Supporting Information

Ligand-Mediated and Copper-Catalyzed C(sp^3)-H Bond Functionalization of Aryl Ketones with Sodium Sulfinates under Mild Conditions

Xing-Wang Lan,¹ Nai-Xing Wang,¹,* Cui-Bing Bai,¹ Wei Zhang,¹ Yalan Xing,²,* Jia-Long Wen³, Yan-Jing Wang¹ & Yi-He Li,¹

¹Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, China
E-Mail: nxwang@mail.ipc.ac.cn; Tel.: +86-10-82543575; Fax: +86-10-62554670.
²Department of Chemistry, William Paterson University of New Jersey, 300 Pompton Road, Wayne, New Jersey 07470, United States.
E-Mail: xingy@wpunj.edu
³Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, 100083, P.R.China.

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1. General Information.

Unless otherwise specified, all commercially available reagents were purchased from chemical suppliers without further purification. In particular, 1,8-diazabicyclo[5.4.1]undec-7-ene (DBU) was dried over 4 Å molecular sieves. \(^1\)H NMR (400 MHz) and \(^{13}\)C NMR (100 MHz) spectra were recorded in CDCl\(_3\) with TMS as internal standard at room temperature. High-resolution mass spectra (HRMS) were obtained by ESI. Column chromatography was performed on silica gel (200-300 mesh). All products were characterized by comparison of \(^1\)H NMR, \(^{13}\)C NMR, and HRMS, especially the 3aa was also characterized by using HSQC and HMBC to further confirm the structure.

2. Experimental Section

General Procedure for Preparation of Sodium Sulfinates (2b-2e, 2g-2i).

4-Chlorobenzenesulfinate (2d) sodium salt was prepared by heating 2.5 g of sodium sulfite, 2.10 g of 4-chlorobenzenesulphonyl chloride, and 1.68 g of sodium bicarbonate in 10.0 mL of water at 70-80 °C for 4 h. After cooling to room temperature, water was removed by filtering under vacuum and the residue was extracted by ethanol, recrystallization or evaporation as a white solid. Similarly, other sodium arenesulfinates (2b, 2c, 2e, 2g-2i) was prepared from their corresponding sulphonyl chlorides.

3. Segmental Experiment Data

<table>
<thead>
<tr>
<th>Table 1 Optimization of reaction conditions a</th>
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a Reaction conditions: 1a (0.5 mmol), 2a (1.0 mmol), and catalyst (20 mol%) and base in 3 mL solvent at room temperature in open flask (air). b Isolated yields.

4. Characterization Data of All Products.

1-phenyl-2-(phenylsulfonyl)propan-1-one (3aa): White solid, mp 85-86°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.96 - 7.94(m, 2H), 7.80 - 7.77(m, 2H), 7.64 - 7.57(m, 2H), 7.52 - 7.43(m, 2H). 5.17 (dd, \(J_1 = 14.0\) Hz, \(J_2 = 6.8\) Hz, 1H), 1.57 (d, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 192.45, 136.23, 134.18, 134.03, 129.73, 129.10, 128.88, 128.74, 64.97, 13.11. HRMS (ESI, m/z) calcd. for C\(_{15}\)H\(_{14}\)O\(_3\)SNa [M+Na] \(^+\) 297.0556, found 297.0559.

1-phenyl-2-tosylpropan-1-one (3ab): White solid, mp 101-102°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.98 - 7.96(m, 2H), 7.65 (d, \(J = 8.4\) Hz, 2H), 7.60 (t, \(J = 7.4\) Hz, 1H), 7.47 (t, \(J = 7.8\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 5.15 (dd, \(J_1 = 13.8\) Hz, \(J_2 = 7.0\) Hz, 1H), 2.42 (s, 3H), 1.55 (d, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 192.60, 145.30, 136.31, 133.94, 133.16, 129.80, 129.50, 129.15, 128.70, 65.03, 21.63, 13.17. HRMS (ESI, m/z) calcd. for C\(_{16}\)H\(_{16}\)O\(_3\)SNa [M+Na] \(^+\) 311.0712.
2-((4-fluorophenyl)sulfonyl)-1-phenylpropan-1-one (3ac): White solid, mp 113-114°C. 1H NMR (400 MHz, CDCl3) δ 7.90 – 7.87 (m, 2H), 7.75 – 7.70 (m, 2H), 7.56 – 7.52 (m, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.13 – 7.09 (m, 2H), 5.10 (dd, J1 = 7.0 Hz, J2 = 3.4 Hz, 1H), 1.49 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 192.57, 167.49, 164.93, 136.09, 134.22, 132.84, 132.74, 132.05, 132.02, 129.13, 128.84, 116.35, 116.12, 65.04, 13.28. HRMS (ESI, m/z) calcd. for C15H14FO5Sn [M+Na]+ 315.0462, found 315.0461.

2-((4-chlorophenyl)sulfonyl)-1-phenylpropan-1-one (3ad): White solid, mp 113-118°C. 1H NMR (400 MHz, CDCl3) δ 7.91 – 7.89 (m, 2H), 7.66 – 7.64 (m, 2H), 7.58 – 7.54 (m, 1H), 7.44 – 7.41 (m, 4H), 5.10 (dd, J1 = 7.0 Hz, J2 = 3.6 Hz, 1H), 1.50 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 192.47, 141.19, 136.06, 134.42, 134.25, 131.35, 129.22, 129.15, 128.86, 65.10, 13.31. HRMS (ESI, m/z) calcd. for C15H13ClO5Sn [M+Na]+ 331.0166, found 331.0166.

2-((4-bromophenyl)sulfonyl)-1-phenylpropan-1-one (3ae): White solid, mp 149-151°C. 1H NMR (400 MHz, CDCl3) δ 7.90 – 7.88 (m, 2H), 7.61 – 7.54 (m, 5H), 7.42 (t, J = 8.0 Hz, 2H), 5.09 (dd, J1 = 13.8 Hz, J2 = 7.0 Hz, 1H), 1.50 (d, J = 7.0 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 192.45, 136.05, 134.97, 134.25, 132.22, 131.39, 130.90, 129.86, 129.15, 128.86, 77.34, 77.02, 76.70, 65.55, 65.09, 30.59, 19.19, 13.71, 13.30. HRMS (ESI, m/z) calcd. for C15H13BrO5Sn [M+Na]+ 376.9642, found 376.9642.

2-(methylsulfonyl)-1-phenylpropan-1-one (3af): Yellow oil liquid. 1H NMR (400 MHz, CDCl3) δ 8.01 – 7.99 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 4.96 (dd, J1 = 14.2 Hz, J2 = 7.0 Hz, 1H), 2.94 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 193.97, 135.73, 134.43, 129.16, 128.93, 63.95, 37.04, 13.76. HRMS (ESI, m/z) calcd. for C10H12O2SNa [M+Na]+ 235.0399, found 235.0397.

2-(cyclopropylsulfonyl)-1-phenylpropan-1-one (3ag): Yellow oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.97 (d, J = 7.7 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 4.99 (dd, J1 = 14.0 Hz, J2 = 7.2 Hz, 1H), 2.52 – 2.46 (m, 1H), 1.69 (d, J = 7.1 Hz, 3H), 1.20 – 1.17 (m, 1H), 1.15 – 1.05 (m, 1H), 1.04 – 0.97 (m, 1H), 0.93 – 0.86 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 194.05, 136.91, 134.87, 129.85, 129.56, 64.88, 28.16, 13.87, 6.30, 4.74. HRMS (ESI, m/z) calcd. for C12H12O2S [M+H]+ 239.0736, found 239.0735.

1-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)propan-1-one (3ah): White solid, mp 94-97°C. 1H NMR (400 MHz, CDCl3) δ 7.90 – 7.85 (m, 4H), 7.72 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 5.13 (dd, J1 = 13.6 Hz, J2 = 6.8 Hz, 1H), 1.52 (d, J = 7.0 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 192.30, 139.49, 135.90, 134.39, 130.60, 129.12, 128.91, 126.02, 125.98, 125.94, 125.91, 65.11, 13.29. HRMS (ESI, m/z) calcd. for C16H13F3O5S [M+H]+ 343.0610, found 343.0608.

2-(naphthalen-2-ylsulfonyl)-1-phenylpropan-1-one (3ai): White solid, mp 119-121°C. 1H NMR (400 MHz, CDCl3) δ 8.29 (s, 1H), 7.91 – 7.83 (m, 5H), 7.68 (dd, J1 = 8.6 Hz, J2 = 0.8 Hz, 1H), 7.63 – 7.47 (m, 3H), 7.36 (t, J = 4.0 Hz, 2H), 5.17 (dd, J1 = 6.8 Hz, J2 = 3.4 Hz, 1H), 1.54 (d, J = 6.9 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 192.64, 136.59, 135.74, 134.05, 133.70, 132.17, 132.07, 129.73, 129.61, 129.25, 129.15, 128.84, 128.09, 127.73, 124.34, 65.56, 13.34. HRMS (ESI, m/z) calcd. for C19H16O3Sn [M+Na]+ 347.0712, found 347.0712.

1-(4-fluorophenyl)-2-(phenylsulfonyl)propan-1-one (3ba): White solid, mp 116-117°C. 1H NMR (400 MHz, CDCl3) δ 8.04 – 8.01 (m, 2H), 7.79 – 7.76 (m, 2H), 7.68 – 7.64 (m, 1H), 7.55 – 7.51 (m, 2H), 7.17 – 7.13 (m, 2H), 5.11 (dd, J1 = 13.8 Hz, J2 = 7.0 Hz, 1H), 1.56 (d, J =
$13^\text{C}$ NMR (100 MHz, CDCl$_3$) $\delta$ 190.79, 167.60, 134.27, 132.04, 131.95, 129.77, 128.90, 116.07, 115.85, 65.10, 13.11. HRMS (ESI, $m/z$) calcd. for C$_{15}$H$_{34}$FO$_3$Sn [M+Na]$^+$ 315.0462, found 315.0464.

1-(3-fluorophenyl)-2-(phenylsulfonyl)propan-1-one (3ea): White solid, mp 110-112 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 - 7.70 (m, 3H), 7.62 - 7.55 (m, 2H), 7.48 - 7.37 (m, 3H), 7.26 - 7.22 (m, 1H), 5.03 (dd, $J_1$ = 13.6 Hz, $J_2$ = 7.6 Hz, 1H), 1.50 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.41, 191.39, 164.03, 161.56, 138.31, 138.25, 135.92, 134.37, 130.50, 130.42, 129.80, 128.98, 125.05, 125.02, 121.27, 121.05, 115.90, 115.67, 65.29, 13.12. HRMS (ESI, $m/z$) calcd. for C$_{13}$H$_{13}$FO$_3$Sn [M+Na]$^+$ 315.0462, found 315.0461.

1-(3-fluorophenyl)-2-(phenylsulfonyl)propan-1-one (3da): Yellow oil liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 - 7.66 (m, 3H), 7.58 - 7.53 (m, 1H), 7.49 - 7.42 (m, 3H), 7.19 - 7.13 (m, 1H), 7.02 (ddd, $J_1$ = 11.6 Hz, $J_2$=8.3 Hz, $J_3$= 0.8 Hz, 1H), 5.15 (dd, $J_1$ = 6.8 Hz, $J_2$ = 0.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.98, 190.94, 162.78, 160.26, 136.82, 135.61, 135.52, 134.13, 131.13, 131.11, 129.55, 128.92, 125.64, 125.53, 124.81, 124.78, 116.88, 116.64, 69.20, 69.11, 12.39. HRMS (ESI, $m/z$) calcd. for C$_{13}$H$_{14}$FO$_3$S [M+H]$^+$ 293.0642, found 293.0641.

1-(4-chlorophenyl)-2-(phenylsulfonyl)propan-1-one (3ea): White solid, mp 148-150 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 - 7.91 (m, 2H), 7.79 - 7.76 (m, 2H), 7.69 - 7.65 (m, 1H), 7.55 - 7.51 (m, 2H), 7.48 - 7.44 (m, 2H), 5.10 (dd, $J_1$ = 13.6 Hz, $J_2$ = 6.8 Hz, 1H), 1.56 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.25, 140.80, 135.90, 134.57, 134.30, 130.56, 129.76, 129.09, 128.92, 65.14, 13.08. HRMS (ESI, $m/z$) calcd. for C$_{16}$H$_{13}$ClO$_3$Sn [M+Na]$^+$ 331.0166, found 331.0162.

2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3fa): White solid, mp 140-142 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J$ = 8.2 Hz, 2H), 7.79 - 7.74 (m, 4H), 7.70 - 7.66 (m, 1H), 7.56 - 7.52 (m, 2H), 5.15 (dd, $J_1$ = 14.0 Hz, $J_2$ = 6.8 Hz, 1H), 1.58 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.73, 138.90, 135.79, 135.34, 134.41, 129.74, 129.51, 129.00, 125.80, 125.76, 65.47, 13.02. HRMS (ESI, $m/z$) calcd. for C$_{16}$H$_{13}$FO$_3$Sn [M+Na]$^+$ 365.0432, found 365.0432.

2-(phenylsulfonyl)-1-(p-tolyl)propan-1-one (3ga): White solid, mp 103-104 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J$ = 8.2 Hz, 2H), 7.80 - 7.78 (m, 2H), 7.65 (t, $J$ = 7.0 Hz, 1H), 7.52 (t, $J$ = 7.8 Hz, 2H), 7.27 (d, $J$ = 9.4 Hz, 2H), 5.14 (dd, $J_1$ = 12.8 Hz, $J_2$ = 6.8 Hz, 1H), 2.42 (s, 3H), 1.56 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.89, 145.22, 136.18, 134.09, 133.78, 129.81, 129.45, 129.29, 128.81, 64.92, 21.69, 13.17. HRMS (ESI, $m/z$) calcd. for C$_{16}$H$_{13}$O$_3$Sn [M+Na]$^+$ 311.0712, found 311.0710.

2-(phenylsulfonyl)-1-(m-tolyl)propan-1-one (3ha): White solid, mp 83-84 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 - 7.86 (m, 4H), 7.57 (t, $J$ = 7.4 Hz, 1H), 7.44 (t, $J$ = 8.0 Hz, 2H), 7.34 - 7.26 (m, 2H), 5.09 (dd, $J_1$ = 14.0 Hz, $J_2$ = 6.8 Hz, 1H), 2.33 (s, 3H), 1.49 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.68, 138.66, 136.26, 134.92, 134.19, 129.84, 129.57, 128.86, 128.67, 126.41, 64.97, 21.34, 13.20. HRMS (ESI, $m/z$) calcd. for C$_{16}$H$_{13}$O$_3$Sn [M+Na]$^+$ 289.0893, found 289.0897.

1-(4-methoxyphenyl)-2-(phenylsulfonyl)propan-1-one (3ia): White solid, mp 75-75 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 - 7.96 (m, 2H), 7.80 - 7.77 (m, 2H), 7.64 - 7.62 (m, 1H), 7.54 - 7.50 (m, 2H), 6.96 - 6.93 (m, 2H), 5.11 (dd, $J_1$ = 14.0 Hz, $J_2$ = 7.2 Hz, 1H), 3.88 (s, 3H), 1.55 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.50, 164.38, 136.18, 134.07,
131.65, 129.80, 129.27, 128.79, 113.99, 64.79, 55.57, 13.17. HRMS (ESI, m/z) calcd. for C_{16}H_{12}O_{2}NaSNa [M+Na]^+ 327.0662, found 327.0658.

2-(phenylsulfonyl)-1-(thiophen-2-yl)propan-1-one (3ja): White solid, mp 109-111 °C. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.83 – 7.81 (m, 3H), 7.74 – 7.73 (m, 1H), 7.67 – 7.63 (m, 1H), 7.52 (t, \( J = 7.8 \) Hz, 2H), 7.17 – 7.14 (m, 1H), 4.90 (dd, \( J_1 = 10.4 \) Hz, \( J_2 = 6.8 \) Hz, 1H), 1.59 (d, \( J = 7.0 \) Hz, 3H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 184.50, 143.55, 135.99, 134.41, 134.23, 129.80, 128.89, 128.56, 67.04, 12.86. HRMS (ESI, m/z) calcd. for C\(_{16}\)H\(_{12}\)O\(_2\)NaS\(_2\) [M+Na]^+ 303.0132, found 303.0127.

1-(furan-2-yl)-2-(phenylsulfonyl)butan-1-one (3ka): White solid, mp 99-100 °C. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.81 – 7.78 (m, 2H), 7.64 – 7.59 (m, 2H), 7.52 – 7.48 (m, 2H), 7.29 (dd, \( J_1 = 3.6 \) Hz, \( J_2 = 0.8 \) Hz, 1H), 6.56 (dd, \( J_1 = 3.6 \) Hz, \( J_2 = 1.6 \) Hz, 1H), 4.79 (dd, \( J_1 = 11.2 \) Hz, \( J_2 = 4.0 \) Hz, 1H), 2.19 – 1.98 (m, 2H), 0.91 (t, \( J = 7.4 \) Hz, 3H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 180.16, 152.93, 147.85, 136.77, 134.08, 129.61, 128.83, 119.62, 113.06, 72.17, 20.94, 11.43. HRMS (ESI, m/z) calcd. for C\(_{16}\)H\(_{12}\)O\(_2\)NaSNa [M+Na]^+ 301.0505, found 301.0501.

1-phenyl-2-(phenylsulfonyl)butan-1-one (3la): White solid, mp 97-99 °C. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.97 – 7.95 (m, 2H), 7.79 – 7.77 (m, 2H), 7.66 – 7.58 (m, 2H), 7.54 – 7.46 (m, 4H), 5.01 (dd, \( J_1 = 10.8 \) Hz, \( J_2 = 3.6 \) Hz, 1H), 2.23 – 2.01 (m, 2H), 0.89 (t, \( J = 7.2 \) Hz, 3H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 192.59, 137.39, 136.57, 134.11, 133.97, 129.77, 128.92, 128.80, 128.76, 71.46, 22.01, 11.49. HRMS (ESI, m/z) calcd. for C\(_{16}\)H\(_{14}\)O\(_2\)SNa [M+Na]^+ 311.0712, found 311.0712.

1-phenyl-2-(phenylsulfonyl)ethaneone (3ma): White solid, mp 94-97 °C. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.96 – 7.89 (m, 4H), 7.69 – 7.60 (m, 2H), 7.57 – 7.53 (m, 2H), 7.50 – 7.46 (m, 2H), 4.74 (s, 2H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 187.91, 138.80, 135.77, 134.32, 134.19, 129.27, 129.17, 128.84, 128.58, 63.49. HRMS (ESI, m/z) calcd. for C\(_{16}\)H\(_{16}\)O\(_2\)SNa [M+Na]^+ 283.0399, found 283.0396.

2-(phenylsulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3na): Light yellow solid, mp 94-97 °C. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.98 (d, \( J = 7.9 \) Hz, 1H), 7.92 (d, \( J = 7.8 \) Hz, 2H), 7.67 (t, \( J = 7.0 \) Hz, 1H), 7.59 – 7.50 (m, 3H), 7.34 – 7.28 (m, 2H), 4.12 (t, \( J = 5.6 \) Hz, 1H), 3.55 – 3.47 (m, 1H), 3.03 – 2.96 (m, 1H), 2.90 – 2.83 (m, 1H), 2.70 – 2.62 (m, 1H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 188.63, 143.56, 139.00, 134.53, 134.02, 131.76, 129.13, 129.02, 128.97, 127.98, 127.09, 69.67, 26.61, 23.65. HRMS (ESI, m/z) calcd. for C\(_{10}\)H\(_8\)O\(_2\)SNa [M+Na]^+ 309.0556, found 309.0554.

(2-(phenylsulfonyl)ethene-1,1-diyl) dibenzene (4a): \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.50 (d, \( J = 7.6 \) Hz, 2H), 7.40 (t, \( J = 7.2 \) Hz, 1H), 7.30-7.18 (m, 8H), 7.13 (d, \( J = 7.6 \) Hz, 2H), 6.95 (s, 1H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 155.25, 141.50, 139.12, 135.49, 132.87, 130.37, 129.79, 128.91, 128.78, 128.71, 128.63, 128.24, 127.89, 127.66. HRMS (ESI, m/z) calcd. for C\(_{20}\)H\(_{17}\)O\(_2\)S [M+H]^+ 321.0944, found 321.0943.

Reference

5. Copies of NMR Spectra of All Products
**H NMR spectrum of product 3a**

**13C NMR spectrum of product 3a**
$^1$H NMR spectrum of product 3ab

$^{13}$C NMR spectrum of product 3ab
H NMR spectrum of product 3ac

\begin{center}
\includegraphics[width=\textwidth]{hnmr.png}
\end{center}

\textbf{1H NMR spectrum of product 3ac}

\begin{center}
\includegraphics[width=\textwidth]{cnmr.png}
\end{center}

\textbf{13C NMR spectrum of product 3ac}
H NMR spectrum of product 3ad

13C NMR spectrum of product 3ad
**H NMR spectrum of product 3ae**

**13C NMR spectrum of product 3ae**
$^1$H NMR spectrum of product 3af

$^{13}$C NMR spectrum of product 3af
$^1$H NMR spectrum of product 3ag

$^{13}$C NMR spectrum of product 3ag
$^{1}$H NMR spectrum of product 3ah

$^{13}$C NMR spectrum of product 3ah
$^1\text{H}$ NMR spectrum of product $3\text{ai}$

$^{13}\text{C}$ NMR spectrum of product $3\text{ai}$
**$^1$H NMR spectrum of product 3ba**

**$^{13}$C NMR spectrum of product 3ba**
$^1$H NMR spectrum of product 3ca

$^{13}$C NMR spectrum of product 3ca
$^{1}$$H$ NMR spectrum of product 3da

$^{13}C$ NMR spectrum of product 3da
$^1$H NMR spectrum of product 3ea

$^{13}$C NMR spectrum of product 3ea
$\text{H NMR spectrum of product 3fa}$

$\text{C NMR spectrum of product 3fa}$
H NMR spectrum of product 3ga

\[ \text{H NMR spectrum of product 3ga} \]

\[ \text{\textsuperscript{13}C NMR spectrum of product 3ga} \]
$^1$H NMR spectrum of product 3ha

$^{13}$C NMR spectrum of product 3ha
\[ \text{H NMR spectrum of product 3ia} \]

\[ \text{\^{13}C NMR spectrum of product 3ia} \]
$^1$H NMR spectrum of product 3ja

$^{13}$C NMR spectrum of product 3ja
$^1$H NMR spectrum of product 3ka

$^{13}$C NMR spectrum of product 3ka
H NMR spectrum of product 3la

\(^{13}\)C NMR spectrum of product 3la
$^1$H NMR spectrum of product 3ma

$^{13}$C NMR spectrum of product 3ma
$^{1}$H NMR spectrum of product 3na

$^{13}$C NMR spectrum of product 3na


**H NMR spectrum of product 4a**

**C NMR spectrum of product 4a**
6. Copies of HRMS Spectra of All Products

HRMS (ESI, m/z) calcd. for C_{16}H_{16}O_3Na [M+Na]^+ 311.0713, found 311.0713.

HRMS (ESI, m/z) calcd. for C_{15}H_{14}O_3Na [M+Na]^+ 297.0556, found 297.0559.
HRMS spectrum of product 3ac

HRMS (ESI, m/z) calcd. for C_{15}H_{13}ClO_3SNa [M+Na]^+ 315.0462, found 315.0461.

HRMS spectrum of product 3ad

HRMS (ESI, m/z) calcd. for C_{15}H_{13}ClO_3SNa [M+Na]^+ 331.0166, found 331.0166.
HRMS spectrum of product 3ae

HRMS (ESI, m/z) calcd. for C₁₀H₁₂BrO₃Na [M+Na]⁺ 376.9641, found 376.9642.

HRMS spectrum of product 3af

HRMS (ESI, m/z) calcd. for C₁₅H₁₃BrO₃Na [M+Na]⁺ 235.0399, found 235.0397.
HRMS (ESI, \textit{m/z}) calcd. for C_{16}H_{14}F_{3}O_{3}S [M+H]^+ 343.0610, found 343.0608.

HRMS spectrum of product 3ag

HRMS (ESI, \textit{m/z}) calcd. for C_{12}H_{15}O_{3}S [M+H]^+ 239.0736, found 239.0735.

HRMS spectrum of product 3ah
HRMS (ESI, m/z) calcd. for C_{19}H_{16}O_{3}SNa [M+Na]^+ 347.0712, found 347.0712.

HRMS spectrum of product 3ai

HRMS (ESI, m/z) calcd. for C_{15}H_{13}FO_{3}SNa [M+Na]^+ 315.0462, found 315.0464.

HRMS spectrum of product 3ba
HRMS (ESI, \(m/z\)) calcd. for $C_{15}H_{14}FO_3S$ [M+H]$^+$ 293.0642, found 293.0641.

HRMS spectrum of product 3ca

HRMS (ESI, \(m/z\)) calcd. for $C_{15}H_{13}FO_3SNa$ [M+Na]$^+$ 315.0462, found 315.0461.

HRMS spectrum of product 3da
HRMS (ESI, m/z) calcd. for C_{16}H_{13}ClO_3SNa [M+Na]^+ 331.0166, found 331.0162.

HRMS spectrum of product 3ea

HRMS (ESI, m/z) calcd. for C_{15}H_{13}ClO_3SNa [M+Na]^+ 365.0430, found 365.0432.

HRMS spectrum of product 3fa
HRMS (ESI, m/z) calcd. for C_{16}H_{16}O_{3}SNa [M+Na]^+ 311.0712, found 311.0710.

HRMS spectrum of product 3ga

HRMS (ESI, m/z) calcd. for C_{16}H_{17}O_{3}S [M+H]^+ 289.0893, found 289.0897.

HRMS spectrum of product 3ha
HRMS (ESI, m/z) calcd. for C_{16}H_{16}O_{3}Na [M+Na]^+ 327.0662, found 327.0658.

HRMS spectrum of product 3ia

HRMS (ESI, m/z) calcd. for C_{16}H_{16}O_{4}Na [M+Na]^+ 327.06, found 327.0658.

HRMS spectrum of product 3ja
HRMS (ESI, m/z) calcd. for C_{16}H_{16}O_{3}Na [M+Na]^+ 311.0712, found 311.0712.

HRMS spectrum of product 3ka

HRMS (ESI, m/z) calcd. for C_{14}H_{14}O_{4}SNa [M+Na]^+ 301.0505, found 301.0501.

HRMS spectrum of product 3la
HRMS (ESI, m/z) calcd. for C_{16}H_{14}O_{3}SNa [M+Na]^+ 309.0556, found 309.0554.

HRMS (ESI, m/z) calcd. for C_{14}H_{12}O_{3}SNa [M+Na]^+ 283.0399, found 283.0396.

HRMS spectrum of product 3ma

HRMS spectrum of product 3ma
HRMS spectrum of product 4a

7. Copy of HSQC Spectrum of 3aa
8. Copy of HMBC Spectrum of 3aa

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<th>C7</th>
<th>C8</th>
<th>C9</th>
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<th>C10</th>
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