Supporting Information

Copper-catalysed direct radical alkenylation of alkyl bromides

Xu Zhang^{*a*+}, Hong Yi^{*a*+}, Zhixiong Liao^{*a*}, Guoting Zhang^{*a*}, Chao Fan^{*a*}, Chu Qin^{*a*}, Jie Liu^{*a*}, and Aiwen

Lei^{a,b}*

^aCollege of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, P. R. China. ^bNational Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022, Jiangxi, P. R. China

aiwenlei@whu.edu.cn,

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General Considerations

All manipulations were carried out using standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. All new compounds were characterized by ¹H NMR, ¹³C NMR and HRMS. The known compounds were characterized by ¹H NMR and ¹³C NMR. The ¹H and ¹³C NMR spectra were recorded on Bruker Advance III 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ¹H), CDCl₃ (77.3 ppm for ¹³C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H). GC yields were recorded with a Varian GC 3900 gas chromatography instrument with a FID detector. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. EPR spectra were recorded on a Bruker X-band A200 spectrometer.

Experimental Procedures

1. General procedure for Copper-catalyzed Heck-type reaction of Alkyl Bromides

A dried schlenk tube equipped with a stir bar was loaded with CuCl (9.9 mg, 0.1 mmol, 20 mol%), 1,10-phenanthroline (36 mg, 0.2 mmol, 40 mol%), anhydrous sodium carbonate (106 mg, 1 mmol, 2 equivalent). The tube was evacuated and refilled with nitrogen before olefin (1 mmol, 2 equivalent) and alkyl bromide (0.5 mmol) were added. Then 2.0 mL DMF was added into the reaction tube via a syringe. The reaction mixture was stirred under an N₂ atmosphere at 100 °C for 24 h. After the completion of the reaction, it was quenched by ethyl acetate and detected by GC analysis.

Table 1. Optimization of conditions for the reaction

	MeO x mmo	CN 20 + Br 20 2.0 2 ml S pl y mmol	mol%[Cu] nol% Ligand equiv Base olvent, 100 °C 24h	MeO	CN
Entry	Substrate ratio(x:y)	[Cu]/Ligand	Base	Solvent	Yield ^a (%)
1	0.5:0.6	CuCl/phen	Na ₂ CO ₃	DMF	56 ^b
2	0.5:0.6	CuCl/phen	Na ₂ CO ₃	DMSO	52
3	0.5:0.6	CuCl/phen	Na ₂ CO ₃	Dioxane	23
4	0.5:0.6	CuCl/phen	Na ₂ CO ₃	Acetonitrile	51
5	0.5:0.6	CuCl/phen	Na ₂ CO ₃	1,3-dichloropropane	55
6	0.5:0.6	CuCl/phen	Na ₂ CO ₃	Nitro-methane	58
7	0.5:0.6	CuCl/phen	NaHCO ₃	DMF	51
8	0.5:0.6	CuCl/phen	K_3PO_4	DMF	45
9	0.5:0.6	CuCl/phen	NaOH	DMF	n.d
10	0.5:0.6	CuCl/phen	Et ₃ N	DMF	52
11	0.5:0.6	CuCl/phen	Pyridine	DMF	30
12	1:0.5	CuCl/phen	Na ₂ CO ₃	DMF	83(80 ^b)
13	1:0.5	CuCl/No	Na ₂ CO ₃	DMF	n.d
14	1:0.5	CuCl/8-Hydroxyquinoline	Na ₂ CO ₃	DMF	<5
15	1:0.5	CuCl/4,4'-Dimethyl-2,2'- dipyridyl	Na ₂ CO ₃	DMF	<5
16	1:0.5	CuCl/TMEDA	Na ₂ CO ₃	DMF	<5
17	1:0.5	CuCl/Acetyl acetone	Na ₂ CO ₃	DMF	<5
18	1:0.5	No/phen	Na ₂ CO ₃	DMF	n.d
19	1:0.5	CuBr/phen	Na ₂ CO ₃	DMF	82

20	1:0.5	CuI/phen	Na ₂ CO ₃	DMF	79
21	1:0.5	CuCl ₂ /phen	Na ₂ CO ₃	DMF	<5
^{<i>a</i>} GC yield with biphenyl as internal standard; ^{<i>b</i>} isolated yield; n.d= no desired product.					

2. General procedure for Copper-catalyzed Heck-type reaction of Alkyl Bromides

A dried schlenk tube equipped with a stir bar was loaded with CuCl (9.9 mg, 0.1 mmol, 20 mol%), 1,10-phenanthroline (36 mg, 0.2 mmol, 40 mol%), anhydrous sodium carbonate (106 mg, 1.0 mmol, 2 equivalent). The tube was evacuated and refilled with nitrogen before olefin (1.0 mmol, 2 equivalent) and alkylbromide (0.5 mmol) were added. Then 2 mL DMF was added into the reaction tube via a syringe. The reaction mixture was stirred under an N₂ atmosphere at 100 °C for 24 h .After the completion of the reaction, the pure product was obtained by flash column chromatography on silica gel.

Mechanism Study

1. The Radical trapping experiments.

A dried schlenk tube equipped with a stir bar was loaded with CuCl (9.9 mg, 0.1 mmol, 20 mol%), 1,10-phenanthroline (36 mg, 0.2 mmol, 40 mol%), additive (1.0 mmol), anhydrous sodium carbonate (106 mg, 1.0 mmol). The tube was evacuated and refilled with nitrogen before olefin (1.0 mmol, 2 equivalent), alkylbromide (0.5 mmol), were added. Then 2.0 mL DMF was added into the reaction tube via a syringe. The reaction mixture was stirred under an N₂ atmosphere at 100 °C for 24 h. After the completion of the reaction, it was quenched by ethyl acetate and detected by GC analysis.

2. The experiment procedure for trapping homo-coupling products

A dried schlenk tube equipped with a stir bar was loaded with 2a (0.6 mmol), CuCl (0.1 mmol), 1,10-phenanthroline (0.2 mmol), Na₂CO₃ (1.0 mmol), DMF (2.0 mL) under the atmosphere of nitrogen. The tube was then stirred at 100°C for 24 h. After the completion of the reaction, it was quenched by ethyl acetate and detected by GC-MS analysis



Total Ion Chromatogram (TIC)



3. EPR experiments

- 3.1 In an oven dried Schlenk tube equipped with a stir-bar, CuCl (0.05 mmol), 1,10phenanthroline (0.1 mmol) and 2.0 mL DMF were combined. After the reaction was stirred at 100 °C for 60 minutes. The solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at 150K on EPR spectrometer operating at 9.419 GHz. Typical spectrometer parameters were: scan range, 2000 G; center field set, 3367 G; time constant, 163.84 ms; scan time, 80.00 s; modulation amplitude 2.0 G; modulation frequency 100 kHz; receiver gain 1.00*10⁵; microwave power, 2.02 mW.
- 3.2 In an oven dried Schlenk tube equipped with a stir-bar, CuCl (0.05 mmol) 1,10-phenanthroline (0.1 mmol) and 2.0 mL DMF were combined. Then bromoacetonitrile (1.0 mmol) was added. After the reaction was stirred at 100 °C for 60 minutes. The solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at 150K on EPR spectrometer operating at 9.419 GHz. Typical spectrometer parameters were: scan range, 2000 G; center field set, 3367 G; time constant, 163.84 ms; scan time, 80.00 s; modulation amplitude 2.0 G; modulation frequency 100 kHz; receiver gain 1.00*10⁵; microwave power, 2.02 mW.

Characterization of Products



(*E*)-2-(3-(4-methoxyphenyl)allyl)benzonitrile (3a) ¹: Following standard conditions, 102.2 mg colorless liquid was obtained in 82% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.64-7.62 (m, 1H), 7.55-7.51 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.33-7.27 (m, 3H), 6.85-6.82 (m, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.16 (dt, *J* = 15.6 Hz, 7.0 Hz, 1H), 3.79 (s, 3H), 3.74 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.4, 144.6, <u>133.1</u> (overlapping signals of two different carbons), 132.2, 130.0, 129.9 (almost overlapped), 127.7, 127.0, 124.5, 118.3, 114.2, 112.7, 55.5, 38.0.



(*E*)-2-(3-(p-tolyl)allyl)benzonitrile (3b) ¹: Following standard conditions, 92.2 mg colorless liquid was obtained in 79% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32-7.24 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.29-6.21 (m, 1H), 3.75 (d, *J* = 7.2 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, in CDCl₃): δ 144.4, 137.5, 134.4, 133.1(3), 133.1(2), 132.7, 129.9, 129.5, 127.0, 126.4, 125.6, 118.2, 112.7, 38.0, 21.4.



(*E*)-2-(3-(4-(tert-butyl)phenyl)allyl)benzonitrile (3c)¹: Following standard conditions, 110.2 mg colorless liquid was obtained in 80% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.64-7.62 (m, 1H), 7.54-7.50 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34-7.29 (m, 5H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.27 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 3.75 (d, *J* = 7.2 Hz, 2H), 1.30 (s, 9H); ¹³C NMR (100 MHz, in CDCl₃): δ 150.8, 144.5, 134.4, <u>133.1</u> (overlapping signals of two different carbons), 132.6, 129.9, 127.0, 126.2, 125.9, 125.7, 118.2, 112.7, 38.0, 34.8, 31.5.



(*E*)-2-(3-(o-tolyl)allyl)benzonitrile (3d) : Following standard conditions, 78.2 mg colorless liquid was obtained in 67% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.65-7.51 (m, 2H), 7.41-7.39 (m, 2H), 7.33-7.13 (m, 4H), 6.74 (d, *J* = 15.6 Hz, 1H) , 6.19-6.12 (m, 1H), 3.78 (d, *J* = 6.8 Hz, 2H), 2.34 (s, 3H); ¹³C NMR (100 MHz, in CDCl₃): δ 144.3, 136.3, 135.6, <u>133.2</u> (overlapping signals of two different carbons), 130.8, 130.5, 129.9, 128.0, 127.6, 127.1, 126.3, 125.8, 118.2, 112.7, 38.3, 20.1; HRMS (ESI) for C₁₇H₁₆N⁺ ([M+H]⁺) calculated: 234.1277, found [M+H]⁺: 234.1287.



2-((1H-inden-2-yl)methyl)benzonitrile (3e): Following standard conditions, 78.6 mg yellow solid was obtained in 68% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.39-7.20 (m, 5H), 7.13-7.10 (m, 1H), 6.54 (s, 1H), 4.04 (s, 2H), 3.33 (s, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 146.7, 145.1, 144.1, 143.5, <u>133.2(0)</u>, <u>133.1(7)</u> (almost overlapped), 130.3, 129.2, 127.2, 126.7, 124.5, 123.8, 120.8, 118.3, 112.9, 41.1, 36.6; HRMS (ESI) calculated for C₁₇H₁₄N⁺ ([M+H]⁺) calculated: 232.1121, found [M+H]⁺: 232.1124.



2-(3,3-diphenylallyl)benzonitrile (3f): Following standard conditions, 104.9 mg colorless liquid was obtained in 71% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42-7.22 (m, 12H), 6.23 (t, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 145.0, 144.5, 142.1, 139.5, <u>133.1(4)</u>, <u>133.1(2)</u> (almost overlapped), 130.0, 129.6, 128.7, 128.4, 127.6(9), 127.6(4), 127.6, 126.9, 125.1, 118.2, 112.6, 34.6; HRMS (ESI) calculated for C₂₂H₁₈N⁺ ([M+H]⁺) calculated: 296.1434, found [M+H]⁺: 296.1434.



(E)-2-(3-phenylbut-2-en-1-yl)benzonitrile(a); 2-(3-phenylbut-3-en-1-yl)benzonitrile(b) (3g):

Following standard conditions ,98.0 mg product (mixture of a and b, a : b = 1 : 1.6) was obtained in 84% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.64-7.59 (m, 2.6H), 7.54-7.23 (m, 21.7H), 5.89 (t, *J* = 7.6 Hz, 1H), 5.31 (s, 1.6H), 5.07 (s, 1.6H), 3.79 (d, *J* = 7.2 Hz, 2.0H), 3.01-2.97 (m, 3.2H), 2.90-2.86 (m, 3.2H), 2.18 (s, 3H); ¹³C NMR (100 MHz, in CDCl₃) of the mixture of **a** and **b**: δ 147.1, 146.0, 145.3, 143.5, 140.7, 137.8, 133.2, 133.1, 132.9, 130.0, 129.6, 128.7, 128.5, 127.9, 127.3, 126.9, 126.8, 126.4, 126.1, 124.3, 118.4, 118.3, 113.8, 112.7, 112.5, 36.6, 33.9, 16.5; HRMS (ESI) calculated for C₁₇H₁₆N⁺ ([M+H]⁺) calculated:234.1277, found [M+H]⁺: 234.1275.



(*E*)-1-fluoro-2-(3-(4-methoxyphenyl)allyl)benzene (3h) ¹: Following standard conditions, 35% NMR yield was obtained. ¹H NMR (400 MHz, in CDCl₃): δ 7.30-7.17 (m, 4H), 7.09-7.01 (m, 2H), 6.84-6.81 (m, 2H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 3.79 (s, 3H), 3.54 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 161.2 (d, *J* = 243.7 Hz), 159.1, 131.0, 130.9 (d, *J* = 4.8 Hz), 130.4, 128.1(d, *J* = 8.0 Hz), 127.7(d, *J* = 3.3 Hz), 127.5, 125.6, 124.3(d, *J* = 3.6 Hz), 115.5(d, *J* = 21.9 Hz), 114.2, 55.6, 32.5 (d, *J* = 3.0 Hz);



(*E*)-1,3-dichloro-2-(3-(4-methoxyphenyl)allyl)benzene (3i)¹: Following standard conditions,
97% NMR yield was obtained. ¹H NMR (400 MHz, in CDCl₃): δ 7.30-7.24 (m, 4H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.82-6.79 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.13 (dt, *J* = 16.0 Hz, 6.6 Hz, 1H), 3.82-3.80 (m, 2H), 3.77 (s, 3H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.1, 136.3, 135.8, 131.3, 130.4, 128.5, 128.1, 127.5, 123.0, 114.1, 55.5, 34.7.



(*E*)-1-bromo-2-(3-(4-methoxyphenyl)allyl)benzene (3j) ¹: Following standard conditions, 82% NMR yield was obtained. ¹H NMR (400 MHz, in CDCl₃): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.31-7.26 (m,

4H), 7.10-7.06 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 3.80 (s, 3 H), 3.64 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.2, 140.1, 133.0, 131.4, 130.8, 128.1, 127.8, 127.5, 125.4, 124.8, 114.2, 55.6, 39.7.



(*E*)-1-(3-(4-methoxyphenyl)allyl)-2-(trifluoromethyl)benzene (3k) ¹: Following standard conditions, 95% NMR yield was obtained. ¹H NMR (400 MHz, in CDCl₃): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.48-7.44 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.31-7.27 (m, 3H), 6.85-6.81 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.17 (dt, *J* = 16.0 Hz, 6.8 Hz, 1H), 3.78 (s, 3H), 3.69 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.2, 139.4(4),139.4(3), 132.1, 131.5, 131.4, 130.3, 128.6 (q, *J* = 29.6 Hz), 127.6, 126.5, <u>126.1(4)</u> (q, *J* = 5.4 Hz), 126.1(1) (overlapped), 114.2, 55.5, 36.0(2), 36.0(0).



(*E*)-1-methoxy-4-(3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)benzene (3l) ¹: Following standard conditions , 77% NMR yield was obtained. ¹H NMR (400 MHz, in CDCl₃): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31-7.28 (m, 2H), 6.86-6.83 (m, 2H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.18 (td, *J* = 6.8 Hz, 15.6 Hz, 1H), 3.80 (s, 3H), 3.58 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.3, 144.9, 131.5, 130.2, 129.2, 128.9, 127.6, 126.0, 125.6(q, *J* = 3.8 Hz), 114.2, 55.6, 39.4.



(*E*)-ethyl -4-(4-methoxyphenyl)but-3-enoate (3m) ²: Following standard conditions , 24.2 mg colorless liquid was obtained in 22% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.19-6.12 (m, 1H), 4.16 (q, *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 3.21 (d, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, in CDCl₃): δ 172.0, 159.3, 132.9, 129.9, 127.6, 119.9, 114.1, 60.9, 55.4, 38.7, 14.4.



(*E*)-4-(4-methoxyphenyl)but-3-enenitrile (3n) ⁴: Following standard conditions , 60.6 mg white powder was obtained in 70% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 15.6 Hz, 1H), 5.90 (dt, *J* = 15.6 Hz, 5.6 Hz, 1H), 3.81 (s, 3H), 3.26 (d, *J* = 5.6 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.9, 134.2, 128.6, 127.9, 117.8, 114.6, 114.3, 55.5, 21.0.



(*E*)-ethyl 4-(4-methoxyphenyl)-2-methylbut-3-enoate (3o) ³: Following standard conditions ,89 mg colorless liquid was obtained in 76% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.13 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.30-3.23 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 3 H), 1.27 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, in CDCl₃): δ 175.1, 159.4, 130.7, 130.0, 127.7, 127.0, 114.2, 60.9, 55.6, 43.6, 17.8, 14.5.



(*E*)-4-(4-methoxyphenyl)-2-methylbut-3-enenitrile (3p): Following standard conditions ,77.7 mg white powder was obtained in 83% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 15.6 Hz, 1H), 5.93 (dd, *J* = 15.6 Hz, 6.0 Hz, 1H), 3.82 (s, 3H), 3.52-3.44 (m, 1H), 1.50 (d, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, in CDCl₃): δ 159.9, 132.2, 129.6, 128.7, 122.3, 121.4, 114.4, 55.6, 28.7, 19.5; HRMS (ESI) calculated for C₁₂H₁₄NO⁺ ([M+H]⁺) calculated:188.1070, found [M+H]⁺: 188.1065.



(*E*)-ethyl-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (3q) ³: Following standard conditions 105.5 mg colourless liquid was obtained in 85% yield. ¹H NMR (400 MHz, in CDCl₃): δ 7.31 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 16.4 Hz, 1H), 6.26 (d, *J* = 16.4 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 3.80 (s, 3H), 1.39 (s, 6H), 1.25 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, in CDCl₃): δ 176.7, 159.3, 132.6, 130.2, 127.7, 127.5, 114.2, 61.0, 55.5, 44.5, 25.4, 14.4.

References

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NMR Spectra of Products























¹H NMR of 3g







¹³C NMR of 3g











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





- 0.000 -



7.313 6.849 6.849 6.444 6.194 6.119 6.119	4.187 4.170 1.152 3.786 3.218 3.200	€ 1.289 1.271 1.254	0.000
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zx-2-24-1-p2





$\int_{6.124}^{7} \int_{7.245}^{7.315} \int_{7.261}^{7.293} \int_{6.855}^{6.855} \int_{6.438}^{6.438} \int_{6.164}^{6.164} \int_{6.124}^{6.124} \int_{6.124}^{6.1$	4.181 4.164 4.164 4.128 3.303 3.230 3.236 3.236 3.231 3.231	1.258 1.286 1.286 1.268	- 0.000 -
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zx-2-24-2-p1



140 130 120 110 100 f1 (ppm) . 50



zx-2-24-5-2-p1



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





NMR yield of 3h-3l

General Procedure: A dried schlenk tube equipped with a stir bar was loaded with CuCl (9.9 mg, 0.1 mmol, 20 mol%), 1,10-phenanthroline (36 mg, 0.2 mmol, 40 mol%), anhydrous sodium carbonate (106 mg, 1.0 mmol, 2 equivalent). The tube was evacuated and refilled with nitrogen before olefin **1a** (1.0 mmol, 2 equivalent) and alkylbromide (0.5 mmol) were added. Then 2.0 mL DMF was added into the reaction tube via a syringe. The reaction mixture was stirred under an N₂ atmosphere at 100 °C for 24 h. After the completion of the reaction, we firstly isolated the mixture of **1a** and **3** by flash column chromatography on silica gel. Then we added CH₂Br₂ into the mixture and did the ¹H NMR using CDCl₃ as the solvent. At last, we calculated the NMR yield of 3h-31 based on the ratio of desired product 3 to CH₂Br₂ (weight known).





¹H NMR yield spectra of 3i







- -0.000 -







¹H NMR yield spectra of 3k



- 0000.0 —