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A simple approach to bis-spirocycles and spiroindole derivatives via green methods such as Fischer indolization, ring-closing metathesis, and Suzuki–Miyaura cross-coupling

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Abstract: We have developed a simple synthetic methodology for bis-spirocycles and spiroindole derivatives starting with a commercially available 6-bromo-2-tetralone. Here, we have used Fischer indolization, ring-closing metathesis, and Suzuki–Miyaura cross-coupling as key steps to assemble a variety of spirocyclic frameworks. The methodology developed here is simple and it may be useful to prepare various spirocycles containing indole moiety.

Key words: Spirocycles, Fischer indolization, ring-closing metathesis, Suzuki coupling, Grubbs' catalyst

1. Introduction

Generating molecular complexity from simple and readily available starting materials has received a great deal of attention from synthetic chemists. Suzuki coupling and its related processes provide intricate molecular architectures by transforming the C – X bond into a new C – C bond under operationally simple reaction conditions.[1–10]

In recent years, spirocycles[11–21] have been found to be useful building blocks in preparative organic chemistry for the construction of theoretically as well as biologically interesting targets. The structures of some biologically important substances (**1**–**6**) containing the spiro-linkage are shown in Figure 1.[22,23] In this context, development of simple and green protocols involving short synthetic sequences and minimum amounts of byproducts is highly desirable.

During the past two decades, olefin metathesis has become a useful synthetic tool for the construction of C – C double bonds.[24–37] Although numerous methods are available for the synthesis of spirocycles,[38–40] there is a continuous need to develop new and simple approaches where one can improve the overall synthetic economy.

We are actively engaged in developing new synthetic strategies for spirocycles. In this regard, spirocycles containing indeno[1,2-*b*]indole frameworks have been reported via Fischer indolization and ring-closing metathesis (RCM) reaction as key steps.[41] Since this strategy is very simple and useful to construct medicinally important compounds, we intended to expand this strategy for the development of new chemical space containing indole and spiro moieties.

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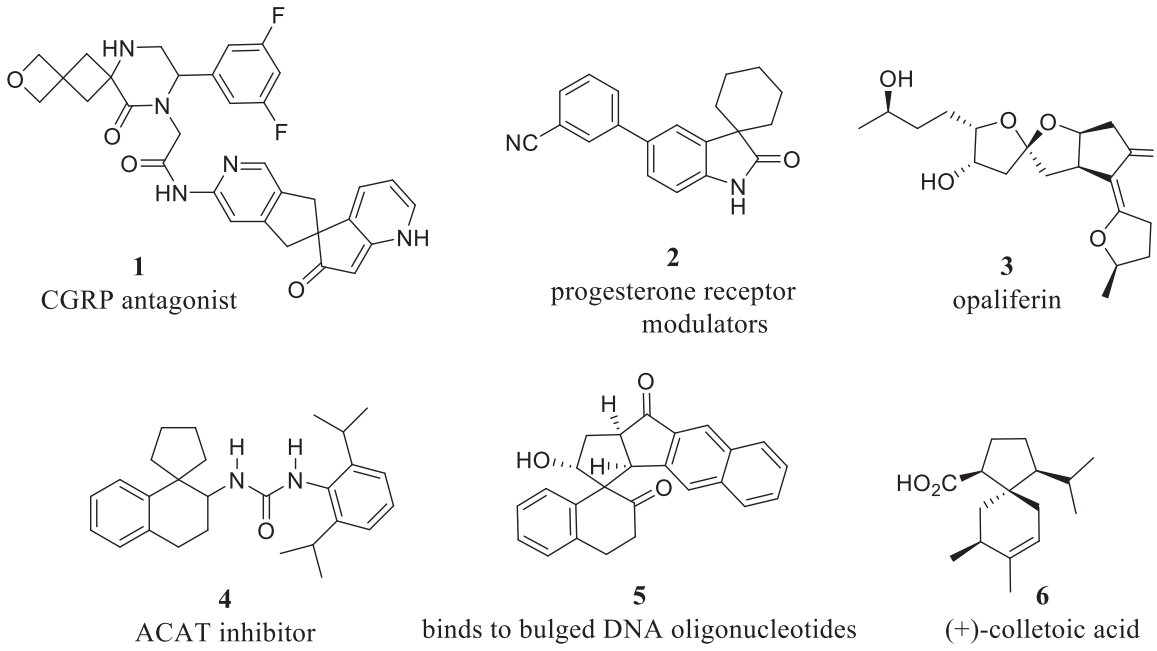
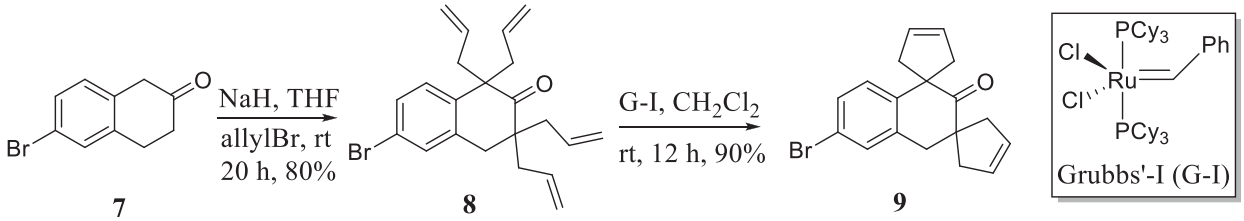


Figure 1. Some important bioactive molecules containing spiro-linkages.

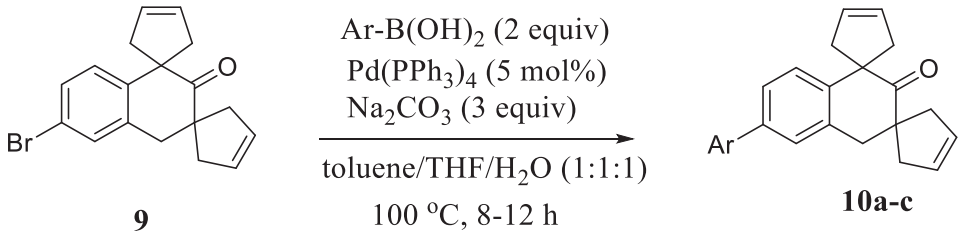
2. Results and discussion

To assemble spirocycles, we began our journey with the synthesis of tetra-allyl building block **8** starting with a readily available β-tetralone **7** under NaH/allyl bromide conditions. The tetra-allyl compound **8** was then subjected to a double RCM sequence with the aid of Grubbs' first-generation (G-I) catalyst to yield the desired bis-spirocyclic compound **9** in excellent yield (Scheme 1). Later, the bromo derivative **9** was subjected to the Suzuki reaction with different boronic acids to deliver the cross-coupling products (Figure 2). To this end, the Suzuki coupling reaction of commercially available phenyl boronic acid was performed with **9** and the desired cross-coupling product **10a** was obtained in 97% yield (Scheme 2; Figure 2). To expand the scope of the coupling reaction, 4-formylphenyl boronic acid and 4-cyanophenyl boronic acid were also used to deliver the desired cross-coupling products **10b** and **10c** in respectable yields (Scheme 2; Figure 2).



Scheme 1. Synthesis of bis-spirocyclic system **9**.

Indoles[42–48] are privileged scaffolds and they are found as critical components in a large number of biologically active substances.[49–56] Recently, many efforts have been directed towards the synthesis of diverse indole derivatives. Therefore, we are interested in synthesizing various spiroindole derivatives by employing RCM, Fischer indolization, and the Suzuki–Miyaura cross-coupling reactions as key steps. To this end, we started our journey by performing the di-allylation of β-ketone **7** with K_2CO_3/allyl bromide to give the



Scheme 2. General approach to spirocycles via the Suzuki coupling reaction.

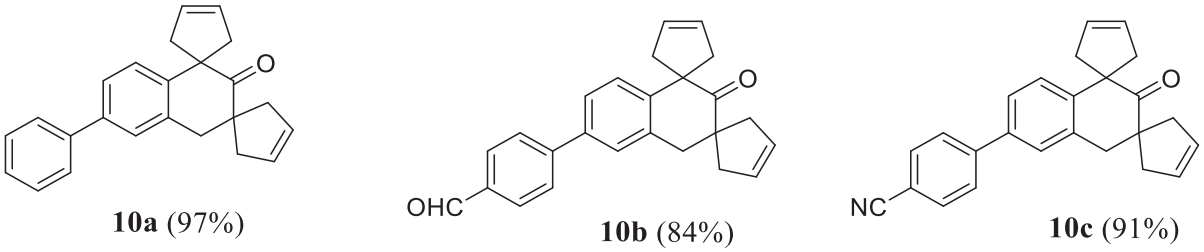
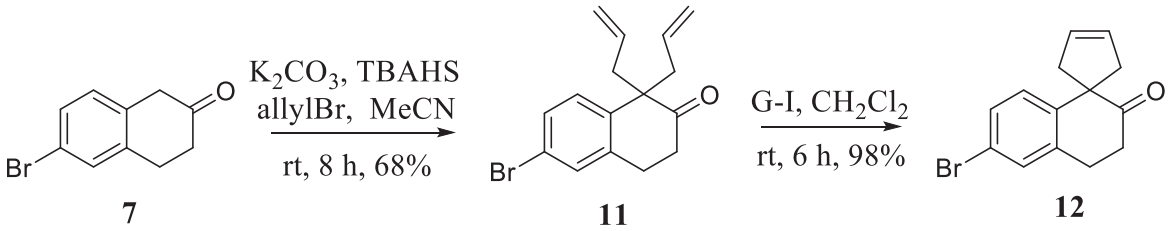


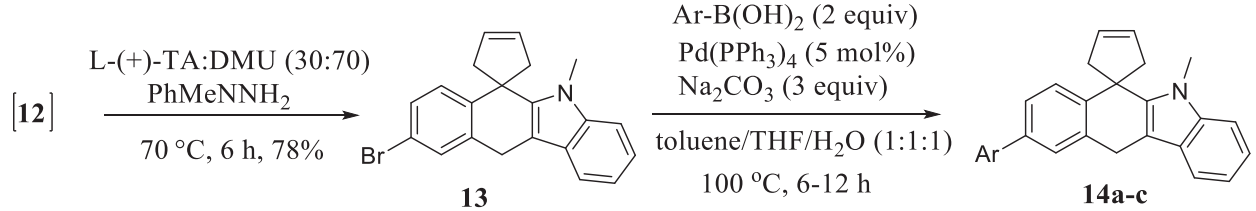
Figure 2. List of cross-coupling products assembled via Scheme 2.

desired product **11** (68%), which on treatment with G-I catalyst in dry CH_2Cl_2 gave the spiro-system **12** in 98% yield (Scheme 3).



Scheme 3. Synthesis of key spiro building block **12**.

Our next task is to use the carbonyl group present in spiro compound **12** for the construction of spiroindole derivatives. For this purpose, we used green conditions to realize the Fischer indolization. To this end, compound **12** was reacted with 1-methyl-1-phenylhydrazine in a low-melting mixture of L-(+)-tartaric acid and *N*,*N*-dimethylurea [L-(+)-TA:DMU] (30:70) to deliver spiroindole derivative **13** (78%). To expand the chemical space of the spiroindoles, bromo derivative **13** was treated with different boronic acids to give the spiroindole derivatives **14a**–**14c** in good to excellent yields (Scheme 4; Figure 3).



Scheme 4. General strategy to spiroindoles.

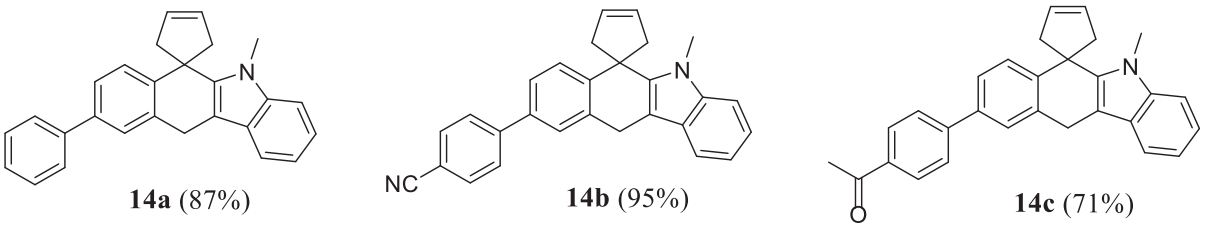


Figure 3. List of cross-coupling products assembled via Scheme 4.

In summary, we have developed a simple methodology to generate bis-spirocycles as well as spiroindole derivatives via RCM, Fischer indolization, and the Suzuki–Miyaura cross-coupling reaction as key steps. The strategy developed here opens up a new and short synthetic sequence to various densely functionalized spirocycles under operationally simple reaction conditions and this methodology is well suited to create a library of novel spiroindole derivatives.

3. Experimental

All commercially accessible reagents were used without further purification and the reactions involving air-sensitive catalysts or reagents were performed in degassed solvents. Moisture-sensitive materials were transferred using the syringe-septum technique and the reactions were maintained under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on glass plates of 7.5 $\times$ 2.5 cm coated with Acme's silica gel GF 254 (containing 13% calcium sulfate as a binder) by using a suitable mixture of EtOAc and petroleum ether for development. Column chromatography was performed by using Acme's silica gel (100–200 mesh) with an appropriate mixture of EtOAc and petroleum ether. The coupling constants (J) are given in hertz and chemical shifts are denoted in parts per million downfield from the internal standard, tetramethylsilane (TMS). The abbreviations s, d, t, q, m, dd, and td refer to singlet, doublet, triplet, quartet, multiplet, doublet of doublets, and triplet of doublets, respectively. Grubbs' catalyst was purchased from Sigma Aldrich. Infrared (IR) spectra were recorded on a Nicolet Impact-400 FT IR spectrometer in $CHCl_3$. Proton nuclear magnetic resonance (^{1}H NMR, 400 MHz, and 500 MHz) spectra and carbon nuclear magnetic resonance (^{13}C NMR, 100 MHz, and 125 MHz) spectra were recorded on a Bruker spectrometer. The high-resolution mass measurements were carried out by using an electrospray ionization (ESI, Q-ToF) spectrometer.

Synthesis of compound 8: To a suspension of sodium hydride (128 mg, 5.33 mmol) in dry THF (20 mL), tetralone **7** (200 mg, 0.89 mmol) was added, and the reaction mixture was stirred for 10 min at room temperature. Allyl bromide (0.5 mL, 5.33 mmol) was then added and the stirring was continued for 20 h at the same temperature. At the conclusion of the reaction (TLC monitoring), the reaction mixture was diluted with EtOAc and the solvent was removed under reduced pressure. The compound was then extracted with CH_2Cl_2 and the crude product was purified by silica gel column chromatography (1% EtOAc-petroleum ether) to afford the desired tetra-allylated compound **8** (273 mg, 80%) as a thick colorless liquid.

R_f = 0.58 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (dd, J_1 = 7.4 Hz, J_2 = 13.9 Hz, 2H), 2.25 (dd, J_1 = 7.4 Hz, J_2 = 14.0 Hz, 2H), 2.43 (dd, J_1 = 7.2 Hz, J_2 = 14.0 Hz, 2H), 2.69 (dd, J_1 = 7.4 Hz, J_2 = 13.9 Hz, 2H), 2.86 (s, 2H), 4.94–5.09 (m, 8H), 5.23–5.41 (m, 2H), 5.61–5.68 (m, 2H), 7.11 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 2.0 Hz, 1H), 7.38 (dd, J_1 = 2.1 Hz, J_2 = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.62, 39.20, 42.30, 48.43, 55.52, 119.15, 119.28, 120.68, 129.16, 129.66, 132.05, 133.12, 133.22, 136.75, 137.86, 213.52; IR ($CHCl_3$): υ_{max} = 1265, 1605, 1639, 1711, 2855, 2926, 3054 cm^{-1};

HRMS (Q-ToF): m/z calcd. for $C_{22}H_{25}BrNaO$ $[M+Na]^+$ 407.0981; found: 407.0983.

Synthesis of compound 9: The solution of compound **8** (150 mg, 0.39 mmol) in CH_2Cl_2 (25 mL) was purged with nitrogen for 15 min. The G-I catalyst (32 mg, 10 mol%) was then added and the reaction mixture was stirred at room temperature for 12 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (2% EtOAc-petroleum ether) to deliver the desired RCM product **9** (115 mg, 90%) as a thick colorless liquid.

R_f = 0.55 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.05 (d, J = 14.7 Hz, 2H), 2.48 (d, J = 14.5 Hz, 2H), 2.69 (d, J = 15.1 Hz, 2H), 2.90 (s, 2H), 3.09 (d, J = 15.2 Hz, 2H), 5.51 (s, 2H), 5.62 (s, 2H), 7.02 (d, J = 8.4 Hz, 1H), 7.21 (s, 1H), 7.25 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.67, 42.87, 47.98, 52.65, 56.37, 120.24, 127.25, 128.05, 128.18, 130.44, 131.46, 136.48, 143.56, 216.30; IR ($CHCl_3$): υ_{max} = 1266, 1652, 1708, 2852, 2921, 3052 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{18}H_{17}BrNaO$ $[M+Na]^+$ 351.0355; found: 351.0355.

General procedure for the Suzuki–Miyaura cross-coupling reaction of 9 and 13: To a solution of bromo derivatives **9** or **13** in THF/toluene/water (1:1:1, each 10 mL) were added Na_2CO_3 (3.0 equiv) and arylboronic acid (2.0 equiv). The reaction mixture was purged with nitrogen for 20 min. $Pd(PPh_3)_4$ (5 mol%) catalyst was then added and the reaction mixture was heated at 100 °C. At the conclusion of the reaction (8–12 h, TLC monitoring), the reaction mixture was diluted with water and the organic layer was extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the crude products were purified by silica gel column chromatography using appropriate mixtures of EtOAc-petroleum ether to afford the desired cross-coupling products.

Compound 10a: Thick colorless liquid; yield = 97% (24 mg, starting from 25 mg of **9**); reaction time = 8 h; R_f = 0.60 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21 (d, J = 14.3 Hz, 2H), 2.68 (d, J = 14.5 Hz, 2H), 2.83 (d, J = 14.1 Hz, 2H), 3.09 (s, 2H), 3.22 (d, J = 14.3 Hz, 2H), 5.62 (s, 2H), 5.75 (s, 2H), 7.31–7.39 (m, 3H), 7.43–7.61 (m, 3H), 7.61 (d, J = 1.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.33, 43.12, 48.00, 52.96, 56.56, 125.94, 126.14, 127.14, 127.40, 127.43, 128.17, 128.29, 128.94, 134.67, 139.40, 140.79, 143.57, 217.16; IR ($CHCl_3$): υ_{max} = 1265, 1435, 1704, 2873, 2929, 3055 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{24}H_{22}NaO$ $[M+Na]^+$ 349.1563; found: 349.1565.

Compound 10b: Thick colorless liquid; yield = 84% (27 mg, starting from 30 mg of **9**); reaction time = 12 h; R_f = 0.51 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.19 (d, J = 14.5 Hz, 2H), 2.66 (d, J = 14.4 Hz, 2H), 2.82 (d, J = 14.7 Hz, 2H), 3.10 (s, 2H), 3.22 (d, J = 14.9 Hz, 2H), 5.61 (s, 2H), 5.75 (s, 2H), 7.35 (d, J = 8.2 Hz, 1H), 7.43 (s, 1H), 7.51 (dd, J_1 = 1.6 Hz, J_2 = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.95 (d, J = 8.2 Hz, 2H), 10.05 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.25, 43.07, 48.03, 52.91, 56.63, 126.23, 126.42, 127.61, 127.66, 128.15, 128.29, 130.47, 135.06, 135.35, 137.88, 145.02, 146.80, 192.05, 216.77; IR ($CHCl_3$): υ_{max} = 1266, 1587, 1712, 1731, 28,71, 2957, 3054 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{25}H_{23}O_2$ $[M+H]^+$ 355.1693; found: 355.1696.

Compound 10c: Thick colorless liquid; yield = 91% (34 mg, starting from 35 mg of **9**); reaction time = 10 h; R_f = 0.55 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.18 (d, J = 15.6 Hz, 2H), 2.64 (d, J = 15.6 Hz, 2H), 2.81 (d, J = 15.6 Hz, 2H), 3.09 (s, 2H), 3.22 (d, J = 15.6 Hz, 2H), 5.61 (s, 2H), 5.74 (s, 2H), 7.35 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.45 (dd, J_1 = 1.8 Hz, J_2 = 8.2 Hz, 1H), 7.68–7.74 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.21, 43.05, 48.02, 52.88, 53.60, 56.61, 111.03, 119.10,

126.28, 126.33, 127.46, 127.70, 128.14, 128.28, 132.78, 135.17, 137.35, 145.23, 145.28, 216.65; IR ($CHCl_3$): υ_{max} = 1265, 1606, 1706, 2229, 2872, 2957, 3055 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{25}H_{21}NNaO$ $[M+Na]^+$ 374.1515; found: 374.1515.

Synthesis of compound 11: To a stirred solution of compound **7** (200 mg, 5.33 mmol) and K_2CO_3 (614 mg, 4.45 mmol) in dry MeCN (15 mL), allyl bromide (0.2 mL, 2.67 mmol) was added and the reaction mixture was stirred for 8 h at room temperature. Later, K_2CO_3 was filtered through the glass sintered funnel and the crude product was purified by silica gel column chromatography (5% EtOAc-petroleum ether) to give the desired di-allylated compound **11** (185 mg, 68%) as a thick colorless liquid.

R_f = 0.51 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45 (dd, J_1 = 6.6 Hz, J_2 = 13.6 Hz, 2H), 2.50–2.53 (m, 2H), 2.74 (dd, J_1 = 8.1 Hz, J_2 = 13.6 Hz, 2H), 2.92 (t, J = 6.9 Hz, 2H), 4.87–4.92 (m, 4H), 5.30–5.38 (m, 2H), 7.19 (d, J = 8.6 Hz, 1H), 7.31 (d, J = 1.1 Hz, 1H), 7.40 (dd, J_1 = 2.2 Hz, J_2 = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.69, 40.06, 45.16, 56.05, 118.90, 120.38, 129.03, 130.15, 131.08, 133.06, 138.46, 139.44, 212.88; IR ($CHCl_3$): υ_{max} = 1265, 1602, 1677, 2855, 2920, 3052 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{16}H_{17}BrNaO$ $[M+Na]^+$ 327.0355; found: 327.0355.

Synthesis of compound 12: The solution of compound **11** (170 mg, 0.56 mmol) in CH_2Cl_2 (20 mL) was purged with nitrogen for 15 min. The G-I catalyst (23 mg, 5 mol%) was then added and the reaction mixture was stirred at room temperature for 6 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (5% EtOAc-petroleum ether) to afford the desired RCM product **12** (151 mg, 98%) as a thick colorless liquid.

R_f = 0.50 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.55 (d, J = 15.0 Hz, 2H), 2.70 (t, J = 7.1 Hz, 2H), 3.06 (t, J = 6.8 Hz, 2H), 3.17 (d, J = 15.3 Hz, 2H), 5.69 (s, 2H), 7.11 (d, J = 8.4 Hz, 1H), 7.30 (s, 1H), 7.33 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.64, 37.38, 46.81, 56.77, 120.20, 128.03, 128.12, 130.49, 130.62, 136.96, 143.91, 212.03; IR ($CHCl_3$): υ_{max} = 1216, 1446, 1592, 1673, 2853, 2925, 3019 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{14}H_{13}BrNaO$ $[M+Na]^+$ 299.1234; found: 299.1238.

Synthesis of compound 13: To a clear melted mixture (1.5 g) of L-(+)-TA-DMU (30:70) at 70 °C, 1-methyl-phenyl hydrazine (0.1 mL, 0.72) and compound **12** (100 mg, 0.36 mmol) were added. The reaction mixture was stirred at 70 °C for 6 h. At the conclusion of the reaction (TLC monitoring), the reaction mixture was diluted with water under hot conditions. The reaction mixture was cooled to room temperature and filtered through a sintered glass funnel, and the solid material was washed with water (4 × 30 mL). The crude product was purified by silica gel column chromatography (103 mg, 78%) as a thick colorless liquid.

R_f = 0.50 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.99, 3.02, (ABq, J = 16.2 Hz, 4H), 3.71 (s, 3H), 4.16 (s, 2H), 6.09 (s, 2H), 7.06–7.11 (m, 1H), 7.17–7.20 (m, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.28 (s, 2H), 7.34 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.69, 30.57, 42.59, 52.96, 105.28, 108.95, 118.37, 119.38, 119.61, 121.82, 126.00, 127.40, 130.67, 131.10, 131.16, 133.88, 138.39, 138.99, 146.93; IR ($CHCl_3$): υ_{max} = 1265, 1642, 2859, 2925, 3053 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{21}H_{19}BrN$ $[M+H]^+$ 364.0690; found: 364.0695.

Compound 14a: Sticky liquid; yield = 87% (17 mg, starting from 20 mg of **13**); reaction time = 6 h; R_f = 0.52 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.98, 3.05, (ABq, J = 15.9 Hz, 4H), 3.60 (s, 3H), 4.14 (s, 2H), 5.98 (s, 2H), 7.07 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.3 Hz, 1H),

7.22–7.27 (m, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.39–7.47 (m, 2H), 7.51 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.95, 30.55, 42.61, 53.00, 105.85, 108.90, 118.39, 119.24, 121.64, 126.02, 126.22, 126.47, 127.06, 127.18, 127.30, 128.92, 131.11, 131.80, 138.38, 138.85, 139.47, 141.02, 147.02; IR ($CHCl_3$): υ_{max} = 1265, 1421, 1650, 2856, 2959, 3055 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{27}H_{24}N$ $[M+H]^+$ 362.1903; found: 362.1909.

Compound 14b: White semisolid; yield = 95% (20 mg, starting from 20 mg of **13**); reaction time = 12 h; R_f = 0.47 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.08, 3.11, (ABq, J = 16.9 Hz, 4H), 3.74 (s, 3H), 4.27 (s, 2H), 6.08 (s, 2H), 7.19 (t, J = 7.0 Hz, 1H), 7.28–7.31 (m, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.52 (dd, J_1 = 2.1 Hz, J_2 = 8.3 Hz, 1H), 7.56 (d, J = 1.7 Hz, 1H), 7.62–7.75 (m, 2H), 7.77 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.97, 30.60, 42.72, 53.03, 105.62, 108.98, 110.87, 118.37, 119.22, 119.36, 121.81, 126.11, 126.43, 126.46, 127.33, 127.70, 131.12, 132.30, 132.79, 136.81, 138.41, 139.16, 145.51, 148.58; IR ($CHCl_3$): υ_{max} = 1266, 1408, 1649, 2148, 2842, 3052 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{28}H_{23}N_2$ $[M+H]^+$ 387.1856; found: 387.1855.

Compound 14c: Thick yellow liquid; yield = 71% (42 mg, starting from 53 mg of **13**); reaction time = 10 h; R_f = 0.45 (silica gel, 10% EtOAc-petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.68 (s, 3H), 3.12, 3.20, (ABq, J = 15.7 Hz, 4H), 3.74 (s, 3H), 4.28 (s, 2H), 6.13 (s, 2H), 7.18–7.21 (m, 1H), 7.27–7.29 (m, 1H), 7.30 (d, J = 1.1 Hz, 1H), 7.56–7.63 (m, 4H), 7.76 (d, J = 4.9 Hz, 2H), 8.08 (d, J = 4.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.85, 26.99, 30.60, 42.73, 53.03, 105.76, 108.96, 118.39, 119.34, 121.76, 126.18, 126.30, 126.53, 127.21, 127.32, 127.47, 129.14, 131.13, 132.13, 135.94, 137.52, 138.43, 139.29, 145.64, 148.14, 197.98; IR ($CHCl_3$): υ_{max} = 1268, 1637, 1681, 2943, 3001 cm^{-1}; HRMS (Q-ToF): m/z calcd. for $C_{29}H_{25}NNaO$ $[M+Na]^+$ 426.1828; found: 426.1827.

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