Triphenylphosphine Promoted Regio and Stereoselective α-Halogenation of Ynamides

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SUPPORTING INFORMATION

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General Information: All the reactions were performed in an oven-dried Schlenk flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using 100–200 Mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I$_2$ chamber.

Proton, carbon, and fluorine nuclear magnetic resonance spectra ($^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, and $^{31}$P NMR) were recorded based on the resonating frequencies as follows: ($^1$H NMR, 400 MHz; $^{13}$C NMR, 101 MHz; $^{19}$F NMR, 376 MHz) and ($^1$H NMR, 500 MHz; $^{13}$C NMR, 126 MHz; $^{19}$F NMR, 470 MHz; $^{31}$P NMR, 202 MHz) having the solvent resonance as internal standard ($^1$H NMR, CHCl$_3$ at 7.26 ppm; $^{13}$C NMR, CDCl$_3$ at 77.0 ppm) and the data for $^1$H, $^{13}$C NMR, $^{19}$F, $^{31}$P NMR were reported in terms of chemical shift (ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for $^1$H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m =multiplet), coupling constants, $J$, in (Hz), and integration. IR spectra were reported in cm$^{-1}$. HRMS were obtained in ESI-TOF analyzer. LC−MS spectra were obtained (EI positive/negative mode) with an ionization voltage of 70 eV; data are reported in the form of m/z (intensity relative to base peak 100). Elemental (C, H, N) analysis was carried out using an EA 1112 analyzer. Melting points were determined by electrothermal heating and are uncorrected.

Materials: Unless otherwise noted, all the reagents were obtained commercially and used without purification. Dichloromethane (CH$_2$Cl$_2$) and carbon tetrachloride (CCl$_4$) used from bottle grade. Iodoform (CH$_3$I), tetrabromomethane (CBr$_4$), carbon tetrachloride (CCl$_4$), and triphenylphosphine (Ph$_3$P) are purchased and used as received.
Experimental Section

Following the known synthetic procedure, 1a–r are prepared. Analytical and spectral data of 1a, 1d, 1h, 1i, 1o, 1p and 1r are exactly matching with the reported values.1

General Procedure for the Synthesis of 1 (GP 1):1 To a mixture of 1″ (2.0 mmol), CuSO₄·5H₂O (0.2 mmol), 1,10-phenanthroline (0.4 mmol) and K₃PO₄ (4.0 mmol) in dry toluene (8.0 mL) was added 1-bromo-2-arylacetylene (1′). The reaction mixture was heated at 70 ºC under the nitrogen atmosphere. Progress of the reaction was monitored periodically by TLC. Upon completion, the reaction mixture was cooled to room temperature and diluted with dichloromethane (10 mL). The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified using column chromatography on silica gel to provide 1.

N-Methyl-N-(m-tolylethynyl)-N-4-methylbenzenesulfonamide (1b):

Pale yellow solid (460 mg, 77% yield); mp 85–88 ºC; Rf = 0.38 (9:1 hexane/EtOAc); [Silica, UV and I₂; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.21–7.14 (m, 3H), 7.12–7.06 (m, 1H), 3.14 (s, 3H), 2.45 (s, 3H), 2.31 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 137.9, 133.2, 131.9, 129.8, 128.7, 128.4, 128.1, 127.8, 122.4, 83.6, 69.1, 39.3, 21.6, 21.2; IR (Neat)νmax 2230, 1687, 1594, 1446, 1167, 1019, 865, 821, 783 cm⁻¹; MS (EI) m/z (%): 300 (M⁺ + 1, 100), 207 (13); Anal. Calcd. for C17H17NO2S: C, 68.20; H, 5.72; N, 4.68; S, 10.71 . Found: C, 68.35; H, 5.75; N, 4.61; S, 10.62.

N-Benzyl-N-((3,4-dimethylphenyl)ethynyl)-4-methylbenzenesulfonamide (1c):

Colorless solid (710 mg, 91% yield); mp 105–107 ºC; Rf = 0.4 (4:1 hexane/EtOAc); [Silica, UV and I₂; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (bd, J = 7.6 Hz, 2H), 7.38–7.24 (m, 7H), 7.03 (s, 1H), 7.00 (s, 2H), 4.56 (s, 2H), 2.43 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.5, 136.6, 136.4, 134.7, 134.5, 132.4, 129.6, 129.4, 128.8, 128.76, 128.4, 128.2,
127.7, 119.9, 81.7, 71.3, 55.7, 21.6, 19.6, 19.5; IR (Neat)νmax 2219, 1594, 1452, 1358, 953, 915, 756, 591, 531; cm⁻¹; MS (El) m/z (%) 390 (M+ + 1, 100); Anal. Calcd. for C₂₄H₂₃NO₂S: C, 78.81; H, 6.19; N, 3.59; O, 8.19; S, 8.21. Found: C, 74.15; H, 5.98; N, 3.65; O, 8.31.

**N-Benzyl-N-((3-cyanophenyl)ethynyl)-4-methylbenzenesulfonamide (1e):**

![Image of the compound](image)

Colorless solid (672 mg, 87% yield); mp 147–148 °C; Rf = 0.41 (4:1 hexane/EtOAc); [Silica, UV and I2]; ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.54–7.47 (m, 3H), 7.44–7.34 (m, 6H), 4.70 (s, 2H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 134.8, 134.2, 133.7, 133.5, 131.8, 130.7, 129.4, 129.1, 128.9, 128.8, 128.0, 126.2, 117.9, 112.7, 89.3, 68.7, 55.8, 21; IR (Neat)νmax 2235, 1693, 1490, 1364, 1304, 1084, 958, 810, 706 cm⁻¹; MS (El) m/z (%) 441 (M+ + 1, 100); Anal. Calcd. for C₂₃H₁₈N₂O₂S: C, 70.93; H, 4.92; N, 3.60; O, 12.32; S, 8.38. Found: C, 71.56; H, 4.61; N, 7.32; S, 8.38.

**N-Benzyl-N-((3-formylphenyl)ethynyl)-4-methylbenzenesulfonamide (1f):**

![Image of the compound](image)

Pale yellow gummy liquid (638 mg, 82 % yield); Rf = 0.62 (4:1 hexane/EtOAc); [Silica, UV and I2]; ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.86–7.80 (m, 1H), 7.73 (bs, 1H), 7.60–7.49 (m, 4H), 7.42–7.34 (m, 5H), 4.67 (s, 2H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 193.1, 145.7, 136.9, 136.4, 135.0, 134.3, 131.8, 130.7, 130.1, 129.3, 129.0, 128.8, 128.0, 123.5, 84.7, 70.4, 55.5, 21.6; IR (Neat)νmax 2235, 1594, 1495, 1260, 1172, 1090, 936, 816, 723, 597 cm⁻¹; MS (El) m/z (%) 389 (M+ + 2, 100); Anal. Calcd. for C₂₃H₁₉N₂O₃S: C, 70.93; H, 4.92; N, 3.60; O, 12.32; S, 8.23. Found: C, 71.56; H, 4.61; N, 7.32; S, 8.38.

**N-((4-Acetylphenyl)ethynyl)-N-benzyl-4-methylbenzenesulfonamide (1g):**

![Image of the compound](image)

Colorless solid (629 mg, 78% yield); mp 146–148 °C; Rf = 0.51 (4:1 hexane/EtOAc); [Silica, UV and I2]; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 12.8 Hz, 2H), 7.41–7.37 (m, 5H), 7.37–7.32 (m, 2H), 4.68 (s, 2H), 2.55 (s, 3H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.5, 145.8, 135.8, 135.0, 134.2, 130.7, 130.6, 129.3, 129.0, 128.9, 128.9, 128.0, 127.3, 86.8, 71.5, 55.5, 27.1, 21.6; IR (Neat)νmax 1682, 1594, 1550, 1452, 1265, 1084, 761 cm⁻¹; MS (El) m/z (%) 461 (M+ + 2, 100); Anal. Calcd. for C₂₄H₂₄N₂O₂S: C, 78.81; H, 6.19; N, 3.59; O, 8.19; S, 8.21. Found: C, 74.15; H, 5.98; N, 3.65; O, 8.31.
N-Benzyl-4-methyl-N-(naphthalen-1-ylethynyl)benzenesulfonamide (1j):

Colorless solid (667 mg, 81% yield); mp 112–114 °C; \( R_f = 0.32 \) (4:1 hexane/EtOAc); [Silica, UV and I2]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.86 (d, \( J = 8.4 \) Hz, 2H), 7.83–7.69 (m, 3H), 7.47–7.42 (m, 2H), 7.41–7.36 (m, 3H), 7.36–7.28 (m, 6H), 4.67 (s, 2H), 2.42 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 144.7, 134.6, 134.4, 133.0, 132.9, 129.8, 129.2, 129.0, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 126.5, 126.2, 126.1, 125.1, 120.5, 87.1, 69.9, 55.7, 21.6; IR (Neat)\( \nu_{\text{max}} \) 2224, 1649, 1594, 1539, 1495, 1446, 1260, 931, 843, 591 cm\(^{-1}\); MS (EI) \( m/z \) (%): 412 (M\(^+\) + 1, 100); Anal. Calcd. for C\(_{26}\)H\(_{2}\)NO\(_3\)S: C, 75.88; H, 5.14; N, 3.40; O, 7.78; S, 7.79. Found: C, 75.73; H, 5.18; N, 3.46; S, 7.71.

N-Methyl-N-(naphthalen-1-ylethynyl)-N-4-Methylbenzenesulfonamide (1k):

Colorless solid (509 mg, 76% yield); mp 119–121 °C; \( R_f = 0.28 \) (4:1 hexane/EtOAc); [Silica, UV and I2]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.26 (d, \( J = 8.4 \) Hz, 1H), 7.83 (d, \( J = 7.6 \) Hz, 2H), 7.73 (d, \( J = 8.0 \) Hz, 1H), 7.67 (d, \( J = 8.0 \) Hz, 1H), 7.57–7.48 (m, 2H), 7.42 (bt, \( J = 7.2 \) Hz, 1H), 7.30 (bt, \( J = 7.2 \) Hz, 1H), 7.19 (d, \( J = 7.6 \) Hz, 2H), 3.18 (s, 3H), 2.26 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 144.9, 133.3, 131.2, 131.1, 130.7, 130.0, 130.0, 129.9, 128.3, 127.8, 127.2, 127.17, 127.03, 126.9, 126.8, 122.7, 122.6, 119.1, 88.2, 67.7, 39.4, 21.6; IR (Neat)\( \nu_{\text{max}} \) 2926, 1600, 1523, 1446, 1167, 1084, 931, 860, 745 cm\(^{-1}\); MS (EI) \( m/z \) (%): 336 (M\(^+\) + 1, 100); Anal. Calcd. for C\(_{20}\)H\(_{1}\)NO\(_2\)S: C, 71.62; H, 5.11; N, 4.18; O, 9.54; S, 9.56. Found: C, 71.56; H, 5.18; N, 4.23; S, 9.49.

N-Methyl-N-(phenanthren-9-ylethynyl)-N-4-Methylbenzenesulfonamide (1l):

Pale yellow solid; (608 mg, 79% yield); mp 120–121 °C; \( R_f = 0.29 \) (9:1 hexane/EtOAc); [Silica, UV and I2]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.68–8.59 (m, 2H), 8.35–8.30 (m, 1H), 7.93–7.85 (m, 3H), 7.82–7.52 (m, 1H), 7.71–7.53 (m, 4H), 7.34 (d, \( J = 8.0 \) Hz, 2H), 3.28 (s, 3H), 2.42 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 144.9, 133.3, 131.2, 131.1, 130.7, 130.0, 130.0, 129.9, 128.3, 127.8, 127.2, 127.17, 127.03, 126.9, 126.8, 122.7, 122.6, 119.1, 88.2, 67.7, 39.4, 21.6; IR (Neat)\( \nu_{\text{max}} \) 2926, 1600, 1523, 1446, 1167, 1084, 931, 860, 745 cm\(^{-1}\); MS (EI) \( m/z \) (%): 386 (M\(^+\) + 5).
(3-Fluorophenyl)ethynyl)-N,N-dimethylbenzenesulfonamide (1m):

Pale yellow semi solid; (533 mg, 88% yield); $R_f = 0.36$ (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.45–7.38 (m, 1H), 7.24–7.18 (m, 3H), 3.15 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3 (d, $J = 245$ Hz, 1C), 145.8, 132.7, 131.2 (d, $J = 9.0$ Hz, 1C), 130.7, 128.1, 127.62, 127.60, 124.4 (d, $J = 10.0$ Hz, 1C), 117.8 (d, $J = 23.0$ Hz, 1C), 117.8 (d, $J = 21$ Hz, 1C), 58.7, 68.1, 21.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –112.6; IR (Neat)$\nu_{max}$ 12241, 1698, 1490, 1347, 1161, 1024, 767, 673 cm$^{-1}$; MS (EI) $m/z$ (%) 304 (M$^+$ + 1, 100); Anal. Calcd. for C$_{16}$H$_{14}$FNO$_2$S: C, 63.35; H, 4.65; F, 6.26; N, 4.62; O, 10.55; S, 10.45. Found: C, 63.41; H, 4.58; N, 4.56; S, 10.45.

N-((4-Fluorophenyl)ethynyl)-N,N-dimethylbenzenesulfonamide (1n):

Brownish gummy solid; (394 mg, 65% yield); $R_f = 0.35$ (9:1 hexane/EtOAc); [Silica, UV and I$_2$]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.46–7.40 (m, 2H), 7.22 (t, $J = 9.2$ Hz, 2H), 3.13 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.4 (d, $J = 247$ Hz, 1C), 145.7, 134.0, 133.9, 132.7, 130.7, 128.1, 118.7, 118.7, 116.4 (d, $J = 22$ Hz, 1C), 84.3, 67.9, 21.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –111.2; IR (Neat)$\nu_{max}$ 2230, 1698, 1600, 1358, 1161, 1024, 767, 673 cm$^{-1}$; MS (EI) $m/z$ (%) 304 (M$^+$ + 1, 100); Anal. Calcd. for C$_{16}$H$_{14}$FNO$_2$S: C, 63.35; H, 4.65; F, 6.26; N, 4.62; O, 10.55; S, 10.57. Found: C, 63.26; H, 4.69; N, 4.58; S, 10.45.

N-Benzyl-N-((5-bromopyridin-2-yl)ethynyl)-4-methylbenzenesulfonamide (1q):

Colorless solid; (573 mg, 65% yield); mp 126–127 °C; $R_f = 0.2$ (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.54 (s, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.39–7.25 (m, 7H), 7.08 (d, $J = 8.4$ Hz, 1H), 4.61 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.8, 144.9, 141.7, 138.6, 134.6, 134.1, 129.8, 128.7, 128.6, 128.4, 127.7, 127.3, 119.0, 84.4, 71.0, 55.6, 29.7, 21.6; IR (Neat)$\nu_{max}$ 2230, 1594, 1161, 1134, 1041, 827, 778, 657 cm$^{-1}$; MS (EI) $m/z$ (%) 304 (M$^+$ + 1, 100); Anal. Calcd. for C$_{24}$H$_{19}$NO$_2$S: C, 74.78; H, 4.97; N, 3.63; O, 8.30; S, 8.32 Found: C, 74.65; H, 4.91; N, 3.72; S, 8.38.
+ 1, 100); Anal. Calcd. for C\textsubscript{21}H\textsubscript{17}BrN\textsubscript{2}O\textsubscript{2}S: C, 71.48; H, 4.69; N, 7.25; O, 8.28; S, 8.30. Found: C, 70.85; H, 4.88; N, 3.56; S, 8.31.

General Procedure for the Chlorination of 1; Synthesis of 2 (GP 2):

\[
\begin{align*}
\text{R}^1= & \quad \text{N} \\
\text{Cl} & \quad \text{R}^2
\end{align*}
\]

To a solution of corresponding ynamide 1 (0.5 mmol), PPh\textsubscript{3} (0.6 mmol), and CCl\textsubscript{4} (1.0 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (2.0 mL for 0.5 mmol) in a Schlenk tube was added H\textsubscript{2}O (0.75 mmol). The resulting mixture was stirred at room temperature (25 °C). Progress of the reaction was monitored periodically by TLC. Upon completion, the reaction mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified through column chromatography on silica gel to provide 2.

(E)-N-Benzyl-N-(1-chloro-2-phenylvinyl)-4-methylbenzenesulfonamide (2a):

Colorless solid; (E/Z = 99:1; 195 mg, 98% yield); mp = 168–169 °C; \( R_f = 0.65 \) (4:1 hexane/EtOAc), [Silica, UV and I\textsubscript{2}]; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.87 (d, \( J = 8.4 \) Hz, 2H), 7.38–7.30 (m, 4H), 7.24–7.19 (m, 5H), 7.18–7.08 (m, 3H), 6.61 (s, 1H), 4.80 (bd, \( J = 9.6 \) Hz, 1H), 4.05 (bd, \( J = 10 \) Hz, 1H), 2.47 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 144.6, 135.0, 134.9, 133.4, 132.9, 129.8, 129.6, 128.9, 128.5, 128.3, 128.2, 128.1, 127.5, 52.4, 21.7; IR (Neat)\( \nu \)\textsubscript{max} 1595, 1348, 1238, 1167, 1085, 937, 816, 740 cm\textsuperscript{-1}; HRMS (ESI) for C\textsubscript{22}H\textsubscript{20}ClNNaO\textsubscript{2}S (M+Na): calcd 420.0801, found 420.0805.

(E)-N-(1-Chloro-2-m-tolylvinyl)-N,4-dimethylbenzenesulfonamide (2b):

Colorless solid; (E/Z = 86:14; 164 mg, 97% yield); mp = 170–172 °C; \( R_f \) = 0.65 (4:1 hexane/EtOAc), [Silica, UV and I\textsubscript{2}]. Major rotamer: \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.77 (d, \( J = 8.0 \) Hz, 2H), 7.44 (d, \( J = 8.0 \) Hz, 1H), 7.35–7.25 (m, 4H), 7.12 (d, \( J = 8.0 \) Hz, 1H), 6.62 (s, 1H), 3.02 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 144.4, 138.1, 134.8, 133.0, 132.5, 129.63, 129.57, 129.5, 128.8, 128.6, 128.3, 125.7, 35.7, 21.6, 21.4 ppm; Minor rotamer (selected signals): \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.40 (d, \( J = 8.0 \) Hz,), 6.9 (s), 3.07 (s), 2.44 (s), 2.36 (s) ppm; IR (Neat)\( \nu \)\textsubscript{max} 2356,
2338, 1631, 1356, 1163, 1087, 739 cm⁻¹; HRMS (ESI) for C₁₇H₂₂ClN₂O₂S (M+NH₄)⁺: calcd 353.1091, found 353.1091.

**(E)-N-Benzyl-N-(1-chloro-2-(3,4-dimethylphenyl)vinyl)-4-methylbenzenesulfonamide (2c):**

![Structure 2c](image)

Colorless solid; (E/Z = 96:4; 183 mg, 86% yield); mp = 180–181 °C; Rƒ = 0.64 (4:1 hexane/EtOAc). [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 8.0 Hz, 2H), 7.36–7.23 (m, 4H), 7.17–7.08 (m, 4H), 7.01 (s, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.54 (s, 1H), 4.78 (bd, J = 12.4 Hz, 1H), 4.07 (bd, J = 12.8 Hz, 1H), 2.41 (s, 3H), 2.17 (s, 3H), 2.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 144.3, 137.2, 135.9, 135.1, 134.8, 133.6, 130.4, 129.7, 129.5, 129.3, 128.7, 128.1, 126.3, 126.2, 52.2, 21.5, 19.5; IR (Neat) v max 1596, 1453, 1359, 1161, 1087, 1020, 852, 731 cm⁻¹; HRMS (ESI) for C₂₄H₂₂ClNO₂SNa (M+Na)⁺: calcd 448.1114, found 448.1112.

**(E)-Ethyl 4-(2-(N-benzyl-4-methylphenylsulfonamido)-2-chlorovinyl)benzoate (2d):**

![Structure 2d](image)

Colorless solid; (E/Z = 98:2; 107 mg, 73% yield); mp = 138–140 °C; Rƒ = 0.34 (4:1 hexane/EtOAc). [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 7.89–7.82 (m, 4H), 7.35 (d, J = 8.4 Hz, 4H), 7.24–7.19 (m, 2H), 7.18–7.10 (m, 3H), 6.64 (s, 1H), 4.81 (bd, J = 12.8 Hz, 1H), 4.36 (q, J = 6.8 Hz, 2H), 4.03 (bd, J = 12.8 Hz, 1H), 2.46 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 166.2, 144.7, 137.2, 134.7, 134.0, 133.2, 130.0, 129.8, 129.7, 129.5, 129.2, 128.9, 128.5, 128.4, 128.3, 60.9, 52.4, 21.6, 14.3; IR (Neat) v max 1704, 1605, 1353, 1233, 1162, 773 cm⁻¹; HRMS (ESI) for C₂₅H₂₄ClNO₄S (M+Na)⁺: calcd 492.1012, found 492.1009.

**(E)-N-Benzyl-N-(1-chloro-2-(3-cyanophenyl)vinyl)-4-methylbenzenesulfonamide (2e):**

![Structure 2e](image)

Pale yellow solid; (E/Z = 100:0; 101 mg, 92% yield); mp = 168–170 °C; Rƒ = 0.44 (4:1 hexane/EtOAc). [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.44 (dt, J = 7.6, 1.2 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.25–7.15 (m, 6H), 6.60 (s, 1H), 4.81 (bd, J = 12.4 Hz, 1H), 4.02 (bd, J = 12.8 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 144.9, 134.6, 134.1, 133.1, 132.7, 132.6, 131.7, 131.5, 130.1, 129.9, 129.7, 128.9, 128.7, 128.6, 128.5, 118.3, 112.2, 52.2, 21.6; IR (Neat) v max 2219, 1595, 1359, 1233, 1162, 1014.
904, 789, 663 cm\(^{-1}\); HRMS (ESI) for C\(_{23}H_{19}ClN_2NaO_2S\) (M+Na): calcd 445.0753, found 445.0757.

\(\text{(E)}\)-N-Benzyl-N-(1-chloro-2-(3-formylphenyl)vinyl)-4-methylbenzenesulfonamide (2f): Colorless solid; (E/Z = 100:0; 90 mg, 82% yield); mp = 185–186 °C; \(R_f = 0.37 \) (4:1 hexane/EtOAc). [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 9.84 \text{ (s, 1H)}, 7.85 \text{ (d, } J = 8.4 \text{ Hz, 2H)}, 7.71 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 7.63 \text{ (bs, 1H)}, 7.60 \text{ (br d, } J = 7.6 \text{ Hz, 1H)}, 7.38–7.32 \text{ (m, 3H)}, 7.25–7.21 \text{ (m, 2H)}, 7.17–7.09 \text{ (m, 3H)}, 6.68 \text{ (s, 1H)}, 4.82 \text{ (bd, } J = 12.4 \text{ Hz, 1H)}, 4.04 \text{ (bd, } J = 12.8 \text{ Hz, 1H)}, 2.46 \text{ (s, 3H)}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 192.0, 144.8, 136.1, 134.7, 133.8, 133.6, 133.3, 130.7, 129.8, 129.7, 129.2, 128.8, 128.5, 128.3, 52.3, 21.6; \) IR (Neat) \(\nu_{\text{max}} \) 2920, 1638, 1348, 1156, 1025 \text{ cm}\(^{-1}\); HRMS (ESI) for C\(_{23}H_{24}ClN_2O_3S\) (M+NH\(_4\)^+): calcd 443.1196, found 443.1194.

\(\text{(E)}\)-N-(2-(4-Acetylphenyl)-1-chlorovinyl)-N-benzyl-4-methylbenzenesulfonamide (2g): Colorless solid; (E/Z = 94:6; 80 mg, 73% yield); mp = 132–134 °C; \(R_f = 0.37 \) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.85 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.77 \text{ (d, } J = 8.4 \text{ Hz, 2H)}, 7.42–7.33 \text{ (m, 4H)}, 7.27–7.21 \text{ (m, 2H)}, 7.20–7.09 \text{ (m, 3H)}, 6.64 \text{ (s, 1H)}, 4.82 \text{ (bd, } J = 12.8 \text{ Hz, 1H)}, 4.03 \text{ (bd, } J = 12.8 \text{ Hz, 1H)}, 2.57 \text{ (s, 3H)}, 2.47 \text{ (s, 3H)}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 197.5, 144.8, 137.4, 136.5, 134.7, 133.9, 133.2, 129.8, 129.7, 129.2, 128.8, 128.5, 128.3, 52.4, 21.6; \) IR (Neat) \(\nu_{\text{max}} \) 1671, 1266, 1162, 1085, 707 \text{ cm}\(^{-1}\); HRMS (ESI) for C\(_{24}H_{22}ClN_2O_3S\) (M+Na)^+: calcd 462.0907, found 462.0909.

\(\text{(E)}\)-N-(1-Chloro-2-phenylnvinyl)-N,4-dimethylbenzenesulfonamide (2h): Colorless solid; (E/Z = 100:0; 151 mg, 93% yield); mp = 201–202 °C; \(R_f = 0.55 \) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.81 \text{ (d, } J = 7.2 \text{ Hz, 2H)}, 7.63 \text{ (d, } J = 7.6 \text{ Hz, 2H)}, 7.45–7.28 \text{ (m, 5H)}, 6.68 \text{ (s, 1H)}, 3.06 \text{ (s, 3H)}, 2.47 \text{ (s, 3H)}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 144.5, 134.2, 133.1, 132.4, 129.8, 129.5, 128.9, 128.82, 128.77, 128.69, 35.7, 21.7; \) IR (Neat) \(\nu_{\text{max}} \) 1638, 1591, 1360, 1167, 1085, 960 \text{ cm}\(^{-1}\); HRMS (ESI) for C\(_{16}H_{20}ClN_2O_2S\) (M+NH\(_4\))^+: calcd 339.0934, found 339.0937.
(E)-N-(1-Chloro-2-(2-methoxyphenyl)vinyl)-N,4-dimethylbenzenesulfonamide (2i):

Colorless solid; (E/Z = 99:1; 118 mg, 67% yield); mp = 130–132 °C; $R_f$ = 0.59 (4:1 hexane/EtOAc), [Silica, UV and I$_2$]; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.32–7.24 (m, 3H), 7.04 (s, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 3.82 (s, 3H), 3.00 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.8, 144.2, 134.3, 129.9, 129.5, 129.4, 128.7, 128.6, 126.5, 122.0, 120.7, 110.6, 55.5, 35.8, 21.6; IR (Neat) $\nu_{\text{max}}$ 1593, 1492, 1349, 1250, 1159, 962, 763 cm$^{-1}$; HRMS (ESI) for C$_{17}$H$_{22}$ClN$_2$O$_3$S (M+NH$_4$)$^+$: calcd 369.1040, found 369.1040.

(E)-N-Benzyl-N-(1-chloro-2-(naphthalen-1-yl)vinyl)-4-methylbenzenesulfonamide (2j):

Colorless solid; (E/Z = 100:0; 202 mg, 90% yield); mp = 193–195 °C; $R_f$ = 0.57 (4:1 hexane/EtOAc), [Silica, UV and I$_2$]; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.76 (d, $J = 6.5$ Hz, 2H), 7.73 (dd, $J = 8.0$, 4.5 Hz, 2H), 7.46 (d, $J = 7.0$ Hz, 1H), 7.42–7.36 (m, 1H), 7.33 (t, $J = 8.0$ Hz, 1H), 7.31–7.27 (m, 1H), 7.25 (bs, 1H), 7.23 (bs, 2H), 6.92–6.87 (m, 2H), 6.86–6.76 (m, 3H), 4.56 (bs, 1H), 4.05 (bs, 1H), 2.40 (s, 3H); $^{13}$C NMR (125.7 MHz, CDCl$_3$) δ 144.4, 134.9, 133.1, 133.03, 132.97, 131.2, 129.8, 129.4, 129.3, 128.8, 128.6, 128.1, 127.84, 127.81, 126.6, 125.9, 125.5, 125.2, 123.9, 52.3, 21.6; IR (Neat)$\nu_{\text{max}}$ 1580, 1345, 1086, 919, 873, 798, 776, 704 cm$^{-1}$; HRMS (ESI) for C$_{26}$H$_{22}$ClNNaO$_2$S (M+Na)$^+$: calcd 470.0957, found 470.0958.

(E)-N-(1-Chloro-2-(naphthalen-1-yl)vinyl)-N,4-dimethylbenzenesulfonamide (2k):

Colorless solid; (E/Z = 100:0; 175 mg, 94% yield); mp = 201–203 °C; $R_f$ = 0.55 (4:1 hexane/EtOAc), [Silica, UV and I$_2$]; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.91–7.86 (m, 1H), 7.85–7.81 (m, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 7.0$ Hz, 1H), 7.53 (bd, $J = 7.0$ Hz, 2H), 7.50–7.46 (m, 2H), 7.44 (t, $J = 7.8$ Hz, 1H), 7.27 (s, 1H), 7.06 (d, $J = 8.0$ Hz, 2H), 2.99 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.0, 134.3, 133.4, 131.9, 131.2, 130.2, 130.1, 129.2, 128.8, 128.5, 128.3, 126.4, 126.3, 125.9, 125.4, 123.8, 36.2, 21.5; IR (Neat)$\nu_{\text{max}}$ 1644, 1594, 1085, 924, 891, 779, 705 cm$^{-1}$; HRMS (ESI) for C$_{20}$H$_{18}$ClNO$_2$SNa (M+Na)$^+$: calcd 394.0644, found 394.0643.
(E)-N-(1-Chloro-2-(phenanthren-9-yl)vinyl)-N,4-dimethylbenzenesulfonamide (2l):

Yellow gummy liquid; (E/Z = 94:6; 177 mg, 84% yield); mp = 223–226 °C; 
$R_f = 0.65$ (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; Major rotamer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.67 (d, $J = 7.6$ Hz, 1H), 8.63 (d, $J = 8.4$ Hz, 1H), 7.93 (dd, $J = 8.0$, 0.8 Hz, 1H), 7.88–7.79 (m, 2H), 7.71–7.55 (m, 4H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.25 (bs, 1H), 6.84 (d, $J = 8.0$ Hz, 2H), 3.04 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.8, 134.7, 132.5, 131.2, 130.28, 130.26, 130.23, 130.17, 129.1, 129.0, 128.8, 128.0, 127.6, 127.1, 126.8, 126.74, 126.66, 124.7, 122.9, 122.5, 122.3, 36.4, 21.4; Minor rotamer (selected signals): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 (s), 3.17 (s), 2.40 (s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 129.7, 128.21, 31.5, 22.6; IR (Neat) $\nu_{\text{max}}$ 2360, 1637, 1353, 1164, 1087, 964 cm$^{-1}$; HRMS (ESI) for C$_{24}$H$_{24}$ClN$_2$O$_2$S (M+NH$_4$)$^+$: calcd 439.1247, found 439.1247.

(E)-N-(1-Chloro-2-(3-fluorophenyl)vinyl)-N,4-dimethylbenzenesulfonamide (2m):

Yellow semi solid; (E/Z = 79:21; 160 mg, 94% yield); mp = 188–190 °C $R_f$ = 0.52 (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; Major rotamer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 8.0$ Hz, 2H), 7.39–7.28 (m, 6H), 6.62 (s, 1H), 3.03 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.8 (d, $J = 244.0$ Hz, 1C), 144.6, 135.1, 134.1, 131.2, 130.1, 129.6, 129.3, 128.2, 124.6 (d, $J = 3.0$ Hz, 1C), 115.8 (d, $J = 21.2$ Hz, 1C), 115.3 (d, $J = 23.2$ Hz, 1C), 35.7, 21.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$–111.5; Minor rotamer (selected signals): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.05–6.98 (m), 6.90 (s), 3.07 (s), 2.45 (s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.5 (d, $J = 247$ Hz, 1C), 144.4, 135.1, 134.4, 131.1, 130.0, 129.7, 129.3, 128.2, 125.6 (d, $J = 2.0$ Hz, 1C), 115.9 (d, $J = 21$ Hz, 1C), 115.7 (d, $J = 19$ Hz, 1C), 35.9; IR (Neat) $\nu_{\text{max}}$ 1448, 1352, 1162, 994, 810, 784, 723, 706 cm$^{-1}$; HRMS (ESI) for C$_{16}$H$_{19}$ClF$_3$N$_2$O$_2$S (M+NH$_4$)$^+$: calcd 357.0840, found 357.0841.

(E)-N-(1-Chloro-2-(4-fluorophenyl)vinyl)-N,4-dimethylbenzenesulfonamide (2n):

Pale yellow solid, (E/Z = 78:22; 155 mg, 91% yield); mp = 170–172 °C $R_f$ = 0.53 (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; Major rotamer: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.71 (d, $J = 8.5$ Hz, 2H), 7.55–7.50 (m, 2H), 7.25 (t, $J = 6.4$ Hz, 2H), 7.19 (s, 1H), 7.0–6.95 (m, 2H), 6.54 (s, 1H), 2.95 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 163.7 (d, $J = 249.1$ Hz, 1C), 144.6, 134.1, 131.2, 130.6
(d, $J = 8.8$ Hz, 1C), 129.6, 128.8, 128.3, 115.72 (d, $J = 21.4$ Hz, 1C), 35.7, 21.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –112.5 (s); Minor rotamer (selected signals): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.68 (d), 6.54 (s), 3.0 (s), $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 131.3 (d, $J = 7.5$ Hz, 1C), 129.7, 129.4, 129.31, 129.28, 115.3 (d, $J = 21.4$ Hz, 1C); IR (Neat) $\nu_{\text{max}}$ 1502, 1349, 1081, 963, 818, 710 cm$^{-1}$; HRMS (ESI) for C$_{16}$H$_{19}$ClFN$_2$O$_2$S (M$+$NH$_4$)$^+$: calcd 357.0840, found 357.0840.

**(E)-tert-Butyl 1-chloro-2-phenylvinyl(phenyl)carbamate (2o):**

![Chemical Structure](image)

Colorless solid; ($E/Z = 99:1$; 213 mg, 97% yield); mp = 182–184 °C; $R_f$ = 0.65 (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43–7.37 (m, 4H), 7.36–7.30 (m, 4H), 7.30–7.27 (m, 1H), 7.25–7.17 (m, 1H), 6.68 (s, 1H), 1.34 (s, 9H), $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.8, 138.9, 133.8, 130.3, 128.90, 128.86, 128.7, 128.5, 127.6, 126.3, 124.4, 82.6, 27.9; IR (Neat) $\nu_{\text{max}}$ 3057, 2980, 2926, 1725, 1638, 1599, 1490, 1451, 1391, 1369, 1287, 1237, 1150, 1002, 892, 843 cm$^{-1}$; HRMS (ESI) for C$_{19}$H$_{20}$ClNNaO$_2$: calcd 352.1080, found 352.1080.

**(E)-N-Benzyl-N-(1-chloropent-1-enyl)-4-methylbenzenesulfonylamine (2p):**

![Chemical Structure](image)

Colorless solid; ($E/Z = 99:1$; 213 mg, 93% yield); mp = 168–170 °C; $R_f$ = 0.35 (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88–7.77 (m, 2H), 7.40–7.26 (m, 7H), 5.74–5.65 (m, 1H), 4.80 (d, $J = 13.2$ Hz, 1H), 3.92 (d, $J = 13.2$ Hz, 1H), 2.45 (s, 3H), 2.08–1.72 (m, 2H), 1.17–0.97 (m, 1H), 0.81–0.67 (m, 1H), 0.67–0.61 (m, 3H), $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.3, 137.8, 135.6, 134.5, 129.6, 128.41, 128.37, 128.2, 125.3, 51.4, 31.3, 21.7, 21.5, 13.5; IR (Neat) $\nu_{\text{max}}$ 1596, 1356, 1261, 1167, 1040, 904, 784, 752, cm$^{-1}$; HRMS (ESI) for C$_{19}$H$_{22}$ClNNaO$_2$ (M$+$Na)$^+$: calcd 386.0957, found 386.0953.

**(E)-N-Benzyl-N-(2-(5-bromopyridin-2-yl)-1-chlorovinyl)-4-ethylbenzenesulfonylamine (2q):**

![Chemical Structure](image)

Brownish gummy liquid; ($E/Z = 94:6$; 213 mg, 77% yield); $R_f$ = 0.51 (30% hexane/EtOAc); [Silica, UV and I$_2$]; Major rotamer: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.45 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 2H), 7.64–7.61 (m, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.28–7.23 (m, 2H), 7.22–7.13 (m, 3H), 6.76 (s, 1H), 4.85 (bs, 1H), 4.06 (bs, 1H), 2.47 (s, 3H), $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.5, 149.98, 144.9, 138.5,
134.7, 132.3, 131.5, 129.8, 129.7, 128.8, 128.6, 128.4, 124.3, 119.8, 52.6, 21.7; Minor rotamer (selected signals): 7.80 (d, \( J = 8.5 \) Hz), 7.65 (bd, \( J = 2.0 \) Hz), 7.60 (bd, \( J = 8.5 \) Hz), 6.72 (s), 2.46 (s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 150.6, 129.8, 128.8, 128.6, 128.1; IR (Neat)\( \nu_{\text{max}} \) 1640, 1548, 1494, 1306, 1287, 1088, 1023, 879, 740 cm\(^{-1}\); HRMS (ESI) for C\(_{21}\)H\(_{18}\)BrClN\(_2\)NaO\(_2\)S (M+Na): calcd 498.9859, found 498.9866.

(E)-N-Benzyl-N-(1-chloro-2-(thiophen-2-yl)vinyl)-4-methylbenzenesulfonamide (2r):

Brownish solid; \((E/Z = 95:5; 174 \text{ mg, 86\% yield})\); mp = 178–180 °C; \( R_f = 0.57 \) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.89 (d, \( J = 8.0 \) Hz, 2H), 7.36 (d, \( J = 7.6 \) Hz, 4H), 7.25 (bd, \( J = 4.8 \) Hz, 1H), 7.16 (bd, \( J = 5.6 \) Hz, 3H), 6.99 (d, \( J = 3.2 \) Hz, 1H), 6.85 (t, \( J = 4 \) Hz, 1H), 6.77 (s, 1H), 4.89 (d, \( J = 12.8 \) Hz, 1H), 3.97 (d, \( J = 12.4 \) Hz, 1H), 2.47 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 144.6, 135.5, 134.6, 133.0, 130.2, 129.9, 129.6, 129.1, 128.7, 128.4, 128.0, 127.8, 125.9, 124.7, 52.4, 21.7; IR (Neat)\( \nu_{\text{max}} \) 1594, 1086, 858, 808, 772, 715, 703 cm\(^{-1}\); HRMS (ESI) for C\(_{20}\)H\(_{19}\)ClNO\(_2\)S\(_2\) (M+H): calcd 404.0546, found 404.0546.

General Procedure for the Bromination of 1; Synthesis of 3 (GP 3):

To a solution of corresponding ynamide 1 (0.5 mmol), PPh\(_3\) (0.6 mmol), and CBr\(_4\) (0.6 mmol) in CH\(_2\)Cl\(_2\) (2.0 mL for 0.5 mmol) in a Schlenk tube was added H\(_2\)O (0.75 mmol). The resulting homogeneous mixture was stirred at room temperature (25 °C). Progress of the reaction was monitored periodically by TLC. The reaction mixture became heterogeneous after stirring for 5 h. Upon completion, the reaction mixture was diluted with CH\(_2\)Cl\(_2\) (10 mL). The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified through column chromatography on silica gel to provide 3.
(E)-N-Benzyl-N-(1-bromo-2-phenylvinyl)-4-methylbenzenesulfonamide (3a):

Colorless solid; (E/Z= 98:2; 213 mg, 96% yield); mp = 168–170 °C; R_f = 0.65 (4:1 hexane/EtOAc); [Silica, UV and I_2]; Mixture of rotamers; \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\) 7.90 (d, \(J = 8.0\) Hz, 2H), 7.38 (bd, \(J = 8.0\) Hz, 3H), 7.34 (bd, \(J = 6.4\) Hz, 2H), 7.28 (bd, \(J = 5.2\) Hz, 2H), 7.23 (bt, \(J = 7.6\) Hz, 2H), 7.18–7.11 (m, 3H), 6.85 (s, 1H), 4.86 (d, \(J = 13.2\) Hz, 1H), 3.97 (d, \(J = 12.8\) Hz, 1H), 2.5 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl_3) \(\delta\) 144.8, 139.8, 134.3, 133.6, 133.2, 129.9, 129.6, 129.2, 128.7, 128.6, 128.4, 128.2, 128.1, 119.7, 53.4, 21.7; IR (Neat) \(\nu_{max}\) 1349, 1164, 1155, 1087, 1012, 866, 820, 747 cm\(^{-1}\); HRMS (ESI) for C\(_{22}\)H\(_{24}\)BrN\(_2\)O\(_2\)S (M+NH\(_4^+\)): calcd 459.0742, found 459.0738.

(3b):

Colorless solid; (E/Z= 88:12; 221 mg, 94% yield); mp = 205–208 °C; R_f = 0.65 (4:1 hexane/EtOAc); [Silica, UV and I_2]; Major rotamer: \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\) 7.84 (d, \(J = 8.4\) Hz, 2H), 7.38–7.27 (m, 4H), 7.21–7.11 (m, 3H), 7.07 (d, \(J = 7.6\) Hz, 1H), 7.00 (s, 1H), 6.93 (d, \(J = 7.6\) Hz, 1H), 6.76 (s, 1H), 4.82 (d, \(J = 13.2\) Hz, 1H), 4.00 (d, \(J = 13.2\) Hz, 1H), 2.43 (s, 3H), 2.19 (s, 3H), 2.11 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl_3) \(\delta\) 144.6, 139.7, 137.5, 136.0, 134.7, 133.6, 131.3, 130.0, 129.8, 129.6, 129.4, 129.1, 128.32, 128.28, 126.3, 118.7, 53.3, 21.7, 19.7, 19.6; Minor rotamer (selected signals): 7.64 (d, \(J = 8.0\) Hz), 7.24 (d, \(J = 9.6\) Hz), 5.06 (s), 3.76 (s), 2.40 (s), 2.20 (s); \(^{13}\)C NMR (101 MHz, CDCl_3) \(\delta\) 129.7, 128.7, 128.5, 128.1, 127.8; IR (Neat) 1363, 1109, 1020, 906, 813, 767, 720 cm\(^{-1}\); HRMS (ESI) for C\(_{24}\)H\(_{24}\)BrNNaO\(_2\)S (M+Na\(^+\)): calcd 492.0609, found 492.0599.

(3c):

Colorless solid; (E/Z= 96:4; 183 mg, 88% yield); mp = 168–171 °C; R_f = 0.5 (4:1 hexane/EtOAc); [Silica, UV and I_2]; Mixture of rotamers; \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\) 7.83–7.69 (m, 4H), 7.60 (d, \(J = 7.2\) Hz, 1H), 7.46–7.39 (m, 5H), 7.35 (bt, \(J = 7.6\) Hz, 1H), 6.96 (d, \(J = 8.0\) Hz, 2H), 2.87 (s, 3H), 2.19 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl_3) \(\delta\) 144.1, 135.1, 133.8, 133.4, 131.02, 130.97, 129.2, 128.8, 128.5, 128.4, 126.3, 126.1, 125.9, 125.4, 123.8, 123.3, 37.0, 21.5; IR (Neat) \(\nu_{max}\)
1593, 1400, 1132, 1021, 893, 927, 775, 704 cm⁻¹; HRMS (ESI) for C₂₀H₁₈BrNO₂SNa (M+Na)⁺: calcd 438.0139, found 438.0139.

**(E)-N-(1-Bromo-2-(phenanthren-9-yl)vinyl)-N,4-dimethylbenzenesulfonylamine (3d):**

Yellow gummy liquid; (E/Z = 98:2; 203 mg, 87% yield); Rᵥ = 0.53 (4:1 hexane/EtOAc); [Silica, UV and I₂]; Major rotamer: ¹H NMR (400 MHz, CDCl₃): δ 8.67 (br, J = 8.0 Hz, 1H), 8.62 (br, J = 8.0 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.87–7.77 (m, 2H), 7.71–7.54 (m, 4H), 7.52–7.39 (m, 3H), 6.83 (d, J = 8.0 Hz, 2H), 3.00 (s, 3H), 2.16 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 143.9, 135.2, 134.4, 131.2, 130.3, 129.9, 129.6, 129.1, 129.0, 128.1, 127.3, 127.1, 126.8, 126.73, 126.67, 124.7, 123.7, 122.9, 122.3, 37.2, 21.4; Minor rotamer (selected signals): 7.30 (d, J = 8.0 Hz), 3.13 (s), 2.40 (s); IR (Neat) νmax 1451, 1163, 826, 768, 715, 704 cm⁻¹; HRMS (ESI) for C₂₄H₂₄BrN₂O₂S(M+NH₄)⁺: calcd 483.0742, found 483.0745.

**(E)-N-Benzyl-N-(1-bromo-2-(5-bromopyridin-2-yl)vinyl)-4-ethylbenzenesulfonamide (3e):**

Pale yellow liquid; (E/Z = 99:1; 201 mg, 77% yield); Rᵥ = 0.50 (2.3:1 hexane/EtOAc); [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 8.42 (br, J = 2.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.64–7.56 (m, 2H), 7.36 (d, J = 8.12 Hz, 2H), 7.33–7.28 (m, 2H), 7.23–7.14 (m, 3H), 7.0 (s, 1H), 4.88 (d, J = 13.2 Hz, 1H), 3.97 (d, J = 13.2 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.9, 150.0, 145.1, 139.3, 138.6, 134.2, 133.2, 129.83, 129.76, 129.1, 128.6, 128.4, 124.2, 123.7, 119.8, 53.6, 21.8; IR (Neat) νmax 1349, 1166, 1091, 812, 738, 700, 658, 638 cm⁻¹; HRMS (ESI) for C₂₁H₁₉Br₂N₂O₂S (M+H)⁺: calcd 520.9534, found 520.9537.

**(E)-N-Benzyl-N-(1-bromo-2-(thiophen-2-yl)vinyl)-4-methylbenzenesulfonamide (3f)**

Brown solid; (E/Z = 96:4; 213 mg, 83% yield); mp = 156–158 °C; Rᵥ = 0.57 (4:1 hexane/EtOAc); [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.0 Hz, 2H), 7.44–7.34 (m, 4H), 7.28–7.23 (m, 1H), 7.21–7.12 (m, 3H), 6.99 (bd, J = 3.6 Hz, 1H), 6.97 (s, 1H), 6.84 (t, J = 4.4 Hz, 1H), 4.92 (d, J = 12.8 Hz, 1H), 3.87 (d, J = 12.8 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 136.2, 134.1, 133.1, 132.9, 130.3, 130.1, 129.6, 129.4, 128.4, 128.0, 127.8, 125.9, 116.6, 53.4,
21.7; IR (Neat) \( \nu_{\text{max}} \) 1455, 1362, 1166, 1021, 742, 703, 671, 609 cm\(^{-1}\); HRMS (ESI) for C\(_{20}\)H\(_{19}\)BrNO\(_2\)S\(_2\) (M+H)\(^+\): calcd 448.0041, found 448.0040.

**(E)-N-Benzyl-N-(1-bromopent-1-ethyl)-4-methylbenzenesulfonamide (3g):**

Colorless solid; \((E/Z) = 99:1\); 201 mg, 85% yield); mp = 76–78 °C; \( R_f = 0.35 \) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.83 (d, \( J = 8.4 \) Hz, 2H), 7.42–7.25 (m, 7H), 5.91 (dd, \( J = 9.2, 6.0 \) Hz, 1H), 4.82 (d, \( J = 13.2 \) Hz, 1H), 3.84 (d, \( J = 13.6 \) Hz, 1H), 2.46 (s, 3H), 2.06–1.88 (m, 1H), 1.87–1.73 (m, 1H), 1.13–0.98 (m, 1H), 0.81–0.68 (m, 1H), 0.63 (br t, \( J = 7.2 \), Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 144.4, 142.8, 135.2, 134.4, 129.7, 129.6, 128.6, 128.4, 128.3, 116.5, 52.2, 32.5, 21.7, 21.3, 13.5; IR (Neat) \( \nu_{\text{max}} \) 1596, 1494, 1356, 1209, 1167, 1027, 747, 699 cm\(^{-1}\); HRMS (ESI) for C\(_{19}\)H\(_{26}\)BrN\(_2\)O\(_2\)S (M+NH\(_4\))\(^+\): calcd 425.0898, found 425.0898.

**General Procedure for the Iodination of 1; Synthesis of 4 (GP 4):**

To a solution of corresponding ynamide 1 (0.5 mmol), PPh\(_3\) (0.6 mmol), and CH\(_I\)\(_3\) (0.6 mmol) in CH\(_2\)Cl\(_2\) (2.0 mL for 0.5 mmol) in a Schlenk tube was added H\(_2\)O (0.75 mmol). The resulting homogeneous mixture was stirred at room temperature (25 °C). Progress of the reaction was monitored periodically by TLC. The reaction mixture became heterogeneous after stirring for 5 h. Upon completion, the reaction mixture was diluted with CH\(_2\)Cl\(_2\) (10 mL). The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified through column chromatography on silica gel to provide 4.

**(E)-N-Benzyl-N-(1-Iodo-2-phenylvinyl)-4-methylbenzenesulfonamide (4a):**

Reddish-orange solid; \((E/Z) = 99:1\); 235 mg, 96% yield); mp = 212–114 °C; \( R_f = 0.65 \) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.85 (d, \( J = 8.0 \) Hz, 2H), 7.36 (d, \( J = 8.0 \) Hz, 2H), 7.29 (bd, \( J = 7.6 \) Hz, 4H), 7.24–7.09 (m, 7H), 4.86 (d, \( J = 13.2 \) Hz, 1H), 3.62 (d, \( J = 13.2 \) Hz, 1H), 2.47 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.3, 144.9, 134.9, 133.3, 132.98, 130.0, 129.63, 129.58,
128.8, 128.7, 128.4, 128.2, 128.0, 98.0, 55.2, 21.8; IR (Neat) νmax 1594, 1349, 1155, 1021, 910, 860, 761 cm⁻¹; HRMS (ESI) for C₂₂H₂₀INaO₂S (M+Na)⁺: calcd 512.0157, found 512.0158.

*(E)-N-Benzyl-N-(1-ido-2-(3,4-dimethylphenyl)vinyl)-4-methylbenzenesulfonamide (4b):* Colorless solid; (E/Z = 91:9; 164 mg, 84% yield); mp = 186–189 °C; Rf = 0.64 (4:1 hexane/EtOAc); [Silica, UV and I₂]; Major rotamer ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 8.4 Hz, 2H), 7.41–7.31 (m, 5H), 7.21–7.13 (m, 3H), 7.09–7.03 (m, 2H), 6.99 (s, 1H), 6.91 (d, J = 7.6 Hz, 1H), 4.85 (d, J = 13.2 Hz, 1H), 3.67 (d, J = 13.2 Hz, 1H), 2.45 (s, 3H), 2.16 (s, 3H), 2.11 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.2, 144.7, 137.6, 135.9, 133.8, 133.3, 132.6, 130.1, 129.9, 129.6, 129.5, 129.3, 128.33, 128.27, 126.4, 96.9, 55.1, 21.7, 19.7, 19.6; Minor rotamer (selected signals) ¹H NMR (400 MHz, CDCl₃): δ 7.24 (s), 2.20 (d, J = 3.2 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 129.7, 129.4, 128.7, 128.5; IR (Neat) νmax 1598, 1401, 1022, 812, 743, 715 cm⁻¹; HRMS (ESI) for C₂₄H₂₅INO₂S (M+H)⁺: calcd 518.0651, found 518.0649.

*(E)-N-(1-Iodo-2-(2-methoxyphenyl)vinyl)-N,4-dimethylbenzenesulfonamide (4c):* Colorless solid; (E/Z = 76:24; 133 mg, 60% yield); mp = 163–165 °C; Rf = 0.48 (4:1 hexane/EtOAc); [Silica, UV and I₂]; Major rotamer: ¹H NMR (400 MHz, CDCl₃): δ 7.86 (dd, J = 7.6, 1.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.51 (s, 1H), 7.29–7.23 (m, 3H), 6.93 (t, J = 5.2 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 2.80 (s, 3H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 156.5, 144.4, 139.7, 130.1, 129.5, 129.3, 129.2, 128.7, 123.9, 120.7, 110.6, 97.7, 55.5, 38.3, 21.6; Minor rotamer (selected signals): 7.85 (d, J = 1.6 Hz), 7.77 (d, J = 8.0 Hz), 7.62 (d, J = 8.0 Hz), 7.57 (d, J = 7.6 Hz), 7.38–7.32 (m), 7.30 (d, J = 1.6 Hz), 6.85 (d, J = 8.4 Hz), 3.83 (s), 2.89 (s), 2.45 (s); ¹³C NMR (101 MHz, CDCl₃) δ 157.1, 144.3, 133.9, 133.0, 130.4, 130.1, 128.7, 127.6, 127.6, 124.9, 121.0, 119.9, 110.5, 101.4, 38.8; IR (Neat) νmax 1437, 1342, 1135, 1086, 892, 751, 705 cm⁻¹; HRMS (ESI) for C₁₇H₁₈INaO₃S (M+Na)⁺: calcd 465.9950, found 465.9951.

*(E)-Ethyl 4-(2-(N,4-dimethylphenylsulfonamido)-2-iodovinyl)benzoate (4d):* Colorless solid (E/Z = 99:1; 133 mg, 94% yield); mp = 176–179 °C; Rf = 0.38 (4:1 hexane/EtOAc); [Silica, UV and I₂]; ¹H NMR (400 MHz,
CDCl$_3$): δ 7.88–7.79 (m, 4H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.33–7.28 (m, 4H), 7.21–7.13 (m, 4H), 4.88 (d, $J = 7.2$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 3.62 (d, $J = 13.2$ Hz, 1H), 2.47 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.2, 147.2, 145.1, 139.0, 133.2, 132.8, 130.1, 129.98, 129.7, 129.5, 128.6, 128.5, 128.4, 100.6, 61.0, 55.3, 21.8, 14.3; IR (Neat) $\nu_{\text{max}}$ 1496, 1456, 1309, 1125, 907, 750, 685 cm$^{-1}$; HRMS (ESI) for C$_{23}$H$_{22}$INaO$_4$S (M+Na)$^+$: calcd 584.0368, found 584.0374.

(E)-N-Benzyl-N-(1-iodo-2-(naphthalen-1-yl)vinyl)-4-methylbenzenesulfonamide (4e):

Pale yellow solid; ($E$/Z = 92:8; 229 mg, 89% yield); mp = 193–195 °C; $R_f = 0.58$ (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; Mixture of rotamers; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.79–7.71 (m, 5H), 7.46–7.35 (m, 2H), 7.33–7.23 (m, 5H), 7.04–6.96 (m, 2H), 6.91–6.79 (m, 3H), 4.66 (d, $J = 12.8$ Hz, 1H), 3.65 (d, $J = 13.6$ Hz, 1H), 2.40 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.0, 144.6, 133.7, 132.9, 132.6, 132.0, 130.7, 129.6, 129.4, 129.4, 128.6, 128.0, 127.9, 126.2, 125.9, 125.5, 125.2, 123.9, 99.1, 54.6, 21.7 IR (Neat)$\nu_{\text{max}}$ 1595, 1345, 1163, 1087, 920, 870, 812, 658 cm$^{-1}$; HRMS (ESI) for C$_{26}$H$_{22}$INO$_2$Na (M+Na)$^+$: calcd 562.0314, found 562.0305.

(E)-N-(1-Iodo-2-(phenanthren-9-yl)vinyl)-N,4-dimethylbenzenesulfonamide(4f):

Yellow semisolid; ($E$/Z = 84:16; 251 mg, 98% yield); $R_f = 0.53$ (4:1 hexane/EtOAc); [Silica, UV and I$_2$]; Major rotamer; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.68 (dd, $J = 8.4$, 1.2 Hz, 1H), 8.63 (d, $J = 8.4$ Hz, 1H), 7.93–7.87 (m, 1H), 7.84–7.78 (m, 2H), 7.75 (bd, $J = 0.8$ Hz, 1H), 7.73–7.56 (m, 4H), 7.40 (d, $J = 8.0$ Hz, 2H), 6.82 (d, $J = 8.0$ Hz, 2H), 2.86 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.0, 134.0, 131.2, 131.0, 130.3, 130.2, 129.7, 129.65, 129.1, 129.0, 128.8, 128.3, 127.2, 127.17, 126.8, 126.7, 126.69, 124.7, 122.9, 122.4, 100.3, 38.8, 21.4; Minor rotamer (selected signals): 8.73–8.70 (m), 8.17–8.13 (m), 7.33 (d, $J = 8.0$ Hz), 3.0 (s), 2.42 (s); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.0, 140.0, 128.0, 127.1, 126.9, 125.5, 122.9, 122.6, 38.9, 21.51; IR (Neat)$\nu_{\text{max}}$ 1449, 1351, 1160, 941, 891, 745, 713 cm$^{-1}$; HRMS (ESI) for C$_{24}$H$_{24}$IN$_2$O$_2$S (M+NH$_4$)$^+$: calcd 531.0603, found 531.0603.
(E)-N-BenzyI-N-(1-iodo-2-(5-bromopyridin-2-yl)vinyl)-4-methylbenzenesulfonamide (4g):
pale yellow liquid; (E/Z = 99:1; 211 mg, 78% yield); \( R_f = 0.5 \) (2.3:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.43 (s, 1H), 7.86 (bd, \( J = 8.0 \) Hz, 2H), 7.74–7.60 (m, 2H), 7.36 (bd, \( J = 8.0 \) Hz, 2H), 7.26 (bd, \( J = 6.0 \) Hz, 2H), 7.24–7.13 (m, 3H), 6.76 (s, 1H), 4.86 (br s, 1H), 4.08 (br s, 1H), 2.47 (s, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 150.5, 150.0, 144.9, 138.5, 134.7, 134.6, 133.3, 131.6, 129.7, 128.5, 128.4, 124.3, 119.8, 52.6, 21.7; IR (Neat) \( \nu_{\text{max}} \) 1456, 1093, 812, 741, 702, 661, 613 cm\(^{-1}\); HRMS (ESI) for C\(_{21}\)H\(_{19}\)BrIN\(_2\)O\(_2\)S (M+H): calcd 568.9395, found 568.9393.

General Procedure for the Suzuki Reaction of 4a; Synthesis of (Z)-N-BenzyI-N-(1,2-diphenyIvinyl)-4-methylbenzenesulfonamide 5 (GP 5):\(^3\)

A mixture of \( \alpha \)-iodoenamide 4a (245 mg, 0.5 mmol), phenylboronic acid (74 mg, 0.6 mmol), Pd[(P(o-Tol)]\(_3\)\(_2\) (15 mg, 10 mol %), and Na\(^+\)OBu (96 mg, 1.0 mmol) was dissolved in EtOH/H\(_2\)O (5:1; 3.0 mL. The resulting solution was stirred at room temperature for 3 h. Progress of the reaction was monitored by TLC. Upon completion, EtOH was removed under vacuum. The reaction mixture was diluted with EtOAc and washed with water and brine. The organic layer was dried over Na\(_2\)SO\(_4\) and evaporated. The residue was purified by flash column chromatography to afford 5. colorless gummy liquid; (E/Z = 81:19; 216 mg, 98% yield); \( R_f = 0.65 \) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; Major rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.79 (d, \( J = 8.4 \) Hz, 2H), 7.35–7.28 (m, 3H), 7.28–7.24 (m, 3H), 7.20–7.15 (m, 3H), 7.14–7.08 (m, 2H), 7.08–7.03 (m, 2H), 6.85 (bd, \( J = 0.8 \) Hz, 1H), 6.84–6.79 (m, 3H), 6.56 (s, 1H), 4.51 (s, 2H), 2.46 (s, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 143.6, 137.5, 137.3, 136.5, 136.3, 135.9, 135.6, 135.3, 130.6, 130.0, 129.7, 129.3, 129.0, 128.4, 128.3, 128.0, 127.9, 127.7, 52.2, 21.7; Minor rotamer (selected signals): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.71 (d, \( J = 8.4 \) Hz), 7.48 (d, \( J = 14.4 \) Hz), 7.24–7.20 (m), 4.64 (s), 2.41 (s); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 128.7, 128.6, 128.4,
127.6, 127.2, 127.0, 126.9, 126.5, 115.3, 112.1, 49.5; IR (Neat)\(\nu_{\text{max}}\) 1643, 1489, 1260, 1057, 942, 810 cm\(^{-1}\); HRMS (ESI) for C\(_{28}\)H\(_{26}\)NO\(_2\)S (M+H): calcd 440.1684, found 440.1687.

**General Procedure for the Sonagashira Reaction of 4; Synthesis of 6 (GP 6):**

To a solution of \(\alpha\)-iodoenamide 4 (245 mg, 0.5 mmol) in toluene/diisopropylamine (2:1; 3.0 mL) was added Pd(PPh\(_3\))\(_4\) (58 mg, 10 mol %). After 2 h, CuI (41 mg, 7 mol %) and phenylacetylene (66 \(\mu\)L, 0.6 mmol) were added to the reaction mixture and stirred for 6 h at room temperature. Upon completion, the crude reaction mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified using column chromatography on silica gel to provide 6.

**Synthesis of (Z)-N-Benzyl-N-(1,2-diphenylvinyl)-4-methylbenzenesulfonamide (6a):**

Brown gummy liquid; \((E/Z = 67:33; 223 \text{ mg}, 96\% \text{ yield); } R_f = 0.65 \text{ (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; Major rotamer (E): } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.88 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.77 \text{ (d, } J = 6.8 \text{ Hz, 2H), 7.41–7.27 \text{ (m, 10H), 7.34–7.28 \text{ (m, 2H), 7.19–7.13 \text{ (m, 3H), 6.99 \text{ (s, 1H), 4.69 \text{ (s, 2H), 2.40 \text{ (s, 3H); } ^13\text{C NMR (101 MHz, CDCl}_3\text{)} } \delta 143.7, 141.5, 135.9, 134.1, 131.4, 130.2, 129.7, 129.6, 129.2, 129.0, 128.8, 128.5, 128.3, 128.2, 127.8, 122.1, 117.0, 96.7, 84.0, 52.01, 21.5; \text{Minor rotamer (selected signals): } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.92 \text{ (d, } J = 8.0 \text{ Hz), 7.71 \text{ (bt, } J = 1.6 \text{ Hz), 7.43 \text{ (d, } J = 7.2 \text{ Hz), 7.34–7.28 \text{ (m), 7.13–7.08 \text{ (m), 6.84 \text{ (s, )}, 2.39 \text{ (s) } ^13\text{C NMR (101 MHz, CDCl}_3\text{)} } \delta 143.9, 140.9, 135.6, 135.0, 134.4, 133.9, 129.2, 129.1, 129.0, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 122.2, 118.3, 91.3, 86.0, 53.4; \text{IR (Neat)}\nu_{\text{max}}\text{ 2356, 1594, 1089, 925, 816, 755 cm}^{-1}; \text{HRMS (ESI) for C}_{30}\text{H}_{25}\text{NO}_2\text{S (M+Na): calcd 486.1504, found 486.1505.}

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General Procedure for the Sequential Iodination and Alkynylation of 1; Synthesis of 6 (GP 7):\(^5\)

To a solution of corresponding ynamide 1 (0.5 mmol), PPh\(_3\) (0.6 mmol, 1.2 equiv), and CHI\(_3\) (0.6 mmol, 1.2 equiv) in CH\(_2\)Cl\(_2\) (2.0 mL) in a Schlenk tube was added H\(_2\)O (0.75 mmol, 1.5 equiv). The homogeneous solution was stirred at 25 °C for 5 h. The reaction mixture turned to heterogeneous. Solvent CH\(_2\)Cl\(_2\) was then completely evaporated. To this reaction mixture, Pd(PPh\(_3\))\(_4\) (10 mol %), toluene/diisopropylamine (2:1; 2.0 mL) was added. After 2 h, CuI (7 mol %) and alkyne (0.6 mmol) were added to the reaction mixture and stirred for 6 h at room temperature. Upon completion, the crude reaction mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified using column chromatography on silica gel to provide 6.

(Z)-Ethyl-4-(2-(N-benzyl-4-methylphenylsulfonamido)-4-phenylbut-1-en-3-ynyl)benzoate (6b)

Colorless gummy liquid; (E/Z = 63:37; 164 mg, 61% yield); \(R_f=0.40\) (4:1 hexane/EtOAc); [Silica, UV and I\(_2\)]; Major rotamer (E): \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.98 (d, \(J=8.4\) Hz, 2H), 7.81 (d, \(J=8.0\) Hz, 2H), 7.76 (d, \(J=8.4\) Hz, 2H), 7.32–7.27 (m, 8H), 7.17–7.08 (m, 4H), 6.96 (s, 1H), 4.64 (s, 2H), 4.43–4.32 (m, 2H), 2.35 (s, 3H), 1.44–1.33 (m, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 166.1, 143.9, 140.0, 138.4, 135.7, 134.2, 131.5, 129.8, 129.7, 129.5, 129.5, 128.9, 128.7, 128.5, 128.3, 128.1, 121.7, 119.2, 97.6, 83.6, 61.0, 52.2, 21.5, 14.3; Minor rotamer (selected signals): 7.92 (d, \(J=8.8\) Hz, 1.4 Hz), 7.85 (d, \(J=8.0\) Hz), (d, \(J=8.4\) Hz), 7.41–7.32 (m), 7.24–7.20 (m), 7.08–7.03 (m), 6.80 (s), 4.43–4.32 (m), 2.33 (s), 1.44–1.33 (m); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 166.3, 144.1, 139.6, 138.2, 125.5, 134.8, 131.5, 130.5, 130.3, 129.6, 129.3, 129.0, 128.9, 128.5, 128.2, 127.8, 121.9, 120.4, 92.4, 85.6, 61.1, 53.4, 14.4; IR (Neat)\(\nu_{\text{max}}\) 2975,
1715, 1605, 1436, 1277, 1101, 1085 cm⁻¹; HRMS (ESI) for C₃₃H₂₉NO₄S (M+Na)⁺: calcd 558.1715, found 558.1716.

(Z)-N-Benzyl-N-(1-(3-cyanophenyl)-4-phenylbut-1-en-3-yn-2-yl)-4-methylbenzene sulfo namide (6c):

Colorless gummy liquid; (E/Z = 53:47; 159 mg, 65% yield) was obtained in as; Rᵥ = 0.65 (4:1 hexane/EtOAc); [Silica, UV and I₂]; Major rotamer ¹H NMR (400 MHz, CDCl₃): δ 8.17 (s, 1H), 7.87 (t, J = 6.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.54 (bs, 1H), 7.39–7.23 (m, 9H), 7.22–7.17 (m, 1H), 7.13–7.04 (m, 2H), 6.74 (s, 1H), 4.63 (s, 2H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.2, 138.3, 135.3, 134.1, 133.6, 132.9, 131.9, 131.6, 131.5, 129.8, 129.7, 129.6, 129.0, 128.6, 128.4, 128.3, 128.1, 127.2, 120.9, 118.6, 112.2, 92.6, 85.0, 53.3, 21.5; Minor rotamer (selected signals): ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, J = 8.0, J = 1.6 Hz), 7.47 (d, J = 7.6 Hz), 7.42 (d, J = 8.0), 7.39–7.23 (m), 7.22–7.17 (m), 7.13–7.04 (m), 6.88 (s), 4.40 (bs), 4.12 (d, J = 6 Hz), 2.37 (s), ¹³C NMR (101 MHz, CDCl₃) δ 144.0, 138.3, 136.9, 136.3, 135.5, 135.1, 134.7, 131.8, 129.2, 129.0, 128.6, 127.9, 121.7, 121.3, 119.6, 112.6, 98.2, 83.1, 52.1, 47.3, IR (Neat)vₘₐₓ 2230, 2192, 1162, 1090, 1052, 1030, 663 cm⁻¹; HRMS (ESI) for C₃₁H₂₄N₂NaO₂S (M+Na)⁺: calcd 511.1456, found 511.1456.

(Z)-N-Benzyl-N-(4-cyclopropyl-1-phenylbut-1-en-3-yn-2-yl)-4-methylbenzene sulfonamide (6d)

Colorless gummy liquid; (E/Z = 86:14; 145 mg, 68% yield); Rᵥ = 0.45 (4:1 hexane/EtOAc); [Silica, UV and I₂]; Major rotamer: ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 8.4 Hz, 2H), 7.67–7.60 (m, 2H), 7.37–7.28 (m, 5H), 7.26–7.18 (m, 5H), 6.80 (s, 1H), 4.5 (s, 2H), 2.45 (s, 3H), 1.24–1.16 (m, 1H), 0.79–0.73 (m, 2H), 0.45–0.40 (m, 2H), ¹³C NMR (101 MHz, CDCl₃) δ 143.7, 140.0, 136.1, 136.0, 134.3, 129.3, 128.9, 128.83, 128.75, 128.6, 128.4, 128.1, 127.6, 117.3, 101.6, 70.4, 51.7, 21.6, 8.6, 0.13; Minor rotamer (selected signals): ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, J = 8.4 Hz), 7.56–7.7.50 (m), 7.15–7.09 (m), 7.02–6.95 (m), 6.6 (s), 3.87 (s), 3.87 (s), 1.31–1.24 (m), 1.15–1.08 (m), 0.73–0.69 (m), 0.40–0.38 (m); ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 139.6, 136.6, 136.6, 134.6, 134.1, 129.8, 129.7, 129.6, 129.2, 128.5, 128.1, 127.98, 127.95, 127.75,
72.4, 53.0, 21.6, 8.5, -0.20; IR (Neat)ν_{max} 2197, 1704, 1452, 1085, 1030, 942 cm^{-1}; HRMS (ESI) for C_{27}H_{25}NNaO_{2}S (M+Na)^{+}: calcd 450.1504, found 450.1506.

Gram Scale Synthesis of 2a:

Following the general procedure (GP-2), a mixture of 1a (1.0 g, 2.8 mmol), PPh\textsubscript{3} (871 mg, 3.3 mmol), and CCl\textsubscript{4} (0.5 mL, 5.5 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (6.0 mL) and H\textsubscript{2}O (75 µL, 4 mmol) was taken in a Schlenk tube. The resulting mixture was stirred at room temperature (25 °C) for 3 h. The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified through column chromatography on silica gel to provide 2a (959 mg) in 87 % yield.

Gram Scale Synthesis of 4a:

Following the general procedure (GP-4), a mixture of 1a (1.0 g, 2.8 mmol), PPh\textsubscript{3} (871 mg, 3.3 mmol), and CHI\textsubscript{3} (1.3 g, 3.3 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (6.0 mL) and H\textsubscript{2}O (75 µL, 4 mmol) was taken in a Schlenk tube. The resulting mixture was stirred at room temperature (25 °C) for 5 h. The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified through column chromatography on silica gel to provide 4a (1.1 g) in 82 % yield.

Synthesis of 2-chloro-1-phenyl-1H-indole 7:\textsuperscript{6}
A solution of enamide 2o (165 mg, 0.5 mmol) and [bis(trifluoroacetoxy)iodo]benzene (259 mg, 0.6 mmol) in CH₂Cl₂ (2.0 mL) was heated in a Schlenk tube at 80 °C for 12 h. Upon completion, the crude mixture filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified using column chromatography on silica gel to provide 7. Brown solid; (74 mg, 65% yield); mp = 210–212 °C; Rf = 0.43 (4:1 hexane/EtOAc); [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 7.6 Hz, 2H), 7.61–7.53 (m, 2H), 7.53–7.44 (m, 5H), 7.40 (t, J = 7.2 Hz, 1H), ¹³C NMR (101 MHz, CDCl₃) δ 151.6, 134.5, 132.0, 129.5, 129.2, 128.8, 128.7, 127.3, 126.3, 124.6, 120.0, 111.3; IR (Neat)νmax 1644, 1594, 1356, 1155, 1085, 958, 924, 844, 799, 779, 730, 705 cm⁻¹; HRMS (ESI) for C₁₄H₁₁ClN (M+H)⁺: calcd 228.0580, found 228.0576.

Chlorination of 1a in D₂O:

The ynamide 1a (181 mg, 0.5 mmol), PPh₃ (158 mg, 0.6 mmol), and CCl₄ (97µL, 1 mmol) were dissolved with CH₂Cl₂ (2.0 mL) in a Schlenk tube followed by the addition of D₂O (14 µL, 0.8 mmol). The reaction mixture was stirred at room temperature (25 °C). After stirring for 2 h, the reaction mixture was diluted with CH₂Cl₂ (10 mL). The crude mixture was filtered through a small pad of Celite and concentrated under the reduced pressure. The crude residue was purified using column chromatography on silica gel to provide 2a-D and 2a (80:20; 192 mg) in 96 % yield as colorless solid. Analytical data is exactly matching with the values mentioned above for 2a.

Ratio of 2a-D and 2a is determined based on the integration of the respective CH₃-proton of N-Ts of 2a-D (δ = 2.46, s, 3H) and alkenyl proton of 2a (δ = 6.60, s, 0.19H).

4-(N-Benzyl-4-methylphenylsulfonamido)-1-phenylbut-3-yn-2-yl acetate (8):⁷

Colorless thick liquid; (192 mg, 86% yield); Rf = 0.40 (4:1 hexane/EtOAc); [Silica, UV and I₂]; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, J = 6.4 Hz, 2H), 7.36–7.21 (m, 10H), 7.13 (dd, J = 5.6, 2.8 Hz, 2H), 5.60 (t, J = 5.2 Hz, 1H), 4.52 (d, J = 11.2 Hz, 1H), 4.39 (d, J = 11.2 Hz, 1H), 3.04–2.90 (m, 2H), 2.45 (s, 3H), 2.01 (s,
Brown gummy liquid \((E/Z = 88:12; 114 \text{ mg}, 96 \% \text{ yield})\); \(R_f = 0.52 \text{ (4:1 hexane/EtOAc)}\); [Silica, UV and I\(_2\)]; Major rotamer: \(^1\)H NMR \((400 \text{ MHz, CDCl}_3\)): \(\delta 7.52 \text{ (bd, } J = 8.4 \text{ Hz, 2H), 7.40–7.25 \text{ (m, 8H), 7.22 \ (d, } J = 8.0 \text{ Hz, 2H), 7.11–7.04 \ (m, 2H), 6.51 \ (d, } J = 14.8 \text{ Hz, 1H ), 5.11 \ (s, 2H), 3.48 \ (br d, } J = 6.0 \text{ Hz, 2H), 2.43 \ (s, 3H)}\); \(^{13}\)C NMR \((101 \text{ MHz, CDCl}_3\)): \(\delta 165.8, 149.1, 144.6, 137.3, 136.9, 136.8, 129.6, 128.9, 128.6, 128.0, 127.9, 127.6, 126.6, 123.3, 49.3, 38.7, 21.6\); Minor rotamer (selected signals): \(^1\)H NMR \((400 \text{ MHz, CDCl}_3\)): \(\delta 7.4–7.28 \ (m, 3H), 6.17 \ (d, } J = 10.8 \text{ Hz), 4.91 \ (s, 2.47 \ (s, 3H)}\); \(^{13}\)C NMR \((101 \text{ MHz, CDCl}_3\)): \(\delta 129.2, 128.5, 127.0, 126.6, 123.2, 122.5, 97.5, 915, 811 \text{ cm}^{-1}\); HRMS (ESI) for \(\text{C}_{24}\text{H}_{23}\text{I}_3\text{NO}_3\text{S} \text{(M+H)}^+\): calcd 532.0443, found 532.0449.

Colorless solid; \((E/Z = 91:09; 103 \text{ mg}, 95\% \text{ yield})\); \(R_f = 0.45 \text{ (4:1 hexane/EtOAc)}\); [Silica, UV and I\(_2\)]; Major rotamer: \(^1\)H NMR \((500 \text{ MHz, DMSO)}\): \(\delta 7.87 \ (d, } J = 8.5 \text{ Hz, 2H), 7.45–7.15 \ (m, 12H), 6.84 \ (bs, 1H), 5.74 \ (bs, 1H), 4.85 \ (bs, 1H), 4.03 \ (bs, 1H), 3.26 \ (bs, 1H), 2.95 \ (bs, 1H), 2.50 \ (s, 3H), 1.76 \ (bs, 3H)}\); \(^{13}\)C NMR \((101 \text{ MHz, CDCl}_3\)): \(\delta 168.8, 144.7, 136.5, 134.8, 133.6, 133.2, 129.8, 128.6, 128.2, 126.6, 122.1, 70.8, 52.0, 39.4, 21.7, 21.0\); Minor rotamer (selected signals): \(^1\)H NMR \((500 \text{ MHz, DMSO)}\): \(\delta 7.52 \ (d, } J = 8.0 \text{ Hz), 7.10–7.06 \ (m), 2.42 \ (s, 1.94 \ (br s)}\); \(^{13}\)C NMR \((101 \text{ MHz, CDCl}_3\)): \(\delta 133.2, 127.7, 69.5, 39.4 \text{ (Neat)}v_{\text{max}} 1732, 1496, 1458, 1359, 1090, 745 \text{ cm}^{-1}\); HRMS (ESI) for \(\text{C}_{26}\text{H}_{25}\text{ClNaO}_4\text{S} \text{(M+Na)}^+\): calcd 506.1169, found 506.1169.
X-ray crystallography:

X-ray reflections for 2a were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-Kα, radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). OLEX2-1.0 and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C−H hydrogens were fixed.

**Figure 1.** Molecular structures of compounds 2a; thermal ellipsoids are set at 30% probability. Oxygen (red), nitrogen (blue), and sulphur (yellow).

**Table 1.** Crystallographic Data for Compound 2a

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References:


(9) (a) SMART (version 5.625), SHELX-TL (version 6.12), Bruker AXS Inc.Madison, WI, 2000; (b) G. M. Sheldrick, *SHELXS-97*, University of Gottingen, Germany, 1997.