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REGULAR ARTICLE

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Rhodium-catalyzed synthesis of C4-chalcogenoalkylated oxindoles *via* Sommelet-Hauser type rearrangement of 3-diazoindolin-2-ones

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Abstract. Efficient rhodium-catalyzed Sommelet-Hauser type rearrangement of 3-diazoindolin-2-ones with α-thioesters has been accomplished for the synthesis of C4-thioalkylated oxindoles. The developed reaction offers the selective functionalization of C4-position of oxindole *via* generation of S-ylide and [2, 3]-sigmatropic rearrangement and allows access to diverse C4-thioalkylated oxindoles in good to excellent yield. Furthermore, the method was successfully extended to the synthesis C4-selenoalkylated oxindoles employing the corresponding α-selenoester.

Keywords. α-Thioesters; α-selenoesters; 3-diazoindolin-2-ones; S-ylide; Se-ylide; oxindoles; Sommelet-Hauser rearrangement.

1. Introduction

Substituted oxindoles have drawn special attention in synthetic organic and medicinal chemistry due to their widespread biological activity.[1] For instance, the drug molecule having oxindoles skeletons exhibits extensive bio-activities,[2] which include anti-HIV, protein kinase inhibitors,[3] anti-bacterial agents, etc.[4] Some of the representative examples of therapeutically important oxindole containing molecules are shown in Figure 1. In addition, aryl sulfonanilide substituted oxindole hybrid also exhibits enhanced activity and inhibits the growth of cancer cells by partial depletion of intracellular calcium stores and phosphorylation of elF2α.[5] Similarly, C4-substituted oxindole derivatives also show diverse biological activities.[6] Due to their biological importance, during past decades, numerous methods for the synthesis of oxindoles have been developed.[7] Most of the known methods are limited to the construction of pyrrolidone ring system of oxindole from functionalized arene and selective functionalization of oxindole is rather limited.[8] Hence, the development of a practical and general method for the selective synthesis of substituted oxindole, which will minimize the number of steps and increases complexity and diversity, is an attractive subject in organic synthesis.[9]

On the other hand, diazocarbonyl compounds, a vital coupling partner in organic synthesis for the construction of various complex molecule,[10] in the presence of metal catalyst generates important reactive intermediate, *viz.,* metal carbeniods. This intermediate undergoes various useful transformations including insertion into C-H[11] and X–H/C bond,[12] ylide generation-*cum*-functionalization,[13] etc. Among these transformations, ylide generation from diazo compound and Lewis base, in particular, sulfides,[14] followed by either [2, 3]/[1, 2]-sigmatrophic rearrangement or Sommelet-Hauser type rearrangement[15] affords an interesting possibility for the construction of diverse sulfur-based building blocks and heterocycles.[16] Although [2, 3]/[1, 2]-sigmatrophic rearrangements of sulfur ylides have been extensively studied, Sommelet-Hauser type rearrangement of sulfur ylides is rather limited. For instance, rhodium-catalyzed Sommlet-Hauser type rearrangement of sulfur ylide was disclosed by Wang and coworkers,[17] wherein the reaction of aryl-substituted diazoacetates with ethyl phenylthioacetate in the presence of $Rh_2(O_2CCF_3)_4$ affords *ortho*-substituted arylacetates

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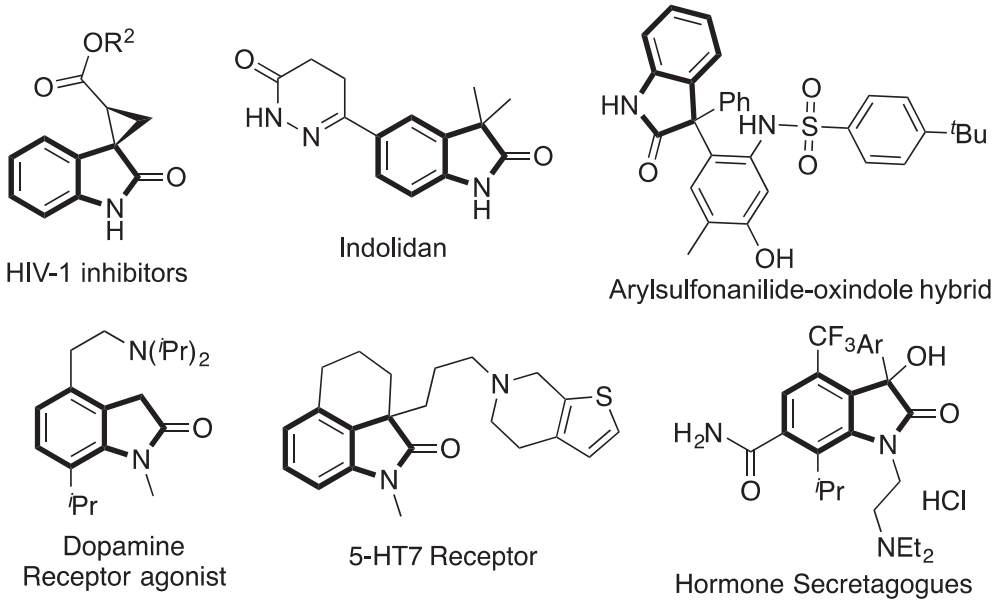


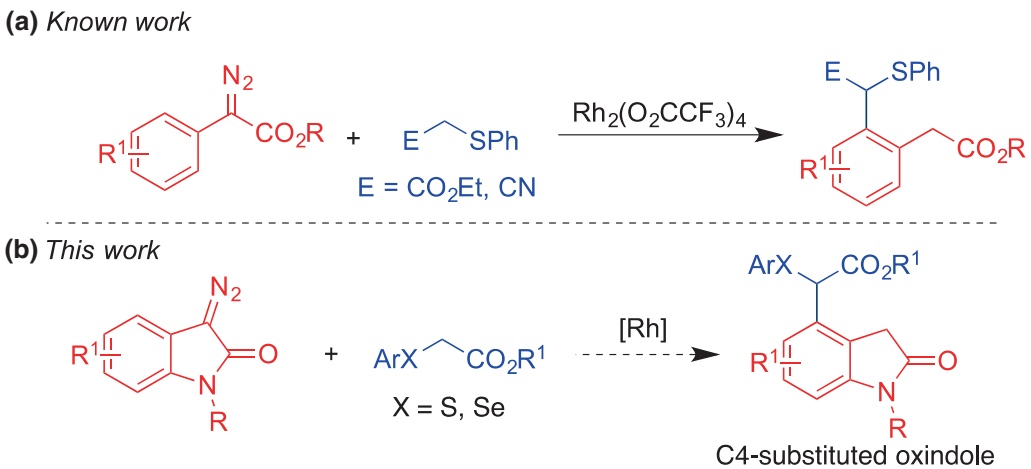
Figure 1. Biologically important oxindole derivatives.

(Scheme 1a). Inspired from this work and our continued interest in functionalization of metal carbenoids,[18] we envisioned the rhodium-catalyzed Sommelet-Hauser type rearrangement of sulfur ylides derived from 3-diazoindolin-2-ones and α-thioester (Scheme 1b). The successful development of the reaction would offer selective rhodium-catalyzed synthesis of C4-thioalkylated oxindole, a biologically important structural motif.

2. Experimental

2.1 *General information*

All reactions were carried out under an atmosphere of dry nitrogen using reaction tubes. Dry dichloromethane (DCM) was prepared by distilling over calcium hydride and stored over 4Å molecular sieves under N_2 atmosphere. All the 3-diazoindolin-2-ones were synthesized from isatin and tosylhydrazine employing literature procedure.[19] α-Thioester[20] and α-selenoester[21] were prepared using literature protocol. Column chromatography was performed using Rankem Silicagel (100–200 mesh) and the solvent system used unless otherwise specified, was ethyl acetate–hexanes with various percentage of polarity depending on the nature of the substrate. NMR data were recorded on Bruker DPX 400 MHz spectrometers. ^{13}C and ^{1}H NMR spectra were referenced to signals of deutero and residual protiated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were



Scheme 1. Rhodium catalyzed Sommelet-Hauser type rearrangement.

recorded by electron spry ionization (ESI) method on a Q-TOF Micro with lock spray source.

2.2 *Typical procedure for the rhodium-catalyzed synthesis of substituted oxindole 3*

α-Thioester/α-selenoester **1** (0.4 mmol, 1 equiv), $Rh_2(OAc)_4$ (0.008 mmol, 2 mol%) and dichloromethane (2 mL) were added under nitrogen atmosphere to an oven-dried 10 mL reaction tube equipped with stir bar. The reaction tube was sealed with septa and stirred at room temperature. Subsequently, the solution of 3-diazoindolin-2-one **2** (0.8 mmol, 2 equiv) in dichloromethane (0.3 mL) was introduced slowly through syringe pump (addition rate = 0.01 mL/min). After the addition of diazo compound, the reaction mixture was stirred for 2 h at same temperature. After the TLC analysis, solvent was removed under reduced pressure. Purification of the resultant crude through column chromatography using mixture of hexane/ethyl acetate as an eluent afforded oxindole **3** in high yield and purity

3a: Brick red solid; yield: 81%; M.p.: 98–100 °C; R_f = 0.55 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3061, 2931, 2362, 1719, 1606, 1469, 1348, 1301, 1253, 1150, 1095, 1026, 982 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.32 (m, 2H), 7.30–7.15 (m, 5H), 6.75 (d, 1H, J = 7.6 Hz), 4.85 (s, 1H), 4.24–4.03 (m, 2H), 3.59 and 3.34 (ABq, 2H, J = 22.1 Hz), 3.18 (s, 3H), 1.18 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 174.6, 169.6, 145.3, 133.2, 133.1, 132.1, 129.1, 128.5, 128.4, 123.7, 122.2, 107.9, 62.0, 54.4, 34.7, 26.3, 14.0; HRMS: calcd. for $C_{19}H_{19}NO_3S$ + Na: 364.0978; found: 364.0982.

3b: Red semi solid; yield: 76%; R_f = 0.39 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3056, 2982, 2850, 2306, 1717, 1605, 1469, 1352, 1262, 1156, 1102, 1030, 900 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 1H), 7.8–7.23 (m, 2H), 7.16 (d, 1H, J = 7.9 Hz), 6.82–6.77 (m, 1H), 6.77–6.70 (m, 2H), 4.71 (s, 1H), 4.24–4.01 (m, 2H), 3.77 (s, 3H), 3.56 and 3.32 (ABq, 2H, J = 21.8 Hz), 3.18 (s, 3H), 1.19 (t, 3H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.6, 169.7, 160.4, 145.3, 136.4, 132.3, 128.4, 123.7, 123.2, 122.2, 114.6, 107.8, 61.9, 55.3(9), 55.3(3), 34.7, 26.3, 14.1; HRMS: calcd. for $C_{20}H_{21}NO_4S$+H: 372.1264; found: 372.1279.

3c: Red semi solid; yield: 64%; R_f = 0.47 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3055, 2980, 2931, 2372, 2307, 1718, 1608, 1468, 1351, 1298, 1262, 1149, 1098, 1031, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.18 (m, 3H), 7.00 (s, 1H), 6.89 (d, 1H, J = 7.7 Hz), 6.74 (d, 1H, J = 7.1 Hz), 4.71 (s, 1H), 4.20–4.02 (m, 2H), 3.58 and 3.29 (ABq, 2H, J = 21.5 Hz), 3.18 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H), 1.17 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.6, 169.8, 145.3, 141.2, 139.0, 134.6, 132.3, 131.4, 128.7, 128.5, 127.4, 123.7, 122.3, 107.8, 61.9, 53.8, 34.7, 26.3, 21.1, 20.6, 14.0; HRMS: calcd. for $C_{21}H_{23}NO_3S$ + Na: 392.1291; found: 392.1298.

3d: Red semi solid; yield: 71%; R_f = 0.34 in 40:60 ethyl acetate/hexane; FTIR (KBr): 3057, 2982, 2928, 2857, 2686, 2522, 2413, 2372, 2306, 2134, 1715, 1610, 1504, 1463, 1422, 1264, 1179, 1147, 1096, 1033, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.23 (m, 1H), 7.16 (d, 1H, J = 7.9 Hz), 7.04–6.96 (dd, 1H, J = 1.5, 8.2 Hz), 6.79 (d, 1H, J = 1.5 Hz), 6.76 (s, 1H), 6.74 (s, 1H), 4.75 (s, 1H), 4.21–4.09 (m, 2H), 3.85 (s, 3H), 3.74 (s, 3H), 3.58 and 3.32 (ABq, 2H, J = 22.2 Hz), 3.19 (s, 3H), 1.20 (t, 3H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 169.7, 150.0, 148.8, 145.3, 132.3, 128.8, 127.8, 123.8, 123.4, 122.3, 117.5, 111.3, 107.8, 62.0, 55.9(6), 55.9(2), 55.3, 34.7, 26.3, 14.1; HRMS: calcd. for $C_{21}H_{23}NO_5S$ + Na: 424.1189; found: 424.1195.

3e: Brick red liquid; yield: 78%; R_f = 0.49 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3057, 2982, 2928, 2857, 2686, 2522, 2413, 2372, 2306, 2134, 1715, 1610, 1504, 1463, 1422, 1264, 1179, 1147, 1096, 1033, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.32 (m, 2H), 7.31–7.18 (m, 3H), 7.14 (t, 1H, J = 7.4 Hz), 6.75 (d, 1H, J = 7.4 Hz), 5.05 (s, 1H), 4.22–4.04 (m, 2H), 3.67 and 3.49 (ABq, 2H, J = 22.1 Hz), 3.19 (s, 3H), 1.16 (t, 3H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.6, 169.3, 145.5, 137.5, 134.7, 132.2, 131.4, 130.1, 129.7, 128.7, 127.3, 123.9, 122.3, 108.1, 62.2, 52.3, 34.8, 26.4, 14.1; HRMS: calcd. for $C_{19}H_{18}ClNO_3S$ + Na: 398.0588; found: 398.0597.

3f: Orange liquid; yield: 75%; R_f = 0.50 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3061, 2977, 2930, 2373, 2181, 2129, 1717, 1656, 1610, 1470, 1354, 1301, 1262, 1225, 1155, 1092, 1029, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, 1H, J = 7.4 Hz), 7.33–7.24 (m, 2H), 7.18 (d, 1H, J = 7.7 Hz), 7.09–7.00 (m, 2H), 6.78 (d, 1H, J = 7.5 Hz), 4.99 (s, 1H), 4.23–4.01 (m, 2H), 3.65 and 3.48 (ABq, 2H, J = 22.3 Hz), 3.19 (s, 3H), 1.15 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.6, 169.5, 145.5, 136.0, 131.7, 131.4 (d, J = 51.2 Hz), 131.1, 128.6, 124.6 (d, J = 3.9 Hz), 123.9, 122.2, 116.1 (d, J = 22.2 Hz), 108.1, 62.1, 52.6, 34.7, 26.4, 14.1; HRMS: calcd. for $C_{19}H_{18}FNO_3S$ + Na: 382.0884; found: 382.0888.

3g: Red solid; yield: 80%; M.p.: 110–112 °C; R_f = 0.49 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3057,

2978, 2937, 2364, 2314, 1719, 1607, 1470, 1350, 1300, 1261, 1152, 1096, 1023, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.18 (m, 5H), 7.13 (d, 1H, J = 8.0 Hz), 6.76 (d, 1H, J = 7.6 Hz), 4.83 (s, 1H), 4.22–4.05 (m, 2H), 3.63 and 3.44 (ABq, 2H, J = 22.5 Hz), 3.19 (s, 3H), 1.19 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.4, 169.3, 145.5, 134.7, 134.5, 131.6(6), 131.6(0), 129.2, 128.6, 123.6, 122.2, 108.1, 62.1, 54.4, 34.7, 26.3, 14.0; HRMS: calcd. for $C_{19}H_{18}ClNO_3S$ + Na: 398.0588; found: 398.0589.

3h: Orange solid; yield: 81%; M.p.: 154–156 °C; R_f = 0.45 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3057, 2983, 2833, 2359, 2309, 1720, 1602, 1463, 1346, 1266, 1153, 1101, 1026, 944, 896 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.10–7.03 (m, 3H), 6.98 (d, 1H, J = 7.9 Hz), 6.59–6.49 (m, 3H), 4.56 (s, 1H), 4.07–3.83 (m, 2H), 3.40 and 3.16 (ABq, 2H, J = 21.6 Hz), 3.01 (s, 3H), 1.01 (t, 3H, J = 7.1 Hz), 0.78 (s, 9H), 0.01 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 169.7, 156.7, 145.3, 136.3, 132.3, 128.4, 124.1, 123.8, 122.3, 120.8, 107.7, 61.9, 55.1, 34.7, 26.3, 25.6, 18.2, 14.1, –4.4; HRMS: calcd. for $C_{25}H_{33}NO_4SSi$ + Na: 494.1792; found: 494.1789.

3i: Red solid; yield: 88%; M.p.: 122–124 °C; R_f = 0.34 in 40:60 ethyl acetate/hexane; FTIR (KBr): 3061, 2971, 2931, 2367, 1717, 1655, 1608, 1464, 1415, 1348, 1298, 1253, 1160, 1128, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, 1H, J = 4.7 Hz), 7.47 (t, 1H, J = 7.8 Hz), 7.27 (t, 1H, J = 7.3 Hz), 7.22 (d, 1H, J = 7.8 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.03–6.95 (m, 1H), 6.75 (d, 1H, J = 7.4 Hz), 5.76 (s, 1H), 4.29–4.09 (m, 2H), 3.73 (s, 2H), 3.19 (s, 3H), 1.22 (t, 3H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.8, 170.0, 156.8, 149.3, 145.4, 136.2, 132.1, 128.6, 124.2, 122.1, 121.9, 120.1, 107.9, 62.1, 48.8, 35.0, 26.3, 14.1; HRMS: calcd. for $C_{18}H_{18}N_2O_3S$ + Na: 343.1111; found: 343.1123.

3m: Red semi solid; yield: 73%; R_f = 0.44 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3057, 2989, 2412, 2359, 2308, 1728, 1608, 1467, 1424, 1354, 1265, 1213, 1159, 1025, 967 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.31 (m, 2H), 7.30–7.19 (m, 5H), 6.64 (d, 1H, J = 7.0 Hz), 4.84 (s, 1H), 4.46 and 4.41 (AB q, 2H, J = 17.6 Hz), 4.26-4.09 (m, 4H), 3.66 and 3.39 (ABq, 2H, J = 22.2 Hz), 1.27 (t, 3H, J = 7.1 Hz), 1.19 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 169.6, 167.6, 144.0, 133.4, 133.2, 132.4, 129.2, 128.6, 123.6, 122.7, 108.0, 62.1, 61.9, 54.5, 41.5, 34.5, 14.2, 14.1; HRMS: calcd. for $C_{22}H_{23}NO_5S$+ H: 414.1370; found: 414.1379.

3n: Red solid; yield: 82%; M.p.: 112–114 °C; R_f = 0.48 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3063, 2977, 2927, 2861, 2360, 1729, 1607, 1468, 1353, 1310, 1207, 1160, 1025, 969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, 2H, J = 6.8 Hz), 7.31–7.20 (m, 4H), 6.67 (d, 1H, J = 8.4 Hz), 5.49 (s, 1H), 4.31–4.07 (m, 2H), 3.77 and 3.29 (ABq, 2H, J = 22.3 Hz), 3.17 (s, 3H), 1.23 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.4, 168.8, 144.4, 134.0, 132.9, 131.3, 129.2, 129.1, 128.7, 127.7, 126.0, 108.7, 62.5, 52.9, 35.7, 26.4, 14.1; HRMS: calcd. for $C_{19}H_{18}ClNO_3S$ + Na: 398.0588; found: 398.0599.

3o: Orange liquid; yield: 81%; R_f = 0.50 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3063, 2974, 2929, 1721, 1601, 1465, 1342, 1291, 1236, 1151, 1100, 1026, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 1H, J = 8.5 Hz), 7.38 (d, 2H, J = 7.9 Hz), 7.30–7.20 (m, 3H), 6.62 (d, 1H, J = 8.2 Hz), 5.54 (s, 1H), 4.27–4.12 (m, 2H), 3.83 and 3.36 (ABq, 2H, J = 22.4 Hz), 3.16 (s, 3H), 1.22 (t, 3H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.2, 168.8, 145.0, 133.9, 133.2, 132.8, 132.4, 129.0, 128.6, 125.9, 117.6, 109.1, 62.4, 55.4, 35.7, 26.3, 14.1; HRMS: calcd. for $C_{19}H_{18}BrNO_3S$ + Na: 442.0083; found: 442.0085.

3p: Red semi solid; yield: 74%; R_f = 0.47 in 30:70 ethyl acetate/hexane; FTIR (KBr): 3057, 2985, 2936, 2306, 1716, 1619, 1472, 1425, 1361, 1265, 1163, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, 2H, J = 7.7 Hz), 7.28–7.22 (m, 3H), 6.95 (t, 1H, J = 9.4 Hz), 6.66 (dd, 1H, J = 3.8, 8.5 Hz), 5.24 (s, 1H), 4.26–4.14 (m, 2H), 3.72 and 3.31 (ABq, 2H, J = 22.9 Hz), 3.17 (s, 3H), 1.22 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.6, 168.8, 156.5 (d, J = 242.5 Hz), 141.5, 133.7, 132.8, 129.1, 128.7, 125.7 (d, J = 3.4 Hz), 121.7 (d, J = 16.6 Hz), 114.4 (d, J = 24.9 Hz), 108.2 (d, J = 8.5 Hz), 62.5, 49.0, 35.6, 26.4, 14.1; HRMS: calcd. for $C_{19}H_{18}FNO_3S$ + Na: 382.0884; found: 382.0893.

3q: Orange solid; yield: 67%; M.p.: 132–134 °C; R_f = 0.42 in 40:60 ethyl acetate/hexane; FTIR (KBr): 3368, 3302, 2926, 2855, 2360, 1713, 1610, 1473, 1358, 1286, 1251, 1160, 1073, 1028, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, 1H, J = 8.3 Hz); 7.39 (d, 2H, J = 7.6 Hz), 7.33–7.21 (m, 3H), 6.82 (d, 1H, J = 8.6 Hz), 5.26 (s, 1H), 4.25 (q, 2H, J = 7.0 Hz), 3.58 and 2.97 (ABq, 2H, J = 21.8 Hz), 3.23 (s, 3H), 1.26 (t, 3H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.0, 168.3, 149.7, 142.3, 134.1, 133.8, 130.8, 129.4, 129.1, 127.8, 125.9, 107.1, 62.7, 54.0, 35.0, 26.6, 14.1; HRMS: calcd. for $C_{19}H_{18}N_2O_5S$ + Na: 409.0829; found: 409.0835.

3r: Orange semi solid; yield: 70%; R_f = 0.41 in 40:60 ethyl acetate/hexane; FTIR (KBr): 3057, 2986, 2308, 1711, 1611, 1472, 1431, 1358, 1266, 1163, 1076, 1029, 897 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ

7.34 (d, 2H), 7.28–7.17 (m, 3H), 6.75 (d, 1H, J = 8.4 Hz), 6.66 (d, 1H, J = 8.4 Hz), 5.33 (s, 1H), 4.18 (q, 2H, J = 7.0 Hz), 3.70 (s, 3H), 3.61 and 3.12 (ABq, 2H, J = 22.0 Hz), 3.15 (s, 3H), 1.21 (t, 3H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 169.6, 152.2, 138.1, 133.8, 133.7, 128.8, 128.3, 125.5, 123.3, 110.1, 107.7, 62.0, 56.4, 49.9, 35.4, 26.2, 14.2; HRMS: calcd. for $C_{20}H_{21}NO_4S$ + H: 372.1264; found: 372.1278.

5a: Red semi solid; yield: 71%; R_f = 0.51 in 40:60 ethyl acetate/hexane; FTIR (Neat): 3426, 3064, 2984, 2252, 1709, 1608, 1470, 1349, 1301, 1251, 1184, 1131, 1027, 984, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.38 (m, 2H), 7.31 (t, 1H, J = 7.3 Hz), 7.27 (m, 4H), 6.76–6.66 (m, 1H), 4.83 (s, 1H), 4.22–4.05 (m, 2H), 3.47 and 3.18 (ABq, 2H, J = 22.1 Hz), 3.18 (s, 3H), 1.19 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 170.3, 145.2, 136.0, 132.7, 129.1, 129.0, 128.4, 128.2, 123.5, 122.6, 107.6, 61.9, 45.9, 34.6, 26.4, 14.1; HRMS: calcd. for $C_{19}H_{19}NO_3Se$+H: 390.0603; found: 390.0608.

5b: Red semi liquid; yield: 76%; R_f = 0.55 in 30:70 ethyl acetate/hexane; FTIR (Neat): 3431, 3061, 2935, 1718, 1618, 1469, 1228, 1125, 1025, 956, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.40 (m, 2H), 7.32 (t, 1H, J = 7.4 Hz), 7.28–7.16 (m, 5H), 6.71 (d, 1H, J = 7.4 Hz), 4.85 (s, 1H), 3.68 (s, 3H), 3.47 and 3.15 (ABq, 2H, J = 22.2 Hz), 3.18 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 170.8, 145.2, 136.1, 132.7, 131.6, 129.2, 129.1, 128.5, 123.5, 122.7, 107.6, 52.9, 45.8, 34.6, 26.4; HRMS: calcd. for $C_{18}H_{16}NO_3Se$ +H: 376.0446; found: 376.0448.

5c: Red semi liquid; yield: 63%; R_f = 0.40 in 40:60 ethyl acetate/hexane; FTIR (Neat): 3433, 3057, 2978, 2932, 2333, 2091, 1730, 1606, 1466, 1355, 1207, 1025, 932, 871 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.39 (m, 2H), 7.36–7.29 (m, 1H), 7.28–7.18 (m, 4H), 6.60 (d, 1H, J = 7.3 Hz), 4.82 (s, 1H), 4.43 (s, 2H), 4.22 (q, 2H, J = 7.1 Hz), 4.18–4.08 (m, 2H), 3.53 and 3.19 (ABq, 2H, J = 22.2 Hz), 1.27 (t, 3H, J = 7.1 Hz), 1.19 (t, 3H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.4, 170.3, 167.5, 143.8, 136.1, 133.0, 131.5, 129.1 (8), 129.1 (1), 128.4, 123.2, 123.0, 107.6, 61.9, 61.8, 45.8, 41.4, 34.3, 14.2, 14.0; HRMS: calcd. for $C_{22}H_{24}NO_5Se$ +H: 462.0814; found: 462.0814.

5d: Red semi liquid; yield: 69%; R_f = 0.51 in 40:60 ethyl acetate/hexane; FTIR (Neat): 3419, 3055, 2980, 2930, 1955, 1717, 1605, 1462, 1340, 1229, 1162, 1026, 965 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.37 (m, 2H), 7.36–7.23 (m, 6H), 7.23–7.15 (m, 3H), 7.11 (t, 1H, J = 7.9 Hz), 6.60 (d, 1H, J = 7.7 Hz), 4.90 and 4.84 (ABq, 2H, J = 15.6 Hz), 4.84 (s, 1H), 4.23–4.03 (m, 2H), 3.53 and 3.20 (ABq, 2H, J = 22.2 Hz), 1.19 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 170.3, 144.1, 136.2, 135.8, 132.8, 129.1, 128.8, 128.3, 128.1, 127.7, 127.4, 123.5, 122.6, 108.5, 61.9, 45.7, 43.8, 34.5, 14.1; HRMS: calcd. for $C_{25}H_{23}NO_3Se$ +H: 466.0916; found: 466.0918.

5e: Red semi liquid; yield: 66%; R_f = 0.51 in 40:60 ethyl acetate/hexane; FTIR (Neat): 3407, 3059, 2926, 2858, 1720, 1602, 1465, 1345, 1302, 1224, 1134, 1027, 806 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.38 (m, 3H), 7.34–7.27 (m, 1H), 7.24–7.15 (m, 2H), 6.57 (d, 1H, J = 8.3 Hz), 5.58 (s, 1H), 4.28–4.09 (m, 2H), 3.69 and 3.17 (ABq, 2H, J = 21.9 Hz), 3.19 (s, 2H), 1.24 (s, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.2, 169.3, 144.8, 136.5, 133.1, 132.4, 129.1, 129.0, 127.8, 126.1, 117.7, 108.8, 62.5, 47.0, 35.8, 26.3, 14.1; HRMS: calcd. for $C_{19}H_{18}BrNO_3Se$ +H: 467.9708; found: 467.9704.

5f: Red semi liquid; yield: 71%; R_f = 0.51 in 40:60 ethyl acetate/hexane; FTIR (Neat): 3454, 3061, 2934, 1718, 1618, 1472, 1347, 1289, 1236, 1125, 1026, 957 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41(d, 2H, J = 7.6 Hz), 7.33–7.24 (m, 1H), 7.18 (t, 2H, J = 7.3 Hz), 6.90 (t, 1H, J = 9.6 Hz), 6.62 (dd, 1H, J = 8.4, 3.7 Hz), 5.27 (s, 1H), 4.20 (q, 2H, J = 6.9 Hz), 3.58 and 3.13 (ABq, 2H, J = 22.2 Hz), 3.16 (s, 3H), 1.23 (t, 3H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 169.3, 156.7 (d, J = 242.7 Hz) 141.3, 136.3, 129.1, 127.9, 125.7, 122.3, 114.3 (d, J = 25.2 Hz), 107.8 (d, J = 8.7 Hz), 62.4, 40.5, 35.5, 26.4, 14.1; HRMS: calcd. for $C_{19}H_{18}FNO_3Se$ +H: 407.0436; found: 407.0439.

Synthesis of sulfone 6: *m*-CPBA (121 mg, 0.7036 mmol) was added to a solution of oxindole **3** (80 g, 0.2345 mmol) in CH_2Cl_2 (10 mL) in 25 mL round bottom flask. The reaction mixture was stirred at room temperature for 2 h and analyzed by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and neutralized by aq. $NaHCO_3$. The organic layer was separated and evaporated under the reduced pressure. The resultant residue was purified by column chromatography using EtOAc/hexane as eluent to give sulfone **6** as green semi-liquid in 78% yield. R_f = 0.38 in 40:70 ethyl acetate/hexane; FTIR (Neat): 3426, 3064, 2984, 2252, 1709, 1608, 1470, 1349, 1301, 1251, 1184, 1131, 1027, 984, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73–7.59 (m, 3H), 7.47 (d, 2H, J = 7.6 Hz), 7.22 (m, 1H, J = 7.8 Hz), 7.15 (d, 1H, J = 8.0 Hz), 6.83 (d, 1H, J = 7.6 Hz), 5.09 (s, 1H), 4.32–4.06 (m, 2H), 3.46 and 3.37 (ABq, 2H, J = 22.0 Hz), 3.19 (s, 3H), 1.21 (t, 3H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.0, 164.3, 145.5, 136.6, 134.5, 130.0, 128.8, 128.4, 126.3, 124.3, 123.2, 109.2, 72.3, 62.8, 34.8, 26.4, 13.9;

HRMS: calcd. for $C_{18}H_{18}NO_5S$ +H: 360.0900; found: 360.0890.

3. Results and Discussion

Initially, α-thioester **1a** derived from thiophenol and 3-diazoindolin-2-one **2a** derived from isatins, were chosen as model substrates to study the rhodium-catalyzed Sommelet-Hauser type rearrangement (Table 1). Thus, one equivalent of α-thioester **1a** was treated with one equivalent of 3-diazoindolin-2-one **2a** in the presence of 2 mol% of rhodium acetate in toluene at 120 °C. To our delight, the formation of expected C4-thioalkylated oxindole product **3a** was observed in 76% yield (Table 1, entry 1). The formation and structure of oxindole **3a** was unambiguously confirmed by X-ray analysis (Figure 2).[22] After the successful confirmation of the product, attempts were devoted to optimize the reaction. The use of DCM as a solvent at 40 °C with equimolar amount of **1a** and **2a** also afforded the expected product **3a** in comparable yield within 4 h (Table 1, entry 2). Next, the reaction temperature was decreased from 40 °C to room temperature in DCM, which gave the product **3a** in decreased yield (Table 1, entry 3). Interestingly, increasing the amount of **2a** in DCM at room temperature showed significant improvement in the reaction (Table 1, entry 4 and 5). The best yield of 81% of **3a** was observed with two equivalents of **2a**.

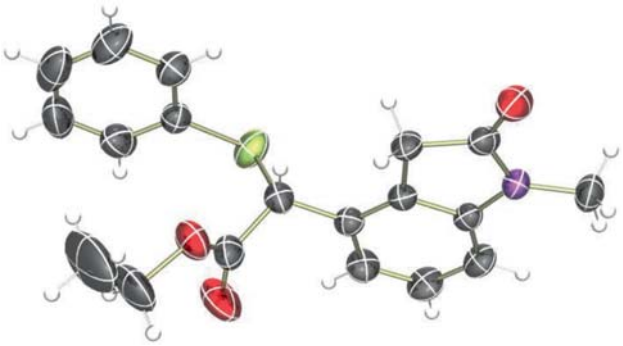
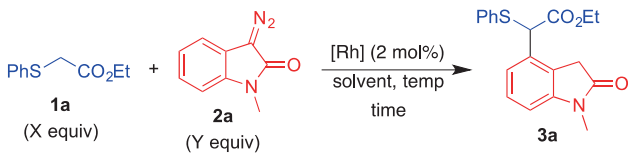


Figure 2. ORTEP diagram of oxindole 3a.

On the other hand, the reaction of two equivalents of **1a** and one equivalent of **2a** gave only 59% of 3a (Table 1, entry 6). Keeping the equivalents of reagents, DCM and room temperature as a constant, decrease the catalyst loading from 2 mol% to 1 mol% gave the product **3a** in diminished yield (Table 1, entry 7). Furthermore, replacing the catalyst $Rh_2(OAc)_4$ with $Rh_2(Oct)_4$ also led to the formation of product **3a** in comparable yield (Table 1, entry 8). Similarly, changing the solvent from DCM to chloroform also gave the product in 78% yield (Table 1, entry 9). From all the above optimization studies, following conditions were chosen for studying the scope and generality of the present Sommelet-Hauser type rearrangement: α-thioester **1a** (1 equiv), 3-diazoindolin-2-one **2a** (2 equiv), $Rh_2(OAc)_4$ (2 mol%), dichloromethane, rt, 2 h.

Table 1. Rhodium-catalyzed Sommelet-Hauser type rearrangemen: optimization studies[a]



Entry	1a (X equiv)	2a (Y equiv)	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	1	2	Toluene	120	6	76
2	1	1	CH_2Cl_2	40	4	72
3	1	1	CH_2Cl_2	rt	4	61
4	1	1.5	CH_2Cl_2	rt	2	70
5	1	2	CH_2Cl_2	rt	2	81
6	2	1	CH_2Cl_2	rt	2	59
7[c]	1	2	CH_2Cl_2	rt	2	68
8[d]	1	2	CH_2Cl_2	rt	2	80
9	1	2	$CHCl_3$	rt	2	78

[a] Reaction conditions: α-thioester **1a** (X equiv), 3-diazoindolin-2-one **2a** (Y equiv), $Rh_2(OAc)_4$ (2 mol%), solvent, temp, time

[b] Isolated yields

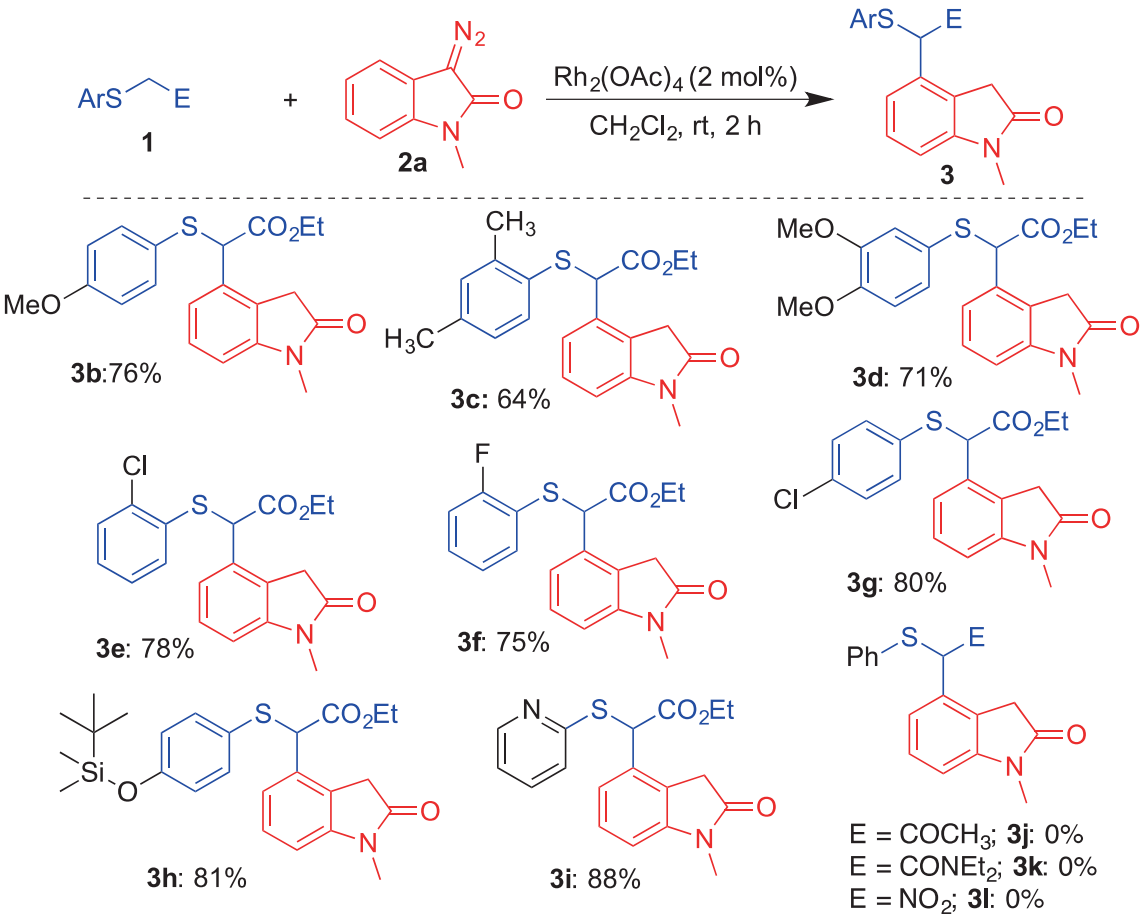
[c] $Rh_2(OAc)_4$ (1 mol%) was used

[d] $Rh_2(Oct)_4$ (2 mol%) was used.

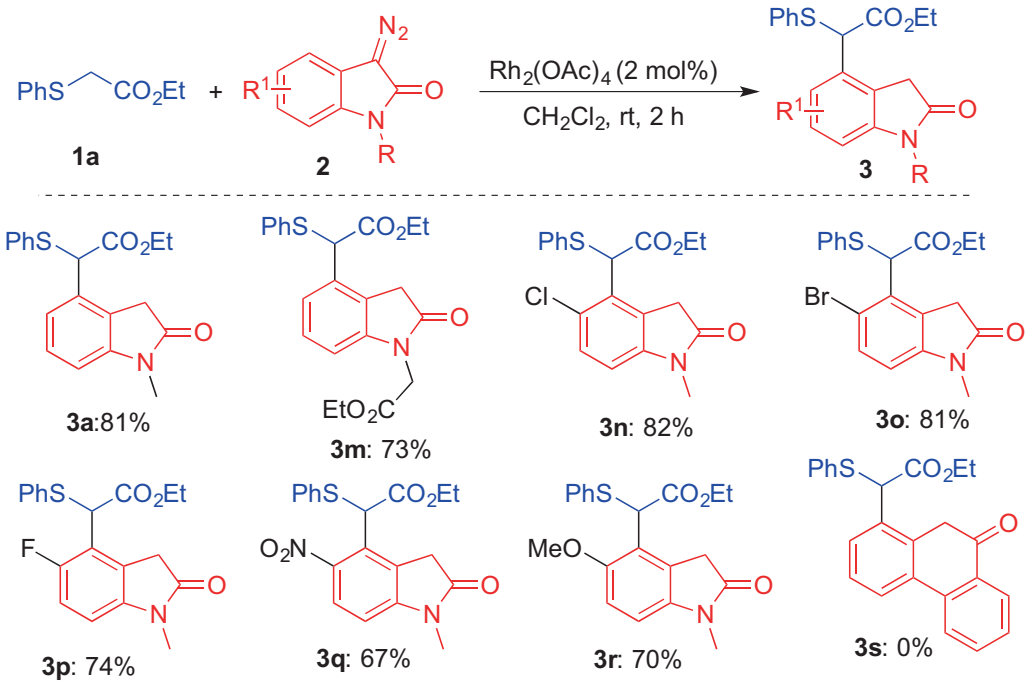
Having found the best-optimized conditions, next, the generality of the developed transformation was examined with respect to various α-thioester **1**. At first, scope of various arene substitutions in α-thioester was investigated. As can be seen in Scheme 2, all the substituted α-thioester **1** afforded the corresponding oxindoles **3** in good yield. For instance, replacing of phenyl with electron-rich arene moieties such as 4-methoxy and 2,3-dimethoxyphenyl substituted α-thioesters afforded corresponding C4-thioalkylated oxindoles **3b** and **3d** in ∼70% yields under the optimized conditions. Similarly, the present method was successfully applied to the haloarene-substituted α-thioesters for the synthesis of synthetically useful halo substituted oxindoles **3e**–**3g** in excellent yields.

Importantly, sterically hindered *ortho*-substituted 2,4-dimethylphenyl substituted α-thioesters underwent smooth reaction with **2a** to provide the corresponding oxindole **3c** in 64% yield. Interestingly, acid-sensitive, silyloxyarene substituted α-thioester was also well-tolerated under the optimized conditions to give oxindole **3h** in 81% yield. Furthermore, α-thioester derived from pyridine-2-thiol also worked well under the optimized conditions to furnish oxindole **3i** in 88% yield. On the other hand, the replacement of ester moiety with other electron-withdrawing groups, such as methyl ketone, carboxamide and nitro group, failed to afford the expected C4-substituted product **3j**–**3l**. This is possibly due to the less acidity of C-H bond in carboxamide and high stability of the anion generated from nitro derivatives.

Successively, the scope of 3-diazoindolin-2-one **2** was also examined under the present optimized conditions (Scheme 3). *N*-substituted diazo derivatives such as methyl and functionalized alkyl group were subjected under rhodium-catalyzed reaction with **1a**, which led to the formation of oxindole products **3a** and **3m** in 81% and 73% yields, respectively. C4-Functionalized chloro, bromo and fluoro substituted oxindole **3n**–**3p** were achieved in good yield from corresponding substituted diazo compounds. It is important to note that both electron-withdrawing, 5-nitro-substituted and electron-donating, 5-methoxy-substituted diazo derivatives underwent smooth reaction to afford the oxindole products **3q** and **3r** in good yields. Unfortunately, the replacement of 3-diazoindolin-2-one **2** with cyclic diazoketone **2s** under the optimized conditions failed to afford the corresponding product **3s**.



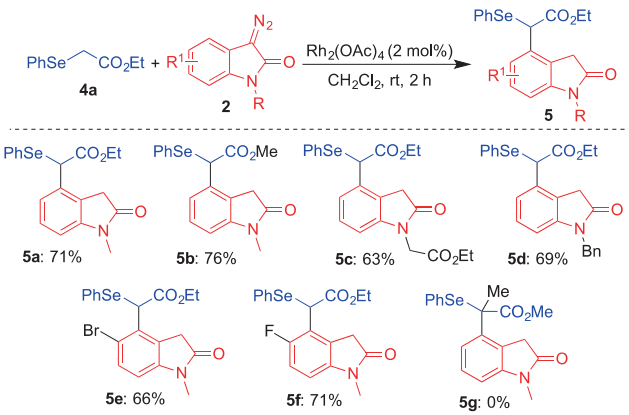
Scheme 2. Synthesis of C4-thioalkylated oxindoles 3: Scope and limitation of α-thioester 1.



Scheme 3. Synthesis of C4-thioalkylated oxindoles 3: Scope and limitation of diazo compound 2.

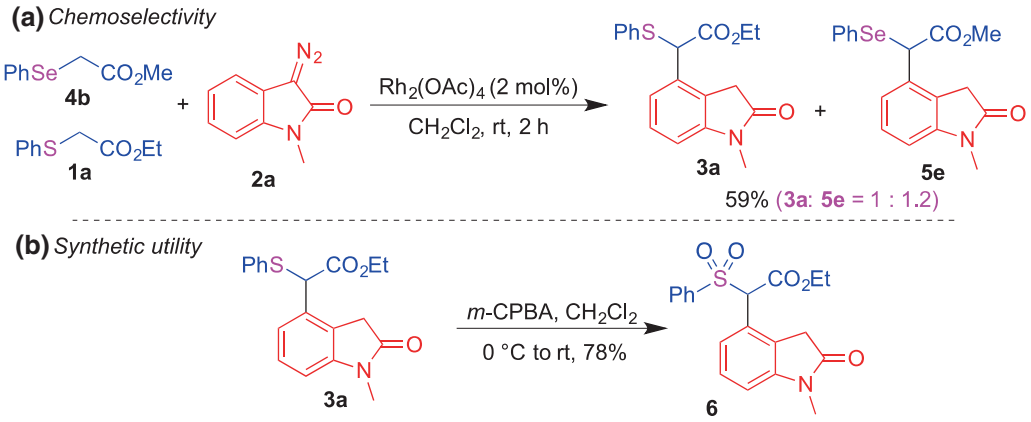
After the successful development of Sommelet-Hauser type rearrangement of 3-diazoindolin-2-one with α-thioester, next, the extension of the present reaction to α-selenoesters was envisaged for the synthesis of C4-selenoalkylated oxindole derivatives. Thus, one equivalent of α-selenoester **4a** was subjected to two equivalents of diazo compound **2a** in the presence of 2 mol% of $Rh_2(OAc)_4$ in dichloromethane at room temperature (Scheme 4). As expected, C4-selenoalkylated oxindole **5a** was observed in 71% yield. This implies that the developed reaction works equally well for selenium-ylide derived the α-selenoesters. Further, the scope of α-selenoesters with various *N*-substituted diazo derivatives as examined. Replacement of ethyl ester with methyl ester in α-selenoesters gave the oxindole **5b** in comparable yield. The reaction of functionalized alkyl and benzyl group containing diazo compound under standard conditions led to the formation of oxindole products **5c** and **5d** in 63% and 69% yields, respectively. Similarly, halo substituted oxindoles **5e–5f** were also synthesized in good yield from corresponding diazo compounds. Unfortunately, α-selenoesters derived from methyl 2-bromopropionate did not afford the expected oxindole **5g**, possibly due to the steric hindrance.

After the successful demonstration of generality of the developed method, chemoselectivity of Sommelet-Hauser type rearrangement was examined with α-thioesters and α-selenoesters (Scheme 5). The



Scheme 4. Synthesis of C4-selenoalkylated oxindoles 5.

reaction of equimolar mixture of **1a** and **4b** with diazo compound **2a** in the presence of 2 mol% of rhodium acetate in DCM afforded the mixture of oxindoles **3a** and **5e** in 59% overall yield with 1:1.2 ratio (Scheme 5a). This observation suggests that reactivity of α-selenoester towards Sommelet-Hauser type rearrangement under the developed conditions is significantly higher compared to α-thioesters. Next, the possible synthetic conversion of oxindole **3a** was also investigated (Scheme 5b). The sulfur moiety in the synthesized oxindole **3a** was readily oxidized in the presence of *m*-CPBA at room temperature in CH_2Cl_2 to corresponding sulfone **6** in 78% yield, which could be readily applied for subsequent synthetic manipulation.



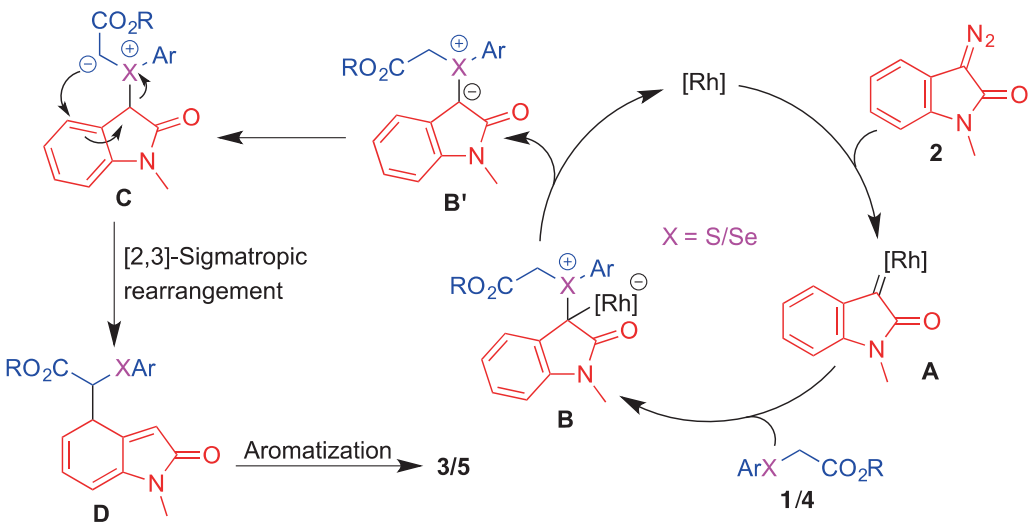
Scheme 5. Chemoselectivity and synthetic utility.

Having demonstrated the efficient synthesis of C4-chalcogenoalkylated oxindoles, based on the literature precedence, the plausible mechanism for the rhodium-catalyzed transformation was postulated (Scheme 6). The reaction starts with the generation of reactive rhodium carbenoid **A** from diazo compound **2** and $Rh_2(OAc)_4$. Subsequent trapping of formed rhodium carbenoid **A** with α-thioester/α-selenoester **1/4** *via* nucleophilic attached would generate the metal-bound S/Se-ylide **B**. Regeneration of rhodium catalyst from metal-bound ylide **B** would form the S/Se-ylide **B′**. Intramolecular proton transfer in **B′** would provide rearranged ylide **C**. Formation of enone intermediate **D** could be readily realized through the [2, 3]-sigmatropic rearrangement of resultant ylide **C**. Finally, the expected oxindole product **3/5** could be achieved *via* the aromatization of intermediate **D**.

In conclusion, a general and efficient synthesis of C4-thioalkylated oxindoles has been accomplished through rhodium-catalyzed Sommelet-Hauser type rearrangement of α-thioester with 3-diazoindolin-2-one. The developed reaction tolerates various reactive functional groups and allowed the selective synthesis of various C4-thioalkylated oxindoles in good yield to excellent yield. Furthermore, the developed reaction was successfully extended to α-selenoester for the synthesis of C4-selenoalkylated oxindoles. Importantly, the chemoselective experiment suggested the significant higher reactivity of α-selenoesters towards metal carbenoids compared to α-thioesters.

Supplementary Information (SI)

^1H and ^{13}C NMR spectra of isolated compounds and CIF file containing crystallographic information of compound 3a are provided in the supporting information. Supplementary information is available at www.ias.ac.in/chemsci.



Scheme 6. A plausible mechanism.

Acknowledgements

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