Supporting Information

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General remarks:
All reactions were performed with dry solvents and the reagents were purified by the usual methods. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merck silica gel plates (60F-254). Column chromatography was performed with silica gel (Fuji Silysia, PSQ-60B) or NH-silica (Fuji Silysia, DM2035). NMR spectra were recorded on spectrometers of JEOL JMN-ECS-400, ECP-400, ECZ-400, ECZ-600, and ECA-600 operating at 400 and 600 MHz for $^1$H NMR and 100 or 150 MHz for $^{13}$C NMR with calibration using residual undeuterated solvent as an internal reference. IR spectra were recorded on JASCO FT/IR-4700. High resolution mass spectra were measured by The AccuTOFLC-plus JMS-T100LP (Ionization method: ESI).

General procedure for hydrocyanative cyclization: EtOH (0.2 M for diene) was added to the mixture of diene 1 (1.0 eq.), Co (2 mol%), TsCN (1.2 eq.) under an argon atmosphere at rt, then PhSiH$_3$ (1.2 eq.) was added at rt and the solution was stirred at room temperature. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography.

N,N-diallylaniline (1a)
(CAS-Reg# 6247-00-3)

\[ ^1\text{H-NMR (CDCl}_3, 400 MHz) \delta: 3.79 \text{ (d, 2H, } J = 4.8 \text{ Hz, 2 H), 5.17-5.33 \text{ (m, 2 H), 5.98 \text{ (m, 1 H), 6.63-6.65 \text{ (m, 2 H), 6.71-6.75 \text{ (m, 1 H), 7.18-7.22 (m, 2 H)}}} \]

N,N-diallyl-4-methylbenzenesulfonamide (1b)
(CAS-Reg# 50487-72-4)

\[ ^1\text{H-NMR (CDCl}_3, 400 MHz) \delta: 2.39 \text{ (s, 3H), 3.77 \text{ (d, 4H, } J = 6.4 \text{ Hz), 5.08-5.51 \text{ (m, 4H), 5.56 \text{ (ddt, 2H, } J = 16.4 \text{ Hz, 10.0 Hz, 6.4 Hz), 7.27 \text{ (d, 2H, } J = 8.0 \text{ Hz), 7.67 \text{ (d, 1H, } J = 8.4 \text{ Hz)}}} \]

Diethyl 2,2-diallylmalonate (1c)
(CAS-Reg# 3195-24-2)

\[ ^1\text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.23 \text{ (t, 6H, } J = 7.2 \text{ Hz), 2.62 \text{ (d, 4 H, } J = 7.2 \text{ Hz), 4.17 \text{ (q, 4 H, } J = 7.2 \text{ Hz), 5.08 \text{ (d, 1 H, } J = 11.2 \text{ Hz), 5.09 \text{ (d, 1 H, } J = 16.0 \text{ Hz), 5.65 \text{ (m, 1 H)}}} \]

Diethyl 2-allyl-2-(3-methylbut-2-en-1-yl)malonate (1d)
(CAS-Reg# 408333-38-0)

\[ ^1\text{H-NMR (CDCl}_3, 400 MHz) \delta:1.23 \text{ (t, } J = 7.2 \text{ Hz, 6H), 1.61 \text{ (s, 3H), 1.69 \text{ (s, 3H), 2.58-2.64 \text{ (m, 2H), 4.12-4.22 \text{ (m, 4H), 4.94-5.00 \text{ (m, 1H), 5.01 \text{ (s, 1H), 5.08-5.12 \text{ (m, 1H), 5.60-5.72 \text{ (m, 1H)}}} \]

Diethyl 2-allyl-2-(2-methylallyl)malonate (1e)
(CAS-Reg# 5309-50-2)
$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 1.25 (t, 6H, $J = 7.2$ Hz), 1.67 (s, 3H), 2.67 (d, 2H, $J = 7.2$ Hz), 2.69-2.71 (m, 2H), 4.13-4.22 (m, 4H), 4.75-4.77 (m, 1H), 4.86-4.89 (m, 1H), 5.06-5.08 (m, 1H), 5.11 (d, 1H, $J = 6.0$ Hz), 5.64-5.75 (m, 1H).

**Synthesis of 1f,g**

![Synthesis of 1f,g](image)

S1 to S2: To a stirred solution of S1 (2 mL, 14.7 mmol) in CH$_2$Cl$_2$ (29 mL) was added pyridine (3.6 mL, 44.1 mmol), and TsCl (3.1 g, 16.2 mmol) at 0 °C, and the reaction mixture was stirred for 2 h at rt. The reaction was quenched with 1 N HCl, extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO$_2$, n-hexane/AcOEt = 2/1) afforded S2 (3.96 g, 94%).

S2 to 1f,g: To a stirred solution of S2 (1.0 eq.) in MeCN (0.3 M for S2) was added K$_2$CO$_3$ (2.0 eq.), and RX (2.0 eq.), and the reaction mixture was stirred at 80 °C. The reaction was quenched with H$_2$O, extracted with AcOEt, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded 1f,g.

**N-allyl-4-methyl-N-(2-(prop-1-en-2-yl)phenyl)benzenesulfonamide (1f)**

(CAS-Reg# 402822-74-6)

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 2.18 (s, 3H), 2.44 (s, 3H), 4.12 (d, 2H, $J = 6.8$ Hz), 4.94 (dd, 1H, $J = 11.2, 1.6$ Hz), 4.98 (d, 1H, $J = 3.2$ Hz), 5.05 (dd, 1H, $J = 1.2, 0.8$ Hz), 5.22 (dd, 1H, $J = 1.6, 1.2$ Hz), 5.69 (ddd, 1H, $J = 17.2, 11.2, 6.8, 6.8$ Hz), 6.74 (d, 1H, $J = 8.0$ Hz), 7.12 (ddd, 1H, $J = 7.8, 6.4, 2.4$ Hz), 7.27-7.31 (m, 4H), 7.67 (d, 2H, $J = 8.4$ Hz); (675 mg, quant.)

**(E)-N-(but-2-en-1-yl)-4-methyl-N-(2-(prop-1-en-2-yl)phenyl)benzenesulfonamide (1g)**

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 1.49 (d, 3H, $J = 5.6$ Hz), 2.17(s, 3H), 2.43 (s, 3H), 4.05 (brs, 2H), 5.05 (s, 1H), 5.21 (s, 1H), 5.26-5.42 (m, 2H), 6.71 (d, 1H, $J = 8.4$ Hz), 7.11 (dd, 1H, $J = 7.6, 2.0$ Hz), 7.21-7.29 (m, 4H), 7.65 (d, 2H, $J = 8.4$ Hz);

$^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 17.5, 21.4, 24.1, 24.2, 54.0, 116.3, 125.0, 127.1, 127.9, 128.0, 128.5, 129.3, 129.8, 130.6, 136.4, 136.8, 143.2, 143.6, 144.9 11; IR (ATR) v: 2982, 1736, 1273, 1044 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{19}$N$_2$O$_2$S, [M+Na]$^+$ 364.1347, found; 364.1360; yellow oil (126.2 mg, 96%).
**Synthesis of 1h**

S3 to S4: Ethylmagnesium bromide (10 mL, 3.0 M in Et₂O, 30 mmol) was added to a solution of S3 (1.18 g, 10 mmol) in THF (20 mL) at 0 °C. Then the reaction was allowed to warm to ambient temperature and allowed to stir at this temperature for 20 h. The reaction was quenched by slow addition of 10% HCl and made basic by the addition of NaOH at 0 °C. The organic layer was separated and the remaining aqueous layer was extracted with AcOEt for three times. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated. The crude S4 (1.68 g) was used in the next step without further purification.

S4 to S5: To a stirred solution of crude S4 (1.68 g) in CH₂Cl₂ (20 mL) was added NEt₃ (4.2 mL, 30 mmol), and TsCl (1.9 g, 10 mmol) at 0 °C, and the reaction mixture was stirred for 7 h at rt. The reaction was quenched with 1 N HCl, extracted with CH₂Cl₂, dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO₂, n-hexane/AcOEt = 4/1) afforded S5 (573 mg, 19%, 2 steps).

S5 to S6: To a stirred solution of S5 (150 mg, 0.49 mmol) in MeCN (1.6 mL) was added K₂CO₃ (136 mg, 0.99 mmol), and allyl bromide (0.08 mL, 0.99 mmol), and the reaction mixture was stirred at 80 °C for 22 h. The reaction was quenched with 1N HCl, extracted with AcOEt, dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded S6 (158 mg, 93%).

S6 to 1h: To a stirred solution of Ph₃PMeBr (357 mg, 1.0 mmol) in THF (2.5 mL) was added n-BuLi (0.63 mL, 1.6 M in hexane, 1.0 mmol) at 0 °C, and the reaction mixture was stirred at rt for 1 h. Then, S6 (158 mg, 0.46 mmol) in THF (1.0 mL) was added at 0 °C, and the reaction mixture was stirred at 60 °C for 24 h. The reaction was quenched with H₂O, extracted with AcOEt, dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded 1h (45.6 mg, 29%).

**N-allyl-N-(2-(but-1-en-2-yl)phenyl)-4-methylbenzenesulfonamide (1h)**

^1H-NMR (CDCl₃, 400 MHz) δ: 1.07 (t, 3H, J = 7.2 Hz), 2.45 (s, 3H), 2.50 (q, 2H, J = 7.2 Hz), 4.11 (d, 2H, J = 6.8 Hz), 4.92-4.98 (m, 2H), 5.04 (s, 1H), 5.21 (d, 1H, J = 6.0 Hz), 5.66 (ddd, 1H, J = 16.8, 10.4, 6.8 Hz), 6.79 (d, 1H, J = 8.0 Hz), 7.14 (ddd, 1H, J =
= 7.6, 7.6, 2.0 Hz), 7.20-7.27 (m, 2H), 7.30 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 8.0 Hz); 13C-NMR (CDCl3, 100 MHz) δ: 12.5, 21.5, 29.7, 54.6, 114.2, 119.1, 127.2, 128.0, 128.2, 128.8, 129.5, 130.7, 132.6, 136.5, 137.1, 143.4, 144.6, 149.8; IR (ATR) ν: 2965, 1349, 1165, 1091 cm⁻¹; HRMS (ESI) Calcd for C20H23NNaO2S, [M+Na]+ 364.1347, found 364.1356; yellow oil

Synthesis of 1i

S7 to S8: To a stirred solution of S7 (1.0 mL, 8.6 mmol) in CCl4 (15 mL) at rt was added NaN3 (1.95 g, 30 mmol) in H2O (15 mL), and the reaction mixture was stirred for 18 h at rt. The reaction mixture was extracted with CH2Cl2, dried over Na2SO4, filtered, and concentrated in vacuo gave crude S8 which was used in the next step without further purification.

S8 to S9: A mixture of the crude S8 (approximately 8.6 mmol), PPh3 (2.7 g, 10.32 mmol), THF (29 mL) was stirred for 16 h. The mixture was extracted with 1 N HCl (3 times). The combined aqueous phases were made basic with NaOH. The aqueous solution was extracted with CH2Cl2. The organic phases were combined, washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure to yield crude S9 (444 mg) which was used in the next step without further purification.

S9 to S10: To a stirred solution of crude S9 (444 mg) in CH2Cl2 (23 mL) was added NEt3 (1.9 mL, 13.71 mmol), and TsCl (1.05 g, 5.48 mmol) at 0 °C, and the reaction mixture was stirred for 8 h at rt. The reaction was quenched with 1 N HCl, extracted with CH2Cl2, dried over Na2SO4, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO2, n-hexane/AcOEt = 5/1) afforded S10 (686 mg, 32%, 3 steps)

S10 to 1i: A solution of crude S10 (234 mg), K2CO3 (259 mg, 1.88 mmol), 4-chloro-2-methyl-1-butene (0.18 mL, 1.88 mmol), NaI (71 mg, 0.47 mmol) in MeCN (3.1 mL) was stirred for 8 h at 80 °C. The reaction was quenched with aqueous sodium thiosulfate, extracted with AcOEt, dried over Na2SO4, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO2, n-hexane/AcOEt = 10/1) afforded 1i (219.9 mg, 72%)

N-(cyclohex-2-en-1-yl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1i)

1H-NMR (CDCl3, 400 MHz) δ: 1.52-1.65 (m, 2H), 1.71-1.75 (m, 1H), 1.77 (s, 3H), 1.85-1.93 (m, 3H), 2.43 (s, 3H), 3.44 (16.4 Hz), 3.80 (d, 1H, J = 16.4 Hz), 4.48-4.55 (m, 1H), 4.88 (s, 1H), 4.93 (d, 1H, J = 10.8 Hz), 5.00 (s, 1H), 5.69-5.81 (m, 1H), 7.28 (d, 2H, J = 8.0 Hz), 7.71 (d, 2H, J = 8.0 Hz); 13C-NMR (CDCl3, 100 MHz) δ: 20.0, 21.3, 21.6, 24.2, 28.5, 49.6,
S12 to S13: A solution of Mg (566 mg, 23.28 mmol) and 1,2-dibromoethane (0.1 mL, 1.16 mmol) in THF (3.6 mL) was stirred at 60 °C for 15 min, then cooled to rt, and a solution of Br(CH₂)₂OTBS (2.95 g, 11.64 mmol) in THF (6 mL) was added slowly at rt, and the mixture was stirred for 10 min at rt. Then the solution was stirred at 60 °C for 1 h, the solution of S12 (850.8 mg, 5.82 mmol) in THF (6 mL) was added at 0 °C, and the solution was stirred for another 2 h at room temperature. The solution was dissolved in AcOEt, sat. NH₄Cl aq. was added and the aqueous phase was extracted with AcOEt. The combined organic phases were washed with water and sat. sodium chloride solution and dried over Na₂SO₄. The solvent was removed in vacuum to leave a crude mixture, which was filtered through a short silica gel column (eluting with hexane/AcOEt = 50/1) to afford crude S13 (940 mg).

S13 to S14: To an oven-dried 100 mL round-bottomed flask equipped with a stir bar was added 13 mL of CH₂Cl₂ and dimethyl sulfoxide (0.89 mL, 12.48 mmol), and the reaction mixture was cooled in a -78 °C. Oxalyl chloride (0.54 mL, 6.24 mmol) was added carefully, and the reaction stirred for 30 min at -78 °C, then crude S13 (940 mg) in CH₂Cl₂ (3 mL) was added, and the reaction mixture was stirred 30 min at -78 °C. Triethylamine (4.3 mL, 31.2 mmol) was added, and the reaction was allowed to warm to r.t. over 13 h. The reaction mixture was concentrated in vacuo and partitioned between EtOAc and 1 M HCl (aq). The layers were separated, and the aqueous layer was extracted with EtOAc (×1). The combined organic layers were washed with sat. NaHCO₃ (aq), water, brine, dried over MgSO₄, and concentrated in vacuo. This crude mixture was filtered through a short silica gel column (eluting with hexane/AcOEt = 20/1) to afford crude S14 (614.6 mg).

S14 to S15: To a suspension of MePPh₃Br (1.38 g, 3.86 mmol) in THF (8 mL) was added NaH in one portion (204 mg, 4.25 mmol) at 0 °C, and the resulting mixture was stirred at 60 °C for 1 h. Then, crude S14 (614.6 mg) in THF (2 mL) was added at 60 °C, and the mixture was stirred 1 h at 60 °C. A saturated ammonium chloride solution was added and the aqueous phase was extracted with AcOEt. The organic
phase was dried over Na$_2$SO$_4$, filtered and concentrated. The compound was purified by flash (10:1 Hex:EtOAc) to give crude S15 (497 mg)

S15 to S16: TBAF (4.7 mL, 1.0 M in THF, 4.7 mmol) was added to the solution of crude S15 (497 mg) in THF (15.7 mL) at 0 °C, and the solution was stirred at rt for 1 h. H$_2$O was added and the aqueous phase was extracted with AcOEt. The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated. The compound was purified by flash (150:1 Hex:EtOAc) to give crude S16 (220 mg)

S16 to 1j: To a solution of crude S16 (78.2 mg), 1H-imidazole (31.6 mg, 0.46 mmol), DMAP (2 blocks) in CH$_2$Cl$_2$ (1.9 mL) was added TBDPSCI (0.1 mL, 0.387 mmol) at 0 °C, and the mixture was stirred at rt for 1 h. sat. NH$_4$Cl aq. was added and the aqueous phase was extracted with CH$_2$Cl$_2$. The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated. The compound was purified by flash (75:1 Hex:EtOAc) to give 1j (147.1 mg, 21%, 5 steps)

$$\text{1H-NMR (CDCl}_3, 400 \text{MHz}} \delta: 1.03 (s, 9H), 1.66 (tt, J = 8.0, 6.4 \text{ Hz}), 2.47 \text{ (t, 2H, J = 8.0 Hz), 3.36 (d, 2H, J = 6.4 Hz), 3.66 (t, 2H, J = 6.4 Hz), 4.86 (d, 1H, J = 1.2 Hz), 4.96-5.04 (m, 2H), 5.16 (d, 1H, J = 1.2 Hz), 5.87-5.97 (m, 1H), 7.03-7.47 (m, 10H), 7.64 (dd, 4H, J = 8.0, 2.0 Hz);}$$

Synthesis of 1k,l

S17 to S18: To a stirred solution of MVK (10.1 mL, 123.1 mmol), Pd(OAc)$_2$ (500 mg, 2.23 mmol) in benzene (50 mL) was added S17 (5 mL, 47.3 mmol) in benzene (40 mL) at 40 °C using dropping funnel over 1 h. Then, Pd(OAc)$_2$ (500 mg, 2.23 mmol) was added and the solution of S18 (5 mL, 47.3 mmol) in benzene (40 mL) was added at 40 °C using dropping funnel over 1 h. The reaction mixture was stirred for 5 h at 40 °C, and the reaction was quenched with sat. Na$_2$CO$_3$, extracted with Et$_2$O, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO$_2$, n-hexane/AcOEt = 10/1) afforded S18 as a yellow oil (5.21 g, 35%).

S18 to S19: To a stirred solution of Ph$_3$PMeBr (5.5 g, 15.4 mmol) in THF (46 mL) was added t-BuOK
(1.73 g, 15.4 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. Then, S18 (1.0 g, 6.4 mmol) in THF (18 mL) was added at 0 °C, and the reaction mixture was stirred at rt for 1 h. The reaction was quenched with H₂O, extracted with Et₂O, dried over Na₂SO₄, filtered, and concentrated in vacuo at 0 °C. Purification by flash column chromatography (Et₂O : pentane = 1 : 4) afforded crude S19 (925 mg) as a colorless liquid.

S19 to S20: LiAlH₄ (456 mg, 12 mmol) was added to a solution of crude S19 (925 mg) in Et₂O (20 mL) at 0 °C under argon atmosphere. After addition, the mixture was warmed to rt, and the mixture was stirred for 16 h. Then, worked up by precipitation with 0.5 mL of water and 0.5 mL of 15% NaOH and 1.5 mL of water at 0 °C, and filtration through celite and washed thoroughly with Et₂O. The solvent was reduced under vacuum at 0 °C. Purification by flash column chromatography (Et₂O) afforded crude S20 (362 mg) as a yellow oil.

S20 to 1k,l: To a stirred solution of S20 (1.0 eq.), S21 (1.3 eq.), PPh₃ (2.0 eq.) in THF (0.1 M for S20) was added DMEAD (2.0 eq.) at 0 °C, and the reaction mixture was stirred for 2 h at rt. The reaction mixture was concentrated in vacuo. Purification by flash column chromatography (hexane/AcOEt = 20/1) gave 1k,l.

N-allyl-4-methyl-N-((2-(prop-1-en-2-yl)cyclopropyl)methyl)benzenesulfonamide (1k)

\[ ^1H-NMR \ (CDCl_3, 400 MHz) \delta: 0.47-0.52 \ (m, 1H), 0.68-0.72 \ (m, 1H), 0.97-1.05 \ (m, 1H), 1.56 \ (s, 3H), 2.42 \ (s, 3H), 2.99 \ (dd, 1H, J = 14.0, 7.2 Hz), 3.18 \ (dd, 1H, J = 14.0, 6.4 Hz), 3.84 \ (dd, 1H, J = 15.6, 6.4 Hz), 3.93 \ (dd, 1H, J = 15.6, 6.4 Hz), 4.62 \ (s, 1H), 4.65 \ (s, 1H), 5.13 \ (d, 1H, J=11.6 Hz), 5.20 \ (d, 1H, J = 16.8 Hz), 5.60-5.70 \ (m, 1H), 7.28 \ (d, 2H, J = 8.4 Hz), 7.69 \ (d, 2H, J = 8.4 Hz); ^13C-NMR \ (CDCl_3, 100 MHz) \delta: 11.0, 17.2, 20.7, 21.3, 24.6, 49.8, 50.6, 108.7, 118.3, 126.9, 129.5, 133.2, 137.3, 142.9, 144.5; IR (ATR) v: 2921, 1735, 1338, 1153, 1090, 658 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₂₃NNaO₂S, [M+Na]⁺ 328.1347, found 328.1342; yellow oil (241.3 mg, 52%).

4-methyl-N-(2-methylallyl)-N-((2-(prop-1-en-2-yl)cyclopropyl)methyl)benzenesulfonamide (1l)

\[ ^1H-NMR \ (CDCl_3, 400 MHz) \delta: 0.43 \ (br, 1H), 0.63 \ (br, 1H), 0.98 \ (br, 1H), 1.18 \ (br, 1H), 1.50 \ (s, 3H), 1.71 \ (s, 3H), 2.40 \ (s, 3H), 2.90-2.96 \ (m, 1H), 3.15-3.19 \ (m, 2H), 3.68-3.86 \ (m, 3H), 4.57 \ (d, 1H, J = 6.4 Hz), 4.63 \ (d, 1H, J = 6.4 Hz), 4.89 \ (s, 2H), 7.28 \ (d, 2H, J = 8.0 Hz), 7.72 \ (d, 2H, J = 8.0 Hz); ^13C-NMR \ (CDCl_3, 100 MHz) \delta:11.1, 16.8, 19.8, 19.9, 21.4, 24.8, 51.1, 53.7, 108.7, 114.0, 127.0, 129.5, 137.3, 140.7, 143.0, 144.7; IR (ATR) v: 2981, 1735, 1337, 1239, 1156 cm⁻¹; HRMS (ESI) Calcd for C₁₈H₂₅NNaO₂S, [M+Na]⁺ 342.1504, found 342.1515; yellow oil (301.6 mg, 69%).
2-4-methyl-1-phenylpyrrolidin-3-yl)acetonitrile (2a)

\[ \text{diethyl (35.2 mg, 68%)} \]

1H-NMR (CDCl3, 400 MHz) \( \delta \): 1.05 (dd, 2.1H, \( J = 6.8, 1.6 \) Hz), 1.16 (d, 0.9H, \( J = 4.4 \) Hz), 2.10-2.72 (m, 4H), 2.97 (dd, 0.3H, \( J = 7.6, 7.6 \) Hz), 3.05 (dd, 0.7H, \( J = 7.2, 7.2 \) Hz), 3.17 (dd, 0.3H, \( J = 7.2, 7.2 \) Hz), 3.25 (dd, 0.7H, \( J = 8.4, 5.6 \) Hz), 3.49 (ddd, 1.4H, \( J = 14.4, 7.2, 7.2 \) Hz), 3.58 (ddd, 0.6H, \( J = 14.4, 7.2, 7.2 \) Hz), 6.52 (d, 2H, \( J = 7.6 \) Hz), 6.69 (dd, 1H, \( J = 7.6, 7.6 \) Hz), 7.23 (dd, 2H, \( J = 7.6, 7.6 \) Hz); 13C-NMR (CDCl3, 100 MHz) \( \delta \): 13.6, (16.8), 17.0, (19.6), 34.9, (38.0), 38.8, (41.8), 51.5, (52.4), 53.7, (54.7), 111.4, 116.0, 118.9, 129.2, 147.2; IR (ATR) \( \nu \): 2974, 1736, 1345 cm\(^{-1} \); HRMS (ESI) Calcd for \( \text{C}_{13}\text{H}_{16}\text{Na}_{2} \text{Na}^+ \) \( 223.1211 \), found \( 223.1203 \); yellow oil (28.9 mg, 47%); (*) in 13C NMR is peak of \( \text{trans-2a} \)

2-4-methyl-1-tosylpyrrolidin-3-yl)acetonitrile (2b)

\[ \text{diethyl (60.3 mg, 82%)} \]

1H-NMR (CDCl3, 400 MHz) \( \delta \): 0.87 (d, 2.1H, \( J = 6.4 \) Hz), 0.98 (d, 0.9H, \( J = 6.4 \) Hz), 1.86-2.48 (m, 7H), 2.85 (dd, 0.3H, \( J = 10.4, 8.0 \) Hz), 3.00 (dd, 0.7H, \( J = 10.4, 5.6 \) Hz), 3.06 (dd, 0.3H, \( J = 10.4, 8.0 \) Hz), 3.20 (dd, 0.7H, \( J = 10.4, 5.6 \) Hz), 3.41-3.58 (m, 2H), 7.34 (d, 2H, \( J = 8.4 \) Hz), 7.72 (d, 2H, \( J = 8.4 \) Hz); 13C-NMR (CDCl3, 100 MHz) \( \delta \): 12.8, (16.2), 16.4, (19.1), 21.5, 35.1, (38.1), 38.7, (41.7), 51.2, (52.0), 53.4, (54.3), 118.1, 127.4, 129.8, 133.4, 143.8; IR (ATR) \( \nu \): 2970, 1711, 1360, 1219 cm\(^{-1} \); HRMS (ESI) Calcd for \( \text{C}_{14}\text{H}_{18}\text{Na}_{2}\text{O}_{2} \) \( 290.1368 \), found \( 290.1372 \); yellow oil (35.2 mg, 68%); (*) in 13C NMR is peak of \( \text{trans-2b} \)

diethyl-3-(cyanomethyl)-4-methylcyclopentane-1,1-dicarboxylate (2c)

1H-NMR (CDCl3, 400 MHz) \( \delta \): 0.94 (dd, 3H, \( J = 7.2, 2.4 \) Hz), 1.25 (t, 6H, \( J = 7.2 \) Hz), 1.99 (ddd, 1H, \( J = 14.0, 7.2, 2.0 \) Hz), 2.16 (ddd, 1H, \( J = 14.0, 7.2, 2.0 \) Hz), 2.25-2.66 (m, 6H), 4.19 (q, 4H, \( J = 7.2 \) Hz); 13C-NMR (CDCl3, 100 MHz) \( \delta \): 13.9, 14.5, 17.9, 35.7, 38.3, 39.3, 40.5, 58.6, 61.6, 119.172, 1, 172.2; IR (ATR) \( \nu \): 2984, 1711, 1360, 1219 cm\(^{-1} \); HRMS (ESI) Calcd for \( \text{C}_{14}\text{H}_{21}\text{NaNO}_{4} \) \( 290.1368 \), found \( 290.1372 \); colorless oil (60.3 mg, 82%)

diethyl-3-(2-cyanopropan-2-yl)-4-methylcyclopentane-1,1-dicarboxylate (2d)

1H-NMR (CDCl3, 400 MHz) \( \delta \): 1.06 (d, 3H, \( J = 6.8 \) Hz), 1.24 (t, 3H, \( J = 7.6 \) Hz), 1.26 (t, 3H, \( J = 7.2 \) Hz), 1.41 (d, 6H, \( J = 4.8 \) Hz), 1.86 (ddd, 1H, \( J = 13.6, 6.8, 6.8 \) Hz), 2.24-2.41 (m, 4H), 2.49 (dd, 1H, \( J = 13.6, 6.8 \) Hz), 4.14-4.26 (m, 4H); 13C-NMR (CDCl3, 100 MHz) \( \delta \): 14.0, 15.3, 25.7, 28.6, 32.7, 34.0, 35.1, 41.4, 51.8, 57.7, 61.6, 124.2, 172.0, 172.9; IR (ATR) \( \nu \): 2980, 1728, 1253 cm\(^{-1} \);
HRMS (ESI) Calcd for C_{16}H_{25}NaO_{4} [M+Na]^+ 318.1681, found 318.1684; colorless oil (22.6 mg, 62%).

diethyl-4-(cyanomethyl)-3,3-dimethycyclopentane-1,1-dicarboxylate (2e)

1H-NMR (CDCl3, 400 MHz) δ: 0.85 (d, 3H, J = 2.0 Hz), 1.10 (d, 3H, J = 2.0 Hz), 1.25 (t, 3H, J = 7.2 Hz), 1.26 (t, 3H, J = 7.2 Hz), 1.90-2.08 (m, 1H), 2.12-2.29 (m, 4H), 2.34 (dddd, 1H, J = 16.4, 5.6, 2.0 Hz), 2.60 (dddd, 1H, J = 13.6, 6.8, 2.0 Hz), 4.18 (q, 2H, J = 7.2 Hz), 4.19 (q, 2H, J = 7.2 Hz); 13C-NMR (CDCl3, 100 MHz) δ: 13.9, 17.1, 21.9, 27.7, 38.7, 41.1, 45.3, 48.4, 57.0, 61.6, 61.7, 119.0, 172.1, 172.4; IR (ATR) ν: 2981, 1716, 1239 cm⁻¹; HRMS (ESI) Calcd for C_{15}H_{23}NaO_{4}, [M+Na]^+ 304.1525, found 304.1520; colorless oil (24.4 mg, 72%).

2-(2,4,4-trimethyl-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)acetonitrile (2f)

1H-NMR (CDCl3, 400 MHz) δ: 1.01 (s, 3H), 1.06 (s, 3H), 1.60-1.72 (m, 1H), 2.06 (dd, 1H, J = 16.8, 10.0 Hz), 2.35 (dd, 1H, J = 16.8, 4.8 Hz), 2.39 (s, 3H), 3.45 (dd, 1H, J = 14.0, 10.4 Hz), 4.22 (dd, 1H, J = 14.0, 3.6 Hz), 7.13-7.26 (m, 5H), 7.53 (d, 2H, J = 8.8 Hz), 7.83 (d, 1H, J = 8.4 Hz); 13C-NMR (CDCl3, 100 MHz) δ: 16.8, 21.5, 25.4, 28.6, 35.8, 39.1, 46.2, 118.3, 124.1, 125.3, 126.8, 127.1, 127.2, 129.8, 134.8, 136.2, 136.5, 144.1; IR (ATR) ν: 3000, 1709, 1357, 1219 cm⁻¹; HRMS (ESI) Calcd for C_{20}H_{22}N_{2}NaO_{2}S, [M+Na]^+ 377.1300, found 377.1297; yellow solid (31.1 mg, 71%).

2-(4,4-dimethyl-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)propanenitrile (2g)

1H-NMR (CDCl3, 400 MHz) δ: 0.05 (t, 2.3H, J = 8.0 Hz), 0.60 (t, 3H, J = 7.6 Hz), 0.98 (s, 3H), 1.03 (s, 2.3H), 1.20-1.39 (m, 2+1.5H), 1.53-1.67 (m, 2+1.5H), 2.36 (s, 2.3H), 2.38 (s, 3H), 3.43 (dd, 0.8H, J = 14.0, 9.6 Hz), 3.65 (dd, 1H, J = 14.0, 9.6 Hz), 4.09 (dd, 1H, J = 13.6, 4.4 Hz), 4.34 (dd, 0.8H, J = 14.0, 3.2 Hz), 7.10-7.24 (m, 5+3.8H), 7.54 (d, 2H, J = 8.0 Hz), 7.59 (d, 1.5H, J = 8.4 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.94

2-((4S)-4-ethyl-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)acetonitrile (2h)

1H-NMR (CDCl3, 400 MHz) δ: 0.05 (t, 2.3H, J = 8.0 Hz), 0.60 (t, 3H, J = 7.6 Hz), 0.98 (s, 3H), 1.03 (s, 2.3H), 1.20-1.39 (m, 2+1.5H), 1.53-1.67 (m, 2+1.5H), 2.36 (s, 2.3H), 2.38 (s, 3H), 3.43 (dd, 0.8H, J = 14.0, 9.6 Hz), 3.65 (dd, 1H, J = 14.0, 9.6 Hz), 4.09 (dd, 1H, J = 13.6, 4.4 Hz), 4.34 (dd, 0.8H, J = 14.0, 3.2 Hz), 7.10-7.24 (m, 5+3.8H), 7.54 (d, 2H, J = 8.0 Hz), 7.59 (d, 1.5H, J = 8.4 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.94
(d, 0.8H, J = 8.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ: 7.6, 9.1, 16.4, 16.6, 21.5, 25.5, 25.8, 28.8, 31.0, 33.8, 38.3, 39.1, 39.7, 45.9, 46.9, 118.4, 123.7, 124.5, 124.7, 125.4, 126.4, 126.8, 127.0, 127.1, 127.4, 129.7, 129.9, 135.3, 136.2, 144.0; IR (ATR) v: 2682, 1721, 1366, 1238 cm⁻¹; HRMS (ESI) Caled for C₂₁H₂₄N₂O₂S⁺ 391.1456, found 391.1469; yellow oil (11.4 mg, 58%).

3,3-dimethyl-1-tosyloctahydro-1H-indene-4-carbonitrile (2i)

¹H-NMR (CDCl₃, 400 MHz) δ: 0.62 (s, 3H), 1.15 (s, 3H), 1.56-1.68 (m, 4H), 1.76 (dd, 1H, J = 9.6, 6.0 Hz), 2.05-2.14 (m, 1H), 2.44 (s, 3H), 2.41-2.48 (m, 2H), 3.06 (dd, 1H, J = 10.8 Hz), 3.27 (d, 1H, J = 10.8 Hz), 3.61 (bbrs, 1H), 7.33 (d, 2H, J = 7.6 Hz), 7.68 (d, 2H, J = 7.6 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ: 18.2, 21.5, 23.0, 26.6, 27.1, 27.9, 28.8, 39.6, 49.6, 57.8, 60.2, 122.8, 127.5, 129.7, 133.1, 143.8; IR (ATR) v: 2938, 1337, 1159, 669 cm⁻¹; HRMS (ESI) Caled for C₁₈H₂₄N₂O₂S⁺ 355.1456, found 355.1450; colorless solid (30.7 mg, 70%, mp: 115-118 °C).

2-(1-(3-((tetr-butylidiphenyloxy)propyl)-1-methyl-2,3-dihydro-1H-inden-2-yl)acetonitrile (2j)

To the solution of 1j (74.3 mg, 0.169 mmol), TscN (36.7 mg, 0.203 mmol), Co (2.0 mg, 0.034 mmol) in EtOH (0.85 mL), PhSiH₂ (25 ul, 0.203 mmol) was added at rt, and the solution was stirred for 16 h at rt. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to give cis-2j (43.2 mg, 55%), and trans-2j (20.1 mg, 25%).

¹H-NMR (CDCl₃, 400 MHz) δ: 1.00 (s, 9H), 1.32 (s, 3H), 1.24-1.45 (m, 4H), 2.33 (dd, 1H, J = 15.6, 8.8 Hz), 2.44 (dddd, 1H, J = 9.6, 8.8, 7.2, 5.2 Hz), 2.50 (dd, 1H, J = 15.6, 5.2 Hz), 2.71 (dd, 1H, J = 15.2, 9.6 Hz), 3.11 (dd, 1H, J = 15.2, 7.2 Hz), 3.56 (dd, 2H, J = 10.4, 5.6 Hz), 7.07 (dd, 1H, J = 8.8, 3.2 Hz), 7.17-7.21 (m, 3H), 7.34-7.44 (m, 6H), 7.58 (d, 4H, J = 7.6 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ: 17.2, 19.1, 24.5, 26.8, 27.5, 31.3, 36.4, 47.9, 48.0, 64.0, 119.5, 123.5, 124.6, 126.4, 126.8, 127.6, 129.6, 133.8, 135.5, 140.1, 149.2; IR (ATR) v: 2930, 2857, 1736, 1427, 1241, 1105, 755, 700 cm⁻¹; HRMS (ESI) Caled for C₃₁H₃₇NaaS₂O₅⁺ [M+N+Na]⁺ 490.2542, found 490.2529; yellow oil.

2-methyl-2-2-tosyloctacycloheptapenta[c]pyrrol-5-yl)propanenitrile (2k)

¹H-NMR (CDCl₃, 400 MHz) δ: 1.21-1.27 (m, 2H), 1.30 (s, 6H), 1.79-1.88 (m, 1H), 1.98-2.08 (m, 2H), 2.44 (s, 3H), 2.54-2.63 (m, 2H), 3.02 (dd, 2H, J = 9.6, 6.8 Hz), 3.09 (dd, 1H, J = 9.6, 1.6 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 8.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ: 21.5, 25.6, 34.5, 35.0, 41.9, 50.5, 53.5, 123.9, 128.0, 129.6, 134.6, 143.6; IR (ATR) v: 2963, 1736, 1240, 1163, 1045, 664 cm⁻¹; HRMS (ESI) Caled for C₁₈H₂₄N₂O₂S⁺ [M+N+Na]⁺ 355.1456, found 355.1451; colorless solid (18.4 mg, 38%, mp: 155-158 °C).

2-methyl-2-3a-methyl-2-tosyloctacycloheptapenta[c]pyrrol-5-yl)propanenitrile (2l)

¹H-NMR (CDCl₃, 400 MHz) δ: 1.05 (s, 3H), 1.21-1.31 (m, 2H), 1.29 (s, 6H), 1.54 (dd, 1H, J = 12.6, 12.6 Hz), 1.67 (dd, 1H, J = 12.6, 7.2 Hz), 1.90-1.99 (m, 1H), 2.01-2.10 (m, 2H), 2.44 (s, 3H), 2.71 (d, 1H, J = 9.0 Hz), 3.10 (d, 2H, J =
4.8 Hz), 3.20 (d, 1H, \( J = 9.0 \) Hz), 7.33 (d, 2H, \( J = 8.4 \) Hz), 7.70 (d, 2H, \( J = 8.4 \) Hz); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta: 21.6, 25.5, 25.6, 26.1, 35.2, 41.2, 48.8, 49.1, 49.2, 53.4, 60.1, 124.0, 128.0, 129.6, 132.6, 143.6; IR (ATR) v: 2969, 1736, 1344, 1158, 664 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{19}\)H\(_{26}\)N\(_2\)NaO\(_2\)S, [M+Na]\(^+\) 369.1613, found 369.1607; colorless solid (16.9 mg, 31%, 124-127 °C)

Synthesis of 3c

Cis-2j to S22: TBAF (1.23 mL, 1.0 M in THF, 1.23 mmol) was added to the solution of cis-2j (191.9 mg) in THF (2.1 mL) at 0 °C, and the solution was stirred at rt for 1 h. H\(_2\)O was added and the aqueous phase was extracted with AcOEt. The organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated. The compound was purified by flash (10:1 Hex:EtOAc) to give crude S22 (79.8 mg)

S22 to 3b: To a solution of crude S22 (79.8 mg) in CH\(_2\)Cl\(_2\) (1.7 mL) was added CBr\(_4\) (23.1 mg, 0.07 mmol) and PPh\(_3\) (18.4 mg, 0.07 mmol) at 0 °C, and the solution was stirred at rt for 1 h. The solution was directly pored to flash column chromatography to give 3b (95.3 mg, 80%, 2 steps)

2-(1-(3-bromopropyl)-1-methyl-2,3-dihydro-1H-inden-2-yl)acetonitrile (3b)

3b to S23: Preparation of LDA: n-BuLi (0.92 mL, 1.43 mmol) was added to a solution of iPr\(_2\)NH (0.2 mL, 1.43 mmol) in THF (6.02 mL) at -78 °C, and the solution was stirred at 0 °C for 1 h. Resulting LDA was added to the solution of 3b (26.4 mg, 0.09 mmol) in THF (3 mL) at -78 °C, and the solution was slowly warmed to rt, and stirred for 2 h. Then, sat. NH\(_4\)Cl aq. was added and the aqueous phase was extracted with AcOEt. The organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated. The compound was purified by flash (20:1 Hex:EtOAc) to give crude S23 (16.9 mg)

S23 to 3c: LDA (prepared by the same scale for the synthesis of S23) was added to the solution of crude S23 (16.9 mg) in THF (0.82 mL) at -78 °C, and stirred for 1 h at the same temperature. Then, MeI (50 \( \mu \)L, 0.803 mmol) was added to the solution at -78 °C, and the solution was slowly warmed to rt, stirred for 6 h. Then, sat. NH\(_4\)Cl aq. was added and the aqueous phase was extracted with AcOEt. The organic phase was
dried over Na₂SO₄, filtered and concentrated. The compound was purified by flash (20:1 Hex:EtOAc) to give 3c (15.2 mg) as a single diastereomer.

1,4a-dimethyl-2,3,4,4a,9,9a-hexahydro-1H-fluorene-1-carbonitrile (3c)

δ H-NMR (CDCl₃, 600 MHz) δ: 1.10-1.29 (m, 3H), 1.39 (s, 3H), 1.43-1.62 (m, 2H), 1.56 (s, 3H), 1.77-1.84 (m, 1H), 2.33-2.36 (m, 1H), 2.64-2.69 (m, 1H), 2.72-2.77 (m, 1H), 7.02-7.19 (m, 4H); ¹³C-NMR (CDCl₃, 150 MHz) δ: 19.8, 23.2, 26.5, 31.7, 32.3, 33.8, 35.5, 45.2, 53.0, 121.5, 124.7, 126.2, 126.5, 126.8, 138.6, 153.0; IR (ATR) ν: 2980, 1755, 1234 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₉NNa [M+Na]⁺ 248.1452, found 248.1414; yellow oil

Optimization of Catalyst

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General procedure for hydroacylation: EtOH (0.2 M for alkenylacylphosphonate) was added to the mixture of alkenylacylphosphonate 4 (1.0 eq.), Co A (5 mol%) under an argon atmosphere at rt, then PhSiH₃ (1.5 eq.) was added at rt and the solution was stirred at rt. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography.

General procedure for the synthesis of acylphosphonate 4

![Chemical equation and diagram]
S24 to S25: To a solution of S24 (1.0 eq.) in EtOH (1.0 M for S24) was added H2O (1.0 M for S24) and NaOH (6.0 eq.) at rt, and the reaction mixture was stirred at 80 ºC for 1 h. The reaction was quenched with 1 N HCl (pH = 1), extracted with CH2Cl2, dried over Na2SO4, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded S25. (*Caution!!: Purification of S25 is necessary even if crude S25 is seems to be pure.)

S27 to S25: To a solution of S27 (1.0 eq.) in CH2Cl2 (0.4 M for S27) was added TFA (10 eq.) at 0 ºC, and the reaction mixture was evaporated under reduced pressure and diluted with CH2Cl2 and 1 N HCl. The organic layer was separated and the mixture was further extracted with CH2Cl2. The combined organic extract was then dried over anhydrous sodium sulfate, concentrated under reduced pressure. Purification by flash column chromatography afforded S25. (*Caution!!: Purification of S25 is necessary even if crude S25 seems to be pure.)

S25 to S26: To a solution of S25 (1.0 eq.) in CH2Cl2 (1.0 M for S25), (COCl)2 (2.0 eq.) followed by DMF (3 drops) was added at 0 ºC, and the reaction mixture was stirred at 0 ºC for 15 min. and then, the reaction mixture was allowed to warm to rt. After 2 h, the reaction mixture was evaporated under reduced pressure gave crude S26, and the resulting volatiles were removed under reduced pressure (at 50 ºC, 1 h) to give S26 which was used in the next step without further purification. (*Caution!!: Careful removal of volatiles under heating condition is necessary even if crude S26 seems to be pure.)

S26 to 4: P(OEt)3 (1.0 eq.) was added to the solution of S26 (1.0 eq.) in CH2Cl2 (1.0 M) at 0 ºC, and stirred for 1 h at the same temperature. Then, the reaction mixture was allowed to warm to rt, and stirred for overnight. Any volatiles were removed under reduced pressure and the crude 4 was purified by column chromatography. (*Caution!!: Excess addition of triethylphosphite gave complex mixture. // Even if TLC indicates the generation of 4 only in a few hours, stirring for overnight is necessary.)

Synthesis of 4a-c

S28 to S29: To a stirred solution of S28 (1.0 eq.) in MeCN (0.2 M for S28) was added K2CO3 (4.0 eq.), and allyl bromide (4.0 eq.), and the reaction mixture was stirred at 80 ºC for 17 h. The reaction was quenched with H2O, extracted with AcOEt, dried over Na2SO4, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded S29 (quant.).

S29 to 4a-c: Same as general procedure (S24 to 4)

diethyl (2-(allyloxy)benzoyl)phosphonate (4a)
diethyl (2-(allyloxy))-5-bromobenzoyl)phosphonate (4b)

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 1.36 (t, 6H, \(J = 7.2\) Hz), 4.63 (d, 2H, \(J = 5.6\) Hz), 5.20 (d, 1H, \(J = 10.0\) Hz), 5.31 (dd, 1H, \(J = 17.2, 1.2\) Hz), 6.09-6.21 (m, 1H), 7.10-7.17 (m, 2H), 7.48 (dd, 1H, \(J = 7.2, 2.4\) Hz); \(^1\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 16.2, 16.2, 55.9, 63.7, 63.8, 75.0, 117.0, 118.0, 121.4, 123.8, 131.9, 132.5, 133.8, 147.2, 152.9, 152.9, 200.2, 202.0; IR (ATR) \(\nu\): 2982, 1724, 1474, 1016 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{15}\)H\(_{21}\)BrNaO\(_5\)P, [M+Na]\(^+\) 351.0973, found 351.0963; yellow oil (492 mg, 45%).

diethyl (2-(allyloxy))-3-methoxybenzoyl)phosphonate (4c)

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 1.34 (t, 6H, \(J = 7.2\) Hz), 3.89 (s, 3H), 4.25 (q, 4H, \(J = 7.2\) Hz), 4.63 (d, 2H, \(J = 5.6\) Hz), 5.20 (d, 1H, \(J = 10.0\) Hz), 5.31 (dd, 1H, \(J = 17.2, 1.2\) Hz), 6.09-6.21 (m, 1H), 7.10-7.17 (m, 2H), 7.48 (dd, 1H, \(J = 7.2, 2.4\) Hz); \(^1\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 16.2, 16.2, 55.9, 63.7, 63.8, 75.0, 117.0, 118.0, 121.4, 123.8, 131.9, 132.5, 133.8, 147.2, 152.9, 152.9, 200.2, 202.0; IR (ATR) \(\nu\): 2982, 1724, 1474, 1016 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{15}\)H\(_{21}\)NaO\(_5\)P, [M+Na]\(^+\) 351.0973, found 351.0963; yellow oil (492 mg, 45%).

**Synthesis of 4d-f**

\[
\begin{array}{c}
\text{S30} \quad \text{Br} \quad \text{MeH} \quad \text{NaH} \quad \text{DMF} (0.5 \text{M}) \quad \text{rt, 16 h, quant} \\
\end{array}
\]

**S30 to S31**: To a solution of S30 (1.0 eq.) in DMF (0.5 M for S30) was added 60% sodium hydride (2.0 eq.) at 0 °C and the mixture was stirred at room temperature for 30 minutes. Allyl bromide (2.0 eq.) was then added and the mixture was stirred for 16 h. Water was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding S31 (quant.).

**S31 to 4d-f**: Same as general procedure (S24 to 4)

diethyl (2-((N-allyl-4-methylphenyl)sulfonamido)benzoyl)phosphonate (4d)

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 1.36 (m, 6H), 2.42 (s, 3H), 4.27 (m, 6H), 5.02 (m, 2H), 5.94 (m, 1H), 6.86 (m, 1H), 7.23 (d, 2H, \(J = 8.4\) Hz), 7.44 (m, 4H), 8.27 (m, 2H).
diethyl (2-((N-allyl-4-methoxyphenyl)sulfonamido)benzoyl)phosphonate (4e)

\[ \text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.37 \text{ (t, 6H, } J = 6.8 \text{ Hz), 3.86 \text{ (s, 3H), 4.21-4.32 (m, 6H), 5.02 \text{ (d, 1H, } J = 16.0 \text{ Hz), 5.03 \text{ (d, 1H, } J = 10.8 \text{ Hz), 5.90-6.00 (m, 1H), 6.86-6.91 \text{ (m, 3H), 7.41-7.47 (m, 2H), 7.51 \text{ (d, 2H, } J = 8.8 \text{ Hz), 8.24-8.27 (m, 1H)), 13C-NMR (CDCl}_3, 100 MHz) \delta: 16.0, 16.1, 54.3, 55.3, 63.9, 113.7, 118.8, 127.8, 129.5, 130.0, 130.2, 131.0, 132.5, 132.8, 136.8, 136.9, 137.0, 137.6, 137.7, 162.7, 199.2, 201.0; IR (ATR) } v: 2969, 1733, 1594, 1158, 1019 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for } C_{21}H_{26}NO_7P_5S_2, [M+Na]^+ 490.1065, \text{found 490.1053; yellow oil (610.6 mg, 42%).} \]

diethyl (2-((N-allyl-4-fluorophenyl)sulfonamido)benzoyl)phosphonate (4f)

\[ \text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.37 \text{ (t, 6H, } J = 6.8 \text{ Hz), 4.26 \text{ (brs, 6H), 5.03 \text{ (d, 1H, } J = 18.4 \text{ Hz), 5.05 \text{ (d, 1H, } J = 9.2 \text{ Hz), 5.88-5.98 (m, 1H), 6.94-6.96 (m, 1H), 7.12 \text{ (dd, 2H, } J = 8.4, 8.4 \text{ Hz), 7.45-7.50 (m, 2H), 7.60-7.63 (m, 2H), 8.30-8.32 \text{ (m, 1H); 13C-NMR (CDCl}_3, 100 MHz) \delta: 16.0, 16.1, 54.5, 64.0, 115.7, 115.9, 119.1, 128.2, 130.0, 130.1, 130.8, 131.5, 132.5, 132.8, 134.8, 134.8, 136.4, 136.4, 137.0, 163.5, 166.1, 198.8, 200.6; IR (ATR) } v: 2984, 1719, 1492, 1154, 839 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for } C_{20}H_{23}FNO_6P_5S_2, [M+Na]^+ 478.0865, \text{found 478.0861; yellow oil (588 mg, 40%).} \]

Synthesis of 4g

S32 to S33: To a stirred solution of S32 (1.0 eq.) in CHCl3 (0.4 M for S32) at 0 °C was added DIBAL (2.5 eq., 1.0 M in toluene) dropwise. The mixture was stirred at 0 °C to rt for 2 h then treated with ice cold Rochelles salt (saturated Na/K tartrate) and allowed to stir at 0 °C open to air. The reaction became a gray-white gelatinous suspension that solubilized over the course of 30 min to 1 h with stirring at room temperature open to air. The mixture was poured into diethyl ether and H2O. The layers were separated, and the aqueous layer was extracted twice more with diethyl ether. The organic layers were combined, dried over Na2SO4, and concentrated to afford a crude S33 which was used without further purification.

S33 to S35: To a stirred solution of S33 (1.5 eq.), S34 (1.0 eq.), PPh3 (2.0 eq.) in THF (0.1 M for S34) was added DMEAD (2.0 eq.) at 0 °C, and the reaction mixture was stirred for 2 h at rt. Then, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography gave S35.

S35 to 4g: Same as general procedure (S24 to 4)
diethyl (2-((N-(cyclopent-1-en-1-ylmethyl)-4-methylphenyl)sulfonamido)benzoyl)phosphonate (4g)

\[
\begin{align*}
\text{1H-NMR (CDCl}_3, 400 \text{ MHz} \delta:} & \, 1.36 \, (t, \, 6H, \, J = 7.2 \, Hz), \, 1.75 \, (dt, \, 2H, \, J = 15.2, \, 7.2 \, Hz), \, 2.11-2.24 \, (m, \, 4H), \, 2.41 \, (s, \, 3H), \, 4.23-4.31 \, (m, \, 6H), \, 5.42 \, (s, \, 1H), \, 6.95-6.98 \, (m, \, 1H), \, 7.21 \, (d, \, 2H, \, J = 8.0 \, Hz), \, 7.42-7.48 \, (m, \, 4H), \, 8.36 \, (s, \, 1H); \, ^{13}\text{C-NMR (CDCl}_3, 100 \text{ MHz} \delta:} & \, 16.3, \, 21.5, \, 23.4, \, 32.2, \, 33.6, \, 51.5, \, 64.2, \, 127.6, \, 127.7, \, 129.2, \, 130.4, \, 131.7, \, 132.7, \, 135.9, \, 136.5, \, 136.9, \, 138.8, \, 143.2, \, 198.3, \, 200.2; \, \text{IR (ATR) \nu:} & \, 2982, \, 1670, \, 1159, \, 1018, \, 750 \text{ cm}^{-1}; \, \text{HRMS (ESI) Calcd for C}_{24}H_{30}N_NaO_6PS, [M+Na]^+ 514.1429, \, \text{found 514.1430; yellow oil (301.5 mg, 65%).}\n\end{align*}
\]

**Synthesis of 4h,i,l**

S36 to S37: To a solution of S36 (1.0 eq.) in THF (0.4 M for S36) was added 60% sodium hydride (1.2 eq.) at 0 °C and the mixture was stirred at room temperature for 30 minutes. tert-Butyl Bromoacetate (1.2 eq.) was then added and the mixture was stirred for 16 h. Water was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding S37.

S37 to 4: Same as general procedure (S24 to 4)

diethyl 2-allyl-2-(2-(diethoxyphosphoryl)-2-oxoethyl)malonate (4h)

\[
\begin{align*}
\text{(CAS-Reg# 593254-57-0)} \quad \text{1H-NMR (CDCl}_3, 400 \text{ MHz} \delta:} & \, 1.25 \, (t, \, 6H, \, J = 7.2 \, Hz), \, 1.37 \, (t, \, 6H, \, J = 7.2 \, Hz), \, 2.76 \, (d, \, 2H, \, J = 7.6 \, Hz), \, 3.50 \, (d, \, 2H, \, J = 2.8 \, Hz), \, 4.21 \, (m, \, 8H), \, 5.10 \, (m, \, 2H), \, 5.66 \, (m, \, 1H); \, (1.60 \, g, \, 84\%)
\end{align*}
\]

diethyl 2-(2-((diethylperoxy)(oxo)-14-phosphanyl)-2-oxoethyl)-2-(2-methylallyl)malonate (4i)

\[
\begin{align*}
\text{1H-NMR (CDCl}_3, 400 \text{ MHz} \delta:} & \, 1.25 \, (t, \, 6H, \, J = 7.2 \, Hz), \, 1.37 \, (t, \, 6H, \, J = 1.62 \, (s, \, 2.4H), \, 1.65 \, (s, \, 6H, s 0.6H), \, 2.84 \, (s, \, 1.6H), \, 2.88 \, (s, \, 0.4H), \, 3.05 \, (s, \, 0.6H), \, 3.55 \, (s, \, 1.6H), \, 4.14-4.24 \, (m, \, 8H), \, 4.65 \, (s, \, 0.8H), \, 4.74 \, (s, \, 0.2H), \, 4.87 \, (s, \, 0.8H), \, 4.90 \, (s, \, 0.2H); \, ^{13}\text{C-NMR (CDCl}_3, 100 \text{ MHz} \delta:} & \, 13.7, \, 16.1, \, 16.2, \, 22.7, \, 40.5, \, 44.8, \, 45.4, \, 54.1, \, 54.2, \, 61.7, \, 63.8, \, 63.9, \, 116.4, \, 140.3, \, 169.8, \, 170.2, \, 207.1, \, 208.8; \, \text{IR (ATR) \nu:} & \, 2982, \, 1731, \, 1183, \, 1019 \text{ cm}^{-1}; \, \text{HRMS (ESI) Calcd for C}_{17}H_{29}NO_8P, [M+Na]^+ 415.1498, \, \text{found 415.1493; yellow oil (357 mg, 25%).}\n\end{align*}
\]

diethyl 2-(but-3-en-1-yl)-2-(2-(diethoxyphosphoryl)-2-oxoethyl)malonate (4l)

\[
\begin{align*}
\text{1H-NMR (CDCl}_3, 400 \text{ MHz} \delta:} & \, 1.25 \, (t, \, 6H, \, J = 6.8 \, Hz), \, 1.38 \, (t, \, 6H, \, J = 7.2 \, Hz), \, 1.92-2.15 \, (m, \, 4H), \, 3.52 \, (s, \, 2H), \, 4.14-4.27 \, (m, \, 8H), \, 4.96 \, (d, \, 1H, \, J = 10.0 \, Hz), \, 5.00 \, (d, \, 1H, \, J = 17.2 \, Hz), \, 5.68-5.81 \, (m, \, 1H); \, ^{13}\text{C-NMR (CDCl}_3, 100 \text{ MHz} \delta:} & \, 13.4, \, 15.8, \, ...
\end{align*}
\]
28.5, 32.1, 44.8, 54.3, 61.2, 63.5, 114.9, 136.5, 169.4, 206.5, 208.2; IR (ATR) ν: 2983, 1731, 1184, 1012 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₂₉NaO₈P, [M+Na]⁺ 415.1498, found 415.1508; colorless oil (794.5 mg, 51%).

Synthesis of 4j

S₃₈ to S₃₉: To a solution of S₃₈ (549 mg, 2.56 mmol) in THF (6.4 mL) was added 60% sodium hydride (123 mg, 3.07 mmol) at 0 °C and the mixture was stirred at room temperature for 30 minutes. Benzyl bromide (0.36 mL, 3.07 mmol) was then added and the mixture was stirred for 3 h. Water was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding S₃₉ (779 mg, quant.).

S₃₉ to S₄₀: To a stirred solution of S₃₉ (779 mg, 2.56 mmol) in EtOH (8.5 mL) at rt, KOH (143 mg, 2.56 mmol) was added. After 15 h, the mixture was acidified with 1 N HCl and filtered. The filter cake (KCl) was washed with EtOH. The combined filtrate was concentrated and residual liquid was subjected to column chromatography to afford S₄₀ (186 mg, 26%) and unreacted S₃₉ (481 mg, 59%).

S₄₀ to 4j: Same as general procedure (S₂₅ to 4).

ethyl 2-benzyl-2-(((diethylperoxy)(oxo)-14-phosphanyl)carbonyl)hex-5-enoate (4j)

1H-NMR (CDCl₃, 400 MHz) δ: 1.19 (t, 3H, J = 7.6 Hz), 1.36 (t, 6H, J = 7.2 Hz), 1.90-2.05 (m, 4H), 3.22 (d, 1H, J = 14.0 Hz), 3.29 (d, 1H, J = 14.0 Hz), 4.10-4.18 (m, 2H), 4.22-4.28 (m, 4H), 4.96 (d, 1H, J = 10.0 Hz), 5.01 (d, 1H, J = 17.2 Hz), 5.69-5.83 (m, 1H), 7.08 (d, 2H, J = 8.0 Hz), 7.20-7.25 (m, 3H); 13C-NMR (CDCl₃, 100 MHz) δ: 13.6, 16.1, 16.1, 27.7, 29.2, 36.2, 61.4, 63.8, 63.8, 63.9, 64.1, 64.6, 115.1, 126.8, 128.0, 129.9, 135.2, 136.8, 169.9, 207.1, 208.8; IR (ATR) ν: 2981, 1731, 1197, 1011, 700 cm⁻¹; HRMS (ESI) Calcd for C₂₀H₂₉NaO₈P, [M+Na]⁺ 419.1599, found 419.1604; yellow oil (165 mg, 55%).

Synthesis of 4k

S₄₁ to S₄₂: To a solution of S₄₁ (2.0 g) in MeOH (100 mL) was added H₂SO₄ (1.0 mL) at rt and the mixture was stirred at 70 °C for 19 h, then MeOH was removed under reduced pressure. sat. NaHCO₃ aq. was added and the mixture was diluted with CH₂Cl₂. The layers were separated and the organic layer was
washed with water and brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude S42 was used in the next step without further purification.

S42 to S43: To a solution of crude S42 (500 mg, 2.21 mmol) in THF (11 mL) was added LHMDS (2.7 mL, 1.0 M in THF, 2.7 mmol) at -78 °C and the mixture was stirred at 0 °C for 1 h. 4-Bromo-1-butene (0.27 mL, 2.65 mmol) and NaI (199 mg, 1.33 mmol) was then added at -78 °C and the mixture was stirred for 1 h at 65 °C. Water was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding S43 (528 mg, 86%).

S43 to 4k: Same as general procedure (S24 to 4).

1-((diethylperoxy)(oxo)-l4-phosphanyl)-2,2-diphenylhex-5-en-1-one (4k)

\[
\text{Ph} \quad \text{P} \quad \text{O} \\
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 1.14 (t, 6H, $J = 7.2$ Hz), 1.76-1.83 (m, 2H), 2.65 (dt, 2H, $J = 8.0, 4.0$ Hz), 3.71-3.92 (m, 4H), 5.73-5.83 (m, 1H), 7.27-7.37 (m, 10H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 16.0, 16.0, 29.2, 29.6, 34.9, 37.1, 63.5, 63.6, 66.6, 67.2, 114.4, 114.8, 126.7, 127.4, 127.7, 128.2, 128.9, 129.8, 137.7, 138.3, 142.7, 207.6, 209.2; IR (ATR) $\nu$: 2981, 1736, 1237, 1016, 700 cm$^{-1}$; HRMS (ESI) Calcd for C$_{22}$H$_{27}$NaO$_4$P, [M+Na]$^+$ 409.1545, found 409.1532; yellow oil (399.8 mg, 55%).

Synthesis of 4m

\[
\begin{array}{c}
\text{Ph} \quad \text{P} \quad \text{O} \\
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

S44 to S45: To a solution of S44 (1.0 mL, 7.6 mmol) and triphosgene (1.35 g, 4.56 mmol) in CH$_2$Cl$_2$ (7 mL), pyridine (1.2 mL, 15.2 mmol) was added using dropping funnel over 1 h at 0 °C. The temperature was allowed to rise to room temperature gradually after the addition of pyridine and the solutions was stirred for 17 h at room temperature (color of the solution: clear yellow to clear dark orange). The reaction was quenched with 1N HCl, extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo gave crude S45 as a deep red oil which was used without further purification.

S45 to 4m: P(OEt)$_3$ (0.18 mL, 1.07 mmol) was directly added to the crude S45 (210 mg, 1.07 mmol) at 0 °C, and the mixture was stirred at rt for 4 h. Any volatiles were removed under reduced pressure and the crude 4m was purified by column chromatography (201 mg, 63%, 2 steps).

2-allylphenyl (dithyrophosphoryl)formate (4m)

\[
\begin{array}{c}
\text{Ph} \quad \text{P} \quad \text{O} \\
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 1.45 (t, 6H, $J = 7.2$ Hz), 3.31 (d, 2H, $J = 6.4$ Hz), 4.40 (q, 4H, $J = 7.2$ Hz), 5.05 (d, 1H, $J = 17.2$ Hz), 5.10 (d, 1H, $J = 10.8$ Hz), 5.84-5.94 (m, 1H), 7.08 (d, 1H, $J = 8.0$ Hz), 7.21-7.29 (m, 3H); $^{13}$C-NMR
(CDCl$_3$, 100 MHz) δ: 16.3, 16.3, 34.3, 64.8, 64.9, 116.7, 121.9, 126.9, 127.5, 130.6, 131.6, 135.3, 147.9, 164.1; IR (ATR) ν: 2982, 1721, 1011, 772 cm$^{-1}$; HRMS (ESI) Calcd for C$_{14}$H$_{19}$NaO$_5$P, [M+Na]$^+$ 321.0868, found 321.0857; yellow oil

**Synthesis of 4n**

[S46 to S47](#): To a stirred solution of S46 (1.0 g, 3.23 mmol) in MeCN (11 mL) was added K$_2$CO$_3$ (891 mg, 6.46 mmol), and trans-1,4-dibromo-2-butene (1.38 g, 6.46 mmol), and the reaction mixture was stirred at 80 °C. The reaction was quenched with H$_2$O, extracted with AcOEt, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded S47 (1.1 g, 77%).

[S47 to 4n](#): Same as general procedure (S24 to 4)

**diethyl(E)-(2-((4-fluoro-N-(2-methylallyl)phenyl)sulfonyl)but-2-en-1-yl)phenyl)sulfonyl)benzoyl)phosphonate (4n)**

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 1.31-1.43 (m, 6H), 1.52 (s, 3H), 2.42 (s, 3H), 3.31-3.69 (br, 4H), 4.15 (q, 4H, J = 6.8 Hz), 4.26 (brs, 2H), 4.63 (s, 1H), 4.79 (s, 1H), 5.30 (dt, 1H, J = 15.2, 6.8 Hz), 5.68 (d, 1H, J = 15.2, 6.8 Hz), 6.84 (d, 1H, J = 6.8 Hz), 7.09 (d, 1H, J = 8.4 Hz), 7.14 (d, 1H, J = 8.8 Hz), 7.21-7.39 (m, 2H), 7.44-7.49 (m, 2H), 7.54 (d, 1H, J = 8.8 Hz), 7.58 (d, 1H, J = 8.8 Hz), 7.61 (d, 2H, J = 8.0 Hz), 8.26 (dd, 1H, J = 6.8, 2.8 Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 16.2, 16.3, 19.7, 21.4, 47.9, 52.7, 53.3, 114.4, 115.9, 116.2, 127.1, 128.3, 129.2, 129.5, 129.5, 130.2, 130.3, 130.7, 131.0, 133.0, 134.5, 136.5, 136.7, 136.9, 137.3, 139.8, 143.2, 163.8, 166.3, 199.2, 201.0; IR (ATR) ν: 2809, 1348, 1158, 1022 cm$^{-1}$; HRMS (ESI) Calcd for C$_{32}$H$_{34}$F$_2$NaO$_8$P, [M+Na]$^+$ 715.1689, found 715.1685; yellow oil (100.2 mg, 11%).

**3-methylchroman-4-one (5a)**

(CAS-Reg# 16982-86-8)

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 1.19 (d, 3H, J = 6.8 Hz), 2.78-2.91 (m, 1H), 4.13 (dd, 1H, J = 11.2, 11.2 Hz), 4.46 (dd, 1H, J = 11.2, 5.2 Hz), 6.93 (d, 1H, J = 8.4 Hz), 6.99 (dd, 1H, J = 7.6, 7.2 Hz), 7.43 (dd, 1H, J = 8.4, 7.2 Hz), 7.89 (d, 1H, J = 7.6 Hz); (28.5 mg, 65%)
6-bromo-3-methylchroman-4-one (5b)

\[
\text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.21 (d, 3H, } J = 7.2 \text{ Hz), 2.82-2.91 (m, 1H), 4.15 (dd, 1H, } J = 11.2, 11.2 \text{ Hz), 4.50 (dd, 1H, } J = 11.2, 5.2 \text{ Hz), 6.87 (d, 1H, } J = 8.4 \text{ Hz), 7.53 (dd, 1H, } J = 8.4, 2.8 \text{ Hz), 8.00 (d, 1H, } J = 2.8 \text{ Hz); } ^{13}\text{C-NMR (CDCl}_3, 100 MHz) \delta: 10.6, 40.4, 72.2, 114.0, 119.8, 121.7, 129.7, 138.3, 160.6, 193.5; \text{ IR (ATR) v: 2991, 1738, 1239, 822 cm}^{-1}; \text{ HRMS (ESI) Calcd for C}_{10}\text{H}_{8}\text{BrNaO}_2, [M+Na]^{+} 262.9684, \text{ found 262.9681; colorless solid (26.4 mg, 59%).}
\]

8-methoxy-3-methylchroman-4-one (5c)

\[
\text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.23 (d, 3H, } J = 7.2 \text{ Hz), 2.84-2.93 (m, 1H), 3.92 (s, 3H), 4.23 (dd, 1H, } J = 10.8, 10.8 \text{ Hz), 4.61 (dd, 1H, } J = 10.8, 4.8 \text{ Hz), 6.96 (dd, 1H, } J = 7.6, 7.6 \text{ Hz), 7.04 (d, 1H, } J = 7.6 \text{ Hz), 7.49 (d, 1H, } J = 7.6 \text{ Hz); } ^{13}\text{C-NMR (CDCl}_3, 100 MHz) \delta: 10.7, 40.5, 56.1, 72.7, 116.2, 118.4, 120.8, 121.0, 148.6, 151.5, 194.7; \text{ IR (ATR) v: 2983, 1736, 1373, 1237, 1045 cm}^{-1}; \text{ HRMS (ESI) Calcd for C}_{11}\text{H}_{13}\text{NaO}_3, [M+Na]^{+} 215.0684, \text{ found 215.0678; colorless solid (15.5 mg, 69%).}
\]

3-methyl-1-tosyl-2,3-dihydroquinolin-4(1H)-one (5d)

(trimethyl Reg# 35043-99; } \text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.13 (d, 3H, } J = 7.2 \text{ Hz), 2.39 (s, 3H), 2.42-2.49 (ddq, 1H), 3.64 (dd, 1H, } J = 13.8, 13.8 \text{ Hz), 4.46 (dd, 1H, } J = 13.8, 4.8 \text{ Hz), 7.22-7.27 (m, 3H), 7.53 (dd, 1H, } J = 8.4, 8.4 \text{ Hz), 7.60 (d, 2H, } J = 8.4 \text{ Hz), 7.84 (d, 1H, } J = 8.4 \text{ Hz), 7.95 (d, 1H, } J = 8.4 \text{ Hz); (28.5 mg, 57%)}
\]

1-((4-methoxyphenyl)sulfonyl)-3-methyl-2,3-dihydroquinolin-4(1H)-one (5e)

\[
\text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.13 (d, 3H, } J = 7.2 \text{ Hz), 2.41-2.51 (m, 1H), 3.63 (dd, 1H, } J = 13.6, 13.6 \text{ Hz), 3.83 (s, 3H), 4.45 (dd, 1H, } J = 13.6, 4.8 \text{ Hz), 6.89 (d, 2H, } J = 9.2 \text{ Hz), 7.22 (dd, 1H, } J = 7.6, 7.6 \text{ Hz), 7.53 (dd, 1H, } J = 8.4, 7.6, 1.6 \text{ Hz), 7.64 (d, 2H, } J = 9.2 \text{ Hz), 7.84 (d, 1H, } J = 8.4 \text{ Hz), 7.95 (dd, 1H, } J = 7.6, 1.6 \text{ Hz); } ^{13}\text{C-NMR (CDCl}_3, 100 MHz) \delta: 12.3, 40.2, 52.2, 55.6, 114.5, 123.1, 124.6, 125.0, 128.1, 128.9, 131.1, 134.4, 142.4, 163.4, 195.5; \text{ IR (ATR) v: 2983, 1736, 1372, 1233, 1043 cm}^{-1}; \text{ HRMS (ESI) Calcd for C}_{17}\text{H}_{17}\text{NNaO}_3, [M+Na]^{+} 354.0776, \text{ found 354.0785; yellow oil (32.6 mg, 56%).}
\]

1-((4-fluorophenyl)sulfonyl)-3-methyl-2,3-dihydroquinolin-4(1H)-one (5f)

\[
\text{H-NMR (CDCl}_3, 400 MHz) \delta: 1.14 (d, 3H, } J = 6.8 \text{ Hz), 2.42-2.52 (m, 1H), 3.65 (dd, 1H, } J = 13.6, 13.6 \text{ Hz), 4.46 (dd, 1H, } J = 13.6, 4.8 \text{ Hz), 7.15 (dd, 2H, } J = 8.8, 8.8 \text{ Hz), 7.23 (dd, 1H, } J = 8.0, 8.0 \text{ Hz), 7.55 (dd, 1H, } J = 8.8, 8.0, 1.6 \text{ Hz), 7.75 (dd, 2H, } J = 8.8, 4.8 \text{ Hz), 7.81 (d, 1H, } J = 8.8 \text{ Hz), 7.97 (dd, 1H, } J = 8.0, 1.6 \text{ Hz); } ^{13}\text{C-NMR (CDCl}_3, 100 MHz) \delta: 12.4, 40.4, 52.4, 116.7, 116.9, 122.9, 124.7, 125.4, 128.3, 129.5, 129.6, 134.5, 135.7, 142.0, 164.5, 166.2, 195.2; \text{ IR (ATR) v: 2932, 1690, 1355, 1170, 734 cm}^{-1}; \text{ HRMS (ESI) Calcd for C}_{10}\text{H}_{16}\text{FNNaO}_3, [M+Na]^{+} 342.0576, \text{ found 342.0586; colorless solid (20.2 mg, 46%).}
\]

1'-tosyl-1',2'-dihydro-4'H-spiro[cyclopentane-1,3'-quinolin]-4'-one (5g)

S21
diethyl 3-methyl-4-oxocyclopentane-1,1-dicarboxylate (5h)

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 1.68-1.87 (m, 6H), 2.00-2.11 (m, 2H), 2.41 (s, 3H), 3.99 (s, 2H), 7.08 (dd, 1H, $J = 7.2$, 7.2 Hz), 7.32 (d, 2H, $J = 8.4$ Hz), 7.39 (dd, 1H, $J = 7.8$, 7.8 Hz), 7.59 (d, 1H, $J = 8.4$ Hz), 7.78 (d, 2H, $J = 8.4$ Hz), 8.00 (d, 1H, $J = 7.8$ Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 21.5, 25.7, 33.2, 53.9, 54.9, 118.4, 122.3, 123.3, 126.8, 129.0, 130.0, 134.2, 136.9, 142.3, 144.4, 197.6; IR (ATR) $v$: 2953, 1683, 1351, 1161 cm$^{-1}$; HRMS (ESI) Caled for C$_{20}$H$_{21}$NaO$_5$ [M+Na]$^+$ 378.1140, found 378.1153; colorless solid (19.5 mg, 30%, mp: 117-119 °C)

diethyl 3,3-dimethyl-4-oxocyclopentane-1,1-dicarboxylate (5i)

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 1.11 (d, 3H, $J = 7.6$ Hz), 1.27 (t, 6H, $J = 7.2$ Hz), 1.97 (dd, 1H, $J = 12.8$, 12.8 Hz), 2.41 (m, 1H), 2.72 (d, 1H, $J = 18.8$ Hz), 2.84 (dd, 1H, $J = 12.8$, 8.8 Hz), 2.95 (d, 1H, $J = 18.8$ Hz), 4.22 (q, 4H, $J = 7.2$ Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 13.9, 38.1, 42.5, 44.4, 54.8, 61.9, 62.0, 170.7, 171.0, 215.8; IR (ATR) $v$: 2984, 1731, 1238, 1044 cm$^{-1}$; HRMS (ESI) Caled for C$_{12}$H$_{18}$NaO$_5$ [M+Na]$^+$ 265.1052, found 265.1060; yellow oil (56 mg, 81%).

ethyl 1-benzyl-3-methyl-2-oxocyclopentan-1-ol (5j)

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 0.62-0.73 (m, 1H), 0.88 (d, 3H, $J = 7.2$ Hz), 1.25 (t, 3H, $J = 7.2$ Hz), 1.89-2.01 (m, 1H), 2.06-2.12 (m, 1H), 2.24-2.41 (m, 2H), 3.11 (d, 1H, $J = 14.0$ Hz), 3.17 (d, 1H, $J = 14.0$ Hz), 4.16 (q, 2H, $J = 7.2$ Hz), 7.11 (d, 2H, $J = 7.6$ Hz), 7.21-7.26 (m, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 26.4, 26.6, 37.6, 39.2, 46.6, 50.5, 64.1, 64.6, 116.9, 118.0, 119.6, 124.6, 152.8, 188.6; IR (ATR) $v$: 2964, 1747, 1722, 1454, 1156, 702 cm$^{-1}$; HRMS (ESI) Caled for C$_{18}$H$_{20}$NaO$_5$ [M+Na]$^+$ 283.1310, found 283.1303; yellow oil (20.4 mg, 50%)

5-methyl-2,2-diphenylcyclopentan-1-one (5k)

(CAS-Reg# 1912-08-9); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 1.16 (d, 3H, $J = 7.6$ Hz), 1.56-1.62 (m, 1H), 2.18-2.26 (m, 1H), 2.37-2.45 (m, 1H), 2.52-2.59 (m, 1H), 2.78-2.84 (m, 1H), 7.18-7.32 (m, 10H); (24.9 mg, 53%)

diethyl 4-methyl-3-oxocyclohexane-1,1-dicarboxylate (5l)

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 1.06 (d, 3H, $J = 6.4$ Hz), 1.22-1.27 (m, 6H), 1.40-1.51 (m, 1H), 2.02-2.11 (m, 1H), 2.18 (dddd, 1H, $J = 13.6$, 13.6, 3.6 Hz), 2.32 (qd, 1H, $J = 6.4$, 6.4 Hz), 2.41 (dd, 1H, $J = 13.6$, 2.8 Hz), 2.51 (d, 1H, $J = 14.8$ Hz), 2.96 (d, 1H, $J = 14.8$ Hz), 4.13-4.26 (m, 4H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 13.9, 13.9, 14.5, 29.9, 30.2, 44.0, 45.1, 57.6, 61.8, 61.8, 170.3, 170.4, 208.2; IR (ATR) $v$: 2980, 1735, 1229, 1045 cm$^{-1}$; HRMS (ESI)
Calcd for C_{13}H_{20}NaO_{5}, [M+Na]^+ 279.1208, found 279.1214; yellow oil (26.4 mg, 37%).

3-methylchroman-2-one (5m)

(CAS-Reg# 66122-70-1)

\[ \text{1H-NMR (CDCl}_3, 400 MHz) \delta: 1.54 \text{ (d, 3H, } J = 6.8 \text{ Hz), 2.89-2.99 \text{ (m, 2H), 4.64-4.73 \text{ (m, 1H), 7.26 \text{ (t, 1H, } J = 6.8 \text{ Hz), 7.39 \text{ (t, 1H, } J = 7.6 \text{ Hz), 7.53 \text{ (dt, 1H, } J = 7.6, 1.6 \text{ Hz), 8.10 \text{ (d, 1H, } J = 7.6 \text{ Hz); (17.8 mg, 52%)}} } \]

3-(4,4-dimethyl-1-tosylpyrrolidin-3-yl)-1-((4-fluorophenyl)sulfonyl)-2,3-dihydroquinolin-4(1H)-one (trans-5n)

\[ \text{1H-NMR (CDCl}_3, 400 MHz) \delta: 0.74 \text{ (s, 3H), 1.07 \text{ (s, 3H), 2.44 \text{ (s, 3H), 2.59-2.68 \text{ (m, 1H), 2.87 \text{ (d, 1H, } J = 9.6 \text{ Hz), 3.10 \text{ (dd, 1H, } J = 13.6, 9.6 \text{ Hz), 4.20 \text{ (d, 1H, } J = 8.0 \text{ Hz); 13C-NMR (CDCl}_3, 100 MHz) } } \]

General procedure for cyclization: EtOH (0.2 M for alkenyloxime) was added to the mixture of alkenyloxime 6 (1.0 eq.), Co (5 mol%) under an argon atmosphere at rt, then PhSiH\(_3\) (1.5 eq.) was added at rt and the solution was stirred at rt. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography.

General procedure for the synthesis of alkenyloximes 6

S50 to S51: To a solution of S50 (1.0 eq.) in H\(_2\)O/EtOH (1/4, 0.2 M for S50), H\(_2\)NOH•HCl (5.0 eq.) and AcONa (5.0 eq.) was added at rt, and the mixture was stirred for 1 h at 80 °C. Then, the mixture was diluted with water and the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), filtered, and concentrated on a rotary evaporator gave crude S51 which was purified by column chromatography.

S51 to 6e,g,h,i: To a solution of S51 (1.0 eq.) in CH\(_2\)Cl\(_2\) (0.2 M for S51), NEt\(_3\) (2.0 eq.) and AcCl (2.0 eq.) was added at 0 °C, and the mixture was stirred for 2 h at rt. Then, the mixture was diluted with 1N HCl and the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with brine, dried
over Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator gave crude $6e,g,h,i$ which was purified by column chromatography.

**S51 to 6d,f,j:** To a solution of $S51$ (1.0 eq.) in CH$_2$Cl$_2$ (0.2 M for $S51$), imidazole (2.0 eq.) and TBSCl (2.0 eq.) was added at 0 °C, and the mixture was stirred for 1 h at rt. Then, the mixture was diluted with H$_2$O and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator gave crude $6d,f,j$ which was purified by column chromatography.

**Synthesis of 6a**

**S52 to S53:** To a stirred solution of $S52$ (3.0 mL, 30.81 mmol) in MeCN (154 mL) was added K$_2$CO$_3$ (17.0 g, 123.2 mmol) and TsNH$_2$ (10.5 g, 61.6 mmol), and the reaction mixture was stirred at 80 °C. The reaction was quenched with H$_2$O, extracted with AcOEt, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded $S53$ (4.5 g, 65%).

**S53 to S54:** To a stirred solution of $S53$ (2.55 g, 10.0 mmol) in acetone (33 mL) was added K$_2$CO$_3$ (2.76 g, 20 mmol), phenyl bromide (2.99 g, 15.0 mmol) and the reaction mixture was stirred at rt for 16 h. The reaction was quenched with H$_2$O, extracted with AcOEt, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded $S54$ (3.42 g, quant.).

**S54 to 6a:** Same as general procedure ($S50$ to $S51$).

1-(4-isopropyl-2,3,5-trimethoxyphenyl)-5-methylhex-5-en-1-ol ($6a$)

**Synthesis of 6b**

To a stirred solution of $6a$ (103.3 mg, 0.289 mmol) in THF (1.4 mL) was added NaH (35 mg, 0.88 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. Then, benzyl bromide (0.1 mL, 0.84 mmol) was added at 0 °C, and the mixture was stirred for 2 h at rt. The reaction mixture was quenched with H$_2$O, extracted with AcOEt, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded $6b$ (E/Z mixture) which was recrystallized from hexane and AcOEt.
to give 6b (Z only, 45.9 mg, 35%).

(Z)-N-(2-((benzoyloxy)imino)-5-phenylethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (6b)

1H-NMR (CDCl3, 400 MHz) δ: 1.31(s, 3H), 2.42(s, 3H), 3.47(s, 2H), 4.46(s, 2H), 4.62(s, 1H), 4.67(s, 1H), 5.14(s, 2H), 7.20-7.41(m, 10H), 7.57-7.72(m, 4H); 13C-NMR (CDCl3, 100 MHz) δ: 19.7, 21.5, 42.7, 55.7, 76.6, 114.4, 127.4, 127.5, 128.0, 128.2, 128.4, 128.5, 129.2, 129.6, 133.4, 135.3, 137.2, 139.9, 143.4, 153.9; IR (ATR) v: 2970, 1738, 1365, 1216, 612 cm⁻¹; HRMS (ESI) Calcd for C26H26N2NaO3Si [M+Na]⁺ 471.1718, found 471.1716; colorless solid

Synthesis of 6c

To a solution of 6a (319 mg, 0.89 mmol) in CH2Cl2 (1.8 mL), NEt₃ (0.25 mL, 1.78 mmol) and BzCl (0.21 mL, 1.78 mmol) was added at 0 °C, and the mixture was stirred for 2 h at rt. Then, the mixture was diluted with water and the aqueous layer was extracted with CH2Cl2. The combined organic layers were washed with brine, dried over Na2SO4, filtered, and concentrated on a rotary evaporator gave crude 6c which was purified by column chromatography (378 mg, 92%).

(Z)-N-(2-((benzoyloxy)imino)-5-phenylethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (6c)

1H-NMR (CDCl3, 400 MHz) δ: 1.76(s, 3H), 2.44(s, 3H), 3.54(s, 2H), 4.70(s, 2H), 4.80(s, 1H), 4.84(s, 1H), 7.24(d, 2H, J = 7.6 Hz), 7.38(dd, 2H, J = 7.6, 6.7 Hz), 7.39-7.66(m, 8H), 8.07(d, 2H, J = 7.6 Hz); 13C-NMR (CDCl3, 100 MHz) δ: 19.5, 21.2, 43.0, 55.4, 115.3, 127.2, 128.1, 128.3, 128.4, 129.4, 129.5, 130.3, 132.2, 133.4, 134.8, 139.0, 143.6, 162.6, 163.0; IR (ATR) v: 2942, 1763, 1344, 1212 cm⁻¹; HRMS (ESI) Calcd for C26H26N2NaO4S [M+Na]⁺ 485.1510, found 485.1506; colorless solid

(Z)-N-(2-(((tert-butyldimethylsilyloxy)imino)-5-phenylethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (6d)

6a to 6d: Same as general procedure (S51 to 6d).

6b to 6d: Same as general procedure (S51 to 6d).

N-(2-(acetoxyimino)-5-phenylethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (6e)

6a to 6e: Same as general procedure (S51 to 6e).
130.5, 132.3, 135.1, 135.3, 139.5, 143.8, 161.4, 161.5, 168.2, 168.9; IR (ATR) v: 2928, 1739,
1349, 1160, 812, 782 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₄N₂NaO₄Si, [M+Na]⁺ 423.1255, found 423.1347;
yellow oil (45.1 mg, 80%).

**Synthesis of 6f**

[Diagram showing the synthesis process from S55 to 6f]

**S55 to S56:** To a stirred solution of S55 (1.0 g, 4.44 mmol) in acetone (22 mL) was added K₂CO₃ (1.23 g, 8.88 mmol), ethyl bromoacetate (0.98 mL, 8.88 mmol) and the reaction mixture was stirred at 55 °C for 18 h. The reaction was quenched with H₂O, extracted with AcOEt, dried over Na₂SO₄, filtered, and concentrated in vacuo. Short column chromatography gave crude S56.

**S56 to S57:** To a solution of crude S56 and MeNHOMe•HCl (866 mg, 8.88 mmol) in THF (9 mL) was added iPrMgCl (2.0 M in THF, 8.9 mL, 17.8 mmol) at -20 °C and the mixture was stirred at room temperature for 2 h. Sat. NH₄Cl aq. was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding S57 as a yellow oil (1.19 g, 82%, 2 steps).

**S57 to S58:** To a solution of S57 (136.4 mg, 0.42 mmol) in THF (2 mL) was added MeMgBr (3.0 M in Et₂O, 0.42 mL, 1.3 mmol) at 0 °C and the mixture was stirred at room temperature for 2 h. Sat. NH₄Cl aq. was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude S58 was used in the next step without further purification.

**S58 to 6f:** Same as general procedure (S50 to 6f). (108.2 mg, 63%, 3 steps)

N-(2-(((tert-butyldimethylsilyl)oxy)imino)propyl)-4-methyl-N-(2-methylallyl)benzenesulfonylamine (6f)

[Compound 6f structure]

[^1]H-NMR (CDCl₃, 400 MHz) δ: 0.13 (s, 5.3H), (s, 0.7H), 0.90 (s, 1.1H), 0.91 (s, 7.9H),
1.65 (s, 2.6H), 1.68 (s, 0.4H), 1.84 (s, 2.6H), 1.92 (s, 0.4H), 2.43 (s, 2.6H), 2.44 (s, 0.4H), 3.62 (s, 0.2H), 3.64 (s, 1.8H), 3.78 (s, 1.8H), 4.04 (s, 0.2H), 4.76 (s, 0.1H), 4.80 (s, 0.9H), 4.87 (s, 1H), 7.29 (d, 2H, J = 8.0 Hz), 7.69(d, 2H, J = 8.0 Hz);[^13]C-NMR (CDCl₃, 100 MHz) δ: -5.3, 12.3, 18.0, 20.0, 21.5, 26.0, 51.9, 54.3, 114.8, 127.3, 129.6, 136.2, 139.7, 143.3, 157.7; IR (ATR) v: 2928, 1342, 1160, 916, 777, 655 cm⁻¹; HRMS (ESI) Calcd for C₂₀H₂₆N₂NaO₄Si ,

S26
Synthesis of 6g,h,i

S59 to S60: To a slurry of phenacyl chloride (3.0 g, 19.4 mmol) and hydroxylamine hydrochloride (4.02 g, 58.2 mmol) in 5 mL of water was added with stirring portionwise methanol (40 mL) to yield a clear solution. The clear solution was stirred for 17 h at room temperature and was added cold water, whereupon an orange solid precipitated out. The oxime product was filtered out, washed several times with water, and dried under reduced pressure gave crude S60 which was used in the next step without further purification.

S60 to S61: To a solution of crude S60 in THF (116 mL), NEt3 (3.3 mL, 23.3 mmol) and AcCl (1.7 mL, 23.3 mmol) was added at 0 °C, and the mixture was stirred for 2 h at rt. Then, the mixture was diluted with H2O and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over Na2SO4, filtered, and concentrated on a rotary evaporator gave crude S61 which was purified by column chromatography (2.2 g, 54%, 2 steps).

S61 to 6g,h,i: To a solution of S61 (1.0 eq.) in THF (0.2 M for S61) was added 60% sodium hydride (1.2 eq.) at 0 °C and the mixture was stirred at room temperature for 30 minutes. S62 (1.2 eq.) was then added and the mixture was stirred for 2 h. Water was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding 6g,h,i.

diethyl 2-(2-(acetoxyimino)-2-phenylethyl)-2-(2-methylallyl)malonate (6g)

\[
\text{HNMR (CDCl}_3, \text{ 400 MHz}) \delta: 1.13 (t, 0.9H, J = 6.8 Hz), 1.22 (t, 5.1H, J = 6.8 Hz), 1.62 (s, 0.45H), 1.65 (s, 2.55H), 2.02 (s, 2.55H), 2.21 (s, 0.45H), 2.65 (s, 0.3H), 2.97 (s, 1.7H), 3.35 (s, 1.7H), 3.61 (s, 0.3H), 3.86-4.18 (m, 4H), 4.72 (s, 0.15H), 4.80 (s, 0.85H), 4.85 (s, 0.15H), 4.88 (s, 0.85H), 7.28-7.59 (m, 5H); \]
\[
\text{C-NMR (CDCl}_3, \text{ 100 MHz}) \delta: 13.7, 19.6, 23.0, 37.6, 39.6, 55.4, 61.5, 116.0, 127.3, 128.0, 129.5, 132.9, 140.6, 162.5, 168.6, 170.3; \]
\[
\text{IR (ATR)} v: 2981, 1770, 1732, 1202, 760 \text{ cm}^{-1}; \]
\[
\text{HRMS (ESI) Calcd for C}_{21}\text{H}_{27}\text{NNaO}_6, [M+Na]^+: 412.1736, \text{found 412.1725; yellow oil (284.2 mg, 78%).} \]

dibenzy l 2-(2-(acetoxyimino)-2-phenylethyl)-2-(2-methylallyl)malonate (6h)

\[
\text{HNMR (CDCl}_3, \text{ 400 MHz}) \delta: 1.56 (s, 3H), 1.98 (s, 2.17H), 2.17 (s, 0.83H), 2.69 (s, 0.56H), 3.03 (s, 1.44H), 3.37 (s, 1.44H), 3.68 (s, 0.56H), 4.58-5.06 (m, 6H), 7.11-7.55 (m, 15H); \]
\[
\text{C-NMR (CDCl}_3, \text{ 100 MHz}) \delta: 14.1, 19.5, 20.9, 22.9, 23.8, 31.3, 37.7, 39.8, 40.9, 55.5, 56.0, 60.2, 67.3, 67.3, 113.8, 116.2, 127.3, 128.0, 128.1, 128.3, 129.5, 130.2, 132.7, 134.1, 134.6, 135.1, 140.3, 140.4, 162.0, 163.5, 168.7, 169.8, 169.9; \]
\[
\text{IR (ATR)} v:}
diethyl 2-(2-(acetoxyimino)-2-phenylethyl)-2-(3-methylbut-3-en-1-yl)malonate (6i)

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{Me} \\
\text{EtO}_2\text{C} & \quad \text{Ph} \quad \text{NOAc} \\
(E/Z = 4:8/1)
\end{align*}
\]

\[\text{\^H-NMR (CDCl}_3, 400 MHz) \delta: 1.17 (t, 6H, \text{J} = 6.8 \text{ Hz}), 1.63 (\text{s}, 0.52\text{H}), 1.67 (\text{s}, 2.48\text{H}), 1.82-2.31 (\text{m}, 7\text{H}), 3.39 (\text{s}, 1.66\text{H}), 3.57 (\text{s}, 0.34\text{H}), 3.80-4.20 (\text{m}, 4\text{H}), 4.58 (\text{s}, 0.17\text{H}), 4.61 (\text{s}, 0.17\text{H}), 4.64 (\text{s}, 1.83\text{H}), 4.68 (\text{s}, 1.83\text{H}), 7.29-7.82 (\text{m}, 5\text{H}); \text{^13C-NMR (CDCl}_3, 100 MHz) \delta: 13.8, 19.5, 22.2, 30.4, 32.0, 37.3, 56.0, 61.4, 110.5, 127.7, 127.9, 129.7, 132.2, 144.5, 162.4, 168.4, 170.1; \text{IR (ATR)} \nu: 2982, 1728, 1183, 903, 697 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{22}\text{H}_{29}\text{NNaO}_6, [M+Na]^+ 426.1893, \text{found 426.1902}; \text{yellow oil (404.0 mg, 76%).}
\]

**Synthesis of 6j**

S63 to S66: To a stirred solution of S63 (1.25 g, 4.83 mmol) in MeCN (16 mL) was added K₂CO₃ (1.33 g, 9.65 mmol), NaI (724 mg, 4.83 mmol) and 3-chloro-2-methyl-1-propene (0.94 mL, 9.65 mmol), and the reaction mixture was stirred at 80 °C for 17 h. The reaction was quenched with H₂O, extracted with AcOEt, dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded S64 (1.2 g, 79%).

S64 to S65: To a stirred solution of S64 (1.2 g, 3.83 mmol) in THF (12 mL) was added 3N HCl (1.5 mL, 4.5 mmol) at rt, and the reaction mixture was stirred at 60 °C for 3 h. The reaction was quenched with H₂O, extracted with AcOEt, dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification by flash column chromatography afforded crude S65 (864 mg) and S64 (223 mg, 19%).

S65 to 6j: Same as general procedure (S50 to 6j).

N-(2-(((tert-butyldimethylsilyl)oxy)imino)ethyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (6j)

\[\text{\^H-NMR (CDCl}_3, 400 MHz) \delta: 0.11 (\text{s}, 3\text{H}), 0.13 (\text{s}, 3\text{H}), 0.90 (\text{s}, 9\text{H}), 1.69 (\text{s}, 1.5\text{H}), 1.75 (\text{s}, 1.5\text{H}), 2.43 (\text{s}, 3\text{H}), 3.68 (\text{s}, 1\text{H}), 3.69 (\text{s}, 1\text{H}), 3.85 (\text{d}, 1\text{H}, \text{J} = 6.0 \text{ Hz}), 4.03 (\text{d}, 1\text{H}, \text{J} = 3.6 \text{ Hz}), 4.86 (\text{s}, 1\text{H}), 4.93 (\text{s}, 1\text{H}), 6.74 (\text{t}, 0.5\text{H}, \text{J} = 4.0 \text{ Hz}), 7.28-7.33 (\text{m}, 2.5\text{H}), 7.69 (\text{d}, 2\text{H}, \text{J} = 8.0 \text{ Hz}); \text{^13C-NMR (CDCl}_3, 100 MHz) \delta: -5.5, -5.5, 17.9, 19.7, 21.4, 25.8, 25.8,
42.5, 45.5, 53.7, 55.2, 115.0, 115.5, 127.1, 129.7, 129.8, 135.8, 136.4, 139.3, 139.3, 143.4, 143.6, 149.9, 152.1; IR (ATR) v: 2929, 1739, 1350, 1249, 1160, 912, 754 cm⁻¹; HRMS (ESI) Calcd for C₉H₁₂Na₂O₃SSi [M+Na]⁺ 419.1801, found 419.1791; colorless oil (250 mg, 32%).

**O-benzoyl-N-(4,4-dimethyl-3-phenyl-1-tosylpyrroloidin-3-yl)hydroxylamine (7c)**

1H-NMR (CDCl₃, 400 MHz) δ: 0.70 (s, 3H), 1.10 (s, 3H), 2.28 (s, 3H), 3.37 (d, 1H, J = 9.2 Hz), 3.46 (d, 1H, J = 9.2 Hz), 3.94 (d, 1H, J = 11.2 Hz), 4.21 (d, 1H, J = 11.2 Hz), 7.17 (d, 2H, J = 8.4 Hz), 7.28-7.38 (m, 7H), 7.53 (dd, 1H, J = 7.2, 7.2 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.76 (d, 2H, J = 7.6 Hz), 7.92 (s, 1H), 13C-NMR (CDCl₃, 100 MHz) δ: 19.6, 21.4, 24.9, 44.8, 53.1, 60.0, 72.8, 126.5, 127.4, 127.8, 128.3, 128.4, 129.0, 129.6, 133.3, 143.5, 165.5; IR (ATR) v: 2924, 1718, 1343, 1157, 705 cm⁻¹; HRMS (ESI) Calcd for C₂₃H₂₃N₂O₃Na₂SSi, [M+Na]⁺ 487.1662, found 487.1160; colorless solid (20.9 mg, 35%).

**O-(tert-butyl(dimethyl)silyl)-N-(4,4-dimethyl-3-phenyl-1-tosylpyrroloidin-3-yl)hydroxylamine (7d)**

1H-NMR (CDCl₃, 400 MHz) δ: 0.70 (s, 3H), 0.09 (s, 3H), 0.46 (s, 3H), 0.71 (s, 3H), 1.25 (s, 3H), 2.43 (s, 3H), 3.26 (d, 1H, J = 9.6 Hz), 3.30 (d, 1H, J = 9.6 Hz), 3.87 (d, 1H, J = 10.0 Hz), 4.19 (d, 1H, J = 10.0 Hz), 4.97 (brs, 1H), 7.19-7.30 (m, 5H), 7.33 (d, 2H, J = 8.0 Hz), 7.79 (d, 2H, J = 8.0 Hz), 13C-NMR (CDCl₃, 100 MHz) δ: -5.53, -5.45, 17.8, 19.6, 21.5, 25.6, 25.9, 44.0, 51.2, 59.9, 73.5, 127.1, 127.3, 127.5, 127.6, 129.2, 134.5, 134.3, 138.4, 143.6, IR (ATR) v: 2926, 1713, 1345, 1158, 1092, 826 cm⁻¹; HRMS (ESI) Calcd for C₂₅H₂₆N₂O₃Si, [M+Na]⁺ 497.2270, found 497.2257; colorless solid (23.7 mg, 60%).

**O-acetyl-N-(4,4-dimethyl-3-phenyl-1-tosylpyrroloidin-3-yl)hydroxylamine (7e)**

1H-NMR (CDCl₃, 400 MHz) δ: 0.58 (s, 3H), 1.04 (s, 3H), 1.80 (s, 3H), 2.44 (s, 3H), 3.28 (d, 1H, J = 9.6 Hz), 3.40 (d, 1H, J = 9.6 Hz), 3.83 (d, 1H, J = 11.2 Hz), 4.08 (d, 1H, J = 11.2 Hz), 7.25-7.31 (m, 4H), 7.33 (d, 2H, J = 8.0 Hz), 7.79-7.81 (m, 3H); 13C-NMR (CDCl₃, 100 MHz) δ: 18.8, 19.7, 21.5, 24.7, 44.6, 53.1, 59.8, 72.4, 126.5, 127.4, 127.7, 128.2, 129.5, 134.2, 136.9, 143.5, 169.7; IR (ATR) v: 2969, 1739, 1343, 1220, 1157, 813 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₀N₂O₃Si, [M+Na]⁺ 425.1511, found 425.1504; colorless solid (32.8 mg, 61%).

**O-(tert-butyl(dimethyl)silyl)-N-(3,4,4-trimethyl-1-tosylpyrroloidin-3-yl)hydroxylamine (7f)**

1H-NMR (CDCl₃, 400 MHz) δ: -0.02 (s, 3H), 0.02 (s, 3H), 0.78 (s, 3H), 0.84 (s, 3H), 0.87 (s, 3H), 0.96 (s, 3H), 2.42 (s, 3H), 3.04 (d, 1H, J = 10.8 Hz), 3.16 (brs, 2H), 3.64 (d, 1H, J = 10.8 Hz), 4.42 (brs, 1H), 4.73 (d, 2H, J = 7.2 Hz), 4.82 (d, 2H, J = 7.6 Hz); 13C-NMR (CDCl₃, 100 MHz) δ: -5.6, -5.5, 16.0, 17.9, 19.1, 21.5, 24.3, 26.1, 43.0, 54.2, 59.9, 68.1, 127.3, 129.6, 132.4, 143.2; IR (ATR) v: 2952, 1542, 1344, 1158, 1094, 665 cm⁻¹; HRMS (ESI) Calcd for C₂₀H₁₈O₃Na₂O₃Si, [M+Na]⁺ 435.2114, found 435.2107; yellow oil (25.7 mg, 66%).

**diethyl 3-(acetoxyamino)-4,4-dimethyl-3-phenylcyclopentane-1,1-dicarboxylate (7g)**

1H-NMR (CDCl₃, 400 MHz) δ: 0.66 (s, 3H), 1.15 (s, 3H), 1.28 (t, 6H, J = 7.2 Hz), 1.79 (s, 3H), 2.17 (d, 1H, J = 14.4 Hz), 2.91 (d, 1H, J = 14.4 Hz), 3.06 (d, 1H, J = 14.4 Hz), 3.35 (d, 1H, J = 14.4 Hz), 4.16-4.32 (m, 4H), 7.24-7.40 (m, 5H), 8.09 (brs, 1H).
$^1$H; $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 14.0, 18.9, 21.4, 27.4, 39.3, 45.7, 47.4, 56.7, 61.5, 61.7, 74.6, 126.5, 127.1, 127.9, 138.8, 172.1, 173.0; IR (ATR) v: 2980, 1730, 1369, 1238, 1044, 700 cm$^{-1}$; HRMS (ESI) Calcd for C$_{21}$H$_{29}$NNaO$_6$, [M+Na]$^+$ 414.1893, found 414.1906; orange oil (57.5 mg, 96%).

dibenzyl 3-(acetoxyamino)-4,4-dimethyl-3-phenylcyclopentane-1,1-dicarboxylate (7h)

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 0.63 (s, 3H), 1.13 (s, 3H), 1.64 (s, 3H), 2.18 (d, 1H, $J = 14.4$ Hz), 2.97 (d, 1H, $J = 14.4$ Hz), 3.11 (d, 1H, $J = 14.4$ Hz), 3.37 (d, 1H, $J = 14.4$ Hz), 5.06-5.20 (m, 4H), 7.24-7.36 (m, 15H), 8.14 (s, 1H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 18.8, 21.4, 27.5, 39.5, 45.6, 47.5, 56.9, 67.3, 67.4, 74.7, 126.4, 127.1, 127.9, 128.0, 128.0, 128.2, 128.4, 128.5, 135.4, 135.8, 138.6, 169.9, 171.8, 172.7; IR (ATR) v: 2969, 1731, 1239, 698 cm$^{-1}$; HRMS (ESI) Calcd for C$_{31}$H$_{33}$NNaO$_6$, [M+Na]$^+$ 538.2206, found 538.2193; yellow oil (69.2 mg, 83%).
TBDPSo-H3Me

cis (major isomer)