**Supporting Information**

**Highly efficient copper-catalyzed benzylic C-H alkoxylation with NFSI**

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## 1. General Information

**General data:** NMR spectra were recorded on a Bruker-400 MHz or Bruker-500 MHz spectrometer. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl3: δH = 7.26 ppm, δC = 77.16 ppm). The high resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker DaltonicsInc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. UV-vis absorption was performed with a Tu-1901 UV-vis spectrophotometer. EPR spectra were measured on a JES-FA 200 (JEOL) at 20 ℃.

**Materials:** All starting materials and reagents were purchased from commercial suppliers (Aldrich, Alfa, TCI, Adamas-beta, Energy chemical) and used as supplied unless otherwise stated. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

## 2. General Procedures

**General procedure for the synthesis of 3:**



To a flame-dried and N2-purged Schlenk tube (10 mL) were added *N*-Fluorobenzenesulfonimide (0.13 mmol) and alkylarene (0.1 mmol, 1.0 equiv.). The vial was sealed, purged and backfilled with N2 three times before adding alcohol (0.5 mmol) and Cu(OAc)2 (2×10-5 M in MeCN, 0.5 mL) through syringes. After being stirred at 80 ℃ for 12-18 hours, the solvent was removed under vacuum to provide the crude product. The residue was purified by flash chromatography (SiO2, ethyl acetate/petroleum ether) to provide the corresponding products.

## 3. Characterization Data of Products

**1-(1-methoxyethyl)naphthalene (3a)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 14.6 mg, 78%.

**1H NMR (**400 MHz, Chloroform-*d*) δ 8.22 – 8.15 (m, 1H), 7.89 (dd, *J* = 7.0, 2.7 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.55-7.47 (m, 3H), 5.07 (q, *J* = 6.5 Hz, 1H), 3.32 (s, 3H), 1.62 (d, *J* = 6.6 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 139.2, 134.1, 131.0, 129.0, 127.9, 126.0, 125.7, 125.6, 123.4, 123.4, 77.5, 56.8, 23.4.

**IR (film, cm-1)** 2977.28, 2928.57, 1511.87, 1447.58, 1370.20,1230.33, 1204.40, 1166.90, 1081.06, 1060.68, 1004.49, 800.77, 777.85.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C13H15O]+ 187.1117; Found 187.1118.

**4-(1-methoxyethyl)-1,1'-biphenyl (3b)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 12.7 mg, 60%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 7.5, 5.6 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 12.9, 7.7 Hz, 3H), 4.36 (q, *J* = 6.5 Hz, 1H), 3.28 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 142.7, 141.1, 140.6, 128.9, 127.4, 127.2, 126.8, 79.5, 56.7, 24.0.

**IR (film, cm-1)** 2926.94, 1454.06, 1309.01, 1191.29, 1155.53, 1096.49, 1008.81, 701.13, 669.98, 504.84, 489.76.

**HRMS** (ESI-TOF) m/z: [M]+ Calcd for [C15H16O]+ 212.1201; Found 212.1181.

**4-bromo-4'-(1-methoxyethyl)-1,1'-biphenyl (3c)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 20.3 mg, 70%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 8.3, 6.6 Hz, 4H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 4.35 (q, *J* = 6.5 Hz, 1H), 3.27 (s, 3H), 1.47 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 143.2, 140.0, 139.3, 132.0, 128.8, 127.1, 126.9, 121.6, 79.4, 56.7, 24.0.

**IR (film, cm-1)** 2976.99, 2855.32, 1483.64, 1387.06, 1112.16, 1087.42, 1002.17, 813.89, 571.19, 521.99.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C15H16BrO]+ 291.0379; Found 291.0370.

**4'-(1-methoxyethyl)-[1,1'-biphenyl]-4-carbonitrile (3d)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 5/1) of crude product gave the title compound. Yield: 15.9 mg, 67%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 4H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 4.36 (q, *J* = 6.5 Hz, 1H), 3.27 (s, 3H), 1.47 (d, *J* = 6.5 Hz, 3H)

**13C NMR** (101 MHz, CDCl3) δ 145.5, 144.4, 138.4, 132.7, 127.8, 127.5, 127.1, 119.1, 111.0, 79.3, 56.7, 23.9.

**IR (film, cm-1)** 3031.25, 2928.02,2819.07, 1726.28, 1599.12, 1479.13, 1452.69, 1210.87, 1115.90, 1100.80, 758.31, 705.26.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C16H16NO]+ 238.1226; Found 238.1226.

**3-(1-methoxyethyl)-1,1'-biphenyl (3e)**

Prepared according to general procedure, stirring at 80 ℃ for 16 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 10.2mg, 48%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.44 (q, *J* = 7.7 Hz, 3H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.37 (q, *J* = 6.5 Hz, 1H), 3.28 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 144.3, 141.5, 141.3, 129.0, 128.9, 127.5, 127.3, 126.4, 125.3, 125.1, 79.8, 56.7, 24.1.

**IR (film, cm-1)** 2975.19, 2926.99, 1479.18, 1210.90, 1115.90, 1100.80, 1074.76, 1002.42, 758.40, 705.35.

**HRMS** (ESI-TOF) m/z: [M]+ Calcd for [C15H16O]+ 212.1201; Found 212.1181.

**(methoxymethylene)dibenzene (3f)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 11.1 mg, 56%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 8H), 7.26 – 7.21 (m, 2H), 5.24 (s, 1H), 3.38 (s, 3H).

**13C NMR** (101 MHz, CDCl3) δ 142.2, 128.5, 127.6, 127.0, 85.6, 57.2.

**IR (film, cm-1)** 2974.52, 2818.07, 1485.92, 1369.97, 1218.41, 1083.72, 1059.96, 1006.81, 991.06, 837.58, 735.12, 576.22.

**HRMS** (ESI-TOF) m/z: [M+Na]+ Calcd for [C14H14ONa]+ 221.0937; Found 221.0940.

**9-methoxy-9H-fluorene (3g)**

Prepared according to general procedure, stirring at 80 ℃ for 18 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 8.2mg, 42%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 5.62 (s, 1H), 3.06 (s, 3H).

**13C NMR** (126 MHz, CDCl3) δ 142.7, 141.1, 129.1, 127.7, 125.6, 120.1, 81.5, 52.4.

**IR (film, cm-1)** 2929.03, 1452.58, 1197.97, 1107.13, 1070.05, 1016.61, 762.06, 742.40, 555.07, 463.04.

**HRMS** (ESI-TOF) m/z: [M]+ Calcd for [C14H12O]+ 196.0888; Found 196.0890.

**2-methoxy-1,2-bis(4-methoxyphenyl)ethan-1-one (3h)**

Prepared according to general procedure, stirring at 80 ℃ for 18 hours. Flash chromatography (SiO2, PE/EtOAc = 3/1) of crude product gave the title compound. Yield: 12.6mg, 44%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.86 (dd, *J* = 9.0, 2.3 Hz, 4H), 5.44 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.42 (s, 3H).

**13C NMR** (101 MHz, CDCl3) δ 195.6, 163.6, 159.8, 131.5, 129.2, 128.6, 128.0, 114.4, 113.8, 85.9, 57.4, 55.6, 55.4.

**IR (film, cm-1)** 2931.07, 1683.32, 1600.28, 1511.06, 1253.93, 1170.60, 1101.46, 1030.12, 829.93, 573.56.

**HRMS** (ESI-TOF) m/z: [M+Na]+ Calcd for [C17H18O4Na]+ 309.1097; Found 309.1105.

**2-(1-methoxyethyl)naphthalene (3i)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 10.6 mg, 57%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 7.89 – 7.80 (m, 3H), 7.74 (s, 1H), 7.53 – 7.44 (m, 3H), 4.47 (q, *J* = 6.5 Hz, 1H), 3.27 (s, 3H), 1.52 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 141.0, 133.4, 133.2, 128.5, 128.0, 127.8, 126.2, 125.9, 125.3, 124.3, 79.9, 56.7, 24.0.

**IR (film, cm-1)** 2975.52, 2927.69, 1112.85, 1092.47, 1058.37, 1018.26, 990.86, 857.28, 820.33, 747.64, 477.54.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C13H15O]+ 187.1117; Found 187.1093.

**1-(1-ethoxyethyl)naphthalene (3j)**

Prepared according to general procedure, stirring at 80 ℃ for 12 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 15.6 mg, 78%.

**1H NMR** (500 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.55 – 7.42 (m, 3H), 5.17 (q, *J* = 6.6 Hz, 1H), 3.45 (q, *J* = 7.0 Hz, 2H), 1.62 (d, *J* = 6.6 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 139.9, 134.0, 130.9, 129.0, 127.8, 125.9, 125.7, 125.5, 123.5, 123.3, 75.6, 64.3, 23.8, 15.7.

**IR (film, cm-1)** 2974.68, 2928.06, 1596.35, 1442.56, 1370.04, 1174.96, 1110.83, 1082.33, 800.62, 777.73.

**HRMS** (ESI-TOF) m/z: [M+Na]+ Calcd for [C14H16ONa]+ 235.1093; Found 223.1076.

**1-(1-(octyloxy)ethyl)naphthalene (3k)**

Prepared according to general procedure, stirring at 80 ℃ for 18 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 20.2 mg, 71%.

**1H NMR** (500 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.88 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.54 – 7.45 (m, 3H), 5.14 (q, *J* = 6.5 Hz, 1H), 3.37 (td, *J* = 6.7, 3.4 Hz, 2H), 1.67 – 1.52 (m, 5H), 1.41 – 1.23 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 140.0, 134.0, 131.0, 129.0, 127.8, 125.9, 125.7, 125.5, 123.6, 123.4, 75.8, 69.1, 32.0, 30.2, 29.6, 29.4, 26.4, 23.7, 22.8, 14.3.

**IR (film, cm-1)** 2927.81, 2855.11, 1465.51, 1369.22, 1230.10, 1171.82, 1102.99, 969.36, 799.42, 777.40.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C20H29O]+ 285.2213; Found 285.2221.

**1-(1-(but-3-en-1-yloxy)ethyl)naphthalene (3l)**

Prepared according to general procedure, stirring at 80 ℃ for 16 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 17.0mg, 75%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 7.1, 2.6 Hz, 1H), 7.92 – 7.83 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 6.4 Hz, 1H), 7.55 – 7.44 (m, 3H), 5.83 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.17 (q, *J* = 6.5 Hz, 1H), 5.08 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.02 (ddt, *J* = 10.3, 2.2, 1.2 Hz, 1H), 3.52 – 3.38 (m, 2H), 2.38 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.62 (d, *J* = 6.6 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 139.7, 135.5, 134.0, 130.9, 129.0, 127.9, 125.9, 125.7, 125.6, 123.5, 123.5, 116.4, 75.9, 68.3, 34.6, 23.7.

**IR (film, cm-1)** 3068.82, 2977.74, 2928.39, 2861.57, 1641.10, 1509.56, 1369.57, 1172.63, 1103.37, 914.11, 800.54, 777.85.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C16H19O]+ 227.1430; Found 227.1453.

**1-(1-(but-3-yn-1-yloxy)ethyl)naphthalene (3m)**

Prepared according to general procedure, stirring at 80 ℃ for 18 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 11.6mg, 75%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.22 – 8.15 (m, 1H), 7.92 – 7.85 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.43 (m, 3H), 5.21 (q, *J* = 6.5 Hz, 1H), 3.63 – 3.45 (m, 2H), 2.50 (td, *J* = 6.9, 2.6 Hz, 2H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.64 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 139.2, 134.1, 130.9, 129.0, 128.0, 126.0, 125.7, 125.6, 123.6, 123.5, 81.6, 76.2, 69.4, 66.9, 29.9, 23.6, 20.3.

**IR (film, cm-1)** 3295.44, 2976.01, 2926.72, 1596.37, 1509.52, 1395.42, 1171.85, 1106.11, 1008.52, 801.68, 778.65, 640.50, 558.84.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C16H17O]+ 225.1274; Found 225.1284.

**1-(1-(2-fluoroethoxy)ethyl)naphthalene (3n)**

Prepared according to general procedure, stirring at 80 ℃ for 16 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 10.5mg, 48%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.53 (m, 1H), 7.56 – 7.44 (m, 3H), 5.23 (q, *J* = 6.6 Hz, 1H), 4.62 (dd, *J* = 4.9, 3.4 Hz, 1H), 4.50 (dd, *J* = 4.9, 3.4 Hz, 1H), 3.66 (dd, *J* = 5.2, 3.2 Hz, 1H), 3.64 – 3.55 (dd, 5.2, 3.2Hz, 1H), 1.66 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (101 MHz, Chloroform-*d*) δ138.9, 134.1, 130.8, 129.1, 128.1, 126.1, 125.7, 125.7, 123.6, 123.4, 83.4 (d, *J* = 169.1 Hz), 67.9 (d, *J* = 19.6 Hz), 67.8, 23.6

**IR (film, cm-1)** 2978349, 2929.02, 1596.33, 1509.98, 1455.47, 1369.76, 1173.48, 1119.56, 1049.28, 942.44, 876.65, 802.42, 779.25.

**HRMS** (ESI-TOF) m/z: [M]+ Calcd for [C14H15FO]+ 218.1107; Found 218.1119.

**methyl 2-(1-(naphthalen-1-yl)ethoxy)acetate (3o)**

Prepared according to general procedure, stirring at 80 ℃ for 16 hours. Flash chromatography (SiO2, PE/EtOAc = 2/1) of crude product gave the title compound. Yield: 13.2mg, 54%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.3 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.43 (m, 3H), 5.33 (q, *J* = 6.5 Hz, 1H), 4.10 (d, *J* = 16.4 Hz, 1H), 3.95 (d, *J* = 16.4 Hz, 1H), 3.73 (s, 3H), 1.70 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 171.1, 138.1, 134.1, 130.9, 129.1, 128.4, 126.2, 125.8, 125.7, 123.8, 123.4, 76.5, 66.0, 51.9, 23.5.

**IR (film, cm-1)** 2979.07, 2951.84, 1754.81, 1437.67, 1371.55, 1171.06, 1120.43, 1003.37802.79, 779.54.

**HRMS** (ESI-TOF) m/z: [M+Na]+ Calcd for [C15H16O3Na]+ 267.0992; Found 267.0999.

**1-(1-((3-bromobenzyl)oxy)ethyl)naphthalene (3p)**

Prepared according to general procedure, stirring at 80 ℃ for 14 hours. Flash chromatography (SiO2, PE/EtOAc = 20/1) of crude product gave the title compound. Yield: 13.9mg, 41%.

**1H NMR** (500 MHz, Chloroform-d) δ 8.21 – 8.16 (m, 1H), 7.93 – 7.87 (m, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.51 (m , 4H), 7.41 (dt, J = 7.7, 1.8 Hz, 1H), 7.30 – 7.18 (m, 2H), 5.25 (q, J = 6.5 Hz, 1H), 4.49 (d, J = 12.1 Hz, 1H), 4.33 (d, J = 12.1 Hz, 1H), 1.68 (d, J = 6.5 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 141.2, 139.0, 134.1, 130.9, 130.7, 130.7, 130.1, 129.1, 128.2, 126.2, 126.1, 125.7, 123.8, 123.5, 122.7, 75.7, 69.9, 23.7.

**IR (film, cm-1)** 2976.03, 2927.20, 1596.21, 1570.36, 1427.32, 1369.49, 1170.91, 1099.98, 1005.85, 800.92, 777.22.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C19H18BrO]+ 341.0536; Found 341.0546.

**1-(1-phenethoxyethyl)naphthalene (3q)**

Prepared according to general procedure, stirring at 80 ℃ for 14 hours. Flash chromatography (SiO2, PE/EtOAc = 20/1) of crude product gave the title compound. Yield: 19.3mg, 70%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (dt, *J* = 7.0, 3.5 Hz, 1H), 7.87 (dt, *J* = 6.2, 3.3 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.39 (m, 4H), 7.31 – 7.23 (m, 3H), 7.24 – 7.16 (m, 3H), 5.17 (q, *J* = 6.5 Hz, 1H), 3.61 (td, *J* = 7.2, 1.8 Hz, 2H), 2.95 (hept, *J* = 6.7 Hz, 2H), 1.61 (d, *J* = 6.5 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 139.6, 139.2, 134.0, 130.9, 129.1, 129.0, 128.4, 127.8, 126.2, 125.9, 125.7, 125.5, 123.5, 76.0, 69.9, 36.8, 23.6.

**IR (film, cm-1)** 2975.19, 2927.35, 1596.32, 1453.29, 1369.38, 1230.47, 1170.96, 1103.26, 800.71, 777.98,749.70, 698.74.

**HRMS** (ESI-TOF) m/z: [M+Na]+ Calcd for [C20H20ONa]+ 299.1406; Found 299.1413.

**1-(1-(4-methylphenethoxy)ethyl)naphthalene (3r)**

Prepared according to general procedure, stirring at 80 ℃ for 16 hours. Flash chromatography (SiO2, PE/EtOAc = 20/1) of crude product gave the title compound. Yield: 17.7mg, 77%.

**1H NMR** (500 MHz, Chloroform-*d*) δ 8.14 (dt, *J* = 7.0, 3.6 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.39 (m, 4H), 7.11 – 7.05 (m, 4H), 5.17 (q, *J* = 6.5 Hz, 1H), 3.67 – 3.53 (m, 2H), 2.97 – 2.83 (m, 2H), 2.32 (s, 3H), 1.61 (d, *J* = 6.6 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 139.6, 136.0, 135.7, 134.0, 130.9, 129.1, 129.0, 127.8, 125.9, 125.7, 125.5, 123.5, 75.9, 70.1, 36.3, 23.6, 21.2.

**IR (film, cm-1)** 2928.61, 2861.15, 1514.62, 1368.99, 1230.42, 1170.96, 1103.57, 1008.67, 800.67, 777.83.

**HRMS** (ESI-TOF) m/z: [M+Na]+ Calcd for [C21H22ONa]+ 313.1563; Found 313.1568.

**1-(1-(4-bromophenethoxy)ethyl)naphthalene (3s)**

Prepared according to general procedure, stirring at 80 ℃ for 14 hours. Flash chromatography (SiO2, PE/EtOAc = 20/1) of crude product gave the title compound. Yield: 27.2mg, 77%.

**1H NMR** (500 MHz, Chloroform-*d*) δ 8.13 – 8.07 (m, 1H), 7.87 (dd, *J* = 7.2, 2.5 Hz, 1H), 7.77 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.55 – 7.39 (m, 4H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.13 (q, *J* = 6.5 Hz, 1H), 3.58 (t, *J* = 6.8 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 3H), 1.60 (d, *J* = 6.6 Hz, 3H).

**13C NMR** (126 MHz, CDCl3) δ 139.4, 138.4, 134.0, 131.4, 130.9, 130.9, 129.0, 128.0, 126.0, 125.7, 125.6, 123.5, 123.5, 120.1, 76.2, 69.4, 36.2, 23.6.

**IR (film, cm-1)** 2975.45, 2928.17, 1508.93, 1488.18, 1440.51, 1369.51, 1230.35, 1170.98, 1104.44, 1072.10, 1011.31, 801.19, 777.95.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C20H20BrO]+ 355.0692; Found 355.0717.

**1-(1-isopropoxyethyl)naphthalene (3t)**

Prepared according to general procedure, stirring at 80 ℃ for 16 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 12.4 mg, 58%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.25 – 8.19 (m, 1H), 7.88 (dd, *J* = 7.1, 2.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.60 – 7.44 (m, 3H), 5.30 (q, *J* = 6.6 Hz, 1H), 3.55 (hept, *J* = 6.1 Hz, 1H), 1.59 (d, *J* = 6.5 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H).

**13C NMR** (101 MHz, CDCl3) δ 140.4, 133.9, 130.8, 128.9, 127.6, 125.7, 125.6, 125.4, 123.5, 123.4, 72.3, 68.8, 24.2, 23.4, 21.4.

**IR (film, cm-1)** 2972.20, 2929.32, 1463.87, 1368.88, 1150.65, 1107.20, 1094.68, 1021.69, 800.45, 777.87.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C15H19O]+ 215.1430; Found 215.1428.

**1-(1-(cyclohexyloxy)ethyl)naphthalene (3u)**

Prepared according to general procedure, stirring at 80 ℃ for 18 hours. Flash chromatography (SiO2, PE/EtOAc = 30/1) of crude product gave the title compound. Yield: 11.7 mg, 46%.

**1H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.43 (m, 3H), 5.35 (q, *J* = 6.5 Hz, 1H), 3.23 (tt, *J* = 9.8, 3.9 Hz, 1H), 2.04 (d, *J* = 12.4 Hz, 1H), 1.85 – 1.64 (m, 2H), 1.58 (d, *J* = 6.5 Hz, 3H), 1.54 – 1.30 (m, 4H), 1.22 – 1.07 (m, 3H).

**13C NMR** (126 MHz, CDCl3) δ 140.8, 134.0, 130.9, 129.0, 127.6, 125.8, 125.7, 125.5, 123.6, 123.5, 75.2, 72.0, 33.7, 32.0, 26.0, 24.6, 24.5, 24.3.

**IR (film, cm-1)** 2930.57, 2854.81, 1449.58, 1367.24, 1259.16, 1170.94, 1100.40, 1024.22, 800.07, 777.70.

**HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for [C18H23O]+ 255.1743; Found 255.1748.

**Unsuccessful substrates**



## 4. Mechanistic Investigations

**General procedure for the dynamic experiment:**



To a flame-dried and N2-purged Schlenk tube (10 mL) were added *N*-FluorobenzenesulfoniMide (0.13 mmol) and **1c** (0.1 mmol, 1.0 equiv.). The vial was sealed, purged and backfilled with N2 three times before adding **2a** (0.5 mmol) and Cu(OAc)2 (2×10-3 to 2×10-7 M in MeCN, 0.5 mL) through syringes. After being stirred at 80 ℃ for several hours, triacetyl benzene was added as an internal standard. The solvent was removed under vacuum to provide the crude product. The concentration of **1c**, **3c**, **4** was monitored by 1H-NMR.

**Table S1** Reaction profiles at 1 mol% loading amount of Cu(OAc)2

|  |  |  |
| --- | --- | --- |
| Time (min) | Conversion of **1c** (10-3 M) | Concentration of **3c** (10-3 M) |
| 10 | 10 | 0 |
| 20 | 20 |  |
| 30 | 30 | 16 |
| 60 | 16 | 30 |
| 90 | 58 |  |
| 120 |  | 46 |
| 180 |  | 60 |

**Table S2** Reaction profiles at 0.1 mol% loading amount of Cu(OAc)2

|  |  |  |
| --- | --- | --- |
| Time (min) | Conversion of **1c** (10-3 M) | Concentration of **3c** (10-3 M) |
| 20 | 0 |  |
| 30 | 6 | 0 |
| 60 | 26 | 14 |
| 90 | 36 |  |
| 120 | 50 | 32 |
| 180 |  | 42 |
| 240 |  | 56 |

**Table S3** Reaction profiles at 0.01 mol% loading amount of Cu(OAc)2

|  |  |  |
| --- | --- | --- |
| Time (min) | Conversion of **1c** (10-3 M) | Concentration of **3c** (10-3 M) |
| 30 | 0 | 0 |
| 60 | 16 | 6 |
| 90 | 24 |  |
| 120 | 34 | 20 |
| 150 | 42 |  |
| 180 | 52 | 32 |
| 240 |  | 42 |
| 300 |  | 52 |

**Table S4** Reaction profiles at 0.001 mol% loading amount of Cu(OAc)2

|  |  |  |
| --- | --- | --- |
| Time (min) | Conversion of **1c** (10-3 M) | Concentration of **3c** (10-3 M) |
| 60 | 0 | 0 |
| 90 | 8 |  |
| 120 | 20 | 14 |
| 150 | 28 |  |
| 180 | 38 | 24 |
| 240 | 48 | 36 |
| 300 |  | 46 |

**Table S5** Reaction profiles at 0.0001 mol% loading amount of Cu(OAc)2

|  |  |  |
| --- | --- | --- |
| Time (min) | Conversion of **1c** (10-3 M) | Concentration of **3c** (10-3 M) |
| 90 | 0 | 0 |
| 120 | 10 | 6 |
| 150 | 14 |  |
| 180 | 20 | 12 |
| 240 | 32 | 22 |
| 300 | 46 | 34 |

**Table S6** Concentration of **4** at 1 mol% loading amount of Cu(OAc)2

|  |  |
| --- | --- |
| Time (h) | Concentration of **4**（10-3 M） |
| 6 | 16 |
| 7 | 28 |
| 8 | 40 |
| 9 | 54 |
| 10 | 62 |

**Table S7** Concentration of **4** at 0.1 mol% loading amount of Cu(OAc)2

|  |  |
| --- | --- |
| Time (h) | Concentration of **4**（10-3 M） |
| 6 | 0 |
| 7 | 12 |
| 8 | 20 |
| 9 | 34 |
| 10 | 44 |
| 12 | 56 |

**Table S8** Concentration of **4** at 0.01 mol% loading amount of Cu(OAc)2

|  |  |
| --- | --- |
| Time (h) | Concentration of **4**（10-3 M） |
| 6 | 0 |
| 7 | 6 |
| 8 | 16 |
| 9 | 24 |
| 10 | 32 |
| 12 | 50 |

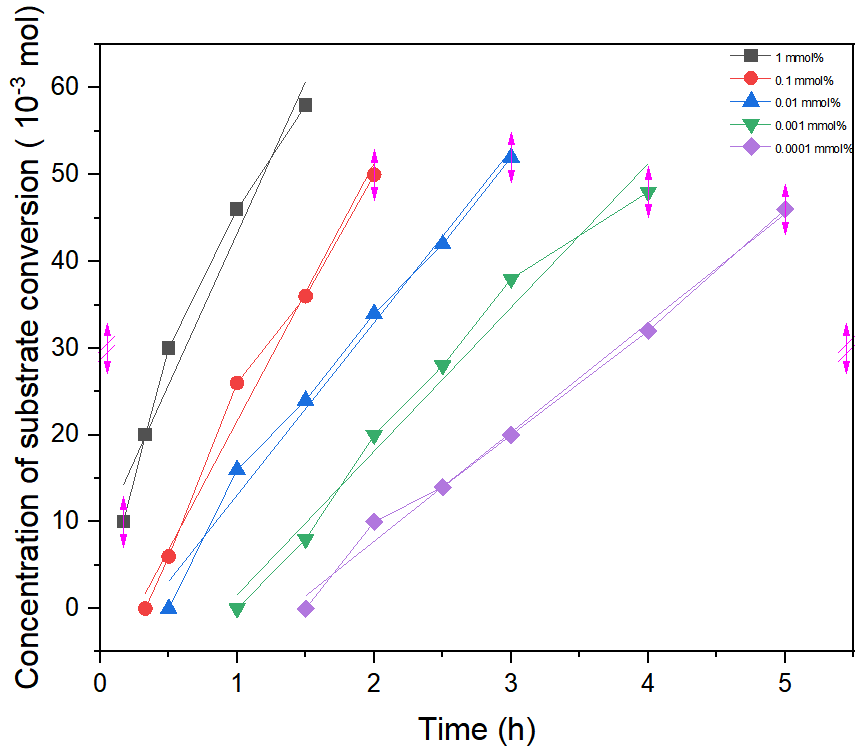
**Table S9** Concentration of **4** at 0.001 mol% loading amount of Cu(OAc)2

|  |  |
| --- | --- |
| Time (h) | Concentration of **4**（10-3 M） |
| 8 | 0 |
| 9 | 10 |
| 10 | 20 |
| 12 | 34 |
| 14 | 52 |

**Table S10** Concentration of **4** at 0.0001 mol% loading amount of Cu(OAc)2

|  |  |
| --- | --- |
| Time (h) | Concentration of **4**（10-3 M） |
| 9 | 0 |
| 10 | 8 |
| 12 | 28 |
| 14 | 44 |
| 16 | 62 |

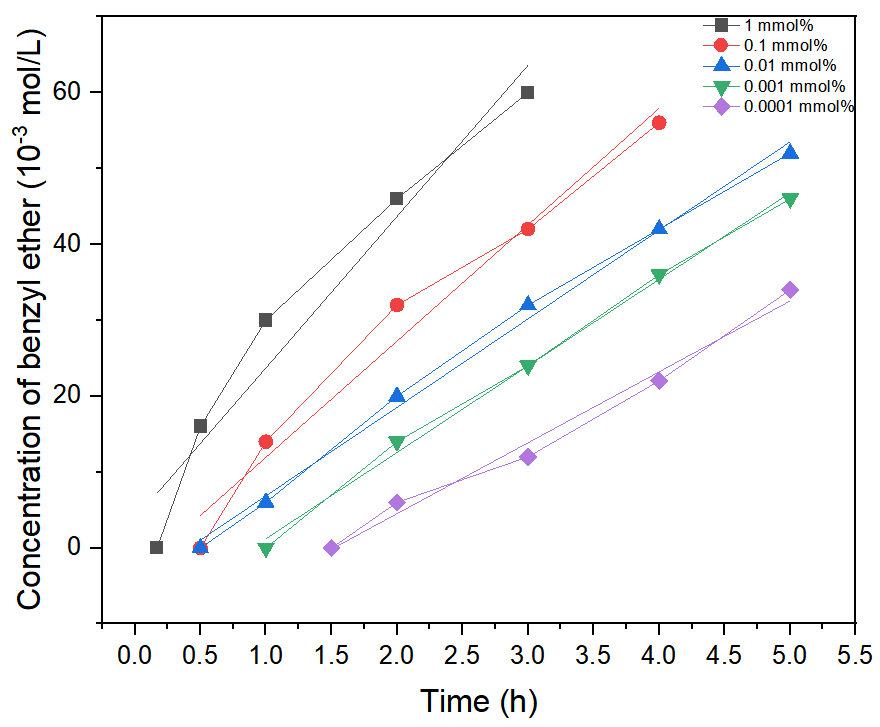
**Fig S1.** Conversion of **1c** at different loading amount of Cu(OAc)2



**Table S11** Linear fitting equation data of conversion of **1c** at different loading amount of Cu(OAc)2

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Linear fitting equation | y = a+bx | | | | |
| catalyst loading | 1 mol% | 0.1 mol% | 0.01 mol% | 0.001 mol% | 0.0001 mol% |
| intercept | 8.343 | -8.047 | -6.8 | -15 | -17.431 |
| slope | 34.939 | 29.688 | 19.886 | 16.571 | 12.588 |
| R2 | 0.966 | 0.986 | 0.987 | 0.98 | 0.993 |

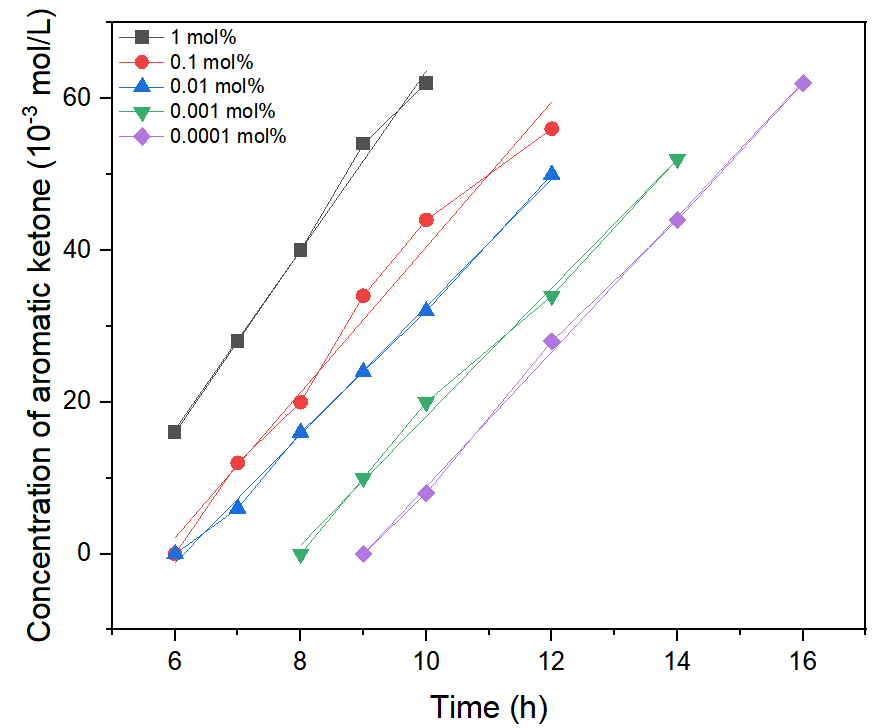
**Fig S2.** Concentration of **3c** at different loading amount of Cu(OAc)2



**Table S12** Linear fitting equation data of concentration of **3c** at different loading amount of Cu(OAc)2

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Linear fitting equation | y = a+bx | | | | |
| catalyst loading | 1 mol% | 0.1 mol% | 0.01 mol% | 0.001 mol% | 0.0001 mol% |
| intercept | 3.817 | -3.366 | -4.789 | -10.2 | -14.159 |
| slope | 19.927 | 15.317 | 11.66 | 11.4 | 9.341 |
| R2 | 0.949 | 0.975 | 0.995 | 0.997 | 0.987 |

**Fig S3.** Concentration of **4** at different loading amount of Cu(OAc)2



**Table S13** Linear fitting equation data of concentration of **4** at different loading amount of Cu(OAc)2

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Linear fitting equation | y = a+bx | | | | |
| catalyst dosage | 1 mol% | 0.1 mol% | 0.01 mol% | 0.001 mol% | 0.0001 mol% |
| intercept | -54.4 | -55.286 | -51.714 | -66.534 | -80.061 |
| slope | 11.8 | 9.571 | 8.429 | 8.466 | 8.89 |
| R2 | 0.995 | 0.981 | 0.998 | 0.996 | 0.999 |

**General procedure for control experiment:**

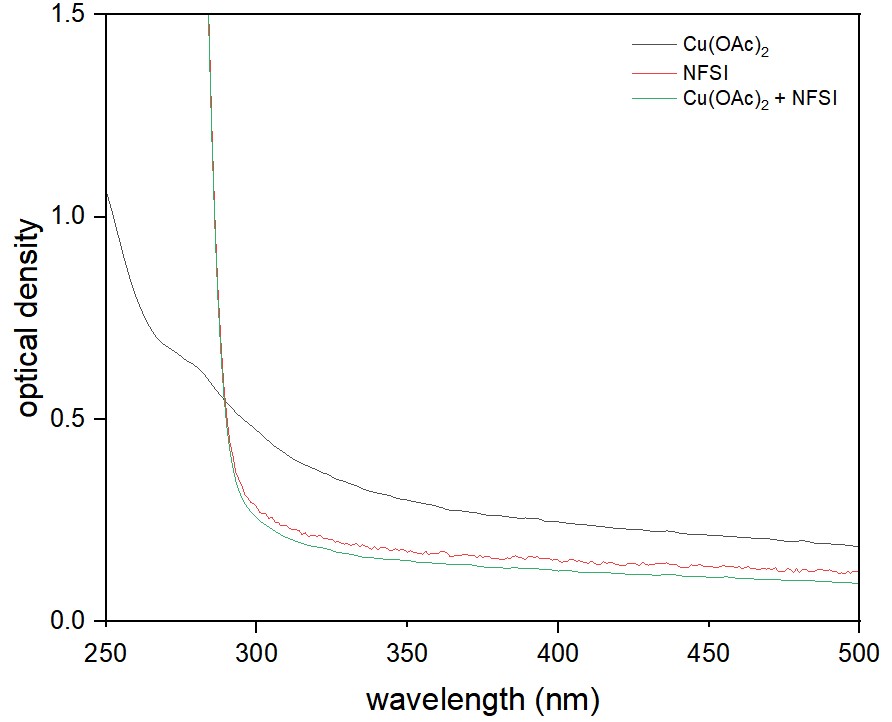


To a flame-dried and N2-purged Schlenk tube (10 mL) were added *N*-FluorobenzenesulfoniMide (0.13 mmol) and 4-bromo-4'-(1-methoxyethyl)-1,1'-biphenyl (0.1 mmol, 1.0 equiv.). The vial was sealed, purged and backfilled with N2 three times before adding Cu(OAc)2 (2×10-3 - 2×10-7 M in MeCN, 0.5 mL) through a syringe. After being stirred at 80 ℃ overnight, triacetyl benzene was added as an internal standard. The solvent was removed under vacuum to provide the crude product. The yield of 1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethan-1-one was monitored by 1H-NMR.

**General procedure for the UV-vis absorption experiment:**

(1) Anhydrous Cu(OAc)2 (0.1mmol, 18.1 mg) and acetonitrile (50 mL) were added in a 100 mL snap vial. After completely dissolved, 20 μl of the solution was extracted with 25 μl syringe and diluted with acetonitrile to 2mL. The solution (2 mL) was transferred into a colorimetric dish. Then the UV-vis measurement was carried out at 20 ℃. (2) NFSI (0.05 mmol, 15.8 mg) and acetonitrile (2 mL) were added in a 5 mL snap vial. After completely dissolved, 0.5 mL of this solution was extracted with 1mL syringe to diluted with acetonitrile to 2 mL. The solution (2 mL) was transferred into a colorimetric dish. Then the UV-vis measurement was carried out at 20 ℃. (3) NFSI (0.05 mmol, 15.8 mg), Cu(OAc)2 (2×10-3 M in MeCN, 80μl) and acetonitrile (2 mL) were added in a 5 mL snap vial. After completely dissolved, 0.5 mL of this solution was extracted with 1mL syringe to diluted with acetonitrile to 2 mL. The solution (2 mL) was transferred into a colorimetric dish. Then the UV-vis measurement was carried out at 20 ℃.

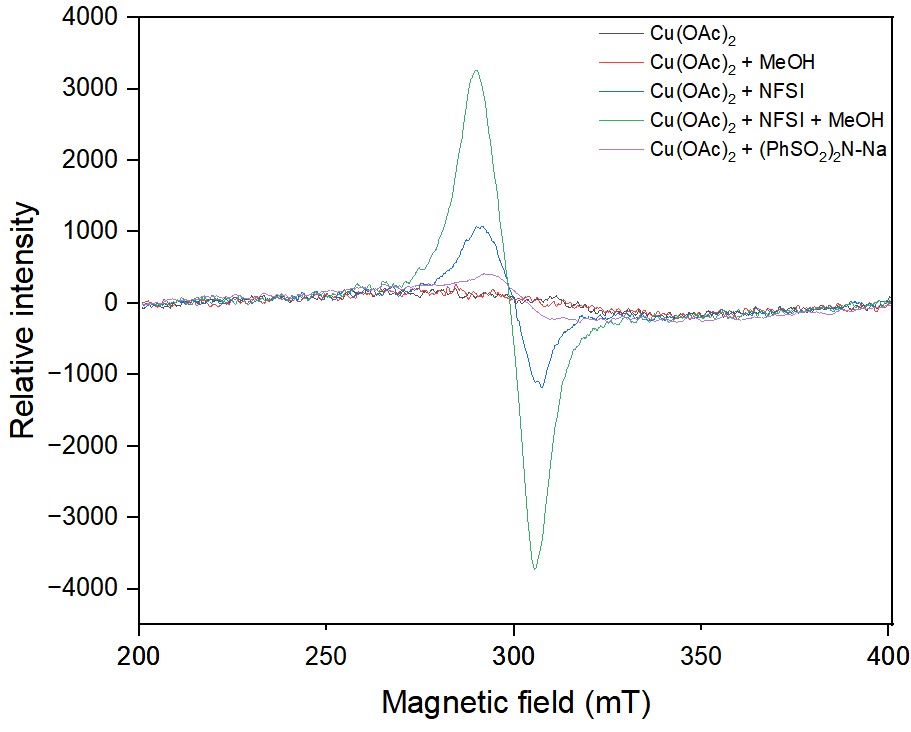
**Fig S4.** UV-visible absorption spectrum



**General procedure for the EPR experiment:**

(1) Anhydrous Cu(OAc)2 (0.1 mmol, 18.1 mg) and acetonitrile (50 mL) were added in a 100 mL snap vial. After completely dissolved, the solution (0.5 mL) was transferred into an EPR tube. Then the EPR measurement was carried out at 20 ℃. (2) Cu(OAc)2 (2×10-3 M in MeCN, 2 mL) and MeOH (40 μl) were added in a 5 mL snap vial. After completely dissolved, the solution (0.5 mL) was transferred into an EPR tube. Then the EPR measurement was carried out at 20 ℃. (3) Cu(OAc)2 (2×10-3 M in MeCN, 2 mL) and NFSI (0.05 mmol, 15.8 mg) were added in a 5 mL snap vial. After completely dissolved, the solution (0.5 mL) was transferred into an EPR tube. Then the EPR measurement was carried out at 20 ℃. (4) Cu(OAc)2 (2×10-3 M in MeCN, 2mL), MeOH (40 μl) and NFSI (0.05 mmol, 15.8 mg) were added in a 5 mL snap vial. After completely dissolved, the solution (0.5 mL) was transferred into an EPR tube. Then the EPR measurement was carried out at 20 ℃. (5) Cu(OAc)2 (2×10-3 M in MeCN, 2 mL) and (PhSO2)2N−Na (0.05 mmol, 16.0 mg) were added in a 5 mL snap vial. After completely dissolved, the solution (0.5 mL) was transferred into an EPR tube. Then the EPR measurement was carried out at 20 ℃.

**Fig S5.** EPR spectroscopy spectrum



**General procedure for the substituent effect experiment:**

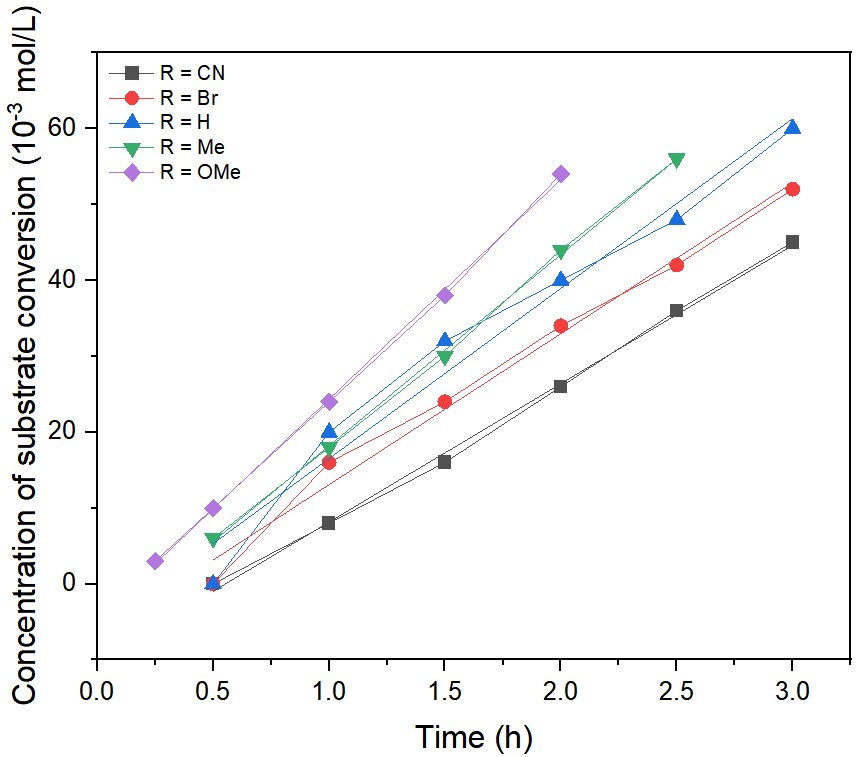


To a flame-dried and N2-purged Schlenk tube (10 mL) were added *N*-Fluorobenzenesulfonimide (0.13 mmol) and **1** (0.1 mmol, 1.0 equiv). The vial was sealed, purged and backfilled with N2 three times before adding **2a** (0.5 mmol) and Cu(OAc)2 (2×10-5 M in MeCN, 0.5 mL). through a syringe. After being stirred at 80 ℃ for several hours, triacetyl benzene was added as an internal standard. The solvent was removed under vacuum to provide the crude product. The concentration of **1** was monitored by 1H-NMR.

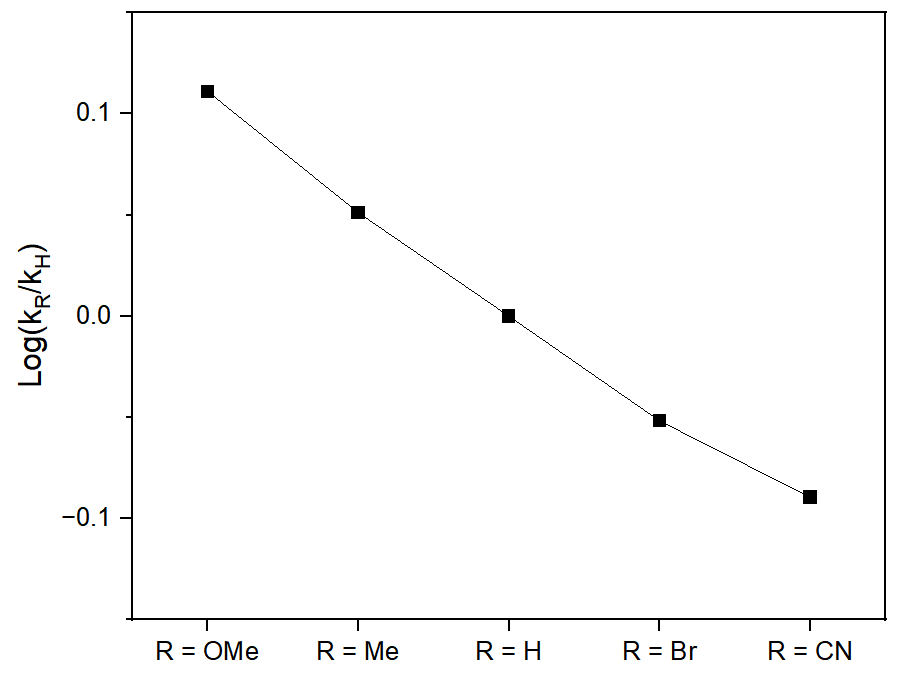
**Table S14** Conversion of **1** at 0.01 mol% loading amount of Cu(OAc)2

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Time (h) | Conversion of **1v** (mM) | Conversion of **1w** (mM) | Conversion of **1b** (mM) | Conversion of **1c** (mM) | Conversion of **1d** (mM) |
| 0.25 | 3 |  |  |  |  |
| 0.5 | 10 | 6 | 0 | 0 | 0 |
| 1 | 24 | 18 | 20 | 16 | 8 |
| 1.5 | 38 | 30 | 32 | 24 | 16 |
| 2 | 54 | 44 | 40 | 34 | 26 |
| 2.5 |  | 56 | 48 | 42 | 36 |
| 3 |  |  | 60 | 52 | 45 |

**Fig S6.** Conversion of **1** at 0.01 mol% loading amount of Cu(OAc)2



**Fig S6.** Effect of substituents on reaction rate constants



**General procedure for the dynamic experiment by using Cu(MeCN)4PF6 as catalyst:**

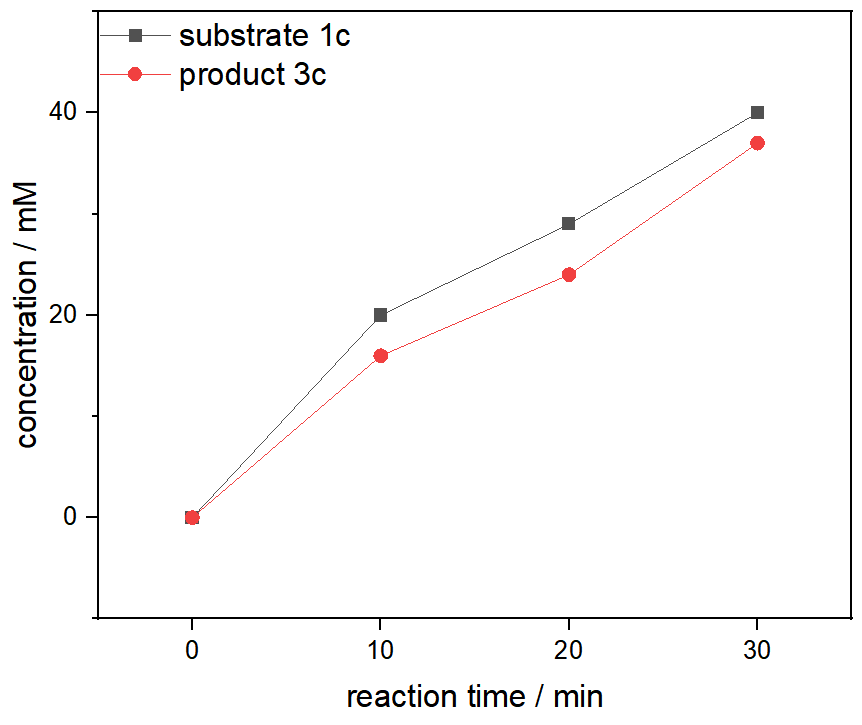


To a flame-dried and N2-purged Schlenk tube (10 mL) were added *N*-FluorobenzenesulfoniMide (0.13 mmol) and **1c** (0.1 mmol, 1.0 equiv.). The vial was sealed, purged and backfilled with N2 three times before adding **2a** (0.5 mmol) and Cu(MeCN)4PF6 (2×10-5 M in MeCN, 0.5 mL) through syringes. After being stirred at 80 ℃ for several hours, triacetyl benzene was added as an internal standard. The solvent was removed under vacuum to provide the crude product. The concentration of **1c**, **3c**, was monitored by 1H-NMR.

**Table S15** Reaction profiles at 0.01 mol% loading amount of Cu(MeCN)4PF6

|  |  |  |
| --- | --- | --- |
| Time (min) | Conversion of **1c** (10-3 M) | Concentration of **3c** (10-3 M) |
| 10 | 20 | 16 |
| 20 | 29 | 24 |
| 30 | 40 | 37 |

**Fig S7.** Conversion of **1c** andconcentration of **3c** at 0.01 mmol% loading amount of Cu(MeCN)4PF6



## NMR Spectra of Products

1H NMR spectrum of **3a**



13C NMR spectrum of **3a**



1H NMR spectrum of **3b**



13C NMR spectrum of **3b**



1H NMR spectrum of **3c**



13C NMR spectrum of **3c**



1H NMR spectrum of **3d**



13C NMR spectrum of **3d**



1H NMR spectrum of **3e**



13C NMR spectrum of **3e**



1H NMR spectrum of **3f**



13C NMR spectrum of **3f**



1H NMR spectrum of **3g**



13C NMR spectrum of **3g**



1H NMR spectrum of **3h**



13C NMR spectrum of **3h**



1H NMR spectrum of **3i**



13C NMR spectrum of **3i**



1H NMR spectrum of **3j**



13C NMR spectrum of **3j**



1H NMR spectrum of **3k**



13C NMR spectrum of **3k**



1H NMR spectrum of **3l**



13C NMR spectrum of **3l**



1H NMR spectrum of **3m**



13C NMR spectrum of **3m**



1H NMR spectrum of **3n**



13C NMR spectrum of **3n**



1H NMR spectrum of **3o**



13C NMR spectrum of **3o**



1H NMR spectrum of **3p**



13C NMR spectrum of **3p**



1H NMR spectrum of **3q**



13C NMR spectrum of **3q**



1H NMR spectrum of **3r**



13C NMR spectrum of **3r**



1H NMR spectrum of **3s**



13C NMR spectrum of **3s**



1H NMR spectrum of **3t**



13C NMR spectrum of **3t**



1H NMR spectrum of **3u**



13C NMR spectrum of **3u**

