Electronic Supplementary Information

Palladium-Catalyzed Regio- and Stereoselective Allylic Alkylation of 5-Vinyloxazolidine-2,4-diones with Azlactones: Synthesis of Chiral (Z)-Trisubstituted Allylic Amino Acid Derivatives

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CONTENTS

General Information

All reactions were performed in Schlenk tubes under an atmosphere of argon using oven-dried glassware. Commercially obtained reagents were used without further purification, unless otherwise noted. Trichloromethane ($CHCl_3$) was distilled over P_2O_5 and stored over 3Å type molecular sieves. Tetrahydrofuran (THF) and toluene were distilled freshly before use over sodium and benzophenone. *m*-Xylene, Ethyl acetate (EA), Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled from CaH_2. Reactions were checked for completion by TLC analysis and plates were visualized with short-wave UV light (254 nm). The ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained in $CDCl_3$ using a Bruker-BioSpin AVANCE III HD NMR spectrometer at 500, 125 and 470 MHz, respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in hertz (Hz). The infrared spectra were recorded on a Bruker VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in cm^{-1}. High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry. Melting points were determined on a Stuard SMP3 melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724+. HPLC analysis was performed on Agilent 1220 series, UV detection monitored at 254 nm, using a Chiralpak AD-H column, Chiralcel OD-H column, Chiralcel OX-H column, Chiralpak IA column, Chiralpak IC column, Chiralpak ID column and Chiralpak IH column with hexane and ^{i}PrOH as the eluent.

General Procedure A for Palladium-Catalyzed Asymmetric Decarboxylative Allylation

To an oven-dried 25 mL of Schlenk tube equipped with a stir bar, $Pd_2dba_3{\cdot}CHCl_3$ (5 mol%) and (1*R*,4*S*,5*S*,6*S*)-5,6-dibenzhydrylbicyclo[2.2.1]hept-2-ene (20 mol%) was added along with γ-vinylaminobutyrolactones **1**[1] (0.15 mmol), 4-*tert*-butyl-2-phenyloxazol-5(4*H*)-ones **2**[2-3] (0.1 mmol) and DCM (1.0 mL). The reaction was stirred at 25 ℃ under argon atmosphere until complete consumption of 4-*tert*-butyl-2-phenyloxazol-5(4*H*)-ones **2** as monitored by thin layer chromatography. The reaction mixture was directly purified by silica gel column chromatography (Ethyl acetate/Petroleum ether = 1:10 or 1:5) to afford the desired products **3**.

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[1] Li, K.; Zhen, S.; Wang, W.; Du, J.; Yu, S.; Wu, Y.; Guo, H. *Chem. Sci*. **2023**, *14*, 3024−3029.

[2] Wang, L.; Liu, M.; Lu, M.; Wang, B.; Han, Q.; Jin, J.; Yu, S.; Wu, Y.; Guo, H. *Org. Chem. Front*. **2023**, *10*, 813−818.

[3] Wakafuji, K.; Lwasa, S.; Ouchida, K. N.; Cho, H.; Dohi, H.; Yamamoto, E.; Kamachi, T.; Tokunaga, M. *ACS Catal*. **2021**, *11*, 14067−14075.

General Procedure B for Scaled-up Asymmetric Decarboxylative Allylation

To an oven-dried 100 mL of Schlenk tube equipped with a stir bar, $Pd_2dba_3 \cdot CHCl_3$ (5 mol%) and (1*R*,4*S*,5*S*,6*S*)-5,6-dibenzhydrylbicyclo[2.2.1]hept-2-ene (20 mol%) was added along with γ-vinylaminobutyrolactone **1k** (1.5 mmol), 4-*tert*-butyl-2-phenyloxazol-5(4*H*)-one **2a** (1.0 mmol) and DCM (10.0 mL). The reaction was stirred at 25 ℃ under argon atmosphere until complete consumption of 4-*tert*-butyl-2-phenyloxazol-5(4*H*)-one **2a** as monitored by thin layer chromatography. The reaction mixture was directly purified by silica gel column chromatography (Ethyl acetate/Petroleum ether = 1:5) to afford the desired product **3ak**.

General Procedure C for Further Transformation

To a sealed tube equipped with compound **3ak** (0.1 mmol) in MeOH (1.0 mL) were added K_2CO_3 (2.5 equiv.). The reaction mixture stirred at room temperature for 20 h. After completion, the resulting mixture was concentrated and the residue was purified by flash chromatography on silica gel (Petroleum ether/Ethyl acetate = 3:1) to give the corresponding product **4a**.

General Procedure D for Further Transformation

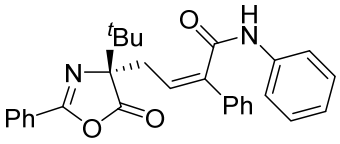
The $NaBH_4$ (1.0 mmol) was added to a solution of **3ak** (0.1 mmol) in MeOH (1.0 mL) at 0 ℃. The reaction was stirring at 0 ℃ for 3 h, The reaction was quenched with saturated aq. NH_4Cl (10.0 mL) and extracted with ethyl acetate (15.0 mL x 3). The combined organic layers were washed with brine (20.0 mL), dried over Na_2SO_4, filtered, concentrated under the reduced pressure. The residue purified by silica gel column chromatography (Petroleum ether/Ethyl acetate = 2:1) to afford desired adduct **4b**.

General Procedure E for Further Transformation

The $NaBH_4$ (1.0 mmol) was added to a solution of **3ak** (0.1 mmol) in MeOH (1.0 mL) at 0 ℃. The reaction was stirring at 0 ℃ for 3 h, The reaction was quenched with saturated aqeous NH_4Cl (5.0 mL) and extracted with ethyl acetate (15.0 mL x 3). The combined organic layers were washed with brine (20.0 mL), dried over Na_2SO_4, filtered, concentrated under the reduced pressure. The residue was dissolved in dichloromethane (1.5 mL) at 0 ℃, and Dess-Martin periodinane (DMP, 0.15 mmol) was added. The reaction mixture was stirred at room temperature for additional 0.5 h, the residue was purified by column chromatography on silica gel (Petroleum ether/Ethyl acetate = 2:1) to afford **4c**.

Characterization Data of Substrates and Products

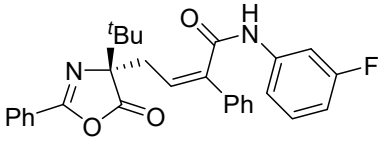
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N,2-diphenylbut-2-enamide



3aa

white solid, 41.3 mg, 91%, Mp: 138 – 140 °C, 94% *ee*, $[\alpha]^{25}_{D}$ = +104.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 7.97 – 7.89 (m, 2H), 7.82 – 7.73 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.29 (m, 2H), 7.22 – 7.17 (m, 2H), 7.16 – 7.11 (m, 3H), 7.11 – 7.06 (m, 1H), 5.68 – 5.62 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.17 – 3.08 (dd, *J* = 13.5, 9.5 Hz, 1H), 2.97 – 2.90 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 166.3, 161.5, 144.0, 138.4, 137.0, 133.4, 129.2, 129.2, 128.5, 128.3, 127.9, 126.9, 125.1, 124.4, 123.2, 119.6, 78.7, 37.8, 32.8, 25.0. IR (film) ν_{max} 3060, 2968, 1819, 1678, 1648, 1598, 1441, 1296, 1018, 755. HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{29}N_2O_3^+$ $[M+H]^+$: 453.2173, found: 453.2171. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 90 : 10, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 12.3 min, t_{minor} = 19.2 min).

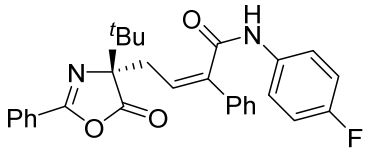
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(3-fluorophenyl)-2-phenylbut-2-enamide



3ab

Colorless oil, 41.8 mg, 89%, 94% *ee*, $[\alpha]^{25}_{D}$ = +96.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.05 – 7.95 (m, 2H), 7.85 – 7.76 (m, 1H), 7.65 – 7.56 (m, 1H), 7.54 – 7.44 (m, 3H), 7.38 – 7.29 (m, 1H), 7.28 – 7.17 (m, 5H), 6.91 – 6.81 (m, 1H), 5.78 – 5.70 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.22 – 3.12 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.06 – 2.95 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 166.4, 163.1 (d, *J* = 243.1 Hz), 161.6, 143.8, 139.8 (d, *J* = 10.6 Hz), 136.8, 133.5, 130.2 (d, *J* = 9.1 Hz), 129.2, 128.5, 128.4, 127.9, 126.9, 125.0, 123.6, 114.8 (d, *J* = 2.9 Hz), 111.2 (d, *J* = 21.3 Hz), 107.1 (d, *J* = 26.1 Hz), 78.7, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –111.1. IR (film) ν_{max} 3062, 2969, 1820, 1683, 1647, 1604, 1540, 1019, 889, 774. HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}FN_2O_3^+$ $[M+H]^+$: 471.2078, found: 471.2076. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 90 : 10, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.1 min, t_{minor} = 10.7 min).

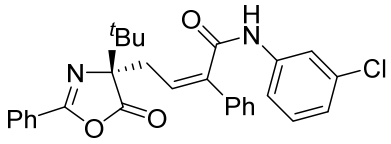
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-fluorophenyl)-2-phenylbut-2-enamide



3ac

Colorless oil, 45.1 mg, 96%, 95% *ee*, $[\alpha]^{25}_{D}$ = +88.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.04 – 7.96 (m, 2H), 7.85 – 7.77 (m, 2H), 7.63 – 7.55 (m, 1H), 7.53 – 7.45 (t, *J* = 7.0 Hz, 2H), 7.28 – 7.19 (m, 5H), 7.13 – 7.05 (m, 2H), 5.79 – 5.68 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.22 – 3.13 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.07 – 2.96 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 166.2, 161.5, 159.4 (d, *J* = 243.5 Hz), 143.9, 136.9, 134.4 (d, *J* = 2.8 Hz), 133.4, 129.2, 128.5, 128.3, 127.9, 126.9, 125.0, 123.4, 121.1 (d, *J* = 7.7 Hz), 115.8 (d, *J* = 22.3 Hz), 78.8, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –117.8. IR (film) ν_{max} 3059, 2970, 1820, 1677, 1652, 1540, 1508, 1295, 1214, 889, 692. HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}FN_2O_3^+$ $[M+H]^+$: 471.2078, found: 471.2075. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 90 : 10, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 11.1 min, t_{minor} = 13.5 min).

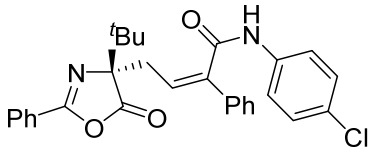
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(3-chlorophenyl)-2-phenylbut-2-enamide



3ad

Colorless oil, 43.3 mg, 89%, 94% *ee*, $[\alpha]^{25}_{D}$ = +112.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (s, 1H), 7.96 – 7.88 (m, 3H), 7.59 – 7.49 (m, 2H), 7.46 – 7.38 (t, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (t, *J* = 8.0 Hz, 1H), 7.19 – 7.12 (m, 5H), 7.09 – 7.03 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.70 – 5.63 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.14 – 3.05 (dd, *J* = 14.0, 10.0 Hz, 1H), 2.97 – 2.89 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 166.4, 161.6, 143.8, 139.5, 136.8, 134.9, 133.5, 130.1, 129.3, 128.5, 128.4, 127.9, 126.9, 125.0, 124.5, 123.6, 119.7, 117.4, 78.7, 37.8, 32.7, 25.0. IR (film) ν_{max} 3060, 2969, 1820, 1677, 1598, 1018, 889, 692, 670. HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}ClN_2O_3^+$ $[M+H]^+$: 487.1783, found: 487.1781. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 95 : 5, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 10.5 min, t_{minor} = 14.6 min).

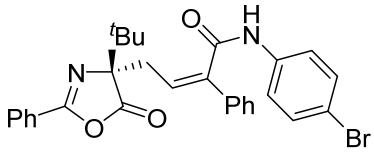
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-chlorophenyl)-2-phenylbut-2-enamide



3ae

Colorless oil, 43.0 mg, 88%, 94% *ee*, $[\alpha]^{25}_{D}$ = +128.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.95 – 7.88 (m, 2H), 7.76 – 7.70 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.47 – 7.37 (t, *J* = 7.0 Hz, 2H), 7.30 – 7.26 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.12 (m, 5H), 5.72 – 5.59 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.14 – 3.04 (dd, *J* = 14.0, 9.5 Hz, 1H), 2.97 – 2.89 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 166.3, 161.6, 143.8, 137.0, 136.9, 133.5, 129.3, 129.2, 129.2, 128.5, 128.4, 127.9, 126.9, 125.0, 123.5, 120.7, 78.7, 37.8, 32.7, 25.0. IR (film) ν_{max} 3034, 2970, 1820, 1681, 1648, 1595, 1527, 1492, 1298, 889, 692. HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}ClN_2O_3^+$ $[M+H]^+$: 487.1783, found: 487.1781. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 90 : 10, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.5 min, t_{minor} = 12.2 min).

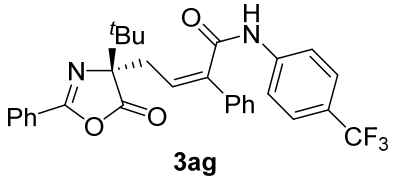
(*S*, *Z*)-N-(4-bromophenyl)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-phenylbut-2-enamide



3af

Colorless oil, 46.3 mg, 87%, 94% *ee*, $[\alpha]^{25}_{D}$ = +104.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (s, 1H), 8.02 – 7.95 (m, 2H), 7.78 – 7.73 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.47 (m, 4H), 7.27 – 7.19 (m, 5H), 5.78 – 5.68 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.21 – 3.10 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.04 – 2.97 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 166.3, 161.6, 143.9, 137.5, 136.8, 133.5, 132.1, 129.2, 128.5, 128.4, 127.9, 126.9, 125.0, 123.5, 121.1, 117.0, 78.7, 37.8, 32.7, 25.0. IR (film) ν_{max} 3033, 2970, 1820, 1681, 1648, 1526, 1488, 1298, 1019, 889. HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{28}BrN_2O_3^+$ $[M+H]^+$: 531.1278, found: 531.1276. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 95 : 5, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 15.2 min, t_{minor} = 22.8 min).

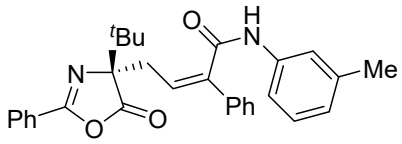
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-phenyl-N-(4-(trifluoro-methyl)phenyl)but-2-enamide



3ag

Colorless oil, 45.7 mg, 88%, 92% *ee*, $[\alpha]^{25}_{D}$ = +104.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 8.03 – 7.95 (m, 4H), 7.69 – 7.58 (m, 3H), 7.54 – 7.47 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 5H), 5.80 – 5.72 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.22 – 3.13 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.07 – 2.98 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 166.6, 161.7, 143.7, 141.4, 136.8, 133.5, 129.3, 128.6, 128.4, 127.9, 126.9, 126.4 (q, *J* = 3.6 Hz), 126.2 (q, *J* = 32.4 Hz), 125.0, 124.2 (q, *J* = 270.0 Hz), 123.8, 119.2, 78.7, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –62.0. IR (film) ν_{max} 2970, 1822, 1685, 1653, 1533, 1322, 1120, 1067, 1017, 692. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{28}F_3N_2O_3^+$ $[M+H]^+$: 521.2047, found: 521.2044. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 95 : 5, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.7 min, t_{minor} = 10.9 min).

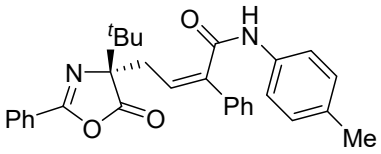
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-phenyl-N-(m-tolyl)but-2-enamide



3ah

Colorless oil, 41.9 mg, 90%, 95% *ee*, $[\alpha]^{25}_{D}$ = +88.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.98 – 7.90 (m, 2H), 7.73 – 7.66 (t, *J* = 2.0 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.45 – 7.38 (t, *J* = 7.0 Hz, 2H), 7.21 – 7.16 (m, 3H), 7.15 – 7.11 (m, 3H), 6.93 – 6.88 (d, *J* = 7.5 Hz, 1H), 5.68 – 5.60 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.15 – 3.06 (dd, *J* = 13.5, 9.5 Hz, 1H), 2.98 – 2.89 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.31 (s, 3H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 166.3, 161.4, 144.0, 139.1, 138.3, 137.0, 133.4, 129.2, 128.9, 128.5, 128.2, 127.9, 126.9, 125.2, 125.1, 123.2, 120.3, 116.6, 78.8, 37.8, 32.7, 25.0, 21.7. IR (film) ν_{max} 2967, 1820, 1683, 1653, 1541, 1489, 1294, 1260, 1019, 888, 764, 750. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{31}N_2O_3^+$ $[M+H]^+$: 467.2329, found: 467.2326. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 90 : 10, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 10.4 min, t_{minor} = 15.4 min).

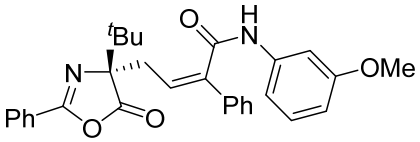
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-phenyl-N-(p-tolyl)but-2-enamide



3ai

White solid, 41.4 mg, 89%, Mp: 150 – 152 °C, 94% *ee*, $[\alpha]^{25}_{D}$ = +136.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.05 – 7.95 (m, 2H), 7.77 – 7.69 (d, *J* = 8.5 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.45 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.17 (m, 5H), 5.75 – 5.67 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.24 – 3.15 (dd, *J* = 14.0, 10.0 Hz, 1H), 3.04 – 2.96 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.35 (s, 3H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 166.1, 161.4, 144.08, 137.1, 135.8, 134.0, 133.4, 129.6, 129.2, 128.5, 128.2, 127.9, 126.9, 125.1, 123.0, 119.5, 78.7, 37.8, 32.7, 25.0, 21.0. IR (film) ν_{max} 2972, 1820, 1772, 1676, 1653, 1540, 1521, 1295, 1276, 1260, 764. HRMS (ESI, *m*/z) calcd for $C_{30}H_{31}N_2O_3^+$ $[M+H]^+$: 467.2329, found: 467.2327. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.3 min, t_{minor} = 14.3 min).

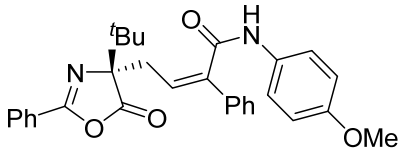
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(3-methoxyphenyl)-2-phenylbut-2-enamide



3aj

Colorless oil, 42.3 mg, 88%, 94% *ee*, $[\alpha]^{25}_{D}$ = +96.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 1H), 7.97 – 7.87 (m, 2H), 7.62 – 7.56 (t, *J* = 2.5 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.44 – 7.38 (m, 2H), 7.25 – 7.11 (m, 7H), 6.69 – 6.61 (m, 1H), 5.70 – 5.60 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.76 (s, 3H), 3.18 – 3.07 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.97 – 2.88 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 166.3, 161.5, 160.3, 144.1, 139.6, 137.1, 133.4, 129.8, 129.2, 128.5, 128.3, 127.9, 126.9, 125.0, 123.3, 111.7, 110.5, 105.2, 78.7, 55.4, 37.8, 32.7, 25.0. IR (film) ν_{max} 2967, 1820, 1672, 1600, 1244, 1064, 965, 752, 693. HRMS (ESI, *m*/z) calcd for $C_{30}H_{31}N_2O_4^+$ $[M+H]^+$: 483.2278, found: 483.2277. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 85 : 15, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 10.2 min, t_{minor} = 15.5 min).

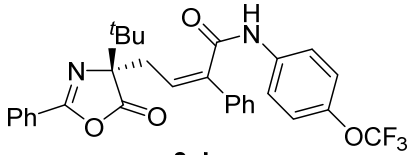
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3ak

White solid, 44.2 mg, 92%, Mp: 106 – 108 °C, 95% *ee*, $[\alpha]^{25}_{D}$ = +112.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.01 (s, 1H), 7.97 – 7.88 (d, *J* = 7.0 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 7.22 – 7.18 (m, 2H), 7.16 – 7.11 (m, 3H), 6.88 – 6.84 (m, 2H), 5.69 – 5.59 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.75 (s, 3H), 3.16 – 3.06 (dd, *J* = 14.0, 10.0 Hz, 1H), 2.99 – 2.87 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 165.9, 161.4, 156.4, 144.1, 137.1, 133.4, 131.6, 129.2, 128.5, 128.2, 127.9, 125.1, 123.1, 121.1, 114.3, 78.8, 55.5, 37.8, 32.7, 25.0. IR (film) ν_{max} 2966, 1819, 1671, 1652, 1510, 1465, 1245, 1178, 889, 830. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{31}N_2O_4^+$ $[M+H]^+$: 483.2278, found: 483.2279. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 12.2 min, t_{minor} = 23.2 min).

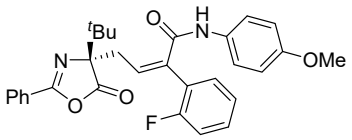
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-phenyl-N-(4-(trifluoromethoxy)phenyl)but-2-enamide



3al

Colorless oil, 48.9 mg, 91%, 95% *ee*, $[\alpha]^{25}_{D}$ = +96.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.03 – 7.95 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.93 – 7.85 (d, *J* = 9.0 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.53 – 7.46 (m, 2H), 7.28 – 7.20 (m, 7H), 5.79 – 5.72 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.22 – 3.13 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.07 – 2.98 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1, 166.4, 161.6, 145.4, 143.8, 137.0, 136.8, 133.5, 129.2, 128.5, 128.4, 127.9, 126.9, 125.0, 123.6, 121.9, 120.6, 120.5 (q, *J* = 256.0 Hz), 78.8, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –58.0. IR (film) ν_{max} 3060, 2970, 1821, 1683, 1653, 1539, 1508, 1263, 1202, 1019, 889, 692. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{28}F_3N_2O_4^+$ $[M+H]^+$: 537.1996, found: 537.1996. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 95 : 5, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.4 min, t_{minor} = 11.9 min).

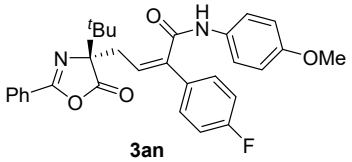
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-(2-fluorophenyl)-N-(4-methoxyphenyl)but-2-enamide



3am

Colorless oil, 44.2 mg, 88%, 96% *ee*, $[\alpha]^{25}_{D}$ = +192.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.95 – 7.88 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.55 – 7.49 (m, 1H), 7.45 – 7.38 (m, 2H), 7.27 – 7.21 (m, 1H), 7.14 – 7.07 (m, 1H), 6.98 – 6.93 (m, 1H), 6.88 – 6.83 (m, 2H), 6.81 – 6.76 (m, 1H), 5.71 – 5.62 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.74 (s, 3H), 3.29 – 3.17 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.98 – 2.87 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.8, 165.0, 161.9, 159.6 (d, *J* = 247.1 Hz), 156.3, 138.8, 133.4, 131.8, 130.6 (d, *J* = 2.9 Hz), 129.8 (d, *J* = 8.4 Hz), 129.1, 128.0, 127.2 (d, *J* = 2.5 Hz), 126.0 (d, *J* = 13.5 Hz), 125.1, 124.1 (d, *J* = 3.5 Hz), 121.0, 115.6 (d, *J* = 21.9 Hz), 114.3, 78.4, 55.5, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –114.3. IR (film) ν_{max} 3062, 2961, 1820, 1671, 1652, 1540, 1510, 1297, 1245, 1020, 964. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}FN_2O_4^+$ $[M+H]^+$: 501.2184, found: 501.2184. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.9 min, t_{minor} = 17.1 min).

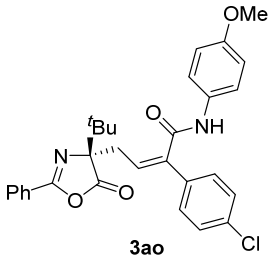
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-(4-fluorophenyl)-N-(4-methoxyphenyl)but-2-enamide



3an

Colorless oil, 45.7 mg, 91%, 96% *ee*, $[\alpha]^{25}_{D}$ = +128.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.03 – 7.97 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.64 – 7.57 (m, 1H), 7.53 – 7.46 (m, 2H), 7.28 – 7.21 (m, 2H), 6.97 – 6.85 (m, 4H), 5.71 – 5.61 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.83 (s, 3H), 3.24 – 3.14 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.04 – 2.94 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 165.7, 162.7 (d, *J* = 246.5 Hz), 161.5, 156.5, 143.1, 133.5, 133.2 (d, *J* = 3.4 Hz), 131.5, 129.2, 128.7 (d, *J* = 8.0 Hz), 127.9, 125.0, 122.9, 121.1, 115.4 (d, *J* = 21.6 Hz), 114.3, 78.7, 55.5, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –113.6. IR (film) ν_{max} 2961, 1820, 1671, 1653, 1601, 1508, 1296, 1235, 1019, 833, 765. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}FN_2O_4^+$ $[M+H]^+$: 501.2184, found: 501.2184. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.4 min, t_{minor} = 11.4 min).

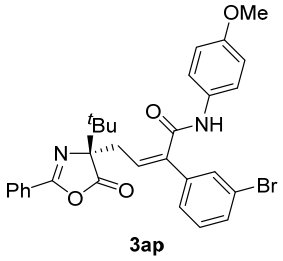
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-2-(4-chlorophenyl)-N-(4-methoxyphenyl)but-2-enamide



3ao

Colorless oil, 46.9 mg, 91%, 97% *ee*, $[\alpha]^{25}_D$ = +88.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.03 – 7.96 (m, 2H), 7.80 – 7.71 (m, 2H), 7.64 – 7.55 (m, 1H), 7.54 – 7.46 (m, 2H), 7.21 – 7.13 (m, 4H), 6.97 – 6.90 (m, 2H), 5.74 – 5.66 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.23 – 3.13 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.04 – 2.94 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 165.4, 161.5, 156.5, 143.0, 135.6, 134.2, 133.5, 131.5, 129.3, 128.6, 128.2, 127.8, 125.0, 123.5, 121.1, 114.3, 78.7, 55.5, 37.8, 32.8, 25.0. IR (film) ν_{max} 2966, 1820, 1670, 1653, 1540, 1510, 1492, 1246, 1018, 830, 765. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}ClN_2O_4^+$ $[M+H]^+$: 517.1889, found: 517.1889. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 85 : 15, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 11.9 min, t_{minor} = 15.9 min).

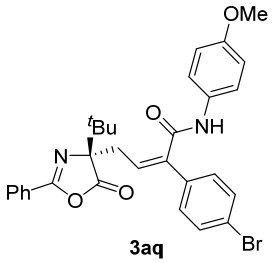
(*S*, *Z*)-2-(3-bromophenyl)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)but-2-enamide



3ap

Colorless oil, 54.5 mg, 97%, 97% *ee*, $[\alpha]^{25}_D$ = +80.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.23 (s, 1H), 8.04 – 7.98 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.79 – 7.73 (d, *J* = 9.0 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.54 – 7.48 (m, 2H), 7.40 – 7.36 (t, *J* = 1.5 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.22 – 7.17 (m, 1H), 7.09 – 7.04 (t, *J* = 8.0 Hz, 1H), 6.97 – 6.91 (m, 2H), 5.73 – 5.67 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.83 (s, 3H), 3.23 – 3.14 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.03 – 2.95 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.9, 165.2, 161.6, 156.5, 142.9, 139.2, 133.5, 131.4, 131.2, 130.0, 129.9, 129.3, 127.9, 125.6, 124.9, 124.3, 122.5, 121.1, 114.3, 78.6, 55.5, 37.8, 32.8, 25.0. IR (film) ν_{max} 3061, 2960, 1820, 1671, 1653, 1539, 1510, 1245, 1019, 830, 692. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}BrN_2O_4^+$ $[M+H]^+$: 561.1383, found: 561.1381. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 7.7 min, t_{minor} = 16.0 min).

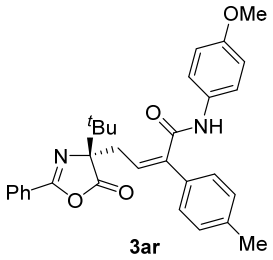
(*S*, *Z*)-2-(4-bromophenyl)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)but-2-enamide



3aq

Colorless oil, 53.8 mg, 96%, 97% *ee*, $[\alpha]^{25}_{D}$ = +80.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.13 (s, 1H), 7.94 – 7.88 (m, 2H), 7.71 – 7.64 (d, *J* = 9.0 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.45 – 7.38 (t, *J* = 7.0 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.07 – 7.03 (m, 2H), 6.88 – 6.83 (m, 2H), 5.67 – 5.58 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.74 (s, 3H), 3.16 – 3.05 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.96 – 2.84 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 165.4, 161.5, 156.5, 143.1, 136.0, 133.5, 131.5, 129.3, 128.5, 127.8, 124.9, 123.5, 122.4, 121.1, 114.3, 78.6, 55.5, 37.8, 32.8, 25.0. IR (film) ν_{max} 2961, 1820, 1671, 1652, 1539, 1510, 1489, 1296, 1245, 1010, 829. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}BrN_2O_4^+$ $[M+H]^+$: 561.1383, found: 561.1381. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 85 : 15, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 12.7 min, t_{minor} = 17.1 min).

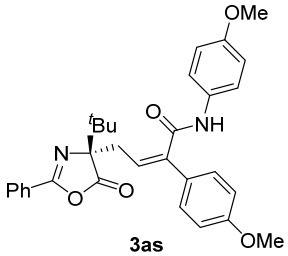
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-(p-tolyl)but-2-enamide



3ar

Colorless oil, 45.8 mg, 92%, 95% *ee*, $[\alpha]^{25}_{D}$ = +120.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.04 – 7.95 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.79 – 7.72 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.45 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.04 – 6.99 (d, *J* = 8.0 Hz, 2H), 6.96 – 6.90 (m, 2H), 5.73 – 5.63 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.82 (s, 3H), 3.24 – 3.13 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.04 – 2.94 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.26 (s, 3H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.1, 161.3, 156.4, 143.9, 138.2, 134.2, 133.3, 131.6, 129.2, 127.9, 126.8, 125.1, 122.2, 121.1, 114.3, 78.8, 55.5, 37.8, 32.7, 25.0, 21.1. IR (film) ν_{max} 2960, 1820, 1671, 1653, 1510, 1246, 1035, 1019, 889, 829. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_2O_4^+$ $[M+H]^+$: 497.2435, found: 497.2434. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.5 min, t_{minor} = 14.6 min).

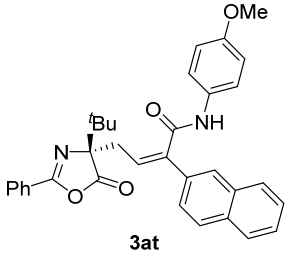
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N,2-bis(4-methoxyphenyl)but-2-enamide



3as

Colorless oil, 43.4 mg, 85%, 96% *ee*, $[\alpha]^{25}_{D}$ = +72.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.04 – 7.96 (m, 2H), 7.80 – 7.71 (m, 2H), 7.64 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 7.23 – 7.19 (m, 2H), 6.96 – 6.91 (m, 2H), 6.76 – 6.71 (m, 2H), 5.69 – 5.58 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.21 – 3.12 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.04 – 2.94 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.2, 161.3, 159.7, 156.4, 143.5, 133.3, 131.6, 129.5, 129.2, 128.1, 127.9, 125.1, 121.2, 121.1, 114.3, 113.8, 78.8, 55.5, 55.3, 37.8, 32.7, 25.0. IR (film) ν_{max} 2959, 1819, 1653, 1603, 1508, 1294, 1246, 1176, 1034, 965, 830. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_2O_5^+$ $[M+H]^+$: 513.2384, found: 513.2385. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OD-H, *n*-hexane/2-propanol = 93 : 7, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 21.3 min, t_{minor} = 27.1 min).

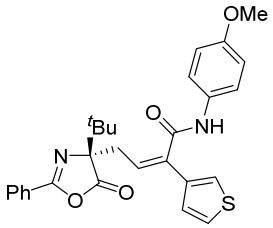
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-(naphthalen-2-yl)but-2-enamide



3at

White solid, 47.5 mg, 89%, Mp: 151 – 153 °C, 96% *ee*, $[\alpha]^{25}_{D}$ = +80.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.04 – 7.98 (m, 2H), 7.82 – 7.78 (m, 2H), 7.75 – 7.69 (m, 2H), 7.69 – 7.64 (m, 2H), 7.59 – 7.54 (m, 1H), 7.50 – 7.45 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.35 (m, 3H), 6.99 – 6.91 (m, 2H), 5.89 – 5.82 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.83 (s, 3H), 3.29 – 3.20 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.11 – 3.02 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.0, 161.4, 156.5, 144.0, 134.3, 133.4, 133.2, 133.0, 131.6, 129.2, 128.3, 128.1, 127.9, 127.5, 126.3, 126.3, 125.1, 124.5, 123.4, 114.3, 78.8, 55.5, 37.8, 32.9, 25.1. IR (film) ν_{max} 2971, 1820, 1670, 1653, 1540, 1510, 1275, 1246, 1171, 1035, 963, 888. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{33}N_2O_4^+$ $[M+H]^+$: 533.2435, found: 533.2433. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 50 : 50, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 10.4 min, t_{minor} = 18.7 min).

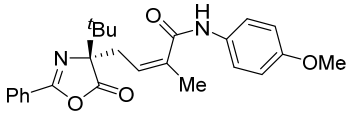
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-(thiophen-3-yl)but-2-enamide



3au

Colorless oil, 45.6 mg, 93%, 93% *ee*, $[\alpha]^{25}_{D}$ = +72.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.07(s, 1H), 8.02 – 7.96 (m, 2H), 7.78 – 7.72 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.47 (m, 2H), 7.31 – 7.28 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.17 – 7.13 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.02 – 6.99 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.96 – 6.92 (m, 2H), 5.79 – 5.71 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.82 (s, 3H), 3.22 – 3.11 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.03 – 2.94 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 165.5, 161.4, 156.4, 138.9, 137.6, 133.4, 131.5, 129.2, 127.9, 125.8, 125.7, 125.0, 123.0, 121.4, 121.2, 114.3, 78.8, 55.5, 37.8, 32.5, 25.0. IR (film) ν_{max} 2965, 1819, 1670, 1653, 1510, 1295, 1246, 1019, 830, 764, 750. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$: 489.1843, found: 489.1842. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 13.9 min, t_{minor} = 18.3 min).

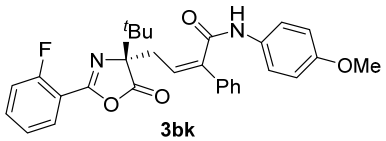
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-methylbut-2-enamide



3av

Colorless oil, 26.7 mg, 64%, 90% *ee*, $[\alpha]^{25}_{D}$ = +304.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.31(s, 1H), 8.04 – 7.96 (m, 2H), 7.79 – 7.71 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.47 (t, *J* = 7.0 Hz, 2H), 6.95 – 6.89 (m, 2H), 5.35 – 5.23 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.82 (s, 3H), 3.13 – 3.03 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.82 – 2.74 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.84 (s, 3H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.9, 166.8, 161.5, 156.2, 140.0, 133.4, 131.9, 129.2, 127.9, 125.1, 122.0, 120.8, 114.2, 78.5, 55.5, 37.6, 32.2, 25.0, 21.1. IR (film) ν_{max} 2959, 1820, 1671, 1648, 1540, 1510, 1298, 1245, 884, 750. HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{29}N_2O_4^+$ $[M+H]^+$: 421.2122, found: 421.2120. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.4 min, t_{minor} = 15.1 min).

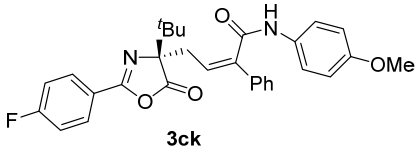
(*S*, *Z*)-4-(4-(tert-butyl)-2-(2-fluorophenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methox-y-phenyl)-2-phenylbut-2-enamide



3bk

White solid, 39.2 mg, 78%, Mp: 90 – 92 °C, 92% *ee*, $[\alpha]^{25}_{D}$ = +136.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.24 (s, 1H), 7.88 – 7.81 (m, 1H), 7.80 – 7.74 (m, 2H), 7.56 – 7.51 (m, 1H), 7.34 – 7.20 (m, 7H), 6.94 – 6.88 (m, 2H), 5.77 – 5.66 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.81 (s, 3H), 3.31 – 3.20 (dd, *J* = 13.5, 11.0 Hz, 1H), 2.98 – 2.89 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.3, 166.0, 161.5 (d, *J* = 260.1 Hz), 157.5 (d, *J* = 6.2 Hz), 156.3, 144.5, 137.1, 134.8 (d, *J* = 9.1 Hz), 131.7, 130.7, 128.5, 128.2, 126.8, 124.8 (d, *J* = 3.8 Hz), 122.2, 121.1 (d, *J* = 2.1 Hz), 117.3 (d, *J* = 21.3 Hz), 114.1, 113.6 (d, *J* = 9.5 Hz), 78.0, 55.5, 37.8, 33.1, 24.9. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –108.7. IR (film) ν_{max} 2965, 1820, 1670, 1653, 1540, 1511, 1496, 1246, 1021, 964, 890. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}FN_2O_4^+$ $[M+H]^+$: 501.2184, found: 501.2181. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 10.8 min, t_{minor} = 22.5 min).

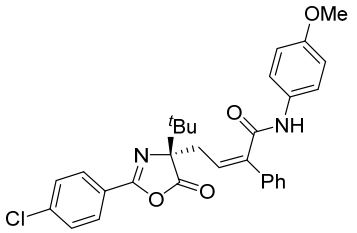
(*S*, *Z*)-4-(4-(tert-butyl)-2-(4-fluorophenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methox-y-phenyl)-2-phenylbut-2-enamide



3ck

Colorless oil, 41.7 mg, 83%, 95% *ee*, $[\alpha]^{25}_{D}$ = +112.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.07 – 7.96 (m, 2H), 7.77 – 7.70 (m, 2H), 7.31 – 7.13 (m, 7H), 6.97 – 6.89 (m, 2H), 5.76 – 5.65 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.22 – 3.12 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.07 – 2.98 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.0, 165.9, 165.8 (d, *J* = 254.0 Hz), 160.4, 156.5, 144.0, 137.0, 131.5, 130.3 (d, *J* = 9.3 Hz), 128.5, 128.3, 126.9, 123.1, 121.3 (d, *J* = 3.1 Hz), 121.1, 116.6 (d, *J* = 22.5 Hz), 114.3, 78.9, 55.5, 37.8, 32.7, 25.0. ^{19}F NMR ($CDCl_3$, 470 MHz): δ –104.0. IR (film) ν_{max} 2966, 1820, 1653, 1602, 1509, 1296, 1276, 1238, 1033, 847, 764, 750. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}FN_2O_4^+$ $[M+H]^+$: 501.2184, found: 501.2181. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.2 min, t_{minor} = 13.4 min).

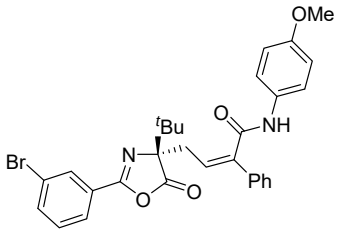
(*S*, *Z*)-4-(4-(tert-butyl)-2-(4-chlorophenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methox-y-phenyl)-2-phenylbut-2-enamide



3dk

White solid, 43.9 mg, 85%, Mp: 58 – 60 °C, 93% *ee*, $[\alpha]^{25}_{D}$ = +104.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.97 – 7.90 (d, *J* = 7.5 Hz, 2H), 7.76 – 7.69 (d, *J* = 9.0 Hz, 2H), 7.51 – 7.44 (d, *J* = 9.0 Hz, 2H), 7.31 – 7.19 (m, 5H), 6.97 – 6.89 (d, *J* = 8.5 Hz, 2H), 5.75 – 5.66 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.23 – 3.13 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.08 – 2.99 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.9, 165.9, 160.5, 156.5, 144.0, 139.8, 137.0, 131.4, 129.6, 129.2, 128.5, 128.3, 126.9, 123.5, 123.0, 121.1, 114.3, 79.0, 55.5, 37.9, 32.7, 25.0. IR (film) ν_{max} 2966, 1820, 1650, 1598, 1312, 1244, 1174, 1091, 1021, 964, 888. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}ClN_2O_4^+$ $[M+H]^+$: 517.1889, found: 517.1889. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 11.0 min, t_{minor} = 20.3 min).

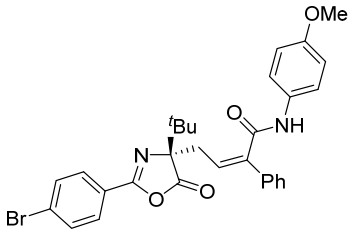
(*S*, *Z*)-4-(2-(3-bromophenyl)-4-(tert-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methox-y-phenyl)-2-phenylbut-2-enamide



3ek

Colorless oil, 41.6 mg, 74%, 92% *ee*, $[\alpha]^{25}_{D}$ = +72.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.19 – 8.14 (t, *J* = 2.0 Hz, 1H), 7.97 – 7.88 (m, 1H), 7.75 – 7.68 (m, 3H), 7.40 – 7.35 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.22 (m, 5H), 6.96 – 6.91 (m, 2H), 5.75 – 5.65 (dd, *J* = 9.5, 8.0 Hz, 1H), 3.82 (s, 3H), 3.22 – 3.12 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.10 – 3.01(dd, *J* = 14.0, 8.0 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.9, 165.9, 156.0, 156.5, 144.0, 136.9, 136.3, 131.3, 130.9, 130.7, 128.6, 128.4, 127.0, 126.9, 126.3, 123.2, 122.9, 121.3, 114.3, 79.1, 55.5, 37.9, 32.6, 25.0. IR (film) ν_{max} 2965, 1824, 1670, 1653, 1559, 1509, 1300, 1275, 1261, 1035, 892. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}BrN_2O_4^+$ $[M+H]^+$: 561.1383, found: 561.1380. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 10.7 min, t_{minor} = 19.8 min).

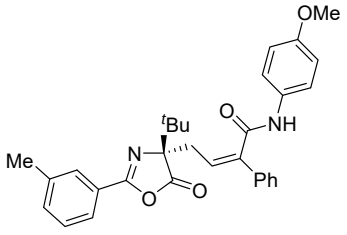
(*S*, *Z*)-4-(2-(4-bromophenyl)-4-(tert-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methox-y-phenyl)-2-phenylbut-2-enamide



3fk

White solid, 41.6 mg, 74%, Mp: 64 – 66 °C, 94% *ee*, $[\alpha]^{25}_{D}$ = +96.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.89 – 7.82 (d, *J* = 8.5 Hz, 2H), 7.75 – 7.68 (d, *J* = 9.0 Hz, 2H), 7.66 – 7.61 (d, *J* = 9.0 Hz, 2H), 7.30 – 7.19 (m, 5H), 6.96 – 6.89 (d, *J* = 9.0 Hz, 2H), 5.73 – 5.67 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.22 – 3.13 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.07 – 2.99 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.9, 165.9, 160.6, 156.5, 144.0, 137.0, 132.6, 131.4, 129.3, 128.5, 128.4, 128.3, 126.9, 124.0, 123.0, 121.1, 114.3, 79.0, 55.5, 37.9, 32.6, 25.0. IR (film) ν_{max} 2963, 1820, 1671, 1648, 1593, 1510, 1399, 1245, 1068, 1009, 831. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{30}BrN_2O_4^+$ $[M+H]^+$: 561.1383, found: 561.1379. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.5 min, t_{minor} = 14.6 min).

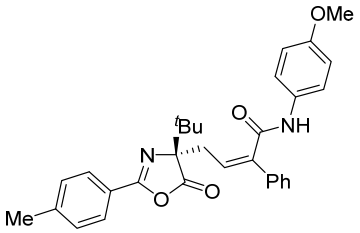
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-(m-tolyl)-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3gk

Colorless oil, 44.5 mg, 90%, 91% *ee*, $[\alpha]^{25}_{D}$ = +96.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (s, 1H), 7.85 – 7.71 (m, 4H), 7.43 – 7.32 (m, 2H), 7.32 – 7.17 (m, 5H), 6.98 – 6.88 (m, 2H), 5.76 – 5.67 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.24 – 3.13 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.06 – 2.97 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.38 (s, 3H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.0, 161.5, 156.4, 144.0, 139.1, 137.1, 134.2, 131.6, 129.1, 128.5, 128.4, 128.2, 126.9, 125.0, 125.0, 123.1, 121.1, 114.3, 78.7, 55.5, 37.8, 32.7, 25.0, 21.4. IR (film) ν_{max} 2962, 1824, 1699, 1684, 1653, 1509, 1473, 1457, 1275, 906, 764. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_2O_4^+$ $[M+H]^+$: 497.2435, found: 497.2433. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 11.6 min, t_{minor} = 22.4 min).

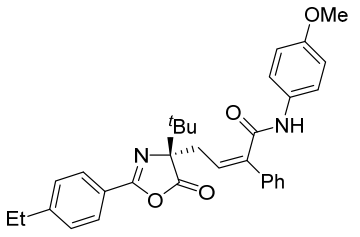
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-(p-tolyl)-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3hk

Colorless oil, 43.0 mg, 87%, 95% *ee*, $[\alpha]^{25}_{D}$ = +136.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 1H), 7.91 – 7.85 (d, *J* = 8.5 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.32 – 7.26 (m, 4H), 7.23 – 7.18 (m, 3H), 6.96 – 6.90 (m, 2H), 5.75 – 5.67 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.22 – 3.13 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.03 – 2.95 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.41 (s, 3H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.0, 161.5, 156.4, 144.3, 144.0, 137.2, 131.7, 129.9, 128.4, 128.2, 127.9, 126.9, 123.1, 122.3, 121.1, 114.3, 78.6, 55.5, 37.8, 32.7, 25.0, 21.8. IR (film) ν_{max} 2961, 1820, 1670, 1653, 1540, 1533, 1260, 968, 830, 724. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{33}N_2O_4^+$ $[M+H]^+$: 497.2435, found: 497.2433. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.3 min, t_{minor} = 17.0 min).

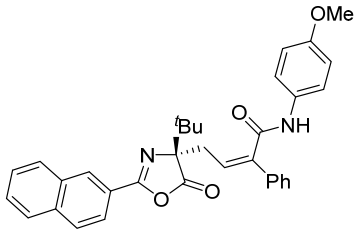
(*S*, *Z*)-4-(4-(tert-butyl)-2-(4-ethylphenyl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methox-yphenyl)-2-phenylbut-2-enamide



3ik

Colorless oil, 38.9 mg, 76%, 93% *ee*, $[\alpha]^{25}_{D}$ = +128.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (s, 1H), 7.94 – 7.88 (d, *J* = 8.5 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.35 – 7.18 (m, 7H), 6.96 – 6.90 (m, 2H), 5.75 – 5.68 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.83 (s, 3H), 3.23 – 3.13 (dd, *J* = 13.5, 10.0 Hz, 1H), 3.03 – 2.95 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.75 – 2.66 (q, *J* = 7.5 Hz, 2H), 1.28 – 1.22 (t, *J* = 7.5 Hz, 3H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.0, 161.5, 156.4, 150.4, 144.0, 137.2, 131.7, 128.7, 128.4, 128.2, 128.0, 126.9, 123.1, 122.4, 121.1, 114.3, 78.6, 55.5, 37.8, 32.8, 29.0, 25.0, 15.2. IR (film) ν_{max} 2965, 1820, 1699, 1652, 1540, 1473, 966, 830, 735. HRMS (ESI, *m*/z) calcd for $C_{32}H_{35}N_2O_4^+$ $[M+H]^+$: 511.2591, found: 511.2590. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.2 min, t_{minor} = 14.5 min).

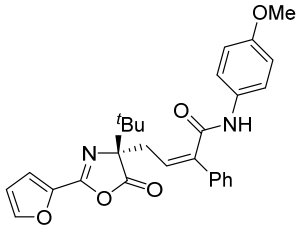
(*S*, *Z*)-4-(4-(tert-butyl)-2-(naphthalen-2-yl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3jk

Colorless oil, 44.2 mg, 83%, 92% *ee*, $[\alpha]^{25}_{D}$ = +104.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.52 – 8.47 (d, *J* = 1.5 Hz, 1H), 8.09 – 8.04 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.95 – 7.85 (m, 3H), 7.83 – 7.77 (m, 2H), 7.64 – 7.54 (m, 2H), 7.30 – 7.25 (m, 2H), 7.19 – 7.13 (m, 3H), 6.99 – 6.93 (m, 2H), 5.82 – 5.70 (dd, *J* =9.5, 7.5 Hz, 1H), 3.83 (s, 3H), 3.29 – 3.18 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.10 – 3.01 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.14 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2, 166.0, 161.5, 156.5, 144.1, 137.1, 135.5, 132.6, 131.6, 129.9, 129.3, 129.2, 128.8, 128.5, 128.2, 128.0, 127.4, 126.9, 123.1, 122.9, 122.1, 121.2, 114.3, 78.9, 55.5, 37.9, 32.8, 25.1. IR (film) ν_{max} 2967, 1824, 1717, 1688, 1652, 1034, 1014, 888, 831. HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{33}N_2O_4^+$ $[M+H]^+$: 533.2435, found: 533.2435. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.7 min, t_{minor} = 19.1 min).

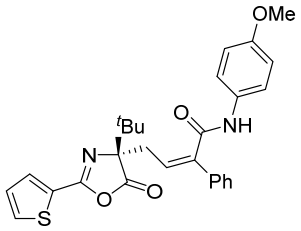
(*S*, *Z*)-4-(4-(tert-butyl)-2-(furan-2-yl)-5-oxo-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3kk

Colorless oil, 37.8 mg, 80%, 92% *ee*, $[\alpha]^{25}_{D}$ = +184.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.30 (s, 1H), 7.85 – 7.79 (d, *J* = 9.0 Hz, 2H), 7.68 – 7.64 (d, *J* = 1.5 Hz, 1H), 7.33 – 7.21 (m, 5H), 7.14 – 7.10 (d, *J* = 3.5 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.61 – 6.56 (dd, *J* = 3.5, 1.5 Hz, 1H), 5.74 – 5.66 (dd, *J* =10.5, 7.0 Hz, 1H), 3.82 (s, 3H), 3.20 – 3.12 (dd, *J* = 13.5, 10.5 Hz, 1H), 3.00 – 2.93 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.0, 165.8, 156.3, 153.2, 147.6, 144.6, 140.1, 137.1, 131.9, 128.5, 128.2, 126.9, 122.3, 120.9, 117.9, 114.2, 112.4, 78.1, 55.5, 37.8, 32.9, 24.9. IR (film) ν_{max} 3127, 2967, 1823, 1666, 1601, 1540, 1510, 1245, 1175, 1034. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{29}N_2O_5^+$ $[M+H]^+$: 473.2071, found: 473.2072. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 70 : 30, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.9 min, t_{minor} = 15.9 min).

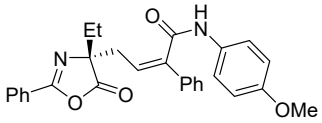
(*S*, *Z*)-4-(4-(tert-butyl)-5-oxo-2-(thiophen-2-yl)-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3lk

Colorless oil, 43.9 mg, 90%, 93% *ee*, $[\alpha]^{25}_{D}$ = +152.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.28 (s, 1H), 7.83 – 7.77 (m, 2H), 7.72 – 7.68 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 7.16 – 7.13 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.96 – 6.90 (m, 2H), 5.75 – 5.67 (dd, *J* =10.5, 6.5 Hz, 1H), 3.82 (s, 3H), 3.23 – 3.14 (dd, *J* = 14.0, 10.5 Hz, 1H), 2.99 – 2.91 (dd, *J* = 14.0, 6.5 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.3, 165.9, 157.3, 156.3, 144.5, 137.2, 132.7, 132.4, 131.8, 128.6, 128.4, 128.2, 127.5, 126.9, 122.6, 121.0, 114.2, 78.5, 55.5, 37.9, 33.0, 25.0. IR (film) ν_{max} 2960, 1819, 1670, 1646, 1539, 1244, 1034, 956, 830, 750. HRMS (ESI, *m*/z) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$: 489.1843, found: 489.1845. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 15.9 min, t_{minor} = 31.0 min).

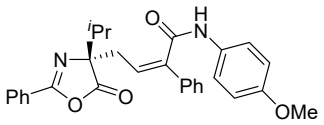
(*R*, *Z*)-4-(4-ethyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3mk

Colorless oil, 28.3 mg, 62%, 89% *ee*, $[\alpha]^{25}_{D}$ = +136 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.03 – 7.96 (m, 2H), 7.71 – 7.64 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.22 (m, 3H), 6.95 – 6.87 (m, 2H), 5.87 – 5.80 (dd, *J* =9.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.18 – 3.08 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.00 – 2.91 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.07 – 1.98 (m, 2H), 0.98 – 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.7, 165.9, 161.5, 156.5, 143.6, 136.9, 133.4, 131.4, 129.1, 128.6, 128.4, 128.0, 127.0, 125.1, 123.3, 121.3, 114.3, 74.0, 55.6, 37.3, 31.1, 8.2. IR (film) ν_{max} 2925, 1818, 1652, 1510, 1451, 1244, 1036, 1019, 830, 696. HRMS (ESI, *m*/z) calcd for $C_{28}H_{27}N_2O_4^+$ $[M+H]^+$: 455.1965, found: 455.1968. The *ee* value was determined by the chiral HPLC analysis (CHIRALPAK IC, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 18.6 min, t_{minor} = 21.6 min).

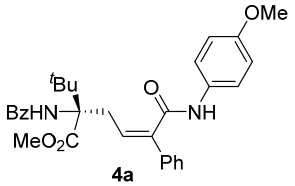
(*S*, *Z*)-4-(4-isopropyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide



3nk

Colorless oil, 35.5 mg, 76%, 91% *ee*, $[\alpha]^{25}_D$ = +128 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.05 – 7.94 (m, 2H), 7.78 – 7.67 (m, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 6.96 – 6.90 (m, 2H), 5.82 – 5.75 (dd, *J* =9.5, 7.5 Hz, 1H), 3.82 (s, 3H), 3.25 – 3.17 (dd, *J* = 14.0, 9.5 Hz, 1H), 2.96 – 2.89 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.29 – 2.19 (m, 1H), 1.13 – 1.07 (d, *J* = 7.0 Hz, 3H), 1.03 – 0.96 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.8, 165.9, 161.6, 156.5, 143.8, 137.0, 133.4, 131.5, 129.1, 128.5, 128.3, 128.0, 126.9, 125.1, 123.1, 121.2, 114.3, 55.5, 35.5, 17.2, 17.0. IR (film) ν_{max} 2924, 1819, 1650, 1511, 1294, 1245, 1037, 738, 698. HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{29}N_2O_4^+$ $[M+H]^+$: 469.2122, found: 469.2123. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 14.6 min, t_{minor} = 19.0 min).

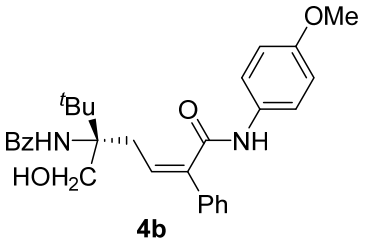
methyl (*S*, *Z*)-2-benzamido-2-(tert-butyl)-6-((4-methoxyphenyl)amino)-6-oxo-5-phenylhex-4-enoate



4a

Colorless oil, 46.5 mg, 90%, 95% *ee*, $[\alpha]^{25}_D$ = +56.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.66 (s, 1H), 7.83 – 7.77 (m, 4H), 7.61 (s, 1H), 7.55 – 7.49 (m, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.34 (m, 2H), 7.26 – 7.18 (m, 3H), 6.94 – 6.89 (m, 2H), 5.64 – 5.58 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.09 – 3.99 (dd, *J* = 16.5, 9.5 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.27 – 3.18 (dd, *J* = 16.5, 3.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 167.3, 166.6, 156.2, 141.2, 137.8, 135.2, 132.2, 131.9, 128.8, 128.4, 127.8, 126.9, 126.6, 125.9, 121.4, 114.2, 71.3, 55.5, 53.3, 40.4, 30.2, 26.8. IR (film) ν_{max} 2957, 1724, 1655, 1602, 1511, 1275, 1235, 1179, 829, 764, 750. HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{35}N_2O_5^+$ $[M+H]^+$: 515.2540, found: 515.2538. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 9.2 min, t_{minor} = 13.0 min).

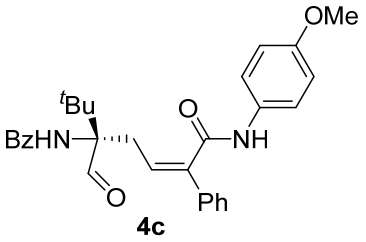
(*S*, *Z*)-N-(3-(hydroxymethyl)-7-((4-methoxyphenyl)amino)-2,2-dimethyl-7-oxo-6-phenyl-hept-5-en-3-yl)benzamide



4b

Colorless oil, 45.4 mg, 93%, 95% *ee*, $[\alpha]^{25}_{D}$ = +96.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.84 – 7.78 (m, 2H), 7.74 (s, 1H), 7.43 – 7.28 (m, 5H), 7.24 – 7.15 (m, 5H), 6.81 – 6.74 (m, 2H), 6.36 – 6.29 (dd, *J* = 10.0, 7.5 Hz, 1H), 4.94 (s, 1H), 4.41 – 4.32 (d, *J* = 12.5 Hz, 1H), 3.93 – 3.83 (d, *J* = 12.5 Hz, 1H), 3.71 (s, 3H), 3.26 – 3.16 (dd, *J* = 14.0, 10.0 Hz, 1H), 2.43 – 2.34 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.1, 167.1, 156.7, 139.1, 137.8, 135.4, 135.3, 131.4, 130.8, 128.8, 128.5, 128.2, 127.5, 127.3, 121.7, 114.2, 67.6, 66.5, 55.5, 39.8, 35.5, 26.5. IR (film) ν_{max} 2960, 1734, 1700, 1653, 1647, 1533, 1521, 1457, 1275, 1261, 764, 750. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{35}N_2O_4^+$ $[M+H]^+$: 487.2591, found: 487.2590. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 8.6 min, t_{minor} = 13.9 min).

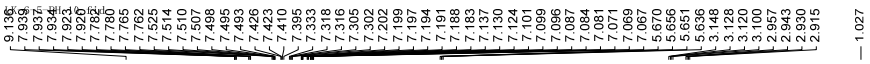
(*S*, *Z*)-N-(3-formyl-7-((4-methoxyphenyl)amino)-2,2-dimethyl-7-oxo-6-phenylhept-5-en-3-yl)benzamide

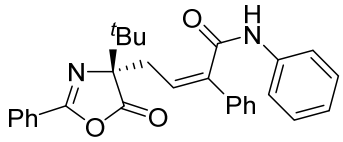


4c

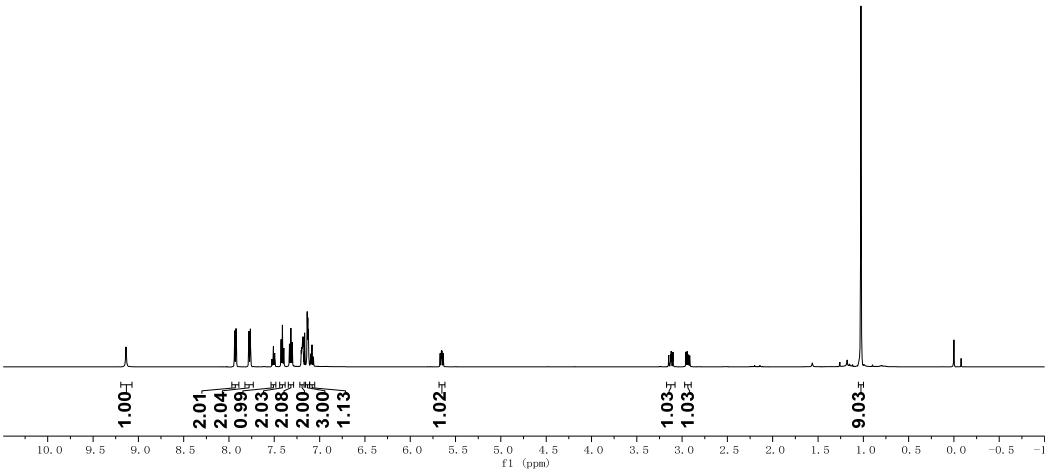
Colorless oil, 36.3 mg, 75%, 95% *ee*, $[\alpha]^{25}_{D}$ = +72.0 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.88 (s, 1H), 8.37 (s, 1H), 7.83 – 7.76 (m, 2H), 7.59 – 7.46 (m, 4H), 7.44 – 7.38 (t, *J* = 7.0 Hz, 2H), 7.25 – 7.20 (m, 5H), 6.90 – 6.85 (m, 2H), 5.90 – 5.81 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.80 (s, 3H), 3.60 – 3.49 (dd, *J* = 14.5, 10.0 Hz, 1H), 3.17 – 3.07 (dd, *J* = 14.5, 5.5 Hz, 1H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 200.3, 168.0, 166.7, 156.5, 140.7, 137.4, 134.0, 131.9, 131.2, 129.2, 128.7, 128.6, 128.1, 127.2, 127.0, 121.7, 114.2, 70.9, 55.5, 39.4, 29.8, 26.3. IR (film) ν_{max} 2967, 1717, 1653, 1602, 1577, 1511, 1489, 1245, 1178, 1033, 830, 764, 750. HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{33}N_2O_4^+$ $[M+H]^+$: 485.2435, found: 485.2433. The *ee* value was determined by the chiral HPLC analysis (CHIRALCEL OX-H, *n*-hexane/2-propanol = 80 : 20, *v* = 1.0 mL/min, λ = 254.0 nm; t_{major} = 12.8 min, t_{minor} = 25.3 min).

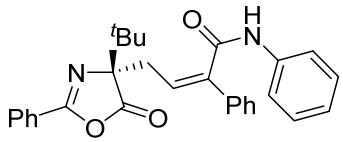
NMR Spectra of Products



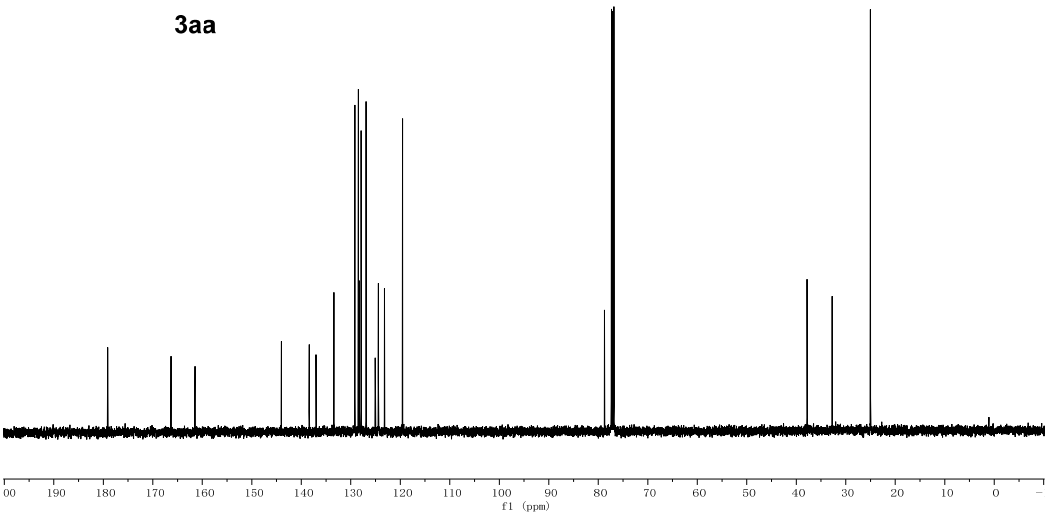


3aa

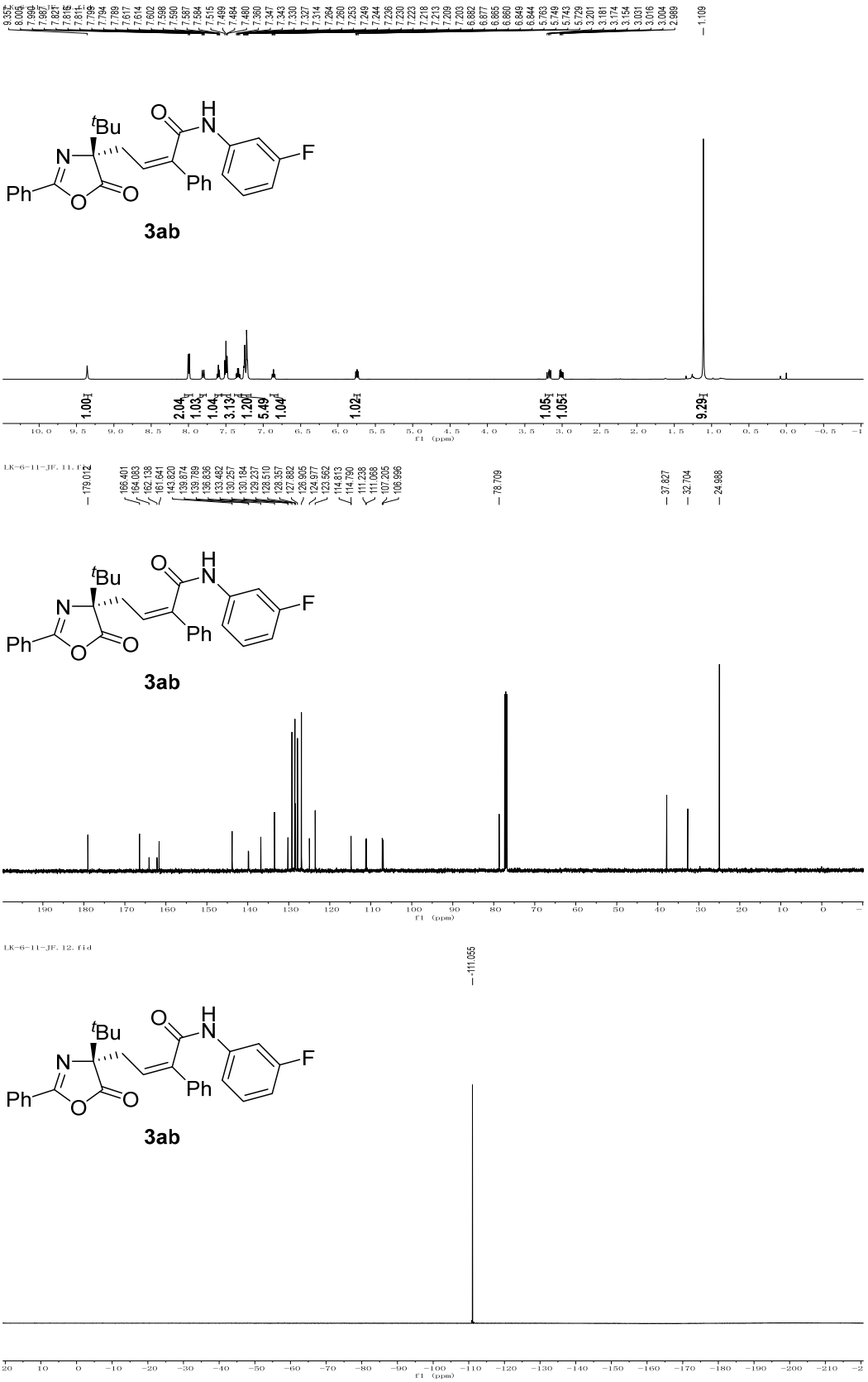




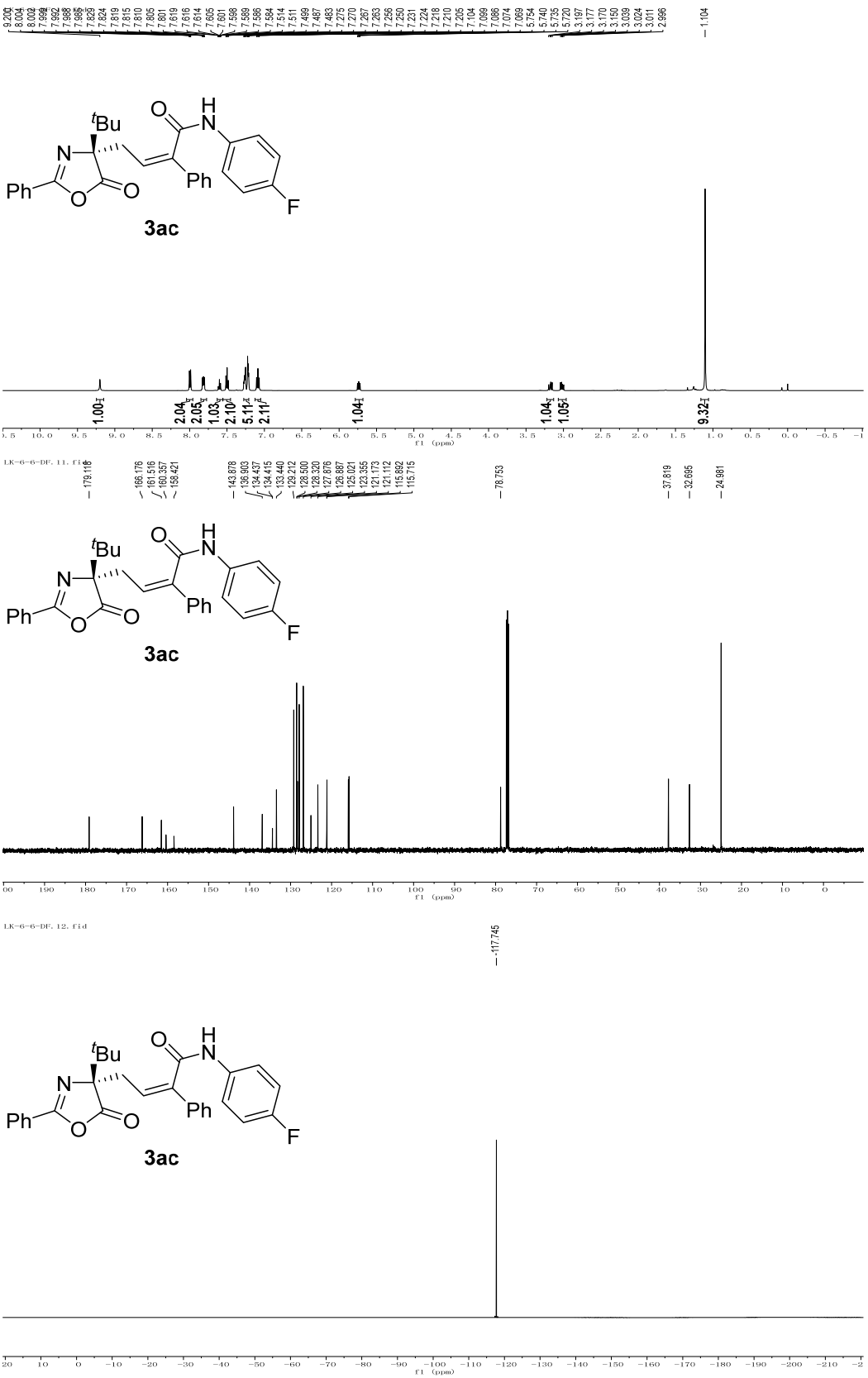
3aa



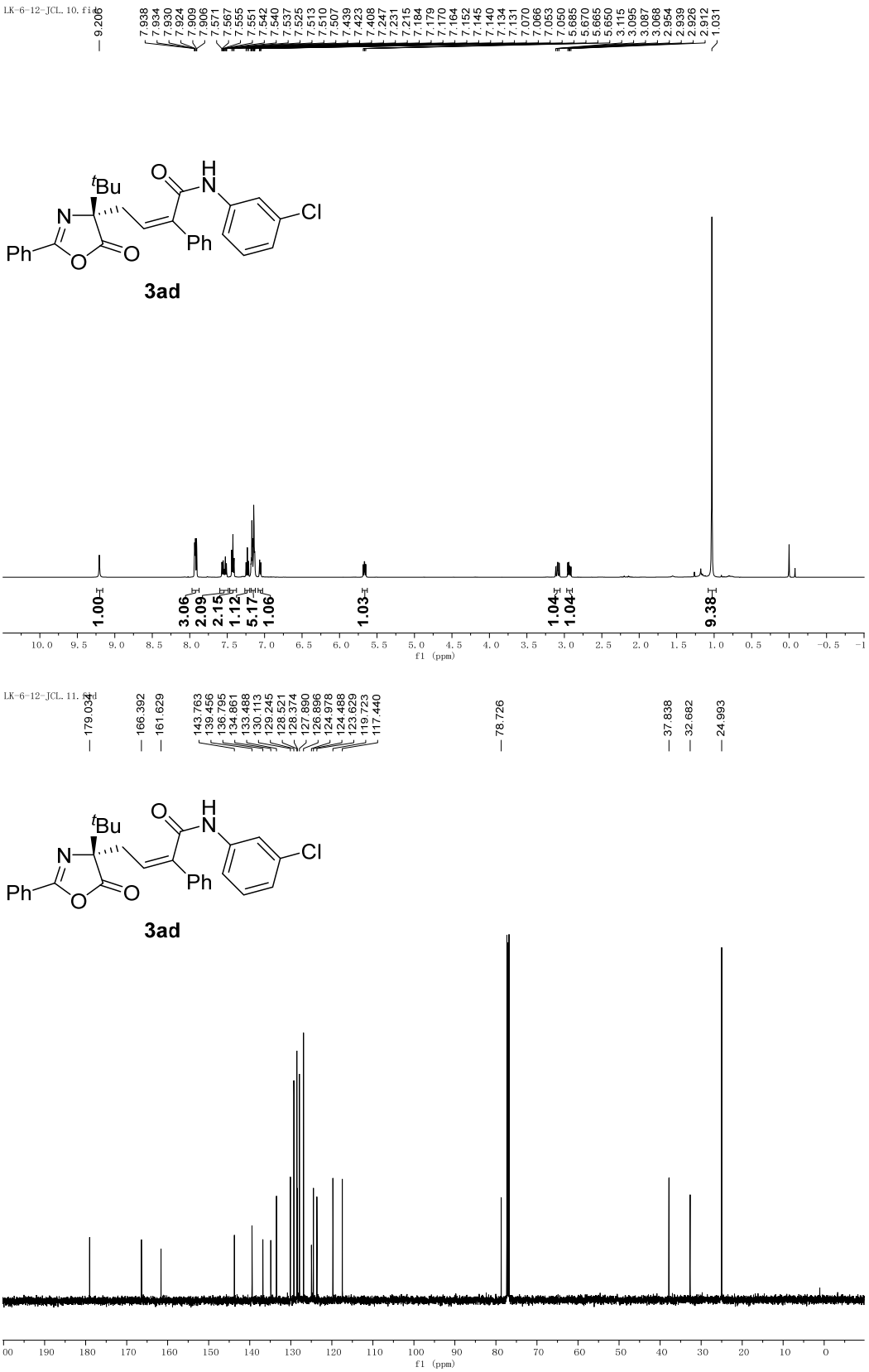
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3aa**



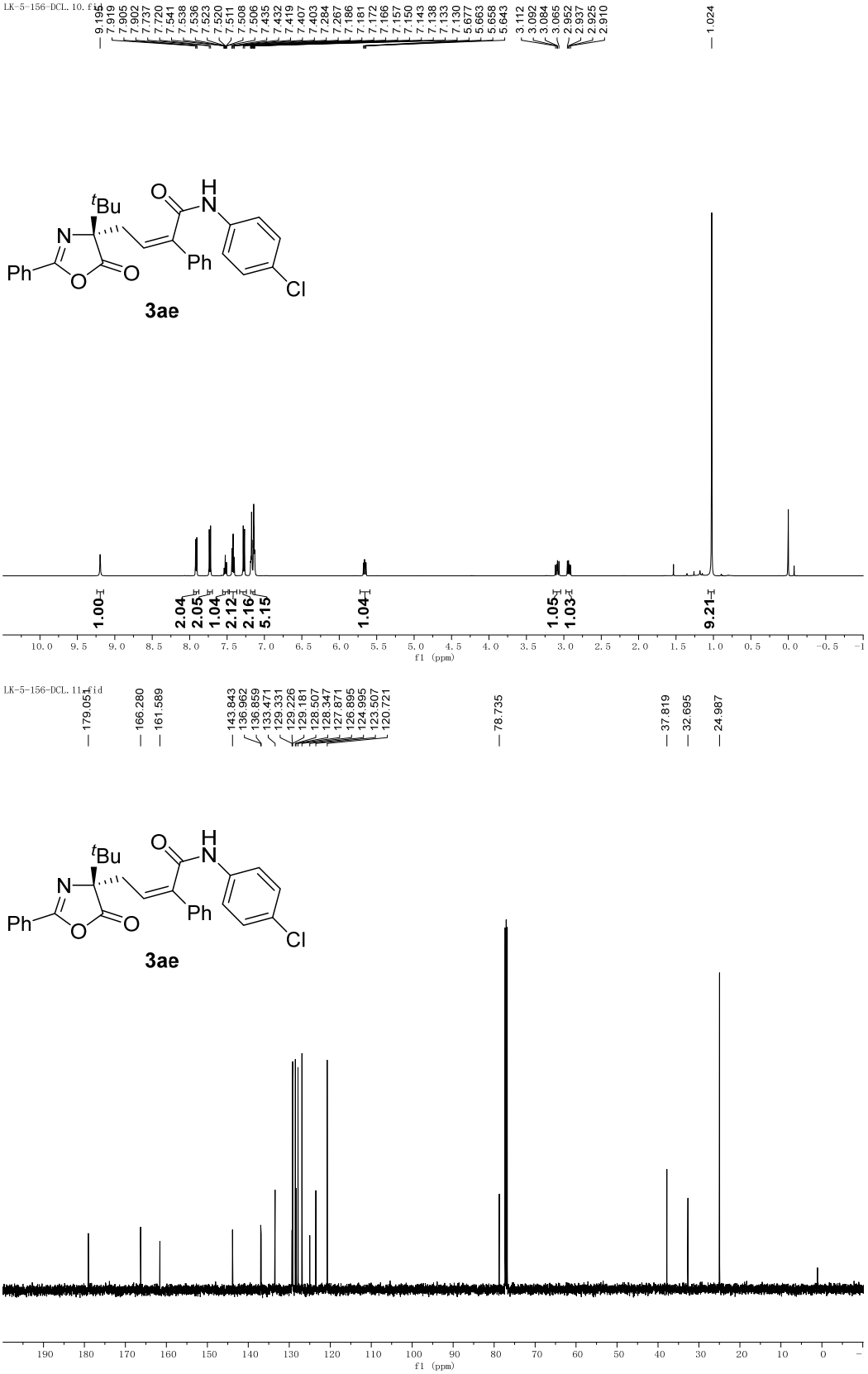
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra of **3ab**



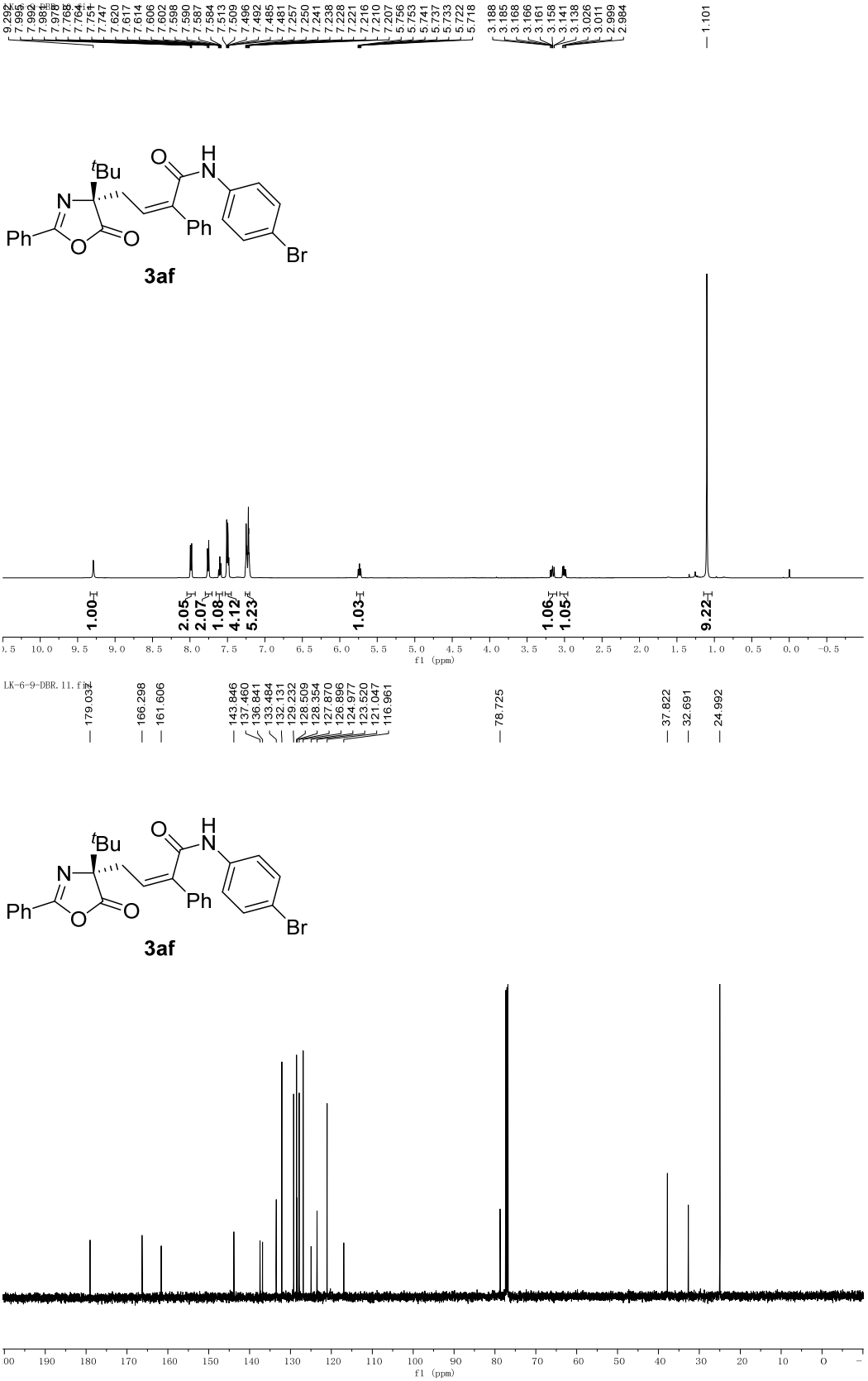
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra of **3ac**



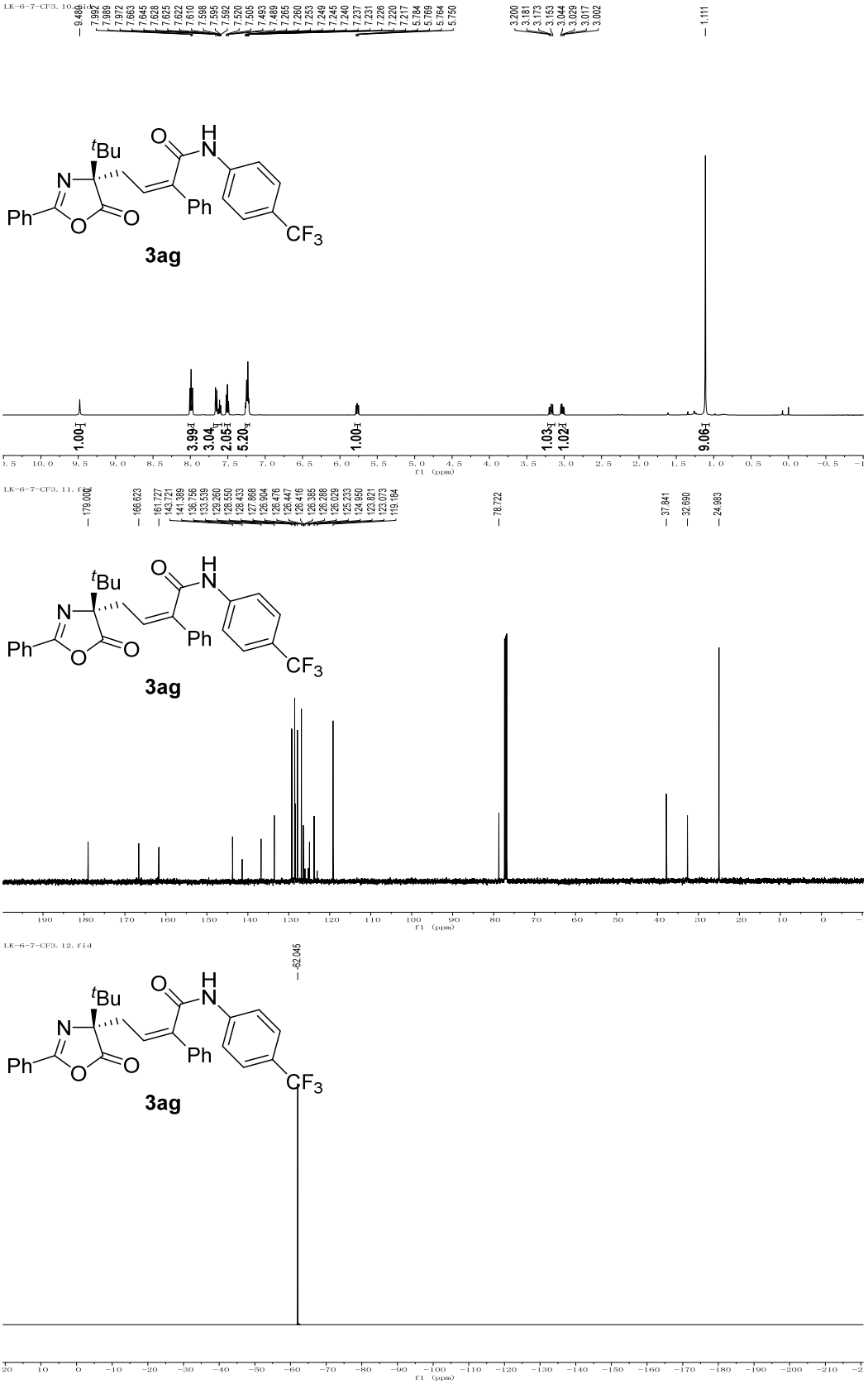
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ad**



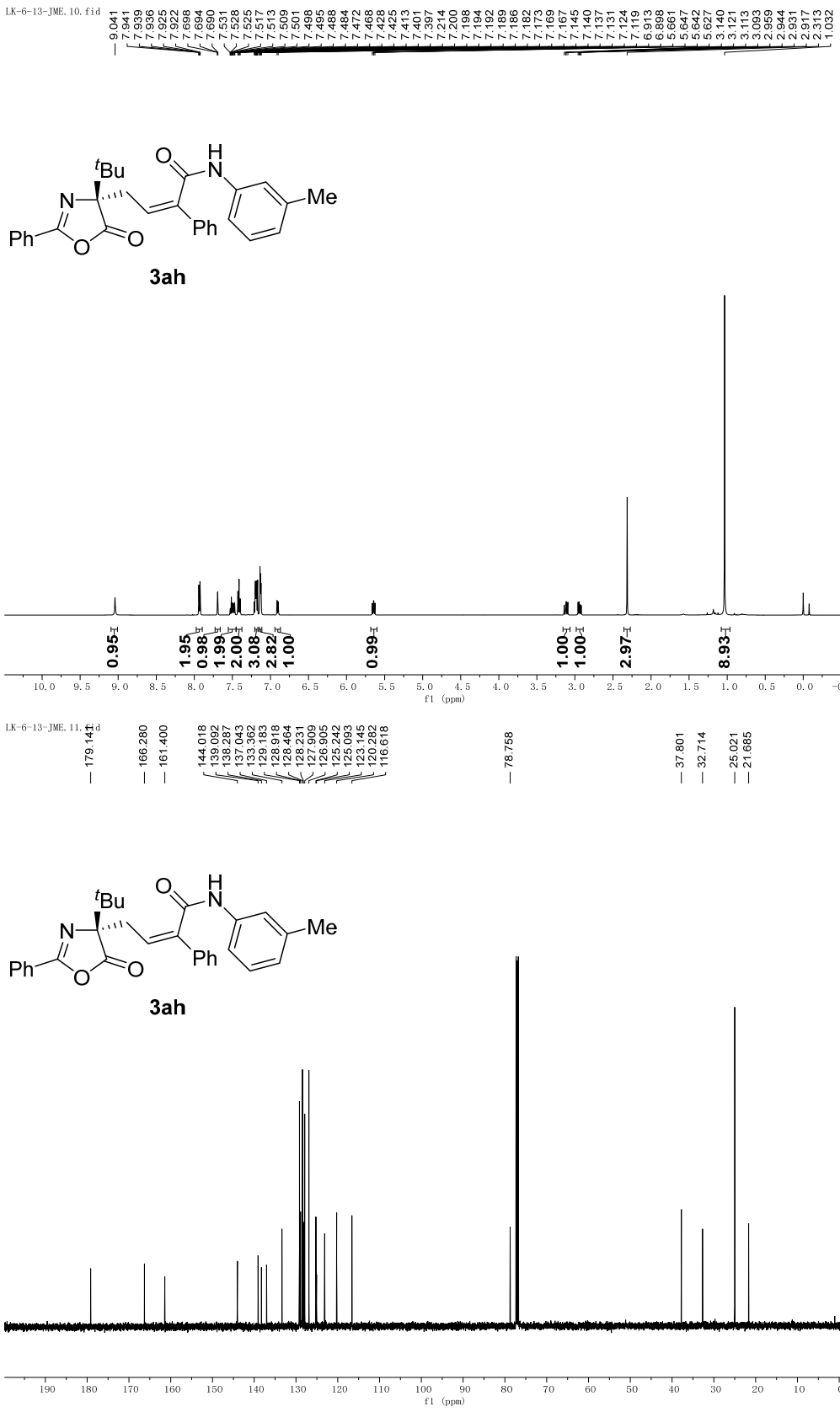
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ae**



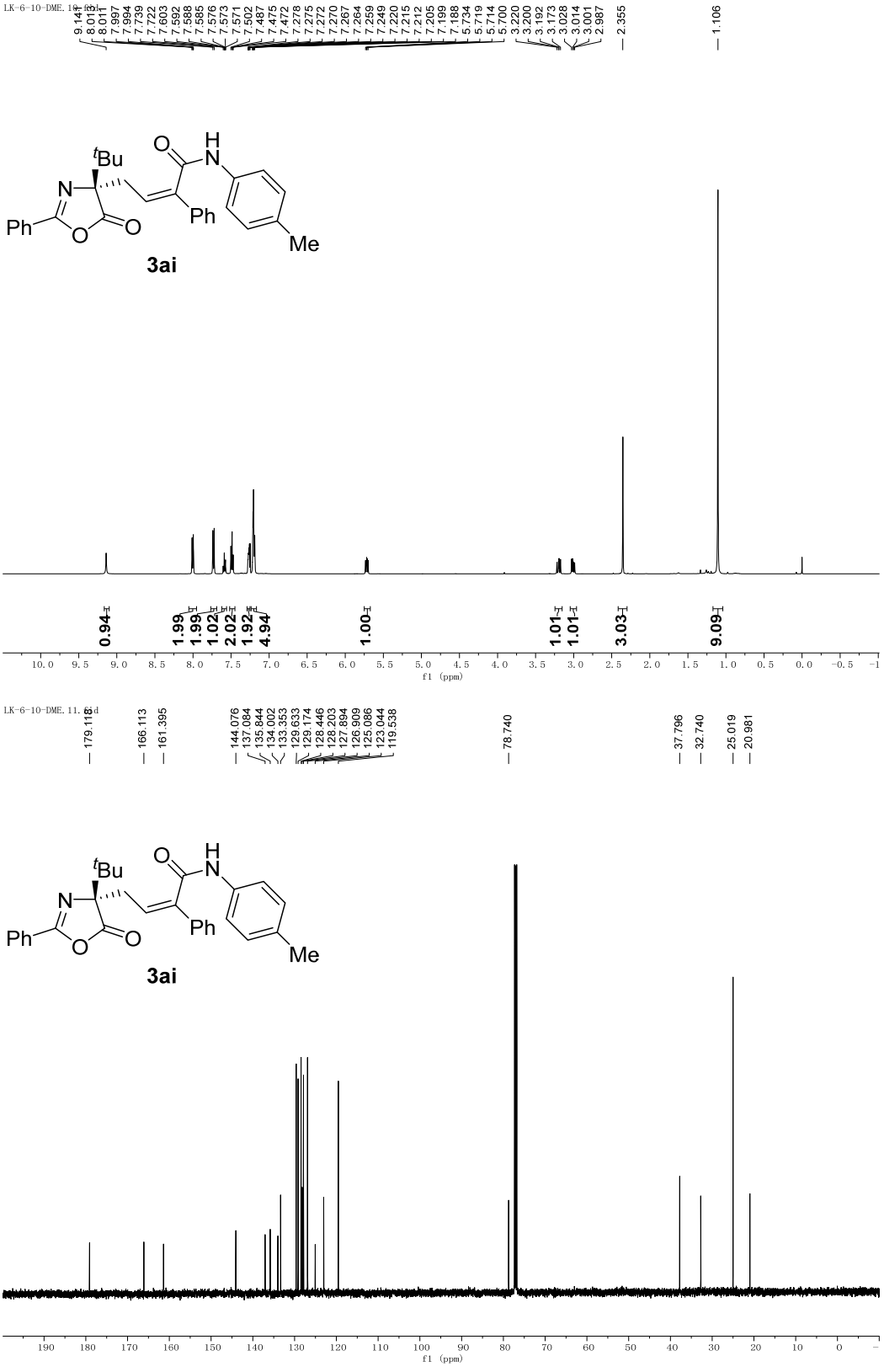
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3af**



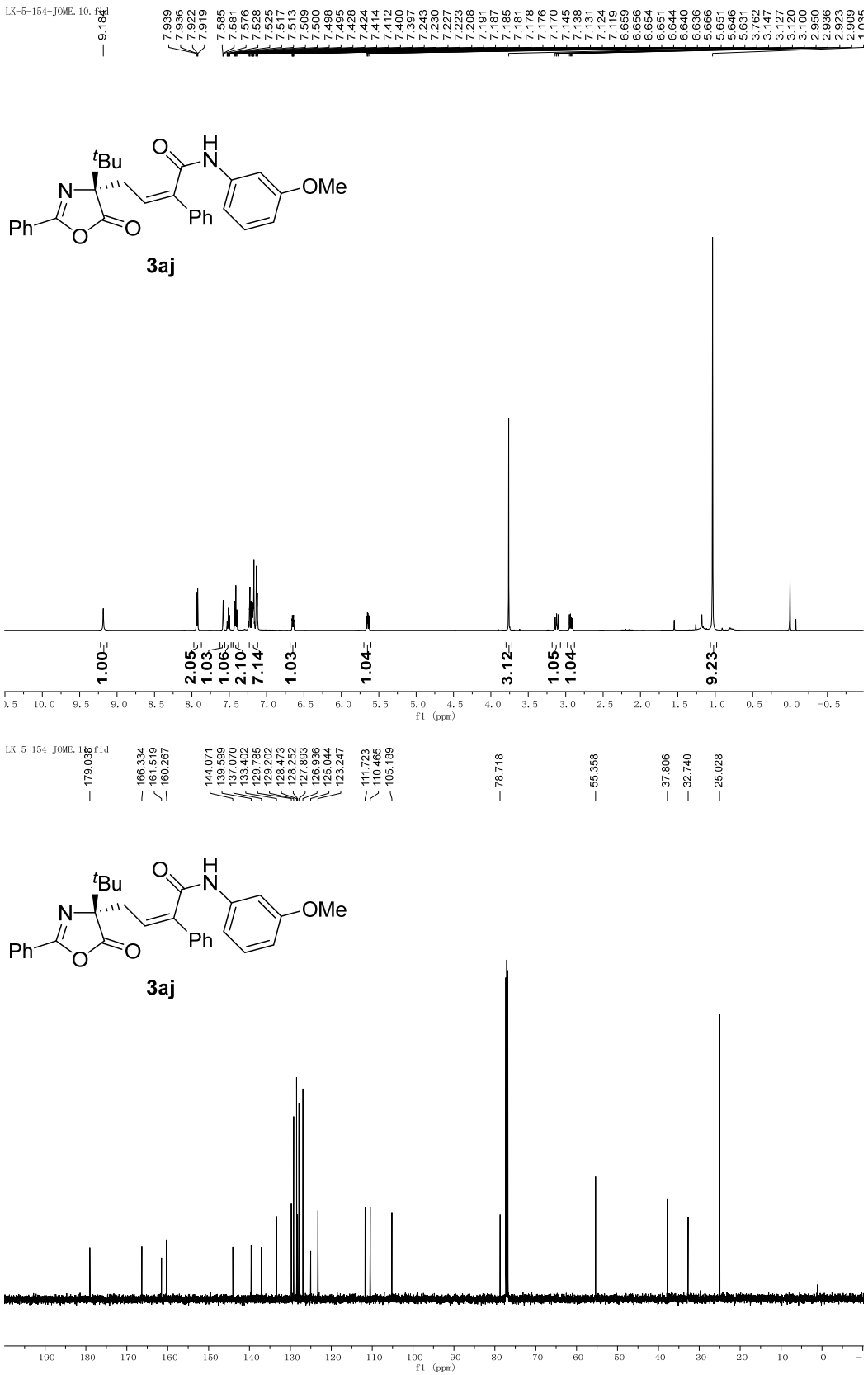
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra of **3ag**



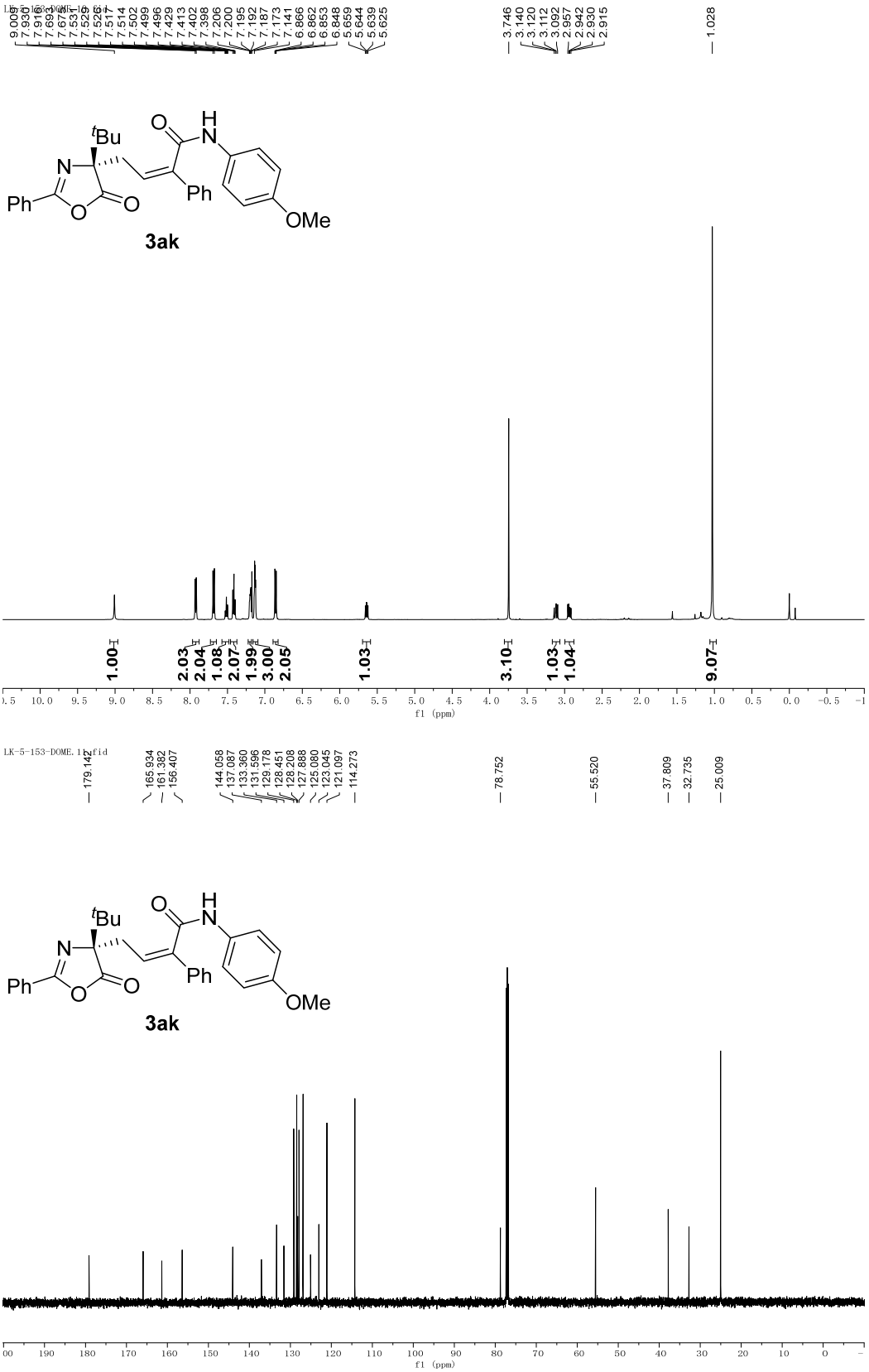
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ah**



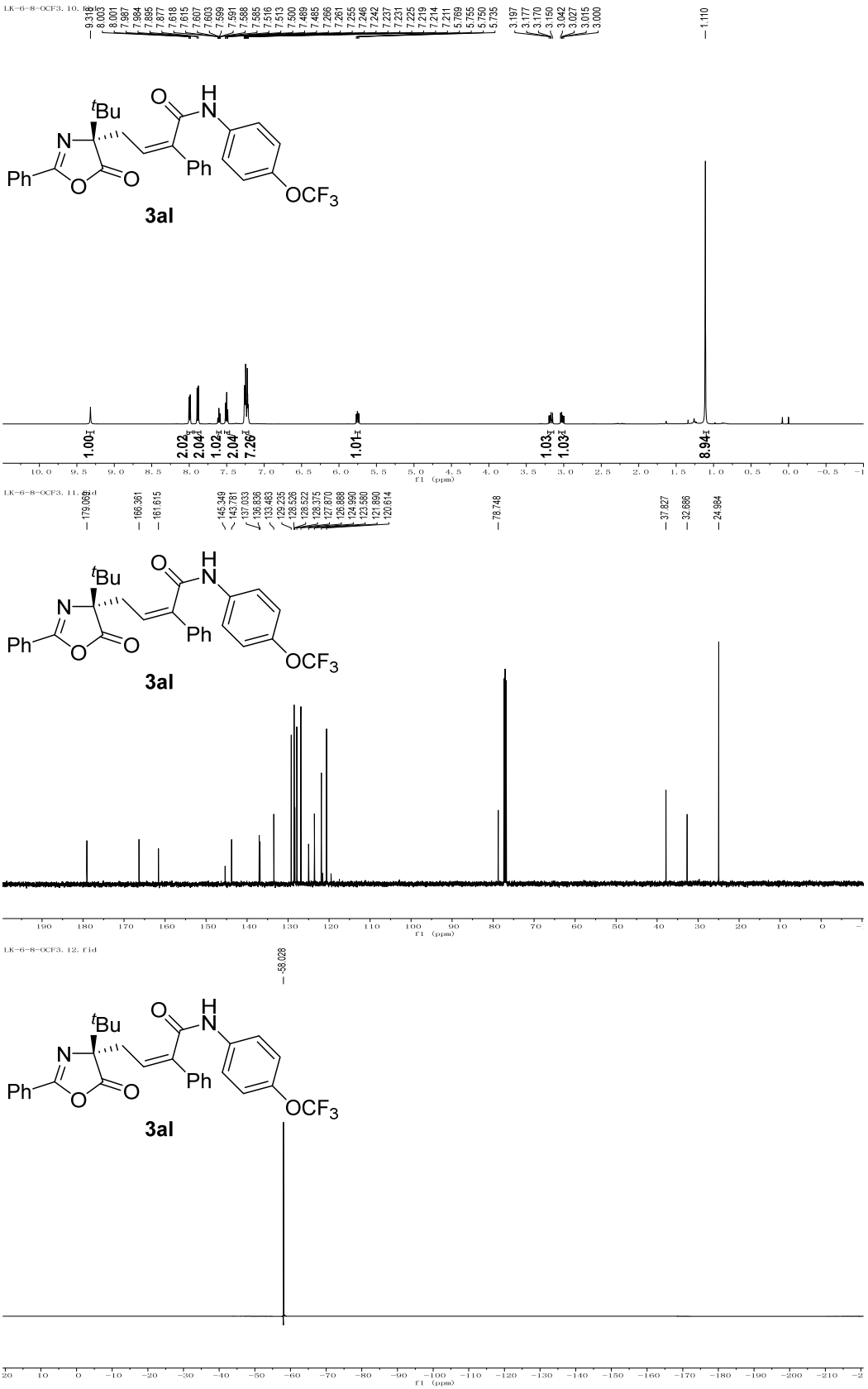
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ai**



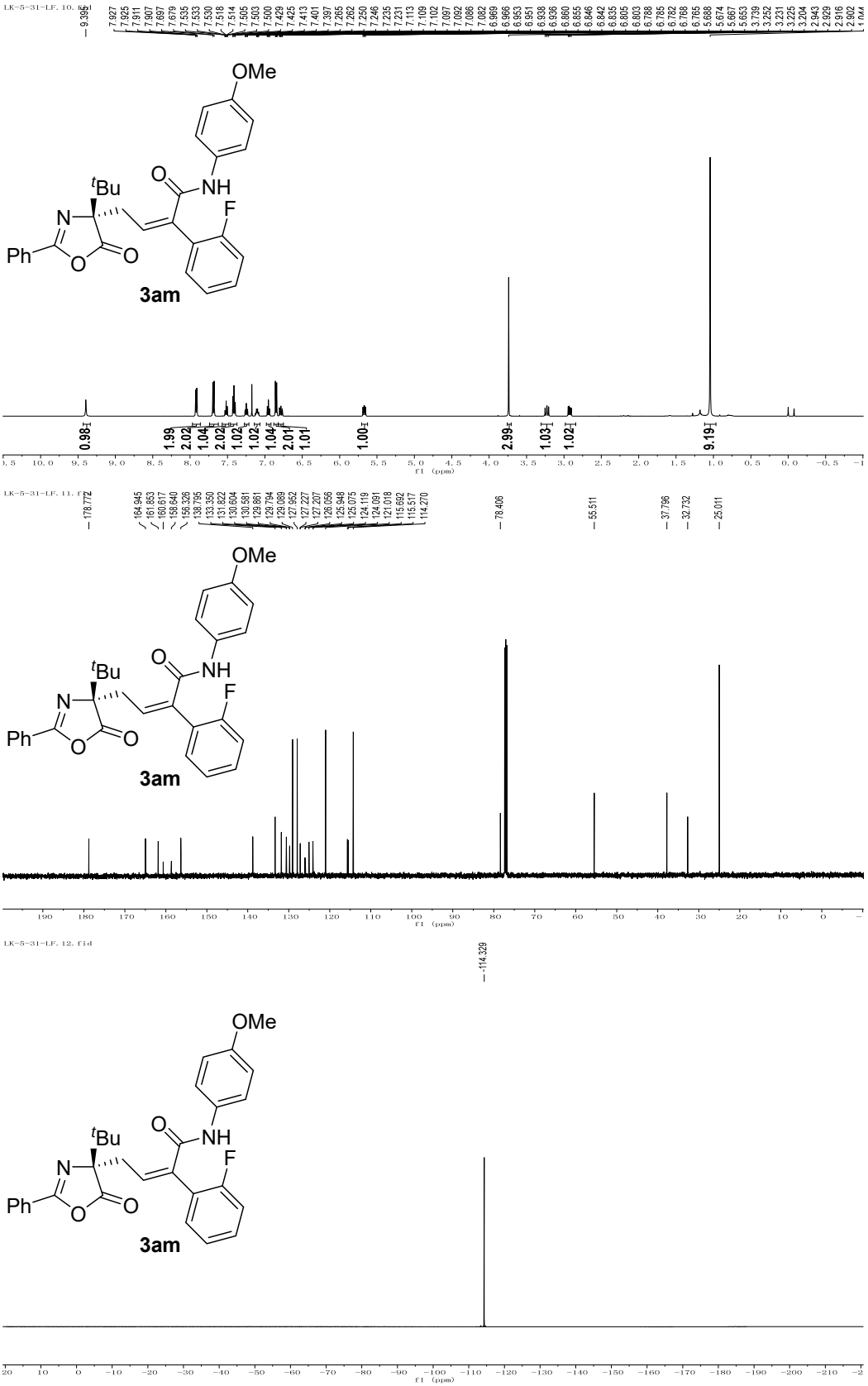
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3aj**



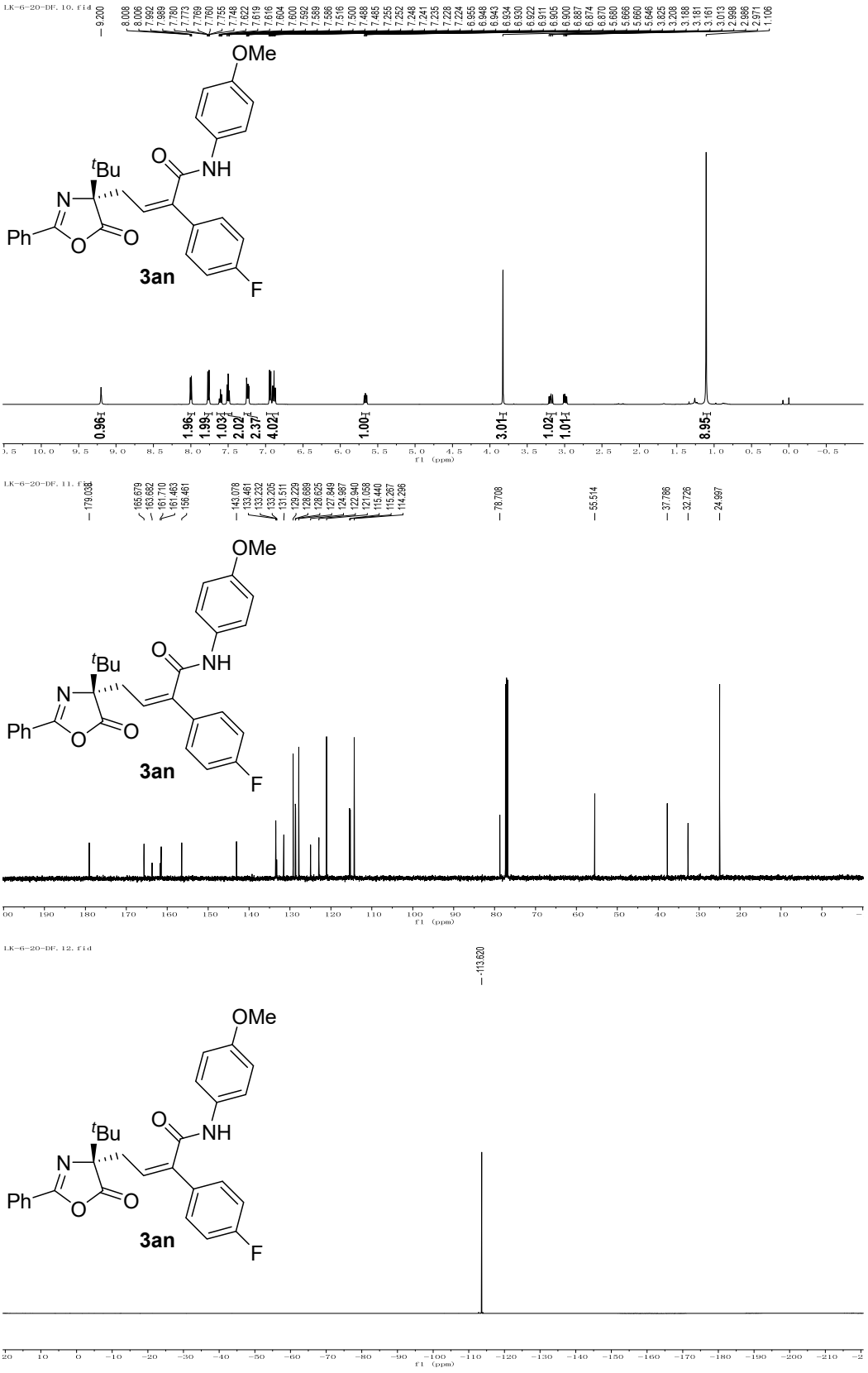
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ak**



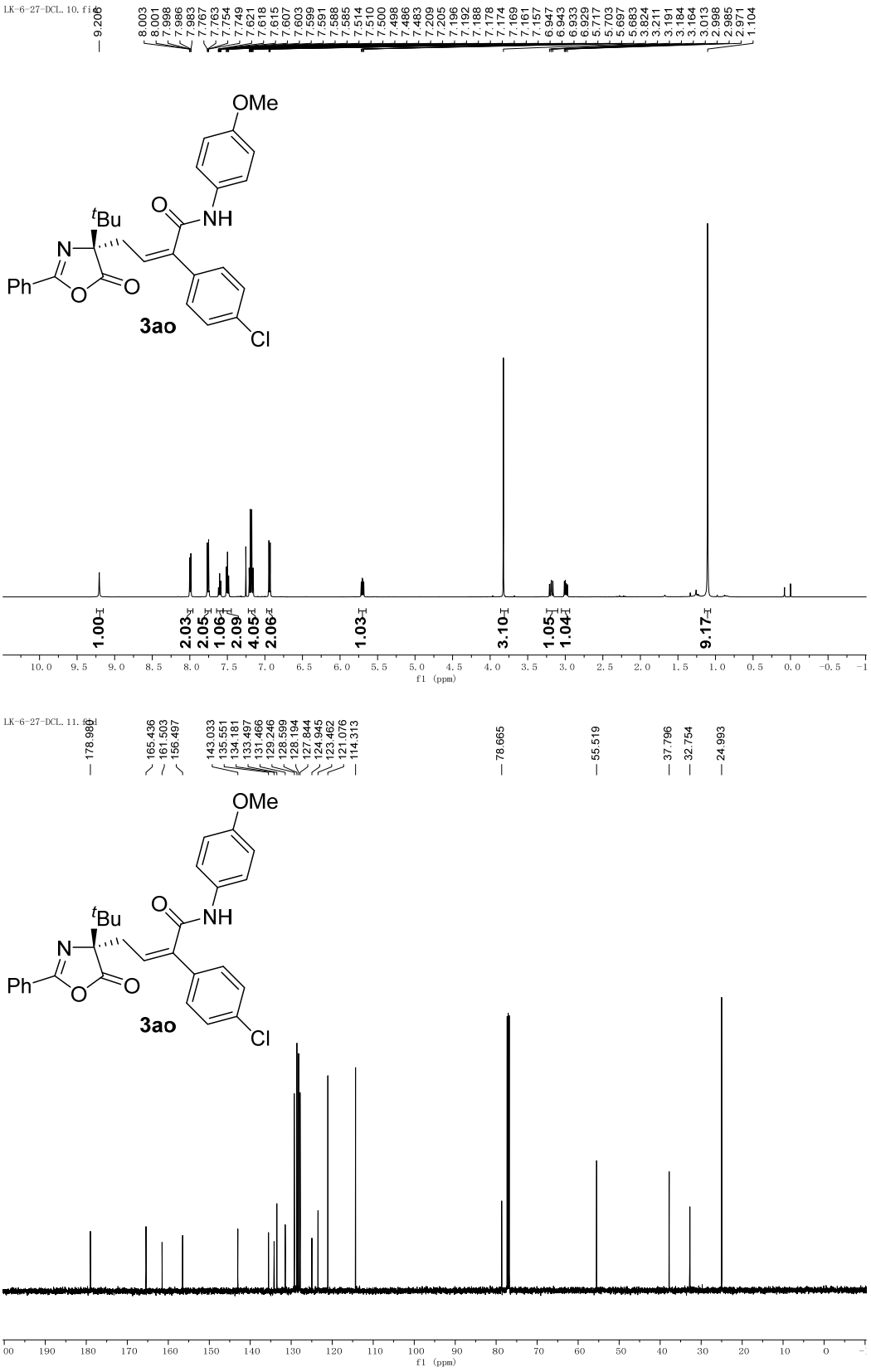
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra of **3al**



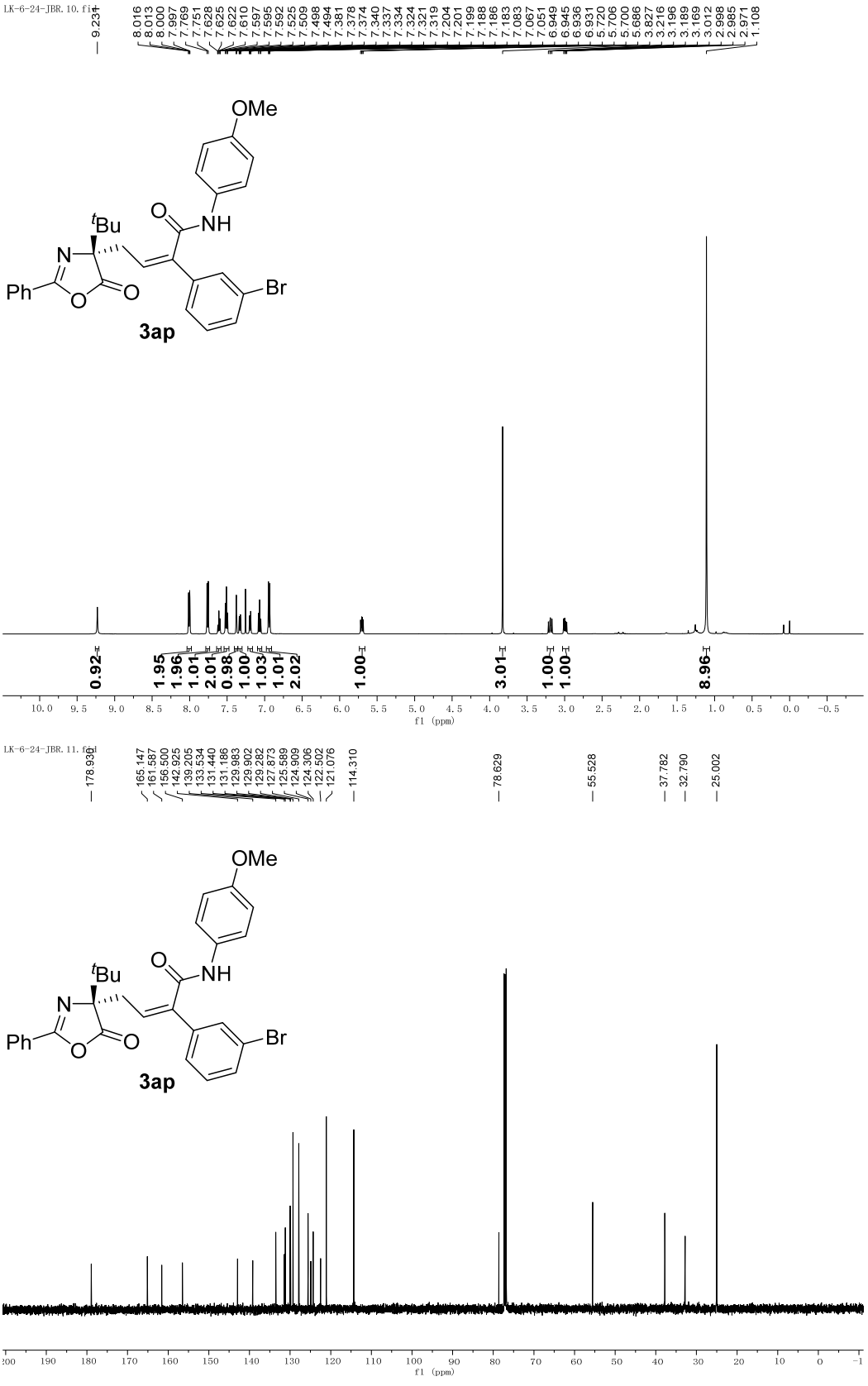
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra of **3am**



^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra of **3an**

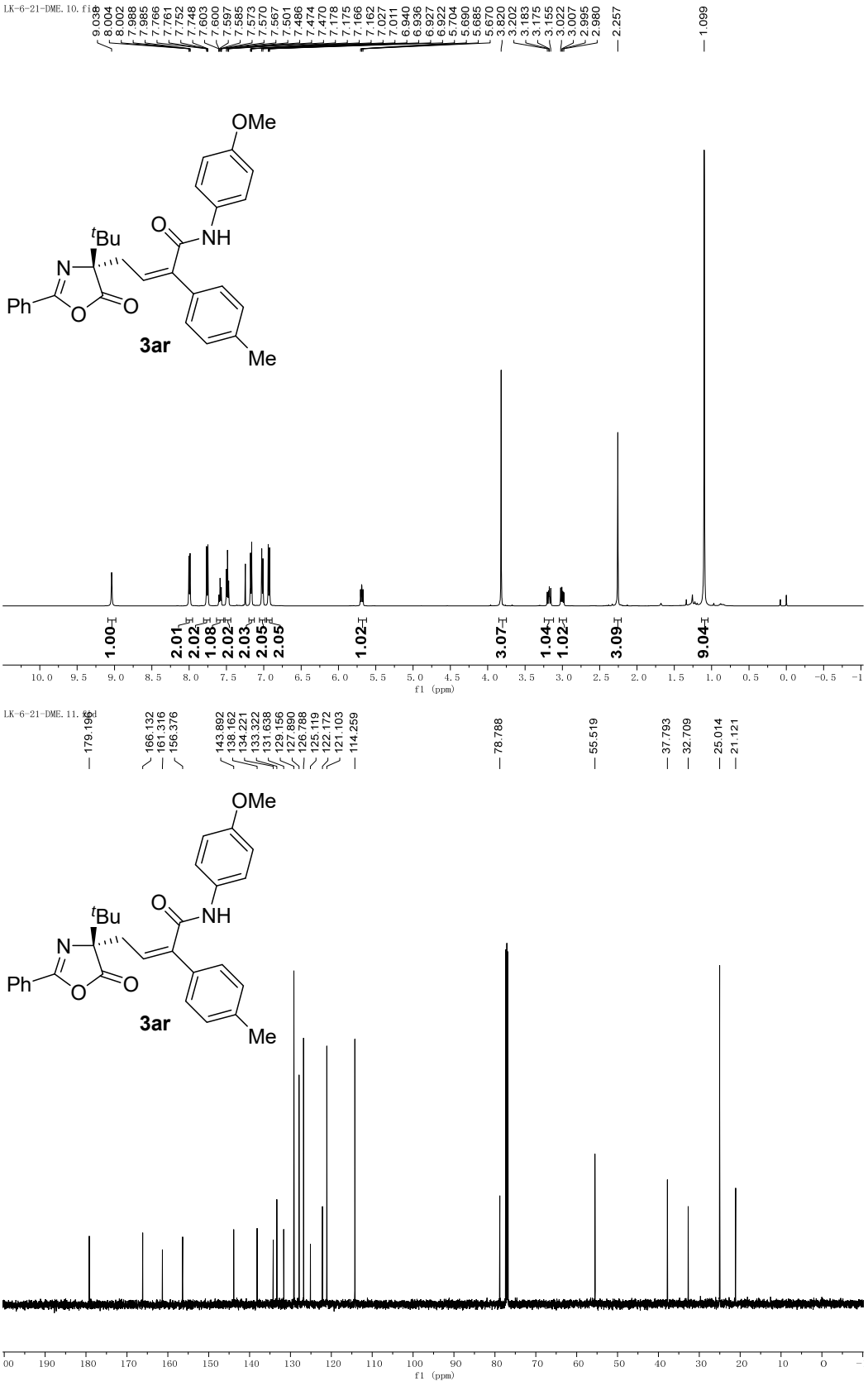


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ao**

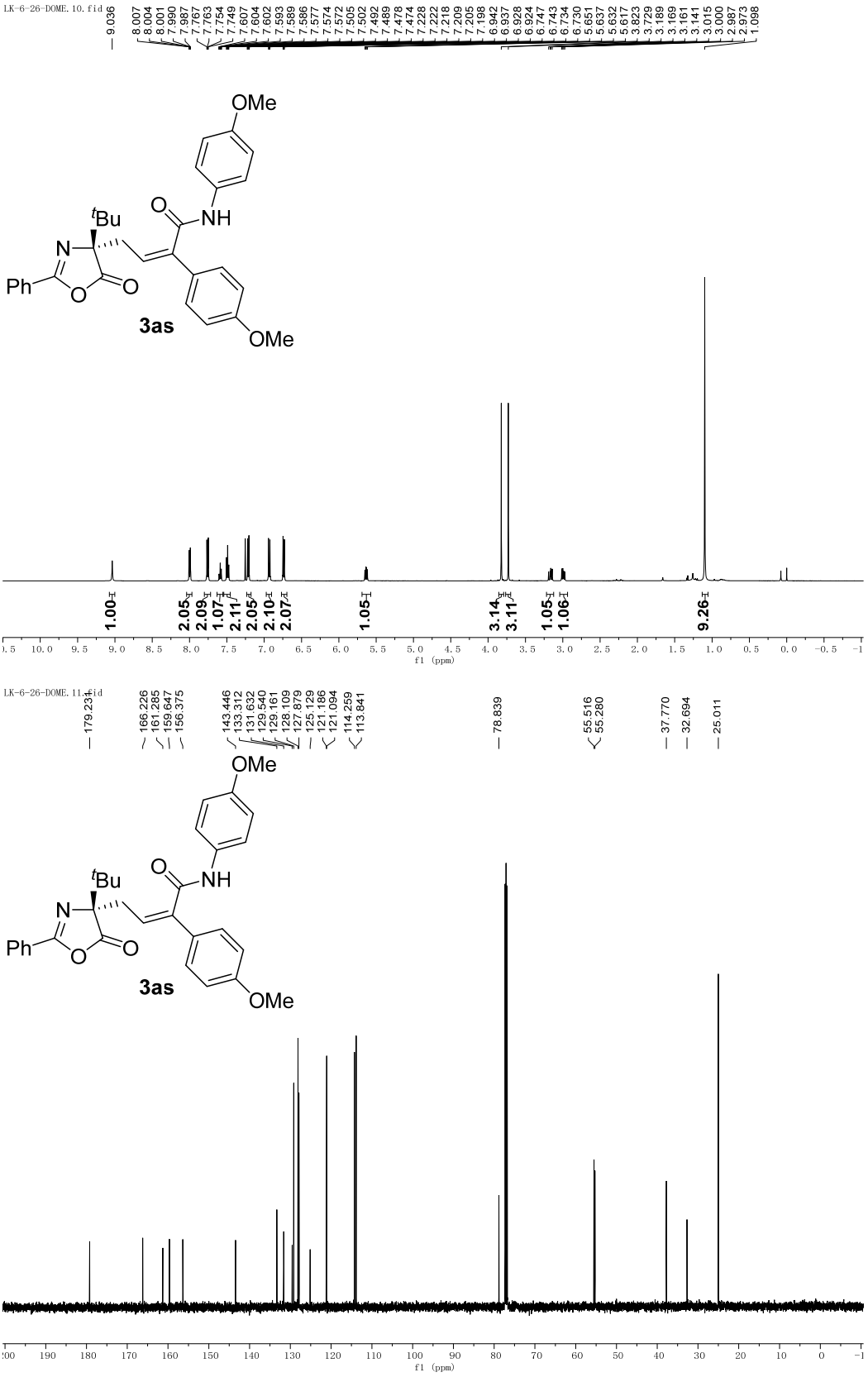


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ap**

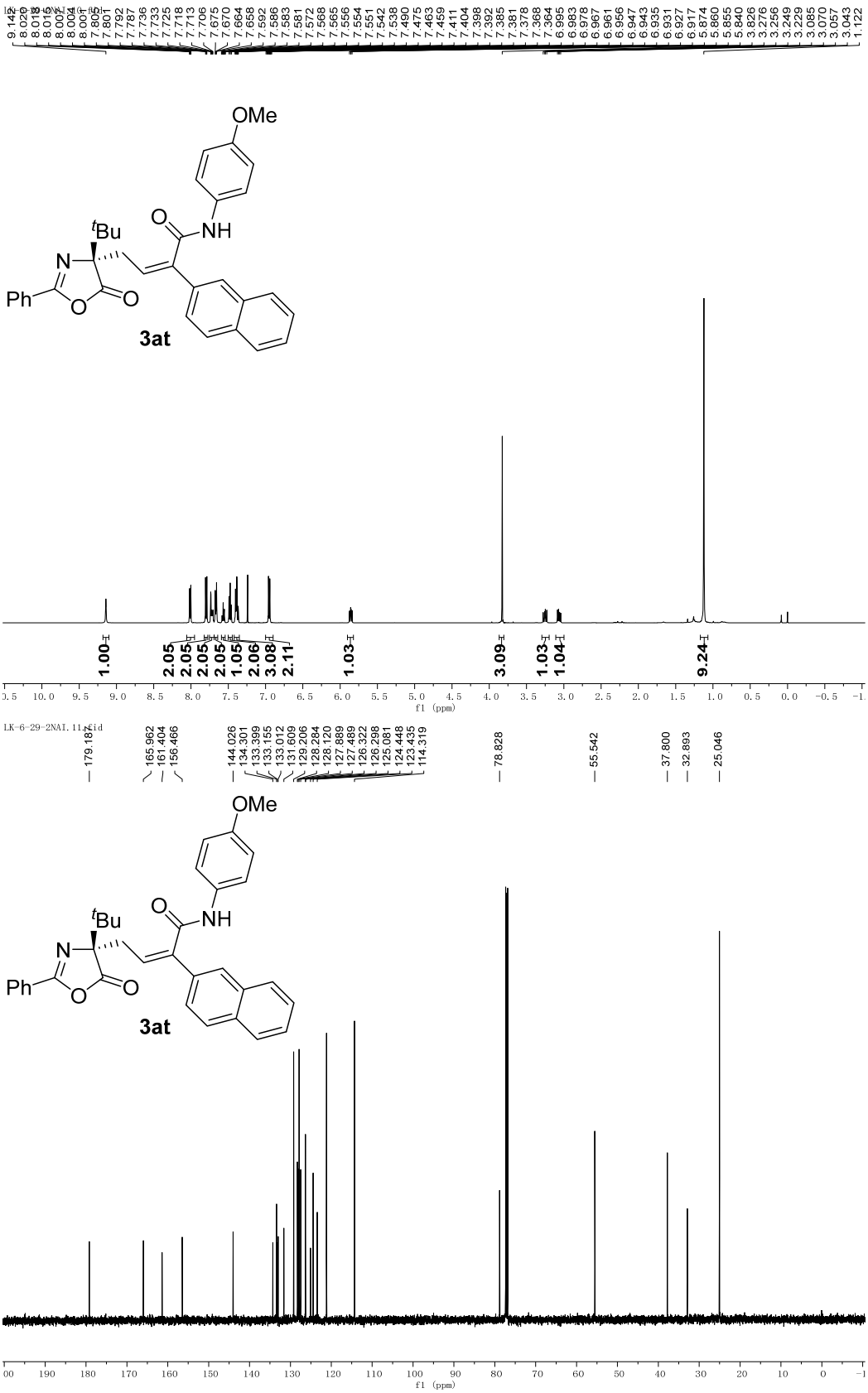
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3aq**



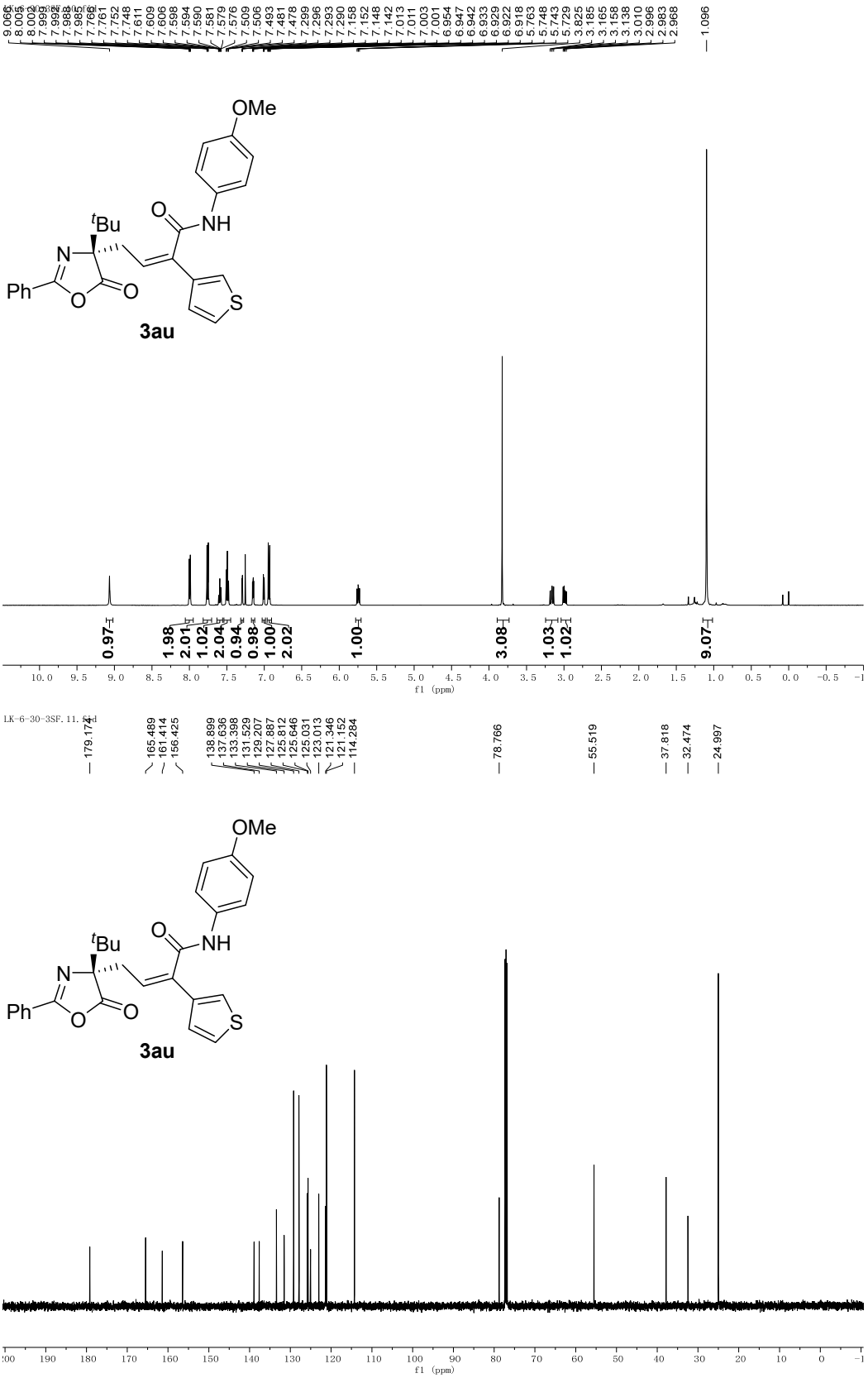
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ar**



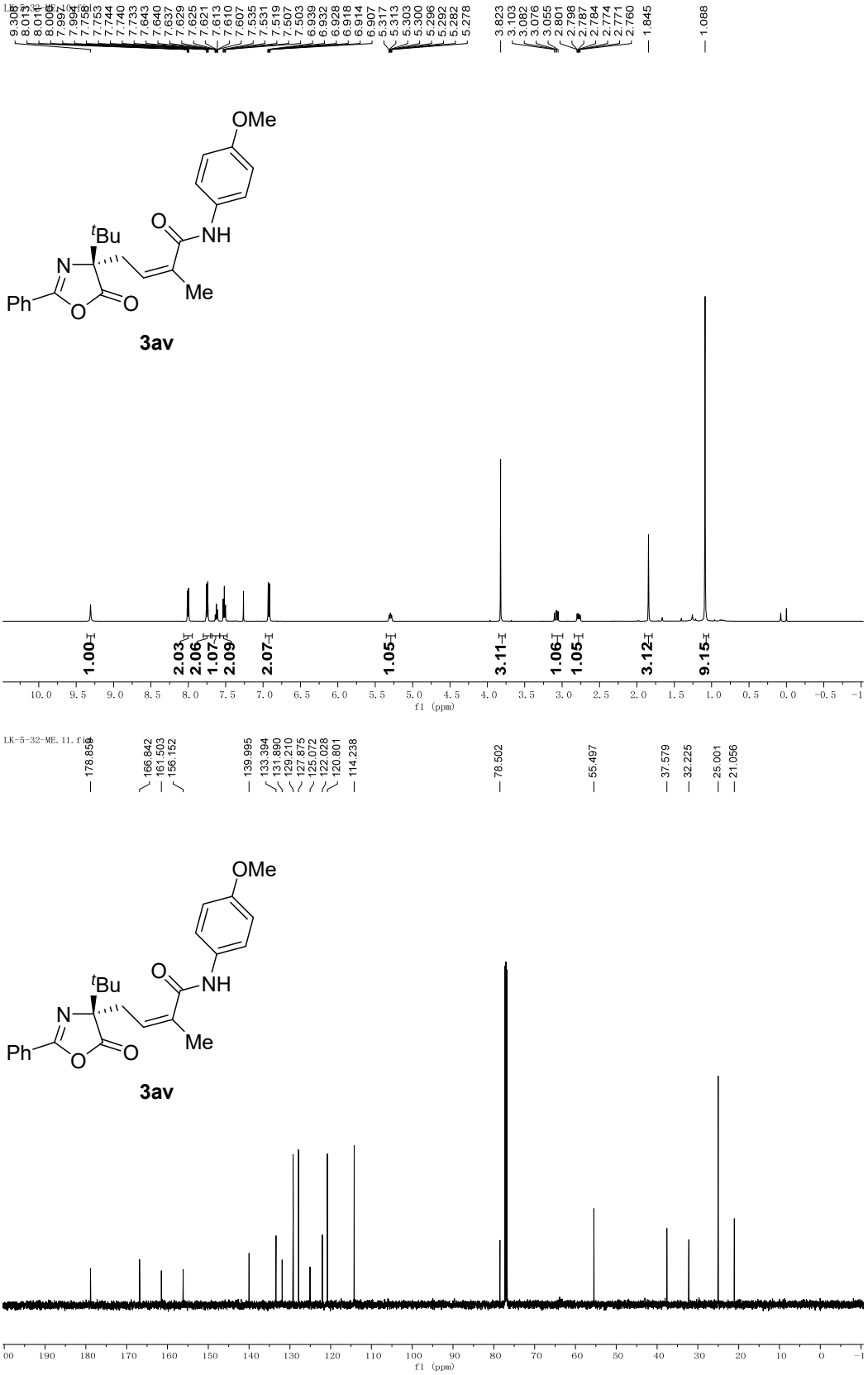
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3as**



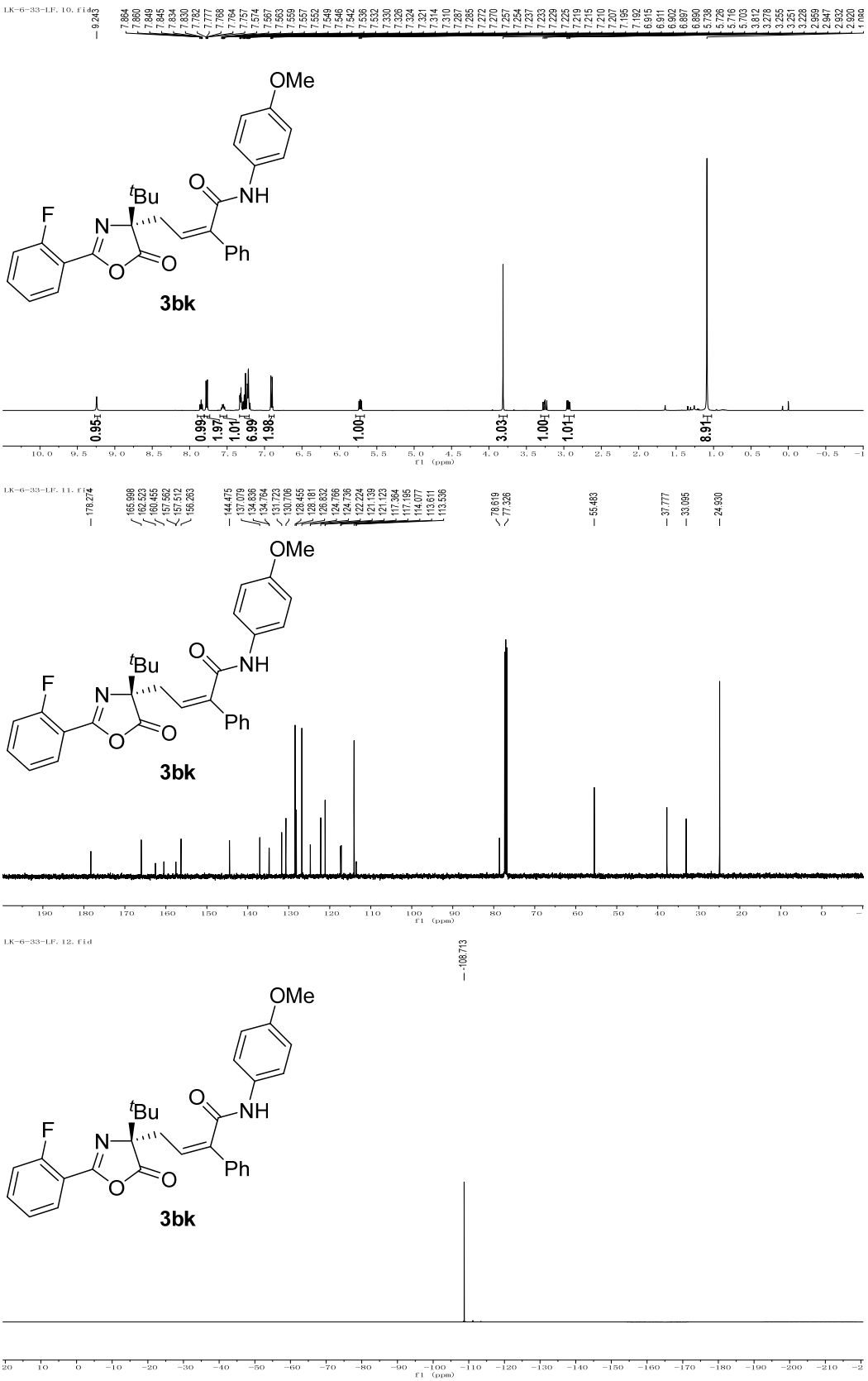
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3at**



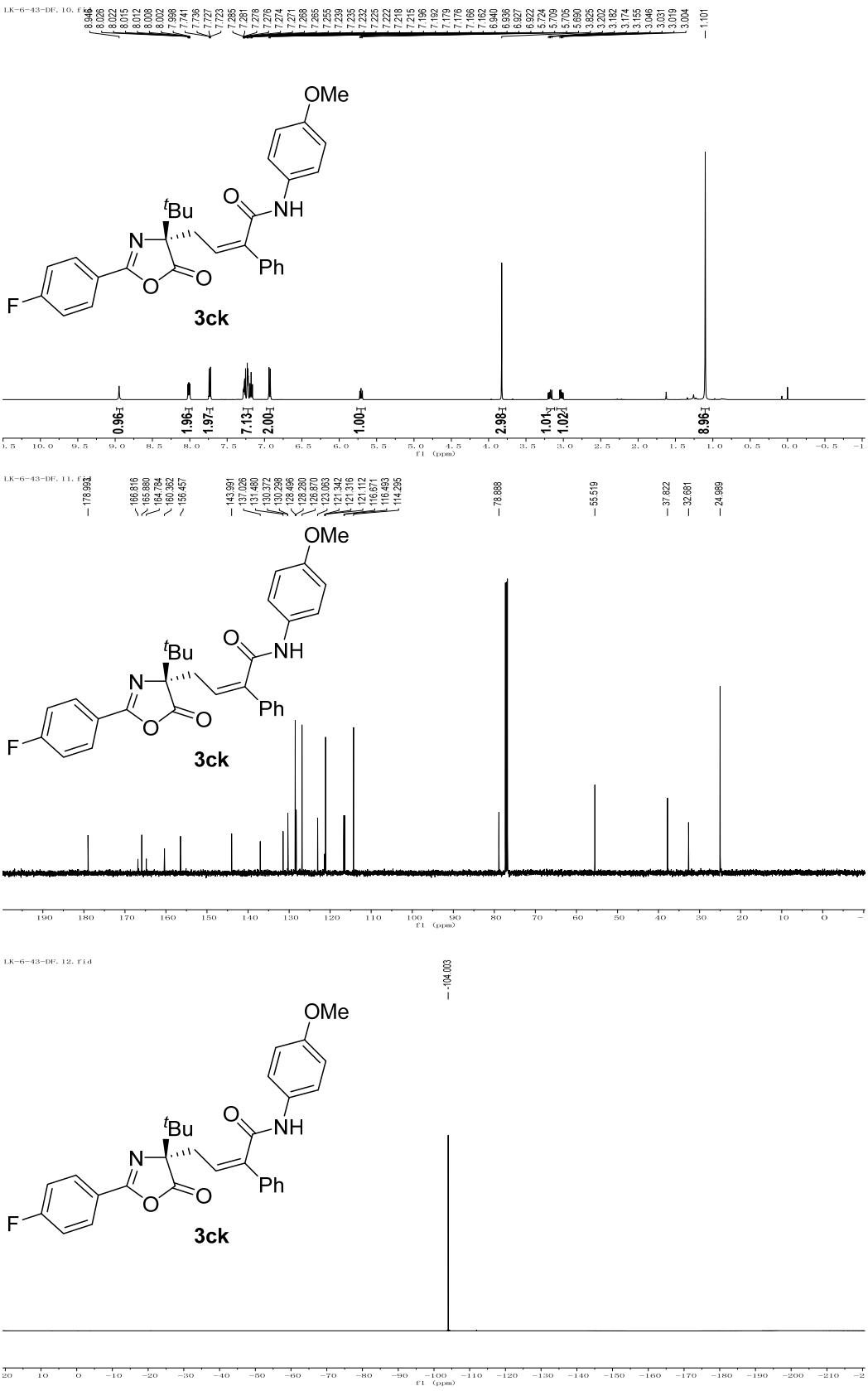
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3au**



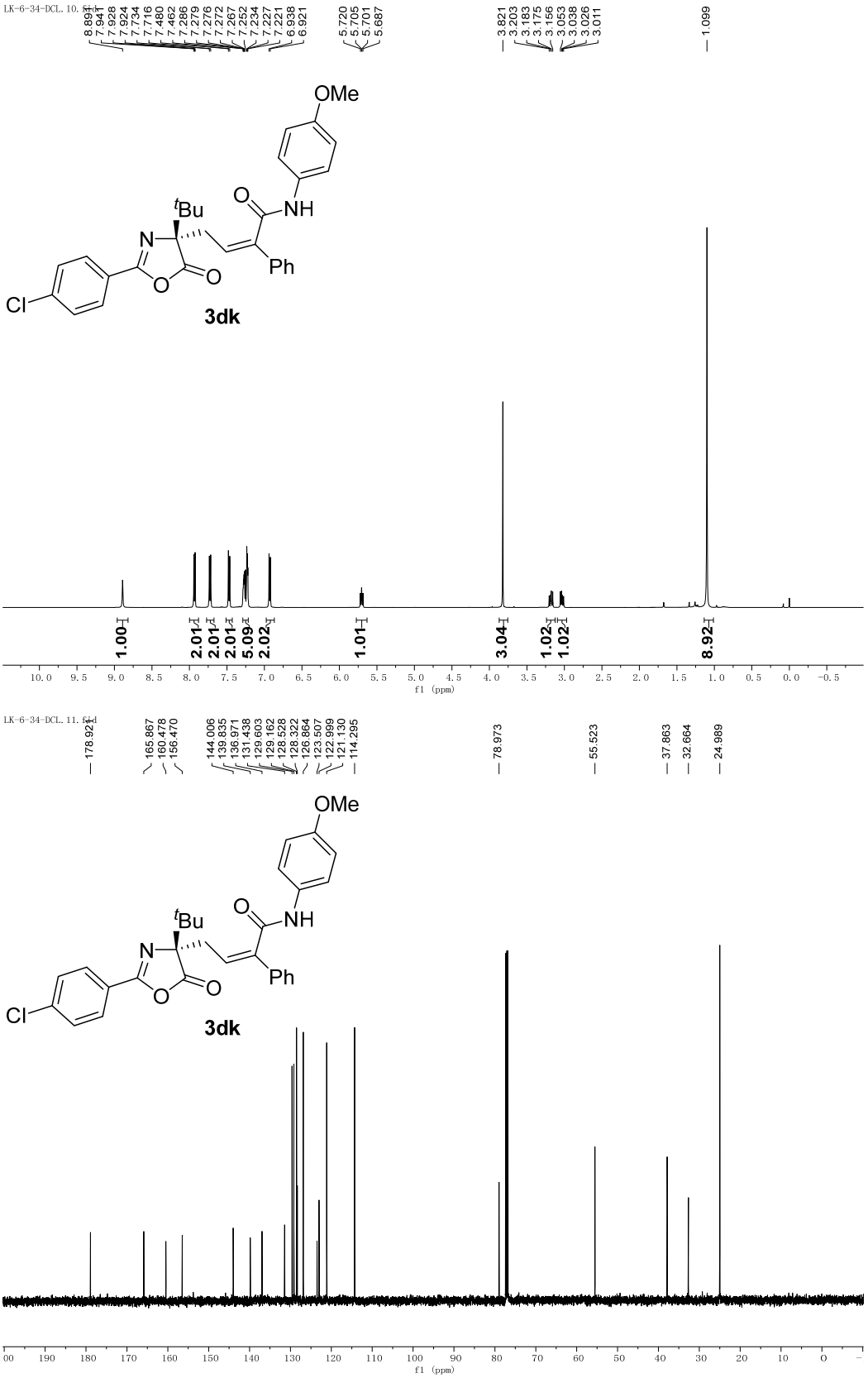
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3av**



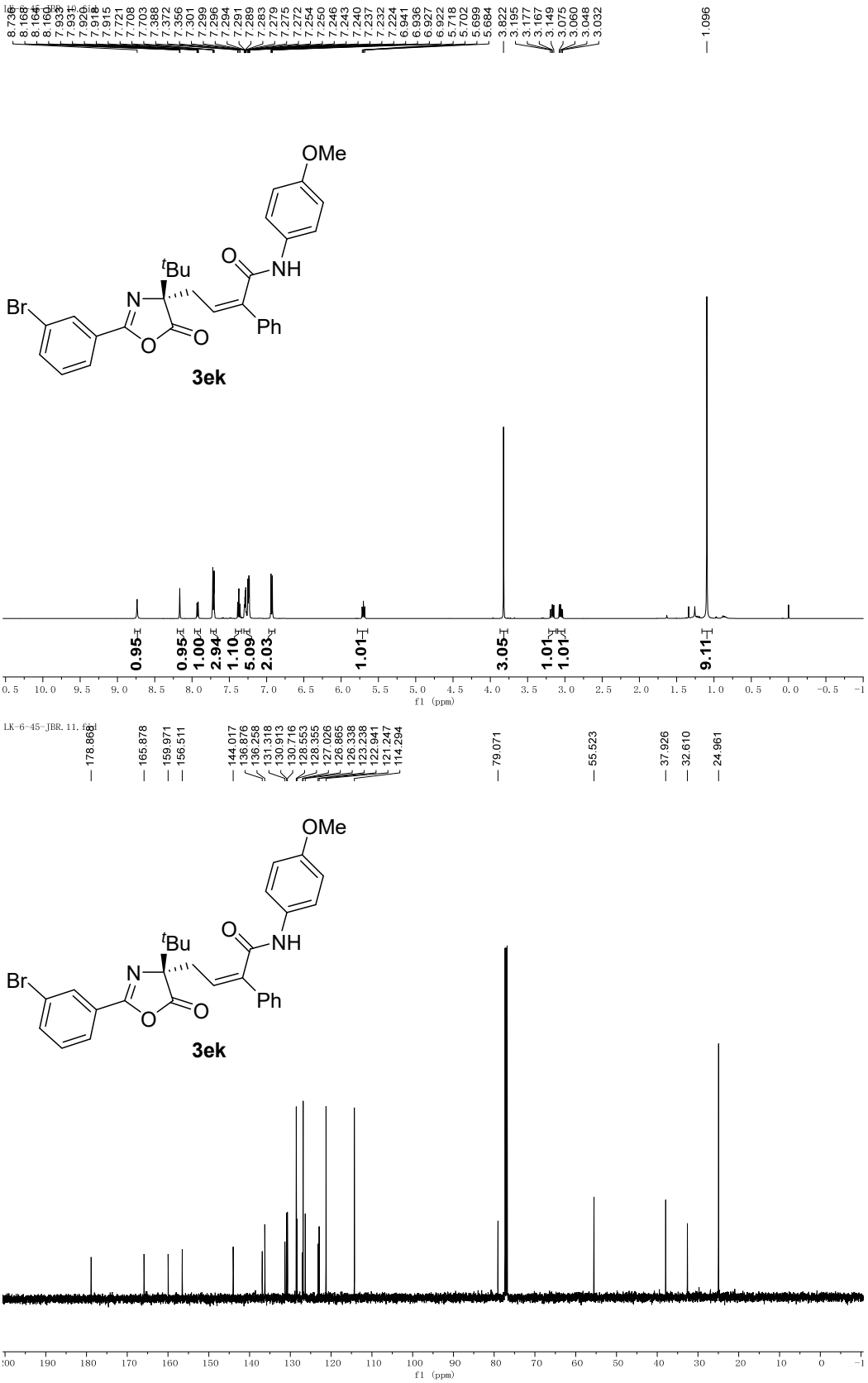
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (125 MHz) spectra of **3bk**



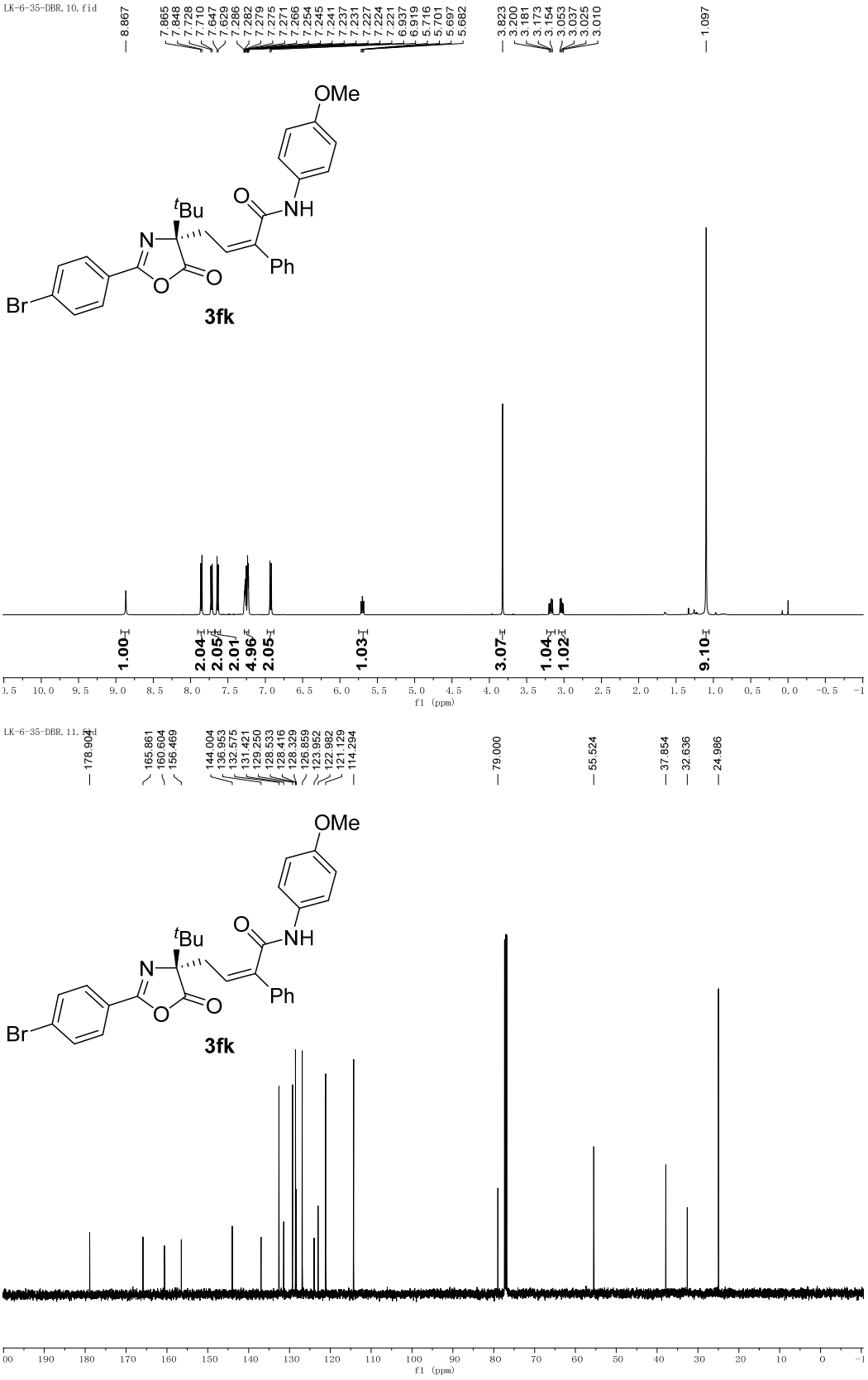
^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (125 MHz) spectra of **3ck**



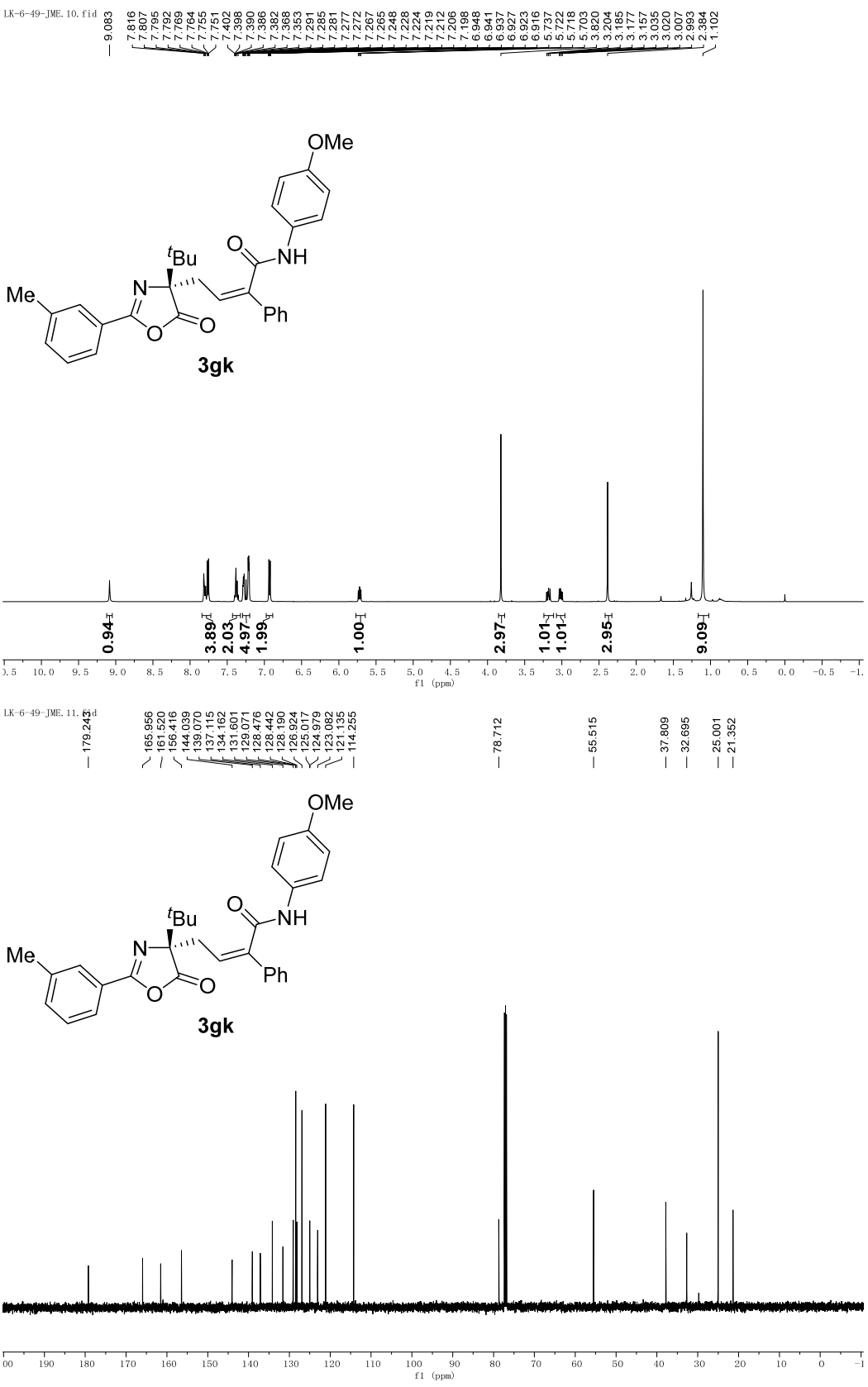
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3dk**



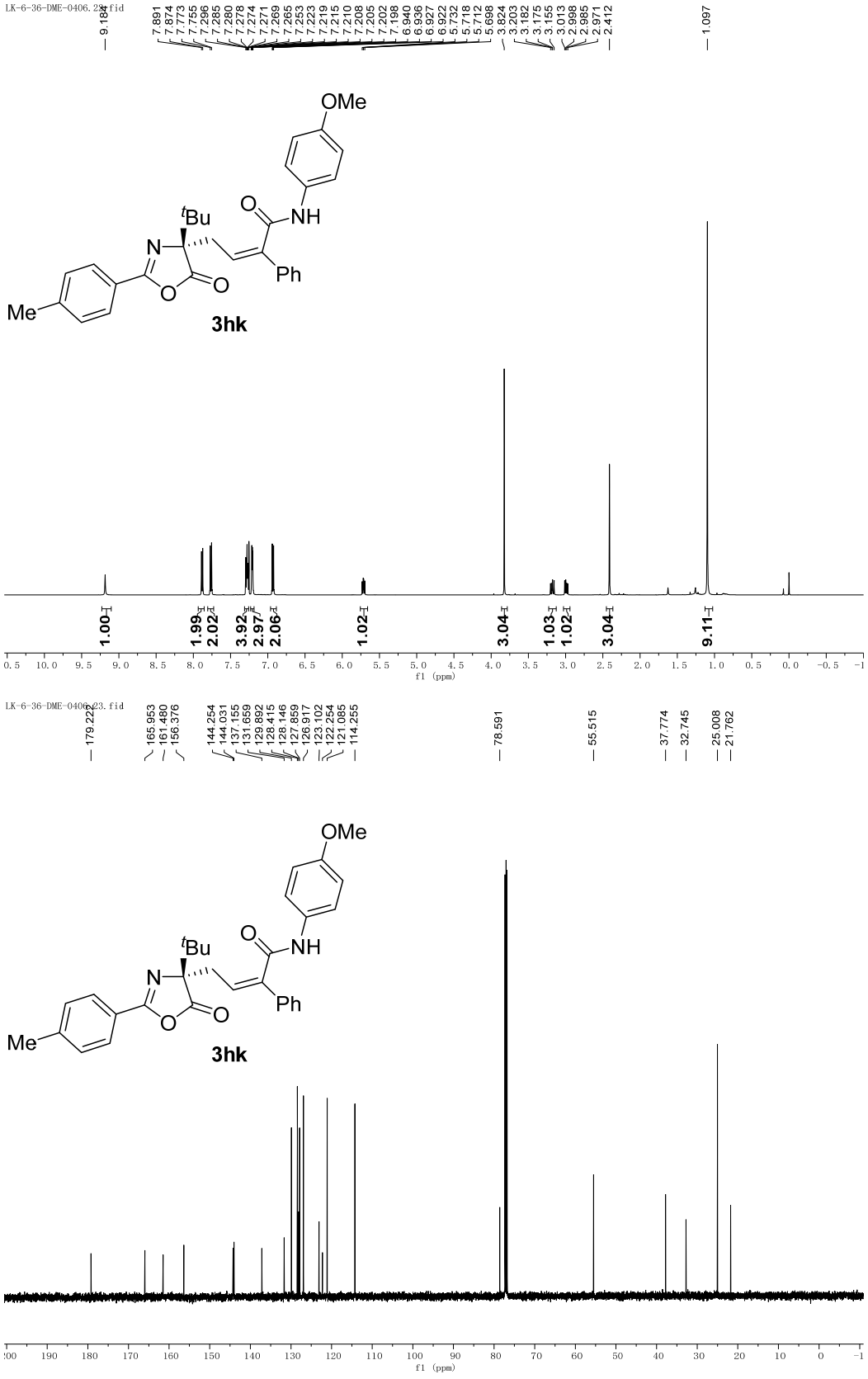
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ek**



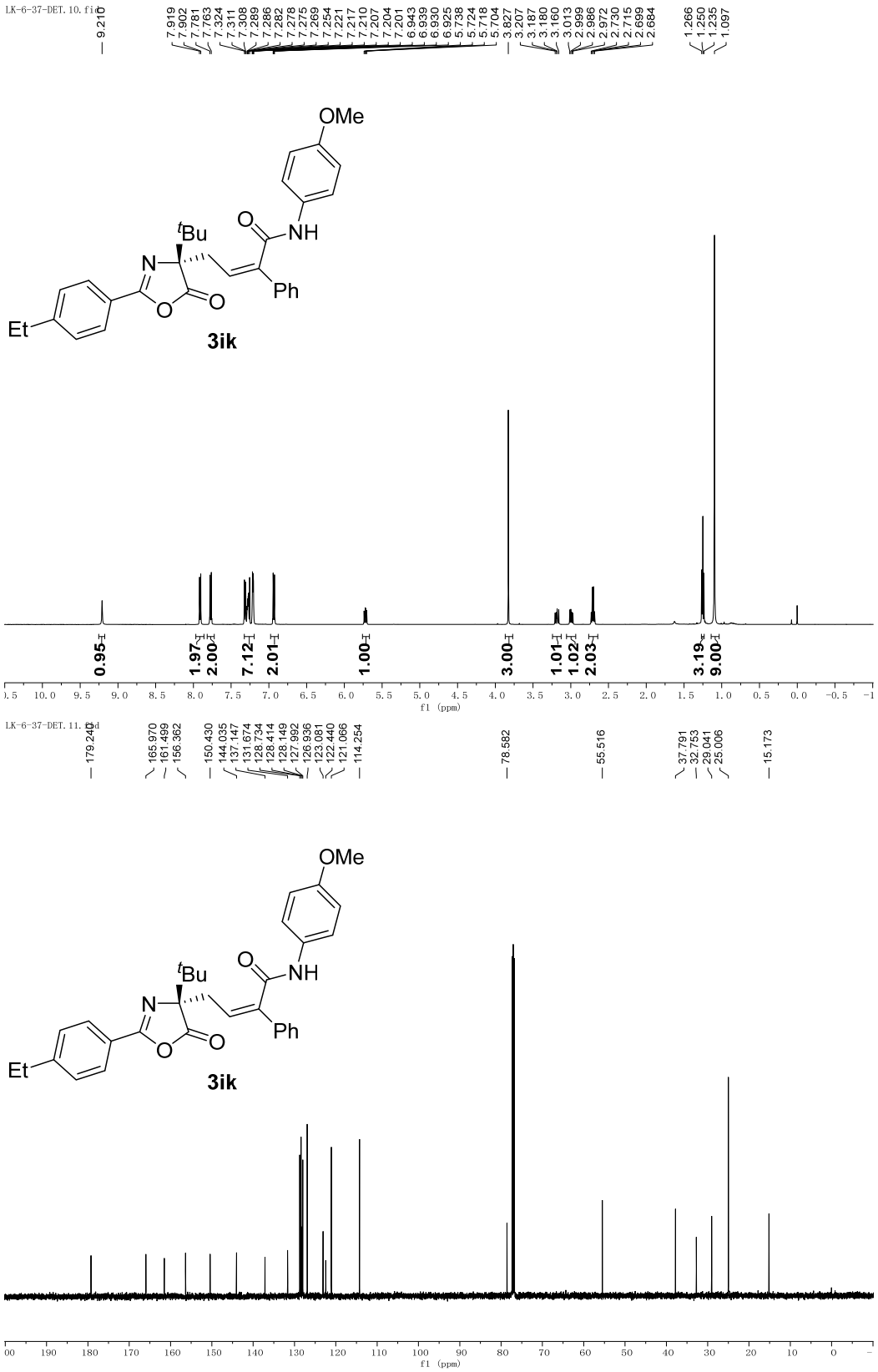
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3fk**



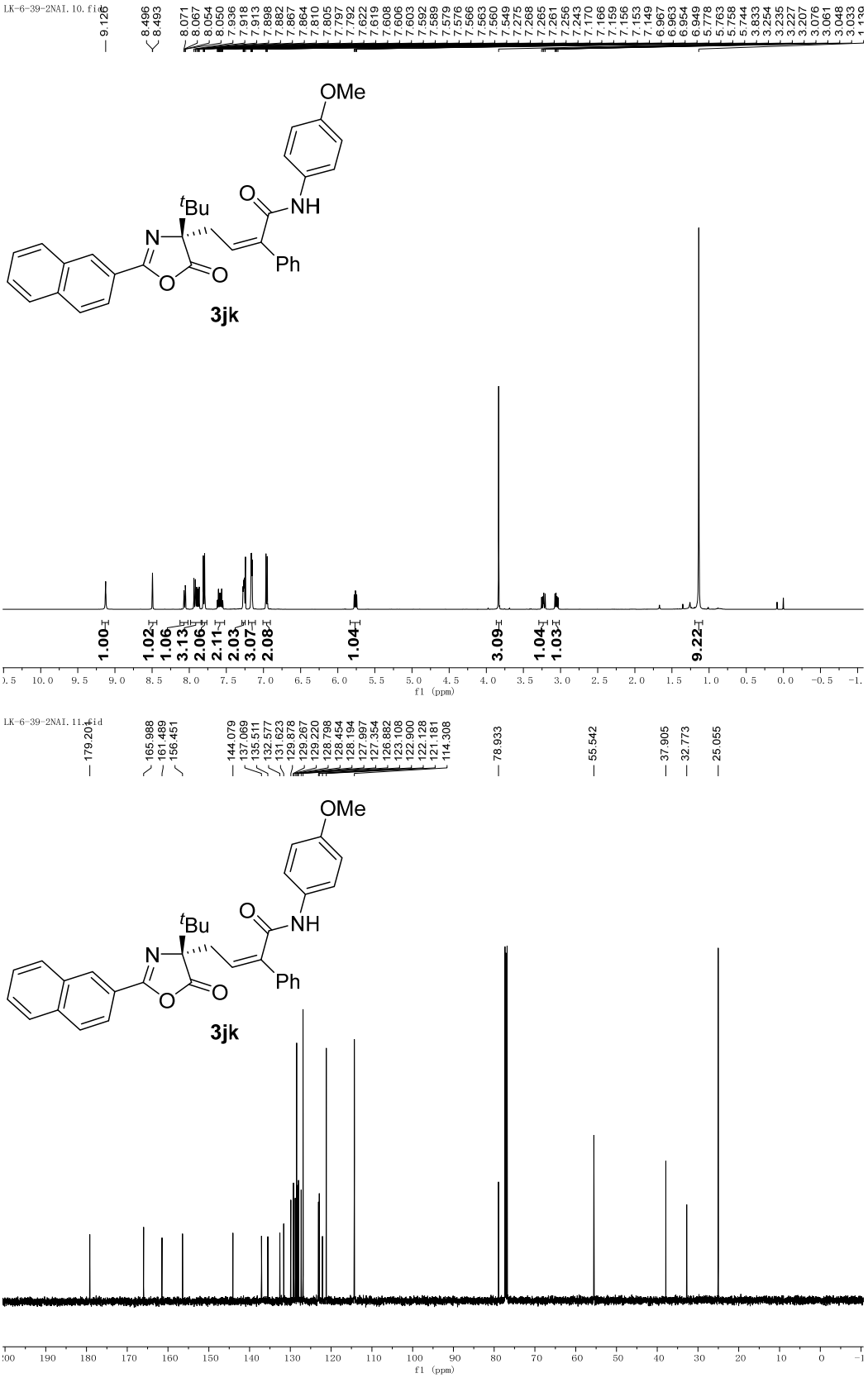
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3gk**



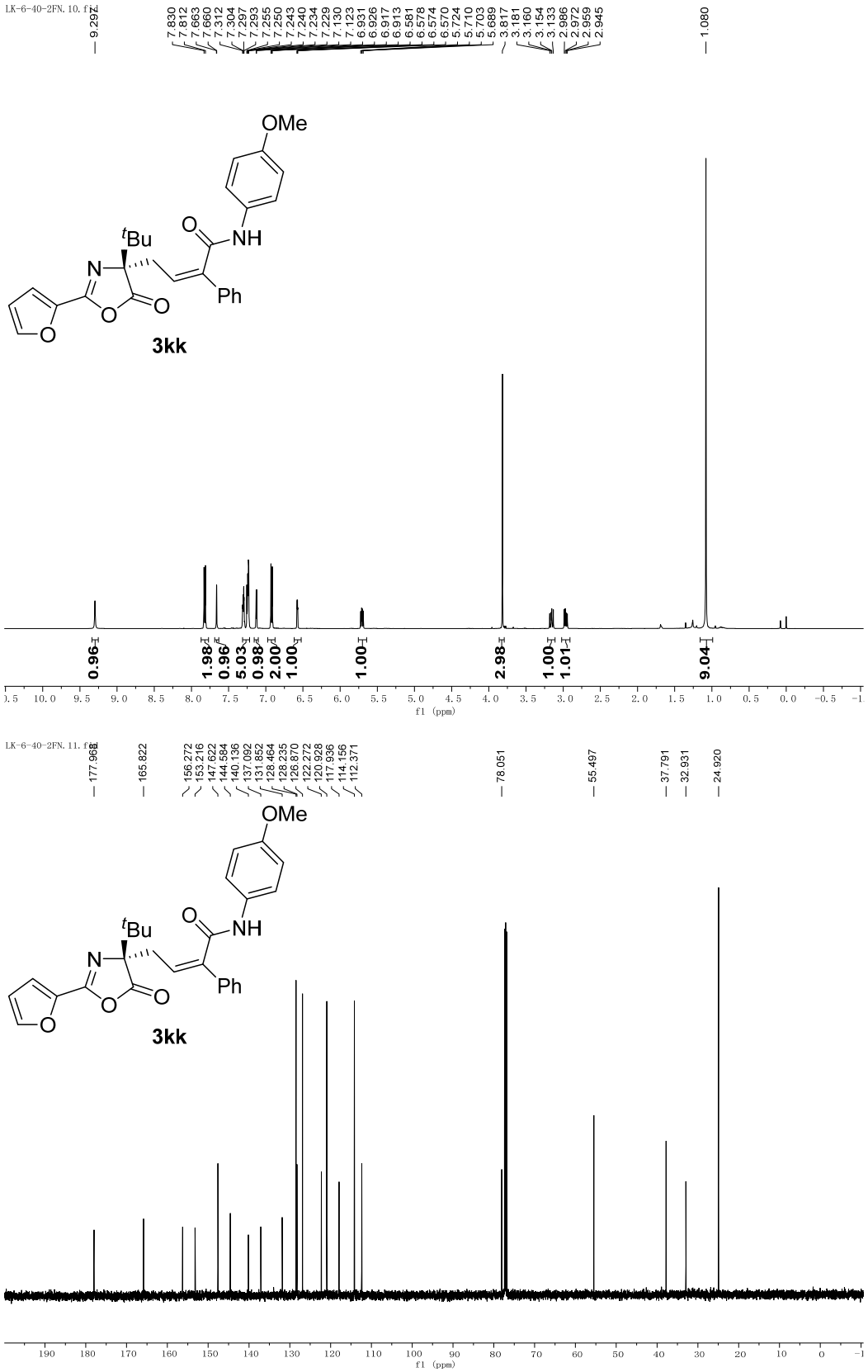
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3hk**



^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3ik**

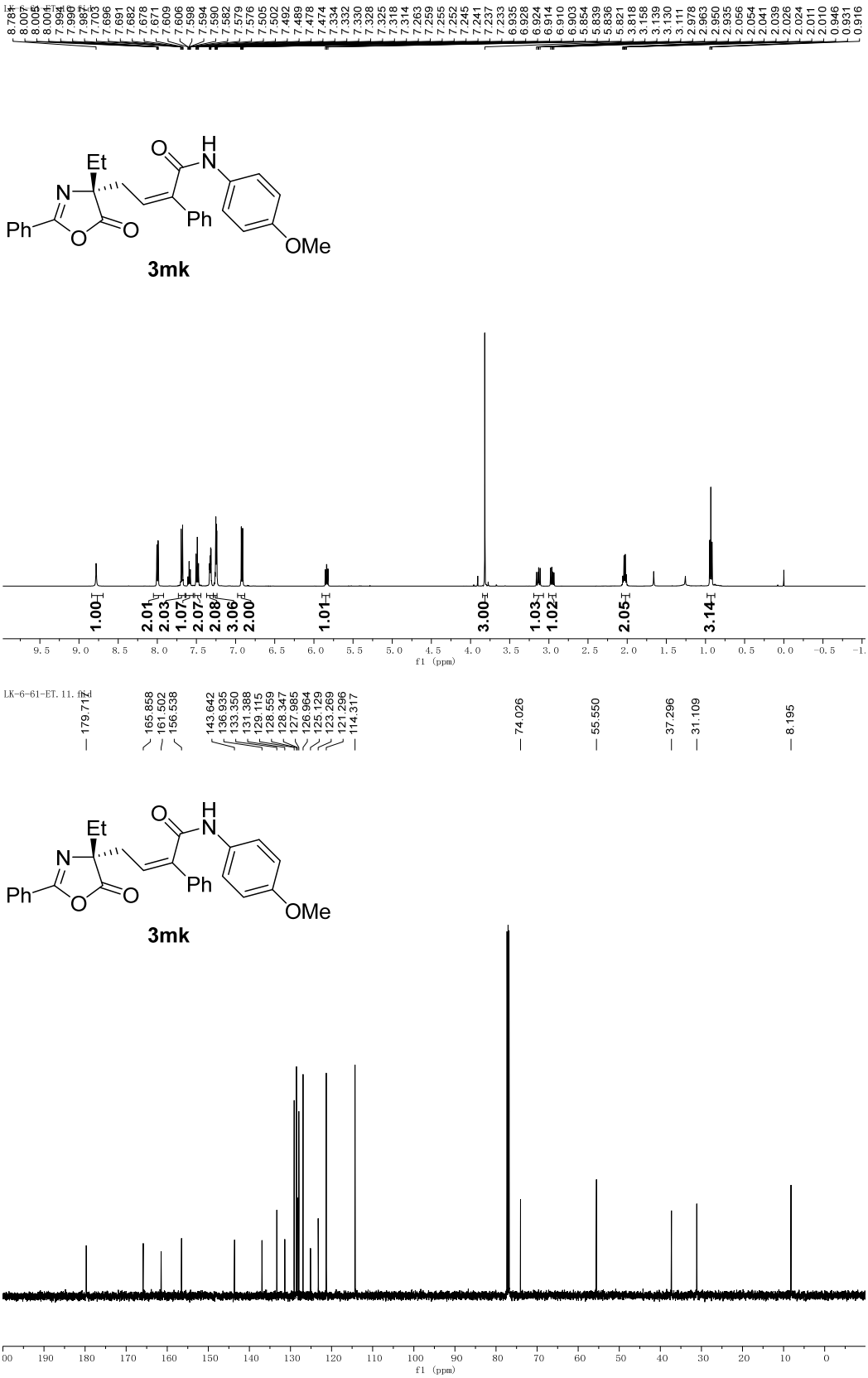


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3jk**

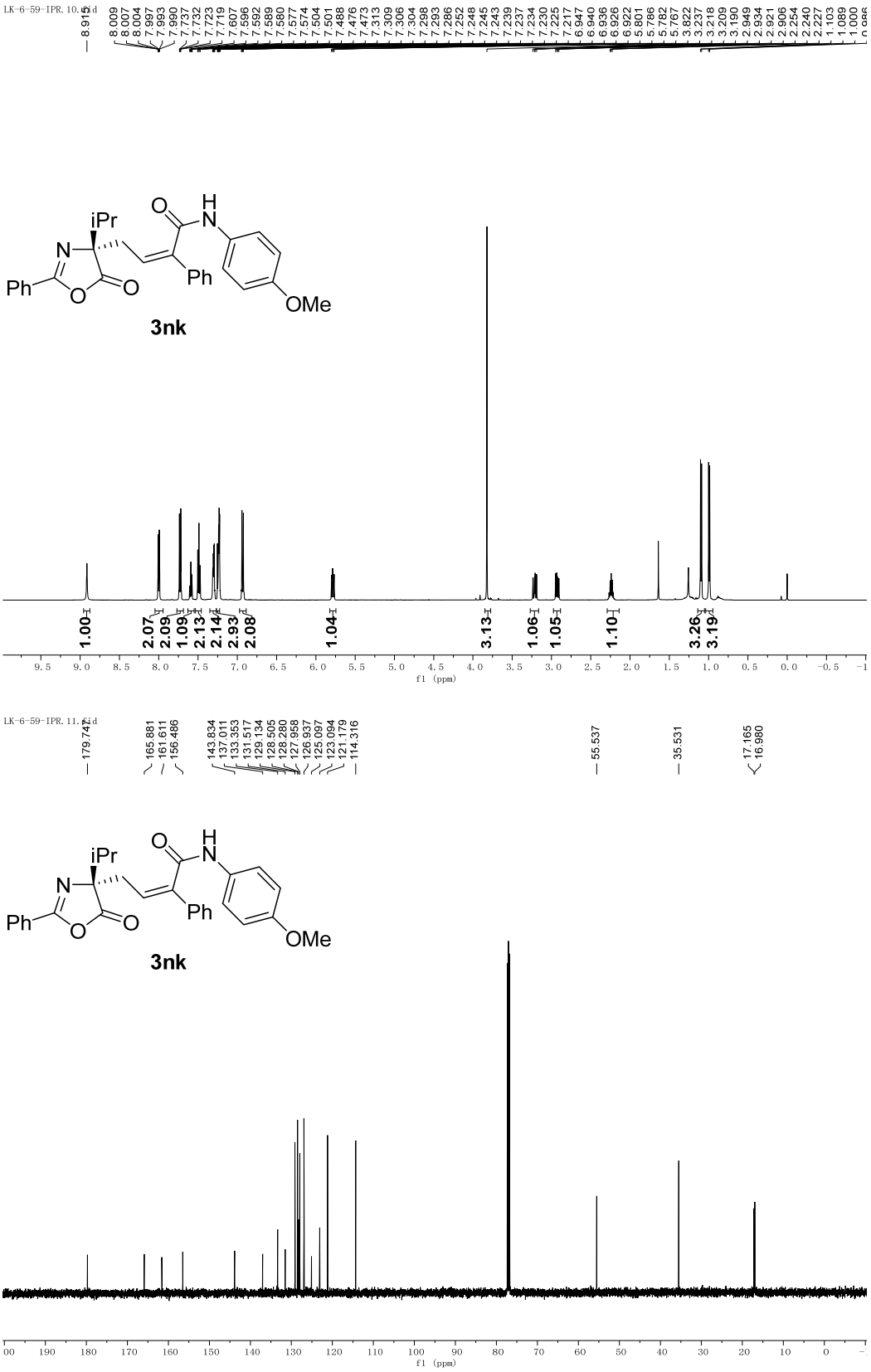


^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3kk**

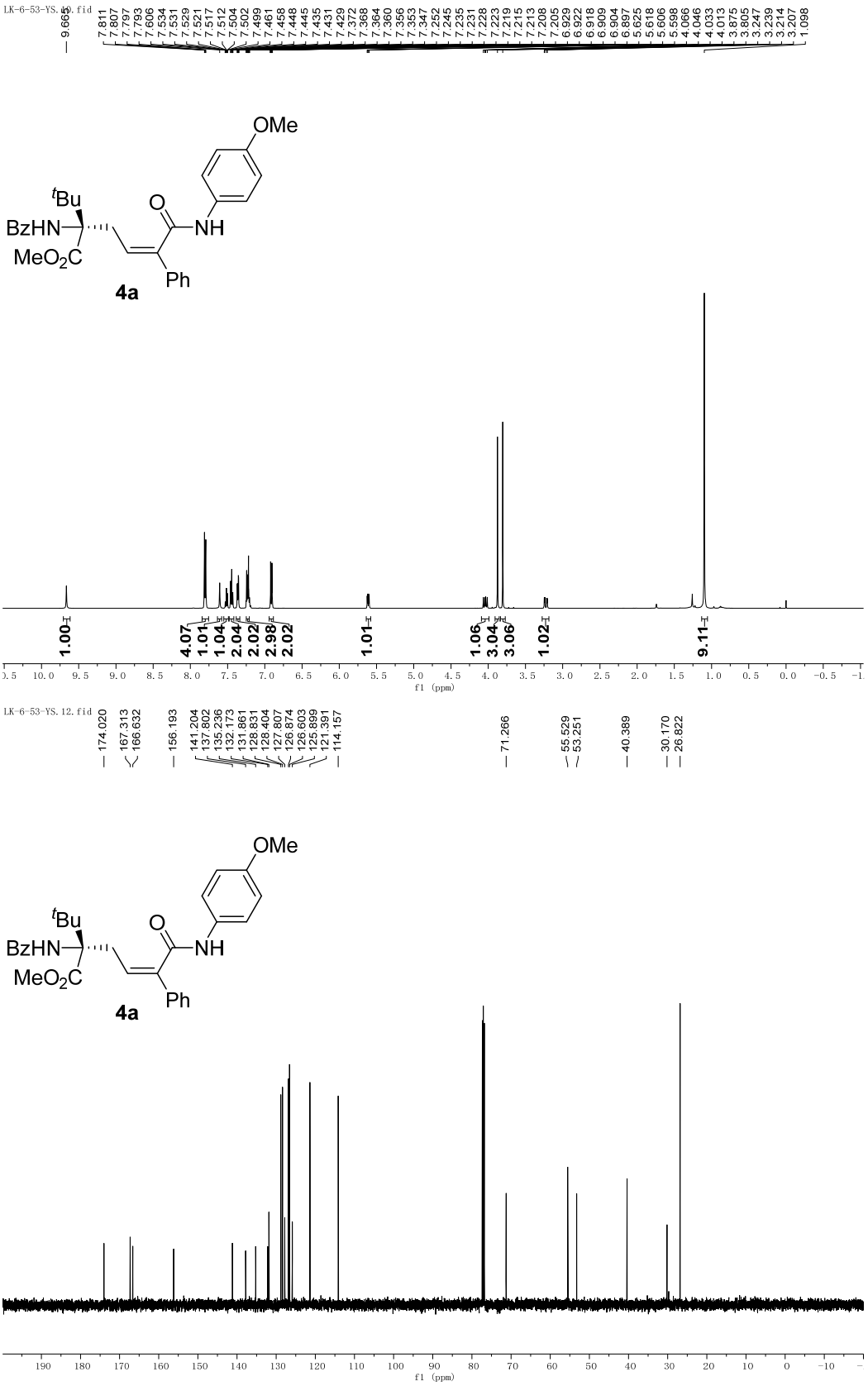
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3lk**



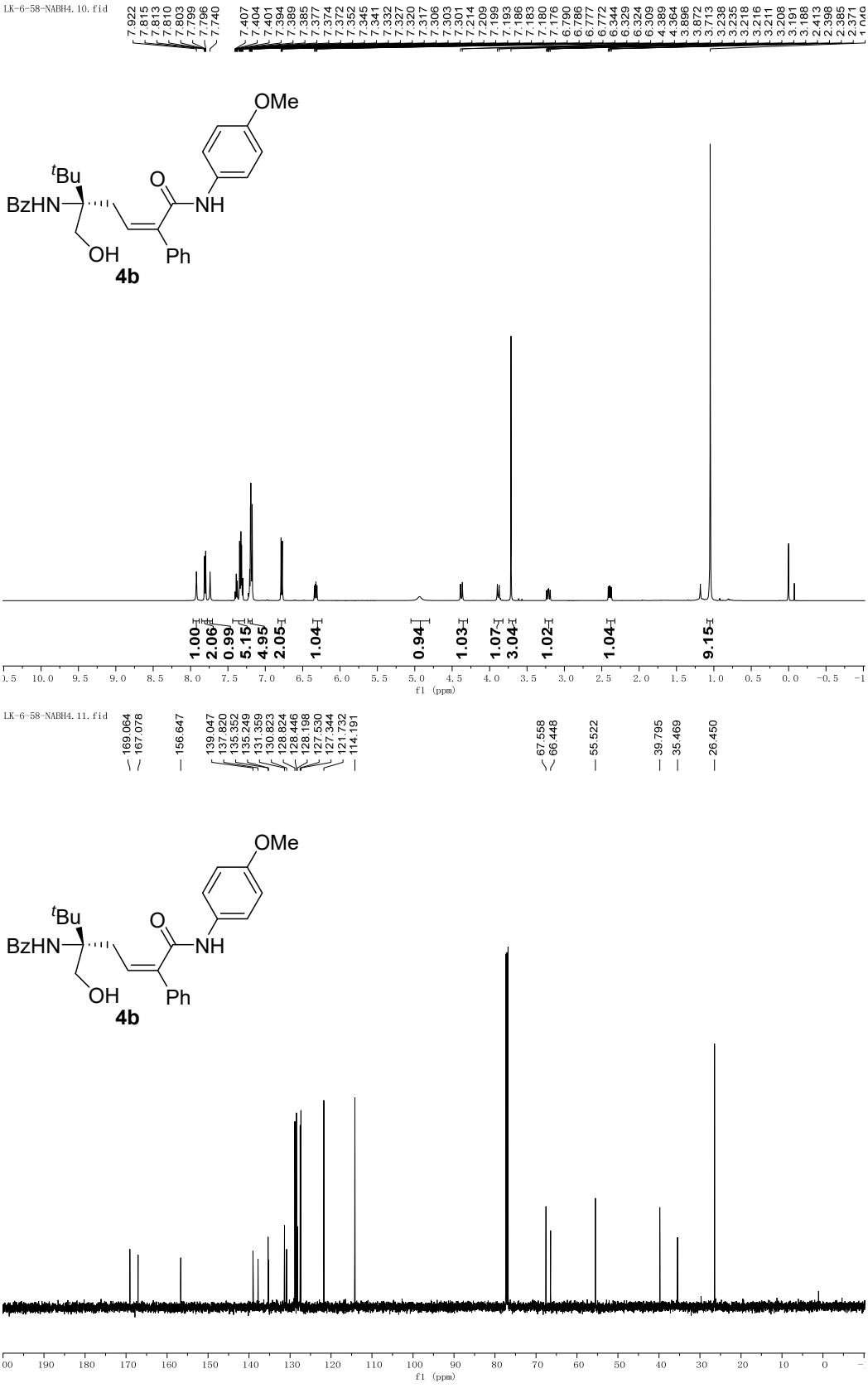
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3mk**



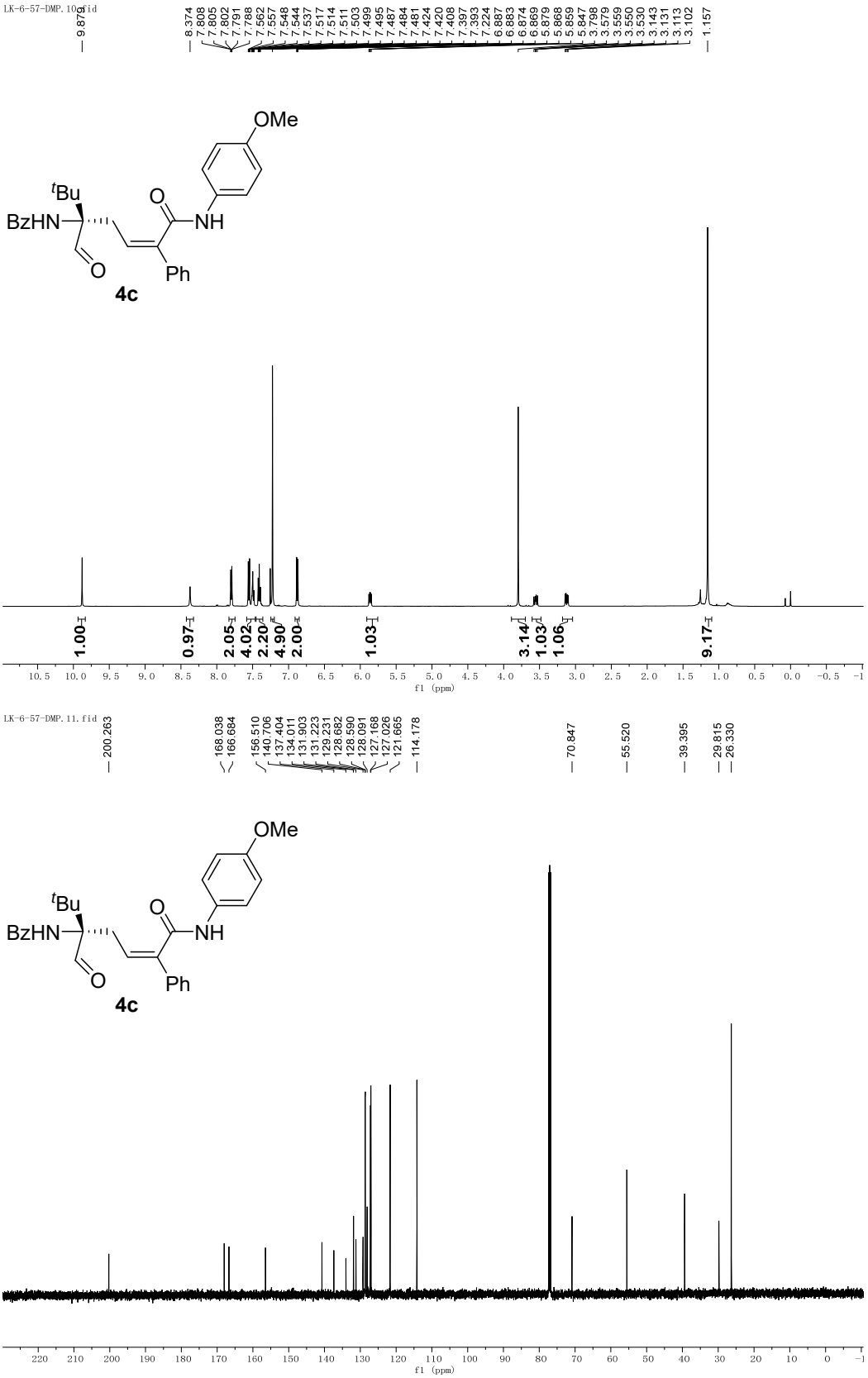
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **3nk**



^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **4a**



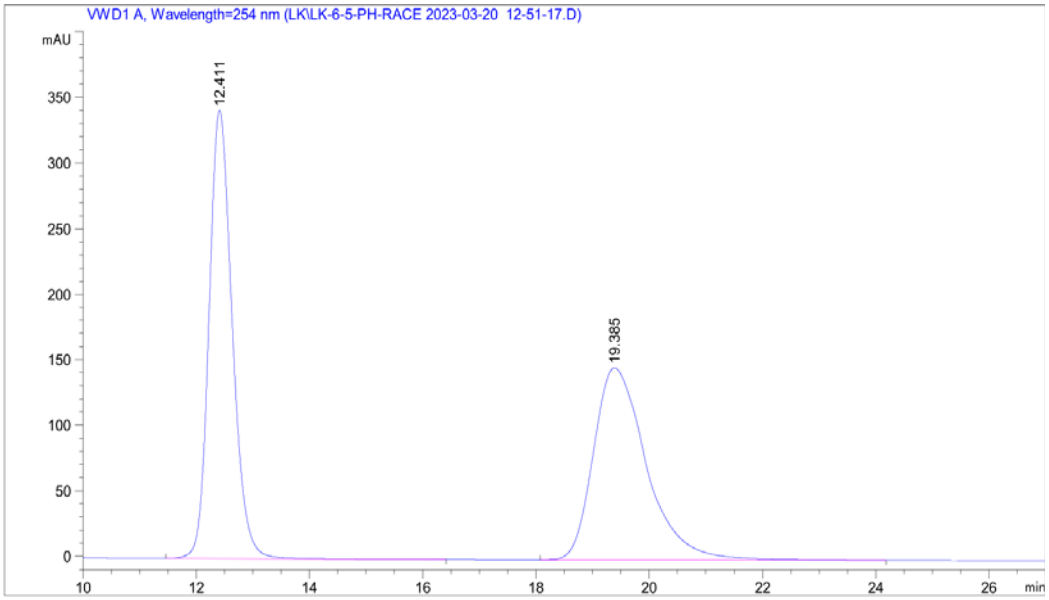
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **4b**



^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of **4c**

HPLC Chromatograms of All Products

HPLC chromatogram of racemic 3aa



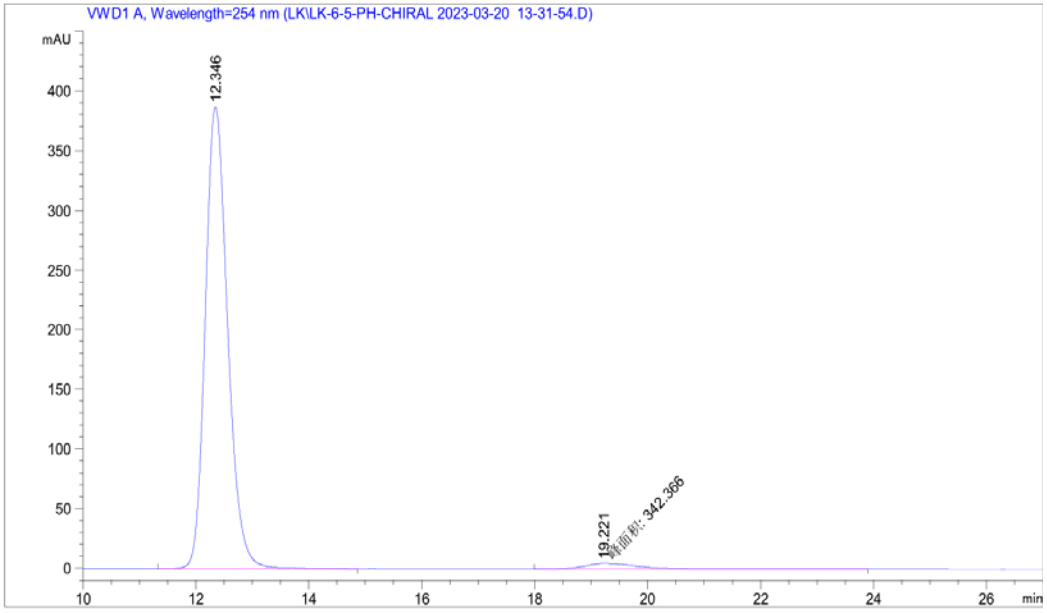
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.411 BB 0.4397 9746.51172 341.81125 50.6016

2 19.385 BB 1.0161 9514.75391 146.23349 49.3984

HPLC chromatogram of chiral 3aa



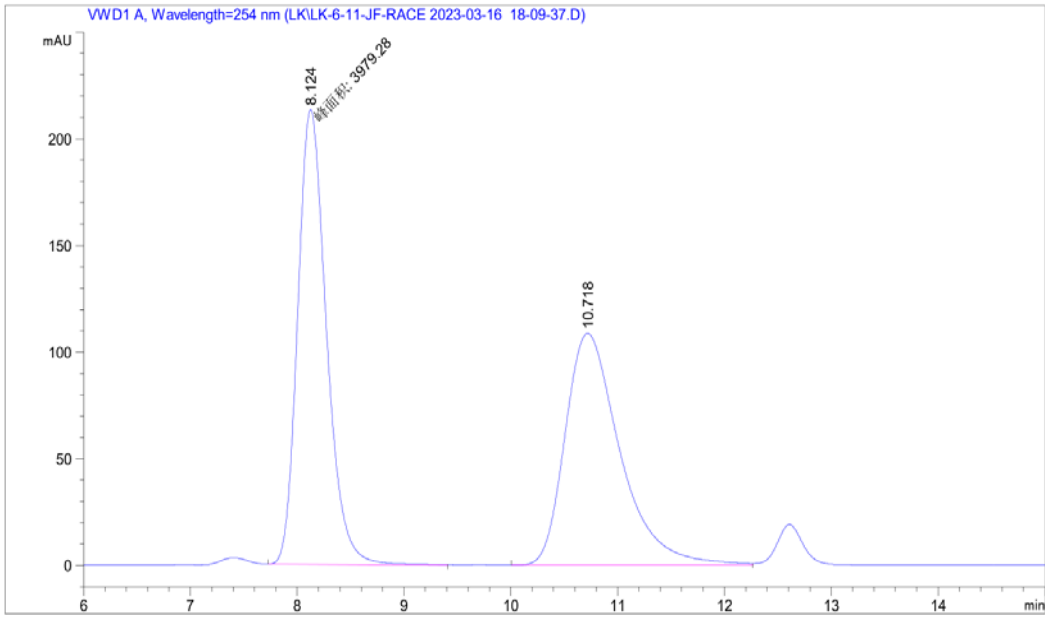
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.346 BB 0.4247 1.06724e4 387.08429 96.8918

2 19.221 MM 1.1784 342.36591 4.84214 3.1082

HPLC chromatogram of racemic 3ab



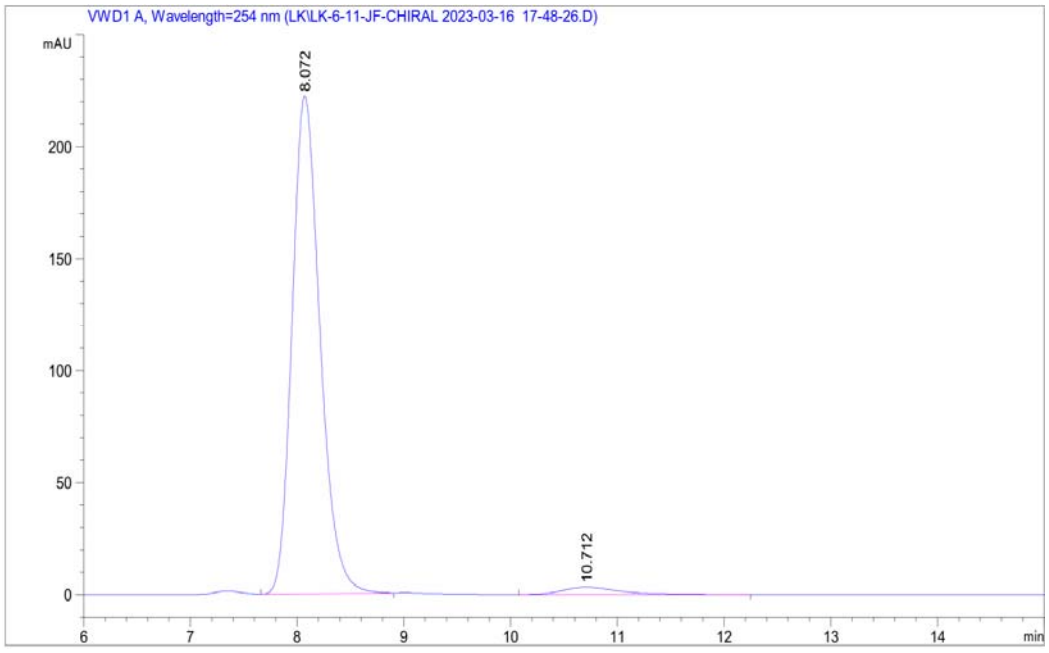
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.124 MM 0.3111 3979.28247 213.18013 50.6601

2 10.718 BV 0.5413 3875.57886 108.60440 49.3399

HPLC chromatogram of chiral 3ab



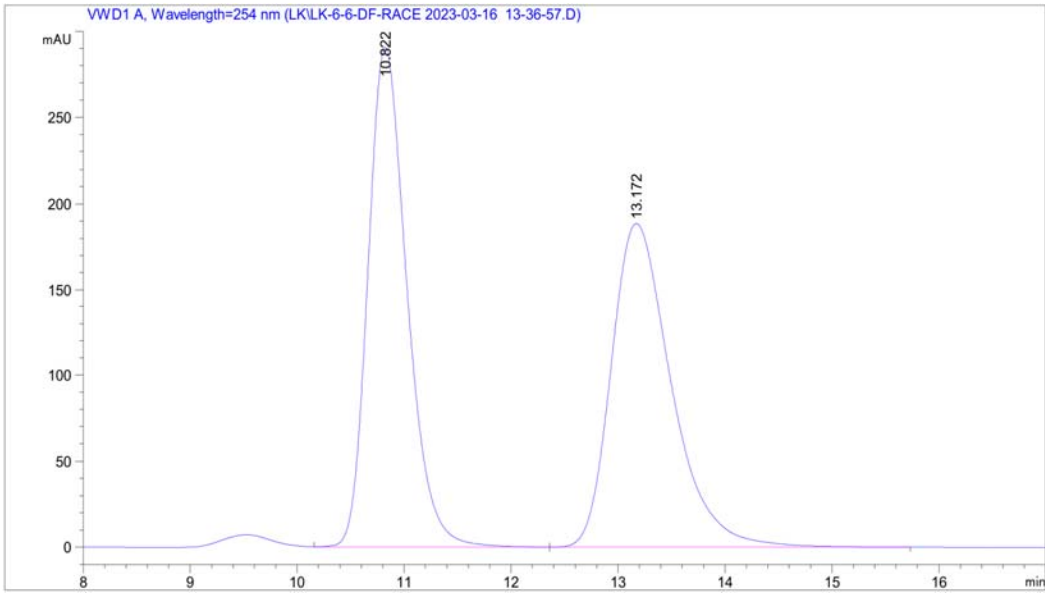
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.072 BB 0.2799 4035.49023 222.22003 97.1276

2 10.712 BB 0.5406 119.34270 3.31068 2.8724

HPLC chromatogram of racemic 3ac



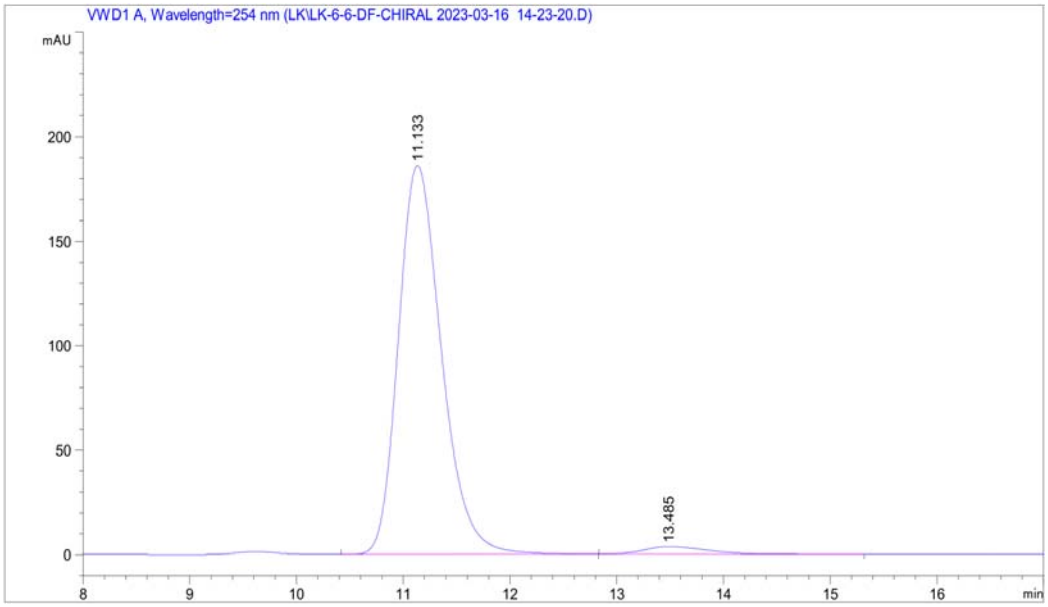
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.822 VB 0.3895 7363.75391 290.68613 50.0828

2 13.172 BB 0.5941 7339.40381 188.54808 49.9172

HPLC chromatogram of chiral 3ac



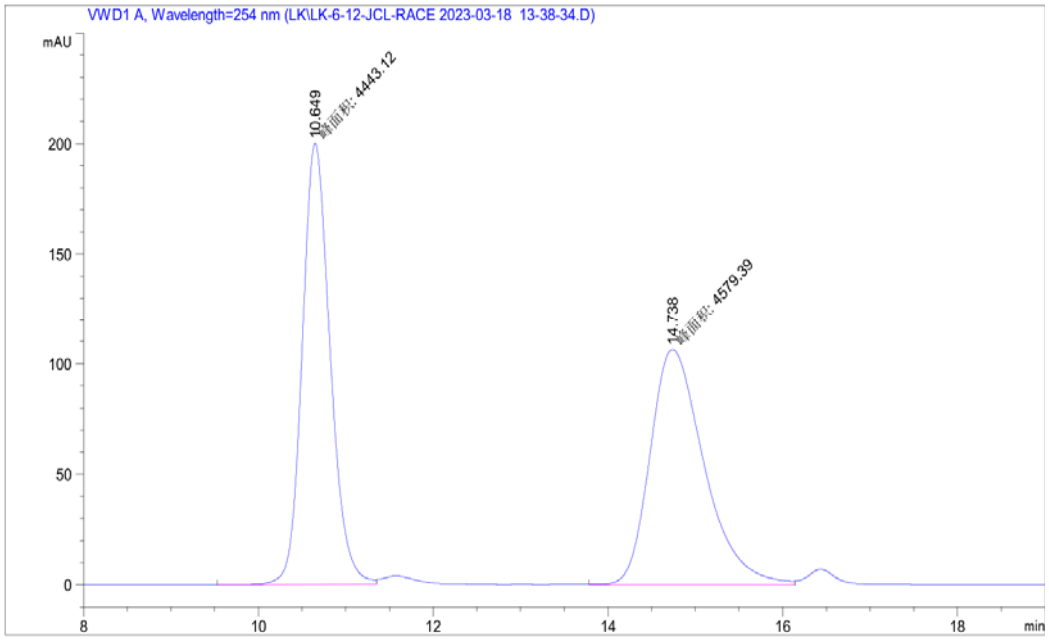
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 11.133 BB 0.4329 5213.42139 186.03273 97.3326

2 13.485 BB 0.6005 142.87244 3.49845 2.6674

HPLC chromatogram of racemic 3ad



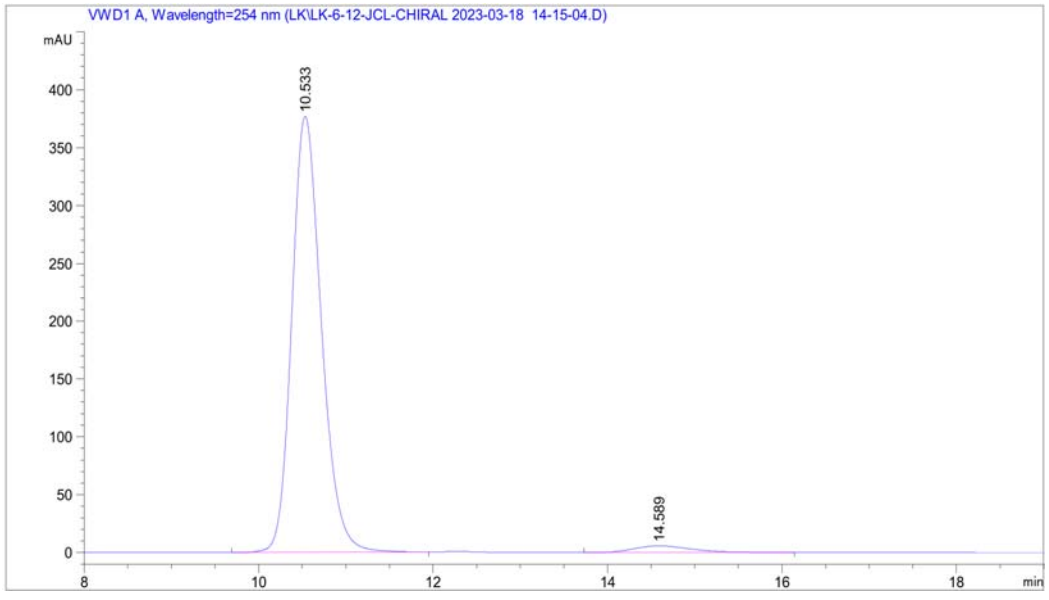
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.649 MM 0.3702 4443.11670 200.05740 49.2448

2 14.738 MM 0.7169 4579.39209 106.46825 50.7552

HPLC chromatogram of chiral 3ad



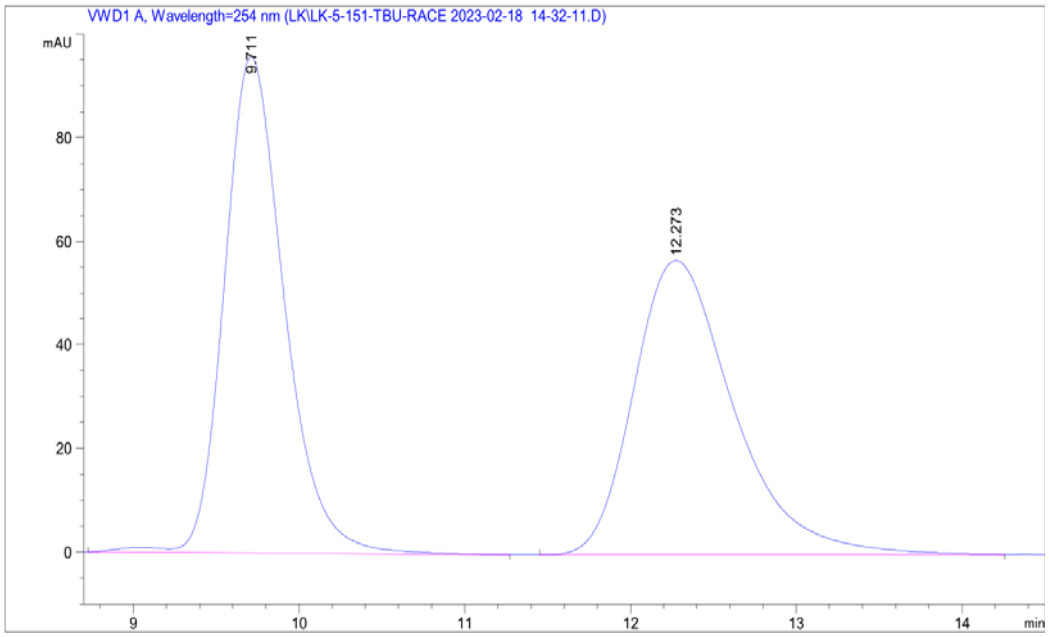
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.533 BB 0.3633 8889.61035 376.77554 97.2114

2 14.589 BB 0.6829 255.00665 5.65725 2.7886

HPLC chromatogram of racemic 3ae



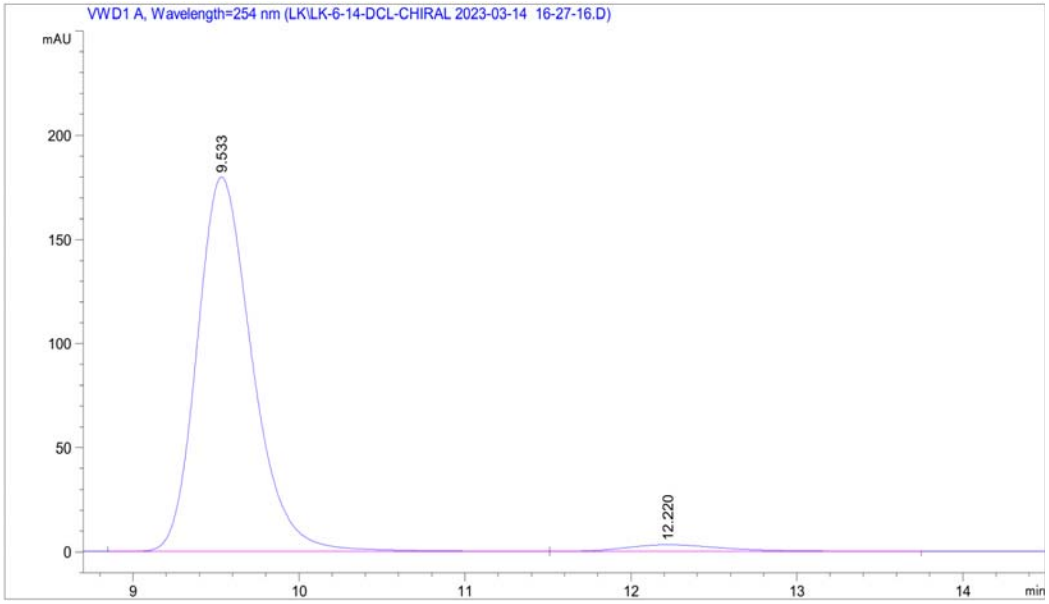
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.711 VB R 0.3845 2410.96289 95.82862 50.4034

2 12.273 BB 0.6301 2372.37231 56.82626 49.5966

HPLC chromatogram of chiral 3ae



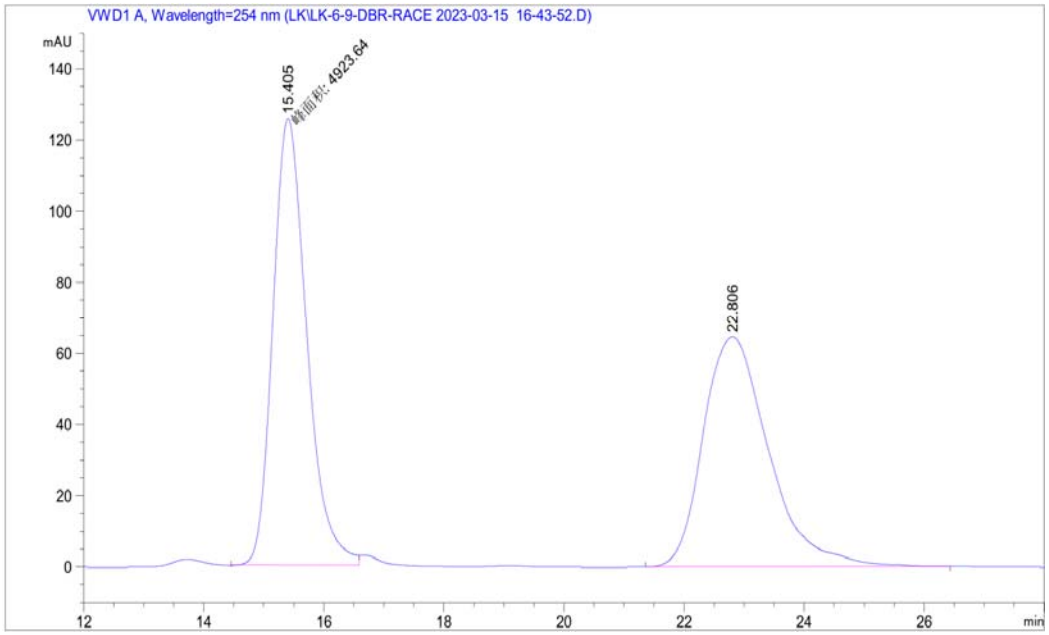
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.533 BB 0.3534 4136.37500 179.76462 97.0808

2 12.220 BB 0.5826 124.38047 3.14363 2.9192

HPLC chromatogram of racemic 3af



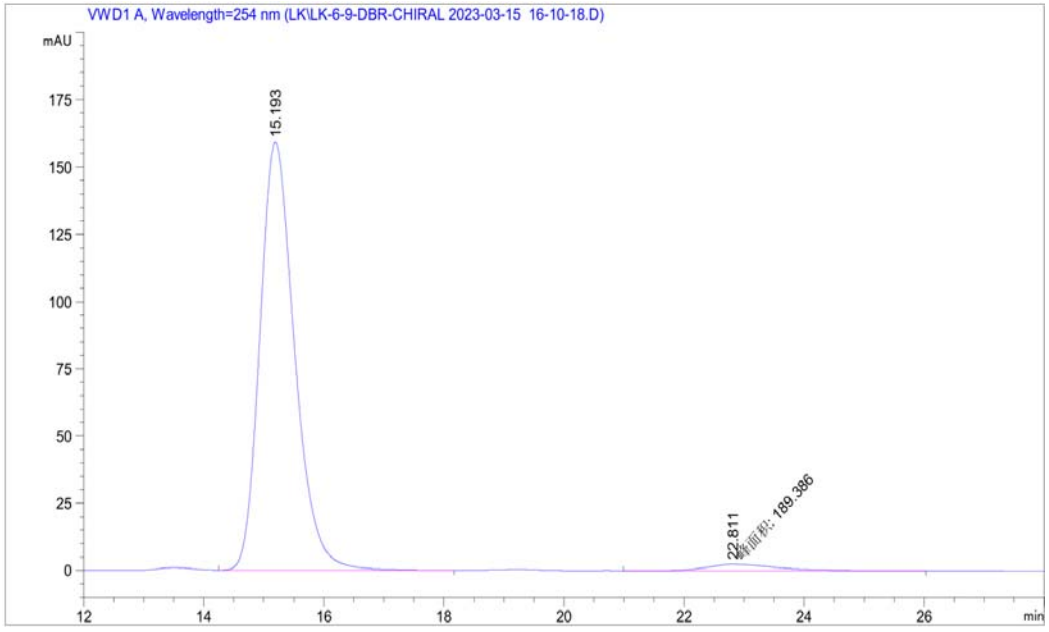
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 15.405 MM 0.6535 4923.63916 125.57277 50.1582

2 22.806 BB 1.1660 4892.58838 64.57186 49.8418

HPLC chromatogram of chiral 3af



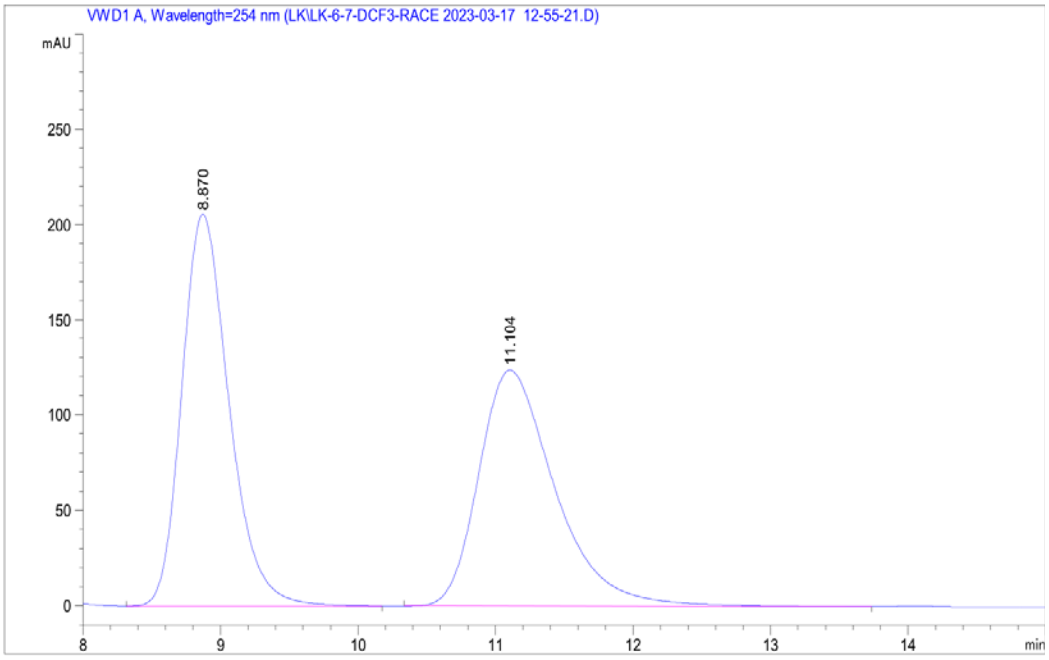
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 15.193 BB 0.6186 6391.42480 159.12971 97.1222

2 22.811 MM 1.2965 189.38553 2.43456 2.8778

HPLC chromatogram of racemic 3ag



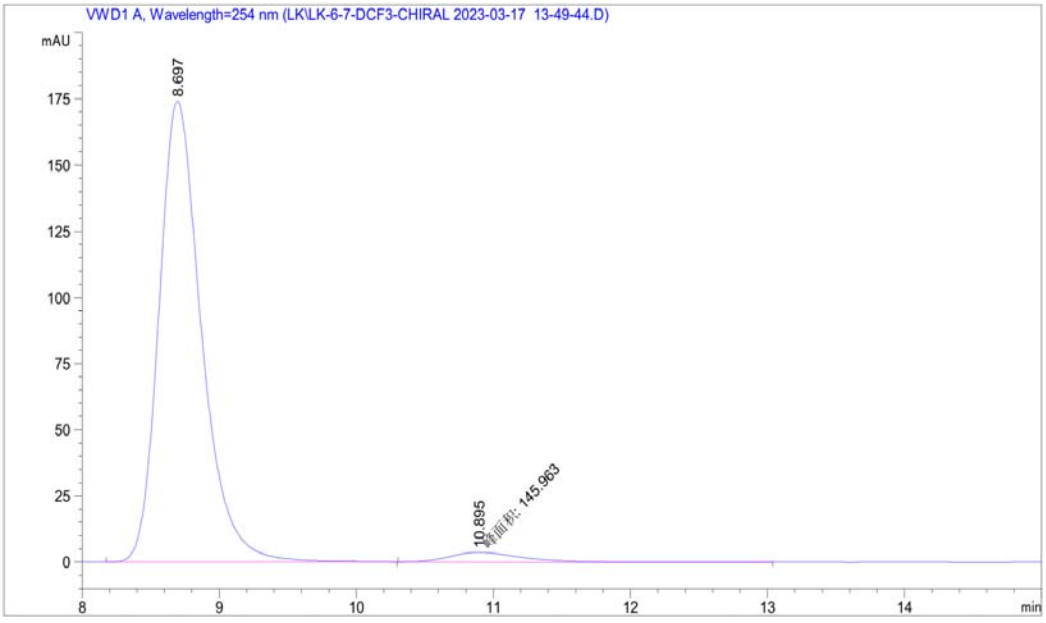
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.870 BB 0.3646 4890.48291 205.54852 50.5890

2 11.104 BB 0.5872 4765.24268 123.48866 49.2934

HPLC chromatogram of chiral 3ag



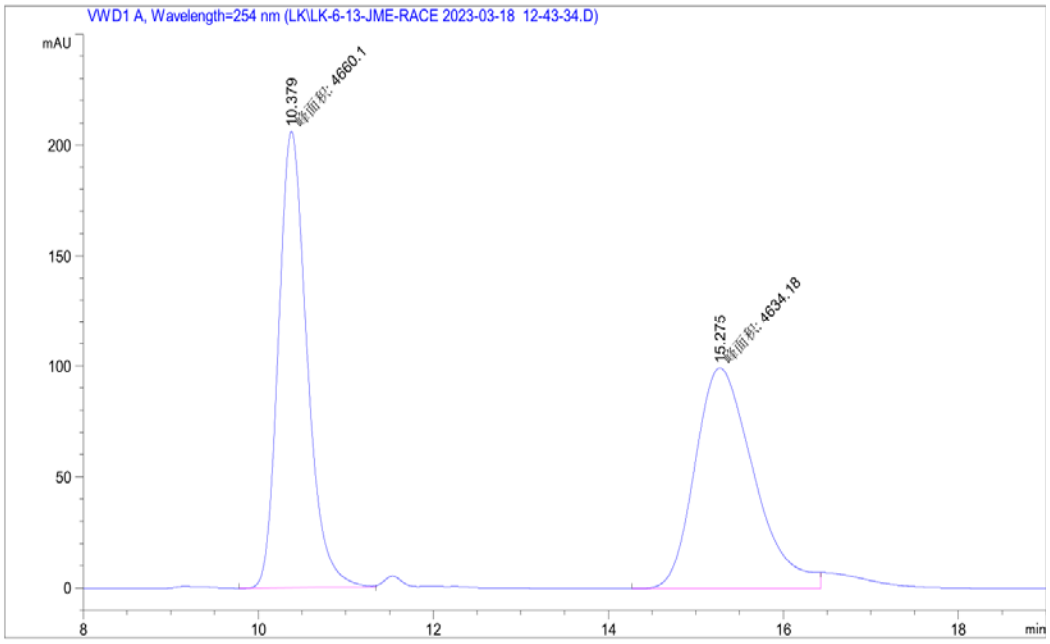
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.697 BB 0.3261 3745.42212 174.03154 96.2491

2 10.895 MM 0.6603 145.96313 3.68409 3.7509

HPLC chromatogram of racemic 3ah



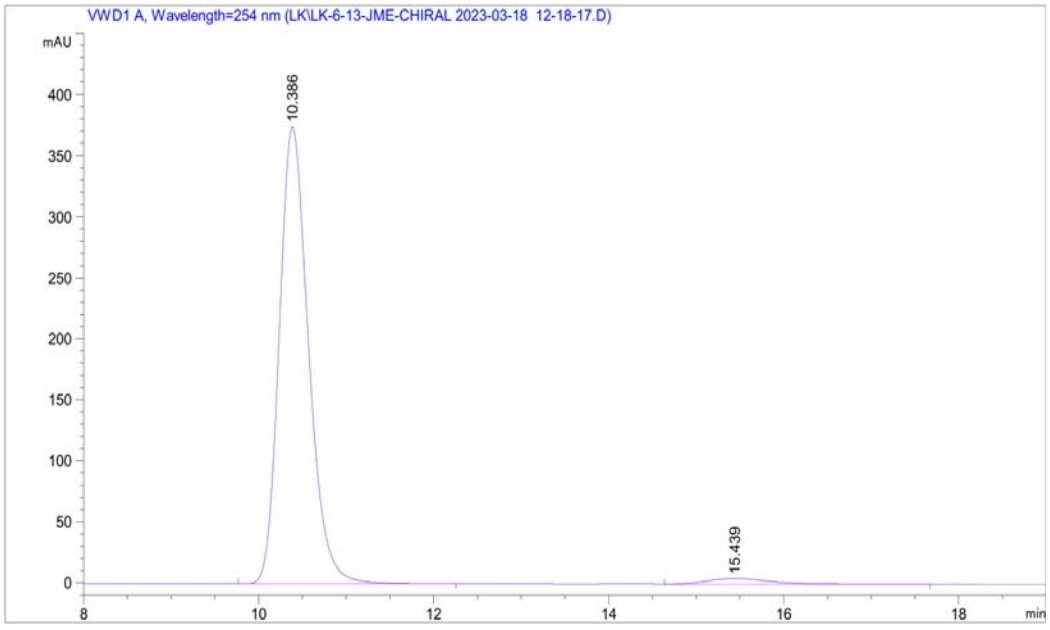
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.379 MM 0.3772 4660.09619 205.93436 50.1394

2 15.275 MM 0.7773 4634.18311 99.36477 49.8606

HPLC chromatogram of chiral 3ah



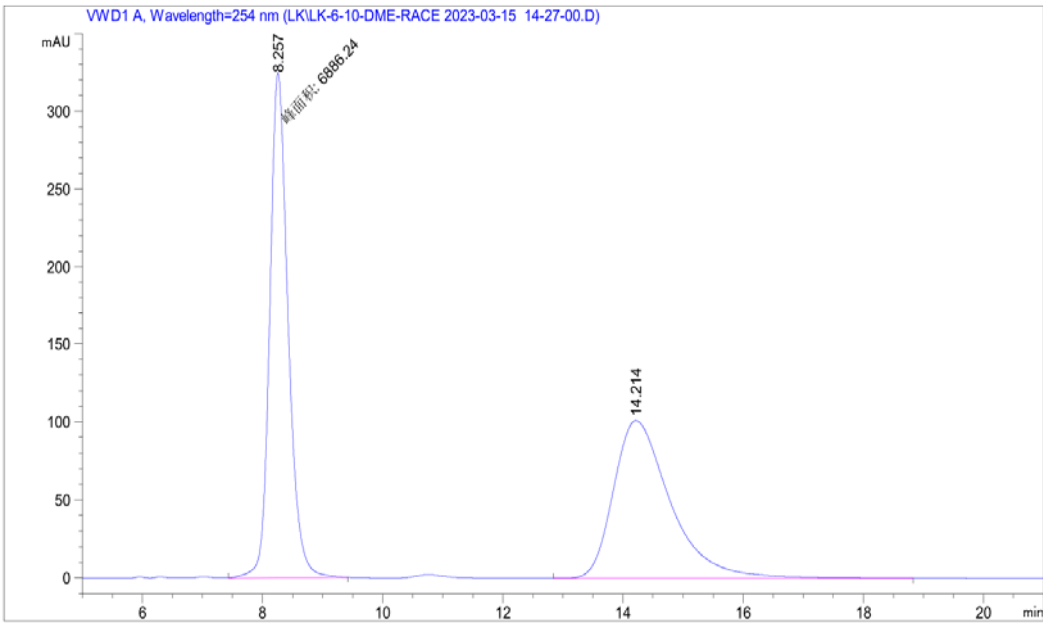
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.386 BB 0.3574 8676.68262 374.31039 97.5986

2 15.439 BB 0.7222 213.48985 4.43024 2.4014

HPLC chromatogram of racemic 3ai



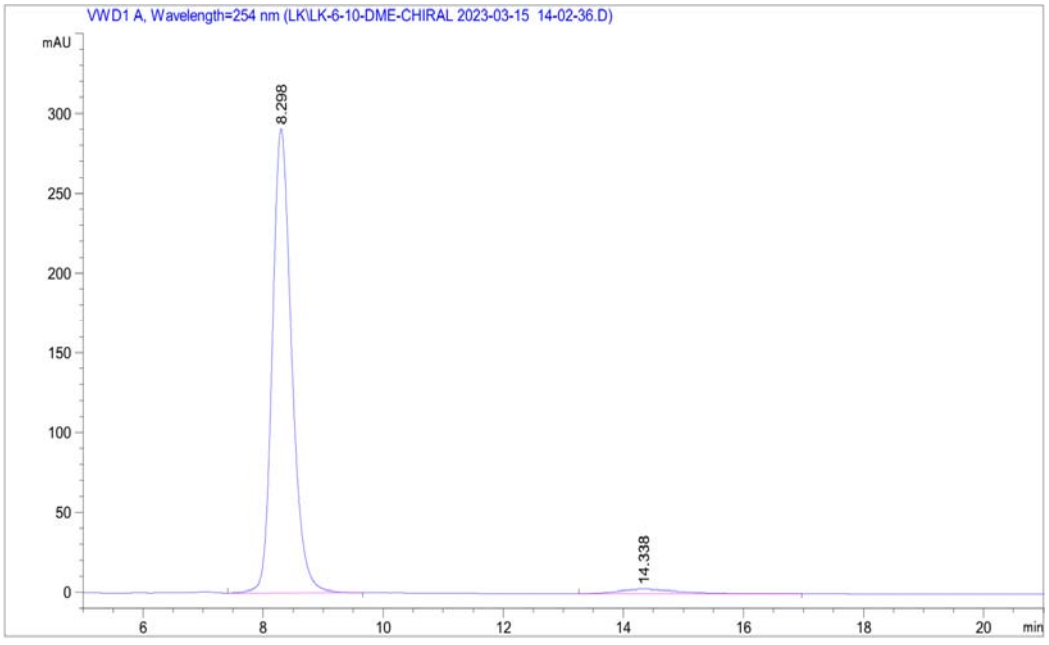
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.257 MM 0.3537 6886.24463 324.51385 50.7771

2 14.214 BB 1.0010 6675.47949 101.14153 49.2229

HPLC chromatogram of chiral 3ai



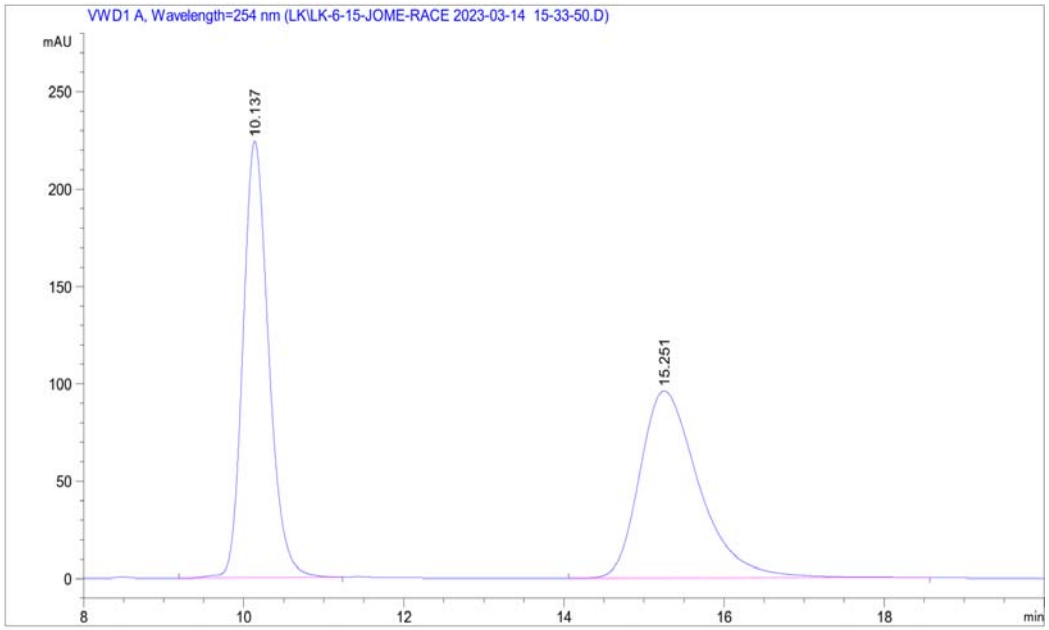
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.298 BB 0.3428 6494.64502 290.53421 97.2380

2 14.338 BB 0.9233 184.47995 2.69597 2.7620

HPLC chromatogram of racemic 3aj



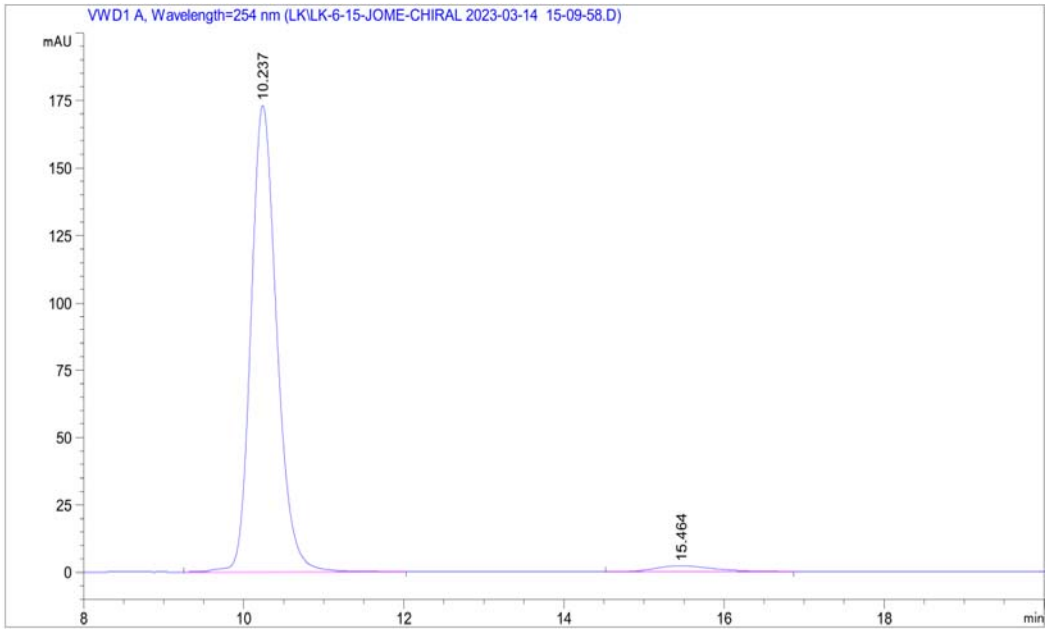
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.137 BB 0.3432 4997.22559 224.04471 50.2172

2 15.251 BB 0.7989 4954.00635 96.02008 49.7828

HPLC chromatogram of chiral 3aj



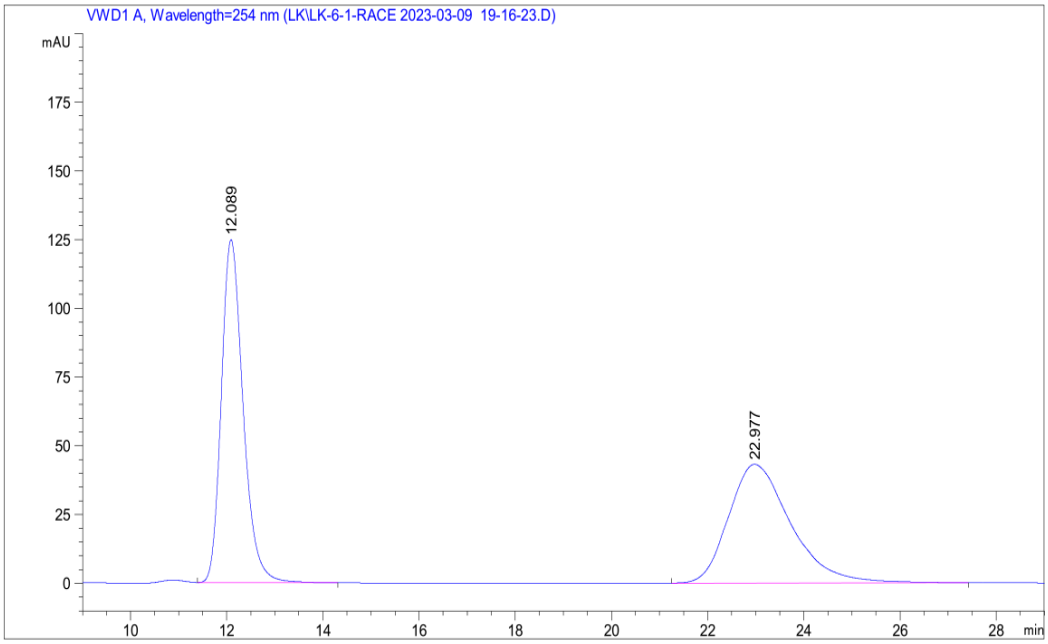
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.237 BB 0.3444 3876.92432 173.04712 97.2453

2 15.464 BB 0.6792 109.82150 2.25879 2.7547

HPLC chromatogram of racemic 3ak



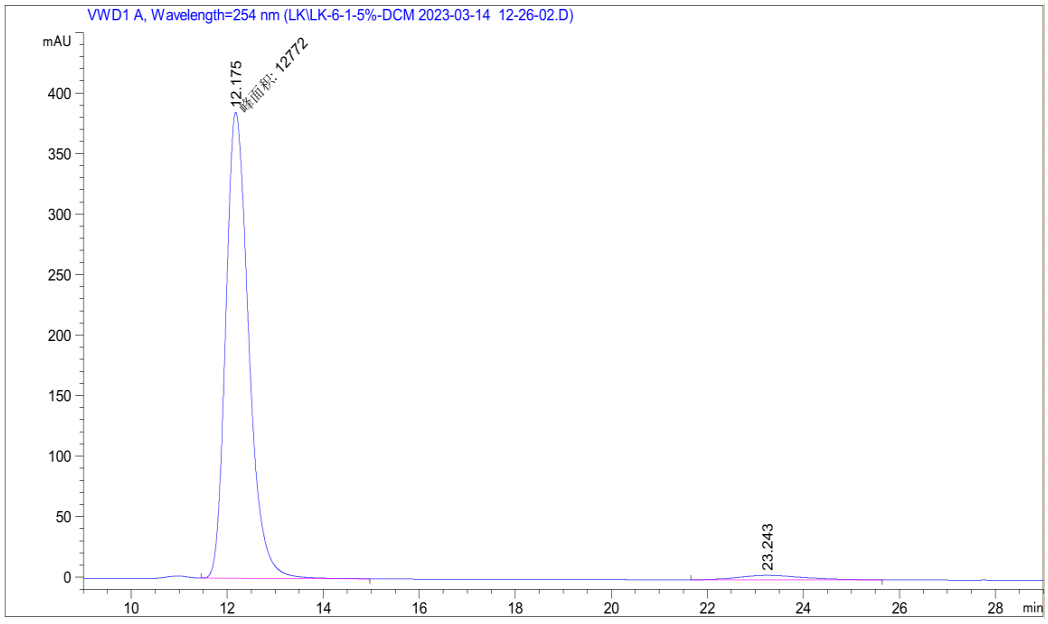
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.089 BB 0.4815 3915.87061 124.65032 50.4042

2 22.977 BB 1.3103 3853.07227 43.12831 49.5958

HPLC chromatogram of chiral 3ak



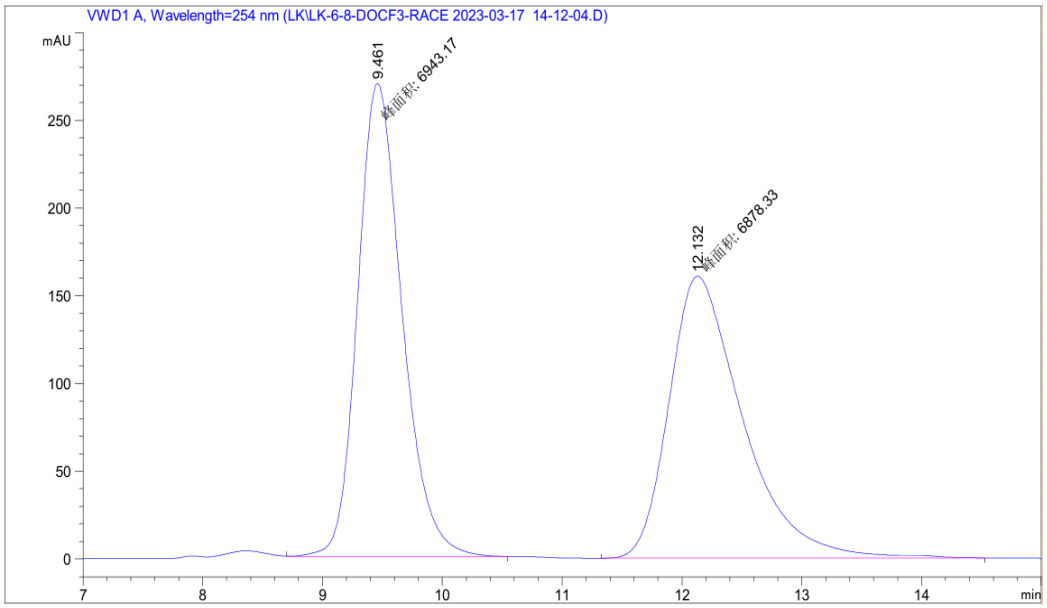
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.175 MM 0.5527 1.27720e4 385.14749 97.3463

2 23.243 BB 1.1427 348.16599 3.75874 2.6537

HPLC chromatogram of racemic 3al



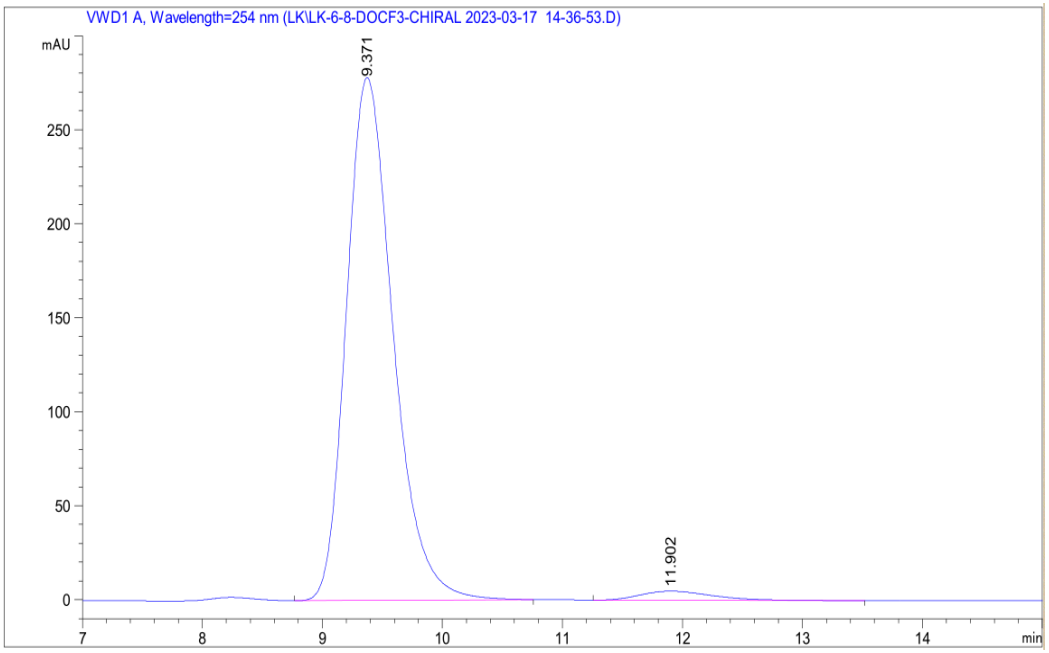
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.461 MM 0.4294 6943.16943 269.47696 50.2346

2 12.132 MM 0.7135 6878.32861 160.67171 49.7654

HPLC chromatogram of chiral 3al



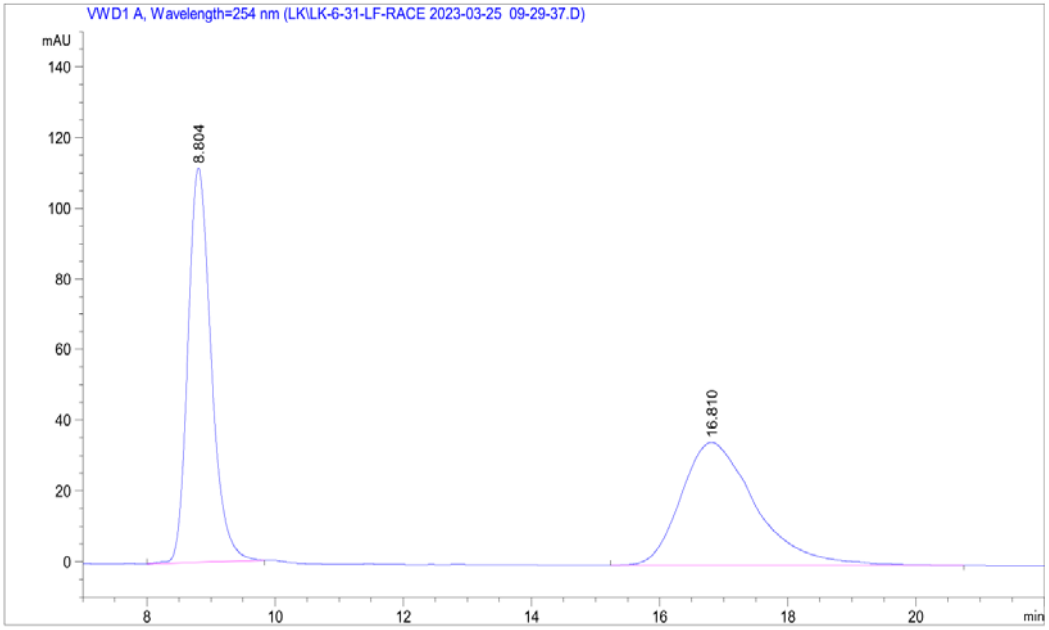
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.371 BB 0.4156 7494.07959 277.94095 97.3069

2 11.902 BB 0.6323 207.40701 4.86603 2.6931

HPLC chromatogram of racemic 3am



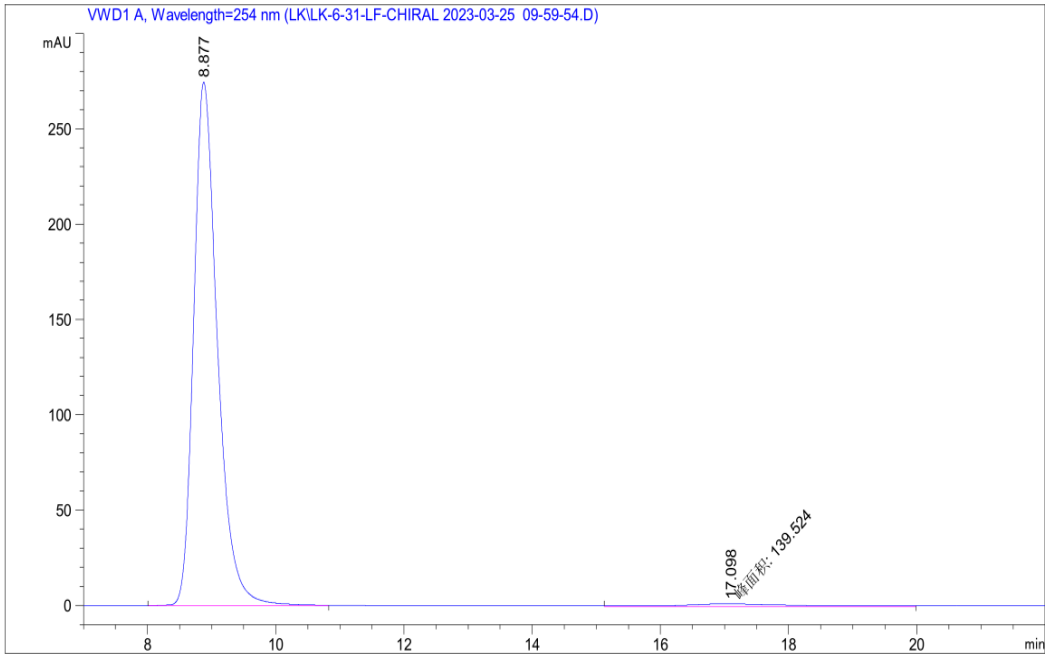
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.804 BB 0.3889 2798.58862 111.47934 50.1383

2 16.810 BB 1.1751 2783.14746 34.61430 49.8617

HPLC chromatogram of chiral 3am



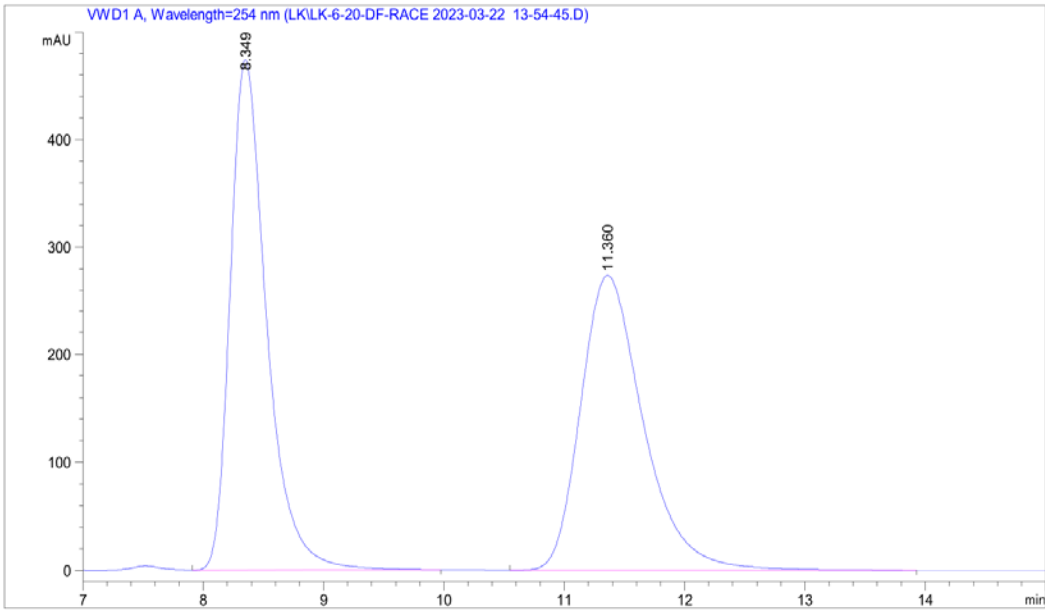
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.877 BB 0.3893 7067.05469 274.51691 98.0639

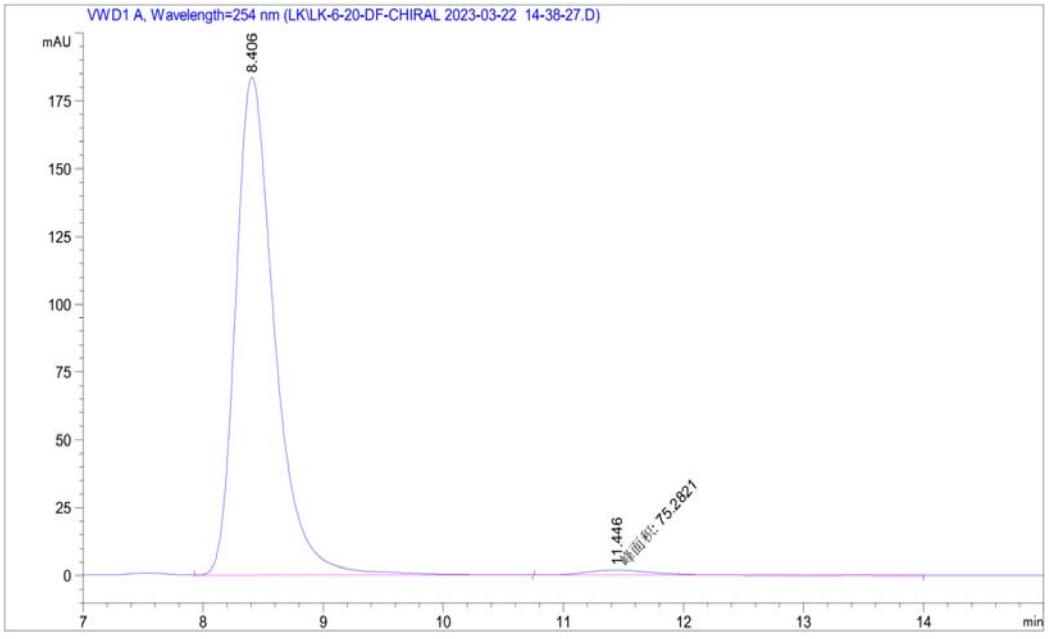
2 17.098 MM 1.8127 139.52391 1.28282 1.9361

HPLC chromatogram of racemic 3an



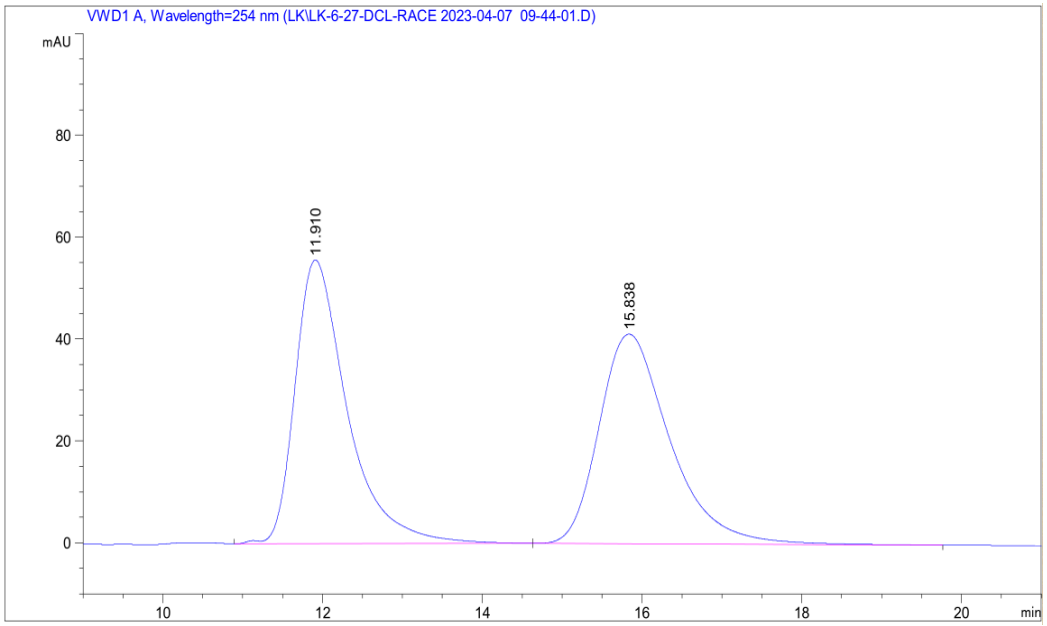
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.349	VB	0.3194	9961.03223	473.59622	50.2937
2	11.360	BB	0.5470	9844.69141	273.48209	49.7063

HPLC chromatogram of chiral 3an



#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.406	BB	0.3416	4132.44189	183.61232	98.2109
2	11.446	MM	0.6703	75.28205	1.87183	1.7891

HPLC chromatogram of racemic 3ao



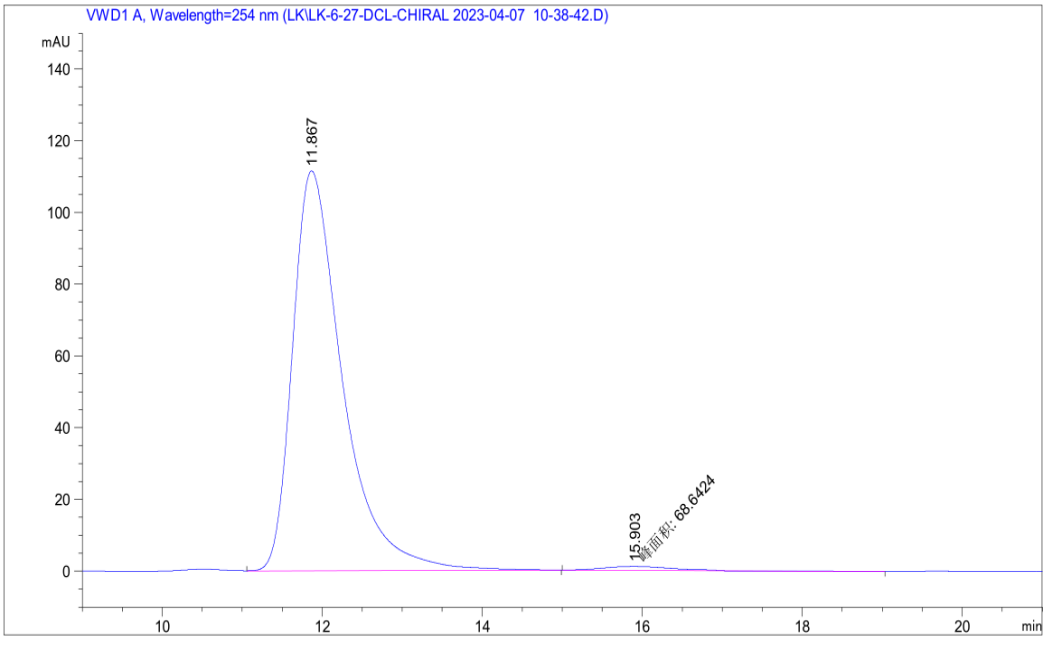
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 11.910 VB R 0.6896 2528.25977 55.69974 49.9118

2 15.838 BB 0.9312 2537.19312 41.15700 50.0882

HPLC chromatogram of chiral 3ao



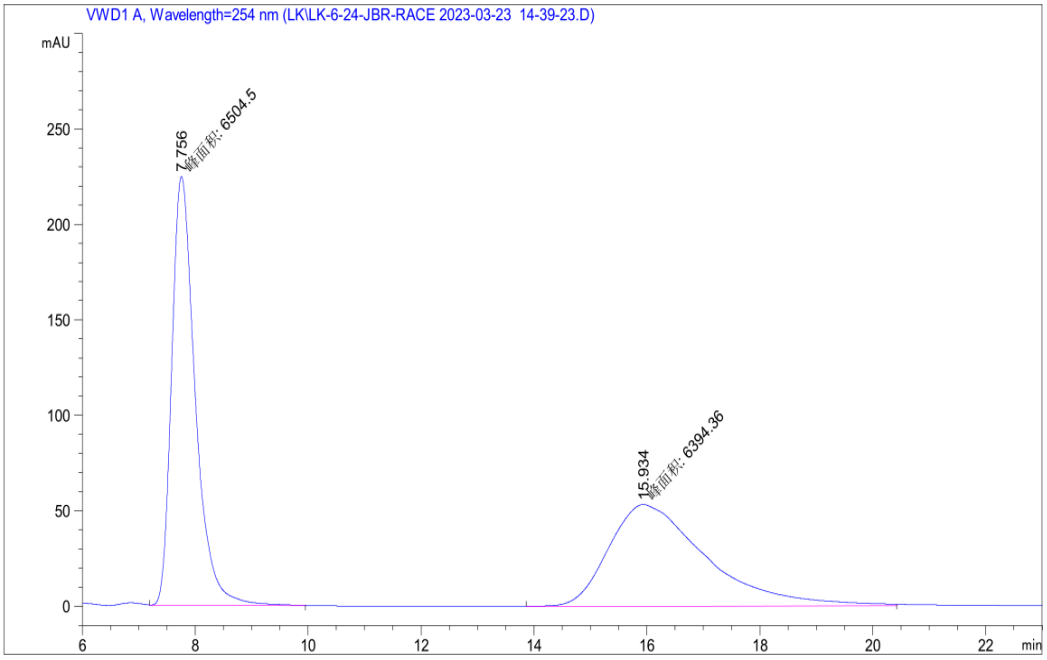
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 11.867 BB 0.6498 4832.34521 111.46315 98.5994

2 15.903 MM 0.9999 68.64243 1.14418 1.4006

HPLC chromatogram of racemic 3ap



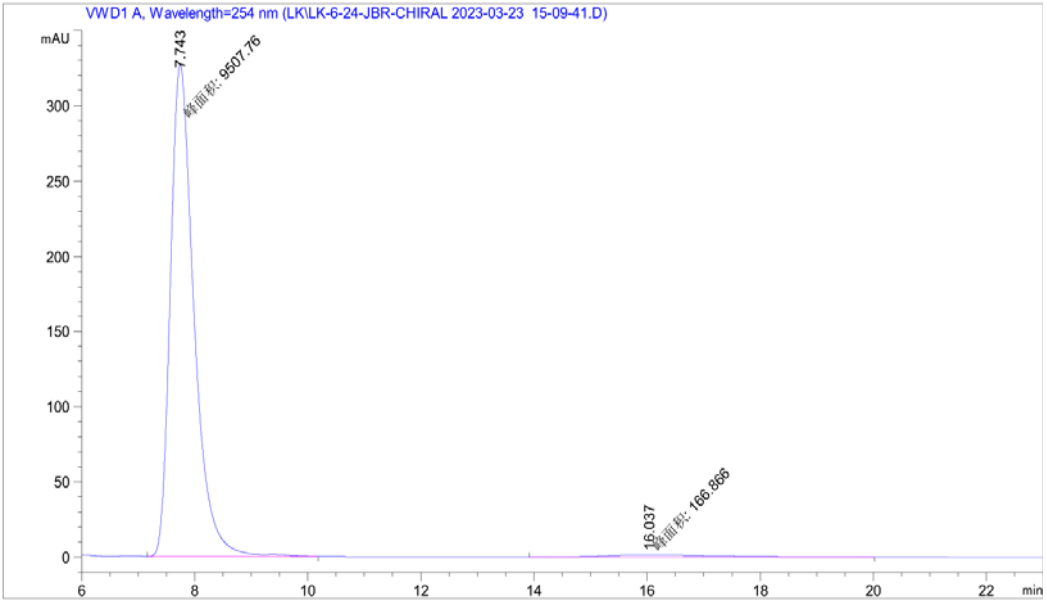
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 7.756 MM 0.4831 6504.49805 224.40334 50.4269

2 15.934 MM 1.9966 6394.36084 53.37725 49.5731

HPLC chromatogram of chiral 3ap



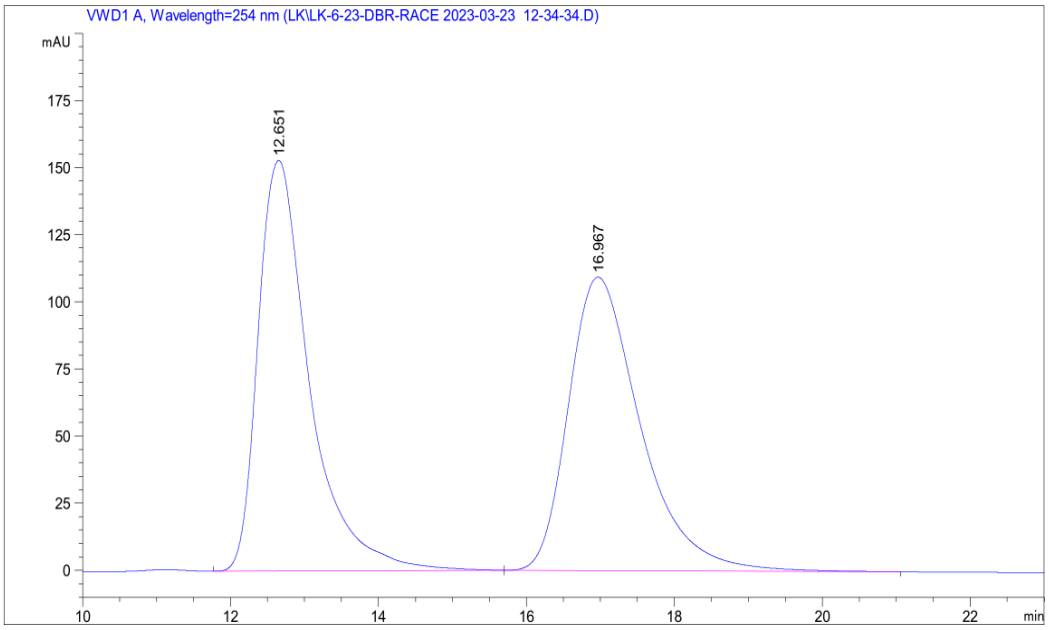
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 7.743 MM 0.4853 9507.76367 326.55042 98.2752

2 16.037 MM 1.9778 166.86604 1.40619 1.7248

HPLC chromatogram of racemic 3aq



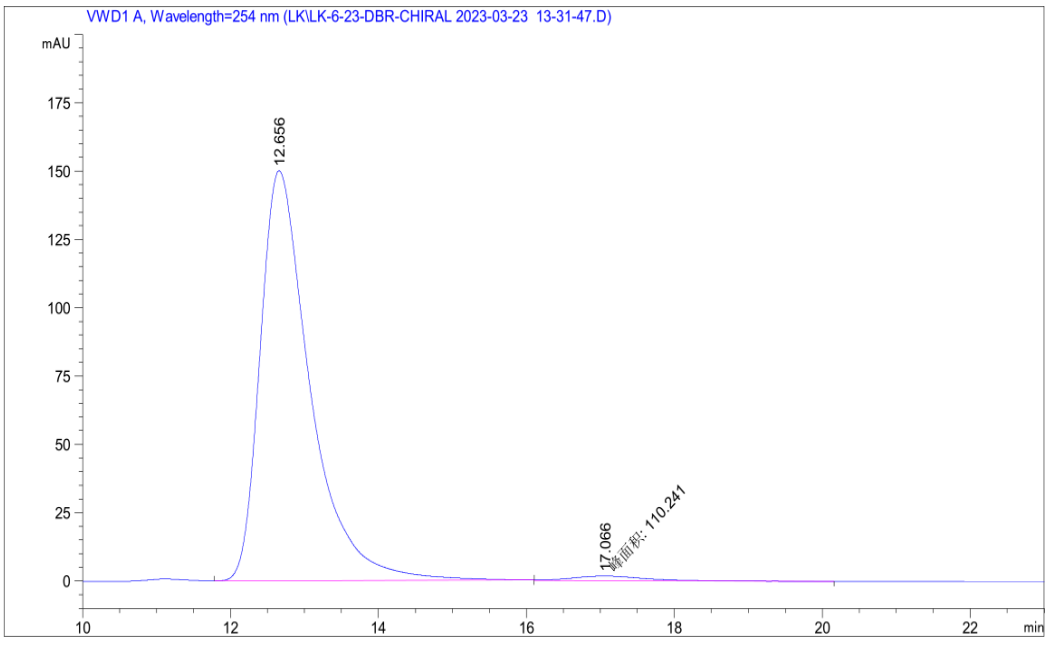
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.651 BB 0.7380 7367.92090 152.95476 49.9532

2 16.967 BB 1.0251 7381.72314 109.26917 50.0468

HPLC chromatogram of chiral 3aq



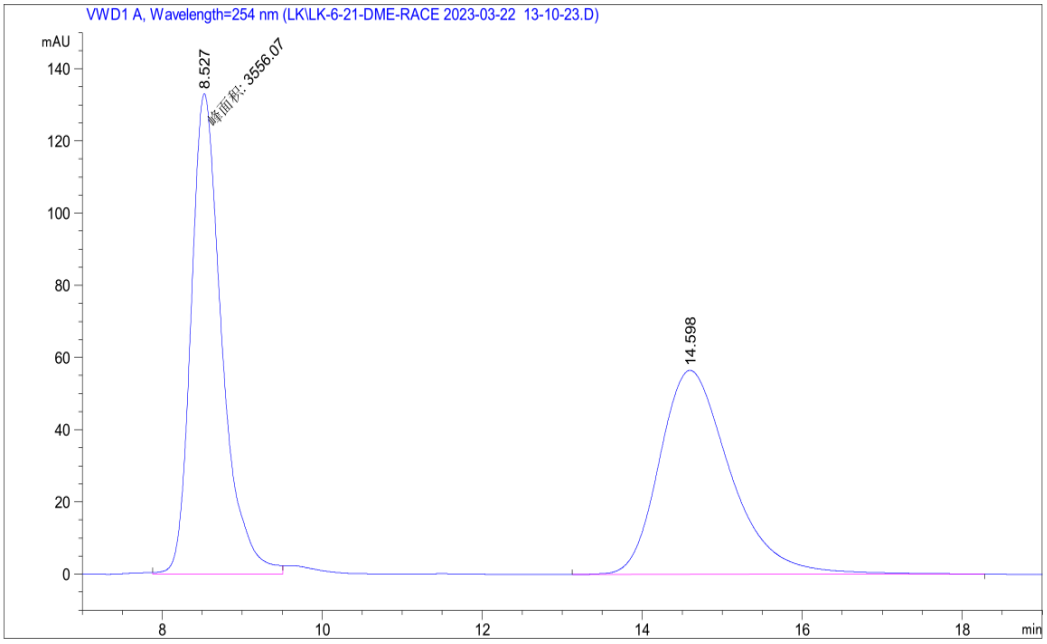
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.656 BB 0.7009 7060.32764 150.05360 98.4626

2 17.066 MM 1.0892 110.24139 1.68686 1.5374

HPLC chromatogram of racemic 3ar



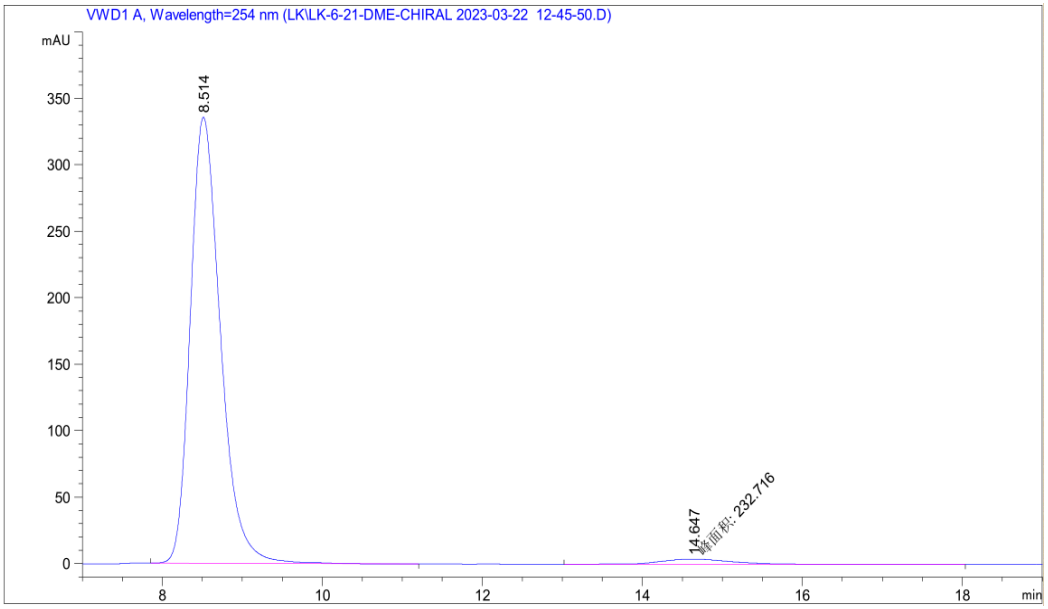
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.527 MM 0.4454 3556.06885 133.05405 50.5521

2 14.598 BB 0.9398 3478.38794 56.53533 49.4479

HPLC chromatogram of chiral 3ar



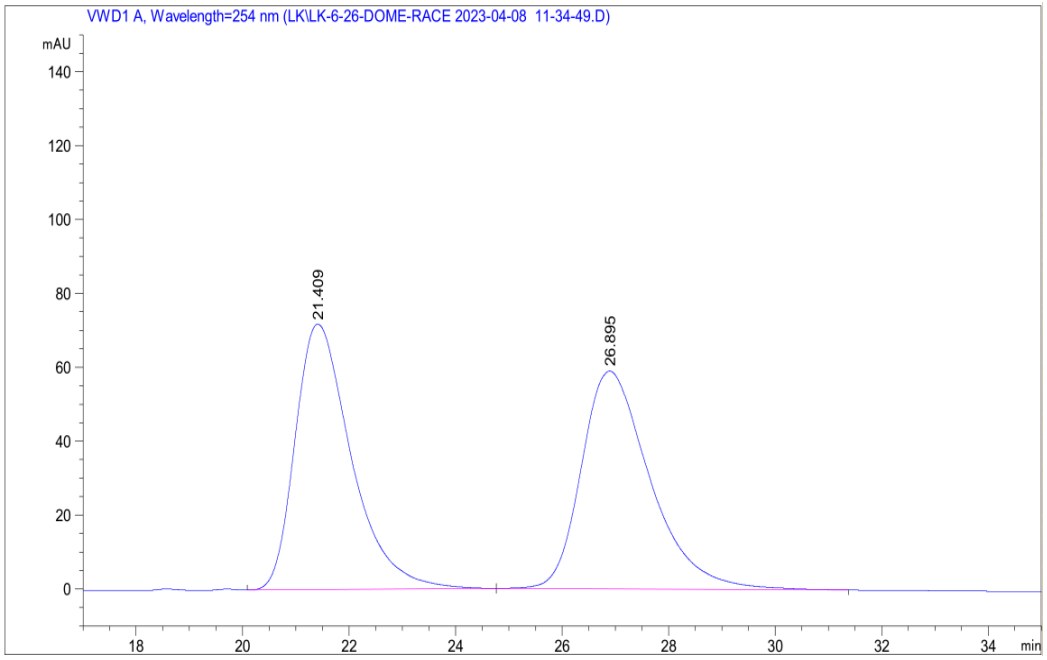
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.514 BB 0.4031 8803.67578 335.54712 97.4247

2 14.647 MM 0.9883 232.71626 3.92439 2.5753

HPLC chromatogram of racemic 3as



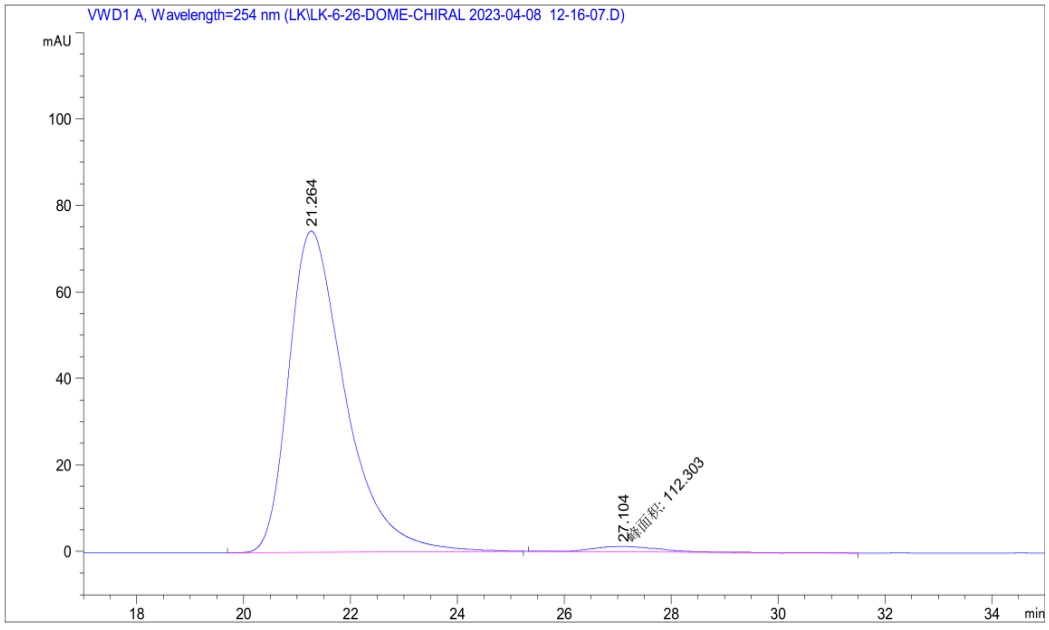
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 21.409 BB 1.1491 5266.14209 71.84633 49.8633

2 26.895 BB 1.3372 5295.01221 58.99105 50.1367

HPLC chromatogram of chiral 3as



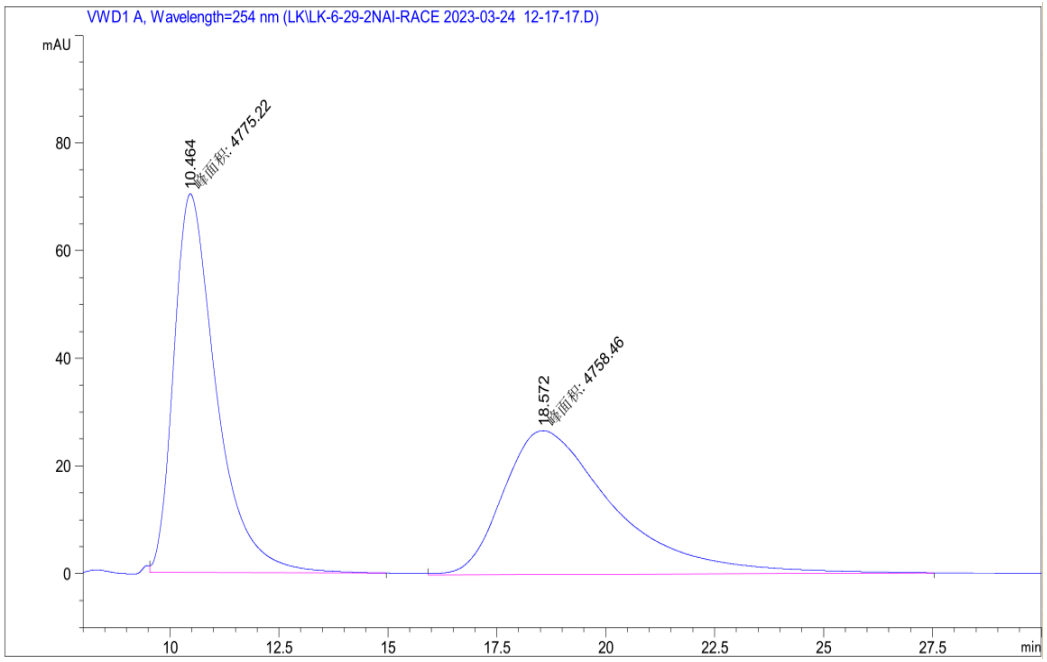
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 21.264 BB 1.0911 5452.08789 74.30270 97.9818

2 27.104 MM 1.5147 112.30274 1.23571 2.0182

HPLC chromatogram of racemic 3at



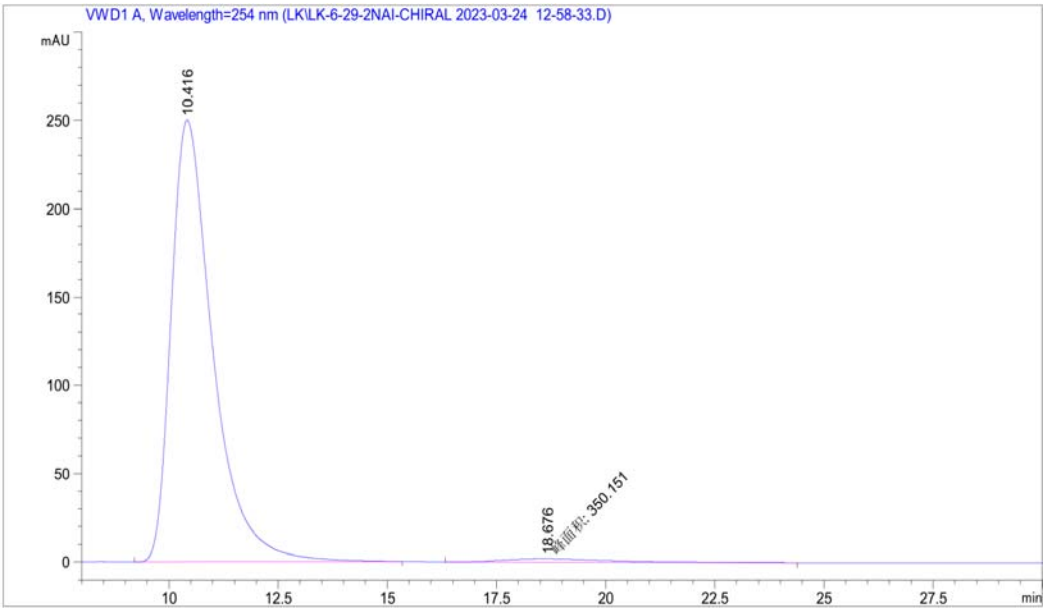
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.464 MM 1.1311 4775.21826 70.36512 50.0879

2 18.572 MM 2.9684 4758.46045 26.71745 49.9121

HPLC chromatogram of chiral 3at



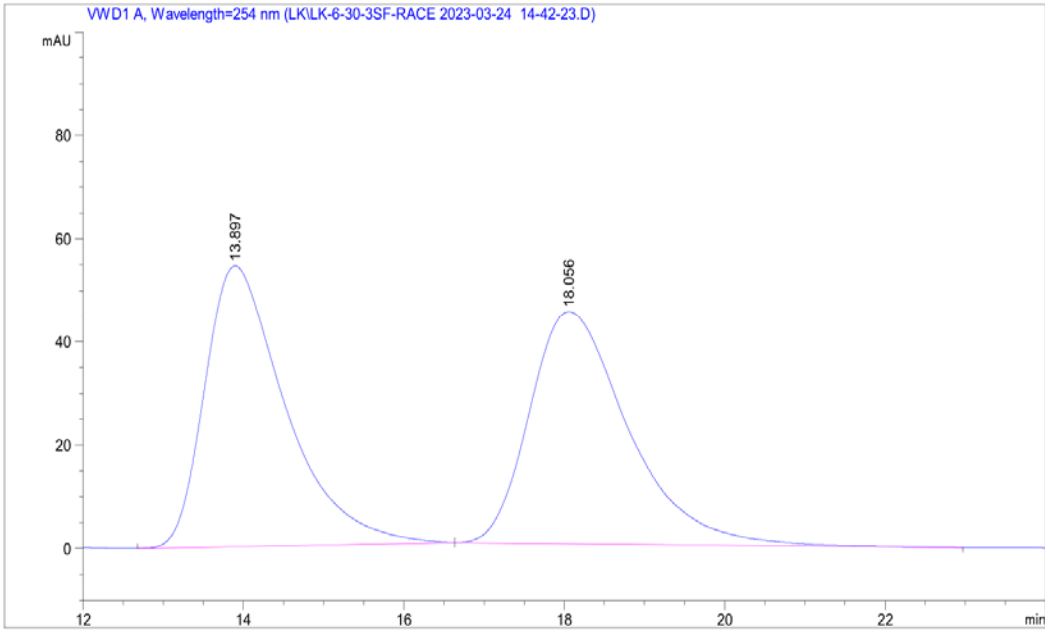
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.416 BB 0.9997 1.65646e4 250.11142 97.9299

2 18.676 MM 2.9922 350.15140 1.95037 2.0701

HPLC chromatogram of racemic 3au



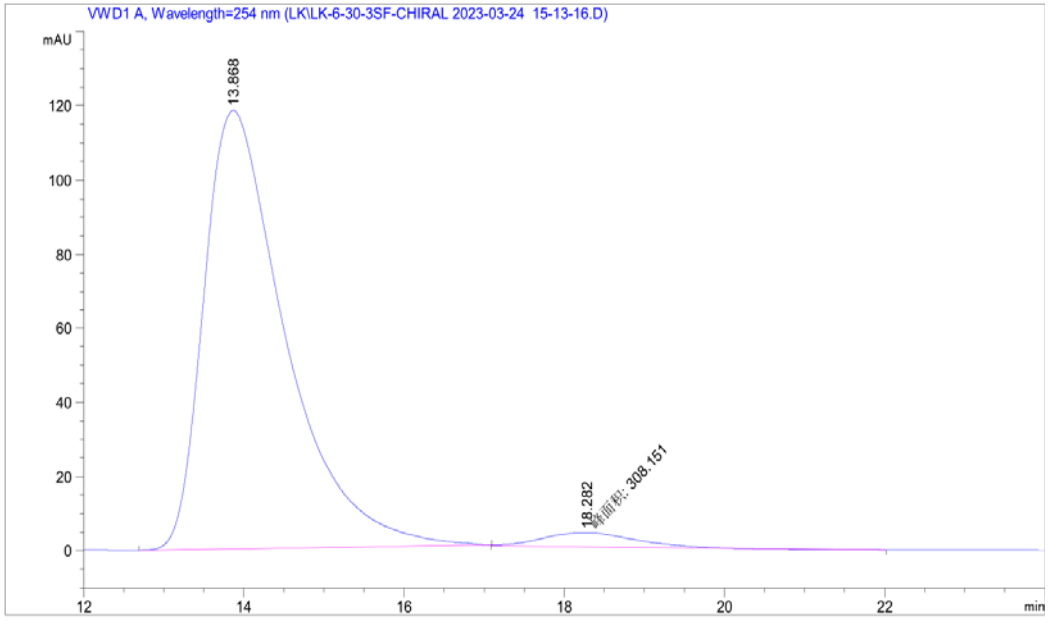
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 13.897 BB 1.0416 3801.03491 54.44036 49.7557

2 18.056 BB 1.3131 3838.36328 44.95751 50.2443

HPLC chromatogram of chiral 3au



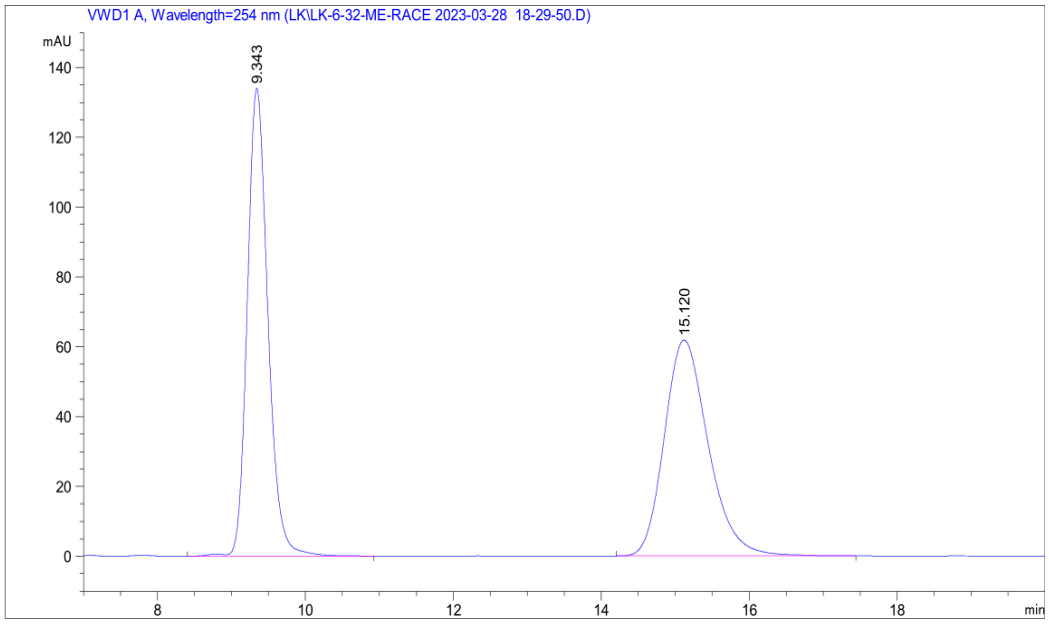
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 13.868 BB 1.0406 8357.58105 118.24073 96.4440

2 18.282 MM 1.3462 308.15146 3.81518 3.5560

HPLC chromatogram of racemic 3av



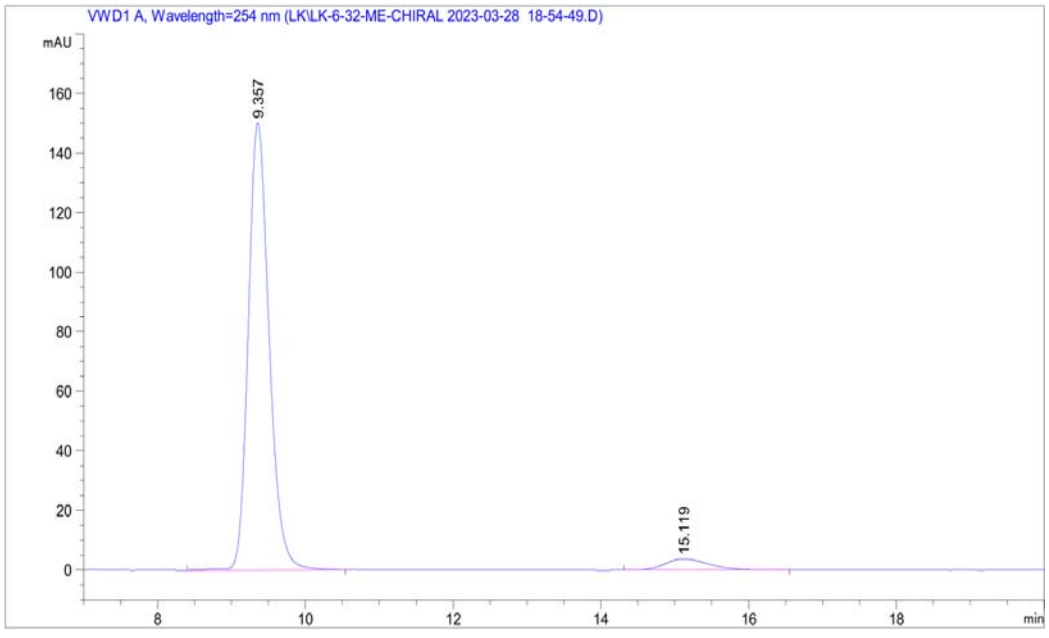
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.343 VB R 0.2975 2589.20361 133.98419 50.3832

2 15.120 BB 0.6341 2549.82227 61.83123 49.6168

HPLC chromatogram of chiral 3av



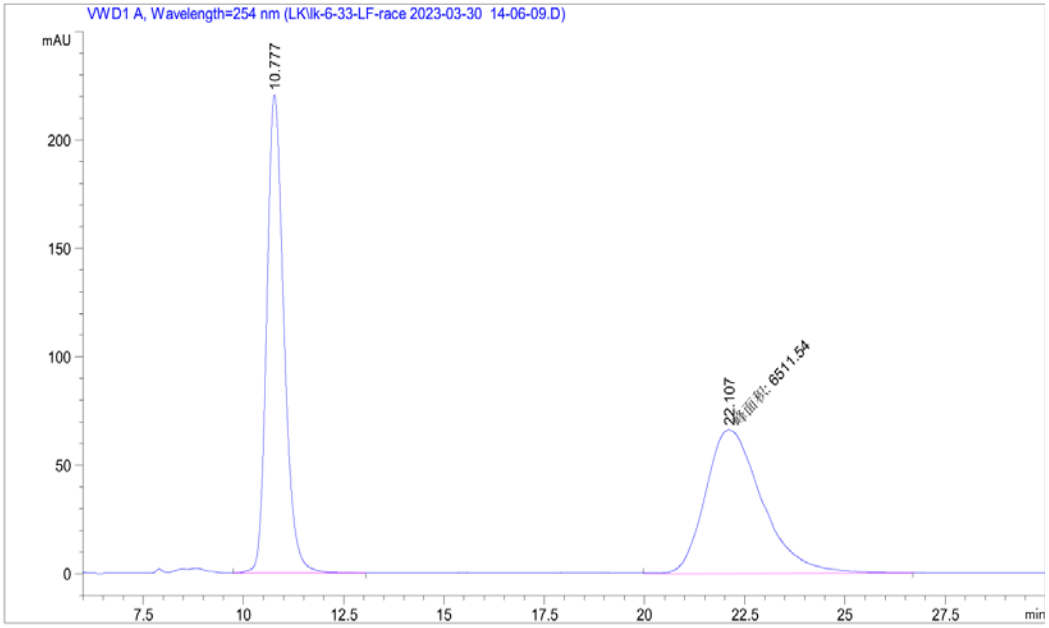
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.357 VB R 0.3009 2932.26001 150.09129 94.9517

2 15.119 BB 0.6309 155.90021 3.73543 5.0483

HPLC chromatogram of racemic 3bk



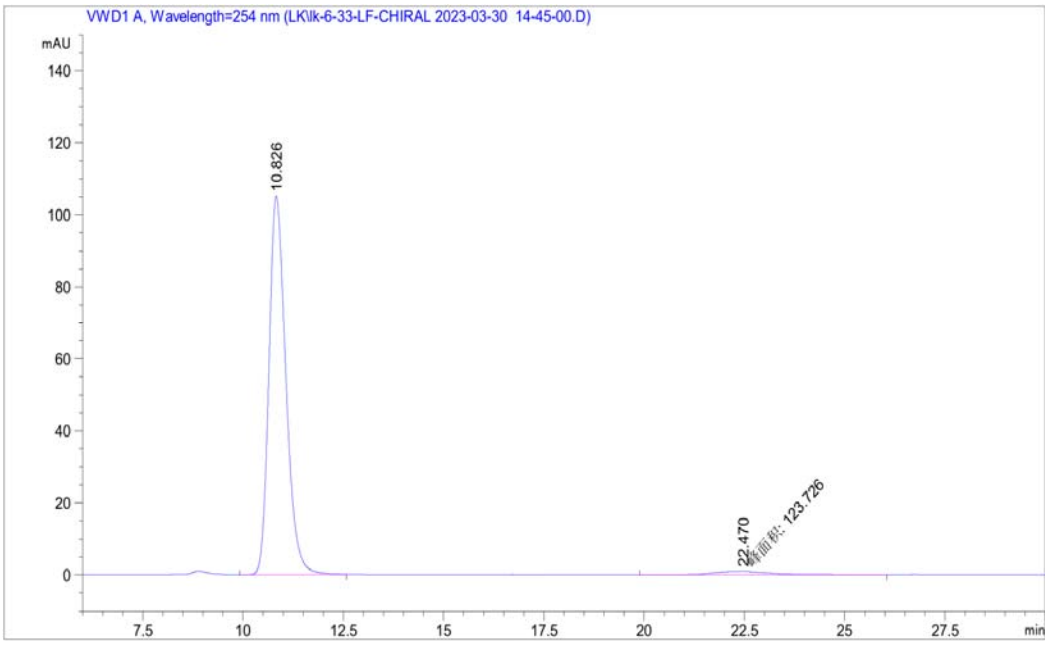
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.777 BB 0.4589 6591.08398 220.40889 50.3035

2 22.107 MM 1.6406 6511.53809 66.15160 49.6965

HPLC chromatogram of chiral 3bk



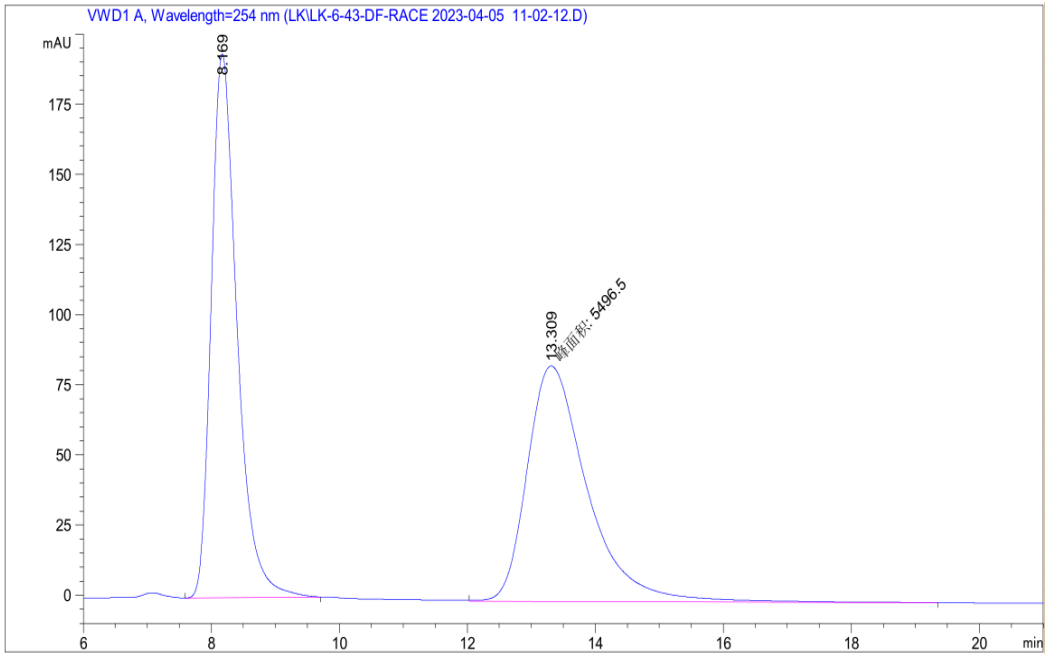
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.826 BB 0.4517 3089.81055 105.18149 96.1498

2 22.470 MM 1.8391 123.72643 1.12124 3.8502

HPLC chromatogram of racemic 3ck



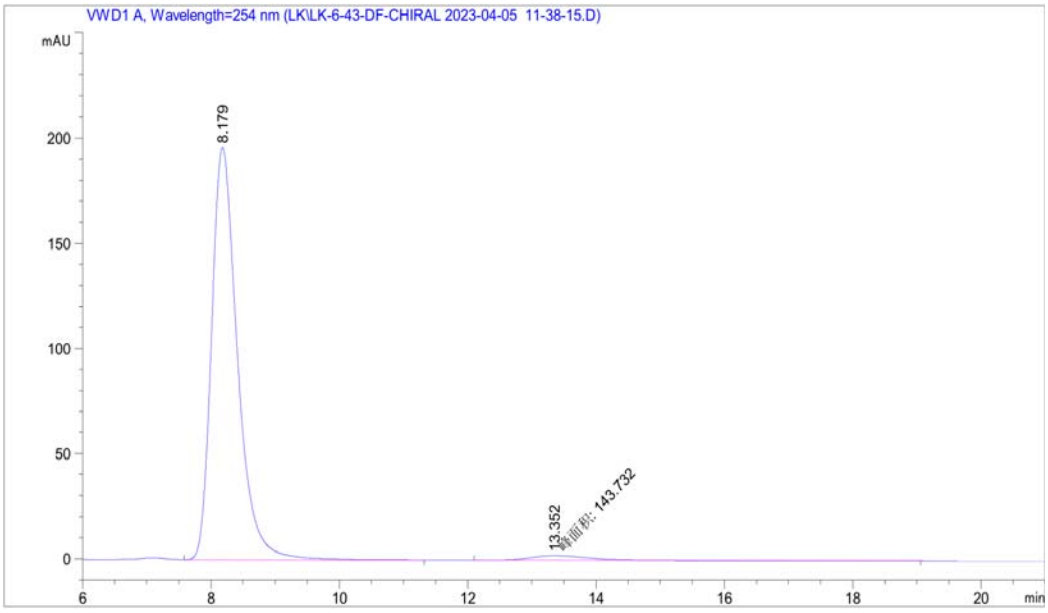
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.169 BB 0.4271 5432.75879 193.74809 49.7084

2 13.309 MM 1.0916 5496.49707 83.92175 50.2916

HPLC chromatogram of chiral 3ck



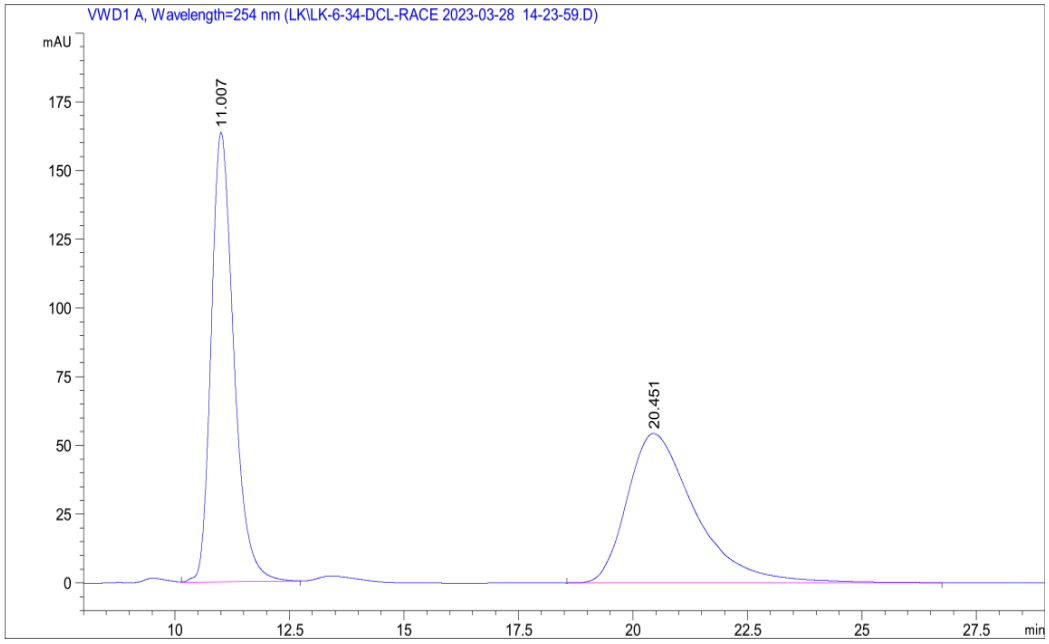
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.179 BB 0.4256 5483.38770 195.90038 97.4457

2 13.352 MM 1.0651 143.73236 2.24916 2.5543

HPLC chromatogram of racemic 3dk



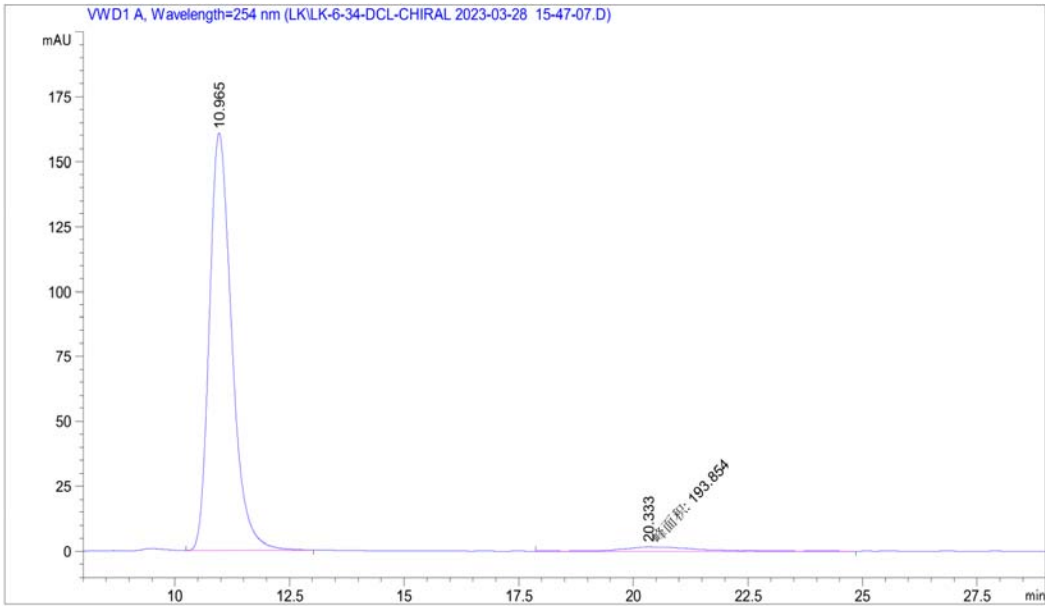
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 11.007 VB 0.5286 5609.83008 163.39287 49.9915

2 20.451 BB 1.5477 5611.73193 54.34380 50.0085

HPLC chromatogram of chiral 3dk



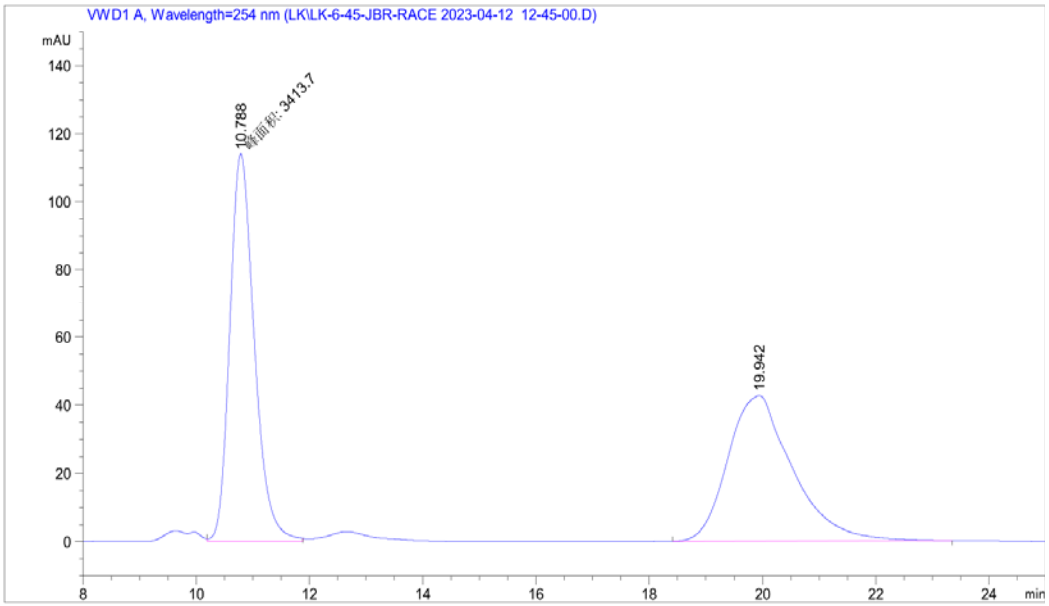
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.965 BB 0.5305 5446.04297 160.64973 96.5628

2 20.333 MM 1.9043 193.85396 1.69664 3.4372

HPLC chromatogram of racemic 3ek



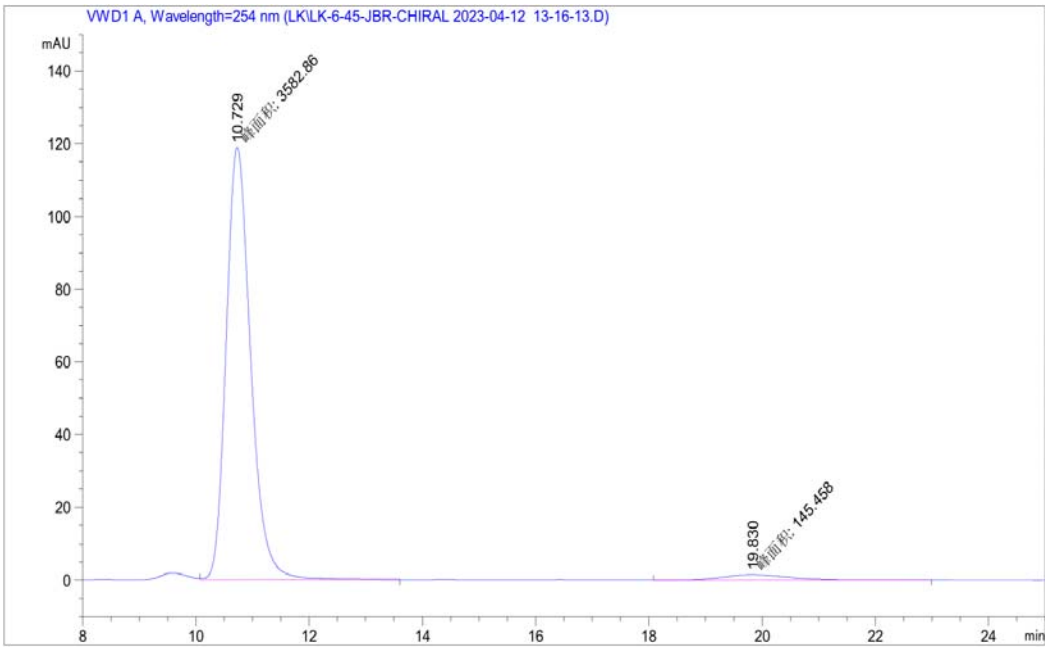
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.788 MM 0.4998 3413.69653 113.83076 50.3019

2 19.942 BB 1.1453 3372.72339 42.66145 49.6981

HPLC chromatogram of chiral 3ek



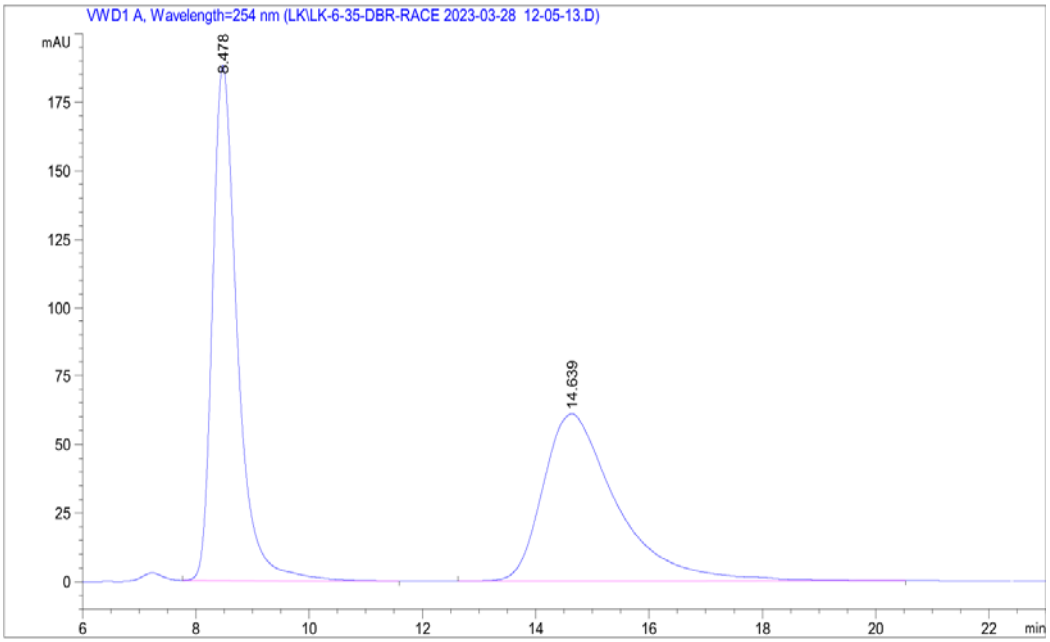
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 10.729 MM 0.5017 3582.85718 119.01801 96.0986

2 19.830 MM 1.5088 145.45807 1.60682 3.9014

HPLC chromatogram of racemic 3fk



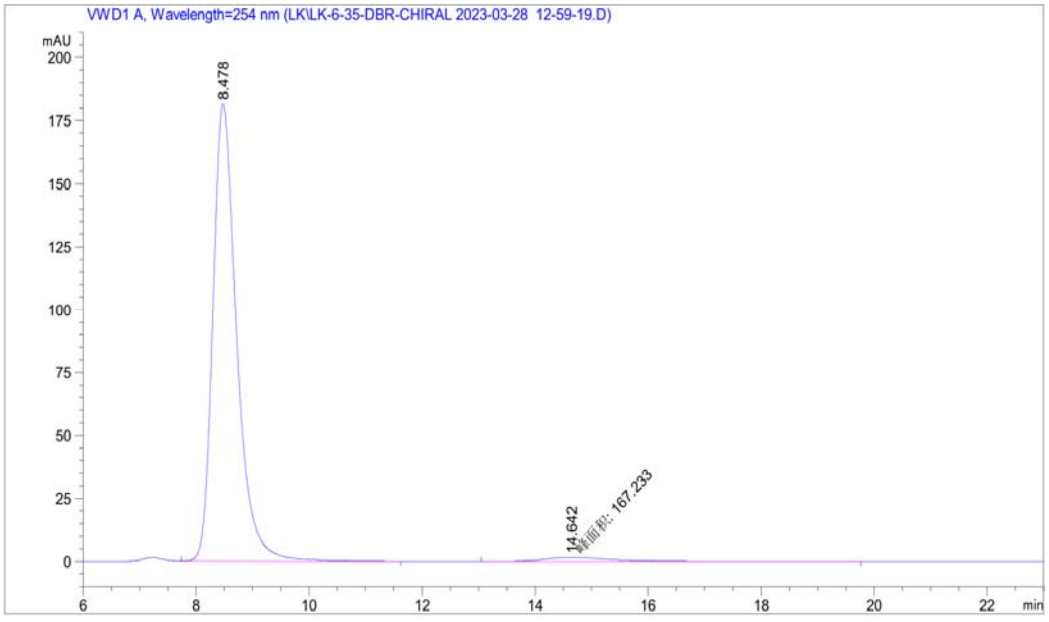
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.478 BB 0.4611 5719.58301 187.92531 50.9621

2 14.639 BB 1.3469 5503.62598 60.86916 49.0379

HPLC chromatogram of chiral 3fk



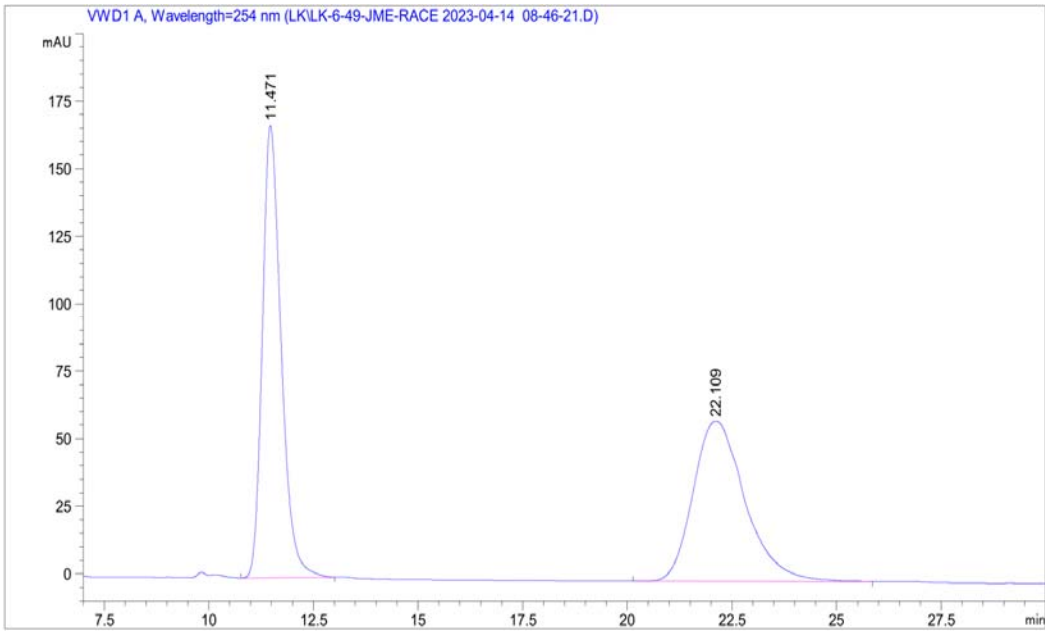
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.478 BB 0.4430 5302.33740 181.41003 96.9425

2 14.642 MM 1.6444 167.23271 1.69495 3.0575

HPLC chromatogram of racemic 3gk



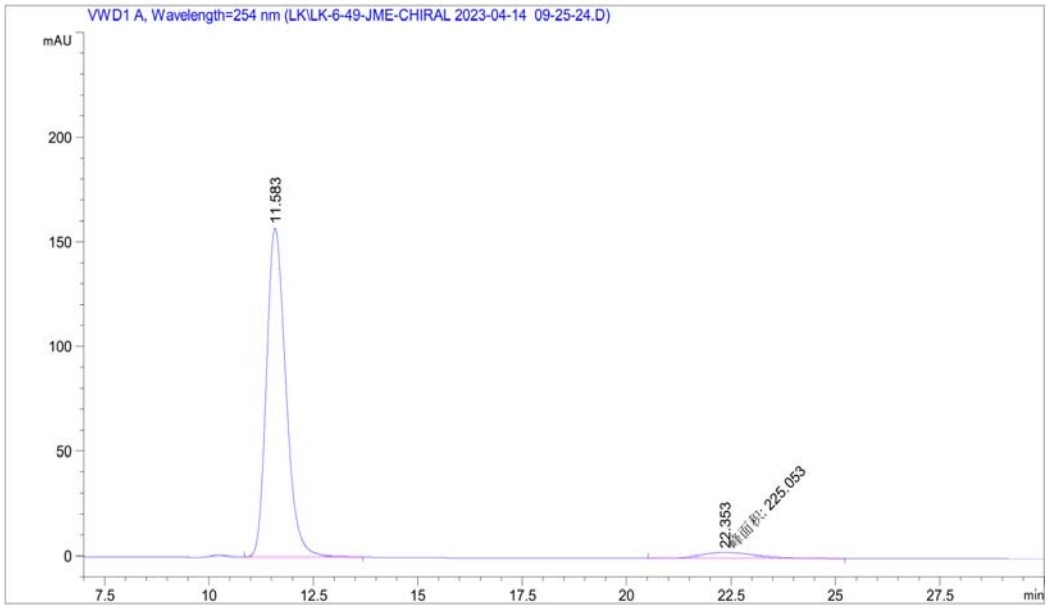
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 11.471 BB 0.4743 5212.81299 167.41412 50.5598

2 22.109 BB 1.2437 5097.38672 59.19217 49.4402

HPLC chromatogram of chiral 3gk



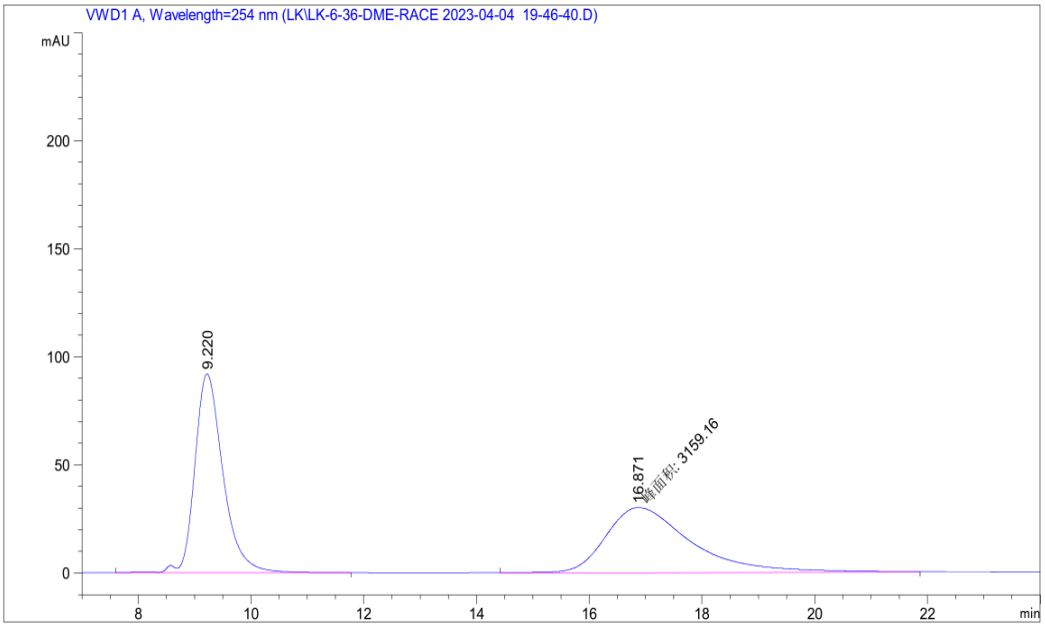
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 11.583 BB 0.4971 5056.63574 157.28792 95.7390

2 22.353 MM 1.4611 225.05284 2.56723 4.2610

HPLC chromatogram of racemic 3hk



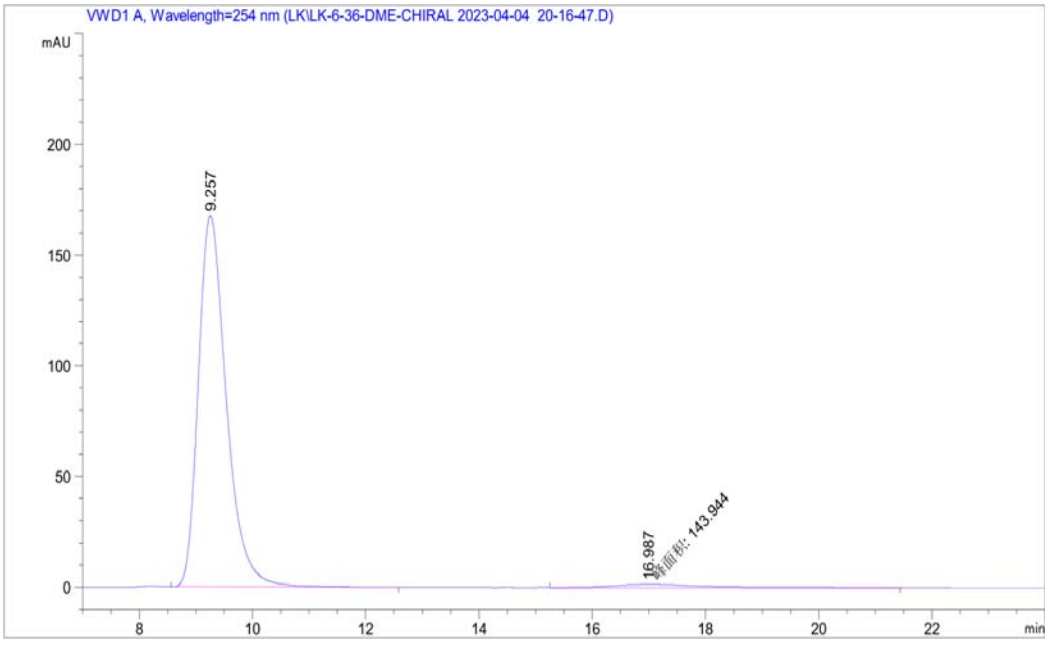
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.220 VB R 0.5262 3210.09717 91.95518 50.3999

2 16.871 MM 1.7513 3159.15942 30.06450 49.6001

HPLC chromatogram of chiral 3hk



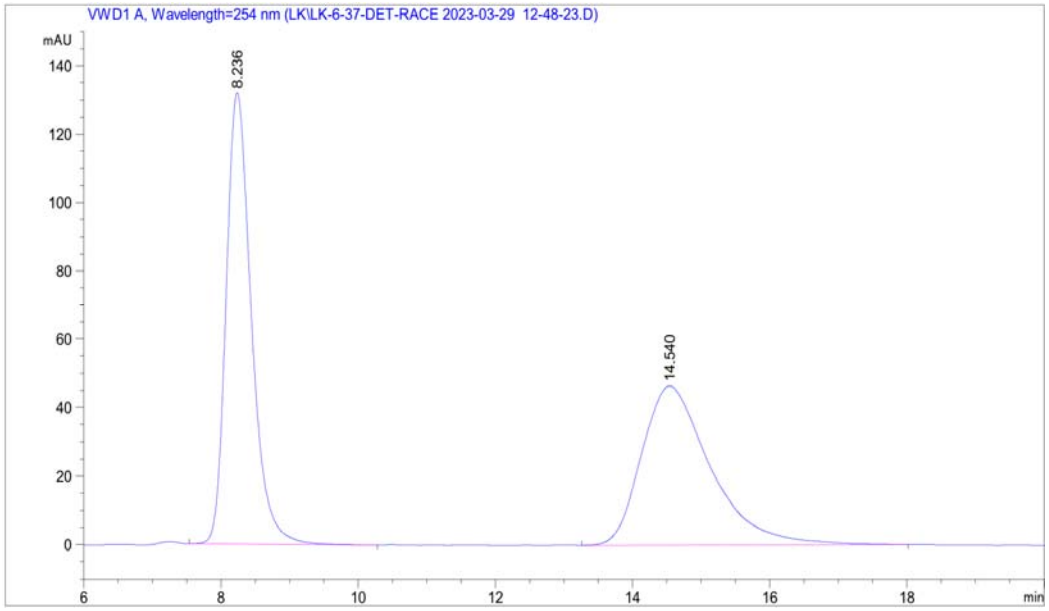
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.257 BB 0.5253 5769.11426 167.73515 97.5657

2 16.987 MM 1.7027 143.94447 1.40902 2.4343

HPLC chromatogram of racemic 3ik



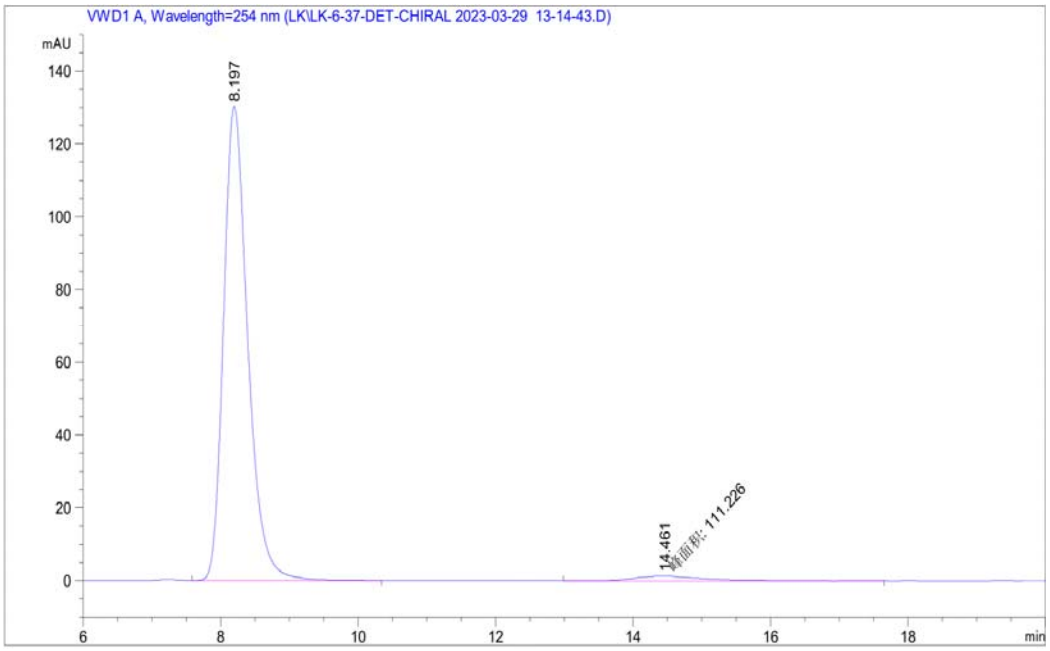
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.236 BB 0.3913 3364.24756 132.01259 50.9355

2 14.540 BB 1.0858 3240.67554 46.45826 49.0645

HPLC chromatogram of chiral 3ik



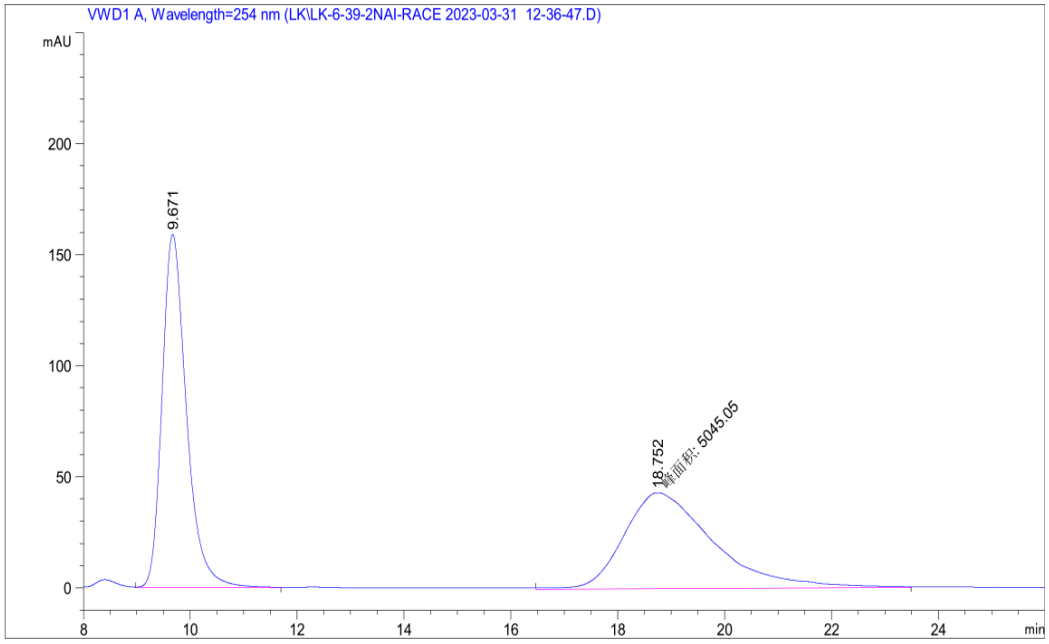
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.197 BB 0.3720 3183.26367 130.29619 96.6239

2 14.461 MM 1.3082 111.22626 1.41706 3.3761

HPLC chromatogram of racemic 3jk



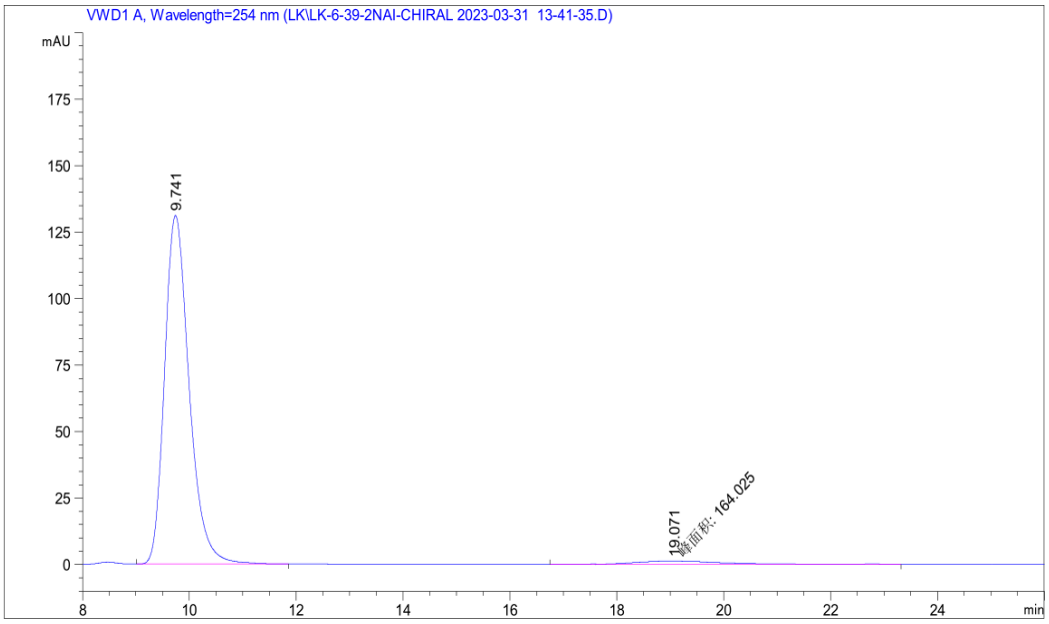
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.671 BB 0.4800 5010.32422 158.83531 49.8273

2 18.752 MM 1.9420 5045.04932 43.29730 50.1727

HPLC chromatogram of chiral 3jk



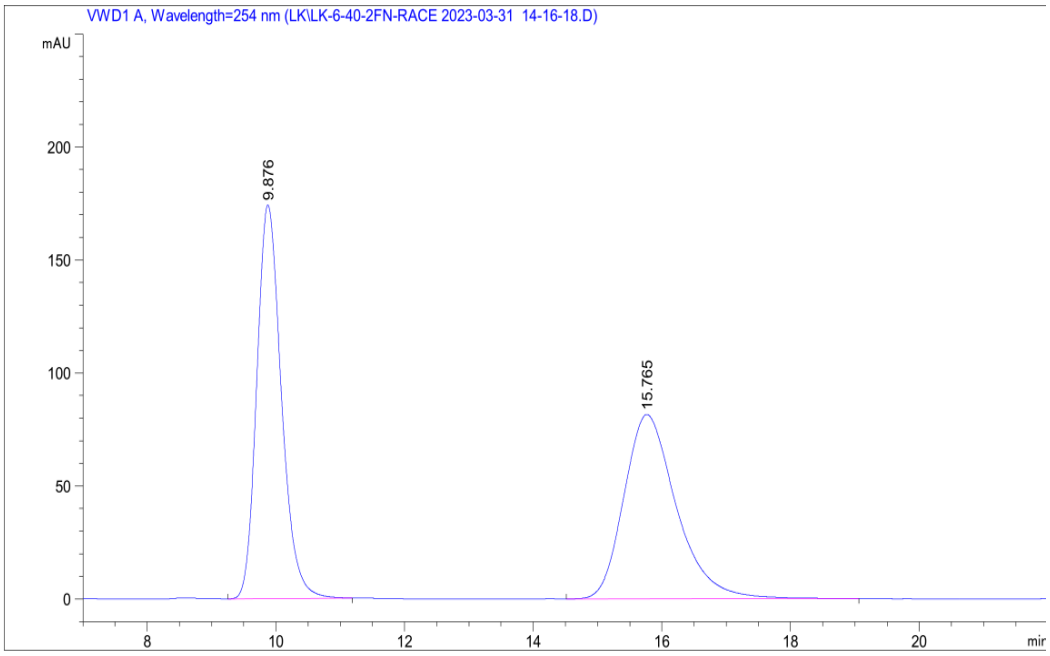
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.741 BB 0.4881 4189.67822 131.02332 96.2325

2 19.071 MM 2.0045 164.02548 1.36380 3.7675

HPLC chromatogram of racemic 3kk



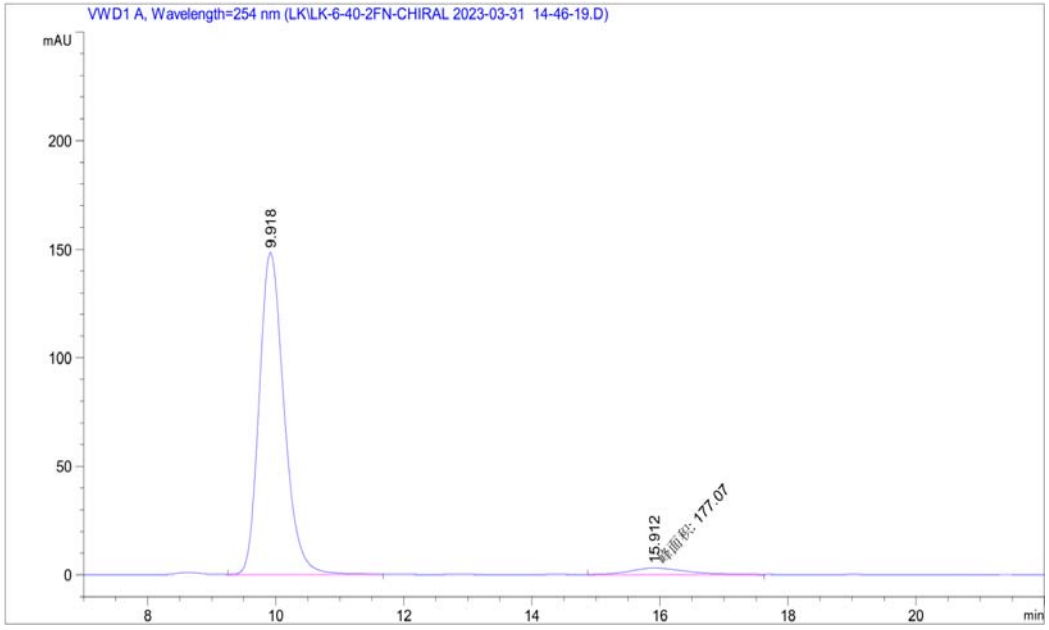
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.876 BB 0.4076 4622.46143 174.20792 50.0131

2 15.765 BB 0.8656 4620.04541 81.59460 49.9869

HPLC chromatogram of chiral 3kk



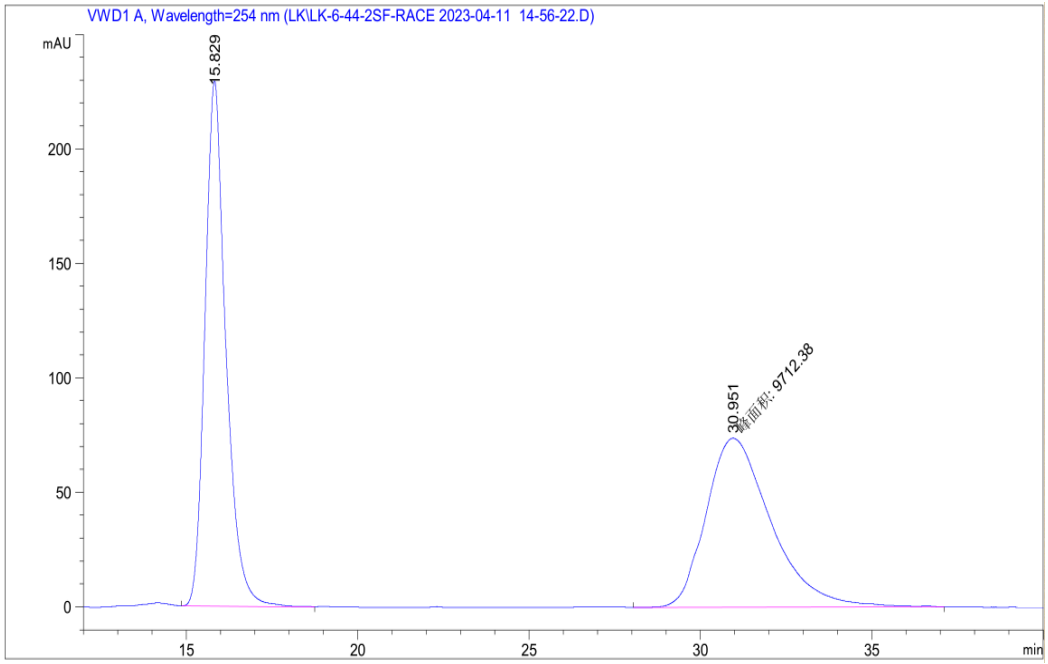
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.918 BB 0.4166 4002.47998 148.41318 95.7634

2 15.912 MM 0.9611 177.07050 3.07052 4.2366

HPLC chromatogram of racemic 3lk



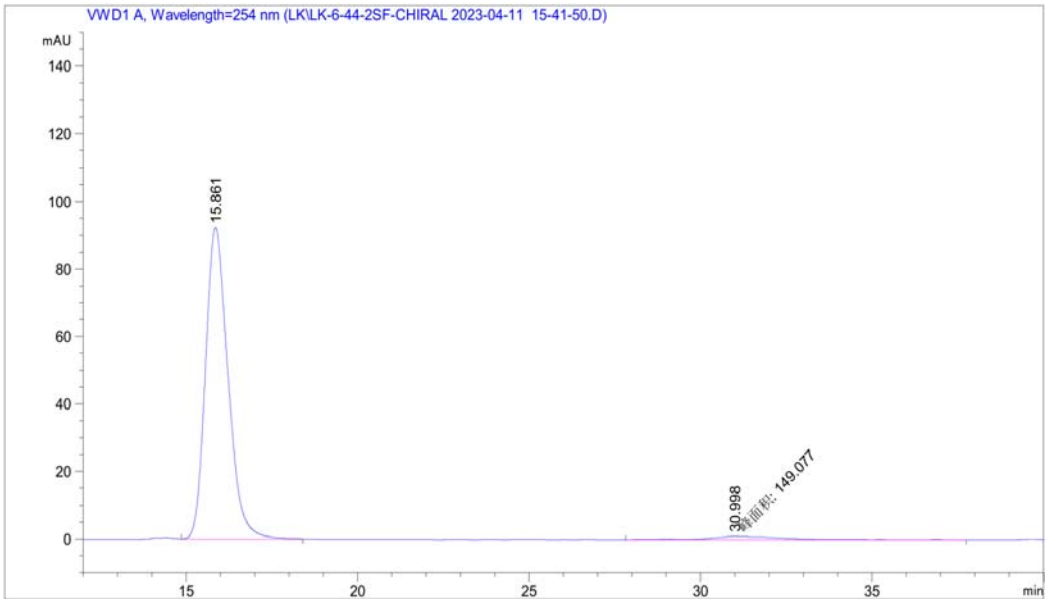
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 15.829 BB 0.6240 9713.27148 229.41214 50.0023

2 30.951 MM 2.1948 9712.38281 73.75340 49.9977

HPLC chromatogram of chiral 3lk



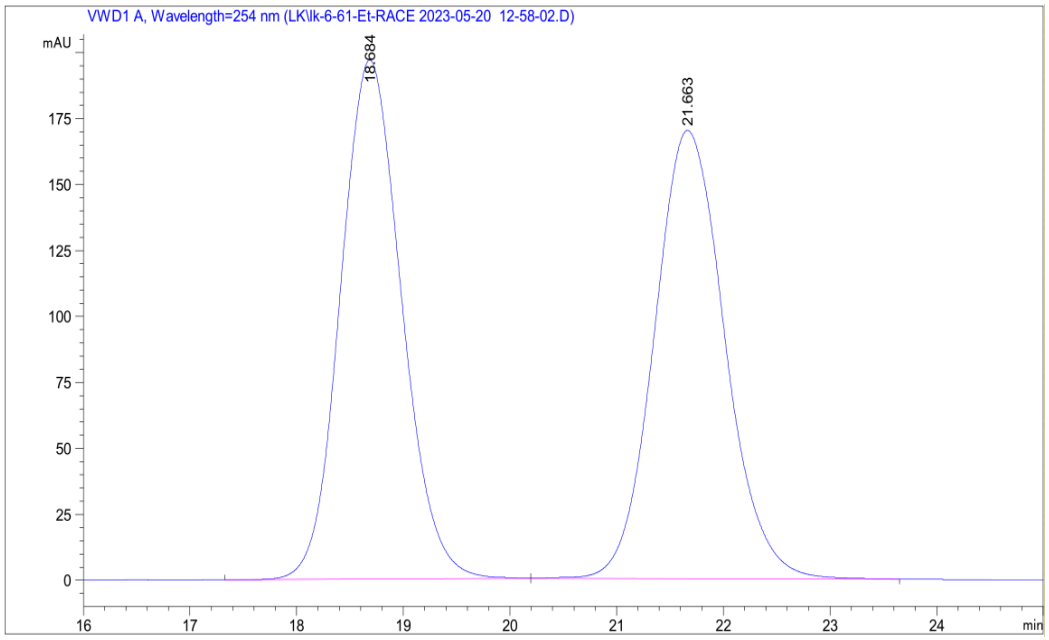
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 15.861 BB 0.6930 4191.94434 92.27579 96.5659

2 30.998 MM 2.3644 149.07654 1.05085 3.4341

HPLC chromatogram of racemic 3mk



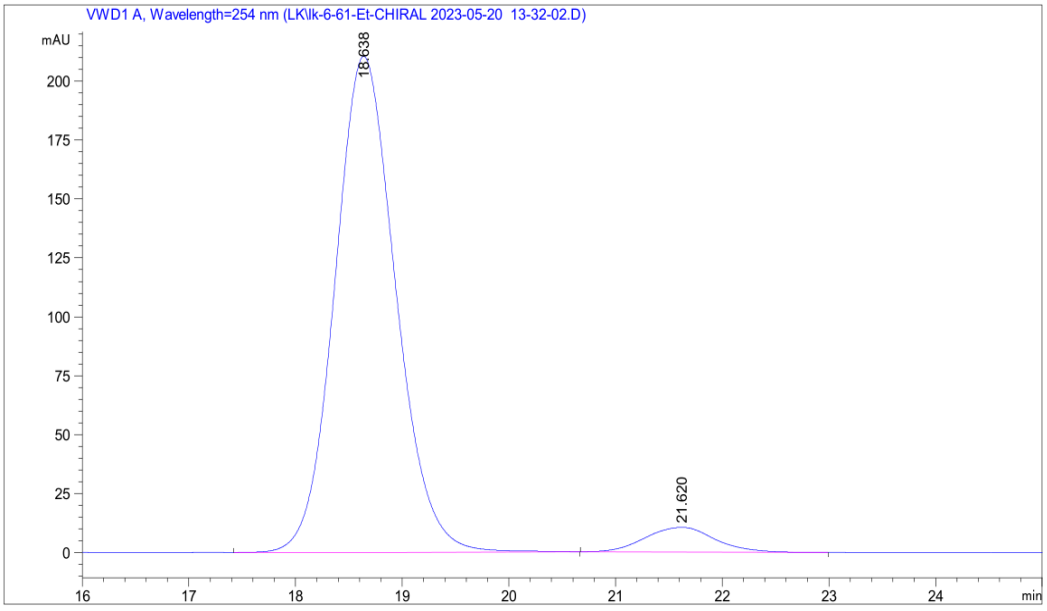
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 18.684 BB 0.6280 7809.15723 196.77307 50.0142

2 21.663 BB 0.7140 7804.70850 169.86447 49.9858

HPLC chromatogram of chiral 3mk



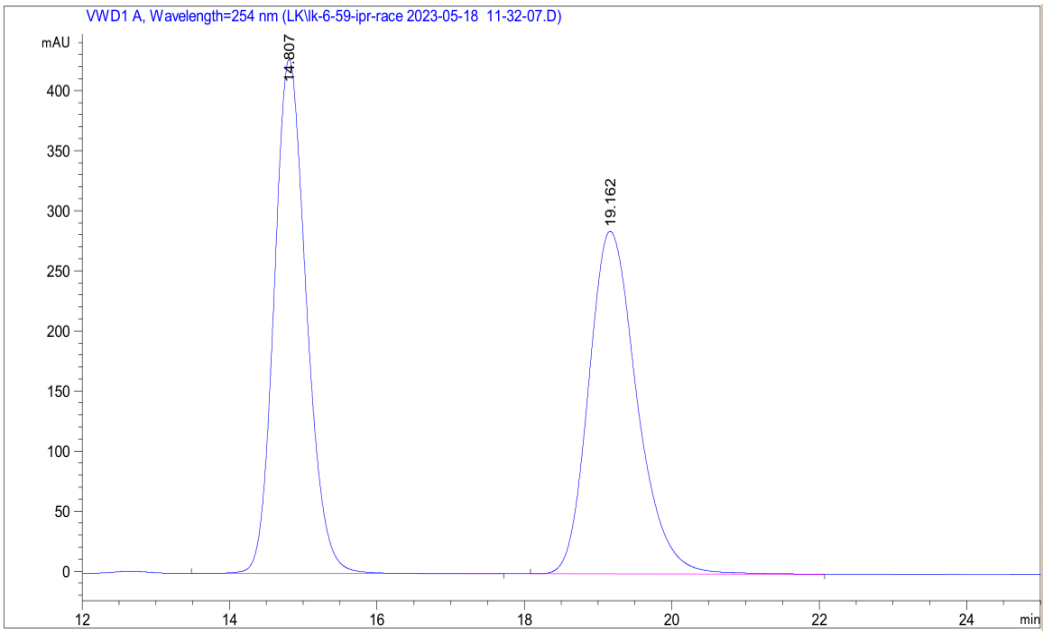
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 18.638 BB 0.6120 8329.90234 210.34508 94.6101

2 21.620 BB 0.7100 474.54932 10.46677 5.3899

HPLC chromatogram of racemic 3nk



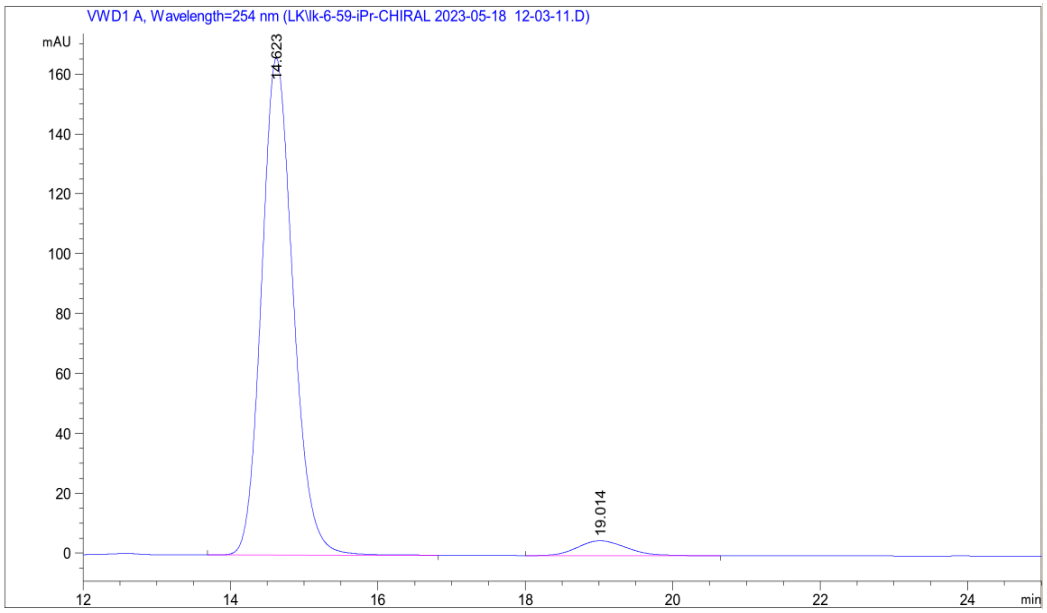
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 14.807 BB 0.4682 1.30333e4 428.05847 50.1462

2 19.162 BB 0.6987 1.29573e4 285.40726 49.8538

HPLC chromatogram of chiral 3nk



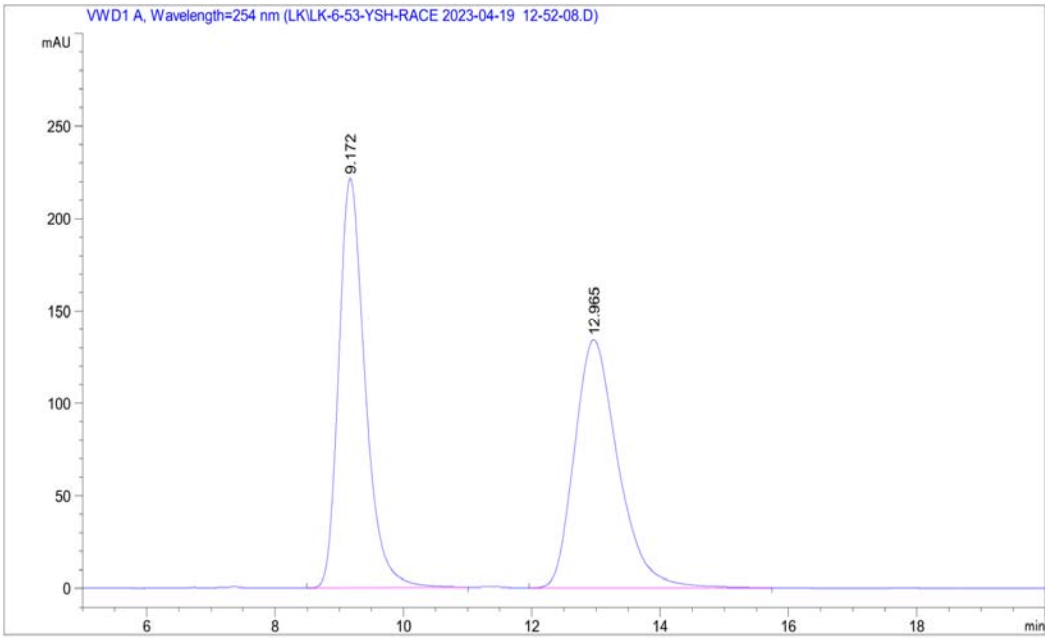
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 14.623 BB 0.4579 4934.23291 165.93445 95.5535

2 19.014 BB 0.7050 229.60878 4.98851 4.4465

HPLC chromatogram of racemic 4a



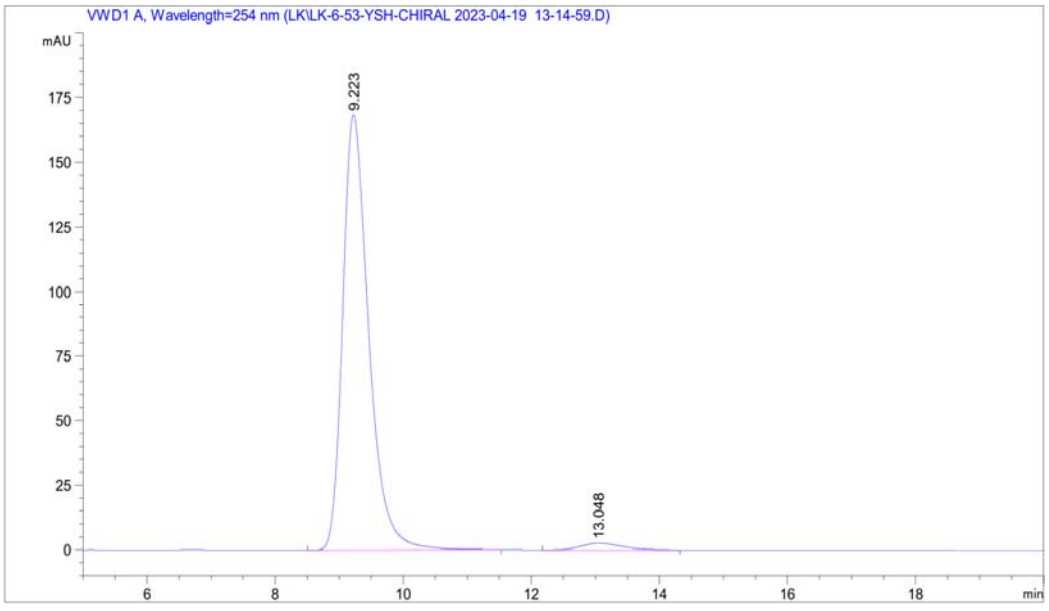
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.172 BB 0.4359 6314.71191 221.30313 50.0226

2 12.965 BB 0.7163 6309.00439 133.99446 49.9774

HPLC chromatogram of chiral 4a



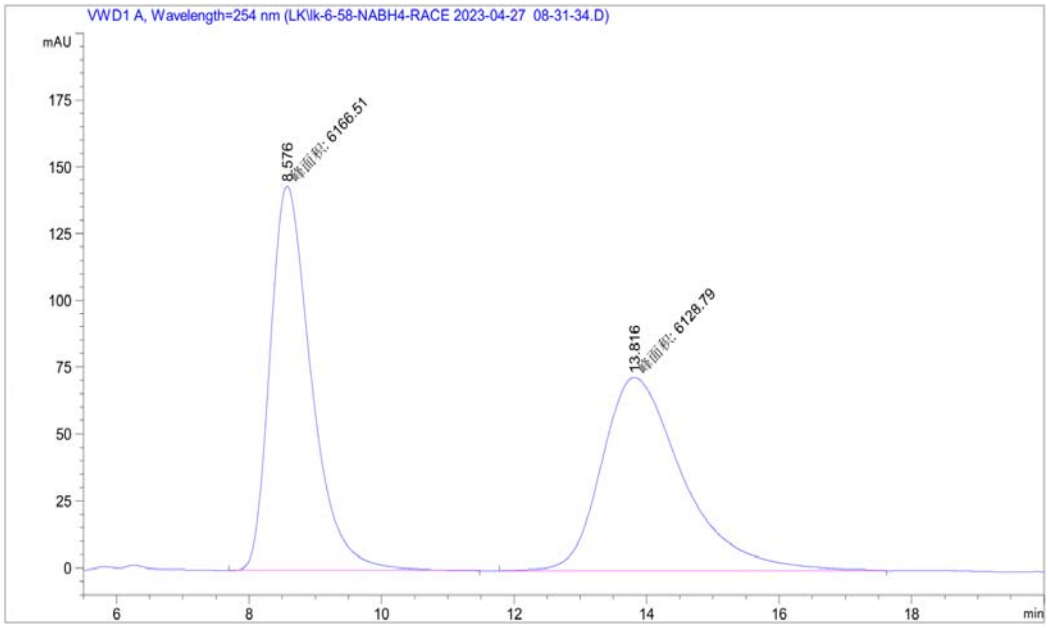
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 9.223 BB 0.4277 4744.22412 168.40855 97.5717

2 13.048 BB 0.6107 118.07159 2.68170 2.4283

HPLC chromatogram of racemic 4b



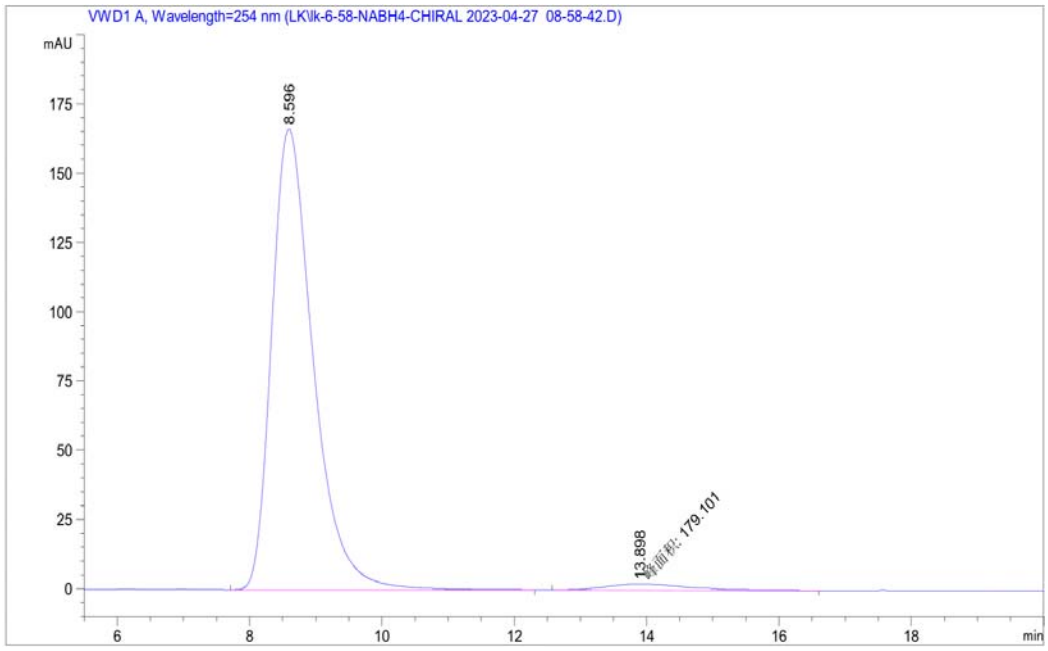
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.576 MM 0.7162 6166.50586 143.50679 50.1534

2 13.816 MM 1.4190 6128.79102 71.98298 49.8466

HPLC chromatogram of chiral 4b



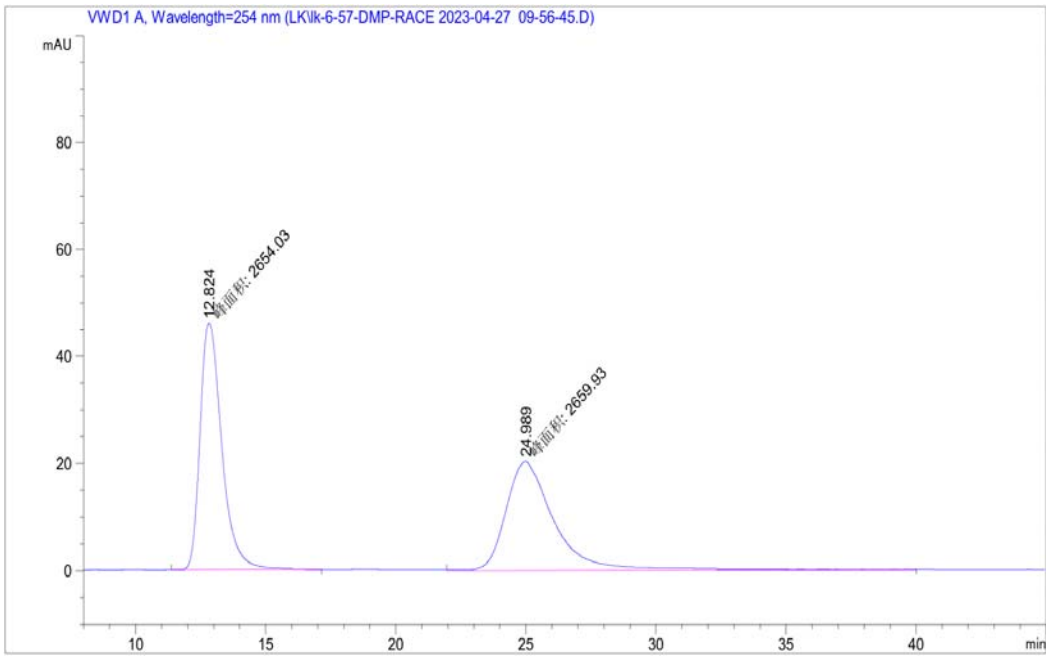
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 8.596 BB 0.6616 7251.37842 166.34438 97.5896

2 13.898 MM 1.3651 179.10065 2.18670 2.4104

HPLC chromatogram of racemic 4c



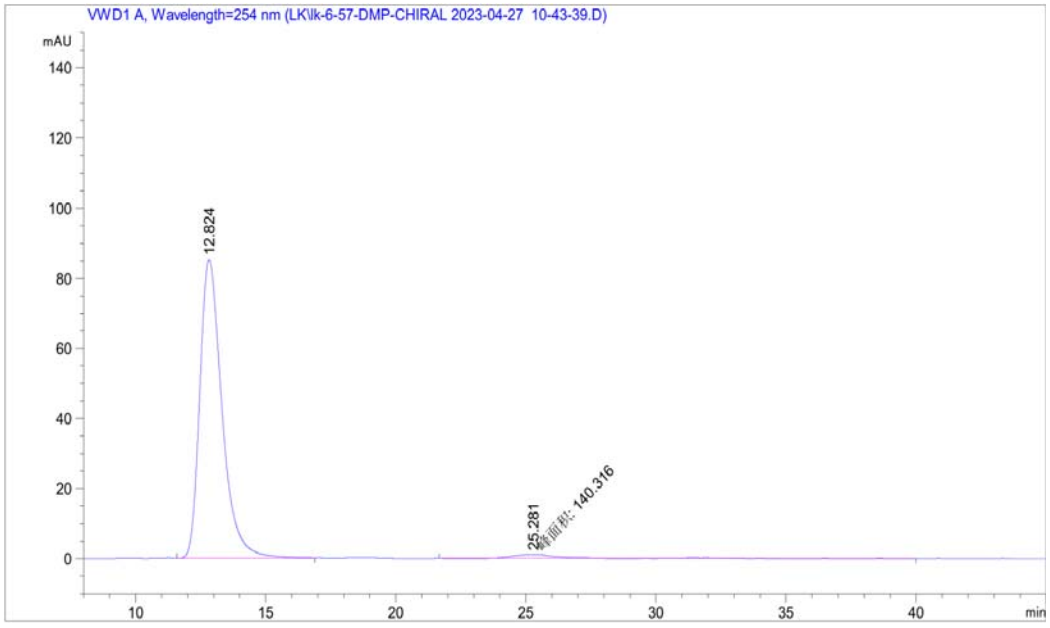
 # [min] [min] [mAU*s] [mAU] %

----|-------|----|-------|----------|----------|--------|

1 12.824 MM 0.9628 2654.02905 45.94079 49.9445

2 24.989 MM 2.1808 2659.92554 20.32876 50.0555

HPLC chromatogram of chiral 4c



 # [min] [min] [mAU*s] [mAU] %

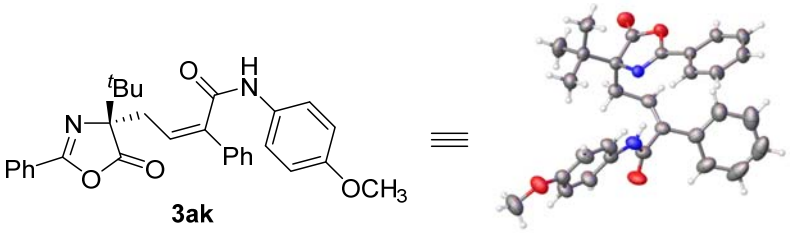
----|-------|----|-------|----------|----------|--------|

1 12.824 BB 0.8990 5044.95654 85.30590 97.2940

2 25.281 MM 2.2291 140.31554 1.04911 2.7060

X-Ray Crystallographic Data of 3ak

Crystallographic data for **3ak** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number 2259613. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3ak

Table S1. Crystal data and structure refinement for 3ak.

Identification code	**3ak**
Empirical formula	$C_{30}H_{30}N_2O_4$
Formula weight	482.56
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.4627(4)
b/Å	23.0018(10)
c/Å	10.8602(4)
α /°	90
β /°	93.636(2)
γ /°	90
Volume/Å^3	2608.36(18)
Z	4
ρ calcg/cm^3	1.229
μ /mm^{-1}	0.418
F(000)	1024.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.686 to 120.48
Index ranges	-12 ⩽ h ⩽ 13, -29 ⩽ k ⩽ 28, -14 ⩽ l ⩽ 13
Reflections collected	45119
Independent reflections	11509 [R_{int} = 0.0496, R_{sigma} = 0.0444]
Data/restraints/parameters	11509/1/658
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.0779
Final R indexes [all data]	R_1 = 0.0639, wR_2 = 0.0875
Largest diff. peak/hole / e Å^{-3}	0.14/-0.14
Flack parameter	-0.12(9)

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ak. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O5	2470.5(19)	3486.1(8)	2848.2(15)	44.3(5)
O2	9501.1(17)	6877.1(8)	7845.9(15)	40.1(4)
N1	9009.5(18)	5935.6(9)	7438.1(17)	31.7(4)
O3	4771.2(19)	5145.2(9)	7761(2)	61.8(6)
O1	9610(2)	6907.8(9)	9914.1(17)	52.8(5)
N3	3114.6(19)	4405.0(9)	2487.3(17)	33.3(5)
O4	8323(2)	2815.9(9)	7001(2)	60.7(6)
O6	2517(2)	3453.3(9)	4919.7(18)	61.2(6)
N2	6749(2)	5125.1(10)	7011(2)	42.6(5)
N4	5364(2)	5202.1(9)	2309(2)	41.4(5)
O7	7407.8(19)	5201.0(9)	3149(2)	74.5(7)
O8	4997(2)	7497.0(9)	674(2)	63.5(6)
C7	9225(2)	6432.7(11)	6999(2)	32.2(5)
C8	9196(2)	6600.1(10)	5702(2)	32.5(5)
C24	7019(2)	4519.7(11)	6972(2)	38.5(6)
C35	3037(2)	4361.7(11)	3837(2)	35.8(6)
C6	9436(3)	6624.3(12)	8995(2)	39.0(6)
C23	5746(3)	5392.8(12)	7470(3)	44.7(7)
C37	2786(2)	3920.1(11)	2027(2)	34.2(6)
C14	7718(2)	5905.2(12)	9258(2)	41.0(6)
C36	2652(3)	3735.1(13)	4011(2)	43.3(6)
C38	2688(2)	3757.3(11)	720(2)	36.0(6)
C15	6764(2)	6249.7(12)	8477(2)	41.0(6)
C46	6263(2)	4309.8(12)	3156(2)	40.8(6)
C5	9085(2)	5988.4(11)	8792(2)	34.1(6)
C45	5379(3)	4112.9(13)	3889(2)	42.4(6)
C54	5275(2)	5791.1(11)	1897(2)	38.0(6)
C44	4379(3)	4458.6(13)	4487(2)	44.2(7)
C53	6402(3)	4947.7(11)	2885(3)	45.1(7)
C9	9093(2)	6166.6(11)	4812(2)	38.2(6)
C32	1976(3)	4787.3(12)	4258(2)	41.0(6)
C16	5914(2)	6039.6(11)	7628(2)	40.2(6)
C57	5049(3)	6922.9(12)	1023(3)	46.2(7)
C55	4623(3)	5908.9(12)	791(3)	45.3(7)

C13	9227(3)	7180.3(12)	5346(2)	41.7(6)
C39	3147(3)	4132.4(12)	-144(2)	40.8(6)
C2	10127(3)	5567.0(12)	9368(2)	40.7(6)
C56	4489(3)	6473.2(13)	350(2)	44.9(7)
C12	9193(3)	7317.5(13)	4106(3)	48.3(7)
C33	680(3)	4601.0(14)	3668(3)	48.6(7)
C47	7188(3)	3926.1(11)	2572(3)	41.0(6)
C11	9126(3)	6884.8(14)	3231(2)	48.0(7)
C25	8000(3)	4341.4(13)	6262(3)	48.3(7)
C29	6411(3)	4113.0(13)	7662(3)	50.8(7)
C10	9064(3)	6309.7(13)	3583(2)	44.9(7)
C4	9835(3)	4942.2(12)	8941(3)	51.1(7)
C27	7825(3)	3368.3(12)	7018(3)	46.3(7)
C28	6812(3)	3533.9(13)	7679(3)	53.5(8)
C31	2276(3)	5402.9(12)	3841(3)	48.1(7)
C52	7667(3)	4071.6(13)	1452(3)	55.1(8)
C26	8410(3)	3771.5(13)	6294(3)	51.3(7)
C48	7576(3)	3398.5(13)	3105(3)	51.1(7)
C58	5704(3)	6809.0(13)	2144(3)	57.4(8)
C59	5812(3)	6246.5(12)	2583(3)	51.4(7)
C1	11426(3)	5743.1(14)	8924(3)	54.7(8)
C49	8376(3)	3028.9(14)	2517(3)	58.5(8)
C50	8833(3)	3179.1(14)	1408(3)	60.0(9)
C40	3033(3)	3997.8(13)	-1382(2)	46.5(7)
C51	8478(3)	3700.7(14)	872(3)	63.8(9)
C43	2120(3)	3242.2(13)	337(3)	55.8(8)
C34	1920(3)	4777.2(15)	5665(2)	56.7(8)
C22	5576(3)	6905.9(15)	6275(3)	59.1(8)
C17	5071(3)	6421.9(13)	6833(3)	45.6(7)
C18	3772(3)	6309.6(15)	6610(3)	60.2(8)
C41	2454(3)	3487.8(15)	-1756(3)	62.7(9)
C3	10169(3)	5588.1(15)	10779(2)	62.2(9)
C19	3017(4)	6671.7(19)	5862(4)	82.3(13)
C21	4810(4)	7269.9(17)	5529(3)	78.3(11)
C20	3524(5)	7147.9(19)	5323(4)	85.4(13)
C30	7818(4)	2397.9(15)	7809(3)	73.4(10)
C60	4431(4)	7632.2(15)	-520(3)	73.0(10)
C42	2002(4)	3110.5(16)	-904(3)	77.5(12)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ak. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U11	U22	U33	U23	U13	U12
O5	60.5(13)	39.4(11)	33.2(10)	2.4(8)	5.9(8)	-9.3(9)
O2	52.7(11)	33.8(10)	33.9(9)	-3.5(8)	3.4(8)	-8.2(9)
N1	32.3(11)	34.2(12)	28.8(10)	1.5(9)	2.6(8)	-2.1(9)
O3	36.3(11)	50.9(13)	99.8(17)	3.3(12)	15.1(11)	-7.3(10)
O1	69.3(14)	52.7(12)	36.4(10)	-12.2(9)	2.8(9)	-9.9(11)
N3	34.2(12)	37.1(12)	28.5(10)	0.2(9)	1.0(8)	-2.5(9)
O4	64.2(14)	42.9(12)	77.0(15)	3.0(11)	20.7(11)	4.1(10)
O6	88.6(17)	56.4(13)	38.6(11)	13.2(10)	5.5(10)	-9.0(12)
N2	40.7(13)	39.9(13)	48.3(13)	-3.4(10)	11.8(10)	-5.7(10)
N4	36.2(12)	35.3(12)	52.2(13)	0.6(10)	-1.5(10)	-3.6(10)
O7	38.2(12)	38.0(12)	144(2)	-3.2(13)	-16.7(13)	-1.3(10)
O8	66.7(15)	39.0(12)	83.9(16)	9.4(11)	-1.1(12)	6.4(10)
C7	30.2(13)	33.2(14)	33.4(13)	-2.5(11)	3.6(10)	-3.5(11)
C8	32.5(13)	32.9(14)	32.2(13)	1.9(10)	3.3(10)	-0.2(10)
C24	37.5(14)	39.7(16)	38.3(14)	-4.1(12)	2.0(11)	-4.8(12)
C35	41.5(15)	39.7(14)	26.0(12)	0.6(10)	-0.5(10)	-1.0(12)
C6	39.3(15)	43.1(16)	34.7(14)	-2.5(12)	3.6(11)	-3.8(12)
C23	37.5(16)	46.0(17)	50.9(16)	-2.5(13)	4.8(13)	-5.5(13)
C37	33.1(14)	36.5(15)	33.5(13)	2.0(11)	4.4(10)	-3.3(11)
C14	41.3(15)	47.9(16)	34.7(13)	-1.7(12)	9.5(11)	-2.5(12)
C36	49.1(17)	46.7(16)	34.1(15)	3.3(13)	3.2(12)	-3.7(13)
C38	36.3(14)	37.8(15)	34.1(13)	-2.4(11)	4.1(11)	-2.9(11)
C15	37.0(15)	41.1(15)	46.1(15)	-3.5(12)	11.7(12)	-0.7(12)
C46	34.2(15)	36.8(15)	50.4(16)	0.2(12)	-5.6(12)	2.5(11)
C5	35.4(14)	39.5(14)	27.5(12)	-0.5(11)	3.8(10)	-2.7(11)
C45	39.9(15)	43.2(15)	42.9(15)	0.4(12)	-6.3(12)	3.9(13)
C54	30.1(14)	37.0(15)	47.2(15)	-1.2(12)	4.5(11)	-0.7(11)
C44	43.3(16)	53.6(18)	34.9(14)	-1.7(12)	-3.7(11)	3.0(13)
C53	32.9(15)	35.2(15)	66.9(19)	-5.1(13)	0.4(13)	-1.0(12)
C9	44.4(16)	34.7(14)	36.0(14)	0.8(11)	7.7(11)	-1.0(11)
C32	40.0(15)	51.6(17)	31.4(13)	-4.8(12)	2.9(11)	1.7(12)
C16	32.5(14)	42.2(16)	46.7(15)	-2.5(12)	9.7(12)	-1.3(12)
C57	43.0(16)	35.8(15)	60.2(18)	4.7(14)	6.9(14)	7.0(13)
C55	42.4(16)	42.6(17)	50.4(17)	-2.1(13)	-0.9(13)	-6.6(13)
C13	47.4(17)	33.9(15)	43.9(15)	2.4(12)	4.8(12)	-2.9(12)

C39	42.2(15)	42.5(15)	37.5(14)	-2.0(12)	1.6(11)	-6.3(12)
C2	43.6(16)	44.8(16)	33.0(14)	4.0(12)	-2.4(12)	0.6(12)
C56	42.9(16)	48.3(17)	43.4(15)	3.4(13)	2.5(12)	1.1(13)
C12	57.4(18)	39.8(16)	48.0(17)	12.9(14)	4.6(14)	-0.6(14)
C33	39.5(16)	62.2(19)	44.2(16)	-0.7(14)	3.1(12)	0.6(14)
C47	33.2(14)	36.4(15)	52.9(16)	0.7(12)	-1.6(12)	-3.3(11)
C11	52.1(18)	56.4(18)	35.5(15)	11.5(14)	3.7(12)	0.7(15)
C25	56.8(18)	44.5(17)	45.3(16)	-3.1(13)	17.2(13)	-7.8(14)
C29	46.7(17)	49.7(18)	57.7(18)	5.4(14)	16.6(14)	-0.6(14)
C10	54.4(18)	47.2(18)	33.5(14)	-0.1(13)	7.0(12)	-4.3(13)
C4	54.1(18)	46.8(18)	52.0(17)	7.7(13)	1.1(14)	3.6(14)
C27	49.9(18)	43.4(17)	45.7(16)	-3.4(13)	3.7(13)	-1.6(14)
C28	50.6(19)	48.8(18)	62.6(19)	10.6(14)	16.2(15)	-0.8(14)
C31	47.4(17)	47.6(17)	49.2(17)	-8.3(13)	1.6(13)	6.2(13)
C52	54.6(19)	38.0(16)	74(2)	12.4(15)	15.6(16)	3.3(14)
C26	55.9(19)	48.6(18)	51.6(17)	-10.2(14)	20.8(14)	-3.2(15)
C48	48.8(18)	48.5(17)	55.8(18)	8.9(14)	2.7(14)	9.2(14)
C58	58(2)	35.3(17)	76(2)	-11.2(15)	-16.1(17)	2.7(14)
C59	56.2(19)	40.2(16)	55.9(18)	-5.1(14)	-11.9(14)	3.5(14)
C1	38.5(16)	63(2)	61.0(19)	6.6(16)	-5.6(14)	-0.8(14)
C49	54(2)	45.5(18)	75(2)	6.9(16)	2.1(17)	14.6(15)
C50	51.5(19)	44.8(19)	85(2)	-6.7(17)	15.0(17)	5.6(15)
C40	52.4(17)	53.7(18)	33.8(14)	1.2(13)	4.7(12)	-7.5(14)
C51	65(2)	51(2)	79(2)	5.1(17)	29.6(18)	4.0(17)
C43	76(2)	50.0(19)	42.7(16)	-8.5(13)	13.8(15)	-24.8(16)
C34	58(2)	78(2)	34.8(15)	-6.9(15)	7.5(13)	6.5(16)
C22	56.1(19)	56.6(19)	65(2)	5.6(17)	6.0(16)	9.8(16)
C17	40.4(16)	47.7(17)	49.2(16)	-9.8(13)	5.7(12)	5.7(13)
C18	44.2(18)	58(2)	77(2)	-19.5(17)	-6.4(15)	7.9(15)
C41	84(2)	68(2)	37.0(16)	-12.1(15)	10.4(15)	-22.4(19)
C3	78(2)	71(2)	35.5(16)	5.5(15)	-8.1(15)	6.2(18)
C19	59(2)	75(3)	109(3)	-38(2)	-29(2)	27(2)
C21	104(3)	58(2)	72(2)	4.6(19)	2(2)	26(2)
C20	102(3)	74(3)	76(3)	-21(2)	-30(2)	43(3)
C30	83(3)	51(2)	89(3)	16.9(19)	22(2)	8.4(18)
C60	90(3)	54(2)	77(2)	21.9(17)	17(2)	20.0(19)
C42	118(3)	64(2)	51(2)	-21.3(17)	15(2)	-45(2)

Table S4. Bond Lengths for 3ak.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
O5	C37	1.392(3)		C5	C2	1.560(4)
O5	C36	1.389(3)		C45	C44	1.495(4)
O2	C7	1.393(3)		C54	C55	1.371(4)
O2	C6	1.383(3)		C54	C59	1.384(4)
N1	C7	1.264(3)		C9	C10	1.374(4)
N1	C5	1.472(3)		C32	C33	1.524(4)
O3	C23	1.227(3)		C32	C31	1.525(4)
O1	C6	1.196(3)		C32	C34	1.532(4)
N3	C35	1.477(3)		C16	C17	1.483(4)
N3	C37	1.261(3)		C57	C56	1.376(4)
O4	C27	1.374(3)		C57	C58	1.383(4)
O4	C30	1.426(4)		C55	C56	1.387(4)
O6	C36	1.196(3)		C13	C12	1.382(4)
N2	C24	1.422(3)		C39	C40	1.378(4)
N2	C23	1.340(3)		C2	C4	1.535(4)
N4	C54	1.428(3)		C2	C1	1.525(4)
N4	C53	1.351(3)		C2	C3	1.531(4)
O7	C53	1.221(3)		C12	C11	1.375(4)
O8	C57	1.374(3)		C47	C52	1.385(4)
O8	C60	1.426(4)		C47	C48	1.394(4)
C7	C8	1.460(3)		C11	C10	1.380(4)
C8	C9	1.387(3)		C25	C26	1.379(4)
C8	C13	1.390(3)		C29	C28	1.396(4)
C24	C25	1.385(4)		C27	C28	1.372(4)
C24	C29	1.379(4)		C27	C26	1.383(4)
C35	C36	1.512(4)		C52	C51	1.383(4)
C35	C44	1.547(4)		C48	C49	1.378(4)
C35	C32	1.570(4)		C58	C59	1.381(4)
C6	C5	1.521(4)		C49	C50	1.368(4)
C23	C16	1.506(4)		C50	C51	1.374(4)
C37	C38	1.466(3)		C40	C41	1.370(4)
C14	C15	1.496(4)		C43	C42	1.379(4)
C14	C5	1.559(3)		C22	C17	1.388(4)
C38	C39	1.383(4)		C22	C21	1.385(5)
C38	C43	1.378(4)		C17	C18	1.390(4)
C15	C16	1.330(4)		C18	C19	1.377(5)

C46	C45	1.337(4)		C41	C42	1.374(4)
C46	C53	1.505(4)		C19	C20	1.365(6)
C46	C47	1.482(4)		C21	C20	1.379(6)

Table S5. Bond Angles for 3ak.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C36	O5	C37	105.22(19)		O7	C53	C46	120.7(2)
C6	O2	C7	105.50(19)		C10	C9	C8	120.0(2)
C7	N1	C5	107.6(2)		C33	C32	C35	109.2(2)
C37	N3	C35	107.6(2)		C33	C32	C31	109.3(2)
C27	O4	C30	117.4(2)		C33	C32	C34	109.0(2)
C23	N2	C24	128.5(2)		C31	C32	C35	109.3(2)
C53	N4	C54	126.1(2)		C31	C32	C34	109.4(2)
C57	O8	C60	117.8(3)		C34	C32	C35	110.7(2)
O2	C7	C8	115.8(2)		C15	C16	C23	120.4(3)
N1	C7	O2	116.7(2)		C15	C16	C17	122.3(3)
N1	C7	C8	127.5(2)		C17	C16	C23	117.3(2)
C9	C8	C7	118.6(2)		O8	C57	C56	124.7(3)
C9	C8	C13	119.9(2)		O8	C57	C58	115.7(3)
C13	C8	C7	121.5(2)		C56	C57	C58	119.7(3)
C25	C24	N2	117.5(2)		C54	C55	C56	121.4(3)
C29	C24	N2	123.3(2)		C12	C13	C8	119.4(3)
C29	C24	C25	119.1(3)		C40	C39	C38	120.7(3)
N3	C35	C36	102.72(19)		C4	C2	C5	109.9(2)
N3	C35	C44	109.7(2)		C1	C2	C5	108.8(2)
N3	C35	C32	109.34(19)		C1	C2	C4	108.5(2)
C36	C35	C44	108.8(2)		C1	C2	C3	109.8(2)
C36	C35	C32	111.1(2)		C3	C2	C5	110.9(2)
C44	C35	C32	114.5(2)		C3	C2	C4	108.9(2)
O2	C6	C5	107.4(2)		C57	C56	C55	119.3(3)
O1	C6	O2	120.7(2)		C11	C12	C13	120.4(3)
O1	C6	C5	131.9(2)		C52	C47	C46	121.0(2)
O3	C23	N2	124.5(3)		C52	C47	C48	117.6(3)
O3	C23	C16	121.5(3)		C48	C47	C46	121.4(3)
N2	C23	C16	114.0(2)		C12	C11	C10	120.2(2)
O5	C37	C38	115.6(2)		C26	C25	C24	120.5(3)
N3	C37	O5	116.8(2)		C24	C29	C28	120.4(3)
N3	C37	C38	127.6(2)		C9	C10	C11	120.0(3)

C15	C14	C5	110.1(2)		O4	C27	C26	115.5(3)
O5	C36	C35	107.6(2)		C28	C27	O4	124.7(3)
O6	C36	O5	120.7(3)		C28	C27	C26	119.7(3)
O6	C36	C35	131.8(3)		C27	C28	C29	120.0(3)
C39	C38	C37	119.5(2)		C51	C52	C47	121.2(3)
C43	C38	C37	121.0(2)		C25	C26	C27	120.2(3)
C43	C38	C39	119.5(2)		C49	C48	C47	120.9(3)
C16	C15	C14	126.4(3)		C59	C58	C57	120.4(3)
C45	C46	C53	121.7(2)		C58	C59	C54	120.1(3)
C45	C46	C47	123.2(2)		C50	C49	C48	120.6(3)
C47	C46	C53	115.1(2)		C49	C50	C51	119.6(3)
N1	C5	C6	102.8(2)		C41	C40	C39	119.4(3)
N1	C5	C14	108.80(19)		C50	C51	C52	120.2(3)
N1	C5	C2	109.9(2)		C38	C43	C42	119.6(3)
C6	C5	C14	106.8(2)		C21	C22	C17	121.2(3)
C6	C5	C2	112.5(2)		C22	C17	C16	120.1(3)
C14	C5	C2	115.2(2)		C22	C17	C18	117.9(3)
C46	C45	C44	127.5(3)		C18	C17	C16	122.0(3)
C55	C54	N4	118.7(2)		C19	C18	C17	120.5(4)
C55	C54	C59	119.0(3)		C40	C41	C42	120.4(3)
C59	C54	N4	122.3(2)		C20	C19	C18	121.0(4)
C45	C44	C35	111.4(2)		C20	C21	C22	119.6(4)
N4	C53	C46	115.4(2)		C19	C20	C21	119.7(4)
O7	C53	N4	123.9(3)		C41	C42	C43	120.4(3)

Table S6. Torsion Angles for 3ak.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O5	C37	C38	C39	-171.2(2)	C36	C35	C32	C33	-49.6(3)
O5	C37	C38	C43	10.2(4)	C36	C35	C32	C31	-169.1(2)
O2	C7	C8	C9	171.7(2)	C36	C35	C32	C34	70.4(3)
O2	C7	C8	C13	-10.4(3)	C38	C39	C40	C41	0.3(4)
O2	C6	C5	N1	1.4(3)	C38	C43	C42	C41	0.4(6)
O2	C6	C5	C14	-113.0(2)	C15	C14	C5	N1	-45.3(3)
O2	C6	C5	C2	119.6(2)	C15	C14	C5	C6	65.0(3)
N1	C7	C8	C9	-9.6(4)	C15	C14	C5	C2	-169.3(2)
N1	C7	C8	C13	168.4(3)	C15	C16	C17	C22	45.4(4)
N1	C5	C2	C4	-56.2(3)	C15	C16	C17	C18	-135.2(3)

N1	C5	C2	C1	62.5(3)	C46	C45	C44	C35	105.5(3)
N1	C5	C2	C3	-176.7(2)	C46	C47	C52	C51	-176.6(3)
O3	C23	C16	C15	110.4(3)	C46	C47	C48	C49	176.1(3)
O3	C23	C16	C17	-67.8(4)	C5	N1	C7	O2	1.8(3)
O1	C6	C5	N1	179.3(3)	C5	N1	C7	C8	-177.0(2)
O1	C6	C5	C14	64.8(4)	C5	C14	C15	C16	105.5(3)
O1	C6	C5	C2	-62.5(4)	C45	C46	C53	N4	-61.3(4)
N3	C35	C36	O5	-3.3(3)	C45	C46	C53	O7	120.5(3)
N3	C35	C36	O6	175.5(3)	C45	C46	C47	C52	150.6(3)
N3	C35	C44	C45	-46.5(3)	C45	C46	C47	C48	-27.3(4)
N3	C35	C32	C33	63.0(3)	C54	N4	C53	O7	1.5(5)
N3	C35	C32	C31	-56.5(3)	C54	N4	C53	C46	-176.6(2)
N3	C35	C32	C34	-177.0(2)	C54	C55	C56	C57	1.6(4)
N3	C37	C38	C39	9.1(4)	C44	C35	C36	O5	-119.5(2)
N3	C37	C38	C43	-169.5(3)	C44	C35	C36	O6	59.3(4)
O4	C27	C28	C29	177.8(3)	C44	C35	C32	C33	-173.3(2)
O4	C27	C26	C25	-178.8(3)	C44	C35	C32	C31	67.2(3)
N2	C24	C25	C26	172.5(3)	C44	C35	C32	C34	-53.3(3)
N2	C24	C29	C28	-173.3(3)	C53	N4	C54	C55	140.8(3)
N2	C23	C16	C15	-68.7(3)	C53	N4	C54	C59	-40.0(4)
N2	C23	C16	C17	113.2(3)	C53	C46	C45	C44	3.3(4)
N4	C54	C55	C56	179.1(2)	C53	C46	C47	C52	-30.5(4)
N4	C54	C59	C58	179.9(3)	C53	C46	C47	C48	151.6(3)
O8	C57	C56	C55	179.1(3)	C9	C8	C13	C12	-1.9(4)
O8	C57	C58	C59	179.9(3)	C32	C35	C36	O5	113.5(2)
C7	O2	C6	O1	-178.7(2)	C32	C35	C36	O6	-67.7(4)
C7	O2	C6	C5	-0.5(3)	C32	C35	C44	C45	-170.0(2)
C7	N1	C5	C6	-1.9(3)	C16	C17	C18	C19	-179.7(3)
C7	N1	C5	C14	111.1(2)	C57	C58	C59	C54	0.6(5)
C7	N1	C5	C2	-121.9(2)	C55	C54	C59	C58	-0.9(4)
C7	C8	C9	C10	-180.0(2)	C13	C8	C9	C10	2.1(4)
C7	C8	C13	C12	-179.8(2)	C13	C12	C11	C10	1.4(4)
C8	C9	C10	C11	-0.5(4)	C39	C38	C43	C42	-0.8(5)

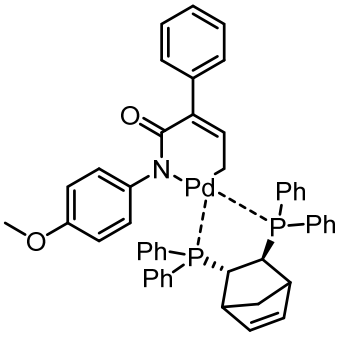
C8	C13	C12	C11	0.1(4)	C39	C40	C41	C42	-0.7(5)
C24	N2	C23	O3	-12.6(5)	C56	C57	C58	C59	0.9(5)
C24	N2	C23	C16	166.4(2)	C12	C11	C10	C9	-1.3(4)
C24	C25	C26	C27	1.4(4)	C47	C46	C45	C44	-177.8(2)
C24	C29	C28	C27	0.8(4)	C47	C46	C53	N4	119.7(3)
C35	N3	C37	O5	-1.0(3)	C47	C46	C53	O7	-58.4(4)
C35	N3	C37	C38	178.7(2)	C47	C52	C51	C50	-0.5(5)
C6	O2	C7	N1	-0.8(3)	C47	C48	C49	C50	1.6(5)
C6	O2	C7	C8	178.1(2)	C25	C24	C29	C28	2.3(4)
C6	C5	C2	C4	-170.1(2)	C29	C24	C25	C26	-3.4(4)
C6	C5	C2	C1	-51.4(3)	C28	C27	C26	C25	1.8(4)
C6	C5	C2	C3	69.4(3)	C52	C47	C48	C49	-1.9(4)
C23	N2	C24	C25	169.1(3)	C26	C27	C28	C29	-2.8(4)
C23	N2	C24	C29	-15.1(4)	C48	C47	C52	C51	1.4(4)
C23	C16	C17	C22	-136.5(3)	C48	C49	C50	C51	-0.7(5)
C23	C16	C17	C18	42.9(4)	C58	C57	C56	C55	-1.9(4)
C37	O5	C36	O6	-176.2(3)	C59	C54	C55	C56	-0.1(4)
C37	O5	C36	C35	2.8(3)	C49	C50	C51	C52	0.1(5)
C37	N3	C35	C36	2.6(3)	C40	C41	C42	C43	0.4(6)
C37	N3	C35	C44	118.1(2)	C43	C38	C39	C40	0.5(4)
C37	N3	C35	C32	-115.4(2)	C22	C17	C18	C19	-0.3(4)
C37	C38	C39	C40	-178.1(3)	C22	C21	C20	C19	0.3(6)
C37	C38	C43	C42	177.7(3)	C17	C22	C21	C20	-0.7(5)
C14	C15	C16	C23	6.7(4)	C17	C18	C19	C20	0.0(5)
C14	C15	C16	C17	-175.3(2)	C18	C19	C20	C21	0.0(6)
C14	C5	C2	C4	67.1(3)	C21	C22	C17	C16	-179.9(3)
C14	C5	C2	C1	-174.2(2)	C21	C22	C17	C18	0.6(5)
C14	C5	C2	C3	-53.3(3)	C30	O4	C27	C28	-5.5(4)
C36	O5	C37	N3	-1.2(3)	C30	O4	C27	C26	175.1(3)
C36	O5	C37	C38	179.1(2)	C60	O8	C57	C56	-6.3(4)
C36	C35	C44	C45	65.1(3)	C60	O8	C57	C58	174.7(3)

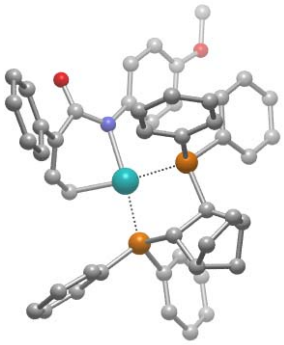
Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3ak.

Atom	x	y	z	U(eq)
H2	7314.89	5354.02	6691.64	51
H4	4677.66	4984.21	2175.41	50
H14A	7483.37	5488.29	9222.17	49
H14B	7709.8	6034.51	10127.06	49
H15	6764.59	6658.7	8598.27	49
H45	5387.45	3706.72	4047.22	51
H44A	4599.77	4876.73	4456.83	53
H44B	4364.35	4344.01	5364.85	53
H9	9043.68	5770.74	5053.94	46
H55	4254.49	5597.59	315.65	54
H13	9270.71	7479.57	5950.11	50
H39	3544.41	4486.35	119.09	49
H56	4015.62	6548.27	-408.63	54
H12	9215.5	7713.08	3856.48	58
H33A	23.66	4879.97	3885.96	73
H33B	463.76	4214.08	3970.23	73
H33C	720.59	4589.16	2769.63	73
H11	9123.03	6982.18	2380.26	58
H25	8394.31	4613.81	5749.25	58
H29	5714.94	4227.45	8128.94	61
H10	9000.96	6012.43	2974.69	54
H4A	8986.22	4828.64	9189.86	77
H4B	10482.27	4678.66	9320.76	77
H4C	9850.27	4920.46	8041.21	77
H28	6382.85	3254.6	8148.26	64
H31A	2311.67	5410.03	2941.56	72
H31B	3103.55	5525.91	4227.49	72
H31C	1604.21	5668.22	4085.66	72
H52	7434.91	4432.51	1076.08	66

H26	9096.79	3655.37	5817.7	62
H48	7284.15	3292.19	3884.41	61
H58	6080.6	7119.77	2614.6	69
H59	6256.24	6172.18	3357.22	62
H1A	11380.65	5750.97	8020.25	82
H1B	12076.58	5461.26	9223.47	82
H1C	11656.83	6130.05	9243.9	82
H49	8612.22	2666.71	2884.51	70
H50	9391.07	2924.5	1010.56	72
H40	3353.82	4256.27	-1971.76	56
H51	8791.04	3806.74	100.98	77
H43	1812.2	2979.22	923.75	67
H34A	1227.75	5031.82	5905.98	85
H34B	2737.35	4914.14	6050.22	85
H34C	1758.95	4379.2	5937.09	85
H22	6463.1	6989.01	6407.15	71
H18	3401.67	5980.23	6977.1	72
H41	2364.03	3394.42	-2609.04	75
H3A	10330.92	5987.87	11058.67	93
H3B	10854.87	5334.2	11120.36	93
H3C	9346.11	5455.58	11060.73	93
H19	2130.56	6588.78	5718.46	99
H21	5168.26	7601.8	5160.83	94
H20	2992.46	7394.34	4809.07	102
H30A	6899.93	2346.8	7598.21	110
H30B	7946.65	2533.67	8663.15	110
H30C	8259.12	2025.83	7720.84	110
H60A	4888.44	7425.61	-1147.51	110
H60B	4483.87	8051.99	-662.2	110
H60C	3530.4	7511.78	-572.25	110
H42	1606.6	2756.84	-1171.86	93

Density functional calculations (DFT)





G = −18.0 kcal/mol

Calculation method

Density functional calculations (DFT) are implemented using the Gaussian 09 package.[4] Geometry optimizations are performed using the Minnesota M06 functional as it has been successful in describing a plethora of transition metal-catalyzed reactions.[5] The LANL2DZ effective core potential method with an extra *f*-polarization function ($\zeta f = 1.472$) is used as the basis set for Pd, and the 6-31G(d) basis set is used for all other atoms.[6]

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