Supporting Information

Palladium-Catalyzed Diastereo- and Enantioselective Formal [3 + 2] Cycloadditions of Vinyl Cyclopropanes with Cyclic 1‑Azadienes

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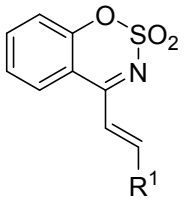
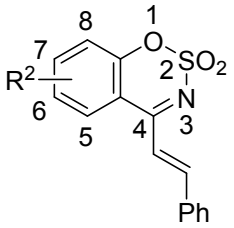
1. General information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All the reagents were obtained from commercial supplier and used as received, without further purification unless otherwise noted. Solvents used in the reactions were distilled from appropriate drying agents prior to use. The chiral phosphoramidite ligands **4a-4f** were prepared according to the literature procedures.[1-2] ^{1}H NMR and ^{13}C NMR spectra were recorded respectively at 400 MHz and 100 MHz on a Bruker AVANCE 400. Enantiomeric excess (*ee*) were determined by HPLC analysis on a Shimadzu LC-20A, using Daicel Chiralcel IA, IB or IC columns. High resolution mass spectra were obtained on Bruker Daltonics micrOTOF-Q II spectrometer in ESI mode. The relative and absolute configuration of **3ia** and **6** were assigned by the X-ray analysis and the configurations of other cycloaddition products were assigned by analogy.

2 **Preparation of the cyclic 1-azadiene substrates**



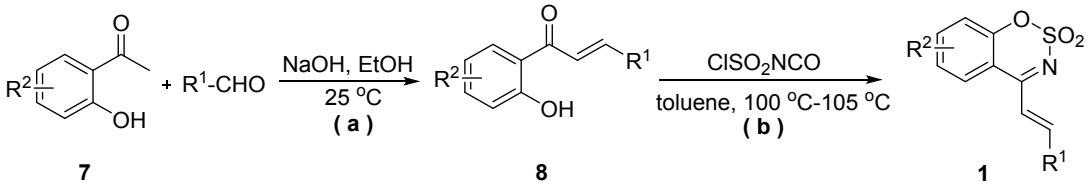
1a: $R^1 = C_6H_5$
1b: $R^1 = 2\text{-}FC_6H_5$
1c: $R^1 = 2\text{-}ClC_6H_5$
1d: $R^1 = 2\text{-}BrC_6H_5$
1e: $R^1 = 2\text{-}CF_3C_6H_5$
1f: $R^1 = 3\text{-}FC_6H_5$
1g: $R^1 = 3\text{-}ClC_6H_5$
1h: $R^1 = 3\text{-}BrC_6H_5$
1i: $R^1 = 3\text{-}NO_2C_6H_5$
1j: $R^1 = 4\text{-}FC_6H_5$
1k: $R^1 = 4\text{-}ClC_6H_5$
1l: $R^1 = 4\text{-}CF_3C_6H_5$
1m: $R^1 = 2\text{-}MeC_6H_5$
1n: $R^1 = 2\text{-}OMeC_6H_5$
1o: $R^1 = 3\text{-}OMeC_6H_5$
1p: $R^1 = 4\text{-}OMeC_6H_5$
1q: $R^1 = 4\text{-}MeC_6H_5$
1r: $R^1 = 3\text{-thienyl}$



1s: $R^2 = 6\text{-Me}$
1t: $R^2 = 6\text{-OMe}$

The cyclic 1-azadiene **1a-1b,**[3a-3b] **1h-1i**,[3c.] **1l-1q,**[3c] **1s-1t**[3d] was prepared according to the literature procedures

General experimental procedure for the synthesis of cyclic 1-azadiene 1.



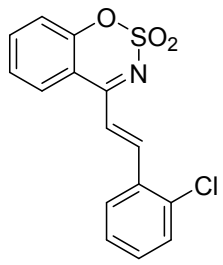
7 **8** **1**

(a) To a 250 mL round-bottomed flask containing a magnetic stir bar were added sequentially **7** (10 mmol), ethanol (20 mL), aromatic benzaldehyde (10 mmol) and aqueous solution of NaOH (6 M, 20 mL). The resulting solution was allowed to stir for 24 h at room temperature, upon the completion of the reaction, the solution was acidified at room temperature with aqueous solution of HCl (6 M, 25 mL). The mixture was extracted with dichloromethane (3 × 60 mL), and the combined organic layers were dried over Na_2SO_4 and filtered and evaporated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/EtOAc = 10:1) afforded the desired **8.**

(b) To a solution of chlorosulphonyl isocyanate (0.9 mL, 10 mmol) in toluene was

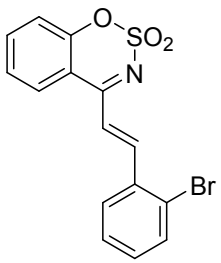
added over a period of 20 minutes another solution of **8 (**10 mmol) in toluene (10 mL) at 100 ^{o}C-105 ^{o}C. Stirring was continued for 3 h at this temperature. The toluene was distilled, and the residue was added to water (40 mL), the solid was filtered and recrystallized from ethanol to desired cyclic 1**-**azadiene **1.**

(*E*)-4-(2-chlorostyryl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1c)



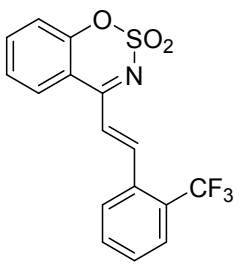
Yellow solid. yield 37%. mp = 192-194 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.50 (d, *J* = 15.5 Hz, 1H), 7.98-7.95 (m, 1H), 7.78-7.75 (m, 2H), 7.49-7.33 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 170.2, 154.4, 142.6, 137.0, 136.0, 132.6, 132.1, 130.6, 128.4, 128.0, 127.3, 125.8, 121.1, 119.5, 116.8. **IR** (KBr): ν_{max} 1620, 1579, 1519, 1374, 1347, 1281, 1180, 974, 928, 864, 774, 756, 672 cm^{-1}**. HRMS (ESI)**: m/z calcd for $C_{15}H_{11}{}^{35}ClNO_3S$ $[M(^{35}Cl)+H]^+$ 320.0143, found 320.0144. $C_{15}H_{11}{}^{37}ClNO_3S$ $[M(^{37}Cl)+H]^+$ 322.0113, found 322.0116**.**

(*E*)-4-(2-bromostyryl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1d)



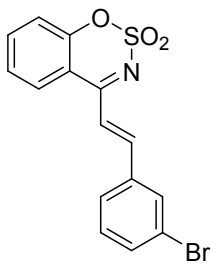
Yellow solid. yield 25%. mp = 197-198 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.46(d, *J* = 15.5 Hz, 1H), 7.98-7.96 (m, 1H), 7.77-7.75 (m, 2H), 7.69-7.67 (m, 1H), 7.46-7.26 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 170.2, 154.4, 145.1, 136.9, 134.5, 133.9, 132.2, 128.4, 128.1, 127.9, 126.4, 125.8, 121.4, 119.5, 116.8. **IR (**KBr**):** ν_{max} 1616, 1579, 1519, 1469, 1434, 1373, 1344, 1278, 1179, 970, 859, 773, 654 cm^{-1}**. HRMS (ESI)**: m/z calcd for $C_{15}H_{10}{}^{79}BrNO_3SNa$ $[M(^{79}Br)+Na]^+$385.9457, found 385.9457. $C_{15}H_{10}{}^{81}BrNO_3SNa$ $[M(^{81}Br)+Na]^+$387.9437, found 387.9436**.**

(*E*)-4-(2-(trifluoromethyl)styryl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1e)



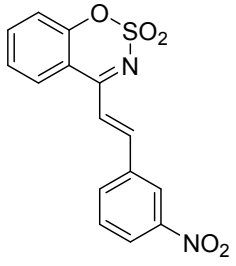
Yellow solid. yield 44%. mp = 204-205 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.45 (d, *J* = 15.4 Hz, 1H), 7.96-7.94 (m,1H), 7.86-7.84(m, 1H), 7.79-7.73 (m, 2H), 7.68-7.64 (m, 1H), 7.60-7.56 (m, 1H), 7.46-7.42 (m, 1H), 7.37-7.32 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 170.1, 154.4, 142.0, 137.0, 133.3, 132.3, 130.6, 129.6 (d, *J* = 30.0 Hz), 128.3, 128.1, 126.5 (q, *J* = 6.0 Hz), 125.8, 123.8 (d, *J* = 170.0 Hz), 123.2, 119.6, 116.7. **IR** (KBr): ν_{max} 1629, 1582, 1525, 1489, 1382, 1313, 1187, 1123, 1038, 977, 865, 771, 651 cm^{-1} **HRMS(ESI)**: m/z calcd for $C_{16}H_{11}F_3NO_3S$ $[M+H]^+$ 354.0406, found 354.0407.

. **(*E*)-4-(3-bromostyryl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1h)**



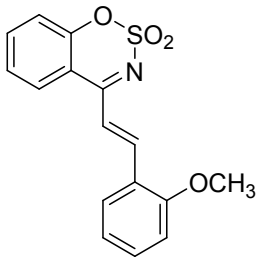
Yellow solid. yield 29%. mp = 196-197 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.09 (d, *J* = 15.5 Hz, 1H), 8.00-7.98 (m, 1H), 7.84 (s, 1H), 7.78-7.74 (m, 1H), 7.61-7.57 (m, 2H), 7.48-7.33 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 169.9, 154.4, 144.9, 137.0, 136.3, 134.3, 131.1, 130.7, 127.9, 127.8, 125.8, 123.4, 119.53, 119.51, 116.8. **IR (**KBr**):** ν_{max} 1626, 1608, 1583, 1526, 1476, 1373, 1331, 1187, 1065, 848, 771, 649 cm^{-1}**. HRMS (ESI)**: m/z calcd for $C_{15}H_{10}{}^{79}BrNO_3SNa$ $[M(^{79}Br)+Na]^+$ 385.9457, found 385.9459. $C_{15}H_{10}{}^{81}BrNO_3SNa$ $[M(^{81}Br)+Na]^+$387.9437, found 387.9438**.**

(*E*)-4-(3-nitrostyryl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1i)



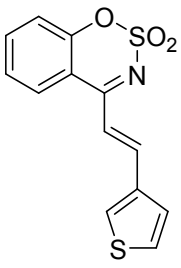
Yellow solid. yield 33%. mp = 198-199 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.59-8.58 (m, 1H), 8.34-8.32 (m, 1H), 8.22 (d, *J* = 15.2 Hz, 1H), 8.04-8.02 (m, 1H), 7.97-7.95 (m, 1H), 7.80-7.77 (m, 1H), 7.71-7.67 (m, 1H), 7.58-7.55 (m, 1H), 7.51-7.49 (m, 1H), 7.39-7.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 169.6, 154.5, 148.9, 143.4, 137.3, 135.9, 134.9, 130.4, 127.9, 126.0, 125.5, 122.4, 121.1, 119.6, 116.6. **IR** (KBr): ν_{max} 1630, 1607, 1581, 1521, 1378, 1351, 1323, 1248, 1179, 926, 862, 776, 697 cm^{-1}**. HRMS (ESI)**: m/z calcd for $C_{15}H_{11}N_2O_5S$ $[M+H]^+$ 331.0383, found 331.0384.

(*E*)-4-(2-methoxystyryl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1n)



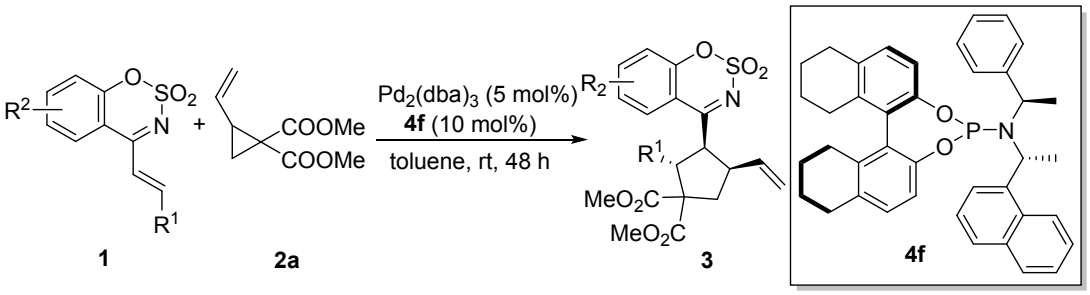
Yellow solid. yield 32%. mp = 190-192 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.45 (d, *J* = 15.5 Hz, 1H), 7.98-7.78 (m,1H), 7.73-7.69 (m, 1H), 7.64-7.56 (m, 2H), 7.46-7.39 (m, 2H), 7.32-7.30 (m, 1H), 7.04-6.97 (m, 2H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 170.9, 159.5, 154.4, 143.1, 136.5, 133.1, 130.5, 128.0, 125.6, 123.4, 121.0, 119.4, 118.9, 117.2, 111.5, 55.7. **IR** (KBr): ν_{max} 1614, 1577, 1509, 1465, 1365, 1289, 1246, 1184, 1026, 935, 752, 835, 688 cm^{-1}**. HRMS(ESI)**: m/z calcd for $C_{16}H_{14}NO_4S$ $[M+H]^+$ 316.0638, found 316.0638.

(*E*)-4-(2-(thiophen-3-yl)vinyl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (1r)



Yellow solid. yield 41%. mp = 197-198 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.20 (d, *J* = 15.2 Hz, 1H), 7.96 (d, *J* = 8 Hz, 1H) 7.75-7.71 (m, 2H), 7.48-7.40 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 15.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 170.5, 154.4, 140.3, 137.8, 136.7, 131.5, 127.8, 127.7, 125.7, 125.2, 119.5, 117.7, 127.0. **IR** (KBr): ν_{max} 1614, 1577, 1509, 1465, 1365, 1289, 1246, 1184, 1026, 935, 752, 835, 688 cm^{-1}**. HRMS (ESI)**: m/z calcd for $C_{13}H_9NO_3S_2Na$ $[M+Na]^+$ 313.9916, found 313.9917.

3. Asymmetric formal [3+2] cycloadditions

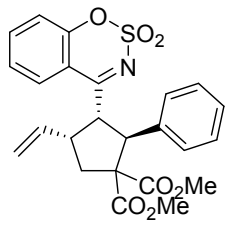


To a dried tube filled with 1-azadiene **1** (0.1 mmol), $Pd_2(dba)_3$ (5 mol%), and chiral phosphoramidite **4f** (10 mol%) was added a solution of vinyl cyclopropane **2a** (0.12 mmol) in toluene (2 mL). The reaction mixture was stirred under an atmosphere of argon at 25 °C. Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 5:1) to give the

corresponding product **3**.

3.1. Products 3aa - 3ta in Table 2

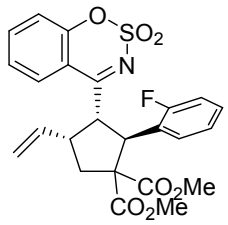
Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-phenyl-4-vinylcyclopentane-1,1-dicarboxylate (3aa)



3aa

white solid, 44 mg, yield 90%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 8:1, mp = 198-200 °C, $[\alpha]_D^{20}$ = -37.1 (c = 0.35, CH_2Cl_2), 98% *ee,* determined by HPLC analysis (chiral IA column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (major) = 14.0 min, t (minor) = 19.6 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.87(d, *J* = 7.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.41-7.39 (m, 1H), 7.31-7.18 (m, 6H), 5.71-5.62 (m, 1H), 4.88-4.86 (m, 2H), 4.77 (d, *J* = 16.8 Hz, 1H), 4.54-4.51 (m, 1H), 3.77 (s, 3H), 3.60-3.53 (m, 1H), 3.30 (s, 3H), 3.13-3.07 (m, 1H), 2.24-2.18 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.1, 171.7, 171.5, 153.7, 137.1, 136.7, 136.1 128.5, 128.2, 127.8, 127.5, 125.7, 119.2, 117.5, 116.9, 64.2, 52.8, 52.3, 51.9, 51.0, 47.0, 41.2. **IR** (KBr): ν_{max} 2956, 1724, 1594, 1549, 1436, 1387, 1281, 1186, 1116, 918, 858, 751, 645 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{23}NO_7SNa$ $[M+Na]^+$ 492.1087, found 492.1089.

Dimethyl(2S,3S,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(2-fluorophenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3ba)

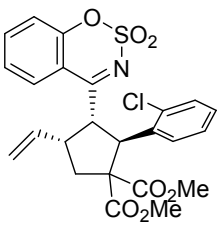


3ba

colorless oil, 40.9 mg, yield 84%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 7:1, $[\alpha]_D^{20}$ = +34.3 (c = 0.35, CH_2Cl_2), 94% ee determined by HPLC analysis (chiral IA column, 2% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (major) = 53.5 min, t (minor) = 64.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, J = 7.9 Hz, 1H), 7.65-7.63 (m, 1H), 7.43-7.37 (m, 2H), 7.21-7.17 (m, 2H), 7.06-7.04 (m, 1H), 6.93-6.91 (m, 1H), 5.68-5.59 (m, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.83 (d, *J* = 10.0 Hz, 1H), 4.78-4.72 (m, 2H), 3,74 (s, 3H), 3.62-3.50 (m, 1H), 3.51 (s, 3H), 3.07-3.02 (m, 1H), 2.19-2.15 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.3, 171.2,

170.9, 161.9 (d, J = 245.0 Hz), 153.7, 136.8, 136.1, 131.9 (d, J = 4.6 Hz), 129.3 (d, J = 8.8 Hz), 127.9, 125.8, 124.0 (d, J = 3.2 Hz), 123.8 (d, J = 12.4 Hz), 119.1, 117.6, 116.9, 115.5 (d, J = 23.2 Hz), 63.3, 52.8, 52.5, 50.3 (d, J = 5.0 Hz), 47.5, 46.4, 41.1. **IR** (KBr): ν_{max} 2956, 1732, 1597, 1553, 1492, 1439, 1390, 1263, 1191, 1109, 924, 854, 759 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}FNO_7SNa$ $[M+Na]^+$ 510.0993, found 510.0993.

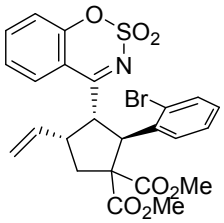
Dimethyl(2*S*,3*S*,4*R*)-2-(2-chlorophenyl)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-4-vinylcyclopentane-1,1-dicarboxylate (3ca)



3ca

colorless oil, 42.7 mg, yield 85%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 7:1, $[\alpha]_D^{20}$ = -142.1 (c = 0.19, CH_2Cl_2), 88% *ee* determined by HPLC analysis (chiral IC column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 29.0 min, t (major) = 46.9 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.70 (d, J = 7.2 Hz, 1H), 7.67-7.64 (m, 1H), 7.38-7.30 (m, 3H), 7.21 (d, J = 8.3 Hz, 1H), 7.14-7.10 (m, 2H), 5.74-5.65 (m, 1H), 5.32 (d, J = 11.0 Hz, 1H), 4.85-4.76 (m, 2H), 4.72-4.66 (m, 1H), 3,73 (s, 3H), 3.61-3.56 (m, 1H), 3.49 (s, 3H), 3.01-2.95 (m, 1H), 2.43-2.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.0, 171.5, 170.7, 153.7, 136.8, 136.4, 135.9, 135.3, 130.3, 128.6, 128.5, 127.9, 126.3, 125.7, 119.2, 117.7, 116.8, 63.7, 53.5, 52.9, 52.5, 47.6, 46.6, 41.6. **IR** (KBr): ν_{max} 2925, 1730, 1596, 1551, 1438, 1387, 1259, 1187, 1105, 922, 852, 793 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}{}^{35}ClNO_7SNa$ $[M(^{35}Cl)+Na]^+$ 526.0698, found 526.0696. $C_{24}H_{22}{}^{37}ClNO_7SNa$ $[M(^{37}Cl)+Na]^+$528.0668, found 528.0672**.**

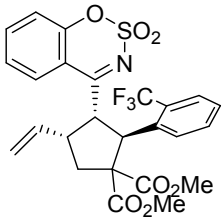
Dimethyl(2*S*,3*S*,4*R*)-2-(2-bromophenyl)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-4-vinylcyclopentane-1,1-dicarboxylate (3da)



3da

white solid, 52.5 mg, yield 96%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), *dr* = 10:1, mp = 150-152 °C, $[\alpha]_D^{20}$ = -220.0 (c = 0.20, CH_2Cl_2), 95% *ee* determined by HPLC analysis (chiral IC column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 31.3 min, t (major) = 43.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.66-7.61 (m, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.37-7.28 (m, 2H), 7.20-7.18 (m, 2H), 7.05-7.02 (m, 1H), 5.74-5.67 (m, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 4.87-4.78 (m, 2H), 4.69-4.64 (m, 1H), 3.76 (s, 3H), 3.63-3.56 (m, 1H), 3.51 (s, 3H), 2.98-2.94 (m, 1H), 2.47-2.41 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.9, 171.5, 170.6, 153.7, 137.2, 136.7, 135.9, 133.8, 128.8, 128.3, 127.9, 127.5, 126.9, 125.7, 119.2, 117.8, 116.8, 63.9, 54.2, 52.9, 52.5, 49.9, 46.5, 41.7. **IR** (KBr): ν_{max} 2953, 1728, 1591, 1552, 1432, 1387, 1277, 1191, 1111, 1020, 938, 854, 757, 675 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{23}{}^{79}BrNO_7S$ [M(^{79}Br)+H]$^+$ 548.0373, found 548.0374.$C_{24}H_{23}{}^{81}BrNO_7S$ [M(^{81}Br)+Na]$^+$550.0353, found 550.0355**.**

Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(2-(trifluoromethyl)phenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3ea)

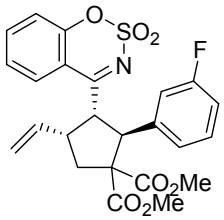


3ea

colorless oil, 47.2 mg, yield 88%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 8:1, $[\alpha]_D^{20}$ = +140.4 (c = 0.47, CH_2Cl_2), 98% *ee*, determined by HPLC analysis (chiral IA column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 24.8 min, t (major) = 26.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.69-7.64 (m, 3H), 7.47-7.46 (m, 2H), 7.35-7.33 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 5.80-5.71 (m, 1H), 5.43 (d, *J* = 8.6 Hz, 1H), 4.90-4.82 (m, 2H), 4.51-4.49 (m, 1H), 3.74 (s, 3H), 3.58-3.56 (m, 1H), 3.25 (s, 3H), 3.14-3.11 (m, 1H), 2.53-2.48 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 179.9, 171.0, 170.7, 153.7, 138.2, 136.8, 135.4, 131.5, 130.6, 130.3,128.3, 127.7, 127.6, 127.0 (q, *J* = 5.8 Hz), 125.6, 119.3, 118.0, 116.7, 65.4, 55.8, 52.9, 52.3, 48.1, 47.2, 41.8. **IR** (KBr): ν_{max} 2925, 1734, 1599, 1553, 1451, 1387, 1310, 1260, 1190, 1124, 1040, 921, 854, 770 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{22}F_3NO_7SNa$ [M+Na]$^+$ 560.0961, found 560.0961.

Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(3-fluorophe

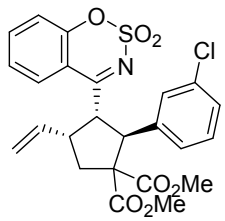
nyl)-4-vinylcyclopentane-1,1-dicarboxylate (3fa)



3fa

yellow solid, 46 mg, yield 95%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 7:1, $[\alpha]_D^{20}$ = -80.8 (c = 0.26, CH_2Cl_2), 94% *ee* determined by HPLC analysis (chiral IB column, 5% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 14.6 min, t (major) = 18.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 6.9 Hz, 1H), 7.70-7.66 (m, 1H), 7.43-7.40 (m, 1H), 7.24-7.17 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 10.3 Hz, 1H), 6.90-6.88 (m, 1H), 5.69-5.62 (m, 1H), 4.88-4.82 (m, 2H), 4.75 (d, *J* = 16.8 Hz, 1H), 4.50-4.45 (m, 1H), 3.77 (s, 3H), 3.60-3.50 (m, 1H), 3.35 (s, 3H), 3.13-3.08 (m, 1H), 2.22-2.17 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.7, 171.5, 171.3, 162.2 (d, *J* = 244.0 Hz), 153.6, 139.7 (d, *J* = 32.7 Hz), 136.9, 135.9, 129.7 (d, *J* = 8.1 Hz), 127.7, 125.8, 124.4 (d, *J* = 2.8 Hz), 119.2, 117.6, 116.8, 115.4 (d, *J* = 21.9 Hz), 114.5 (d, *J* = 20.7 Hz), 64.0, 52.9, 52.4, 51.7, 50.4, 46.7, 41.1. **IR** (KBr): ν_{max} 2955, 1728, 1595, 1551, 1488, 1442, 1390, 1264, 1190, 1110, 928, 856, 785, 699 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}FNO_7SNa$ $[M+Na]^+$ 510.0993, found 510.0992.

Dimethyl(2*S*,3*S*,4*R*)-2-(3-chlorophenyl)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-4-vinylcyclopentane-1,1-dicarboxylate (3ga)

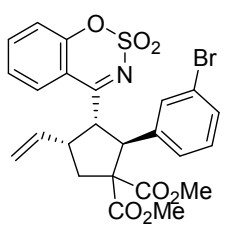


3ga

colorless oil, 44 mg, yield 88%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 5:1, $[\alpha]_D^{20}$ = -86.2 (c = 0.26, CH_2Cl_2), 90% *ee*, determined by HPLC analysis (chiral IB column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) =9.7 min, t (major) =11.9 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, *J* = 14.8 Hz, 1H), 7.70-7.66 (m, 1H), 7.43-7.39 (m, 1H), 7.26-7.14 (m, 5H), 5.65-5.58 (m, 1H), 4.87-4.80 (m, 2H), 4.76 (d, *J* = 16.8 Hz, 1H), 4.50-4.45 (m, 1H), 3,77 (s, 3H), 3.58-3.55 (m, 1H), 3.39 (s, 3H), 3.12-3.06 (m, 1H), 2.21-2.16 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.7, 171.6, 171.2, 153.7, 139.3, 136.9, 135.9, 134.0, 129.5, 128.0, 127.8, 127.7, 127.5, 125.9, 119.2, 117.7, 116.8, 64.0, 52.9, 52.4, 51.7, 50.5, 46.8, 41.1. **IR** (KBr): ν_{max} 2954, 1729, 1597, 1551, 1479, 1435, 1390, 1265, 1190, 1110, 927, 854, 759 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}{}^{35}ClNO_7SNa$

[M(^{35}Cl)+Na]$^+$ 526.0698, found 526.0698. $C_{24}H_{22}{}^{37}ClNO_7SNa$ [M(^{37}Cl)+Na]$^+$528.0668, found 528.0674**.**

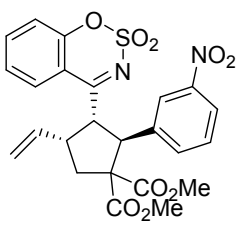
Dimethyl(2*S*,3*S*,4*R*)-2-(3-bromophenyl)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-4-vinylcyclopentane-1,1-dicarboxylate (3ha)



3ha

white solid, 52 mg, yield 96%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 5:1, mp = 168-170 °C, $[\alpha]_D^{25}$ = -34.3 (c = 0.35, CH_2Cl_2), 94% *ee,* determined by HPLC analysis (chiral IA column, 3% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 22.5 min, t (major) = 31.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.68-7.66 (m, 1H), 7.43-7.40 (m, 2H), 7.33-7.30 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.14-7.12 (m, 1H), 5.64-5.59 (m, 1H), 4.87-4.72 (m, 3H), 4.45-4.44 (m, 1H), 3.76 (s, 3H), 3.60-3.56 (m, 1H), 3.39 (s, 3H), 3.11-3.06 (m, 1H), 2.20-2.15 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.7, 171.6, 171.2, 153.7, 139.5, 136.9, 135.8, 130.8, 130.7, 129.8, 128.1, 127.8, 125.9, 122.1, 119.2, 117.7, 116.6, 64.0, 52.9, 52.4, 51.8, 50.5, 46.8, 41.1. **IR** (KBr): ν_{max} 2953, 1728, 1591, 1552, 1432, 1387, 1277, 1191, 1111, 1020, 938, 854, 757, 675 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}{}^{79}BrNO_7SNa$ [M(^{79}Br)+Na]$^+$ 570.0193, found 570.0193. $C_{24}H_{22}{}^{81}BrNO_7SNa$ [M(^{81}Br)+Na]$^+$572.0172, found 387.572.0174**.**

Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(3-nitrophenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3ia)

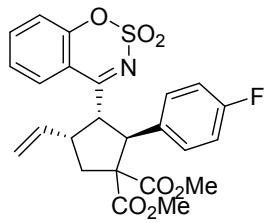


3ia

yellow solid, 44 mg, yield 85%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 4:1, mp = 147-149 °C, $[\alpha]_D^{20}$ = +18.5 (c = 0.54, CH_2Cl_2), 90% *ee*, determined by HPLC analysis (chiral IB column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 15.2 min, t (major) = 17.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.09-8.07 (m, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.72-7.68 (m, 1H), 7.49-7.43 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 5.64-5.59 (m, 1H), 4.90-4.85 (m, 2H), 4.77 (d, *J* = 16.8 Hz, 1H), 4.60-4.55 (m, 1H), 3.77 (s, 3H), 3.64-3.62 (m, 1H), 3.43 (s, 3H), 3.14-3.08 (m, 1H), 2.22-2.17 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.3, 171.1, 171.0, 153.6, 148.0, 139.2, 137.1, 136.5, 135.6,

129.3, 127.9, 126.0, 122.8, 122.3, 119.2, 118.0, 116.6, 63.8, 53.0, 52.6, 51.6, 50.3, 46.3, 41.0. **IR** (KBr): ν_{max} 2955, 1727, 1599, 1555, 1529, 1439, 1390, 1350, 1266, 1189, 1095, 935, 856, 747, 684 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}N_2O_9SNa$ $[M+Na]^+$ 537.0938, found 537.0937.

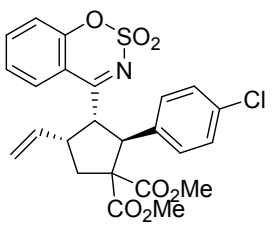
Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(4-fluorophenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3ja)



3ja

colorless oil, 46 mg, yield 96%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 6:1, $[\alpha]_D^{20}$ = -95.8 (c = 0.24, CH_2Cl_2), 96% *ee* determined by HPLC analysis (chiral IA column, 3% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 26.5 min, t (major) = 33.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.67-7.65 (m, 1H), 7.42-7.40 (m, 1H), 7.30-7.27 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.94-6.90 (m, 2H), 5.70-5.60 (m, 1H), 4.88-4.84 (m, 2H) 4.76 (d, *J* = 16.8 Hz, 1H), 4.47-4.46 (m, 1H), 3.76 (s, 3H), 3.56-3.53 (m, 1H), 3.34 (s, 3H), 3.12-3.07 (m, 1H), 2.22-2.17 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.8, 171.7, 171.5, 162.1 (d, *J* = 249.0 Hz), 153.7, 136.9, 135.9, 132.7 (d, *J* = 3.3 Hz), 130.1, 130.0, 127.7, 125.8, 119.2, 117.6, 116.8, 115.2, 115.0, 63.9, 52.8, 52.4, 51.9, 50.2, 46.7, 41.1. **IR** (KBr): ν_{max} 2956, 1728, 1598, 1553, 1512, 1439, 1391, 1265, 1190, 1109, 1066, 923, 852, 801, 646 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}FNO_7SNa$ $[M+Na]^+$ 510.0993, found 510.0993

Dimethyl(2*S*,3*S*,4*R*)-2-(4-chlorophenyl)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-4-vinylcyclopentane-1,1-dicarboxylate (3ka)

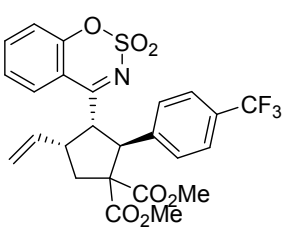


3ka

colorless oil, 49 mg, yield 97%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 5:1, $[\alpha]_D^{20}$ = -55.6 (c = 0.27, CH_2Cl_2), 95% *ee*, determined by HPLC analysis (chiral IA column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (major) = 12.2 min, t (minor) = 15.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm), 7.86 (d, *J* = 7.0 Hz, 1H), 7.68-7.65 (m, 1H), 7.42-7.40 (m, 1H), 7.26-7.21 (m, 5H), 5.68-5.59 (m, 1H), 4.87-4.72 (m, 3H), 4.48-4.45 (m, 1H), 3.76 (s, 3H), 3.57-3.54 (m, 1H), 3.36 (s, 3H), 3.12-3.06 (m, 1H), 2.22-2.17 (m, 1H). **^{13}C NMR** (100 MHz,

$CDCl_3$, ppm) δ 177.7, 171.7, 171.3, 153.7, 136.9, 135.9, 135.5, 135.4, 129.9, 128.4, 127.8, 125.9, 119.3, 117.6, 116.8, 63.9, 52.9, 52.4, 51.8, 50.3, 46.8, 41.1. **IR** (KBr): ν_{max} 2957, 1729, 1597, 1552, 1491, 1439, 1391, 1264, 1190, 1094, 922, 856, 798 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}{}^{35}ClNO_7SNa$ $[M(^{35}Cl)+Na]^+$ 526.0698, found 526.0698. $C_{24}H_{22}{}^{37}ClNO_7SNa$ $[M(^{37}Cl)+Na]^+$528.0668, found 528.0673**.**

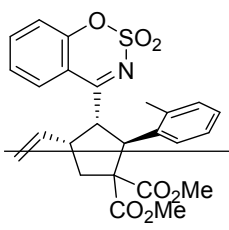
Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(4-(trifluoro methyl)phenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3la)



3la

colorless oil, 49 mg, yield 94%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 5:1, $[\alpha]_D^{20}$ = -83.3 (c = 0.54, CH_2Cl_2), 96% *ee,* determined by HPLC analysis (chiral IB column, 2% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 19.1 min, t (major) =21.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.70-7.66 (m, 1H), 7.51-7.42 (m, 5H), 7.22 (d, *J* = 8.3 Hz, 1H), 5.69-5.60 (m, 1H), 4.92-4.86 (m, 2H), 4.76 (d, *J* = 16.8 Hz, 1H), 4.53-4.50 (m, 1H), 3.77 (s, 3H), 3.62-3.57 (m, 1H), 3.32 (s, 3H), 3.15-3.10 (m, 1H), 2.25-2.20 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 177.6, 171.5,171.3, 153.7, 141.2, 137.0, 135.7, 129.8 (d, *J* = 32.2 Hz), 129.0, 127.7, 125.9, 125.1 (q, *J* = 3.6 Hz), 119.3, 117.8, 116.7, 74.0, 52.9, 52.4, 51.7, 50.5, 46.8, 41.1. **IR** (KBr): ν_{max} 2957, 1731, 1598, 1553, 1432, 1391, 1327, 1268, 1191, 1120, 1069, 1019, 923, 853, 762 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{22}F_3NO_7SNa$ $[M+Na]^+$ 560.0961, found 560.0960.

Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(o-tolyl)-4-vinylcyclopentane-1,1-dicarboxylate (3ma)

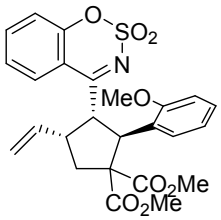


3ma

colorless oil, 45 mg, yield 84%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 9:1, $[\alpha]_D^{20}$ = -50.0 (c = 0.28, CH_2Cl_2), 97% *ee,* determined by HPLC analysis (chiral IA column, 5% IPA in hexane,

rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 21.5 min, t (major) = 30.1 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.63-7.60 (m, 1H), 7.37-7.35 (m, 1H), 7.20-7.14 (m, 2H), 7.06-7.02 (m, 3H), 5.73-5.66 (m, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 4.87 (d, *J* = 10.1 Hz, 1H), 4.76 (d, *J* = 16.8 Hz, 1H), 4.43-4.42 (m, 1H), 3,73 (s, 3H), 3.60-3.56 (m, 1H), 3.30 (s, 3H), 3.20-3.17 (m, 1H), 2.67 (s, 3H), 2.30-2.25 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.3, 171.8, 171.5, 153.6, 139.4, 136.7, 136.5, 135.9, 131.1, 127.8, 127.2, 125.8, 125.7, 125.3, 119.1, 117.6, 116.8, 64.5, 55.6, 52.8, 52.3, 47.6, 46.2, 41.9, 20.1. **IR** (KBr): ν_{max} 2955, 1730, 1597, 1553, 1438, 1390, 1261, 1190, 1099, 921, 856, 758 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_7SNa$ $[M+Na]^+$ 506.1244, found 506.1245.

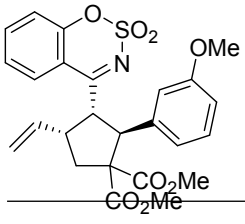
Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(2-meth oxyphenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3na)



3na

colorless oil, 36 mg, yield 72%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 20:1, $[\alpha]_D^{20}$ = -67.9 (c = 0.56, CH_2Cl_2), 89% *ee* determined by HPLC analysis (chiral IB column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 11.2 min, t (major) = 13.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.67-7.62 (m, 1H), 7.36-7.32 (m, 2H), 7.22-7.14 (m, 2H), 6.85-6.78 (m, 2H), 5.71-5.64 (m, 1H), 5.10 (d, *J* = 10.7 Hz, 1H), 4.86-4.76 (m, 3H), 3,78 (s, 3H), 3,72 (s, 3H), 3.58-3.53 (m, 1H), 3.41 (s, 3H), 3.04-2.98 (m, 1H), 2.29-2.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 179.3, 171.4, 171.3, 158.3, 153.6, 137.3, 136.6, 136.4, 128.6, 127.9, 125.6, 120.6, 119.1, 117.3, 117.1, 110.9, 63.2, 55.5, 52.7, 52.1, 50.9, 48.0, 47.0, 41.3. **IR** (KBr): ν_{max} 2955, 1731, 1597, 1551, 1493, 1438, 1388, 1256, 1190, 1112, 1027, 924, 854, 756 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_8SNa$ $[M+Na]^+$ 522.1193, found 522.1189.

Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(3-methoxyp henyl)-4-vinylcyclopentane-1,1-dicarboxylate (3oa)

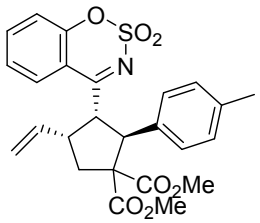


3oa

colorless oil, 47 mg, yield 95%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 7:1, $[\alpha]_D^{20}$ = -120.0 (c = 0.25, CH_2Cl_2), 94% *ee* determined by HPLC analysis (chiral IC column, 5% IPA in

hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 23.9 min, t (major) = 26.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.67-7.64 (m, 1H), 7.42-7.38 (m, 1H), 7.21-7.20 (m, 1H), 7.12-7.10 (m, 1H) , 6.91 (s, 1H) , 6.84 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 5.70-5.61 (m, 1H), 4.87-4.73 (m, 1H), 4.51-4.48 (m, 3H), 3.76-3.75 (m, 6H), 3.58-3.54 (m, 1H), 3.33 (s, 3H), 3.12-3.06 (m, 1H), 2.22-2.17 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.1, 171.6, 171.4, 159.3, 153.6, 138.7, 136.7, 136.1, 129.0, 127.8, 125.8, 120.3, 119.2, 117.4, 116.8, 114.9, 112.9, 64.1, 55.1, 52.8, 52.3, 51.9, 51.0, 46.9, 41.2. **IR** (KBr): ν_{max} 2953, 1728, 1597, 1551, 1489, 1438, 1389, 1264, 1190, 1110, 1047, 928, 855, 775 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_8SNa$ $[M+Na]^+$ 522.1193, found 522.1193.

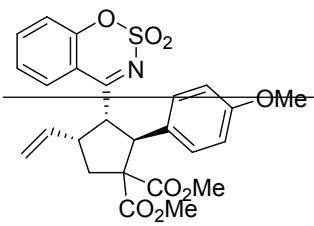
Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(p-tolyl)-4-vinylcyclopentane-1,1-dicarboxylate (3pa)



3pa

colorless oil, 44 mg, yield 92%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 7:1, $[\alpha]_D^{20}$ = +32.9 (c = 0.79, CH_2Cl_2), 95% *ee*, determined by HPLC analysis (chiral IA column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (major) = 11.5 min, t (minor) = 15.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, *J* = 7.2 Hz, 1H), 7.65-7.63 (m, 1H), 7.40-7.36 (m, 1H), 7.21-7.16 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.68-5.63 (m, 1H), 4.86-4.73 (m, 3H), 4.50-4.47 (m, 1H), 3.75 (s, 3H),3.59-3.34 (m, 1H), 3.34 (s, 3H), 3.10-3.04 (m, 1H), 2.24 (s, 3H), 2.21-2.16 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.3, 171.8, 171.5, 153.6, 137.1, 136.7, 136.2, 133.9. 128.9, 128.3, 127.8, 125.7, 119.1, 117.4, 116.9, 64.1, 52.7, 52.3, 51.9, 50.8, 46.9, 41.3, 21.0. **IR** (KBr): ν_{max} 2924, 1728, 1598, 1553, 1438, 1387, 1263, 1189, 1110, 1064, 922, 854, 763, 646 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_7SNa$ $[M+Na]^+$ 506.1244, found 506.1244.

Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(4-methoxyphenyl)-4-vinylcyclopentane-1,1-dicarboxylate (3qa)

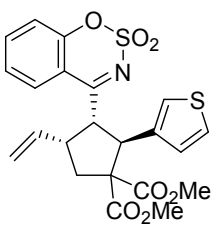


3qa

colorless oil, 48 mg, yield 97%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 8:1, $[\alpha]_D^{20}$ = +120.0 (c = 0.30,

CH_2Cl_2), 96% *ee*, determined by HPLC analysis (chiral IA column, 5% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 24.5 min, t (major) = 27.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.66-7.63 (m, 1H), 7.41-7.38 (m, 1H), 7.23-7.21 (m, 3H), 6.75 (d, *J* = 8.7 Hz, 2H), 5.70-5.61 (m, 1H), 4.86-4.73 (m, 3H), 4.50-4.45 (m, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.59-3.57 (m, 1H), 3.35 (s, 3H), 3.10-3.05 (m, 1H), 2.21-2.16 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.2, 171.8, 171.5, 158.8, 153.6, 136.7, 136.2, 129.5, 128.9, 127.8, 125.8, 119.2, 117.4, 116.9, 113.5, 64.0, 55.1, 52.7, 52.4, 52.0, 50.4, 46.8, 41.1. **IR** (KBr): ν_{max} 2955, 1728, 1598,1152, 1514, 1439, 1390, 1258, 1188, 1113, 1065, 1033, 922, 854, 798 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_8SNa$ $[M+Na]^+$ 522.1193, found 522.1193.

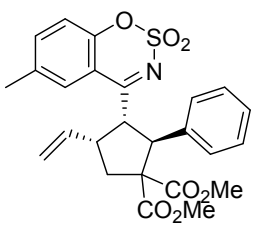
Dimethyl(2*S*,3*S*,4*R*)-3-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-(thiophen-3-yl)-4-vinylcyclopentane-1,1-dicarboxylate (3ra)



3ra

yellow solid, 45 mg, yield 95%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 4:1, mp = 158-159 °C, $[\alpha]_D^{20}$ = +50.0 (c = 0.20, CH_2Cl_2), 90% *ee*, determined by HPLC analysis (chiral IA column, 7% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (major) = 16.8 min, t (minor) = 20.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.68-7.66 (m, 1H), 7.42-7.40 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.18-7.16 (m, 1H), 7.09-7.02 (m, 2H), 5.65-5.58 (m, 1H), 4.94-4.84 (m, 2H), 4.75 (d, *J* = 16.7 Hz, 1H), 4.72-4.47 (m, 1H), 3.79 (s, 3H), 3.56-3.52 (m, 1H), 3.37 (s, 3H), 3.08-3.04 (m, 1H), 2.22-2.18 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.1, 171.9, 171.4, 153.7, 137.9, 136.8, 136.1, 127.8, 127.7, 125.8, 125.1, 122.5, 119.2, 117.4, 116.9, 63.8, 52.8, 52.5, 52.3, 46.8, 46.7, 41.0. **IR** (KBr): ν_{max} 2952, 1734, 1591, 1549, 1435, 1387, 1260, 1184, 1135, 1067, 1032, 923, 848 ,775, 669 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{22}H_{21}NO_7S_2Na$ $[M+Na]^+$ 498.0652, found 498.0651.

Dimethyl(2*S*,3*S*,4*R*)-3-(6-methyl-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-phenyl-4-vinylcyclopentane-1,1-dicarboxylate (3sa)

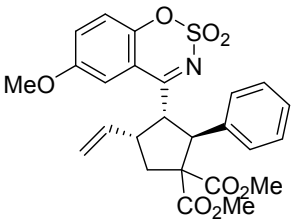


3sa

colorless oil, 27 mg, yield 56%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 7:1, $[\alpha]_D^{20}$ = -157.1 (c = 0.14, CH_2Cl_2), 93% *ee,* determined by HPLC analysis (chiral IB column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm).

Retention time: t (minor) = 19.9 min, t (major) = 37.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.60 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.33-7.31 (m, 2H), 7.26-7.19 (m, 3H), 7.10 (d, *J* = 8.6 Hz, 1H), 5.69-5.62 (m, 1H), 4.88 (d, *J* = 11.5 Hz, 2H), 4.77 (d, *J* = 16.7 Hz, 1H), 4.51-4.48 (m, 1H), 3.78 (s, 3H), 3.55-3.54 (m, 1H), 3.29 (s, 3H), 3.15-3.11 (m, 1H), 2.45 (s, 3H), 2.27-2.22 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ. 178.1, 171.9, 171.6, 151.6, 137.5, 137.1, 136.1, 135.8, 128.5, 128.2, 118.9, 117.4, 116.6, 64.2, 52.8, 52.3, 51.8, 51.0, 46.9, 41.1, 21.0. **IR** (KBr): ν_{max} 2959, 1728, 1598, 1558, 1434, 1388, 1262, 1188, 1095, 1022, 931, 800, 751, 700 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_7SNa$ $[M+Na]^+$ 506.1244, found 506.1243.

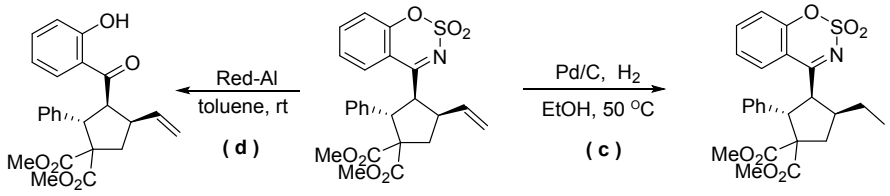
Dimethyl(2*S*,3*S*,4*R*)-3-(6-methoxy-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)-2-phenyl-4-vinylcyclopentane-1,1-dicarboxylate (3ta)



3ta

colorless oil, 25 mg, yield 50%. R_f = 0.3 (petroleum ether/ethyl acetate = 4:1), dr = 6:1, $[\alpha]_D^{20}$ = -245.8 (c = 0.24, CH_2Cl_2), 93% *ee,* determined by HPLC analysis (chiral IB column, 5% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 15.8 min, t (major) = 22.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.33-7.17 (m, 8H), 5.71-5.64 (m, 1H), 4.92-4.85 (m, 3H), 4.48-4.45 (m, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.61-3.59 (m, 1H), 3.30 (s, 3H), 3.14-3.10 (m, 1H), 2.27-2.22 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ. 178.0, 171.6, 171.5, 156.8, 147.3, 137.2, 136.1, 128.5, 127.5, 122.2, 120.1, 117.5, 117.4, 112.1, 64.2, 56.2, 52.8, 52.0, 51.2, 47.0, 41.2. **IR** (KBr): ν_{max} 2925, 1728, 1599, 1557, 1457, 1387, 1262, 1183, 1109, 1031,931, 833, 700 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{25}H_{25}NO_8SNa$ $[M+Na]^+$ 522.1193, found 522.1193.

3.2 The Compound 5 and 6 in Scheme 2



6 **3aa** **5**

(c) 3aa (47 mg, 0.1 mmol) was hydrogenated in EtOH (2 mL) over atmosphere of

hydrogen at 50 °C in the presence of Pd/C catalyst (10%，18 mg) for 3 h. The catalyst was filtered off，the filtrate was concentrated and chromatographed over silica gel column to give compound **5** (44 mg, 93% yield, 96% ee) as a white solid. dr = 8:1. R_f = 0.5 (petroleum ether/ethyl acetate = 4:1), mp = 172-174 °C, $[\alpha]_D^{20}$ = -24.3 (c = 0.37, CH_2Cl_2), 96% *ee,* determined by HPLC analy*sis (*chiral IC column, 10% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 16.4 min, t (major) = 27.3 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.70-7.67 (m, 1H), 7.43-7.41 (m, 1H), 7.28-7.16 (m, 6H), 4.82 (d, *J* = 11.6 Hz, 1H), 4.47-4.46 (m, 1H), 3.77 (S, 3H), 3.27 (S, 3H), 3.05-3.00 (m, 1H), 2.85-2.82 (m, 1H), 2.15-2.10 (m, 1H), 1.21-1.15 (m, 2H), 0.82-0.78 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 178.7, 171.8, 171.7, 153.6, 137.4, 136.8, 128.5, 128.1, 127.6, 127.4, 125.9, 119.4, 117.0, 64.1, 52.7, 52.2, 51.7, 51.1, 44.3, 40.3, 29.9, 24.1, 12.1. **IR** (KBr): ν_{max} 2925, 1727, 1596, 1551, 1438, 1386, 1261, 1188, 1096, 856, 752, 698 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{25}NO_7SNa$ $[M+Na]^+$ 494.1244, found 494.1242.

(d) To a solution of **3aa** (67 mg, 0.14 mmol) in toluene (2 mL) was slowly added sodium bis-(2-methoxyethoxy) aluminiumhydride (85 mg, 0.42mmol) in toluene (5 mL) at 0 °C. The reaction mixture was stirred at room temperature for about 2 h. The reaction was quenched with water (15 mL), the mixture was extracted with ethyl acetate (3 × 15 mL), the combined organic layer was dried $MgSO_4$. After removal of the solvents under reduced pressure, the residual was purified by column chromatography. affording the title compound **6** (32 mg, 77% yield, 97% *ee*) as a white solid. dr = 8:1. Rf = 0.4 (petroleum ether/ethyl acetate = 10:1), mp = 98-100 °C, $[\alpha]_D^{20}$ = －259.6 (c = 0.47, CH_2Cl_2). 97% *ee* determined by HPLC analysis (chiral IA column,2 % IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (major) = 8.3 min, t (minor) = 9.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 12.14 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.47-7.44 (m, 1H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.26-7.19 (m, 3H), 6.95-6.92 (m, 2H), 5.70-5.61 (m, 1H), 4.90-4.78 (m, 3H), 4.66-4.61 (m, 1H), 3.78 (s, 3H), 3.57-3.50 (m, 1H), 3.25 (s, 3H), 3.17-3.11 (m, 1H), 2.23-2.19 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.0, 172.1, 171.6, 162.7, 138.0, 136.9, 136.3, 129.8, 128.4, 128.1, 127.3, 120.0, 118.9, 118.6, 116.8, 64.2, 54.4, 52.7, 52.1, 50.4, 46.0, 41.0. **IR** (KBr): ν_{max} 3443, 2952,

1722, 1634, 1489, 1443, 1392, 1261, 1208, 1159, 1111, 927, 828, 755, 699 cm^{-1}. **HRMS (ESI)**: m/z calcd for $C_{24}H_{24}O_6Na$ $[M+Na]^+$ 431.1465, found 431.1466.

References

[1] B. M. Trost, S. M. Silverman, J. P. Stambuli. *J. Am. Chem. Soc.* **2011**, *133*, 19483–19497.

[2] Z. Yang, J. Zhou. *J. Am. Chem. Soc*. **2012**, *134*, 11833−11835.

[3] (a) X. Feng, Z. Zhou, C. Ma, X. Yin, R. Li, Y.-C. Chen. *Angew. Chem. Int. Ed.* **2013**, *52*, 14173. (b) C. Ma, J. Gu, B. Teng, Q. Zhou, R. Li, Y.-C. Chen. *Org. Lett.* **2013**, *15*, 6206. (c) Y. Wu, Y. Liu, W. Yang, H. Liu, L. Zhou, Z. Sun, H. Guo. *Adv. Synth. Catal*. **2016**, *358*, 3517. (d) Q. An, J. Shen, N. Butt, D. Liu, Y. Liu, W. Zhang. *Adv. Synth. Catal.* **2015**, *357*, 3627.

4.NMR spectra of the products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7.9746
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7.7876
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7.7468
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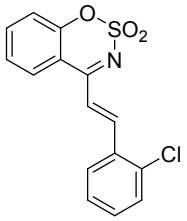
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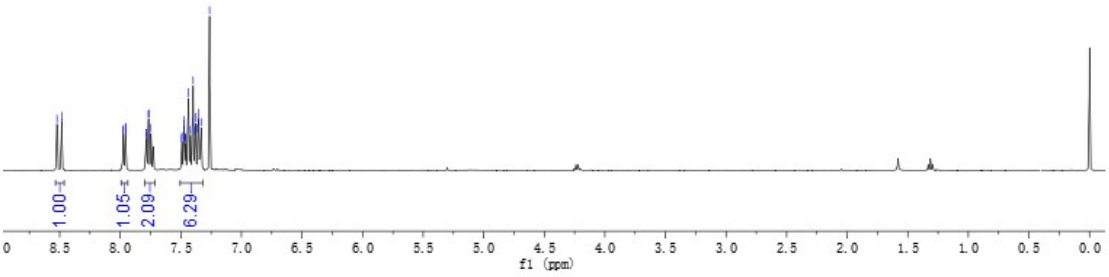
Cl

1c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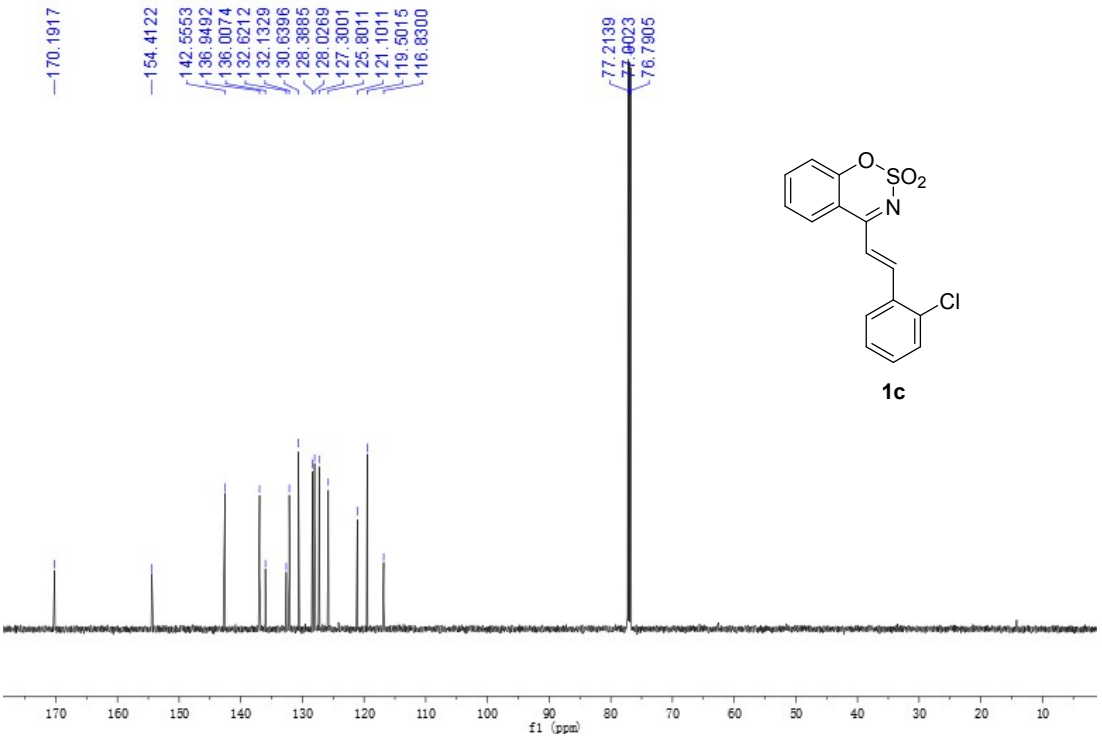
f1 (ppm)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121.1011
119.5015
116.8300
77.2139
77.0023
76.7905
f1 (ppm)

O
SO2
N
Cl

1c


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7.9756
7.9589
7.9557
7.7712
7.7677
7.7488
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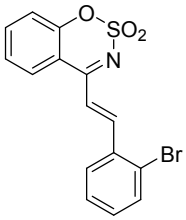
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SO2
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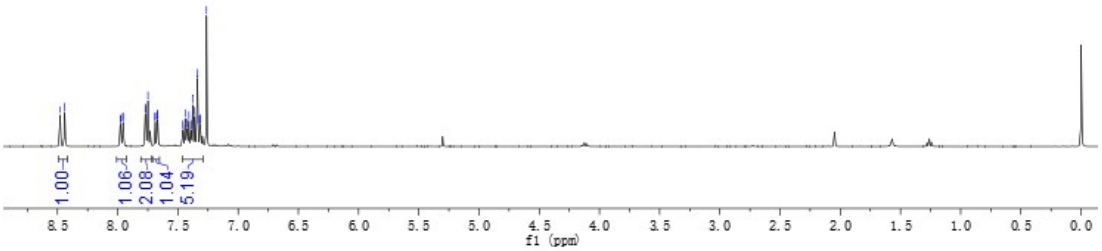
Br

1d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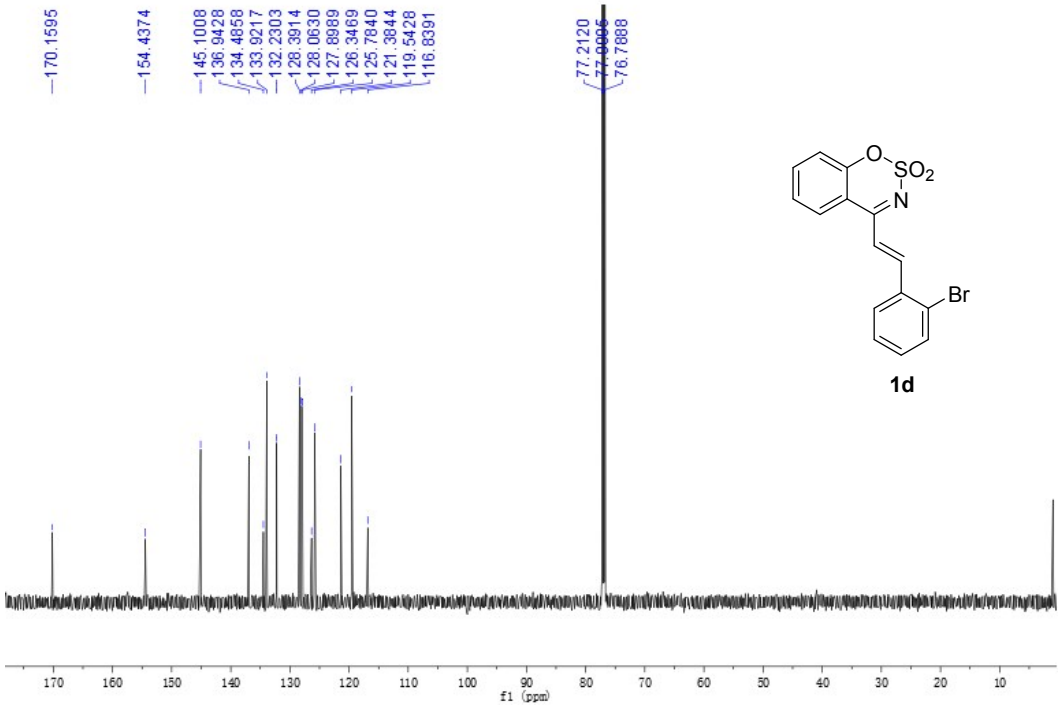
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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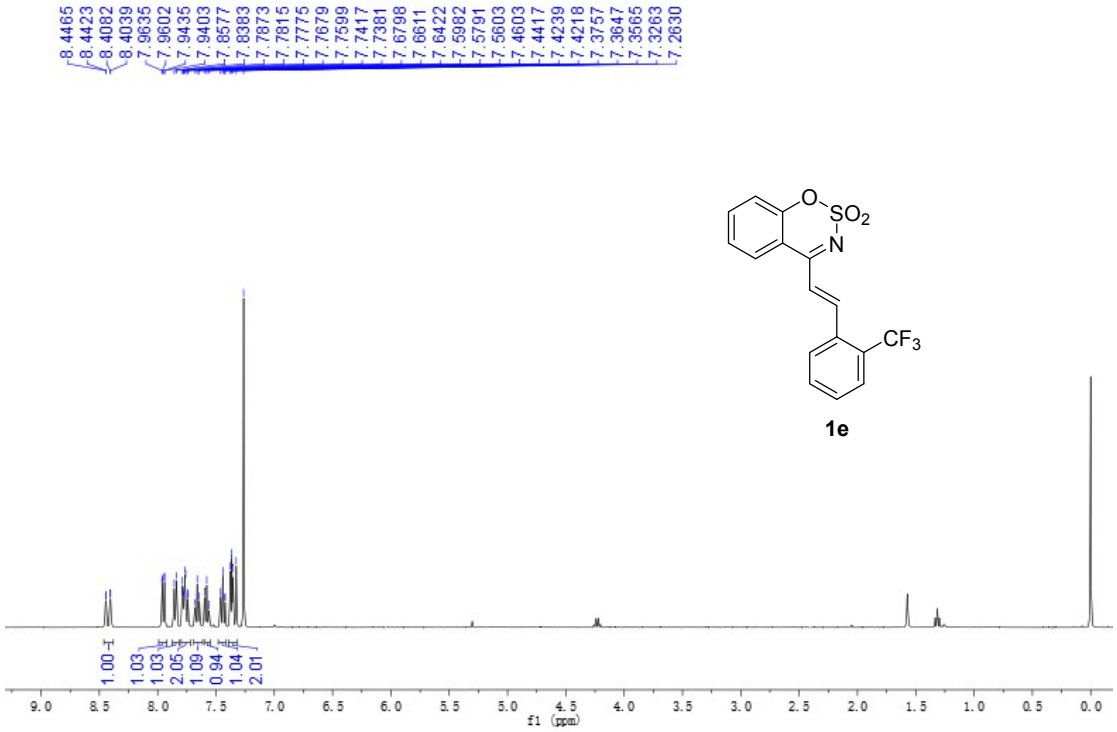
145.1008
136.9428
134.4858
133.9217
132.2303
128.3914
128.0630
127.8989
126.3469
125.7840
121.3844
119.5428
116.8391
77.2120
77.0006
76.7888
O
SO2
N
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1d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8.4082
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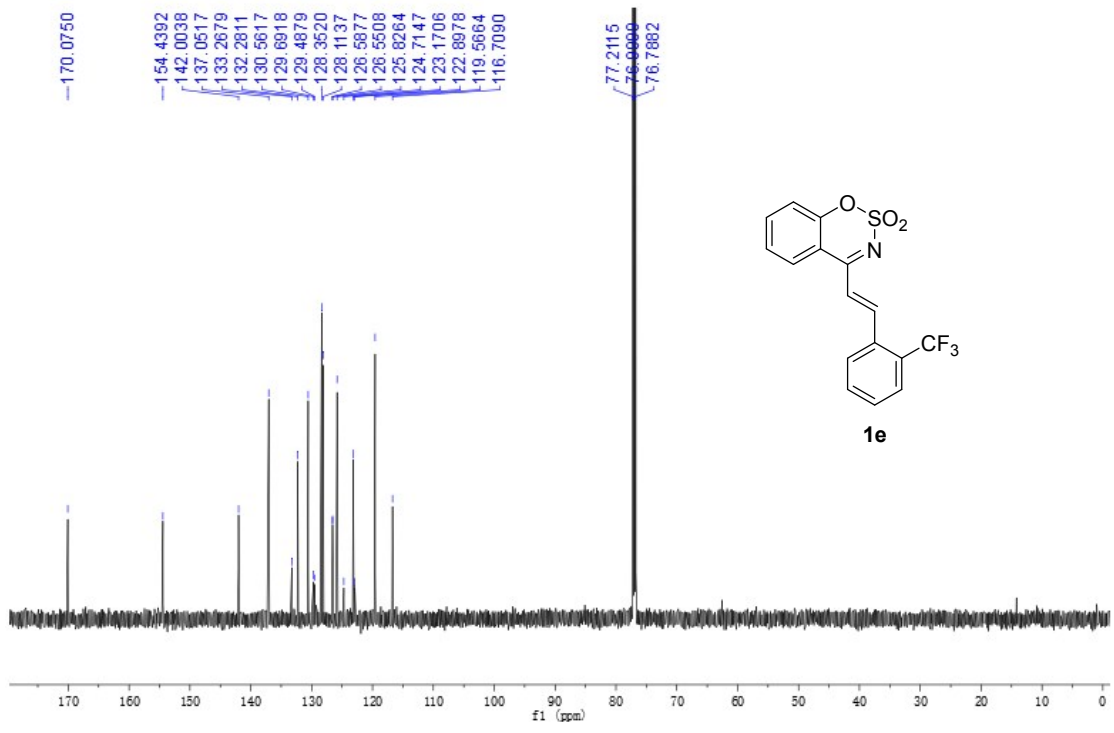
7.9635
7.9602
7.9435
7.9403
7.8577
7.8383
7.7873
7.7815
7.7775
7.7679
7.7599
7.7417
7.7381
7.6798
7.6611
7.6422
7.5982
7.5791
7.5603
7.4603
7.4417
7.4239
7.4218
7.3757
7.3647
7.3565
7.3263
7.2630
O
SO2
N
CF3
1e
1.00
1.03
1.03
2.05
1.09
0.94
1.04
2.01
f1 (ppm)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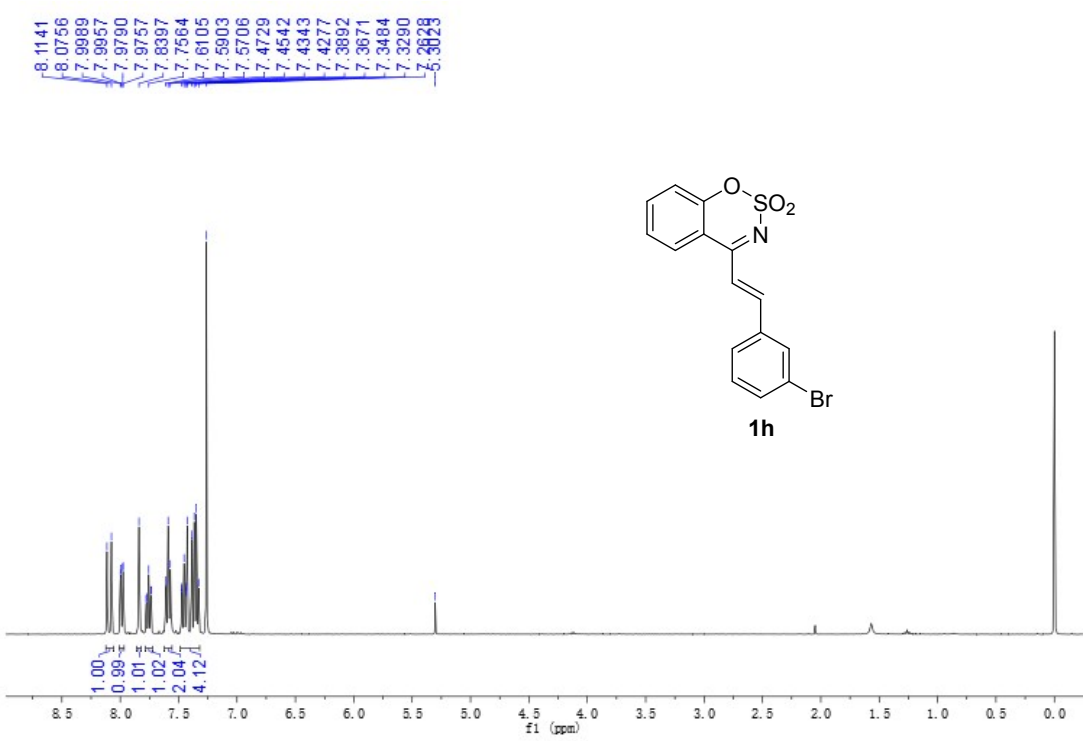
132.2811
130.5617
129.6918
129.4879
128.3520
128.1137
126.5877
126.5508
125.8264
124.7147
123.1706
122.8978
119.5664
116.7090
77.2115
76.9999
76.7882
O
SO2
N
CF3
1e
f1 (ppm)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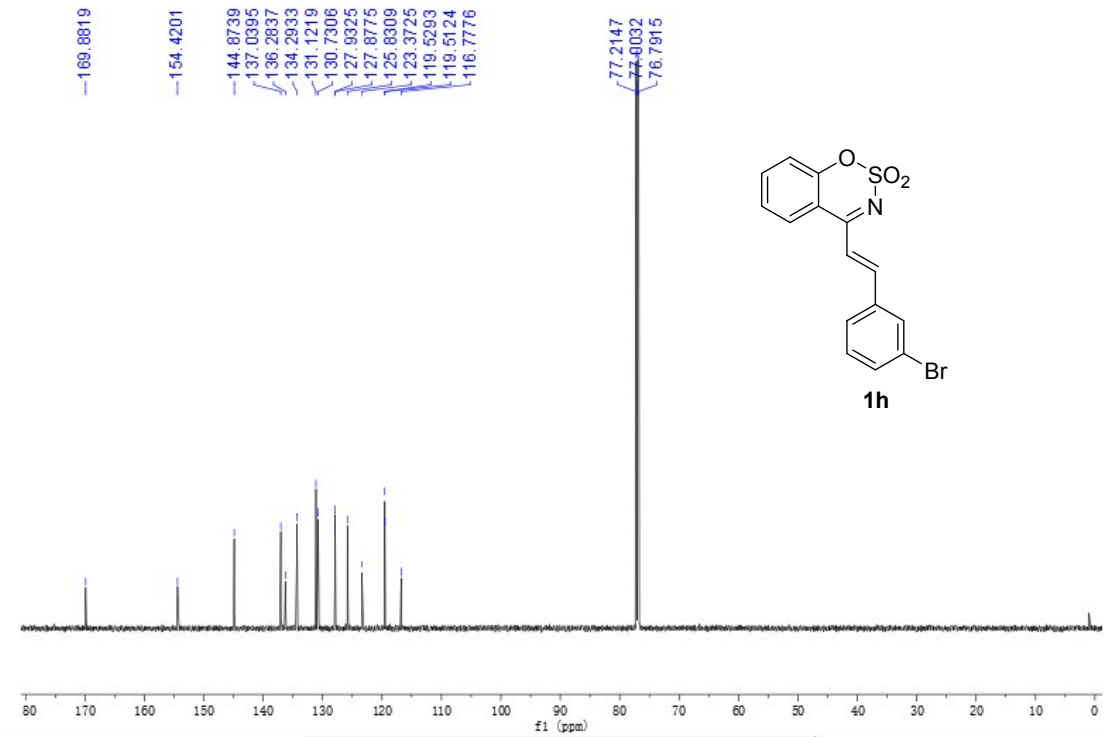
8.0756
7.9989
7.9957
7.9790
7.9757
7.8397
7.7564
7.6105
7.5903
7.5706
7.4729
7.4542
7.4343
7.4277
7.3892
7.3671
7.3484
7.3290
1.00
0.99
1.01
1.02
2.04
4.12
f1 (ppm)
1h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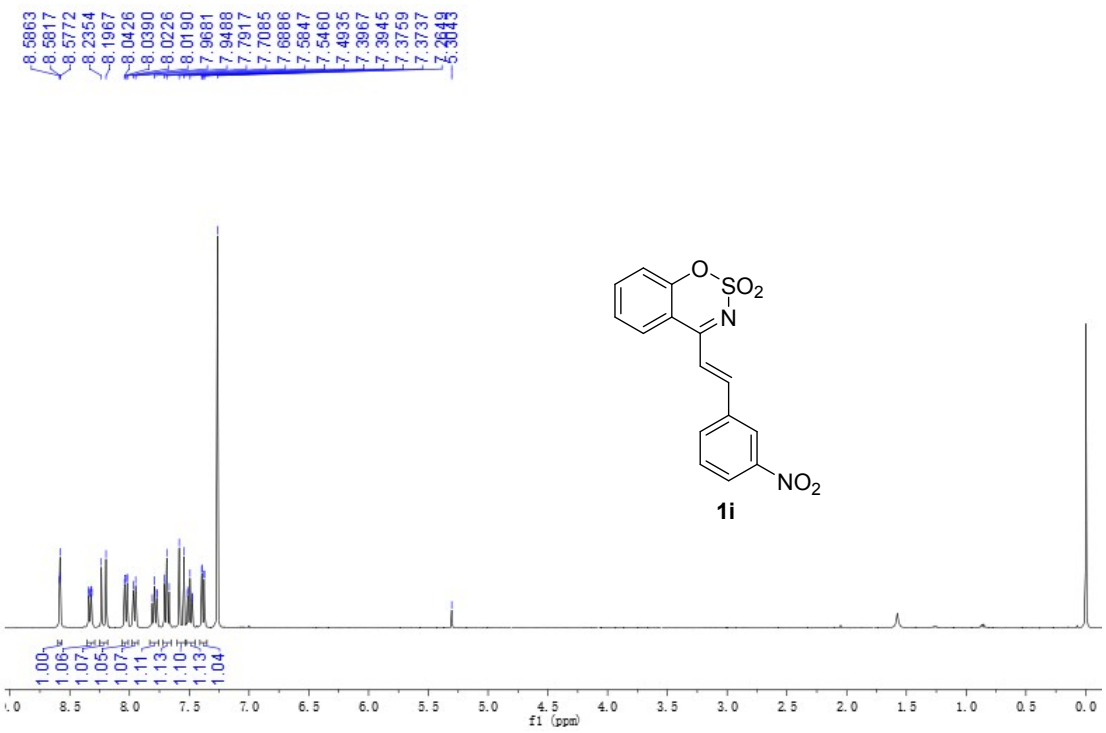
154.4201
144.8739
137.0395
136.2837
134.2933
131.1219
130.7306
127.9325
127.8775
125.8309
123.3725
119.5293
119.5124
116.7776
77.2147
77.0032
76.7915
f1 (ppm)
1h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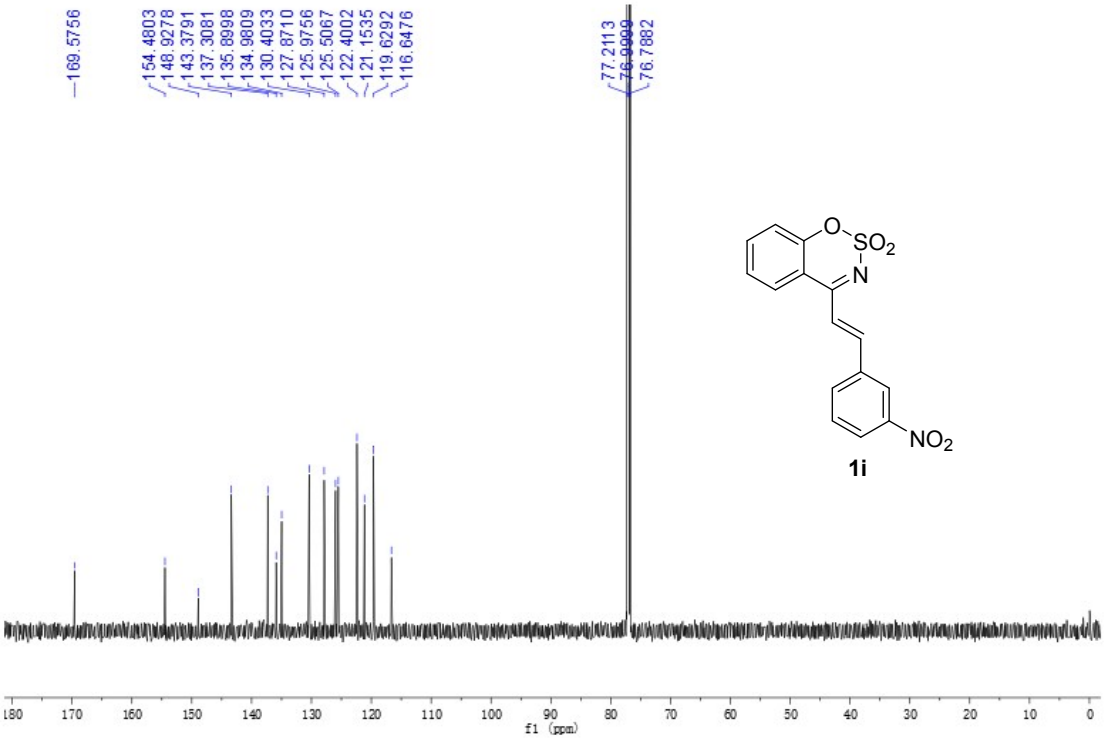
8.5817
8.5772
8.2354
8.1967
8.0426
8.0390
8.0226
8.0190
7.9681
7.9488
7.7917
7.7085
7.6886
7.5847
7.5460
7.4935
7.3967
7.3945
7.3759
7.3737
1.00
1.06
1.07
1.05
1.07
1.11
1.13
1.10
1.13
1.04
f1 (ppm)
O
SO2
N
NO2
1i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143.3791
137.3081
135.8998
134.9809
130.4033
127.8710
125.9756
125.5067
122.4002
121.1535
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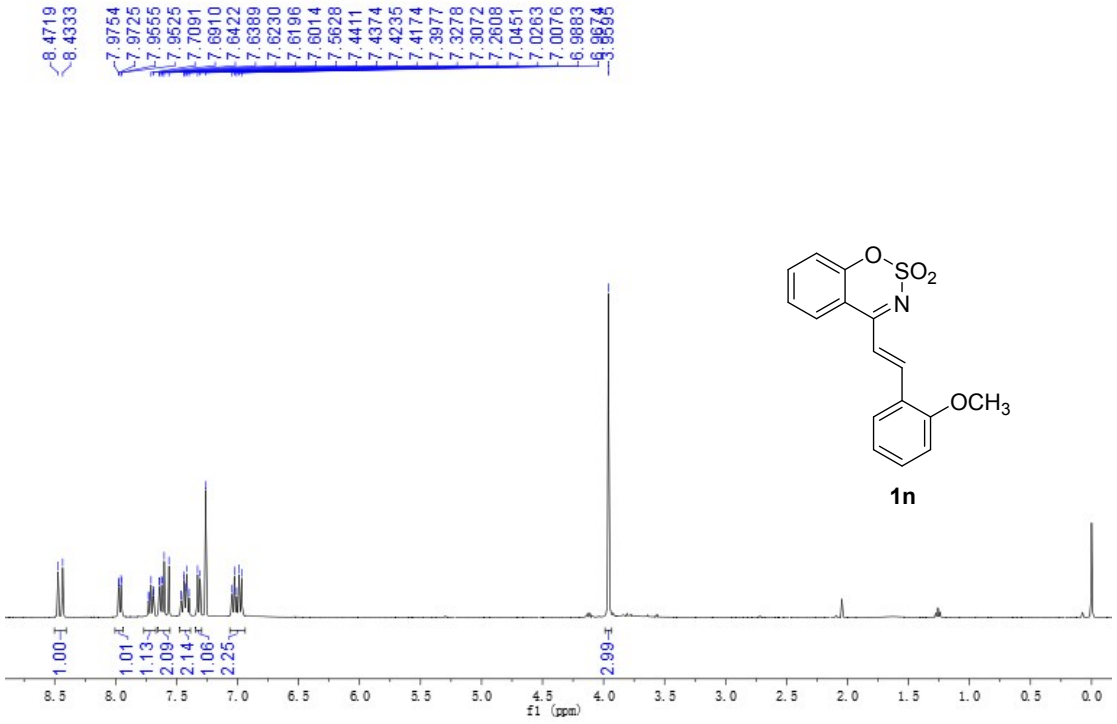
116.6476
77.2113
76.9999
76.7882
f1 (ppm)
O
SO2
N
NO2
1i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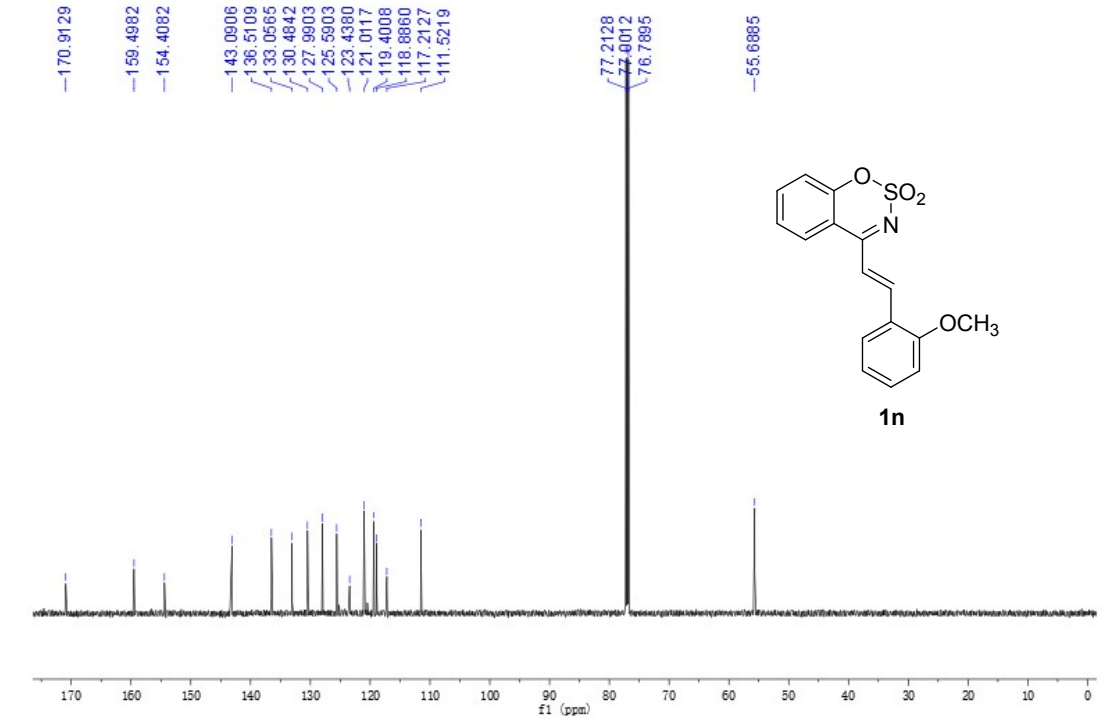
7.9754
7.9725
7.9555
7.9525
7.7091
7.6910
7.6422
7.6389
7.6230
7.6196
7.6014
7.5628
7.4411
7.4374
7.4235
7.4174
7.3977
7.3278
7.3072
7.2608
7.0451
7.0263
7.0076
6.9883
O
SO2
N
OCH3
1n
1.00
1.01
1.13
2.09
2.14
1.06
2.25
2.99
f1 (ppm)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154.4082
143.0906
136.5109
133.0565
130.4842
127.9903
125.5903
123.4380
121.0117
119.4008
118.8860
117.2127
111.5219
77.2128
77.0012
76.7895
55.6885
O
SO2
N
OCH3
1n
f1 (ppm)


8.2197
8.1816
7.9702
7.9668
7.9502
7.9468
7.7497
7.7457
7.7280
7.7104
7.7066
7.4780
7.4755
7.4652
7.4628
7.4441
7.4361
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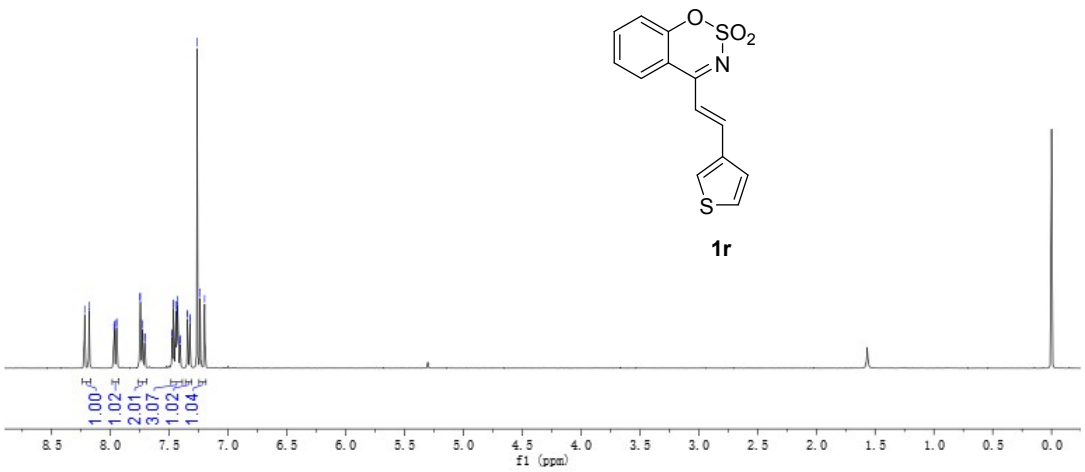
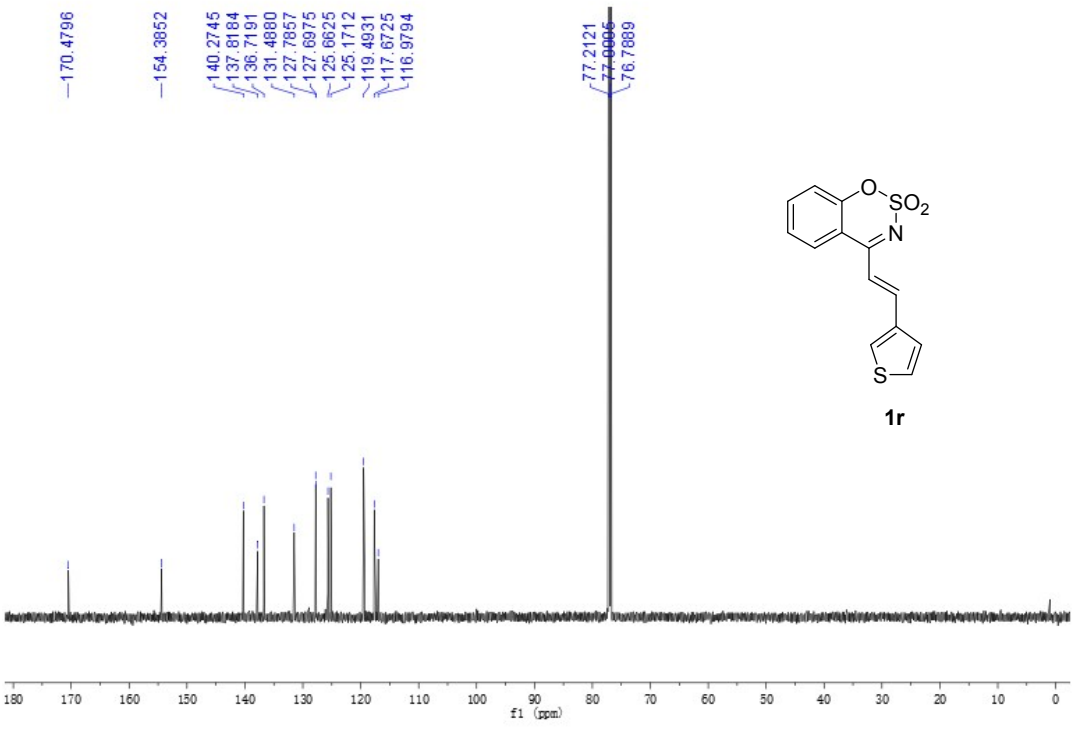
7.3255
7.3237
7.2629
7.2376
7.1995


1.00
1.02
2.01
3.07
1.02
1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

O
SO2
N
S

1r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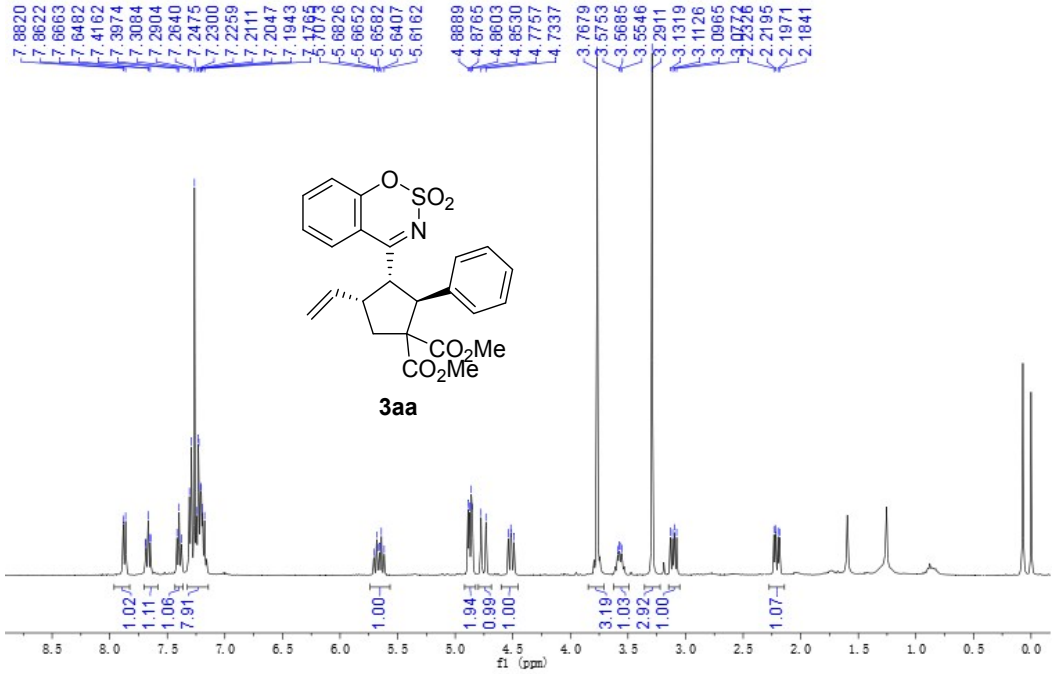
140.2745
137.8184
136.7191
131.4880
127.7857
127.6975
125.6625
125.1712
119.4931
117.6725
116.9794
77.2121
77.0006
76.7889
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

O
SO2
N
S

1r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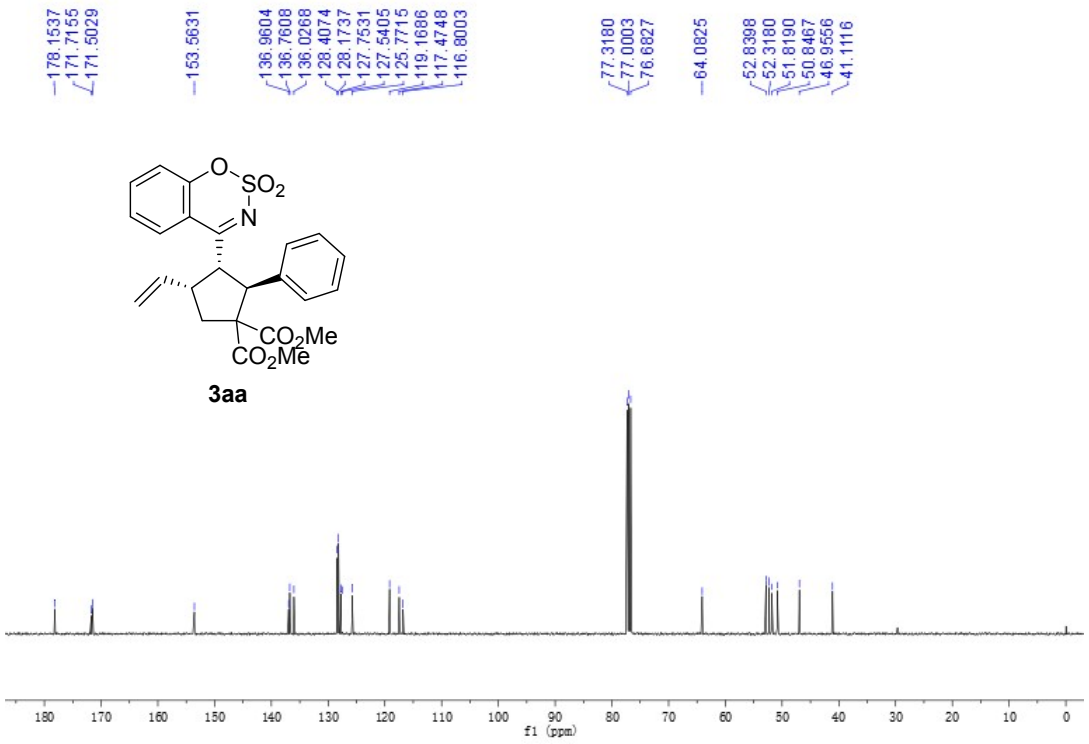
7.8622
7.6663
7.6482
7.4162
7.3974
7.3084
7.2904
7.2640
7.2475
7.2300
7.2259
7.2111
7.2047
7.1943
5.6826
5.6652
5.6582
5.6407
5.6162
4.8889
4.8765
4.8603
4.8530
4.7757
4.7337
3.7679
3.5753
3.5685
3.5546
3.2911
3.1319
3.1126
3.0965
2.2195
2.1971
2.1841
O
SO2
N
CO2Me
CO2Me
1.02
1.11
1.06
7.91
1.00
1.94
0.99
1.00
3.19
1.03
2.92
1.00
1.07
f1 (ppm)

3aa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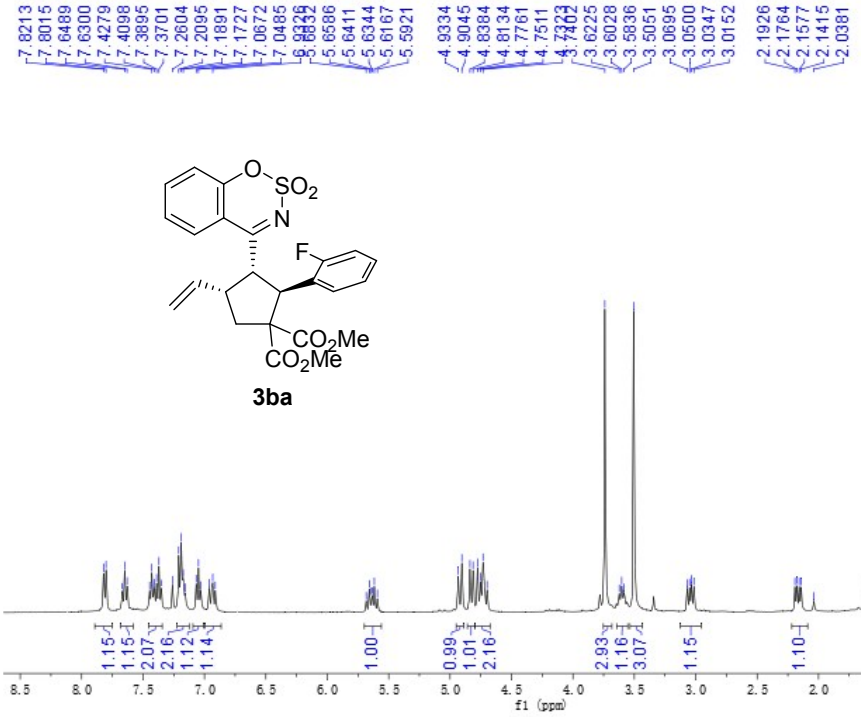
171.7155
171.5029
153.5631
136.9604
136.7608
136.0268
128.4074
128.1737
127.7531
127.5405
125.7715
119.1686
117.4748
116.8003
77.3180
77.0003
76.6827
64.0825
52.8398
52.3180
51.8190
50.8467
46.9556
41.1116
O
SO2
N
CO2Me
CO2Me
f1 (ppm)

3aa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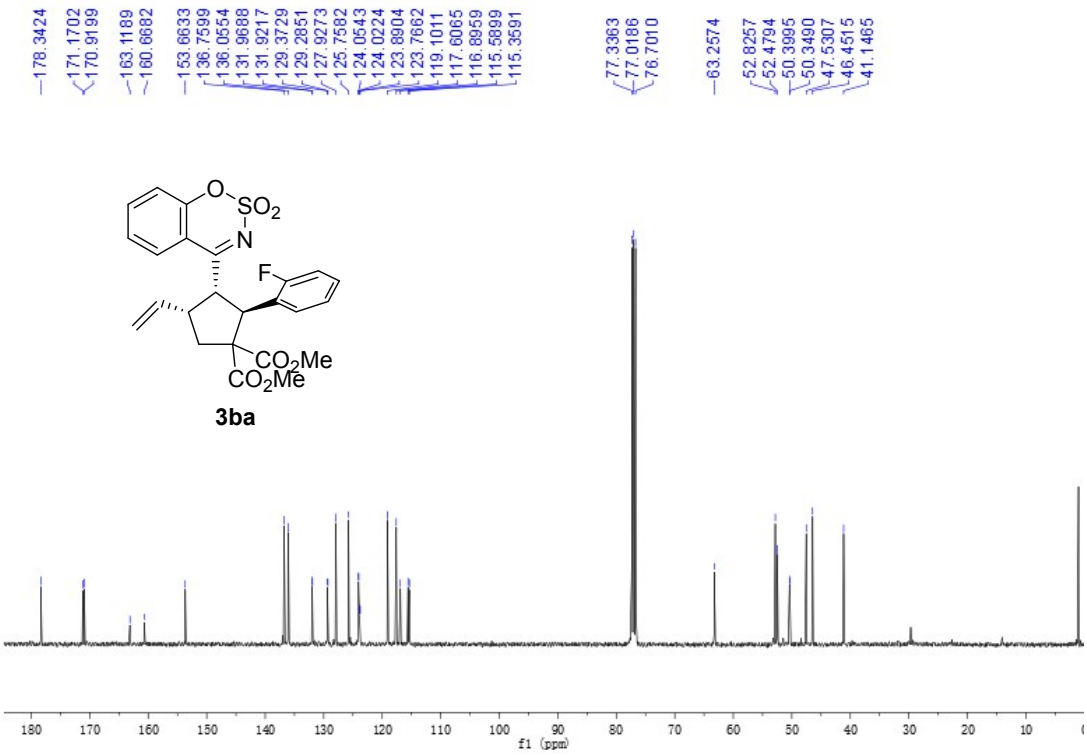
7.6489
7.6300
7.4279
7.4098
7.3895
7.3701
7.2604
7.2095
7.1891
7.1727
7.0672
7.0485
5.6586
5.6411
5.6344
5.6167
5.5921
4.9334
4.9045
4.8384
4.8134
4.7761
4.7511
3.6225
3.6028
3.5836
3.5051
3.0695
3.0500
3.0347
3.0152
2.1926
2.1764
2.1577
2.1415
2.0381
O
SO2
N
F
CO2Me
CO2Me
1.15
1.15
2.07
2.16
1.12
1.14
1.00
0.99
1.01
2.16
2.93
1.16
3.07
1.15
1.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ba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170.9199
163.1189
160.6682
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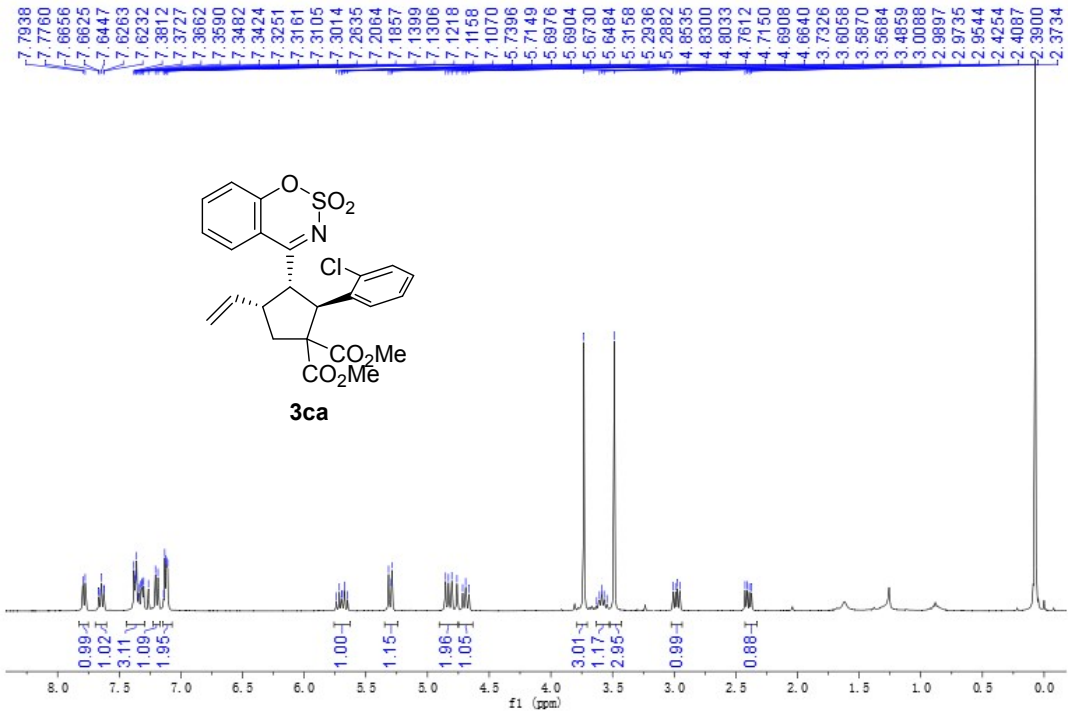
136.7599
136.0554
131.9688
131.9217
129.3729
129.2851
127.9273
125.7582
124.0543
124.0224
123.8904
123.7662
119.1011
117.6065
116.8959
115.5899
115.3591
77.3363
77.0186
76.7010
63.2574
52.8257
52.4794
50.3995
50.3490
47.5307
46.4515
41.1465
O
SO2
N
F
CO2Me
CO2Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3ba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7.6447
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7.6232
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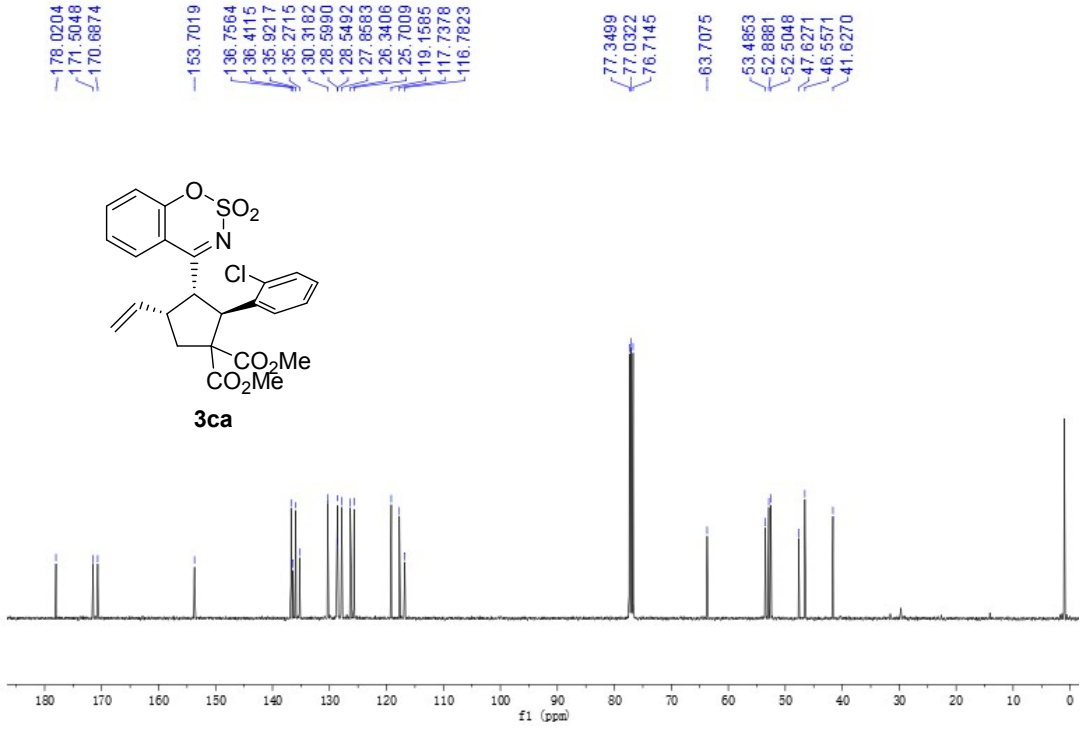
7.3727
7.3662
7.3590
7.3482
7.3424
7.3251
7.3161
7.3105
7.3014
7.2635
7.2064
7.1857
7.1399
7.1306
7.1218
7.1158
7.1070
5.7396
5.7149
5.6976
5.6904
5.6730
5.6484
5.3158
5.2936
5.2882
4.8535
4.8300
4.8033
4.7612
4.7150
4.6908
4.6640
3.7326
3.6058
3.5870
3.5684
3.4859
3.0088
2.9897
2.9735
2.9544
2.4254
2.4087
2.3900
2.3734
O
SO2
N
Cl
CO2Me
CO2Me
0.99
1.02
3.11
1.09
1.95
1.00
1.15
1.96
1.05
3.01
1.17
2.95
0.99
0.88
f1 (ppm)

3ca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136.4115
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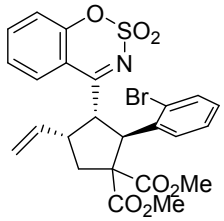
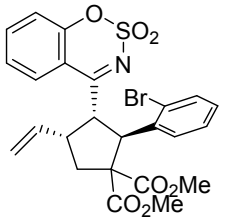
130.3182
128.5990
128.5492
127.8583
126.3406
125.7009
119.1585
117.7378
116.7823
77.3499
77.0322
76.7145
63.7075
53.4853
52.8881
52.5048
47.6271
46.5571
41.6270
O
SO2
N
Cl
CO2Me
CO2Me
f1 (ppm)

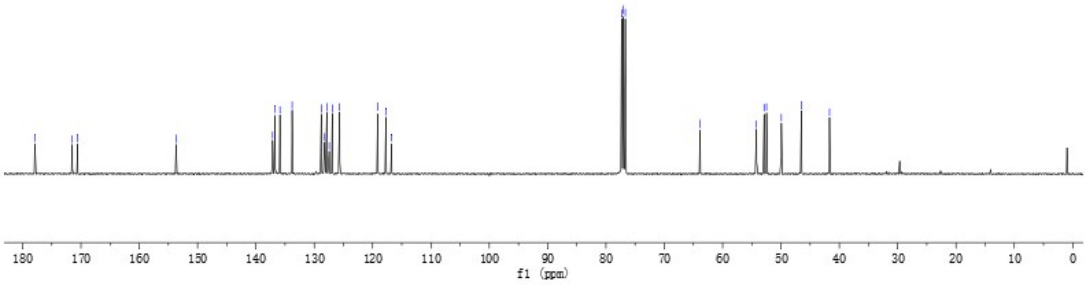
3ca

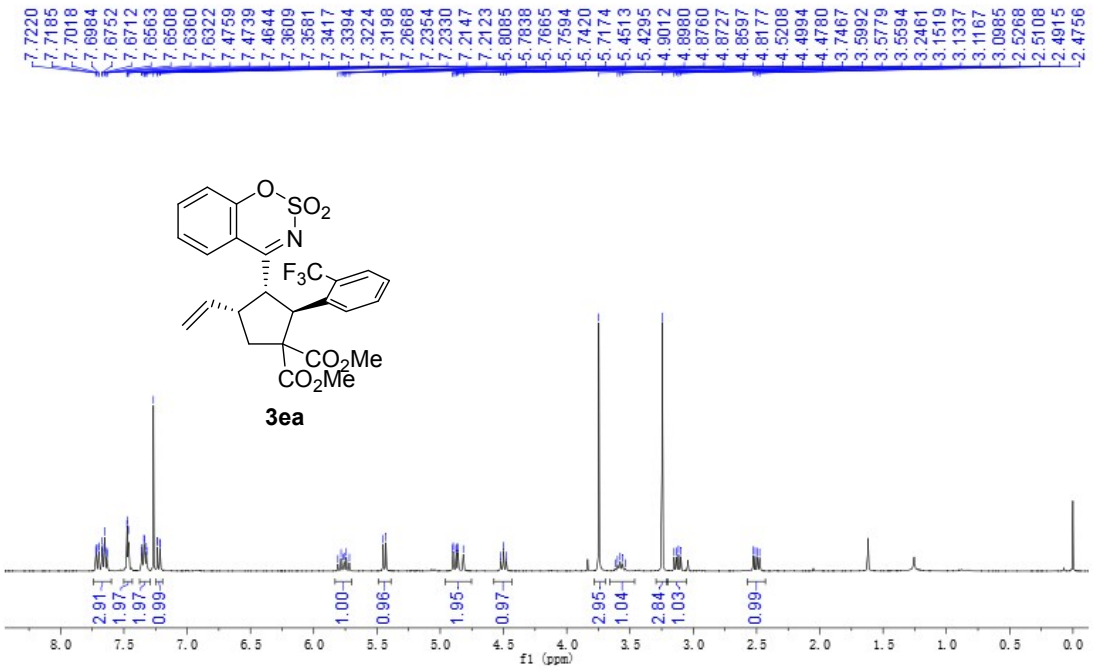


3da



3da

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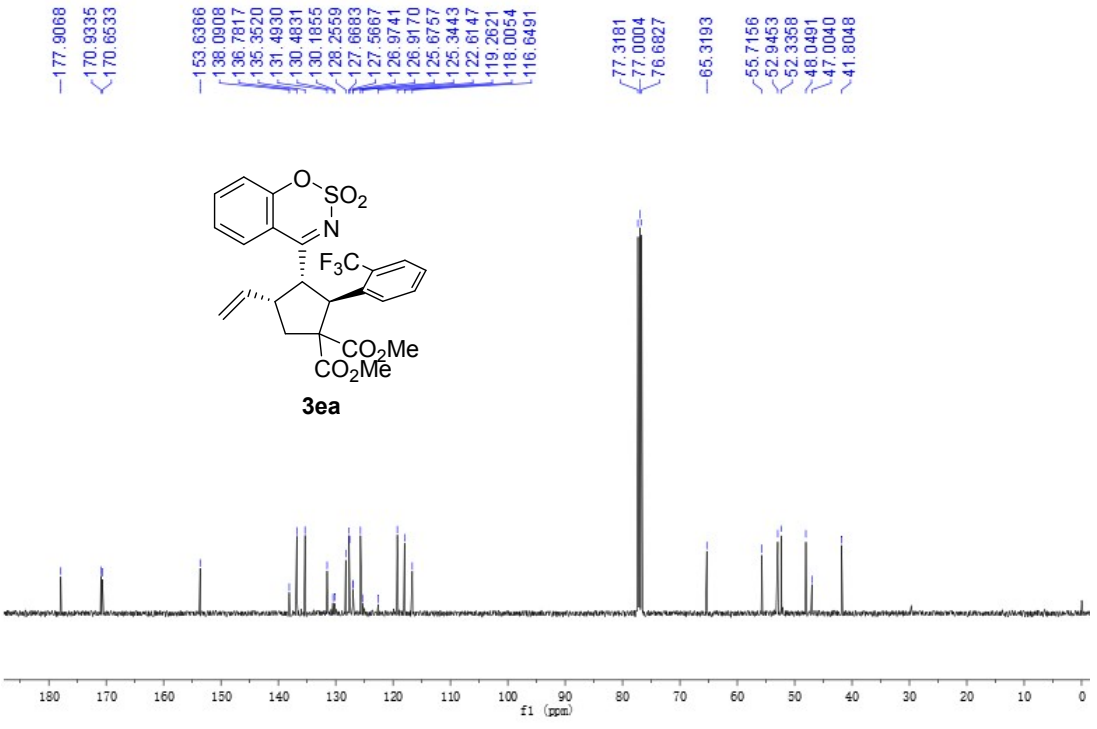
7.6508
7.6360
7.6322
7.4759
7.4739
7.4644
7.3609
7.3581
7.3417
7.3394
7.3224
7.3198
7.2668
7.2354
7.2330
7.2147
7.2123
5.8085
5.7838
5.7665
5.7594
5.7420
5.7174
5.4513
5.4295
4.9012
4.8980
4.8760
4.8727
4.8597
4.8177
4.5208
4.4994
4.4780
3.7467
3.5992
3.5779
3.5594
3.2461
3.1519
3.1337
3.1167
3.0985
2.5268
2.5108
2.4915
2.4756
O
SO2
N
F3C
CO2Me
CO2Me
2.91
1.97
1.97
0.99
1.00
0.96
1.95
0.97
2.95
1.04
2.84
1.03
0.99
f1 (ppm)

3ea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170.6533
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138.0908
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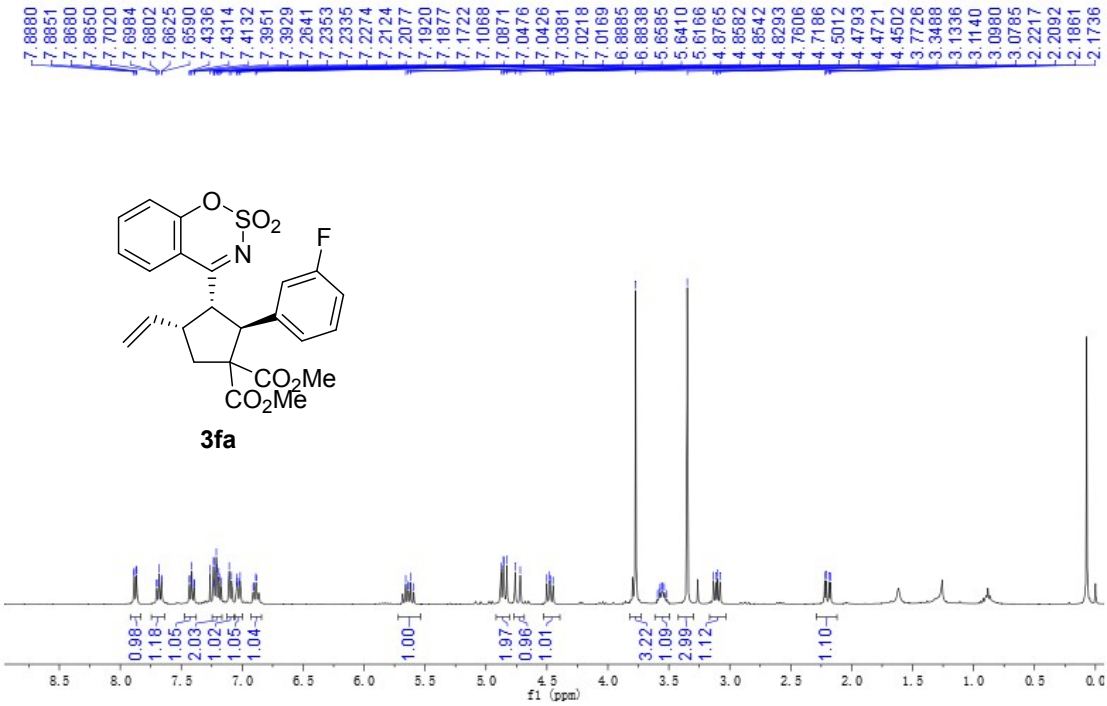
135.3520
131.4930
130.4831
130.1855
128.2559
127.6683
127.5667
126.9741
126.9170
125.6757
125.3443
122.6147
119.2621
118.0054
116.6491
77.3181
77.0004
76.6827
65.3193
55.7156
52.9453
52.3358
48.0491
47.0040
41.8048
O
SO2
N
F3C
CO2Me
CO2Me
f1 (ppm)

3ea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7.6590
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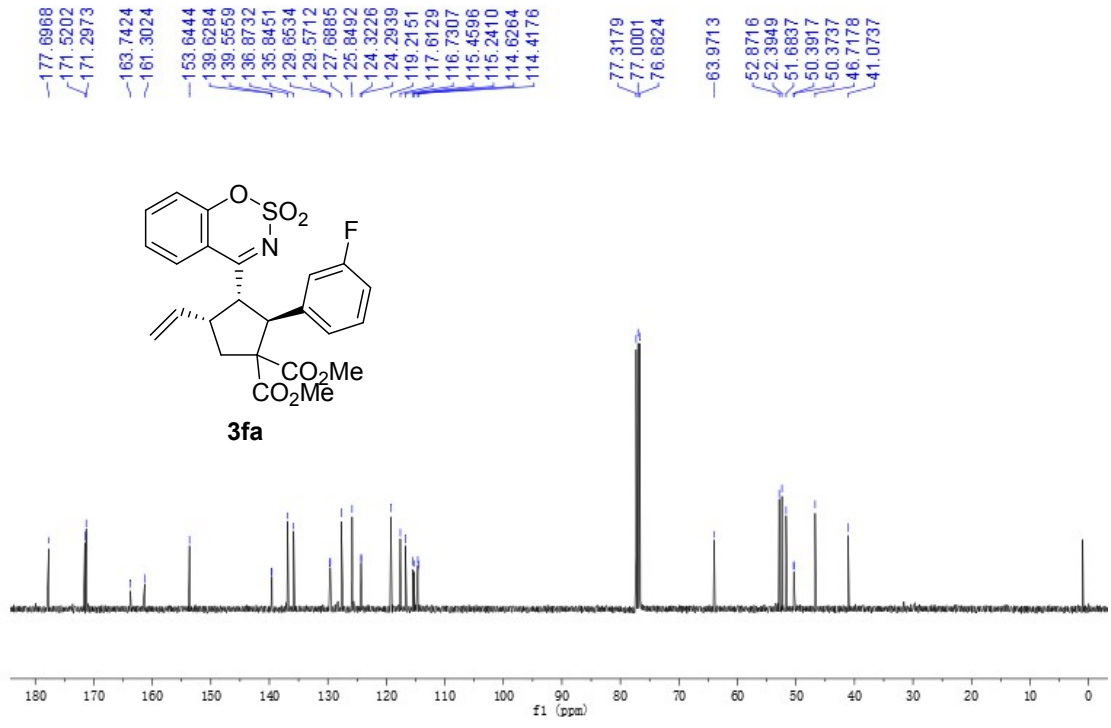
7.4132
7.3951
7.3929
7.2641
7.2353
7.2335
7.2274
7.2124
7.2077
7.1920
7.1877
7.1722
7.1068
7.0871
7.0476
7.0426
7.0381
7.0218
7.0169
6.8885
6.8838
5.6585
5.6410
5.6166
4.8765
4.8582
4.8542
4.8293
4.7606
4.7186
4.5012
4.4793
4.4721
4.4502
3.7726
3.3488
3.1336
3.1140
3.0980
3.0785
2.2217
2.2092
2.1861
2.1736
O
SO2
N
F
CO2Me
CO2Me
0.98
1.18
1.05
2.03
1.02
1.05
1.04
1.00
1.97
0.96
1.01
3.22
1.09
2.99
1.12
1.10
f1 (ppm)

3fa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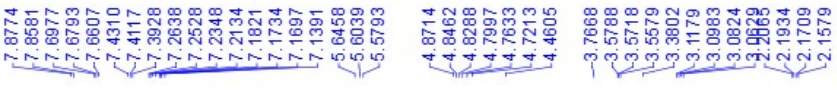
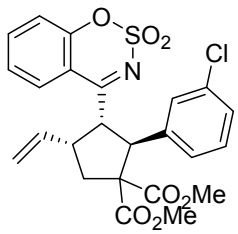
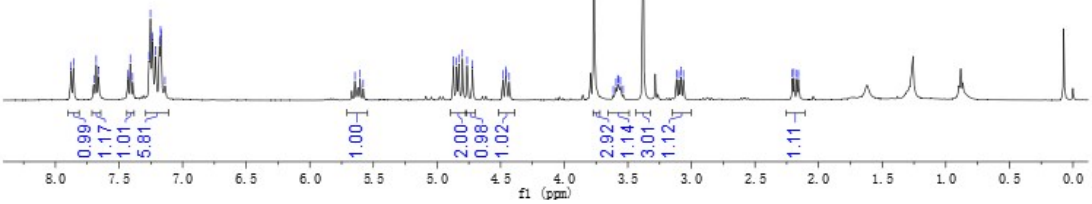
129.6534
129.5712
127.6885
125.8492
124.3226
124.2939
119.2151
117.6129
116.7307
115.4596
115.2410
114.6264
114.4176
77.3179
77.0001
76.6824
63.9713
52.8716
52.3949
51.6837
50.3917
50.3737
46.7178
41.0737
O
SO2
N
F
CO2Me
CO2Me
f1 (ppm)

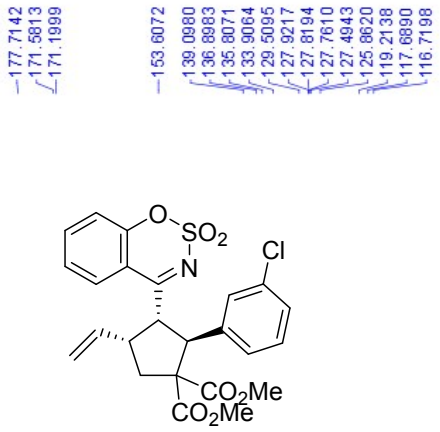
3fa


7.8774
7.8581
7.6977
7.6793
7.6607
7.4310
7.4117
7.3928
7.2638
7.2528
7.2348
7.2134
7.1821
7.1734
7.1697
7.1391
5.6458
5.6039
5.5793
4.8714
4.8462
4.8288
4.7997
4.7633
4.7213
4.4605
3.7668
3.5788
3.5718
3.5579
3.3802
3.1179
3.0983
3.0824
2.2065
2.1934
2.1709
2.1579


O
SO2
N
Cl
CO2Me
CO2Me

3ga


0.99
1.17
1.01
5.81
1.00
2.00
0.98
1.02
2.92
1.14
3.01
1.12
1.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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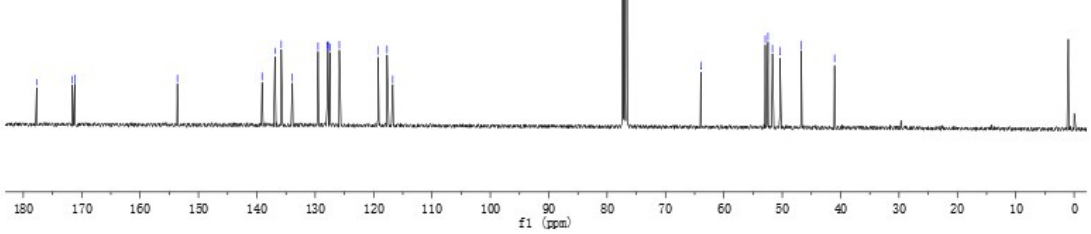
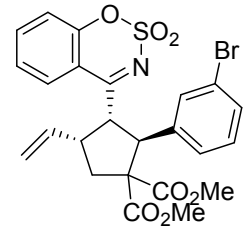
171.5813
171.1999
153.6072
139.0980
136.8983
135.8071
133.9064
129.5095
127.9217
127.8194
127.7610
127.4943
125.8620
119.2138
117.6890
116.7198
77.3176
77.0001
76.6824
63.9436
52.9106
52.4487
51.6839
50.3816
46.7453
41.0441

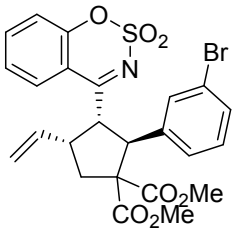
O
SO2
N
Cl
CO2Me
CO2Me

3ga

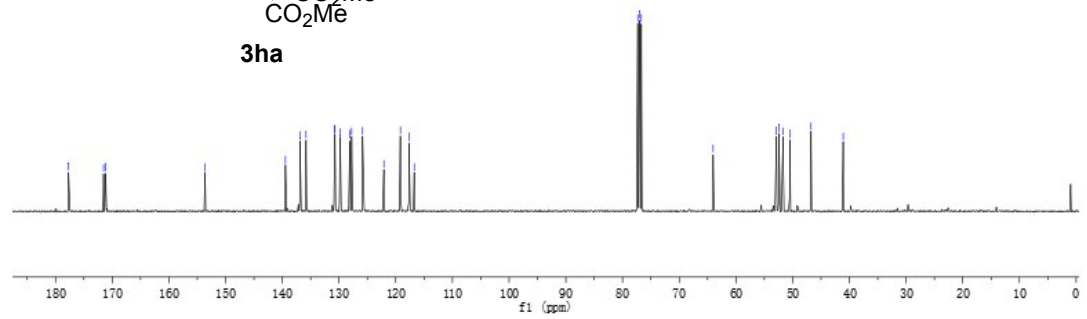

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

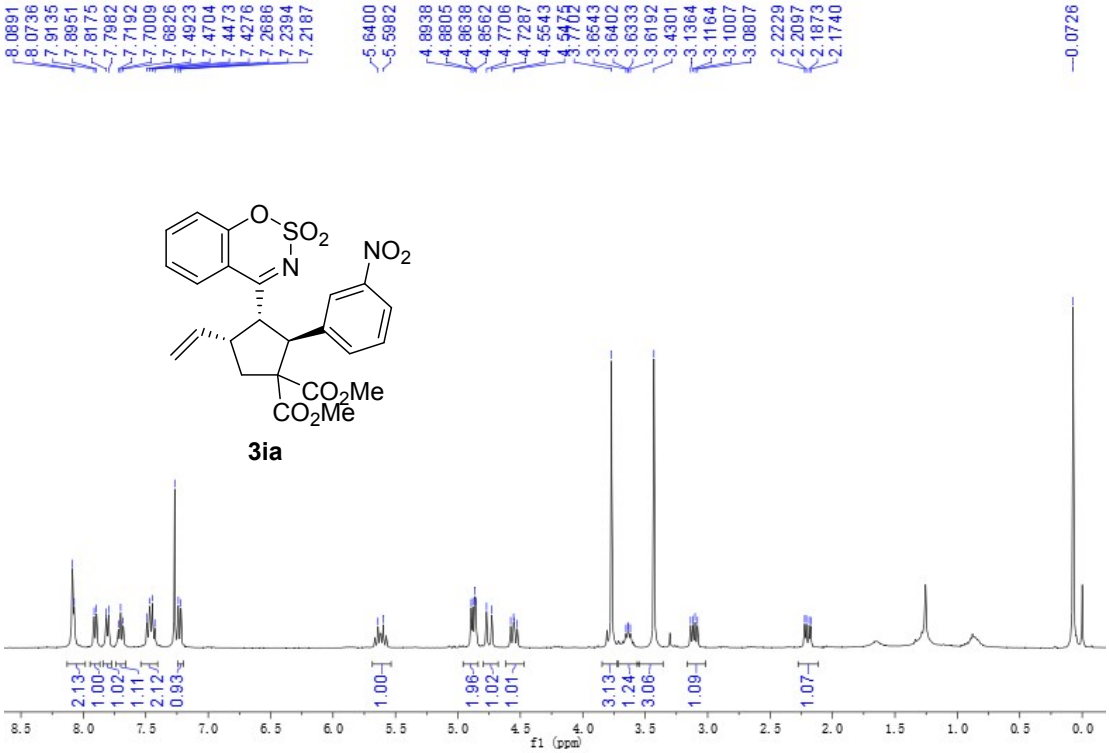


3ha



3ha

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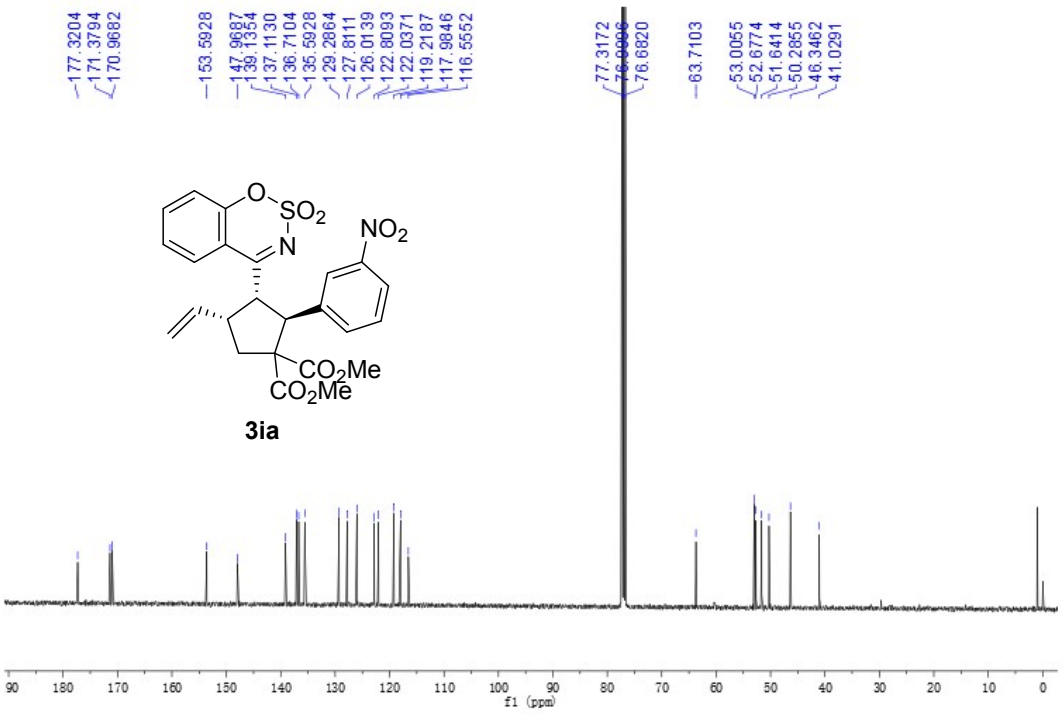
7.8951
7.8175
7.7982
7.7192
7.7009
7.6826
7.4923
7.4704
7.4473
7.4276
7.2686
7.2394
7.2187
5.6400
5.5982
4.8938
4.8805
4.8638
4.8562
4.7706
4.7287
4.5543
3.7702
3.6543
3.6402
3.6333
3.6192
3.4301
3.1364
3.1164
3.1007
3.0807
2.2229
2.2097
2.1873
2.1740
-0.0726
O
SO2
N
NO2
CO2Me
CO2Me
2.13
1.00
1.02
1.11
2.12
0.93
1.00
1.96
1.02
1.01
3.13
1.24
3.06
1.09
1.07
f1 (ppm)

3ia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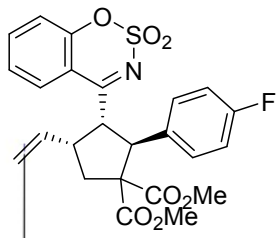
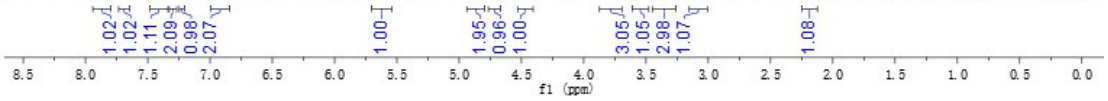
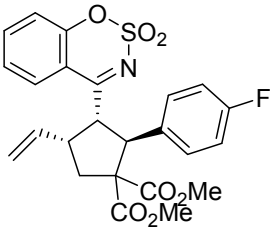
171.3794
170.9682
153.5928
147.9687
139.1354
137.1130
136.7104
135.5928
129.2864
127.8111
126.0139
122.8093
122.0371
119.2187
117.9846
116.5552
77.3172
76.9996
76.6820
63.7103
53.0055
52.6774
51.6414
50.2855
46.3462
41.0291
O
SO2
N
NO2
CO2Me
CO2Me
f1 (ppm)

3ia

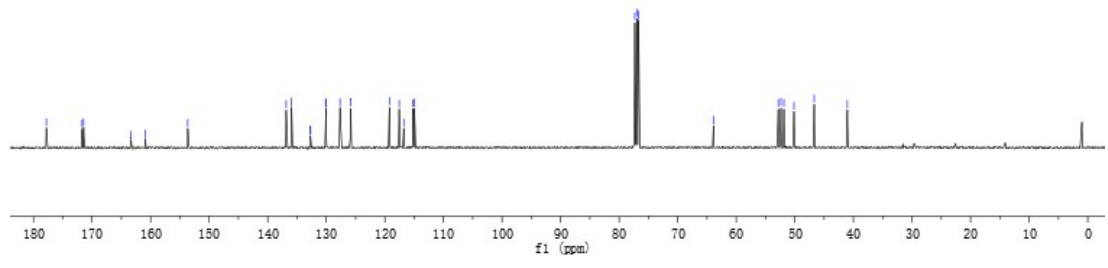


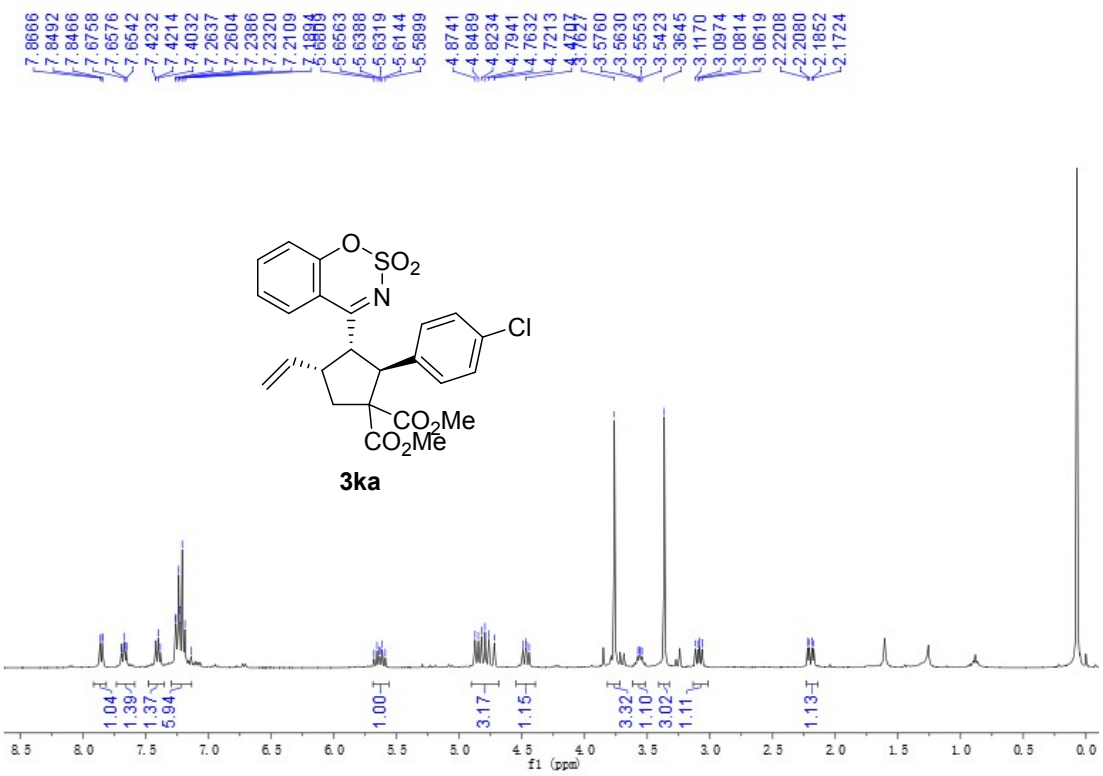
3ja





3ja

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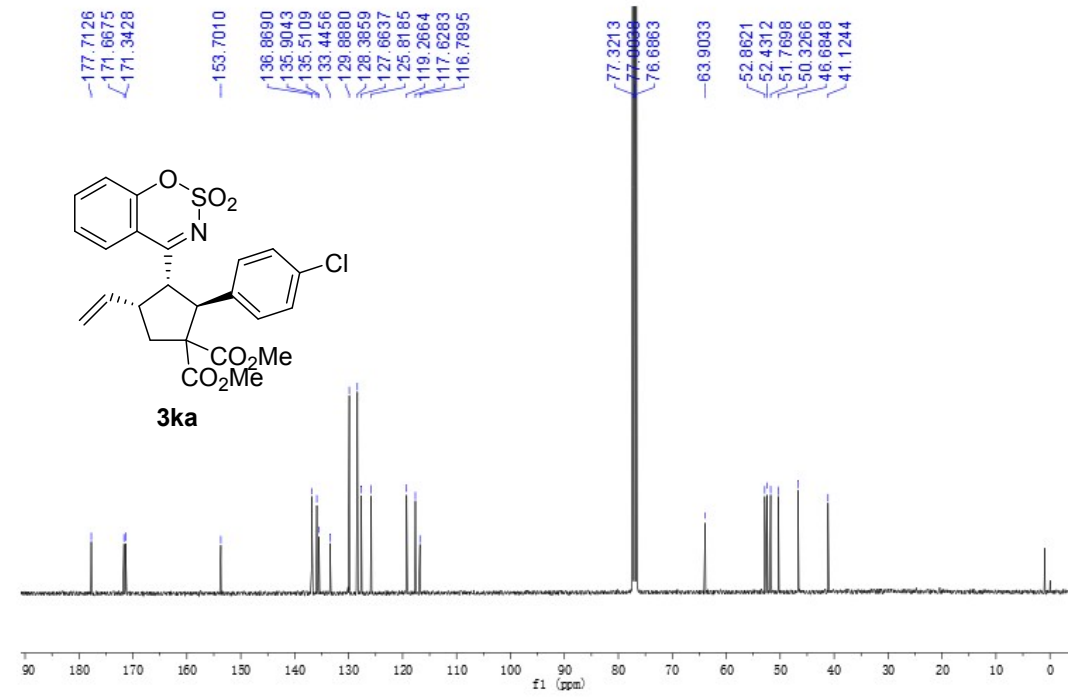
7.6576
7.6542
7.4232
7.4214
7.4032
7.2637
7.2604
7.2386
7.2320
7.2109
5.6663
5.6388
5.6319
5.6144
5.5899
4.8741
4.8489
4.8234
4.7941
4.7632
4.7213
3.5760
3.5630
3.5553
3.5423
3.3645
3.1170
3.0974
3.0814
3.0619
2.2208
2.2080
2.1852
2.1724
O
SO2
N
Cl
CO2Me
CO2Me
3ka
1.04
1.39
1.37
5.94
1.00
3.17
1.15
3.32
1.10
3.02
1.11
1.13
f1 (ppm)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171.3428
153.7010
136.8690
135.9043
135.5109
133.4456
129.8880
128.3859
127.6637
125.8185
119.2664
117.6283
116.7895
77.3213
76.6863
63.9033
52.8621
52.4312
51.7698
50.3266
46.6848
41.1244
O
SO2
N
Cl
CO2Me
CO2Me
3ka
f1 (ppm)


7.8912
7.8714
7.7038
7.6840
7.6648
7.5078
7.4872
7.4547
7.4349
7.4168
7.3976
7.2659
7.2308
7.2101
5.6872
5.6626
5.6448
5.6385
5.6208
5.5962
4.9202
4.8895
4.8620
4.7758
4.7339
4.5354
3.7689
3.5927
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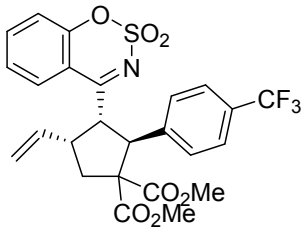
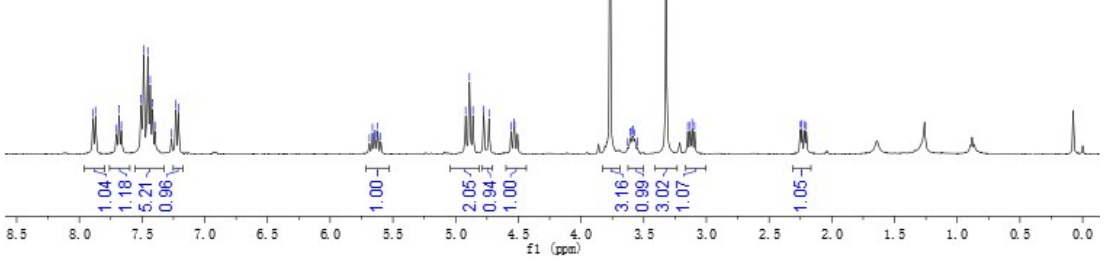
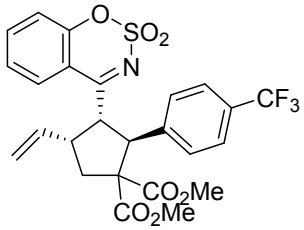
3.5722
3.3213
3.1489
3.1295
3.1133
2.2387
2.2155
2.2030


O
SO2
N
CF3
CO2Me
CO2Me

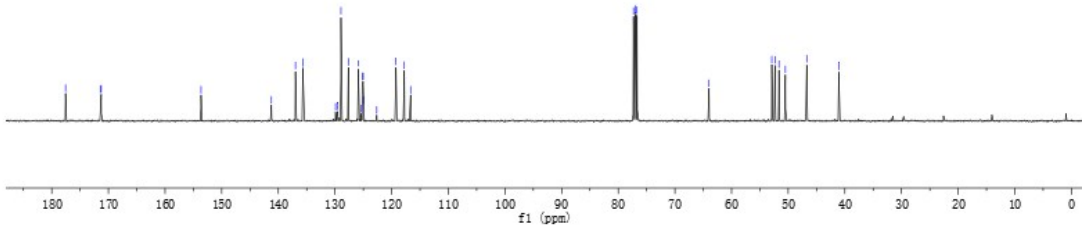
3la

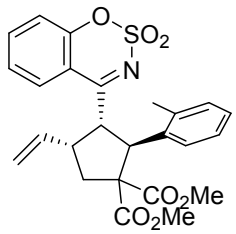

1.04
1.18
5.21
0.96
1.00
2.05
0.94
1.00
3.16
0.99
3.02
1.07
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.5625
171.4239
171.2649
153.6447
141.2206
136.9836
135.6815
129.9000
129.5778
128.9494
127.6507
125.8902
125.3315
125.0799
125.0430
125.0065
122.6275
119.2337
117.7602
116.6588
77.3175
76.9998
76.6819
63.9706
52.8993
52.3480
51.6439
50.4994
46.7334
41.0749

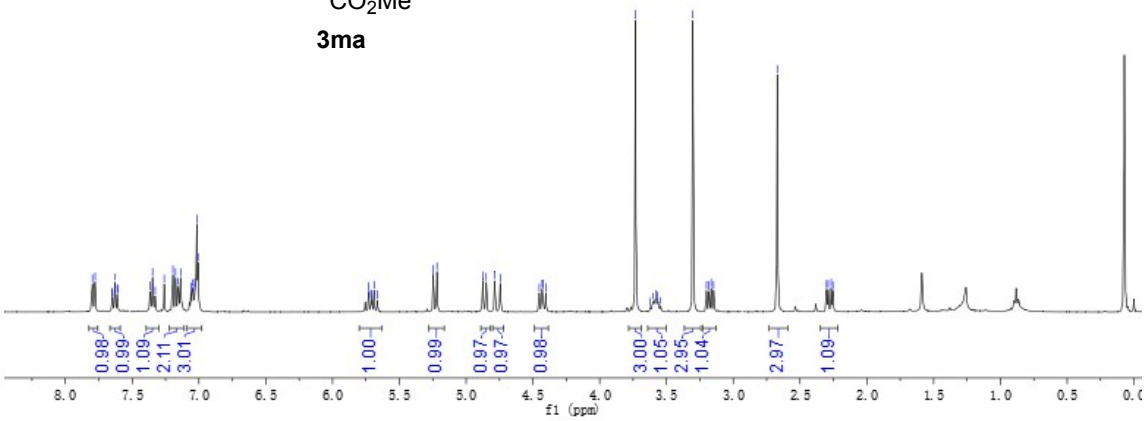

O
SO2
N
CF3
CO2Me
CO2Me

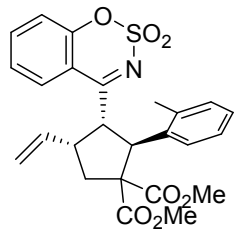
3la


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

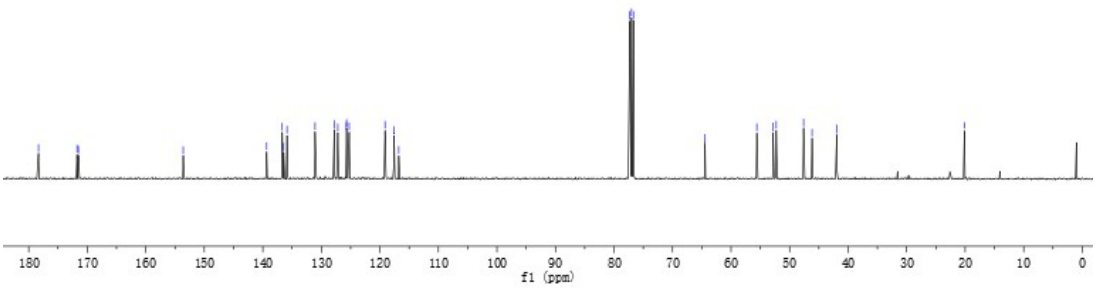


3ma

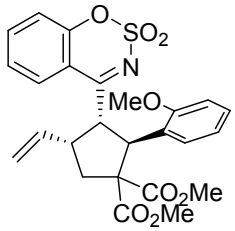




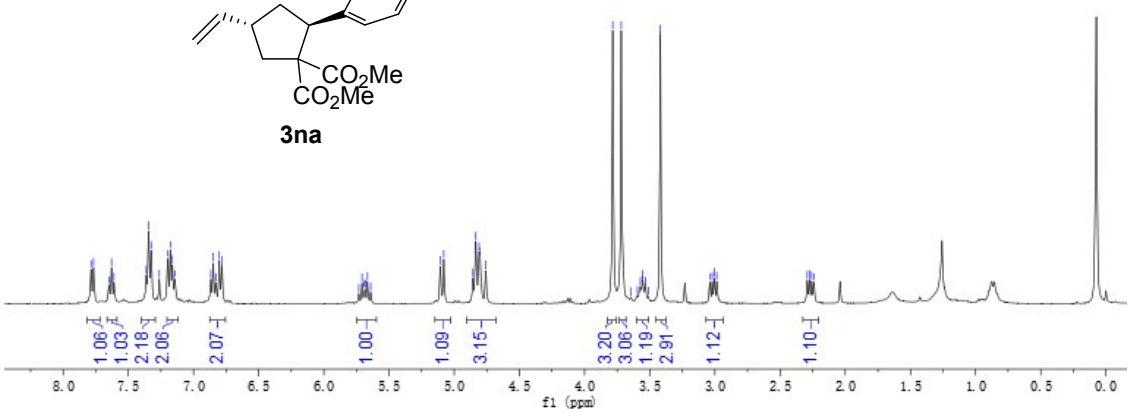
3ma




7.7864
7.7670
7.6293
7.3621
7.3439
7.3254
7.2626
7.1977
7.1778
7.1618
7.1433
6.8483
6.8021
6.7817
5.7070
5.6894
5.6827
5.6651
5.0799
4.8559
4.8341
4.8091
4.8006
4.7572
3.7843
3.7186
3.5720
3.5534
3.5327
3.0206
3.0047
2.9861
2.2918
2.2752
2.2572
2.2406


O
SO2
N
MeO
CO2Me
CO2Me

3na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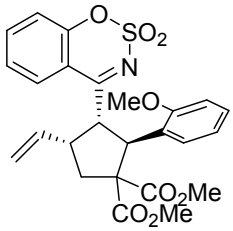
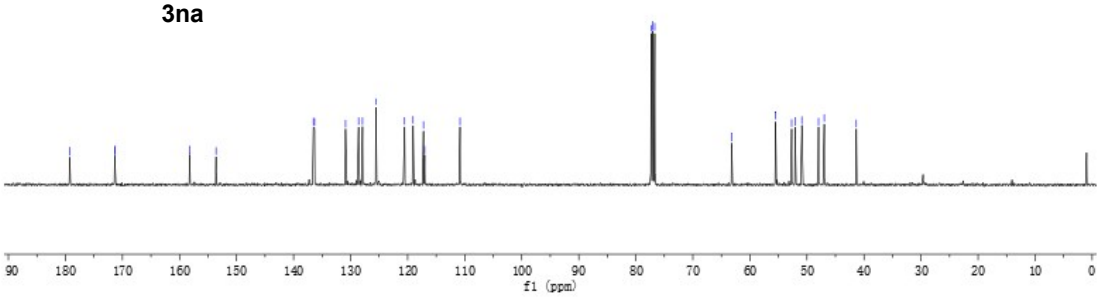
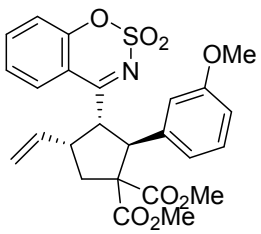
1.03
2.18
2.06
2.07
1.00
1.09
3.15
3.20
3.06
1.19
2.91
1.12
1.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


179.2509
171.3515
171.3008
158.2174
153.5969
136.5196
136.3256
130.8873
128.6009
127.9160
125.5642
120.5336
119.0426
117.2266
117.0243
110.8206
77.3175
76.9998
76.6820
63.1966
55.4952
52.6771
52.0882
50.8994
47.9689
46.9637
41.3436

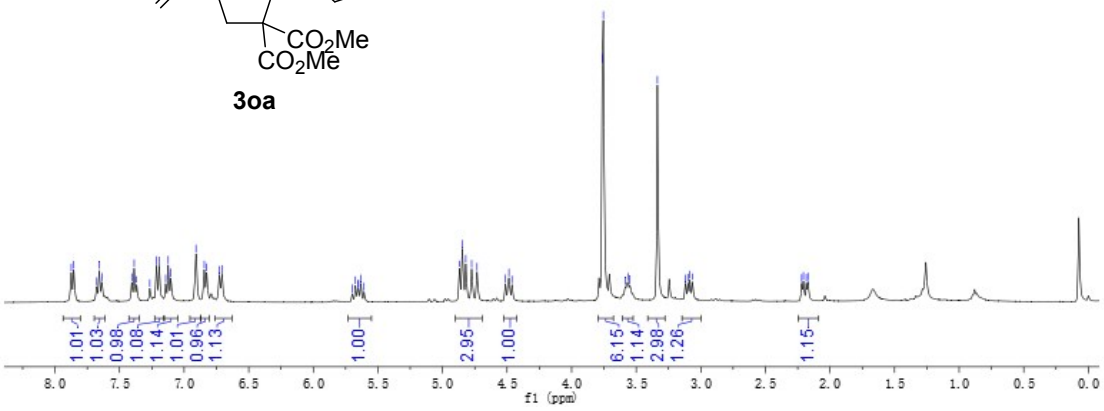

O
SO2
N
MeO
CO2Me
CO2Me

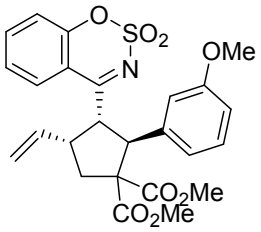
3na


90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

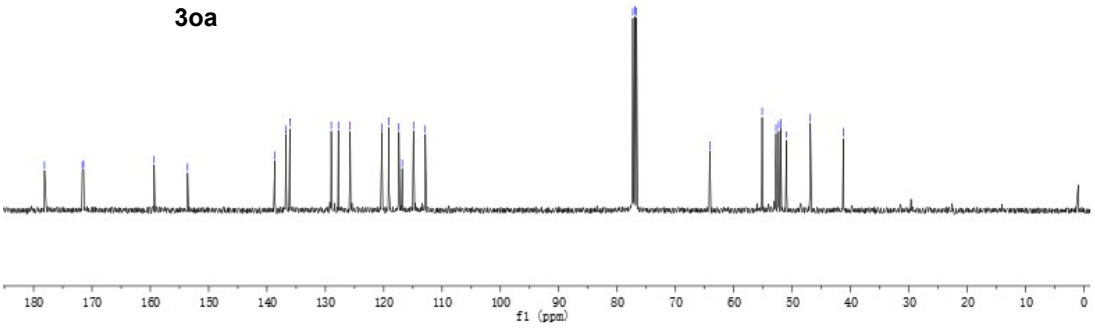


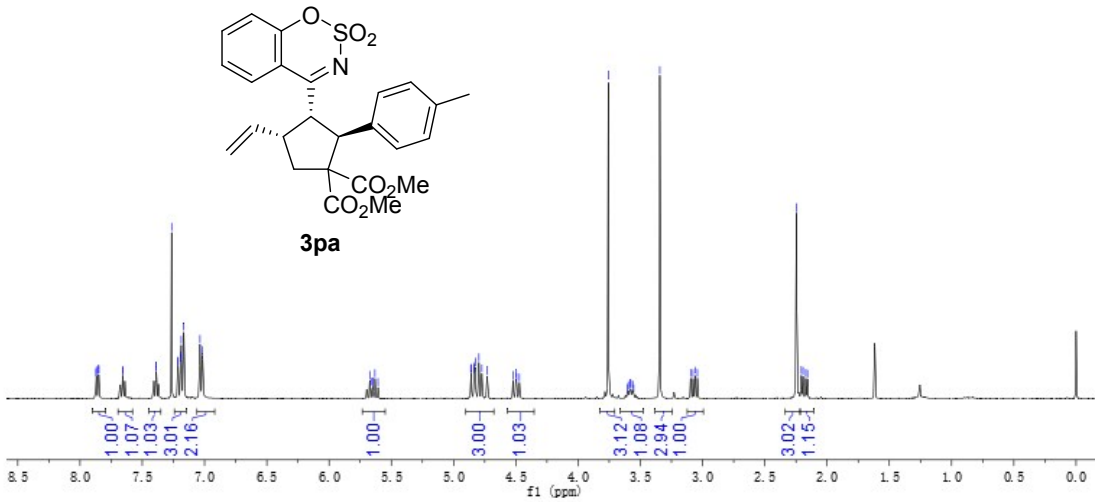
3oa



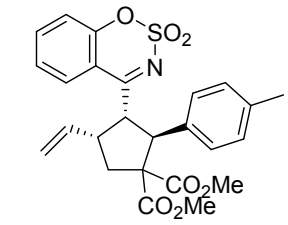


3oa

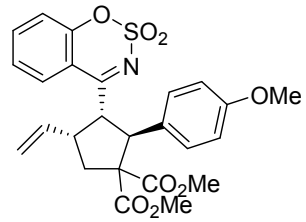




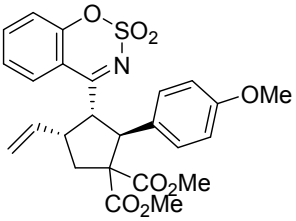
3pa



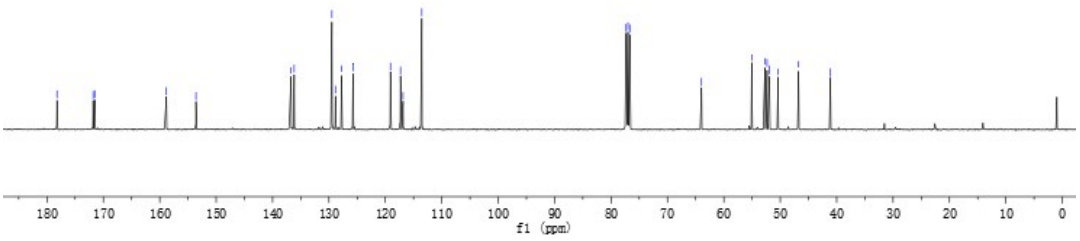
3pa

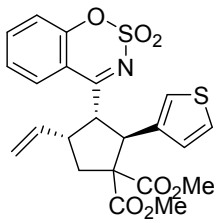


3qa

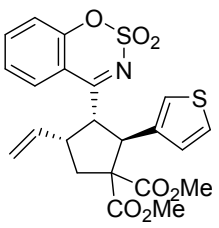


3qa





3ra



3ra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7.1702
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7.0847
5.6876
5.6696
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5.6456
5.6213
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4.4802
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2.2351
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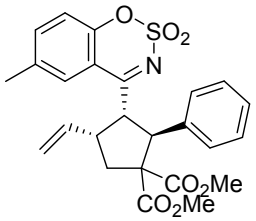
2.1998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N
CO2Me
CO2Me

3sa

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1.97
3.06
1.02
1.00
1.97
1.01
1.07
3.11
1.11
3.00
1.02
2.95
1.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
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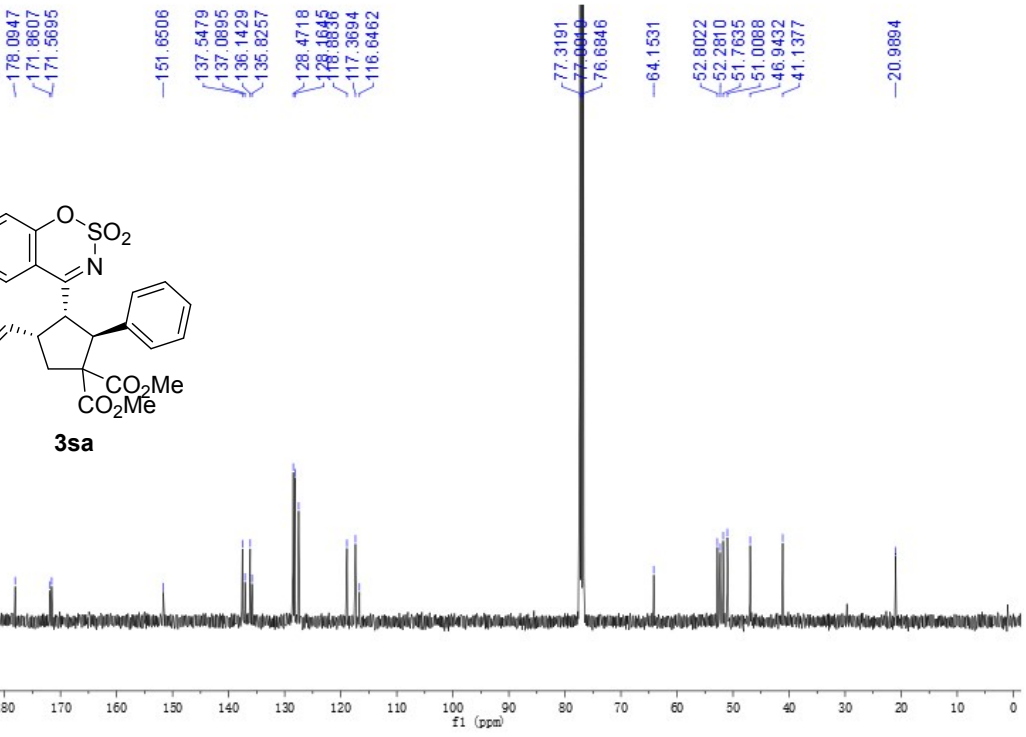
f1 (ppm)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51.0088
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41.1377
20.9894
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
SO2
N
CO2Me
CO2Me

3sa


7.3259
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7.2740
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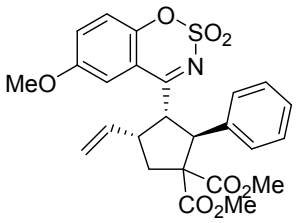
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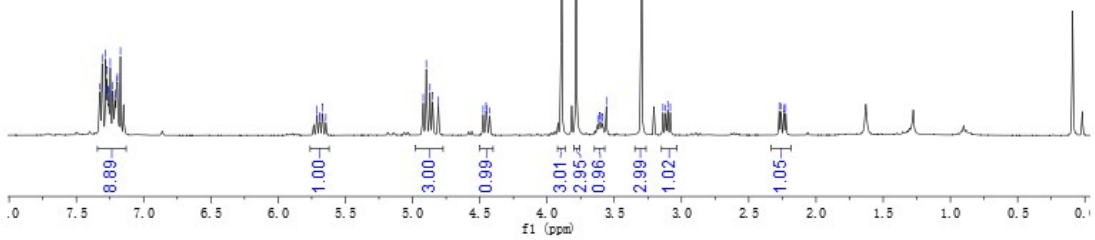
SO2
N
MeO
CO2Me
CO2Me

3ta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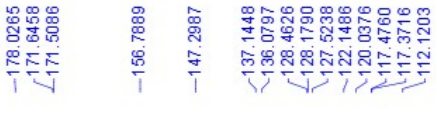
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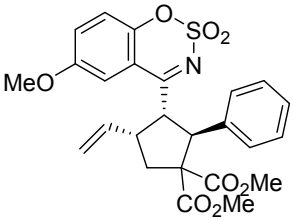
41.1733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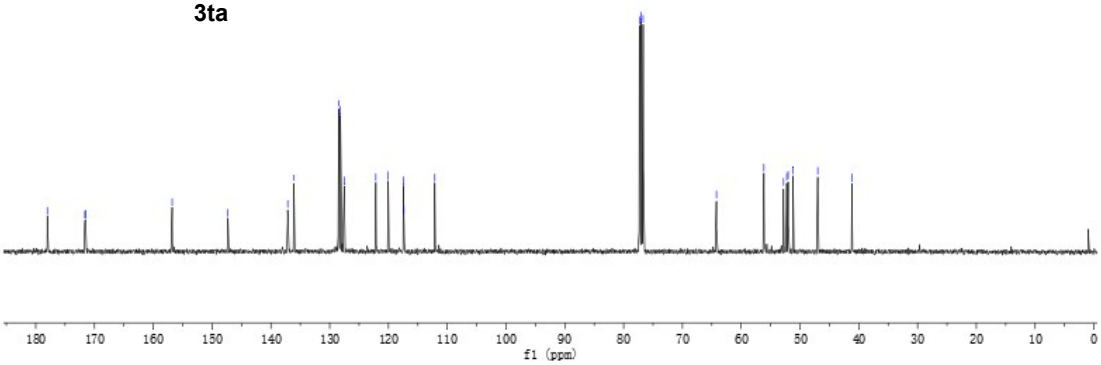
SO2
N
MeO
CO2Me
CO2Me

3ta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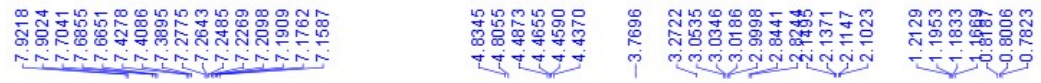
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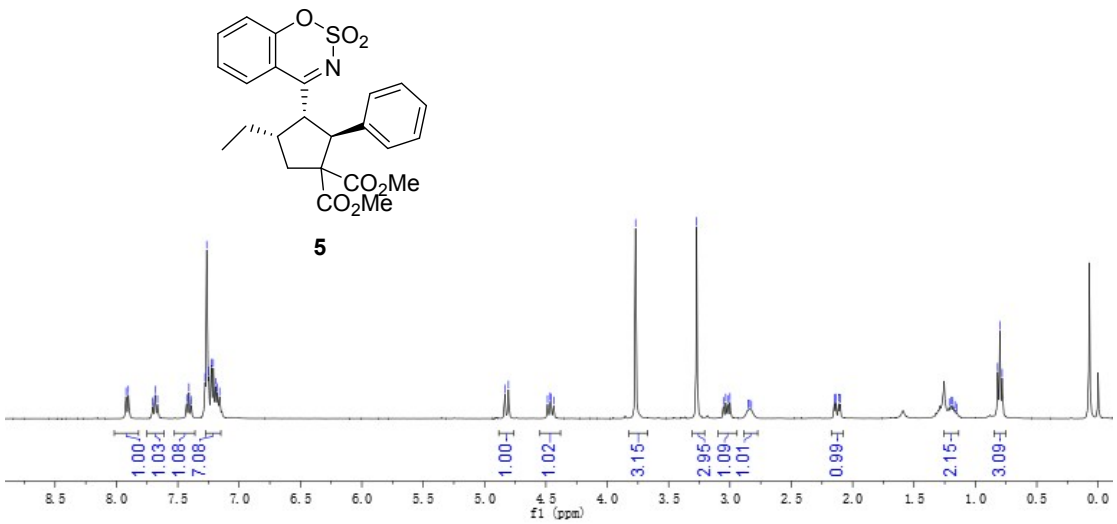
7.2269
7.2098
7.1909
7.1762
7.1587
4.8345
4.8055
4.4873
4.4655
4.4590
4.4370
3.7696
3.2722
3.0535
3.0346
3.0186
2.9998
2.8441
2.1371
2.1147
2.1023
1.2129
1.1953
1.1833
0.8006
0.7823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N
CO2Me
CO2Me
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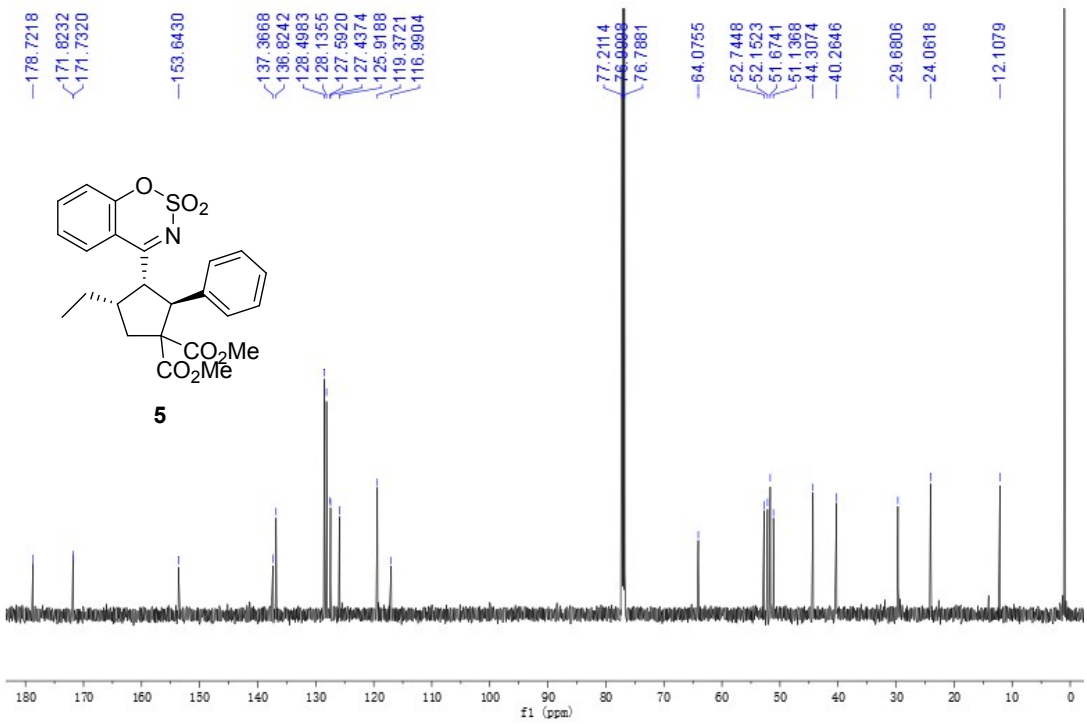
1.08
7.08
1.00
1.02
3.15
2.95
1.09
1.01
0.99
2.15
3.09
f1 (ppm)

5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127.5920
127.4374
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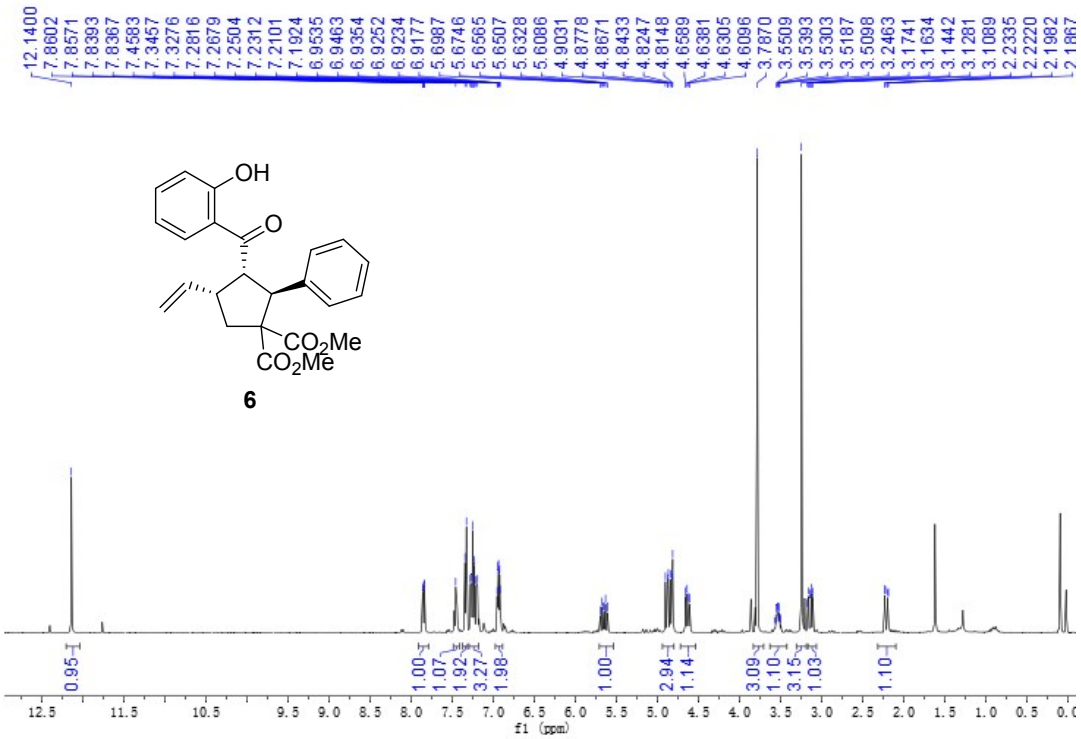
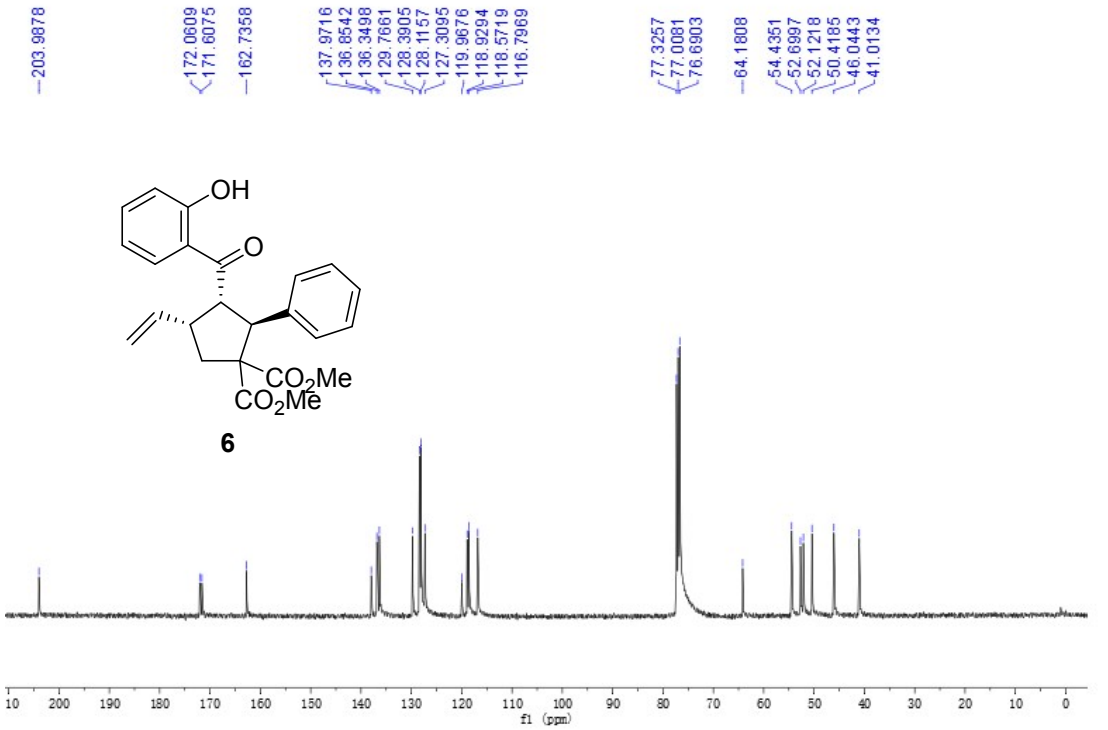
119.3721
116.9904
77.2114
76.9988
76.7881
64.0755
52.7448
52.1523
51.6741
51.1368
44.3074
40.2646
29.6806
24.0618
12.1079
O
SO2
N
CO2Me
CO2Me
f1 (ppm)

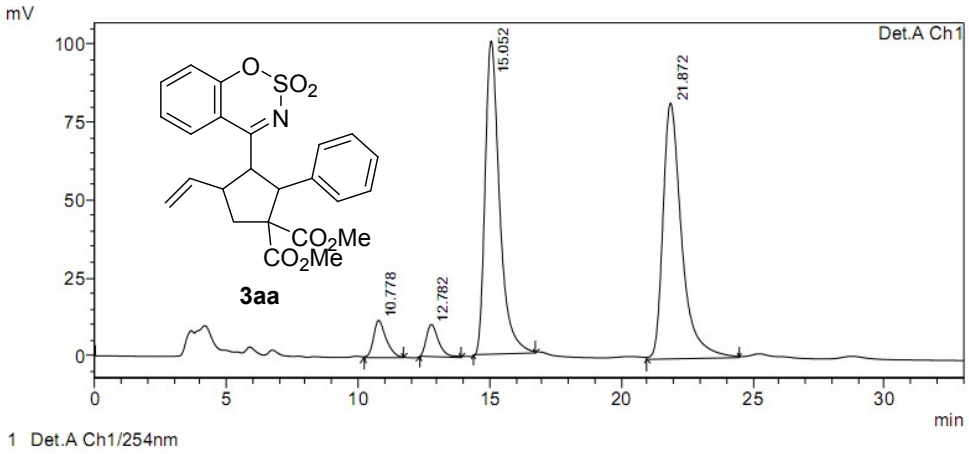
5


OH
O
CO2Me
CO2Me
6
f1 (ppm)


OH
O
CO2Me
CO2Me
6
f1 (ppm)

5.HPLC spectra of the products

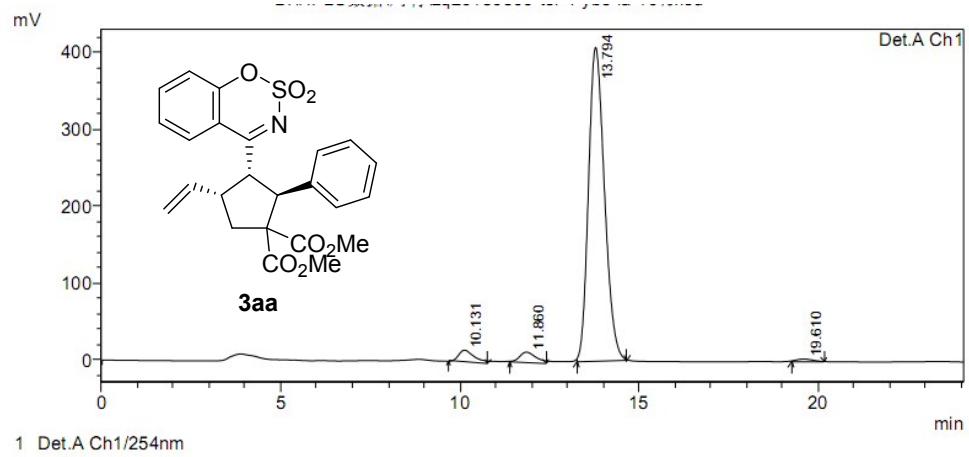
HPLC of **3aa**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.778	401785	11994	4.647	5.854
2	12.782	336359	10336	3.890	5.045
3	15.052	3832471	100490	44.324	49.051
4	21.872	4075895	82047	47.139	40.049
Total		8646509	204867	100.000	100.000

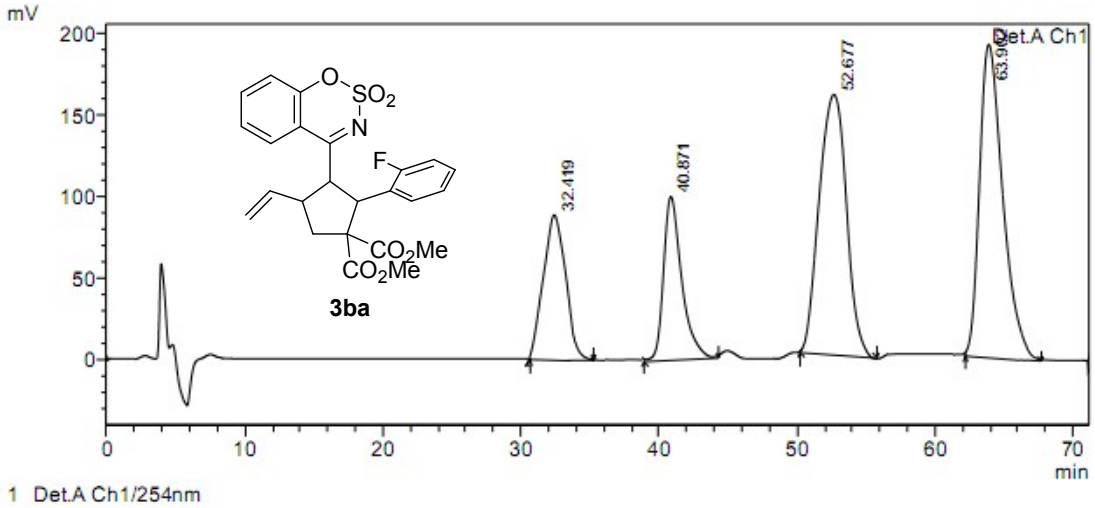


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.131	442305	14773	3.239
2	11.860	436182	13545	3.194
3	13.794	12653363	407665	92.655
4	19.610	124547	3635	0.912
Total		13656397	439617	100.000

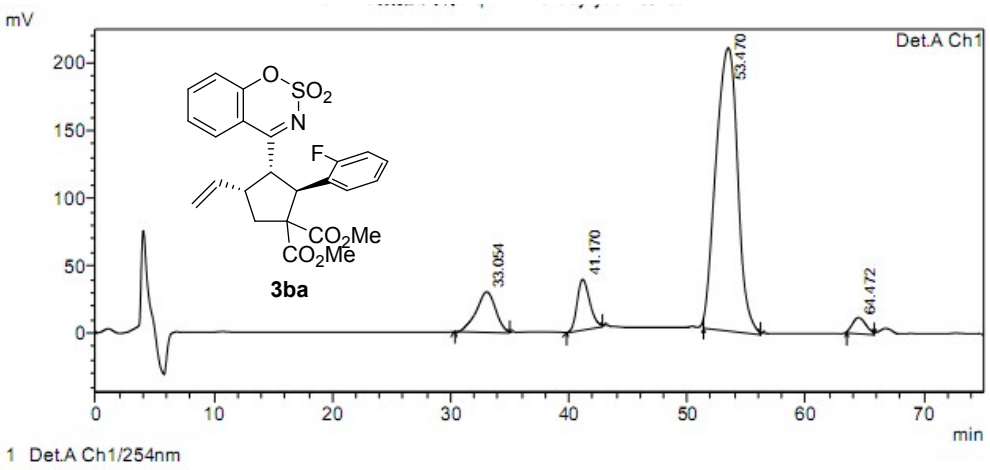
HPLC of **3ba**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	32.419	9908759	89232	15.538
2	40.871	9257646	100401	14.517
3	52.677	21972611	159718	34.455
4	63.902	22633094	192240	35.491
Total		63772111	541592	100.000

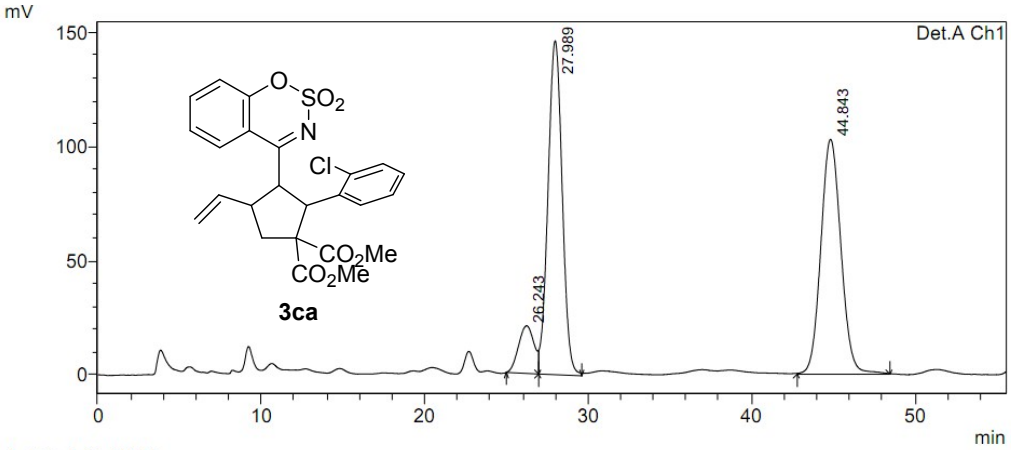


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	33.054	3432125	30030	10.098
2	41.170	2802407	37688	8.245
3	53.470	26795798	209539	78.836
4	64.472	958755	12015	2.821
Total		33989085	289272	100.000

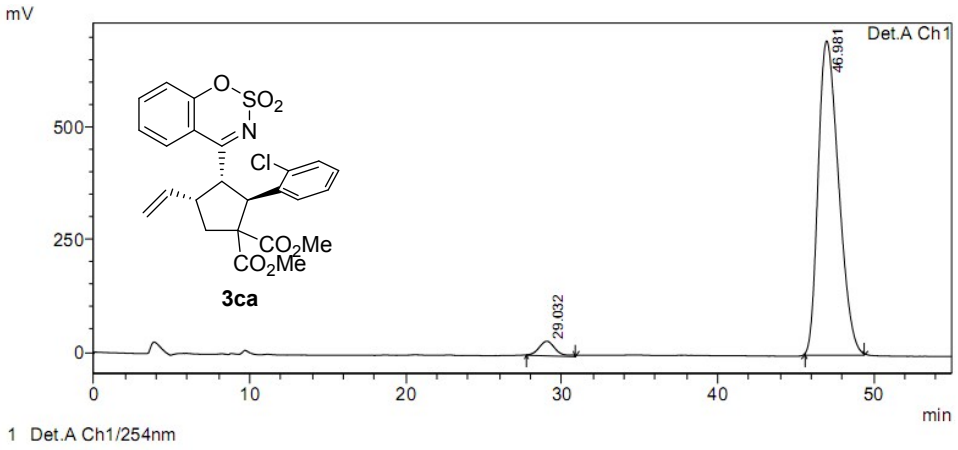
HPLC of **3ca**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	26.243	1358696	20866	7.135
2	27.989	8875708	146363	46.612
3	44.843	8807138	102977	46.252
Total		19041542	270206	100.000

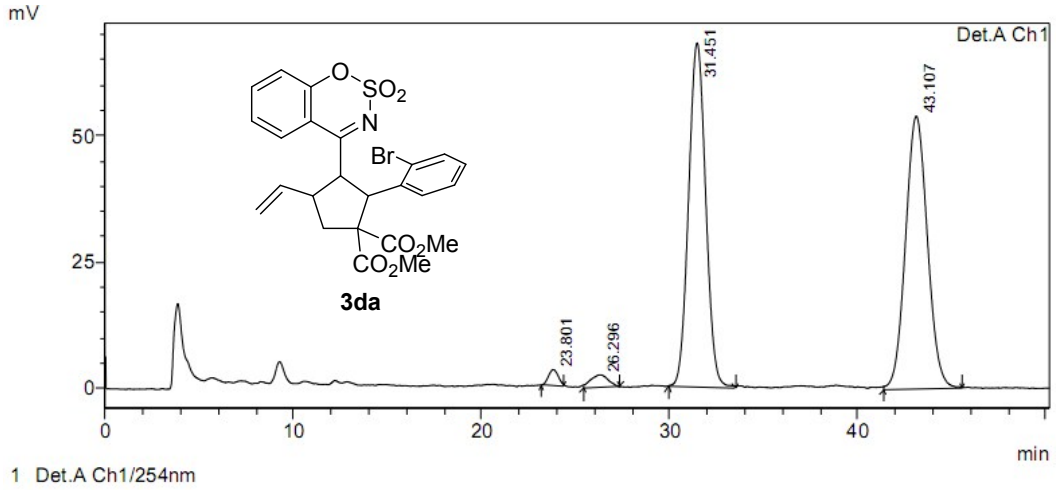


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	29.032	2396171	32387	3.619
2	46.981	63807171	698641	96.381
Total		66203341	731028	100.000

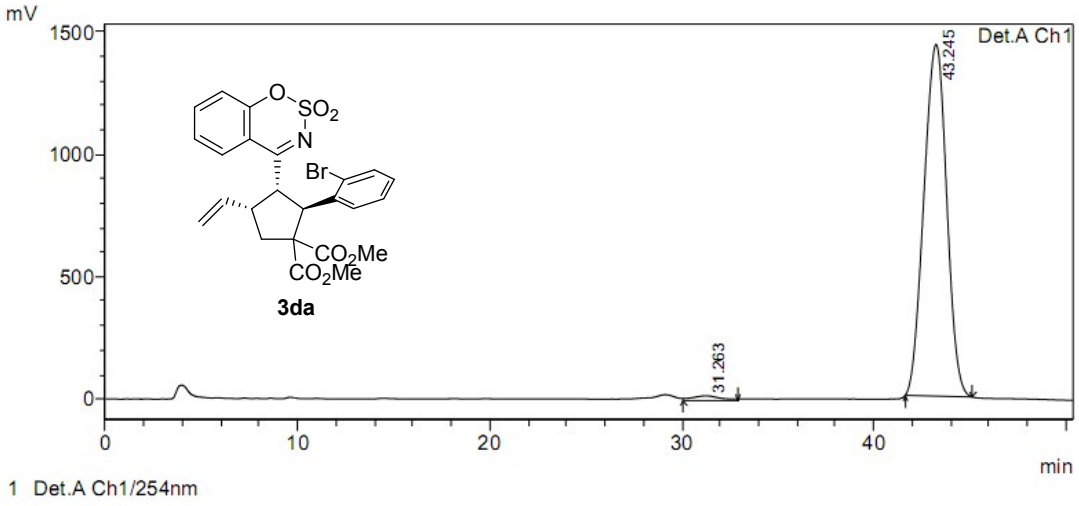
HPLC of **3da**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	23.801	114392	3164	1.276
2	26.296	160330	2451	1.788
3	31.451	4315978	68202	48.130
4	43.107	4376673	54090	48.807
Total		8967373	127907	100.000

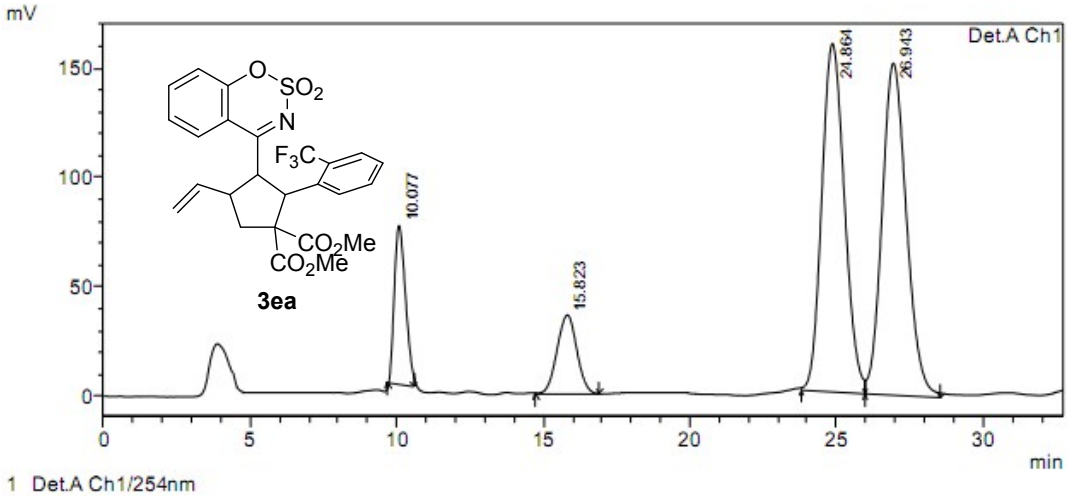


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	31.263	2061510	19284	1.710
2	43.245	118460858	1437849	98.290
Total		120522368	1457133	100.000

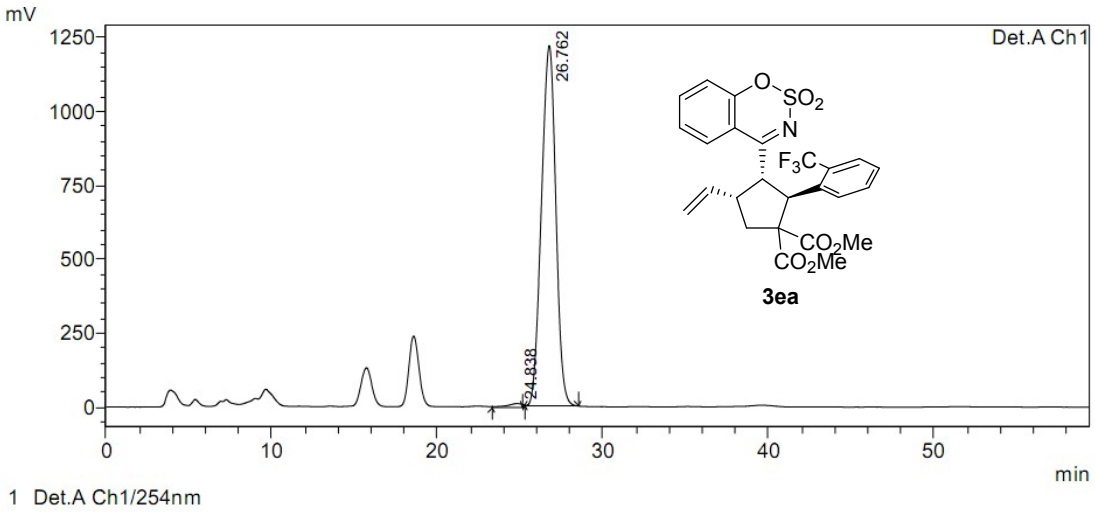
HPLC of **3ea**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.077	1919076	72642	9.157
2	15.823	1702307	36123	8.122
3	24.864	8549580	159275	40.793
4	26.943	8787354	151738	41.928
Total		20958317	419778	100.000

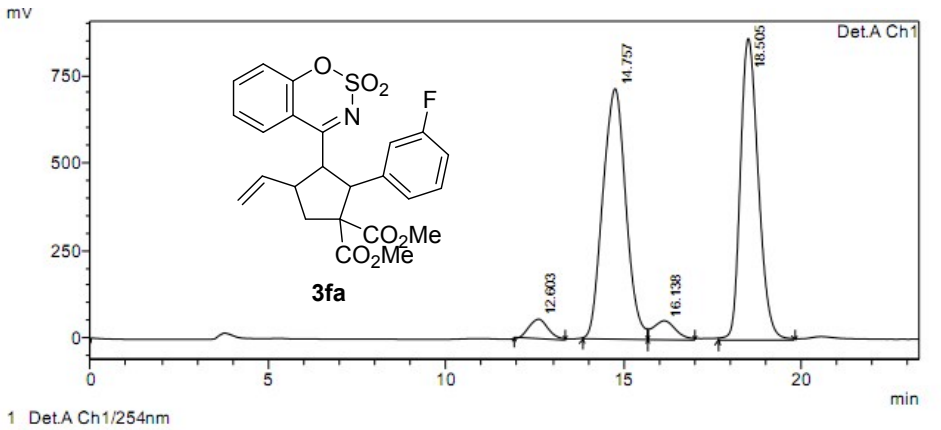


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.838	872797	13162	1.173
2	26.762	73534485	1218262	98.827
Total		74407282	1231425	100.000

HPLC of **3fa**

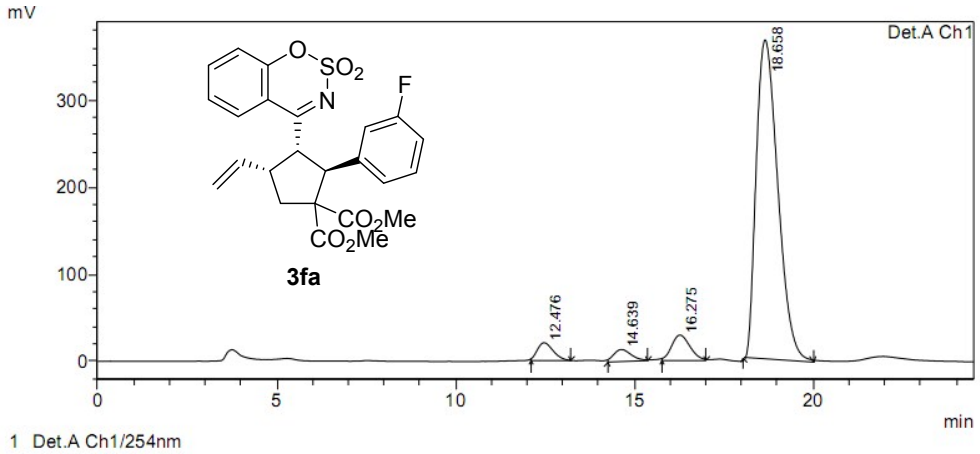


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.603	2049439	55353	3.051
2	14.757	32331141	715257	48.134
3	16.138	2403219	54138	3.578
4	18.505	30385181	861555	45.237
Total		67168981	1686303	100.000



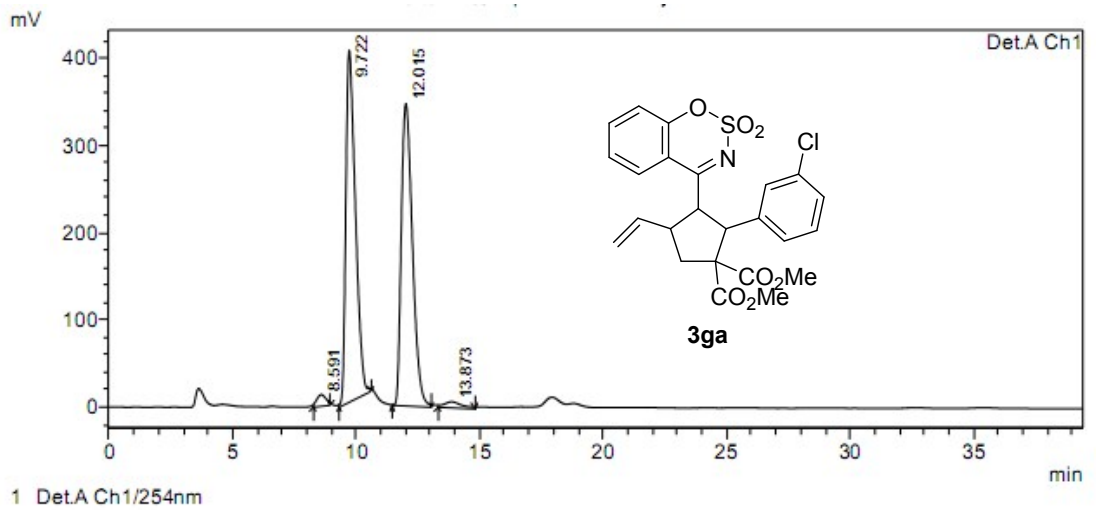
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.476	628915	20395	3.584
2	14.639	474535	13805	2.704
3	16.275	1044523	29193	5.952
4	18.658	15399773	366416	87.759
Total		17547746	429809	100.000

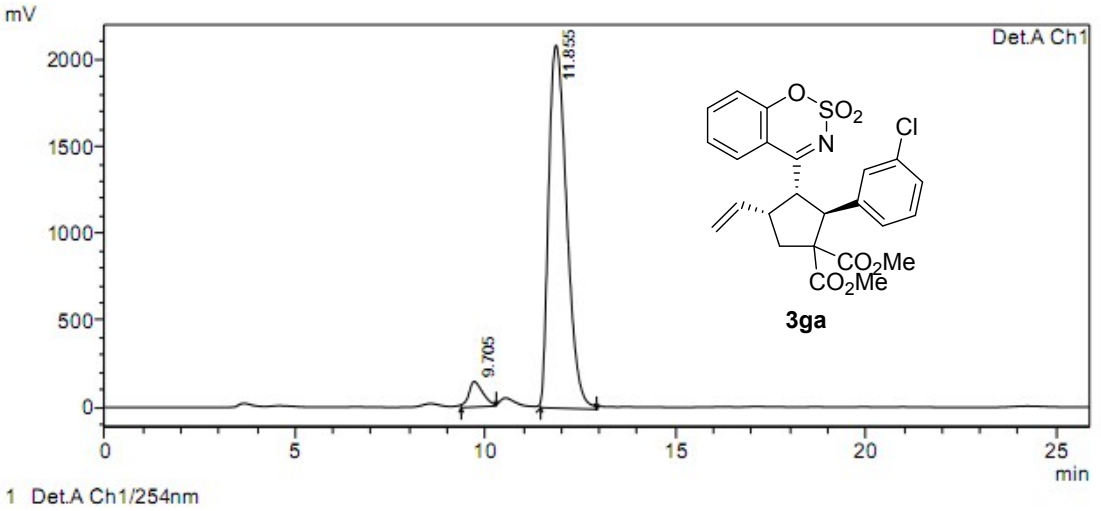
HPLC of **3ga**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.591	363061	13465	1.620
2	9.722	10825515	403453	48.300
3	12.015	10861248	346656	48.459
4	13.873	363363	7014	1.621
Total		22413188	770589	100.000

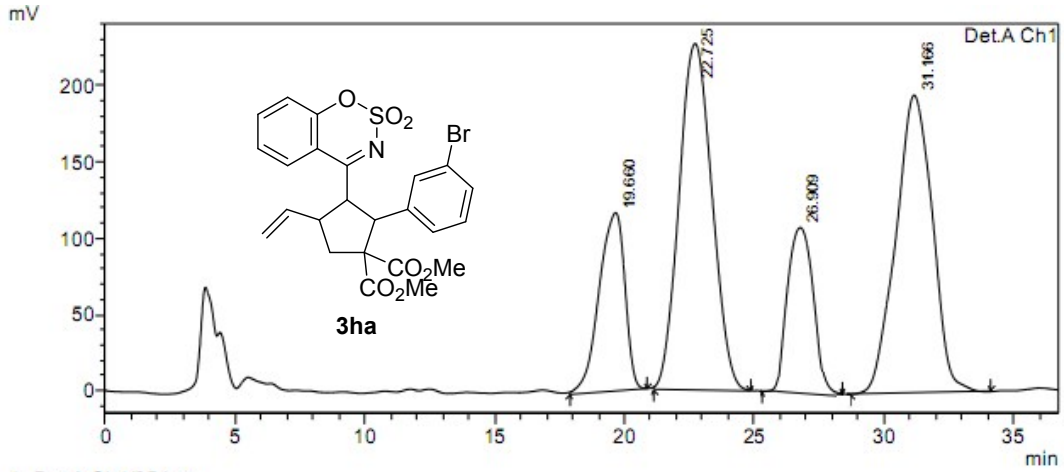


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.705	3792216	145600	5.225
2	11.855	68791485	2087480	94.775
Total		72583701	2233081	100.000

HPLC of **3ha**

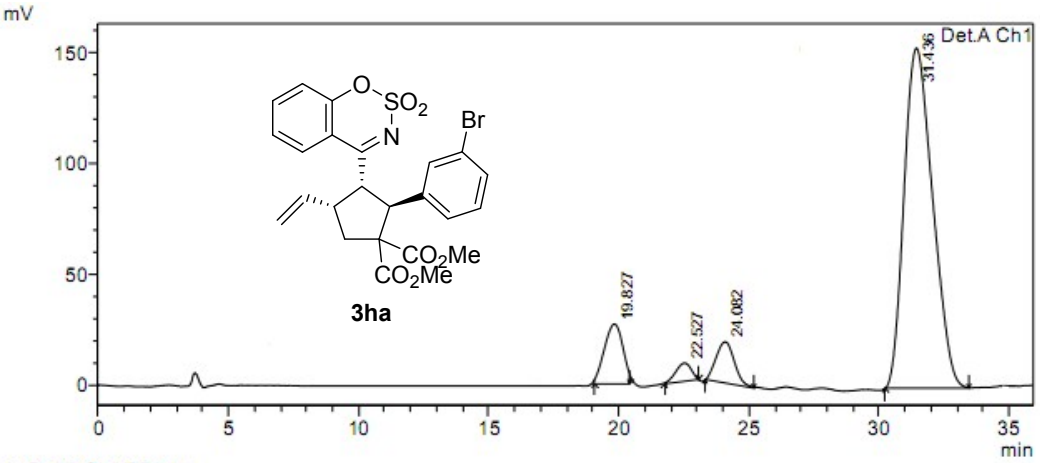


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.660	8100181	116864	14.528
2	22.725	20049852	227092	35.960
3	26.909	8562657	120161	15.358
4	31.166	19042817	194929	34.154
Total		55755507	659047	100.000



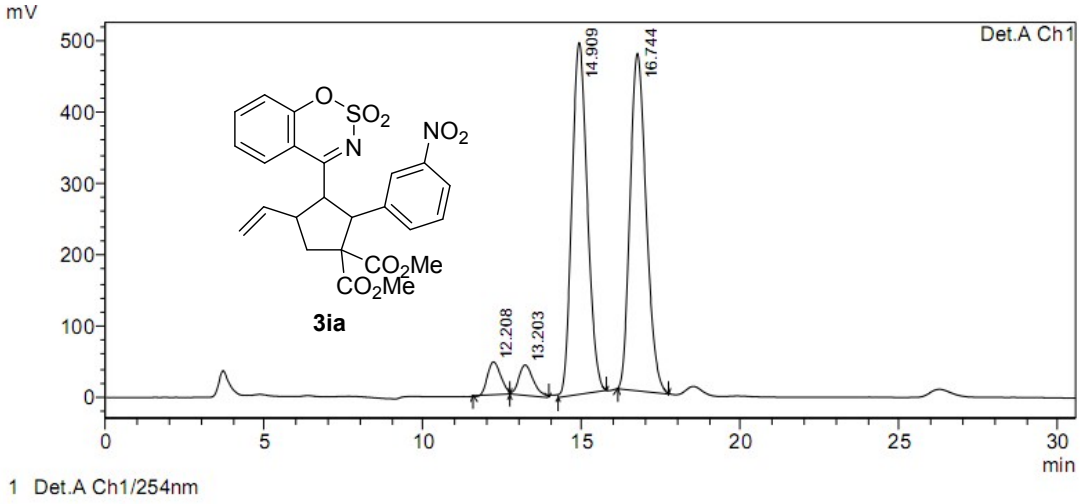
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.827	1326710	27042	9.280
2	22.527	338105	8201	2.365
3	24.082	905325	18600	6.332
4	31.436	11726593	153788	82.023
Total		14296733	207632	100.000

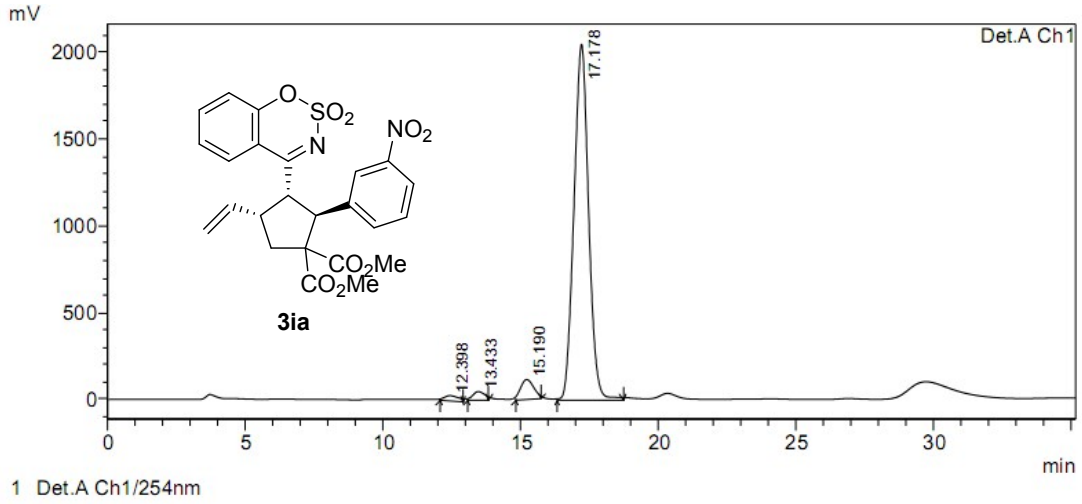
HPLC of **3ia**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.208	1326514	46118	3.669
2	13.203	1359824	42624	3.761
3	14.909	16717059	493273	46.234
4	16.744	16754112	473452	46.336
Total		36157508	1055467	100.000

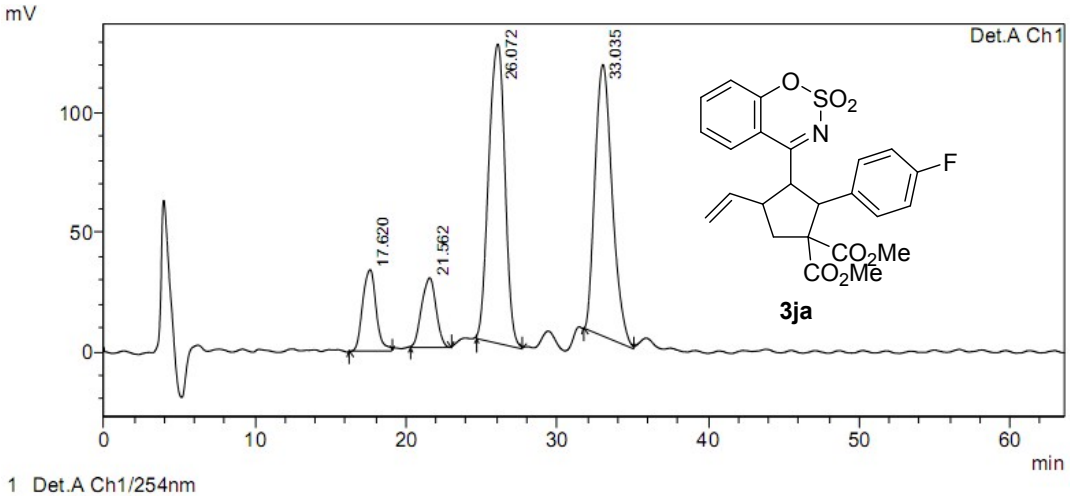


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.398	1155958	30679	1.403
2	13.433	1517661	49684	1.842
3	15.190	3854231	115151	4.677
4	17.178	75876127	2050380	92.078
Total		82403977	2245894	100.000

HPLC of **3ja**

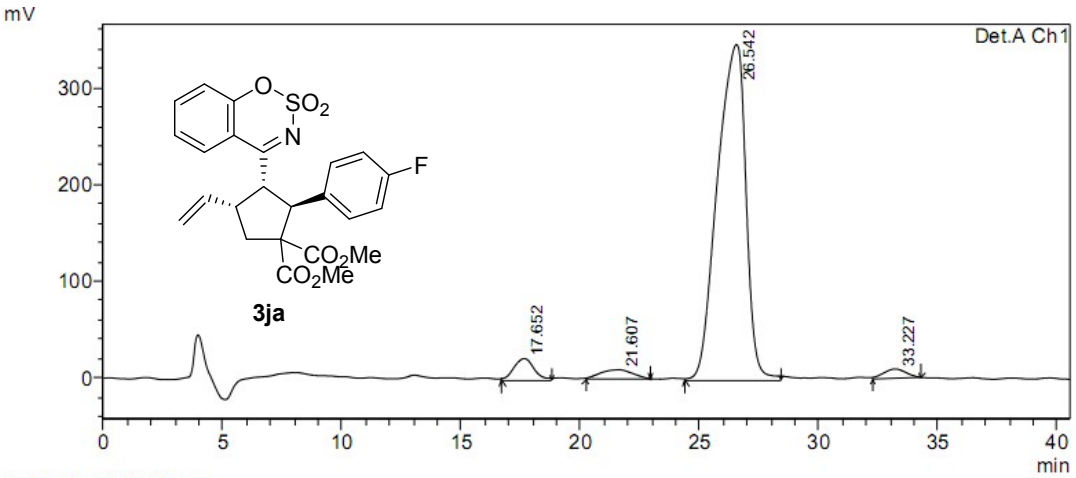


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.620	2109416	34064	9.371
2	21.562	1944229	29197	8.637
3	26.072	9406253	125427	41.786
4	33.035	9050739	113808	40.206
Total		22510637	302497	100.000



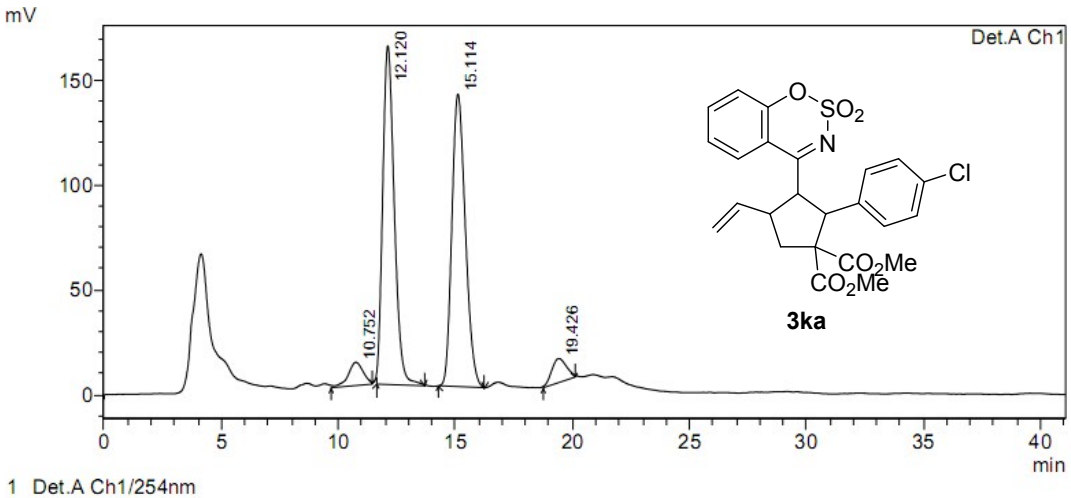
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.652	1381477	22896	4.325
2	21.607	903209	9552	2.827
3	26.542	29035540	347501	90.893
4	33.227	624539	9462	1.955
Total		31944764	389411	100.000

HPLC of **3ka**

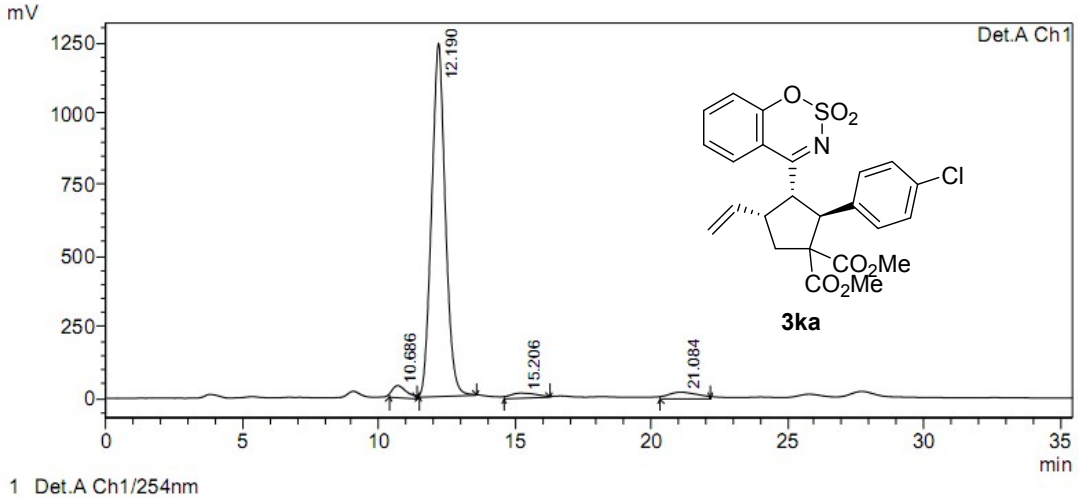


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.752	495556	11060	4.081
2	12.120	5564375	161635	45.829
3	15.114	5582008	139507	45.974
4	19.426	499733	11388	4.116
Total		12141672	323590	100.000



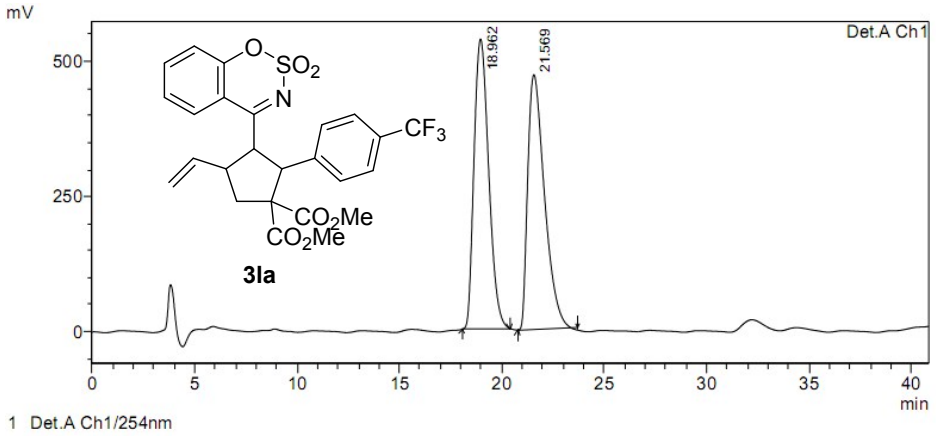
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.686	1571805	42550	3.267
2	12.190	43516261	1241507	90.450
3	15.206	1216442	17765	2.528
4	21.084	1806330	23498	3.755
Total		48110838	1325320	100.000

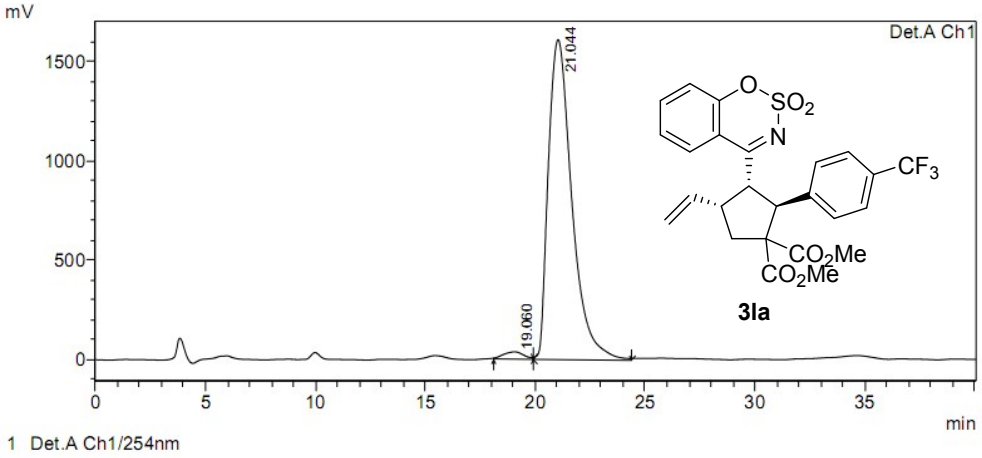
HPLC of **3la**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.962	26722442	536132	49.963
2	21.569	26761783	471511	50.037
Total		53484225	1007643	100.000

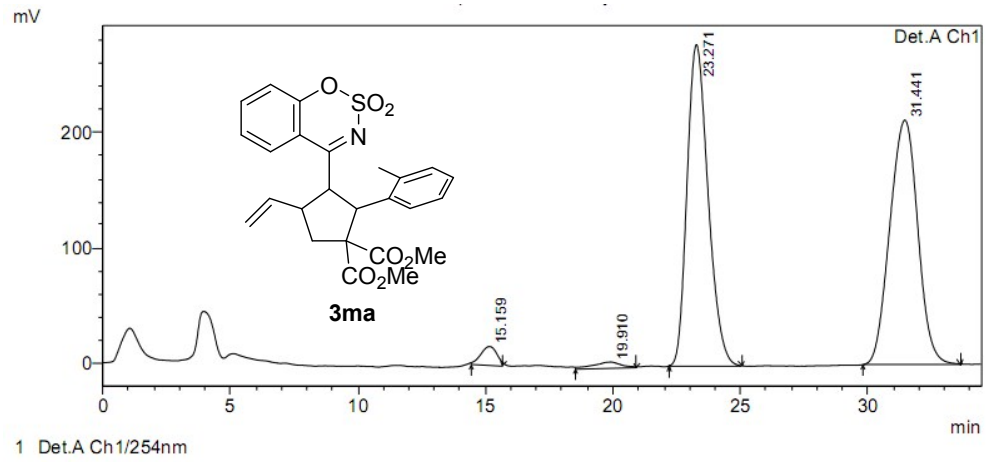


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.060	2385415	36633	1.950
2	21.044	119971220	1607261	98.050
Total		122356634	1643893	100.000

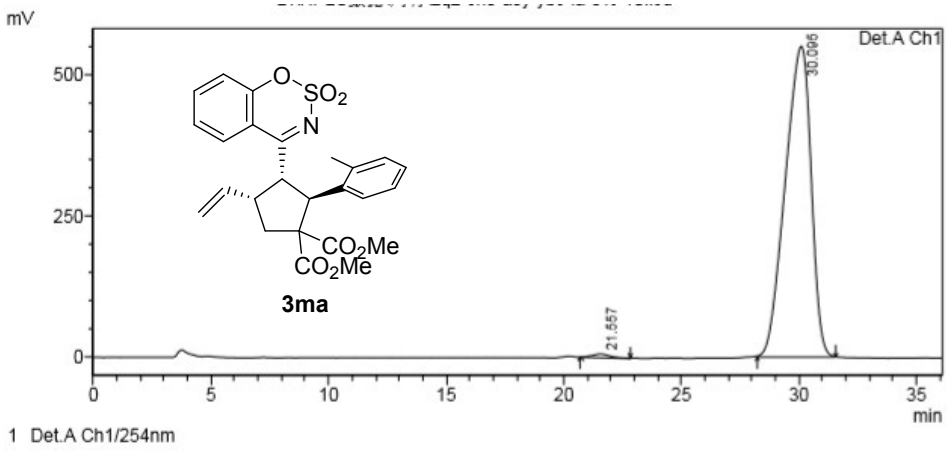
HPLC of **3ma**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.159	727217	16436	2.173
2	19.910	437796	5492	1.308
3	23.271	16078248	279867	48.049
4	31.441	16218942	212738	48.469
Total		33462203	514533	100.000

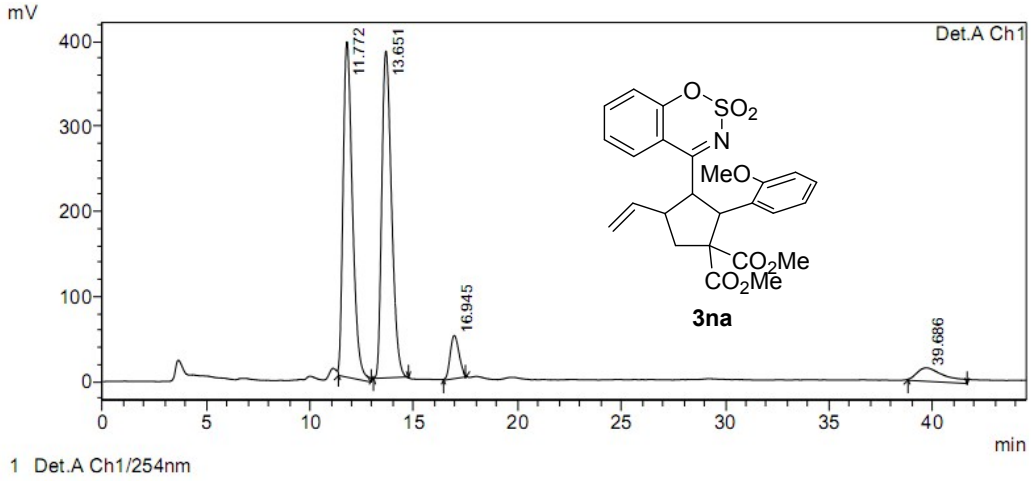


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.557	346040	6421	0.813
2	30.095	42215573	550847	99.187
Total		42561613	557268	100.000

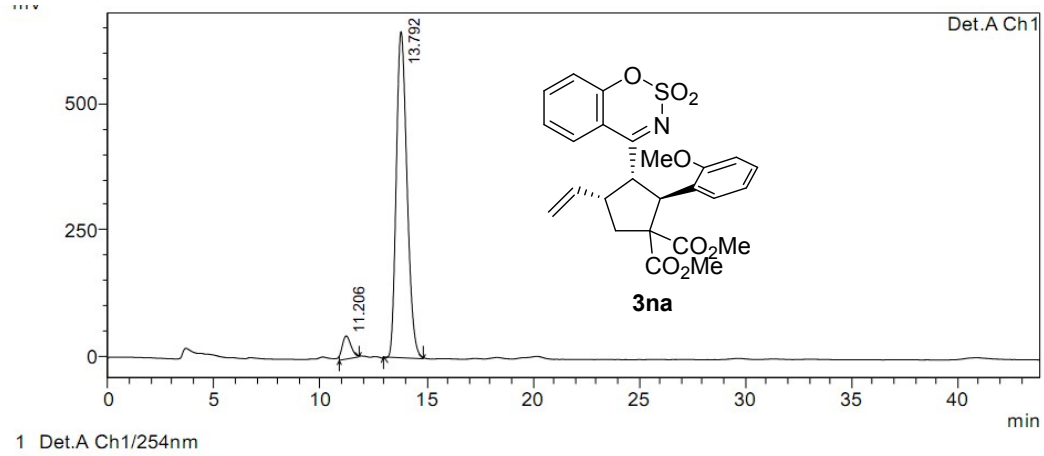
HPLC of **3na**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.772	12356478	394162	44.228
2	13.651	12563460	384499	44.969
3	16.945	1514199	50747	5.420
4	39.686	1504179	15669	5.384
Total		27938316	845076	100.000

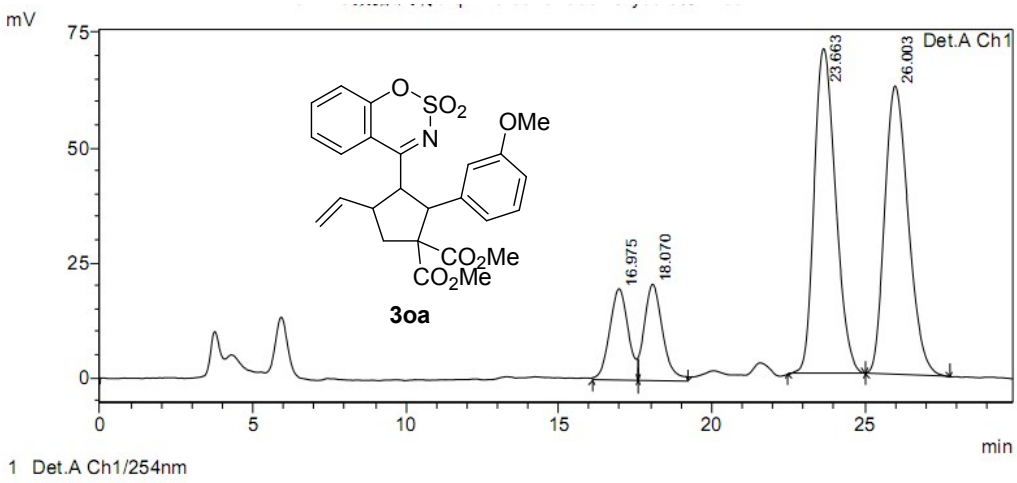


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.206	1302578	45622	5.453
2	13.792	22582811	642587	94.547
Total		23885389	688210	100.000

HPLC of **3oa**

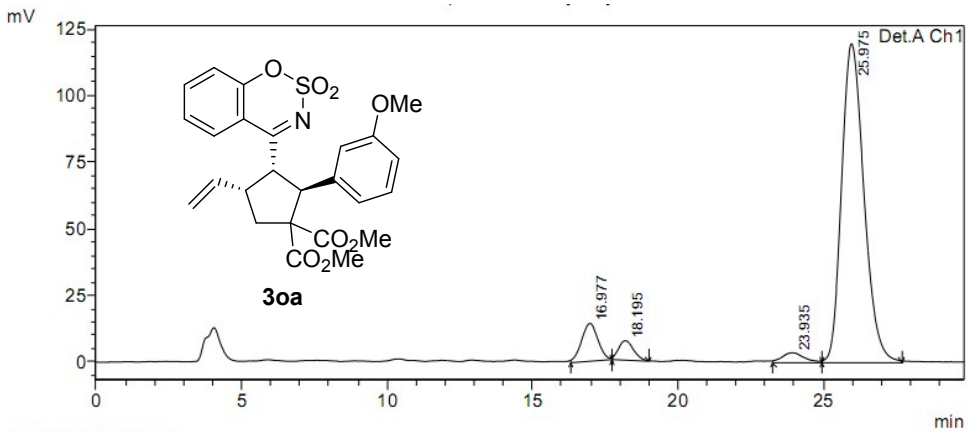


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.975	837296	19832	9.856
2	18.070	873970	20942	10.288
3	23.663	3423066	70509	40.294
4	26.003	3360897	62620	39.562
Total		8495229	173902	100.000



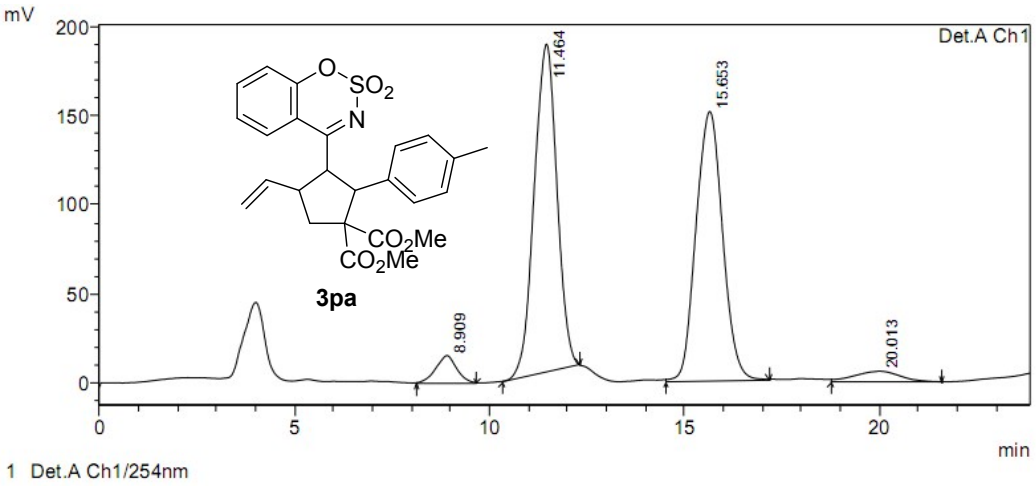
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.977	561342	14201	7.556
2	18.195	264265	7286	3.557
3	23.935	200576	3731	2.700
4	25.975	6403274	119661	86.188
Total		7429456	144879	100.000

HPLC of **3pa**

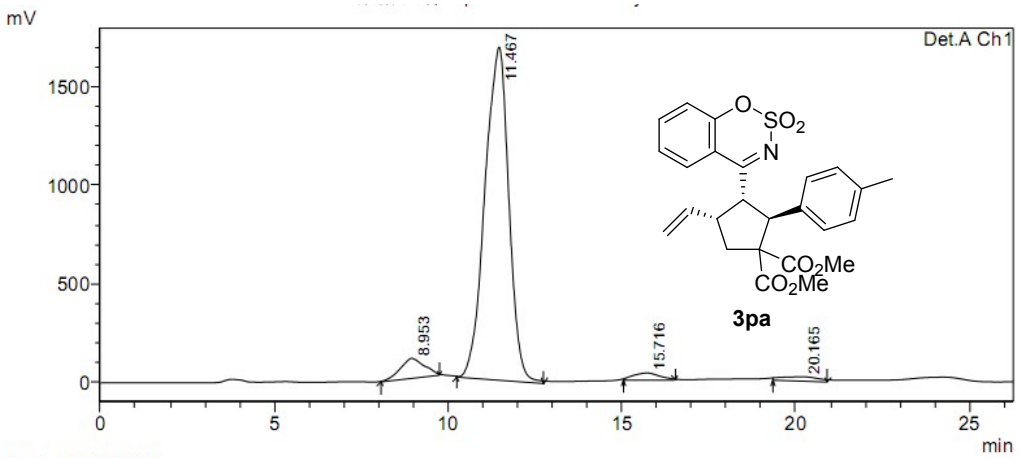


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.909	594498	15712	3.767
2	11.464	7485442	184365	47.432
3	15.653	7216392	151614	45.727
4	20.013	485010	5946	3.073
Total		15781342	357637	100.000



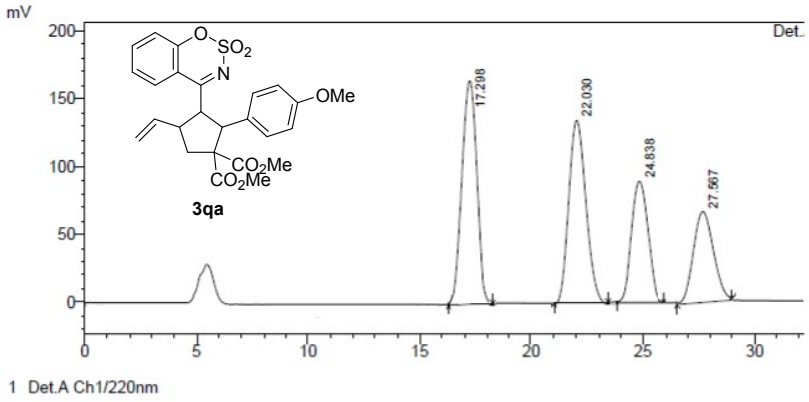
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.953	4933292	101640	5.525
2	11.467	80646774	1687231	90.327
3	15.716	2025122	36913	2.268
4	20.165	1678435	22138	1.880
Total		89283622	1847922	100.000

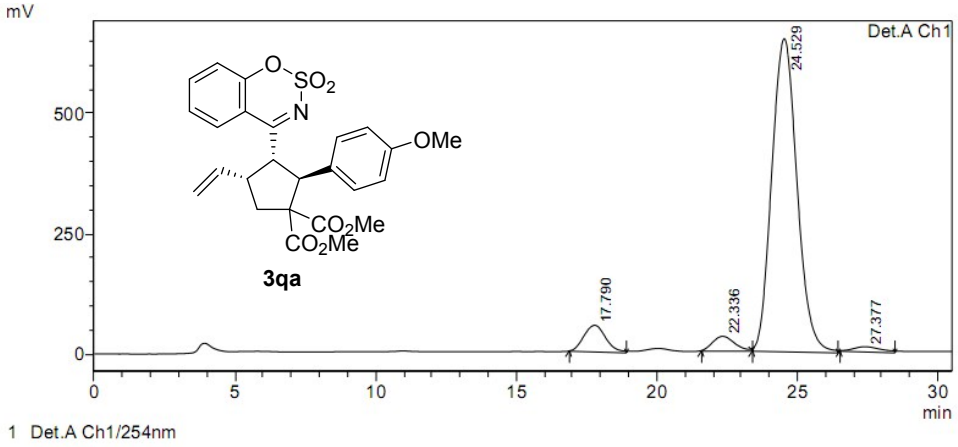
HPLC of **3qa**



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	17.298	7391413	163736	31.832
2	22.030	7145343	134617	30.772
3	24.838	4487520	88704	19.326
4	27.567	4195767	66811	18.070
Total		23220044	453868	100.000

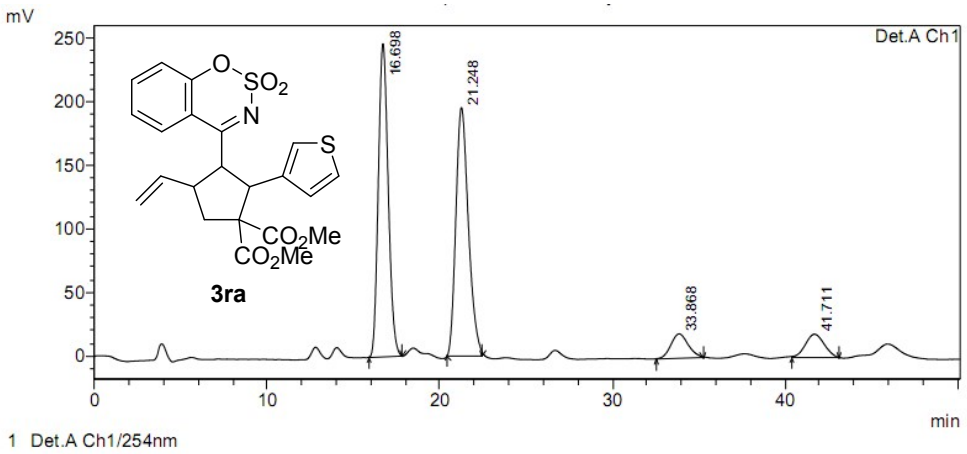


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.790	3024050	55449	6.544
2	22.336	1715233	31092	3.712
3	24.529	40692980	650789	88.062
4	27.377	776991	10885	1.681
Total		46209254	748216	100.000

HPLC of **3ra**

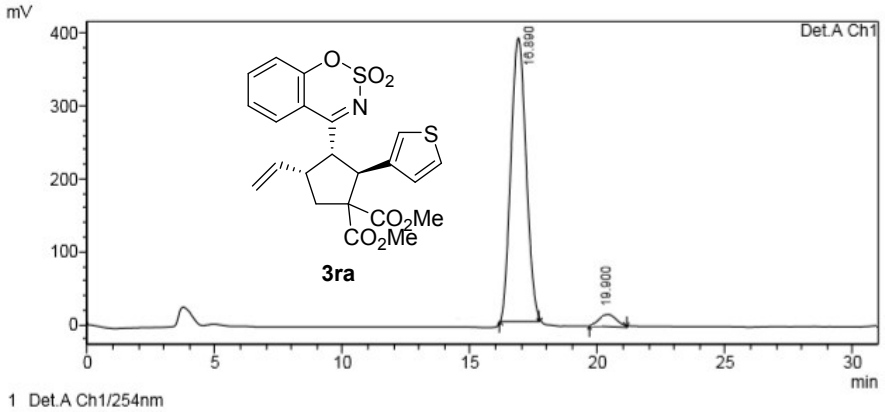


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.698	9818642	246119	43.799
2	21.248	9853824	195299	43.956
3	33.868	1350524	19222	6.024
4	41.711	1394675	18311	6.221
Total		22417666	478951	100.000



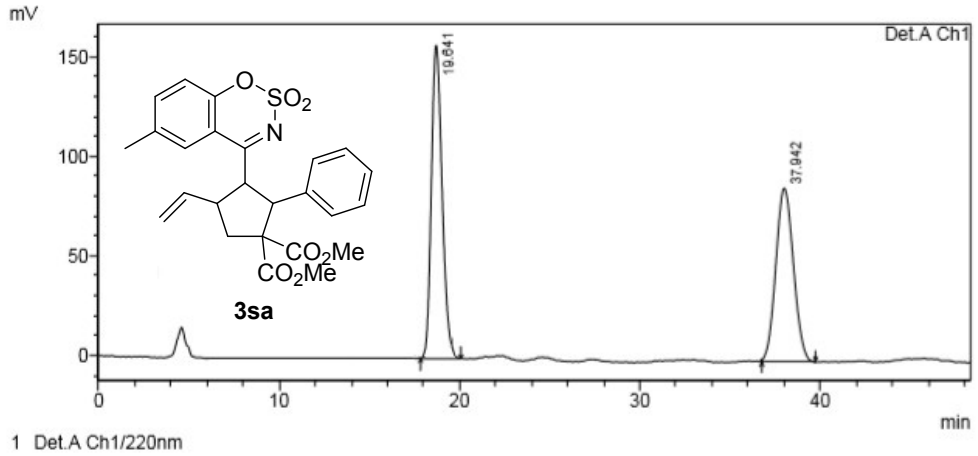
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.890	16140816	389110	94.731
2	19.900	897789	22068	5.269
Total		17038605	411178	100.000

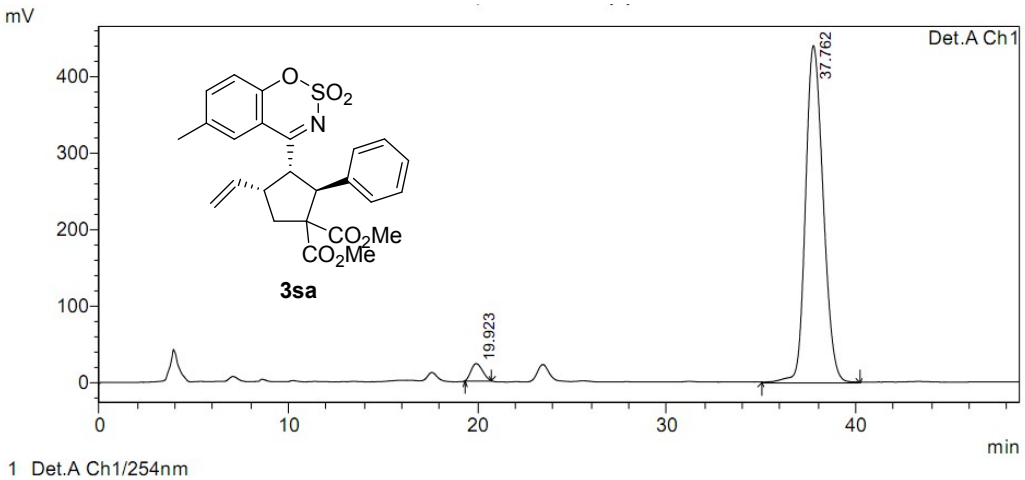
HPLC of **3sa**



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	19.641	6060491	153083	50.676
2	37.942	5898711	87064	49.324
Total		11959202	240148	100.000

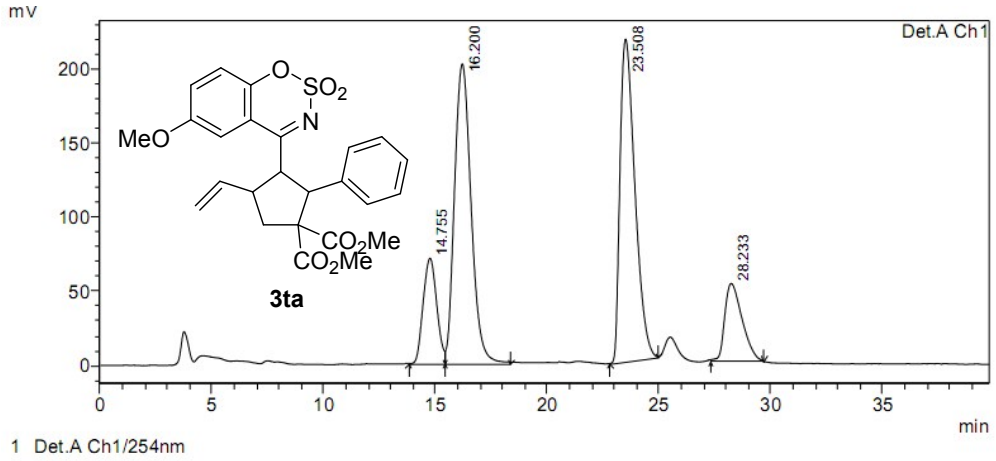


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.923	988615	23002	3.323
2	37.762	28757861	440841	96.677
Total		29746476	463844	100.000

HPLC of **3ta**

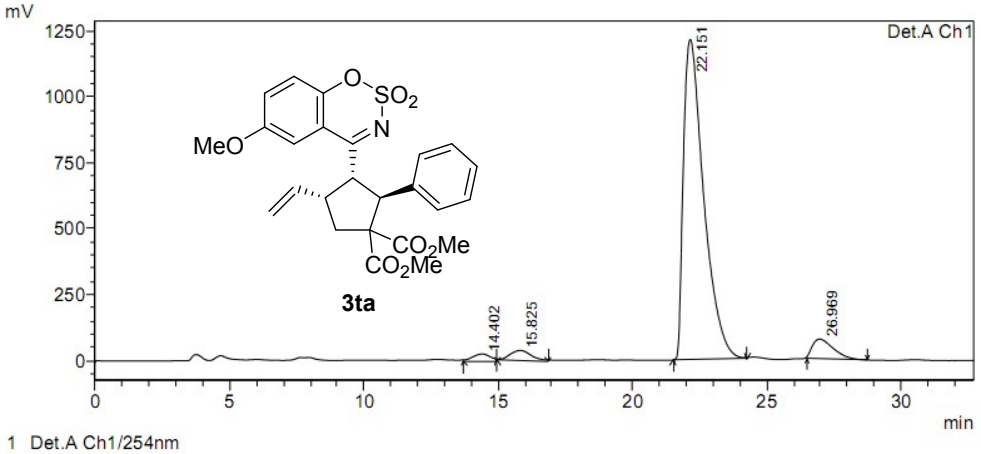


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.755	3049255	71650	11.485
2	16.200	10521637	202827	39.628
3	23.508	10147682	218101	38.220
4	28.233	2832359	52379	10.668
Total		26550932	544957	100.000



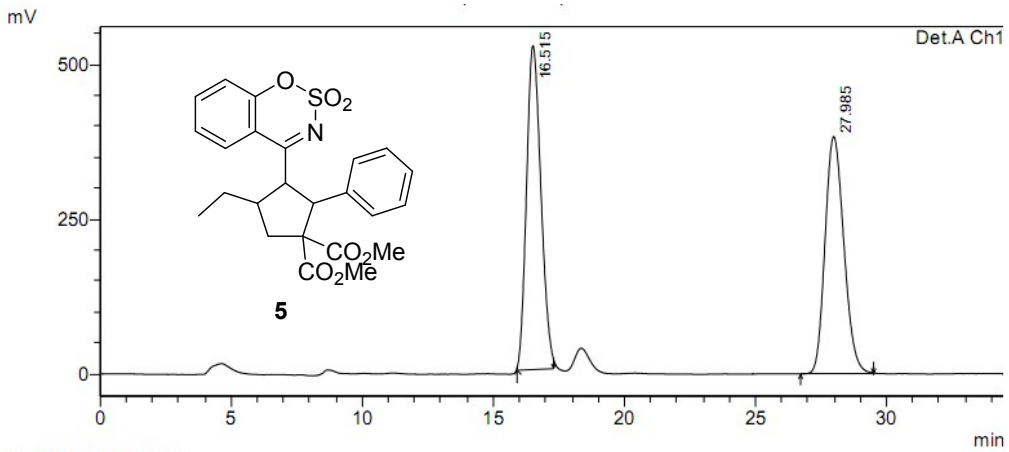
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.402	1326827	28108	1.864
2	15.825	2128330	38288	2.990
3	22.151	63724325	1213662	89.537
4	26.969	3991210	73909	5.608
Total		71170693	1353967	100.000

HPLC of **5**

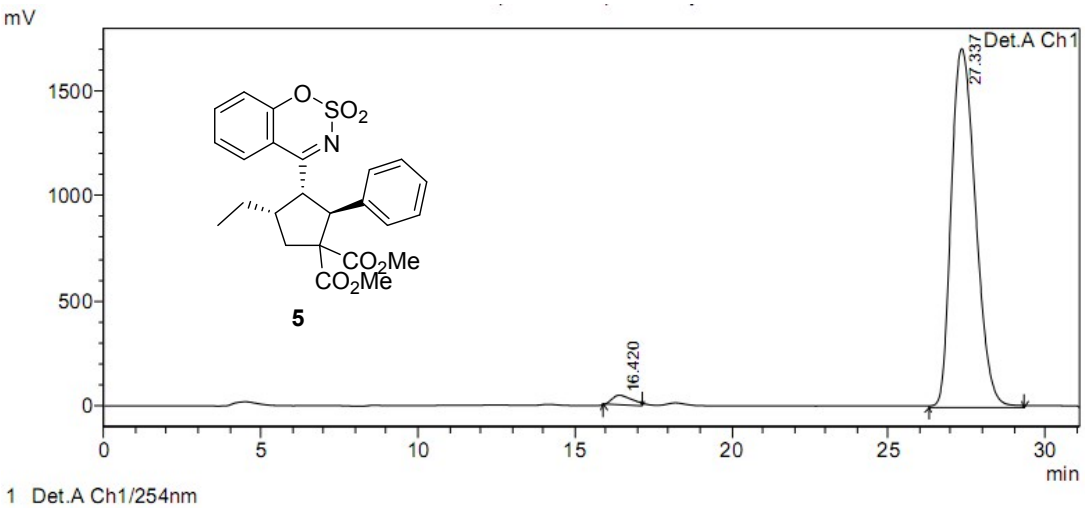


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.515	19944246	523483	51.071
2	27.985	19107659	382871	48.929
Total		39051906	906354	100.000



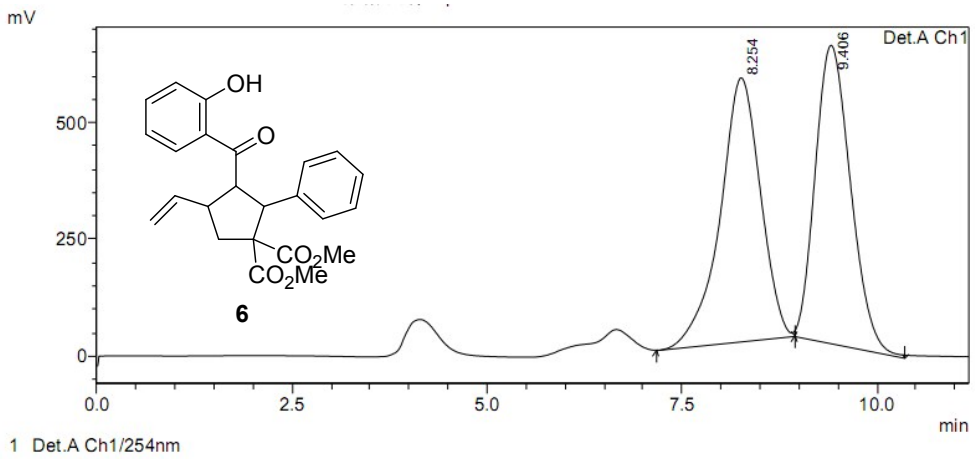
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.420	1977603	45281	2.096
2	27.337	92389683	1708305	97.904
Total		94367286	1753587	100.000

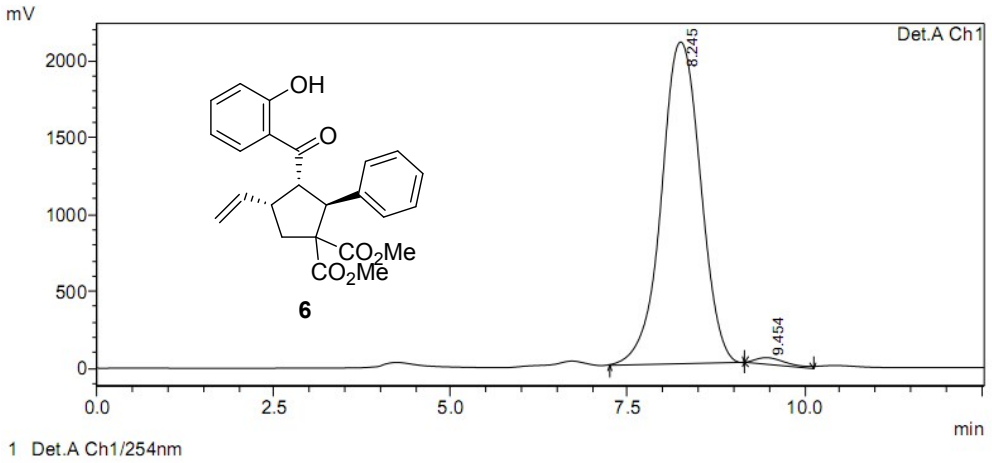
HPLC of **6**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.254	20340377	565415	50.310
2	9.406	20089560	638875	49.690
Total		40429937	1204290	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.245	80736080	2093078	98.401
2	9.454	1312127	42013	1.599
Total		82048206	2135091	100.000

3.X-ray crystallographic data of 3ia and 6.

A single crystal of **3ia** or **6** was obtained via evaporation of its hexane/isopropanol solvent mixture. The intensity data were collected on an (Dual, Cu at zero, Eos) diffractometer using graphite-monochromated Cu Kα radiation. Crystallographic data collection and structure solution parameters are summarized in Table S1. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.uk/data_request/cif.

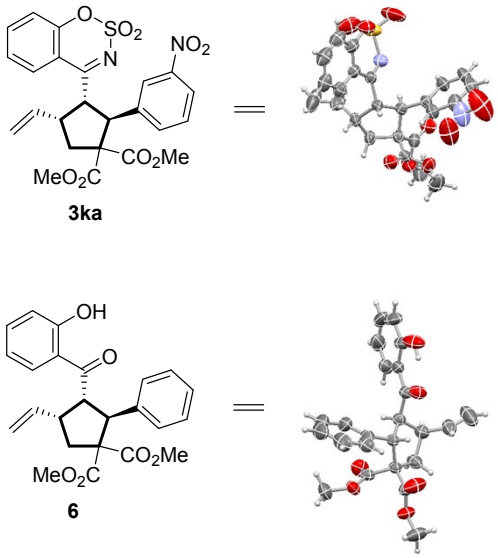


Figure S1. ORTEP diagram of **3ia** and **6**; thermal ellipsoids are drawn at the 50% probability level

Table S1 Crystal data and structure refinement for Compounds **3ia**, **6**.

Identification code	**3ia**	**6**
CCDC Deposit number	1873121	1874838
Empirical formula	$C_{24}H_{22}N_2O_9S$	$C_{24}H_{24}O_6$
Formula weight	514.49	408.43
Temperature (K)	273(2)	293(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	orthorhombic	monoclinic
space group	P 21 21 21	P 1 21/c 1
Unit cell dimensions	a = 12.2161(5)	10.3133(4)

Å	b = 12.5468(5)	11.2328(4)
	c = 16.7879(7)	19.0954(8)
(°)	α = 90	α = 90
	β = 90	99.604(2)
	γ = 90	γ = 90
Volume	2573.13(18) $Å^3$	2181.14(15) $Å^3$
Z	4	4
Calcd. density (Mg/m^3)	1.328	1.244
F(000)	1072	864
Limiting indices	$-13 \leq h \leq 13$	$-12 \leq h \leq 12$
	$-13 \leq k \leq 14$	$-13 \leq k \leq 13$
	$-17 \leq l \leq 19$	$-22 \leq l \leq 19$
GOOF	1.088	1.038
R(int)	15.18%	2.90%
R_1	5.79%	4.99%
$_wR_2$	15.31%	13.72%