

Supporting Information

for

Enantioselective Copper-Catalyzed Alkynylation of Benzylic C-H Bonds via Radical Relay

Liang Fu,^a Zhihan, Zhang,^b Pinhong Chen,^a Zhenyang Lin,^{*b} and Guosheng Liu^{*a,c}

^aState Key Laboratory of Organometallic Chemistry and Shanghai Hongkong Joint Laboratory in Chemical Synthesis, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. ^bDepartment of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China. ^cChang-Kung Chuang Institute, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China.

Email: gliu@mail.sioc.ac.cn

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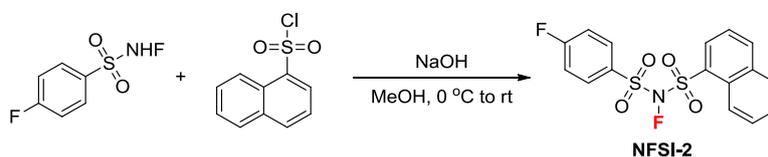
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1. General

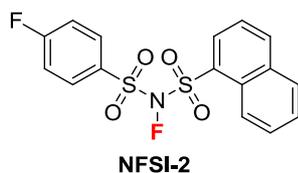
All commercially available compounds were purchased from Aldrich, Alfa Aesar or Adamas. NMR spectra was recorded on Bruker 400, Varian Inova 400 or Aglient 400 (400 MHz for ^1H ; 376 MHz for ^{19}F ; 100 MHz for ^{13}C) spectrometer. The chemical shifts (δ) are given in parts per million relative to CDCl_3 (7.26 ppm for ^1H) and CDCl_3 (77.0 ppm for ^{13}C) and $\text{DMSO-}d_6$ (2.50 ppm for ^1H) and $\text{DMSO-}d_6$ (39.5 ppm for ^{13}C). High performance liquid chromatography was performed on Waters 2487-600E, Thermo UltiMate 3000 or Waters ACQUITY UPC2, using AD-H, OD-H and OJ-H chiral columns eluted with a mixture of hexane and isopropyl alcohol (for SFC, CO_2 and MeOH were used as eluent). Optical rotation was measured on a Rudolph-Autopol I. Melting point was measured on SMP30. Flash column chromatography was performed on silica gel (particle size 200-300 mesh, purchased from Canada) and eluted with petroleum ether/ethyl acetate. Solvent was purified according to the procedure from a book named "Purification of Laboratory Chemicals". DMA and 1,2,4,5-tetrafluorobenzene were deoxygenated with anhydrous Ar bubble for at least 30 min before they were used.

2. Synthesis and Characterization of Substrates and N-F Reagents

2.1. Synthesis of N-F Reagents

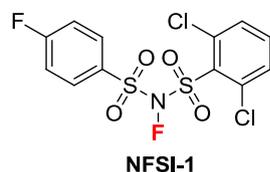


To a solution of NaOH (3.16 g, 79 mmol) in MeOH (80 mL) was added *N*-fluoro-4-fluorobenzenesulfonamide (13.9 g, 72 mmol) at 0 °C under N_2 . After that, naphthalene-1-sulfonyl chloride (17.9 g, 79 mmol) was added to the homogenous solution in portions. The reaction was then warmed up to room temperature and stirred for 2 hours. The reaction mixture was filtered, the filter cake was crystallized from DCM to yield **NFSI-2** (11.08 g, 40% yield).



N-Fluoro-*N*-((4-fluorophenyl)sulfonyl)naphthalene-1-sulfonamide (**NFSI-2**): ^1H NMR (400 MHz, CDCl_3) δ 8.75 (d, $J = 8.4$ Hz, 1H), 8.31-8.29 (m, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 8.15-8.11 (m, 2H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.81-7.77 (m, 1H), 7.70-7.66 (m, 1H), 7.60 (t, $J = 8.0$ Hz, 1H), 7.33-7.28 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.14 (d, $J = 258.6$ Hz), 137.95,

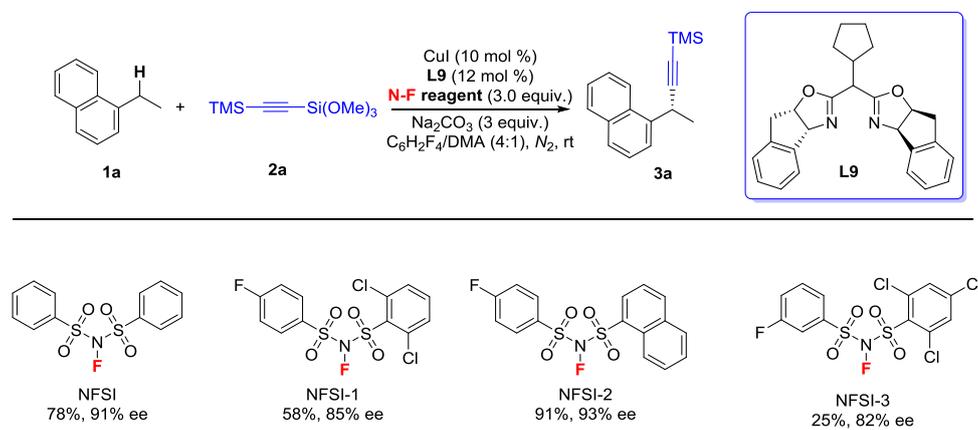
134.15, 133.49, 133.14 (d, $J = 9.4$ Hz), 130.47 (d, $J = 2.8$ Hz), 129.70, 129.66, 129.09, 128.63, 127.66, 124.46, 123.99, 116.94 (d, $J = 23.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -36.06 (s, 1F), -98.72-98.79 (m, 1F); IR (neat): $\nu = 3108, 1587, 1488, 1409, 1373, 1240, 1191, 1174, 1084, 786, 762, 673, 582, 550, 496$; Anal. calcd for $\text{C}_{16}\text{H}_{11}\text{F}_2\text{NO}_4\text{S}_2$: C 50.13, H 2.89, N 3.65, found: C 50.08, H 3.13, N 3.63; melting point: 144-146 $^\circ\text{C}$.



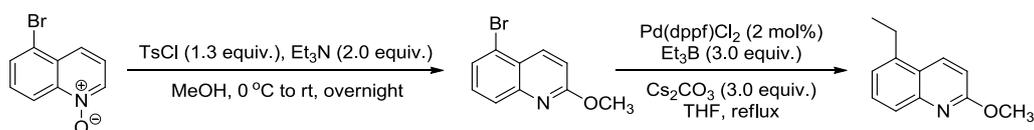
2,6-Dichloro-*N*-fluoro-*N*-((4-fluorophenyl)sulfonyl)benzenesulfonamide (**NFSI-1**): ^1H NMR (400 MHz, CDCl_3) δ 8.18-8.14 (m, 2H), 7.56-7.49 (m, 3H), 7.36-7.32 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.33 (d, $J = 259.3$ Hz), 138.06 (d, $J = 3.6$ Hz), 135.53, 135.47, 133.36 (d, $J = 10.0$ Hz), 132.07, 132.06, 117.12 (d, $J = 22.9$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -36.71 (s, 1F), -98.23-98.30 (m, 1F); IR (neat): $\nu = 3088, 1586, 1559, 1489, 1431, 1404, 1395, 1245, 1197, 1185, 1158, 1086, 853, 784, 676, 590, 543$; Anal. calcd for $\text{C}_{12}\text{H}_7\text{Cl}_2\text{F}_2\text{NO}_4\text{S}_2$: C 35.84, H 1.75, N 3.48, found: C 35.95, H 1.86, N 3.61; melting point: 121-123 $^\circ\text{C}$.

2.2. Effect of N-F Reagents on the Reaction

Scheme S1. The effect of N-fluoroarenesulfonimides



2.3. Synthesis of Alkylarenes

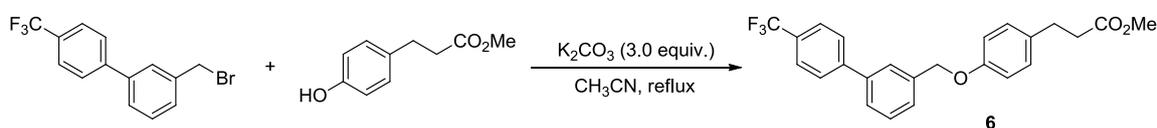


5-Bromo-2-methoxyquinoline was synthesized according to the literature.^{S1} To an ice-cooled solution of 5-bromoquinoline 1-oxide (3.36 g, 15 mmol) and TsCl (3.8 g, 20 mmol) in

MeOH (90 mL), Et₃N (4.2 mL, 30 mmol) was added at 0 °C. The reaction mixture was then stirred at room temperature overnight. After reaction completion, MeOH was removed under vacuum, and the residue was quenched by 10% HCl. Then HCl solution was neutralized with aq. Na₂CO₃ and extracted with CHCl₃. The combined organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was then purified by column chromatography on silica gel (PE/EA = 20:1) to yield 5-bromo-2-methoxyquinoline (2.49 g, 70% yield) as a white solid.

5-Ethyl-2-methoxyquinoline was prepared according to the literature.^{S2} To a solution of Pd(dppf)Cl₂ (146 mg, 0.2 mmol), Cs₂CO₃ (9.77 g, 30 mmol) and 5-bromo-2-methoxyquinoline (2.38 g, 10 mmol) in dried THF (30 mL), BEt₃ (30 mL, 30 mmol, 1.0 M in THF) was added under N₂. Then, the mixture was heated up to reflux and monitored by TLC. After cooling down to room temperature, the mixture was filtered through a short pad of celite, and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 20:1) to yield 5-ethyl-2-methoxyquinoline (1.81 g, 97% yield) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 9.2 Hz, 1H), 4.07 (s, 3H), 3.02 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.92, 147.08, 140.63, 134.80, 129.31, 125.54, 123.33, 123.07, 112.37, 53.25, 25.49, 15.34; IR (neat): ν = 2966, 2943, 2877, 1609, 1579, 1505, 1400, 1321, 1270, 1241, 1027, 808, 763, 716, 446, 432 cm⁻¹; HRMS: *m/z* (ESI) calculated for (C₁₂H₁₄NO) [M+H]⁺: 188.1070, found: 188.1068.



To a solution of 3-(bromomethyl)-4'-(trifluoromethyl)-1,1'-biphenyl (1.74 g, 5.5 mmol) and methyl 3-(4-hydroxyphenyl)propanoate (0.9 g, 5 mmol) in CH₃CN (20 mL), K₂CO₃ (2.07 g, 15 mmol) was added. The mixture was then heated up to reflux for 6 hours. After cooling down to room temperature, CH₃CN was removed under vacuum and the residue was purified by column chromatography on silica gel (PE/EA = from 40:1 to 15:1) to yield methyl 3-(4-((4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)methoxy)phenyl)propanoate **6** (1.85 g, 89% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 4H), 7.66 (s, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.51-7.45 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.2 Hz, 2H), 5.10 (s, 2H), 3.66 (s, 3H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 173.31, 157.16, 144.36, 140.03, 137.96, 133.05, 129.39 (q, *J* = 32.3 Hz), 129.27, 129.18, 127.41, 127.18, 126.79, 126.26, 125.65 (q, *J* = 4.0 Hz), 124.24 (q, *J* = 270.7 Hz), 114.83, 69.79, 51.50, 35.86, 30.04; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.42 (s, 3F); IR (neat): ν = 2951, 1733, 1613, 1583, 1322, 1238, 1163, 1110, 1068, 1014, 810, 783, 699, 518, 429 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₄H₂₁F₃O₃) [M]⁺: 414.1437, found: 414.1445; melting point: 62-64 °C.

3. Optimization of the Reaction Conditions

Table S1. Evaluation of copper catalysts.^{a,b}

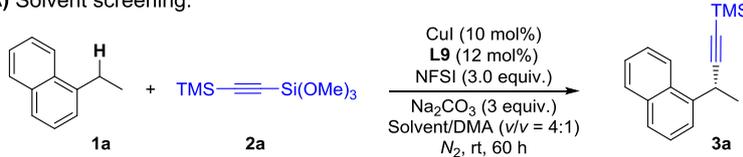


Entry	Copper catalyst	Conv. (1a) ^b	Yield of 3a ^b	ee ^c
1	CuOAc	84%	75%	91%
2	CuI	84%	78%	91%
3	[CuOTf] ₂ PhH	75%	75%	89%
4	Cu(CH ₃ CN) ₄ PF ₆	73%	70%	84%
5	Cu(CH ₃ CN) ₄ BF ₄	70%	63%	87%
6	Cu(CH ₃ CN) ₄ OTf	74%	72%	87%
7	CuTc	84%	74%	91%
8	Cu(OAc) ₂	86%	69%	91%
9	Cu(OTf) ₂	69%	69%	87%

^aReaction conditions: copper catalyst (10 mol%), **L9** (12 mol%), **1a** (0.2 mmol), **2a** (0.8 mmol), NFSI (0.6 mmol) and Na₂CO₃ (0.6 mmol) in 1,2,4,5-C₆H₂F₄/DMA (2.5 mL, v/v = 4:1) under N₂ at rt for 60 h. ^b¹H NMR yield and conversion were determined by using CH₂Br₂ as an internal standard. ^c ee value was determined by HPLC on a chiral stationary phase.

Table S2. Evaluation of solvents.^{a,b}

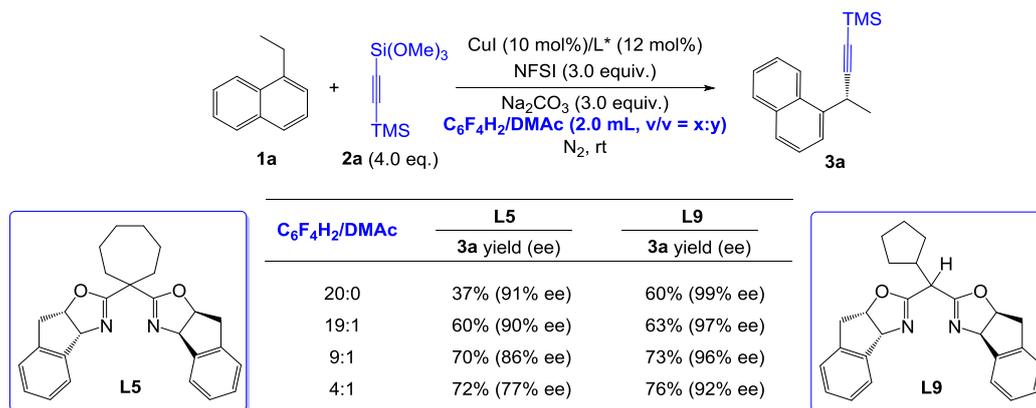
A) Solvent screening.



Entry	Solvent	Conv. (1a) ^b	Yield of 3a ^b	ee ^c
1	C ₆ H ₆	73%	66%	91%
2	Ph-Cl	78%	71%	89%
3	Ph-CH ₃	67%	61%	90%
4	Ph-CF ₃	78%	65%	83%
5	Ph-F	84%	65%	89%
6	1,2-C ₆ H ₄ F ₂	83%	70%	82%
7	1,2,3,4-C ₆ H ₂ F ₄	77%	68%	76%
8	1,2,4,5-C₆H₂F₄	84%	78%	91%
9	C ₆ F ₆	53%	55%	91%
10	1,4-C ₆ H ₄ -(CH ₃) ₂	47%	42%	89%
11 ^d	C ₆ F ₆	84%	31%	99%

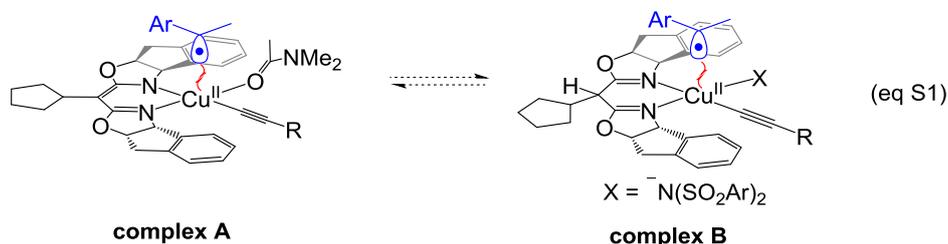
^aReaction conditions: CuI (10 mol%), **L9** (12 mol%), **1a** (0.2 mmol), **2a** (0.8 mmol), NFSI (0.6 mmol) and Na₂CO₃ (0.6 mmol) in solvent/DMA (2.5 mL, v/v = 4:1) under N₂ at rt for 60 h. ^b¹H NMR yield and conversion were determined by using CH₂Br₂ as an internal standard. ^c ee value was determined by HPLC on a chiral stationary phase. ^d Pure C₆F₆ (2 mL) was used.

B) The effect of DMAc and Box ligands on the asymmetric reaction.



The experimental results in Figure S2-B suggested that the covalent complex is less likely involved in the catalytic reaction, and more elaborations are given as follows:

(1) During the ligand screening (Table S2-B), we found that the ligand **L5** without *gem*-C-H bonds also exhibited excellent enantioselectivity (up to 91% ee) as **L9** (up to 99% ee). In addition, DMAc as co-solvent played an essential role in yields and enantioselectivities of the alkylation products. Increasing the amount of DMAc could lead to better yields, but lower enantioselectivities; notably, a similar trend towards the DMAc effect on the reaction using **L5** or **L9** was observed (see Table S2B).



(2) For **L9**, if a covalent Cu(II) complex **A** (eq S1) was involved in the radical trapping step, a neutral solvent molecule such as DMAc, instead of an anionic ligand, should coordinate to the Cu(II) center. However, the excellent enantioselectivity (up to 99% ee) was obtained in the absence of DMAc as co-solvent (see Table S2-B), and the ee values were decreased by increasing the concentration of DMAc, which are difficult to be addressed by the model of a covalent Cu(II) complex **A** (eq S1). In addition, the results presented in the manuscript showed that different N-F reagents could slightly change the ee values (see Table 1c, also see Scheme S1), suggesting that the non-covalent Cu(II) complex **B** containing the anion of bisarenesulfonamide (eq S1) is more likely involved. In view of the effect of N-F reagents on the ee values, we employed an anionic bisarylsulfonamide ligand instead of fluoride for our DFT mechanistic calculations (*vide infra*). As shown in Figure 2, the difference in the computed activation free energy ($\Delta\Delta G^\ddagger$) for the benzylic radical trapping by chiral Cu(II) species with a bismethylsulfonimide anion (2.6 kcal/mol) is pretty consistent with the

experimental result observed in the absence of DMAc (99% ee in Table S2-B), which also strongly support this mode.

Collected all, the additional experimental results suggest that a covalent complex is less likely involved in our reaction. However, we have to mention that it is difficult to explain the effect of co-solvent DMAc on yields and enantioselectivity at the moment.

Table S3. Evaluation of inorganic bases.^{a,b}

Entry	Base	Conv. (1a) ^b	Yield of 3a ^b	ee ^c
1	Na₂CO₃	84%	78%	91%
2	NaHCO ₃	88%	58%	85%
3	K ₂ CO ₃	88%	73%	91%
4	Li ₂ CO ₃	85%	75%	90%
5	Cs ₂ CO ₃	88%	71%	91%
6	CsF	65%	39%	92%

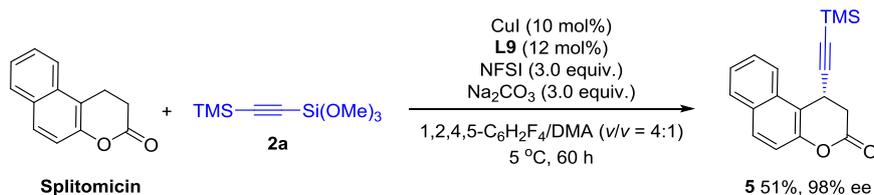
^aReaction conditions: CuI (10 mol%), **L9** (12 mol%), **1a** (0.2 mmol), **2a** (0.8 mmol), NFSI (0.6 mmol) and base (0.6 mmol) in 1,2,4,5-C₆H₂F₄/DMA (2.5 mL, v/v = 4:1) under N₂ at rt for 60 h. ^b¹H NMR yield and conversion were determined by using CH₂Br₂ as an internal standard. ^c ee value was determined by HPLC on a chiral stationary phase.

4. General Procedure for the Asymmetric Alkylation of Benzylic C-H Bonds

In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol, 3.0 equiv.) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, v/v = 4:1) under N₂, and the mixture was stirred for 30 min. Then, alkylarenes **1** (0.2 mmol, 1.0 equiv.), NFSI-2 (230 mg, 0.6 mmol, 3.0 equiv.) and alkynylating reagents **2** (0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction was stirred at room temperature for 60 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate, solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to give the desired product **3** or **4**. These results were summarized in Table 2.

5. Late-Stage Functionalization and Synthetic Applications

5.1. Late-Stage Functionalization of Splitomicin



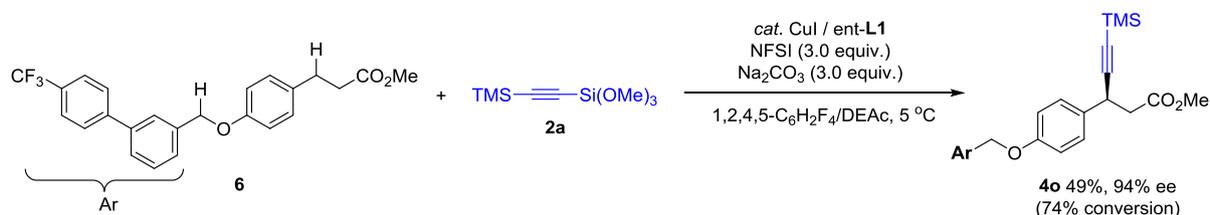
In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol, 3.0 equiv.) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, v/v = 4:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, Splitomicin (39.7 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction was stirred at 5 °C for 60 h. According to the above-mentioned workup procedure by column chromatography (PE/EA = 15:1), product **5** (29.8 mg, 51% yield, 98% ee) was obtained as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 4.58 (dd, *J* = 6.8, 1.6 Hz, 1H), 3.20 (dd, *J* = 15.6, 1.6 Hz, 1H), 2.92 (dd, *J* = 15.6, 6.8 Hz, 1H), 0.07 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 166.33, 148.89, 130.93, 130.30, 129.96, 128.71, 127.58, 125.34, 122.74, 117.69, 115.41, 102.41, 89.16, 35.14, 24.77, -0.20; IR (neat): ν = 2962, 2161, 1755, 1465, 1352, 1259, 1159, 1081, 1046, 1017, 837, 797, 760, 750 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₈H₁₈O₂Si) [M]⁺: 294.1071, found: 294.1070; melting point: 109-111 °C.

[α]_D^{30.7} = -131.96 (*c* 0.9, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 98/2, flow 0.7 mL/min, detection at 214 nm) retention time = 10.01 min (major) and 11.68 min (minor).

5.2. Synthetic Applications



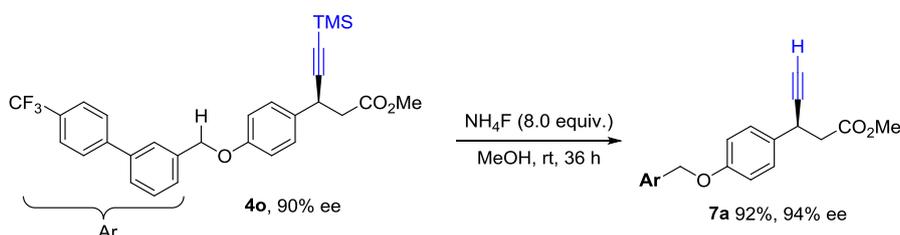
In a dried sealed 10 mL Schlenk tube, ent-**L1** (12.3 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol, 3.0 equiv.) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DEAc (*N,N*-diethylacetamide) (2.5 mL, v/v = 4:1) under N₂, the mixture was stirred for 30 min and cooled down to 5 °C. Then, methyl

3-(4-((4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)methoxy)phenyl)propanoate **6** (82.9 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction was stirred at 5 °C for 4.5 d. According to the same workup process by column chromatography (PE/EA = 8:1), product **4o** (50.5 mg, 49% yield, 94% ee) was obtained as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 4H), 7.66 (s, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.52-7.46 (m, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 2H), 4.15 (t, *J* = 7.6 Hz, 1H), 3.66 (s, 3H), 2.80 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.69 (dd, *J* = 15.2, 7.6 Hz, 1H), 0.17 (s, 9H); ¹³C NMR (400 MHz, CDCl₃) δ 171.26, 157.80, 144.37, 140.14, 137.83, 132.67, 129.46 (q, *J* = 32.2 Hz), 129.26, 128.52, 127.47, 127.23, 126.92, 126.34, 125.72 (q, *J* = 3.9 Hz), 124.24 (q, *J* = 269.7 Hz), 114.91, 106.64, 87.60, 69.84, 51.71, 43.40, 34.33, 0.01; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.44 (s, 3F); IR (neat): ν = 2955, 2174, 1738, 1611, 1509, 1324, 1247, 1163, 1122, 1111, 1070, 1016, 839, 789, 759, 699 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₉H₂₉F₃O₃Si) [M]⁺: 510.1833, found: 510.1840.

[α]_D^{23.1} = 16.3 (*c* 0.67, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 95/5, flow 0.7 mL/min, detection at 254 nm) retention time = 7.74 min (minor) and 10.25 min (major).



To a solution of **4o** (51 mg, 0.1 mmol) in MeOH (2 mL), NH₄F (29.6 mg, 0.8 mmol) was added. The mixture was stirred at room temperature for 36 h. After the reaction was completed, the organic solvent was removed under vacuum, and the residue was purified by column chromatography (PE/EA = 8:1) to give the product **7a** (40.1 mg, 92% yield, 94% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 4H), 7.65 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.51-7.45 (m, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.11 (s, 2H), 4.16-4.11 (m, 1H), 3.67 (s, 3H), 2.83 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.71 (dd, *J* = 15.2, 6.8 Hz, 1H), 2.28 (d, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 171.19, 157.89, 144.36, 140.13, 137.77, 132.29, 129.45 (q, *J* = 32.1 Hz), 129.26, 128.44, 127.46, 127.22, 126.92, 126.31, 125.71 (q, *J* = 3.7 Hz), 124.23 (q, *J* = 271.1 Hz), 115.00, 84.62, 71.24, 69.84, 51.81, 42.86, 33.04; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.42 (s, 3F); IR (neat): ν = 3294, 1736, 1612, 1509, 1323, 1241, 1161, 1110, 1070, 1016, 842, 830, 789, 643 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₆H₂₁F₃O₃) [M]⁺: 438.1437, found: 438.1450.

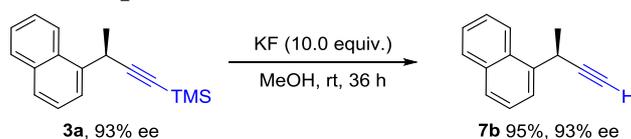
These data are consistent with the reports in the literature.^{S3}

$[\alpha]_D^{20.0} = 3.40$ (*c* 1.06, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 95/5, flow 0.7 mL/min, detection at 254 nm) retention time = 17.56 min (minor) and 22.94 min (major).

6. Synthetic Transformations

6.1. Removing the TMS Group in 3a



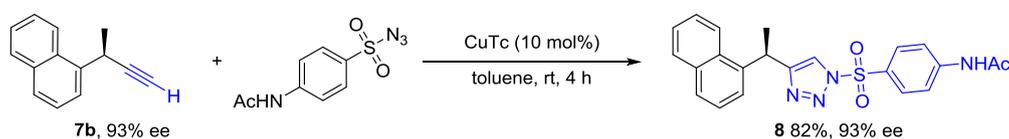
KF (116 mg, 2.0 mmol) was added to a solution of **3a** (50.5 mg, 0.2 mmol) in MeOH (2 mL), and the mixture was stirred at room temperature for 36 h. After the reaction was completed, the organic solvent was removed under vacuum, and the residue was purified by column chromatography (PE/EA = 100:1) to give product **7b** (34.2 mg, 95% yield, 93% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.88-7.86 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.56-7.45 (m, 3H), 4.56-4.50 (qd, *J* = 7.2, 2.4 Hz, 1H), 2.31 (d, *J* = 2.4 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.13, 133.95, 130.43, 129.00, 127.58, 126.06, 125.62, 125.53, 124.10, 122.98, 87.23, 70.39, 28.13, 23.10; IR (neat): ν = 3293, 3048, 2977, 2931, 2113, 1596, 1510, 1449, 1395, 797, 774, 632, 517, 433 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₄H₁₂) [M]⁺: 180.0934, found: 180.0932.

$[\alpha]_D^{30.8} = 18.40$ (*c* 0.71, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 12.10 min (minor) and 13.02 min (major).

6.2. Click Reaction



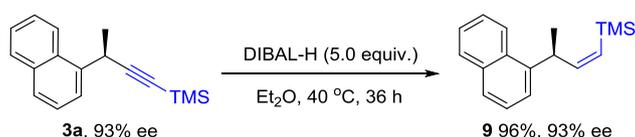
To a solution of CuTc (3.8 mg, 0.02 mmol) and **7b** (36 mg, 0.2 mmol) in toluene (2 mL), 4-acetamidobenzenesulfonyl azide (39.5 mg, 0.2 mmol) was added, and the mixture was stirred at room temperature for 4 h. After the reaction was completed, the organic solvent was removed under vacuum, and the residue was purified by column chromatography (PE/EA = 3:1) to give the product **8** (69.2 mg, 82% yield, 93% ee) as a white solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.58 (s, 1H), 8.74 (s, 1H), 8.21-8.19 (m, 1H), 8.08-8.05 (m, 2H), 7.93-7.86 (m, 3H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.55-7.48 (m, 2H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 7.6$ Hz, 1H), 5.13 (q, $J = 7.2$ Hz, 1H), 2.10 (s, 3H), 1.70 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 169.61, 152.16, 146.17, 140.05, 133.59, 130.62, 130.02, 128.84, 127.97, 127.16, 126.31, 125.72, 125.70, 124.30, 123.29, 122.20, 119.24, 31.61, 24.34, 20.99; IR (neat): $\nu = 3326, 3119, 1699, 1589, 1527, 1392, 1319, 1193, 1174, 1018, 1004, 776, 728, 647, 631, 579, 541$ cm^{-1} ; HRMS: m/z (ESI) calculated for $(\text{C}_{22}\text{H}_{21}\text{N}_4\text{O}_3\text{S})$ $[\text{M}+\text{H}]^+$: 421.1329, found: 421.1337. The melting point (**8**) couldn't be determined, for it went bad at high temperature.

$[\alpha]_{\text{D}}^{30.1} = -85.15$ (c 0.69, MeOH).

HPLC (AD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 85/15, flow 0.7 mL/min, detection at 214 nm) retention time = 27.52 min (major) and 38.21 min (minor).

6.3. Reduction of the C-C Triple Bond by DIBAL-H



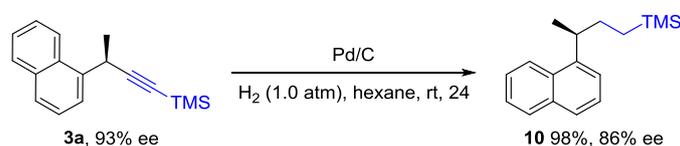
To a solution of **3a** (50.5 mg, 0.2 mmol) in Et_2O (2 mL), DIBAL-H (1.0 mL, 1.0 M solution in hexanes) was added, then the mixture was stirred at 40 $^\circ\text{C}$ for 36 h. After the reaction was completed, aqueous solution of NaOH was added to quench extra DIABL-H, and the solution was extracted by Et_2O . The combined organic layer was dried over MgSO_4 , and filtered. After the removal of the solvent, the residue was purified by column chromatography (PE) to give product **9** (48.7 mg, 96% yield, 93% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 1H), 7.89-7.87 (m, 1H), 7.76-7.72 (m, 1H), 7.57-7.44 (m, 4H), 6.68 (dd, $J = 14.0, 9.6$ Hz, 1H), 5.64 (d, $J = 14.0$ Hz, 1H), 4.50-4.43 (qd, $J = 9.6, 6.4$ Hz, 1H), 1.51 (d, $J = 6.8$ Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.70, 142.29, 133.95, 131.24, 128.92, 128.56, 126.62, 125.65, 125.61, 125.31, 123.44, 122.93, 38.21, 23.09, 0.25; IR (neat): $\nu = 2955, 1597, 1247, 832, 794, 773, 689, 671$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{17}\text{H}_{22}\text{Si})$ $[\text{M}]^+$: 254.1485, found: 254.1491.

$[\alpha]_{\text{D}}^{30.8} = 39.11$ (c 0.93, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 19.31 min (major) and 21.57 min (minor).

6.4. Pd/C-Catalyzed Hydrogenation of the C-C Triple Bond



To a solution of **3a** (50.5 mg, 0.2 mmol) in hexane (2.0 mL), 10 wt% Pd/C (5.1 mg) was added under H₂ (1.0 atm), and the hydrogenation was performed at room temperature for 24 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The residue was purified by column chromatography (PE) to give product **10** (50.5 mg, 98% yield, 86% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.90-7.88 (m, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.56-7.47 (m, 3H), 7.40 (d, *J* = 7.2 Hz, 1H), 3.60-3.52 (m, 1H), 1.91-1.82 (m, 1H), 1.73-1.64 (m, 1H), 1.41 (d, *J* = 7.2 Hz, 3H), 0.67-0.59 (m, 1H), 0.55-0.47 (m, 1H), -0.01 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 143.85, 133.94, 131.86, 128.91, 126.12, 125.60, 125.58, 125.17, 123.25, 122.41, 36.78, 31.99, 21.28, 14.75, -1.79; IR (neat): ν = 3047, 2953, 2917, 1596, 1509, 1454, 1246, 1024, 859, 830, 795, 775, 690, 437 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₇H₂₄Si) [M]⁺: 256.1642, found: 256.1648.

[α]_D^{30.9} = -43.96 (*c* 1.0, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 24.25 min (major) and 33.73 min (minor).

6.5. TBD-Catalyzed Isomerization



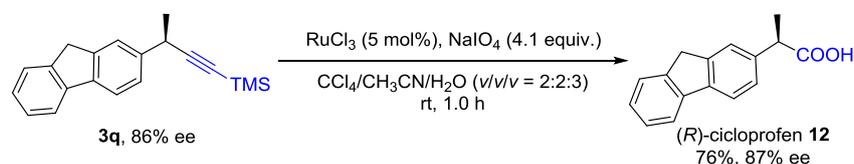
To a solution of **4k** (55 mg, 0.2 mmol) in THF (4 mL), triazabicyclodecene (TBD, 5.6 mg, 0.04 mmol) was added, and the mixture was stirred at room temperature for 48 h. After the reaction was completed, the organic solvent was removed under vacuum, and the residue was purified by column chromatography (PE/EA = 100:1) to give product **11** (51.2 mg, 93% yield, 91% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 7.6 Hz, 1H), 7.90-7.88 (m, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.56-7.49 (m, 4H), 7.32-7.26 (m, 1H), 7.17-7.11 (m, 2H), 6.95-6.90 (m, 1H), 6.30 (q, *J* = 2.8 Hz, 1H), 2.38 (d, *J* = 2.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 205.50, 163.15 (d, *J* = 243.5 Hz), 137.47 (d, *J* = 7.7 Hz), 135.91, 133.94, 130.83, 129.96 (d, *J* = 8.0 Hz), 128.51, 127.84, 126.09, 125.81, 125.46, 125.30, 125.14, 122.67 (d, *J* = 2.6 Hz), 113.66 (d, *J* = 20.6 Hz), 113.41 (d, *J* = 21.8 Hz), 103.66, 93.29 (d, *J* = 2.0 Hz), 21.13; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.53-113.60 (m, 1F); IR (neat): ν = 2980, 1610, 1584, 1487, 1445, 1247, 1131, 872, 798, 772, 741, 681 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₀H₁₅F) [M]⁺: 274.1152, found: 274.1155.

[α]_D^{31.0} = -478.84 (*c* 0.94, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μ m, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 6.28 min (minor) and 7.04 min (major).

6.6. Oxidation of the C-C Triple Bond



To a solution of **3q** (23.8 mg, 0.082 mmol) in a mixed solvent of CCl₄, CH₃CN and H₂O (0.7 mL, v/v/v 2:2:3), RuCl₃ (0.8 mg, 5 mol%) and sodium periodate (72 mg, 4.1 equiv.) were added, then the mixture was stirred vigorously at room temperature for 1 h. After reaction completion, the mixture was extracted with dichloromethane (3x5 mL). The combined organic phase was dried over Na₂SO₄. The organic solvent was removed under vacuum, and the residue was purified via a preparative plate (PE/EA = 3:2) to give **(R)-cicloprofen 12** (14.8 mg, 76%, 86% ee) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.76-7.72 (m, 2H), 7.52 (d, *J* = 10.4 Hz, 2H), 7.38-7.29 (m, 3H), 3.88 (s, 2H), 3.82 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.95, 143.76, 143.29, 141.27, 141.09, 138.33, 126.73, 126.70, 126.31, 124.99, 124.19, 119.99, 119.86, 45.32, 36.84, 18.33; IR (neat): ν = 2962, 1692, 1410, 1259, 1014, 794, 766, 733, 611, 460 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₆H₁₄O₂) [M]⁺: 238.0988, found: 238.0995.

These data are consistent with those reported in the literature.^{S4}

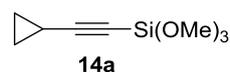
$[\alpha]_D^{30.9} = -26.76$ (*c* 0.33, MeOH).

HPLC (AD-H, 0.46*25 cm, 5 μ m, hexane/isopropanol/TFA = 90/10/0.1, flow 0.7 mL/min, detection at 254 nm) retention time = 12.76 min (major) and 13.80 min (minor).

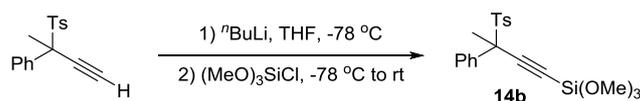
7. Mechanistic Studies

7.1. Synthesis of Alkynylsilanes

Alkynylsilanes were synthesized according to the reported literature.^{S5a}

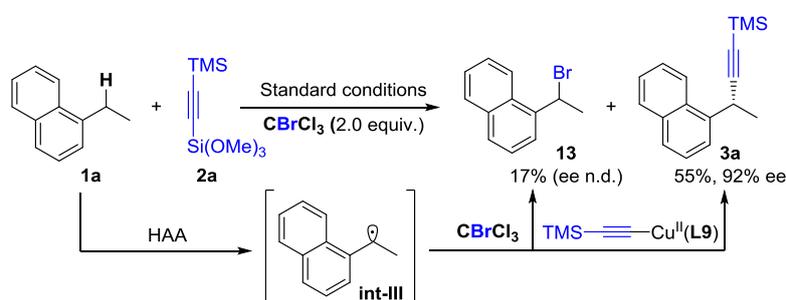


(Cyclopropylethynyl)trimethoxysilane (**14a**): ¹H NMR (400 MHz, CDCl₃) δ 3.58 (s, 9H), 1.36-1.29 (m, 1H), 0.86-0.81 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 111.05, 69.35, 50.71, 8.89, 0.08; IR (neat): ν = 2944, 2843, 2166, 1456, 1352, 1191, 1072, 983, 712, 566, 486 cm⁻¹; HRMS: m/z (EI) calculated for (C₈H₁₄O₃Si) [M]⁺: 186.0712, found: 186.0709.



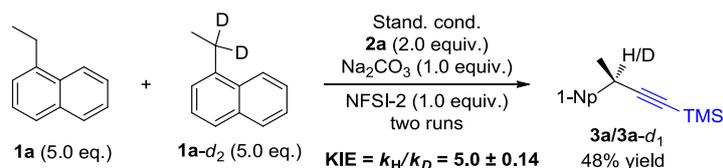
1-Methyl-4-((2-phenylbut-3-yn-2-yl)sulfonyl)benzene was synthesized according to the literature.^{S5b} To a solution of 1-methyl-4-((2-phenylbut-3-yn-2-yl)sulfonyl)benzene (1.422 g, 5 mmol) in dried THF (10 mL) was slowly added ⁿBuLi (2.4 mL, 2.5 M in solution in hexanes) at -78 °C under N₂, the reaction mixture was warmed up to room temperature and stirred at room temperature for 30 min. Then, (MeO)₃SiCl (10 mmol, 2.0 equiv.) was dropwise added to the mixture at -78 °C, and the reaction was warmed up to room temperature and stirred at room temperature overnight. After reaction completion, THF was removed under vacuum, dried Et₂O (50 mL) was then poured into the residue, the resulting mixture was sonicated for 30 min. After filtration, Et₂O was removed and 1.97 g the residue was used directly for the enantioselective benzylic C-H bond alkylation. IR (neat): ν = 2944, 2844, 2182 (C-C triple bond), 1596, 1492, 1451, 1315, 1188, 1144, 1065, 946, 815, 763, 708, 683, 670, 573, 527, 450; HRMS: m/z (EI) calculated for (C₂₀H₂₄O₅SSi) [M]⁺: 404.1114, found: 404.1110. Note: The product **14b** can not be isolated by flash column chromatography or distillation under high vacuum. THF and Et₂O should be very dry, all the apparatuses should be dried before they were used.

7.2. Using CBrCl₃ as a Radical Scavenger



In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, v/v = 4:1) under N₂, and the mixture was stirred for 30 min. Then, **1a** (31.2 mg, 0.2 mmol, 1.0 equiv.), NFSI-2 (230 mg, 0.6 mmol, 3.0 equiv.), **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) and CBrCl₃ (79.3 mg, 0.4 mmol, 2.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred at room temperature for 39 h. The reaction was quenched by a short pad of silica gel (PE/EA = 10:1), the solvent was removed under vacuum, and the residue was analyzed by ¹H NMR using CH₂Br₂ as an internal standard. The formation of **13** indicated the involvement of a benzylic radical.

7.3. Competition KIE Experiment



The reaction was performed using NFSI-2 as a limiting reagent. In a dried sealed 10 mL Schlenk tube, **L9** (4.8 mg, 0.012 mmol, 12 mol %), CuI (1.9 mg, 0.01 mmol, 10 mol %) and anhydrous Na₂CO₃ (10.6 mg, 0.1 mmol) were dissolved in 1,2,4,5-C₆H₂F₄ and DMA (1.25 mL, *v/v* = 4:1) under N₂, and the mixture was stirred for 30 min. Then, **1a** (78.1 mg, 0.5 mmol, 5.0 equiv.), **1a-d₂** (79.1 mg, 0.5 mmol, 5.0 equiv.), NFSI-2 (38.3 mg, 0.1 mmol, 1.0 equiv.) and **2a** (43.7 mg, 0.2 mmol, 2.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred at room temperature for 38 h. The reaction was quenched by a short pad of silica gel (PE/EA = 10:1), the solvent was removed under vacuum, and the residue was purified by column chromatography (PE) to give the mixture products **3a/3a-d₁** as colorless oil. The KIE ratio was determined by ¹H qNMR spectroscopy.

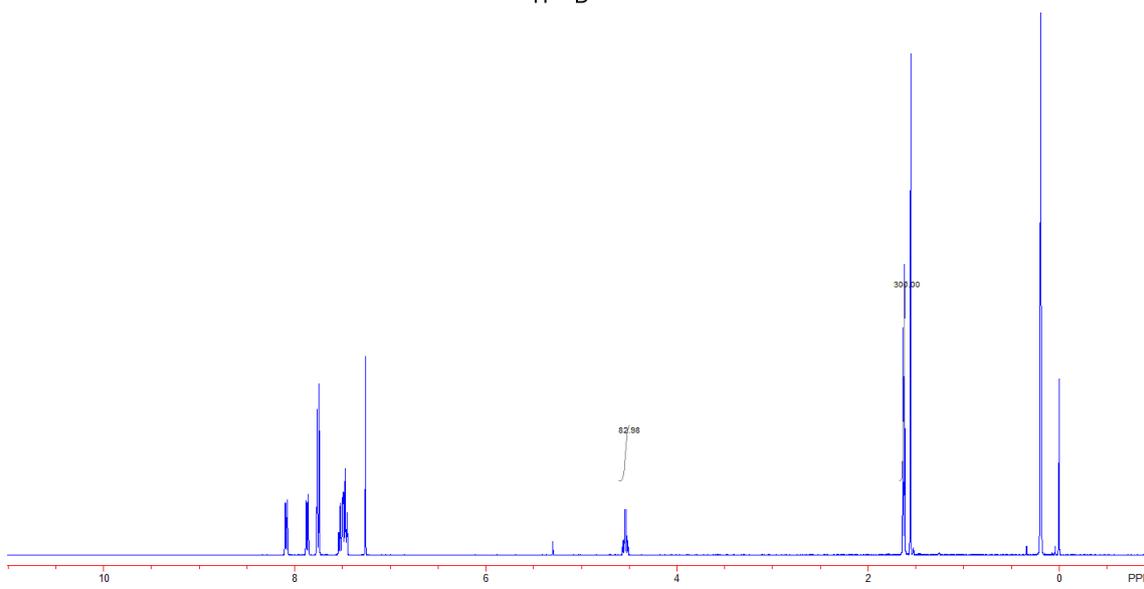
First run: KIE = 4.86 (48% isolated yield); second run: KIE = 5.14 (49% isolated yield).

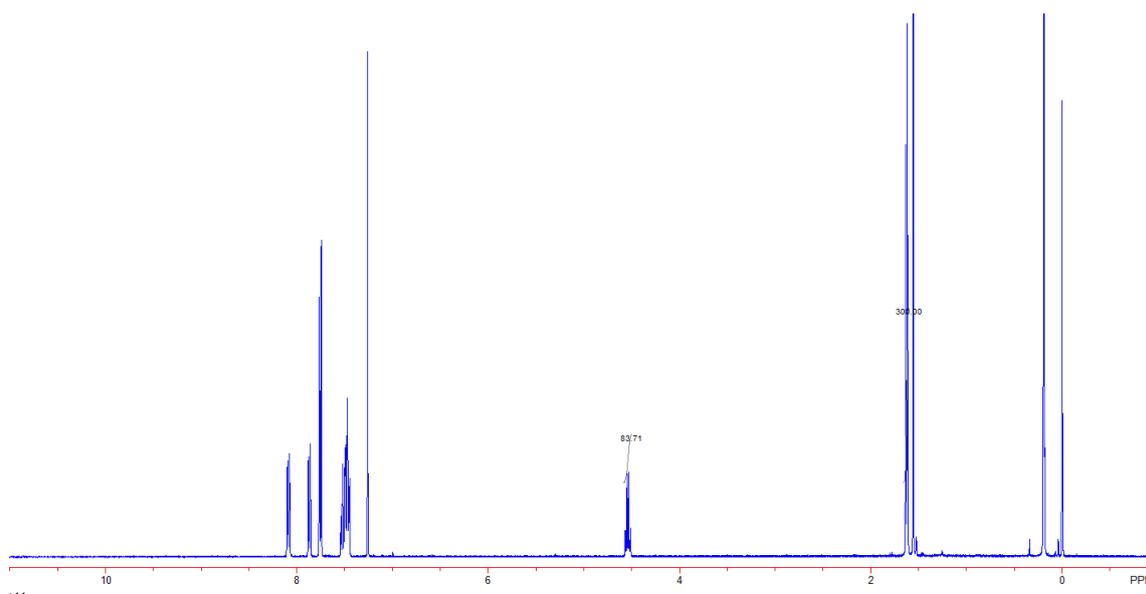
Ratio of the products (%)

Run	3a	3a-d₁	K _H /K _D
1	82.98	17.02	4.86
2	83.71	16.29	5.14

Average = 5.0

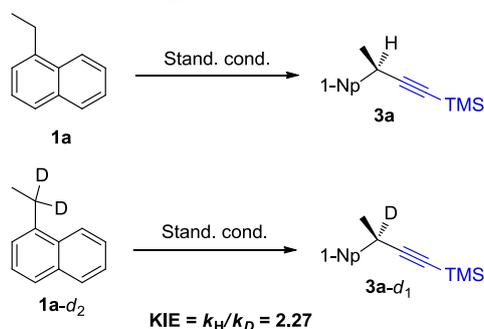
$$\text{KIE} = K_{\text{H}}/K_{\text{D}} = 5.0 \pm 0.14$$

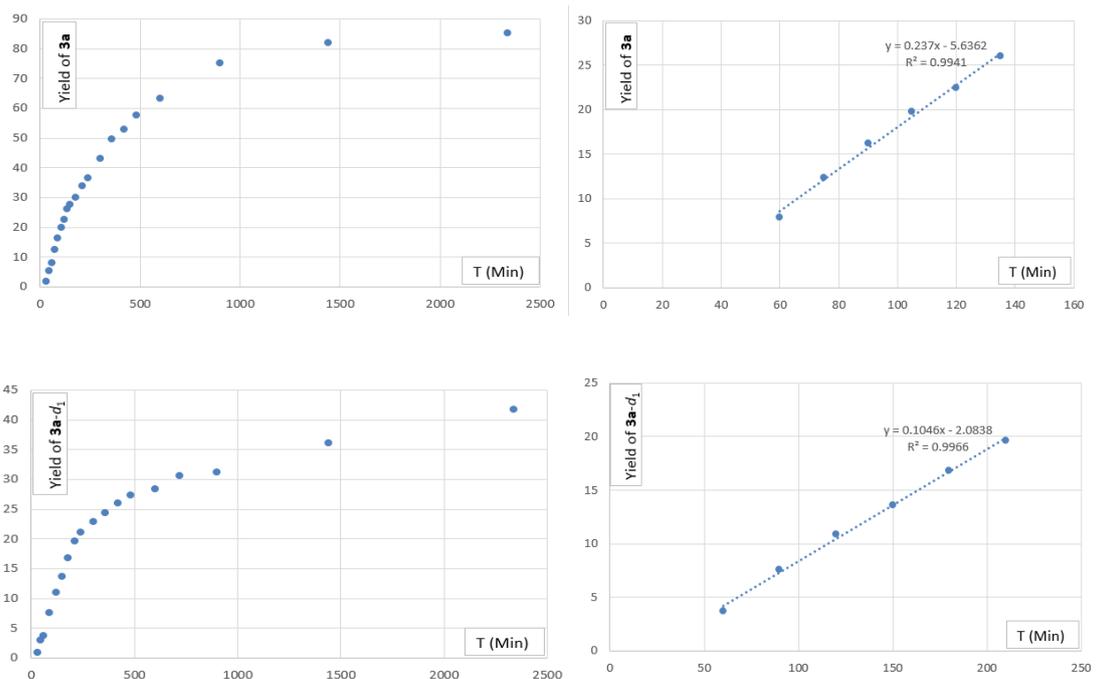




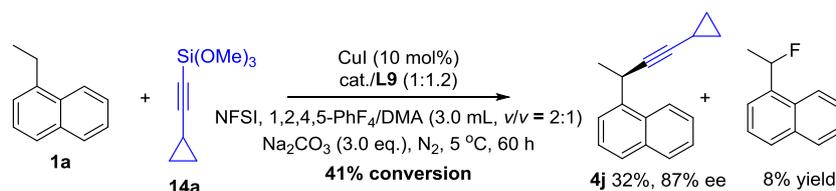
7.4. Independent-Rate KIE Experiments

For the enantioselective benzylic C-H bond alkylation is heterogeneous, the reaction of **1a** and the reaction of **1a-d₂** under the standard conditions were carried out at various time independently. In a glove box, a homogenous solution of CuI (38.1 mg, 0.2 mmol) and **L9** (95.6 mg, 0.24 mmol) in dried and degassed DCM was prepared in a 2.0 mL volumetric flask. In the glove box, anhydrous Na₂CO₃ (31.8 mg, 3.0 equiv.) and 100 μL the solution of Cu/**L9** in DCM were added to a dried sealed 10 mL Schlenk tube, and DCM was removed under high vacuum very carefully. Then, the residue was dissolved in 1,2,4,5-C₆H₂F₄/DMA (1.25 mL, v/v = 4:1) under N₂, **1a/1a-d₂** (0.1 mmol, 1.0 equiv.), NFSI-2 (115 mg, 0.3 mmol, 3.0 equiv.) and **2a** (87.4 mg, 0.4 mmol, 4.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred at room temperature for the indicated time. All the reactions were quenched through a short pad of silica gel (PE/EA = 10:1) and solvent was removed under vacuum. The residue was analyzed by GC using dodecane as an internal standard. These studies revealed an independent KIE of 2.27, suggesting that C-H bond cleavage is only partially rate-determining.





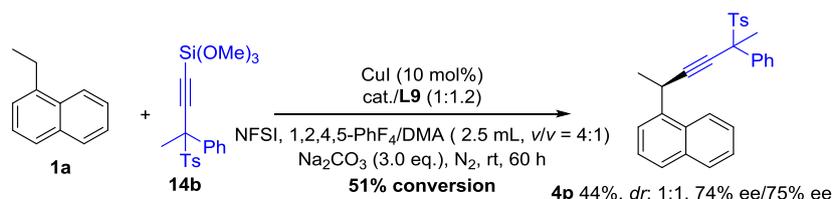
7.5. Experimental Mechanistic Studies



In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol, 3.0 equiv.) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (3.0 mL, v/v = 2:1) under N₂, and the mixture was stirred for 30 min. Then, **1a** (31.2 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and (cyclopropylethynyl)trimethoxysilane **14a** (149 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, the tube was sealed with Teflon septum, and the reaction was stirred at 5 °C for 60 h. The reaction was quenched by a short pad of silica gel (PE/EA = 4:1), the solvent was removed under vacuum and the residue was purified by column chromatography (PE) to give product **4j** (14.2 mg, 32% yield, 87% ee) as colorless oil. 41% Conversion (**1a**) and 8% yield of the C-H fluorination product were determined by ¹H NMR using CH₂Br₂ as an internal standard. Excellent mass balance was observed for the reaction.

$$[\alpha]_{\text{D}}^{25.5} = 14.99 \text{ (} c \text{ 0.41, CHCl}_3 \text{)}.$$

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 8.93 min (major) and 13.88 min (minor).



In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol, 3.0 equiv.) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, *v/v* = 4:1) under N₂, and the mixture was stirred for 30 min. Then, **1a** (31.2 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and the unisolable alkyne **14b** (0.8 mmol, 4.0 equiv.) were added sequentially, the tube was sealed with Teflon septum, and the reaction was stirred at room temperature for 60 h. The reaction was quenched by a short pad of silica gel (PE/EA = 4:1), the solvent was removed under vacuum. The residue was purified by RP-HPLC (CH₃CN/H₂O = 9:1) to give product **4p** (25.5 mg, 29% yield, dr: 1.1:1, 74% ee/75% ee) as very sticky colorless oil. 51% Conversion (**1a**) and 44% ¹H NMR yield (**4p**) were determined by using CH₂Br₂ as an internal standard. Excellent mass balance was also observed for the reaction.

¹H NMR (400 MHz, CDCl₃) δ 8.10-8.06 (m, 1H), 7.91-7.87 (m, 1H), 7.80-7.78 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 6.8 Hz, 1H), 7.55-7.44 (m, 5H), 7.34-7.24 (m, 5H), 6.91 (t, *J* = 6.8 Hz, 2H), 4.62 (q, *J* = 7.2 Hz, 1H), 2.31-2.30 (diastereomers, 3H), 2.13 (s, 3H), 1.71-1.69 (diastereomers, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.44, 144.41, 137.98, 137.93, 134.79, 133.97, 131.69, 131.66, 130.82, 130.80, 130.49, 130.48, 129.07, 128.97, 128.78, 128.45, 128.42, 127.84, 127.63, 126.12, 126.07, 125.63, 125.60, 124.32, 124.29, 123.12, 92.77, 92.74, 79.67, 79.62, 67.24, 28.70, 28.63, 22.68, 22.61, 22.36, 22.30, 21.55, 21.53; IR (neat): *ν* = 3054, 2980, 2932, 2248, 1593, 1498, 1448, 1386, 1142, 1061, 909, 783, 731, 690, 642, 576, 517 cm⁻¹; HRMS: *m/z* (ESI) calculated for (C₂₉H₂₆O₂NaS) [M+Na]⁺: 461.1546, found: 461.1549.

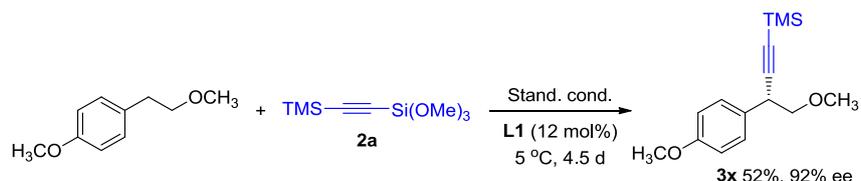
$[\alpha]_{\text{D}}^{25.5} = -11.71$ (*c* 0.64, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 97/3, flow 0.7 mL/min, detection at 214 nm) retention time = 23.41 min (minor) and 33.84 min (major), 25.94 min (major) and 29.58 min (minor).

7.6. Equimolar Complex of CuI and L9 in the Presence of Anhydrous Na₂CO₃

In a glove box, CuI (7.6 mg, 0.04 mmol), **L9** (15.9 mg, 0.04 mmol) and anhydrous Na₂CO₃ (127.2 mg, 1.2 mmol) were dissolved in 2 mL CDCl₃, and the mixture was stirred at room temperature for 2 h. After filtration in the glove box, the filtrate was directly measured by ¹H NMR. The ¹H NMR results clearly demonstrated that **L9** couldn't generate a covalent complex with CuI in the presence of anhydrous Na₂CO₃, for Na₂CO₃ is probably not basic enough for the deprotonation process.

to give product **3h** (1.03 g, 66% yield, 94% ee) as colorless oil. 75% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.



In a dried sealed 250 mL Schlenk tube, **L1** (612.8 mg, 1.2 mmol, 12 mol %), CuI (190.5 mg, 1.0 mmol, 10 mol %) and anhydrous Na_2CO_3 (3.18 g, 30 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (125 mL, $v/v = 4:1$) under N_2 , and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 1-methoxy-4-(2-methoxyethyl)benzene **1x** (1.66 g, 10.0 mmol, 1.0 equiv.), NFSI (9.46 g, 30.0 mmol, 3.0 equiv.) and **2a** (8.74 g, 40 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. According to the same workup procedure, the residue was purified by column chromatography (PE/EA = 10:1) to give product **3x** (1.36 g, 52% yield, 92% ee) as colorless oil. 57% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

8.2. Using PhCl and DMA as Solvents



In a dried sealed 250 mL Schlenk tube, **L1** (612.8 mg, 1.2 mmol, 12 mol %), CuI (190.5 mg, 1.0 mmol, 10 mol %) and anhydrous Na_2CO_3 (3.18 g, 30 mmol) were dissolved in a mixed solvent of PhCl and DMA (105 mL, $v/v = 20:1$) under N_2 , and the mixture was stirred at room temperature for 30 min and cooled down to 5 °C. Then, 4-ethyl-1,1'-biphenyl (1.83 g, 10 mmol, 1.0 equiv.), NFSI (9.46 g, 30 mmol, 3.0 equiv.) and **2a** (8.74 g, 40 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. According to the same workup procedure, the residue was purified by column chromatography (PE/EA = 50:1) to give product **3r** (1.82 g, 65% yield, 80% ee) as colorless oil. 80% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

$$[\alpha]_{\text{D}}^{24.6} = -0.19 \text{ (} c \text{ 1.1, CHCl}_3\text{)}.$$

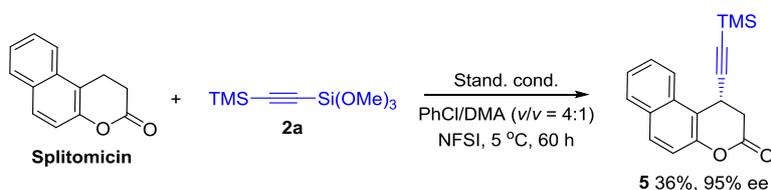
HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 20.49 min (major) and 26.82 min (minor).



In a dried sealed 250 mL Schlenk tube, **L9** (669.5 mg, 1.68 mmol, 24 mol %), CuI (266.6 mg, 1.4 mmol, 20 mol %) and anhydrous Na₂CO₃ (4.45 g, 42 mmol) were dissolved in a mixed solvent of PhCl and DMA (87.5 mL, *v/v* = 4:1) under N₂, and the mixture was stirred at room temperature for 30 min and cooled down to 5 °C. Then, 5-ethyl-2-methoxyquinoline (1.31 g, 7 mmol, 1.0 equiv.), NFSI (13.24 g, 42 mmol, 6.0 equiv.) and **2a** (12.23 g, 56 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. According to the same workup procedure, the residue was purified by column chromatography (PE/EA = 60:1) to give product **4e** (950.2 mg, 48% yield, 86% ee) as colorless oil. 50% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

$$[\alpha]_{\text{D}}^{23.5} = -6.32 \text{ (} c \text{ 1.04, CHCl}_3\text{)}.$$

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 5.27 min (minor) and 5.50 min (major).

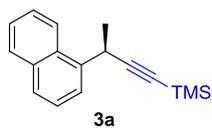


In a dried sealed 250 mL Schlenk tube, **L9** (334.7 mg, 0.84 mmol, 12 mol %), CuI (133.3 mg, 0.7 mmol, 10 mol %) and anhydrous Na₂CO₃ (2.23 g, 21 mmol) were dissolved in a mixed solvent of PhCl and DMA (87.5 mL, *v/v* = 4:1) under N₂, and the mixture was stirred at room temperature for 30 min and cooled down to 5 °C. Then, Splitomicin (1.39 g, 7 mmol, 1.0 equiv.), NFSI (6.62 g, 21 mmol, 3.0 equiv.) and **2a** (6.12 g, 28 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 60 h. According to the same workup procedure, the residue was purified by column chromatography (PE/EA = 15:1) to give product **5** (743.7 mg, 36% yield, 95% ee) as a white solid.

$$[\alpha]_{\text{D}}^{26.1} = -127.24 \text{ (} c \text{ 0.79, CHCl}_3\text{)}.$$

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 98/2, flow 0.7 mL/min, detection at 214 nm) retention time = 9.55 min (major) and 11.12 min (minor).

9. Product Characterization

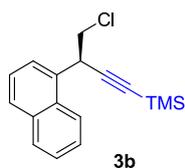


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE) yielded product **3a** (45.0 mg, 89% yield, 93% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.54-7.46 (m, 3H), 4.55 (q, $J = 6.8$ Hz, 1H), 1.63 (d, $J = 6.8$ Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.64, 133.94, 130.45, 128.93, 127.41, 125.90, 125.65, 125.44, 124.31, 123.13, 109.71, 86.57, 29.52, 23.56, 0.16; IR (neat): $\nu = 2959, 2165, 1248, 1115, 1007, 912, 838, 797, 774, 758, 654, 425$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{17}\text{H}_{20}\text{Si})$ $[\text{M}]^+$: 252.1329, found: 252.1331.

$[\alpha]_{\text{D}}^{25.9} = 1.33$ (c 0.94, CHCl_3).

HPLC (AD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 6.43 min (major) and 7.39 min (minor).

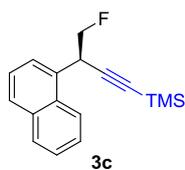


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE) yielded product **3b** (48.5 mg, 85% yield, 94% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.82 (t, $J = 8.4$ Hz, 2H), 7.59-7.49 (m, 3H), 4.80 (dd, $J = 8.4, 5.6$ Hz, 1H), 3.90 (dd, $J = 10.4, 5.2$ Hz, 1H), 3.80 (dd, $J = 10.0, 8.4$ Hz, 1H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.93, 133.44, 130.55, 129.15, 128.58, 126.50, 126.32, 125.75, 125.48, 122.43, 104.76, 89.54, 47.92, 38.63, -0.01; IR (neat): $\nu = 2959, 1248, 1089, 1075, 979, 951, 880, 859, 835, 783, 757, 409$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{17}\text{H}_{19}\text{ClSi})$ $[\text{M}]^+$: 286.0939, found: 286.0941.

$[\alpha]_{\text{D}}^{26.5} = 29.88$ (c 0.8, CHCl_3).

HPLC (AD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 7.80 min (major) and 8.60 min (minor).

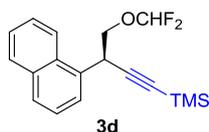


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE) yielded product **3c** (30.4 mg, 56% yield, 96% ee) as colorless oil. 72% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84-7.79 (m, 2H), 7.58-7.49 (m, 3H), 4.90-4.83 (m, 1H), 4.76-4.69 (m, 1H), 4.65-4.57 (m, 1H), 0.23 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 133.88, 132.00 (d, *J* = 5.8 Hz), 130.90, 129.05, 128.47, 126.44, 126.40, 125.73, 125.54, 122.59, 103.97 (d, *J* = 6.4 Hz), 89.22, 85.42 (d, *J* = 179.8 Hz), 36.57 (d, *J* = 22.5 Hz), -0.01; ¹⁹F NMR (376 MHz, CDCl₃) δ -211.63 (td, *J* = 47.4, 14.7 Hz, 1F); IR (neat): ν = 2959, 2165, 1250, 1017, 993, 905, 836, 796, 778, 758, 413 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₇H₁₉FSi) [M]⁺: 270.1235, found: 270.1230.

[α]_D^{24.8} = 7.71 (*c* 0.72, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 8.24 min (major) and 9.74 min (minor).

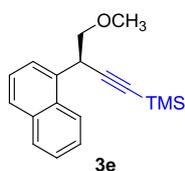


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE/EA = 50:1) yielded product **3d** (38.0 mg, 60% yield, 96% ee) as colorless oil. 64% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.58-7.48 (m, 3H), 6.26 (t, *J* = 74.8 Hz, 1H), 4.78 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.21 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.12 (dd, *J* = 9.6, 8.4 Hz, 1H), 0.22 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 133.88, 132.61, 130.78, 129.07, 128.45, 126.46, 126.29, 125.72, 125.51, 122.53, 115.84 (t, *J* = 259.6 Hz), 104.73, 89.11, 66.60 (t, *J* = 5.7 Hz), 35.79, -0.03; ¹⁹F NMR (376 MHz, CDCl₃) δ -84.15 (d, *J* = 73.70 Hz, 1F), -84.18 (d, *J* = 74.1 Hz, 1F); IR (neat): ν = 2960, 2170, 1395, 1250, 1185, 1016, 839, 798, 775, 759, 652, 423 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₈H₂₀F₂OSi) [M]⁺: 318.1246, found: 318.1249.

[α]_D^{26.9} = 21.15 (*c* 1.0, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 6.94 min (minor) and 8.32 min (major).

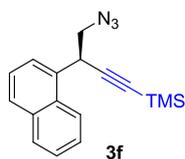


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE/EA = 40:1) yielded product **3e** (40.8 mg, 72% yield, 92% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.4$ Hz, 1H), 7.89-7.87 (m, 1H), 7.80-7.77 (m, 2H), 7.56-7.47 (m, 3H), 4.73 (dd, $J = 8.0, 5.6$ Hz, 1H), 3.80-3.71 (m, 2H), 3.41 (s, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.10, 133.88, 130.93, 128.93, 127.94, 126.08, 126.00, 125.53, 125.51, 122.97, 106.53, 87.97, 76.74, 59.17, 36.32, 0.08; IR (neat): $\nu = 2957, 2168, 1248, 1191, 1115, 838, 798, 775, 758, 422$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{18}\text{H}_{22}\text{OSi})$ $[\text{M}]^+$: 282.1434, found: 282.1438.

$[\alpha]_{\text{D}}^{27.1} = 33.64$ (c 0.78, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 44.51 min (minor) and 69.63 min (major).

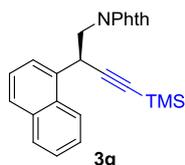


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE/EA = 50:1) yielded product **3f** (37.7 mg, 64% yield, 94% ee) as colorless oil. 65% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.91-7.88 (m, 1H), 7.84-7.81 (m, 2H), 7.57-7.49 (m, 3H), 4.74 (t, $J = 6.8$ Hz, 1H), 3.60 (d, $J = 7.6$ Hz, 1H), 3.60 (d, $J = 5.6$ Hz, 1H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.93, 133.28, 130.41, 129.17, 128.47, 126.47, 126.21, 125.75, 125.55, 122.29, 104.97, 90.15, 56.13, 36.58, -0.12; IR (neat): $\nu = 2958, 2174, 2096, 1597, 1511, 1315, 1280, 1249, 838, 798, 775, 759$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{17}\text{H}_{19}\text{NSi})$ $[\text{M}-\text{N}_2]^+$: 265.1281, found: 265.1281.

$[\alpha]_{\text{D}}^{27.4} = 46.68$ (c 0.87, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 7.34 min (minor) and 8.25 min (major).



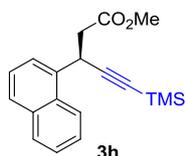
The reaction was conducted on a 0.2 mmol scale according to the general conditions. **L9** (19.1 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol%), anhydrous Na_2CO_3 (127.2 mg, 1.2 mmol), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0

equiv.) were used. Column chromatography (PE/EA = 4:1) yielded product **3g** (51.2 mg, 64% yield, 90% ee) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, J = 8.4 Hz, 1H), 7.93-7.87 (m, 4H), 7.82 (d, J = 8.4 Hz, 1H), 7.76-7.72 (m, 2H), 7.63-7.59 (m, 1H), 7.54-7.48 (m, 2H), 5.15 (dd, J = 10.8, 5.2 Hz, 1H), 4.17 (dd, J = 13.2, 10.8 Hz, 1H), 3.99 (dd, J = 13.6, 5.2 Hz, 1H), 0.08 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.12, 133.98, 133.83, 133.37, 132.04, 130.85, 128.87, 128.38, 126.64, 126.09, 125.74, 125.60, 123.25, 122.98, 104.73, 89.72, 43.48, 34.62, -0.30; IR (neat): ν = 2955, 1770, 1713, 1391, 1260, 1247, 1102, 1085, 983, 836, 796, 768, 715, 653, 530, 462, 417 cm^{-1} ; HRMS: m/z (ESI) calculated for ($\text{C}_{25}\text{H}_{24}\text{NO}_2\text{Si}$) $[\text{M}+\text{H}]^+$: 398.1571, found: 398.1575; melting point: 110-112 $^\circ\text{C}$.

$[\alpha]_{\text{D}}^{23.4} = -141.69$ (c 0.86, CHCl_3).

HPLC (AD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 97/3, flow 0.7 mL/min, detection at 214 nm) retention time = 8.46 min (major) and 8.82 min (minor).

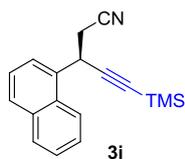


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE/EA = 20:1) yielded product **3h** (43.5 mg, 70% yield, 94% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 8.4 Hz, 1H), 7.89-7.86 (m, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.57-7.44 (m, 3H), 4.96 (dd, J = 9.6, 5.2 Hz, 1H), 3.72 (s, 3H), 2.93 (dd, J = 15.2, 5.2 Hz, 1H), 2.84 (dd, J = 15.2, 9.6 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.50, 135.55, 133.97, 130.26, 129.04, 128.06, 126.31, 125.68, 125.54, 125.32, 122.84, 106.34, 88.54, 51.86, 42.24, 32.06, 0.00; IR (neat): ν = 2954, 2174, 1737, 1436, 1397, 1348, 1248, 1168, 1149, 838, 800, 775, 759, 637 cm^{-1} ; HRMS: m/z (EI) calculated for ($\text{C}_{19}\text{H}_{22}\text{O}_2\text{Si}$) $[\text{M}]^+$: 310.1384, found: 310.1376.

$[\alpha]_{\text{D}}^{25.7} = 12.57$ (c 0.58, CHCl_3).

HPLC (AD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 6.47 min (minor) and 6.76 min (major).



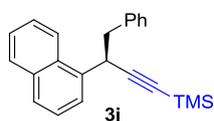
The reaction was conducted on a 0.2 mmol scale according to the general conditions. NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) was used. Column chromatography (PE/EA = 25:1) yielded

product **3i** (34.6 mg, 62% yield, 97% ee) as colorless oil. 65% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 2H), 7.60-7.51 (m, 3H), 4.83 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.01 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.88 (dd, *J* = 16.4, 7.6 Hz, 1H), 0.25 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 133.96, 133.18, 129.81, 129.39, 128.91, 126.75, 125.89, 125.86, 125.61, 121.76, 117.16, 103.61, 90.87, 32.04, 26.00, -0.13; IR (neat): ν = 2960, 2184, 1597, 1510, 1413, 1250, 1076, 874, 840, 804, 778, 762, 613, 423 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₈H₁₉NSi) [M]⁺: 277.1281, found: 277.1285.

[α]_D^{27.9} = 45.96 (*c* 0.55, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 98/2, flow 0.7 mL/min, detection at 214 nm) retention time = 10.13 min (major) and 12.39 min (minor).

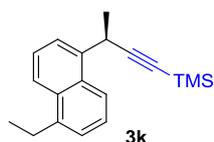


The reaction was conducted on a 0.2 mmol scale according to the general conditions. NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) was used. Column chromatography (PE/EA = 100:1) yielded product **3j** (36.6 mg, 56% yield, 91% ee) as colorless oil. 60% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.90-7.88 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.57-7.47 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.29-7.20 (m, 5H), 4.65 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.22 (dd, *J* = 12.8, 4.4 Hz, 1H), 3.05 (dd, *J* = 13.2, 9.2 Hz, 1H), 0.17 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 139.01, 136.59, 133.95, 130.45, 129.56, 129.08, 127.91, 127.65, 126.46, 126.09, 125.65, 125.50, 125.48, 122.80, 107.73, 89.13, 43.45, 37.69, 0.02; IR (neat): ν = 2956, 2172, 1248, 837, 794, 774, 758, 730, 696, 496, 422, cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₃H₂₄Si) [M]⁺: 328.1642, found: 328.1646.

[α]_D^{28.1} = 37.15 (*c* 0.45, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 6.09 min (minor) and 7.11 min (major).



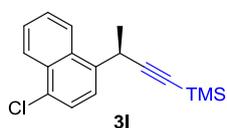
The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE) yielded product **3k** (40.8 mg, 73% yield, 91% ee) as colorless oil. (Note: the reaction was monitored by TLC plate until 1,5-diethylnaphthalene was consumed, and the

yield (21%) of α,α' -dialkynylation product **3k'** was determined by ^1H NMR spectroscopy of the crude mixture using CH_2Br_2 as an internal standard).

^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 6.8$ Hz, 1H), 7.54-7.44 (m, 2H), 7.36 (d, $J = 6.8$ Hz, 1H), 4.58 (q, $J = 6.8$ Hz, 1H), 3.14 (q, $J = 7.2$ Hz, 2H), 1.64 (d, $J = 7.2$ Hz, 3H), 1.40 (t, $J = 7.6$ Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.09, 139.26, 132.20, 130.74, 125.68, 125.42, 124.63, 123.95, 123.02, 121.35, 109.91, 86.47, 29.73, 26.39, 23.71, 15.14, 0.16; IR (neat): $\nu = 2962, 2167, 1248, 1097, 1004, 919, 836, 782, 757, 697, 642, 462$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{19}\text{H}_{24}\text{Si})$ $[\text{M}]^+$: 280.1642, found: 280.1646.

$[\alpha]_{\text{D}}^{28.4} = 12.55$ (c 0.58, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 5.09 min (minor) and 5.37 min (major).

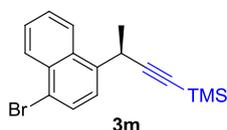


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE) yielded product **3l** (47.7 mg, 83% yield, 93% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.36-8.34 (m, 1H), 8.13-8.10 (m, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.63-7.57 (m, 3H), 4.52 (q, $J = 6.8$ Hz, 1H), 1.63 (d, $J = 7.2$ Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.01, 131.54, 131.00, 130.95, 126.68, 126.59, 125.94, 125.35, 124.34, 123.51, 109.09, 86.98, 29.35, 23.49, 0.11; IR (neat): $\nu = 2958, 2168, 1509, 1381, 1248, 934, 888, 836, 754, 698, 651, 420$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{17}\text{H}_{19}\text{ClSi})$ $[\text{M}]^+$: 286.0939, found: 286.0944.

$[\alpha]_{\text{D}}^{28.6} = 8.03$ (c 0.97, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 14.77 min (major) and 17.29 min (minor).

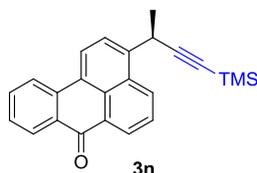


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE) yielded product **3m** (53.9 mg, 81% yield, 93% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 7.6$ Hz, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.64-7.56 (m, 3H), 4.52 (q, $J = 7.2$ Hz, 1H), 1.63 (d, $J = 7.2$ Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.79, 132.07, 131.68, 129.76, 128.13, 126.89, 126.73, 124.86, 123.51, 121.97, 109.00, 87.00, 29.37, 23.43, 0.10; IR (neat): $\nu = 2958, 2163, 1592,$

1507, 1449, 1378, 1247, 1124, 1101, 1009, 920, 877, 862, 830, 751, 655, 426 cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{17}\text{H}_{19}\text{BrSi}) [\text{M}]^+$: 330.0434, found: 330.0438. $[\alpha]_{\text{D}}^{28.8} = 10.54$ (c 1.0, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 17.40 min (major) and 20.40 min (minor).

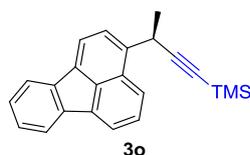


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE/EA = 15:1) yielded product **3n** (42.3 mg, 60% yield, 95% ee) as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 8.0$ Hz, 1H), 8.51 (d, $J = 8.4$ Hz, 1H), 8.47 (d, $J = 8.4$ Hz, 1H), 8.43 (d, $J = 8.0$ Hz, 1H), 8.31 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.81 (t, $J = 8.0$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 1H), 4.61 (q, $J = 7.6$ Hz, 1H), 1.69 (d, $J = 7.2$ Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.99, 141.54, 136.16, 133.40, 130.63, 130.23, 130.20, 129.50, 129.16, 128.42, 128.11, 127.99, 126.41, 125.83, 125.04, 124.24, 122.91, 108.72, 87.47, 29.81, 23.91, 0.09; IR (neat): $\nu = 2957, 2174, 1650, 1577, 1313, 1245, 838, 777, 762, 752, 702, 632, 469$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{24}\text{H}_{22}\text{OSi}) [\text{M}]^+$: 354.1434, found: 354.1436; melting point: 168-170 $^\circ\text{C}$.

$[\alpha]_{\text{D}}^{28.9} = 12.64$ (c 0.54, CHCl_3).

HPLC (AD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 98/2, flow 0.7 mL/min, detection at 214 nm) retention time = 11.52 min (minor) and 13.08 min (major).



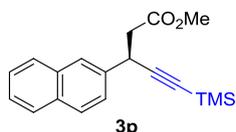
The reaction was conducted on a 0.2 mmol scale according to the general conditions. NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) was used. Column chromatography (PE) yielded product **3o** (48.0 mg, 74% yield, 94% ee) as a white solid. 82% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.93-7.87 (m, 4H), 7.82 (d, $J = 7.2$ Hz, 1H), 7.64 (dd, $J = 8.4, 7.2$ Hz, 1H), 7.39-7.36 (m, 2H), 4.59 (q, $J = 6.8$ Hz, 1H), 1.70 (d, $J = 7.2$ Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.87, 139.46, 139.17, 137.50, 136.05, 132.89, 127.82, 127.71, 127.56, 127.32, 125.98, 123.15, 121.39, 121.27, 120.22, 119.80, 109.56, 86.77, 29.56, 24.79, 0.14; IR (neat): $\nu = 2959, 2167, 1449, 1440, 1248, 1076$ cm^{-1} .

938, 900, 838, 779, 755, 743 cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{23}\text{H}_{22}\text{Si})$ $[\text{M}]^+$: 326.1485, found: 326.1491; melting point: 69-71 $^{\circ}\text{C}$.

$[\alpha]_{\text{D}}^{29.1} = 42.50$ (c 0.60, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 8.81 min (major) and 11.94 min (minor).

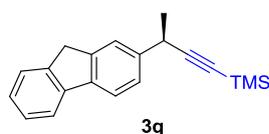


The reaction was conducted on a 0.2 mmol scale according to the general conditions. CuI (7.6 mg, 20 mol%), **L1** (24.5 mg, 24 mol%), **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) and NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) were used. Column chromatography (PE/EA = 15:1) yielded product **3p** (25.0 mg, 40% yield, 92% ee) as colorless oil. 43% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 7.83-7.81 (m, 4H), 7.51-7.44 (m, 3H), 4.36 (t, $J = 8.0$ Hz, 1H), 3.66 (s, 3H), 2.90 (dd, $J = 15.2, 8.0$ Hz, 1H), 2.81 (dd, $J = 15.6, 7.6$ Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.23, 137.45, 133.35, 132.58, 128.44, 127.84, 127.60, 126.17, 125.87, 125.47, 106.35, 88.06, 51.79, 43.07, 35.23, 0.02; IR (neat): $\nu = 2958, 2172, 1735, 1435, 1351, 1293, 1019, 839, 812, 799, 760, 739, 704, 472$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{19}\text{H}_{22}\text{O}_2\text{Si})$ $[\text{M}]^+$: 310.1384, found: 310.1391.

$[\alpha]_{\text{D}}^{29.3} = -2.78$ (c 0.71, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 98/2, flow 0.7 mL/min, detection at 214 nm) retention time = 8.62 min (minor) and 9.24 min (major).



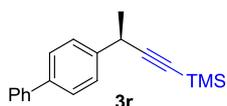
In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na_2CO_3 (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (4.2 mL, $v/v = 20:1$) under N_2 , and the mixture was stirred for 30 min and cooled down to 5 $^{\circ}\text{C}$. Then, 2-ethyl-9H-fluorene (38.9 mg, 0.2 mmol, 1.0 equiv.), NFSI-2 (230 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 $^{\circ}\text{C}$ for 4.5 d. The crude product was purified via a preparative plate (PE/EA = 50:1) to yield pure product **3q** (28.6 mg, 49% yield, 86% ee) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.57 (s, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.29 (t, $J = 7.2$ Hz,

1H), 3.90(s, 2H), 3.88 (q, $J = 6.8$ Hz, 1H), 1.54 (d, $J = 6.8$ Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.59, 143.27, 141.77, 141.50, 140.29, 126.68, 126.44, 125.56, 124.96, 123.54, 119.81, 119.72, 109.74, 86.20, 36.86, 32.92, 24.83, 0.18; IR (neat): $\nu = 2959, 2166, 1455, 1247, 1087, 1013, 879, 839, 762, 735, 421$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{20}\text{H}_{22}\text{Si})$ $[\text{M}]^+$: 290.1485, found: 290.1493.

$[\alpha]_{\text{D}}^{29.5} = 9.45$ (c 0.65, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 20.59 min (major) and 27.26 min (minor).

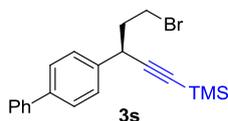


In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol %), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na_2CO_3 (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (2.1 mL, $v/v = 20:1$) under N_2 , and the mixture was stirred for 30 min and cooled down to 5 $^\circ\text{C}$. Then, 4-ethyl-1,1'-biphenyl (36.5 mg, 0.2 mmol, 1.0 equiv.), NFSI-2 (230 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 $^\circ\text{C}$ for 4.5 d. Column chromatography (PE/EA = 50:1) yielded product **3r** (36.8 mg, 66% yield, 90% ee) as colorless oil. 71% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 7.63-7.58 (m, 4H), 7.50-7.45 (m, 4H), 7.37 (t, $J = 7.6$ Hz, 1H), 3.87 (q, $J = 7.2$ Hz, 1H), 1.56 (d, $J = 7.2$ Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.11, 140.90, 139.56, 128.72, 127.28, 127.24, 127.13, 127.04, 109.35, 86.29, 32.47, 24.58, 0.16; IR (neat): $\nu = 2960, 2164, 1487, 1248, 1092, 1007, 918, 835, 761, 729, 697, 656, 569, 490$ cm^{-1} ; HRMS: m/z (EI) calculated for $(\text{C}_{19}\text{H}_{22}\text{Si})$ $[\text{M}]^+$: 278.1485, found: 278.1490.

$[\alpha]_{\text{D}}^{29.4} = -0.81$ (c 0.59, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane / isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 19.31 min (major) and 26.02 min (minor).



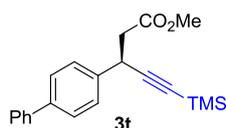
In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na_2CO_3 (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (2.1 mL, $v/v = 20:1$) under N_2 , and the mixture was stirred for 30 min. Then, 4-(3-bromopropyl)-1,1'-biphenyl (55.1 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at

room temperature for 60 h. Column chromatography (PE) yielded a mixture of 4-(3-bromopropyl)-1,1'-biphenyl and the product **3s**. Then, the mixture was further purified via a preparative plate (PE) to yield product **3s** (40.4 mg, 54% yield, 95% ee) as a white solid. 74% Conversion (alkylarene) and 69% ¹H NMR yield (**3s**) were determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 4H), 7.46-7.42 (m, 4H), 7.37-7.33 (m, 1H), 3.98 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.63-3.57 (m, 1H), 3.48-3.43 (m, 1H), 2.34-2.22 (m, 2H), 0.21 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 140.73, 140.09, 139.29, 128.76, 127.87, 127.41, 127.27, 127.05, 106.23, 88.43, 41.08, 36.87, 31.11, 0.10; IR (neat): ν = 2957, 2168, 1487, 1248, 929, 840, 830, 758, 728, 689, 415 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₀H₂₃BrSi) [M]⁺: 370.0747, found: 370.0753; melting point: 75-77 °C.

[α]_D^{29.4} = -17.83 (*c* 0.8, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 5.97 min (major) and 6.49 min (minor).

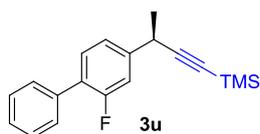


In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol %) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (4.2 mL, *v/v* = 20:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, methyl 3-([1,1'-biphenyl]-4-yl)propanoate (48.1 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 10:1) yielded product **3t** (38.1 mg, 57% yield, 97% ee) as a white solid. 62% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.57 (t, *J* = 8.4 Hz, 4H), 7.47-7.42 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 4.24 (t, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 2.86 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.76 (dd, *J* = 15.2, 7.2 Hz, 1H), 0.18 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.21, 140.68, 140.13, 139.14, 128.73, 127.81, 127.36, 127.25, 127.02, 106.29, 87.89, 51.75, 43.21, 34.76, 0.01; IR (neat): ν = 2954, 2174, 1736, 1487, 1452, 1359, 1248, 1201, 1152, 841, 762, 689, 471 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₁H₂₄O₂Si) [M]⁺: 336.1540, found: 336.1550; melting point: 63-65 °C.

[α]_D^{29.6} = -5.96 (*c* 0.67, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 8.52 min (major) and 9.44 min (minor).

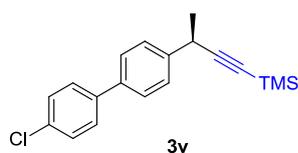


In a dried sealed 10 mL Schlenk tube, **L1** (24.5 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol %) and anhydrous Na₂CO₃ (127.2 mg, 1.2 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, *v/v* = 20:1) under N₂, and the mixture was stirred for 30 min. Then, 4-ethyl-2-fluoro-1,1'-biphenyl (40.1 mg, 0.2 mmol, 1.0 equiv.), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at room temperature for 60 h. Column chromatography (PE/EA = 50:1) yielded product **3u** (23.9 mg, 40% yield, 79% ee) as colorless oil. 60% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.46-7.34 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 11.6 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.20 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 159.68 (d, *J* = 247.0 Hz), 144.57 (d, *J* = 7.7 Hz), 135.68 (d, *J* = 1.2 Hz), 130.69 (d, *J* = 3.9 Hz), 128.95 (d, *J* = 2.6 Hz), 128.42, 127.54, 127.23 (d, *J* = 14.0 Hz), 122.83 (d, *J* = 3.5 Hz), 114.63 (d, *J* = 23.8 Hz), 108.52, 86.85, 32.32, 24.33, 0.11; ¹⁹F NMR (376 MHz, CDCl₃) δ -117.96-118.01 (m, 1F); IR (neat): *ν* = 2959, 2166, 1484, 1416, 1249, 886, 838, 759, 696, 565 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₉H₂₁FSi) [M]⁺: 296.1391, found: 296.1397.

[α]_D^{30.9} = -0.19 (*c* 0.72, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 13.45 min (major) and 17.27 min (minor).



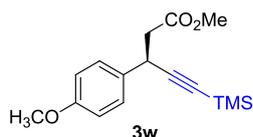
In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, *v/v* = 20:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 4-chloro-4'-ethyl-1,1'-biphenyl (43.4 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 50:1) yielded product **3v** (38.0 mg, 61% yield, 88% ee) as a white solid. 70% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.54-7.51 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 3.84 (q, *J* = 7.2 Hz, 1H), 1.53 (d, *J* = 7.6 Hz, 3H), 0.21 (s, 9H); ¹³C NMR (100 MHz,

CDCl₃) δ 142.55, 139.35, 138.32, 133.23, 128.88, 128.26, 127.43, 127.08, 109.22, 86.43, 32.48, 24.53, 0.15; IR (neat): ν = 2956, 2165, 1484, 1247, 1090, 1005, 916, 837, 813, 757 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₉H₂₁ClSi) [M]⁺: 312.1096, found: 312.1105; melting point: 65-67 °C.

$[\alpha]_D^{29.5} = -0.99$ (*c* 0.63, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μ m, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 8.60 min (major) and 9.26 min (minor).

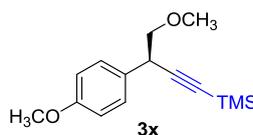


In a dried sealed 10 mL Schlenk tube, **L1** (24.5 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol%) and anhydrous Na₂CO₃ (127.2 mg, 1.2 mmol, 6.0 equiv.) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, *v/v* = 4:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, methyl 3-(4-methoxyphenyl)propanoate (38.9 mg, 0.2 mmol, 1.0 equiv.), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 10:1) yielded product **3w** (29.3 mg, 50% yield, 92% ee) as colorless oil. 80% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard. For the accurate determination of the enantiomeric excess, the TMS group in **3w** was successfully removed using NH₄F (8.0 equiv.) and using MeOH as solvent at room temperature for 36 h.

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.13 (t, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.79 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.68 (dd, *J* = 15.2, 7.2 Hz, 1H), 0.16 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.27, 158.68, 132.18, 128.41, 113.97, 106.74, 87.51, 55.24, 51.68, 43.44, 34.33, 0.02; IR (neat): ν = 2956, 2174, 1738, 1611, 1510, 1246, 1176, 1155, 1028, 838, 759 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₆H₂₂O₃Si) [M]⁺: 290.1333, found: 290.1341.

$[\alpha]_D^{29.7} = -3.16$ (*c* 0.81, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μ m, hexane/isopropanol = 98/2, flow 0.7 mL/min, detection at 214 nm) retention time = 13.71 min (major) and 16.02 min (minor).



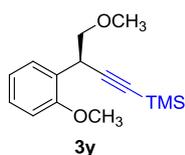
In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed

solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, v/v = 4:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 1-methoxy-4-(2-methoxyethyl)benzene (33.3 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 10:1) yielded product **3x** (27.0 mg, 51% yield, 92% ee) as colorless oil. 53% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.87 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.61 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.50 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.35 (s, 3H), 0.18 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 158.65, 130.72, 128.90, 113.82, 106.04, 87.65, 77.54, 59.00, 55.22, 38.65, 0.09; IR (neat): ν = 2957, 2174, 1612, 1510, 1246, 1177, 1114, 1035, 838, 758 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₅H₂₂O₂Si) [M]⁺: 262.1384, found: 262.1391.

[α]_D^{29.8} = 1.03 (*c* 0.98, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 6.97 min (minor) and 7.67 min (major).

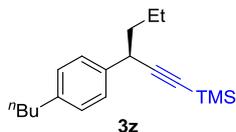


In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, v/v = 20:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 1-methoxy-2-(2-methoxyethyl)benzene (33.3 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 10:1) yielded product **3y** (28.6 mg, 54% yield, 92% ee) as colorless oil. 57% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.33 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.82 (s, 3H), 3.55 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.42 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.40 (s, 3H), 0.19 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 156.34, 129.07, 128.27, 126.46, 120.66, 110.32, 106.85, 86.74, 76.02, 58.98, 55.39, 32.92, 0.15; IR (neat): ν = 2957, 2172, 1600, 1588, 1492, 1462, 1439, 1243, 1114, 1029, 838, 751, 698, 656 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₅H₂₂O₂Si) [M]⁺: 262.1384, found: 262.1386.

[α]_D^{29.9} = 23.78 (*c* 0.55, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μ m, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 5.32 min (minor) and 5.98 min (major).

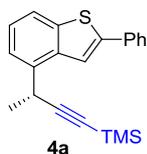


In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DEAc (*N,N*-diethylacetamide) (2.5 mL, *v/v* = 4:1) under N₂, and the mixture was stirred for 30 min. Then, 1,4-dibutylbenzene (38.1 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at room temperature for 60 h. Column chromatography (PE) yielded product **3z** (22.7 mg, 40% yield, 94% ee) as colorless oil. For the determination of the enantiomeric excess, the TMS group in **3z** was successfully removed using K₂CO₃ (3.0 equiv.) and using MeOH as solvent at room temperature for 36 h.

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.61 (dd, *J* = 8.0, 6.8 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.74-1.55 (m, 4H), 1.51-1.31 (m, 4H), 0.94-0.89 (m, 6H), 0.17 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 141.09, 139.20, 128.37, 127.26, 108.82, 86.73, 40.87, 38.15, 35.23, 33.64, 22.39, 20.46, 13.95, 13.77, 0.19; IR (neat): ν = 2957, 2930, 2170, 1511, 1459, 1259, 1249, 1093, 1019, 870, 839, 803, 759 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₉H₃₀Si) [M]⁺: 286.2111, found: 286.2115.

$[\alpha]_D^{30.0} = 3.34$ (*c* 0.63, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μ m, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 8.08 min (major) and 8.80 min (minor).

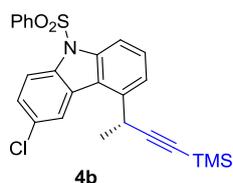


In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, *v/v* = 20:1) under N₂, and the mixture was stirred for 30 min. Then, 4-ethyl-2-phenylbenzo[*b*]thiophene (47.7 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at room temperature for 60 h. Column chromatography (PE/EA = 100:1) yielded product **4a** (31.7 mg, 47% yield, 91% ee) as colorless oil. 79% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.74-7.71 (m, 3H), 7.46-7.41 (m, 3H), 7.36-7.28 (m, 2H), 4.26 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.00, 140.10, 138.18, 137.58, 134.30, 128.93, 128.28, 126.47, 124.58, 122.53, 120.88, 117.20, 109.14, 86.53, 31.37, 23.49, 0.12; IR (neat): $\nu = 2957, 2167, 1488, 1459, 1417, 1248, 1073, 925, 837, 755, 687, 640$ cm^{-1} ; HRMS: m/z (EI) calculated for ($\text{C}_{21}\text{H}_{22}\text{SSi}$) $[\text{M}]^+$: 334.1206, found: 334.1211.

$[\alpha]_{\text{D}}^{29.8} = -26.05$ (c 0.67, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 29.41 min (minor) and 32.08 min (major).

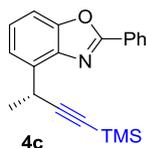


In a dried sealed 10 mL Schlenk tube, **L9** (19.1 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol%) and anhydrous Na_2CO_3 (127.2 mg, 1.2 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (2.1 mL, $v/v = 20:1$) under N_2 , and the mixture was stirred for 30 min. Then, 3-chloro-5-ethyl-9-(phenylsulfonyl)-9H-carbazole (74 mg, 0.2 mmol, 1.0 equiv.), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at room temperature for 60 h. 48% ^1H NMR yield (**4b**) was determined by using CH_2Br_2 as an internal standard. The product **4b** was purified by RP-HPLC ($\text{CH}_3\text{CN}/\text{H}_2\text{O} = 9:1$) as a white solid. 72% ee was determined by HPLC on a chiral stationary phase.

^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, $J = 8.8$ Hz, 1H), 8.29 (d, $J = 8.8$ Hz, 1H), 8.04 (s, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.54-7.45 (m, 3H), 7.33 (t, $J = 7.6$ Hz, 2H), 4.48 (q, $J = 6.8$ Hz, 1H), 1.62 (d, $J = 6.8$ Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.23, 138.11, 137.50, 136.83, 134.01, 129.58, 129.12, 128.11, 126.91, 126.89, 126.43, 122.97, 122.54, 122.31, 115.95, 113.69, 107.63, 87.48, 30.16, 21.81, -0.03; IR (neat): $\nu = 2960, 2166, 1583, 1446, 1438, 1411, 1373, 1247, 1227, 1213, 1179, 1168, 1130, 1088, 1070, 1018, 935, 903, 839, 758, 722, 681, 594, 585, 566, 554, 535, 476$ cm^{-1} ; HRMS: m/z (EI) calculated for ($\text{C}_{25}\text{H}_{24}\text{ClNO}_2\text{SSi}$) $[\text{M}]^+$: 465.0980, found: 465.0984; melting point: 73-75 $^\circ\text{C}$.

$[\alpha]_{\text{D}}^{30.2} = -50.08$ (c 1.0, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 13.33 min (major) and 14.22 min (minor).

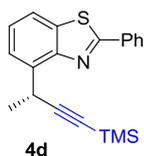


In a dried sealed 10 mL Schlenk tube, **L9** (19.1 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol%) and anhydrous Na₂CO₃ (127.2 mg, 1.2 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, v/v = 20:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 4-ethyl-2-phenylbenzo[d]oxazole (44.7 mg, 0.2 mmol, 1.0 equiv.), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 30:1) yielded product **4c** (29.6 mg, 46% yield, 90% ee) as colorless oil. 57% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.28-8.23 (m, 2H), 7.56-7.50 (m, 4H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 4.60 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 6.8 Hz, 3H), 0.21 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 162.34, 150.54, 139.86, 135.28, 131.33, 128.82, 127.65, 127.37, 125.06, 122.18, 109.01, 108.75, 86.24, 28.34, 23.79, 0.19; IR (neat): ν = 2958, 2169, 1623, 1556, 1488, 1450, 1427, 1245, 1061, 1010, 902, 863, 837, 748, 703, 687 cm⁻¹; HRMS: *m/z* (ESI) calculated for (C₂₀H₂₂NOSi) [M+H]⁺: 320.1465, found: 320.1470.

[α]_D^{30.5} = -54.15 (*c* 0.56, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 11.34 min (minor) and 14.31 min (major).



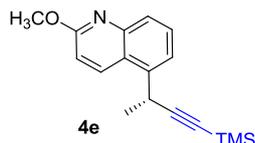
In a dried sealed 10 mL Schlenk tube, **L9** (19.1 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol%) and anhydrous Na₂CO₃ (127.2 mg, 1.2 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, v/v = 20:1) under N₂, and the mixture was stirred for 30 min. Then, 4-ethyl-2-phenylbenzo[d]thiazole (47.9 mg, 0.2 mmol, 1.0 equiv.), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at room temperature for 60 h. Column chromatography (PE/EA = 40:1) yielded product **4d** (43.5 mg, 65% yield, 90% ee) as a white solid. 83% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.11-8.08 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.52-7.48 (m, 3H), 7.38 (t, *J* = 8.0 Hz, 1H), 4.92 (q, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 6.8 Hz, 3H), 0.21 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 166.81, 151.58, 138.04, 135.05, 133.83,

130.79, 128.92, 127.51, 125.44, 124.05, 119.87, 109.68, 86.10, 29.38, 24.08, 0.22; IR (neat): $\nu = 2956, 2171, 1479, 1409, 1249, 1104, 973, 859, 841, 783, 757, 684 \text{ cm}^{-1}$; HRMS: m/z (ESI) calculated for $(\text{C}_{20}\text{H}_{22}\text{NSSi})$ $[\text{M}+\text{H}]^+$: 336.1237, found: 336.1241; melting point: 99-101 °C

$[\alpha]_{\text{D}}^{31.0} = -67.08$ (c 0.65, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 11.75 min (minor) and 13.24 min (major).

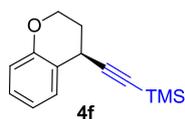


In a dried sealed 10 mL Schlenk tube, **L9** (19.1 mg, 0.048 mmol, 24 mol%), CuI (7.6 mg, 0.04 mmol, 20 mol%) and anhydrous Na_2CO_3 (127.2 mg, 1.2 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (2.5 mL, $v/v = 4:1$) under N_2 , and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 5-ethyl-2-methoxyquinoline (37.5 mg, 0.2 mmol, 1.0 equiv.), NFSI (378.4 mg, 1.2 mmol, 6.0 equiv.) and **2a** (349.4 mg, 1.6 mmol, 8.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 60:1) yielded product **4e** (33.8 mg, 60% yield, 92% ee) as colorless oil. 63% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.8$ Hz, 1H), 7.78-7.76 (m, 1H), 7.61-7.56 (m, 2H), 6.93 (d, $J = 9.2$ Hz, 1H), 4.38 (q, $J = 7.2$ Hz, 1H), 4.08 (s, 3H), 1.60 (d, $J = 7.2$ Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.92, 147.27, 138.96, 134.41, 129.31, 126.65, 122.35, 122.30, 112.54, 109.20, 86.83, 53.30, 29.59, 23.57, 0.09; IR (neat): $\nu = 2957, 2169, 1610, 1578, 1402, 1269, 1249, 1107, 1030, 907, 838, 809, 759, 661, 449 \text{ cm}^{-1}$; HRMS: m/z (ESI) calculated for $(\text{C}_{17}\text{H}_{22}\text{NOSi})$ $[\text{M}+\text{H}]^+$: 284.1465, found: 284.1470.

$[\alpha]_{\text{D}}^{30.2} = -16.81$ (c 0.52, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 5.51 min (minor) and 5.79 min (major).



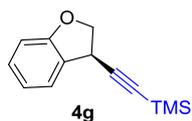
In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na_2CO_3 (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (2.5 mL, $v/v = 4:1$) under N_2 , and the mixture was stirred for 30 min and cooled down to 5 °C. Then, chroman (26.8 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added

sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE) yielded product **4f** (24.1 mg, 52% yield, 87% ee) as colorless oil. 57% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.36-4.31 (m, 1H), 4.19-4.13 (m, 1H), 3.86 (t, *J* = 6.4 Hz, 1H), 2.25-2.18 (m, 1H), 2.16-2.08 (m, 1H), 0.16 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 153.72, 129.65, 128.30, 121.53, 120.47, 116.85, 107.86, 86.03, 64.36, 29.01, 28.40, 0.06; IR (neat): ν = 2958, 2169, 1607, 1582, 1488, 1453, 1310, 1267, 1248, 1224, 1070, 898, 837, 750 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₄H₁₈OSi) [M]⁺: 230.1121, found: 230.1124.

[α]_D^{29.8} = -1.60 (*c* 0.68, CHCl₃).

SFC (OJ-H, 0.46*25 cm, 5 μm, column T: 40 °C, background press: 2000 psi, CO₂/MeOH = 95/5, flow 1.0 mL/min, detection at 214 nm) retention time = 9.38 min (minor) and 9.93 min (major).

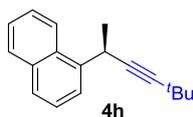


In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, *v/v* = 4:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 2,3-dihydrobenzofuran (24 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and **2a** (174.7 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 100:1) yielded product **4g** (19.4 mg, 45% yield, 61% ee) as colorless oil. 85% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.76 (t, *J* = 12.8 Hz, 1H), 4.43-4.37 (m, 2H), 0.16 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 159.36, 128.87, 127.29, 124.66, 121.04, 109.88, 104.24, 87.22, 76.47, 34.80, -0.03; IR (neat): ν = 2959, 2178, 1598, 1480, 1459, 1249, 1223, 837, 747 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₃H₁₆OSi) [M]⁺: 216.0965, found: 216.0968.

[α]_D^{29.9} = -45.94 (*c* 0.83, CHCl₃).

HPLC (OD-H+OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.5 mL/min, detection at 214 nm) retention time = 24.79 min (minor) and 25.52 min (major).

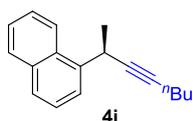


The reaction was conducted on a 0.2 mmol scale according to the general conditions. NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) was used. Column chromatography (PE) yielded product **4h** (27.7 mg, 59% yield, 88% ee) as colorless oil. 83% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.88-7.85 (m, 1H), 7.75 (t, *J* = 7.2 Hz, 2H), 7.54-7.45 (m, 3H), 4.49 (q, *J* = 6.8 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 139.89, 133.91, 130.53, 128.87, 127.15, 125.74, 125.64, 125.33, 124.16, 123.27, 91.32, 81.43, 31.33, 28.50, 27.48, 24.13; IR (neat): ν = 2967, 1454, 1361, 1264, 797, 774, 489, 438 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₈H₂₀) [M]⁺: 236.1560, found: 236.1562.

[α]_D^{30.1} = 11.86 (*c* 0.67, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 6.14 min (major) and 6.72 min (minor).

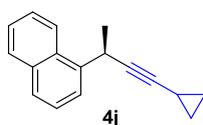


The reaction was conducted on a 0.2 mmol scale according to the general conditions. NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) was used and the reaction was performed at 5 °C for 4.5 d. Column chromatography (PE) yielded product **4i** (20.1 mg, 43% yield, 91% ee) as colorless oil. 68% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.87-7.85 (m, 1H), 7.76-7.73 (m, 2H), 7.53-7.44 (m, 3H), 4.52-4.47 (m, 1H), 2.27-2.23 (m, 2H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.56-1.39 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.66, 133.93, 130.55, 128.89, 127.21, 125.81, 125.62, 125.36, 124.08, 123.27, 83.02, 82.62, 31.16, 28.51, 23.76, 21.97, 18.56, 13.63; IR (neat): ν = 2957, 2930, 2870, 1597, 1511, 1451, 797, 774, 733, 573, 503, 428 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₈H₂₀) [M]⁺: 236.1560, found: 236.1557.

[α]_D^{26.4} = -1.01 (*c* 0.92, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 214 nm) retention time = 8.64 min (major) and 9.61 min (minor).

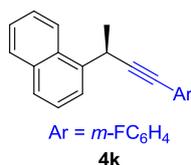


The reaction was conducted on a 0.2 mmol scale according to the general conditions. The reaction in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DEAc (*N,N*-diethylacetamide) (3.0 mL, *v/v* = 2:1) was performed at 5 °C for 4.5 d and NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) was used. Column chromatography (PE) yielded product **4i** (22.9 mg, 52% yield, 89% ee) as colorless oil. 89% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.2 Hz, 2H), 7.53-7.43 (m, 3H), 4.46 (q, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.33-1.26 (m, 1H), 0.77-0.71 (m, 2H), 0.69-0.65 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 139.52, 133.91, 130.51, 128.89, 127.23, 125.82, 125.62, 125.37, 124.08, 123.20, 85.55, 78.34, 28.41, 23.68, 8.16, 8.13, -0.33; IR (neat): *ν* = 2974, 1596, 1510, 1449, 1359, 1027, 999, 797, 774 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₁₇H₁₆) [M]⁺: 220.1247, found: 220.1244.

$[\alpha]_D^{26.9} = 12.46$ (*c* 0.34, CHCl₃).

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 8.12 min (major) and 12.10 min (minor).

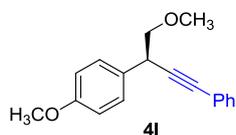


The reaction was conducted on a 0.2 mmol scale according to the general conditions. Column chromatography (PE/EA = 100:1) yielded product **4k** (30.4 mg, 55% yield, 91% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 6.8 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.25-7.19 (m, 2H), 7.14 (d, *J* = 9.6 Hz, 1H), 6.99-6.94 (m, 1H), 4.71 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.35 (d, *J* = 244.8 Hz), 138.48, 134.00, 130.50, 129.71 (d, *J* = 8.9 Hz), 129.01, 127.60, 127.49 (d, *J* = 2.6 Hz), 126.08, 125.59 (d, *J* = 9.9 Hz), 124.24, 123.08, 118.42 (d, *J* = 22.0 Hz), 115.07 (d, *J* = 21.2 Hz), 93.91, 81.51 (d, *J* = 2.9 Hz), 29.01, 23.16; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.31-113.38 (m, 1F); IR (neat): *ν* = 2977, 1607, 1578, 1486, 1433, 1235, 1176, 1150, 868, 798, 774, 734, 681, 504 cm⁻¹; HRMS: *m/z* (EI) calculated for (C₂₀H₁₅F) [M]⁺: 274.1152, found: 274.1155.

$[\alpha]_D^{30.5} = -76.60$ (*c* 0.88, CHCl₃).

HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 100/0, flow 0.7 mL/min, detection at 254 nm) retention time = 14.62 min (major) and 24.17 min (minor).

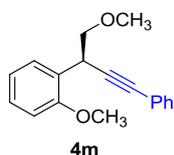


In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.5 mL, v/v = 4:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 1-methoxy-4-(2-methoxyethyl)benzene (33.3 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and trimethoxy(phenylethynyl)silane (177.9 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 10:1) yielded product **4l** (19.4 mg, 36% yield, 92% ee) as colorless oil. 50% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.47-7.44 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.30-7.27 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.07 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 3.70 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.60 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.70, 131.72, 130.88, 128.94, 128.14, 127.86, 123.44, 113.89, 89.34, 83.43, 77.50, 59.06, 55.26, 38.29; IR (neat): ν = 2930, 2895, 2834, 1600, 1584, 1510, 1247, 1176, 1109, 1032, 829, 756, 734, 691, 569, 541 cm⁻¹; HRMS: m/z (EI) calculated for (C₁₈H₁₈O₂) [M]⁺: 266.1301, found: 266.1305.

$$[\alpha]_D^{30.4} = -13.34 (c 0.70, \text{CHCl}_3).$$

HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 15.30 min (major) and 17.27 min (minor).



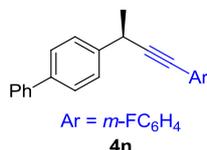
In a dried sealed 10 mL Schlenk tube, **L9** (9.6 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na₂CO₃ (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5-C₆H₂F₄ and DMA (2.1 mL, v/v = 20:1) under N₂, and the mixture was stirred for 30 min and cooled down to 5 °C. Then, 1-methoxy-2-(2-methoxyethyl)benzene (33.3 mg, 0.2 mmol, 1.0 equiv.), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv.) and trimethoxy(phenylethynyl)silane (177.9 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 °C for 4.5 d. Column chromatography (PE/EA = 10:1) yielded product **4m** (16.2 mg, 30% yield, 92% ee) as colorless oil. 32% Conversion (alkylarene) was determined by using CH₂Br₂ as an internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.48-7.46 (m, 2H), 7.31-7.24 (m, 4H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.62 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.86 (s, 3H), 3.67 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.59 (t, *J* = 8.0 Hz, 1H), 3.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.38, 131.80, 129.18, 128.35, 128.09, 127.70, 126.67, 123.73, 120.73, 110.43, 90.06, 82.65, 76.01, 59.00, 55.46, 32.54; IR (neat): ν = 2925, 2888, 2836, 1598, 1588, 1491,

1460, 1439, 1242, 1110, 1050, 1026, 751, 691, 503 cm^{-1} ; HRMS: m/z (EI) calculated for ($\text{C}_{18}\text{H}_{18}\text{O}_2$) [M] $^+$: 266.1301, found: 266.1301.

$[\alpha]_{\text{D}}^{30.3} = -17.06$ (c 0.65, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 11.93 min (major) and 22.32 min (minor).



In a dried sealed 10 mL Schlenk tube, **L1** (12.3 mg, 0.024 mmol, 12 mol%), CuI (3.8 mg, 0.02 mmol, 10 mol%) and anhydrous Na_2CO_3 (63.6 mg, 0.6 mmol) were dissolved in a mixed solvent of 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ and DMA (2.1 mL, $v/v = 20:1$) under N_2 , and the mixture was stirred for 30 min and cooled down to 5 $^\circ\text{C}$. Then, 4-ethyl-1,1'-biphenyl (36.5 mg, 0.2 mmol, 1.0 equiv.), NFSI-2 (230 mg, 0.6 mmol, 3.0 equiv.) and ((3-fluorophenyl)ethynyl)trimethoxysilane (192.2 mg, 0.8 mmol, 4.0 equiv.) were added sequentially, and the tube was sealed with Teflon septum. The reaction mixture was stirred at 5 $^\circ\text{C}$ for 4.5 d. Column chromatography (PE/EA = 100:1) yielded product **4n** (24.0 mg, 40% yield, 80% ee) as colorless oil. 59% Conversion (alkylarene) was determined by using CH_2Br_2 as an internal standard.

^1H NMR (400 MHz, CDCl_3) δ 7.60-7.56 (m, 4H), 7.51-7.49 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.36-7.32 (m, 1H), 7.29-7.22 (m, 2H), 7.17-7.14 (m, 1H), 7.02-6.97 (m, 1H), 4.02 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.36 (d, $J = 244.6$ Hz), 142.03, 140.86, 139.79, 129.73 (d, $J = 8.9$ Hz), 128.75, 127.51 (d, $J = 3.0$ Hz), 127.37, 127.32, 127.20, 127.07, 125.53 (d, $J = 9.1$ Hz), 118.45 (d, $J = 23.0$ Hz), 115.11 (d, $J = 20.8$ Hz), 93.60, 81.36 (d, $J = 3.4$ Hz), 32.10, 24.26; ^{19}F NMR (376 MHz, CDCl_3) δ -113.30-113.36 (m, 1F); IR (neat): $\nu = 2975, 1607, 1578, 1485, 1263, 1169, 1150, 836, 782, 763, 731, 696, 681, 570, 518$ cm^{-1} ; HRMS: m/z (EI) calculated for ($\text{C}_{22}\text{H}_{17}\text{F}$) [M] $^+$: 300.1309, found: 300.1314.

$[\alpha]_{\text{D}}^{30.6} = -13.99$ (c 0.52, CHCl_3).

HPLC (OD-H, 0.46*25 cm, 5 μm , hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 8.89 min (minor) and 9.57 min (major).

10. Single Crystal X-Ray Diffraction Data (3s, 4d and 8)

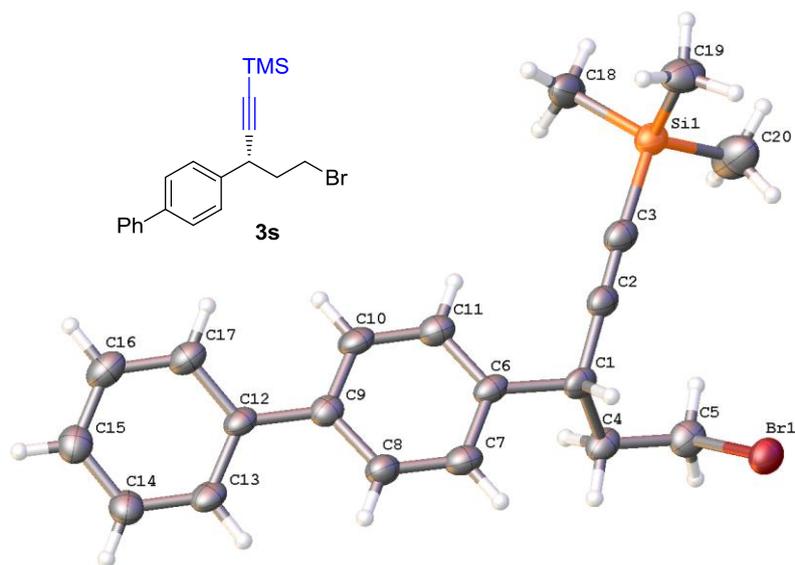


Table 1. Crystal data and structure refinement for mj19476_0m.

Identification code	mj19476_0m	
Empirical formula	C ₂₀ H ₂₃ Br Si	
Formula weight	371.38	
Temperature	170.01 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.2063(10) Å	α = 90 °
	b = 8.2335(13) Å	β = 98.177(9) °
	c = 18.476(3) Å	γ = 90 °
Volume	934.5(3) Å ³	
Z	2	
Density (calculated)	1.320 Mg/m ³	
Absorption coefficient	2.416 mm ⁻¹	
F(000)	384	
Crystal size	0.1 x 0.08 x 0.005 mm ³	
Theta range for data collection	4.206 to 55.424 °	
Index ranges	-7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -22 ≤ l ≤ 19	
Reflections collected	8682	
Independent reflections	3429 [R(int) = 0.1262]	
Completeness to theta = 53.594 °	98.4 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7508 and 0.3477
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3429 / 1 / 202
Goodness-of-fit on F ²	1.122
Final R indices [I>2sigma(I)]	R1 = 0.0841, wR2 = 0.2090
R indices (all data)	R1 = 0.1007, wR2 = 0.2314
Absolute structure parameter	0.07(5)
Extinction coefficient	n/a
Largest diff. peak and hole	1.062 and -0.743 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for mj19476_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	415(2)	2342(2)	8055(1)	66(1)
Si(1)	7941(5)	6421(4)	8983(2)	56(1)
C(1)	4305(16)	3591(14)	7100(6)	53(2)
C(2)	5479(18)	4590(14)	7702(6)	55(2)
C(3)	6432(19)	5369(14)	8188(6)	58(3)
C(4)	4170(20)	1793(13)	7336(6)	58(3)
C(5)	3356(19)	1526(16)	8058(6)	64(3)
C(6)	5364(17)	3717(12)	6404(5)	51(2)
C(7)	4240(20)	3023(15)	5757(6)	63(3)
C(8)	5170(20)	3047(15)	5119(6)	59(3)
C(9)	7203(19)	3746(13)	5091(5)	53(2)
C(10)	8260(20)	4427(14)	5739(6)	59(3)
C(11)	7353(19)	4418(14)	6379(6)	60(3)
C(12)	8233(18)	3731(12)	4418(5)	52(2)
C(13)	7430(20)	2754(12)	3819(6)	60(3)
C(14)	8430(20)	2699(13)	3190(6)	65(3)
C(15)	10220(20)	3635(18)	3140(6)	68(3)
C(16)	11010(20)	4630(17)	3720(6)	71(3)
C(17)	10010(20)	4714(16)	4340(6)	65(3)
C(18)	10870(20)	6510(20)	8905(7)	79(4)
C(19)	6930(30)	8499(17)	9012(9)	86(4)
C(20)	7440(30)	5300(30)	9799(7)	108(6)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for mj19476_0m.

Br(1)-C(5)	1.944(12)
Si(1)-C(3)	1.841(11)
Si(1)-C(18)	1.842(13)
Si(1)-C(19)	1.827(15)
Si(1)-C(20)	1.831(15)
C(1)-H(1)	1.0000
C(1)-C(2)	1.487(15)
C(1)-C(4)	1.549(16)
C(1)-C(6)	1.530(15)
C(2)-C(3)	1.191(16)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.507(17)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.416(14)
C(6)-C(11)	1.369(16)
C(7)-H(7)	0.9500
C(7)-C(8)	1.386(17)
C(8)-H(8)	0.9500
C(8)-C(9)	1.394(17)
C(9)-C(10)	1.398(15)
C(9)-C(12)	1.477(15)
C(10)-H(10)	0.9500
C(10)-C(11)	1.382(17)
C(11)-H(11)	0.9500
C(12)-C(13)	1.402(15)
C(12)-C(17)	1.392(16)
C(13)-H(13)	0.9500
C(13)-C(14)	1.394(17)
C(14)-H(14)	0.9500
C(14)-C(15)	1.369(18)
C(15)-H(15)	0.9500
C(15)-C(16)	1.382(18)
C(16)-H(16)	0.9500
C(16)-C(17)	1.382(18)

C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(3)-Si(1)-C(18)	110.6(5)
C(19)-Si(1)-C(3)	109.0(6)
C(19)-Si(1)-C(18)	108.3(8)
C(19)-Si(1)-C(20)	110.4(9)
C(20)-Si(1)-C(3)	107.1(7)
C(20)-Si(1)-C(18)	111.5(8)
C(2)-C(1)-H(1)	107.9
C(2)-C(1)-C(4)	111.1(9)
C(2)-C(1)-C(6)	111.6(10)
C(4)-C(1)-H(1)	107.9
C(6)-C(1)-H(1)	107.9
C(6)-C(1)-C(4)	110.4(9)
C(3)-C(2)-C(1)	179.1(13)
C(2)-C(3)-Si(1)	175.4(11)
C(1)-C(4)-H(4A)	108.5
C(1)-C(4)-H(4B)	108.5
H(4A)-C(4)-H(4B)	107.5
C(5)-C(4)-C(1)	115.3(10)
C(5)-C(4)-H(4A)	108.5
C(5)-C(4)-H(4B)	108.5
Br(1)-C(5)-H(5A)	109.2
Br(1)-C(5)-H(5B)	109.2
C(4)-C(5)-Br(1)	112.2(7)
C(4)-C(5)-H(5A)	109.2
C(4)-C(5)-H(5B)	109.2
H(5A)-C(5)-H(5B)	107.9
C(7)-C(6)-C(1)	117.6(11)

C(11)-C(6)-C(1)	123.6(9)
C(11)-C(6)-C(7)	118.8(10)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-C(6)	119.8(12)
C(8)-C(7)-H(7)	120.1
C(7)-C(8)-H(8)	119.1
C(7)-C(8)-C(9)	121.8(10)
C(9)-C(8)-H(8)	119.1
C(8)-C(9)-C(10)	116.8(10)
C(8)-C(9)-C(12)	122.0(9)
C(10)-C(9)-C(12)	121.1(11)
C(9)-C(10)-H(10)	118.9
C(11)-C(10)-C(9)	122.1(11)
C(11)-C(10)-H(10)	118.9
C(6)-C(11)-C(10)	120.7(10)
C(6)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7
C(13)-C(12)-C(9)	121.4(10)
C(17)-C(12)-C(9)	121.7(10)
C(17)-C(12)-C(13)	116.9(10)
C(12)-C(13)-H(13)	119.2
C(14)-C(13)-C(12)	121.6(11)
C(14)-C(13)-H(13)	119.2
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-C(13)	120.1(10)
C(15)-C(14)-H(14)	119.9
C(14)-C(15)-H(15)	120.5
C(14)-C(15)-C(16)	118.9(11)
C(16)-C(15)-H(15)	120.5
C(15)-C(16)-H(16)	119.3
C(15)-C(16)-C(17)	121.4(12)
C(17)-C(16)-H(16)	119.3
C(12)-C(17)-H(17)	119.6
C(16)-C(17)-C(12)	120.9(11)
C(16)-C(17)-H(17)	119.6
Si(1)-C(18)-H(18A)	109.5
Si(1)-C(18)-H(18B)	109.5
Si(1)-C(18)-H(18C)	109.5

H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mj19476_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	54(1)	62(1)	86(1)	-2(1)	19(1)	3(1)
Si(1)	48(2)	52(2)	69(1)	-1(1)	11(1)	2(1)
C(1)	30(5)	50(6)	82(6)	-4(5)	12(4)	3(4)
C(2)	43(6)	49(6)	76(6)	-4(5)	18(4)	1(5)
C(3)	44(6)	53(6)	80(6)	-1(5)	13(5)	1(5)
C(4)	52(7)	40(6)	85(6)	5(4)	18(5)	3(4)
C(5)	54(7)	56(6)	83(6)	6(5)	11(5)	11(6)
C(6)	39(6)	36(5)	78(6)	3(4)	8(4)	-1(4)
C(7)	58(7)	49(6)	79(6)	-2(5)	5(5)	-10(5)
C(8)	52(7)	55(6)	72(5)	-6(5)	10(4)	-6(5)
C(9)	52(6)	40(5)	69(5)	2(4)	11(4)	2(5)
C(10)	56(7)	41(5)	80(6)	1(4)	10(5)	-13(5)
C(11)	56(7)	52(6)	72(5)	0(5)	5(5)	-6(5)
C(12)	48(6)	36(5)	73(5)	3(4)	13(4)	-5(4)
C(13)	58(7)	36(6)	87(6)	3(4)	16(5)	-5(4)

C(14)	76(8)	48(8)	75(5)	-2(4)	22(5)	0(5)
C(15)	72(9)	57(7)	77(6)	8(5)	21(5)	8(6)
C(16)	56(8)	66(8)	89(7)	17(6)	9(6)	-8(6)
C(17)	59(8)	58(7)	78(6)	8(5)	8(5)	-11(6)
C(18)	47(7)	88(9)	105(8)	-33(8)	19(5)	-3(7)
C(19)	66(10)	54(8)	137(12)	-19(7)	13(8)	4(7)
C(20)	109(14)	130(16)	80(7)	17(9)	-5(8)	-30(12)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mj19476_0m.

	x	y	z	U(eq)
H(1)	2787	4020	6988	64
H(4A)	3192	1207	6952	70
H(4B)	5632	1302	7363	70
H(5A)	4346	2078	8449	77
H(5B)	3385	349	8169	77
H(7)	2848	2542	5761	75
H(8)	4403	2575	4689	71
H(10)	9651	4912	5738	70
H(11)	8115	4904	6807	72
H(13)	6164	2113	3842	72
H(14)	7862	2010	2796	78
H(15)	10913	3602	2713	81
H(16)	12273	5269	3691	85
H(17)	10541	5452	4719	78
H(18A)	11350	5443	8754	119
H(18B)	11687	6799	9380	119
H(18C)	11115	7325	8541	119
H(19A)	6811	8982	8523	129
H(19B)	7938	9141	9355	129
H(19C)	5491	8489	9174	129
H(20A)	5898	5014	9757	162
H(20B)	7846	5978	10233	162
H(20C)	8323	4306	9844	162

Table 6. Torsion angles [$^\circ$] for mj19476_0m.

C(2)-C(1)-C(4)-C(5)	49.8(14)
C(6)-C(1)-C(4)-C(5)	174.2(9)
C(1)-C(4)-C(5)-Br(1)	61.2(12)
C(2)-C(1)-C(6)-C(11)	10.9(15)
C(4)-C(1)-C(6)-C(11)	-113.1(11)
C(2)-C(1)-C(6)-C(7)	-170.9(10)
C(4)-C(1)-C(6)-C(7)	65.1(13)
C(11)-C(6)-C(7)-C(8)	0.8(17)
C(1)-C(6)-C(7)-C(8)	-177.4(10)
C(6)-C(7)-C(8)-C(9)	-0.2(18)
C(7)-C(8)-C(9)-C(10)	-0.1(18)
C(7)-C(8)-C(9)-C(12)	178.1(11)
C(8)-C(9)-C(10)-C(11)	-0.1(17)
C(12)-C(9)-C(10)-C(11)	-178.3(10)
C(7)-C(6)-C(11)-C(10)	-1.0(17)
C(1)-C(6)-C(11)-C(10)	177.1(10)
C(9)-C(10)-C(11)-C(6)	0.7(18)
C(8)-C(9)-C(12)-C(17)	165.9(11)
C(10)-C(9)-C(12)-C(17)	-15.9(17)
C(8)-C(9)-C(12)-C(13)	-12.3(17)
C(10)-C(9)-C(12)-C(13)	165.8(11)
C(17)-C(12)-C(13)-C(14)	3.5(16)
C(9)-C(12)-C(13)-C(14)	-178.1(10)
C(12)-C(13)-C(14)-C(15)	-1.2(17)
C(13)-C(14)-C(15)-C(16)	-0.1(18)
C(14)-C(15)-C(16)-C(17)	-1.0(19)
C(15)-C(16)-C(17)-C(12)	3.5(19)
C(13)-C(12)-C(17)-C(16)	-4.6(17)
C(9)-C(12)-C(17)-C(16)	177.1(11)

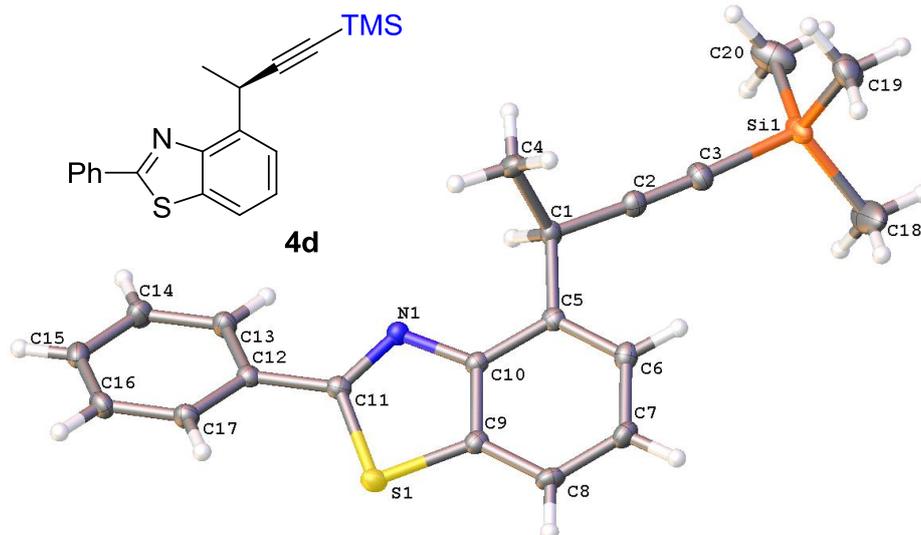


Table 1. Crystal data and structure refinement for mj19475.

Identification code	mj19475	
Empirical formula	C ₂₀ H ₂₁ N S Si	
Formula weight	335.53	
Temperature	169.97 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 9.5614(2) Å	α = 90 °
	b = 26.9394(5) Å	β = 90 °
	c = 7.32500(10) Å	γ = 90 °
Volume	1886.76(6) Å ³	
Z	4	
Density (calculated)	1.181 Mg/m ³	
Absorption coefficient	1.367 mm ⁻¹	
F(000)	712	
Crystal size	0.12 x 0.1 x 0.08 mm ³	
Theta range for data collection	4.269 to 54.961 °	
Index ranges	-11 ≤ h ≤ 11, -32 ≤ k ≤ 32, -8 ≤ l ≤ 7	
Reflections collected	20486	
Independent reflections	3571 [R(int) = 0.0626]	
Completeness to theta = 53.594 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5859	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3571 / 0 / 212	

Goodness-of-fit on F^2	1.093
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0391, wR2 = 0.0796
R indices (all data)	R1 = 0.0472, wR2 = 0.0831
Absolute structure parameter	0.036(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.228 and -0.291 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for mj19475. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4929(1)	4824(1)	2949(1)	30(1)
Si(1)	-666(1)	7191(1)	8333(2)	39(1)
N(1)	4586(2)	5299(1)	6007(3)	25(1)
C(1)	2875(3)	6160(1)	6963(5)	27(1)
C(2)	1673(3)	6486(1)	7342(4)	29(1)
C(3)	730(3)	6760(1)	7702(5)	35(1)
C(4)	4243(3)	6441(1)	7364(5)	38(1)
C(5)	2888(3)	5943(1)	5056(4)	24(1)
C(6)	2127(3)	6131(1)	3626(5)	30(1)
C(7)	2202(3)	5929(1)	1864(5)	32(1)
C(8)	3035(3)	5522(1)	1503(5)	31(1)
C(9)	3801(3)	5325(1)	2947(5)	26(1)
C(10)	3740(3)	5529(1)	4709(4)	23(1)
C(11)	5270(3)	4931(1)	5274(4)	25(1)
C(12)	6244(3)	4610(1)	6271(5)	25(1)
C(13)	6101(3)	4551(1)	8138(5)	31(1)
C(14)	6997(4)	4244(1)	9095(5)	37(1)
C(15)	8053(3)	3991(1)	8176(5)	34(1)
C(16)	8210(3)	4053(1)	6331(5)	34(1)
C(17)	7313(3)	4357(1)	5364(5)	31(1)
C(18)	-2278(4)	7004(2)	7106(8)	88(2)
C(19)	-110(4)	7823(1)	7653(6)	56(1)
C(20)	-916(5)	7154(2)	10849(6)	64(1)

Table 3. Bond lengths [Å] and angles [$^\circ$] for mj19475.

S(1)-C(9)	1.729(3)
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S(1)-C(11)	1.758(3)
Si(1)-C(3)	1.830(3)
Si(1)-C(18)	1.854(4)
Si(1)-C(19)	1.852(4)
Si(1)-C(20)	1.862(4)
N(1)-C(10)	1.394(4)
N(1)-C(11)	1.303(4)
C(1)-H(1)	1.0000
C(1)-C(2)	1.473(4)
C(1)-C(4)	1.540(4)
C(1)-C(5)	1.515(4)
C(2)-C(3)	1.194(4)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-C(6)	1.373(4)
C(5)-C(10)	1.403(4)
C(6)-H(6)	0.9500
C(6)-C(7)	1.403(5)
C(7)-H(7)	0.9500
C(7)-C(8)	1.379(4)
C(8)-H(8)	0.9500
C(8)-C(9)	1.392(4)
C(9)-C(10)	1.404(4)
C(11)-C(12)	1.466(4)
C(12)-C(13)	1.384(5)
C(12)-C(17)	1.396(4)
C(13)-H(13)	0.9500
C(13)-C(14)	1.382(4)
C(14)-H(14)	0.9500
C(14)-C(15)	1.392(5)
C(15)-H(15)	0.9500
C(15)-C(16)	1.370(5)
C(16)-H(16)	0.9500
C(16)-C(17)	1.381(4)
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(9)-S(1)-C(11)	89.28(15)
C(3)-Si(1)-C(18)	108.13(18)
C(3)-Si(1)-C(19)	107.86(17)
C(3)-Si(1)-C(20)	107.99(19)
C(18)-Si(1)-C(20)	111.0(2)
C(19)-Si(1)-C(18)	111.0(2)
C(19)-Si(1)-C(20)	110.68(19)
C(11)-N(1)-C(10)	110.4(3)
C(2)-C(1)-H(1)	107.2
C(2)-C(1)-C(4)	109.5(2)
C(2)-C(1)-C(5)	114.3(3)
C(4)-C(1)-H(1)	107.2
C(5)-C(1)-H(1)	107.2
C(5)-C(1)-C(4)	111.0(3)
C(3)-C(2)-C(1)	177.4(4)
C(2)-C(3)-Si(1)	177.5(3)
C(1)-C(4)-H(4A)	109.5
C(1)-C(4)-H(4B)	109.5
C(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(6)-C(5)-C(1)	123.8(3)
C(6)-C(5)-C(10)	117.6(3)
C(10)-C(5)-C(1)	118.6(3)
C(5)-C(6)-H(6)	119.0
C(5)-C(6)-C(7)	122.1(3)
C(7)-C(6)-H(6)	119.0
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-C(6)	120.9(3)

C(8)-C(7)-H(7)	119.5
C(7)-C(8)-H(8)	121.2
C(7)-C(8)-C(9)	117.5(3)
C(9)-C(8)-H(8)	121.2
C(8)-C(9)-S(1)	128.9(3)
C(8)-C(9)-C(10)	121.8(3)
C(10)-C(9)-S(1)	109.4(2)
N(1)-C(10)-C(5)	124.5(3)
N(1)-C(10)-C(9)	115.4(3)
C(5)-C(10)-C(9)	120.1(3)
N(1)-C(11)-S(1)	115.6(2)
N(1)-C(11)-C(12)	124.2(3)
C(12)-C(11)-S(1)	120.2(2)
C(13)-C(12)-C(11)	119.8(3)
C(13)-C(12)-C(17)	119.1(3)
C(17)-C(12)-C(11)	121.1(3)
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-C(12)	120.6(3)
C(14)-C(13)-H(13)	119.7
C(13)-C(14)-H(14)	120.1
C(13)-C(14)-C(15)	119.8(3)
C(15)-C(14)-H(14)	120.1
C(14)-C(15)-H(15)	120.1
C(16)-C(15)-C(14)	119.8(3)
C(16)-C(15)-H(15)	120.1
C(15)-C(16)-H(16)	119.7
C(15)-C(16)-C(17)	120.7(3)
C(17)-C(16)-H(16)	119.7
C(12)-C(17)-H(17)	120.0
C(16)-C(17)-C(12)	120.0(3)
C(16)-C(17)-H(17)	120.0
Si(1)-C(18)-H(18A)	109.5
Si(1)-C(18)-H(18B)	109.5
Si(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(1)-C(19)-H(19A)	109.5

Si(1)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mj19475. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	38(1)	28(1)	25(1)	-3(1)	0(1)	2(1)
Si(1)	25(1)	33(1)	59(1)	-14(1)	3(1)	2(1)
N(1)	26(1)	26(1)	22(1)	1(1)	0(1)	2(1)
C(1)	30(2)	27(2)	24(2)	3(1)	-1(2)	6(1)
C(2)	32(2)	31(2)	25(2)	4(2)	1(1)	1(1)
C(3)	33(2)	31(2)	40(2)	-1(2)	3(2)	2(2)
C(4)	32(2)	46(2)	35(2)	-14(2)	-8(2)	5(2)
C(5)	20(2)	25(2)	27(2)	1(1)	2(1)	-2(1)
C(6)	26(2)	31(2)	32(2)	7(2)	1(2)	0(1)
C(7)	33(2)	36(2)	28(2)	5(2)	-9(2)	-1(1)
C(8)	39(2)	35(2)	20(2)	-1(1)	-3(2)	-7(2)
C(9)	26(1)	25(2)	26(2)	3(2)	-2(1)	-4(1)
C(10)	24(1)	25(2)	20(2)	2(1)	0(1)	-3(1)
C(11)	27(2)	25(2)	23(2)	1(1)	3(1)	-3(1)
C(12)	26(2)	21(2)	28(2)	-1(1)	1(1)	-2(1)
C(13)	33(2)	34(2)	27(2)	-2(2)	1(2)	7(1)
C(14)	44(2)	39(2)	29(2)	1(2)	-5(2)	7(2)
C(15)	33(2)	28(2)	43(2)	-1(2)	-10(2)	4(1)
C(16)	32(2)	30(2)	41(2)	-6(2)	2(2)	7(1)

C(17)	34(2)	31(2)	27(2)	-2(2)	2(2)	3(1)
C(18)	36(2)	89(3)	138(5)	-57(4)	-23(3)	14(2)
C(19)	63(2)	36(2)	69(3)	2(2)	-1(2)	9(2)
C(20)	70(3)	55(3)	65(3)	-14(2)	31(2)	-11(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mj19475.

	x	y	z	U(eq)
H(1)	2822	5876	7839	32
H(4A)	5039	6216	7201	56
H(4B)	4229	6564	8623	56
H(4C)	4332	6722	6522	56
H(6)	1532	6408	3835	35
H(7)	1671	6073	905	39
H(8)	3085	5383	314	38
H(13)	5381	4724	8768	37
H(14)	6893	4206	10377	45
H(15)	8663	3776	8826	41
H(16)	8943	3885	5710	41
H(17)	7423	4394	4082	37
H(18A)	-2121	7027	5787	132
H(18B)	-3048	7224	7454	132
H(18C)	-2516	6661	7429	132
H(19A)	750	7912	8305	83
H(19B)	-848	8061	7960	83
H(19C)	64	7831	6335	83
H(20A)	-1209	6817	11182	95
H(20B)	-1637	7391	11226	95
H(20C)	-34	7233	11465	95

Table 6. Torsion angles [$^\circ$] for mj19475.

C(2)-C(1)-C(5)-C(6)	18.4(4)
C(4)-C(1)-C(5)-C(6)	-106.0(3)
C(2)-C(1)-C(5)-C(10)	-162.7(3)
C(4)-C(1)-C(5)-C(10)	72.9(3)

C(10)-C(5)-C(6)-C(7)	-1.0(4)
C(1)-C(5)-C(6)-C(7)	177.9(3)
C(5)-C(6)-C(7)-C(8)	1.0(5)
C(6)-C(7)-C(8)-C(9)	-0.4(4)
C(7)-C(8)-C(9)-C(10)	-0.3(4)
C(7)-C(8)-C(9)-S(1)	180.0(2)
C(11)-S(1)-C(9)-C(8)	178.5(3)
C(11)-S(1)-C(9)-C(10)	-1.3(2)
C(11)-N(1)-C(10)-C(5)	-179.0(3)
C(11)-N(1)-C(10)-C(9)	-0.1(4)
C(6)-C(5)-C(10)-N(1)	179.2(3)
C(1)-C(5)-C(10)-N(1)	0.2(4)
C(6)-C(5)-C(10)-C(9)	0.4(4)
C(1)-C(5)-C(10)-C(9)	-178.6(3)
C(8)-C(9)-C(10)-N(1)	-178.7(3)
S(1)-C(9)-C(10)-N(1)	1.1(3)
C(8)-C(9)-C(10)-C(5)	0.3(4)
S(1)-C(9)-C(10)-C(5)	-179.9(2)
C(10)-N(1)-C(11)-C(12)	-179.6(3)
C(10)-N(1)-C(11)-S(1)	-1.0(3)
C(9)-S(1)-C(11)-N(1)	1.4(2)
C(9)-S(1)-C(11)-C(12)	-179.9(2)
N(1)-C(11)-C(12)-C(13)	25.2(4)
S(1)-C(11)-C(12)-C(13)	-153.4(2)
N(1)-C(11)-C(12)-C(17)	-155.5(3)
S(1)-C(11)-C(12)-C(17)	26.0(4)
C(17)-C(12)-C(13)-C(14)	-0.4(5)
C(11)-C(12)-C(13)-C(14)	179.0(3)
C(12)-C(13)-C(14)-C(15)	0.0(5)
C(13)-C(14)-C(15)-C(16)	0.8(5)
C(14)-C(15)-C(16)-C(17)	-1.3(5)
C(15)-C(16)-C(17)-C(12)	0.8(5)
C(13)-C(12)-C(17)-C(16)	0.0(5)
C(11)-C(12)-C(17)-C(16)	-179.4(3)

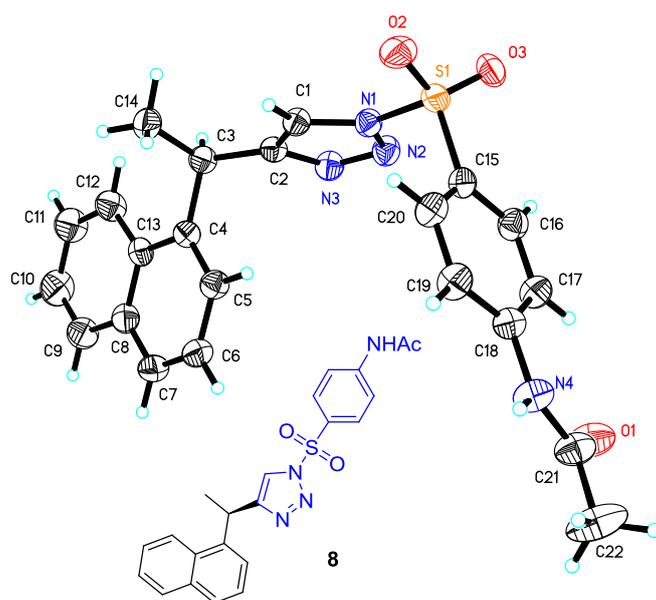


Table 1. Crystal data and structure refinement for mo_d8v18878_0m.

Identification code	mo_d8v18878_0m	
Empirical formula	C ₂₂ H ₂₀ N ₄ O ₃ S	
Formula weight	420.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.7177(4) Å	α = 90 °
	b = 10.0431(5) Å	β = 90 °
	c = 22.0386(10) Å	γ = 90 °
Volume	2150.88(17) Å ³	
Z	4	
Density (calculated)	1.298 Mg/m ³	
Absorption coefficient	0.181 mm ⁻¹	
F(000)	880	
Crystal size	0.180 x 0.110 x 0.070 mm ³	
Theta range for data collection	2.290 to 25.998 °	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27	
Reflections collected	19750	
Independent reflections	4215 [R(int) = 0.0473]	
Completeness to theta = 25.242 °	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6291	

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4215 / 0 / 274
Goodness-of-fit on F ²	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1017
R indices (all data)	R1 = 0.0559, wR2 = 0.1118
Absolute structure parameter	0.06(4)
Extinction coefficient	0.030(3)
Largest diff. peak and hole	0.246 and -0.235 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v18878_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2679(1)	8055(1)	3471(1)	55(1)
O(1)	5507(3)	10436(4)	6088(1)	83(1)
O(2)	1339(2)	7530(2)	3374(1)	71(1)
O(3)	3257(3)	9049(2)	3089(1)	73(1)
N(1)	3731(3)	6706(2)	3384(1)	48(1)
N(2)	5100(3)	6878(3)	3328(1)	56(1)
N(3)	5636(3)	5694(3)	3304(1)	55(1)
N(4)	3389(3)	9511(3)	6043(1)	61(1)
C(1)	3402(3)	5396(3)	3405(1)	47(1)
C(2)	4624(3)	4750(3)	3347(1)	45(1)
C(3)	4940(3)	3288(3)	3316(1)	52(1)
C(4)	5778(3)	2825(3)	3862(1)	47(1)
C(5)	5654(4)	3436(4)	4414(1)	55(1)
C(6)	6356(4)	2983(4)	4929(2)	63(1)
C(7)	7187(4)	1910(4)	4892(2)	68(1)
C(8)	7372(3)	1241(4)	4334(2)	59(1)
C(9)	8232(5)	111(4)	4284(2)	82(1)
C(10)	8385(5)	-552(5)	3753(2)	91(1)
C(11)	7668(5)	-119(4)	3243(2)	83(1)
C(12)	6824(4)	959(4)	3266(2)	69(1)
C(13)	6655(3)	1685(3)	3811(2)	50(1)
C(14)	3622(4)	2475(3)	3247(2)	72(1)
C(15)	2909(3)	8470(3)	4230(1)	51(1)
C(16)	3996(4)	9285(3)	4396(2)	57(1)

C(17)	4186(4)	9627(4)	4990(2)	56(1)
C(18)	3292(3)	9163(3)	5433(1)	51(1)
C(19)	2207(4)	8325(4)	5263(2)	60(1)
C(20)	2012(4)	7978(4)	4664(2)	58(1)
C(21)	4436(4)	10146(4)	6332(2)	66(1)
C(22)	4156(5)	10434(7)	6990(2)	111(2)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for mo_d8v18878_0m.

S(1)-O(2)	1.422(3)
S(1)-O(3)	1.421(3)
S(1)-N(1)	1.708(3)
S(1)-C(15)	1.737(3)
O(1)-C(21)	1.208(4)
N(1)-N(2)	1.348(4)
N(1)-C(1)	1.355(4)
N(2)-N(3)	1.300(4)
N(3)-C(2)	1.369(4)
N(4)-C(21)	1.359(5)
N(4)-C(18)	1.394(4)
N(4)-H(4)	0.8600
C(1)-C(2)	1.359(4)
C(1)-H(1)	0.9300
C(2)-C(3)	1.501(4)
C(3)-C(4)	1.525(4)
C(3)-C(14)	1.527(5)
C(3)-H(3)	0.9800
C(4)-C(5)	1.367(4)
C(4)-C(13)	1.432(4)
C(5)-C(6)	1.400(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.350(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.413(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.414(5)
C(8)-C(13)	1.418(5)
C(9)-C(10)	1.356(6)

C(9)-H(9)	0.9300
C(10)-C(11)	1.392(6)
C(10)-H(10)	0.9300
C(11)-C(12)	1.359(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.416(5)
C(12)-H(12)	0.9300
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.386(5)
C(15)-C(20)	1.386(5)
C(16)-C(17)	1.365(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.387(5)
C(17)-H(17)	0.9300
C(18)-C(19)	1.400(5)
C(19)-C(20)	1.378(5)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(22)	1.504(6)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
O(2)-S(1)-O(3)	122.18(17)
O(2)-S(1)-N(1)	103.70(13)
O(3)-S(1)-N(1)	104.72(15)
O(2)-S(1)-C(15)	110.63(17)
O(3)-S(1)-C(15)	110.53(16)
N(1)-S(1)-C(15)	102.83(14)
N(2)-N(1)-C(1)	111.2(3)
N(2)-N(1)-S(1)	119.9(2)
C(1)-N(1)-S(1)	128.7(2)
N(3)-N(2)-N(1)	106.3(3)
N(2)-N(3)-C(2)	110.1(2)
C(21)-N(4)-C(18)	128.4(3)
C(21)-N(4)-H(4)	115.8

C(18)-N(4)-H(4)	115.8
N(1)-C(1)-C(2)	104.7(3)
N(1)-C(1)-H(1)	127.6
C(2)-C(1)-H(1)	127.6
C(1)-C(2)-N(3)	107.7(3)
C(1)-C(2)-C(3)	130.5(3)
N(3)-C(2)-C(3)	121.8(3)
C(2)-C(3)-C(4)	111.9(3)
C(2)-C(3)-C(14)	110.9(3)
C(4)-C(3)-C(14)	111.3(3)
C(2)-C(3)-H(3)	107.5
C(4)-C(3)-H(3)	107.5
C(14)-C(3)-H(3)	107.5
C(5)-C(4)-C(13)	118.7(3)
C(5)-C(4)-C(3)	121.1(3)
C(13)-C(4)-C(3)	120.0(3)
C(4)-C(5)-C(6)	122.2(3)
C(4)-C(5)-H(5)	118.9
C(6)-C(5)-H(5)	118.9
C(7)-C(6)-C(5)	120.2(3)
C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(6)-C(7)-C(8)	120.5(3)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(9)-C(8)-C(7)	121.6(4)
C(9)-C(8)-C(13)	118.6(3)
C(7)-C(8)-C(13)	119.7(3)
C(10)-C(9)-C(8)	121.8(4)
C(10)-C(9)-H(9)	119.1
C(8)-C(9)-H(9)	119.1
C(9)-C(10)-C(11)	119.3(4)
C(9)-C(10)-H(10)	120.3
C(11)-C(10)-H(10)	120.3
C(12)-C(11)-C(10)	121.4(4)
C(12)-C(11)-H(11)	119.3
C(10)-C(11)-H(11)	119.3
C(11)-C(12)-C(13)	120.8(4)

C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(12)-C(13)-C(8)	118.1(3)
C(12)-C(13)-C(4)	123.2(3)
C(8)-C(13)-C(4)	118.7(3)
C(3)-C(14)-H(14A)	109.5
C(3)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(3)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	120.4(3)
C(16)-C(15)-S(1)	119.7(3)
C(20)-C(15)-S(1)	119.9(3)
C(17)-C(16)-C(15)	120.4(3)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(16)-C(17)-C(18)	120.3(3)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(17)-C(18)-N(4)	123.5(3)
C(17)-C(18)-C(19)	119.1(3)
N(4)-C(18)-C(19)	117.4(3)
C(20)-C(19)-C(18)	120.8(3)
C(20)-C(19)-H(19)	119.6
C(18)-C(19)-H(19)	119.6
C(19)-C(20)-C(15)	119.1(3)
C(19)-C(20)-H(20)	120.5
C(15)-C(20)-H(20)	120.5
O(1)-C(21)-N(4)	123.4(3)
O(1)-C(21)-C(22)	122.6(4)
N(4)-C(21)-C(22)	114.0(4)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v18878_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	64(1)	46(1)	55(1)	-4(1)	-11(1)	12(1)
O(1)	50(2)	129(3)	69(2)	-7(2)	-4(1)	-12(2)
O(2)	57(2)	72(2)	83(2)	-17(1)	-22(1)	21(1)
O(3)	113(2)	48(1)	58(1)	9(1)	-7(1)	9(1)
N(1)	46(2)	44(1)	53(2)	-3(1)	-2(1)	3(1)
N(2)	51(2)	51(2)	67(2)	-2(1)	-2(1)	-3(1)
N(3)	46(2)	56(2)	64(2)	-1(1)	0(1)	0(1)
N(4)	45(2)	86(2)	52(2)	-9(2)	4(1)	-2(2)
C(1)	42(2)	46(2)	52(2)	-3(1)	-1(1)	1(1)
C(2)	46(2)	48(2)	42(2)	0(1)	-1(1)	3(1)
C(3)	57(2)	49(2)	49(2)	-4(1)	2(1)	9(2)
C(4)	46(2)	50(2)	46(2)	0(1)	5(1)	2(1)
C(5)	56(2)	56(2)	53(2)	-2(2)	2(2)	1(2)
C(6)	73(2)	65(2)	52(2)	-4(2)	-4(2)	-5(2)
C(7)	69(2)	71(2)	63(2)	6(2)	-18(2)	-6(2)
C(8)	46(2)	55(2)	75(2)	2(2)	-6(2)	1(2)
C(9)	73(3)	67(3)	104(3)	5(2)	-29(2)	16(2)
C(10)	81(3)	73(3)	118(4)	-13(3)	-9(3)	29(2)
C(11)	92(3)	72(3)	85(3)	-13(2)	7(2)	25(2)
C(12)	76(3)	63(2)	67(2)	-3(2)	4(2)	18(2)
C(13)	48(2)	45(2)	58(2)	3(1)	4(1)	2(1)
C(14)	81(3)	49(2)	86(3)	-4(2)	-22(2)	1(2)
C(15)	57(2)	42(2)	54(2)	-3(1)	-3(2)	5(2)
C(16)	59(2)	54(2)	57(2)	-1(2)	4(2)	-5(2)
C(17)	50(2)	60(2)	58(2)	-5(2)	3(2)	-5(2)
C(18)	43(2)	58(2)	52(2)	-3(2)	2(1)	6(2)
C(19)	52(2)	66(2)	63(2)	-4(2)	10(2)	-10(2)
C(20)	56(2)	58(2)	62(2)	-6(2)	1(2)	-6(2)
C(21)	44(2)	91(3)	64(2)	-11(2)	-6(2)	7(2)
C(22)	71(3)	197(6)	66(3)	-44(3)	1(2)	-7(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mo_d8v18878_0m.

	x	y	z	U(eq)
H(4)	2697	9296	6266	73
H(1)	2533	5021	3450	56
H(3)	5500	3138	2953	62
H(5)	5086	4177	4448	66
H(6)	6248	3423	5297	76
H(7)	7642	1608	5237	81
H(9)	8705	-186	4625	98
H(10)	8962	-1289	3729	109
H(11)	7769	-577	2878	100
H(12)	6352	1222	2919	82
H(14A)	3031	2637	3588	108
H(14B)	3848	1545	3230	108
H(14C)	3160	2731	2881	108
H(16)	4599	9601	4102	68
H(17)	4920	10172	5098	67
H(19)	1611	7998	5558	72
H(20)	1290	7422	4553	70
H(22A)	4230	11375	7062	167
H(22B)	4814	9972	7238	167
H(22C)	3244	10140	7092	167

Table 6. Torsion angles [$^\circ$] for mo_d8v18878_0m.

O(2)-S(1)-N(1)-N(2)	167.0(2)
O(3)-S(1)-N(1)-N(2)	37.9(3)
C(15)-S(1)-N(1)-N(2)	-77.7(3)
O(2)-S(1)-N(1)-C(1)	-18.4(3)
O(3)-S(1)-N(1)-C(1)	-147.5(3)
C(15)-S(1)-N(1)-C(1)	96.9(3)
C(1)-N(1)-N(2)-N(3)	0.9(4)
S(1)-N(1)-N(2)-N(3)	176.4(2)
N(1)-N(2)-N(3)-C(2)	-0.2(3)

N(2)-N(1)-C(1)-C(2)	-1.2(4)
S(1)-N(1)-C(1)-C(2)	-176.2(2)
N(1)-C(1)-C(2)-N(3)	1.0(3)
N(1)-C(1)-C(2)-C(3)	-177.7(3)
N(2)-N(3)-C(2)-C(1)	-0.5(3)
N(2)-N(3)-C(2)-C(3)	178.4(3)
C(1)-C(2)-C(3)-C(4)	-114.8(4)
N(3)-C(2)-C(3)-C(4)	66.6(4)
C(1)-C(2)-C(3)-C(14)	10.0(5)
N(3)-C(2)-C(3)-C(14)	-168.6(3)
C(2)-C(3)-C(4)-C(5)	29.8(4)
C(14)-C(3)-C(4)-C(5)	-94.9(4)
C(2)-C(3)-C(4)-C(13)	-153.8(3)
C(14)-C(3)-C(4)-C(13)	81.6(4)
C(13)-C(4)-C(5)-C(6)	0.0(5)
C(3)-C(4)-C(5)-C(6)	176.4(3)
C(4)-C(5)-C(6)-C(7)	0.0(6)
C(5)-C(6)-C(7)-C(8)	0.7(6)
C(6)-C(7)-C(8)-C(9)	-179.7(4)
C(6)-C(7)-C(8)-C(13)	-1.3(6)
C(7)-C(8)-C(9)-C(10)	178.4(4)
C(13)-C(8)-C(9)-C(10)	0.0(6)
C(8)-C(9)-C(10)-C(11)	-0.6(7)
C(9)-C(10)-C(11)-C(12)	0.4(8)
C(10)-C(11)-C(12)-C(13)	0.5(7)
C(11)-C(12)-C(13)-C(8)	-1.1(6)
C(11)-C(12)-C(13)-C(4)	-179.9(4)
C(9)-C(8)-C(13)-C(12)	0.8(5)
C(7)-C(8)-C(13)-C(12)	-177.6(3)
C(9)-C(8)-C(13)-C(4)	179.6(3)
C(7)-C(8)-C(13)-C(4)	1.3(5)
C(5)-C(4)-C(13)-C(12)	178.2(3)
C(3)-C(4)-C(13)-C(12)	1.7(5)
C(5)-C(4)-C(13)-C(8)	-0.6(5)
C(3)-C(4)-C(13)-C(8)	-177.1(3)
O(2)-S(1)-C(15)-C(16)	-164.4(3)
O(3)-S(1)-C(15)-C(16)	-25.9(3)
N(1)-S(1)-C(15)-C(16)	85.4(3)

O(2)-S(1)-C(15)-C(20)	16.1(3)
O(3)-S(1)-C(15)-C(20)	154.6(3)
N(1)-S(1)-C(15)-C(20)	-94.1(3)
C(20)-C(15)-C(16)-C(17)	-0.8(5)
S(1)-C(15)-C(16)-C(17)	179.7(3)
C(15)-C(16)-C(17)-C(18)	-0.1(5)
C(16)-C(17)-C(18)-N(4)	-177.4(3)
C(16)-C(17)-C(18)-C(19)	1.0(5)
C(21)-N(4)-C(18)-C(17)	-11.5(6)
C(21)-N(4)-C(18)-C(19)	170.0(4)
C(17)-C(18)-C(19)-C(20)	-1.0(5)
N(4)-C(18)-C(19)-C(20)	177.5(3)
C(18)-C(19)-C(20)-C(15)	0.1(5)
C(16)-C(15)-C(20)-C(19)	0.8(5)
S(1)-C(15)-C(20)-C(19)	-179.6(3)
C(18)-N(4)-C(21)-O(1)	-4.7(7)
C(18)-N(4)-C(21)-C(22)	176.5(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v18878_0m [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
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11. DFT Calculations

Computational details

All of the calculations were performed using the Gaussian 09 D.01 program.^{S6} Structures were optimized at the (U)wB97XD^{S7} level of density functional theory. The keyword “int=ultrafine” in the Gaussian 09 D.01 program was used to increase the accuracy of the calculations. The SDD basis set^{S8} with f polarization ($\zeta_f = 3.525$)^{S9} was used for Cu, while the 6-31G(d) basis set was used for all other atoms. Frequency calculations have been performed to verify the optimized structures as local minima or transition states and to obtain Gibbs free energy at 298 K. Intrinsic reaction coordinate (IRC) calculations^{S10} were carried out to make sure that every transition state links relevant intermediates. The more accurate relative

stabilities were further refined by carrying out single-point energy calculations using (U)wB97XD functional, def2TZVP basis set for Cu^{S11}, and 6-311G(d,p) basis set for all nonmetal atoms. CPCM solvation model^{S12-13} with perfluorobenzene as solvent was employed in the single-point energy calculations.

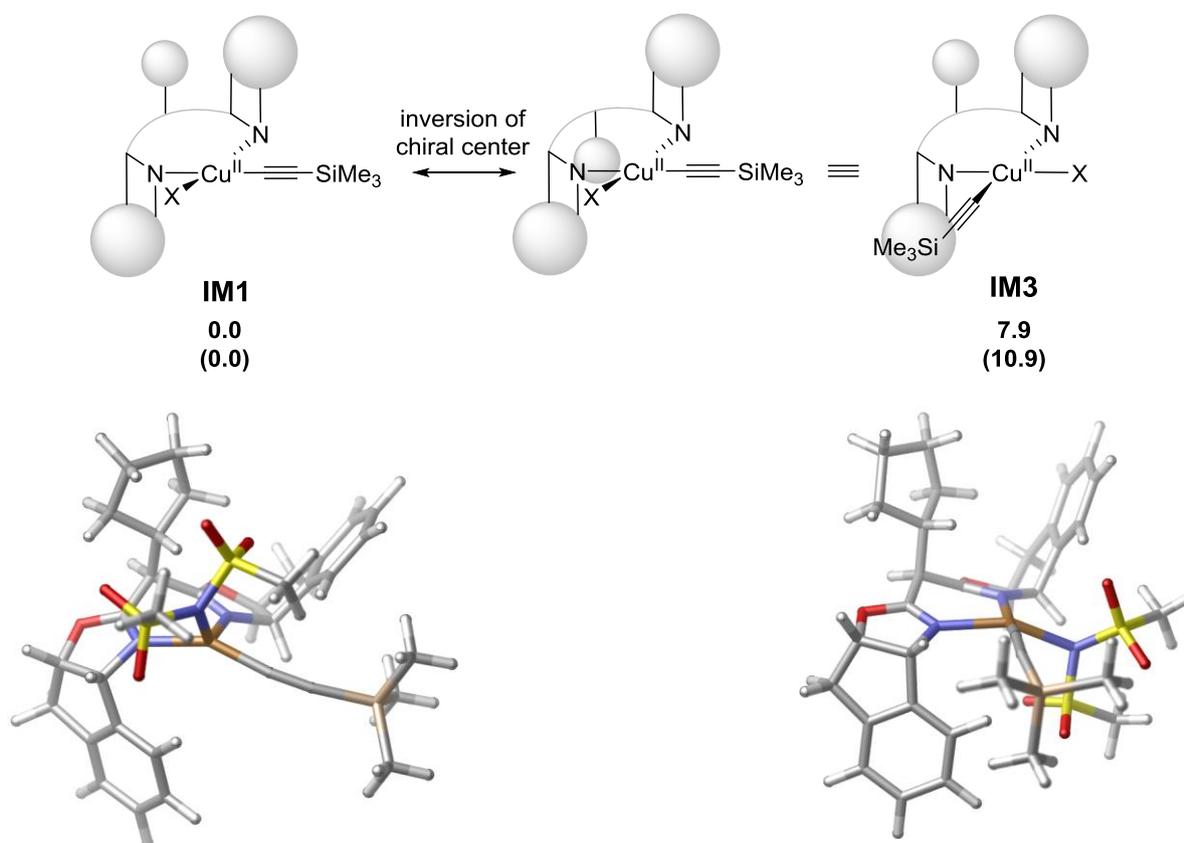


Figure S1. Comparison of the two diastereomers **IM1** and **IM3** calculated for L*Cu(alkynyl)(bismethylsulfonamide).

Notes on Figure S1: In the main text, we presented the calculation results considering how the chiral L*CuII-alkynyl (L* = **L9**, **IM1**) reacts with a benzyl radical. As a diastereomer of **IM1**, **IM3** was also calculated. **IM3** is lying 7.9 kcal/mol higher than **IM1**, and thus we do not consider further the corresponding reaction from **IM3** in view of the fact that the barriers from **IM1** are relatively low.

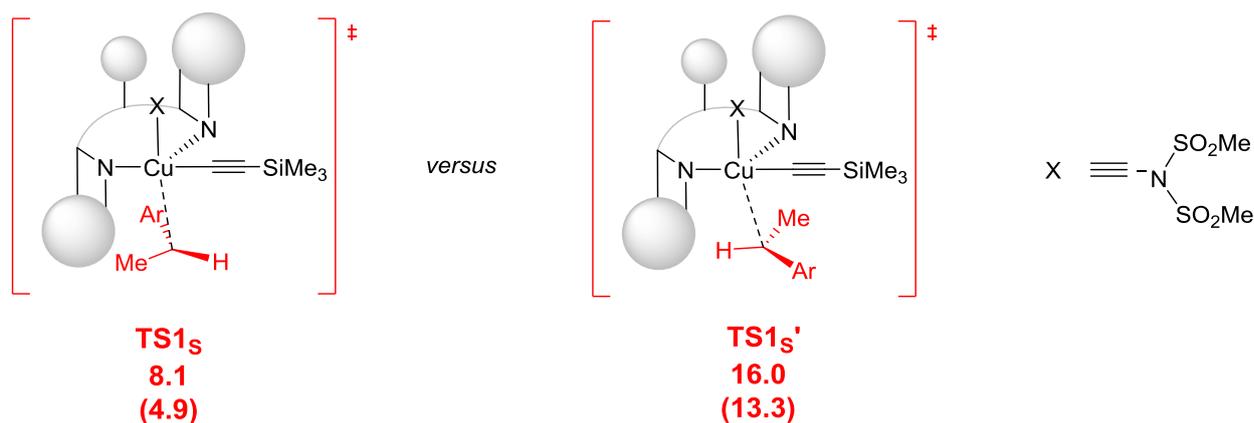


Figure S2. Transition state structures (leading to the S product) in different conformations. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

Notes on Figure S2: The conformations of the transition states presented in the main text are the most stable ones. Here, we showed a higher energy conformation, **TS1_s'**, which is lying 7.9 kcal/mol higher in free energy than **TS1_s** (presented in the main text).

XYZ coordinate

IM1+int1			
E = -5087.967606		G = -5087.158135	
O	3.36126800	2.44476000	0.71758700
O	-0.80053000	1.93179500	1.80738000
N	2.33656400	1.35907400	-0.94852200
N	-0.37857800	0.87453500	-0.11616400
C	3.75826200	0.98853100	-1.10210500
C	4.00337600	-0.48593500	-0.93425800
C	3.70768600	-1.50182000	-1.83808500
C	4.00567700	-2.81351900	-1.47633900
C	4.56978400	-3.09565200	-0.23091600
C	4.87017300	-2.07068000	0.66441300
C	4.59454600	-0.75745300	0.29809100
C	4.87397600	0.50748500	1.07809100
C	4.42338000	1.64395600	0.13624600
C	2.24757000	2.16003300	0.04519700
C	-0.08613300	1.81983400	0.69595600
C	-1.65917300	0.75708000	1.87241400
C	-3.10664200	1.16668900	2.13108100
C	-3.72653500	1.18700500	0.75645900
C	-4.98660600	1.65461500	0.39839100
C	-5.39126000	1.55234400	-0.92971100
C	-4.54343500	0.98775700	-1.88303200
C	-3.28249000	0.52101200	-1.52441400
C	-2.87832400	0.62553300	-0.19806700
C	-1.56609000	0.19142900	0.43017700
H	4.10837200	1.36965000	-2.06076300
H	3.26577900	-1.26254000	-2.80066700
H	3.78822100	-3.62398500	-2.16505500

H	4.78322600	-4.12499600	0.04172000
H	5.31776200	-2.29622700	1.62827900
H	4.31596600	0.54285100	2.01981900
H	5.93525400	0.60153900	1.33066900
H	5.22643800	2.33684700	-0.11153300
H	-1.23551500	0.11492800	2.64381500
H	-3.59243500	0.42476300	2.77609100
H	-3.15393200	2.13001300	2.64849300
H	-5.64459400	2.09469500	1.14301400
H	-6.37056000	1.91745800	-1.22528300
H	-4.86395100	0.92125800	-2.91880800
H	-2.61499300	0.09382800	-2.26064000
H	-1.40729400	-0.88884900	0.38297800
C	0.98970200	2.84168700	0.48330200
Cu	0.69548500	0.52769700	-1.86749900
C	-0.29659300	-1.01256100	-2.39377700
C	-1.07486900	-1.94006900	-2.59358500
Si	-2.40592500	-3.19582800	-2.61705500
C	-3.06773600	-3.34544900	-0.85696800
H	-2.27159700	-3.58452900	-0.14212000
H	-3.51183400	-2.39061200	-0.55051300
H	-3.84135000	-4.11846200	-0.77816100
C	-3.78882400	-2.59549500	-3.74909400
H	-4.60002900	-3.33128200	-3.80276500
H	-4.21277300	-1.65693800	-3.37486500
H	-3.42178700	-2.42302400	-4.76704300
C	-1.75885700	-4.85043000	-3.24435400
H	-1.38458600	-4.75410600	-4.26961300
H	-0.93827400	-5.22761300	-2.62514100
H	-2.55553700	-5.60387300	-3.24578900
H	1.17351300	3.35851400	1.42862300
C	0.55429600	3.84403300	-0.60908700
C	-0.75764100	4.57437100	-0.31972600
C	1.54776700	4.97079700	-0.88942500
H	0.42052200	3.27589400	-1.53285500
C	-0.75685200	5.71931500	-1.35559000
H	-0.74369500	4.96973800	0.70553800
H	-1.62732900	3.91798900	-0.42027400
C	0.72401600	5.90305900	-1.79377400
H	2.45980700	4.61814200	-1.38011700
H	1.82416900	5.46934200	0.05070100
H	-1.37096800	5.44007800	-2.21562800
H	-1.17883600	6.63613000	-0.93298100
H	0.84744600	5.58437400	-2.83331500
H	1.05826900	6.94234800	-1.72502300
C	1.08630800	-2.77718100	0.37320800
H	1.68528100	-1.93668400	0.04191200
C	0.94152700	-3.89774100	-0.60339700
H	1.16377000	-3.54866200	-1.61330500
H	1.62810900	-4.72348300	-0.36393600
H	-0.07287700	-4.31101100	-0.61655500
C	0.55460300	-2.77866800	1.66815100
C	0.78148800	-1.67558100	2.60125900
C	-0.23524100	-3.86036400	2.12412900
C	1.56916500	-0.54736200	2.27564600
C	0.18352900	-1.71925900	3.89238500
C	-0.80725300	-3.88169400	3.39832400
H	-0.40578600	-4.70297700	1.46296600
C	1.73764600	0.49425700	3.16289300
H	2.04809800	-0.49136000	1.30500000
C	0.37370800	-0.63482300	4.78601800

C	-0.61413200	-2.83588400	4.27398900
H	-1.41151600	-4.73397400	3.69535300
C	1.12890500	0.45614900	4.43093300
H	2.33597500	1.35547400	2.87858100
H	-0.09647100	-0.68189400	5.76510000
H	-1.06146100	-2.84844900	5.26397100
H	1.25906200	1.28331700	5.12186200
N	0.78336500	1.54371100	-3.66232200
S	-0.60985000	2.32907200	-4.05087700
S	2.25988900	1.97750600	-4.23624300
O	-0.35783600	3.50694200	-4.88014000
O	-1.38363300	2.49372100	-2.82279000
O	3.10946000	0.80301400	-4.00965600
O	2.71988400	3.24915300	-3.68195300
C	-1.46782000	1.11532500	-5.04106400
H	-0.92532900	0.98212200	-5.97877100
H	-1.49598200	0.17829600	-4.47967600
H	-2.47380200	1.49576200	-5.23132500
C	2.10480800	2.16476200	-6.00600000
H	1.73623700	1.22455900	-6.42002300
H	1.43174200	2.99366100	-6.22169900
H	3.11168900	2.36995000	-6.37506800

IM2

E = -4138.712968

G = -4138.200802

O	3.30725600	2.79089200	0.50105800
O	-0.88771600	1.80973500	2.01327400
N	2.24479900	1.29938300	-0.79785500
N	-0.49896600	0.79400900	0.05727700
C	3.65818200	1.15584900	-1.16506200
C	4.24866300	-0.12872000	-0.63793800
C	3.88894200	-1.42679800	-0.98419400
C	4.53440200	-2.48307100	-0.34541000
C	5.51918700	-2.23967700	0.61452900
C	5.87649100	-0.93557500	0.95042100
C	5.23182500	0.12188200	0.31640200
C	5.46903300	1.60429700	0.49548300
C	4.36880700	2.27020900	-0.34439700
C	2.17510500	2.18894900	0.10770800
C	-0.14903900	1.68763300	0.90524100
C	-1.96251300	0.84210300	1.93236100
C	-3.32770400	1.54735000	1.93234500
C	-3.76452900	1.51410100	0.48607600
C	-4.85649200	2.14746700	-0.09936000
C	-5.08691000	1.97212300	-1.46226600
C	-4.23984600	1.17109000	-2.23070100
C	-3.14620600	0.53628800	-1.64664800
C	-2.92065500	0.71936000	-0.28643500
C	-1.75820300	0.20469100	0.52899100
H	3.74795700	1.25415100	-2.24965800
H	3.12245100	-1.60640500	-1.73355900
H	4.27071700	-3.50548800	-0.59955500
H	6.01379700	-3.07488600	1.10240800
H	6.64622800	-0.75059300	1.69532600
H	5.40722800	1.93036500	1.53892000
H	6.45855400	1.89497000	0.12358900
H	4.72552300	3.11064400	-0.94193500
H	-1.82777300	0.15353200	2.76749300
H	-4.03631000	1.00960800	2.57292500
H	-3.23259400	2.56206600	2.33139900
H	-5.51842100	2.77255000	0.49362900

H	-5.93368300	2.46392100	-1.93160700
H	-4.43246300	1.04530300	-3.29190100
H	-2.46898100	-0.06853700	-2.24440200
H	-1.67804600	-0.88508900	0.53645800
C	0.90890100	2.73108800	0.70810500
Cu	0.42110700	0.60531400	-1.67621800
H	1.13750600	3.18632100	1.67596100
C	0.32282900	3.80468100	-0.24975600
C	-0.98908300	4.44228900	0.23177800
C	1.23316800	5.00320800	-0.52067900
H	0.15186000	3.30929500	-1.21267900
C	-1.10181700	5.75395300	-0.58372600
H	-0.92182300	4.65821100	1.30583000
H	-1.85103600	3.78094900	0.08836100
C	0.28427600	5.96494300	-1.24642100
H	2.10308900	4.73945500	-1.12710300
H	1.58754600	5.43108600	0.42726000
H	-1.89041000	5.68276200	-1.33906000
H	-1.36498500	6.59140500	0.06956000
H	0.24771300	5.67896400	-2.30278200
H	0.62055500	7.00446600	-1.19796700
N	0.43537100	0.71374400	-3.64510400
S	0.46231000	2.25606900	-4.24459800
S	1.53950700	-0.39394700	-4.17040800
O	0.75258600	2.25730600	-5.67775700
O	1.22421100	3.16861200	-3.38751000
O	1.31252700	-1.55501200	-3.30164200
O	2.89630400	0.14313800	-4.25232200
C	-1.26162300	2.68225400	-4.02458900
H	-1.87031800	2.02245400	-4.64347800
H	-1.53373900	2.57547700	-2.97275000
H	-1.37039100	3.72122000	-4.34376600
C	1.02643600	-0.83618400	-5.82098500
H	0.01565400	-1.24266500	-5.76824600
H	1.06005300	0.06323800	-6.43699100
H	1.72813700	-1.58995300	-6.18335100

IM3+int1

E = -5087.950221

G = -5087.145583

O	-4.95799500	2.10615200	-0.73925800
O	-2.22897900	3.38844600	-4.10368100
N	-3.57157000	0.52025900	-1.48587300
N	-1.61908600	1.39068100	-3.31694800
C	-4.66224400	-0.23904100	-0.85494700
C	-5.49411000	-0.99100300	-1.86331500
C	-5.11095500	-2.09079800	-2.62221100
C	-6.02966400	-2.62414700	-3.52225700
C	-7.30075700	-2.06245000	-3.65862900
C	-7.68013700	-0.96455700	-2.88677200
C	-6.76690600	-0.43548700	-1.97952900
C	-6.97334200	0.70153400	-1.00479700
C	-5.60601000	0.87466700	-0.31928600
C	-3.84350000	1.76248200	-1.38639900
C	-2.27762200	2.47797300	-3.14184000
C	-1.53202800	2.77318300	-5.22867400
C	-0.44555800	3.71456600	-5.73881700
C	0.74319300	3.36135600	-4.87437800
C	1.91019500	4.08616000	-4.66180500
C	2.85870500	3.59022300	-3.76839200
C	2.63587500	2.39201200	-3.08872700
C	1.46619500	1.66245700	-3.29868700

C	0.53600800	2.15099000	-4.21034400
C	-0.83228400	1.58691000	-4.54094800
H	-4.23006600	-0.89007500	-0.09252600
H	-4.12291700	-2.52644700	-2.51621400
H	-5.74149100	-3.48176600	-4.12212300
H	-8.00394600	-2.48531800	-4.37043100
H	-8.67385000	-0.53672500	-2.98899600
H	-7.28231000	1.63376800	-1.48962300
H	-7.74443200	0.45570600	-0.26599800
H	-5.67346100	0.92203100	0.76802000
H	-2.29224800	2.50455700	-5.96292400
H	-0.25383700	3.51176700	-6.79965500
H	-0.75592700	4.76039700	-5.65633300
H	2.07493800	5.03287000	-5.16930100
H	3.77178200	4.15001100	-3.58811800
H	3.37280100	2.02678300	-2.37985700
H	1.28219700	0.74642500	-2.74165600
H	-0.81671600	0.66662700	-5.12294500
C	-2.97617200	2.87508200	-1.88125000
Cu	-1.85484800	-0.33541000	-2.29190200
C	-1.96654800	-1.79399200	-1.07549200
C	-2.16388100	-2.85025300	-0.48563100
Si	-2.38500900	-4.60579000	-0.01838600
C	-3.02885200	-4.74799100	1.75102100
H	-2.32670800	-4.29973300	2.46287000
H	-3.99324200	-4.23913200	1.86272000
H	-3.16912000	-5.79865900	2.03251300
C	-3.64397300	-5.33525500	-1.21678100
H	-3.78081700	-6.41110100	-1.05374500
H	-4.61992400	-4.84724600	-1.10985000
H	-3.30200700	-5.17777900	-2.24557300
C	-0.73234000	-5.48669600	-0.18398200
H	-0.31283200	-5.29792300	-1.17787700
H	-0.01455200	-5.11237300	0.55435600
H	-0.83589600	-6.56947600	-0.04325800
H	-3.60126100	3.74650800	-2.08893400
C	-1.89981400	3.23696800	-0.82648300
C	-0.93446600	4.33893400	-1.28041900
C	-2.47369200	3.78116500	0.49038800
H	-1.31890500	2.32654400	-0.62530000
C	-0.23344600	4.72878200	0.02630900
H	-1.50858300	5.18442400	-1.68374100
H	-0.23563400	4.00885700	-2.05582300
C	-1.31197300	4.58108400	1.13032200
H	-2.85040000	2.98542700	1.13975100
H	-3.32084200	4.44241100	0.26985500
H	0.59372100	4.03426600	0.21038900
H	0.19379500	5.73457600	-0.01427700
H	-0.90773500	4.06286700	2.00445700
H	-1.66409500	5.55741600	1.47624000
N	-0.73187300	-1.41861300	-3.72021100
S	0.66456800	-2.14442800	-3.21077400
S	-1.85745700	-2.19026600	-4.64233000
O	0.58824700	-3.59973500	-3.20831300
O	1.08014000	-1.41213400	-2.01818400
O	-2.79481700	-1.10760500	-4.96359100
O	-2.40139900	-3.41931700	-4.08250800
C	1.85192400	-1.69824500	-4.48384900
H	1.60326600	-2.19628000	-5.42123100
H	1.85531100	-0.61427400	-4.60767000
H	2.82765900	-2.04111000	-4.13261100

C	-1.02184100	-2.65951600	-6.15374000
H	-0.54232000	-1.78463800	-6.59615700
H	-0.30031200	-3.44560100	-5.92185300
H	-1.78929300	-3.05227600	-6.82407600
C	-5.36401100	0.19507900	-5.88126200
H	-5.71339000	0.02469900	-4.86928500
C	-5.27837000	-1.00757400	-6.76378400
H	-5.63445800	-1.89246700	-6.23313900
H	-5.87640700	-0.88618200	-7.67763400
H	-4.24154000	-1.20453200	-7.06239000
C	-4.99709500	1.48537700	-6.28617300
C	-5.18071000	2.65687500	-5.43128600
C	-4.44157600	1.69885800	-7.56918000
C	-5.74364900	2.57836500	-4.13633800
C	-4.80414500	3.94141600	-5.91737800
C	-4.06837400	2.96859100	-8.01948100
H	-4.29529800	0.84656200	-8.22399700
C	-5.94091400	3.70770100	-3.37045300
H	-6.04538900	1.61528900	-3.73698800
C	-4.99923000	5.08195600	-5.10084300
C	-4.23804500	4.07701300	-7.21744000
H	-3.64302200	3.07747400	-9.01335600
C	-5.56216200	4.97462400	-3.85314600
H	-6.37400400	3.61849300	-2.37936400
H	-4.70145000	6.05342800	-5.48756200
H	-3.95553200	5.06626500	-7.56713200
H	-5.71893100	5.85898900	-3.24240600

TS1R

E = -5087.962625

G = -5087.149309

O	3.29922700	2.80866800	0.53823200
O	-0.73231100	2.01520500	2.04835300
N	2.39763400	1.12611900	-0.64738400
N	-0.50367100	0.86695400	0.13304100
C	3.86883100	1.03951800	-0.89857800
C	4.53912400	-0.26301200	-0.53906100
C	4.66105700	-1.41094500	-1.31365600
C	5.33100800	-2.50990800	-0.78038800
C	5.88371600	-2.45155500	0.49951800
C	5.80405800	-1.28153600	1.25270900
C	5.13881900	-0.18404900	0.71927900
C	4.99057100	1.19526900	1.31286500
C	4.43853400	2.03187800	0.13928100
C	2.21882300	2.15668200	0.10022400
C	-0.11562400	1.82461200	0.87736000
C	-1.65508400	0.90236100	2.20845200
C	-3.05953600	1.40992300	2.53593000
C	-3.73672900	1.48195200	1.18859000
C	-4.95241900	2.07624400	0.86699800
C	-5.39554100	2.03157400	-0.45289600
C	-4.62766100	1.40650000	-1.43645100
C	-3.41209400	0.81001200	-1.11393000
C	-2.97963200	0.84541100	0.20618000
C	-1.69028000	0.29570600	0.78238700
H	4.03831400	1.33596500	-1.93338900
H	4.23507900	-1.43205300	-2.30995000
H	5.43015800	-3.41642000	-1.37021500
H	6.40160200	-3.31660900	0.90325500
H	6.26779200	-1.22620300	2.23377800
H	4.27552200	1.20941700	2.14434100
H	5.93620200	1.59083400	1.69571300

H	5.17430900	2.72103200	-0.27379000
H	-1.22818500	0.25318700	2.97407400
H	-3.56521600	0.69840600	3.20052200
H	-3.01924400	2.37159700	3.05693500
H	-5.54334800	2.57656400	1.62971700
H	-6.33896400	2.49866300	-0.72050100
H	-4.97053800	1.40132900	-2.46696900
H	-2.79395700	0.34879900	-1.87317700
H	-1.64616500	-0.79607700	0.75404400
C	0.93515200	2.81495200	0.49692900
Cu	0.79128600	-0.01307100	-1.44719100
C	-0.50854000	-1.27082000	-1.92307400
C	-1.50642400	-1.93752400	-2.17474800
Si	-3.06620500	-2.87138900	-2.35367700
C	-3.99031600	-2.80748400	-0.71336200
H	-3.35958800	-3.17357600	0.10473400
H	-4.27938600	-1.77762100	-0.47679400
H	-4.89986900	-3.41926400	-0.74473700
C	-4.11709100	-2.09045600	-3.70926900
H	-5.06106300	-2.63287300	-3.83825700
H	-4.36009100	-1.05212400	-3.45619000
H	-3.59296600	-2.09149200	-4.67166300
C	-2.66996400	-4.66160800	-2.79674900
H	-2.09459700	-4.71966800	-3.72726100
H	-2.07900000	-5.14233500	-2.00813200
H	-3.58746100	-5.24724900	-2.92888700
H	1.14349200	3.46212300	1.35310200
C	0.42273500	3.65227300	-0.69726500
C	-0.86663000	4.42441500	-0.40454600
C	1.38162300	4.72027500	-1.22395400
H	0.21497400	2.94922600	-1.50475500
C	-0.94981200	5.44790400	-1.55874900
H	-0.78161500	4.93351900	0.56593400
H	-1.73944000	3.76513100	-0.36531700
C	0.47525300	5.52161900	-2.17272200
H	2.24865300	4.29562300	-1.73988100
H	1.74424600	5.34608600	-0.39595500
H	-1.66615800	5.10650200	-2.30964900
H	-1.28946700	6.42297500	-1.19553300
H	0.48006000	5.04268000	-3.15704400
H	0.82521000	6.54974900	-2.30568500
C	1.45938500	-2.01436000	-0.53549100
H	2.30580400	-1.37722900	-0.29942800
C	1.79005600	-2.99071600	-1.63316800
H	2.19932100	-2.46224300	-2.49618200
H	2.55474600	-3.68507600	-1.25583300
H	0.92766000	-3.56332000	-1.97332700
C	0.67178400	-2.42614600	0.62565700
C	0.81360600	-1.78194900	1.91011800
C	-0.23295900	-3.47278400	0.51278300
C	1.70610900	-0.70423100	2.14831700
C	0.02084100	-2.23598500	3.00525700
C	-1.00824200	-3.91448800	1.59781200
H	-0.37163900	-3.94981600	-0.44932400
C	1.78626200	-0.09800500	3.37726300
H	2.33364800	-0.34113300	1.34588600
C	0.14214700	-1.60451900	4.27202900
C	-0.89103500	-3.30623200	2.82141200
H	-1.70446800	-4.73557600	1.45593300
C	0.99881800	-0.55110800	4.45783700
H	2.46316000	0.73885200	3.52349300

H	-0.46743800	-1.97124600	5.09397900
H	-1.49062400	-3.63660900	3.66550000
H	1.07612700	-0.06789400	5.42679100
N	0.68130700	1.07667500	-3.30684400
S	-0.59070900	1.88153100	-3.95807700
S	2.15725200	1.04339000	-3.99788200
O	-0.15225800	2.85501200	-4.96017100
O	-1.44347500	2.33937200	-2.86742100
O	2.77622600	-0.18742300	-3.47286700
O	2.91081200	2.28191100	-3.80220600
C	-1.51113200	0.60530600	-4.80780800
H	-0.93496200	0.25705600	-5.66673800
H	-1.68198000	-0.21280100	-4.10515700
H	-2.45267300	1.04799600	-5.14025600
C	1.97146100	0.79856700	-5.75927500
H	1.44518600	-0.14313600	-5.92466600
H	1.43435600	1.64674900	-6.18359700
H	2.98450200	0.73888100	-6.16174100

TS1S

E = -5087.959851

G = -5087.145293

O	-2.01836400	1.40449700	2.04954700
O	0.66793300	3.09917700	-0.84559400
N	-0.78715200	-0.35075200	1.42154100
N	1.29342500	0.99998900	-0.36869300
C	-1.28031000	-0.71139800	2.77802800
C	-2.14325800	-1.94385800	2.85422600
C	-1.72885100	-3.26814500	2.94728300
C	-2.69789100	-4.26593800	3.03867800
C	-4.05394000	-3.93678400	3.06236800
C	-4.46048700	-2.60363100	3.03170100
C	-3.49408300	-1.60764000	2.94051300
C	-3.68954300	-0.11172000	3.00294300
C	-2.25370500	0.44747000	3.09984200
C	-1.25466400	0.81605500	1.14052800
C	0.36211000	1.86361700	-0.43276100
C	2.08986800	3.12223200	-1.06176900
C	2.80806300	3.99776400	-0.02251600
C	3.89564100	3.10192400	0.50879200
C	4.99281200	3.46699500	1.28105600
C	5.90051600	2.48666700	1.67755800
C	5.69484900	1.15422200	1.31758500
C	4.59110600	0.79088100	0.54762500
C	3.69889500	1.77326800	0.13482400
C	2.53014100	1.64713000	-0.82384200
H	-0.43572500	-0.75491700	3.46117400
H	-0.66803700	-3.50141300	2.96258400
H	-2.39373600	-5.30612400	3.10734400
H	-4.79835200	-4.72427800	3.13763100
H	-5.51487000	-2.34907300	3.10157800
H	-4.18089000	0.28476800	2.10665800
H	-4.30010500	0.18321200	3.86228400
H	-2.02770000	0.94519400	4.04076000
H	2.24753300	3.46668200	-2.08526300
H	3.19002000	4.92856700	-0.45324100
H	2.10379300	4.25215300	0.77690900
H	5.14543700	4.50467700	1.56548900
H	6.76782100	2.76065600	2.27134400
H	6.40228400	0.39257400	1.63511900
H	4.41785300	-0.24181000	0.27511000
H	2.84563900	1.13377900	-1.73955000

C	-1.09363800	1.56510200	-0.16347700
Cu	0.95926900	-0.98218500	0.62246900
C	2.45233300	-1.78156700	-0.20314800
C	3.43727900	-2.16739100	-0.82537300
Si	4.98546400	-2.48475600	-1.74477600
C	5.23793700	-1.02810000	-2.91670400
H	4.39967800	-0.94532500	-3.61870900
H	5.29964500	-0.09170800	-2.34952300
H	6.15926100	-1.13143200	-3.50170000
C	6.41749600	-2.57353400	-0.52261100
H	7.36345400	-2.78245600	-1.03585000
H	6.53086000	-1.62377900	0.01264300
H	6.25440800	-3.36254200	0.21990400
C	4.85551300	-4.09348100	-2.71330700
H	4.68912200	-4.94232300	-2.04110500
H	4.02074400	-4.05914700	-3.42219500
H	5.77316200	-4.28650200	-3.28137500
H	-1.36779900	0.83784300	-0.93466300
C	-2.06854100	2.74941800	-0.30667300
C	-2.01722600	3.43165100	-1.69288100
C	-3.55645500	2.30098400	-0.14931300
H	-1.83151600	3.49066400	0.46300400
C	-3.42623000	3.99367700	-1.88591500
H	-1.80644900	2.68479600	-2.47047500
H	-1.23893100	4.19212800	-1.75283700
C	-4.32290100	2.87147000	-1.35827700
H	-3.96100200	2.67685700	0.79351000
H	-3.64305900	1.20912100	-0.11645900
H	-3.55314600	4.89746100	-1.27577200
H	-3.63883000	4.26545800	-2.92484400
H	-5.33039100	3.20874200	-1.09626200
H	-4.42803400	2.09979500	-2.13015200
C	0.05915300	-2.44744600	-0.89883700
H	0.89751500	-2.64522700	-1.55096000
C	-0.26957800	-3.62864400	-0.03561100
H	-0.63662900	-4.43756900	-0.68550700
H	0.62392500	-3.98146400	0.48328300
H	-1.03707800	-3.42383500	0.70754400
C	-0.97360200	-1.63714300	-1.52477300
C	-0.64882800	-0.78705900	-2.64767400
C	-2.29580500	-1.71618500	-1.10172900
C	0.68545700	-0.54557800	-3.06886300
C	-1.70303200	-0.12407500	-3.33767300
C	-3.32711800	-1.05275300	-1.78989800
H	-2.54636300	-2.31341700	-0.23150800
C	0.95064900	0.29701500	-4.12060100
H	1.51362200	-0.99305200	-2.52923200
C	-1.39736300	0.72672000	-4.43209200
C	-3.04249700	-0.29047600	-2.89664500
H	-4.35147100	-1.15708700	-1.44555000
C	-0.09847500	0.93742600	-4.81614000
H	1.98058300	0.47556300	-4.41673300
H	-2.21466600	1.22194500	-4.95018900
H	-3.83849200	0.20820400	-3.44312000
H	0.12640200	1.59810800	-5.64777900
N	1.92532500	-0.32484600	2.49686600
S	1.66397900	1.10309700	3.28119500
S	2.33782200	-1.67296100	3.33856200
O	0.66990000	0.99477900	4.35021800
O	1.39128000	2.10320200	2.24707300
O	1.52020300	-2.77269600	2.80813300

O	2.35809900	-1.46086300	4.78487300
C	3.21643100	1.52620700	4.05037000
H	3.44389200	0.76511700	4.79860000
H	3.98394600	1.58232900	3.27811000
H	3.07880200	2.49907900	4.52651700
C	4.02156200	-1.98861600	2.83180200
H	4.03541600	-2.14792400	1.75312400
H	4.63137400	-1.12611900	3.10770900
H	4.35600500	-2.88206500	3.36372300

TS1S'

E = -5087.946426

G = -5087.132558

O	-2.07605000	1.60077400	2.06858900
O	0.67812900	3.40561100	-0.67340700
N	-0.70793300	-0.06735900	1.49744800
N	1.33696900	1.30011800	-0.27620000
C	-1.26708500	-0.49424900	2.80319700
C	-2.13806500	-1.72120700	2.70600000
C	-1.73611600	-3.04756500	2.58679200
C	-2.71003800	-4.03708400	2.47584100
C	-4.06442400	-3.70191000	2.51690700
C	-4.46145500	-2.37908600	2.70404300
C	-3.48831300	-1.39016500	2.80677800
C	-3.68053900	0.07701100	3.11380200
C	-2.25114200	0.65288600	3.14931800
C	-1.23612700	1.06481000	1.19930700
C	0.38985900	2.14865400	-0.32908600
C	2.10810800	3.46670700	-0.85568200
C	2.78882700	4.32497000	0.22136400
C	3.88005600	3.43093300	0.75017300
C	4.96216500	3.79159900	1.54600100
C	5.86812600	2.80944700	1.94224800
C	5.67778600	1.48106200	1.55818800
C	4.59578700	1.12292800	0.75669600
C	3.70663800	2.10835500	0.34532000
C	2.57604200	1.99349100	-0.65699000
H	-0.45911600	-0.60599500	3.52163700
H	-0.68198500	-3.30284300	2.62689800
H	-2.41164700	-5.07632200	2.37584600
H	-4.81533300	-4.48214900	2.43282500
H	-5.51619800	-2.12901300	2.78358100
H	-4.27916200	0.60011800	2.35986500
H	-4.18451800	0.21411800	4.07655400
H	-1.99149600	1.17605000	4.06706100
H	2.27732300	3.84732200	-1.86441500
H	3.16351800	5.27253800	-0.17781400
H	2.06505300	4.54474800	1.01337400
H	5.10200100	4.82488500	1.85207500
H	6.72224700	3.07847300	2.55695600
H	6.38708000	0.72100800	1.87503300
H	4.44176300	0.09631100	0.44798000
H	2.93988300	1.52105400	-1.57525900
C	-1.06333500	1.79329800	-0.11550100
Cu	1.03151300	-0.66002100	0.66496800
C	2.45143900	-1.42296900	-0.25166100
C	3.47120800	-1.80697500	-0.81174500
Si	5.02181200	-2.52634600	-1.46542100
C	4.72468900	-3.21926900	-3.18978200
H	3.96553700	-4.00759200	-3.16138300
H	4.37336500	-2.43817900	-3.87323600
H	5.64707800	-3.64320000	-3.60471900

C	6.35087300	-1.19010600	-1.54230600
H	7.27765100	-1.58843600	-1.97238500
H	6.02708500	-0.34545100	-2.16072800
H	6.58495800	-0.79702500	-0.54679300
C	5.55288800	-3.89682500	-0.28851300
H	5.73896600	-3.49900300	0.71576400
H	4.77126300	-4.65953400	-0.20279500
H	6.47249400	-4.38453500	-0.63351200
H	-1.26958700	1.03473200	-0.88273200
C	-2.08546600	2.92274400	-0.32287800
C	-1.98232100	3.60039900	-1.70959000
C	-3.55314900	2.38944100	-0.25265800
H	-1.93236500	3.67490400	0.45656900
C	-3.41664400	4.02086200	-2.03552600
H	-1.63761400	2.87259100	-2.45886100
H	-1.27367100	4.42888000	-1.71397500
C	-4.23901900	2.82069700	-1.56265600
H	-4.05933500	2.81772900	0.61638300
H	-3.59014600	1.30114100	-0.12535200
H	-3.68418200	4.91390600	-1.45600900
H	-3.56184900	4.25746100	-3.09404500
H	-5.30065300	3.04673500	-1.42569000
H	-4.17061000	2.01793500	-2.30761200
C	0.07843800	-2.45010600	-0.34068200
H	-0.24139300	-2.66838900	0.67373100
C	-0.95085400	-1.70169600	-1.15330600
H	-1.58526300	-2.41987000	-1.68831400
H	-1.59507300	-1.11662200	-0.49799000
H	-0.49488800	-1.04132600	-1.89943400
C	0.78915200	-3.56099700	-0.98361400
C	1.50733400	-4.53903300	-0.20858100
C	0.71647700	-3.72737600	-2.35613100
C	1.72185900	-4.40058700	1.18306200
C	2.06031100	-5.67455400	-0.86389000
C	1.27445600	-4.84744800	-3.00057000
H	0.21307300	-2.98451200	-2.96483100
C	2.41563800	-5.34983600	1.89266000
H	1.38043000	-3.52013200	1.71300200
C	2.76111100	-6.64737100	-0.10394100
C	1.92180100	-5.80990700	-2.26998500
H	1.18368500	-4.94331500	-4.07811600
C	2.93416000	-6.49362800	1.24812100
H	2.56644100	-5.20448700	2.95818900
H	3.16934800	-7.51373300	-0.61830600
H	2.34747800	-6.68277900	-2.75839700
H	3.47792400	-7.24007500	1.81920300
N	2.00537500	0.07088200	2.66088800
S	1.57763800	1.47832700	3.39855800
S	2.39603900	-1.21573500	3.59922900
O	0.56292900	1.28794200	4.43937000
O	1.23511600	2.42680400	2.33309200
O	1.37862900	-2.26687000	3.42157700
O	2.73740200	-0.84879000	4.97420100
C	3.04550300	2.09845100	4.19755500
H	3.33224200	1.39187700	4.97631900
H	3.82681100	2.20646500	3.44583900
H	2.78358700	3.06852900	4.62507300
C	3.89091500	-1.81443400	2.83188400
H	3.69529100	-2.05964100	1.78731100
H	4.64576000	-1.03034400	2.91062500
H	4.19531000	-2.70270100	3.39014200

3a

E = -949.266655	G = -948.993317		
C	1.21389700	-0.76134500	-0.08950400
C	2.38112500	-0.45039800	0.03869800
Si	4.13376200	0.05975700	0.24676600
C	4.24178100	1.92287000	0.00093900
H	3.90481700	2.20917700	-1.00139100
H	3.61896200	2.45298000	0.72966100
H	5.27401900	2.27221500	0.12178100
C	4.70409000	-0.39905600	1.97997500
H	5.74745200	-0.10034600	2.13620800
H	4.09290700	0.09866300	2.74048900
H	4.63411100	-1.47932100	2.14689700
C	5.18532900	-0.82492200	-1.03883500
H	5.12239300	-1.91216700	-0.92174300
H	4.85920100	-0.57689600	-2.05466200
H	6.23859900	-0.53583100	-0.94261900
C	-5.28613900	-0.52716200	0.64234900
C	-4.79971200	0.72040400	0.35232800
C	-3.42523900	0.92255200	0.06087500
C	-2.53469100	-0.19116400	0.07154000
C	-3.07561800	-1.47053700	0.37937600
C	-4.40935100	-1.63447400	0.65608000
H	-3.61728300	3.05663200	-0.24474200
H	-6.33989400	-0.66822100	0.86297000
H	-5.46364500	1.58118100	0.34066500
C	-2.92702900	2.21702200	-0.23977300
C	-1.14854500	0.02752200	-0.22181900
H	-2.42921500	-2.34166100	0.39803100
H	-4.79435800	-2.62288700	0.88886200
C	-0.71329100	1.29940500	-0.50434100
C	-1.59996600	2.39956200	-0.51556600
H	-1.21663400	3.38977100	-0.74298300
C	-0.18535100	-1.15631800	-0.27843400
H	-0.42899400	-1.84316100	0.54209100
C	-0.33680000	-1.92171100	-1.61226800
H	0.31554200	-2.79969800	-1.62847900
H	-1.37234100	-2.24486900	-1.75314000
H	-0.06436000	-1.26898700	-2.44653100
H	0.33912000	1.46331800	-0.71581000

12. References

- (S1) Hayashida, M.; Honda, H.; Hamana, M. *Heterocycles* **1990**, *31*, 1325.
- (S2) Sun, H.-X.; Sun, Z.-H.; Wang, B. *Tetrahedron Lett.* **2009**, *50*, 1596.
- (S3) Yazaki, R.; Kumagai, N.; Shibasaki, M. *Org. Lett.* **2011**, *13*, 952.
- (S4) (a) Guin, J.; Varseev, G.; List, B. *J. Am. Chem. Soc.* **2013**, *135*, 2100. (b) Iwamoto, T.; Okuzono, C.; Adak, L.; Jin, M.; Nakamura, M. *Chem. Commun.* **2019**, *55*, 1128.
- (S5) (a) Fu, L.; Zhou, S.; Wan, X.; Chen, P.; Liu, G. *J. Am. Chem. Soc.* **2018**, *140*, 10965. (b) Liu, Y.; Xie, P.; Sun, Z.; Wo, X.; Gao, C.; Fu, W.; Loh, T.-P. *Org. Lett.* **2018**, *20*, 5353.
- (S6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.;

Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M. E., M.; ; Toyota, K. F., R.; ; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.;; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., *Gaussian 09*, Gaussian, Inc., Wallingford CT, 2009.

(S7) Chai, J.-D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10* (44), 6615-6620.

(S8) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H., Energy-adjusted ab initio pseudopotentials for the first row transition elements. *The Journal of Chemical Physics* **1987**, *86* (2), 866-872.

(S9) Ehlers, A.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K.; Stegmann, R.; Veldkamp, A.; Frenking, G., A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc-Cu, Y-Ag and La-Au. *Chemical physics letters* **1993**, *208* (1), 111-114.

(S10) Fukui, K., The path of chemical reactions-the IRC approach. *Accounts of chemical research* **1981**, *14* (12), 363-368.

(S11) Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297-3305.

(S12) Barone, V.; Cossi, M., Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A* **1998**, *102* (11), 1995-2001.

(S13) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V., Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* **2003**, *24* (6), 669-681.