## Supplementary Information

# Nickel-catalysed denitrogenative alkyne insertion reaction of *N*-sulfonyl-1,2,3-triazoles

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**General.** Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian Gemini 2000 ($^{1}H$ at 300 MHz and $^{13}C$ at 75 MHz) spectrometer using $CHCl_3$ ($^{1}H$, $\delta = 7.26$) and $CDCl_3$ ($^{13}C$, $\delta = 77.0$) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) or a JEOL JMS-HX110A (FAB) spectrometer. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF254 (Merck).

**Materials.** Toluene was distilled from sodium/benzophenone ketyl. Trimethylphosphine (Aldrich), tricyclohexylphosphine (Strem), tri-*t*-butylphosphine (Wako), *n*-butyl-di-1-adamantylphosphine (Strem), triphenylborane (Aldrich), diphenylzinc (Aldrich), trimethylaluminium toluene solution (Kanto) and diphenylethyne (**2b**) (Aldrich) were used as received from the commercial sources. $Ni(cod)_2$ (Kanto) was obtained from the commercial sources and purified by recrystallisation from toluene before use. Triphenylaluminium was prepared according to the literature procedure.[1] *N*-Sulfonyl-1,2,3-triazoles (**1a**-**1k**) were prepared according to the literature procedure.[2] **1a**, **1f** and **1g** have been already reported.[2] Alkynylboranes (**2f**) was prepared according to the literature procedure.[3] All other alkynes were purchased from the commercial sources and purified by bulb-to-bulb distillation prior to use.

**1b**: IR (KBr): 3129, 1451, 1393, 1181 $cm^{-1}$; $^{1}H$ NMR: $\delta = 7.33$–$7.48$ (m, 3H), 7.56–7.66 (m, 2H), 7.69–7.77 (m, 1H), 7.80–7.86 (m, 2H), 8.12–8.19 (m, 2H), 8.33 (s, 1H); $^{13}C$ NMR: $\delta = 119.0$, 126.0, 128.4, 128.6, 128.9, 129.0, 129.7, 135.6, 136.0, 147.3; HRMS ($EI^+$): Calcd for $C_{14}H_{11}N_3O_2S$, $M^+$ 285.0572. Found m/z 285.0567.

**1c**: IR (KBr): 3144, 1586, 1493, 1395, 1244, 1188 $cm^{-1}$; $^{1}H$ NMR: $\delta = 7.23$–$7.33$ (m, 2H), 7.34–7.48 (m, 3H), 7.79–7.86 (m, 2H), 8.15–8.24 (m, 2H), 8.32 (s, 1H); $^{13}C$ NMR: $\delta = 117.3$ (d, $J = 23.0$ Hz), 118.9, 126.0, 128.6, 129.0, 129.2, 131.8 (d, $J = 10.4$ Hz), 132.0 (d, $J = 2.3$ Hz), 147.5, 166.8 (d, $J = 258.2$ Hz); HRMS ($EI^+$): Calcd for $C_{14}H_{10}FN_3O_2S$, $M^+$ 303.0478. Found m/z 303.0474.

**1d**: IR (KBr): 3092, 1592, 1397, 1271, 1202, 1167, 1090 $cm^{-1}$; $^{1}H$ NMR: $\delta = 3.87$ (s, 3H), 6.99–7.06 (m, 2H), 7.32–7.46 (m, 3H), 7.79–7.85 (m, 2H), 8.03–8.11 (m, 2H), 8.31 (s, 1H); $^{13}C$ NMR: $\delta = 55.9$, 115.0, 118.8, 126.0, 126.9, 128.9, 129.0, 131.1, 147.2, 165.3; HRMS ($EI^+$): Calcd for $C_{15}H_{13}N_3O_3S$, $M^+$ 315.0678. Found m/z 315.0678.

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**1e**: IR (KBr): 3125, 1395, 1179, 995 $cm^{-1}$; $^1H$ NMR: δ = 7.31–7.47 (m, 3H), 7.61–7.75 (m, 2H), 7.78–7.86 (m, 2H), 7.87–7.94 (m, 1H), 7.96–8.08 (m, 3H), 8.38 (s, 1H), 8.74–8.80 (m, 1H); $^{13}C$ NMR: δ = 119.0, 122.1, 126.0, 128.0, 128.2, 128.7, 128.9, 129.0, 129.7, 130.2, 130.4, 131.2, 131.8, 132.7, 135.9, 147.4; HRMS ($EI^+$): Calcd for $C_{18}H_{13}N_3O_2S$, $M^+$ 335.0728. Found m/z 335.0731.

**1h**: IR (KBr): 3115, 1497, 1393, 1256, 1179 $cm^{-1}$; $^1H$ NMR: δ = 2.40 (s, 3H), 3.81 (s, 3H), 6.90–6.97 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.70–7.78 (m, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 8.23 (s, 1H); $^{13}C$ NMR: δ = 21.7, 55.2, 114.3, 117.9, 121.3, 127.3, 128.5, 130.3, 133.0, 147.1, 147.2, 160.1; HRMS ($EI^+$): Calcd for $C_{16}H_{15}N_3O_3S$, $M^+$ 329.0834. Found m/z 329.0833.

**1i**: IR (KBr): 3139, 1593, 1483, 1389, 1177 $cm^{-1}$; $^1H$ NMR: δ = 2.43 (s, 3H), 7.33–7.41 (m, 3H), 7.42–7.50 (m, 2H), 7.59–7.70 (m, 4H), 7.88–7.95 (m, 2H), 8.01–8.07 (m, 2H), 8.38 (s, 1H); $^{13}C$ NMR: δ = 21.7, 118.9, 126.4, 126.8, 127.5, 127.6, 127.7, 128.5, 128.8, 130.4, 132.9, 140.1, 141.6, 147.0, 147.3; HRMS ($EI^+$): Calcd for $C_{21}H_{17}N_3O_2S$, $M^+$ 375.1041. Found m/z 375.1045.

**1j**: IR (KBr): 3141, 1389, 1325, 1198, 1175 $cm^{-1}$; $^1H$ NMR: δ = 2.43 (s, 3H), 7.34–7.41 (m, 2H), 7.45–7.55 (m, 2H), 7.79–7.92 (m, 4H), 8.01–8.08 (m, 2H), 8.34–8.38 (m, 1H), 8.43 (s, 1H); $^{13}C$ NMR: δ = 21.8, 119.1, 123.5, 125.2, 126.1, 126.60, 126.63, 127.7, 128.2, 128.6, 128.8, 130.4, 133.0, 133.3, 133.4, 147.3, 147.4; HRMS ($EI^+$): Calcd for $C_{19}H_{15}N_3O_2S$, $M^+$ 349.0885. Found m/z 349.0889.

**1k**: IR (neat): 2930, 1595, 1395, 1194 $cm^{-1}$; $^1H$ NMR: δ = 0.87 (t, *J* = 6.8 Hz, 3H), 1.21–1.40 (m, 6H), 1.64 (quint, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 2.64–2.75 (m, 2H), 7.34–7.40 (m, 2H), 7.82–7.84 (m, 1H), 7.94–8.01 (m, 2H); $^{13}C$ NMR: δ = 14.0, 21.8, 22.5, 25.4, 28.75, 28.84, 31.4, 120.2, 128.5, 130.3, 133.3, 147.0, 148.3; HRMS ($EI^+$): Calcd for $C_{15}H_{21}N_3O_2S$, $M^+$ 307.1354. Found m/z 307.1344.

**General procedure for the nickel-catalysed reaction of *N*-sulfonyl-1,2,3-triazoles with alkynes**: In a glove-box, **1** (0.20 mmol) and $AlPh_3$ (2.6 mg, 10 μmol) were charged into an oven-dried 4 mL-vial equipped with a stir bar. A solution of $Ni(cod)_2$ (5.5 mg, 20 μmol) and P(*n*-Bu)$Ad_2$ (14.3 mg, 40 μmol) in toluene (2 mL) and **2** (0.40 mmol) were added, and then the vial capped with a Teflon film was removed from the glove-box. The reaction mixture was heated at 100 °C for 12 h. After this time, the reaction mixture was cooled to room temperature and stirred in open air for 30 min. The resulting mixture was passed through a pad of Florisil and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/dichloromethane) to give the product **3**.

**3aa**: IR (neat): 2957, 1597, 1368, 1175, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.77 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.10–1.53 (m, 8H), 2.35–2.46 (m, 2H), 2.41 (s, 3H), 2.60–2.70 (m, 2H), 7.24–7.42 (m, 8H), 7.61–7.67 (m, 2H); $^{13}C$ NMR: δ = 13.7, 13.8, 21.6, 22.6, 22.8, 24.3, 25.3, 32.6, 33.1, 119.3, 125.2, 126.5, 126.7, 128.0, 128.3, 129.8, 132.3, 134.9, 136.8, 144.4; HRMS ($EI^+$): Calcd for $C_{25}H_{31}NO_2S$, $M^+$ 409.2075. Found m/z 409.2073.

**3ba**: IR (neat): 2957, 1368, 1175, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.10–1.54 (m, 8H), 2.36–2.48 (m, 2H), 2.62–2.72 (m, 2H), 7.26–7.42 (m, 6H), 7.45–7.53 (m, 2H), 7.55–7.63 (m, 1H), 7.73–7.80 (m, 2H); $^{13}C$ NMR: δ = 13.7, 13.8, 22.6, 22.8, 24.3, 25.3, 32.6, 33.1, 119.4, 125.5, 126.4, 126.8, 128.1, 128.4, 128.6, 129.2, 132.4, 133.4, 134.8, 139.8; HRMS ($EI^+$): Calcd for $C_{24}H_{29}NO_2S$, $M^+$ 395.1919. Found m/z 395.1920.

**3ca**: IR (neat): 2957, 1593, 1495, 1372, 1183, 1092 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.10–1.56 (m, 8H), 2.35–2.47 (m, 2H), 2.59–2.71 (m, 2H), 7.12–7.22 (m, 2H), 7.25–7.43 (m, 6H), 7.74–7.83 (m, 2H); $^{13}C$ NMR: δ = 13.7, 13.8, 22.6, 22.8, 24.3, 25.4, 32.6, 33.2, 116.6 (d, *J* = 21.9 Hz), 119.3, 125.8, 126.9, 128.1, 128.4, 129.0, 129.3 (d, *J* = 10.4 Hz), 132.4, 134.6, 135.8 (d, *J* = 3.5 Hz), 165.4 (d, *J* = 254.7 Hz); HRMS ($EI^+$): Calcd for $C_{24}H_{28}FNO_2S$, $M^+$ 413.1825. Found m/z 413.1824.

**3da**: IR (neat): 2957, 1595, 1499, 1366, 1264, 1167, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H), 1.11–1.53 (m, 8H), 2.36–2.45 (m, 2H), 2.60–2.70 (m, 2H), 3.85 (s, 3H), 6.90–6.97 (m, 2H), 7.25–7.41 (m, 6H), 7.67–7.74 (m, 2H); $^{13}C$ NMR: δ = 13.75, 13.83, 22.6, 22.9, 24.3, 25.3, 32.6, 33.1, 55.7, 114.4, 119.2, 125.2, 126.7, 128.1, 128.3, 128.4, 128.8, 131.3, 132.2, 134.9, 163.4; HRMS ($EI^+$): Calcd for $C_{25}H_{31}NO_3S$, $M^+$ 425.2025. Found m/z 425.2026.

**3ea**: IR (neat): 2957, 1366, 1177, 1076 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H), 1.12–1.57 (m, 8H), 2.38–2.49 (m, 2H), 2.68–2.79 (m, 2H), 7.28–7.45 (m, 6H), 7.58–7.74 (m, 3H), 7.85–8.01 (m, 3H), 8.42 (d, *J* = 2.1 Hz, 1H); $^{13}C$ NMR: δ = 13.7, 13.8, 22.5, 22.8, 24.2, 25.3, 32.5, 33.1, 119.4, 121.4, 125.4, 126.7, 127.7, 127.9, 128.0, 128.1, 128.3, 128.5, 129.2, 129.3, 129.6, 131.9, 132.4, 134.8, 135.0, 136.5; HRMS ($EI^+$): Calcd for $C_{28}H_{31}NO_2S$, $M^+$ 445.2075. Found m/z 445.2076.

**3fa**: IR (neat): 2957, 1368, 1175, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.09–1.52 (m, 8H), 2.32–2.45 (m, 2H), 2.37 (s, 3H), 2.40 (s, 3H), 2.60–2.69 (m, 2H), 7.14–7.20 (m, 2H), 7.22–7.30 (m, 5H), 7.60–7.66 (m, 2H); $^{13}C$ NMR: δ = 13.75, 13.81, 21.1, 21.57, 22.60, 22.8, 24.3, 25.3, 32.6, 33.1, 119.1, 125.3, 126.5, 127.9, 128.3, 129.1, 129.8, 131.9, 132.3, 136.3, 136.9, 144.3; HRMS ($EI^+$): Calcd for $C_{26}H_{33}NO_2S$, $M^+$ 423.2232. Found m/z 423.2235.

**3ga**: IR (neat): 2959, 1619, 1370, 1325, 1175, 1127, 1073 $cm^{-1}$; $^1H$ NMR: δ = 0.79 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.10–1.52 (m, 8H), 2.36–2.48 (m, 2H), 2.42 (s, 3H), 2.61–2.71 (m, 2H), 7.27–7.33 (m, 2H), 7.34 (s, 1H), 7.45–7.52 (m, 2H), 7.60–7.70 (m, 4H); $^{13}C$ NMR: δ = 13.7, 13.8, 21.6, 22.6, 22.8, 24.3, 25.2, 32.7, 33.1, 119.8, 124.3 (q, *J* = 270.1 Hz), 124.8, 125.3 (q, *J* = 3.5 Hz), 126.6, 126.9, 128.2, 128.8 (q, *J* = 31.7 Hz), 129.9, 132.7, 136.6, 138.7, 144.7; HRMS ($EI^+$): Calcd for $C_{26}H_{30}F_3NO_2S$, $M^+$ 477.1949. Found m/z 477.1946.

**3ha**: IR (neat): 2957, 1539, 1368, 1246, 1173, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H), 1.10–1.52 (m, 8H), 2.32–2.43 (m, 2H), 2.40 (s, 3H), 2.59–2.68 (m, 2H), 3.83 (s, 3H), 6.87–6.95 (m, 2H), 7.22 (s, 1H), 7.23–7.31 (m, 4H), 7.60–7.67 (m, 2H); $^{13}C$ NMR: δ = 13.77, 13.81, 21.6, 22.6, 22.8, 24.3, 25.3, 32.6, 33.1, 55.3, 113.8, 118.9, 125.4, 126.5, 127.3, 128.0, 129.2, 129.8, 132.2, 136.9, 144.3, 158.5; HRMS ($EI^+$): Calcd for $C_{26}H_{33}NO_3S$, $M^+$ 439.2181. Found m/z 439.2179.

**3ia**: IR (neat): 2957, 1368, 1175, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.82 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H), 1.16–1.56 (m, 8H), 2.42 (s, 3H), 2.43–2.52 (m, 2H), 2.64–2.74 (m, 2H), 7.27–7.32 (m, 2H), 7.33–7.40 (m, 2H), 7.43–7.51 (m, 4H), 7.60–7.71 (m, 6H); $^{13}C$ NMR: δ = 13.77, 13.83, 21.6, 22.6, 22.8, 24.4, 25.3, 32.7, 33.1, 119.3, 125.2, 126.6, 126.9, 127.0, 127.2, 127.9, 128.3, 128.7, 129.8, 132.5, 133.9, 136.8, 139.5, 140.7, 144.5; HRMS ($EI^+$): Calcd for $C_{31}H_{35}NO_2S$, $M^+$ 485.2389. Found m/z 485.2390.

**3ja**: IR (neat): 2957, 1368, 1173, 1094 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 1.12–1.56 (m, 8H), 2.42 (s, 3H), 2.46–2.56 (m, 2H), 2.65–2.75 (m, 2H), 7.26–7.33 (m, 2H), 7.41 (s, 1H), 7.43–7.56 (m, 3H), 7.65–7.72 (m, 2H), 7.80–7.89 (m, 4H); $^{13}C$ NMR: δ = 13.7, 13.8, 21.6, 22.6, 22.9, 24.4, 25.3, 32.6, 33.1, 119.6, 125.3, 125.6, 126.1, 126.3, 126.60, 126.63, 127.6, 127.8, 127.9, 128.2, 129.8, 132.3, 132.4, 132.5, 133.5, 136.8, 144.5; HRMS ($EI^+$): Calcd for $C_{29}H_{33}NO_2S$, $M^+$ 459.2232. Found m/z 459.2233.

**3ka**: IR (neat): 2930, 1466, 1368, 1175, 1094, 1065 $cm^{-1}$; $^1H$ NMR: δ = 0.78–0.98 (m, 9H), 1.18–1.62 (m, 16H), 2.16–2.35 (m, 4H), 2.38 (s, 3H), 2.51–2.61 (m, 2H), 6.93–6.97 (m, 1H), 7.20–7.27 (m, 2H), 7.52–7.58 (m, 2H); $^{13}C$ NMR: δ = 13.8, 13.9, 14.1, 21.5, 22.65, 22.73, 22.8, 24.2, 25.3, 29.1, 29.2, 31.7, 32.8, 33.2, 118.4, 126.3, 126.5, 127.7, 129.6, 131.8, 137.2, 144.0; HRMS ($EI^+$): Calcd for $C_{25}H_{39}NO_2S$, $M^+$ 417.2702. Found m/z 417.2702.

**3ab**: IR (neat): 2961, 1368, 1175, 1092 $cm^{-1}$; $^1H$ NMR: δ = 0.77 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 1.21–1.36 (m, 2H), 1.46–1.62 (m, 2H), 2.35–2.46 (m, 2H), 2.41 (s, 3H), 2.59–2.69 (m, 2H), 7.25–7.42 (m, 8H), 7.62–7.68 (m, 2H); $^{13}C$ NMR: δ = 14.0, 14.2, 21.6, 23.6, 24.3, 26.7, 27.5, 119.4, 125.2, 126.5, 126.7, 128.0, 128.3, 129.8, 132.3, 134.9, 136.8, 144.4; HRMS ($EI^+$): Calcd for $C_{23}H_{27}NO_2S$, $M^+$ 381.1762. Found m/z 381.1758.

**3ac**: IR (KBr): 1368, 1171, 1103 $cm^{-1}$; $^1H$ NMR: δ = 2.38 (s, 3H), 6.83–6.91 (m, 2H), 6.98–7.08 (m, 5H), 7.10–7.34 (m, 12H), 7.65 (s, 1H); $^{13}C$ NMR: δ = 21.6, 119.9, 126.3, 126.6, 126.9, 127.1, 127.5, 127.6, 127.7, 128.2, 128.4, 129.4, 130.2, 130.4, 132.1, 132.6, 133.3, 133.7, 135.7, 144.7; HRMS ($EI^+$): Calcd for $C_{29}H_{23}NO_2S$, $M^+$ 449.1449. Found m/z 449.1447.

**3ad (mixture)**: IR (neat): 2965, 1364, 1173, 1094 $cm^{-1}$; $^1H$ NMR: δ = 1.125 (d, *J* = 7.2 Hz, 3H), 1.132 (d, *J* = 6.9 Hz, 3H), 2.10 (s, 1.5H), 2.36 (s, 1.5H), 2.42 (s, 1.5H), 2.43 (s, 1.5H), 2.92 (sept, *J* = 7.2 Hz, 0.5H), 3.61 (sept, *J* = 7.1 Hz, 0.5H), 7.23 (s, 0.5H), 7.27–7.44 (m, 7.5H), 7.64–7.74 (m, 2H); $^{13}C$ NMR: δ = 11.5, 12.0, 21.0, 21.6, 22.4, 25.1, 25.5, 118.2, 118.7, 119.1, 125.8, 126.6, 126.7, 126.8, 126.9, 128.0, 128.2, 128.3, 128.5, 128.8, 129.4, 129.86, 129.89, 130.2, 134.4, 135.2, 136.0, 136.5, 136.9, 144.5; HRMS ($EI^+$): Calcd for $C_{21}H_{23}NO_2S$, $M^+$ 353.1449. Found m/z 353.1447.

**3ae (major)**: IR (KBr): 2953, 1360, 1173, 1011 $cm^{-1}$; $^1H$ NMR: δ = 0.00 (s, 9H), 2.41 (s, 3H), 2.44 (s, 3H), 7.23–7.37 (m, 8H), 7.71–7.78 (m, 2H); $^{13}C$ NMR: δ = 1.2, 14.3, 21.7, 120.1, 126.9, 127.1, 127.7, 129.6, 130.0, 133.0, 136.1, 136.4, 136.8, 144.8; HRMS ($EI^+$): Calcd for $C_{21}H_{25}NO_2SSi$, $M^+$ 383.1375. Found m/z 383.1374.

**3ae (minor)**: IR (KBr): 2953, 1356, 1169, 1100 $cm^{-1}$; $^1H$ NMR: δ = 0.37 (s, 9H), 2.17 (s, 3H), 2.40 (s, 3H), 7.22–7.42 (m, 7H), 7.42 (s, 1H), 7.49–7.55 (m, 2H); $^{13}C$ NMR: δ = 2.4, 13.2, 21.6, 125.4, 126.0, 126.9, 128.3, 128.9, 129.6, 131.4, 131.7, 134.0, 134.6, 137.6, 144.1; HRMS ($EI^+$): Calcd for $C_{21}H_{25}NO_2SSi$, $M^+$ 383.1375. Found m/z 383.1371.

**3af (major)**: IR (neat): 2930, 1374, 1173, 1111 $cm^{-1}$; $^1H$ NMR: δ = 0.78 (t, *J* = 7.4 Hz, 3H), 1.13–1.39 (m, 4H), 1.39 (s, 12H), 2.40 (s, 3H), 2.53–2.63 (m, 2H), 7.23–7.39 (m, 8H), 7.88–7.94 (m, 2H); $^{13}C$ NMR: δ = 13.7, 21.6, 22.7, 24.9, 25.6, 33.7, 84.1, 122.6, 126.7, 127.6, 128.3, 129.4, 130.0, 134.4, 136.4, 137.9, 144.3 (The boron-bound carbon was not detected due to the quadrupolar relaxation); HRMS ($EI^+$): Calcd for $C_{27}H_{34}BNO_4S$, $M^+$ 479.2302. Found m/z 479.2303.

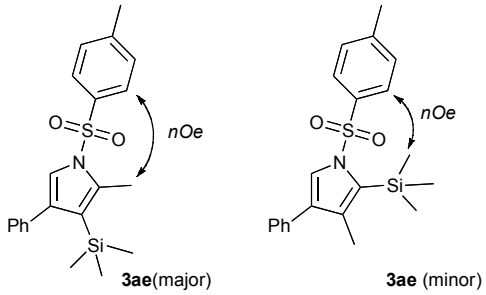
**3af (minor)**: IR (neat): 2977, 1372, 1306, 1175, 1117 $cm^{-1}$; $^1H$ NMR: $\delta$ = 0.90 (t, $J$ = 7.2 Hz, 3H), 1.25 (s, 12H), 1.29–1.54 (m, 4H), 2.40 (s, 3H), 2.84–2.94 (m, 2H), 7.21–7.35 (m, 5H), 7.36 (s, 1H), 7.40–7.46 (m, 2H), 7.66–7.72 (m, 2H); $^{13}C$ NMR: $\delta$ = 13.8, 21.6, 22.9, 24.7, 27.3, 34.4, 83.2, 119.7, 126.6, 126.9, 127.7, 128.4, 129.9, 131.9, 134.9, 136.5, 144.8, 145.3 (The boron-bound carbon was not detected due to the quadrupolar relaxation); HRMS ($EI^+$): Calcd for $C_{27}H_{34}BNO_4S$, $M^+$ 479.2302. Found m/z 479.2303.

**Determination of regiochemistries.**

Regiochemistries of the products were determined by nOe experiments. Curved arrows shown below indicate the observed nOe.

**[Compound 3ae]**

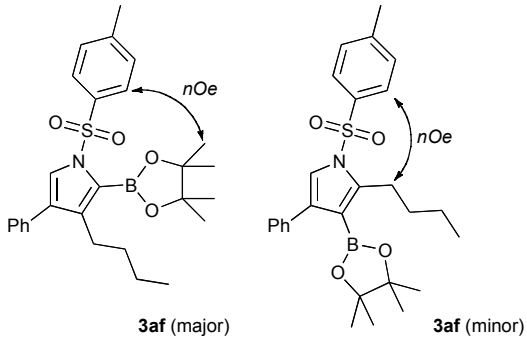
The following results of **3ae** (major product) and **3ae** (minor product) suggested that the methyl group was bound to C(2) in the major product.




**3ae**(major) **3ae** (minor)

**[Compound 3af]**

The following results of **3af** (major product) and **3af** (minor product) suggested that the boryl group was bound to C(2) in the major product.




**3af** (major) **3af** (minor)