Oxidative Radical Addition-Cyclization of Sulfonyl Hydrazones with Simple Olefins by Binary Acid Catalysis

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General Experimental

Commercial reagents were used as received, unless otherwise indicated. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-400 and AV-500 spectrometers. ¹H and ¹³C, NMR spectra were measured on a NMR instrument (400 MHz and 500 MHz for ¹H NMR, 100 or 125 MHz for ¹³C NMR). Tetramethylsilane (TMS) served as the internal standard for ¹H NMR, and CDCl₃ served as the internal standard for ¹H NMR, and CDCl₃ served as the internal standard for ¹³C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d= doublet; t = triplet; q = quartet; m = multiplet; br = broad. HRMS was recorded on a commercial apparatus (ESI).

Sulfonyl hydrazones 2 were prepared according to literature procedure.^[1] Simple olefins (**3a-j**, **3l**) and ketones (**6a-f**) were received from commercial sources without further purification, except for 2-vinylthiophene **3k**, which was prepare according to the literature procedure.^[2] Sulfonyl hydrazines **5a**, **b** were received from commercial sources without further purification, **5c**, **d** were prepared according to the literature procedure.^[3] Solvents were freshly dried according to *the Purification Handbook Purification of Laboratory Chemicals before using*.

Oxidative Radical [4+2] Cycloaddition

Table S1. Influence of reaction parameters on the catalytic oxidative [4+2]cycloaddition of N-tosylhydrazones 2a and styrene 3a.

Ts N N H F Ph 2a	LA (5 mol %), 1 (5 mol %) Ph l ₂ (5 mol %), TBHP (4 equ 3a solvent, rt, t	iv) Ph 4a		
entry	Lewis acid/1	solvent	<i>t</i> (h)	yield (%) ^b
1	Cu(CH ₃ CN) ₄ BF ₄	CH3CN	6	63
2	CuX (X = Cl, Br, or I)	CH ₃ CN	6	< 20
3	Cu(OTf) ₂	CH ₃ CN	6	9
4	In(OTf) ₃	CH ₃ CN	6	1
5	Mg(OTf) ₂	CH ₃ CN	6	3
6	Zn(OTf) ₂	CH ₃ CN	6	3
7	FeCl ₃	CH ₃ CN	6	6
8	FeBr ₂	CH ₃ CN	6	NR
9 ^d	Cu(CH ₃ CN) ₄ BF ₄	CH ₃ CN	6	32

^{*a*} General conditions: Cu(CH₃CN)₄BF₄ (5 mol %), **1** (5 mol %), I₂ (5 mol %), TBHP (0.8 mmol), **2a** (0.2 mmol), and **3a** (1.0 mmol) at room temperature. ^{*b*} Determined by ¹H NMR analysis with an internal standard, 1,3,5-trimethyloxylbenzene. ^{*c*} **1** (10 mol%). ^{*d*} TBHP (0.4 mmol). Tf = Trifluoro-methanesulfonate. NR = No reaction



General procedure for oxidative [4+2] cycloaddition of sulfonyl hydrazones 2a with simple olefins 3: To an oven-dried reaction tube was added Cu(CH₃CN)₄BF₄ (0.01 mmol, 5 mol%) and diphenyl phosphate 1 (0.01 mmol, 5 mol%). Distilled anhydrous CH₃CN (0.5 mL) was added. After stirring for 0.5 h, sulfonyl hydrazine 2a (0.2 mmol, in 0.4 mL CH₃CN), simple olefin 3 (1.0 mmol), I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. The mixture was stirred for 12-24 hours at room temperature. Purification of mixture by column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 to 10:1 as eluent) gave 4a-l, 4u.



67.9 mg, yield: 87%; ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.72 (m, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.39-7.33 (m, 3H), 7.19-7.13 (m, 5H), 6.98-6.96 (m, 2H), 5.64 (s, 1H), 2.61-2.52 (m, 1H), 2.36 (s, 3H), 2.17-2.04 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.3, 143.5, 140.3, 137.0, 136.0, 129.2, 128.5, 128.4, 128.1, 127.3, 126.1, 125.3, 55.2, 24.9, 21.6, 17.9 ppm; IR (KBr, cm⁻¹): 3062, 3029, 2929, 1598, 1495, 1448, 1356, 894, 754, 695, 672; HRMS (ESI) calcd for C₂₃H₂₃N₂O₂S⁺ (M+H)⁺ 391.1475, found 391.1469.



49.7 mg, yield: 59%; ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.72 (m, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.39-7.34 (m, 3H), 7.17 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 5.59 (s, 1H), 3.75 (s, 3H), 2.61-2.56 (m, 1H), 2.37 (s, 3H), 2.19-2.04 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 158.8, 147.2, 143.4, 137.0, 136.0, 132.5, 129.1, 128.4, 128.1, 127.3, 125.3, 113.8, 55.3, 54.7, 25.1, 21.6, 17.9

ppm; IR (KBr, cm⁻¹): 3067, 2956, 2929, 2836, 1612, 1356, 1251, 1095, 897, 758, 694, 578, 548; HRMS (ESI) calcd for C₂₄H₂₅N₂O₃S⁺ (M+H)⁺421.1580, found 421.1575.



61.9 mg, yield: 77%; ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.68 (m, 4H), 7.38-7.33 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 5.60 (s, 1H), 2.60-2.54 (m, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 2.17-2.02 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.2, 143.5, 137.4, 137.1, 137.0, 136.0, 129.2, 129.1, 128.4, 128.1, 126.0, 125.3, 55.0, 24.9, 21.6, 21.0, 17.9 ppm; IR (KBr, cm⁻¹): 3056, 3029, 2924, 2862, 1597, 1514, 1447, 987, 938, 898, 757, 694; HRMS (ESI) calcd for C₂₄H₂₅N₂O₂S⁺ (M+H)⁺ 405.1631, found 405.1624.



70.9 mg, yield: 84%; ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.69 (m, 4H), 7.39-7.35 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 2.63-2.54 (m, 1H), 2.38 (s, 3H), 2.14-2.03 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.4, 143.8,138.9, 136.8, 135.8, 133.2, 129.3, 128.6, 128.5, 128.0, 127.5, 125.3, 54.6, 24.8, 21.6, 17.8 ppm; IR (KBr, cm⁻¹): 3065, 2929, 2859, 1597, 1492, 1358, 1171, 1094, 1014, 939, 898, 756, 681, 575; HRMS (ESI) calcd for C₂₃H₂₂ClN₂O₂S⁺ (M+H)⁺ 425.1085, found 425.1077.

74.5 mg, yield: 80%; ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.69 (m, 4H), 7.39-7.35 (m, 3H), 7.29 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.59 (s, 1H), 2.63-2.54 (m, 1H), 2.39 (s, 3H), 2.14-2.03 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.4, 143.8, 139.5, 136.8, 135.8, 131.6, 129.3, 128.5, 128.0, 127.9, 125.3, 121.3, 54.7, 24.7, 21.6, 17.8 ppm; IR (KBr, cm⁻¹): 3065, 2929, 2862, 1596, 1488,

1010, 939, 898, 771, 693, 644; HRMS (ESI) calcd $forC_{23}H_{22}BrN_2O_2S^+$ (M+H)⁺ 469.0580, found 469.0572.



78.5 mg, yield: 84%; ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.68 (m, 4H), 7.39-7.37 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.07-7.02 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 5.60 (d, *J* = 3.2 Hz, 1H), 2.65-2.55 (m, 1H), 2.39 (s, 3H), 2.17-2.06 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.4, 143.9, 142.5, 136.9, 135.7, 130.6, 130.1, 129.3, 129.3, 129.1, 128.4, 128.0, 125.4, 124.9, 122.6, 54.6, 24.8, 21.6, 17.8 ppm; IR (KBr, cm⁻¹): 3065, 2924, 2854, 1595, 1093, 940, 899, 776, 756, 677, 583; HRMS (ESI) calcd for C₂₃H₂₂BrN₂O₂S⁺ (M+H)⁺ 469.0580, found 469.0578.



42.5 mg, yield: 50%; ¹H NMR (400 MHz, CDCl₃): δ 7.77-7.73 (m, 4H), 7.40-7.35 (m, 4H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18-7.13 (m, 1H), 6.96-6.92 (m, 1H), 6.76-6.74 (m, 1H), 5.97-5.96 (m, 1H), 2.64-2.59 (m, 1H), 2.39 (s, 3H), 2.35-2.30 (m, 1H), 2.09-1.92 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 143.7, 137.6, 136.8, 135.9, 131.1, 130.0, 129.3, 129.3, 128.7, 128.4, 128.2, 128.1, 126.7, 125.3, 52.9, 22.2, 21.6, 17.9 ppm; IR (KBr, cm⁻¹): 3065, 2926, 2865, 1445, 1359, 1095, 941, 898, 754, 694, 579; HRMS (ESI) calcd for C₂₃H₂₂ClN₂O₂S⁺ (M+H)⁺ 425.1085, found 425.1079.



76.3 mg, yield: 91%; ¹H NMR (400 MHz, CDCl₃): δ 7.78-7.75 (m, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.41-7.36 (m, 3H), 7.13 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.7 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.13 (s, 1H), 5.78 (s, 1H), 2.65-2.60 (m, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 2.22-2.03 (m, 3H), 1.85 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 143.3, 137.9, 137.2, 136.0, 135.1, 130.7, 129.1, 129.0, 128.4, 128.1, 128.0, 127.2, 125.4, 52.2, 22.9, 21.5, 20.9, 18.6, 17.7 ppm; IR (KBr, cm⁻¹): 3026, 2924, 2868,

1597, 1446, 944, 808, 762, 693, 645, 582; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_2S^+$ (M+H)⁺ 419.1788, found 419.1782.

75.0 mg, yield: 93%; ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, J = 8.1 Hz, 2H), 7.69-7.67 (m, 2H), 7.38-7.34 (m, 6H), 7.28-7.26 (m, 4H), 2.57-2.49 (m,1H), 2.40 (s, 3H), 2.38-2.29 (m, 1H), 2.16-2.09 (m, 1H), 2.03 (s, 3H), 2.01-1.95 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 145.6, 145.6, 143.4, 137.4, 137.0, 129.0, 129.0, 128.6, 128.4, 128.4, 127.0, 125.3, 125.3, 62.4, 37.6, 25.0, 21.6, 20.2 ppm; IR (KBr, cm⁻¹): 3062, 2924, 2854, 1597, 1494, 1446, 1087, 1037, 863, 781, 695, 565; HRMS (ESI) calcd for C₂₄H₂₅N₂O₂S⁺ (M+H)⁺ 405.1631, found 405.1626.



69.9 mg, yield: 99%; ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.2 Hz, 2H), 7.69-7.66 (m, 2H), 7.37-7.32 (m, 5H), 5.92-5.87 (m, 2H), 4.76 (d, J = 7.7 Hz, 1H), 2.69-2.63 (m, 2H), 2.44-2.37 (m, 4H), 2.19-2.10 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 154.2, 144.0, 136.4, 134.2, 132.7, 131.8, 129.5, 129.4, 128.8, 128.4, 125.8, 64.0, 38.6, 33.6, 27.3, 21.6 ppm; IR (KBr, cm⁻¹): 3067, 2922, 2851, 1598, 1095, 813, 694, 634, 583, 555, 538; HRMS (ESI) calcd for C₂₀H₂₁N₂O₂S⁺ (M+H)⁺ 353.1318, found 353.1313.



48.8 mg, yield: 62%; ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.72 (m, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.39-7.36 (m, 3H), 7.12 (d, J = 8.1 Hz, 2H), 7.06-7.05 (m, 1H), 6.79-6.77 (m, 1H), 6.75-6.74 (m, 1H), 5.86 (t, J = 3.5 Hz, 1H), 2.72-2.65 (m, 1H), 2.52-2.45 (m, 1H), 2.34 (s, 3H), 2.23-2.19 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 143.4, 141.8, 136.9, 135.4, 129.3, 129.0, 128.4, 128.0, 126.3, 126.1, 125.4, 124.8, 51.1, 25.4, 21.6, 18.5 ppm; IR (KBr, cm⁻¹): 3065, 2924, 2854, 1597, 1446, 937,

891, 757, 693, 670, 561; HRMS (ESI) calcd for $C_{21}H_{21}N_2O_2S_2^+$ (M+H)⁺ 397.1039, found 397.1034.



The compound 4u was used, when a Hammett plot was constructed to probe the electronic effects of the substrate alkene on the reaction rate (see, Figure 1D). 43.8 mg, yield: 53%; ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.71 (m, 4H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.38-7.37 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.67 (s, 1H), 2.62 (d, *J* = 17.4 Hz, 1H), 2.40 (s, 3H), 2.20-1.95 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.5, 145.8, 144.1, 136.6, 135.6, 132.4, 129.5, 129.4, 128.5, 128.0, 126.9, 125.3, 118.5, 111.4, 54.8, 24.5, 21.6, 17.7 ppm; IR (KBr, cm⁻¹): 3065, 2928, 2856, 2228, 1608, 1447, 987, 940, 844, 757, 694; HRMS (ESI) calcd for C₂₄H₂₂N₃O₂S⁺ (M+H)⁺ 416.1427, found 416.1435.



In a 30 ml stainless steel reactor with a magnetic stirring bar was charged with Cu(MeCN)₄BF₄ (5 mol%, 0.01 mmol) and diphenyl phosphate **1** (5 mol%, 0.01 mmol) in 0.5 mL CH₃CN, stirred for 0.5 h. Then, sulfonyl hydrazone **2a** (0.2 mmol in 0.4 mL CH₃CN), I₂ (5 mol%, 2.54 mg in 0.1 mL CH₃CN), TBHP (0.8 mmol in decane) were added successively to the reaction mixture. Next, the reaction mixture was charged with 8 atm propene **3l** atmosphere and stirred at room temperature for 24 h. After carefully releasing the propene, the mixture was evaporated and loaded on a silica column to give the final product **4l**. 41.3 mg, yield: 63%; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.73-7.70 (m, 2H), 7.38-7.35 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.61-4.58 (m, 1H), 2.65-2.59 (m, 1H), 2.48-2.41 (m, 1H), 2.39 (s, 3H), 1.91-1.88 (m, 2H), 1.15 (d, *J* = 6.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.2, 143.5,

137.0, 136.3, 129.4, 129.1, 128.3, 128.1, 125.2, 47.3, 24.3, 21.6, 18.2, 17.4 ppm; IR (KBr, cm⁻¹): 3065, 2930, 2870, 1597, 1446, 1234, 912, 836, 762, 694, 592; HRMS (ESI) calcd for $C_{18}H_{21}N_2O_2S^+$ (M+H)⁺ 329.1318, found 329.1314.



General procedure for one-pot oxidative [4+2] cvcloaddition of sulfonyl hydrazides 5 and ketones 6 with simple olefins 3: To an oven-dried reaction tube was added Cu(CH₃CN)₄BF₄ (0.01 mmol, 5 mol%) and diphenyl phosphate 1 (0.01 mmol, 5 mol%). Distilled anhydrous CH₃CN (0.5 mL) was added. After stirring for 0.5 h, sulfronyl hydrazide 5 (0.2 mmol, in 0.2 mL CH₃CN), ketone 6 (0.22 mmol, in 0.2 mL CH₃CN) were added to the reaction mixture. After stirring for 0.5 h, simple olefin 3 (1.0 mmol), I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. The mixture was stirred for 24-48 hours at room temperature. Purification of mixture by column chromatography on silica gel (petroleum ether:ethyl acetate = 20:1 to 10:1 as eluent) gave **4a**, **m-t**.



54.8 mg, yield: 68%; ¹H NMR (400 MHz, CDCl₃): δ 7.68-7.62 (m, 4H), 7.18-7.12 (m, 7H), 6.96 (d, J = 6.5 Hz, 2H), 5.63 (s, 1H), 2.60-2.51 (m, 1H), 2.36 (s, 6H), 2.15-2.05 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.4, 143.4, 140.3, 139.3, 136.0, 134.3, 129.1, 129.1, 128.4, 128.1, 127.3, 126.1, 125.2, 55.2, 24.9, 21.5, 21.3, 17.8 ppm; IR (KBr, cm⁻¹): 3062, 3029, 2924, 2862, 1598, 1495, 1451, 938, 895, 815, 749, 702, 548; HRMS (ESI) calcd for C₂₄H₂₅N₂O₂S⁺ (M+H)⁺ 405.1631, found 405.1626.

55.3 mg, yield: 65%; ¹H NMR (400 MHz, CDCl₃): δ 7.67-7.64 (m, 4H), 7.33 (d, J = 8.6 Hz, 2H), 7.20-7.14 (m, 5H), 6.96-6.94 (m, 2H), 5.64 (d, J = 2.8 Hz, 1H), 2.57-2.46 (m, 1H), 2.37 (s, 3H), 2.18-2.01 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 146.1, 143.7, 140.2, 135.9, 135.5, 135.1, 129.2, 128.6, 128.5, 128.0, 127.4, 126.5, 126.0, 55.2, 24.8, 21.6, 17.8 ppm; IR (KBr, cm⁻¹): 3065, 2926, 2856, 1600, 1493,

1356, 1012, 939, 895, 814, 707, 664, 569; HRMS (ESI) calcd for $C_{23}H_{22}CIN_2O_2S^+$ (M+H)⁺ 425.1085, found 425.1079.



56.8 mg, yield: 61%; ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.20-7.15 (m, 5H), 6.96-6.94 (m, 2H), 5.65 (d, *J* = 3.2 Hz, 1H), 2.57-2.48 (m, 1H), 2.38 (s, 3H), 2.18-2.06 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 146.1, 143.7, 140.1, 135.9, 135.9, 131.5, 129.2, 128.5, 128.1, 127.4, 126.8, 126.0, 123.4, 55.2, 24.8, 21.6, 17.7 ppm; IR (KBr, cm⁻¹): 3065, 2926, 2856, 1599, 1490, 1007, 939, 895, 787, 688, 661, 564; HRMS (ESI) calcd for C₂₃H₂₂BrN₂O₂S⁺ (M+H)⁺ 469.0580, found 469.0573.



54.2 mg, yield: 58%; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25-7.15 (m, 6H), 6.96-6.94 (m, 2H), 5.65 (d, *J* = 3.3 Hz, 1H), 2.57-2.47 (m, 1H), 2.38 (s, 3H), 2.18-2.05 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 145.7, 143.7, 140.1, 139.1, 135.8, 131.9, 129.9, 129.3, 128.5, 128.4, 128.1, 127.4, 126.0, 123.8, 122.7, 55.2, 24.8, 21.6, 17.9 ppm; IR (KBr, cm⁻¹): 3062, 2929, 2854, 1597, 1451, 1101, 995, 940, 894, 801, 697, 589; HRMS (ESI) calcd for C₂₃H₂₂BrN₂O₂S⁺ (M+H)⁺ 469.0580, found 469.0573.



64.4 mg, yield: 69%; ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.32-7.13 (m, 10H), 5.60 (d, *J* = 1.4 Hz, 1H), 2.41 (s, 3H), 2.37-2.31 (m, 1H), 2.26-2.17 (m, 1H), 2.11-2.06 (m, 1H), 1.97-1.89 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 151.1, 143.6, 140.7, 140.0, 136.0, 133.1, 130.3, 129.9, 129.3, 128.5, 128.0, 127.4, 127.4, 126.1, 121.5, 55.5, 24.3, 21.9, 21.6 ppm; IR (KBr, cm⁻¹):

3062, 2926, 2859, 1597, 1494, 1451, 987, 936, 891, 789, 703, 584; HRMS (ESI) calcd for $C_{23}H_{22}BrN_2O_2S^+(M+H)^+$ 469.0580, found 469.0574.

54.2 mg, yield: 72%; ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.78 (m, 2H), 7.75-7.73 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.39-7.36 (m, 5H), 7.19-7.13 (m, 3H), 6.95 (d, *J* = 6.6 Hz, 2HHHH), 5.66 (d, *J* = 2.3 Hz, 1H), 2.64-2.56 (m, 1H), 2.18-2.11 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.5, 140.1, 138.9, 137.0, 132.6, 129.2, 128.5, 128.5, 128.4, 128.0, 127.3, 126.0, 125.3, 55.2, 24.9, 17.9 ppm; IR (KBr, cm⁻¹): 3065, 2924, 2854, 1447, 939, 894, 792, 754, 721, 689, 654, 555; HRMS (ESI) calcd for C₂₂H₂₁N₂O₂S⁺ (M+H)⁺ 377.1318, found 377.1314.



45.3 mg, yield: 50%; ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.72 (m, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.39-7.38 (m, 3H), 7.21-7.14 (m, 3H), 6.92 (d, J = 7.0 Hz, 2HHHH), 5.63 (s, 1H), 2.68-2.58 (m, 1H), 2.24-2.14 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.0, 139.9, 137.8, 136.8, 131.7, 129.6, 129.4, 128.6, 128.5, 127.7, 127.5, 126.1, 125.3, 55.3, 25.0, 17.9 ppm; IR (KBr, cm⁻¹): 3065, 2923, 2854, 1574, 1361, 1094, 792, 739, 700, 599, 554; HRMS (ESI) calcd for C₂₂H₂₀BrN₂O₂S⁺ (M+H)⁺ 455.0423, found 455.0417.



29.0 mg, yield: 46%; ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.78 (m, 2H), 7.43-7.39 (m, 3H), 7.34-7.26 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 2H), 5.60 (d, *J* = 3.1 Hz, 1H), 3.08 (s, 3H), 2.76-2.65 (m, 1H), 2.32-2.22 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.5, 140.8, 136.8, 129.4, 128.8, 128.5, 127.7, 125.9, 125.4, 54.4, 39.3, 25.1, 18.1

ppm; IR (KBr, cm⁻¹): 3062, 3029, 2929, 1495, 1448, 1242, 1069, 939, 894, 796, 695; HRMS (ESI) calcd for $C_{17}H_{19}N_2O_2S^+(M+H)^+$ 315.1162, found 315.1159.



Transformation of Product 4a: To LiAlH₄ (3.0 equiv, 22.8 mg, 0.6 mmol) solution in THF (2 mL) was added tetrahydropyridazine **4a** (78.0 mg, 0.2 mmol) at room temperature. After refluxing for 4 h, the reaction mixture was quenched by cold water, then extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na₂SO₄), evaporated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether:ethyl acetate = 10:1 as eluent) to afford the desired product **8** as a white solid.

46.5 mg, yield: 98%; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, J = 7.8 Hz, 2H), 7.41-7.27 (m, 8H), 5.81 (br, 1H), 4.17-4.14 (m, 1H), 2.84-2.75 (m, 1H), 2.71-2.64 (m, 1H), 2.26-2.13 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 143.2, 142.1, 138.6, 128.7, 128.3, 127.9, 127.8, 127.0, 124.5, 56.4, 28.6, 23.4 ppm; IR (KBr, cm⁻¹): 3055, 3031, 2926, 2854, 1681, 1581, 1494, 1408, 1126, 867, 589; HRMS (ESI) calcd for C₁₆H₁₇N₂⁺ (M+H)⁺ 237.1386, found 237.1383.



Mechanistic Studies of Binary-acid Catalysis

Figure S1. ESI-MS Analysis of Binary acid Cu(CH₃CN)₄BF₄/1.



the complexes of *N*-tosylhydrazone 2a, Cu(CH₃CN)₄BF₄ and diphenyl phosphate 1 (1:1:1).

Weak but noticeable shift of the hydrazine signals were observed, in particular, shift of hydrazine N-H was clearly noted.

Ts N N Ph 2a	Cu(C Ph 🔨 [l] (5 r 3a	CH ₃ CN) ₄ BF ₄ (5 mol %) <u>1</u> (5 mol %) nol %), TBHP (4 equiv) CH ₃ CN, rt, 6h	Ts N ^N h Ph 4a	
Entry		I source		Yield [%] ^[b]
1		None		NR
2		I ₂		63
3		KI		NR
4		n-Bu ₄ NI		NR
5		NIS		57

Table S2. Results of different iodine source^[a]

[a] Standard reaction condition: Cu(CH₃CN)₄BF₄ (5 mol %), **1** (5 mol %), I source (5mol %), TBHP (0.8 mmol), **2a** (0.2 mmol), and **3a** (1.0 mmol) at room temperature in CH₃CN for 6 h. [b] Determined by ¹H NMR analysis with an internal standard, 1,3,5-trimethyloxylbenzene.



Figure S3. Reaction conditions: (A) 2a (0.1 mmol) in CD₃CN; (B) Cu(CH₃CN)₄BF₄ (5 mol%), 1 (5 mol%), 2a (0.1 mmol) and I₂ (0.1 mmol) in CD₃CN, stirring at 1h; (C) Adding TBHP (4.0 equiv) in B' mixture; (D) Cu(CH₃CN)₄BF₄ (5 mol%), 1 (5 mol%), 2a (0.1 mmol), (n-Bu)₄NI₂ (0.1 mmol) and TBHP (0.4 equiv) in CD₃CN

Control experiment



Procedure A: To an oven-dried reaction tube was added $Cu(CH_3CN)_4BF_4$ (5 mol%) and diphenyl phosphate **1** (5 mol%). Anhydrous CD₃CN (0.3 mL) was added. After stirring for 0.5 h, sulfonyl hydrazine **2a** (0.1 mmol), I₂ (50 mol%, in 0.2 mL CD₃CN), and TBHP (0.4 mmol in decane) were added successively to the stirring reaction mixture. The mixture was stirred for 0.5-3 hours at room temperature. The reaction progress was monitored by ¹H NMR (Scheme 4B).



Procedure B: To an oven-dried reaction tube was added hydrazine **2a** (0.1 mmol). Anhydrous CH₃CN (0.2 mL) was added. And then I₂ (50 mol%, in 0.2 mL CH₃CN), and TBHP (0.4 mmol in decane) were added successively to the stirring reaction mixture. After stirring for 3 hours at room temperature, Cu(CH₃CN)₄BF₄ (5 mol%) and diphenyl phosphate **1** (5 mol%, in 0.1 mL) was added to the mixture. Anhydrous CD₃CN (0.4 mL) was added. And then styrene **3a** (0.5 mmol) was added. The reaction progress was monitored by ¹H NMR (Scheme 4C), and yield was determined by ¹H NMR analysis with an internal standard (1,3,5-trimethyloxyl benzene).

Kinetics study: iodination reaction



Procedure A for catalyst-free iodination reaction of sulfonyl hydrazine 2a, monitored by *in-situ* **IR:** To an oven-dried reaction tube was added hydrazine **2a** (0.2 mmol). Anhydrous CH₃CN (0.8 mL) was added. And then I₂ (100 mol%, in 0.2 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. At the same time, transformation of **C-2a** was also tracked by in situ IR in this reaction (see Figure 1A). The reaction progress was monitored by in-situ IR at 1269 cm⁻¹ (Figure S4).



Figure S4. Representative 3D stacking plots of spectra obtained by React-IR



Procedure B for iodination reaction of sulfonyl hydrazine 2a catalyzed by Cu(CH₃CN)₄BF₄, monitored by *in-situ* **IR:** To an oven-dried reaction tube was added Cu(CH₃CN)₄BF₄ (5 mol%) and hydrazine **2a** (0.2 mmol). Anhydrous CH₃CN (0.8 mL) was added. And then I₂ (100 mol%, in 0.2 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. At the same time, transformation of **C-2a** was also tracked by in situ IR in this reaction (see Figure 1A). The reaction progress was monitored by in-situ IR at 1269 cm⁻¹ (Figure S4).



Procedure C for iodination reaction of sulfonyl hydrazine 2a catalyzed by binary-acids, monitored by *in-situ* **IR:** To an oven-dried reaction tube was added $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%) and diphenyl phosphate **1** (0.01 mmol, 5 mol%). Distilled anhydrous CH₃CN (0.6 mL) was added. After stirring for 0.5 h, sulfonyl hydrazine **2a** (0.2 mmol, in 0.2 mL CH₃CN), I₂ (100 mol%, in 0.2 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. At the same time, transformation of C-2a was also tracked by in situ IR in this reaction (see Figure 1A). The reaction progress was monitored by in-situ IR at 1269 cm⁻¹ (Figure S4).

Kinetics study: oxidative [4+2] cylcoaddition reaction



Procedure A for catalyst-free oxidative [4+2] reaction of sulfonyl hydrazine 2a and styrene 3a, monitored by *in-situ* **IR:** To an oven-dried reaction tube was added hydrazine **2a** (0.2 mmol). Anhydrous CH₃CN (0.9 mL) was added. And then styrene **3a** (1.0 mmol), I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. At the same time, transformation of **4a** was also tracked by in situ IR in this reaction (see Figure 1B). The reaction progress was monitored by in-situ IR at 895 cm⁻¹ (Figure S5).



Procedure B for oxidative [4+2] reaction of sulfonyl hydrazine 2a and styrene 3a, catalyzed by Cu(CH₃CN)₄BF₄, monitored by *in-situ* **IR:** To an oven-dried reaction tube was added Cu(CH₃CN)₄BF₄ (5 mol%) and hydrazine **2a** (0.2 mmol). Anhydrous CH₃CN (0.9 mL) was added. And then styrene **3a**, I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. At the same time, transformation of **4a** was also tracked by in situ IR in this reaction (see Figure 1B). The reaction progress was monitored by in-situ IR at 895 cm⁻¹ (Figure S5).



Procedure C for oxidative [4+2] reaction of sulfonyl hydrazine 2a and styrene 3a, catalyzed by Cu(CH₃CN)₄BF₄/1, monitored by *in-situ* **IR:** To an oven-dried reaction tube was added Cu(CH₃CN)₄BF₄ (0.01 mmol, 5 mol%) and diphenyl phosphate **1** (0.01 mmol, 5 mol%). Distilled anhydrous CH₃CN (0.8 mL) was added. After stirring for 0.5 h, sulfonyl hydrazine **2a** (0.2 mmol, in 0.1 mL CH₃CN), styrene **3a** (1.0 mmol), I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. At the same time, transformation of **4a** was also tracked by in situ IR in this reaction (see Figure 1B). The reaction progress was monitored by in-situ IR at 895 cm⁻¹ (Figure S5).



Figure S5. Representative 3D stacking plots of spectra obtained by React-IR

Procedure D for oxidative [4+2] reaction of sulfonyl hydrazine 2a and styrene 3a, catalyzed by Cu(CH₃CN)₄BF₄/1, monitored by *continuous* ¹*H NMR*: To be added Cu(CH₃CN)₄BF₄ (0.005 mmol, 5 mol%) and diphenyl phosphate **1** (0.005 mmol, 5 mol%), anhydrous CD₃CN (0.2 mL) was added. After stirring for 0.5 h, binary-acids, sulfonyl hydrazine **2a** (0.1 mmol, in 0.1 mL CD₃CN), styrene **3a** (1.0 mmol), I₂ (50 mol%, in 0.4 mL CD₃CN), and TBHP (0.4 mmol in decane) were added successively to the NMR tube. At the same time, transformation of **4a** and **C-2a** was also tracked by continuous ¹H NMR in this reaction (see Figure 1C). The reaction progress was monitored by continuous ¹H NMR at 4.13 ppm (adduct **C-2a** generated) and 5.60 ppm (adduct **4a**) cm⁻¹ (see some selected examples in Figure S6).



Figure S6. Selected ¹H NMR spectra monitored the oxidative [4+2] cycloaddition

Radical trapping experiment



<u>General procedure:</u> To an oven-dried reaction tube was added $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%) and diphenyl phosphate **1** (0.01 mmol, 5 mol%). Distilled anhydrous CH₃CN (0.5 mL) was added. After stirring for 0.5 h, sulfonyl hydrazine **2a** (0.2 mmol, in 0.4 mL CH₃CN), styrene **3a** (1.0 mmol), TEMPO (3.0 mmol), I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. The mixture was stirred for 15 hours at room temperature, and no product **4a** was obtained.

Radical clock test



General procedure: To an oven-dried reaction tube was added Cu(CH₃CN)₄BF₄ (0.01 mmol, 5 mol%) and diphenyl phosphate **1** (0.01 mmol, 5 mol%). Distilled anhydrous CH₃CN (0.5 mL) was added. After stirring for 0.5 h, sulfonyl hydrazine **2a** (0.2 mmol, in 0.4 mL CH₃CN), vinylcyclopropane (1.0 mmol), I₂ (5 mol%, in 0.1 mL CH₃CN), and TBHP (0.8 mmol in decane) were added successively to the stirring reaction mixture. The mixture was stirred for 12 hours at room temperature, and product **9** was obtained, which was a known compound.⁴ 22.3 mg, yield: 50%, *E/Z* = 82/18. ¹H NMR (400 MHz, CDCl₃, major-*E*): δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1, 2H), 5.59-5.52 (m, 1H), 5.43-5.36 (m, 1H), 3.72 (d, *J* = 7.3 Hz, 2H), 2.44 (s, 3H), 2.05-1.98 (m, 2 H), 0.91 (t, *J* = 7.5 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 144.5, 143.0, 135.5, 129.6, 128.6, 115.2, 60.2, 25.6, 21.6, 12.9 ppm.

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NMR spectrum

























| 150

ppm (t1)

Γ

| 100

50

0





























































