Ru(II)-Catalyzed Intermolecular C-H Amidation of Weakly Coordinating Ketones

(Supporting Information)

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Table of Contents

<table>
<thead>
<tr>
<th>General remarks</th>
<th>S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental procedure and characterization data</td>
<td>S3-S17</td>
</tr>
<tr>
<td>References</td>
<td>S18</td>
</tr>
<tr>
<td>$^1$H NMR and $^{13}$C NMR spectra for products</td>
<td>S19-S68</td>
</tr>
</tbody>
</table>
General remarks

All manipulations were conducted with schlenk tubes. $^1$H-NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with CDCl$_3$. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
Experimental procedure and characterization data

1) **N-(2-Isobutrylphenyl)-4-methylbenzenesulfonamide (3a)**

**Typical procedure:**
The reaction of isobutyrophenone (1a) (0.2 mmol, 30 uL), 4-methylbenzenesulfonyl azide (2a) (0.4 mmol, 81 uL), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 2.9 mg), AgSbF₆ (10 mol %, 6.9 mg), Cu(OAc)₂ (30 mol %, 10.9 mg), in 1.0 mL DCE at 80 °C under Ar for 21 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 46.7 mg (74%) of 3a as solid: ¹H NMR (400 MHz, CDCl₃): δ 11.39 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.73-7.68 (m, 3H), 7.44 (t, J = 8.4 Hz, 1H), 7.19 (t, J = 8.4 Hz, 2H), 7.08 (d, J = 7.2 Hz, 1H), 3.55-3.45 (m, 1H), 2.34 (s, 3H), 1.08 (d, J = 6.8 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 208.6, 143.7, 140.3, 136.6, 134.4, 130.6, 129.5, 127.1, 122.7, 121.7, 120.1, 36.0, 21.4, 19.1 ppm. IR (KBr) νmax = 3087, 2975, 1648, 1601, 1492, 1165, 565 cm⁻¹. HRMS m/z (ESI): Calcd. for C₁₇H₂₀NO₃S [M+H]+ 318.1164, Found: 318.1164.

2) **4-Methyl-N-(2-pivaloylphenyl)benzenesulfonamide (3b)**

The reaction of 2,2-dimethyl-1-phenylpropan-1-one (1b) (0.3 mmol, 49.7 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5
mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 82.5 mg (83%) of 3b as solid: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.78 (s, 1H), 7.75 (d, $J = 9.2$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 2H), 2.34 (s, 3H), 1.14 (s, 9H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 210.9, 143.7, 137.6, 136.4, 132.5, 129.5, 129.2, 127.0, 126.0, 123.1, 123.0, 44.7, 28.2, 21.3 ppm. MS (70 eV): m/z (%): 331.1 (7) [M$^+$], 274.1 (100).

3) 4-Methyl-N-(2-propionylphenyl)benzenesulfonamide (3c)

The reaction of propiophenone (1c) (0.3 mmol, 40.7 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru($p$-Cymene)Cl$_2$]$_2$ (2.5 mol %, 4.3 mg), AgSbF$_6$ (10 mol %, 10.4 mg), Cu(OAc)$_2$ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 77.0 mg (85%) of 3c as solid: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.44 (s, 1H), 7.80 (d, $J = 6.8$ Hz, 1H), 7.71-7.66 (m, 3H), 7.43 (t, $J = 8.8$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 2.91 (q, $J = 7.2$ Hz, 2H), 2.34 (s, 3H), 1.12 (t, $J = 6.8$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 204.9, 143.7, 139.7, 136.5, 134.4, 130.7, 129.5, 127.1, 122.6, 122.2, 119.4, 32.7, 21.3, 8.1 ppm. IR:(KBr) $\nu_{\text{max}}$ = 3434, 2977, 1983, 1817, 1650, 1455, 929, 662 cm$^{-1}$. HRMS m/z (ESI): Calcd. for C$_{16}$H$_{18}$NO$_3$S [M+H]$^+$ 304.1007, Found: 304.1002.

4) N-(2-Butyrylphenyl)-4-methylbenzenesulfonamide (3d)

The reaction of 1-phenylbutan-1-one (1d) (0.3 mmol, 44.9 mg),
4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl]_2 (2.5 mol %, 4.3 mg), AgSbF_6 (10 mol %, 10.4 mg), Cu(OAc)_2 (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 38 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 76.9 mg (81%) of 3d as solid: ^1H NMR (400 MHz, CDCl_3): δ 11.45 (s, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.70-7.67 (m, 3H), 7.43 (t, J = 8.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 8.0 Hz, 1H), 2.85 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.69-1.60 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H) ppm. ^13C NMR (100 MHz, CDCl_3): δ 204.5, 143.7, 139.8, 136.5, 134.4, 130.9, 129.5, 127.1, 122.6, 122.4, 119.5, 41.4, 21.3, 17.7, 13.5 ppm. MS (70 eV): m/z (%): 317.1 (35) [M]^+, 91.1 (100).

5) 4-Methyl-N-(2-pentanoylphenyl)benzenesulfonamide (3e)

The reaction of 1-phenylpentan-1-one (1e) (0.3 mmol, 49.2 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl]_2 (2.5 mol %, 4.3 mg), AgSbF_6 (10 mol %, 10.4 mg), Cu(OAc)_2 (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 64.6 mg (65%) of 3e as solid: ^1H NMR (400 MHz, CDCl_3): δ 11.43 (s, 1H), 7.80 (d, J = 6.8 Hz, 1H), 7.70-7.68 (m, 3H), 7.43 (t, J = 6.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.2 Hz, 1H), 2.86 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.62-1.54 (m, 2H), 1.37-1.29 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H) ppm. ^13C NMR (100 MHz, CDCl_3): δ 204.7, 143.7, 139.7, 136.5, 134.4, 130.9, 129.5, 127.1, 122.6, 122.4, 119.6, 39.2, 26.4, 22.1, 21.3, 13.7 ppm. MS (70 eV): m/z (%): 331.1 (30) [M]^+, 91.1 (100).
6) N-(2-Hexanoylphenyl)-4-methylbenzenesulfonamide (3f)

The reaction of 1-phenylhexan-1-one (1f) (0.3 mmol, 54.0 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 38 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 73.45 mg (71%) of 3f as solid: ¹H NMR (400 MHz, CDCl₃): δ 11.35 (s, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.62-7.59 (m, 3H), 7.35 (t, J = 6.8 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 2.77 (t, J = 7.2 Hz, 2H), 2.26 (s, 3H), 1.56-1.48 (m, 2H), 1.27-1.17 (m, 4H), 0.82 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 204.7, 143.7, 139.8, 136.5, 134.4, 130.9, 129.5, 127.1, 122.7, 122.4, 119.5, 39.5, 31.2, 24.0, 22.3, 21.3, 13.8 ppm. IR (KBr) v_max = 3062, 2956, 1712, 1649, 1493, 1168, 918, 562 cm⁻¹.


7) N-(2-Heptanoylphenyl)-4-methylbenzenesulfonamide (3g)

The reaction of 1-phenylheptan-1-one (1g) (0.3 mmol, 58.3 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 30 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 80.9 mg (75%) of 3g as solid: ¹H NMR (400 MHz, CDCl₃): δ 11.35 (s, 1H), 7.71 (d, J = 6.8
Hz, 1H), 7.61-7.59 (m, 3H), 7.34 (t, \( J = 7.2 \) Hz, 1H), 7.11 (d, \( J = 4.0 \) Hz, 2H), 6.97 (t, \( J = 8.0 \) Hz, 1H), 2.77 (t, \( J = 7.2 \) Hz, 2H), 2.25 (s, 3H), 1.53-1.47 (m, 2H), 1.25-1.16 (m, 6H), 0.80 (t, \( J = 6.4 \) Hz, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 204.7, 143.6, 139.8, 136.5, 134.4, 130.9, 129.4, 127.1, 122.7, 122.4, 119.5, 39.5, 31.5, 28.7, 24.3, 22.3, 21.3, 13.9 ppm.

IR (KBr) \( \nu_{\text{max}} \) = 3430, 3084, 1740, 1649, 1495, 1158, 930, 568 cm\(^{-1}\).

HRMS m/z (ESI): Calcd. for \( \text{C}_{20}\text{H}_{26}\text{NO}_3\text{S} \) [M+H]\(^{+}\) 360.1633, Found: 360.1631.

8) N-(2-(Cyclohexanecarbonyl)phenyl)-4-methylbenzenesulfonamide (3h) \(^4\)

The reaction of cyclohexyl(phenyl)methanone (1h) (0.3 mmol, 57.6 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 \( \mu \)L), [Ru(\( p \)-Cymene)Cl\(_2\)]\(_2\) (2.5 mol \%, 4.3 mg), AgSbF\(_6\) (10 mol \%, 10.4 mg), Cu(OAc)\(_2\) (30 mol \%, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 86.6 mg (81\%) of 3h as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 11.39 (s, 1H), 7.79 (d, \( J = 6.8 \) Hz, 1H), 7.72-7.66 (m, 3H), 7.43 (d, \( J = 8.4 \) Hz, 1H), 7.19 (d, \( J = 8.0 \) Hz, 2H), 7.08 (t, \( J = 8.0 \) Hz, 1H), 3.21-3.15 (m, 1H), 2.33 (s, 3H), 1.80-1.77 (m, 2H), 1.73-1.68 (m, 3H), 1.35-1.18 (m, 5H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 207.9, 143.6, 140.1, 136.6, 134.2, 130.5, 129.4, 127.1, 122.8, 121.9, 120.1, 46.2, 29.3, 25.7, 25.5, 21.3 ppm.

MS (70 eV): m/z (%): 357.1 (25) [M]\(^{+}\), 274.0 (100);

9) N-(2-(Cyclopentanecarbonyl)phenyl)-4-methylbenzenesulfonamide (3i)
The reaction of cyclopentyl(phenyl)methanone (1i) (0.3 mmol, 54.5 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 μL), [Ru(\(p\)-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 60.4 mg (59%) of 3i as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 11.41 (s, 1H), 7.84 (d, \(J = 6.8\) Hz, 1H), 7.71-7.66 (m, 3H), 7.43 (t, \(J = 7.2\) Hz, 1H), 7.18 (d, \(J = 8.0\) Hz, 2H), 7.08 (t, \(J = 6.8\) Hz, 1H), 3.66-3.59 (m, 1H), 2.34 (s, 3H), 1.84-1.76 (m, 2H), 1.70-1.58 (m, 6H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 206.9, 143.6, 140.0, 136.6, 134.1, 131.0, 129.4, 127.1, 122.8, 122.6, 120.1, 46.9, 30.0, 26.1, 21.3 ppm. IR: (KBr) \(\nu_{\text{max}}\) = 3441, 2951, 1738, 1644, 1491, 1156, 659, 566 cm\(^{-1}\). HRMS m/z (ESI): Calcd. for C\(_{19}\)H\(_{22}\)NO\(_3\)S [M+H]\(^+\) 344.1320, Found: 344.1321.

Electronic Supplementary Material (ESI) for Chemical Communications
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The reaction of cyclobutyl(phenyl)methanone (1j) (0.3 mmol, 49.6 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 μL), [Ru(\(p\)-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 63.1 mg (64%) of 3j as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 11.49 (s, 1H), 7.71-7.67 (m, 3H), 7.60 (d, \(J = 6.8\) Hz, 1H), 7.41 (t, \(J = 7.2\) Hz, 1H), 7.20 (d, \(J = 8.0\) Hz, 2H), 7.03 (t, \(J = 8.4\) Hz, 1H), 3.94-3.86 (m, 1H), 2.34 (s, 3H), 2.25-2.19 (m, 4H), 3.08-1.97 (m, 1H), 1.86-1.77 (m, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 205.1, 143.7, 140.1, 136.5, 134.3, 130.8, 129.4, 127.1, 122.7, 121.0, 119.7, 42.9, 25.0, 21.3, 17.7 ppm. IR: (KBr) \(\nu_{\text{max}}\) = 3452, 2948, 1710, 1639, 1600, 1453, 934, 663 cm\(^{-1}\). HRMS m/z (ESI): Calcd. for C\(_{18}\)H\(_{20}\)NO\(_3\)S [M+H]\(^+\) 330.1164, Found: 330.1165.
11) N-(2-(Cyclopropanecarbonyl)phenyl)-4-methylbenzenesulfonamide (3k) \(^{4,5}\)

The reaction of cyclopropyl(phenyl)methanone (1k) (0.3 mmol, 45.2 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 38 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 76.0 mg (80%) of 3k as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.21 (s, 1H), 7.98 (d, \(J = 6.8\) Hz, 1H), 7.67-7.65 (m, 3H), 7.44 (t, \(J = 8.4\) Hz, 1H), 7.19 (d, \(J = 8.0\) Hz, 2H), 7.10 (t, \(J = 8.0\) Hz, 1H), 2.54-2.47 (m, 1H), 2.34 (s, 3H), 1.18-1.45 (m, 2H), 1.03-0.99 (m, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 203.7, 143.6, 139.0, 136.4, 134.1, 130.8, 129.4, 127.0, 124.0, 122.9, 119.8, 21.3, 18.0, 12.3 ppm. MS (70 eV): m/z (%): 315.1 (70) [M]\(^+\), 132.0 (100).

12)

N-(2-(Cyclopropanecarbonyl)-5-methoxyphenyl)-4-methylbenzenesulfonamide (3l) \(^6\)

The reaction of cyclopropyl(4-methoxyphenyl)methanone (1l) (0.3 mmol, 53.9 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 33.2 mg (32%) of 3l as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.84 (s, 1H), 7.93 (d, \(J = 9.2\) Hz,
1H), 7.72 (d, J = 8.4 Hz, 2H), 7.22-7.17 (m, 3H), 6.59-6.56 (m, 1H), 3.81 (s, 3H), 2.51-2.45 (m, 1H), 2.35 (s, 3H), 1.18-1.14 (m, 2H), 1.03-0.95 (m, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 202.0, 164.0, 143.7, 142.0, 136.6, 133.0, 129.5, 127.2, 116.7, 109.1, 103.3, 55.5, 21.4, 17.4, 11.6 ppm. MS (70 eV): m/z (%): 345.1 (50) [M]\(^+\), 91.0.

13) N-(2-Acetyl-5-methoxyphenyl)-4-methylbenzenesulfonamide (3m)

The reaction of 1-(4-methoxyphenyl)ethanone (1m) (0.3 mmol, 46.0 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 48 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 28.9 mg (30%) of 3m as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.90 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.24-7.17 (m, 3H), 6.54-6.51 (m, 1H), 3.81 (s, 3H), 2.51 (s, 3H), 2.36 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 200.7, 164.3, 143.2, 142.7, 136.5, 133.9, 130.2, 129.6, 127.4, 127.2, 115.4, 108.9, 102.6, 55.5, 27.7, 21.4 ppm. IR:(KBr) \(\nu_{max}\) = 3267, 2922, 1689, 1640, 1569, 1265, 1090, 660 cm\(^{-1}\). HRMS m/z (ESI): Calcd. for C\(_{16}\)H\(_{18}\)NO\(_4\)S [M+H]\(^+\) 320.0957, Found: 320.0958.

14) N-(2-Acetyl-5-fluorophenyl)-4-methylbenzenesulfonamide (3n)

The reaction of 1-(4-fluorophenyl)ethanone (1n) (0.3 mmol, 42.3 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 48 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 28.9 mg (30%) of 3n as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.90 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.24-7.17 (m, 3H), 6.54-6.51 (m, 1H), 3.81 (s, 3H), 2.51 (s, 3H), 2.36 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 200.7, 164.3, 143.2, 142.7, 136.5, 133.9, 130.2, 129.6, 127.4, 127.2, 115.4, 108.9, 102.6, 55.5, 27.7, 21.4 ppm. IR:(KBr) \(\nu_{max}\) = 3267, 2922, 1689, 1640, 1569, 1265, 1090, 660 cm\(^{-1}\). HRMS m/z (ESI): Calcd. for C\(_{16}\)H\(_{18}\)NO\(_4\)S [M+H]\(^+\) 320.0957, Found: 320.0958.
mol %, 4.3 mg), AgSbF$_6$ (10 mol %, 10.4 mg), Cu(OAc)$_2$ (30 mol %, 16.4 mg), in 1.5 mL DCE at 100 °C under Ar for 48 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 65.7 mg (71%) of 3n as solid: $^1$H NMR (400 MHz, CDCl$_3$): δ 11.80 (s, 1H), 7.85-7.82 (m, 1H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.42-7.38 (m, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.72 (d, $J = 9.2$ Hz, 1H), 2.56 (s, 3H), 2.37 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 201.1, 165.9 (d, $J = 254.8$ Hz), 142.8 (d, $J = 11.2$ Hz), 134.6 (d, $J = 11.0$ Hz), 118.3 (d, $J = 1.9$ Hz), 109.6 (d, $J = 22.1$ Hz), 105.4 (d, $J = 26.9$ Hz), 28.0, 21.4 ppm. IR:(KBr) $\nu_{\text{max}}$ = 3443, 1941, 1650, 1588, 1159, 894, 820, 657 cm$^{-1}$. HRMS m/z (ESI): Calcd. for C$_{15}$H$_{15}$FNO$_3$S [M+H]$^+$ 308.0757, Found: 308.0757.

![Image of 3n](image-url)

**15) N-(2-Acetyl-5-chlorophenyl)-4-methylbenzenesulfonamide (3o)**

The reaction of 1-(4-chlorophenyl)ethanone (1o) (0.3 mmol, 47.3 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl$_2$)$_2$ (2.5 mol %, 4.3 mg), AgSbF$_6$ (10 mol %, 10.4 mg), Cu(OAc)$_2$ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 36 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 64.1 mg (66%) of 3o as solid: $^1$H NMR (400 MHz, CDCl$_3$): δ 11.59 (s, 1H), 7.75-7.69 (m, 4H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.69 (t, $J = 6.4$ Hz, 1H), 2.55 (s, 3H), 2.37 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 201.4, 144.2, 141.2, 141.0, 136.2, 133.0, 129.7, 127.1, 122.6, 120.1, 118.4, 28.0, 21.4 ppm. MS (70 eV): m/z (%): 323.0 (22) [M]$^+$, 91.1 (100).

![Image of 3o](image-url)
16) N-(2-Acetyl-5-bromophenyl)-4-methylbenzenesulfonamide (3p)

The reaction of 1-(4-bromophenyl)ethanone (1p) (0.3 mmol, 60.9 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 100 °C under Ar for 48 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 50.7 mg (46%) of 3p as solid: ¹H NMR (400 MHz, CDCl₃): δ 11.54 (s, 1H), 7.87 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.8 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.18-7.15 (m, 1H), 2.54 (s, 3H), 2.37 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 201.6, 144.2, 141.0, 136.1, 129.7, 127.1, 125.6, 121.5, 120.5, 28.0, 21.4 ppm. IR:(KBr) νmax 3427, 2922, 1644, 1491, 1166, 1090, 930, 661 cm⁻¹. HRMS m/z (ESI): Calcd. for C₁₅H₁₅BrNO₃S [M+H]+ 367.9956, Found: 367.9956.

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17) N-(3-Acetyl-naphthalen-2-yl)-4-methylbenzenesulfonamide (3q)

The reaction of 1-(naphthalen-2-yl)ethanone (1q) (0.3 mmol, 51.6 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 66.5 mg (65%) of 3q as solid: ¹H NMR (400 MHz, CDCl₃): δ 11.02 (s, 1H), 8.31 (s, 1H), 8.00 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.72-7.68 (m, 3H), 7.55 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 6.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 2.63 (s, 3H), 2.29 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 202.3, 143.6, 136.2, 135.9, 134.8, 134.3, 129.8, 129.4, 128.9, 128.5, 127.2, 127.1, 125.8, 123.2, 117.0, 27.9, 21.3 ppm. IR:(KBr) νmax = 3429, 3088, 2919, 1654, 1597, 1156, 665 cm⁻¹. HRMS m/z (ESI): Calcd. for C₁₉H₁₈NO₃S [M+H]+ 340.1007, Found: 340.1005.
18) N-(2-Benzoylphenyl)-4-methylbenzenesulfonamide (3r)\(^3,8\)

The reaction of benzophenone (1r) (0.3 mmol, 55.8 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 30 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 78.0 mg (74%) of 3r as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 9.99 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.58-7.49 (m, 4H), 7.42-7.36 (m, 5H), 7.10 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.4 Hz, 2H), 2.22 (s, 3H) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 198.4, 143.6, 138.8, 137.4, 135.7, 133.6, 132.9, 132.5, 129.7, 129.4, 127.9, 127.0, 126.2, 123.4, 123.0, 21.2 ppm. MS (70 eV): m/z (%): 351.1 (35) [M]+, 91.0 (100).

19) N-(5-Methoxy-2-(4-methoxybenzoyl)phenyl)-4-methylbenzenesulfonamide (3s)

The reaction of bis(4-methoxyphenyl)methanone (1s) (0.3 mmol, 74.2 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru(p-Cymene)Cl\(_2\)]\(_2\) (2.5 mol %, 4.3 mg), AgSbF\(_6\) (10 mol %, 10.4 mg), Cu(OAc)\(_2\) (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 90.1 mg (73%) of 3s as solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 10.64 (s, 1H), 7.62 (d, J = 7.6 Hz, 2H), 7.41-7.36 (m, 3H), 7.27 (s, 1H), 7.08 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 8.8 Hz, H), 3.87 (s, 3H), 3.85 (s, 3H), 2.27 (s, 3H) ppm. \(^13\)C NMR
(100 MHz, CDCl$_3$): $\delta$ 196.4, 163.4, 162.9, 143.6, 141.6, 135.9, 135.1, 131.9, 130.6, 129.4, 127.1, 118.5, 113.2, 109.1, 106.4, 55.5, 55.4, 21.2 ppm. IR:(KBr) $\nu_{\text{max}}$ = 344, 3222, 1921, 1684, 1572, 1159, 852, 705 cm$^{-1}$. HRMS m/z (ESI): Calcd. for C$_{22}$H$_{22}$NO$_5$S $[\text{M+H}]^+$ 412.1219, Found: 412.1212.

20) N-(5-Fluoro-2-(4-fluorobenzoyl)phenyl)-4-methylbenzenesulfonamide (3t)

The reaction of bis(4-fluorophenyl)methanone (1t) (0.3 mmol, 67.5 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru($p$-Cymene)Cl$_2$]$_2$ (2.5 mol %, 4.3 mg), AgSbF$_6$ (10 mol %, 10.4 mg), Cu(OAc)$_2$ (30 mol %, 16.4 mg), in 1.5 mL DCE at 100 $^\circ$C under Ar for 48 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 90.9 mg (78%) of 3t as solid: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.41 (s, 1H), 7.65 (d, $J$ = 8.0 Hz, 2H), 7.52-7.41 (m, 4H), 7.15-7.09 (m, 4H), 6.76 (t, $J$ = 10.0 Hz, 1H), 2.30 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.2, 165.4 (d, $J$ = 254.9 Hz), 165.3 (d, $J$ = 253.8 Hz), 144.2, 142.1 (d, $J$ = 1.9 Hz), 135.8, 135.6 (d, $J$ = 11.3 Hz), 133.9 (d, $J$ = 3.0 Hz), 132.2 (d, $J$ = 8.4 Hz), 129.7, 127.2, 121.1 (d, $J$ = 3.5 Hz), 115.4 (d, $J$ = 21.6 Hz), 110.3 (d, $J$ = 22.0 Hz), 108.8 (d, $J$ = 27.2 Hz), 21.4 ppm. IR:(KBr) $\nu_{\text{max}}$ = 3233, 3094, 1712, 1633, 1502, 1173, 1091, 682 cm$^{-1}$. HRMS m/z (ESI): Calcd. for C$_{20}$H$_{16}$F$_2$NO$_5$S $[\text{M+H}]^+$ 388.0819, Found: 388.0825.

21) N-(2-Pivaloylphenyl)benzenesulfonamide (3u)
The reaction of 2,2-dimethyl-1-phenylpropan-1-one (1b) (0.3 mmol, 49.7 mg), benzenesulfonyl azide (2b) (0.6 mmol, 109.9 mg), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 25 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 83.8 mg (88%) of 3u as solid: ¹H NMR (400 MHz, CDCl₃): δ 9.83 (s, 1H), 7.78-7.69 (m, 4H), 7.50 (t, J = 7.2 Hz, 1H), 7.44-7.38 (m, 3H), 7.10 (t, J = 6.8 Hz, 1H), 1.12 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 211.0, 139.4, 137.4, 132.8, 132.5, 129.2, 128.9, 126.9, 126.1, 123.3, 123.2, 44.7, 28.2 ppm. MS (70 eV): m/z (%): 317.1 (5) [M]+, 260.0 (100).

22) 4-nitro-N-(2-pivaloylphenyl)benzenesulfonamide (3v)¹

The reaction of 2,2-dimethyl-1-phenylpropan-1-one (1b) (0.3 mmol, 49.7 mg), 4-nitrobenzenesulfonyl azide (2c) (0.6 mmol, 136.9 mg), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 100 °C under Ar for 26 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 78.3 mg (72%) of 3v as solid: ¹H NMR (400 MHz, CDCl₃): δ 10.18 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.83 (t, J = 8.4 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 1.19 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 211.0, 150.0, 145.1, 137.0, 133.0, 129.8, 128.4, 125.4, 124.1, 123.6, 122.4, 44.9, 28.4 ppm. MS (70 eV): m/z (%): 362.2 (4) [M]+, 305.1 (100).
23) 1-Phenyl-N-(2-pivaloylphenyl)methanesulfonamide (3w)

The reaction of 2,2-dimethyl-1-phenylpropan-1-one (1b) (0.3 mmol, 49.7 mg), phenylmethanesulfonyl azide (2d) (0.6 mmol, 118.3 mg), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 25 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 69.6 mg (70%) of 3w as solid: ¹H NMR (400 MHz, CDCl₃): δ 10.00 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 8.4 Hz, 1H), 7.32-7.21 (m, 5H), 7.08 (t, J = 8.0 Hz, 1H), 4.38 (s, 2H), 1.35 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 210.6, 139.2, 133.1, 130.5, 130.2, 128.8, 128.7, 128.2, 122.9, 121.7, 119.2, 58.4, 45.1, 28.6 ppm. IR (KBr) ʋ max = 3033, 2932, 1711, 1639, 1491, 1153, 922, 697 cm⁻¹. HRMS m/z (ESI): Calcd. for C₁₈H₂₁KNO₃S [M+K]⁺ 370.0879, Found: 370.0880.

24) N-(2-Pivaloylphenyl)butane-1-sulfonamide (3x)

The reaction of 2,2-dimethyl-1-phenylpropan-1-one (1b) (0.3 mmol, 49.7 mg), butane-1-sulfonyl azide (2e) (0.6 mmol, 97.9 mg), [Ru(p-Cymene)Cl₂]₂ (2.5 mol %, 4.3 mg), AgSbF₆ (10 mol %, 10.4 mg), Cu(OAc)₂ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 °C under Ar for 25 h as monitored by TLC. The resulting mixture was
concentrated and purified by flash chromatography on silica gel to afford 55.3 mg (62%) of 3x as solid: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.76 (s, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.75 (d, $J$ = 8.4 Hz, 1H), 7.47 (t, $J$ = 8.0 Hz, 1H), 7.12 (t, $J$ = 7.6 Hz, 1H), 3.11 (t, $J$ = 4.8 Hz, 2H), 1.79-1.72 (m, 2H), 1.44-1.23 (m, 11H), 0.89 (t, $J$ = 7.2 Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 211.0, 138.7, 133.0, 129.9, 124.1, 122.1, 120.0, 52.0, 45.2, 28.6, 25.3, 21.2, 13.4 ppm. IR (KBr) $\nu_{\text{max}}$ = 3424, 2920, 2055, 1639, 1452, 1061, 759, 505 cm$^{-1}$. HRMS m/z (ESI): Calcd. for C$_{15}$H$_{24}$NO$_3$S [M+H]$^+$ 298.1477, Found: 298.1475.

![3y](image)

**25) N-(2-Acetylphenyl)-4-methylbenzenesulfonamide (3y)**

The reaction of acetophenone (1y) (0.3 mmol, 36.4 mg), 4-methylbenzenesulfonyl azide (2a) (0.6 mmol, 122 uL), [Ru($p$-Cymene)Cl$_2$]$_2$ (2.5 mol %, 4.3 mg), AgSbF$_6$ (10 mol %, 10.4 mg), Cu(OAc)$_2$ (30 mol %, 16.4 mg), in 1.5 mL DCE at 80 $^\circ$C under Ar for 24 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 64.8 mg (75%) of 3y as solid: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.47 (s, 1H), 7.79 (d, $J$ = 9.2 Hz, 1H), 7.72 (d, $J$ = 8.0 Hz, 2H), 7.67 (d, $J$ = 8.0 Hz, 1H), 7.41 (t, $J$ = 7.2 Hz, 1H), 7.21 (d, $J$ = 8.0 Hz, 2H), 7.05 (t, $J$ = 8.8 Hz, 1H), 2.55 (s, 3H), 2.35 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.3, 143.8, 139.9, 136.4, 134.8, 131.8, 129.5, 127.1, 1225.5, 122.1, 118.9, 28.0, 21.4 ppm. MS (70 eV): m/z (%): 289.1 (50) [M]$^+$, 91.1 (100).
Reference

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