Rhodium(III)-Catalyzed Sequential Cleavage of Double C-H Bonds for the Synthesis of Multiple Arylated Naphthols

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Supporting Information

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**General** The reagents and solvents were purchased from common commercial sources and used without additional purification, if there is no special version. The starting materials were prepared according to the known method\(^{[1-4]}\). NMR spectra were recorded for \(^1\text{H}\) NMR at 400 MHz, and \(^{13}\text{C}\) NMR at 100 MHz using TMS as internal standard. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), quintuplet (q), multiplet (m), doublet of doublet (dd), broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-EI-TOF instrument. Infrared spectra were recorded on a FTIR spectrometer.

**Experimental Procedures**

**General Procedure for Preparation of products (4)**

A 25 mL sealed tube with a magnetic stir bar was charged with \([\text{Cp}^*\text{RhCl}_2]_2\) (3 mg, 0.005 mmol), \(\text{AgSbF}_6\) (7 mg, 0.02 mmol), \(\text{Cu(OAc)}_2\) (80 mg, 0.4 mol), \(\text{1}\) (0.2 mmol), \(\text{2}\) (0.5 mmol), \(\text{PhF}\) (2.0 mL). Then the tube was sealed and heated to 110 °C with stirring for 12 h. After cooling down, the mixture was filtered through a plug of Celite, and then the residue was washed with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (2 × 20 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.
Removal of the carbamate group

A 25 mL sealed tube with a magnetic stir bar was charged with 4ia (120 mg, 0.2 mmol), KOH (224 mg, 4 mmol), EtOH (5 mL). Then the sealed tube was sealed and heated to 110 °C with stirring for 12 h. After cooling down, Ethyl acetate (10 mL) was added, and then the excess of NaOH was neutralized at room temperature by using a solution of 2 M HCl. The aqueous solution was extracted with EA (3 × 20 mL), and the combined organic layers were washed with brine, dried with Na2SO4, and concentrated under reduced pressure. The crude product was washed with EtOAc/petroleum ether (1:30) to afford 5 (86 mg, 82%) as a white solid.

Isotopically labeled experiment

A 25 mL sealed tube with a magnetic stir bar was charged with [Cp*RhCl2]2 (3 mg, 0.005 mmol), AgSbF6 (7 mg, 0.1 mmol), HOAc-d4 (384 mg, 6 mmol), 1a (43 mg, 0.2 mmol), PhF (2.0 mL). Then the sealed tube was sealed and heated to 110 °C with stirring for 2 h. After cooling down, the mixture was filtered through a plug of Celite, and then the residue was washed with ethyl acetate (3 × 20 mL). Then the organic layer was removed. The crude product was purified by flash column chromatography.

A 25 mL sealed tube with a magnetic stir bar was charged with [Cp*RhCl2]2 (3 mg, 0.005 mmol), AgSbF6 (7 mg, 0.1 mmol), HOAc-d4 (384 mg, 6 mmol), 1a (43 mg, 0.2 mmol), 2a (53 mg, 0.3 mmol), PhF (2.0 mL). Then the sealed tube was sealed under air and heated to 110 °C with stirring for 2 h. After cooling down, the mixture was
filtered through a plug of Celite, and then the residue was washed with ethyl acetate (3 × 20 mL). Then the organic layer was removed. The crude product was purified by flash column chromatography.

References


(2) Feng, C.; Loh, T.-P. Chem. Commun. 2011, 47, 10458.


Characterization data of products

5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4ba) yellow solid (47 mg, 45%); mp (°C) 214–215; \(^1\)H NMR (400 Hz, CDCl\(_3\), TMS) δ 2.26 (s, 3H), 2.66 (s, 3H), 6.69–6.71 (m, 2H), 6.75–6.81 (m, 8H), 7.05–7.09 (m, 4H), 7.14–7.23 (m, 7H), 7.33–7.37 (m, 1H), 7.52–7.55 (m, 1H); \(^{13}\)C NMR (100 Hz, CDCl\(_3\), TMS) δ 35.9, 36.2, 121.0, 125.0, 125.3, 125.4, 125.5, 125.7, 126.0, 126.2, 126.4, 126.5, 127.5, 130.2, 131.0, 131.2 (2C), 134.3, 135.1, 138.7, 139.3, 139.9, 140.3, 140.4, 141.2, 142.2, 148.1, 154.5; IR ν 1719, 1162 cm\(^{-1}\). HRMS (EI) Calcd for C\(_{37}\)H\(_{29}\)NO\(_2\) (M\(^+\)) 519.2198, Found 519.2192.

2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4ca) yellow solid (44 mg, 41%); mp (°C) 236–237; \(^1\)H NMR (400 Hz, CDCl\(_3\), TMS) δ 2.25 (s, 3H), 2.35 (s, 3H), 2.65 (s, 3H), 6.69–6.71 (m, 2H), 6.73–6.80 (m, 8H), 6.94–6.95 (m, 1H), 7.04–7.05 (m, 3H), 7.13–7.22 (m, 7H), 7.30 (m, 1H); \(^{13}\)C NMR (100 Hz, CDCl\(_3\), TMS) δ 21.5, 35.9, 36.2, 123.0, 124.2, 124.7, 124.9, 125.2, 125.3, 126.2, 126.4 (2C), 127.5, 130.2, 131.1, 131.3 (2C), 134.3, 135.0, 135.5, 138.1, 139.4, 140.0, 140.2, 140.4, 140.6, 142.3, 147.9, 154.2; IR ν 1719, 1370, 1162 cm\(^{-1}\). HRMS (EI) Calcd for C\(_{38}\)H\(_{31}\)NO\(_2\) (M\(^+\)) 533.2355, Found 533.2355.

2-chloro-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4da) yellow solid (53 mg, 48%); mp (°C) 225–226; \(^1\)H NMR (400 Hz, CDCl\(_3\), TMS) δ 2.34 (s, 3H), 2.68 (s, 3H), 6.66–6.69 (m, 1H), 6.74–6.81 (m, 9H), 7.00–7.02 (m, 1H), 7.06–7.20 (m, 7H), 7.24 (m, 2H), 7.37–7.40 (m, 1H), 7.47–7.49 (m, 1H); \(^{13}\)C NMR (100 Hz, CDCl\(_3\), TMS) δ 36.0, 36.4, 125.2, 125.4, 125.5, 126.2, 126.3, 126.5, 126.6, 126.7, 127.6, 129.6, 130.8, 130.9, 131.0, 131.2, 131.3, 132.7, 135.2, 138.9, 139.3, 139.6, 140.0, 140.1, 141.8, 142.2, 144.0, 152.8; IR ν 1727, 1150 cm\(^{-1}\). HRMS (EI) Calcd for C\(_{37}\)H\(_{28}\)ClNO\(_2\) (M\(^+\)) 553.1809, Found 553.1807.

2-bromo-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4ea) yellow solid (63 mg, 53%); mp (°C) 202–203; \(^1\)H NMR (400 Hz, CDCl\(_3\), TMS) δ 2.28 (s, 3H), 2.60 (s, 3H), 6.58–6.59 (m, 1H), 6.67–6.74 (m, 9H), 6.91–6.93 (m, 1H), 7.00–7.12 (m, 7H), 7.18 (m, 2H), 7.33–7.35 (m, 1H), 7.44–7.47 (m, 1H); \(^{13}\)C NMR (100 Hz, CDCl\(_3\),
TMS) δ 36.0, 36.4, 116.6, 125.2, 125.4, 125.5, 126.2, 126.3, 126.5, 126.6, 126.7, 127.6, 129.6, 130.8, 130.9, 131.0, 131.2, 131.4, 133.2, 135.2, 138.9, 139.3, 139.7, 140.0, 140.1, 141.8, 145.3, 152.7 ; IR ν 1728, 1146 cm⁻¹. HRMS (EI) Calcd for C₃₇H₂₈BrNO₂ (M⁺) 597.1303, Found 597.1298.

### 3-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4fa)

Yellow solid (49 mg, 46%); mp (°C) 207–208; ¹H NMR (400 Hz, CDCl₃, TMS) δ 2.21 (s, 3H), 2.31 (s, 3H), 2.66 (s, 3H), 6.65–6.67 (m, 1H), 6.73–6.79 (m, 9H), 6.98–7.00 (m, 1H), 7.02–7.05 (m, 1H), 7.08–7.25 (m, 9H), 7.44 (d, 1H, J = 8.8 Hz); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 16.7, 35.9, 36.2, 124.9, 125.2 (2C), 126.1, 126.2, 126.4, 126.5, 127.5, 128.5, 128.7, 129.7, 131.0, 131.1 (2C), 131.2, 131.4 (2C), 132.9, 134.8, 138.4, 138.5, 139.9, 140.5, 141.2, 142.5, 145.6, 153.5; IR ν 1728, 1158 cm⁻¹. HRMS (EI) Calcd for C₃₈H₃₁NO₂ (M⁺) 533.2355, Found 533.2355.

### 3-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4ga)

Yellow solid (56 mg, 51%); mp (°C) > 280; ¹H NMR (400 Hz, CDCl₃, TMS) δ 2.28 (s, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 6.72–6.74 (m, 2H), 6.76–6.84 (m, 9H), 6.91–6.92 (m, 1H), 7.07–7.09 (m, 1H), 7.16–7.19 (m, 3H), 7.24–7.25 (m, 4H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 35.9, 36.2, 55.3, 105.2, 113.0, 121.7, 124.9, 125.2, 125.4, 126.2, 126.4 (2C), 127.6, 130.2, 131.0, 131.1, 131.4, 135.0, 135.2, 137.6, 138.9, 139.7, 140.0, 140.4, 140.7, 142.2, 149.2, 154.2, 156.8; IR ν 1739, 1598, 1439, 1373, 1239, 1046 cm⁻¹. HRMS (EI) Calcd for C₃₈H₃₃NO₃ (M⁺) 549.2304, Found 549.2312.

### 3-chloro-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4ha)

Yellow solid (74 mg, 67%); mp (°C) 229–230; ¹H NMR (400 Hz, CDCl₃, TMS) δ 2.24 (s, 3H), 2.65 (s, 3H), 6.67–6.69 (m, 2H), 6.74–6.81 (m, 8H), 7.05–7.07 (m, 4H), 7.11–7.13 (m, 2H), 7.16–7.19 (m, 2H), 7.51–7.52 (m, 1H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 36.0, 36.2, 122.1, 124.4, 124.7, 125.2, 125.5, 125.6, 126.3, 126.5, 126.6, 126.7, 126.8, 127.7, 130.2, 130.8, 130.9, 131.1, 134.7, 135.4, 138.1, 139.1, 139.9, 140.1, 140.5, 141.4, 141.7, 148.9, 153.9; IR ν 1723, 1111 cm⁻¹. HRMS (EI) Calcd for C₃₇H₂₈ClNO₂ (M⁺) 553.1809, Found 553.1812.

### 3-bromo-5,6,7,8-tetraphenylnaphthalen-1-yl dimethylcarbamate (4ia)

Yellow solid (78 mg, 65%); mp (°C) 238–239; ¹H NMR (400 Hz, CDCl₃, TMS) δ 2.24 (s, 3H),
2.65 (s, 3H), 6.67–6.69 (m, 2H), 6.74–6.81 (m, 8H), 7.05–7.07 (m, 3H), 7.11–7.12 (m, 2H), 7.16–7.19 (m, 3H), 7.21–7.24 (m, 3H), 7.68 (m, 1H); $^{13}$C NMR (100 Hz, CDCl$_3$, TMS) $\delta$ 36.0, 36.2, 118.7, 124.5, 124.9, 125.2, 125.5, 125.6, 126.3, 126.5, 126.6, 126.8, 127.7 (2C), 130.2, 130.9, 131.1 (2C), 135.1, 135.4, 138.0, 139.1, 139.9, 140.1, 140.5, 141.6 (2C), 148.7, 153.9; IR $\nu$ 1723, 1158 cm$^{-1}$. HRMS (EI) Calcd for C$_{37}$H$_{28}$BrNO$_2$ (M$^+$) 597.1303, Found 597.1301.

1,2,3,4-tetraphenylanthracen-9-yl dimethylcarbamate (4aa) yellow solid (86 mg, 76%); mp ($^{\circ}$C) 227–229; $^1$H NMR (400 Hz, CDCl$_3$, TMS) $\delta$ 2.47 (s, 3H), 2.71 (s, 3H), 6.67–6.69 (m, 1H), 6.77–6.84 (m, 9H), 7.00–7.03 (m, 1H), 7.07–7.11 (m, 1H), 7.15–7.17 (m, 2H), 7.23 (m, 2H), 7.27–7.43 (m, 6H), 7.77–7.80 (m, 2H), 8.12 (s, 1H); $^{13}$C NMR (100 Hz, CDCl$_3$, TMS) $\delta$ 36.1, 36.4, 121.4, 123.7, 124.7, 125.0, 125.3, 125.5, 125.8, 126.2, 126.4, 126.6, 127.6, 127.7, 128.6, 129.8, 131.1, 131.2, 131.4, 131.7, 132.1, 134.8, 138.4, 138.6, 139.9, 140.4, 140.6, 141.1, 142.5, 143.5, 154.2; IR $\nu$ 1727, 1160 cm$^{-1}$. HRMS (EI) Calcd for C$_{41}$H$_{31}$NO$_2$ (M$^+$) 569.2355, Found 569.2358.

5,6,7,8-tetraphenylphenanthren-9-yl dimethylcarbamate (4ja) yellow solid (85 mg, 75%); mp ($^{\circ}$C) 225–226; $^1$H NMR (400 Hz, CDCl$_3$, TMS) $\delta$ 2.26 (s, 3H), 2.67 (s, 3H), 6.63–6.68 (m, 4H), 6.77–6.82 (m, 6H), 6.93–6.97 (m, 1H), 7.04–7.14 (m, 10H), 7.32–7.36 (m, 2H), 7.51–7.53 (m, 1H), 7.69–7.71 (m, 1H); $^{13}$C NMR (100 Hz, CDCl$_3$, TMS) $\delta$ 36.0, 36.2, 120.9, 124.1, 125.0, 125.1, 125.4, 126.1, 126.3, 126.4, 126.5, 127.1, 127.3, 128.2, 129.2, 129.6, 130.4, 131.3, 131.4 (2C), 132.9, 135.8, 138.4, 140.3, 140.6, 140.9, 141.1, 142.5, 143.3, 146.1, 154.2; IR $\nu$ 1727, 1160 cm$^{-1}$. HRMS (EI) Calcd for C$_{41}$H$_{31}$NO$_2$ (M$^+$) 569.2355, Found 569.2352.

3-bromo-5,6,7,8-tetrakis(4-chlorophenyl)naphthalen-1-yl dimethylcarbamate (4ib) yellow solid (75 mg, 51%); mp ($^{\circ}$C) > 280; $^1$H NMR (400 Hz, CDCl$_3$, TMS) $\delta$ 2.40 (s, 3H), 2.70 (s, 3H), 6.58–6.65 (m, 4H), 6.84–6.88 (m, 4H), 7.01–7.12 (m, 6H), 7.24–7.27 (m, 3H), 7.59 (m, 1H); $^{13}$C NMR (100 Hz, CDCl$_3$, TMS) $\delta$ 35.9, 36.2, 119.6, 125.1, 125.3, 127.0, 127.2, 127.4, 127.5, 128.4, 131.3, 131.9 (2C), 132.1 (3C), 132.2, 133.3, 134.8, 134.9, 136.9, 137.4, 137.7, 137.8, 139.1, 139.5, 139.9, 148.6, 153.7; IR $\nu$ 1726, 1492, 1155 cm$^{-1}$. HRMS (EI) Calcd for C$_{37}$H$_{24}$BrCl$_4$NO$_2$ (M$^+$)
3-bromo-5,6,7,8-tetrakis(4-fluorophenyl)naphthalen-1-yl dimethylcarbamate (4ic)
yellow solid (75 mg, 56%); mp (°C) > 280; ¹H NMR (400 Hz, CDCl₃, TMS) δ 2.39 (s, 3H), 2.69 (s, 3H), 6.52–6.68 (m, 8H), 6.80–6.84 (m, 2H), 6.94–6.99 (m, 2H), 7.04–7.12 (m, 4H), 7.24–7.26 (m, 1H), 7.62–7.63 (m, 1H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 35.9, 36.2, 113.5, 113.7, 113.9, 114.1, 115.0, 115.2, 119.3, 125.0, 125.2, 127.6, 131.5, 132.1, 132.2, 132.3, 132.4, 132.5, 132.6, 134.6, 135.0, 135.1, 135.5, 135.7, 137.2, 137.6, 139.8, 140.7, 148.6, 153.8, 159.4, 159.6, 160.2, 160.5, 161.9, 162.0, 162.6, 163.0; IR ν 1725, 1600, 1508, 1365, 1266, 1222, 820, 737 cm⁻¹. HRMS (EI) Calcd for C₅₇H₄₂BrF₄NO₂ (M⁺) 669.0927, Found 669.0925.

3-bromo-5,8-diethyl-6,7-diphenylnaphthalen-1-yl dimethylcarbamate (4id)
yellow solid (48 mg, 48%); mp (°C) 160–161; ¹H NMR (400 Hz, CDCl₃, TMS) δ 1.10 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.6 Hz, 3H), 2.80 (q, J = 14.8 Hz, 3H), 2.88 (q, J = 14.8 Hz, 3H), 3.08 (s, 3H), 3.21 (s, 3H), 6.94–7.00 (m, 3H), 7.07–7.14 (m, 5H), 7.28–7.32 (m, 1H), 7.36 (m, 1H), 7.40–7.52 (m, 1H), 8.22–8.23 (m, 1H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 15.4, 16.5, 24.0, 25.8, 36.5, 37.0, 118.3, 124.3, 124.8, 125.7, 126.0 (2C), 127.1, 127.3, 129.8, 130.1, 134.9, 135.3, 140.7, 141.1, 141.2, 141.5, 149.2, 155.1; IR ν 1735, 1596, 1442, 1373, 1240, 1155, 1046 cm⁻¹. HRMS (EI) Calcd for C₂₉H₂₈BrNO₂ (M⁺) 501.1303, Found 501.1306.

3-bromo-5,6,7,8-tetraphenylnaphthalen-1-ol (5) white solid (86 mg, 82%); mp (°C) > 280; ¹H NMR (400 Hz, CDCl₃, TMS) δ 5.62 (s, 1H), 6.77–6.89 (m, 3H), 7.07 (d, J = 2.0 Hz, 1H), 7.18–7.21 (m, 2H), 7.23–7.33 (m, 6H), 7.35–7.38 (m, 3H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 115.6, 120.1, 120.6, 122.0, 125.6, 126.6 (2C), 126.8, 127.7, 128.4, 128.6, 130.9 (2C), 131.0, 134.0, 135.0, 138.5, 138.8, 139.2, 139.3, 139.9, 140.0, 140.1, 143.2, 154.3; IR ν 3475, 2924, 1740, 1600, 1560, 1492, 1374, 1239 cm⁻¹. HRMS (EI) Calcd for C₃₄H₂₃BrO (M⁺) 526.0932, Found 526.0935.
$^1$H NMR and $^{13}$C NMR spectra

5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4ba
2-methyl-5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4ca
2-chloro-5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4da
2-bromo-5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4ea
3-methyl-5,6,7,8-tetraphenyl-1-yl dimethylcarbamate 4fa
3-methoxy-5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4ga
3-chloro-5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4ha
3-bromo-5,6,7,8-tetraphenynaphthalen-1-yl dimethylcarbamate 4ia
1,2,3,4-tetraphenylanthracen-9-yl dimethylcarbamate 4aa
5,6,7,8-tetraphenylphenanthren-9-yl dimethylcarbamate 4ja
3-bromo-5,6,7,8-tetrakis(4-chlorophenyl)naphthalen-1-yl dimethylcarbamate 4ib
3-bromo-5,8-diethyl-6,7-diphenylnapthalen-1-yl dimethylcarbamate 4id
3-bromo-5,6,7,8-tetraphenynaphthalen-1-ol
Mechanism studies