Catalytic asymmetric coupling of vinylogous species via deconjugated butenolides addition to vinylogous imines *in situ* generated from arylsulfonyl indoles

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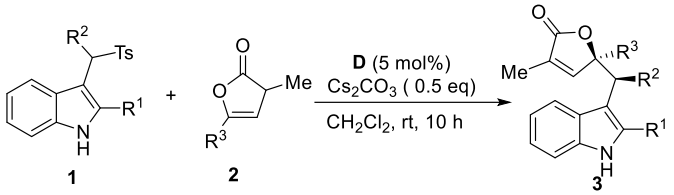
Supporting Information

Contents

1. General Information

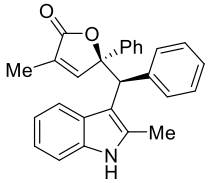
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. 13C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm, DMSO-d_6 at 39.51 ppm). The enantiomeric excesses were determined by chiral HPLC analysis. HPLC analysis was performed on Shimadzu SCL-10AVP HPLC systems consisting of the followings: pump, LC-10AD; detector, SPD-10A measured at 254 nm. HRMS was recorded on Bruker Q TOF. Optical rotations were measured with a Perkin-Elmer-341 polarimeter. Melting points were recorded on a Büchi Melting Point B-545.

2. General procedure for the synthesis of 3



In an ordinary vial equipped with a magnetic stirring bar, the *β,γ*-unsaturated butenolides **2** (0.3 mmol, 1.5 equiv) were added to a solution of arylsulfonyl indoles **1** (0.2 mmol, 1.0 equiv), catalyst **D** (5 mol %) and Cs_2CO_3 (0.1 mmol, 0.5 equiv) in CH_2Cl_2 (2 mL) at the room temperature. And then, the mixture was stirred at the same temperature for 10 h. After completion of the reaction, as indicated by TLC, the products **3** were isolated by flash chromatography on silica gel (PE/EA/CH_2Cl_2 = 10/1/1 ~ 6/1/1).

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)-5-phenylfuran-2(5*H*)-one (3a)



Light yellow solid; 75.5 mg, 96% yield; 75:25 dr, 97% ee; $[\alpha]_D^{20}$ = -479.2 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 132.8-133.5 ℃;

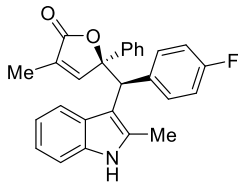
The ee was determined by HPLC (Chiralpak IB, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 10.7 min, t_{major} = 12.6 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.76 (s, 1H), 7.70 (s, 1H), 7.60-7.58 (m, 3H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.33-7.28 (m, 2H), 7.18 (dd, *J* = 14.6, 7.4 Hz, 2H), 7.12-7.07 (m, 2H), 7.00-6.90 (m, 3H), 5.29 (s, 1H), 2.35 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.5, 140.0, 139.8, 135.0, 133.4, 129.7, 128.5, 127.9, 127.5, 127.3, 125.6, 125.2, 125.1, 119.8, 119.4, 118.4, 110.1, 108.6, 91.6, 48.9, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{23}NNaO_2$ $[M + Na]^+$ 416.1626; found: 416.1632.

(*S*)-5-((*S*)-(4-fluorophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3b)



Light yellow solid; 63.8 mg, 78% yield; 70:30 dr, 94% ee; $[\alpha]_D^{20}$ = -364.7 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 114.3-115.2 ℃;

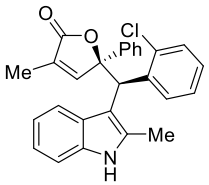
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 8.0 min, t_{major} = 26.6 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.78 (s, 1H), 7.68 (s, 1H), 7.60-7.58 (m, 3H), 7.43 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.35-7.29 (m, 2H), 7.23-7.15 (m, 2H), 6.95-6.90 (m, 4H), 5.31 (s, 1H), 2.36 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.0, 160.1 (d, *J* = 242.2 Hz, 1C), 154.4, 139.6, 136.2 (d, *J* = 3.1 Hz, 1C), 135.0, 133.5, 131.5 (d, *J* = 7.9 Hz, 1C), 128.5, 128.2, 127.4, 125.3, 125.1, 119.8, 119.3, 118.4, 114.2 (d, *J* = 21.0 Hz, 1C), 110.2, 108.3, 91.6, 48.2, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}FNNaO_2$ $[M + Na]^+$ 434.1527; found: 434.1509.

(*S*)-5-((*S*)-(2-chlorophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3c)



Light yellow solid; 82.2 mg, 96% yield; 77:23 dr, 95% ee; $[\alpha]_D^{20}$ = -516.4 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 137.8-139.4 ℃;

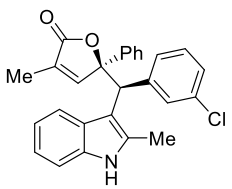
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 0.5 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 50.4 min, t_{major} = 54.6 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.81 (s, 1H), 8.14 (s, 1H), 7.71-7.67 (m, 2H), 7.56-7.53 (d, *J* = 7.7 Hz, 2H), 7.33-7.28 (m, 2H), 7.20-7.15 (m, 4H), 7.06-7.00 (m, 1H), 6.92-6.90 (m, 2H), 5.57 (s, 1H), 2.38 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 172.8, 154.2, 139.2, 136.9, 134.9, 134.4, 133.9, 131.7, 129.3, 128.6, 127.6, 127.4, 126.0, 125.6, 125.0, 124.8, 119.7, 119.2, 118.4, 110.2, 105.1, 91.8, 45.8, 12.4, 9.5.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}ClNNaO_2$ $[M + Na]^+$ 450.1237; found: 450.1234.

(*S*)-5-((*S*)-(3-chlorophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3d)



Light yellow solid; 60.6 mg, 71% yield; 68:32 dr, 92% ee; $[\alpha]_D^{20}$ = -291.2 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 108.5-109.7 ℃;

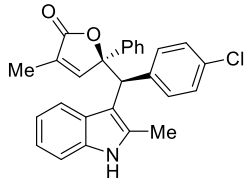
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.1 min, t_{major} = 10.1 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.83 (s, 1H), 7.67-7.58 (m, 4H), 7.41-7.31 (m, 4H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.19-7.11 (m, 2H), 7.06-7.04 (m, 1H), 6.91 (q, *J* = 9.4, 8.3 Hz, 2H), 5.32 (s, 1H), 2.37 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.4, 142.6, 139.5, 135.1, 133.8, 132.2, 129.6, 129.5, 128.7, 128.5, 127.6, 127.4, 125.8, 125.5, 125.1, 120.0, 119.3, 118.6, 110.4, 107.9, 91.5, 48.6, 12.1, 9.7.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}ClNNaO_2$ $[M + Na]^+$ 450.1237; found: 450.1240.

(*S*)-5-((*S*)-(4-chlorophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3e)



Light red solid; 57.1 mg, 67% yield; 63:37 dr, 89% ee; $[\alpha]_D^{20}$ = -322.1 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 132.2-132.9 ℃;

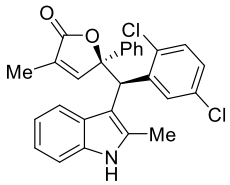
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 8.1 min, t_{major} = 15.4 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.81 (s, 1H), 7.67-7.59 (m, 4H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.35-7.30 (m, 2H), 7.24 (d, *J* = 1.3 Hz, 1H), 7.17-7.15 (m, 3H), 6.95-6.90 (m, 2H), 5.32 (s, 1H), 2.37 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.0, 154.3, 139.5, 139.1, 135.0, 133.5, 131.5, 130.2, 128.6, 127.6, 127.5, 127.4, 125.3, 125.1, 119.8, 119.2, 118.4, 110.2, 108.0, 91.4, 48.2, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}ClNNaO_2$ $[M + Na]^+$ 450.1231; found: 450.1236.

(*S*)-5-((*S*)-(2,5-dichlorophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3f)



White solid; 74.0 mg, 80% yield; 73:27 dr, 89% ee; $[\alpha]_D^{20}$ = -640.1 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 222.3-223.7 ℃;

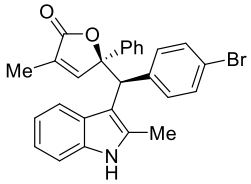
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 6.8 min, t_{major} = 8.7 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.89 (s, 1H), 8.11 (s, 1H), 7.68 (s, 2H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.37-7.32 (m, 2H), 7.24-7.10 (m, 4H), 6.94-6.92 (m, 2H), 5.54 (s, 1H), 2.39 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 172.6, 153.8, 138.9, 138.8, 134.8, 134.7, 132.6, 131.3, 130.8, 130.5, 128.8, 127.7, 127.6, 127.4, 125.8, 124.7, 119.8, 118.7, 118.6, 110.3, 104.2, 91.5, 46.0, 12.3, 9.5.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}Cl_2NO_2$ $[M + H]^+$ 462.1028; found: 462.1032.

(*S*)-5-((*S*)-(4-bromophenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3g)



Light yellow solid; 77.3 mg, 82% yield; 67:33 dr, 94% ee; $[\alpha]_D^{20}$ = -373.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 108.7-109.8 ℃;

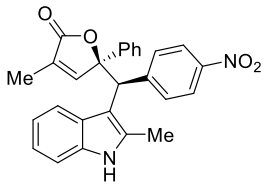
The ee was determined by HPLC (Chiralpak IB, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 11.7 min, t_{major} = 18.4 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.80 (s, 1H), 7.65-7.57 (m, 4H), 7.37-7.32 (m, 3H), 7.30-7.27 (m, 3H), 7.23-7.14 (m, 2H), 6.94-6.86 (m, 2H), 5.28 (s, 1H), 2.37 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.4, 139.6, 139.5, 135.1, 133.6, 132.0, 130.5, 128.7, 128.5, 127.5, 127.4, 125.2, 119.9, 119.3, 118.8, 118.6, 110.3, 108.0, 91.5, 48.4, 12.1, 9.7.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}BrNNaO_2$ $[M + Na]^+$ 494.0726; found: 494.0731.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(4-nitrophenyl)methyl)-5-phenylfuran-2(5*H*)-one (3h)



Yellow solid; 54.0 mg, 62% yield; 60:40 dr, 87% ee; $[\alpha]_D^{20}$ = -270.7 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 79.9-80.6 ℃;

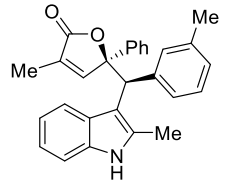
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 30.0 min, t_{major} = 43.7 min);

^{1}H NMR (400 MHz, DMSO-d_6) δ (major diastereomer) 10.87 (s, 1H), 8.04-7.95 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.67-7.54 (m, 4H), 7.37-7.29 (m, 2H), 7.25-7.19 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.99-6.83 (m, 2H), 5.50 (s, 1H), 2.38 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 172.8, 154.1, 148.1, 145.3, 139.1, 135.0, 134.0, 130.9, 128.7, 128.5, 127.6, 125.5, 125.1, 122.7, 120.0, 119.1, 118.6, 110.3, 107.2, 91.0, 48.7, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}N_2NaO_4$ $[M + Na]^+$ 461.1477; found: 461.1484.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(m-tolyl)methyl)-5-phenylfuran-2(5*H*)-one (3i)



Light yellow solid; 67.7 mg, 83% yield; 63:37 dr, 92% ee; $[\alpha]_D^{20}$ = -325.9(*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 97.7-98.9 ℃;

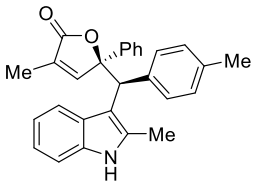
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 12.1 min, t_{major} = 16.2 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.74 (s, 1H), 7.70 (s, 1H), 7.60-7.58 (m, 3H), 7.35-7.26 (m, 3H), 7.24-7.10 (m, 3H), 7.04-6.83 (m, 3H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.24 (s, 1H), 2.35 (s, 3H), 2.11 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.5, 139.8, 136.3, 134.9, 133.3, 130.5, 128.6, 128.4, 127.6, 127.3, 127.2, 126.7, 126.2, 125.2, 125.1, 119.7, 119.3, 118.3, 110.1, 108.6, 91.7, 48.8, 21.0, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{28}H_{25}NNaO_2$ $[M + Na]^+$ 430.1778; found: 430.1783.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(p-tolyl)methyl)-5-phenylfuran-2(5*H*)-one (3j)



White solid; 72.6 mg, 89% yield; 58:42 dr, 91% ee; $[\alpha]_D^{20}$ = -436.3 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 126.7-127.3 ℃;

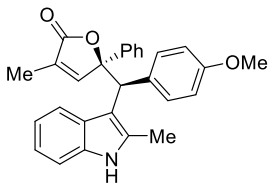
The ee was determined by HPLC (Chiralpak IB, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.6 min, t_{major} = 11.1 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.74 (s, 1H), 7.66 (s, 1H), 7.58-7.55 (m, 3H), 7.34-7.25 (m, 4H), 7.17 (dd, *J* = 14.7, 7.5 Hz, 2H), 6.93-6.84 (m, 4H), 5.22 (s, 1H), 2.35 (s, 3H), 2.09 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.5, 154.8, 140.0, 137.1, 135.2, 134.7, 133.5, 129.8, 128.7, 128.3, 127.9, 127.5, 125.4, 125.3, 119.9, 119.6, 118.5, 110.3, 108.9, 92.0, 48.8, 20.6, 12.3, 9.8.

HRMS (ESI-TOF) calcd. for $C_{28}H_{25}NNaO_2$ $[M + Na]^+$ 430.1783; found: 430.1764.

(*S*)-5-((*S*)-(4-methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3k)



Light yellow solid; 79.3 mg, 94% yield; 55:45 dr, 88% ee; $[\alpha]_D^{20}$ = -205.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 110.9-111.3 ℃;

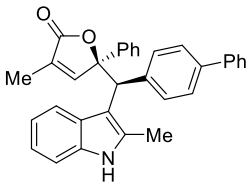
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.3 min, t_{major} = 9.4 min);

^{1}H NMR (600 MHz, DMSO-d_6) δ (major diastereomer)10.74 (s, 1H), 7.67-7.57 (m, 4H), 7.35-7.26 (m, 4H), 7.24-7.18 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.98-6.81 (m, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 5.22 (s, 1H), 3.60 (s, 3H), 2.35 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ (major diastereomer) 173.2, 156.9, 154.7, 139.9, 133.3, 132.0, 130.7, 130.6, 128.5, 128.4, 127.3, 125.2, 119.9, 119.7, 119.6, 118.3, 112.9, 110.1, 108.9, 91.9, 54.8, 48.8, 12.1, 9.7.

HRMS (ESI-TOF) calcd. for $C_{28}H_{25}NNaO_3$ $[M + Na]^+$ 446.1727; found: 446.1726.

(*S*)-5-((*S*)-[1,1'-biphenyl]-4-yl(2-methyl-1*H*-indol-3-yl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3l)



White solid; 79.8 mg, 85% yield; 52:48 dr, 86% ee; $[\alpha]_D^{20}$ = -187.6 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 124.6-125.3 ℃;

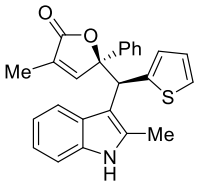
The ee was determined by HPLC (Chiralpak IB, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 8.6 min, t_{major} = 12.1 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.75 (s, 1H), 7.73-7.55 (m, 4H), 7.51-7.45 (m, 4H), 7.41-7.35 (m, 3H), 7.34-7.30 (m, 3H), 7.29-7.20 (m, 2H), 7.19-7.13 (m, 2H), 6.90-6.87 (m, 1H), 5.28 (s, 1H), 2.41 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 174.1, 155.3, 140.1, 139.9, 139.8, 137.8, 135.6, 134.0, 130.9, 129.5, 129.3, 128.1, 127.9, 127.0, 126.8, 126.2, 125.9, 125.6, 120.5, 120.0, 119.1, 110.8, 109.0, 92.4, 49.3, 12.5, 10.1.

HRMS (ESI-TOF) calcd. for $C_{33}H_{27}NNaO_2$ $[M + Na]^+$ 492.1939; found: 492.1933.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(thiophen-2-yl)methyl)-5-phenylfuran-2(5*H*)-one (3m)



Light red solid; 68.5 mg, 86% yield; 53:47 dr, 93% ee; $[\alpha]_D^{20}$ = -583.2 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p.72.8-73.4 ℃;

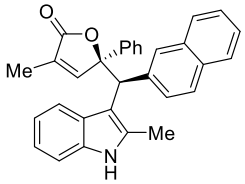
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 31.5 min, t_{minor} = 35.8 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.83 (s, 1H), 7.67 (d, *J* = 6.6 Hz, 1H), 7.59 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 2H), 7.28-7.23 (m, 1H), 7.22-7.14 (m, 2H), 6.94 (q, *J* = 8.4, 7.9 Hz, 2H), 6.86 (d, *J* = 3.6 Hz, 1H), 6.75 (dd, *J* = 5.2, 3.5 Hz, 1H), 5.42 (s, 1H), 2.27 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 172.8, 153.1, 142.0, 139.7, 135.1, 133.7, 128.8, 128.4, 127.6, 126.9, 126.1, 125.8, 125.5, 125.3, 124.3, 119.9, 118.4, 110.3, 108.0, 91.6, 45.5, 11.8, 9.7.

HRMS (ESI-TOF) calcd. for $C_{25}H_{21}NNaO_2S$ $[M + Na]^+$ 422.1191; found: 422.1189.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(naphthalen-2-yl)methyl)-5-phenylfuran-2(5*H*)-one (3n)



Light yellow solid; 69.3 mg, 78% yield; 60:40 dr, 95% ee/(minor 30% ee); $[\alpha]_D^{20}$ = -529.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 214.7-215.4 ℃;

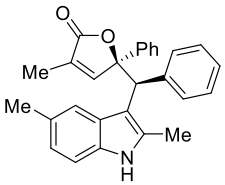
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomers: t_{minor} = 7.9 min, t_{major} = 12.5 min, minor diastereomers: t_{minor} = 13.7 min, t_{major} = 19.7 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.79 (s, 1H), 7.98 (s, 1H), 7.74-7.62 (m, 5H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.44-7.35 (m, 2H), 7.35-7.25 (m, 2H), 7.21-7.12 (m, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 5.50 (s, 1H), 2.39 (s, 3H) ,1.38 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.5, 139.7, 137.6, 134.9, 133.6, 132.4, 131.1, 128.6, 128.5, 127.8, 127.6, 127.5, 127.3, 127.1, 126.8, 125.8, 125.4, 125.3, 125.1, 119.7, 119.2, 118.4, 110.1, 108.3, 91.7, 48.8, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{31}H_{25}NNaO_2$ $[M + Na]^+$ 466.1783; found: 466.1791.

(*S*)-5-((*S*)-(2,5-dimethyl-1*H*-indol-3-yl)(phenyl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3o)



Light yellow solid; 75.9 mg, 93% yield; 64:36 dr, 90% ee/(minor 23% ee); $[\alpha]_D^{20}$ = -345.4 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 104.7-105.6 ℃;

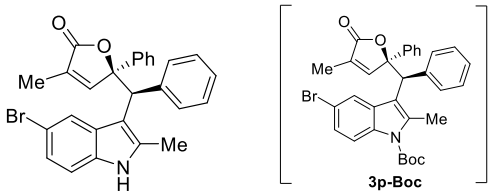
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomers: t_{minor} = 14.5 min, t_{major} = 16.5 min, minor diastereomers: t_{minor} = 11.6 min, t_{major} = 13.5 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.60 (s, 1H), 7.63-7.51 (m, 4H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.36-7.26 (m, 3H), 7.23-7.16 (m, 1H), 7.12-7.05 (m, 2H), 7.03-6.94 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.26 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.2, 154.5, 140.1, 139.9, 133.4, 133.3, 129.6, 128.4, 127.8, 127.6, 127.5, 127.3, 126.5, 125.5, 125.1, 121.3, 119.0, 109.8, 108.1, 91.6, 48.9, 21.5, 12.2, 9.6.

HRMS (ESI-TOF) calcd. for $C_{28}H_{25}NNaO_2$ $[M + Na]^+$ 430.1783; found: 430.1786.

(*S*)-5-((*S*)-(5-bromo-2-methyl-1*H*-indol-3-yl)(phenyl)methyl)-3-methyl-5-phenylfuran-2(5*H*)-one (3p)



Light yellow solid; 69.7 mg, 74% yield; 71:29 dr, 96% ee; $[\alpha]_D^{20}$ = -330.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 215.9-216.3 ℃;

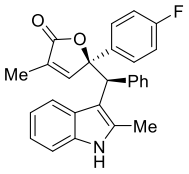
The ee was determined by HPLC (3p-Boc) (Chiralpak IA, EtOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomers: t_{minor} = 5.6 min, t_{major} = 6.2 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 11.01 (s, 1H), 7.84 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.56 (s, 1H), 7.42-7.26 (m, 4H), 7.24-7.16 (m, 1H), 7.15-7.06 (m, 3H), 7.05-6.94 (m, 2H), 5.31 (s, 1H), 2.37 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.6, 139.7, 139.5, 135.4, 133.6, 129.7, 128.5, 128.1, 127.6, 127.3, 125.7, 125.2, 125.1, 122.3, 121.6, 112.0, 111.3, 108.6, 91.5, 48.2, 12.2, 9.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}BrNNaO_2$ $[M + Na]^+$ 494.0732; found: 494.0739.

(*S*)-5-(4-fluorophenyl)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)furan-2(5*H*)-one (3q)



Light yellow solid; 80.3 mg, 97% yield; 72:28 dr, 92% ee/(minor 34% ee); $[\alpha]_D^{20}$ = -387.0 (*c* 1.00, CH_2Cl_2) for major diastereomers; m.p. 213.5-214.7 ℃;

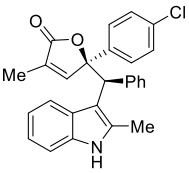
The ee was determined by HPLC (Chiralpak IA, *i*-PrOH/hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.3 min, t_{minor} = 7.7 min, minor diastereomers: t_{minor} = 8.7 min, t_{major} = 24.1 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomers) 10.77 (s, 1H), 7.72 (s, 1H), 7.68-7.56 (m, 3H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.18-7.07 (m, 5H), 7.04-6.96 (m, 1H), 6.97-6.87 (m, 2H), 5.26 (s, 1H), 2.35 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 161.2 (d, *J* = 244.1 Hz, 1C), 154.4, 140.0, 136.0 (d, *J* = 2.4 Hz, 1C), 135.0, 133.5, 129.8, 127.7, 127.5, 127.4 (d, *J* = 8.2 Hz, 1C), 125.7, 125.6, 125.5, 119.8, 118.4, 115.3 (d, *J* = 21.5 Hz, 1C), 110.2, 108.5, 91.4, 48.9, 12.2, 9.7.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}FNNaO_2$ $[M + Na]^+$ 434.1527; found: 434.1536.

(*S*)-5-(4-chlorophenyl-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)furan-2(5*H*)-one (3r)



Light yellow solid; 82.9 mg, 97% yield; 73:27 dr, 94% ee/(minor 31% ee); $[\alpha]_D^{20}$ = -423.1 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 204.1-205.5 ℃;

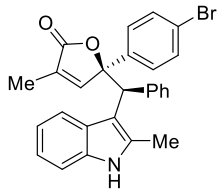
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 12.7 min, t_{major} = 19.9 min, minor diastereomers: t_{minor} = 33.9 min, t_{major} = 39.2 min);

^{1}H NMR (600 MHz, DMSO-d_6) δ (major diastereomer) 10.78 (s, 1H), 7.84-7.53 (m, 4H), 7.43-7.30 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.12-7.07 (m, 2H), 7.02-6.97 (m, 1H), 6.96-6.77 (m, 2H), 5.26 (s, 1H), 2.36 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.2, 139.9, 138.9, 135.0, 133.6, 132.1, 129.8, 128.6, 127.8, 127.7, 127.4, 127.3, 125.9, 125.7, 119.9, 118.5, 110.3, 108.4, 91.4, 49.0, 12.2, 9.8.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}ClNNaO_2$ $[M + Na]^+$ 450.1231; found: 450.1241.

(*S*)-5-(4-bromophenyl)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)furan-2(5*H*)-one (3s)



Light yellow solid; 90.2 mg, 95% yield; 73:27 dr, 92% ee/(minor 28% ee); $[\alpha]_D^{20}$ = -214.7 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 204.9-205.8 ℃;

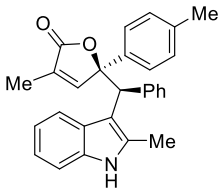
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.9 min, t_{major} = 25.0 min, minor diastereomers: t_{minor} = 44.9 min, t_{major} = 48.5 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.76 (s, 1H), 7.70 (s, 1H), 7.58-7.55 (m, 3H), 7.51-7.50 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.12 (q, *J* = 7.8 Hz, 3H), 7.05-6.96 (m, 1H), 6.90 (q, *J* = 8.7, 7.8 Hz, 2H), 5.27 (s, 1H), 2.35 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 172.8, 154.0, 139.8, 139.3, 135.1, 134.9, 133.5, 131.3, 129.7, 127.6, 127.5, 125.7, 125.6, 120.5, 119.8, 119.3, 118.4, 110.1, 108.3, 91.3, 48.8, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{22}BrNNaO_2$ $[M + Na]^+$ 494.0726; found: 494.0742.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)-5-(p-tolyl)furan-2(5*H*)-one (3t)



Light yellow solid; 70.1 mg, 86% yield; 77:23 dr, 96% ee/(minor 21% ee); $[\alpha]_D^{20}$ = -412.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 120.8-121.3 ℃;

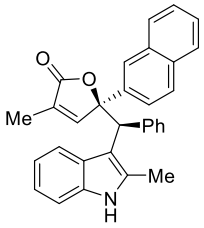
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 10.4 min, t_{major} = 14.4 min, minor diastereomers: t_{minor} = 23.7 min, t_{major} = 29.9 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.84 (s, 1H), 7.71-7.57 (m, 1H), 7.45-7.40 (m, 2H), 7.40-7.33 (m, 2H), 7.20-7.13 (m, 1H), 7.13-7.00 (m, 8H), 5.30 (s, 1H), 2.26 (s, 3H), 2.12 (s, 3H), 1.38 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 174.3, 153.7, 139.3, 137.5, 136.3, 134.8, 133.9, 130.2, 129.6, 129.0, 127.8, 126.6, 126.0, 125.1, 121.1, 119.7, 118.0, 110.4, 109.9, 91.9, 48.7, 21.1, 12.8, 10.0.

HRMS (ESI-TOF) calcd. for $C_{28}H_{25}NNaO_2$ $[M + Na]^+$ 430.1778; found: 430.1793.

(*S*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)-5-(naphthalen-2-yl)furan-2(5*H*)-one (3u)



Light red solid; 69.1 mg, 78% yield; 72:28 dr, 93% ee/(minor 30% ee); $[\alpha]_D^{20}$ = -396.1 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 116.3-117.2 ℃;

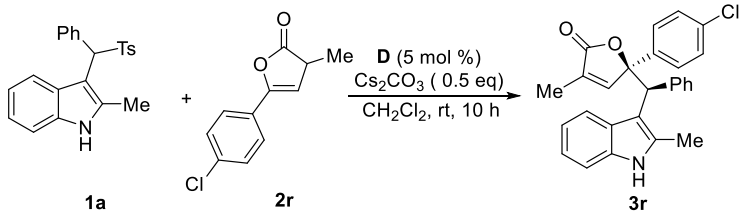
The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 0.5 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 34.7 min, t_{major} = 54.0 min, minor diastereomers: t_{minor} = 97.0 min, t_{major} = 105.3 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 10.78 (s, 1H), 8.12 (s, 1H), 7.95-7.77 (m, 5H), 7.69 (s, 1H), 7.51-7.43 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.10-7.01 (m, 2H), 6.95-6.91 (m, 3H), 5.45 (s, 1H), 2.39 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 173.1, 154.3, 140.0, 137.3, 134.9, 133.5, 132.7, 131.9, 129.7, 128.1, 127.9, 127.6, 127.4, 127.3, 126.3, 126.2, 125.5, 125.4, 123.8, 123.4, 119.7, 119.3, 118.3, 110.1, 108.5, 91.7, 48.8, 12.1, 9.6.

HRMS (ESI-TOF) calcd. for $C_{31}H_{25}NNaO_2$ $[M + Na]^+$ 466.1778; found: 466.1764.

3. Scale-up experiment

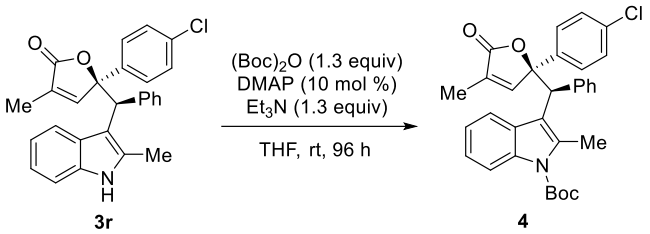


In an ordinary vial equipped with a magnetic stirring bar, the *β,γ*-unsaturated butenolide **2r** (4.5 mmol, 1.5 equiv) was added to a solution of arylsulfonyl indole **1a** (3.0 mmol, 1.0 equiv), catalyst **D** (5 mol %) and Cs_2CO_3 (1.5 mmol, 0.5 equiv) in CH_2Cl_2 (30 mL) at the room temperature. And then, the whole was stirred for 10 h until the completion of the reaction, as indicated by TLC. Finally, the reaction mixture was directly purified by flash chromatography on silica gel (PE/EA/DCM = 8:1:1) and obtained the product **3r** (0.85 g, 66% yield, 61:39 dr, 94% ee).

4. Procedure for the synthesis of 4, 5 and 6

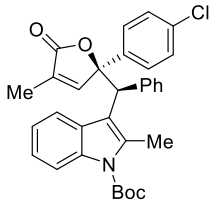
4.1 Synthesis of compound 4

A solution of **3r** (85.6 mg, 0.2 mmol, 1.0 equiv) in dry THF (2 mL) was added DMAP (24.4 mg, 10 mol %), Et_3N (36 μL, 0.26 mmol, 1.3 equiv) and di-*tert*-butyl carbonate (60 μL, 0.26 mmol, 1.3 equiv) dropwise at room temperature and stirred for 96 h. After completion of the reaction, as indicated by TLC, the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 10/1) to afford product **4** (71.2 mg, 67% yield) as a light red solid.



3r **4**

***tert*-butyl 3-((*S*)-((*S*)-2-(4-chlorophenyl)-4-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)-2-methyl-1*H*-indole-1-carboxylate (4)**



White solid; 71.2 mg, 67% yield; >20:1 dr, 94% ee; $[\alpha]_D^{20}$ = -552.8 (*c* 1.00, CH_2Cl_2); m.p. 119.9-120.7 ℃;

The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 0.5 mL/min, λ = 254 nm, t_{minor} = 10.2 min, t_{major} = 12.1 min);

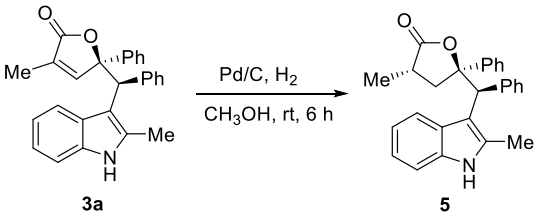
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 8.04 (s, 1H), 7.66-7.56 (m, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.34-7.22 (m, 3H), 7.19 (s, 1H), 7.14-7.08 (m, 2H), 7.07-6.98 (m, 2H), 5.31 (s, 1H), 2.57 (s, 3H), 1.65 (s, 9H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer)173.4, 152.6, 150.7, 138.1, 138.0, 135.7, 135.6, 133.8, 130.0, 129.2, 129.1, 128.9, 128.1, 127.9, 127.2, 126.5, 126.4, 123.6, 122.7, 116.5, 115.2, 90.7, 48.2, 28.3, 14.6, 10.2.

HRMS (ESI-TOF) calcd. for $C_{32}H_{30}ClNNaO_4$ $[M + Na]^+$ 550.1761; found: 550.1762.

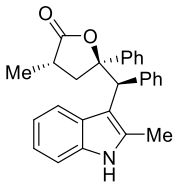
4.2 Synthesis of compound 5

A solution of **3a** (0.5 mmol, 196.7 mg) in MeOH (6 mL) was treated with 10% palladium on charcoal (10 wt %) and hydrogenated for 6 h at room temperature. The mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure, and then purified by column chromatography (PE/EA = 6/1) to give the target product **5** (133.8 mg, 68% yield) as a white solid.



3a **5**

(3*S*,5*R*)-3-methyl-5-((*S*)-(2-methyl-1*H*-indol-3-yl)(phenyl)methyl)-5-phenyldihydrofuran-2(3*H*)-one (5)



White solid; 133.8 mg, 68% yield; >20:1 dr, 91% ee; $[\alpha]_D^{20}$ = -137.5 (*c* 1.00, CH_2Cl_2); m.p. 78.2-79.3 ℃;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 17.1 min, t_{major} = 18.6 min);

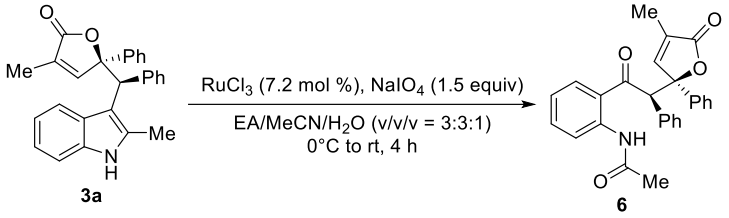
^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.02-7.76 (m, 2H), 7.53-7.37 (m, 2H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.28-7.19 (m, 3H), 7.19-7.07 (m, 3H), 7.07-6.91 (m, 3H), 4.91 (s, 1H), 2.60-2.47 (m, 1H), 2.47-2.34 (m, 1H), 2.28 (s, 3H), 2.26-2.16 (m, 1H), 0.82 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 179.6, 143.4, 139.9, 135.1, 133.8, 130.0, 128.8, 128.5, 128.4, 127.9, 127.7, 127.3, 125.9, 125.3, 121.2, 119.9, 110.4, 89.8, 52.0, 42.6, 33.9, 14.4, 13.1.

HRMS (ESI-TOF) calcd. for $C_{27}H_{25}NNaO_2$ $[M + Na]^+$ 418.1783; found: 418.1775.

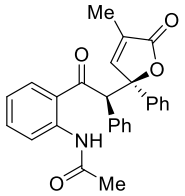
4.3 Synthesis of compound 6

A solution of **3a** (0.3 mmol, 117.9 mg) in a mixture of EA (1.5 mL) and MeCN (1.5 mL) was added dropwise to a solution of $RuCl_3$ (7.2 mol %, 4.5 mg) and $NaIO_4$ (0.45 mmol, 96.0 mg, 1.5 equiv) in H_2O (0.5 mL) at 0°C, and the mixture was stirred vigorously for 15 min, and then moved to room temperature with stirring for 4 h. After the addition of a saturated $Na_2S_2O_3$ aqueous solution, the mixture was extracted with EA and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography (PE/EA = 4/1), affording product **6** (38.8 mg, 30% yield) as a light red solid.



3a 6

***N*-(2-((*S*)-2-((*R*)-4-methyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl)-2-phenylacetyl)phenyl)acetamide (6)**



Light yellow solid; 38.8 mg, 30% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = +205.5 (*c* 1.00, CH_2Cl_2); m.p. 213.8-214.7 ℃;

The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 24.1 min, t_{major} = 28.4 min);

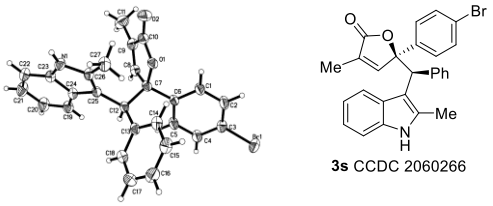
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 11.14 (s, 1H), 8.55 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 6.6 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.45-7.38 (m, 1H), 7.33-7.24 (m, 8H), 7.02-6.84 (m, 1H), 5.59 (s, 1H), 2.21 (s, 3H), 1.72 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 201.6, 171.9, 169.2, 149.0, 141.2, 138.7, 135.3, 132.4, 131.6, 130.8, 130.2, 128.8, 128.7, 128.6, 128.5, 127.0, 122.6, 121.9, 121.1, 89.3, 64.2, 25.6, 10.6.

HRMS (ESI-TOF) calcd. for $C_{27}H_{23}NNaO_4$ $[M + Na]^+$ 448.1525; found: 448.1503.

5. X-ray crystal data for compounds 3s and 6

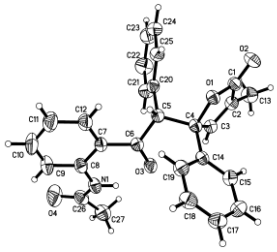
Crystal data and structure refinement for **3s** (CCDC 2060266)

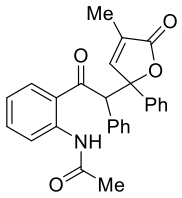


3s CCDC 2060266

Identification code	**3s**
Empirical formula	$C_{27}H_{22}BrNO_2$
Formula weight	472.36
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5545(2)
b/Å	10.0115(3)
c/Å	24.6214(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2355.17(10)
Z	4
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	2.551
F(000)	968.0
Crystal size/mm^3	0.17 × 0.13 × 0.009
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.18 to 134.142
Index ranges	$-7 \le h \le 11$, $-11 \le k \le 10$, $-20 \le l \le 29$
Reflections collected	8533
Independent reflections	4210 [R_{int} = 0.0293, R_{sigma} = 0.0392]
Data/restraints/parameters	4210/2/290
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.0954
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1053
Largest diff. peak/hole / e Å^{-3}	0.30/-0.28
Flack parameter	-0.029(13)

Crystal data and structure refinement for **6** (CCDC 2060270)



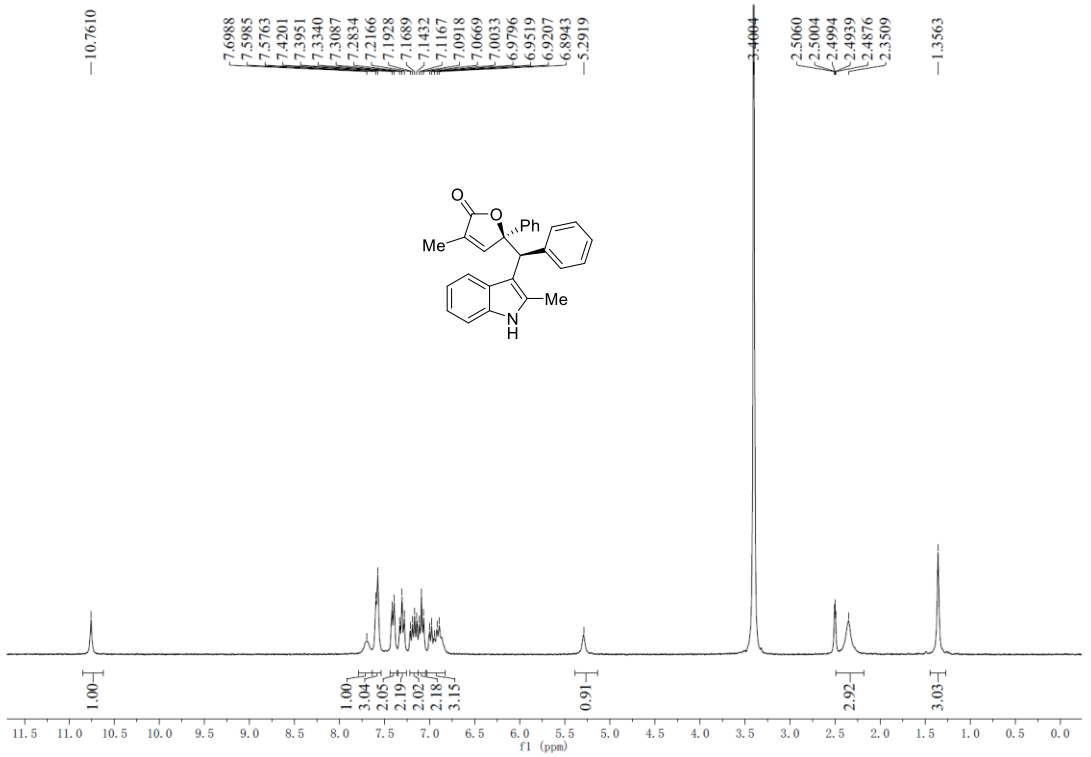


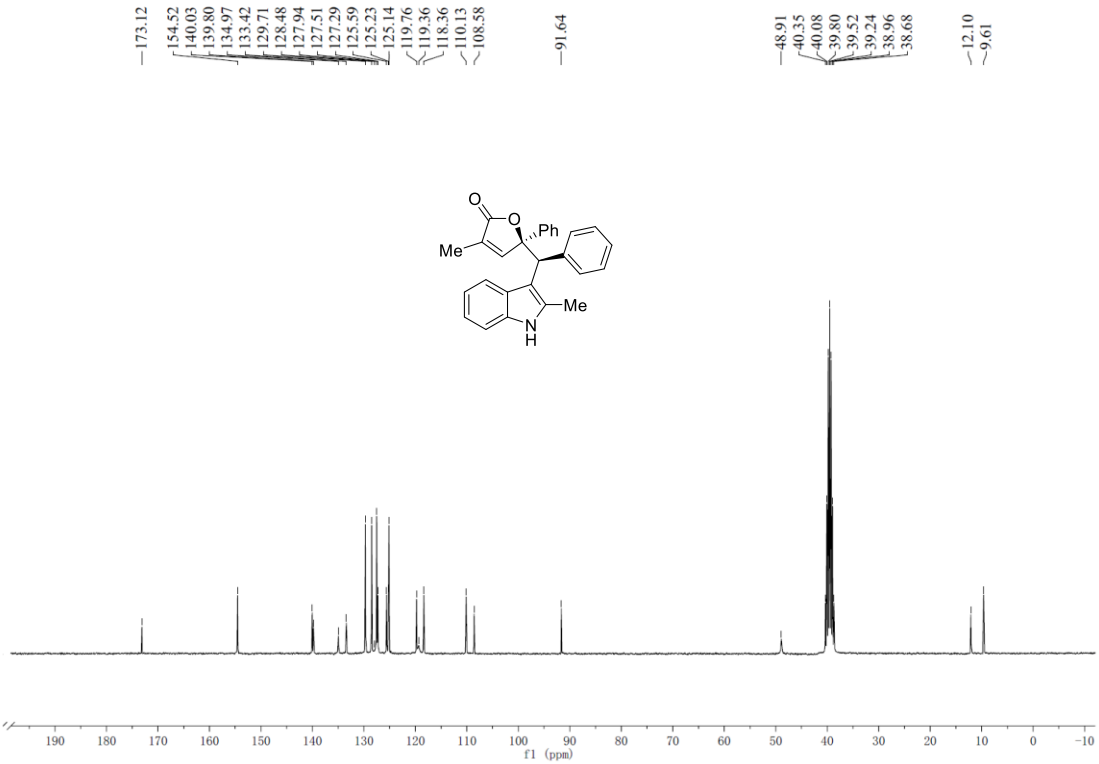
6 CCDC 2060270

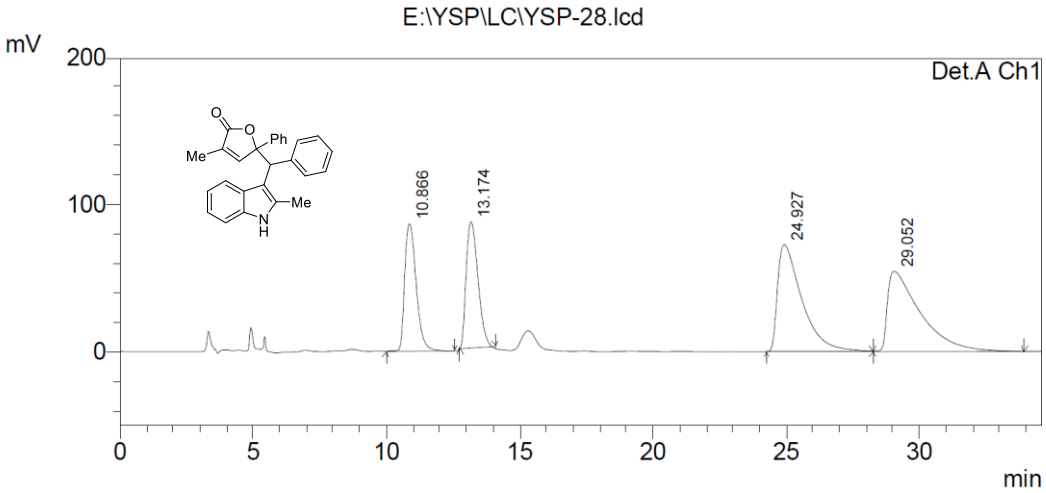
Identification code	6
Empirical formula	$C_{27}H_{23}NO_4$
Formula weight	425.46
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.2533(10)
b/Å	10.7469(10)
c/Å	11.7360(9)
α/°	93.016(7)
β/°	99.314(7)
γ/°	116.142(10)
Volume/Å^3	1134.4(2)
Z	2
ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	0.676
F(000)	448.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.71 to 134.122
Index ranges	$-12 \le h \le 10$, $-7 \le k \le 12$, $-14 \le l \le 13$
Reflections collected	7932
Independent reflections	4034 [R_{int} = 0.0358, R_{sigma} = 0.0519]
Data/restraints/parameters	4034/0/295
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0525, wR_2 = 0.1223
Final R indexes [all data]	R_1 = 0.0874, wR_2 = 0.1505
Largest diff. peak/hole / e Å^{-3}	0.18/-0.16

6. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra of compounds 3, 4, 5 and 6

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3a





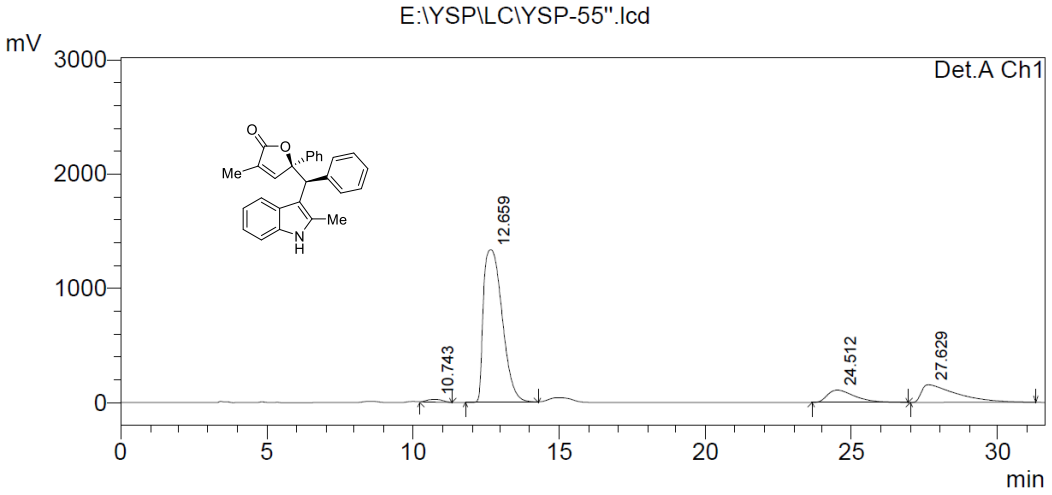


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.866	2608990	86740	17.900
2	13.174	2640939	85806	18.119
3	24.927	4648150	72947	31.890
4	29.052	4677329	54652	32.091
Total		14575408		100.000



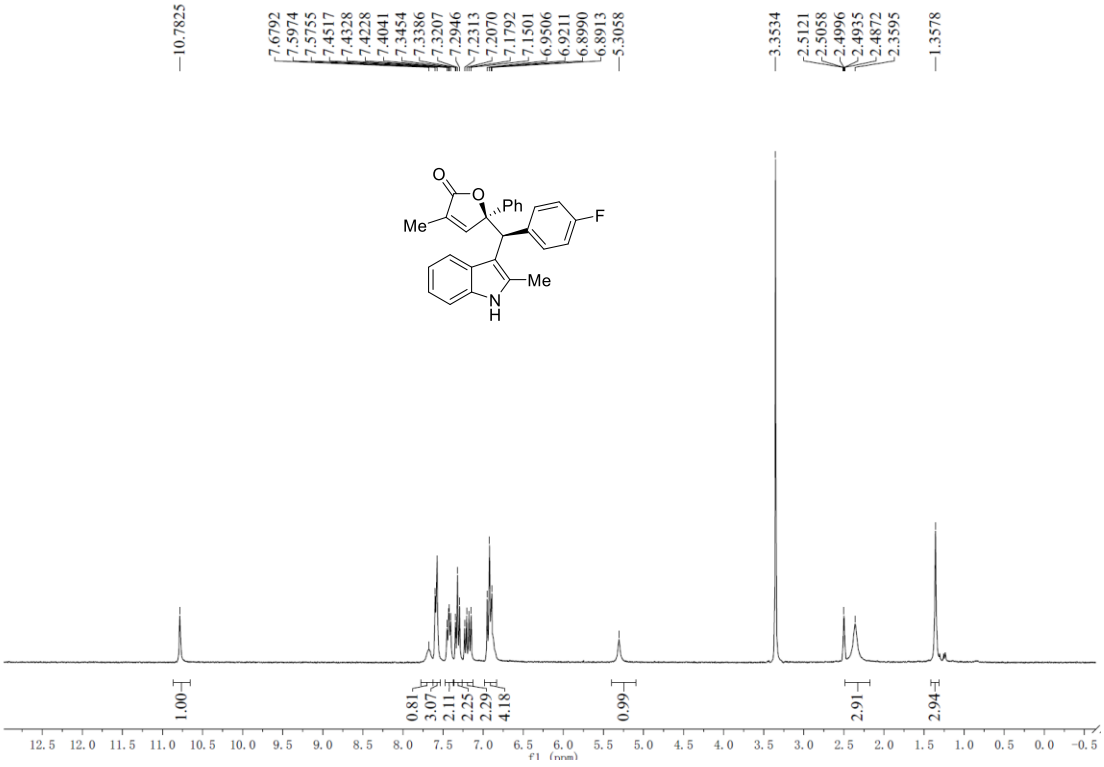
1 Det.A Ch1/254nm

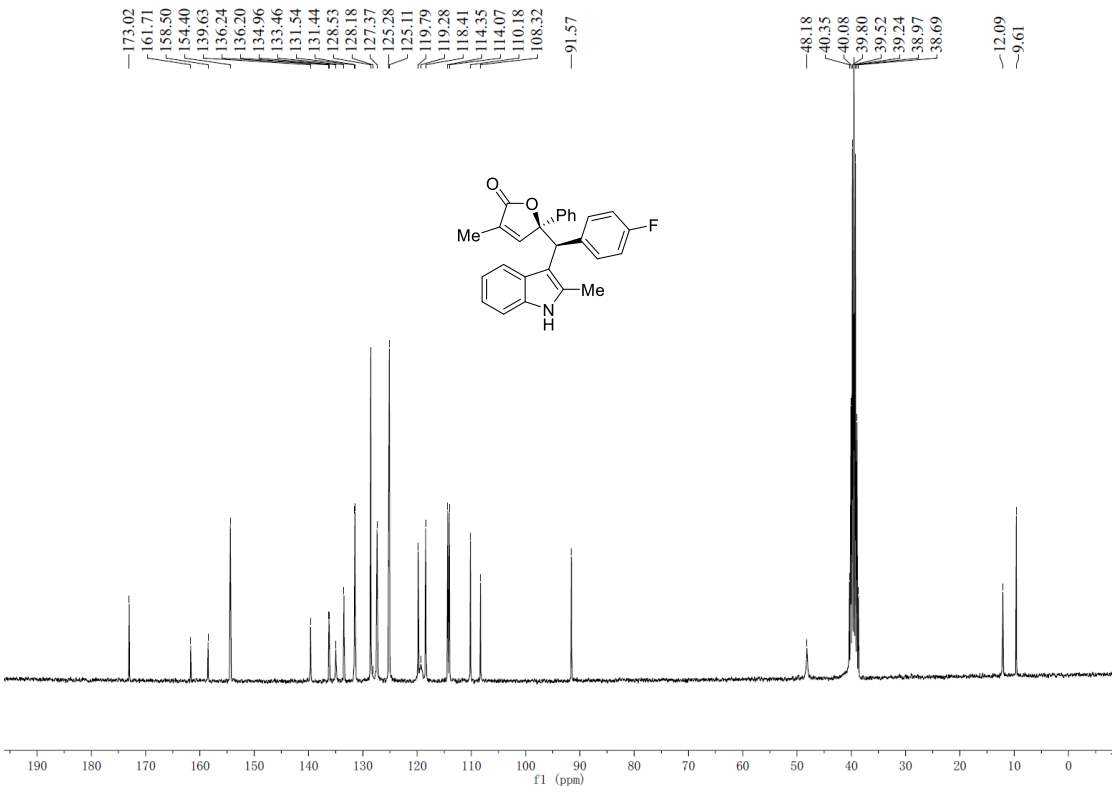
PeakTable

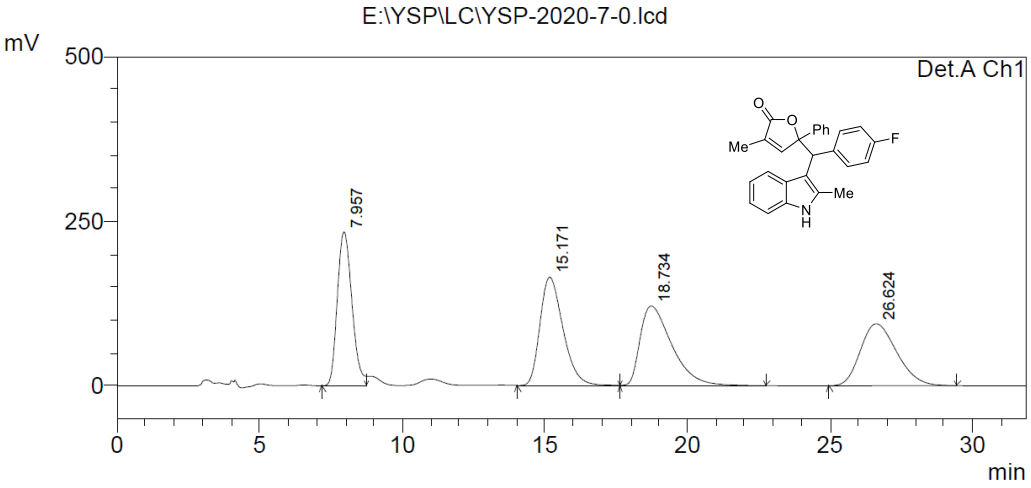
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.743	918616	23982	1.141
2	12.659	59714592	1334460	74.189
3	24.512	7032579	108388	8.737
4	27.629	12823503	153932	15.932
Total		80489290		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3b





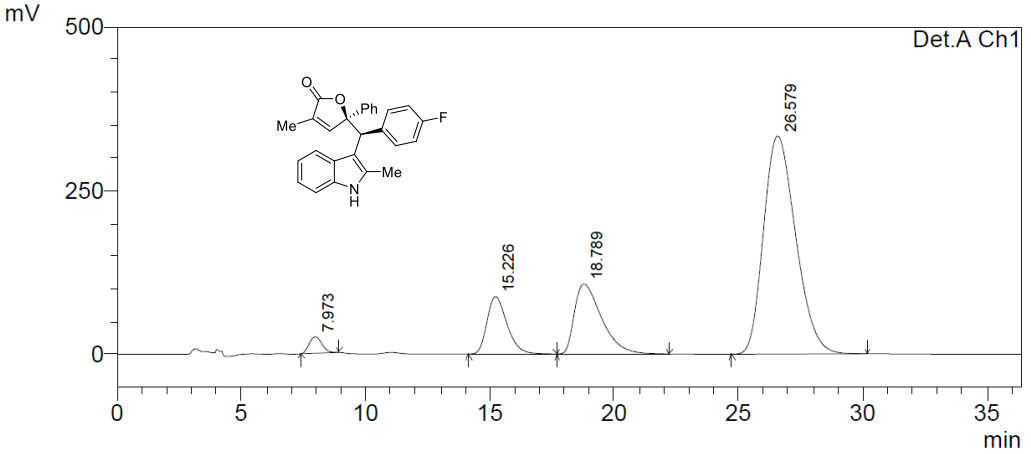


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.957	8345581	233260	23.694
2	15.171	9229461	164247	26.204
3	18.734	9321212	120669	26.464
4	26.624	8325670	94004	23.638
Total		35221924		100.000



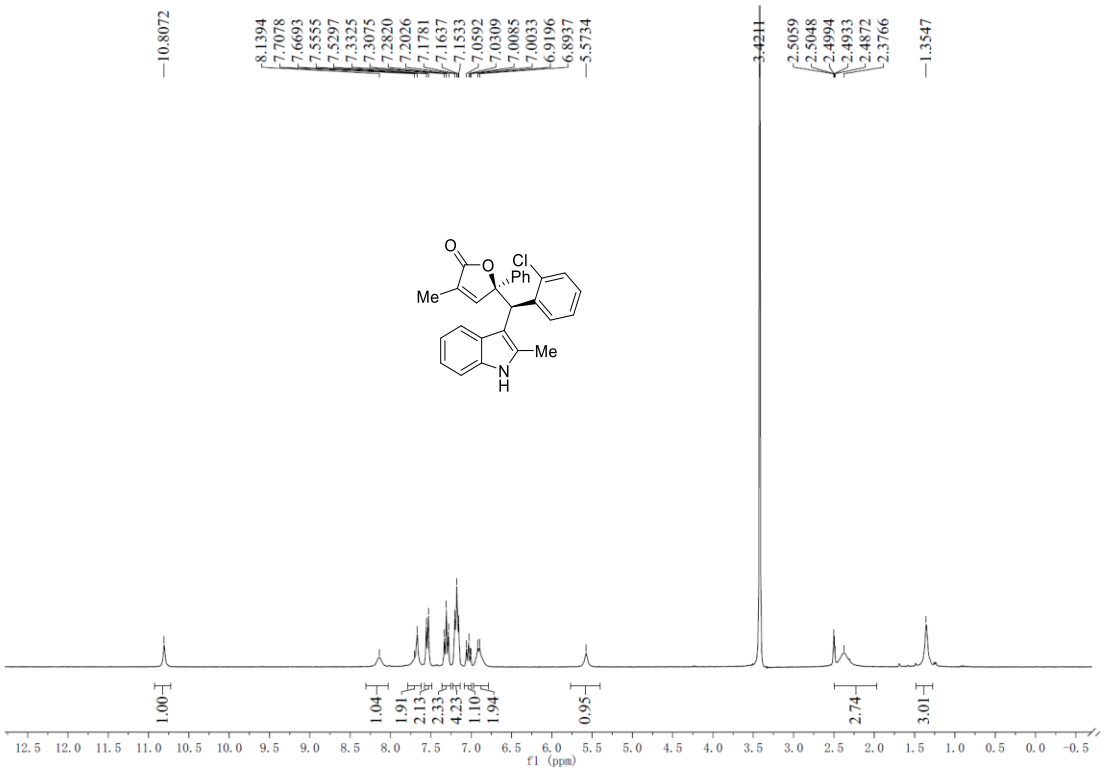
1 Det.A Ch1/254nm

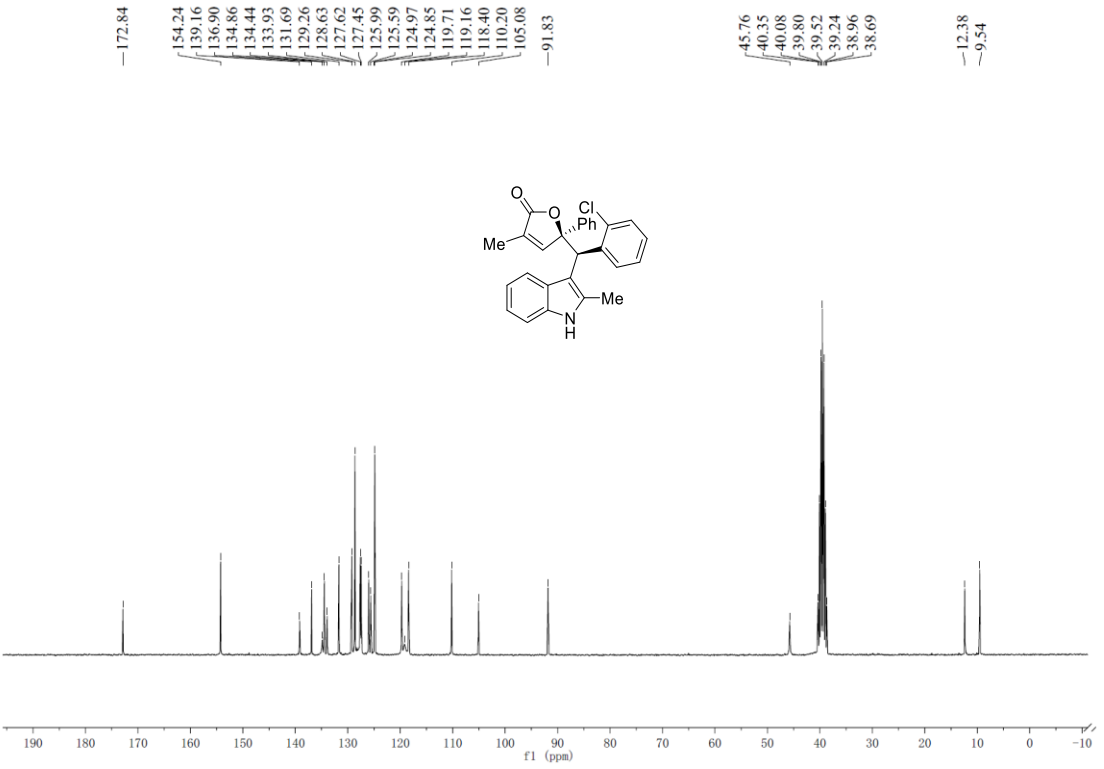
PeakTable

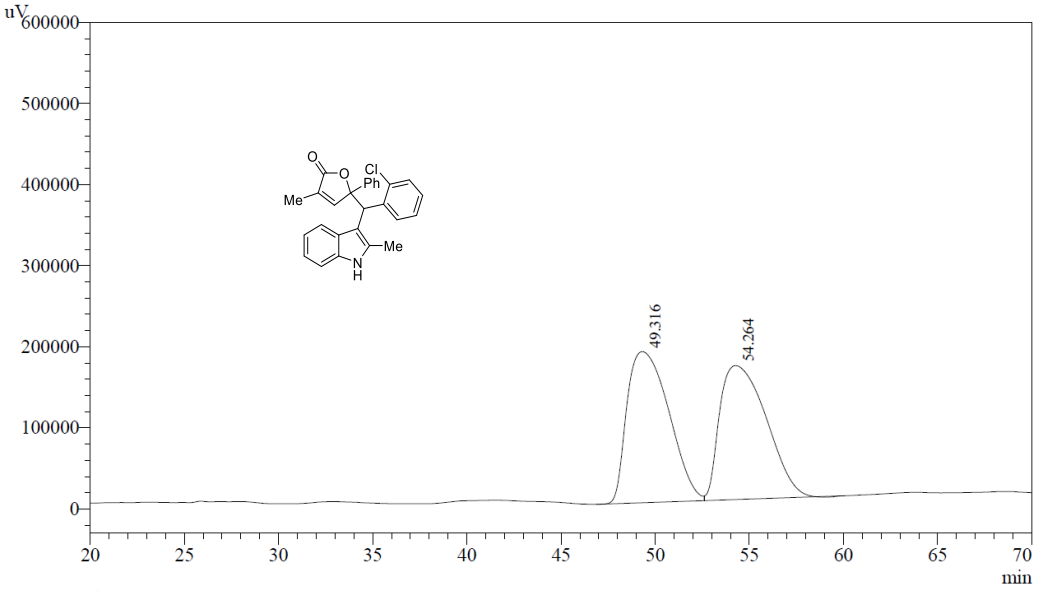
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.973	893973	25145	2.041
2	15.226	4897382	87405	11.180
3	18.789	8101475	106665	18.495
4	26.579	29910564	332421	68.284
Total		43803394		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3c



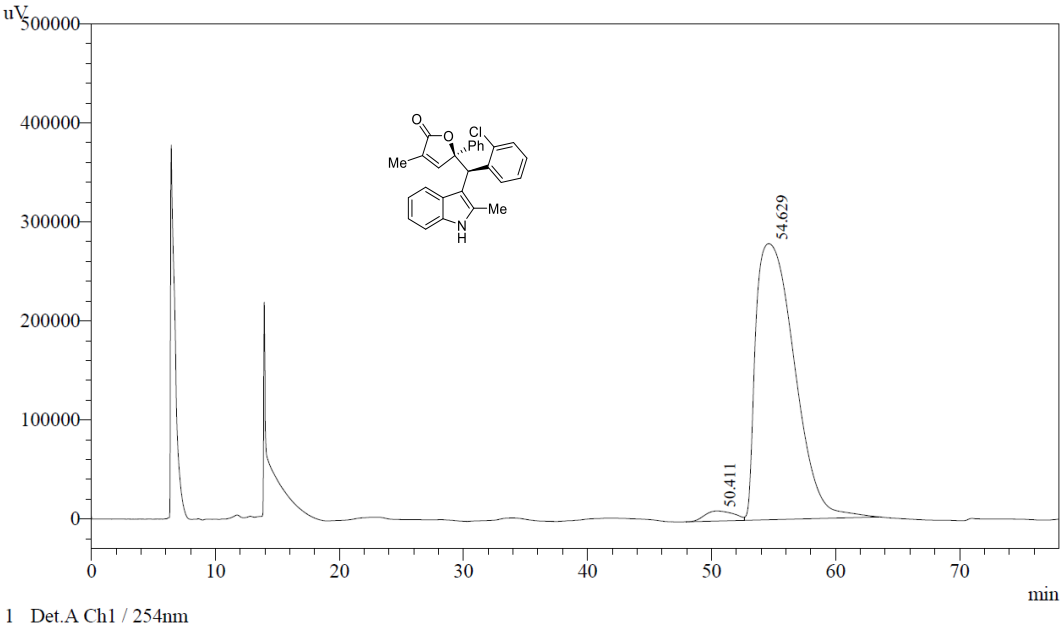




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.316	28943729	186436	50.441	53.019
2	54.264	28437983	165202	49.559	46.981
Total		57381711	351637	100.000	100.000

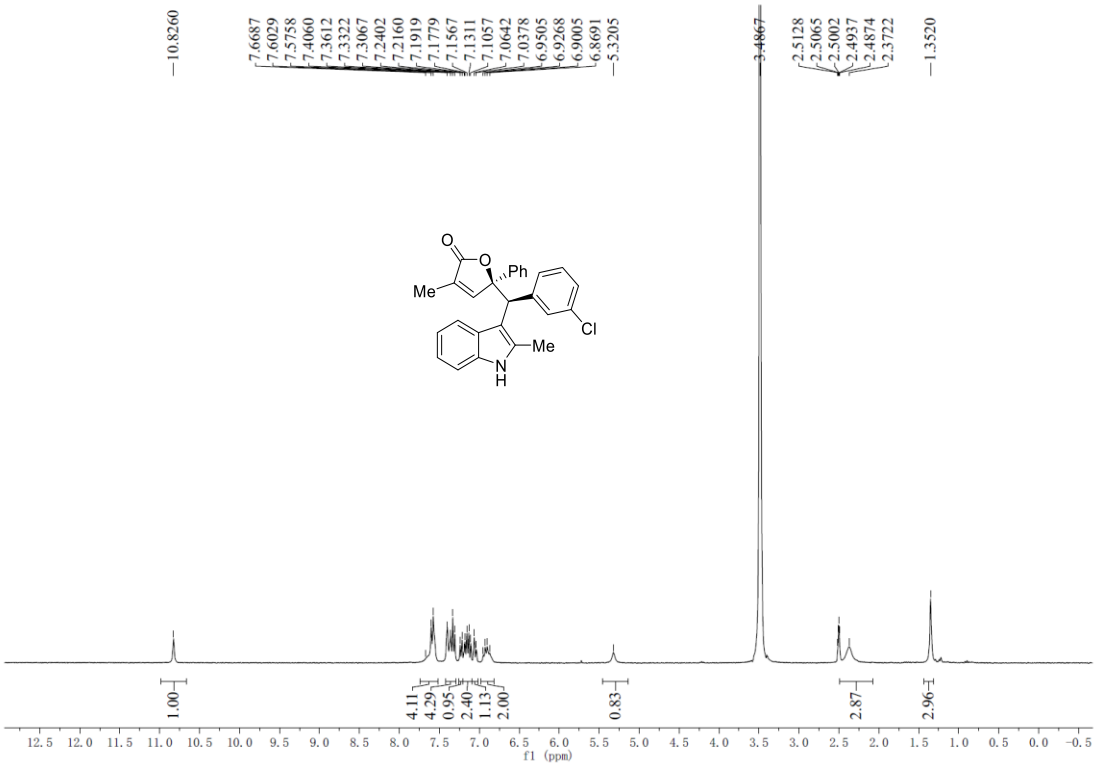


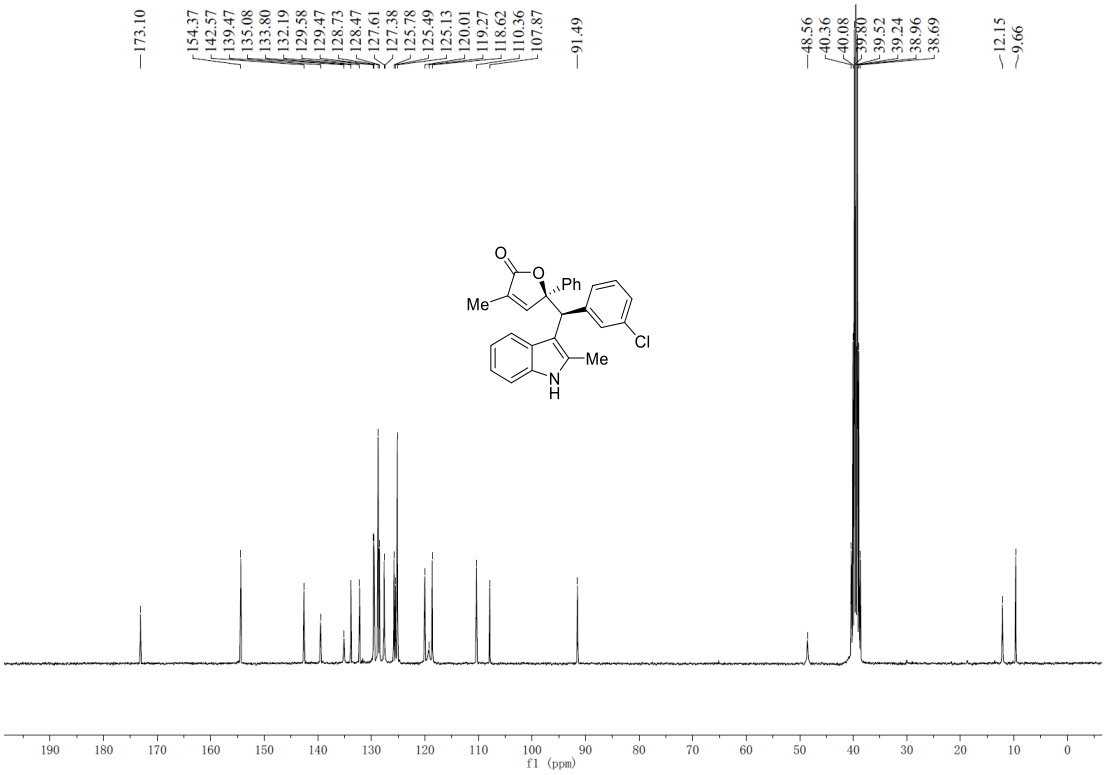
1 Det.A Ch1 / 254nm

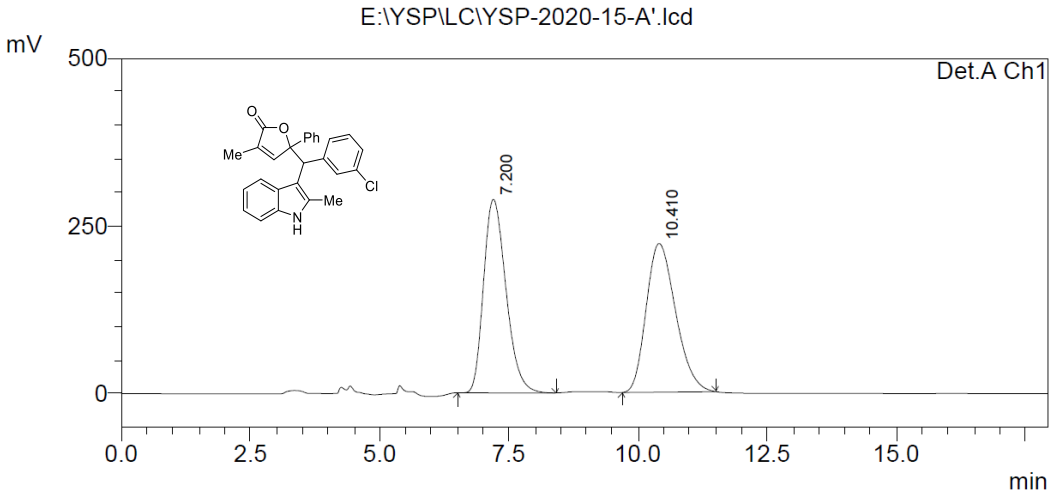
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.411	1661946	10201	2.672	3.531
2	54.629	60548124	278710	97.328	96.469
Total		62210069	288911	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3d



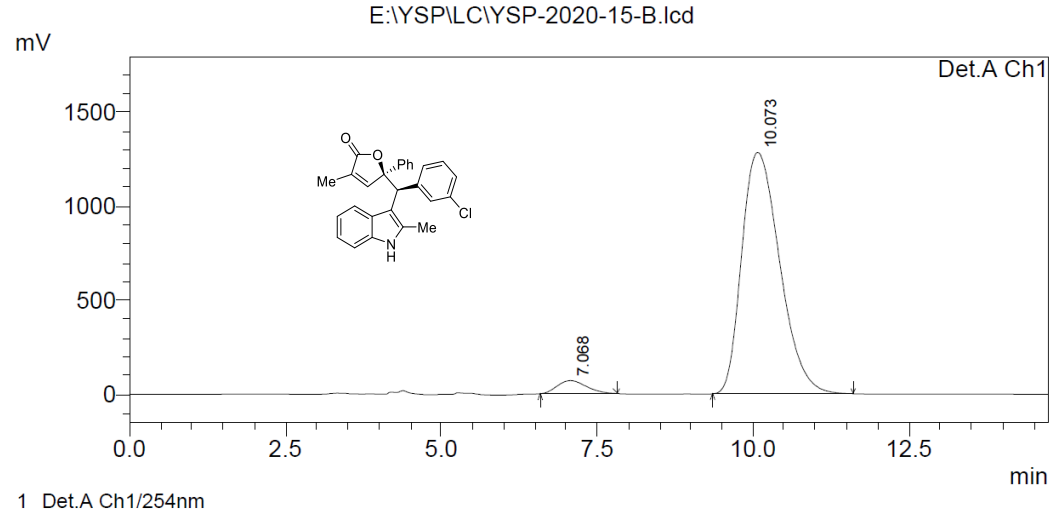




PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.200	8706669	287832	49.829
2	10.410	8766439	221223	50.171
Total		17473107		100.000

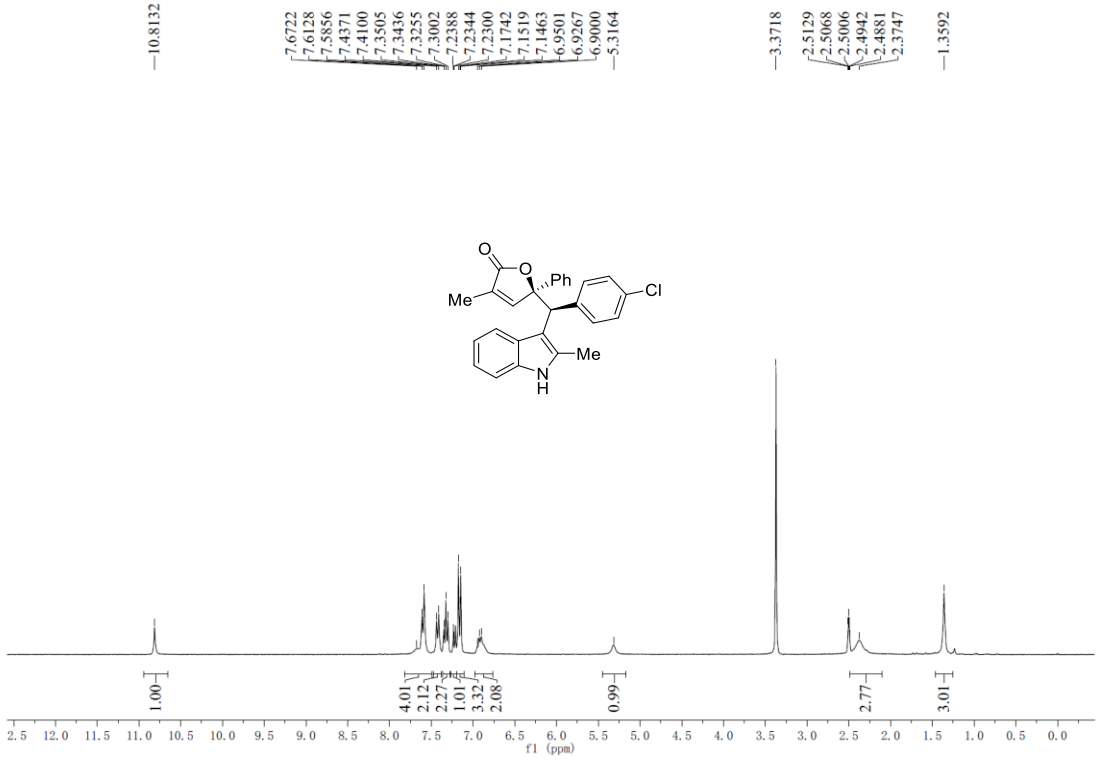


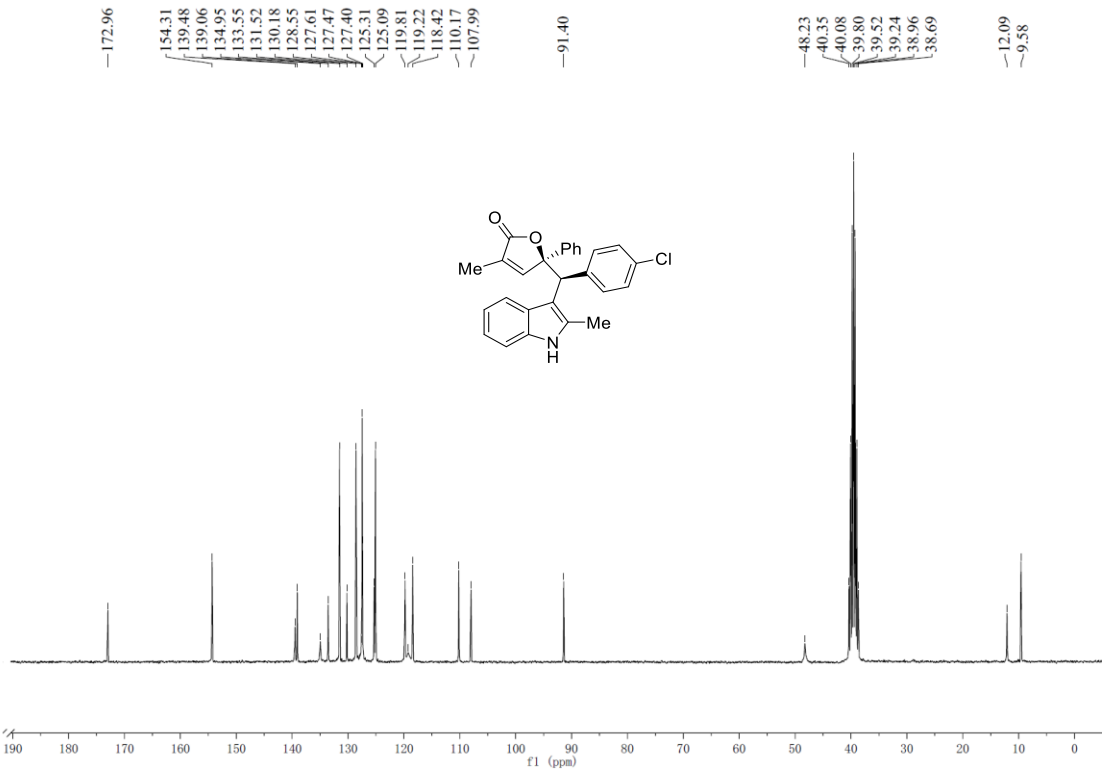
PeakTable

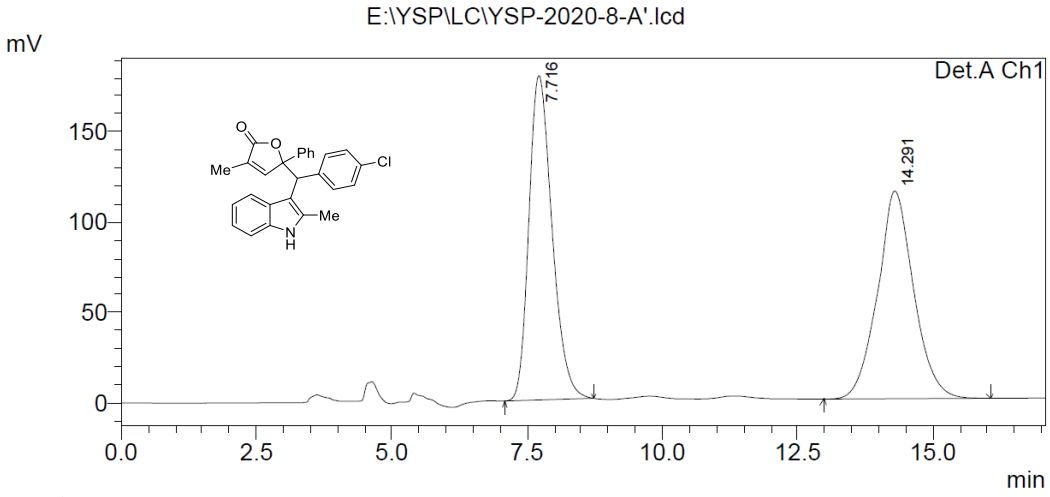
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.068	2253076	69245	3.969
2	10.073	54516058	1283944	96.031
Total		56769134		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3e





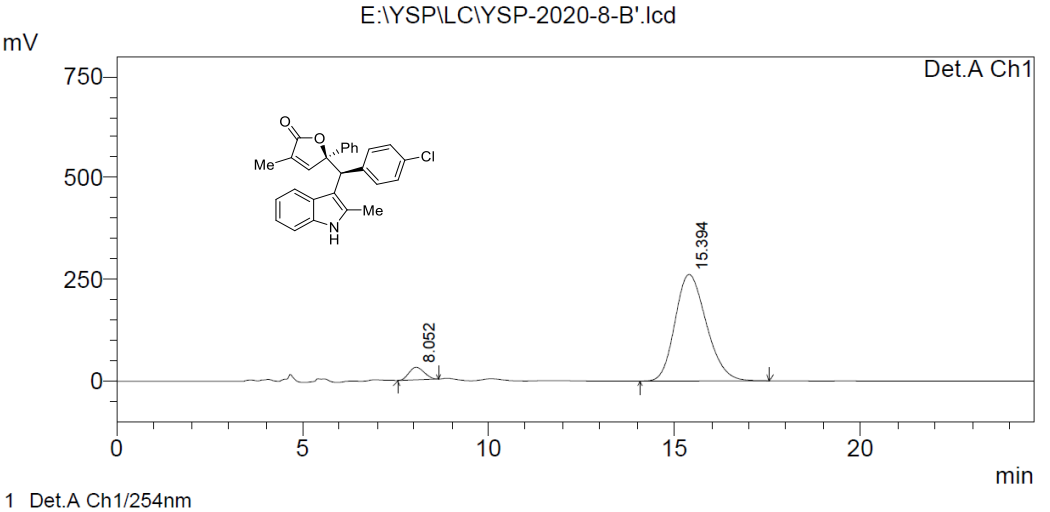


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.716	5338398	179392	50.029
2	14.291	5332227	114871	49.971
Total		10670625		100.000



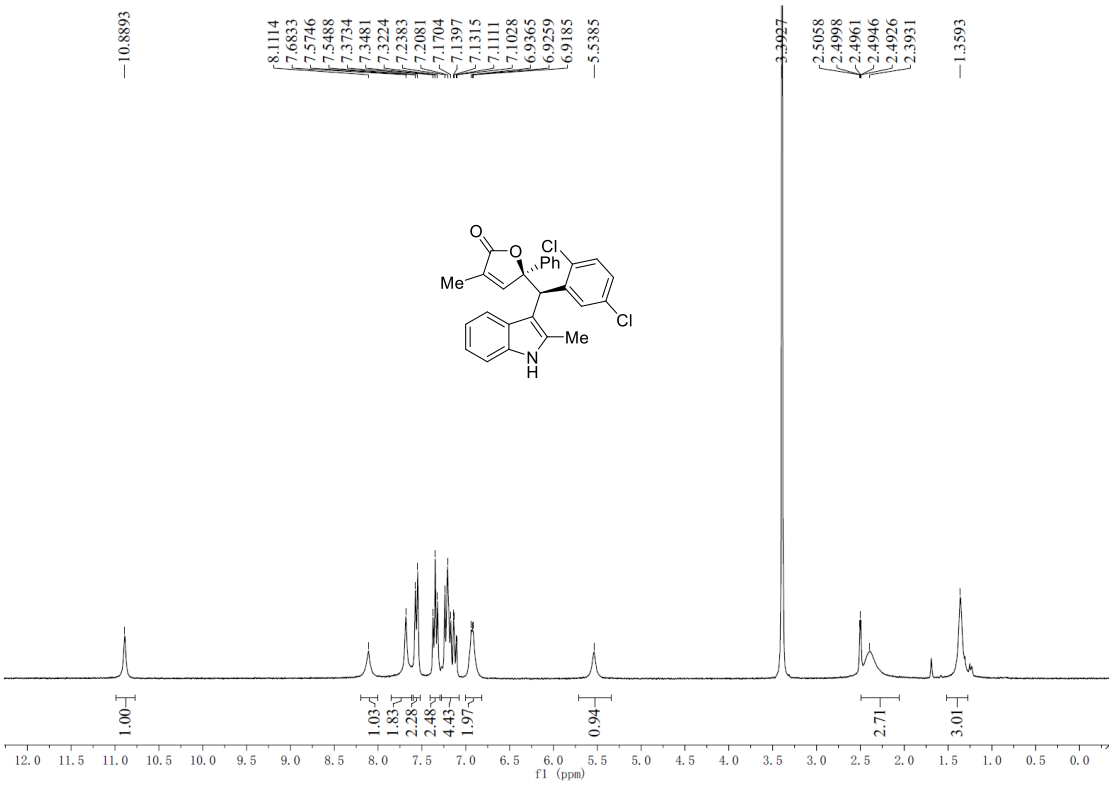
1 Det.A Ch1/254nm

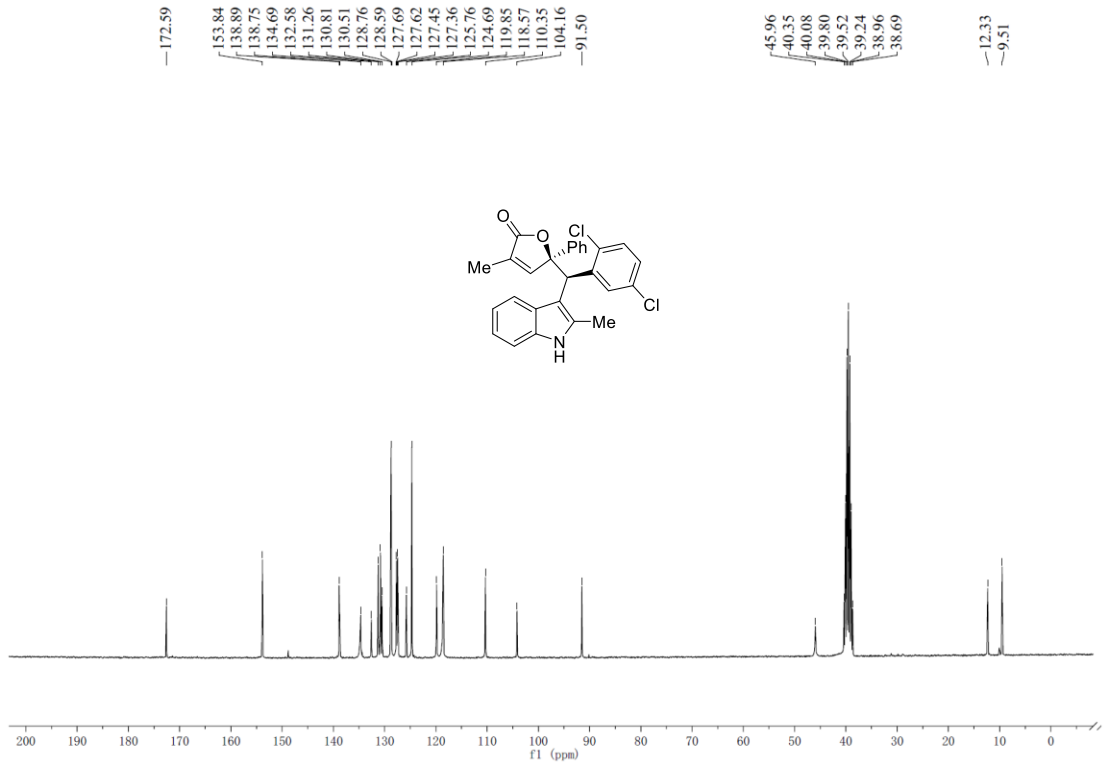
PeakTable

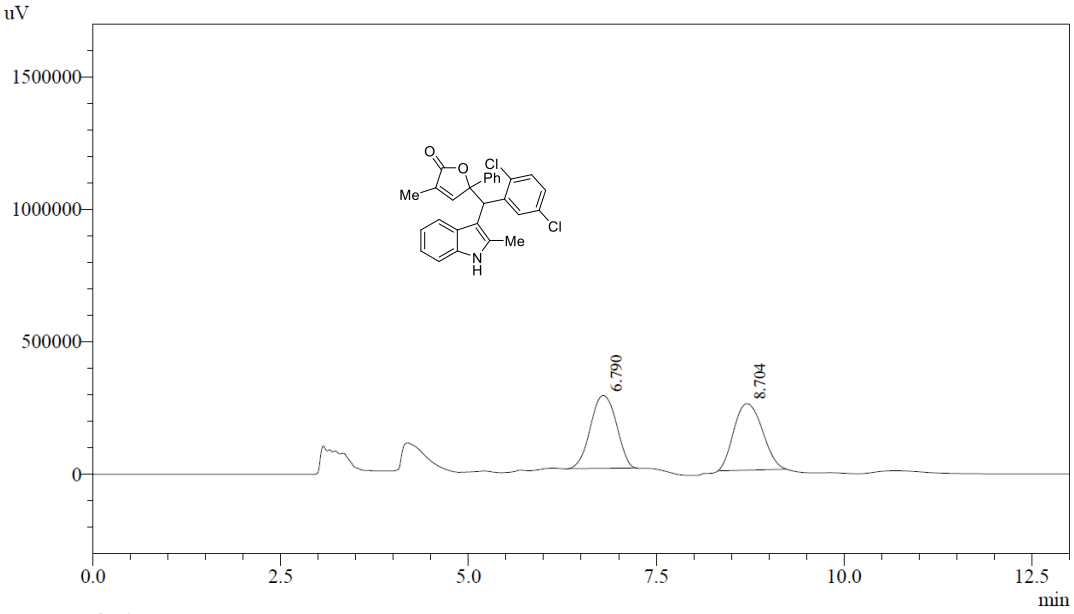
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.052	866797	30718	5.355
2	15.394	15318636	261689	94.645
Total		16185433		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3f



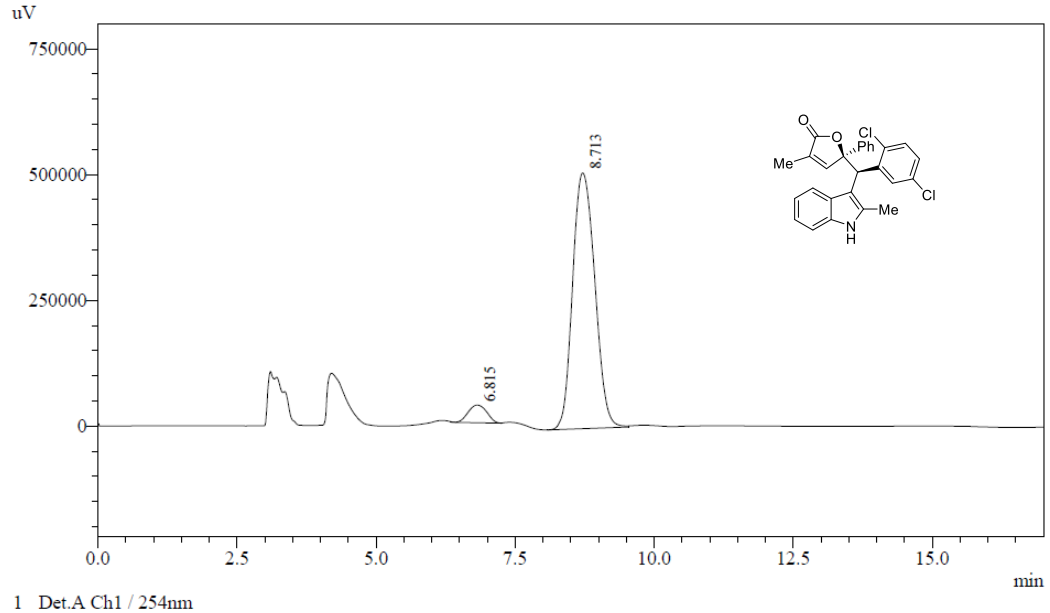




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.790	6631213	275123	49.913	52.285
2	8.704	6654258	251073	50.087	47.715
Total		13285472	526196	100.000	100.000

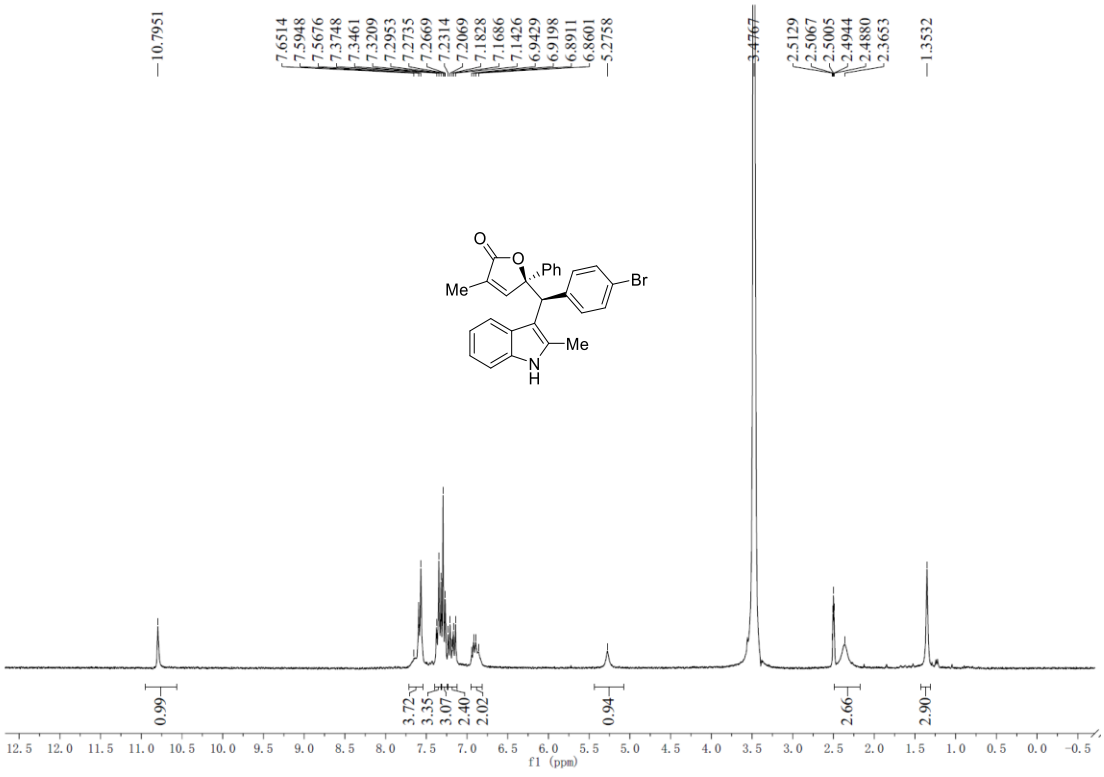


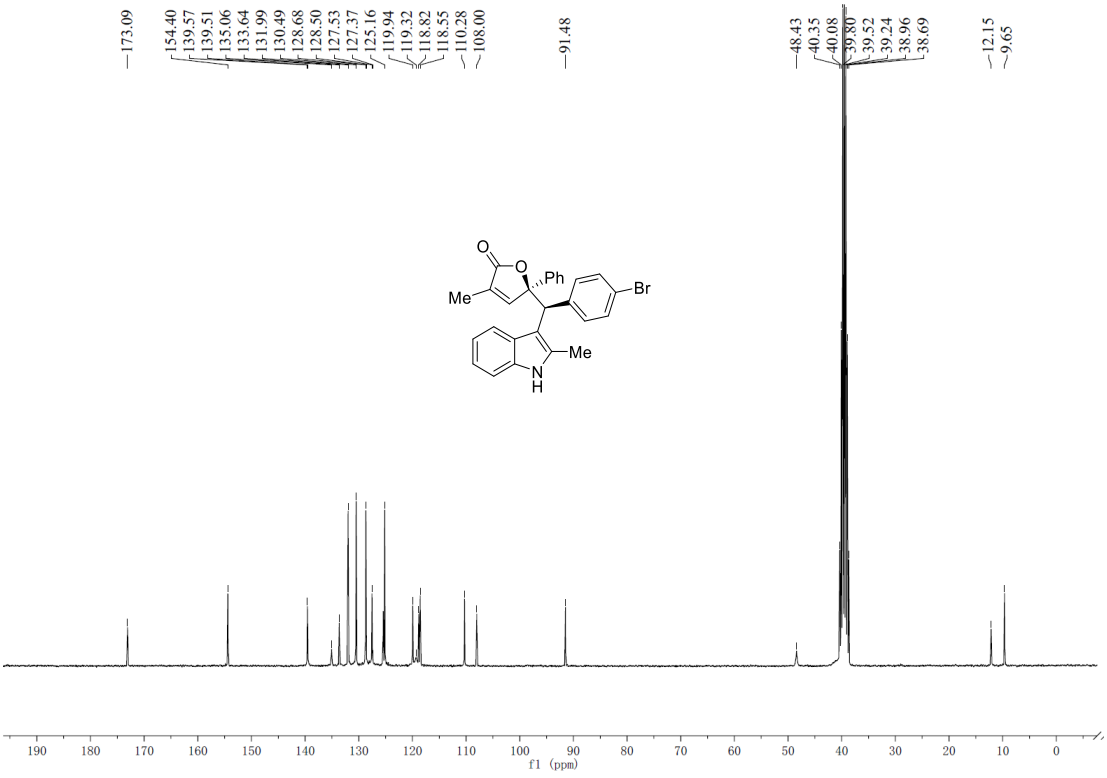
1 Det.A Ch1 / 254nm

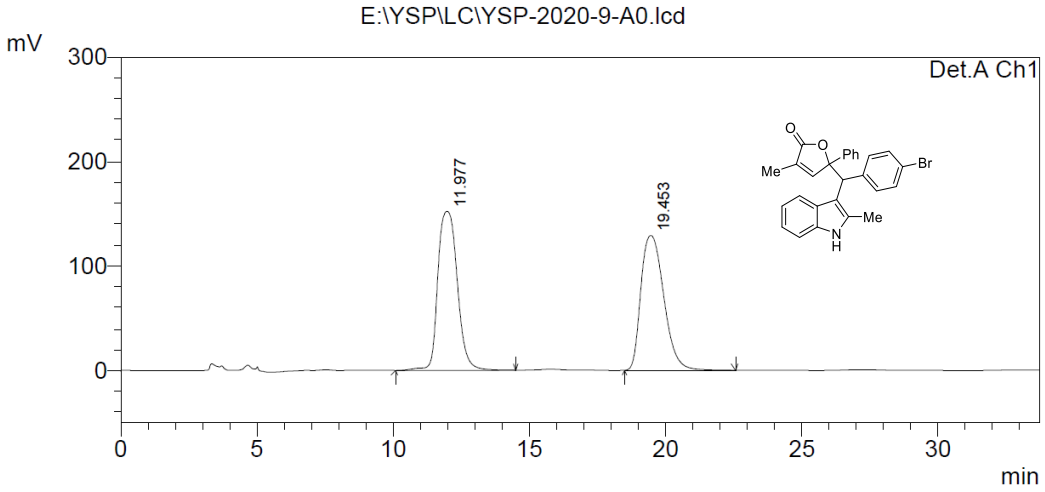
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.815	820694	35036	5.492	6.447
2	8.713	14122028	508382	94.508	93.553
Total		14942722	543418	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3g





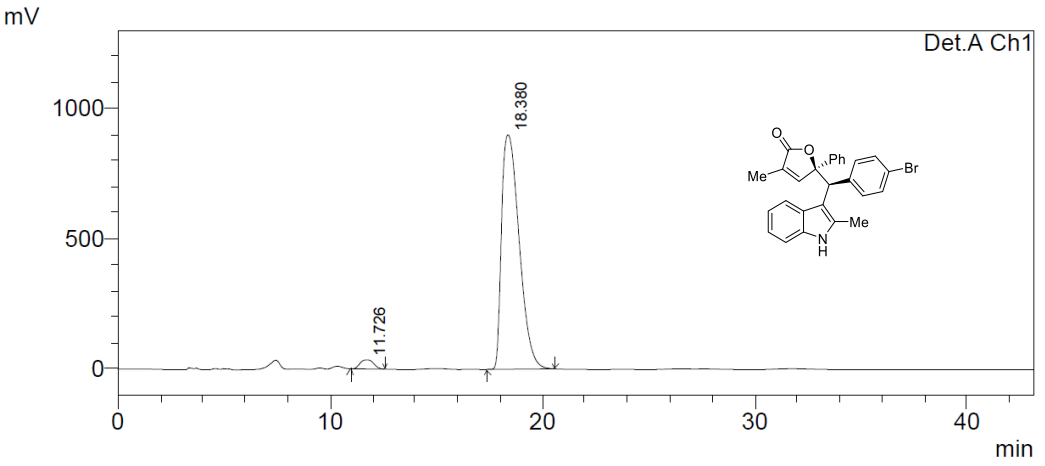


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.977	7559073	151868	50.085
2	19.453	7533455	128901	49.915
Total		15092527		100.000



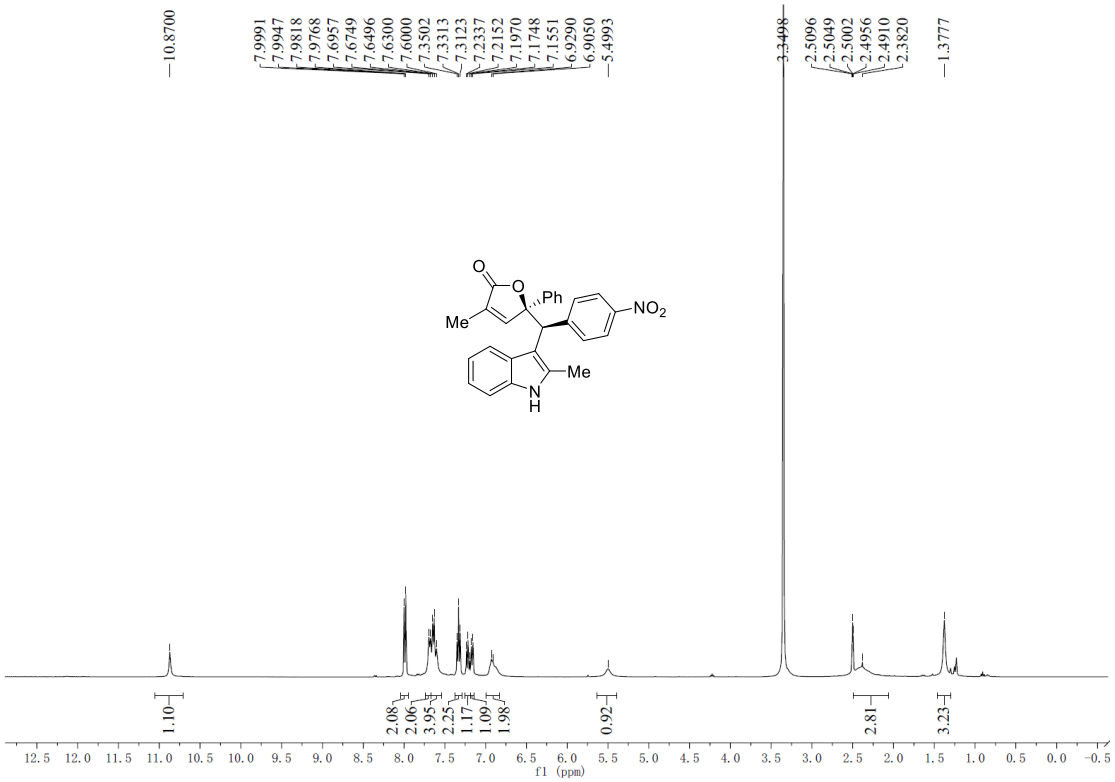
1 Det.A Ch1/254nm

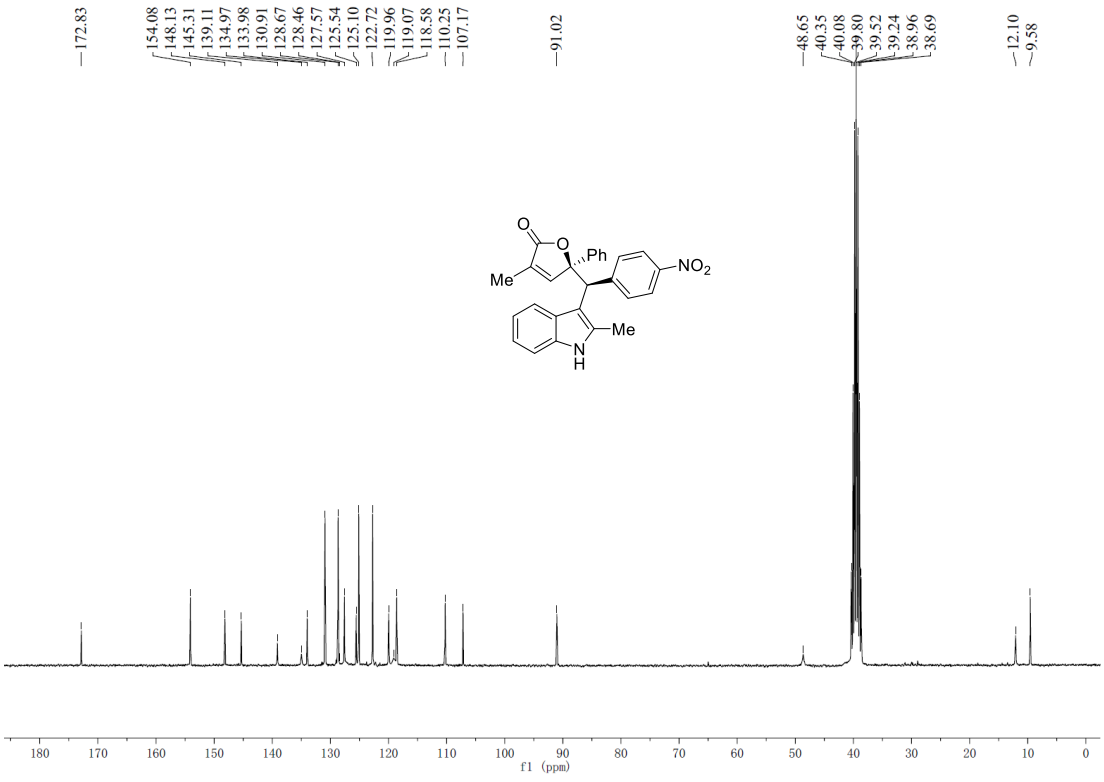
PeakTable

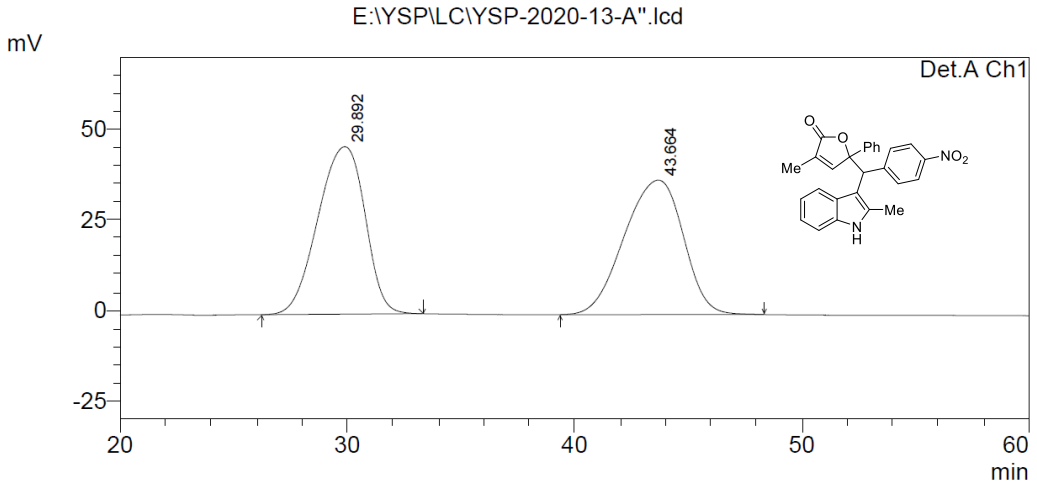
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.726	1556727	34937	2.918
2	18.380	51793224	898439	97.082
Total		53349951		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3h





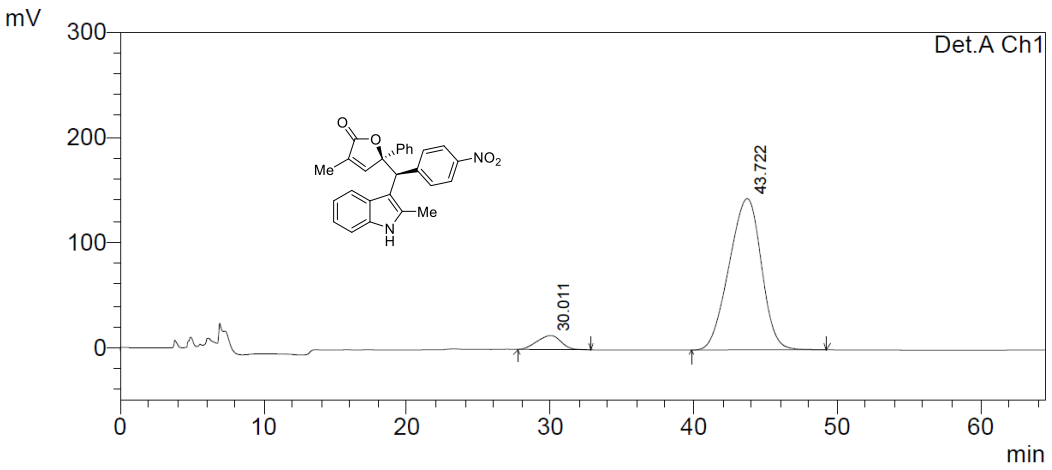


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	29.892	6684332	46245	49.846
2	43.664	6725551	37107	50.154
Total		13409883		100.000



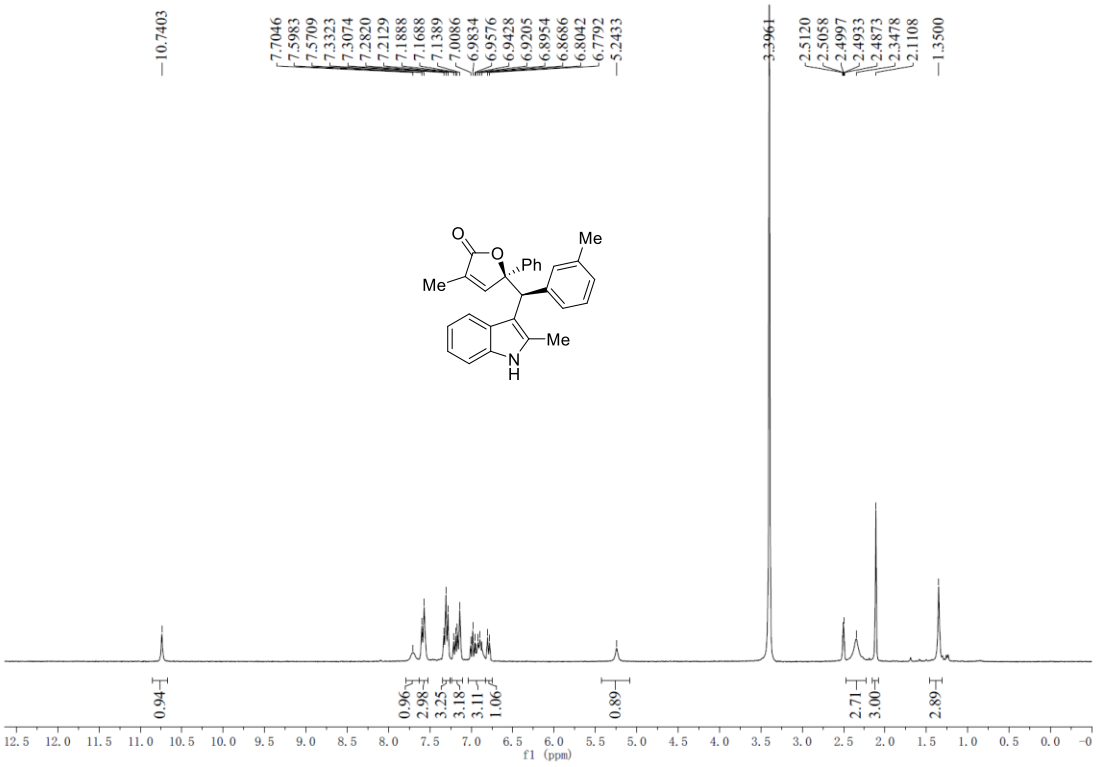
1 Det.A Ch1/254nm

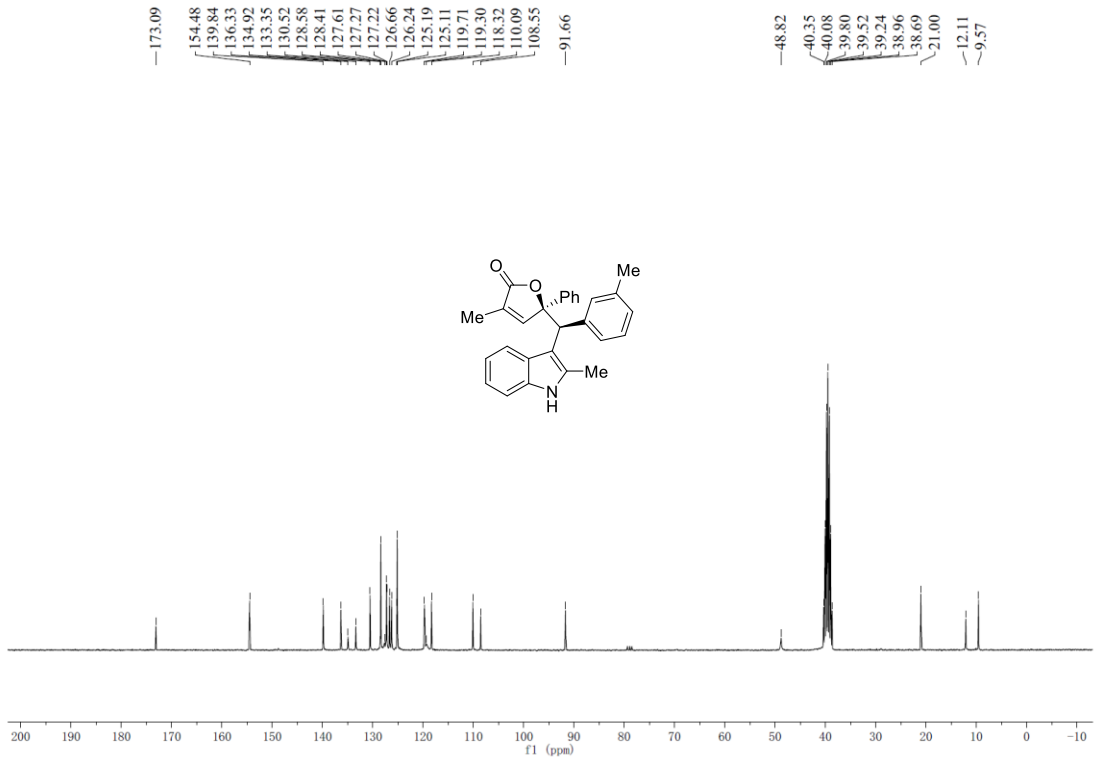
PeakTable

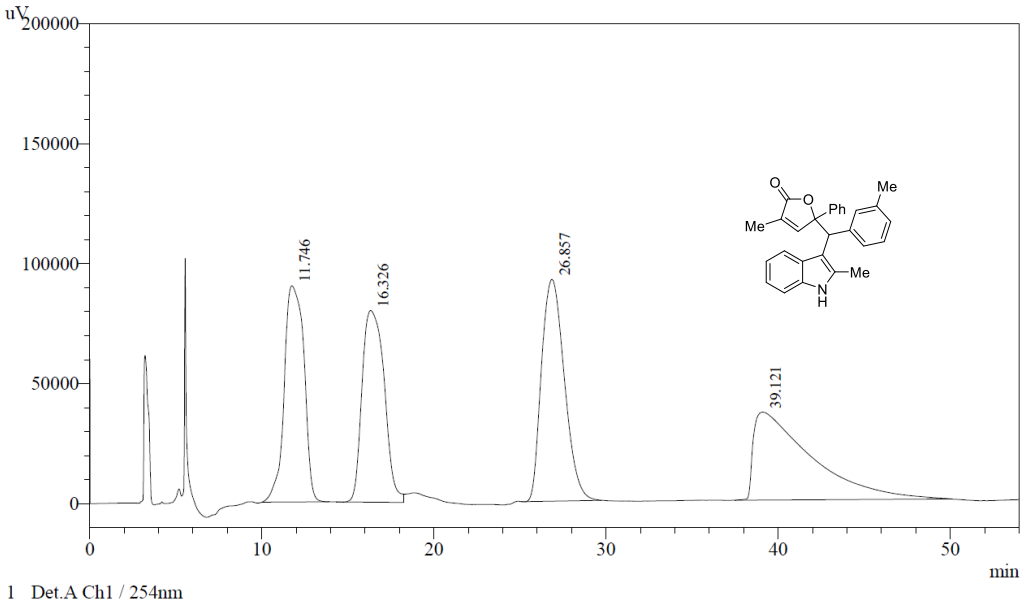
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	30.011	1538829	13293	6.401
2	43.722	22502670	143623	93.599
Total		24041499		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3i



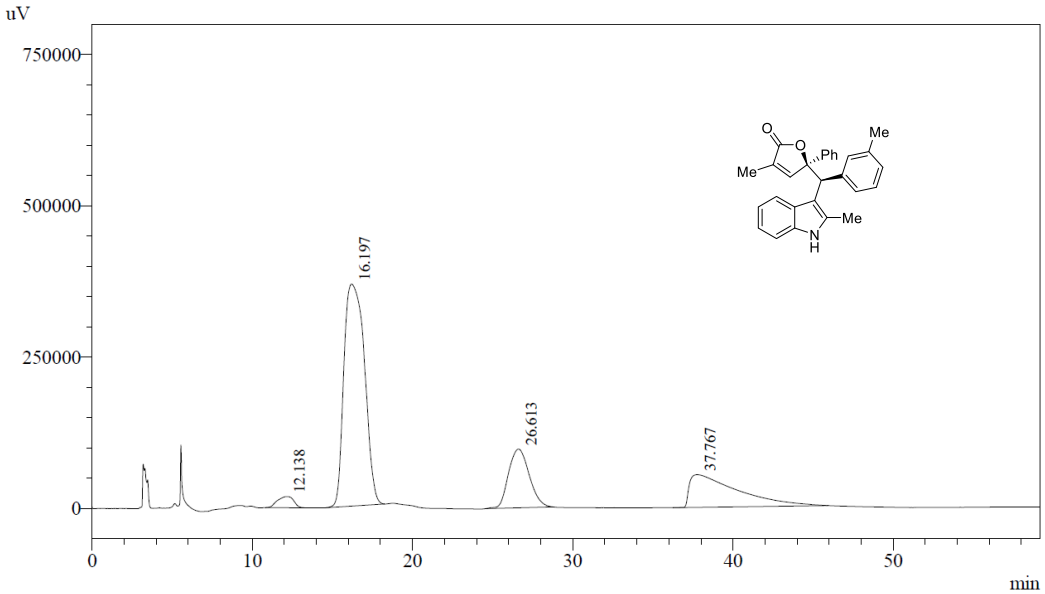




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.746	7199775	90109	22.807	30.136
2	16.326	7186139	79902	22.763	26.723
3	26.857	8563701	92358	27.127	30.888
4	39.121	8619078	36637	27.303	12.253
Total		31568693	299007	100.000	100.000

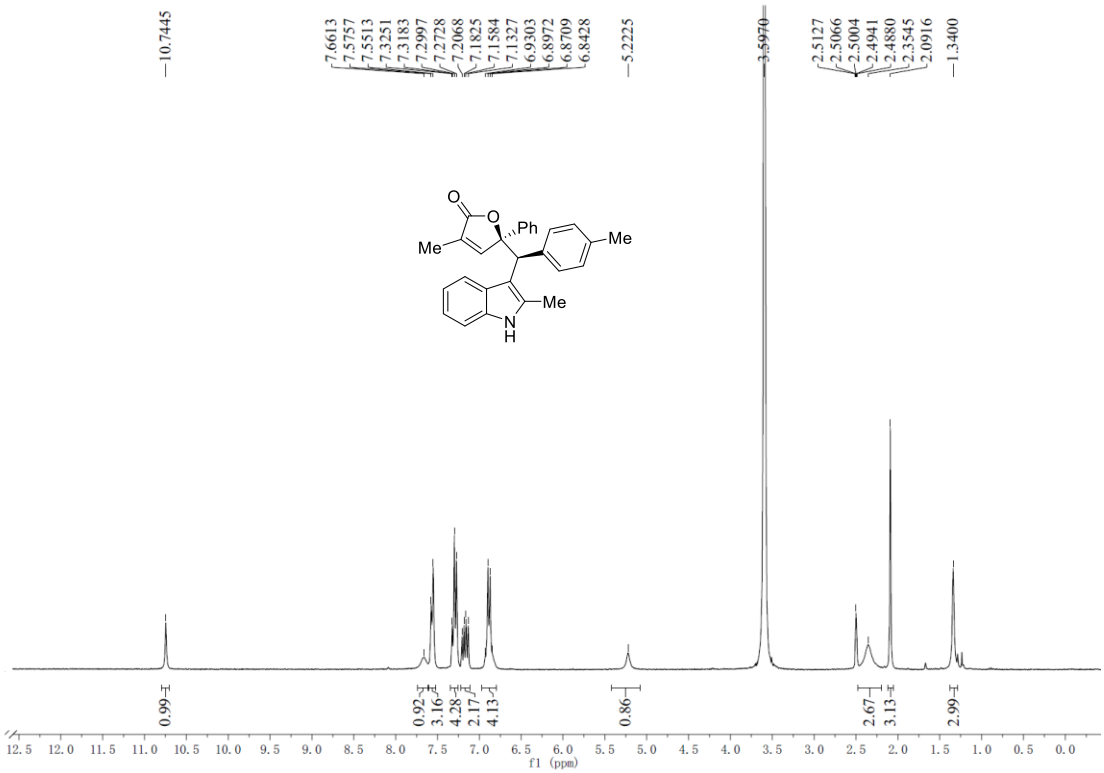


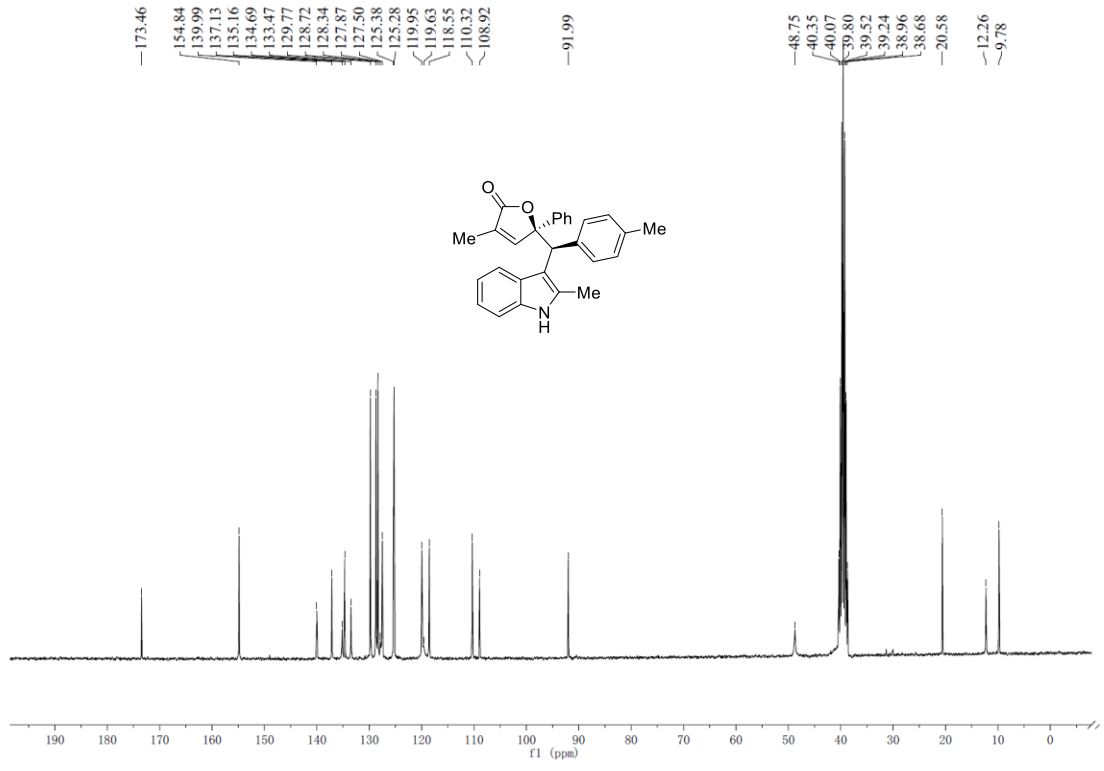
1 Det.A Ch1 / 254nm

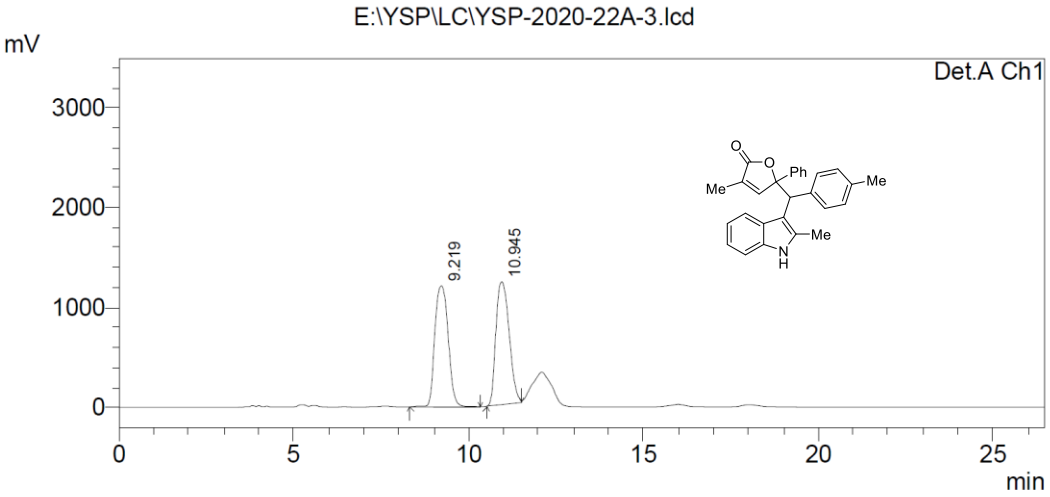
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.138	1292931	18343	2.386	3.421
2	16.197	32795708	366736	60.527	68.390
3	26.613	8744238	97156	16.138	18.118
4	37.767	11350987	54006	20.949	10.071
Total		54183864	536240	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3j





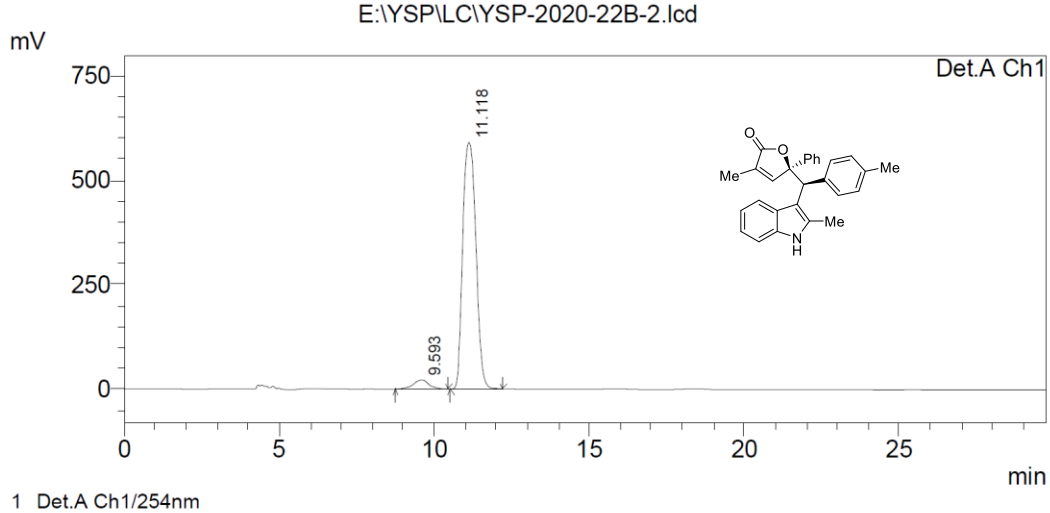


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.219	32535785	1214550	50.048
2	10.945	32473279	1230594	49.952
Total		65009063		100.000



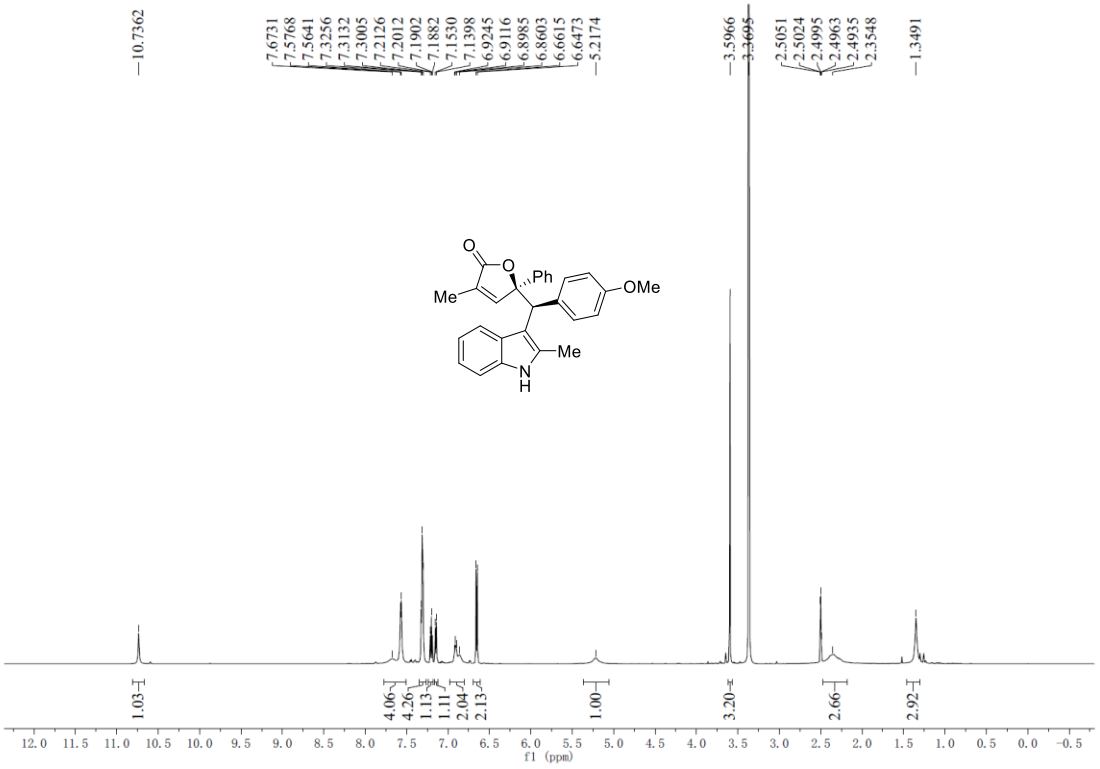
1 Det.A Ch1/254nm

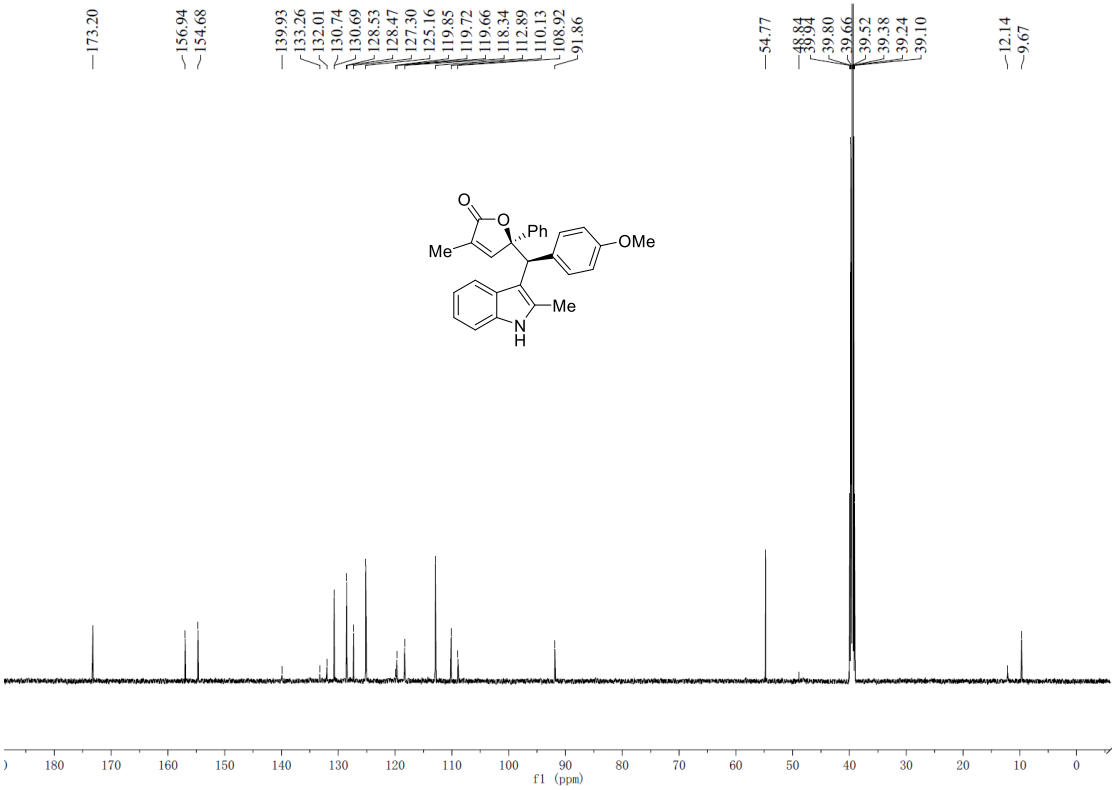
PeakTable

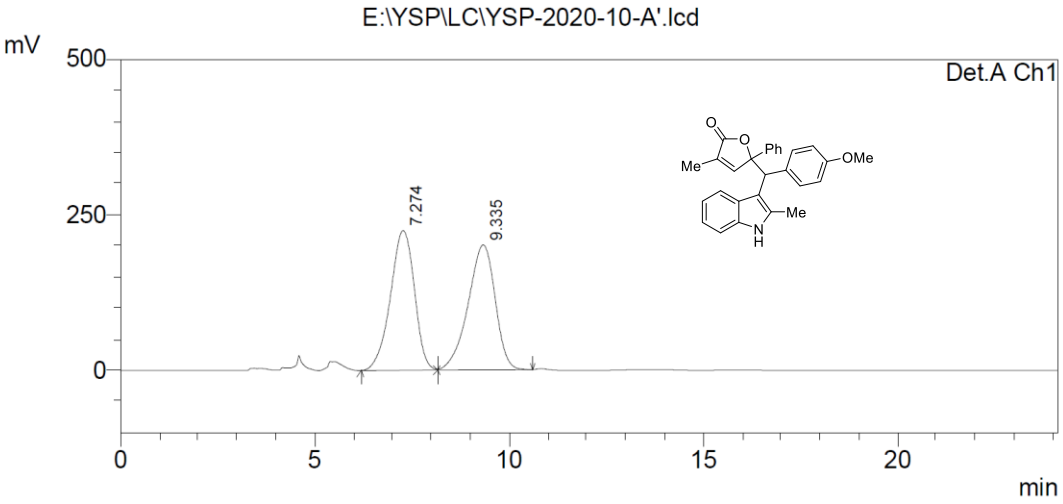
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.593	791130	21712	4.340
2	11.118	17439354	590343	95.660
Total		18230485		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3k





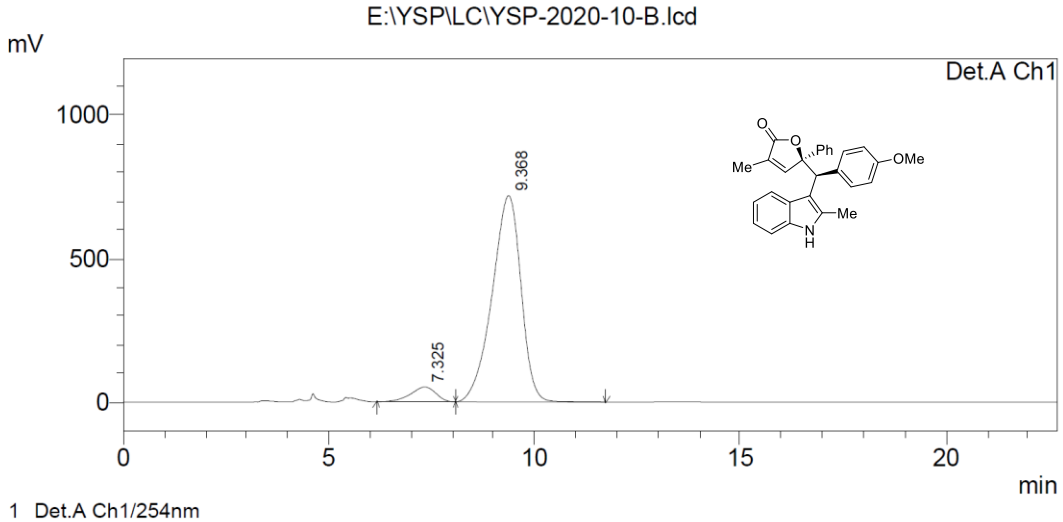


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.274	9650333	224266	49.763
2	9.335	9742447	200554	50.237
Total		19392780		100.000



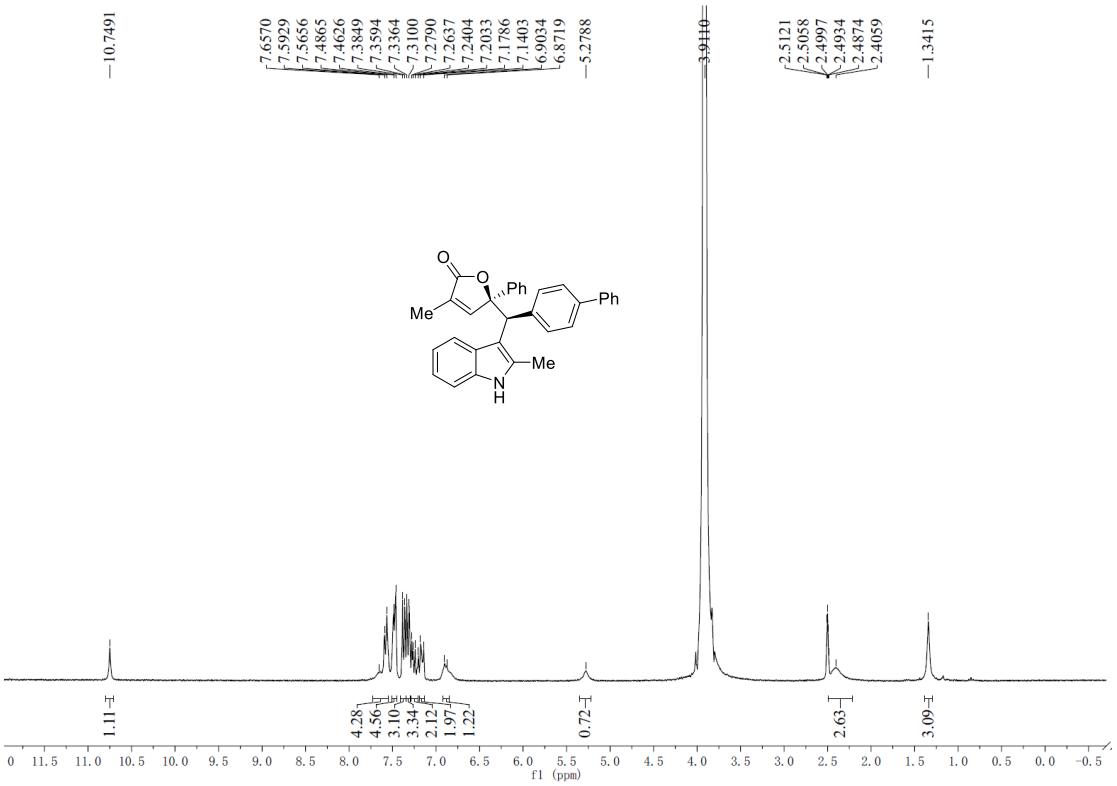
1 Det.A Ch1/254nm

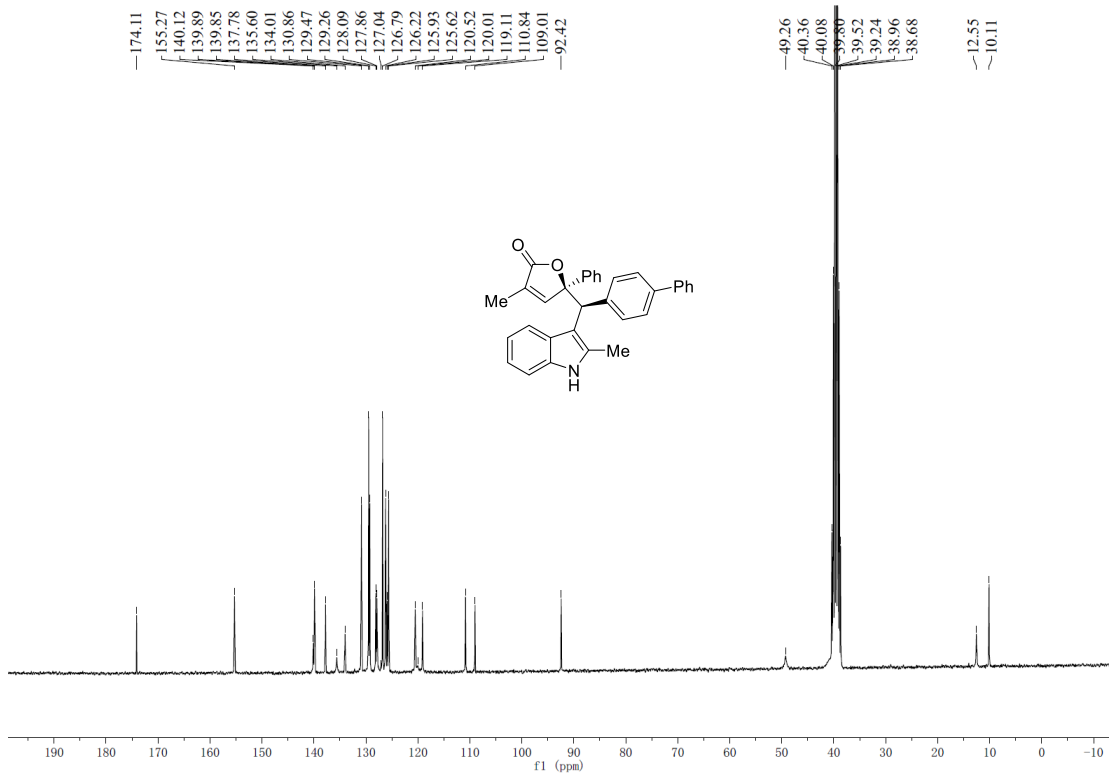
PeakTable

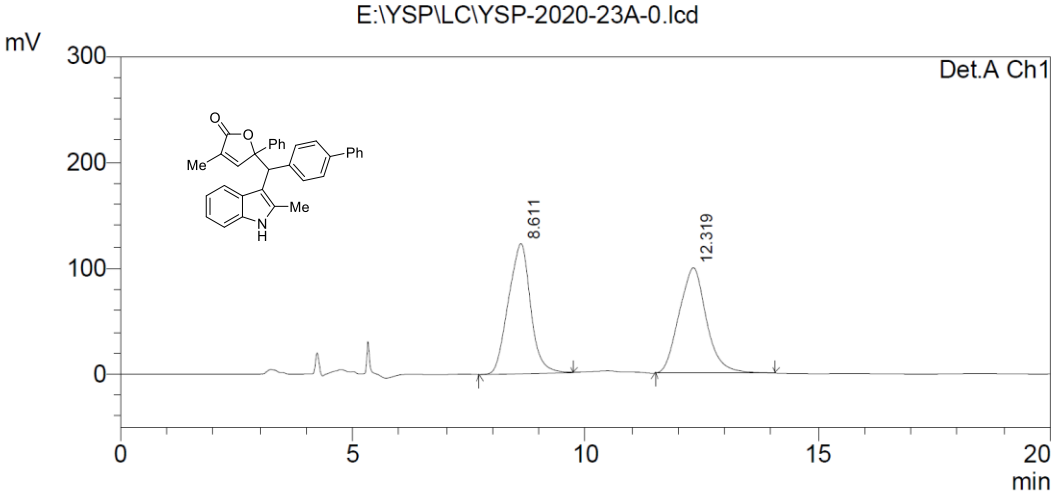
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.325	2194649	51379	5.888
2	9.368	35076888	718780	94.112
Total		37271537		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3l





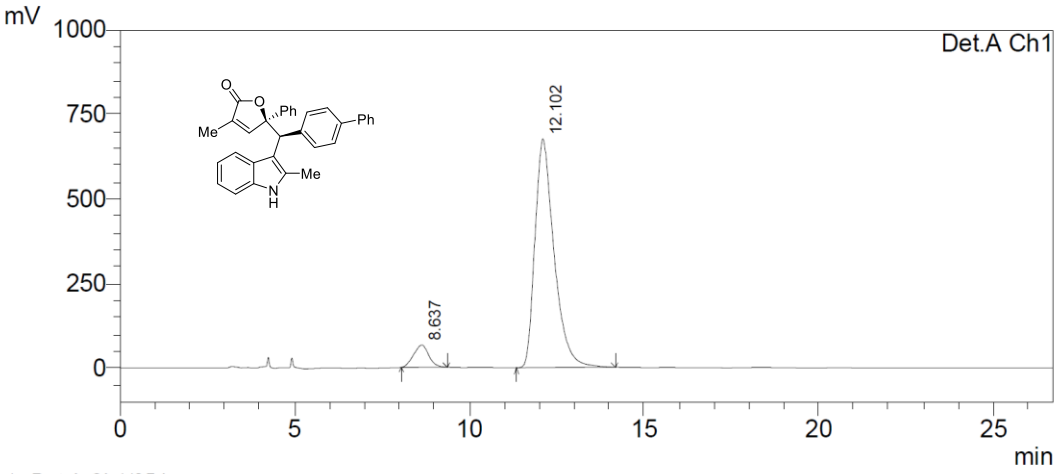


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.611	4084566	122819	50.113
2	12.319	4066168	99409	49.887
Total		8150733		100.000



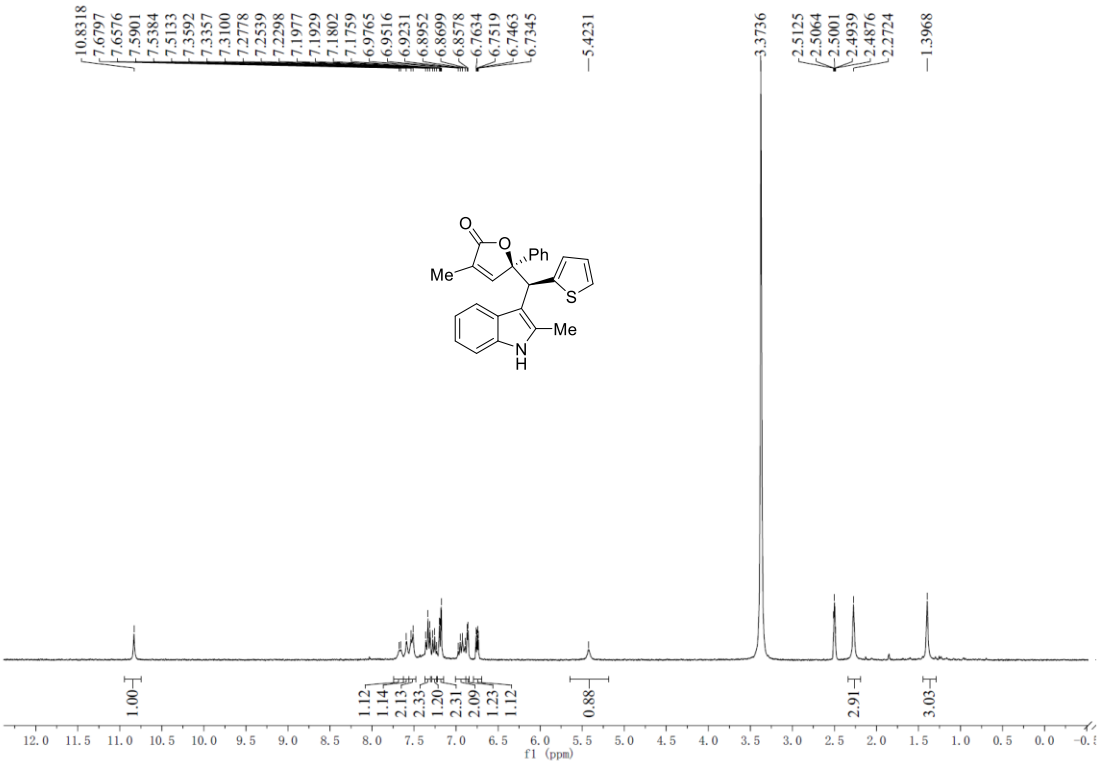
1 Det.A Ch1/254nm

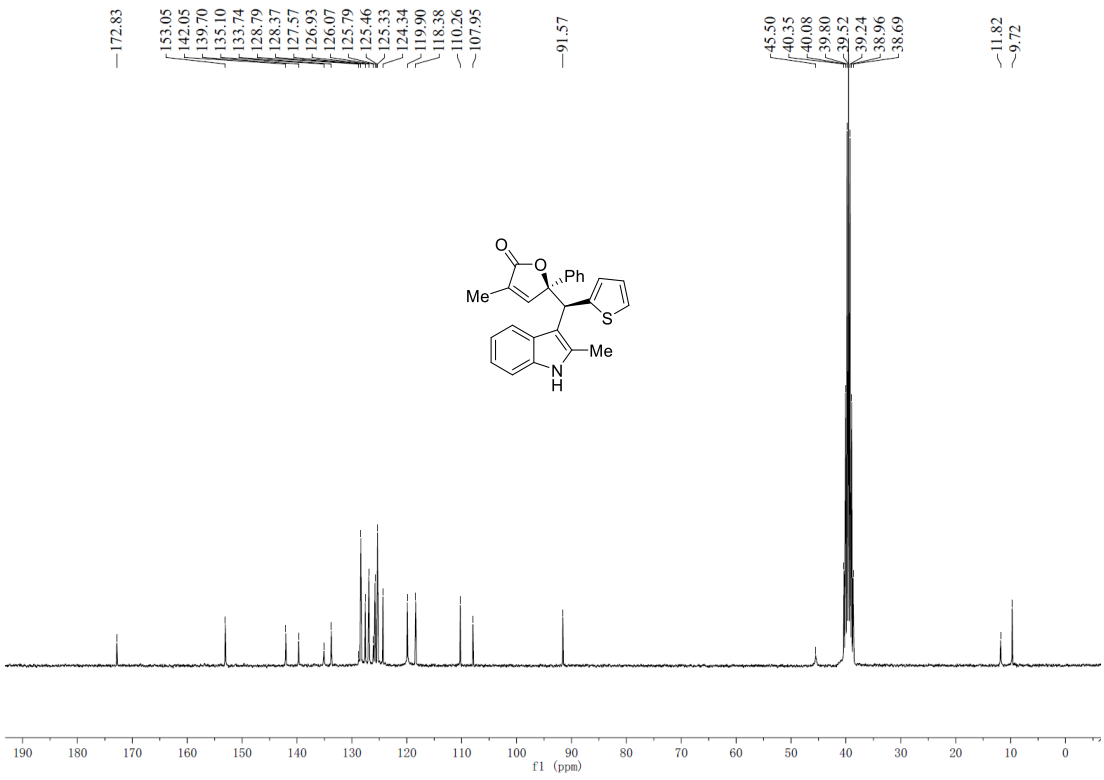
PeakTable

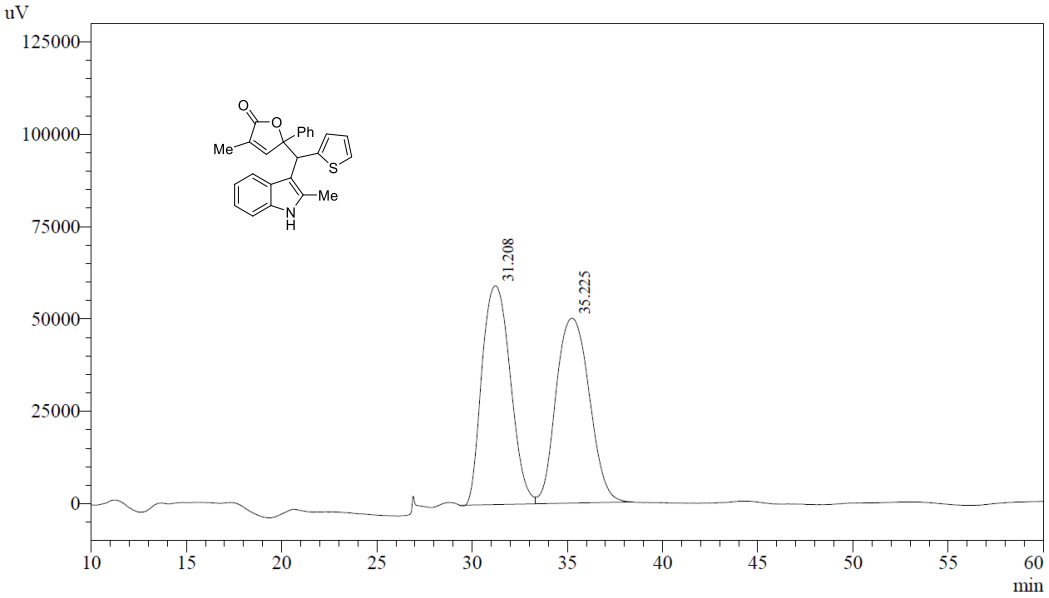
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.637	1995741	66018	7.197
2	12.102	25734176	675830	92.803
Total		27729917		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3m



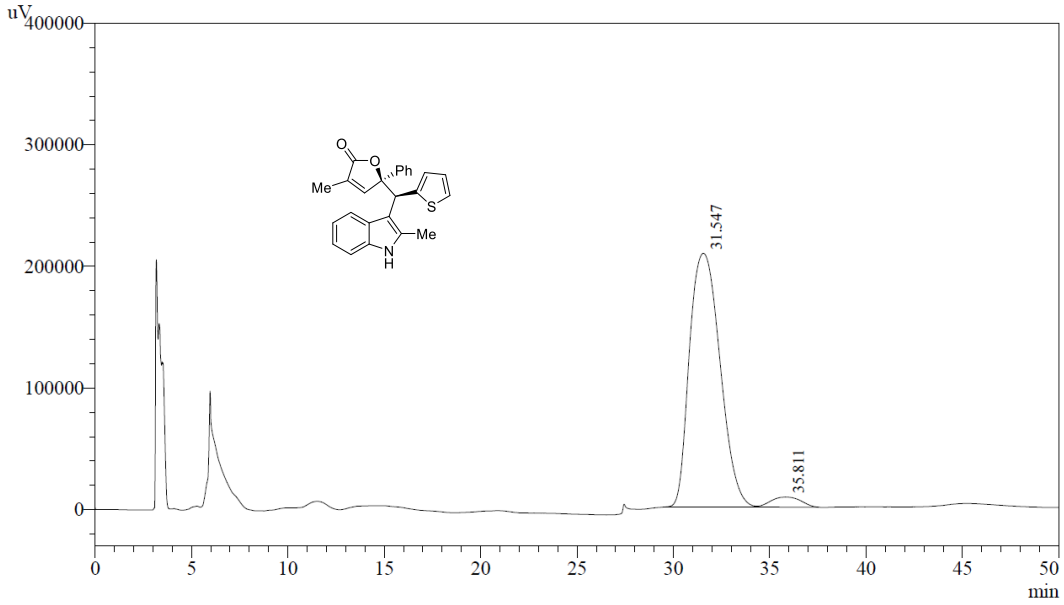




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.208	6174210	59272	50.269	54.228
2	35.225	6108132	50030	49.731	45.772
Total		12282342	109302	100.000	100.000

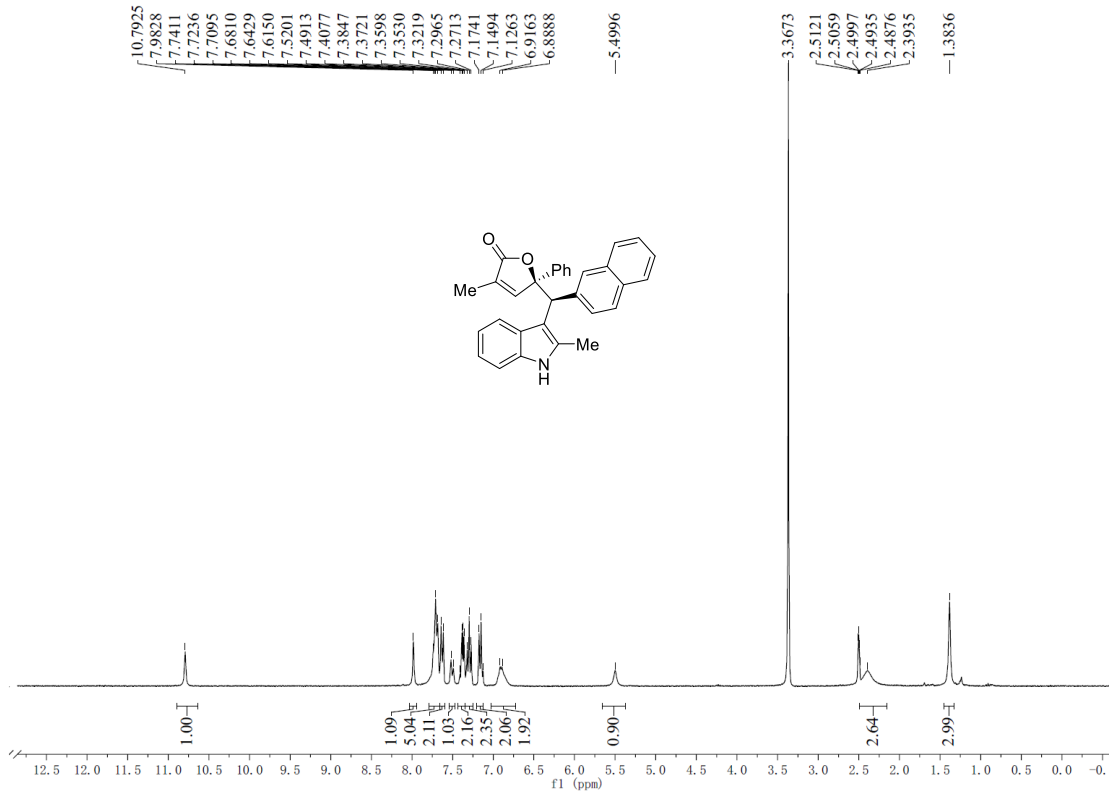


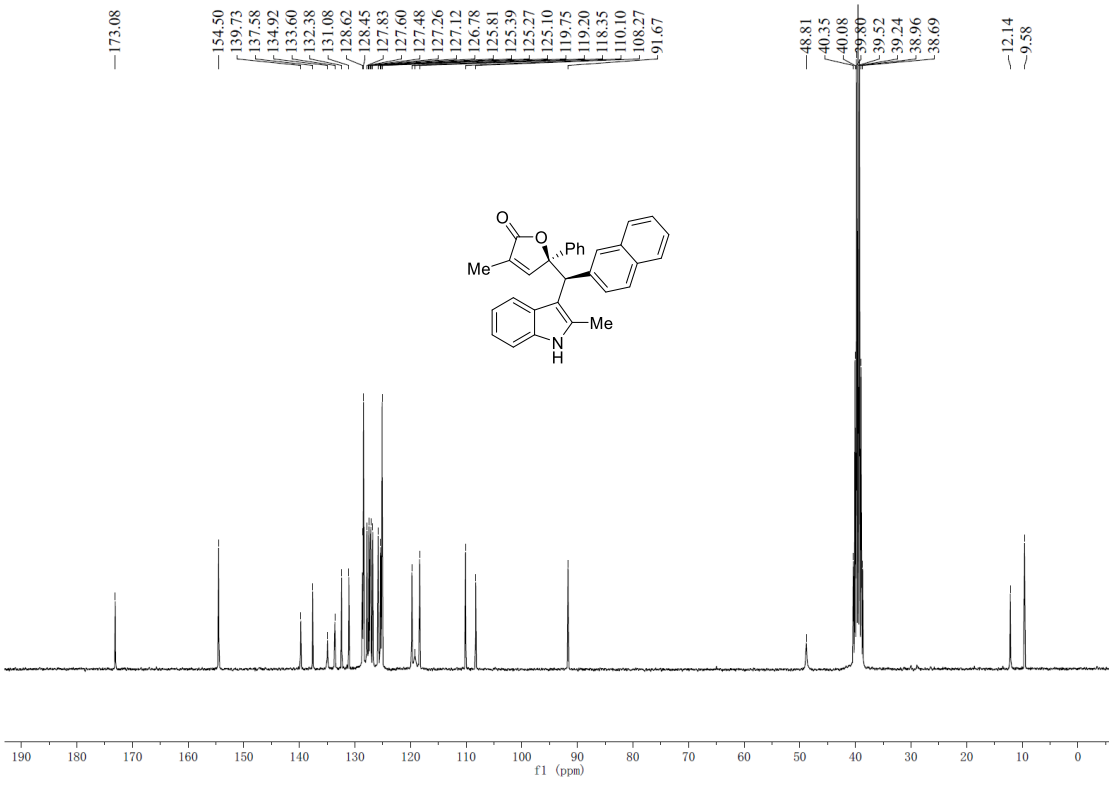
1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

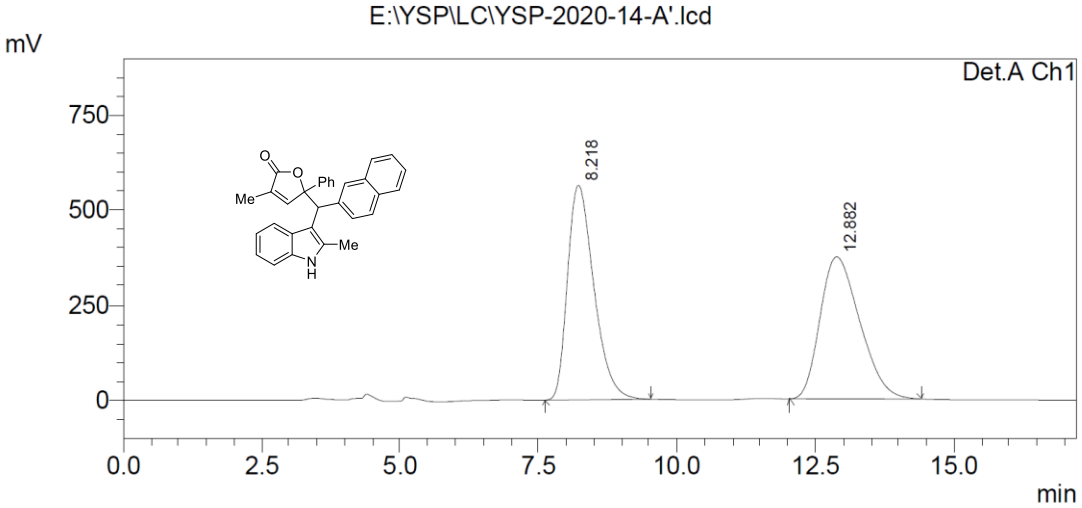
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.547	23015564	208584	96.262	96.172
2	35.811	893666	8302	3.738	3.828
Total		23909230	216886	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3n





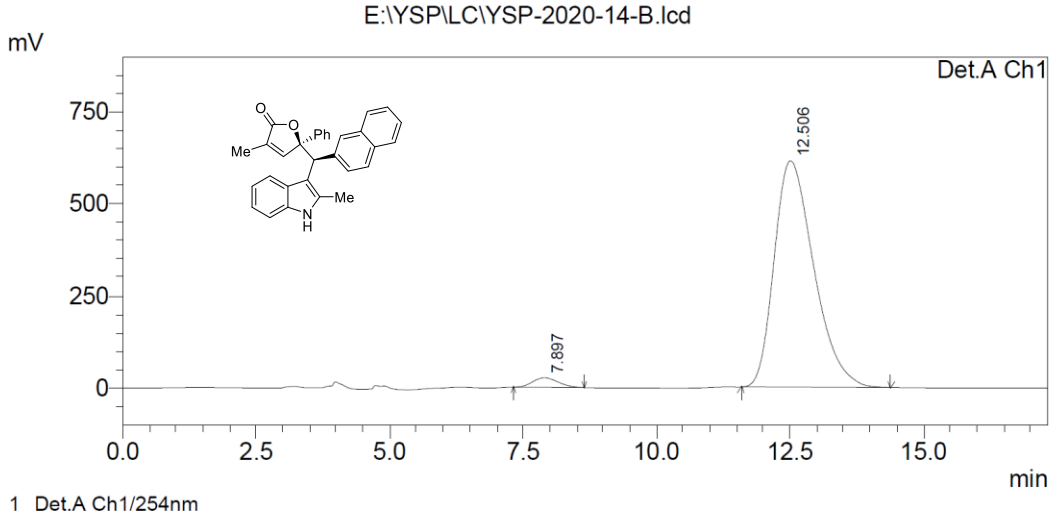
HPLC of major 3n



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.218	18729163	564340	50.125
2	12.882	18636074	373536	49.875
Total		37365237		100.000

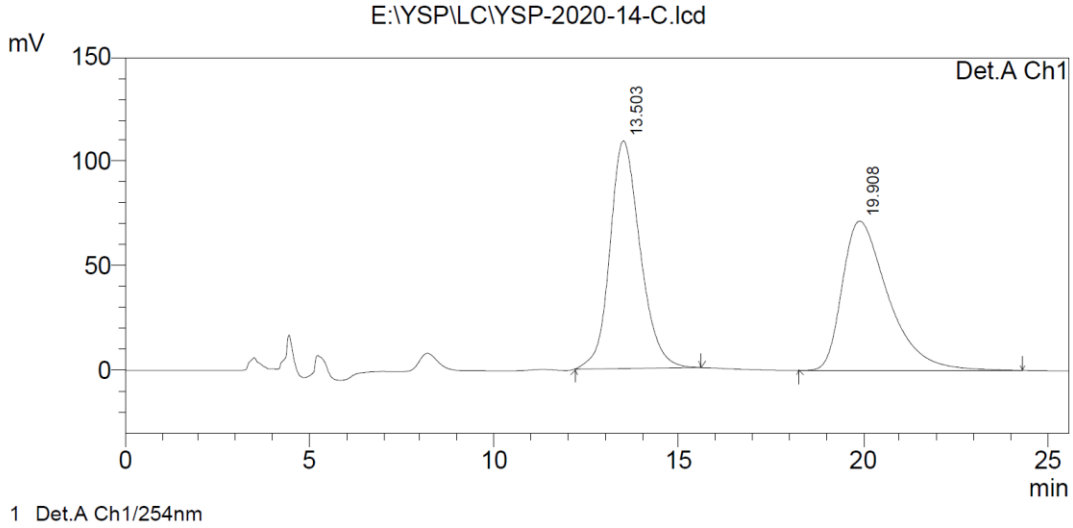


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.897	851279	25608	2.616
2	12.506	31689272	614082	97.384
Total		32540552		100.000

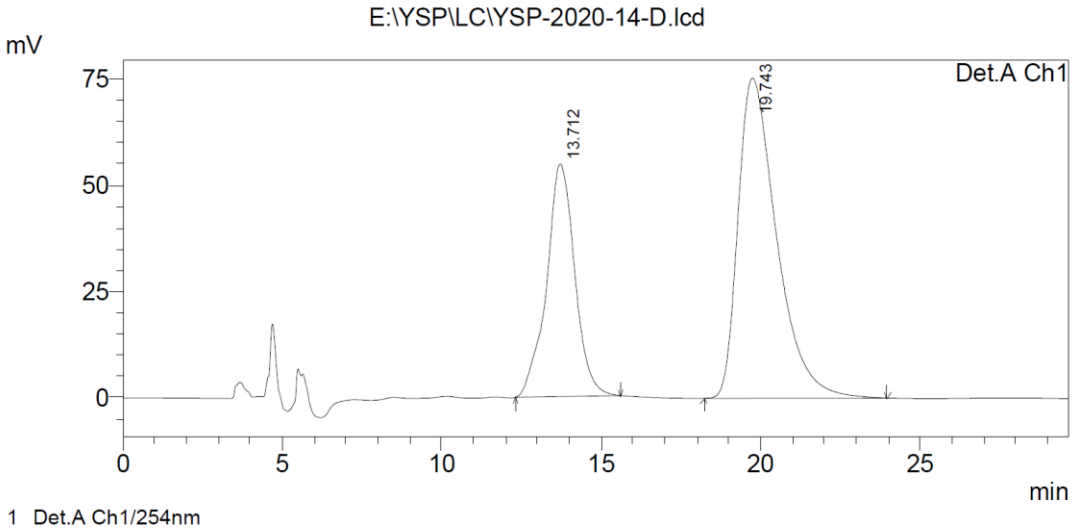
HPLC of minor 3n



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.503	6238017	109034	50.182
2	19.908	6192886	71425	49.818
Total		12430904		100.000

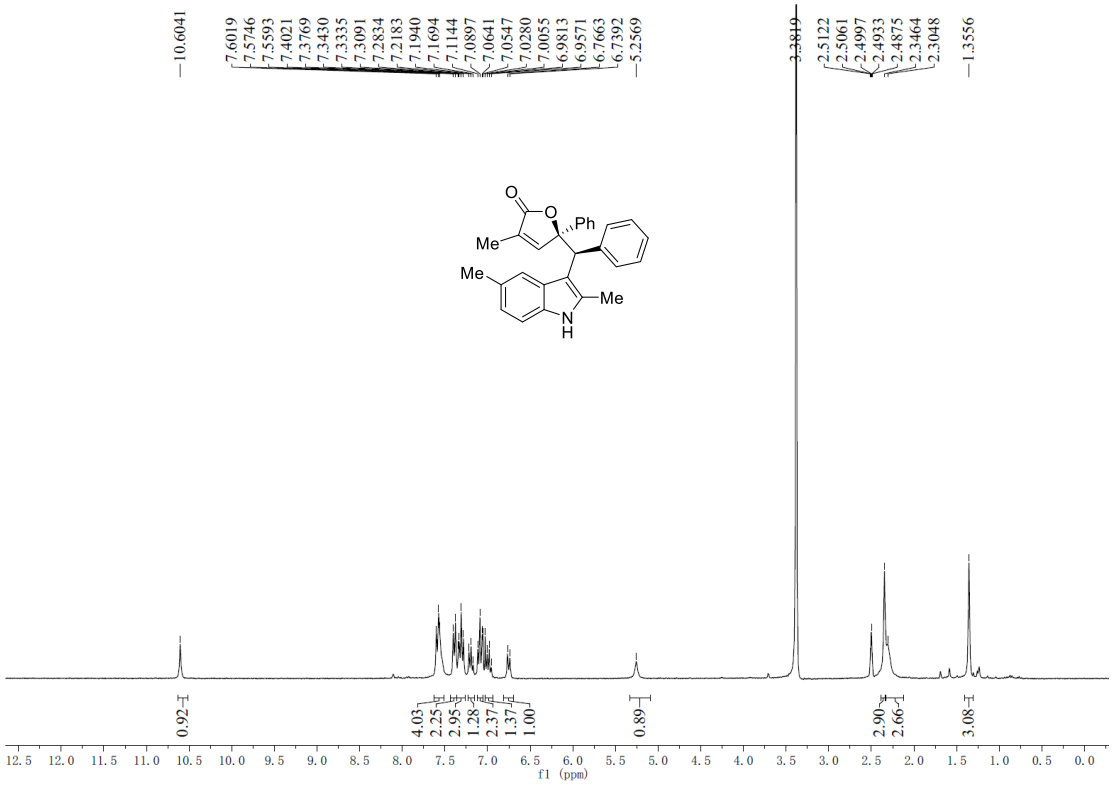


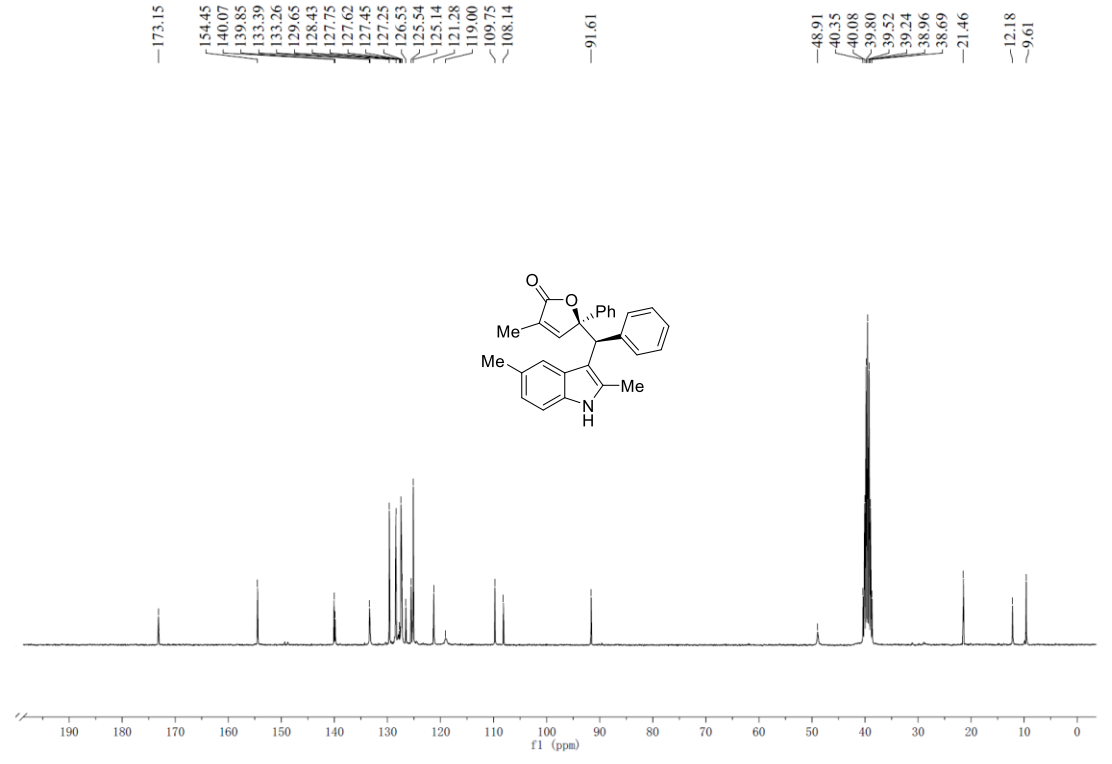
PeakTable

Detector A Ch1 254nm

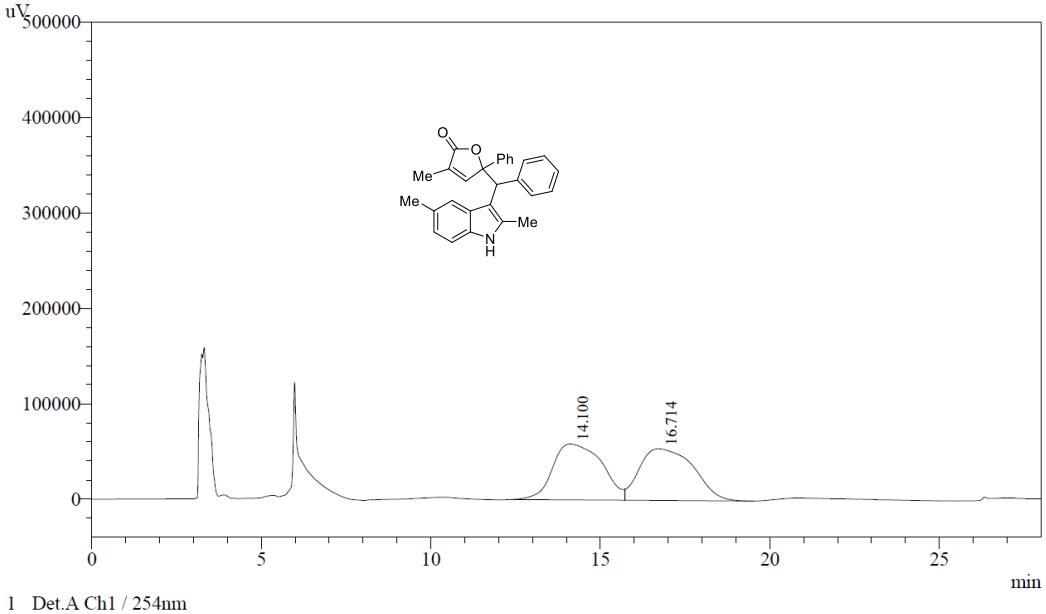
Peak#	Ret. Time	Area	Height	Area %
1	13.712	3377401	54716	34.773
2	19.743	6335194	75281	65.227
Total		9712595		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3o





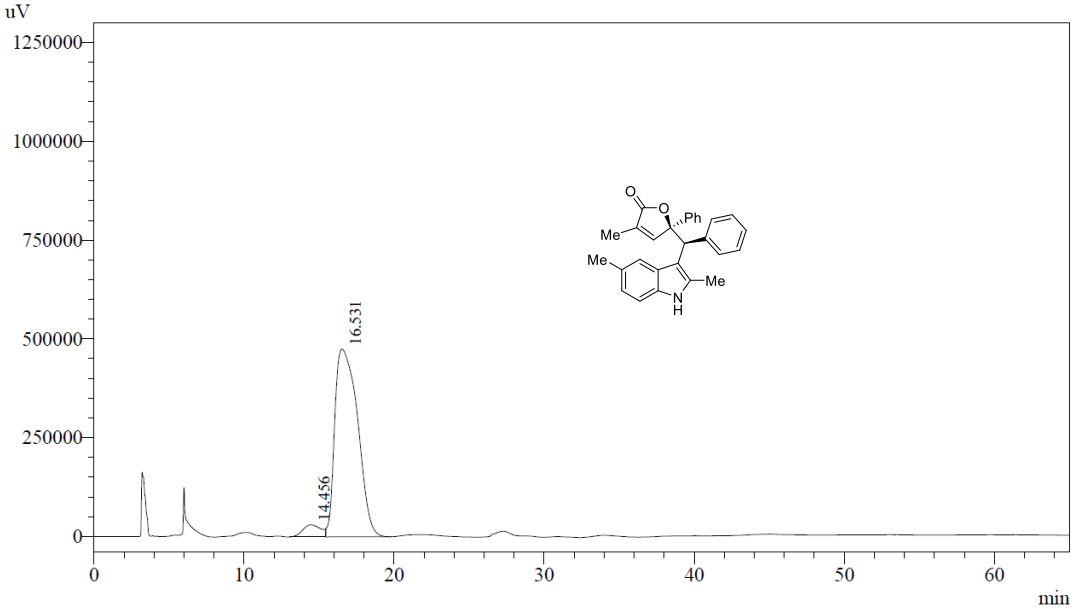
HPLC of major 3o



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.100	5934430	58564	49.733	51.995
2	16.714	5998073	54070	50.267	48.005
Total		11932504	112634	100.000	100.000

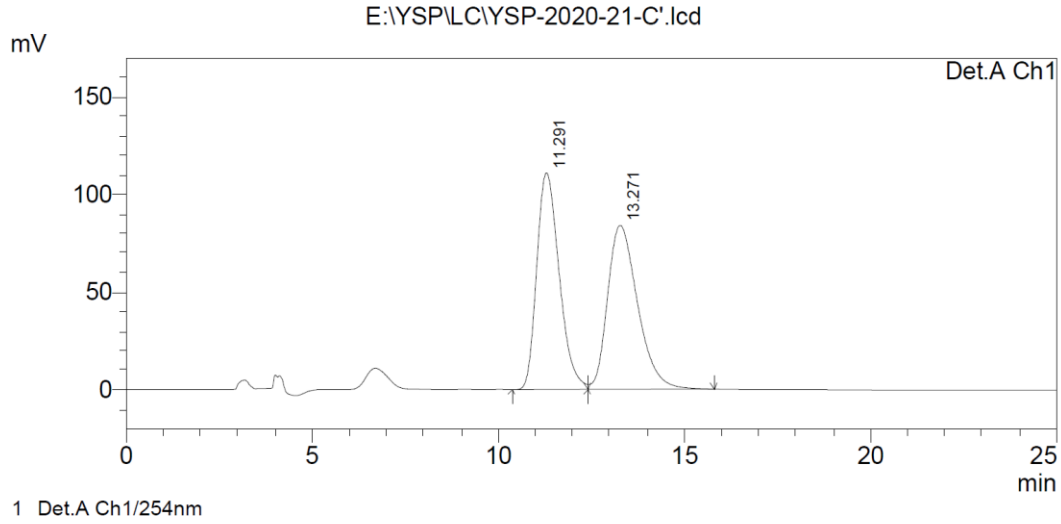


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.456	2572219	30497	4.866	6.031
2	16.531	50291293	475194	95.134	93.969
Total		52863512	505691	100.000	100.000

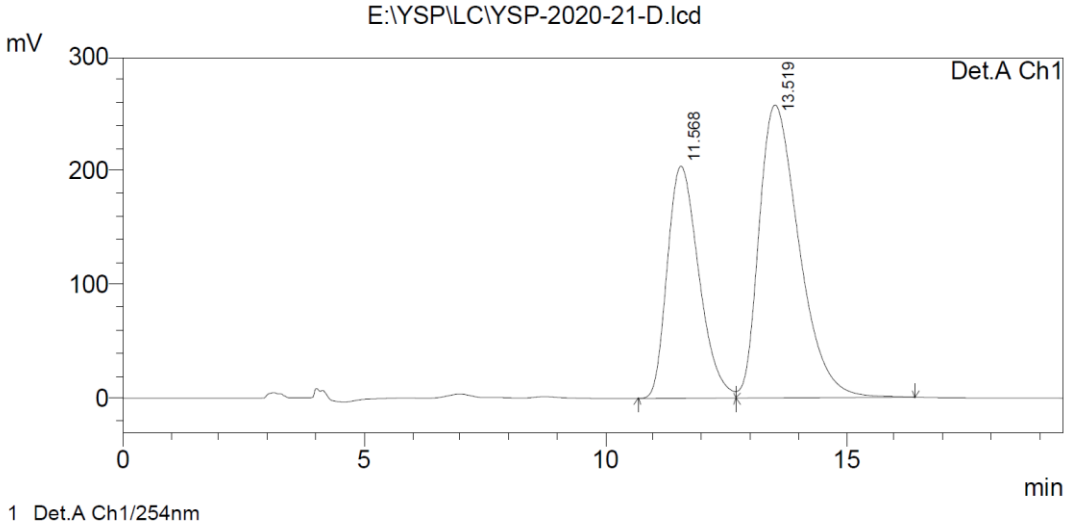
HPLC of minor 3o



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.291	4659489	110935	49.687
2	13.271	4718178	83988	50.313
Total		9377667		100.000

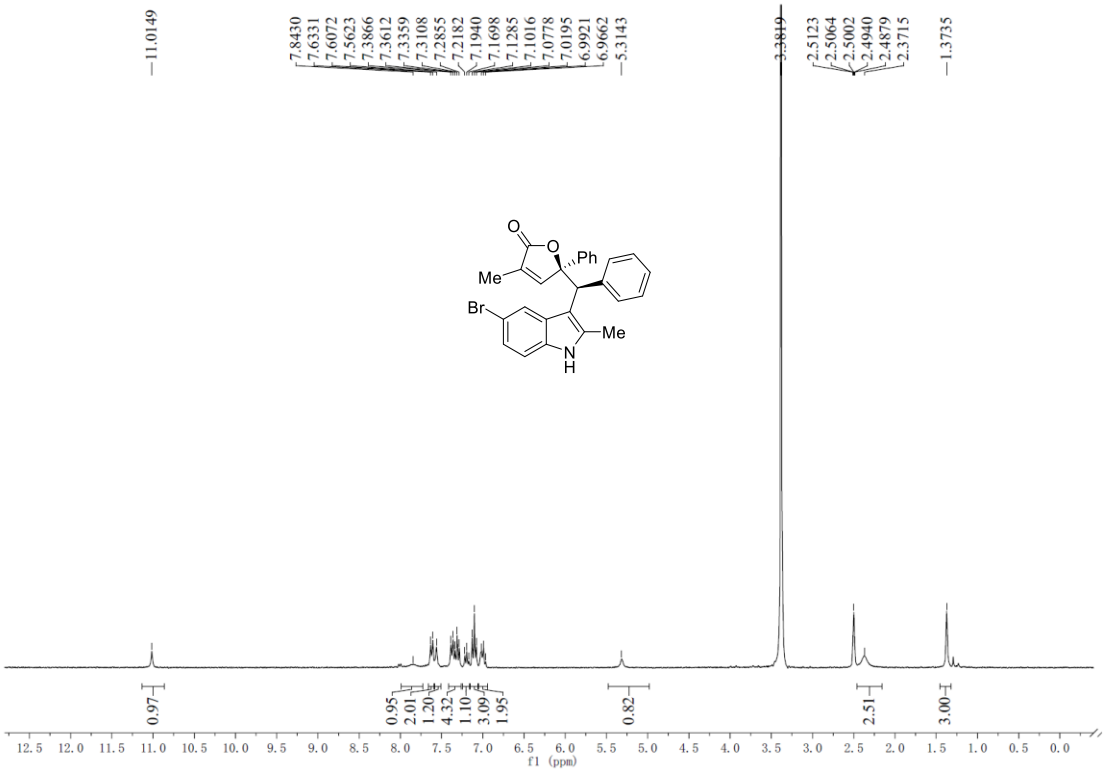


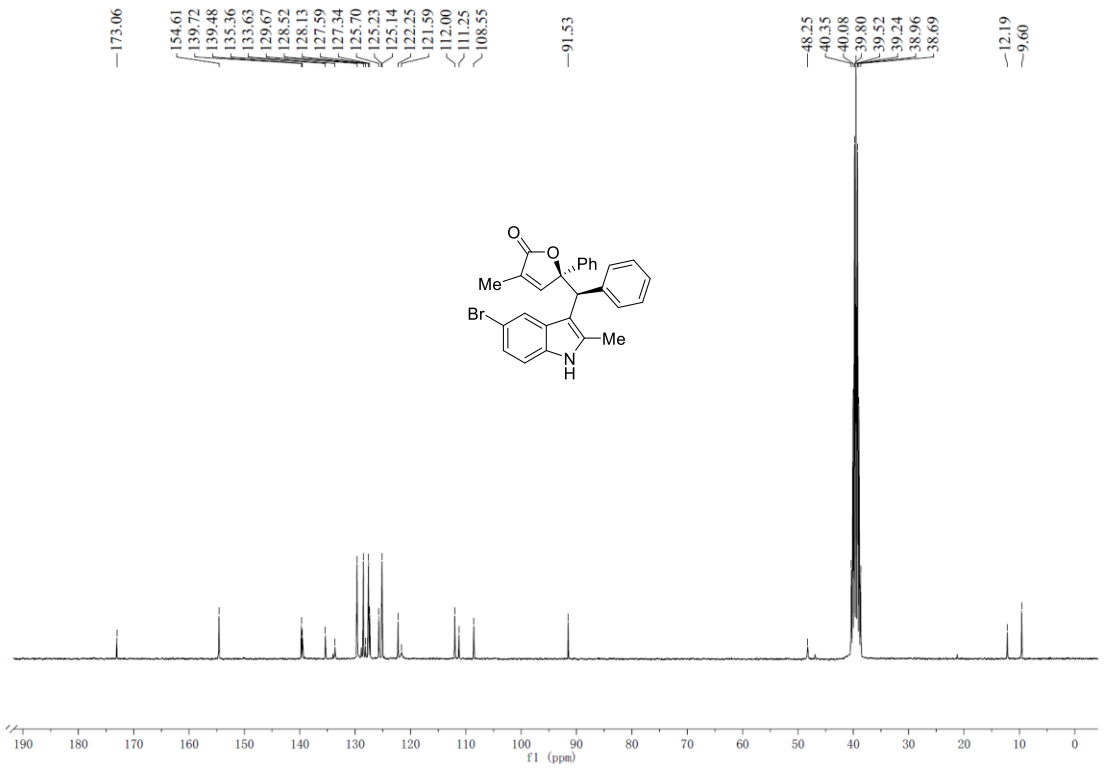
PeakTable

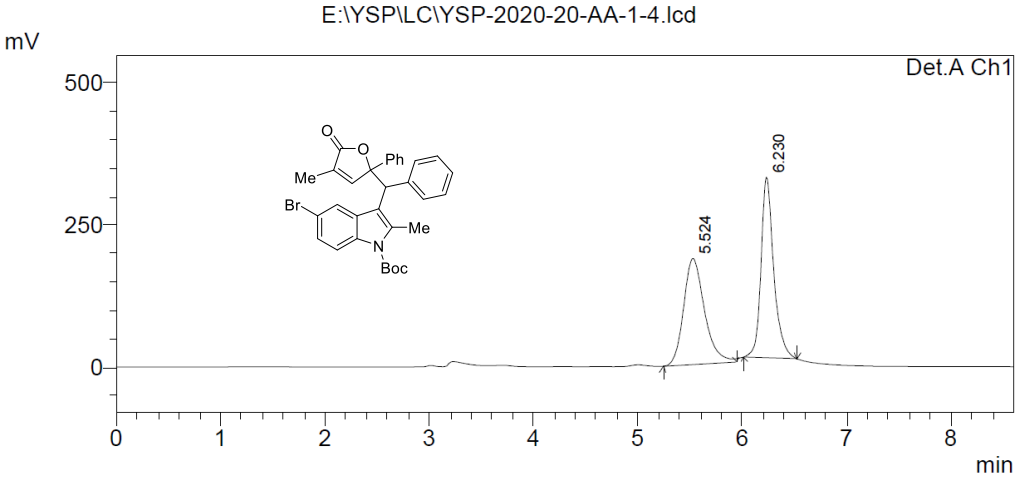
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.568	9301351	204055	38.540
2	13.519	14833029	257464	61.460
Total		24134380		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3p





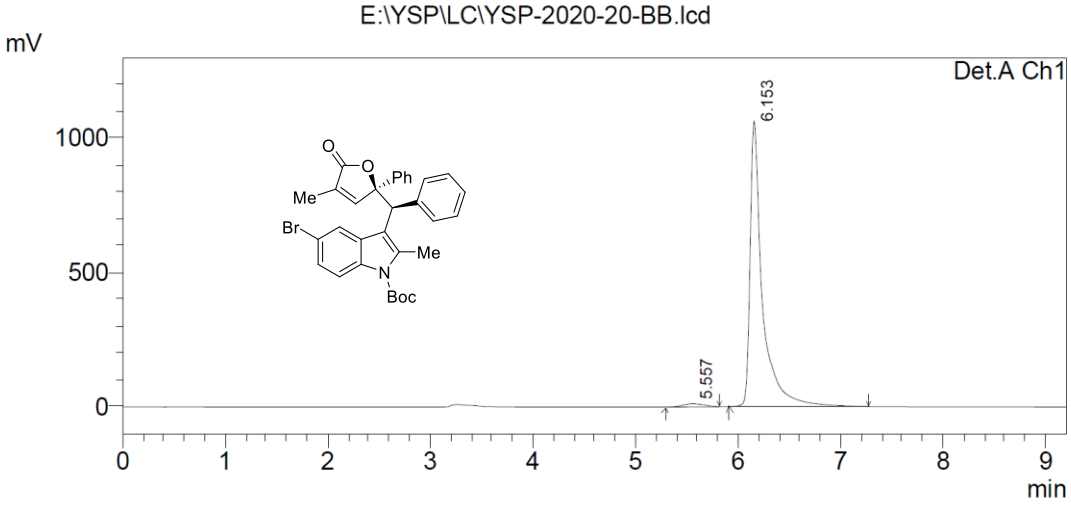


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.524	2610528	186660	49.306
2	6.230	2684017	317594	50.694
Total		5294546		100.000



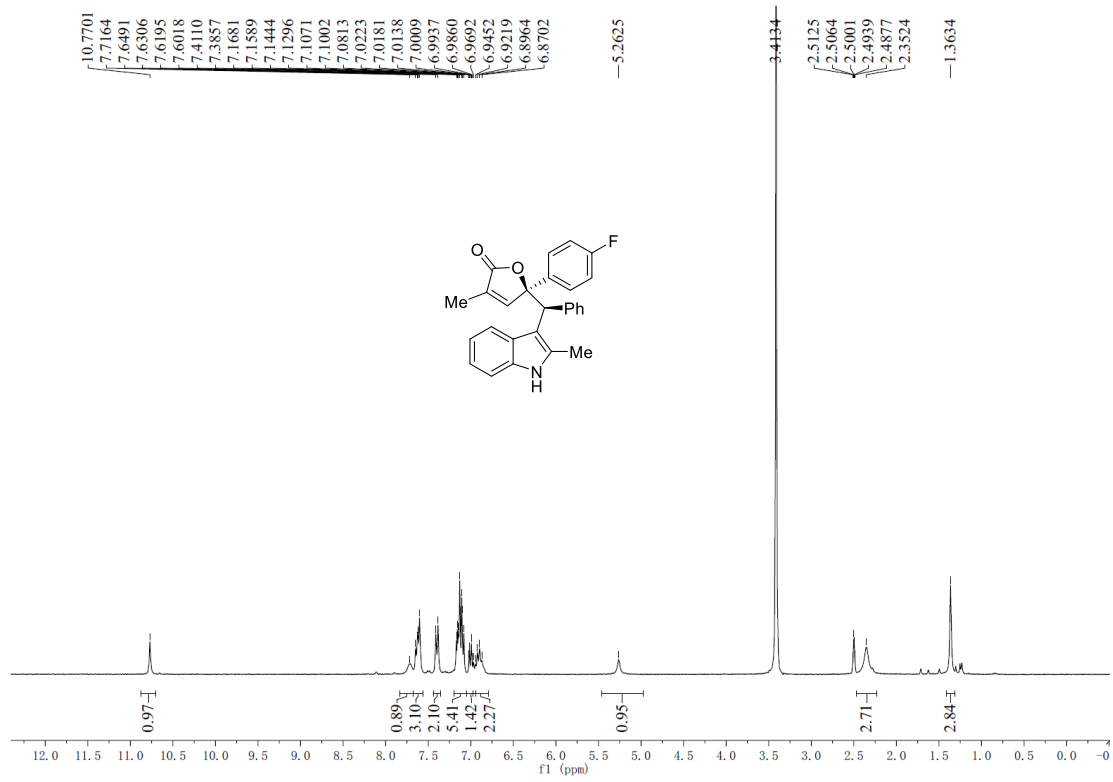
1 Det.A Ch1/254nm

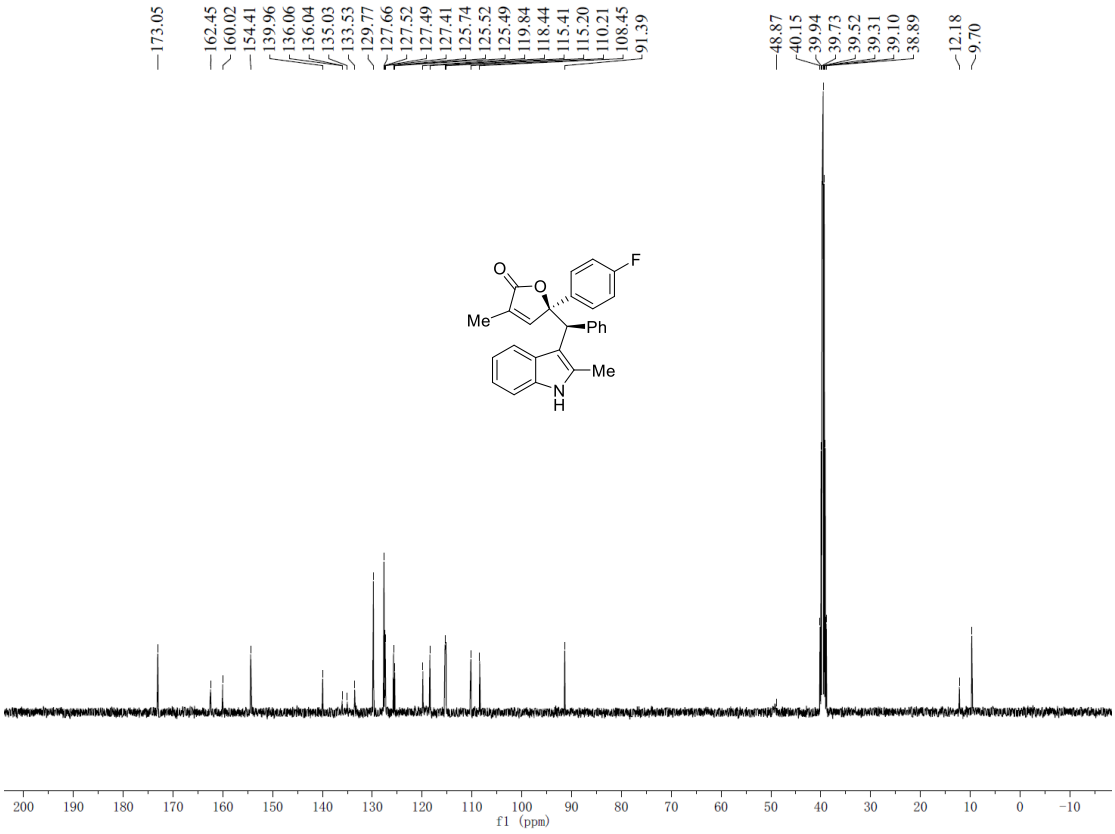
PeakTable

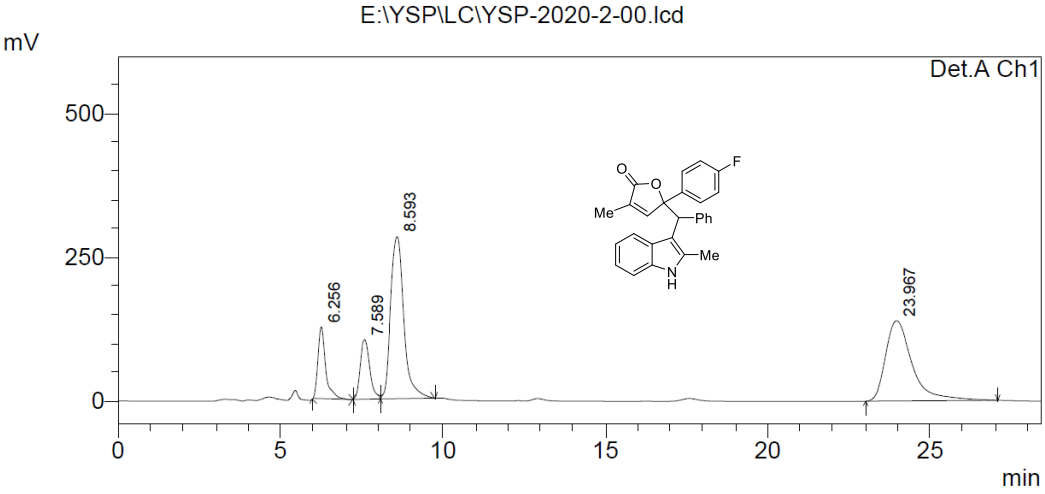
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.557	171778	11749	1.909
2	6.153	8825149	1061484	98.091
Total		8996926		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3q





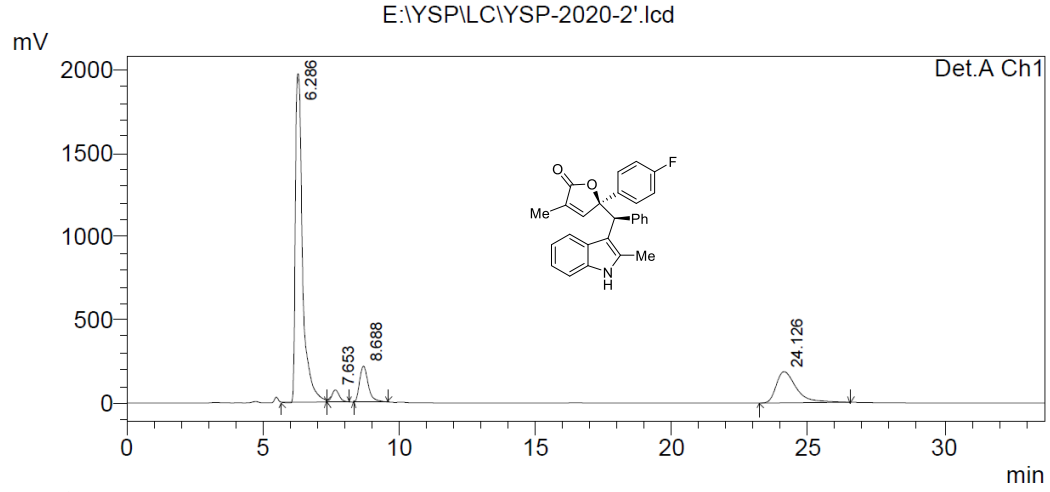


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.256	2056830	124858	10.214
2	7.589	2139048	103931	10.623
3	8.593	7983768	281929	39.648
4	23.967	7957086	139724	39.515
Total		20136731		100.000



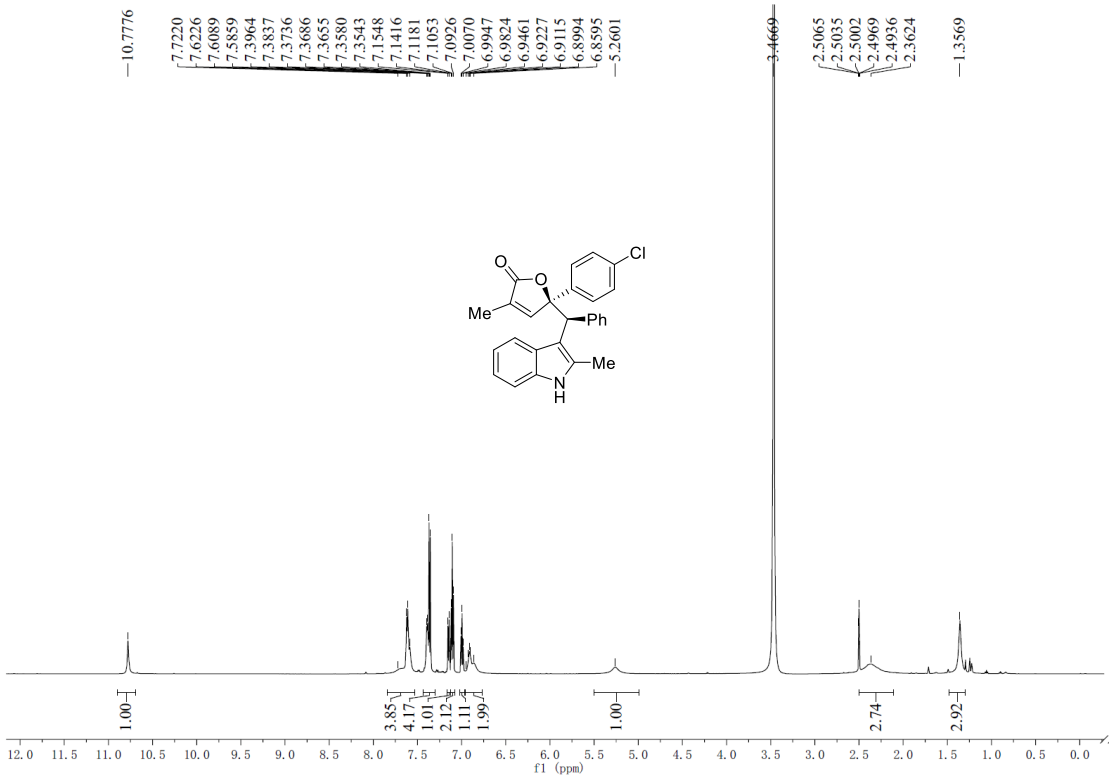
1 Det.A Ch1/254nm

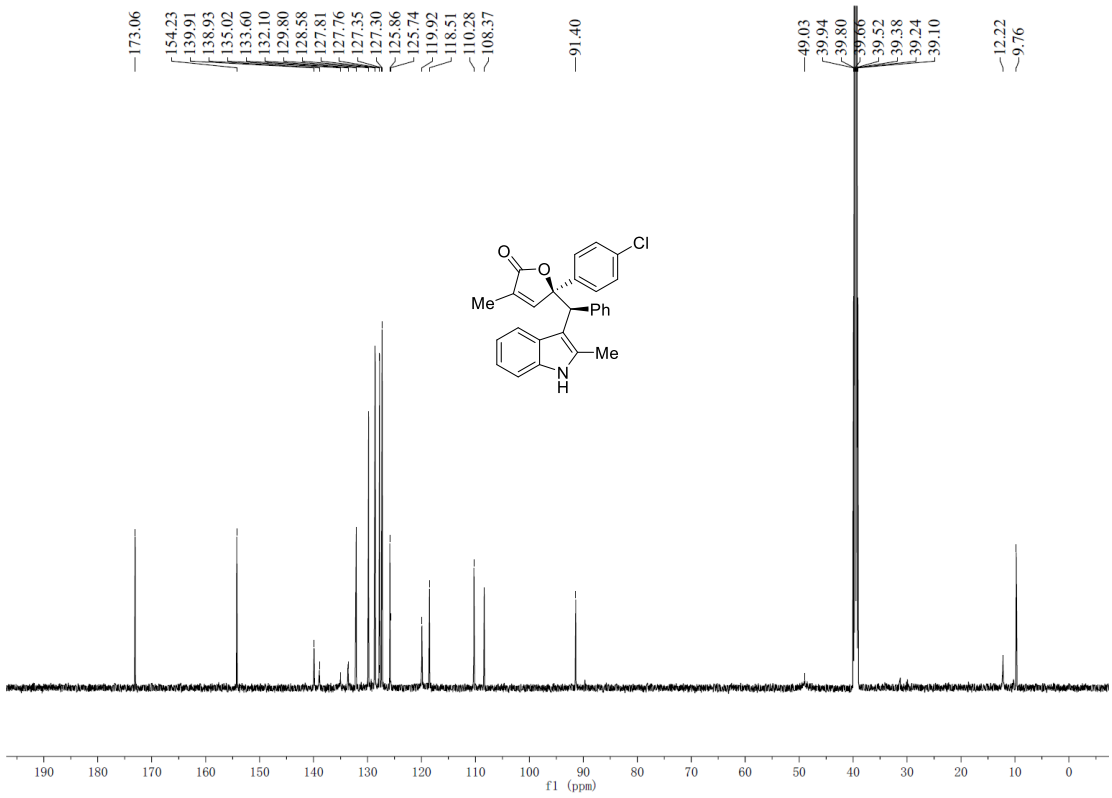
PeakTable

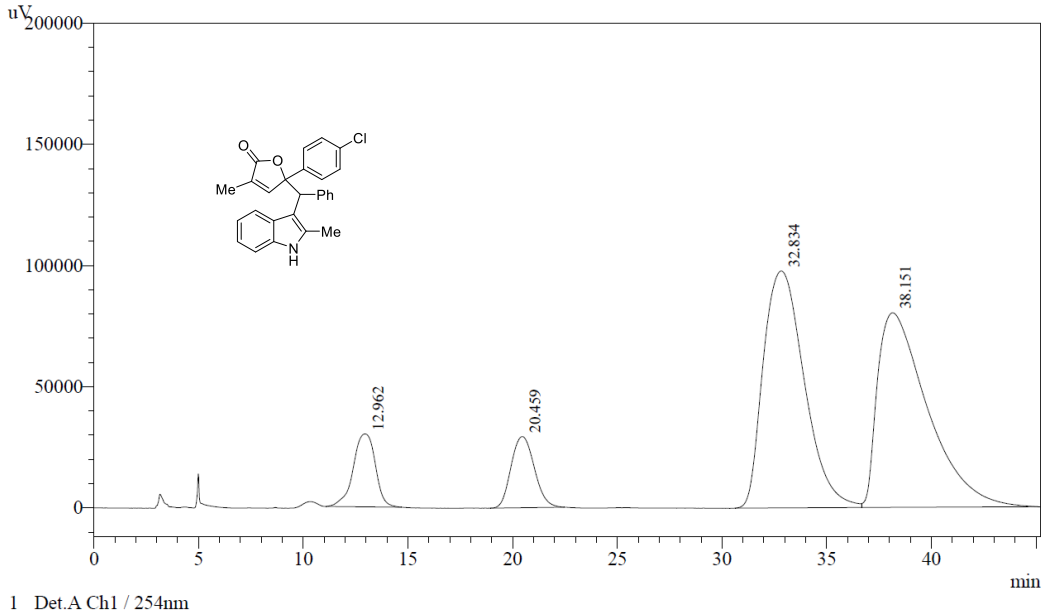
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.286	36452823	1974457	69.668
2	7.653	1423375	72519	2.720
3	8.688	4776712	215115	9.129
4	24.126	9670705	187252	18.482
Total		52323615		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3r



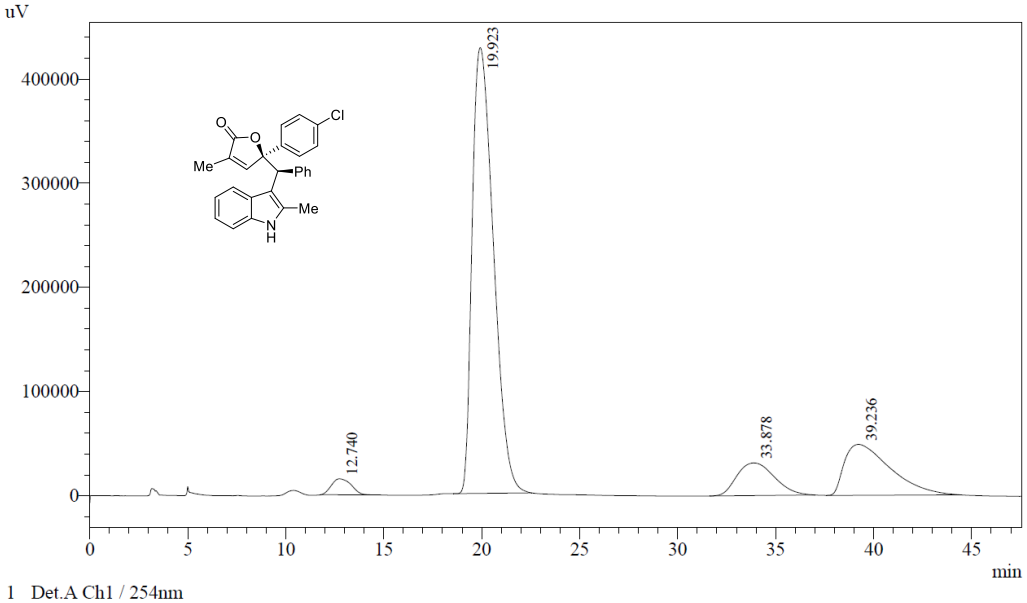




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.962	2216509	30083	7.096	12.666
2	20.459	2271329	29387	7.272	12.373
3	32.834	13358313	97738	42.768	41.151
4	38.151	13388180	80305	42.864	33.811
Total		31234331	237513	100.000	100.000



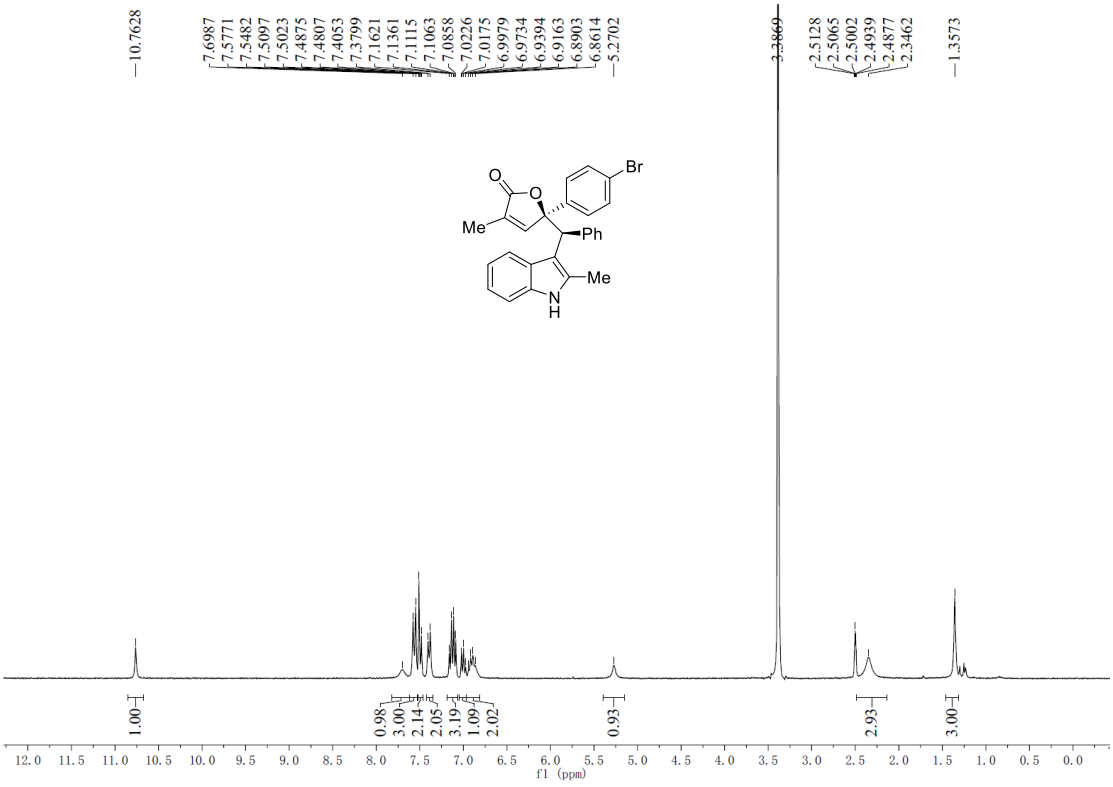
1 Det.A Ch1 / 254nm

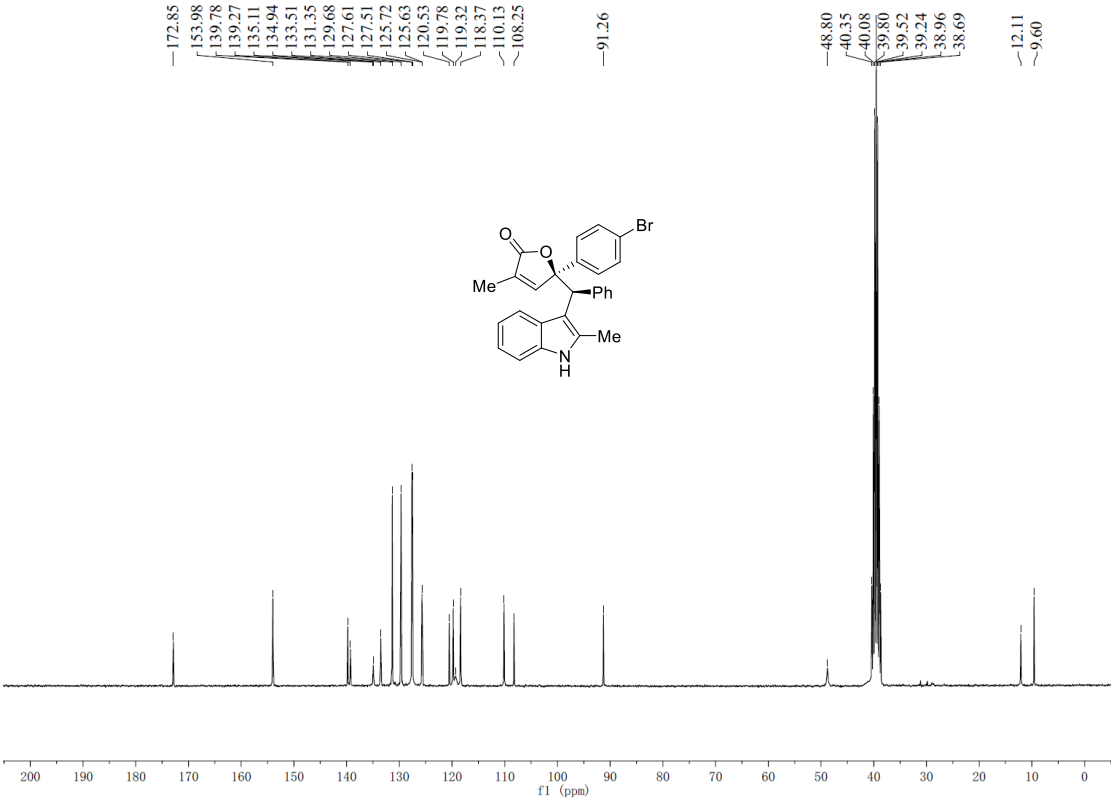
Detector A Ch1 254nm

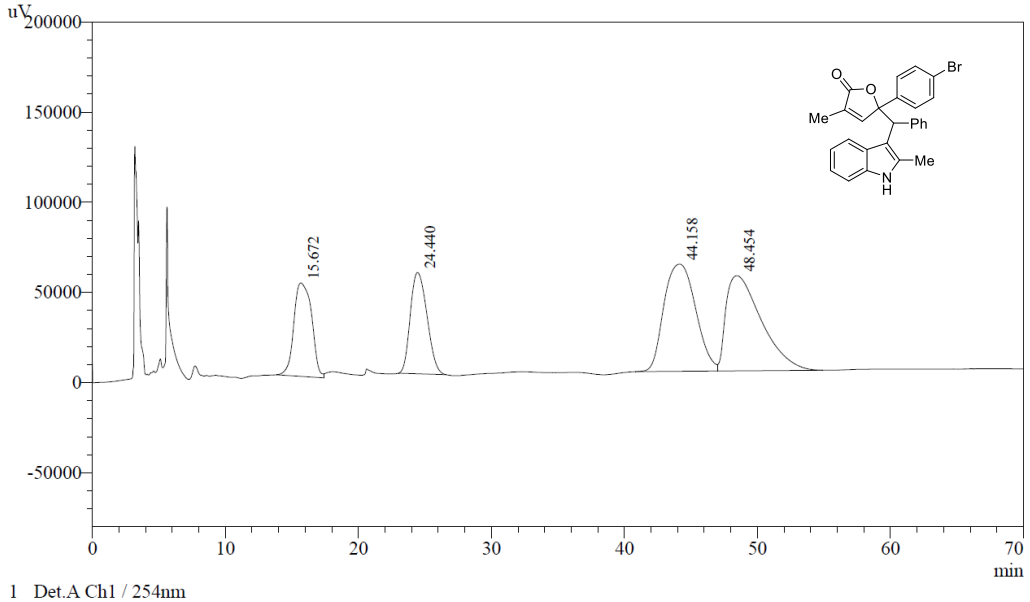
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.740	1067493	15300	2.346	2.923
2	19.923	32273092	427984	70.911	81.759
3	33.878	4187421	31308	9.201	5.981
4	39.236	7984291	48878	17.543	9.337
Total		45512297	523470	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3s

.



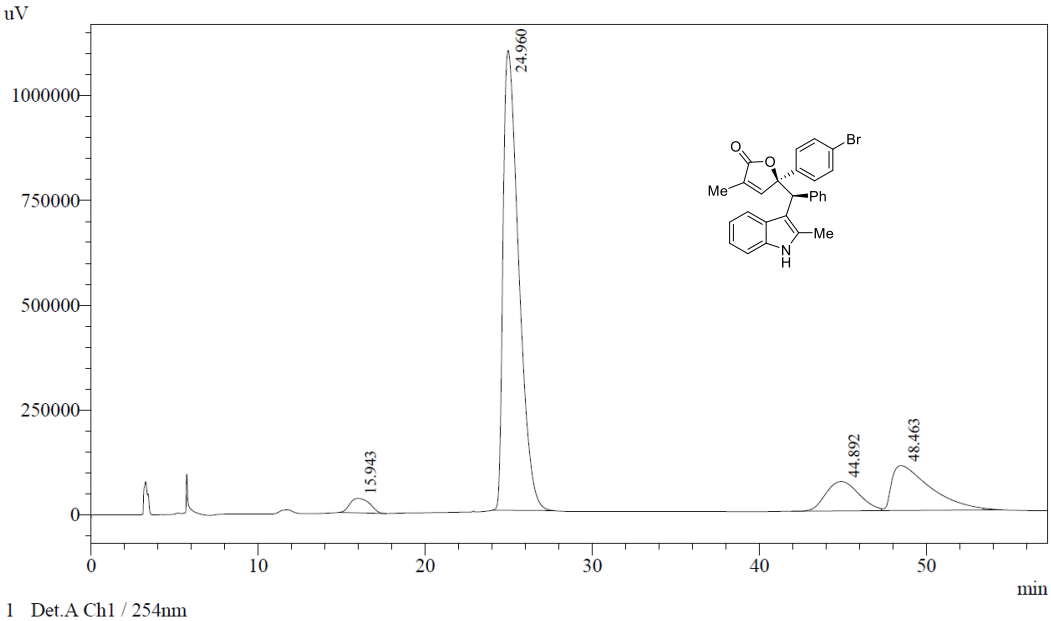




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.672	4820066	51822	16.415	23.533
2	24.440	4912528	56176	16.730	25.511
3	44.158	9864787	59449	33.595	26.997
4	48.454	9766643	52761	33.261	23.959
Total		29364024	220208	100.000	100.000

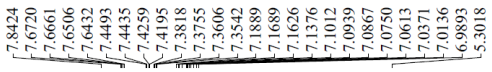


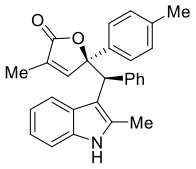
1 Det.A Ch1 / 254nm

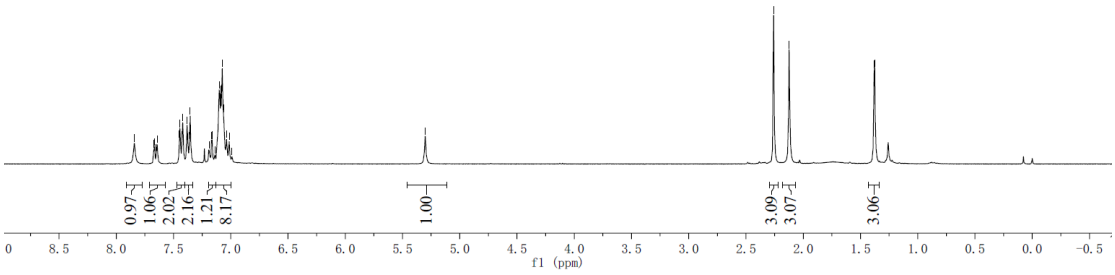
Detector A Ch1 254nm

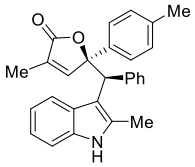
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.943	2859076	34669	2.822	2.648
2	24.960	71508524	1097126	70.578	83.804
3	44.892	9656530	70290	9.531	5.369
4	48.463	17294729	107077	17.070	8.179
Total		101318860	1309162	100.000	100.000

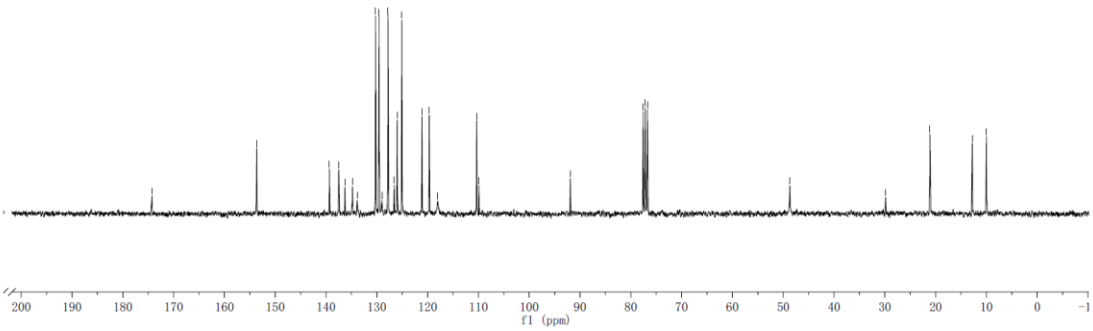
^{1}H NMR, ^{13}C NMR and HPLC spectra of 3t

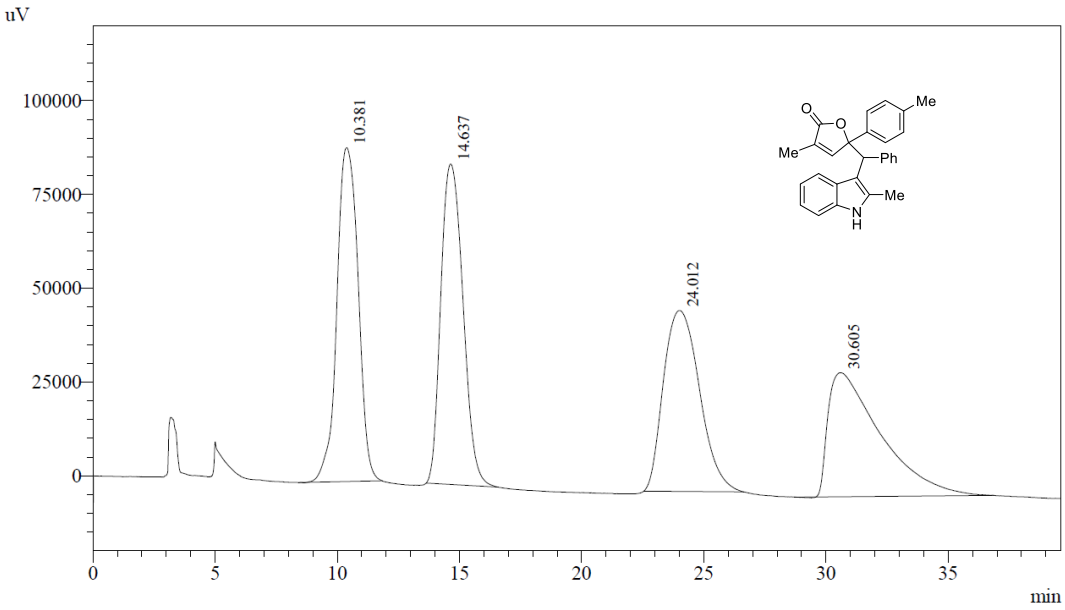








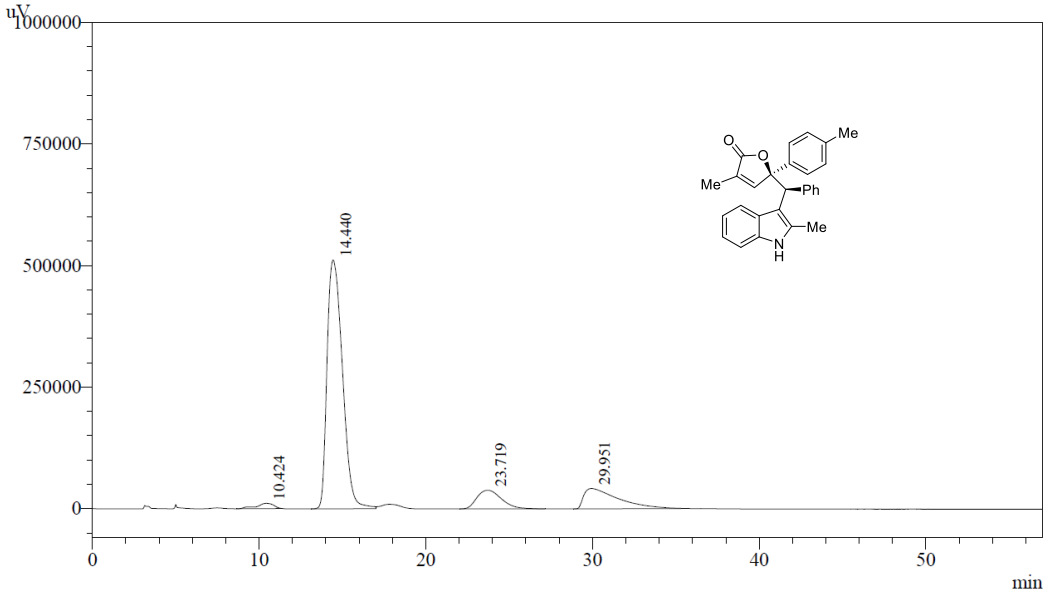




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.381	5392637	89052	26.038	34.808
2	14.637	5398037	85450	26.064	33.400
3	24.012	4969463	48252	23.995	18.860
4	30.605	4950481	33082	23.903	12.931
Total		20710619	255836	100.000	100.000

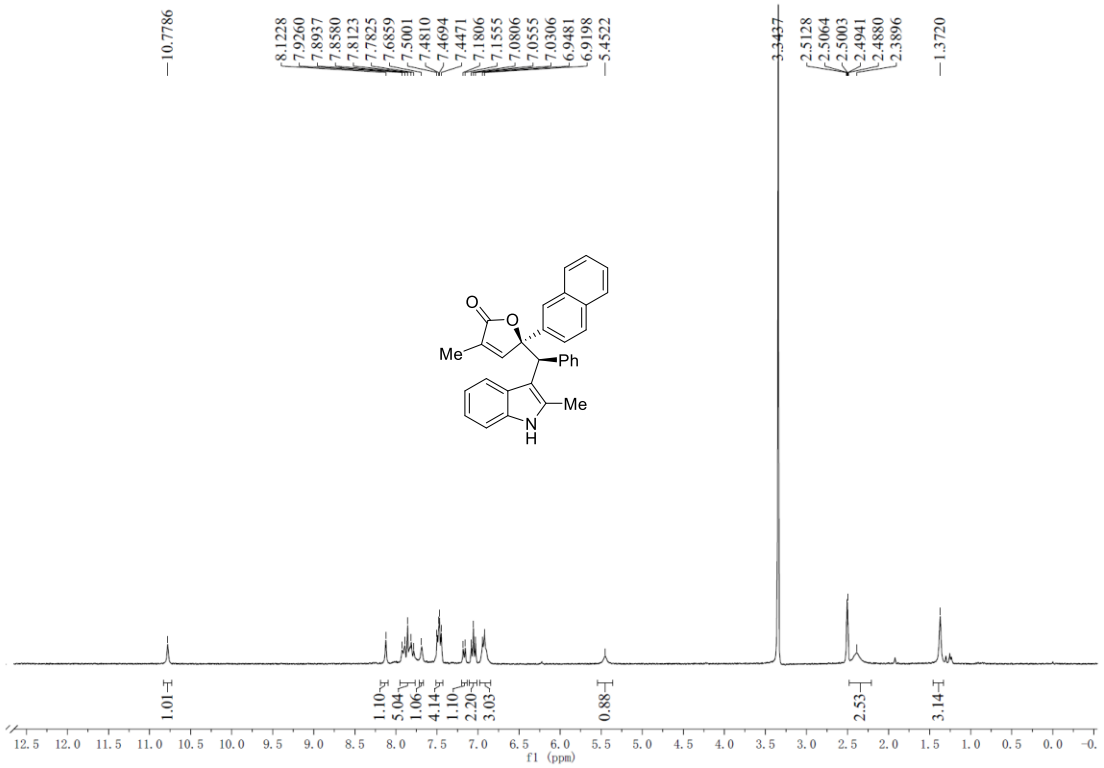


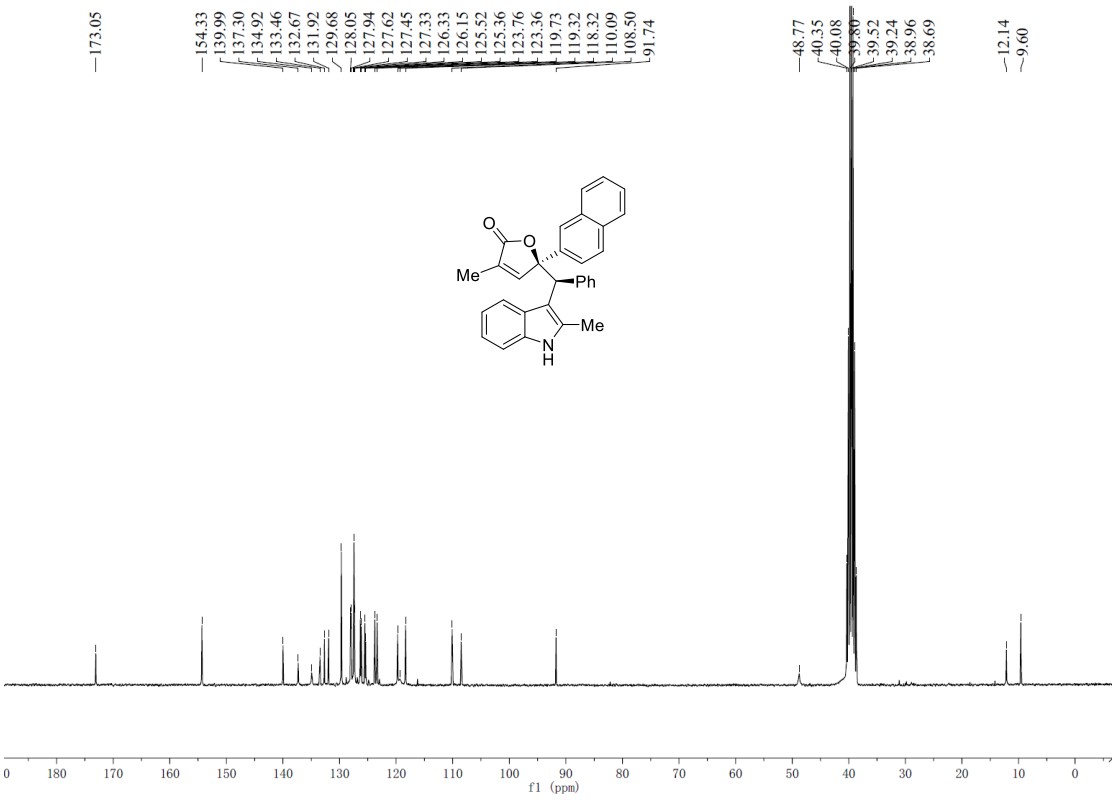
1 Det.A Ch1 / 254nm

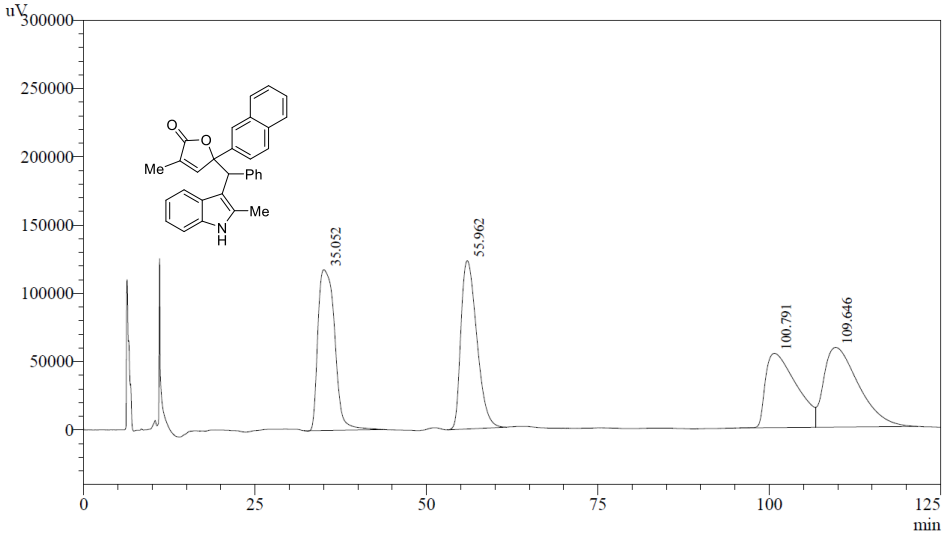
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.424	744545	10621	1.711	1.764
2	14.440	32867902	511555	75.518	84.949
3	23.719	3921602	38253	9.010	6.352
4	29.951	5989098	41763	13.761	6.935
Total		43523147	602192	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3u



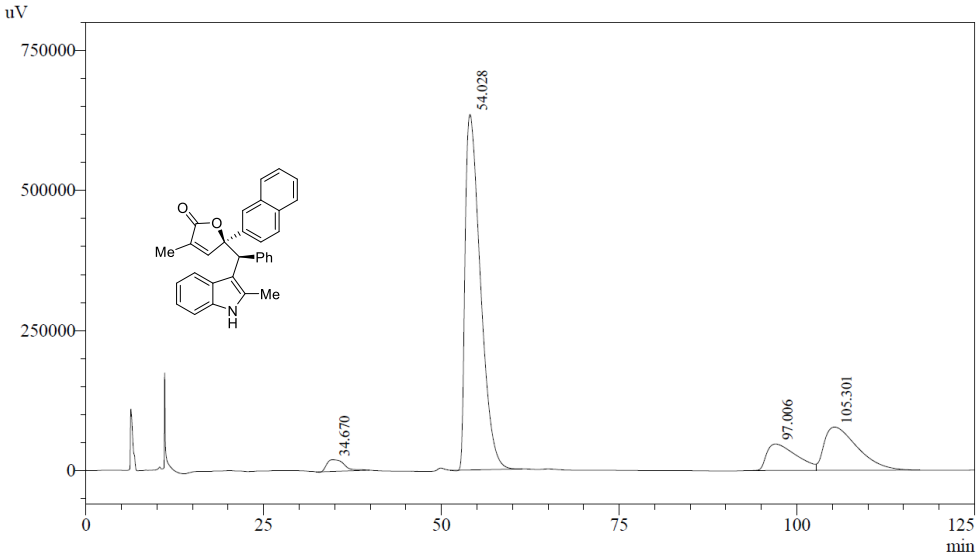




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.052	20015748	117708	25.800	33.275
2	55.962	19896069	123281	25.646	34.851
3	100.791	17046766	54385	21.973	15.374
4	109.646	20622194	58364	26.582	16.499
Total		77580778	353739	100.000	100.000

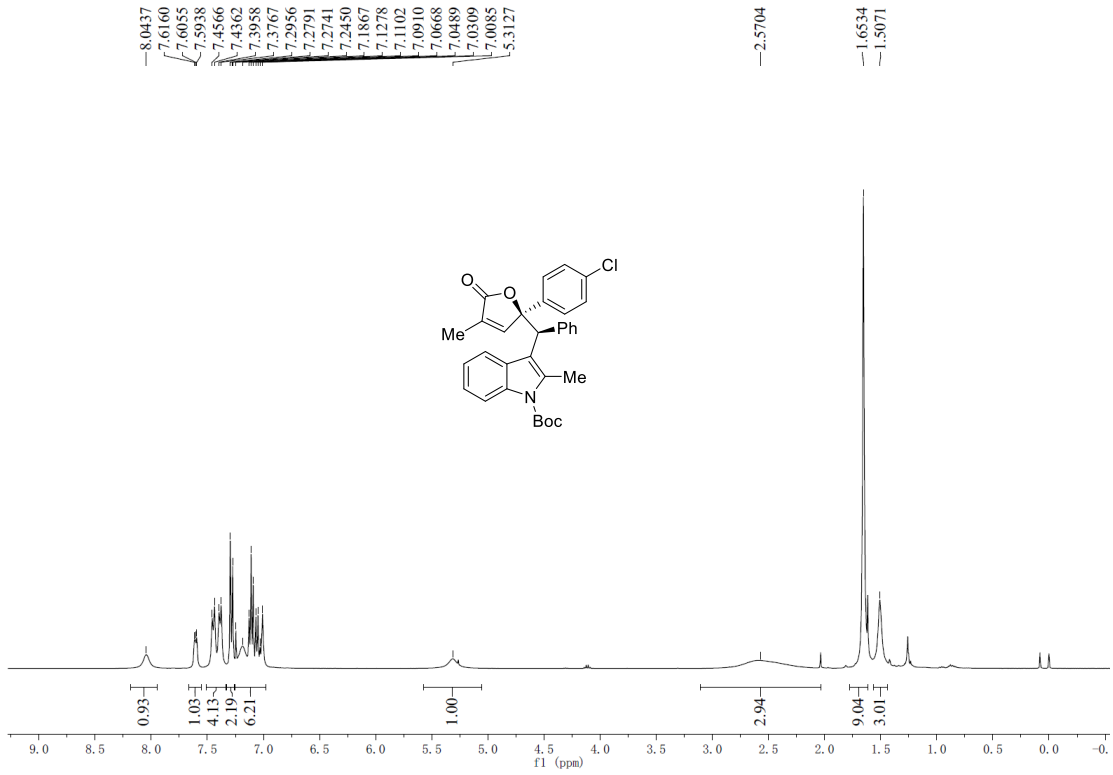


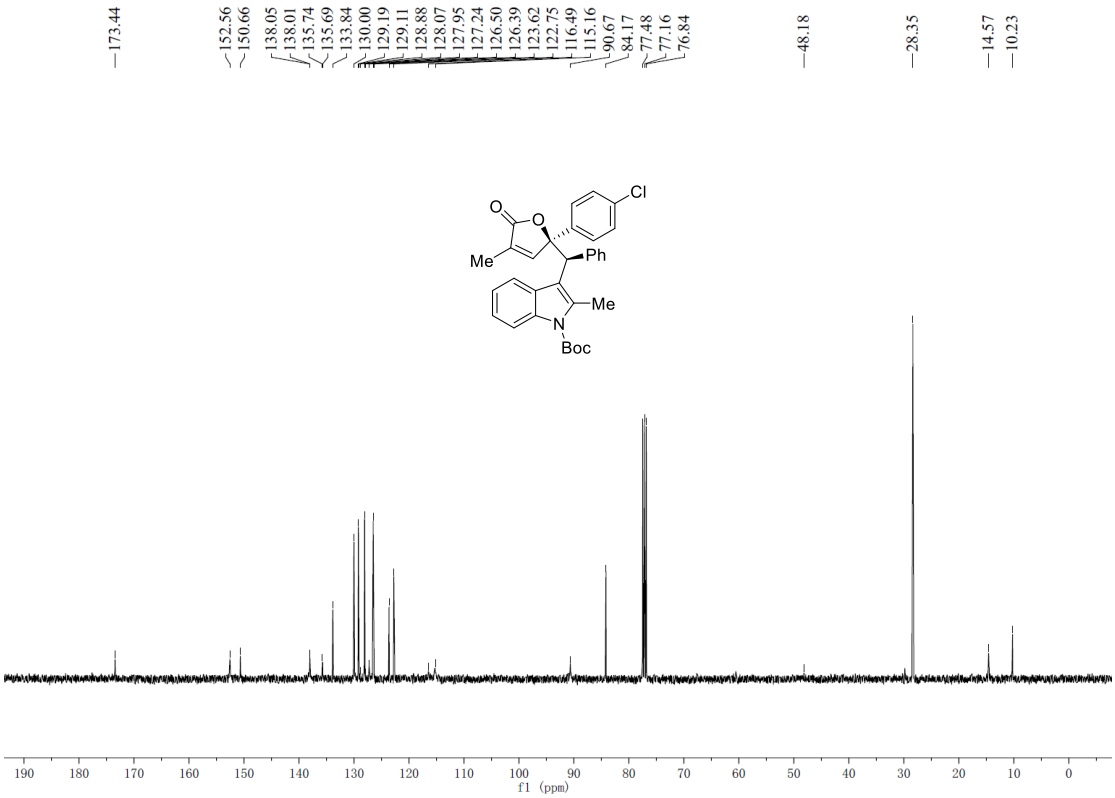
1 Det.A Ch1 / 254nm

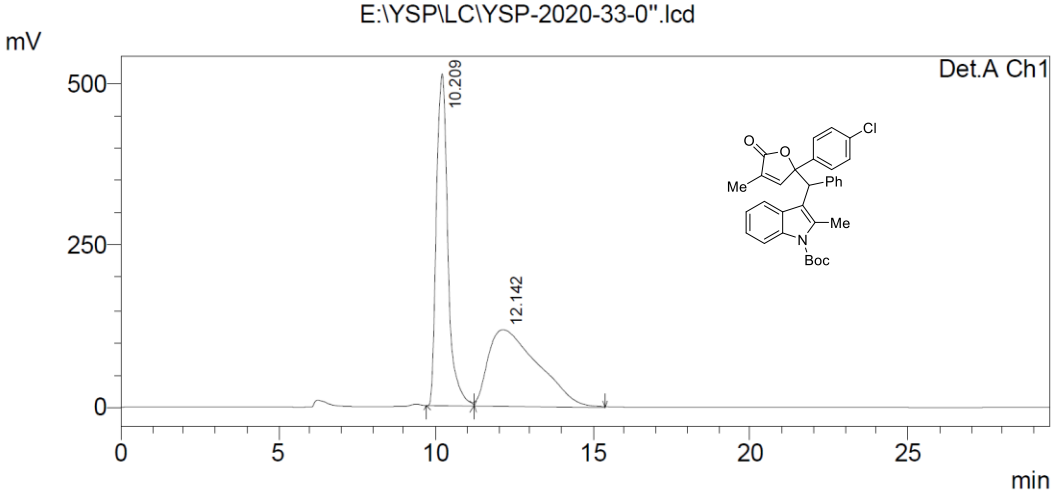
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.670	3510310	20859	2.556	2.676
2	54.028	94858525	634316	69.074	81.364
3	97.006	13717278	47194	9.989	6.054
4	105.301	25242699	77236	18.381	9.907
Total		137328812	779605	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 4





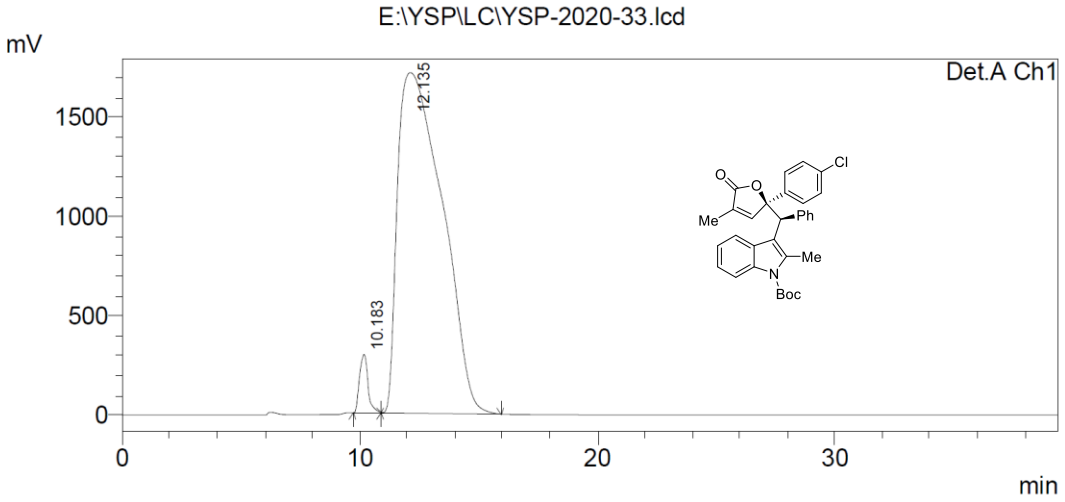


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.209	13086858	514312	49.945
2	12.142	13115442	118883	50.055
Total		26202300		100.000



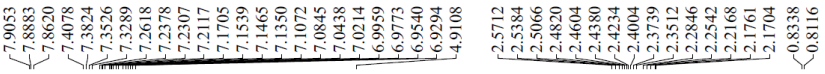
1 Det.A Ch1/254nm

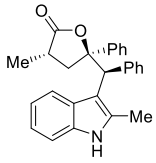
PeakTable

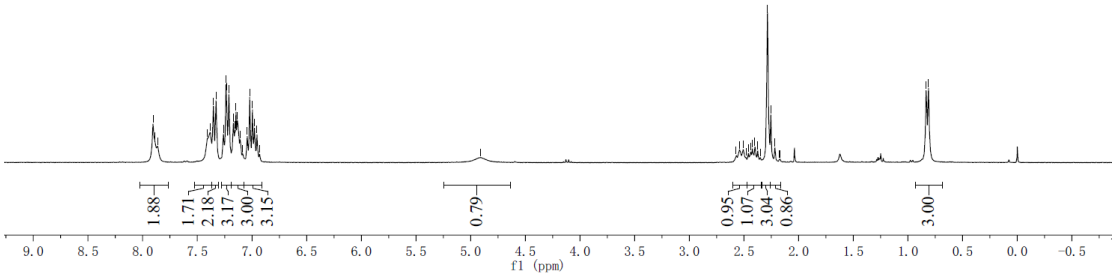
Detector A Ch1 254nm

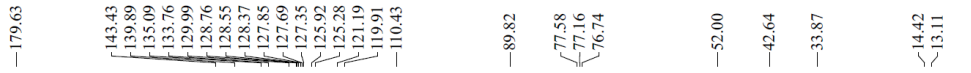
Peak#	Ret. Time	Area	Height	Area %
1	10.183	7407057	295733	3.187
2	12.135	225017026	1717722	96.813
Total		232424083		100.000

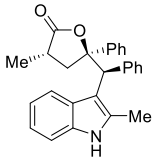
^{1}H NMR, ^{13}C NMR and HPLC spectra of 5

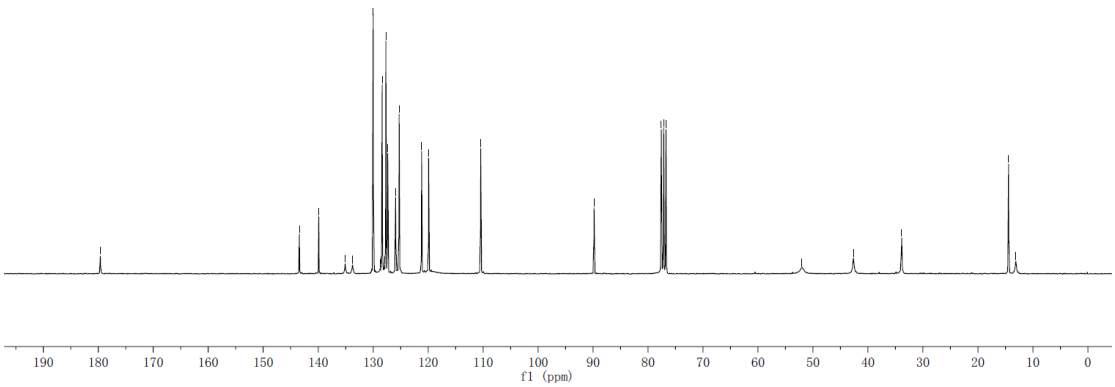


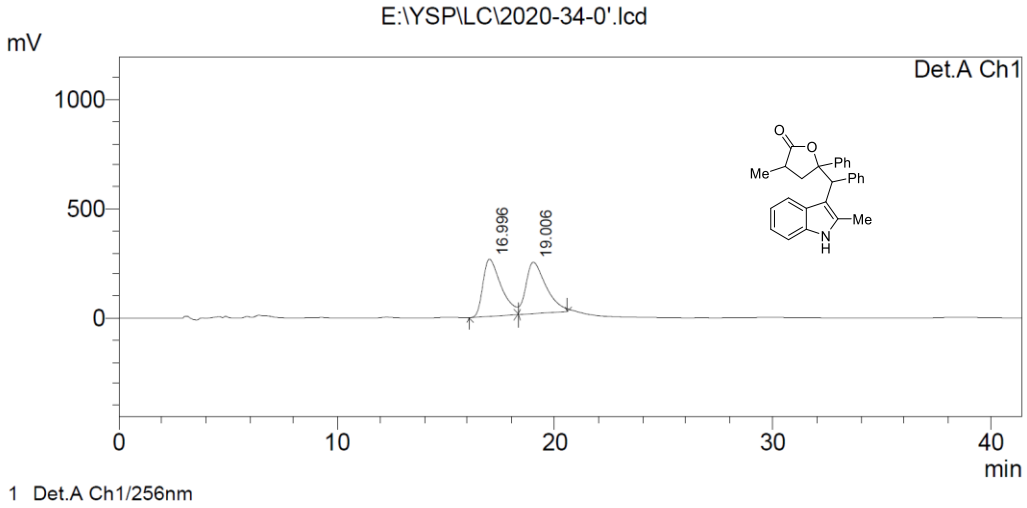








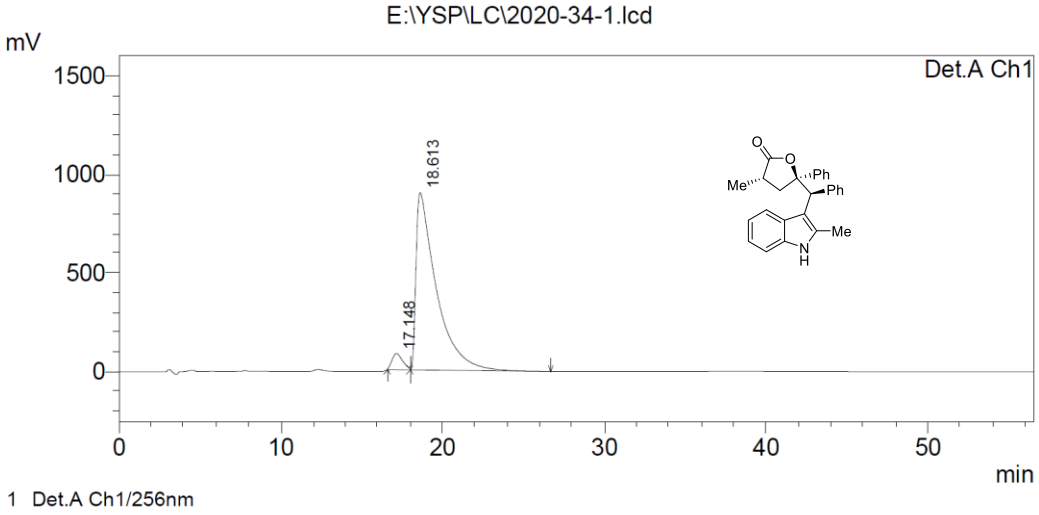




PeakTable

Detector A Ch1 256nm

Peak#	Ret. Time	Area	Height	Area %
1	16.996	15183329	262192	49.919
2	19.006	15232614	235660	50.081
Total		30415943		100.000

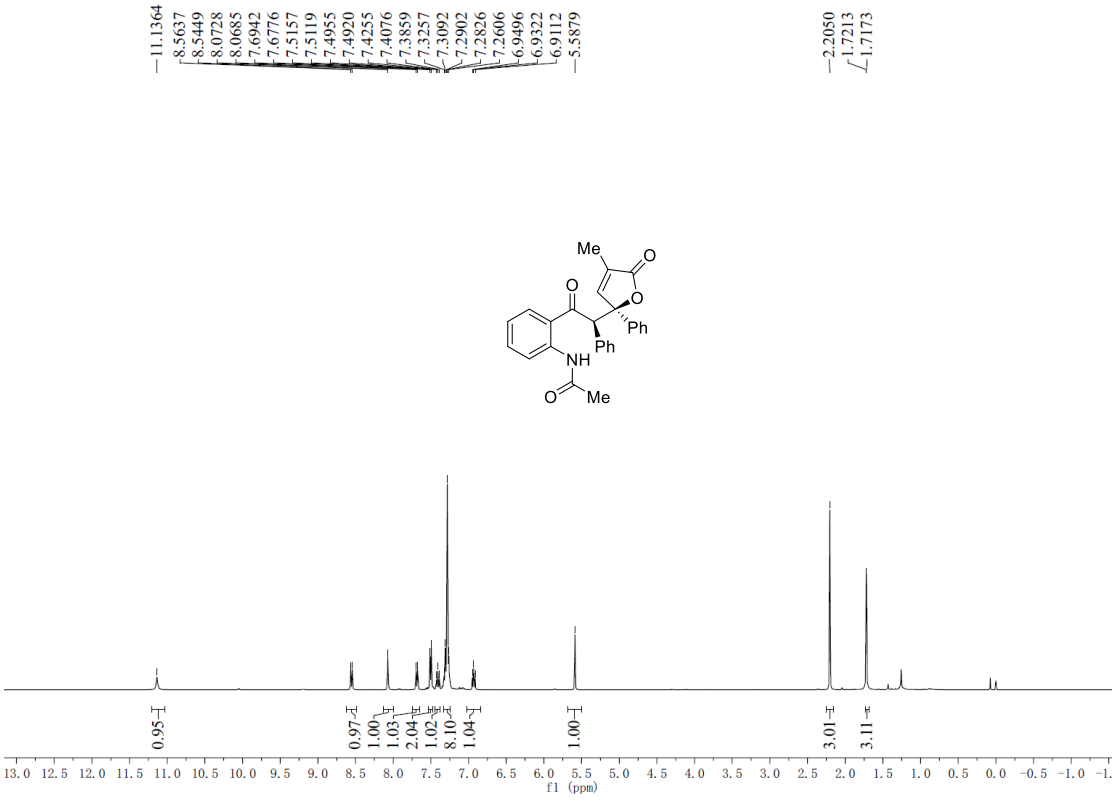


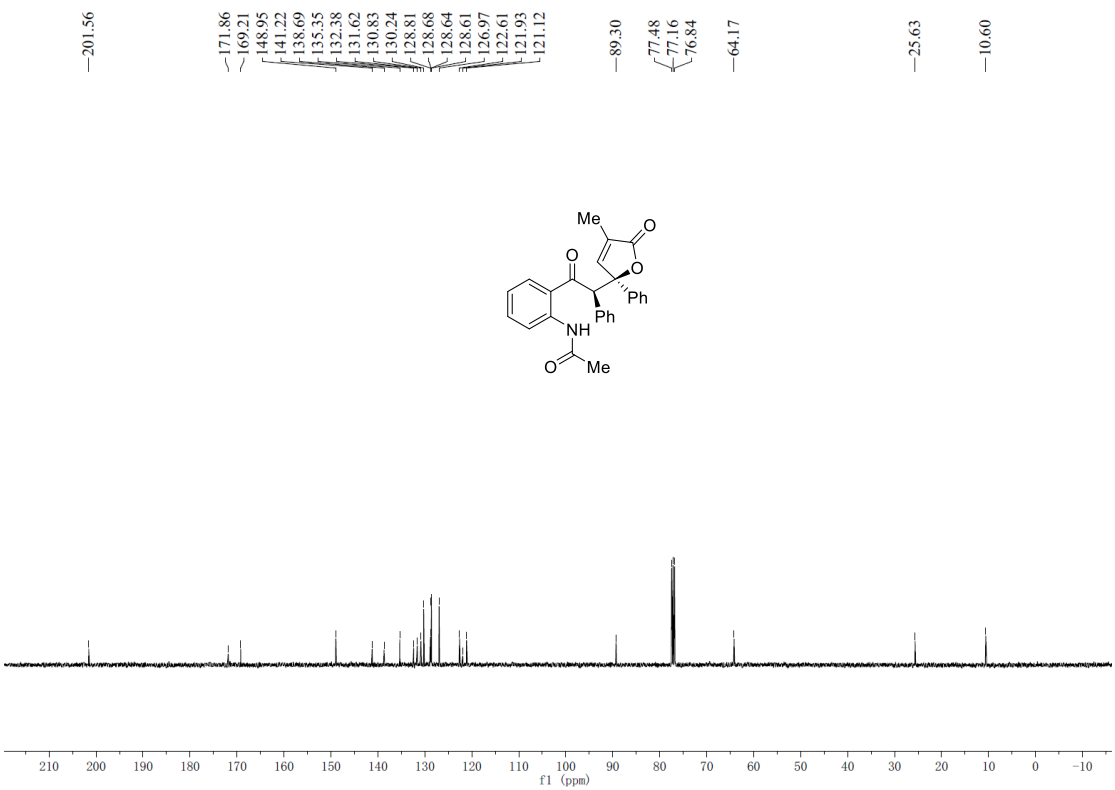
PeakTable

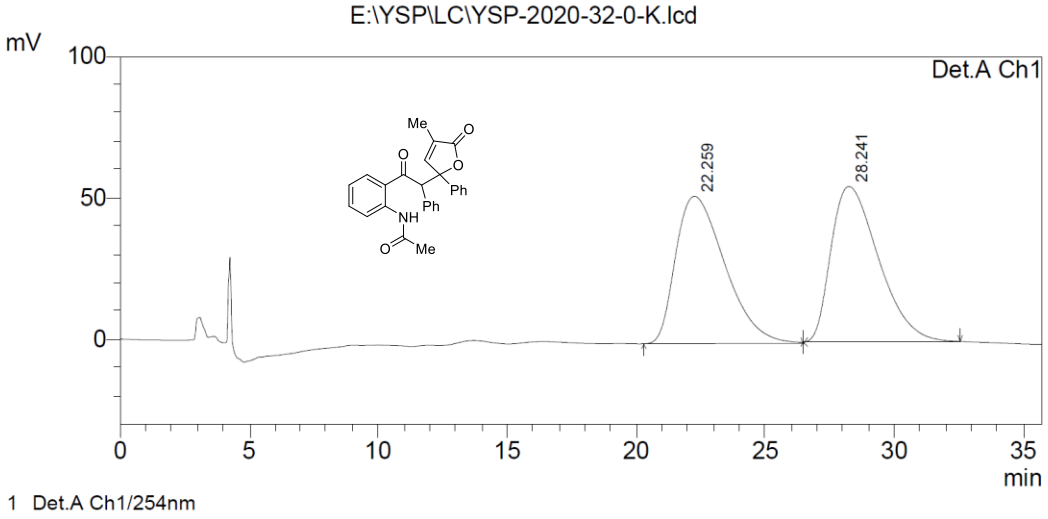
Detector A Ch1 256nm

Peak#	Ret. Time	Area	Height	Area %
1	17.148	3718210	81210	4.540
2	18.613	78188266	898412	95.460
Total		81906476		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 6



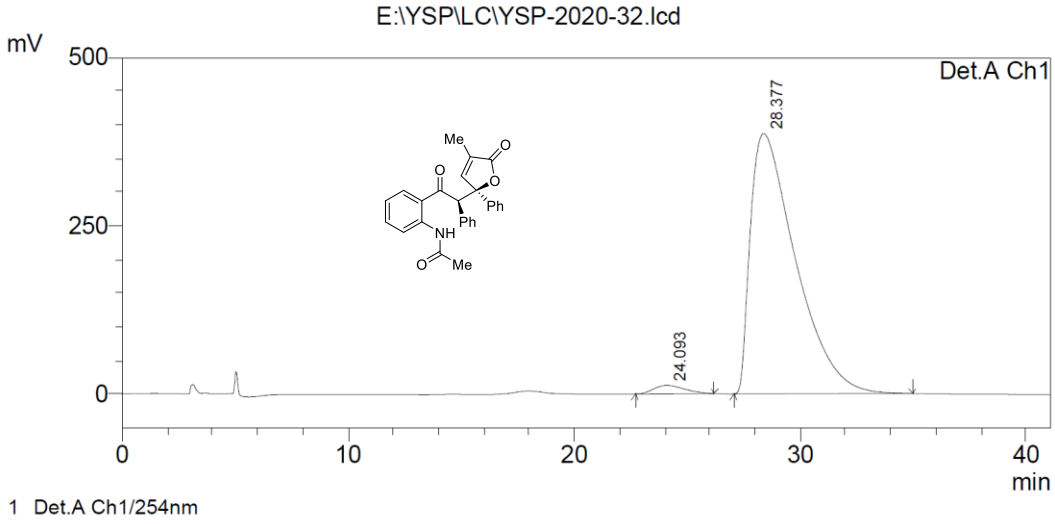




PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	22.259	6927620	52106	49.773
2	28.241	6990867	54769	50.227
Total		13918487		100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.093	1210852	12627	2.202
2	28.377	53769169	386588	97.798
Total		54980021		100.000