Electronic Supporting Information

Palladium-Catalyzed Desulfitative Arylation of Azoles with Arylsulfonyl Hydrazides

Xinzhang Yu, Xingwei Li*, Boshun Wan*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

E-mail: bswan@dicp.ac.cn; xwli@dicp.ac.cn

Table of Contents

<table>
<thead>
<tr>
<th>Table of Contents</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>S-2</td>
</tr>
<tr>
<td>Experimental Section</td>
<td>S-2</td>
</tr>
<tr>
<td>Mechanism Experiments Data</td>
<td>S-3</td>
</tr>
<tr>
<td>Analytical Data</td>
<td>S-4</td>
</tr>
<tr>
<td>References</td>
<td>S-7</td>
</tr>
<tr>
<td>$^1$H and $^{13}$C spectra</td>
<td>S-8</td>
</tr>
</tbody>
</table>
General.
Commercially available reagents were used without further purification. Solvents were purified prior to use according to the standard methods. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. For TLC, silica gel GF-254 was used and visualized by fluorescence quenching under UV light. NMR spectra were recorded at room temperature in CDCl$_3$ on 400 MHz Bruker DRX-400 or 500 MHz Bruker DRX-500 NMR spectrometers. The chemical shifts for $^1$H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for CDCl$_3$). The chemical shifts for $^{13}$C NMR were recorded in ppm downfield using the central peak of CDCl$_3$ (77.16 ppm) as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications. The abbreviations $s$, $d$, $t$, $q$, and $m$ stand for singlet, doublet, triplet, quartet, and multiplet in that order. HRMS data were obtained with Micromass HPLC–Q–TOF mass spectrometer.

Experimental Section.

![Chemical Structure](image)

**Preparation of Arylsulfonyl Hydrazides.** Arylsulfonyl hydrazides were prepared according to a literature procedure.$^{[1]}$ Hydrazine monohydrate (80%) (275 mg, 4.4 mmol) was added water (260 mg) and was cooled to 0 °C. To this solution was added dropwise a solution of arylsulfonyl chloride (2.0 mmol) in THF (10 mL) at 0 °C. The mixture was further stirred at 0 °C for 30 min., then flowed by addition of diethyl ether (10 mL). The mixture was extracted with saturated brine (3 × 10 mL). The organic layer was dried over sodium sulfate, filtered through Celite. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. (Yield: 75-91 %)

![Chemical Structure](image)

**General procedure for Arylation of Azoles with Arylsulfonyl Hydrazides.** A flame-dried Schlenk tube with a magnetic stirring bar was charged with Pd(CH$_3$CN)$_2$Cl$_2$ (6.5 mg, 0.025 mmol), phenanthroline hydrate (6 mg, 0.03 mmol), Na$_2$CO$_3$ (80 mg, 0.75 mmol), azoles (0.5 mmol), arylsulfonyl hydrazide (0.75 mmol), Cu(OAc)$_2$ (545 mg, 3 mmol), DMSO (0.6 mL) and 1,4-dioxane (5 mL) in presence or absence of TBAB (32mg, 0.1 mmol) under N$_2$. The reaction mixture was stirred for 5 min. at room temperature, and then stirred at 100°C for 4.5 h. The reaction mixture was then cooled to ambient temperature, diluted with diethyl ether (20 mL), filtered through a Celite pad, and washed with 10-20 mL of diethyl ether. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.
**Experimental data for mechanistic studies**

1. Decomposition of TsNHNH$_2$*

   ![Equation Image]

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<td>Cu(OAc); (4 equiv.)</td>
<td>13% 25%</td>
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<td>2</td>
<td>Pd(CH$_3$CN)$_2$Cl$_2$ (10 mol%), Phen. H$_2$O (12 mol%).</td>
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<td>trace ---$^b$</td>
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<td>3</td>
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<td>Cu(OAc)$_2$ (4 equiv.)</td>
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*a Condition: 1a (0.5 mmol), catalyst, oxidant, Dioxane/DMSO (9:1) (6mL), 100 °C, N$_2$, 4h.

*b Isolated yield.

*c Not detected.

2. Effects of Radical Inhibitors.*

   ![Equation Image]

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<tr>
<td>2</td>
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<tr>
<td>3</td>
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*a Condition: 1a (0.5 mmol), 2a (1.5 equiv.), Pd(CH$_3$CN)$_2$Cl$_2$ (5 mol%), Phen.H$_2$O (6 mol%), Na$_2$CO$_3$ (1.5 equiv.), TBAB (0.2 equiv.), Cu(OAc)$_2$ (6 equiv.), additive (20 mol%).

$b$ HPLC yield.
Analytical Data

2-p-Tolybenzodioxazole (3a),[2] white solid, yield: 90%; 1H NMR (400 MHz, CDCl3) δ 8.15 (d, J = 8.2 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.61 – 7.54 (m, 1H), 7.38 – 7.28 (m, 4H), 2.44 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.4, 150.8, 142.3, 142.1, 129.7, 127.7, 127.6, 124.5, 124.5, 119.9, 110.6, 21.7.

5-Methyl-2-p-tolybenzodioxazole (3b),[2] white solid, yield: 92%; 1H NMR (400 MHz, CDCl3) δ 8.13 (d, J = 7.6 Hz, 2H), 7.54 (s, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.5, 151.1, 141.9, 140.1, 135.4, 129.7, 127.6, 125.8, 124.75, 119.3, 110.8, 21.9, 21.8.

6-Methyl-2-p-tolybenzodioxazole (3c), white solid, yield: 89%; 1H NMR (400 MHz, CDCl3) δ 8.15 – 8.08 (m, 2H), 7.62 (dd, J = 8.1, 2.0 Hz, 1H), 7.36 (s, 1H), 7.32 (d, J = 6.8 Hz, 2H), 7.15 (d, J = 8.1 Hz, 1H), 2.50 (d, J = 1.8 Hz, 3H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.0, 151.1, 141.9, 140.1, 135.4, 129.7, 127.6, 125.8, 124.75, 119.3, 110.8, 21.9, 21.8.

4-Methyl-2-p-tolybenzodioxazole (3d), pink solid, yield: 88%; 1H NMR (400 MHz, CDCl3) δ 8.16 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 162.65, 150.60, 141.83, 141.64, 130.52, 129.66, 127.69, 125.07, 124.84, 124.61, 107.86, 21.73, 16.69; RMS (ESI) calculated for C15H14NO+ (M+H): 224.1075, found 224.1079.

5-Chloro-2-p-tolybenzodioxazole (3e),[2] white solid, yield: 85%; 1H NMR (400 MHz, CDCl3) δ 8.12 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 5.8 Hz, 1H), 7.47 (dd, J = 11.6, 4.8 Hz, 1H), 7.37 – 7.27 (m, 3H), 2.44 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 164.6, 149.3, 143.4, 142.5, 129.9, 127.7, 125.1, 123.9, 119.8, 111.2, 21.7.

6-Nitro-2-p-tolybenzodioxazole (3f),[5] white solid, yield: 40%; 1H NMR (400 MHz, CDCl3) δ 8.44 (d, J = 2.1 Hz, 1H), 8.29 (dd, J = 8.8, 2.1 Hz, 1H), 8.14 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 167.90, 150.60, 141.83, 141.64, 130.52, 129.66, 127.69, 125.07, 124.84, 124.61, 107.86, 21.73, 16.69; RMS (ESI) calculated for C15H14NO+ (M+H): 224.1075, found 224.1079.

2-p-Tolyloxazole (3g),[6] colorless oil, yield: 88%; 1H NMR (400 MHz, CDCl3) δ 7.99 (d, J = 7.3 Hz, 2H), 7.71 (s, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.26 (s, 1H), 2.44 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 162.2, 140.6, 138.3, 129.5, 128.3, 126.3, 124.9, 21.5.

Ethyl 2-p-tolyloxazole-4-carboxylate (3h),[2] white solid, yield: 91%; 1H NMR (400 MHz, CDCl3) δ 8.24 (s, 1H), 7.99 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 162.7, 161.5, 143.4, 141.6, 134.6, 129.5, 126.9, 123.8, 61.3, 21.6 14.4.

5-Phenyl-2-p-tolyloxazole (3i),[8] white solid, yield: 84%; 1H NMR (400 MHz, CDCl3) δ
8.00 (d, J = 8.1 Hz, 2H), 7.72 (dd, J = 5.1, 3.3 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.37 – 7.26 (m, 3H), 2.41 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 161.4, 150.9, 140.6, 129.5, 128.9, 128.3, 127.6, 126.3, 124.8, 124.1, 123.4, 21.5.

5-(4-Methoxyphenyl)-2-p-tolyloxazole (3j).16 yellow solid, yield: 78%; 1H NMR (400 MHz, CDCl3) δ 6.98 (d, J = 7.3 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.96 (d, J = 7.5 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 160.8, 159.8, 151.0, 140.4, 129.5, 126.1, 125.7, 125.0, 121.9, 121.0, 114.4, 55.3, 21.5.

2-p-Tolythiazole (3k).23 yellow oil, yield: 87%; 1H NMR (500 MHz, CDCl3) δ 7.88 – 7.85 (m, 2H), 7.84 (d, J = 3.3 Hz, 1H), 7.27 (d, J = 3.3 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 168.7, 143.6, 140.3, 131.1, 129.7, 126.6, 118.4, 21.5.

4, 5-Dimethyl-2-p-tolythiazole (3l).21 white solid, yield: 71%; 1H NMR (400 MHz, CDCl3) δ 7.76 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.37 (d, J = 2.5 Hz, 9H); 13C NMR (100 MHz, CDCl3) δ 163.7, 149.1, 139.5, 131.5, 129.6, 126.1, 126.0, 21.4, 14.9, 11.5.

4-Methyl-2-p-tolythiazole (3m).22 colorless oil, yield 86%; 1H NMR (400 MHz, CDCl3) δ 7.87 – 7.80 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 0.9 Hz, 1H), 2.50 (d, J = 1.0 Hz, 3H), 2.37 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.8, 153.7, 140.0, 131.2, 129.6, 126.4, 113.0, 21.4, 17.3.

4-Methyl-2-p-toly-5-vinylthiazole (3n), yellow solid, m.p. 66-68 °C, yield: 43%; 1H NMR (400 MHz, CDCl3) δ 7.81 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.84 – 6.72 (m, 1H), 5.45 (d, J = 17.1 Hz, 1H), 5.22 (d, J = 10.9 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 164.7, 150.8, 140.3, 131.0, 130.9, 129.6, 126.9, 126.4, 115.3, 21.5, 15.4; HRMS (ESI) calculated for C13H13NS+ (M+H): 216.0847, found 216.0842.

2-(4-Methyl-2-p-tolythiazol-5-yl)ethyl acetate (3o), yellow oil, yield: 78%; 1H NMR (400 MHz, CDCl3) δ 7.74 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 4.21 (t, J = 6.7 Hz, 2H), 3.03 (t, J = 6.7 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 2.03 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 170.8, 165.0, 150.2, 139.9, 131.3, 129.6, 126.7, 126.2, 64.2, 26.1, 21.5, 21.0, 15.2; HRMS (ESI) calculated for C15H18NO,S+ (M+H): 276.1058, found 276.1054 (M+H).

2-p-Tolybenzo[d]thiazole (3p).22 white solid, yield: 71%; 1H NMR (400 MHz, CDCl3) δ 8.07 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 7.4 Hz, 2H), 7.90 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.31 (d, J = 7.2 Hz, 2H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 168.2, 154.2, 141.3, 135.0, 131.0, 129.7, 127.5, 126.2, 125.0, 123.0, 121.5, 21.5.

6-Nitro-2-p-tolybenzo[d]thiazole (3q).22 yellow solid, yield: 54%; 1H NMR (400 MHz, CD2Cl2) δ 8.81 (d, J = 2.2 Hz, 1H), 8.33 (dd, J = 9.0, 2.3 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H), 8.01 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 174.05, 158.07, 144.90, 143.16, 135.35, 130.23, 130.10, 128.00, 123.18, 121.96, 118.25, 21.75.
1,3,7-Trimethyl-8-p-tolyl-1H-purine-2,6-(3H,7H)-dione (3r), [3] white solid, yield: 93%; 1H NMR (400 MHz, CDCl3) δ 7.57 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 4.03 (s, 3H), 3.61 (s, 3H), 3.42 (s, 3H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 155.7, 152.5, 151.9, 148.4, 140.8, 129.7, 129.2, 125.7, 108.6, 34.0, 29.9, 28.1, 21.6.

2-Phenylbenz[d]oxazole (3s), [2] white solid, yield: 92%; 1H NMR (400 MHz, CDCl3) δ 8.26 (d, J = 3.1 Hz, 2H), 7.79 (d, J = 4.4 Hz, 1H), 7.57 (s, 1H), 7.53 (s, 3H), 7.41 – 7.30 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 163.1, 150.9, 142.2, 131.6, 129.0, 127.7, 127.3, 125.2, 124.7, 120.1, 110.7, 104.0, 77.5, 77.2, 76.8.

2-m-Tolylbenz[d]oxazole (3t), [2] white solid, yield: 86%; 1H NMR (400 MHz, CDCl3) δ 8.10 (s, 1H), 8.06 (d, J = 7.7 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.62 – 7.54 (m, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.38 – 7.31 (m, 3H), 2.46 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.4, 150.9, 142.3, 138.9, 132.5, 129.0, 128.3, 127.2, 125.2, 124.9, 124.7, 120.1, 110.7, 21.5.

2-(3,5-Dimethylphenyl)benz[d]oxazole (3u), [1] white solid, yield: 84%; 1H NMR (400 MHz, CDCl3) δ 7.90 (s, 2H), 7.81 – 7.74 (m, 1H), 7.62 – 7.54 (m, 1H), 7.35 (dd, J = 6.0, 3.3 Hz, 2H), 7.17 (s, 1H), 2.42 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 163.6, 150.8, 142.2, 138.7, 133.4, 127.0, 125.1, 124.6, 120.0, 110.6, 21.4.

2-o-Tolylbenz[d]oxazole (3v), [2] white solid, yield: 67%; 1H NMR (400 MHz, CDCl3) δ 8.20 (d, J = 7.3 Hz, 1H), 7.83 (d, J = 3.1 Hz, 1H), 7.60 (d, J = 3.6 Hz, 1H), 7.46 – 7.30 (m, 5H), 2.84 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.5, 150.4, 142.3, 139.0, 131.9, 131.0, 130.0, 126.3, 126.2, 125.1, 124.5, 120.2, 110.6, 22.3.

2-(4-Methoxyphenyl)benz[d]oxazole (3w), [2] white solid, yield: 86%; 1H NMR (400 MHz, CDCl3) δ 8.20 (d, J = 8.2 Hz, 2H), 7.73 (s, 1H), 7.55 (s, 1H), 7.33 (s, 2H), 7.03 (d, J = 8.1 Hz, 2H), 3.89 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.3, 162.5, 150.8, 142.5, 129.5, 124.7, 124.5, 119.8, 119.7, 114.5, 110.5, 55.5.

2-(Naphthalen-2-yl)benz[d]oxazole (3x), [4] white solid, yield: 90%; 1H NMR (400 MHz, CDCl3) δ 8.75 (s, 1H), 8.30 (d, J = 8.6 Hz, 1H), 7.95 (t, J = 8.1 Hz, 2H), 7.82 (ddd, J = 8.8, 8.1, 4.3 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.41 – 7.31 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 163.2, 150.9, 142.3, 134.8, 133.0, 129.0, 128.8, 128.2, 128.0, 127.8, 126.9, 125.2, 124.7, 124.5, 124.0, 120.1, 110.7.

2-(Naphthalen-1-yl)benz[d]oxazole (3y), [7] white solid, yield: 47%; 1H NMR (400 MHz, CDCl3) δ 8.75 (s, 1H), 8.30 (d, J = 8.6 Hz, 1H), 7.95 (t, J = 8.1 Hz, 2H), 7.82 (ddd, J = 8.8, 8.1, 4.3 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.41 – 7.31 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 163.2, 150.9, 142.3, 134.8, 133.0, 129.0, 128.8, 128.2, 127.96, 127.8, 126.9, 125.2, 124.7, 124.5, 124.0, 120.1, 110.7.

2-(4-tert-Butylphenyl)benz[d]oxazole (3z), [2] white solid, yield: 73%; 1H NMR (400 MHz, CDCl3) δ 8.25 – 8.14 (m, 2H), 7.81 – 7.73 (m, 1H), 7.63 – 7.51 (m, 3H), 7.40 – 7.29 (m, 2H), 1.38 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 163.3, 155.1, 150.8, 142.3, 127.6, 126.0, 124.9, 124.5,
2-(4-Chlorophenyl)benzo[d]oxazole (3aa) \(^2\) white solid, yield: 83%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (d, \(J = 7.4\) Hz, 2H), 7.77 (d, \(J = 3.4\) Hz, 1H), 7.58 (d, \(J = 3.4\) Hz, 1H), 7.51 (d, \(J = 7.6\) Hz, 2H), 7.37 (d, \(J = 3.3\) Hz, 2H); \(^1\)^1C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.1, 150.8, 142.1, 137.8, 129.3, 128.9, 125.7, 125.4, 124.8, 120.2, 110.7.

2-(4-(Trifluoromethyl)phenyl)benzo[d]oxazole (3ab), \(^4\) white solid, yield: 70%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.37 (d, \(J = 8.1\) Hz, 2H), 7.84 – 7.73 (m, 3H), 7.61 (dd, \(J = 5.1, 3.7\) Hz, 1H), 7.40 (dd, \(J = 6.6, 2.7\) Hz, 2H); \(^1\)^1C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.5, 150.9, 142.0, 133.01 (dd, \(J = 63.6, 31.0\) Hz), 130.5, 127.9, 125.9, 125.0, 122.5, 120.5, 110.8; \(^1\)^19F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -63.57.

2-(3-(Trifluoromethyl)phenyl)benzo[d]oxazole (3ac), \(^8\) white solid, yield: 87%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.53 (s, 1H), 8.43 (d, \(J = 7.2\) Hz, 1H), 7.78 (d, \(J = 5.9\) Hz, 2H), 7.64 – 7.53 (m, 1H), 7.41 – 7.31 (m, 2H); \(^1\)^1C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 161.60, 150.96, 142.02, 131.75 (q, \(J = 33.0\) Hz), 130.72, 129.64, 128.20, 128.01 (dd, \(J = 7.1, 3.5\) Hz), 125.83, 125.03, 124.61 (q, \(J = 3.7\) Hz), 122.77, 120.45, 110.88; \(^1\)^19F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -63.95.

2-(4-Bromophenyl)benzo[d]oxazole (3ad): \(^2\) white solid, yield: 65%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (d, \(J = 8.6\) Hz, 2H), 7.82 – 7.72 (m, 1H), 7.65 (d, \(J = 8.6\) Hz, 2H), 7.61 – 7.53 (m, 1H), 7.41 – 7.31 (m, 2H); \(^1\)^1C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.3, 150.9, 142.2, 132.4, 129.1, 126.4, 126.2, 125.5, 124.9, 120.3, 110.8.

2-(4-Fluorophenyl)benzo[d]oxazole (3ae), \(^2\) white solid, yield: 92%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.26 (dd, \(J = 8.7, 5.4\) Hz, 2H), 7.83 – 7.72 (m, 1H), 7.57 (dt, \(J = 7.5, 3.9\) Hz, 1H), 7.42 – 7.31 (m, 2H), 7.21 (t, \(J = 8.6\) Hz, 2H); \(^1\)^1C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.86 (d, \(J = 252.9\) Hz), 162.17, 150.83, 142.15, 129.87 (d, \(J = 8.8\) Hz), 125.17, 124.70, 123.58, 120.06, 116.21 (d, \(J = 22.2\) Hz), 110.61; \(^1\)^19F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -108.06.

References:
$^1$H and $^{13}$C spectra

$^1$H NMR (400 MHz, CDCl$_3$)

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

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -200.0, max = 200.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

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<td>224.1075</td>
<td>0.4</td>
<td>1.8</td>
<td>9.5</td>
<td>16.4</td>
<td>C15H14NO</td>
</tr>
</tbody>
</table>

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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S-13
$^1$H NMR (400 MHz, CDCl$_3$)

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

$3h$

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

$\text{OEt}$

$3h$

$^{13}\text{C NMR (100 MHz, CDCl}_3)$
3m

$^1$H NMR (400 MHz, CDCl$_3$)

3m

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

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -200.0, max = 200.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-150  H: 0-150  N: 1-1  S: 1-1

33447
12051721 46 (0.857) AM (Cen,2, 80.00, H,5.0000,0.00,1.000); Sm (Mn,2x1.00); Cm (44.57)

% 0 100 139.0937 139.1368 218.0910 217.0960 303.1236 317.1311 385.0849 401.0594 402.0618 549.0843 570.0527 695.1578 721.1646 747.1784 793.1353
1148.43 8.36e3

Minimum: 5.0 5.0 5.0 5.0
Maximum: -200.0 200.0 200.0

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  Formula
216.0842  216.0847  -0.5  -2.3  7.5  100.2  Cl3H14N3S
Elemental Composition Report

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -200.0, max = 200.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-150  H: 0-150  N: 1-1  O: 2-2  S: 1-1

3285T
12051722 ? (0.130 AM (Cen,2, 80.00, H,5000.0,0.0,1.00); Sm (Mn, 2x1.00); Cm (7:10)
1: TOF MS ES+

11:53:47
1.86k3

Minimum: 150
Maximum: 150

Mass     Calc. Mass     mDa     PPM     DBE     i-FIT
276.1054 276.1058     -0.4     -1.4     7.5     0.5     C15 H18 N O2 S
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$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
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**1H NMR (400 MHz, CDCl₃)**

![1H NMR spectrum for compound 3u](image1)

**13C NMR (100 MHz, CDCl₃)**

![13C NMR spectrum for compound 3u](image2)

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S-31
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
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**$^1$H NMR (400 MHz, CDCl$_3$)**

**$^{13}$C NMR (100 MHz, CDCl$_3$)**
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$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
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$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**3ab**

$^1$H NMR (400 MHz, CDCl$_3$)

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

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$\text{3ab}$

$^{19}\text{F NMR (377 MHz, CDCl$_3$)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)
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$\text{F}$

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$^{19}$F NMR (377 MHz, CDCl$_3$)