Ir-Catalyzed Asymmetric Formal (3+2) Cycloaddition of Esters with Vinylcyclopropanes

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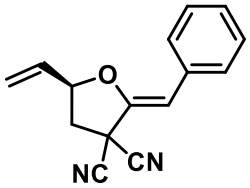
I. General Considerations

Unless noted, all reactions were conducted under inert atmosphere employing standard Schlenk technique or by the use of a N_2-filled glovebox. All glassware was oven-dried prior to use. Flash chromatography was performed as described by Still and co-workers (SiliaFlash P60, 40-63μm, 60A silica gel, Silicycle).[1] Analytical thin-layer chromatography was performed using glass plates pre-coated with silica (SiliaPlate G TLC - Glass-Backed, 250μm, Silicycle). NMR spectra (^1H, ^{13}C) were obtained on a Bruker AVANCE III 400 MHz spectrometer. The chemical shifts are given as parts per million (ppm) and were referenced to the residual solvent signal ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). HRMS analyses of compounds were performed on a Waters Xevo G2 Q-tof instrument (ESI) in positive or negative ionization mode. Specific Rotation was determined using an Autopol III Automatic polarimeter (Rudolph Research Analytical) and was reported as follows: $[\alpha]_D^T$ (c in g per 100 mL solvent). All starting materials, reagents and solvents were purchased from commercial suppliers (Alfa, TCI, etc.) and used as supplied unless otherwise stated. The carboxylic esters were synthesized by condensation from the corresponding carboxylic acids and phenols as described by Smith and co-workers.[2] The vinylcyclopropanes were synthesized as described according to the literature procedure.[3]

II. General Procedure of Asymmetric Formal (3+2) Cycloaddition of Esters and Vinylcyclopropanes

General Procedure: In an atmosphere-controlled glovebox carboxylic ester (0.2 mmol, 1.0 equiv.), vinylcyclopropane (0.4 mmol, 2.0 equiv.), **Ir-1** (0.002 mmol, 1.0 mol%) and DIPEA (0.2 mmol, 1.0 equiv.) were added to a 2-dram vial charged with a stir bar, followed by the addition of anhydrous DMA (2.0 mL). The vial was sealed with a PTFE-lined cap and removed from the glovebox. The reaction was stirred at room temperature for 4 hours. Then the mixture was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed sequentially with H_2O (3 × 20 mL) and saturated brine (3 × 20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo.* The residue was purified by flash column chromatography on silica gel. The ee values were determined by HPLC using a Daicel chiral column.

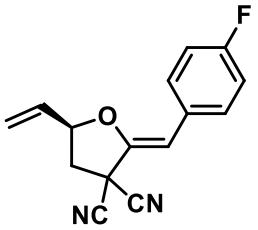
III. Specific Experimental Details and Product Characterization Data



3 prepared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 95% yield (44.9 mg) and 96% ee as an off-white solid. Spectroscopic data for **3** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.05 - 5.91 (m, 1H), 5.88 (s, 1H), 5.57 (d, *J* = 17.1 Hz, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 5.21 - 5.11 (m, 1H), 3.01 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.58 (dd, *J* = 12.9, 9.2 Hz, 1H);

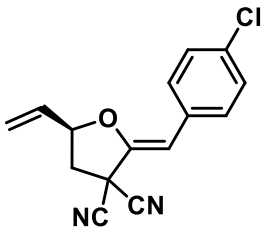
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 16.8 min (major), t_r = 21.1 min (minor);



4 prepared according to **General Procedure** from corresponding carboxylic ester (64.0 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 95% yield (48.3 mg) and 97% ee as an off-white solid. Spectroscopic data for **4** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 - 7.54 (m, 2H), 7.09 - 7.00 (m, 2H), 6.03 - 5.89 (m, 1H), 5.84 (s, 1H), 5.57 (d, *J* = 17.1 Hz, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 5.20 - 5.10 (m, 1H), 3.02 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.58 (dd, *J* = 12.9, 9.2 Hz, 1H);

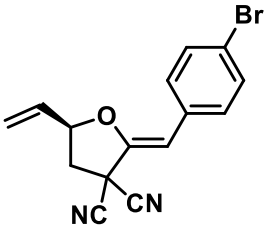
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.8 min (major), t_r = 24.7 min (minor);



5 prepared according to **General Procedure** from corresponding carboxylic ester (67.2 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 90% yield (48.6 mg) and 96% ee as an off-white solid. Spectroscopic data for **5** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.04 - 5.91 (m, 1H), 5.83 (s, 1H), 5.57 (d, *J* = 17.1 Hz, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.23 - 5.13 (m, 1H), 3.02 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.59 (dd, *J* = 12.9, 9.2 Hz, 1H);

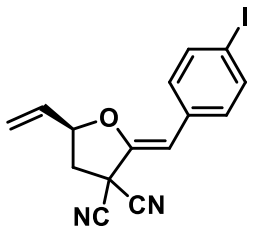
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.5 min (major), t_r = 25.4 min (minor);



6 prepared according to **General Procedure** from corresponding carboxylic ester (76.0 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 90% yield (56.5 mg) and 96% ee as an off-white solid. Spectroscopic data for **6** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 - 7.43 (m, 4H), 6.02 - 5.91 (m, 1H), 5.82 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.22 - 5.13 (m, 1H), 3.02 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.58 (dd, *J* = 12.9, 9.2 Hz, 1H);

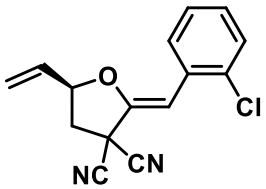
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 22.0 min (major), t_r = 27.1 min (minor));



7 prepared according to **General Procedure** from corresponding carboxylic ester (85.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 95% yield (68.8 mg) and 96% ee as an off-white solid. Spectroscopic data for **7** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.00 - 5.90 (m, 1H), 5.80 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.21 - 5.13 (m, 1H), 3.02 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.58 (dd, *J* = 12.9, 9.2 Hz, 1H);

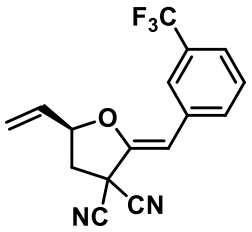
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 23.0 min (major), t_r = 28.5 min (minor);



8 prepared according to **General Procedure** from corresponding carboxylic ester (67.2 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 92% yield (49.7 mg) and 95% ee as an off-white solid. Spectroscopic data for **8** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.26 - 7.23 (m, 1H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 6.36 (s, 1H), 6.01 - 5.91 (m, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 5.23 - 5.13 (m, 1H), 3.04 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.60 (dd, *J* = 12.9, 9.2 Hz, 1H);

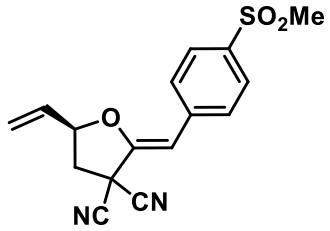
Chiral HPLC: Daicel Chiral pak ID column (1% IPA in hexanes, 1.0 mL/min), t_r = 11.2 min (major), t_r = 10.1 min (minor);



9 prepared according to **General Procedure** from corresponding carboxylic ester (74.0 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 87% yield (52.9 mg) and 96% ee as an off-white solid. Spectroscopic data for **9** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (s, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.55 - 7.46 (m, 2H), 6.04 - 5.91 (m, 2H), 5.58 (d, *J* = 17.1 Hz, 1H), 5.48 (d, *J* = 10.4 Hz, 1H), 5.25 - 5.19 (m, 1H), 3.05 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.61 (dd, *J* = 12.9, 9.2 Hz, 1H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 15.5 min (major), t_r = 19.0 min (minor);

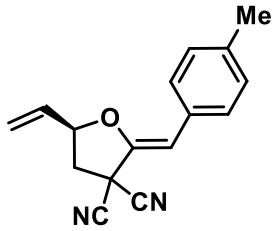


10 prepared according to **General Procedure** from corresponding carboxylic ester (76.0 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The

reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 41% yield (25.8 mg) and 89% ee as an off-white solid. Spectroscopic data for **10** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 6.03 - 5.92 (m, 2H), 5.59 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.4 Hz, 1H), 5.28 - 5.20 (m, 1H), 3.09 (d, *J* = 5.4 Hz, 1H), 3.05 (s, 3H), 2.63 (dd, *J* = 13.0, 9.2 Hz, 1H)

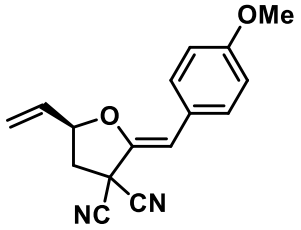
Chiral HPLC: Daicel Chiral pak IG column (30% IPA in hexanes, 1.0 mL/min), t_r = 29.9 min (major), t_r = 27.1 min (minor);



11 prepared according to **General Procedure** from corresponding carboxylic ester (63.2 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 93% yield (46.5 mg) and 97% ee as an off-white solid. Spectroscopic data for **11** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.03 - 5.91 (m, 1H), 5.85 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.19 - 5.10 (m, 1H), 3.00 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.57 (dd, *J* = 12.8, 9.1 Hz, 1H), 2.35 (s, 3H);

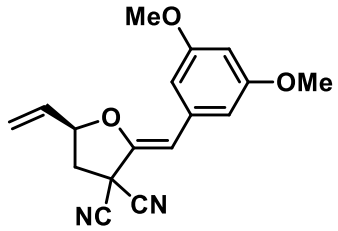
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 15.4 min (major), t_r = 19.3 min (minor);



12 prepared according to **General Procedure** from corresponding carboxylic ester (66.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 90% yield (47.9 mg) and 97% ee as an off-white solid. Spectroscopic data for **12** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.02 - 5.90 (m, 1H), 5.85 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.44 (d, *J* = 10.4 Hz, 1H), 5.19 - 5.09 (m, 1H), 3.04 - 2.97 (m, 1H), 2.57 (dd, *J* = 12.9, 9.1 Hz, 1H), 2.35 (s, 3H);

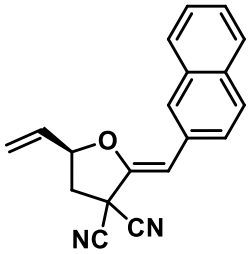
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 30.4 min (major), t_r = 38.4 min (minor);



13 prepared according to **General Procedure** from corresponding carboxylic ester (72.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 86% yield (50.9 mg) and 96% ee as an off-white solid. Spectroscopic data for 1**3** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.77 (d, *J* = 2.2 Hz, 2H), 6.40 (t, *J* = 2.2 Hz, 1H), 6.01 - 5.91 (m, 1H), 5.81 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.44 (d, *J* = 10.4 Hz, 1H), 5.21 - 5.12 (m, 1H), 3.80 (s, 6H), 3.01 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.57 (dd, *J* = 12.9, 9.2 Hz, 1H);

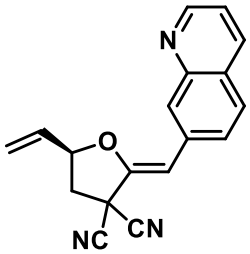
Chiral HPLC: Daicel Chiral pak IC column (5% IPA in hexanes, 1.0 mL/min), t_r = 18.9 min (major), t_r = 21.4 min (minor);



14 prepared according to **General Procedure** from corresponding carboxylic ester (70.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 87% yield (49.8 mg) and 96% ee as an off-white solid. Spectroscopic data for **14** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 1H), 7.86 - 7.79 (m, 3H), 7.75 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.52 - 7.44 (m, 2H), 6.09 - 5.94 (m, 2H), 5.61 (d, *J* = 17.1 Hz, 1H), 5.48 (d, *J* = 10.4 Hz, 1H), 5.27 - 5.18 (m, 1H), 3.04 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.62 (dd, *J* = 12.9, 9.1 Hz, 1H);

Chiral HPLC: Daicel Chiral pak IE column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.2 min (major), t_r = 19.1 min (minor);

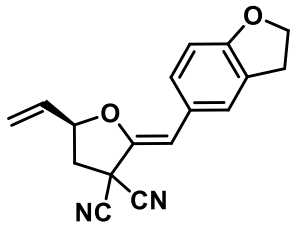


15 prepared according to **General Procedure** from corresponding carboxylic ester (70.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 76% yield (43.6 mg) and 96% ee as an off-white solid. Spectroscopic data for **15** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.89 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.10 - 8.04 (m, 1H), 8.04 - 7.96 (m, 2H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.09 - 5.93 (m, 2H), 5.62 (d, *J* =

17.1 Hz, 1H), 5.51 (d, *J* = 10.4 Hz, 1H), 5.30 - 5.19 (m, 1H), 3.07 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.64 (dd, *J* = 12.9, 9.2 Hz, 1H);

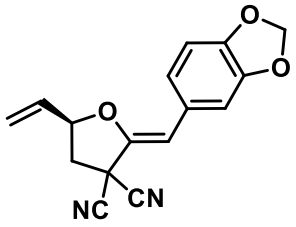
Chiral HPLC: Daicel Chiral pak IE column (10% IPA in hexanes, 1.0 mL/min), t_r = 27.5 min (major), t_r = 25.6 min (minor);



16 prepared according to **General Procedure** from corresponding carboxylic ester (68.8 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 8/1, R_f = 0.3), the desired product was obtained in 81% yield (45.1 mg) and 97% ee as an off-white solid. Spectroscopic data for **16** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.01 - 5.91 (m, 1H), 5.81 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.44 (d, *J* = 10.4 Hz, 1H), 5.16 - 5.09 (m, 1H), 4.59 (t, *J* = 8.7 Hz, 2H), 3.22 (t, *J* = 8.7 Hz, 2H), 2.99 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.56 (dd, *J* = 12.9, 9.1 Hz, 1H);

Chiral HPLC: Daicel Chiral pak IC column (3% IPA in hexanes, 1.0 mL/min), t_r = 24.2 min (major), t_r = 28.7 min (minor);

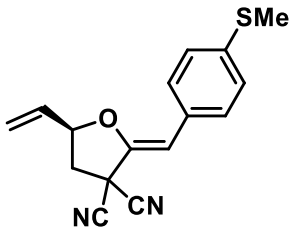


17 prepared according to **General Procedure** from corresponding carboxylic ester (69.2 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 8/1, R_f = 0.3), the desired product was obtained in

91% yield (51.0 mg) and 97% ee as an off-white solid. Spectroscopic data for **17** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, *J* = 1.5 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.01 - 5.91 (m, 3H), 5.79 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.17 - 5.09 (m, 1H), 3.00 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.57 (dd, *J* = 12.9, 9.1 Hz, 1H);

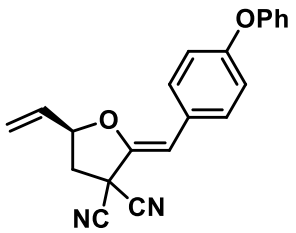
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 36.4 min (major), t_r = 44.3 min (minor);



18 prepared according to **General Procedure** from corresponding carboxylic ester (69.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 61% yield (34.4 mg) and 97% ee as an off-white solid. Spectroscopic data for **18** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.00 - 5.91 (m, 1H), 5.83 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.19 - 5.12 (m, 1H), 3.01 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.58 (dd, *J* = 12.9, 9.1 Hz, 1H), 2.49 (s, 3H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 32.4 min (major), t_r = 40.3 min (minor);

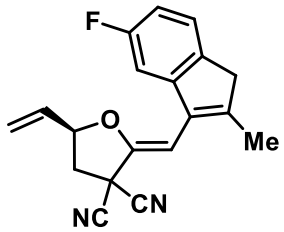


19 prepared according to **General Procedure** from corresponding carboxylic ester (78.8 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg,

0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 93% yield (61.0 mg) and 97% ee as an off-white solid. Spectroscopic data for **19** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, *J* = 8.7 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 - 6.94 (m, 4H), 6.00 - 5.91 (m, 1H), 5.85 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.18 - 5.11 (m, 1H), 3.01 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.58 (dd, *J* = 12.9, 9.2 Hz, 1H);

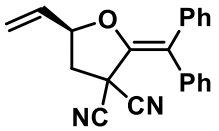
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 28.2 min (major), t_r = 34.6 min (minor);



20 prepared according to **General Procedure** from corresponding carboxylic ester (74.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 71% yield (43.5 mg) and 97% ee as an off-white solid. Spectroscopic data for **20** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 - 7.26 (m, 1H), 7.01 (dd, *J* = 9.5, 2.3 Hz, 1H), 6.87 - 6.77 (m, 1H), 5.97 - 5.87 (m, 1H), 5.83 (s, 1H), 5.50 (d, *J* = 17.1 Hz, 1H), 5.41 (d, *J* = 10.4 Hz, 1H), 5.11 - 5.05 (m, 1H), 3.35 (s, 2H), 3.05 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.62 (dd, *J* = 12.9, 9.3 Hz, 1H), 2.13 (s, 3H);

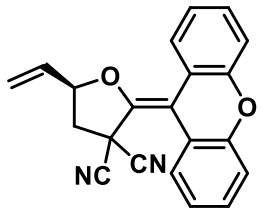
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.1 min (major), t_r = 23.1 min (minor);



21 prepared according to **General Procedure** from corresponding carboxylic ester (75.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 90% yield (56.2 mg) and >99% ee as an off-white solid. Spectroscopic data for **21** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 - 7.36 (m, 7H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 - 7.21 (m, 1H), 6.06 - 5.93 (m, 1H), 5.55 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.12 - 4.99 (m, 1H), 3.07 (dd, *J* = 12.8, 5.1 Hz, 1H), 2.67 (dd, *J* = 12.8, 9.7 Hz, 1H);

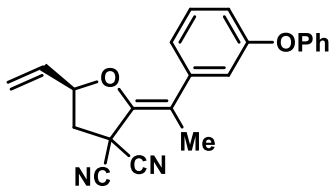
Chiral HPLC: Daicel Chiral pak ID column (1% IPA in hexanes, 1.0 mL/min), t_r = 14.8 min (major), t_r = 18.0 min (minor);



22 prepared according to **General Procedure** from corresponding carboxylic ester (78.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 8/1, R_f = 0.3), the desired product was obtained in 51% yield (33.3 mg) and 99% ee as an off-white solid. Spectroscopic data for **22** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.41 - 7.36 (m, 1H), 7.33 - 7.26 (m, 2H), 7.25 - 7.13 (m, 3H), 5.96 - 5.86 (m, 1H), 5.55 (d, *J* = 17.1 Hz, 1H), 5.41 (d, *J* = 10.4 Hz, 1H), 5.18 (dt, *J* = 9.2, 6.0 Hz, 1H), 3.12 (dd, *J* = 12.9, 5.5 Hz, 1H), 2.60 (dd, *J* = 12.9, 9.2 Hz, 1H);

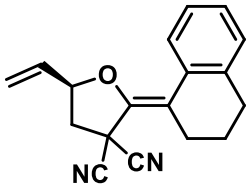
Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 18.2 min (major), t_r = 20.6 min (minor);



23 prepared according to **General Procedure** from corresponding carboxylic ester (78.8 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 39% yield (26.7 mg), 98% ee and 9:1 Z/E as an off-white solid. Spectroscopic data for **23** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 - 7.32 (m, 3H), 7.27 - 7.20 (m, 2H), 7.17 - 7.10 (m, 1H), 7.08 - 7.02 (m, 2H), 6.98 - 6.92 (m, 1H), 5.91 - 5.81 (m, 1H), 5.39 (dd, *J* = 17.3, 13.9 Hz, 2H), 4.90 - 4.82 (m, 1H), 3.10 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.69 (dd, *J* = 13.1, 8.8 Hz, 1H), 2.30 (s, 3H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 17.3 min (major), t_r = 20.2 min (minor);



24 prepared according to **General Procedure** from corresponding carboxylic ester (68.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 87% yield (48.0 mg) and 98% ee as an off-white solid.

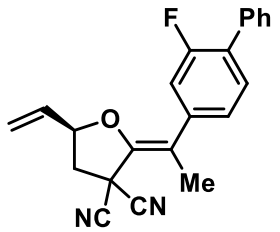
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 - 8.03 (m, 1H), 7.21 - 7.13 (m, 3H), 6.00 - 5.90 (m, 1H), 5.51 (d, *J* = 17.2 Hz, 1H), 5.42 (d, *J* = 10.5 Hz, 1H), 4.96 - 4.89 (m, 1H), 3.10 (dd, *J* = 13.0, 5.4 Hz, 1H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.74 - 2.67 (m, 3H), 2.05 - 1.97 (m, 2H);

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.1, 138.2, 133.1, 132.3, 129.3, 129.1, 127.6, 125.9, 120.4, 113.8, 113.6, 113.5, 81.0, 44.3, 35.8, 30.4, 28.6, 22.7;

HRMS (ESI): Calcd for $C_{18}H_{17}N_2O$ $[M+H]^+$: 277.1335, found 277.1333;

Chiral HPLC: Daicel Chiral pak IG column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.0 min (major), t_r = 16.0 min (minor);

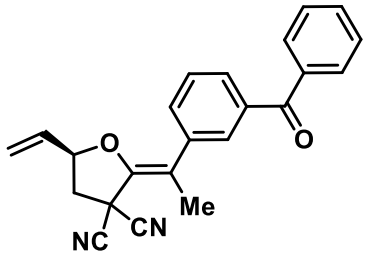
Optical Rotation: $[\alpha]_D^{20}$ = -46.60 (c = 1.0, CH_2Cl_2).



25 prepared according to **General Procedure** from corresponding carboxylic ester (82.0 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 51% yield (35.1 mg) and 97% ee as an off-white solid. Spectroscopic data for **25** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 - 7.56 (m, 2H), 7.49 - 7.42 (m, 3H), 7.41 - 7.35 (m, 3H), 5.96 - 5.86 (m, 1H), 5.48 (d, *J* = 17.2 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 4.98 - 4.87 (m, 1H), 3.12 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.72 (dd, *J* = 13.1, 8.7 Hz, 1H), 2.34 (s, 3H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 18.1 min (major), t_r = 19.7 min (minor);

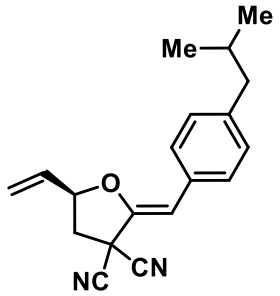


26 prepared according to **General Procedure** from corresponding carboxylic ester (84.0 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 8/1, R_f = 0.3), the desired product was obtained in

83% yield (58.8 mg) and 98% ee as an off-white solid. Spectroscopic data for **26** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (s, 1H), 7.89 - 7.80 (m, 2H), 7.75 - 7.68 (m, 2H), 7.63 - 7.57 (m, 1H), 7.52 - 7.45 (m, 3H), 5.96 - 5.81 (m, 1H), 5.39 (dd, *J* = 19.6, 13.8 Hz, 2H), 4.90 - 4.83 (m, 1H), 3.10 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.69 (dd, *J* = 13.1, 8.8 Hz, 1H), 2.32 (s, 3H);

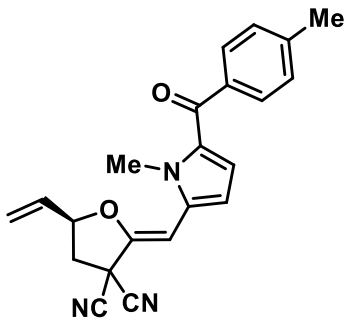
Chiral HPLC: Daicel Chiral pak IG column (5% IPA in hexanes, 1.0 mL/min), t_r = 48.1 min (major), t_r = 52.8 min (minor);



27 prepared according to **General Procedure** from corresponding carboxylic ester (71.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 87% yield (50.8 mg) and 97% ee as an off-white solid. Spectroscopic data for **27** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.01 - 5.91 (m, 1H), 5.86 (s, 1H), 5.57 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.18 - 5.11 (m, 1H), 3.00 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.57 (dd, *J* = 12.9, 9.1 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.91 - 1.80 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 6H);

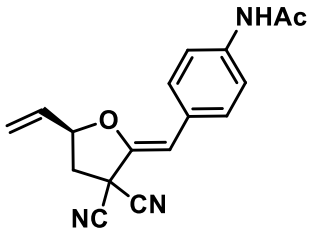
Chiral HPLC: Daicel Chiral pak IG column (1% IPA in hexanes, 1.0 mL/min), t_r = 23.2 min (major), t_r = 17.0 min (minor);



28 prepared according to **General Procedure** from corresponding carboxylic ester (84.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 5/1, R_f = 0.3), the desired product was obtained in 40% yield (28.6 mg) and 84% ee as an off-white solid. Spectroscopic data for **28** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.24 (s, 2H), 6.72 (d, *J* = 4.2 Hz, 1H), 6.66 (d, *J* = 4.2 Hz, 1H), 6.01 - 5.91 (m, 2H), 5.58 (d, *J* = 17.1 Hz, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.23 - 5.16 (m, 1H), 4.03 (s, 3H), 3.07 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.63 (dd, *J* = 12.9, 9.2 Hz, 1H), 2.43 (s, 3H);

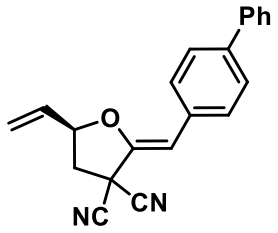
Chiral HPLC: Daicel Chiral pak IE column (10% IPA in hexanes, 1.0 mL/min), t_r = 41.5 min (major), t_r = 35.6 min (minor);



29 prepared according to **General Procedure** from corresponding carboxylic ester (71.8 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 5/1, R_f = 0.3), the desired product was obtained in 63% yield (36.9 mg) and 97% ee as an off-white solid. Spectroscopic data for **29** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 - 7.47 (m, 4H), 7.26 (s, 1H), 6.01 - 5.91 (m, 1H), 5.82 (s, 1H), 5.56 (d, *J* = 17.1 Hz, 1H), 5.45 (d, *J* = 10.4 Hz, 1H), 5.19 - 5.12 (m, 1H), 3.01 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.57 (dd, *J* = 12.9, 9.1 Hz, 1H), 2.18 (s, 3H)

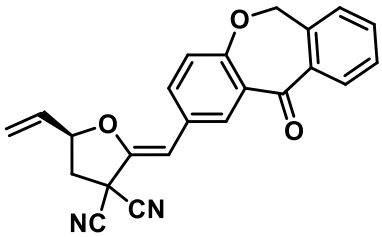
Chiral HPLC: Daicel Chiral pak IE column (10% IPA in hexanes, 1.0 mL/min), t_r = 17.1 min (major), t_r = 14.5 min (minor);



30 prepared according to **General Procedure** from corresponding carboxylic ester (75.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 90% yield (56.2 mg) and 97% ee as an off-white solid. Spectroscopic data for **30** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.64 - 7.58 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.05 - 5.91 (m, 2H), 5.59 (d, *J* = 17.1 Hz, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.26 - 5.14 (m, 1H), 3.03 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.60 (dd, *J* = 12.9, 9.1 Hz, 1H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 32.8 min (major), t_r = 39.2 min (minor);

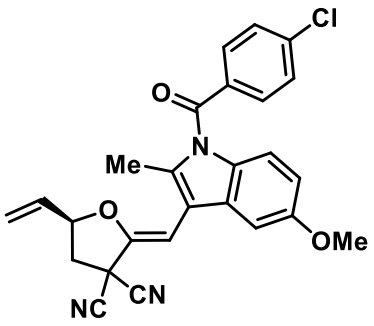


31 prepared according to **General Procedure** from corresponding carboxylic ester (86.8 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by

silica gel column chromatography (PE/EA = 5/1, R_f = 0.3), the desired product was obtained in 83% yield (61.1 mg) and 98% ee as an off-white solid. Spectroscopic data for **31** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (d, *J* = 2.3 Hz, 1H), 7.90 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.78 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.61 - 7.55 (m, 1H), 7.51 - 7.46 (m, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.04 - 5.94 (m, 1H), 5.91 (s, 1H), 5.60 (d, *J* = 17.1 Hz, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.23 - 5.16 (m, 3H), 3.03 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.59 (dd, *J* = 12.9, 9.2 Hz, 1H);

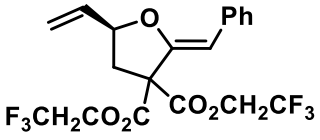
Chiral HPLC: Daicel Chiral pak IC column (10% IPA in hexanes, 1.0 mL/min), t_r = 48.7 min (major), t_r = 45.4 min (minor);



32 prepared according to **General Procedure** from corresponding carboxylic ester (104.6 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (47.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 5/1, R_f = 0.3), the desired product was obtained in 87% yield (79.5 mg) and 98% ee as an off-white solid. Spectroscopic data for **32** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.02 - 5.88 (m, 2H), 5.53 (d, *J* = 17.1 Hz, 1H), 5.43 (d, *J* = 10.4 Hz, 1H), 5.16 - 5.06 (m, 1H), 3.83 (s, 3H), 3.08 (dd, *J* = 12.9, 5.3 Hz, 1H), 2.66 (dd, *J* = 12.9, 9.3 Hz, 1H), 2.34 (s, 3H);

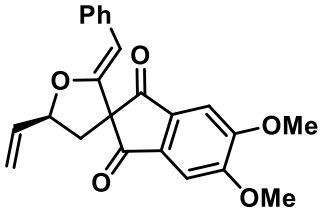
Chiral HPLC: Daicel Chiral pak IA column (10% IPA in hexanes, 1.0 mL/min), t_r = 24.1 min (major), t_r = 20.3 min (minor);



33 prepared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (128.0 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 93% yield (81.5 mg) and 95% ee as an off-white solid. Spectroscopic data for **33** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.02 - 5.90 (m, 1H), 5.70 (s, 1H), 5.46 (d, *J* = 17.1 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.95 (dd, *J* = 14.8, 6.5 Hz, 1H), 4.68 - 4.54 (m, 4H), 2.94 (dd, *J* = 13.1, 5.9 Hz, 1H), 2.52 (dd, *J* = 12.9, 9.3 Hz, 1H);

Chiral HPLC: Daicel Chiral pak IA column (1% IPA in hexanes, 1.0 mL/min), t_r = 8.7 min (major), t_r = 7.9 min (minor);



34 prepared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (103.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 93% yield (70.0 mg) and 95% ee as an off-white solid.

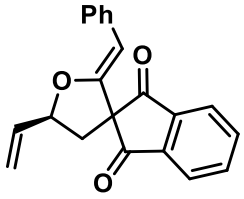
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (dd, *J* = 9.9, 5.1 Hz, 4H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.19 - 6.07 (m, 1H), 5.51 (d, *J* = 17.1 Hz, 1H), 5.41 - 5.31 (m, 2H), 4.62 (s, 1H), 4.07 (d, *J* = 5.6 Hz, 6H), 2.52 - 2.37 (m, 2H);

^{13}C NMR ($CDCl_3$, 101 MHz) δ 196.9, 196.59, 156.69, 156.5, 155.6, 138.2, 137.3, 136.4, 135.6, 128.2, 127.9, 125.8, 125.8, 118.6, 104.5, 104.2, 100.5, 84.4, 64.0, 57.0, 37.0;

HRMS (ESI): Calcd for $C_{23}H_{21}O_5$ $[M+H]^+$: 377.1384, found 377.1385;

Chiral HPLC: Daicel Chiral pak IC column (10% IPA in hexanes, 1.0 mL/min), t_r = 12.9 min (major), t_r = 14.9 min (minor);

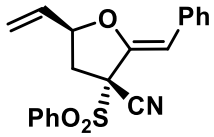
Optical Rotation: $[\alpha]_D^{20}$ = -66.70 (c = 1.0, CH_2Cl_2).



35 prepared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (79.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 93% yield (58.8 mg) and 97% ee as an off-white solid. Spectroscopic data for **35** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 - 8.07 (m, 2H), 7.99 - 7.92 (m, 2H), 7.44 - 7.37 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.07 (dd, *J* = 10.5, 4.2 Hz, 1H), 6.19 - 6.08 (m, 1H), 5.52 (d, *J* = 17.1 Hz, 1H), 5.42 - 5.34 (m, 2H), 4.57 (s, 1H), 2.54 (dd, *J* = 12.6, 6.2 Hz, 1H), 2.45 (dd, *J* = 12.6, 9.4 Hz, 1H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.7 min (major), t_r = 22.5 min (minor);

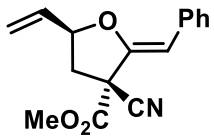


36 prepared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (93.2 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 73% yield (51.3 mg) and 97% ee as an off-white solid. Spectroscopic data for **36** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.86 - 7.80 (m, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.42 - 7.40 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.98 - 5.90 (m, 1H), 5.52

(d, *J* = 17.1 Hz, 1H), 5.38 (d, *J* = 10.3 Hz, 1H), 5.34 - 5.29 (m, 1H), 4.92 (s, 1H), 3.36 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.58 (dd, *J* = 14.3, 10.2 Hz, 1H);

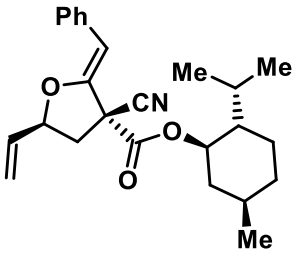
Chiral HPLC: Daicel Chiral pak IA column (1% IPA in hexanes, 1.0 mL/min), t_r = 18.3 min (major), t_r = 16.7 min (minor);



37 prepared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (60.4 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 73% yield (39.3 mg), 93% ee and 7:3 dr as an off-white solid. Spectroscopic data for **37** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz, 7:3 dr) δ 7.62 - 7.54 (m, 2H), 7.37 - 7.29 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.08 - 5.92 (m, 1H), 5.76 (s, 0.3H), 5.62 (s, 0.7H), 5.55 - 5.48 (m, 1H), 5.42 - 5.35 (m, 1H), 5.22 - 5.15 (m, 0.3H), 5.10 - 5.03 (m, 0.7H), 3.94 (s, 2.1H), 3.90 (s, 0.9H), 2.99 (dd, *J* = 12.9, 5.7 Hz, 0.3H), 2.80 - 2.73 (m, 1.4H), 2.37 (dd, *J* = 12.8, 9.6 Hz, 0.3H);

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.7 min (major), t_r = 18.1 min (minor);



38 repared according to **General Procedure** from corresponding carboxylic ester (60.4 mg, 0.2 mmol, 1.0 equiv.), vinylcyclopropane (110.0 mg, 0.4 mmol, 2.0 equiv.), **Ir-1** (2.2 mg, 0.002 mmol, 1.0 mol%) and DIPEA (25.8 mg, 0.2 mmol, 1.0 equiv.) in DMA (2.0 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 56%

yield (44.0 mg) and 2:1 dr as an off-white solid. Spectroscopic data for **38** match those previously reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.07 - 5.96 (m, 1H), 5.64 (s, 1H), 5.51 (d, *J* = 17.1 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 5.06 (dd, *J* = 15.3, 7.0 Hz, 1H), 4.83 (td, *J* = 10.9, 4.4 Hz, 1H), 2.78 - 2.70 (m, 2H), 2.09 - 2.04 (m, 1H), 2.00 - 1.92 (m, 1H), 1.77 - 1.70 (m, 2H), 1.62 - 1.56 (m, 1H), 1.53 - 1.47 (m, 1H), 1.28 - 1.25 (m, 1H), 1.16 - 1.06 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H);

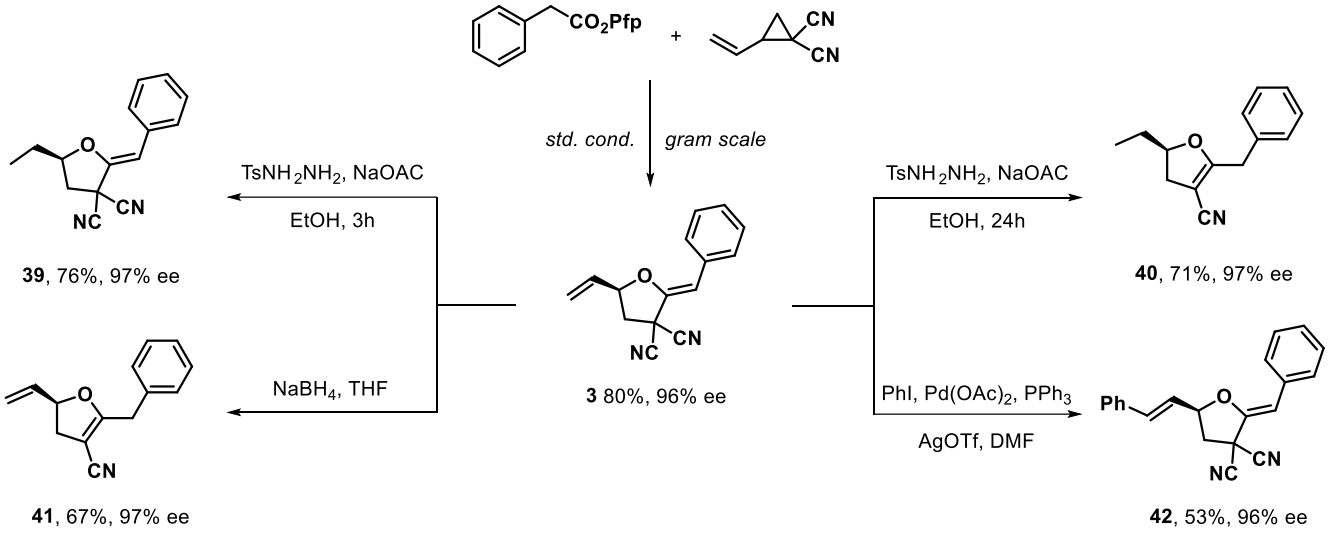
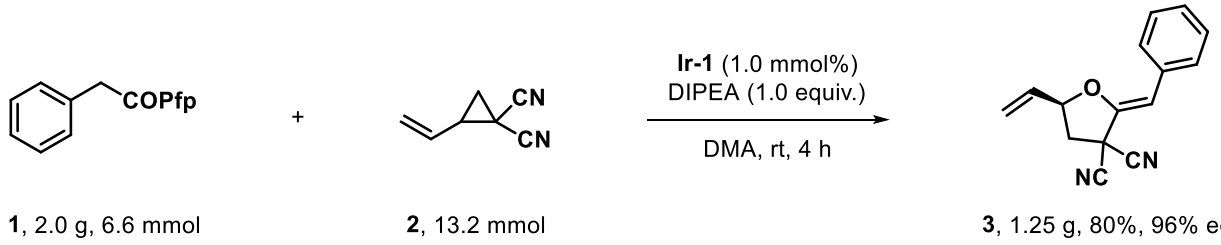
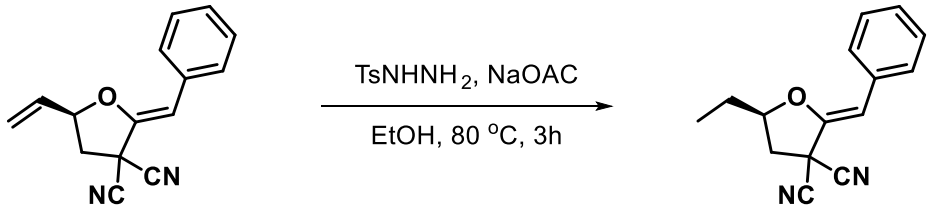


Fig. S1. Scale-up and synthetic applications.



3 prepared according to **General Procedure** from corresponding carboxylic ester (2.0 g, 6.6 mmol, 1.0 equiv.), vinylcyclopropane (1.56 g, 13.2 mmol, 2.0 equiv.), **Ir-1** (73.9 mg, 0.066 mmol, 1.0 mol%) and DIPEA (0.85 g, 6.6 mmol, 1.0 equiv.) in DMA (20 mL). The reaction mixture was allowed to stir at room temperature for 4 hours. After purification by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3), the desired product was obtained in 80% yield (1.25 g) and 96% ee as an off-white solid.



3, 96% ee

39, 76%, 97% ee

3 (47.2 mg, 96% ee, 0.20 mmol, 1.0 equiv.), $TsNHNH_2$ (186.2 mg, 1.00 mmol, 5.0 equiv.) and NaOAc (82.0 mg, 1.00 mmol, 5.0 equiv.) were added to a 2-dram vial charged with a stir bar, followed by the addition of EtOH (2.0 mL). The resulting mixture was stirred at 80 °C under reflux for 3 hours. Upon completion of the reaction, H_2O (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with brine (3 × 10 mL) and H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3) to give **39** in 76% yield (36.2 mg) and 97% ee as a colourless oil.

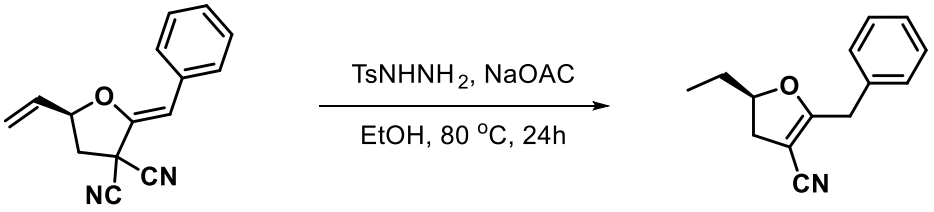
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 - 7.55 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 - 7.22 (m, 1H), 5.83 (s, 1H), 4.71 - 4.63 (m, 1H), 2.95 (dd, *J* = 12.8, 5.0 Hz, 1H), 2.44 (dd, *J* = 12.8, 9.8 Hz, 1H), 1.99 - 1.81 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.3, 133.6, 128.7, 128.5, 127.6, 113.7, 113.6, 104.3, 84.0, 42.2, 27.4, 10.0;

HRMS (ESI): Calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179, found 239.1178;

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 15.1 min (major), t_r = 19.6 min (minor);

Optical Rotation: $[\alpha]_D^{20}$ = -33.56 (c = 1.0, CH_2Cl_2).



3, 96% ee

40, 71%, 97% ee

3 (47.2 mg, 96% ee, 0.20 mmol, 1.0 equiv.), $TsNHNH_2$ (186.2 mg, 1.00 mmol, 5.0 equiv.) and NaOAc (82.0 mg, 1.00 mmol, 5.0 equiv.) were added to a 2-dram vial charged with a stir bar, followed by the addition of EtOH (2.0 mL). The resulting mixture was stirred at 80 °C under reflux for 24 hours. Upon completion of the reaction, H_2O (10 mL) was added and the

aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with brine (3 × 10 mL) and H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3) to give **40** in 71% yield (30.3 mg) and 97% ee as a colourless oil.

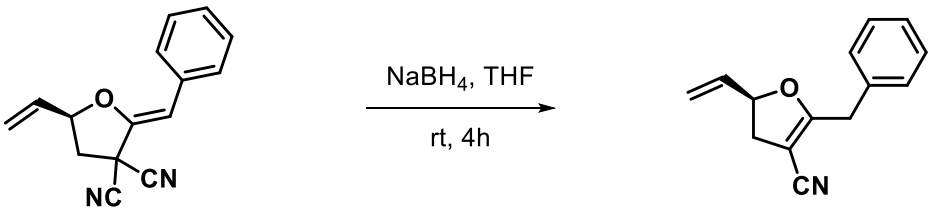
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 - 7.26 (m, 5H), 4.71 - 4.62 (m, 1H), 3.73 - 3.62 (m, 2H), 2.95 (dd, *J* = 13.8, 10.1 Hz, 1H), 2.52 (dd, *J* = 13.9, 7.5 Hz, 1H), 1.72 - 1.59 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.3, 129.0, 128.8, 127.3, 117.2, 85.8, 81.5, 35.1, 34.4, 28.7, 9.0;

HRMS (ESI): Calcd for $C_{14}H_{16}NO$ $[M+H]^+$: 214.1226, found 214.1225;

Chiral HPLC: Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.5 min (major), t_r = 21.8 min (minor);

Optical Rotation: $[\alpha]_D^{20}$ = + 26.34 (c = 1.0, CH_2Cl_2)



3, 96% ee

41, 67%, 97% ee

To a stirring solution of **3** (47.2 mg, 96% ee, 0.20 mmol, 1.0 equiv.) in THF (2.0 mL) was slowly added $NaBH_4$ (7.6 mg, 0.20 mmol, 1.0 equiv.) at 0 °C. The resulting mixture was stirred at room temperature for 4 hours. Upon completion of the reaction, H_2O (10 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with brine (3 × 10 mL) and H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3) to give **41** in 67% yield (28.3 mg) and 97% ee as a colourless oil.

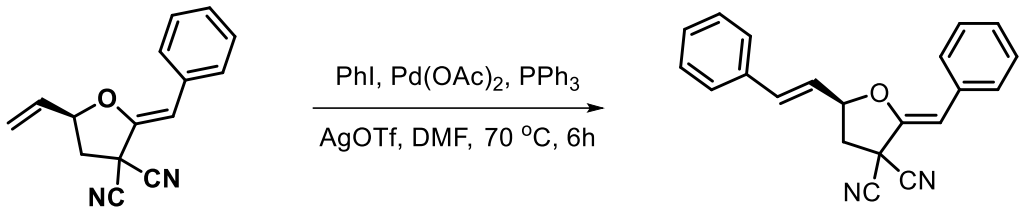
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 - 7.26 (m, 5H), 5.90 - 5.79 (m, 1H), 5.24 - 5.10 (m, 3H), 3.72 - 3.64 (m, 2H), 3.07 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.66 (dd, *J* = 14.0, 7.7 Hz, 1H);

^{13}C NMR ($CDCl_3$, 101 MHz) δ 172.1, 135.7, 135.1, 129.0, 128.9, 127.4, 117.7, 84.4, 81.7, 36.0, 34.4;

HRMS (ESI): Calcd for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1070, found 212.1071;

Chiral HPLC: Daicel Chiral pak IG column (5% IPA in hexanes, 1.0 mL/min), t_r = 9.4 min (major), t_r = 8.7 min (minor);

Optical Rotation: $[\alpha]_D^{20}$ = -55.34 (c = 1.0, CH_2Cl_2).



3, 96% ee

42, 53%, 96% ee

In an atmosphere-controlled glovebox **3** (70.8 mg, 96% ee, 0.3 mmol, 1.0 equiv.), PhI (183.5 mg, 0.9 mmol, 3.0 equiv.), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol%), PPh_3 (15.7 mg, 0.06 mmol, 20 mol%) and AgOTf (154.1 mg, 0.6 mmol, 2.0 quiv.) were added to a 2-dram vial charged with a stir bar, followed by the addition of anhydrous DMF (3.0 mL). The vial was sealed with a PTFE-lined cap and removed from the glovebox. The reaction was stirred at 70 °C for 6 hours. Then the mixture was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed sequentially with H_2O (3 × 10 mL) and saturated brine (3 × 10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo.* The residue was purified by silica gel column chromatography (PE/EA = 10/1, R_f = 0.3) to give **42** in 53% yield (49.6 mg) and 96% ee as an off-white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.47 - 7.42 (m, 2H), 7.40 - 7.31 (m, 5H), 7.27 - 7.26 (m, 1H), 6.85 (d, *J* = 15.8 Hz, 1H), 6.25 (dd, *J* = 15.8, 7.6 Hz, 1H), 5.90 (s, 1H), 5.37 - 5.30 (m, 1H), 3.08 (dd, *J* = 12.9, 5.2 Hz, 1H), 2.67 (dd, *J* = 12.9, 9.5 Hz, 1H);

^{13}C NMR ($CDCl_3$, 101 MHz) δ 146.1, 136.5, 135.1, 133.4, 129.2, 129.0, 128.7, 128.7, 127.7, 127.2, 123.3, 113.5, 104.8, 83.2, 43.0, 38.4;

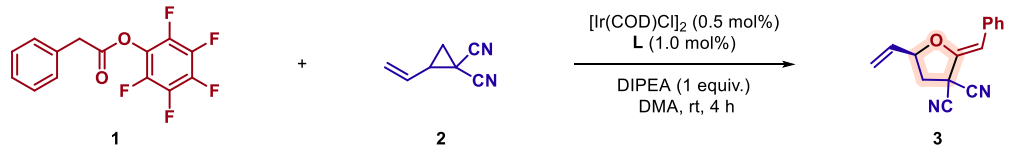
HRMS (ESI): Calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$: 313.1335, found 313.1336;

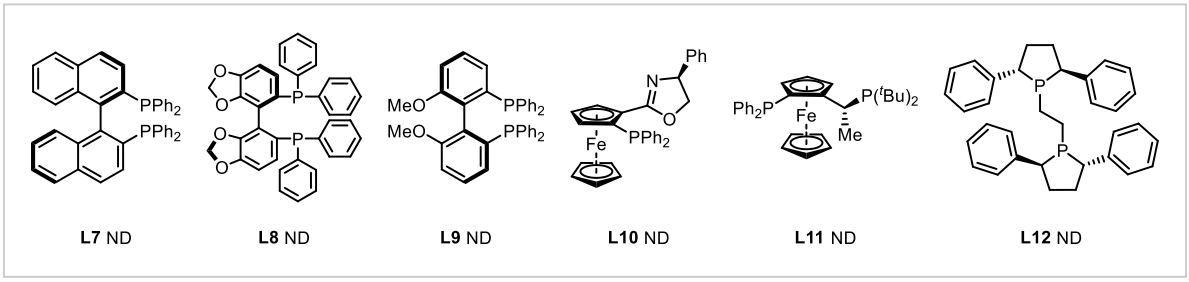
Chiral HPLC: Daicel Chiral pak IA column (5% IPA in hexanes, 1.0 mL/min), t_r = 10.2 min (major), t_r = 9.2 min (minor);

Optical Rotation: $[\alpha]_D^{20}$ = -66.77 (c = 1.0, CH_2Cl_2).

IV. Additional Studies

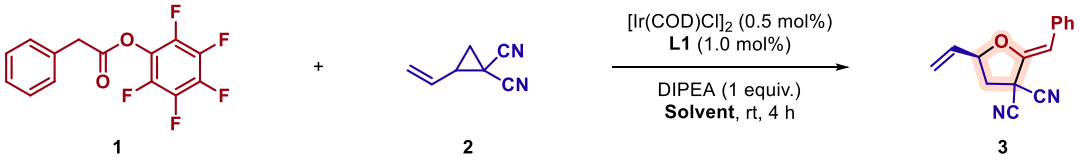
Table S1. Screening of ligands





Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $[Ir(COD)Cl]_2$ (0.5 mol%), **L** (1.0 mol%), DIPEA (0.2 mmol, 1.0 equiv.), DMA (2.0 mL), room temperature, 4 h. Isolated yield. The enantiomeric excess (ee) was determined by HPLC analysis.

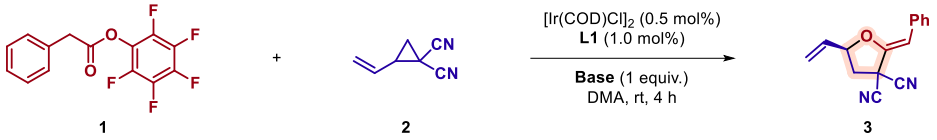
Table S2. Solvent effect in the (3+2) cycloaddition of **1** and **2**



Entry	Solvent	yield (%) [a]	ee (%) [b]
1	**none**	**80**	**96**
2	DMSO	61	91
3	MeCN	53	96
4	DCM	ND	/
5	PhMe	ND	/
6	1,4-dioxane	ND	/
7	Et_2O	ND	/

Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $[Ir(COD)Cl]_2$ (0.5 mol%), **L1** (1.0 mol%), DIPEA (0.2 mmol, 1.0 equiv.), **Solvent** (2.0 mL), room temperature, 4 h. [a] Isolated yield. [b] The enantiomeric excess (ee) was determined by HPLC analysis.

Table S3. Effect of base in the (3+2) cycloaddition of **1** and **2**

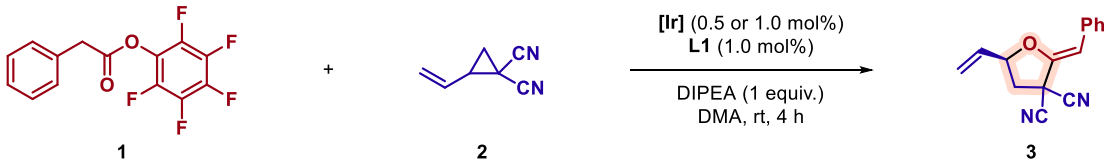


1 2 3

Entry	Base	yield (%) [a]	ee (%) [b]
1	**none**	**80**	**96**
2	DBU	55	96
3	Pyridine	21	96
4	K_3PO_4	ND	/
5	^tBuOK	ND	/
6	Cs_2CO_3	ND	/
7	KOH	ND	/
8	Na_2CO_3	ND	/

Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $[Ir(COD)Cl]_2$ (0.5 mol%), **L1** (1.0 mol%), **Base** (0.2 mmol, 1.0 equiv.), DMA (2.0 mL), room temperature, 4 h. [a] Isolated yield. [b] The enantiomeric excess (ee) was determined by HPLC analysis.

Table S4. Effect of ridium precursors in the (3+2) cycloaddition of **1** and **2**

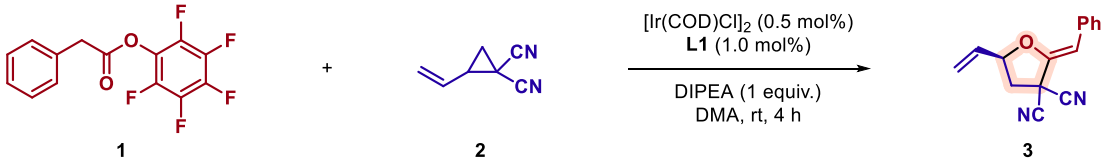


1 2 3

Entry	[Ir]	yield (%) [a]	ee (%) [b]
1	**$[Ir(COD)Cl]_2$**	**80**	**96**
2	**$Ir(COD)_2BF_4$**	72	96
3	**$[Ir(COD)OMe]_2$**	0	-
4	**$Ir(COD)_2BAr_4$**	0	-

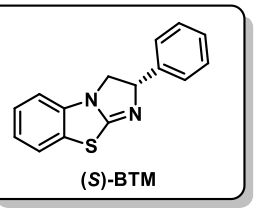
Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), **[Ir]** (0.5 or 1.0 mol%), **L1** (1.0 mol%), DIPEA (0.2 mmol, 1.0 equiv.), DMA (2.0 mL), room temperature, 4 h. [a] Isolated yield. [b] The enantiomeric excess (ee) was determined by HPLC analysis.

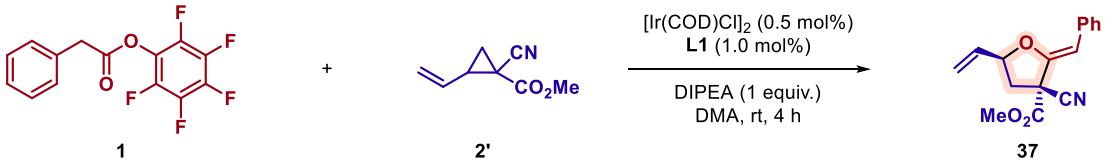
Table S5. Effect of chiral isothiourea organocatalyst in the (3+2) cycloaddition



1 2 3

Entry	Variation	yield (%) [a]	ee (%) [b]
1	**none**	**80**	**96**
2	add 10 mol% **(*S*)-BTM**	76	96
3	10 mol% **(*S*)-BTM** instead of 1 equiv. DIPEA	10	96
4	1 equiv. **(*S*)-BTM** instead of 1 equiv. DIPEA	10	96



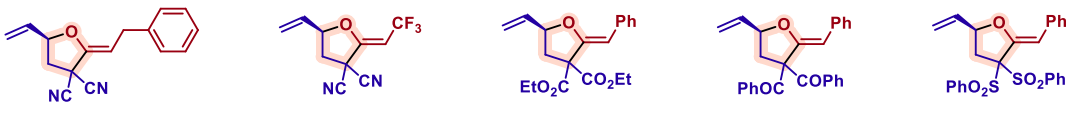


1 2' 37

Entry	Variation	yield (%) [a]	ee (%) [b]	dr
1	**none**	**73**	**93**	**2:1**
2	add 10 mmol% **(*S*)-BTM**	70	93	2:1
3	add 10 mmol% **(*R*)-BTM**	70	93	2:1
4	10 mmol% **(*S*)-BTM** instead of 1 equiv. DIPEA	0	-	-
5	10 mmol% **(*R*)-BTM** instead of 1 equiv. DIPEA	0	-	-
6	1 equiv. **(*S*)-BTM** instead of 1 equiv. DIPEA	0	-	-
7	1 equiv. **(*R*)-BTM** instead of 1 equiv. DIPEA	0	-	-

Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $[Ir(COD)Cl]_2$ (0.5 mol%), **L1** (1.0 mol%), DIPEA (0.2 mmol, 1.0 equiv.), DMA (2.0 mL), room temperature, 4 h. [a] Isolated yield. [b] The enantiomeric excess (ee) was determined by HPLC analysis.

Table S6. Unsuccessful examples



ND ND ND ND ND

Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), **Ir-1** (1.0 mol%), DIPEA (0.2 mmol, 1.0 equiv.), DMA (2.0 mL), room temperature, 4 h.

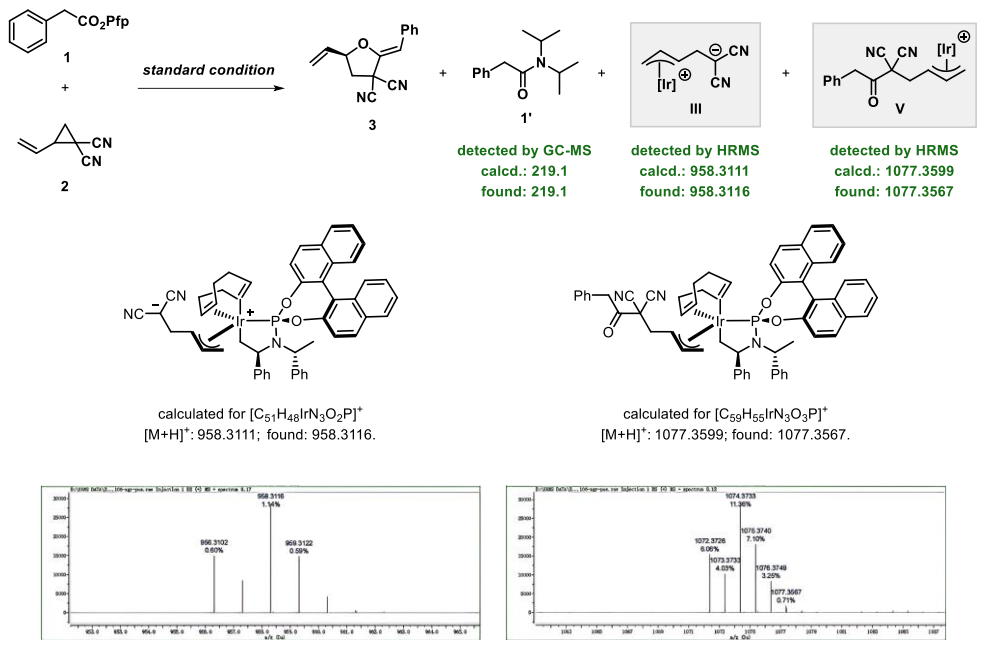
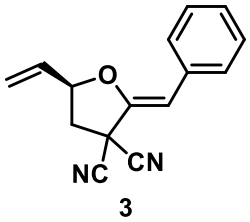


Fig. S2 Verification of intermediates.

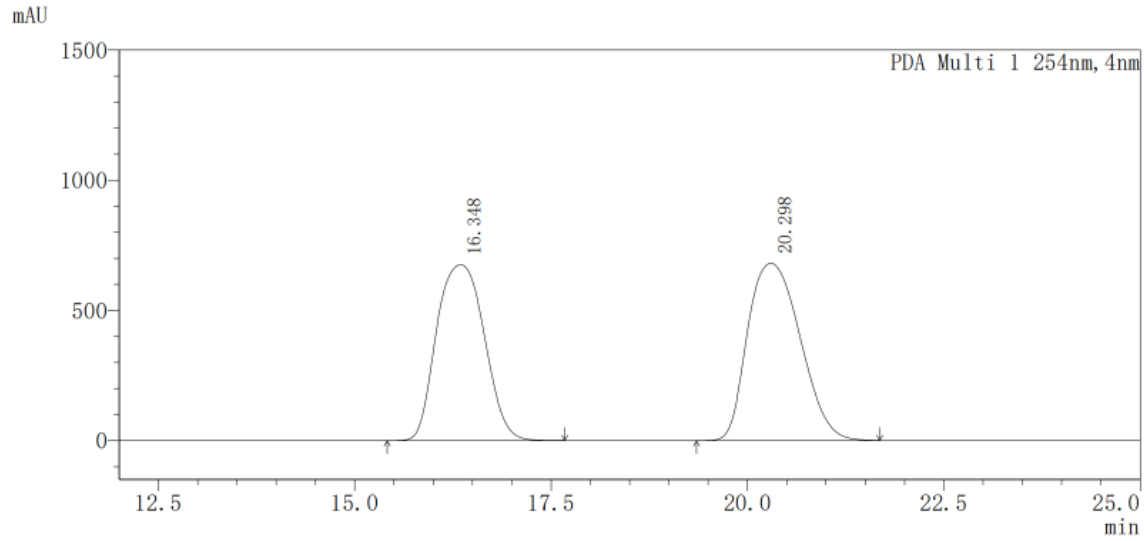
In a N_2-filled glovebox, an oven-dried vial (1 dram) equipped with a magnet stir bar was charged with carboxylic ester (0.1 mmol, 1.0 equiv.), vinylcycloproane (0.2 mmol, 2.0 equiv.), **Ir-1** (0.001 mmol, 1.0 mmol%), DIPEA (0.1 mmol, 1.0 equiv.) and dry DMA (0.1 M). The reaction mixture was stirred at room temperature for 10 min. The reaction system was subjected to HRMS and GC-MS analysis *in situ*.

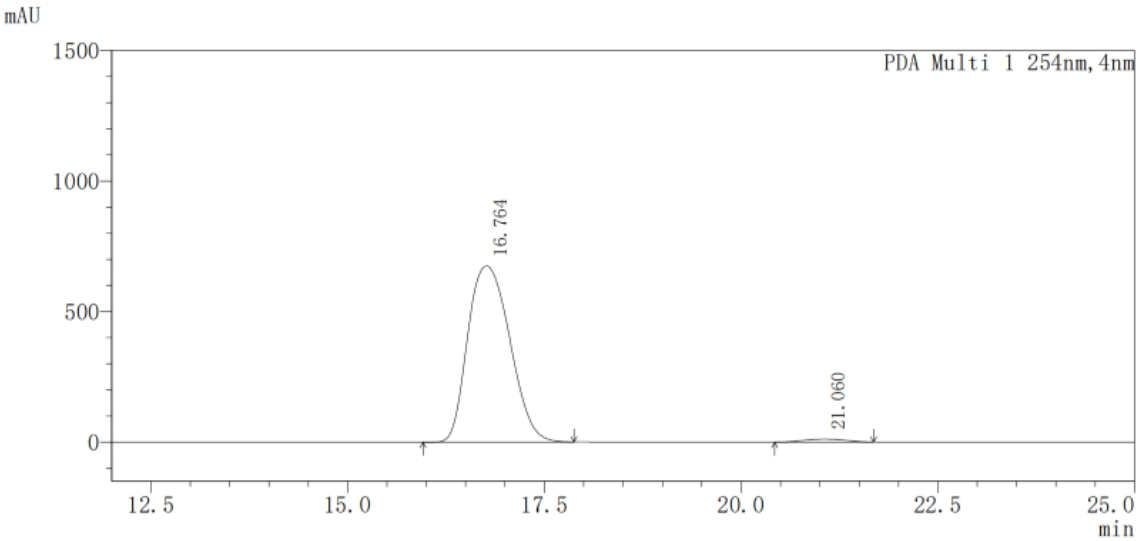
V. HPLC Chromatograms



3

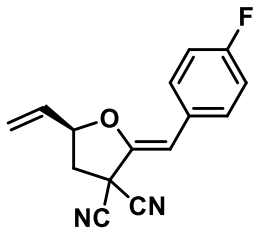
Chiral HPLC: 96% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 16.8 min (major), t_r = 21.1 min (minor);





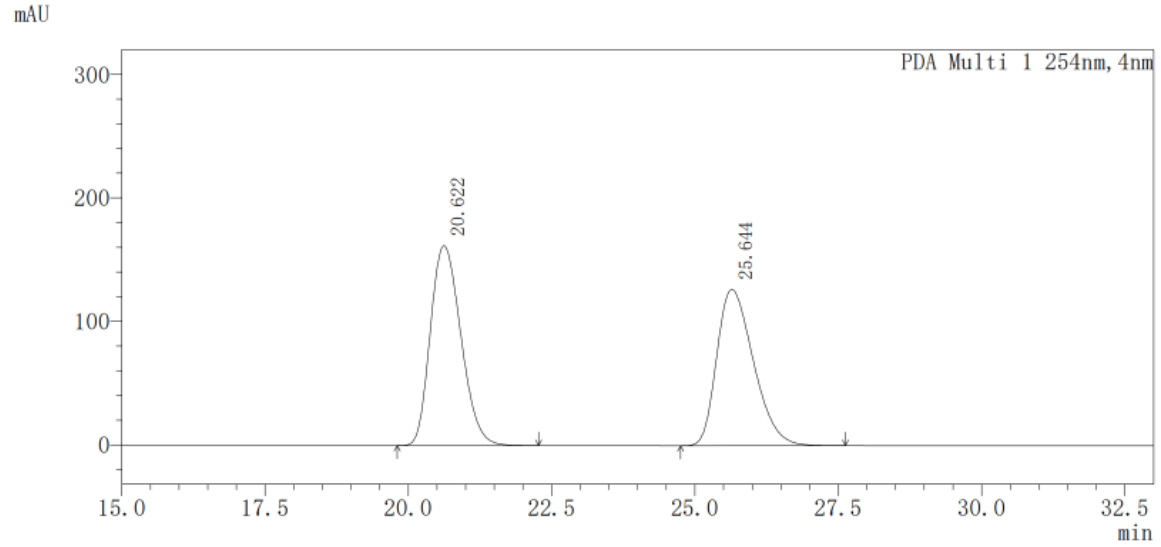
PDA Ch1 254nm

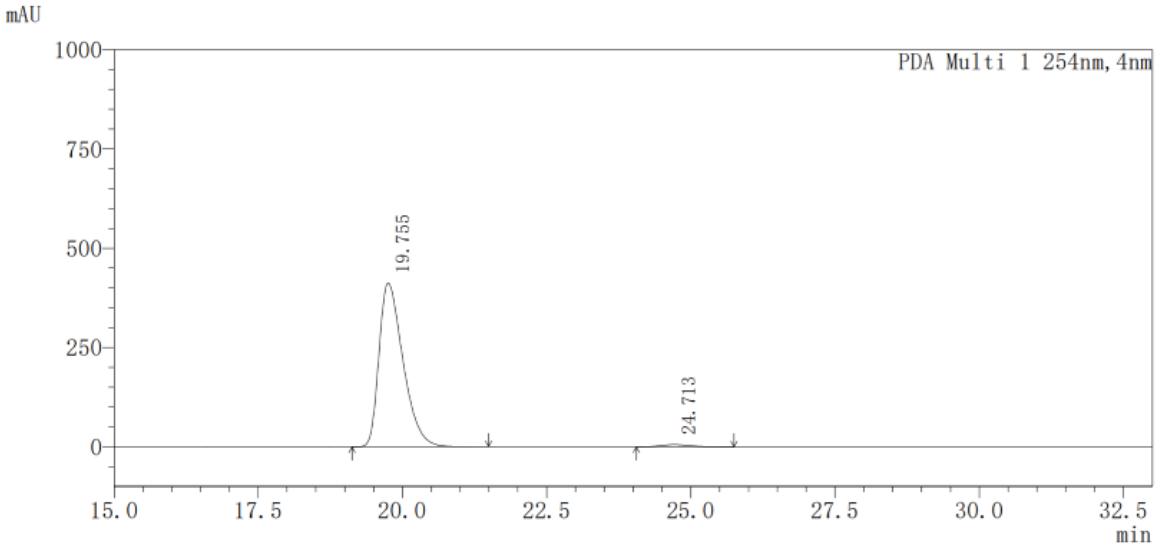
Peak #	Ret. Time	Area	Height	Area%	Height%
1	16.764	25228969	675101	98.221	98.312
2	21.060	457038	11591	1.779	1.688
总计		25686007	686691	100.000	100.000



4

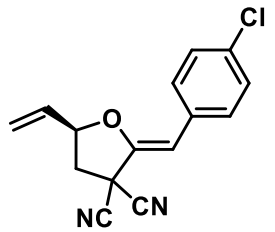
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.8 min (major), t_r = 24.7 min (minor);





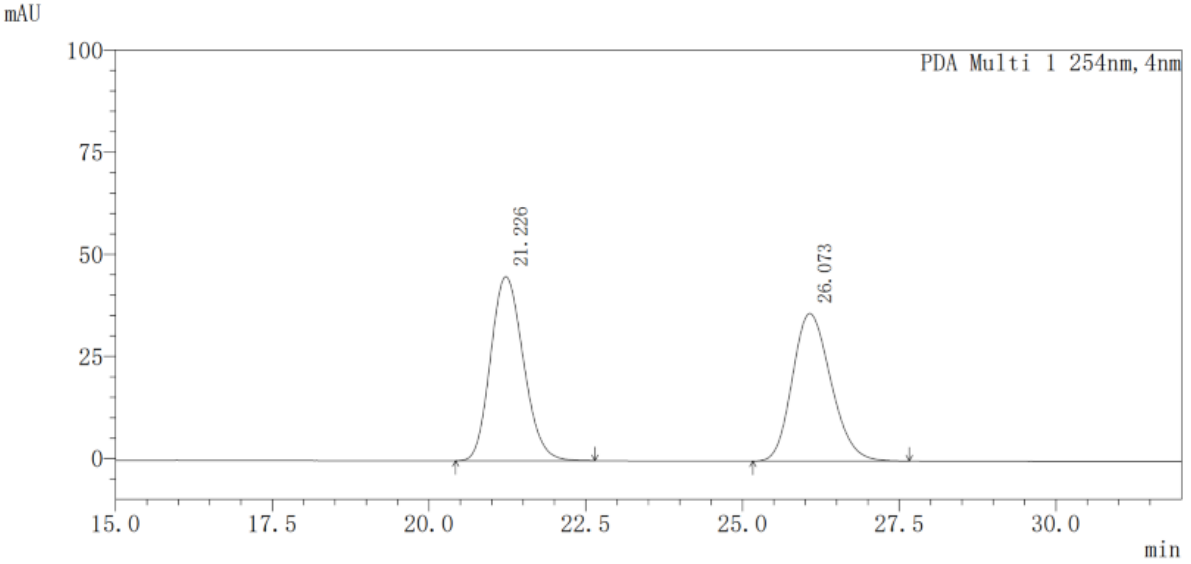
PDA Ch1 254nm

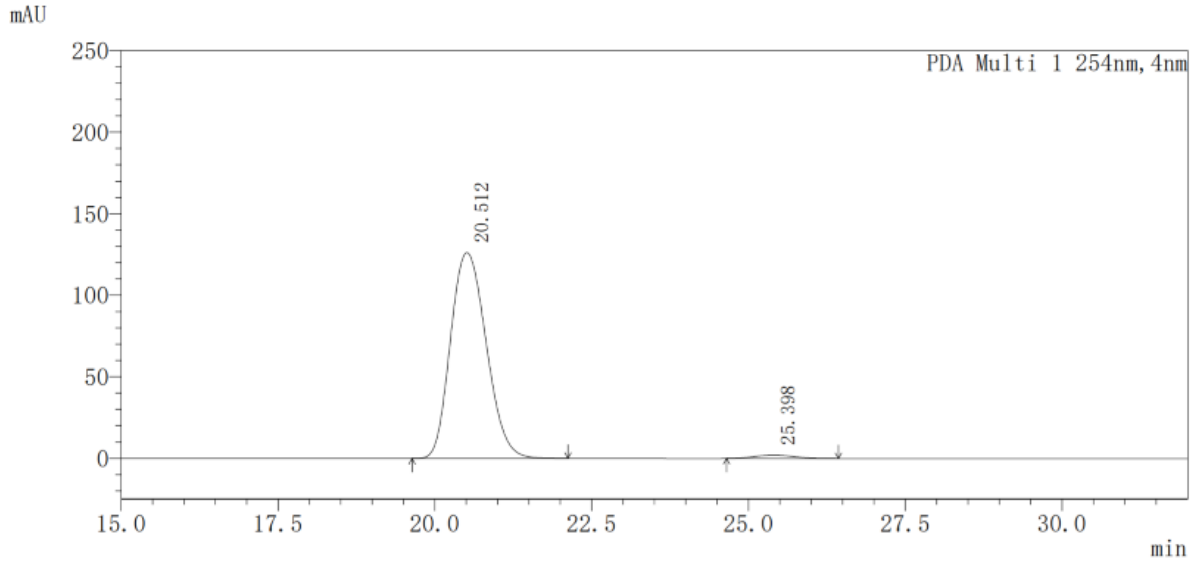
Peak #	Ret. Time	Area	Height	Area%	Height%
1	19.755	11957047	412539	98.472	98.689
2	24.713	185545	5481	1.528	1.311
总计		12142592	418020	100.000	100.000



5

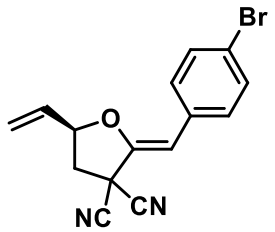
Chiral HPLC: 96% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.5 min (major), t_r = 25.4 min (minor);





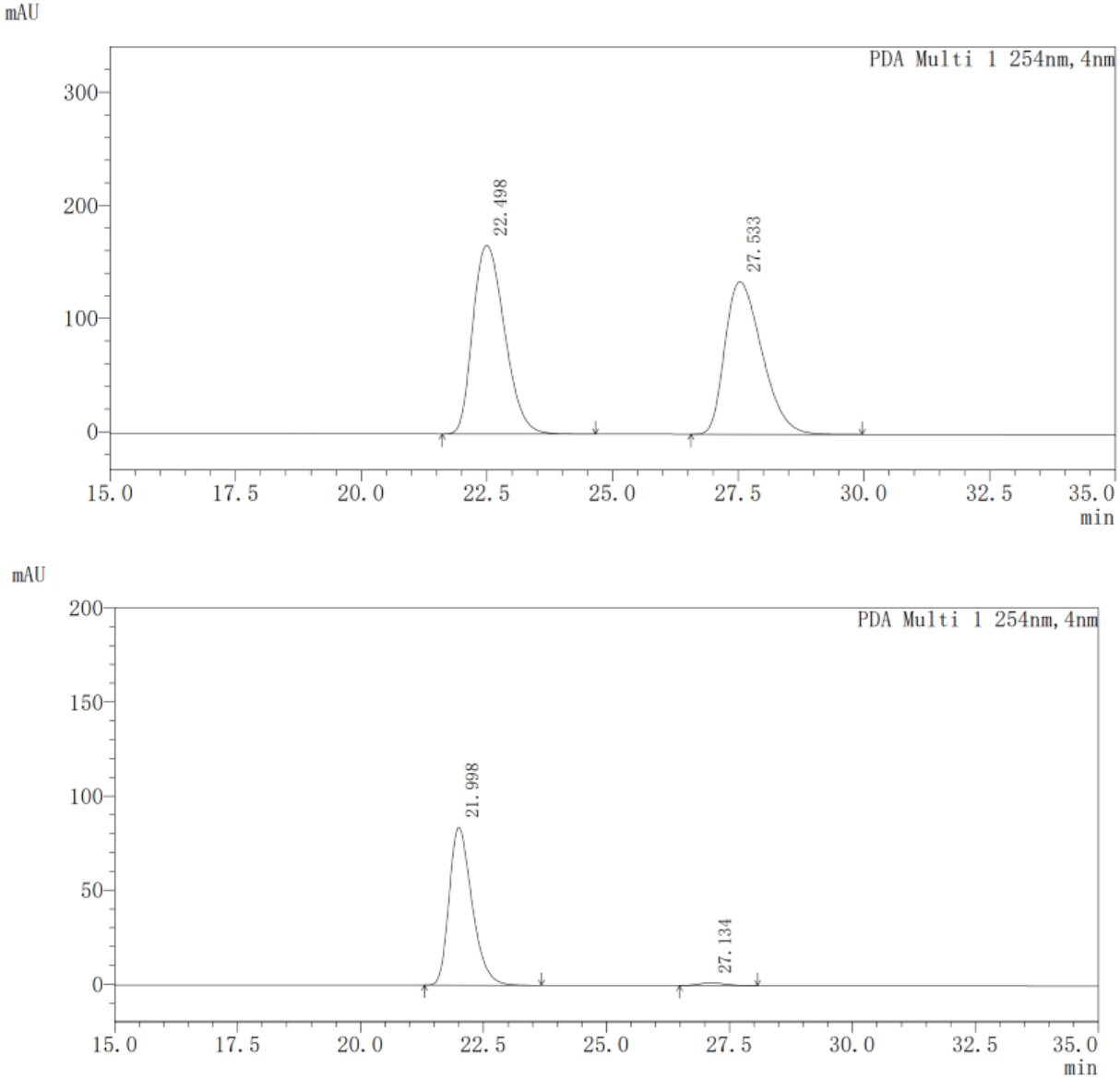
PDA Ch1 254nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	20.512	5008416	126283	98.211	98.376
2	25.398	91207	2085	1.789	1.624
总计		5099624	128368	100.000	100.000



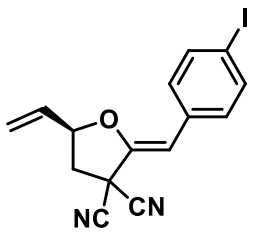
6

Chiral HPLC: 96% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 22.0 min (major), t_r = 27.1 min (minor);



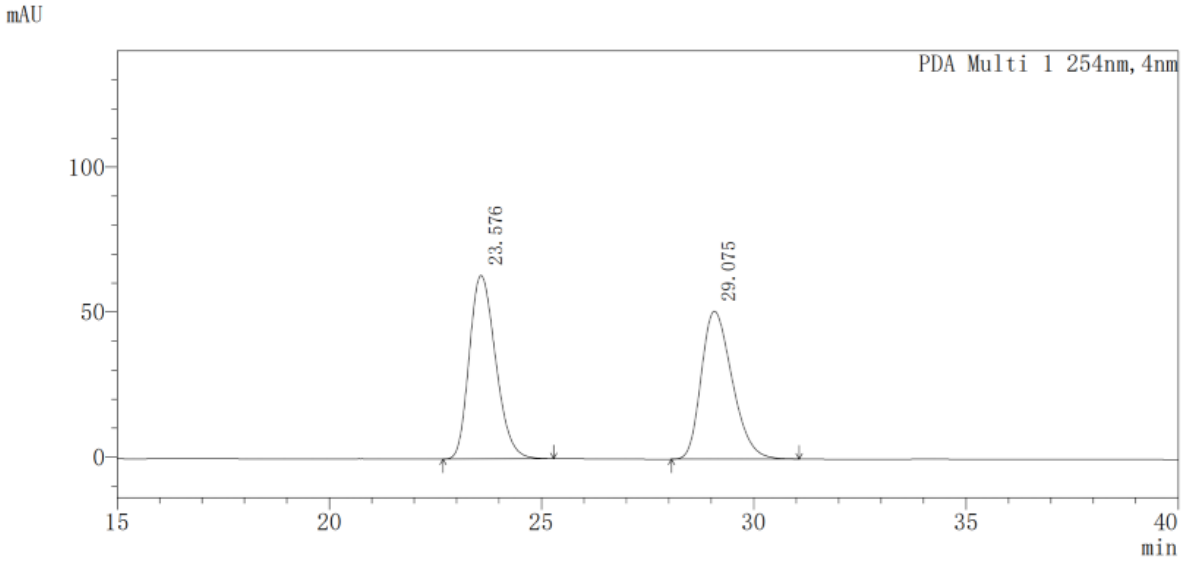
PDA Ch1 254nm

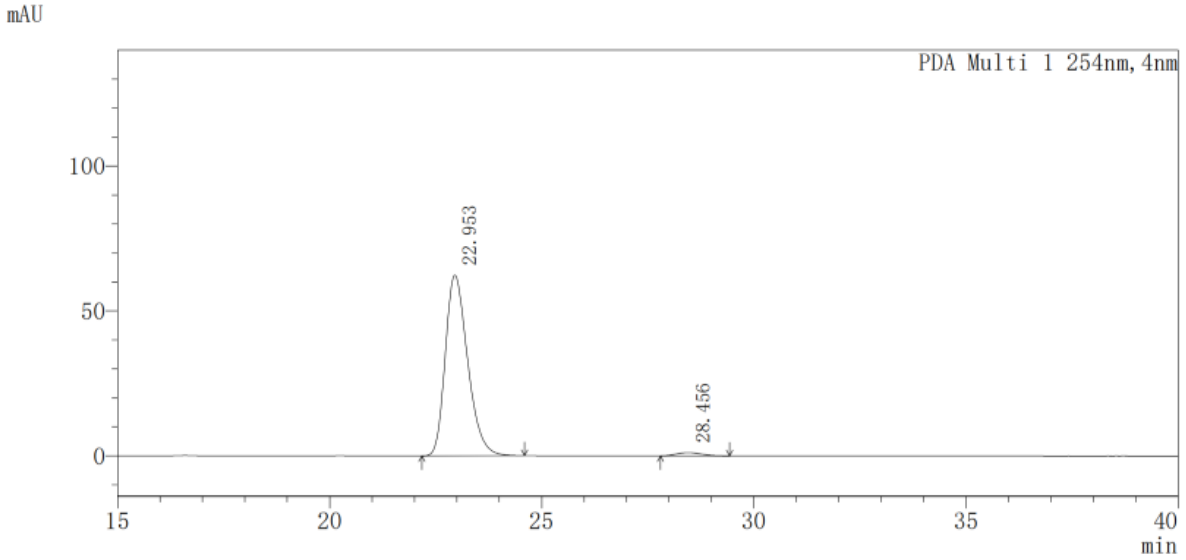
Peak #	Ret. Time	Area	Height	Area%	Height%
1	21.998	2720835	83951	97.918	98.212
2	27.134	57853	1528	2.082	1.788
总计		2778688	85479	100.000	100.000



7

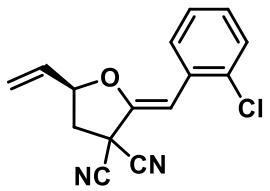
Chiral HPLC: 96% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 23.0 min (major), t_r = 28.5 min (minor);





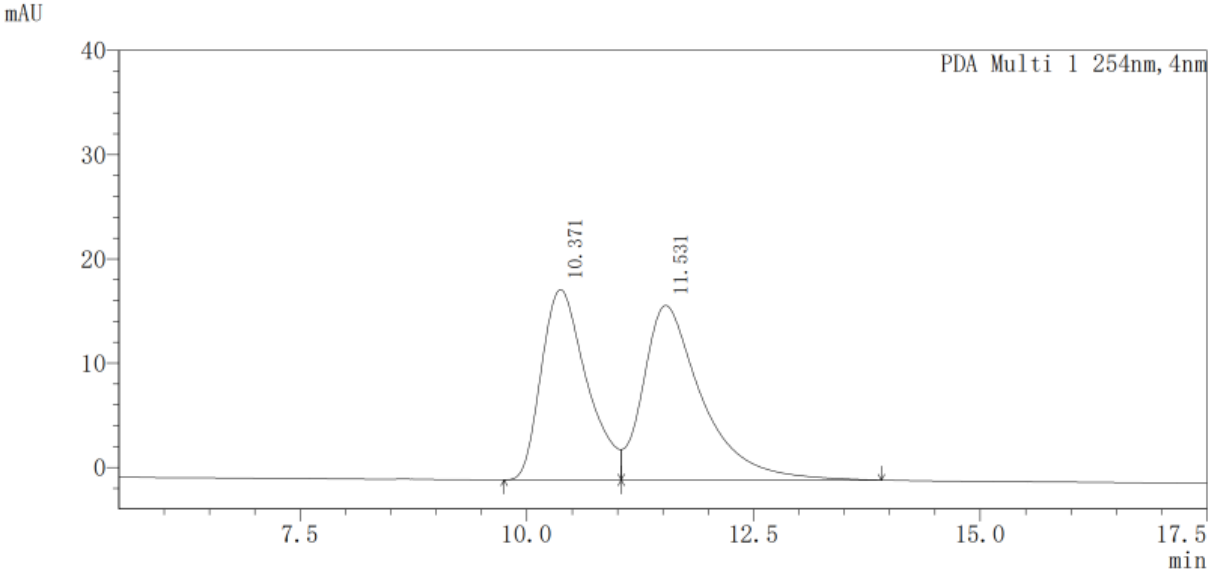
PDA Ch1 254nm

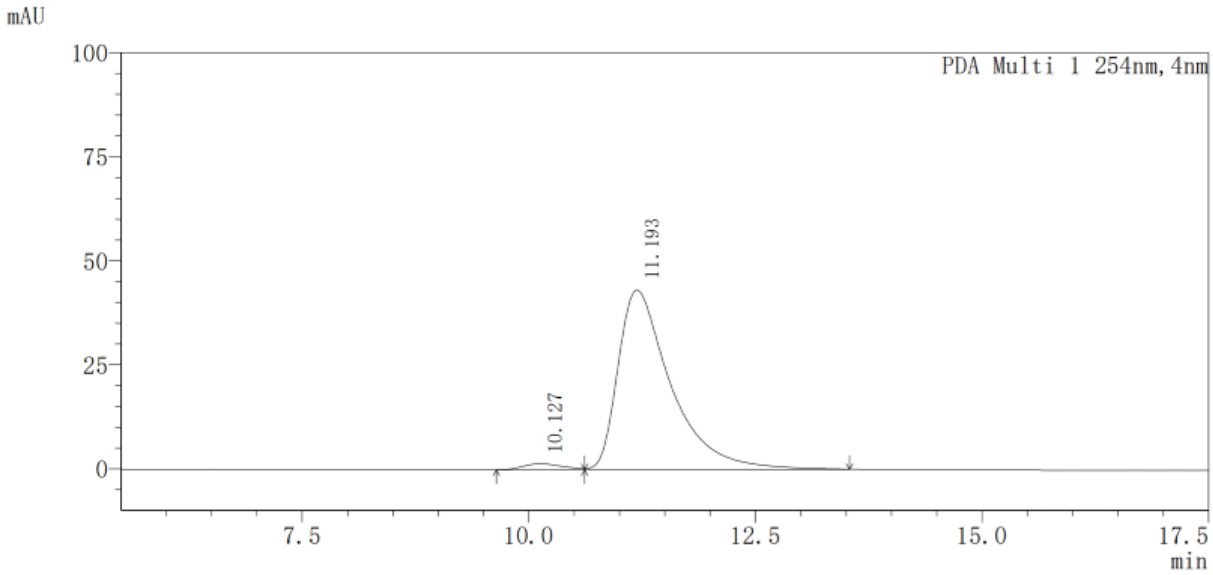
Peak #	Ret. Time	Area	Height	Area%	Height%
1	22.953	2288588	62360	98.014	98.235
2	28.456	46373	1121	1.986	1.765
总计		2334962	63481	100.000	100.000



8

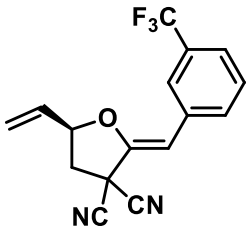
Chiral HPLC: 95% ee, Daicel Chiral pak ID column (1% IPA in hexanes, 1.0 mL/min), t_r = 11.2 min (major), t_r = 10.1 min (minor);





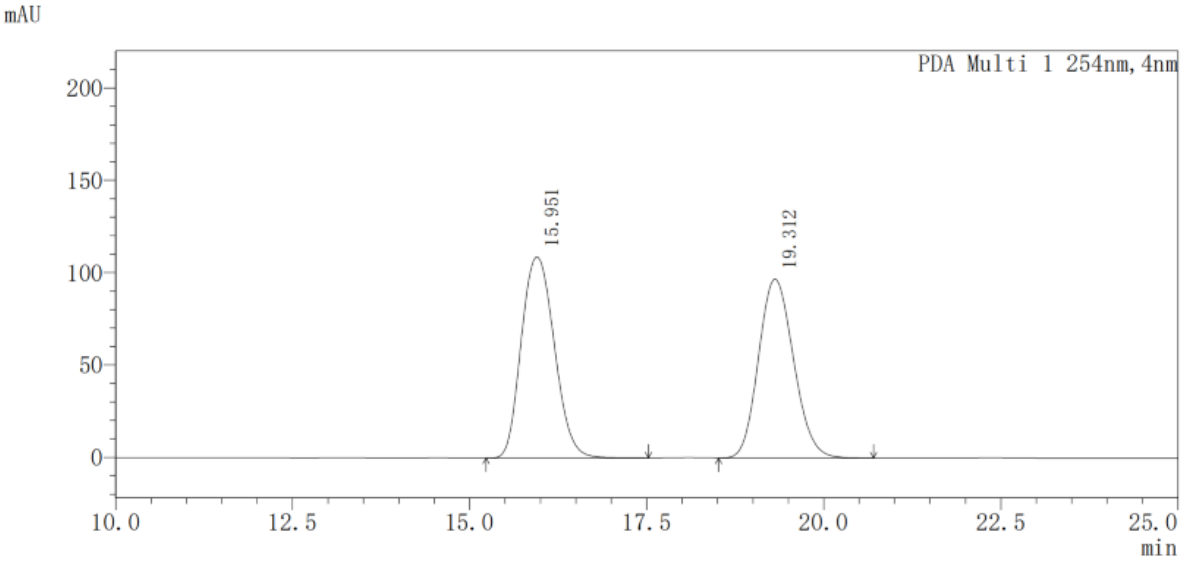
PDA Ch1 254nm

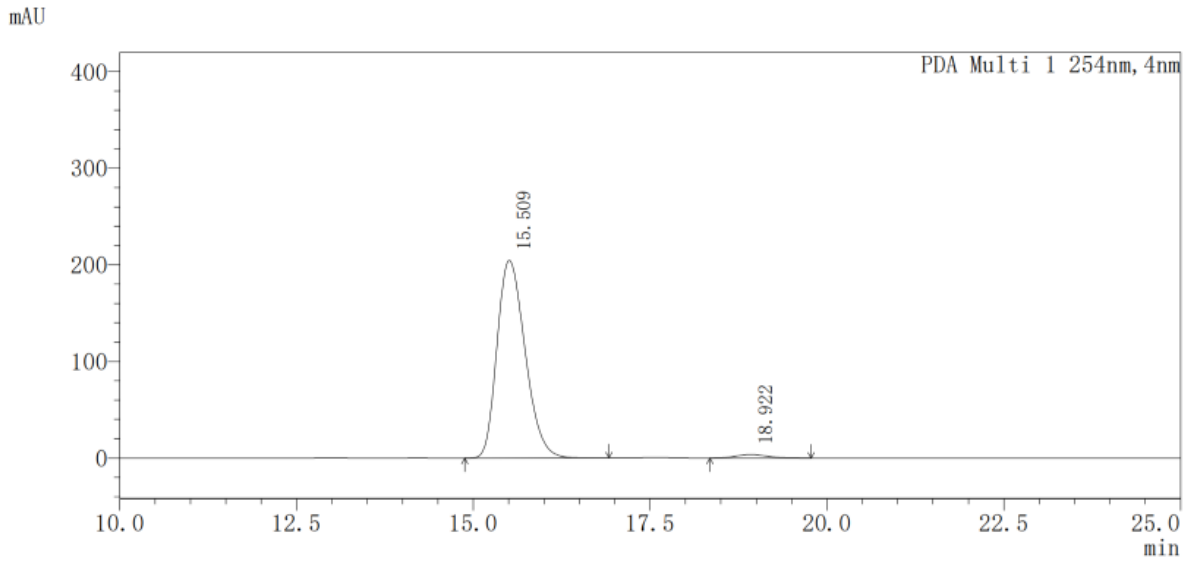
Peak #	Ret. Time	Area	Height	Area%	Height%
1	10.127	44620	1459	2.467	3.265
2	11.193	1764426	43219	97.533	96.735
总计		1809047	44677	100.000	100.000



9

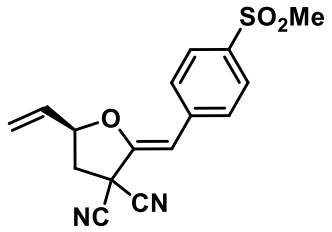
Chiral HPLC: 96% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 15.5 min (major), t_r = 19.0 min (minor);





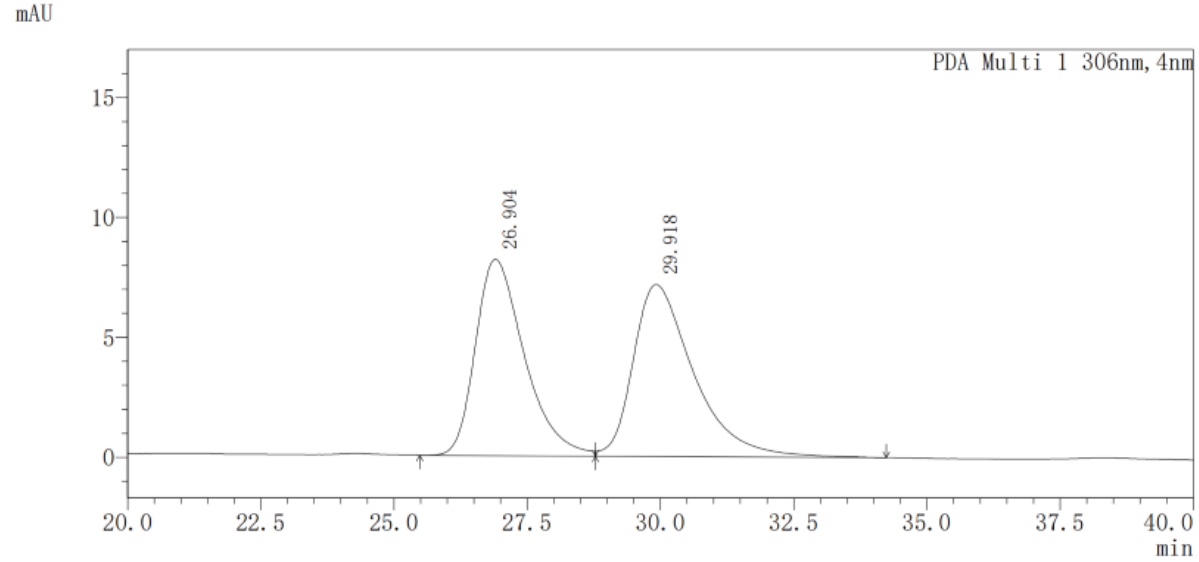
PDA Ch1 254nm

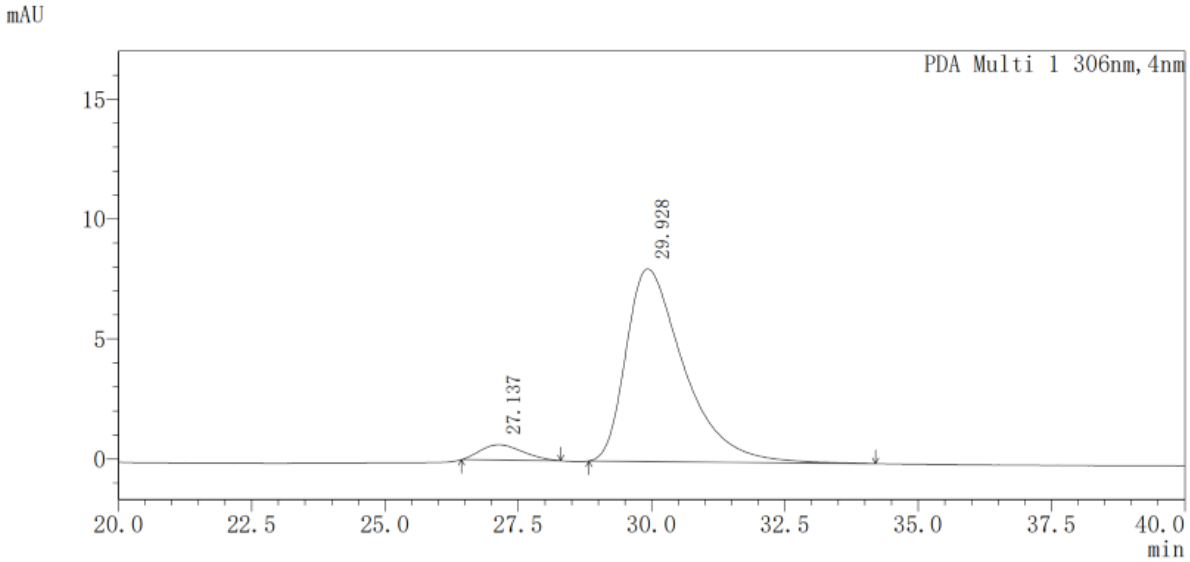
Peak #	Ret. Time	Area	Height	Area%	Height%
1	15.509	5662662	204714	98.109	98.274
2	18.922	109173	3596	1.891	1.726
总计		5771834	208310	100.000	100.000



10

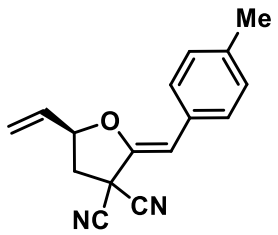
Chiral HPLC: 89% ee, Daicel Chiral pak IG column (30% IPA in hexanes, 1.0 mL/min), t_r = 29.9 min (major), t_r = 27.1 min (minor);





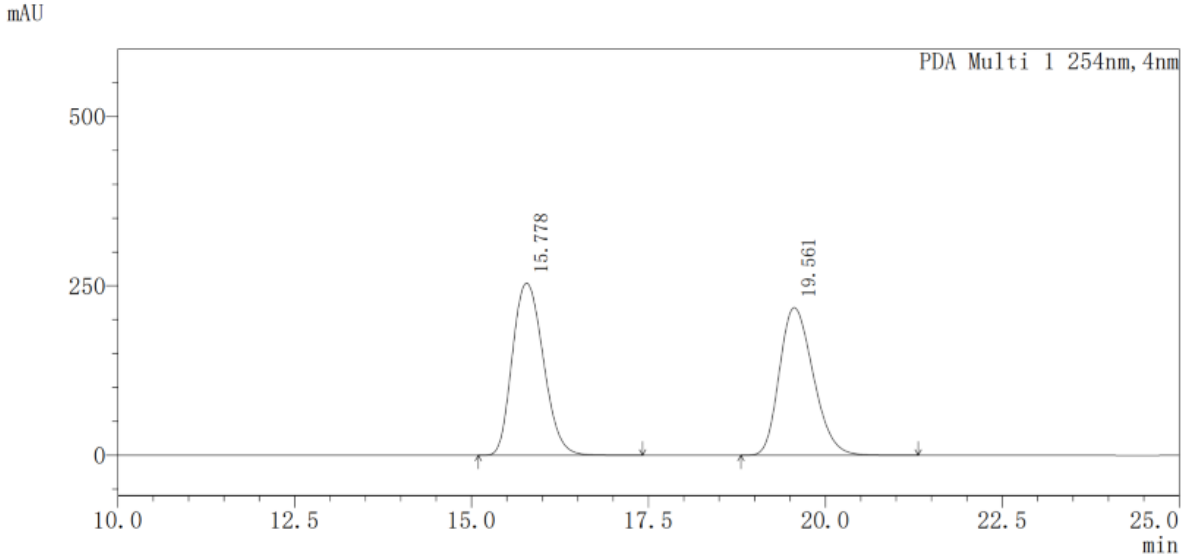
PDA Ch1 306nm

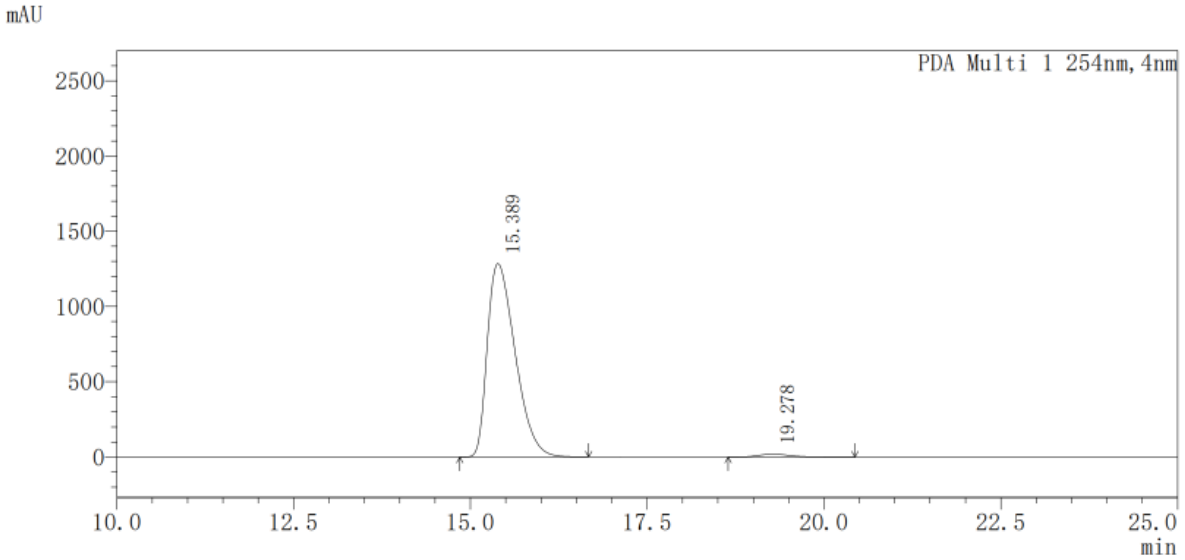
Peak #	Ret. Time	Area	Height	Area%	Height%
1	27.137	35221	636	5.474	7.343
2	29.928	608225	8027	94.526	92.657
总计		643445	8664	100.000	100.000



11

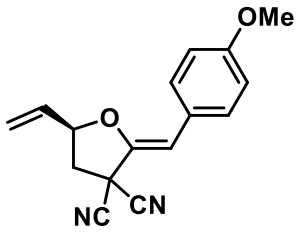
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 15.4 min (major), t_r = 19.3 min (minor);





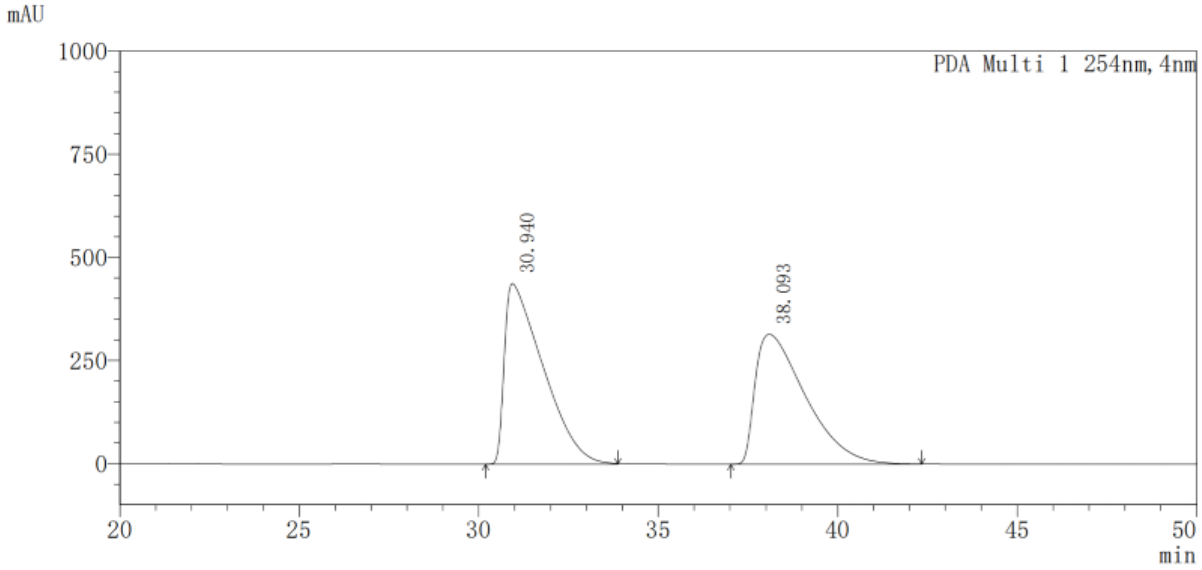
PDA Ch1 254nm

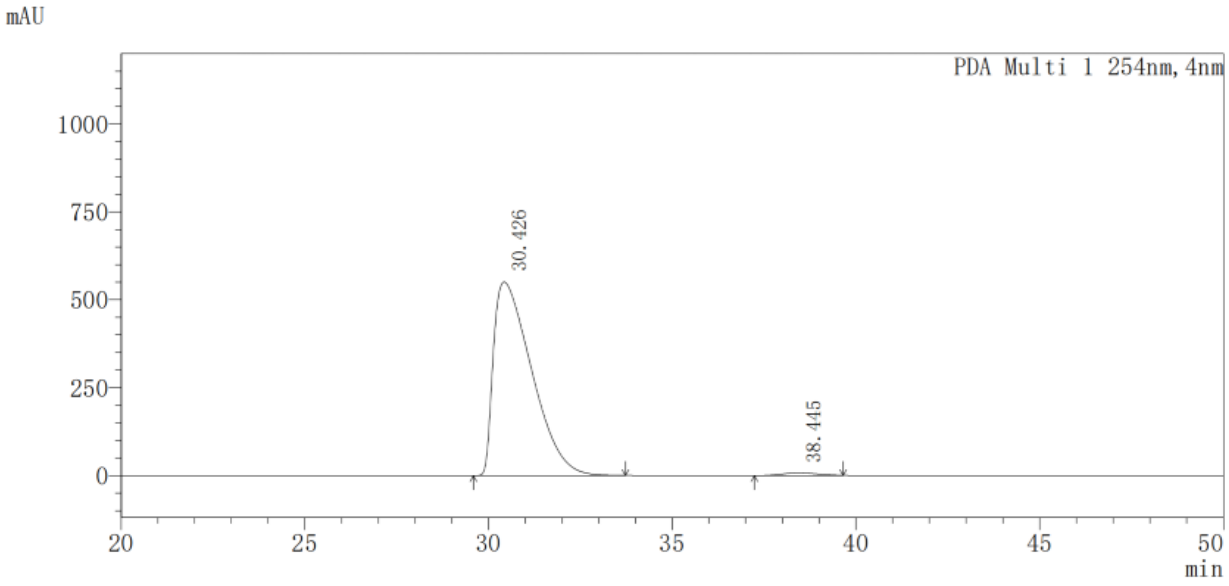
Peak #	Ret. Time	Area	Height	Area%	Height%
1	15.389	35212736	1284552	98.412	98.519
2	19.278	568254	19316	1.588	1.481
总计		35780990	1303867	100.000	100.000



12

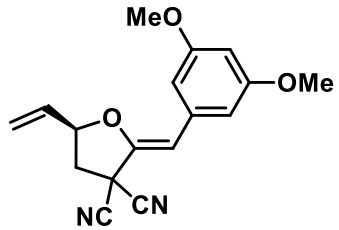
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 30.4 min (major), t_r = 38.4 min (minor);





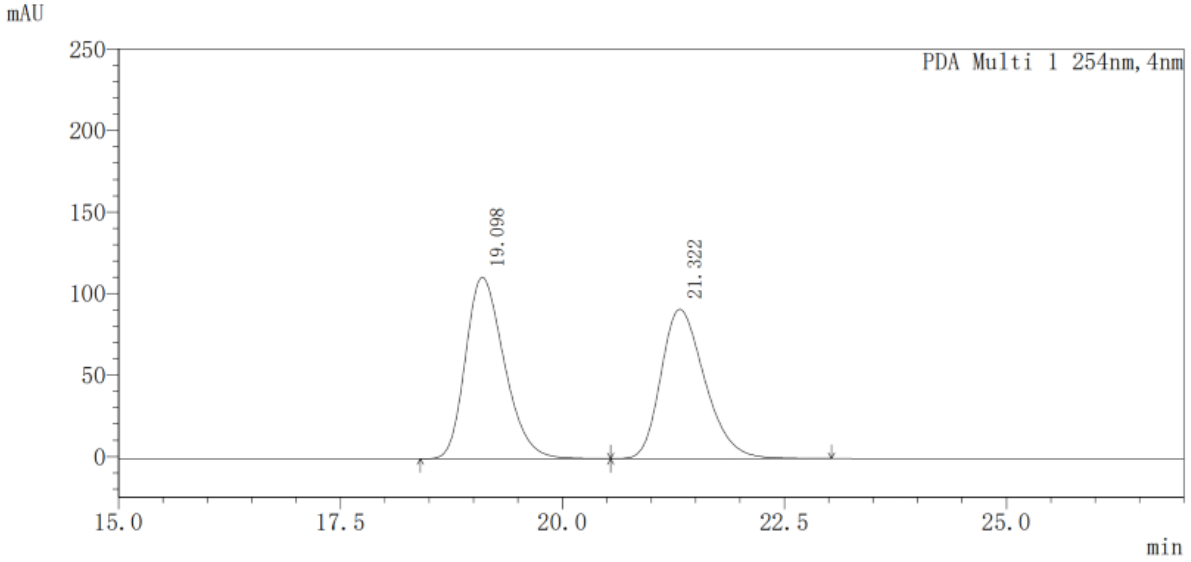
PDA Ch1 254nm

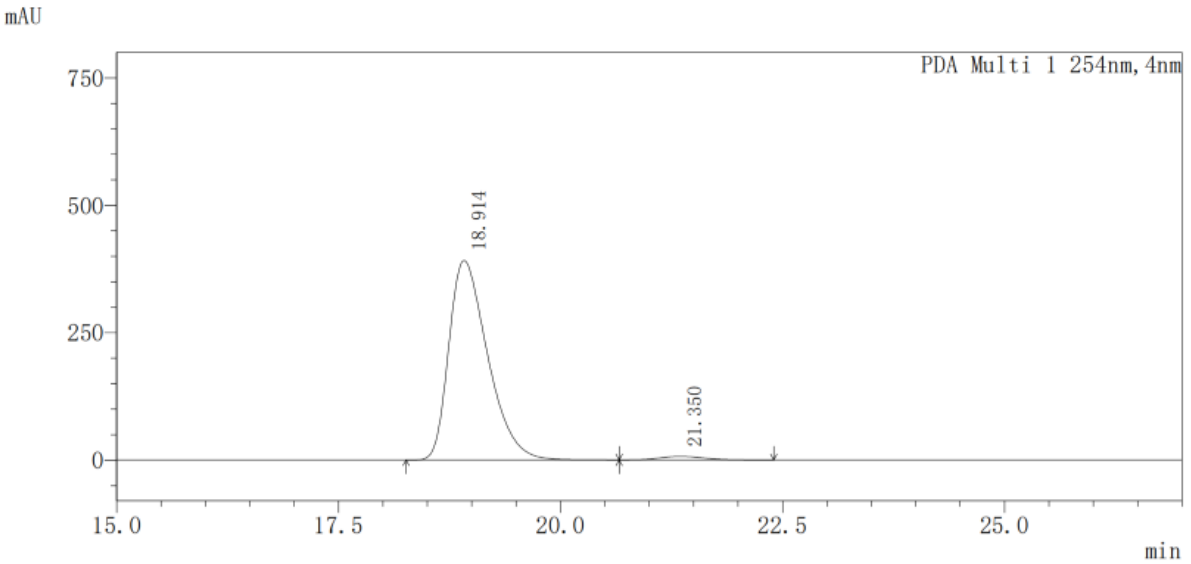
Peak #	Ret. Time	Area	Height	Area%	Height%
1	30.426	39928367	550875	98.671	98.621
2	38.445	537895	7701	1.329	1.379
总计		40466262	558576	100.000	100.000



13

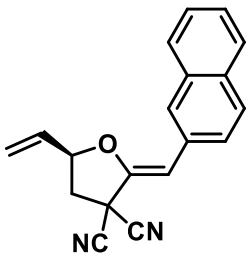
Chiral HPLC: 96% ee, Daicel Chiral pak IC column (5% IPA in hexanes, 1.0 mL/min), t_r = 18.9 min (major), t_r = 21.4 min (minor);





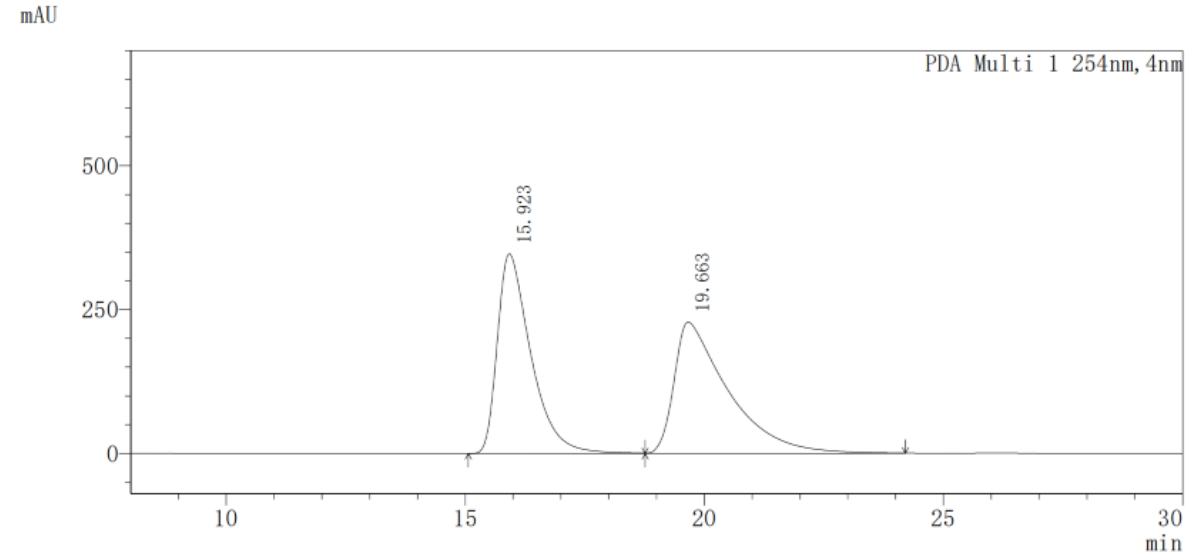
PDA Ch1 254nm

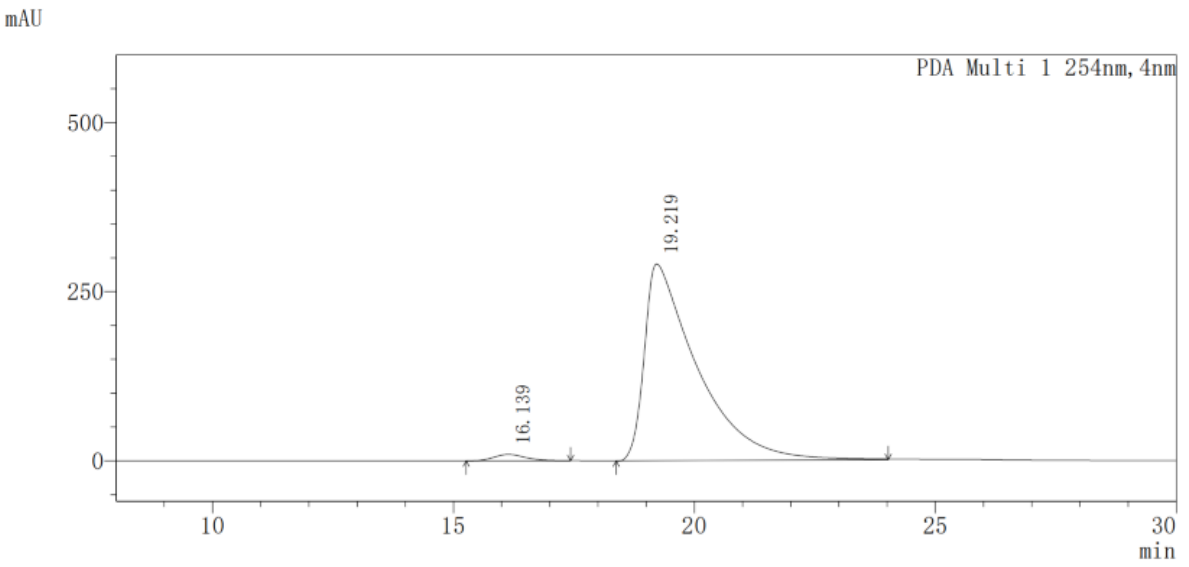
Peak #	Ret. Time	Area	Height	Area%	Height%
1	18.914	11911909	391535	97.998	98.235
2	21.350	243313	7036	2.002	1.765
总计		12155222	398570	100.000	100.000



14

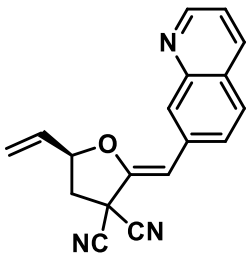
Chiral HPLC: 96% ee, Daicel Chiral pak IE column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.2 min (major), t_r = 19.1 min (minor);





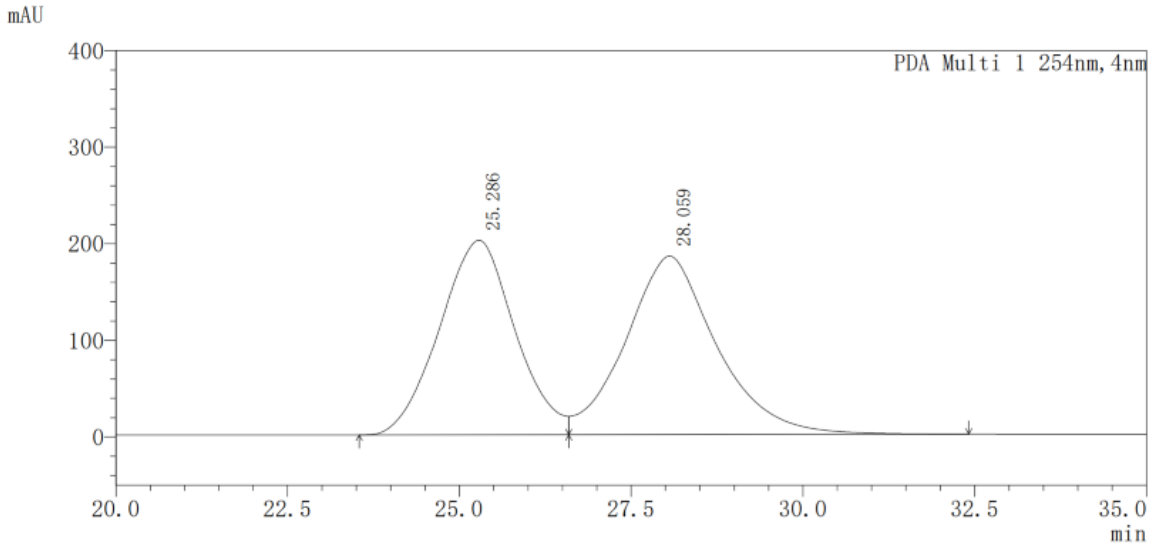
PDA Ch1 254nm

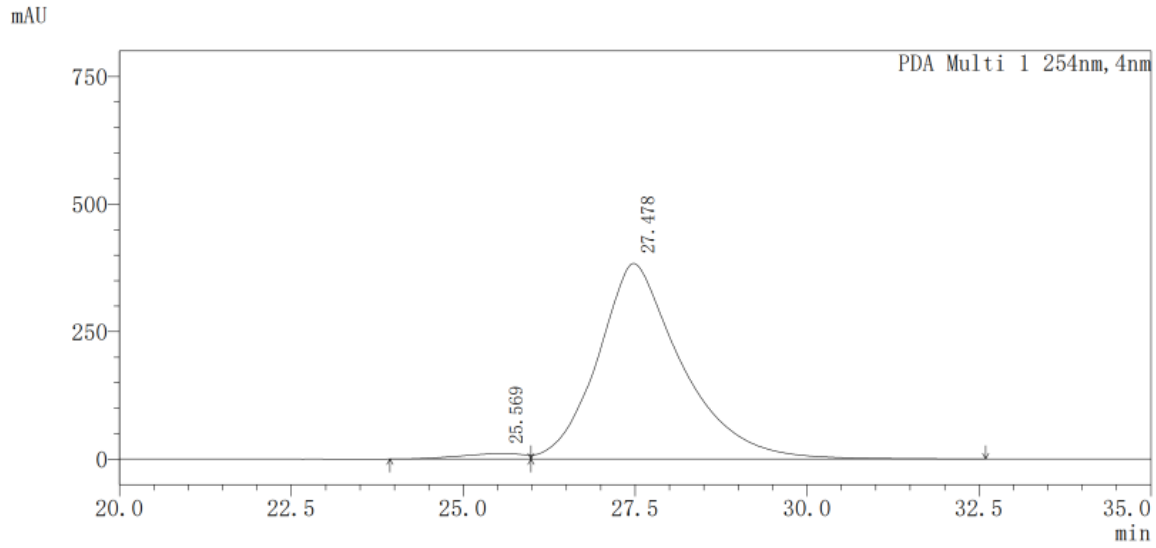
Peak #	Ret. Time	Area	Height	Area%	Height%
1	16.139	447064	9544	1.973	3.178
2	19.219	22211678	290813	98.027	96.822
总计		22658742	300357	100.000	100.000



15

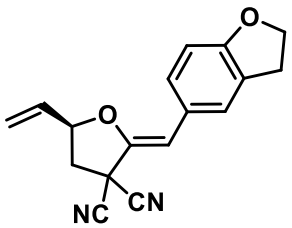
Chiral HPLC: 96% ee, Daicel Chiral pak IE column (10% IPA in hexanes, 1.0 mL/min), t_r = 27.5 min (major), t_r = 25.6 min (minor);





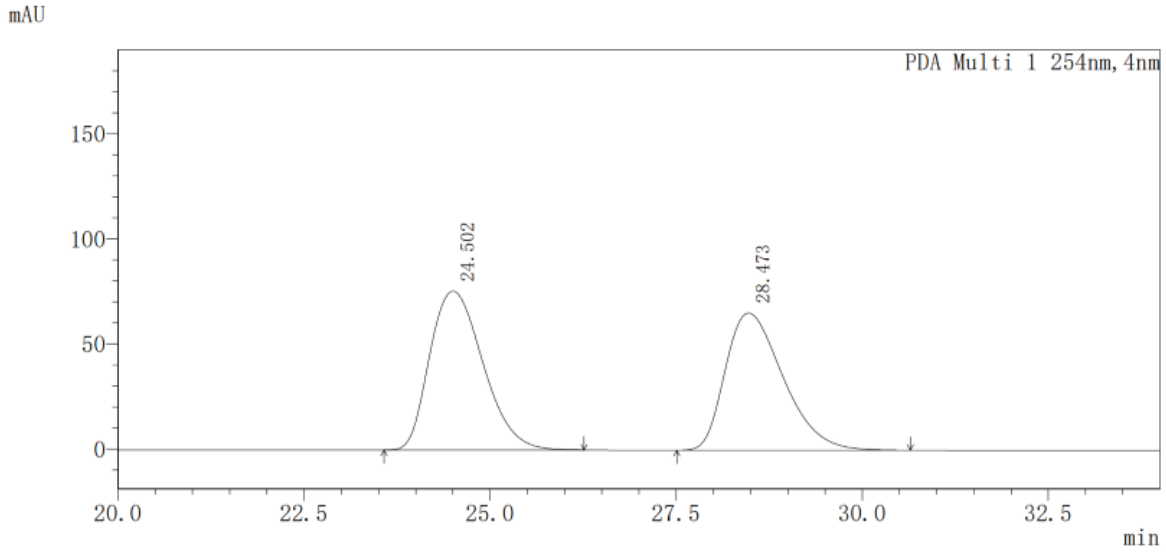
PDA Ch1 254nm

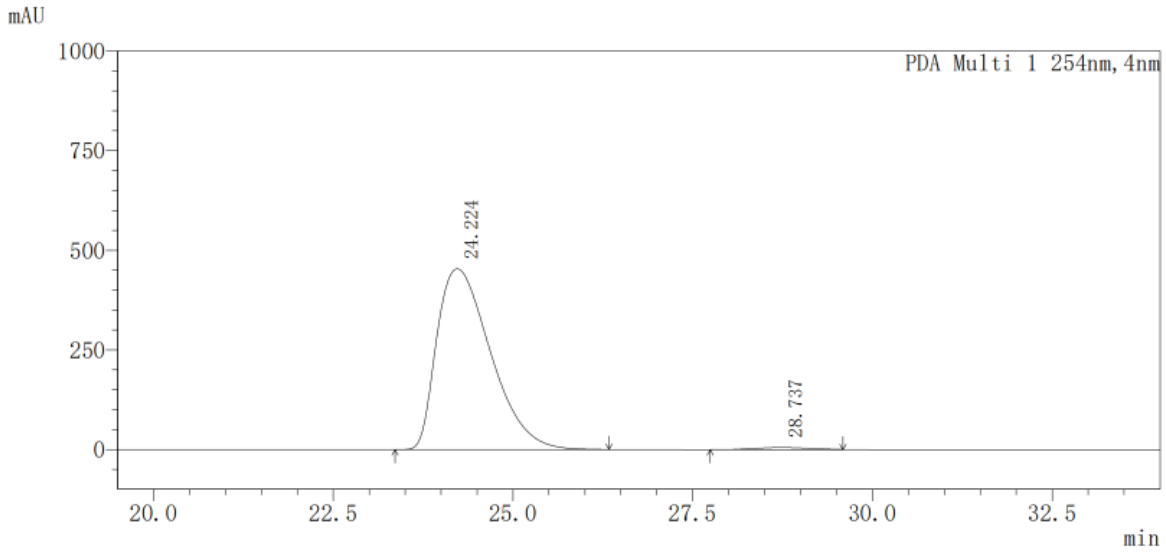
Peak #	Ret. Time	Area	Height	Area%	Height%
1	25.569	678768	10491	2.047	2.665
2	27.478	32481909	383115	97.953	97.335
总计		33160677	393606	100.000	100.000



16

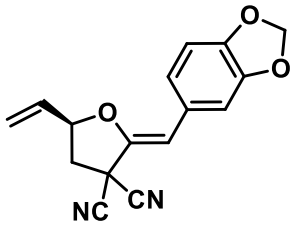
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (3% IPA in hexanes, 1.0 mL/min), t_r = 24.2 min (major), t_r = 28.7 min (minor);





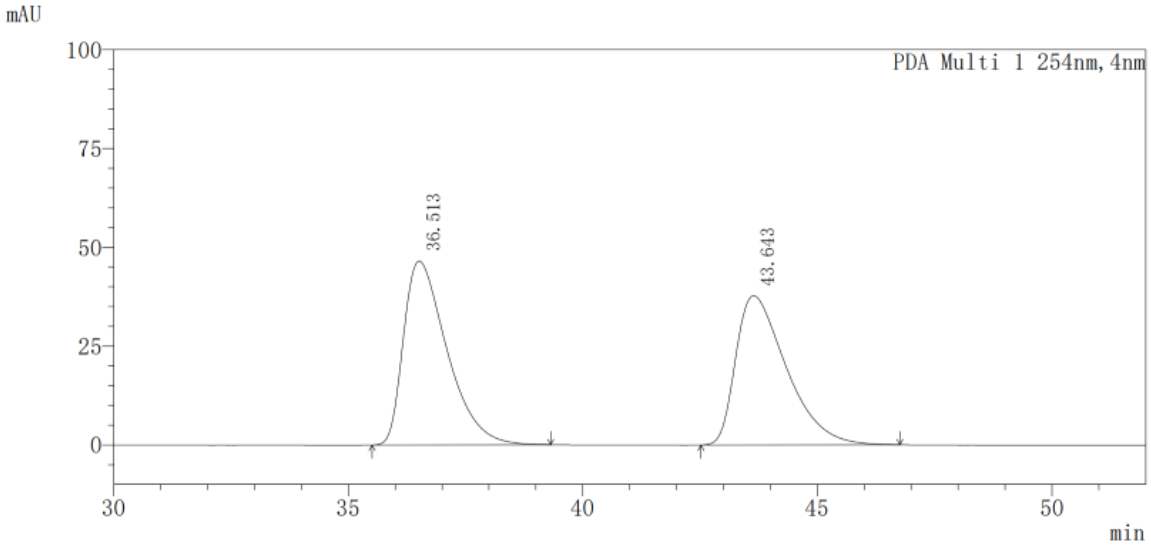
PDA Ch1 254nm

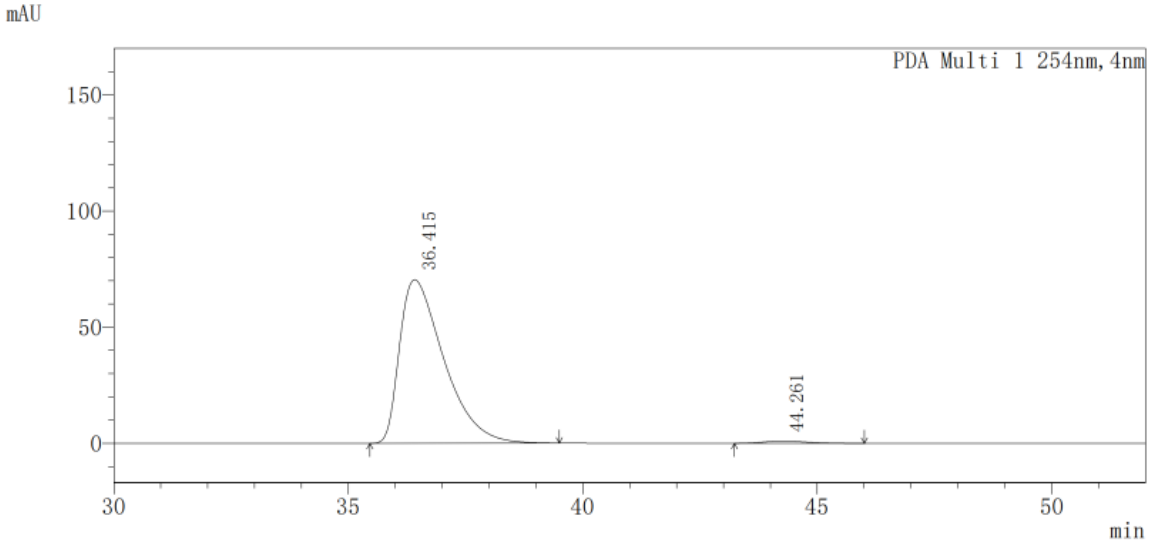
Peak #	Ret. Time	Area	Height	Area%	Height%
1	24.224	23677591	453961	98.704	98.824
2	28.737	310884	5400	1.296	1.176
总计		23988475	459361	100.000	100.000



17

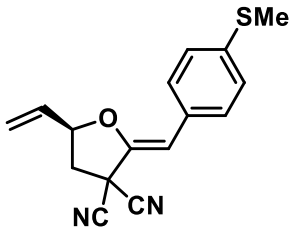
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 36.4 min (major), t_r = 44.3 min (minor);





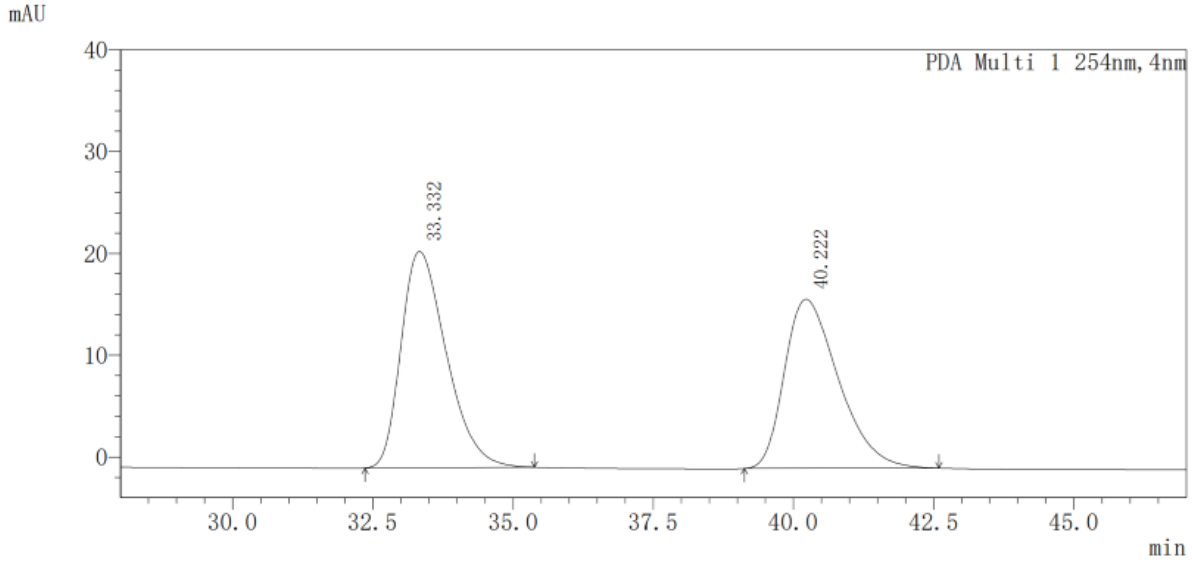
PDA Ch1 254nm

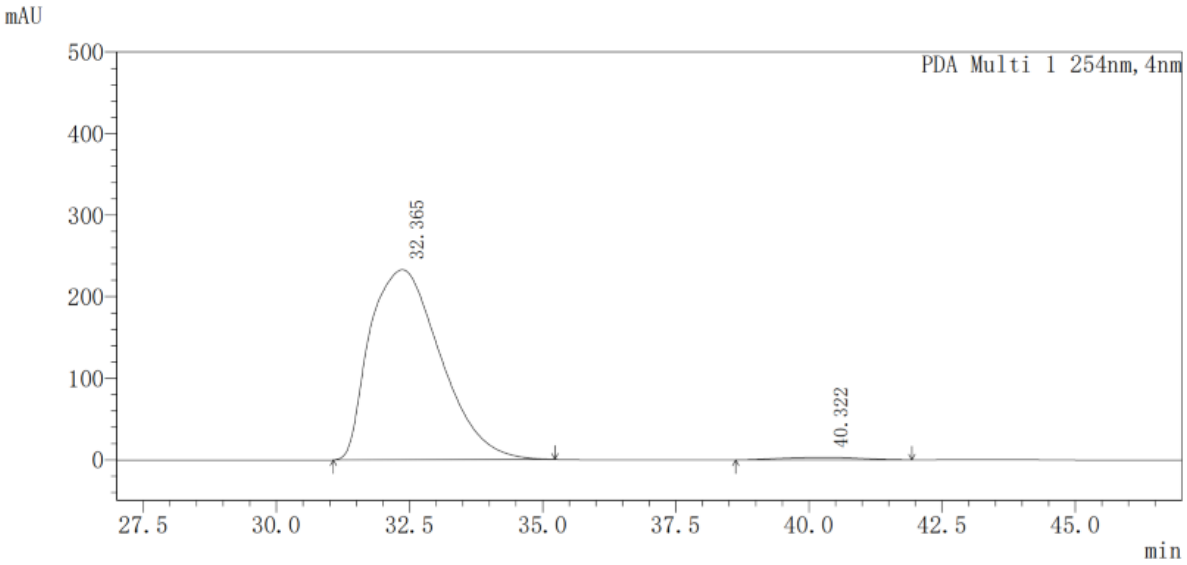
Peak #	Ret. Time	Area	Height	Area%	Height%
1	36.415	4629526	70471	98.665	98.749
2	44.261	62648	893	1.335	1.251
总计		4692174	71364	100.000	100.000



18

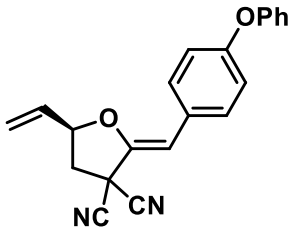
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 32.4 min (major), t_r = 40.3 min (minor);





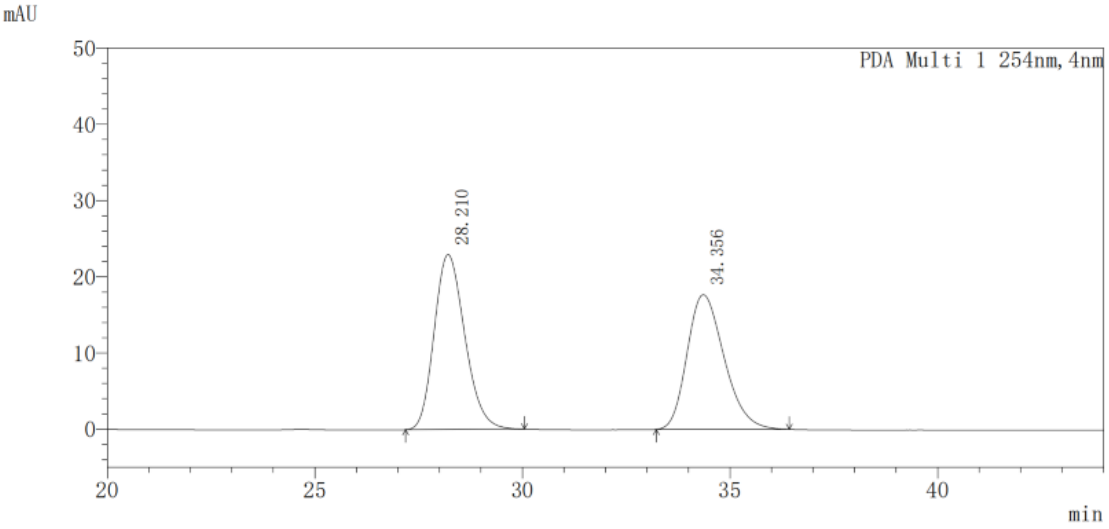
PDA Ch1 254nm

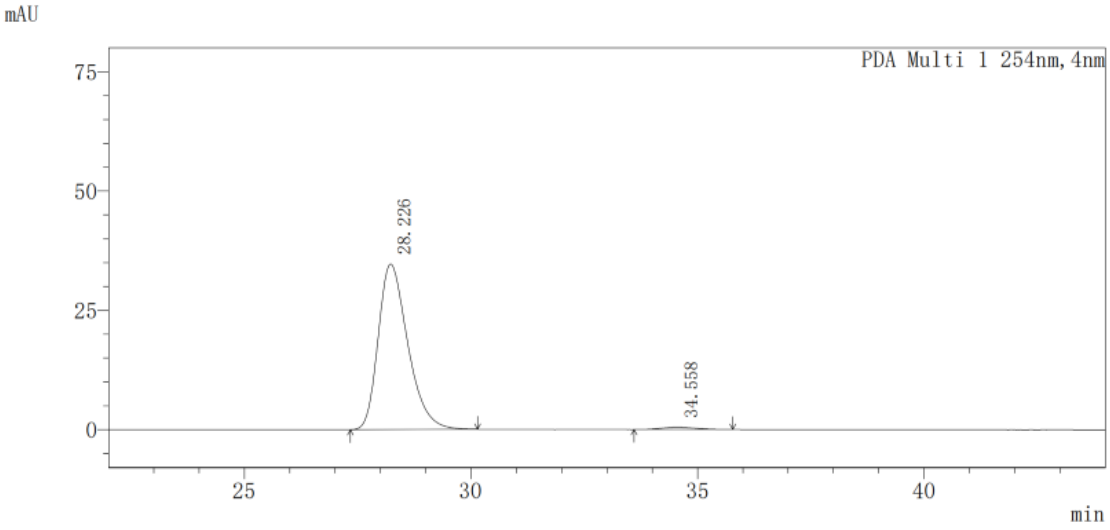
Peak #	Ret. Time	Area	Height	Area%	Height%
1	32.365	21615328	233008	98.599	98.745
2	40.322	307138	2961	1.401	1.255
总计		21922466	235969	100.000	100.000



19

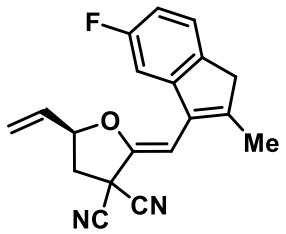
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 28.2 min (major), t_r = 34.6 min (minor);





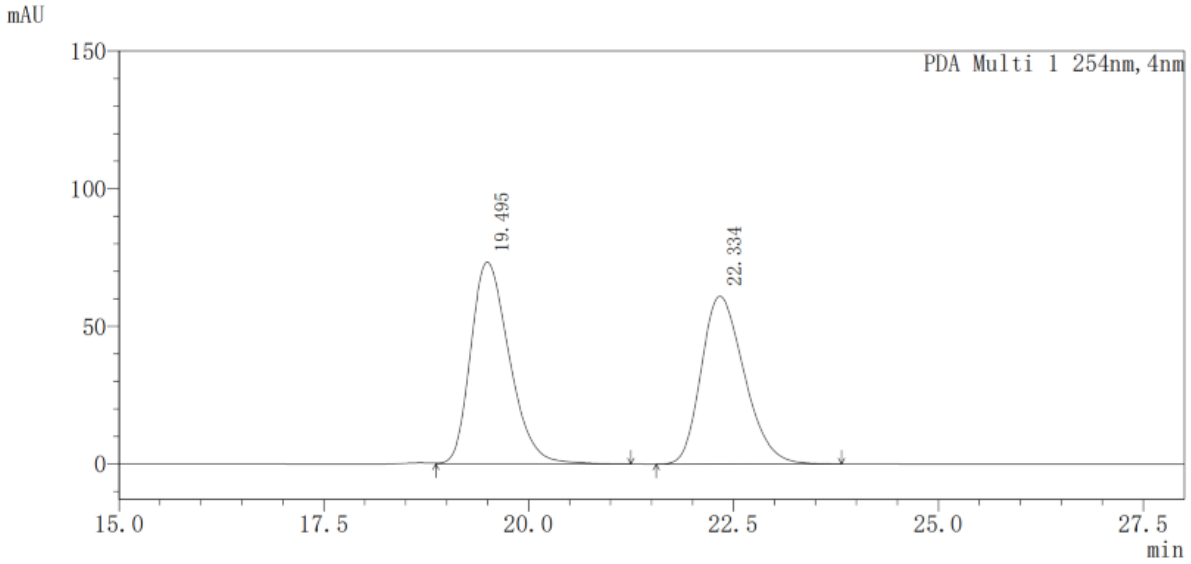
PDA Ch1 254nm

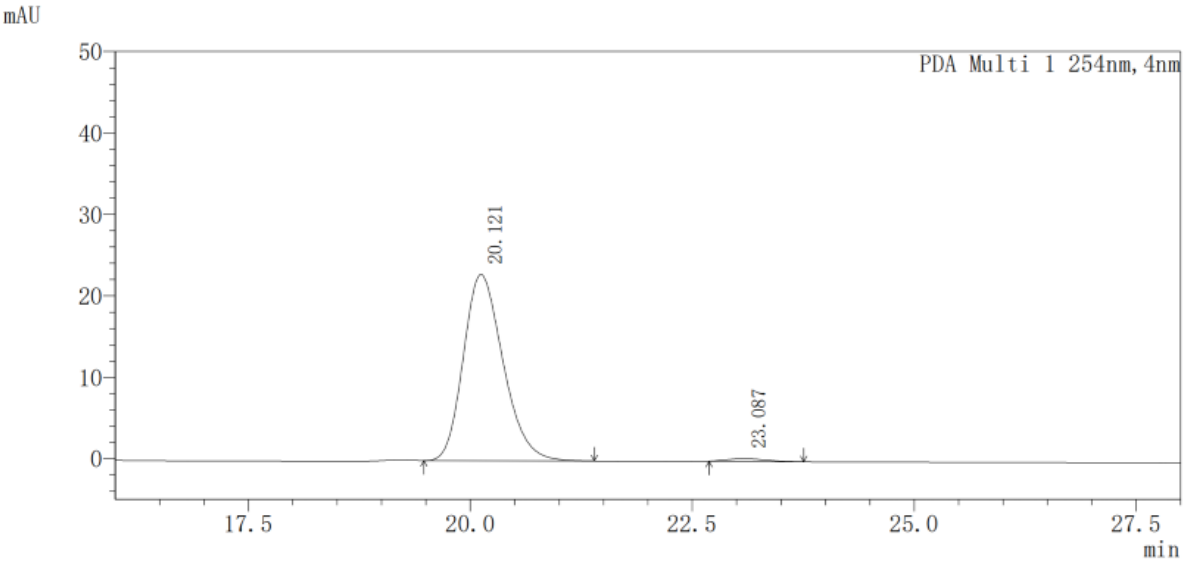
Peak #	Ret. Time	Area	Height	Area%	Height%
1	28.226	1573483	34700	98.395	98.618
2	34.558	25665	486	1.605	1.382
总计		1599148	35186	100.000	100.000



20

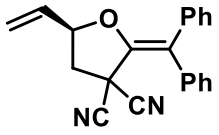
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.1 min (major), t_r = 23.1 min (minor);





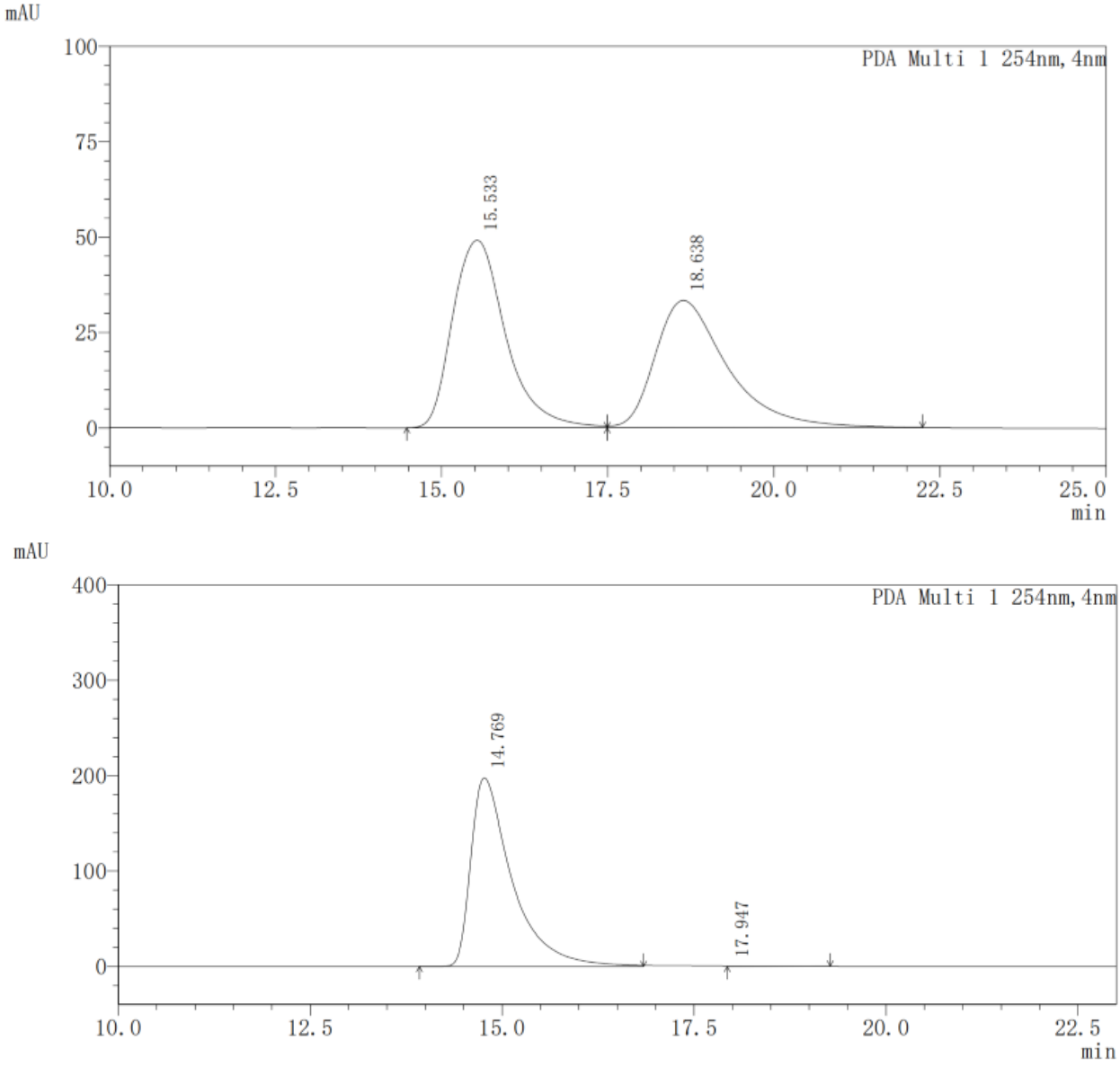
PDA Ch1 254nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	20.121	713174	22874	98.576	98.540
2	23.087	10301	339	1.424	1.460
总计		723475	23213	100.000	100.000



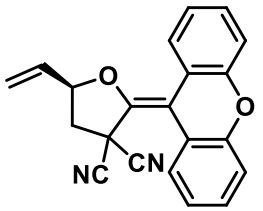
21

Chiral HPLC: >99% ee, Daicel Chiral pak ID column (1% IPA in hexanes, 1.0 mL/min), t_r = 14.8 min (major), t_r = 18.0 min (minor);



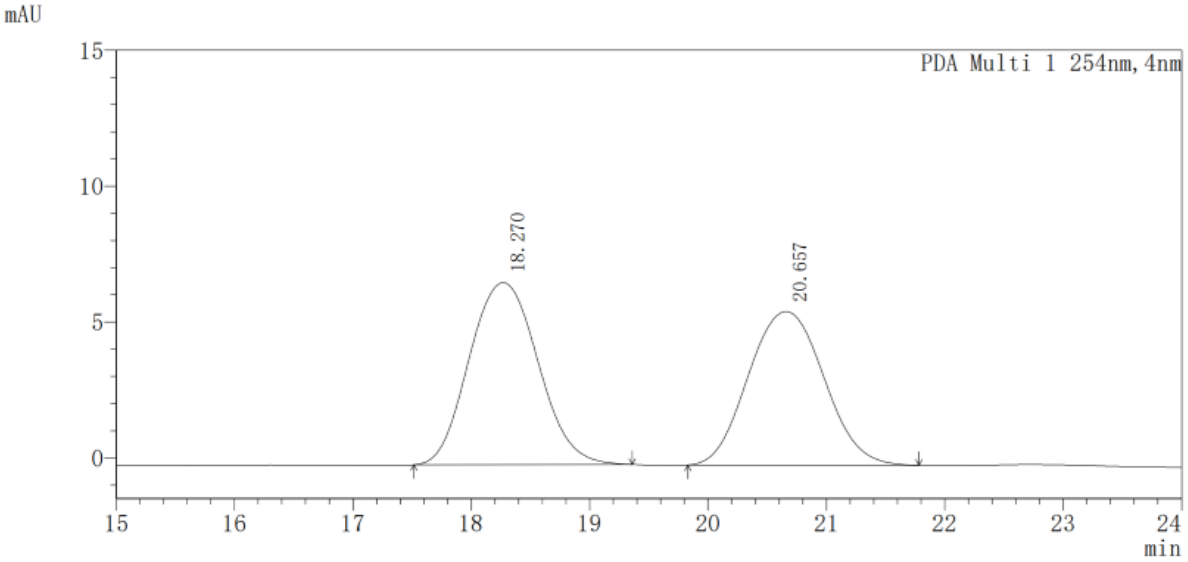
PDA Ch1 254nm

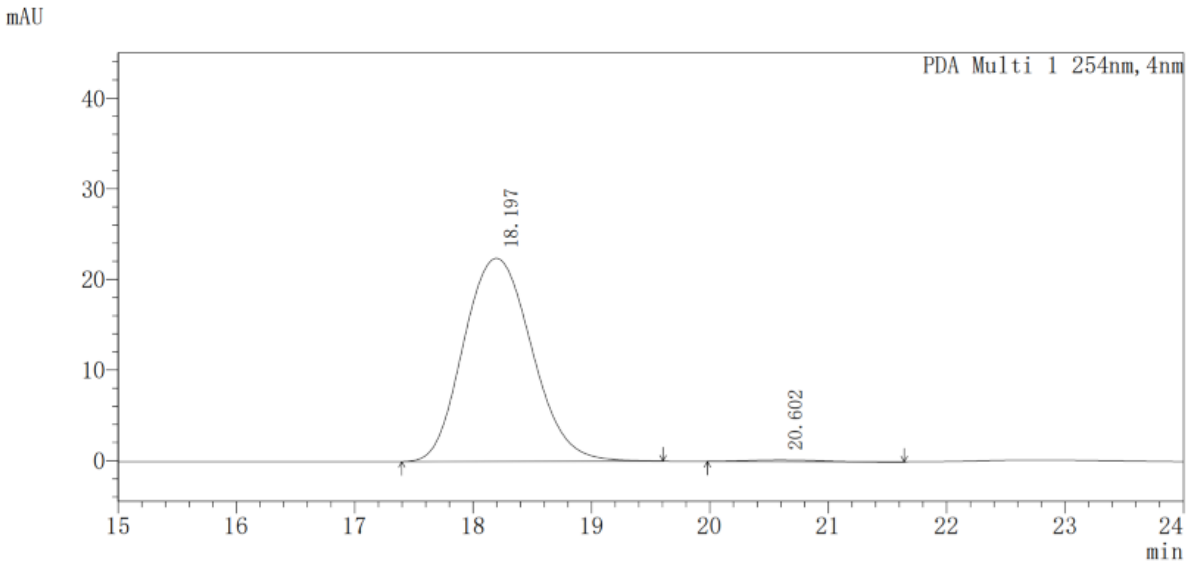
Peak #	Ret. Time	Area	Height	Area%	Height%
1	14.769	7370568	197633	99.898	99.862
2	17.947	7524	273	0.102	0.138
总计		7378092	197906	100.000	100.000



22

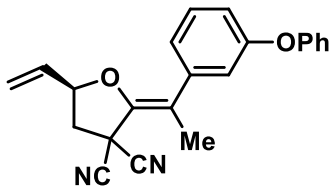
Chiral HPLC: 99% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 18.2 min (major), t_r = 20.6 min (minor);





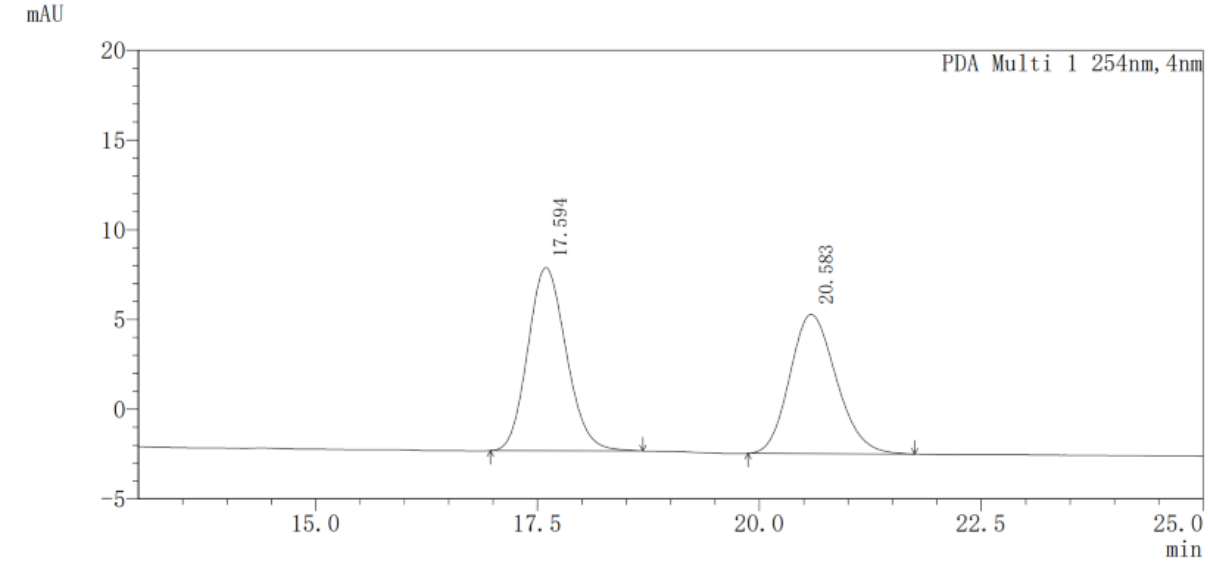
PDA Ch1 254nm

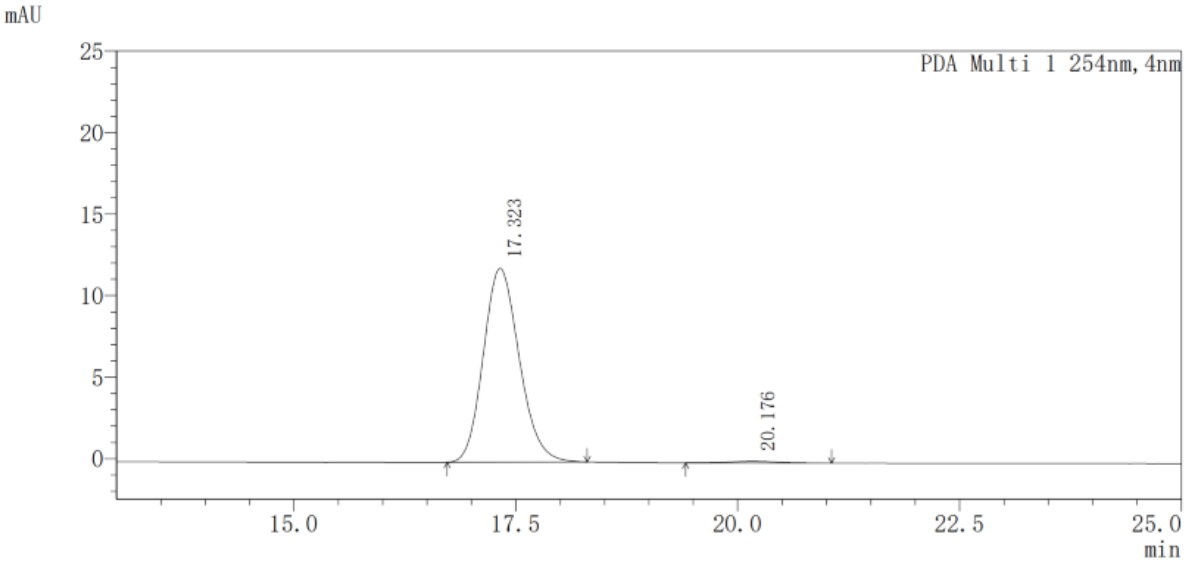
Peak #	Ret. Time	Area	Height	Area%	Height%
1	18.197	898683	22405	99.252	99.226
2	20.602	6769	175	0.748	0.774
总计		905452	22580	100.000	100.000



23

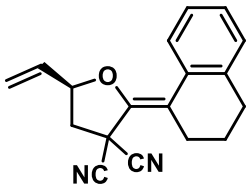
Chiral HPLC: 98% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 17.3 min (major), t_r = 20.2 min (minor);





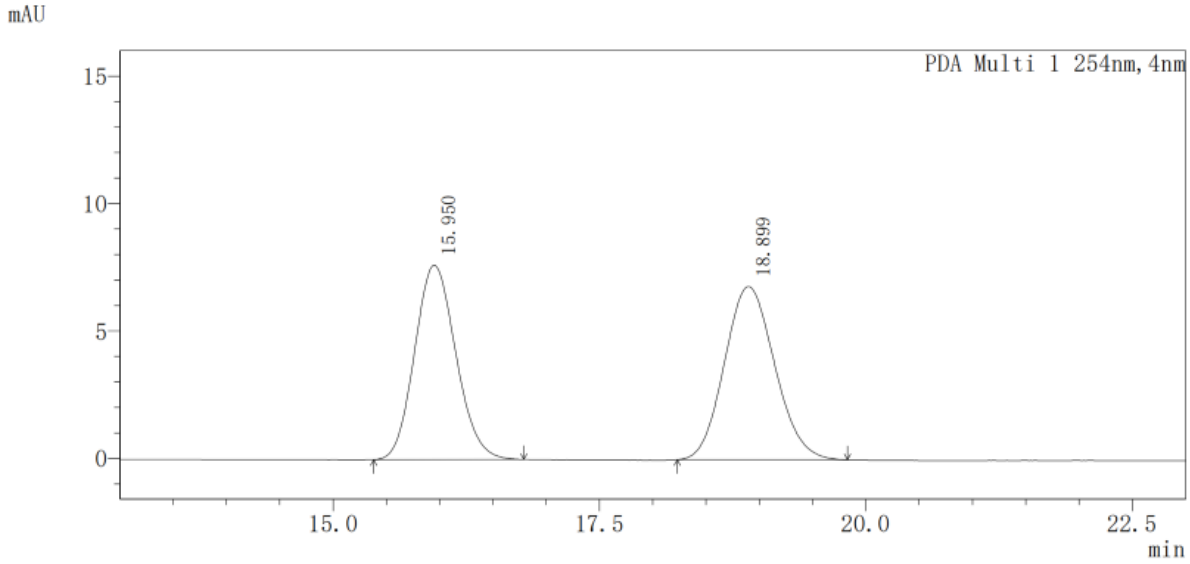
PDA Ch1 254nm

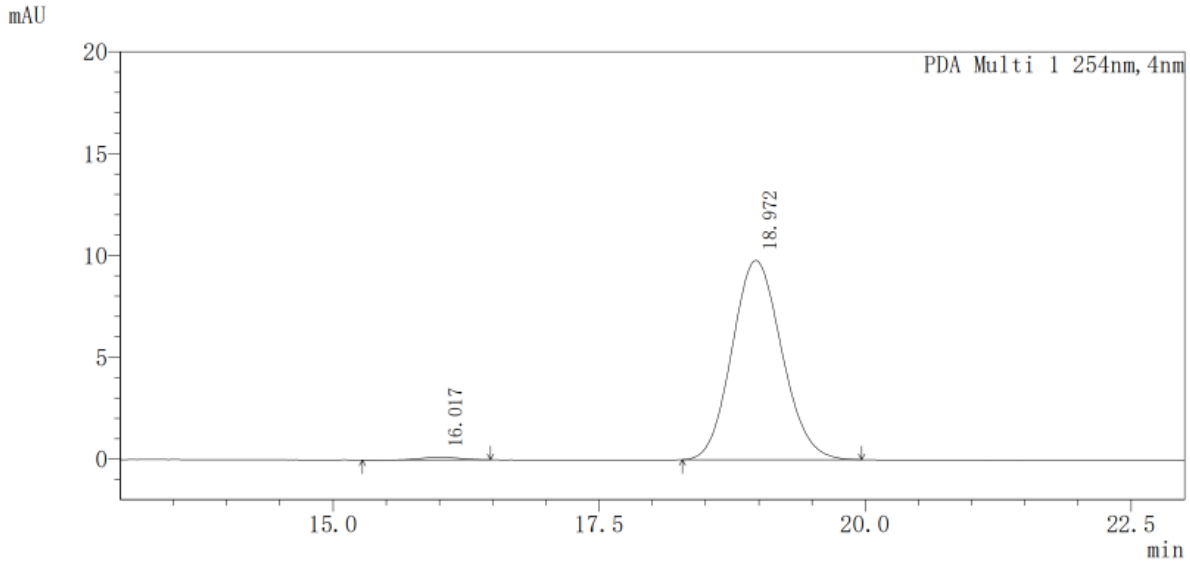
Peak #	Ret. Time	Area	Height	Area%	Height%
1	17.323	335113	11887	98.912	99.072
2	20.176	3685	111	1.088	0.928
总计		338798	11999	100.000	100.000



24

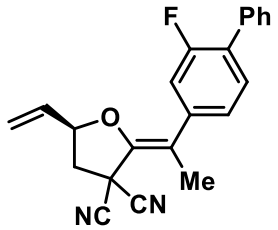
Chiral HPLC: 98% ee, Daicel Chiral pak IG column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.0 min (major), t_r = 16.0 min (minor);





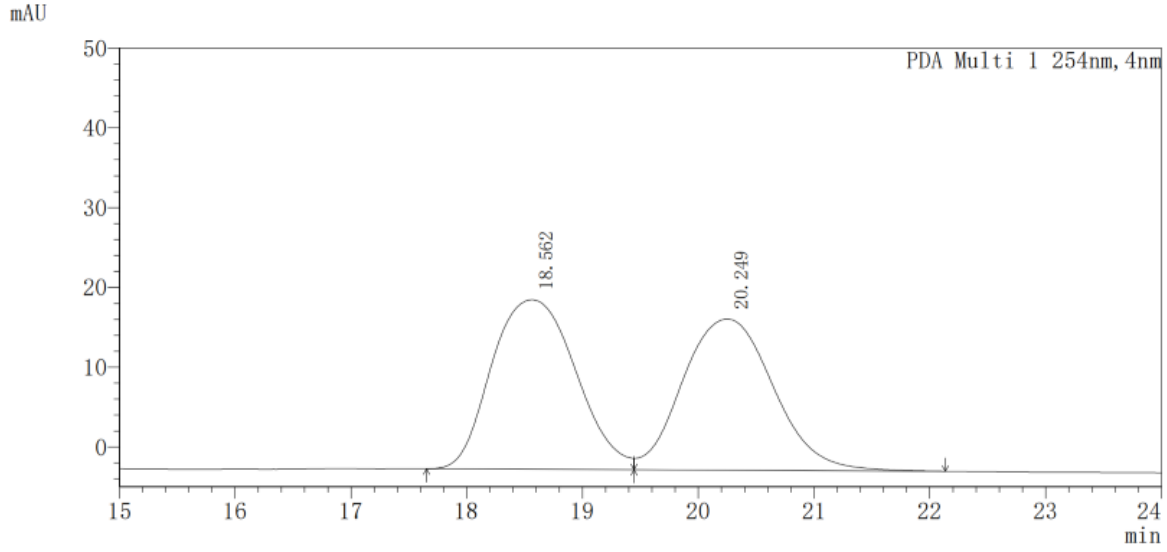
PDA Ch1 254nm

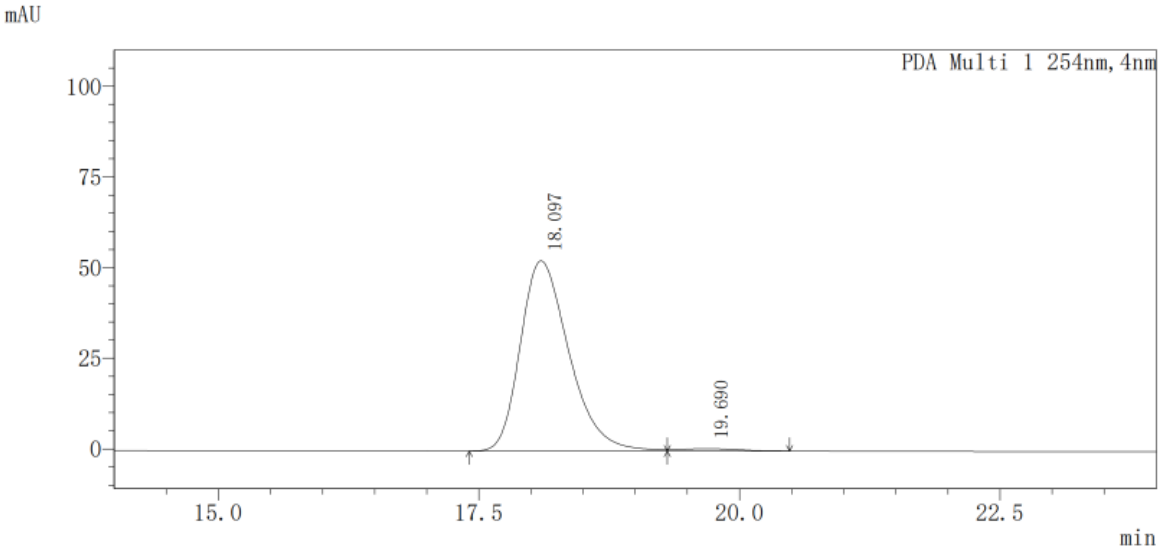
Peak #	Ret. Time	Area	Height	Area%	Height%
1	16.017	3108	128	0.967	1.290
2	18.972	318353	9787	99.033	98.710
总计		321461	9915	100.000	100.000



25

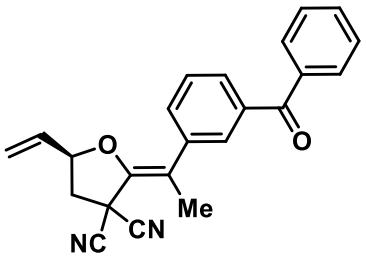
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 18.1 min (major), t_r = 19.7 min (minor);





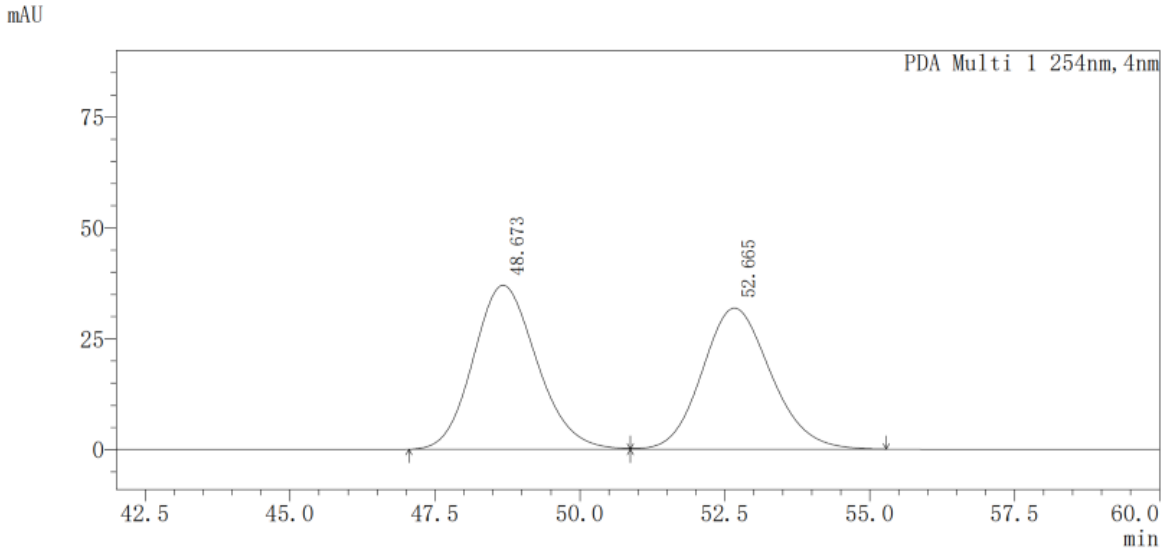
PDA Ch1 254nm

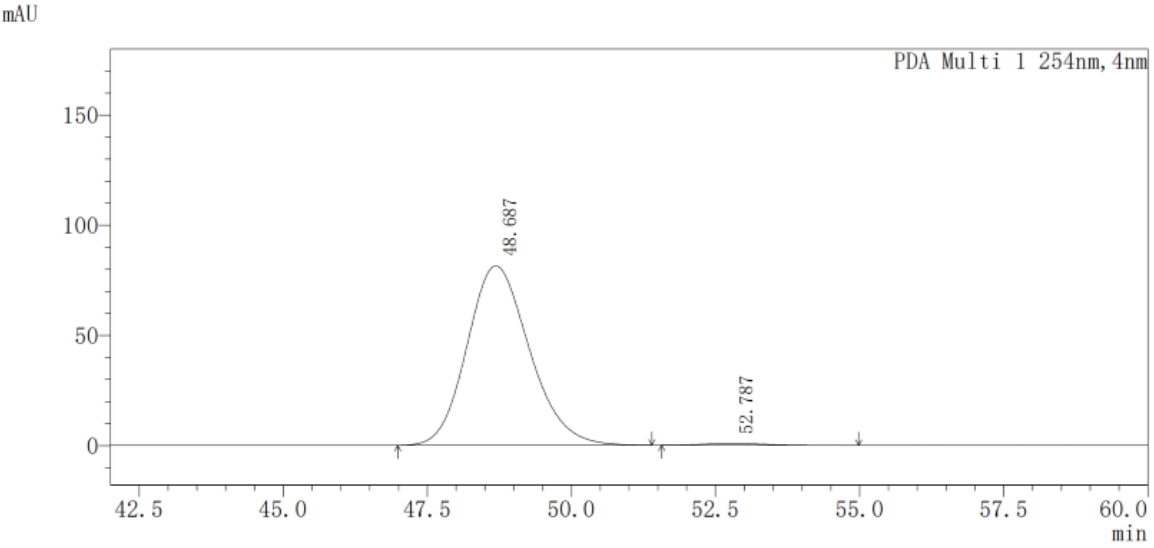
Peak #	Ret. Time	Area	Height	Area%	Height%
1	18.097	1701568	52406	98.581	98.776
2	19.690	24495	649	1.419	1.224
总计		1726064	53055	100.000	100.000



26

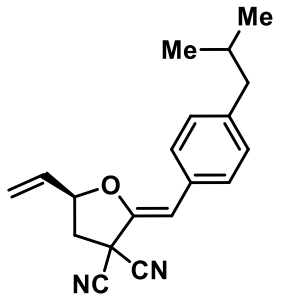
Chiral HPLC: 98% ee, Daicel Chiral pak IG column (5% IPA in hexanes, 1.0 mL/min), t_r = 48.1 min (major), t_r = 52.8 min (minor);





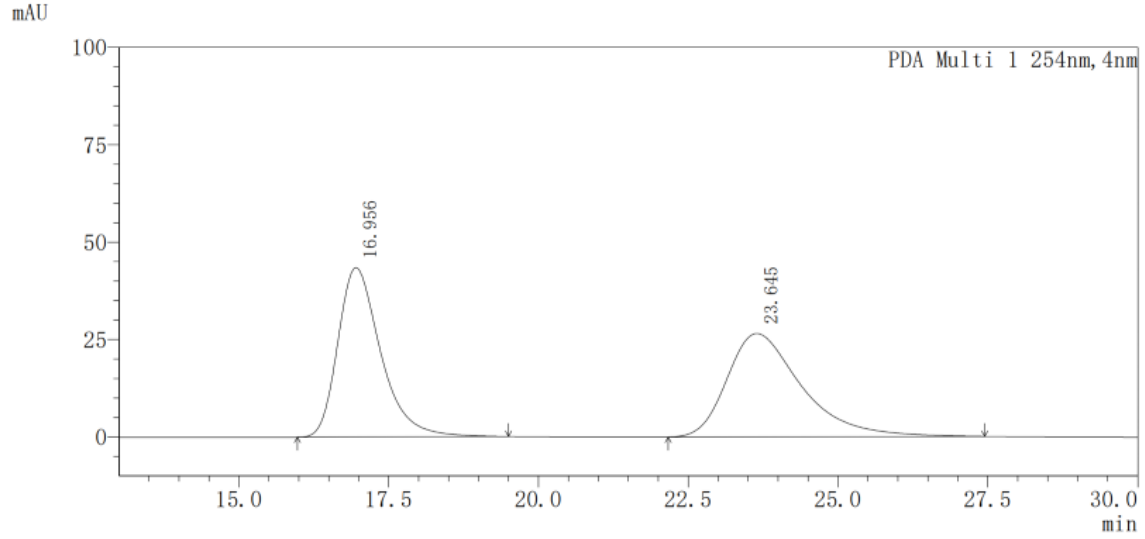
PDA Ch1 254nm

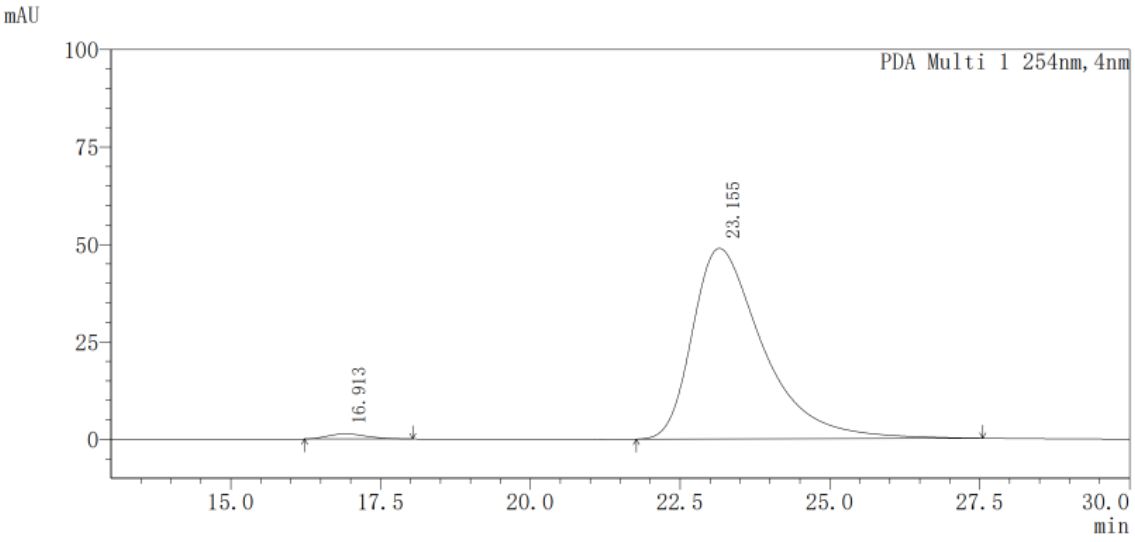
Peak #	Ret. Time	Area	Height	Area%	Height%
1	48.687	6139658	81450	99.064	99.067
2	52.787	58039	767	0.936	0.933
总计		6197697	82217	100.000	100.000



27

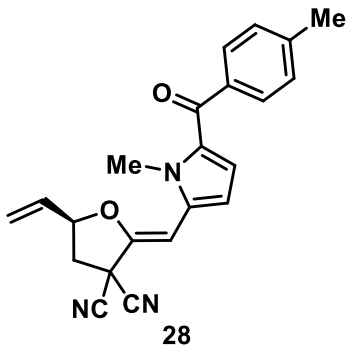
Chiral HPLC: 97% ee, Daicel Chiral pak IG column (1% IPA in hexanes, 1.0 mL/min), t_r = 23.2 min (major), t_r = 17.0 min (minor);





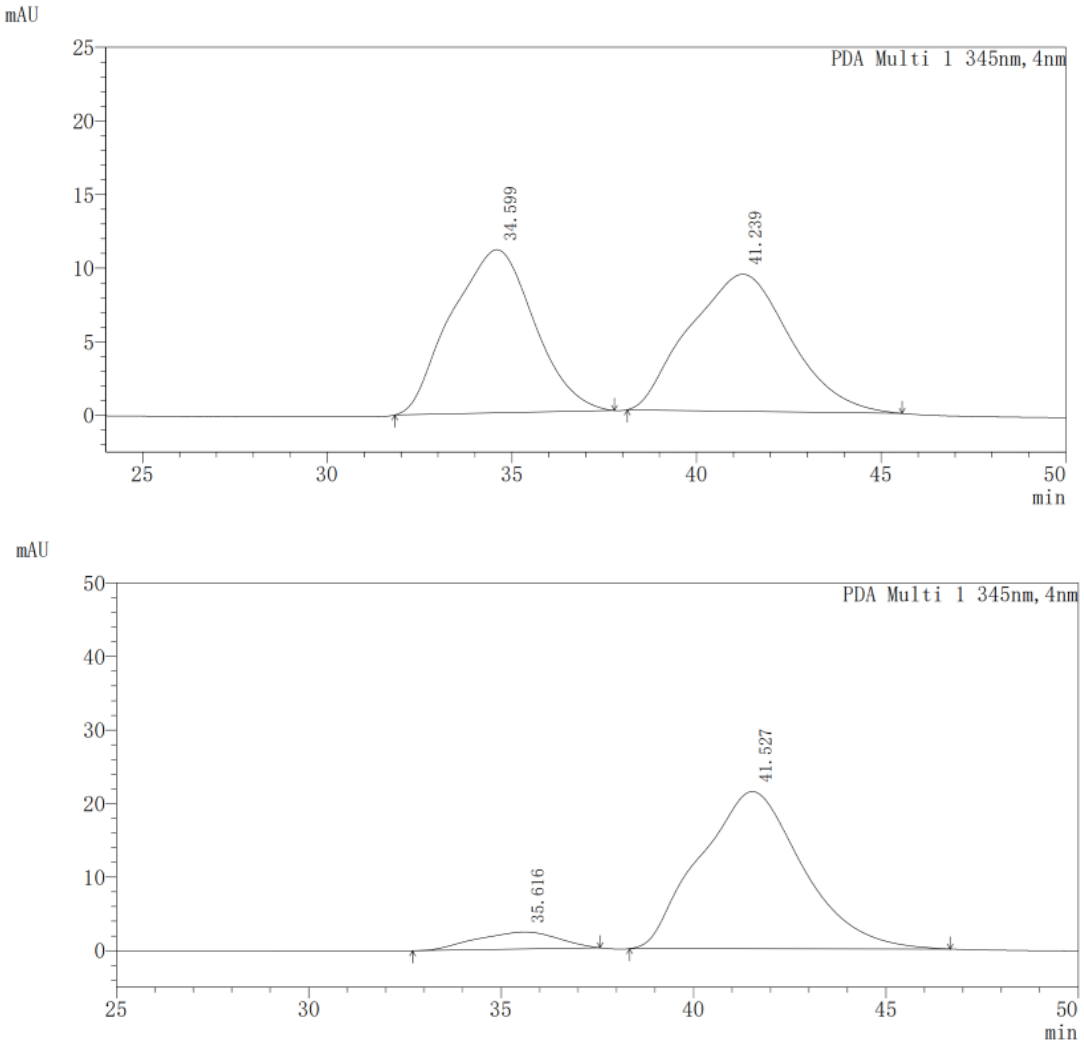
PDA Ch1 254nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	16.913	60140	1334	1.479	2.656
2	23.155	4005752	48905	98.521	97.344
总计		4065892	50239	100.000	100.000



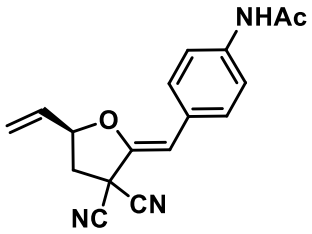
28

Chiral HPLC: 84% ee, Daicel Chiral pak IE column (10% IPA in hexanes, 1.0 mL/min), t_r = 41.5 min (major), t_r = 35.6 min (minor);



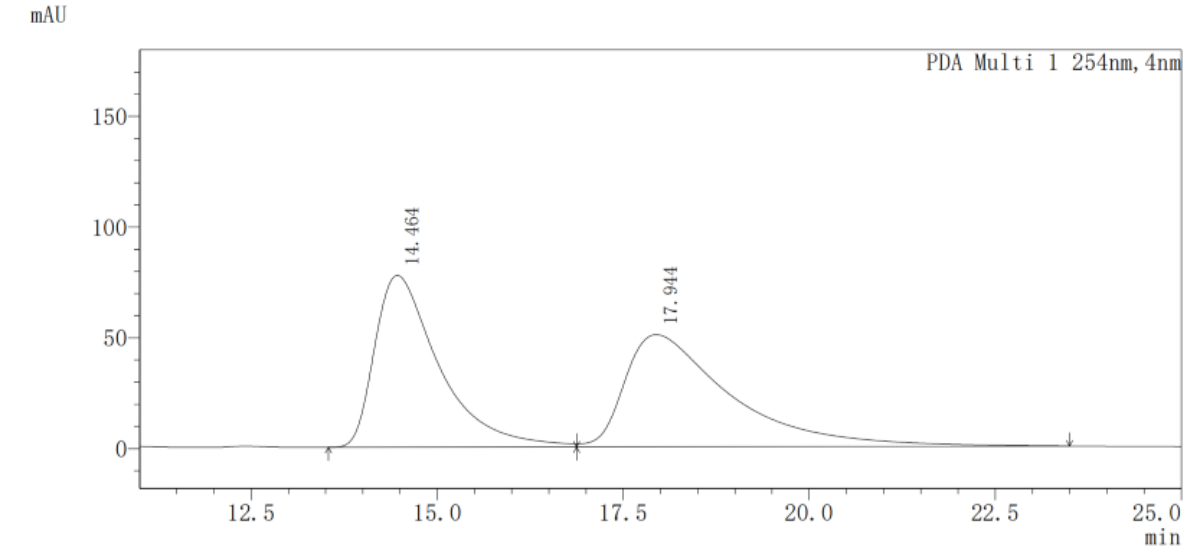
PDA Ch1 345nm

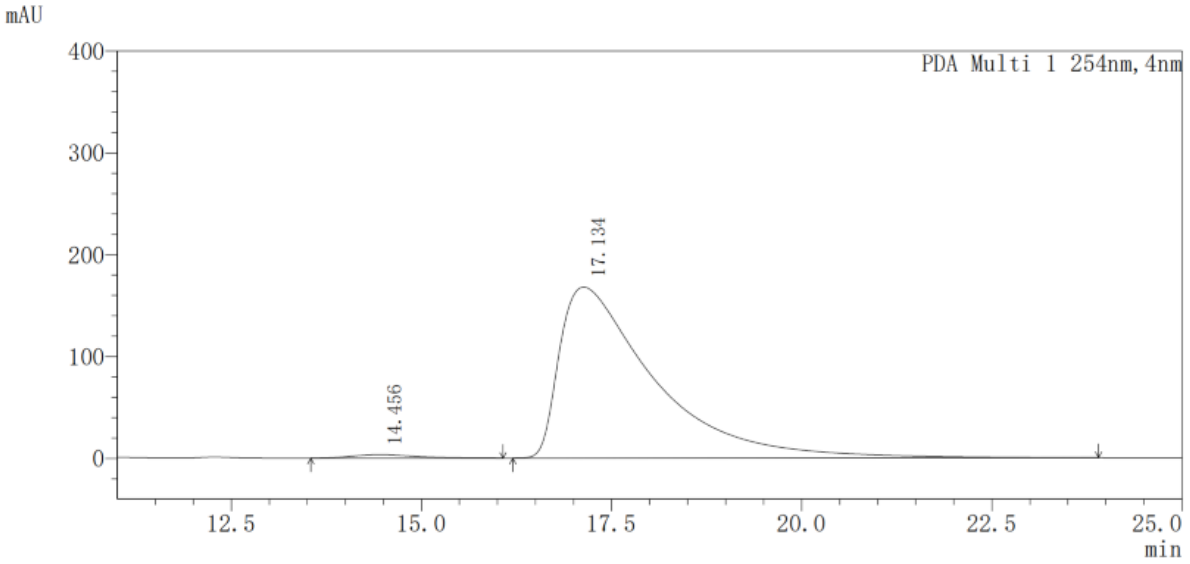
Peak #	Ret. Time	Area	Height	Area%	Height%
1	35.616	343380	2315	7.925	9.766
2	41.527	3989500	21389	92.075	90.234
总计		4332881	23703	100.000	100.000



29

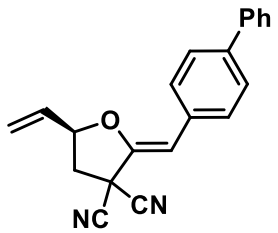
Chiral HPLC: 97% ee, Daicel Chiral pak IE column (10% IPA in hexanes, 1.0 mL/min), t_r = 17.1 min (major), t_r = 14.5 min (minor);





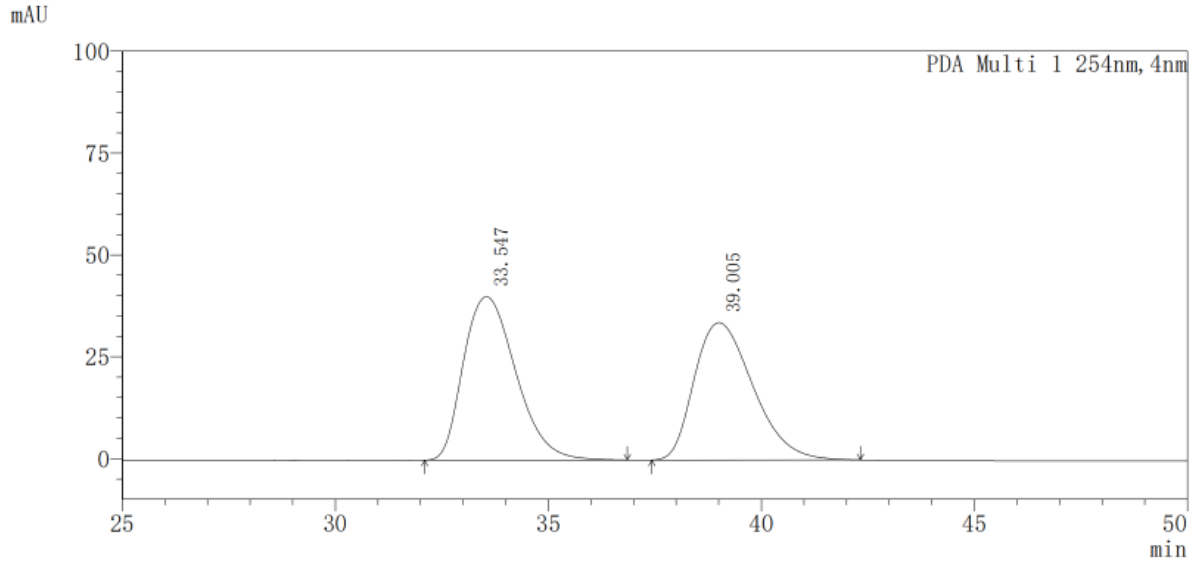
PDA Ch1 254nm

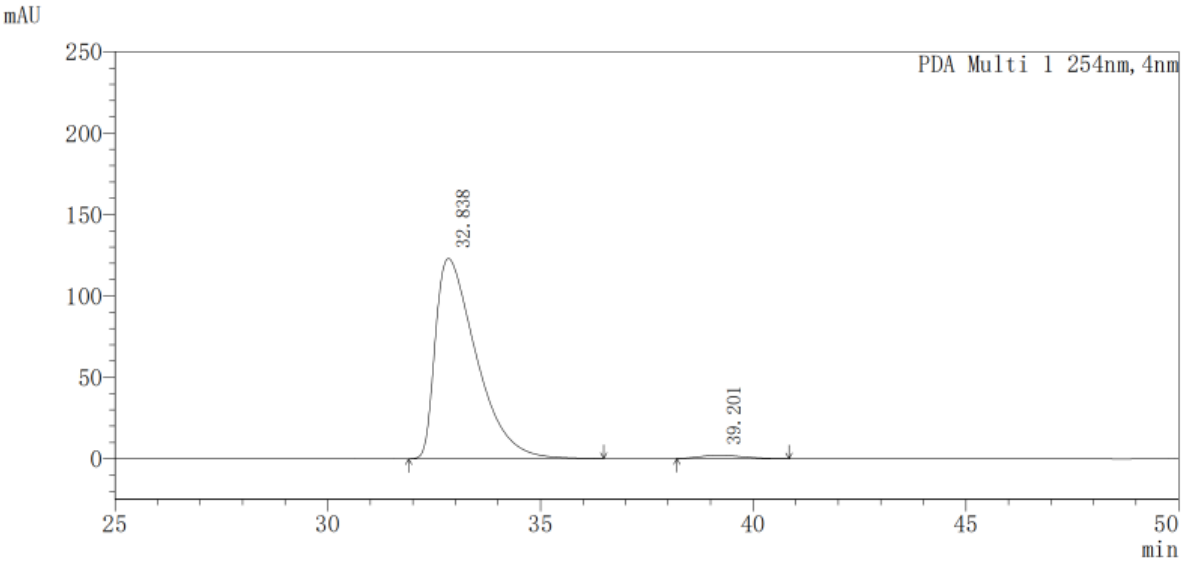
Peak #	Ret. Time	Area	Height	Area%	Height%
1	14.456	199043	3448	1.346	2.012
2	17.134	14585654	167904	98.654	97.988
总计		14784697	171352	100.000	100.000



30

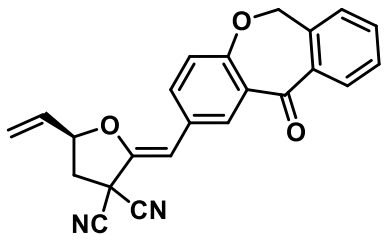
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 32.8 min (major), t_r = 39.2 min (minor);





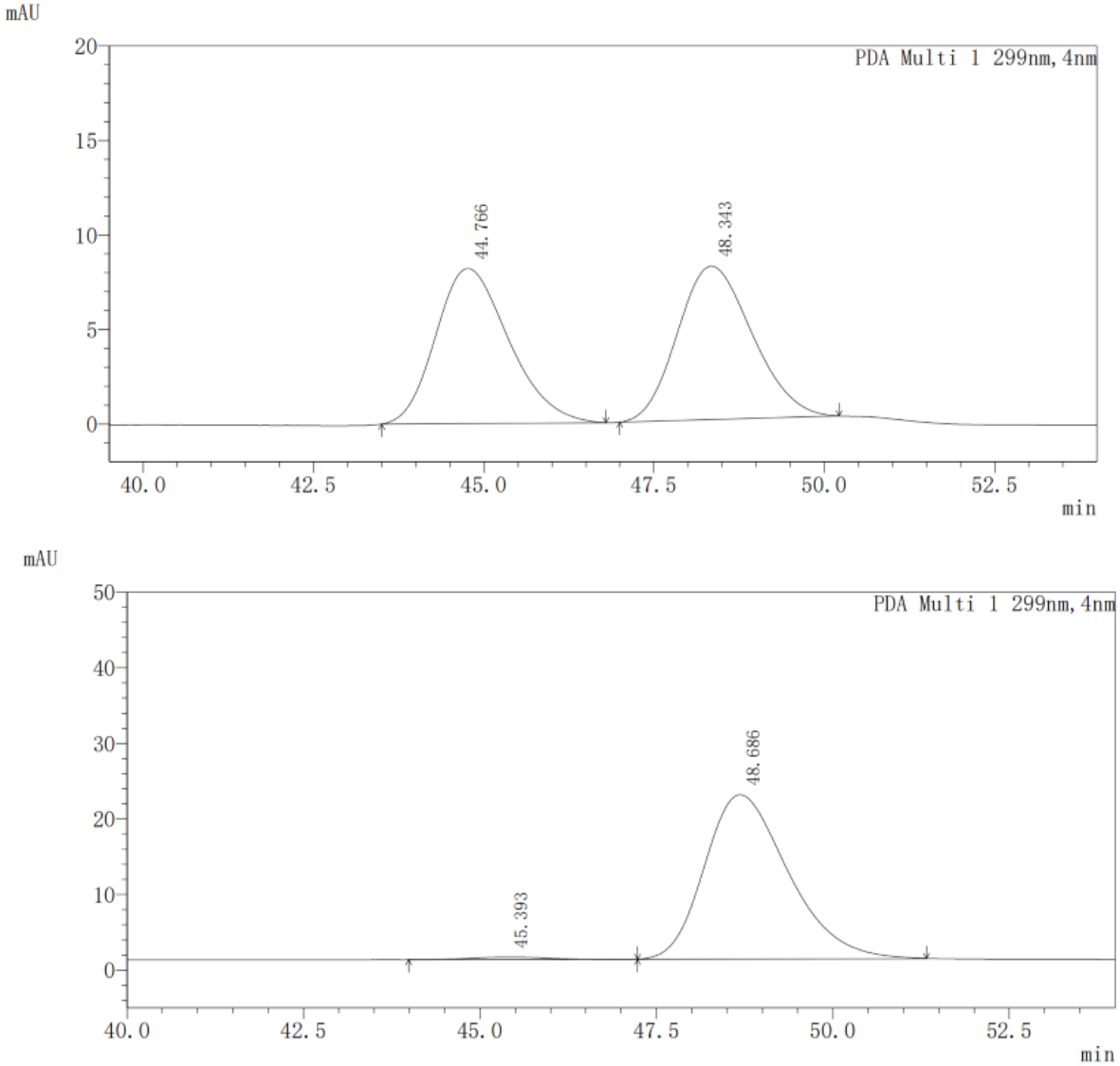
PDA Ch1 254nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	32.838	8221303	122934	98.316	98.351
2	39.201	140831	2061	1.684	1.649
总计		8362134	124996	100.000	100.000



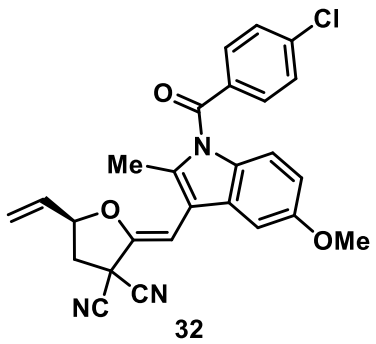
31

Chiral HPLC: 98% ee, Daicel Chiral pak IC column (10% IPA in hexanes, 1.0 mL/min), t_r = 48.7 min (major), t_r = 45.4 min (minor);



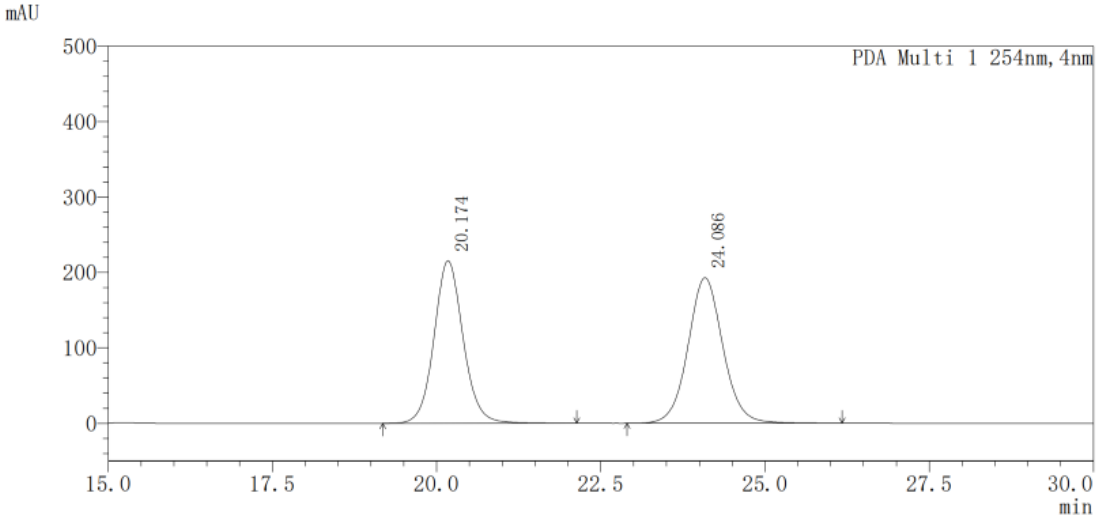
PDA Ch1 299nm

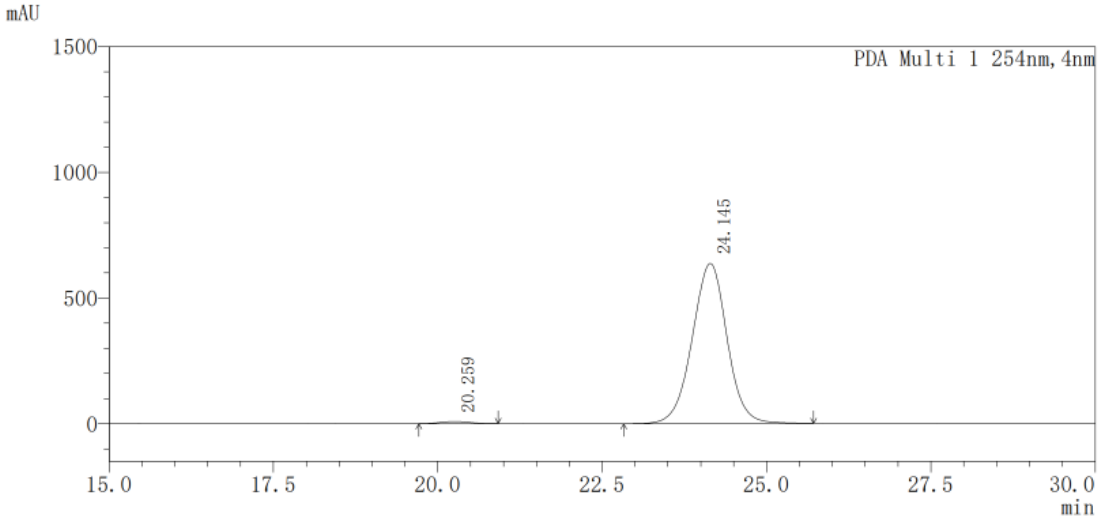
Peak #	Ret. Time	Area	Height	Area%	Height%
1	45.393	21168	327	1.165	1.482
2	48.686	1795918	21731	98.835	98.518
总计		1817086	22058	100.000	100.000



32

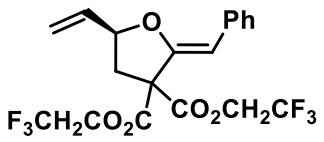
Chiral HPLC: 98% ee, Daicel Chiral pak IA column (10% IPA in hexanes, 1.0 mL/min), t_r = 24.1 min (major), t_r = 20.3 min (minor);





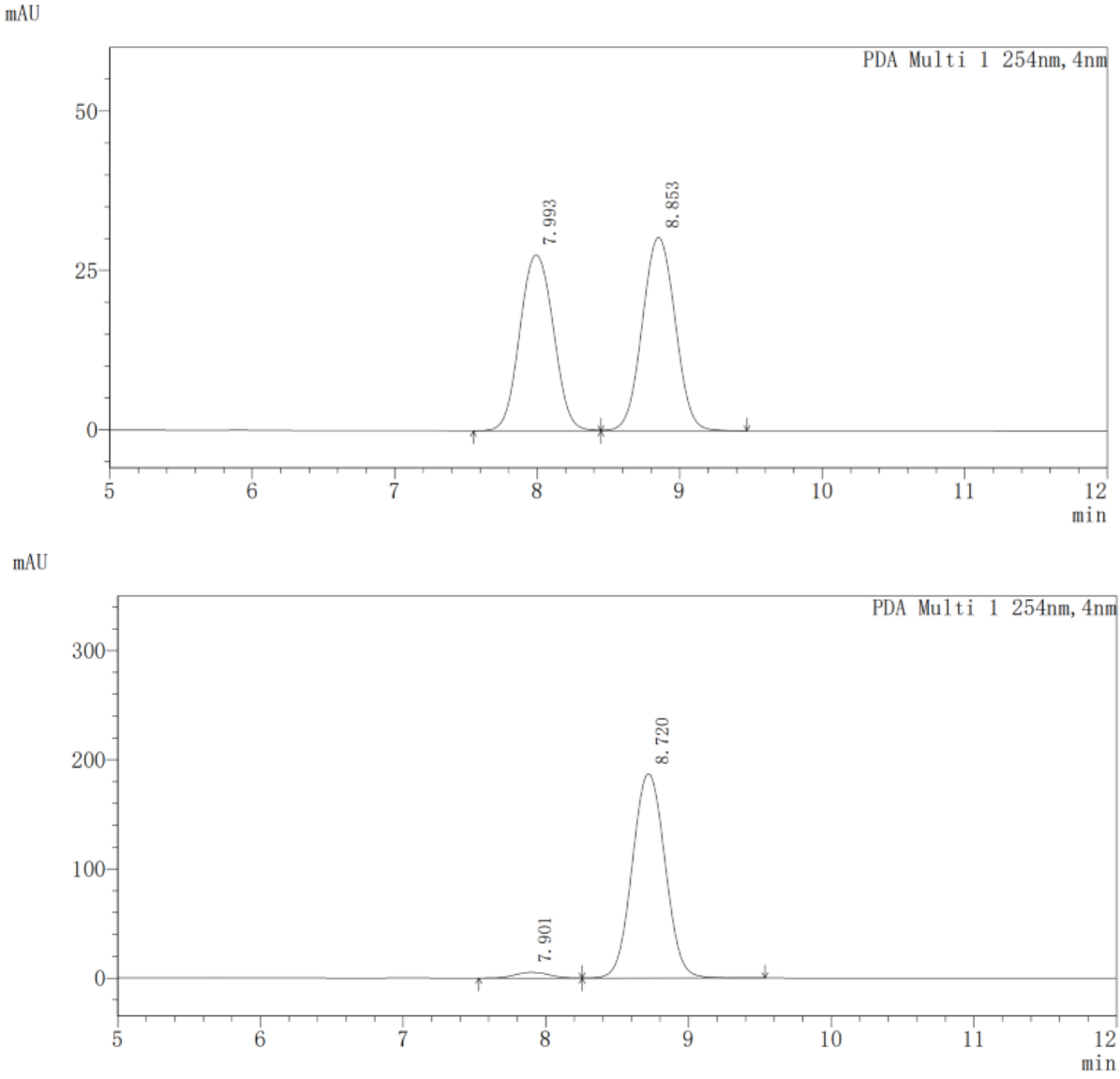
PDA Ch1 254nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	20.259	268134	8759	1.124	1.355
2	24.145	23588471	637576	98.876	98.645
总计		23856605	646335	100.000	100.000



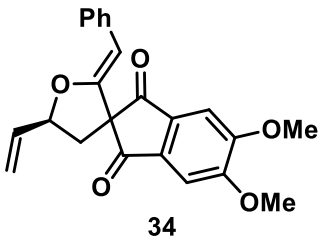
33

Chiral HPLC: 95% ee, Daicel Chiral pak IA column (1% IPA in hexanes, 1.0 mL/min), t_r = 8.7 min (major), t_r = 7.9 min (minor);



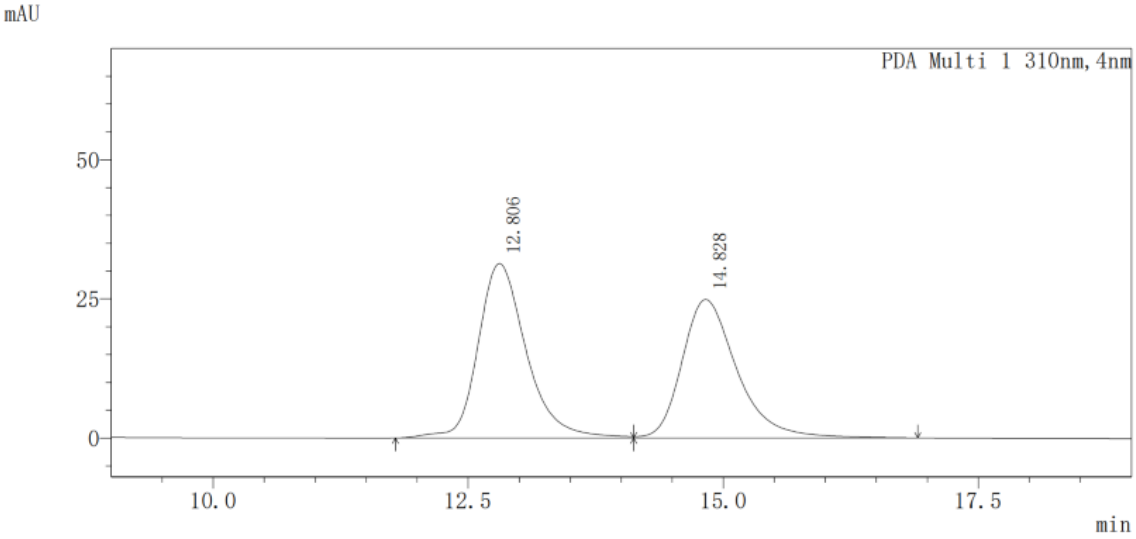
PDA Ch1 254nm

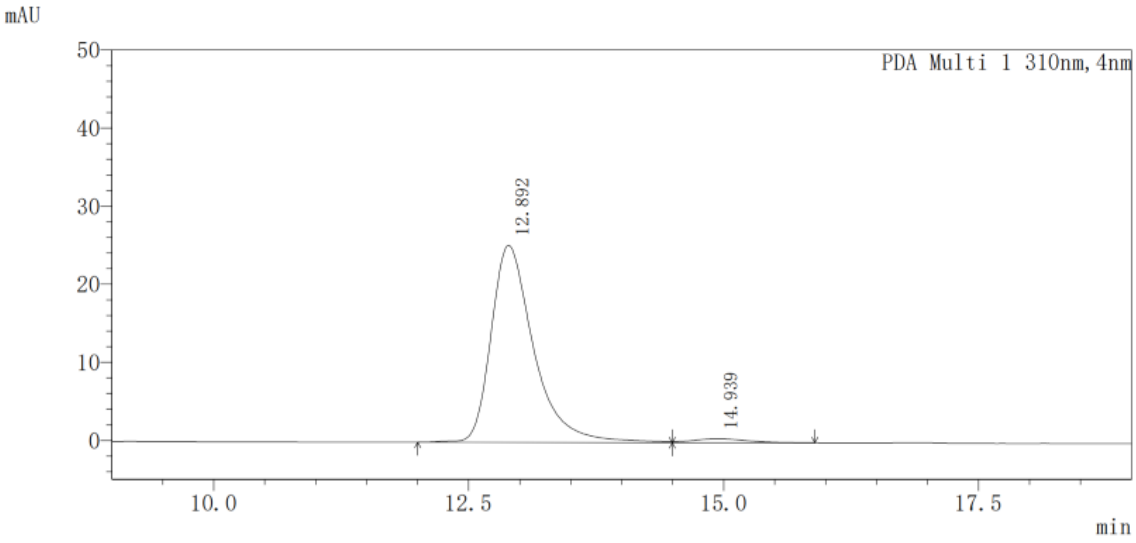
Peak #	Ret. Time	Area	Height	Area%	Height%
1	7.901	84453	5171	2.739	2.689
2	8.720	2998480	187157	97.261	97.311
总计		3082932	192328	100.000	100.000



34

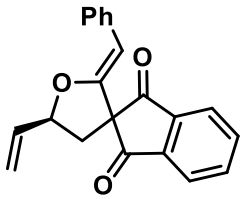
Chiral HPLC: 95% ee, Daicel Chiral pak IC column (10% IPA in hexanes, 1.0 mL/min), t_r = 12.9 min (major), t_r = 14.9 min (minor);





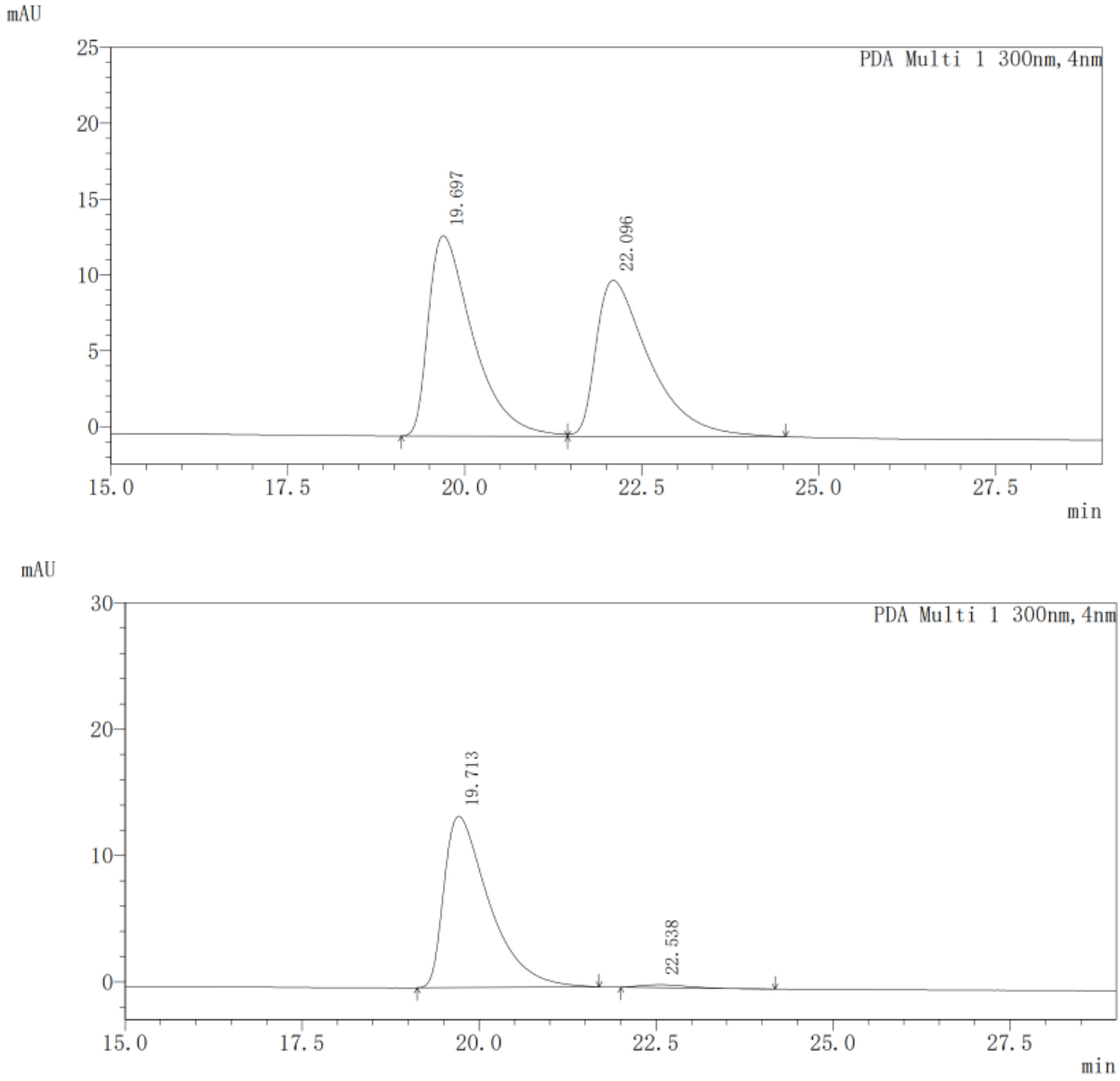
PDA Ch1 310nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	12.892	735862	25234	97.499	97.988
2	14.939	18873	518	2.501	2.012
总计		754735	25753	100.000	100.000



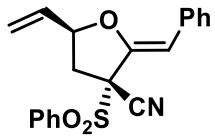
35

Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 19.7 min (major), t_r = 22.5 min (minor);



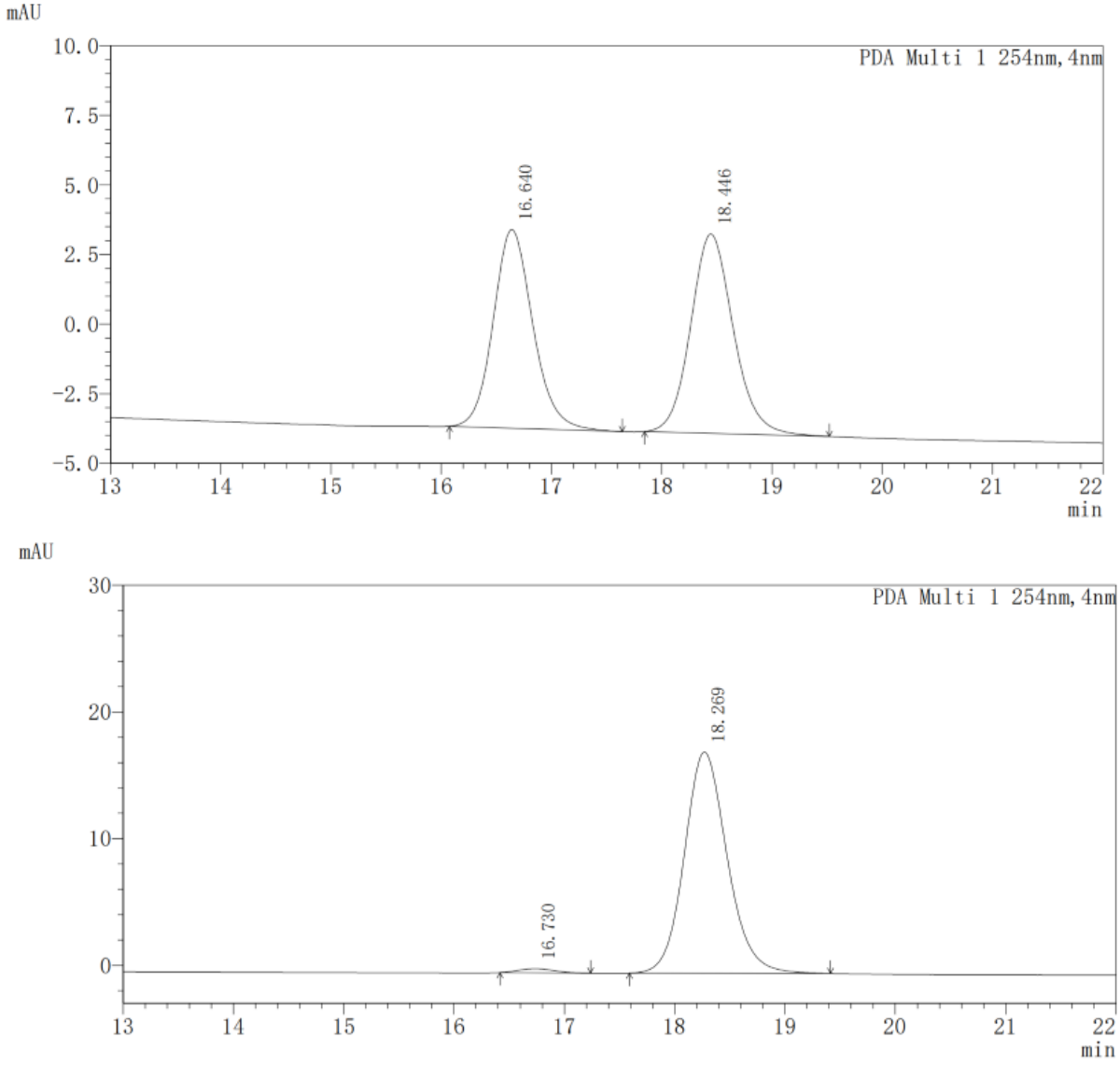
PDA Ch1 300nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	19.713	603004	13565	98.446	98.373
2	22.538	9517	224	1.554	1.627
总计		612520	13790	100.000	100.000



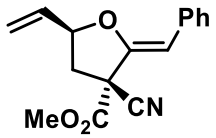
36

Chiral HPLC: 97% ee, Daicel Chiral pak IA column (1% IPA in hexanes, 1.0 mL/min), t_r = 18.3 min (major), t_r = 16.7 min (minor);



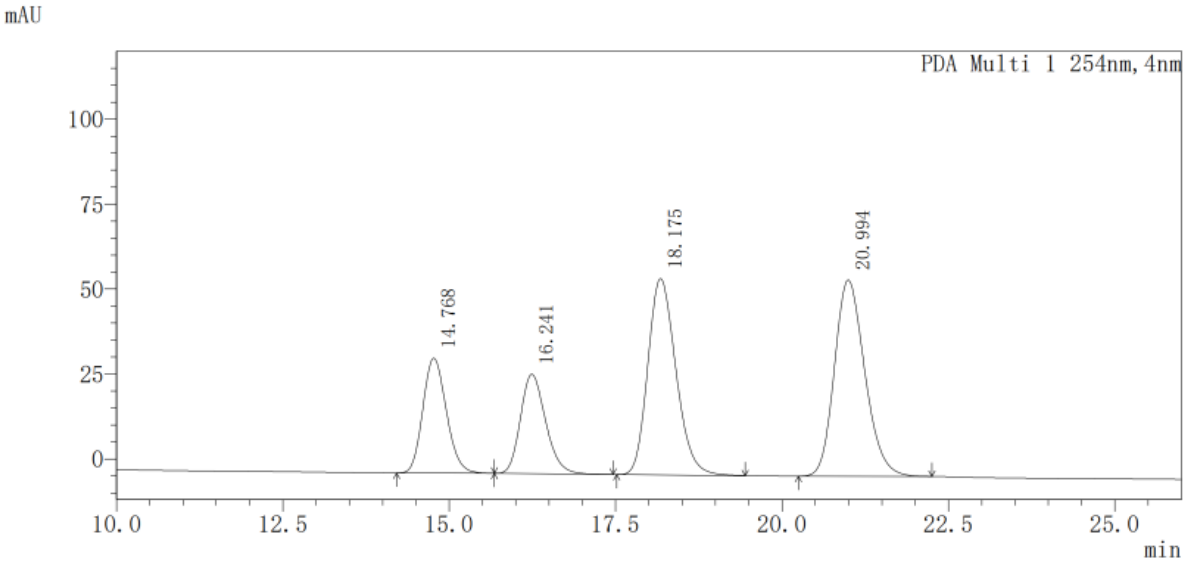
PDA Ch1 254nm

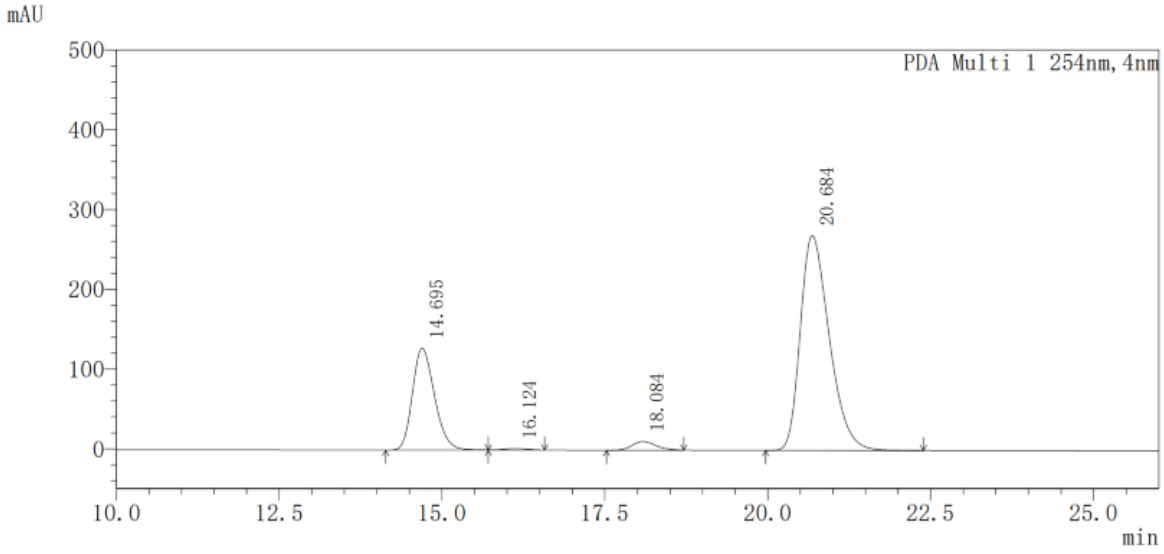
Peak #	Ret. Time	Area	Height	Area%	Height%
1	16.730	7335	328	1.528	1.844
2	18.269	472648	17466	98.472	98.156
总计		479983	17794	100.000	100.000



37

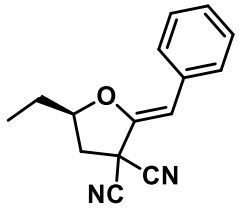
Chiral HPLC: 93% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.7 min (major), t_r = 18.1 min (minor);





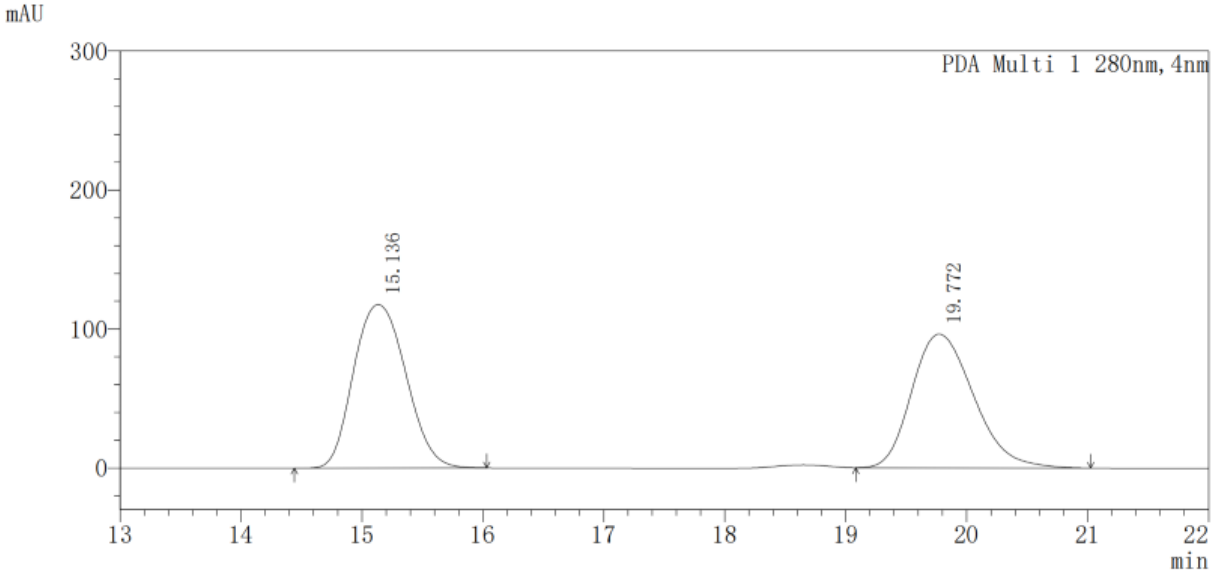
PDA Ch1 254nm

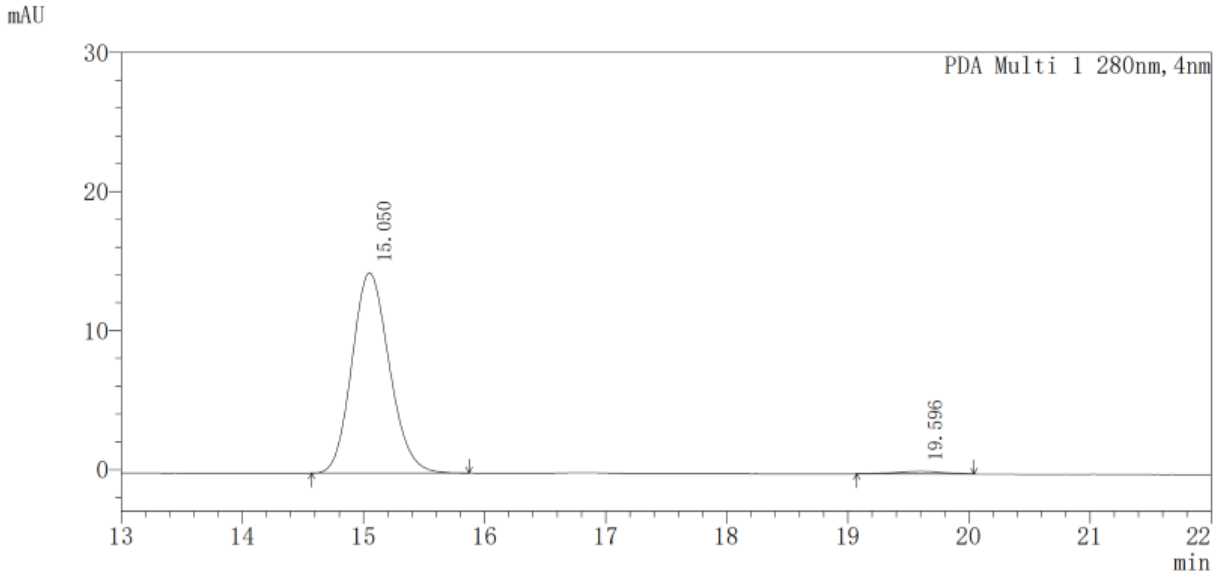
Peak #	Ret. Time	Area	Height	Area%	Height%
1	14.695	3018567	127655	25.770	31.118
2	16.124	53698	2038	0.458	0.497
3	18.084	290262	11059	2.478	2.696
4	20.684	8351139	269474	71.294	65.689
总计		11713665	410226	100.000	100.000



39

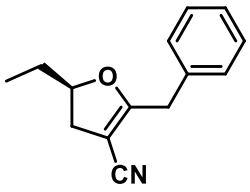
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 15.1 min (major), t_r = 19.6 min (minor);





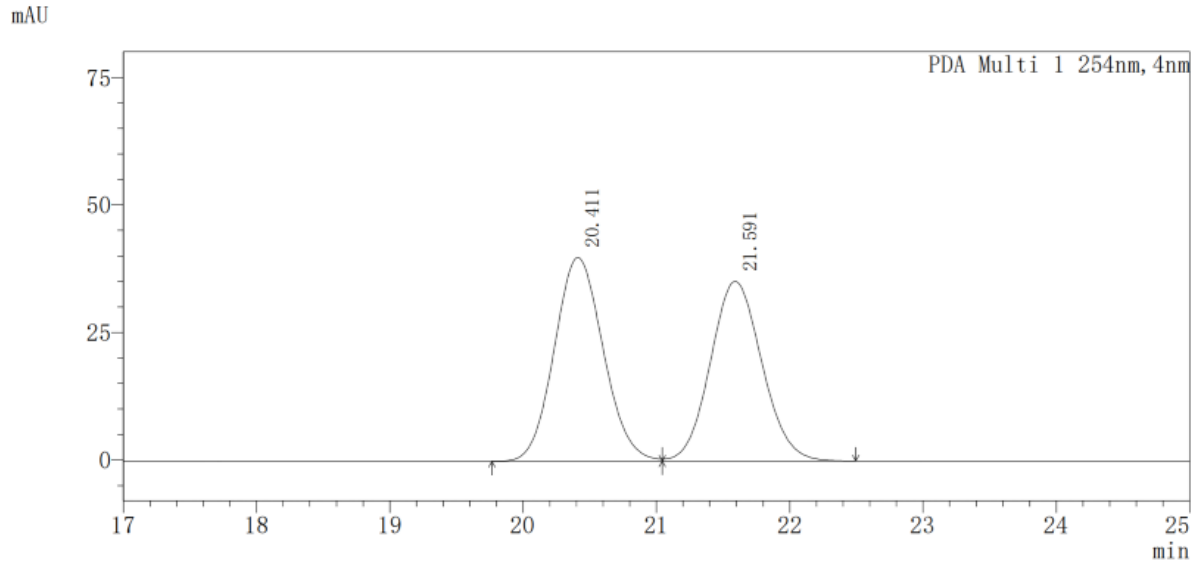
PDA Ch1 280nm

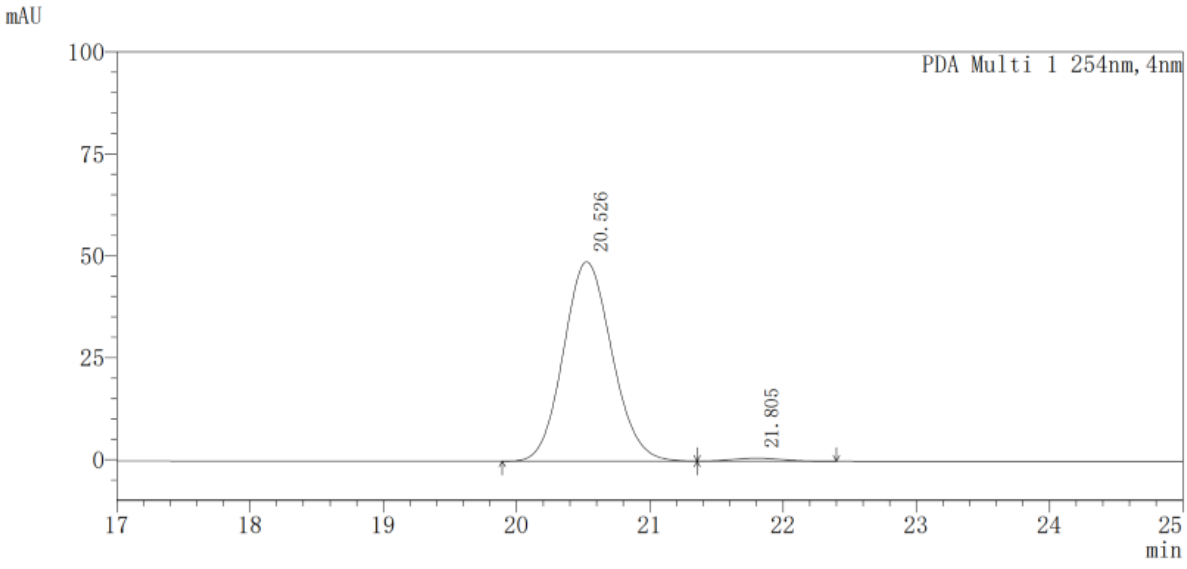
Peak #	Ret. Time	Area	Height	Area%	Height%
1	15.050	309354	14421	98.377	98.729
2	19.596	5102	186	1.623	1.271
总计		314456	14607	100.000	100.000



40

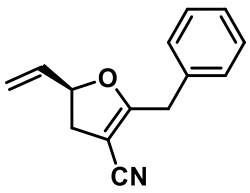
Chiral HPLC: 97% ee, Daicel Chiral pak IC column (1% IPA in hexanes, 1.0 mL/min), t_r = 20.5 min (major), t_r = 21.8 min (minor);





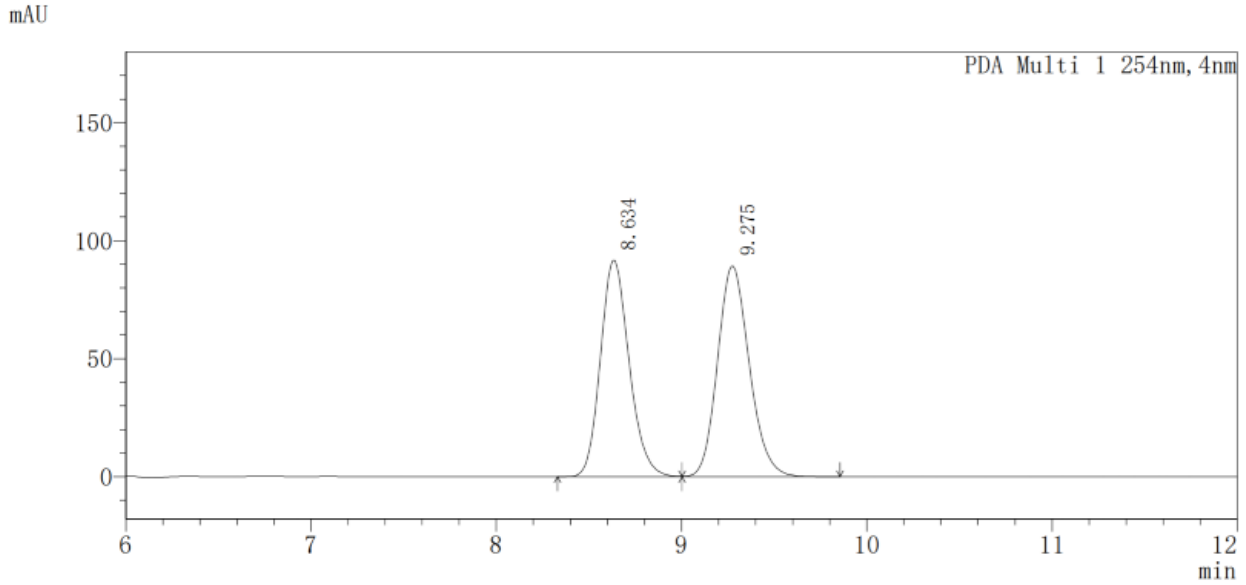
PDA Ch1 254nm

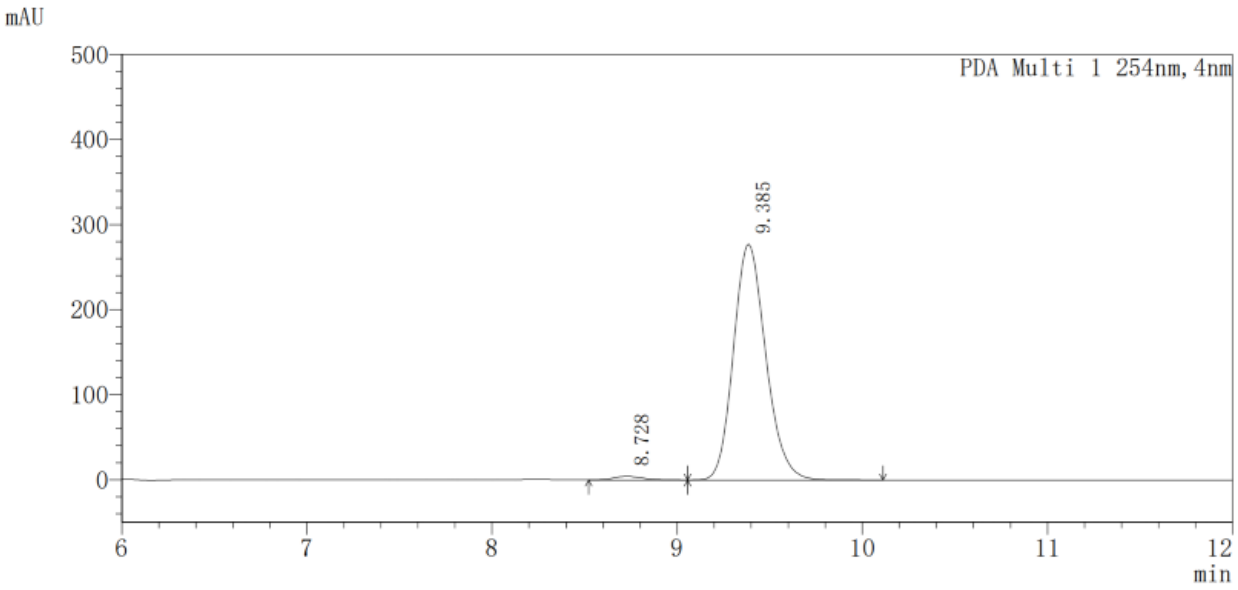
Peak #	Ret. Time	Area	Height	Area%	Height%
1	20.526	1239650	48906	98.384	98.476
2	21.805	20356	757	1.616	1.524
总计		1260006	49663	100.000	100.000



41

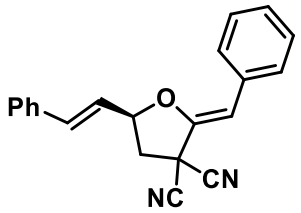
Chiral HPLC: 97% ee, Daicel Chiral pak IG column (5% IPA in hexanes, 1.0 mL/min), t_r = 9.4 min (major), t_r = 8.7 min (minor);





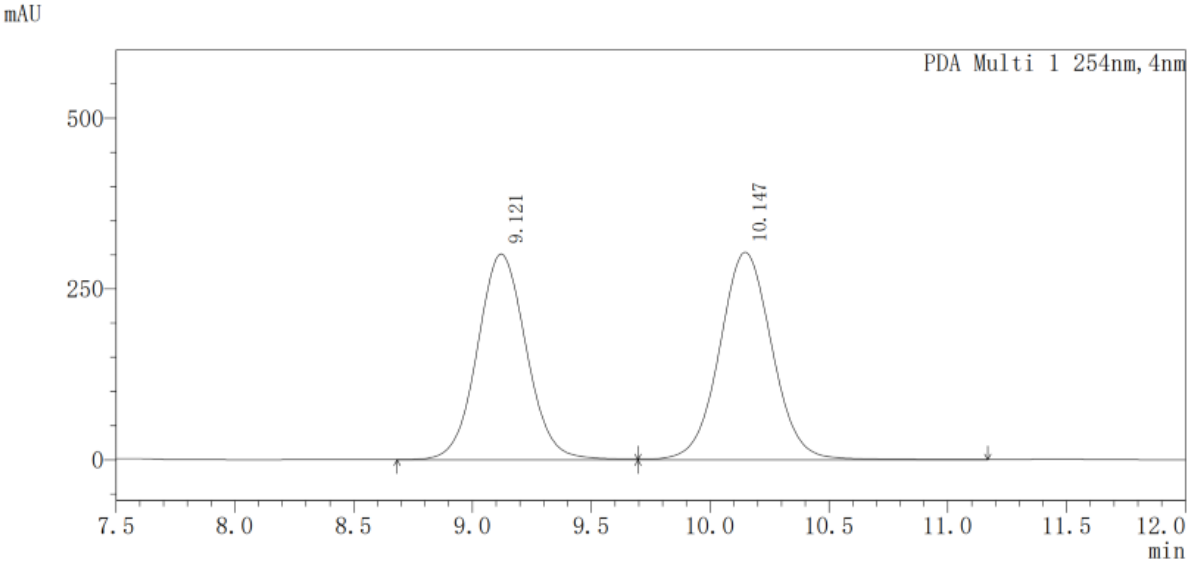
PDA Ch1 254nm

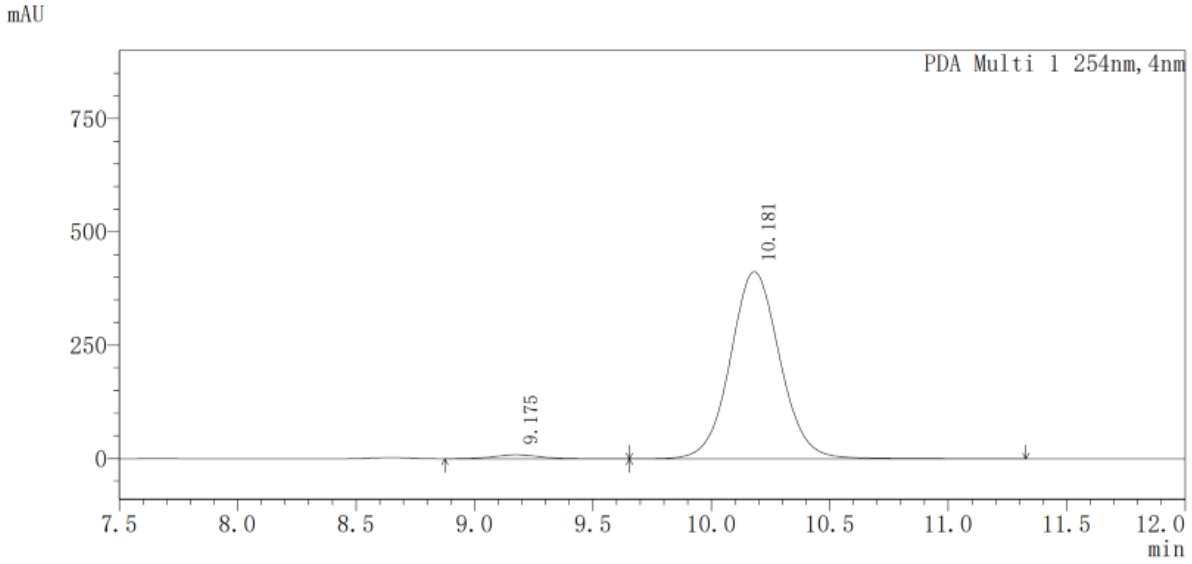
Peak #	Ret. Time	Area	Height	Area%	Height%
1	8.728	45445	4200	1.333	1.492
2	9.385	3362906	277318	98.667	98.508
总计		3408351	281518	100.000	100.000



42

Chiral HPLC: 96% ee, Daicel Chiral pak IA column (5% IPA in hexanes, 1.0 mL/min), t_r = 10.2 min (major), t_r = 9.2 min (minor);

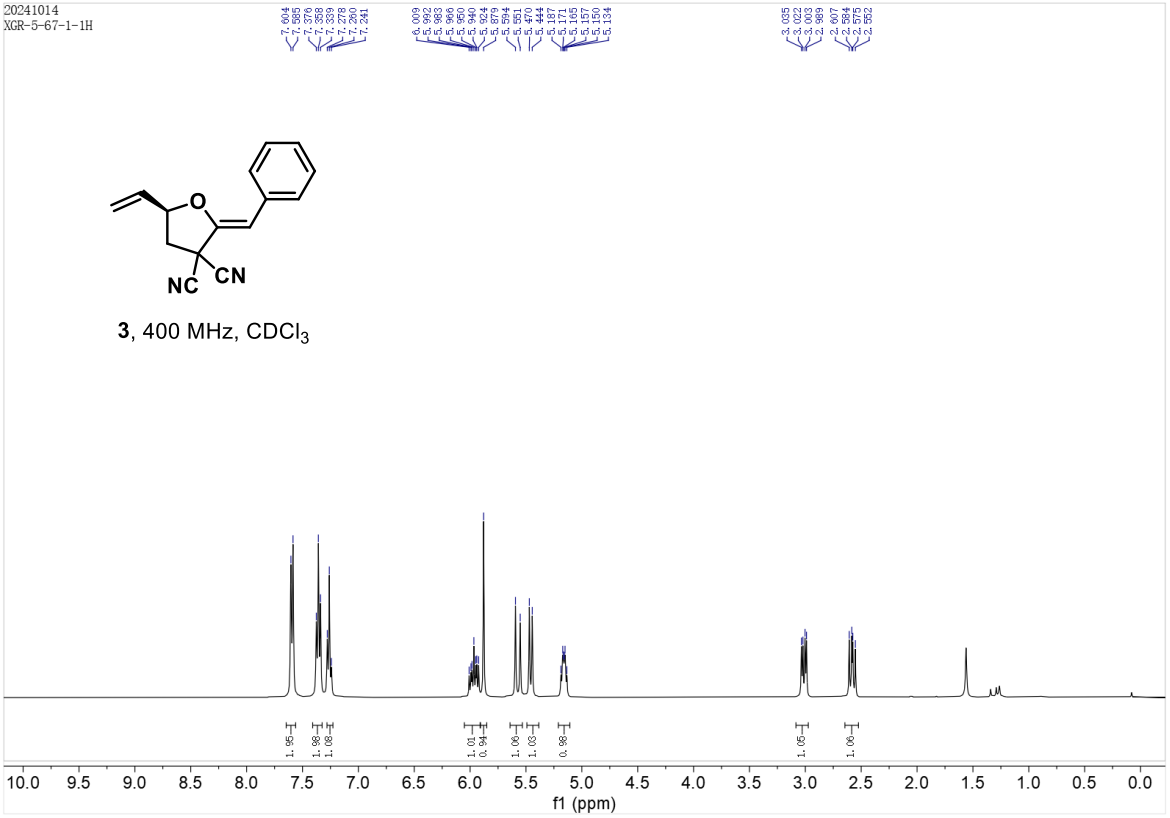




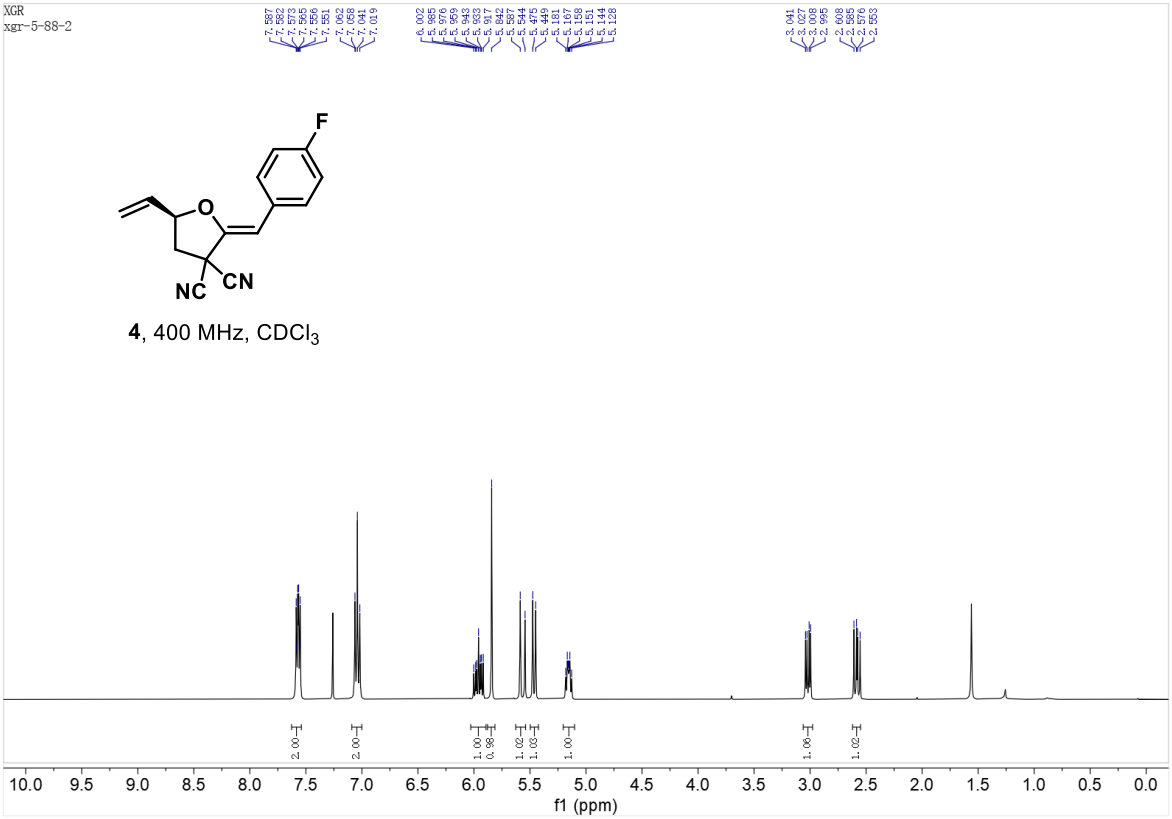
PDA Ch1 254nm

Peak #	Ret. Time	Area	Height	Area%	Height%
1	9.175	122123	8904	1.986	2.111
2	10.181	6028108	412875	98.014	97.889
总计		6150232	421779	100.000	100.000

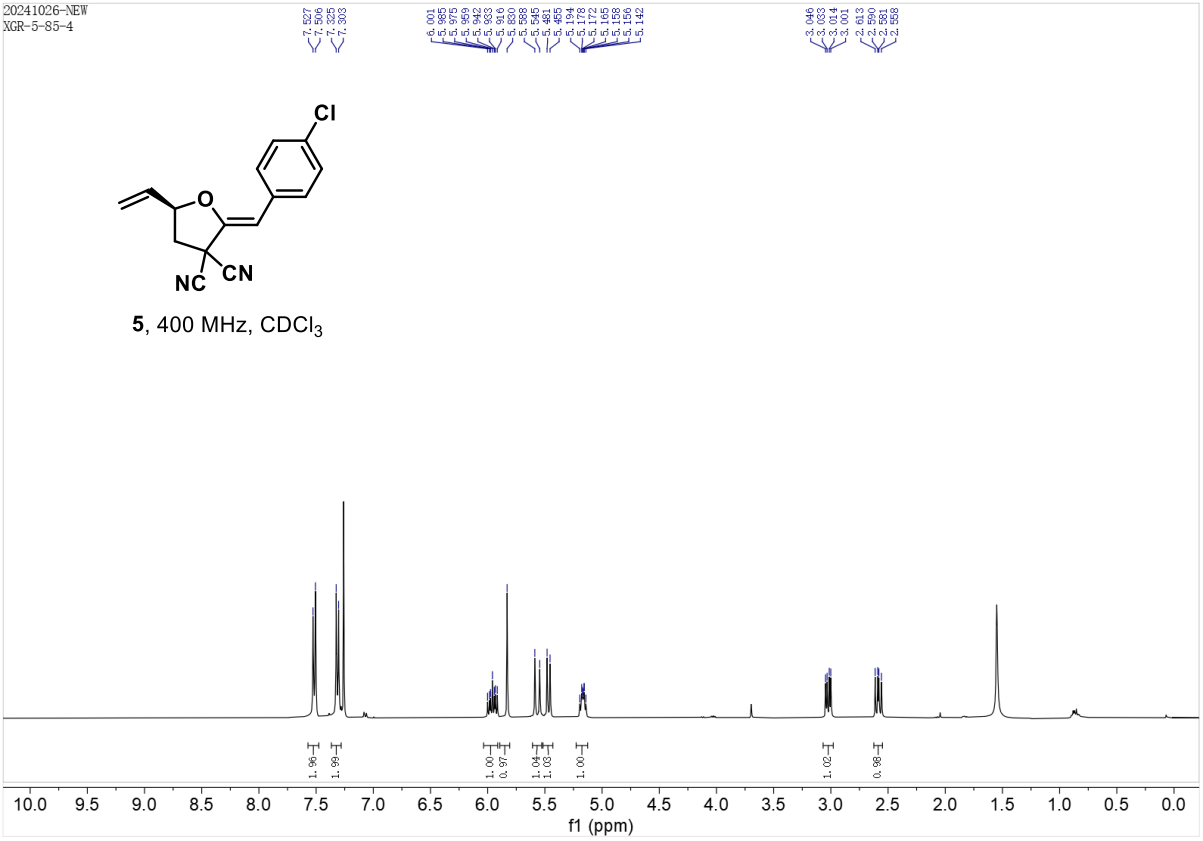
VIII. NMR Spectra



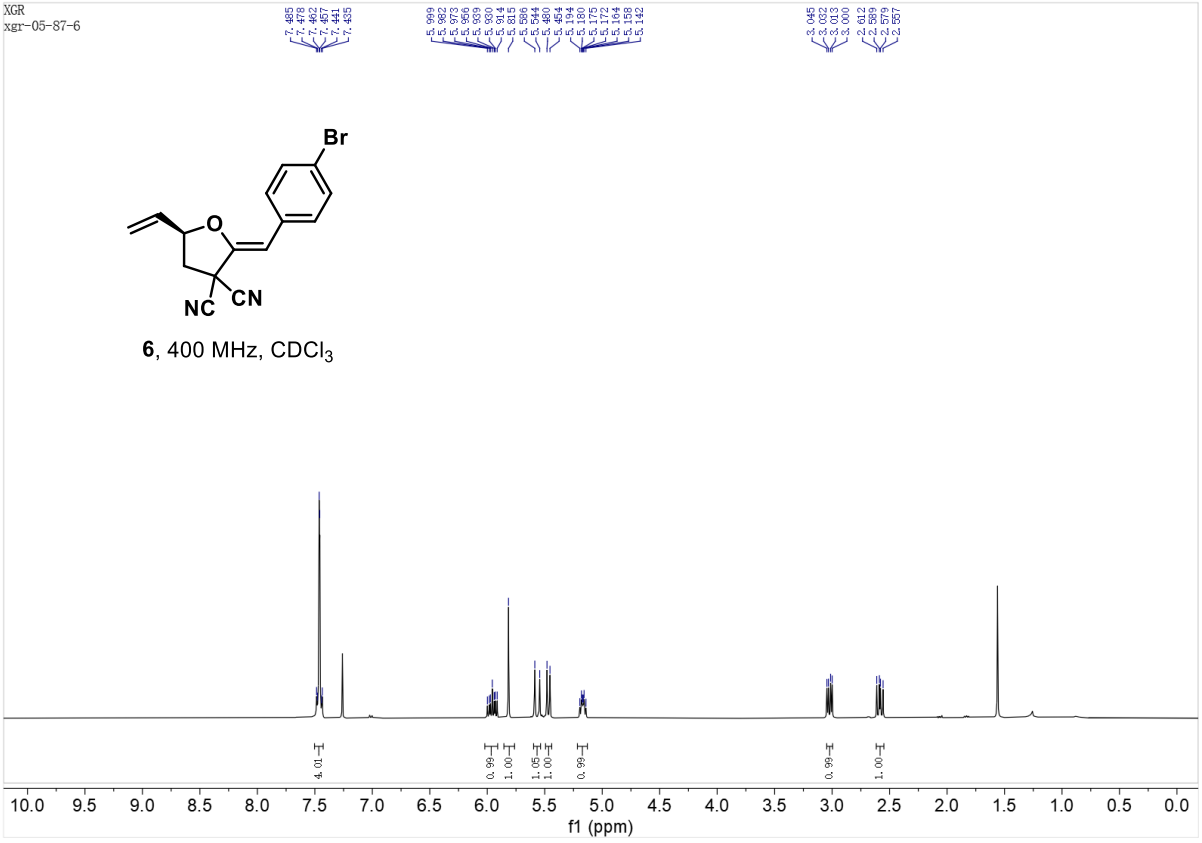
3, 400 MHz, $CDCl_3$



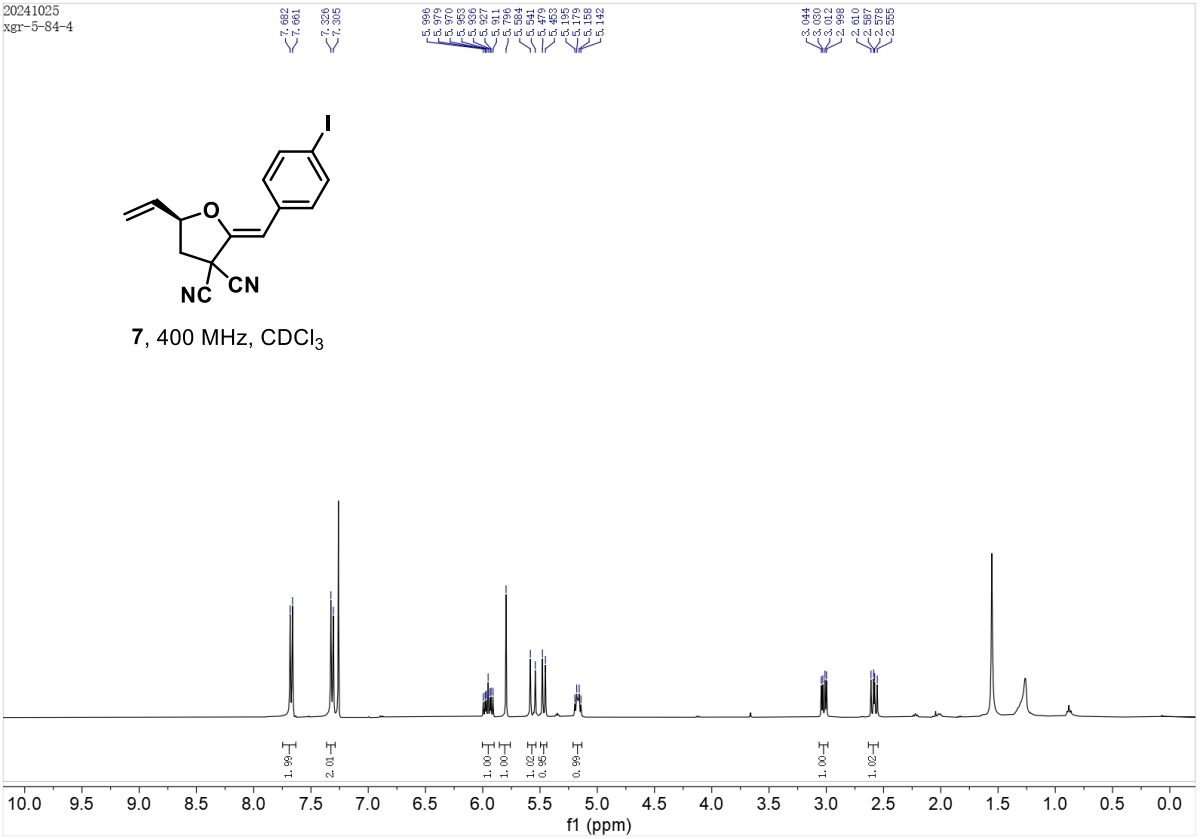
4, 400 MHz, $CDCl_3$



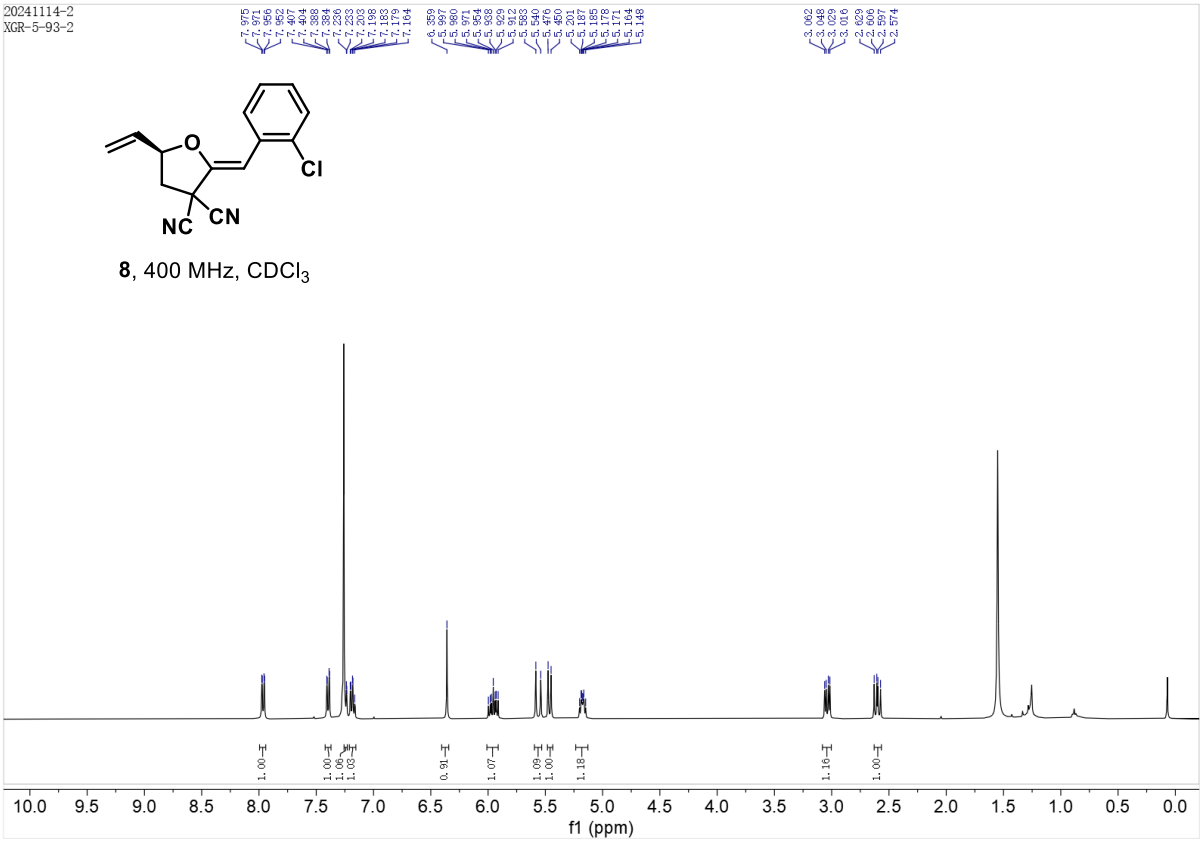
5, 400 MHz, $CDCl_3$



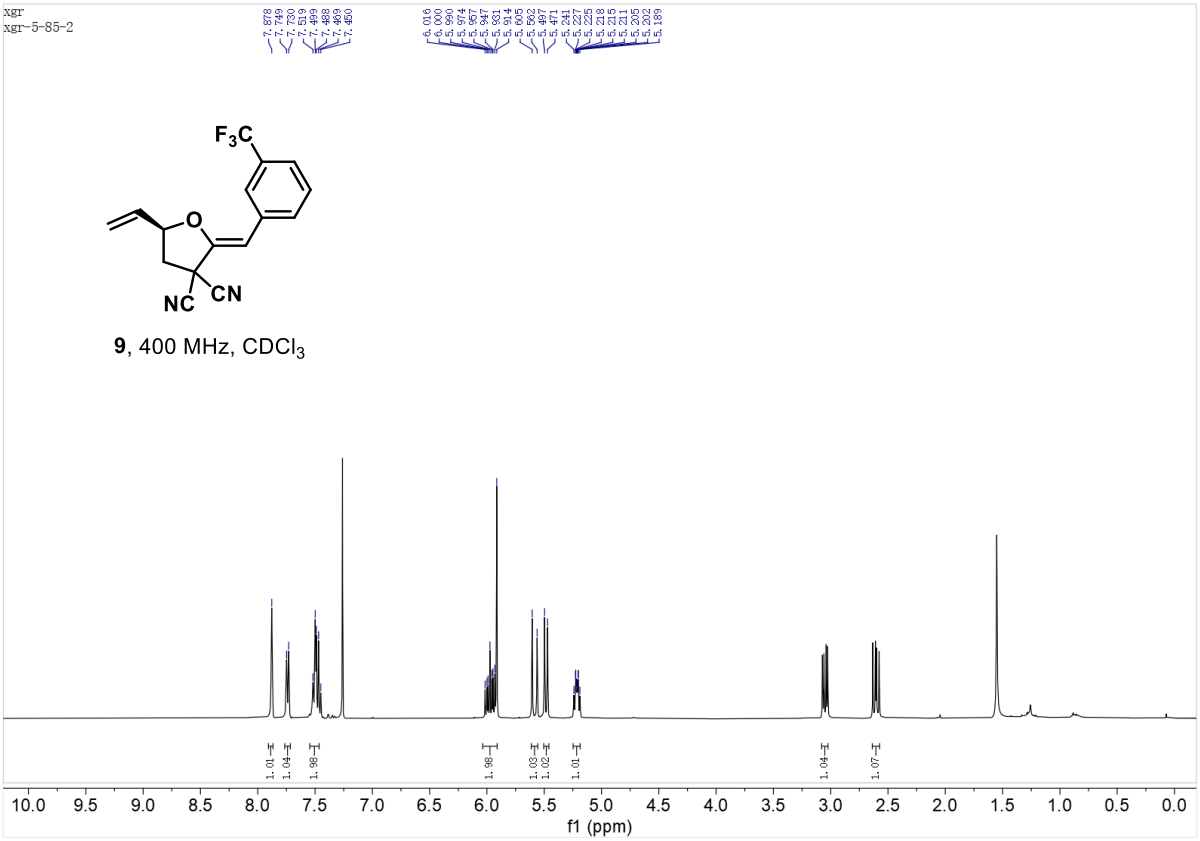
6, 400 MHz, $CDCl_3$



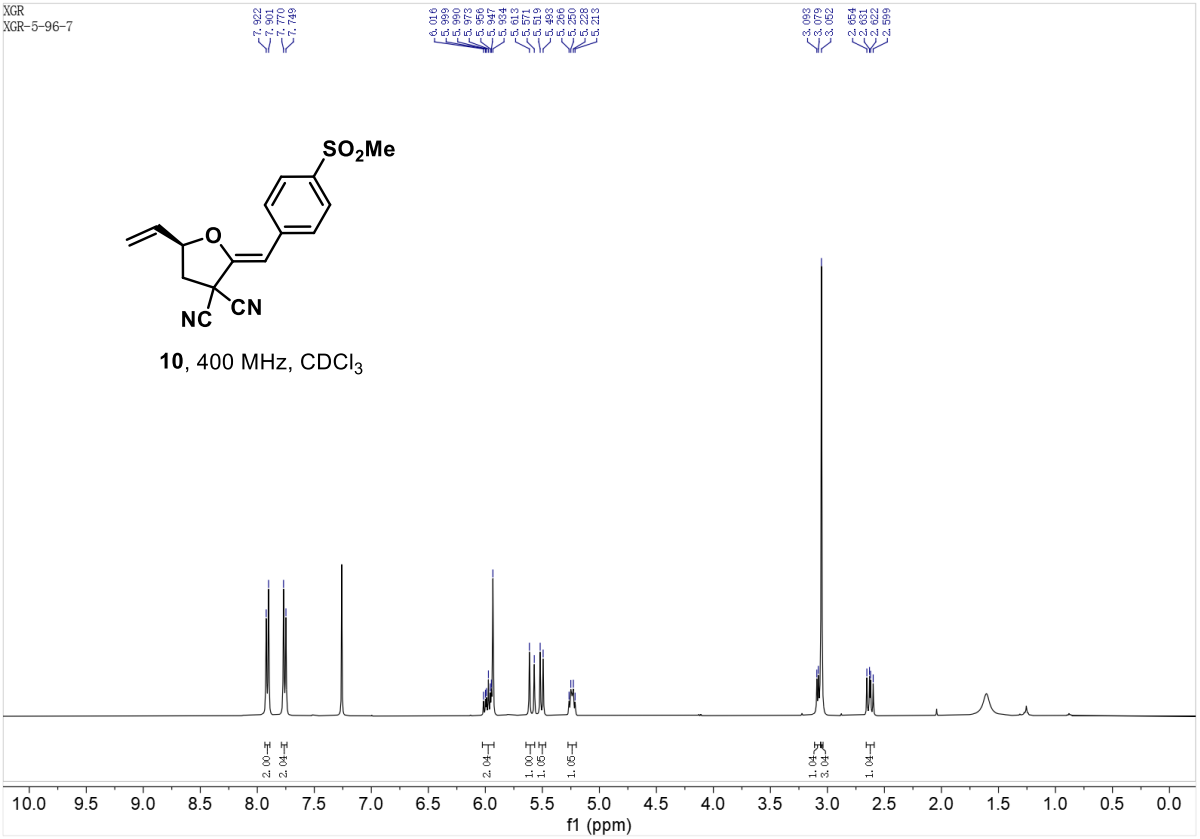
7, 400 MHz, $CDCl_3$



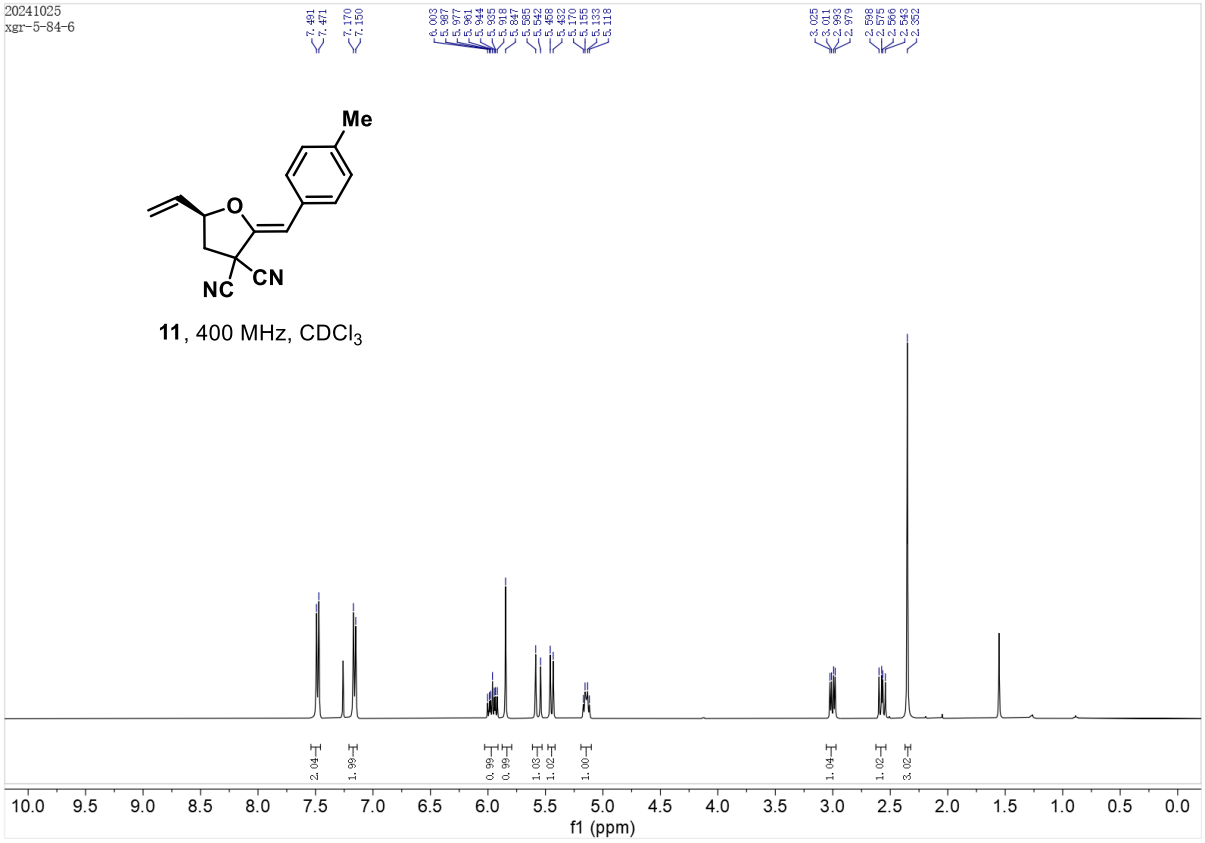
8, 400 MHz, $CDCl_3$



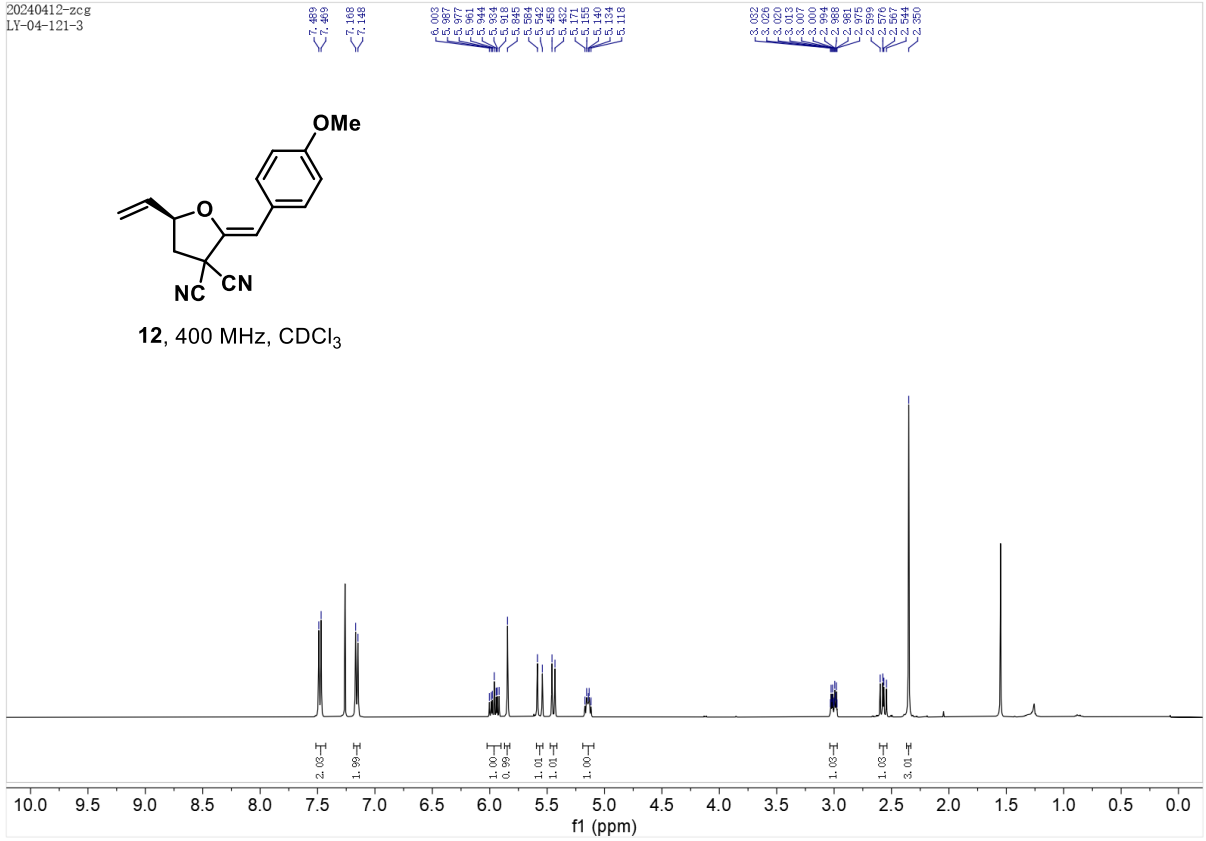
9, 400 MHz, $CDCl_3$



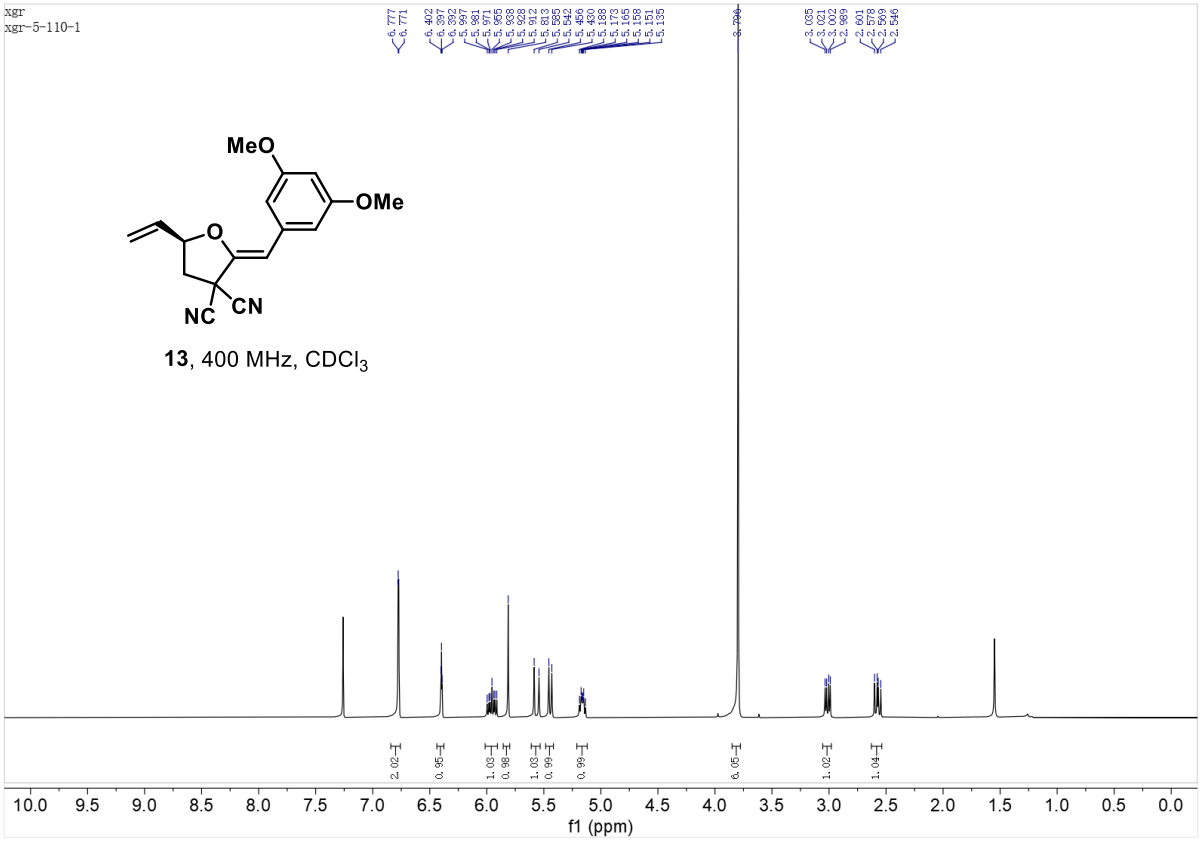
10, 400 MHz, $CDCl_3$



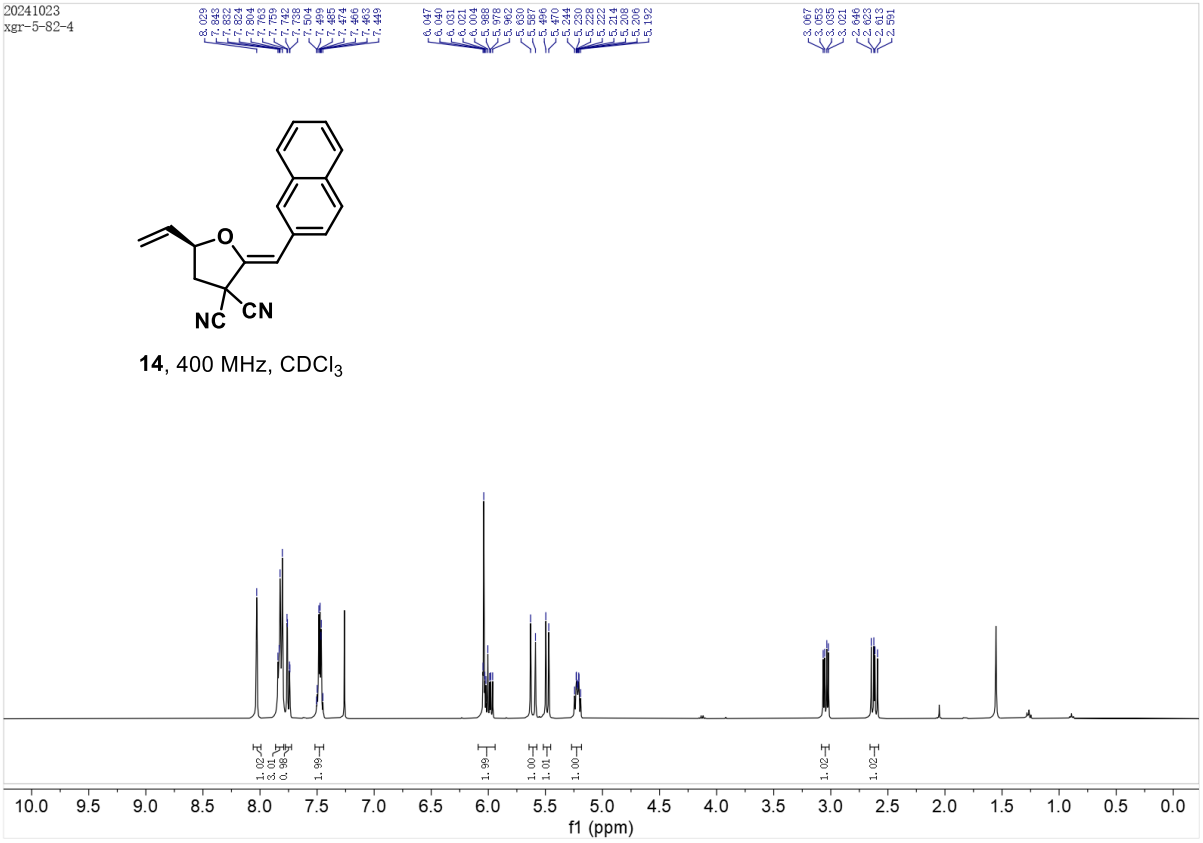
11, 400 MHz, $CDCl_3$



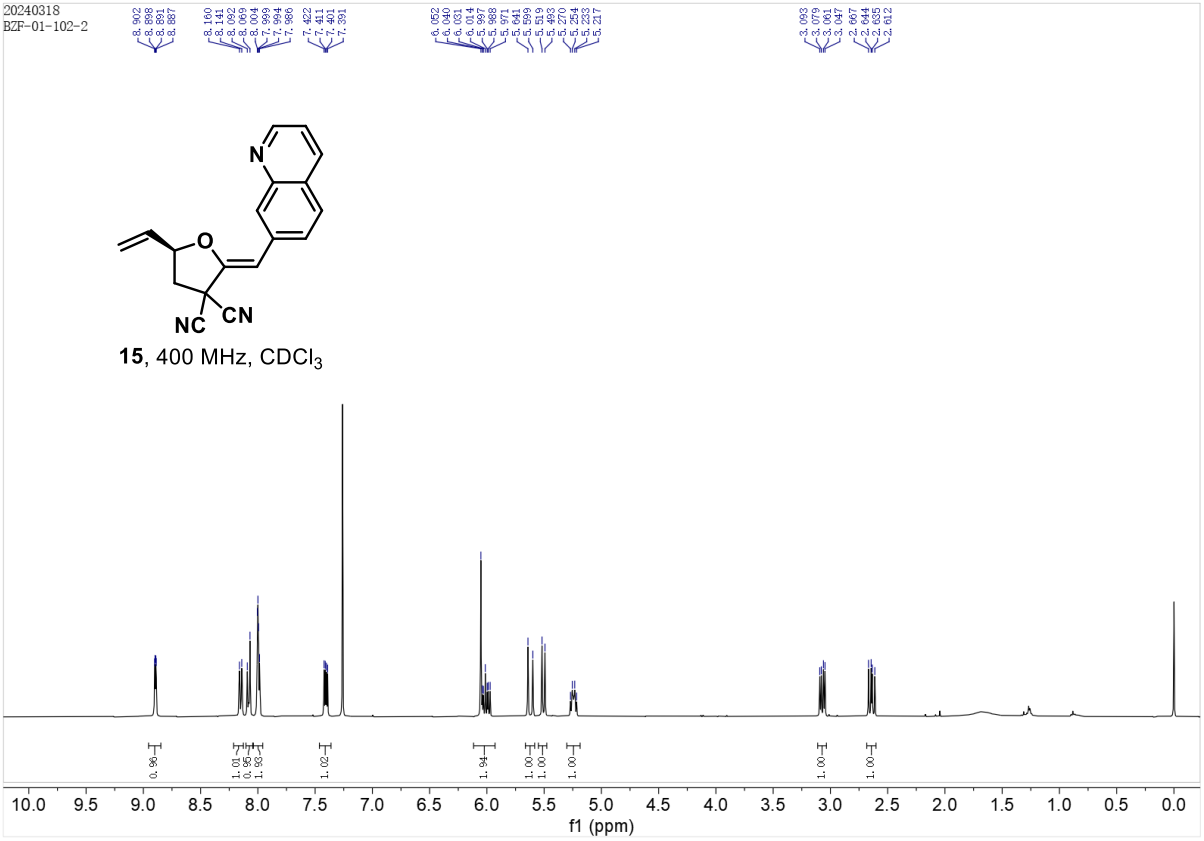
12, 400 MHz, $CDCl_3$



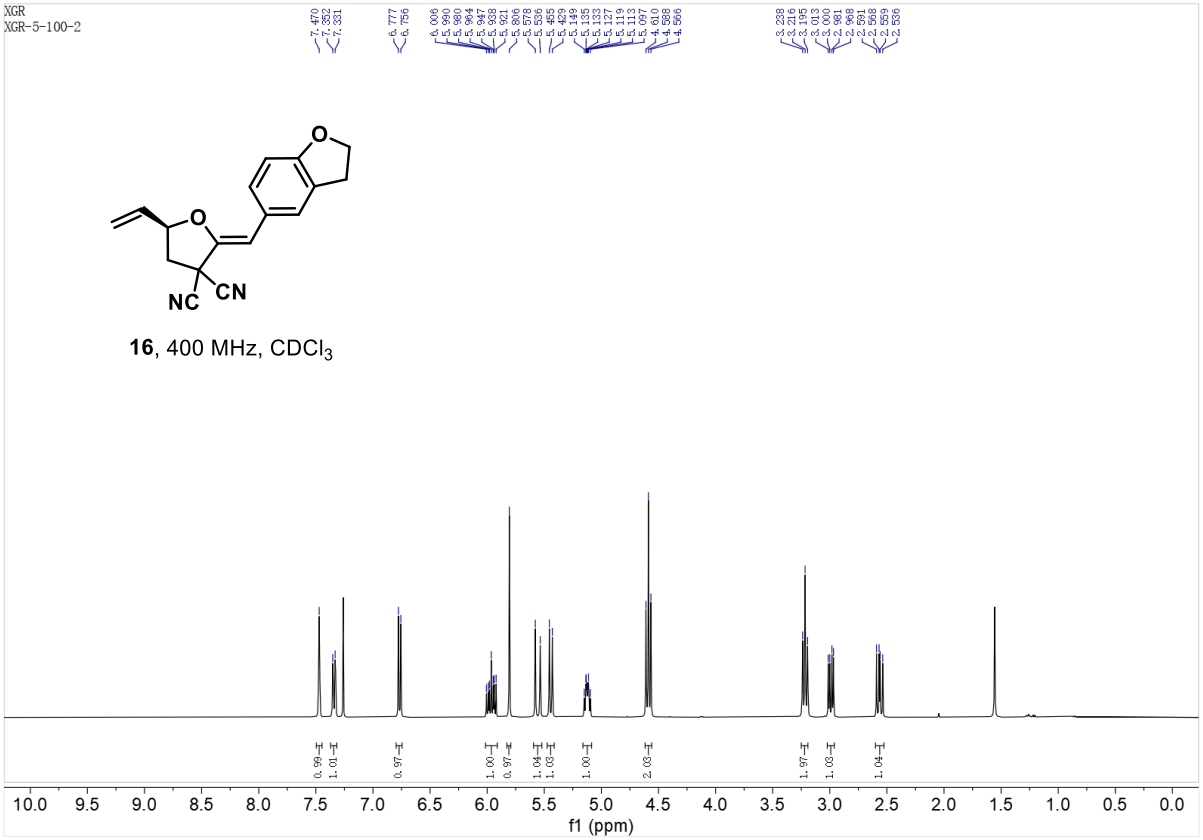
13, 400 MHz, $CDCl_3$



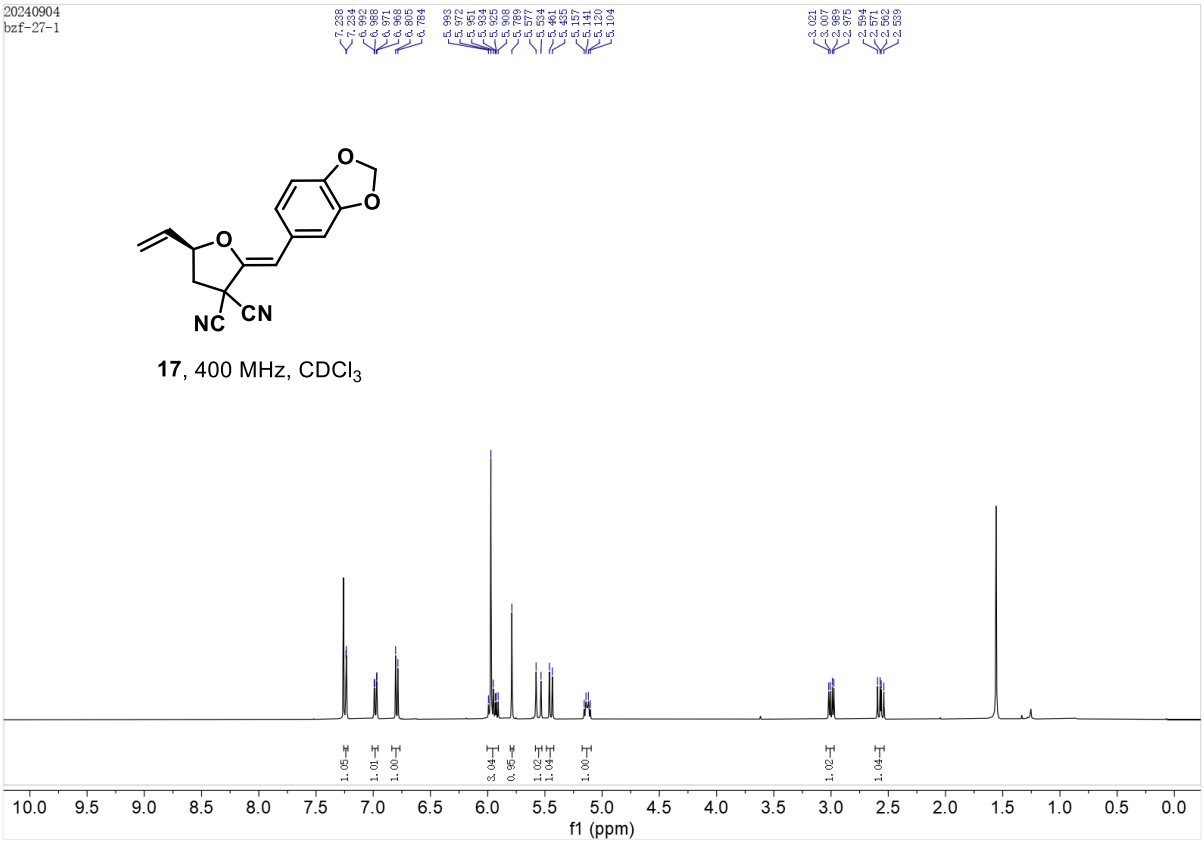
14, 400 MHz, $CDCl_3$



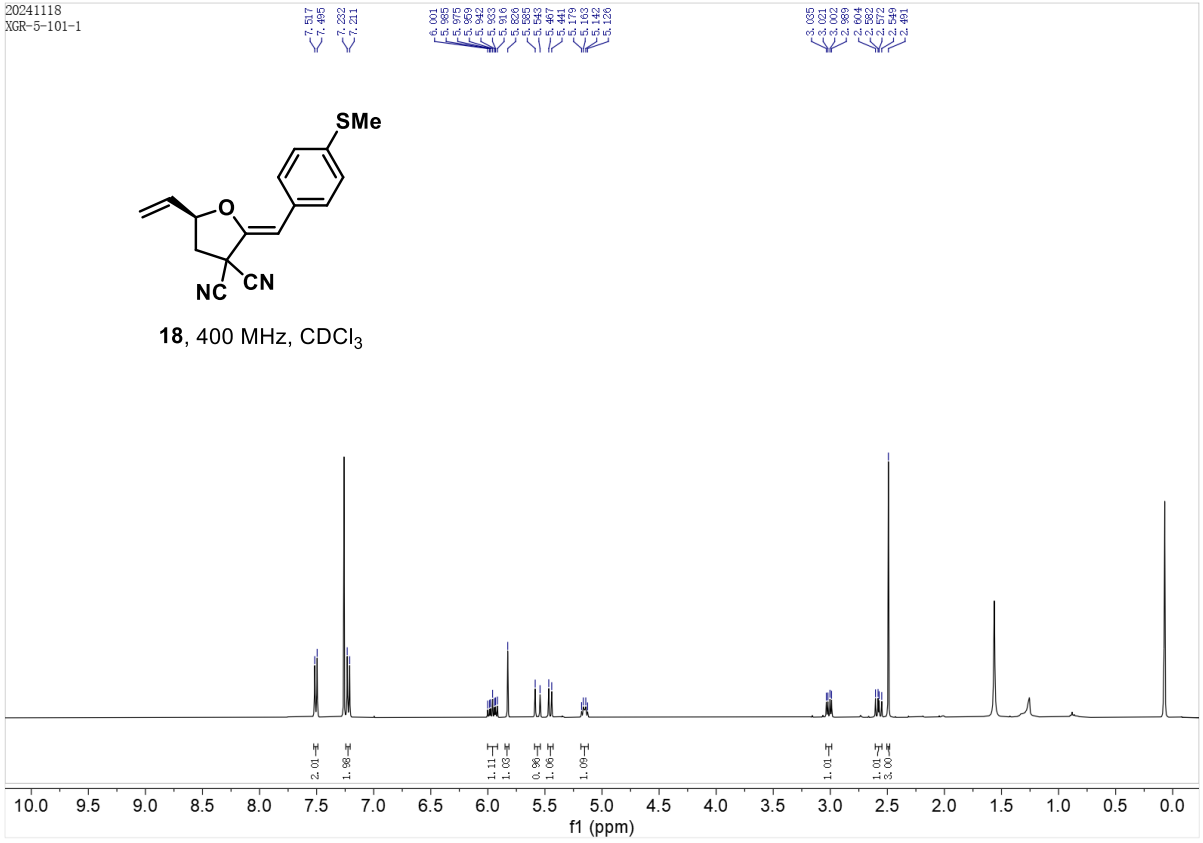
15, 400 MHz, $CDCl_3$



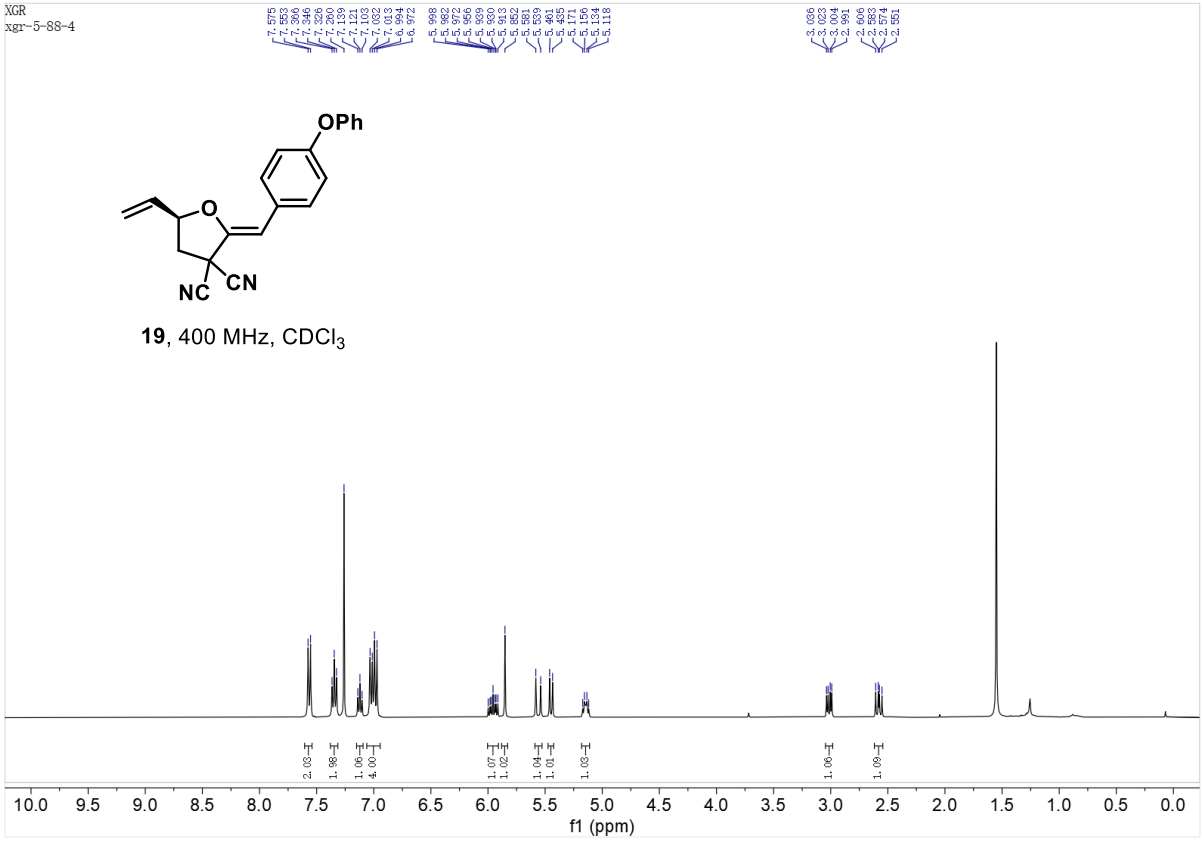
16, 400 MHz, $CDCl_3$



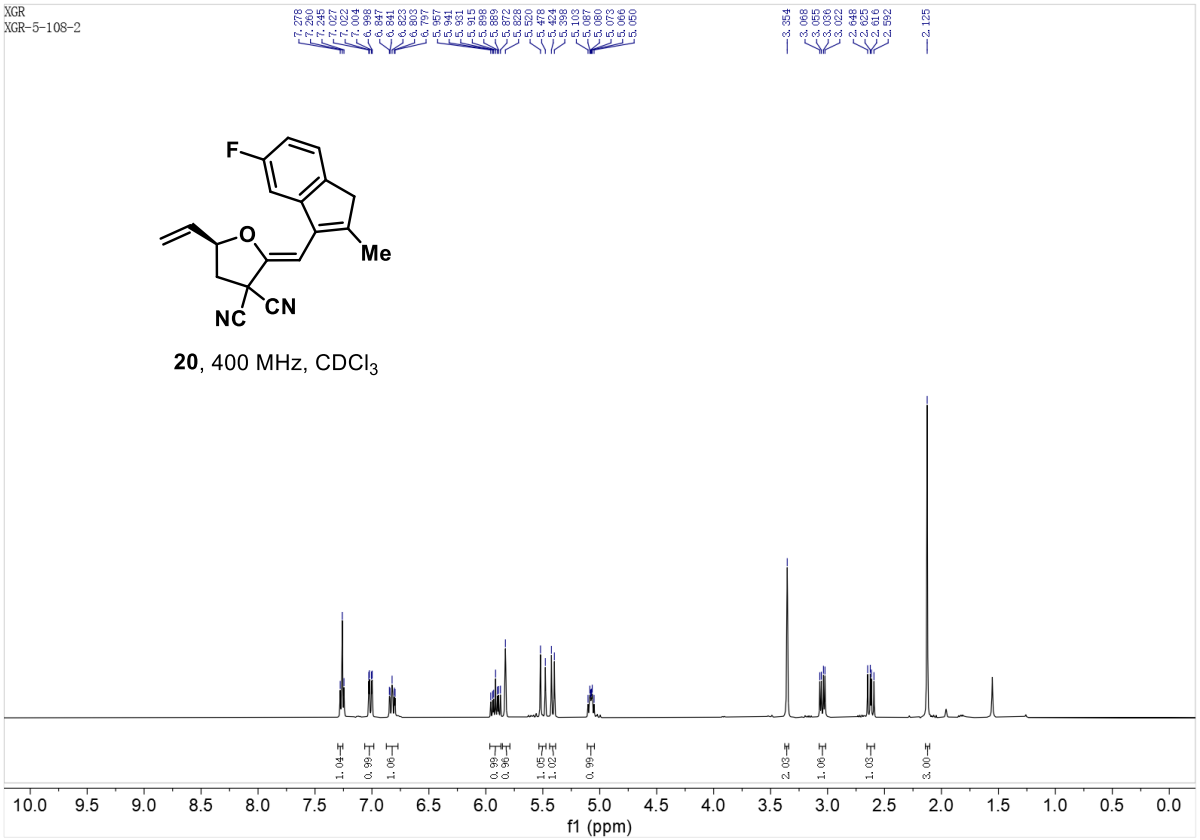
17, 400 MHz, $CDCl_3$



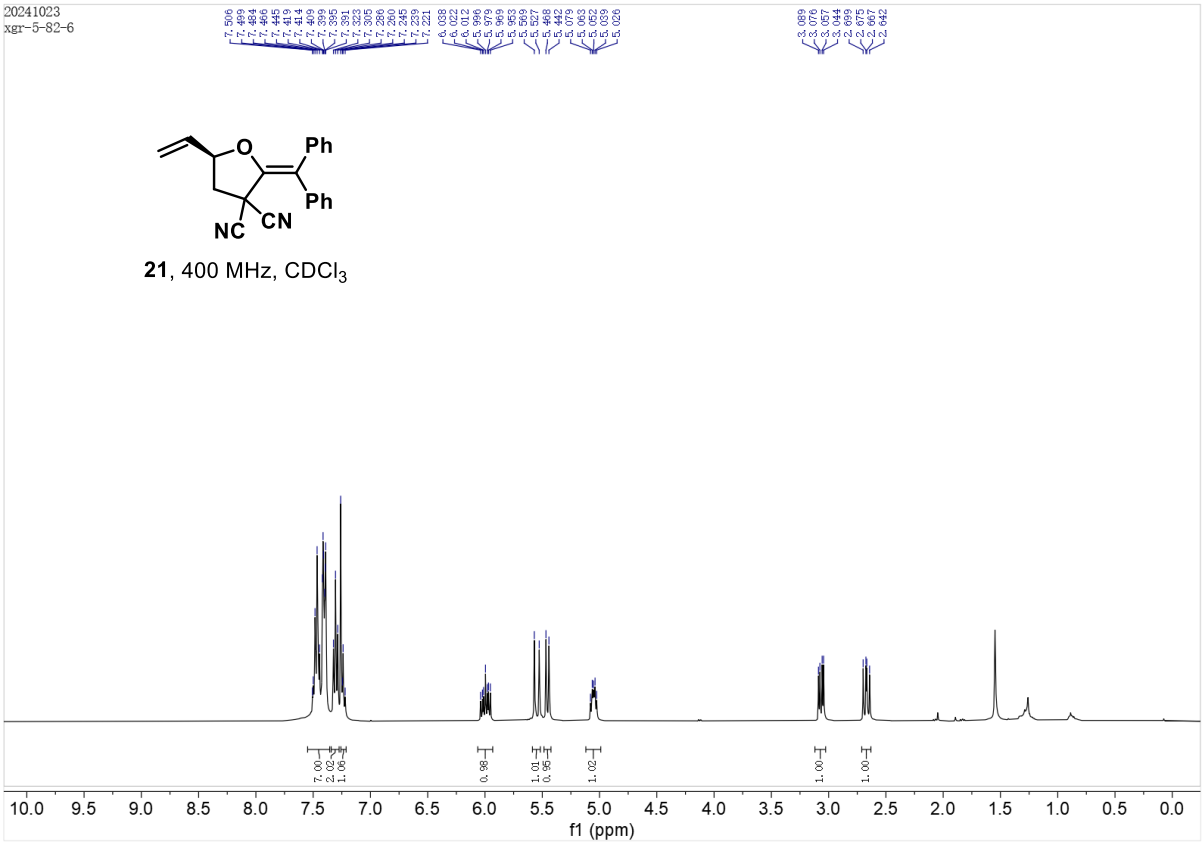
18, 400 MHz, $CDCl_3$



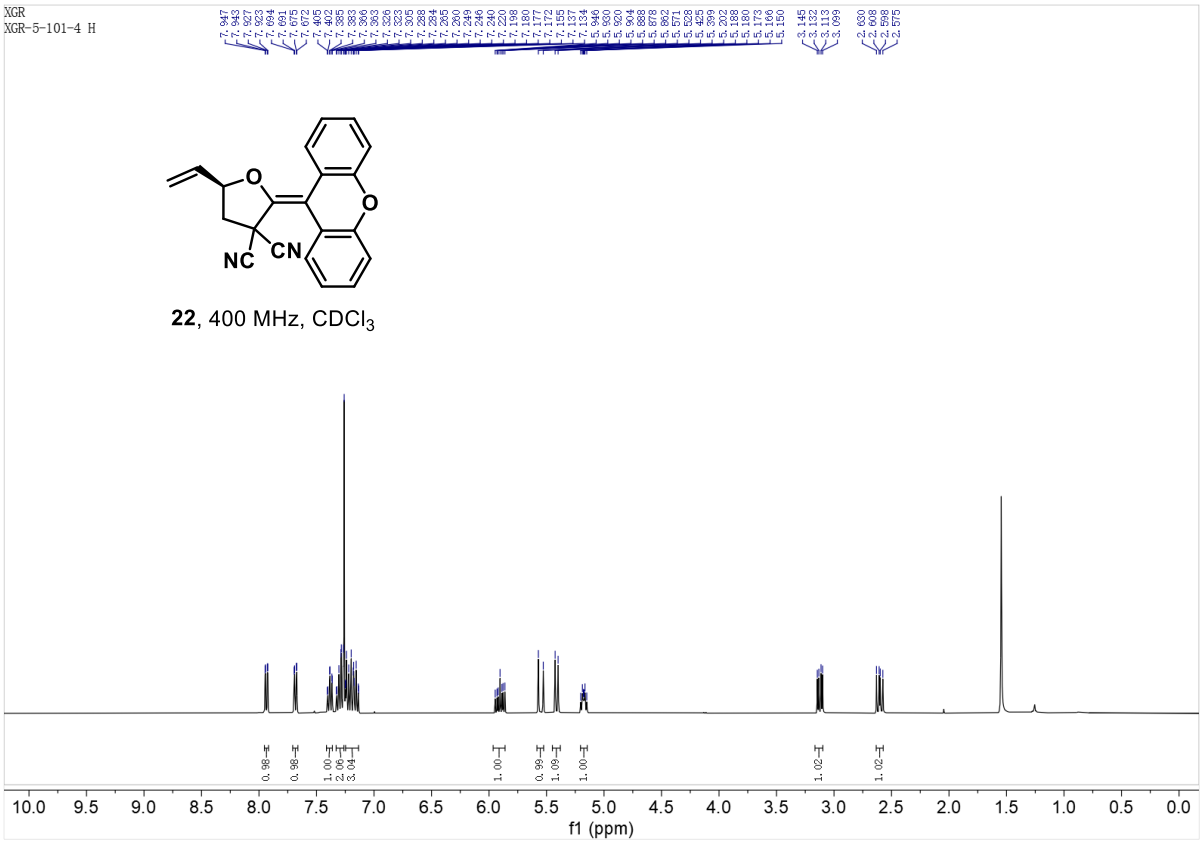
19, 400 MHz, $CDCl_3$



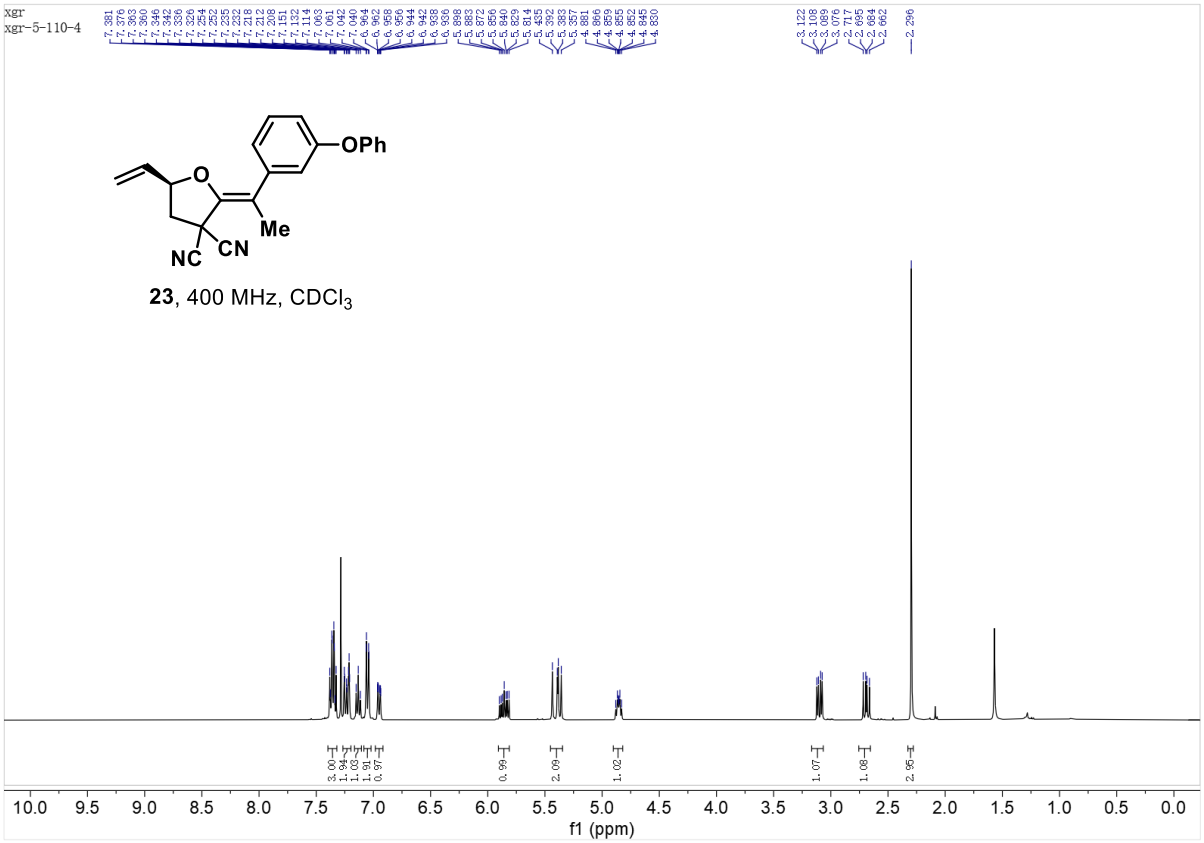
20, 400 MHz, $CDCl_3$



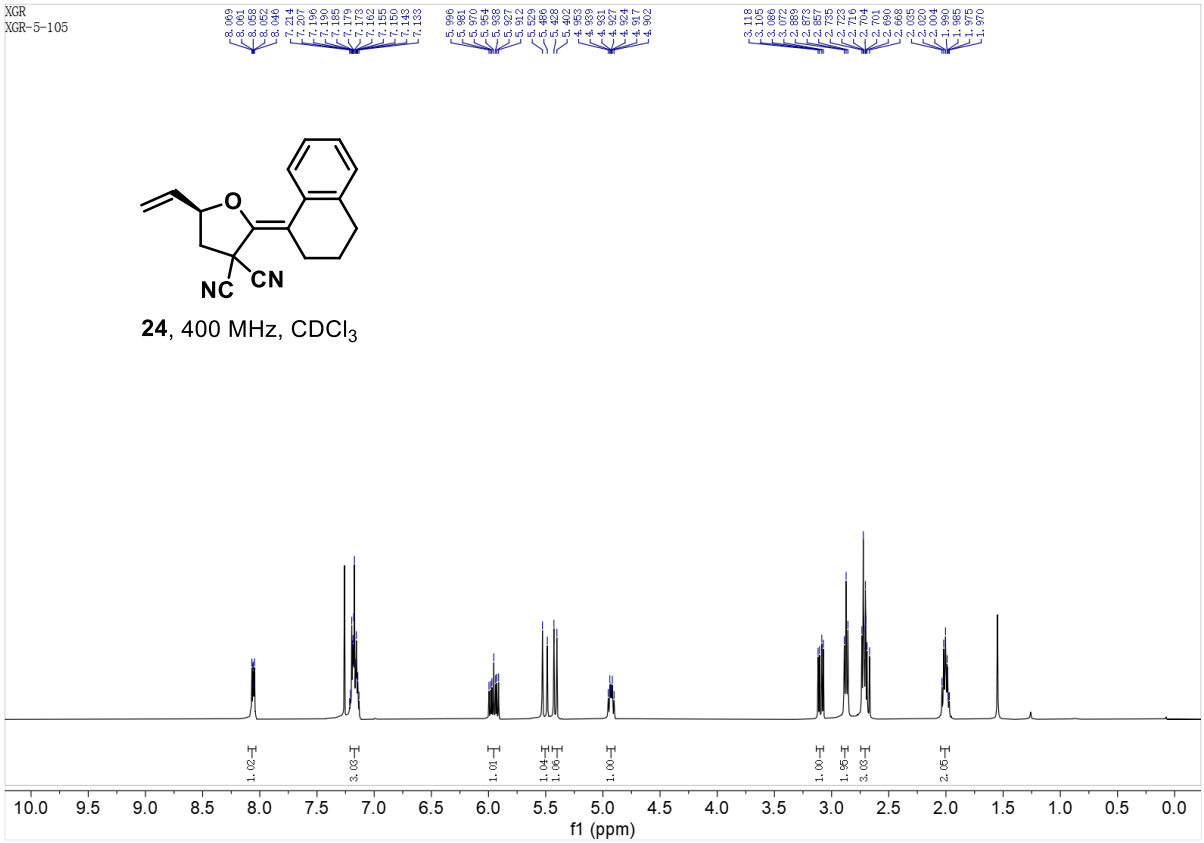
21, 400 MHz, $CDCl_3$



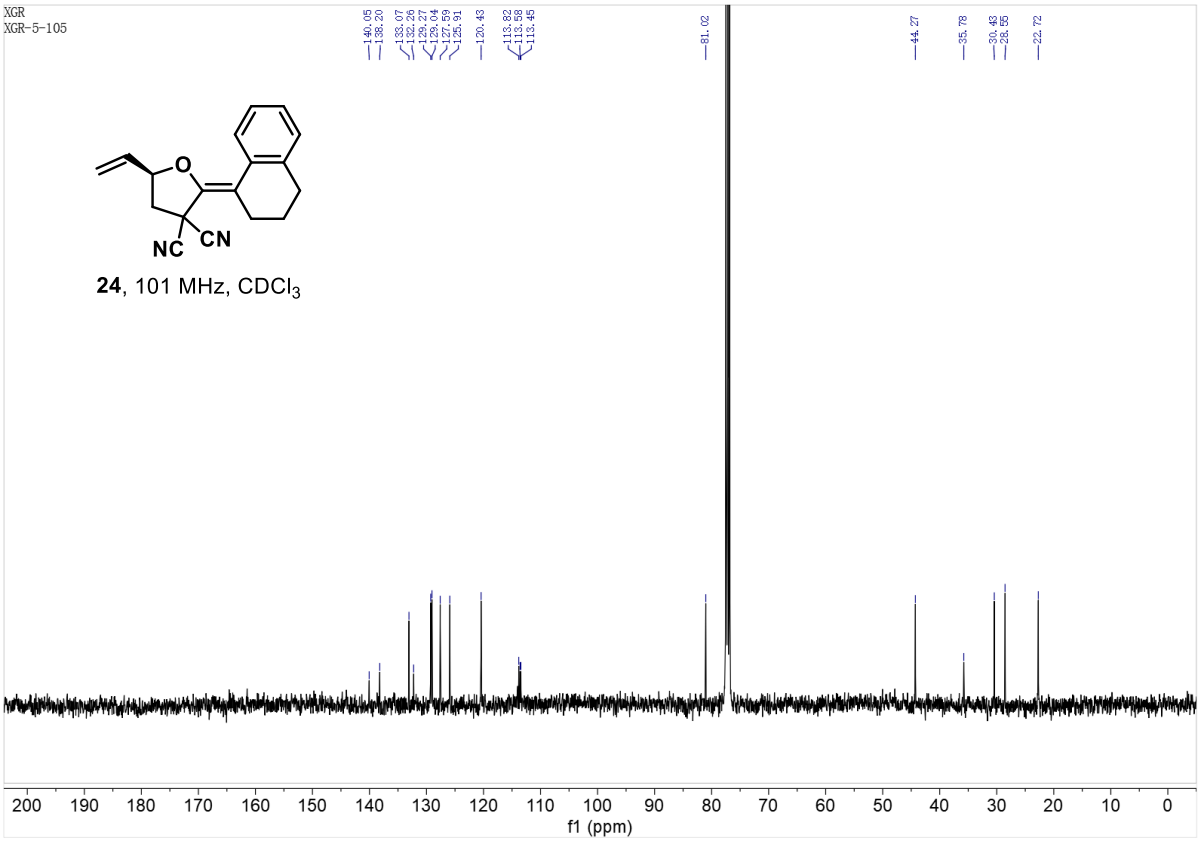
22, 400 MHz, $CDCl_3$



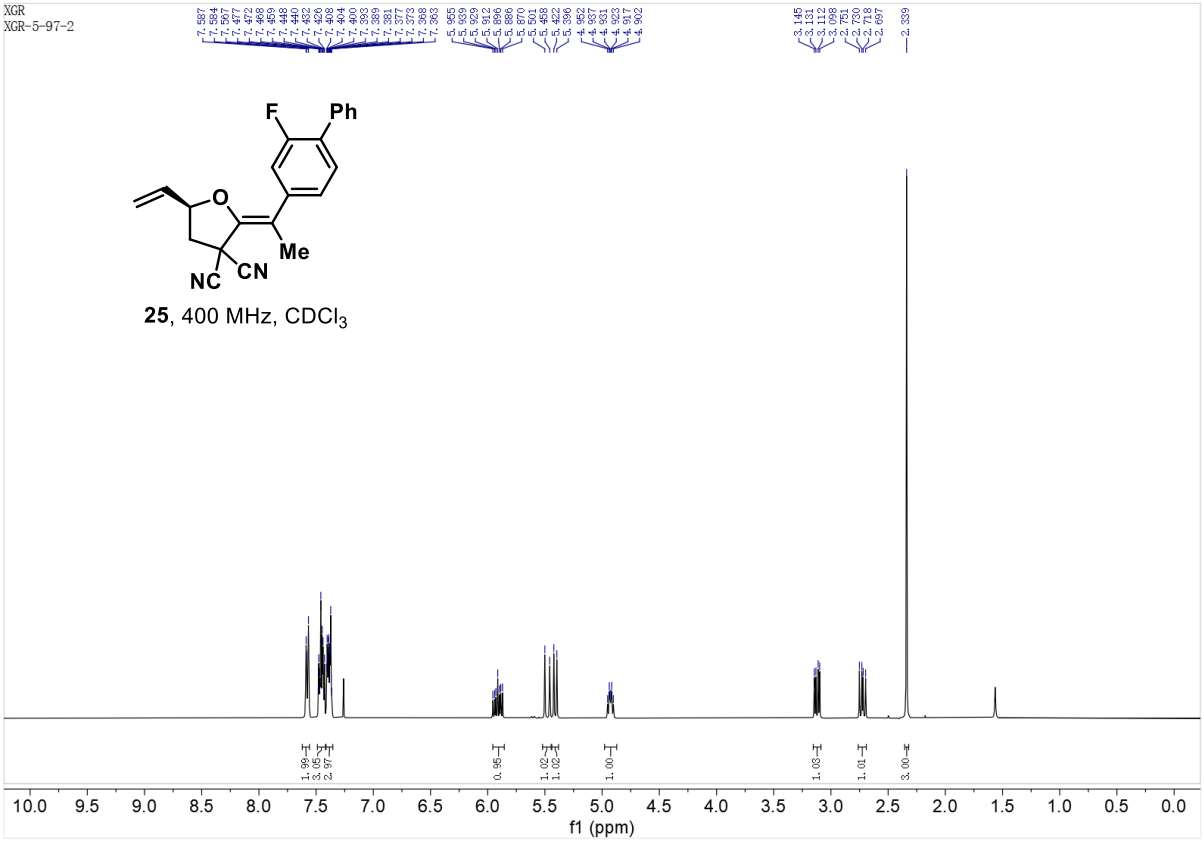
23, 400 MHz, $CDCl_3$



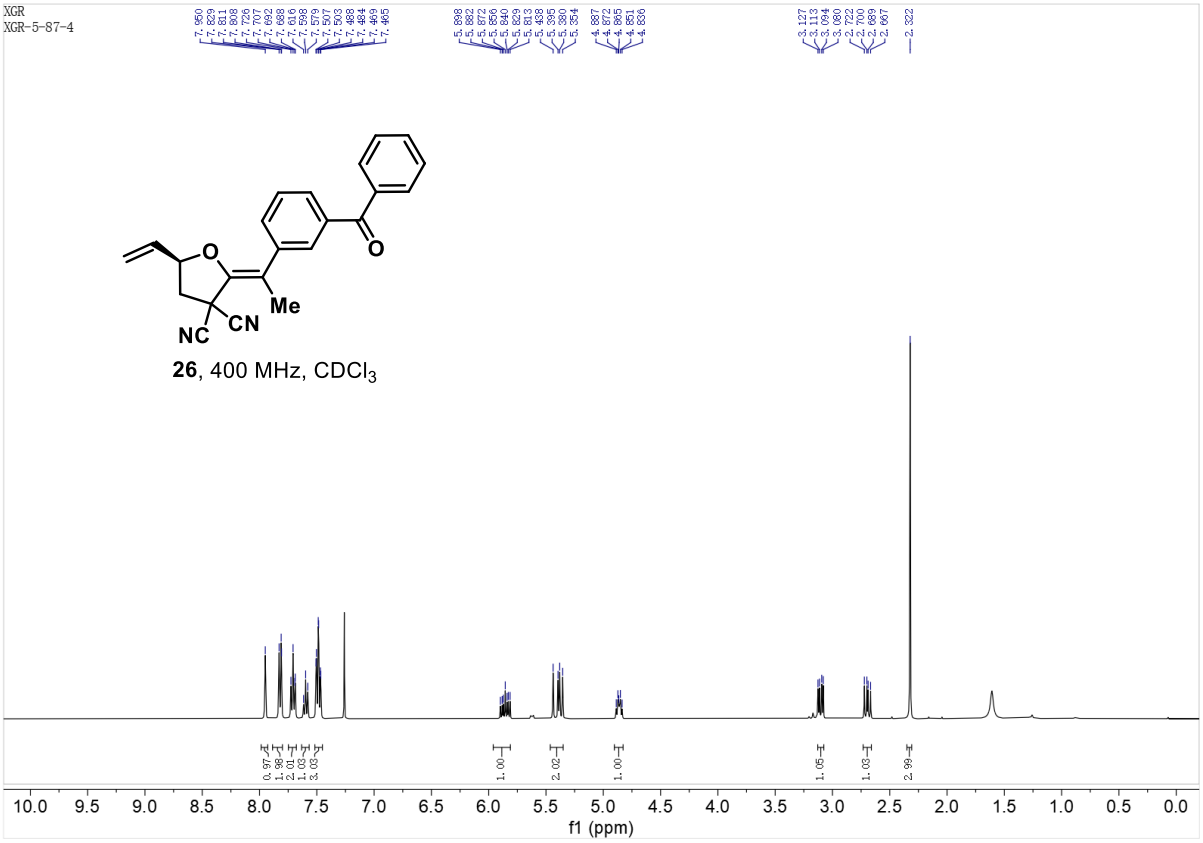
24, 400 MHz, $CDCl_3$



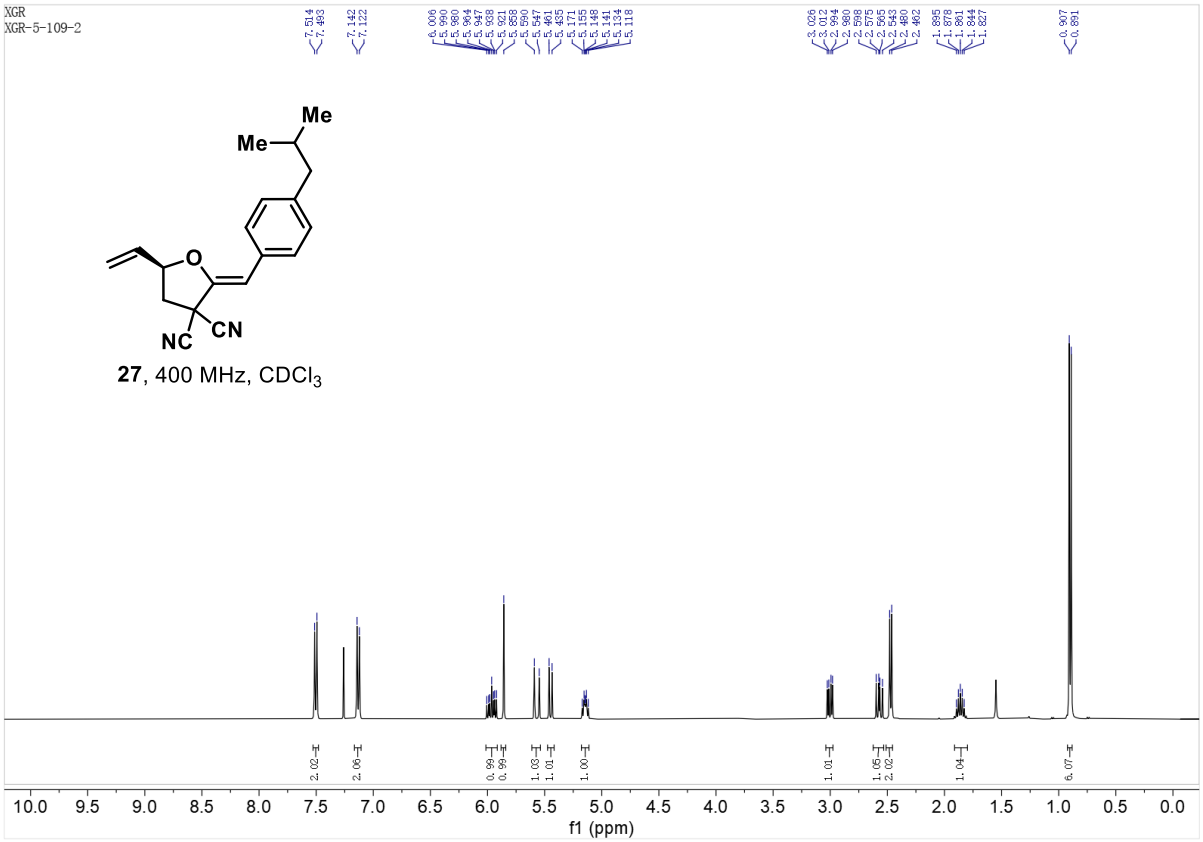
24, 101 MHz, $CDCl_3$



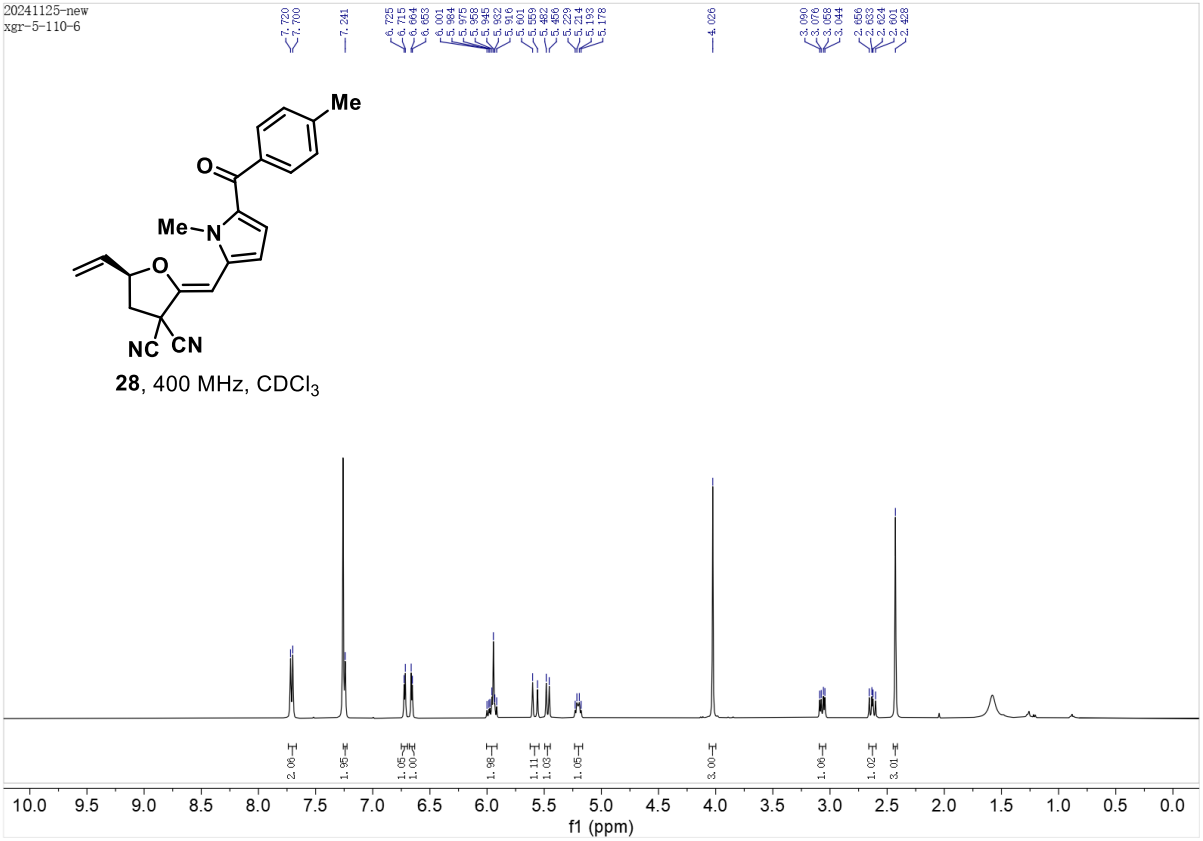
25, 400 MHz, $CDCl_3$



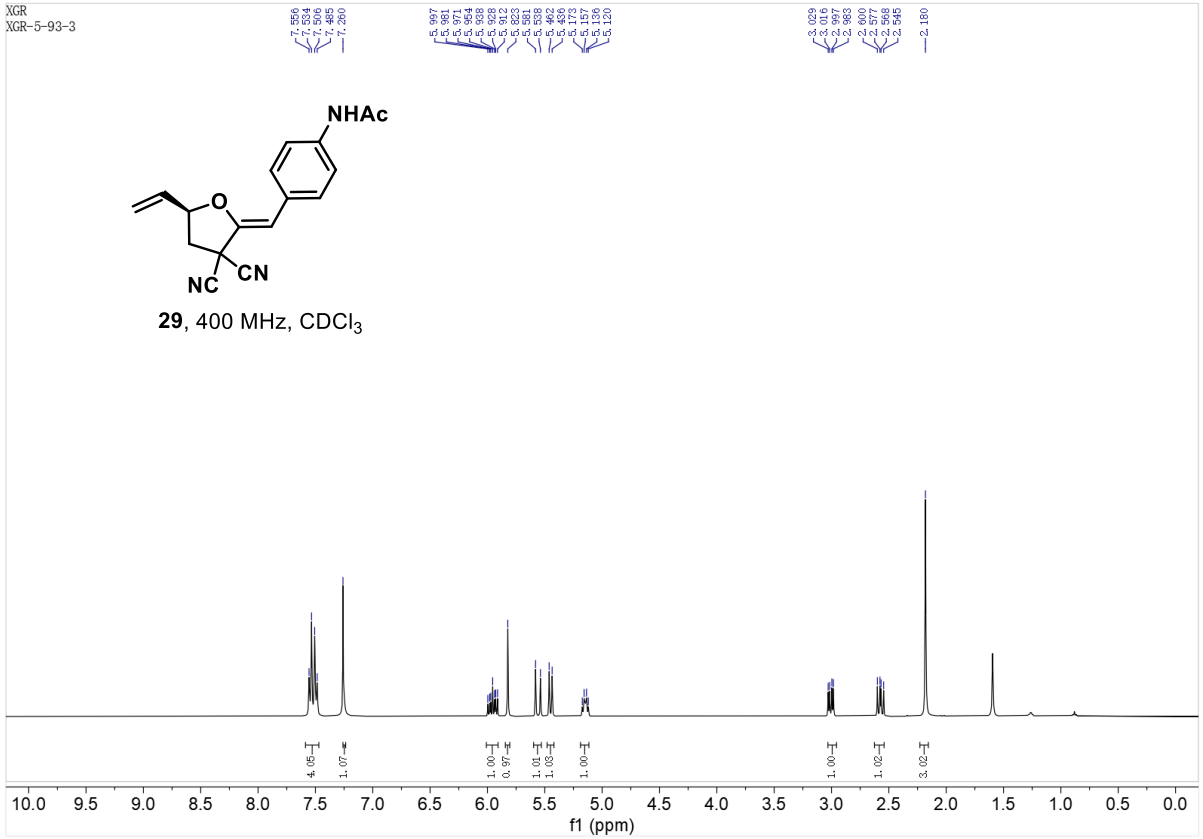
26, 400 MHz, $CDCl_3$



27, 400 MHz, $CDCl_3$



28, 400 MHz, $CDCl_3$



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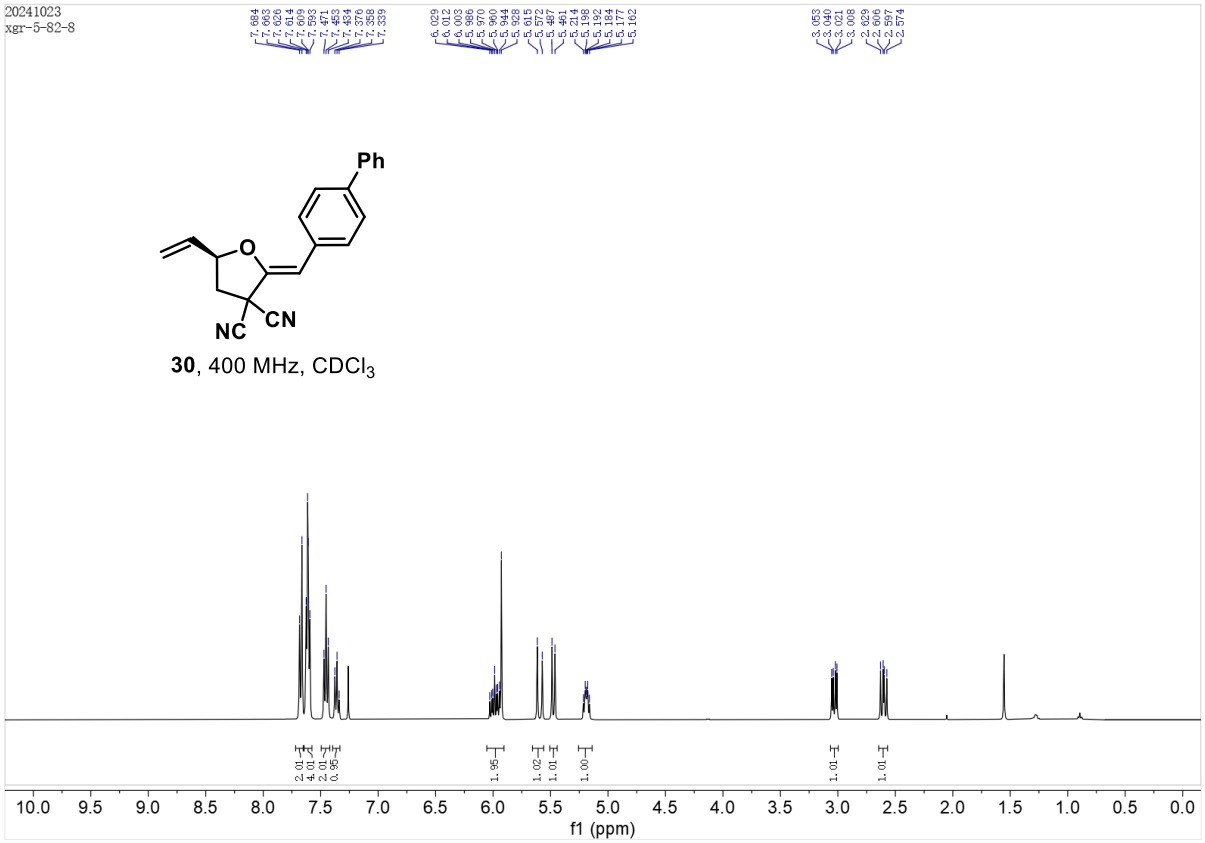
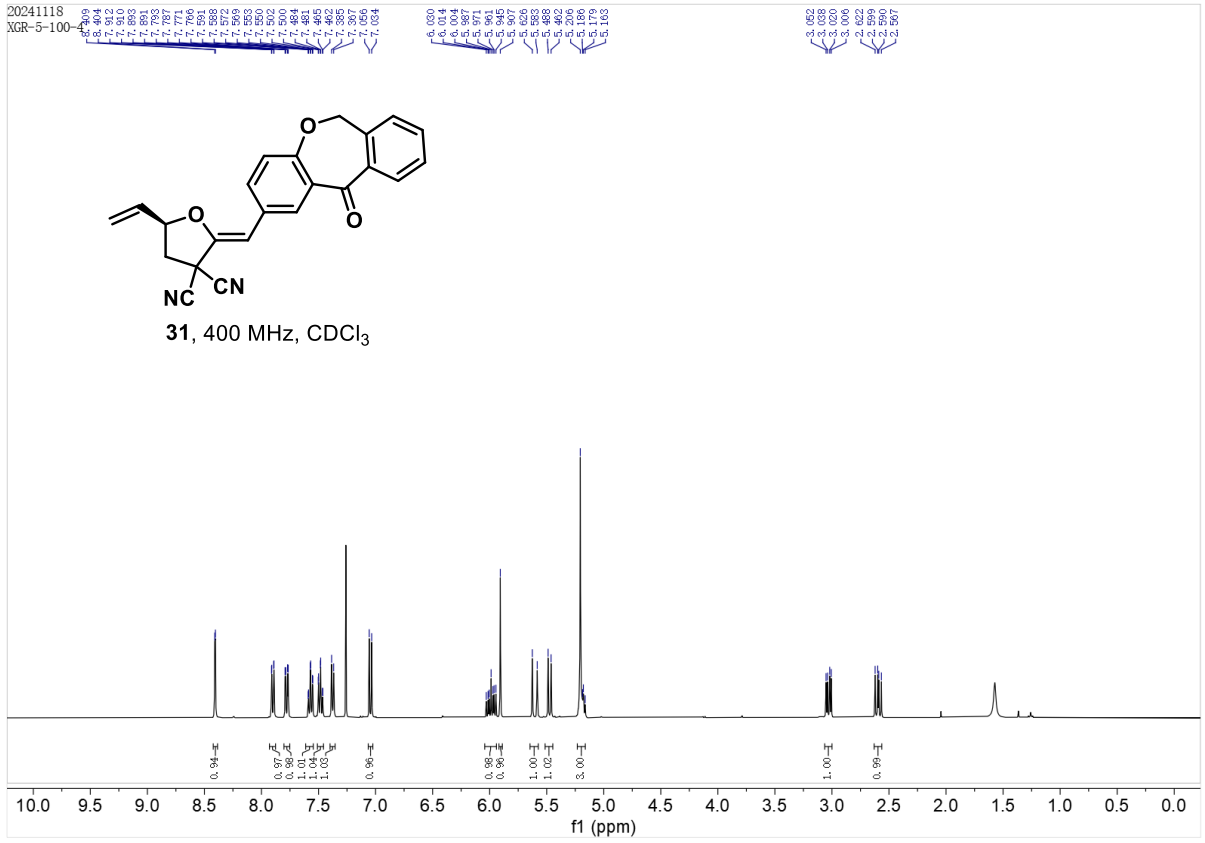
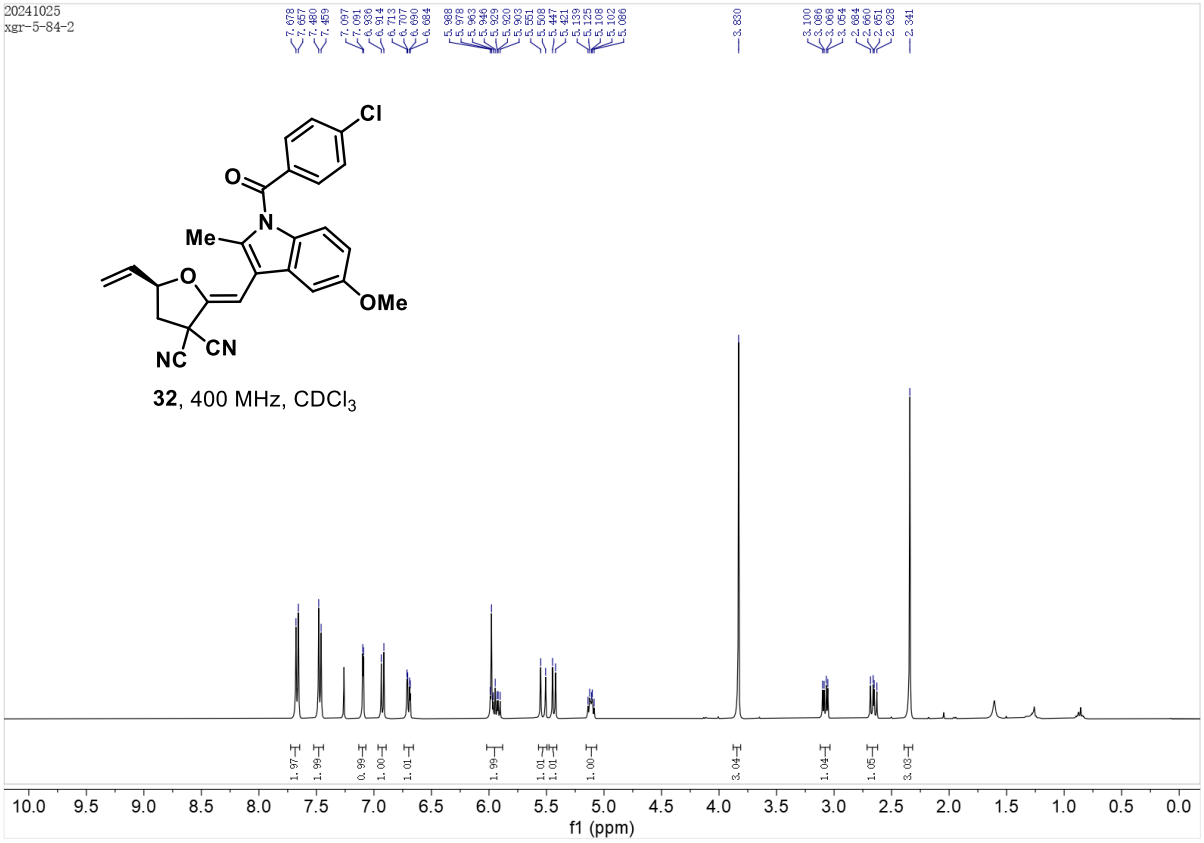


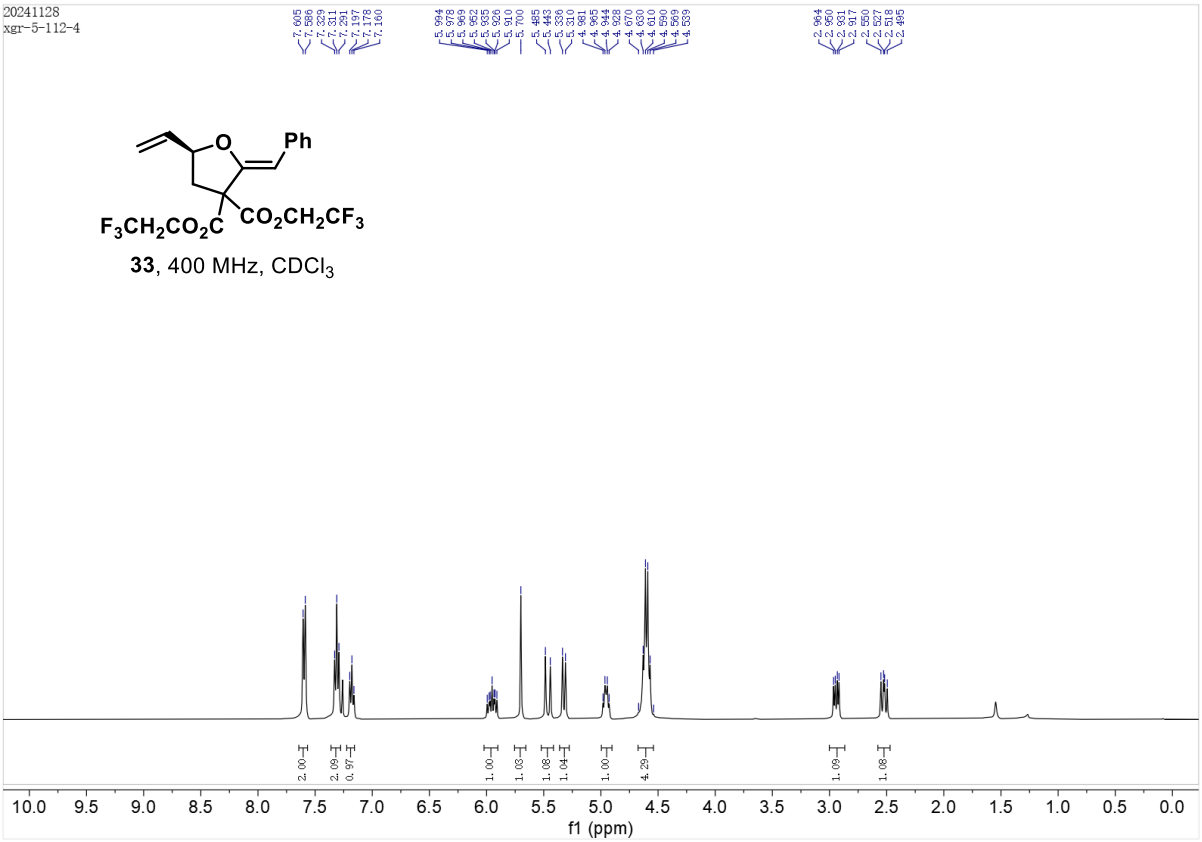
30, 400 MHz, $CDCl_3$



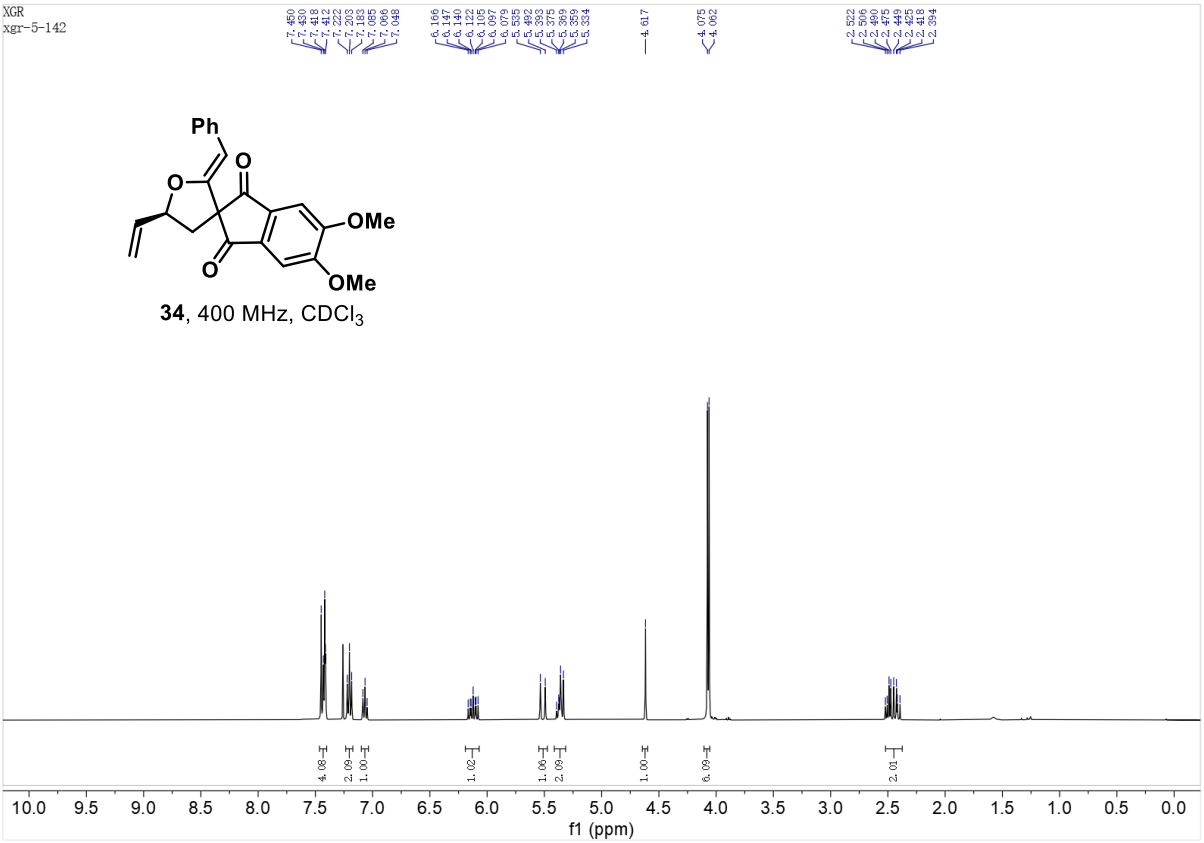
31, 400 MHz, $CDCl_3$



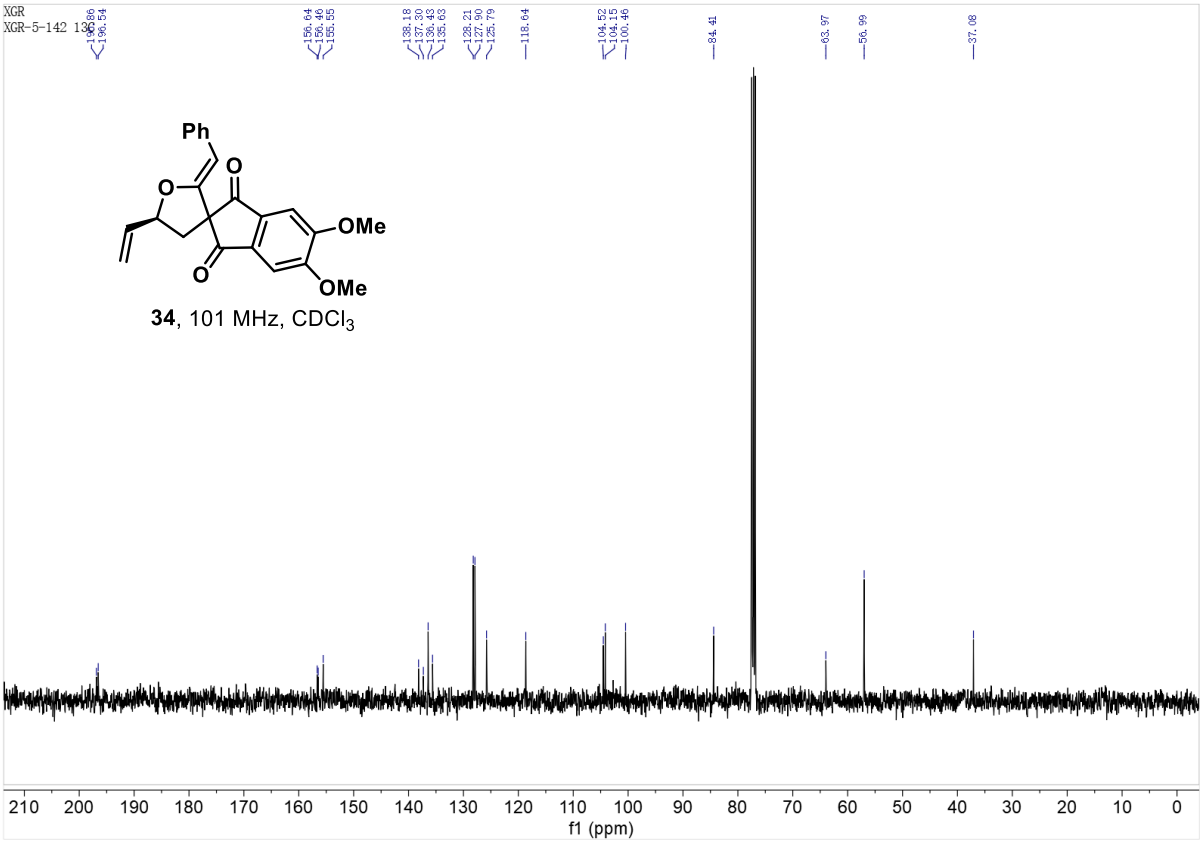
32, 400 MHz, $CDCl_3$



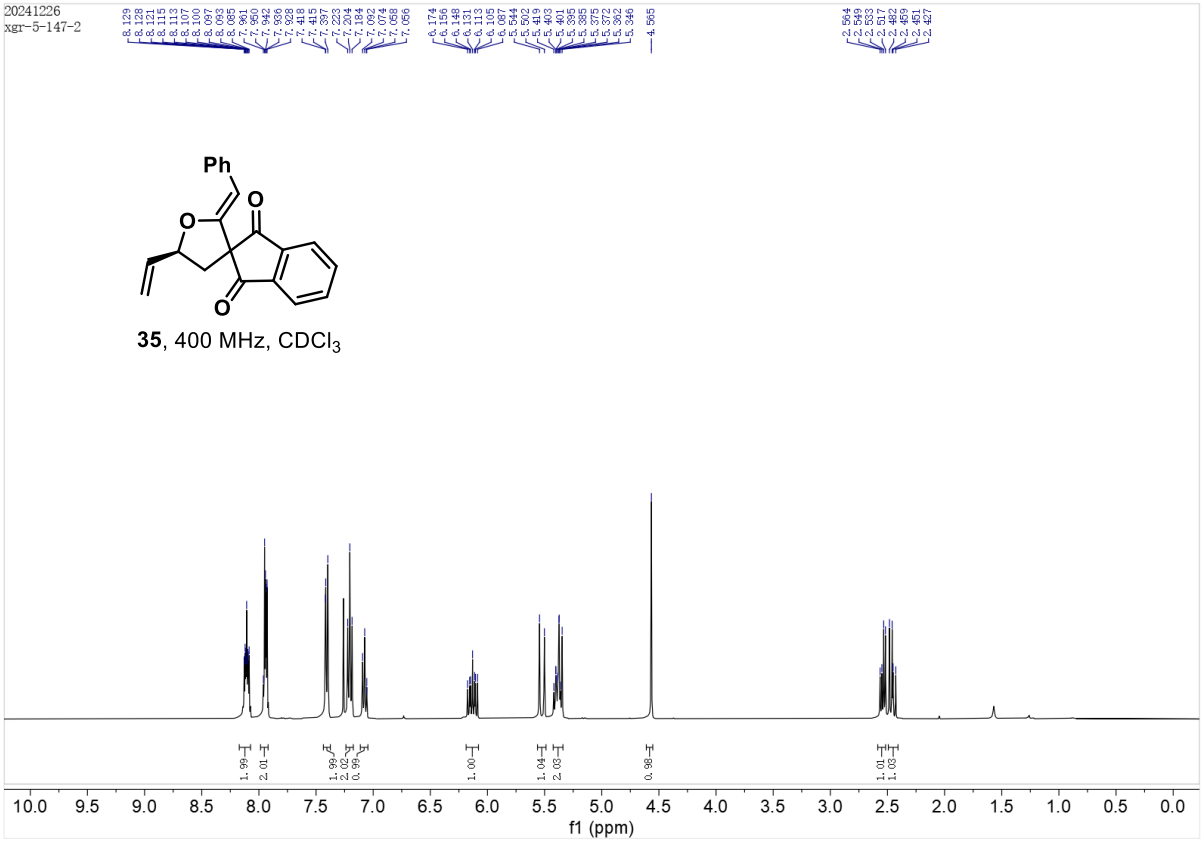
33, 400 MHz, $CDCl_3$



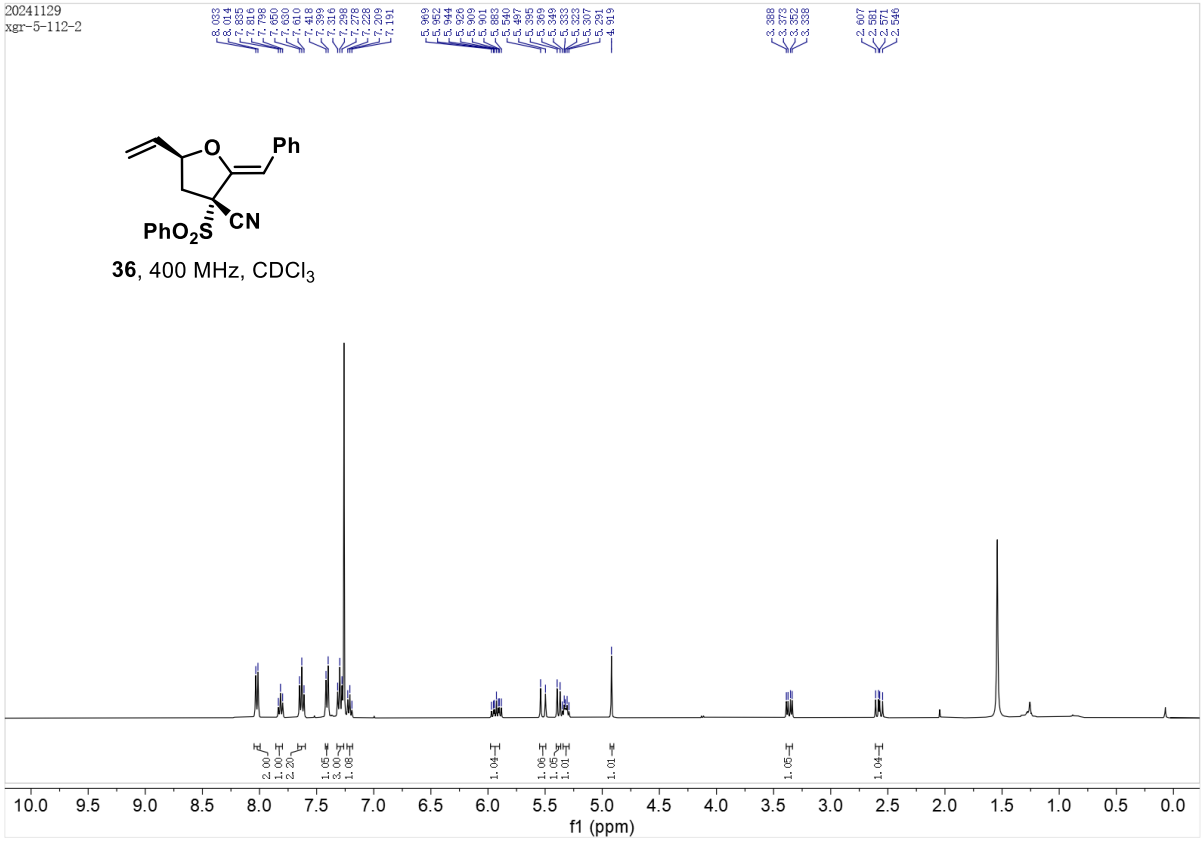
34, 400 MHz, $CDCl_3$



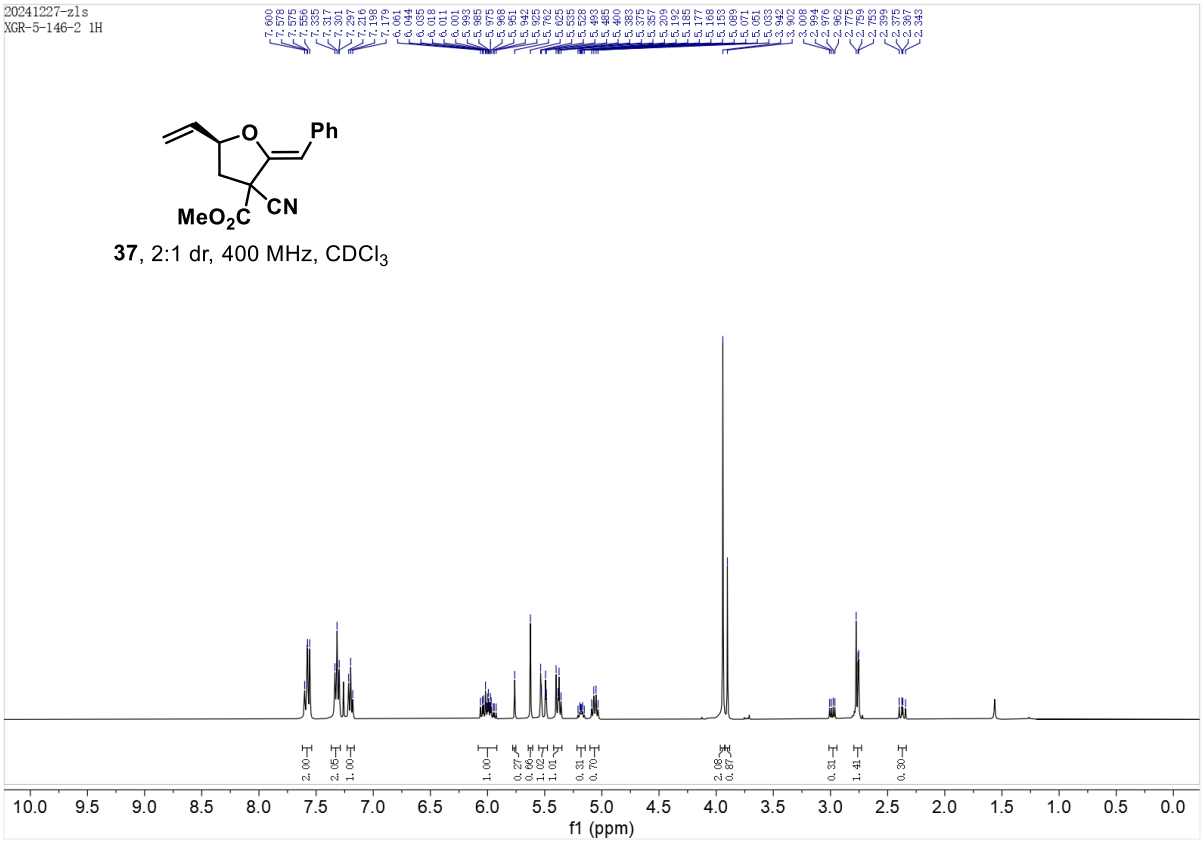
34, 101 MHz, $CDCl_3$



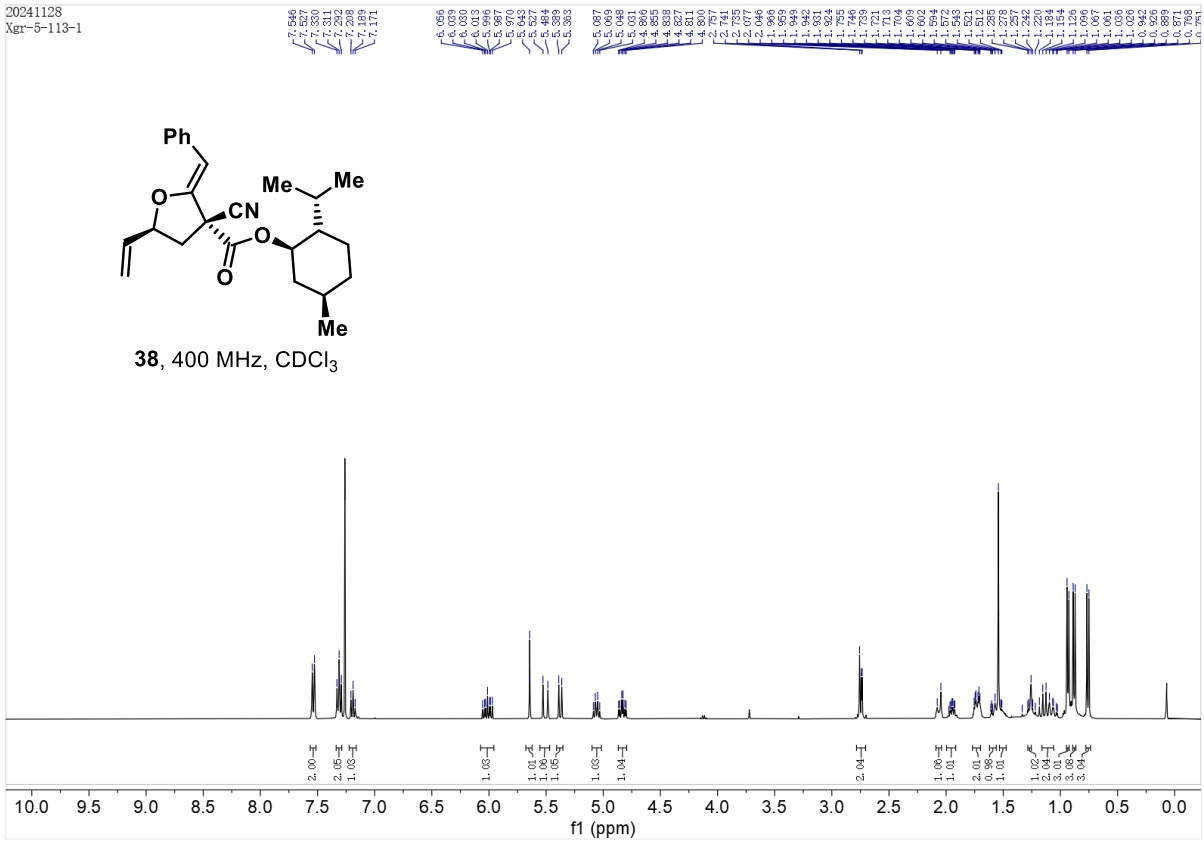
35, 400 MHz, $CDCl_3$



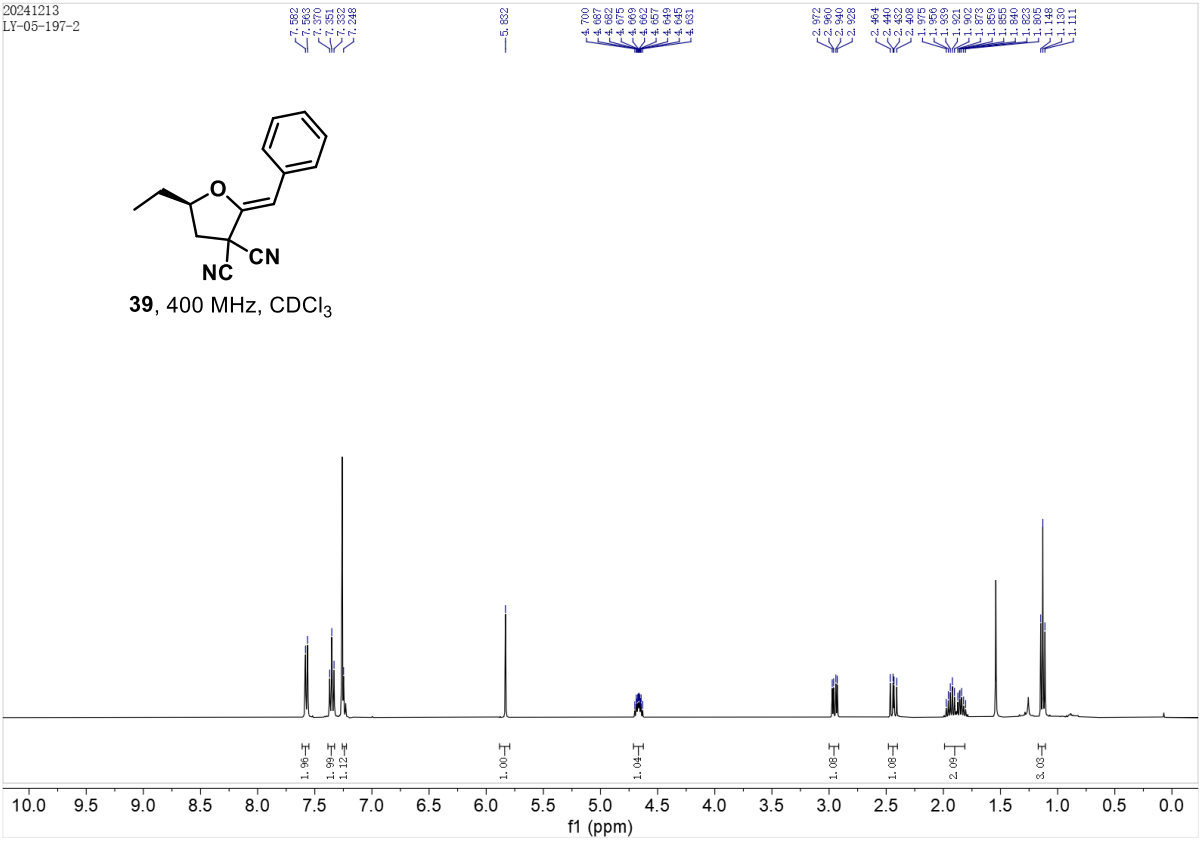
36, 400 MHz, $CDCl_3$



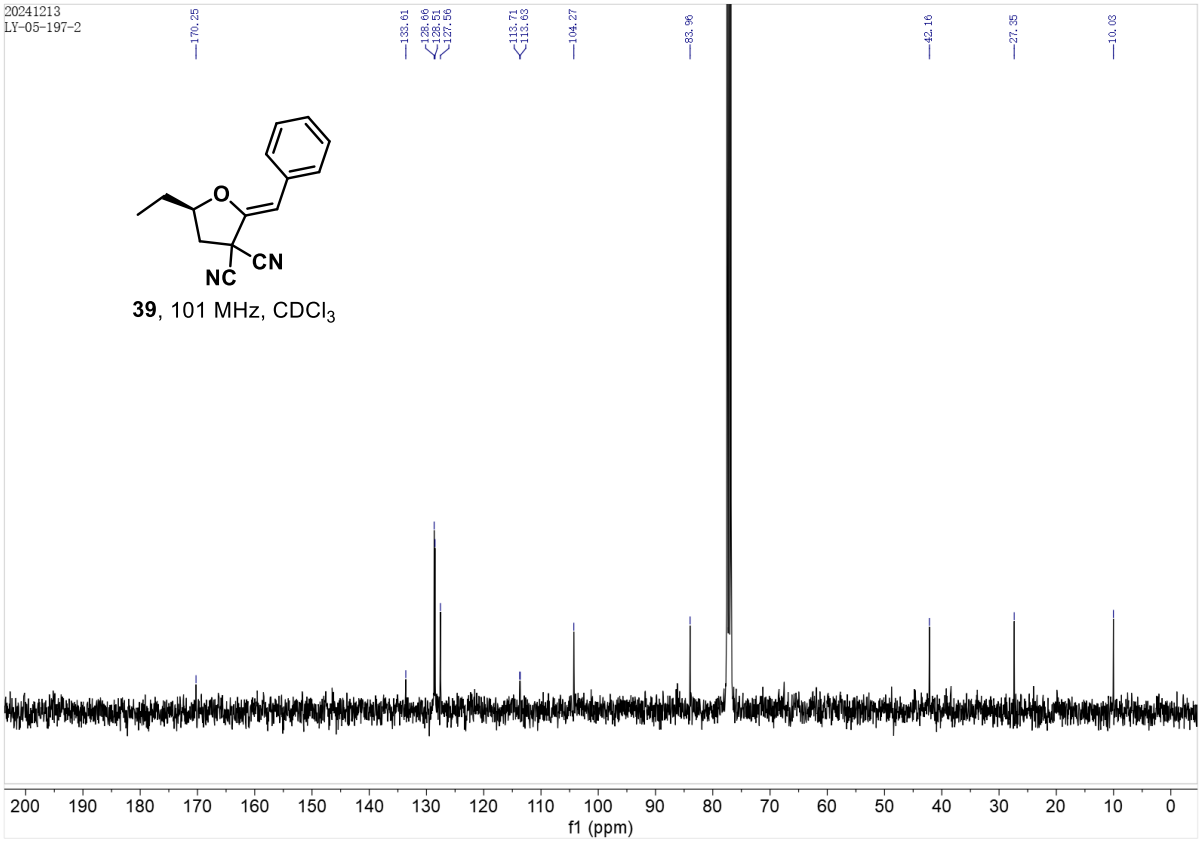
37, 2:1 dr, 400 MHz, $CDCl_3$



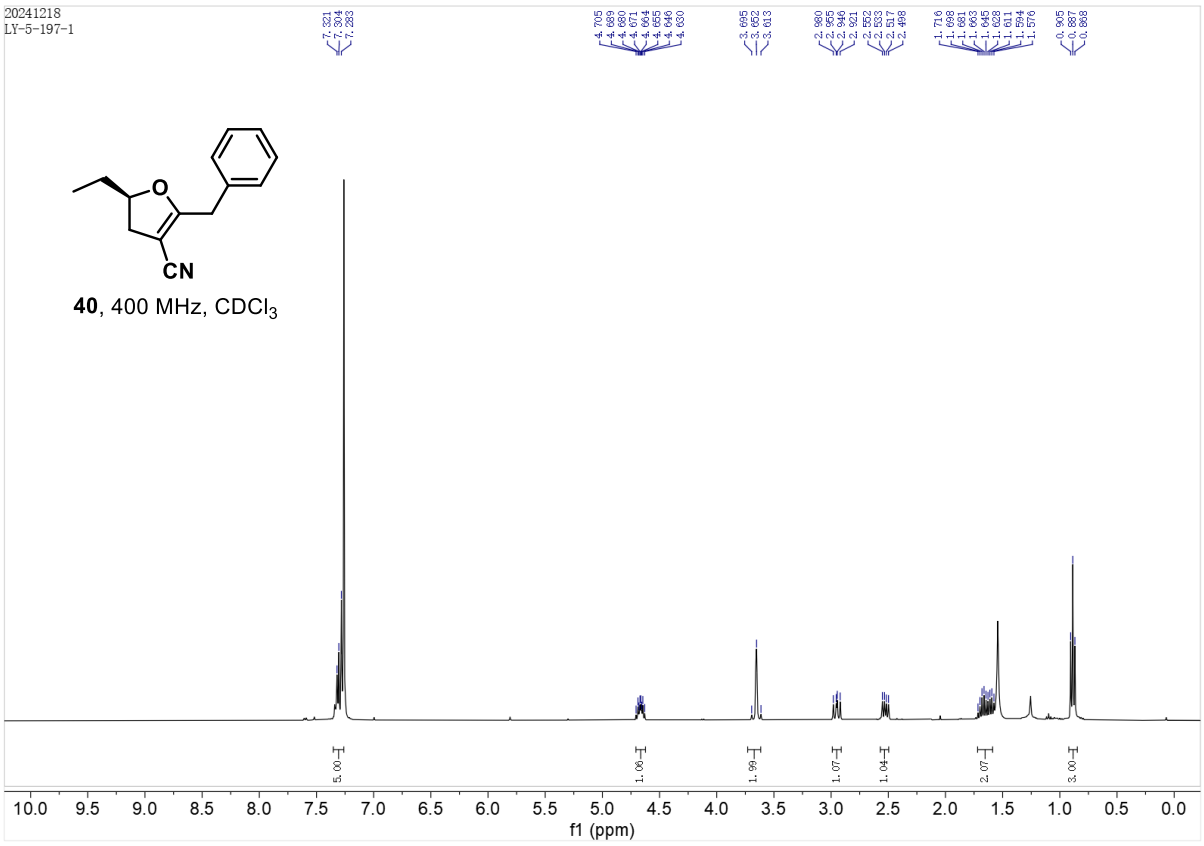
38, 400 MHz, $CDCl_3$

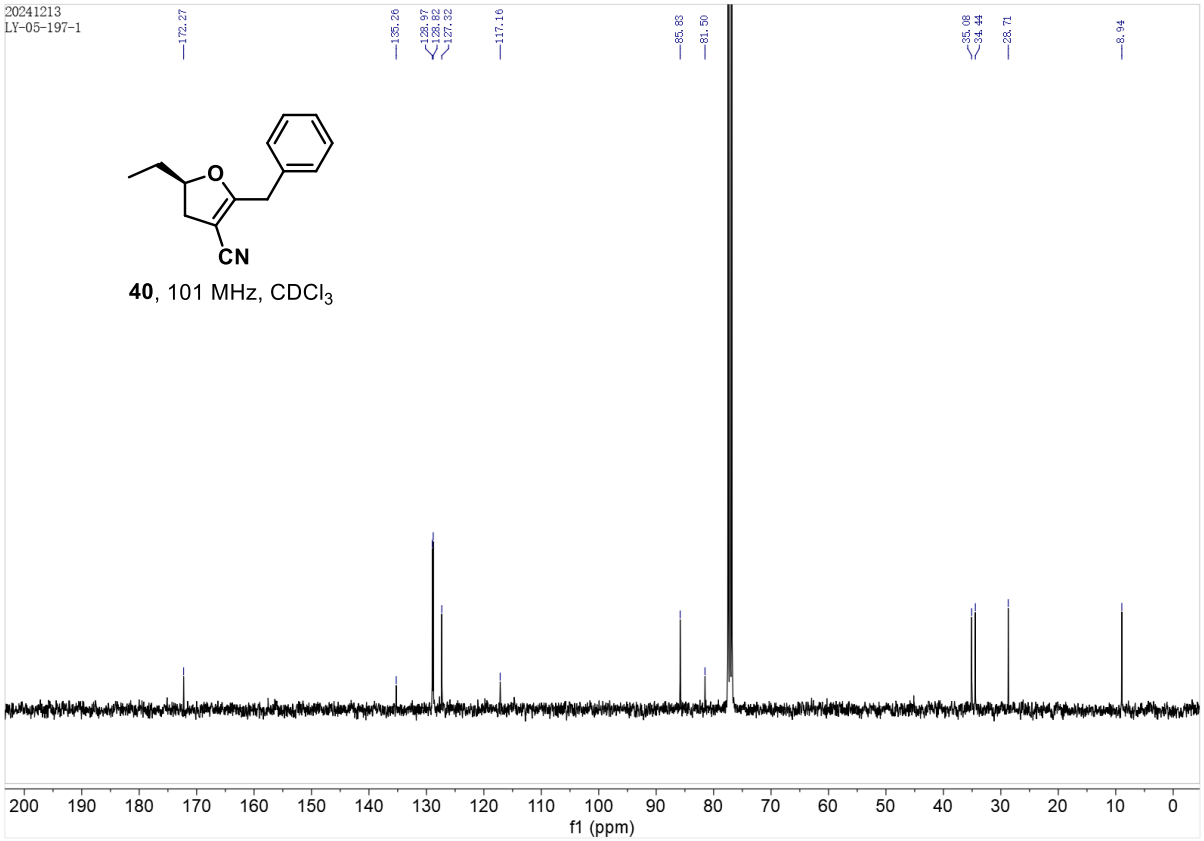


39, 400 MHz, $CDCl_3$



39, 101 MHz, $CDCl_3$


20241218
LY-5-197-1
O
CN
40, 400 MHz, CDCl3
f1 (ppm)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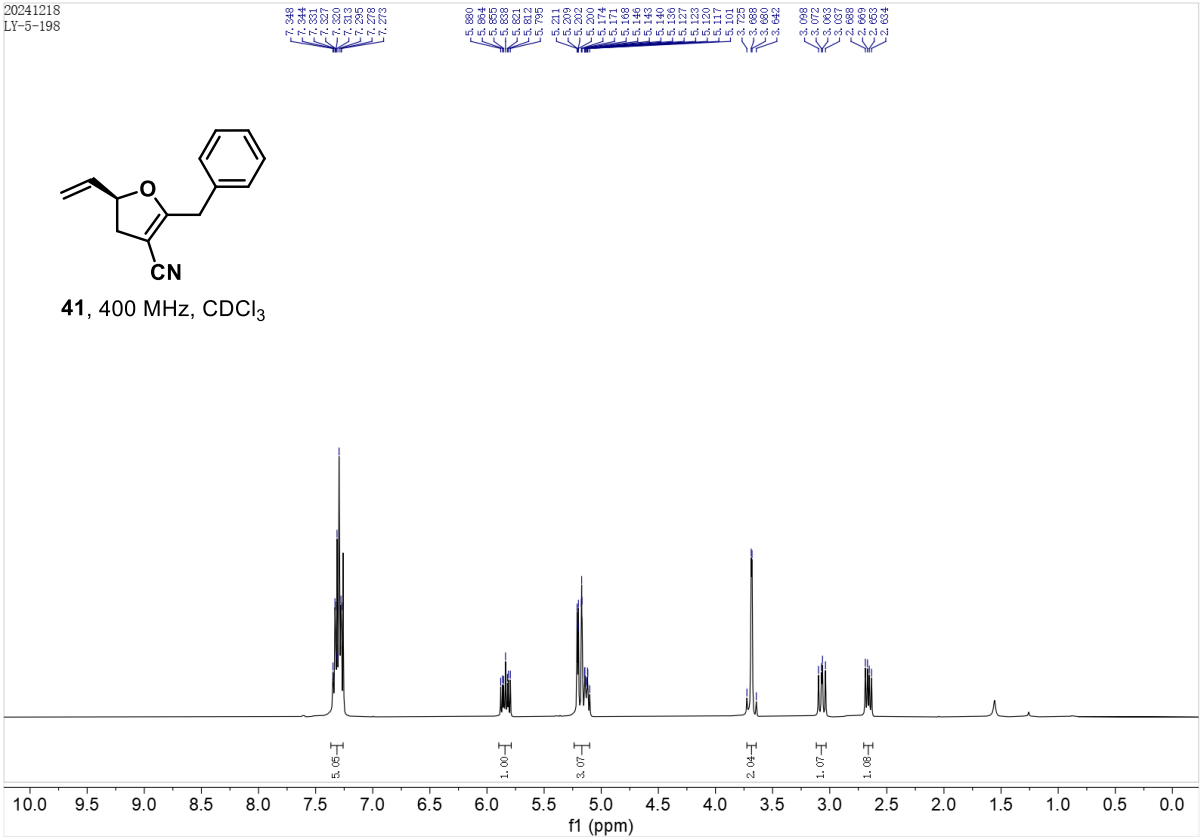
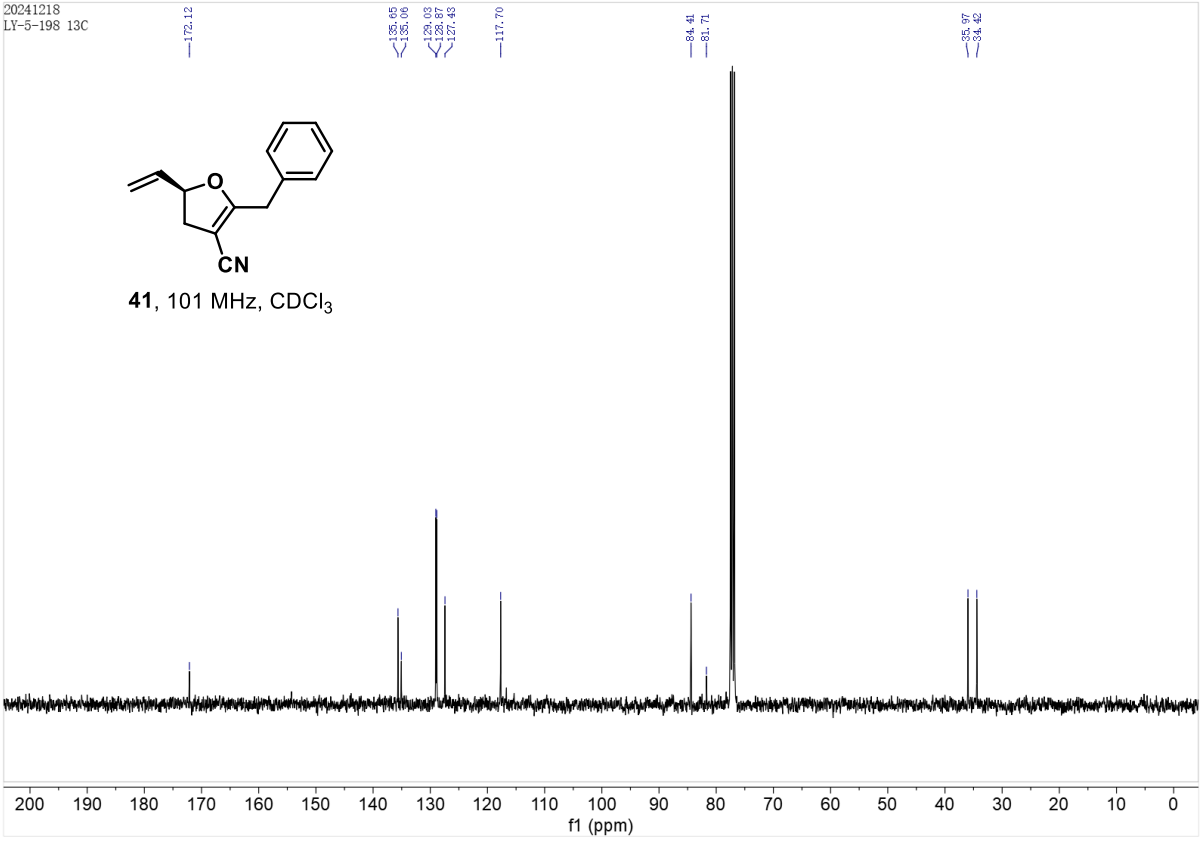
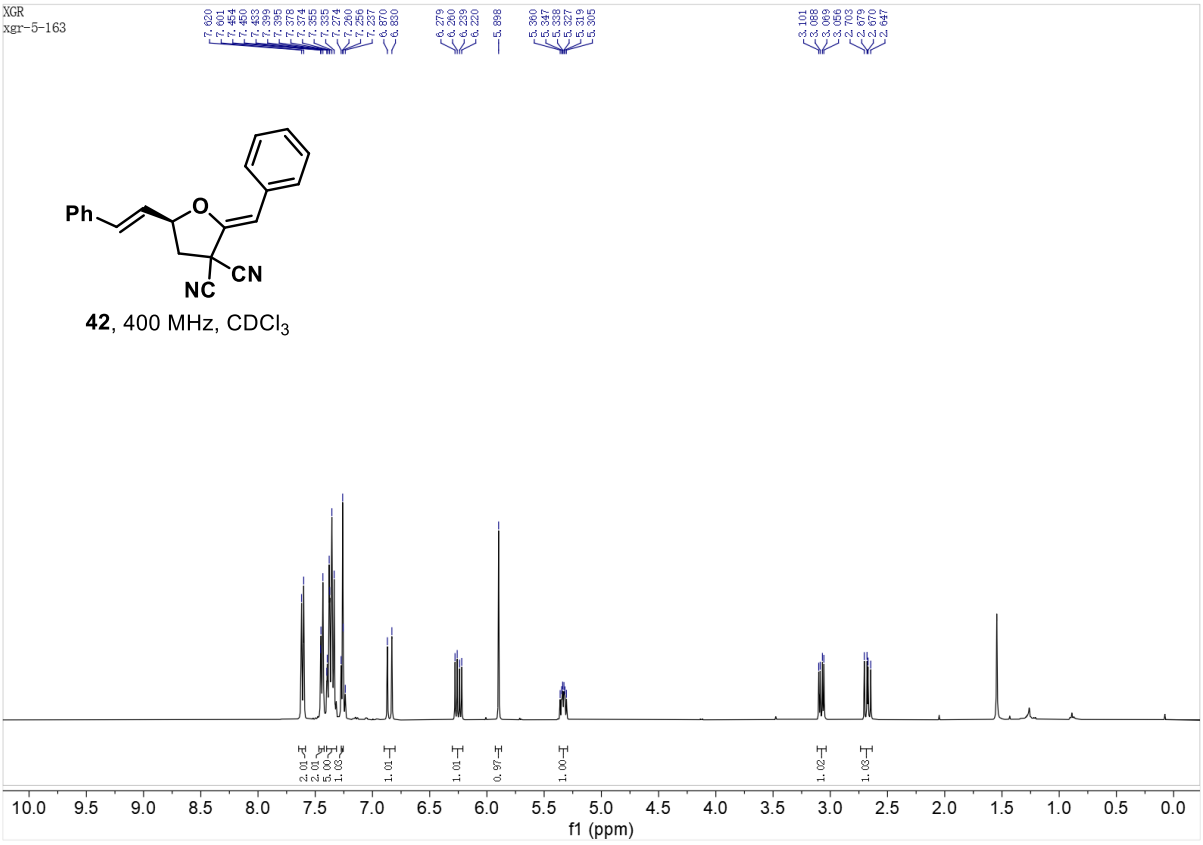
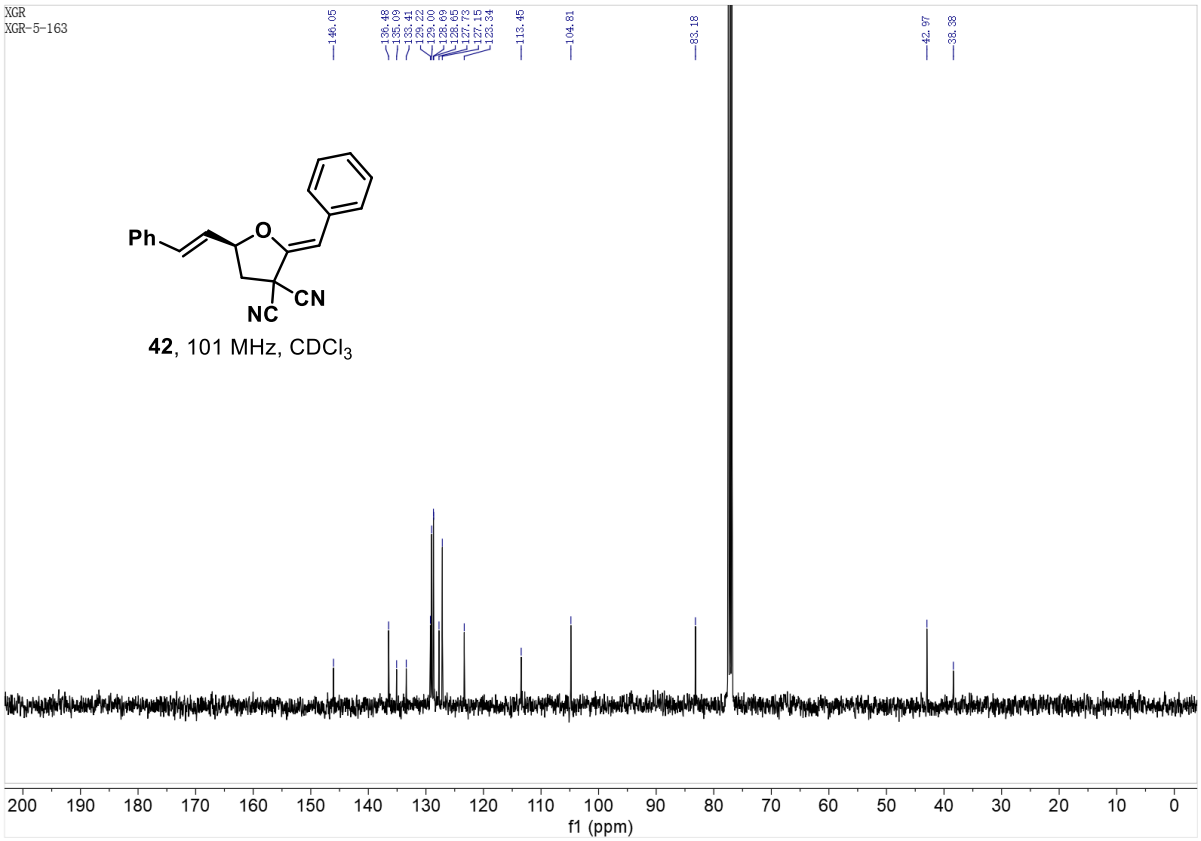
LY-05-197-1
O
CN
40, 101 MHz, CDCl3
f1 (ppm)


20241218
LY-5-198
O
CN
41, 400 MHz, CDCl3
5.05
1.00
3.07
2.04
1.07
1.08
f1 (ppm)


20241218
LY-5-198 13C
172.12
135.65
135.06
129.03
128.87
127.43
117.70
84.41
81.71
35.97
34.42
O
CN
41, 101 MHz, CDCl3
f1 (ppm)


XGR
xgr-5-163
Ph
O
CN
NC
42, 400 MHz, CDCl3
f1 (ppm)


XGR
XGR-5-163
Ph
O
CN
NC
42, 101 MHz, CDCl3
f1 (ppm)

VII. References

1. Clark Still, W.; Kahn, M.; Mitra, A., Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution. *J. Org. Chem.* **1978,** *43*, 2923-2925.

2. McLaughlin, C.; Slawin, A. M. Z.; Smith, A. D., Base-free Enantioselective C(1)-Ammonium Enolate Catalysis Exploiting Aryloxides: A Synthetic and Mechanistic Study. *Angew. Chem. Int. Ed.* **2019,** *58* (42), 15111-15119.

3. Liu, Y.; Xiao, G.; Bai, Z.; Sa, Y.; Yang, M.; Kong, D., Asymmetric Deoxygenative Formal [3 +2] Cycloaddition of Carboxylic Acids and Vinylcyclopropanes. *J. Am. Chem. Soc.*, **2025**, *147* (32), 28564-28569.