

Electronic Supplementary Information

Table of contents

I. General Information.....	S2
II. Experimental Section.....	S2
III. References and Notes.....	S16
IV. ^1H and ^{13}C NMR Spectra.....	S17

I. General Information

All the solvents and commercially available reagents were purchased from commercial sources and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III–400 or 300 spectrometer. ^1H NMR data were reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data were reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and reported as wave number (cm^{-1}). Mass (MS) analysis was obtained using SHIMADZU-2020 LC/MS system with Electrospray Ionization (ESI).

II. Experimental Section

Synthesis of starting materials:

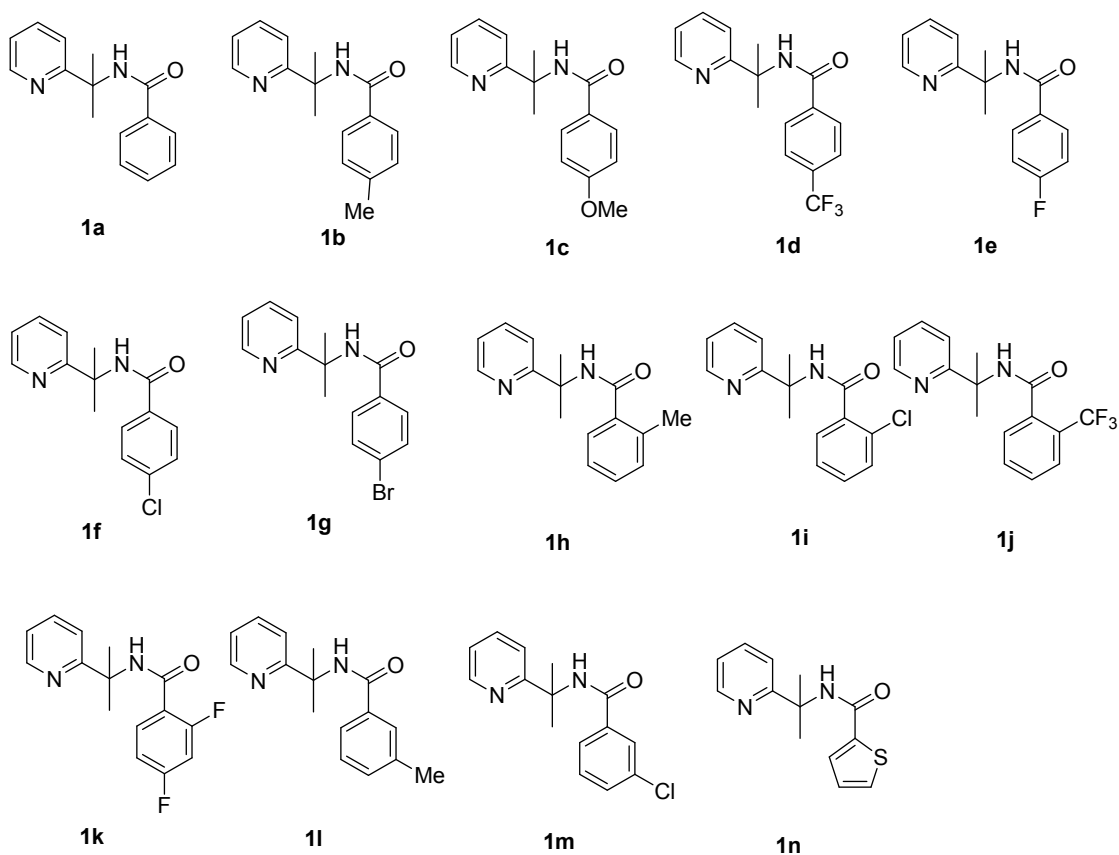


Figure 1 Benzamides (**1**)

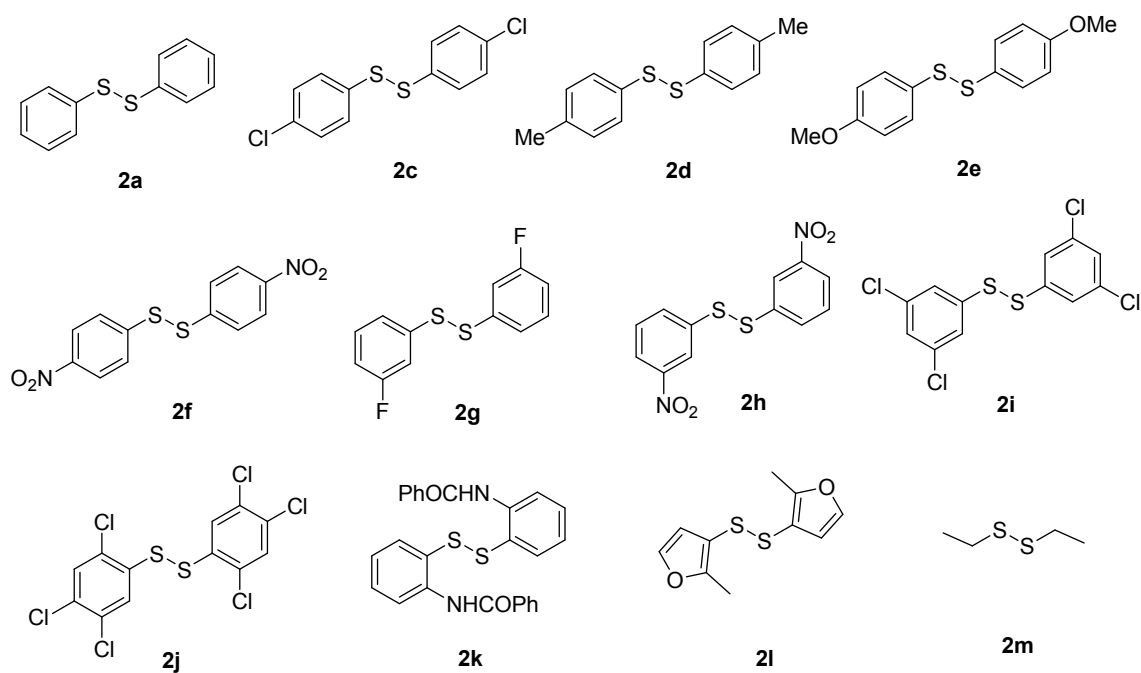


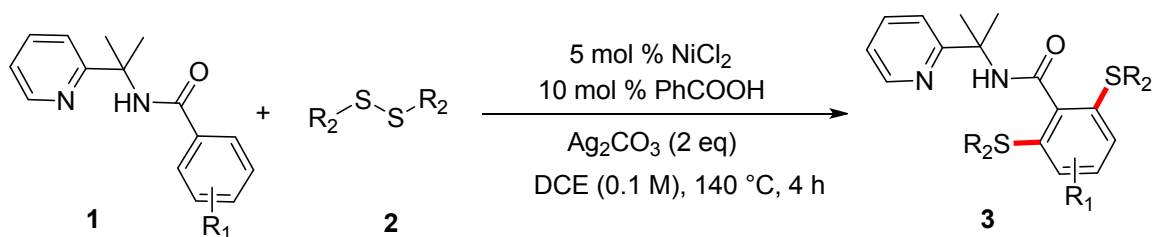
Figure 2 Disulfides (**2**)

Benzamides (**1**) were prepared from 2-(pyridine-2-yl)-isopropylamine and the corresponding benzaldehydes according to the reported procedure.¹⁻³ Disulfides (**2**) were all purchased from Adamas-beta, TCI or J&K@.

Optimization of the reaction conditions

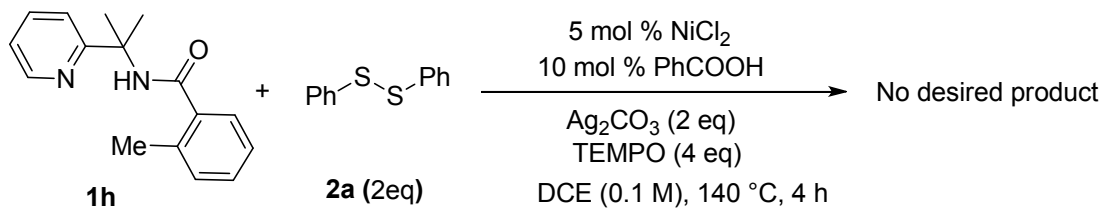
A 35 mL oven-dried pressure tube was charged with benzamides **1a** (0.2 mmol), diphenyl disulfide (0.6 mmol), Ni source (0.005 - 0.01 mmol), ligand (0.02 mmol), additives (0.2 - 0.4 mmol), and solvent (2.0 mL). The tube was then sealed and stirred vigorously at 120-140 °C for 4-10 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of celite. The filtrate was concentrated in *vacuo*, and the crude product was analyzed by ¹H NMR in CDCl₃. Yields and conversions are based on **1a**, determined by crude ¹H NMR using dibromomethane as the internal standard. And the residue was purified by flash chromatography on silica gel (gradient eluent of 10% EtOAc in hexanes, v/v) to yield the product **3a**.

General procedure for the scope study



A 35 mL oven-dried pressure tube was charged with benzamides (**1**, 0.2 mmol), disulfide (**2**, 0.4 mmol), NiCl_2 (1.3 mg, 0.01 mmol), PhCOOH (2.4 mg, 0.02 mmol), Ag_2CO_3 (110.3 mg, 0.4 mmol), and DCE (2.0 mL). The tube was then sealed and stirred vigorously at 140 °C for 4 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of Celite, and then the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (gradient eluent of 10% EtOAc in hexanes, *v/v*) to give the desired product **3**.

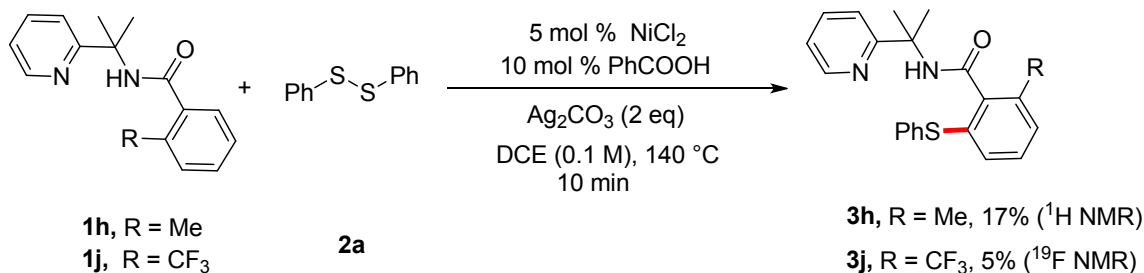
Radical Trapping Experiment



Scheme S1

A 35 mL oven-dried pressure tube was charged with benzamides **1h** (0.2 mmol), diphenyl disulfide **2a** (0.4 mmol), TEMPO (0.8 mmol), NiCl_2 (1.3 mg, 0.01 mmol), PhCOOH (2.4 mg, 0.02 mmol), Ag_2CO_3 (110.3 mg, 0.4 mmol), and DCE (2.0 mL). The tube was then sealed and stirred vigorously at 140 °C for 4 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of Celite, and then the filtrate was concentrated in *vacuo*, and the crude product was analyzed by ^1H NMR in CDCl_3 , no desired product **3h** was found in the ^1H NMR.

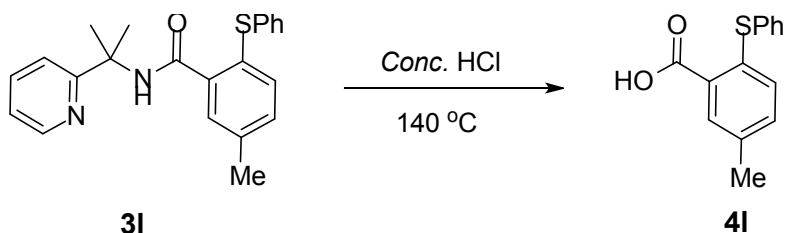
Intermolecular Competition Experiment



Scheme S2

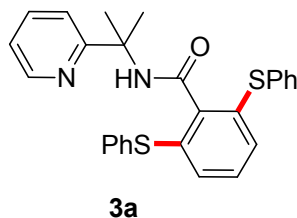
A 35 mL oven-dried pressure tube was charged with benzamides **1h** (0.2 mmol), benzamides **1j** (0.2 mmol), diphenyl disulfide **2a** (0.4 mmol), NiCl_2 (1.3 mg, 0.01 mmol), PhCOOH (2.4 mg, 0.02 mmol), Ag_2CO_3 (110.3 mg, 0.4 mmol), and DCE (2.0 mL). The tube was then sealed and stirred vigorously at 140 °C for 10 min. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of Celite, and then the filtrate was concentrated in *vacuo*, yields are determined by crude ^1H NMR and ^{19}F NMR using CH_2Br_2 and PhCF_3 as the internal standard..

Removal of Directing Group

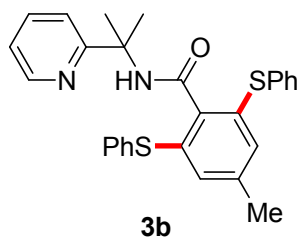


To a 35 mL Schlenk tube was added **3I** (0.1 mmol) and conc. HCl (2 mL). The mixture was then heated at 140 °C for 72 hours. The reaction mixture was cooled to room temperature, aqueous NaOH (1 M) was added and the aqueous phase was extracted with DCM (10 mL). Then, conc. HCl was added slowly into the aqueous phase (pH = 2) and the aqueous phase was as extracted with DCM (10 mL $\times$ 3). The combined organic phase was dried with anhydrous magnesium sulfate. After concentration, the desired product **4I** was obtained. White solid, yield 81%.⁴ ^1H NMR (400 MHz, CDCl_3) δ 10.47 (s, 1H), 7.97 (s, 1H), 7.58 (d, J = 4.4 Hz, 2H), 7.45 (d, J = 3.6 Hz, 3H), 7.14 (d, J = 7.2 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.80, 140.67, 135.46, 134.40, 134.22, 132.73, 132.49, 129.74, 129.04, 127.75, 125.55, 20.56.

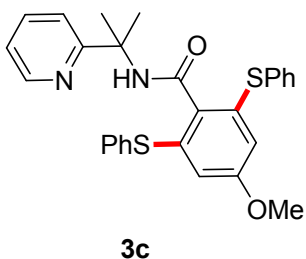
Data of new products



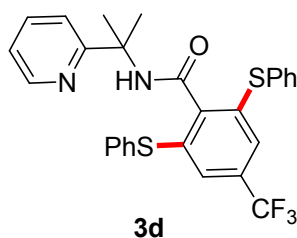
White solid, m.p.: 130-131 °C, yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, J = 4.4 Hz, 1H), 8.09 (s, 1H), 7.67 (td, J = 8.0, 1.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.30 – 7.17 (m, 7H), 7.15 – 7.05 (m, 4H), 1.87 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.60, 163.98, 147.18, 141.22, 137.07, 135.12, 134.67, 131.76, 130.57, 129.56, 129.24, 127.40, 121.72, 119.53, 57.56, 27.27. IR (neat) ν 3318, 2979, 1669, 1498, 1471, 1428, 998, 885, 750, 693, 591 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}^+$): 457.1408, found: 457.1410.



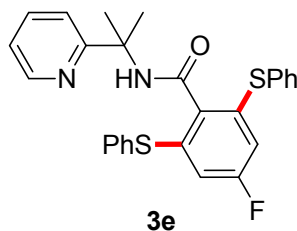
White solid, m.p.: 108-110 °C, yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 8.40 – 8.32 (m, 1H), 7.94 (s, 1H), 7.66 (td, J = 8.0, 1.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.38 (dd, J = 5.2, 3.2 Hz, 4H), 7.29 – 7.24 (m, 4H), 7.22 – 7.17 (m, 2H), 7.12 (m, 1H), 6.97 (s, 2H), 2.16 (s, 3H), 1.83 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.84, 164.17, 147.29, 139.85, 139.75, 136.98, 135.77, 133.89, 132.18, 131.28, 129.22, 127.14, 121.67, 119.56, 57.60, 27.31, 21.14. IR (neat) ν 3385, 2981, 1650, 1535, 1475, 1435, 1300, 1026, 790, 740, 689 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{28}\text{H}_{27}\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}^+$): 471.1565, found: 471.1565.



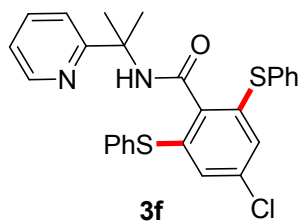
Colorless oil, yield: 83%. ^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, $J = 4.4$ Hz, 1H), 7.98 (s, 1H), 7.69 – 7.65 (m, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.2$ Hz, 4H), 7.32 – 7.21 (m, 6H), 7.18 – 7.10 (m, 1H), 6.57 (s, 2H), 3.55 (s, 3H), 1.85 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.66, 164.24, 159.77, 147.35, 136.99, 136.24, 134.83, 133.87, 132.10, 129.33, 127.62, 121.69, 119.59, 115.58, 57.61, 55.28, 27.34. IR (neat) ν 3312, 2965, 1653, 1578, 1544, 1472, 1423, 1295, 1240, 1063, 1023, 911, 742, 689 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_2\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 487.1514, found: 487.1514.



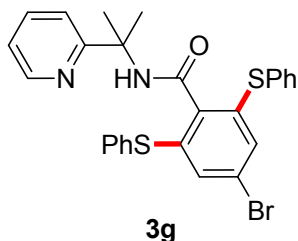
White solid, m.p.: 128-129 $^{\circ}\text{C}$, yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 8.48 – 8.35 (m, 2H), 7.70 (td, $J = 8.0, 1.6$ Hz, 1H), 7.54 – 7.39 (m, 5H), 7.36 – 7.24 (m, 6H), 7.16 (m, 3H), 1.93 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.55, 163.84, 147.26, 142.17, 137.25, 133.16, 132.89, 131.69 (q, $J_{\text{C},\text{F}} = 33.0$ Hz), 129.64, 128.46, 125.29 (q, $J_{\text{C},\text{F}} = 3.5$ Hz), 123.08 (q, $J_{\text{C},\text{F}} = 272.0$ Hz), 121.93, 119.51, 57.72, 27.30. IR (neat) ν 3283, 2977, 1647, 1539, 1475, 1293, 1128, 1109, 746, 687 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{28}\text{H}_{24}\text{F}_3\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 525.1282, found: 525.1281.



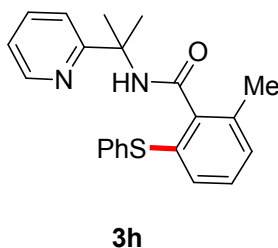
Yellow oil, yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, $J = 4.8$ Hz, 1H), 8.33 (s, 1H), 7.74 – 7.67 (m, 1H), 7.51 – 7.45 (m, 5H), 7.38 – 7.27 (m, 6H), 7.19 – 7.15 (m, 1H), 6.55 (d, $J = 9.2$ Hz, 2H), 1.93 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.99, 164.06, 162.47 (d, $J_{\text{C},\text{F}} = 250.0$ Hz), 147.35, 138.60 (d, $J_{\text{C},\text{F}} = 9.0$ Hz), 137.21, 134.58 (d, $J_{\text{C},\text{F}} = 3.0$ Hz), 133.49, 133.09, 129.65, 128.57, 121.91, 119.62, 114.71 (d, $J_{\text{C},\text{F}} = 24.0$ Hz), 57.67, 27.38. IR (neat) ν 3320, 2984, 1661, 1564, 1550, 1471, 1428, 748, 691 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{24}\text{FN}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 475.1314, found: 475.1313.



Yellow oil, yield: 95%. ^1H NMR (400 MHz, CDCl_3) δ 8.45 – 8.39 (m, 1H), 8.32 (s, 1H), 7.70 (td, $J = 8.0, 1.6$ Hz, 1H), 7.49 – 7.42 (m, 5H), 7.35 – 7.26 (m, 6H), 7.17 (m, 1H), 6.88 (s, 2H), 1.91 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.87, 163.99, 147.31, 137.66, 137.54, 137.21, 135.22, 133.40, 133.02, 129.61, 128.37, 128.22, 121.90, 119.58, 57.66, 27.34. IR (neat) ν 3299, 2971, 1653, 1559, 1535, 1472, 1439, 1127, 887, 786, 743, 688 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{24}\text{ClN}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 491.1019, found: 491.1019.

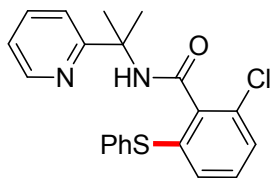


White solid, m.p.: 117-119 $^{\circ}\text{C}$, yield: 89%. ^1H NMR (400 MHz, CDCl_3) δ 8.42 (m, 1H), 8.33 (s, 1H), 7.70 (td, $J = 8.0, 1.6$ Hz, 1H), 7.50 – 7.42 (m, 5H), 7.37 – 7.25 (m, 6H), 7.16 (m, 1H), 7.06 (s, 2H), 1.90 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.88, 163.96, 147.29, 138.36, 137.58, 137.23, 133.51, 132.88, 131.24, 129.62, 128.34, 123.29, 121.92, 119.58, 57.65, 27.34. IR (neat) ν 3280, 2981, 1647, 1559, 1475, 1435, 1300, 1026, 790, 740 689 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{24}\text{BrN}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 537.0493, found: 537.0493.



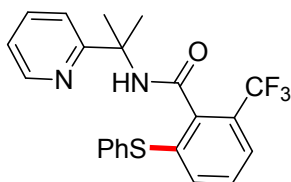
White solid, m.p.: 80-81 $^{\circ}\text{C}$, yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 8.45 – 8.30 (m, 1H), 7.92 (s, 1H), 7.68 (td, $J = 8.0, 2.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.31 – 7.09 (m, 9H), 2.41 (s, 3H), 1.86 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.36, 164.18, 147.42, 141.32, 137.05, 136.80,

136.11, 131.61, 130.93, 130.32, 129.73, 129.09, 126.60, 121.79, 119.49, 57.30, 27.35, 19.36. IR (neat) ν 3280, 2980, 1662, 1506, 1470, 1438, 1047, 997, 886, 786, 765, 690 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{OS}$ ($\text{M}+\text{H}$) $^{+}$: 363.1531, found: 363.1531.



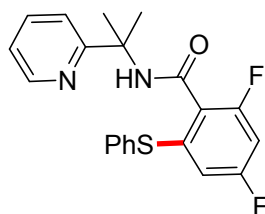
3i

Yellow oil, yield: 82%. ^1H NMR (400 MHz, CDCl_3) δ 8.46 – 8.38 (m, 1H), 8.16 (s, 1H), 7.72 (td, $J = 8.0, 1.6$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.41 – 7.36 (m, 2H), 7.31 – 7.25 (m, 3H), 7.24 – 7.14 (m, 3H), 7.08 (dd, $J = 8.0, 1.2$ Hz, 1H), 1.91 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.47, 163.90, 147.23, 138.78, 137.27, 136.04, 134.66, 132.05, 131.72, 130.11, 129.86, 129.35, 128.06, 127.68, 121.90, 119.59, 57.55, 27.30. IR (neat) ν 3299, 2982, 1653, 1506, 1472, 1429, 1195, 886, 785, 747, 690 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{21}\text{H}_{20}\text{ClN}_2\text{OS}$ ($\text{M}+\text{H}$) $^{+}$: 383.0985, found: 383.0986.



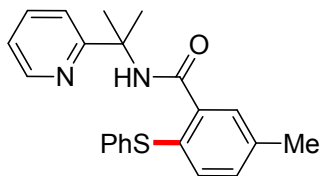
3j

White solid, m.p.: 127-129 $^{\circ}\text{C}$, yield: 93%. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (s, 1H), 8.43 (d, $J = 4.4$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.57 – 7.55 (m, 1H), 7.50 – 7.44 (m, 3H), 7.36 – 7.27 (m, 5H), 7.22 – 7.19 (m, 1H), 1.94 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.37, 163.85, 147.09, 137.38, 137.07, 134.85, 134.20, 132.68, 129.48, 129.14, 128.02 (q, $J_{\text{C},\text{F}} = 32.0$ Hz), 128.03, 124.46 (q, $J_{\text{C},\text{F}} = 4.8$ Hz), 123.59 (q, $J_{\text{C},\text{F}} = 273.0$ Hz), 121.97, 119.60, 57.51, 26.98. IR (neat) ν 3308, 2982, 2924, 1670, 1504, 1474, 1430, 1312, 1171, 1158, 1071, 887, 790, 749, 691 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{22}\text{H}_{20}\text{F}_3\text{N}_2\text{OS}$ ($\text{M}+\text{H}$) $^{+}$: 417.1248, found: 417.1248.



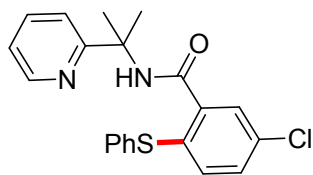
3k

Colorless oil, yield: 91%. ^1H NMR (400 MHz, CDCl_3) δ 8.49 (dd, $J = 4.8, 0.8$ Hz, 1H), 8.45 (s, 1H), 7.73 (td, $J = 8.0, 1.6$ Hz, 1H), 7.55 – 7.46 (m, 3H), 7.43 – 7.35 (m, 3H), 7.21 – 7.18 (m, 1H), 6.63 (td, $J = 9.2, 2.4$ Hz, 1H), 7.44 – 7.41 (m, 1H), 1.91 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.94, 162.71 (dd, $J = 252.0, 13.0$ Hz), 161.90, 159.98 (dd, $J = 250.0, 13.0$ Hz), 147.48, 142.29 (dd, $J = 10.0, 6.0$ Hz), 137.26, 134.55, 131.99, 129.83, 129.19, 121.99, 121.30 (dd, $J = 20.0, 4.0$ Hz), 119.53, 111.41 (dd, $J = 24.0, 3.0$ Hz), 101.36 (t, $J = 26.0$ Hz), 57.65, 27.50. IR (neat) ν 3296, 2980, 1653, 1606, 1440, 1415, 1104, 995, 848, 747 691 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{21}\text{H}_{19}\text{F}_2\text{N}_2\text{OS}$ ($\text{M}+\text{H}$) $^+$: 385.1186, found: 385.1188.



3l

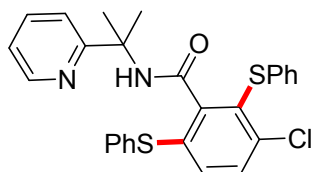
White solid, m.p.: 118-120 $^{\circ}\text{C}$, yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 4.0$ Hz, 1H), 8.27 (s, 1H), 7.57 (dd, $J = 12.0, 4.0$ Hz, 1H), 7.44 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.20 – 7.00 (m, 8H), 2.27 (s, 3H), 1.68 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.00, 163.31, 146.59, 138.12, 136.84, 135.91, 135.49, 132.57, 130.20, 129.06, 128.67, 128.15, 128.03, 125.64, 120.67, 118.36, 56.32, 26.37, 19.94. IR (neat) ν 3269, 2980, 1637, 1533, 1549, 1320, 1211, 818, 747, 694, 683 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{OS}$ ($\text{M}+\text{H}$) $^+$: 363.1531, found: 363.1531.



3ma

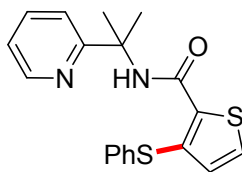
Colorless oil, yield: 47%. ^1H NMR (400 MHz, CDCl_3) δ 8.52 (s, 1H), 8.47 (d, $J = 4.8$ Hz, 1H), 7.73 (td, $J = 8.0, 1.6$ Hz, 1H), 7.64 (d, $J = 2.4$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.39 – 7.26 (m,

5H), 7.25 – 7.17 (m, 2H), 7.08 (d, $J = 8.4$ Hz, 1H), 1.83 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.73, 164.01, 147.45, 139.20, 137.35, 134.58, 133.50, 132.85, 132.70, 132.08, 130.32, 129.49, 128.54, 127.80, 121.99, 119.52, 57.37, 27.36. IR (neat) ν 3296, 2977, 1653, 1506, 1473, 1439, 1306, 1098, 1048, 786, 746, 691 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{21}\text{H}_{20}\text{ClN}_2\text{OS}$ ($\text{M}+\text{H}$) $^+$: 383.0985, found: 383.0985.



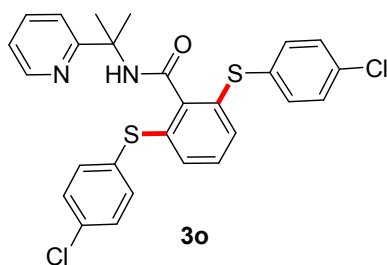
3mb

Colorless oil, yield: 30%. ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 4.4$ Hz, 1H), 8.07 (s, 1H), 7.66 (td, $J = 8.0, 1.6$ Hz, 1H), 7.44 – 7.39 (m, 3H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.32 – 7.25 (m, 3H), 7.23 – 7.05 (m, 7H), 1.84 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.00, 163.91, 147.17, 147.04, 139.82, 137.04, 136.24, 134.46, 133.91, 133.83, 132.25, 130.88, 129.67, 129.45, 128.93, 128.19, 127.88, 126.01, 121.72, 119.43, 57.65, 27.19. IR (neat) ν 3299, 2923, 1662, 1501, 1472, 1293, 1023, 787, 737, 688 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{24}\text{ClN}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 491.1019, found: 491.1019.

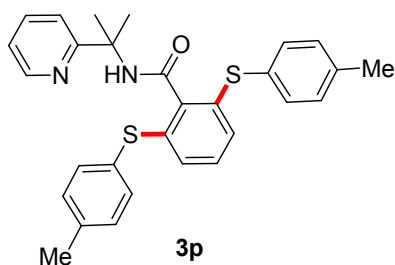


3n

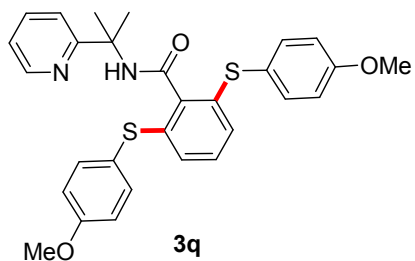
White solid, m.p.: 64-66 $^{\circ}\text{C}$, yield: 52%. ^1H NMR (400 MHz, CDCl_3) δ 9.23 (s, 1H), 8.47 (d, $J = 4.8$ Hz, 1H), 7.64 (td, $J = 7.6, 1.6$ Hz, 1H), 7.41 (d, $J = 5.2$ Hz, 1H), 7.34 – 7.20 (m, 6H), 7.14 (dd, $J = 7.2, 4.8$ Hz, 1H), 6.95 (d, $J = 5.2$ Hz, 1H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.30, 160.41, 147.91, 140.47, 136.89, 135.47, 133.62, 129.31, 129.19, 128.77, 128.55, 127.04, 121.76, 119.30, 57.87, 27.73. IR (neat) ν 3218, 1993, 2964, 1627, 1569, 1501, 1477, 1431, 999, 731, 694, 626 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 355.0939, found: 355.0939.



White solid, m.p.: 147-148 °C, yield: 92%. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 4.8 Hz, 1H), 8.17 (s, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.25 – 7.12 (m, 8H), 1.88 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.36, 163.73, 147.00, 142.25, 137.39, 134.05, 134.00, 133.44, 132.68, 131.68, 129.85, 129.40, 121.92, 119.55, 57.44, 27.19. IR (neat) ν 3318, 2977, 1653, 1473, 1429, 1092, 1013, 824, 785, 750, 623 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₂₇H₂₃Cl₂N₇OS₂ (M+H)⁺: 525.0629, found: 525.0629.

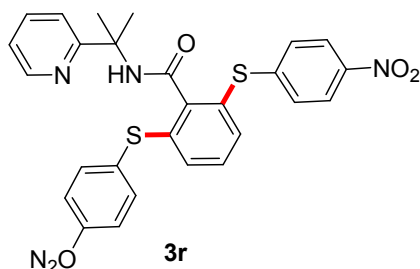


White solid, m.p.: 134-135 °C, yield: 93%. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 4.4 Hz, 1H), 8.09 (s, 1H), 7.74 – 7.65 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.18 – 7.01 (m, 6H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.30 (s, 6H), 1.91 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.76, 164.09, 147.12, 139.50, 137.85, 137.22, 135.77, 132.81, 130.90, 130.10, 129.35, 128.87, 121.75, 119.69, 57.58, 27.35, 21.13. IR (neat) ν 3317, 2974, 1656, 1490, 1471, 1427, 814, 784, 760 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₂₉H₂₉N₂OS₂ (M+H)⁺: 485.1721, found: 485.1721.

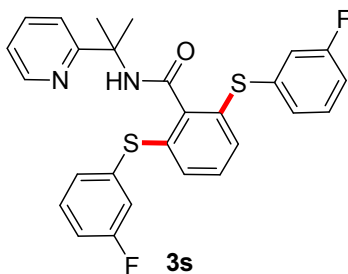


White solid, m.p.: 132-134 °C, yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 4.4 Hz, 1H), 8.21 (s, 1H), 7.79 – 7.67 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 4H), 7.19 (dd,

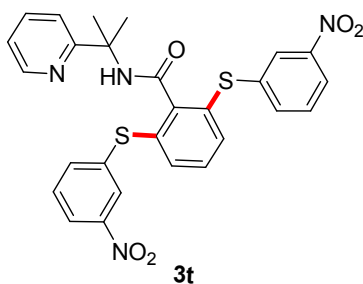
$J = 6.8, 5.2$ Hz, 1H), 6.98 (t, $J = 8.0$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 4H), 6.76 (d, $J = 8.0$ Hz, 2H), 3.77 (s, 6H), 1.97 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.90, 164.14, 159.98, 147.18, 137.42, 137.30, 137.12, 135.77, 129.25, 126.84, 124.05, 121.94, 119.84, 115.05, 57.65, 55.37, 27.48. IR (neat) ν 3342, 2971, 1654, 1588, 1502, 1426, 1249, 1171, 1023, 826, 775, 747 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_3\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 517.1620, found: 517.1621.



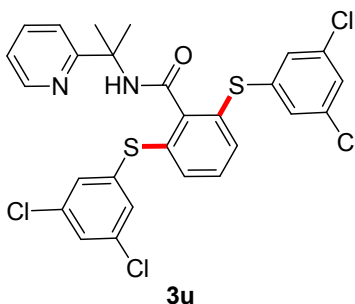
Yellow solid, m.p.: 86-87 $^{\circ}\text{C}$, yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 4.4$ Hz, 1H), 8.03 (s, 1H), 7.95 (d, $J = 8.8$ Hz, 4H), 7.61 – 7.58 (m, 3H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.15 (d, $J = 8.8$ Hz, 4H), 7.08 – 7.00 (m, 1H), 1.64 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.59, 161.98, 147.07, 146.24, 145.25, 144.59, 136.92, 136.75, 130.03, 129.07, 126.50, 123.12, 121.17, 118.48, 56.16, 25.82. IR (neat) ν 3275, 1972, 1651, 1574, 1506, 1473, 1330, 1080, 849, 740, 625 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{23}\text{N}_4\text{O}_5\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 547.1110, found: 547.1104.



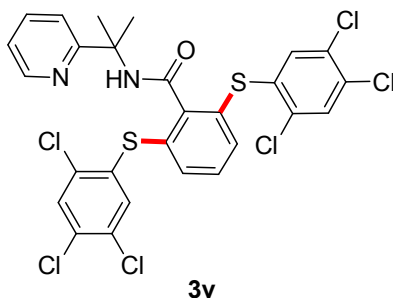
Colorless oil, yield: 85%. ^1H NMR (400 MHz, CDCl_3) δ 8.34 – 8.33 (m, 1H), 8.16 (s, 1H), 7.67 (td, $J = 8.0, 1.6$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.33 – 7.25 (m, 3H), 7.23 – 7.07 (m, 5H), 7.04 – 6.95 (m, 2H), 6.86 – 6.81 (m, 2H), 1.83 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.26, 163.72, 162.98 (d, $J = 247.0$ Hz), 147.06, 144.11, 138.49 (d, $J = 8.0$ Hz), 137.24, 133.52, 132.88, 130.43 (d, $J = 8.0$ Hz), 130.12, 125.94 (d, $J = 3.0$ Hz), 121.84, 119.39, 117.12 (d, $J = 23.0$ Hz), 113.95 (d, $J = 21.0$ Hz), 57.46, 27.16. IR (neat) ν 3310, 2980, 1662, 1597, 1506, 1472, 1429, 1215, 877, 774, 677 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{23}\text{F}_2\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 493.1120, found: 493.1121.



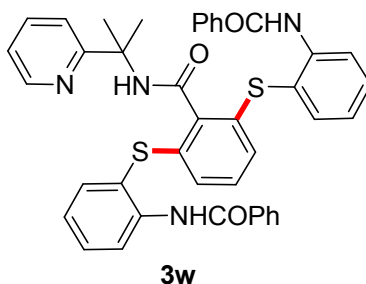
White solid, m.p.: 153-154 °C, yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 8.18 – 8.16 (m, 2H), 8.02 (t, J = 2.0 Hz, 2H), 7.96 – 7.91 (m, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 4H), 7.47 – 7.39 (m, 3H), 7.34 (d, J = 8.0 Hz, 1H), 7.18 – 7.08 (m, 1H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.79, 163.36, 148.53, 146.86, 146.79, 139.86, 137.39, 136.24, 134.71, 131.23, 130.86, 129.90, 123.33, 122.00, 121.23, 119.29, 57.33, 26.99. IR (neat) ν 3312, 2982, 1663, 1533, 1344, 1124, 876, 785, 731, 676 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{23}\text{N}_4\text{O}_5\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 547.1110, found: 547.1105.



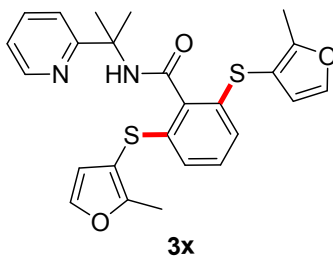
White solid, m.p.: 165-167 °C, yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, J = 4.4 Hz, 1H), 8.17 (s, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.51 – 7.32 (m, 4H), 7.22 – 7.14 (m, 1H), 7.13 – 7.07 (m, 6H), 1.82 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.81, 163.41, 146.95, 145.72, 140.27, 137.48, 135.41, 135.33, 131.57, 130.57, 127.41, 126.80, 121.95, 119.31, 57.32, 27.03. IR (neat) ν 3329, 2980, 1667, 1473, 1430, 1420, 767, 746, 622 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{21}\text{Cl}_4\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 594.9820, found: 594.9816.



White solid, m.p.: 219-220 °C, yield: 87%. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, J = 3.6 Hz, 1H), 8.14 (s, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.33 (d, J = 6.8 Hz, 3H), 7.18 – 7.10 (m, 1H), 6.99 (s, 2H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.54, 163.17, 147.15, 146.70, 137.74, 137.09, 136.65, 131.86, 131.22, 131.03, 130.67, 130.60, 130.44, 130.34, 121.95, 119.33, 57.13, 26.93. IR (neat) ν 3300, 2969, 1661, 1507, 1432, 1156, 1055, 887, 871, 787, 757, 638, 621 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{19}\text{Cl}_6\text{N}_2\text{OS}_2$ ($\text{M}+\text{H}$) $^+$: 662.9040, found: 662.9023.



White solid, m.p.: 191-193 °C, yield: 88%. ^1H NMR (400 MHz, CDCl_3) δ 9.16 (s, 2H), 8.65 – 8.63 (m, 3H), 8.31 (d, J = 4.4 Hz, 1H), 8.78 – 8.74 (m, 5H), 7.61 (dd, J = 7.6, 0.8 Hz, 2H), 7.52 – 7.35 (m, 3H), 7.19 (dd, J = 6.8, 5.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 1.99 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.29, 165.05, 163.81, 147.26, 140.18, 137.40, 136.83, 136.21, 134.87, 134.35, 131.93, 131.31, 130.21, 128.79, 127.18, 125.44, 124.67, 122.09, 121.13, 119.95, 119.62, 57.74, 27.45. IR (neat) ν 3372, 2974, 1658, 1515, 1424, 1300, 1251, 757, 700 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{41}\text{H}_{34}\text{N}_4\text{O}_3\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 717.1970, found: 717.1982.



Yellow solid, m.p.: 115-116 °C, yield: 94%. ^1H NMR (400 MHz, CDCl_3) δ 8.53 – 8.45 (m, 1H), 8.39 (s, 1H), 7.75 (td, J = 8.0, 1.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 2.0 Hz, 2H), 7.23 – 7.16 (m, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.69 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 2.0 Hz, 2H), 2.33 (s, 6H), 2.01 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.53, 164.29, 157.29, 147.36, 141.28, 137.17, 136.84, 134.68, 129.06, 123.66, 121.91, 119.69, 115.50, 107.73, 57.71, 27.50, 11.84. IR (neat) ν 3329, 3296, 2923, 1658, 1498, 1429, 1120, 1087, 885, 792, 668, 658 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_3\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 465.1307, found: 465.1303.

III. References and notes:

- (1) Q. Zhang, K. Chen, W. H. Rao, Y. Zhang, F. J. Chen, B.-F. Shi, *Angew. Chem., Int. Ed.*, 2013, **52**, 13588.
- (2) F. J. Chen, G. Liao, X. Li, J. Wu, B.-F. Shi, *Org. Lett.*, 2014, **16**, 5644.
- (3) X. Li, Y. H. Liu, W. J. Gu, B. Li, F. J. Chen, B.-F. Shi, *Org. Lett.*, 2014, **16**, 3904;
- (4) V. Valenta, J. Jílek, J. Pomykáček, A. Dlabač, M. Valchář, J. Metyš, M. Protiva, *Collect. Czech. Chem. Commun.* 1979, **44**, 2677.

IV. ¹H and ¹³C NMR Spectra

