Electronic Supplementary Information

Access to 2-Naphthols via Ru(II)-Catalyzed C-H Annulation of Nitrones with α-Diazo Sulfonyl Ketones

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I. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on a 600 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless $\delta$ values and is frequency referenced relative to TMS in $^1$H and $^{13}$C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate/hexanes. Aryl nitrones $^1$ and $\alpha$-diazo sulfonyl ketones$^2$ were prepared according to literature reports.

II. Experimental Procedures and Characterizations

A mixture of aryl nitrone ($^1$, 0.3 mmol), $\alpha$-diazo sulfonyl ketone ($^2$, 0.2 mmol), [Ru($\rho$-cymene)Cl$_2$)$_2$ (5.0 mol %), AgNTf$_2$ (20.0 mol %), AgPF$_6$ (20.0 mol %), PivOH (2.0 equiv), and DCE (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred under N$_2$ at 120 ºC for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (25:1) to afford the product $^3$.

1-Tosylnaphthalen-2-ol ($^3$aa)

$^3$aa was obtained according to the general procedure in 79% yield (47.1 mg), white solid, mp = 123.6-125.3 ºC, $R_f$ = 0.25 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 11.14 (s, 1H), 8.34 (d, $J$ = 8.5 Hz, 1H), 7.91 (d, $J$ = 9.0 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.71 (d, $J$ = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.34 – 7.31 (m, 1H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.17 (d, $J$ = 9.0 Hz, 1H), 2.35 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 158.9, 144.8, 139.4, 137.5, 130.0, 129.7, 129.2, 128.9, 128.8, 126.8, 124.5, 123.2, 120.4, 112.3, 21.7. HRMS: m/z: [M + H]$^+$ calculated for C$_{17}$H$_{15}$O$_3$S$: 299.0736, found 299.0736.

7-Methoxy-1-tosylnaphthalen-2-ol ($^3$ba)

$^3$ba was obtained according to the general procedure in 66% yield (43.1 mg), white solid, mp = 90.8-91.8 ºC, $R_f$ = 0.25 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 11.09 (s, 1H), 7.84 - 7.81 (m, 3H), 7.66 (d, $J$ = 2.4 Hz, 1H), 7.27 (d, $J$ = 8.2 Hz, 2H), 7.02 (d, $J$ = 9.0 Hz, 1H), 6.94 (dd, $J$ = 8.8, 2.4 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.8, 159.5, 144.8, 139.2, 137.2, 131.4, 130.6, 129.9,
126.8, 124.0, 117.5, 116.3, 111.3, 103.3, 55.5, 21.8. HRMS: m/z: [M + Na]$^+$ calculated for C$_{18}$H$_{16}$NaO$_4$S$^+$: 351.0662, found 351.0659.

7-(tert-Butyl)-1-tosylnaphthalen-2-ol (3ca)

3ca was obtained according to the general procedure in 74% yield (52.5 mg), white solid, mp = 154.5-155.3 °C, R$_f$ = 0.30 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) δ 11.15 (s, 1H), 8.26 (s, 1H), 7.86 – 7.85 (m, 3H), 7.63 (d, $J$ = 8.5 Hz, 1H), 7.39 (dd, $J$ = 8.5, 1.8 Hz, 1H), 7.26 (d, $J$ = 8.1 Hz, 2H), 7.11 (d, $J$ = 9.0 Hz, 1H), 2.35 (s, 3H), 1.30 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.9, 151.7, 144.7, 139.4, 137.0, 129.8, 129.5, 128.7, 127.0, 126.9, 123.0, 119.5, 119.1, 112.2, 35.6, 31.3, 21.7. HRMS: m/z: [M + Na]$^+$ calculated for C$_{21}$H$_{22}$NaO$_3$S$^+$: 377.1182, found 377.1177.

7-Phenyl-1-tosylnaphthalen-2-ol (3da)

3da was obtained according to the general procedure in 67% yield (50.4 mg), yellow solid, mp = 160.0-161.5 °C, R$_f$ = 0.25 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) δ 11.18 (s, 1H), 8.54 (s, 1H), 7.91 (d, $J$ = 9.0 Hz, 1H), 7.87 (d, $J$ = 8.0 Hz, 2H), 7.74 (d, $J$ = 8.3 Hz, 1H), 7.56 (d, $J$ = 8.3 Hz, 1H), 7.52 (d, $J$ = 7.6 Hz, 2H), 7.45 (t, $J$ = 7.6 Hz, 2H), 7.38 (t, $J$ = 7.4 Hz, 1H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 9.0 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 159.2, 144.9, 141.4, 140.9, 139.4, 137.2, 130.0, 129.9, 129.6, 129.1, 128.0, 127.9, 127.7, 126.9, 124.1, 121.5, 120.3, 112.5, 21.7. HRMS: m/z: [M + Na]$^+$ calculated for C$_{23}$H$_{20}$NaO$_3$S$^+$: 397.0869, found 397.0863.

7-Fluoro-1-tosyl naphthalen-2-ol (3ea)

3ea was obtained according to the general procedure in 51% yield (32.3 mg), yellow solid, mp = 159.5-160.4 °C, R$_f$ = 0.25 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) δ 11.14 (s, 1H), 8.05 (dd, $J$ = 12.2, 2.4 Hz, 1H), 7.88 (d, $J$ = 9.0 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.69 (dd, $J$ = 8.9, 6.0 Hz, 1H), 7.28 (d, $J$ = 8.1 Hz, 2H), 7.13 (d, $J$ = 9.1 Hz, 1H), 7.09 (m, 1H), 2.37 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 162.5 (d, $J_{C,F}$ = 248.4 Hz), 159.7, 145.1, 138.9, 137.2, 131.5 (d, $J_{C,F}$ = 10.0 Hz), 131.1 (d, $J_{C,F}$ = 10.6 Hz), 130.1, 126.8, 125.8, 119.6 (d, $J_{C,F}$ =
2.7 Hz), 114.3 (d, \( J_{C-F} = 24.9 \) Hz), 112.3, 108.3 (d, \( J_{C-F} = 25.8 \) Hz), 21.8. \(^1\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -108.2. HRMS: m/z: [M + Na\(^+\)] calculated for C\(_{17}\)H\(_{13}\)FNaO\(_3\)S\(^+\): 339.0462, found 339.0461.

7-Bromo-1-tosylnaphthalen-2-ol (3fa)
3fa was obtained according to the general procedure in 60% yield (45.1 mg), yellow solid, mp = 166.7-168.6 °C, \( R_f = 0.25 \) (hexanes/ethyl acetate = 15/1).
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 11.16 (s, 1H), 8.56 (d, \( J = 1.8 \) Hz, 1H), 7.86 – 7.83 (m, 3H), 7.54 (d, \( J = 8.5 \) Hz, 1H), 7.40 (dd, \( J = 8.6, 1.8 \) Hz, 1H), 7.29 (d, \( J = 8.1 \) Hz, 2H), 7.16 (d, \( J = 9.0 \) Hz, 1H), 2.37 (s, 3H).
\(^1\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 159.3, 145.2, 138.8, 137.2, 130.8, 130.5, 130.1, 128.0, 127.3, 126.9, 125.7, 123.8, 120.8, 112.0, 21.8. HRMS: m/z: [M + Na\(^+\)] calculated for C\(_{17}\)H\(_{13}\)BrNaO\(_3\)S\(^+\): 398.9661, found 398.9656.

1-Tosyl-7-(trifluoromethyl)naphthalen-2-ol (3ga)
3ga was obtained according to the general procedure in 61% yield (45.0 mg), yellow solid, mp = 148.6-150.2 °C, \( R_f = 0.25 \) (hexanes/ethyl acetate = 15/1).
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 11.22 (s, 1H), 8.76 – 8.70 (m, 1H), 7.96 (d, \( J = 9.1 \) Hz, 1H), 7.89 – 7.84 (m, 2H), 7.82 (d, \( J = 8.4 \) Hz, 1H), 7.51 (dd, \( J = 8.3, 1.7 \) Hz, 1H), 7.33 – 7.27 (m, 3H), 2.38 (s, 3H).
\(^1\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 159.4, 145.4, 138.8, 136.9, 130.2, 130.1, 130.0, 128.9, 127.0, 124.2 (q, \( J_{C-F} = 272.9 \) Hz), 122.8, 120.9 (q, \( J_{C-F} = 4.6 \) Hz), 120.4 (q, \( J_{C-F} = 3.3 \) Hz), 113.8, 100.2, 21.8. \(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -62.6. HRMS: m/z: [M + Na\(^+\)] calculated for C\(_{18}\)H\(_{13}\)F\(_3\)NaO\(_3\)S\(^+\): 389.0430, found 389.0422.

Methyl 7-hydroxy-8-tosyl-2-naphthoate (3ha)
3ha was obtained according to the general procedure in 69% yield (48.3 mg), white solid, mp = 169.2-170.3 °C, \( R_f = 0.20 \) (hexanes/ethyl acetate = 15/1).
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 11.20 (s, 1H), 9.15 (s, 1H), 7.95 – 7.89 (m, 4H), 7.74 (d, \( J = 8.4 \) Hz, 1H), 7.29 (d, \( J = 8.1 \) Hz, 2H), 7.28 – 7.23 (m, 1H), 3.97 (s, 3H), 2.36 (s, 3H).
\(^1\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 166.8, 159.0, 145.1, 139.0, 136.9, 131.1, 130.1, 129.9, 129.3, 128.9, 127.3, 126.8, 21.8. HRMS: m/z: [M + Na\(^+\)] calculated for C\(_{19}\)H\(_{16}\)NaO\(_3\)S\(^+\): 379.0611, found 379.0601.
1-Tosyl naphthalene-2,7-diol (3ia)

3ia was obtained according to the general procedure in 56% yield (35.4 mg), white solid, mp = 194.9-195.8 oC, Rf = 0.10 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.04 (s, 1H), 7.84 – 7.81 (m, 4H), 7.58 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.9 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.34 (s, 1H), 2.31 (s, 3H).

13C NMR (151 MHz, CDCl3) δ 159.6, 156.6, 144.9, 138.9, 137.5, 131.5, 131.3, 130.1, 126.7, 124.0, 117.4, 115.8, 110.8, 106.7, 21.7. HRMS: m/z: [M + Na]+ calculated for C17H14NaO4S: 337.0505, found 337.0498.

6-Methyl-1-tosyl naphthalen-2-ol (3ja)

3ja was obtained according to the general procedure in 64% yield (40.2 mg), yellow solid, mp = 126.0-127.7 oC, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.03 (s, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.88 – 7.78 (m, 3H), 7.47 (s, 1H), 7.29 (dd, J = 8.9, 1.9 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.13 (d, J = 9.1 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H).

13C NMR (151 MHz, CDCl3) δ 158.2, 144.7, 139.4, 137.0, 134.1, 130.9, 130.0, 129.2, 128.4, 127.6, 126.7, 123.0, 120.2, 112.2, 21.7, 21.1. HRMS: m/z: [M + Na]+ calculated for C18H16NaO3S: 335.0712, found 335.0705.

6-Chloro-1-tosyl naphthalen-2-ol (3ka)

3ka was obtained according to the general procedure in 66% yield (44.1 mg), white solid, mp = 142.0-143.6 oC, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.11 (s, 1H), 8.30 (d, J = 9.2 Hz, 1H), 7.82 – 7.80 (m, 3H), 7.67 (d, J = 2.3 Hz, 1H), 7.39 (dd, J = 9.3, 2.3 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 9.1 Hz, 1H), 2.36 (s, 3H).

13C NMR (151 MHz, CDCl3) δ 158.8, 145.1, 139.0, 136.4, 130.4, 130.1, 129.8, 129.4, 127.9, 127.8, 126.7, 124.8, 121.7, 112.7, 21.8. HRMS: m/z: [M + Na]+ calculated for C18H16ClNaO3S: 355.0166, found 355.0160.
Methyl 6-hydroxy-5-tosyl-2-naphthoate (3la)

3ma was obtained according to the general procedure in 81% yield (71.2 mg), white solid, mp = 154.2-155.7 °C, Rf = 0.10 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.31 (s, 1H), 8.42 (s, 1H), 8.39 (d, J = 9.2 Hz, 1H), 8.01 (m, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.25 (m, 3H), 3.93 (s, 3H), 2.36 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 166.6, 160.4, 145.1, 138.9, 138.4, 132.3, 131.7, 130.1, 128.4, 128.1, 126.8, 126.1, 123.3, 121.3, 112.8, 52.4, 21.7. HRMS: m/z: [M + Na]+ calculated for C19H16NaO5S+: 379.0611, found 379.0604.

6-Methoxy-1-tosyl-naphthalen-2-ol (3ma)

3ka was obtained according to the general procedure in 80% (20:1) yield (52.6 mg), white solid, mp = 131.1-133.2 °C, Rf = 0.25 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 10.90 (s, 1H), 8.27 (d, J = 9.4 Hz, 1H), 7.82 – 7.79 (m, 3H), 7.25 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 9.0 Hz, 1H), 7.12 (dd, J = 9.4, 2.8 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 3.82 (s, 3H), 2.34 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 157.0, 156.3, 144.7, 139.3, 136.3, 130.3, 130.0, 126.7, 124.6, 124.3, 120.7, 120.4, 112.5, 108.2, 55.4, 21.7. HRMS: m/z: [M + Na]+ calculated for C18H16NaO4S+: 351.0662, found 351.0655.

5-Methyl-1-tosyl-naphthalen-2-ol (3na)

3na was obtained according to the general procedure in 74% yield (46.4 mg), yellow solid, mp = 160.2-161.4 °C, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.16 (s, 1H), 8.21 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 9.4 Hz, 1H), 7.82 – 7.80 (m, 2H), 7.34 – 7.31 (m, 1H), 7.25 – 7.23 (m, 2H), 7.20 (d, J = 9.3 Hz, 1H), 7.16 – 7.14 (m, 1H), 2.61 (s, 3H), 2.34 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 158.5, 144.7, 139.4, 135.6, 133.5, 130.0, 129.9, 128.6, 127.9, 126.7, 125.7, 121.5, 119.9, 112.7, 21.7, 19.9. HRMS: m/z: [M + Na]+ calculated for C18H16NaO3S+: 335.0712, found 335.0704.

5-Methoxy-1-tosyl-naphthalen-2-ol (3oa)
3oa was obtained according to the general procedure in 90% yield (59.0 mg), white solid, mp = 142.2-143.0 °C, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 11.14 (s, 1H), 8.42 (d, $J = 9.3$ Hz, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.35 (t, $J = 8.3$ Hz, 1H), 7.25 – 7.23 (m, 2H), 7.13 (d, $J = 9.3$ Hz, 1H), 6.67 (d, $J = 7.8$ Hz, 1H), 3.90 (s, 3H), 2.34 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.1, 156.0, 144.5, 139.2, 131.4, 130.9, 129.8, 129.3, 126.6, 120.5, 118.9, 115.3, 111.9, 103.2, 55.6, 21.6. HRMS: m/z: [M + Na]$^+$ calculated for C$_{18}$H$_{16}$NaO$_4$S$^+$: 351.0662, found 351.0658.

5-Fluoro-1-tosynylnaphthalen-2-ol (3pa)

3pa was obtained according to the general procedure in 53% yield (33.4 mg), white solid, mp = 146.1-146.6 °C, Rf = 0.25 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 11.21 (s, 1H), 8.23 (d, $J = 9.3$ Hz, 1H), 8.12 (d, $J = 8.8$ Hz, 1H), 7.40 – 7.36 (m, 1H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 9.3$ Hz, 1H), 7.01 – 6.98 (m, 1H), 2.37 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.5, 159.2 (d, $J_{C-F} = 253.0$ Hz), 145.0, 139.1, 131.2 (d, $J_{C-F} = 3.5$ Hz), 130.1, 129.7 (d, $J_{C-F} = 7.3$ Hz), 129.2 (d, $J_{C-F} = 9.1$ Hz), 126.8, 120.8 (d, $J_{C-F} = 2.1$ Hz), 119.1 (d, $J_{C-F} = 16.7$ Hz), 119.0 (d, $J_{C-F} = 4.3$ Hz), 112.5, 108.7 (d, $J_{C-F} = 19.7$ Hz), 21.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -120.8. HRMS: m/z: [M + Na]$^+$ calculated for C$_{17}$H$_{13}$FNaO$_3$S$^+$: 339.0462, found 339.0454.

5-Bromo-1-tosynylnaphthalen-2-ol (3qa)

3qa was obtained according to the general procedure in 76% yield (57.4 mg), white solid, mp = 158.0-1158.8 °C, Rf = 0.25 (hexanes/ethyl acetate = 15/1).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 11.23 (s, 1H), 8.42 (d, $J = 9.4$ Hz, 1H), 8.35 (d, $J = 8.8$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.28 – 7.25 (m, 4H), 2.36 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.2, 145.0, 139.1, 136.4, 131.2, 130.1, 129.1, 128.8, 127.2, 126.7, 124.0, 122.9, 121.8, 112.6, 21.8. HRMS: m/z: [M + Na]$^+$ calculated for C$_{17}$H$_{13}$BrNaO$_3$S$^+$: 398.9661, found 398.9648.

S7
1-Tosyl-5-(trifluoromethyl)naphthalen-2-ol (3ra)

3ra was obtained according to the general procedure in 63% yield (46.4 mg), white solid, mp = 98.0-99.2 °C, R<sub>f</sub> = 0.30 (hexanes/ethyl acetate = 15/1).

1<sup>H</sup> NMR (600 MHz, CDCl<sub>3</sub>) δ 11.25 (s, 1H), 8.61 (d, J = 8.9 Hz, 1H), 8.30 (d, J = 9.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 7.4 Hz, 1H), 7.49 (t, J = 8.1 Hz, 1H), 7.33 (d, J = 9.5 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H).

13<sup>C</sup> NMR (151 MHz, CDCl<sub>3</sub>) δ 158.9, 145.2, 139.0, 133.0 (q, J<sub>C-F</sub> = 3.0 Hz), 130.8, 130.2, 127.5, 127.3, 127.2 (q, J<sub>C-F</sub> = 42.2 Hz), 126.8, 124.7, 124.4 (q, J<sub>C-F</sub> = 274.1 Hz), 123.01 (q, J<sub>C-F</sub> = 6.1 Hz), 122.3, 113.4, 21.8. 19<sup>F</sup> NMR (376 MHz, CDCl<sub>3</sub>) δ -58.8. HRMS: m/z: [M + Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>13</sub>F<sub>3</sub>NaO<sub>3</sub>S<sub>3</sub>: 389.0430, found 389.0424.

4-Tosylbenzo[<i>b</i>]thiophen-5-ol (3sa)

3sa was obtained according to the general procedure in 22% yield (13.2 mg), yellow solid, mp = 179.3-179.9 °C, R<sub>f</sub> = 0.25 (hexanes/ethyl acetate = 15/1).

1<sup>H</sup> NMR (600 MHz, CDCl<sub>3</sub>) δ 10.21 (s, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 5.6 Hz, 1H), 7.57 (d, J = 5.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.8 Hz, 1H), 2.38 (s, 3H).

13<sup>C</sup> NMR (151 MHz, CDCl<sub>3</sub>) δ 156.0, 145.0, 139.0, 136.3, 133.3, 130.8, 130.1, 129.9, 126.7, 122.8, 117.1, 115.1, 21.8. HRMS: m/z: [M + Na]<sup>+</sup> calculated for C<sub>15</sub>H<sub>12</sub>NaO<sub>2</sub>S<sub>2</sub>: 327.0120, found 327.0116.

1-Tosyldibenzo[<i>b,d</i>]furan-2-ol (3ta)

3ta was obtained according to the general procedure in 23% yield (15.7 mg), white solid, mp = 163.5-164.0 °C, R<sub>f</sub> = 0.25 (hexanes/ethyl acetate = 15/1).

1<sup>H</sup> NMR (600 MHz, CDCl<sub>3</sub>) δ 10.32 (s, 1H), 8.59 (d, J = 8.1 Hz, 1H), 7.85 – 7.83 (m, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.32 – 7.28 (m, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 9.0 Hz, 1H), 2.34 (s, 3H). 13<sup>C</sup> NMR (151 MHz, CDCl<sub>3</sub>) δ 157.4, 154.8, 145.1, 138.8, 130.1, 128.5, 126.2, 125.8, 123.2, 121.8, 121.4, 120.1, 119.1, 114.2, 111.8, 21.8. HRMS: m/z: [M + Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>14</sub>NaO<sub>4</sub>S<sub>2</sub>: 361.0505, found 361.0509.

1-Tosylanthracen-2-ol (3ua)
3ua was obtained according to the general procedure in 61% yield (42.8 mg), yellow solid, mp = 136.2-137.0 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.38 (s, 1H), 8.83 (s, 1H), 8.24 (s, 1H), 8.04 (d, J = 9.2 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.88 (t, J = 8.6 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.43 -7.40 (m, 1H), 7.23 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 9.2 Hz, 1H), 2.30 (s, 3H).

13C NMR (151 MHz, CDCl3) δ 159.6, 144.8, 139.2, 138.2, 133.1, 130.1, 129.9, 128.6, 128.3, 127.9, 127.7, 126.9, 126.8, 126.4, 125.8, 122.0, 120.9, 109.9, 21.7.

HRMS: m/z: [M + Na]+ calculated for C21H16NaO3S+: 371.0712, found 371.0708.

7-Tosylbenzo[pqr]tetraphen-8-ol (3va)

3va was obtained according to the general procedure in 62% yield (52.4 mg), yellow solid, mp = 222.1-222.9 °C, R_f = 0.30 (hexanes/ethyl acetate = 5/1).

1H NMR (600 MHz, DMSO-d6) δ 11.42 (s, 1H), 9.67 (s, 1H), 9.41 (d, J = 9.3 Hz, 1H), 9.09 (d, J = 9.1 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.35 (d, J = 7.6 Hz, 1H), 8.24 (d, J = 7.3 Hz, 1H), 8.15 – 8.09 (m, 2H), 8.06 (t, J = 7.9 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 9.3 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H).

13C NMR (151 MHz, DMSO-d6) δ 157.9, 144.0, 140.2, 132.2, 130.9, 130.6, 130.3, 129.6, 129.1, 128.6, 128.4, 127.7, 126.9, 126.6, 126.2, 125.8, 123.7, 122.3, 120.9, 119.3, 119.3, 115.2, 21.1.

HRMS: m/z: [M + H]+ calculated for C27H19O3S+: 423.1049, found 423.1049.

1-((4-Fluorophenyl)sulfonyl)naphthalen-2-ol (3ab)

3ab was obtained according to the general procedure in 76% yield (46.0 mg), white solid, mp = 118.4-119.2 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl3) δ 11.05 (s, 1H), 8.31 (d, J = 8.7 Hz, 1H), 7.98 – 7.95 (m, 2H), 7.94 (d, J = 9.1 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 9.1 Hz, 1H), 7.15 (t, J = 8.5 Hz, 2H).

13C NMR (151 MHz, CDCl3) δ 165.7 (d, J_C-F = 256.6 Hz), 159.0, 138.3 (d, J_C-F = 3.4 Hz), 137.9, 129.6 (d, J_C-F = 31.4 Hz), 129.5, 129.4, 129.1, 128.9, 124.7, 122.9, 120.4, 116.8 (d, J_C-F = 22.7 Hz), 111.8.

19F NMR (376 MHz, CDCl3) δ -103.3. HRMS: m/z: [M + Na]+ calculated for C16H11FNaO3S+: 325.0305, found 325.0302.
1-((4-Bromophenyl)sulfonyl)naphthalen-2-ol (3ac)

3ac was obtained according to the general procedure in 72% yield (52.5 mg), white solid, mp = 157.0-157.6 °C, Rf = 0.25 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl₃) δ 11.02 (s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 9.1 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.49 – 7.46 (m, 1H), 7.36 – 7.33 (m, 1H), 7.18 (d, J = 9.1 Hz, 1H). 13C NMR (151 MHz, CDCl₃) δ 159.2, 141.2, 138.0, 132.7, 129.5, 129.4, 129.1, 128.91, 128.90, 128.2, 124.7, 122.9, 120.3, 111.4. HRMS: m/z: [M + Na]+ calculated for C₁₆H₁₁BrNaO₃S: 384.9504, found 384.9506.

1-((4-(Trifluoromethyl)phenyl)sulfonyl)naphthalen-2-ol (3ad)

3ad was obtained according to the general procedure in 69% yield (48.5 mg), white solid, mp = 151.8-152.3 °C, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

1H NMR (600 MHz, CDCl₃) δ 10.99 (s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 9.0 Hz, 1H), 7.75 – 7.72 (m, 3H), 7.50 – 7.47 (m, 1H), 7.38 – 7.35 (m, 1H), 7.20 (d, J = 9.1 Hz, 1H). 13C NMR (151 MHz, CDCl₃) δ 159.5, 145.7, 138.4, 135.3 (q, J_C-F = 33.1 Hz), 129.5, 129.4, 129.3, 128.9, 127.2, 126.6 (q, J_C-F = 3.8 Hz), 124.8, 123.1 (q, J_C-F = 273.1 Hz), 122.8, 120.4, 110.9. 19F NMR (376 MHz, CDCl₃) δ -63.3. HRMS: m/z: [M + Na]+ calculated for C₁₇H₁₁F₃NaO₃S: 375.0273, found 375.0272.

1-(Phenylsulfonyl)naphthalen-2-ol (3ae)

3ae was obtained according to the general procedure in 65% yield (36.8 mg), yellow solid, mp = 123.9-
125.2 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

^1^H NMR (600 MHz, CDCl_3) δ 11.12 (s, 1H), 8.33 (d, J = 8.7 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.93 (d, J = 9.1 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.49 – 7.43 (m, 3H), 7.34 – 7.31 (m, 1H), 7.18 (d, J = 9.0 Hz, 1H). ^1^C NMR (151 MHz, CDCl_3) δ 159.1, 142.2, 137.7, 133.7, 129.6, 129.4, 129.3, 128.9, 128.9, 126.7, 124.5, 123.1, 120.3, 111.9. HRMS: m/z: [M + Na]^+ calculated for C_{16}H_{12}NaO_3S: 307.0399, found 307.0397.

![Image](image1.png)

1-(Naphthalen-2-ylsulfonyl)naphthalen-2-ol (3af)

3af was obtained according to the general procedure in 76% yield (50.5 mg), white solid, mp = 164.7-165.1 °C, R_f = 0.25 (hexanes/ethyl acetate = 15/1).

^1^H NMR (600 MHz, CDCl_3) δ 11.22 (s, 1H), 8.62 (s, 1H), 8.42 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 9.1 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.82 – 7.78 (m, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.44 – 7.40 (m, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 9.0 Hz, 1H). ^1^C NMR (151 MHz, CDCl_3) δ 159.1, 138.9, 137.8, 135.3, 132.1, 129.9, 129.7, 129.6, 129.5, 129.3, 129.0, 128.9, 128.1, 128.0, 127.9, 124.5, 123.1, 121.6, 120.4, 111.9. HRMS: m/z: [M + Na]^+ calculated for C_{20}H_{14}NaO_3S: 357.0556, found 357.0551.

![Image](image2.png)

1-((2,3-Dihydro-1H-inden-5-yl)sulfonyl)naphthalen-2-ol (3ag)

3ag was obtained according to the general procedure in 74% yield (48.1 mg), white solid, mp = 143.4-144.0 °C, R_f = 0.30 (hexanes/ethyl acetate = 15/1).

^1^H NMR (600 MHz, CDCl_3) δ 11.18 (s, 1H), 8.36 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 9.1 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.33 – 7.30 (m, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 2.89 – 2.87 (m, 2H), 2.87 – 2.85 (m, 2H), 2.07 – 2.01 (m, 2H). ^1^C NMR (151 MHz, CDCl_3) δ 158.7, 151.2, 145.9, 140.0, 137.4, 129.7, 129.2, 128.9, 128.8, 125.03, 125.00, 124.4, 123.2, 122.5, 120.3, 112.5, 33.0, 32.7, 25.4. HRMS: m/z: [M + Na]^+ calculated for
1-(Phenethylsulfonyl)naphthalen-2-ol (3ah)

3ah was obtained according to the general procedure in 72% yield (44.9 mg), white solid, mp = 91.9-92.6 °C, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

\[ ^1H \text{NMR (600 MHz, CDCl}_3 \delta 10.85 (s, 1H), 8.51 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.45 – 7.41 (m, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.13 (m, 1H), 7.12 (d, J = 9.0 Hz, 1H), 7.04 – 7.02 (m, 2H), 3.66 – 3.62 (m, 2H), 3.09 – 3.05 (m, 2H).} \]

\[ ^13C \text{NMR (151 MHz, CDCl}_3 \delta 159.2, 137.7, 136.9, 130.0, 129.6, 129.4, 128.9, 128.8, 128.3, 127.1, 124.7, 122.7, 120.3, 110.2, 57.5, 28.6.} \]

HRMS: m/z: [M + Na]^+ calculated for C_{18}H_{16}NaO_{3}S^+: 335.0712, found 335.0705.

1-(Cyclohexylsulfonyl)naphthalen-2-ol (3ai)

3ai was obtained according to the general procedure in 65% yield (37.9 mg), yellow solid, mp = 91.4-92.3 °C, Rf = 0.30 (hexanes/ethyl acetate = 15/1).

\[ ^1H \text{NMR (600 MHz, CDCl}_3 \delta 10.85 (s, 1H), 8.55 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.612 – 7.59 (m, 1H), 7.44 – 7.41 (m, 1H), 7.13 (d, J = 9.0 Hz, 1H), 3.27 – 3.22 (m, 1H), 2.04 – 1.86 (m, 4H), 1.67 – 1.63 (m, 3H), 1.25 – 1.18 (m, 3H).} \]

\[ ^13C \text{NMR (151 MHz, CDCl}_3 \delta 159.8, 137.4, 130.4, 129.5, 129.1, 129.0, 124.5, 123.2, 120.1, 109.0, 63.82, 63.80, 25.2, 25.1.} \]

HRMS: m/z: [M + Na]^+ calculated for C_{16}H_{18}NaO_{3}S^+: 313.0869, found 313.0864.

1-(Thiophen-2-ylsulfonyl)naphthalen-2-ol (3aj)

3aj was obtained according to the general procedure in 73% yield (42.6 mg), white solid, mp = 135.3-136.5 °C, Rf = 0.25 (hexanes/ethyl acetate = 15/1).

\[ ^1H \text{NMR (600 MHz, CDCl}_3 \delta 10.87 (s, 1H), 8.60 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.78 –} \]
7.77 (m, 1H), 7.74 (d, \( J = 8.0 \text{ Hz}, 1 \text{H} \)), 7.56 – 7.54 (m, 2H), 7.39 (t, \( J = 7.5 \text{ Hz}, 1 \text{H} \)), 7.16 (d, \( J = 9.0 \text{ Hz}, 1 \text{H} \)), 7.04 (t, \( J = 4.6 \text{ Hz}, 1 \text{H} \)). \(^{13}\text{C} \text{ NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) 158.2, 143.6, 137.9, 133.5, 133.0, 129.5, 129.4, 129.1, 128.9, 127.7, 124.7, 123.2, 120.4, 113.4. HRMS: m/z: \([M + Na]^+ \) calculated for \( \text{C}_{14}\text{H}_{10}\text{NaO}_{3}\text{S}^2^+ \): 312.9964, found 312.9958.

[Diagram of 3-Methyl-1-(phenylsulfonyl)naphthalen-2-ol (3ak)]

3ak was obtained according to the general procedure in 66% yield (39.2 mg), white solid, mp = 141.6–142.4 °C, \( R_f = 0.30 \) (hexanes/ethyl acetate = 15/1)

\(^1\text{H} \text{ NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 11.41 (s, 1H), 8.27 (d, \( J = 8.7 \text{ Hz}, 1 \text{H} \)), 7.94 (d, \( J = 7.8 \text{ Hz}, 2 \text{H} \)), 7.78 (s, 1H), 7.63 (d, \( J = 8.0 \text{ Hz}, 1 \text{H} \)), 7.53 (t, \( J = 7.4 \text{ Hz}, 1 \text{H} \)), 7.46 (t, \( J = 7.7 \text{ Hz}, 2 \text{H} \)), 7.38 (t, \( J = 7.9 \text{ Hz}, 1 \text{H} \)), 7.29 (t, \( J = 7.5 \text{ Hz}, 1 \text{H} \)), 2.43 (s, 3H). \(^{13}\text{C} \text{ NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) 158.5, 142.4, 136.9, 133.6, 129.4, 129.0, 128.5, 128.48, 128.44, 127.9, 126.6, 124.4, 122.9, 111.2, 17.2. HRMS: m/z: \([M + Na]^+ \) calculated for \( \text{C}_{17}\text{H}_{14}\text{NaO}_{3}\text{S}^+ \): 321.0556, found 321.0552.

[Diagram of 3-Benzyl-1-tosynaphthalen-2-ol (3al)]

3al was obtained according to the general procedure in 45% yield (34.9 mg), white solid, mp = 166.7–167.2 °C, \( R_f = 0.30 \) (hexanes/ethyl acetate = 15/1)

\(^1\text{H} \text{ NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 11.50 (s, 1H), 8.29 (dd, \( J = 8.7, 1.0 \text{ Hz}, 1 \text{H} \)), 7.83 – 7.79 (m, 2H), 7.63 (s, 1H), 7.58 (dd, \( J = 8.1, 1.4 \text{ Hz}, 1 \text{H} \)), 7.40 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H), 7.29 – 7.27 (m, 2H), 7.27 – 7.22 (m, 4H), 4.16 (s, 2H), 2.34 (s, 3H). \(^{13}\text{C} \text{ NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) 157.7, 144.7, 139.5, 139.4, 136.8, 132.0 130.0, 129.3, 128.8, 128.7, 128.66, 128.4, 128.1, 126.7, 126.5, 124.4, 122.9, 112.0, 36.5, 21.7. HRMS: m/z: \([M + Na]^+ \) calculated for \( \text{C}_{24}\text{H}_{20}\text{NaO}_{3}\text{S}^+ \): 411.1025, found 411.1034.

### III. Derivatization Reaction

[Diagram of Derivatization Reaction]

To a 15 mL tube equipped with a magnetic stirrer was charged with 3qa (37.7 mg, 0.1 mmol), NBS (21.4 mg, 0.12 mmol), and KOAc (14.7 mg, 0.15 mmol) in 1.0 mL H\(_2\)O. Then the mixture
was stirred at room temperature for the desired time (monitored by TLC). After the reaction, the resulting mixture was extracted three times with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous MgSO$_4$, after which the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (20:1) as the eluent to afford the desired product 5 as brown solid in 98% yield (44.5 mg), mp = 82.3-84.1 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.05 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 10.3 Hz, 1H), 7.72 (dd, J = 8.1, 1.2 Hz, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.38 – 7.36 (m, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.31 (d, J = 10.2 Hz, 1H), 2.46 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 186.6, 146.9, 143.7, 135.4, 135.0, 134.2, 132.0, 131.1, 130.4, 129.2, 126.7, 125.7, 124.9, 81.1, 22.0. HRMS: m/z: [M + H]$^+$ calculated for C$_{17}$H$_{13}$Br$_2$O$_3$S: 454.8947, found 454.8947.

IV. Mechanistic Studies

(a) H/D Exchange Experiment

Aryl nitrone (1, 0.3 mmol), $\alpha$-diazo sulfonyl ketone (2, 0.2 mmol), [Ru($p$-cymene)Cl$_2$]$_2$ (5 mol %), AgNTf$_2$ (20 mol %), AgPF$_6$ (20 mol %), and CD$_3$COOD (2.0 equiv) were dissolved in DCE in a pressure tube under N$_2$ atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the recovered 1a and the product 3aa, which was characterized by $^1$H NMR spectroscopy. The ortho’ positions of the recovered 1a and the product 3aa were deuterated (43% D, and 38% D respectively).
(b) The intermolecular competition experiment

\[ \text{[Ru(p-cymene)Cl}_2]_2 (5 \text{ mol } \%) + \text{AgNTf}_2 (20 \text{ mol } \%), \text{AgPF}_6 (20 \text{ mol } \%) \]

PivOH (2.0 equiv), DCE, 120 °C, 16 h

1b + 1g + 2a → 3ab:3ga = 10:1
An equimolar mixture of aryl nitrone 1b (0.1 mmol) and 1g (0.1 mmol), \( \alpha \)-diazo sulfonyl ketone (2, 0.2 mmol), \([\text{Ru}(p\text{-cymene})\text{Cl}_2]\) (5 mol %), AgNTf\(_2\) (20 mol %), AgPF\(_6\) (20 mol %), PivOH (2.0 equiv), and DCE (2 mL) were charged into a pressure tube under \( \text{N}_2 \). The reaction mixture was stirred at 120 \(^\circ\text{C}\) for 12 h. The solvent was rapidly removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the mixed product. The yield ratio (3ba/3ga = 11:1) was determined on the basis of \(^1\text{H NMR}\) analysis.

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(c) Isolation of Intermediate 6 and Control Experiments

Aryl nitrone 1a (0.3 mmol), diazo sulfonylketone 2a (0.2 mmol), \([\text{Ru}(p\text{-cymene})\text{Cl}_2]\) (5 mol %), AgNTf\(_2\) (20 mol %), AgPF\(_6\) (20 mol %), PivOH (2.0 equiv), and DCE (2 mL) were charged into a pressure tube. The reaction mixture was stirred under \( \text{N}_2 \) at 80 \(^\circ\text{C}\) for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (2:1) to afford the product 6 in 49% yield (38.1 mg). \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \( \delta \) 7.78 (s, 1H), 7.63 – 7.61 (m, 1H), 7.43 – 7.40 (m, 3H), 7.28 – 7.25 (m, 1H), 7.21 – 7.16 (m, 3H), 5.84 (s, 1H), 2.41 (s, 3H), 2.37 (s, 3H), 1.64 (s, 9H). \(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \( \delta \) 199.3, 145.0, 134.3, 132.5, 130.8, 130.2, 130.1, 129.7, 129.5, 129.4, 129.1, 127.9, 78.1, 71.2, 31.7, 28.2, 21.8. HRMS: \( \text{m/z: [M + H]}^+ \) calculated for \( \text{C}_{21}\text{H}_{26}\text{NO}_4\text{S}^- \): 388.1577, found 388.1576.
Intermediate 6 (0.14 mmol), AgNTf$_2$ (20 mol %), AgPF$_6$ (20 mol %), PivOH (2.0 equiv), and DCE (1.4 mL) were charged into a pressure tube. The reaction mixture was stirred under N$_2$ at 120 ºC for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (2:1) to afford the product 3aa in 69% yield (28.8 mg). What’s more, the intermediate 6 could be converted to the final product 3aa without Ru(II) catalyst.

(d) KIE Study

Aryl nitrone 1a (0.15 mmol), diazo sulfonylketone 2a (0.1 mmol), [Ru(p-cymene)Cl$_2$]$_2$ (5 mol %), AgNTf$_2$ (20 mol %), AgPF$_6$ (20 mol %), and CH$_3$COOH (2.0 equiv) were dissolved in DCE (1 mL) in a pressure tube under N$_2$ atmosphere, while the other pressure tube was changed with 1a-$d_5$ (0.1 mmol), 2a (0.1 mmol), [Ru(p-cymene)Cl$_2$]$_2$ (5 mol %), AgNTf$_2$ (20 mol %), AgPF$_6$ (20 mol %), and CD$_3$COOD (2.0 equiv) in DCE (1 mL) under N$_2$ atmosphere. The two reaction mixtures were stirred side by side in an oil bath preheated at 100 ºC for 15 min. The two reaction tubes were chilled in an ice bath and the resulting mixtures in the two tubes were rapidly combined. The solvent was rapidly removed under reduced pressure. The resulting residue was purified by silica gel chromatography using EA/PE to afford the crude products. The KIE value was determined to be $k_H/k_D = 0.9$ on the basis of $^1$H NMR analysis.
Aryl nitrone 1a (0.2 mmol), 1a-d₅ (0.2 mmol), diazo sulfonylketone 2a (0.2 mmol), [Ru(p-cymene)Cl₂]₂ (5 mol %), AgNTf₂ (20 mol %), AgPF₆ (20 mol %), and CH₃COOH (1.0 equiv), and CD₃COOD (1.0 equiv) were dissolved in DCE (2 mL) in a pressure tube under N₂ atmosphere. The reaction mixture was stirred at 100 ºC for 15 min. After the solvent was removed under reduced pressure, the resulting residue was purified by silica gel chromatography using EA/PE to afford the rude products. The KIE value was determined to be $k_{H}/k_{D} = 2.0$ on the basis of $^1$H NMR analysis.
V. Reference


VI. NMR Spectra

$^1$H and $^{13}$C NMR spectra for compound 3aa

![NMR Spectra](image)

$^{13}$C NMR spectra for compound 3aa

![NMR Spectra](image)
$^{1}$H and $^{13}$C NMR spectra for compound 3ba

![NMR Spectra](image)
$^1$H and $^{13}$C NMR spectra for compound $3\text{ca}$

3ca

3ca
$^1$H and $^{13}$C NMR spectra for compound 3da

Ph

Ts

3da

OH

Tso

3da

Ph

Ts

OH
$^1$H, $^{13}$C and $^{19}$F NMR spectra for compound 3ea
$^1$H and $^{13}$C NMR spectra for compound 3fa
$^1$H, $^{13}$C and $^{19}$F NMR spectra for compound 3ga
$\mathrm{F}_3\mathrm{C}$

$\mathrm{Ts}$

$\mathrm{OH}$

$3\text{ga}$
$^1$H and $^{13}$C NMR spectra for compound 3ha

3ha

Ts

MeOOC

OH

3ha

Ts

MeOOC
$^{1}$H and $^{13}$C NMR spectra for compound 3ia
$^1$H and $^{13}$C NMR spectra for compound 3ja

3ja

3ja
$^1$H and $^{13}$C NMR spectra for compound 3ka

![H and C NMR spectra for compound 3ka](image)

3ka
$^1$H and $^{13}$C NMR spectra for compound 3la
**H and **C NMR spectra for compound 3ma

![NMR Spectra](image)

**3ma**

**MeO**

**Ts**

**OH**

**Ts**

**MeO**
$^1$H and $^{13}$C NMR spectra for compound 3na
$^{1}\text{H}$ and $^{13}\text{C}$ NMR spectra for compound 3oa

![NMR Spectra](image)

**3oa**

- Chemical shifts for $^{1}\text{H}$ NMR spectrum:
  - 7.8000, 7.8133, 7.8719, 7.8865, 8.4156, 8.4311

- Chemical shifts for $^{13}\text{C}$ NMR spectrum:
  - 21.5857, 55.6186, 103.1755, 111.8852, 115.2729, 118.9199, 120.4565, 126.5839, 129.3261, 129.7856, 130.8536, 131.4224, 139.2351, 144.5034, 155.9500, 159.1005

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S36
$^1$H, $^{13}$C and $^{19}$F NMR spectra for compound 3pa
F

Ts

3pa

-120.7638
$^{1}$H and $^{13}$C NMR spectra for compound 3qa
$^1$H, $^{13}$C and $^{19}$F NMR spectra for compound 3ra

![NMR spectra](image)

3ra

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
$\text{CF}_3$

$3\text{ra}$

$\text{T}s\text{OH}$

$f_1$ (ppm)

-58.7807
$^1$H and $^{13}$C NMR spectra for compound 3sa

![NMR spectra](image)

**3sa**
$^1$H and $^{13}$C NMR spectra for compound 3ta
$^1$H and $^{13}$C NMR spectra for compound 3ua

![NMR spectra for compound 3ua](image)

3ua

![NMR spectra for compound 3ua](image)

3ua
$^1$H and $^{13}$C NMR spectra for compound 3va
$^1$H, $^{13}$C and $^{19}$F NMR spectra for compound 3ab
$f_1$ (ppm)
$^1$H and $^{13}$C NMR spectra for compound 3ac

3ac

S48
$^1$H, $^{13}$C and $^{19}$F NMR spectra for compound 3ad
$^1$H and $^{13}$C NMR spectra for compound 3ae

3ae

3ae
$^1$H and $^{13}$C NMR spectra for compound 3af
$^1$H and $^{13}$C NMR spectra for compound \textit{3ag}
$^1$H and $^{13}$C NMR spectra for compound 3ah

![NMR spectra of compound 3ah](image)

**3ah**
\( \text{H and } ^{13}\text{C NMR spectra for compound } 3\text{ai} \)

![NMR spectra for compound 3ai](image)

\( 3\text{ai} \)
$^1$H and $^{13}$C NMR spectra for compound 3aj
$^1$H and $^{13}$C NMR spectra for compound 3ak

![NMR spectra of compound 3ak](image-url)
$^1$H and $^{13}$C NMR spectra for compound 3al
$^1$H and $^{13}$C NMR spectra for compound 5

![NMR Spectra](image-url)
$^1$H and $^{13}$C NMR spectra for compound 6