Multiligand Enabled, Copper-Catalyzed Hiyama Coupling of Arylsilanes with Unactivated Secondary Alkyl Halides: Reaction Development and Mechanistic Insights

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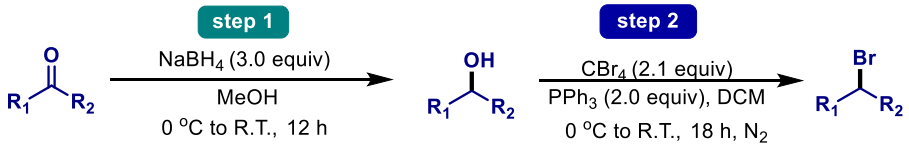
I. General Methods

All the reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. Commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated. High Resolution Mass (HRMS) analyses were obtained using electron impact ionization (EI) and reported as m/z (relative intensity) for the molecular ion $[M]^+$, with electrospray ionization (ESI) and reporting the molecular ion $[MH]^+$ or a suitable fragment ion. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plate. Column chromatography was undertaken on silica gel (200-300 mesh) using proper eluents. ^1H, ^{13}C and ^{19}F NMR spectroscopic data were recorded on Bruker Avance 400 (400 MHz) or Bruker Avance 600 (600 MHz), and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak [$CHCl_3$ in $CDCl_3$: 7.26 ppm, pyridine in pyridine-d_5: 8.74, 7.58, 7.22 ppm, C_6D_6: 7.16 ppm].

II. Procedures for the Preparation of the Starting Materials

a) Preparation of Alkyl Halides

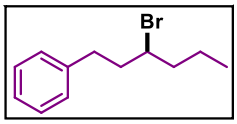
General Procedure A



Step 1: Following the reported procedures,[1] to an oven-dried round-bottom flask equipped with a stir bar was added the ketone (10 mmol) and MeOH (20 mL). Then, $NaBH_4$ (1.1 g, 30 mmol, 3.0 equiv) was slowly added to the mixture in an ice bath. The reaction mixture was stirred overnight at room temperature. Finally, the above solution was quenched with saturated $NaHCO_3$ and extracted with dichloromethane (DCM, 3 x 20 mL). The combined organics were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used for the next step without further purification.

Step 2: Following the reported procedures,[2] to an oven-dried flask equipped with a stir bar were charged with PPh_3 (5.3 g, 20 mmol, 2.0 equiv) and CBr_4 (7.0 g, 21 mmol, 2.1 equiv) under a nitrogen atmosphere. Then, anhydrous DCM (30 mL) was added, and the flask was cooled in an ice bath. The corresponding alcohol in DCM (20 mL) was slowly added to the above solution at 0 °C. Finally, the ice bath was removed and the reaction mixture was stirred for 18 h at room temperature. The reaction was concentrated under reduced pressure and purified by column chromatography.

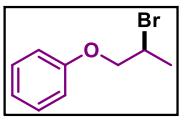
(3-Bromohexyl)benzene



Following the **General Procedure A** using 1-phenylhexan-3-one (1.76 g, 10 mmol) as the reagent. Column chromatography (petroleum ether) afforded colorless liquid (70%), R_f = 0.74 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.01 (tt, *J* = 8.7, 4.6 Hz, 1H), 2.91 (ddd, *J* = 14.1, 8.8, 5.6 Hz, 1H), 2.76 (ddd, *J* = 13.7, 8.8, 7.3 Hz, 1H), 2.20 – 2.04 (m, 2H), 1.93 – 1.73 (m, 2H), 1.66 – 1.55 (m, 1H), 1.44 (dddd, *J* = 13.3, 9.9, 7.4, 6.0 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H).
The spectral data is similar to that previously reported in the literature.[3]

(2-Bromopropoxy)benzene



Following the **General Procedure A** using 1-phenoxypropan-2-one (1.5 g, 10 mmol) as the reagent. Column chromatography (petroleum ether) afforded colorless oil (52%), R_f = 0.83 (petroleum ether).

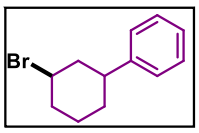
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 4.39 – 4.29 (m, 1H), 4.24 (dd, *J* = 10.0, 5.7 Hz, 1H), 4.07 (dd, *J* = 9.9, 7.1 Hz, 1H), 1.81 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 158.18, 129.62, 121.40, 114.78, 73.12, 45.35, 22.74.

(4-Bromocyclohexyl)benzene

Following the **General Procedure A** using 4-phenylcyclohexan-1-one (1.74 g, 10 mmol) as the reagent. Column chromatography (petroleum ether) afforded pale yellow oil (70%), diastereomeric ratio was determined to be 24:1 by NMR spectrum analyses. R_f = 0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 4.77 – 4.74 (m, 1H), 2.56 (ddt, *J* = 15.5, 12.0, 3.2 Hz, 1H), 2.27 – 2.17 (m, 2H), 2.15 – 2.02 (m, 2H), 2.01 – 1.89 (m, 2H), 1.75 (d, *J* = 12.6 Hz, 2H).
The spectral data is similar to that previously reported in the literature.[3]

(3-Bromocyclohexyl)benzene

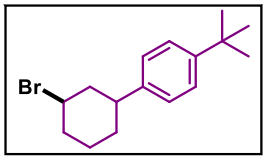


Following the **General Procedure A** using 3-phenylcyclohexan-1-one (1.74 g, 10 mmol) as the reagent. Column chromatography (petroleum ether) afforded pale yellow oil (40%), diastereomeric ratio was determined to be 9:1 by NMR spectrum analyses. R_f = 0.57 (petroleum ether).

Major isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H, overlap), 7.22 – 7.19 (m, 3H, overlap), 4.83 – 4.82 (m, 1H, overlap), 3.20 – 3.15 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.28 – 2.24 (m, 1H), 2.15 – 2.12 (m, 1H), 2.05 – 2.00 (m, 1H), 1.98 – 1.92 (m, 2H, overlap), 1.85 – 1.80 (m, 1H, overlap), 1.75 – 1.71 (m, 1H, overlap), 1.52 – 1.47 (m, 1H, overlap). ^{13}C NMR (600 MHz, $CDCl_3$) δ 146.10 (overlap), 128.49 (overlap), 127.04, 126.24, 54.76, 42.03, 38.31, 34.33 (overlap), 33.42, 21.37 (overlap).
Minor isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H, overlap), 7.22 – 7.19 (m, 3H, overlap), 4.83 – 4.82 (m, 1H, overlap), 4.17 – 4.11 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.63 – 2.59 (m, 1H), 2.52 – 2.50 (m,

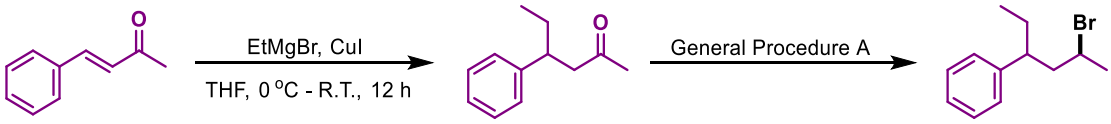
1H), 2.40 – 2.38 (m, 1H), 1.98 – 1.92 (m, 2H, overlap), 1.85 – 1.80 (m, 1H, overlap), 1.75 – 1.71 (m, 1H, overlap), 1.52 – 1.47 (m, 1H, overlap). ^{13}C NMR (600 MHz, $CDCl_3$) δ 146.10 (overlap), 128.49 (overlap), 126.72, 126.44, 51.41, 42.03 (overlap), 37.89, 34.33 (overlap), 32.65, 27.25.
HRMS (EI) calcd. for $C_{12}H_{15}Br$ $[M]^+$: 238.0352, found: 238.0351.

1-(3-Bromocyclohexyl)-4-(*tert*-butyl)benzene



Following the **General Procedure A** using 3-(4-(*tert*-butyl)phenyl) cyclohexan-1-one (2.3 g, 10 mmol) as the reagent. Column chromatography (petroleum ether) afforded pale yellow oil (45%), diastereomeric ratio was determined to be 5:1 by NMR spectrum analyses. R_f = 0.55 (petroleum ether).
major: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H, overlap), 7.15 (d, *J* = 8.3 Hz, 2H, overlap), 4.82 (t, *J* = 3.3 Hz, 1H, overlap), 3.15 (tt, *J* = 12.1, 3.3 Hz, 1H), 2.27 – 2.25 (m, 1H), 2.14 – 2.11 (m, 1H), 2.05 – 1.99 (m, 1H), 1.97 – 1.90 (m, 3H, overlap), 1.85 – 1.79 (m, 1H, overlap), 1.70 – 1.74 (m, 1H, overlap), 1.31 (s, 9H, overlap). ^{13}C NMR (600 MHz, $CDCl_3$) δ 148.97 (overlap), 143.01 (overlap), 126.63, 125.33, 54.91, 44.88, 42.00 (overlap), 37.71, 34.35, 33.45, 31.40, 21.40.
minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H, overlap), 7.15 (d, *J* = 8.3 Hz, 2H, overlap), 4.82 (t, *J* = 3.3 Hz, 1H, overlap), 4.13 (tt, *J* = 12.1, 3.3 Hz, 1H), 2.61 – 2.57 (m, 1H), 2.51 – 2.49 (m, 1H), 2.37 – 2.39 (m, 1H), 1.97 – 1.90 (m, 3H, overlap), 1.85 – 1.79 (m, 1H, overlap), 1.70 – 1.74 (m, 1H, overlap), 1.31 (s, 9H, overlap). ^{13}C NMR (600 MHz, $CDCl_3$) δ 148.97 (overlap), 143.01 (overlap), 126.32, 125.39, 51.60, 45.78, 42.00 (overlap), 37.91, 34.39, 32.61, 29.73, 27.26.
HRMS (EI) calcd. for $C_{16}H_{23}Br$ $[M]^+$: 294.0978, found: 294.0978.

(5-Bromohexan-3-yl)benzene

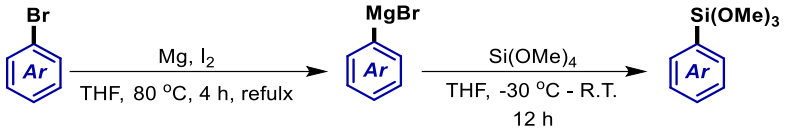


Following the reported procedures,[4] to an oven-dried round-bottom flask equipped with a stir bar was added EtMgBr (20 mmol, 2 M, 10 mL, 2.0 equiv), CuI (950 mg, 5 mmol, 0.5 equiv), and THF (30 mL) under a nitrogen atmosphere at 0 °C. Then, 4-phenylbut-3-en-2-one (1.46 g, 10 mmol, 1.0 equiv) was slowly added to the above solution. The reaction mixture was stirred overnight at room temperature. After completion, the solution was quenched with water and extracted with DCM (3 x 10 mL). The combined organics were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to obtain the crude product 4-phenylhexan-2-one.

Next, following the **General Procedure A** to obtain the final product (5-bromohexan-3-yl)benzene as colorless oil (768 mg, 32%), diastereomeric ratio was determined to be 6:1 by NMR spectrum analyses. R_f = 0.67 (petroleum ether). major: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H, overlap), 7.23 – 7.14 (m, 3H, overlap), 3.69 – 3.64 (m, 1H), 2.83 – 2.78 (m, 1H), 2.13 – 2.07 (m, 1H, overlap), 1.91 – 1.86 (m, 1H), 1.74 – 1.65 (m, 2H, overlap), 1.63 (d, *J* = 6.7 Hz, 3H, overlap), 0.81 – 0.76 (m, 3H, overlap). ^{13}C NMR (600 MHz, $CDCl_3$) δ 143.95 (overlap), 128.49, 127.88, 126.37 (overlap), 50.73 (overlap), 47.99, 46.18, 29.70, 27.27, 12.15. minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H, overlap),

7.23 – 7.14 (m, 3H, overlap), 3.99 – 3.93 (m, 1H), 2.65 – 2.60 (m, 1H), 2.30 – 2.25 (m, 1H), 2.13 – 2.07 (m, 1H, overlap), 1.74 – 1.65 (m, 2H, overlap), 1.63 (d, J = 6.7 Hz, 3H, overlap), 0.81 – 0.76 (m, 3H, overlap). ^{13}C NMR (600 MHz, $CDCl_3$) δ 143.95 (overlap), 128.57, 127.66, 126.37 (overlap), 50.73 (overlap), 48.92, 45.94, 29.23, 25.67, 11.93. HRMS (EI) calcd. for $C_{12}H_{17}Br$ $[M]^+$: 240.0509, found: 240.0514.

b) Preparation of trimethoxy(aryl)silanes



Following the reported procedures,[5] to a flame dried 3-neck round bottom flask equipped with a stir bar was added $Si(OMe)_4$ (13.7 g, 90 mmol, 3.0 equiv) and THF (20 mL) at -30 ˚C. Then, a solution of aryl Grignard reagent in THF [prepared from 30 mmol (1.0 equiv) of the corresponding arylbromide and magnesium turnings [1.1 g, 45 mmol, (1.5 equiv)] by heating at 80°C for 4 h.] was dropwise added to the solution. The resulting mixture was warmed to room temperature and stirred overnight. Finally, the reaction solution was diluted with H_2O (10 mL) and extracted with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by distillation.

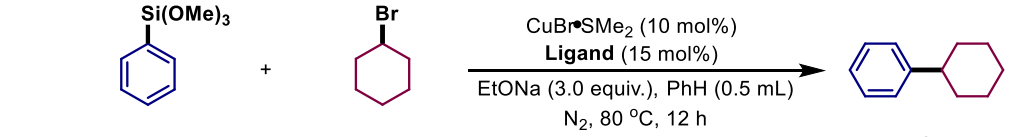
III. Optimization of Reaction Conditions

a) Evaluation of ligand effect

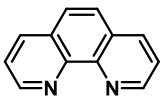
i) Preliminary screening of the ligand effect

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (8.2 mg, 0.04 mmol), the indicated ligand (0.06 mmol) and EtONa (82 mg, 1.20 mmol). Then, anhydrous benzene (0.50 mL) was added, followed by the addition of phenyl trimethoxysilane (160 mg, 0.80 mmol) and bromocyclohexane (65 mg, 0.40 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields were determined by GC analyses against *n*-hexadecane as a calibrated internal standard.

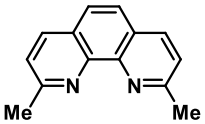
Table S1. Evaluation of ligand effect for the Cu-catalyzed Hiyama cross-couplings.



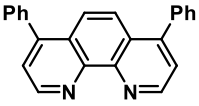
1 2 3



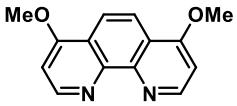
L1, 32%



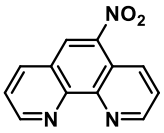
L2, <1%



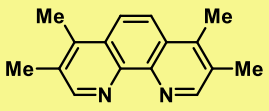
L3, 34%



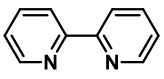
L4, 19%



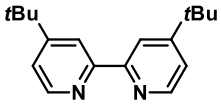
L5, <1%



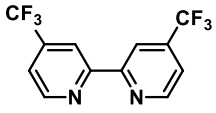
L6, 35%



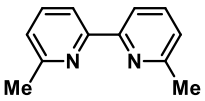
L7, 11%



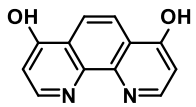
L8, 18%



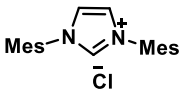
L9, 11%



L10, 6%

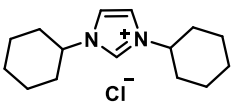


L11, 13%

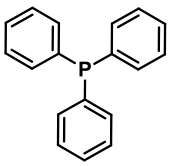


Mes = 2,4,6-$Me_3C_6H_2$

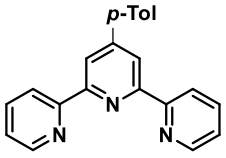
NHC-1, ＜1%



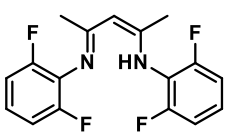
NHC-5, <1 %



L12, <1 %



L13, 6%

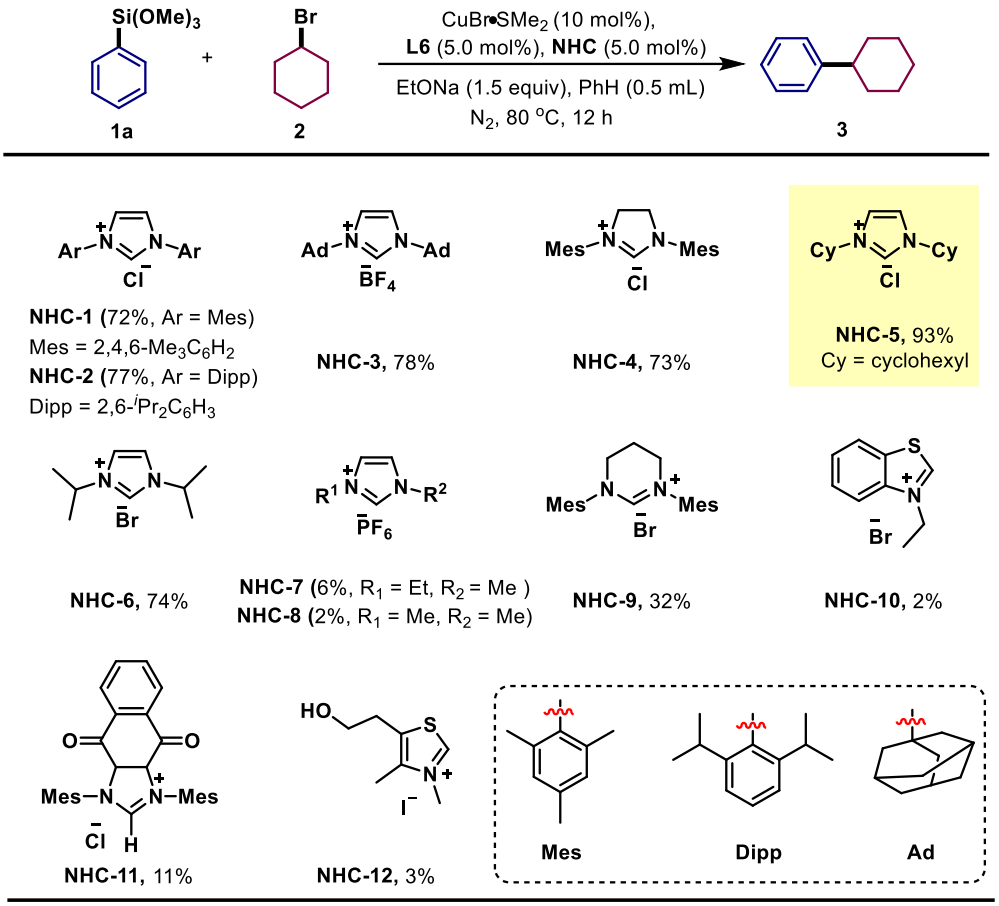


L14, 1%

ii) Evaluation of NHC ligand effect in Me_4Phen-Cu catalysis

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (8.2 mg, 0.04 mmol), ligand **L6** (4.8 mg, 0.02 mmol), the indicated **NHC** ligand (0.02 mmol) and EtONa (82 mg, 1.20 mmol). Then, anhydrous benzene (0.50 mL) was added, followed by the addition of phenyl trimethoxysilane (160 mg, 0.80 mmol) and bromocyclohexane (65 mg, 0.40 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields were determined by GC analyses against *n*-hexadecane as a calibrated internal standard.

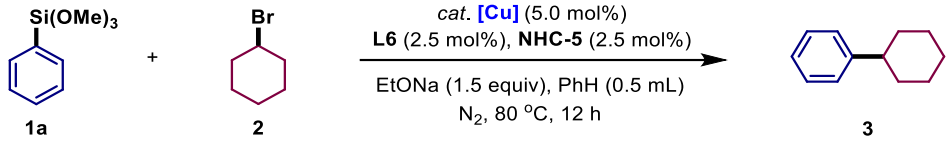
Table S2. Evaluation of NHC ligand effect for the Cu-catalyzed Hiyama cross-couplings.



b) Evaluation of copper catalyst effect

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the indicated copper catalyst (0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added, followed by the addition of phenyl trimethoxysilane (160 mg, 0.80 mmol) and bromocyclohexane (65 mg, 0.40 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields were determined by GC analyses against *n*-hexadecane as a calibrated internal standard.

Table S3. Evaluation of the copper catalyst effect for the Cu-catalyzed Hiyama cross-couplings.



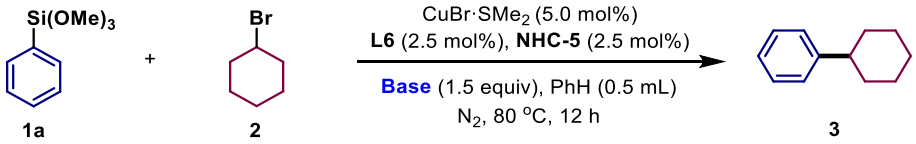
1a 2 3

Entry	*cat.* **[Cu]**	Yield (%)
1	$CuBr•SMe_2$	90
2	CuBr	78
3	CuCl	38
4	$CuBr_2$	＜1
5	CuI	57
6	$Cu(acac)_2$	85
7	CuTc	75
8	CuOTf	42

c) Evaluation of base effect

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and the indicated base (0.60 mmol). Then, anhydrous benzene (0.50 mL) was added, followed by the addition of phenyl trimethoxysilane (160 mg, 0.80 mmol) and bromocyclohexane (65 mg, 0.40 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields were determined by GC analyses against *n*-hexadecane as a calibrated internal standard.

Table S4. Evaluation of base effect for the Cu-catalyzed Hiyama cross-couplings.



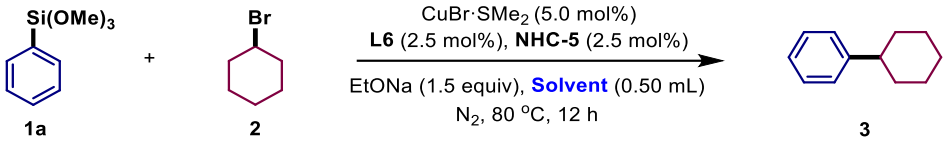
Entry	Base	Yield (%)
1	EtONa	90
2[a]	EtONa	54
3[b]	EtONa	70
4[c]	EtONa	88
5	*t*BuONa	72
6	*t*BuOK	28
7	MeONa	89
8	MeOK	36
9	MeOLi	<1
10	Na_2CO_3	<1
11	K_2CO_3	<1
12	$(Me)_3SiOK$	<1
13	CsF	3

[a]EtONa (2.0 equiv). [b]EtONa (1.2 equiv). [c]EtONa (1.0 equiv).

d) Evaluation of solvent effect

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous solvent (0.50 mL) was added, followed by the addition of phenyl trimethoxysilane (160 mg, 0.80 mmol) and bromocyclohexane (65 mg, 0.40 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields were determined by GC analyses against *n*-hexadecane as a calibrated internal standard.

Table S5. Evaluation of solvent effect for the Cu-catalyzed Hiyama cross-couplings.

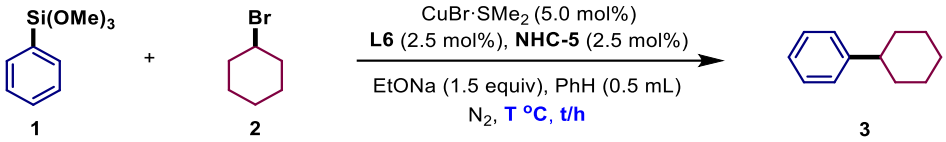


Entry	Solvent	Yield (%)
1	PhH	90
2	DCM	<1
3	Toluene	83
4	THF	23
5	*t*BuOMe	75
6	1,4-Dioxane	64
7	CyH	80
8	*n*-Hexane	42
9	DMSO	<1

e) Evaluation of reaction temperature and reaction time effect

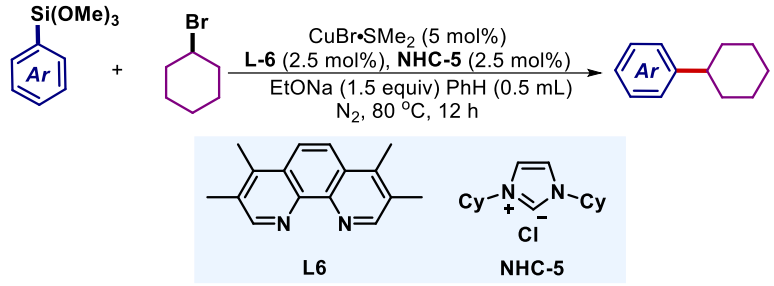
In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added, followed by the addition of phenyl trimethoxysilane (160 mg, 0.80 mmol) and bromocyclohexane (65.2 mg, 0.40 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at the indicated temperature over a certain time. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields were determined by GC analyses against *n*-hexadecane as a calibrated internal standard.

Table S6. Evaluation of reaction temperature and reaction time effect for the Cu-catalyzed Hiyama cross-couplings.



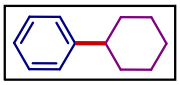
Entry	T/°C	t/h	Yield (%)[b]
1	RT	12	＜1
2	40 °C	12	＜1
3	60 °C	12	45
4	80 °C	12	90
5	100 °C	12	71
6	80 °C	1	3
7	80 °C	3	83
8	80 °C	6	89
9	80 °C	12	90

V. Substrate Scope of Arylsilanes



In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added, and followed by the addition of bromocyclohexane (65 mg, 0.40 mmol) and the corresponding arylsilane (0.80 mmol). The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction solution was cooled to room temperature, passed through a pad of silica gel with dichloromethane, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired products.

Cyclohexylbenzene (Table 2, 3)

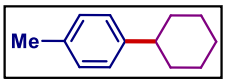


Column chromatography (petroleum ether) afforded colorless oil (89%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.19 – 7.12 (m, 3H), 2.68 – 2.63 (m, 1H), 1.92 – 1.76 (m, 5H), 1.47 – 1.23 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$): 143.05, 128.21, 126.82, 125.74, 44.63, 34.52, 26.89, 26.24.

The spectral data is similar to that previously reported in the literature.[6b]

1-Cyclohexyl-4-methylbenzene (Table 2, 4)

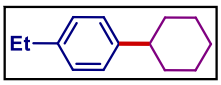


Column chromatography (petroleum ether) afforded colorless oil (90%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.2 Hz, 4H), 2.51 – 2.44 (m, 1H), 2.33 (s, 3H), 1.89 – 1.74 (m, 5H), 1.47 – 1.30 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.20, 135.22, 129.00, 126.73, 44.20, 34.62, 26.99, 26.23, 21.03.

The spectral data is similar to that previously reported in the literature.[6a]

1-Cyclohexyl-4-ethylbenzene (Table 2, 5)

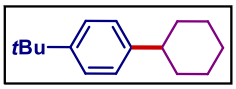


Column chromatography (petroleum ether) afforded colorless oil (89%). R_f = 0.6 (petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (s, 4H), 2.65 – 2.59 (m, 2H), 2.51 – 2.43 (m, 1H), 1.88 – 1.73 (m, 5H), 1.46 – 1.28 (m, 5H), 1.23 (t, J = 7.6 Hz, 3H).^{13}C NMR (400 MHz, $CDCl_3$) δ 145.42, 141.60, 127.79, 126.78, 44.22, 34.62, 28.46, 27.02, 26.26, 15.63.

The spectral data is similar to that previously reported in the literature.[7]

1-(*t*ert-Butyl)-4-cyclohexylbenzene (Table 2, 6)

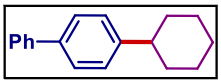


Column chromatography (petroleum ether) afforded colorless oil (81%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 2.55 – 2.47 (m, 1H), 1.95 – 1.73 (m, 5H), 1.51 – 1.37 (m, 4H), 1.35 (s, 9H), 1.28 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.42, 145.05, 126.43, 125.14, 43.99, 34.50, 34.35, 31.45, 26.98, 26.23.

The spectral data is similar to that previously reported in the literature.[11]

4-Cyclohexyl-1,1'-biphenyl (Table 2, 7)

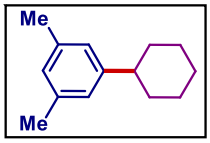


Column chromatography (petroleum ether) afforded white solid (64%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 4H), 7.47 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 2.59 – 2.53 (m, 1H), 1.94 – 1.76 (m, 5H), 1.52 – 1.29 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.27, 141.20, 138.74, 128.71, 127.27, 127.06, 127.05, 126.96, 44.26, 34.49, 26.94, 26.19.

The spectral data is similar to that previously reported in the literature.[6a]

1-Cyclohexyl-3,5-dimethylbenzene (Table 2, 8)

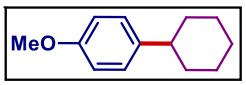


Column chromatography (petroleum ether) afforded colorless oil (86%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87-6.82 (m, 3H), 2.46 – 2.39 (m, 1H), 2.30 (s, 6H), 1.87 – 1.68 (m, 5H), 1.46 – 1.28 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.19, 137.73, 127.51, 124.73, 44.59, 34.56, 27.02, 26.27, 21.43.

The spectral data is similar to that previously reported in the literature.[8]

1-Cyclohexyl-4-methoxybenzene (Table 2, 9)

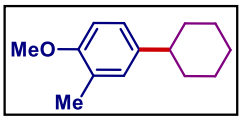


Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6**, 5.0 mol% **NHC-5**. Column chromatography (petroleum ether/ethyl acetate = 10:1) afforded white solid (78%). R_f = 0.75 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.49 – 2.41 (m, 1H), 1.87 – 1.73 (m, 5H), 1.41 – 1.22 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.64, 140.41, 127.66, 113.65, 55.26, 43.71, 34.75, 26.99, 26.20.

The spectral data is similar to that previously reported in the literature.[6]

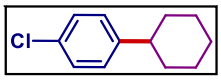
4-Cyclohexyl-1-methoxy-2-methylbenzene (Table 2, 10)



Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6**, 5.0 mol% **NHC-5**. Column chromatography (petroleum ether/ethyl acetate = 10:1) afforded white solid (72%). R_f = 0.75 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 6.4 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 1H), 3.82 (s, 3H), 2.46 – 2.38 (m, 1H), 2.22 (s, 3H), 1.87 – 1.72 (m, 5H), 1.45 – 1.31 (m, 5H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 155.88, 140.05, 129.31, 126.26, 124.67, 109.82, 55.36, 43.79, 34.83, 27.05, 26.27, 16.39. HRMS (EI) calcd. for $C_{14}H_{20}O$ $[M]^+$: 204.1509, found: 204.1507.

1-Chloro-4-cyclohexylbenzene (Table 2, 12)

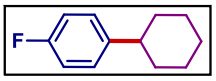


Column chromatography (petroleum ether) afforded colorless oil (77%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.50 – 2.43 (m, 1H), 1.86 – 1.72 (m, 5H), 1.37 (td, *J* = 9.0, 3.0 Hz, 4H), 1.29 – 1.21 (m, 1H, overlap). ^{13}C NMR (400 MHz, $CDCl_3$) δ 146.88, 128.45, 126.89, 126.17, 59.25, 43.71, 34.26, 27.70.

The spectral data is similar to that previously reported in the literature.[8]

1-Cyclohexyl-4-fluorobenzene (Table 2, 13)

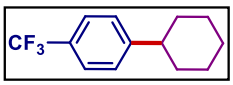


Column chromatography (petroleum ether) afforded colorless oil (35%), R_f = 0.6 (petroleum ether). The NMR yield of the crude mixture is 71% using 1,4-dioxane as the internal standard.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.5, 5.7 Hz, 2H), 6.97 (t, *J* = 8.8 Hz, 2H), 2.53 – 2.42 (m, 1H), 1.86 – 1.81 (m, 4H), 1.78 – 1.72 (m, 1H), 1.43 – 1.33 (m, 4H), 1.29 – 1.22 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 161.11 (d, *J* = 968 Hz), 143.74 (d, *J* = 8 Hz), 128.07 (d, *J* = 28 Hz), 114.91 (d, *J* = 84 Hz), 43.85, 34.66, 26.87, 26.10.

The spectral data is similar to that previously reported in the literature.[9]

1-Cyclohexyl-4-(trifluoromethyl)benzene (Table 2, 14)

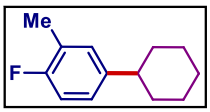


Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6,** 5.0 mol% **NHC-5**. Column chromatography (petroleum ether) afforded colorless oil (22%). R_f = 0.6 (petroleum ether). The NMR yield of the crude mixture is 50% using 1,4-dioxane as the internal standard.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.56 (m, 1H), 1.90 – 1.84 (m, 4H), 1.79 – 1.75 (m, 1H), 1.45 – 1.35 (m, 4H), 1.29 – 1.24 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 152.04, 128.16, 127.32, 125.20, 124.58, 44.51, 34.21, 26.74, 26.02.

The spectral data is similar to that previously reported in the literature.[8]

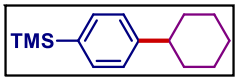
4-Cyclohexyl-1-fluoro-2-methylbenzene (Table 2, 15)



Column chromatography (petroleum ether) afforded colorless oil (64%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.88 (m, 3H), 2.47 – 2.41 (m, 1H), 2.25 (s, 3H), 1.88 – 1.72 (m, 5H), 1.44 – 1.28 (m, 5H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 160.47, 158.87, 143.53, 129.76, 125.29, 114.65, 43.90, 34.72, 26.94, 26.16, 14.67. HRMS (EI) calcd. for $C_{13}H_{17}F$ $[M]^+$: 192.1309, found: 192.1313.

(4-Cyclohexylphenyl)trimethylsilane (Table 2, 16)

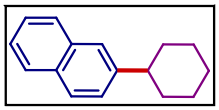


Column chromatography (petroleum ether) afforded colorless oil (74%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 2.51 – 2.45 (m, 1H), 1.89 – 1.72 (m, 5H), 1.48 – 1.33 (m, 5H), 0.25 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.61, 137.79, 133.39, 126.53, 44.59, 34.42, 27.02, 26.12, -1.05.

The spectral data is similar to that previously reported in the literature.[10]

2-Cyclohexylnaphthalene (Table 2, 17)

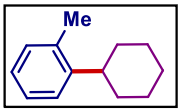


Column chromatography (petroleum ether) afforded colorless oil (82%). R_f = 0.25 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 3H), 7.65 (d, J = 1.7 Hz, 1H), 7.47 – 7.38 (m, 3H), 2.71 – 2.65 (m, 1H), 2.01 – 1.79 (m, 5H), 1.60 – 1.28 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.62, 133.71, 132.13, 127.93, 127.76, 127.64, 126.26, 125.88, 125.07, 124.56, 44.72, 34.47, 27.00, 26.28.

The spectral data is similar to that previously reported in the literature.[9]

1-Cyclohexyl-2-methylbenzene (Table 2, 18)

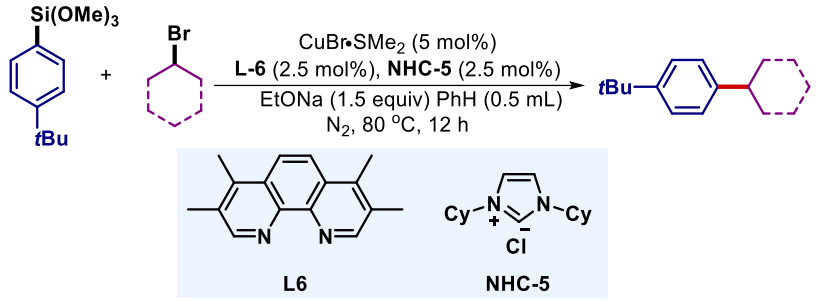


Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6,** 5.0 mol% **NHC-5**. Column chromatography (petroleum ether) afforded colorless oil (45%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 6.98 (m, 4H), 2.69 – 2.60 (m, 1H), 2.26 (s, 3H), 1.82 – 1.67 (m, 5H), 1.40 – 1.29 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.96, 135.16, 130.24, 126.14, 125.51, 125.41, 40.13, 33.70, 27.23, 26.40, 19.42.

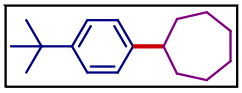
The spectral data is similar to that previously reported in the literature.[9]

IV. Substrate Scope of Alkyl Halides



In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, 4-*tert*-butylphenyltrimethoxysilane (203 mg, 0.80 mmol) and the corresponding alkyl bromides (0.40 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction solution was cooled to room temperature, passed through a pad of silica gel with dichloromethane, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired products.

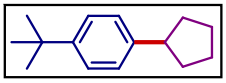
[4-(*tert*-Butyl)phenyl]cycloheptane (Table 3, 20)



Column chromatography (petroleum ether) afforded colorless oil (82%). R_f = 0.55 (petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 2.67 – 2.62 (m, 1H), 1.93 – 1.89 (m, 2H), 1.83 – 1.76 (m, 2H), 1.73 – 1.52 (m, 8H), 1.31 (s, 9H).
^{13}C NMR (400 MHz, $CDCl_3$) δ 145.61, 144.41, 123.75, 122.60, 43.90, 34.29, 31.78, 28.92, 25.47, 24.68.
The spectral data is similar to that previously reported in the literature.[11]

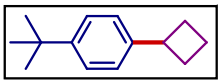
[1-(*tert*-Butyl)-4-cyclopentyl]benzene (Table 3, 21)



Column chromatography (petroleum ether) afforded colorless oil (78%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.06 – 2.93 (m, 1H), 2.16 – 2.03 (m, 2H), 1.88 – 1.78 (m, 2H), 1.78 – 1.56 (m, 4H), 1.35 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.41, 143.41, 126.77, 125.12, 45.49, 34.61, 34.36, 31.46, 25.51.
The spectral data is similar to that previously reported in the literature.[11]

[1-(*tert*-Butyl)-4-cyclobutyl]benzene (Table 3, 22)

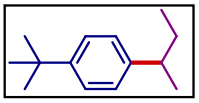


Column chromatography (petroleum ether) afforded colorless oil (83%). R_f = 0.55 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 3.55 (q, *J* = 8.8 Hz, 1H), 2.40 – 2.31 (m, 2H), 2.26 – 2.11 (m, 2H), 2.11 – 1.97 (m, 1H), 1.94 – 1.81 (m, 1H), 1.35 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.51, 143.27, 126.05, 125.12, 40.05, 34.41, 31.47, 29.94, 18.34.

The spectral data is similar to that previously reported in the literature.[11]

[1-(*sec*-Butyl)-4-(*tert*-butyl)]benzene (Table 3, 23)

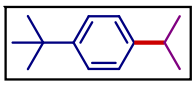


Column chromatography (petroleum ether) afforded colorless oil (61%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.64 – 2.55 (m, 1H), 1.61 (dq, *J* = 7.2, 2.9 Hz, 2H), 1.34 (s, 9H), 1.25 (d, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.33, 143.55, 125.58, 124.01, 40.01, 33.28, 30.40, 30.19, 20.64, 11.30.

The spectral data is similar to that previously reported in the literature.[20]

[1-(*tert*-Butyl)-4-isopropyl]benzene (Table 3, 24)

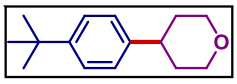


Column chromatography (petroleum ether) afforded colorless oil (55%). R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 2.97 – 2.85 (m, 1H), 1.35 (s, 9H), 1.29 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.60, 145.89, 126.21, 125.32, 34.49, 33.70, 31.63, 24.21.

The spectral data is similar to that previously reported in the literature.[21]

[1-(*tert*-Butyl)-4-isopropyl]benzene (Table 3, 25)

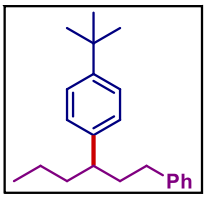


Column chromatography (petroleum ether) afforded colorless oil (50%). R_f = 0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.25 – 7.15 (m, 2H), 4.23 – 4.02 (m, 2H), 3.56 (td, J = 11.5, 2.9 Hz, 2H), 2.89 – 2.65 (m, 1H), 1.97 – 1.76 (m, 4H), 1.35 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 149.10, 142.85, 126.39, 125.41, 68.50, 41.00, 34.41, 33.98, 31.42.

The spectral data is similar to that previously reported in the literature.[11]

[1-(*tert*-Butyl)-4-(1-phenylhexan-3-yl)]benzene (Table 3, 26)

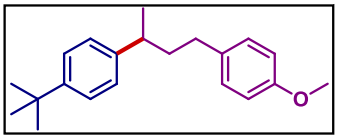


Column chromatography (petroleum ether) afforded colorless oil (70%). R_f = 0.4 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.30 – 7.21 (m, 2H), 7.21 – 7.06 (m, 5H), 2.54 (m, 1H), 2.51– 2.42 (m, 2H), 2.02 – 1.81 (m, 2H), 1.69 – 1.52 (m, 2H), 1.34 (s, 9H), 1.24 – 1.12 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.5, 141.7, 141.5, 127.3, 127.1, 126.2, 124.5, 124.0, 43.7, 38.3, 37.5, 33.3, 32.9, 30.4, 19.6, 13.1.

The spectral data is similar to that previously reported in the literature.[3]

[1-(5-Bromohexan-2-yl)-4-(*tert*-butyl)]benzene (Table 3, 27)

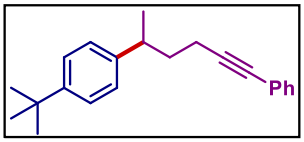


Column chromatography (petroleum ether) afforded colorless oil (66%). R_f = 0.2 (petroleum ether/Et_2O = 150:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.76 – 2.65 (m, 1H), 2.49 (m, 2H), 1.98 – 1.79 (m, 2H), 1.34 (s, 9H), 1.28 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.68, 148.63, 144.34, 134.78, 129.32, 126.73, 125.28, 113.73, 55.28, 40.34, 38.90, 34.43, 33.10, 31.54, 22.51.

The spectral data is similar to that previously reported in the literature.[3]

[1-(*tert*-Butyl)-4-(6-phenylhex-5-yn-2-yl)]benzene (Table 3, 28)

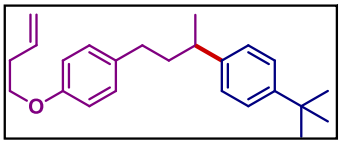


Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6,** 5.0 mol% **NHC-5**. Column chromatography (petroleum ether) afforded colorless oil (51%). R_f = 0.45 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 5.2, 2.1 Hz, 3H), 7.17 (d, *J* = 8.3 Hz, 2H), 2.97 – 2.86 (m, 1H), 2.39 – 2.22 (m, 2H), 1.94 – 1.83 (m, 2H), 1.33 (s, 9H), 1.31 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.74, 142.28, 130.49, 127.13, 126.43, 125.64, 124.21, 123.04, 89.14, 79.78, 37.33, 36.25, 33.30, 30.38, 20.89, 16.70.

The spectral data is similar to that previously reported in the literature.[3]

[1-(But-3-en-1-yloxy)-4-{2-[4-(*tert*-butyl)phenyl]propyl}benzene (Table 3, 29)



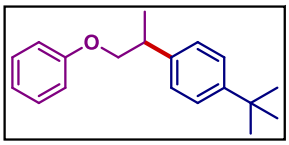
Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6,** 5.0 mol% **NHC-5**. Column chromatography (petroleum ether) afforded colorless oil (57%). R_f = 0.21 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.93 (m, 1H), 5.19 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.12 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.01 (t, *J* = 6.7 Hz, 2H), 2.76 – 2.65 (m, 1H), 2.52 (m, 4H), 1.98 – 1.80 (m, 2H), 1.34 (s, 9H), 1.28 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.05, 148.64,

144.36, 134.85, 134.67, 129.32, 126.75, 125.29, 117.01, 114.49, 67.31, 40.35, 38.93, 34.44, 33.84, 33.14, 31.57, 22.51.

The spectral data is similar to that previously reported in the literature.[3]

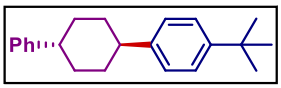
[1-(*tert*-Butyl)-4-(1-phenoxypropan-2-yl)]benzene (Table 3, 30)



Using a modified method with 10 mol% CuBr•SMe_2 and 5.0 mol% **L6,** 5.0 mol% **NHC-5**. Column chromatography (petroleum ether) afforded colorless oil (39%). R_f = 0.54 (petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.29 – 7.23 (m, 4H), 6.95 – 6.90 (m, 3H), 4.10 (dd, *J* = 9.1, 5.5 Hz, 1H), 3.94 (t, *J* = 8.6 Hz, 1H), 3.26 – 3.20 (m, 1H), 1.42 (d, *J* = 6.9 Hz, 3H), 1.33 (s, 9H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 159.03, 149.40, 140.54, 129.44, 127.09, 125.39, 120.62, 114.64, 73.49, 39.04, 34.44, 31.42, 18.17. HRMS (ESI) calcd. for $C_{19}H_{25}O$ $[M+H]^+$: 269.1900, found: 269.1904.

[1-(*tert*-Butyl)-4-(4-(4-methoxyphenyl)butyl)]benzene (Table 3, 31)

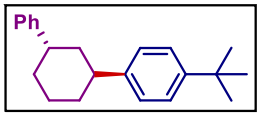


Column chromatography (petroleum ether) afforded white solid (64%). The diastereomeric ratio was 20:1 determined to be by NMR analyses. R_f = 0.3 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 14.0, 7.8 Hz, 4H), 7.27 (d, *J* = 6.1 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 3H), 2.70 – 2.51 (m, 2H), 2.09 – 1.99 (m, 4H), 1.64 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.68, 147.58, 144.41, 128.41, 126.91, 126.50, 125.99, 125.27, 44.12, 43.46, 34.64, 34.60, 34.42, 31.49.

The spectral data is similar to that previously reported in the literature.[3]

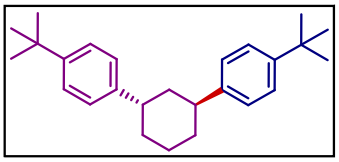
[1-(*tert*-Butyl)-4-(4-(4-methoxyphenyl)butyl)]benzene (Table 3, 32)



Column chromatography (petroleum ether) afforded white solid (55%). The diastereomeric ratio was determined to be 22:1 by NMR analyses. R_f = 0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 15.3, 7.8 Hz, 4H), 7.27 – 7.23 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 3H), 2.72 (m, 2H), 2.20 – 1.92 (m, 4H), 1.68 – 1.45 (m, 4H), 1.32 (s, 9H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 148.67, 147.38, 144.24, 128.35, 126.86, 126.44, 125.94, 125.23, 44.70, 44.06, 42.07, 34.38, 33.87, 33.74, 31.45, 27.02. HRMS (EI) calcd. for $C_{22}H_{28}$ $[M]^+$: 292.2186, found: 292.2190.

[1-(*tert*-Butyl)-4-(4-(4-methoxyphenyl)butyl)]benzene (Table 3, 33)

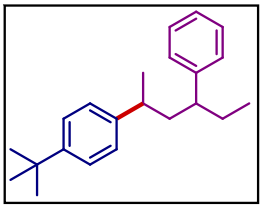


Column chromatography (petroleum ether) afforded white solid (60%). The diastereomeric ratio was determined to be 50:1 by NMR analyses. R_f = 0.55 (petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 4H), 2.72 – 2.66 (m, 2H), 2.25 – 1.79 (m, 5H), 1.51 – 1.36 (m, 3H), 1.30 (s, 18H). ^{13}C NMR (600

MHz, $CDCl_3$) δ 148.61, 144.30, 126.43, 125.18, 44.04, 42.09, 34.36, 33.79, 31.47, 31.44, 30.21, 27.03. HRMS (EI) calcd. for $C_{26}H_{36}$ $[M]^+$: 348.2812, found: 348.2813.

[1-(*tert*-Butyl)-4-(4-(4-methoxyphenyl)butyl)]benzene (Table 3, 34)

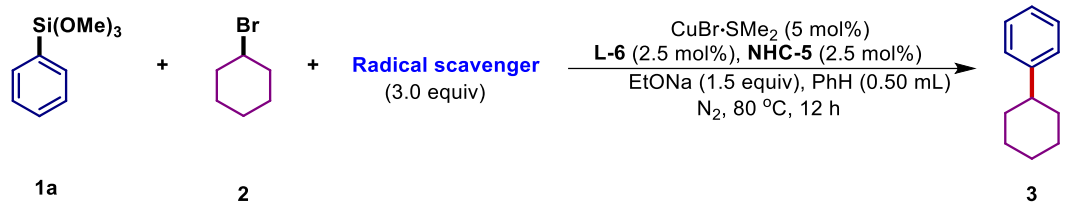


Column chromatography (petroleum ether) afforded colorless oil (65%). The diastereomeric ratio was determined to be 8:1 by NMR analyses. R_f = 0.55 (petroleum ether).

major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H, overlap), 7.20 (d, *J* = 7.3 Hz, 1H, overlap), 7.15 – 7.12 (m, 2H, overlap), 7.03 (d, *J* = 8.2 Hz, 2H, overlap), 2.50 (m, 2H, overlap), 1.85 (ddd, *J* = 24.1, 9.2, 5.2 Hz, 2H, overlap), 1.71 – 1.61 (m, 2H, overlap), 1.30 (s, 9H, overlap), 1.20 (d, *J* = 6.9 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 148.42 (overlap), 145.49, 145.22, 128.27, 127.80, 126.40, 125.89, 125.14 (overlap), 45.35, 36.28, 34.33 (overlap), 31.44, 30.16, 29.69, 20.99 (overlap), 12.11. minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H, overlap), 7.20 (d, *J* = 7.3 Hz, 1H, overlap), 7.15 – 7.12 (m, 2H, overlap), 7.03 (d, *J* = 8.2 Hz, 2H, overlap), 2.50 (m, 2H, overlap), 1.85 (ddd, *J* = 24.1, 9.2, 5.2 Hz, 2H, overlap), 1.71 – 1.61 (m, 2H, overlap), 1.30 (s, 9H, overlap), 1.13 (d, *J* = 6.9 Hz, 3H), 0.67 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 148.42 (overlap), 145.77, 144.12, 128.17, 128.04, 126.83, 125.83, 125.14 (overlap), 45.29, 37.00, 34.33 (overlap), 31.49, 30.22, 29.73, 20.99 (overlap), 12.02. HRMS (EI) calcd. for $C_{22}H_{30}$ $[M]^+$: 294.2343, found 294.2341.

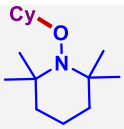
VII. Mechanistic Investigations

a) Influence of the Radical Scavenger

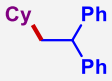


1a 2 3

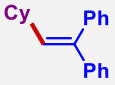
	Yield of **3**	Yield of **Radical Adduct**
standard conditions	90%	—
w **TEMPO**	<1%	**35** (58%)
w **1,1-Diphenylethylene**	6%	**36** (29%) **and 37** (4%)



35



36

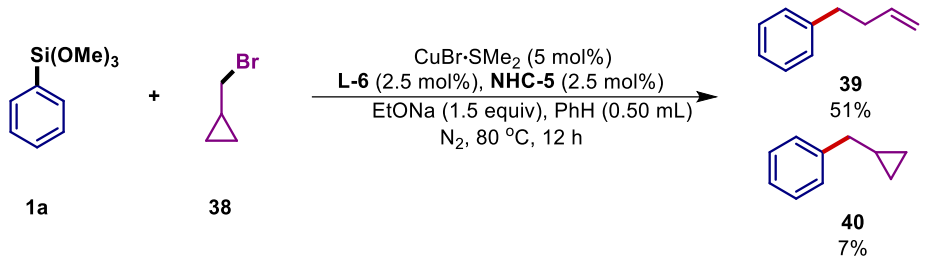


37

In the glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65 mg, 0.40 mmol) and phenyl trimethoxysilane (160 mg, 0.80 mmol) were added. Then, radical scavenger **TEMPO** (187 mg, 1.20 mmol) were added to the solution. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction solution was cooled to room temperature, passed through a pad of silica gel with dichloromethane, and the solvent was removed under reduced pressure. The crude yield of **3** was measured to be <1% by using NMR spectroscopy with 1,4-dioxane as an internal standard, while the scavenger was observed to form cyclohexyl-substituted TEMPO (**35**) in 58% NMR yield.

The same reactions were repeated in the presence of 1,1-diphenylethene (216 mg, 1.20 mmol) under otherwise identical conditions which revealed that the crude NMR yields of the alkylation product **3** were 6% with 1,4-dioxane as an internal standard, and the scavenger was observed to form (2-cyclohexylethane-1,1-diyl)dibenzene (**36**) and (2-cyclohexylethene-1,1-diyl)dibenzene (**37**) in 29% and 4% NMR yields, respectively.

b) Radical Clock Experiment



In the glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.1 mg, 0.02 mmol), **L6** (2.4 mg, 0.01 mmol), **NHC-5** (2.7 mg, 0.01 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, (bromomethyl)cyclopropane (54 mg, 0.40 mmol) and phenyl trimethoxysilane (160 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction solution was cooled to room temperature, passed through a pad of silica gel with dichloromethane, and the solvent was removed under reduced pressure. The crude yield of **39** was measured to be 51 % by using NMR spectroscopy with 1,4-dioxane as an internal standard, while the other produt of **40** was observed in 7% NMR yield.

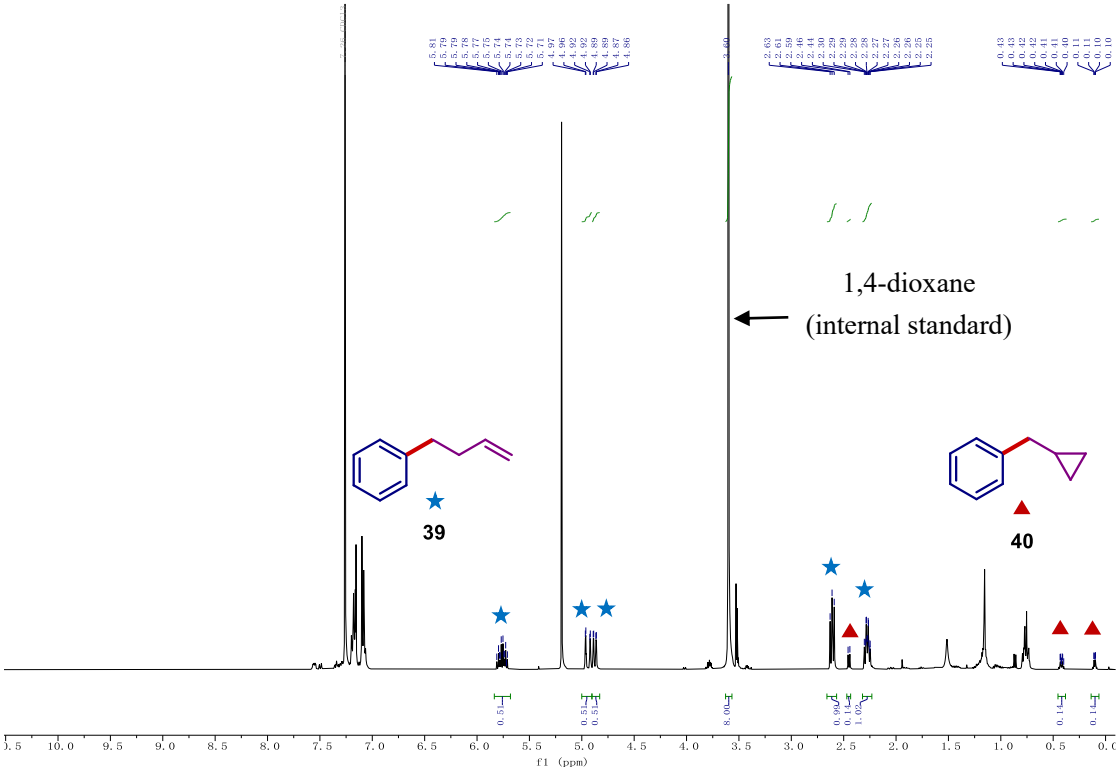


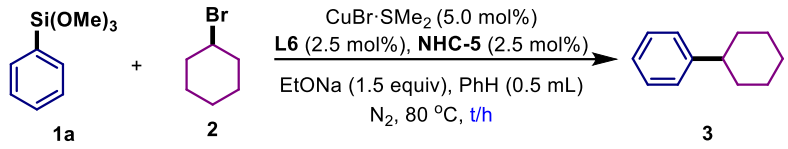
Fig. S1.[1]H NMR Spectrum of the products **39** and **40** in the radical clock experiment.

c) Comparison of the reaction course of L6 and multiligands

In the glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.0 mg, 0.02 mmol), the indicated ligand (0.02 mmol) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65 mg, 0.40 mmol) and phenyl trimethoxysilane (160 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for the indicated reaction time. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **3** was measured by GC analyses against *n*-hexadecane as a calibrated internal standard.

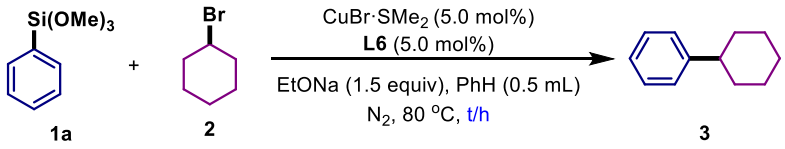
*Notably, the reactions were also repeated with **NHC-5** alone as the ligand under otherwise identical conditions, the yields of **3** to be <1%, measured by GC analyses against n-hexadecane as a calibrated internal standard.*

Table S7. The reaction course of multiligands



Entry	t/h	Yield of **3** (%)
1	1	0
2	2	4
3	3	17
4	4	89
5	5	90
6	6	90

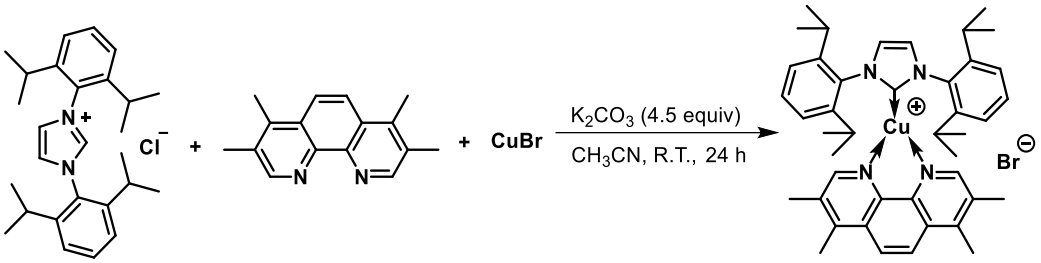
Table S8. The reaction course of L6



Entry	t/h	Yield of **3** (%)
1	1	0
2	2	2
3	3	5
4	4	5
5	5	15
6	6	18

d) Catalytic Reaction with Copper Complexes

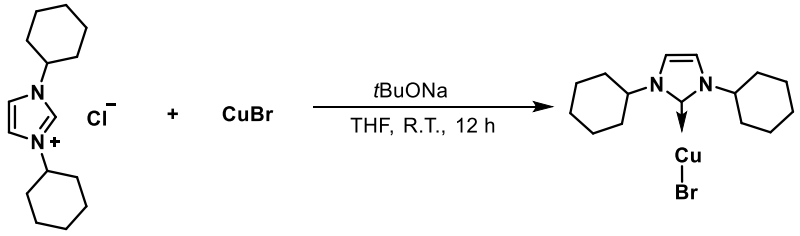
Preparation of Copper Complexes Cu-1



Following the reported procedures,[15] in a glove box, to an oven-dried flask equipped with a stir bar were added CuBr (142 mg, 1.0 mmol, 1.0 equiv), ligand **L6** (283 mg, 1.2 mmol, 1.2 equiv), K_2CO_3 (621 mg, 4.5 mmol, 4.5 equiv), ligand **NHC-2** (424 mg, 1.0 mmol, 1.0 equiv) in CH_3CN (20 mL). The mixture was stirred for 24 h at room temperature. The solution was filtered off. The precipitate was washed with dichloromethane, evaporated in reduced pressure. The precipitate obtained as yellow powder (460 mg, 60%). The single crystals of complex **Cu-1** were grown by slow cooling of the toluene solution. X-Ray crystallographic data are in *Appendix I.*

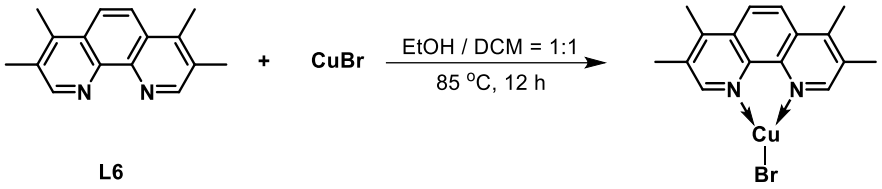
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.78 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 4H), 7.41 (s, 2H), 6.58 (s, 2H), 2.74 – 2.67 (m, 4H, overlap), 2.68 (s, 6H, overlap), 2.33 (s, 6H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.08 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 183.45, 150.44, 146.63, 145.68, 142.28, 136.15, 133.17, 130.68, 127.15, 124.54, 123.54, 122.93, 28.86, 25.12, 23.66, 17.54, 15.01. Elem. Anal.: calcd. for [(**Cu-1**)•$(CH_3CN)_2$] $C_{47}H_{59}BrCuN_6$: C: 66.22%, H: 7.09%, N: 9.86%, found: C: 66.00%, H: 7.02%, N: 9.58%.

Preparation of Copper Complexes Cu-2



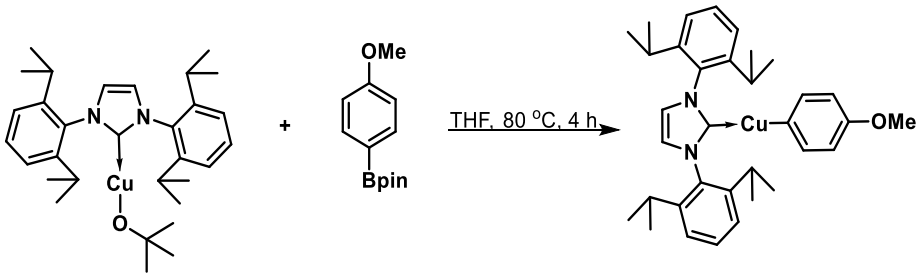
Following the reported procedures,[16] in the glove box, to an oven-dried flask equipped with a stir bar were added CuBr (781 mg, 5.5 mmol, 1.1 equiv), *t*BuONa (781 mg, 5.5 mmol, 1.1 equiv) and THF (20 mL). The mixture was stirred for 12 h at room temperature. The reaction solution was filtered through diatomite and concentrated under reduced pressure. Then, the obtained product was recrystallized in THF/*n*-hexane to afford white solid (1.31 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 4.31 – 4.23 (m, 2H), 2.10 – 2.05 (m, 4H), 1.90 – 1.84 (m, 4H), 1.76 – 1.61 (m, 6H), 1.50 – 1.38 (m, 4H), 1.27 – 1.16 (m, 2H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 174.78, 117.42, 61.19, 34.79, 25.42, 25.10. Elem. Anal.: calcd. for (**Cu-2**) $C_{15}H_{25}BrCuN_2$: C: 47.68%, H: 6.94%, N: 7.41%, found: C: 47.06%, H: 6.19%, N: 6.94%.

Preparation of Copper Complexes Cu-3



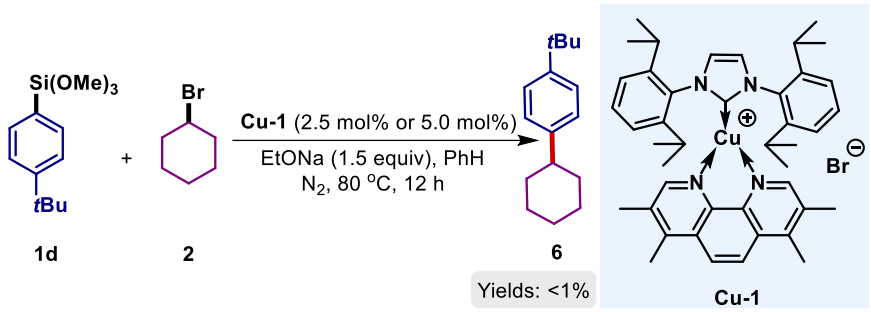
Following the reported procedures,[17] in the glove box, to an oven-dried flask equipped with a stir bar were added CuBr (284 mg, 2.0 mmol, 1.0 equiv) and ethanol (20 mL) under nitrogen atmosphere. Next, ligand **L6** (472 mg, 2.0 mmol, 1.0 equiv) in DCM (20 mL) was added to the above solution. The reaction vial was sealed and taken out of the glove box, and stirred at 85 °C for 12 h and then cooled to room temperature. The solution was filtered off. The precipitate was washed with dichloromethane, evaporated in vacuo to give the orange solid. (529 mg, 70 %) ^{1}H NMR (600 MHz, Pyridine-d_5) δ 9.07 (s, 2H), 8.17 (s, 2H), 2.46 (s, 6H), 2.32 (s, 6H). Elem. Anal.: calcd. for **Cu-3**, $C_{16}H_{16}BrCuN_2$: C: 50.60%, H: 4.25%, N: 7.38%, found: C: 50.08%, H: 3.92%, N: 7.11%.

Preparation of Copper Complexes Cu-4



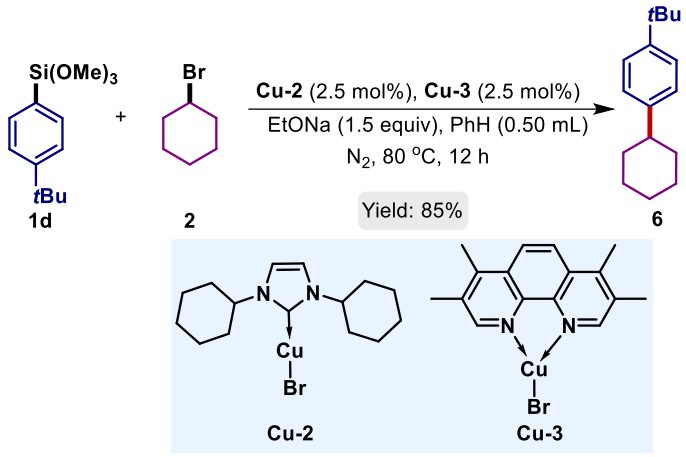
Following the reported procedures,[18] in the glove box, 4-methoxybenzeneboronic acid, pinacol ester (468 mg, 4.0 mmol, 2.0 equiv) was added to a solution of [(IPr)Cu(O^{t}Bu)] [prepared from [(IPr)CuCl] and ^{t}BuOK by stirring at room temperature for 12 h.] (1.05 g, 2.0 mmol, 1.0 equiv) in THF (8.0 mL) at 80 °C. The reaction mixture was stirred for 4 h, and then the volatiles were removed under reduced pressure. The resulting white solid was washed with dry *n*-hexane, dried under reduced pressure to give complex **Cu-4** as white solid in 50 % yield (559 mg). ^{1}H NMR (600 MHz, C_6D_6) δ 7.55 (d, J = 6.7 Hz, 2H), 7.24 (t, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 4H), 6.89 (ddd, J = 8.4, 3.7, 1.9 Hz, 2H), 6.31 (d, J = 4.1 Hz, 2H), 3.38 (s, 3H), 2.66 (m, 4H), 1.43 (d, J = 6.9 Hz, 12H), 1.11 (d, J = 6.9 Hz, 12H).
The spectral data is similar to that previously reported in the literature.

e) Evaluation of the catalytic activity of copper complexes

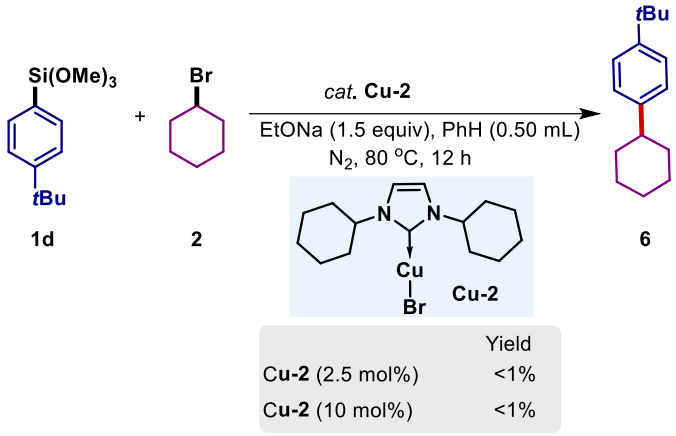


In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the copper complex **Cu-1** (7.7 mg, 0.01 mmol, 2.5 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added, followed by the addition of bromocyclohexane (65 mg, 0.40 mmol) and 4-*tert*-butylphenyltrimethoxysilane (203 mg, 0.80 mmol). The reaction vial was sealed and taken out of the glove box. The reaction was further stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **6** was measured to be **<1%** by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with 5.0 mol% of the complex **Cu-1** (15.4 mg, 0.02 mmol) as the catalyst under otherwise identical conditions, and the yield of **6** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.



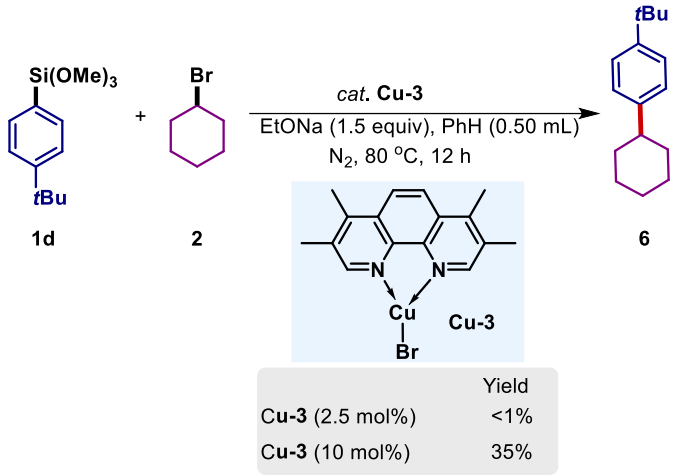
In a glove box, to an oven-dried screw capped vial charged with a stir bar were added complex **Cu-2** (3.8 mg, 0.01 mmol, 2.5 mol%)**,** complex **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and 4-*tert*-butylphenyltrimethoxysilane (203 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **6** was measured to be 85% by NMR analyses against 1,4-dioxane as a calibrated internal standard.



	Yield
Cu-2 (2.5 mol%)	<1%
Cu-2 (10 mol%)	<1%

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added complex **Cu-2** (3.8 mg, 0.01 mmol, 2.5 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and 4-*tert*-butylphenyltrimethoxysilane (203 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **6** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

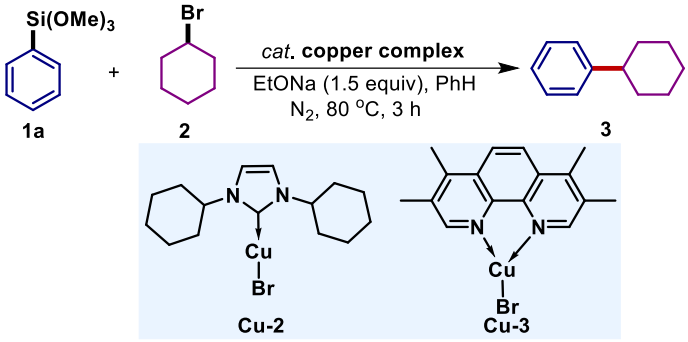
The reaction was repeated with 10 mol% of the complex **Cu-2** (15.2 mg, 0.04 mmol) as the catalyst under otherwise identical conditions, and the yield of **6** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.



In ta glove box, to an oven-dried screw capped vial charged with a stir bar were added complex **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and 4-*tert*-butylphenyltrimethoxysilane (203 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **6** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with 10 mol% of the complex **Cu-3** (15.2 mg, 0.04 mmol) as the catalyst under otherwise identical conditions, and the yield of **6** was measured to be 35% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

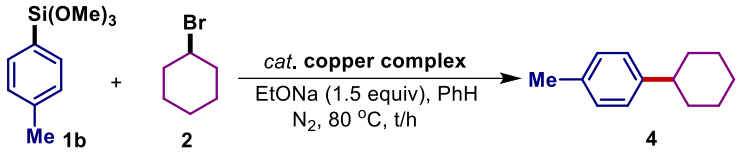
f) Comparation the catalytic activity of copper complexes with arysilanes

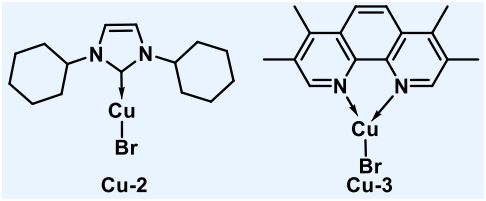


	Yield
Cu-2 (2.5 mol%) + **Cu-3** (2.5 mol%)	41%
Cu-3 (2.5 mol%)	5%

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the complexes of **Cu-2** (3.8 mg, 0.01 mmol, 2.5 mol%) and **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalysts. Then, EtONa (41 mg, 0.60 mmol) and anhydrous benzene (0.50 mL) were added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and phenyl trimethoxysilane (160 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 3 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **3** was measured to be 41% by GC analyses against *n*-hexadecane as a calibrated internal standard.

The reaction was repeated with **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalyst under otherwise identical conditions, and the yield of **3** was measured to be 5% by NMR analyses against 1,4-dioxane as a calibrated internal standard.





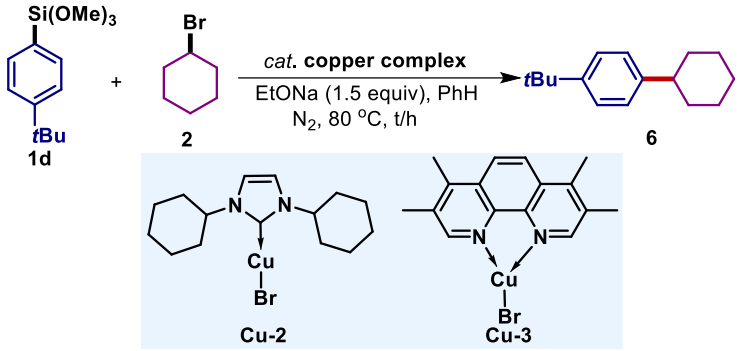
	Yield
Cu-2 (2.5 mol%) + **Cu-3** (2.5 mol%)	63% (3 h)
Cu-2 (2.5 mol%) + **Cu-3** (2.5 mol%)	92% (12 h)
Cu-3 (2.5 mol%)	9% (3 h)
Cu-3 (2.5 mol%)	14% (12 h)

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the complexes of **Cu-2** (3.8 mg, 0.01 mmol, 2.5 mol%) and **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalyst. Then, EtONa (41 mg, 0.60 mmol) and anhydrous benzene (0.50 mL) were added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and trimethoxy(*p*-tolyl)silane (170 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C in 3 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields of **4** was measured to be 63% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with an elongated reaction time of 12 h under otherwise identical conditions, and the yield of **4** was measured to be 92% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalyst in 3 h under otherwise identical conditions, and the yield of **4** was measured to be 9% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalyst in 12 h under otherwise identical conditions, and the yield of **4** was measured to be 14% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

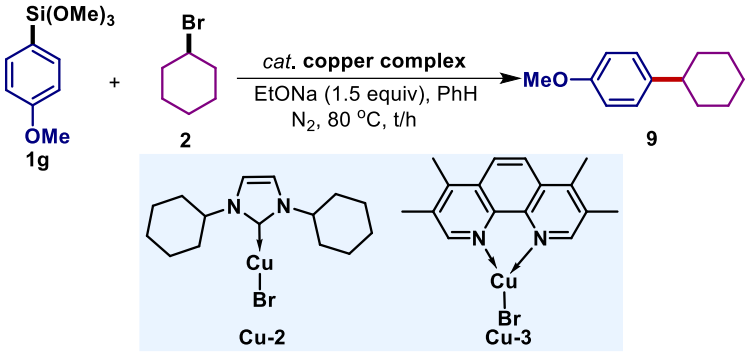


	Yield
Cu-2 (2.5 mol%) + **Cu-3** (2.5 mol%)	85%
Cu-3 (2.5 mol%)	<1%
Cu-3 (10 mol%)	35%

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the complexes of **Cu-2** (3.8 mg, 0.01 mmol, 2.5 mol%) and **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalysts. Then, EtONa (41 mg, 0.60 mmol) and anhydrous benzene (0.50 mL) were added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and 4-*tert*-butylphenyltrimethoxysilane (203 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **6** was measured to be 85% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with **Cu-3** (3.8 mg, 0.01 mmol, 2.5 mol%) as the catalyst under otherwise identical conditions, and the yield of **6** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

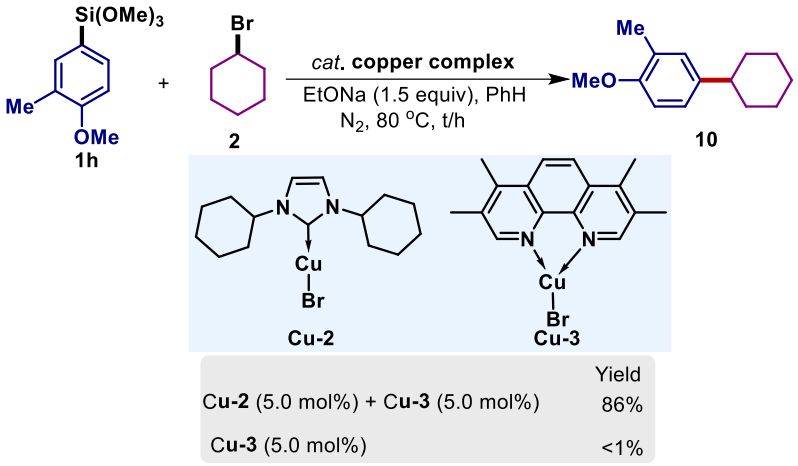
The reaction was repeated with **Cu-3** (15.2 mg, 0.04 mmol, 10 mol%) as the catalyst under otherwise identical conditions, and the yield of **6** was measured to be 35% by NMR analyses against 1,4-dioxane as a calibrated internal standard.



	Yield
Cu-2 (5.0 mol%) + **Cu-3** (5.0 mol%)	83%
Cu-3 (5.0 mol%)	18%

In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the complexes of **Cu-2** (7.6 mg, 0.02 mmol, 5.0 mol%) and **Cu-3** (7.6 mg, 0.02 mmol, 5.0 mol%) as the catalysts. Then, EtONa (41 mg, 0.60 mmol) and anhydrous benzene (0.50 mL) were added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and trimethoxy(4-methoxyphenyl)silane (182 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 ºC for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **9** was measured to be 83% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

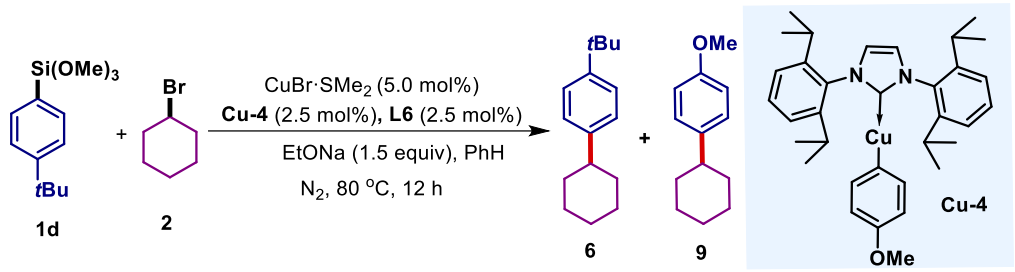
The reaction was repeated with **Cu-3** (7.6 mg, 0.02 mmol, 5.0 mol%) as the catalyst under otherwise identical conditions, and the yield of **9** was measured to be 18% by NMR analyses against 1,4-dioxane as a calibrated internal standard.



In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the complexes of **Cu-2** (7.6 mg, 0.02 mmol) and **Cu-3** (7.6 mg, 0.02 mmol) as the catalysts. Then, EtONa (41 mg, 0.60 mmol) and anhydrous benzene (0.50 mL) were added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and trimethoxy(4-methoxy-3-methylphenyl)silane (194 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **10** was measured to be 86% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with **Cu-3** (7.6 mg, 0.02 mmol, 5.0 mol%) as the catalyst under otherwise identical conditions, and the yield of **10** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

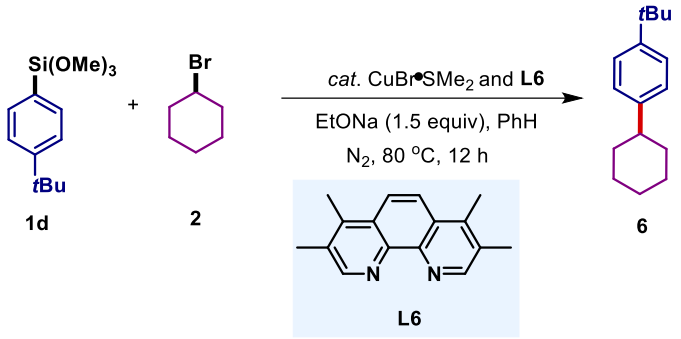
g) NHC-Cu-Aryl Complex accelerated the Hiyama coupling



In the glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (4.0 mg, 0.02 mmol, 5.0 mol%), **L6** (2.4 mg, 0.01 mmol, 2.5 mol%), **Cu-4** (5.6 mg, 0.01 mmol, 2.5 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and [4-(*tert*-butyl)phenyl] trimethoxysilane (206 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields of **6** and **9** were measured to be 86% and <1%, respectively, by NMR analyses against 1,4-dioxane as a calibrated internal standard.

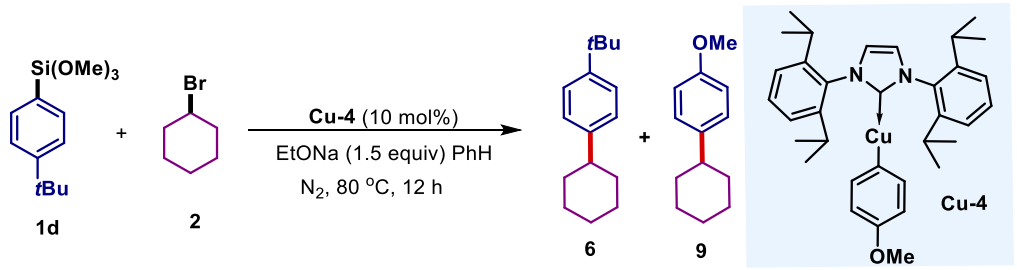
The reaction was repeated with CuBr•SMe_2 (4.0 mg, 0.02 mmol, 5.0 mol%), **L6** (4.8 mg, 0.02 mmol, 5.0 mol%), **Cu-4** (22.4 mg, 0.04 mmol, 10 mol%) as the catalyst under otherwise identical conditions, and the yields of **6** and **9** were measured to be 89% and <1%, respectively, by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with CuBr•SMe_2 (4.0 mg, 0.02 mmol, 5.0 mol%), **L6** (4.8 mg, 0.02 mmol, 5.0 mol%), **Cu-4** (44.8 mg, 0.08 mmol, 20 mol%) as the catalyst under otherwise identical conditions, and the yields of **6** and **9** were measured to be 87% and 7%, respectively, by NMR analyses against 1,4-dioxane as a calibrated internal standard.



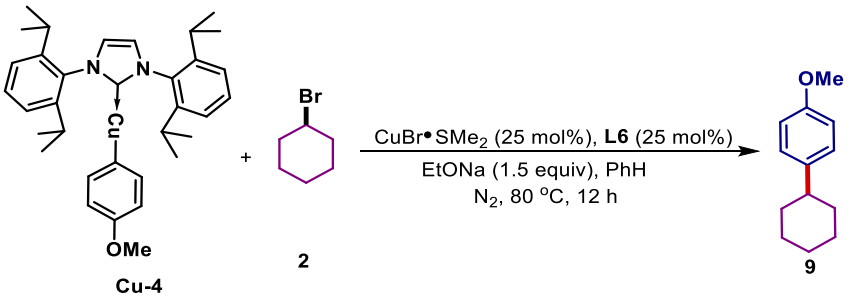
In the glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (2.0 mg, 0.01 mmol, 2.5 mol%), **L6** (2.4 mg, 0.01 mmol, 2.5 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and (4-(*tert*-butyl)phenyl) trimethoxysilane (206 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **6** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

The reaction was repeated with CuBr•SMe_2 (8.0 mg, 0.04 mmol, 10 mol%), **L6** (9.6 mg, 0.04 mmol, 10 mol%) as the catalyst under otherwise identical conditions, and the yield of **6** was measured to be 28% by NMR analyses against 1,4-dioxane as a calibrated internal standard.



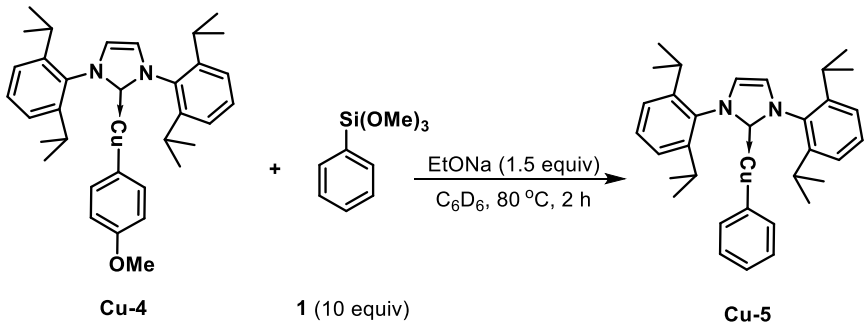
In a glove box, to an oven-dried screw capped vial charged with a stir bar were added the complex **Cu-4** (22.4 mg, 0.04 mmol, 10 mol%) and EtONa (41 mg, 0.60 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (65.2 mg, 0.40 mmol) and [4-(*tert*-butyl)phenyl] trimethoxysilane (206 mg, 0.80 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yields of **6** and **9** were both measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

h) Evaluation the reaction of NHC-Cu-Aryl Complex with alkyl halides under copper-catalysis



In a glove box, to an oven-dried screw capped vial charged with a stir bar were added CuBr•SMe_2 (2.0 mg, 0.01 mmol), **L6** (2.4 mg, 0.01 mmol)**, Cu-4** (22.4 mg, 0.04 mmol) and EtONa (4.1 mg, 0.06 mmol). Then, anhydrous benzene (0.50 mL) was added. Next, bromocyclohexane (6.5 mg, 0.04 mmol) were added. The reaction vial was sealed and taken out of the glove box, and stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through silica gel with EtOAc. The yield of **9** was measured to be <1% by NMR analyses against 1,4-dioxane as a calibrated internal standard.

i) Aryl group exchange in NHC-Cu-Aryl Complex with arylsilanes



In the glove box, to an oven-dried screw capped vial were added **Cu-4** (5.6 mg, 0.01 mmol, 1.0 equiv.), phenyl trimethoxysilane (20 mg, 0.1 mmol, 10.0 equiv.) and EtONa (1 mg, 0.015 mmol). Then, benzene-d_6 (0.50 mL) was added. The solution was added to an NMR tube and taken out of the glove box, and heated at 80 °C for 2 h. The reaction mixture was cooled to room temperature and the complex of **Cu-5** was observed by using NMR spectroscopy with almost quantitive conversion.

The spectral data of **Cu-5** is similar to that previously reported in the literature.[19]

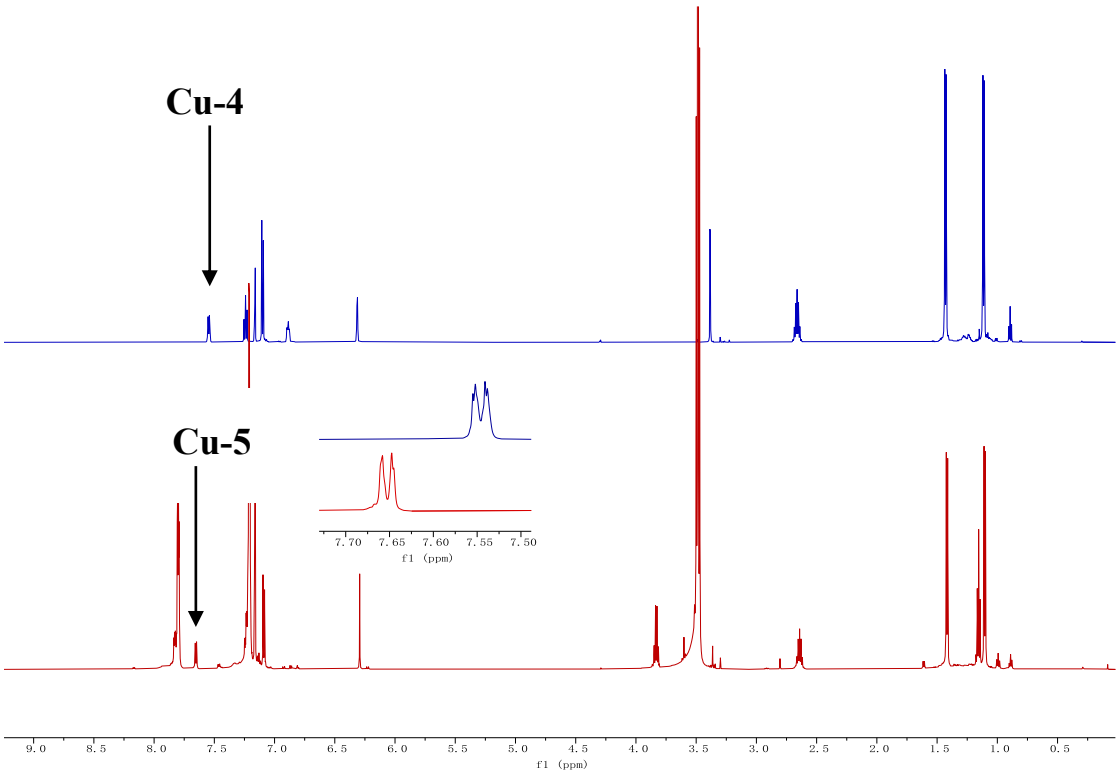


Fig. S2. ^{1}H NMR Spectrum of the aryl exchange in NHC-copper complex with arylsilane

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Appendix I

Crystallographic Data

Copper Complexes Cu-1

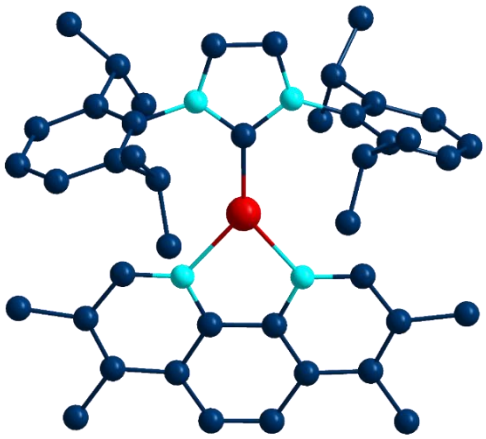


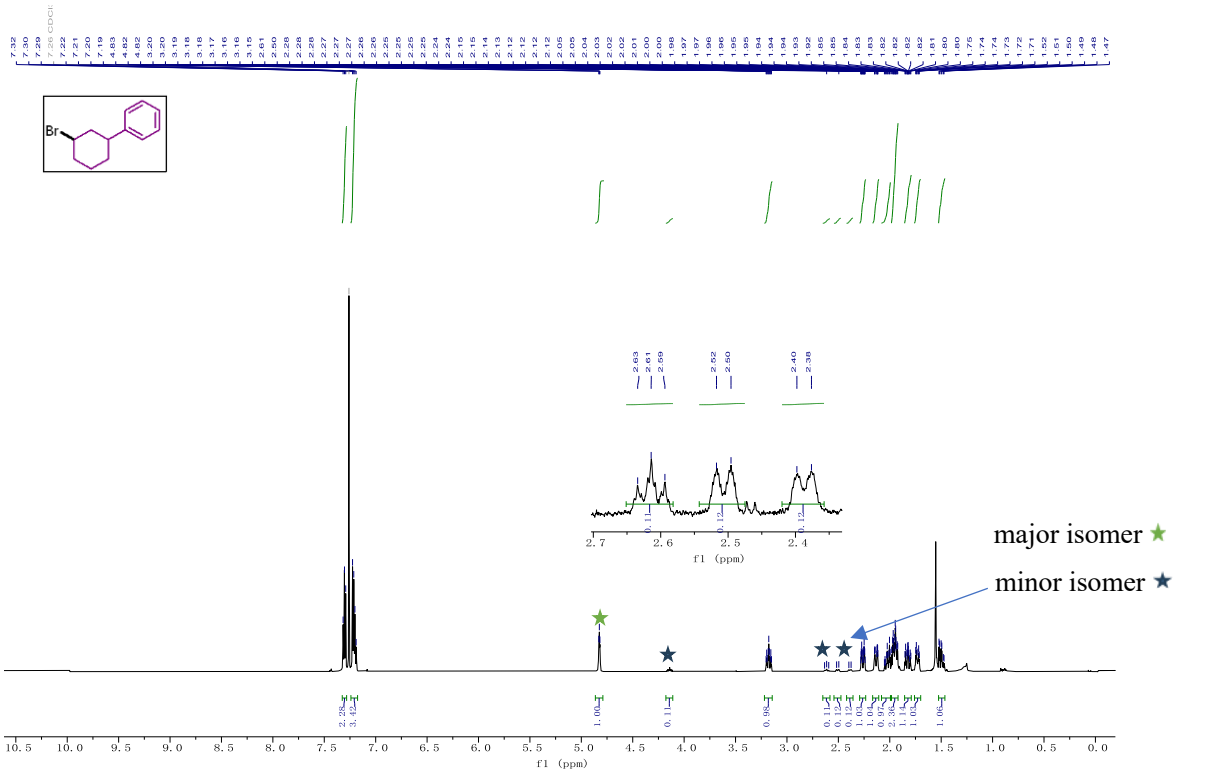
Table S9. Crystal data and structure refinement for **Cu-1**.

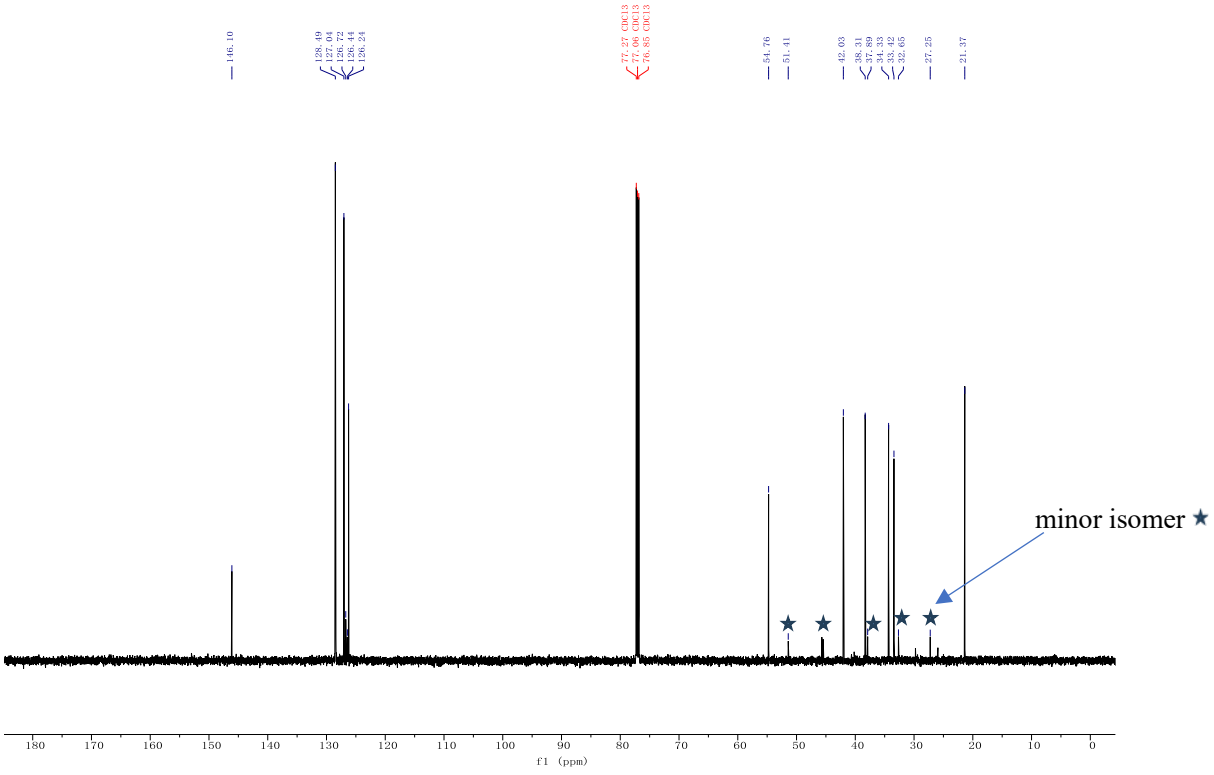
Empirical formula	$C_{43}H_{53}BrCuN_4$	
Formula weight	767.2750	
Temperature	180 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.3872 (19) Å	α = 90°
	b = 15.6834 (19) Å	β = 106.820°
	c = 16.433 (3) Å	γ = 90°
Volume	2735.2 (7) $Å^3$	
Z	2	
Density (calculated)	1.157 Mg m^{-3}	
Absorption coefficient	1.167 mm^{-1}	
F(000)	1004.0	
Crystal size	0.15 × 0.15 × 0.1 mm^3	
Theta range for data collection	2.6–25.3°.	
Index ranges	-14<=h<=14, –18<=k<=18, –19<=l<=19	
Reflections collected	77805	
Independent reflections	9776[R_{int} = 0.1169, R_{sigma} = 0.0641]	
Data / restraints / parameters	9776 / 331 / 626	
Goodness-of-fit on F^2	1.12	
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.2151	
R indices (all data)	R1 = 0.0830, wR2 = 0.2258	
Largest diff. peak and hole	2.78 e $Å^{-3}$ and -1.16 e $Å^{-3}$	

Appendix II

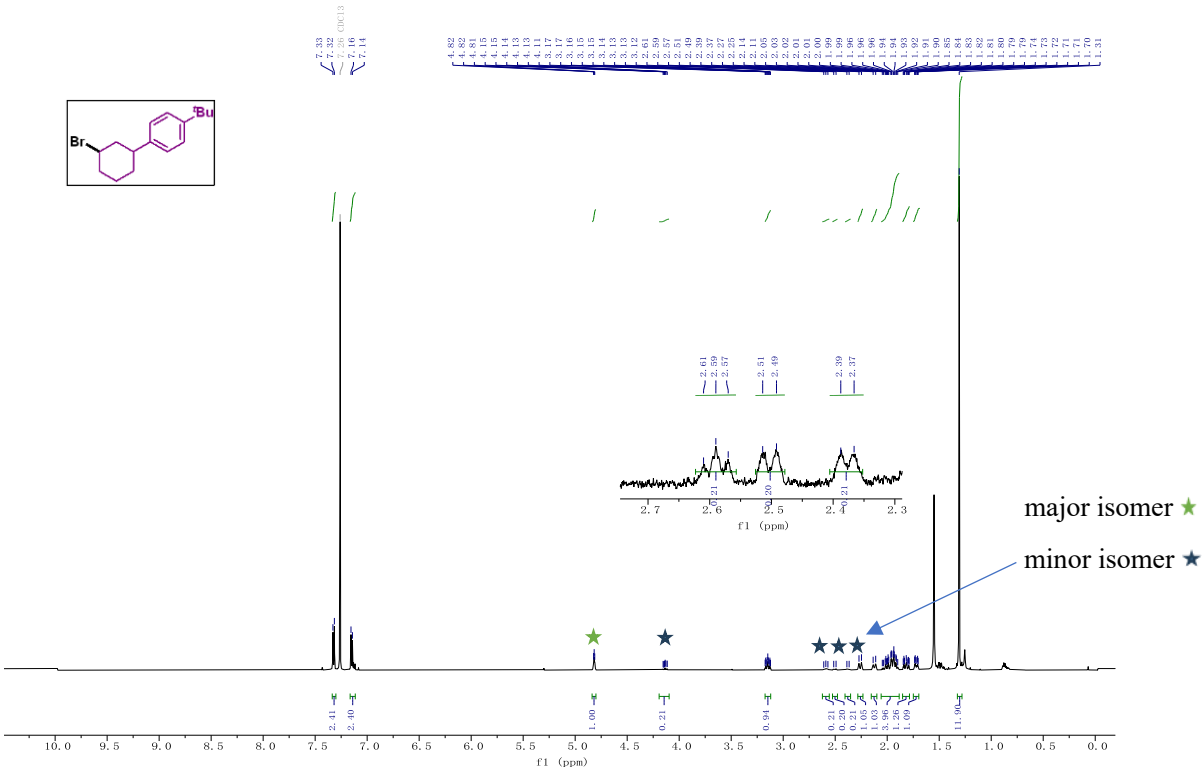
Spectral Copies of NMR of Newly Obtained Compounds

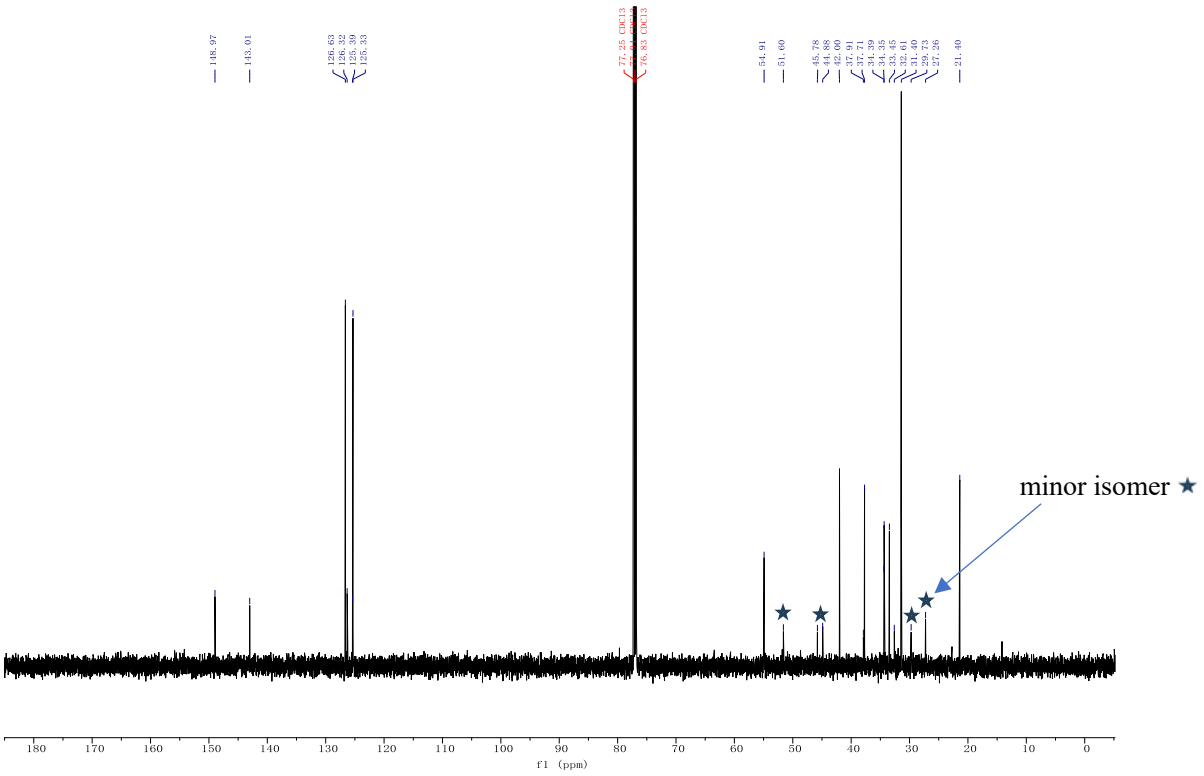
(3-Bromocyclohexyl)benzene) (dr = 9:1)



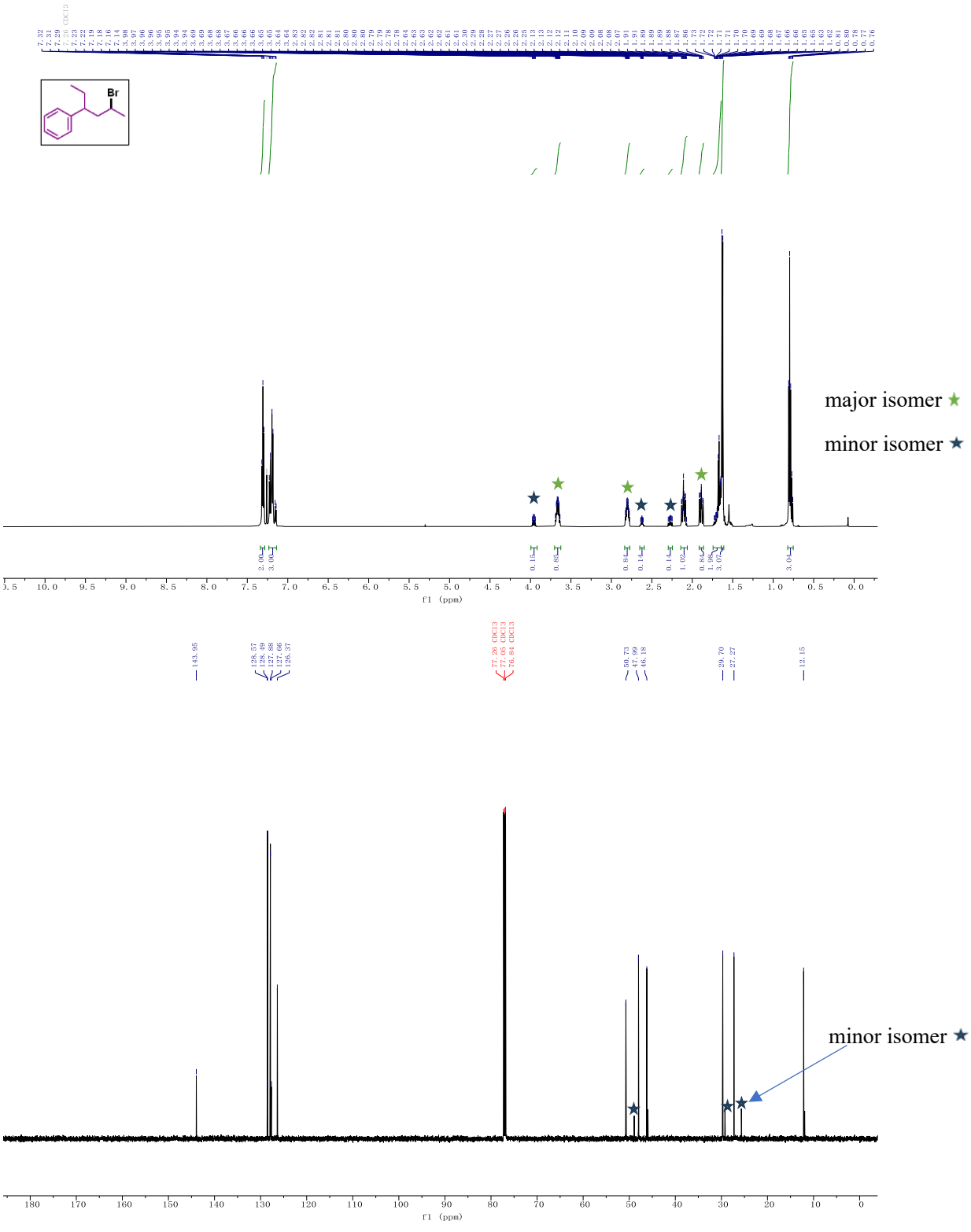


1-(3-Bromocyclohexyl)-4-(*t*ert-butyl)benzene (dr = 5:1)

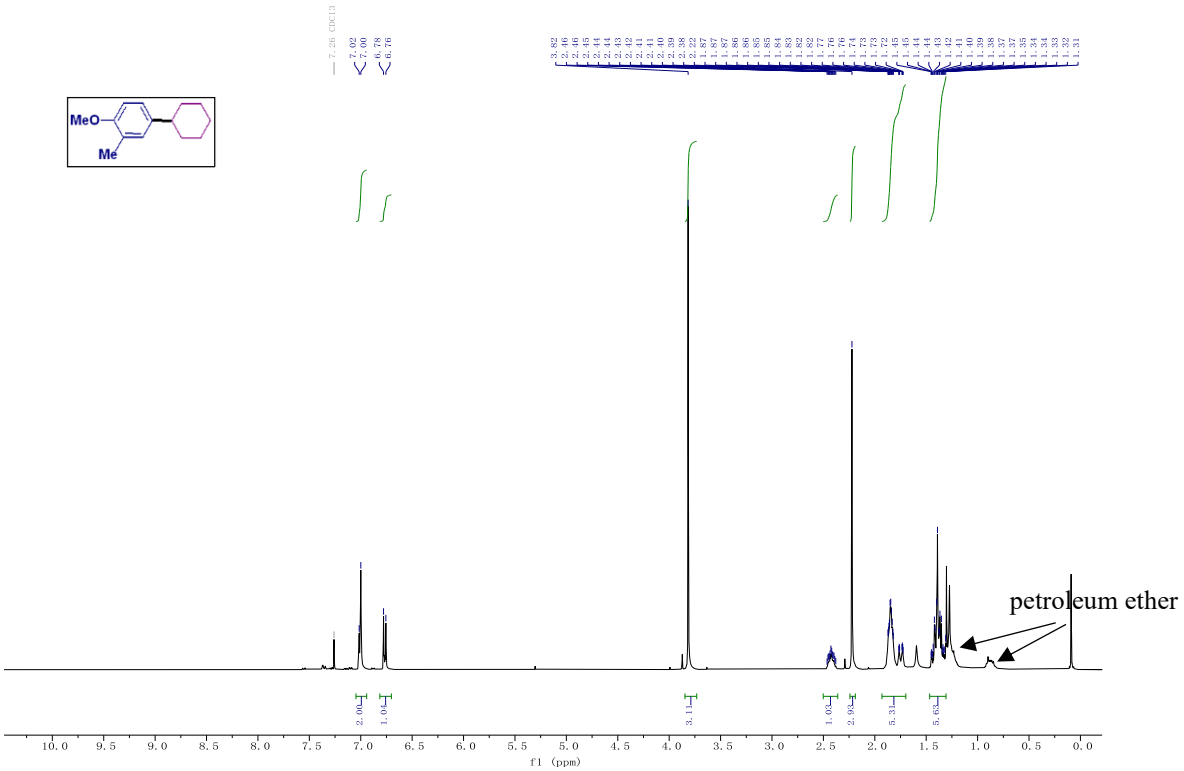


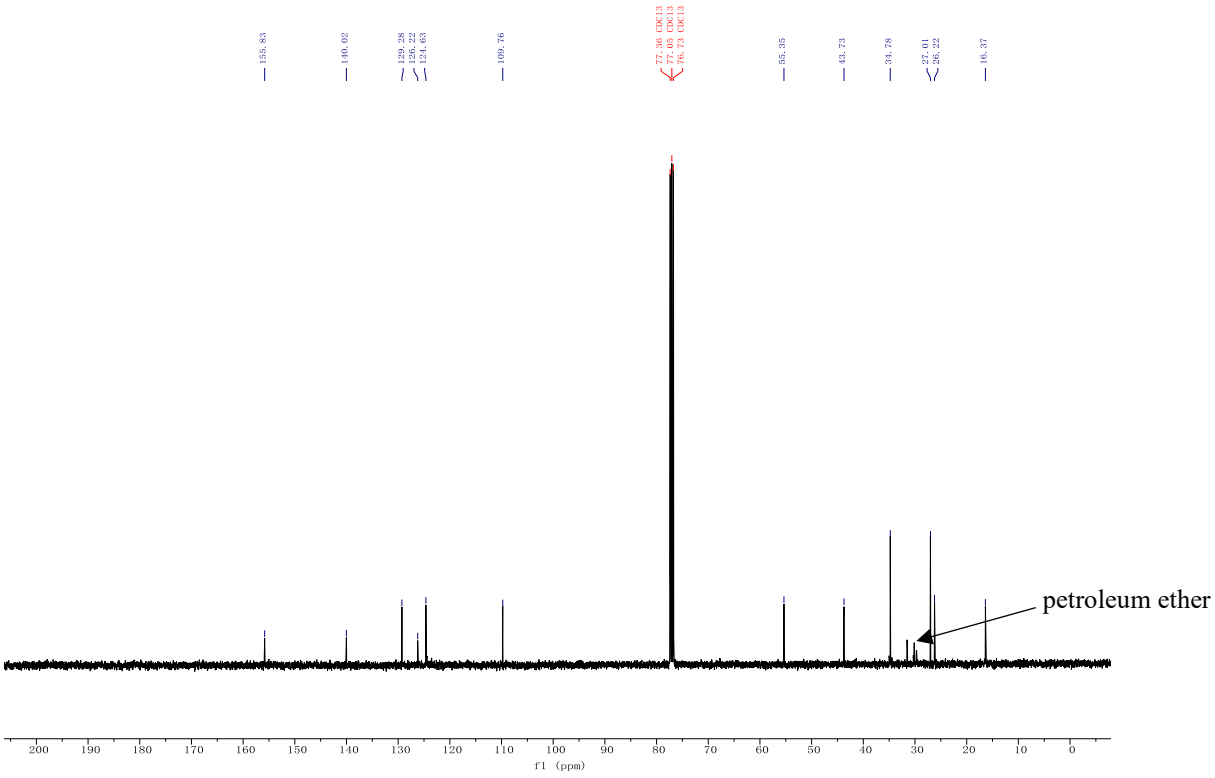


(5-Bromohexan-3-yl)benzene (dr = 6:1)

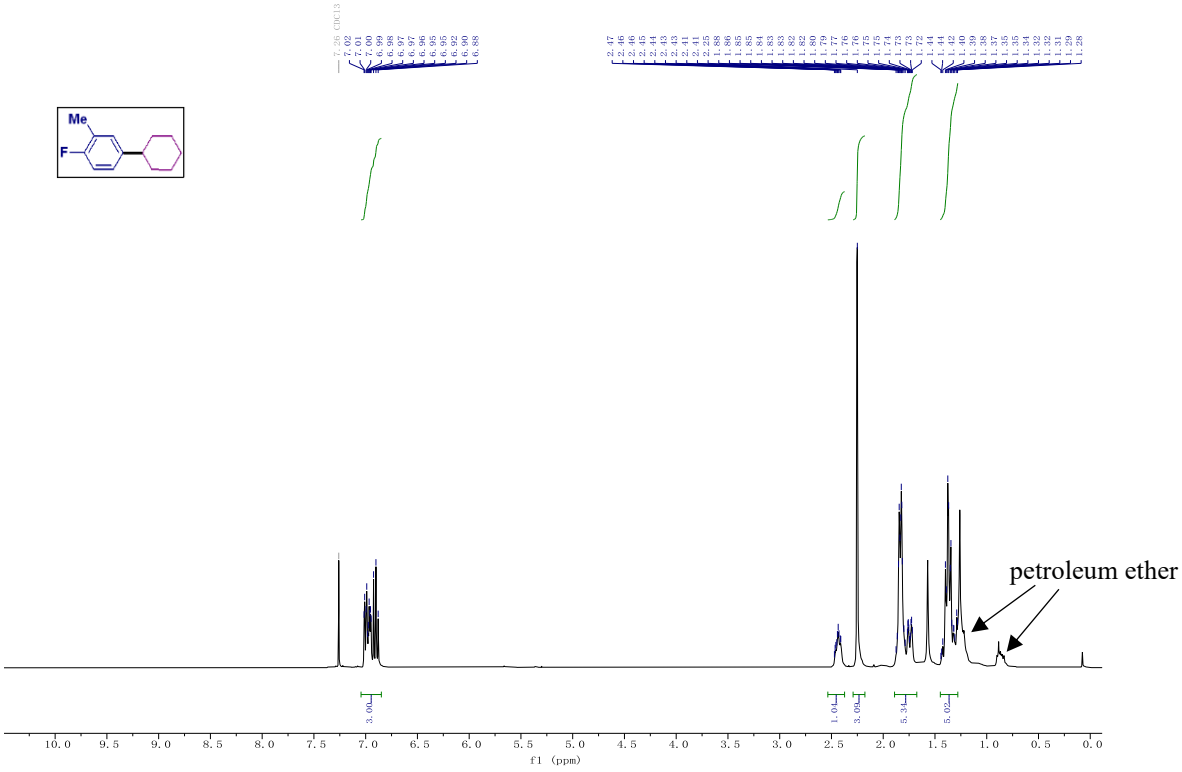


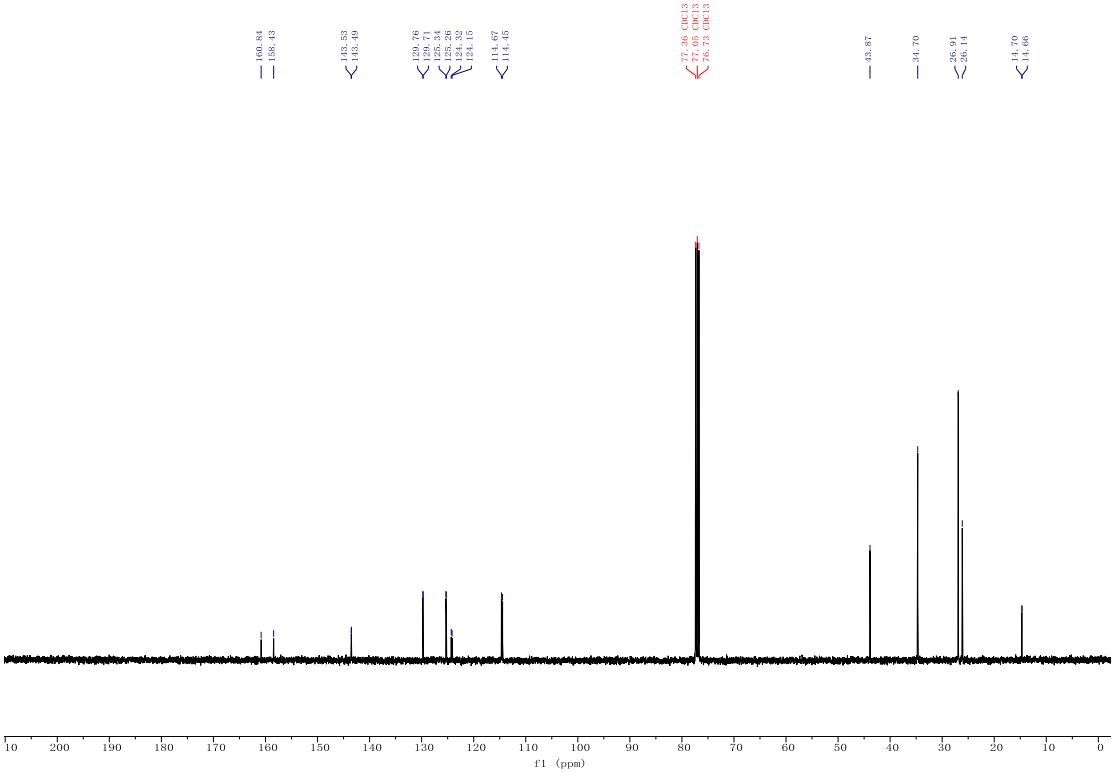
4-Cyclohexyl-1-methoxy-2-methylbenzene (Table 2, 10, containing small amount of petroleum ether**)**

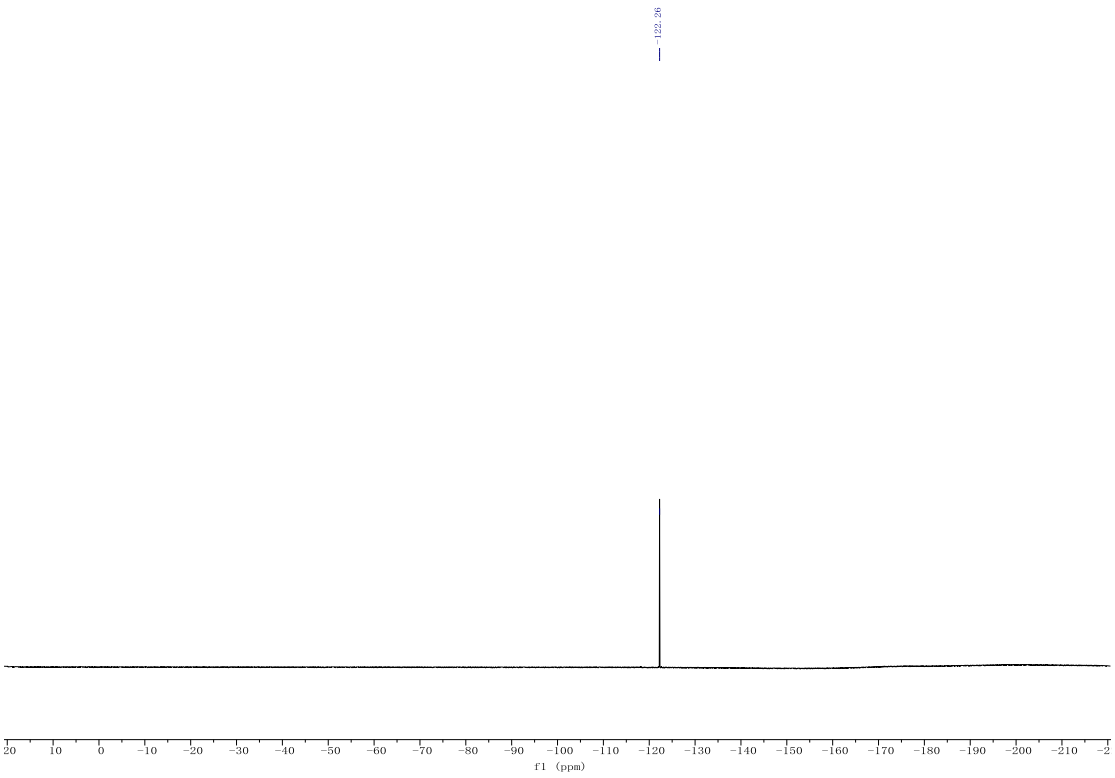




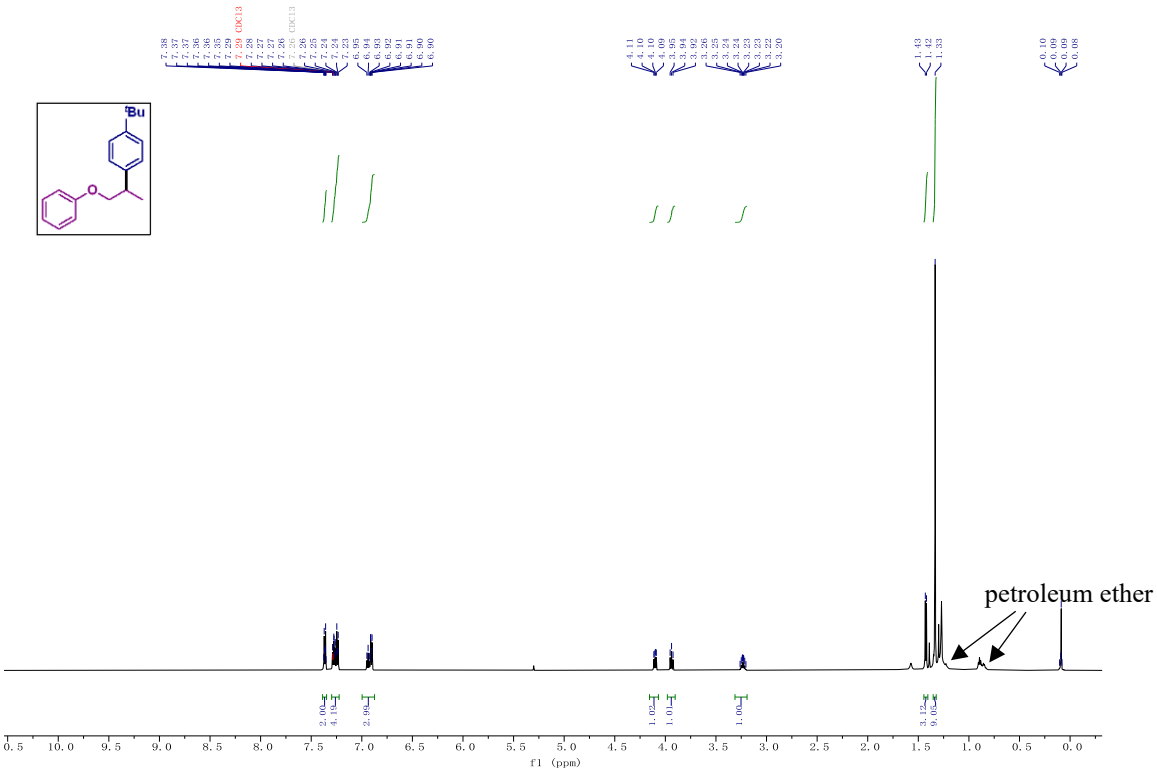
4-Cyclohexyl-1-fluoro-2-methylbenzene (Table 2, 15)

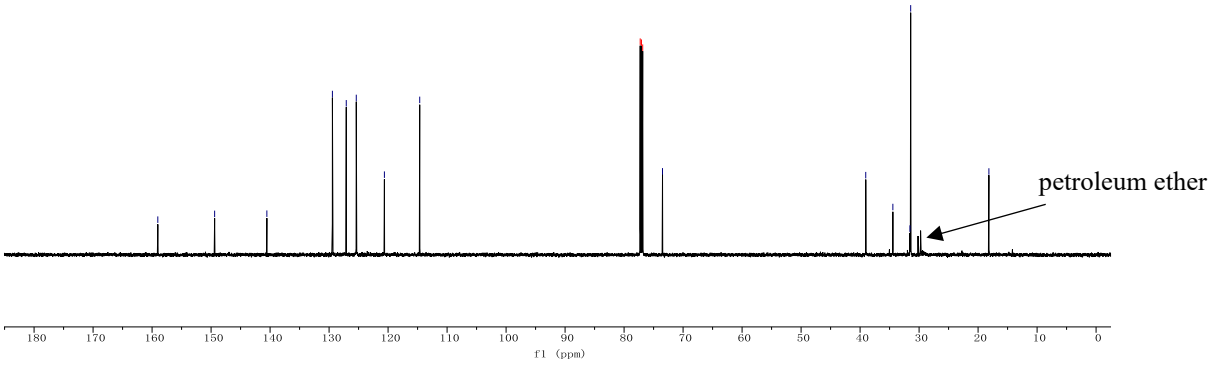




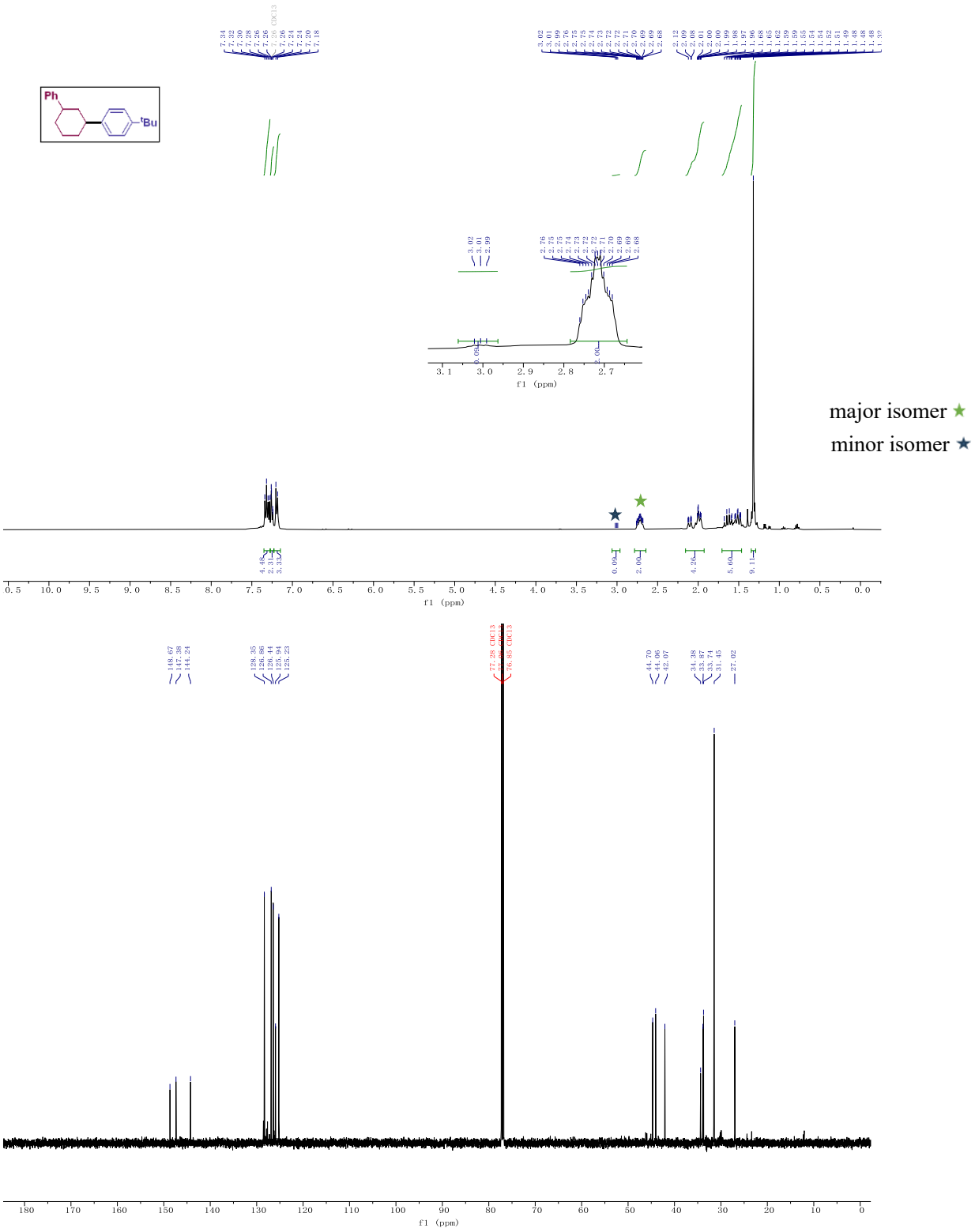

-122.26
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

(*t*ert-Butyl)-4-(1-phenoxypropan-2-yl)benzene (Table 3, 30, containing small amount of petroleum ether**)**

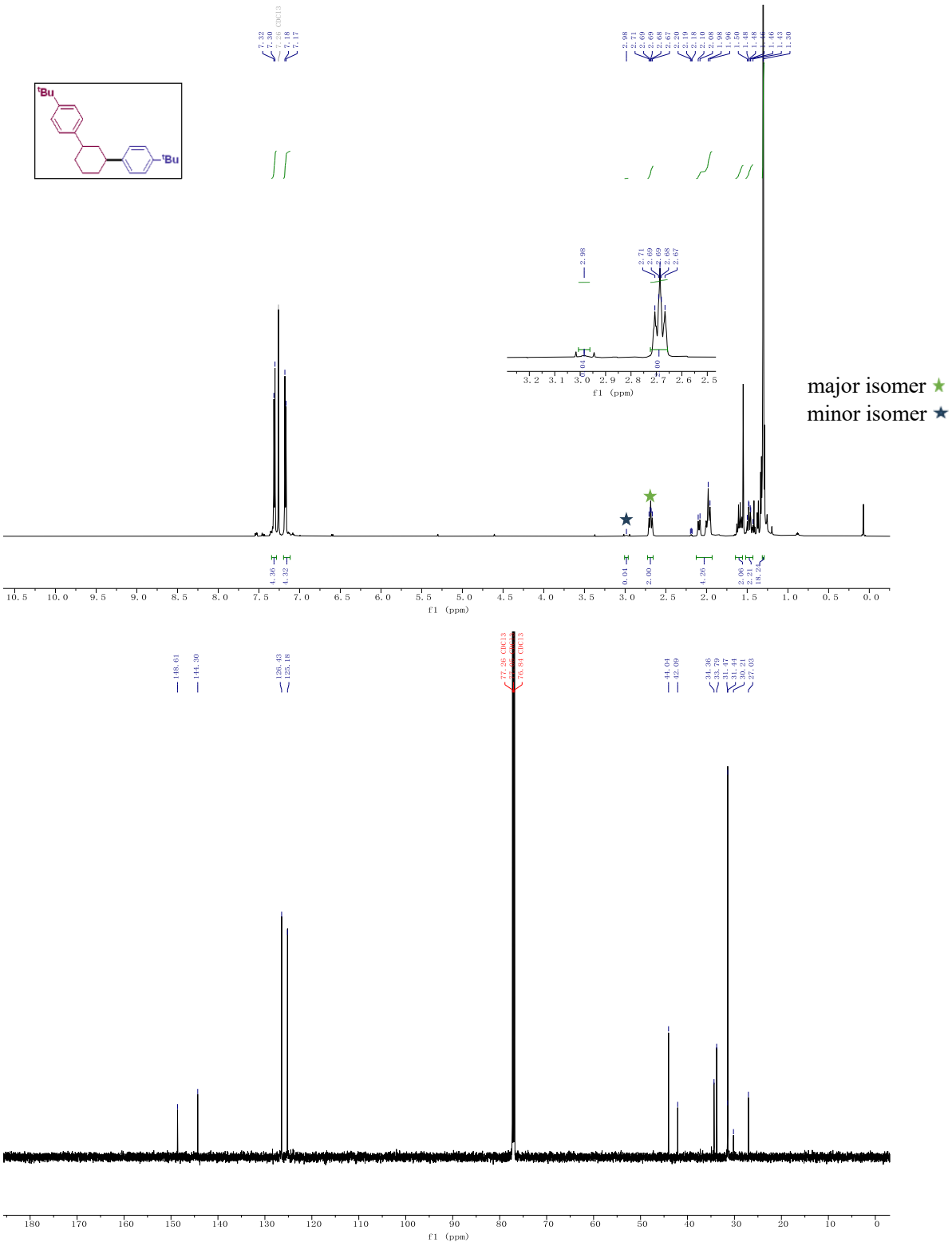




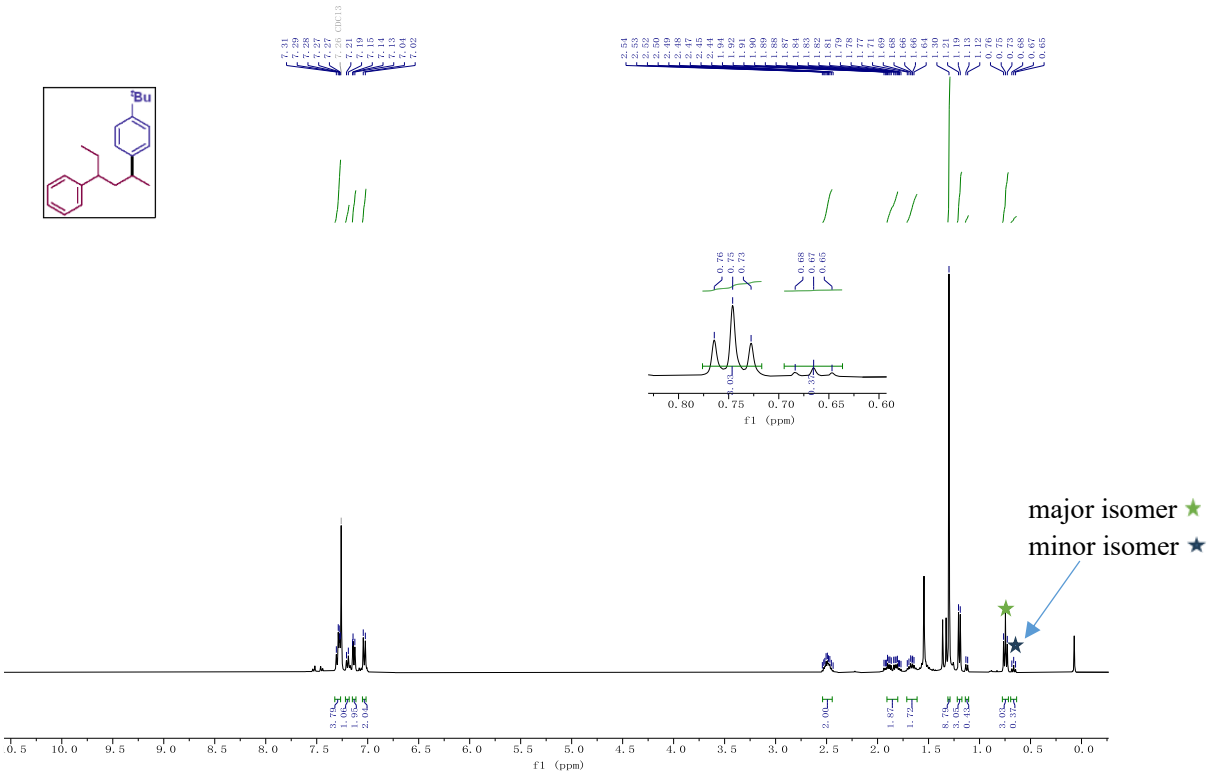
1-(*t*ert-Butyl)-4-(3-phenylcyclohexyl)benzene (Table 3, 32) (dr = 22:1)

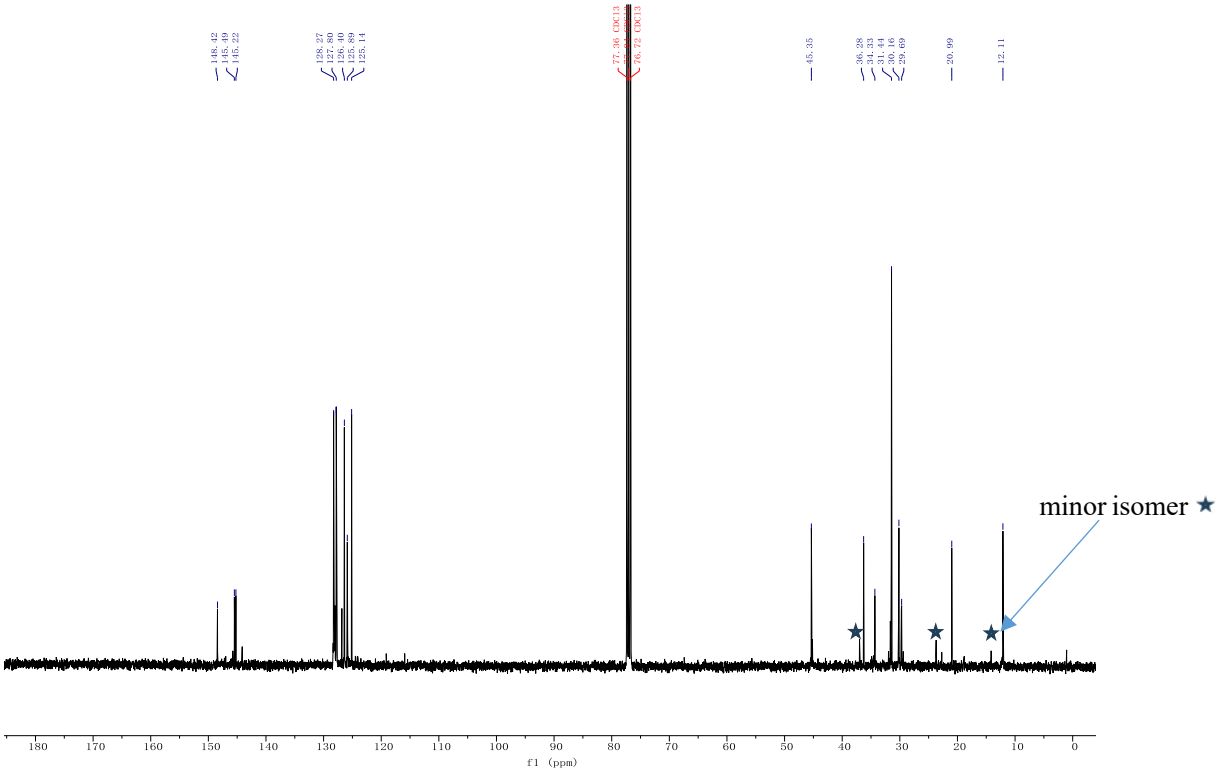


1,3-bis(4-(*t*ert-Butyl)phenyl)cyclohexane (Table 3, 33) (dr = 50:1)

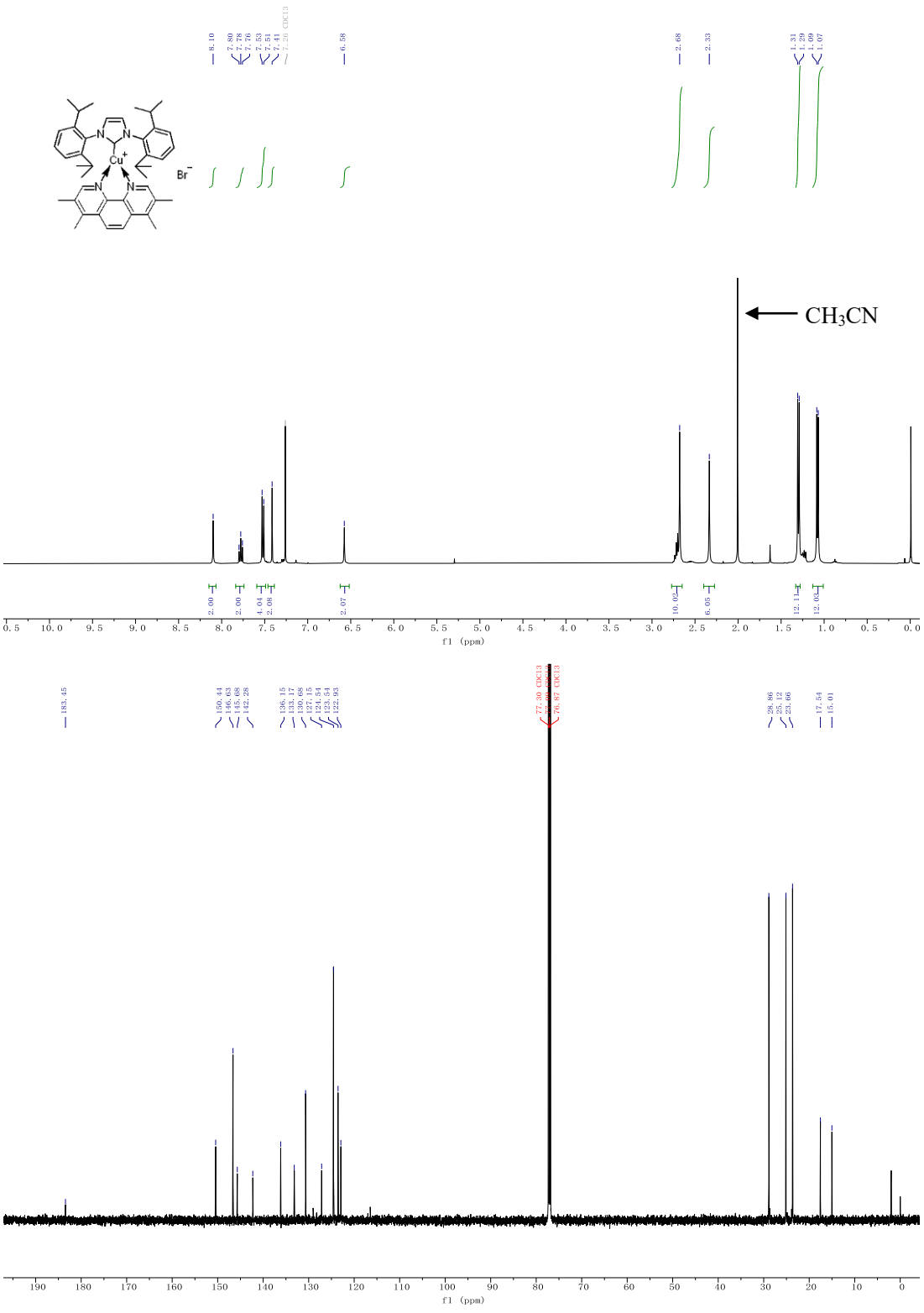


1-(*t*ert-Butyl)-4-(4-phenylhexan-2-yl)benzene (Table 3, 34) (dr = 8:1)

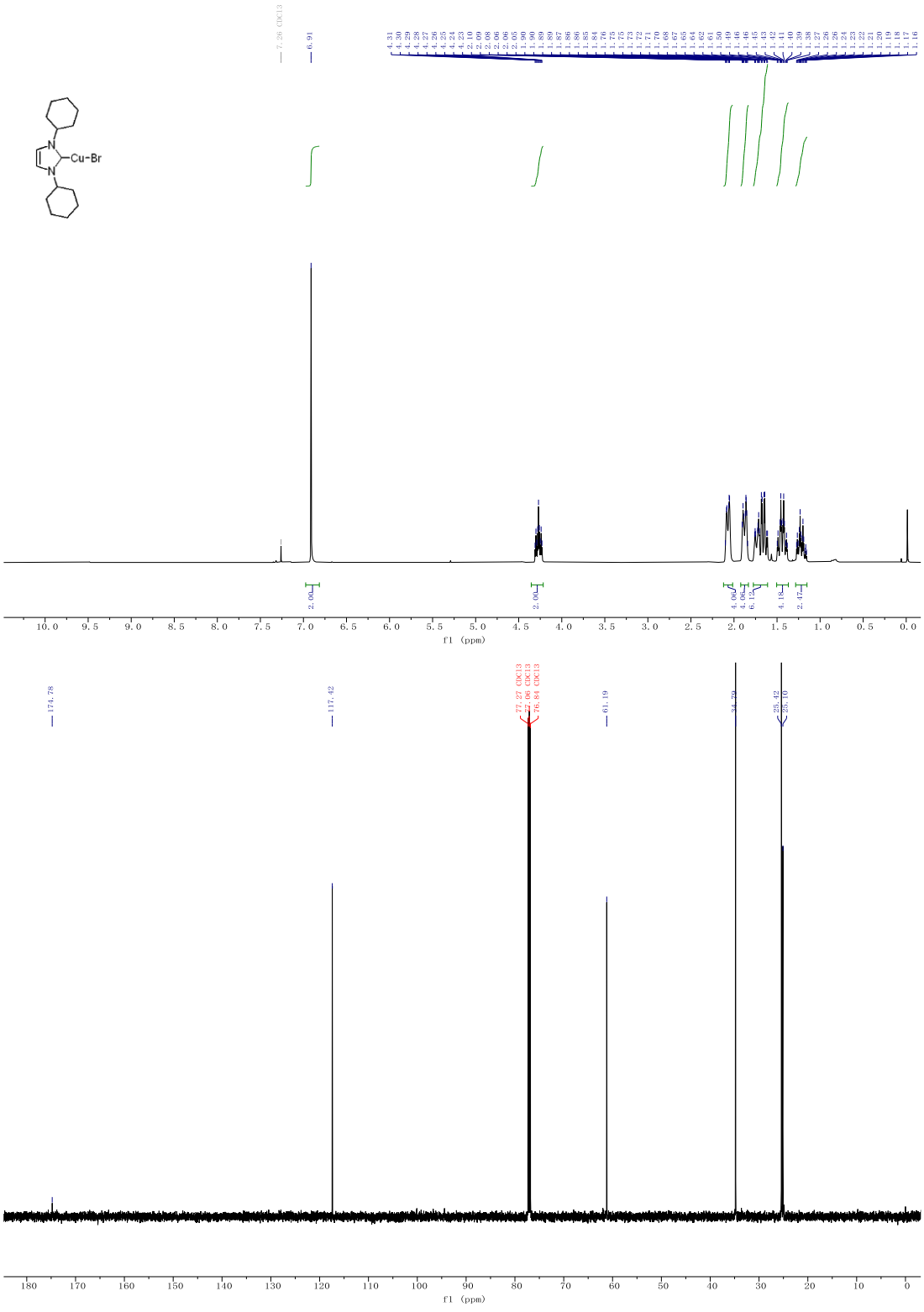




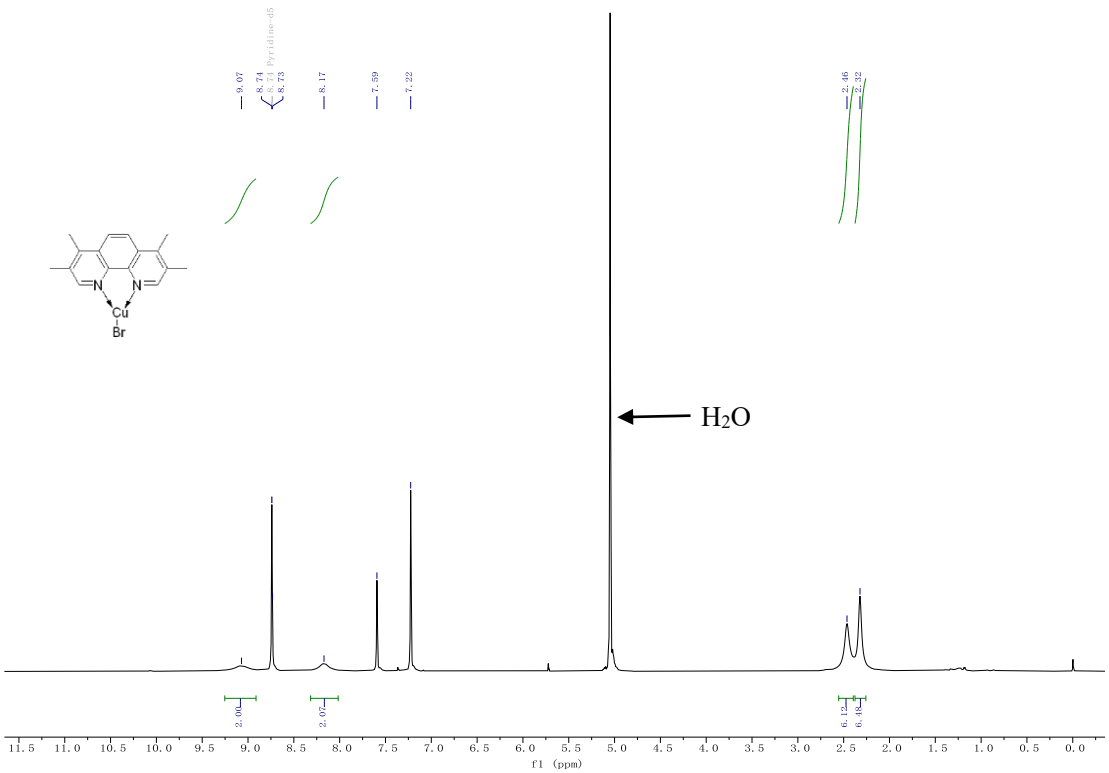
Cu-1



Cu-2



Cu-3


9.07
8.74
8.73
8.17
7.59
7.22
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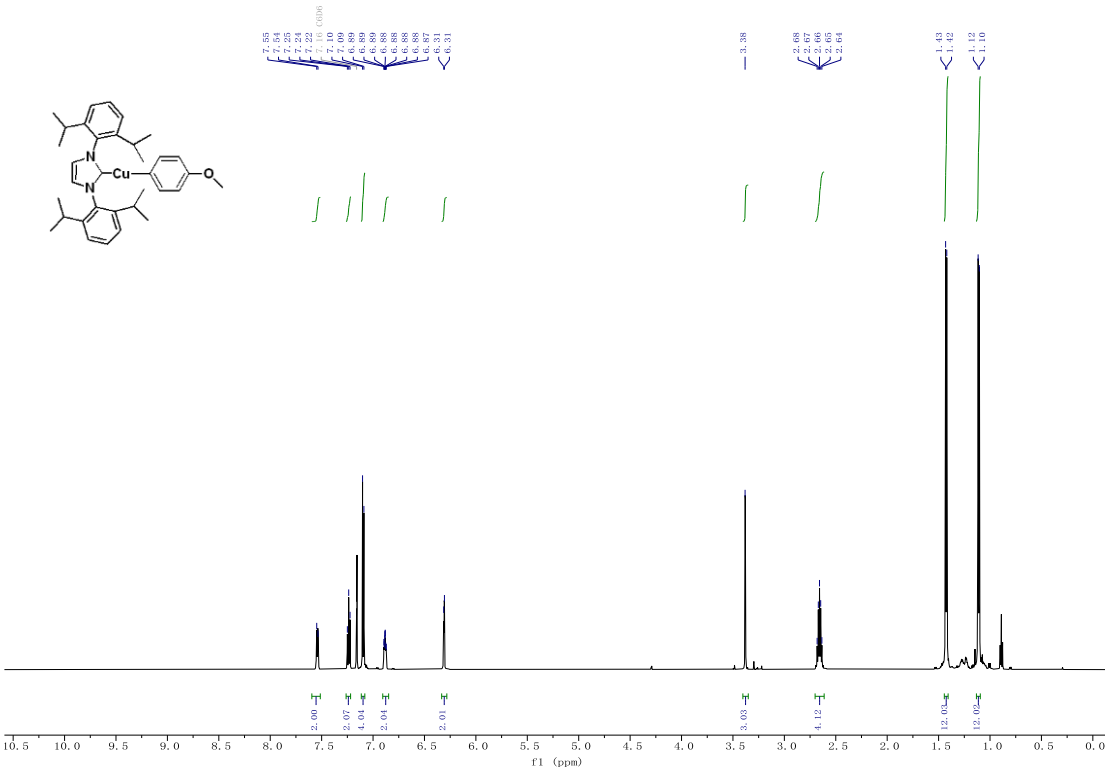
2.32
Cu
Br
H2O
2.00
2.07
6.12
6.48
f1 (ppm)

Cu-4


7.55
7.54
7.25
7.24
7.22
7.10
7.09
6.89
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6.88
6.88
6.87
6.31
6.31
3.38
2.68
2.67
2.66
2.65
2.64
1.43
1.42
1.12
1.10
Cu
O
2.00
2.07
4.04
2.04
2.01
3.03
4.12
12.03
12.00
f1 (ppm)