Supporting Information

Asymmetric synthesis of 4-aryl-1,2,5-thiadiazolidin-3-one 1,1-dioxides by Pd-catalyzed hydrogenation of cyclic ketimines
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S0
1. General

All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. $^1$H NMR, $^{13}$C NMR, $^{31}$P NMR and $^{19}$F NMR spectra were recorded at room temperature in CDCl$_3$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Optical rotations were measured with JASCO P-1010 polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis.

2. General Procedure for Synthesis of Cyclic Ketimines 1

Cyclic ketimines 1 can be conveniently synthesized according to the known literature procedures. Among them, 1a, 1d and 1g-h are the known compounds. Following a known literature procedure,$^1$ to a solution of sulfamide (1.920 g, 20 mmol) in ethanol (30 mL) was slowly added sodium ethoxide (1.360 g, 20 mmol) in ethanol (5 mL). The suspension was stirred at room temperature for 15 min and then ethyl arylglyoxylate (20 mmol) in ethanol (15 mL) was added. After stirring for 15 min, the mixture was refluxed overnight and concentrated on a rotary evaporator. The residue was suspended in diethyl ether for 0.5 h and the resulting white solid was filtered, which was used for the next reaction without further purification. To a suspension of the above white solid (5.0 mmol) in dimethylformamide (10 mL) was added alkyl halide (7.5 mmol), and the mixture was stirred at room temperature for 24 h. Water was added to the mixture and it was extracted with ethyl acetate. The organic extracts were washed with water, brine, dried over anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with hexanes/ethyl acetate (100:1) to give the product 1.

2-ethyl-4-phenyl-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1b): unknown compound, white solid, m.p. = 133-134 °C, yield: 7%, R$_f$ = 0.60 (petroleum ether/ethyl acetate 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, $J = 7.7$ Hz, 2H), 7.74 (t, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 2H), 3.87 (q, $J = 7.3$ Hz, 2H), 1.46 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.6, 156.1, 136.4, 132.3, 129.5, 127.1, 37.6, 13.2. HRMS Calculated for C$_{10}$H$_{11}$N$_2$O$_3$S (M+H)$^+$ 239.0485, found: 239.0483.

2-benzyl-4-phenyl-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1c): unknown compound, white solid, m.p. = 134-135 °C, yield: 18%, R$_f$ = 0.46 (petroleum ether/ethyl acetate 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, $J = 7.4$ Hz, 2H), 7.74 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 2H), 7.52-7.45 (m, 2H), 7.43-7.31 (m, 3H), 4.91 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.6, 156.4, 136.6, 133.2, 132.4, 129.6, 129.2, 129.1, 129.0, 127.0, 45.8. HRMS Calculated for C$_{13}$H$_{10}$N$_2$O$_3$S (M+NH$_4$)$^+$ 318.0907, found: 318.0909.
2-methyl-4-(m-tolyl)-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1e): New compound, white solid, m.p. = 119-120 °C, yield: 26%, R_f = 0.48 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, J = 7.9 Hz, 1H), 8.35 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 3.32 (s, 3H), 2.45 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 165.0, 156.3, 139.6, 137.5, 132.5, 129.8, 129.5, 126.9, 26.4, 21.5. HRMS Calculated for C_{10}H_{11}N_2O_3S (M+H)^+ 239.0485, found: 239.0481.

2-methyl-4-(o-tolyl)-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1f): New compound, yellow solid, m.p. = 123-124 °C, yield: 22%, R_f = 0.28 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, J = 7.9 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.44-7.35 (m, 2H), 3.33 (s, 3H), 2.67 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.1, 156.6, 143.0, 134.9, 134.3, 132.7, 126.5, 125.2, 26.5, 22.7. HRMS Calculated for C_{10}H_{11}N_2O_3S (M+H)^+ 239.0485, found: 239.0486.

4-(4-bromophenyl)-2-methyl-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1i): New compound, yellowish solid, m.p. = 202-203 °C, yield: 37%, R_f = 0.51 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 3.33 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 164.1, 156.0, 133.5, 133.1, 132.9, 125.8, 26.5. HRMS Calculated for C_9H_8BrN_2O_3S [M+H]^+ 302.9434, found: 302.9433.

4-(4-methoxyphenyl)-2-methyl-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1j): New compound, greenish yellow solid, m.p. = 169-170 °C, yield: 16%, R_f = 0.33 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, J = 9.1 Hz, 2H), 7.03 (d, J = 9.1 Hz, 2H), 3.94 (s, 3H), 3.30 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.9, 163.3, 156.9, 135.3, 119.6, 115.3, 56.1, 26.3. HRMS Calculated for C_{10}H_{11}N_2O_4S [M+H]^+ 255.0434, found: 255.0435.

2-methyl-4-(naphthalen-2-yl)-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1k): New compound, yellow solid, m.p. = 209-210 °C, yield: 21%, R_f = 0.42 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 9.44 (s, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 3.36 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 164.4, 156.5, 137.2, 137.1, 132.7, 130.9, 130.9, 129.7, 128.3, 127.8, 125.3, 124.4, 26.5. HRMS Calculated for C_{13}H_{11}N_2O_3S [M+H]^+ 275.0485, found: 275.0485.
3. Screen of Optimizations for the Acid Additives

![Chemical Reaction]

<table>
<thead>
<tr>
<th>Acid additives</th>
<th>Yield (%)</th>
<th>Ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-CSA</td>
<td>96</td>
<td>94</td>
</tr>
<tr>
<td>TFA</td>
<td>23</td>
<td>92</td>
</tr>
<tr>
<td>PhCOOH</td>
<td>41</td>
<td>92</td>
</tr>
</tbody>
</table>

4. General Procedure for Asymmetric Hydrogenation

Pd(OCOCF\textsubscript{3})\textsubscript{2} (1.3 mg, 0.004 mmol) and (R\textsubscript{c},R\textsubscript{p})-WalPhos (4.5 mg, 0.0048 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, then the solvent was removed under vacuum to give the catalyst. In a glove box, to 1 (0.20 mmol) was added the above catalyst with 3.0 mL TFE. The hydrogenation was performed at 40 °C under hydrogen gas (600 psi) in a stainless steel autoclave for 12 h. After carefully releasing the hydrogen, the autoclave was opened and the reaction mixture was evaporated in vacuo. Flash chromatography on silica gel using dichloromethane/methanol 100:1 as the eluent gave the products 2.

(R)-2-methyl-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2a): known compound,\textsuperscript{2} yellow solid, m.p. = 69-70 °C, >99% yield, 98% ee, [\(\alpha\)]\textsuperscript{D} = -3.7 (c 0.90, CHCl\textsubscript{3}), R\textsubscript{f} = 0.48 (petroleum ether/ethyl acetate 3:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.47-7.33 (m, 5H), 5.78 (s, 1H), 5.16 (s, 1H), 3.08 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.6, 133.5, 129.6, 129.3, 127.3, 64.1, 25.8. HPLC (AD-H column, \textsuperscript{1}PrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): \(t_1\) = 11.9 min, \(t_2\) = 13.4 min (major). HRMS Calculated for C\textsubscript{9}H\textsubscript{11}N\textsubscript{2}O\textsubscript{3}S (M+H)\textsuperscript{+} 227.0485, found: 227.0486.

(R)-2-ethyl-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2b): known compound,\textsuperscript{2} yellow solid, m.p. = 94-95 °C, 98% yield, 96% ee, [\(\alpha\)]\textsuperscript{D} = +2.2 (c 0.94, CHCl\textsubscript{3}), R\textsubscript{f} = 0.48 (petroleum ether/ethyl acetate 3:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.57-7.35 (m, 5H), 5.34 (s, 1H), 5.20 (s, 1H), 3.71 (q, \(J\) = 7.3 Hz, 2H), 1.37 (t, \(J\) = 7.3 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.3, 133.6, 129.8, 129.5, 127.4, 63.9, 36.9, 13.6. HPLC (IC column, \textsuperscript{1}PrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): \(t_1\) = 11.5 min, \(t_2\) = 12.6 min (major). HRMS Calculated for C\textsubscript{10}H\textsubscript{13}N\textsubscript{2}O\textsubscript{3}S (M+H)\textsuperscript{+} 241.0641, found: 241.0643.

(R)-2-benzyl-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2c): New compound, white solid, m.p. = 82-83 °C, 94% yield, 94% ee, [\(\alpha\)]\textsuperscript{D} = +19.4 (c 1.14, CHCl\textsubscript{3}), R\textsubscript{f} = 0.48 (petroleum ether/ethyl acetate 3:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.53-7.28 (m, 10H), 5.27 (s, 1H), 5.16 (s, 1H), 3.07 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.3, 133.6, 129.8, 129.5, 127.4, 63.9, 36.9, 13.6. HPLC (IC column, \textsuperscript{1}PrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): \(t_1\) = 11.5 min, \(t_2\) = 12.6 min (major). HRMS Calculated for C\textsubscript{10}H\textsubscript{13}N\textsubscript{2}O\textsubscript{3}S (M+H)\textsuperscript{+} 241.0641, found: 241.0643.
12.1 min, t = 18.5 min, t_2 = 19.6 min (major). HRMS Calculated for C_{10}H_{13}N_{2}O_{3}S (M+H)^+ 303.0798, found: 303.0796.

(R)-2-methyl-4-(p-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2d): New compound, yellow solid, m.p. = 103-104 °C, >99% yield, 97% ee, [α]^{20D} = +3.5 (c 0.95, CHCl_3). R_<t> = 0.52 (petroleum ether/ethyl acetate 3:1). ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.27 (s, 1H), 5.18 (s, 1H), 3.15 (s, 3H), 2.36 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.7, 139.9, 130.4, 130.2, 127.3, 164.2, 25.9, 21.4. HPLC (AD-H column, PrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t_1 = 12.7 min, t_2 = 14.5 min (major). HRMS Calculated for C_{10}H_{13}N_{2}O_{3}S (M+H)^+ 241.0641, found: 241.0642.

(R)-2-methyl-4-(m-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2e): New compound, yellow solid, m.p. = 81-82 °C, 98% yield, 98% ee, [α]^{20D} = -2.4 (c 0.95, CHCl_3). R_<t> = 0.61 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.27 (m, 1H), 7.26-7.18 (m, 3H), 5.38 (s, 1H), 5.17 (s, 1H), 3.16 (s, 3H), 2.37 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.6, 139.5, 133.3, 130.6 129.4, 128.0, 124.5, 64.4, 25.9, 21.6. HPLC (AD-H column, PrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t_1 = 12.1 min, t_2 = 13.8 min (major). HRMS Calculated for C_{10}H_{13}N_{2}O_{3}S (M+H)^+ 241.0641, found: 241.0641.

(R)-2-methyl-4-(o-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2f): New compound, yellow solid, m.p. = 145-146 °C, 99% yield, 80% ee, [α]^{20D} = +28.6 (c 0.94, CHCl_3). R_<t> = 0.60 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.21 (m, 4H), 5.48 (s, 1H), 4.97 (s, 1H), 3.20 (s, 3H), 2.45 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 167.0, 137.5, 131.8, 131.6, 130.1, 127.4, 127.3, 61.9, 26.0, 19.6. HPLC (AS-H column, PrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t_1 = 13.1 min (major), t_2 = 16.6 min. HRMS Calculated for C_{10}H_{13}N_{2}O_{3}S (M+H)^+ 241.0641, found: 241.0643.

(R)-4-(4-fluorophenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2g): New compound, yellow solid, m.p. = 108-109 °C, 99% yield, 97% ee, [α]^{20D} = -7.9 (c 0.96, CHCl_3). R_<t> = 0.20 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.43 (m, 2H), 7.16-7.06 (m, 2H), 5.42 (s, 1H), 5.26 (s, 1H), 3.16 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.2, 163.5 (d, J_FC = 249.4 Hz), 129.3 (d, J_FC = 8.5 Hz), 129.1 (d, J_FC = 3.3 Hz), 116.5 (d, J_FC = 22.0 Hz), 63.5, 26.0. ^19F NMR (376 MHz, CDCl_3) δ -111.5. HPLC (AD-H column, PrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t_1 = 11.8 min, t_2 = 13.3 min (major). HRMS Calculated for C_{10}F_{10}N_{2}O_{3}S (M+H)^+ 245.0391, found: 245.0391.

(R)-4-(4-chlorophenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2h): New compound, yellow solid, m.p. = 100-101 °C, 99% yield, 96% ee, [α]^{20D} = -5.9 (c 0.97, CHCl_3). R_<t> = 0.26 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.33 (m, 4H), 5.66 (s, 1H), 5.23 (s, 1H), 3.14 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.0, 135.8, 131.8, 129.6, 128.6, 63.4, 26.0. HPLC (AD-H column, PrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): t_1 = 18.0 min, t_2 = 19.8 min (major). HRMS Calculated for C_{10}H_{10}ClN_{2}O_{3}S (M+H)^+ 261.0095, found: 261.0095.

(R)-4-(4-bromophenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2i): New compound,
yellow solid, m.p. = 95-96 °C, 96% yield, 94% ee, [α]D20 = -5.7 (c 1.21, CHCl3), Rf = 0.21 (DCM). 1H NMR (400 MHz, CDCl3) δ 7.55 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 5.46 (s, 1H), 5.23 (s, 1H), 3.15 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 166.0, 132.5, 132.3, 128.9, 124.0, 63.4, 26.0. HPLC (AD-H column, iPrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): t1 = 19.8 min, t2 = 21.4 min (major). HRMS Calculated for C9H10BrN2O3S (M+H)+ 304.9590, found: 304.9591.

(R)-4-(4-methoxyphenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2j): New compound, yellow solid, m.p. = 111-112 °C, 98% yield, 97% ee, [α]D20 = +8.1 (c 0.80, CHCl3), Rf = 0.50 (dichloromethane). 1H NMR (400 MHz, CDCl3) δ 7.36 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.20 (s, 1H), 5.08 (s, 1H), 3.81 (s, 3H), 3.18 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 166.9, 160.8, 128.9, 125.3, 114.9, 64.0, 55.6, 25.9. HPLC (AD-H column, iPrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t1 = 17.1 min, t2 = 18.6 min (major). HRMS Calculated for C10H13N2O4S (M+H)+ 257.0591, found: 257.0594.

(R)-2-methyl-4-(naphthalen-2-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2k): New compound, yellow solid, m.p. = 153-154 °C, 95% yield, 93% ee, [α]D20 = +2.0 (c 1.04, CHCl3), Rf = 0.42 (dichloromethane). 1H NMR (400 MHz, CDCl3) δ 7.90 (s, 1H), 7.88-7.80 (m, 3H), 7.56-7.44 (m, 3H), 5.51 (s, 1H), 5.35 (s, 1H), 3.16 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 166.4, 133.7, 133.2, 130.6, 129.6, 128.4, 128.0, 127.3, 127.1, 124.0, 64.5, 26.0. HPLC (OJ-H column, iPrOH/hexane 30/70, 0.7 mL/min, 220 nm, 30 °C): t1 = 37.6 min (major), t2 = 46.2 min. HRMS Calculated for C13H13N2O3S (M+H)+ 277.0641, found: 277.0641.

5. Gram Scale Experiment

Pd(OOCF3)2 (8.3 mg, 0.025 mmol) and (Rc,Rp)-Walphos (28 mg, 0.030 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, then, the solvent was removed under vacuum to give the catalyst. In a glove box, to the mixture of 1a (1.121 g, 5.0 mmol) and L-CSA (0.116 g, 0.5 mmol) was added the above catalyst with 25 mL TFE. The hydrogenation was performed at 40 °C under hydrogen (600 psi) in a stainless steel autoclave for 2.5 d. After carefully releasing the hydrogen, the autoclave was opened and the reaction mixture was evaporated in vacuo. Flash chromatography on silica gel using dichloromethane/methanol 100:1 as the eluent gave the product 2a with 97% yield and 97% ee.
6. Determination of the Absolute Configuration of 2a

To a suspension of LiAlH₄ (30 mg, 0.8 mmol, 2.0 equiv) in THF (2 mL), a solution of 2a (93 mg, 0.4 mmol, 1.0 equiv) in THF (4 mL) was added dropwise at 0 °C. After stirring for 10 min, the mixture was cooled, quenched with ice water and 10% sodium hydroxide was then added. The aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound 3a.

(R)-2-Amino-N-methyl-2-phenylacetamide: 30 mg, 45% yield, 95% ee, [α]²⁰_D = -104.16 (c 0.60, MeOH), [lit.]: [α]²⁰_D = +93.56 (c 0.79, MeOH) for the (S)-enantiomer], known compound, yellow oil, R_f = 0.20 (dichloromethane/methanol 15/1). ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.27 (m, 5H), 7.21 (brs, 1H), 4.58 (s, 1H), 2.78 (d, J = 4.9 Hz, 3H), 2.65 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 140.7, 129.0, 128.2, 127.1, 59.7, 26.2. HPLC (AS-H column, PrOH/hexane 30/70, 0.7 mL/min, 220 nm, 30 °C): t₁ = 16.3 min (major), t₂ = 23.3 min.

7. References

8. Copy of NMR and HPLC for the Compounds

1H NMR 2Z-1-15A in CDCl3

1b 1H NMR (400 MHz, CDCl3)
$^{13}$C NMR ZZ-1-15A in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)

![NMR spectrum](image-url)
$^1$H NMR ZZ-1-168 in CDCl$_3$

$^{1c}$ $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR ZZ-1-16B in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)

1c

S10
1H NMR ZZ-1-33B in CDCl3

1e 1H NMR (400 MHz, CDCl3)
$^{13}$C NMR ZZ-1-33B in CDCl$_3$

1e $^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{H NMR ZZ-1-528 in CDCl}_3$

$1H \text{ NMR (400 MHz, CDCl}_3$
$^{13}$C NMR ZZ-1-52B in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR ZZ-1-268 in CDCl$_3$
$^{13}$C NMR ZZ-1-26B in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR ZZ-1-23B in CDCl$_3$
$^{13}$C NMR ZZ-1-23B in CDCl$_3$
$^1$H NMR ZZ-1-S18 In CDCl$_3$
S20

$^{13}$C NMR of 1k in CDCl$_3$
$^{1}H$ NMR ZZ-1-17 in CDCl$_3$
$^{13}$C NMR ZZ-1-17 in CDCl$_3$

2a $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR ZZ-1-32 in CDCl$_3$

2b $^{1}$H NMR (400 MHz, CDCl$_3$)
$\text{EtN} \overset{\text{SO}}{\text{SO}} \overset{\text{NH}}{\text{NH}}$

$\text{2b} \overset{\text{13C NMR (100 MHz, CDCl₃)}}{\text{(100 MHz, CDCl₃)}}$

13C NMR ZZ-1-32 In CDCl₃

$\text{f1 (ppm)}$

$\begin{align*}
130.6 & \quad 130.0 \\
129.4 & \quad 128.8 \\
128.4 & \quad 128.0
\end{align*}$
$\text{BnNH} \cdot \text{NH}$

$\text{O}$

$\text{O}$

$2c \ H N M R \ (400 \ MHz, \ C D C l _ { 3 } )$

$1H \ N M R \ Z Z - 1 - 3 4 \ I n \ C D C l _ { 3 }$
$\text{13C NMR ZZ-1-34 in CDCl3}$

$2c$ $^{13}$C NMR (100 MHz, CDCl3)
1H NMR 2d in CDCl3

1H NMR 2d 1H NMR (400 MHz, CDCl3)
13C NMR 2Z-1-35 In CDCl3

2d 13C NMR (100 MHz, CDCl3)
$^{1}H$ NMR ZZ-1-48 in CDCl$_3$

2e $^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR Z2-1-48 in CDCl$_3$

2e $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR ZZ-1-S8 in CDCl3

2f 1H NMR (400 MHz, CDCl3)
$^{13}$C NMR 2f-58n CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR ZZ-1-41 in CDCl$_3$

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl$_3$)
13C NMR of compound 2g in CDCl₃.
$^{1}H$ NMR ZZ-1-27 in CDCl$_3$

$^{2}h\ {^1}H$ NMR (400 MHz, CDCl$_3$)
$\text{MeN}$

S37

$\text{Cl}$

$2h \ {^{13}C} \text{NMR (100 MHz, CDCl}_3)$

$13C \text{ NMR ZZ-1-27 in CDCl}_3$
1H NMR ZZ-1-39 in CDCl₃

2H NMR (400 MHz, CDCl₃)
$^{13}$C NMR Z2-1-39 in CDCl$_3$
$^1H$ NMR ZZ-1-36 in CDCl$_3$

2j $^1H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR ZZ-1-36 in CDCl$_3$
1H NMR ZZ-1-56 in CDCl₃

2k 1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR ZZ-1-56 in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{MeHN} \quad \text{NH}_2$

$3a \quad ^1\text{H NMR} \ (400 \text{ MHz}, \text{CDCl}_3)$

$1\text{H NMR} \ ZZ-1-75 \ ln \ \text{CDCl}_3$
$^{13}$C NMR 22-1-75 in CDCl$_3$

![Chemical Structure](image)

$^{13}$C NMR (100 MHz, CDCl$_3$)
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**Graphic:**

[Graph depicting chemical analysis]

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***End of Report***