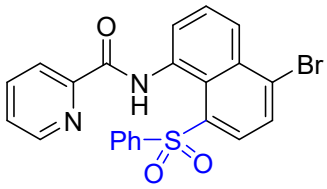
N-(4-(hydrazine-1,2-dicarboxylate)-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3da**): white solid (53%), mp 138-140 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.18 (s, 1H), 8.95-8.59 (m, 2H), 8.56-8.48 (m, 1H), 7.90-7.72 (m, 4H), 7.71-7.53 (m, 2H), 7.51-7.44 (m, 1H), 7.41-7.31 (m, 2H), 7.26-7.19 (m, 1H), 7.11-6.96 (m, 2H), 5.15-4.85 (m, 2H), 1.22 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.3, 156.0, 155.3, 149.7, 148.1, 142.6, 138.1, 136.8, 133.8, 133.2, 132.3, 131.9, 131.7, 130.0, 128.4, 126.8, 126.4, 124.7, 124.5, 122.9, 71.4, 70.1, 21.9, 21.8; HRMS (ESI$^+$): calcd for $C_{30}H_{30}N_4O_7S$ $[M+H]^+$: 591.1908, Found: 591.1904



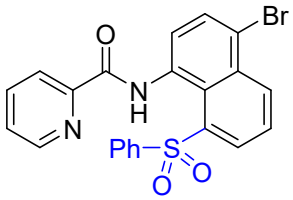
N-(2-methyl-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3ea**): white solid (25%), mp 240-242 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.06 (s, 1H), 8.75-8.68 (m, 1H), 8.66-8.57 (m, 1H), 8.51 (s, 1H), 8.32 (d, $J$ =7.81 Hz, 1H), 8.07-7.89 (m, 4H), 7.62-7.40 (m, 6H), 2.58 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.6, 149.1, 148.3, 141.7, 137.8, 136.2, 134.4, 133.1, 133.0, 132.0, 131.3, 129.1, 127.8, 127.5, 127.4, 127.4, 126.9, 124.6, 123.5, 122.8, 19.1; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_3S$ $[M+H]^+$: 403.1111, Found: 403.1110.



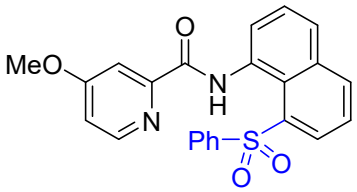
N-(7-methoxy-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3fa**): white solid (41%), mp 208-210 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.39 (s, 1H), 8.68 (d, $J$ = 4.08 Hz, 1H), 8.17 (d, $J$ = 7.78 Hz, 1H), 8.01 (d, $J$ = 8.17 Hz, 1H),7.87 (d, $J$ = 7.30 Hz, 1H), 7.84-7.76 (m, 2H), 7.70 (d, $J$ = 7.55 Hz, 2H), 7.57 (t, $J$ = 7.64 Hz, 1H), 7.44-7.30 (m, 4H), 7.07 (d, $J$ = 8.03 Hz, 1H), 3.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.2, 158.8, 150.3, 148.3, 145.6, 137.3, 136.9, 132.2, 132.0, 130.9, 130.4, 128.7, 128.0, 127.6, 126.7, 126.0, 125.3, 122.5, 121.0, 113.1, 56.2; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_4S$ $[M+H]^+$: 441.0879, Found: 441.0884.



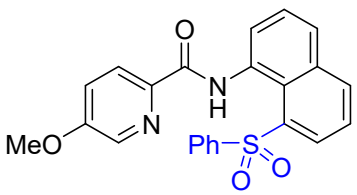
N-(5-Bromo-8-(phenylsulfonyl)naphthalen-1-yl) picolinamide (**3ga**): white solid (55%), mp 170-172 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.25 (s, 1H), 8.83 (d, $J$ = 4.37 Hz, 1H), 8.63-8.53 (m, 2H), 8.38-8.29 (m, 1H), 8.27-8.21 (m, 1H), 8.21-8.09 (m, 2H), 8.01 (d, $J$ = 7.42 Hz, 2H), 7.82-7.70 (m, 3H), 7.67-7.60 (m, 2H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 163.4, 149.5, 149.2, 141.7, 139.8, 138.9, 134.0, 131.9, 130.9, 130.1, 129.1, 128.8, 128.0, 127.8, 127.6, 127.5, 124.6, 123.5, 123.0, 118.9; HRMS (ESI$^+$): calcd for $C_{22}H_{15}BrN_2O_3S$ [M+H]$^+$: 467.0060, Found: 467.0058.



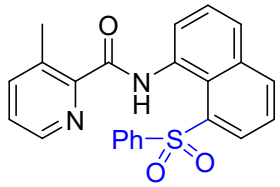
N-(4-bromo-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**3ha**): white solid (53%), mp 175-177 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.05 (s, 1H), 8.75-8.71 (m, 1H), 8.54-8.48 (m, 1H), 8.33 (d, $J$ = 8.13 Hz, 1H), 7.98 (d, $J$ =8.16 Hz, 1H), 7.87-7.74 (m, 4H), 7.49-7.44 (m, 1H), 7.38-7.32 (m, 2H), 7.25-7.20 (m, 1H), 7.08-7.00 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.2, 149.7, 148.1, 142.4, 136.8, 134.3, 133.1, 132.9, 132.5, 132.3, 132.0, 131.5, 128.7, 128.5, 128.5, 128.0, 127.5, 126.4, 124.5, 122.8; HRMS (ESI$^+$): calcd for $C_{22}H_{15}BrN_2O_3S$ [M+H]$^+$: 467.0060, Found: 467.0059.



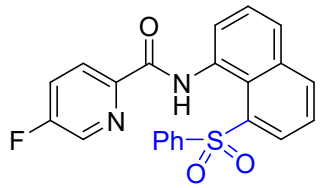
N-(8-(phenylsulfonyl)naphthalen-1-yl)-4-methoxypicolinamide (**3ia**): white solid (50%), mp 204-206 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.08 (s, 1H), 8.57-8.50 (m, 2H), 8.24 (d, $J$ = 7.60 Hz, 1H), 7.95 (d, $J$ = 7.89 Hz, 1H), 7.80 (d, $J$ = 7.38 Hz, 1H), 7.70-7.59 (m, 2H), 7.39-7.32 (m, 3H), 7.28-7.23 (m, 1H), 7.09-7.02 (m, 2H), 6.99-6.95 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.5, 164.0, 151.9, 149.2, 142.7, 136.8, 136.3, 133.6, 132.7, 132.0, 131.4, 130.5, 128.7, 128.4, 127.3, 126.2, 124.6, 123.9, 113.0, 108.0, 55.5; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_4S$ [M+H]$^+$: 419.1060, Found: 419.1060.



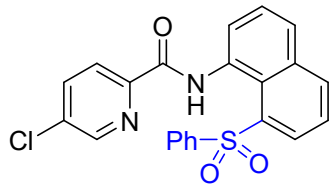
N-(8-(phenylsulfonyl)naphthalen-1-yl)-5-methoxypicolinamide (**3ja**): white solid (52%), mp 210-212 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.08 (s, 1H), 8.72 (d, $J$ = 4.62 Hz, 1H), 8.62 (d, $J$ = 8.52 Hz, 1H), 8.53-8.36 (m, 1H), 7.82-7.69 (m, 1H), 7.49-7.40 (m, 1H), 7.29 (d, $J$ = 7.53 Hz, 2H), 7.19-7.10 (m, 1H), 6.98-6.89 (m, 3H), 4.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 161.2, 150.0, 148.0, 143.6, 136.6, 136.1, 131.7, 131.2, 131.0, 128.2, 128.2, 127.6, 126.6, 126.2, 124.1, 123.3, 122.7, 122.2, 122.0, 102.0, 56.3; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_4S$ $[M+H]^+$: 419.1060, Found: 419.1058.



N-(8-(phenylsulfonyl)naphthalen-1-yl)-3-methylpicolinamide (**3ka**): white solid (42%), mp 240-242 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.13 (s, 1H), 8.61-8.56 (m, 2H), 8.27-8.21 (m, 1H), 7.97-7.91 (m, 1H), 7.84 (d, $J$ = 7.48 Hz, 1H), 7.70-7.60 (m, 2H), 7.53-7.48 (m, 1H), 7.40-7.34 (m, 1H), 7.29-7.24 (m, 3H), 7.05-6.91 (m, 2H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.4, 147.2, 145.5, 143.0, 140.3, 137.0, 136.4, 135.8, 133.9, 132.4, 131.7, 131.6, 130.3, 128.4, 128.3, 127.2, 126.4, 125.8, 124.1, 123.9, 20.4; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_3S$ $[M+H]^+$: 403.1111, Found: 403.1112.

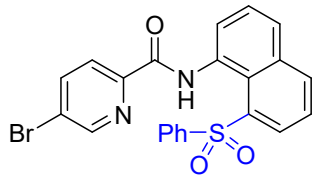


N-(8-(phenylsulfonyl)naphthalen-1-yl)-5-fluoropicolinamide (**3la**): yellow solid (32%), mp 160-162 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.98 (s, 1H), 8.55 (d, $J$ =2.68 Hz, 1H), 8.52-8.45 (m, 1H), 8.26-8.21 (m, 1H), 7.98-7.94 (m, 1H), 7.90-7.85 (m, 1H), 7.80 (d, $J$ = 7.21 Hz, 1H), 7.71-7.59 (m, 2H), 7.52-7.42 (m, 2H), 7.41-7.35 (m, 2H), 7.11-7.05 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.0, 161.1 (d, $J$ = 261.8 Hz), 146.4 (d, $J$ = 3.91 Hz), 142.7, 136.9, 136.5 (d, $J$ = 24.99 Hz), 136.3, 133.5, 132.7, 132.3, 131.2, 130.5, 128.8, 128.4, 127.3, 126.1, 124.7, 124.5 (d, $J$ = 5.51 Hz), 124.0, 123.3 (d, $J$ = 19.08 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ -121.86 (s, 1F); HRMS (ESI$^+$): calcd for $C_{22}H_{15}FN_2O_3S$ $[M+H]^+$: 407.0860, Found: 407.0861.

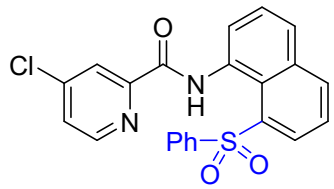


N-(8-(phenylsulfonyl)naphthalen-1-yl)-5-chloropicolinamide (**3ma**): white solid (38%), mp 170-172 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.86 (s, 1H), 8.76-8.65 (m, 3H), 8.60 (d, $J$ = 8.32 Hz, 1H), 8.36-8.30 (m, 1H), 8.15-8.07 (m, 1H), 7.99-7.93 (m, 3H), 7.69-7.60 (m, 2H), 7.52-7.44 (m, 3H);

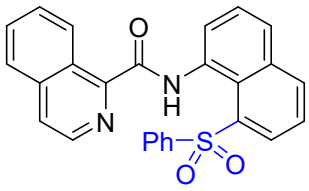
$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.4, 147.4, 147.3, 142.0, 138.1, 137.7, 136.0, 132.9, 131.4, 131.1, 129.4, 129.1, 128.3, 127.3, 126.0, 125.4, 123.7, 120.7, 115.4; HRMS ($ESI^+$): calcd for $C_{22}H_{15}ClN_2O_3S$ $[M+H]^+$: 423.0565, Found: 423.0569.



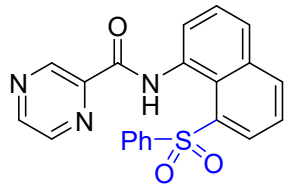

N-(8-(phenylsulfonyl)naphthalen-1-yl)-5-bromopicolinamide (**3na**): white solid (38%), mp 125-127 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.87 (s, 1H), 8.80-8.77 (m, 1H), 8.75-8.71 (m, 1H), 8.62-8.58 (m, 1H), 8.28-8.23 (m, 1H), 8.13-8.08 (m, 2H), 7.99-7.94 (m, 2H), 7.67-7.62 (m, 2H), 7.53-7.44 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.6, 149.5, 147.8, 142.0, 140.7, 138.1, 132.9, 131.4, 131.1, 129.4, 129.1, 128.3, 127.3, 127.2, 126.0, 125.4, 125.0, 124.1, 120.7, 115.5; HRMS ($ESI^+$): calcd for $C_{22}H_{15}BrN_2O_3S$ $[M+H]^+$: 467.0060, Found: 467.0064.



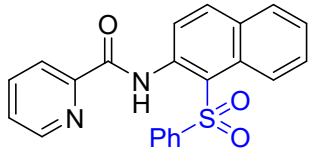

N-(8-(phenylsulfonyl)naphthalen-1-yl)-4-chloropicolinamide (**3oa**): white solid (52%), mp 194-196 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.03 (s, 1H), 8.62 (d, $J$ = 5.16 Hz, 1H), 8.56-8.44 (m, 1H), 8.25 (dd, $J_1$ = 8.18 Hz, $J_2$ =1.06 Hz, 1H), 8.01-7.96 (m, 1H), 7.82-7.76 (m, 2H), 7.72-7.66 (m, 1H), 7.65-7.60 (m, 1H), 7.49-7.45 (m, 1H), 7.37-7.33 (m, 2H), 7.33-7.28 (m, 1H), 7.12-7.04 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.0, 151.4, 149.0, 145.3, 142.8, 136.9, 136.3, 133.7, 132.6, 132.2, 131.0, 130.6, 129.0, 128.5, 127.3, 126.3, 126.2, 124.6, 124.1, 123.3,; HRMS ($ESI^+$): calcd for $C_{22}H_{15}ClN_2O_3S$ $[M+H]^+$: 423.0565, Found: 423.0565.



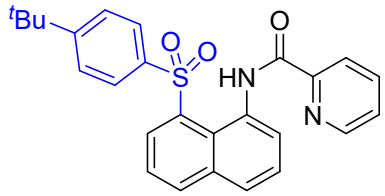

N-(8-(phenylsulfonyl)naphthalen-1-yl)isoquinoline-1-carboxamide (**3pa**): white solid (48%), mp 228-230 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.30 (s, 1H), 9.00-8.92 (m, 1H), 8.67 (d, $J$ = 5.54 Hz, 1H), 8.64-8.61 (m, 1H), 8.27 (dd, $J_1$ = 8.20 Hz, $J_2$ = 1.20 Hz, 1H), 8.00-7.95 (m, 2H), 7.90-7.85 (m, 2H), 7.74-7.69 (m, 2H), 7.68-7.62 (m, 1H), 7.58-7.53 (m, 1H), 7.15-7.09 (m, 2H), 7.76-6.75 (m, 1H), 6.65-6.59 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.4, 148.3, 142.8, 140.4, 137.2, 137.0, 136.4, 134.1, 132.4, 131.7, 131.5, 130.3, 130.0, 128.5, 128.2, 128.2, 127.5, 127.2, 127.1, 126.7, 126.2, 124.4, 124.0, 123.8; HRMS (ESI+): calcd for $C_{26}H_{18}N_2O_3S$ $[M+H]^+$: 439.1111, Found: 439.1114.



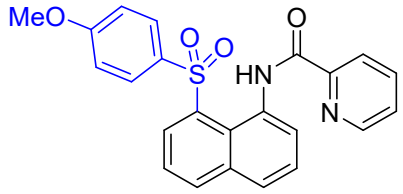
N-(8-(phenylsulfonyl)naphthalen-1-yl)pyrimidine-3-carboxamide (**3qa**): white solid (50%), mp 235-237 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.66 (s, 1H), 9.59 (d, $J$ = 1.24 Hz, 1H), 8.90 (d, $J$ = 2.41 Hz, 1H), 8.77-8.72 (m, 1H), 8.72-8.67 (m, 2H), 8.61 (d, $J$ = 8.25 Hz, 1H), 8.14-8.07 (m, 1H), 8.00-7.95 (m, 2H), 7.69-7.61 (m, 2H), 7.55-7.44 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.0, 148.2, 144.9, 143.9, 142.5, 141.9, 137.7, 133.0, 131.9, 131.0, 129.4, 129.1, 128.4, 127.3, 127.3, 126.0, 125.5, 120.5, 115.9; HRMS (ESI$^+$): calcd for $C_{21}H_{15}N_3O_3S$ [M+H]$^+$: 390.0907, Found: 390.0911.



N-(1-(phenylsulfonyl)naphthalen-2-yl) picolinamide (**3ra**): light yellow solid (57%), mp 162-165 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 12.98 (s, 1H), 9.01-8.85 (m, 2H), 8.80 (d, $J$ = 4.24 Hz, 1H), 8.37-8.23 (m, 1H), 8.08 (d, $J$ = 9.18 HZ 1H), 7.98-7.88 (m, 3H), 7.86-7.77 (m, 1H), 7.59-7.50 (m, 2H), 7.50-7.42 (m, 2H), 7.40-7.32 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.4, 149.8, 148.7, 142.5, 139.7, 137.5, 135.8, 133.2, 130.9, 130.0, 129.0, 128.9, 128.6, 126.8, 126.3, 125.5, 124.5, 122.9, 121.2, 120.0; HRMS (ESI$^+$): calcd for $C_{22}H_{16}N_2O_3S$ [M+Na]$^+$: 411.0774, Found: 411.0771.

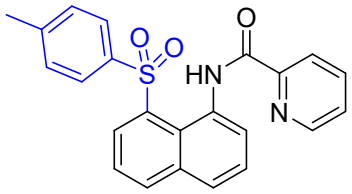


N-(8-(4-(tert-butyl)phenylsulfonyl)naphthalen-1-yl)picolinamide (**3ab**): light yellow solid (42%), mp 198-200 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.18 (s 1H), 8.82-8.68 (m, 1H), 8.57 (dd, $J_1$ = 7.48 Hz, $J_2$ = 1.31 Hz, 1H), 8.28-8.19 (m, 1H), 8.00-7.89 (m, 1H), 7.87-7.71 (m, 3H), 7.71-7.56 (m, 2H), 7.51-7.43 (m, 1H), 7.28-7.21 (m, 2H), 7.02-6.98 (m, 2H), 1.15 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.9, 155.5, 150.0, 148.1, 139.8, 136.8, 136.7, 136.3, 133.6, 132.7, 131.3, 130.5, 128.7, 127.2, 126.2, 125.4, 124.2, 123.9, 122.6, 34.8, 30.8; HRMS (ESI$^+$): calcd for $C_{26}H_{24}N_2O_3S$ [M+H]$^+$: 445.1580, Found: 445.1583.

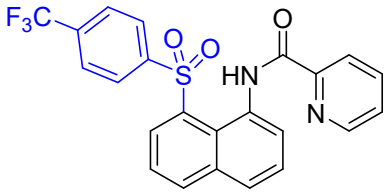


N-(8-(4-methoxyphenylsulfonyl)naphthalen-1-yl)picolinamide (**3ac**): white solid (37%), mp 157-

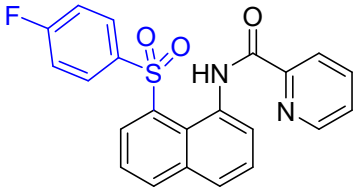
159 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.10 (s, 1H), 8.78-8.67 (m, 3H), 8.55 (d, $J$ = 8.31 Hz, 1H), 8.37 (d, $J$ = 7.79 Hz, 1H), 8.19-8.13 (m, 1H), 8.02-7.95 (m, 1H), 7.93-7.88 (m, 2H), 7.68-7.60 (m, 2H), 7.60-7.54 (m, 1H), 6.96-6.88 (m, 2H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.1, 162.3, 149.4, 148.2, 138.1, 138.0, 133.6, 131.9, 130.7, 129.6, 129.3, 128.1, 127.0, 127.0, 126.0, 125.4, 122.7, 120.8, 115.3, 114.3, 55.6; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_4S$ $[M+H]^+$: 419.1060, Found: 419.1060.




N-(8-(4-methylphenylsulfonyl)naphthalen-1-yl)picolinamide (**3ad**): white solid (47%), mp 200-202 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.09 (s, 1H), 8.77-8.70 (m, 1H), 8.50 (dd, $J_1$ = 7.49 Hz, $J_2$ = 1.28 Hz, 1H), 8.26-8.18 (m, 1H), 7.98-7.93 (m, 1H), 7.85-7.80 (m, 2H), 7.80-7.74 (m, 1H), 7.70-7.64 (m, 1H), 7.64-7.57 (m, 1H), 7.50-7.43 (m, 1H), 7.24-7.22 (m, 2H), 6.79 (d, $J$ = 8.07 Hz, 2H), 7.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 150.2, 148.1, 142.8, 139.9, 136.7, 136.4, 136.3, 133.4, 133.1, 131.4, 130.6, 128.9, 128.7, 127.2, 126.2, 126.2, 124.7, 123.9, 122.6; HRMS (ESI$^+$): calcd for $C_{23}H_{18}N_2O_3S$ $[M+H]^+$: 403.1111, Found: 403.1108.

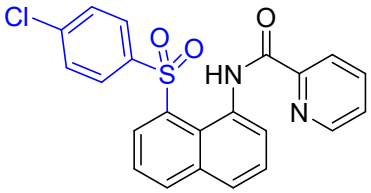



N-(8-(4-(trifluoromethyl)phenylsulfonyl)naphthalen-1-yl)picolinamide (**3ae**): white solid (37%), mp 215-217 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.89 (s, 1H), 8.75-8.66 (m, 2H), 8.32 (dd, $J_1$ = 8.17 Hz, $J_2$ = 1.16 Hz, 1H), 8.05-7.96 (m, 1H), 7.79-7.66 (m, 5H), 7.53-7.45 (m, 1H), 7.42 (d, $J$ = 8.25 Hz, 2H), 7.18 (d, $J$ = 8.40 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 149.4, 148.0, 146.7, 137.6, 137.0, 136.4, 134.7, 133.4 (d, $J$ = 33.1 Hz), 131.4, 131.0, 129.2, 127.5, 126.7 126.5, 125.4, 125.3, 124.4, 124.2, 122.7; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ -63.36 (s, 3F); HRMS (ESI$^+$): calcd for $C_{23}H_{15}F_3N_2O_3S$ $[M+H]^+$: 457.0828, Found: 457.0829.

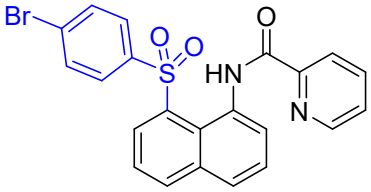



N-(8-(4-fluorophenylsulfonyl)naphthalen-1-yl)picolinamide (**3af**): light yellow solid (32%), mp 220-222 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.02 (s, 1H), 8.77-8.70 (m, 1H), 8.58-8.49 (m, 1H), 8.31-8.21 (m, 1H), 7.98 (dd, $J_1$ = 8.08 Hz, $J_2$ = 1.08 Hz, 1H), 7.91-7.86 (m, 1H), 7.84-7.78 (m, 2H), 7.73-7.60 (m, 2H), 7.51-7.46 (m, 1H), 7.39-7.34 (m, 2H), 6.72-6.59 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 163.1, 149.9, 148.1, 139.0, 137.1, 136.9, 136.4, 133.8, 132.4, 131.3, 130.9,

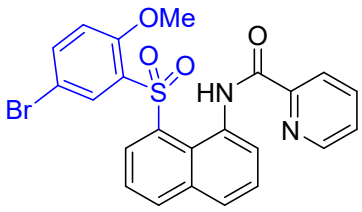
128.9, 127.3 (d, $J$ = 10.93 Hz), 127.2, 126.4, 126.3, 124.0, 122.7, 115.5 (d, $J$ = 22.82 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ -105.54 (s, 1F); HRMS ($ESI^+$): calcd for $C_{22}H_{15}FN_2O_3S$ $[M+H]^+$: 407.0860, Found: 407.0861.



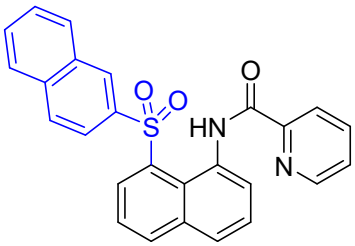

N-(8-(4-chlorophenylsulfonyl)naphthalen-1-yl)picolinamide (**3ag**): light yellow solid (62%), mp 208-210 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.94 (s, 1H), 8.73-8.69 (m, 1H), 8.63-8.56 (m, 1H), 8.34-8.23 (m, 1H), 7.99 (dd, $J_1$ = 8.08 Hz, $J_2$ = 1.11 Hz, 1H), 7.85-7.76 (m, 3H), 7.73-7.62 (m, 2H), 7.52-7.47 (m, 1H), 7.26-7.23 (m, 2H), 6.96-6.85 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 149.8, 148.0, 141.6, 138.3, 137.3, 136.8, 136.3, 134.1, 131.9, 131.2, 131.1, 129.0, 128.5, 127.4, 126.5, 126.5, 125.7, 124.0, 122.8; HRMS ($ESI^+$): calcd for $C_{22}H_{15}ClN_2O_3S$ $[M+H]^+$: 423.0565, Found: 423.0562.



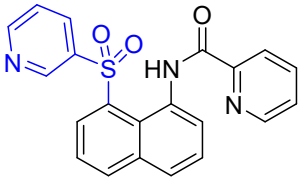

N-(8-(4-bromophenylsulfonyl)naphthalen-1-yl)picolinamide (**3ah**): light yellow solid (48%), mp 192-197 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.92 (s, 1H), 8.70 (d, $J$ =4.60 Hz,1H), 8.60 (d, $J$ = 6.89 Hz, 1H), 8.28 (d, $J$ = 7.82 Hz, 1H), 7.99 (d, $J$ = 7.70 Hz, 1H), 7.85-7.77 (m, 3H), 7.74-7.63 (m, 2H), 7.52-7.46 (m, 1H), 7.22-7.16 (m, 2H), 7.09-7.04 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 149.8, 148.0, 142.2, 137.3, 136.8, 136.4, 134.2, 131.8, 131.4, 131.2, 129.0, 127.4, 126.8, 126.6, 126.5, 125.7, 124.1, 122.8; HRMS ($ESI^+$): calcd for $C_{22}H_{15}BrN_2O_3S$ $[M+H]^+$: 467.0060, Found: 467.0059.



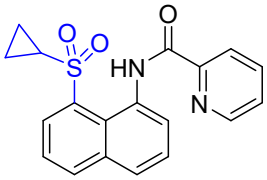

N-(8-(2-methoxy-5-bromophenylsulfonyl)naphthalen-1-yl)picolinamide (**3ai**): yellow solid (20%), mp 206-208 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.10 (s, 1H), 8.76 (d, $J$ = 4.15 Hz, 1H), 8.63 (d, $J$ = 7.30 Hz, 1H), 8.20 (d, $J$ = 7.72 Hz, 1H), 8.04 (d, $J$ = 7.75 Hz, 1H), 7.92 (d, $J$ = 7.99 Hz, 1H), 7.84 (d, $J$ = 7.49 Hz, 2H), 7.67-7.65 (m, 4H), 7.50-7.45 (m, 1H), 6.48 (d, $J$ = 8.83 Hz, 1H), 3.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.2, 154.7, 149.8, 148.3, 137.1, 136.8, 136.4, 136.1, 135.4, 133.4, 132.5, 131.6, 130.0, 129.7, 128.5, 127.0, 126.4, 125.9, 124.0, 123.0, 113.8, 112.2, 56.0; HRMS ($ESI^+$): calcd for $C_{23}H_{17}BrN_2O_4S$ $[M+H]^+$: 497.0165, Found: 497.0163.



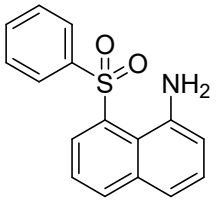
N-(8-(naphthalen-2-ylsulfonyl)naphthalen-1-yl)picolinamide (**3aj**): yellow solid (50%), mp 222-224 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.04 (s, 1H), 8.68 (d, $J$ = 4.28 Hz, 1H), 8.59 (d, $J$ = 7.25 Hz, 1H), 8.28 (d, $J$ = 8.02 Hz, 1H), 7.99 (d, $J$ = 7.68 Hz, 1H),7.95 (s, 1H), 7.78 (d, $J$ = 7.49 Hz, 1H), 7.73-7.59 (m, 3H), 7.53-7.48 (m, 2H), 7.46-7.27 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$164.2, 149.6, 147.9, 140.0, 136.9, 136.4, 134.3, 133.9, 132.8, 131.5, 131.4, 130.8, 129.1, 128.9, 128.7, 128.4, 127.6, 127.3, 127.1, 126.6, 126.1, 125.5, 124.0, 122.2, 120.4; HRMS (ESI$^+$): calcd for $C_{26}H_{18}N_2O_3S$ $[M+H]^+$: 439.1111, Found: 439.1112.



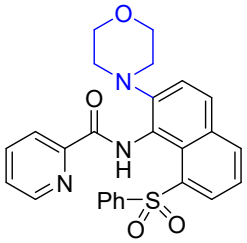
N-(8-(3-pyridylsulfonyl)naphthalen-1-yl)picolinamide (**3ak**): yellow solid (23%), mp 172-174 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.19 (s, 1H), 9.20 (d, $J$ = 2.02 HZ, 1H), 8.82-8.76 (m, 1H), 8.76 - 8.70 (m, 3H), 8.67-8.61 (m, 1H), 8.40-8.35 (m, 1H), 8.24-8.17 (m, 2H), 8.02-7.96 (m, 1H), 7.72-7.65 (m, 2H), 7.61-7.56 (m, 1H), 7.43-7.38 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.3, 153.4, 149.2, 148.3, 139.0, 138.6, 138.0, 134.9, 131.8, 130.0, 129.3, 128.7, 127.3, 127.1, 125.9, 124.8, 123.6, 122.8, 121.0, 115.1; HRMS (ESI$^+$): calcd for $C_{21}H_{15}N_3O_3S$ $[M+Na]^+$: 412.0726, Found: 412.0727.



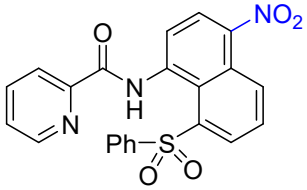
N-(8-(cyclopropylsulfonyl)naphthalen-1-yl)picolinamide (**3al**): white solid (53%), mp 184-186 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.83 (s, 1H), 8.85-8.77 (m, 1H), 8.43-8.34 (m, 1H), 8.28 (d, $J$ = 7.88 Hz, 1H), 8.20-8.13 (m, 1H), 8.06 (d, $J$ = 7.54 Hz, 1H), 7.96-7.86 (m, 2H), 7.74-7.66 (m, 1H), 7.59-7.49 (m, 2H), 2.94-2.80 (m, 1H), 1.30-1.25 (m, 2H), 0.82-0.69 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.6, 150.1, 148.6, 137.3, 136.3, 136.2, 135.3, 131.7, 131.0, 129.5, 128.6, 126.9, 126.5, 125.3, 123.9, 123.0, 33.3, 6.6; HRMS (ESI$^+$): calcd for $C_{19}H_{16}N_2O_3S$ $[M+H]^+$: 353.0954, Found: 353.0952.



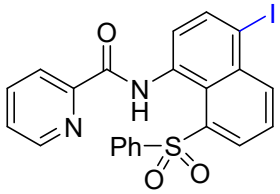
8-phenylsulfonyl-1-naphthylamine (**4a**): yellow paste (85%), mp 50 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 7.51 Hz, $J$ = 1.13 Hz, 1H), 8.09-7.96 (m, 1H), 7.76-7.65 (m, 2H), 7.56-7.41 (m, 4H), 7.36-7.27 (m, 2H), 6.79-6.70 (m, 1H), 5.29 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.8, 142.7, 136.9, 136.6, 134.8, 132.5, 131.4, 128.8, 127.7, 126.4, 123.4, 119.7, 119.6, 115.5; HRMS (ESI$^+$): calcd for $C_{16}H_{13}NO_2S$ $[M+H]^+$: 284.0740, Found: 284.0740.



N-(2-morpholine-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**5a**): yellow solid (76%), mp 228-230 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.25 (s, 1H), 8.68-8.60 (m, 1H), 8.59-8.48 (m, 1H), 8.18-8.11 (m, 1H), 7.97 (d, $J$ =8.48 HZ, 1H), 7.75-7.62 (m, 2H), 7.56-7.48 (m, 2H), 7.46-7.40 (m, 3H), 7.16-7.07 (m, 1H), 7.00-6.88 (m, 2H), 3.51-3.42 (m, 2H), 3.42-3.33 (m, 2H), 3.31-3.22 (m, 2H), 2.95-2.85 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.7, 151.3, 150.0, 147.8, 143.9, 136.7, 136.4, 135.0, 132.5, 131.8, 131.6, 130.5, 130.2, 128.1, 126.1, 124.2, 124.0, 122.5, 121.5, 67.1, 51.5; HRMS (ESI$^+$): calcd for $C_{26}H_{23}N_3O_4S$ $[M+H]^+$: 474.1482, Found: 474.1483.

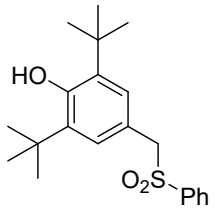


N-(4-nitro-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**6a**): yellow solid (40%), mp 225-227 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.41 (s, 1H), 8.86-8.70 (m, 2H), 8.62-8.52 (m, 1H), 8.29-8.20 (m, 1H), 8.03-7.95 (m, 1H), 7.95-7.88 (m, 2H), 7.86-7.77 (m, 2H), 7.56-7.48 (m, 1H), 7.42-7.29 (m, 3H), 7.18-7.05 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 149.3, 148.3, 145.9, 141.7, 137.1, 137.0, 134.8, 133.9, 132.8, 130.3, 128.7, 128.0, 127.6, 126.9, 126.8, 126.2, 125.1, 124.5, 123.0; HRMS (ESI$^+$): calcd for $C_{22}H_{15}N_3O_5S$ $[M+H]^+$: 434.0805, Found: 434.0802.



N-(4-iodo-8-(phenylsulfonyl)naphthalen-1-yl)picolinamide (**7a**): red solid (43%), mp 220-222 °C;

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.55 (s, 1H), 8.80 (s, 1H), 8.72-8.64 (m, 1H), 8.55-8.47 (m, 1H), 8.30-8.22 (m, 1H), 7.83-7.76 (m, 1H), 7.76-7.68 (m, 1H), 7.66-7.59 (m, 1H), 7.59-7.51 (m, 2H), 7.49-7.41 (m,1H), 7.27-7.22 (m, 2H), 7.17-7.06 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 149.2, 148.0, 148.0, 142.2, 140.3, 136.8, 136.1, 135.8, 134.7, 134.7, 132.5, 129.9, 128.4, 126.5, 126.2, 125.6, 122.7, 105.9, 100.8; HRMS (ESI$^+$): calcd for $C_{22}H_{15}IN_2O_3S$ $[M+H]^+$: 514.9921, Found: 514.9920.




2, 6-ditert-butyl-4-phenylsulfonylmethylphenol (**8a**): yellow solid (51%), mp 114-115 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66-7.51 (m, 3H), 7.48-7.34 (m, 2H), 6.74 (s, 2H), 5.24 (s, 1H), 4.22 (s, 2H), 1.31 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 154.2, 137.8, 136.0, 133.3, 128.8, 128.6, 127.6, 118.7, 63.1, 34.1, 30.0; HRMS (ESI$^+$): calcd for $C_{21}H_{28}O_3S$ $[M+Na]^+$: 383.1651, Found: 383.1652.

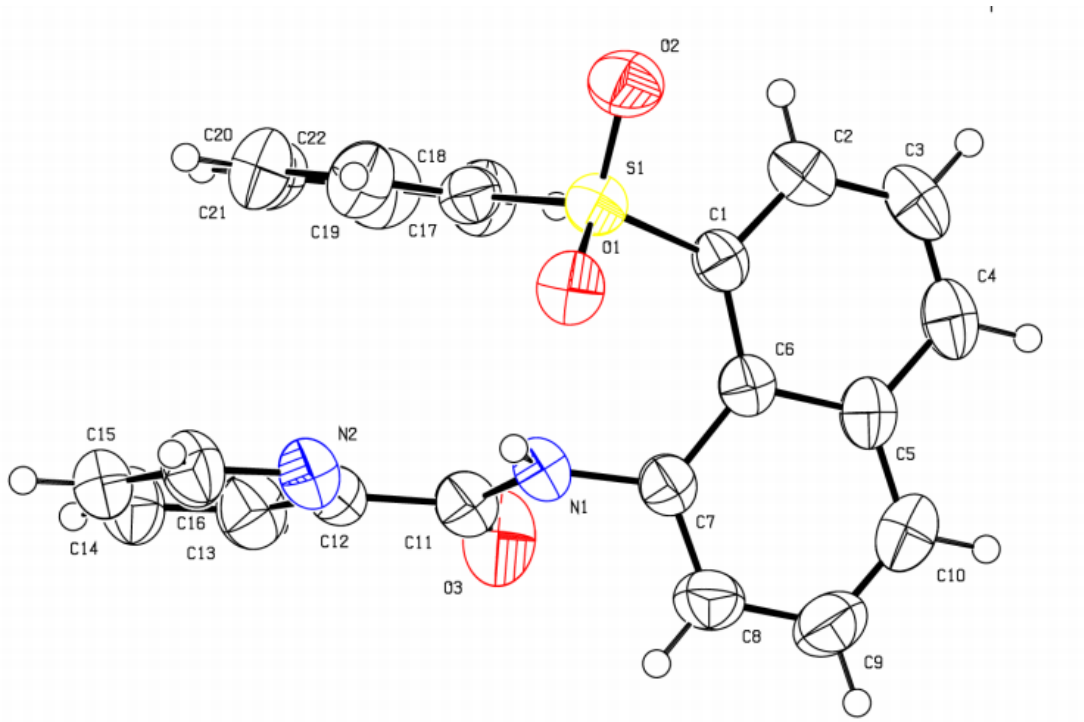
## 5. References

[1]. R. Shang, L. Ilies and E. Nakamura, *J. Am. Chem. Soc*. 2015, **137**, 7660.

[2]. (a) B. Du, P. Qian, Y. Wang, H. Mei, J. Han, Y. Pan, *Org. Lett.* 2016, **18**, 4144; (b) P. R. Bai, S. Y. Sun, Z. X. Li, H. J. Qiao, X. X. Su, F. Yang, Y. S. Wu and Y. J. Wu, *J. Org. Chem*. 2017, **82**, 12119.

## 6. The Single Crystal X-ray Diffraction Study

The Single Crystal X-ray Diffraction Study of **3aa**



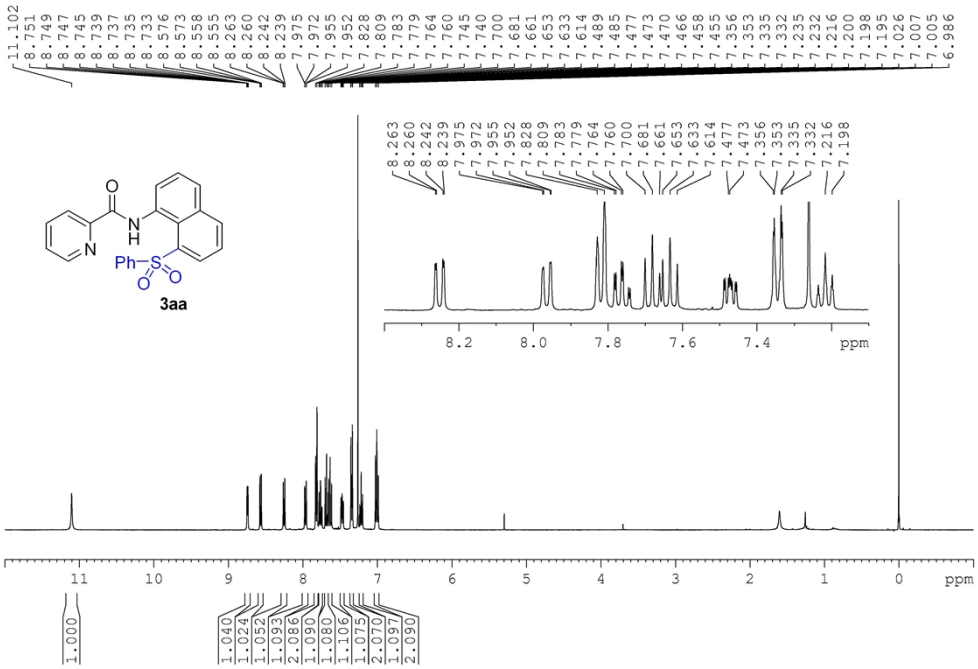

CCDC 2078508 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

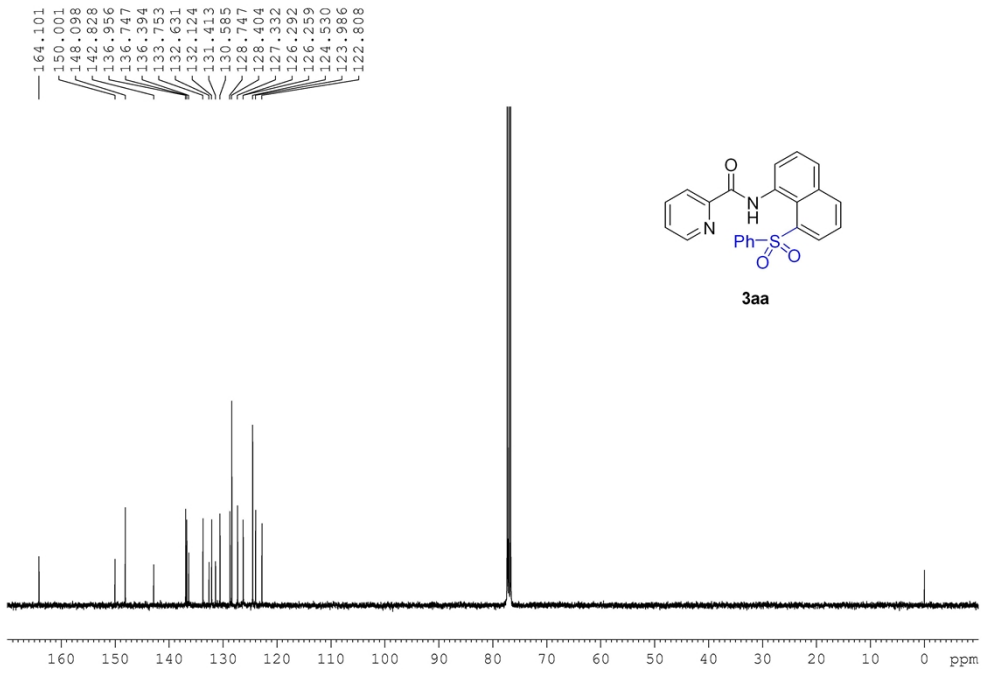
**Table S3 Crystal Data and Structure Refinement for CCDC 2078508.**

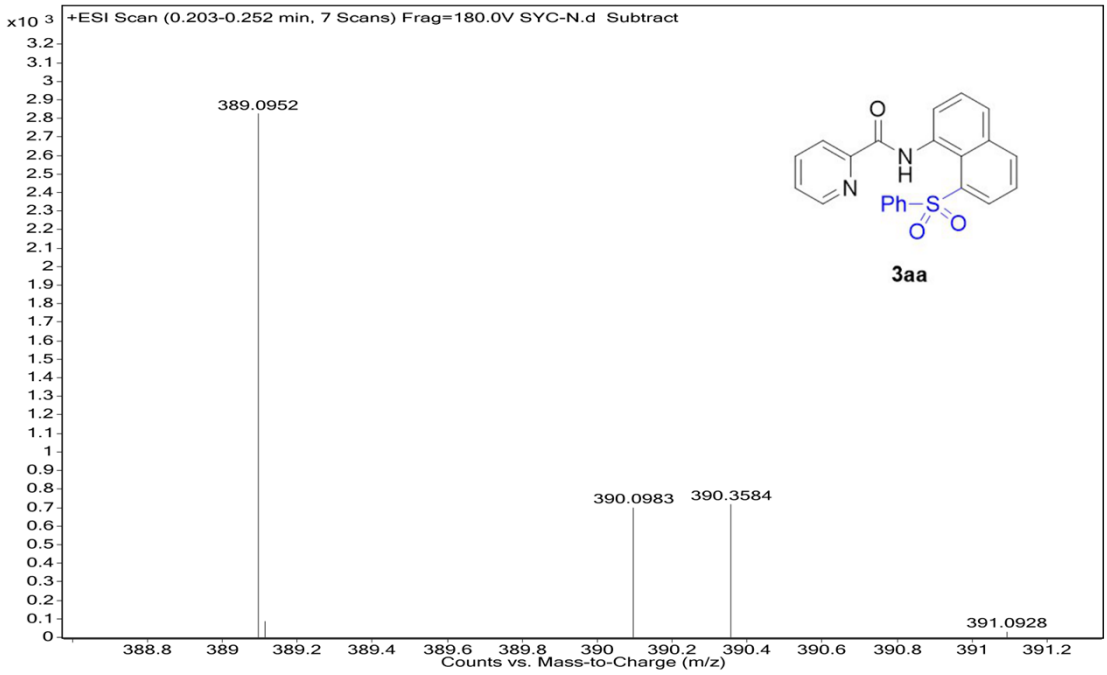
| | |
|---|---|
| Empirical formula | $C_{22}H_{16}N_2O_3S$ |
| Formula weight | 388.43 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 8.8921(4) |
| b/Å | 14.4512(7) |
| c/Å | 14.9303(6) |
| α/° | 90 |
| β/° | 105.182(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 1851.62 (14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.393 |

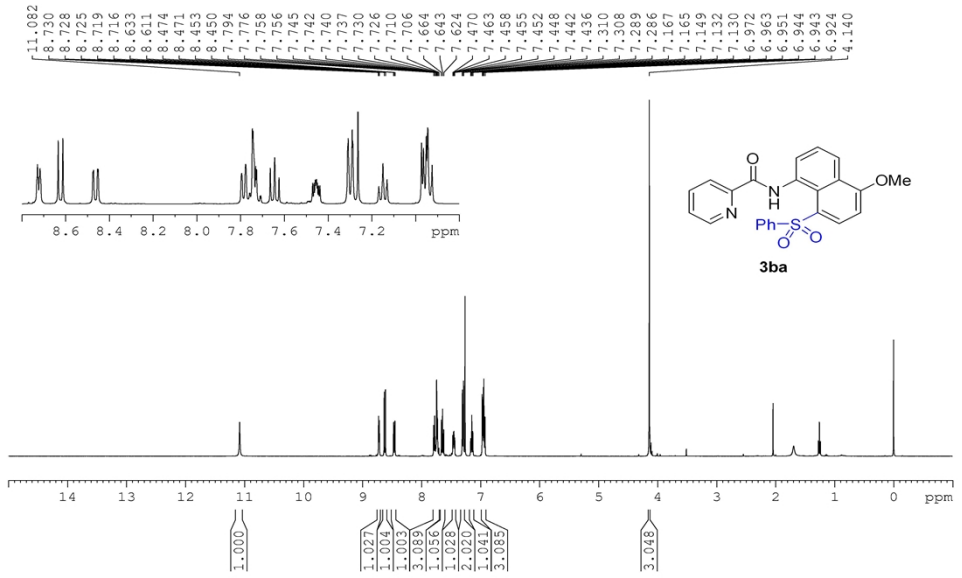
| | |
|---|---|
| μ/mm$^{-1}$ | 1.775 |
| F(000) | 808.0 |
| Crystal size/mm$^3$ | 0.15 × 0.12 × 0.1 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.666 to 134.02 |
| Index ranges | -10 ≤ h ≤ 8, -16 ≤ k ≤ 17, -17 ≤ l ≤ 17 |
| Reflections collected | 7015 |
| Independent reflections | 3301 [$R_{int}$ = 0.0249, $R_{sigma}$ = 0.0339] |
| Data/restraints/parameters | 3301/1/257 |
| Goodness-of-fit on F$^2$ | 1.035 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0486, $wR_2$ = 0.1342 |
| Final R indexes [all data] | $R_1$ = 0.0580, $wR_2$ = 0.1457 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.35/-0.29 |

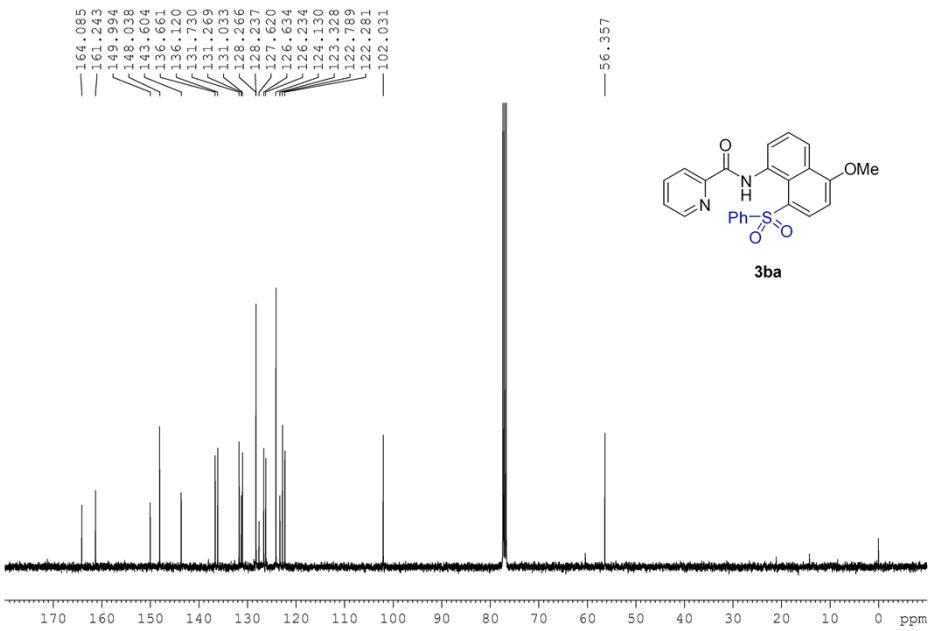
## 7. Copies of $^1$H, $^{13}$C NMR Spectra for the Products

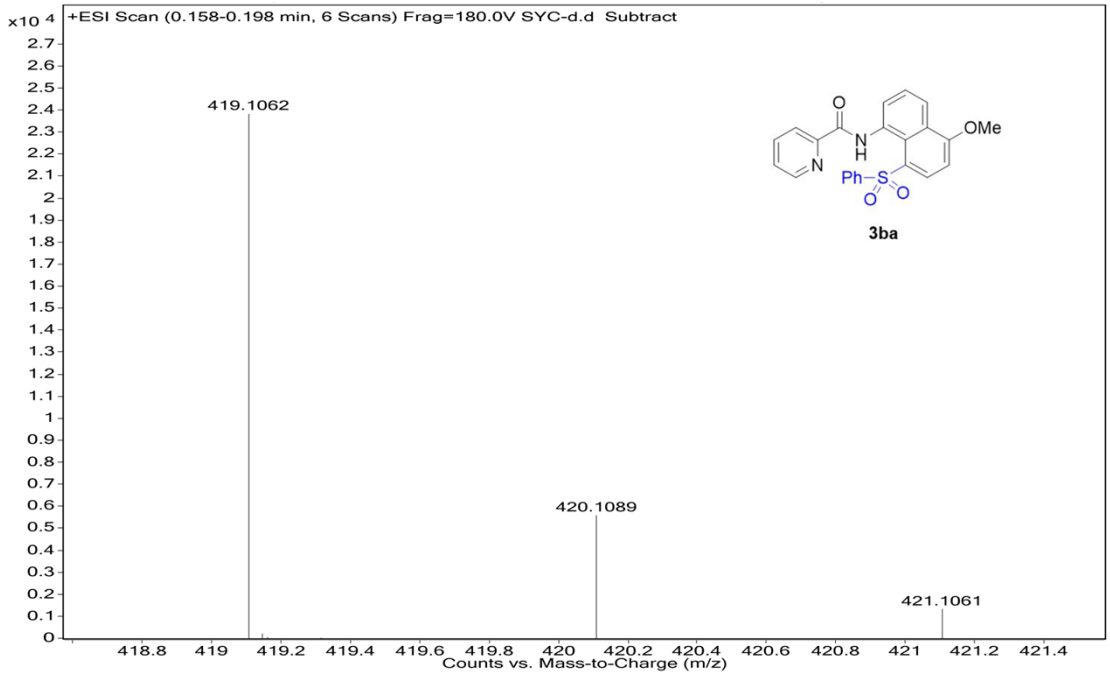


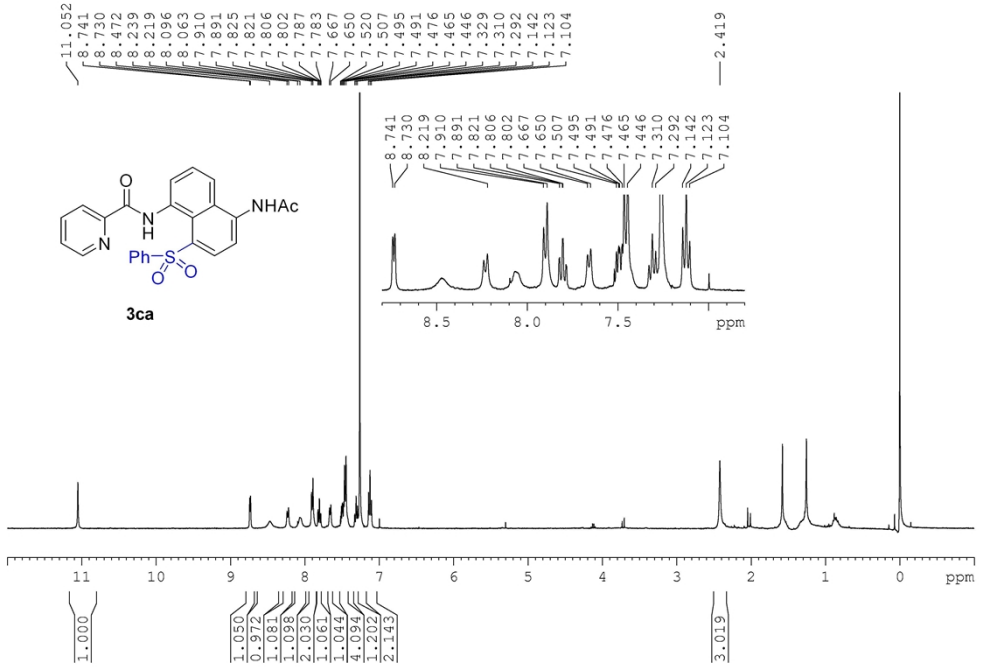

164.101
150.001
148.098
142.828
136.956
136.747
136.394
133.753
132.631
132.124
131.413
130.585
128.747
128.404
127.332
126.292
126.259
124.530
123.986
122.808
O
N
H
N
Ph—S
O
O
3aa
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

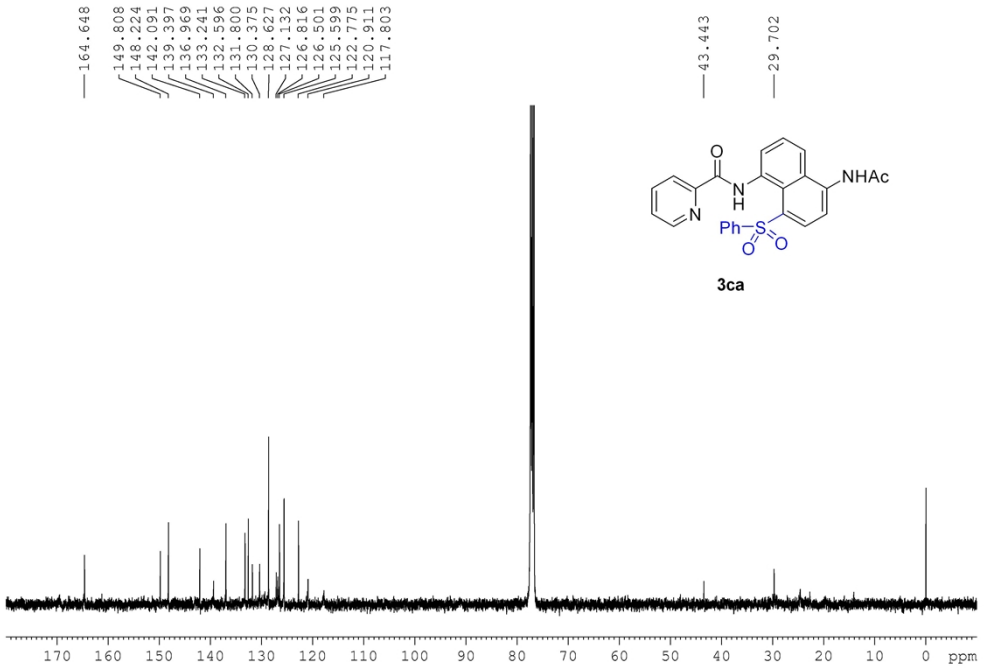

x10 3
+ESI Scan (0.203-0.252 min, 7 Scans) Frag=180.0V SYC-N.d Subtract
389.0952
390.0983
390.3584
391.0928
O
N
H
N
Ph—S
O
O
3aa
Counts vs. Mass-to-Charge (m/z)

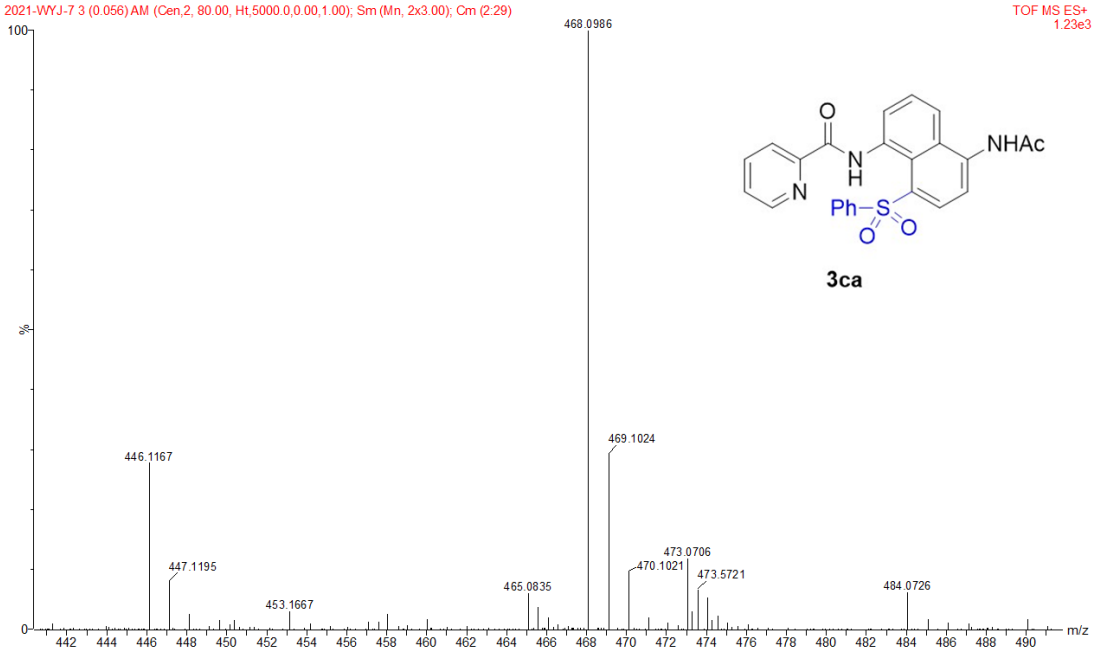

11.082
8.730
8.728
8.725
8.719
8.716
8.633
8.611
8.474
8.471
8.453
8.450
7.794
7.776
7.758
7.756
7.745
7.742
7.740
7.737
7.730
7.726
7.710
7.706
7.664
7.643
7.624
7.470
7.463
7.458
7.455
7.452
7.448
7.442
7.436
7.310
7.308
7.289
7.286
7.167
7.165
7.149
7.132
7.130
6.972
6.963
6.951
6.944
6.943
6.924
4.140
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
OMe
Ph
S
O
N
H
3ba
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.027
1.004
1.003
3.089
1.056
1.028
2.020
1.041
3.085
3.048

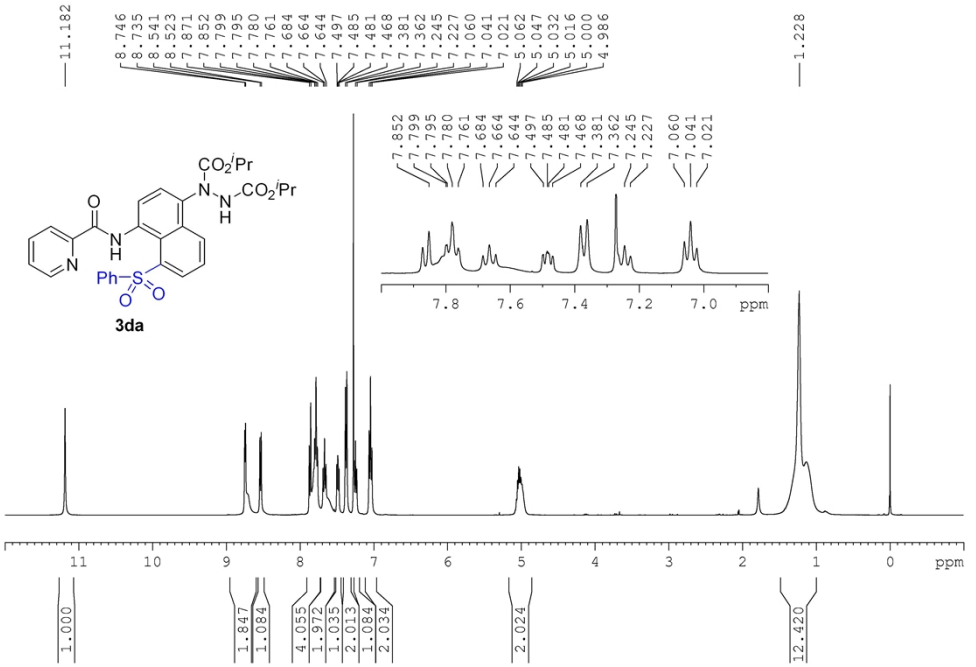

164.085
161.243
149.994
148.038
143.604
136.661
136.120
131.730
131.269
131.033
128.266
128.237
127.620
126.634
126.234
124.130
123.328
122.789
122.281
102.031
56.357
OMe
Ph
S
O
N
H
3ba
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

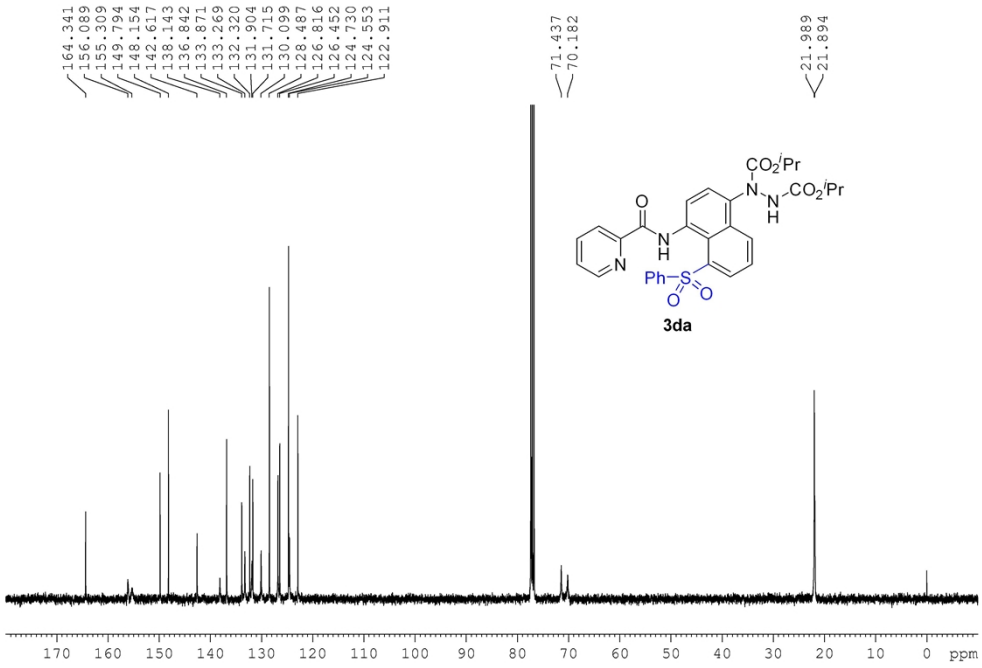

+ESI Scan (0.158-0.198 min, 6 Scans) Frag=180.0V SYC-d.d Subtract
x10 4
419.1062
420.1089
421.1061
OMe
Ph—S
3ba
Counts vs. Mass-to-Charge (m/z)

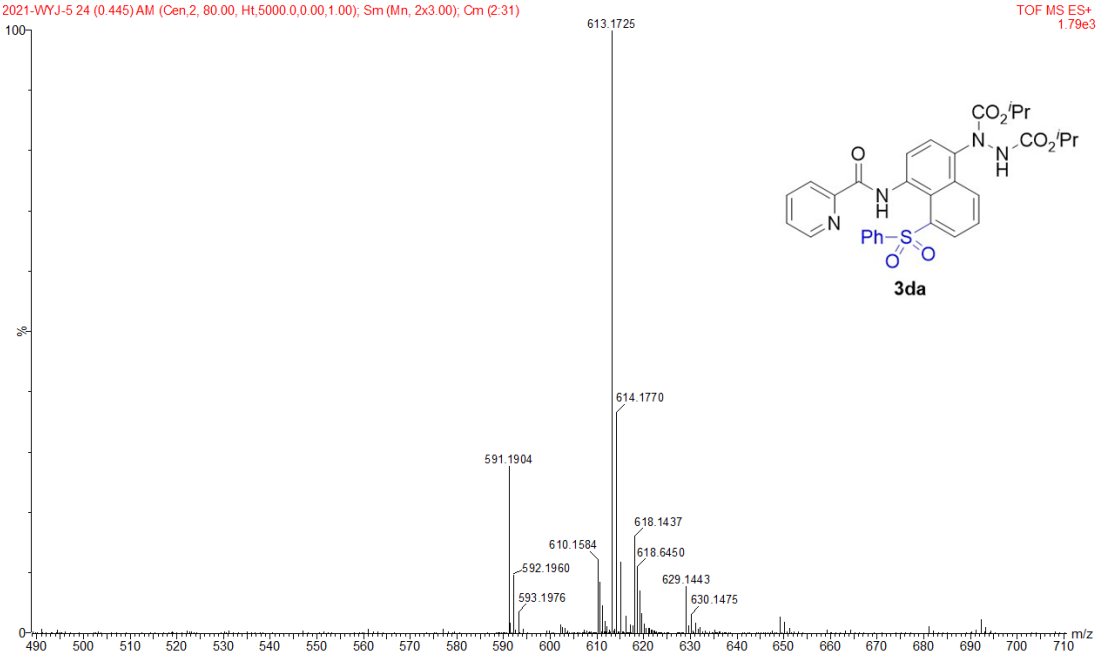

NHAc
Ph—S
3ca
ppm

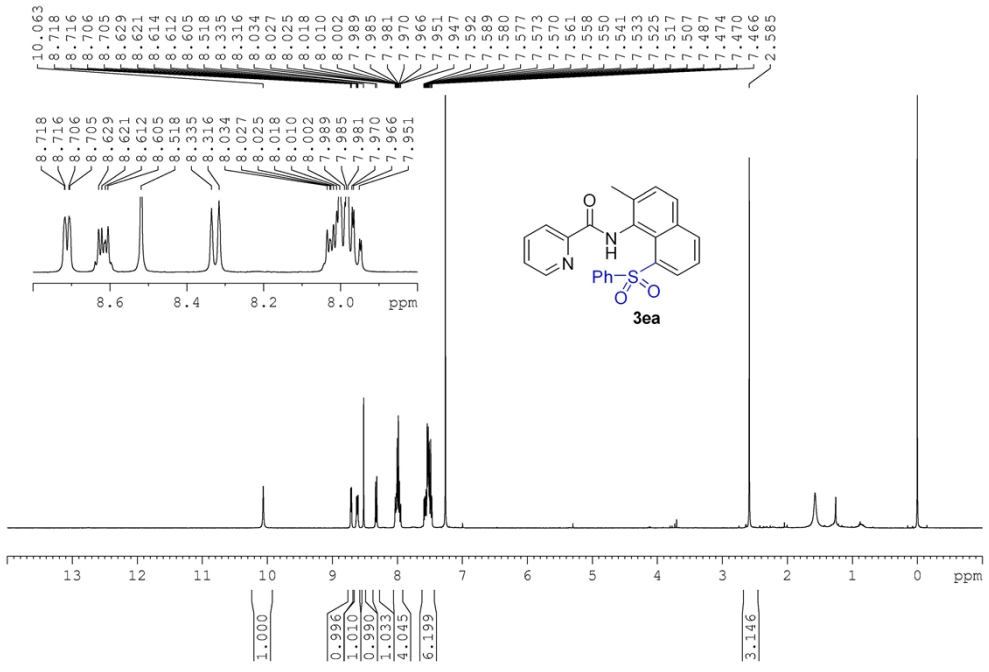

164.648
149.808
148.224
142.091
139.397
136.969
133.241
132.596
131.800
130.375
128.627
127.132
126.816
126.501
125.599
122.775
120.911
117.803
43.443
29.702
NHAc
Ph—S
3ca
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

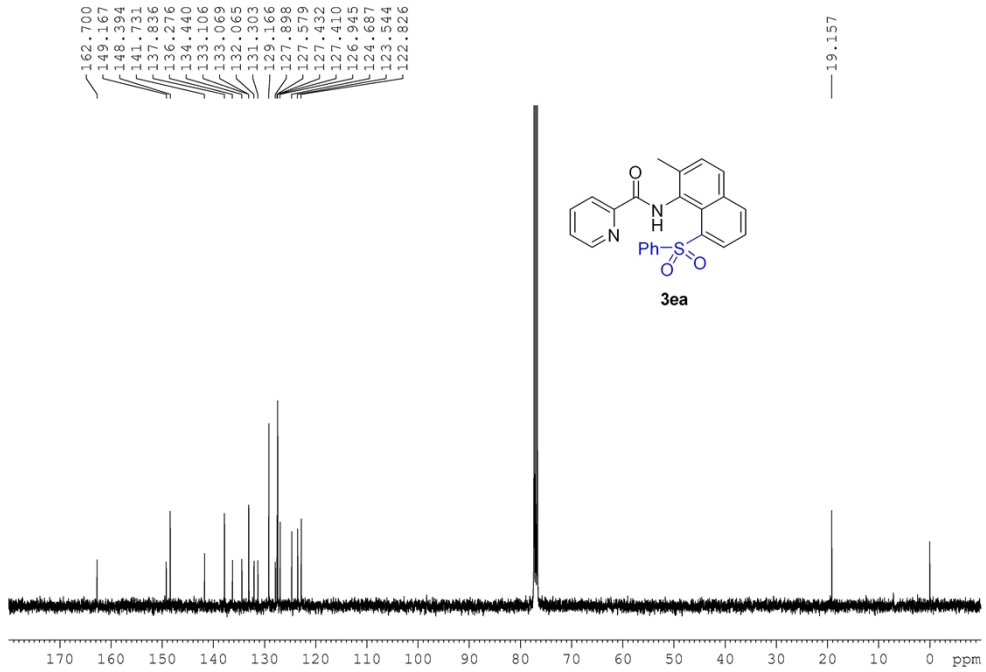

2021-WYJ-7 3 (0.056) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (2:29)
TOF MS ES+
1.23e3
100
%
0
468.0986
469.1024
446.1167
447.1195
453.1667
465.0835
470.1021
473.0706
473.5721
484.0726
NHAc
Ph—S
3ca
442 444 446 448 450 452 454 456 458 460 462 464 466 468 470 472 474 476 478 480 482 484 486 488 490 m/z

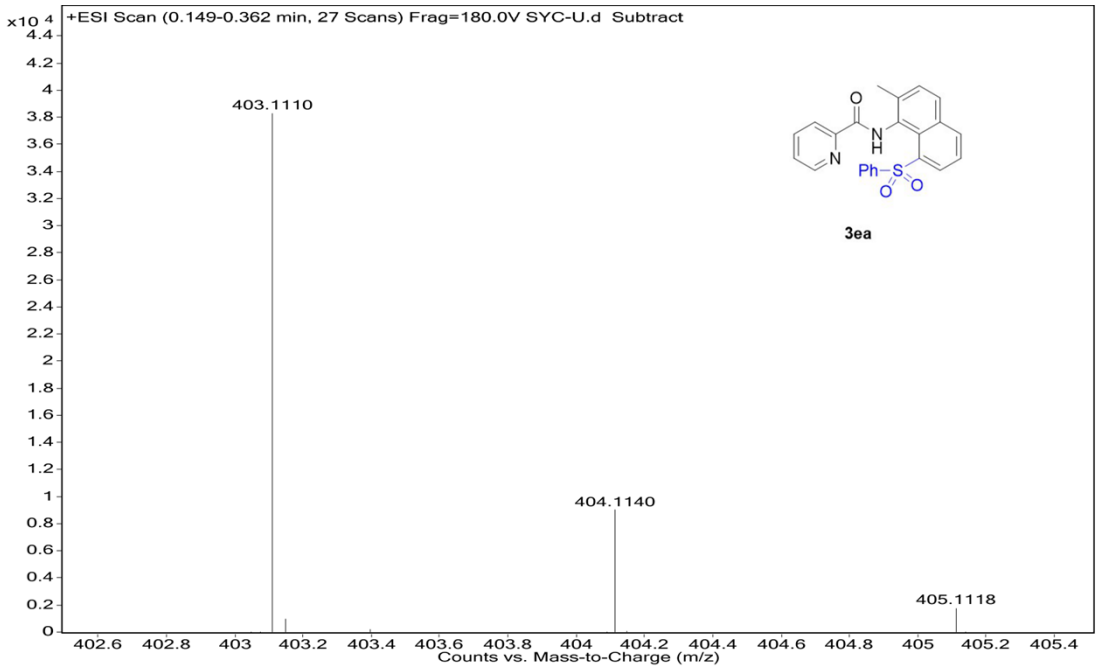

11.182
8.746
8.735
8.541
8.523
7.871
7.852
7.799
7.795
7.780
7.761
7.684
7.664
7.644
7.497
7.485
7.481
7.468
7.381
7.362
7.245
7.227
7.060
7.041
7.021
5.062
5.047
5.032
5.016
5.000
4.986
1.228
3da
ppm
1.000
1.847
1.084
4.055
1.972
1.035
2.013
1.084
2.034
2.024
12.420

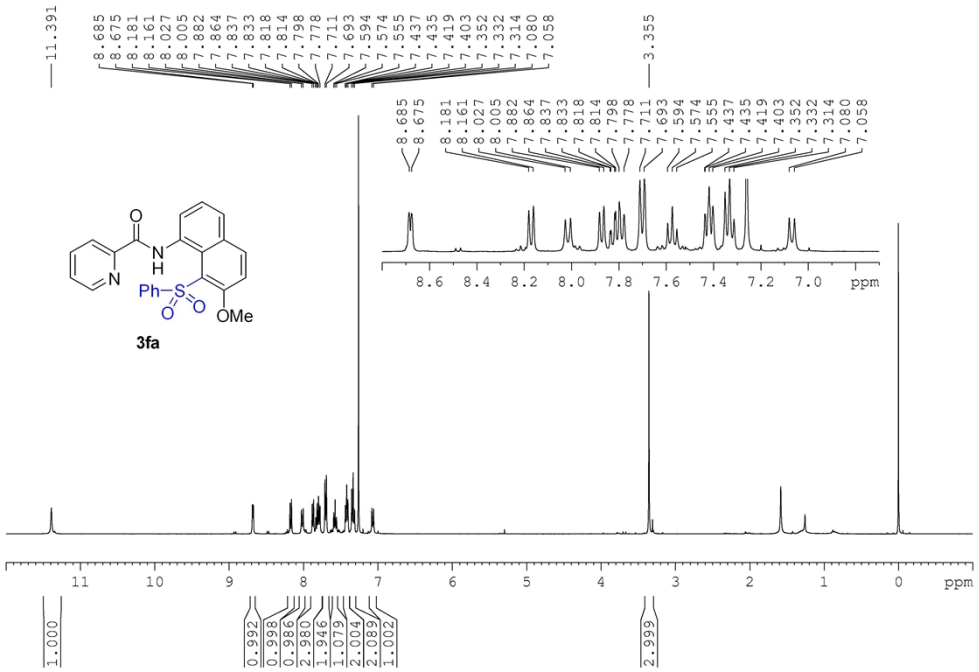

164.341
156.089
155.309
149.794
148.154
142.617
138.143
136.842
133.871
133.269
132.320
131.904
131.715
130.099
128.487
126.816
126.452
124.730
124.553
122.911
71.437
70.182
21.989
21.894
3da
ppm

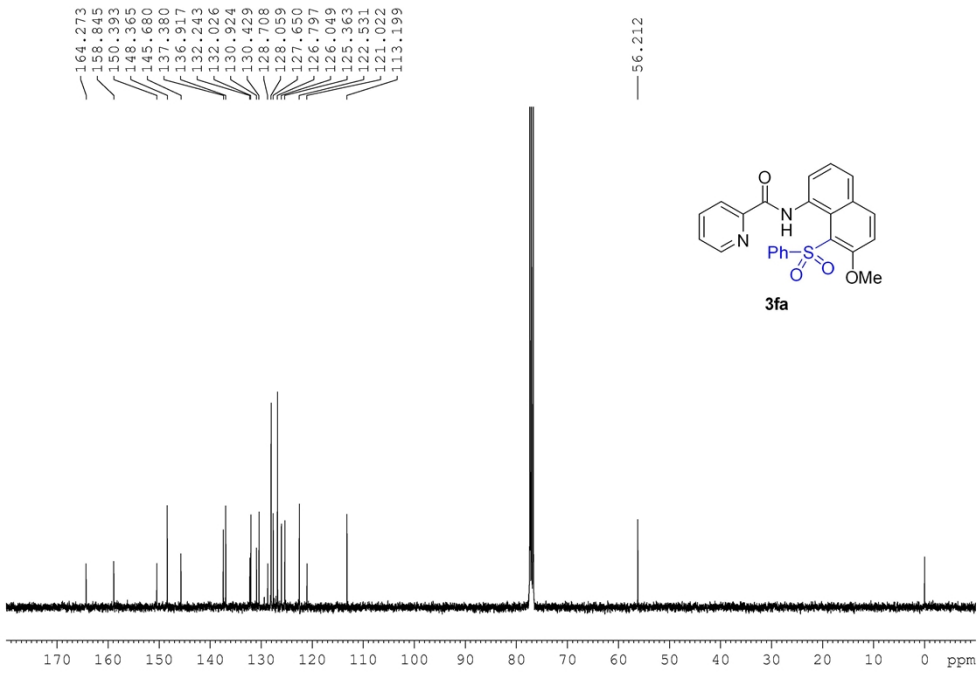

2021-WYJ-5 24 (0.445) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (2:31)
TOF MS ES+
1.79e3
613.1725
614.1770
591.1904
618.1437
610.1584
618.6450
592.1960
629.1443
593.1976
630.1475
%
m/z
3da

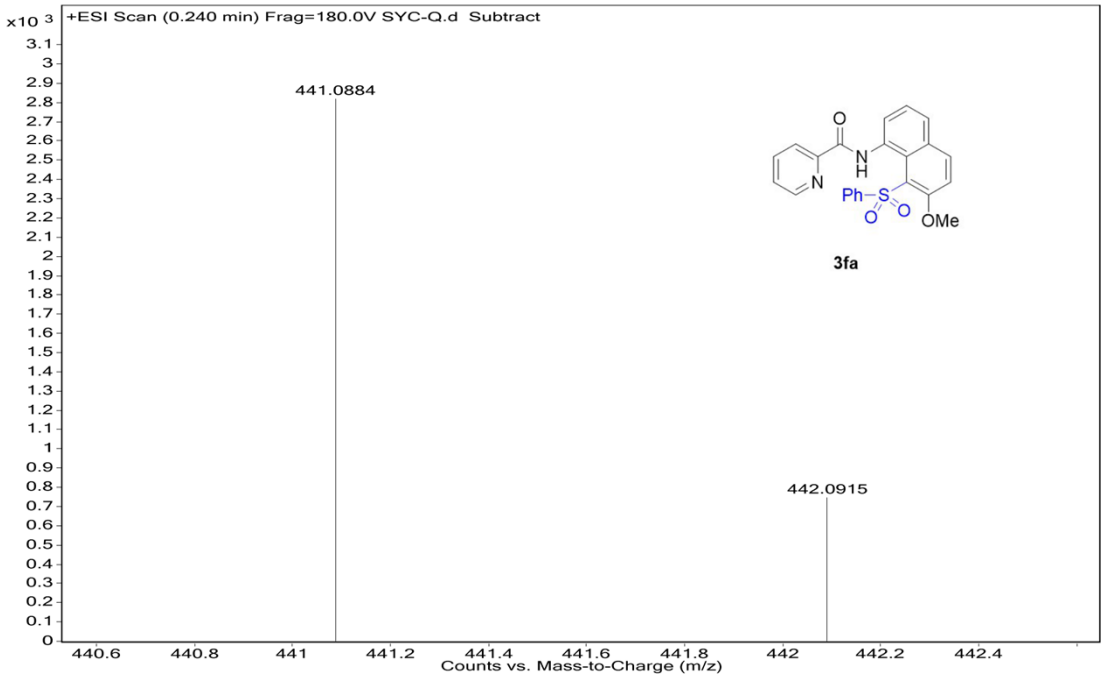

10.063
8.718
8.716
8.706
8.705
8.629
8.621
8.614
8.612
8.605
8.518
8.335
8.316
8.034
8.027
8.025
8.018
8.010
8.002
7.989
7.985
7.981
7.970
7.966
7.951
7.947
7.592
7.589
7.580
7.577
7.573
7.570
7.561
7.558
7.550
7.541
7.533
7.525
7.517
7.507
7.487
7.474
7.470
7.466
2.585
ppm
3ea

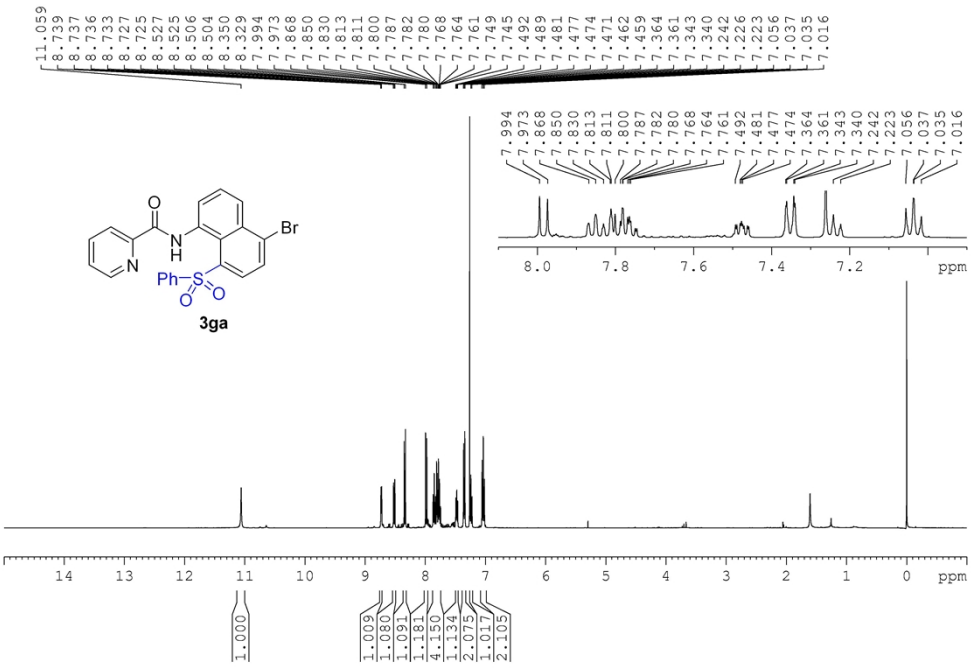

162.700
149.167
148.394
141.731
137.836
136.276
134.440
133.106
133.069
132.065
131.303
129.166
127.898
127.579
127.432
127.410
126.945
124.687
123.544
122.826
19.157
3ea
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

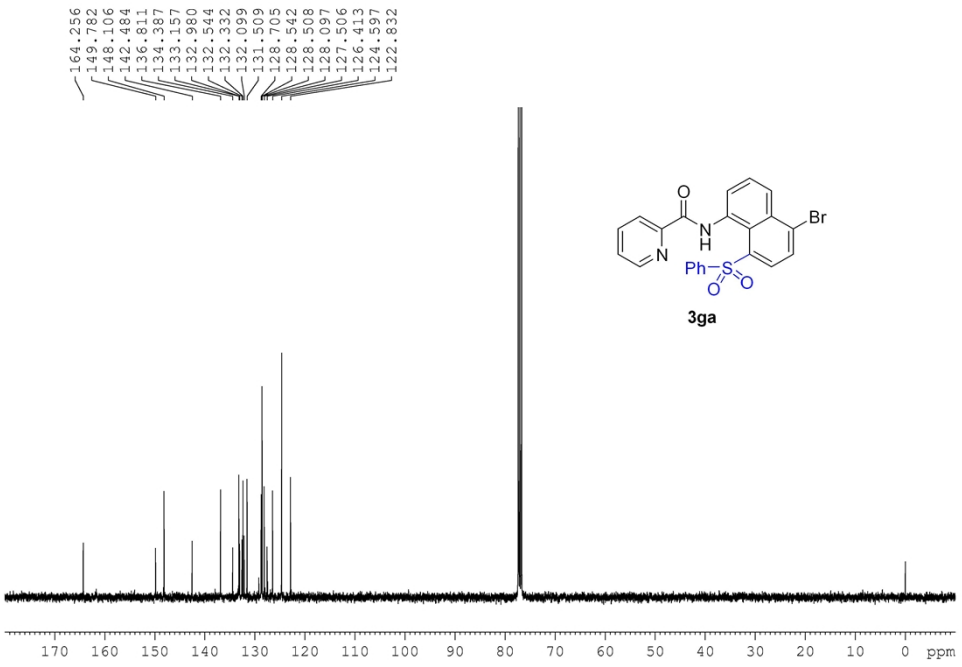

+ESI Scan (0.149-0.362 min, 27 Scans) Frag=180.0V SYC-U.d Subtract
x10 4
403.1110
404.1140
405.1118
3ea
Counts vs. Mass-to-Charge (m/z)

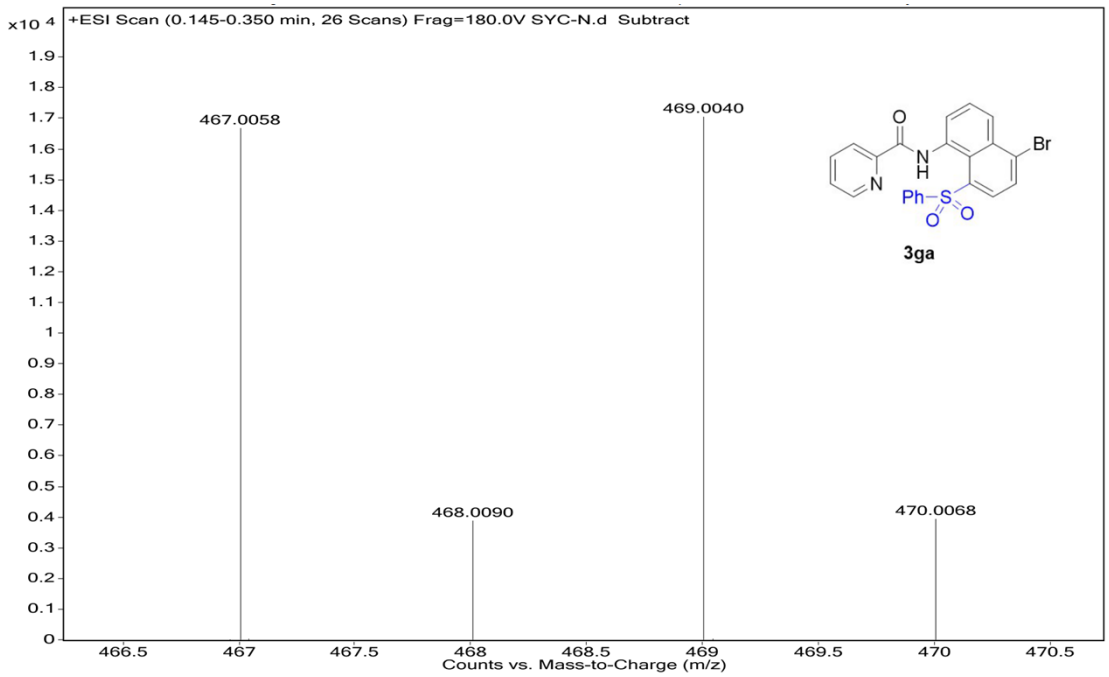

11.391
8.685
8.675
8.181
8.161
8.027
8.005
7.882
7.864
7.837
7.833
7.818
7.814
7.798
7.778
7.711
7.693
7.594
7.574
7.555
7.437
7.435
7.419
7.403
7.352
7.332
7.314
7.080
7.058
3.355
ppm
1.000
0.992
0.998
0.986
2.980
1.946
1.079
2.004
2.089
1.002
2.999
3fa

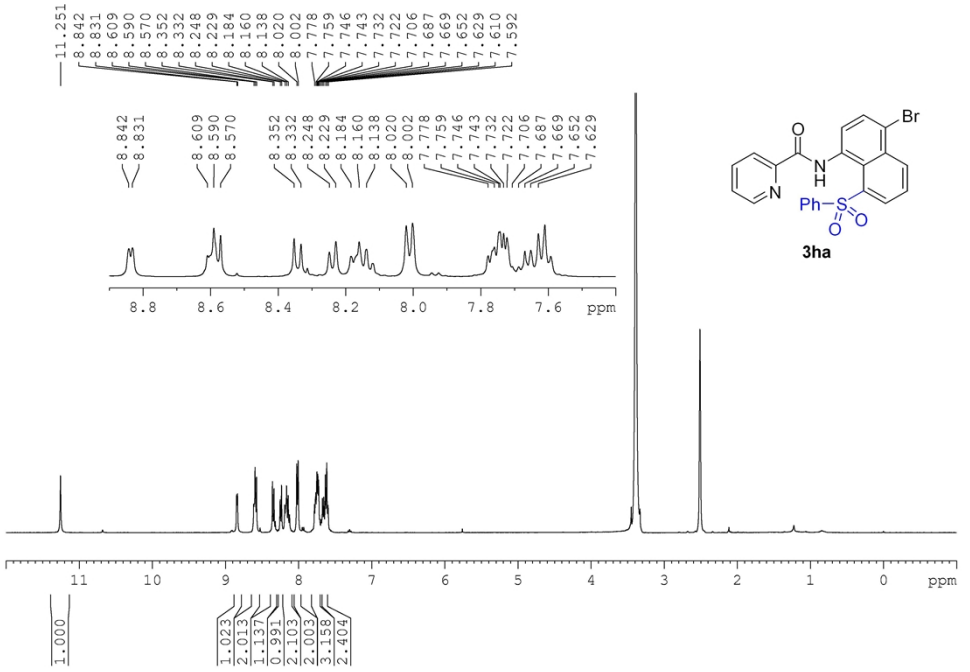

164.273
158.845
150.393
148.365
145.680
137.380
136.917
132.243
132.026
130.924
130.429
128.708
128.059
127.650
126.797
126.049
125.363
122.531
121.022
113.199
56.212
ppm
3fa

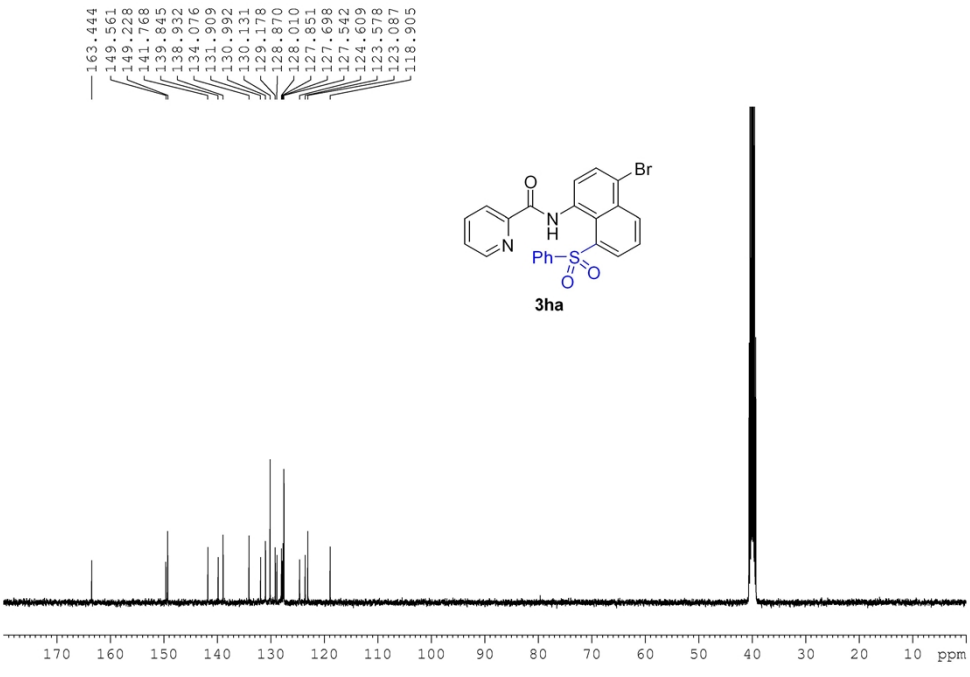

+ESI Scan (0.240 min) Frag=180.0V SYC-Q.d Subtract
441.0884
442.0915
Counts vs. Mass-to-Charge (m/z)
3fa

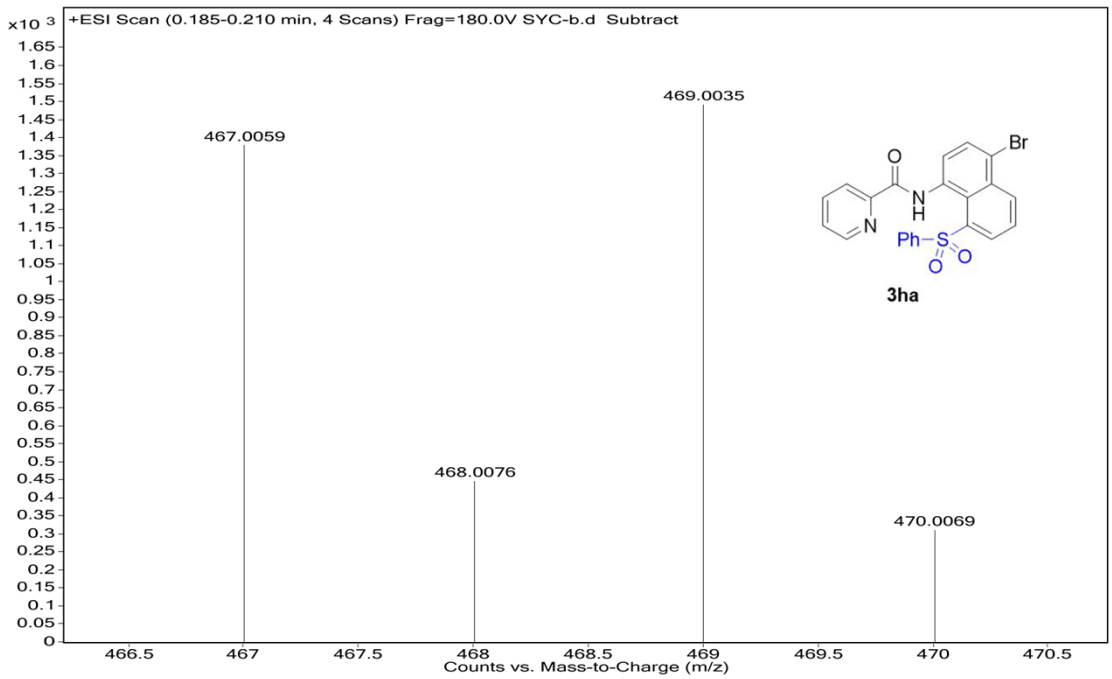

3ga
ppm

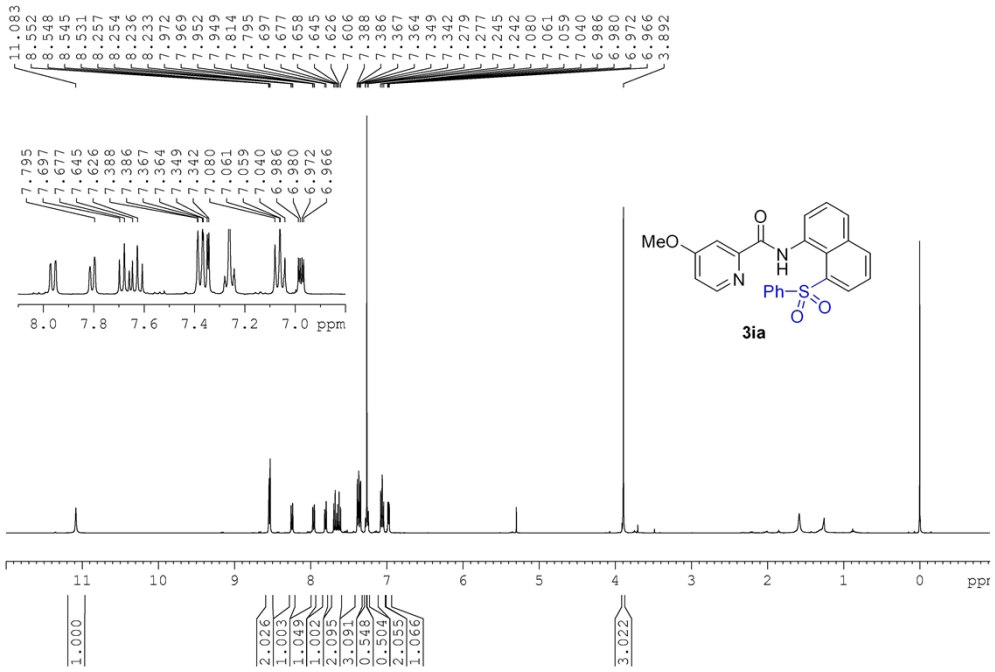

164.256
149.782
148.106
142.484
136.811
134.387
133.157
132.980
132.544
132.332
132.099
131.509
128.705
128.542
128.508
128.097
127.506
126.413
124.597
122.832
Br
Ph
S
O
N
H
3ga
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

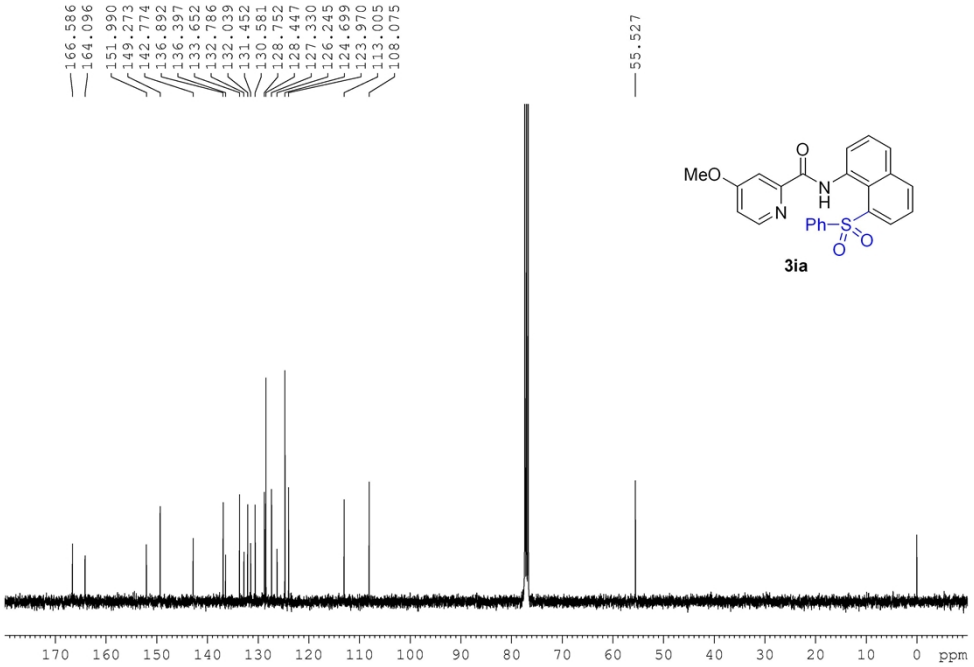

+ESI Scan (0.145-0.350 min, 26 Scans) Frag=180.0V SYC-N.d Subtract
x10 4
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
467.0058
468.0090
469.0040
470.0068
Br
Ph
S
O
N
H
3ga
466.5 467 467.5 468 468.5 469 469.5 470 470.5
Counts vs. Mass-to-Charge (m/z)

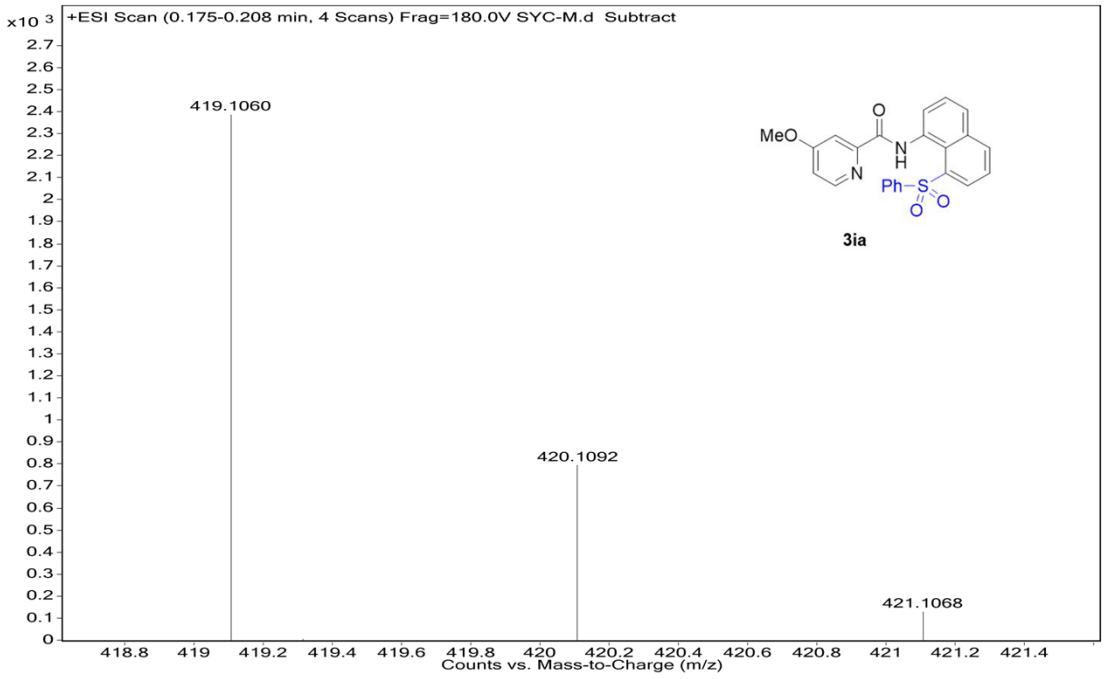

11.251
8.842
8.831
8.609
8.590
8.570
8.352
8.332
8.248
8.229
8.184
8.160
8.138
8.020
8.002
7.778
7.759
7.746
7.743
7.732
7.722
7.706
7.687
7.669
7.652
7.629
7.610
7.592
Br
N
H
O
Ph—S
O
O
3ha
ppm
1.000
1.023
2.013
1.137
0.991
2.103
2.003
3.158
2.404

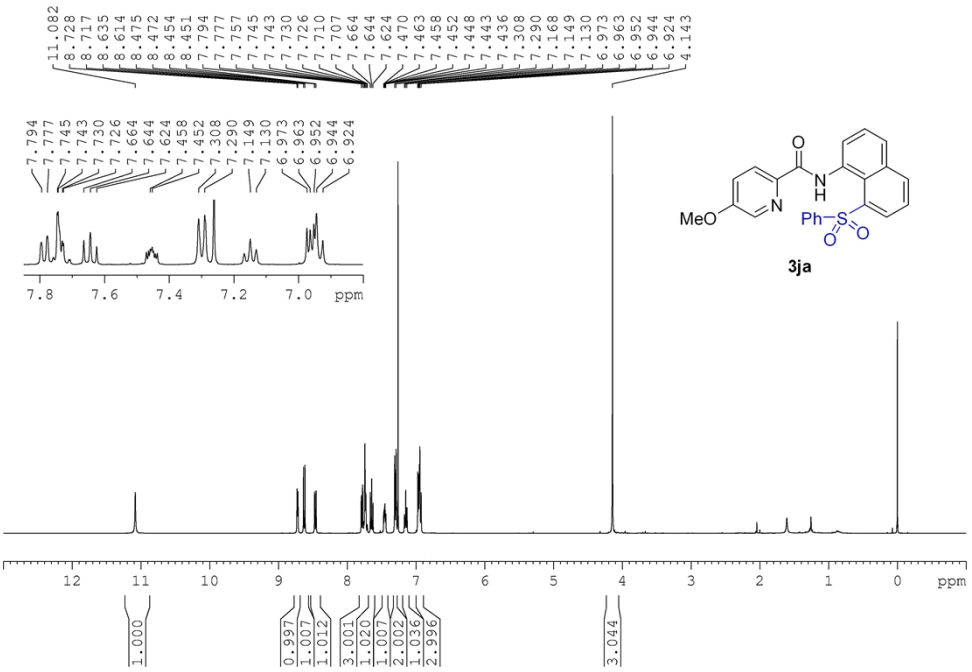

163.444
149.561
149.228
141.768
139.845
138.932
134.076
131.909
130.992
130.131
129.178
128.870
128.010
127.851
127.698
127.542
124.609
123.578
123.087
118.905
Br
N
H
O
Ph—S
O
O
3ha
ppm

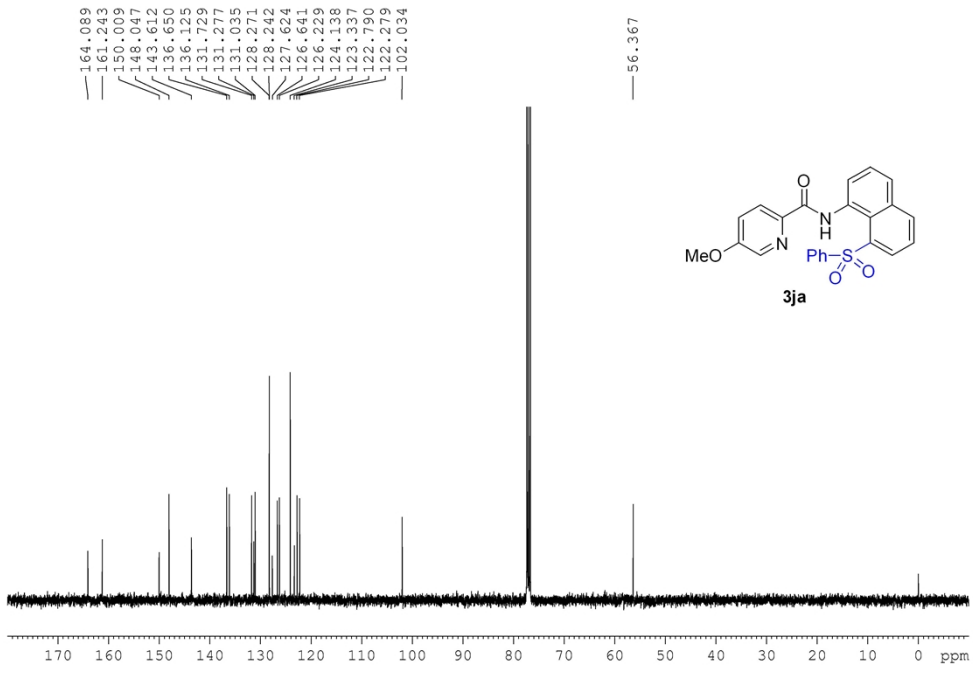

+ESI Scan (0.185-0.210 min, 4 Scans) Frag=180.0V SYC-b.d Subtract
x10 3
467.0059
469.0035
468.0076
470.0069
Counts vs. Mass-to-Charge (m/z)
3ha

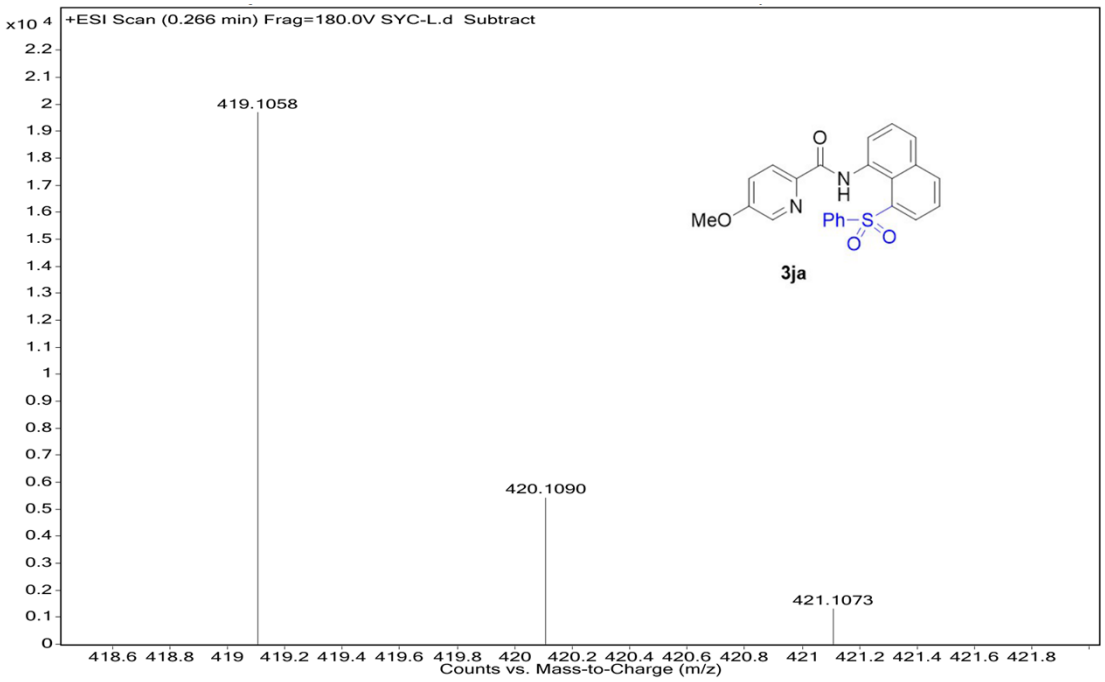

3ia

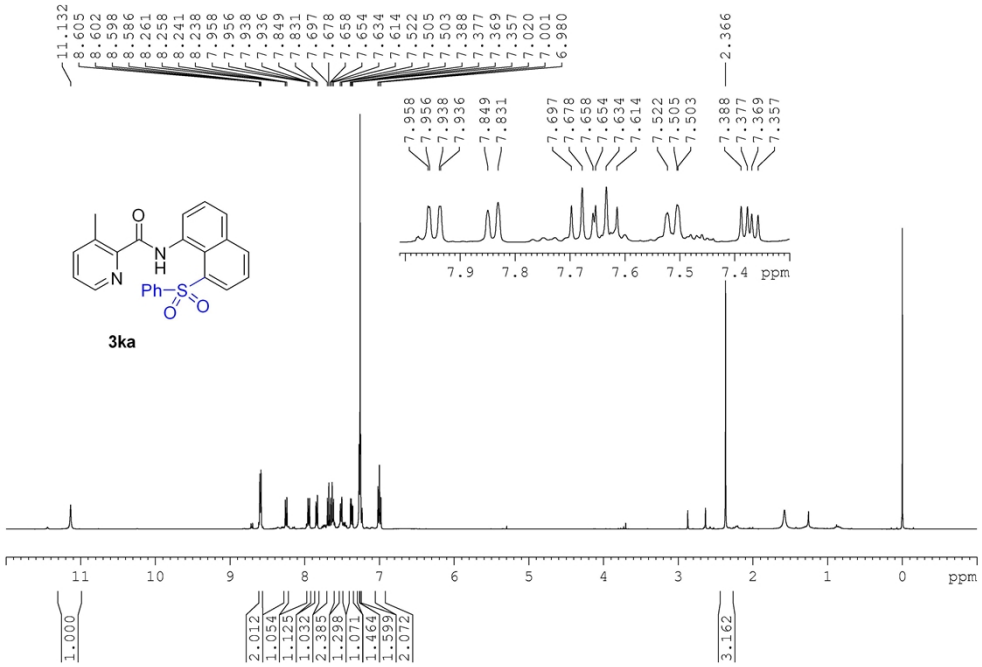

166.586
164.096
151.990
149.273
142.774
136.892
136.397
133.652
132.786
132.039
131.452
130.581
128.752
128.447
127.330
126.245
124.699
123.970
113.005
108.075
55.527
MeO
N
H
O
Ph–S
O
O
3ia
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

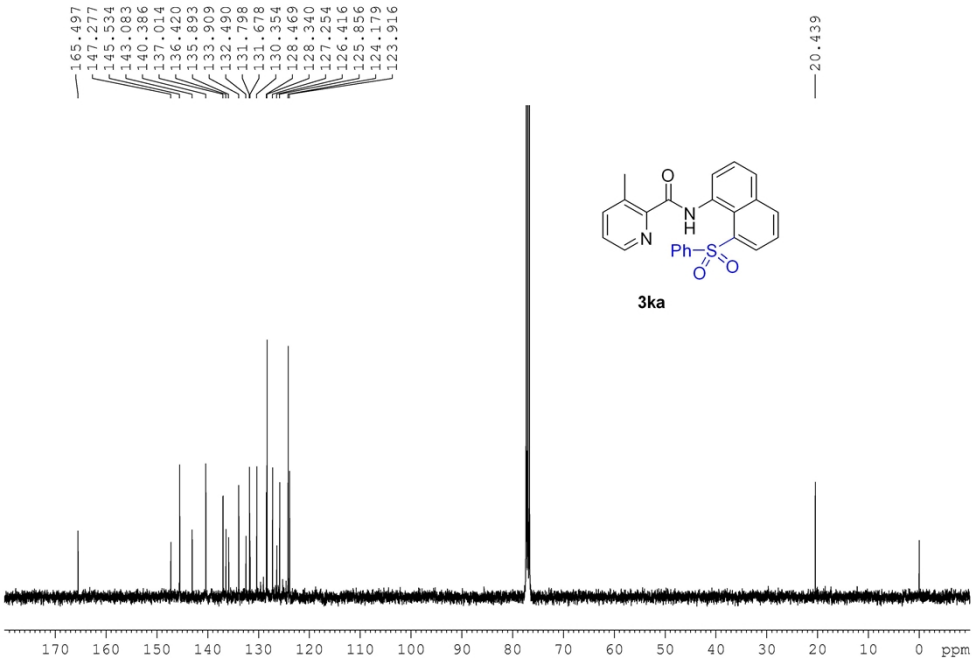

x10 3
+ESI Scan (0.175-0.208 min, 4 Scans) Frag=180.0V SYC-M.d Subtract
419.1060
420.1092
421.1068
MeO
N
H
O
Ph–S
O
O
3ia
Counts vs. Mass-to-Charge (m/z)

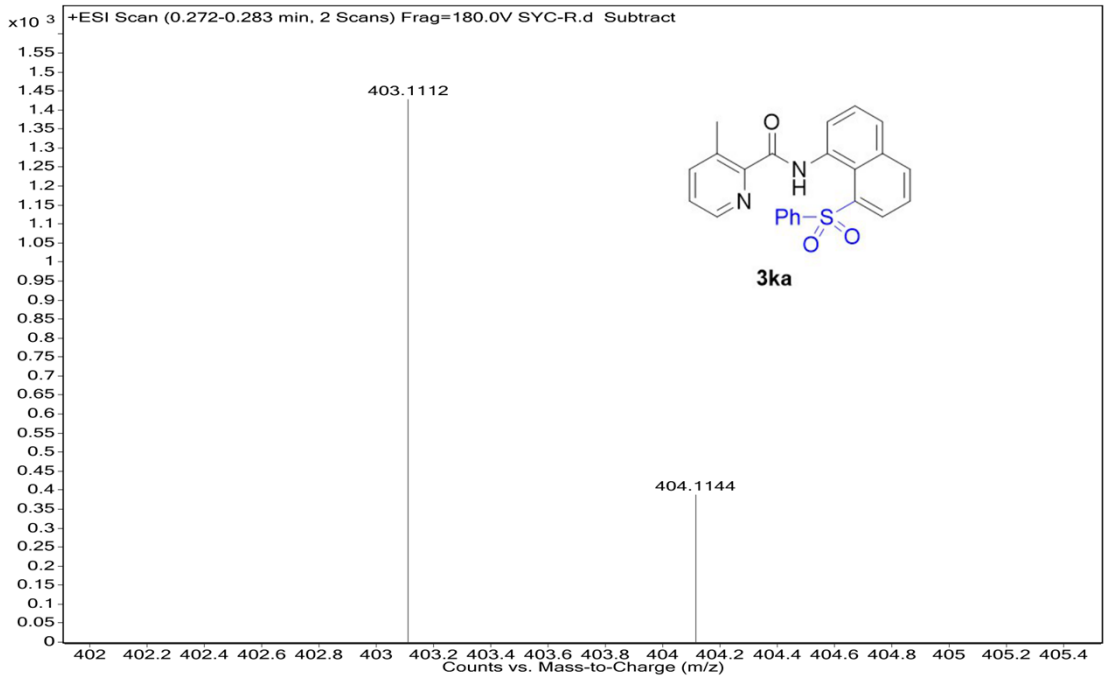

11.082
8.728
8.717
8.635
8.614
8.475
8.472
8.454
8.451
7.794
7.777
7.757
7.745
7.743
7.730
7.726
7.710
7.707
7.664
7.644
7.624
7.470
7.463
7.458
7.452
7.448
7.443
7.436
7.308
7.290
7.168
7.149
7.130
6.973
6.963
6.952
6.944
6.924
4.143
7.8
7.6
7.4
7.2
7.0
ppm
MeO
Ph
S
O
N
H
3ja
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.997
1.007
1.012
3.001
1.020
1.007
2.002
1.036
2.936
3.044

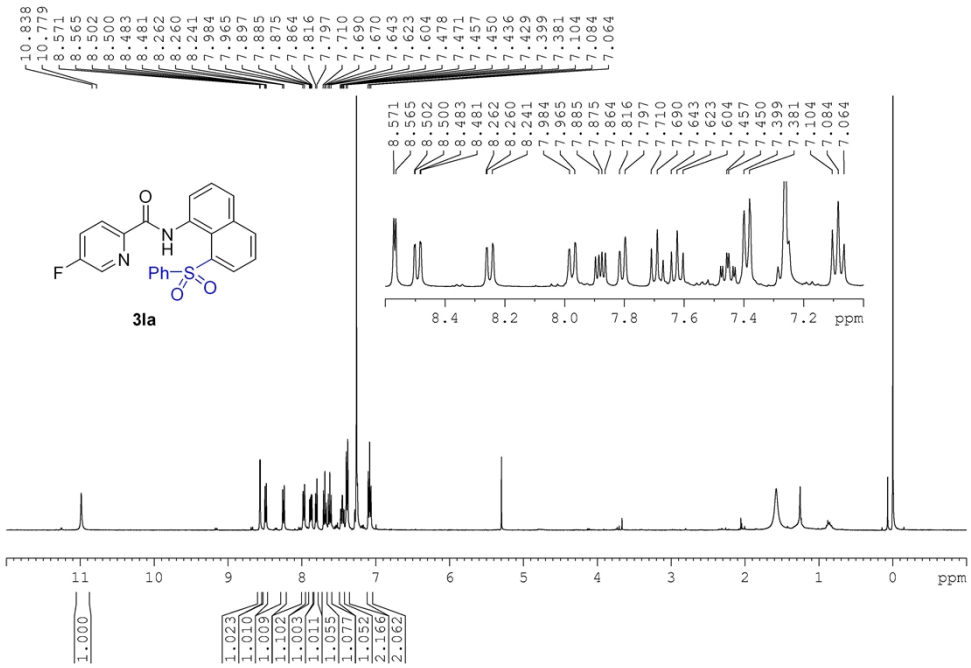

164.089
161.243
150.009
148.047
143.612
136.650
136.125
131.729
131.277
131.035
128.271
128.242
127.624
126.641
126.229
124.138
123.337
122.790
122.279
102.034
56.367
MeO
Ph
S
O
N
H
3ja
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

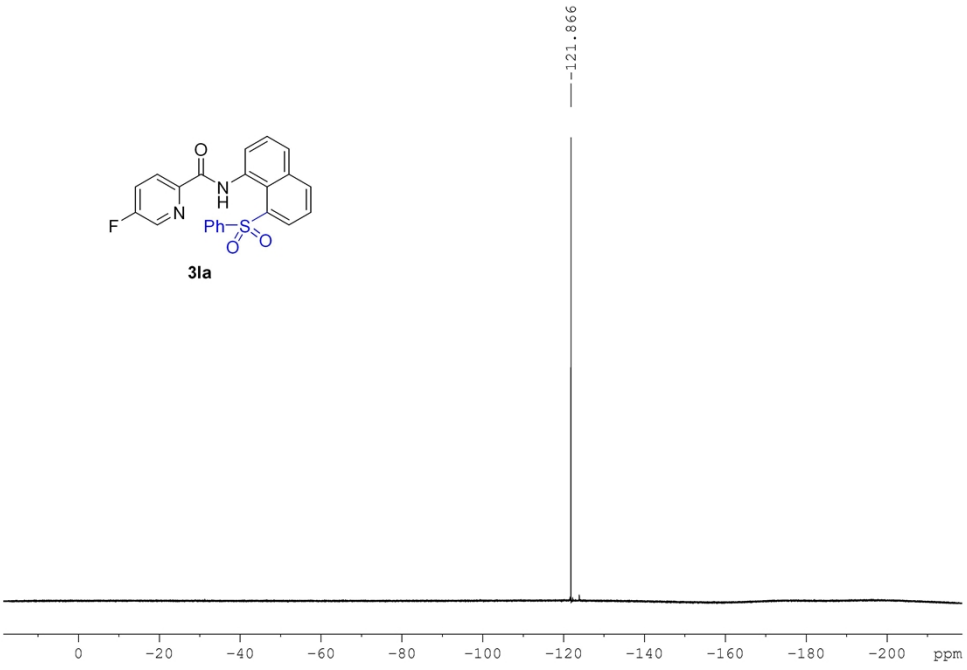

+ESI Scan (0.266 min) Frag=180.0V SYC-L.d Subtract
x10 4
419.1058
420.1090
421.1073
Counts vs. Mass-to-Charge (m/z)
MeO
Ph
3ja

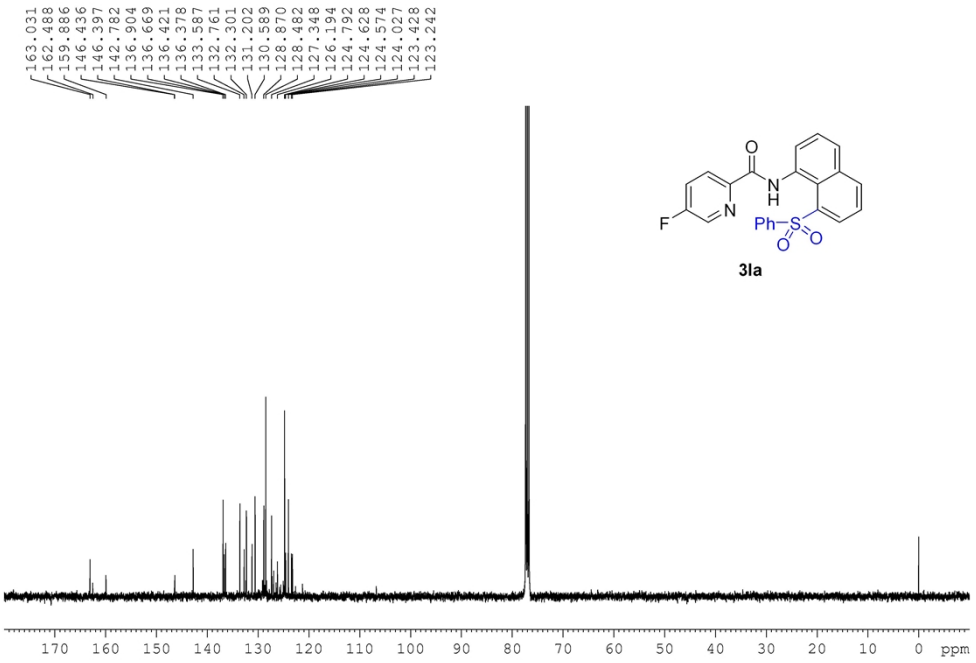

11.132
8.605
8.602
8.598
8.586
8.261
8.258
8.241
8.238
7.958
7.956
7.938
7.936
7.849
7.831
7.697
7.678
7.658
7.654
7.634
7.614
7.522
7.505
7.503
7.388
7.377
7.369
7.357
7.020
7.001
6.980
2.366
7.9 7.8 7.7 7.6 7.5 7.4 ppm
3ka
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
2.012
1.054
1.125
1.032
2.385
1.298
1.071
1.464
1.599
2.072
3.162

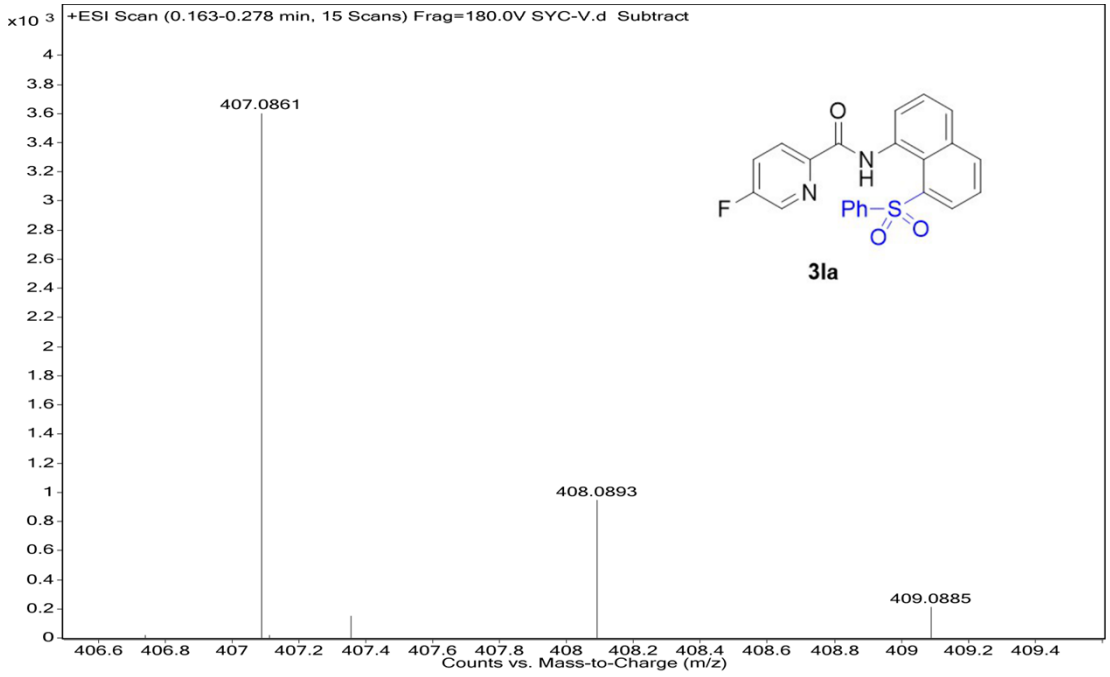

165.497
147.277
145.534
143.083
140.386
137.014
136.420
135.893
133.909
132.490
131.798
131.678
130.354
128.469
128.340
127.254
126.416
125.856
124.179
123.916
20.439
O
N
H
N
Ph—S
O
O
3ka
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

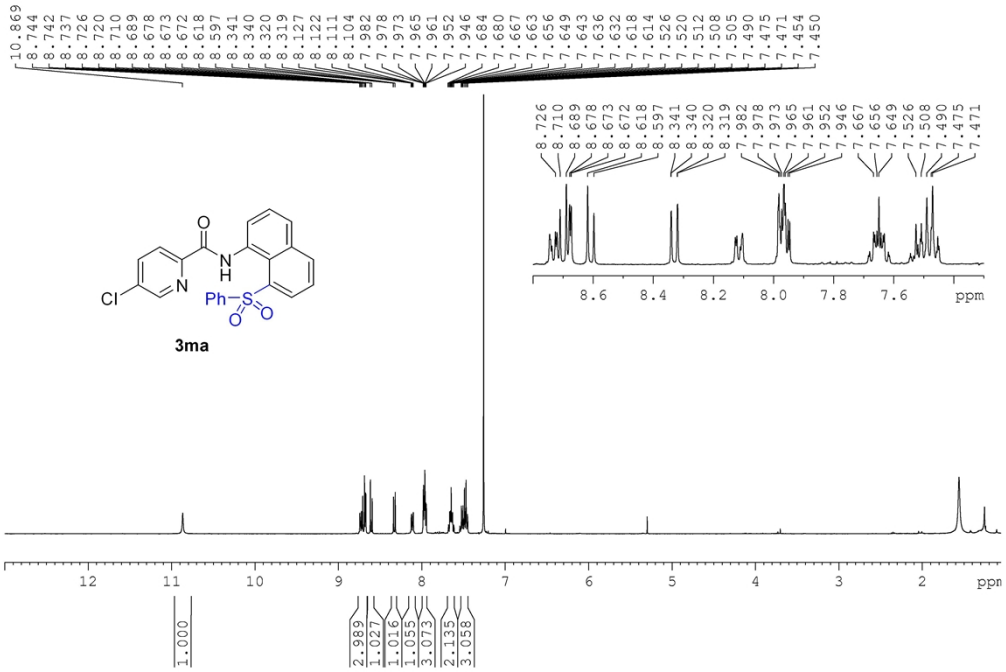

x10 3
+ESI Scan (0.272-0.283 min, 2 Scans) Frag=180.0V SYC-R.d Subtract
403.1112
404.1144
O
N
H
N
Ph—S
O
O
3ka
Counts vs. Mass-to-Charge (m/z)

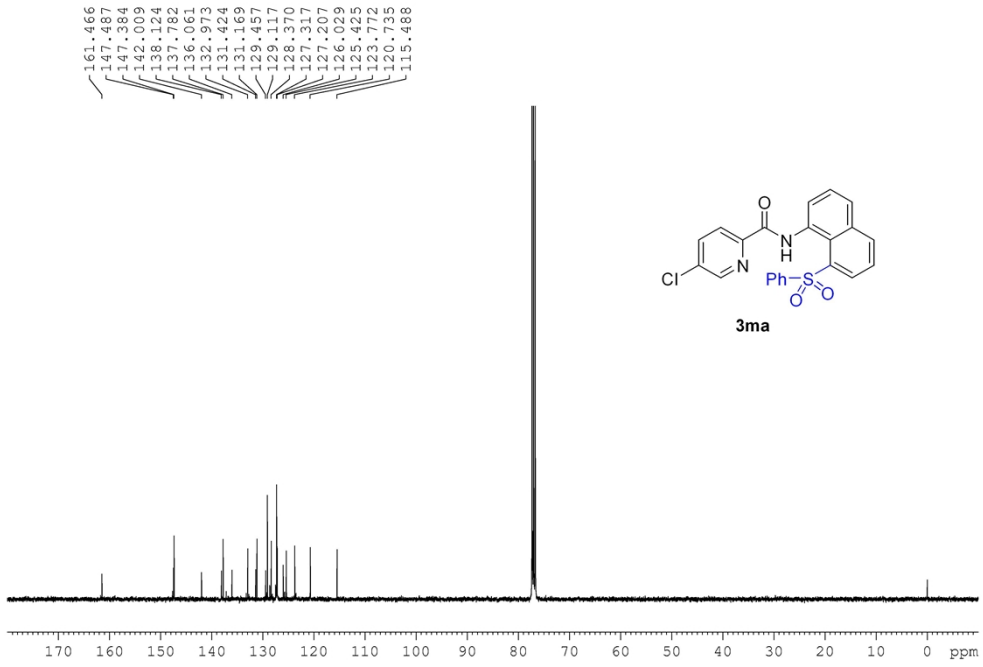

10.838
10.779
8.571
8.565
8.502
8.500
8.483
8.481
8.262
8.260
8.241
7.984
7.965
7.897
7.885
7.875
7.864
7.816
7.797
7.710
7.690
7.670
7.643
7.623
7.604
7.478
7.471
7.457
7.450
7.436
7.429
7.399
7.381
7.104
7.084
7.064
3Ia
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.023
1.010
1.009
1.102
1.003
1.011
1.055
1.077
1.052
2.166
2.062

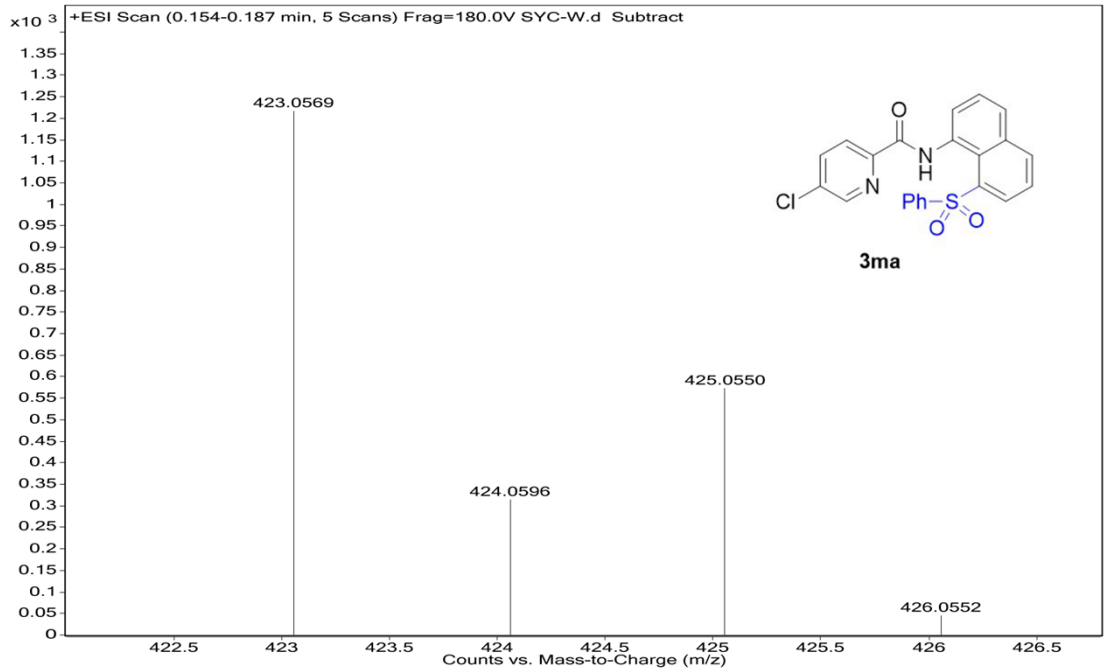

-121.866
3Ia
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

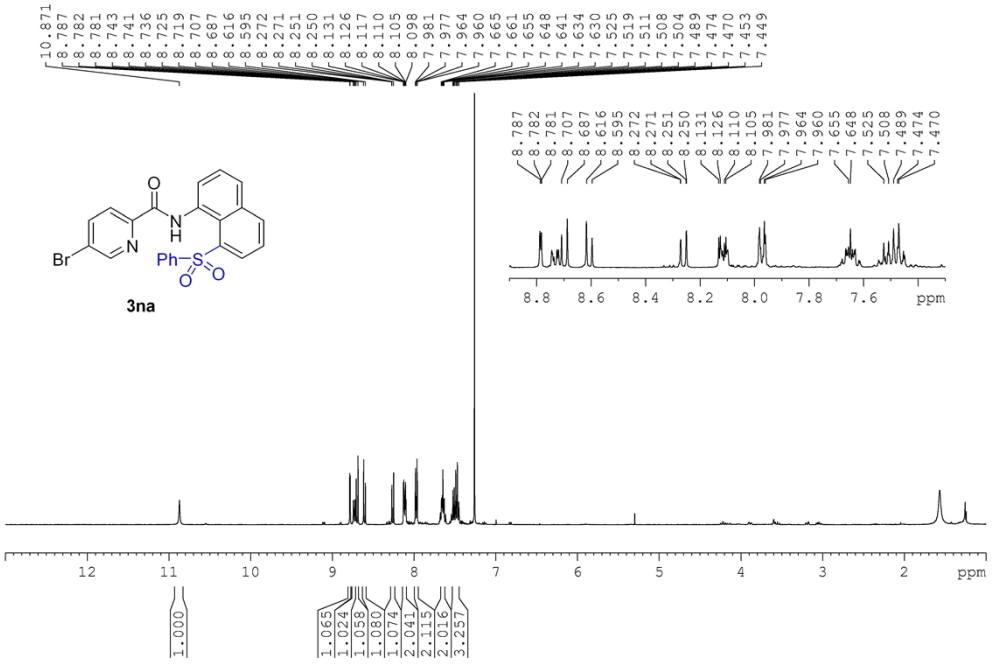

163.031
162.488
159.886
146.436
146.397
142.782
136.904
136.669
136.421
136.378
133.587
132.761
132.301
131.202
130.589
128.870
128.482
127.348
126.194
124.792
124.628
124.574
124.027
123.428
123.242
3la
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

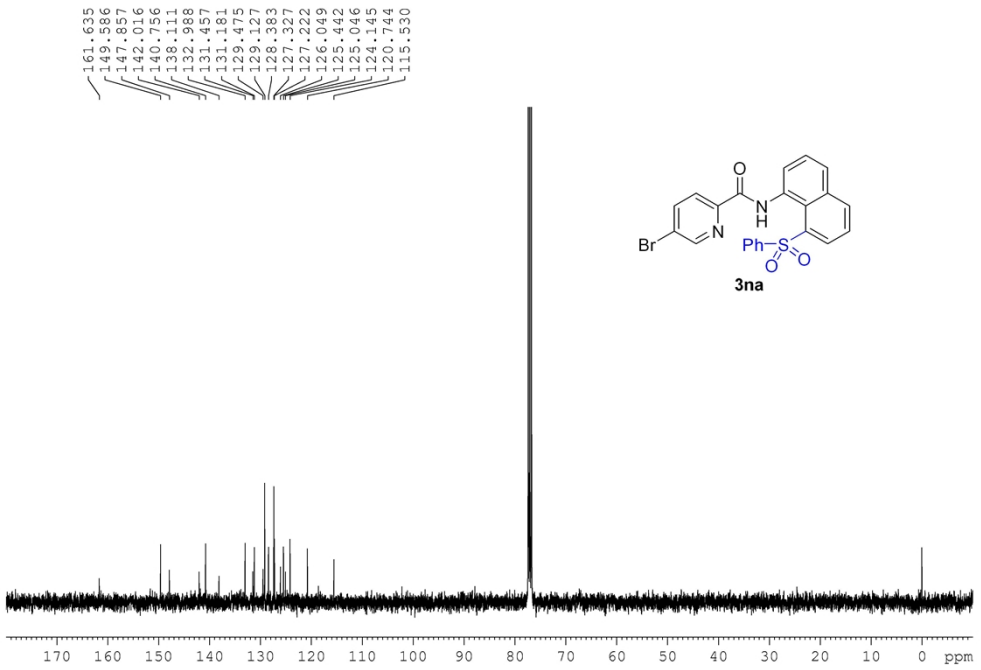

x10 3
+ESI Scan (0.163-0.278 min, 15 Scans) Frag=180.0V SYC-V.d Subtract
407.0861
408.0893
409.0885
3la
Counts vs. Mass-to-Charge (m/z)

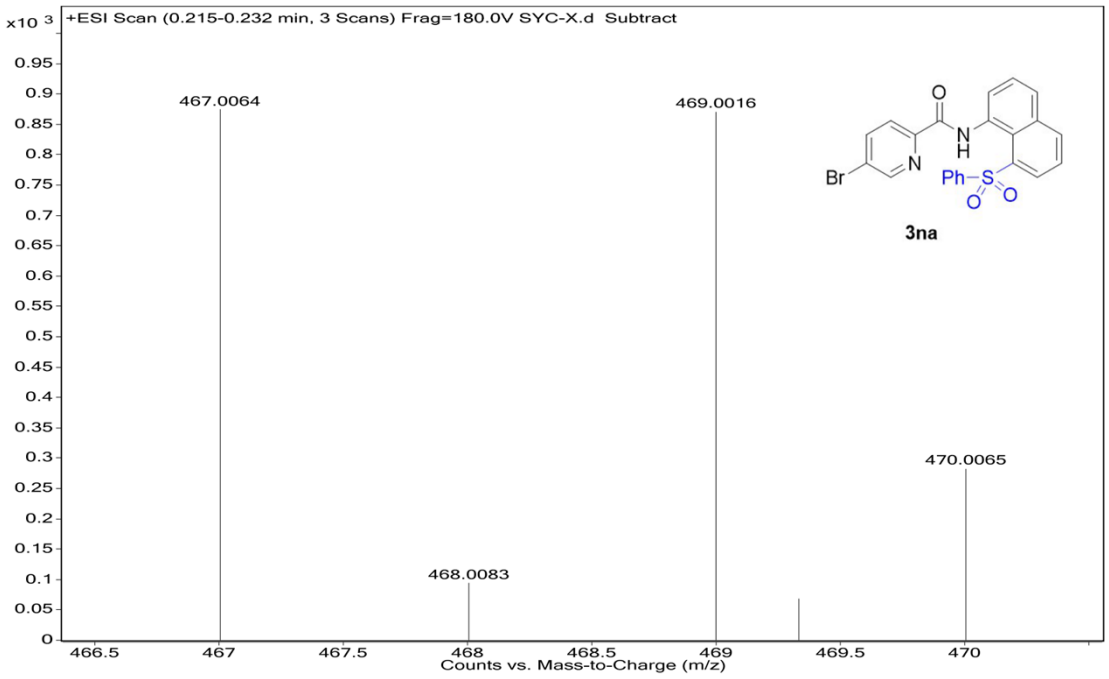

10.869
8.744
8.742
8.737
8.726
8.720
8.710
8.689
8.678
8.673
8.672
8.618
8.597
8.341
8.340
8.320
8.319
8.127
8.122
8.111
8.104
7.982
7.978
7.973
7.965
7.961
7.952
7.946
7.684
7.680
7.667
7.663
7.656
7.649
7.643
7.636
7.632
7.618
7.614
7.526
7.520
7.512
7.508
7.505
7.490
7.475
7.471
7.454
7.450
3ma
1.000
2.989
1.027
1.016
1.055
3.073
2.135
3.058
ppm

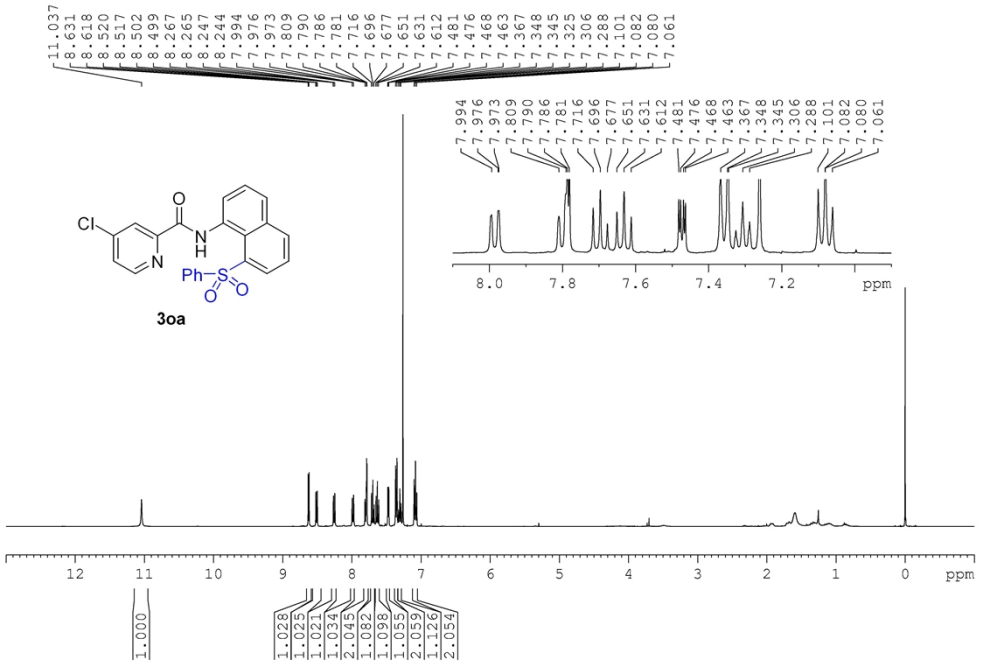

161.466
147.487
147.384
142.009
138.124
137.782
136.061
132.973
131.424
131.169
129.457
129.117
128.370
127.317
127.207
126.029
125.425
123.772
120.735
115.488
3ma
ppm

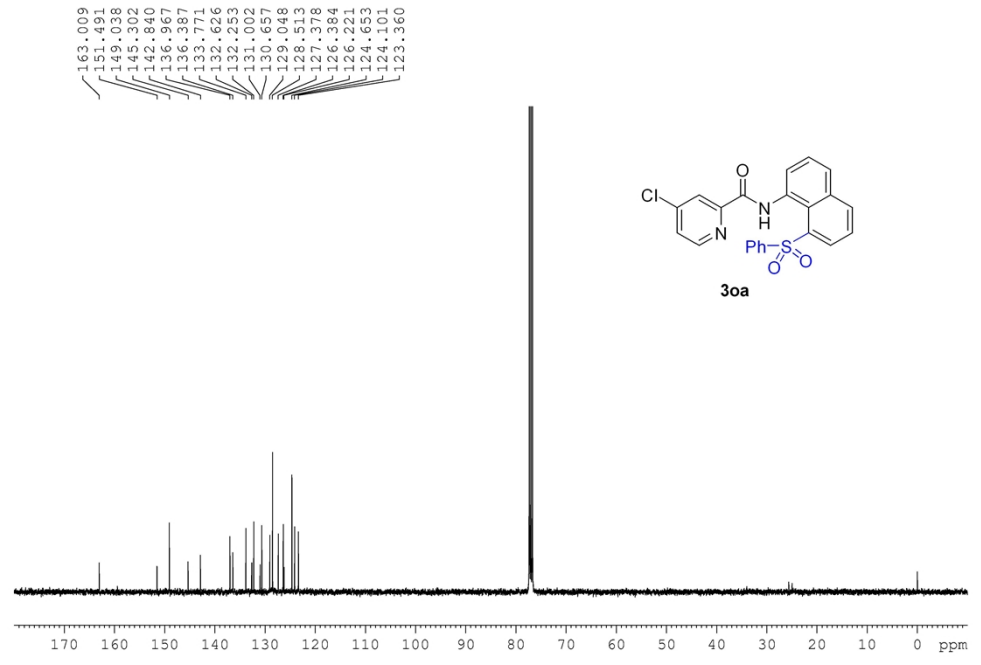

+ESI Scan (0.154-0.187 min, 5 Scans) Frag=180.0V SYC-W.d Subtract
x10 3
423.0569
425.0550
424.0596
426.0552
Counts vs. Mass-to-Charge (m/z)
3ma

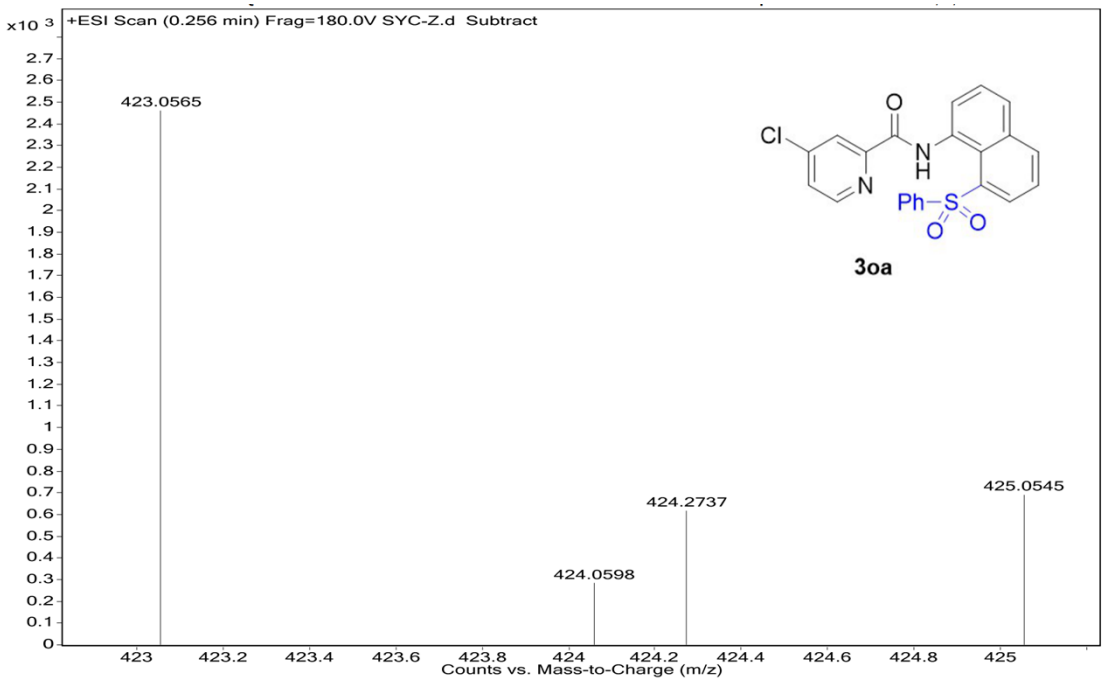

3na
ppm

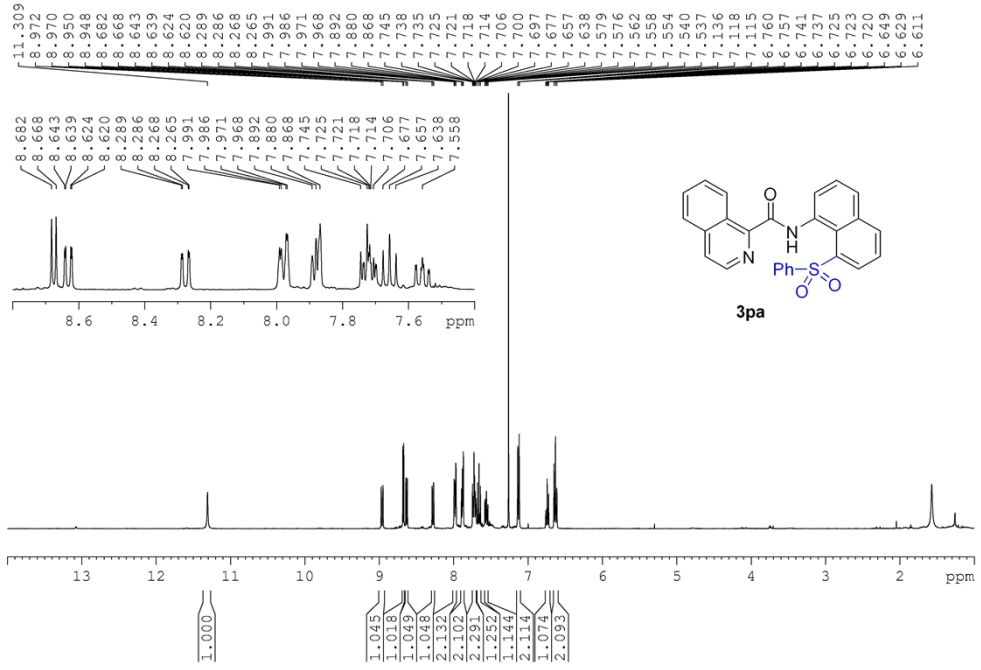

161.635
149.586
147.857
142.016
140.756
138.111
132.988
131.457
131.181
129.475
129.127
128.383
127.327
127.222
126.049
125.442
125.046
124.145
120.744
115.530
Br
N
O
N
H
Ph—S
O
O
3na
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

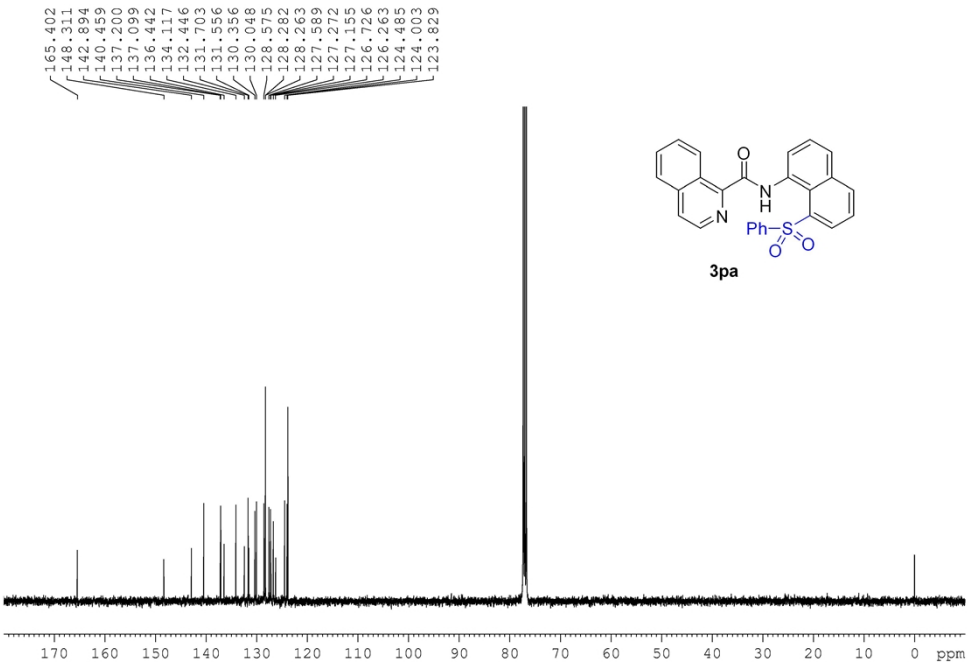

x10 3
+ESI Scan (0.215-0.232 min, 3 Scans) Frag=180.0V SYC-X.d Subtract
467.0064
469.0016
470.0065
468.0083
Br
N
O
N
H
Ph—S
O
O
3na
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
466.5
467
467.5
468
468.5
469
469.5
470
Counts vs. Mass-to-Charge (m/z)

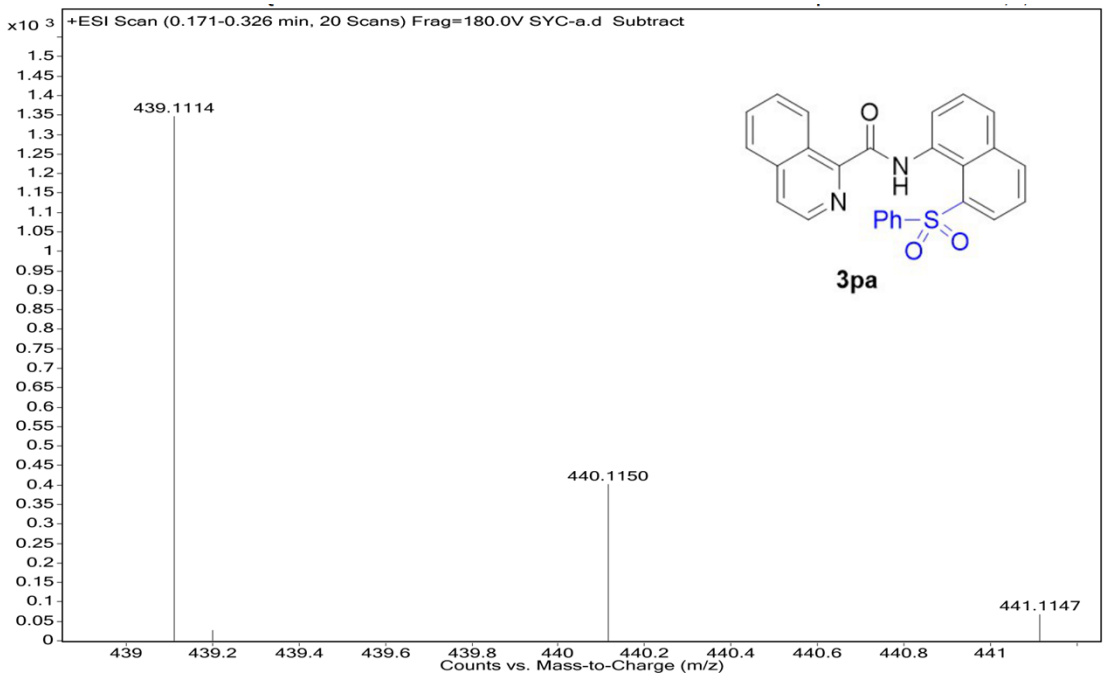

11.037
8.631
8.618
8.520
8.517
8.502
8.499
8.267
8.265
8.247
8.244
7.994
7.976
7.973
7.809
7.790
7.786
7.781
7.716
7.696
7.677
7.651
7.631
7.612
7.481
7.476
7.468
7.463
7.367
7.348
7.345
7.325
7.306
7.288
7.101
7.082
7.080
7.061
Cl
N
O
N
H
Ph
S
O
O
3oa
8.0
7.8
7.6
7.4
7.2
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.028
1.025
1.021
1.034
2.045
1.082
1.098
1.055
2.059
1.126
2.054

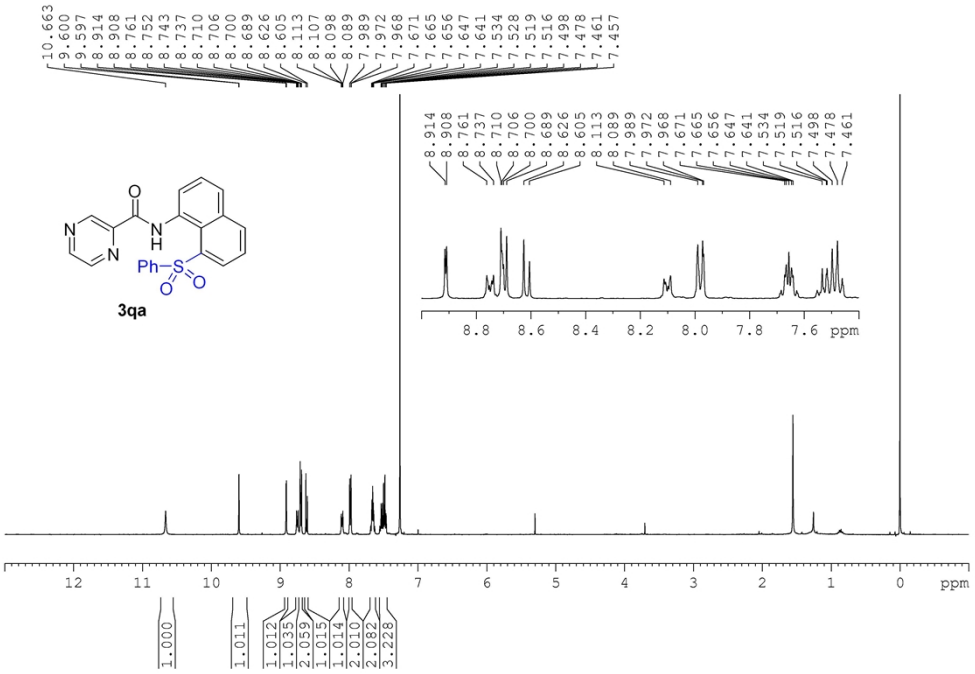

163.009
151.491
149.038
145.302
142.840
136.967
136.387
133.771
132.626
132.253
131.002
130.657
129.048
128.513
127.378
126.384
126.221
124.653
124.101
123.360
Cl
N
O
N
H
Ph
S
O
O
3oa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

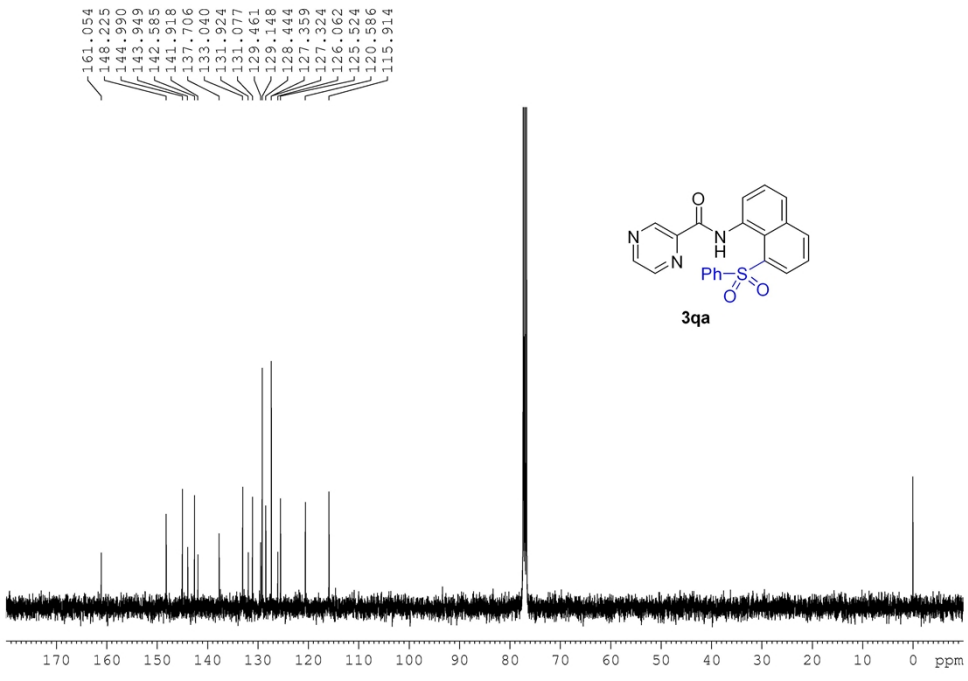

+ESI Scan (0.256 min) Frag=180.0V SYC-Z.d Subtract
x10 3
423.0565
424.0598
424.2737
425.0545
Counts vs. Mass-to-Charge (m/z)
3oa

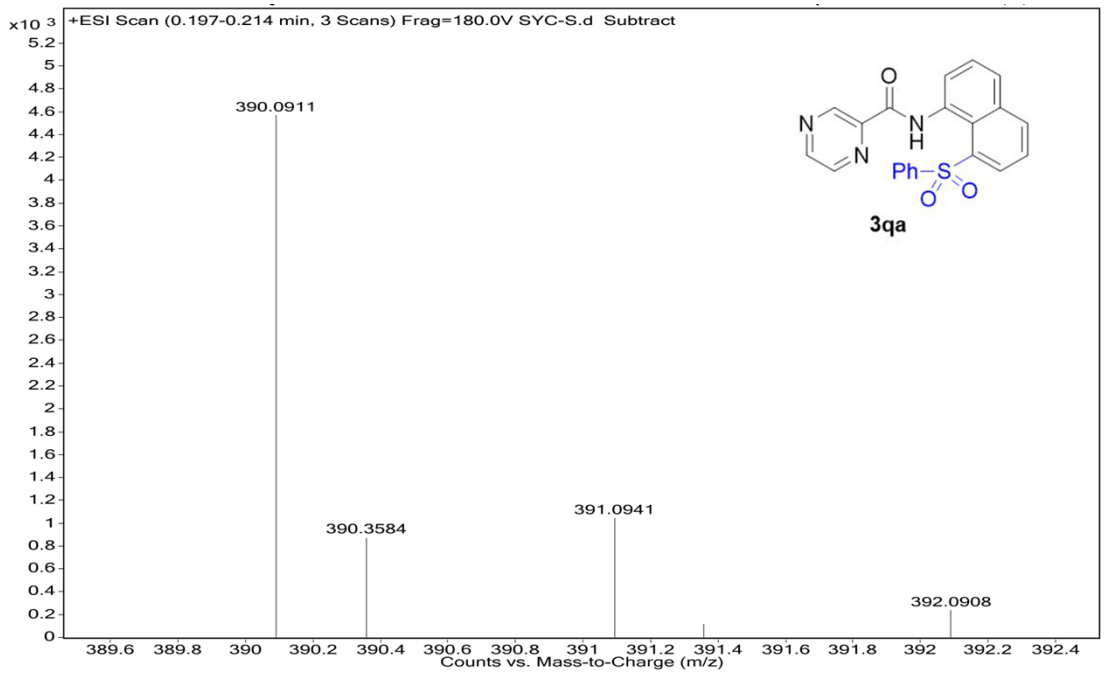

3pa
ppm

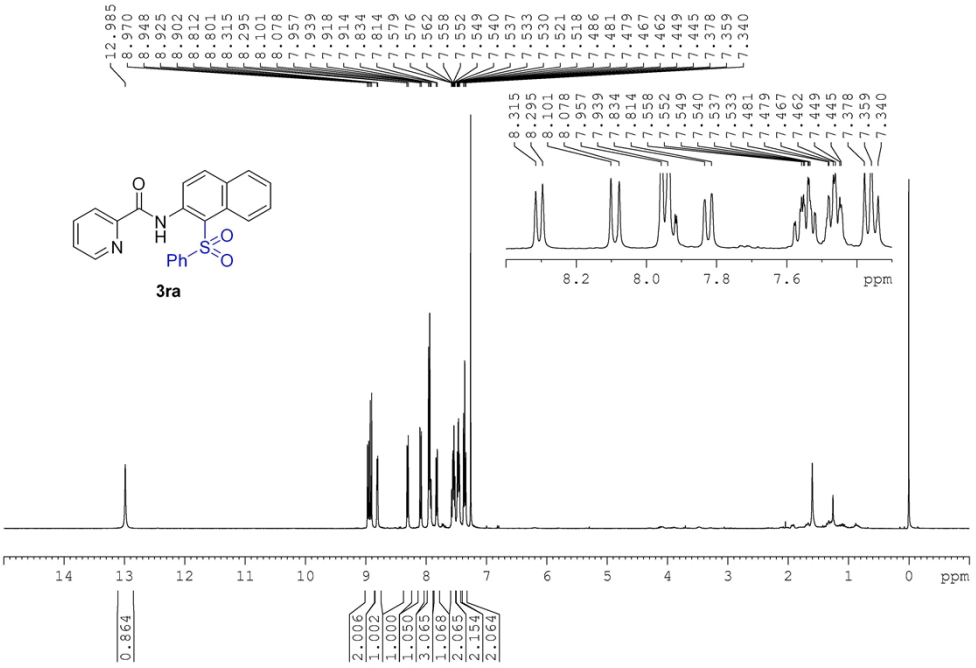

165.402
148.311
142.894
140.459
137.200
137.099
136.442
134.117
132.446
131.703
131.556
130.356
130.048
128.575
128.282
128.263
127.589
127.272
127.155
126.726
126.263
124.485
124.003
123.829
O
N
H
N
Ph—S
O
O
3pa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

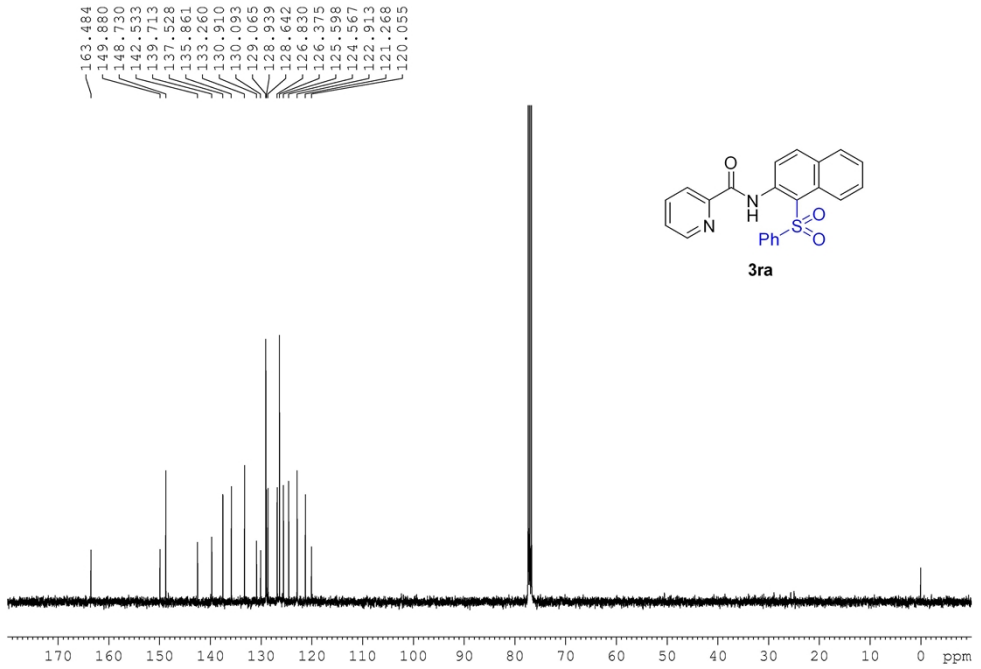

x10 3
+ESI Scan (0.171-0.326 min, 20 Scans) Frag=180.0V SYC-a.d Subtract
439.1114
440.1150
441.1147
O
N
H
N
Ph—S
O
O
3pa
Counts vs. Mass-to-Charge (m/z)

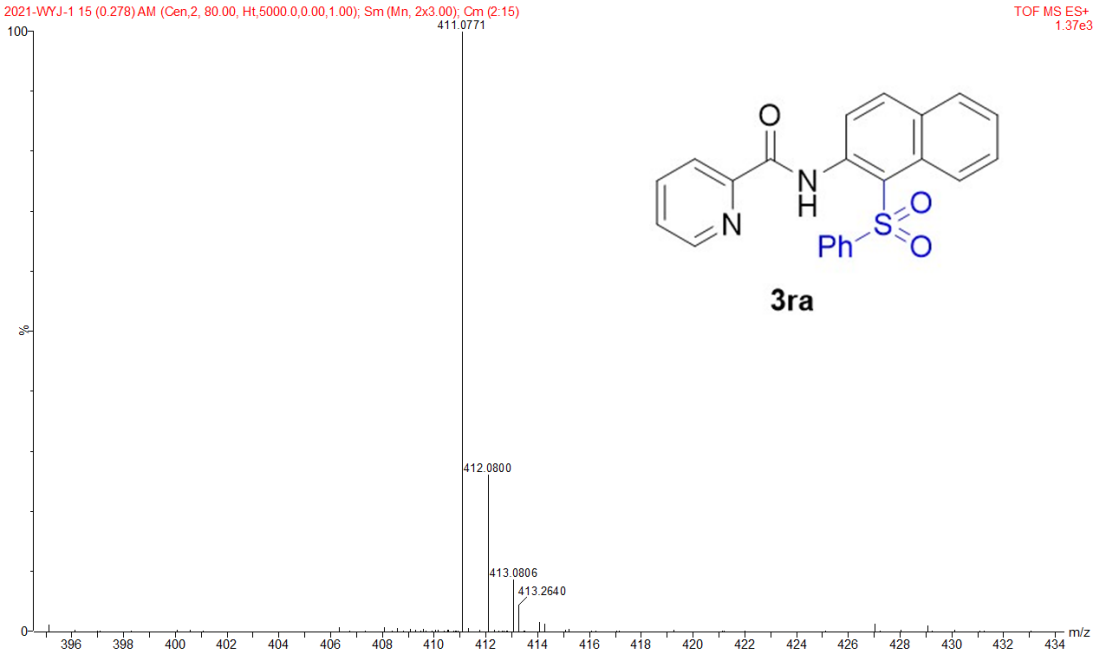

10.663
9.600
9.597
8.914
8.908
8.761
8.752
8.743
8.737
8.710
8.706
8.700
8.689
8.626
8.605
8.113
8.107
8.098
8.089
7.989
7.972
7.968
7.671
7.665
7.656
7.647
7.641
7.534
7.528
7.519
7.516
7.498
7.478
7.461
7.457
3qa
8.8 8.6 8.4 8.2 8.0 7.8 7.6 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.011
1.012
1.035
2.059
1.015
1.014
2.010
2.082
3.228

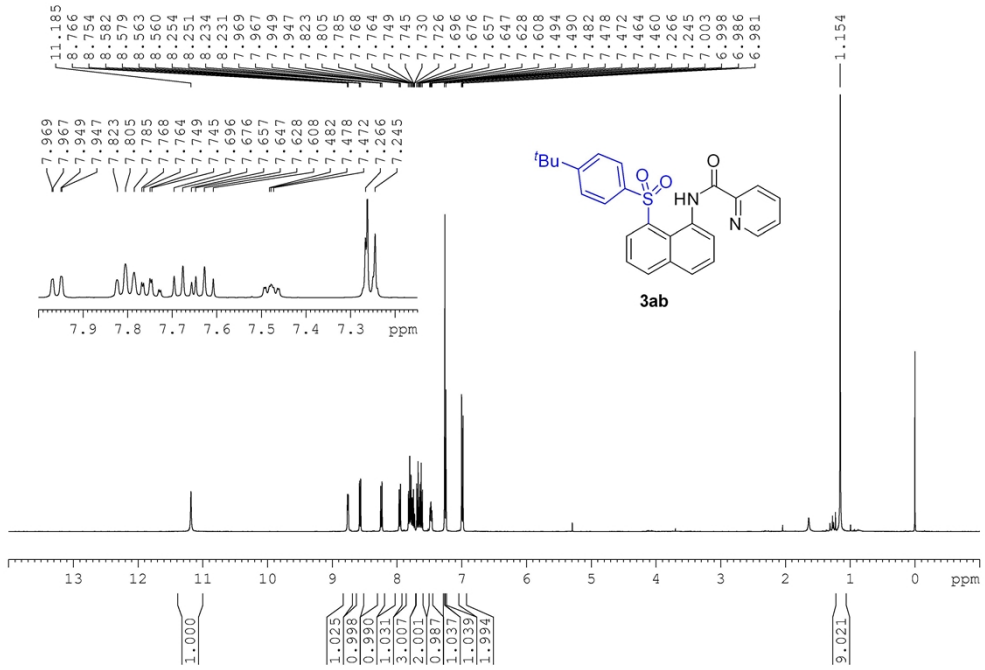

161.054
148.225
144.990
143.949
142.585
141.918
137.706
133.040
131.924
131.077
129.461
129.148
128.444
127.359
127.324
126.062
125.524
120.886
115.914
3qa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

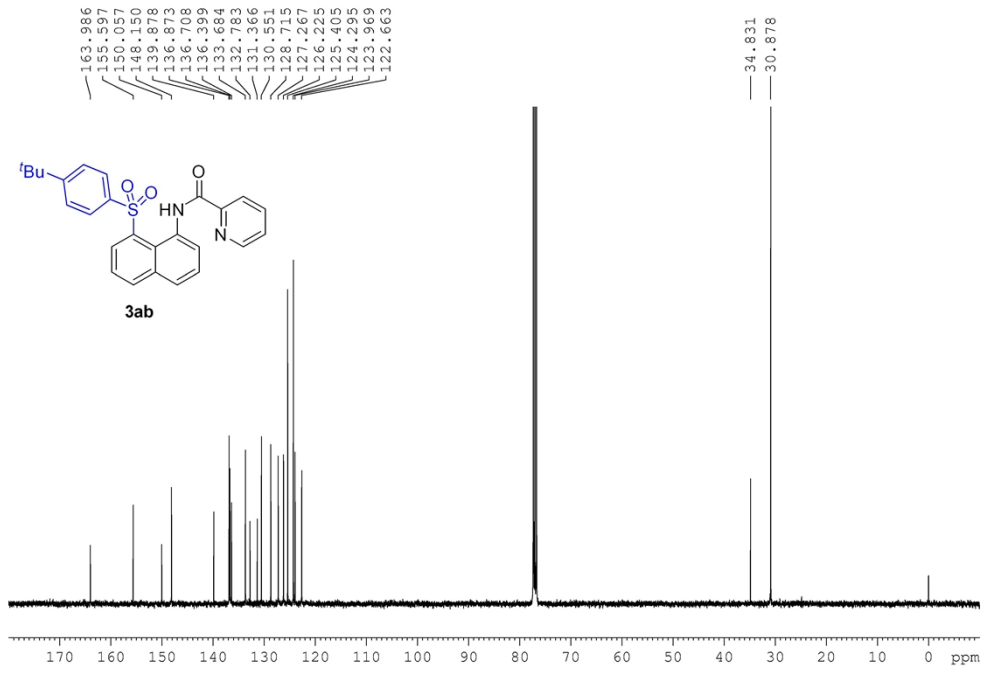

+ESI Scan (0.197-0.214 min, 3 Scans) Frag=180.0V SYC-S.d Subtract
x10 3
390.0911
390.3584
391.0941
392.0908
Counts vs. Mass-to-Charge (m/z)
3qa

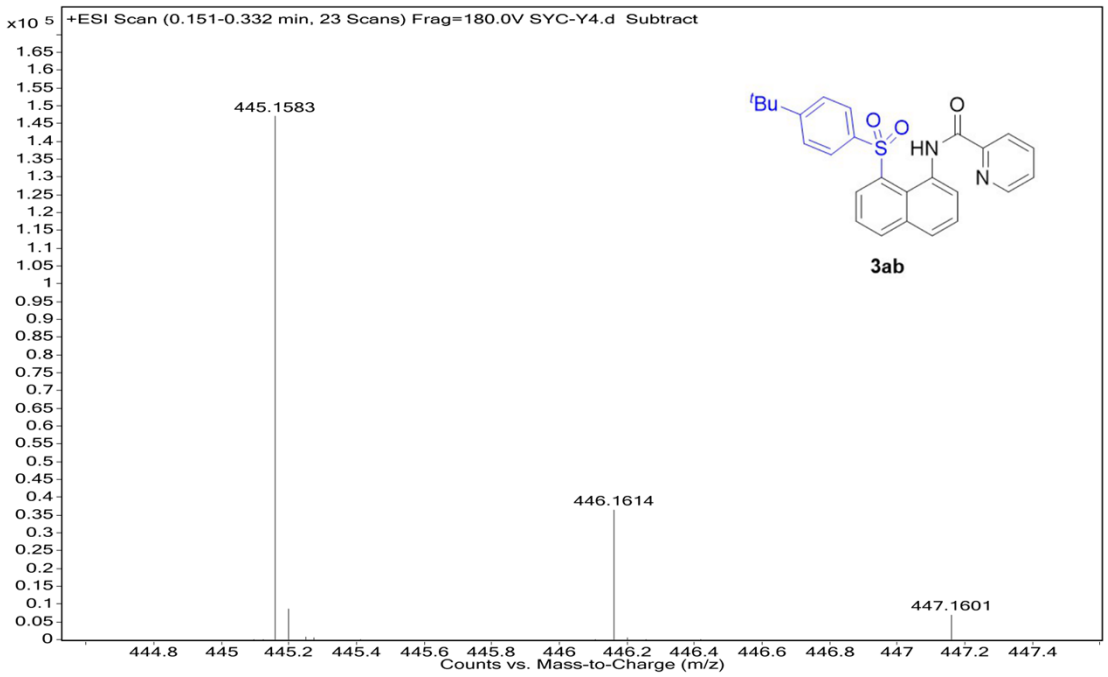

3ra
ppm

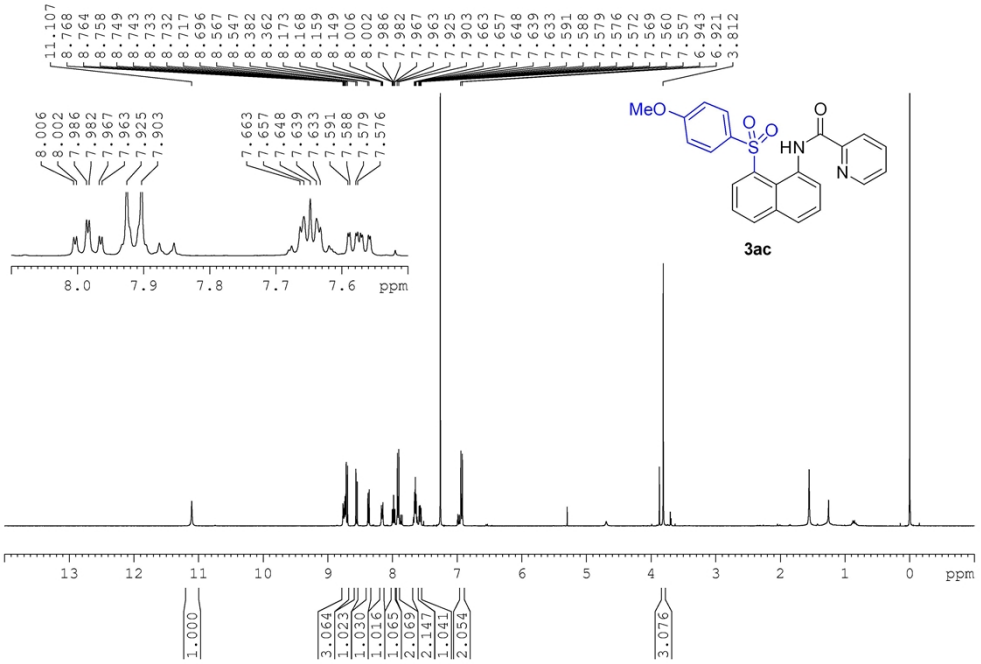

163.484
149.880
148.730
142.533
139.713
137.528
135.861
133.260
130.910
130.093
129.065
128.939
128.642
126.830
126.375
125.598
124.567
122.913
121.268
120.055
O
N
H
N
S
O
O
Ph
3ra
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

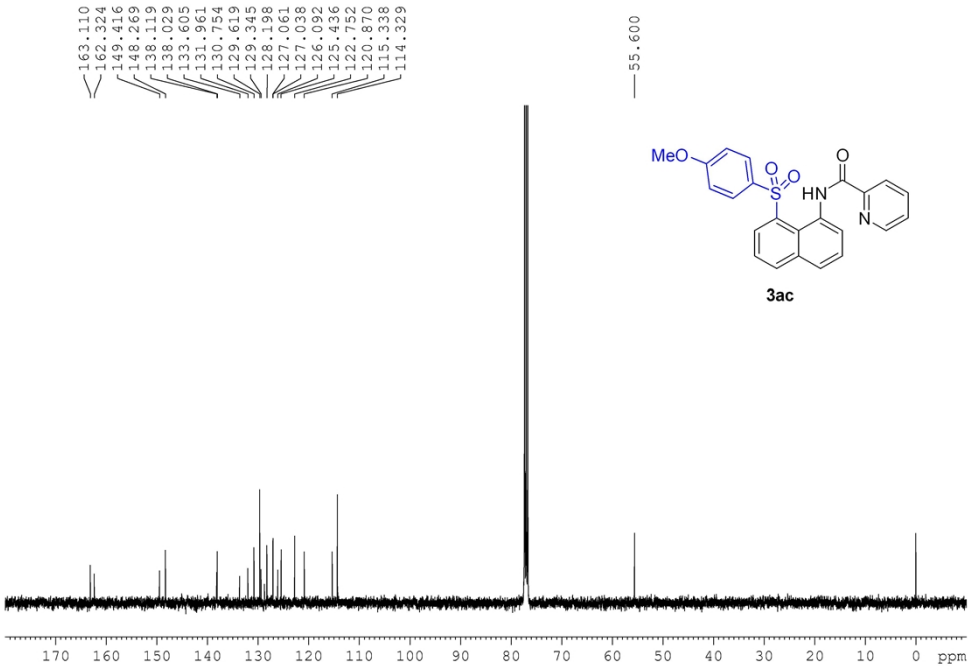

2021-WYJ-1 15 (0.278) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (2:15)
TOF MS ES+
1.37e3
100
%
0
411.0771
412.0800
413.0806
413.2640
O
N
H
N
S
O
O
Ph
3ra
396 398 400 402 404 406 408 410 412 414 416 418 420 422 424 426 428 430 432 434 m/z

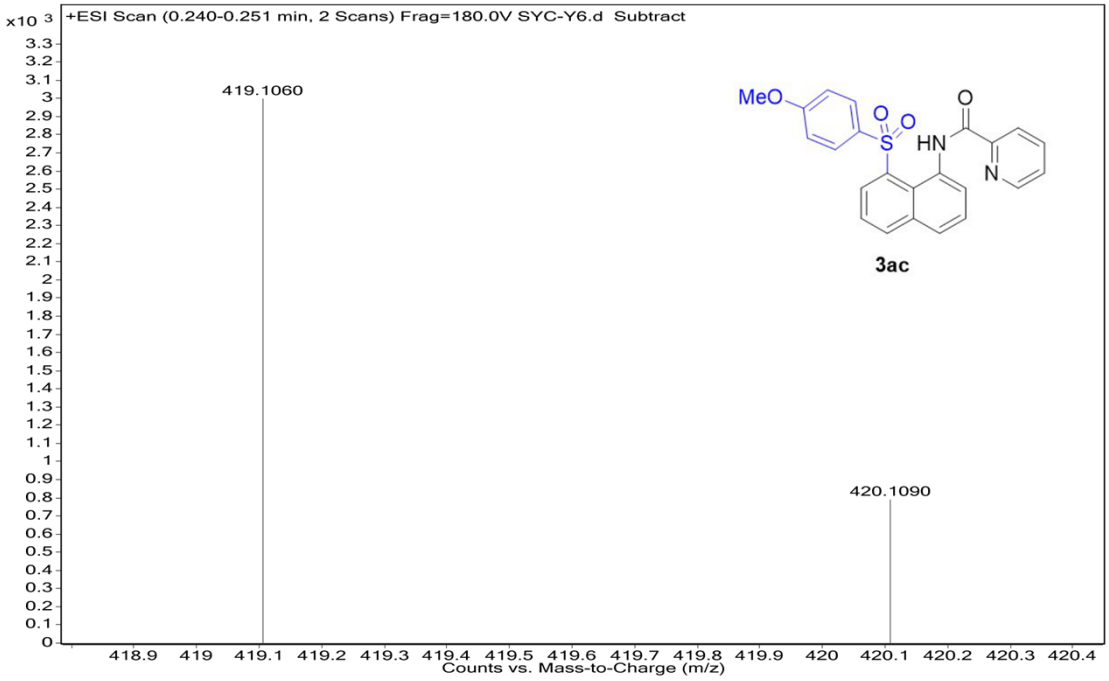

11.185
8.766
8.754
8.582
8.579
8.563
8.560
8.254
8.251
8.234
8.231
7.969
7.967
7.949
7.947
7.823
7.805
7.785
7.768
7.764
7.749
7.745
7.730
7.726
7.696
7.676
7.657
7.647
7.628
7.608
7.494
7.490
7.482
7.478
7.472
7.464
7.460
7.266
7.245
7.003
6.998
6.986
6.981
1.154
7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
3ab
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.025
0.998
0.990
1.031
3.007
2.001
0.987
1.037
1.039
1.994
9.021

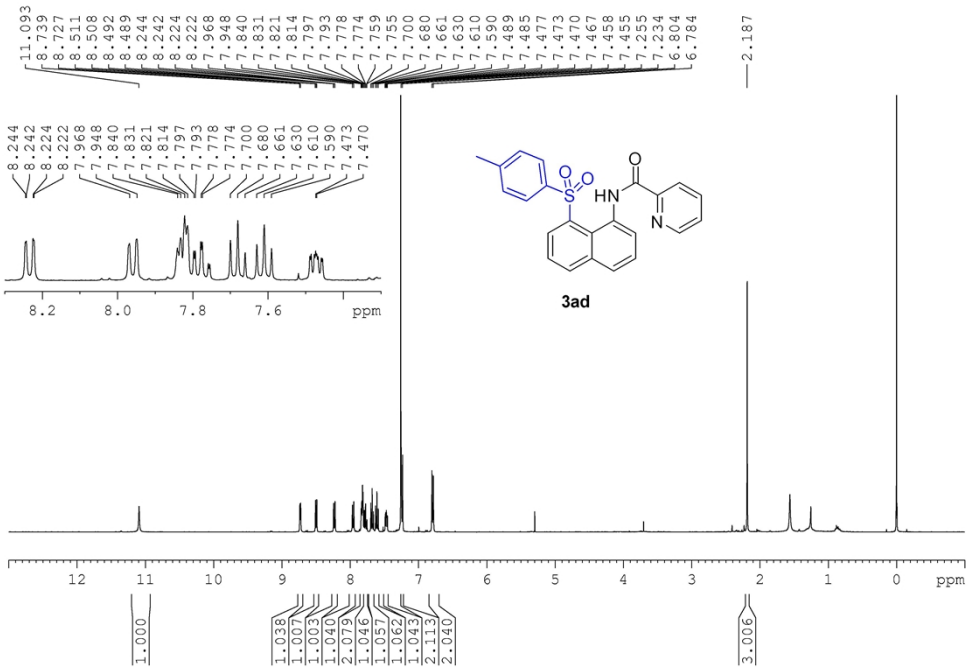

163.986
155.597
150.057
148.150
139.878
136.873
136.708
136.399
133.684
132.783
131.366
130.551
128.715
127.267
126.225
125.405
124.295
123.969
122.663
34.831
30.878
3ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

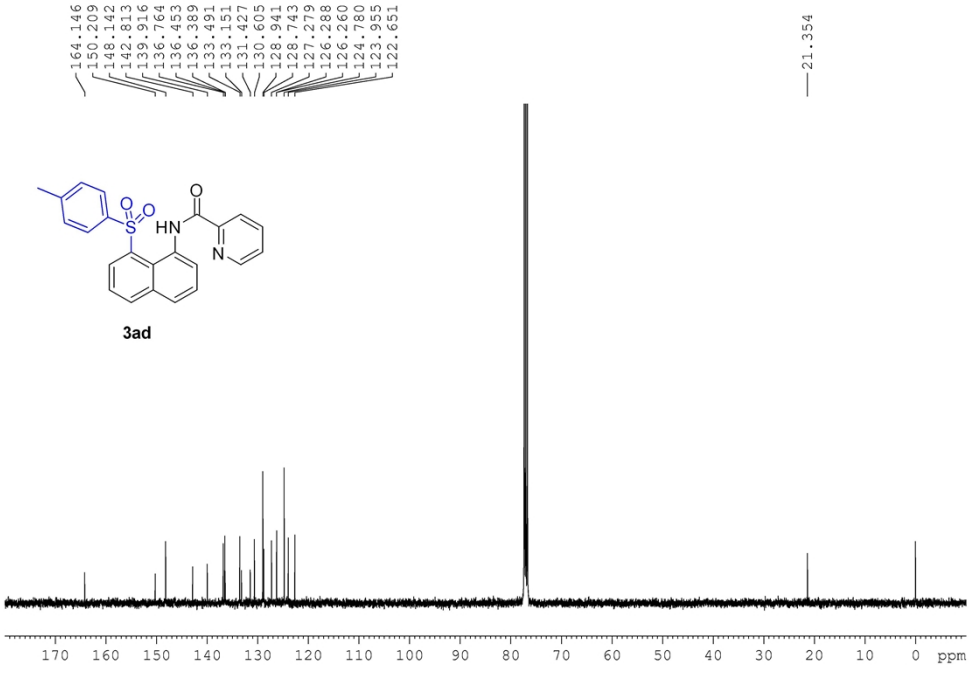

x10 5
+ESI Scan (0.151-0.332 min, 23 Scans) Frag=180.0V SYC-Y4.d Subtract
445.1583
446.1614
447.1601
Counts vs. Mass-to-Charge (m/z)
tBu
HN
N
3ab

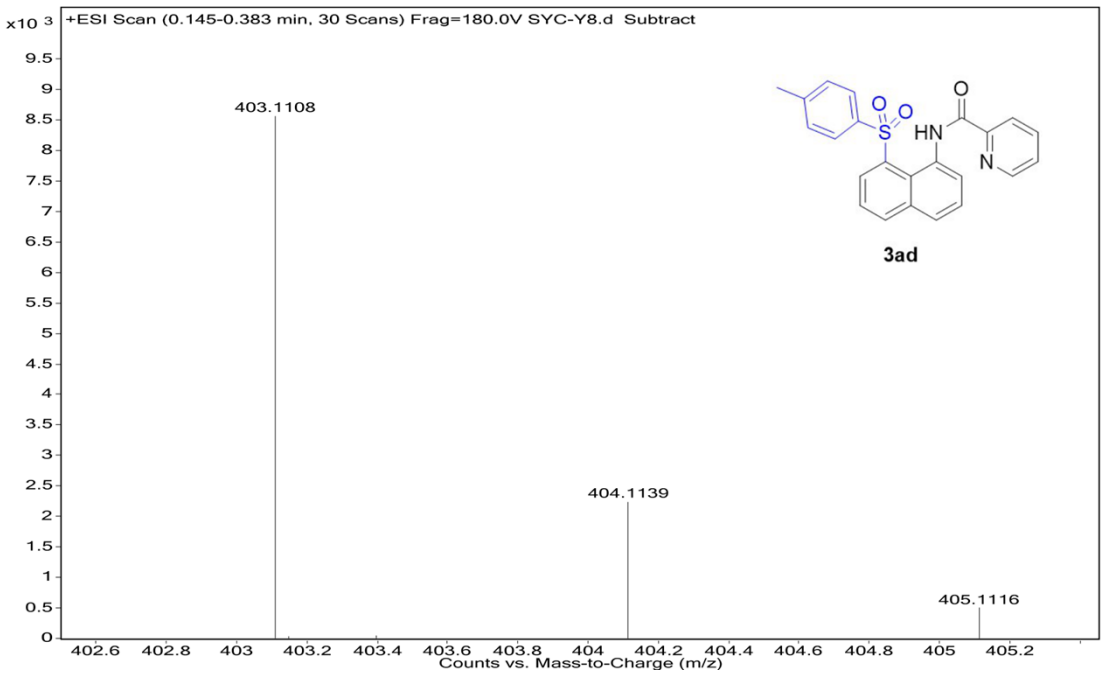

MeO
HN
N
3ac
ppm

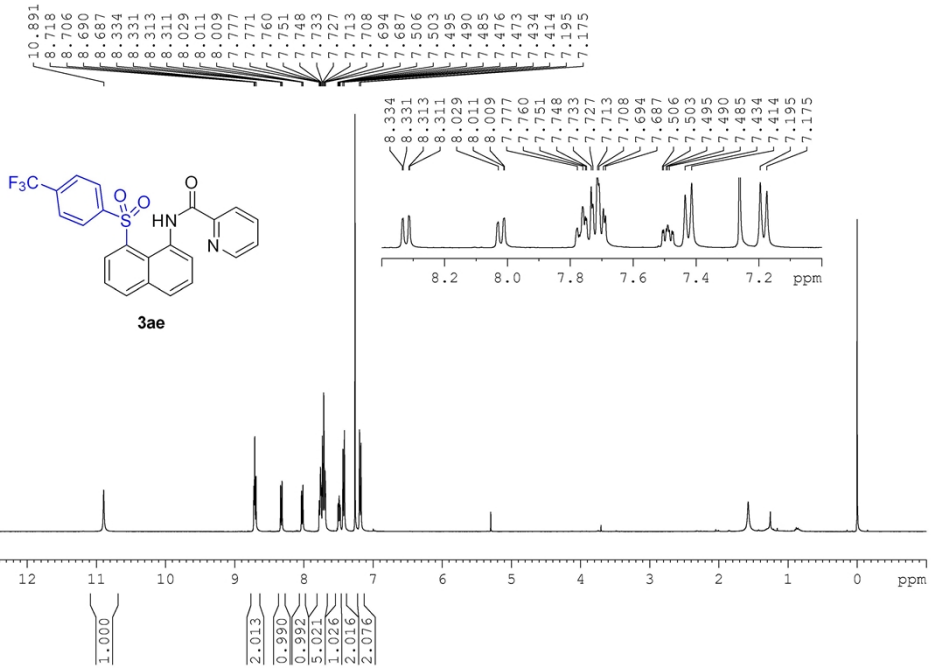

163.110
162.324
149.416
148.269
138.119
138.029
133.605
131.961
130.754
129.619
129.345
128.198
127.061
127.038
126.092
125.436
122.752
120.870
115.338
114.329
55.600
MeO
O
S
O
HN
O
N
3ac
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

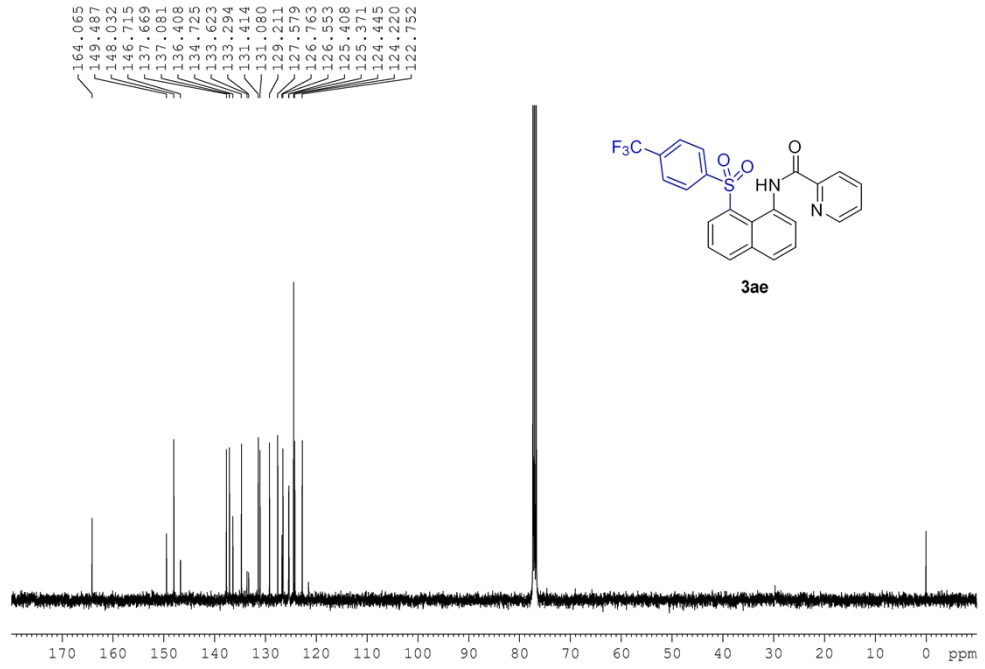

x10 3
+ESI Scan (0.240-0.251 min, 2 Scans) Frag=180.0V SYC-Y6.d Subtract
419.1060
420.1090
MeO
O
S
O
HN
O
N
3ac
Counts vs. Mass-to-Charge (m/z)

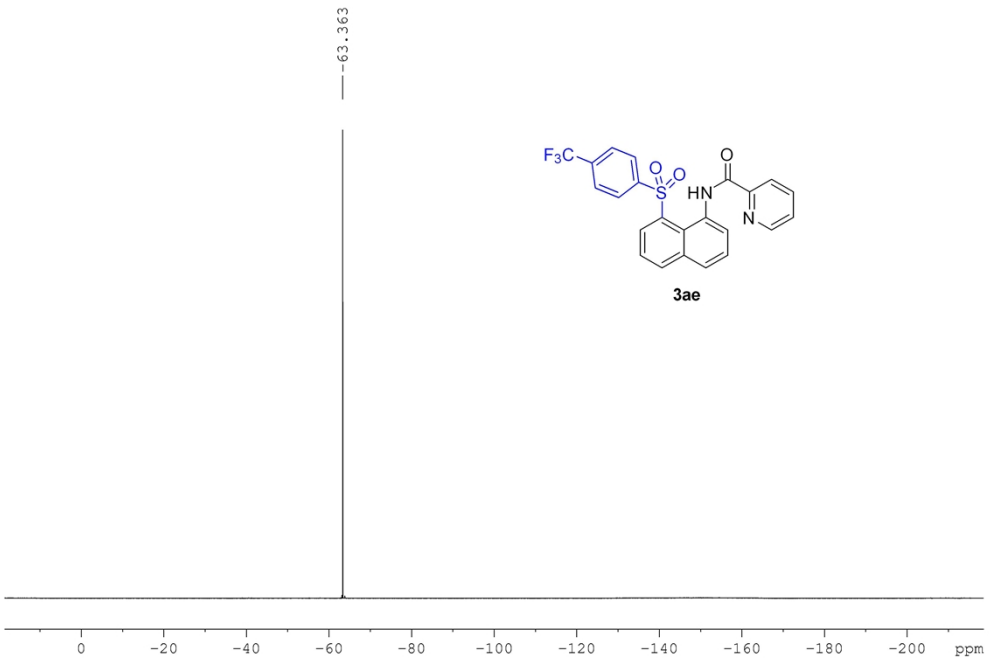

11.093
8.739
8.727
8.511
8.508
8.492
8.489
8.244
8.242
8.224
8.222
7.968
7.948
7.840
7.831
7.821
7.814
7.797
7.793
7.778
7.774
7.759
7.755
7.700
7.680
7.661
7.630
7.610
7.590
7.473
7.470
2.187
HN
O
S
N
3ad
ppm
1.000
1.038
1.007
1.003
1.040
2.079
1.046
1.057
1.062
1.043
2.113
2.040
3.006

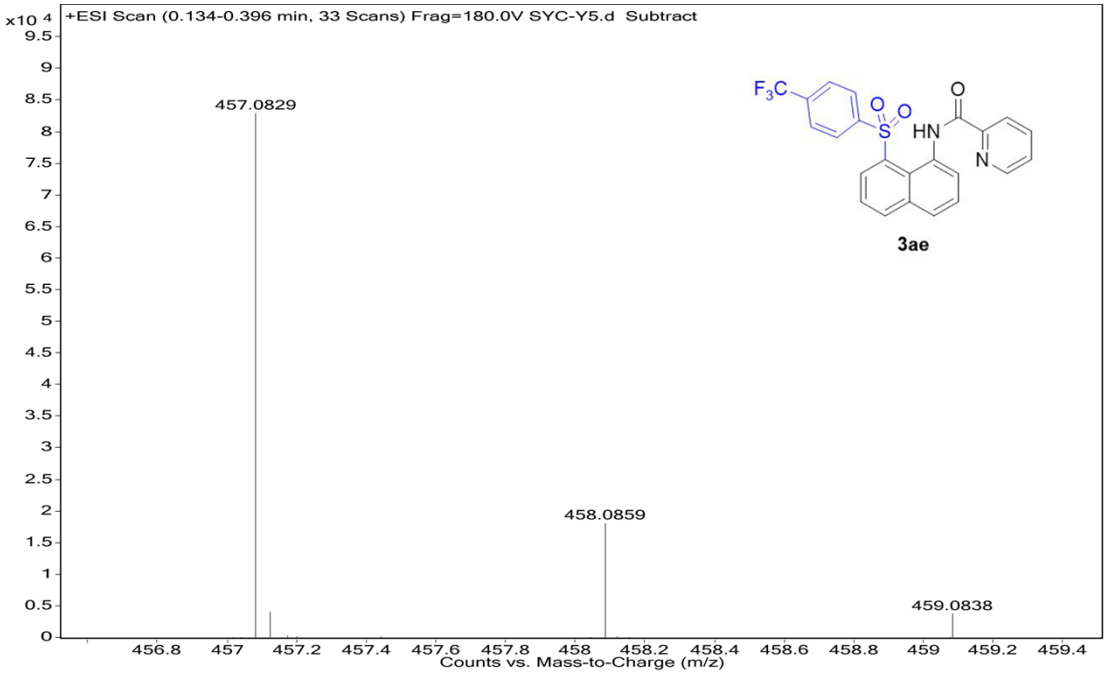

164.146
150.209
148.142
142.813
139.916
136.764
136.453
136.389
133.491
133.151
131.427
130.605
128.941
128.743
127.279
126.288
126.260
124.780
123.955
122.651
21.354
HN
O
S
N
3ad
ppm

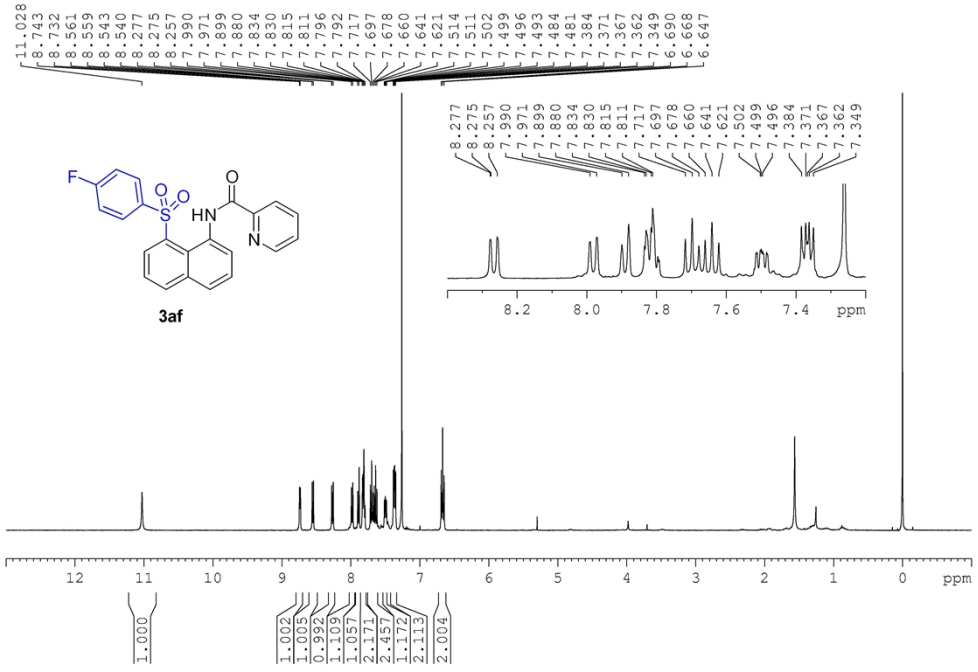

x10 3
+ESI Scan (0.145-0.383 min, 30 Scans) Frag=180.0V SYC-Y8.d Subtract
403.1108
404.1139
405.1116
Counts vs. Mass-to-Charge (m/z)
3ad

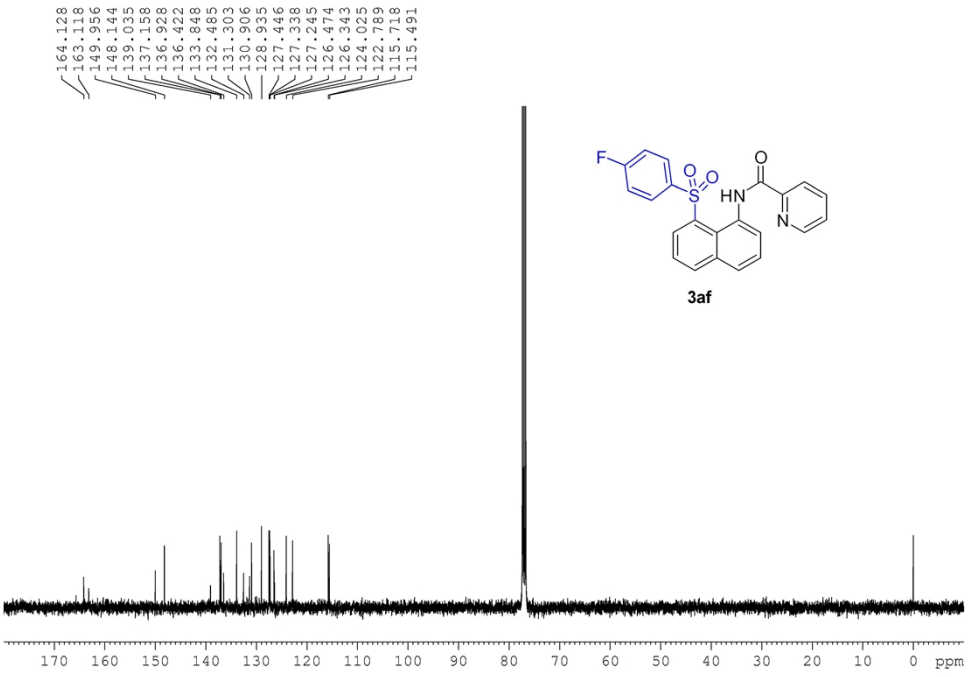

3ae
ppm

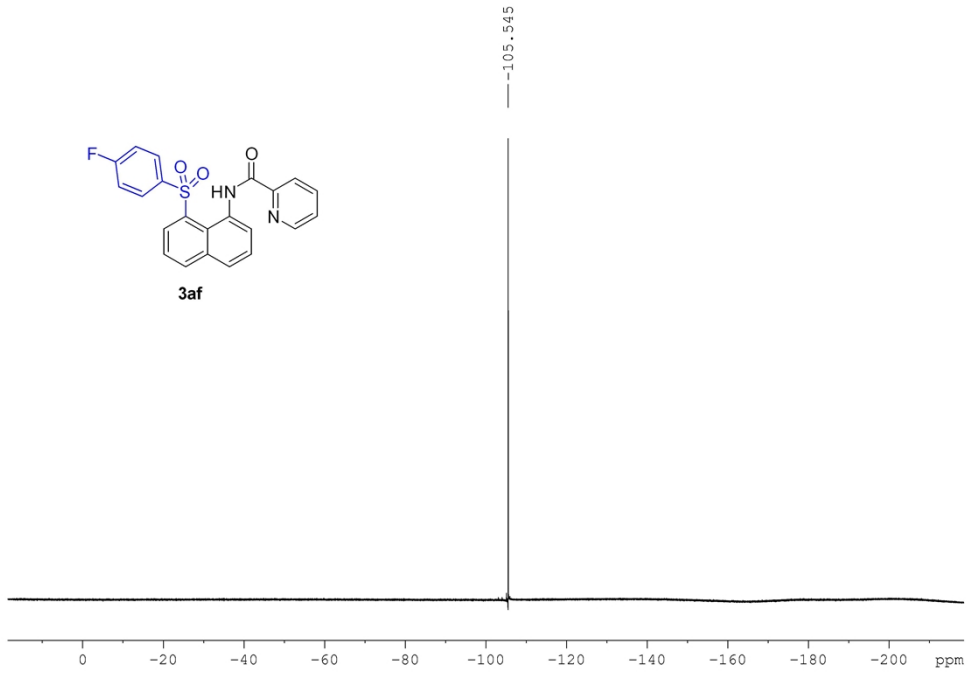

164.065
149.487
148.032
146.715
137.669
137.081
136.408
134.725
133.623
133.294
131.414
131.080
129.211
127.579
126.763
126.553
125.408
125.371
124.445
124.220
122.752
F3C
O
S
O
HN
O
N
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

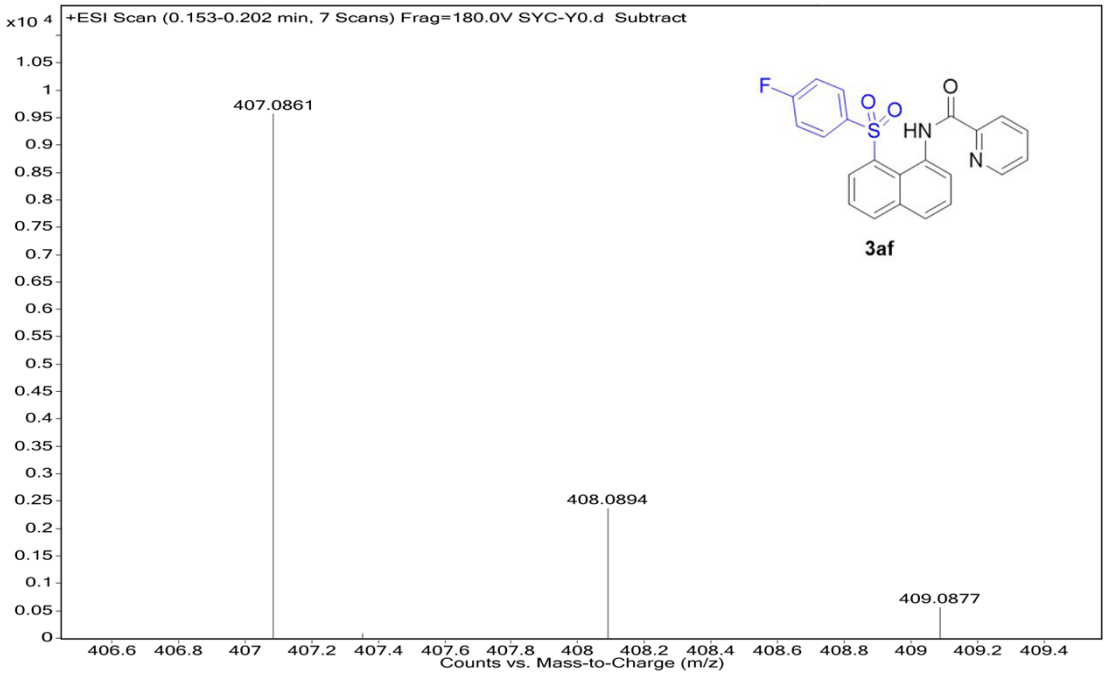

-63.363
F3C
O
S
O
HN
O
N
3ae
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

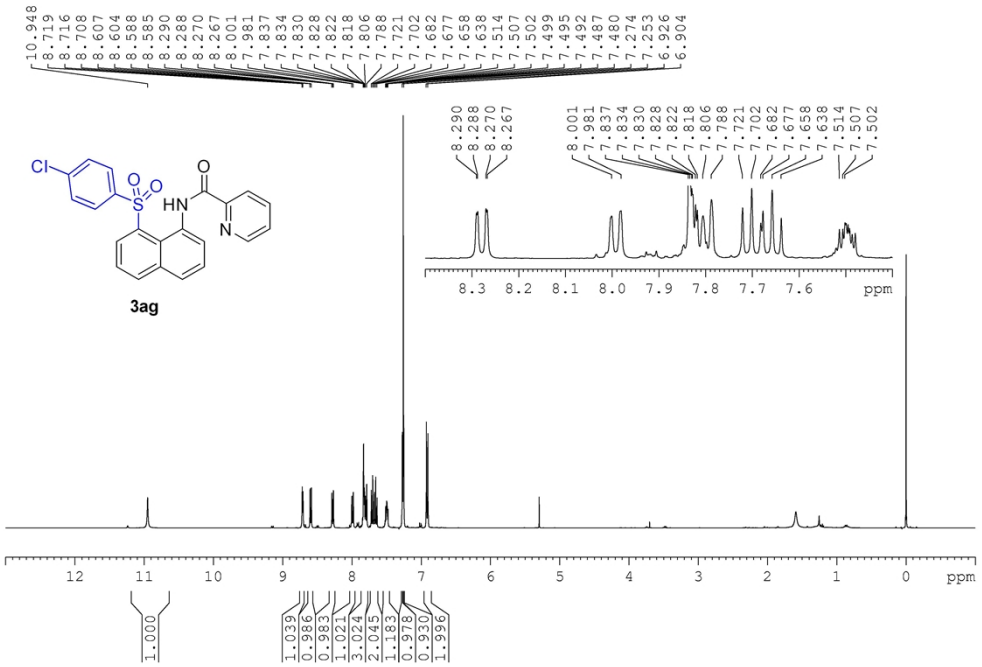

x10 4
+ESI Scan (0.134-0.396 min, 33 Scans) Frag=180.0V SYC-Y5.d Subtract
457.0829
458.0859
459.0838
Counts vs. Mass-to-Charge (m/z)
3ae

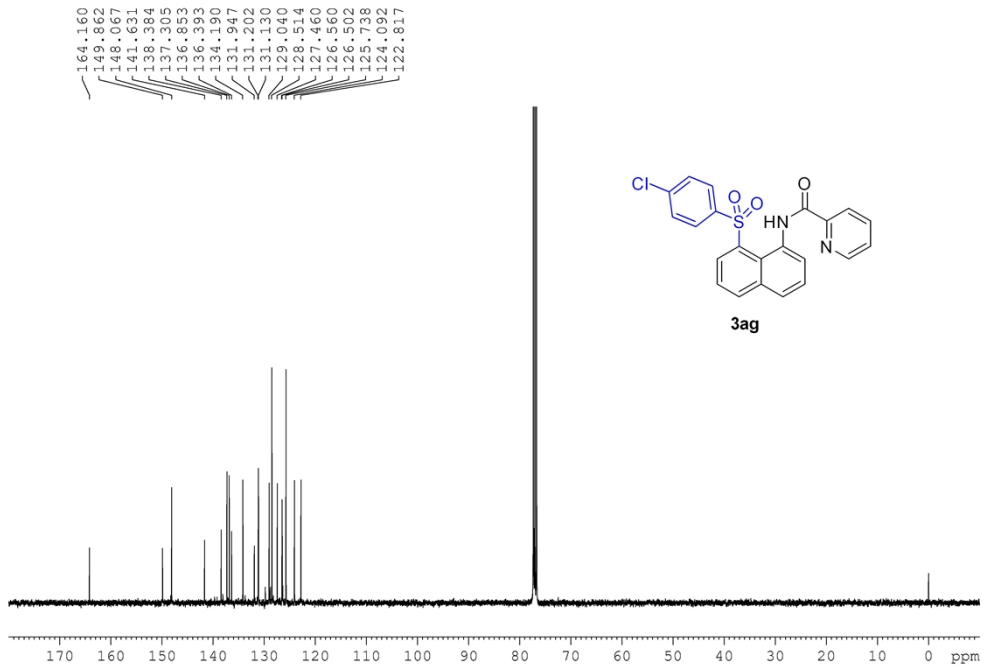

3af
ppm

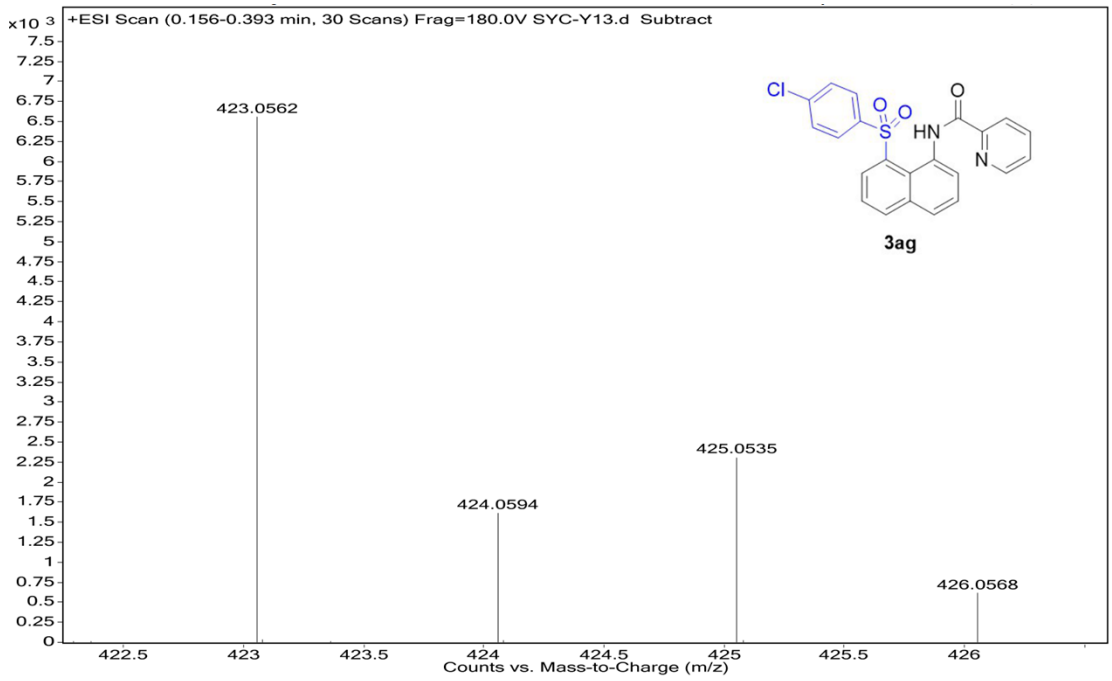

164.128
163.118
149.956
148.144
139.035
137.158
136.928
136.422
133.848
132.485
131.303
130.906
128.935
127.446
127.338
127.245
126.474
126.343
124.025
122.789
115.718
115.491
F
O
O
S
HN
O
N
3af
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

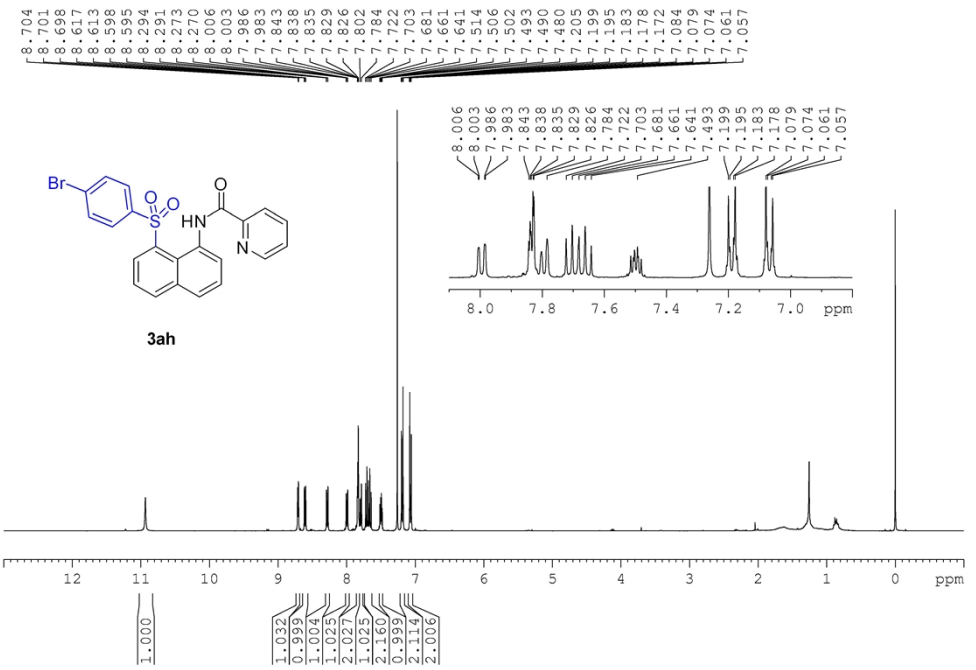

-105.545
F
O
O
S
HN
O
N
3af
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

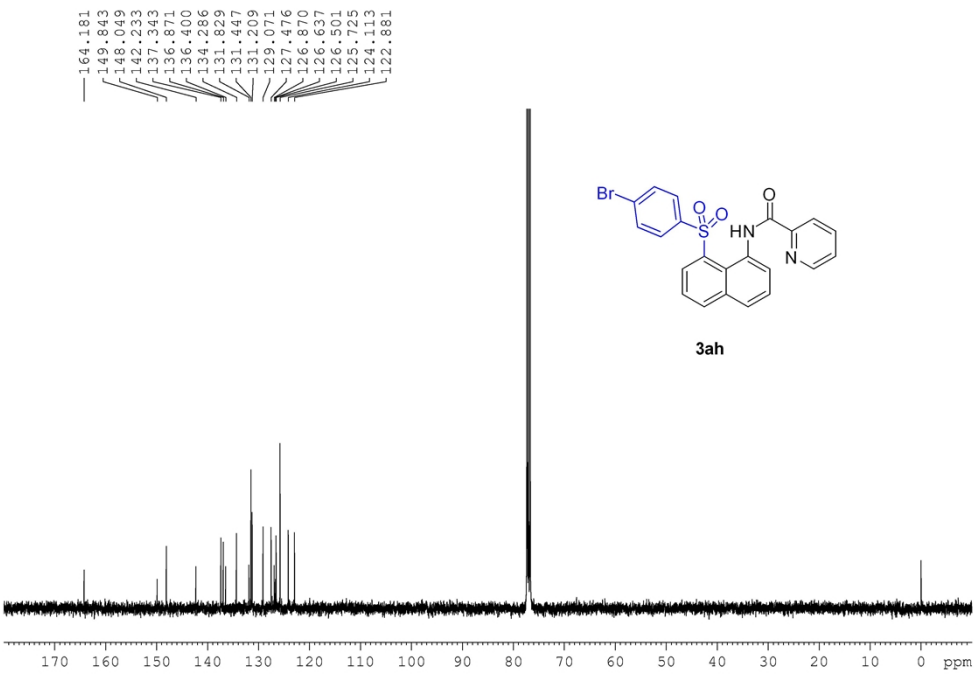

x10 4
+ESI Scan (0.153-0.202 min, 7 Scans) Frag=180.0V SYC-Y0.d Subtract
407.0861
408.0894
409.0877
Counts vs. Mass-to-Charge (m/z)
3af

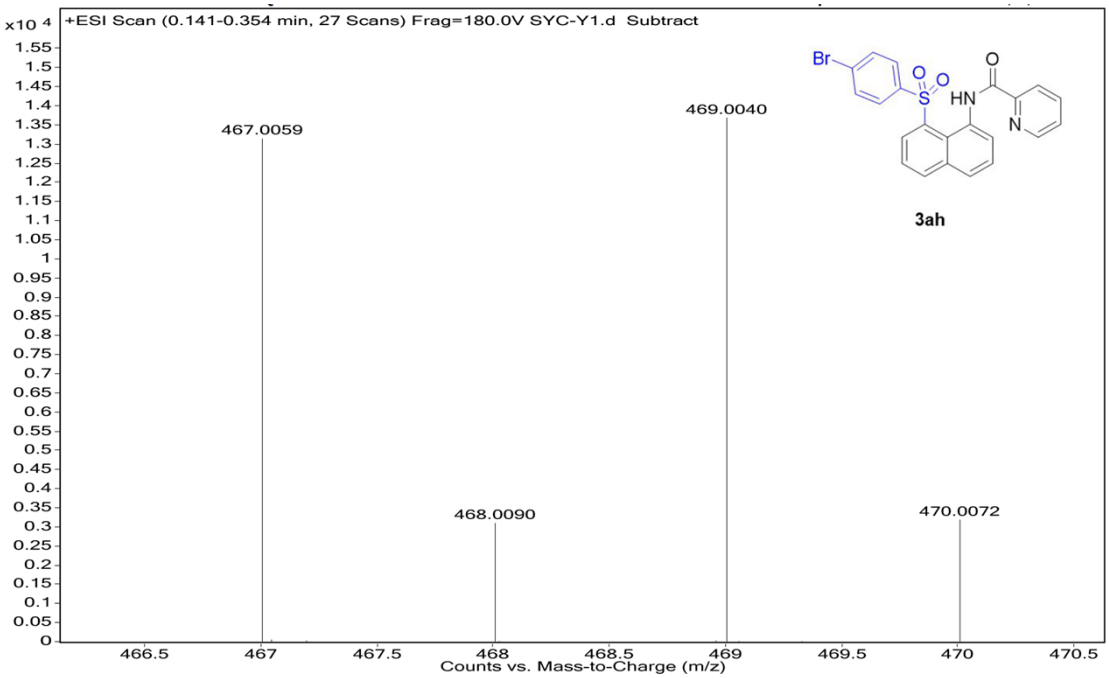

3ag
ppm

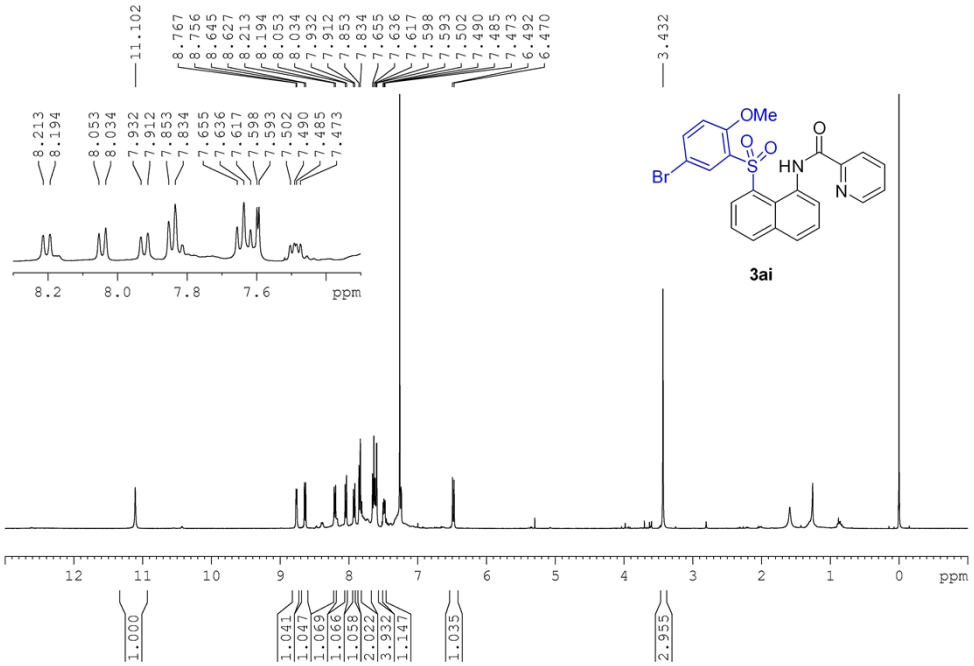

164.160
149.862
148.067
141.631
138.384
137.305
136.853
136.393
134.190
131.947
131.202
131.130
129.040
128.514
127.460
126.560
126.502
125.738
124.092
122.817
Cl
O
O
S
HN
O
N
3ag
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

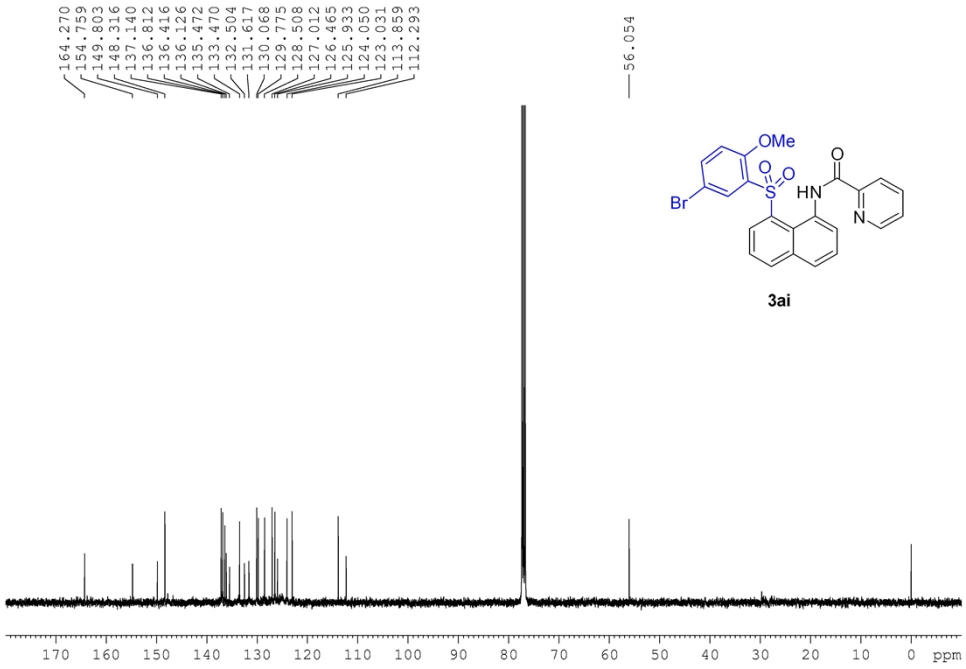

x10 3
+ESI Scan (0.156-0.393 min, 30 Scans) Frag=180.0V SYC-Y13.d Subtract
423.0562
424.0594
425.0535
426.0568
Cl
O
O
S
HN
O
N
3ag
Counts vs. Mass-to-Charge (m/z)

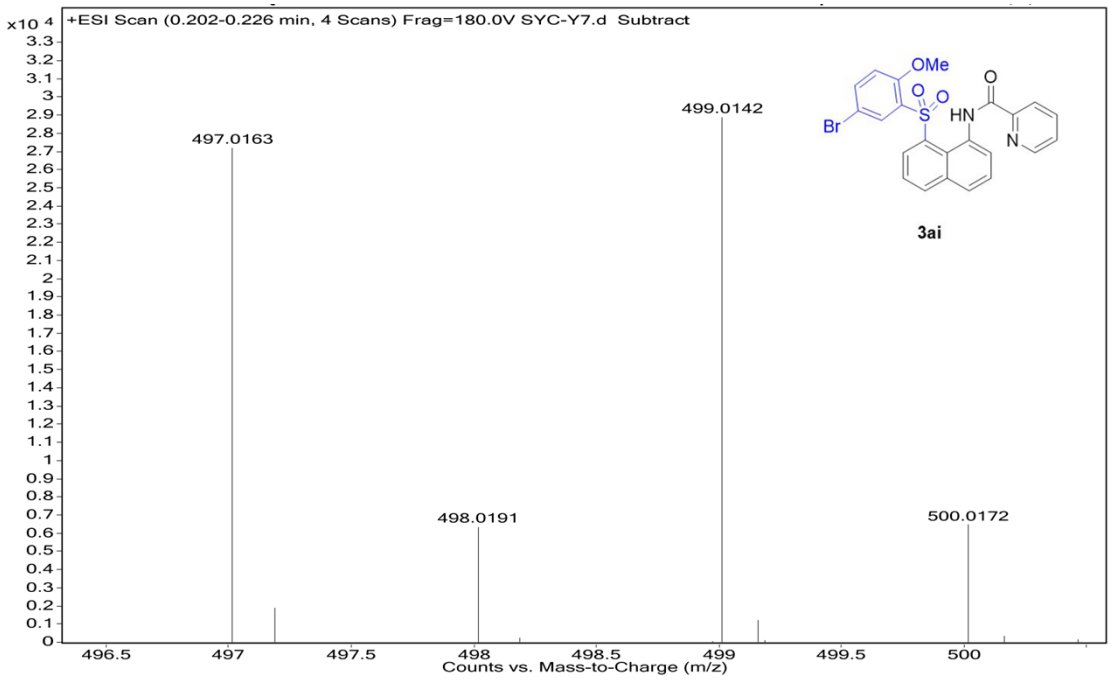

8.704
8.701
8.698
8.617
8.613
8.598
8.595
8.294
8.291
8.273
8.270
8.006
8.003
7.986
7.983
7.843
7.838
7.835
7.829
7.826
7.802
7.784
7.722
7.703
7.681
7.661
7.641
7.514
7.506
7.502
7.493
7.490
7.480
7.205
7.199
7.195
7.183
7.178
7.172
7.084
7.079
7.074
7.061
7.057
Br
O
S
O
HN
O
N
3ah
8.0
7.8
7.6
7.4
7.2
7.0
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.032
0.999
1.004
1.025
2.027
1.025
2.160
0.999
2.114
2.006

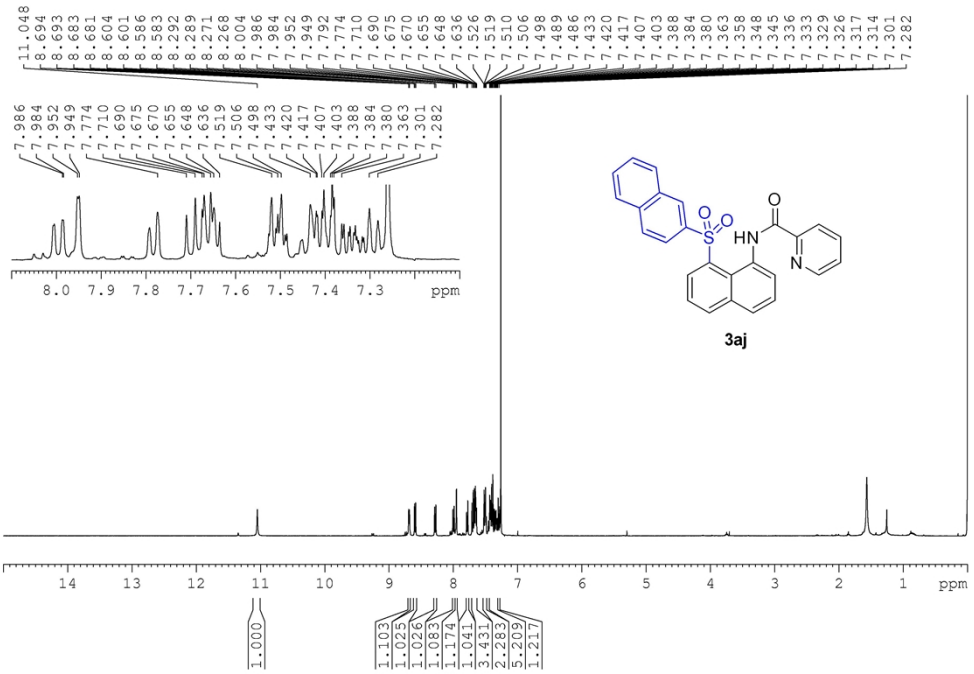

164.181
149.843
148.049
142.233
137.343
136.871
136.400
134.286
131.829
131.447
131.209
129.071
127.476
126.870
126.637
126.501
125.725
124.113
122.881
Br
O
S
O
HN
O
N
3ah
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

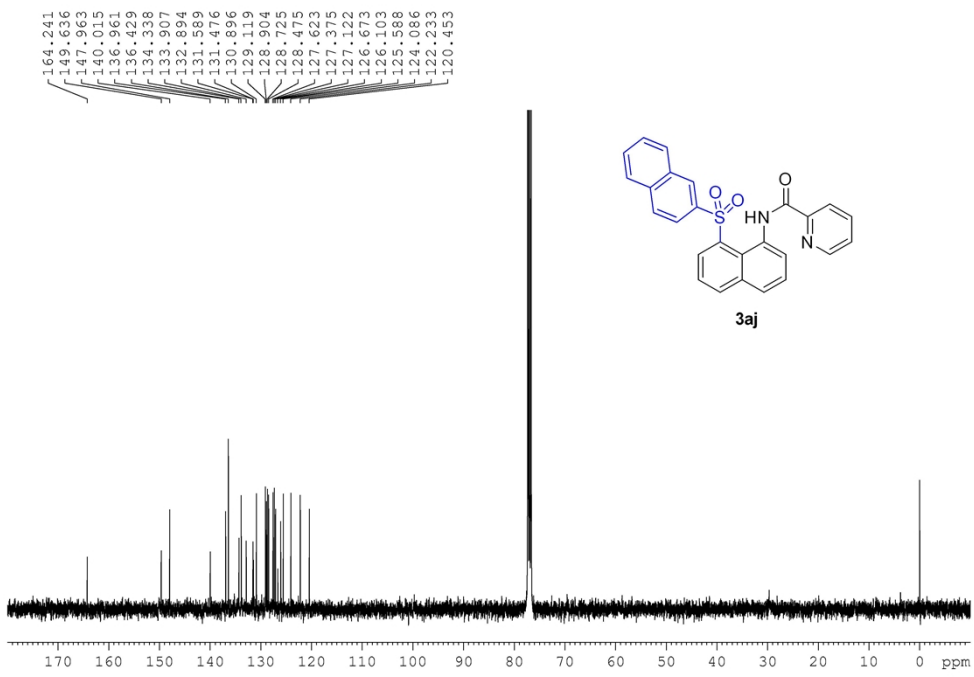

+ESI Scan (0.141-0.354 min, 27 Scans) Frag=180.0V SYC-Y1.d Subtract
x10 4
467.0059
468.0090
469.0040
470.0072
Counts vs. Mass-to-Charge (m/z)
3ah

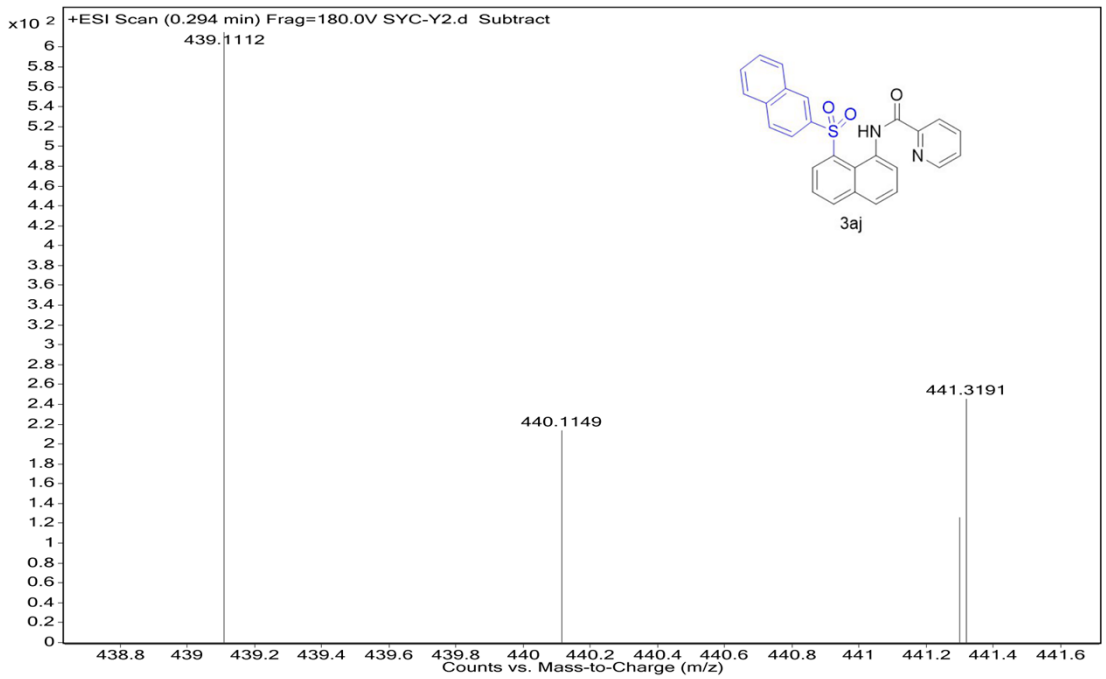

11.102
3.432
3ai
ppm

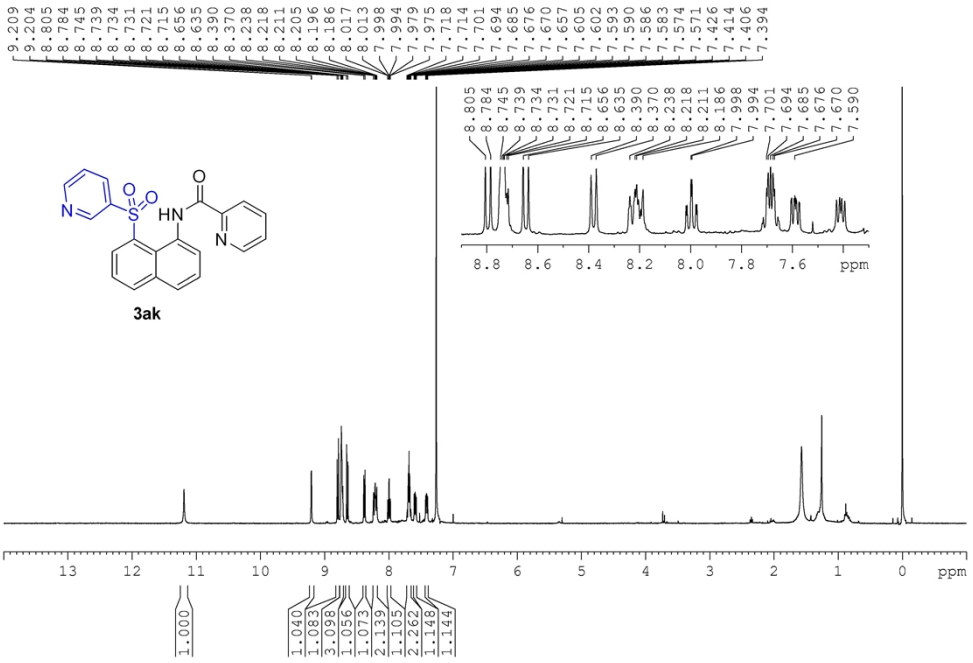

164.270
154.759
149.803
148.316
137.140
136.812
136.416
136.126
135.472
133.470
132.504
131.617
130.068
129.775
128.508
127.012
126.465
125.933
124.050
123.031
113.859
112.293
56.054
OMe
Br
S
O
O
HN
O
N
3ai
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

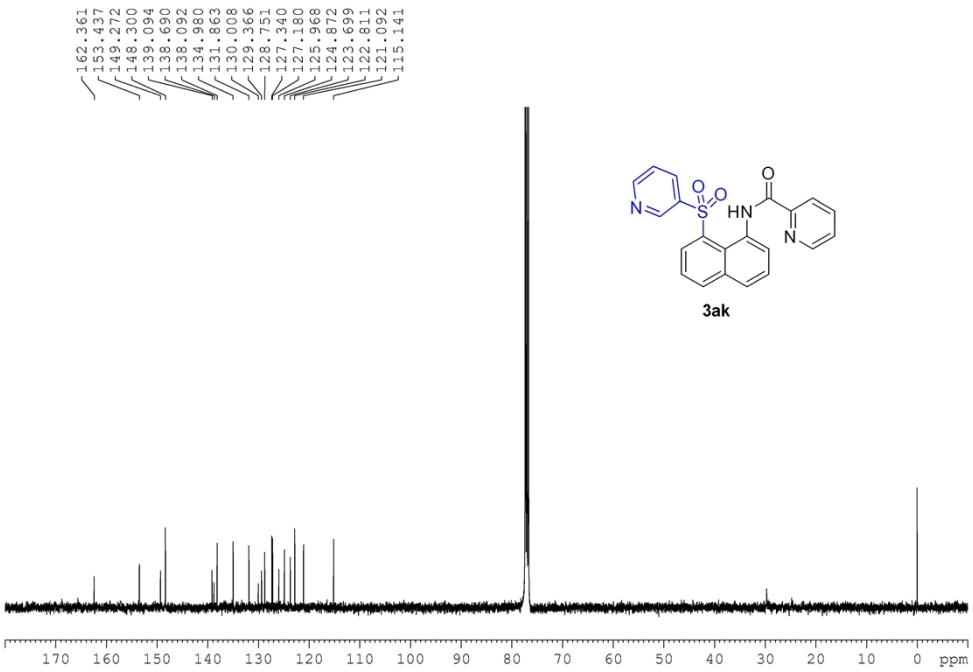

+ESI Scan (0.202-0.226 min, 4 Scans) Frag=180.0V SYC-Y7.d Subtract
x10 4
497.0163
498.0191
499.0142
500.0172
OMe
Br
S
O
O
HN
O
N
3ai
Counts vs. Mass-to-Charge (m/z)

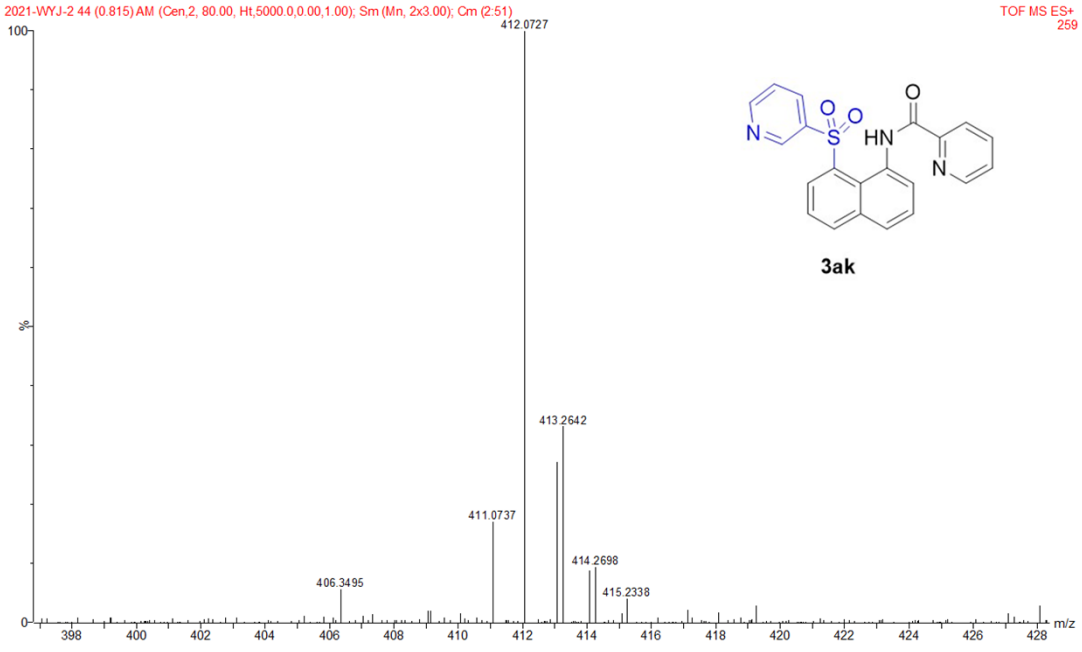

11.048
8.694
8.693
8.683
8.681
8.604
8.601
8.586
8.583
8.292
8.289
8.271
8.268
8.004
7.986
7.984
7.952
7.949
7.792
7.774
7.710
7.690
7.675
7.670
7.655
7.648
7.636
7.526
7.519
7.510
7.506
7.498
7.489
7.486
7.433
7.420
7.417
7.407
7.403
7.388
7.384
7.380
7.363
7.358
7.348
7.345
7.336
7.333
7.329
7.326
7.317
7.314
7.301
7.282
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.000
1.103
1.025
1.026
1.083
1.174
1.041
3.431
2.283
5.209
1.217
3aj

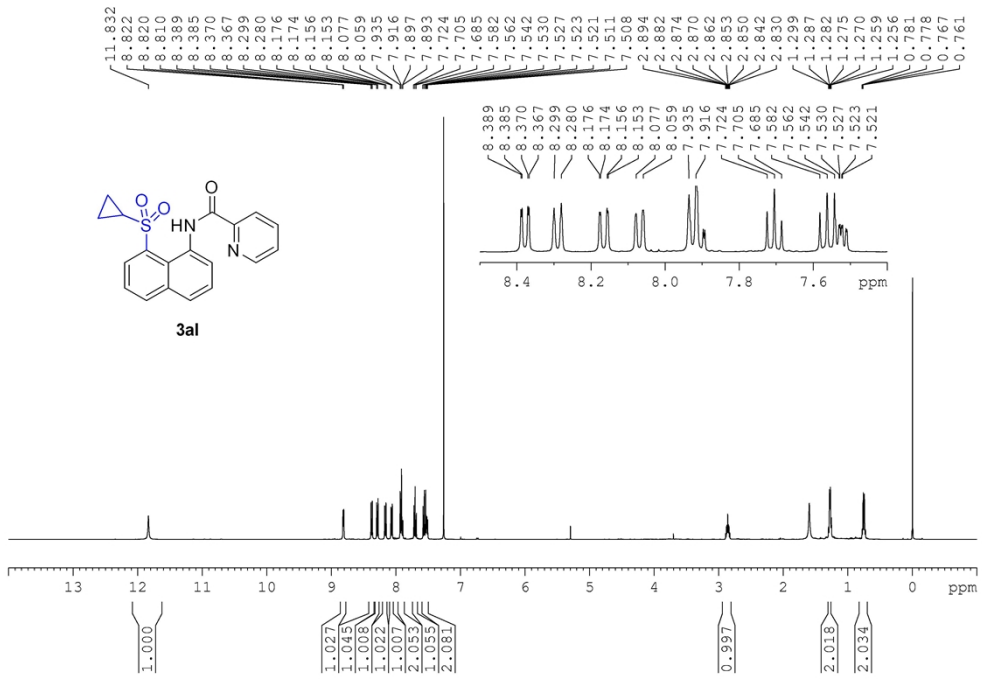

164.241
149.636
147.963
140.015
136.961
136.429
134.338
133.907
132.894
131.589
131.476
130.896
129.119
128.904
128.725
128.475
127.623
127.375
127.122
126.673
126.103
125.588
124.086
122.233
120.453
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
3aj


+ESI Scan (0.294 min) Frag=180.0V SYC-Y2.d Subtract
439.1112
440.1149
441.3191
3aj
Counts vs. Mass-to-Charge (m/z)

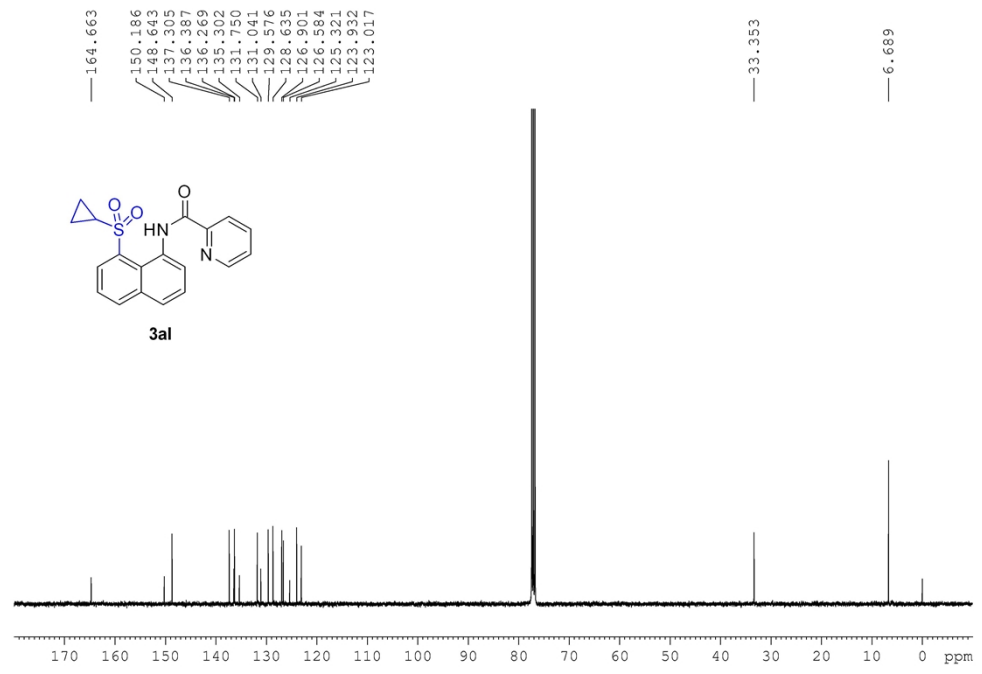

3ak
ppm


162.361
153.437
149.272
148.300
139.094
138.690
138.092
134.980
131.863
130.008
129.366
128.751
127.340
127.180
125.968
124.872
123.699
122.811
121.092
115.141
3ak
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

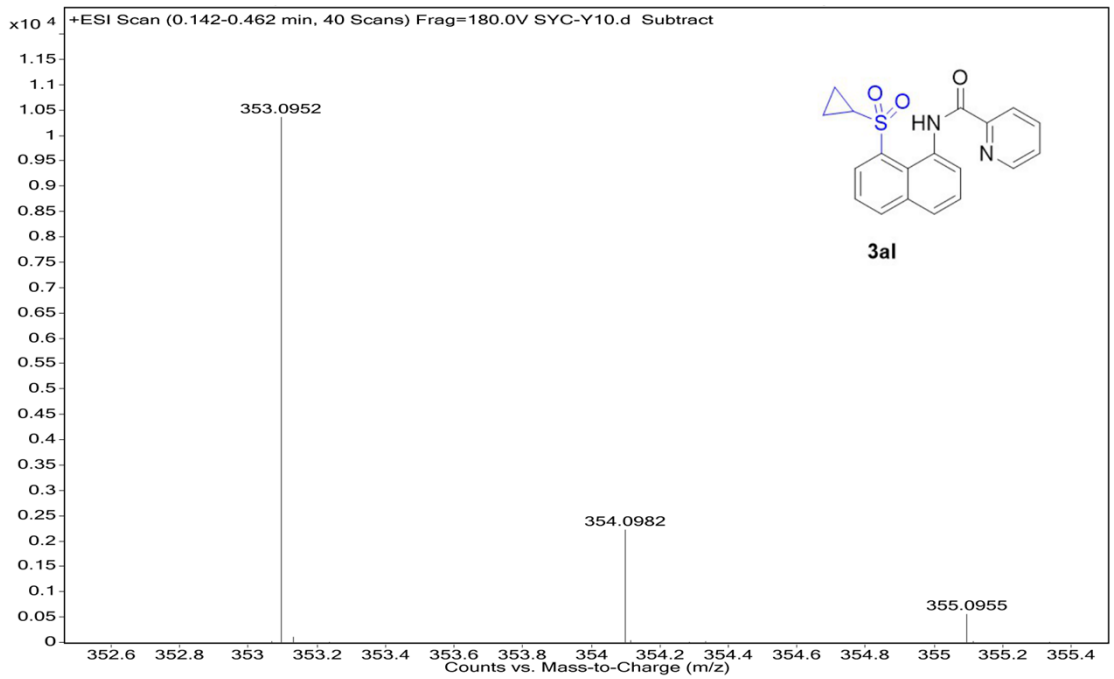

2021-WYJ-2 44 (0.815) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (2:51)
TOF MS ES+
259
412.0727
413.2642
411.0737
414.2698
406.3495
415.2338
3ak
100
%
0
398 400 402 404 406 408 410 412 414 416 418 420 422 424 426 428 m/z

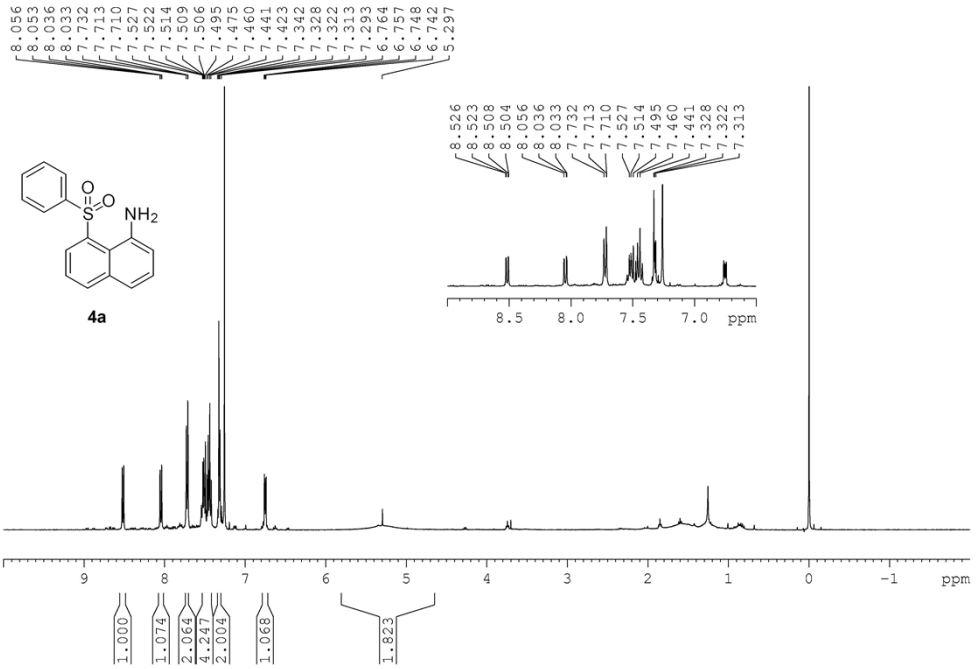

11.832
8.822
8.820
8.810
8.389
8.385
8.370
8.367
8.299
8.280
8.176
8.174
8.156
8.153
8.077
8.059
7.935
7.916
7.897
7.893
7.724
7.705
7.685
7.582
7.562
7.542
7.530
7.527
7.523
7.521
7.511
7.508
2.894
2.882
2.874
2.870
2.862
2.853
2.850
2.842
2.830
1.299
1.287
1.282
1.275
1.270
1.259
1.256
0.781
0.778
0.767
0.761
8.4
8.2
8.0
7.8
7.6
ppm
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.027
1.045
1.008
1.022
1.007
2.053
1.055
2.081
0.997
2.018
2.034

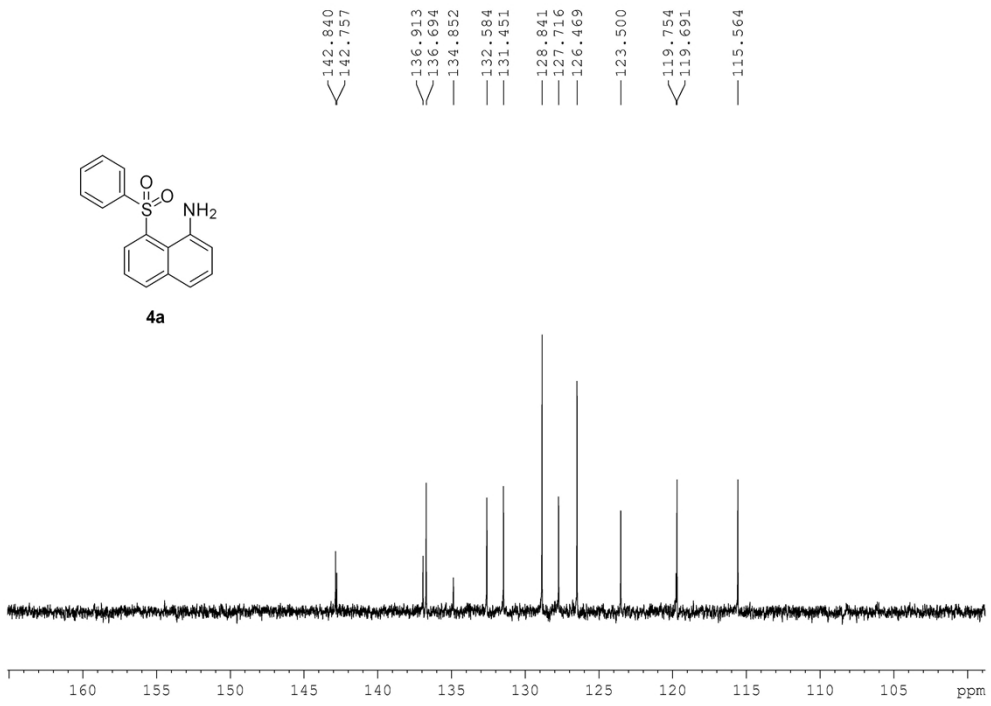
3al


164.663
150.186
148.643
137.305
136.387
136.269
135.302
131.750
131.041
129.576
128.635
126.901
126.584
125.321
123.932
123.017
33.353
6.689
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

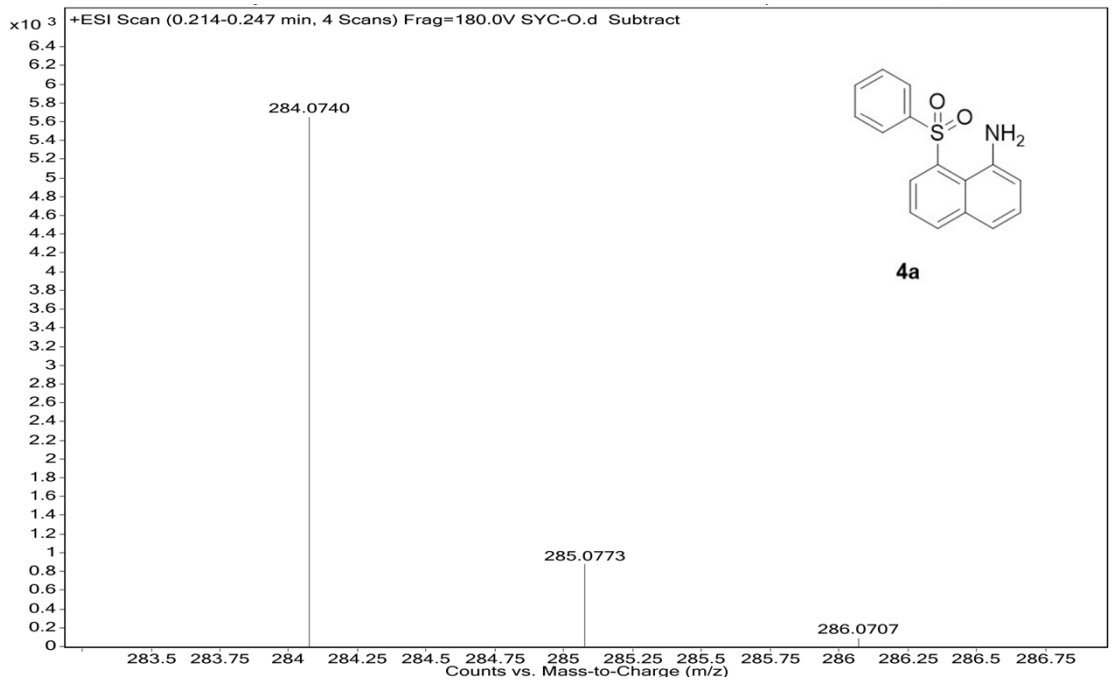
3al


x10 4
+ESI Scan (0.142-0.462 min, 40 Scans) Frag=180.0V SYC-Y10.d Subtract
353.0952
354.0982
355.0955
Counts vs. Mass-to-Charge (m/z)
3al

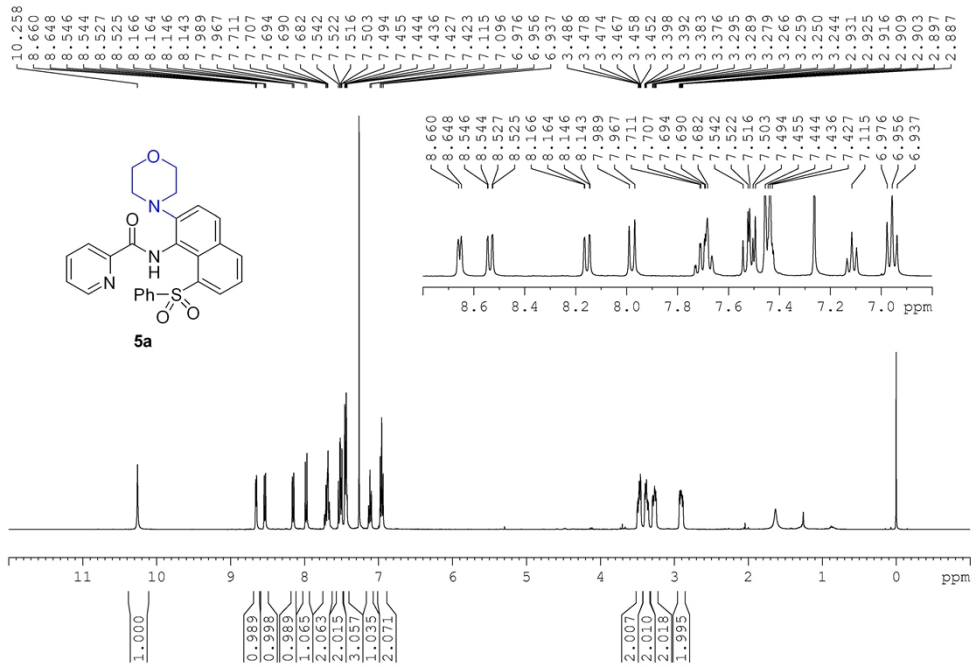

4a
ppm

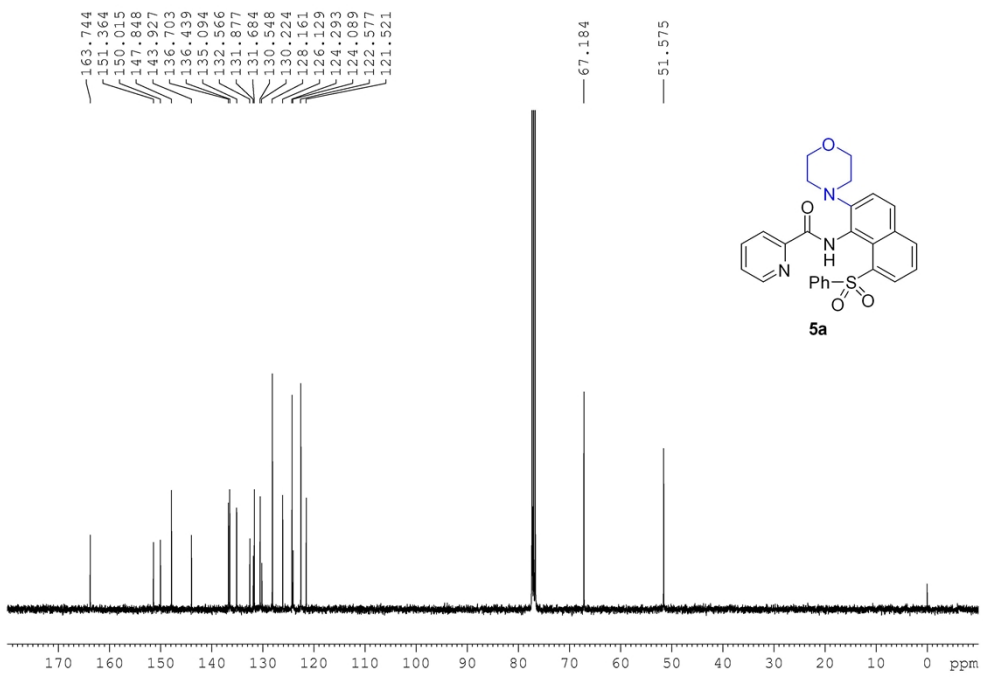

142.840
142.757
136.913
136.694
134.852
132.584
131.451
128.841
127.716
126.469
123.500
119.754
119.691
115.564
O
S
O
NH2
160
155
150
145
140
135
130
125
120
115
110
105
ppm

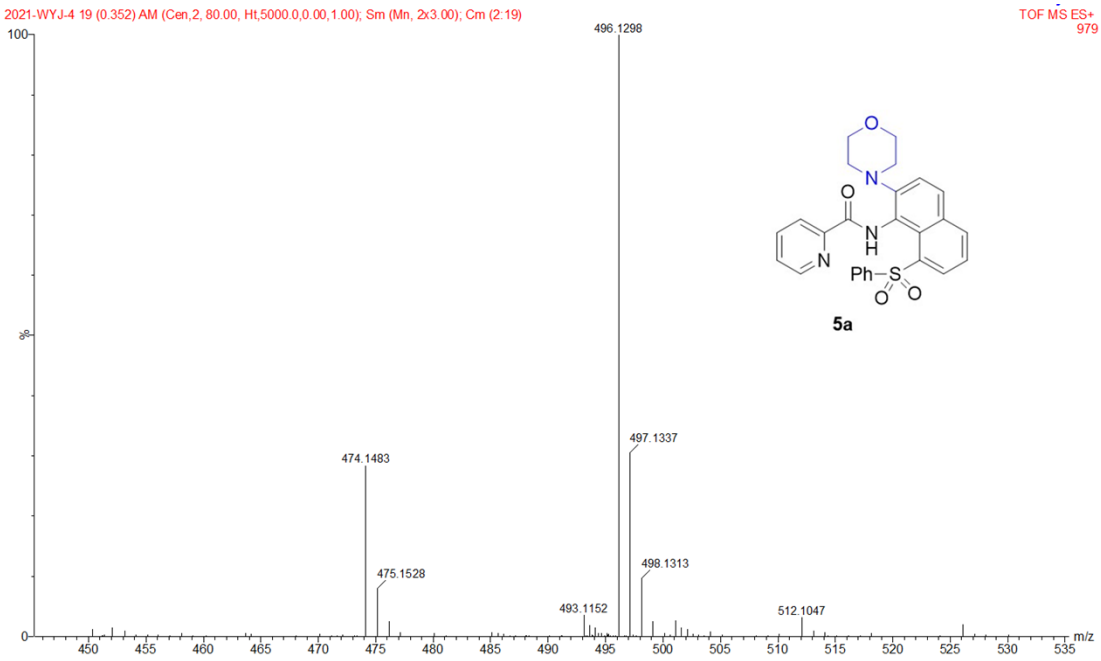
**4a**

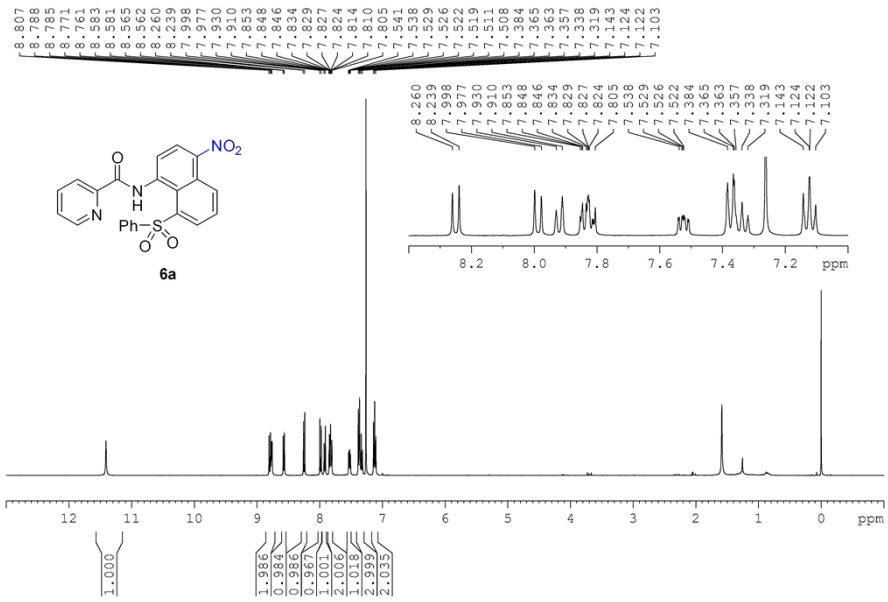

x10 3
+ESI Scan (0.214-0.247 min, 4 Scans) Frag=180.0V SYC-O.d Subtract
284.0740
285.0773
286.0707
O
S
O
NH2
283.5
283.75
284
284.25
284.5
284.75
285
285.25
285.5
285.75
286
286.25
286.5
286.75
Counts vs. Mass-to-Charge (m/z)

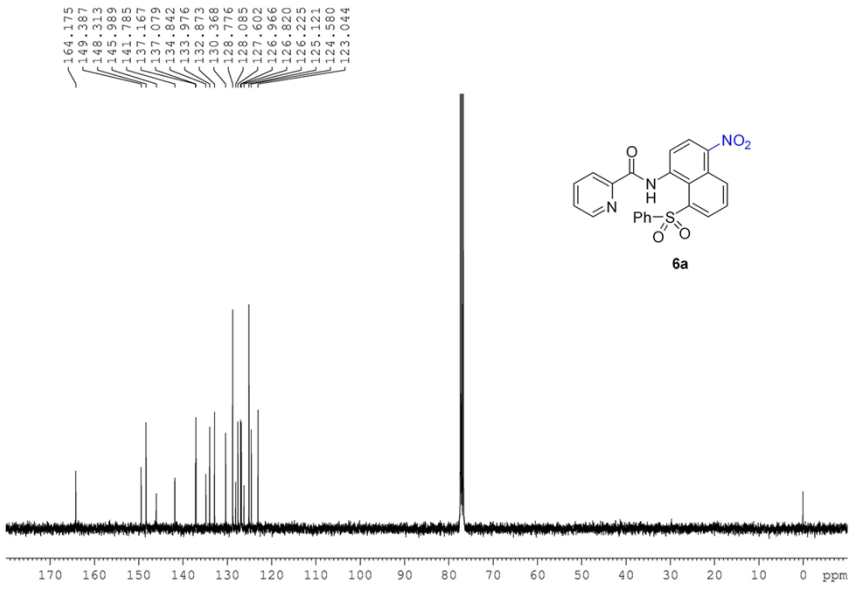
**4a**

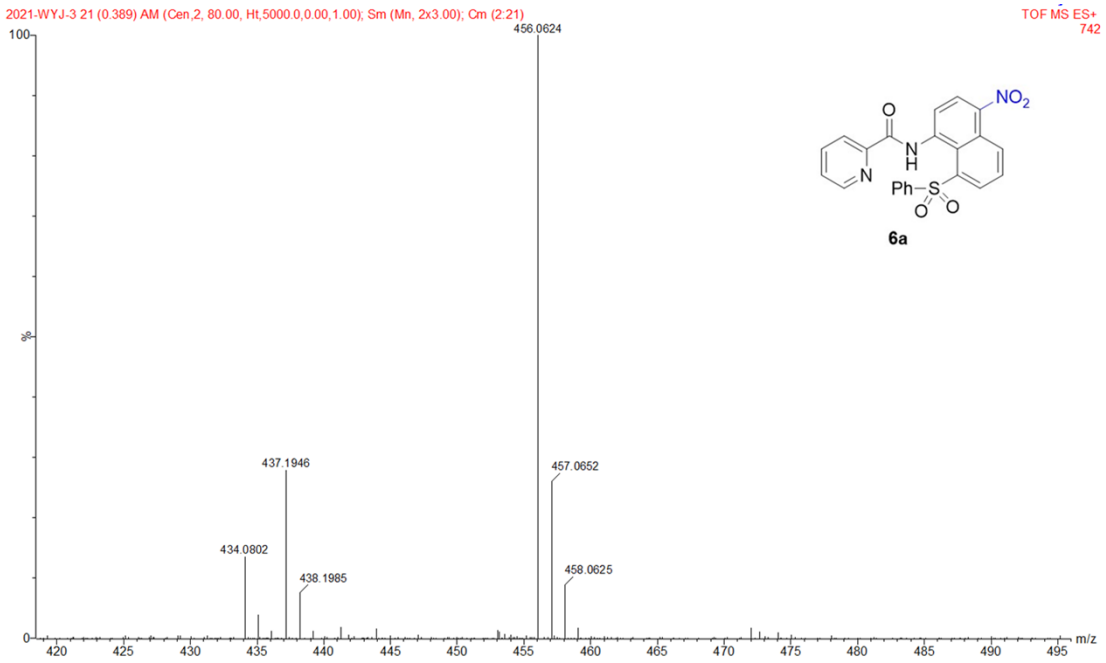

10.258
8.660
8.648
8.546
8.544
8.527
8.525
8.166
8.164
8.146
8.143
7.989
7.967
7.711
7.707
7.694
7.690
7.682
7.542
7.522
7.516
7.503
7.494
7.455
7.444
7.436
7.427
7.423
7.115
7.096
6.976
6.956
6.937
3.486
3.478
3.474
3.467
3.458
3.452
3.398
3.392
3.383
3.376
3.295
3.289
3.279
3.266
3.259
3.250
3.244
2.931
2.925
2.916
2.909
2.903
2.897
2.887
5a
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
0.989
0.998
0.989
1.065
2.063
2.015
3.057
1.035
2.071
2.007
2.010
2.018
1.995

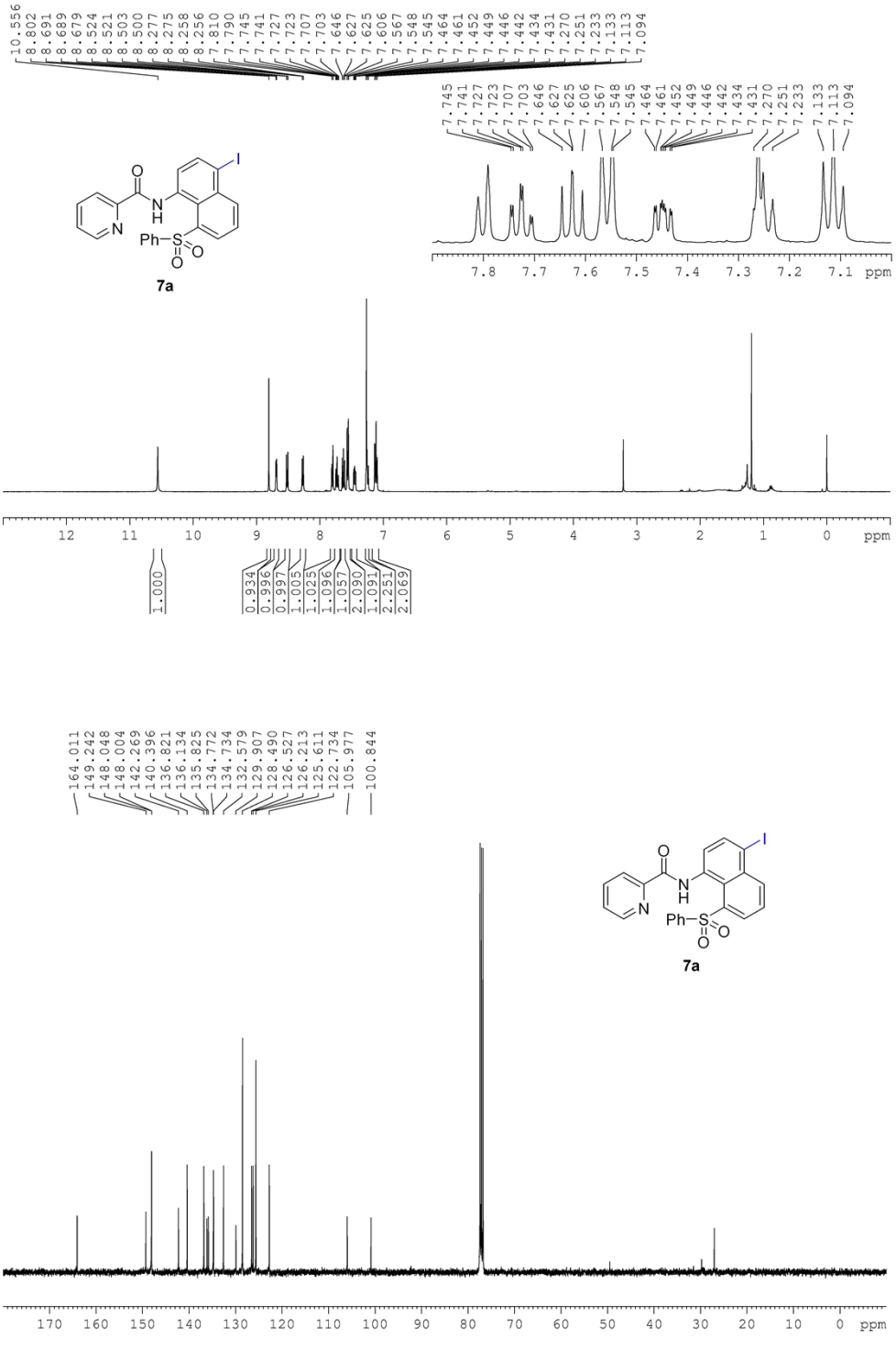

163.744
151.364
150.015
147.848
143.927
136.703
136.439
135.094
132.566
131.877
131.684
130.548
130.224
128.161
126.129
124.293
124.089
122.577
121.521
67.184
51.575
5a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

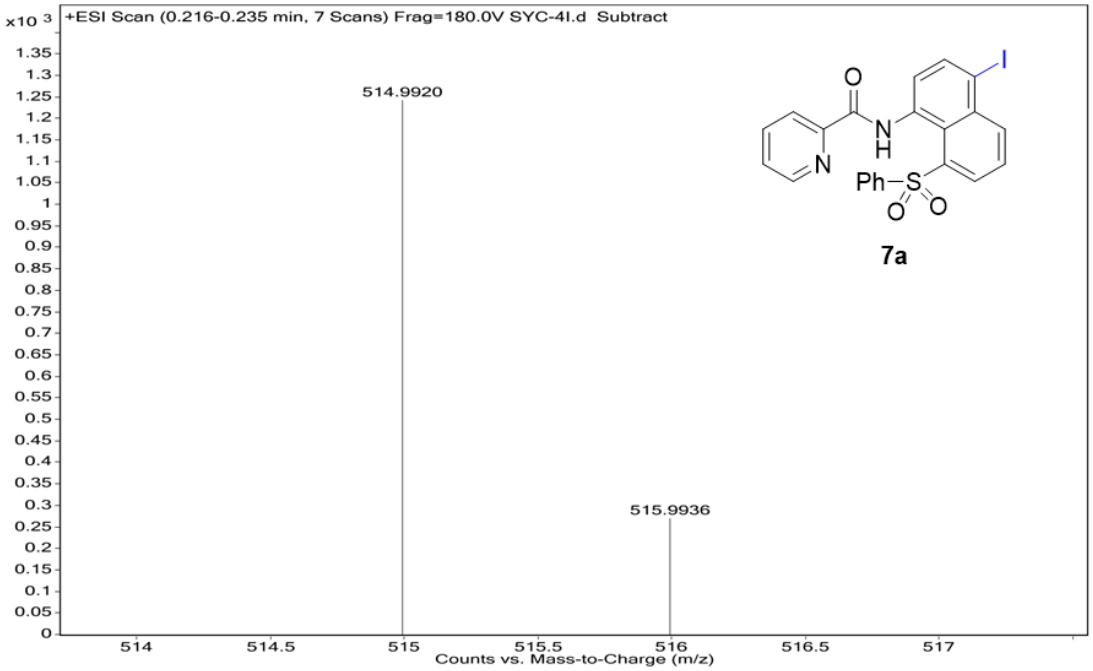

2021-WYJ-4 19 (0.352) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (2:19)
TOF MS ES+
979
496.1298
497.1337
474.1483
475.1528
498.1313
493.1152
512.1047
%
m/z
5a

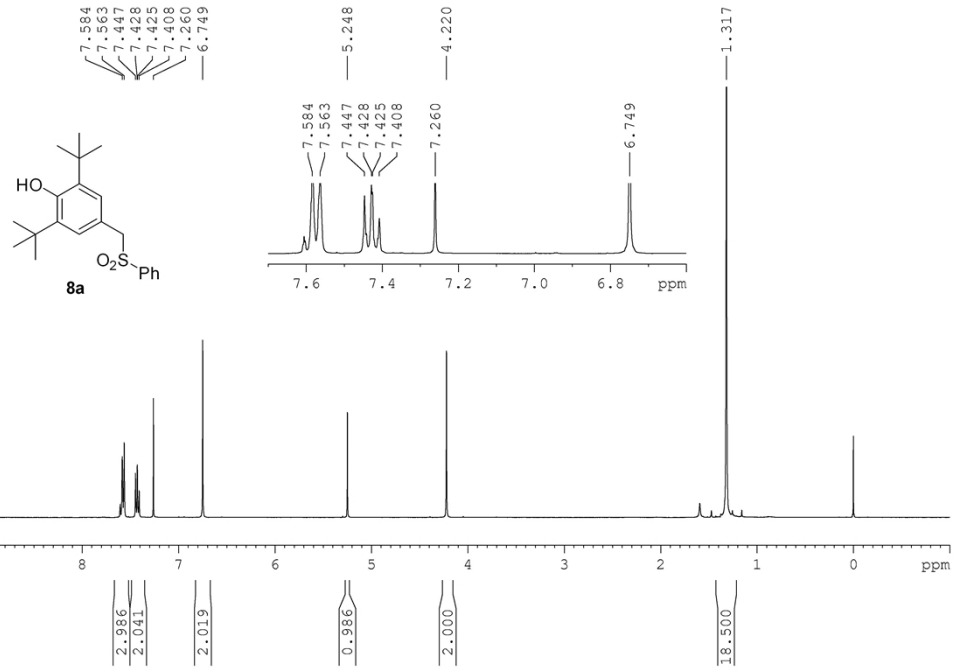

6a
ppm

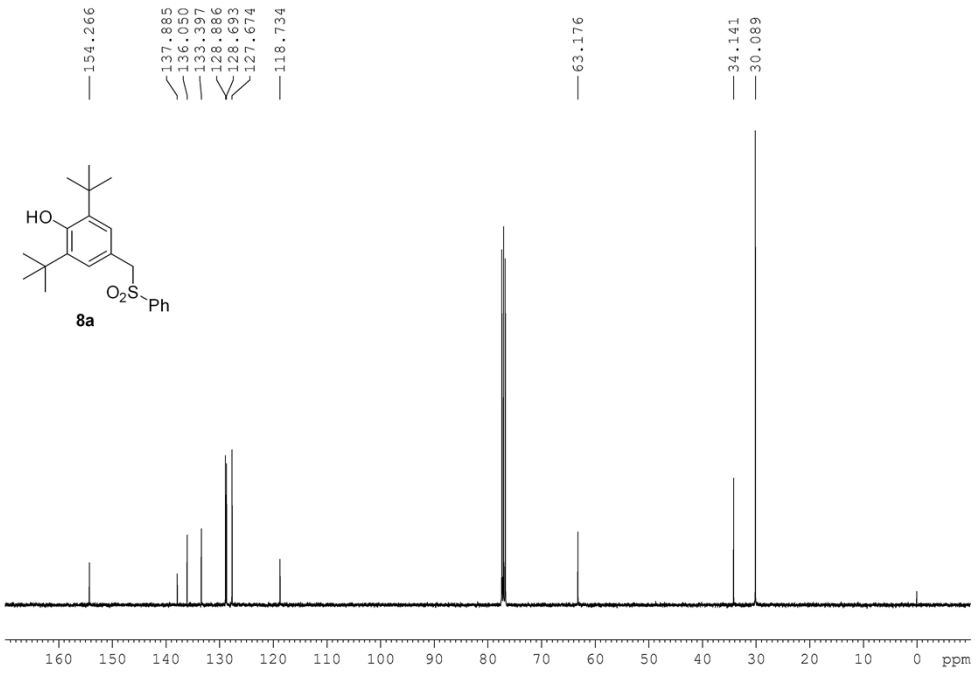

164.175
149.387
148.313
145.989
141.785
137.167
137.079
134.842
133.976
132.873
130.368
128.776
128.085
127.602
126.966
126.820
126.225
125.121
124.580
123.044
NO2
O
N
H
N
Ph–S
O
O
6a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


2021-WYJ-3 21 (0.389) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (2:21)
TOF MS ES+
742
456.0624
NO2
O
N
H
N
Ph–S
O
O
6a
100
%
0
437.1946
457.0652
434.0802
438.1985
458.0625
420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 m/z


10.556
8.802
8.691
8.689
8.679
8.524
8.521
8.503
8.500
8.277
8.275
8.258
8.256
7.810
7.790
7.745
7.741
7.727
7.723
7.707
7.703
7.646
7.627
7.625
7.606
7.567
7.548
7.545
7.464
7.461
7.452
7.449
7.446
7.442
7.434
7.431
7.270
7.251
7.233
7.133
7.113
7.094
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
7a
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
0.934
0.996
0.997
1.005
1.025
1.096
1.057
2.090
1.091
2.251
2.069
164.011
149.242
148.048
148.004
142.269
140.396
136.821
136.134
135.825
134.772
134.734
132.579
129.907
128.490
126.527
126.213
125.611
122.734
105.977
100.844
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
7a


+ESI Scan (0.216-0.235 min, 7 Scans) Frag=180.0V SYC-4I.d Subtract
x10 3
514.9920
515.9936
Counts vs. Mass-to-Charge (m/z)
7a


7.584
7.563
7.447
7.428
7.425
7.408
7.260
6.749
5.248
4.220
1.317
8a
ppm
2.986
2.041
2.019
0.986
2.000
18.500


154.266
137.885
136.050
133.397
128.886
128.693
127.674
118.734
63.176
34.141
30.089
HO
O2S
Ph
8a
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm