**Catalytic Intermolecular Amination of C–H Bonds:
Method Development and Mechanistic Insights**

Supplementary Material
(12 pages)

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General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of nitrogen. Organic solutions were concentrated under reduced pressure (~15 Torr) by rotary evaporation. Freshly distilled solvents were employed unless otherwise noted. Dichloromethane, benzene, and toluene were dried by passage through activated alumina columns under 12 psi of N₂. The preparation of Rh₂(esp)₂ followed a previously published protocol.¹

Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35-75 μm). Thin-layer chromatography (TLC) was performed on EM Science silica gel 60 F₂₅₄ plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

Nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury spectrometer operating at 400 and 100 MHz for ¹H and ¹³C, respectively, or on a Varian Inova spectrometer operating at 500 and 125 MHz for ¹H and ¹³C, respectively, and are referenced internally according to residual solvent signals. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; br d, broad doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet), integration, and coupling constant (Hz). Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Thermo Nicolet IR300 spectrometer and are reported in terms of frequency of absorption. Sample preparation was done either as a thin film on a NaCl salt plate or as a KBr pellet. UV/Visible spectra were collected on a Varian Cary 6000i UV-vis-NIR spectrophotometer. High-resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

PhI(O₂C^tBu)₂:² A 500 mL round bottom flask was charged with PhI(OAc)₂ (15.0 g, 46.5 mmol), 180 mL of chlorobenzene, and trimethylacetic acid (16.5 g, 0.16 mol, 3.0 equiv). The flask was fitted with a short-path distillation head and a 250 mL receiving flask. The reaction was stirred at 50 °C under reduced pressure (30 torr) and the chlorobenzene was slowly distilled (ca. 8–10 h) until ~20–30 mL of solvent remained. After cooling to 23 °C, 150 mL of hexanes was added to precipitate a white solid. The desired product was collected upon filtration and dried *in vacuo* (17.9 g, 95%). ¹H NMR (CDCl₃, 400 MHz) δ 8.02-7.99 (m, 2H), 7.57-7.52 (m, 1H), 7.50-7.44 (m, 2H), 1.11 (s, 18H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 183.5, 134.2, 131.2, 130.6, 122.0, 38.9, 27.7 ppm; IR (thin film) ν 2974, 2931, 2870, 1644, 1477, 1443, 1393, 1364, 1291, 1175, 994, 890 cm⁻¹.

H₂NSO₃CH₂CCl₃:³ To a 100 mL three-neck flask equipped with a 25 mL addition funnel, a CaSO₄-filled drying tube, and a rubber septum were added 10 mL of CH₃CN and ClSO₂NCO (2.7 mL, 31.3 mmol, 1.5 equiv). After cooling the solution to 0 °C, HCO₂H (1.2 mL, 31.3 mmol, 1.5 equiv) in 6 mL of CH₃CN was added dropwise from the addition funnel over a 10 min period. Following this time, the mixture was warmed to 23 °C and stirred for 8 h. The reaction vessel was then returned to the ice bath before a solution of 2,2,2-trichloroethanol (2.0 mL, 20.8 mmol) in 12 mL of DMA was added via cannula. Transfer of the alcohol was made quantitative with an additional 4 mL of DMA. The contents were warmed to 23 °C and stirred vigorously for 1.5 h. The reaction mixture was quenched by the addition of 50 mL of H₂O and poured into a separatory funnel containing 100 mL of Et₂O. The organic phase was collected and the aqueous layer was extracted with 2 x 100 mL of Et₂O. The combined ethereal extracts were washed with 5 x 50 mL of H₂O, dried over MgSO₄, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel using 2:1 hexanes/EtOAc as eluent afforded the desired product as a white solid (4.35 g, 91%). TLC R_f = 0.35 (15:1 CH₂Cl₂/EtOAc); mp = 52–54 °C; ¹H NMR (CDCl₃, 400 MHz) δ 5.40 (br s, 2H), 4.69 (s, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 93.0, 78.6 ppm; IR (thin film) ν 3404, 3296, 3095, 1551, 1371, 1267, 1189, 1089, 1016, 932, 860, 770 cm⁻¹; HRMS (EI) calcd for C₂H₄Cl₃NO₃S 226.8977 found 227.9069 (MH⁺).

Preparation of $\text{H}_2^{15}\text{NSO}_3\text{CH}_2\text{CCl}_3$: A 50 mL 2-neck flask fitted with a gas inlet (glass pipette) and a rubber septum was charged with 7 mL of THF and $\text{Cl}_3\text{CCH}_2\text{OSO}_2\text{Cl}$ (0.60 g, 2.4 mmol).⁴ The solution was cooled to 0 °C and gaseous $^{15}\text{NH}_3$ was bubbled into the mixture for 15 s. A white precipitate formed almost immediately upon addition of $^{15}\text{NH}_3$. The gas inlet was quickly removed and the reaction flask was sealed with a glass stopper. The white suspension stirred vigorously while the contents slowly warmed from 0° to 23 °C over the course of 1 h. The reaction mixture was then quenched with 10 mL of H_2O , transferred to a separatory funnel, and extracted with 2 x 25 mL of Et_2O . The organic extracts were combined and washed with 1 x 10 mL of saturated aqueous NaCl, dried over MgSO_4 , and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (3:1 hexanes/ EtOAc) afforded the desired sulfamate as a white solid (420 mg, 76%). TLC R_f = 0.35 (15:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); ^1H NMR (CDCl_3 , 400 MHz) δ 5.00 (d, 2H, J_{NH} = 83.5 Hz), 4.71 (s, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 94.4, 78.7 ppm; IR (thin film) ν 3287, 2957, 1619, 1547, 1448, 1371, 1267, 1188, 1089, 1047, 1016, 921, 858, 769 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_2\text{H}_4\text{Cl}_3^{15}\text{NO}_3\text{S}$ 227.8947 found 250.8850 (MNa^+).

Experimental procedure and characterization data intermolecular C–H amination reactions

A flask containing $\text{H}_2\text{NSO}_3\text{CH}_2\text{CCl}_3$ (137 mg, 0.60 mmol) in 0.6 mL of C_6H_6 was charged with $\text{Rh}_2(\text{esp})_2$ (9 mg, 12 μmol , 0.02 equiv) and substrate (0.60 mmol). To this bright green mixture was added 1.4 mL of a 0.83 M C_6H_6 solution of $\text{PhI}(\text{O}_2\text{C}^t\text{Bu})_2$ (1.2 mmol, 2.0 equiv) via syringe pump over 3 h. During the addition of $\text{PhI}(\text{O}_2\text{C}^t\text{Bu})_2$, a change in the reaction color to brown or red was generally observed. Following the transfer of oxidant, the solution was stirred at 23 °C for 1–2 h. Dichloromethane (5 mL) and 2 mL of a saturated aqueous solution of thiourea were then added and the orange biphasic mixture was stirred vigorously for 30 min.⁵ The contents were transferred to a separatory funnel and the organic phase was collected. The aqueous layer was extracted with 2 x 10 mL of CH_2Cl_2 . The combined organic extracts were washed with 2 x 10 mL of a 0.1 M pH 7 $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ buffer, dried over MgSO_4 , and concentrated under reduced pressure. Purification of the isolated material by chromatography on silica gel (conditions given below) afforded the desired product.

Purified by chromatography on silica gel (9:1 hexanes/ EtOAc); pale yellow oil (72%): TLC R_f = 0.38 (4:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.41–7.30 (m, 5H), 4.89 (br d, 1H, J = 6.8 Hz), 4.74 (quint, 1H, J = 6.8 Hz), 4.44 (d, 1H, J = 10.8 Hz), 4.43 (d, 1H, J = 10.8 Hz), 1.63 (d, 3H, J = 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.3, 129.0, 128.3, 126.2, 93.2, 78.1, 54.9, 22.8 ppm; IR (thin film) ν 3304, 3066, 3033, 2981, 2950, 1496, 1433, 1365, 1273, 1182, 1121, 1086, 1047, 1015, 976, 854 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{12}\text{Cl}_3\text{NO}_3\text{S}$ 330.9603 found 353.9503 (MNa^+).

Purified by chromatography on silica gel (9:1 hexanes/ EtOAc); pale yellow oil (47%): TLC R_f = 0.41 (4:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.38–7.33 (m, 3H), 7.33–7.28 (m, 2H), 4.64 (quint, 1H, J = 6.7 Hz), 4.58 (br d, 1H, J = 6.7 Hz), 3.68 (d, 1H, J = 8.8 Hz), 3.57 (d, 1H, J = 8.8 Hz), 1.58 (d, 3H, J = 6.7 Hz) 0.83(s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 142.3, 128.7, 127.8, 126.1, 79.4, 54.3, 31.3, 25.9, 23.3 ppm; IR (thin film) ν 3292, 2961, 1460, 1433, 1357, 1174, 1122, 1086, 963, 880, 826 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3\text{S}$ 271.1242 found 294.1138 (MNa^+).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); pale yellow oil (20%): TLC R_f = 0.35 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.30 (m, 5H), 7.11-7.07 (m, 2H), 6.98-6.94 (m, 2H), 5.03 (br d, 1H, J = 6.9 Hz), 4.74 (quint, 1H, J = 6.9 Hz), 2.32 (s, 3H), 1.59 (d, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 147.8, 141.7, 136.6, 130.1, 128.8, 128.1, 126.2, 121.5, 55.0, 23.1, 20.8 ppm; IR (thin film) ν 3299, 3033, 2980, 2927, 1504, 1456, 1432, 1364, 1197, 1176, 1152, 1120, 1105, 1084, 1020, 1001, 976, 869, 831, 795 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3\text{S}$ 291.0929 found 314.0839 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 9:1→4:1 hexanes/EtOAc); white solid (29%): TLC R_f = 0.35 (2:1 hexanes/EtOAc); mp = 84–88 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.71 (dd, 1H, J = 7.9, 1.2 Hz), 7.66 (dd, 1H, J = 7.8, 1.4 Hz), 7.53 (td, 1H, J = 7.9, 1.4 Hz), 7.40 (td, 1H, J = 7.8, 1.2 Hz), 7.12-7.05 (m, 5H), 5.78 (br d, 1H, J = 8.4 Hz), 4.69 (dq, 1H, J = 8.4, 7.0 Hz), 1.52 (d, 3H, J = 7.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 147.2, 141.1, 134.3, 132.9, 132.4, 130.7, 128.4, 127.6, 126.0, 124.8, 54.9, 23.6 ppm; IR (thin film) ν 3347, 3096, 3030, 2979, 2927, 1594, 1540, 1496, 1456, 1415, 1361, 1339, 1302, 1208, 1170, 1119, 1084, 1061, 1017, 1000, 961, 854 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ 306.0674 found 329.0574 (MNa^+).

Purified by chromatography on silica gel (3:1 hexanes/EtOAc); pale yellow oil (20%): TLC R_f = 0.26 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.28 (m, 5H), 4.95 (br s, 1H), 4.64 (quint, 1H, J = 6.9 Hz), 2.61 (s, 3H), 1.54 (d, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 142.4, 128.9, 128.0, 126.2, 53.7, 41.7, 24.0 ppm; IR (thin film) ν 3278, 2977, 2932, 1495, 1454, 1316, 1152, 1120, 1086, 1021, 981, 862 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$ 199.0667 found 222.0556 (MNa^+).

Purified by chromatography on silica gel (9:1 hexanes/EtOAc); pale yellow oil (35%): TLC R_f = 0.69 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.36 (m, 2H), 7.36-7.30 (m, 3H), 5.24 (br s, 1H), 4.80 (quint, 1H, J = 7.0 Hz), 1.64 (d, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.9, 129.0, 128.4, 125.7, 119.5 (q, J_{CF} = 320.4 Hz), 55.3, 23.4 ppm; IR (thin film) ν 3307, 1433, 1372, 1231, 1195, 1147, 1080, 1023, 980, 868 cm^{-1} .

Purified by chromatography on silica gel (gradient elution: 9:1→4:1 hexanes/EtOAc); clear oil (70%): TLC R_f = 0.48 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.35 (m, 2H), 7.33-7.29 (m, 3H), 5.87 (br d, 1H, J = 7.7 Hz), 4.58 (dt, 1H, J = 7.7, 6.3 Hz), 4.34 (d, 1H, J = 10.8 Hz), 4.29 (d, 1H, J = 10.8 Hz), 3.69 (s, 3H), 2.51-2.38 (m, 2H), 2.30-2.20 (m, 1H), 2.12 (dq, 1H, J = 14.3, 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.2, 140.0, 129.0, 128.4, 126.5, 93.2, 77.9, 59.0, 52.1, 31.5, 30.6 ppm; IR (thin film) ν 3286, 2954, 1717, 1440, 1369, 1260, 1182, 1089, 1048, 1019, 990, 910, 855 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_5\text{S}$ 402.9815 found 425.9699 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 13:1→4:1 hexanes/EtOAc); white solid (70%): TLC R_f = 0.34 (4:1 hexanes/EtOAc); mp = 130–132 °C; ^1H NMR (CDCl_3 , 400 MHz, 50 °C) δ 7.73 (br d, 1H, J = 7.8 Hz), 7.57 (dd, 1H, J = 7.8, 1.5 Hz), 7.36 (td, 1H, J = 7.5, 1.5 Hz), 7.30 (dt, 1H, J = 7.5, 1.5 Hz), 5.09 (br d, 1H, J = 7.5 Hz), 4.88 (q, 1H, J = 6.8 Hz), 4.70 (d, 1H, J = 11.1 Hz), 4.69 (d, 1H, J = 11.1 Hz), 3.98–3.86 (m, 2H), 2.50–2.41 (m, 1H), 2.38–2.30 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz, 50 °C) δ 156.0 (q, 1C, J_{CF} = 37.4 Hz), 136.7, 129.1, 129.0, 128.6, 127.3, 124.6, 116.5 (q, J_{CF} = 288.4 Hz), 93.5, 78.3, 50.9, 42.6 (q, J_{CF} = 3.4 Hz), 31.2 ppm; IR (thin film) ν 3267, 1686, 1495, 1433, 1366, 1292, 1267, 1205, 1182, 1149, 1085, 997, 948, 855 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{12}\text{Cl}_3\text{F}_3\text{N}_2\text{O}_4\text{S}$ 453.9535 found 476.9416 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 9:1→4:1 hexanes/EtOAc); white solid (57%): TLC R_f = 0.52 (2:1 hexanes/EtOAc); mp = 179–181 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.90 (dd, 1H, J = 2.0, 1.1 Hz), 7.48 (dd, 1H, J = 8.3, 2.0 Hz), 6.86 (d, 1H, J = 8.3 Hz), 4.90 (br d, 1H, J = 10.1 Hz), 4.82 (td, 1H, J = 10.1, 6.0 Hz), 4.78 (d, 1H, J = 10.8 Hz), 4.74 (d, 1H, J = 10.8 Hz), 2.47 (dd, 1H, J = 13.6, 6.0 Hz), 1.92 (dd, 1H, J = 13.6, 10.1 Hz), 1.48 (s, 3H), 1.33 (s, 3H) ppm; ^{13}C NMR (d_6 -acetone, 100 MHz) δ 210.0, 158.4, 133.8, 133.5, 123.3, 119.5, 104.2, 94.8, 78.7, 77.8, 69.2, 48.3, 40.1, 24.6 ppm; IR (thin film) ν 3169, 2980, 2229, 1611, 1489, 1372, 1302, 1269, 1182, 1129, 1084, 1005, 909, 847 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_3\text{N}_2\text{O}_4\text{S}$ 411.9818 found 434.9727 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 13:1→4:1 hexanes/EtOAc); white solid (51%, 7:1 C1/C4 mixture): TLC R_f = 0.36_{C1}, 0.38_{C4} (4:1 hexanes/EtOAc); C1 isomer: mp = 120–125 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.39 (d, 1H, J = 8.5 Hz), 6.77 (dd, 1H, J = 8.6, 2.7 Hz), 6.61 (d, 1H, J = 2.7 Hz), 4.84 (br d, 1H, J = 7.6 Hz), 4.74 (dt, 1H, J = 7.6, 4.8 Hz), 4.68 (s, 2H), 3.78 (s, 3H), 2.82–2.63 (m, 2H), 2.17–1.99 (m, 2H), 1.90–1.79 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.2, 139.1, 130.6, 126.6, 113.6, 113.0, 93.6, 78.0, 55.2, 53.0, 30.3, 29.1, 18.7 ppm; IR (thin film) ν 3305, 2943, 1609, 1579, 1503, 1447, 1432, 1363, 1277, 1257, 1235, 1183, 1076, 1027, 988, 946, 853 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_4\text{S}$ 386.9866 found 409.9760 (MNa^+).

C4 isomer: mp = 92–96 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.02 (d, 1H, J = 8.5 Hz), 6.99 (d, 1H, J = 2.6 Hz), 6.80 (dd, 1H, J = 8.5, 2.6 Hz), 4.85 (br d, 1H, J = 7.6 Hz), 4.75 (dt, 1H, J = 7.6, 5.2 Hz), 4.70 (s, 2H), 3.79 (s, 3H), 2.80–2.61 (m, 2H), 2.14–2.02 (m, 2H), 1.89–1.81 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.2, 135.2, 130.4, 129.6, 115.4, 112.9, 93.6, 78.1, 55.4, 53.7, 30.2, 28.0, 19.1 ppm; IR (thin film) ν 3308, 2935, 2860, 1612, 1503, 1448, 1363, 1252, 1234, 1182, 1078, 1034, 991, 946, 852 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_4\text{S}$ 386.9866 found 409.9763 (MNa^+).

Purified by chromatography on silica gel (gradient elution: hexanes→9:1 hexanes/EtOAc); white solid (60%, 1:1 *cis/trans* mixture): TLC R_f = 0.44, 0.52 (4:1 hexanes/EtOAc); higher R_f diastereomer: ^1H NMR (CDCl_3 , 400 MHz) δ 7.48-7.45 (m, 1H), 7.37-7.28 (m, 3H), 5.57 (br d, 1H, J = 8.5 Hz), 4.78 (t, 1H, J = 5.4 Hz), 4.74 (dt, 1H, J = 8.5, 4.8 Hz), 4.63 (d, 1H, J = 10.7 Hz), 4.54 (d, 1H, J = 10.7 Hz), 2.38-2.30 (m, 1H), 2.07 (ddd, 1H, J = 14.2, 7.1, 4.8 Hz), 2.05-1.97 (m, 2H), 0.93 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.0, 135.0, 128.8, 128.6, 128.3, 128.0, 93.5, 77.9, 69.0, 53.2, 28.7, 26.6, 25.8, 18.1, -4.3, -4.6 ppm; IR (thin film) ν 3308, 2954, 2930, 2857, 1454, 1363, 1256, 1183, 1125, 1080, 1048, 1019, 995, 939, 838 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{18}\text{H}_{28}\text{Cl}_3\text{NO}_4\text{SSi}$ 487.0574 found 510.0476 (MNa^+); lower R_f diastereomer: ^1H NMR (C_6D_6 , 400 MHz) δ 7.38 (d, 1H, J = 7.7 Hz), 7.35 (d, 1H, J = 7.7 Hz), 7.08 (td, 1H, J = 7.8, 1.4 Hz), 7.00 (td, 1H, J = 7.8, 1.4 Hz), 4.65-4.59 (m, 1H), 4.58-4.50 (m, 1H), 4.36 (d, 1H, J = 11.0 Hz), 4.32 (d, 1H, J = 11.0 Hz), 3.95 (br d, 1H, J = 8.0 Hz), 2.22 (ddd, 1H, J = 10.5, 8.7, 5.3 Hz), 1.64 (ddd, 1H, J = 10.5, 8.0, 4.5 Hz), 1.52-1.48 (m, 2H), 0.95 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.3, 134.2, 128.43, 128.42, 128.2, 128.0, 93.5, 78.0, 68.1, 53.6, 29.8, 27.2, 25.8, 18.1, -4.2, -4.6 ppm; IR (thin film) ν 3292, 2956, 2930, 2857, 1454, 1363, 1255, 1180, 1127, 1085, 1051, 995, 926, 861, 837 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{18}\text{H}_{28}\text{Cl}_3\text{NO}_4\text{SSi}$ 487.0574 found 510.0479 (MNa^+).

Purified by chromatography on silica gel (gradient elution: hexanes→9:1 hexanes/EtOAc); white solid (53%, 1:6 *cis/trans* mixture): TLC R_f = 0.46_{*trans*}, 0.51_{*cis*} (4:1 hexanes/EtOAc); *trans* isomer: ^1H NMR (CDCl_3 , 400 MHz) δ 7.54-7.50 (m, 1H), 7.27-7.22 (m, 2H), 7.12-7.08 (m, 1H), 5.00 (dt, 1H, J = 7.9, 5.6 Hz), 4.82 (br d, 1H, J = 7.9 Hz), 4.70 (s, 2H), 4.31-4.24 (m, 1H), 3.04 (dd, 1H, J = 16.6, 4.6 Hz), 2.74 (dd, 1H, J = 16.6, 6.9 Hz), 2.21-2.17 (m, 2H), 0.88 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 135.3, 133.9, 129.7, 128.3, 128.2, 126.8, 93.5, 78.1, 64.7, 53.0, 38.9, 38.5, 25.8, 18.1, 1.0, -4.7 ppm; IR (thin film) ν 3304, 2954, 2930, 2889, 2857, 1452, 1361, 1255, 1184, 1120, 1088, 1047, 1017, 990, 905, 837 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{18}\text{H}_{28}\text{Cl}_3\text{NO}_4\text{SSi}$ 487.0574 found 510.0467 (MNa^+).

Cis isomer: ^1H NMR (CDCl_3 , 400 MHz) δ 7.54-7.48 (m, 1H), 7.28-7.22 (m, 2H), 7.12-7.04 (m, 1H), 6.55 (br d, 1H, J = 9.4 Hz), 4.81 (ddd, 1H, J = 9.4, 5.3, 2.7 Hz), 4.63 (d, 1H, J = 10.7 Hz), 4.60 (d, 1H, J = 10.7 Hz), 4.54-4.50 (m, 1H), 2.98 (dd, 1H, J = 17.0, 3.8 Hz), 2.74 (br d, 1H, J = 17.0 Hz), 2.49 (dddd, 1H, J = 14.3, 4.7, 2.7, 1.9 Hz), 2.10 (ddd, 1H, J = 14.3, 5.3, 1.9 Hz), 0.88 (s, 9H), 0.16 (s, 3H), 0.11 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 134.3, 132.8, 130.1, 129.5, 128.3, 126.8, 93.7, 77.8, 66.8, 51.5, 37.3, 34.9, 25.8, 18.0, -4.9, -5.0 ppm; IR (thin film) ν 3304, 2954, 2930, 2896, 2857, 1456, 1362, 1255, 1184, 1120, 1089, 1047, 1016, 990, 837 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{18}\text{H}_{28}\text{Cl}_3\text{NO}_4\text{SSi}$ 487.0574 found 510.0475 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 13:1→4:1 hexanes/EtOAc); white solid (50%, 8:1 C4/C1 mixture): TLC R_f = 0.44_{C4}, 0.52_{C1} (4:1 hexanes/EtOAc); C4 isomer: mp = 143–146 °C; ^1H NMR (CDCl_3 , 400 MHz,

40 °C) δ 8.13 (ddd, 1H, J = 7.7, 1.3, 0.7 Hz), 7.76 (ddd, 1H, J = 7.7, 1.6, 0.7 Hz), 7.30 (td, 1H, J = 7.7, 1.6 Hz), 7.25 (td, 1H, J = 7.7, 1.3 Hz), 5.01 (ddd, 1H, J = 6.0, 5.0, 4.4 Hz), 4.75 (d, 1H, J = 11.0 Hz), 4.75 (br d, 1H, J = 6.0 Hz), 4.74 (d, 1H, J = 11.0 Hz), 3.18 (dt, 1H, J = 18.4, 4.4 Hz), 2.95-2.84 (m, 1H), 2.34-2.28 (m, 1H), 2.13-1.90 (m, 3H), 1.68 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.2, 139.1, 135.7, 127.3, 124.2, 123.1, 118.1, 115.4, 113.8, 93.6, 84.2, 77.9, 48.1, 29.1, 28.2, 25.5, 18.5 ppm; IR (thin film) ν 3280, 2979, 2947, 1732, 1610, 1458, 1430, 1396, 1371, 1325, 1258, 1224, 1180, 1161, 1142, 1118, 1076, 1021, 1001, 964, 911, 849 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{19}\text{H}_{23}\text{Cl}_3\text{N}_2\text{O}_5\text{S}$ 496.0393 found 519.0290 (MNa^+).

C1 isomer: mp = 116–120 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.01 (dt, 1H, J = 8.4, 0.8 Hz), 7.47 (ddd, 1H, J = 7.2, 1.2, 0.8 Hz), 7.34 (ddd, 1H, J = 8.4, 7.2, 1.2 Hz), 7.24 (ddd, 1H, J = 8.4, 7.2, 1.2 Hz), 5.26 (m, 2H), 4.85 (d, 1H, J = 10.7 Hz), 4.71 (d, 1H, J = 10.7 Hz), 2.85 (ddd, 1H, J = 16.9, 5.3, 2.2 Hz), 2.77-2.70 (m, 1H), 2.60 (ddd, 1H, J = 16.9, 10.4, 6.7 Hz), 2.14-1.93 (m, 2H), 1.88-1.79 (m, 1H), 1.72 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.5, 135.8, 131.1, 128.6, 125.4, 122.9, 121.8, 118.9, 115.8, 93.6, 85.0, 78.3, 49.5, 28.3, 28.2, 20.9, 16.8 ppm; IR (thin film) ν 3309, 2934, 1728, 1455, 1370, 1313, 1256, 1222, 1175, 1141, 1119, 1087, 1022, 1002, 964, 911, 853 cm^{-1} .

Purified by chromatography on silica gel (gradient elution: 13:1→4:1 hexanes/EtOAc); white solid (46%): TLC R_f = 0.44 (4:1 hexanes/EtOAc); mp = 89–91 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 4.78 (br s, 1H), 4.60 (s, 2H), 1.92-1.85 (m, 2H), 1.70-1.60 (m, 4H), 1.46-1.36 (m, 1H), 1.42 (s, 3H), 1.16-1.04 (m, 2H), 0.90 (d, 3H, J = 6.6 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 93.4, 78.1, 58.5, 37.5, 31.5, 30.8, 22.8, 21.6 ppm; IR (thin film) ν 3296, 2928, 2861, 1448, 1357, 1186, 1175, 1126, 1090, 1045, 1018, 984, 851 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{18}\text{Cl}_3\text{NO}_3\text{S}$ 337.0073 found 359.9985 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 9:1→4:1 hexanes/EtOAc); pale yellow solid (25%): TLC R_f = 0.52 (2:1 hexanes/EtOAc); mp = 70–75 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.41-7.36 (m, 2H), 7.26-7.22 (m, 1H), 7.10-7.06 (m, 2H), 5.08 (br s, 1H), 4.64 (s, 2H), 2.73 (t, 2H, J = 7.6 Hz), 2.09 (t, 2H, J = 7.6 Hz), 1.47 (s, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.3, 150.5, 129.5, 126.0, 121.4, 93.4, 78.0, 57.5, 36.5, 29.3, 27.3 ppm; IR (thin film) ν 3295, 2976, 1751, 1594, 1493, 1406, 1389, 1374, 1268, 1193, 1165, 1087, 1046, 1004, 957, 855 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{14}\text{H}_{18}\text{Cl}_3\text{NO}_5\text{S}$ 416.9971 found 439.9864 (MNa^+).

Purified by chromatography on silica gel (gradient elution: CH_2Cl_2 →10:1 CH_2Cl_2 /EtOAc); colorless oil (10%): TLC R_f = 0.46 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.49-7.46 (m, 2H), 7.43-7.38 (m, 2H), 7.36-7.31 (m, 1H), 5.59 (br s, 1H), 4.56 (d, 1H, J = 10.8 Hz), 4.54 (d, 1H, J = 10.8 Hz), 4.50 (d, 1H, J = 11.7 Hz), 4.24 (d, 1H, J = 11.7 Hz), 2.08 (s, 3H), 1.88 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.8, 140.6, 128.8, 128.2, 125.8, 93.3, 78.1, 70.2, 61.9, 22.7, 20.8 ppm; IR (thin film) ν 3289, 1743, 1446, 1374, 1239, 1185, 1087, 1045, 1029, 997, 928, 857 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_5\text{S}$ 402.9815 found 425.9710 (MNa^+).

Reaction performed with 1.8 mmol (1 equiv) of cyclohexane. Purified by chromatography on silica gel (19:1 hexanes/EtOAc); white solid (38%): TLC R_f = 0.52 (4:1 hexanes/EtOAc); mp = 79–81 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 4.62 (s, 2H), 4.46 (br d, 1H, J = 7.3 Hz), 3.49–3.39 (m, 1H), 2.12–2.04 (m, 2H), 1.79–1.71 (m, 2H), 1.65–1.56 (m, 1H), 1.41–1.12 (m, 5H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 93.5, 78.1, 54.2, 33.6, 25.0, 24.6 ppm; IR (thin film) ν 3305, 2932, 2857, 1452, 1360, 1182, 1080, 1048, 1022, 998, 933, 890, 855, 757 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_8\text{H}_{14}\text{Cl}_3\text{NO}_3\text{S}$ 308.9760 found 331.9663 (MNa^+).

Purified by chromatography on silica gel (19:1 hexanes/EtOAc); white solid (70%): TLC R_f = 0.50 (4:1 hexanes/EtOAc); mp = 71–73 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.39–7.34 (m, 2H), 7.32–7.28 (m, 3H), 5.35 (br d, 1H, J = 7.8 Hz), 4.56 (q, 1H, J = 7.8 Hz), 4.28 (d, 1H, J = 10.8 Hz), 4.20 (d, 1H, J = 10.8 Hz), 1.80 (dt, 1H, J = 13.7, 7.5 Hz), 1.66 (dt, 1H, J = 13.7, 7.0 Hz), 1.56 (sept, 1H, J = 6.7 Hz), 0.94 (d, 6H, J = 6.6 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.9, 129.0, 128.2, 126.6, 93.2, 77.9, 57.8, 46.1, 24.7, 22.4, 22.2 ppm; IR (thin film) ν 3308, 2959, 1496, 1457, 1427, 1366, 1270, 1181, 1137, 1087, 1050, 1005, 971, 941, 855, 757 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{18}\text{Cl}_3\text{NO}_3\text{S}$ 373.0073 found 395.9977 (MNa^+).

Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (75%): TLC R_f = 0.32 (2:1 hexanes/EtOAc); mp = 89–92 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.32–7.27 (m, 2H), 7.25–7.20 (m, 1H), 7.12–7.09 (m, 2H), 4.82 (br s, 2H), 4.18 (ddd, 1H, J = 6.7, 3.3, 2.6 Hz), 2.55 (ddd, 1H, J = 10.7, 7.3, 2.6 Hz), 1.60 (ddd, 1H, J = 10.7, 7.0, 3.3 Hz), 1.29 (q, 1H, J = 7.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 138.3, 128.6, 126.7, 126.5, 60.6, 22.7, 13.8 ppm; IR (thin film) ν 3379, 3281, 1355, 1176, 1130, 1049, 976, 949, 923, 844, 790 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_9\text{H}_{11}\text{NO}_3\text{S}$ 213.0460 found 236.0361 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 11:1→4:1 hexanes/EtOAc); clear oil (78%, 3:2 diastereomeric mixture): TLC R_f = 0.47, 0.53 (4:1 hexanes/EtOAc); higher R_f diastereomer: ^1H NMR (CDCl_3 , 400 MHz) δ 7.28–7.24 (m, 2H), 7.19–7.14 (m, 1H), 7.08–7.04 (m, 2H), 4.71 (br d, 1H, J = 6.0 Hz), 4.61 (d, 1H, J = 10.8 Hz), 4.58 (d, 1H, J = 10.8 Hz), 3.24–3.14 (m, 1H), 2.09–2.04 (m, 1H), 1.43 (d, 3H, J = 6.6 Hz), 1.29–1.21 (m, 1H), 1.05 (dt, 1H, J = 8.7, 5.3 Hz), 0.98 (dt, 1H, J = 9.0, 5.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.6, 128.5, 126.0, 125.7, 93.5, 78.0, 56.2, 29.1, 22.2, 20.9, 14.4 ppm; IR (thin film) ν 3308, 2932, 1605, 1498, 1429, 1364, 1263, 1182, 1118, 1088, 1002, 853, 753 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_3\text{S}$ 370.9916 found 393.9808 (MNa^+); lower R_f diastereomer: ^1H NMR (CDCl_3 , 400 MHz) δ 7.29–7.25 (m, 2H), 7.20–7.16 (m, 1H), 7.08–7.05 (m, 2H), 4.74 (br s, 1H), 4.65 (s, 2H), 3.27–3.17 (m, 1H), 1.89 (dt, 1H, J = 9.3, 4.7 Hz), 1.43 (d, 3H, J = 6.6 Hz), 1.28–1.21 (m, 1H), 1.17 (dt, 1H, J = 8.9, 5.4 Hz), 1.05 (dt, 1H, J = 8.3, 5.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.5, 128.4, 126.0, 125.7, 93.5, 78.1, 55.9, 28.9, 22.0, 21.1, 14.6 ppm; IR (thin film) ν 3302, 2977, 2929, 1605, 1498, 1431, 1363, 1264, 1181, 1119, 1088, 1046, 1027, 998, 852, 753 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_3\text{S}$ 370.9916 found 393.9818 (MNa^+).

Experimental procedure and characterization data for ^{15}N -trichloroethoxysulfonamide and ^{15}N -amine:

Purified by chromatography on silica gel (19:1 hexanes/EtOAc); white solid (80%): TLC R_f = 0.48 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.38 (m, 2H), 7.31-7.27 (m, 2H), 5.21 (br dd, 1H, J = 6.9 Hz, J_{HN} = 87.4 Hz), 4.70 (quint, 1H, J = 6.9 Hz), 4.33 (d, 1H, J = 10.8 Hz), 4.31 (d, 1H, J = 10.8 Hz), 1.62 (dd, 3H, J = 6.9 Hz, J_{HN} = 3.5), 1.31 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.3, 138.3, 126.0, 125.9, 93.3, 78.0, 54.6 (d, J_{CN} = 5.3 Hz), 34.5, 31.3, 22.7 ppm; IR (thin film) ν 3296, 2965, 1429, 1365, 1269, 1181, 1114, 1086, 1013, 967, 848, 757, 726 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{14}\text{H}_{20}\text{Cl}_3^{15}\text{NO}_3\text{S}$ 388.0199 found 411.0096 (MNa^+).

A solution of alkoxysulfonamide (70 mg, 0.18 mmol) in 3.0 mL of 1:1 MeOH/AcOH was transferred via cannula into a flask containing Zn(Cu) couple (118 mg, 1.8 mmol, 10.0 equiv). Transfer of the starting material was made quantitative with an additional 2.0 mL of 1:1 MeOH/AcOH. The resulting suspension was stirred vigorously for 48 h. After this time, the reaction contents were filtered through a small pad of Celite and the filter cake was rinsed with MeOH. The combined filtrates were concentrated under reduced pressure to afford a white solid, which was redissolved in 7.5 mL of anhydrous methanolic HCl (prepared with 0.56 mL of CH_3COCl in 7.5 mL of MeOH). The solution was heated to 40 $^\circ\text{C}$ for 12 h and then concentrated under reduced pressure. The resulting viscous oil was dissolved in 25 mL of EtOAc and transferred to a separatory funnel containing 5 mL of saturated aqueous K_2CO_3 . The organic phase was collected and the aqueous layer was extracted with 2 x 25 mL of EtOAc. The combined organic extracts were dried over MgSO_4 , filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (7:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$) afforded the desired amine as a white solid (87%): TLC R_f = 0.33 (6.7:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39 (br s, 4H), 4.33 (q, 1H, J = 6.8 Hz), 1.60 (dd, 3H, J = 6.8 Hz, J_{HN} = 2.9 Hz), 1.27 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.9, 138.6, 126.5, 126.0, 51.4 (d, J_{CN} = 4.8 Hz), 22.7 ppm; IR (thin film) ν 3279, 2796, 1608, 1508, 1459, 1362, 1320, 1231, 1111, 1076, 1021, 831 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{12}\text{H}_{19}^{15}\text{N}$ 178.1487 found 179.1566 (M^+).

Experimental procedure and characterization data for Hammett study

A flask containing $\text{H}_2\text{NSO}_3\text{CH}_2\text{CCl}_3$ (27 mg, 0.12 mmol) in 0.6 mL of C_6H_6 was charged with $\text{Rh}_2(\text{esp})_2$ (9 mg, 12 μmol , 0.02 equiv), ethylbenzene (127 mg, 1.2 mmol), and a *p*-substituted ethylbenzene substrate (1.2 mmol). To this bright green mixture was added 0.22 mL of a 0.83 M C_6H_6 solution of $\text{PhI}(\text{O}_2\text{C}^t\text{Bu})_2$ (0.18 mmol, 0.15 equiv) via syringe pump over 3 h. The color of the solution remained deep green throughout the addition of $\text{PhI}(\text{O}_2\text{C}^t\text{Bu})_2$. Following the transfer of oxidant, the solution was stirred at 23 $^\circ\text{C}$ for 1–2 h then concentrated under reduced pressure to an oily green residue. Product ratios were determined by ^1H NMR integration (400 MHz) of the unpurified reaction mixture. Reactions were performed in triplicate and the average product ratio used to generate the Hammett plot.

Purified by chromatography on silica gel (19:1 hexanes/EtOAc); white solid (78%): TLC R_f = 0.48 (4:1 hexanes/EtOAc); mp = 88–90 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.38 (m, 2H), 7.31-7.25 (m, 2H), 4.80 (br d,

1H, $J = 6.9$ Hz), 4.71 (quint, 1H, $J = 6.9$ Hz), 4.37 (s, 2H), 1.63 (d, 3H, $J = 6.9$ Hz), 1.31 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.4, 138.3, 126.0, 125.9, 93.3, 78.0, 54.6, 34.6, 31.3, 22.6 ppm; IR (thin film) ν 3325, 2965, 2870, 1615, 1513, 1433, 1365, 1269, 1182, 1132, 1115, 1083, 1047, 1015, 977, 879, 851, 758 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{14}\text{H}_{20}\text{Cl}_3\text{NO}_3\text{S}$ 387.0229 found 410.0129 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 11:1 $\rightarrow$ 4:1 hexanes/EtOAc); white solid (61%): TLC R_f = 0.38 (4:1 hexanes/EtOAc); mp = 55–57 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.53–7.49 (m, 2H), 7.26–7.22 (m, 2H), 4.83 (br s, 1H), 4.71 (quint, 1H, $J = 6.8$ Hz), 4.50 (d, 1H, $J = 10.8$ Hz), 4.49 (d, 1H, $J = 10.8$ Hz), 1.61 (d, 3H, $J = 6.8$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.4, 132.0, 128.0, 122.1, 93.2, 78.0, 54.3, 22.7 ppm; IR (thin film) ν 3289, 3046, 1489, 1433, 1363, 1181, 1123, 1077, 1012, 977, 854, 759 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{10}\text{H}_{11}\text{BrCl}_3\text{NO}_3\text{S}$ 408.8709 found 431.8605 (MNa^+).

Purified by chromatography on silica gel (gradient elution: 11:1 $\rightarrow$ 4:1 hexanes/EtOAc); clear oil (40%): TLC R_f = 0.40 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.65 (d, 2H, $J = 8.2$ Hz), 7.49 (d, 2H, $J = 8.2$ Hz), 4.95 (br d, 1H, $J = 7.0$ Hz), 4.81 (quint, 1H, $J = 7.0$ Hz), 4.51 (d, 1H, $J = 10.8$ Hz), 4.49 (d, 1H, $J = 10.8$ Hz), 1.64 (d, 3H, $J = 7.0$ Hz) ppm; IR (thin film) ν 3287, 2925, 1622, 1435, 1365, 1327, 1181, 1127, 1103, 1070, 1016, 977, 881, 843, 762 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{11}\text{H}_{11}\text{Cl}_3\text{F}_3\text{NO}_3\text{S}$ 398.9477 found 421.9387 (MNa^+).

Ar = *p*-RC₆H₄Et

<u>R</u>	<u>σ^+</u>	<u>σ_p</u>	<u>product ratio Ar/C₆H₅Et</u>
MeO	−0.78	−0.27	5.0/1.0
^t Bu	−0.26	−0.20	2.3/1.0
Br	0.15	0.23	1.0/1.0
CF ₃	0.61	0.54	1.0/2.3
NO ₂	0.79	0.78	1.0/2.6

Hammet plot fit against σ^+ values

Hammet plot fit against σ_p values

UV-visible spectroscopic data

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 - (5) Thiourea is used to decomplex any remaining $\text{Rh}_2(\text{esp})_2$ catalyst, thereby facilitating product purification.