Supporting Information for:

Selective6-Endo-digandRing-expansionCycloisomerizationsofortho-DisubstitutedThiophenesBearing 1-En-3-yne Moieties

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Experimental section

1. Materials and reagents.

All chemicals and reagents were purchased from commercial sources and used as received unless otherwise specified. Anhydrous tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. *N*,*N*-dimethylformamide (DMF) was distilled from CaH₂. Other materials and reagents were obtained from Energy Chemical. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

2. Characterizations.

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). High-resolution mass spectroscopy (HRMS) were performed on an Agilent QTOF-6550 spectrometer using ESI for ionization. The single crystals suitable for X-ray analysis were obtained by the slow solvent volatilization method. The X-ray measurement of single crystals was recorded on a Bruker Sc XRD D8 venture.

3. Synthesis.



Scheme S1. General synthetic route of benzo[*b*]thiophene derivatives 3 via 6-*endo*-dig cyclizations.

Synthesis of 1a.



Under nitrogen atmosphere, in a mixture of compound **S1a**^{S1} (661 mg, 2.61 mmol), 2,2'-(2,5-dihexylthieno[3,2-*b*]thiophene-3,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (666 mg, 1.19 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (139 mg, 0.12 mmol), and K₂CO₃ (493 mg, 3.57 mmol) were added degassed toluene (20 mL) and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room

temperature, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the resulting crude product was proceeded directly to the next step without further purification due to the easy deprotection of the trimethylsilyl group. Then crude product S2a (565 mg, 0.87 mmol) and K₂CO₃ (481 mg, 3.48 mmol) were added to the mixture of MeOH (20 mL) and THF (20 mL). After stirring at room temperature for 12 h, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound 1a as yellowish oil in 76% yield (460 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.65 (d, J = 7.7 Hz, 2H), 7.51–7.40 (m, 4H), 7.36 (t, J = 6.4 Hz, 2H), 3.02 (d, J= 11.2 Hz, 2H), 2.87–2.63 (m, 4H), 1.69–1.44 (m, 4H), 1.31–1.08 (m, 12H), 0.81 (t, J = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.11, 143.00, 138.71, 136.49, 133.83, 130.21, 129.17, 127.79, 122.37, 82.89, 80.60, 31.85, 31.71, 30.03, 29.03, 22.75, 14.29. HRMS (ESI, m/z): $[M + H]^+$ calcd for C₃₄H₃₇S₂, 509.2337; found 509.2344.

Synthesis of 1b.

Under nitrogen atmosphere, in a mixture of compound **S1b**^{S2} (714 mg, 2.36 mmol), 2,2'-(2,5-dihexylthieno[3,2-*b*]thiophene-3,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (600 mg, 1.07 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (127 mg, 0.11 mmol), and K₂CO₃ (443 mg, 3.21 mmol) were added degassed toluene (20 mL)



and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the resulting crude product was proceeded directly to the next step without further purification due to the easy deprotection of the trimethylsilyl group. Then crude product S2b (475 mg, 0.63 mmol) and K₂CO₃ (348 mg, 2.52 mmol) were added to the mixture of MeOH (16 mL) and THF (16 mL). After stirring at room temperature for 12 h, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound **1b** as yellowish oil in 51% yield (334 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.52 (d, J = 8.3 Hz, 2H), 7.99–7.90 (m, 4H), 7.69–7.55 (m, 6H), 3.49 (d, J = 9.9 Hz, 2H), 2.95–2.70 (m, 4H), 1.71–1.46 (m, 4H), 1.35–1.05 (m, 12H), 0.77 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.27, 137.72, 136.11, 134.11, 132.79, 129.77, 129.28, 128.44, 127.71, 127.62, 127.52, 126.83, 119.43, 85.98, 80.77, 31.75,

31.69, 30.21, 29.04, 22.72, 14.27. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₄₂H₄₁S₂, 609.2650; found 609.2643.

Synthesis of 1c.



Under nitrogen atmosphere, in a mixture of compound S1a^{S1} (1.68 g, 6.64 mmol), 2-(2-hexylbenzo[b]thien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.43 g, 9.96 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (763 mg, 0.66 mmol), and K₂CO₃ (2.75 g, 19.92 mmol) were added degassed toluene (40 mL) and H₂O (8 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the resulting crude product was proceeded directly to the next step without further purification due to the easy deprotection of the trimethylsilyl group. Then crude product S2c (3.06 g, 7.84 mmol) and K₂CO₃ (2.79 g, 20.16 mmol) were added to the mixture of MeOH (20 mL) and THF (20 mL). After stirring at room temperature for 12 h, the mixture was diluted with dichloromethane (80 mL), washed with water (3×20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound 1c as yellowish oil in 84% yield (2.67 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.82 (d, J =

7.9, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.51–7.43 (m, 1H), 7.43–7.37 (m, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.31–7.24 (m, 3H), 2.87 (s, 1H), 2.85–2.71 (m, 2H), 1.77–1.57 (m, 2H), 1.26 (d, J = 6.3 Hz, 6H), 0.85 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 144.09, 140.68, 138.97, 138.39, 133.63, 132.17, 131.29, 129.02, 127.84, 124.26, 123.82, 123.36, 122.80, 122.25, 82.71, 80.31, 31.77, 31.43, 29.30, 29.07, 22.81, 14.37. HRMS (ESI, m/z): $[M + H]^+$ calcd for C₂₂H₂₃S, 319.1520; found 319.1515.

Synthesis of 1d.



Under nitrogen atmosphere, in a mixture of compound **S1b**^{S2} (1.76 g, 5.79 mmol), 2-(2-hexylbenzo[*b*]thien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.99 g, 8.69 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (670 mg, 0.58 mmol), and K₂CO₃ (2.40 g, 17.37 mmol) were added degassed toluene (40 mL) and H₂O (8 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water (3×20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the resulting crude product was proceeded directly to the next step without further purification due to the easy deprotection of the trimethylsilyl group. Then crude product **S2d** (2.91 g, 6.60 mmol) and K₂CO₃ (3.25 g, 23.52 mmol) were added to the mixture of MeOH (20 mL) and THF (20 mL). After stirring at room temperature for 12 h, the mixture was diluted with

dichloromethane (80 mL), washed with water (3 × 20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound **1d** as yellowish oil in 65% yield (2.09 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.52 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.91–7.83 (m, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.64–7.58 (m, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.35–7.24 (m, 3H), 3.31 (s, 1H), 2.94–2.76 (m, 2H), 1.78–1.61 (m, 2H), 1.33–1.17 (m, 6H), 0.81 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 144.33, 140.57, 138.35, 138.05, 134.23, 132.65, 132.50, 129.08, 128.56, 128.48, 127.53, 126.88, 126.74, 124.23, 123.87, 122.89, 122.30, 120.49, 85.80, 80.59, 31.74, 31.45, 29.49, 29.04, 22.77, 14.27. HRMS (ESI, *m/z*): [M + H]⁺ calcd for C₂₆H₂₅S, 369.1677; found 369.1675.

General synthetic procedure for the 6-endo-dig cycloisomerization.

As shown in Scheme S1, under nitrogen atmosphere, $PtCl_2$ (0.10 eq) and compound 1 (1.00 eq) were added to dry toluene, and the concentration of compound 1 was 0.06 mmol/mL. The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene by a rotary evaporator, the residue was purified by chromatography on silica gel to afford target compound **3**.

Synthesis of 3a.

Under nitrogen atmosphere, PtCl₂ (16 mg, 0.061 mmol) and compound **1a** (309 mg, 0.61 mmol) were added to dry toluene (10 mL). The mixture was stirred at 110 °C



overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound **3a** as a white solid in 42% yield (131 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.61 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.81–7.71 (m, 2H), 7.68 (s, 2H), 7.61 (t, J = 7.0 Hz, 2H), 3.29–2.98 (m, 4H), 2.10–1.93 (m, 4H), 1.45–1.30 (m, 4H), 1.23–0.98 (m, 8H), 0.93 (t, J = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.11, 143.00, 138.71, 136.49, 133.83, 133.80, 130.33, 130.21, 129.71, 127.79, 122.37, 31.85, 31.71, 30.04, 29.03, 22.75, 14.29. HRMS (ESI, *m*/z): [M]⁺ calcd for C₃₄H₃₆S₂, 508.2258; found 508.2277.

Synthesis of 3b.



Under nitrogen atmosphere, PtCl₂ (14 mg, 0.052 mmol) and compound **1b** (314 mg, 0.52 mmol) were added to dry toluene (9 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound **3b** as a white solid in 35% yield (109 mg). ¹H NMR (400 MHz, CDCl₃) δ

(ppm): 8.66 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.8 Hz, 1H), 8.30 (s, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.69–7.58 (m, 2H), 3.09–2.99 (m, 2H), 1.97–1.82 (m, 2H), 1.59–1.35 (m, 6H), 0.95 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.56, 137.54, 136.28, 132.65, 131.54, 129.17, 129.05, 128.41, 127.18, 127.09, 126.93, 126.81, 125.44, 125.19, 124.74, 34.36, 31.92, 29.48, 29.37, 22.83, 14.36. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₄₂H₄₁S₂, 609.2650; found 609.2695.

Synthesis of 3c.



Under nitrogen atmosphere, PtCl₂ (48 mg, 0.18 mmol) and compound **1c** (556 mg, 1.75 mmol) were added to dry toluene (29 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound **3c** as a white solid in 45% yield (252 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.96 (d, *J* = 4.8 Hz, 1H), 8.88 (d, *J* = 8.2 Hz, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 8.58 (d, *J* = 4.8 Hz, 1H), 8.07–7.90 (m, 3H), 7.73 (t, *J* = 8.2 Hz, 1H), 7.69–7.57 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 3.20–2.99 (m, 2H), 1.99–1.91 (m, *J* = 7.5 Hz, 2H), 1.62–1.30 (m, 6H), 0.98 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.01, 139.35, 137.31, 134.86, 132.55, 129.36, 129.16, 128.98, 126.27, 125.84, 125.10, 124.83, 124.78, 124.72, 123.19, 122.99, 35.13, 31.79, 29.36, 29.14, 22.71, 14.21. HRMS (ESI,

m/z): [M]⁺ calcd for C₂₂H₂₂S, 318.1442; found 318.1460.

Synthesis of 3d.



Under nitrogen atmosphere, PtCl₂ (50 mg, 0.19 mmol) and compound **1d** (711 mg, 1.93 mmol) were added to dry toluene (32 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford compound **3d** as a white solid in 38% yield (270 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.03 (d, *J* = 8.5 Hz, 1H), 8.90 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.75–7.68 (m, 2H), 7.63–7.58 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 3.10–2.99 (m, 2H), 1.94 (t, *J* = 7.6 Hz, 2H), 1.53 (t, *J* = 9.1, 2H), 1.42 (t, *J* = 8.0, 4H), 0.96 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.74, 139.65, 137.23, 135.05, 131.08, 130.74, 128.49, 127.63, 127.04, 126.66, 126.11, 125.40, 125.05, 124.69, 123.22, 123.04, 121.99, 120.45, 35.77, 31.83, 29.45, 29.38, 22.75, 14.25. HRMS (ESI, *m*/z): [M]⁺ calcd for C₂₆H₂₄S, 368.1599; found 368.1609.



Scheme S2. General synthetic route of cyclopenta[*c*]thiapyran derivatives via ringexpansion cyclizations.

Synthesis of S4a.



Under nitrogen atmosphere, in a mixture of compound **S3a**^{S3} (998 mg, 5.28 mmol), 2,2'-(2,5-dihexylthieno[3,2-*b*]thiophene-3,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (988 mg, 1.76 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (203 mg, 0.18 mmol), and K₂CO₃ (730 mg, 5.28 mmol) were added degassed toluene (20 mL) and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water (3×20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/20) to afford compound **S4a** as yellowish oil in 86% yield (782 mg). ¹H NMR

(400 MHz, CDCl₃) δ (ppm): 9.42 (d, J = 15.3 Hz, 2H), 2.73–2.50 (m, 6H), 2.43–2.18 (m, 6H), 1.77–1.51 (m, 12H), 1.22 (d, J = 8.4 Hz, 12H), 0.79 (t, J = 6.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.23, 152.99, 152.50, 143.27, 138.05, 128.33, 32.01, 31.68, 31.59, 29.57, 29.00, 22.63, 22.49, 22.33, 21.70, 14.20. MALDI-TOF Mass: m/z calcd for C₃₂H₄₄O₂S₂: 524.2783; found: 524.1476.

Synthesis of S4b.



Under nitrogen atmosphere, in a mixture of compound **S3b**^{S3} (814 mg, 3.75 mmol), 2,2'-(2,5-dihexylthieno[3,2-*b*]thiophene-3,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (700 mg, 1.25 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (145 mg, 0.13 mmol), and K₂CO₃ (518 mg, 3.75 mmol) were added degassed toluene (20 mL) and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water (3 × 20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/20) to afford compound **S4b** as yellowish oil in 58% yield (415 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.43 (d, *J* = 22.8 Hz, 2H), 2.92–2.49 (m, 12H), 1.84–1.51 (m, 20H), 1.37–1.19 (m, 12H), 0.86 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.20, 156.33, 143.92, 141.21, 136.51, 128.50, 34.56, 32.11, 31.68, 29.98, S14

29.93, 29.79, 29.28, 27.19, 26.76, 23.78, 22.72, 14.29. MALDI-TOF Mass: *m*/*z* calcd for C₃₆H₅₂O₂S₂: 580.3409; found: 580.2342.

Synthesis of S4c.



Under nitrogen atmosphere, in a mixture of compound S3a^{S3} (613 mg, 3.24 mmol), 2-(2-hexylbenzo[b]thien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.45 g, 4.21 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (187 mg, 0.16 mmol), and K₂CO₃ (1.34 g, 9.72 mmol) were added degassed toluene (20 mL) and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound S4c as yellowish oil in 88% yield (919 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.38 (s, 1H), 7.79 (d, J = 7.0 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.37–7.25 (m, 2H), 2.85-2.77 (m, 2H), 2.65-2.29 (m, 4H), 1.92-1.64 (m, 6H), 1.41-1.23 (m, 6H), 0.90 (t, J = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.42, 154.20, 143.01, 139.91, 138.90, 138.61, 130.74, 124.74, 124.35, 122.54, 122.02, 33.26, 31.73, 31.45, 29.26, 29.21, 22.75, 22.68, 22.37, 21.98, 14.31. MALDI-TOF Mass: m/z calcd for $C_{21}H_{26}OS: 326.1704; found: 326.1738.$

Synthesis of S4d.



Under nitrogen atmosphere, in a mixture of compound **S3b**^{S3} (462 mg, 2.13 mmol), 2-(2-hexylbenzo[b]thien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.10 g, 3.19 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (122 mg, 0.11 mmol), and K₂CO₃ (883 mg, 6.39 mmol) were added degassed toluene (15 mL) and H₂O (3 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound S4d as yellowish oil in 79% yield (590 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.37 (s, 1H), 7.79 (d, J = 6.8 Hz, 1H), 7.46 (d, J = 8.7 Hz, 1H), 7.36–7.28 (m, 2H), 2.90–2.51 (m, 6H), 1.85–1.55 (m, 10H), 1.43–1.23 (m, 6H), 0.89 (t, J = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.26, 157.12, 143.90, 141.90, 140.05, 138.51, 130.92, 124.68, 124.32, 122.58, 122.50, 35.23, 31.78, 31.75, 29.93, 29.74, 29.42, 29.33, 27.31, 26.74, 23.83, 22.73, 14.28. MALDI-TOF Mass: m/z calcd for C₂₃H₃₀OS: 354.2017; found: 354.3051.

Synthesis of S4e.

Under nitrogen atmosphere, in a mixture of compound $\mathbf{S3c}^{S3}$ (555 mg, 2.34 mmol),



2-(2-hexylbenzo[b]thien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.21 g, 3.51 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (135 mg, 0.12 mmol), and K₂CO₃ (970 mg, 7.02 mmol) were added degassed toluene (20 mL) and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water $(3 \times 20 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound S4e as yellowish oil in 82% yield (711 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.50 (s, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.34–7.22 (m, 5H), 7.06 (t, J = 8.4, 1H), 6.82 (d, J = 7.7 Hz, 1H), 3.09-2.91 (m, 2H), 2.88-2.64 (m, 4H), 1.68-1.61 (m, 2H), 1.31–1.19 (m, 6H), 0.82 (t, J = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.08, 148.69, 145.63, 140.86, 138.61, 138.42, 137.09, 134.12, 130.70, 128.19, 127.62, 127.15, 126.67, 124.87, 124.49, 122.58, 122.43, 31.58, 31.14, 29.44, 29.10, 27.85, 22.65, 20.39, 14.22. MALDI-TOF Mass: *m*/*z* calcd for C₂₅H₂₆OS: 374.1704; found: 374.1769.

Synthesis of S4f.

Under nitrogen atmosphere, in a mixture of compound **S3d**^{S4} (481 mg, 2.28 mmol), 2-(2-hexylbenzo[*b*]thien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.18 g, 3.42 S17



mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (132 mg, 0.11 mmol), and K₂CO₃ (945 mg, 6.84 mmol) were added degassed toluene (20 mL) and H₂O (4 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water (3 × 20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound **S4f** as yellowish oil in 85% yield (668 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.43 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.48–7.20 (m, 8H), 6.91 (d, *J* = 8.0 Hz, 1H), 2.85–2.68 (m, 2H), 1.73–1.60 (m, 2H), 1.33–1.19 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.50, 155.85, 146.55, 140.47, 138.44, 138.11, 131.10, 129.22, 129.06, 127.96, 127.76, 125.06, 124.62, 122.70, 122.47, 31.61, 31.32, 29.50, 29.16, 22.71, 14.25. MALDI-TOF Mass: *m*/z calcd for C₂₃H₂₄OS: 348.1548; found: 348.0998.

Synthesis of 2a.



Ohira-Bestmann reagent (754 mg, 3.93 mmol) was added dropwisely to the MeOH (22 mL) solution of compound **S4a** (685 mg, 1.31 mmol) and K₂CO₃ (724 mg, 5.24 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄, filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **2a** as a yellowish solid in 68% yield (462 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.88–2.57 (m, 8H), 2.37–2.34 (m, 4H), 2.18–2.08 (m, 2H), 1.83–1.58 (m, 12H), 1.37–1.26 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 141.60, 140.77, 134.74, 131.22, 118.85, 84.82, 79.18, 31.83, 31.72, 30.66, 30.12, 30.10, 29.24, 22.81, 22.65, 22.54, 14.35. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₃₄H₄₅S₂, 517.2963; found 517.2967.

Synthesis of 2b.



Ohira-Bestmann reagent (478 mg, 2.49 mmol) was added dropwisely to the MeOH (14 mL) solution of compound **S4b** (480 mg, 0.83 mmol) and K₂CO₃ (459 mg, 3.32 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with S19

diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄, filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **2b** as a yellowish solid in 68% yield (323 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.95–2.35 (m, 14H), 1.85–1.48 (m, 20H), 1.41–1.30 (m, 12H), 0.91 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.98, 142.30, 134.99, 131.61, 121.99, 85.39, 79.14, 32.36, 32.17, 31.92, 30.69, 30.01, 29.95, 29.48, 29.12, 27.17, 26.38, 22.81, 14.34. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₃₈H₅₃S₂, 573.3589; found 573.3583.

Synthesis of 2c.



Ohira-Bestmann reagent (1.75 g, 9.12 mmol) was added dropwisely to the MeOH (50 mL) solution of compound **S4c** (994 mg, 3.04 mmol) and K₂CO₃ (1.68 g, 12.16 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄, filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **2c** as yellowish oil in 89% yield (873 mg). ¹H NMR (400 MHz,

CDCl₃) δ (ppm): 7.78 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.37–7.24 (m, 2H), 2.93–2.76 (m, 2H), 2.70 (s, 1H), 2.54–2.36 (m, 3H), 2.32–2.14 (m, 1H), 1.92–1.66 (m, 6H), 1.48–1.28 (m, 6H), 0.93 (t, J = 6.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 141.67, 141.18, 139.22, 138.41, 133.83, 123.82, 123.36, 122.15, 121.96, 120.03, 84.14, 78.59, 31.64, 31.12, 31.01, 30.23, 29.08, 22.59, 22.47, 14.13. HRMS (ESI, m/z): [M + H]⁺ calcd for C₂₂H₂₇S, 323.1833; found 323.1837.

Synthesis of 2d.



Ohira-Bestmann reagent (1.01 g, 5.28 mmol) was added dropwisely to the MeOH (30 mL) solution of compound **S4d** (623 mg, 1.76 mmol) and K₂CO₃ (0.97 g, 7.04 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄, filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **2d** as yellowish oil in 85% yield (524 mg). ¹H NMR (400 MHz, CDCl3) δ (ppm): 7.78 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.36–7.22 (m, 2H), 3.01–2.85 (m, 2H), 2.75 (s, 1H), 2.74–2.63 (m, 2H), 2.62–2.45 (m, 2H), 1.91–1.57 (m, 9H), 1.56–1.31 (m, 7H), 0.94 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm):

144.53, 142.81, 139.59, 138.51, 134.26, 124.01, 123.58, 123.01, 122.76, 122.37, 85.13, 78.86, 33.20, 32.40, 31.96, 31.78, 30.13, 29.63, 29.61, 29.22, 27.25, 26.45, 22.85, 14.38. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₂₄H₃₁S, 351.2146; found 351.2144.

Synthesis of 2e.



Ohira-Bestmann reagent (1.05 g, 5.49 mmol) was added dropwisely to the MeOH (31 mL) solution of compound **S4e** (686 mg, 1.83 mmol) and K₂CO₃ (1.01 g, 7.32 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄, filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **2e** as yellowish oil in 83% yield (562 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.80 (d, *J* = 8.6 Hz, 1H), 7.27–7.12 (m, 5H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 3.11–2.92 (m, 3H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.75–1.60 (m, 2H), 1.33–1.20 (m, 6H), 0.83 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 144.59, 140.04, 139.41, 138.48, 135.68, 134.59, 1219.89, 128.12, 127.67, 126.95, 126.26, 124.14, 123.73, 122.81, 122.24, 121.06, 83.43, 83.28,

31.74, 31.10, 29.57, 29.22, 28.83, 28.23, 22.75, 14.27. HRMS (ESI, m/z): [M + H]⁺ calcd for C₂₆H₂₇S, 371.1833; found 371.1839.

Synthesis of 2f.



Ohira-Bestmann reagent (0.99 g, 5.16 mmol) was added dropwisely to the MeOH (31 mL) solution of compound **S4f** (600 mg, 1.72 mmol) and K₂CO₃ (0.95 g, 6.88 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄, filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **2f** as a yellowish solid in 81% yield (480 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.81 (d, *J* = 7.3 Hz, 1H), 7.37–7.19 (m, 8H), 6.44 (d, *J* = 2.4 Hz, 1H), 2.97 (d, *J* = 2.4 Hz, 1H), 2.84 (t, *J* = 7.7 Hz, 2H), 1.85–1.63 (m, 2H), 1.39–1.19 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.41, 145.22, 139.70, 139.24, 138.50, 130.20, 129.03, 128.88, 126.72, 124.25, 123.83, 123.03, 122.25, 109.25, 83.29, 82.21, 31.77, 31.23, 29.71, 29.29, 22.80, 14.31. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₂₄H₂₅S, 345.1677; found 345.1676.

General synthetic procedure for the ring-expansion cycloisomerization.

As shown in Scheme S2, under nitrogen atmosphere, $PtCl_2$ (0.10 eq) and compound **2** (1.00 eq, 0.06 mmol/mL) were added to dry toluene. The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel to afford compound **4**.

Synthesis of 4a.



Under nitrogen atmosphere, PtCl₂ (3 mg, 0.013 mmol) and compound **2a** (70 mg, 0.13 mmol) were added to dry toluene (2 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/5) to afford compound **4a** as an orange solid in 56% yield (39 mg).¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.14 (s, 1H), 3.44 (t, *J* = 6.7 Hz, 2H), 3.20 (t, *J* = 6.0 Hz, 1H), 3.05–2.91 (m, 3H), 2.05–1.81 (m, 6H), 1.47–1.34 (m, 6H), 0.96–0.91 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.99, 152.50, 143.27, 138.05, 135.97, 131.98, 128.33, 32.01, 31.68, 31.59, 29.57, 29.00, 22.63, 22.49, 22.33, 21.70, 14.20. HRMS (ESI, *m*/z): [M]⁺ calcd for C₃₄H₄₄S₂, 516.2884; found 516.2895.

Synthesis of 4b.



Under nitrogen atmosphere, PtCl₂ (7 mg, 0.025 mmol) and compound **2b** (145 mg, 0.25 mmol) were added to dry toluene (4 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/5) to afford compound **4b** as an orange solid in 76% yield (110 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.02 (s, 1H), 3.64–3.40 (m, 1H), 3.26–3.18 (m, 2H), 2.96–2.90 (m, 3H), 2.01–1.69 (m, 6H), 1.58–1.31 (m, 10H), 0.91 (t, *J* = 7.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.55, 135.37, 134.96, 134.22, 132.51, 131.51, 126.47, 34.84, 33.62, 32.85, 30.99, 29.96, 29.52, 28.88, 26.59, 26.15, 24.89, 22.87, 14.37. HRMS (ESI, *m*/z): [M]⁺ calcd for C₃₈H₅₂S₂, 572.3510; found 572.3563.

Synthesis of 4c.



Under nitrogen atmosphere, $PtCl_2$ (21 mg, 0.078 mmol) and compound **2c** (250 mg, 0.78 mmol) were added to dry toluene (13 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent:

dichloromethane/petroleum ether = 1/10) to afford compound **4c** as an orange solid in 88% yield (221 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.30 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 6.62 (s, 1H), 3.22 (t, J = 6.4 Hz, 2H), 3.12–3.04 (m, 2H), 2.93 (t, J = 6.2 Hz, 2H), 1.99–1.92 (m, 2H), 1.90–1.80 (m, 4H), 1.52–1.40 (m, 2H), 1.39–1.28 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 146.41, 144.57, 134.08, 130.90, 130.29, 128.09, 127.08, 126.35, 126.19, 123.32, 120.71, 106.50, 35.03, 31.83, 31.51, 29.46, 28.24, 27.06, 24.54, 23.46, 22.80, 14.35. HRMS (ESI, m/z): [M + NH₄]⁺ calcd for C₂₂H₃₀SN, 340.2099; found 340.2097.

Synthesis of 4d.



Under nitrogen atmosphere, PtCl₂ (11 mg, 0.042 mmol) and compound 2d (146 mg, 0.42 mmol) were added to dry toluene (7 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/10) to afford compound 4d as an orange solid in 95% yield (138 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.37 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 9.1 Hz, 1H), 7.50–7.42 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 6.64 (s, 1H), 3.20– 3.13 (m, 2H), 3.11–3.03 (m, 2H), 2.88–2.80 (m, 2H), 1.98–1.82 (m, 4H), 1.78–1.70 (m, 2H), 1.63–1.55 (m, 2H), 1.51–1.42 (m, 4H), 1.39–1.33 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). S26

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 150.05, 144.92, 134.62, 134.44, 130.01, 128.08, 127.22, 126.42, 125.71, 123.47, 120.76, 108.35, 34.94, 33.20, 31.83, 31.36, 29.49, 29.17, 28.91, 26.88, 26.47, 25.58, 22.83, 14.36. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₂₄H₃₁S, 351.2146; found 351.2150.

Synthesis of 4e.



Under nitrogen atmosphere, PtCl₂ (37 mg, 0.14 mmol) and compound **2e** (518 mg, 1.40 mmol) were added to dry toluene (23 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/10) to afford compound **4e** as an orange solid in 83% yield (432 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.76 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.36–7.13 (m, 6H), 3.13–3.03 (m, 2H), 2.95 (t, *J* = 6.0 Hz, 2H), 2.86 (t, *J* = 6.2 Hz, 2H), 1.94–1.83 (m, 2H), 1.51–1.33 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 146.93, 146.74, 139.21, 136.12, 134.26, 129.28, 128.95, 128.76, 128.55, 126.56, 126.41, 126.36, 126.31, 126.20, 124.84, 120.74, 106.44, 35.21, 31.82, 31.61, 31.48, 29.46, 25.77, 22.79, 14.34. HRMS (ESI, *m*/z): [M]⁺ calcd for C₂₆H₂₆S, 370.1755; found 370.1750.

Synthesis of 4f.



Under nitrogen atmosphere, PtCl₂ (3 mg, 0.01 mmol) and compound **2f** (35 mg, 0.10 mmol) were added to dry toluene (2 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/10) to afford compound **4f** as an orange solid in 86% yield (30 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.05 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.24–7.09 (m, 3H), 6.98 (d, *J* = 4.9 Hz, 1H), 3.23–3.14 (m, 2H), 1.99–1.89 (m, 2H), 1.55–1.43 (m, 2H), 1.42–1.33 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H).¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.64, 140.30, 135.52, 134.79, 134.01, 129.46, 129.41, 128.83, 128.07, 127.01, 126.97, 126.30, 126.17, 124.40, 120.64, 111.26, 35.35, 31.80, 31.63, 29.46, 22.79, 14.34. HRMS (ESI, *m*/z): [M]⁺ calcd for C₂₄H₂₄S, 344.1599; found 344.1541.

Synthesis of S5.



Under nitrogen atmosphere, in a mixture of compound $S3c^{S3}$ (1.10 g, 4.64 mmol), 4,4,5,5-tetramethyl-2-(2-methylbenzo[*b*]thien-3-yl)-1,3,2-dioxaborolane (1.53 g, 5.57 S28

mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (268 mg, 0.23 mmol), and K₂CO₃ (1.92 g, 13.92 mmol) were added degassed toluene (25 mL) and H₂O (5 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water (3 × 20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound **S5** as yellowish oil in 81% yield (1.14 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.26 (s, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.81–7.68 (m, 2H), 7.47–7.31 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 2.86–2.81 (m, 2H), 2.66–2.60 (m, 2H), 2.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.46, 139.31, 137.39, 135.44, 134.76, 133.25, 131.62, 129.00, 127.85, 127.39, 125.13, 124.98, 123.84, 122.79, 122.37, 115.12, 106.81, 27.42, 23.12, 15.75. MALDI-TOF Mass: *m/z* calcd for C₂₀H₁₆OS: 304.0922; found: 304.0929.

Synthesis of S6.



Ohira-Bestmann reagent (1.74 g, 9.06 mmol) was added dropwisely to the MeOH (50 mL) solution of compound **S5** (920 mg, 3.02 mmol) and K_2CO_3 (1.67 g, 12.08 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄,

filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **S6** as yellowish oil in 79% yield (717 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.81 (d, *J* = 7.7 Hz, 1H), 7.28–7.21 (m, 4H), 7.21–7.15 (m, 1H), 7.03 (t, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 3.15–3.05 (m, 2H), 3.03–2.94 (m, 1H), 2.77–2.67 (m, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.86, 138.87, 138.39,138.27, 135.51, 134.15, 130.23, 127.95, 127.52, 126.78, 126.02, 123.96, 123.58, 122.67, 121.91, 121.02, 84.15, 82.89, 28.60, 28.00, 14.75. HRMS (ESI, m/z): [M + H]⁺ calcd for C₂₁H₁₇S, 301.1051; found 301.1055.

Synthesis of S7.



Under nitrogen atmosphere, PtCl₂ (64 mg, 0.24 mmol) and compound **S6** (705 mg, 2.35 mmol) were added to dry toluene (40 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/10) to afford compound **S7** as an orange solid in 84% yield (592 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.79 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.36–7.20 (m, 5H), 6.70 (s, 1H), 3.00–2.94 (m, 2H), 2.92–2.85 (m, 2H), 2.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 147.51, 146.91, 140.75, 139.03, 136.20, 133.99, 129.09, 128.71, 128.54, 128.35, 126.40, 126.22, 126.16, 126.01, S30

125.98, 125.66, 124.67, 106.45, 31.40, 25.56, 20.32. HRMS (ESI, *m*/z): [M]⁺ calcd for C₂₁H₁₆S, 300.0973; found 300.0977.

Synthesis of S8.



Under nitrogen atmosphere, phosphoryl trichloride (129 mg, 0.84 mmol) was slowly added to anhydrous DMF (10 mL) at 0 °C, and the mixture was stirred for 30 min before **S7** (210 mg, 0.70 mmol) dissolved in CHCl₃ (7 mL) was added to the reaction system. The reaction mixture was allowed to warm to room temperature, and the stirring was maintained for an additional 3 h. When the completion of the reaction was indicated by TLC, the reaction was quenched by addition of 10% aqueous NaOH (20 mL) and 10 min successive stirring. Then the mixture was extracted with ethyl acetate $(3 \times 30 \text{ mL})$, and the combined organic phase was washed with brine. After drying over Na₂SO₄, the solvent was removed under reduced pressure. the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound **S8** as a red solid in 65% yield (149 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.39 (s, 1H), 8.78 (d, J = 9.4 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.76 (d, J = 7.8Hz, 1H), 7.47–7.34 (m, 3H), 7.27–7.18 (m, 2H), 3.29 (t, *J* = 6.1 Hz, 2H), 3.16 (s, 3H), 3.01 (t, J = 6.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 184.08, 160.73, 147.62, 138.30, 132.84, 132.37, 130.91, 129.98, 128.82, 128.24, 127.61, 127.38, 127.04, 126.79, 126.65, 126.14, 125.97, 125.38, 120.41, 30.05, 24.80, 24.27. MALDI-TOF Mass: *m*/*z* calcd for C₂₂H₁₆OS: 328.0922; found: 328.0940.

Synthesis of S9.



Under nitrogen atmosphere, DDQ (6 mg, 0.024 mmol) and compound **S8** (80 mg, 0.24 mmol) were added to dry 1,4-dioxane (10 mL). The mixture was stirred at 100 °C for 12 h and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: eluent: EtOAc/petroleum ether = 1/30) to afford compound **S9** as a red solid in 50% yield (39 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.77 (s, 1H), 7.85 (d, *J* = 6.4 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 3.5 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.23–7.15 (m, 2H), 6.98 (t, *J* = 7.1 Hz, 1H), 2.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 181.97, 140.57, 137.39, 136.74, 135.44, 133.00, 131.68, 129.96, 129.74, 129.68, 129.64, 129.32, 129.28, 128.63, 128.48, 125.55, 125.24, 125.13, 124.99, 122.79, 122.38, 15.75. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₂₂H₁₅OS, 327.0844; found 327.0847.

Synthesis of S11.



Under nitrogen atmosphere, PtCl₂ (13 mg, 0.05 mmol) and compound S10^{S5} (115 mg, 0.49 mmol) were added to dry toluene (8 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue purified chromatography silica gel (eluent: was by on dichloromethane/petroleum ether = 1/10) to afford compound S11 as a white solid in 56% yield (64 mg). ¹H NMR (400 MHz, Benzene- d_6) δ (ppm): 8.82 (d, J = 8.1 Hz, 1H), 8.60 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 15.3 Hz, 1H), 7.18–7.11 (m, 2H). ¹³C NMR (100 MHz, Benzene- d_6) δ (ppm): 140.22, 139.60, 137.65, 134.86, 133.00, 129.86, 129.64, 129.15, 126.40, 126.13, 125.20, 124.98, 124.89, 123.30, 123.23. HRMS (ESI, m/z): $[M + H]^+$ calcd for C₁₆H₁₁S, 235.0581; found 235.0583.

Synthesis of S13.



Under nitrogen atmosphere, in a mixture of compound **S12**^{S3} (334 mg, 1.54 mmol), 2-(benzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (600 mg, 2.31 mmol), Aliquat 336 (two drops), Pd(PPh₃)₄ (89 mg, 0.08 mmol), and K₂CO₃ (638 mg, 4.62

mmol) were added degassed toluene (15 mL) and H₂O (3 mL). The mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with dichloromethane (80 mL), washed with water (3 × 20 mL) and dried over Na₂SO₄. The solvent was removed by a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/30) to afford compound **S13** as yellowish oil in 75% yield (312 mg). ¹H NMR (400 MHz, CDCl₃) *δ* (ppm): 9.43 (s, 1H), 7.95–7.84 (m, 1H), 7.68–7.59 (m, 1H), 7.44–7.36 (m, 2H), 7.24 (s, 1H), 2.96–2.85 (m, 1H), 2.84–2.76 (m, 1H), 2.68–2.61 (m, 1H), 2.52–2.41 (m, 1H), 1.88–1.76 (m, 1H), 1.75–1.68 (m, 1H), 1.66–1.52 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) *δ* (ppm): 193.05, 156.68, 142.09, 140.30, 138.59, 134.87, 125.55, 125.05, 124.93, 123.18, 123.03, 34.32, 30.16, 29.33, 26.95, 26.72, 24.07. MALDI-TOF Mass: *m/z* calcd for C₁₇H₁₈OS: 270.1078; found: 270.1062.

Synthesis of S14.



Ohira-Bestmann reagent (617 mg, 3.21 mmol) was added dropwisely to the MeOH (20 mL) solution of compound **S13** (289 mg, 1.07 mmol) and K₂CO₃ (0.59 g, 4.28 mmol) at 0 °C. The reaction mixture was stirred at room temperature for around 24 h. After TLC analysis indicating full conversion of the aldehyde, the mixture was diluted with diethyl ether, and washed with water twice. The organic layer was dried over MgSO₄,

filtered through celite pad, and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane/petroleum ether = 1/7) to give compound **S14** as yellowish oil in 83% yield (236 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 7.3 Hz, 1H), 7.40–7.32 (m, 2H), 7.30 (s, 1H), 2.73 (s, 1H), 2.67–2.60 (m, 2H), 2.60–2.53 (m, 2H), 1.84–1.76 (m, 2H), 1.69–1.53 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 144.16, 140.20, 138.49, 138.05, 124.28, 124.00, 123.98, 123.54, 122.96, 122.08, 85.14, 79.30, 32.70, 32.64, 29.47, 26.72, 26.70. HRMS (ESI, m/z): [M + H]⁺ calcd for C₁₈H₁₉S, 267.1207; found 267.1203.

Synthesis of S15.



Under nitrogen atmosphere, PtCl₂ (8 mg, 0.03 mmol) and compound **S14** (80 mg, 0.30 mmol) were added to dry toluene (5 mL). The mixture was stirred at 110 °C overnight and then cooled to room temperature. After removing toluene in vacuum, the residue was purified by chromatography on silica gel (eluent: dichloromethane/petroleum ether = 1/10) to afford compound **S15** as a white solid in 66% yield (52 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.89 (d, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.40–7.32 (m, 3H), 2.99–2.91 (m, 2H), 2.52–2.45 (m, 2H), 1.84–1.77 (m, 2H), 1.55–1.45 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 147.43, 146.87, 139.92, 139.80, 138.45, 126.52, 124.42, 124.37, 124.29, 124.07, 123.83, 122.71, 39.91, 30.09, S35

28.49, 26.77, 26.41, 25.76. HRMS (ESI, *m*/z): [M + H]⁺ calcd for C₁₈H₁₉S, 267.1207; found 267.1209.
4. Crystallographic data for 3b and 4a.

Fig. S1. ORTEP diagram for the crystal structure of **3b** with an ellipsoid contour probability level of 50%.



Fig. S2. ORTEP diagram for the crystal structure of 4a with an ellipsoid contour probability level of 50%.



Table S1

	3b	4 a
CCDC No.	2254334	2254335
formula	$C_{42}H_{40}S_2$	$C_{34}H_{44}S_2$
formula wt.	608.86	514.55
<i>T</i> (K)	173	302
wavelength (Å)	1.54178	1.34139
crystal syst.	Monoclinic	Monoclinic
space group	<i>C2/m</i>	$P2_1/c$
<i>a</i> (Å)	26.534(6)	5.050(1)
<i>b</i> (Å)	7.135(12)	23.714(3)
<i>c</i> (Å)	25.949(8)	12.344(2)
α (deg.)	90	90
β (deg.)	118.26(1)	93.778(1)
γ (deg.)	90	90
$V(Å^3)$	4327.1(19)	1475.04(4)
Z	4	2
$\mu \text{ (mm}^{-1})$	1.270	1.16
<i>F</i> (000)	1296.0	556.0
final R indices	R1 = 0.0500	R1 = 0.0531
$[I > 2\theta(I)]$	wR2 = 0.1247	wR2 = 0.2390
R indices (all data)	R = 0.0464	R = 0.0898
	wR2 = 0.1470	wR2 = 0.2419

Crystal data and structure refinement details for **3b** and **4a**.

Table S2

Selected bond lengths for **3b**.

Bond	Length / Å	Bond	Length / Å
S1-C3	1.737(3)	C9-C10	1.425(4)
S1-C1	1.735(2)	C10-C15	1.414(4)
C2-C7	1.417(3)	C10-C11	1.416(4)
C2-C3	1.403(3)	C11-C12	1.411(4)
C3-C4	1.414(3)	C12-C13	1.365(4)
C4-C5	1.377(4)	C13-C14	1.399(4)
C4-C16	1.506(3)	C14-C15	1.364(4)
C5-C6	1.411(3)	C16-C17	1.525(3)
C1-C2	1.441(3)	C17-C18	1.522(3)
C6-C11	1.456(3)	C18-C19	1.526(4)
C6-C7	1.418(4)	C19-C20	1.536(4)
C7-C8	1.423(3)	C20-C21	1.510(5)
C8-C9	1.341(4)		
		1	

Table S3

Selected bond lengths for 4a.

Bond	Length / Å	Bond	Length / Å
S1-C2	1.718(4)	C8-C9	1.499(7)
S1-C1	1.713(6)	C9-C10	1.521(5)
C1-C4	1.416(3)	C10-C11	1.517(5)
C2-C3	1.360(3)	C6-C11	1.421(5)
C3-C4	1.478(7)	C1-C14	1.514(7)
C3-C11	1.387(5)	C14-C15	1.509(5)
C4-C5	1.462(7)	C15-C16	1.499(4)
C5-C6	1.376(5)	C16-C17	1.494(5)
C6-C7	1.493(5)	C17-C18	1.504(5)
C7-C8	1.486(6)	C18-C19	1.489(6)

5. Absorption and PL spectra of 3b and 4a.





6. Density funcational theory calculations.

Density-functional theory (DFT) calculations were performed with the B3LYP-D3(BJ) functional with Gaussian 16 programs (LANL2DZ for Pt atom and 6-31G* for other atoms).^{S6} Frequency calculations were performed at the same level of theory as for geometry optimization in toluene solutions to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency) on the potential energy surface, as well as to obtain thermal Gibbs free energy corrections. Intrinsic reaction coordinate calculations were performed to ensure that the first-order saddle points found were true transition states (TS) connecting the reactants and the products.



Fig. S4. Calculated pathway of the reactions of 6-*endo*-dig and ring-expansion and the relative Gibbs free energies (in kcal/mol) of the starting material and the transition state.

Atomic	C	oordinates (Angstrom	us)
Name	Х	Y	Z
С	0.59224	3.91903	-0.57419
С	1.8913	3.70934	-1.05555
С	2.52803	2.47997	-0.87957
С	1.89212	1.41825	-0.2255
С	0.56446	1.63492	0.24562
С	-0.07069	2.8908	0.07652
С	2.5988	0.12952	-0.01904
С	-0.15959	0.58889	0.85623
С	-0.77664	-0.3186	1.49037
С	2.92758	-0.77362	-1.10265
С	3.61938	-1.86118	-0.65286
S	3.88728	-1.81888	1.06062
С	3.04747	-0.30048	1.21231
С	2.49303	-0.58146	-2.53109
С	2.95038	0.37613	2.55021
Pt	-2.01321	-0.54245	-0.05646
Cl	-3.48835	1.15556	0.63317
Cl	-0.85077	-2.31413	-1.0459
Н	0.10333	4.87803	-0.71428
Н	2.41477	4.51382	-1.56495
Н	3.54398	2.33997	-1.23634
Н	-1.08942	3.00963	0.4319
Н	-0.82193	-0.85269	2.42659
Н	3.95996	-2.7087	-1.23283
Н	2.92517	-1.35455	-3.17318
Н	1.4017	-0.65025	-2.61586
Н	2.79668	0.39401	-2.92881
Н	2.36882	-0.21854	3.26557
Н	3.94102	0.53636	2.99216
Н	2.46801	1.35293	2.45516

Table S4. Calculated orientation for intermediate 5a.

Atomic	C	oordinates (Angstrom	us)
Name	Х	Y	Z
С	0.66767	3.75969	-0.89179
С	2.06132	3.66904	-0.91226
С	2.69781	2.45763	-0.62139
С	1.93911	1.32664	-0.31687
С	0.52742	1.42843	-0.30098
С	-0.10656	2.64048	-0.5845
С	2.54099	0.00243	0.00363
С	-0.14471	0.18313	0.03289
С	0.37949	-0.91969	0.45254
С	3.05085	-0.92316	-0.99272
С	3.6255	-2.01529	-0.41242
S	3.5651	-1.97	1.32841
С	2.74257	-0.43716	1.31611
С	2.90046	-0.71185	-2.4735
С	2.46761	0.29758	2.59493
Pt	-2.03151	-0.36621	0.016
Cl	-2.65271	1.09525	1.74063
Cl	-1.84566	-1.88763	-1.75945
Н	0.18129	4.70472	-1.11427
Н	2.6587	4.54365	-1.15349
Н	3.78232	2.394	-0.63095
Н	-1.18904	2.69631	-0.55138
Н	0.53392	-1.96762	0.61575
Н	4.06018	-2.87217	-0.9107
Н	3.41915	-1.4936	-3.03528
Н	1.84233	-0.73237	-2.76189
Н	3.30349	0.25892	-2.78326
Н	2.07892	-0.37227	3.36822
Н	3.38564	0.75737	2.98236
Н	1.734	1.09014	2.43052

Table S5. Calculated orientation for transition state 5b.

Atomic	C	oordinates (Angstrom	s)
Name	Х	Y	Z
С	0.53551	3.81385	-0.58244
С	1.93479	3.73414	-0.61268
С	2.60014	2.50862	-0.46833
С	1.8391	1.35506	-0.33495
С	0.42157	1.43217	-0.29237
С	-0.23639	2.66684	-0.41143
С	2.27974	-0.05533	-0.11659
С	-0.11955	0.10509	-0.08101
С	0.95899	-0.85105	0.08186
С	3.40198	-0.76187	-0.78618
С	3.87385	-1.78773	-0.05114
S	3.12767	-2.00442	1.53298
С	1.98421	-0.63514	1.2596
С	3.84118	-0.41261	-2.17892
С	1.59567	0.11132	2.51793
Pt	-1.92827	-0.3786	-0.09094
Cl	-2.69313	1.10274	1.55561
Cl	-1.76761	-2.03743	-1.73674
Н	0.05054	4.77926	-0.68895
Н	2.51734	4.64084	-0.75134
Н	3.68534	2.46742	-0.47569
Н	-1.31834	2.71144	-0.35986
Н	0.82889	-1.87044	-0.26242
Н	4.63068	-2.49834	-0.36329
Н	4.68359	-1.03515	-2.49321
Н	3.02258	-0.55888	-2.89577
Н	4.14523	0.63837	-2.25552
Н	0.89054	0.9185	2.3084
Н	1.1093	-0.57214	3.22166
Н	2.48443	0.53026	3.00049

Table S6. Calculated orientation for intermediate 5c.

Atomic	C	oordinates (Angstrom	us)
Name	Х	Y	Z
С	-0.32552	3.77341	0.53508
С	-1.70245	3.78428	0.73975
С	-2.44755	2.6013	0.60653
С	-1.7891	1.42173	0.27764
С	-0.39245	1.40631	0.0643
С	0.33948	2.58402	0.20102
С	-2.45942	0.12912	0.01093
С	0.12527	0.05579	-0.25056
С	-0.75521	-0.89118	-0.71833
С	-3.3411	-0.59058	0.85651
С	-3.83199	-1.71107	0.21852
S	-3.2509	-1.98458	-1.37592
С	-2.1545	-0.50703	-1.29151
С	-3.6347	-0.23458	2.28983
С	-2.15314	0.27929	-2.60024
Pt	1.93516	-0.43675	0.11588
Cl	3.03269	0.97705	-1.4079
Cl	1.36932	-2.03353	1.74092
Н	0.24594	4.69026	0.64482
Н	-2.2077	4.7067	1.01078
Н	-3.52425	2.6147	0.74965
Н	1.41313	2.56658	0.04936
Н	-0.5175	-1.94558	-0.66318
Н	-4.49759	-2.44039	0.66834
Н	-4.40196	-0.89345	2.70552
Н	-2.7297	-0.33741	2.89992
Н	-3.98206	0.798	2.39145
Н	-1.4853	1.13996	-2.51354
Н	-1.78171	-0.35306	-3.41222
Н	-3.1595	0.62897	-2.85285

 Table S7. Calculated orientation for transition state 5d.

Atomic	C	oordinates (Angstrom	s)
Name	Х	Y	Z
С	0.60616	3.92127	-0.14402
С	2.01982	3.82993	-0.18024
С	2.67952	2.61071	-0.20143
С	1.91789	1.4251	-0.20776
С	0.47725	1.51936	-0.17405
С	-0.16922	2.77967	-0.13465
С	2.31209	0.04667	-0.24582
С	-0.07639	0.2158	-0.17528
С	1.05145	-0.77393	-0.18355
С	3.55579	-0.60247	-0.56204
С	3.75385	-1.86349	-0.07849
S	2.73851	-2.45023	1.21655
С	1.48579	-1.26704	1.16161
С	4.61656	0.0733	-1.40345
С	0.75183	-0.93755	2.4215
Pt	-1.88715	-0.29193	-0.18235
Cl	-2.59855	0.98048	1.6519
Cl	-1.73021	-1.75167	-2.00856
Н	0.13657	4.8995	-0.1163
Н	2.60407	4.74651	-0.18392
Н	3.76324	2.57627	-0.21512
Н	-1.25131	2.82265	-0.08416
Н	0.91058	-1.55536	-0.94007
Н	4.58321	-2.50408	-0.35464
Н	5.35745	-0.65596	-1.74392
Н	4.18959	0.56609	-2.28316
Н	5.15555	0.8347	-0.82522
Н	0.52707	0.1372	2.45659
Н	-0.2252	-1.43886	2.4459
Н	1.32499	-1.20839	3.31198

Table S8. Calculated orientation for transition state 5d'.

Atomic	C	oordinates (Angstrom	us)
Name	Х	Y	Z
С	0.36015	3.59121	-0.46976
С	1.76314	3.69626	-0.4624
С	2.52776	2.56312	-0.28069
С	1.91947	1.29218	-0.07622
С	0.47653	1.19104	-0.06693
С	-0.26479	2.36674	-0.28047
С	2.68001	0.09578	0.06892
С	-0.19462	-0.10085	0.1273
С	0.53313	-1.18335	0.48613
С	3.99987	-0.20268	-0.36007
С	4.26547	-1.56003	-0.25164
S	3.02767	-2.56311	0.35315
С	2.00156	-1.05877	0.7431
С	5.01149	0.73417	-0.96954
С	2.18146	-0.84185	2.30677
Pt	-2.11871	-0.28784	-0.10022
Cl	-2.68072	0.84134	1.89515
Cl	-1.95095	-1.46168	-2.12914
Н	-0.24629	4.47998	-0.61913
Н	2.24161	4.66224	-0.59109
Н	3.60465	2.65363	-0.24064
Н	-1.34554	2.29493	-0.27734
Н	0.05985	-2.12924	0.7238
Н	5.21077	-2.01085	-0.53859
Н	5.85288	0.16953	-1.38106
Н	4.56995	1.31861	-1.78374
Н	5.41704	1.43791	-0.23348
Н	1.66995	0.08365	2.58106
Н	1.71641	-1.67242	2.84136
Н	3.23992	-0.77916	2.57634

Table S9. Calculated orientation for intermediate 5e.

Atomic	C	oordinates (Angstrom	s)
Name	Х	Y	Z
С	-0.54725	3.99506	0.02218
С	-1.96788	3.94685	0.0631
С	-2.66344	2.75463	0.09697
С	-1.94304	1.5326	0.09305
С	-0.49372	1.58762	0.0622
С	0.18927	2.83354	0.0198
С	-2.37119	0.18009	0.13772
С	0.03518	0.28579	0.07188
С	-1.11776	-0.68515	0.16193
С	-3.64115	-0.40206	0.2858
С	-3.81411	-1.76244	0.06273
S	-2.66615	-2.70645	-0.79701
С	-1.26009	-1.79216	-0.83531
С	-4.8671	0.41091	0.64482
С	-0.19553	-2.17934	-1.80492
Pt	1.8578	-0.22099	0.17994
Cl	2.66633	0.94392	-1.68236
Cl	1.55339	-1.57964	2.07337
Н	-0.04873	4.95875	-0.01266
Н	-2.52319	4.88132	0.05759
Н	-3.74621	2.76425	0.11349
Н	1.27211	2.8418	-0.03164
Н	-0.96236	-1.14403	1.16505
Н	-4.75092	-2.27499	0.24461
Н	-5.69607	-0.24409	0.92768
Н	-4.67	1.09242	1.47846
Н	-5.20312	1.01252	-0.20898
Н	0.09519	-1.30551	-2.40579
Н	0.71343	-2.48955	-1.27378
Н	-0.51832	-2.98065	-2.47623

Table S10. Calculated orientation for intermediate 5e'.

Atomic	С	oordinates (Angstrom	s)
Name	Х	Y	Z
С	0.45974	3.55145	0.82572
С	1.87333	3.59064	0.83436
С	2.60706	2.4615	0.55823
С	1.97973	1.21718	0.25533
С	0.52216	1.17627	0.25541
С	-0.19202	2.37602	0.54512
С	2.72455	0.04099	-0.0617
С	-0.18667	-0.03341	-0.02275
С	0.54771	-1.21318	-0.23493
С	4.14526	-0.17407	-0.27576
С	4.4072	-1.44329	-0.70572
S	3.00541	-2.46433	-0.91527
С	1.99096	-1.18014	-0.23861
С	5.26439	0.8206	-0.10257
С	1.41605	-1.70692	1.55992
Pt	-2.11152	-0.20686	-0.10025
Cl	-2.1827	-1.84037	1.61666
Cl	-2.51031	1.3063	-1.84071
Н	-0.11011	4.45011	1.04115
Н	2.38692	4.52034	1.06317
Н	3.68474	2.52331	0.58123
Н	-1.27369	2.33342	0.53157
Н	0.03762	-2.13207	-0.49392
Н	5.38416	-1.84723	-0.9396
Н	6.22271	0.35347	-0.34738
Н	5.14222	1.68659	-0.76312
Н	5.33146	1.19104	0.9269
Н	0.58297	-2.39508	1.68393
Н	2.3809	-2.17182	1.74914
Н	1.26669	-0.77035	2.08686

Table S11. Calculated orientation for transition state 5f.

Atomic	C	oordinates (Angstrom	s)
Name	Х	Y	Z
С	0.59194	3.98369	0.29798
С	2.00709	3.95242	0.26012
С	2.70199	2.76268	0.16157
С	1.98144	1.54196	0.09074
С	0.54881	1.58838	0.14833
С	-0.14017	2.81404	0.24677
С	2.39809	0.17824	-0.00974
С	-0.00371	0.26809	0.04144
С	1.152	-0.65059	0.00559
С	3.69079	-0.37698	-0.03561
С	3.88458	-1.74087	-0.19101
S	2.64336	-2.87124	-0.47187
С	1.18082	-2.03593	-0.39409
С	4.93117	0.48235	0.07178
С	-0.03624	-2.85374	-0.7
Pt	-1.88071	-0.15371	0.06032
Cl	-1.63678	-1.26399	2.13389
Cl	-2.49832	0.83872	-1.96164
Н	0.08144	4.93969	0.36739
Н	2.55866	4.88752	0.30366
Н	3.78305	2.78235	0.12933
Н	-1.22428	2.8172	0.26287
Н	0.60901	-0.53443	1.12372
Н	4.87446	-2.18209	-0.20322
Н	5.83288	-0.13579	0.07542
Н	5.00539	1.17538	-0.77382
Н	4.92464	1.07688	0.99157
Н	-0.64938	-2.34468	-1.4535
Н	0.23163	-3.85023	-1.06529
Н	-0.66115	-2.95539	0.19565

Table S12. Calculated orientation for transition state 5f'.

Atomic	Coordinates (Angstroms)		
Name	Х	Y	Z
С	0.43474	3.63725	-0.41653
С	1.83516	3.68256	-0.39498
С	2.58842	2.5236	-0.2449
С	1.98617	1.26117	-0.10755
С	0.53931	1.2114	-0.10529
С	-0.19754	2.41917	-0.27226
С	2.76119	0.0293	0.01556
С	-0.14662	-0.02687	0.06413
С	0.59736	-1.29704	0.37118
С	4.2027	-0.17654	-0.07517
С	4.52254	-1.49316	0.08801
S	3.14448	-2.51377	0.34862
С	2.08099	-1.15418	0.23673
С	5.28068	0.84612	-0.33223
С	0.2026	-1.83441	1.78571
Pt	-2.02256	-0.20629	-0.10442
Cl	-2.72598	1.03757	1.74691
Cl	-1.98428	-1.57152	-2.00864
Н	-0.14694	4.54567	-0.53384
Н	2.34793	4.63552	-0.49579
Н	3.66386	2.61102	-0.23193
Н	-1.27856	2.36506	-0.26207
Н	0.23502	-2.03649	-0.35969
Н	5.51233	-1.92932	0.0589
Н	6.25257	0.34963	-0.40909
Н	5.11741	1.39134	-1.26916
Н	5.35726	1.58307	0.4766
Н	-0.87603	-1.99336	1.83944
Н	0.71647	-2.78282	1.96653
Н	0.49492	-1.12168	2.56179

 Table S13. Calculated orientation for intermediate 5g.

Atomic	Coordinates (Angstroms)		
Name	Х	Y	Z
С	0.2134	4.01255	-0.4691
С	-1.10658	4.15501	-0.00095
С	-1.93966	3.05274	0.12941
С	-1.44273	1.77786	-0.21648
С	-0.09959	1.64524	-0.66315
С	0.72687	2.76168	-0.79839
С	-2.063	0.46702	-0.25037
С	0.21653	0.22081	-0.94895
С	-1.09574	-0.46903	-0.74548
С	-3.38396	0.08523	0.12369
С	-3.79056	-1.2194	-0.03439
S	-2.86262	-2.50515	-0.66899
С	-1.33284	-1.80161	-1.0087
С	-4.37326	1.06693	0.7056
С	-0.29343	-2.75237	-1.53226
Pt	1.60543	-0.40342	0.41226
Cl	3.32092	0.06409	-1.13508
Cl	0.15197	-0.99695	2.18385
Н	0.84253	4.89309	-0.56528
Н	-1.47901	5.14108	0.26064
Н	-2.95093	3.19423	0.48651
Н	1.75305	2.63495	-1.12884
Н	0.68405	0.04032	-1.92204
Н	-4.79331	-1.5261	0.24735
Н	-5.30637	0.56569	0.97636
Н	-3.969	1.53863	1.60753
Н	-4.61396	1.86066	-0.01049
Н	0.46961	-2.90518	-0.75952
Н	-0.7234	-3.71861	-1.81205
Н	0.21326	-2.32679	-2.4043

Table S14. Calculated orientation for intermediate 5g'.

Atomic	C	oordinates (Angstrom	s)
Name	Х	Y	Z
С	-0.50245	3.61509	-0.46815
С	-1.9012	3.67475	-0.40188
С	-2.64558	2.51727	-0.24778
С	-2.02669	1.25065	-0.1484
С	-0.59627	1.19685	-0.21176
С	0.13537	2.39087	-0.37579
С	-2.77511	0.01366	0.00675
С	0.12158	-0.07925	-0.08878
С	-0.63498	-1.29506	0.04745
С	-4.20558	-0.20579	0.0925
С	-4.495	-1.53765	0.22741
S	-3.11556	-2.57349	0.25051
С	-2.0662	-1.19216	0.08066
С	-5.31264	0.81693	0.05827
Pt	2.0707	-0.12891	0.03826
Cl	2.18268	-0.94053	-2.18186
Cl	2.3005	0.60415	2.24324
Н	0.0813	4.52216	-0.59033
Н	-2.41019	4.63185	-0.47342
Н	-3.72096	2.59738	-0.20524
Н	1.21653	2.32892	-0.41961
Н	-5.48285	-1.96952	0.32616
Н	-6.28195	0.32001	0.15968
Н	-5.22863	1.5413	0.87644
Н	-5.32837	1.37478	-0.8851
С	0.03639	-2.62368	0.29555
Н	0.9933	-2.68219	-0.2253
Н	0.23586	-2.71484	1.36955
Н	-0.59571	-3.45862	-0.02047
Н	-0.14823	-0.797	-1.14473

Table S15. Calculated orientation for transition state 5h.

Atomic	Coordinates (Angstroms)		
Name	Х	Y	Z
С	-1.21297	3.92263	-0.53647
С	-2.48112	3.5199	-0.10501
С	-2.8057	2.16984	-0.02415
С	-1.87202	1.17019	-0.36156
С	-0.58001	1.59152	-0.78677
С	-0.27399	2.95853	-0.87756
С	-2.15821	-0.26346	-0.32559
С	0.4411	0.61436	-1.17029
С	0.1257	-0.8032	-1.21513
С	-3.35773	-0.94619	0.09154
С	-3.23184	-2.30814	-0.04423
S	-1.71225	-2.82612	-0.66087
С	-1.17329	-1.17061	-0.75428
С	-4.62915	-0.34819	0.6366
Pt	1.55314	-0.08942	0.48317
Cl	3.51034	0.19235	-0.79854
Cl	0.11985	-0.4021	2.31472
Н	-0.96354	4.97728	-0.60403
Н	-3.22522	4.26339	0.16626
Н	-3.79838	1.90047	0.30396
Н	0.7201	3.2511	-1.20494
Н	-3.98744	-3.04395	0.20031
Н	-5.32991	-1.14294	0.90905
Н	-4.4424	0.24827	1.53657
Н	-5.13183	0.29392	-0.09635
С	0.91092	-1.76182	-2.0797
Н	1.89534	-1.36417	-2.32632
Н	1.04805	-2.72713	-1.58203
Н	0.34763	-1.94124	-3.00589
Н	1.19516	0.97099	-1.86975

 Table S16. Calculated orientation for intermediate 5i.

Atomic	С	oordinates (Angstrom	us)
Name	Х	Y	Z
С	0.46189	3.75587	-0.17228
С	1.83217	3.57132	-0.87507
С	2.73886	2.53131	-0.16751
С	2.00422	1.29846	0.28699
С	0.79702	1.53872	0.94648
С	0.37444	2.98507	1.16191
С	2.5733	-0.02172	0.06163
С	-0.06801	0.50934	1.24102
С	-0.98374	-0.3482	1.48959
С	3.07463	-0.46684	-1.2331
С	3.58934	-1.72591	-1.16254
S	3.53265	-2.38512	0.44069
С	2.74535	-0.97546	1.06476
С	2.9367	0.28552	-2.53256
С	2.45766	-0.90908	2.53745
Pt	-2.04751	-0.50315	-0.15586
Cl	-3.00705	1.64689	-0.09737
Cl	-1.33074	-2.70116	-0.55426
Н	0.26438	4.81684	0.01401
Н	1.68097	3.25241	-1.91166
Н	3.60995	2.27862	-0.77435
Н	1.03096	3.45033	1.91205
Н	-1.19336	-0.97263	2.35103
Н	3.96682	-2.32572	-1.98013
Н	3.14166	-0.37868	-3.37686
Н	1.92108	0.6768	-2.66078
Н	3.63067	1.13124	-2.60864
Н	1.5924	-1.52997	2.79727
Н	3.31107	-1.27116	3.12122
Н	2.23936	0.1142	2.85251
Н	-0.64612	3.01754	1.548
Н	-0.34671	3.39248	-0.81418
Н	2.38185	4.51759	-0.91927
Н	3.13806	2.9901	0.75284

 Table S17. Calculated orientation for intermediate 6a.

Atomic	С	oordinates (Angstrom	us)
Name	Х	Y	Z
С	0.80352	3.85295	-0.32619
С	2.10456	3.57566	-1.0908
С	2.84133	2.36001	-0.50517
С	1.90425	1.20324	-0.23627
С	0.55785	1.35139	-0.20237
С	-0.1602	2.65923	-0.41226
С	2.47125	-0.14993	0.01897
С	-0.15582	0.10897	0.06743
С	0.31767	-1.03675	0.42505
С	2.92488	-1.0504	-1.03043
С	3.51353	-2.16627	-0.51455
S	3.53515	-2.17695	1.22818
С	2.73237	-0.63653	1.30406
С	2.69547	-0.79582	-2.49434
С	2.49918	0.04589	2.61909
Pt	-2.06278	-0.36231	0.00501
Cl	-2.57934	0.77974	1.99013
Cl	-1.94362	-1.53974	-2.02063
Н	1.03896	4.05477	0.728
Н	1.87104	3.38211	-2.14659
Н	3.64572	2.03376	-1.17814
Н	-0.96316	2.74908	0.32836
Н	0.44703	-2.09127	0.56277
Н	3.91521	-3.01027	-1.06024
Н	3.15643	-1.57776	-3.10427
Н	1.6221	-0.77855	-2.71927
Н	3.11241	0.16845	-2.80824
Н	2.11513	-0.65013	3.37149
Н	3.43125	0.47506	3.00847
Η	1.77187	0.8529	2.50139
Н	-0.65828	2.63414	-1.39275
Н	0.31283	4.75167	-0.71599
Н	2.76333	4.45136	-1.06719
Н	3.34366	2.63574	0.43579

Table S18. Calculated orientation for transition state 6b.

Atomic	Coordinates (Angstroms)		
Name	Х	Y	Z
С	0.73765	3.79704	-0.75594
С	2.04271	3.68514	0.04754
С	2.77725	2.36815	-0.26673
С	1.83549	1.20252	-0.30508
С	0.46771	1.33961	-0.3231
С	-0.24199	2.66392	-0.40134
С	2.23078	-0.22848	-0.17357
С	-0.12919	0.03796	-0.16473
С	0.9085	-0.984	-0.05393
С	3.37455	-0.92347	-0.8293
С	3.79434	-1.99924	-0.13929
S	2.99359	-2.28793	1.40909
С	1.87324	-0.89245	1.17773
С	3.8853	-0.513	-2.18152
С	1.4496	-0.23033	2.47073
Pt	-1.96015	-0.33446	-0.08073
Cl	-2.44511	0.79788	1.91972
Cl	-2.09705	-1.62066	-2.03123
Н	0.26053	4.76556	-0.57174
Н	2.70327	4.53277	-0.16579
Н	3.28043	2.44326	-1.24355
Н	-0.73863	2.85887	0.55771
Н	0.74765	-1.96696	-0.48241
Н	4.54974	-2.70575	-0.46404
Н	4.687	-1.17833	-2.51447
Н	3.08501	-0.54361	-2.93228
Н	4.28145	0.50998	-2.17378
Н	0.76885	0.60572	2.29778
Н	0.91129	-0.95244	3.09372
Н	2.32507	0.11986	3.027
Н	-1.04874	2.59755	-1.14092
Н	0.97071	3.75977	-1.8293
Н	1.81384	3.72348	1.12098
Н	3.57826	2.17192	0.45884

Table S19. Calculated orientation for intermediate 6c.

Atomic	Coordinates (Angstroms)		
Name	Х	Y	Z
С	0.82599	3.8962	-0.45013
С	2.15815	3.70067	0.28798
С	2.85821	2.40909	-0.17261
С	1.91498	1.2388	-0.21053
С	0.51306	1.4084	-0.19412
С	-0.15878	2.75535	-0.14065
С	2.26014	-0.14559	-0.25609
С	-0.09796	0.14185	-0.20295
С	0.96803	-0.91063	-0.21959
С	3.48988	-0.83596	-0.62224
С	3.67774	-2.07453	-0.10529
S	2.65477	-2.59756	1.22603
С	1.46491	-1.33073	1.12914
С	4.47822	-0.2245	-1.58705
С	0.79422	-0.90972	2.39552
Pt	-1.93956	-0.27285	-0.16411
Cl	-2.49111	0.79347	1.85612
Cl	-1.9164	-1.51304	-2.15518
Н	0.37426	4.85491	-0.17323
Н	2.82487	4.55373	0.11964
Н	3.26441	2.55639	-1.18515
Н	-0.60333	2.88866	0.85383
Н	0.80675	-1.7082	-0.94955
Н	4.47755	-2.74931	-0.38754
Н	5.28429	-0.92855	-1.81218
Н	3.99986	0.06062	-2.53152
Н	4.93675	0.67873	-1.16687
Н	0.53264	0.15517	2.34984
Н	-0.16772	-1.42821	2.50659
Н	1.4184	-1.09697	3.27265
Н	-1.00244	2.76396	-0.83984
Н	1.01679	3.93891	-1.53176
Н	1.97418	3.65028	1.36974
Н	3.71943	2.17326	0.46487

Table S20. Calculated orientation for transition state 6d.

Atomic	С	oordinates (Angstrom	ls)
Name	Х	Y	Z
С	0.42719	3.84081	-0.04579
С	1.65248	3.71522	-0.96146
С	2.56566	2.5616	-0.51218
С	1.75439	1.32232	-0.20416
С	0.42213	1.32378	0.01061
С	-0.42625	2.56276	-0.06775
С	2.41131	0.00713	0.01871
С	-0.1295	-0.02491	0.32735
С	0.69208	-0.98055	0.85693
С	3.19146	-0.74683	-0.88657
С	3.67446	-1.89649	-0.28528
S	3.18524	-2.16181	1.33403
С	2.14788	-0.63848	1.32648
С	3.39237	-0.41491	-2.34176
С	2.25186	0.12609	2.64487
Pt	-1.93519	-0.44425	-0.14044
Cl	-3.02614	0.61565	1.6492
Cl	-1.34811	-1.66084	-2.06466
Н	0.76357	4.03895	0.98179
Н	1.31971	3.52893	-1.99121
Н	3.31917	2.3504	-1.28117
Н	-1.15265	2.55405	0.75397
Н	0.40145	-2.02265	0.8812
Н	4.27708	-2.64841	-0.78448
Н	4.02032	-1.16548	-2.82951
Н	2.42601	-0.39281	-2.85824
Н	3.86789	0.56141	-2.47895
Н	1.62084	1.01707	2.59669
Н	1.88855	-0.49868	3.4661
Н	3.28466	0.42457	2.85433
Н	3.1339	2.85606	0.38475
Н	2.22612	4.64913	-0.97444
Н	-0.18553	4.69846	-0.34472
Н	-1.03336	2.51285	-0.98321

 Table S21. Calculated orientation for transition state 6d'.

Atomic	С	oordinates (Angstrom	s)
Name	Х	Y	Z
С	-0.72165	3.81633	-0.50067
С	-2.27126	3.69734	-0.39882
С	-2.77014	2.58504	0.56433
С	-1.97604	1.32559	0.37662
С	-0.54892	1.46772	0.32166
С	0.04556	2.83973	0.42136
С	-2.34542	-0.01218	0.26191
С	0.04611	0.23186	0.16249
С	-1.04831	-0.81651	0.16619
С	-3.60052	-0.67138	0.33307
С	-3.71433	-1.98537	-0.06927
S	-2.51044	-2.79584	-1.00827
С	-1.1274	-1.85589	-0.90107
С	-4.85615	0.02168	0.81868
С	-0.00999	-2.16947	-1.83209
Pt	1.91172	-0.18751	0.179
Cl	2.54822	1.09969	-1.67783
Cl	1.69856	-1.65608	2.01077
Н	-0.4102	3.61505	-1.53099
Н	-2.71053	4.6456	-0.07015
Н	-2.62446	2.92289	1.60178
Н	1.10574	2.82022	0.16056
Н	-0.85339	-1.36246	1.11741
Н	-4.63376	-2.55154	0.02137
Н	-5.64692	-0.70775	1.01605
Н	-4.67532	0.58796	1.73698
Н	-5.23641	0.7198	0.06343
Н	0.2791	-1.25803	-2.37525
Н	0.88149	-2.45803	-1.26022
Н	-0.2668	-2.95644	-2.54711
Н	-3.84318	2.4348	0.43357
Н	-2.68681	3.49508	-1.39239
Н	-0.4047	4.84026	-0.2758
Н	-0.02573	3.18363	1.46473

 Table S22. Calculated orientation for intermediate 6e.

Atomic	C	oordinates (Angstrom	us)
Name	Х	Y	Z
С	0.44953	3.65209	0.36255
С	1.76659	3.52269	1.12156
С	2.64099	2.46409	0.44298
С	1.92721	1.13001	0.24282
С	0.50785	1.07603	0.21325
С	-0.31367	2.32547	0.38232
С	2.65258	-0.04891	0.00514
С	-0.21499	-0.1677	0.0137
С	0.47483	-1.34112	-0.03812
С	4.02666	-0.23355	-0.38302
С	4.25103	-1.51675	-0.82451
S	2.91853	-2.60979	-0.81659
С	1.94177	-1.36041	0.15793
С	5.1369	0.78961	-0.41633
С	2.12666	-1.79624	1.68043
Pt	-2.15648	-0.24535	-0.1131
Cl	-2.34804	-1.35201	1.95795
Cl	-2.33456	0.81372	-2.21217
Н	-0.18305	4.43667	0.79121
Н	2.30831	4.47502	1.14884
Н	2.96749	2.85401	-0.53161
Н	-0.85412	2.20581	1.33449
Н	-0.04663	-2.29173	-0.05701
Н	5.21278	-1.87677	-1.17563
Н	6.04117	0.34348	-0.84056
Н	4.87667	1.65549	-1.03187
Н	5.38968	1.15744	0.5837
Н	1.65539	-1.04488	2.31815
Н	1.64073	-2.75901	1.84788
Н	3.19186	-1.87481	1.91431
Н	-1.10415	2.30628	-0.37875
Н	0.6547	3.94669	-0.67559
Н	1.57184	3.23465	2.16393
Н	3.54688	2.30432	1.03335

 Table S23. Calculated orientation for intermediate 6e'.

Atomic	Coordinates (Angstroms)		
Name	Х	Y	Z
С	0.80753	3.97765	-0.11921
С	2.14486	3.83231	0.61467
С	2.91014	2.58059	0.14707
С	2.01722	1.35936	0.07623
С	0.61361	1.48104	0.11984
С	-0.11698	2.79182	0.19468
С	2.36896	-0.00325	-0.01431
С	-0.0093	0.20681	0.04558
С	1.09563	-0.78626	0.01432
С	3.64402	-0.62834	-0.07984
С	3.76147	-1.98973	-0.24393
S	2.45774	-3.08571	-0.44116
С	1.03718	-2.17583	-0.30586
С	4.93401	0.16187	-0.00756
С	-0.22788	-2.95662	-0.48957
Pt	-1.91611	-0.11463	0.05057
Cl	-1.75077	-1.08379	2.20449
Cl	-2.41092	0.75042	-2.06655
Н	0.313	4.91413	0.1618
Н	2.77484	4.71583	0.45904
Н	3.33612	2.77212	-0.84908
Н	-0.53662	2.89843	1.20636
Н	0.52539	-0.5883	1.11847
Н	4.72811	-2.47677	-0.30656
Н	5.79517	-0.49127	-0.17284
Н	4.96275	0.95317	-0.7622
Н	5.05674	0.63419	0.97289
Н	-0.85815	-2.47273	-1.24513
Н	-0.02204	-3.98835	-0.79119
Н	-0.80712	-2.96155	0.44184
Н	-0.97664	2.76443	-0.4836
Н	0.98785	4.0281	-1.202
Н	1.95909	3.76287	1.69563
Н	3.76017	2.40701	0.81328

Table S24. Calculated orientation for transition state 6f.

Atomic	Coordinates (Angstroms)			
Name	Х	Y	Z	
С	0.54194	3.67969	0.20568	
С	1.84207	3.54439	0.99156	
С	2.69605	2.42387	0.39013	
С	1.95315	1.11362	0.15525	
С	0.52069	1.10747	0.12626	
С	-0.27175	2.3894	0.31843	
С	2.6783	-0.07044	-0.07016	
С	-0.20025	-0.08787	-0.06375	
С	0.50477	-1.30136	-0.23847	
С	4.11152	-0.31876	-0.23403	
С	4.35982	-1.59266	-0.64094	
S	2.94631	-2.6038	-0.88121	
С	1.93474	-1.30126	-0.23008	
С	5.2504	0.64885	-0.02474	
С	1.33248	-1.78255	1.55163	
Pt	-2.13363	-0.23448	-0.06996	
Cl	-2.19227	-1.35754	2.01608	
Cl	-2.49868	0.79269	-2.14846	
Н	-0.05862	4.51964	0.57179	
Н	2.41901	4.47642	0.98248	
Н	3.09791	2.76761	-0.57443	
Н	-0.74745	2.33534	1.30854	
Н	-0.03185	-2.20794	-0.49042	
Н	5.33542	-2.01668	-0.84352	
Н	6.19804	0.16639	-0.28162	
Н	5.15357	1.54156	-0.65012	
Н	5.32368	0.98107	1.01701	
Н	0.48162	-2.44625	1.69229	
Н	2.27883	-2.27745	1.7597	
Н	1.20405	-0.83698	2.06757	
Н	-1.0966	2.38549	-0.40037	
Н	0.77003	3.89026	-0.84846	
Н	1.61696	3.31946	2.04345	
Н	3.56045	2.24022	1.03217	

Table S25. Calculated orientation for transition state 6f'.

Atomic	Coordinates (Angstroms)			
Name	Х	Y	Z	
С	-0.12882	4.01415	-0.95121	
С	-1.11091	4.03963	0.22685	
С	-2.14511	2.9018	0.12922	
С	-1.49684	1.5917	-0.25806	
С	-0.18798	1.51894	-0.69895	
С	0.68706	2.71231	-0.93326	
С	-2.05939	0.26516	-0.26845	
С	0.20828	0.11985	-0.95895	
С	-1.04991	-0.65112	-0.73097	
С	-3.37386	-0.16982	0.09043	
С	-3.71689	-1.49232	-0.04593	
S	-2.72087	-2.76499	-0.61526	
С	-1.20892	-1.99637	-0.94167	
С	-4.42557	0.7728	0.6343	
С	-0.11171	-2.92454	-1.38715	
Pt	1.629	-0.34803	0.43874	
Cl	3.30565	-0.16223	-1.20149	
Cl	0.22174	-0.64491	2.31362	
Н	-0.68435	4.09546	-1.89629	
Н	-0.54859	3.93555	1.16429	
Н	-2.66683	2.80819	1.08726	
Н	1.25806	2.56848	-1.85993	
Н	0.70099	-0.05107	-1.9217	
Н	-4.71425	-1.83355	0.21503	
Н	-5.37644	0.25063	0.7726	
Н	-4.12316	1.17629	1.60623	
Н	-4.60096	1.61781	-0.03749	
Н	0.50891	-3.19237	-0.52381	
Н	-0.51058	-3.84133	-1.83288	
Н	0.54352	-2.43466	-2.1118	
Н	-2.91171	3.1703	-0.61304	
Н	-1.63602	5.00039	0.27606	
Н	0.5478	4.87468	-0.90735	
Н	1.44311	2.74958	-0.13795	

Table S26. Calculated orientation for intermediate 6g.

Atomic	Coordinates (Angstroms)			
Name	Х	Y	Z	
С	0.58891	3.57631	-0.85327	
С	1.81774	3.68901	0.04354	
С	2.6901	2.44105	-0.11701	
С	1.94948	1.12102	-0.08815	
С	0.54569	1.10336	-0.16947	
С	-0.25463	2.37996	-0.41023	
С	2.72092	-0.10103	0.01264	
С	-0.15292	-0.11213	-0.00789	
С	0.54825	-1.43128	0.15733	
С	4.17092	-0.30025	-0.00538	
С	4.48163	-1.62422	0.0939	
S	3.09337	-2.66062	0.21971	
С	2.03326	-1.30474	0.12446	
С	5.27064	0.7252	-0.13676	
С	0.06114	-2.23108	1.40229	
Pt	-2.05226	-0.1846	-0.04377	
Cl	-2.55416	0.88598	1.98108	
Cl	-2.16163	-1.3713	-2.06674	
Н	-0.01915	4.48635	-0.80954	
Н	2.41613	4.57568	-0.19487	
Н	3.23168	2.49766	-1.07334	
Н	-0.79719	2.62394	0.51146	
Н	0.22661	-2.00779	-0.73033	
Н	5.47197	-2.06013	0.09606	
Н	6.23716	0.21794	-0.209	
Н	5.15881	1.34532	-1.03211	
Н	5.32162	1.39875	0.72613	
Н	-1.01866	-2.37919	1.34955	
Н	0.55462	-3.20722	1.43133	
Н	0.29657	-1.68681	2.3208	
Н	-1.02667	2.16095	-1.15528	
Н	0.90599	3.45515	-1.89884	
Н	1.50095	3.78932	1.09019	
Н	3.46372	2.4221	0.65693	

Table S27. Calculated orientation for intermediate 6g'.

Atomic	Coordinates (Angstroms)			
Name	Х	Y	Z	
С	-0.59771	3.57713	-0.84834	
С	-1.83418	3.69009	0.03932	
С	-2.72613	2.45807	-0.14492	
С	-1.98047	1.13216	-0.11274	
С	-0.59651	1.1022	-0.20911	
С	0.22618	2.35877	-0.42704	
С	-2.72045	-0.0996	0.01587	
С	0.1357	-0.15093	-0.07631	
С	-0.58877	-1.39556	0.06868	
С	-4.15764	-0.32725	0.06379	
С	-4.44224	-1.65865	0.18842	
S	-3.05924	-2.69576	0.24761	
С	-2.0107	-1.31228	0.09458	
С	-5.27799	0.68196	-0.0147	
Pt	2.08614	-0.15058	0.04626	
C1	2.21304	-0.97595	-2.16801	
C1	2.26914	0.62354	2.24699	
Н	-0.90556	3.48165	-1.89914	
Н	-1.52384	3.76881	1.08989	
Н	-3.49723	2.45015	0.63027	
Н	1.00029	2.13656	-1.17022	
Н	-5.43056	-2.09579	0.2551	
Н	-6.2386	0.1608	-0.06573	
Н	-5.30999	1.33744	0.86245	
Н	-5.20211	1.31892	-0.90094	
С	0.11479	-2.70584	0.32384	
Н	1.0661	-2.74932	-0.20869	
Н	0.32928	-2.78401	1.3958	
Н	-0.50343	-3.55696	0.02268	
Н	-0.13583	-0.88023	-1.12145	
Н	-3.25892	2.53806	-1.10345	
Н	-2.41436	4.59125	-0.19027	
Н	0.02279	4.47733	-0.78005	
Н	0.77074	2.57163	0.50277	

Table S28. Calculated orientation for transition state 6h'.

Atomic	Coordinates (Angstroms)			
Name	Х	Y	Z	
С	-1.41308	3.85364	-0.89	
С	-2.30784	3.4628	0.28595	
С	-2.86403	2.04476	0.09979	
С	-1.82759	1.0313	-0.35551	
С	-0.59689	1.44556	-0.8058	
С	-0.2128	2.90573	-0.9494	
С	-2.12181	-0.39313	-0.31392	
С	0.42285	0.47882	-1.19492	
С	0.14635	-0.94919	-1.18717	
С	-3.34018	-1.06719	0.07562	
С	-3.21865	-2.4306	-0.04517	
S	-1.68604	-2.97132	-0.61214	
С	-1.13419	-1.3189	-0.7132	
С	-4.63742	-0.46898	0.56336	
Pt	1.60237	-0.07995	0.48455	
Cl	3.52357	0.2228	-0.84074	
Cl	0.18854	-0.38332	2.33378	
Н	-1.98581	3.7932	-1.82623	
Н	-1.72352	3.50579	1.21477	
Н	-3.30243	1.71041	1.04442	
Н	0.33987	3.03777	-1.88934	
Н	-3.98925	-3.15773	0.17824	
Н	-5.38971	-1.25613	0.67162	
Н	-4.52498	0.01034	1.54186	
Н	-5.03885	0.27806	-0.12789	
С	0.97489	-1.92556	-1.98795	
Н	1.94674	-1.50638	-2.24917	
Н	1.14254	-2.85451	-1.43325	
Н	0.43099	-2.18115	-2.90785	
Н	1.15998	0.82731	-1.91736	
Н	-3.6892	2.06944	-0.62718	
Н	-3.14132	4.16537	0.40175	
Н	-1.0661	4.88883	-0.79527	
Н	0.49904	3.16074	-0.15145	

Table S29. Calcula	ted orientation	for interm	ediate 6i'.
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7. ¹H and ¹³C NMR spectra.

Fig. S5. ¹ H NMR spectrum of	1a in CDCl ₃ .
7.66 7.64 7.749 7.747 7.745 7.745 7.738 7.736 7.736	3.04 3.01 2.28 2.29 2.79 2.77 1.66 1.56 1.156 1.



Fig. S6	. ¹³ C NMR	spectrum	of 1a	in CDCl ₃ .



Fig. S7. ¹H NMR spectrum of 1b in CDCl₃.








Fig. S11. ¹H NMR spectrum of **1d** in CDCl₃.



Fig. S12. ¹³C NMR spectrum of 1d in CDCl₃.

144.33 140.57 138.55 138.55 138.05 132.65 132.65 132.65 132.65 132.65 132.65 122.88 127.53 122.89 122.89 122.89 122.89 122.89 122.89 122.89	85.80 80.59 77.61 CDCI 77.29 CDCI 76.97 CDCI	31.74 31.45 39.49 29.04 29.04 22.77



Fig. S13. ¹H NMR spectrum of 3a in CDCl₃.



Fig. S14. ¹³C NMR spectrum of **3a** in CDCl₃.

	888	
143.11 138.72 136.45 136.45 133.85 133.38 122.37 122.37	77.28 77.27 76.95	∠ 31.85 23.71 23.04 29.03 - 22.75 - 14.29







	CDCI3 CDCI3 CDCI3	
140.56 137.54 132.65 132.65 131.54 123.15 125.19 125.19 125.19 125.19 125.19	77.56 77.24 76.92	34.36 31.92 31.92 29.37 29.37 22.83





Fig. S18. ¹³C NMR spectrum of 3c in CDCl₃.

140.01 137.31 137.31 133.55 133.486 133.486 133.486 129.16 129.16 128.98 128.98 124.78 124.78 124.78 124.78 122.99	77.40 CDCI3 77.08 CDCI3 76.76 CDCI3	35.13 31.79 29.14	22.71	14.21
			Ĩ	Ī



Fig. S19. ¹H NMR spectrum of **3d** in CDCl₃.





S79



Fig. S24. ¹³C NMR spectrum of S4b in CDCl₃.

- 193.20	- 156.33	- 143.92 - 141.21 - 136.51 - 128.50	 77.60 CDCI3 77.28 CDCI3 √ 76.96 CDCI3 	34.56 31.68 31.68 73.11 72.9.98 72.9.93 72.9.3 72.9.3 72.71 23.78 72.77 72.77 14.29
1		$(< < \land)$		



Fig. S25. ¹H NMR spectrum of **S4c** in CDCl₃.



Fig. S26. ¹³C NMR spectrum of S4c in CDCl₃.





Fig. S27. ¹H NMR spectrum of S4d in CDCl₃.

9.37	7,7,7,80 7,7,7,45 7,7,45 7,7,45 7,7,45 7,7,45 7,7,45 7,7,33 7,2,2,55 7,7,33 7,2,2,55 7,7,33 7,2,2,55 7,7,33 7,2,2,55 7,7,33 7,2,2,55 7,2,55 7,55 7
I	



Fig. S28. ¹³C NMR spectrum of S4d in CDCl₃.







S83

Fig. S31. ¹H NMR spectrum of S4f in CDCl₃.





Fig. S32. ¹³C NMR spectrum of S4f in CDCl₃





Fig. S33. ¹H NMR spectrum of 2a in CDCl₃.



Fig. S34. ¹³C NMR spectrum of 2a in CDCl₃









Fig. S38. ¹³C NMR spectrum of 2c in CDCl₃.

141.67 141.18 133.22 133.83 133.83 133.83 133.83 133.83 123.36 123.36 123.36 122.15 123.15 122.15 122.15	84.14 77.36 CDCI3 77.05 CDCI3 76.73 CDCI3	$\begin{array}{c} 31.64\\ 31.12\\ 31.12\\ 31.12\\ 30.23\\ 22.08\\ 22.47\\ 22.47\\ 22.47\end{array}$









Fig. S41. ¹H NMR spectrum of 2e in CDCl₃.

7.7.8 7.7.7 7.7.12 7.7.12 7.7.12 7.7.11 7.7.



Fig. S43. ¹H NMR spectrum of 2f in CDCl₃.

 $\begin{array}{c} 7.38\\ 7.38\\ 7.38\\ 7.33\\ 7.73\\ 7.73\\ 7.73\\ 7.73\\ 7.72\\ 1.13\\ 1.17\\ 1.17\\ 1.17\\ 1.17\\ 1.17\\ 1.17\\ 1.17\\ 1.17\\ 1.13\\$



S90

Fig. S45.¹H NMR spectrum of 4a in CDCl₃.









Fig. S47.¹H NMR spectrum of 4b in CDCl₃.

7.26	7.02	3.53 3.52 3.52 3.29 3.29 3.29 3.29 3.29 3.29 3.29 3.2	1.34 1.34 0.93 0.91 0.89
	1		



Fig. S48. ¹³C NMR spectrum of 4b in CDCl₃.

8	62	85	66	96	52	88	59	15	89	87	37
3.	33.	32.	30.	29.	29.	28.	26.	26.	24.	22.	14.
_	5	-	-	÷	2	7	ŀ	4	_	_	





Fig. S49. ¹H NMR spectrum of **4c** in CDCl₃.



Fig. S52. ¹³C NMR spectrum of 4d in CDCl₃.



Fig. S51. ¹H NMR spectrum of 4d in CDCl₃.







Fig. S54. ¹³C NMR spectrum of 4e in CDCl₃.





Fig. S56. ¹³C NMR spectrum of 4f in CDCl₃.

11.64 11.64 14.79 14.79 14.70 14.70 14.40 14.40 11.26 11.26	1.59 C	5.35 1.80 1.46 1.34 1.34
	552	14 53 53 33



Fig. S57. ¹H NMR spectrum of **S5** in CDCl₃.

10.20	7.91 7.7.88 7.7.78 7.7.78 7.7.35 7.7.35 7.7.35 7.7.35 7.7.37 7.7.37 7.7.37 7.7.37 7.7.37 7.7.37 7.7.37 7.7.37 7.7.37 7.7.38 7.7.37 7.7.38 7.7.38 7.7.41 7.7.73 7.7.741 7.7417	2.86 2.84 2.65 2.63 2.63 2.63 2.63



Fig. S58. ¹³C NMR spectrum of S5 in CDCl₃.

139.31 137.39 137.39 137.39 137.44 137.56 133.25 131.62 131.62 132.53 127.39 127.39 127.38 127.38 127.38 122.37 115.12 106.81	77.59 CDC 76.96 CDC 76.96 CDC	~ 27.42 ~ 23.12 16.76
	139.31 137.39 137.39 137.39 137.39 137.39 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 137.55 125.13 125.13 125.34 125.34 125.37 125.37 115.12 106.81	139.31 137.39 137.39 134.76 135.44 135.45 135.45 135.45 135.62 135.62 135.62 135.62 135.62 135.62 125.73 127.39 127.39 127.39 122.73 127.35 127.35 127.35 106.81 122.73 106.81 106.81 106.81 106.81 106.81 106.81 106.81 106.81 106.81 106.81 106.81 106.82 106.8





140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

Fig. S61. ¹H NMR spectrum of S7 in CDCl₃.

8.8. 8.78 8.10 7.65 7.165 7.165 7.165 7.165 7.165 7.165 7.136 7.132 7.132 7.123 7.12

2.99 2.95 2.95 2.95 2.95 2.95 2.99 2.89 2.89 2.89



Fig. S62. ¹³C NMR spectrum of S7 in CDCl₃.

147.51 140.75 140.75 139.00 139.00 139.00 133.99 133.99 133.99 133.99 133.99 133.99 128.35 128.35 128.35 128.35 128.35 126.40 126.40 126.40 126.66 126.66 126.66 126.40	77.37 CDCI: 77.05 CDCI: 76.74 CDCI:	\
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Fig. S64. ¹³C NMR spectrum of S8 in CDCl₃.





Fig. S65. ¹H NMR spectrum of S9 in CDCl₃. - 2.55 сно 3.14-00.1 0.89 1.05 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.(5.5 4.5 5.0 4.0 Fig. S66. ¹³C NMR spectrum of S9 in CDCl₃. -181.97135.44 133.00 131.68 129.96 129.74 128.63 128.48 122.79 122.38 140.57 129.68 125.55 125.13 - 15.75 129.64 129.32 129.28 125.24 124.99 137.39 СНО



Fig. S67. ¹H NMR spectrum of **S11** in Benzene- d_6 .





		Benzene Benzene Benzene	
140.22 139.60 137.65 134.86	133.00 129.86 129.64 129.15	128.14 127.90 127.66 126.40	126.13 125.20 124.98 124.89 124.89 123.30



 Fig. S69. 1 H NMR spectrum of S13 in CDCl₃.

 \mathfrak{S}_{0}
 \mathfrak{S}_{0}



Fig. S70. ¹³C NMR spectrum of S13 in CDCl₃.

3.05	6.68	2.09 0.30 0.30 5.48 7.49 3.18 3.03 3.03	62 CDCl3 36 CDCl3 39 CDCl3	
193	150	124 125 126 127 138	77. 76.	34. 26.29.
1		VICC V		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~



Fig. S71. ¹H NMR spectrum of S14 in CDCl₃.



8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4



	5 5 5 5 5 5	
144.10 140.20 138.05 138.05 124.00 123.55 123.55 122.00 122.00	85.14 79.30 77.59 77.27 76.96	32.70 32.64 29.47 26.72
		VIE



Fig. S73. ¹H NMR spectrum of **S15** in CDCl₃.

$\begin{array}{c} 2.36\\ 2.94\\ 2.93\\ 2.93\\ 2.94\\ 2.94\\ 2.94\\ 2.94\\ 2.94\\ 1.77\\ 1.77\\ 1.77\\ 1.77\\ 1.77\\ 1.77\\ 1.54\\ 1.54\\ 1.54\\ 1.56\\$



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