Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information I

Remote Electronic Effect on the N-Heterocyclic Carbene-catalyzed Asymmetric Intramolecular Stetter Reaction and Structural Revision of Products

Tsubasa Inokuma,[a,b] Kohei Iritani,[a] Yuki Takahara,[a] Chunzhao Sun,[a] Yousuke Yamaoka,[c] Satoru Kuwano,[c] and Ken-ichi Yamada[,a,b]*

[a]Graduate School of Pharmaceutical Sciences, Tokushima University, Shomachi, Tokushima 770-8505, Japan.

[b]Research Cluster on "Key Material Development", Tokushima University, Shomachi, Tokushima 770-8505, Japan.

[c]Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.

yamak@tokushima-u.ac.jp

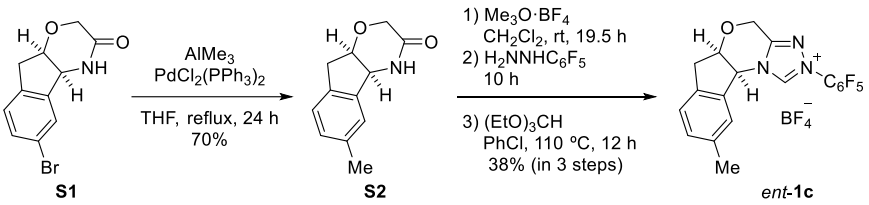
Contents

Supporting Information I

1. General procedure

All non-aqueous reactions were carried out under a positive atmosphere of argon in dried glassware. Dehydrated solvents were purchased for the reactions and used without further desiccation. Reagents were purchased and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck TLC silica gel 60 F_{254}. Column chromatography was performed using Kanto Chem. Co. Silica Gel 60N (particle size 0.040–0.050 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-400N instrument. The chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (0 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm), DMSO-d_6 (39.5 ppm), or acetone-d_6 (206.7 and 30.4 ppm) for ^{13}C. The coupling constants (*J*) are presented in hertz. The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a Waters MICROMASS® LCT PREMIERTM (ESI-TOF). IR was measured using a JASCO FT-IR 6200, and the wavenumbers of maximum absorption peaks are reported in cm^{-1}. Optical rotations were measured using a JASCO P-2200 polarimeter (concentration in g dL^{-1}). High performance liquid chromatography (HPLC) analyses were performed on a SHIMADZU analytical system equipped with two LC-20AT pumps. The catalysts **1a**,[1] **1b**,[2] **1d**[3] and the substrates **2a**,[4] **2c**[5] were prepared according to the literature procedures.

2. Preparation of the NHC precursors *ent*-**1c** and *ent*-**1e**



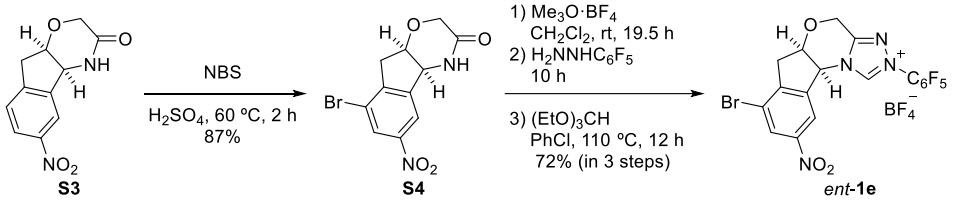
(4a*S*,9a*R*)-6-Methyl-4,4a,9,9a-tetrahydroindeno[2,1-*b*][1,4]oxazin-3(2*H*)-one (S2)

A stirring bar, **S1**[6] (885 mg, 3.30 mmol), and $PdCl_2(PPh_3)_2$ (116 mg, 0.165 mmol) were placed in a dried 200 mL flask. The flask was evacuated and filled with argon three times. Distilled THF (66 mL) was added, and the mixture was stirred at 60 °C for 30 min. A 1.07 M hexane solution of $AlMe_3$ (5.0 mL, 1.6 mmol) was added and the mixture was heated under reflux in an oil-bath (90 °C) for 24 h. The mixture was then cooled in an ice–water bath and 2 M HCl was dropwise added until bubbling ceased. The mixture was extracted three times with $CHCl_3$. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the residue by silica gel column chromatography ($CHCl_3$/EtOAc 1:3) gave pale brown solid, which was then recrystallized from hexane–acetone (5:1) to give **S2** (470 mg, 70%) as glossy white solid of mp 248–250 °C: $[\alpha]_D^{28}$ +12.6 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 7.0 Hz, 1H), 7.11–7.09 (m, 2H), 6.60 (m, 1H), 4.74 (dd, *J* = 4.0, 4.0 Hz, 1H), 4.53 (dd, *J* = 4.5, 4.0 Hz, 1H), 4.16 (s, 2H), 3.17 (dd, *J* = 17.0, 4.5 Hz, 1H), 3.05 (d, *J* = 17.0 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.8 (C), 140.9 (C), 137.3 (C), 136.2 (C), 129.3 (CH), 125.0 (CH), 124.6 (CH), 76.5 (CH), 66.6 (CH_2), 58.7 (CH), 37.3 (CH_2), 21.4 (CH_3). **LRMS** (ESI) *m/z* 226 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{12}H_{13}NNaO_2$, 226.0844; found, 226.0833. **IR** (KBr): 2922, 1692, 1498, 1417, 1328, 1267, 1109, 1045, 802.

(5a*S*,10b*R*)-9-Methyl-2-(perfluorophenyl)-5a,10b-dihydro-4*H*,6*H*-indeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-2-ium tetrafluoroborate (*ent*-1c)

To a solution of **S2** (102 mg, 0.502 mmol) in distilled CH_2Cl_2 (5.0 mL) was added $Me_3O{\cdot}BF_4$ (77 mg, 0.51 mmol), and the mixture was stirred at rt for 19.5 h. $C_6F_5NHNH_2$ (103 mg, 0.504 mmol) was then added, and the mixture was stirred for

another 10 h. The mixture was concentrated *in vacuo,* and the residue was dissolved in distilled PhCl (3.0 mL) followed by addition of $(EtO)_3CH$ (0.43 mL, 2.5 mmol). The mixture was heated at 110 °C and stirred for 12 h open to the atmosphere. The whole mixture was directly purified by column chromatography ($CHCl_3$/MeOH 20:1) to give brown solid. The solid was dissolved in hot toluene. The mixture was cooled to rt followed by addition of hexane to give **1c** (91 mg, 38%) as pale brown solid of mp 117–119 °C: $[\alpha]_D^{25}$ +120 (*c* 1.00, CH_3CN). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.7 (s, 1H), 7.26–7.18 (m, 3H), 6.02 (d, *J* = 4.5 Hz, 1H), 5.11–5.06 (m, 3H), 3.35 (dd, *J* = 17.0, 4.5 Hz, 1H), 3.21 (d, *J* = 17.0 Hz, 1H), 2.36 (s, 3 H). **^{13}C NMR** (100 MHz, acetone-d_6): δ 152.5 (C), 147.1 (CH), 138.5 (C), 138.0 (C), 136.1 (C), 131.2 (CH), 126.1 (CH), 125.5 (CH), 78.3 (CH), 63.3 (CH), 60.7 (CH_2), 37.4 (CH_2), 21.1 (CH_3). **LRMS** (ESI) *m/z* 394 (M – BF_4). **HRMS** (ESI) *m/z* [M – BF_4]$^+$ calcd for $C_{19}H_{13}F_5N_3O$, 394.0979; found, 394.0982. **IR** (KBr): 2948, 1594, 1525, 1483, 1390, 1324, 1077, 1005, 861, 824, 801.



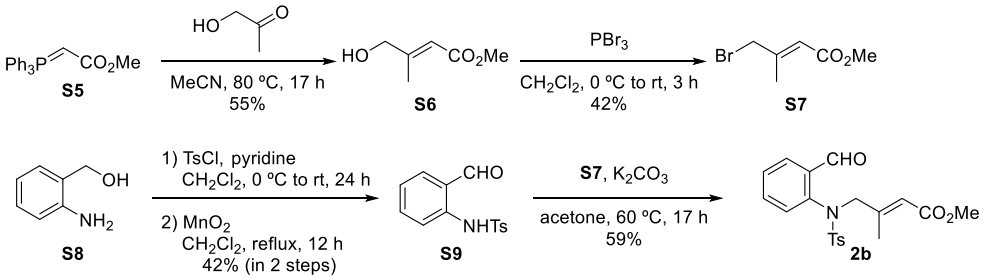
(4a*R*,9a*S*)-8-Bromo-6-nitro-4,4a,9,9a-tetrahydroindeno[2,1-b][1,4]oxazin-3(2*H*)-one (S4)

To a solution of **S3**[7] (468 mg, 2.0 mmol) in H_2SO_4 (2.0 mL) was added NBS (360 mg, 2.02 mmol) in three additions at 60 ^{O}C. After attired for 2 h, the reaction mixture was poured into ice water. The resulting mixture was filtered, washed with cold water and hexane. Solvent was concentrated under reduced pressure to give the title compound **S4** (544 mg, 1.74 mmol, 87%) as a light brown powder of mp 246–252 °C: $[\alpha]_D^{29}$ +77.96 (*c* 0.14, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 1.5 Hz, 1H), 8.19 (s, 1H), 4.89 (t, *J* = 4.0 Hz, 1H), 4.62 (m, 1H), 4.20 (s, 2H), 3.23 (m, 2H).**^{13}C NMR** (125 MHz, acetone-d_6): δ 167.1 (C), 148.6 (C), 148.1 (C), 146.0 (C), 126.1 (CH), 119.5 (C), 118.6 (CH), 75.4 (CH), 66.3 (CH_2), 59.2 (CH), 39.0 (CH_2). **LRMS** (ESI) *m/z* 335 (M + Na). **HRMS** (ESI) *m/z* [M + Na]$^+$ calcd for $C_{11}H_9BrN_2NaO_4$, 334.9643; found, 334.9654.. **IR** (KBr): 3442, 3087, 2911, 1691, 1631, 1531, 1347.

(5a*S*,10b*R*)-7-Bromo-9-nitro-2-(perfluorophenyl)-5a,10b-dihydro-4*H*,6*H*-indeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-2-ium tetrafluoroborate (1e)

To a solution of **S4** (157 mg, 0.501 mmol) in CH_2Cl_2 (10 mL) was added $Me_3O{\cdot}BF_4$ (84 mg, 0.55 mmol), and the mixture was stirred at rt for 19.5 h. $C_6F_5NHNH_2$ (112 g, 0.551 mmol) was then added, and the mixture was stirred for another 10 h. The mixture was concentrated *in vacuo,* and the residue was dissolved in distilled PhCl (3.0 mL) followed by addition of $(EtO)_3CH$ (0.86 mL, 5.0 mmol). The mixture was heated at 110 °C and stirred for 12 h open to the atmosphere. The whole mixture was directly purified by column chromatography ($CHCl_3$/MeOH 20:1) to give brown solid. The solid was triturated in Et_2O and collected by filtration to give **1e** (212 mg, 72%) as pale brown solid of mp 147–149 °C: $[\alpha]_D^{20}$ +135 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.7 (s, 1H), 8.33 (s, 1H), 8.25 (s, 1H), 6.34 (d, *J* = 4.0 Hz, 1H), 5.15 (dd, *J* = 4.5, 4.0 Hz, 1H), 5.12 (s, 2H), 3.42 (dd, *J* = 18.5, 4.5 Hz, 1H), 3.34 (d, *J* = 18.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.7 (C), 148.5 (C), 148.2 (C), 146.2 (CH), 138.2 (C), 128.3 (CH), 120.9 (C), 119.2 (CH), 76.5 (CH), 62.8 (CH), 60.4 (CH_2), 39.1 (CH_2). **LRMS** (ESI) *m/z* 503 (M – BF_4). **HRMS** (ESI) *m/z* [M – BF_4]$^+$ calcd for $C_{18}H_9BrF_5N_4O_3$, 502.9778; found, 502.9780. **IR** (KBr): 2943, 1593, 1529, 1483, 1447, 1351, 1079, 1004, 893, 862, 843, 756.

3. Preparation of the substrate **2b**



Methyl (*E*)-4-hydroxy-3-methylbut-2-enoate (S6)

To a solution of **S5** (44.3 g, 132 mmol) in MeCN (235 mL) was added hydroxyacetone (7.7 mL, 0.11 mol). The obtained solution was stirred at 80 °C for 17 h. After this time solvent was evaporated and the residue was treated with diethyl ether (200 mL) and cooled down to 0 °C. Precipitated triphenylphosphine oxide was filtered off. The solvent was evaporated under reduced pressure. The crude product was distilled (160 °C at 7 mmHg) to give the title compound **S6** (7.9 g, 61 mmol, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.01–5.99 (m, 1H), 4.16 (dd, *J* = 6.0, 1.0 Hz, 2H), 3.72 (s, 3H), 2.10 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.5 (C), 158.1 (C), 113.0 (CH), 66.8 (CH_2), 51.0 (CH_3), 15.6 (CH_3). **LRMS** (ESI) *m/z*: 153 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_6H_{10}NaO_3$, 153.0528; found, 153.0522. **IR** (neat): 3443, 2952, 1719, 1659, 1438, 1227, 1151.

Methyl (*E*)-4-bromo-3-methylbut-2-enoate (S7)

To a solution of **S6** (7.9 g, 61 mmol) in CH_2Cl_2 (180 mL) was added dropwise a solution of PBr_3 (6.9 mL, 73 mmol) in CH_2Cl_2 (64 mL) at 0 °C. After stirring at room temperature for 3 h, the reaction was quenched with water, and the whole solution was extracted with ethyl acetate twice. The combined organic layers were dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash column chromatography (hexane/ethyl acetate 19:1) to give the title compound **S7** (5.7 g, 26 mmol, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.97 (m 1H), 3.95 (d, *J* = 1.0 Hz, 2H), 3.72 (s, 3H), 2.28 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3 (C), 152.7 (C), 119.0 (CH), 51.3 (CH_3), 38.1 (CH_2), 17.2 (CH_3). **LRMS** (ESI) *m/z*: 215 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_6H_9BrNaO_2$, 214.9684; found, 214.9691. **IR** (neat): 1720, 1646, 1435, 1360, 1287, 1232, 1159, 1037.

***N*-(2-Formylphenyl)-4-methylbenzenesulfonamide (S9)**

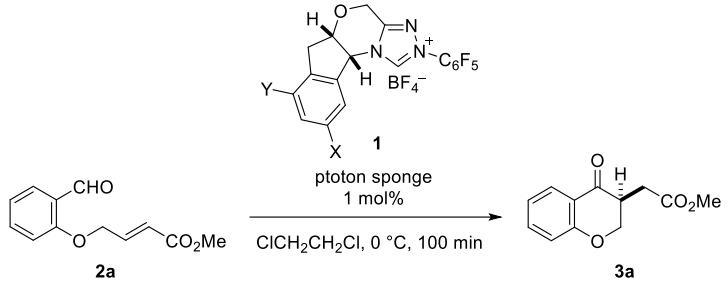
To a solution of **S8** (1.2 g, 10 mmol) in $CHCl_3$ (33 mL) at 0 °C were added pyridine (1.0 mL, 13 mmol) and TsCl (2.3 g, 12 mmol) and the reaction mixture was stirred under an argon atmosphere. After 22 h, the reaction mixture was diluted with ethyl acetate, washed with saturated aqueous NH_4Cl, water, and then dried over Na_2SO_4. The organic solvent was removed under reduced pressure and the obtained crude product was used to the next step without further purification.

The above-obtained crude product (3.0 g, 10 mmol) was dissolved in CH_2Cl_2 (23 mL). MnO_2 (3.5 g, 40 mmol) was added under argon atmosphere and the solution was refluxed for 12 h. The progress of the reaction was monitored by TLC analysis. After completion, the reaction mixture was filtered off with Celite® and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate 3:1) to give the title compound **S9** (1.16 g, 4.21 mmol, 2 steps 42%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 10.8 (s, 1H), 9.83 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.51 (td, *J* = 8.0, 1.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (td, *J* = 8.0, 1.0 Hz, 1H), 2.37 (s, 3H). The ^{1}H NMR data of **S9** was in good agreement with that of the literature.[8]

Methyl (*E*)-4-((N-(2-formylphenyl)-4-methylphenyl)sulfonamido)-3-methylbut-2-enoate (2b)

A round bottom flask was charged with **S9** (1.2 g, 4.2 mmol) and K_2CO_3 (1.5 g, 11 mmol) under argon atmosphere. To this flask was added acetone (28 mL). After 10 min, **S7** (0.69 mL, 5.0 mmol) was added, and the resulting solution was stirred at 60 °C for 17 h. After this time, solvent was evaporated. The residue was diluted with ethyl acetate, washed with saturated aqueous $Na_2S_2O_3$, water, brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate 2:1 and then 1:2) to give the title compound **2b** (955 mg, 2.5 mmol, 59%) as white solid of mp 108–118 °C. **^{1}H NMR** (400 MHz, DMSO-d_6, 80 °C): δ 10.26 (s, 1H), 7.87 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.60 (ddd, *J* = 9.5, 7.5, 1.5 Hz, 1H), 7.52 (m, 1H), 7.46–7.38 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 4.34 (s, 2H), 3.56 (s, 3H), 2.43 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (125MHz, $CDCl_3$): δ 189.3 (CH), 165.9 (C), 151.2 (C), 144.6 (C), 140.8 (C), 135.7 (C), 134.0 (CH), 133.5 (C), 129.8 (CH), 129.0 (CH), 128.7 (CH), 128.1 (CH), 127.1 (CH), 119.9 (CH), 59.0 (CH_2), 51.2 (CH_3), 21.6 (CH_3), 17.1 (CH_3). **LRMS** (ESI) *m/z*: 410 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{20}H_{21}NNaO_5S$, 410.1038; found, 410.1056. **IR** (KBr): 2952, 1722, 1690, 1597, 1347, 1227, 1159.

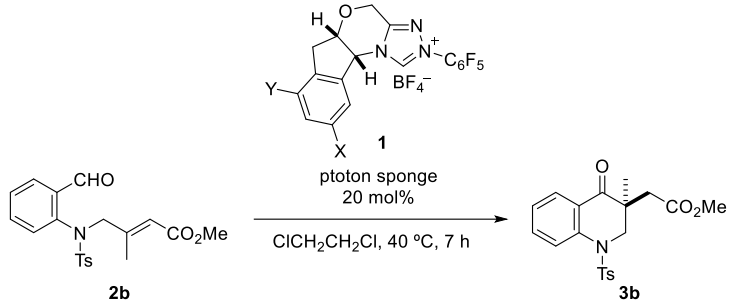
4. Typical procedure for asymmetric intramolecular Stetter reaction of **2a** (Table 1, entry 2)



A flame-dried round bottom flask was charged with triazolium salt **1a** (2.3 mg, 5.0 μmol, 1 mol%), proton sponge (1.1 mg, 5.0 μmol, 1 mol%), and a magnetic stirring bar under argon. To this flask was added $ClCH_2CH_2Cl$ (20 mL) via syringe, and the mixture was stirred at ambient temperature for 1 h and then cooled in an ice–brine bath. After 15 min, the substrate **2a** (110 mg, 0.50 mmol) was added, and the resulting mixture was stirred at 0 °C for 100 min. Acetic acid (1.0 mL) was added, and the reaction mixture was stirred at 0 °C for 10 min. The reaction mixture was diluted with ethyl acetate, washed with H_2O twice, saturated aqueous $NaHCO_3$, brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure. The mixture was purified by silica gel flash column chromatography (hexane/ethyl acetate = 5:1) to give the title compound **3a** (58.6 mg, 53%) with 96% ee as light yellow oil: $[\alpha]_D^{19}$ –9.38 (*c* 1.14, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 4.60 (dd, *J* = 11.0, 5.5 Hz, 1H), 4.30 (dd, *J* = 12.0, 11.0 Hz, 1H), 3.74 (s, 3H), 3.34 (ddt, *J* = 12.0, 8.0, 5.0 Hz, 1H), 2.95 (dd, *J* = 17.0, 5.0 Hz, 1H), 2.41 (dd, *J* = 17.0, 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.5 (C), 171.8 (C), 161.7 (C), 136.0 (CH), 127.4 (CH), 121.5 (CH), 120.5 (C), 117.8 (CH), 70.2 (CH_2), 52.0 (CH_3), 42.5 (CH), 30.1 (CH_2). **LRMS** (ESI) *m/z*: 243 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{12}H_{12}NaO_4$, 243.0633; found, 243.0645. **IR** (neat): 2952, 1738, 1692, 1606, 1480, 1325, 1301, 1216.

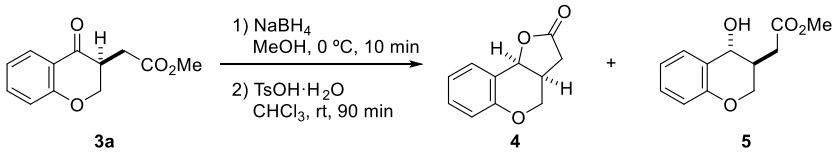
The ee was determined by HPLC analysis (Daicel Chiralcel AD-H; hexane/*i*-PrOH 19:1; 1.0 mL/min; 254 nm; (*S*) 12.2 min, (*R*) 15.3 min).

5. Typical procedure for asymmetric intramolecular Stetter reaction of **2b** (Table 2, entry 2)



A flame-dried test tube was charged with triazolium salt **1a** (4.7 mg, 0.010 mmol, 20 mol%), proton sponge (2.3 mg, 0.010 mmol, 20 mol%), and a magnetic stirring bar under argon. To this flask was added $ClCH_2CH_2Cl$ (1.0 mL) via syringe. After 1 h at rt, the substrate **2b** (19 mg, 0.050 mmol) was added, and the resulting mixture was stirred at 40 °C for 7 h. Acetic acid (0.5 mL) was added, and the reaction mixture was stirred 10 min at rt. The reaction mixture was diluted with ethyl acetate, washed with H_2O twice, saturated aqueous $NaHCO_3$, brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate 3:1) to give the title compound **3b** (10.1 mg, 52%) with 78% ee as a yellow solid of mp 99–103 °C. $[\alpha]_D^{16}$ –35.4 (*c* = 1.01, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5, Hz, 1H), 7.42 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.12 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1H), 4.27 (d, *J* = 1.0, 2H), 3.67 (s, 3H), 3.04 (d, *J* = 17.0 Hz, 1H) 2.55 (d, *J* = 17.0 Hz, 1H), 2.44 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.1 (C), 171.2 (C), 144.4 (C), 142.3 (C), 137.3 (C), 134.5 (CH), 130.1 (CH), 129.2 (CH), 126.8 (CH), 123.6 (CH), 122.2 (C), 118.8 (CH), 54.7 (CH_2), 51.8 (CH_3), 44.8 (C), 39.2 (CH_2), 21.6 (CH_3), 20.7 (CH_3). **LRMS** (ESI) *m/z*: 410 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{20}H_{21}NNaO_5S$, 410.1038; found, 410.1052. **IR** (KBr) 1743, 1696, 1602, 1481, 1342, 1163. The ee was determined by HPLC analysis (Daicel Chiralcel OD-H; hexane/*i*-PrOH 17:3; 1.0 mL/min; 254 nm; (*R*) 13.8 min, (*S*) 25.9 min).

6. Conversion of **3a** into **7**



(3a*S*,9b*S*)-3a,9b-Dihydro-4*H*-furo[3,2-c]chromen-2(3*H*)-one (4) and Methyl 2-((3*S*,4*R*)-4-hydroxychroman-3-yl)acetate (5)

To a solution of **3a** (176 mg, 0.80 mmol, 96% ee) in MeOH (4.0 mL) was slowly added $NaBH_4$ (30 mg, 0.80 mmol) at 0 °C, and then stirred for 10 min. The reaction mixture was diluted with ethyl acetate, washed with brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure. The crude mixture was diluted with $CHCl_3$ (4.0 mL), and $TsOH{\cdot}H_2O$ (8.0 mg) was added. After stirred for 90 min at room temperature, the solvent was concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography ($CHCl_3$/acetone = 20/1 and then 10/1) to obtain the lactone **4** (59 mg, 0.31 mmol, 39%) as a white solid and the alcohol **5** (91 mg, 0.41 mmol, 51%) as colorless oil.

Supporting Information I

(3a*S*,9b*S*)-3a,9b-Dihydro-4*H*-furo[3,2-c]chromen-2(3*H*)-one (4)

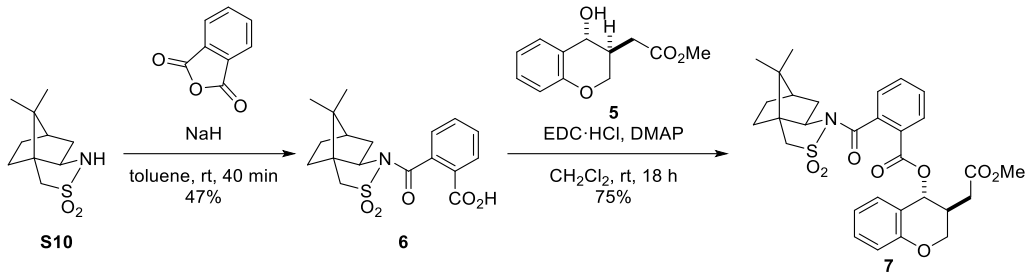
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 7.5 ,1.5 Hz, 1H)**,** 7.29 (ddd, *J* = 8.5, 7.5 ,1.5 Hz, 1H), 7.03 (td, *J* = 7.5 ,1.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 5.49 (d, *J* = 6.5, 1H), 4.22 (dd, *J* = 11.5, 4.5, 1H), 3.83 (dd, *J* = 11.5, 9.5, 1H), 3.02 (m, 1H), 2.87 (dd, *J* = 17.5, 8.5, 1H), 2.46 (dd, *J* = 17.5, 4.0, 1H). $[\alpha]_D^{28}$ +102.23 (*c* 1.02, $CHCl_3$).

The ^{1}H NMR data of **4** was in good agreement with that of the literature.[9]

Methyl 2-((3*S*,4*R*)-4-hydroxychroman-3-yl)acetate (5)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.22 (m, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 8.5, 1H), 4.51 (m, 1H), 4.33 (dd, *J* = 11.0, 2.5 Hz, 1H), 4.08 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.70 (s, 3H), 2.49 (m, 1H), 2.40-2.36 (m, 2H), 2.13 (m, 1H). $[\alpha]_D^{20}$ = +37.70 (*c* 1.06, $CHCl_3$).

The ^{1}H NMR data of **5** was in good agreement with that of the literature.[10]



2-((6*R*,7a*R*)-8,8-Dimethyl-2,2-dioxidohexahydro-3*H*-3a,6-methanobenzo[c]isothiazole-1-carbonyl)benzoic acid (6)

To a solution of **S10** (0.40 g, 1.8 mmol) and freshly distilled toluene (6.0 mL) was added 60% NaH in paraffin liquid (0.16 g, 4.0 mmol), and then the mixture was stirred at room temperature. After 30 min, phthalic anhydride (0.27 g, 1.8 mmol) was added, and the resulting mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with 2M HCl to pH 1-2, and was decantated. The white solid was diluted with $CHCl_3$ and washed with H_2O. The solvent was concentrated under reduced pressure. The resulting mixture was recrystallized from $CHCl_3$/hexane to obtain the title compound **6** (0.32 g, 0.87 mmol, 47%) as a white solid of mp 195–211 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.57 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.0 Hz, 1H), 4.08 (m, 1H), 3.41 (d, *J* = 2.0 Hz, 2H), 2.49–2.39 (m, 1H), 2.21–2.08 (m, 1H), 1.93 (m, 3H), 1.49–1.37 (m, 2H), 1.22 (s, 3H), 0.96 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.2 (C), 167.5 (C), 136.0 (C), 132.9 (CH), 130.6 (CH), 130.4 (CH), 129.3 (CH), 127.6 (C), 65.7 (CH), 53.0 (CH_2), 48.4 (C), 47.8 (C), 44.7 (CH), 37.7 (CH_2), 33.1 (CH_2), 26.5 (CH_2), 20.3 (CH_3), 20.0 (CH_3). **LRMS** (ESI) *m/z*: 362 (M – H). **HRMS** (ESI) *m/z* [M – H] calcd for $C_{18}H_{20}NO_5S$, 362.1062; found, 362.1080. **IR** (KBr) 2950, 2687, 2554, 1684, 1333, 1315, 1302, 1255, 1169, 1154.

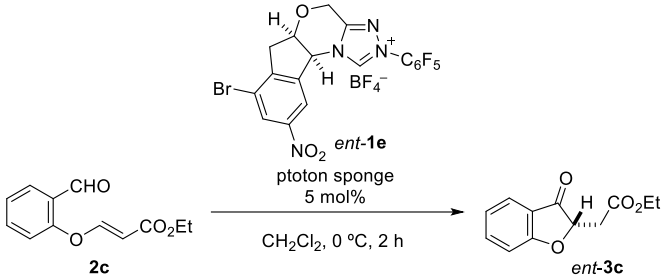
(3*S*,4*R*)-3-(2-Methoxy-2-oxoethyl)chroman-4-yl 2-((6*R*,7a*R*)-8,8-dimethyl-2,2-dioxidohexahydro-3*H*-3a,6-methanobenzo[c]isothiazole-1-carbonyl)benzoate (7)

To the mixture of alcohol **5** (44 mg, 0.20 mmol), EDC·HCl (58 mg, 0.30 mmol), and DMAP (59 mg, 0.48 mmol) in CH_2Cl_2 (2.0 mL) was added the carboxylic acid **6** (80 mg, 0.22 mmol), and then the mixture was stirred at room temperature for 18 h. The resulting mixture was added H_2O and 2M HCl to pH 3-4. The reaction mixture was extracted with CH_2Cl_2 three times, washed with brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure. The mixture was purified by silica gel flash column chromatography ($CHCl_3$/acetone = 30:1 and then Hex/EtOAc = 2/1) to obtain the title compound **7** as white solid of mp 83–98 °C. $[\alpha]_D^{20}$ +16.95 (*c* = 0.89, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.59 (td, *J* = 7.5, 1.0 Hz, 1H), 7.52 (td, *J* = 7.5, 1.0 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.25 (m, 1H), 6.94–6.88 (m, 2H), 5.86 (s, 1H), 4.42 (dd, *J* = 11.5, 2.5 Hz, 1H), 4.26 (ddd, *J* = 11.5, 3.0, 1.0

Hz, 1H), 3.71–3.61 (m, 4H), 3.37 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 2.71 (m, 1H), 2.51–2.34 (m, 3H), 2.18–2.05 (m, 1H), 1.93–1.80 (m, 3H), 1.37–1.20 (m, 5H), 0.96 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.8 (C), 167.4 (C), 164.3 (C), 155.0 (C), 135.5 (C), 132.2 (CH), 132.1 (CH), 131.7 (CH), 130.5 (CH), 130.2 (CH), 129.0 (CH), 128.3 (C), 120.8 (CH), 118.1 (C), 116.8 (CH), 69.9 (CH), 65.5 (CH), 65.0 (CH_2), 52.9 (CH_2), 51.9 (CH_3), 48.2 (C), 47.6 (C), 45.0 (CH), 37.9 (CH_2), 34.1 (CH), 32.8 (CH_2), 32.4 (CH_2), 26.3 (CH_2), 21.1 (CH_3), 20.0 (CH_3). **LRMS** (ESI) *m/z*: 590 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{30}H_{33}NNaO_8S$, 590.1825; found, 590.1828. **IR** (KBr) 2955, 1717, 1684, 1584, 1490, 1336, 1301, 1227, 1170, 1138, 1077.

The single crystal of **7** for X-ray crystallography analysis was obtained by slow evaporation from acetone/hexane. The Absolute stereochemistry was determined *S* by X-ray crystallography analysis.

7. Typical procedure for asymmetric intramolecular Stetter reaction of **2c** (Scheme 3, entry 3)



A flame-dried round bottom flask was charged with triazolium salt *ent*-**1e** (2.3 mg, 5.0 μmol, 5 mol%), proton sponge (1.1 mg, 5.0 μmol, 5 mol%), and a magnetic stirring bar under argon atmosphere. To this flask was added CH_2Cl_2 (6.0 mL) via syringe, and the mixture was stirred at ambient temperature for 1 h and then cooled in an ice–brine bath. After 15 min, A solution of the substrate **2c** (22 mg, 0.10 mmol) in CH_2Cl_2 (1.5 mL) cooled at 0 °C was added via cannula then CH_2Cl_2 (0.5 mL) was also added via cannula. The resulting mixture was stirred at 0 °C for 2 h. The reaction mixture was purified directly by silica gel flash column chromatography (hexane/ethyl acetate = 1:1) at 5 °C to give the title compound *ent*-**3c** (25 mg, quant) with 91% ee as yellow oil: $[\alpha]_D^{27}$ –60.83 (*c* 2.06, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (ddd, *J* = 7.5, 1.5, 0.5 Hz, 1H), 7.62 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.15–7.09 (m, 2H), 4.88 (dd, *J* = 4.0, 8.0 Hz, 1H), 4.19–4.11 (m, 2H), 3.08 (dd, *J* = 4.0, 17 Hz, 1H), 2.83 (dd, *J* = 8.0, 17 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.3 (C), 172.5 (C), 169.3 (C), 138.0 (CH), 124.3 (CH), 122.2 (CH), 120.9 (C), 113.5 (CH), 81.1 (CH), 61.2 (CH_2), 36.1 (CH_2), 14.0 (CH_3). **LRMS** (ESI) *m/z*: 243 (M + Na). **HRMS** (ESI) *m/z* $[M + Na]^+$ calcd for $C_{12}H_{12}NaO_4$, 243.0633; found, 243.0623. **IR** (neat) 3026, 1724, 1616, 1477, 1463.

The ee was determined by HPLC analysis (Daicel Chiralcel AS-3; hexane/*i*-PrOH 19:1; 1.0 mL/min; 254 nm; (*R*) 21.2 min, (*S*) 36.6 min).

8. X-ray diffraction

Preparation of 3b for X-ray diffraction analysis: A flame-dried test tube was charged with triazolium salt **1d** (5.1 mg, 0.010 mmol), proton sponge (2.2 mg, 0.010 mmol), and a magnetic stirring bar under argon. To this flask was added $ClCH_2CH_2Cl$ (1.0 mL) via syringe. After 1 h at rt, the substrate **2b** (19 mg, 0.050 mmol) was added, and the resulting mixture was stirred at 40 °C for 24 h. Acetic acid (0.5 mL) was added, and the reaction mixture was stirred 10 min at rt. The reaction mixture was diluted with ethyl acetate, washed with H_2O twice, saturated aqueous $NaHCO_3$, brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate 3:1) to give the title compound **3b** (19.8 mg, 97%) with 94% ee. The single crystal of **3b** for X-ray crystallography analysis was obtained by slow evaporation from *i*-PrOH/hexane. The Absolute stereochemistry was determined *S* by X-ray crystallography analysis.

Data collection and Structure solution details: Single crystal X-ray data for compounds **3b** and **7** were collected on a Rigaku XtaLaB P200 diffractometer Cu-Kα radiation. Data collection, cell refinement, data reduction and analysis were carried out with the CrysAlisPro (Rigaku Oxford Diffraction). These structures were solved by intrinsic phasing methods with the SHELXT program and refines using SHELXL[11] with anisotropic displacement parameters for non-H atoms. CCDC 2208224 (for **3b**) and 2208225 (for **7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

X-ray crystallographic data for compound **3b** (CCDC 2208224).

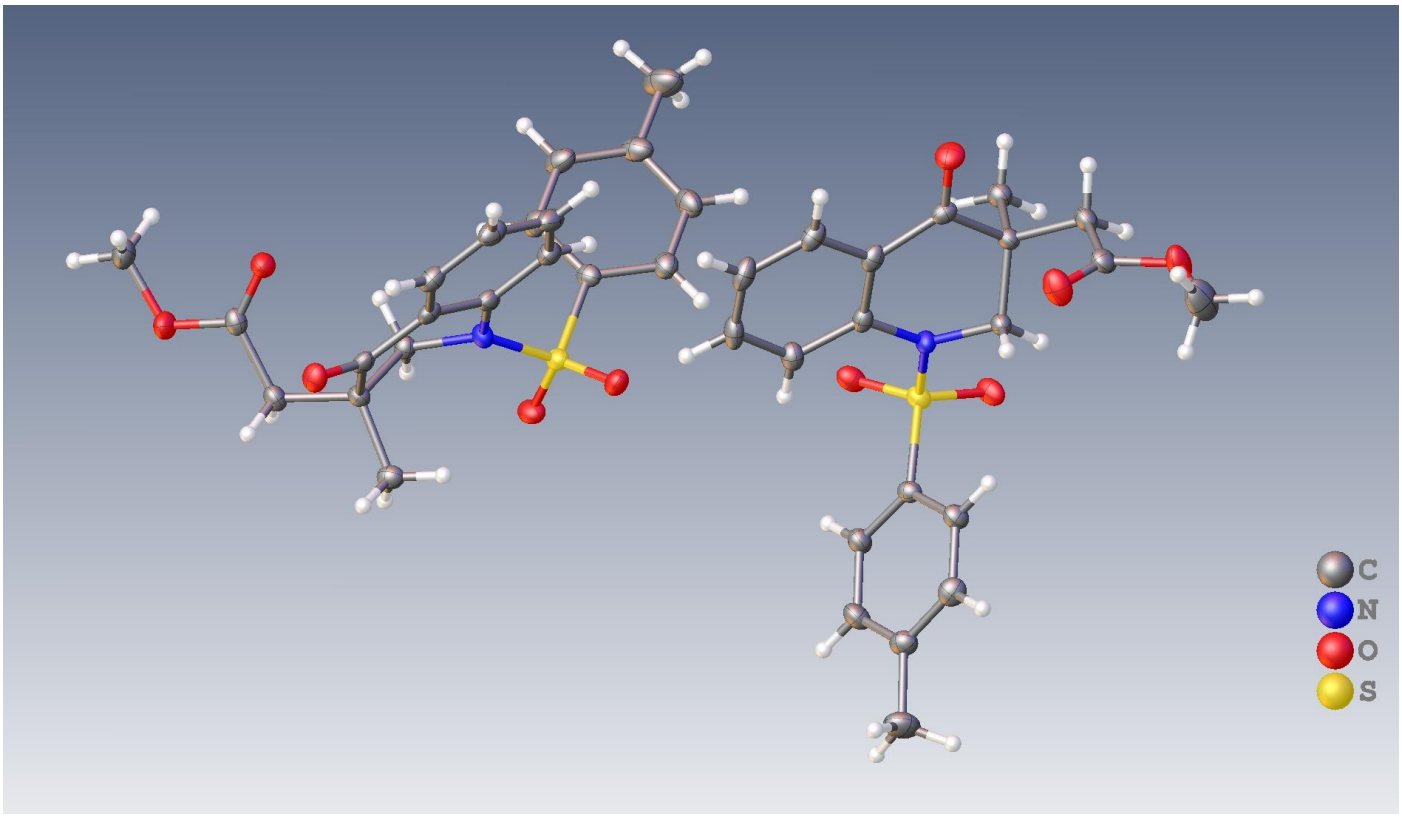


Figure S1. ORTEP view of the compound **3b** with thermal ellipsoids drawn at the 50% probability level

Supporting Information I

Table S1 Crystal data and structure refinement for 3b.

Identification code	3b
Empirical formula	$C_{20}H_{21}NO_5S$
Formula weight	387.44
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.21970(10)
b/Å	9.6414(2)
c/Å	21.4651(2)
α/°	90
β/°	100.6270(10)
γ/°	90
Volume/Å^3	1875.32(5)
Z	4
ρ_{calc}g/cm^3	1.372
μ/mm^{-1}	1.808
F(000)	816.0
Crystal size/mm^3	0.02 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.382 to 146.47
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 11, -24 ≤ l ≤ 26
Reflections collected	24711
Independent reflections	6656 [R_{int} = 0.0906, R_{sigma} = 0.0517]
Data/restraints/parameters	6656/1/493
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0423, wR_2 = 0.1079
Largest diff. peak/hole / e Å^{-3}	0.49/-0.50
Flack parameter	0.033(10)

Supporting Information I

X-ray crystallographic data for compound **7** (CCDC2208225).

Figure S2. ORTEP view of the compound **7** with thermal ellipsoids drawn at the 50% probability level

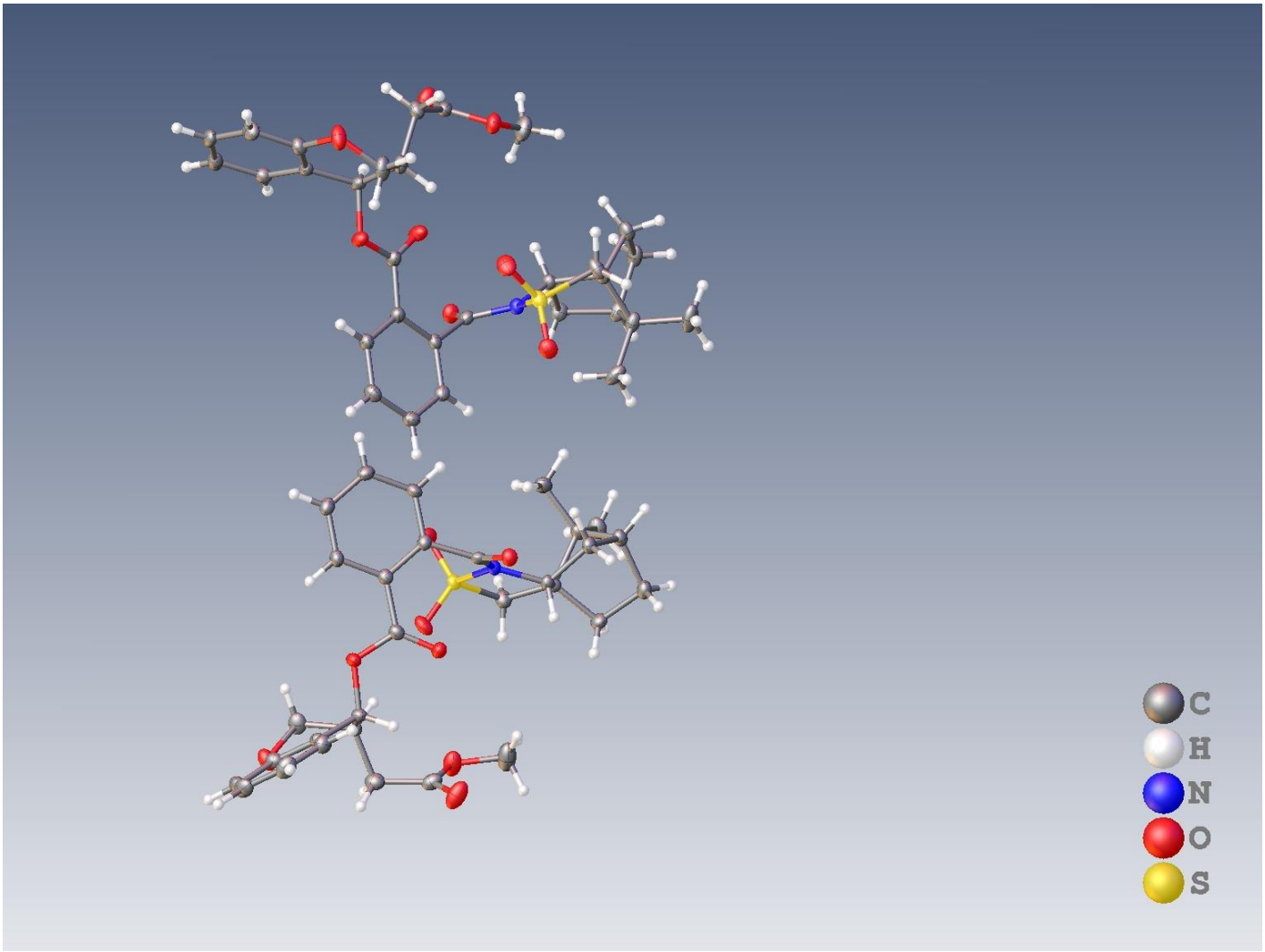


Table S2 Crystal data and structure refinement for 7.

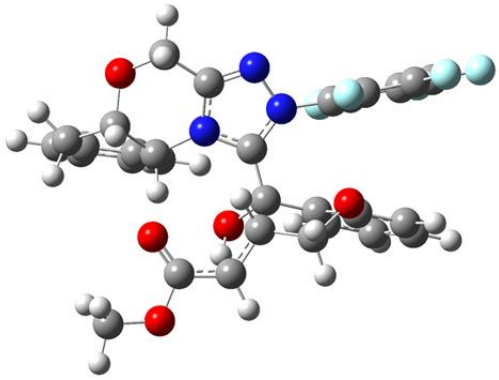
Identification code	7
Empirical formula	$C_{30}H_{33}NO_8S$
Formula weight	567.63
Temperature/K	93.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.4269(3)
b/Å	11.0986(2)
c/Å	20.8157(5)
α/°	90
β/°	107.341(2)
γ/°	90
Volume/Å^3	2740.44(11)
Z	4
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	1.502
F(000)	1200.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.448 to 144.112
Index ranges	-14 ≤ h ≤ 15, -13 ≤ k ≤ 12, -22 ≤ l ≤ 24
Reflections collected	20845
Independent reflections	8222 [R_{int} = 0.0346, R_{sigma} = 0.0390]
Data/restraints/parameters	8222/1/727
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0782
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0794
Largest diff. peak/hole / e Å^{-3}	0.16/-0.29
Flack parameter	0.034(10)

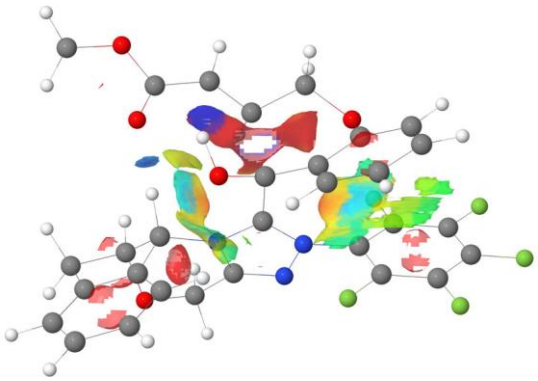
Supporting Information I

9. DFT calculation

The initial transition state (TS) search was conducted using Spartan'18W program at the B3LYP/6-31G(d) theoretical level. After conformational search, the geometry optimization of the conformers at the HF/3-21G theoretical level was performed with restriction of the forming C–C bond lengths. Finally, TS search was performed at the B3LYP/6-31G(d) levels of theory using Gaussian 09W program[11] to give the TS_{major} and TS_{minor}. The TS geometries were verified by vibrational frequency analysis. Single-point-energy calculations were performed at the B3LYP-D3/6-311+G(2df,2p) theoretical level. The NCI plots[12] were visualized using a Java application, Jmol, downloaded from http://www.jmol.org/.

TS_{major} that gives 3a by the catalysis of 1a





NCI plot of TS_{major}

Energies (RB3LYP) =	–2195.85217976
Zero-point correction =	0.479310 (Hartree/Particle)
Thermal correction to Energy =	0.514386
Thermal correction to Enthalpy =	0.515330
Thermal correction to Gibbs Free Energy =	0.411694
Energies (B3LYP-D3) =	–2196.69893438
Sum of electronic and zero-point Energies =	–2196.219624
Sum of electronic and thermal Energies =	–2196.184548
Sum of electronic and thermal Enthalpies =	–2196.183604
Sum of electronic and thermal Free Energies =	–2196.287240

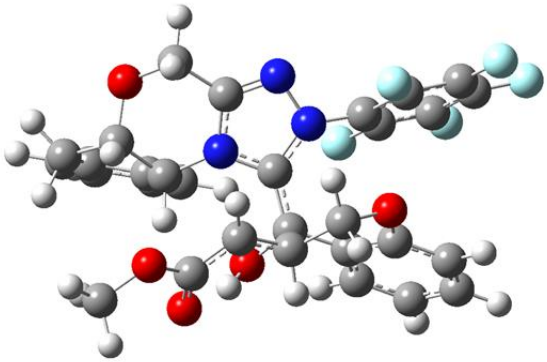
Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
H	0.523966	0.228996	3.211294
C	1.341831	0.733942	2.707550
C	3.411797	2.083198	1.402686
C	1.162197	1.141387	1.378463
C	2.546496	0.968888	3.368701
C	3.586943	1.632100	2.710551
C	2.201309	1.842904	0.749734
H	2.675721	0.634031	4.393978
H	4.527506	1.816406	3.222694
H	4.188171	2.632982	0.879281
O	2.035938	2.295114	–0.538169
C	0.879997	3.154002	–0.654521
H	0.973614	3.955006	0.089243
H	0.965454	3.597901	–1.650609
C	–0.466476	2.467679	–0.514691
C	–1.491573	3.225818	0.111334
H	–1.232827	4.041716	0.780054
C	–2.856760	3.133848	–0.321602
O	–3.334267	2.300810	–1.104017
C	–0.128058	0.877558	0.652382
C	–0.181969	–0.226184	–0.283474
N	0.833021	–0.810377	–0.992759
N	–1.319636	–0.753528	–0.850810

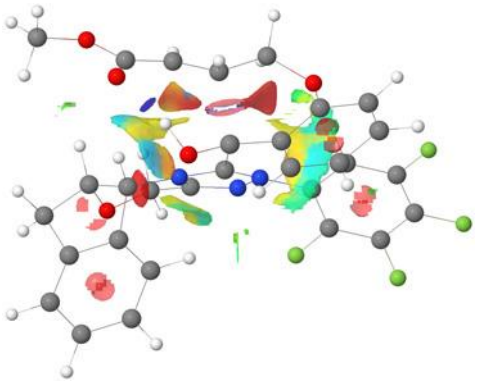
C	–0.926386	–1.562567	–1.893495
N	0.362918	–1.635896	–2.007915
C	2.225213	–0.844216	–0.743250
C	4.977882	–1.050890	–0.340488
C	2.729986	–1.520328	0.370267
C	3.115346	–0.302208	–1.673337
C	4.488781	–0.398318	–1.470879
C	4.100178	–1.607624	0.588353
C	–2.741493	–0.608712	–0.472950
H	–2.924385	0.449920	–0.284458
C	–1.933314	–2.153631	–2.838158
C	–3.651413	–1.033674	–1.653811
H	–3.709984	–0.250608	–2.420353
O	–1.239235	0.885333	1.481229
H	–1.624107	1.810829	1.355530
H	–0.786475	1.948355	–1.417923
F	1.888937	–2.071901	1.248878
F	4.577288	–2.240446	1.663427
F	6.293770	–1.138932	–0.143633
F	5.340111	0.130021	–2.354462
F	2.657440	0.316566	–2.757789
C	–3.238608	–1.488336	0.663499
C	–4.987699	–1.348894	–0.969164
H	–5.569878	–2.059332	–1.564407
H	–5.575914	–0.427024	–0.869266
C	–4.553897	–1.882565	0.380811
O	–3.198708	–2.265341	–2.232493
H	–1.618203	–3.153783	–3.145370
C	–2.618474	–1.872454	1.847955
H	–1.606031	–1.557025	2.073457
C	–5.266884	–2.660456	1.287829
H	–6.285938	–2.971343	1.070483
C	–3.331335	–2.667233	2.751699
H	–2.858031	–2.982336	3.677732
C	–4.645574	–3.054344	2.477224
H	–5.187076	–3.671006	3.189744
H	–1.977432	–1.516325	–3.738147
O	–3.646134	4.098781	0.246733
C	–5.024456	4.057709	–0.121135
H	–5.489080	3.115108	0.187250
H	–5.149630	4.168153	–1.202698
H	–5.493763	4.894251	0.400327
H	0.523966	0.228996	3.211294
C	1.341831	0.733942	2.707550
C	3.411797	2.083198	1.402686
C	1.162197	1.141387	1.378463
C	2.546496	0.968888	3.368701
C	3.586943	1.632100	2.710551
C	2.201309	1.842904	0.749734
H	2.675721	0.634031	4.393978
H	4.527506	1.816406	3.222694
H	4.188171	2.632982	0.879281
O	2.035938	2.295114	–0.538169
C	0.879997	3.154002	–0.654521
H	0.973614	3.955006	0.089243
H	0.965454	3.597901	–1.650609
C	–0.466476	2.467679	–0.514691
C	–1.491573	3.225818	0.111334
H	–1.232827	4.041716	0.780054
C	–2.856760	3.133848	–0.321602
O	–3.334267	2.300810	–1.104017
C	–0.128058	0.877558	0.652382
C	–0.181969	–0.226184	–0.283474

N	0.833021	–0.810377	–0.992759
N	–1.319636	–0.753528	–0.850810
C	–0.926386	–1.562567	–1.893495
N	0.362918	–1.635896	–2.007915
C	2.225213	–0.844216	–0.743250
C	4.977882	–1.050890	–0.340488
C	2.729986	–1.520328	0.370267
C	3.115346	–0.302208	–1.673337
C	4.488781	–0.398318	–1.470879
C	4.100178	–1.607624	0.588353
C	–2.741493	–0.608712	–0.472950
H	–2.924385	0.449920	–0.284458
C	–1.933314	–2.153631	–2.838158
C	–3.651413	–1.033674	–1.653811
H	–3.709984	–0.250608	–2.420353
O	–1.239235	0.885333	1.481229
H	–1.624107	1.810829	1.355530
H	–0.786475	1.948355	–1.417923
F	1.888937	–2.071901	1.248878
F	4.577288	–2.240446	1.663427
F	6.293770	–1.138932	–0.143633
F	5.340111	0.130021	–2.354462
F	2.657440	0.316566	–2.757789
C	–3.238608	–1.488336	0.663499
C	–4.987699	–1.348894	–0.969164
H	–5.569878	–2.059332	–1.564407
H	–5.575914	–0.427024	–0.869266
C	–4.553897	–1.882565	0.380811
O	–3.198708	–2.265341	–2.232493
H	–1.618203	–3.153783	–3.145370
C	–2.618474	–1.872454	1.847955
H	–1.606031	–1.557025	2.073457
C	–5.266884	–2.660456	1.287829
H	–6.285938	–2.971343	1.070483
C	–3.331335	–2.667233	2.751699
H	–2.858031	–2.982336	3.677732
C	–4.645574	–3.054344	2.477224
H	–5.187076	–3.671006	3.189744
H	–1.977432	–1.516325	–3.738147
O	–3.646134	4.098781	0.246733
C	–5.024456	4.057709	–0.121135
H	–5.489080	3.115108	0.187250
H	–5.149630	4.168153	–1.202698
H	–5.493763	4.894251	0.400327

Supporting Information I

TS_{minor} that gives 3a by the catalysis of 1a





NCI plot of TS_{minor}

Energies (RB3LYP) =	–2195.84703001
Zero-point correction =	0.479292 (Hartree/Particle)
Thermal correction to Energy =	0.514621
Thermal correction to Enthalpy =	0.515565
Thermal correction to Gibbs Free Energy =	0.412010
Energies (B3LYP-D3) =	–2196.69577236
Sum of electronic and zero-point Energies =	–2196.216480
Sum of electronic and thermal Energies =	–2196.181151
Sum of electronic and thermal Enthalpies =	–2196.180207
Sum of electronic and thermal Free Energies =	–2196.283762

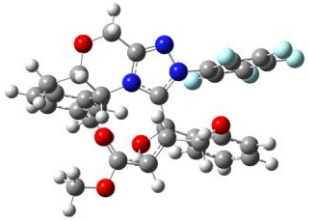
Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
H	0.612860	–0.163271	3.402482
C	1.421335	0.405242	2.955536
C	3.450736	1.936170	1.805374
C	1.218986	0.962534	1.684266
C	2.628274	0.576857	3.629074
C	3.648017	1.336690	3.047136
C	2.237212	1.759094	1.133551
H	2.773218	0.123281	4.605374
H	4.591480	1.476543	3.567961
H	4.215174	2.552084	1.341737
O	2.118095	2.310705	–0.114323
C	0.907089	3.007649	–0.476611
H	0.786160	2.808786	–1.545112
H	1.102528	4.081428	–0.352717
C	–0.359054	2.663014	0.277668
C	–1.563273	2.894272	–0.423686
H	–1.564389	3.055389	–1.496763
C	–2.793123	2.985492	0.278783
O	–2.989745	2.634796	1.463050
C	–0.095439	0.821640	0.984097
C	–0.227721	0.025851	–0.200367
N	0.719012	–0.296371	–1.146940
N	–1.428397	–0.219364	–0.835387
C	–1.133467	–0.622763	–2.121744
N	0.139141	–0.690224	–2.351518
C	2.088264	–0.582201	–0.961182
C	4.798094	–1.210713	–0.675617
C	3.046680	0.022617	–1.779389
C	2.506828	–1.519178	–0.011879
C	3.855270	–1.820684	0.148889
C	4.394782	–0.289570	–1.641539
C	–2.781259	–0.410306	–0.268507
H	–2.992870	0.432204	0.387043
C	–2.236366	–0.822863	–3.116388

C	–3.841661	–0.464443	–1.400491
H	–4.091341	0.538354	–1.773767
O	–1.163245	0.636913	1.867300
H	–1.744769	1.442608	1.878263
H	–0.361083	3.004633	1.314827
F	1.607007	–2.130486	0.767361
F	4.243784	–2.711501	1.065685
F	6.092027	–1.504527	–0.537365
F	5.306603	0.297428	–2.422474
F	2.675861	0.918522	–2.692539
O	–3.404682	–1.296172	–2.480555
H	–1.940781	–1.560887	–3.864933
C	–5.015787	–1.210854	–0.747689
H	–5.619860	–1.714169	–1.509016
H	–5.666741	–0.500903	–0.218915
C	–3.015626	–1.718826	0.469615
C	–4.322503	–2.153739	0.215157
C	–2.177609	–2.424476	1.326511
H	–1.166143	–2.085380	1.525031
C	–2.664404	–3.591148	1.924907
H	–2.021608	–4.161684	2.589632
C	–3.969152	–4.027116	1.677716
H	–4.332445	–4.935966	2.150001
C	–4.809234	–3.308027	0.821446
H	–5.820675	–3.655032	0.624377
H	–2.428265	0.135520	–3.628851
O	–3.826930	3.470716	–0.473496
C	–5.082064	3.584492	0.201571
H	–5.789502	3.936039	–0.551936
H	–5.022052	4.302326	1.025190
H	–5.405602	2.620983	0.607946
H	0.612860	–0.163271	3.402482
C	1.421335	0.405242	2.955536
C	3.450736	1.936170	1.805374
C	1.218986	0.962534	1.684266
C	2.628274	0.576857	3.629074
C	3.648017	1.336690	3.047136
C	2.237212	1.759094	1.133551
H	2.773218	0.123281	4.605374
H	4.591480	1.476543	3.567961
H	4.215174	2.552084	1.341737
O	2.118095	2.310705	–0.114323
C	0.907089	3.007649	–0.476611
H	0.786160	2.808786	–1.545112
H	1.102528	4.081428	–0.352717
C	–0.359054	2.663014	0.277668
C	–1.563273	2.894272	–0.423686
H	–1.564389	3.055389	–1.496763
C	–2.793123	2.985492	0.278783
O	–2.989745	2.634796	1.463050
C	–0.095439	0.821640	0.984097
C	–0.227721	0.025851	–0.200367
N	0.719012	–0.296371	–1.146940
N	–1.428397	–0.219364	–0.835387
C	–1.133467	–0.622763	–2.121744
N	0.139141	–0.690224	–2.351518
C	2.088264	–0.582201	–0.961182
C	4.798094	–1.210713	–0.675617
C	3.046680	0.022617	–1.779389
C	2.506828	–1.519178	–0.011879
C	3.855270	–1.820684	0.148889
C	4.394782	–0.289570	–1.641539
C	–2.781259	–0.410306	–0.268507

H	–2.992870	0.432204	0.387043
C	–2.236366	–0.822863	–3.116388
C	–3.841661	–0.464443	–1.400491
H	–4.091341	0.538354	–1.773767
O	–1.163245	0.636913	1.867300
H	–1.744769	1.442608	1.878263
H	–0.361083	3.004633	1.314827
F	1.607007	–2.130486	0.767361
F	4.243784	–2.711501	1.065685
F	6.092027	–1.504527	–0.537365
F	5.306603	0.297428	–2.422474
F	2.675861	0.918522	–2.692539
O	–3.404682	–1.296172	–2.480555
H	–1.940781	–1.560887	–3.864933
C	–5.015787	–1.210854	–0.747689
H	–5.619860	–1.714169	–1.509016
H	–5.666741	–0.500903	–0.218915
C	–3.015626	–1.718826	0.469615
C	–4.322503	–2.153739	0.215157
C	–2.177609	–2.424476	1.326511
H	–1.166143	–2.085380	1.525031
C	–2.664404	–3.591148	1.924907
H	–2.021608	–4.161684	2.589632
C	–3.969152	–4.027116	1.677716
H	–4.332445	–4.935966	2.150001
C	–4.809234	–3.308027	0.821446
H	–5.820675	–3.655032	0.624377
H	–2.428265	0.135520	–3.628851
O	–3.826930	3.470716	–0.473496
C	–5.082064	3.584492	0.201571
H	–5.789502	3.936039	–0.551936
H	–5.022052	4.302326	1.025190
H	–5.405602	2.620983	0.607946

Supporting Information I

TS_{major} that gives 3a by the catalysis of 1c



Energies (RB3LYP) =	–2235.17009109
Zero-point correction =	0.506891 (Hartree/Particle)
Thermal correction to Energy =	0.543840
Thermal correction to Enthalpy =	0.544784
Thermal correction to Gibbs Free Energy =	0.436924
Energies (B3LYP-D3) =	–2236.03191394
Sum of electronic and zero-point Energies =	–2235.525023
Sum of electronic and thermal Energies =	–2235.488074
Sum of electronic and thermal Enthalpies =	–2235.487130
Sum of electronic and thermal Free Energies =	–2235.594990

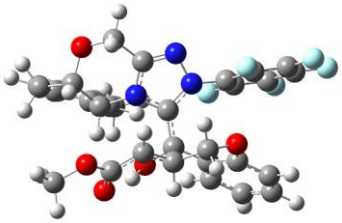
Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
H	0.502998	–0.453652	3.087627
C	1.349212	0.129493	2.739219
C	3.493279	1.681997	1.844757
C	1.217907	0.856213	1.547950
C	2.542405	0.151120	3.459888
C	3.619759	0.917579	3.004320
C	2.293889	1.653018	1.130431
H	2.633839	–0.429119	4.373682
H	4.551497	0.936757	3.563259
H	4.299649	2.315517	1.487842
O	2.174930	2.414535	–0.007958
C	1.046785	3.314057	0.072982
H	1.144297	3.902058	0.994026
H	1.169499	3.987961	–0.779794
C	–0.321289	2.659352	0.014462
C	–1.342098	3.274512	0.788169
H	–1.079788	3.893632	1.641241
C	–2.697441	3.331573	0.320485
O	–3.175278	2.727921	–0.649706
C	–0.060417	0.826667	0.755575
C	–0.121592	–0.008583	–0.426446
N	0.896622	–0.427584	–1.240689
N	–1.256847	–0.334977	–1.131528
C	–0.857478	–0.863768	–2.338608
N	0.431992	–0.950595	–2.442634
C	2.273197	–0.598931	–0.963906
C	4.991625	–1.054633	–0.530730
C	2.693526	–1.550147	–0.030658
C	3.230350	0.098764	–1.704133
C	4.586830	–0.123043	–1.485260
C	4.046138	–1.766075	0.206073
C	–2.682974	–0.271164	–0.745519
H	–2.855460	0.704768	–0.290249
C	–1.856461	–1.159212	–3.419870
C	–3.582874	–0.365677	–2.004908
H	–3.628801	0.590176	–2.542040
O	–1.190958	0.664702	1.541622
H	–1.546041	1.604804	1.645398
H	–0.631690	2.391700	–0.995496
F	1.786923	–2.247400	0.659660
F	4.441452	–2.664989	1.111378

F	6.291362	–1.262768	–0.317389
F	5.502587	0.551757	–2.185682
F	2.854120	0.985941	–2.620546
C	–3.199291	–1.410706	0.119212
C	–4.929477	–0.836065	–1.437689
H	–5.507603	–1.363377	–2.203102
H	–5.514413	0.033878	–1.110460
C	–4.513736	–1.704418	–0.268301
O	–3.132590	–1.408235	–2.881088
H	–1.550124	–2.044324	–3.982549
C	–2.592733	–2.091886	1.166428
H	–1.578557	–1.849721	1.467603
C	–5.232405	–2.683552	0.407512
H	–6.253150	–2.923288	0.119152
C	–3.301874	–3.095612	1.846428
C	–4.619673	–3.372215	1.459042
H	–5.175371	–4.144684	1.985855
H	–1.877375	–0.301294	–4.113878
O	–3.477343	4.152715	1.092196
C	–4.846498	4.242389	0.699968
H	–5.338266	3.265175	0.751105
H	–4.942540	4.625453	–0.320780
H	–5.311072	4.932854	1.406701
C	–2.642786	–3.869684	2.965498
H	–2.062977	–3.209888	3.620928
H	–1.949420	–4.626382	2.574646
H	–3.382409	–4.391069	3.581692
H	0.502998	–0.453652	3.087627
C	1.349212	0.129493	2.739219
C	3.493279	1.681997	1.844757
C	1.217907	0.856213	1.547950
C	2.542405	0.151120	3.459888
C	3.619759	0.917579	3.004320
C	2.293889	1.653018	1.130431
H	2.633839	–0.429119	4.373682
H	4.551497	0.936757	3.563259
H	4.299649	2.315517	1.487842
O	2.174930	2.414535	–0.007958
C	1.046785	3.314057	0.072982
H	1.144297	3.902058	0.994026
H	1.169499	3.987961	–0.779794
C	–0.321289	2.659352	0.014462
C	–1.342098	3.274512	0.788169
H	–1.079788	3.893632	1.641241
C	–2.697441	3.331573	0.320485
O	–3.175278	2.727921	–0.649706
C	–0.060417	0.826667	0.755575
C	–0.121592	–0.008583	–0.426446
N	0.896622	–0.427584	–1.240689
N	–1.256847	–0.334977	–1.131528
C	–0.857478	–0.863768	–2.338608
N	0.431992	–0.950595	–2.442634
C	2.273197	–0.598931	–0.963906
C	4.991625	–1.054633	–0.530730
C	2.693526	–1.550147	–0.030658
C	3.230350	0.098764	–1.704133
C	4.586830	–0.123043	–1.485260
C	4.046138	–1.766075	0.206073
C	–2.682974	–0.271164	–0.745519
H	–2.855460	0.704768	–0.290249
C	–1.856461	–1.159212	–3.419870
C	–3.582874	–0.365677	–2.004908
H	–3.628801	0.590176	–2.542040

O	–1.190958	0.664702	1.541622
H	–1.546041	1.604804	1.645398
H	–0.631690	2.391700	–0.995496
F	1.786923	–2.247400	0.659660
F	4.441452	–2.664989	1.111378
F	6.291362	–1.262768	–0.317389
F	5.502587	0.551757	–2.185682
F	2.854120	0.985941	–2.620546
C	–3.199291	–1.410706	0.119212
C	–4.929477	–0.836065	–1.437689
H	–5.507603	–1.363377	–2.203102
H	–5.514413	0.033878	–1.110460
C	–4.513736	–1.704418	–0.268301
O	–3.132590	–1.408235	–2.881088
H	–1.550124	–2.044324	–3.982549
C	–2.592733	–2.091886	1.166428
H	–1.578557	–1.849721	1.467603
C	–5.232405	–2.683552	0.407512
H	–6.253150	–2.923288	0.119152
C	–3.301874	–3.095612	1.846428
C	–4.619673	–3.372215	1.459042
H	–5.175371	–4.144684	1.985855
H	–1.877375	–0.301294	–4.113878
O	–3.477343	4.152715	1.092196
C	–4.846498	4.242389	0.699968
H	–5.338266	3.265175	0.751105
H	–4.942540	4.625453	–0.320780
H	–5.311072	4.932854	1.406701
C	–2.642786	–3.869684	2.965498
H	–2.062977	–3.209888	3.620928
H	–1.949420	–4.626381	2.574646
H	–3.382409	–4.391069	3.581692

Supporting Information I

TS_{minor} that gives 3a by the catalysis of 1c



Energies (RB3LYP) =	–2235.16498172
Zero-point correction =	0.506954 (Hartree/Particle)
Thermal correction to Energy =	0.544140
Thermal correction to Enthalpy =	0.545084
Thermal correction to Gibbs Free Energy =	0.437042
Energies (B3LYP-D3) =	–2236.02897405
Sum of electronic and zero-point Energies =	–2235.522020
Sum of electronic and thermal Energies =	–2235.484834
Sum of electronic and thermal Enthalpies =	–2235.483890
Sum of electronic and thermal Free Energies =	–2235.591932

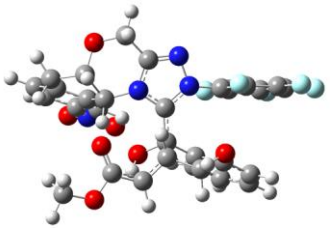
Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
H	–0.590653	0.757386	3.249298
C	–1.426153	0.140012	2.937252
C	–3.526403	–1.518226	2.149401
C	–1.263882	–0.676869	1.808445
C	–2.627239	0.158758	3.642061
C	–3.682411	–0.666543	3.240397
C	–2.318588	–1.531041	1.444521
H	–2.739972	0.810729	4.503524
H	–4.621444	–0.659772	3.787307
H	–4.319183	–2.188547	1.831756
O	–2.240800	–2.335009	0.338853
C	–1.061052	–3.136117	0.114771
H	–0.955295	–3.168230	–0.973105
H	–1.290094	–4.152588	0.462293
C	0.231382	–2.690277	0.764250
C	1.411535	–3.101258	0.105619
H	1.383784	–3.474868	–0.912782
C	2.652881	–3.094947	0.793297
O	2.887757	–2.518345	1.878085
C	0.044763	–0.735738	1.085860
C	0.189468	–0.204366	–0.237522
N	–0.758716	–0.052872	–1.225068
N	1.388753	–0.139457	–0.916528
C	1.090551	–0.003273	–2.257188
N	–0.181915	0.059579	–2.488836
C	–2.114974	0.312817	–1.093868
C	–4.800314	1.075288	–0.920761
C	–3.103953	–0.415684	–1.761194
C	–2.490732	1.439276	–0.356053
C	–3.826797	1.811036	–0.248709
C	–4.439753	–0.037873	–1.679088
C	2.751923	0.133735	–0.410024
H	2.951917	–0.557944	0.406525
C	2.187524	–0.054631	–3.276211
C	3.803548	–0.074492	–1.533527
H	4.032203	–1.138217	–1.687307
O	1.130689	–0.419939	1.907659
H	1.689373	–1.226396	2.065239
H	0.245854	–2.815184	1.848976
F	–1.561327	2.170906	0.270415
F	–4.173927	2.884523	0.467144

F	–6.082485	1.433660	–0.834459
F	–5.380552	–0.743901	–2.313367
F	–2.775025	–1.493608	–2.471257
O	3.372797	0.516540	–2.764481
H	1.902430	0.508323	–4.167384
C	4.997823	0.769009	–1.058824
H	5.603333	1.087844	–1.913131
H	5.640449	0.171590	–0.397225
C	3.019580	1.562401	0.035603
C	4.331044	1.906165	–0.311967
C	2.199994	2.448019	0.724310
H	1.182988	2.172218	0.987053
C	2.690289	3.715700	1.073802
C	4.006175	4.050795	0.722546
H	4.389165	5.034737	0.984089
C	4.832101	3.155977	0.036339
H	5.844666	3.445612	–0.234360
H	2.351181	–1.106891	–3.565887
O	3.651808	–3.763243	0.141216
C	4.918977	–3.779692	0.802815
H	5.592203	–4.318662	0.133388
H	4.853607	–4.294539	1.765948
H	5.290058	–2.765005	0.979207
C	1.821157	4.688131	1.838137
H	0.762108	4.555920	1.592282
H	2.092800	5.726702	1.621232
H	1.922742	4.544214	2.922175
H	–0.590653	0.757386	3.249298
C	–1.426153	0.140012	2.937252
C	–3.526403	–1.518226	2.149401
C	–1.263882	–0.676869	1.808445
C	–2.627239	0.158758	3.642061
C	–3.682411	–0.666543	3.240397
C	–2.318588	–1.531041	1.444521
H	–2.739972	0.810729	4.503524
H	–4.621444	–0.659772	3.787307
H	–4.319183	–2.188547	1.831756
O	–2.240800	–2.335009	0.338853
C	–1.061052	–3.136117	0.114771
H	–0.955295	–3.168230	–0.973105
H	–1.290094	–4.152588	0.462293
C	0.231382	–2.690277	0.764250
C	1.411535	–3.101258	0.105619
H	1.383784	–3.474868	–0.912782
C	2.652881	–3.094947	0.793297
O	2.887757	–2.518345	1.878085
C	0.044763	–0.735738	1.085860
C	0.189468	–0.204366	–0.237522
N	–0.758716	–0.052872	–1.225068
N	1.388753	–0.139457	–0.916528
C	1.090551	–0.003273	–2.257188
N	–0.181915	0.059579	–2.488836
C	–2.114974	0.312817	–1.093868
C	–4.800314	1.075288	–0.920761
C	–3.103953	–0.415684	–1.761194
C	–2.490732	1.439276	–0.356053
C	–3.826797	1.811036	–0.248709
C	–4.439753	–0.037873	–1.679088
C	2.751923	0.133735	–0.410024
H	2.951917	–0.557944	0.406525
C	2.187524	–0.054631	–3.276211
C	3.803548	–0.074492	–1.533527
H	4.032203	–1.138217	–1.687307

O	1.130689	–0.419939	1.907659
H	1.689373	–1.226396	2.065239
H	0.245854	–2.815184	1.848976
F	–1.561327	2.170906	0.270415
F	–4.173927	2.884523	0.467144
F	–6.082485	1.433660	–0.834459
F	–5.380552	–0.743901	–2.313367
F	–2.775025	–1.493608	–2.471257
O	3.372797	0.516540	–2.764481
H	1.902430	0.508323	–4.167384
C	4.997823	0.769009	–1.058824
H	5.603333	1.087844	–1.913131
H	5.640449	0.171590	–0.397225
C	3.019580	1.562401	0.035603
C	4.331044	1.906165	–0.311967
C	2.199994	2.448019	0.724310
H	1.182988	2.172218	0.987053
C	2.690289	3.715700	1.073802
C	4.006175	4.050795	0.722546
H	4.389165	5.034737	0.984089
C	4.832101	3.155977	0.036339
H	5.844666	3.445612	–0.234360
H	2.351181	–1.106891	–3.565887
O	3.651808	–3.763243	0.141216
C	4.918977	–3.779692	0.802815
H	5.592203	–4.318662	0.133388
H	4.853607	–4.294539	1.765948
H	5.290058	–2.765005	0.979207
C	1.821157	4.688131	1.838137
H	0.762108	4.555920	1.592282
H	2.092800	5.726702	1.621232
H	1.922742	4.544214	2.922174

Supporting Information I

TS_{major} that gives 3a by the catalysis of 1d



Energies (RB3LYP) =	–2400.35478873
Zero-point correction =	0.481955 (Hartree/Particle)
Thermal correction to Energy =	0.519600
Thermal correction to Enthalpy =	0.520544
Thermal correction to Gibbs Free Energy =	0.410789
Energies (B3LYP-D3) =	–2401.28033558
Sum of electronic and zero-point Energies =	–2400.798381
Sum of electronic and thermal Energies =	–2400.760736
Sum of electronic and thermal Enthalpies =	–2400.759791
Sum of electronic and thermal Free Energies =	–2400.869546

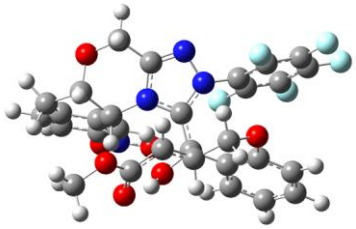
Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
H	0.347398	1.426990	–2.603060
C	1.261427	0.844857	–2.539579
C	3.597727	–0.683355	–2.390701
C	1.292498	–0.281975	–1.705430
C	2.388426	1.220194	–3.269238
C	3.560506	0.462177	–3.185160
C	2.464398	–1.051200	–1.663265
H	2.353864	2.104525	–3.898806
H	4.440573	0.752950	–3.752437
H	4.483090	–1.309128	–2.331641
O	2.514026	–2.180383	–0.878922
C	1.466923	–3.113459	–1.216202
H	1.518496	–3.313706	–2.293683
H	1.731083	–4.031337	–0.682738
C	0.061572	–2.688542	–0.833124
C	–0.975098	–3.114524	–1.704873
H	–0.744480	–3.381750	–2.732107
C	–2.272393	–3.470599	–1.206657
O	–2.712712	–3.265874	–0.065904
C	0.086917	–0.682386	–0.899802
C	0.038143	–0.310864	0.496884
N	1.066456	–0.083838	1.371377
N	–1.075040	–0.342873	1.308204
C	–0.645923	–0.190697	2.608881
N	0.635781	–0.020810	2.691574
C	2.419214	0.256459	1.129577
C	5.089432	0.994172	0.816585
C	2.750530	1.507316	0.602798
C	3.439082	–0.609070	1.530521
C	4.772464	–0.245913	1.369003
C	4.080157	1.872331	0.424244
C	–2.506101	–0.449193	0.969108
H	–2.616884	–1.259766	0.246116
C	–1.597909	–0.337542	3.760486
C	–3.328739	–0.833676	2.226563
H	–3.252709	–1.906289	2.444279
O	–1.117302	–0.404281	–1.530583
H	–1.387044	–1.289608	–1.935111
H	–0.160490	–2.816931	0.226141
F	1.781934	2.353192	0.246753
F	4.393516	3.061410	–0.095077

F	6.366873	1.340804	0.657699
F	5.748692	–1.077447	1.742641
F	3.142835	–1.790385	2.065716
C	–3.188870	0.826266	0.504347
C	–4.747800	–0.363983	1.876651
H	–5.324135	–0.153376	2.782578
H	–5.270669	–1.149537	1.315448
C	–4.497771	0.850770	1.009751
O	–2.921473	–0.060995	3.361254
H	–1.335181	0.362125	4.557230
C	–2.721220	1.843753	–0.314161
H	–1.724318	1.845186	–0.730560
C	–5.362264	1.897050	0.692895
H	–6.374915	1.920369	1.085618
C	–3.600561	2.887168	–0.608470
C	–4.908777	2.931599	–0.125054
H	–5.543324	3.768327	–0.389254
H	–1.510665	–1.362362	4.159184
O	–3.043232	–4.081941	–2.158345
C	–4.358624	–4.448446	–1.743159
H	–4.941997	–3.568456	–1.451642
H	–4.328475	–5.140974	–0.896350
H	–4.817067	–4.930592	–2.608607
N	–3.126121	3.981749	–1.469544
O	–1.968118	3.924544	–1.884888
O	–3.913503	4.893112	–1.725360
H	0.347398	1.426990	–2.603060
C	1.261427	0.844857	–2.539579
C	3.597727	–0.683355	–2.390701
C	1.292498	–0.281975	–1.705430
C	2.388426	1.220194	–3.269238
C	3.560506	0.462177	–3.185160
C	2.464398	–1.051200	–1.663265
H	2.353864	2.104525	–3.898806
H	4.440573	0.752950	–3.752437
H	4.483090	–1.309128	–2.331641
O	2.514026	–2.180383	–0.878922
C	1.466923	–3.113459	–1.216202
H	1.518496	–3.313706	–2.293683
H	1.731083	–4.031337	–0.682738
C	0.061572	–2.688542	–0.833124
C	–0.975098	–3.114524	–1.704873
H	–0.744480	–3.381750	–2.732107
C	–2.272393	–3.470599	–1.206657
O	–2.712712	–3.265874	–0.065904
C	0.086917	–0.682386	–0.899802
C	0.038143	–0.310864	0.496884
N	1.066456	–0.083838	1.371377
N	–1.075040	–0.342873	1.308204
C	–0.645923	–0.190697	2.608881
N	0.635781	–0.020810	2.691574
C	2.419214	0.256459	1.129577
C	5.089432	0.994172	0.816585
C	2.750530	1.507316	0.602798
C	3.439082	–0.609070	1.530521
C	4.772464	–0.245913	1.369003
C	4.080157	1.872331	0.424244
C	–2.506101	–0.449193	0.969108
H	–2.616884	–1.259766	0.246116
C	–1.597909	–0.337542	3.760486
C	–3.328739	–0.833676	2.226563
H	–3.252709	–1.906289	2.444279
O	–1.117302	–0.404281	–1.530583

H	–1.387044	–1.289608	–1.935111
H	–0.160490	–2.816931	0.226141
F	1.781934	2.353192	0.246753
F	4.393516	3.061410	–0.095077
F	6.366873	1.340804	0.657699
F	5.748692	–1.077447	1.742641
F	3.142835	–1.790385	2.065716
C	–3.188870	0.826266	0.504347
C	–4.747800	–0.363983	1.876651
H	–5.324135	–0.153376	2.782578
H	–5.270669	–1.149537	1.315448
C	–4.497771	0.850770	1.009751
O	–2.921473	–0.060995	3.361254
H	–1.335181	0.362125	4.557230
C	–2.721220	1.843753	–0.314161
H	–1.724318	1.845186	–0.730560
C	–5.362264	1.897050	0.692895
H	–6.374915	1.920369	1.085618
C	–3.600561	2.887168	–0.608470
C	–4.908777	2.931599	–0.125054
H	–5.543324	3.768327	–0.389254
H	–1.510665	–1.362362	4.159184
O	–3.043232	–4.081941	–2.158345
C	–4.358624	–4.448446	–1.743159
H	–4.941997	–3.568456	–1.451642
H	–4.328475	–5.140974	–0.896350
H	–4.817067	–4.930592	–2.608607
N	–3.126121	3.981749	–1.469544
O	–1.968118	3.924544	–1.884888
O	–3.913503	4.893112	–1.725360

Supporting Information I

TS_{minor} that gives 3a by the catalysis of 1d



Energies (RB3LYP) =	–2400.34808555
Zero-point correction =	0.481783 (Hartree/Particle)
Thermal correction to Energy =	0.519761
Thermal correction to Enthalpy =	0.520706
Thermal correction to Gibbs Free Energy =	0.410041
Energies (B3LYP-D3) =	–2401.27562592
Sum of electronic and zero-point Energies =	–2400.793842
Sum of electronic and thermal Energies =	–2400.755865
Sum of electronic and thermal Enthalpies =	–2400.754920
Sum of electronic and thermal Free Energies =	–2400.865584

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
H	–0.500261	1.273567	2.929991
C	–1.389093	0.668444	2.787148
C	–3.643902	–0.937251	2.434071
C	–1.339859	–0.385761	1.862544
C	–2.553676	0.940254	3.500698
C	–3.685037	0.138868	3.317327
C	–2.473037	–1.203507	1.717545
H	–2.579102	1.772878	4.197475
H	–4.596219	0.343507	3.872983
H	–4.500353	–1.588353	2.288543
O	–2.510207	–2.225287	0.805433
C	–1.411996	–3.155337	0.718848
H	–1.361066	–3.421810	–0.340576
H	–1.702410	–4.054214	1.279622
C	–0.057716	–2.701619	1.219479
C	1.051385	–3.344372	0.626860
H	0.940565	–3.923583	–0.284177
C	2.321803	–3.309359	1.257568
O	2.661742	–2.536145	2.180717
C	–0.073540	–0.707497	1.134298
C	0.059541	–0.467041	–0.270100
N	–0.906467	–0.426498	–1.249801
N	1.237084	–0.631231	–0.973991
C	0.904553	–0.715561	–2.311714
N	–0.366274	–0.592445	–2.522988
C	–2.229251	0.060694	–1.163717
C	–4.841740	1.047558	–1.095029
C	–3.290436	–0.712081	–1.642455
C	–2.492498	1.341474	–0.669229
C	–3.794042	1.830092	–0.613519
C	–4.591717	–0.223312	–1.611721
C	2.632577	–0.418666	–0.545220
H	2.799834	–0.981674	0.371596
C	1.958318	–1.027239	–3.329916
C	3.620289	–0.907121	–1.639436
H	3.742877	–1.998561	–1.618386
O	1.072416	–0.332006	1.844801
H	1.565206	–1.136726	2.155651
H	–0.001698	–2.595107	2.304727
F	–1.488352	2.106989	–0.231143
F	–4.038468	3.050562	–0.131388

F	–6.090558	1.514223	–1.057976
F	–5.603663	–0.969280	–2.064518
F	–3.063131	–1.934448	–2.121470
O	3.203190	–0.481619	–2.938699
H	1.692456	–0.592167	–4.295283
C	4.905445	–0.120997	–1.333837
H	5.509544	–0.001352	–2.238240
H	5.512286	–0.658354	–0.592493
C	3.055355	1.027267	–0.339509
C	4.382041	1.180979	–0.766618
C	2.355179	2.082098	0.227596
H	1.333531	1.990848	0.571371
C	3.024029	3.302061	0.343361
C	4.344114	3.482220	–0.071571
H	4.806509	4.454476	0.044638
C	5.032371	2.406068	–0.631377
H	6.058427	2.532895	–0.965036
H	2.031039	–2.121577	–3.447882
O	3.225253	–4.193376	0.736309
C	4.511859	–4.203843	1.359593
H	5.101787	–4.933849	0.802164
H	4.437723	–4.502145	2.409542
H	4.985682	–3.217896	1.315144
N	2.305819	4.444772	0.930985
O	1.142406	4.265513	1.290098
O	2.910469	5.512856	1.028320
H	–0.500261	1.273567	2.929991
C	–1.389093	0.668444	2.787148
C	–3.643902	–0.937251	2.434071
C	–1.339859	–0.385761	1.862544
C	–2.553676	0.940254	3.500698
C	–3.685037	0.138868	3.317327
C	–2.473037	–1.203507	1.717545
H	–2.579102	1.772878	4.197475
H	–4.596219	0.343507	3.872983
H	–4.500353	–1.588353	2.288543
O	–2.510207	–2.225287	0.805433
C	–1.411996	–3.155337	0.718848
H	–1.361066	–3.421810	–0.340576
H	–1.702410	–4.054214	1.279622
C	–0.057716	–2.701619	1.219479
C	1.051385	–3.344372	0.626860
H	0.940565	–3.923583	–0.284177
C	2.321803	–3.309359	1.257568
O	2.661742	–2.536145	2.180717
C	–0.073540	–0.707497	1.134298
C	0.059541	–0.467041	–0.270100
N	–0.906467	–0.426498	–1.249801
N	1.237084	–0.631231	–0.973991
C	0.904553	–0.715561	–2.311714
N	–0.366274	–0.592445	–2.522988
C	–2.229251	0.060694	–1.163717
C	–4.841740	1.047558	–1.095029
C	–3.290436	–0.712081	–1.642455
C	–2.492498	1.341474	–0.669229
C	–3.794042	1.830092	–0.613519
C	–4.591717	–0.223312	–1.611721
C	2.632577	–0.418666	–0.545220
H	2.799834	–0.981674	0.371596
C	1.958318	–1.027239	–3.329916
C	3.620289	–0.907121	–1.639436
H	3.742877	–1.998561	–1.618386
O	1.072416	–0.332006	1.844801

H	1.565206	–1.136726	2.155651
H	–0.001698	–2.595107	2.304727
F	–1.488352	2.106989	–0.231143
F	–4.038468	3.050562	–0.131388
F	–6.090558	1.514223	–1.057976
F	–5.603663	–0.969280	–2.064518
F	–3.063131	–1.934448	–2.121470
O	3.203190	–0.481619	–2.938699
H	1.692456	–0.592167	–4.295283
C	4.905445	–0.120997	–1.333837
H	5.509544	–0.001352	–2.238240
H	5.512286	–0.658354	–0.592493
C	3.055355	1.027267	–0.339509
C	4.382041	1.180979	–0.766618
C	2.355179	2.082098	0.227596
H	1.333531	1.990848	0.571371
C	3.024029	3.302061	0.343361
C	4.344114	3.482220	–0.071571
H	4.806509	4.454476	0.044638
C	5.032371	2.406068	–0.631377
H	6.058427	2.532895	–0.965036
H	2.031039	–2.121577	–3.447882
O	3.225253	–4.193376	0.736309
C	4.511859	–4.203843	1.359593
H	5.101787	–4.933849	0.802164
H	4.437723	–4.502145	2.409542
H	4.985682	–3.217896	1.315144
N	2.305819	4.444772	0.930985
O	1.142406	4.265513	1.290098
O	2.910469	5.512856	1.028320

9. References

1. Kerr, M. S.; Read de Alaniz, J.; Rovis, T. An Efficient Synthesis of Achiral and Chiral 1,2,4-Triazolium Salts: Bench Stable Precursors for N-Heterocyclic Carbenes. *J. Org. Chem.* **2005**, *70*, 5725–5728.
2. Carmine, G. D.; Ragno, D.; Bortolini, O.; Giovannini, P. P.; Mazzanti, A.; Massi, A.; Fogagnolo, M. Enantioselective Dearomatization of Alkylpyridiniums by N-Heterocyclic Carbene-Catalyzed Nucleophilic Acylation. *J. Org. Chem.* **2018**, *83*, 2050–2057.
3. Wang, Y.; Yamauchi, A.; Hashimoto, K.; Fujiwara, T.; Inokuma, T.; Mitani, Y.; Ute, K.; Kuwano, S.; Yamaoka, Y.; Takasu, K.; Yamada, K. Enhanced Molecular Recognition through Substrate–Additive Complex Formation in N-Heterocyclic-Carbene-Catalyzed Kinetic Resolution of α-Hydroxythioamides. *ACS Catal.* **2022**, *12*, 6100–6107.
4. Pospíšil, J.; Potáček, M. Microwave-assisted solvent-free intramolecular 1,3-dipolar cycloaddition reactions leading to hexahydrochromeno[4,3-b]-pyrroles: scope and limitations. *Tetrahedron* **2007**, *63*, 337–346.
5. Cui, S-L.; Wang, J.; Lin, X-F.; Wang, Y-G. Domino Reaction of 3-(2-Formylphenoxy)propenoates and Amines: A Novel Synthesis of 1,4-Dihydropyridines from Salicaldehydes, Ethyl Propiolate, and Amines. *J. Org. Chem.* **2007**, *72*, 7779–7782.
6. Heieh, S-Y.; Binanzer, M.; Kreituss, I.; Bode, J. W. Expanded substrate scope and catalyst optimization for the catalytic kinetic resolution of N-heterocycles. *Chem. Commun.* **2012**, *48*, 8892–8894.
7. Kuwano, S.; Harada, S.; Kang, B.; Oriez, R.; Yamaoka, Y.; Takasu, K.; Yamada, K. Enhanced Rate and Selectivity by Carboxylate Salt as a Basic Cocatalyst in Chiral N-Heterocyclic Carbene-Catalyzed Asymmetric Acylation of Secondary Alcohols. *J. Am. Chem. Soc.* **2013**, *135*, 11485–11488.
8. Lee, Y-T.; Jang, Y-J.; Syu, S-e.; Chou, S-C.; Lee, C-J.; Lin, W. Preparation of functional benzofurans and indolesvia chemoselective intramolecular Wittig reactions. *Chem. Commun.* **2012**, *48*, 8135–8137.
9. Xiong, Z.; Tian, J.; Xue, P.; Zhang, X.; Lv, H. Enantioselective synthesis of chiral multicyclic γ-lactones via dynamic kinetic resolution of racemic γ-keto carboxylic acids. *Org. Chem. Front.* **2020**, *7*, 104–108.
10. Santoso, H.; Casana, M. I.; Donner, C. D. Exploring O-stannyl ketyl and acyl radical cyclizations for the synthesis of γ-lactone-fused benzopyrans and benzofurans. *Org. Biomol. Chem.* **2014**, *12*, 171–176.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.
12. Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W. Revealing Noncovalent Interactions. *J. Am. Chem. Soc*. **2010**, *132*, 6498.