
Supplementary Materials

**Organocatalytic regio- and enantioselective formal [4+2]-
annulation of chiral nitrogen-containing dipoles**

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Content

I. General information.....	S2
II. Experimental section.....	S3
III. Characterization Data of the Compounds 3 and 5.....	S8
IV. Characterization Data of the Compounds 6.....	S17
V. ECD Calculated of 3aa.....	S18
VI. Reference.....	S32
VII. NMR Copies of Compounds 3 and 5.....	S33
VIII. NMR Copies of Compounds 6.....	S53
IX. HPLC Spectra of compounds 3-6.....	S54

I. General information

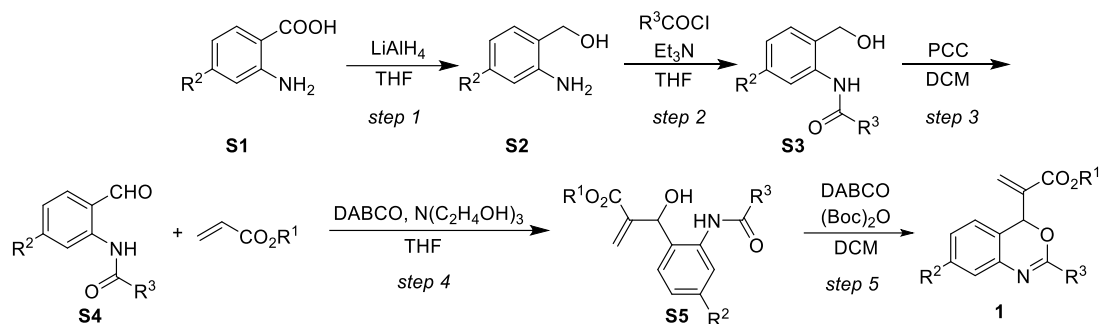
Flash column chromatography was performed over silica gel (200-300 mesh). All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using anhydrous solvents. Anhydrous tetrahydrofuran and common solvents were purchased from Energy Chemical, China. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. ^1H , ^{13}C , and ^{19}F spectra were collected on a Bruker AV 400 MHz or 500 MHz NMR spectrometer using residue solvent peaks as an internal standard (^1H NMR: CDCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.16 ppm). The enantiomeric excess values were determined by chiral HPLC using an Agilent 1200 LC instrument with Daicel CHIRALPAK®IB, IF-3.

II. Experimental section

Substrate Preparation

General procedure for the synthesis of substrates 1

o-Aminobenzoic acid is commercially available. The substrates **1** were synthesized following the general procedure reported earlier.^{[1],[2]}



Step 1: To a solution of LiAlH_4 (60 mmol, 2.0 equiv) in THF (60 mL) was added dropwise a solution of substituted 2-aminobenzoic acid (30 mmol, 1.0 equiv) in THF (60 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was hydrolyzed by addition of water (6 mL) and 5% NaOH (aqueous solution) (10.0 mL). Filter the resulting suspension and wash the residue with EtOAc. The organic phase was washed with water and saturated NaCl aqueous solution, dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 1/1) to afford product **S2**.

Step 2: To a solution of **S2** (20 mmol, 1.0 equiv) and Et_3N (40 mmol, 2.0 equiv) in THF (100 mL) at 0 °C, R^3COCl (20.0 mmol, 1.0 equiv) was added slowly. After addition was completed, the mixture was allowed to gradually warm to room temperature and stirred for 12 h. The solvent was removed under vacuum and the crude product **S2** was used in the following step without further purification.

Step 3: To a 500 mL round-bottomed flask was added **S3** (20 mmol, 1.0 equiv), PCC (30 mmol, 1.5 equiv) and DCM (250 mL). The mixture was stirred at room temperature for 24 h and filtered through a plug of diatomite. The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20/1) to afford product **S4**.

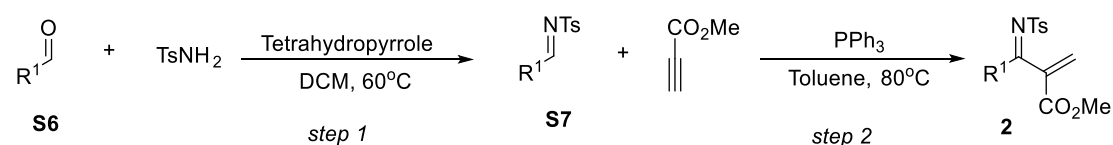
Step 4: To a 250 mL round-bottomed flask was added **S4** (10 mmol, 1.0 equiv), DABCO (10 mmol, 1.0 equiv), $N(C_2H_4OH)_3$ (8 mmol, 0.8 equiv), THF (100 mL) and methyl acrylate (30 mmol, 3.0 equiv). The mixture was stirred at room temperature for 72 h, the mixture was concentrated and dissolved in DCM (50 mL), following washed with saturated $NaHCO_3$ aqueous solution, saturated NaCl aqueous solution, dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product.

Step 5: To a 250 mL round-bottomed flask was added **S4** (10 mmol, 1.0 equiv), DABCO (2 mmol, 0.2 equiv), DCM (100 mL) and $(Boc)^2O$ (15 mmol, 2.0 equiv). The mixture was stirred at room temperature for 4 - 24 h, following washed with saturated $NaHCO_3$ aqueous solution, saturated NaCl aqueous solution, dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product **1**.

General procedure for the synthesis of substrates **2** and **4**

The unsaturated olefins **2** and **4** were synthesized following the general procedure reported earlier.^{[3],[4]}

General procedure for the synthesis of substrates **2**

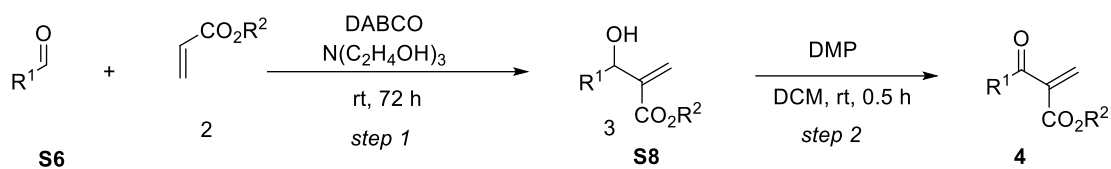


Step 1: To a 100 mL pressure tube was added **S6** (60 mmol, 1.2 equiv), $TsNH_2$ (50 mmol, 1.0 equiv), Tetrahydropyrrole (6 mmol, 0.1 equiv), DCM (30 mL) and Molecular sieve (1g/ mmol). The mixture was stirred at 60°C for 48 h, the mixture was filtered by diatomite. The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product.

Step 2: Under Ar atmosphere, to a 250 mL two mouth flask was added **S7** (10 mmol, 1.0 equiv), PPh_3 (2 mmol, 0.2 equiv), Toluene (100 mL), and Methyl propiolate (30 mmol, 3.0 equiv) was added in 3h.

The mixture was stirred at 80°C for 3 h, the mixture was no need to concentrated and purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **2**.

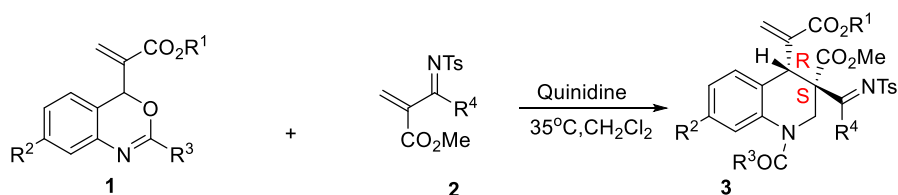
General procedure for the synthesis of substrates **4**



Step 1: To a 250 mL two mouth flask was added **S6** (50 mmol, 1.0 equiv), **2** (50 mmol, 3.0 equiv), $N(C_2H_4OH)_3$ (40 mmol, 0.8 equiv) and DABCO (50 mmol, 1.0 equiv), stirred in rt for 48 h. The solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford the desired product.

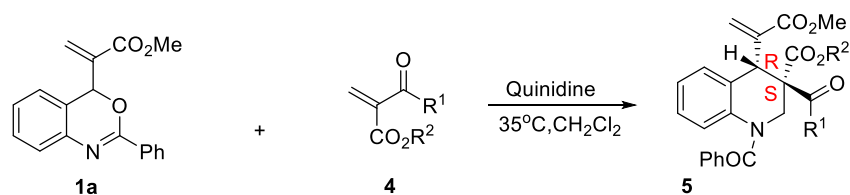
Step 2: To a 250 mL round-bottomed flask was added **S8** (10 mmol, 1.0 equiv), DCM (50mL) and Dess-Martin periodinane (30 mmol, 3.0 equiv). The mixture was stirred at 0°C for 1 h, the mixture was no need to concentrated and purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **4**.

General procedure for the synthesis of **3**



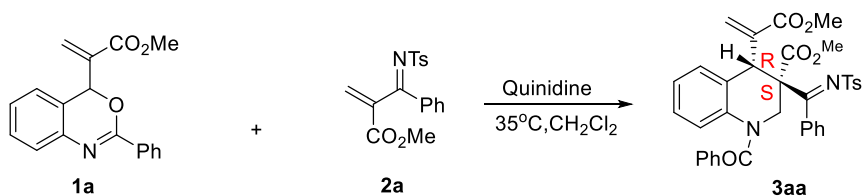
To a mixture of **1** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv) and quinidine (0.01 mmol, 0.1 equiv) in the CH_2Cl_2 (0.1 mL), stirred 96 h in 35°C. The mixture purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **3**.

General procedure for the synthesis of **5**



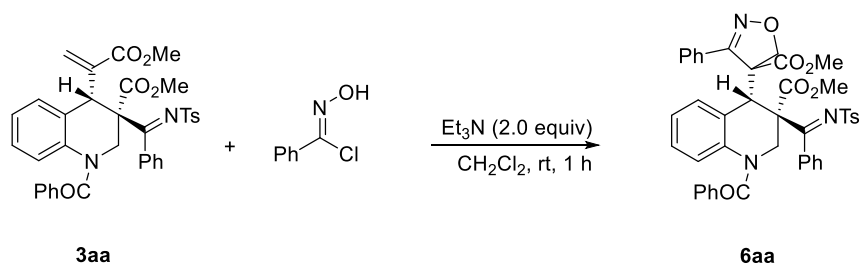
To a mixture of **1a** (0.1 mmol, 1.0 equiv), **4** (0.2 mmol, 2.0 equiv) and quinidine (0.01 mmol, 0.1 equiv) in the CH₂Cl₂ (0.1 mL), stirred 96 h in 35°C. The mixture purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **5**.

General procedure for the gram-scale synthesis of **3aa**



To a 250 mL round-bottomed flask was added **1a** (5 mmol, 1.0 equiv), **2a** (10 mmol, 2.0 equiv) and quinidine (0.5 mmol, 0.1 equiv) in the CH₂Cl₂ (5 mL), stirred 96 h in 35°C. The mixture purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **3aa** (2.4 g, 75% yield, 89% ee).

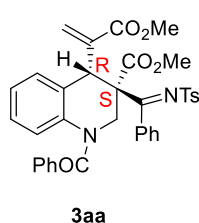
Transformation of the product **3aa**



To a stirred solution of N-hydroxybenzimidoyl chloride (15.6 mg, 0.1 mmol, 2.0 equiv) in 1 mL CH₂Cl₂ was added Et₃N (0.1 mmol, 2.0 equiv) at room temperature. After stirred for 10 min, **3aa** (31.8 mg, 0.05 mmol, 1.0 equiv) in 1 mL CH₂Cl₂ was added to the solution. The mixture was stirred for 1 h then evaporated to give the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate = 3/1) to provide the desired product **6aa** (36 mg, 96% yield, 79% ee).

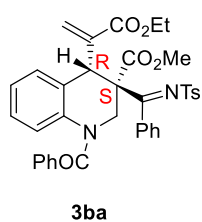
III. Characterization Data of the Compounds 3 and 5

Methyl (3S,4R)-1-benzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-((Z)-phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3aa).



3aa was prepared according to the general Procedure purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 176.4-176.9 °C 60.7 mg, 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 2H), 7.70 – 7.59 (m, 2H), 7.53 – 7.36 (m, 4H), 7.31 (m, 3H), 7.18 – 7.06 (m, 2H), 6.93 (m, 1H), 6.79 (m, 1H), 6.54 (m, 1H), 6.23 (s, 1H), 5.48 (s, 1H), 5.15 (s, 1H), 5.11 (m, 1H), 3.79 (m, 1H), 3.66 (s, 3H), 3.20 (s, 3H), 2.42 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 181.6, 170.7, 170.4, 166.7, 143.8, 142.2, 138.1, 137.4, 135.4, 132.3, 131.2, 130.4, 129.4, 129.0, 128.9, 128.5, 127.9, 127.8, 127.5, 126.2, 124.8, 123.9, 61.2, 52.8, 52.6, 45.7, 44.0, 21.7 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₆H₃₃N₂O₇S 637.2003; Found 637.1998. Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR (minor) = 21.119 min, tR (major) = 22.668 min, 89 % ee. [α]²⁰_D = 295.0 (c = 1.00, CH₂Cl₂).

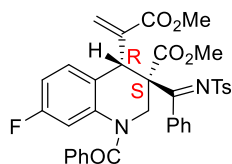
Methyl (3S,4R)-1-benzoyl-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ba).



3ba was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 177.4-178.6 °C, 50.9 mg, 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 2H), 7.65 – 7.53 (m, 2H), 7.49 – 7.35 (m, 4H), 7.35 – 7.26 (m, 6H), 7.12 (m, 1H), 6.93 (m, 1H), 6.78 (m, 1H), 6.53 (m, 1H), 6.30 (s, 1H), 5.47 (s, 1H), 5.23 (s, 1H), 5.09 (m, 1H), 4.10 (m, 2H), 3.84 (m, 1H), 3.24 (s, 3H), 2.42 (s, 3H), 1.20 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 181.6, 170.7, 170.3, 166.3, 143.8, 142.2, 138.0, 137.3, 135.4, 135.2, 131.9, 131.0, 130.2, 129.3, 129.2, 129.2, 128.9, 128.4, 127.9, 127.6, 127.4, 126.1, 124.7, 124.0, 61.6, 61.4, 52.8, 45.6, 43.9, 21.7, 21.6, 14.1 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₇H₃₅N₂O₇S 651.2160; Found 651.2157. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol =

60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR (minor) = 22.068 min, tR (major) = 23.398 min, 86% ee. $[\alpha]^{20}_D = 205.48$ ($c = 1.00$, CH_2Cl_2).

Methyl (3S,4R)-1-benzoyl-7-fluoro-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ca)

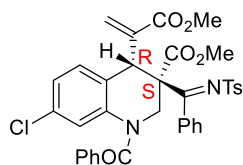


3ca

3ca was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 141.4-142.1 °C, 60.9 mg, 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (m, 2H), 7.63 – 7.54 (m, 2H), 7.52 – 7.31 (m, 8H),

7.29 – 7.24 (m, 2H), 7.11 – 7.03 (m, 1H), 6.70 – 6.65 (m, 1H), 6.49 – 6.34 (m, 1H), 6.26 (s, 1H), 5.43 (s, 1H), 5.19 (s, 1H), 5.00 (m, 1H), 3.80 (m, 1H), 3.65 (s, 3H), 3.21 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 181.4, 170.6, 170.5, 166.6, 160.3 ($J_{CF} = 24.6$ Hz), 143.9, 142.1, 138.5 ($J_{CF} = 10.1$ Hz), 137.93, 135.2, 134.9, 132.4, 131.6 ($J_{CF} = 9.1$ Hz), 131.5, 131.2, 129.37, 128.89, 128.74, 127.92, 127.67, 127.43, 124.7 ($J_{CF} = 3.1$ Hz), 112.3 ($J_{CF} = 22.2$ Hz), 110.5 ($J_{CF} = 26.3$ Hz), 60.9, 52.8, 52.6, 46.0, 43.6, 21.7. ppm. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{32}\text{FN}_2\text{O}_7\text{S}$ 655.1909; Found 655.1902. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 34.340 min, tR(major) = 36.271 min, 88% ee. $[\alpha]^{20}_D = 246.71$ ($c = 1.00$, CH_2Cl_2).

Methyl (3S,4R)-1-benzoyl-7-chloro-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3da)



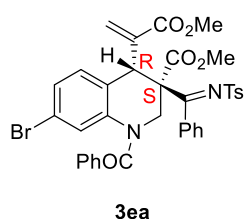
3da

3da was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 142.7-143.1 °C, 62.9 mg, 94% yield. ^1H NMR (400 MHz, Chloroform- d) δ 7.71 (m, 2H), 7.56 (s, 2H), 7.50 – 7.32 (m, 8H), 7.26 (m, 2H), 7.04 (m, 1H), 6.92 (m, 1H), 6.67 (s, 1H), 6.26 (s, 1H), 5.42 (s,

1H), 5.19 (s, 1H), 5.01 (m, 1H), 3.78 (m, 1H), 3.65 (s, 3H), 3.21 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 181.3, 170.6, 170.5, 166.6, 143.9, 141.9, 138.2, 137.9, 135.2, 134.8, 132.5, 131.7, 131.6, 131.3, 131.2, 129.4, 128.7, 128.7, 127.9, 127.7, 127.4, 127.4, 124.9, 123.6, 60.8, 52.9, 52.6,

45.9, 43.7, 21.7 ppm. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{36}H_{32}ClN_2O_7S$ 671.1613; Found 670.1609. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $tR(\text{minor})$ = 38.883 min, $tR(\text{major})$ = 41.090 min, 82% ee. $[\alpha]_D^{20}$ = 134.00 (c = 1.00, CH_2Cl_2).

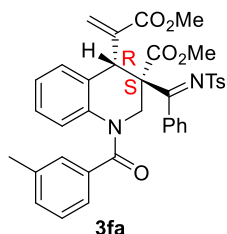
Methyl (3S, 4R)-1-benzoyl-7-bromo-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ea)



3ea

3ea was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 146.4-147.1 °C, 52.1 mg, 73% yield. 1H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.59 – 7.55 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 – 7.34 (m, 6H), 7.26 (m, 2H), 7.07 – 7.05 (m, 1H), 6.97 (m, 1H), 6.87 – 6.76 (m, 1H), 6.26 (s, 1H), 5.40 (s, 1H), 5.20 (s, 1H), 5.02 – 4.99 (m, 1H), 3.82 – 3.71 (m, 1H), 3.65 (s, 3H), 3.22 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.3, 170.6, 170.4, 166.5, 143.9, 141.8, 138.4, 137.9, 135.2, 134.7, 132.6, 131.6, 131.5, 131.2, 129.4, 128.7, 128.7, 128.0, 127.9, 127.8, 127.7, 127.4, 126.5, 119.5, 60.8, 52.9, 52.6, 45.9, 43.7, 21.7 ppm. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{36}H_{32}BrN_2O_7S$ 715.1107; Found 715.1106. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $tR(\text{minor})$ = 37.205 min, $tR(\text{major})$ = 41.713 min, 82% ee. $[\alpha]_D^{20}$ = 138.33 (c = 1.00, CH_2Cl_2).

Methyl (3S, 4R)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1-(3-methylbenzoyl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3fa)

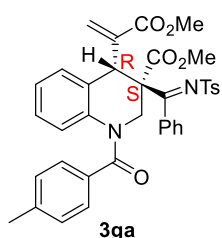


3fa

3fa was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 116.4-117.1 °C, 63.3 mg, 97% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m 2H), 7.64 – 7.61 (m, 2H), 7.47 – 7.37 (m, 3H), 7.30 – 7.20 (m, 5H), 7.09 (s, 2H), 6.95 – 6.90 (m, 1H), 6.80 (m, 1H), 6.57 (m, 1H), 6.22 (m, 1H), 5.48 (s, 1H), 5.13 (s, 1H), 5.08 (m, 1H), 3.80 – 3.76 (m, 1H), 3.65 (m,

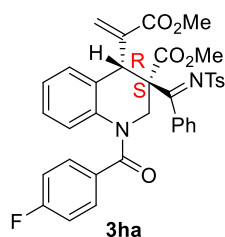
3H), 3.17 (m, 3H), 2.42 (m, 3H), 2.34 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 181.7, 170.7, 170.5, 166.7, 143.8, 142.3, 141.7, 138.1, 137.6, 135.4, 135.4, 132.4, 131.2, 130.4, 129.3, 129.3, 129.2, 129.1, 128.9, 128.9, 127.9, 127.8, 127.5, 126.2, 124.6, 123.9, 61.2, 52.7, 52.6, 45.8, 44.0, 21.8, 21.7 ppm. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{35}\text{N}_2\text{O}_7\text{S}$ 651.2160; Found 651.2156. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_R(\text{minor})$ = 60.367 min, $t_R(\text{major})$ = 53.985 min, 92% ee. $[\alpha]_D^{20}$ = 311.53 (c = 1.00, CH_2Cl_2).

Methyl (3S, 4R)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1-(4-methylbenzoyl)-3-(phenyl (tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ga)



3ga was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 124.9-125.6 °C, 60.5 mg, 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.70 (m, 2H), 7.68 – 7.57 (m, 2H), 7.51 – 7.35 (m, 4H), 7.26 – 7.20 (m, 3H), 7.09 (m, 3H), 6.92 (m, 1H), 6.84 – 6.78 (m, 1H), 6.58 (m, 1H), 6.22 (s, 1H), 5.48 (s, 1H), 5.14 (s, 1H), 5.08 (m, 1H), 3.78 (m, 1H), 3.65 (s, 3H), 3.18 (s, 3H), 2.42 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 181.7, 170.7, 170.5, 166.7, 143.8, 142.3, 141.7, 138.1, 137.6, 135.4, 132.4, 131.2, 130.4, 129.3, 129.3, 129.2, 129.1, 128.9, 127.9, 127.8, 127.5, 126.2, 124.6, 123.9, 61.2, 52.7, 52.6, 45.8, 44.0, 21.8, 21.7 ppm. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{35}\text{N}_2\text{O}_7\text{S}$ 651.2160; Found 651.2157. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_R(\text{minor})$ = 24.821 min, $t_R(\text{major})$ = 21.538 min, 84% ee. $[\alpha]_D^{20}$ = 341.26 (c = 1.00, CH_2Cl_2).

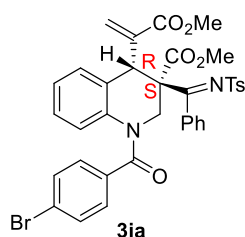
Methyl (3S, 4R)-1-(4-fluorobenzoyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(phenyl (tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ha)



3ha was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 116.4-116.7 °C, 61.6 mg, 94% yield. ^1H NMR (500 MHz,

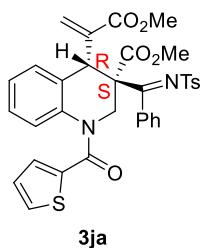
CDCl₃) δ 7.78 – 7.69 (m, 2H), 7.66 – 7.58 (m, 2H), 7.48 – 7.39 (m, 3H), 7.28 – 7.24 (m, 6H), 7.11 (m, 1H), 6.95 (m, 1H), 6.87 – 6.76 (m, 1H), 6.51 (m, 1H), 6.23 (s, 1H), 5.46 (s, 1H), 5.15 (s, 1H), 5.07 (m, 1H), 3.80 (m, 1H), 3.65 (s, 3H), 3.19 (s, 3H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.4, 170.0 (*J*_{CF} = 164.6 Hz), 166.6, 143.9, 142.1, 138.0, 137.3, 137.1, 135.3, 133.7, 132.3, 131.2, 130.4, 129.3, 129.2 (*J*_{CF} = 17.1 Hz), 128.8, 127.8 (*J*_{CF} = 18.2 Hz), 127.6, 127.3 (*J*_{CF} = 28.3 Hz), 126.3, 125.0, 123.9, 61.2, 52.8, 52.6, 45.7, 44.0, 21.7 ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -107.86 ppm. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₂FN₂O₇S 655.1909; Found 655.1904. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 47.330 min, tR(major) = 45.114 min, 88% ee. [α]²⁰_D = 198.0 (*c* = 0.50, CH₂Cl₂).

Methyl (3S, 4R)-1-(4-bromobenzoyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ia).



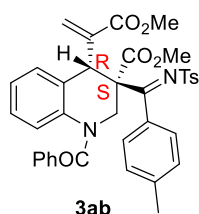
3ia was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 134.4-134.6 °C, 58.2 mg, 82% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.82 – 7.70 (m, 2H), 7.68 – 7.57 (m, 2H), 7.47 – 7.44 (m, 1H), 7.43 – 7.38 (m, 4H), 7.27 – 7.25 (m, 2H), 7.24 – 7.17 (m, 2H), 6.96 (m, 1H), 6.83 (m, 1H), 6.51 (m, 1H), 6.23 (s, 1H), 5.46 (s, 1H), 5.15 (s, 1H), 5.07 (m, 1H), 3.79 (m, 1H), 3.65 (s, 3H), 3.19 (s, 3H), 2.42 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 181.4, 170.8, 169.2, 166.7, 143.9, 142.1, 138.0, 137.1, 135.3, 134.2, 132.3, 131.8, 131.2, 130.6, 130.5, 129.4, 129.2, 128.0, 127.8, 127.5, 126.3, 125.8, 125.1, 123.9, 61.2, 52.8, 52.6, 45.7, 43.98, 21.8 ppm. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₂BrN₂O₇S 715.1108; Found 715.1105. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 54.776 min, tR(major) = 48.586 min, 90% ee. [α]²⁰_D = 341.5 (*c* = 1.00, CH₂Cl₂).

Methyl (Z)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(phenyl(tosylimino)methyl)-1-(thiophene-2-carbonyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ja).



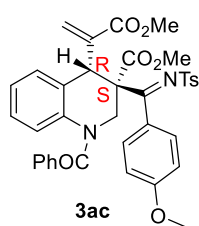
3ja was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 169.4-169.7 °C, 60.3 mg, 94% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.69 (m, 2H), 7.68 – 7.59 (m, 2H), 7.52 – 7.35 (m, 4H), 7.27 (m, 2H), 7.13 (m, 1H), 7.03 – 6.81 (m, 5H), 6.23 (s, 1H), 5.47 (s, 1H), 5.16 (s, 1H), 5.02 (m, 1H), 3.88 (m, 1H), 3.65 (s, 3H), 3.14 (s, 3H), 2.42 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 181.5, 170.4, 166.7, 164.1, 143.9, 142.0, 138.0, 137.5, 137.5, 135.3, 132.2, 131.8, 131.1, 131.0, 130.4, 129.4, 129.3, 127.89, 127.73, 127.45, 127.2, 126.3, 125.0, 123.9, 61.4, 52.7, 52.6, 46.7, 44.0, 21.7 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₄H₃₁N₂O₇S₂ 643.1567; Found 643.1564. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 22.590 min, tR(major) = 26.031 min, 89% ee. [α]_D²⁰ = 308.667 (c = 0.50, CH₂Cl₂).

Methyl (3S, 4R)-1-benzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(p-tolyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ab)



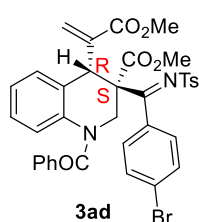
3ab was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 126.4-127.1 °C, 42.3 mg, 65% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.66 (m, 2H), 7.62 – 7.49 (m, 2H), 7.40 – 7.37 (m, 1H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 4H), 7.22 – 7.19 (m, 2H), 7.11 – 7.07 (m, 1H), 6.94 – 6.91 (m, 1H), 6.80 – 6.76 (m, 1H), 6.53 (m, 1H), 6.18 (s, 1H), 5.48 (s, 1H), 5.17 – 5.04 (m, 2H), 3.79 (m, 1H), 3.63 (s, 3H), 3.21 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 181.6, 170.9, 170.4, 166.6, 143.7, 142.2, 141.9, 138.3, 137.4, 135.4, 132.7, 132.3, 131.1, 130.4, 129.3, 129.1, 128.9, 128.6, 128.5, 128.1, 127.42, 126.11, 124.7, 123.9, 61.2, 52.8, 52.5, 45.8, 44.0, 21.7, 21.7 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₇H₃₅N₂O₇S 651.2160; Found 651.2158. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 34.340 min, tR(major) = 36.271 min, 88% ee. [α]_D²⁰ = 128.12 (c = 1.00, CH₂Cl₂).

Methyl (3S, 4R)-1-benzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-((4-methoxyphenyl)(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ac)



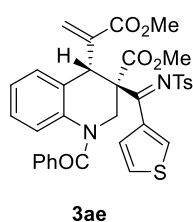
3ac was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 131.1-131.6 °C, 32.0 mg, 48% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.70 (m, 4H), 7.40 – 7.37 (m, 1H), 7.34 (m, 2H), 7.30 – 7.26 (m, 4H), 7.09 – 7.07 (m, 1H), 6.94 – 6.90 (m, 3H), 6.80 – 6.76 (m, 1H), 6.53 (m, 1H), 6.10 (s, 1H), 5.49 (s, 1H), 5.18 – 5.10 (m, 1H), 5.03 (s, 1H), 3.77 (m, 1H), 3.60 (s, 3H), 3.21 (s, 3H), 2.42 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 180.7, 171.1, 170.4, 166.5, 162.2, 143.6, 142.2, 138.5, 137.5, 135.4, 132.3, 131.1, 130.7, 130.5, 129.3, 129.1, 129.0, 128.5, 128.0, 127.3, 126.1, 124.7, 123.8, 113.3, 61.1, 55.5, 52.8, 52.5, 45.9, 44.0, 21.7 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₇H₃₅N₂O₈S 667.2109; Found 667.2104. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: retention time: tR(minor) = 32.223 min, tR(major) = 29.134 min, 88% ee. [α]²⁰_D = 206.04 (c = 1.00, CH₂Cl₂).

Methyl (3S, 4R)-1-benzoyl-3-((4-bromophenyl)(tosylimino)methyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ad)



3ad was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 134.1-135.2 °C, 53.6 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.70 (m, 2H), 7.55 (s, 4H), 7.42 – 7.37 (m, 1H), 7.33 – 7.26 (m, 6H), 7.13 – 7.08 (m, 1H), 6.95 – 6.91 (m, 1H), 6.81 – 6.77 (m, 1H), 6.53 (m, 1H), 6.21 (s, 1H), 5.47 (s, 1H), 5.14 – 5.00 (m, 2H), 3.78 – 3.71 (m, 1H), 3.66 (s, 3H), 3.21 (s, 3H), 2.43 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 180.4, 170.6, 170.4, 166.7, 144.1, 142.2, 137.8, 137.3, 135.2, 134.1, 132.6, 131.2, 131.2, 130.5, 129.5, 129.4, 128.9, 128.7, 128.5, 127.4, 126.2, 126.1, 124.8, 123.8, 61.0, 52.9, 52.7, 45.6, 44.0, 21.8 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₆H₃₂BrN₂O₇S 715.1108; Found 715.1107. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 25.688 min, tR(major) = 23.970 min, 93% ee. [α]²⁰_D = 157.64 (c = 1.00, CH₂Cl₂).

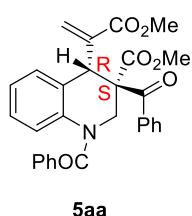
Methyl (3S, 4R)-1-benzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-3-(thiophen-3-yl(tosylimino)methyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ae)



3ae

3ae was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 141.6-142.4 °C, 30.2mg, 47% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.16 (m, 1H), 7.86 – 7.73 (m, 2H), 7.55 (m, 1H), 7.41 – 7.37 (m, 1H), 7.36 – 7.31 (m, 3H), 7.31 – 7.26 (m, 4H), 7.09 (m, 1H), 6.95 – 6.91 (m, 1H), 6.78 (m, 1H), 6.51 (m, 1H), 6.20 (s, 1H), 5.47 (s, 1H), 5.18 – 5.09 (m, 1H), 5.02 (s, 1H), 3.73 (m, 1H), 3.62 (s, 3H), 3.28 (s, 3H), 2.42 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 174.6, 171.3, 170.3, 166.4, 143.7, 142.1, 138.5, 137.5, 135.7, 135.4, 132.5, 132.3, 131.1, 130.4, 129.4, 129.0, 128.9, 128.5, 128.5, 127.2, 126.1, 125.3, 124.8, 123.9, 60.8, 52.9, 52.5, 45.6, 43.8, 21.7 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₄H₃₁N₂O₇S₂ 643.1567; Found 643.1564. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 20.538 min, tR(major) = 22.544 min, 87% ee. [α]_D²⁰ = 159.6 (c = 1.00, CH₂Cl₂).

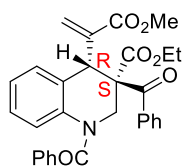
Methyl (3S, 4R)-1,3-dibenzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (5aa)



5aa

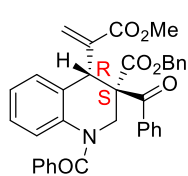
5aa was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 115.9-116.5 °C, 33.9 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.85 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.41 (m, 4H), 7.41 – 7.35 (m, 1H), 7.35 – 7.27 (m, 2H), 7.18 – 7.11 (m, 1H), 7.00 – 6.96 (m, 1H), 6.88 – 6.84 (m, 1H), 6.69 (m, 1H), 6.27 (s, 1H), 5.51 (s, 1H), 5.27 (s, 1H), 5.21 (m, 1H), 4.00 (m, 1H), 3.47 (s, 3H), 3.32 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 194.2, 172.1, 170.3, 166.8, 142.4, 137.8, 136.2, 135.6, 133.5, 131.8, 130.9, 130.0, 129.6, 129.0, 128.8, 128.6, 128.4, 126.1, 124.9, 124.3, 61.4, 53.2, 52.0, 45.6, 43.0 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₉H₂₆NO₆ 484.1755; Found 484.1754. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR (minor) = 15.052 min, tR (major) = 11.996 min, 81% ee. [α]_D²⁰ = 242.31 (c = 0.50, CH₂Cl₂).

Ethyl (3S, 4R)-1,3-dibenzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (5ab).



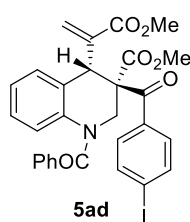
5ab was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 117.6-118.4 °C, 30.2 mg, 61% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.96 – 7.86 (m, 2H), 7.60 – 7.49 (m, 1H), 7.48 – 7.35 (m, 5H), 7.35 – 7.28 (m, 2H), 7.20 – 7.01 (m, 1H), 6.98 – 6.95 (m, 1H), 6.85 – 6.82 (m, 1H), 6.65 (m, 1H), 6.27 (s, 1H), 5.51 (s, 1H), 5.26 (s, 1H), 5.23 (m, 1H), 4.07 – 3.93 (m, 2H), 3.88 (m, 1H), 3.33 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 194.7, 171.6, 170.3, 166.8, 142.5, 137.8, 136.3, 135.7, 133.4, 131.8, 130.9, 130.0, 129.6, 129.0, 128.8, 128.5, 128.4, 126.0, 124.8, 124.2, 62.5, 61.6, 52.0, 45.4, 43.0, 13.6 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₀H₂₈NO₆ 498.1911 Found 498.1912. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 14.955 min, tR(major) = 12.704 min, 88% ee. [α]_D²⁰ = 253.71 (c = 1.00, CH₂Cl₂).

Benzyl (3S, 4R)-1,3-dibenzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (5ac).



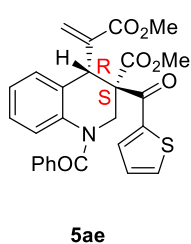
5ac was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 181.4-119.4 °C, 37.5 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.73 (m, 2H), 7.52 – 7.36 (m, 4H), 7.35 – 7.24 (m, 4H), 7.18 – 7.11 (m, 2H), 7.11 – 7.02 (m, 2H), 7.00 – 6.96 (m, 1H), 6.93 – 6.81 (m, 3H), 6.73 (m, 1H), 6.28 (s, 1H), 5.49 (s, 1H), 5.26 (s, 1H), 5.20 (m, 1H), 5.05 (m, 1H), 4.71 (m, 1H), 4.05 (m, 1H), 3.31 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 194.34, 171.42, 170.37, 166.73, 142.34, 137.78, 136.07, 135.63, 134.13, 133.34, 131.86, 130.85, 129.97, 129.45, 128.98, 128.75, 128.64, 128.44, 128.39, 128.33, 128.31, 126.07, 124.80, 124.21, 68.28, 61.41, 52.0, 45.7, 43.2 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₅H₃₀NO₆ 560.2078; Found 560.2064. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 16.311 min, tR(major) = 14.468 min, 82% ee. [α]_D²⁰ = 292.21 (c = 1.00, CH₂Cl₂).

Methyl (3S, 4R)-1-benzoyl-3-(4-iodobenzoyl)-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (5ad).



5ad was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 124.4-124.9 °C, 41.7 mg, 68% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.86 – 7.73 (m, 2H), 7.66 – 7.52 (m, 2H), 7.47 – 7.36 (m, 3H), 7.35 – 7.27 (m, 2H), 7.14 – 7.12 (m, 1H), 7.00 – 6.96(m, 1H), 6.88 – 6.80 (m, 1H), 6.67 (m, 1H), 6.29 (s, 1H), 5.47 (s, 1H), 5.26 (s, 1H), 5.18 (m, 1H), 3.96 (m, 1H), 3.47 (s, 3H), 3.38 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 193.8, 171.9, 170.3, 166.8, 142.2, 137.9, 137.7, 135.5, 135.4, 132.1, 131.0, 130.0, 129.3, 128.9, 128.4, 126.1, 124.9, 124.2, 101.7, 61.4, 53.3, 52.2, 45.4, 42.9 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₉H₂₅NO₆ 610.0721; Found 610.0717. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 18.291 min, tR(major) = 14.114 min, 91% ee. [α]_D²⁰ = 312.73 (c = 1.00, CH₂Cl₂).

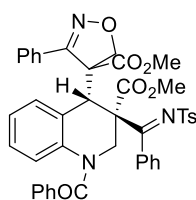
Methyl (3S, 4R)-3-benzoyl-4-(3-methoxy-3-oxoprop-1-en-2-yl)-1-(thiophene-2-carbonyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (5ae).



5ae was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 109.4-110.6 °C, 23.3 mg, 48% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.76 – 7.75 (m, 1H), 7.68 – 7.67 (m, 1H), 7.50 – 7.37 (m, 3H), 7.37 – 7.29 (m, 2H), 7.17 – 7.15 (m, 1H), 7.13 – 7.11 (m, 1H), 7.00 – 6.96 (m, 1H), 6.90 – 6.79 (m, 1H), 6.70 (m, 1H), 6.27 (s, 1H), 5.54 (s, 1H), 5.29 (s, 1H), 5.23 (m, 1H), 3.99 (m, 1H), 3.56 (s, 3H), 3.42 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 186.4, 171.7, 170.4, 167.2, 142.8, 142.4, 137.8, 135.6, 135.2, 132.9, 131.5, 131.0, 130.1, 129.5, 129.0, 128.6, 128.5, 126.2, 124.9, 124.2, 61.7, 53.4, 52.1, 45.2, 42.9 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₂₄NO₆S 490.1309; Found 490.1315. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 21.887 min, tR(major) = 14.433 min, 85% ee. [α]_D²⁰ = 292.21 (c = 0.50, CH₂Cl₂).

IV. Characterization Data of the Compounds 6

Methyl (3S, 4R)-4-(1-benzoyl-3-(methoxycarbonyl)-3-(phenyl(tosylimino)methyl)-1,2,3,4-tetrahydroquinolin-4-yl)-3-phenyl-4,5-dihydroisoxazole-4-carboxylate (6aa).



6aa

6aa was prepared according to the general procedure, purified by flash chromatography (petroleum ether/ethyl acetate = 3/1) and obtained as white solid, melting point 158.4-159.6 °C, 36.1 mg, 96% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.56 (m, 2H), 7.47 – 7.32 (m, 9H), 7.31 – 7.22 (m, 6H), 7.19 – 7.15 (m, 1H), 7.15 – 7.07 (m, 1H), 7.00 – 6.97 (m, 4H), 4.94 (m, 1H), 4.41 – 4.38 (m, 1H), 4.29 – 4.13 (m, 2H), 3.73 (m, 1H), 3.41 (s, 3H), 3.34 (s, 3H), 2.31 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 181.4, 171.1, 171.0, 169.0, 157.7, 143.6, 137.6, 137.2, 136.0, 134.1, 131.1, 130.8, 130.3, 130.2, 129.3, 128.8, 128.4, 128.3, 128.0, 127.9, 127.6, 127.3, 127.0, 125.8, 124.7, 124.0, 90.7, 62.1, 53.5, 53.2, 51.5, 48.9, 47.1, 21.7 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₄₃H₃₈N₃O₈S 756.2374; Found 756.2379. HPLC conditions: Daicel CHIRALPAK IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 23.235 min, tR(major) = 30.810 min, 79% ee. [α]_D²⁰ = 98.70 (c = 0.50, CH₂Cl₂).

VI. ECD Calculated off 3aa

Determination of the absolute configuration.

The absolute configuration of **3aa** was determined by ECD. Conformations of **(3S,4R)-3aa** was searched using Grimme's programs xTB 6.3. Next, Conformers within 5 kcal/mol were conducted at the M06-2X/6-31+G(d) level in DCM solvent by a self-consistent reaction field (SCRF) using the SMD implicit solvent model with *Gaussian 16*. Then, conformers with distinct conformations were further subjected to TD-DFT calculation at at the M06-2X/6-311+G(d,p) level in DCM solvent as aforementioned for dipole and rotational strengths of the first 30 excited states in the UV range. Next, ECD spectra of **(3S,4R)-3aa** (Figure 1) were calculated from excitation energies and rotational strengths as averages weighed on Boltzmann conformer relative populations as a sum of Gaussian functions centered at the wavelength of each transition with appropriate widths of the band at half-height using SpecDis (version 1.71), respectively.

Samples of compound **3aa** for ECD were dissolved in DCM solvent, and spectra were acquired in a 1.0-mm pathlength cuvette, respectively. The UV and ECD spectra were recorded using a Chirascan Spectrophotometer with the following instrumental parameters: 220–380 nm with a 1 nm step and a 2 nm bandwidth with data averaging over 1.0 sec per point. Three spectral acquisitions were taken for each sample and were averaged and smoothed thereafter.

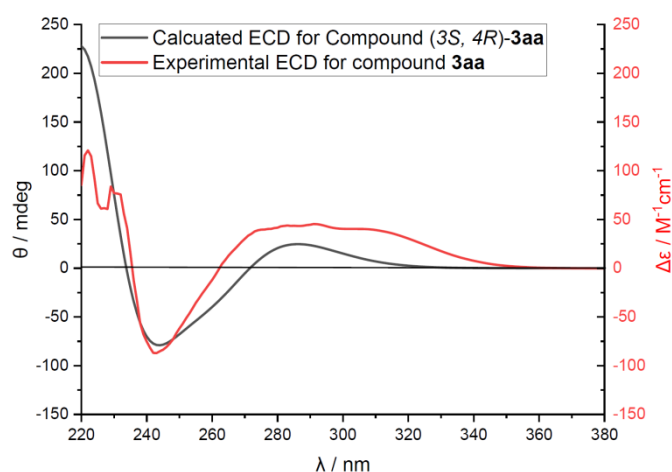


Figure S1. Comparison of the calculated ECD of compound (3S,4R)-3aa with the experimental one of compound 3aa. Width of the band at half-height σ : 0.35 eV; Shift: 20 nm.

The calculated spectrum for **(3*S*,4*R*)-3aa** was same to the experimental one, and thus, the absolute configuration of compound **3aa** was assigned to **3*S*,4*R*** accordingly. The absolute configurations of other chiral products were assigned by analogue to that of **3aa**.

Table S1. Energies of calculated conformers of (3*S*,4*R*)-3aa. Energies (E) (in Hartree) of the structures calculated at the SMD_(DCM)/M06-2X/6-31+G(d) level of theory.

Structure (3 <i>S</i> ,4 <i>R</i>)-3aa	E _(solv-M06-2X)	G _(corr-solv-M06-2X)	G _(solv-M06-2X)	Boltzmann distribution(%)
conformer-1	-2424.570539	0.546315	-2424.024224	59.31%
conformer-2	-2424.567952	0.544247	-2424.023705	32.75%
conformer-3	-2424.565856	0.544019	-2424.021837	4.72%
conformer-4	-2424.563397	0.544456	-2424.018941	0.23%

Cartesian coordinates for DFT-optimized structures for all the optimized compounds and transition states

3aa-conformer-1

C	1.51571800	4.92803900	-0.03746400
C	0.78204200	4.04250900	-0.81321100
C	0.99059100	2.66155700	-0.69194900
C	2.00592900	2.16625800	0.13127000
C	2.73502900	3.07770600	0.90633400
C	2.48550100	4.44229900	0.84560600
H	1.33861500	5.99577100	-0.12737300
H	0.03503100	4.40979100	-1.51040400
C	2.40100000	0.69772600	0.18212700
H	3.51724100	2.69707800	1.56033500

H	3.05918400	5.12767600	1.46243600
C	1.46869800	-0.22362400	-0.68024700
C	0.94202200	0.56416600	-1.90079800
H	0.28692300	-0.04431800	-2.52103800
N	0.21658200	1.73716600	-1.44302200
C	-1.14495900	1.79295500	-1.63009400
C	-1.96617900	2.77107200	-0.84210300
C	-1.77381900	2.97065600	0.52872500
C	-3.03764000	3.38802300	-1.49451100
C	-2.64828200	3.79087700	1.23815300
H	-0.96523600	2.46666400	1.05056500
C	-3.89319400	4.23031400	-0.78775300
H	-3.19377600	3.20393900	-2.55386700
C	-3.70005600	4.43055500	0.58044700
H	-2.50797900	3.92496400	2.30687600
H	-4.71504900	4.72113600	-1.30112900
H	-4.37404400	5.07754200	1.13510700
O	-1.70585400	1.02572900	-2.41075100
C	3.85786700	0.52764700	-0.23745000
C	4.41433300	1.11766900	-1.29819900
H	3.85367500	1.81375600	-1.91769900
H	5.45261100	0.94133800	-1.56200800
C	4.69082500	-0.33176000	0.66330300
O	4.48289000	-0.45990700	1.85146400
O	5.70601600	-0.92240800	0.02675100
C	6.58098300	-1.71153800	0.84319400

H	6.02207000	-2.50760000	1.34037700
H	7.31762000	-2.13216600	0.15993100
H	7.06952600	-1.08267500	1.59120500
H	2.32662800	0.36168100	1.22030600
C	2.24992700	-1.43130800	-1.20572000
O	2.79504600	-2.11244300	-0.19771600
O	2.35610400	-1.73565200	-2.36941200
C	3.51267300	-3.30532900	-0.54806300
H	4.36830600	-3.05668400	-1.18049100
H	3.84272000	-3.73416100	0.39727600
H	2.84865300	-3.99826400	-1.07106500
C	0.27591600	-0.76593800	0.12922400
C	-0.31868800	-2.06659100	-0.32170900
C	-1.19130100	-2.11962700	-1.41498900
C	0.03918100	-3.24072600	0.35099600
C	-1.70216200	-3.34831100	-1.82910900
H	-1.49346900	-1.20560000	-1.92044800
C	-0.47165200	-4.46545300	-0.07594100
H	0.71096400	-3.19300700	1.20331300
C	-1.34085900	-4.52130400	-1.16529400
H	-2.39031000	-3.38412000	-2.66916600
H	-0.19202800	-5.37446700	0.44918700
H	-1.74031900	-5.47677300	-1.49361700
N	-0.09500800	-0.05598100	1.12495200
S	-1.32671000	-0.51534800	2.21585700
O	-0.77017100	-1.57574300	3.05335800

O	-1.71841600	0.74899600	2.82726000
C	-2.72406100	-1.14982900	1.32508300
C	-3.46175300	-0.28037400	0.52583100
C	-3.05944600	-2.49564700	1.45182600
C	-4.54370700	-0.78590000	-0.18856000
H	-3.19896600	0.77214900	0.45981800
C	-4.15552500	-2.97642700	0.74381400
H	-2.46972100	-3.14938900	2.08710000
C	-4.90190400	-2.13642200	-0.09401500
H	-5.12082800	-0.11857500	-0.82394800
H	-4.43042900	-4.02486300	0.83365500
C	-6.04989600	-2.68804900	-0.89557600
H	-5.67526100	-3.19821500	-1.79140400
H	-6.62165100	-3.41904500	-0.31601600
H	-6.72537400	-1.89244500	-1.22096900
H	1.79718200	0.87232700	-2.51075900

3aa-conformer-2

C	2.82249800	4.15897000	0.25600800
C	1.95840200	3.45540900	-0.57299800
C	1.73794500	2.08972300	-0.36274700
C	2.45607400	1.39703800	0.61742300
C	3.32005900	2.12355000	1.44420000
C	3.49358400	3.49415500	1.28469300
H	2.97878600	5.22124300	0.09253700
H	1.44314300	3.95976800	-1.38477700

C	2.37294700	-0.11460600	0.79430000
H	3.87012400	1.59609100	2.22051200
H	4.16619400	4.03629300	1.94288200
C	1.37373500	-0.81129400	-0.20204000
C	1.24849600	0.00801400	-1.50783900
H	0.52598300	-0.43301200	-2.19168900
N	0.82875600	1.36265100	-1.17697100
C	-0.41553200	1.79489800	-1.56475100
C	-1.01440600	3.00978000	-0.91734200
C	-0.95951900	3.21728900	0.46473400
C	-1.76116200	3.87304600	-1.72416600
C	-1.64401500	4.29019700	1.03136400
H	-0.41172800	2.52969100	1.10318900
C	-2.42167600	4.96115600	-1.15757500
H	-1.81926700	3.68645100	-2.79296200
C	-2.36480100	5.16944800	0.22174200
H	-1.61672400	4.43454400	2.10760600
H	-2.98786700	5.63929800	-1.78966500
H	-2.88911300	6.01080600	0.66636100
O	-1.06653800	1.17825500	-2.40755500
C	3.77317900	-0.72155500	0.77257300
C	4.24350200	-1.41701000	1.81218100
H	3.62976000	-1.57681800	2.69535200
H	5.24386100	-1.83794700	1.81202700
C	4.63115700	-0.49875000	-0.43459800
O	4.34291100	0.24912100	-1.34639900

O	5.76021500	-1.21269100	-0.41295900
C	6.62791500	-1.04026500	-1.54099200
H	6.94496300	0.00204500	-1.61962800
H	7.48425200	-1.68569600	-1.35028200
H	6.11742100	-1.34306700	-2.45804900
H	1.98874800	-0.31011700	1.79975100
C	1.92474000	-2.19678700	-0.53313800
O	1.86534100	-2.99235500	0.53106100
O	2.39917000	-2.51516000	-1.59900600
C	2.41330900	-4.30760600	0.37415100
H	3.47922900	-4.24165100	0.13999700
H	2.26287100	-4.80360400	1.33200800
H	1.88731400	-4.84161100	-0.42094900
C	-0.03393500	-0.97699700	0.40365900
C	-0.90416200	-2.06906200	-0.14945100
C	-1.56802300	-1.91792700	-1.37248400
C	-1.04295900	-3.25712300	0.57930700
C	-2.35651400	-2.95815100	-1.86372200
H	-1.50302000	-0.98303000	-1.92260500
C	-1.82521200	-4.29378300	0.07567300
H	-0.53872800	-3.36667900	1.53447400
C	-2.48039100	-4.14805900	-1.14750900
H	-2.87994900	-2.82925200	-2.80710300
H	-1.92551000	-5.21378800	0.64464000
H	-3.09309600	-4.95655600	-1.53656900
N	-0.34620000	-0.15124800	1.32860000

S	-1.81774700	-0.18882600	2.19402000
O	-1.73531700	-1.32463600	3.11071500
O	-1.91802200	1.16113300	2.73618800
C	-3.17855300	-0.43371400	1.08141000
C	-3.49401900	0.57516800	0.17511300
C	-3.90666800	-1.61938600	1.14400100
C	-4.54656800	0.37111600	-0.71228700
H	-2.93085100	1.50438600	0.15947400
C	-4.96538700	-1.79592700	0.25988500
H	-3.64348700	-2.38652900	1.86571100
C	-5.29071300	-0.81474100	-0.68681800
H	-4.79370800	1.14813200	-1.43140100
H	-5.54334100	-2.71651700	0.29669500
C	-6.40395700	-1.05054300	-1.67168200
H	-6.05829600	-1.70066600	-2.48472900
H	-7.25501100	-1.54567200	-1.19438300
H	-6.74783200	-0.11259300	-2.11578300
H	2.22263900	0.03407600	-1.99635700

3aa-conformer-3

C	0.66699500	-4.72363600	-0.24712300
C	0.86389000	-3.59754000	-1.03263100
C	0.09984400	-2.44345600	-0.81057100
C	-0.94194100	-2.44836500	0.11997600
C	-1.11913400	-3.59375400	0.90836600
C	-0.31356800	-4.71347800	0.75031100

H	1.27163400	-5.60988400	-0.41588000
H	1.61811500	-3.59575100	-1.81364100
C	-1.93863600	-1.30636400	0.26958400
H	-1.91707000	-3.60021100	1.64837200
H	-0.46720500	-5.58605400	1.37834300
C	-1.65020000	-0.08325300	-0.67621300
C	-0.89451100	-0.55408900	-1.94007000
H	-0.64105300	0.28091800	-2.59073400
N	0.31974600	-1.25634300	-1.56101900
C	1.54162100	-0.68731500	-1.82890100
C	2.77965700	-1.28345800	-1.22601500
C	2.86604900	-1.64009500	0.12270000
C	3.89853200	-1.40593300	-2.05404300
C	4.06081800	-2.14597700	0.62878700
H	2.00695900	-1.51903100	0.77839600
C	5.08843000	-1.92620800	-1.54797800
H	3.82758200	-1.09902600	-3.09400600
C	5.16829000	-2.30256600	-0.20658700
H	4.12764000	-2.41365400	1.67968100
H	5.95153500	-2.03468300	-2.19884300
H	6.09579400	-2.70587000	0.19106900
O	1.63344900	0.30012400	-2.55669700
C	-3.35401300	-1.83668100	0.05265900
C	-3.71826200	-2.60550600	-0.97629200
H	-2.99349400	-2.93964400	-1.71536500
H	-4.74426200	-2.93825600	-1.09846400

C	-4.34988000	-1.46412200	1.10660700
O	-4.04955000	-1.18424900	2.24834700
O	-5.61074400	-1.49226200	0.66602900
C	-6.61996200	-1.19732500	1.63987600
H	-7.56539500	-1.23128500	1.09999300
H	-6.60802100	-1.94610200	2.43548900
H	-6.45868400	-0.20482700	2.06672400
H	-1.88731200	-0.94253300	1.29961000
C	-2.96878800	0.54556700	-1.14284000
O	-3.71879500	0.90011600	-0.09912400
O	-3.29065000	0.70426300	-2.29561700
C	-4.97324300	1.52814800	-0.40247000
H	-4.80214400	2.44187700	-0.97746700
H	-5.60769900	0.84207200	-0.96852400
H	-5.42283000	1.76296400	0.56160900
C	-0.83672800	1.03012000	0.01678500
C	-1.02778400	2.41929100	-0.52865800
C	-0.28654400	2.82929500	-1.63970400
C	-1.97742500	3.27894400	0.03542700
C	-0.49268300	4.10035000	-2.17969100
H	0.45454900	2.16548000	-2.07875800
C	-2.17750500	4.54308500	-0.50943300
H	-2.54052000	2.96506500	0.90960200
C	-1.43736600	4.95644800	-1.61941600
H	0.08993800	4.41516700	-3.04072700
H	-2.90822400	5.21012600	-0.06077500

H	-1.59644300	5.94447500	-2.04202600
N	-0.05929600	0.65290400	0.96007400
S	0.80828600	1.74958000	1.94637700
O	0.48185000	3.14675700	1.67488400
O	0.59331100	1.23678000	3.29640000
C	2.49132600	1.46263000	1.48147700
C	3.36875300	0.93875600	2.42677400
C	2.91852000	1.84363300	0.21136200
C	4.70941000	0.79665600	2.08095900
H	3.00742700	0.64908400	3.40879500
C	4.25766500	1.67251000	-0.12048500
H	2.21975100	2.25806600	-0.51114800
C	5.17008300	1.15295400	0.80766100
H	5.40692300	0.38482300	2.80640000
H	4.59898600	1.94243600	-1.11703700
C	6.62194900	0.99345600	0.44457300
H	6.73997900	0.77399900	-0.62071200
H	7.17231400	1.91831000	0.65653800
H	7.08840500	0.18995500	1.02203800
H	-1.54580100	-1.23579400	-2.49632500

3aa-conformer-4

C	-0.16261400	-4.62936600	0.30721200
C	0.09326100	-3.59927800	-0.58859900
C	-0.42151600	-2.31991100	-0.35364500
C	-1.29017700	-2.08724000	0.71666700

C	-1.52714000	-3.13464700	1.61456500
C	-0.95578200	-4.38945100	1.43124600
H	0.25135100	-5.61677200	0.12490100
H	0.70490600	-3.77488300	-1.46839900
C	-2.03942200	-0.77116000	0.90775400
H	-2.18384700	-2.96111600	2.46389900
H	-1.15215500	-5.18407500	2.14508200
C	-1.74161200	0.30549100	-0.20580300
C	-1.26095500	-0.36810700	-1.51252600
H	-0.96852900	0.36801500	-2.25909500
N	-0.12734100	-1.23541900	-1.22470200
C	1.11490600	-0.92246200	-1.71632700
C	2.31363300	-1.67650500	-1.21753500
C	2.53522400	-1.92804800	0.13946400
C	3.26603700	-2.06448000	-2.16343300
C	3.69226700	-2.59140100	0.54039600
H	1.81090900	-1.60385500	0.88295400
C	4.41592900	-2.74162000	-1.76075700
H	3.09622000	-1.83962500	-3.21283800
C	4.62711800	-3.01069200	-0.40794700
H	3.86558700	-2.77717500	1.59682800
H	5.14595500	-3.05627800	-2.50131000
H	5.52387500	-3.53672600	-0.09134700
O	1.26144300	-0.03468500	-2.55625800
C	-3.52582000	-1.07026600	1.08888100
C	-4.17697700	-0.73018800	2.20452000

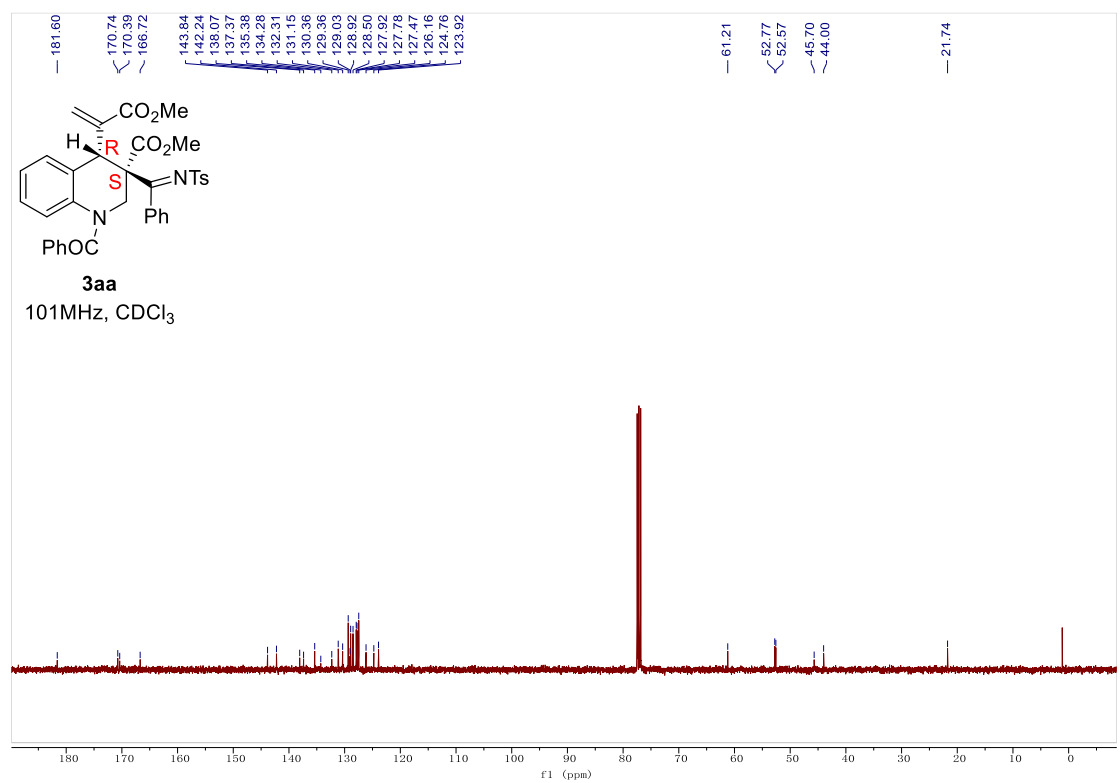
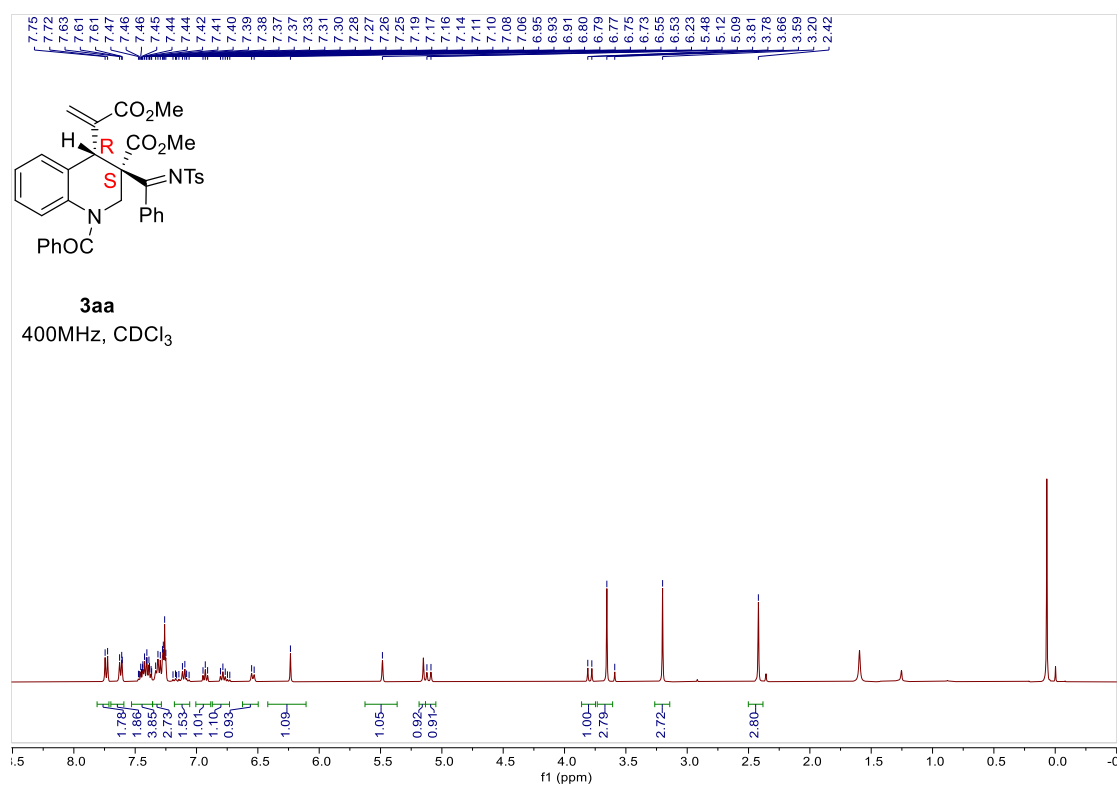
H	-3.66405900	-0.20615900	3.00746000
H	-5.22743700	-0.96363300	2.34585500
C	-4.23693100	-1.79857200	-0.00975500
O	-3.68475800	-2.25343600	-0.99055700
O	-5.55399500	-1.89780600	0.19222600
C	-6.29042700	-2.58395200	-0.82875300
H	-7.32821900	-2.56843700	-0.49877500
H	-6.18474100	-2.06346500	-1.78333000
H	-5.93552000	-3.61241300	-0.92579800
H	-1.71134900	-0.33194800	1.85433600
C	-3.03460500	1.06919900	-0.49736700
O	-3.40439000	1.78376200	0.56214200
O	-3.66109400	1.00566400	-1.52922400
C	-4.63997500	2.50029400	0.44638700
H	-4.58972300	3.20673200	-0.38595500
H	-5.46386500	1.79821600	0.29198500
H	-4.76201300	3.02913100	1.39077200
C	-0.67938100	1.33893600	0.23161700
C	-0.71485900	2.67481200	-0.46671000
C	-0.08778800	2.81849000	-1.70719000
C	-1.37709200	3.76747900	0.10695500
C	-0.12727600	4.04745200	-2.36991400
H	0.44592600	1.98271300	-2.15246400
C	-1.41372200	4.98719500	-0.55931000
H	-1.84302500	3.66626000	1.08211800
C	-0.79178300	5.13039000	-1.80198400

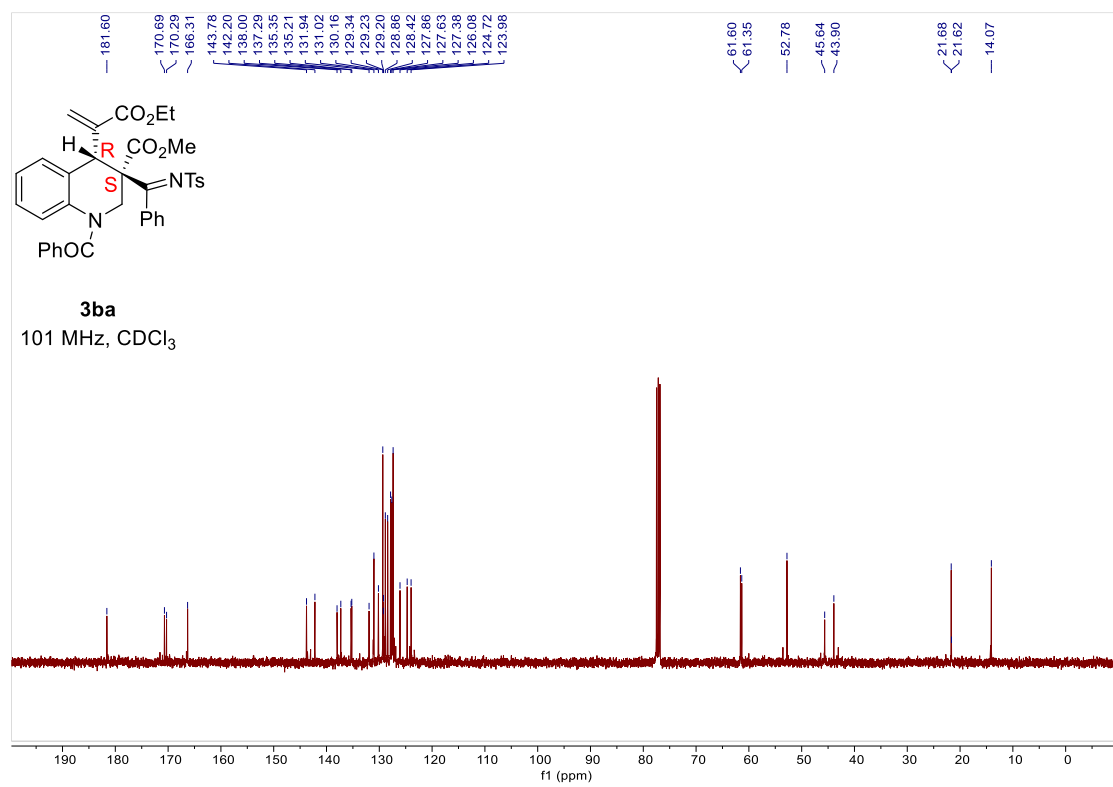
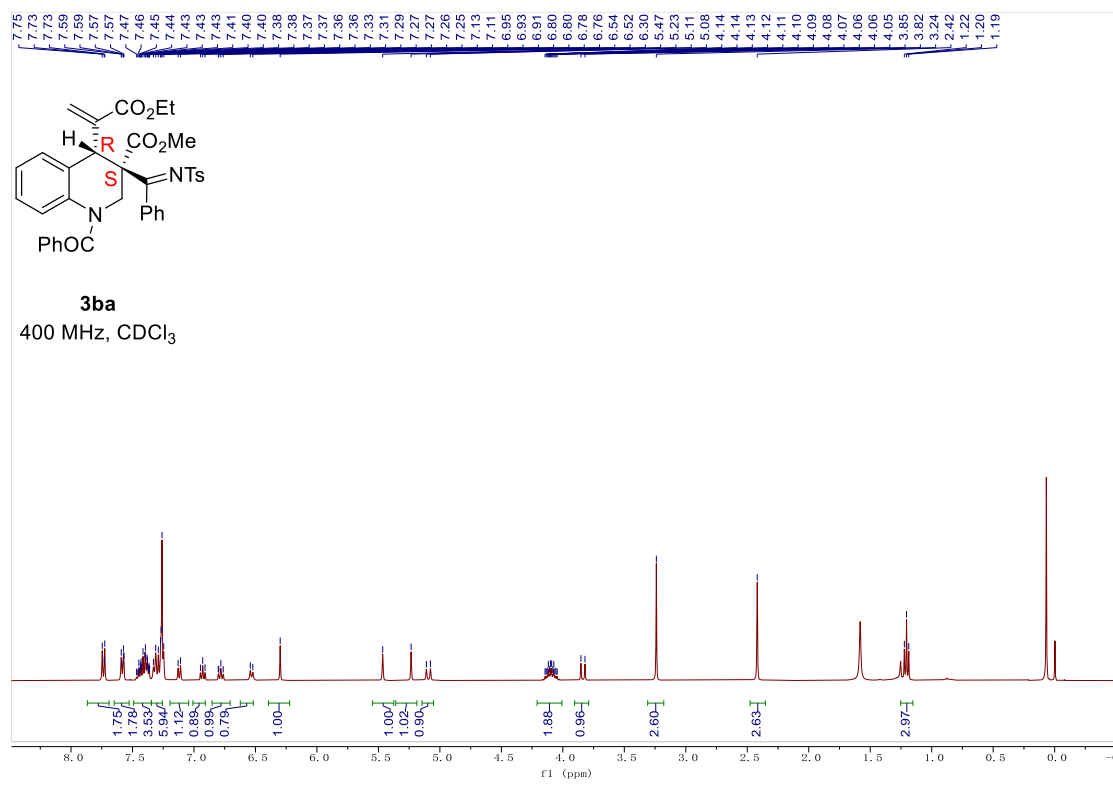
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H	-1.92183600	5.83148500	-0.10198600
H	-0.82231600	6.08504400	-2.31945500
N	0.16238600	0.94121700	1.10975400
S	1.33800600	1.96066400	1.81845800
O	1.21657700	3.35654800	1.40734900
O	1.24297600	1.64694700	3.24190800
C	2.86091900	1.31865600	1.18573800
C	3.76245000	0.73284900	2.07062200
C	3.16069700	1.49226700	-0.16355200
C	4.99585700	0.31415300	1.58085900
H	3.50216200	0.61069800	3.11760500
C	4.39035700	1.04694100	-0.63596100
H	2.44750600	1.95910900	-0.83834300
C	5.32418700	0.45854800	0.22711100
H	5.70987300	-0.14800600	2.25837300
H	4.62675600	1.15409000	-1.69187300
C	6.66219300	0.00216000	-0.28906500
H	6.59869800	-0.29628000	-1.33954900
H	7.39633800	0.81394900	-0.21685900
H	7.04321100	-0.84199000	0.29321000
H	-2.08046300	-0.96754300	-1.91089700

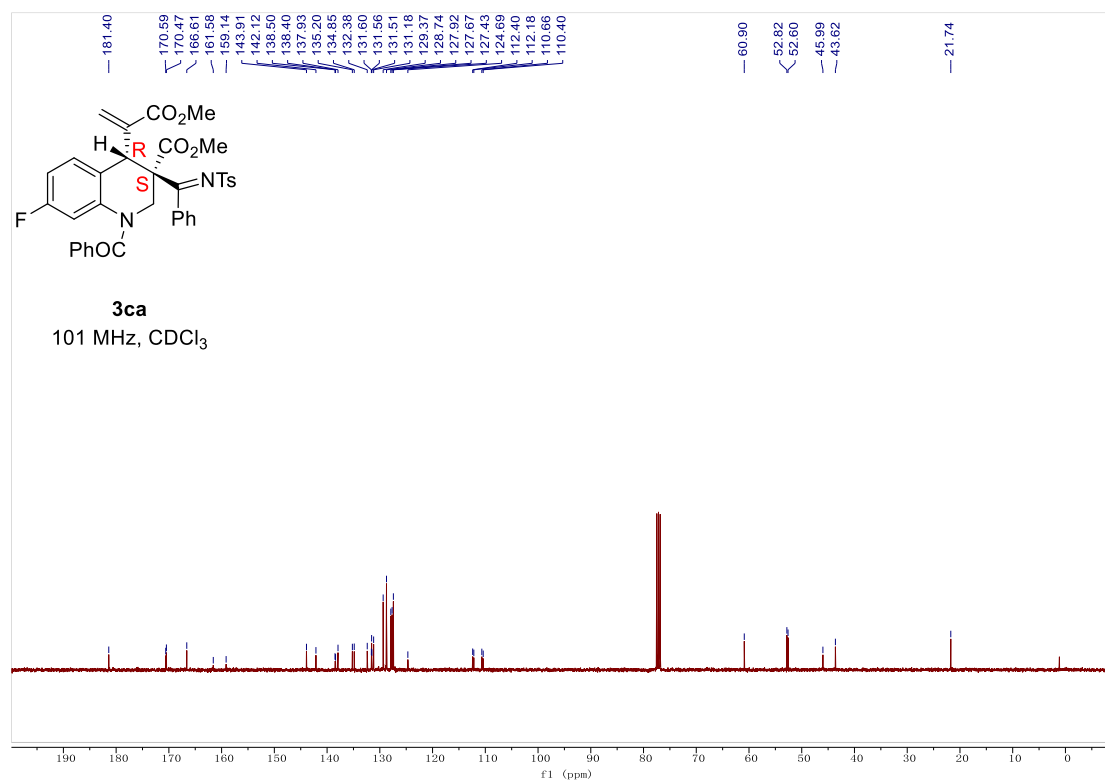
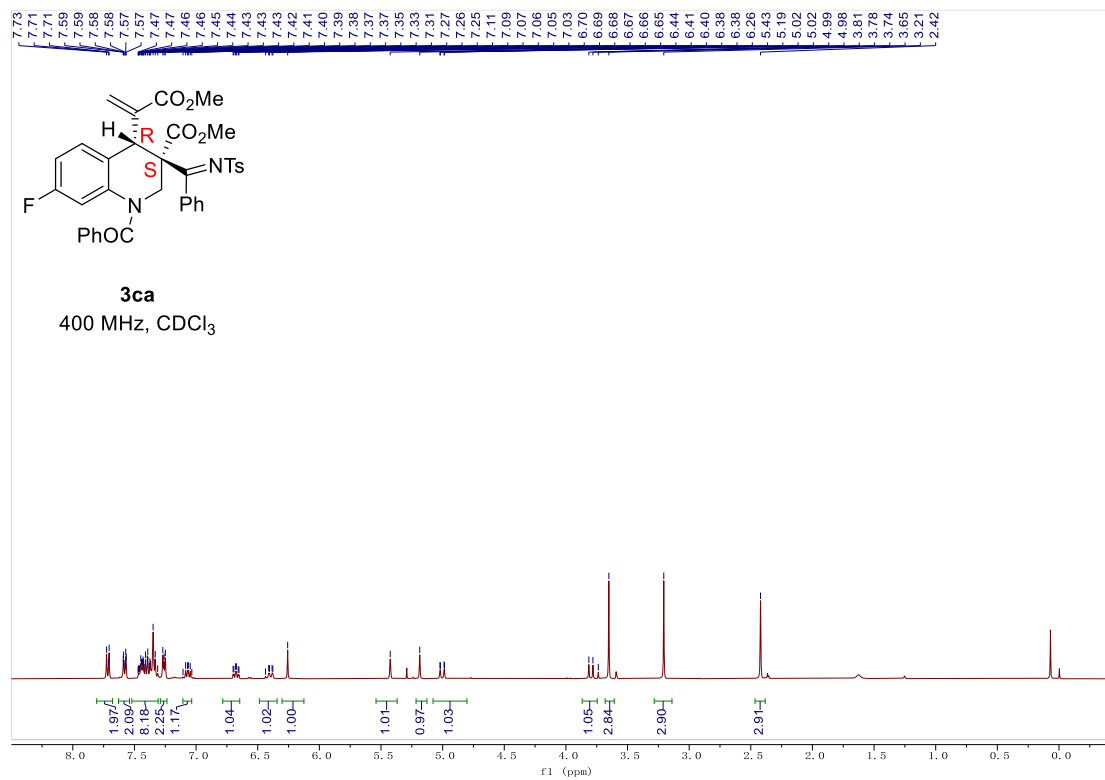
VI. References

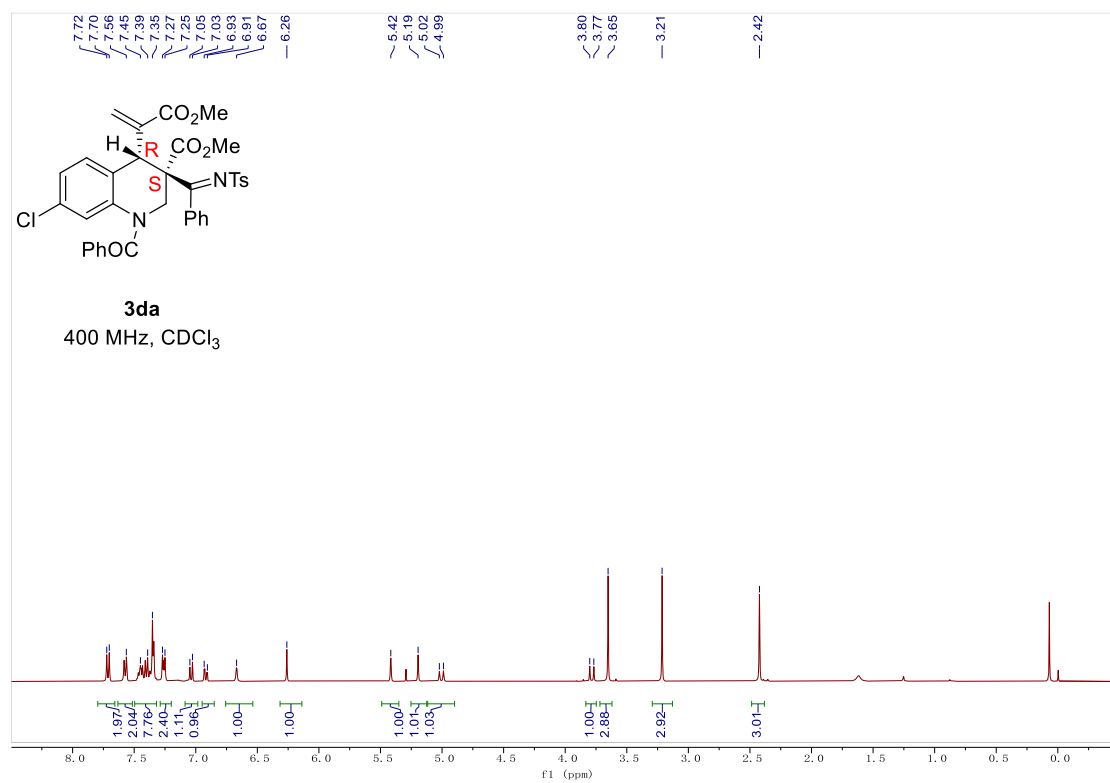
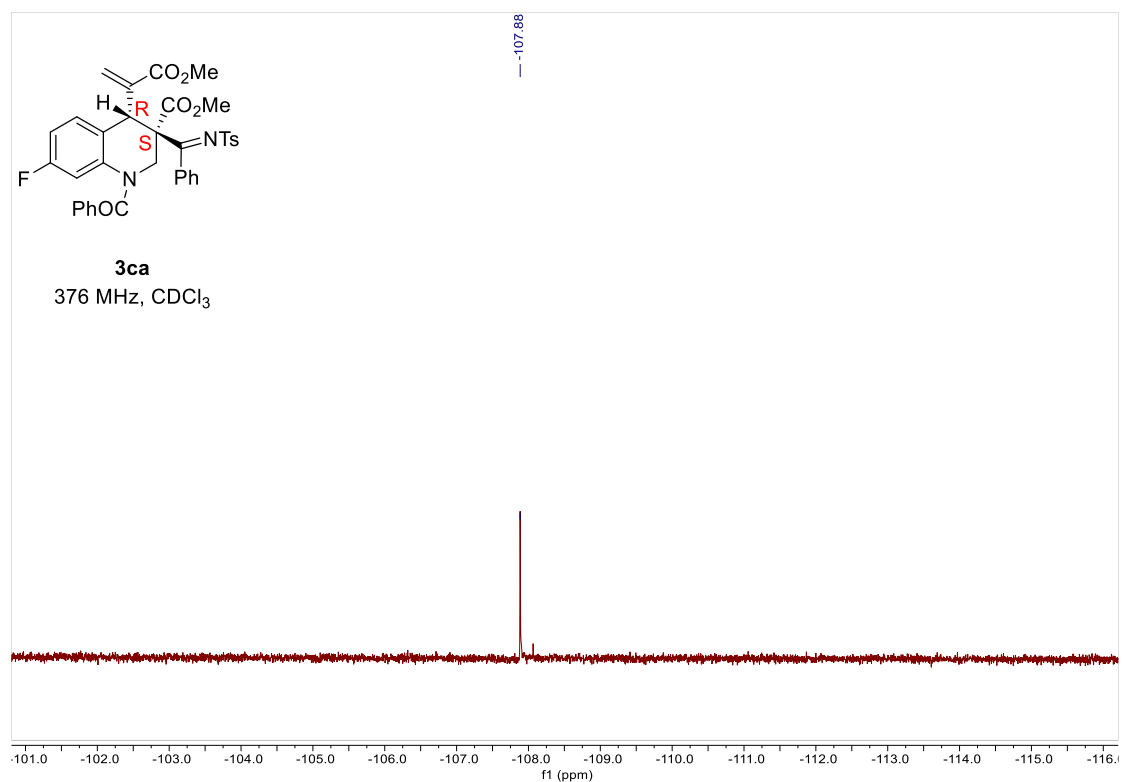
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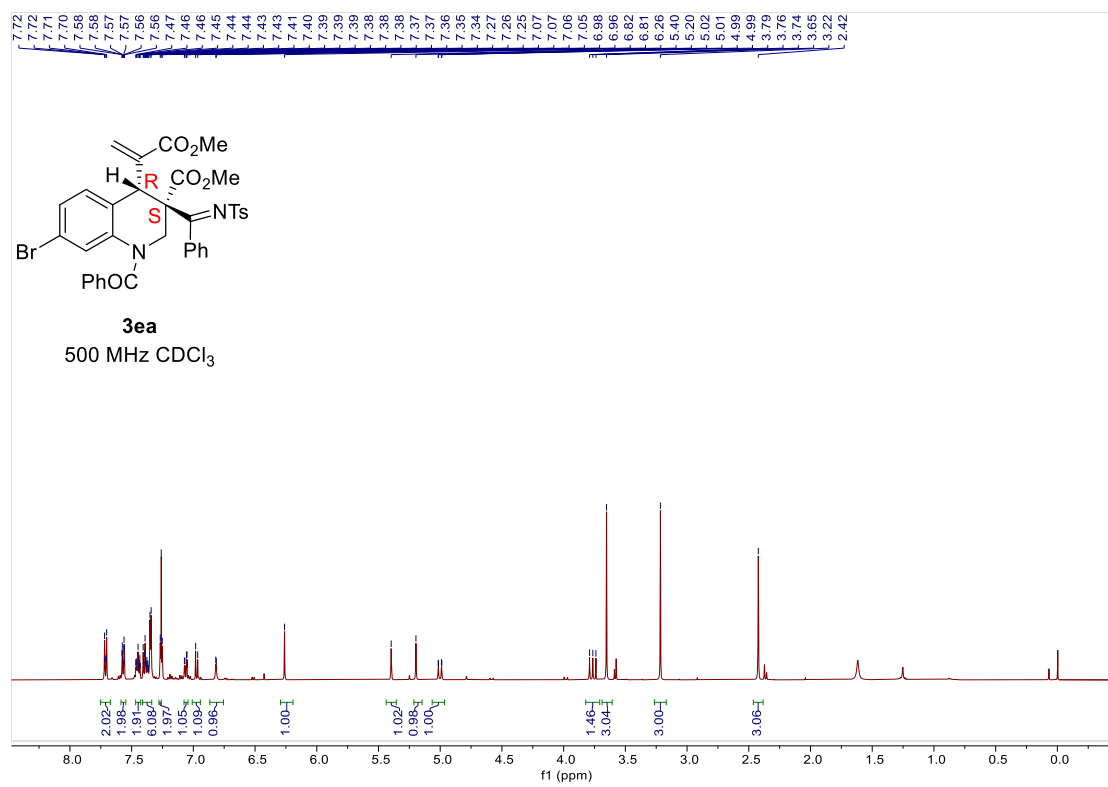
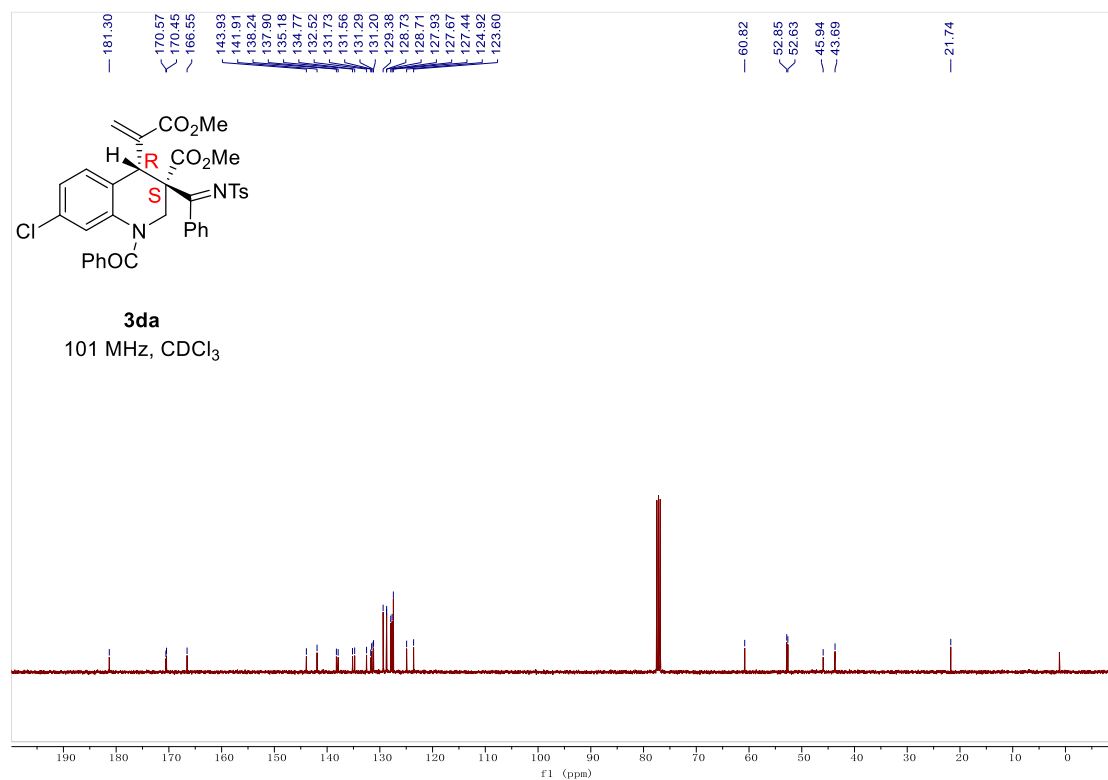
VII. NMR Copies of Compounds 3 and 5

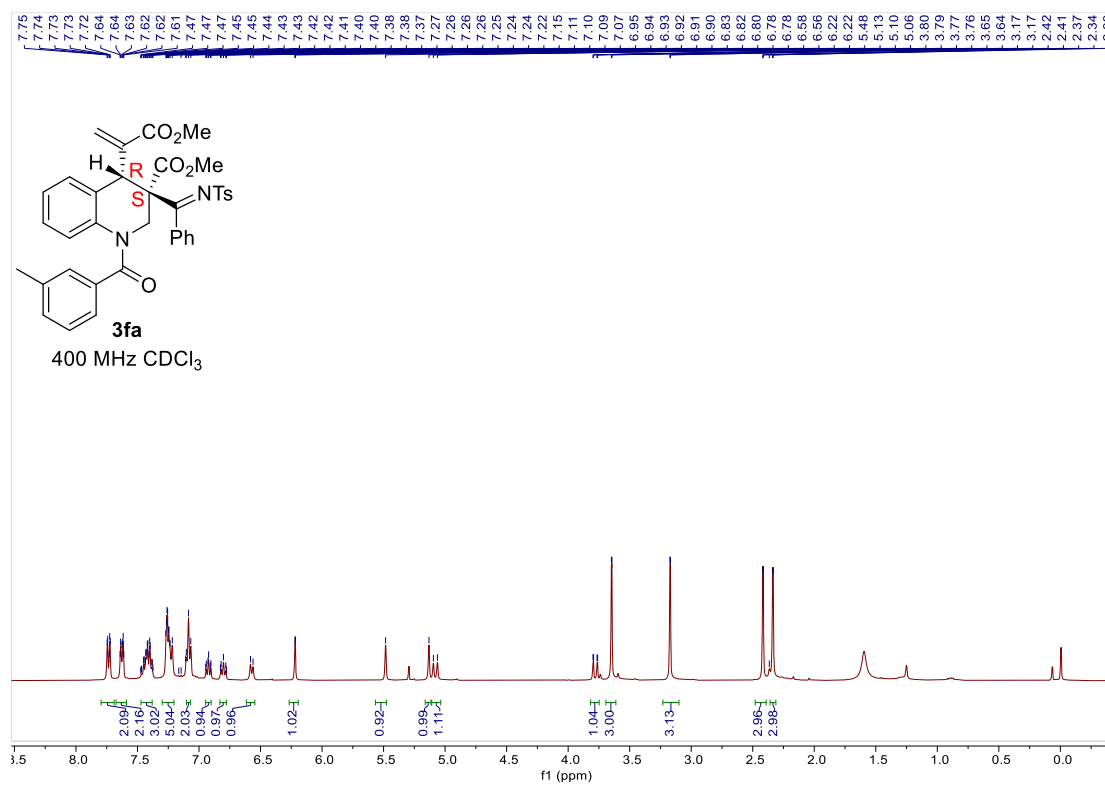
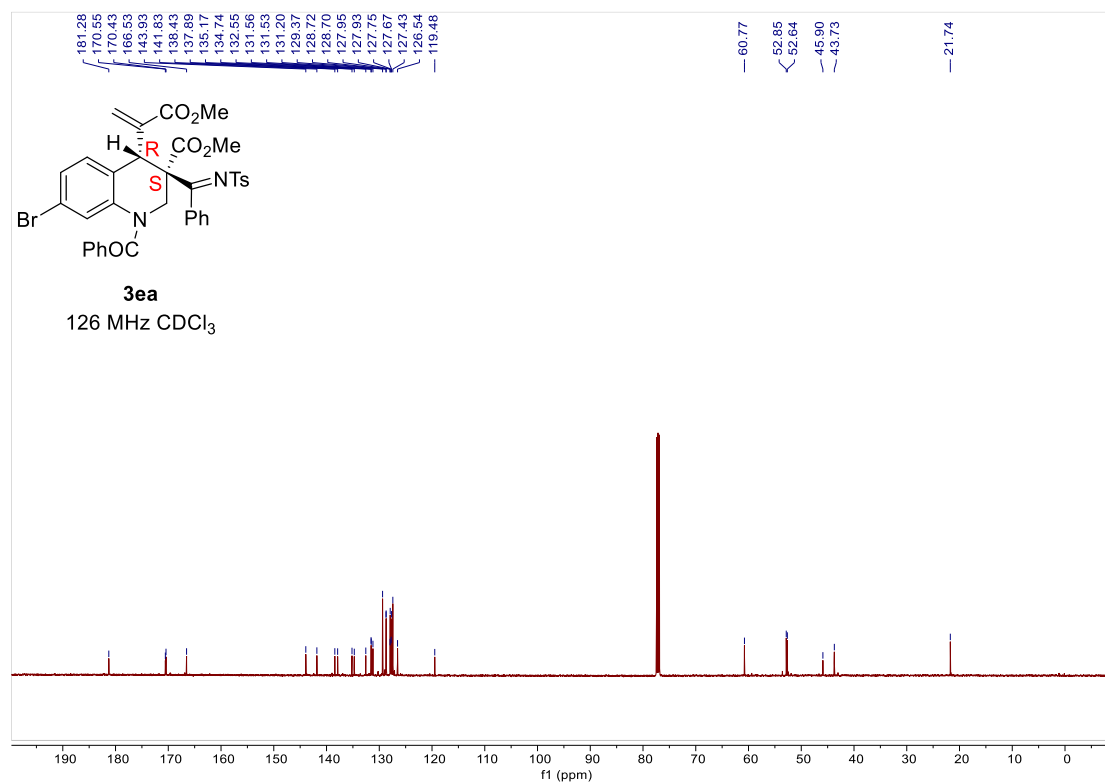


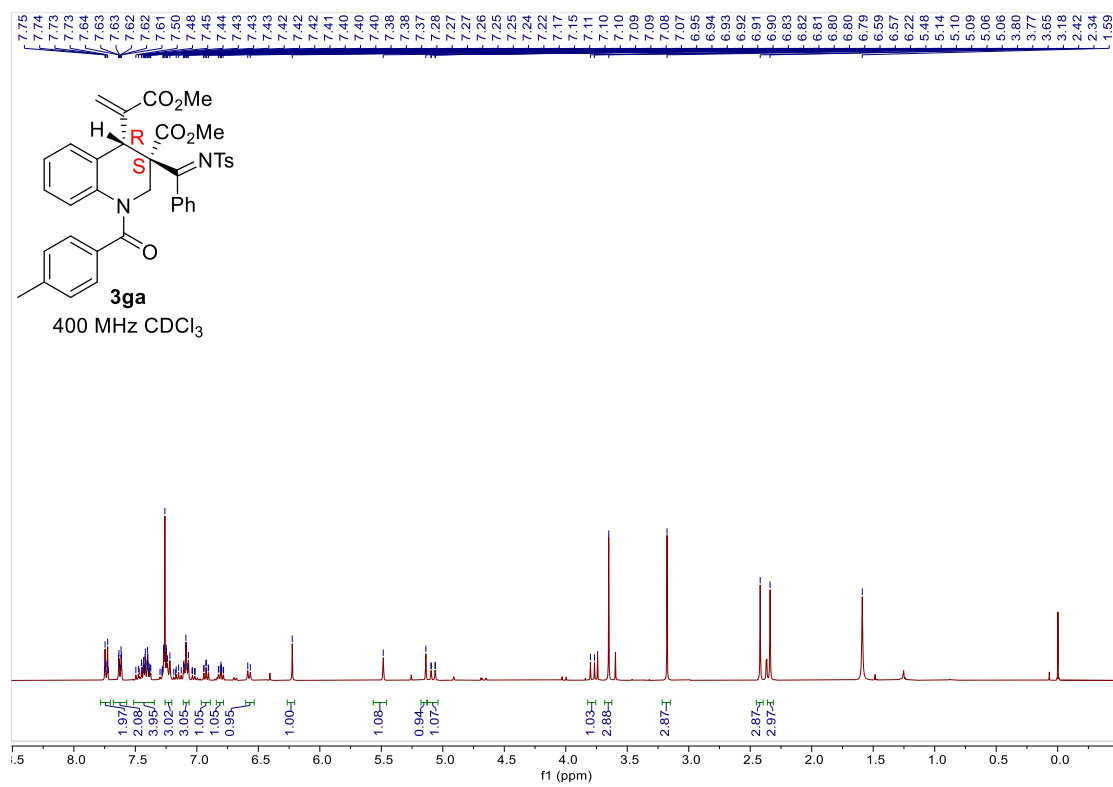
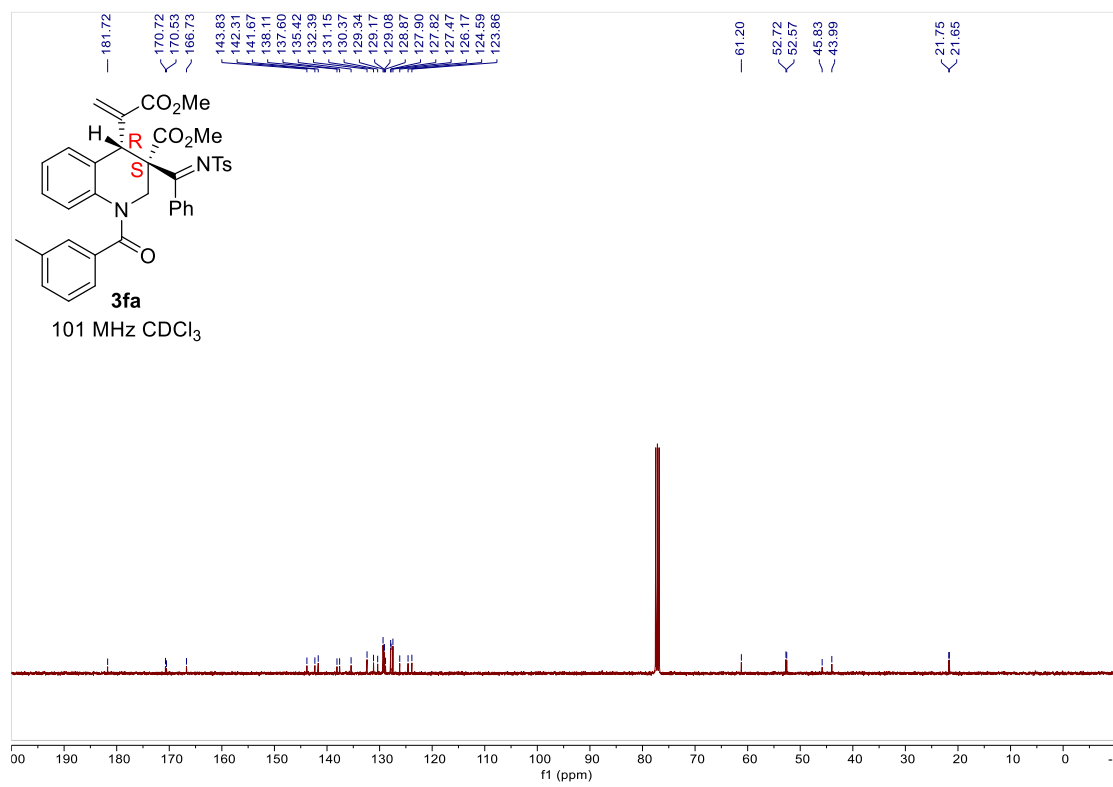


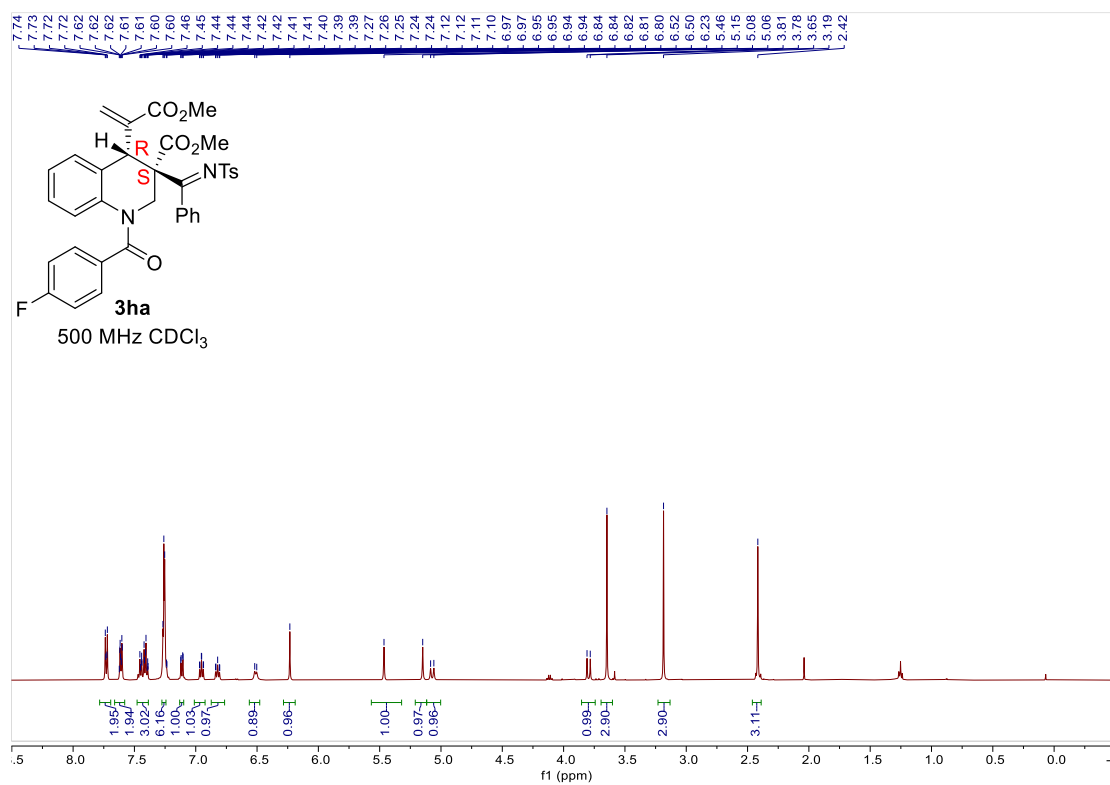
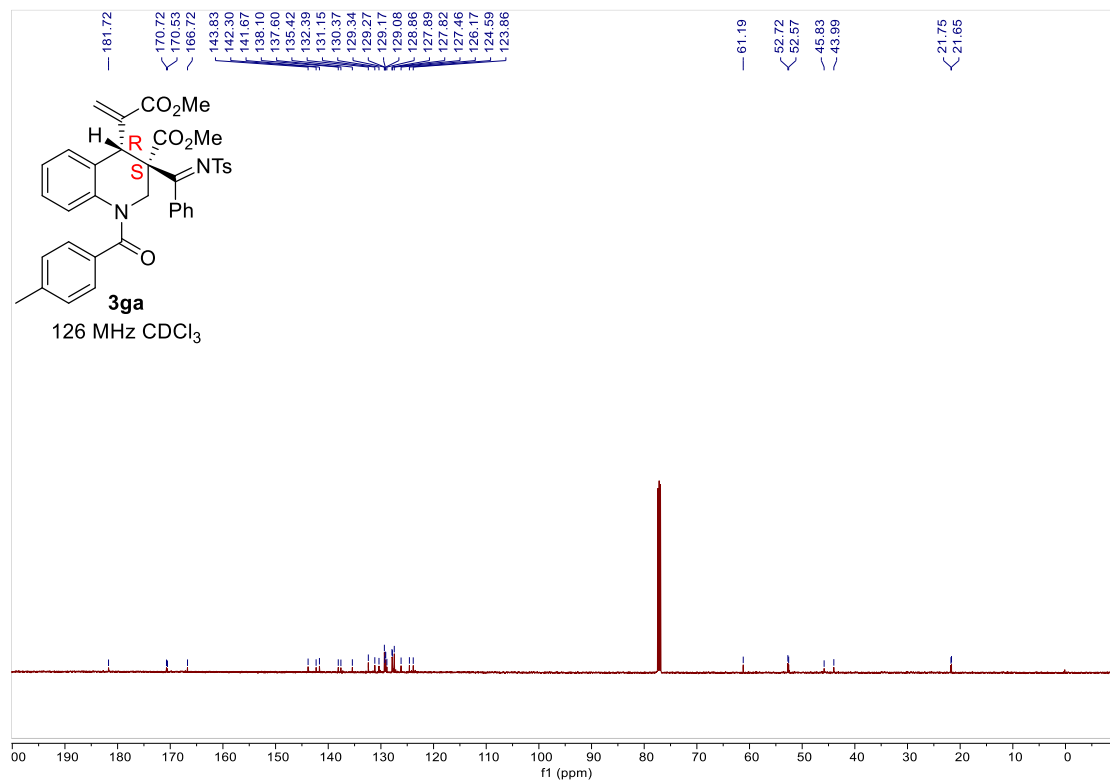


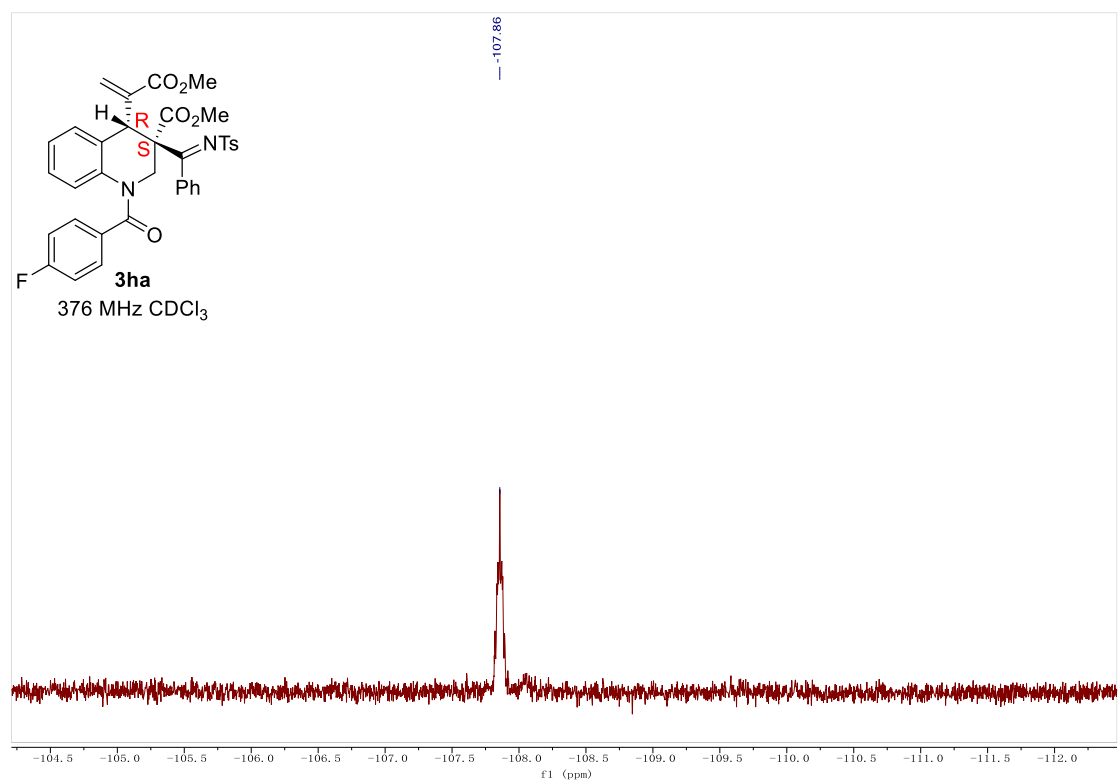
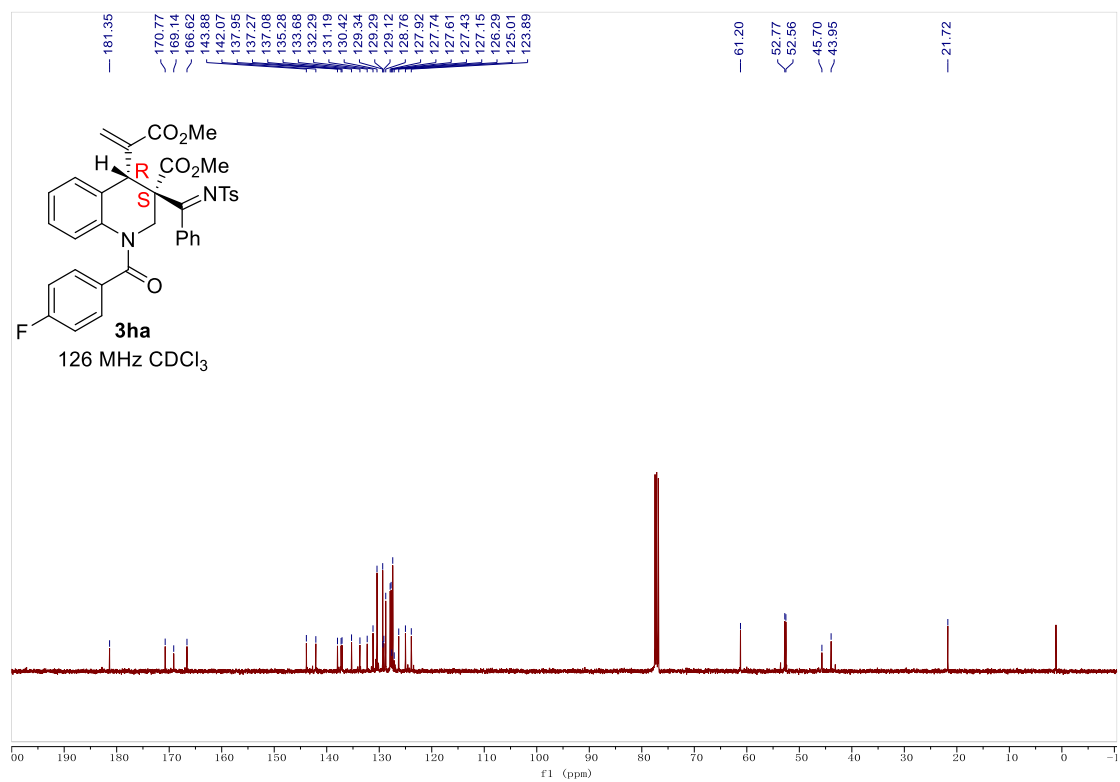


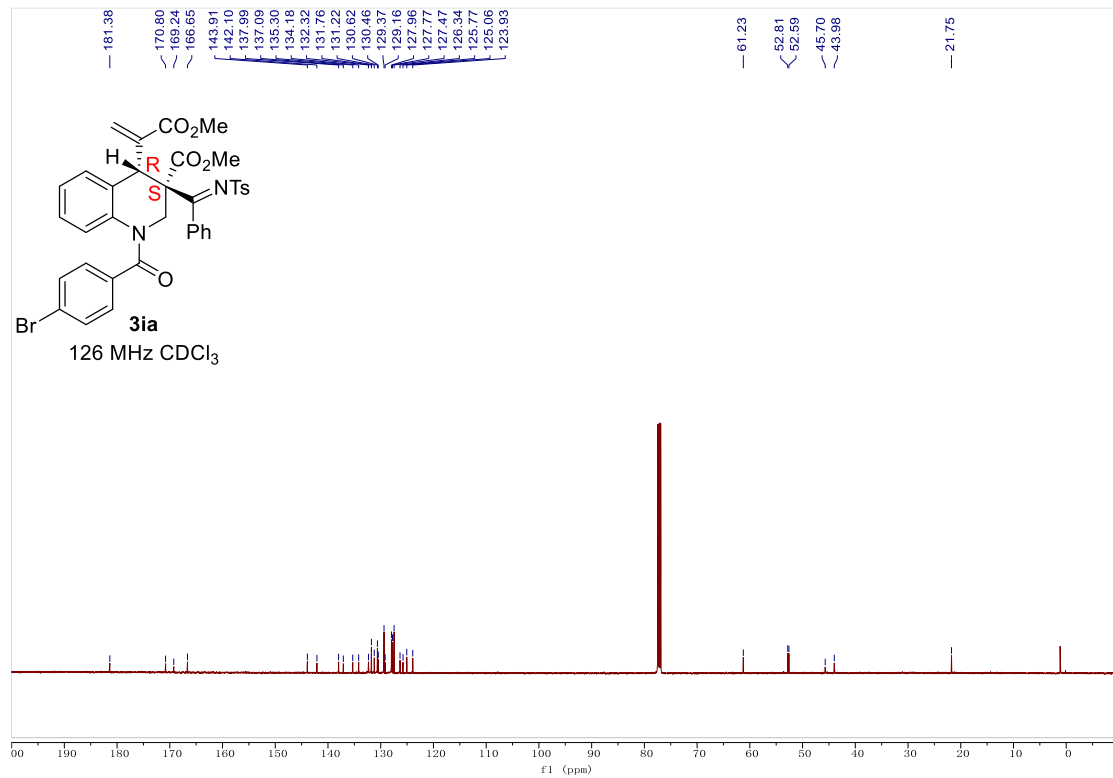
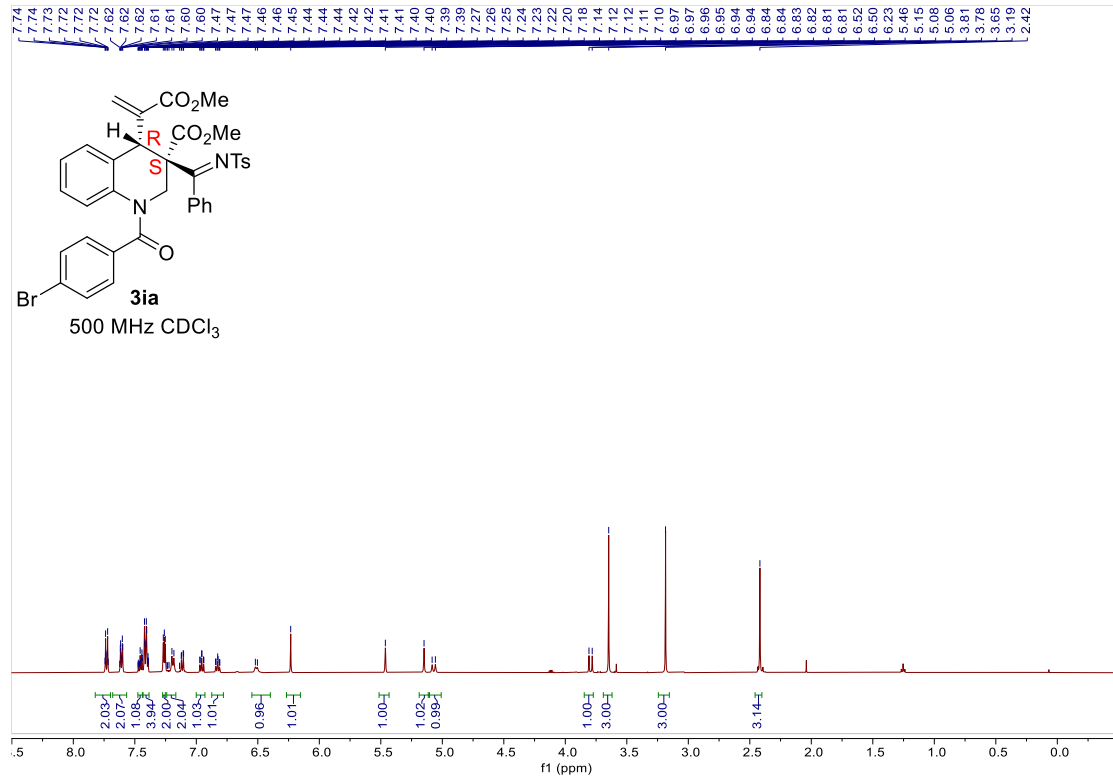


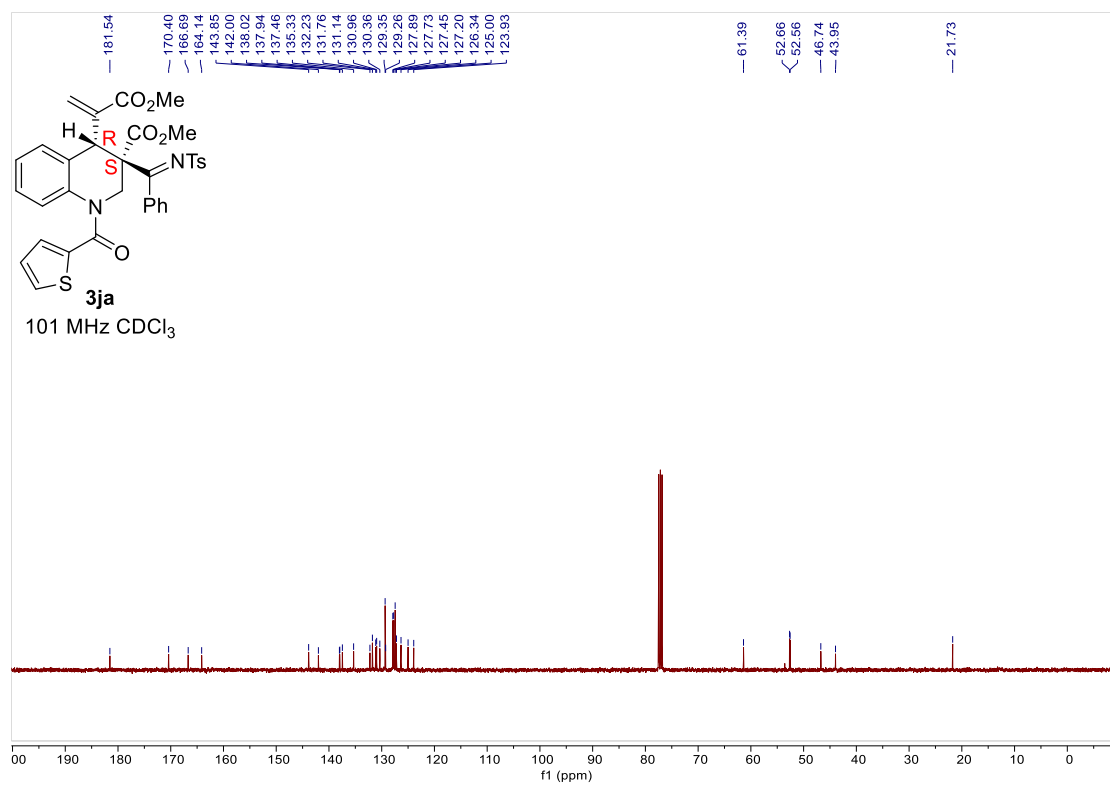
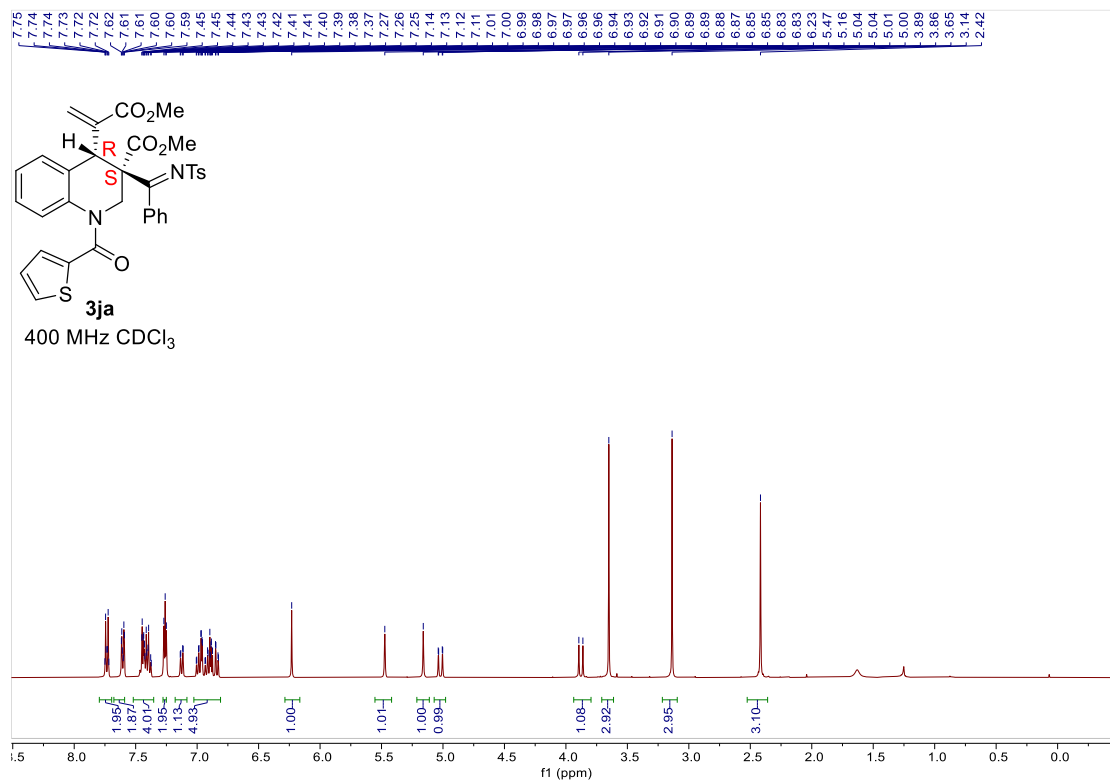


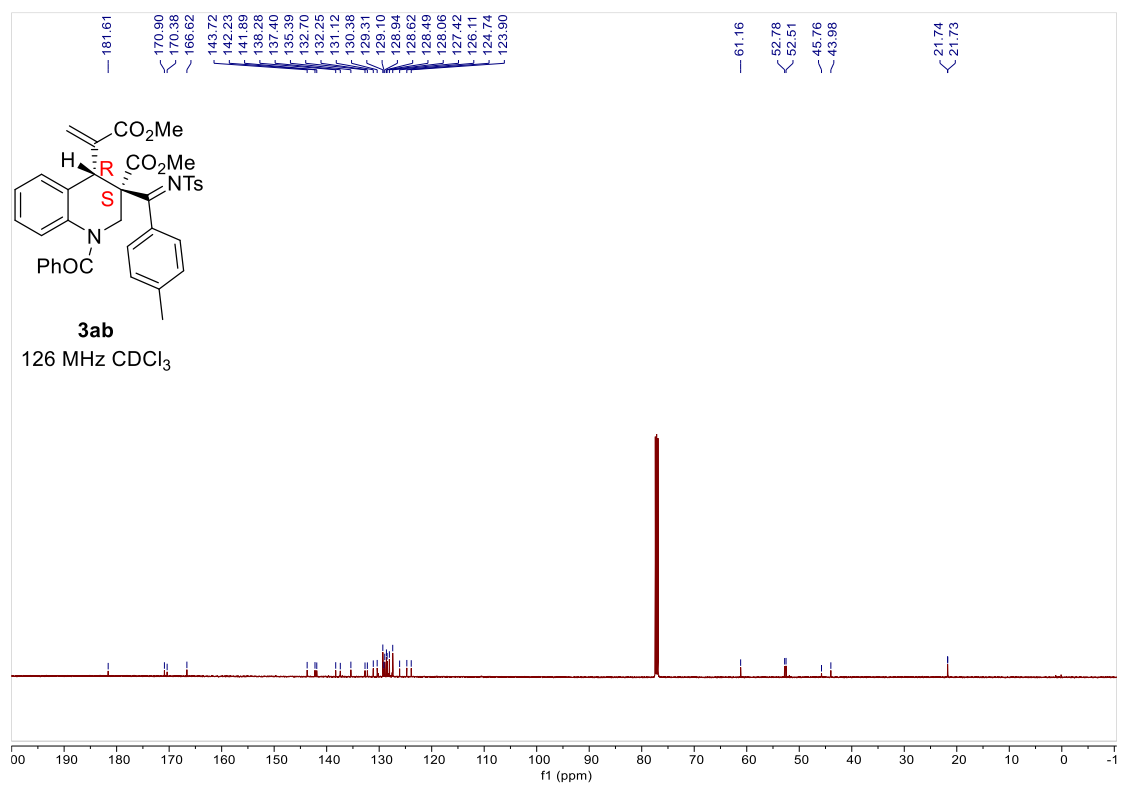
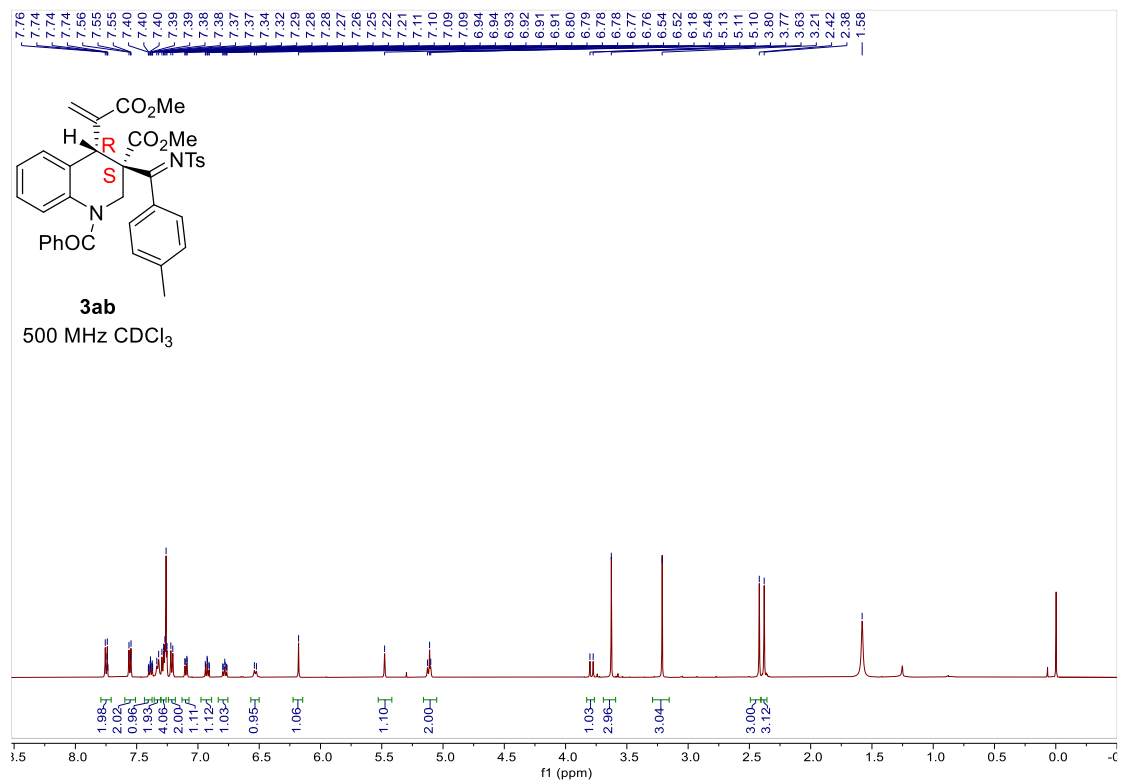


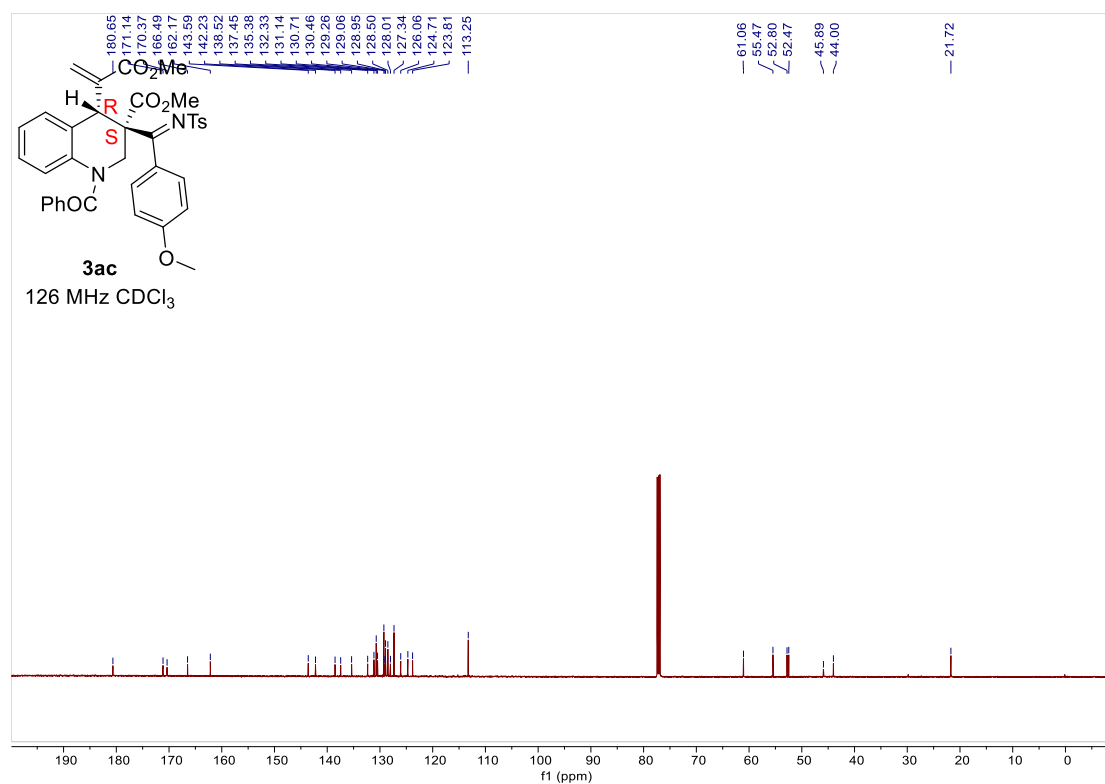
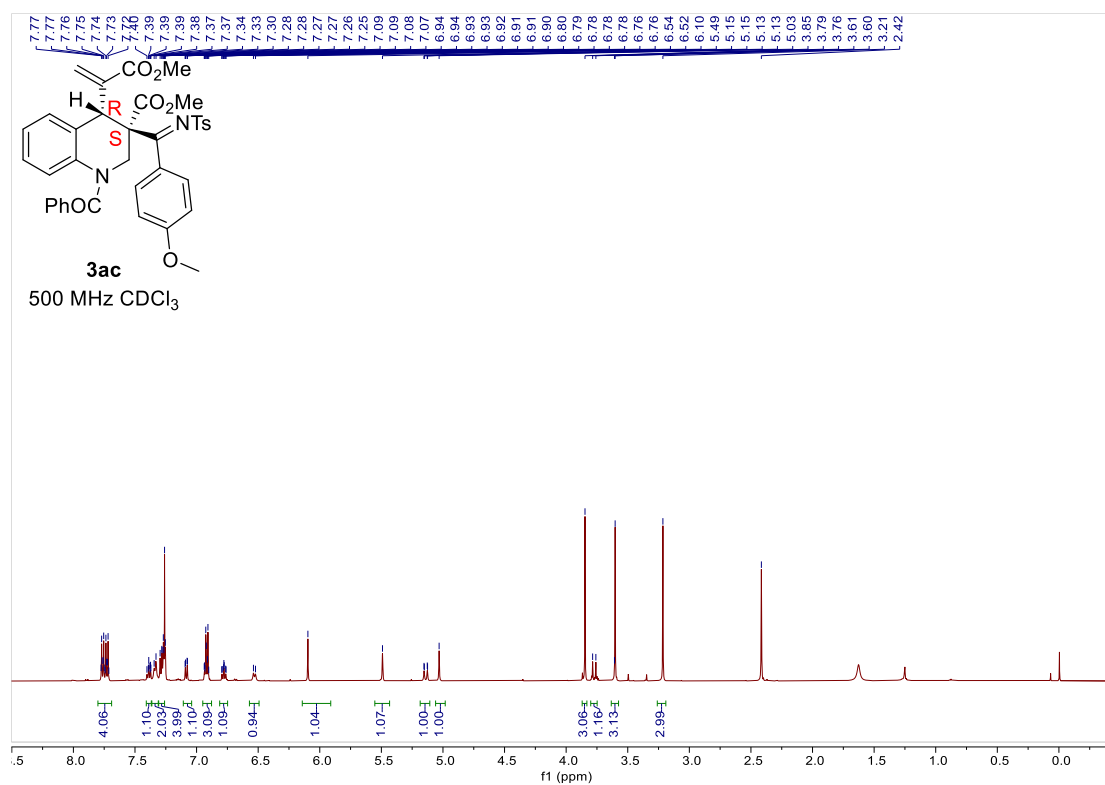


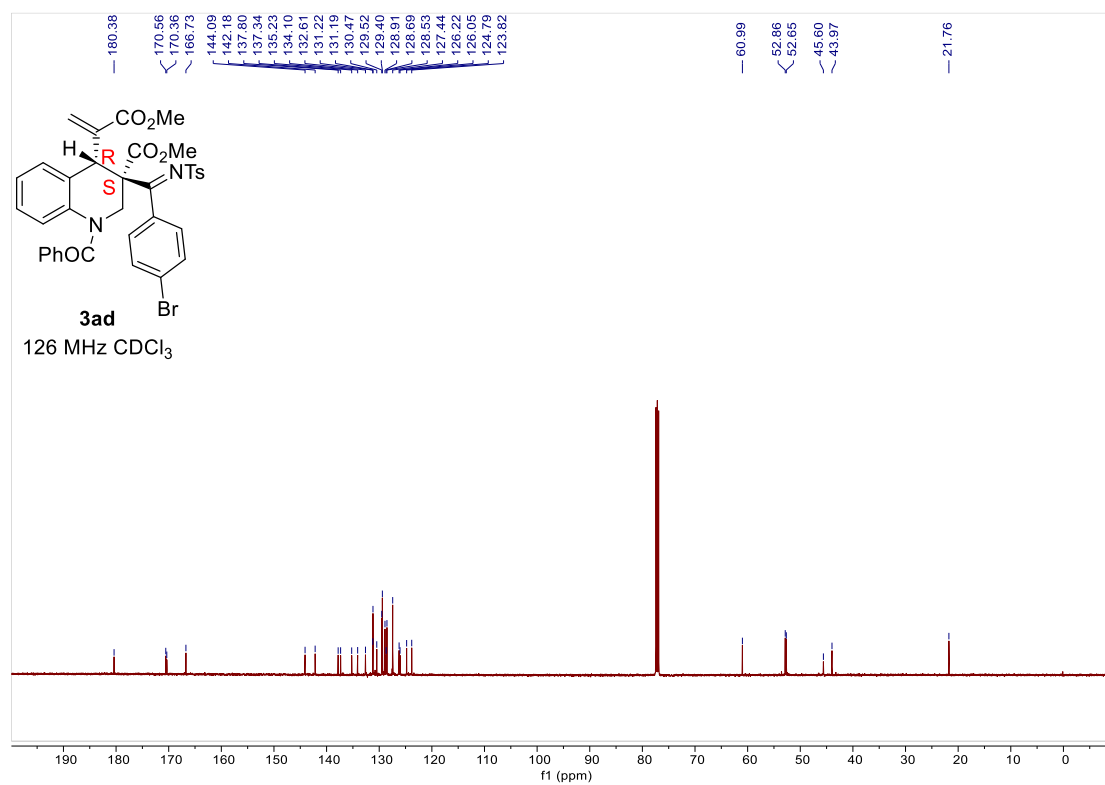
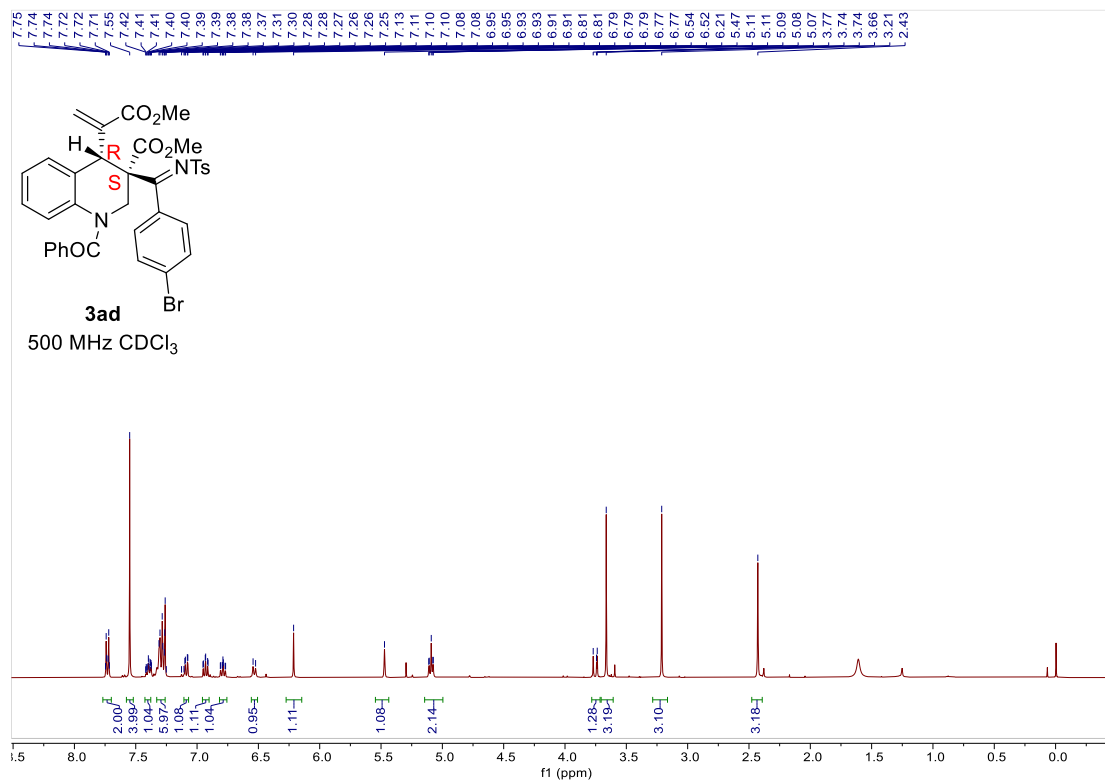


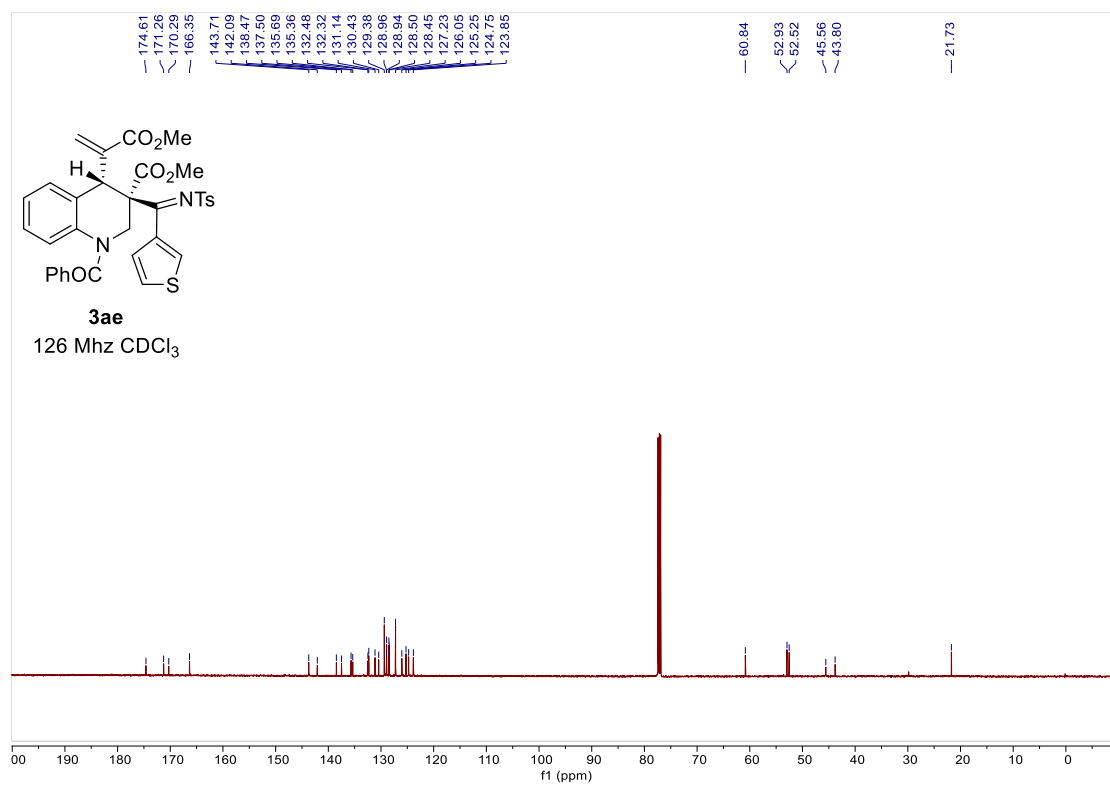
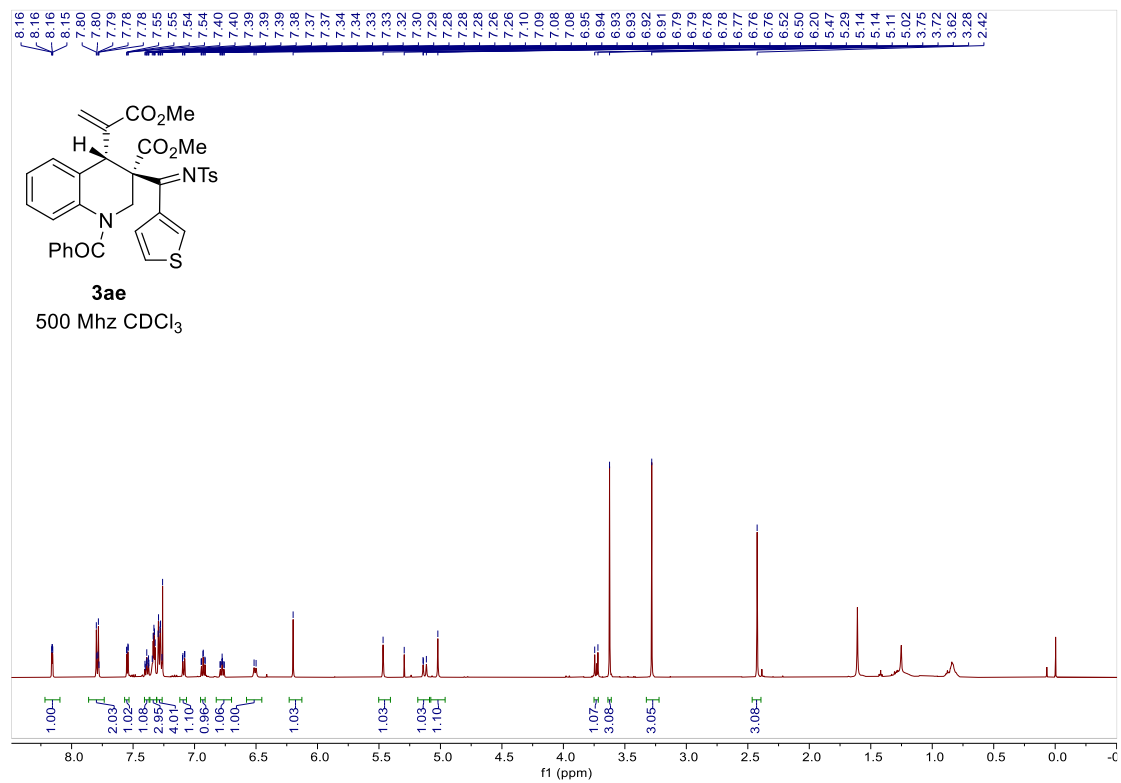


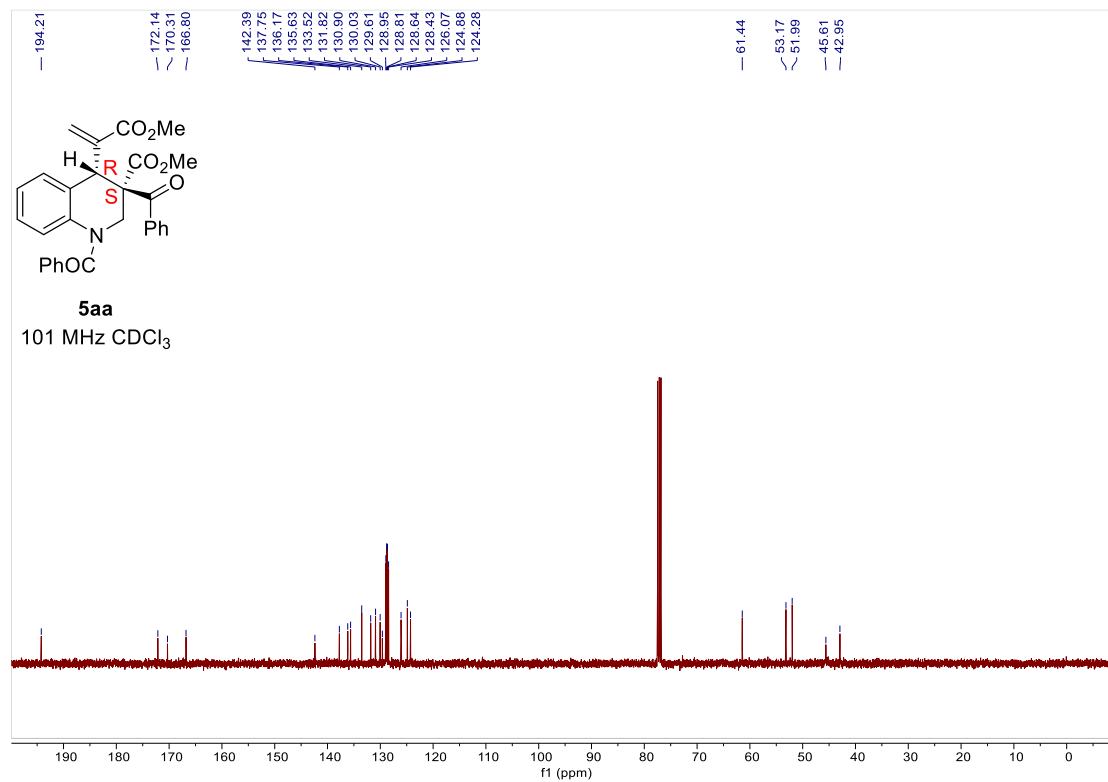
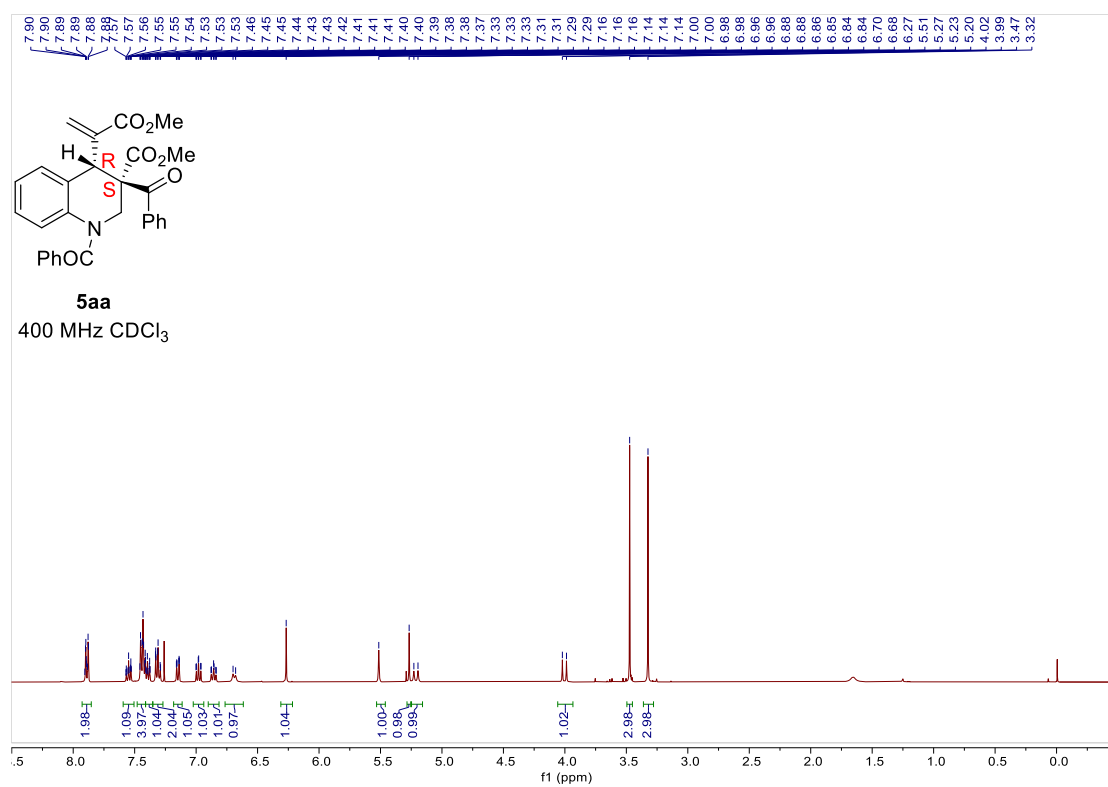


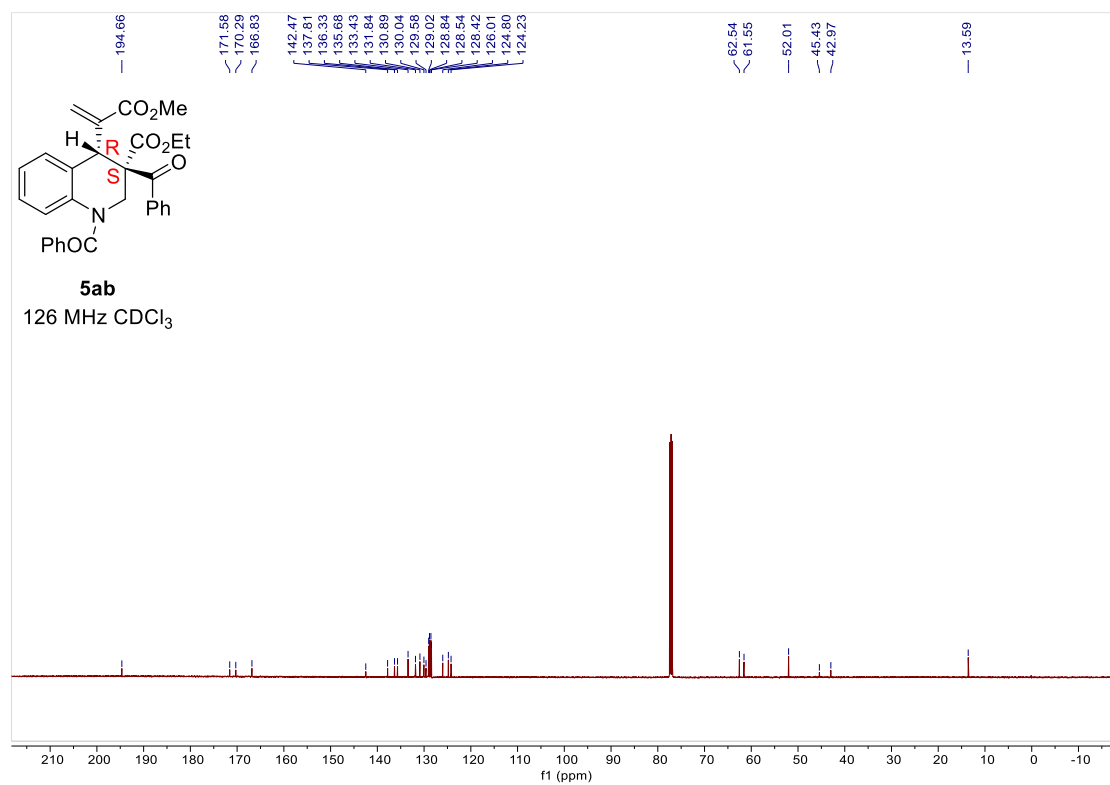
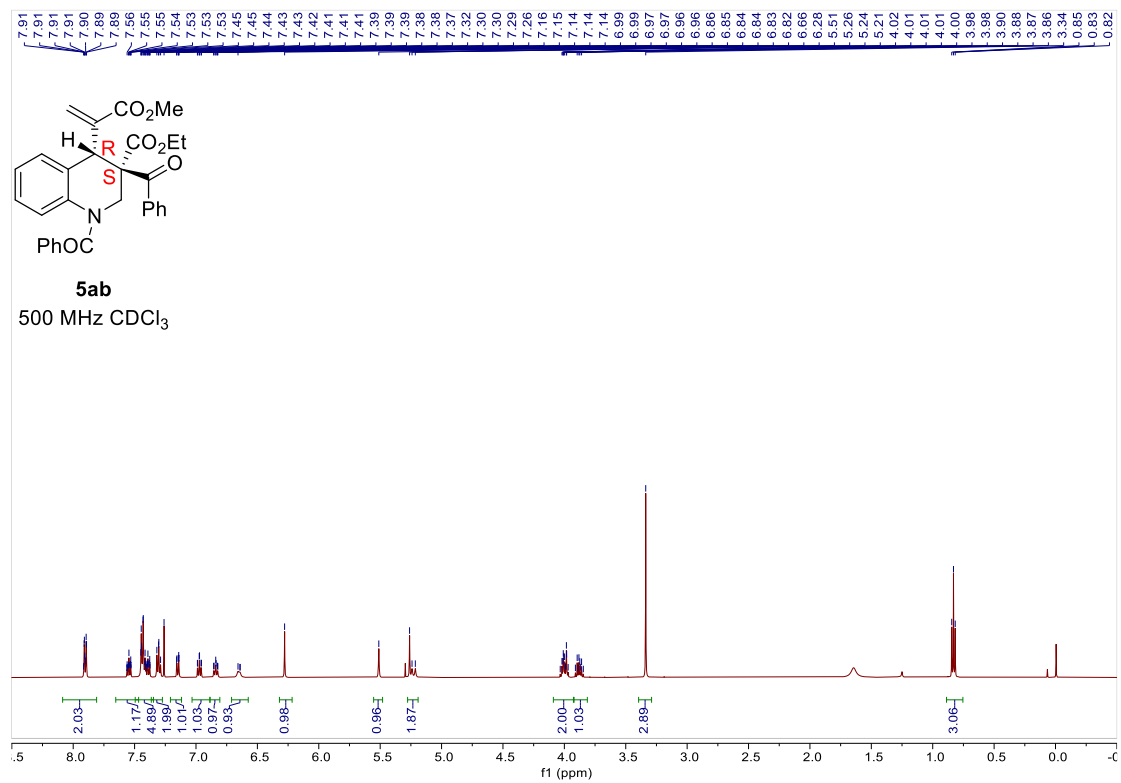


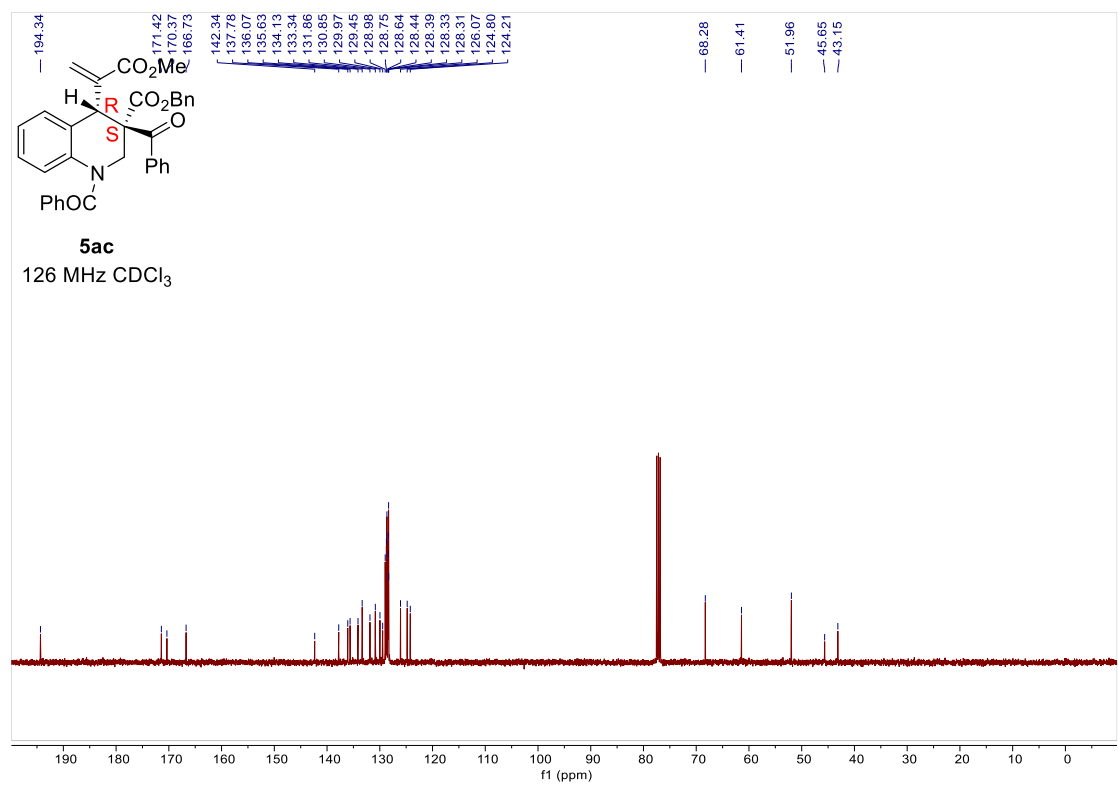
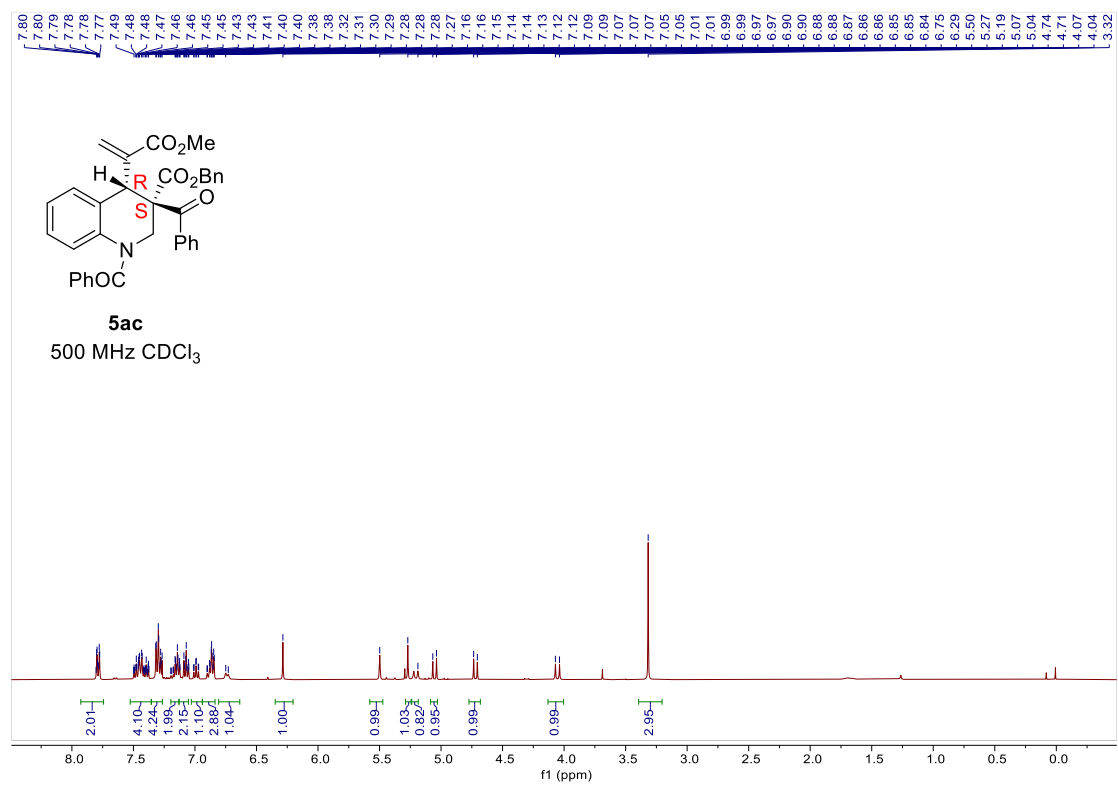


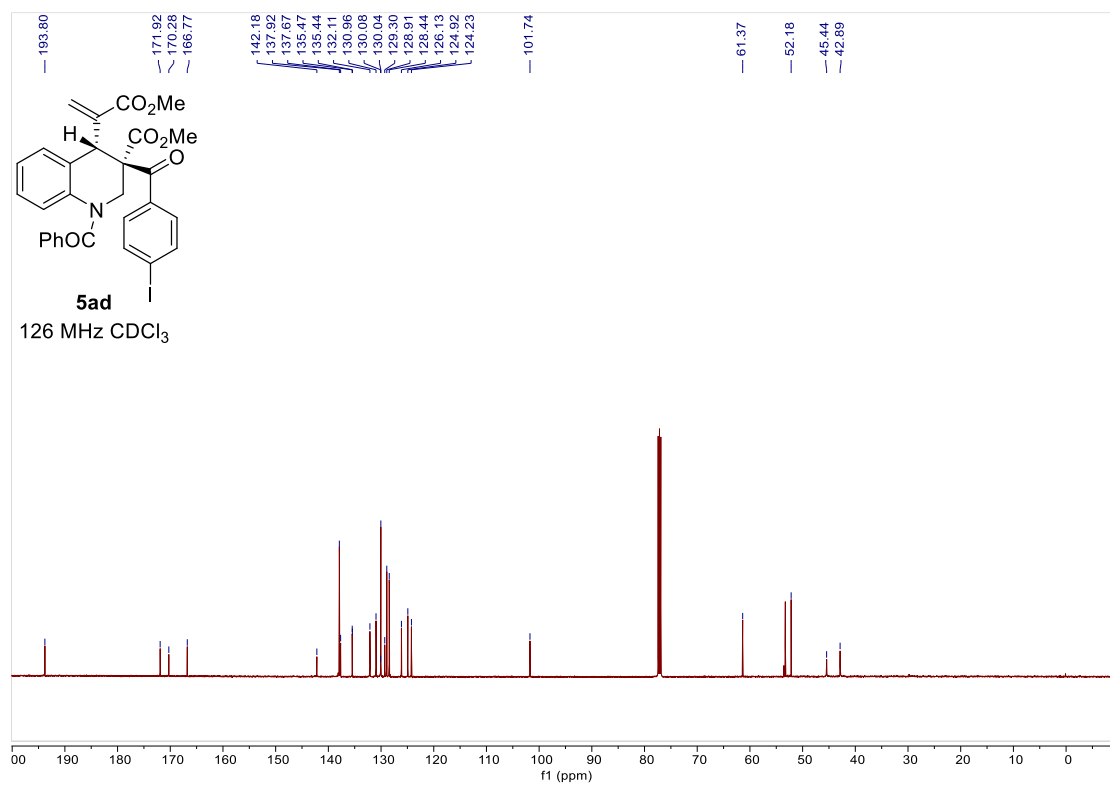
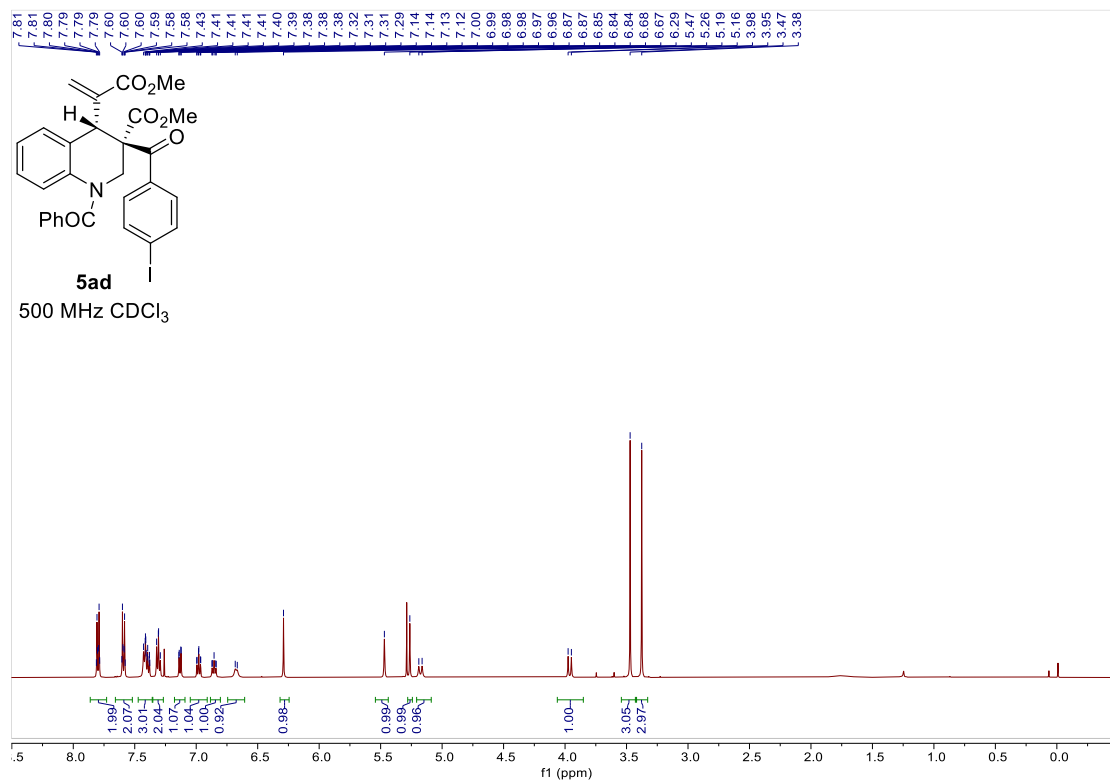


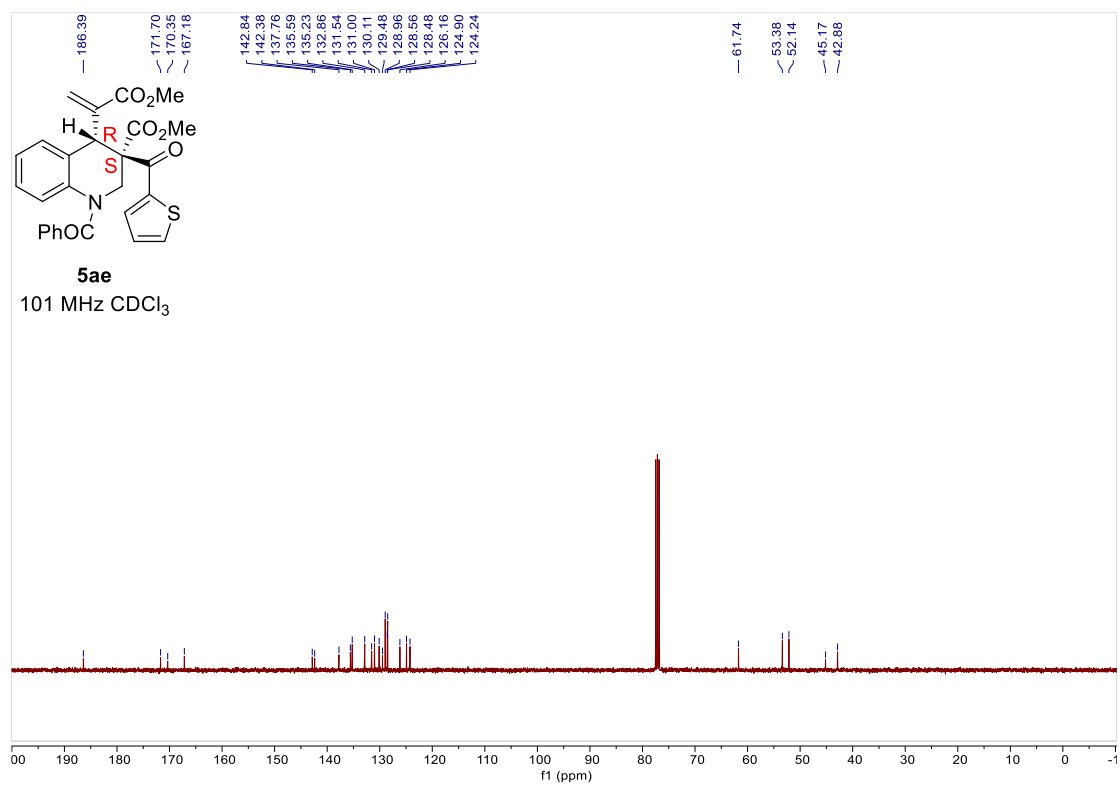
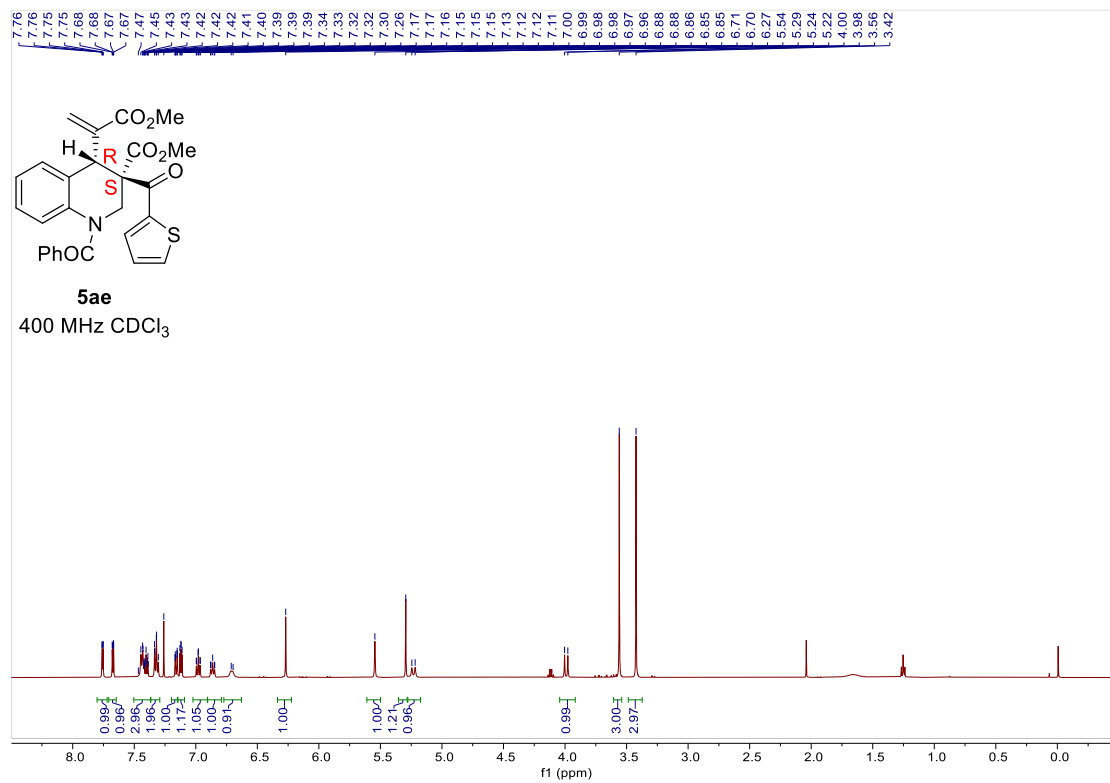




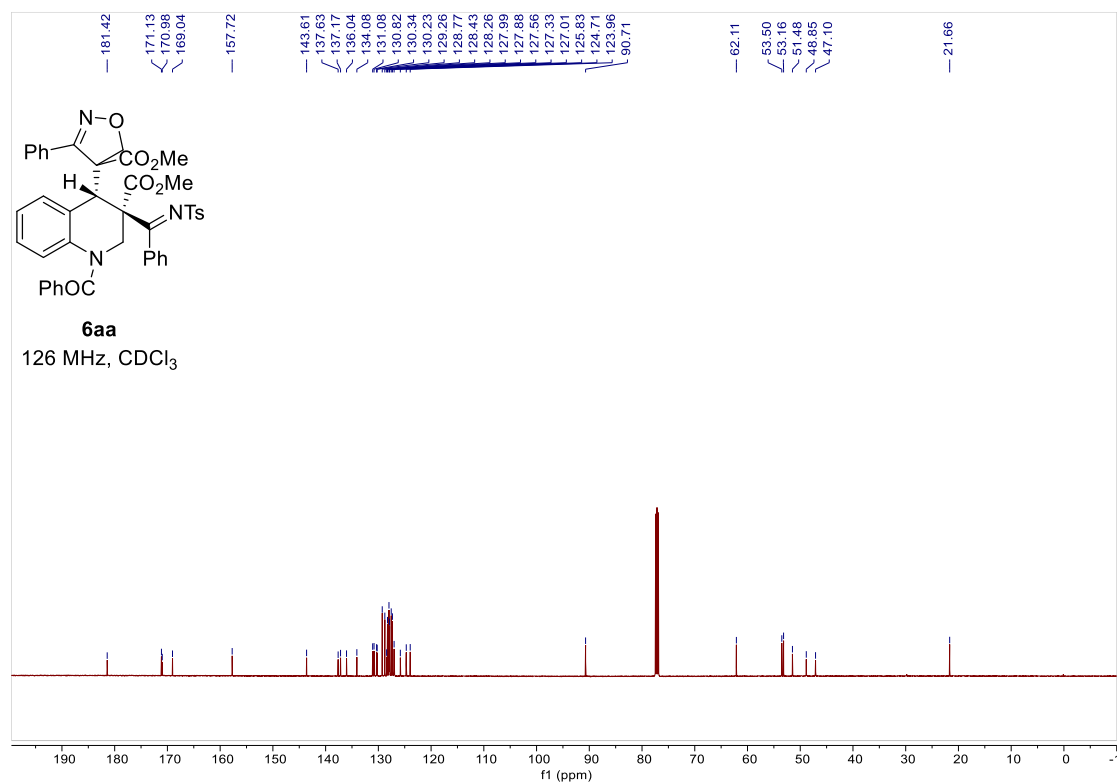
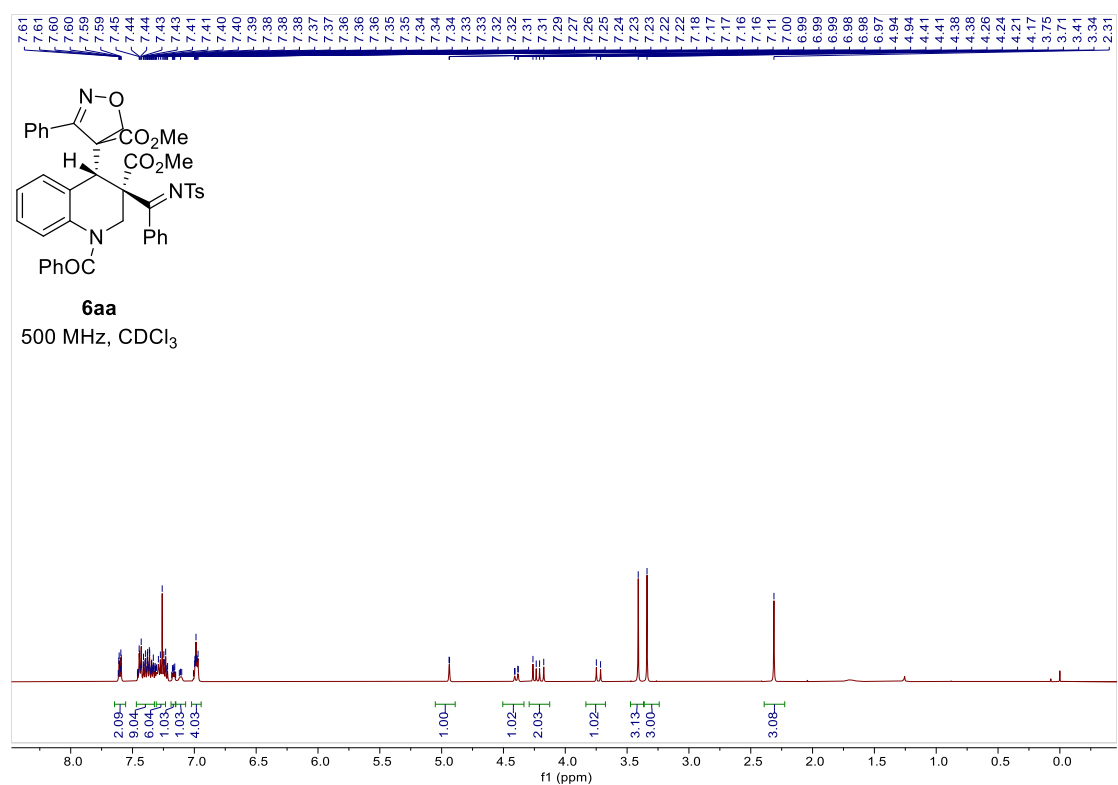




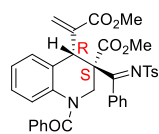




VIII. NMR Copies of Compounds 6



IX. HPLC Spectra of compounds 3-6

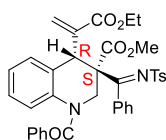
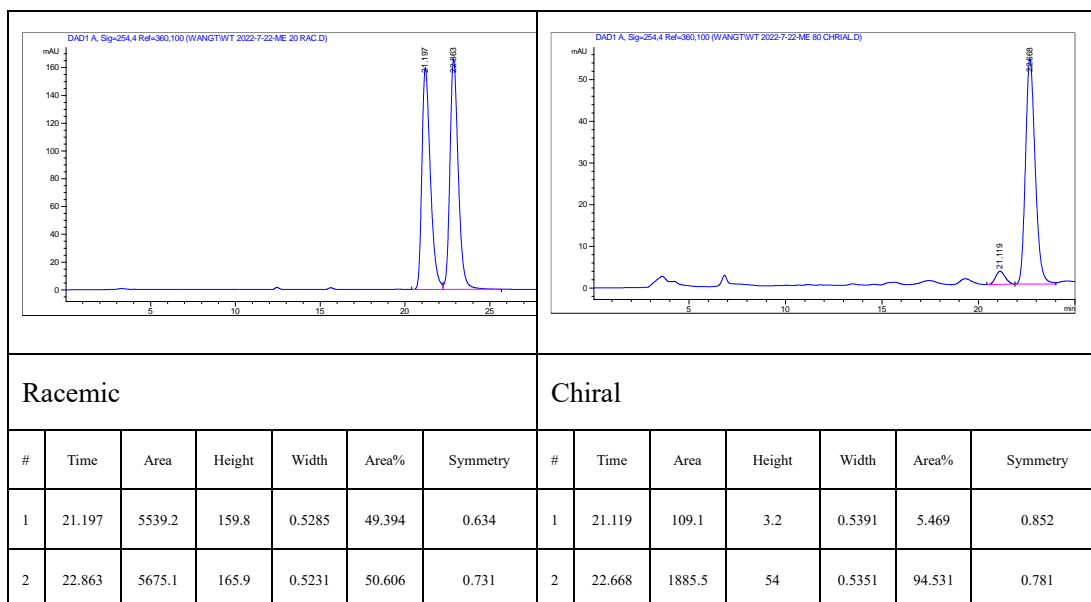


3aa

HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,

flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 21.119$ min,

$t_R(\text{major}) = 22.668$ min.

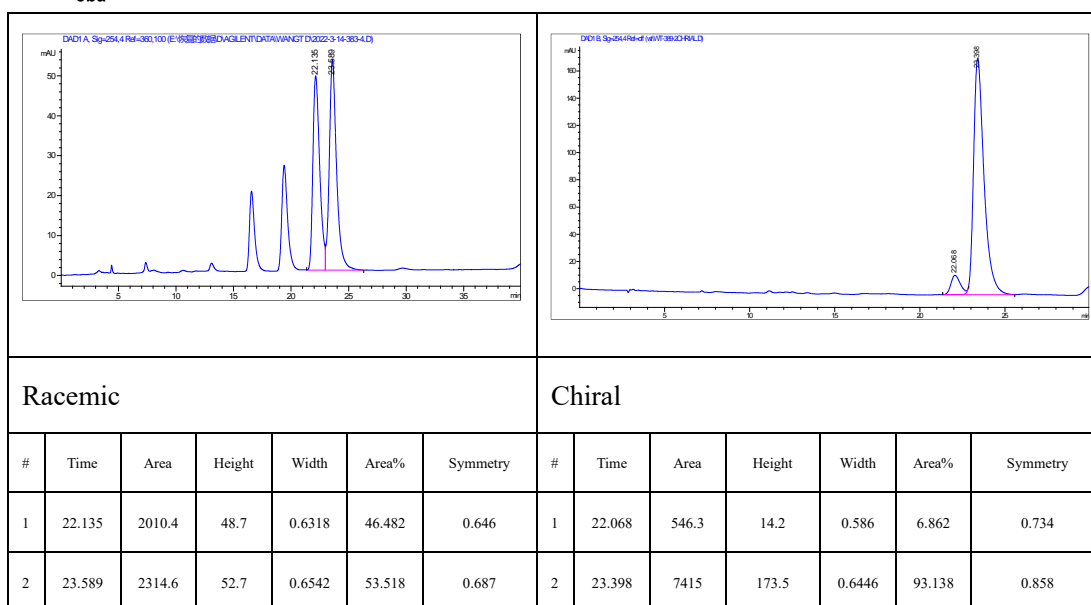


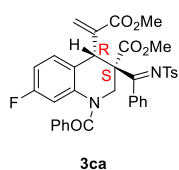
3ba

HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,

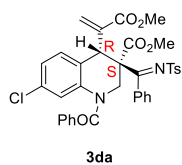
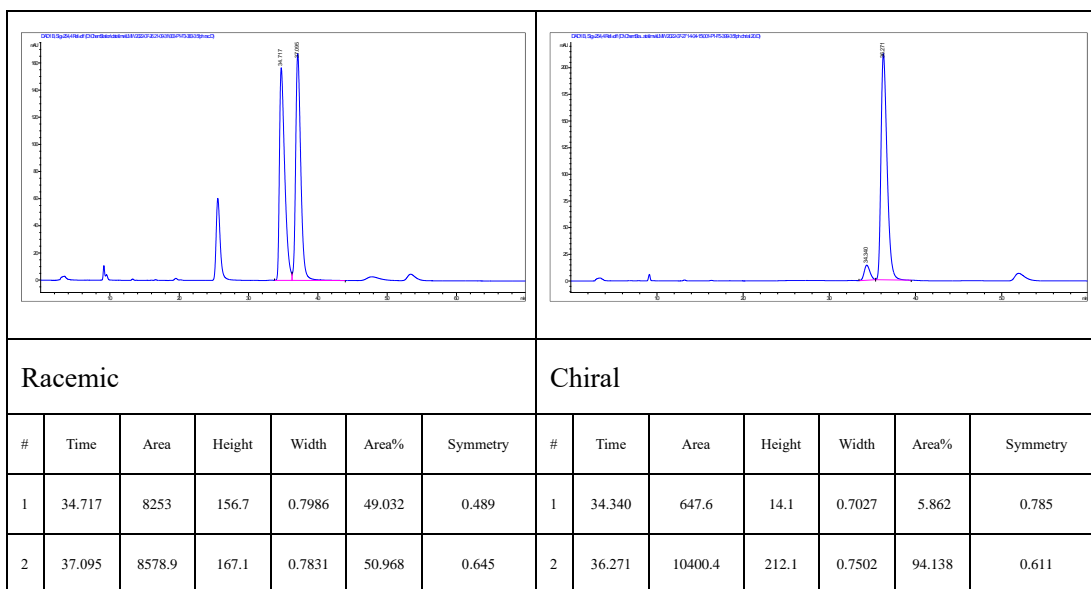
flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 22.068$ min,

$t_R(\text{major}) = 23.398$ min.

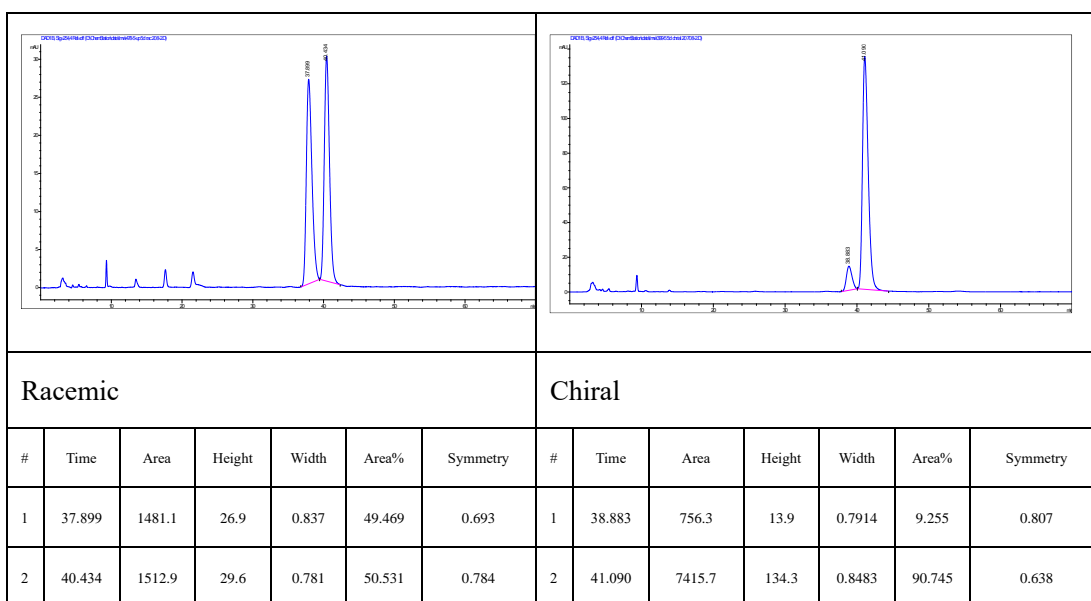


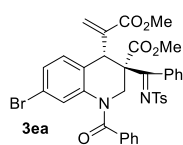


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 80/20,
 flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 34.340 min,
 tR(major) = 36.271 min.

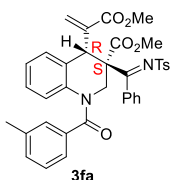
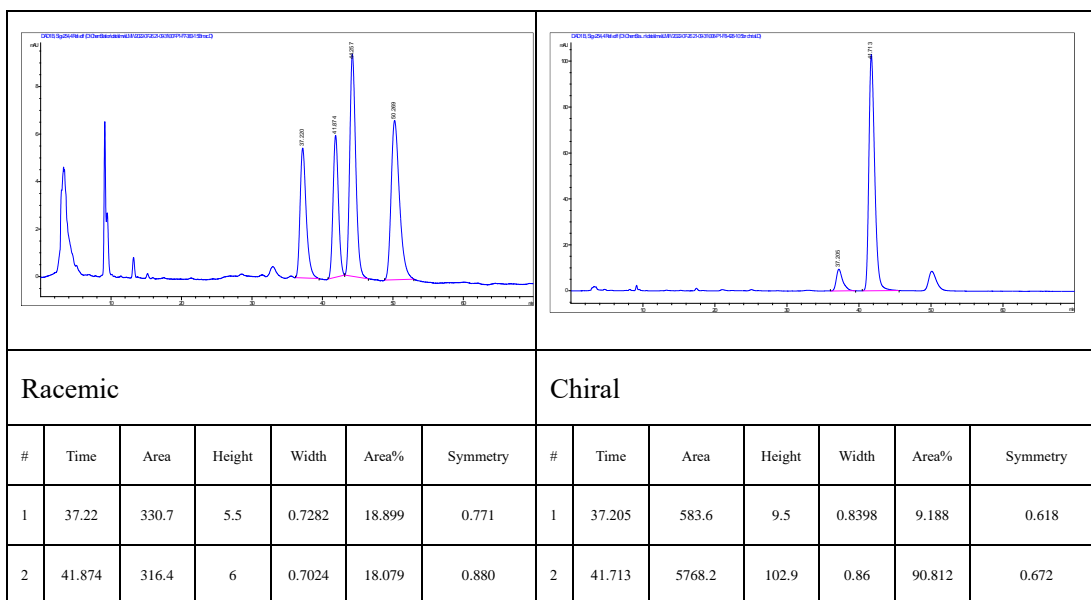


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 80/20,
 flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR(minor) = 38.883 min,
 tR(major) = 41.090 min.

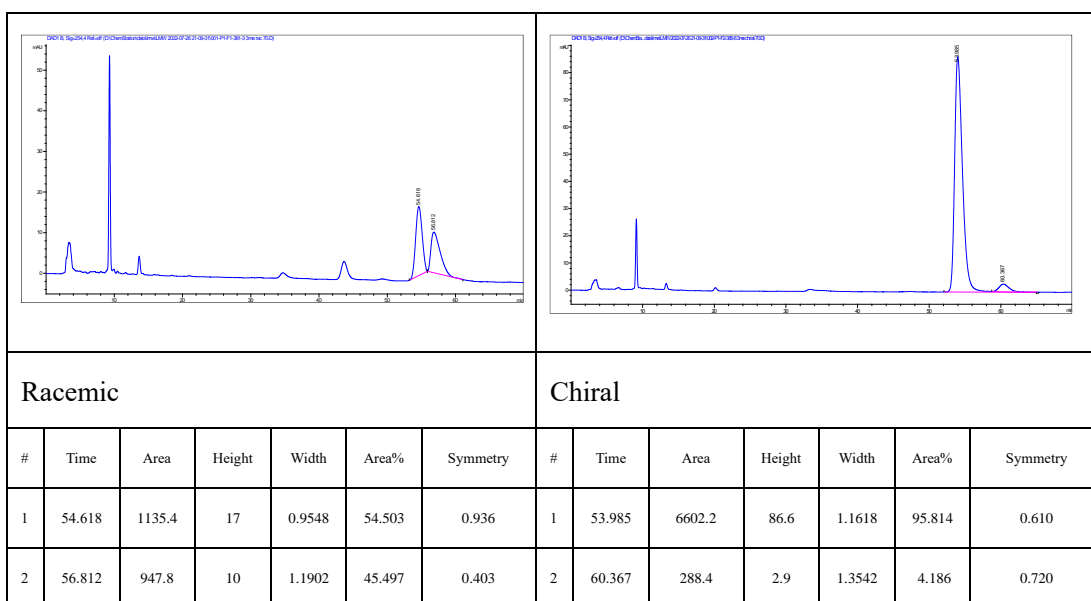


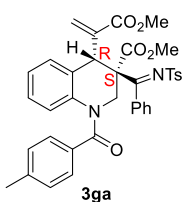


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 80/20,
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 $tR(\text{major}) = 41.713$ min.

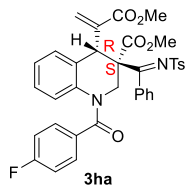
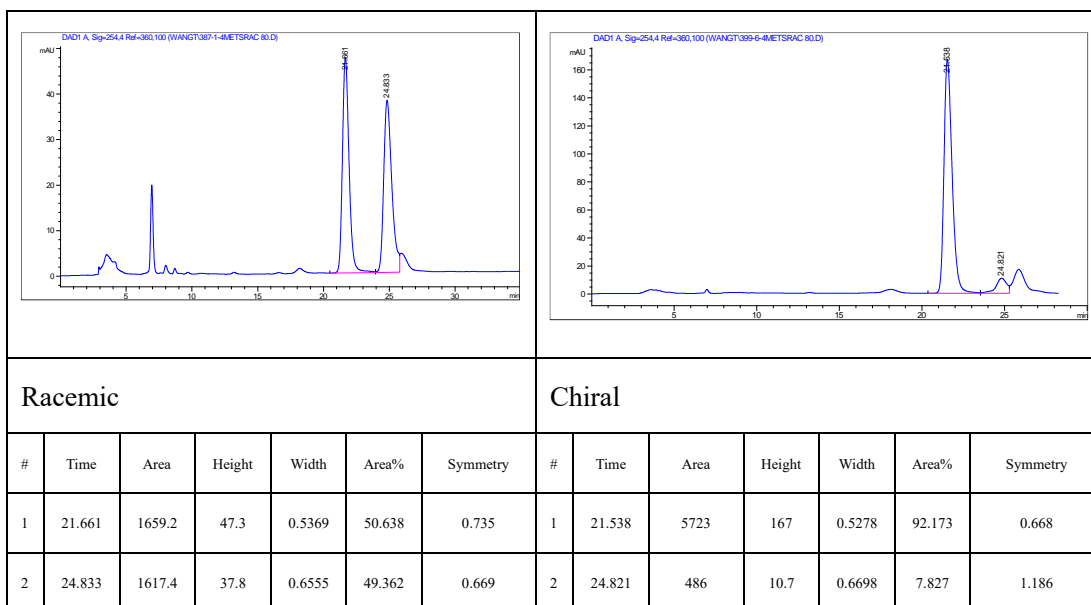


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 80/20,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $tR(\text{minor}) = 60.367$ min,
 $tR(\text{major}) = 53.985$ min.

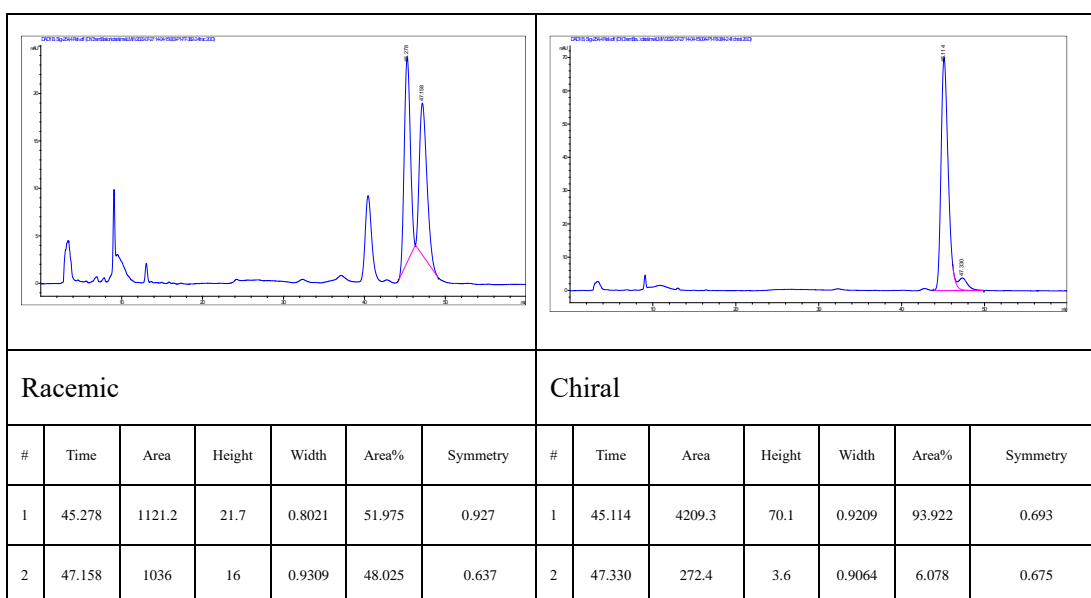


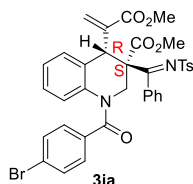


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
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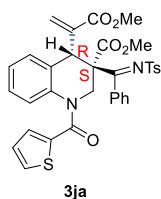
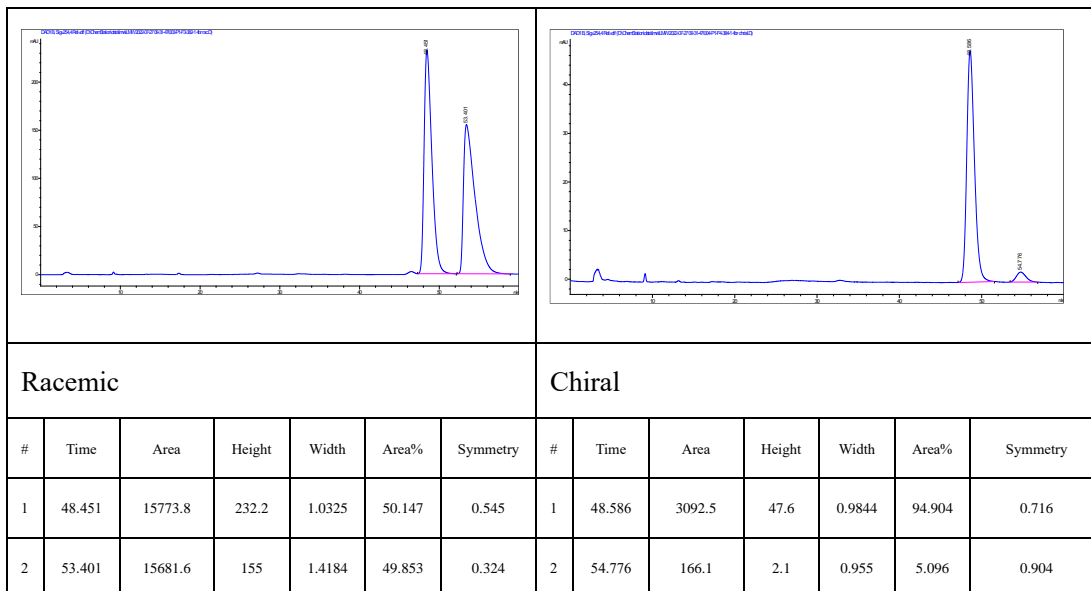


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 80/20,
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 $tR(\text{major}) = 45.114$ min.

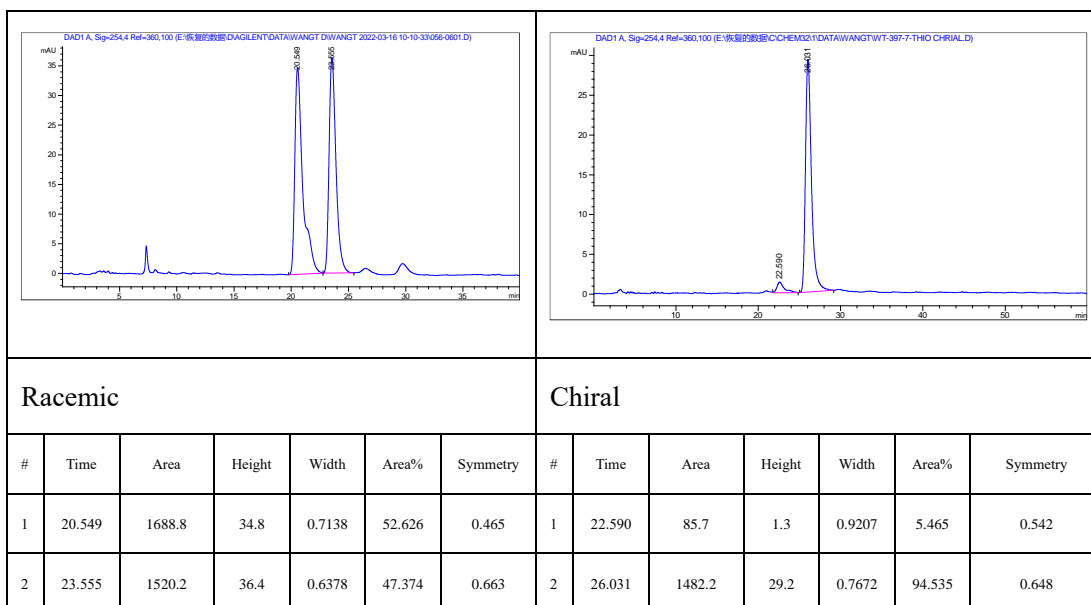


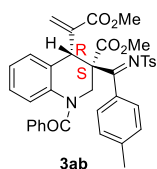


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 54.776$ min, $t_R(\text{major}) = 48.586$ min.

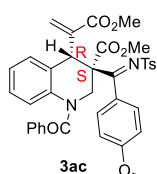
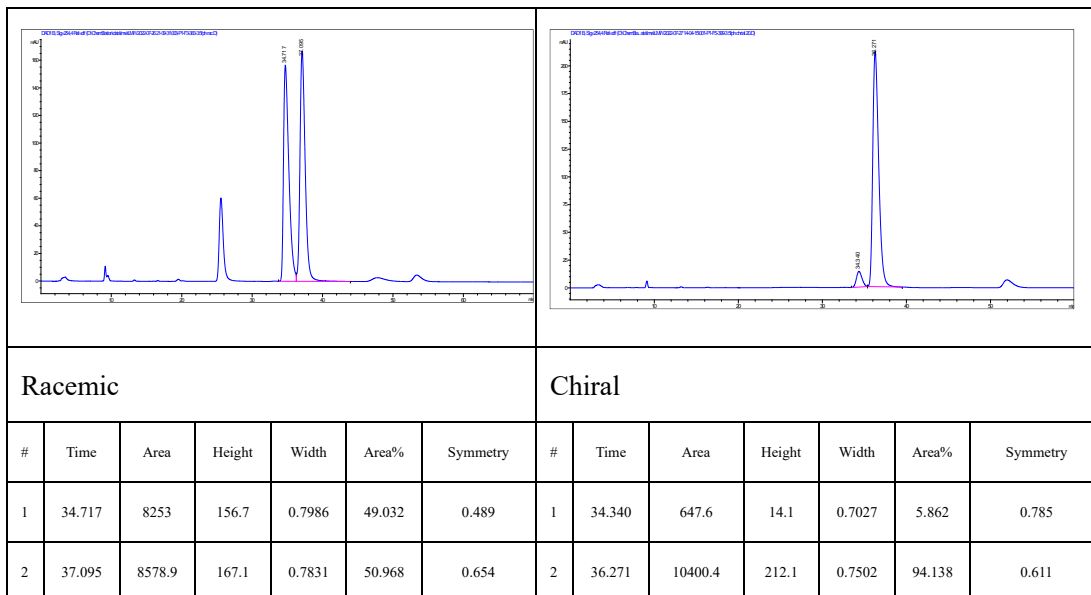


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 22.590$ min, $t_R(\text{major}) = 26.031$ min.

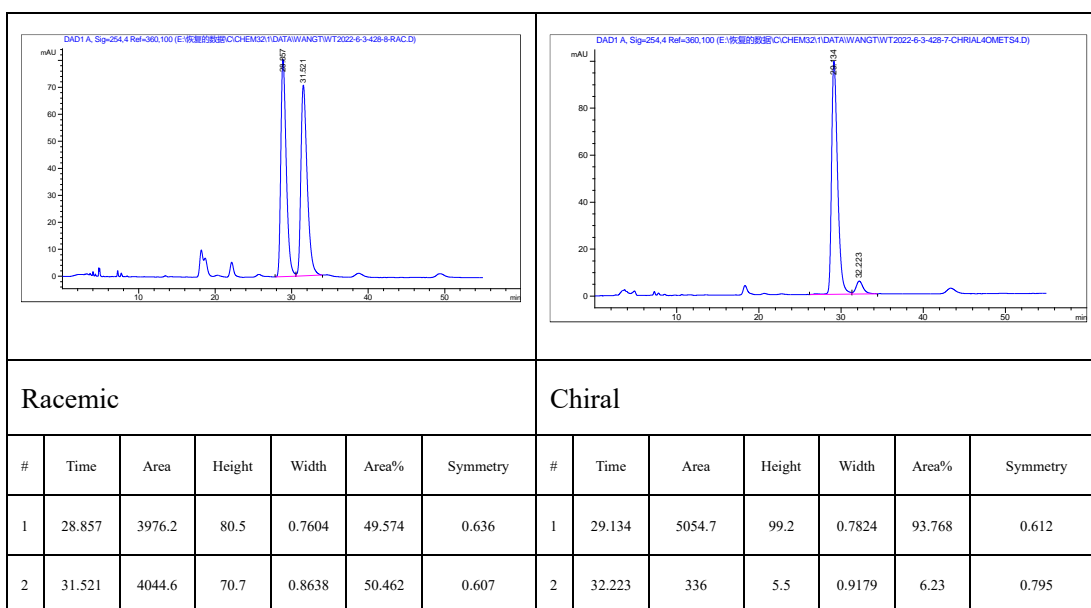


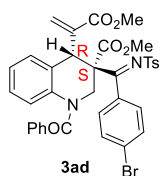


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 34.340$ min,
 $t_R(\text{major}) = 36.271$ min.

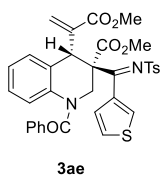
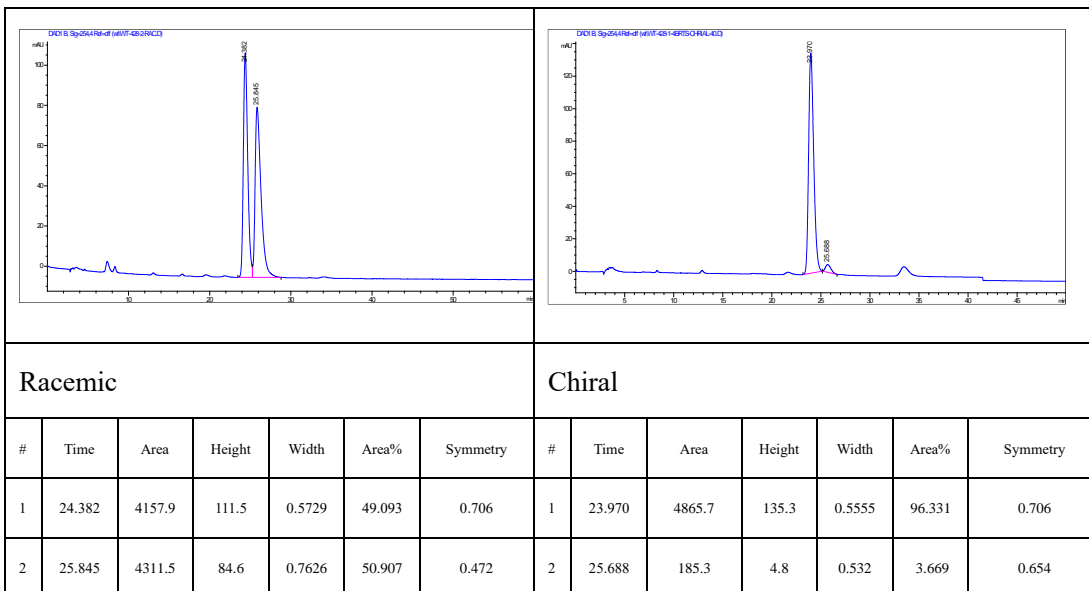


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 32.223$ min,
 $t_R(\text{major}) = 29.134$ min.

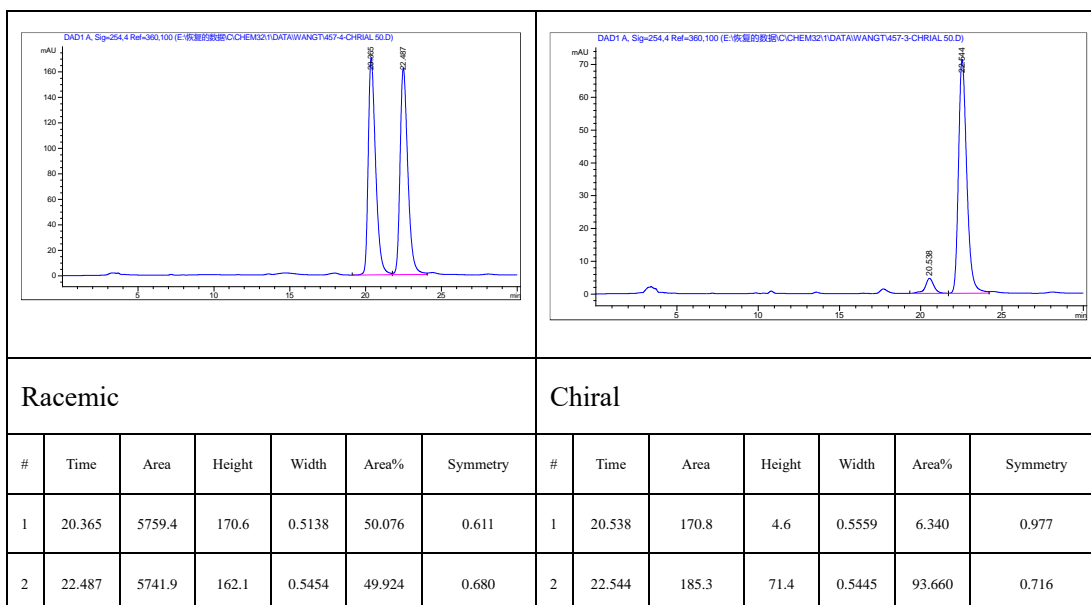


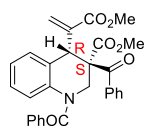


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 25.688$ min,
 $t_R(\text{major}) = 23.970$ min.



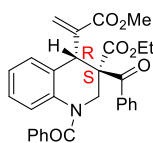
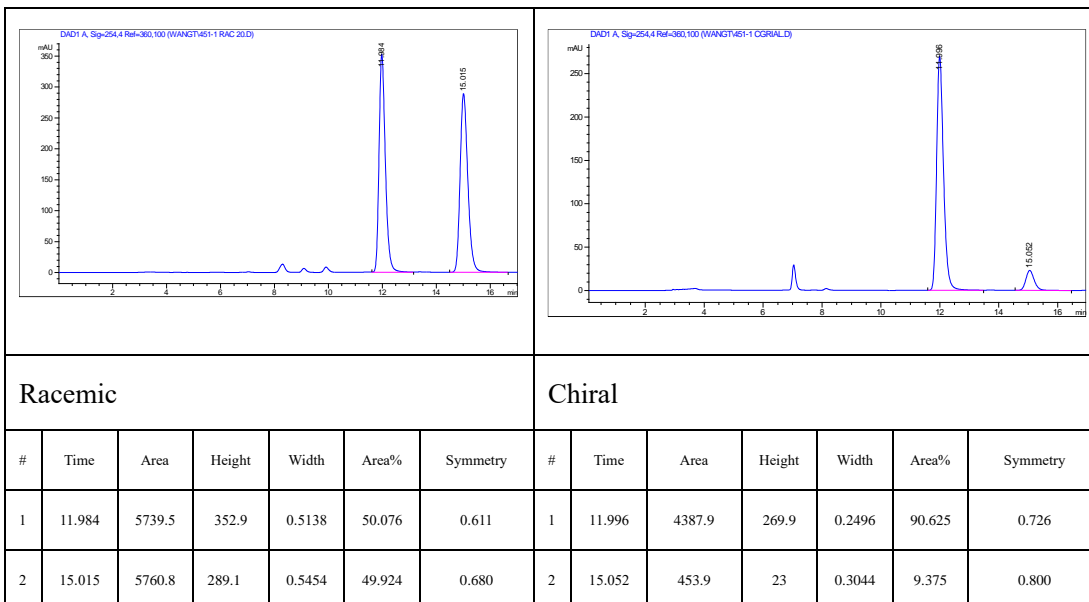
HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 20.538$ min,
 $t_R(\text{major}) = 22.544$ min.





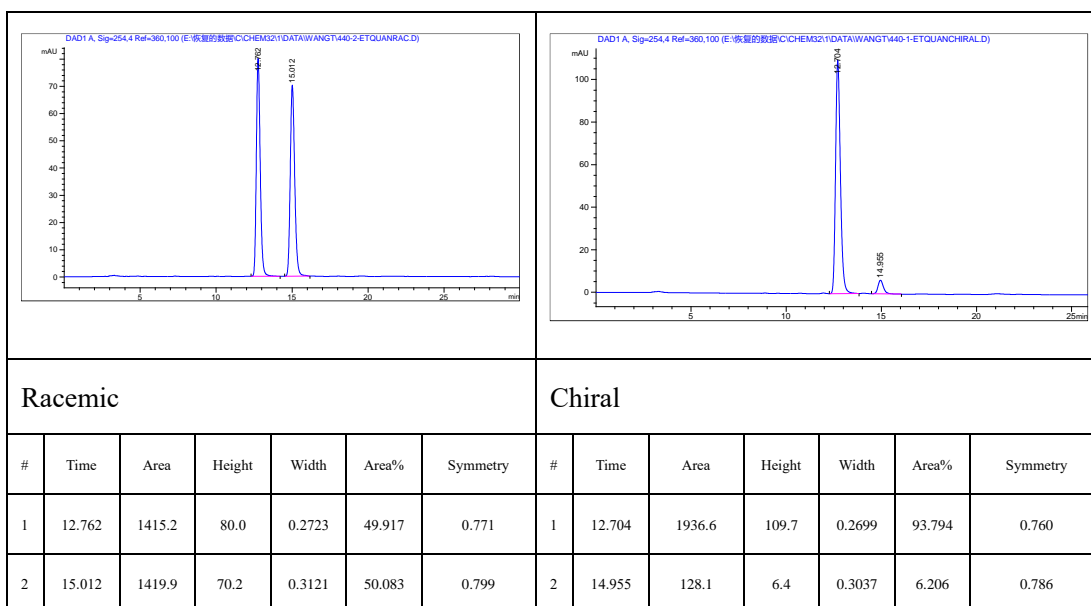
5aa

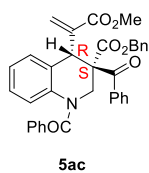
HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $tR(\text{minor}) = 15.052$ min,
 $tR(\text{major}) = 11.996$ min.



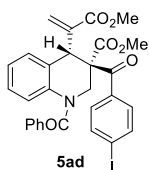
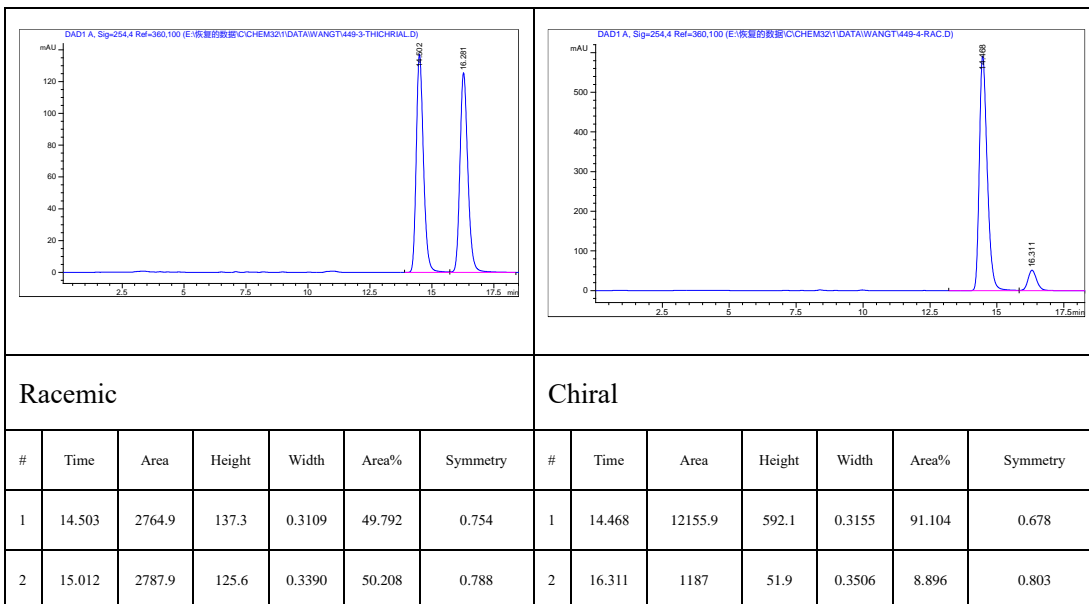
5ab

HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $tR(\text{minor}) = 14.955$ min,
 $tR(\text{major}) = 12.704$ min.

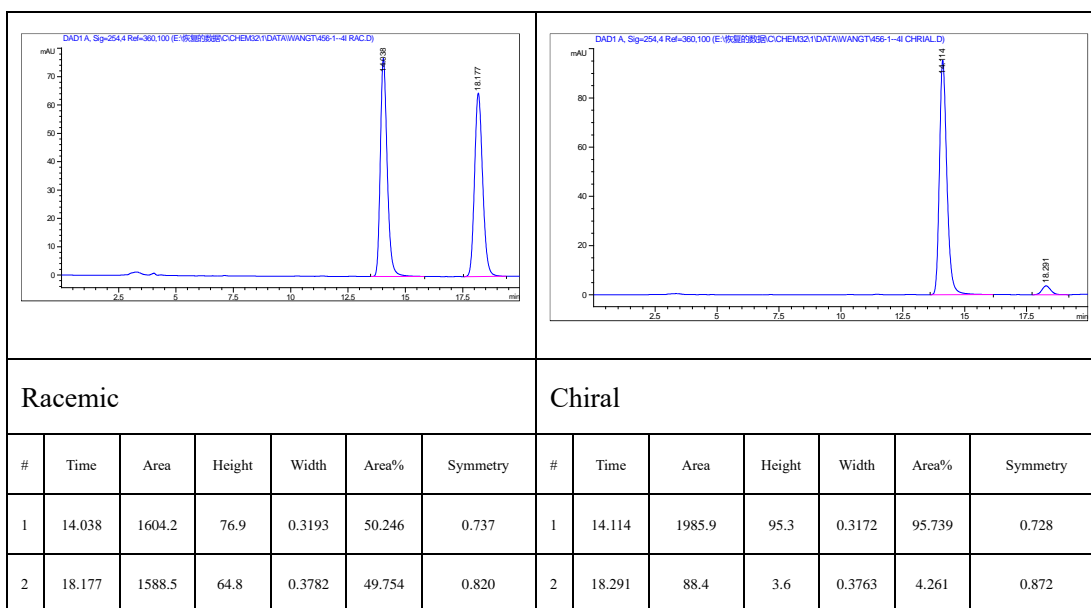


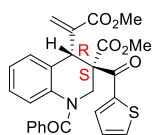


HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 16.311$ min,
 $t_R(\text{major}) = 14.468$ min.



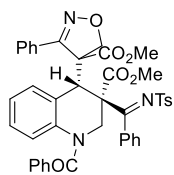
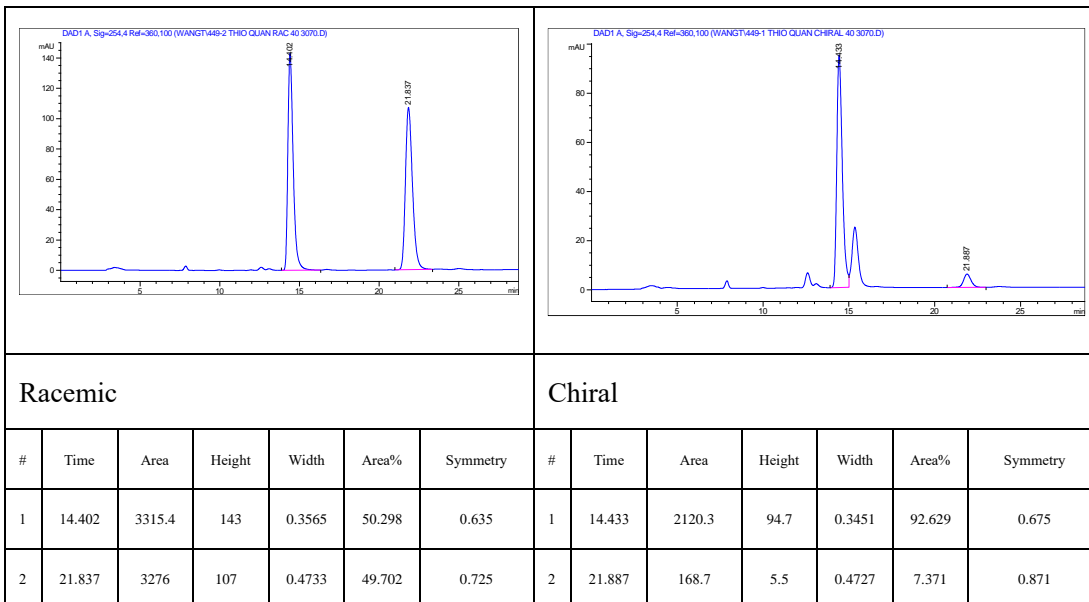
HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 70/30,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R(\text{minor}) = 18.291$ min,
 $t_R(\text{major}) = 14.114$ min.





HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 70/30,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $tR(\text{minor}) = 21.887$ min,
 $tR(\text{major}) = 14.433$ min.

5ae



HPLC conditions: Daicel Chiralpak IF-3 column, n-hexane/2-propanol = 60/40,
 flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $tR(\text{minor}) = 23.235$ min,
 $tR(\text{major}) = 30.810$ min.

6aa

