Supporting Information

Silver-Copper Co-catalyzed Cascade Intramolecular Cyclization/Desulfinamide/Dehydrogenation: One-Pot Synthesis of Substituted Carbazoles

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1. General procedure for the synthesis of substrate

To a three-necked flask were added \((\text{PPh}_3)_2\text{PdCl}_2\) (5.0 mol%), CuI (5.0 mol%), DMF, \(\text{Et}_3\text{N}\) (4.0 equiv), and 2-iodoaniline (1.0 equiv). After degassing with argon and four evacuation/backfill-cycles with argon, 5-hexyn-1-ol was then added and the resulting mixture was stirring at room temperature. The reaction was complete as monitored by TLC. Then it was diluted with saturated aqueous \(\text{NH}_4\text{Cl}\) and EtOAc. The aqueous phase was extracted with an additional of EtOAc, and the combined
organic layers were washed with water. The organic phase was dried over MgSO$_4$ and filtered. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the product A.

To a flask were added A (1.0 equiv)/DCM, pyridine (2.0 equiv) and TsCl (1.2 equiv) sequentially at room temperature. The reaction was complete as monitored by TLC. H$_2$O were added to the resulting mixture. After separation of the organic layer, the water layer was extracted with DCM. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product B.

To a flask were added B (1.0 equiv)/DMSO and IBX (3.0 equiv) sequentially at room temperature. The reaction was complete as monitored by TLC. H$_2$O and EtOAc were added to the resulting mixture. The aqueous phase was extracted with an additional of EtOAc, and the combined organic layers were washed with water. The organic phase was dried over MgSO$_4$ and filtered. The filtrate was concentrated in vacuo yielding the crude extract C without further purification.

To a flask were added C (1.0 equiv), (R)-(+)2-Methyl-2-propanesulfinamide (1.2 equiv) and CuSO$_4$ (3.0 equiv). After degassing with argon and four evacuation/backfill-cycles with argon, dry DCM was then added, and the resulting mixture was stirring at room temperature. After 48 h, the reaction was stopped and filtrated through Celite, washing with DCM. The solution was evaporated with a rotary evaporator to remove the solvent, yielding the crude extract which was further purified by flash column (eluent: petroleum ether/ethyl acetate) to yield the desired product as a yellow oil.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 (t, $J = 4.0$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.28 – 7.18 (m, 5H), 6.99 (t, $J = 7.2$ Hz, 1H), 2.71 – 2.63 (m, 2H), 2.53 (t, $J = 6.8$ Hz, 2H),
2.37 (s, 3H), 1.99 – 1.91 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 144.0, 137.6, 136.2, 132.1, 129.6, 129.1, 127.2, 124.3, 119.5, 114.6, 96.2, 76.4, 56.7, 35.0, 24.3, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C$_{23}$H$_{20}$N$_2$O$_3$S$_2$ [M+H]$^+$ 445.1614, found 445.1618.

[Chemical structure image]

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J = 4.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.54 (dd, $J = 8.8$, 5.2 Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.02 (s, 1H), 6.95 (d, $J = 8.4$ Hz, 2H), 2.64 (td, $J = 7.2$, 4.4 Hz, 2H), 2.49 (t, $J = 7.2$ Hz, 2H), 2.38 (s, 3H), 1.97 – 1.89 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.2, 159.3 (d, $J_{C-F} = 243.6$ Hz), 144.1, 136.0, 133.7, 129.6, 127.2, 122.6 (d, $J_{C-F} = 8.8$ Hz), 118.5 (d, $J_{C-F} = 24.2$ Hz), 117.0 (d, $J_{C-F} = 9.8$ Hz), 116.3 (d, $J_{C-F} = 22.5$ Hz), 96.9, 75.6, 56.7, 35.0, 24.1, 22.4, 21.6, 19.0, HRMS (ESI) calcd for C$_{23}$H$_{28}$FN$_2$O$_3$S$_2$ [M+H]$^+$ 463.1520, found 463.1526.

[Chemical structure image]

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (t, $J = 4.0$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.27 – 7.21 (m, 4H), 7.15 (s, 1H), 2.73 – 2.63 (m, 2H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 2.01 – 1.92 (m, 2H), 1.24 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 144.3, 136.2, 136.0, 131.8, 129.7, 129.6, 129.2, 127.2, 121.2, 116.5, 97.5, 75.3, 56.8, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C$_{23}$H$_{28}$ClN$_2$O$_3$S$_2$ [M+H]$^+$ 479.1224, found 479.1232.

[Chemical structure image]

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J = 4.0$ Hz, 1H), 7.65 (d, $J = 7.2$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.39 (s, 1H), 7.34 (d, $J = 8.4$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 2H), 7.14 (s, 1H), 2.69 – 2.62 (m, 2H), 2.53 (t, $J = 6.8$ Hz, 2H), 2.39 (s, 3H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.1, 144.3, 136.7, 135.9, 134.6, 132.1, 129.7, 127.2, 121.0, 117.0, 116.4, 97.6, 76.7, 56.7, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C$_{23}$H$_{28}$BrN$_2$O$_3$S$_2$
[M+H]$^+$ 523.0719, found 523.0721.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J = 4.4$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 12.0$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 1H), 2.69 – 2.62 (m, 2H), 2.50 (t, $J = 7.2$ Hz, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 1.97 – 1.87 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 143.9, 136.3, 135.0, 134.3, 132.5, 129.9, 129.6, 127.3, 120.2, 114.9, 95.6, 76.6, 56.7, 35.0, 24.3, 22.4, 21.6, 20.6, 19.1, HRMS (ESI) calcd for C$_{24}$H$_{31}$N$_2$O$_3$S$_2$ [M+H]$^+$ 459.1771, found 459.1779.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J = 4.4$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 9.2$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.95 (s, 1H), 6.82 (dd, $J = 8.8$, 3.2 Hz, 1H), 6.76 (d, $J = 2.8$ Hz, 1H), 3.74 (s, 3H), 2.63 (td, $J = 7.2$, 4.4 Hz, 2H), 2.46 (t, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.97 – 1.82 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 156.7, 143.7, 136.2, 130.6, 129.4, 127.2, 123.4, 117.3, 116.4, 115.4, 95.5, 76.5, 56.7, 55.5, 35.0, 24.2, 22.4, 21.6, 19.0, HRMS (ESI) calcd for C$_{26}$H$_{35}$N$_2$O$_4$S$_2$ [M+H]$^+$ 475.1720, found 475.1721.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (t, $J = 4.4$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.15 – 7.06 (m, 3H), 2.83 – 2.74 (m, 1H), 2.70 – 2.63 (m, 2H), 2.51 (t, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 2.00 – 1.89 (m, 2H), 1.22 (s, 9H), 1.17 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 145.1, 143.8, 136.4, 135.2, 129.9, 129.6, 127.4, 127.2, 120.0, 114.6, 95.4, 76.7, 56.7, 35.0, 33.3, 24.3, 23.8, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C$_{26}$H$_{35}$N$_2$O$_4$S$_2$ [M+H]$^+$ 487.2084, found 487.2089.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (t, $J = 4.4$ Hz, 1H),
7.71 (d, \( J = 8.0 \) Hz, 2H), 7.62 (d, \( J = 8.8 \) Hz, 1H), 7.53 – 7.45 (m, 4H), 7.40 (t, \( J = 7.2 \) Hz, 2H), 7.33 (d, \( J = 7.2 \) Hz, 1H), 7.25 – 7.19 (m, 3H), 2.72 – 2.64 (m, 2H), 2.55 (t, \( J = 7.2 \) Hz, 2H), 2.37 (s, 3H), 2.03 – 1.91 (m, 2H), 1.22 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.4, 144.1, 139.4, 137.2, 136.7, 136.2, 130.6, 129.7, 128.9, 127.8, 127.6, 127.3, 126.7, 119.8, 114.9, 96.2, 76.4, 56.8, 35.0, 24.3, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C\(_{29}\)H\(_{33}\)N\(_2\)O\(_3\)S\(_2\) [M+H]\(^{+}\) 521.1927, found 521.1931.

Yellow Oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.13 (t, \( J = 4.4 \) Hz, 1H), 7.67 (d, \( J = 8.4 \) Hz, 2H), 7.44 (d, \( J = 8.8 \) Hz, 1H), 7.27 (d, \( J = 0.8 \) Hz, 2H), 7.23 (d, \( J = 8.0 \) Hz, 2H), 7.10 (s, 1H), 2.70 – 2.64 (m, 2H), 2.52 (t, \( J = 7.2 \) Hz, 2H), 2.38 (s, 3H), 1.91 – 1.99 (m, 2H), 1.24 (s, 9H), 1.22 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.4, 147.3, 143.9, 136.5, 135.0, 129.6, 128.9, 127.2, 126.4, 119.3, 114.1, 95.3, 76.9, 56.7, 35.0, 34.3, 31.2, 24.3, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C\(_{27}\)H\(_{37}\)N\(_2\)O\(_5\)S\(_2\) [M+H]\(^{+}\) 501.2240, found 501.2246.

Yellow Oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.14 (t, \( J = 4.0 \) Hz, 1H), 7.96 (s, 1H), 7.87 (d, \( J = 8.8 \) Hz, 1H), 7.72 (d, \( J = 8.0 \) Hz, 2H), 7.57 (d, \( J = 8.8 \) Hz, 1H), 7.46 (s, 1H), 7.25 (d, \( J = 8.0 \) Hz, 2H), 3.87 (s, 3H), 2.74 – 2.67 (m, 2H), 2.59 (t, \( J = 7.2 \) Hz, 2H), 2.38 (s, 3H), 2.06 – 1.94 (m, 2H), 1.23 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.2, 165.8, 144.5, 141.4, 135.8, 133.8, 130.4, 129.8, 127.3, 125.5, 117.3, 113.5, 97.4, 75.5, 56.7, 52.2, 35.0, 24.2, 22.4, 21.6, 19.1, HRMS (ESI) calcd for C\(_{25}\)H\(_{31}\)N\(_2\)O\(_5\)S\(_2\) [M+H]\(^{+}\) 503.1669, found 503.1675.

Yellow Oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.13 (t, \( J = 4.0 \) Hz, 1H), 7.70 (d, \( J = 8.0 \) Hz, 2H), 7.57 (d, \( J = 8.0 \) Hz, 2H), 7.18 (d, \( J = 8.4 \) Hz, 1H), 6.97 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 2.67 (td, \( J = 6.8, 4.4 \) Hz, 2H), 2.54 (t, \( J = 7.2 \) Hz, 2H), 2.39 (s, 3H), 2.00 – 1.91 (m, 2H), 1.22 (s,
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (t, $J = 4.4$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.62 – 7.55 (m, 3H), 7.47 (d, $J = 8.5$ Hz, 1H), 7.29 (d, $J = 6.4$ Hz, 2H), 2.72 – 2.65 (m, 2H), 2.60 (t, $J = 7.2$ Hz, 2H), 2.40 (s, 3H), 2.05 – 1.93 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.0, 144.9, 141.4, 135.9, 135.6, 132.6, 130.0, 127.2, 117.8, 117.8, 114.3, 107.2, 99.2, 74.4, 56.7, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcld for C$_{23}$H$_{28}$ClN$_2$O$_3$S$_2$ [M+H]$^+$ 479.1224, found 479.1224.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J = 4.4$ Hz, 1H), 7.80 – 7.74 (m, 2H), 7.59 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.29 – 7.19 (m, 3H), 7.01 (td, $J = 7.6$, 1.2 Hz, 1H), 2.70 – 2.62 (m, 2H), 2.51 (t, $J = 7.2$ Hz, 2H), 1.98 – 1.88 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 139.1, 137.4, 133.1, 132.1, 129.1, 129.0, 127.2, 124.5, 120.0, 114.9, 96.2, 76.3, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcld for C$_{23}$H$_{27}$N$_2$O$_3$S$_2$ [M+H]$^+$ 431.1458, found 431.1466.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (t, $J = 4.4$ Hz, 1H), 7.83 – 7.74 (m, 2H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.29 – 7.21 (m, 3H), 7.13 – 7.07 (m, 2H), 7.04 (td, $J = 7.6$, 0.8 Hz, 1H), 2.70 – 2.64 (m, 2H), 2.52 (t, $J = 7.2$ Hz, 2H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 165.3 (d, $J_{C-F} = 254$ Hz), 137.1, 135.1 (d, $J_{C-F} = 3.2$ Hz), 132.3, 130.0 (d, $J_{C-F} = 9.4$ Hz), 129.2, 124.8, 120.3, 116.2 (d, $J_{C-F} = 22.5$ Hz), 115.2, 96.3, 76.2, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcld for C$_{22}$H$_{26}$FN$_2$O$_3$S$_2$
[M+H]$^+$ 449.1363, found 449.1369.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (t, $J$ = 4.4 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.55 (d, $J$ = 8.4 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 7.05 (td, $J$ = 7.6, 0.8 Hz, 1H), 2.67 (td, $J$ = 7.6, 4.4 Hz, 2H), 2.51 (t, $J$ = 7.2 Hz, 2H), 2.00 – 1.87 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.2, 139.7, 137.6, 137.0, 132.3, 129.3, 129.2, 128.6, 124.9, 120.3, 115.2, 96.3, 76.3, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for C$_{22}$H$_{26}$ClN$_2$O$_3$S$_2$ [M+H]$^+$ 465.1068, found 465.1071.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (t, $J$ = 4.4 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.58 – 7.53 (m, 3H), 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 7.05 (td, $J$ = 7.6, 0.8 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.51 (t, $J$ = 7.2 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 138.2, 137.0, 132.3, 129.2, 128.7, 128.2, 124.9, 120.3, 115.2, 96.3, 76.3, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for C$_{22}$H$_{26}$BrN$_2$O$_3$S$_2$ [M+H]$^+$ 509.0563, found 509.0562.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (t, $J$ = 4.4 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.54 (d, $J$ = 8.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.30 – 7.19 (m, 3H), 7.00 (td, $J$ = 7.6, 0.8 Hz, 1H), 2.72 – 2.65 (m, 2H), 2.53 (t, $J$ = 7.2 Hz, 2H), 2.01 – 1.90 (m, 2H), 1.29 (s, 9H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 157.0, 137.7, 136.2, 132.1, 129.1, 127.0, 126.0, 124.0, 119.0, 114.2, 96.2, 76.4, 56.7, 35.2, 35.0, 31.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for C$_{26}$H$_{35}$N$_2$O$_3$S$_2$ [M+H]$^+$ 487.2084, found 487.2092.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (t, $J$ = 4.4 Hz, 1H),
7.87 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.32 (s, 1H), 7.31 – 7.27 (m, 2H), 7.13 – 7.04 (m, 1H), 2.68 (td, $J = 7.2, 4.4$ Hz, 2H), 2.50 (t, $J = 7.2$ Hz, 2H), 2.05 – 1.87 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 143.3, 136.4, 132.7, 132.5, 129.3, 127.8, 125.4, 120.8, 117.2, 116.8, 115.6, 96.5, 76.2, 56.8, 35.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for C$_{23}$H$_{26}$N$_3$O$_3$S$_2$ [M+H]$^+$ 456.1410, found 456.1415.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (t, $J = 4.4$ Hz, 1H), 7.71 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.28 – 7.20 (m, 2H), 7.17 (s, 1H), 7.00 (td, $J = 7.6, 1.2$ Hz, 1H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H), 2.71 – 2.64 (m, 2H), 2.54 (t, $J = 7.2$ Hz, 2H), 2.01 – 1.91 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 163.2, 137.7, 132.1, 130.7, 129.4, 129.1, 124.2, 119.5, 114.5, 114.1, 96.2, 76.4, 56.7, 55.6, 35.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for C$_{23}$H$_{29}$N$_2$O$_4$S$_2$ [M+H]$^+$ 461.1563, found 461.1573.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (t, $J = 4.4$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.54 (dd, $J = 4.8, 1.2$ Hz, 1H), 7.48 (dd, $J = 4.0, 1.2$ Hz, 1H), 7.34 – 7.25 (m, 3H), 7.06 (td, $J = 7.6, 0.8$ Hz, 1H), 6.99 (dd, $J = 4.8, 4.0$ Hz, 1H), 2.67 (td, $J = 7.6, 4.4$ Hz, 2H), 2.53 (t, $J = 7.2$ Hz, 2H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 139.5, 137.1, 132.8, 132.6, 132.1, 129.1, 127.3, 124.9, 120.3, 115.2, 96.3, 76.2, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for C$_{20}$H$_{25}$N$_2$O$_3$S$_3$ [M+H]$^+$ 437.1022, found 437.1026.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (t, $J = 4.4$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.42 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.35 – 7.29 (m, 1H), 7.11 (td, $J = 7.6, 1.0$ Hz, 1H), 7.04 (s, 1H), 3.02 (s, 3H), 2.75 – 2.69 (m, 2H), 2.54 (t, $J = 7.2$ Hz, 2H), 2.06 – 1.95 (m, 2H), 1.21 (s, 9H); $^{13}$C NMR
(100 MHz, CDCl$_3$) $\delta$ 168.3, 137.7, 132.5, 129.5, 124.6, 119.1, 114.5, 96.8, 76.4, 56.7, 39.6, 35.0, 24.3, 22.4, 19.2, HRMS (ESI) calcd for C$_{17}$H$_{25}$N$_2$O$_3$S$_2$ [M+H]$^+$ 369.1301, found 369.1305.

Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (t, $J$ = 4.4 Hz, 1H), 7.61 (d, $J$ = 8.0 Hz, 1H), 7.41 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.10 (td, $J$ = 7.6, 1.2 Hz, 1H), 6.98 (s, 1H), 2.75 – 2.69 (m, 2H), 2.61 (t, $J$ = 7.2 Hz, 2H), 2.51 – 2.43 (m, 1H), 2.06 – 1.96 (m, 2H), 1.21 (s, 9H), 1.20 – 1.17 (m, 2H), 0.99 – 0.92 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 137.9, 132.3, 129.3, 124.5, 120.1, 115.0, 96.4, 76.7, 56.7, 35.0, 30.1, 24.4, 22.4, 19.2, 5.8, HRMS (ESI) calcd for C$_{19}$H$_{27}$N$_2$O$_3$S$_2$ [M+H]$^+$ 395.1458, found 395.1459.

2. General procedure for the synthesis of products

To a microwave rotor were added DCE, substrate (1.0 equiv), Cu(OAc)$_2$ (20 mol%), AgSbF$_6$ (10 mol %) and chloranil (0.6 equiv) sequentially. The mixture was heated at 80 °C in microwave for 2.5 h. After the reaction was complete as monitored by TLC. CH$_2$Cl$_2$ and H$_2$O were added to the resulting mixture. After separation of the organic layer, the water layer was extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product as a solid.

Pale grey solid; yield: 86%; mp: 134-135 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J$ = 8.4 Hz, 2H), 7.87 (d, $J$ = 7.6 Hz, 2H), 7.63 (d, $J$ = 7.6 Hz, 2H),
7.48 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.34 (td, J = 7.6, 0.8 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 2.21 (s, 3H); ^13^C NMR (100 MHz, CDCl\_3) \(\delta\) 144.9, 138.4, 134.9, 129.7, 127.4, 126.5, 126.4, 123.9, 120.0, 115.2, 21.5, HRMS (ESI) calcd for C\(_{19}\)H\(_{16}\)NO\(_2\)S [M+H]^+ 322.0896, found 322.0902.

White solid; yield: 82%; mp: 171-172 °C. \(^1\)H NMR (400 MHz, CDCl\_3) \(\delta\) 8.32 (d, J = 8.4 Hz, 1H), 8.28 (dd, J = 9.2, 4.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.39 – 7.33 (m, 1H), 7.20 (td, J = 8.8, 2.4 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H); \(^13^C\) NMR (100 MHz, CDCl\_3) \(\delta\) 159.9 (d, \(J_{C-F}\) = 240.6 Hz), 145.0, 139.2, 134.7, 134.5 (d, \(J_{C-F}\) = 1.3 Hz), 129.7, 128.0, 127.8 (d, \(J_{C-F}\) = 9.6 Hz), 126.5, 125.9 (d, \(J_{C-F}\) = 3.6 Hz), 124.0, 120.2, 116.4 (d, \(J_{C-F}\) = 8.8 Hz), 115.47, 114.8 (d, \(J_{C-F}\) = 24.6 Hz), 106.2 (d, \(J_{C-F}\) = 4.0 Hz), 21.5, HRMS (ESI) calcd for C\(_{19}\)H\(_{15}\)FNO\(_2\)S [M+H]^+ 340.0802, found 340.0803.

White solid; yield: 84%; mp: 135-136 °C. \(^1\)H NMR (400 MHz, CDCl\_3) \(\delta\) 8.31 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.43 (dd, J = 9.2, 2.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H); \(^13^C\) NMR (100 MHz, CDCl\_3) \(\delta\) 145.2, 138.9, 136.7, 134.7, 129.8, 129.7, 128.1, 127.8, 127.4, 126.5, 125.3, 124.2, 120.2, 119.9, 116.3, 115.3, 21.5, HRMS (ESI) calcd for C\(_{19}\)H\(_{15}\)ClNO\(_2\)S [M+H]^+ 356.0507, found 356.0504.

White solid; yield: 83%; mp: 143-144 °C. \(^1\)H NMR (400 MHz, CDCl\_3) \(\delta\) 8.31 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.57 (dd, J = 8.8, 2.0 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H); \(^13^C\) NMR (100 MHz, CDCl\_3) \(\delta\) 145.2, 138.7, 137.1, 134.6, 130.1, 129.8, 128.3, 128.2,
White solid; yield: 56%; mp: 121-122 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.30 (d, $J = 8.0$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 7.6$ Hz, 1H),
7.70 – 7.63 (m, 3H), 7.49 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 7.29 (dd, $J = 8.4$, 1.2
Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz,
CDCl$_3$) $\delta$ 144.7, 138.7, 136.5, 135.0, 133.6, 129.6, 128.6, 127.2, 126.6, 126.5, 123.8,
120.1, 119.9, 115.2, 114.9, 21.5, 21.3, HRMS (ESI) calcd for C$_{19}$H$_{15}$BrNO$_2$S [M+H]$^+$
356.0507, found 356.0504.

White solid; yield: 48%; mp: 129-130 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.30 (d, $J = 8.4$ Hz, 1H), 8.22 (d, $J = 8.8$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H),
7.64 (d, $J = 8.4$ Hz, 2H), 7.52 – 7.44 (m, 1H), 7.37 – 7.30 (m, 2H), 7.09 – 7.05 (m,
3H), 3.89 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.8, 144.7, 139.1,
134.8, 132.7, 129.6, 127.6, 127.4, 126.6, 126.5, 123.8, 119.9, 116.3, 115.5, 115.3,
103.2, 55.8, 21.5, HRMS (ESI) calcd for C$_{20}$H$_{17}$NNaO$_3$S [M+Na]$^+$ 374.0821, found
374.0825.

White solid; yield: 74%; mp: 94-95 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.30 (d, $J = 8.4$ Hz, 1H), 8.22 (d, $J = 8.8$ Hz, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.73
(s, 1H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.38 – 7.31 (m, 1H), 7.08 (d,
$J = 8.0$ Hz, 2H), 3.11 – 2.98 (m, 1H), 2.25 (s, 3H), 1.32 (d, $J = 6.8$ Hz, 6H); $^{13}$C NMR
(100 MHz, CDCl$_3$) $\delta$ 144.74, 144.72, 138.6, 136.7, 135.1, 129.6, 127.1, 126.6, 126.5,
126.4, 126.3, 123.7, 119.9, 117.3, 115.1, 114.9, 34.0, 24.3, 21.5, HRMS (ESI) calcd
for C$_{22}$H$_{22}$NO$_2$S [M+H]$^+$ 364.1366, found 364.1370.
White solid; yield: 70%; mp: 139-140 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.38 (d, $J = 8.8$ Hz, 1H), 8.34 (d, $J = 8.4$ Hz, 1H), 8.09 (d, $J = 1.6$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.75 – 7.70 (m, 3H), 7.69 – 7.64 (m, 2H), 7.54 – 7.45 (m, 3H), 7.41 – 7.34 (m, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.0, 140.9, 138.8, 137.8, 137.3, 135.0, 129.7, 128.9, 127.6, 127.3, 127.3, 126.9, 126.8, 126.5, 126.4, 124.0, 120.1, 118.4, 115.4, 115.2, 21.6, HRMS (ESI) calcd for C$_{25}$H$_{20}$NO$_2$S [M+H]$^+$ 398.1209, found 398.1211.

White solid; yield: 72%; mp: 158-159 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.30 (d, $J = 8.4$ Hz, 1H), 8.22 (d, $J = 8.8$ Hz, 1H), 7.94 – 7.86 (m, 2H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 2.24 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.0, 144.7, 138.6, 136.3, 135.1, 129.7, 127.1, 126.7, 126.5, 126.0, 125.2, 123.7, 119.8, 116.3, 115.1, 114.6, 34.8, 31.7, 21.5, HRMS (ESI) calcd for C$_{23}$H$_{24}$NO$_2$S [M+H]$^+$ 378.1522, found 378.1525.

White solid; yield: 84%; mp: 176-177 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.61 (s, 1H), 8.35 (dd, $J = 16.0$, 8.8 Hz, 2H), 8.18 (d, $J = 8.8$ Hz, 1H), 7.97 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 3.97 (s, 3H), 2.47 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.0, 145.3, 141.2, 138.9, 134.8, 129.8, 128.7, 128.0, 126.5, 126.3, 125.8, 125.7, 124.3, 122.0, 120.4, 115.1, 114.7, 52.3, 21.6, HRMS (ESI) calcd for C$_{21}$H$_{18}$NO$_4$S [M+H]$^+$ 380.0951, found 380.0948.

White solid; yield: 85%; mp: 170-171 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
8.36 (s, 1H), 8.29 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.35 (dd, $J = 14.4$, 7.6 Hz, 2H), 7.13 (d, $J = 7.6$ Hz, 2H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.2,
138.8, 138.5, 134.8, 133.1, 129.8, 127.7, 126.5, 125.5, 124.9, 124.4, 124.1, 120.7, 120.0, 115.4, 115.1, 21.6, HRMS (ESI) calcd for C_{19}H_{13}ClNO_{2}S [M+H]^+ 356.0507, found 356.0507.

White solid; yield: 82%; mp: 189-190 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.44 (d, \(J = 8.8\) Hz, 1H), 8.35 (d, \(J = 8.4\) Hz, 1H), 8.22 (d, \(J = 1.2\) Hz, 1H), 7.94 (d, \(J = 7.6\) Hz, 1H), 7.76 (dd, \(J = 8.8, 1.6\) Hz, 1H), 7.72 (d, \(J = 8.4\) Hz, 2H), 7.63 – 7.56 (m, 1H), 7.44 (t, \(J = 7.2\) Hz, 1H), 7.16 (d, \(J = 8.2\) Hz, 2H), 2.30 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.7, 140.4, 138.8, 134.6, 130.6, 130.0, 128.9, 126.7, 126.5, 124.6, 124.5, 120.4, 119.1, 115.7, 115.1, 107.3, 21.6, HRMS (ESI) calcd for C\(_{20}\)H\(_{15}\)N\(_2\)O\(_2\)S [M+H]^+ 347.0849, found 347.0853.

White solid; yield: 81%; mp: 134-135 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.33 (d, \(J = 8.4\) Hz, 2H), 7.90 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 7.48 (ddd, \(J = 8.4, 7.2, 1.2\) Hz, 2H), 7.45 – 7.39 (m, 1H), 7.35 (td, \(J = 7.6, 0.8\) Hz, 2H), 7.32 – 7.26 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.4, 137.9, 133.8, 129.0, 127.5, 126.5, 126.4, 124.0, 120.0, 115.2, HRMS (ESI) calcd for C\(_{18}\)H\(_{14}\)NO\(_2\)S [M+H]^+ 308.0740, found 308.0741.

White solid; yield: 80%; mp: 152-153 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 8.4\) Hz, 2H), 7.90 (d, \(J = 7.2\) Hz, 2H), 7.84 – 7.76 (m, 2H), 7.49 (ddd, \(J = 8.8, 7.6, 1.2\) Hz, 2H), 7.40 – 7.33 (m, 2H), 6.96 (t, \(J = 8.4\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.7 (d, \(J_{C,F} = 255.3\) Hz), 138.3, 133.8 (d, \(J_{C,F} = 3.0\) Hz), 129.3 (d, \(J_{C,F} = 9.6\) Hz), 127.6, 126.6, 124.2, 120.1, 116.4 (d, \(J_{C,F} = 22.7\) Hz), 115.2, HRMS (ESI) calcd for C\(_{18}\)H\(_{13}\)FNO\(_2\)S [M+H]^+ 326.0646, found 326.0651.

White solid; yield: 83%; mp: 135-136 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.30

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(d, J = 8.4 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.53 – 7.46 (m, 2H), 7.41 – 7.34 (m, 2H), 7.29 – 7.21 (m, 2H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 140.5, 138.2, 136.1, 129.4, 127.8, 127.6, 126.6, 124.3, 120.2, 115.2, HRMS (ESI) calcd for C\textsubscript{18}H\textsubscript{13}ClNO\textsubscript{2}S [M+H]\(^+\) 342.0350, found 326.0351.

White solid; yield: 81%; mp: 145-146 °C. \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.30 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.49 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.45 – 7.35 (m, 2H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 138.2, 136.7, 132.4, 129.1, 127.9, 127.6, 126.6, 124.3, 120.2, 115.2, HRMS (ESI) calcd for C\textsubscript{18}H\textsubscript{13}BrNO\textsubscript{2}S [M+H]\(^+\) 385.9845, found 385.9839.

White solid; yield: 78%; mp: 184-185 °C. \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.35 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.50 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.39 – 7.30 (m, 4H), 1.19 (s, 9H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 157.7, 138.4, 135.2, 127.4, 126.4, 126.3, 126.1, 123.8, 120.0, 115.0, 35.1, 30.9, HRMS (ESI) calcd for C\textsubscript{22}H\textsubscript{22}NO\textsubscript{2}S [M+H]\(^+\) 364.1366, found 364.1371.

White solid; yield: 72%; mp: 181-182 °C. \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.29 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 141.3, 138.0, 132.8, 127.8, 127.0, 126.8, 124.8, 120.4, 117.5, 116.9, 115.2, HRMS (ESI) calcd for C\textsubscript{19}H\textsubscript{13}N\textsubscript{2}O\textsubscript{2}S [M+H]\(^+\) 333.0692, found 333.0637.

White solid; yield: 77%; mp: 175-176 °C. \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.33 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.77 – 7.70 (m, 2H), 7.48 (ddd, J = 8.8, 7.6, 1.2 Hz, 2H), 7.39 – 7.31 (m, 2H), 6.75 – 6.65 (m, 2H), 3.67 (s, 3H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 163.7, 138.4, 129.5, 128.7, 127.4, 126.4,
123.9, 120.0, 115.2, 114.2, 55.5, HRMS (ESI) calcd for C_{19}H_{16}NO_{3}S [M+H]^+ 338.0845, found 338.0842.

White solid; yield: 74%; mp: 157-158 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.32 (d, \(J = 8.4\) Hz, 2H), 7.92 (d, \(J = 7.6\) Hz, 2H), 7.58 (dd, \(J = 4.0, 1.2\) Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 – 7.36 (m, 3H), 6.88 (dd, \(J = 4.8, 4.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.2, 137.3, 132.9, 132.5, 127.5, 127.3, 126.8, 124.4, 120.1, 115.5, HRMS (ESI) calcd for C_{16}H_{12}NO_{2}S \[M+H\]^+ 314.0304, found 314.0304.

White solid; yield: 60%; mp: 108-109 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.17 (d, \(J = 8.4\) Hz, 2H), 8.01 (d, \(J = 7.2\) Hz, 2H), 7.55 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 2.98 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.4, 127.6, 126.3, 124.2, 120.2, 114.7, 38.7, HRMS (ESI) calcd for C_{13}H_{11}NNaO_{2}S \[M+Na\]^+ 268.0403, found 268.0407.

White solid; yield: 65%; mp: 59-60 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J = 8.4\) Hz, 2H), 7.91 – 7.85 (m, 2H), 7.39 – 7.33 (m, 2H), 7.28 (td, \(J = 7.6, 0.8\) Hz, 2H), 2.48 – 2.41 (m, 1H), 1.24 – 1.18 (m, 2H), 0.74 – 0.67 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.7, 127.4, 126.2, 123.8, 120.2, 114.8, 30.2, 5.2, HRMS (ESI) calcd for C_{13}H_{14}NO_{2}S \[M+H\]^+ 272.0740, found 272.0742.

3. Scale-up Synthesis and Further Transformations

Under nitrogen, to a round flask containing 2d, Pd(PPh\(_3\))\(_2\)Cl\(_2\) (5 mol%), and CuI (5 mol%) were added acetonitrile, piperidine (V/V = 2:1, 0.75 M) and phenylacetylene (1.1 eq). The reaction mixture was stirred and heated to reflux for 12 hours. After the reaction mixture was cooled down to room temperature, saturated
aqueous NH₄Cl was added to quench the reaction. The mixture was then extracted with ethyl acetate. All organic fractions were combined and washed with water and brine, dried over Na₂SO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to afford product 2d′.

Yellow solid; yield: 82%; mp: 72-73 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.32 (dd, J = 8.4, 4.0 Hz, 2H), 8.08 (d, J = 1.0 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.66 (dd, J = 8.8, 1.6 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.42 – 7.33 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 138.8, 137.9, 134.8, 131.6, 130.8, 129.8, 128.4, 128.3, 127.9, 126.6, 126.5, 125.8, 124.2, 123.3, 123.2, 120.2, 118.9, 115.2, 115.2, 89.3, 89.2, 21.5, HRMS (ESI) calcd for C₂₇H₁₉NNaO₂S [M+Na]⁺ 444.1029, found 444.1032.

4. NMR spectra

¹H NMR spectrum of 1a
\[ ^{13}C \text{ NMR spectrum of 1a} \]
$^1$H NMR spectrum of 1b

$^{13}$C NMR spectrum of 1b
$^1$H NMR spectrum of 1c
$^{13}$C NMR spectrum of 1c

$^1$H NMR spectrum of 1d
$^{13}$C NMR spectrum of 1d
$^1$H NMR spectrum of 1e

$^{13}$C NMR spectrum of 1e
$^1$H NMR spectrum of 1f
$^{13}$C NMR spectrum of 1f

$^{1}$H NMR spectrum of 1g
$^{13}$C NMR spectrum of 1g
$^{1}H$ NMR spectrum of 1h

$^{13}C$ NMR spectrum of 1h
$^1$H NMR spectrum of 1i
$^{13}$C NMR spectrum of 1i

$^1$H NMR spectrum of 1j
$^{13}$C NMR spectrum of 1j
$^1$H NMR spectrum of 1k

$^{13}$C NMR spectrum of 1k
H NMR spectrum of 11

\[ \text{1H NMR spectrum of 11} \]
$^{13}$C NMR spectrum of 1l

$^{1}$H NMR spectrum of 1m
$^{13}$C NMR spectrum of 1m
$^1$H NMR spectrum of 1n

$^{13}$C NMR spectrum of 1n
$^1$H NMR spectrum of 1o
$^{13}$C NMR spectrum of 1o

$^1$H NMR spectrum of 1p
$^{13}$C NMR spectrum of 1p
$^{1}$H NMR spectrum of 1q

$^{13}$C NMR spectrum of 1q
H NMR spectrum of 1r
$^{13}$C NMR spectrum of 1r

$^1$H NMR spectrum of 1s
$^{13}$C NMR spectrum of 1s
$^1$H NMR spectrum of 1t

$^{13}$C NMR spectrum of 1s
^1H NMR spectrum of 1u
$^{13}\text{C} \text{ NMR spectrum of 1u}$

$^{1}\text{H} \text{ NMR spectrum of 1v}$
$^{13}$C NMR spectrum of 1v
$^{1}$H NMR spectrum of 2a

$^{13}$C NMR spectrum of 2a
\[ \text{\textsuperscript{1}H NMR spectrum of 2b} \]
\(^{13}\text{C} \) NMR spectrum of 2b

\(^{1}\text{H} \) NMR spectrum of 2c
$^{13}$C NMR spectrum of 2c
$^{1}$H NMR spectrum of 2d

$^{13}$C NMR spectrum of 2d
$^1$H NMR spectrum of 2e
$^{13}$C NMR spectrum of 2e

$^1$H NMR spectrum of 2f
$^{13}$C NMR spectrum of 2f
$^1$H NMR spectrum of 2g

$^{13}$C NMR spectrum of 2g
$^1$H NMR spectrum of 2h
$^{13}$C NMR spectrum of 2h

$^{1}$H NMR spectrum of 2i
$^{13}$C NMR spectrum of 2i
$^1$H NMR spectrum of 2j

$^{13}$C NMR spectrum of 2j
$^1$H NMR spectrum of 2k
$^{13}$C NMR spectrum of 2k

$^{1}$H NMR spectrum of 2l
$^{13}$C NMR spectrum of 2l
$^{1}H$ NMR spectrum of $2m$

$^{13}C$ NMR spectrum of $2m$
$^1$H NMR spectrum of 2n
$^{13}$C NMR spectrum of 2n

$^1$H NMR spectrum of 2o
$^{13}$C NMR spectrum of 2o
$^1$H NMR spectrum of 2p

$^{13}$C NMR spectrum of 2p
$^{1}$H NMR spectrum of 2q
$^{13}$C NMR spectrum of 2q

$^{1}$H NMR spectrum of 2r
$^{13}$C NMR spectrum of 2r
$^{1}H$ NMR spectrum of 2s

$^{13}C$ NMR spectrum of 2s
'H NMR spectrum of 2t
$^{13}$C NMR spectrum of 2t

$^{1}$H NMR spectrum of 2u
\[ ^{13}\text{C NMR spectrum of 2u} \]
$^{1}H$ NMR spectrum of 2v

$^{13}C$ NMR spectrum of 2v
$^1$H NMR spectrum of 2d'}
$\text{${}^{13}$C NMR spectrum of 2d'}$
5. X-ray single crystal data for product

<table>
<thead>
<tr>
<th>Identification code</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{19}H_{15}NO_{3}S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>337.38</td>
</tr>
<tr>
<td>Temperature</td>
<td>113(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>17.5290(4) Å</td>
</tr>
<tr>
<td>b</td>
<td>10.1840(2) Å</td>
</tr>
<tr>
<td>c</td>
<td>18.2727(4) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>3214.79(13) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.394 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.218 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1408</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.18 x 0.12 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.53 to 35.68 deg.</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-28 &lt;= h &lt;= 27, -16 &lt;= k &lt;= 16, -28 &lt;= l &lt;= 29</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td><strong>Reflections collected / unique</strong></td>
<td>49049 / 14126 [R(int) = 0.0435]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 27.90</strong></td>
<td>94.9 %</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>0.9743 and 0.9577</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>14126 / 0 / 435</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F^2</strong></td>
<td>1.019</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R1 = 0.0532, wR2 = 0.1437</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.0990, wR2 = 0.1653</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.261 and -0.306 e. Å^{-3}</td>
</tr>
</tbody>
</table>