Supporting Information

Palladium Catalysed [3+2]-Annulation Reaction of Vinylcyclopropanes with Pentafulvenes: Synthesis of Polysubstituted Spiro[4,4]nona-6,8-dienes

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1. General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. $^1$H NMR, $^{13}$C NMR spectra were recorded on 400 MHz or 100 MHz spectrometers. The spectra were recorded in CDCl$_3$ as solvent at room temperature, $^1$H and $^{13}$C NMR chemical shifts are reported in ppm relative to either the residual solvent peak or TMS as an internal standard. Data for $^1$H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = double, t = triplet, m = multiplet, dd = double doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for $^{13}$C NMR were reported as chemical shift. HRMS were performed on Bruker Apex II mass instrument (ESI).
2. Procedure for the palladium catalysed [2+3]-annulation reaction

\[
\text{R}^1 \text{R}^2 + \text{R}^3 \text{R}^4 \xrightarrow{\text{Pd}_2(\text{dba})_3 (2.5 \text{ mmol } \%), \text{dppp (5 mmol %)}} \text{CH}_3\text{CN, 0 °C}, 4\text{Å MS}} \\
\text{1a, R}^3 = \text{CN}; \text{R}^4 = \text{CN}; \text{1b, R}^3 = \text{CO}_2\text{Me}; \text{R}^4 = \text{CN}; \text{1c, R}^3 = \text{CO}_2\text{Pr}, \text{R}^4 = \text{CN}; \text{1d, R}^3 = \text{CO}_2\text{Bu}, \text{R}^4 = \text{CN};
\]

Under an atmosphere of dry nitrogen, tris(dibenzylideneacetone)dipalladium (Pd$_2$dba$_3$) (4.6 mg, 0.005 mmol), 1,3-bis (diphenylphosphino) propane (4.1 mg, 0.01 mmol), 4 Å MS (100 mg), and 0.5 mL of anhydrous CH$_3$CN were added into an oven-dried reaction tube equipped with a stir bar, and the solution was stirred at 30 °C for half an hour. When the solution changed to green, the reaction tube was cooled to 0 °C. Next, a solution of vinylcyclopropane 1 (0.4 mmol) and pentafulvene 2 (0.2 mmol) in anhydrous CH$_3$CN (1.5 mL) was transferred into the reaction tube via syringe, and mixture was stirred at 0°C until the material exhausted completely. Filtration of the reaction mixture through silica gel and removal of the solvent in vacuo offered the crude mixture of products. Isolation of this mixture by silica gel chromatography offered the title products. The dr value was determined by $^1$H NMR spectrum of the diastereomeric mixture of products.

For the reaction of vinylcyclopropane 1e with pentafulvene 2a, the solvent was changed into dimethyl sulfoxide and the temperature was increased to 30 °C.

3. Procedure for the Diels-Alder reactions of annulation products

\[
\text{major-3aa} \xrightarrow{\text{DCM, rt, 3 days}} \text{anti-endo-5 (48% yield)} + \text{sym-endo-5 (50% yield)}
\]

In a 5 mL reaction tube equipped with a stir bar was charged with the compound major-3aa (60.4
mg, 0.20 mmol) and the N-phenyl maleimide (45.0 mg, 0.26 mmol) in DCM (0.2 M). Then the solution was stirred at ambient temperature for 3 days. After completion of the reaction as detected by TLC, the mixture was concentrated under reduced pressure, the product \textit{anti-end\textsubscript{o}-5} was isolated in 48% yield (45.9 mg, 0.10 mmol) and the product \textit{syn-end\textsubscript{o}-5} was isolated in 39% yield (36.8 mg, 0.08 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:5 / V:V).

In a 5 mL reaction tube equipped with a stir bar was charged with the compound \textit{major-3ba} (67.2 mg, 0.20 mmol) and the N-phenyl maleimide (45.0 mg, 0.26 mmol) in DCM (0.2 M). Then the solution was stirred at 30 °C for overnight. After completion of the reaction as detected by TLC, the mixture was concentrated under reduced pressure, the product \textit{anti-end\textsubscript{o}-6} was isolated in 40% yield (40.8 mg, 0.08 mmol) and the product \textit{syn-end\textsubscript{o}-6} was isolated in 40% yield (39.5 mg, 0.08 mmol) by silica gel chromatography (EtOAc:petroleum ether:DCM = 1:10:4/V:V:V).

\textbf{4. Procedure for the RCM reaction of annulation product 3ao}

In a 5 mL reaction tube equipped with a stir bar, Grubbs-II catalyst (8.5 mg, 0.01 mmol) was added to a stirred solution of \textit{3ao} (26.5 mg, 0.1 mmol) in anhydrous benzene (1 mL) under argon. The mixture was refluxed for 3h with stirring. After completion of the reaction as detected by TLC, distilled water was added, and the mixture was extracted with EtOAc (10×3 mL). The combined organic phase was washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}. After filtration, the solvent was removed by rotary evaporator, and the product \textit{7} was isolated as a colorless oil in 51% yield (13.5 mg, 0.05 mmol) by silica gel chromatography (EtOAc:petroleum ether =1:15/ V:V).
5. Procedure for the synthesis of thiobarbital 8

The compound 3ea was prepared according to general procedure with vinylcyclopropane 1e (94.4 mg, 0.8 mmol) and pentafuvene 2a (72.2 mg, 0.4 mmol) in DMSO (0.1 M) at 30°C for 10h. After completion of the reaction as detected by TLC, the product mixture was isolated in 66% yield (99.2 mg, 0.26 mmol) with 1:1.1 dr as a colorless oil by silica gel chromatography (EtOAc: petroleum ether =1:35 /V:V).

Thiourea (91.3 mg, 1.2 mmol) and t-BuOK (49.4 mg, 0.44 mmol) were added into the solution of 3ea (73.7 mg, 0.2 mmol) in 0.4 mL DMSO, and the reaction mixture was stirred at 30 °C for 1 hour. Then the reaction mixture was diluted with 10 mL of hydrochloric acid (0.1 N) and extracted with EtOAc (10×3 mL). The combined organic phase was washed with water and brine successively, and dried over Na₂SO₄. After removal of the solvent in vacuo, the products trans-8 and cis-8 was isolated respectively in 41% and 37% yields by silica gel chromatography (EtOAc:petroleum ether = 1:5/V:V).

6. Characterization data of compounds

1-(4-Methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3aa)

The products trans-3aa and cis-3aa were obtained in 98% total yield (59.2 mg, 0.19 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3aa is a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.31 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 4.8 Hz, 1H), 6.30 (d, J = 5.2 Hz, 1H), 6.25–6.20 (m, 2H), 5.82–5.74 (m, 1H), 5.13–5.06 (m, 2H), 4.06 (s, 1H), 3.76 (s, 3H), 3.24 (dd, J = 14.8, 7.2 Hz, 1H), 3.03 (dd, J = 14.0, 7.6 Hz, 1H), 2.73 (dd, J = 14.0, 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 159.9, 139.2, 138.2, 136.4, 132.5, 132.4, 130.0, 124.6, 116.5, 116.5,
116.3, 116.0, 113.7, 67.9, 59.2, 55.2, 46.6, 43.0, 40.2. HRMS (ESI) m/z calcd. for C_{20}H_{19}N_{2}O [M+H]^+ 303.1492, found: 303.1484.

1-(2-Methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ab)

The products trans-3ab and cis-3ab were obtained in 90% total yield (54.4 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V).

The major product trans-3ab is a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.47 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.30–7.26 (m, 1H), 6.89–6.86 (m, 2H), 6.64 (td, \(J = 3.2, 1.6\) Hz, 1H), 6.33–6.31 (m, 1H), 6.27–6.23 (m, 2H), 5.82 (dd, \(J = 17.2, 10.4, 7.6\) Hz, 1H), 5.12–5.07 (m, 2H), 4.89 (s, 1H), 3.84 (s, 3H), 3.25 (dd, \(J = 14.8, 7.2\) Hz, 1H), 3.07 (dd, \(J = 14.0, 7.2\) Hz, 1H), 2.78 (dd, \(J = 14.0, 7.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.3, 139.3, 138.4, 136.5, 132.3, 131.9, 130.0, 129.0, 121.9, 120.2, 116.7, 116.6, 116.3, 110.8, 68.3, 55.6, 50.2, 47.4, 44.2, 39.4. HRMS (ESI) m/z calcd. for C_{20}H_{19}N_{2}O [M+H]^+ 303.1492, found 303.1499.

1-(3-Methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ac)

The products trans-3ac and cis-3ac were obtained in 85% total yield (51.4 mg, 0.17 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V).

The major product trans-3ac is a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.24 (t, \(J = 8.0\) Hz, 1H), 6.96 (d, \(J = 7.6\) Hz, 1H), 6.91–6.88 (m, 1H), 6.87–6.85 (m, 1H), 6.62–6.60 (m, 1H), 6.33–6.31 (m, 1H), 6.30–6.28 (m, 1H), 6.26–6.24 (m, 1H), 5.82–5.73 (m, 1H), 5.14–5.07 (m, 2H), 4.06 (s, 1H), 3.77 (s, 3H), 3.27 (dd, \(J = 14.8, 7.6\) Hz, 1H), 3.05 (dd, \(J = 14.0, 7.6\) Hz, 1H), 2.76 (dd, \(J = 14.0, 7.6\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.3, 139.3, 138.2, 136.2, 134.3, 132.6, 132.4, 129.4, 121.0, 116.6, 116.3, 116.0, 114.4, 114.3, 67.9, 59.5, 55.3, 46.8, 43.4, 39.8. HRMS (ESI) m/z calcd. for C_{20}H_{19}N_{2}O [M+H]^+ 303.1492, found 303.1499.

1-(P-tolyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ad)

The products trans-3ad and cis-3ad were obtained in 97% total yield (57.2 mg, 0.194 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3ad is a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.26 (d, \(J = 6.8\) Hz, 2H), 7.10 (d, \(J = 8.0\) Hz, 2H), 6.62–6.02 (m, 1H), 0.194 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3ad is a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.26 (d, \(J = 6.8\) Hz, 2H), 7.10 (d, \(J = 8.0\) Hz, 2H), 6.62–6.02 (m, 1H), 6.31–6.29 (m,
1H), 6.27–6.21 (m, 2H), 5.81–5.73 (m, 1H), 5.13–5.07 (m, 2H), 4.05 (s, 1H), 3.27 (dd, J = 14.8, 7.2 Hz, 1H), 3.04 (dd, J = 14.0, 7.6 Hz, 1H), 2.74 (dd, J = 14.0, 7.6 Hz, 1H), 2.31 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 139.3, 138.9, 138.2, 136.3, 132.5, 132.4, 129.8, 129.1, 128.6, 116.6, 116.3, 116.0, 67.9, 59.5, 46.8, 43.3, 40.1, 21.2. HRMS (ESI) m/z calcd. for C20H19N2 [M+H]+ 287.1543, found 287.1540.

1-Phenyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ae)

The products trans-3ae and cis-3ae were obtained in 90% total yield (48.0 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3ae is a colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.38–7.29 (m, 5H), 6.61 (d, J = 5.2 Hz, 1H), 6.30 (d, J = 5.2 Hz, 1H), 6.23–6.26 (m, 2H), 5.77 (ddd, J = 17.6, 10.4, 7.6 Hz, 1H), 5.12 (d, J = 8.0 Hz, 1H), 5.09 (d, J = 14.4 Hz, 1H), 4.08 (s, 1H), 3.28 (dd, J = 14.8, 7.6 Hz, 1H), 3.06 (dd, J = 14.0, 7.6 Hz, 1H), 2.76 (dd, J = 14.0, 7.6 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 139.2, 138.1, 136.2, 132.6, 132.5, 131.0, 129.1, 128.7, 128.4, 116.6, 116.2, 116.0, 67.8, 59.7, 46.8, 43.4, 39.9, 19.3. HRMS (ESI) m/z calcd. for C19H16N2Na [M+Na]+ 295.1206, found 295.1208.

1-(4-Fluorophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3af)

The products trans-3af and cis-3af were obtained in 96% total yield (55.7 mg, 0.192 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3af is a colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.38–7.35 (m, 2H), 6.98 (t, J = 8.4 Hz, 2H), 6.64 (d, J = 5.2 Hz, 1H), 6.32 (d, J = 5.2 Hz, 1H), 6.26 (d, J = 5.2 Hz, 1H), 6.20 (d, J = 5.2 Hz, 1H), 5.79 (ddd, J = 17.6, 10.4, 7.2 Hz, 1H), 5.16–5.09 (m, 2H), 4.08 (s, 1H), 3.24 (dd, J = 14.4, 7.2 Hz, 1H), 3.05 (dd, J = 14.0, 7.2 Hz, 1H), 2.76 (dd, J = 14.0, 7.2 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 164.3 (d, J = 247.0 Hz, 1C), 161.8, 138.9, 138.0, 136.3, 132.8, 130.5 (d, J = 8.2 Hz, 1C), 128.4 (d, J = 3.0 Hz, 1C), 116.7, 116.0, 115.8, 115.4 (d, J = 21.0 Hz, 1C), 67.8, 58.9, 46.6, 43.0, 39.9. HRMS (ESI) m/z calcd. for C19H16FN2 [M+H]+ 291.1292, found 291.1292.

1-(4-Chlorophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ag)
The products *trans*-3ag and *cis*-3ag were obtained in 95% total yield (58.2 mg, 0.19 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/V:V). The major product *trans*-3ag is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.62 (d, $J = 5.2$ Hz, 1H), 6.32 (d, $J = 5.2$ Hz, 1H), 6.26 (d, $J = 5.2$ Hz, 1H), 6.20 (d, $J = 5.2$ Hz, 1H), 5.78 (ddd, $J = 17.2$, 10.4, 7.2 Hz, 1H), 5.15–5.08 (m, 2H), 4.06 (s, 1H), 3.24 (dd, $J = 14.2$, 7.2 Hz, 1H), 3.05 (dd, $J = 14.0$, 7.2 Hz, 1H), 2.75 (dd, $J = 14.0$, 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.8, 138.0, 136.2, 135.0, 132.8, 132.7, 131.0, 130.0, 128.6, 116.7, 116.0, 115.8, 67.7, 58.9, 46.6, 43.0, 39.7. HRMS (ESI) $m/z$ calcd. for C$_{19}$H$_{16}$ClN$_2$ [M+H]$^+$ 307.0997, found 307.0997.

1-(4-Bromophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ah)

The products *trans*-3ah and *cis*-3ah were obtained in 91% total yield (63.7 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/V:V). The major product *trans*-3ah is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.62 (d, $J = 5.2$ Hz, 1H), 6.32 (d, $J = 5.2$ Hz, 1H), 6.26 (d, $J = 5.2$ Hz, 1H), 6.20 (d, $J = 5.2$ Hz, 1H), 5.78 (ddd, $J = 17.2$, 10.4, 7.2 Hz, 1H), 5.15–5.08 (m, 2H), 4.05 (s, 1H), 3.24 (dd, $J = 14.4$, 7.2 Hz, 1H), 3.05 (dd, $J = 14.0$, 7.2 Hz, 1H), 2.75 (dd, $J = 14.0$, 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.8, 138.0, 136.2, 135.0, 132.8, 132.7, 131.0, 130.0, 128.6, 116.7, 116.0, 115.8, 67.7, 58.9, 46.6, 43.0, 39.7. HRMS (ESI) $m/z$ calcd. for C$_{19}$H$_{16}$BrN$_2$ [M+H]$^+$ 351.0491, found 351.0493.

1-(4-(Trifluoromethyl)phenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ai)

The products *trans*-3ai and *cis*-3ai were obtained in 76% total yield (51.7 mg, 0.15 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/V:V). The major product *trans*-3ai is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 5.2$ Hz, 1H), 6.33 (d, $J = 5.2$ Hz, 1H), 6.28 (d, $J = 5.2$ Hz, 1H), 6.22 (d, $J = 5.2$ Hz, 1H), 5.80 (ddd, $J = 17.2$, 10.4, 7.2 Hz, 1H), 5.17–5.10 (m, 2H), 4.14 (s, 1H), 3.28 (dd, $J = 14.8$, 7.2 Hz, 1H), 3.08 (dd, $J = 14.0$, 7.6 Hz, 1H), 2.78 (dd, $J = 14.0$, 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.8, 137.9, 136.6,
136.1, 133.0, 129.1, 125.5, 125.4, 122.5, 116.9, 115.8, 115.7, 67.7, 59.1, 46.7, 43.3, 39.6. HRMS (ESI) calcd for C$_{20}$H$_{16}$F$_3$N$_4$Na [M+Na]$^+$ 363.1080, found 363.1080.

1-(4-Nitrophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3aj)

The products trans-3aj and cis-3aj were obtained in 68% total yield (43.1 mg, 0.14 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:20/ V:V). The major product trans-3aj is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, $J$ = 8.8 Hz, 2H), 7.57 (d, $J$ = 8.8 Hz, 2H), 6.64 (d, $J$ = 5.6 Hz, 1H), 6.35 (d, $J$ = 5.6 Hz, 1H), 6.29 (d, $J$ = 5.6 Hz, 1H), 6.23 (d, $J$ = 5.2 Hz, 1H), 5.80 (ddd, $J$ = 17.2, 10.4, 7.2 Hz, 1H), 5.19–5.11 (m, 2H), 4.19 (s, 1H), 3.29 (dd, $J$ = 14.4, 7.2 Hz, 1H), 3.09 (dd, $J$ = 14.0, 7.6 Hz, 1H), 6.29 (d, $J$ = 14.0, 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.3, 139.7, 138.6, 137.8, 136.0, 133.3, 133.2, 129.6, 123.6, 117.1, 115.5, 67.7, 58.8, 46.7, 43.3, 39.3. HRMS (ESI) calcd for C$_{19}$H$_{15}$N$_3$O$_2$Na [M+Na]$^+$ 340.1056, found 340.1057.

1-(Furan-2-yl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ak)

The products trans-3ak and cis-3ak were obtained in 84% total yield (44.1 mg, 0.168 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3ak is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.44 (d, $J$ = 0.8 Hz, 1H), 6.40–6.33 (m, 4H), 6.28 (d, $J$ = 3.2 Hz, 1H), 6.21 (d, $J$ = 5.2 Hz, 1H), 5.57 (ddd, $J$ = 17.2, 10.4, 7.2 Hz, 1H), 5.09–5.04 (m, 2H), 4.13 (s, 1H), 3.60 (dd, $J$ = 16.4, 7.6 Hz, 1H), 3.09 (dd, $J$ = 14.0, 7.6 Hz, 1H), 2.71 (dd, $J$ = 14.0, 9.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.6, 143.1, 138.3, 137.3, 134.5, 132.7, 117.2, 116.7, 115.0, 110.6, 109.8, 68.4, 53.3, 47.4, 43.8, 38.7. HRMS (ESI) m/z calcd. for C$_{17}$H$_{15}$N$_3$O$_2$ [M+H]$^+$ 263.1179, found 263.1177.

1-(Thiophen-2-yl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3al)

The products trans-3al and cis-3al were obtained in 92% total yield (51.2 mg, 0.184 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product trans-3al is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.21 (d, $J$ = 5.2 Hz, 1H), 7.14 (d, $J$ = 3.2 Hz, 1H), 6.97–6.94 (m, 1H), 6.63 (d, $J$ = 5.6 Hz, 1H), 6.39 (d, $J$ = 5.6 Hz, 1H), 6.32 (d, $J$ = 5.2 Hz, 1H), 6.23 (d, $J$ = 5.2 Hz, 1H), 5.78 (ddd, $J$ = 17.6,
10.4, 7.2 Hz, 1H), 5.14–5.08 (m, 2H), 4.45 (s, 1H), 3.28 (dd, \( J = 14.4, 7.2 \) Hz, 1H), 3.04 (dd, \( J = 14.0, 7.6 \) Hz, 1H), 2.74 (dd, \( J = 14.0, 7.2 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.9, 137.7, 136.3, 133.9, 133.6, 133.1, 128.1, 126.7, 125.9, 125.9, 116.8, 116.0, 115.6, 68.1, 55.3, 46.5, 42.7, 41.2. HRMS (ESI) \( m/z \) calcd. for \( C_{17}H_{14}N_2Sn [M+Na]^+ \) 301.0770, found 301.0773.

**(E)-1-Styryl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3am)**

The product cis-3am were obtained in 93% yield (55.5 mg, 0.186 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.34–7.25 (m, 5H), 6.54–6.50 (m, 2H), 6.36 (d, \( J = 5.6 \) Hz, 1H), 6.32 (d, \( J = 5.2 \) Hz, 1H), 6.21 (d, \( J = 5.6 \) Hz, 1H), 6.03 (dd, \( J = 15.6, 9.6 \) Hz, 1H), 5.70 (ddd, \( J = 17.2, 10.0, 7.2 \) Hz, 1H), 5.08–5.02 (m, 2H), 3.59 (d, \( J = 9.2 \) Hz, 1H), 3.24 (dd, \( J = 15.2, 7.6 \) Hz, 1H), 2.94 (dd, \( J = 13.6, 6.8 \) Hz, 1H), 2.61 (dd, \( J = 13.6, 8.4 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.0, 137.6, 136.2, 135.7, 135.6, 132.9, 132.6, 128.7, 128.4, 126.9, 119.8, 116.4, 116.0, 115.1, 67.7, 57.9, 46.4, 43.1, 39.9. HRMS (ESI) \( m/z \) calcd. for \( C_{21}H_{19}N_2 [M+H]^+ \) 299.1543, found 299.1548.

**1-Propyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3an)**

The products trans-3an and cis-3an were obtained in 92% total yield (43.8 mg, 0.184 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V). The major product trans-3an is a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.40–6.35 (m, 2H), 6.30 (dt, \( J = 5.2, 1.6 \) Hz, 1H), 6.17 (dt, \( J = 5.6, 1.6 \) Hz, 1H), 5.63 (ddd, \( J = 17.6, 10.4, 7.6 \) Hz, 1H), 5.03–4.96 (m, 2H), 3.10 (dd, \( J = 15.2, 7.6 \) Hz, 1H), 2.94 (dd, \( J = 13.6, 8.8 \) Hz, 1H), 2.61 (dd, \( J = 13.6, 8.4 \) Hz, 1H), 2.34 (dd, \( J = 15.2, 7.6 \) Hz, 1H), 1.65–1.52 (m, 1H), 1.48–1.38 (m, 1H), 1.31–1.21 (m, 2H), 0.88 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 139.0, 138.8, 135.3, 132.3, 131.6, 116.7, 116.1, 115.0, 67.1, 53.3, 47.0, 43.3, 38.6, 30.7, 20.9, 13.9. HRMS (ESI) calcd for \( C_{16}H_{18}N_2Na [M+Na]^+ \) 261.1362, found 261.1361.

**1-(But-3-en-1-yl)-1-methyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ao)**

The diastereomeric mixture of the product 3ao was obtained in 72% total yield (38.0 mg, 0.144 mmol) by silica gel chromatography (EtOAc:petroleum ether =
The major product is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.55 (ddd, $J$ = 5.2, 2.4, 1.6 Hz, 1H), 6.32–6.27 (m, 2H), 6.26–6.24 (m, 1H), 5.77–5.70 (m, 1H), 5.52 (ddd, $J$ = 17.2, 11.2, 8.0 Hz, 1H), 5.04–4.95 (m, 2H), 4.91–4.84 (m, 2H), 3.35–3.30 (m, 1H), 2.84 (ddd, $J$ = 13.6, 8.0 Hz, 1H), 2.60 (dd, $J$ = 13.6, 10.8 Hz, 1H), 2.14–2.05 (m, 1H), 2.00–1.92 (m, 1H), 1.83 (td, $J$ = 14.8, 10.8 Hz, 1H), 1.7 (td, $J$ = 16.4, 12.0 Hz, 1H), 1.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.4, 137.9, 137.4, 135.7, 131.6, 130.7, 116.1, 115.6, 115.4, 70.2, 55.3, 45.4, 45.1, 41.7, 36.8, 28.5, 22.8. HRMS (ESI) $m/z$ calcd. for C$_{18}$H$_{21}$N$_2$[M+H]$^+$ 265.1699, found 265.1703.

1,1-Dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ap)

The product 3ap was obtained in 97% yield (45.8 mg, 0.19 mmol) as a colorless oil by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.54 (d, $J$ = 4.8 Hz, 1H), 6.44 (d, $J$ = 5.2 Hz, 1H), 6.34 (d, $J$ = 5.6 Hz, 1H), 6.14–6.13 (m, 1H), 5.34 (ddd, $J$ = 17.2, 9.6, 7.2 Hz, 1H), 4.91–4.88 (m, 2H), 3.36 (dd, $J$ = 17.6, 9.6 Hz, 1H), 3.02 (dd, $J$ = 14.8, 9.6 Hz, 1H), 2.69 (dd, $J$ = 14.8, 10.0 Hz, 1H), 1.51 (s, 3H), 1.11 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.7, 133.9, 133.8, 132.7, 132.7, 117.3, 116.7, 115.6, 72.7, 52.9, 46.1, 44.1, 43.0, 26.7, 21.5. HRMS (ESI) $m/z$ calcd. for C$_{15}$H$_{17}$N$_2$ [M+H]$^+$ 225.1386, found 225.1387.

Methyl 2-cyano-1-(4-methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3ba)

The diastereomeric mixture of 3ba was obtained in 90% total yield (57.4 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V). The major product is a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25 (d, $J$ = 2.0 Hz, 2H), 6.76–6.73 (m, 3H), 6.23–6.19 (m, 2H), 6.16 (dt, $J$ = 7.2, 1.6 Hz, 1H), 5.81 (ddd, $J$ = 16.8, 10.4, 8.0 Hz, 1H), 5.00–4.96 (m, 2H), 4.13 (s, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.32 (dd, $J$ = 16.0, 8.0 Hz, 1H), 2.80 (dd, $J$ = 17.6, 7.2 Hz, 1H), 2.55 (dd, $J$ = 13.6, 8.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.4, 159.3, 140.5, 139.6, 137.4, 131.4, 131.3, 130.0, 126.6, 120.0, 115.2, 113.3, 68.2, 58.0, 55.1, 54.1, 53.9, 46.7, 43.0. HRMS (ESI) $m/z$ calcd.
for C$_{21}$H$_{22}$NO$_3$ [M+H]$^+$ 336.1594, found 336.1603.

**Methyl 2-cyano-1-(p-tolyl)-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bd)**

The diastereomeric mixture of 3bd was obtained in 90% total yield (57.4 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/V:V). The major product is a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.22 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.73 (d, $J = 5.6$ Hz, 1H), 6.23 (d, $J = 5.2$ Hz, 1H), 6.19 (d, $J = 5.2$ Hz, 1H), 6.16 (d, $J = 5.2$ Hz, 1H), 5.81 (ddd, $J = 17.2, 10.4, 8.4$ Hz, 1H), 5.00–4.96 (m, 2H), 4.14 (s, 1H), 3.74 (s, 3H), 3.34 (dd, $J = 16.0, 7.6$ Hz, 1H), 2.80 (dd, $J = 13.6, 7.2$ Hz, 1H), 2.56 (dd, $J = 13.6, 8.8$ Hz, 1H), 2.27 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.4, 140.6, 139.6, 131.6, 131.4, 131.3, 128.7, 128.6, 120.0, 115.3, 68.2, 58.2, 54.0, 53.8, 46.9, 43.2, 21.2. HRMS (ESI) m/z calcd for C$_{21}$H$_{22}$NO$_3$ [M+H]$^+$ 320.1645, found 320.1652.

**Methyl 2-cyano-1-(furan-2-yl)-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bk)**

The diastereomeric mixture of 3bk was obtained in 67% total yield (39.5 mg, 0.13 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/V:V). The major product is a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.11 (d, $J = 5.2$ Hz, 1H), 7.03 (d, $J = 3.2$ Hz, 1H), 6.87 (dd, $J = 5.2, 3.6$ Hz, 1H), 6.77 (d, $J = 5.2$ Hz, 1H), 6.30 (d, $J = 5.6$ Hz, 1H), 6.25–6.21 (m, 2H), 5.83 (ddd, $J = 17.6, 9.2, 7.6$ Hz, 1H), 5.00–4.96 (m, 2H), 4.56 (s, 1H), 3.80 (s, 3H), 3.30 (dd, $J = 16.0, 8.0$ Hz, 1H), 2.82 (dd, $J = 13.6, 7.2$ Hz, 1H), 2.54 (dd, $J = 13.6, 8.0$ Hz, 1H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.1, 140.4, 139.1, 137.4, 136.0, 132.2, 126.9, 126.4, 124.7, 119.5, 115.5, 68.3, 55.0, 54.1, 53.7, 46.6, 42.7. HRMS (ESI) calcd for C$_{18}$H$_{17}$NO$_3$K [M+K]$^+$ 334.0840 found 334.0870.

**(E)-Methyl 2-cyano-1-styryl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bm)**

The diastereomeric mixture of 3bm was obtained in 95% total yield (62.9 mg, 0.19 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/V:V). The major product is a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31–7.19 (m, 5H), 6.64–6.61 (m, 1H), 6.30–6.22 (m, 4H), 6.10 (dd, $J = 15.2, 9.2$ Hz, 1H), 5.73 (ddd, $J = 17.6, 9.6, 8.0$ Hz, 1H), 4.97–4.93 (m, 2H), 3.83 (s, 3H), 3.64 (d, $J = 9.6$ Hz,
1H), 3.27 (dd, $J = 16.4, 8.0$ Hz, 1H), 2.71 (dd, $J = 13.6, 7.2$ Hz, 1H), 2.49 (dd, $J = 13.6, 10.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$169.1, 139.1, 138.7, 136.7, 136.3, 133.8, 131.8, 131.6, 128.6, 127.9, 126.7, 122.0, 118.9, 115.2, 68.1, 56.4, 54.0, 46.8, 42.7. HRMS (ESI) $m/z$ calcd. for C$_{22}$H$_{22}$NO$_2$[M+H]$^+$ 332.1645, found 332.1653.

**Methyl 2-cyano-1,1-dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bp)**

The product 3bp was obtained in 58% total yield (29.8 mg, 0.116 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/V:V) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.46 (ddd, $J = 5.6, 2.4, 1.6$ Hz, 1H), 6.35 (dt, $J = 5.6, 1.6$ Hz, 1H), 6.22 (dt, $J = 5.6, 1.6$ Hz, 1H), 6.16 (ddd, $J = 5.2, 2.0, 1.2$ Hz, 1H), 5.39 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 4.97–4.87 (m, 2H), 3.84 (s, 3H), 3.32–3.25 (m, 1H), 2.90 (dd, $J = 13.6, 12.4$ Hz, 1H), 2.60 (dd, $J = 14.0, 7.2$ Hz, 1H, 1.55 (s, 3H), 0.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.3, 138.3, 137.9, 134.9, 132.6, 131.2, 120.4, 116.1, 72.9, 56.4, 53.6, 52.3, 46.6, 41.8, 29.8, 22.5. HRMS (ESI) $m/z$ calcd. for C$_{16}$H$_{20}$NO$_2$ [M+H]$^+$ 258.1489, found 258.1497.

**Isopropyl 2-cyano-1,1-dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3cp)**

The product 3cp was obtained in 31% yield (17.7 mg, 0.062 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/V:V) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.46 (d, $J = 5.2$ Hz, 1H), 6.34–6.31 (m, 1H), 5.44–5.34 (m, 1H), 5.14–5.08 (m, 2H), 3.29–3.23 (m, 1H), 2.89 (t, $J = 14.0$ Hz, 1H), 2.58 (dd, $J = 14.0, 7.2$ Hz, 1H), 1.52 (s, 3H), 1.35 (d, $J = 6.4$ Hz, 3H), 1.30 (d, $J = 6.0$ Hz, 1H), 0.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 168.1, 138.5, 138.2, 135.2, 132.3, 131.0, 120.5, 115.6, 73.0, 71.3, 56.6, 52.0, 46.3, 41.7, 29.6, 22.8, 21.7, 21.6. HRMS (ESI) $m/z$ calcd. for C$_{18}$H$_{23}$NO$_2$Na [M+Na]$^+$ 308.1621, found 308.1626.

**tert-Butyl 2-cyano-1,1-dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3dp)**

The product 3dp was obtained in 30% yield (17.9 mg, 0.06 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/V:V) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.46 (ddd, $J = 5.2, 2.0, 1.2$ Hz, 1H), 6.34–6.31 (m, 1H),
6.21–6.18 (m, 2H), 5.40 (ddd, \( J = 17.6, 10.4, 7.2 \) Hz, 1H), 4.94–4.85 (m, 2H), 3.28–3.21 (m, 1H), 2.84 (dd, \( J = 14.0, 12.4 \) Hz, 1H), 2.55 (dd, \( J = 14.0, 7.2 \) Hz, 1H), 1.53 (s, 9H), 1.50 (s, 3H), 0.86 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 167.4, 138.6, 138.5, 135.4, 132.1, 131.0, 120.9, 115.7, 84.3, 73.0, 57.2, 46.2, 41.5, 29.5, 27.9, 23.0. HRMS (ESI) \( m/z \) calcd. for C\(_{19}\)H\(_{25}\)NO\(_2\)Na \([M+Na]^+\) 322.1778, found 322.1785.

Diels-Alder cycloadducts of 3aa (5)

\( \text{anti-endo-5} \) as a white solid. m.p.: 148–152 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.42–7.29 (m, 4H), 7.21 (dd, \( J = 8.4, 2.4 \) Hz, 1H), 7.06–7.00 (m, 3H), 6.95 (dd, \( J = 8.4, 2.8 \) Hz, 1H), 6.02 (dd, \( J = 5.6, 2.8 \) Hz, 1H), 5.95 (dt, \( J = 16.8, 10.0 \) Hz, 1H), 5.04 (dd, \( J = 10.4, 0.4 \) Hz, 1H), 4.92 (d, \( J = 16.8 \) Hz, 1H), 3.85 (s, 3H), 3.69 (s, 1H), 3.58 (s, 1H), 3.54 (dd, \( J = 7.6, 4.4 \) Hz, 1H), 3.40 (s, 1H), 3.21 (td, \( J = 9.2, 6.0 \) Hz, 1H), 2.90–2.79 (m, 2H), 2.39 (dd, \( J = 14.0, 6.0 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 175.6, 160.5, 140.6, 137.0, 132.7, 131.7, 129.2, 128.8, 127.9, 126.5, 126.4, 116.9, 116.2, 115.3, 114.8, 114.3, 79.6, 59.5, 55.4, 52.0, 51.1, 48.0, 44.8, 44.6, 42.6, 40.4. HRMS (ESI) \( m/z \) calcd. for C\(_{30}\)H\(_{25}\)N\(_3\)O\(_3\)Na \([M+Na]^+\) 498.1788, found 498.1798.

\( \text{syn-endo-5} \) as a white solid. m.p.: 156–160 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.41–7.33 (m, 3H), 7.21 (d, \( J = 8.0 \) Hz, 1H), 7.04 (d, \( J = 7.6 \) Hz, 2H), 6.97–7.21 (m, 2H), 6.85 (d, \( J = 8.0 \) Hz, 1H), 6.27–6.17 (m, 2H), 5.80 (dd, \( J = 6.0, 2.8 \) Hz, 1H), 5.33–5.25 (m, 2H), 3.92 (dd, \( J = 7.2, 4.4 \) Hz, 1H), 3.81 (s, 4H), 3.78 (s, 1H), 3.40–3.35 (m, 2H), 3.10–3.00 (m, 2H), 2.48 (dd, \( J = 12.4, 2.8 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 175.9, 159.8, 138.4, 135.3, 134.3, 132.8, 131.7, 129.3, 128.8, 127.8, 126.5, 118.0, 117.0, 114.9, 114.5, 114.3, 79.4, 61.1, 55.3, 53.2, 51.1, 47.5, 46.1, 44.7, 44.0, 38.9. HRMS (ESI) \( m/z \) calcd. for C\(_{30}\)H\(_{25}\)N\(_3\)O\(_3\)Na \([M+Na]^+\) 498.1788, found 498.1810.

Diels-Alder cycloadducts of 3ba (6)

\( \text{anti-endo-6} \) as a white solid. m.p.: 217–220 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.61 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 7.41–7.31 (m, 3H), 7.09–7.03 (m, 4H), 6.87 (dd, \( J = 8.4, 2.4 \) Hz, 1H), 6.19 (dd, \( J = 5.6, 2.4 \) Hz, 1H), 6.07 (dd, \( J = 5.6, 3.2 \) Hz,
1H), 5.66–5.57 (m, 1H), 4.92–4.86 (m, 2H), 3.85 (s, 3H), 3.79 (s, 3H), 3.62 (s, 1H), 3.44–3.39 (m, 3H), 3.18 (dd, J = 18.0, 8.4 Hz, 1H), 2.82 (dd, J = 7.2, 4.8 Hz, 1H), 2.49 (dd, J = 13.6, 7.2 Hz, 1H), 2.29 (dd, J = 13.2, 11.2 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 176.4, 169.2, 159.7, 140.8, 135.3, 133.1, 132.0, 131.0, 128.8, 128.5, 126.5, 118.8, 114.7, 113.7, 107.9, 79.7, 67.7, 57.2, 55.3, 54.1, 51.0, 50.6, 49.2, 45.0, 44.4, 41.8. HRMS (ESI) m/z calcd. for C31H28N2O5Na [M+Na]+ 531.1890, found 531.1889.

syn-endo-6 as a colorless solid. m.p.: 209–212 °C. 1H NMR (400 MHz, CDCl3): δ 7.38 (dd, J = 6.8, 1.6 Hz, 1H), 7.37–7.31 (m, 3H), 7.04–7.02 (m, 2H), 6.91 (dd, J = 8.4, 2.0 Hz, 1H), 6.75 (ddd, J = 14.4, 8.4, 1.6 Hz, 2H), 6.06–5.97 (m, 1H), 5.86 (dd, J = 6.0, 3.2 Hz, 1H), 5.66 (dd, J = 5.6, 2.4 Hz, 1H), 5.30 (d, J = 16.8 Hz, 1H), 5.20 (dd, J = 10.0, 1.6 Hz, 1H), 3.86–3.83 (m, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.65 (s, 1H), 3.60 (s, 1H), 3.51 (dd, J = 7.2, 4.4 Hz, 1H), 3.40 (s, 1H), 3.03 (dd, J = 18.0, 8.8 Hz, 1H), 2.64 (dd, J = 13.6, 8.0 Hz, 1H), 2.36 (dd, J = 13.6, 8.8 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 176.4, 169.1, 158.9, 138.5, 135.0, 132.2, 131.7, 131.3, 129.1, 128.7, 128.2, 126.5, 119.4, 117.2, 114.4, 113.8, 79.3, 58.9, 55.2, 54.0, 52.6, 52.1, 50.4, 48.1, 45.7, 44.4, 43.1. HRMS (ESI) m/z calcd. for C31H28N2O5Na [M+Na]+ 531.1890, found 531.1889.

RCM-derivative of 3ao (7)
as a pale yellow oil. 1H NMR (400 MHz, CDCl3): δ 6.08 (dd, J = 9.6, 5.6 Hz, 1H), 6.00 (dd, J = 9.6, 5.6 Hz, 1H), 5.80 (dd, J = 9.6, 5.6 Hz, 1H), 5.70–5.64 (m, 2H), 5.39–5.36 (m, 1H), 2.95–2.88 (m, 2H), 2.44–2.36 (m, 1H), 2.23–2.18 (m, 2H), 1.87–1.82 (m, 1H), 1.76–1.68 (m, 1H), 1.42 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 131.1, 127.4, 125.8, 125.4, 124.7, 122.8, 116.5, 115.6, 52.5, 48.9, 44.4, 43.3, 30.3, 22.8, 17.7. HRMS (ESI) m/z calcd. for C16H17N2 [M+H]+ 237.1386, found 237.1392.

Thiobarbital derivatives from 3ea (8)

trans-8 as a white waxy substance. 1H NMR (400 MHz, CDCl3): δ 9.17 (s, 1H), 8.74 (s, 1H), 7.06 (d, J = 8.8 Hz, 2H), 6.76 (ddd, J = 3.2, 2.0, 1.2 Hz, 1H), 6.70 (d, J = 8.8 Hz, 2H), 6.32–6.30 (m, 1H), 6.18–6.16 (m, 2H), 6.04 (ddd, J = 18.4, 10.0, 4.8 Hz, 1H).
cis-8 as a white waxy substance. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.20 (s, 1H), 8.71 (s, 1H), 7.06–7.03 (m, 3H), 6.66 (d, \(J = 8.8\) Hz, 2H), 6.36 (d, \(J = 5.2\) Hz, 1H), 6.24 (d, \(J = 5.2\) Hz, 1H), 6.03 (d, \(J = 5.2\) Hz, 1H), 5.97 (t, \(J = 4.0\) Hz, 1H), 5.50–5.41 (m, 1H), 5.03–4.92 (m, 2H), 4.18 (s, 1H), 3.72 (s, 3H), 3.48–3.41 (m, 1H), 2.85 (t, \(J = 12.8\) Hz, 1H), 2.67 (dd, \(J = 13.6, 7.6\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 175.4, 171.8, 169.0, 159.9, 138.8, 136.2, 134.6, 133.1, 132.8, 129.6, 125.6, 116.4, 113.7, 71.6, 67.4, 62.1, 55.3, 50.2, 38.2. HRMS (ESI) \(m/z\) calcd. for C\(_{21}\)H\(_{20}\)N\(_2\)O\(_3\)SNa [M+Na]\(^+\) 403.1087, found 403.1097.
7. Crystallographic information of compounds anti-endo-5 and syn-endo-6

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wR2 (reflections) = 0.1086 (3845)
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8. Copies of $^1$H NMR and $^{13}$C NMR spectrogram

$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound $trans$-3aa

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound $trans$-3aa
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound trans-3ab

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound trans-3ab
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound trans -3ac

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound trans -3ac
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound $\textit{trans}$-3ad

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound $\textit{trans}$-3ad
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound *trans*-3ae

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound *trans*-3ae
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound $trans$ -3af

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound $trans$ -3af
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound trans-3ag

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound trans-3ag
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound *trans*-3ah

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound *trans*-3ah
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound trans -3ai

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound trans -3ai
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound $trans$-3aj

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound $trans$-3aj
\( ^1\)H NMR (400 MHz, CDCl\(_3\)) spectra of compound \textit{trans} -3ak

\[ \text{Diagram of H NMR spectrum} \]

\( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectra of compound \textit{trans} -3ak

\[ \text{Diagram of C NMR spectrum} \]
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound trans-3al

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound trans-3al
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound trans-3am

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound trans-3am
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound $trans$-3an

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound $trans$-3an
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound major-3ao

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound major-3ao
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3ap

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$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound major-3ba

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound major-3ba
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound major-3bd

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound major-3bd
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound *major-3bk*

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound *major-3bk*
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound major-3bm

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound major-3bm
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3bp

$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 3bp
$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3cp

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$^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 3dp

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\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectra of compound \textit{anti-endo-5}
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