

**Organocatalytic Asymmetric [3+2] Cycloaddition of *N*-2,2,2-Trifluoroethylsatin
Ketimines with 3-Alkenyl-5-arylfuran-2(3*H*)-ones: Efficient Synthesis of
Spiro[pyrrolidin-3,2'-oxindoles] Bearing Four Consecutive Stereocenters with Two
Vicinal Spiro-quaternary Chiral Centers**

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Supporting Information

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1. General experimental information

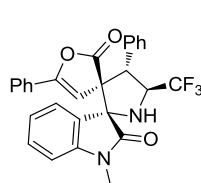
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 and $\text{DMSO-}d_6$. ^1H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl_3 at 7.26 ppm, $\text{DMSO-}d_6$ 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. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl_3 at 77.20 ppm, $\text{DMSO-}d_6$ at 39.51 ppm). Melting points were recorded on a melting point apparatus.

2. General procedure for the synthesis of starting materials.

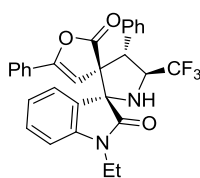
1a-1p were prepared according to the literature.^{1,2} **2a-2k** were prepared according to literature reported by Wang and co-workers and slightly modified.³

3. General procedure for the synthesis of compounds 3a-z.

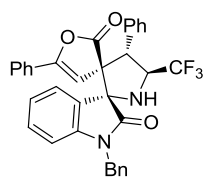
In an ordinary vial equipped with a magnetic stirring bar, the compounds **1** (0.20 mmol, 2.0 equiv), compounds **2** (0.10 mmol, 1.0 equiv) and catalyst **C** (1~5 mol %) were dissolved in DCE (1 mL), and then the mixture was stirred at room temperature for the indicated time. After completion of the reaction as indicated by TLC, the products **3** were isolated by flash chromatography on silica gel (petroleum ether/acetone = 10/1~2/1).



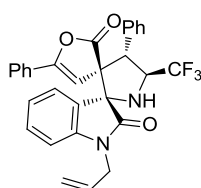
Compound **3a**: White solid; 47.8 mg, 98% yield; >20:1 dr, 97% ee; $[\alpha]_{\text{D}}^{20} = -195.6$ (c. 0.960, acetone); m.p. 199.8-200.7 °C; HPLC (AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 22.1$ min (minor), 30.4 min (major); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 3.10 (s, 3H), 4.52 (d, $J = 8.6$ Hz, 1H), 4.77-4.97 (m, 1H), 5.17 (d, $J = 10.8$ Hz, 1H), 6.84-7.02 (m, 3H), 7.15-7.34 (m, 6H), 7.34-7.42 (m, 5H), 7.51 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 25.9, 50.7, 60.6 (q, $J = 29.7$ Hz, 1C), 67.5, 72.1, 102.9, 108.4, 121.4, 124.3, 124.4, 126.1 (q, $J = 278.2$ Hz, 1C), 126.3, 126.9, 128.1, 128.3, 128.6, 129.0, 130.1, 130.3, 133.4, 143.6, 150.9, 172.7, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{21}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 513.1396, found: 513.1397.



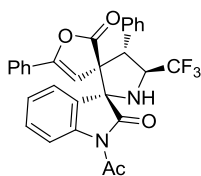
Compound **3b**: White solid; 49.9 mg, 99% yield; >20:1 dr, 95% ee; $[\alpha]_{\text{D}}^{20} = -183.9$ (c. 0.543, acetone); m.p. 211.7-212.5 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 5/5/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 18.2$ min (minor), 38.4 min (major); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 1.12 (t, $J = 7.0$ Hz, 3H), 3.53-3.60 (m, 1H), 3.74-3.81 (m, 1H), 4.49 (d, $J = 8.6$ Hz, 1H), 4.85-4.92 (m, 1H), 5.17 (d, $J = 10.8$ Hz, 1H), 6.89-6.98 (m, 3H), 7.18-7.32 (m, 6H), 7.36 (s, 5H), 7.53 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 12.2, 33.9, 50.7, 60.6 (q, $J = 29.7$ Hz, 1C), 67.5, 71.8, 102.8, 108.3, 121.1, 124.4, 124.5, 126.1 (q, $J = 278.3$ Hz, 1C), 126.4, 126.9, 128.0, 128.3, 128.6, 128.9, 130.0, 130.3, 133.4, 142.6, 150.9; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 527.1553, found: 527.1530.



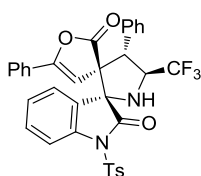
Compound **3c**: White solid; 59.1 mg, 99% yield; >20:1 dr, 97% ee; $[\alpha]_{\text{D}}^{20} = -171.8$ (c. 0.554, acetone); m.p. 220.2-220.8 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 5/5/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 25.1$ min (minor), 40.4 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 4.62 (d, $J = 8.6$ Hz, 1H), 4.73 (d, $J = 15.7$ Hz, 1H), 4.84-5.00 (m, 1H), 5.04 (d, $J = 15.7$ Hz, 1H), 5.26 (d, $J = 10.8$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 6.91 (t, $J = 7.6$ Hz, 1H), 7.03 (s, 1H), 7.10-7.23 (m, 2H), 7.24-7.43 (m, 14H), 7.56 (d, $J = 7.5$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 43.0, 51.0, 60.6 (q, $J = 29.3$ Hz, 1C), 67.5, 72.0, 102.9, 109.1, 121.6, 124.5, 126.2 (q, $J = 279.0$ Hz, 1C), 126.7, 126.9, 127.5, 127.5, 128.1, 128.4, 128.6, 128.7, 129.0, 130.1, 130.2, 133.4, 136.1, 142.8, 151.0, 172.8, 174.7; HRMS (ESI-TOF) calcd. for $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 589.1709, found: 589.1713.



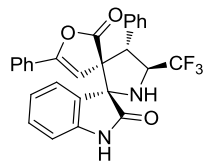
Compound **3d**: White solid; 56.9 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_{\text{D}}^{20} = -114.3$ (c. 0.589, acetone); m.p. 193.2-194.1 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 18.0$ min (minor), 35.0 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 4.16 (dd, $J = 16.3, 5.7$ Hz, 1H), 4.41 (dd, $J = 16.2, 4.7$ Hz, 1H), 4.56 (d, $J = 8.5$ Hz, 1H), 4.79-5.01 (m, 1H), 5.09-5.30 (m, 3H), 5.66-5.89 (m, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 6.93 (t, $J = 7.6$ Hz, 1H), 6.99 (s, 1H), 7.13-7.43 (m, 11H), 7.54 (d, $J = 7.4$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 41.6, 50.8, 60.6 (q, $J = 30.0$ Hz, 1C), 67.6, 72.0, 102.9, 109.0, 117.5, 121.4, 124.4, 124.5, 126.1 (q, $J = 278.2$ Hz, 1C), 126.5, 126.9, 128.1, 128.4, 128.7, 129.0, 130.1, 130.2, 131.7, 133.4, 142.8, 151.0, 172.7, 174.3; HRMS (ESI-TOF) calcd. for $\text{C}_{30}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 539.1553, found: 539.1557.



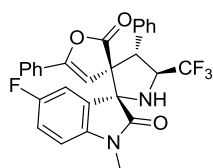
Compound **3e**: White solid; 50.9 mg, 98% yield; 12:1 dr, 98% ee; $[\alpha]_{\text{D}}^{20} = -227.9$ (c. 0.523, acetone); m.p. 171.2-171.5 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 5/5/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 18.1$ min (minor), 19.2 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 2.66 (s, 3H), 4.77 (d, $J = 7.4$ Hz, 1H), 4.85 (d, $J = 10.8$ Hz, 1H), 4.90-5.06 (m, 1H), 6.98 (s, 1H), 7.12-7.23 (m, 2H), 7.23-7.40 (m, 10H), 7.69 (d, $J = 7.6$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 51.2, 60.8 (q, $J = 29.3$ Hz, 1C), 68.5, 72.4, 102.3, 115.4, 124.3, 124.3, 124.5, 126.0 (q, $J = 278.3$ Hz, 1C), 126.5, 126.6, 128.3, 128.4, 128.7, 129.0, 130.3, 130.5, 132.7, 139.2, 151.4, 170.1, 173.4, 176.4; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{21}\text{F}_3\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 541.1346, found: 541.1351.



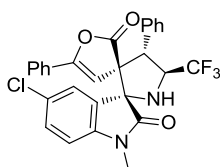
Compound **3f**: White solid; 57.4 mg, 91% yield; >20:1 dr, 88% ee; $[\alpha]_{\text{D}}^{20} = -45.6$ (c. 1.435, acetone); m.p. 222.4-223.2 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 31.0$ min (minor), 36.1 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 2.38 (s, 3H), 4.68 (d, $J = 7.3$ Hz, 1H), 4.74 (d, $J = 10.8$ Hz, 1H), 4.83-4.99 (m, 1H), 6.93 (s, 1H), 7.09-7.22 (m, 2H), 7.22-7.40 (m, 10H), 7.49 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 7.4$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 2H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 21.1, 51.1, 60.5 (q, $J = 30.0$ Hz, 1C), 67.9, 72.2, 102.0, 112.5, 124.0, 124.5, 125.8 (q, $J = 279.0$ Hz, 1C), 126.6, 127.4, 127.5, 128.2, 128.3, 128.6, 128.9, 130.2, 130.2, 130.9, 132.5, 134.3, 137.8, 146.0, 151.5, 172.5, 173.5; HRMS (ESI-TOF) calcd. for $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M} + \text{Na}]^+$ 653.1328, found: 653.1336.



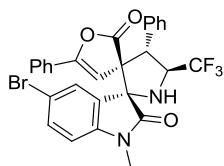
Compound **3g**: White solid; 43.5 mg, 91% yield; >20:1 dr, 83% ee; $[\alpha]_D^{20} = -128.6$ (c. 0.435, acetone); m.p. 119.3-119.8 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 10/10/80, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 19.6$ min (minor), 36.1 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 4.42 (d, $J = 8.6$ Hz, 1H), 4.84-4.89 (m, 1H), 5.14 (d, $J = 10.8$ Hz, 1H), 6.73 (d, $J = 7.7$ Hz, 1H), 6.84 (t, $J = 7.6$ Hz, 1H), 6.94 (s, 1H), 7.12-7.21 (m, 2H), 7.22-7.28 (m, 4H), 7.30-7.40 (m, 5H), 7.46 (d, $J = 7.6$ Hz, 1H), 10.41 (s, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 50.6, 60.6 (q, $J = 29.7$ Hz, 1C), 67.4, 72.3, 103.0, 109.4, 120.7, 125.0, 126.2 (q, $J = 275.3$ Hz, 1C), 126.7, 127.0, 128.0, 128.3, 128.6, 129.0, 130.0, 130.2, 133.5, 142.3, 150.8, 176.1; HRMS (ESI-TOF) calcd. for $\text{C}_{27}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 499.1240, found: 499.1240.



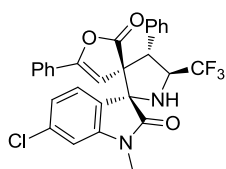
Compound **3h**: White solid; 49.4 mg, 97% yield; >20:1 dr, 99% ee; $[\alpha]_D^{20} = -155.4$ (c. 0.579, acetone); m.p. 207.4-208.1 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 21.9$ min (minor), 33.9 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.09 (s, 3H), 4.63 (d, $J = 8.2$ Hz, 1H), 4.76-4.92 (m, 1H), 5.12 (d, $J = 10.7$ Hz, 1H), 6.94 (dd, $J = 8.6, 4.3$ Hz, 1H), 6.98 (s, 1H), 7.07-7.23 (m, 2H), 7.23-7.32 (m, 4H), 7.34-7.46 (m, 6H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.2, 50.7, 60.6 (q, $J = 29.9$ Hz, 1C), 67.4, 72.2, 102.6, 109.3 (d, $J = 8.2$ Hz, 1C), 114.5 (d, $J = 26.0$ Hz, 1C), 116.5 (d, $J = 23.3$ Hz, 1C), 124.4, 126.0 (q, $J = 278.2$ Hz, 1C), 126.2 (d, $J = 8.4$ Hz, 1C), 126.8, 128.2, 128.4, 128.6, 129.0, 130.3, 133.2, 139.9 (d, $J = 1.6$ Hz, 1C), 151.2, 157.4 (d, $J = 237.2$ Hz, 1C), 172.5, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{F}_4\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 531.1302, found: 531.1308.



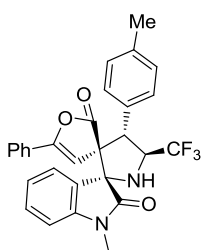
Compound **3i**: White solid; 53.0 mg, 99% yield; >20:1 dr, >99% ee; $[\alpha]_D^{20} = -36.8$ (c. 0.572, acetone); m.p. 222.5-222.9 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 5/5/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 15.6$ min (minor), 35.2 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.09 (s, 3H), 4.66 (d, $J = 8.2$ Hz, 1H), 4.76-4.95 (m, 1H), 5.09 (d, $J = 10.8$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 7.02 (s, 1H), 7.14-7.23 (m, 1H), 7.23-7.34 (m, 5H), 7.35-7.43 (m, 5H), 7.61 (d, $J = 2.2$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.1, 50.6, 60.6 (q, $J = 30.0$ Hz, 1C), 67.4, 72.2, 102.6, 109.8, 124.4, 125.4, 126.0 (q, $J = 278.2$ Hz, 1C), 126.3, 126.7, 126.8, 128.1, 128.4, 128.6, 128.9, 129.9, 130.2, 133.1, 142.5, 151.3, 172.4, 174.3; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{ClF}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 547.1007, found: 547.1013



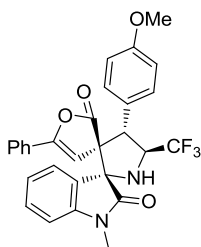
Compound **3j**: White solid; 49.2 mg, 86% yield; >20:1 dr, >99% ee; $[\alpha]_D^{20} = -37.5$ (c. 0.512, acetone); m.p. 220.8-220.9 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 19.4$ min (minor), 35.3 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.08 (s, 3H), 4.65 (d, $J = 8.2$ Hz, 1H), 4.76-4.98 (m, 1H), 5.07 (d, $J = 10.7$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 7.02 (s, 1H), 7.15-7.33 (m, 5H), 7.38 (s, 5H), 7.44 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.74 (d, $J = 2.0$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.1, 50.5, 60.6 (q, $J = 28.5$ Hz, 1C), 67.4, 72.2, 102.7, 110.3, 113.0, 124.4, 126.0 (q, $J = 279.0$ Hz, 1C), 126.6, 126.8, 128.2, 128.4, 128.6, 129.0, 129.6, 130.3, 132.8, 133.2, 142.9, 151.3, 172.5, 174.2; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{BrF}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 591.0502, found: 591.0510



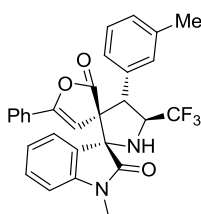
Compound **3k**: White solid; 51.3 mg, 98% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20} = -144.7$ (c. 0.647, acetone); m.p. 211.6-211.9 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 16.7$ min (minor), 25.0 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.11 (s, 3H), 4.62 (d, $J = 8.3$ Hz, 1H), 4.74-4.98 (m, 1H), 5.12 (d, $J = 10.6$ Hz, 1H), 6.94 (s, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 7.10 (s, 1H), 7.14-7.34 (m, 5H), 7.37 (s, 5H), 7.50 (d, $J = 8.0$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.1, 50.8, 60.5 (q, $J = 30.0$ Hz, 1C), 67.4, 71.7, 102.5, 108.9, 121.0, 123.1, 124.5, 126.0 (q, $J = 279.0$ Hz, 1C), 126.8, 127.7, 128.1, 128.3, 128.6, 128.9, 130.2, 133.2, 134.9, 145.2, 151.2, 172.5, 174.6; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{ClF}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 547.1007, found: 547.1012.



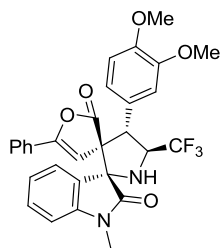
Compound **3l**: White solid; 48.3 mg, 95% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20} = -205.7$ (c. 0.483, acetone); m.p. 197.4-198.1 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 1/9/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 22.4$ min (minor), 35.7 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 2.16 (s, 3H), 3.09 (s, 3H), 4.49 (d, $J = 8.7$ Hz, 1H), 4.73-4.91 (m, 1H), 5.13 (d, $J = 10.9$ Hz, 1H), 6.88-6.97 (m, 3H), 7.06 (d, $J = 7.9$ Hz, 2H), 7.15-7.29 (m, 3H), 7.32-7.42 (m, 5H), 7.50 (d, $J = 7.5$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 20.5, 25.9, 50.3, 60.7 (q, $J = 29.6$ Hz, 1C), 67.4, 72.1, 102.9, 108.3, 121.3, 124.3, 124.4, 126.1 (q, $J = 279.0$ Hz, 1C), 126.2, 127.0, 127.1, 128.5, 128.9, 129.0, 130.0, 130.3, 137.2, 143.6, 150.9, 172.6, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 527.1553, found: 527.1554.



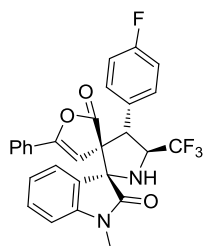
Compound **3m**: White solid; 42.3 mg, 81% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20} = -154.4$ (c. 0.416, acetone); m.p. 198.5-199.6 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 8/8/84, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 12.7$ min (minor), 21.0 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.09 (s, 3H), 3.63 (s, 3H), 4.48 (d, $J = 8.5$ Hz, 1H), 4.65-4.91 (m, 1H), 5.11 (d, $J = 10.8$ Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 2H), 6.88-7.00 (m, 3H), 7.17-7.30 (m, 3H), 7.38 (s, 5H), 7.51 (d, $J = 7.5$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 25.9, 50.1, 54.9, 60.9 (q, $J = 30.0$ Hz, 1C), 67.5, 72.0, 103.0, 108.4, 113.7, 121.4, 124.4, 125.1, 126.2 (q, $J = 279.0$ Hz, 1C), 126.3, 127.0, 129.0, 129.8, 130.1, 130.3, 143.6, 150.9, 158.8, 172.8, 174.6; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 543.1502, found: 543.1519.



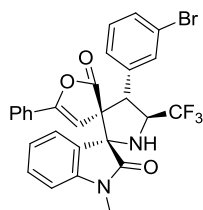
Compound **3n**: White solid; 55.9 mg, 99% yield; >20:1 dr, 97% ee; $[\alpha]_D^{20} = -143.4$ (c. 0.597, acetone); m.p. 199.5-200.2 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 1/9/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 18.8$ min (minor), 33.1 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 2.16 (s, 3H), 3.05 (s, 3H), 4.48 (d, $J = 8.7$ Hz, 1H), 4.71-4.90 (m, 1H), 5.09 (d, $J = 10.8$ Hz, 1H), 6.83-7.00 (m, 4H), 7.02-7.15 (m, 3H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.29-7.39 (m, 5H), 7.47 (d, $J = 7.2$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 20.9, 25.9, 50.7, 60.7 (q, $J = 30.0$ Hz, 1C), 67.5, 72.1, 103.0, 108.3, 121.4, 124.3, 124.4, 125.6, 126.1 (q, $J = 278.3$ Hz, 1C), 126.2, 127.0, 128.1, 128.7, 128.9, 129.4, 130.0, 130.3, 133.4, 137.4, 143.6, 150.9, 172.7, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 527.1553, found: 527.1560.



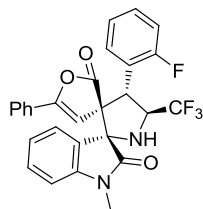
Compound **3o**: White solid; 47.6 mg, 86% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20} = -163.7$ (c. 0.427, acetone); m.p. 192.7-193.5 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 6/6/88, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 21.7$ min (minor), 34.8 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.09 (s, 3H), 3.63 (s, 3H), 3.66 (s, 3H), 4.48 (d, $J = 8.2$ Hz, 1H), 4.75-4.93 (m, 1H), 5.08 (d, $J = 10.8$ Hz, 1H), 6.79 (q, $J = 8.2$ Hz, 2H), 6.87-6.99 (m, 3H), 7.11 (s, 1H), 7.25 (t, $J = 7.7$ Hz, 1H), 7.33-7.44 (m, 5H), 7.47 (d, $J = 7.5$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 25.9, 50.6, 55.2, 55.6, 60.9 (q, $J = 29.3$ Hz, 1C), 67.5, 71.9, 103.4, 108.4, 111.2, 112.0, 121.3, 121.4, 124.3, 124.5, 125.5, 126.6 (q, $J = 279.0$ Hz, 1C), 126.3, 127.1, 129.0, 130.1, 130.3, 143.6, 148.0, 148.4, 150.7, 172.8, 174.7; HRMS (ESI-TOF) calcd. for $\text{C}_{30}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5$ $[\text{M} + \text{Na}]^+$ 573.1608, found: 573.1609.



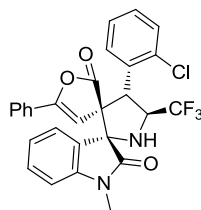
Compound **3p**: White solid; 47.3 mg, 99% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20} = -172.1$ (c. 0.564, acetone); m.p. 198.8-199.3 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 25.5$ min (minor), 37.3 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.10 (s, 3H), 4.56 (d, $J = 8.5$ Hz, 1H), 4.76-4.95 (m, 1H), 5.17 (d, $J = 10.9$ Hz, 1H), 6.88-7.00 (m, 3H), 7.11 (t, $J = 8.7$ Hz, 2H), 7.25 (t, $J = 7.7$ Hz, 1H), 7.30-7.44 (m, 7H), 7.50 (d, $J = 7.3$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 50.0, 60.8 (q, $J = 29.2$ Hz, 1C), 67.4, 72.0, 102.7, 108.4, 115.3 (d, $J = 21.4$ Hz, 1C), 121.4, 124.3, 124.5, 126.1 (q, $J = 279.0$ Hz, 1C), 126.3, 126.9, 129.0, 129.6 (d, $J = 3.1$ Hz, 1C), 130.2, 130.4, 130.7 (d, $J = 8.2$ Hz, 1C), 143.6, 151.1, 161.7 (d, $J = 244.7$ Hz, 1C), 172.6, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{F}_4\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 531.1302, found: 531.1305.



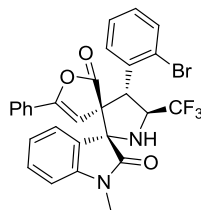
Compound **3q**: White solid; 59.5 mg, 96% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20} = -160.8$ (c. 1.282, acetone); m.p. 204.1-204.5 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 15/85, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 13.1$ min (minor), 21.7 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.09 (s, 3H), 4.59 (d, $J = 8.3$ Hz, 1H), 4.79-5.03 (m, 1H), 5.14 (d, $J = 10.8$ Hz, 1H), 6.94 (t, $J = 7.4$ Hz, 2H), 7.02 (s, 1H), 7.18-7.29 (m, 2H), 7.30-7.45 (m, 7H), 7.48 (d, $J = 7.4$ Hz, 1H), 7.56 (s, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 50.4, 60.6 (q, $J = 29.2$ Hz, 1C), 67.4, 72.0, 102.6, 108.5, 121.5, 124.2, 124.5, 126.0, 126.3, 126.8, 127.9, 129.0, 130.3, 130.4, 130.6, 131.2, 131.3, 136.1, 143.6, 151.3, 172.6, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{BrF}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 591.0502, found: 591.0510.



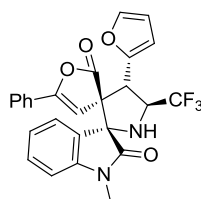
Compound **3r**: White solid; 40.7 mg, 81% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20} = -78.5$ (c. 0.407, acetone); m.p. 188.5-188.9 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 6/6/88, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 14.2$ min (minor), 24.5 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.10 (s, 3H), 4.58 (d, $J = 8.8$ Hz, 1H), 4.77-4.97 (m, 1H), 5.61 (d, $J = 10.7$ Hz, 1H), 6.89-6.99 (m, 3H), 7.06-7.19 (m, 2H), 7.20-7.32 (m, 2H), 7.32-7.45 (m, 5H), 7.46-7.62 (m, 2H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 40.9, 60.6 (q, $J = 31.5$ Hz, 1C), 66.9, 72.0, 102.7, 108.4, 115.6 (d, $J = 22.5$ Hz, 1C), 120.3 (d, $J = 12.8$ Hz, 1C), 121.5, 124.1, 124.2, 124.5, 126.1 (q, $J = 269.2$ Hz, 1C), 126.3, 126.9, 129.1, 130.1, 130.3, 130.4, 130.8, 143.7, 151.2, 160.4 (d, $J = 244.5$ Hz, 1C), 172.2, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{F}_4\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 531.1302, found: 531.1313.



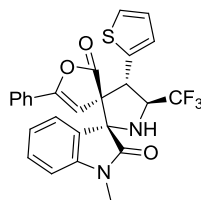
Compound **3s**: White solid; 55.4 mg, 99% yield; >20:1 dr, 94% ee; $[\alpha]_{\text{D}}^{20} = -67.4$ (c. 0.583, acetone); m.p. 205.2-205.9 °C; HPLC (AD-H, *i*-propanol/*n*-hexane = 9/91, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 59.9$ min (minor), 65.0 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.10 (s, 3H), 4.59 (d, $J = 8.5$ Hz, 1H), 4.66-4.86 (m, 1H), 6.15 (d, $J = 10.6$ Hz, 1H), 6.93 (t, $J = 8.5$ Hz, 2H), 7.11 (s, 1H), 7.15-7.30 (m, 3H), 7.32-7.48 (m, 6H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.76 (d, $J = 7.1$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 45.4, 62.2 (q, $J = 30.0$ Hz, 1C), 66.6, 72.3, 103.0, 108.4, 121.4, 124.2, 124.5, 126.0 (q, $J = 278.2$ Hz, 1C), 126.3, 126.5, 127.0, 129.0, 129.6, 129.7, 130.2, 130.4, 130.9, 131.2, 134.1, 143.8, 151.1, 172.0, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{ClF}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 547.1007, found: 547.1003.



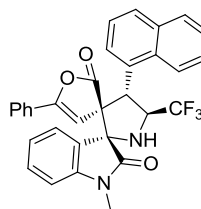
Compound **3t**: White solid; 61.2 mg, 98% yield; >20:1 dr, 98% ee; $[\alpha]_{\text{D}}^{20} = -10.6$ (c. 0.731, acetone); m.p. 196.8-197.3 °C; HPLC (AD-H, *i*-propanol/*n*-hexane = 9/91, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 69.5$ min (major), 77.4 min (minor); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.10 (s, 3H), 4.57 (d, $J = 8.6$ Hz, 1H), 4.63-4.82 (m, 1H), 6.14 (d, $J = 10.7$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 2H), 7.10 (d, $J = 10.3$ Hz, 2H), 7.21-7.32 (m, 2H), 7.34-7.48 (m, 5H), 7.51 (d, $J = 7.5$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.73 (d, $J = 7.8$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 48.2, 62.6, 66.7, 72.3, 103.0, 108.4, 121.4, 124.2, 124.5, 125.1, 126.1, 126.4, 126.9, 127.0, 129.0, 129.9, 130.2, 130.4, 131.0, 133.0, 133.1, 143.8, 151.0, 171.9, 174.4; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{BrF}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 591.0502, found: 591.0505.



Compound **3u**: White solid; 45.6 mg, 95% yield; >20:1 dr, 94% ee; $[\alpha]_{\text{D}}^{20} = -203.5$ (c. 0.450, acetone); m.p. 192.9-193.7 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 1/9/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 18.6$ min (minor), 37.5 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.09 (s, 3H), 4.59 (d, $J = 9.1$ Hz, 1H), 4.63-4.84 (m, 1H), 5.25 (d, $J = 10.5$ Hz, 1H), 6.26-6.43 (m, 2H), 6.72 (s, 1H), 6.87-6.99 (m, 2H), 7.27 (t, $J = 7.7$ Hz, 1H), 7.35-7.47 (m, 5H), 7.47-7.58 (m, 2H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 25.9, 44.7, 60.2 (q, $J = 30.0$ Hz, 1C), 66.2, 71.9, 102.7, 108.4, 108.5, 110.6, 121.4, 123.7, 124.5, 125.8 (q, $J = 278.3$ Hz, 1C), 126.2, 126.9, 129.0, 130.2, 130.4, 143.2, 143.6, 148.0, 151.3, 172.3, 174.2; HRMS (ESI-TOF) calcd. for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 503.1189, found: 503.1184.

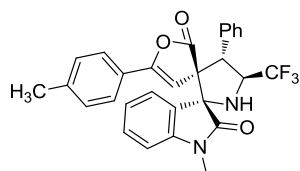


Compound **3v**: White solid; 49.3 mg, 99% yield; >20:1 dr, >99% ee; $[\alpha]_{\text{D}}^{20} = -134.7$ (c. 0.501, acetone); m.p. 198.0-198.3 °C; HPLC (IA-H, DCM/*i*-propanol/*n*-hexane = 1/9/90, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 19.2$ min (minor), 34.6 min (major); $^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ 3.05 (s, 3H), 4.50 (d, $J = 8.8$ Hz, 1H), 4.54-4.70 (m, 1H), 5.45 (d, $J = 10.3$ Hz, 1H), 6.84-6.96 (m, 4H), 7.03 (d, $J = 3.5$ Hz, 1H), 7.23 (t, $J = 7.7$ Hz, 1H), 7.31-7.45 (m, 6H), 7.50 (d, $J = 7.5$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ 26.0, 46.1, 63.1 (q, $J = 30.0$ Hz, 1C), 67.3, 71.8, 102.8, 108.5, 121.5, 124.1, 124.6, 125.9 (q, $J = 278.3$ Hz, 1C), 126.3, 126.4, 126.9, 127.0, 127.4, 129.1, 130.3, 130.4, 143.6, 151.8, 172.4, 174.4; HRMS (ESI-TOF) calcd. for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_3\text{S}$ $[\text{M} + \text{Na}]^+$ 519.0961, found: 519.0964.



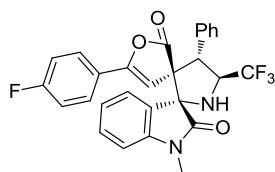
Compound **3w**: White solid; 51.0 mg, 94% yield; >20:1 dr, 98% ee; $[\alpha]_{\text{D}}^{20} = +103.1$ (c. 0.483, acetone); m.p. 207.1-207.5 °C; HPLC (IA-H,

i-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 31.6 min (minor), 49.8 min (major); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 3.17 (s, 3H), 4.65 (d, J = 8.4 Hz, 1H), 4.86-5.09 (m, 1H), 6.52 (d, J = 10.6 Hz, 1H), 6.85-7.06 (m, 2H), 7.20 (s, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.31-7.42 (m, 5H), 7.42-7.49 (m, 1H), 7.49-7.68 (m, 3H), 7.78 (d, J = 8.1 Hz, 1H), 7.87 (t, J = 7.1 Hz, 2H), 8.36 (d, J = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 26.1, 43.2, 62.2 (q, J = 30.0 Hz, 1C), 67.0, 72.4, 103.3, 108.5, 121.5, 122.5, 124.3, 124.4, 124.7, 125.8, 126.2, 126.4, 126.6, 126.9, 128.4, 128.8, 129.0, 129.0, 130.1, 130.4, 131.8, 133.4, 143.7, 151.3, 172.6, 174.9; HRMS (ESI-TOF) calcd. for $\text{C}_{32}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 563.1553, found: 563.1542.



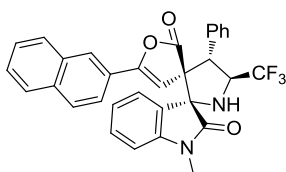
Compound **3x**: White solid; 51.8 mg, 99% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20}$ = -159.7 (c. 0.619, acetone); m.p. 217.2-218.1 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 22.1 min (minor), 37.3 min (major); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 2.24 (s, 3H), 3.09 (s, 3H), 4.52 (d, J = 8.7 Hz,

1H), 4.77-4.96 (m, 1H), 5.17 (d, J = 10.8 Hz, 1H), 6.86 (s, 1H), 6.92 (t, J = 8.2 Hz, 2H), 7.11-7.21 (m, 3H), 7.21-7.34 (m, 7H), 7.51 (d, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 20.9, 25.9, 50.7, 60.6 (q, J = 30.0 Hz, 1C), 67.5, 72.1, 101.8, 108.4, 121.4, 124.2, 124.4, 126.2 (q, J = 278.5 Hz, 1C), 126.3, 128.0, 128.3, 128.6, 129.5, 130.3, 133.5, 140.0, 143.6, 151.1, 172.8, 174.6; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 527.1553, found: 527.1547.



Compound **3y**: White solid; 49.8 mg, 98% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20}$ = -151.4 (c. 0.606, acetone); m.p. 197.2-197.5 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 24.4 min (minor), 42.2 min (major); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 3.09 (s, 3H), 4.56 (d, J = 8.4 Hz, 1H), 4.76-4.96 (m, 1H), 5.17 (d, J =

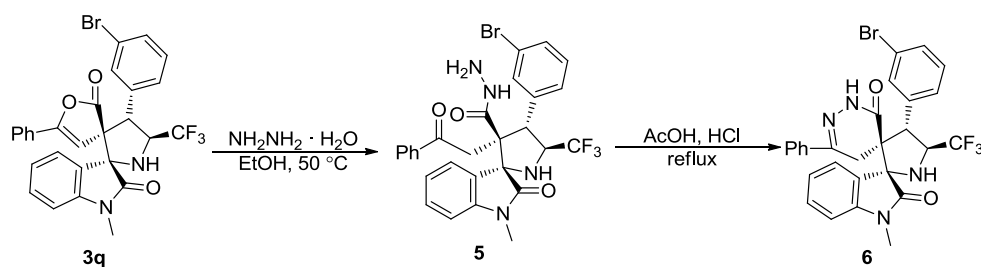
10.8 Hz, 1H), 6.86-6.99 (m, 3H), 7.14-7.35 (m, 8H), 7.37-7.47 (m, 2H), 7.51 (d, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 25.9, 60.2 (q, J = 30.0 Hz, 1C), 61.2, 67.6, 72.1, 102.7 (d, J = 2.3 Hz, 1C), 108.4, 116.1, 121.4, 123.5 (d, J = 3.0 Hz, 1C), 124.3, 126.1 (q, J = 279.0 Hz, 1C), 126.3, 126.9 (d, J = 8.2 Hz, 1C), 128.1, 128.4, 128.6, 130.3, 133.4, 143.7, 150.0, 162.9 (d, J = 246.7 Hz, 1C), 172.6, 174.5; HRMS (ESI-TOF) calcd. for $\text{C}_{28}\text{H}_{20}\text{F}_4\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 531.1302, found: 531.1309



Compound **3z**: White solid; 52.2 mg, 96% yield; >20:1 dr, 97% ee; $[\alpha]_D^{20}$ = -165.7 (c. 0.652, acetone); m.p. 199.5-199.8 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 29.1 min (minor), 43.5 min (major); ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 3.11 (s, 3H), 4.59 (d, J = 8.2 Hz, 1H), 4.80-5.03 (m, 1H), 5.22 (d, J =

10.7 Hz, 1H), 6.82-7.00 (m, 2H), 7.07-7.30 (m, 5H), 7.31-7.42 (m, 2H), 7.43-7.62 (m, 3H), 7.68 (d, J = 8.5 Hz, 1H), 7.74 (s, 1H), 7.87 (t, J = 6.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 26.0, 50.8, 60.7 (q, J = 29.3 Hz, 1C), 67.7, 72.2, 103.8, 108.4, 121.4, 121.7, 123.9, 124.2, 124.4, 126.2 (q, J = 279.0 Hz, 1C), 126.4, 127.1, 127.5, 127.7, 128.1, 128.4, 128.6, 128.7, 128.9, 130.4, 132.4, 133.3, 133.5, 143.7, 151.0, 172.7, 174.6; HRMS (ESI-TOF) calcd. for $\text{C}_{32}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3$ $[\text{M} + \text{Na}]^+$ 563.1553, found: 563.1547.

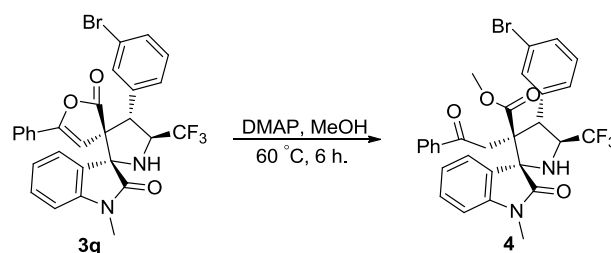
4. Procedure for the synthesis of compounds **4**⁴ and **6**⁵.



Hydrazine hydrate (80%, 1.0 mL) was added to a stirred solution of **3q** (0.4 mmol, 228.8 mg) in absolute ethanol (13.0 mL) and the reaction mixture was stirred for 20 min at 50 °C. The white solid disappears. After completion of the reaction as indicated by TLC. The resulting mixture concentrated under reduced pressure and obtained pale yellow oil **5**.

A mixture of glacial acetic acid (1.0 mL), hydrochloric acid (34%, 4.0 mL) and pale yellow oil was refluxed for 20 min. White precipitate was formed. After completion of the reaction and mixture was allowed to cool and ice-cold water (15 mL) was poured into. The aqueous phase extracted with DCM (3 x 10 mL). The organic phase were combined and dried over Na₂SO₄, then the solvent was evaporated. The crude product was purified on a column of silica gel and eluted with petroleum ether/EtOAc (8:1). Afforded 231.9 mg of **6**.

Compound **6**: White solid; 231.9 mg, 99% yield; >20:1 dr, >99% ee; [α]_D²⁰ = -360.1 (c. 1.150, acetone); m.p. 199.8-200.7 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 15/85, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.0 min (major), 14.6 min (minor); ¹H NMR (300 MHz, CDCl₃) δ 2.45 (s, 3H), 2.74 (d, J = 16.6 Hz, 1H), 2.87 (d, J = 8.7 Hz, 1H), 3.20 (d, J = 16.7 Hz, 1H), 4.50 (d, J = 10.7 Hz, 1H), 5.30 (dq, J = 15.8, 7.1 Hz, 1H), 6.40 (d, J = 7.8 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 7.15-7.29 (m, 6H), 7.29-7.36 (m, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.84 (s, 1H), 9.23 (s, 1H); ¹³C NMR (75 MHz, DMSO) δ 24.7, 49.8, 55.9, 61.6 (q, J = 29.1 Hz, 1C), 71.0, 79.1, 108.0, 121.4, 122.3, 124.7, 124.9, 125.3, 126.2 (q, J = 279.0 Hz, 1C), 128.1, 129.4, 129.7, 129.8, 130.1, 130.8, 132.8, 135.1, 136.4, 143.2, 149.0, 165.5, 175.5; HRMS (ESI-TOF) calcd. for C₂₈H₂₂BrF₃N₄NaO₂ [M + Na]⁺ 605.0707, found: 605.0765.



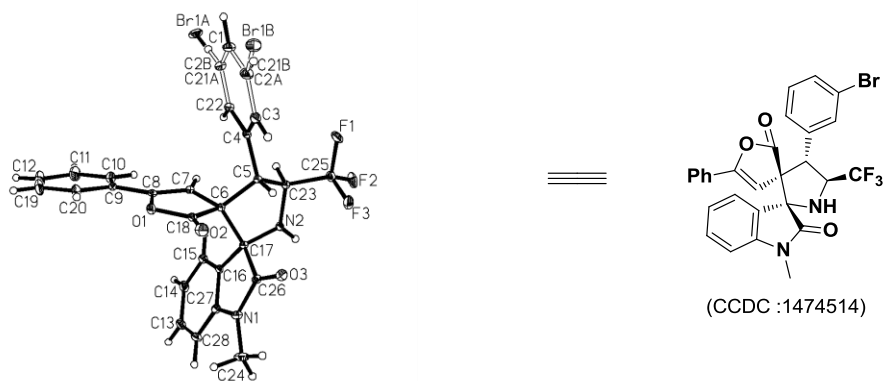
To a solution of **3q** (113.7 mg, 0.20 mmol) (>99:1 dr) in methanol (3 mL) was added DMAP (24.4 mg, 0.2 mmol). The reaction mixture was stirred at 60 °C for 5 h before being concentrated in vacuo to give crude product. Chromatographic purification (eluent PE/EA 3:1) gave product as a white solid.

Compound **6**: White solid; 116.7 mg, 97% yield; >20:1 dr, 98% ee; [α]_D²⁰ = -154.5 (c. 2.334, CHCl₃); m.p. 199.8-200.7 °C; HPLC (IA-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min,

$\lambda = 254 \text{ nm}$ $t_R = 21.8 \text{ min}$ (minor), 29.5 min (major); $^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 3.06 (s, 3H), 3.18 (d, $J = 18.1 \text{ Hz}$, 1H), 3.32 (s, 3H), 3.88 (d, $J = 8.8 \text{ Hz}$, 1H), 4.54 (d, $J = 18.1 \text{ Hz}$, 1H), 4.87 (dq, $J = 18.1, 7.8 \text{ Hz}$, 1H), 5.09 (d, $J = 11.0 \text{ Hz}$, 1H), 6.99 (d, $J = 7.7 \text{ Hz}$, 2H), 7.10-7.19 (m, 1H), 7.19-7.29 (m, 1H), 7.38 (t, $J = 7.4 \text{ Hz}$, 2H), 7.46-7.57 (m, 3H), 7.59-7.65 (m, 1H), 7.73 (d, $J = 7.2 \text{ Hz}$, 2H), 7.78 (d, $J = 7.3 \text{ Hz}$, 1H); $^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 25.8, 47.1, 51.4, 60.7 (q, $J = 29.2 \text{ Hz}$, 1C), 60.9, 73.5, 108.4, 120.8, 121.6, 121.8, 126.1, 126.3, 126.4 (q, $J = 279.0 \text{ Hz}$, 1C), 127.4, 128.6, 128.9, 129.9, 130.0, 130.1, 133.2, 135.7, 139.0, 144.5, 170.4, 175.3, 194.4; HRMS (ESI-TOF) calcd. for $\text{C}_{29}\text{H}_{24}\text{BrF}_3\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 623.0764, found: 623.0786.

1. Koch, R.; Berstermann, H. M.; Wentrup, C. *J. Org. Chem.* 2014, **79**, 65.
2. Deo, U.; Inam, F.; Masahsabde, R. P.; Jadhav, A. N. *Asian Journal of Chemistry.* 2010, **22**, 3362.
3. Ma, M.; Zhu, Y.; Sun, Q.; Li, X.; Su, J.; Zhao, L.; Zhao, Y.; Qiu, S.; Yan, W.; Wang, K.; Wang, R. *Chem. Commun.* 2015, **51**, 8789.
4. Farag, A. M.; Elkholy, Y. M.; Ali, K. A. *Heterocyclic Chem.* 2008, **45**, 279.
5. Morrill, L. C.; Douglas, J.; Lebl, T.; Slawin, A. M. Z.; Fox, D. J.; Smith, A. D. *Chem. Sci.*, 2013, **4**, 4146.

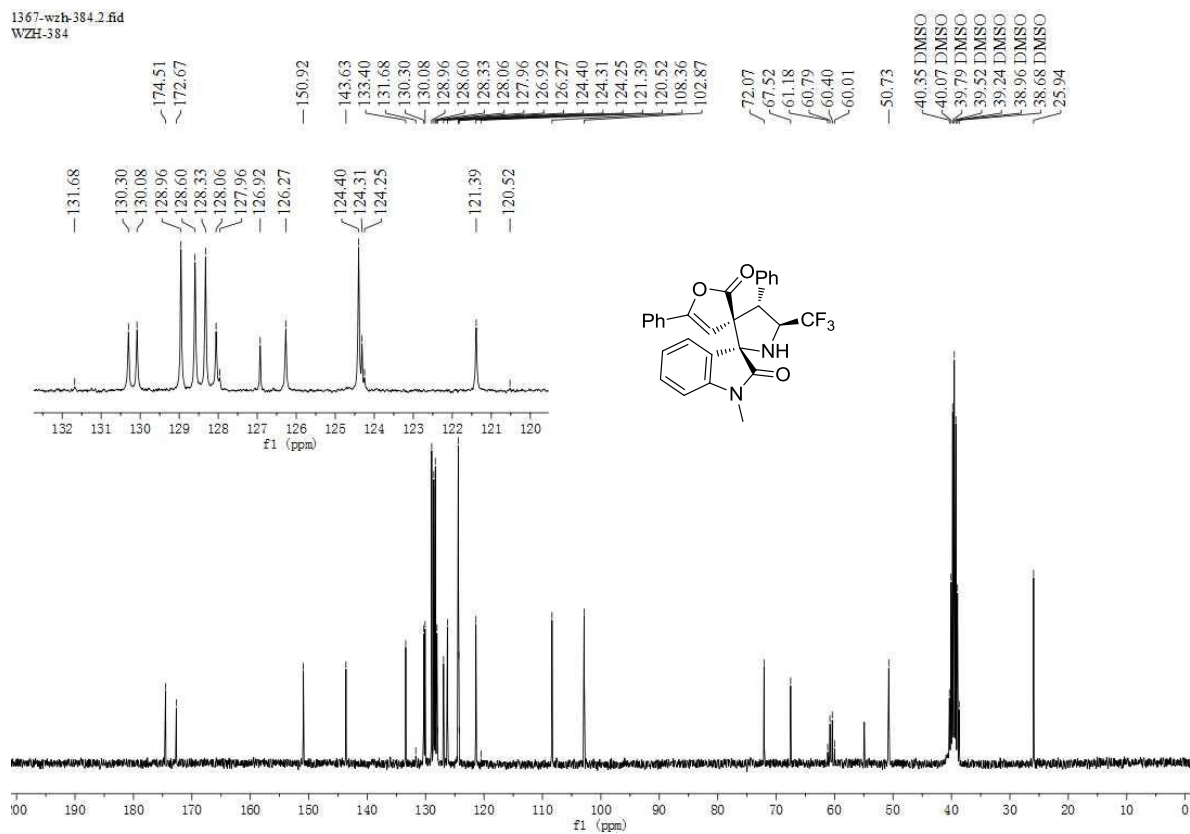
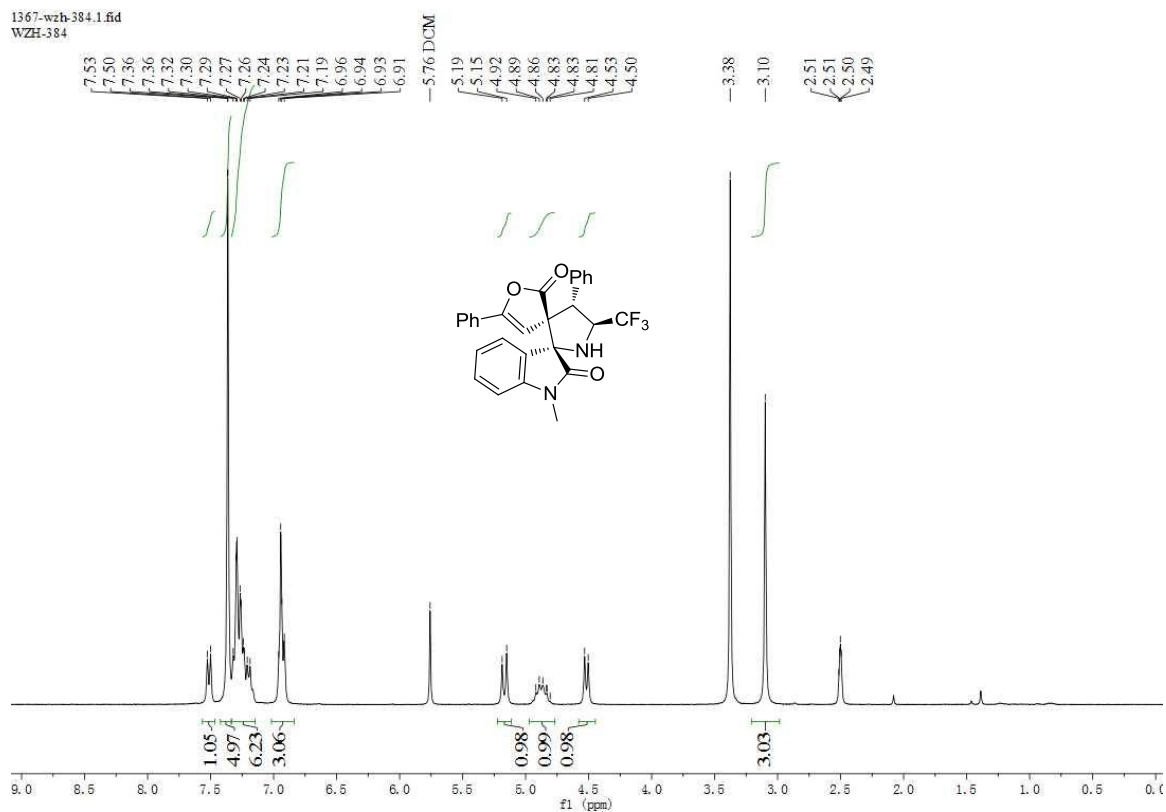
5. X-ray crystal structure of compound **3q**

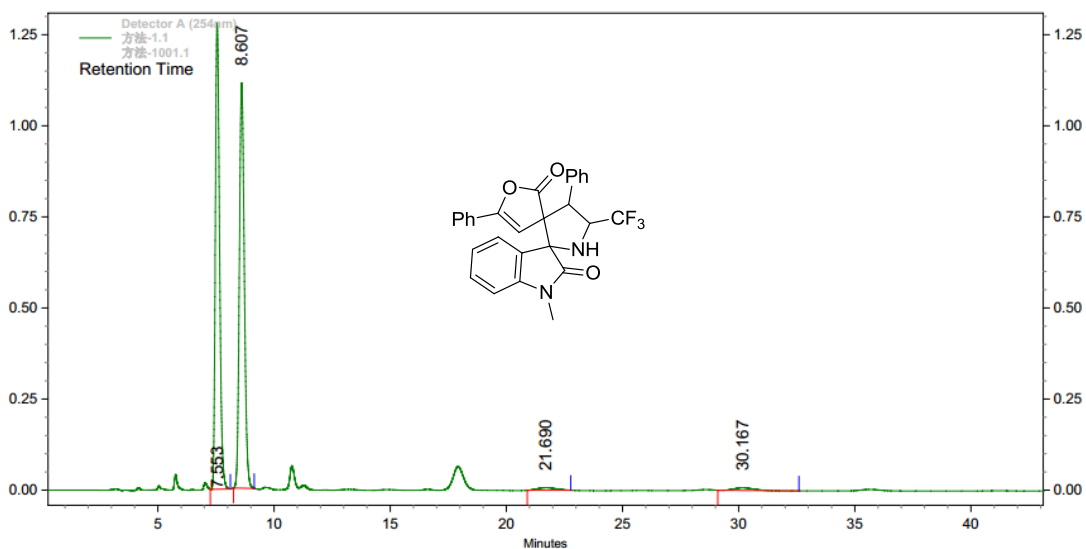


Empirical formula	$C_{28}H_{20}BrF_3N_2O_3$
Formula weight	688.74
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 12.0262(12)$ Å = 90°. $b = 13.8263(14)$ Å = 90°. $c = 17.0090(17)$ Å = 90°.
Volume	2828.2(5) Å ³
Z	4
Density (calculated)	1.618 Mg/m ³
Absorption coefficient	1.792 mm ⁻¹
F(000)	1384
Crystal size	0.620 x 0.290 x 0.290 mm ³
Theta range for data collection	1.898 to 31.013 °
Index ranges	-17<=h<=17, -19<=k<=18, -24<=l<=24
Reflections collected	31413
Independent reflections	8298 [R(int) = 0.0349]
Completeness to theta = 25.242 °	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8298 / 0 / 381
Goodness-of-fit on F ²	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0866
R indices (all data)	R1 = 0.0478, wR2 = 0.0902
Absolute structure parameter	0.021(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.734 d -0.601 e. Å ⁻³

6. ^1H , ^{13}C NMR and HPLC spectra for compounds 3a-z and compounds 5, 6.

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

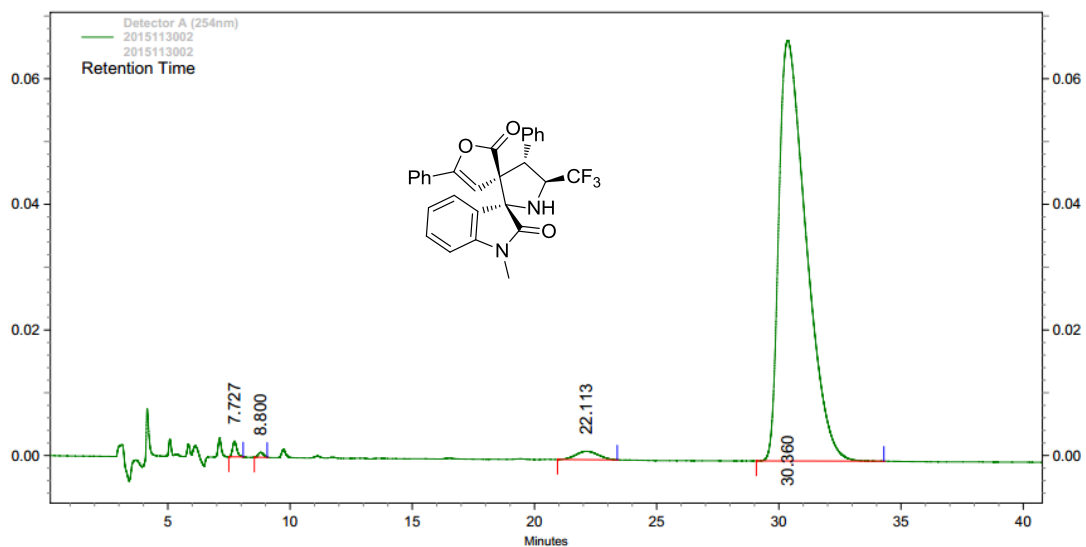




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.553	1281849	53.25	16181023	48.43
2	8.607	1111282	46.17	16418205	49.14
3	21.690	6926	0.29	402212	1.20
4	30.167	7103	0.30	408224	1.22

Totals					
		2407160	100.00	33409664	100.00

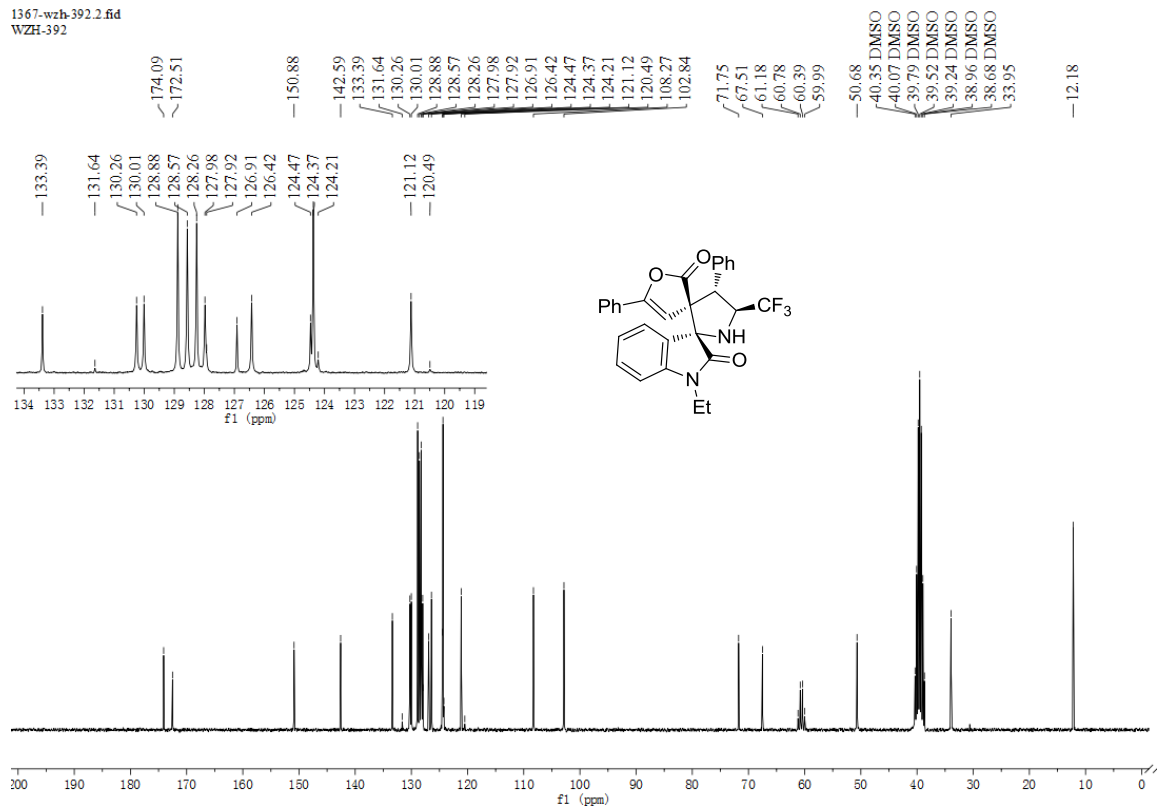
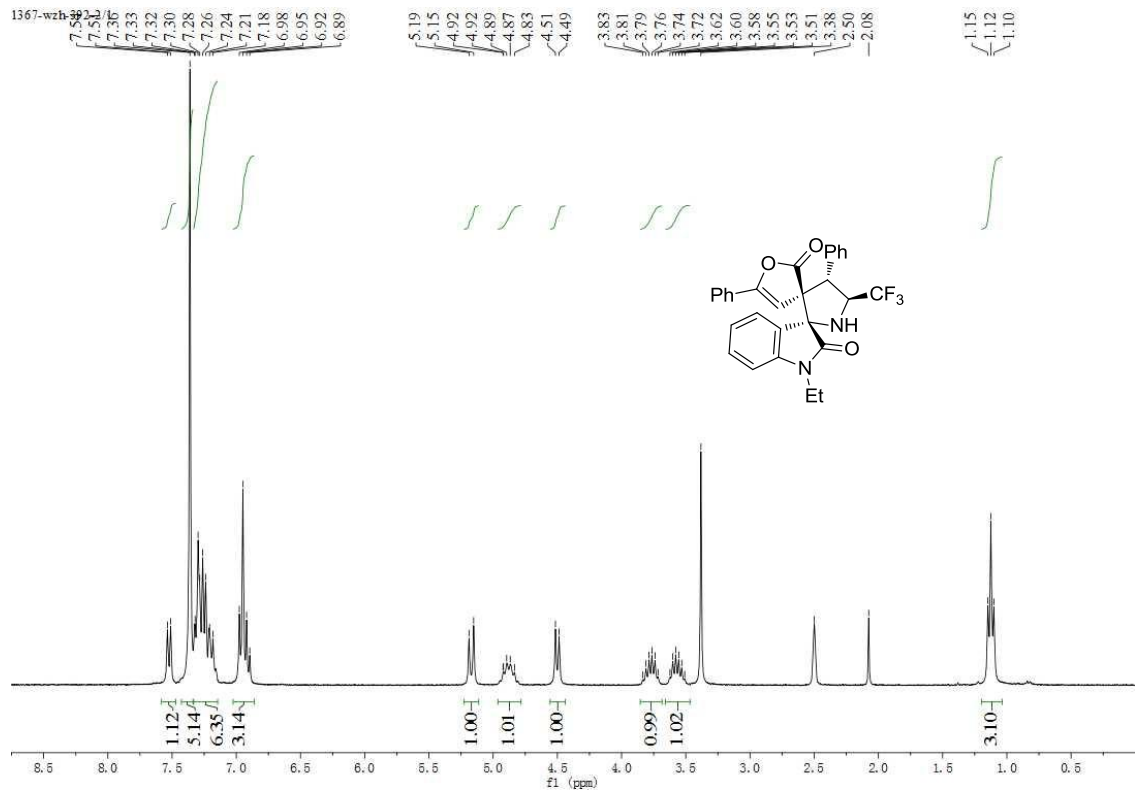


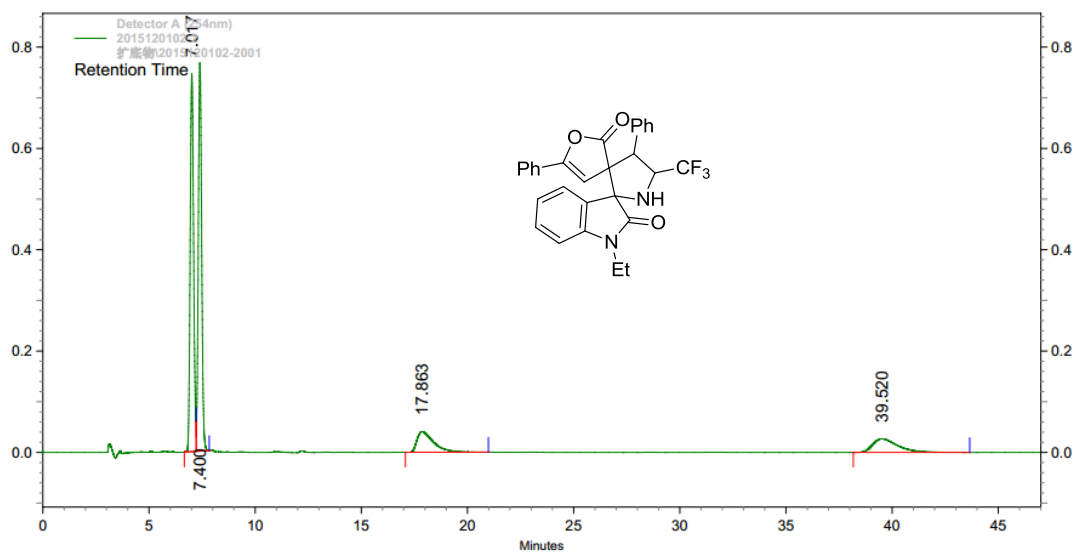
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.727	2516	3.51	30744	0.58
2	8.800	796	1.11	11413	0.22
3	22.113	1331	1.86	84997	1.60
4	30.360	66967	93.52	5174778	97.60

Totals					
		71610	100.00	5301932	100.00

¹H NMR, ¹³C NMR and HPLC of 3b





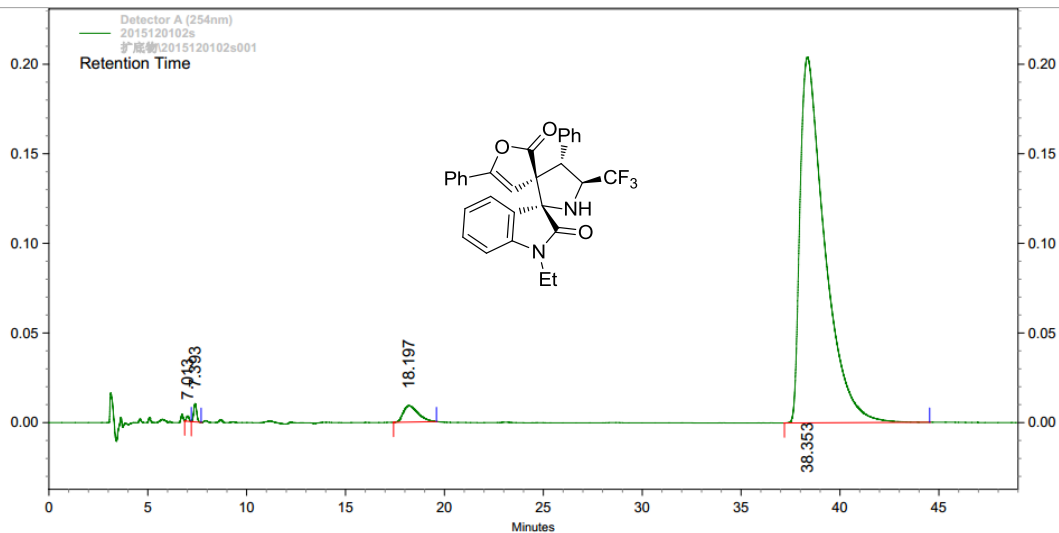
Detector

A

(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.017	745605	47.20	8272368	39.20
2	7.400	766480	48.52	8437496	39.98
3	17.863	40843	2.59	2179844	10.33
4	39.520	26805	1.70	2214321	10.49

Totals		1579733	100.00	21104029	100.00
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Detector

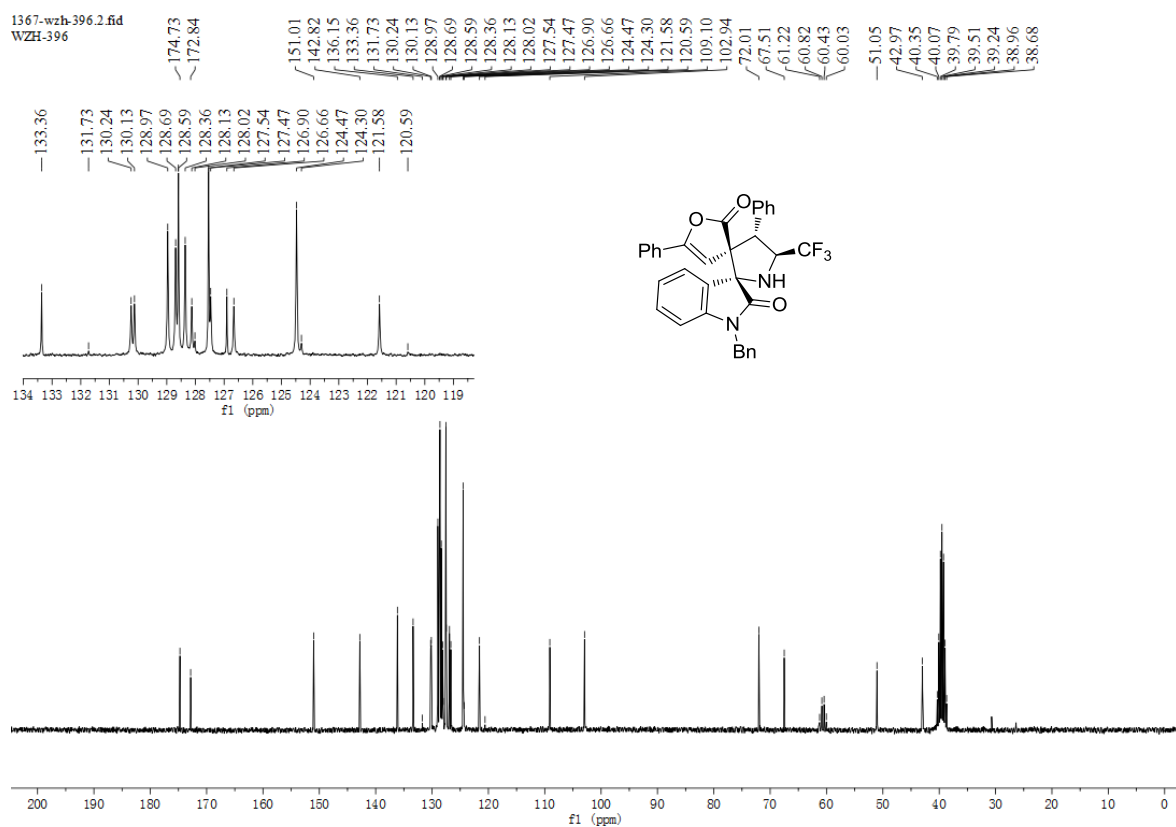
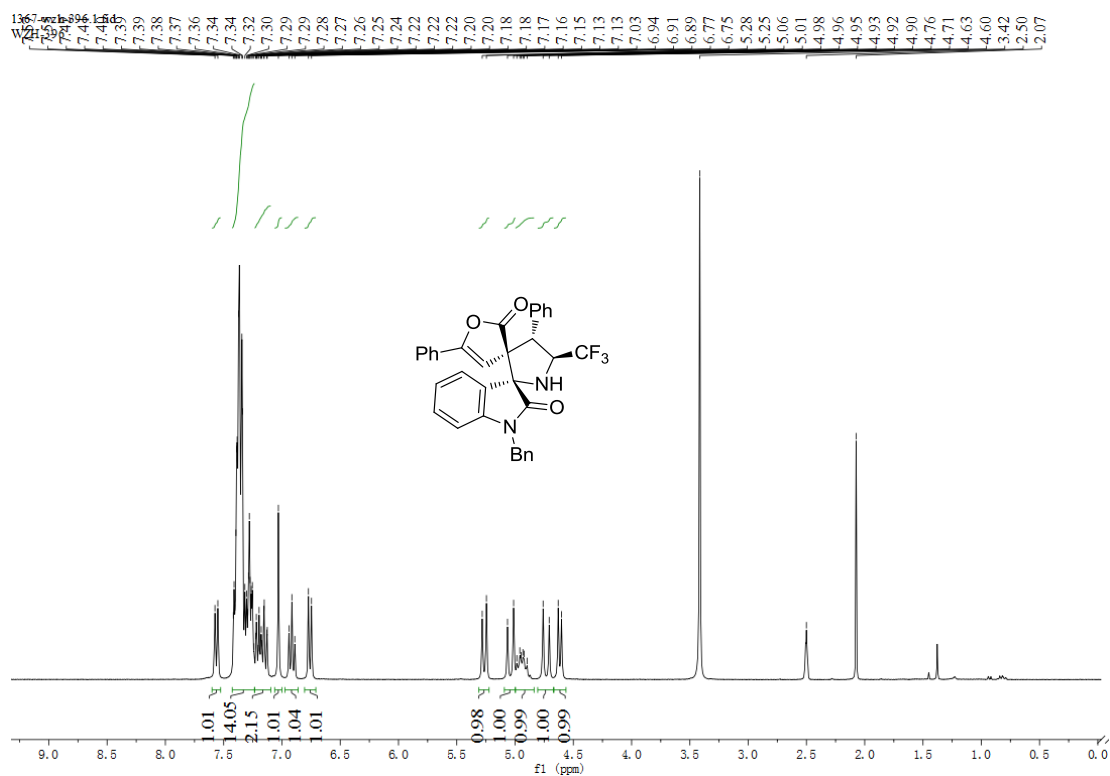
A

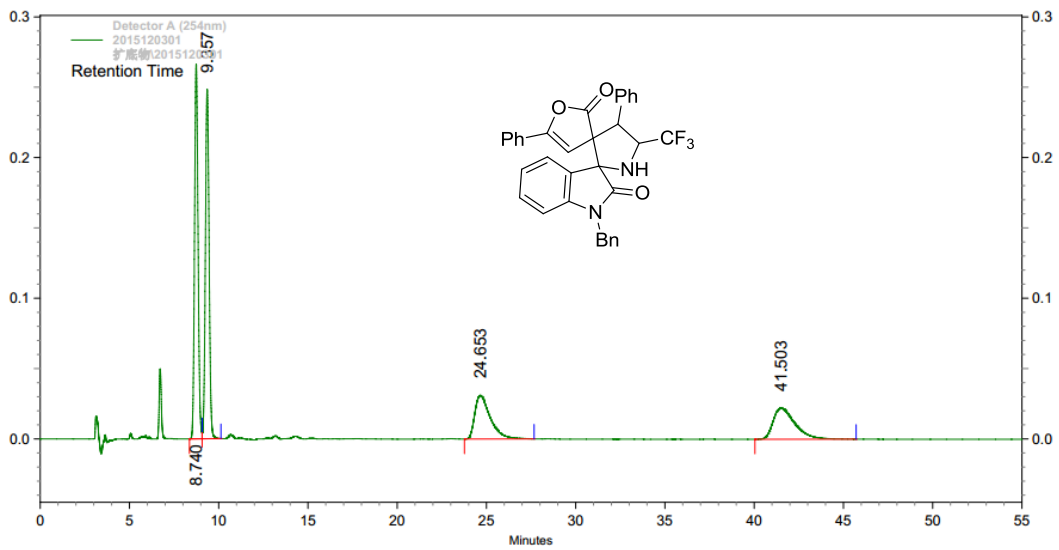
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.013	2988	1.32	27474	0.15
2	7.393	10181	4.50	105154	0.58
3	18.197	9144	4.04	470779	2.59
4	38.353	204135	90.15	17602826	96.69

Totals		226448	100.00	18206233	100.00
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¹H NMR, ¹³C NMR and HPLC of 3c

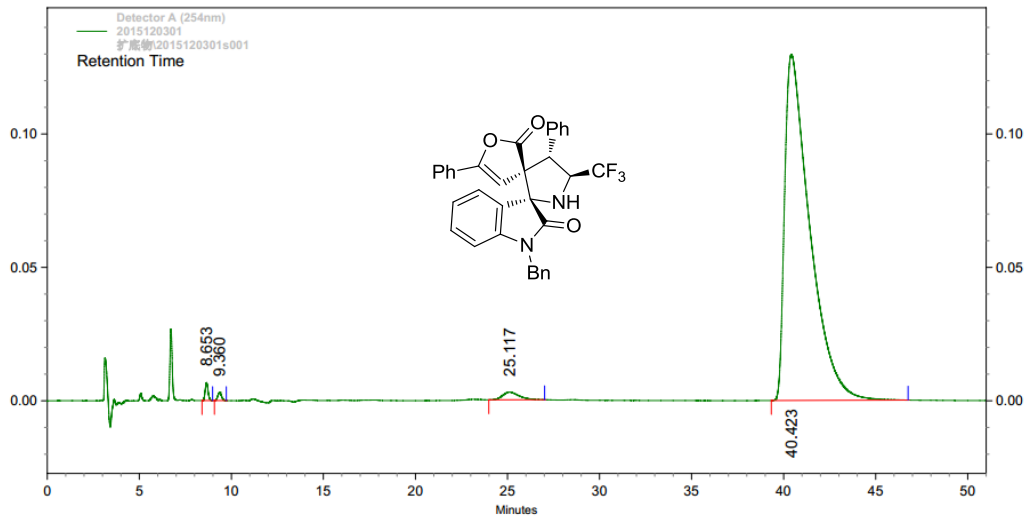




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.740	266406	46.89	3623056	33.21
2	9.357	248421	43.72	3545098	32.50
3	24.653	31058	5.47	1868820	17.13
4	41.503	22282	3.92	1871425	17.16

Totals		568167	100.00	10908399	100.00
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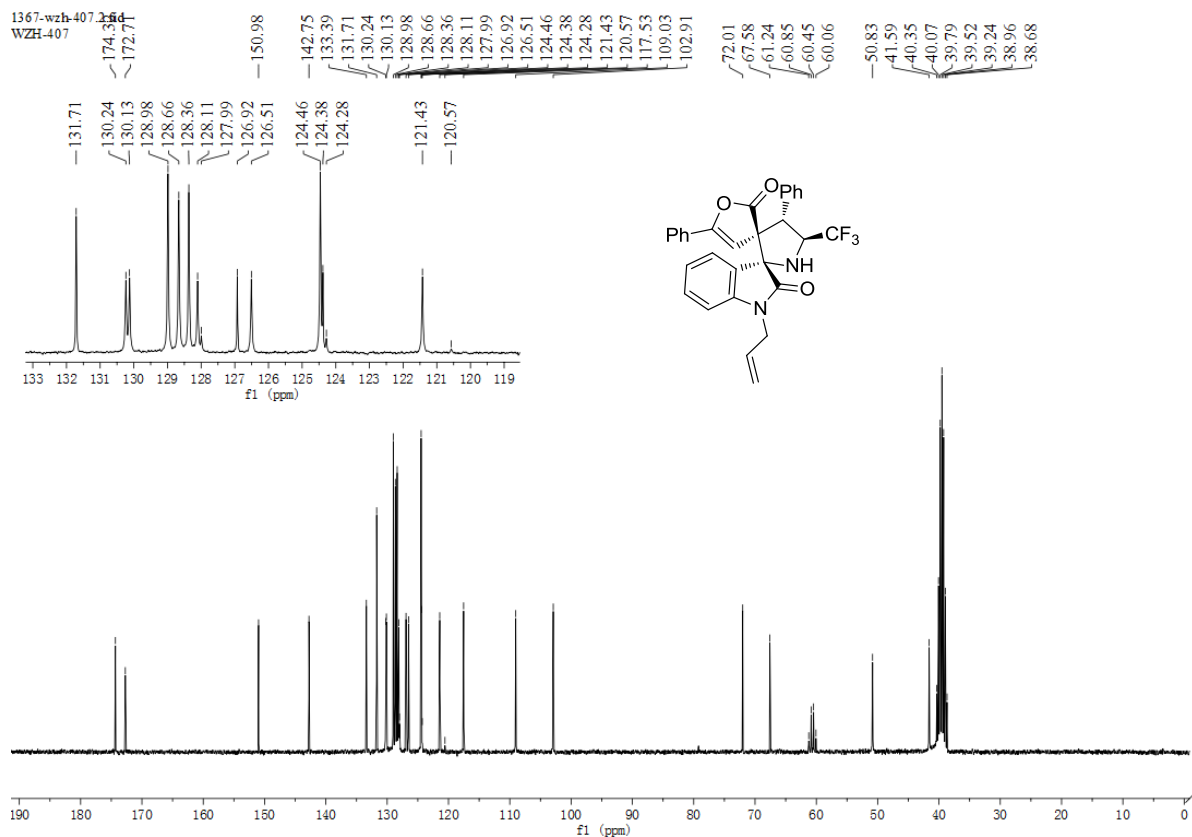
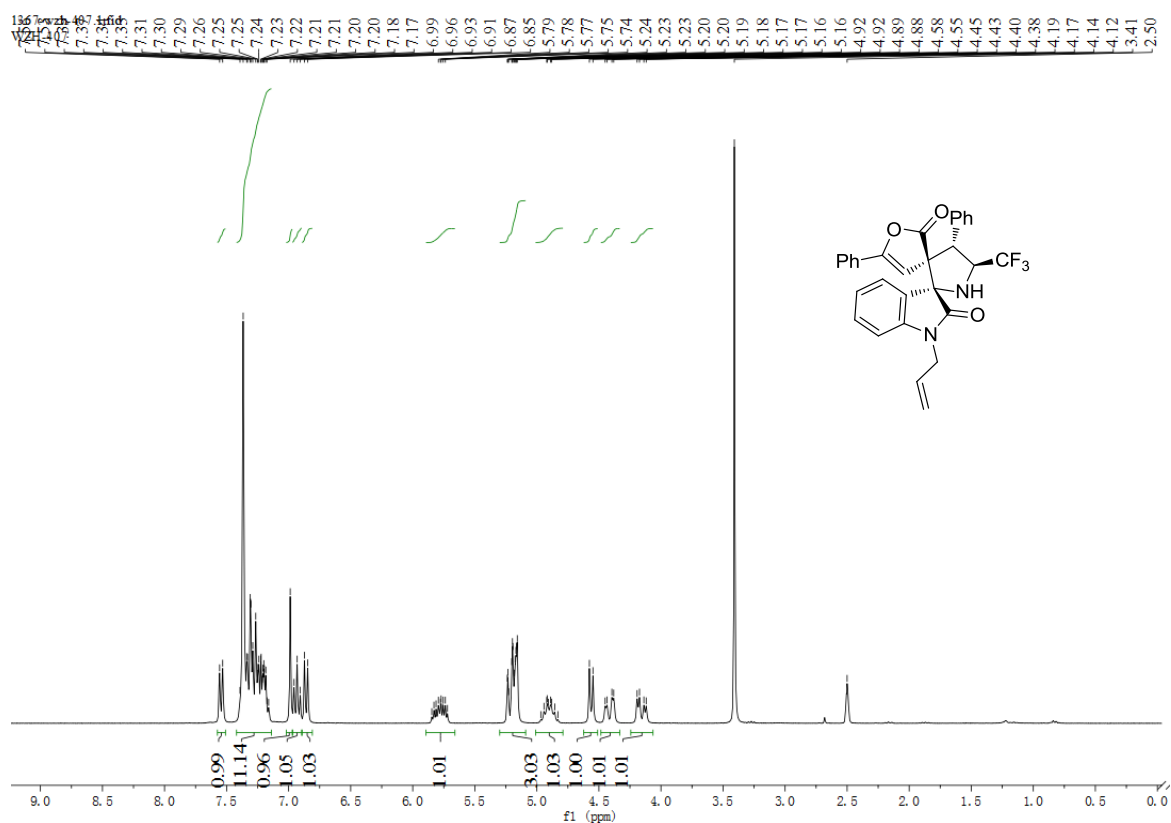


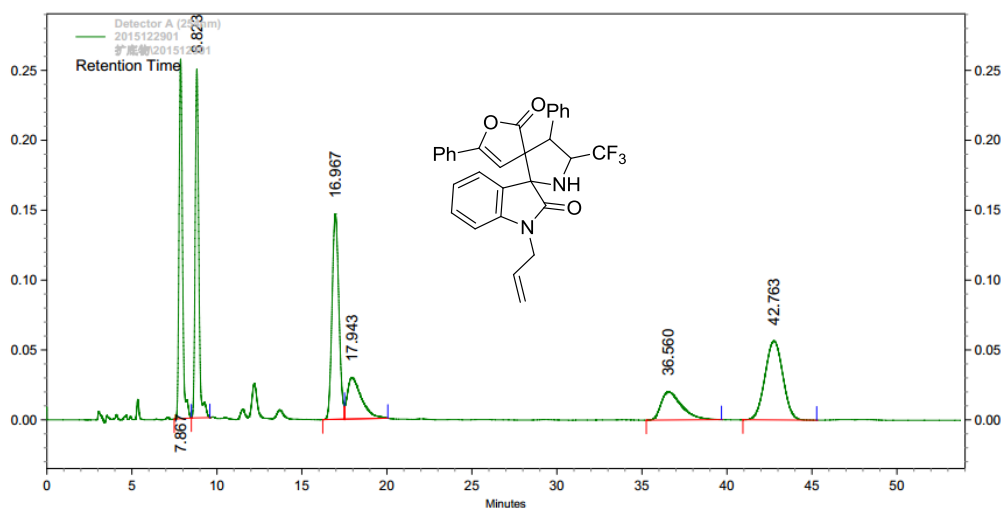
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.653	6726	4.72	73914	0.59
2	9.360	3050	2.14	43077	0.34
3	25.117	2857	2.01	178417	1.42
4	40.423	129752	91.13	12296992	97.65

Totals		142385	100.00	12592400	100.00
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¹H NMR, ¹³C NMR and HPLC of 3d

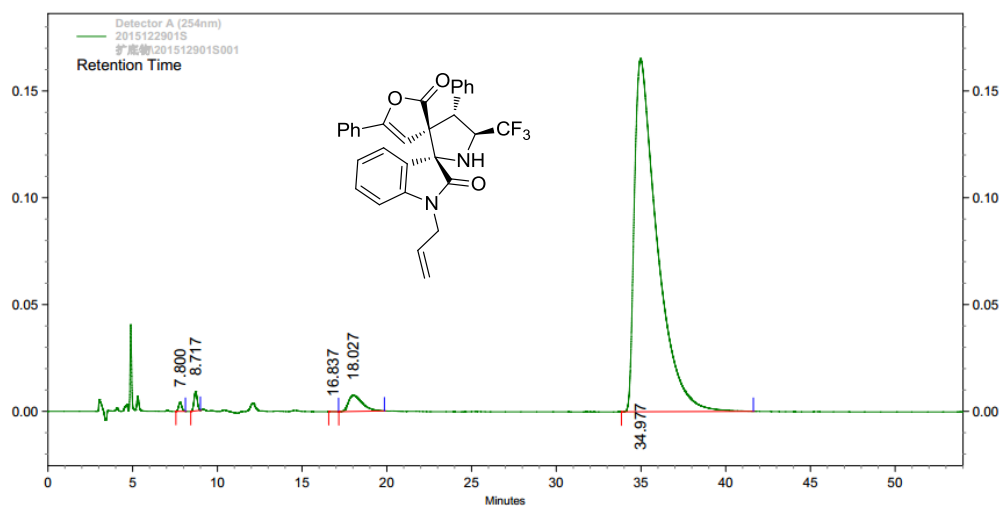




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.867	257178	33.82	3611404	19.10
2	8.823	249587	32.82	3671934	19.42
3	16.967	146954	19.33	4118620	21.79
4	17.943	29820	3.92	1697848	8.98
5	36.560	20202	2.66	1676837	8.87
6	42.763	56631	7.45	4127015	21.83

Totals		760372	100.00	18903658	100.00
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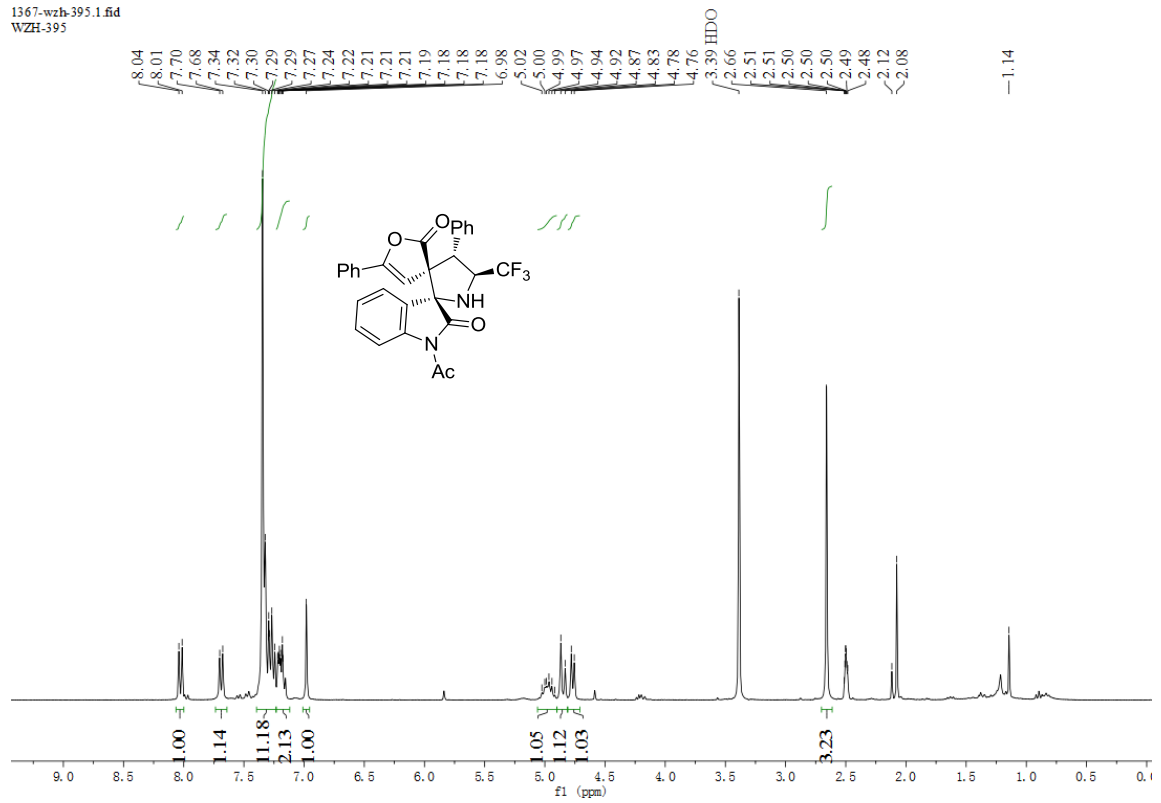
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.800	4301	2.31	55370	0.35
2	8.717	9047	4.86	119811	0.75
3	16.837	32	0.02	596	0.00
4	18.027	7590	4.08	422661	2.66
5	34.977	165266	88.74	15320082	96.24

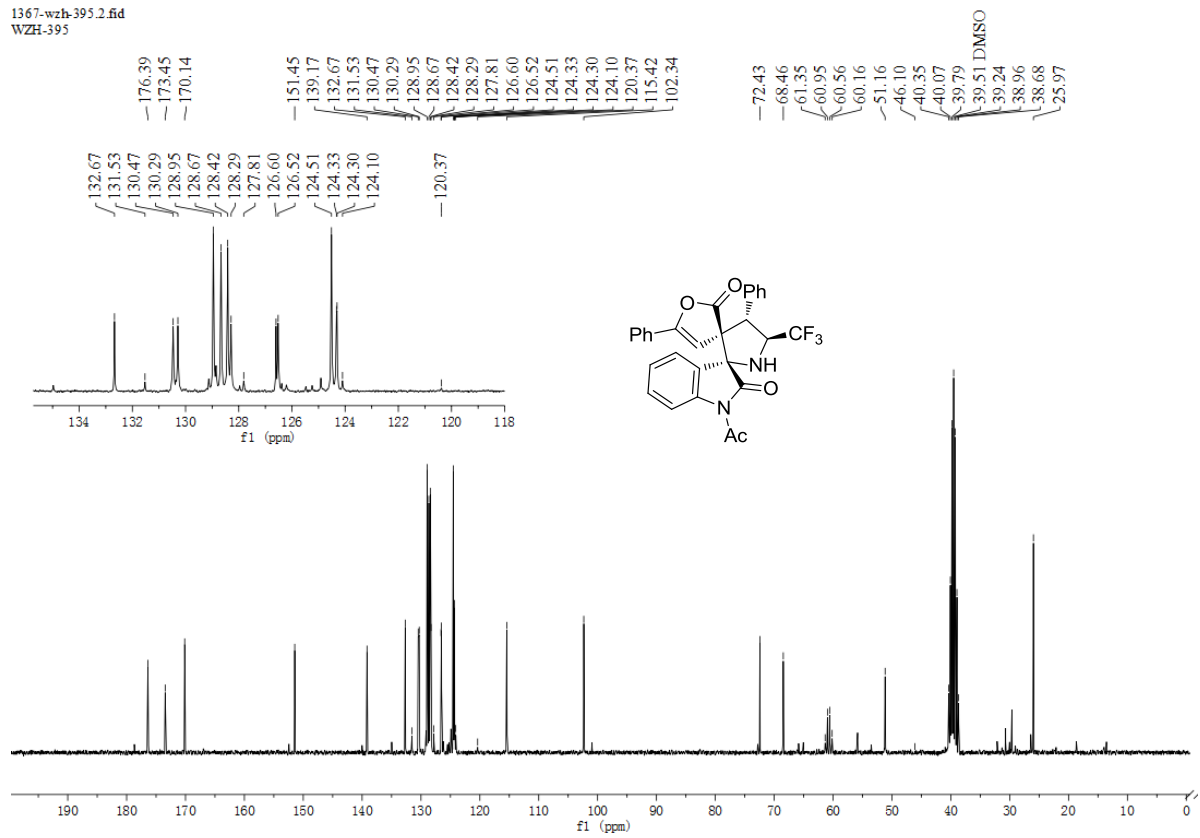
Totals		186236	100.00	15918520	100.00
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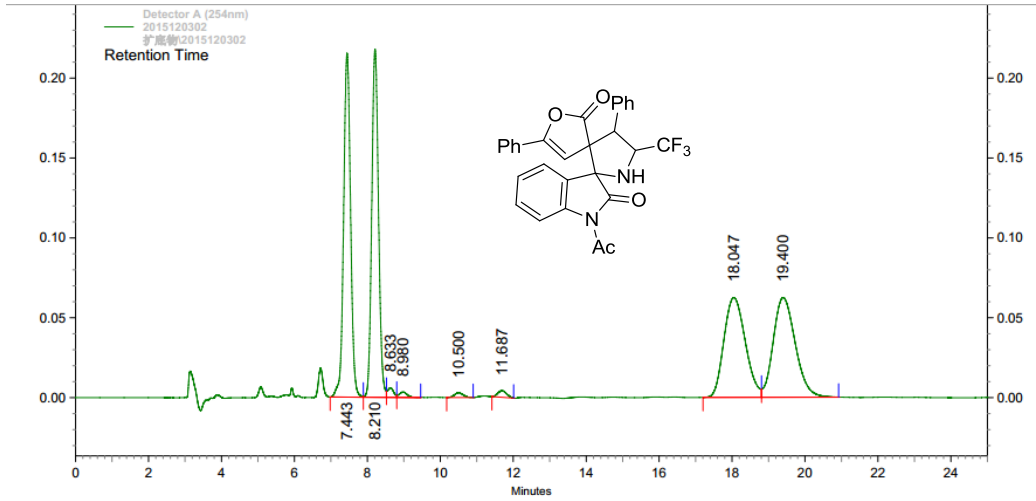
¹H NMR, ¹³C NMR and HPLC of 3e

1367-wzh-395.1.fid
WZH-395



1367-wzh-395.2.fid
WZH-395

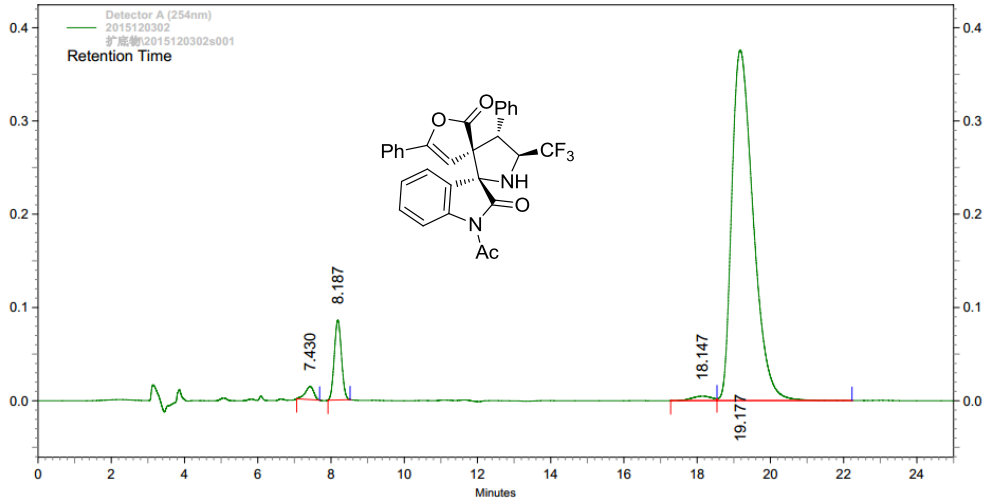




Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.443	215216	37.47	2849739	25.84
2	8.210	217839	37.93	2782201	25.22
3	8.633	5952	1.04	67687	0.61
4	8.980	3326	0.58	49604	0.45
5	10.500	2994	0.52	48511	0.44
6	11.687	4124	0.72	68370	0.62
7	18.047	62432	10.87	2543479	23.06
8	19.400	62439	10.87	2620056	23.75

Totals		574322	100.00	11029647	100.00
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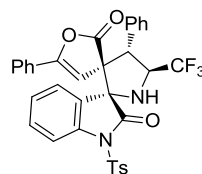
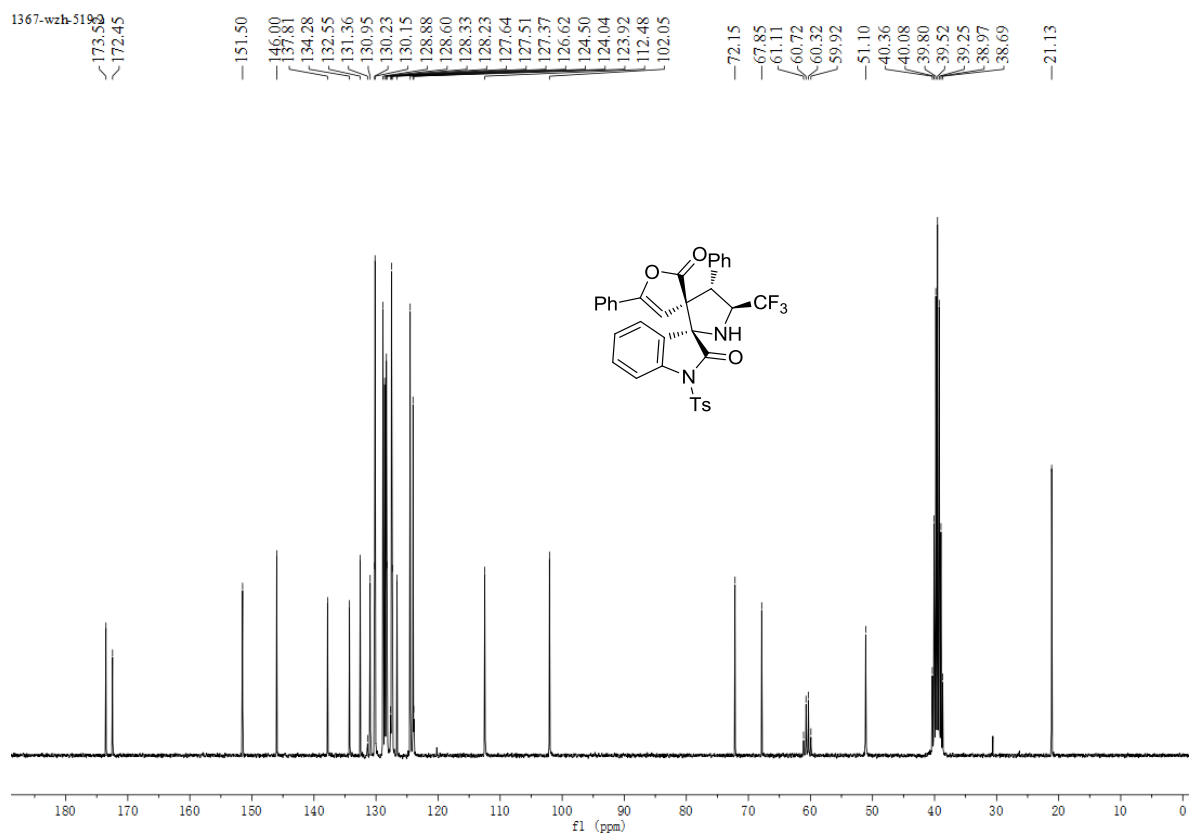
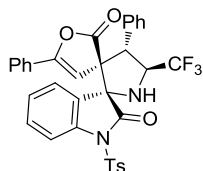
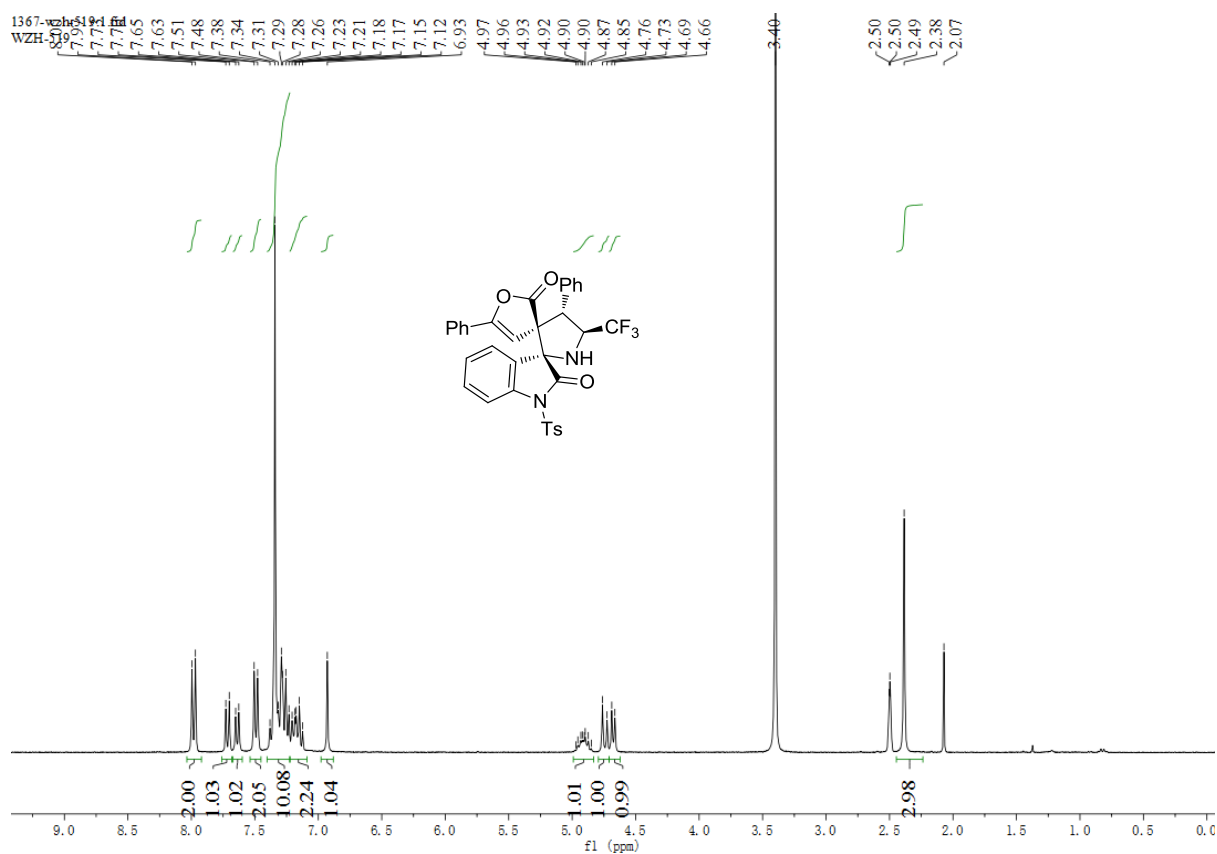


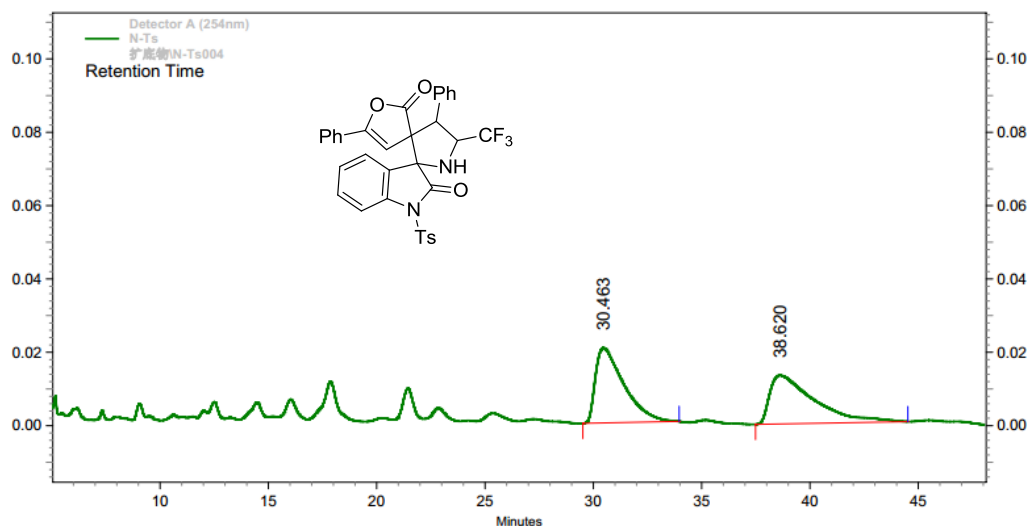
Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.430	14019	2.92	229015	1.36
2	8.187	85583	17.82	1162895	6.91
3	18.147	4823	1.00	180488	1.07
4	19.177	375960	78.26	15267866	90.66

Totals		480385	100.00	16840264	100.00
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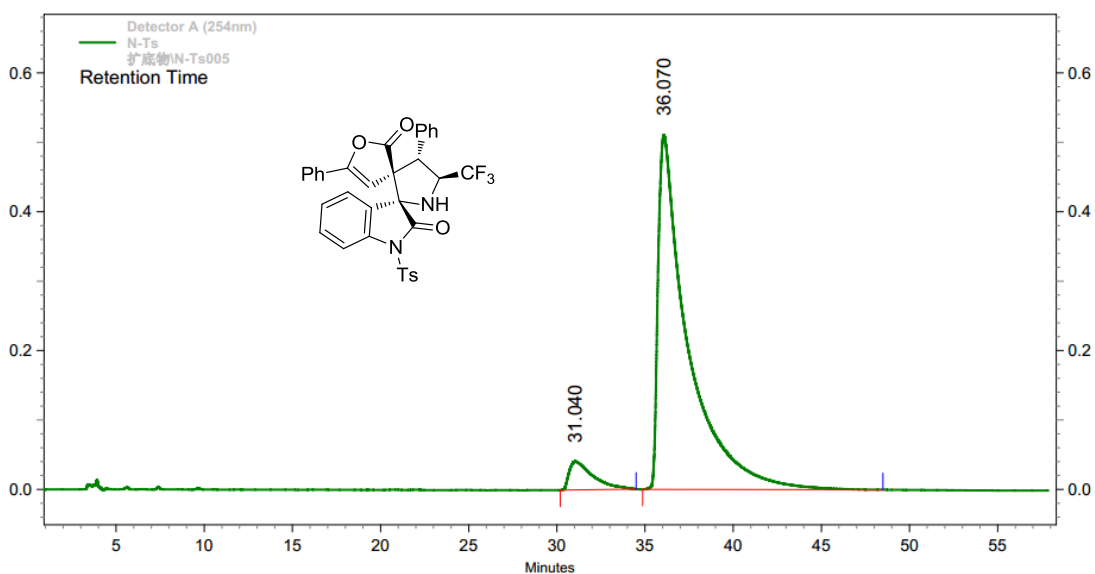
¹H NMR, ¹³C NMR and HPLC of 3f





Detector A (254nm)	Pk #	Retention Time	Height	Height Percent	Area	Area Percent
	1	30.463	20468	60.72	1864131	49.85
	2	38.620	13242	39.28	1875243	50.15

Totals						
			33710	100.00	3739374	100.00

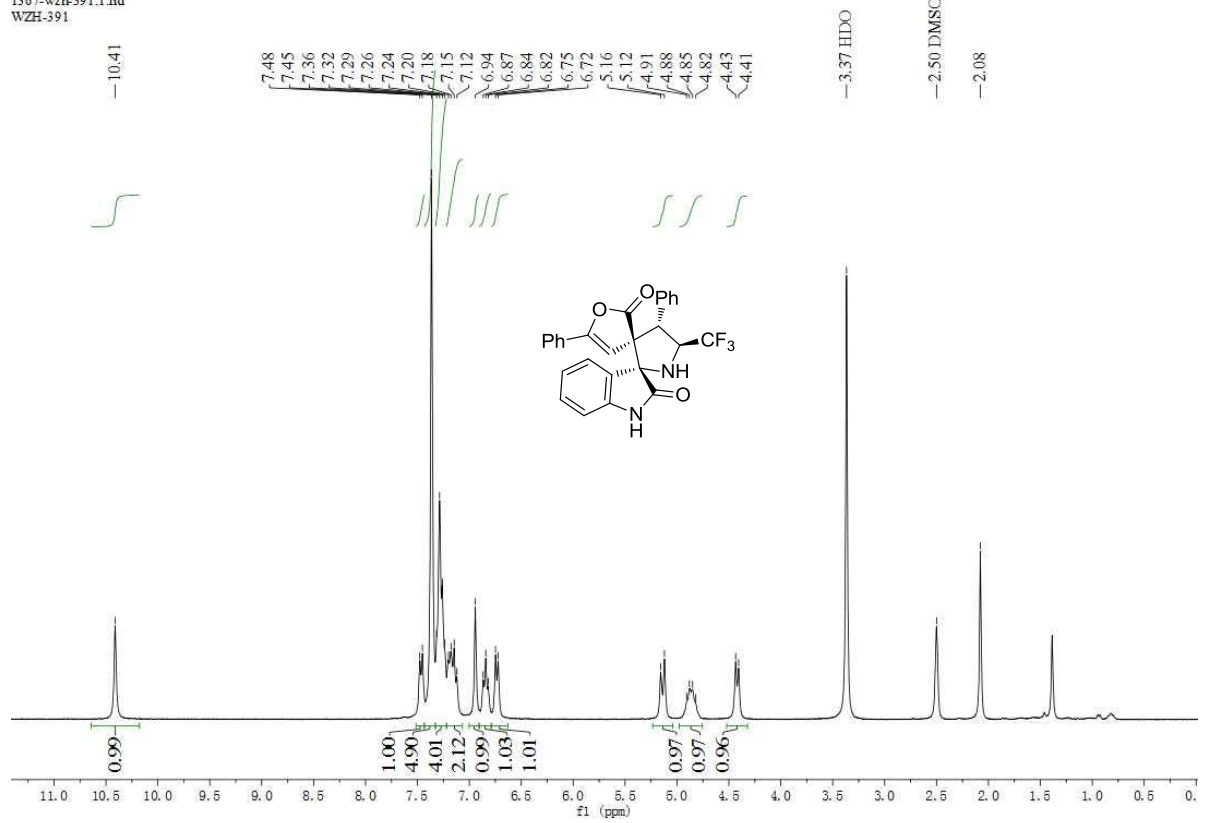


Detector A (254nm)	Pk #	Retention Time	Height	Height Percent	Area	Area Percent
	1	31.040	41147	7.46	3826010	6.02
	2	36.070	510556	92.54	59700004	93.98

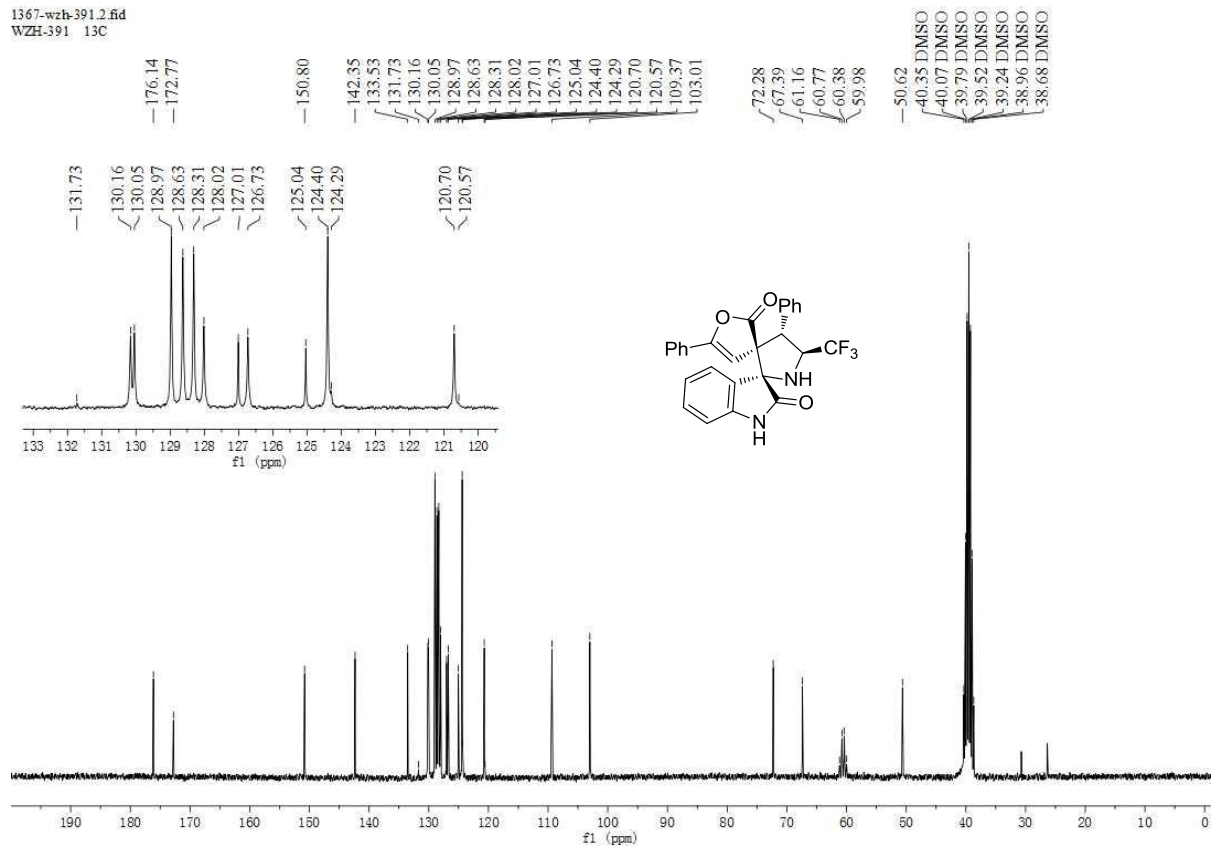
Totals						
			551703	100.00	63526014	100.00

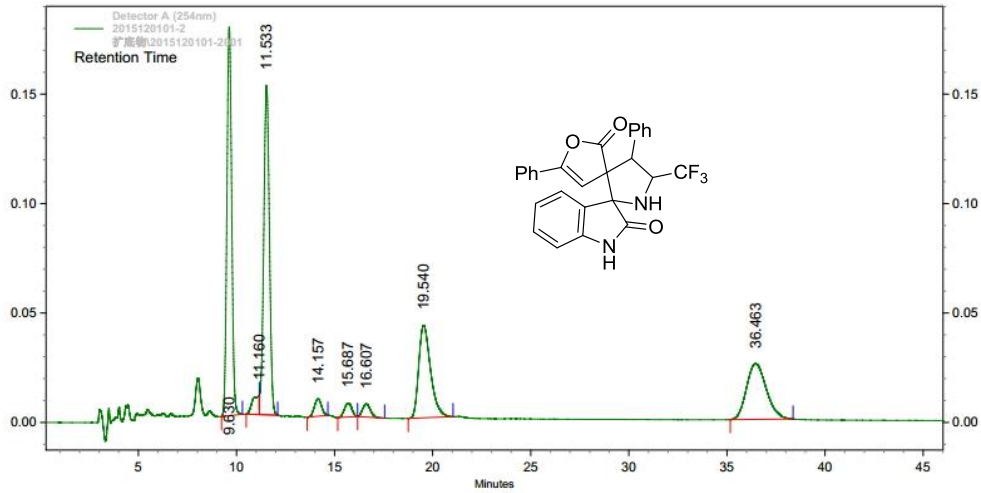
¹H NMR, ¹³C NMR and HPLC of 3g

1367-wzh-391.1.fid
WZH-391



1367-wzh-391.2.fid
WZH-391 13C

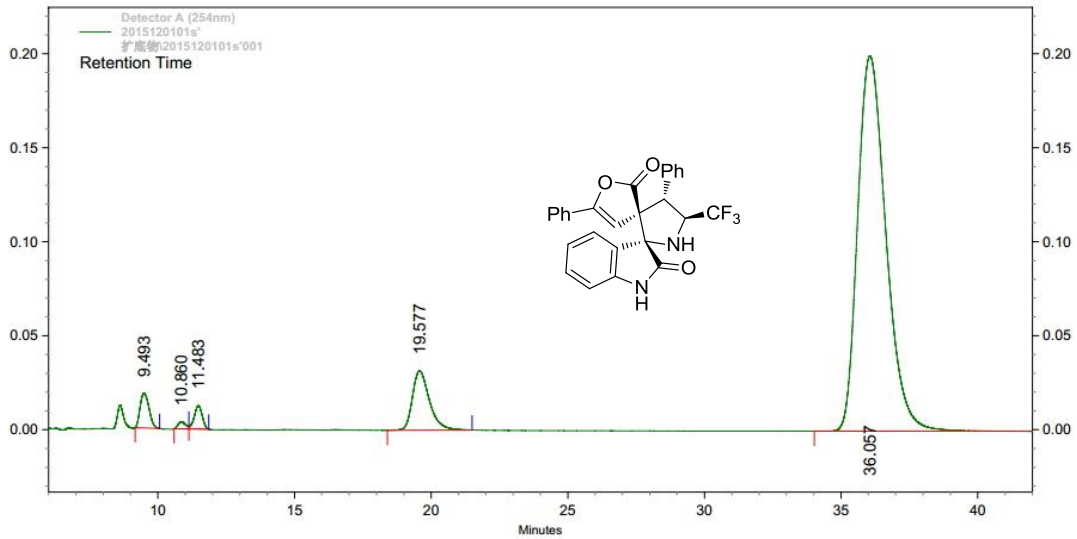




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.630	177384	41.76	3000456	29.08
2	11.160	8711	2.05	207236	2.01
3	11.533	150528	35.44	3020504	29.27
4	14.157	7958	1.87	201581	1.95
5	15.687	6422	1.51	165828	1.61
6	16.607	6023	1.42	165094	1.60
7	19.540	42282	9.95	1770008	17.15
8	36.463	25437	5.99	1787586	17.32

Totals		424745	100.00	10318293	100.00
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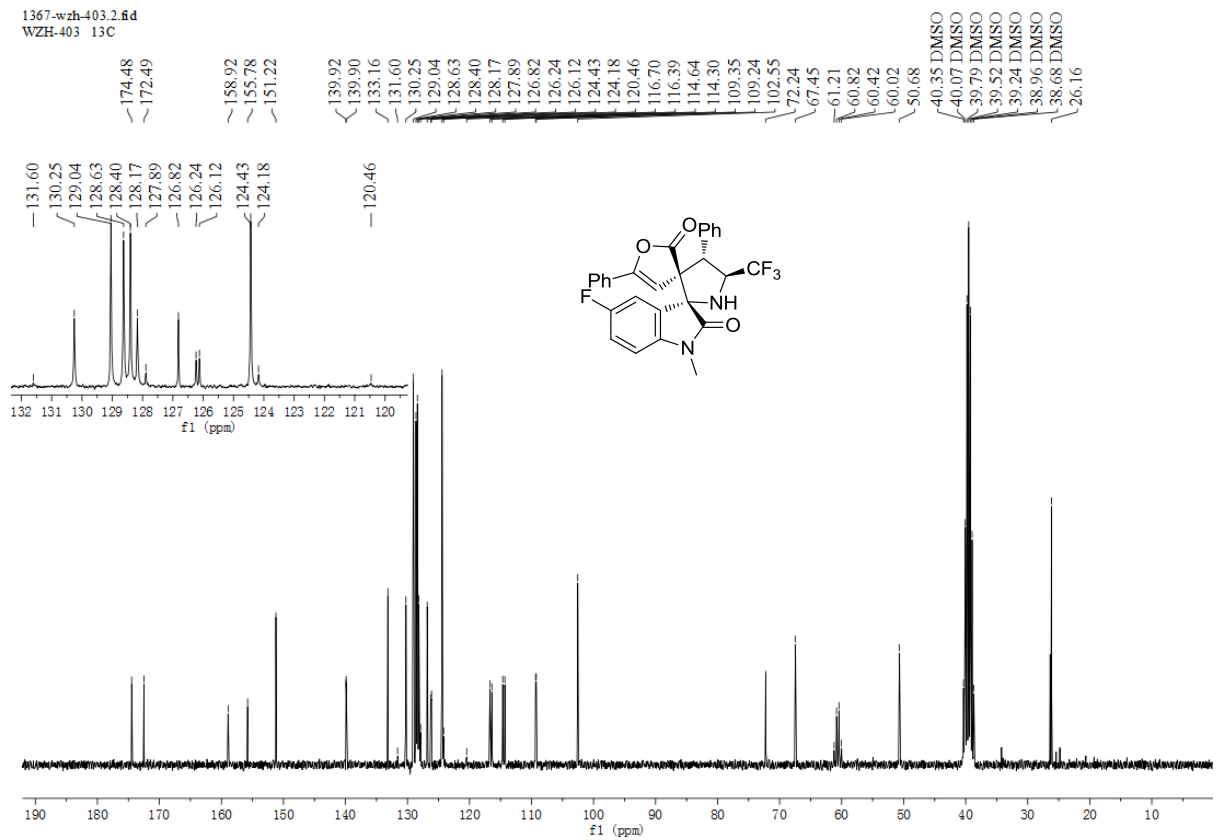
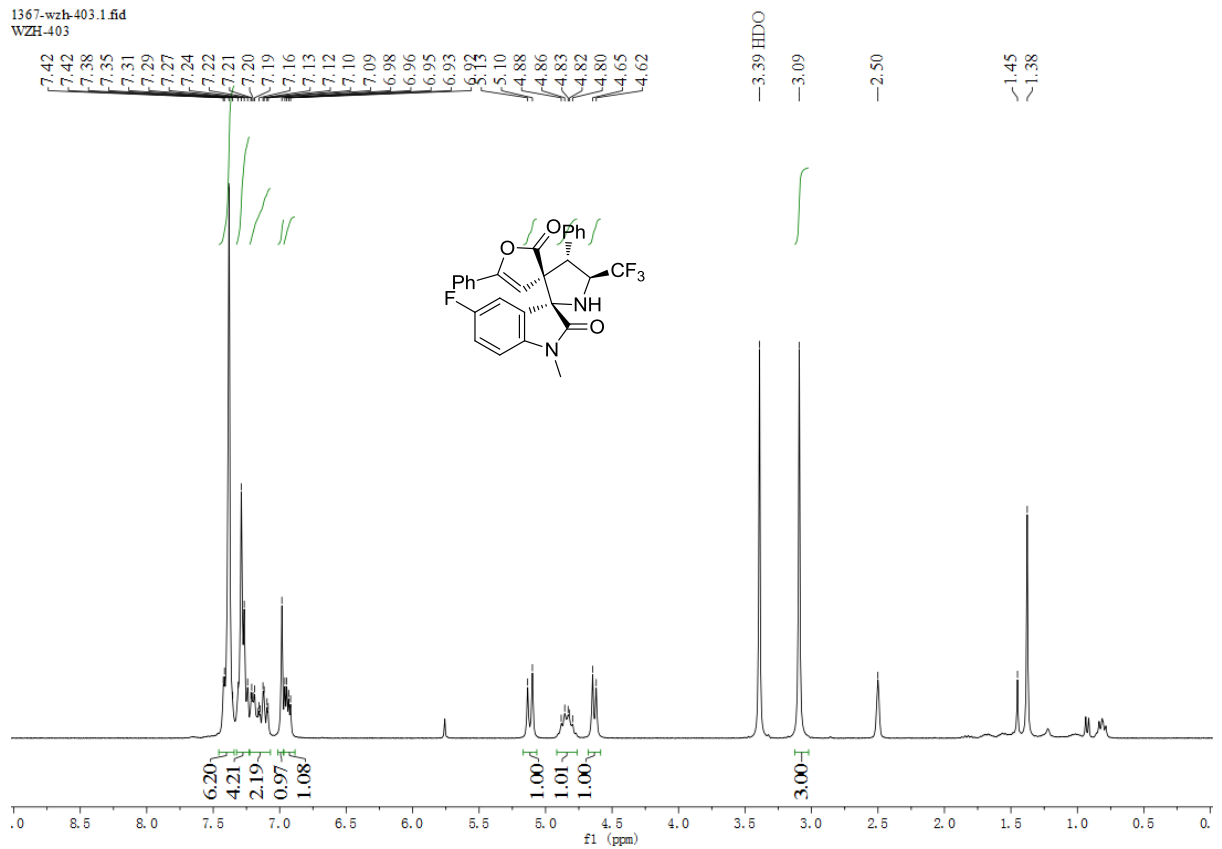


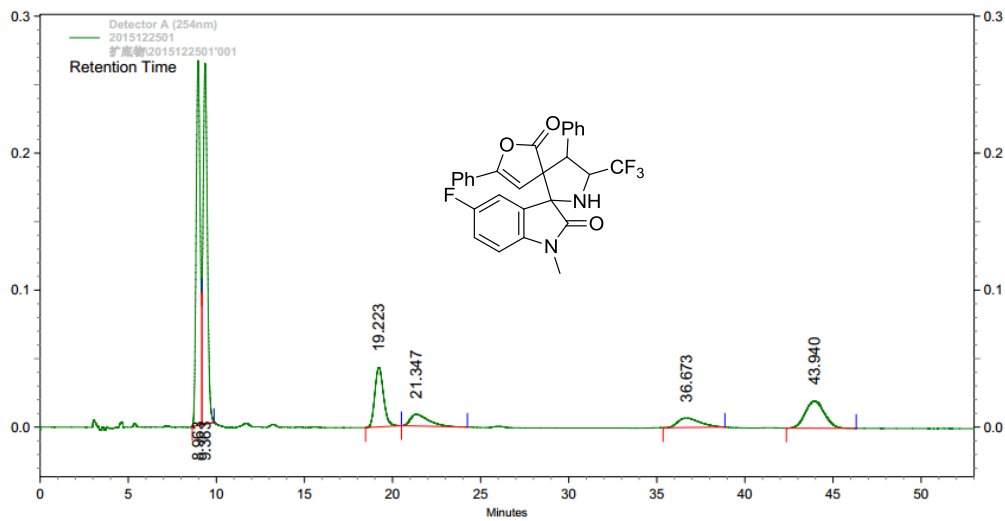
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.493	18414	6.92	418207	2.54
2	10.860	3766	1.42	72204	0.44
3	11.483	12416	4.67	252072	1.53
4	19.577	31624	11.89	1364549	8.28
5	36.057	199696	75.10	14368842	87.21

Totals		265916	100.00	16475874	100.00
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¹H NMR, ¹³C NMR and HPLC of 3h

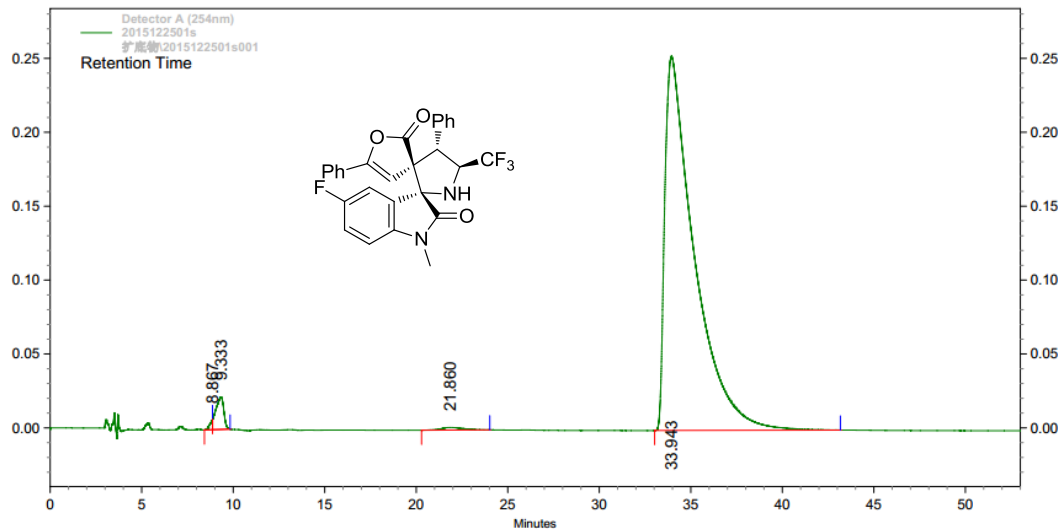




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.963	266314	43.79	4238591	32.93
2	9.363	263132	43.27	4419339	34.33
3	19.223	43462	7.15	1489549	11.57
4	21.347	8506	1.40	617197	4.79
5	36.673	6925	1.14	611407	4.75
6	43.940	19814	3.26	1496369	11.62

Totals					
		608153	100.00	12872452	100.00



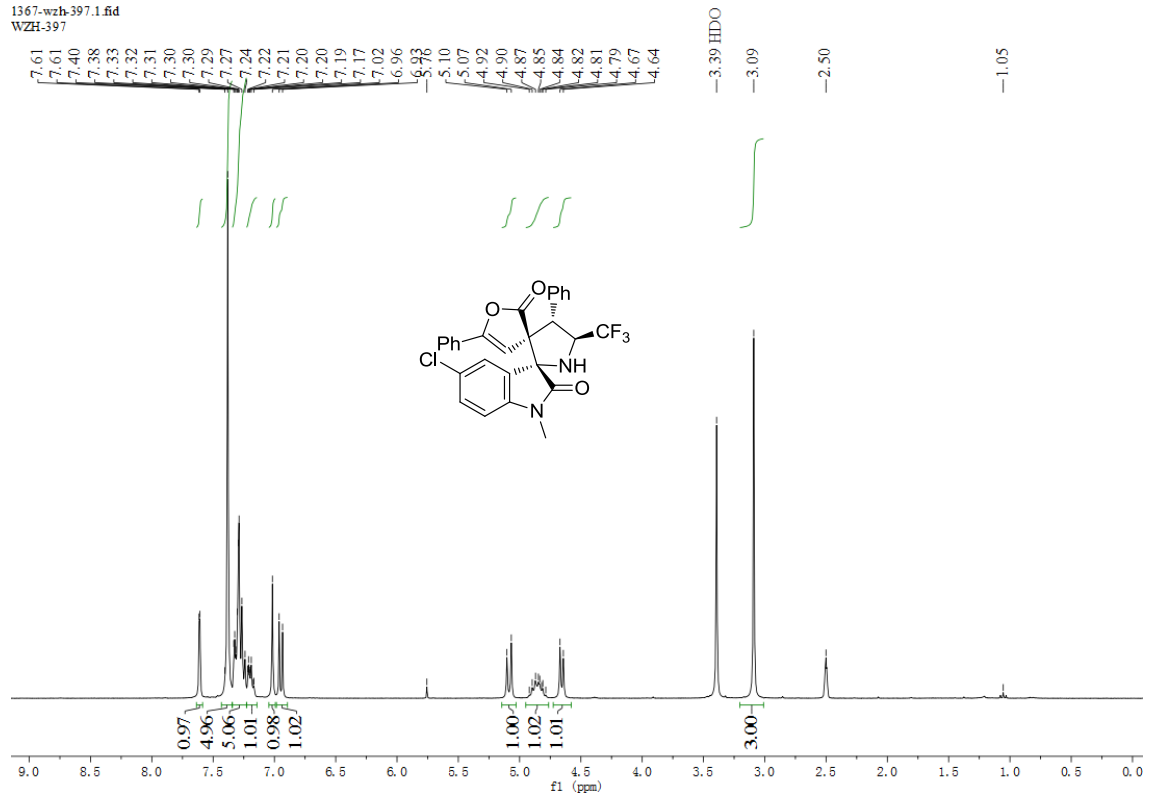
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.867	6766	2.39	67682	0.23
2	9.333	21920	7.73	659681	2.27
3	21.860	1755	0.62	147825	0.51
4	33.943	253062	89.26	28198518	96.99

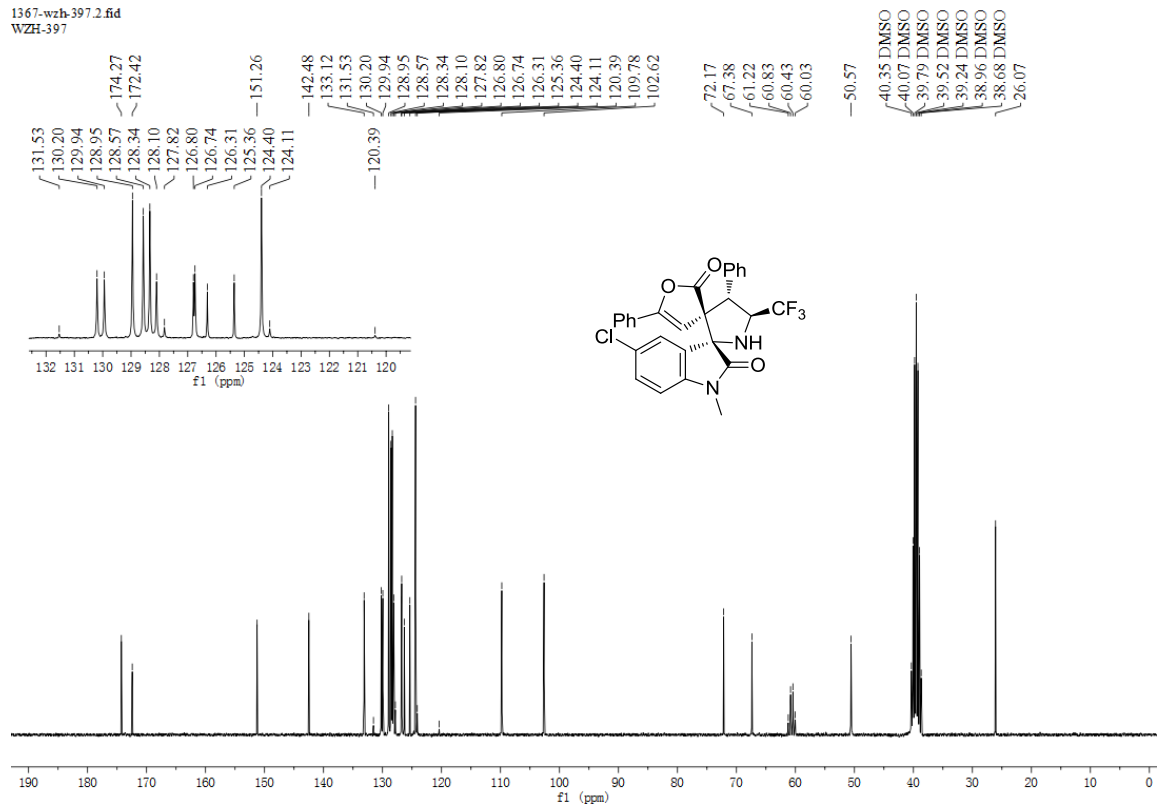
Totals					
		283503	100.00	29073706	100.00

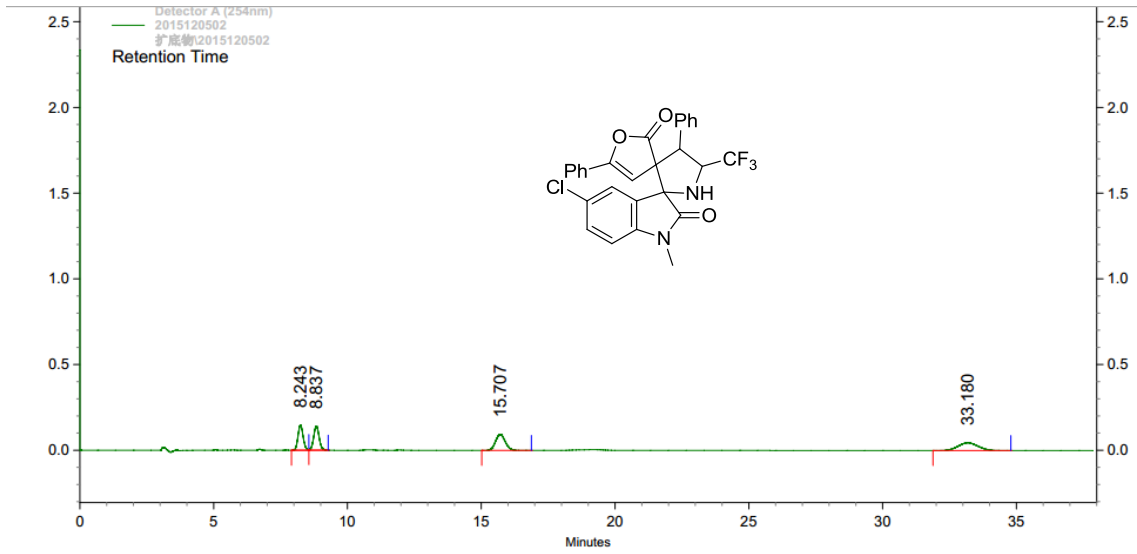
¹H NMR, ¹³C NMR and HPLC of 3i

1367-wzh-397.1.fid
WZH-397



1367-wzh-397.2.fid
WZH-397

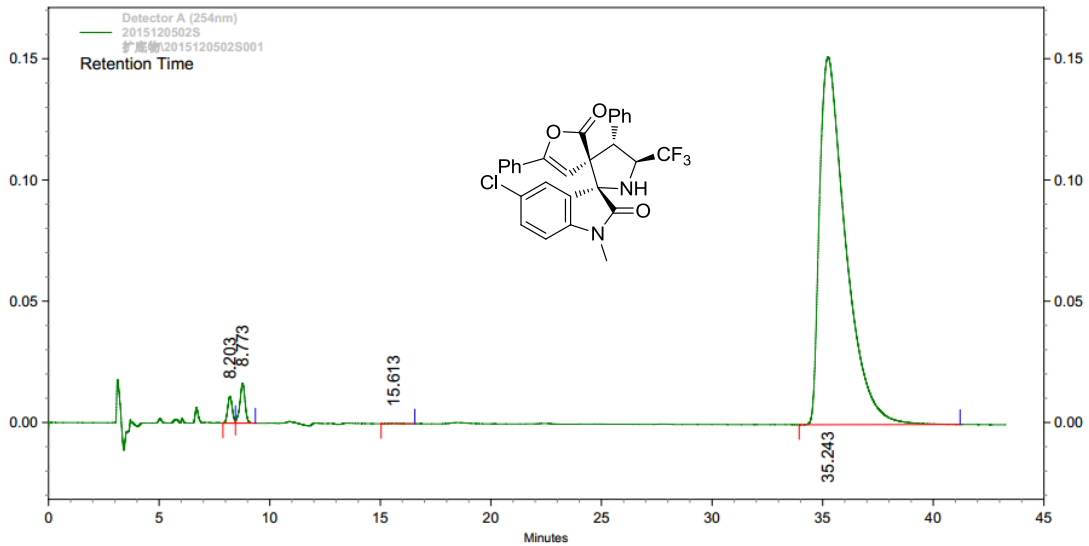




Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.243	147133	34.55	1975587	22.70
2	8.837	140920	33.09	2004156	23.02
3	15.707	92966	21.83	2358577	27.10
4	33.180	44857	10.53	2366024	27.18

Totals		425876	100.00	8704344	100.00
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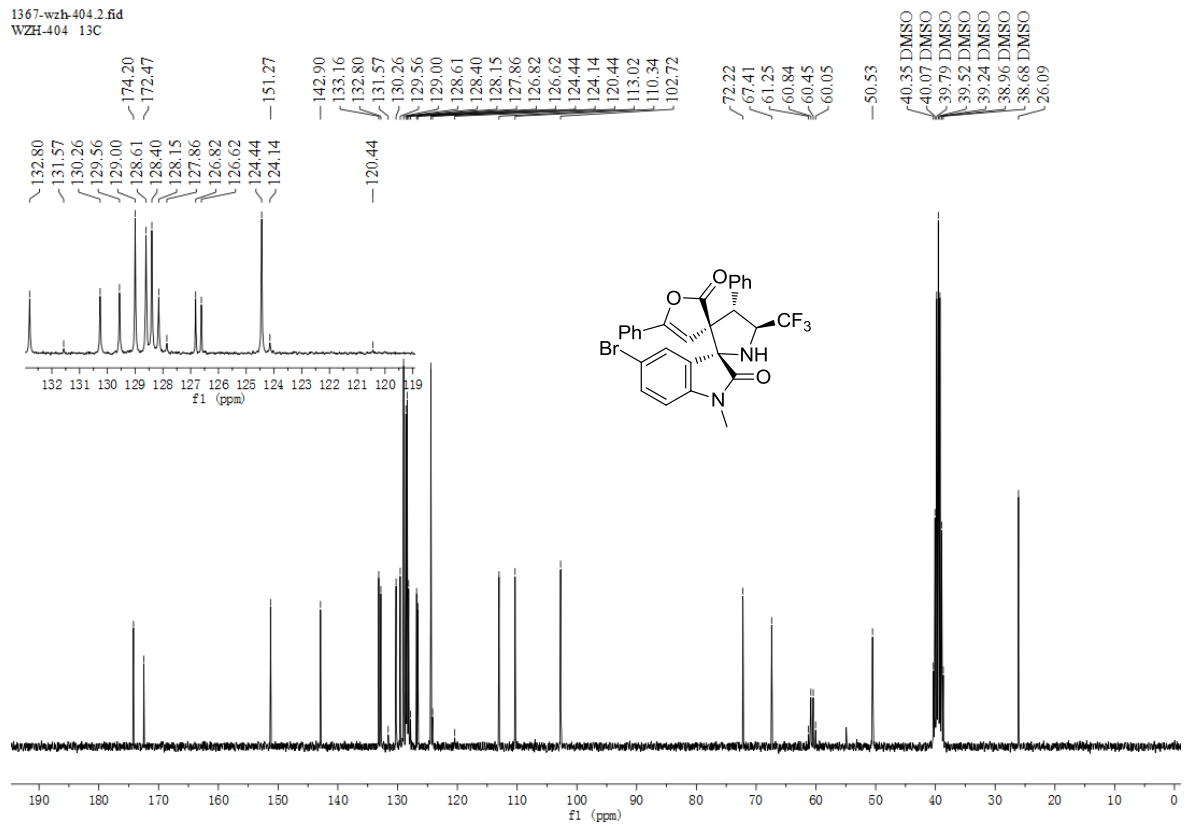
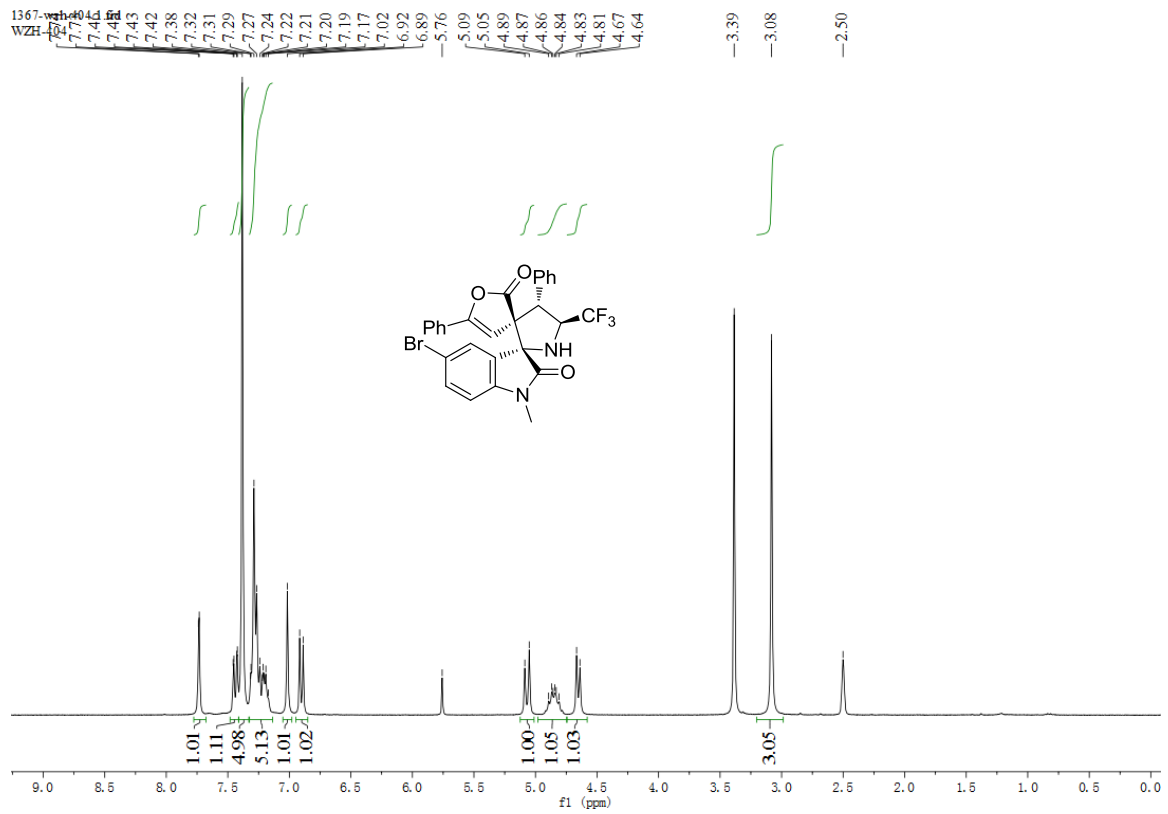


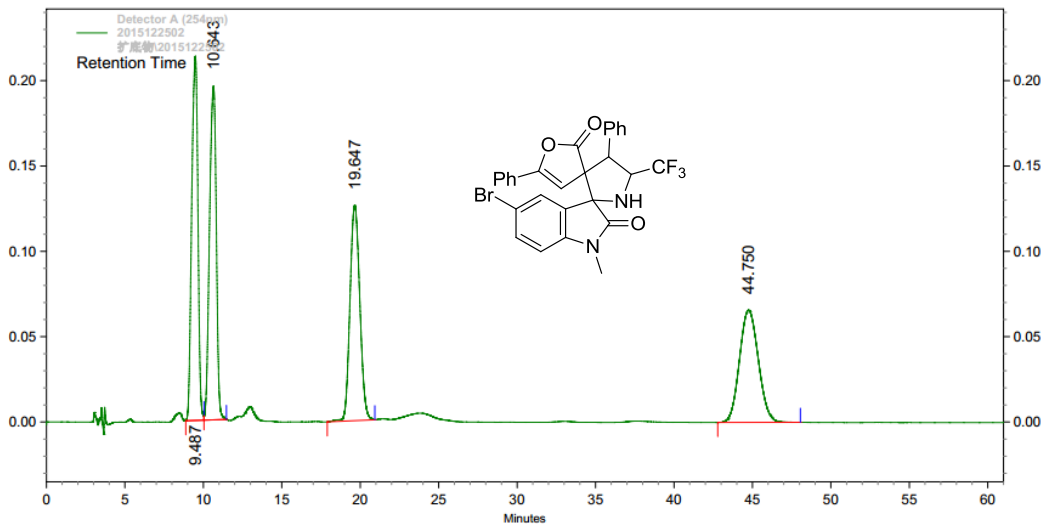
Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.203	11053	6.16	158612	1.23
2	8.773	16466	9.18	267321	2.08
3	15.613	180	0.10	5916	0.05
4	35.243	151722	84.56	12428539	96.64

Totals		179421	100.00	12860388	100.00
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¹H NMR, ¹³C NMR and HPLC of 3j

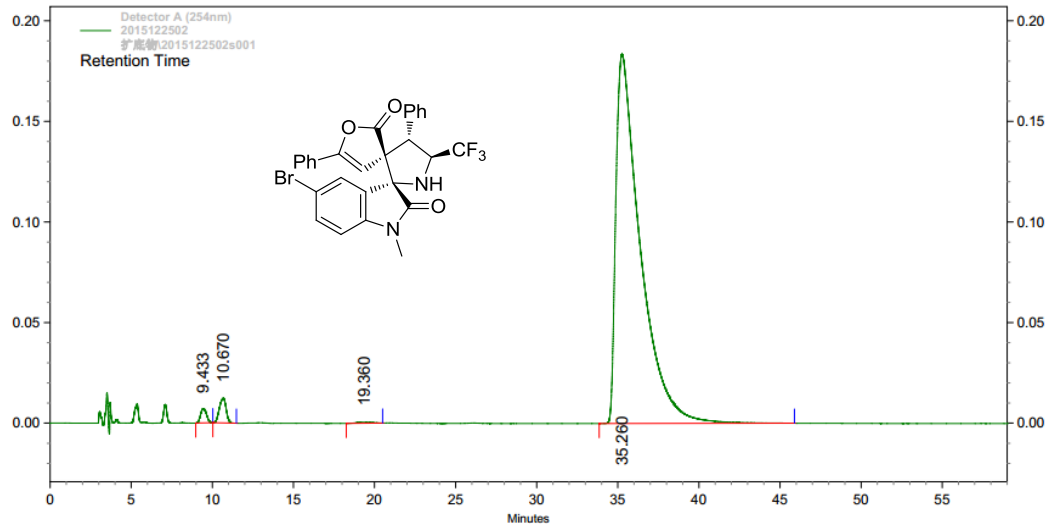




Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.487	213353	35.52	5853233	25.79
2	10.643	195451	32.54	5848578	25.77
3	19.647	126129	21.00	5494824	24.21
4	44.750	65807	10.95	5501387	24.24

Totals	Height	Area	Area Percent
	600740	22698022	100.00

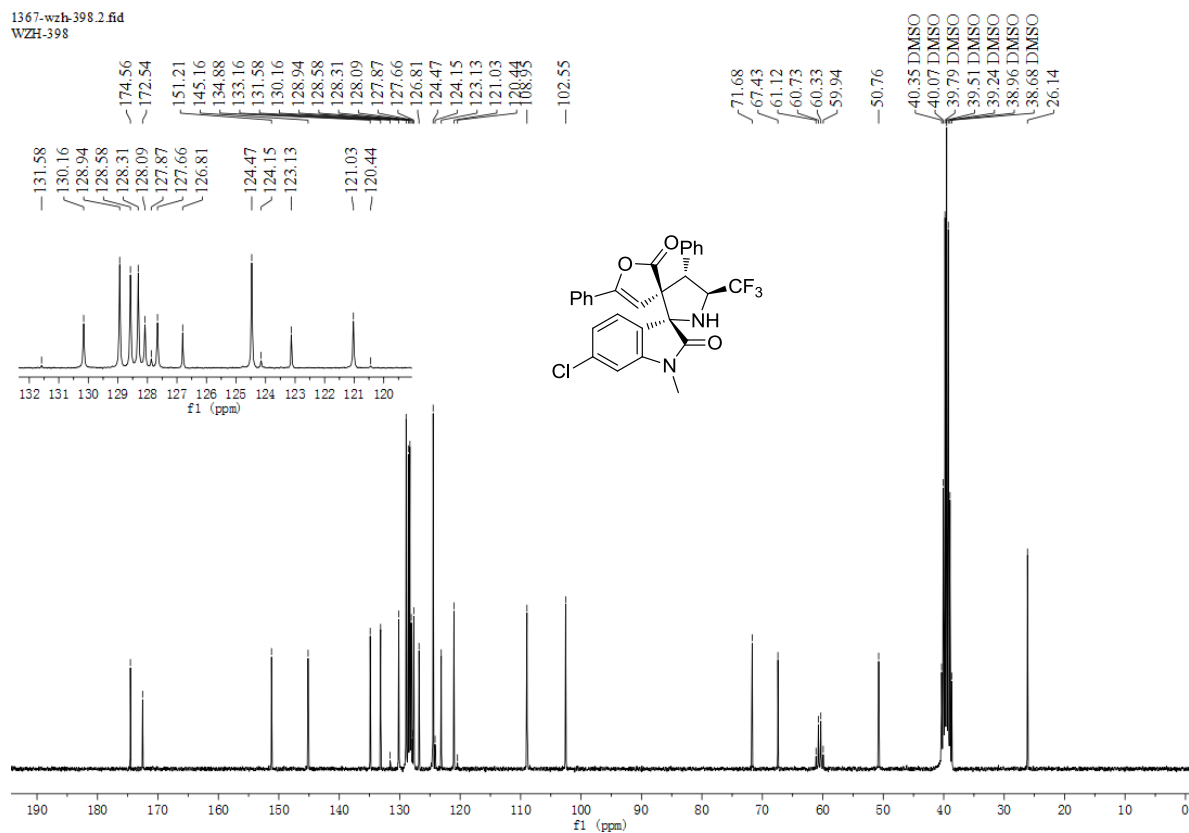
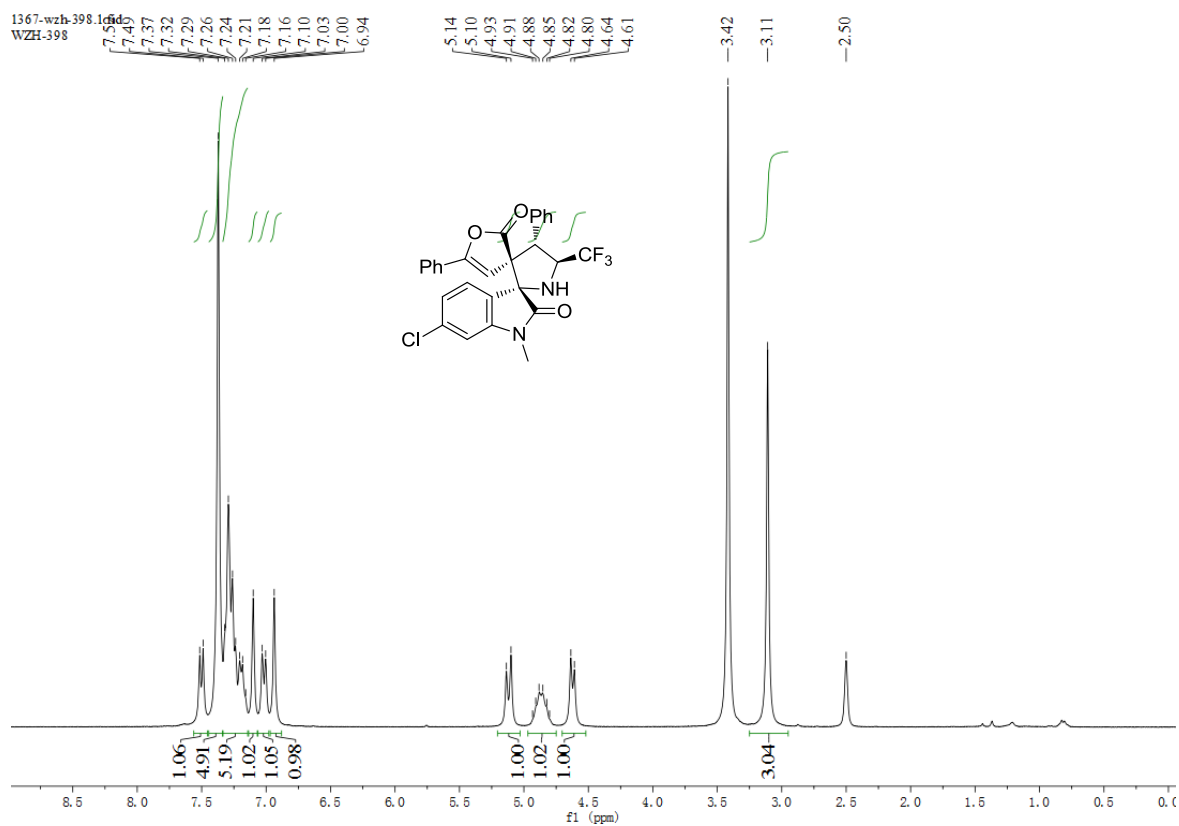


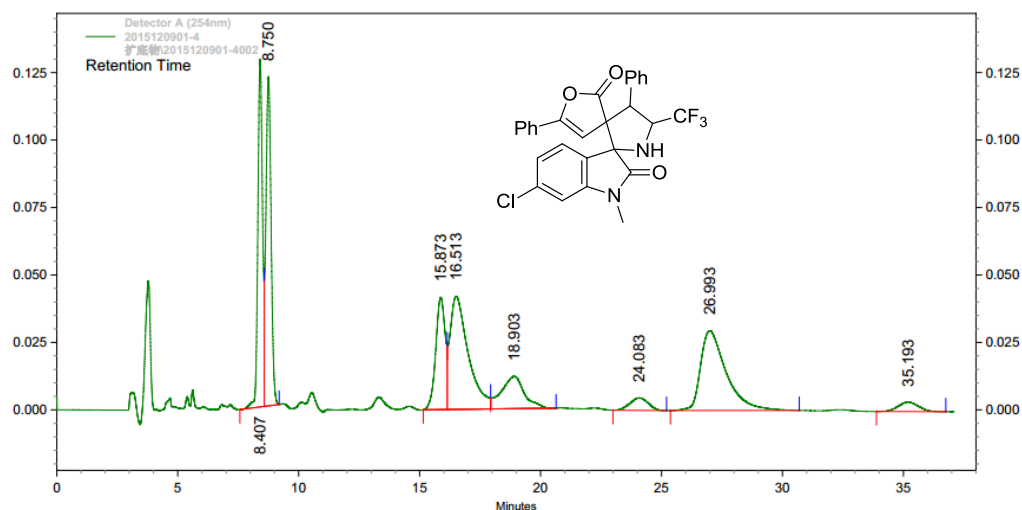
Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.433	6968	3.43	177920	0.90
2	10.670	12233	6.02	355022	1.80
3	19.360	526	0.26	32525	0.16
4	35.260	183629	90.30	19185114	97.14

Totals	Height	Area	Area Percent
	203356	19750581	100.00

¹H NMR, ¹³C NMR and HPLC of 3k

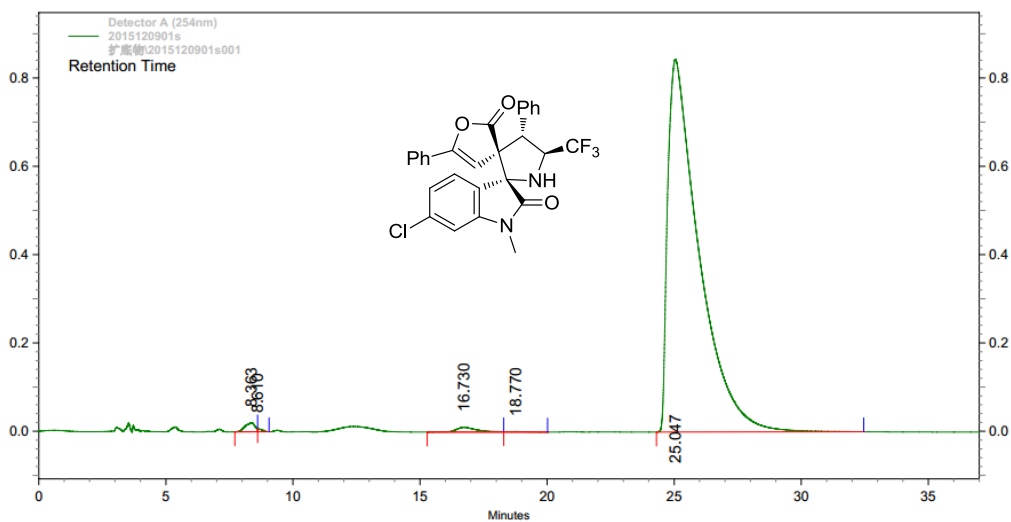




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.407	128902	33.55	1711242	16.62
2	8.750	121993	31.75	1828359	17.76
3	15.873	41629	10.84	1123876	10.91
4	16.513	41976	10.93	2220186	21.56
5	18.903	11972	3.12	791098	7.68
6	24.083	4620	1.20	243876	2.37
7	26.993	29592	7.70	2172455	21.10
8	35.193	3500	0.91	205579	2.00

Totals		384184	100.00	10296671	100.00
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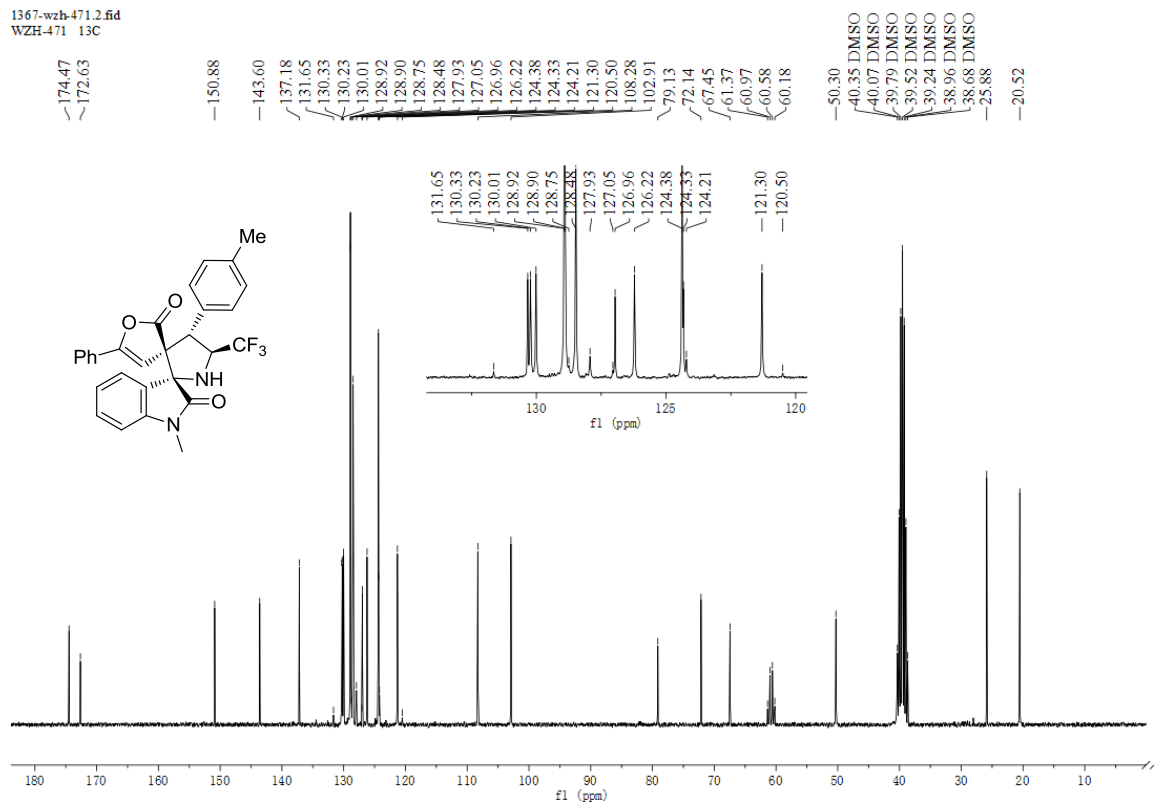
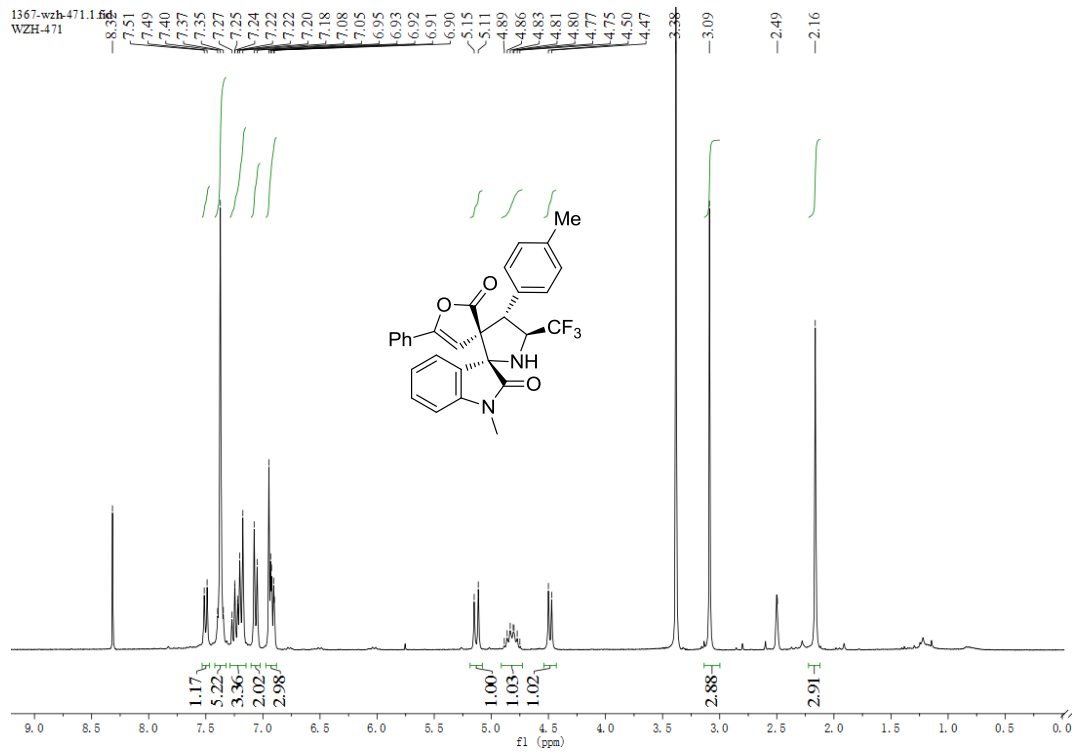


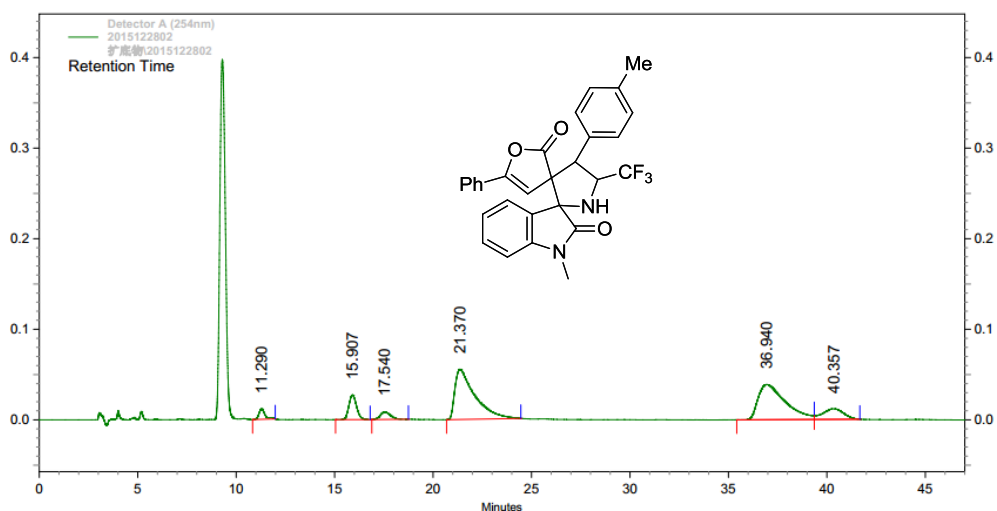
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.363	20777	2.35	557871	0.76
2	8.610	6805	0.77	81652	0.11
3	16.730	10381	1.18	580192	0.79
4	18.770	856	0.10	50616	0.07
5	25.047	844226	95.60	71949952	98.27

Totals		883045	100.00	73220283	100.00
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¹H NMR, ¹³C NMR and HPLC of 3I

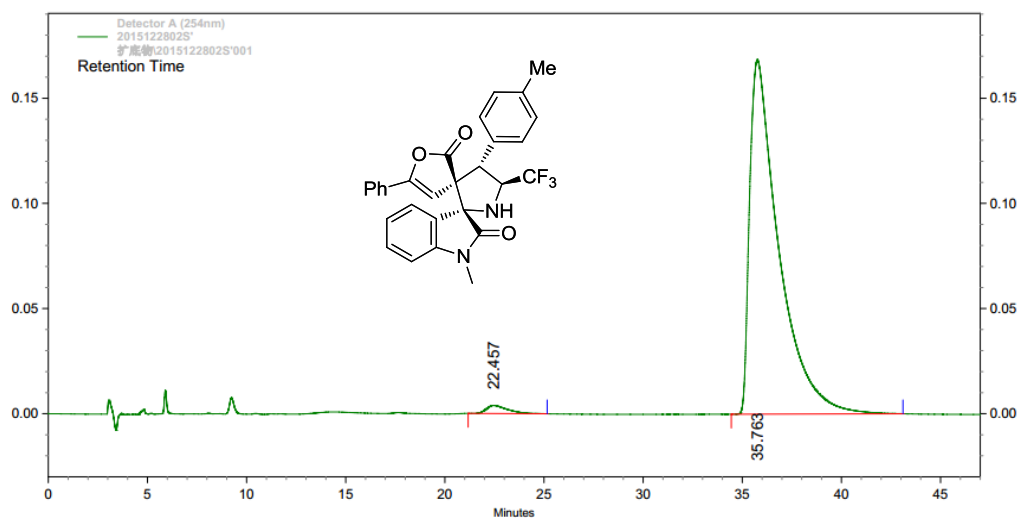




Detector A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.290	11524	7.52	248295	2.56
2	15.907	27227	17.76	739848	7.62
3	17.540	8402	5.48	299371	3.08
4	21.370	55437	36.16	3874709	39.88
5	36.940	38973	25.42	3691692	38.00
6	40.357	11733	7.65	861423	8.87

Totals	Area	Area Percent
	153296	100.00
	9715338	100.00

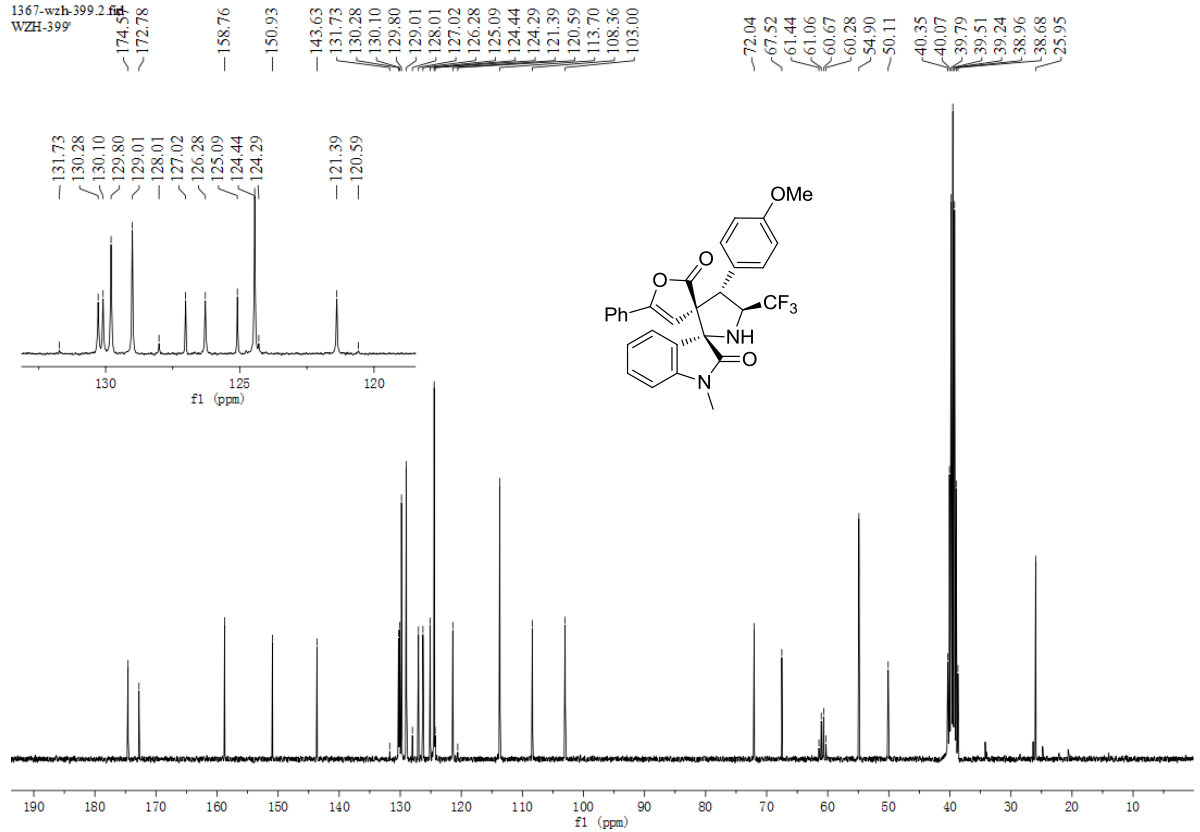
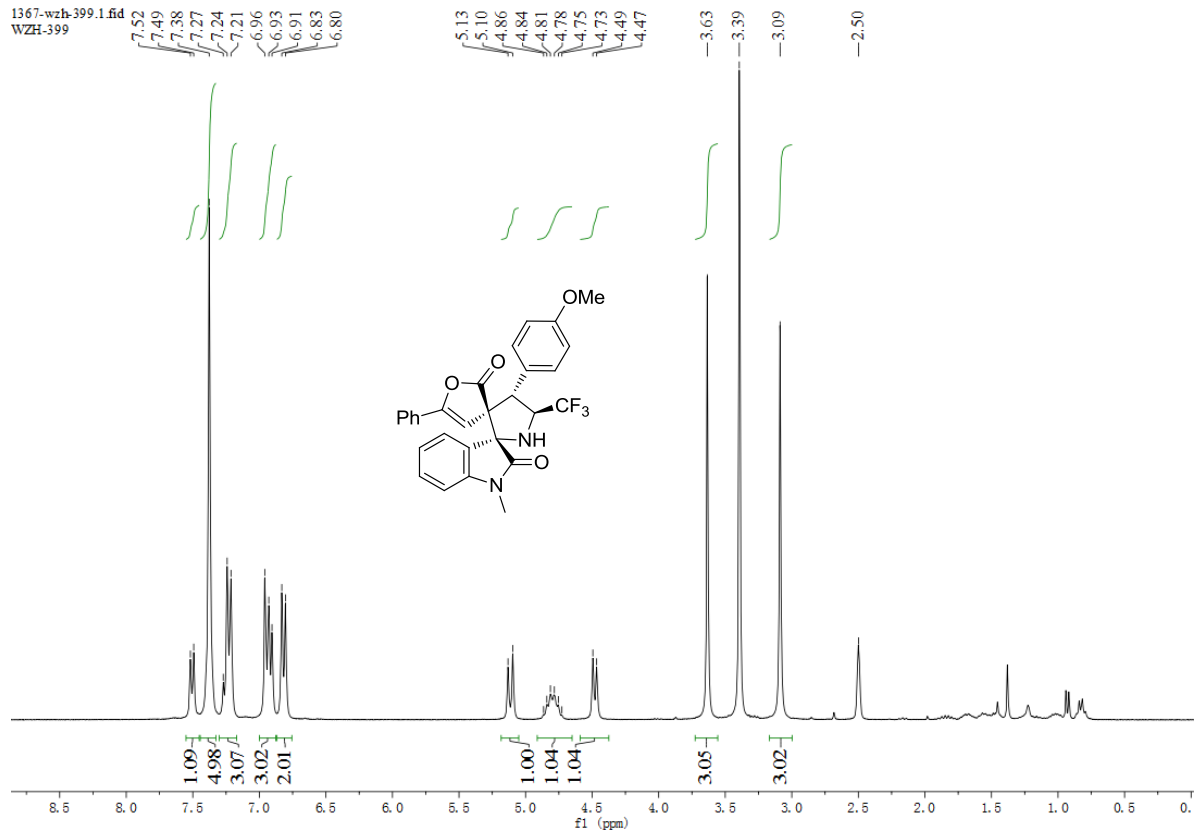


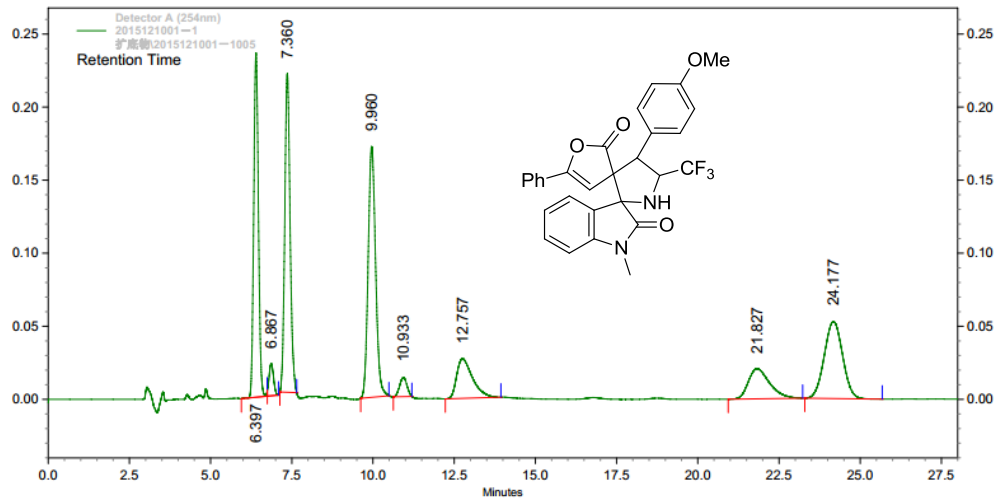
Detector A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	22.457	3824	2.22	288920	1.65
2	35.763	168546	97.78	17182045	98.35

Totals	Area	Area Percent
	172370	100.00
	17470965	100.00

¹H NMR, ¹³C NMR and HPLC of 3m

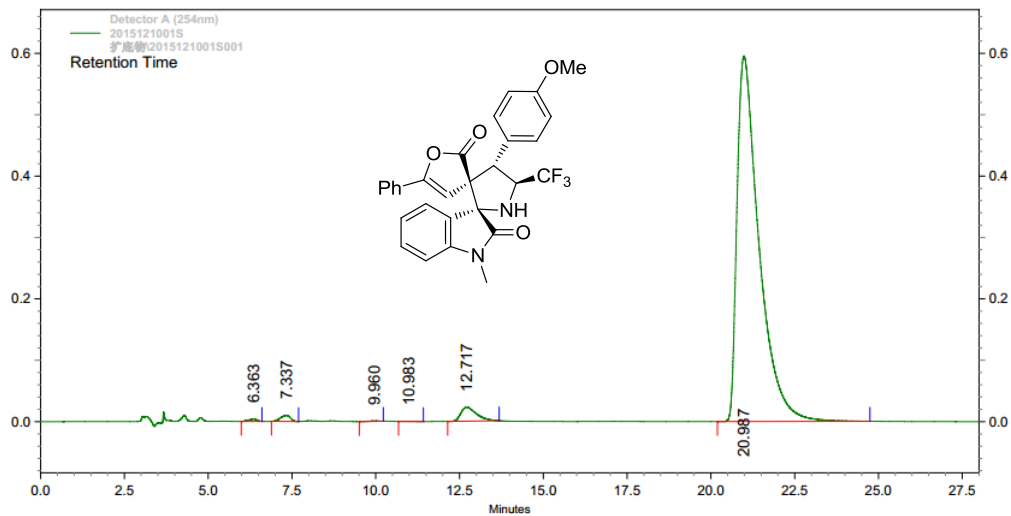




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.397	235650	30.96	2354168	19.77
2	6.867	22098	2.90	211611	1.78
3	7.360	217989	28.64	2490085	20.91
4	9.960	171625	22.55	2722143	22.86
5	10.933	13184	1.73	207472	1.74
6	12.757	27162	3.57	915212	7.69
7	21.827	20568	2.70	938702	7.88
8	24.177	52804	6.94	2068292	17.37

Totals		761080	100.00	11907685	100.00
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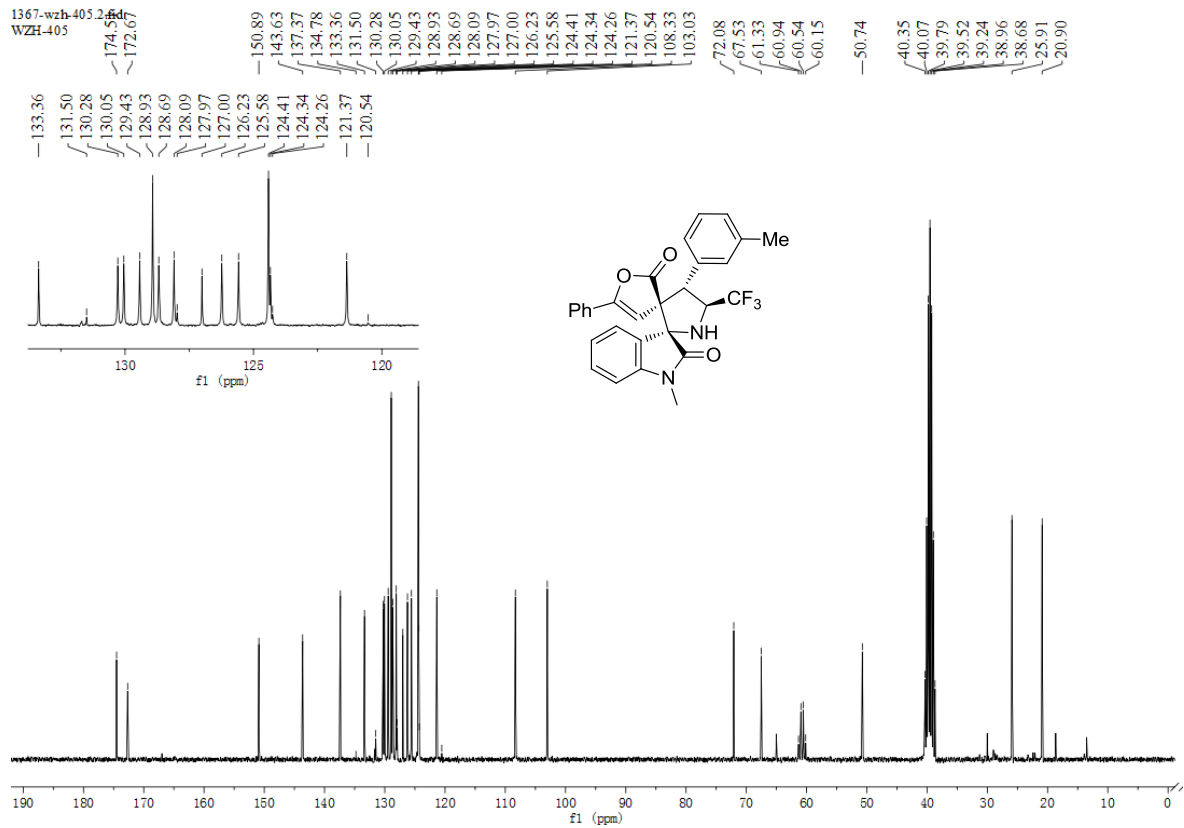
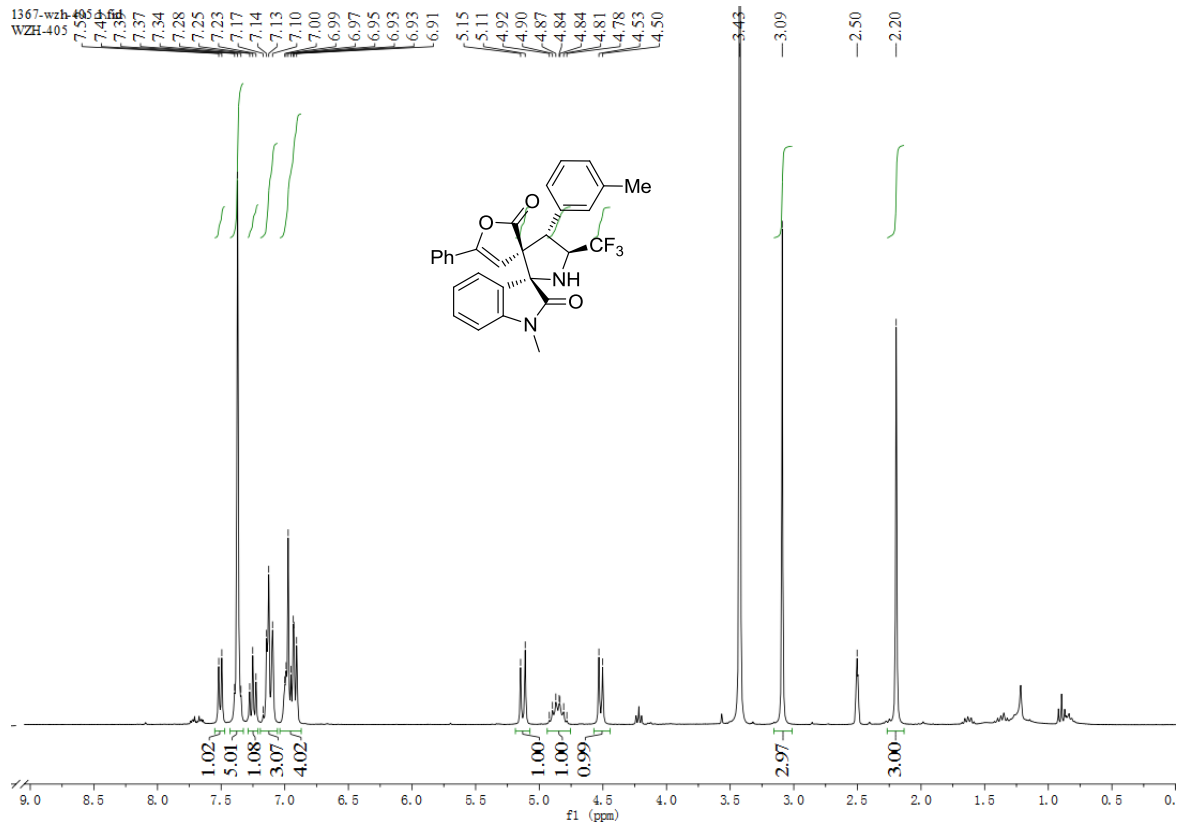


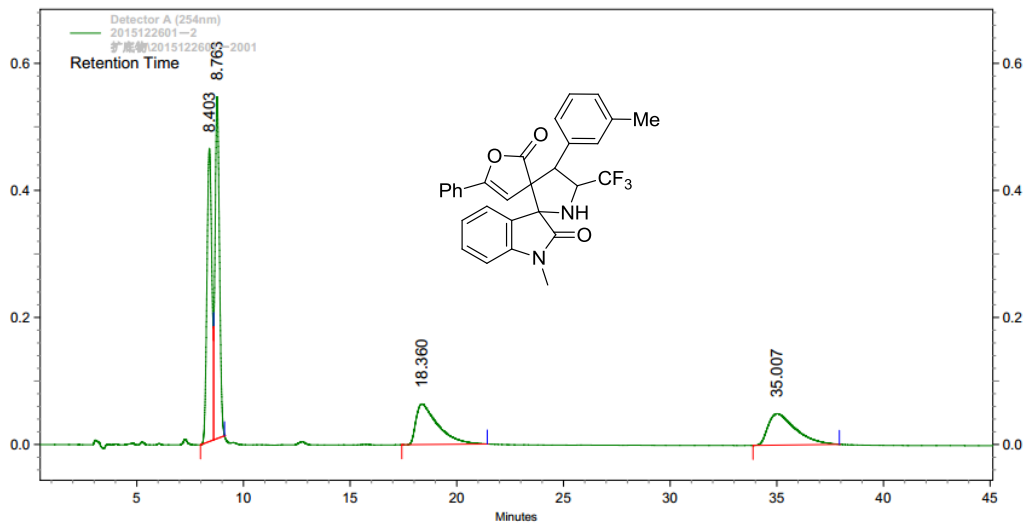
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.363	3739	0.59	63416	0.23
2	7.337	9859	1.56	200213	0.71
3	9.960	811	0.13	12833	0.05
4	10.983	96	0.02	1627	0.01
5	12.717	22579	3.57	740409	2.63
6	20.987	595421	94.14	27132935	96.38

Totals		632505	100.00	28151433	100.00
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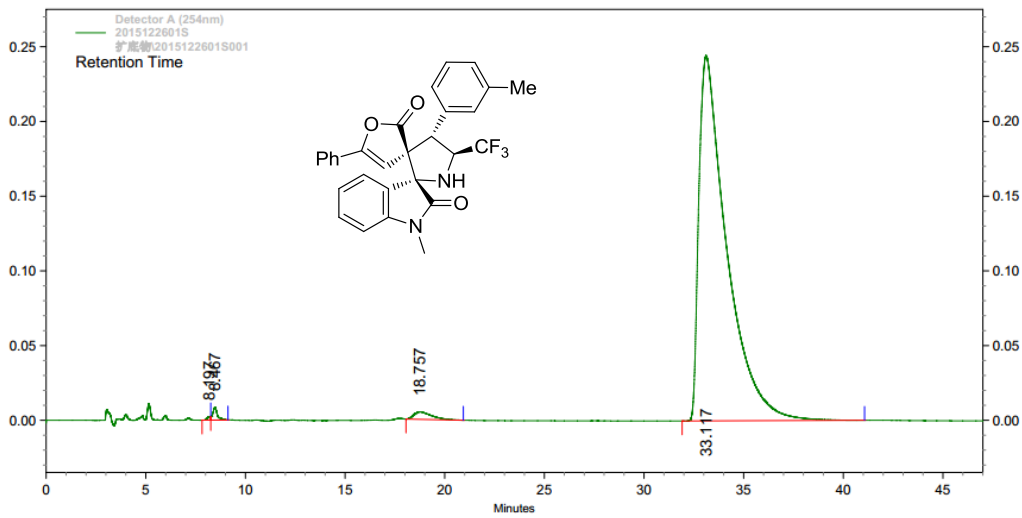
¹H NMR, ¹³C NMR and HPLC of 3n





PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.403	461319	41.46	7369679	30.74
2	8.763	537818	48.34	7694116	32.10
3	18.360	63967	5.75	4501667	18.78
4	35.007	49525	4.45	4405459	18.38

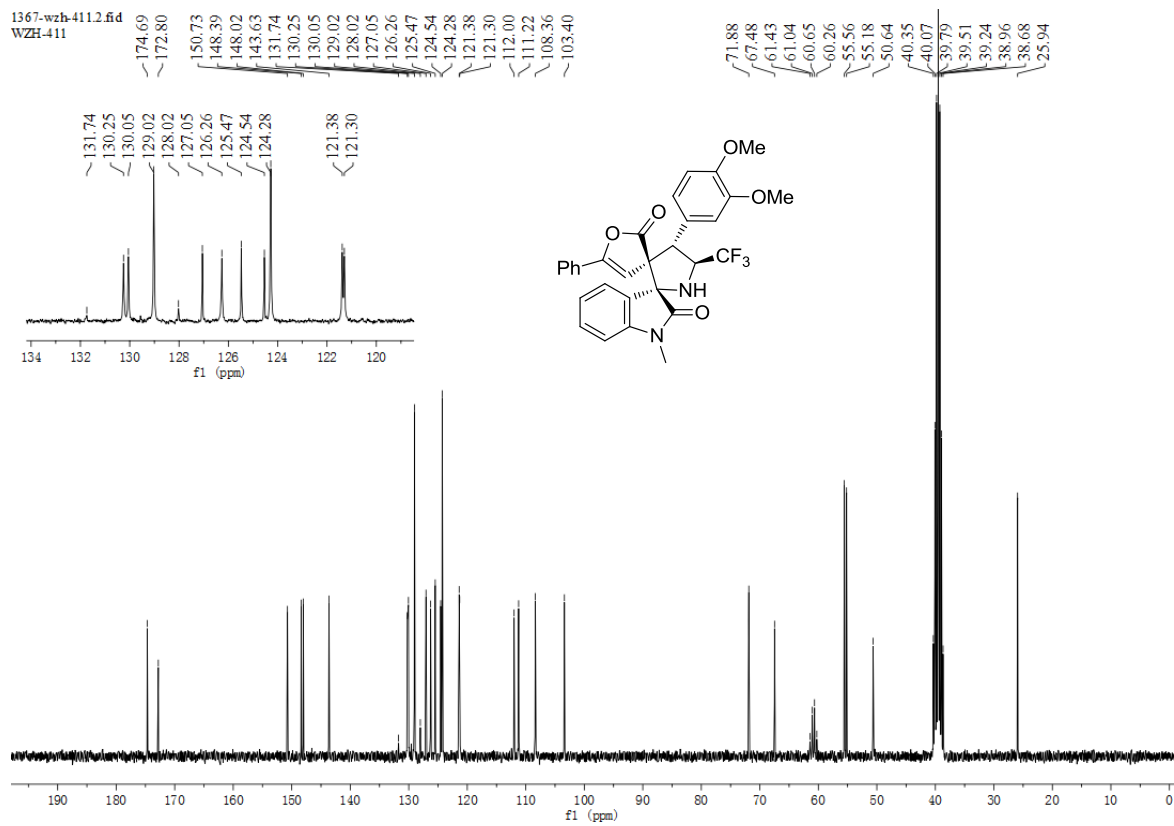
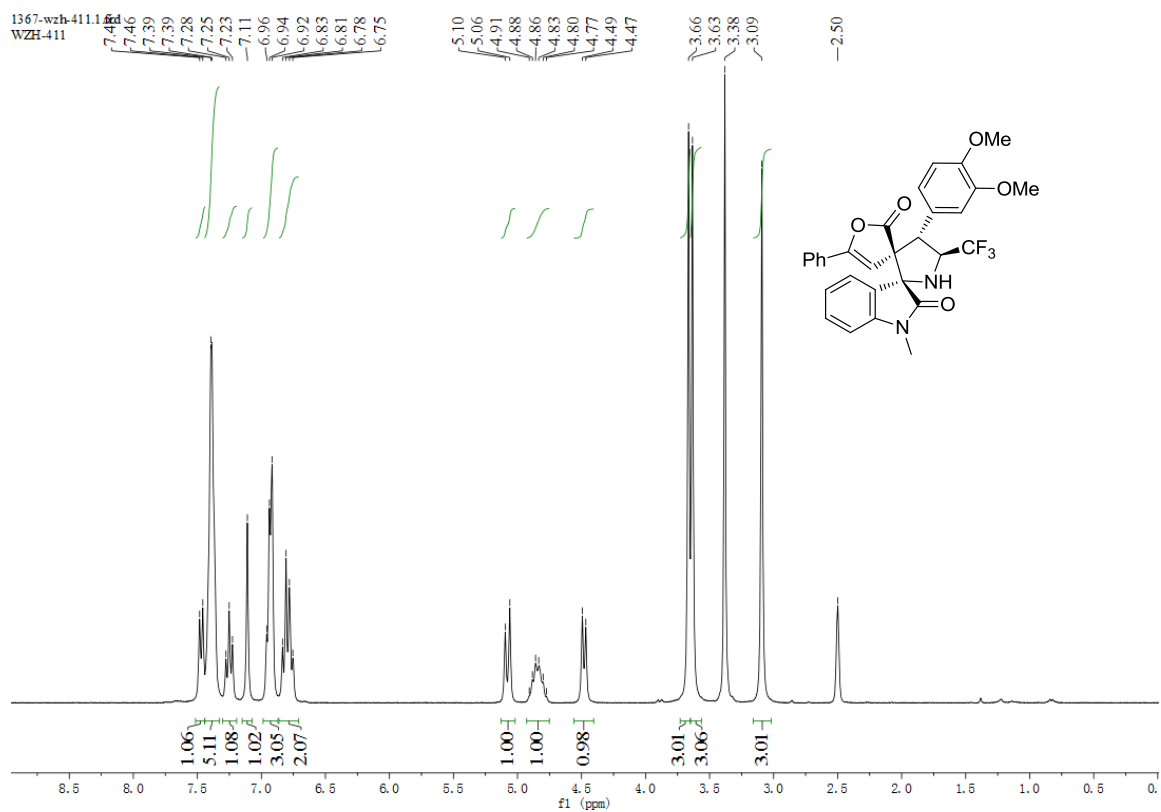
Totals	1112629	100.00	23970921	100.00
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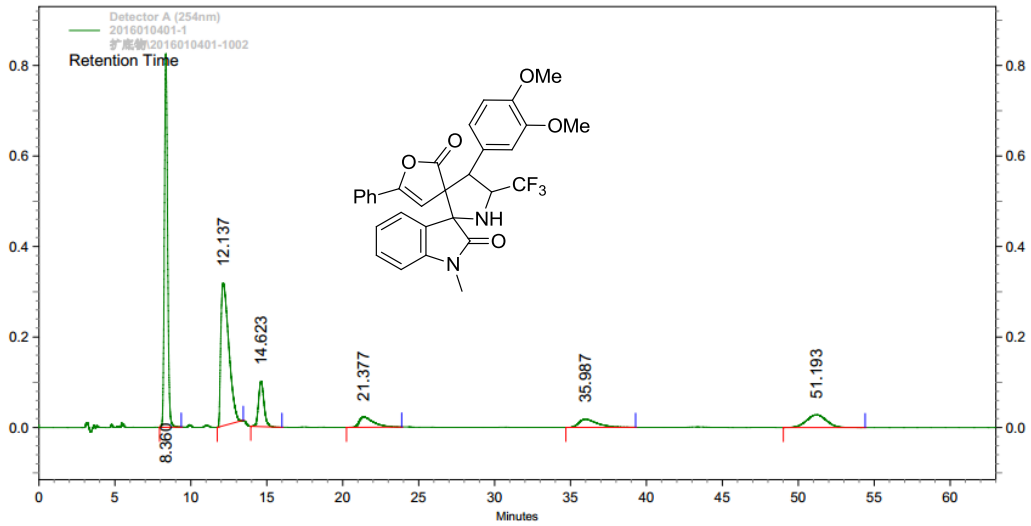


PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.197	2425	0.93	27581	0.11
2	8.467	8545	3.28	137025	0.57
3	18.757	4901	1.88	310807	1.29
4	33.117	244448	93.90	23612689	98.03

Totals	260319	100.00	24088102	100.00
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^1H NMR, ^{13}C NMR and HPLC of 3o

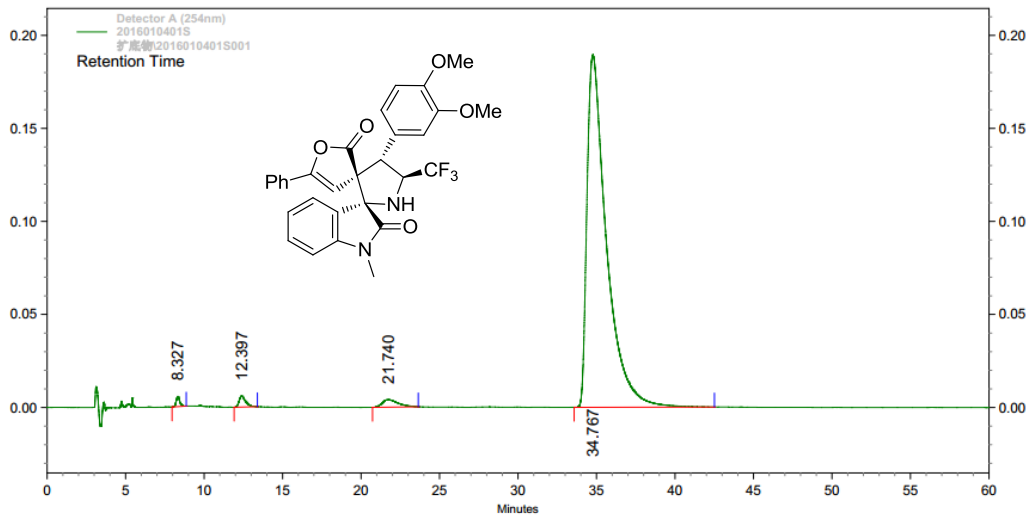




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.360	824981	62.97	11991395	37.89
2	12.137	315668	24.09	11580814	36.60
3	14.623	100506	7.67	2481663	7.84
4	21.377	22816	1.74	1498602	4.74
5	35.987	18063	1.38	1549375	4.90
6	51.193	28161	2.15	2543038	8.04

Totals	Height	Height Percent	Area	Area Percent
	1310195	100.00	31644887	100.00



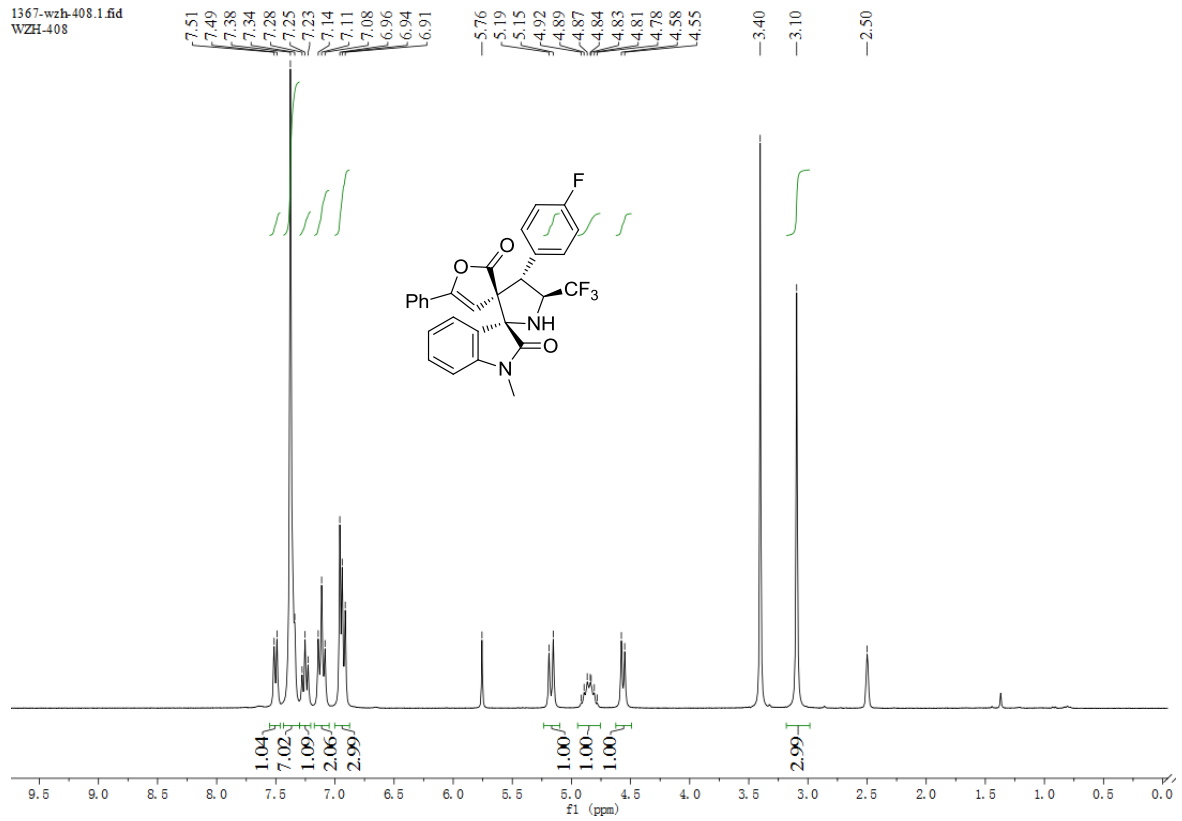
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.327	5477	2.67	85544	0.51
2	12.397	5989	2.92	171562	1.02
3	21.740	4019	1.96	281646	1.68
4	34.767	189375	92.44	16271474	96.80

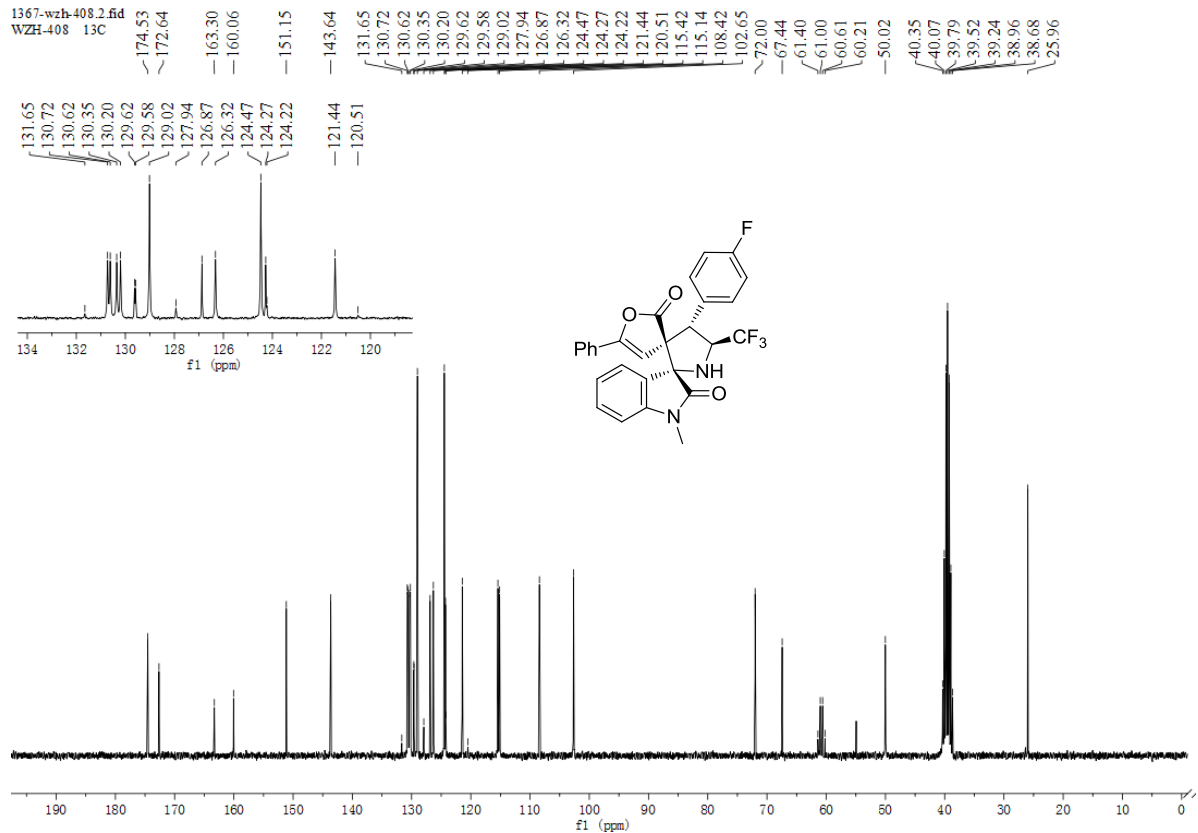
Totals	Height	Height Percent	Area	Area Percent
	204860	100.00	16810226	100.00

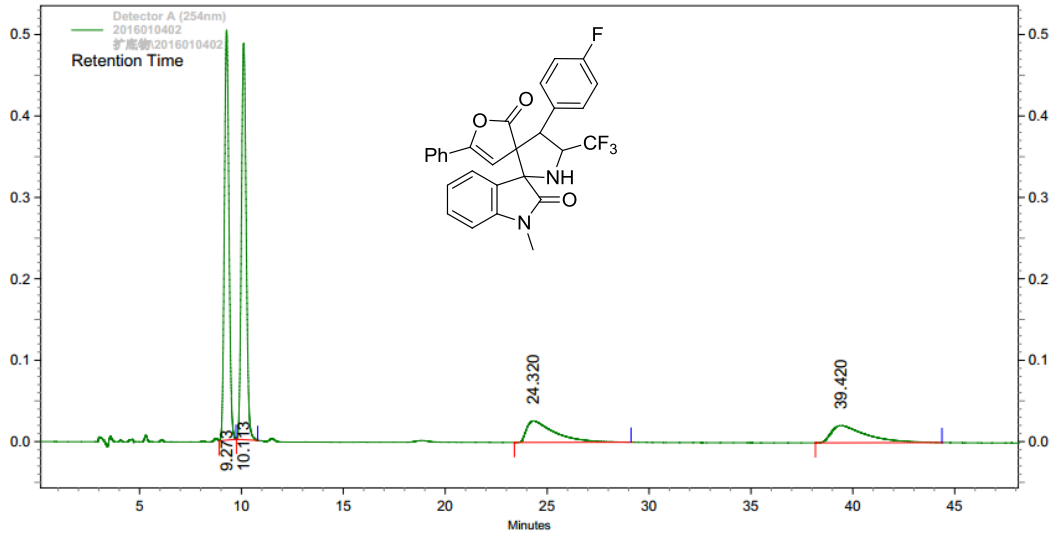
¹H NMR, ¹³C NMR and HPLC of 3p

1367-wzh-408.1.fid
WZH-408



1367-wzh-408.2.fid
WZH-408 13C

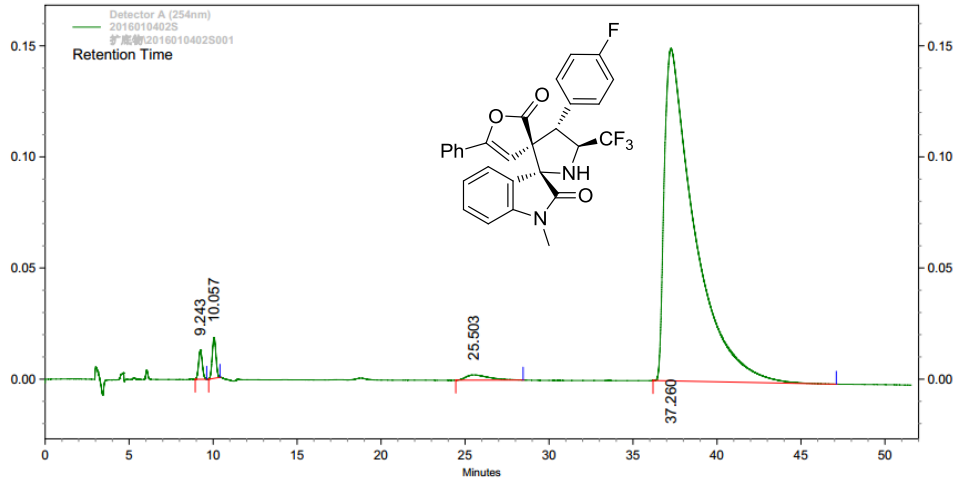




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.273	503442	48.52	7860409	37.69
2	10.113	486763	46.91	7972570	38.22
3	24.320	26399	2.54	2534449	12.15
4	39.420	21069	2.03	2490360	11.94

Totals	1037673	100.00	20857788	100.00
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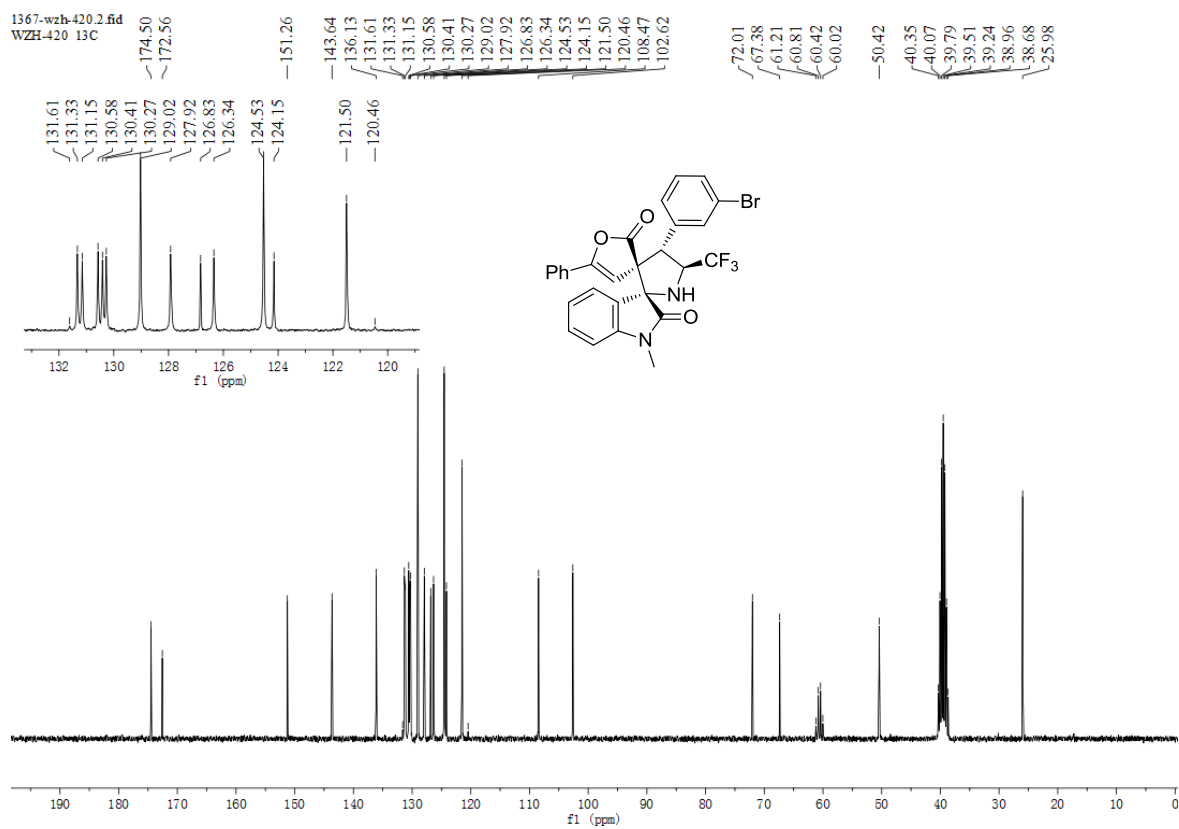
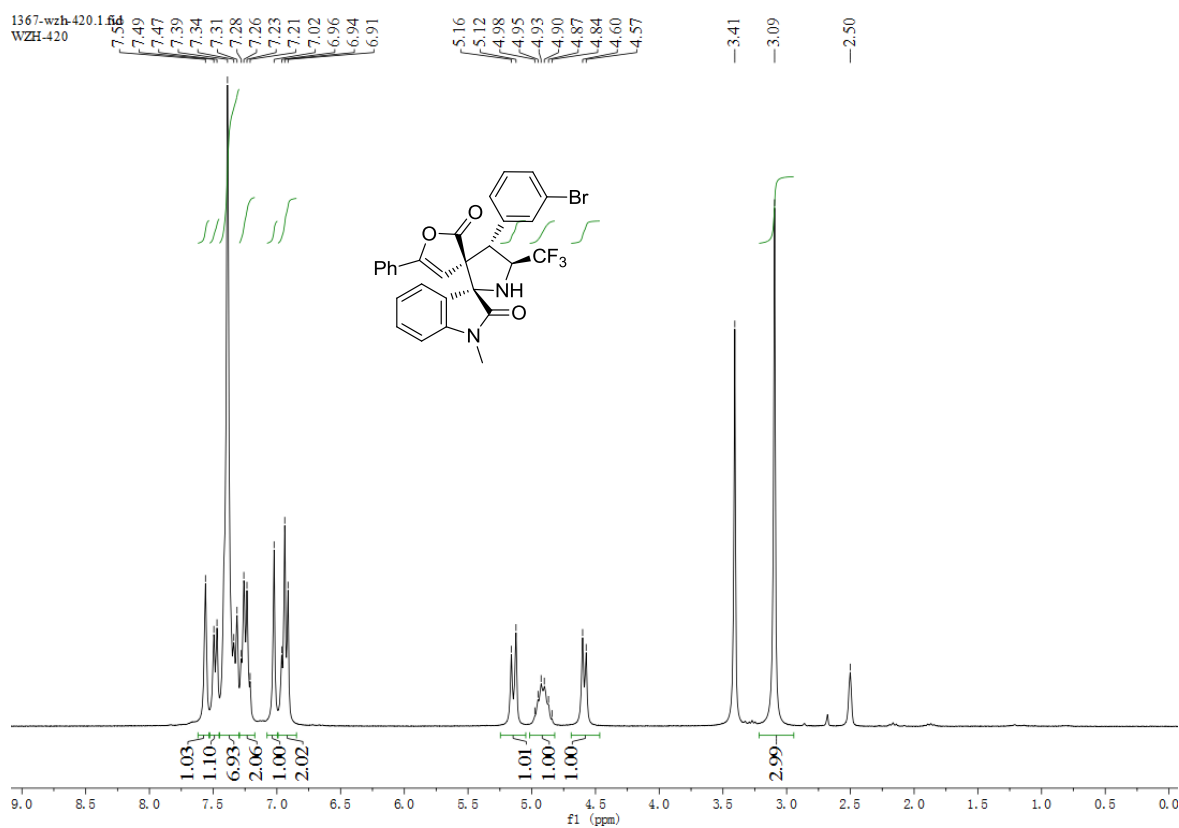


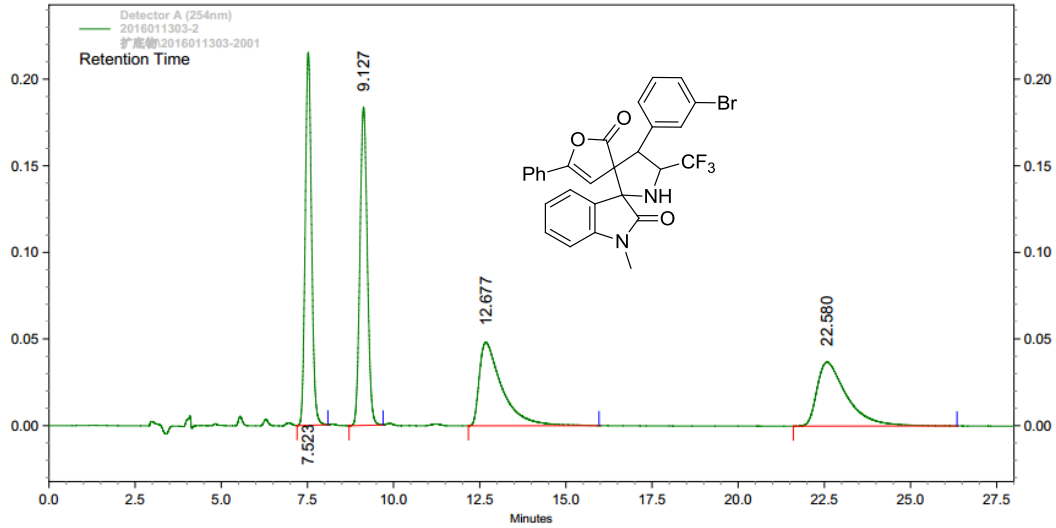
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.243	12997	7.09	199040	1.03
2	10.057	18288	9.98	282160	1.46
3	25.503	2350	1.28	225162	1.17
4	37.260	149582	81.64	18608706	96.34

Totals	183217	100.00	19315068	100.00
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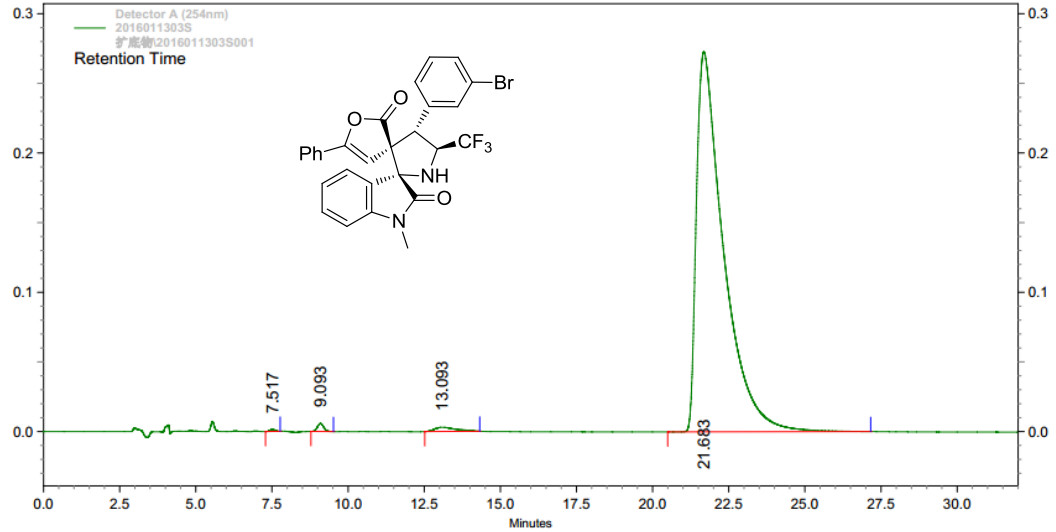
¹H NMR, ¹³C NMR and HPLC of 3q





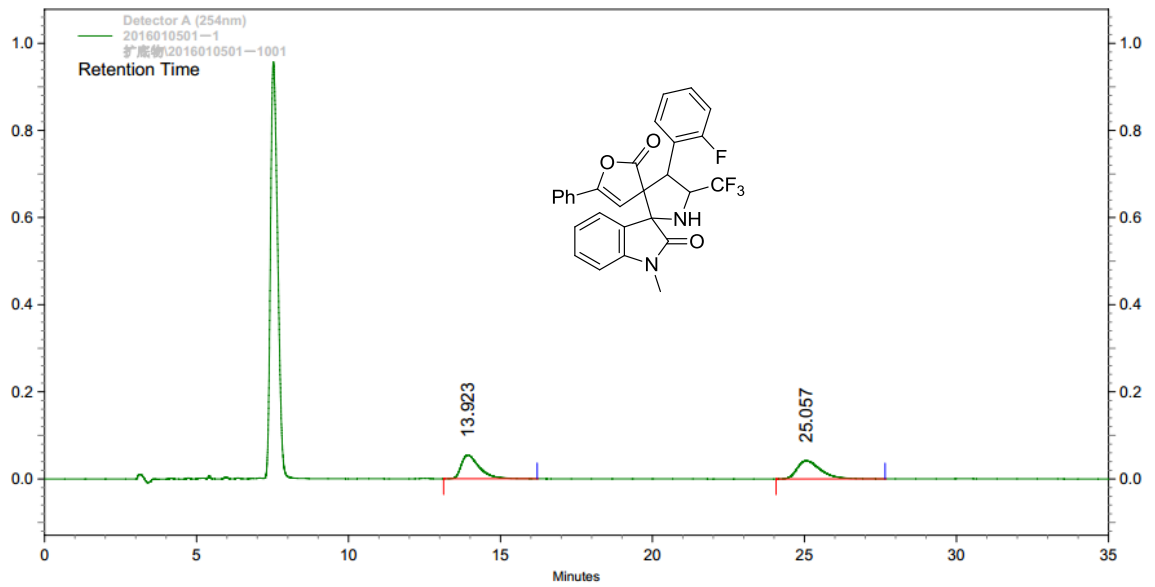
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.523	215203	44.49	2738782	27.72
2	9.127	183484	37.93	2725045	27.58
3	12.677	48136	9.95	2205362	22.32
4	22.580	36878	7.62	2210282	22.37
Totals		483701	100.00	9879471	100.00



Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.517	1402	0.50	16385	0.10
2	9.093	5737	2.03	82721	0.48
3	13.093	3024	1.07	148991	0.87
4	21.683	272842	96.41	16895269	98.55
Totals		283005	100.00	17143366	100.00



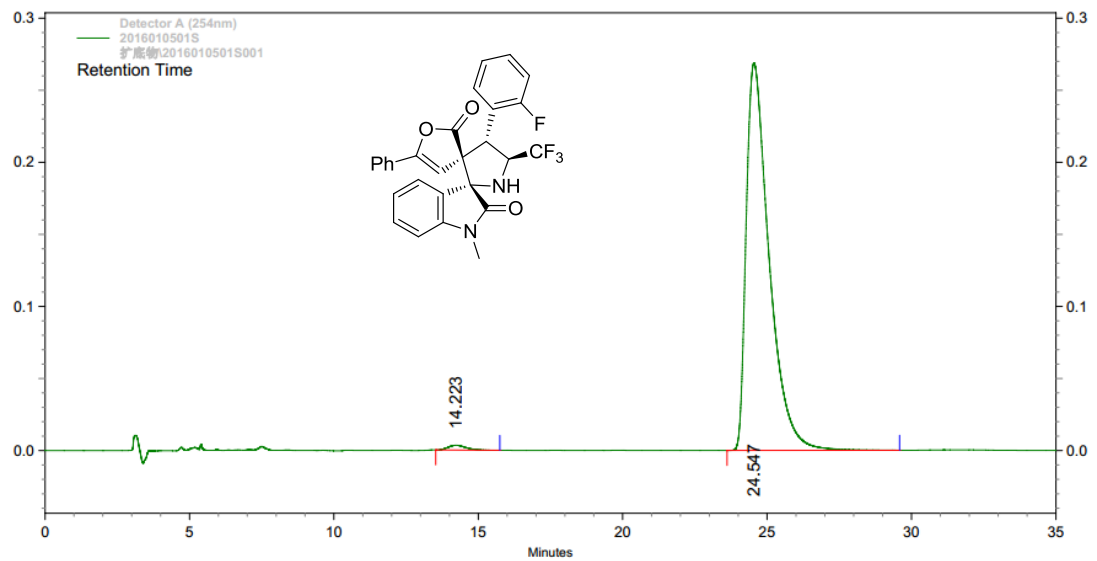
Detector

A

(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	13.923	54505	56.69	2246977	50.23
2	25.057	41634	43.31	2226127	49.77

Totals		96139	100.00	4473104	100.00
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Detector

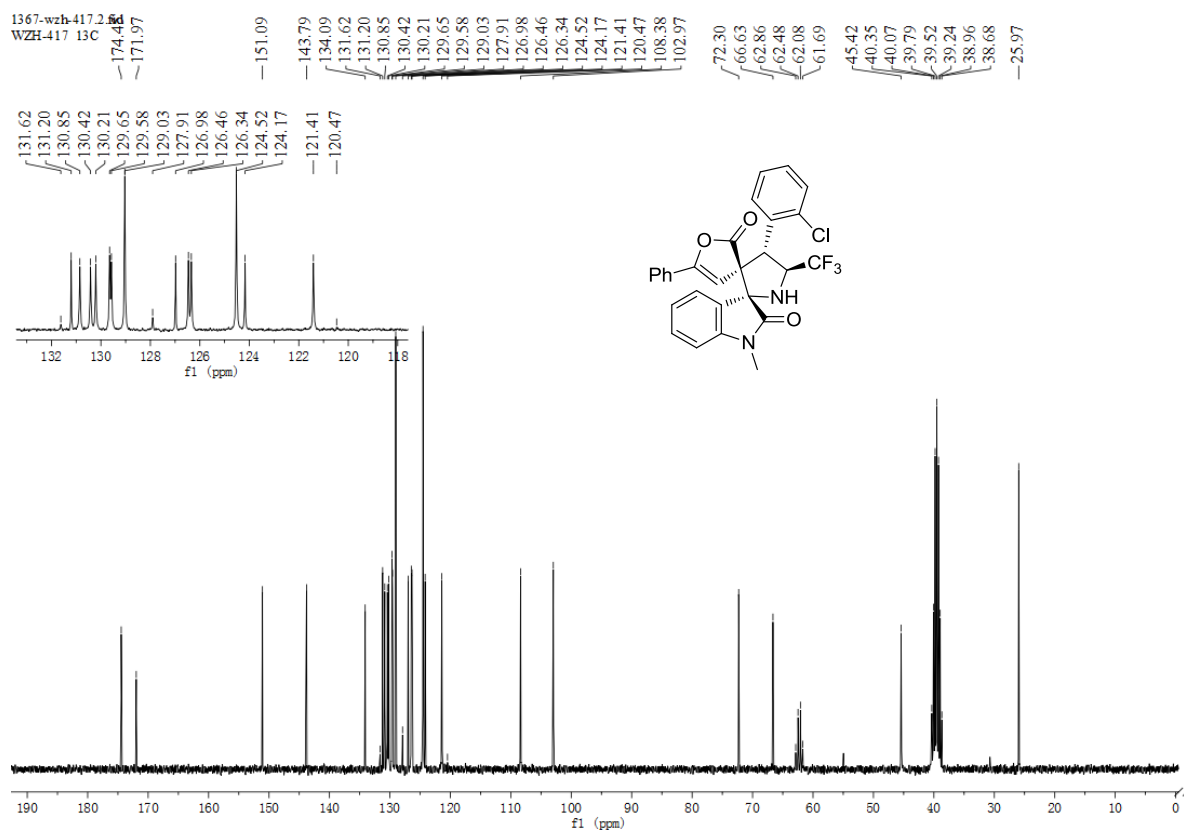
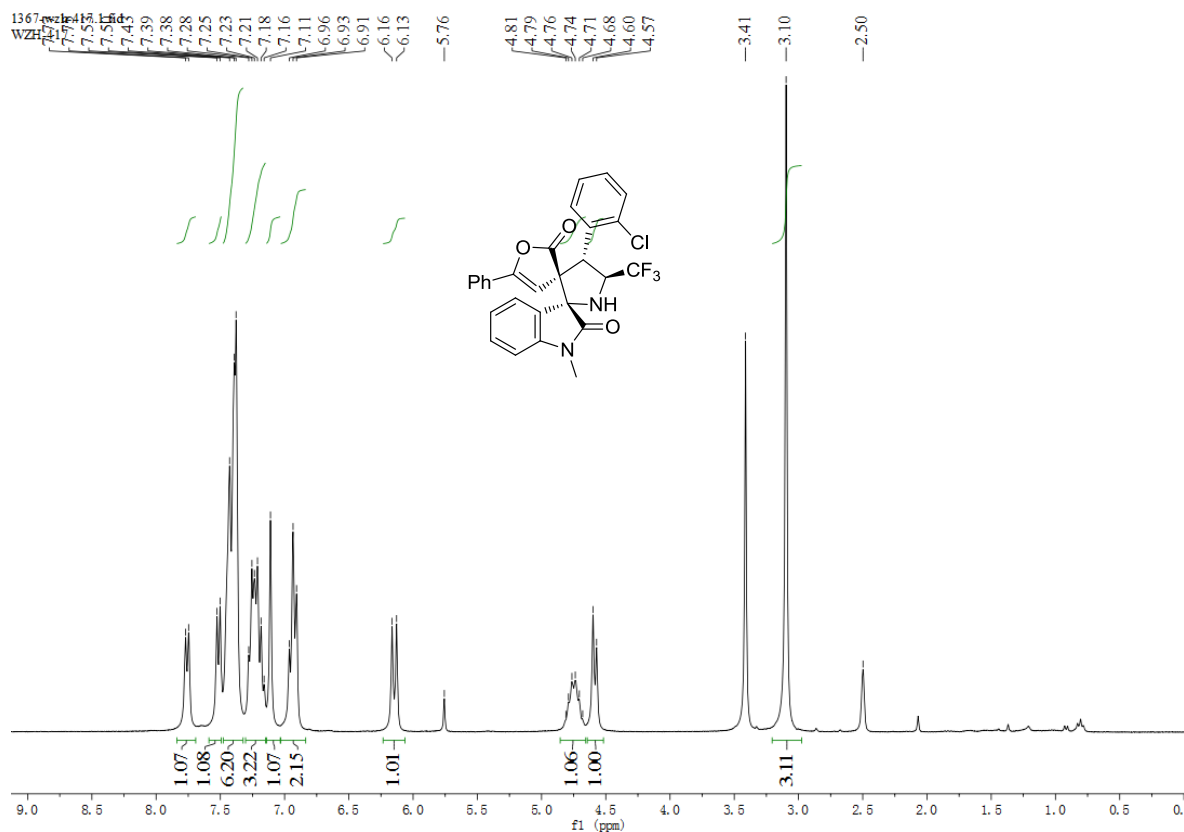
A

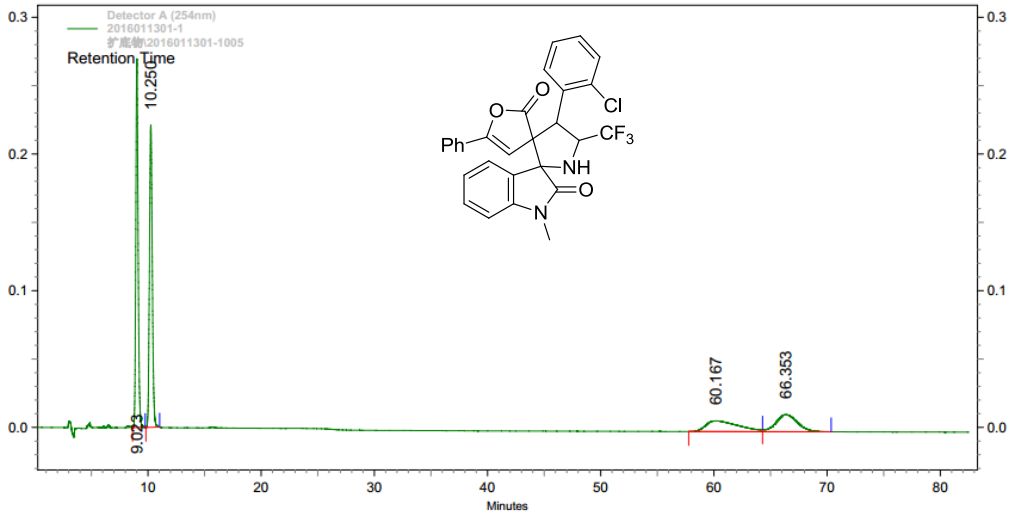
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	14.223	3297	1.21	141602	0.95
2	24.547	268906	98.79	14819795	99.05

Totals		272203	100.00	14961397	100.00
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¹H NMR, ¹³C NMR and HPLC of 3s

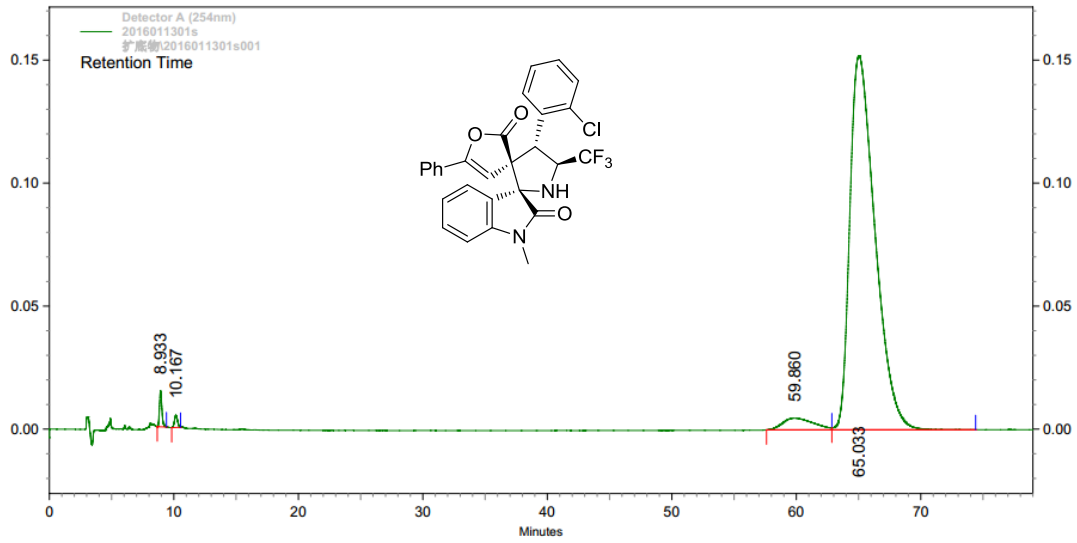




Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.023	269640	52.80	3810775	35.23
2	10.250	220817	43.24	3839878	35.50
3	60.167	7778	1.52	1542150	14.26
4	66.353	12471	2.44	1622917	15.01

Totals		510706	100.00	10815720	100.00
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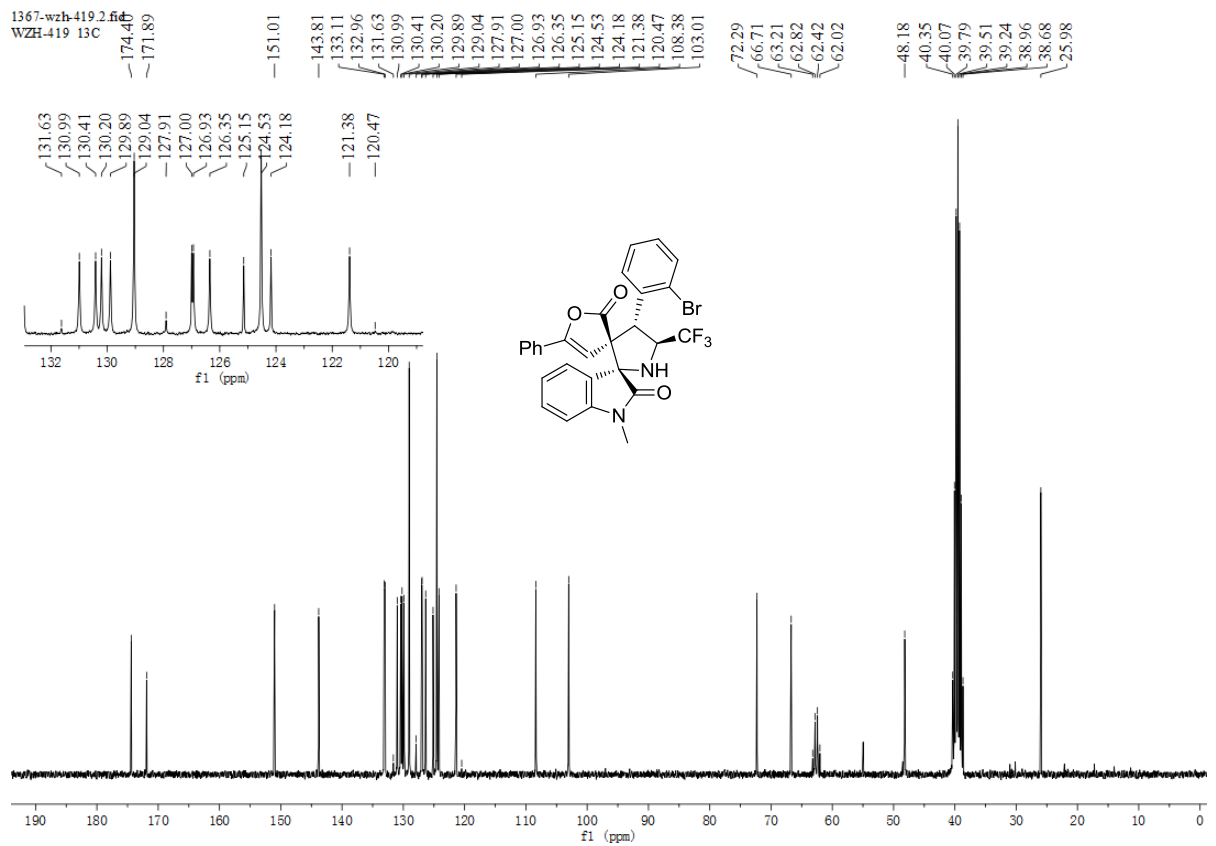
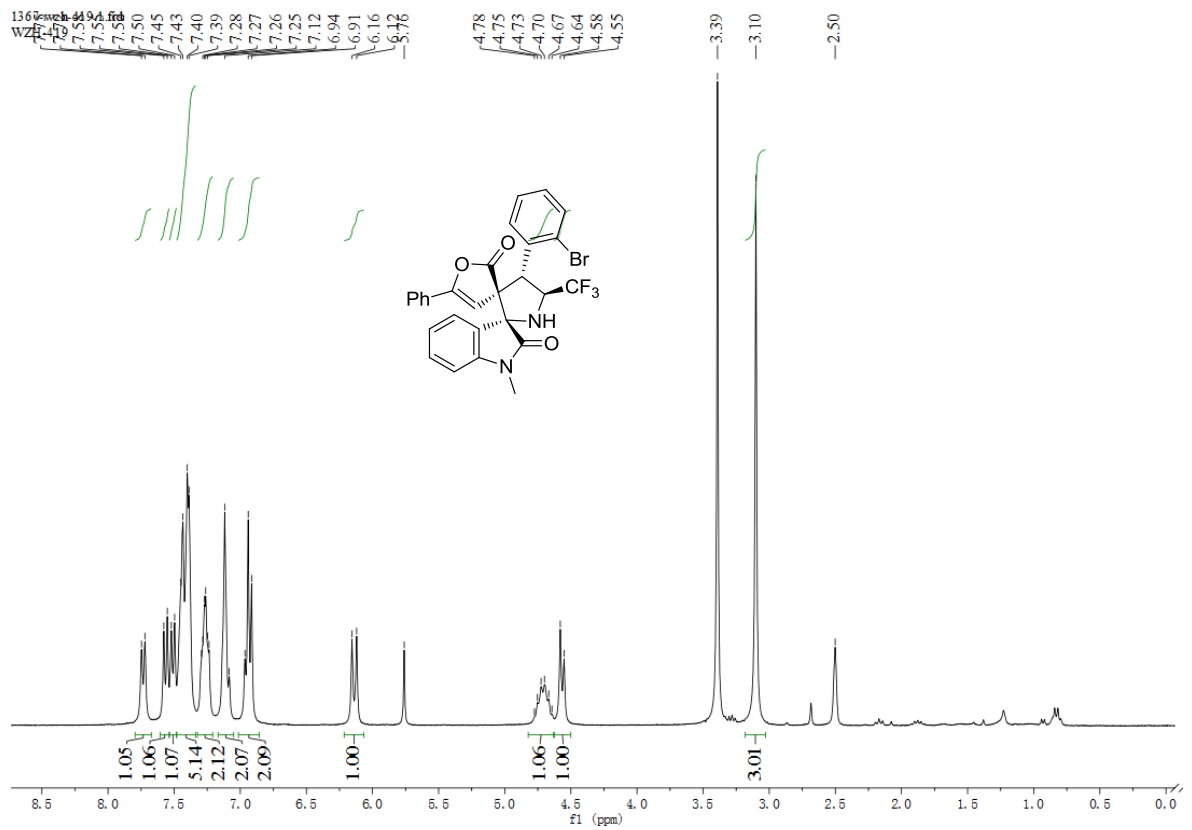


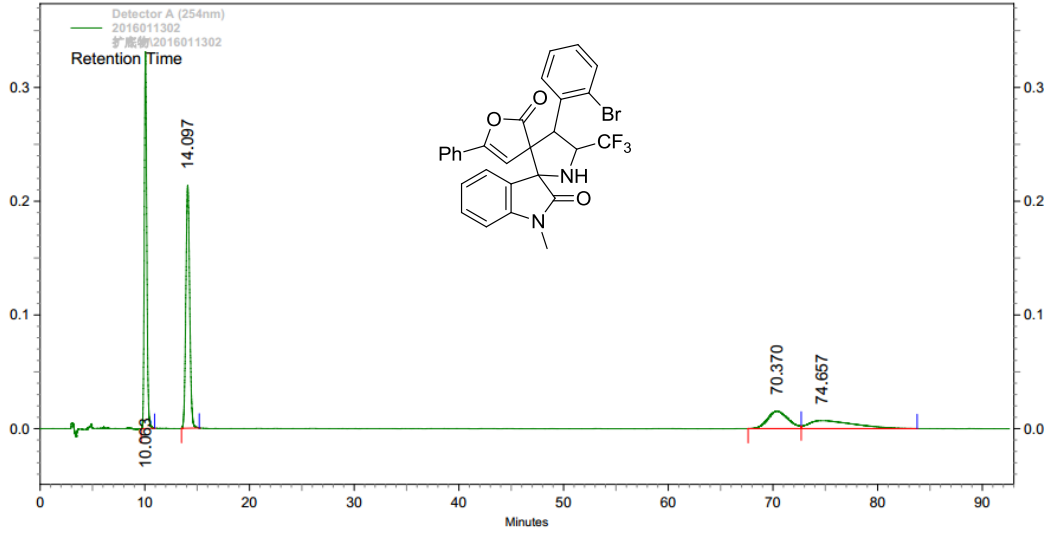
Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.933	14560	8.26	196452	0.88
2	10.167	4978	2.82	84852	0.38
3	59.860	4744	2.69	816717	3.64
4	65.033	152062	86.23	21342553	95.11

Totals		176344	100.00	22440574	100.00
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¹H NMR, ¹³C NMR and HPLC of 3t

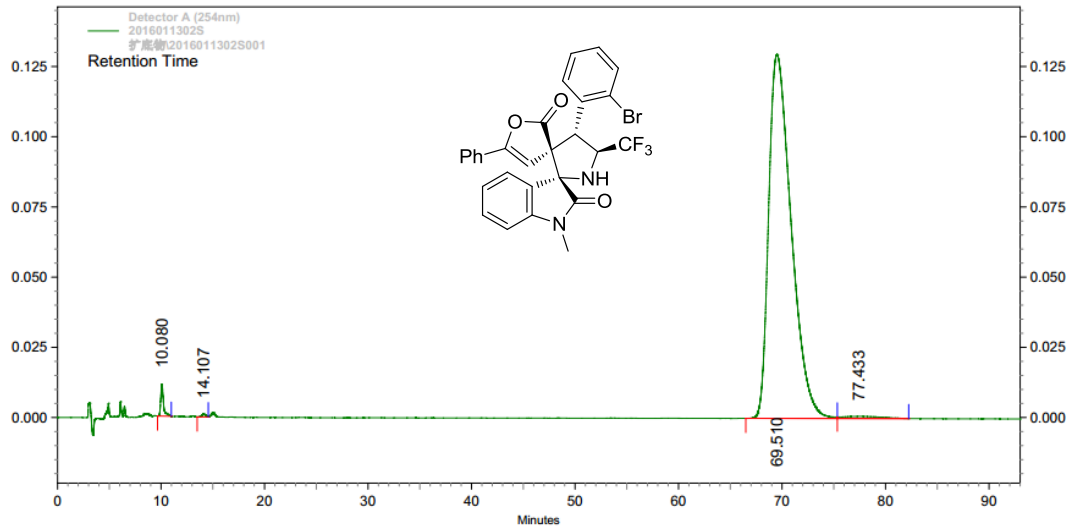




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.063	331274	58.43	5401052	36.04
2	14.097	213537	37.66	5404869	36.06
3	70.370	15178	2.68	2072674	13.83
4	74.657	6976	1.23	2109026	14.07

Totals		566965	100.00	14987621	100.00
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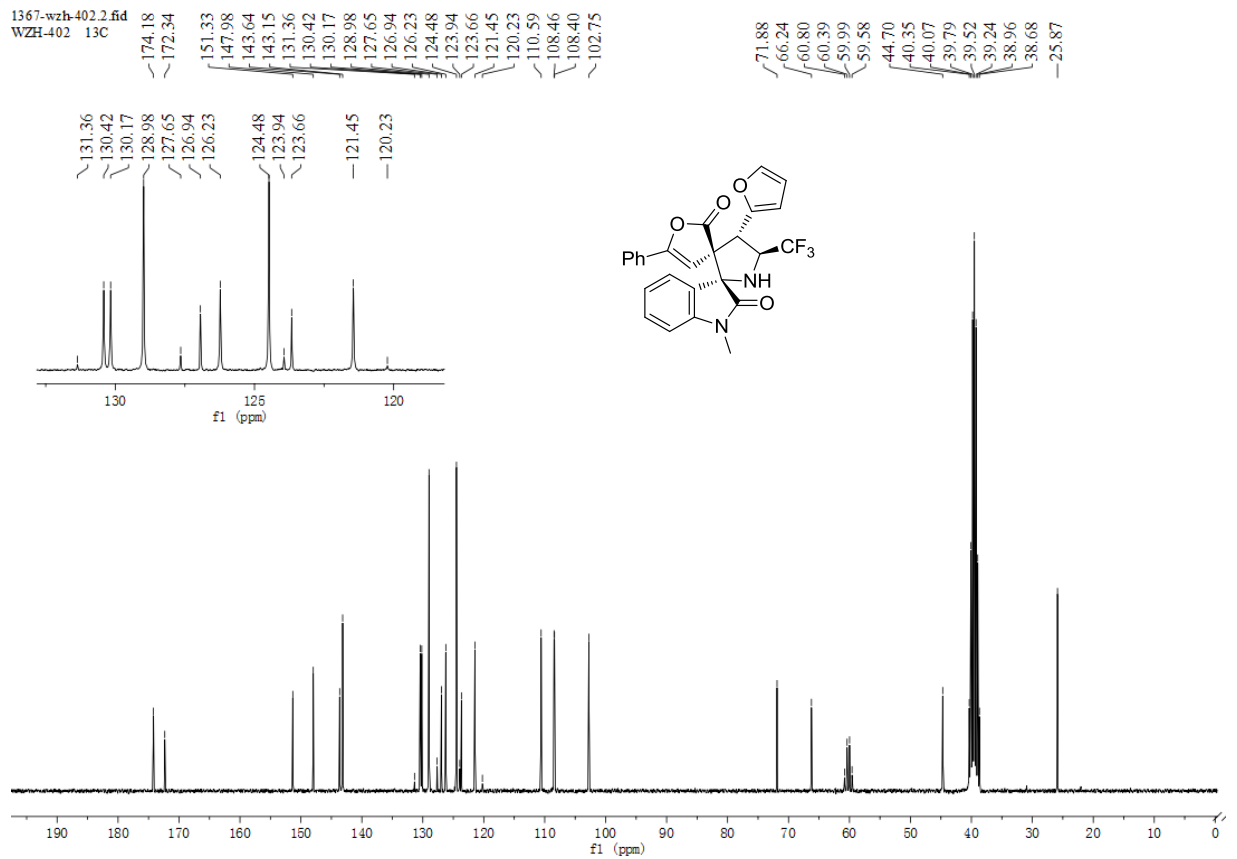
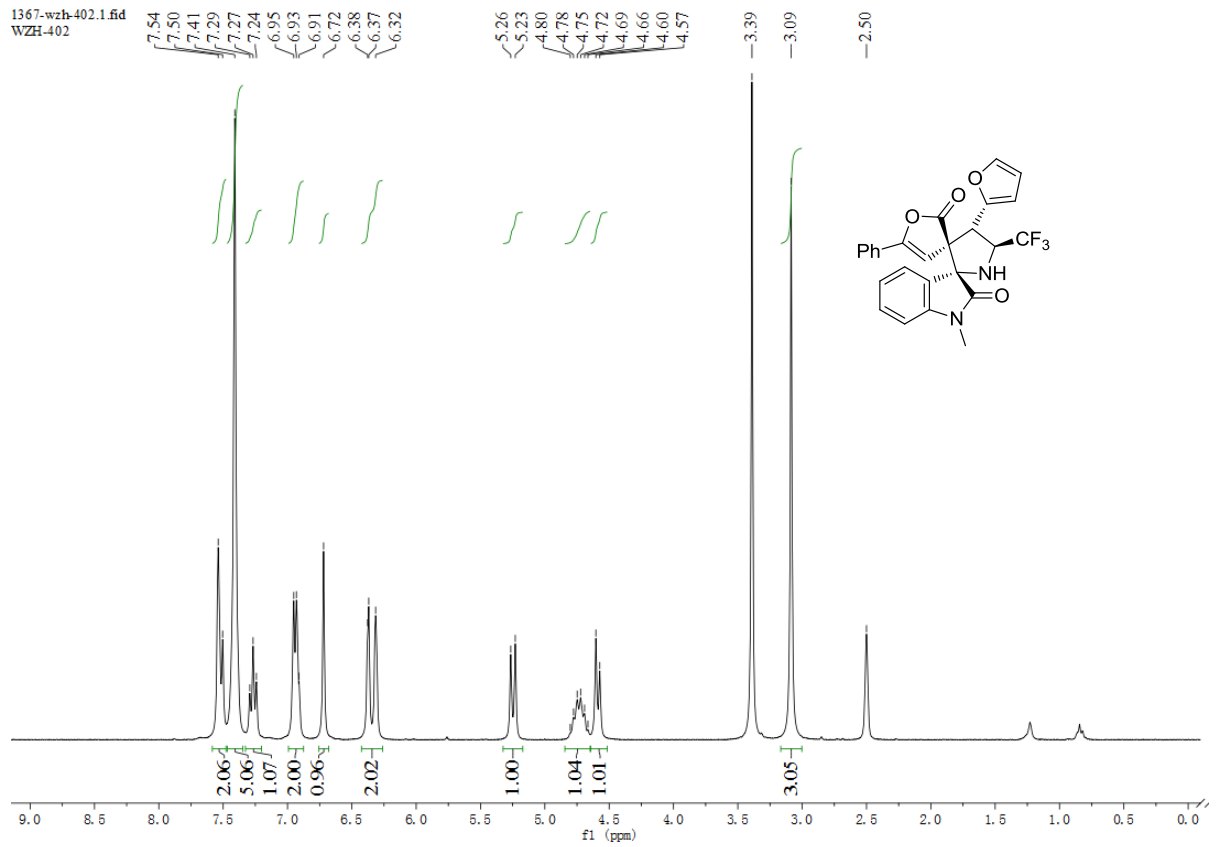


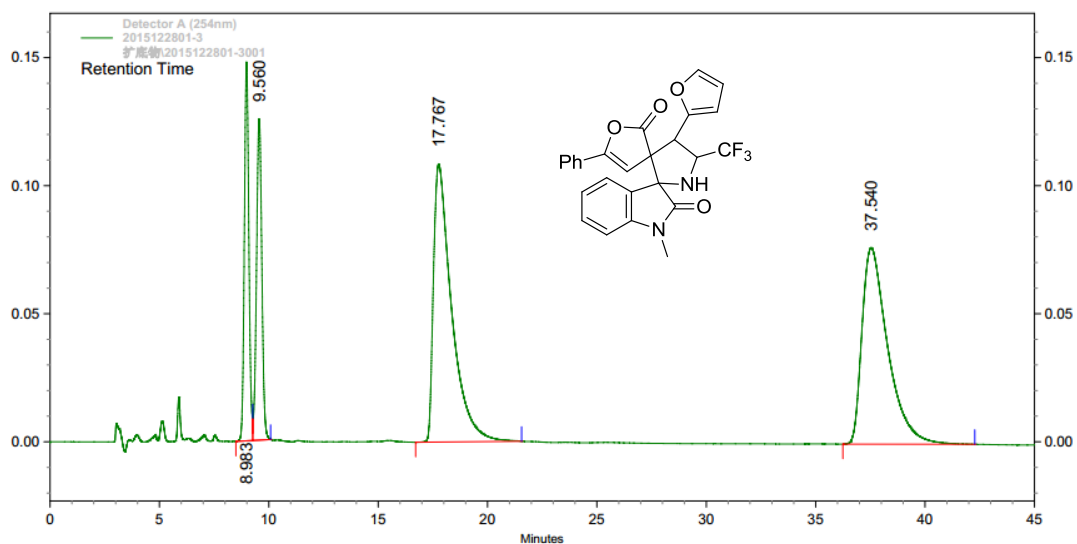
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.080	11349	7.95	208110	1.04
2	14.107	1091	0.76	26019	0.13
3	69.510	129594	90.77	19562602	97.88
4	77.433	735	0.51	190589	0.95

Totals		142769	100.00	19987320	100.00
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¹H NMR, ¹³C NMR and HPLC of 3u



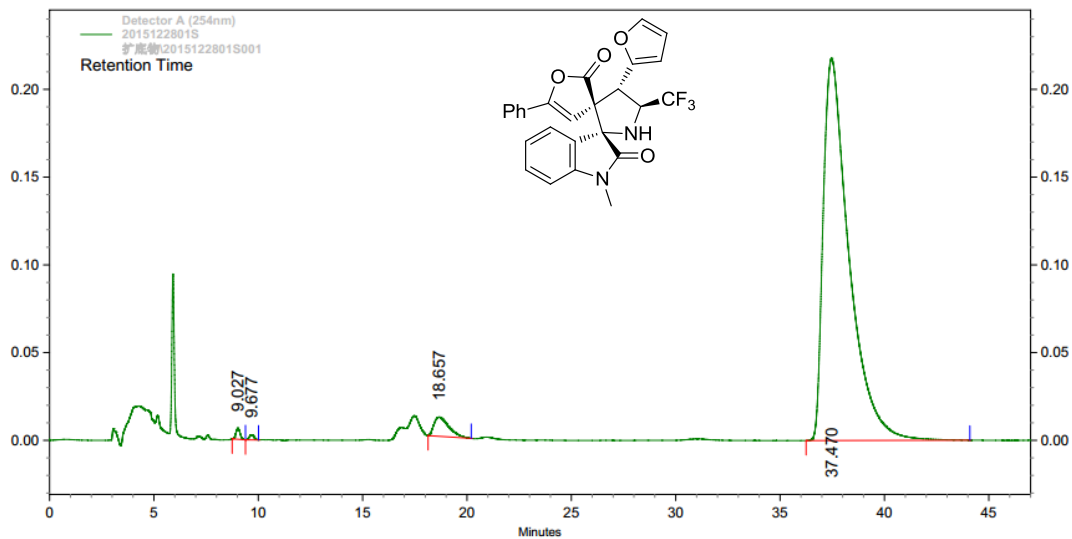


Detector
A

(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.983	147854	32.24	2109765	12.58
2	9.560	125491	27.36	2116534	12.62
3	17.767	108583	23.68	6267182	37.37
4	37.540	76709	16.73	6275385	37.42

Totals	Area	Height Percent	Area	Area Percent
	458637	100.00	16768866	100.00



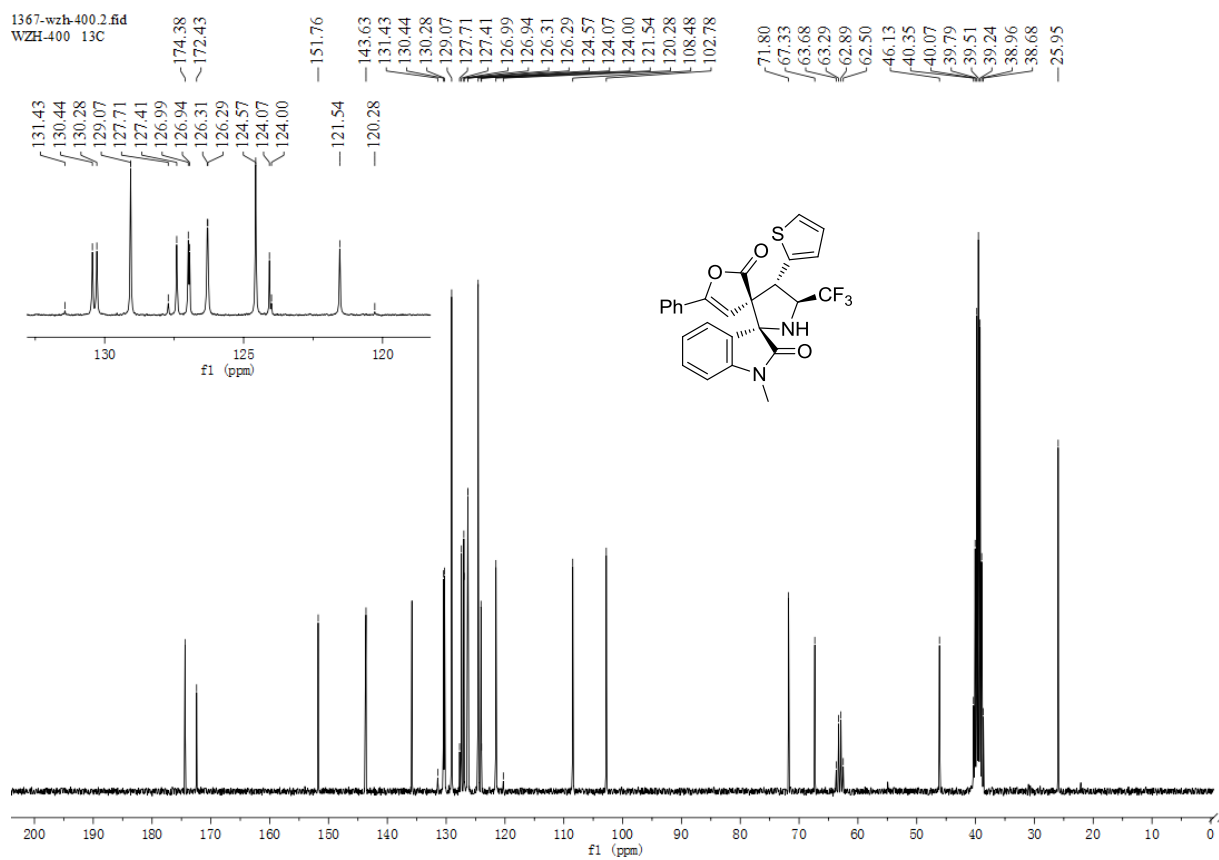
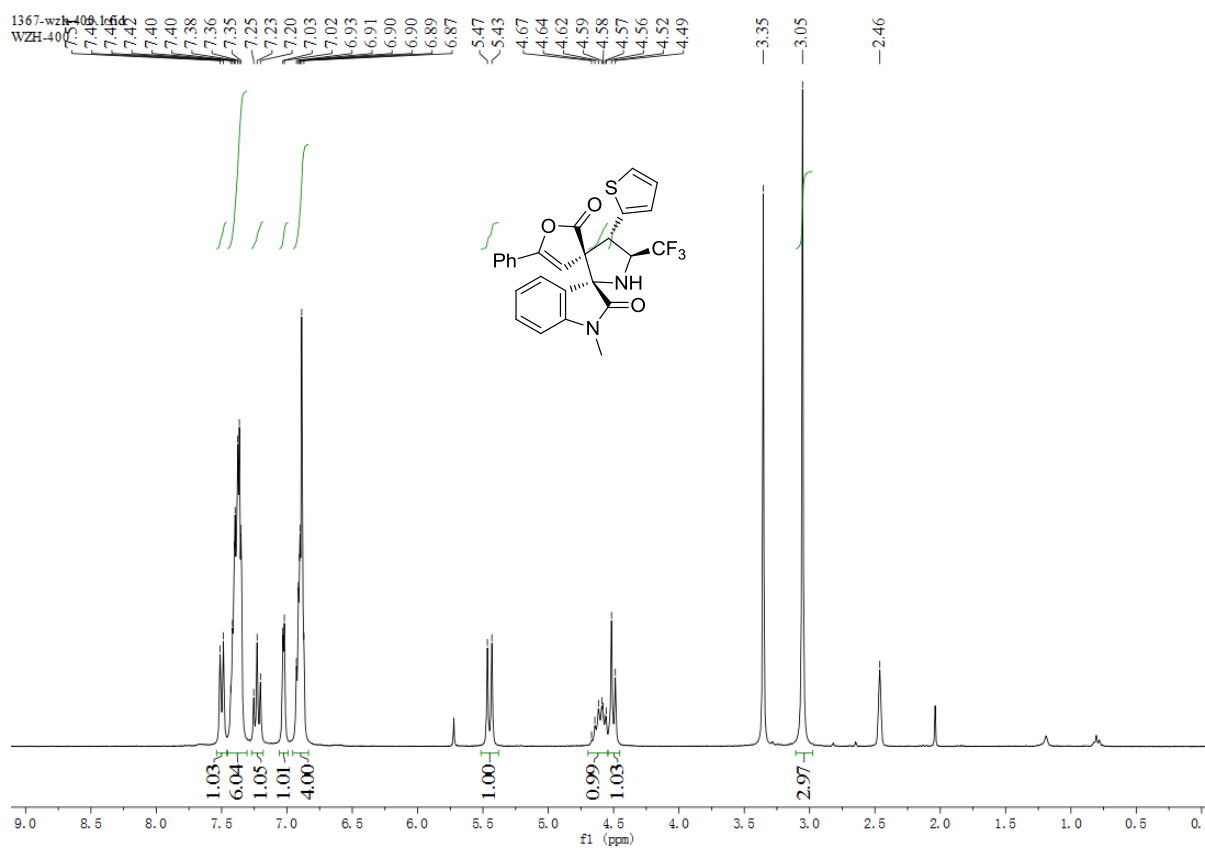
Detector
A

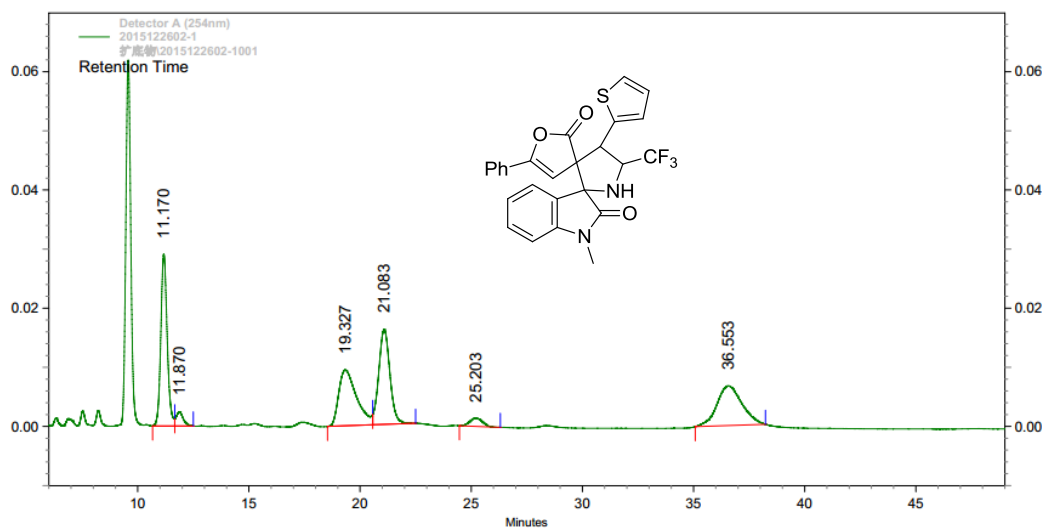
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.027	6396	2.69	88261	0.46
2	9.677	2810	1.18	42842	0.22
3	18.657	10931	4.60	538531	2.78
4	37.470	217709	91.53	18694871	96.54

Totals	Area	Height Percent	Area	Area Percent
	237846	100.00	19364505	100.00

¹H NMR, ¹³C NMR and HPLC of 3v

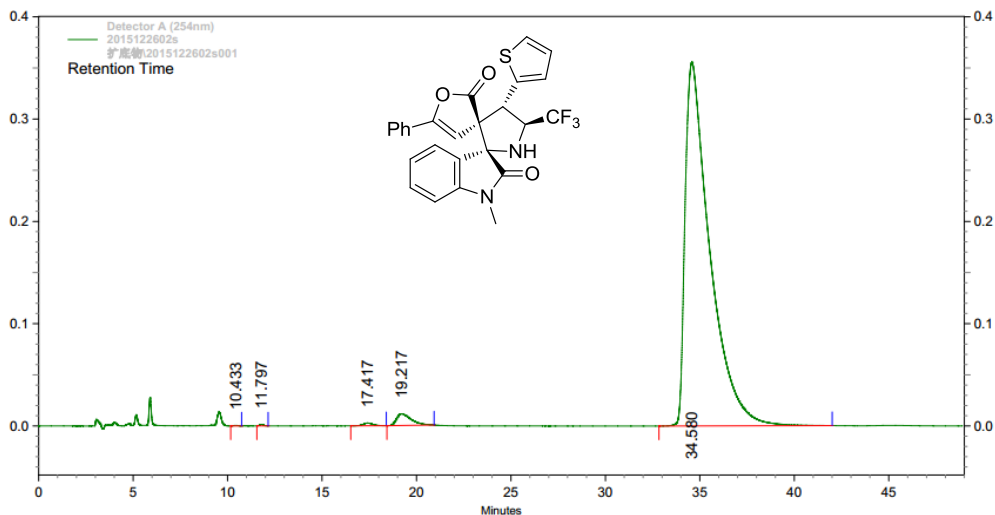




Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.170	29061	44.63	578280	25.18
2	11.870	2416	3.71	52623	2.29
3	19.327	9448	14.51	524794	22.85
4	21.083	16074	24.69	560179	24.39
5	25.203	1385	2.13	54861	2.39
6	36.553	6725	10.33	525777	22.89

Totals		65109	100.00	2296514	100.00
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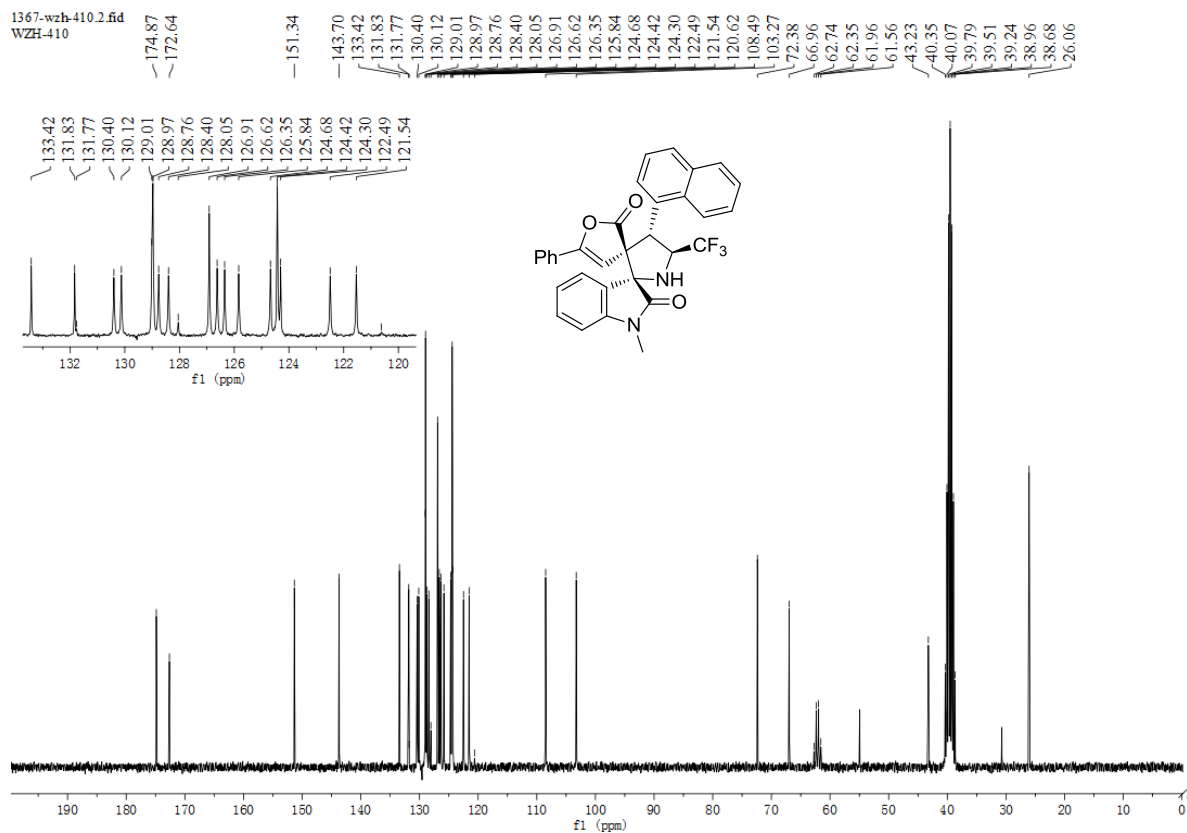
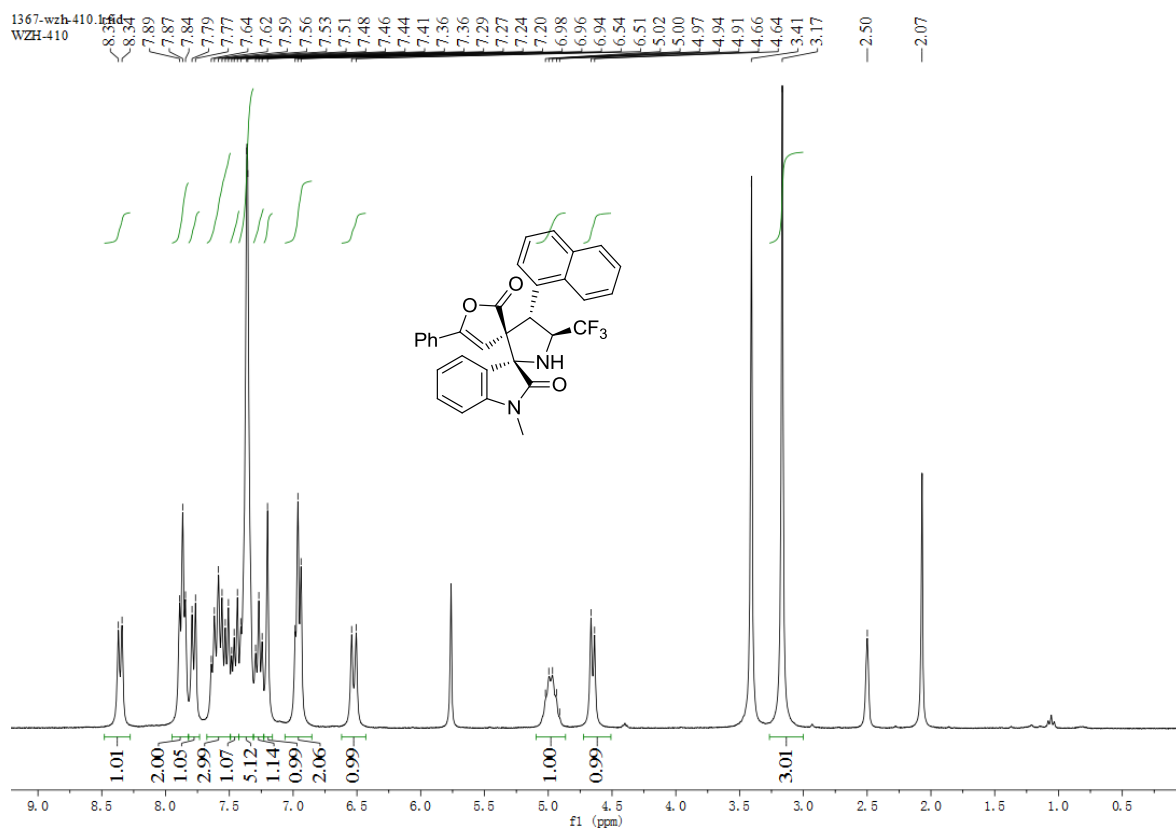


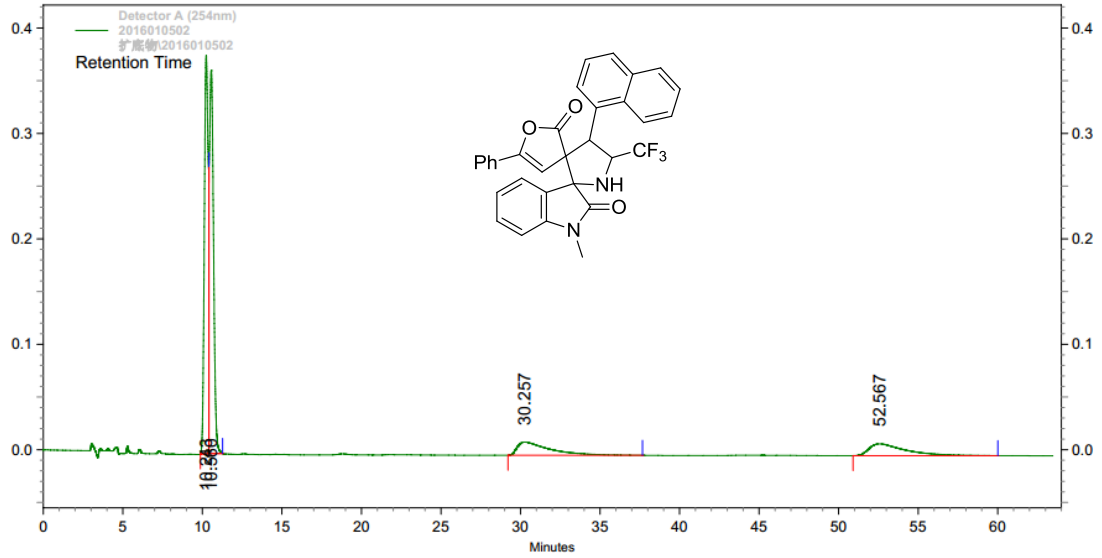
Detector
A
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.433	505	0.14	8336	0.03
2	11.797	1386	0.37	20594	0.06
3	17.417	2712	0.73	97561	0.30
4	19.217	11436	3.08	623096	1.89
5	34.580	355518	95.68	32265447	97.73

Totals		371557	100.00	33015034	100.00
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¹H NMR, ¹³C NMR and HPLC of 3w

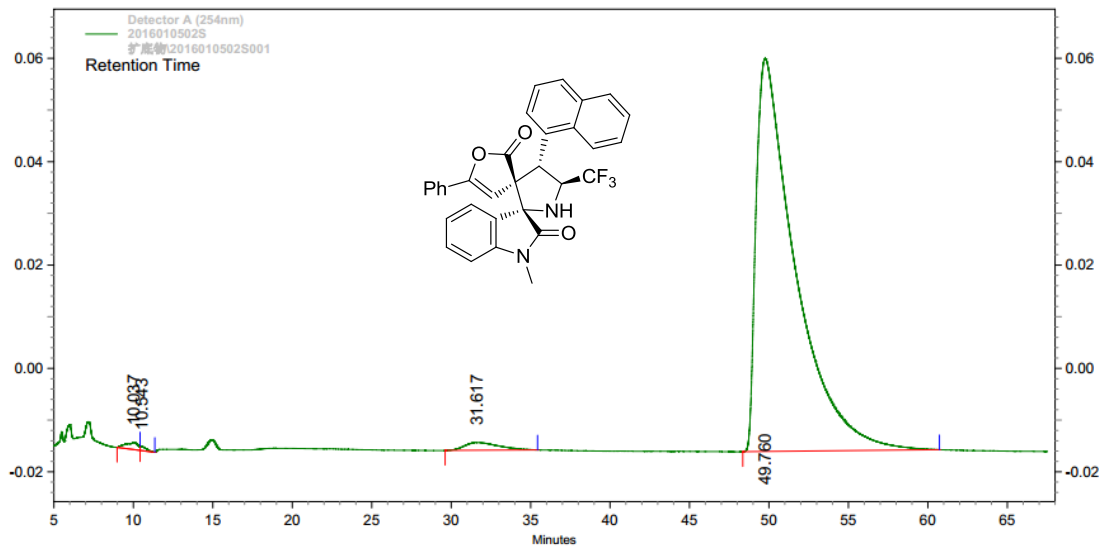




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.243	377903	49.40	6373869	38.61
2	10.560	363369	47.50	6553730	39.70
3	30.257	12550	1.64	1788987	10.84
4	52.567	11191	1.46	1793084	10.86

Totals		765013	100.00	16509670	100.00
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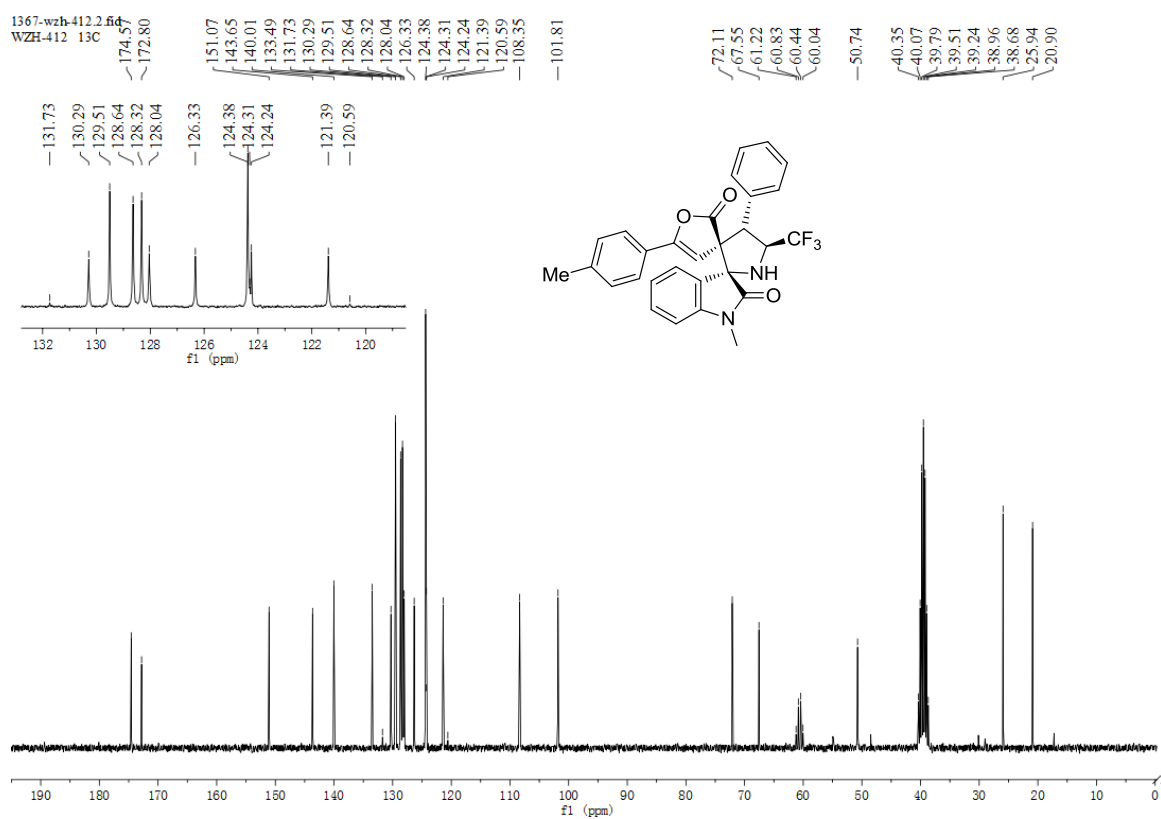
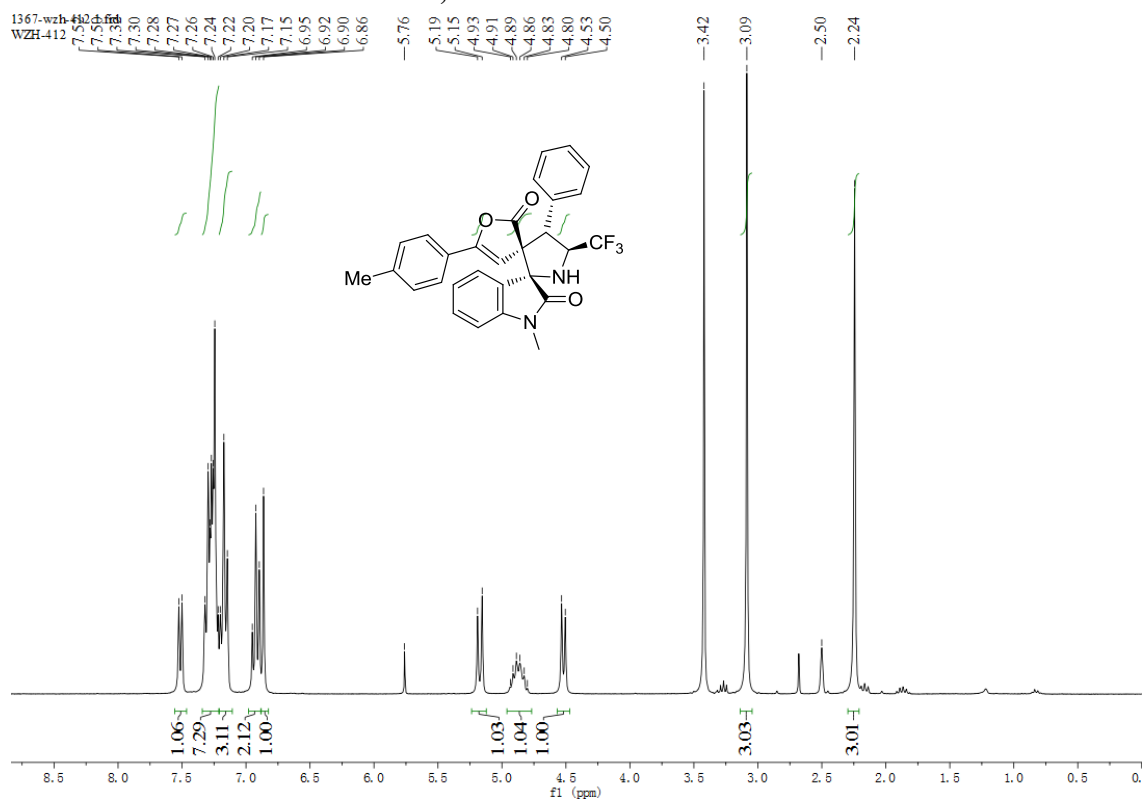


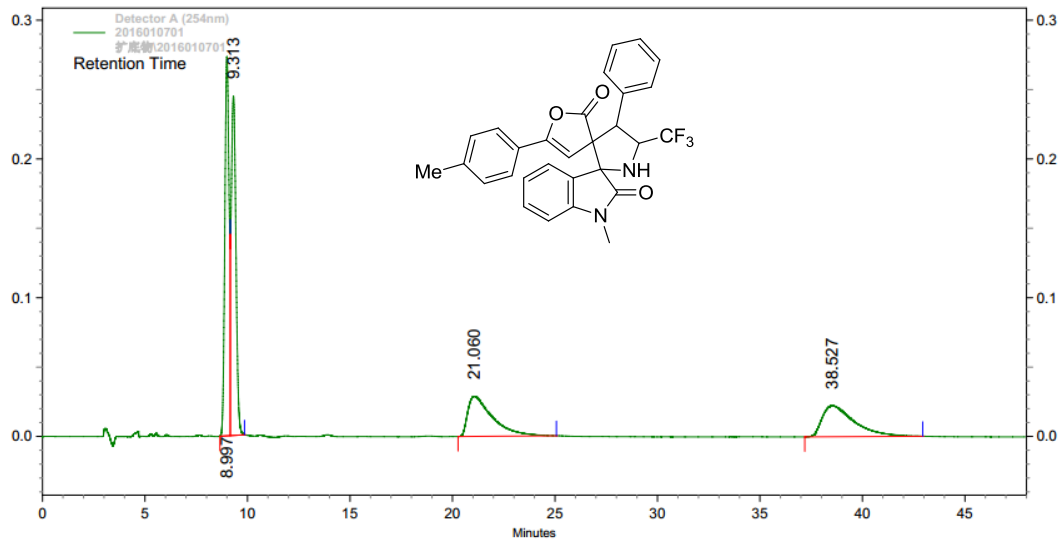
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.037	1386	1.74	71764	0.54
2	10.543	778	0.98	21340	0.16
3	31.617	1496	1.88	223545	1.68
4	49.760	76071	95.41	12981225	97.62

Totals		79731	100.00	13297874	100.00
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¹H NMR, ¹³C NMR and HPLC of 3x

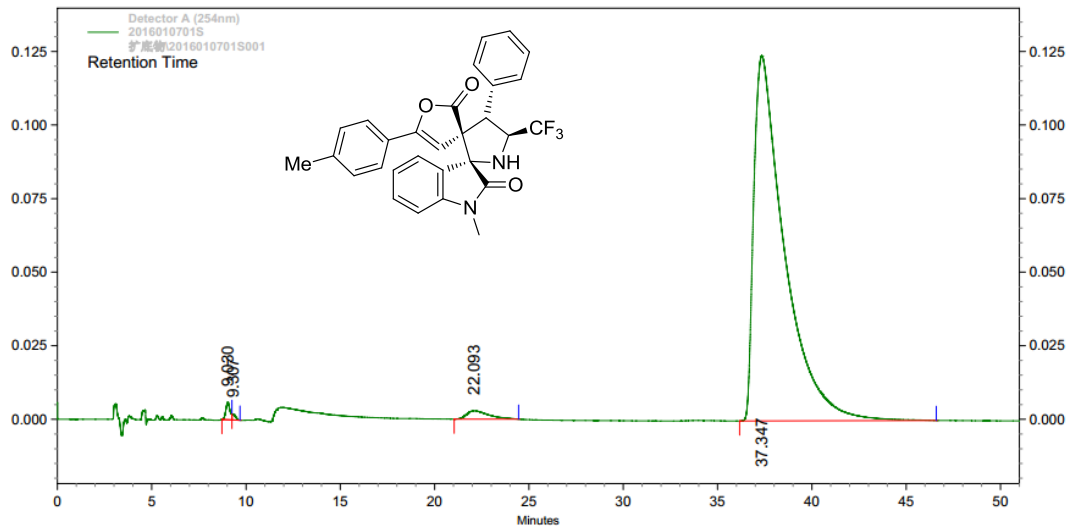




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.997	273171	48.00	3923065	30.95
2	9.313	244524	42.97	3944205	31.11
3	21.060	28888	5.08	2391013	18.86
4	38.527	22489	3.95	2418178	19.08

Totals		569072	100.00	12676461	100.00
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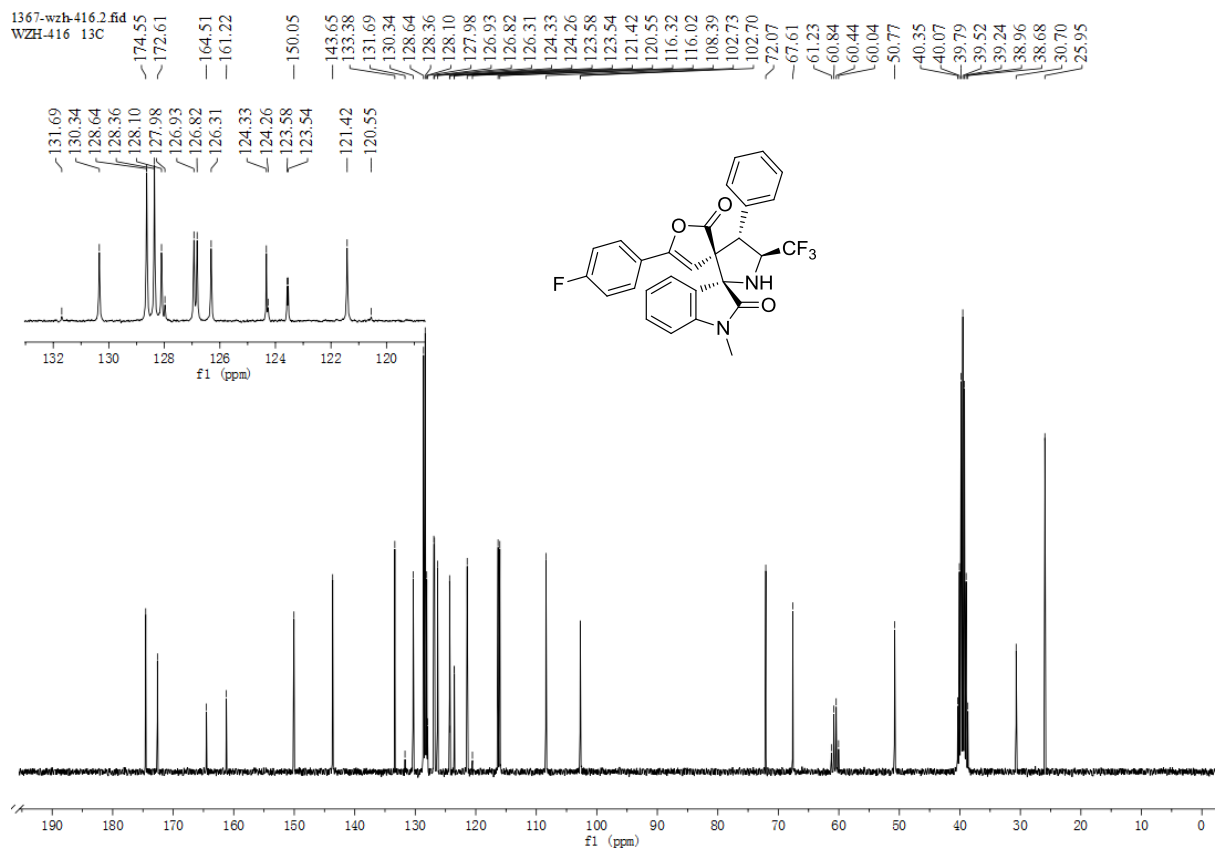
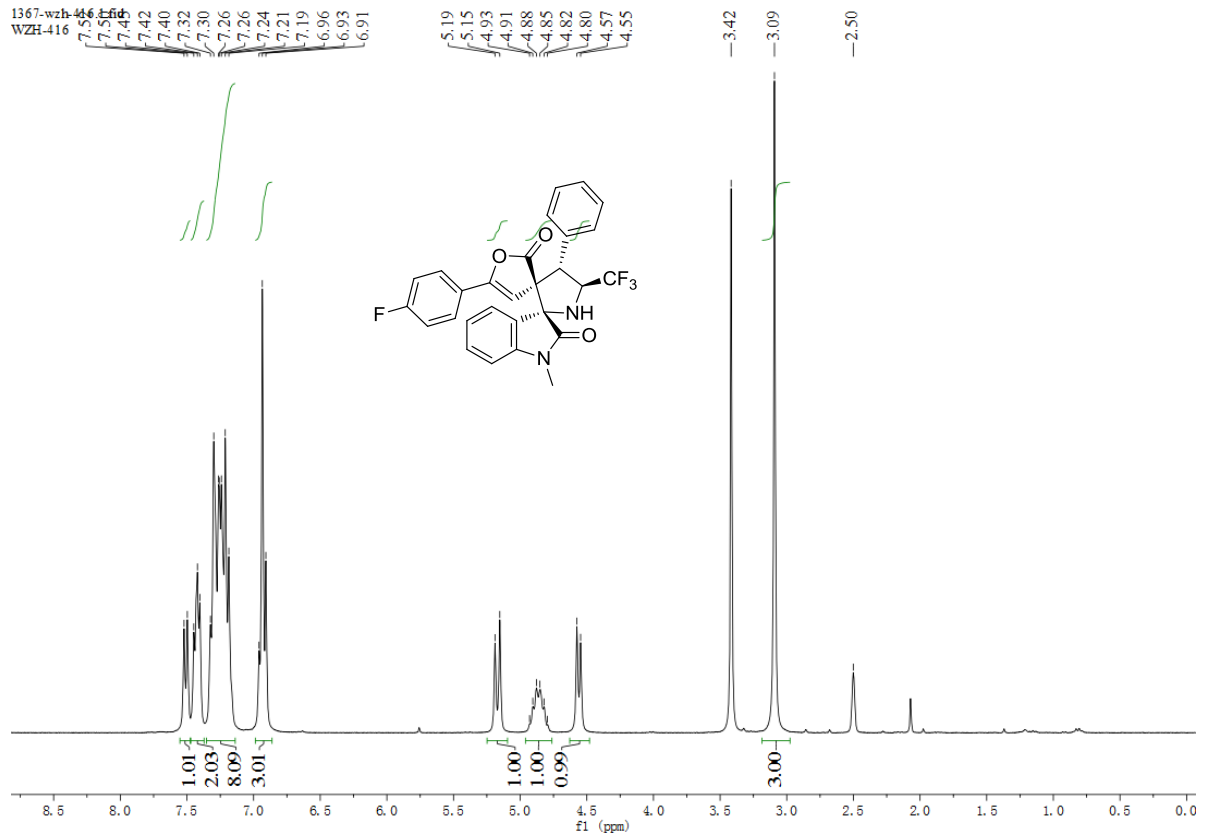


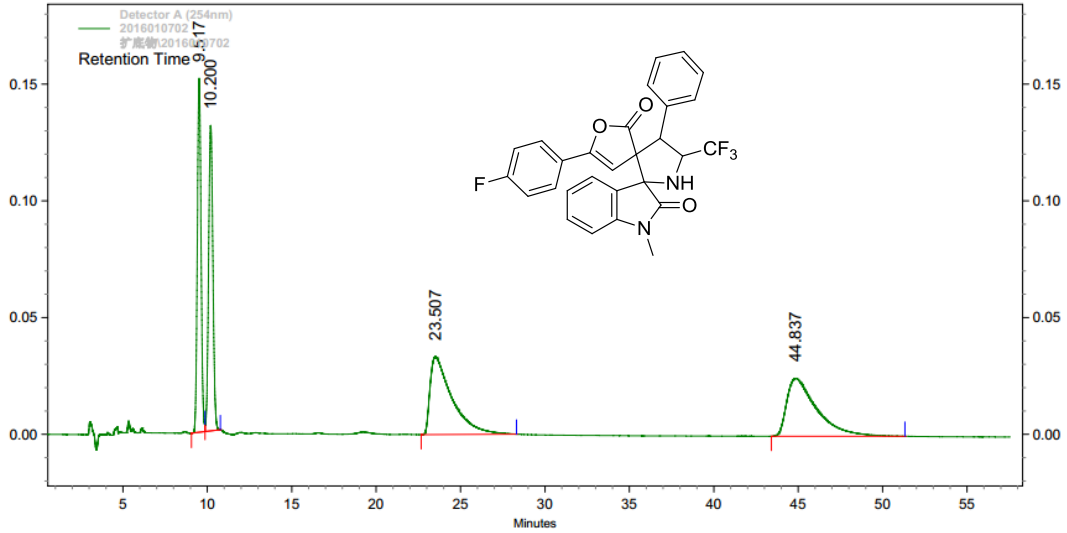
Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.030	5861	4.35	89164	0.62
2	9.307	1920	1.43	24129	0.17
3	22.093	2820	2.09	232069	1.62
4	37.347	124108	92.13	13998595	97.59

Totals		134709	100.00	14343957	100.00
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¹H NMR, ¹³C NMR and HPLC of 3y



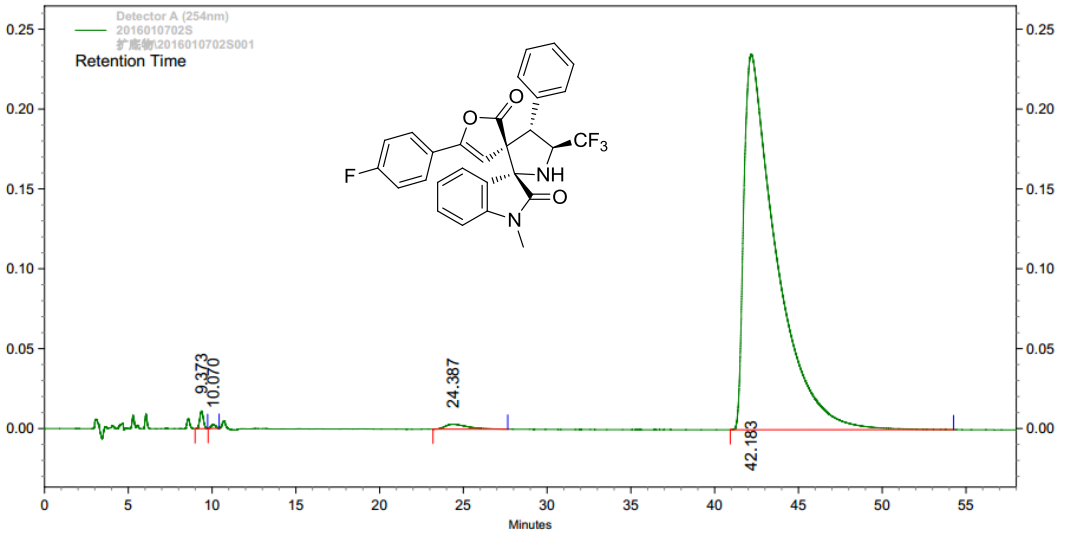


Detector
A

(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.517	151572	44.51	2305924	21.66
2	10.200	130788	38.40	2307428	21.68
3	23.507	33374	9.80	2998887	28.17
4	44.837	24833	7.29	3032845	28.49

Totals		340567	100.00	10645084	100.00
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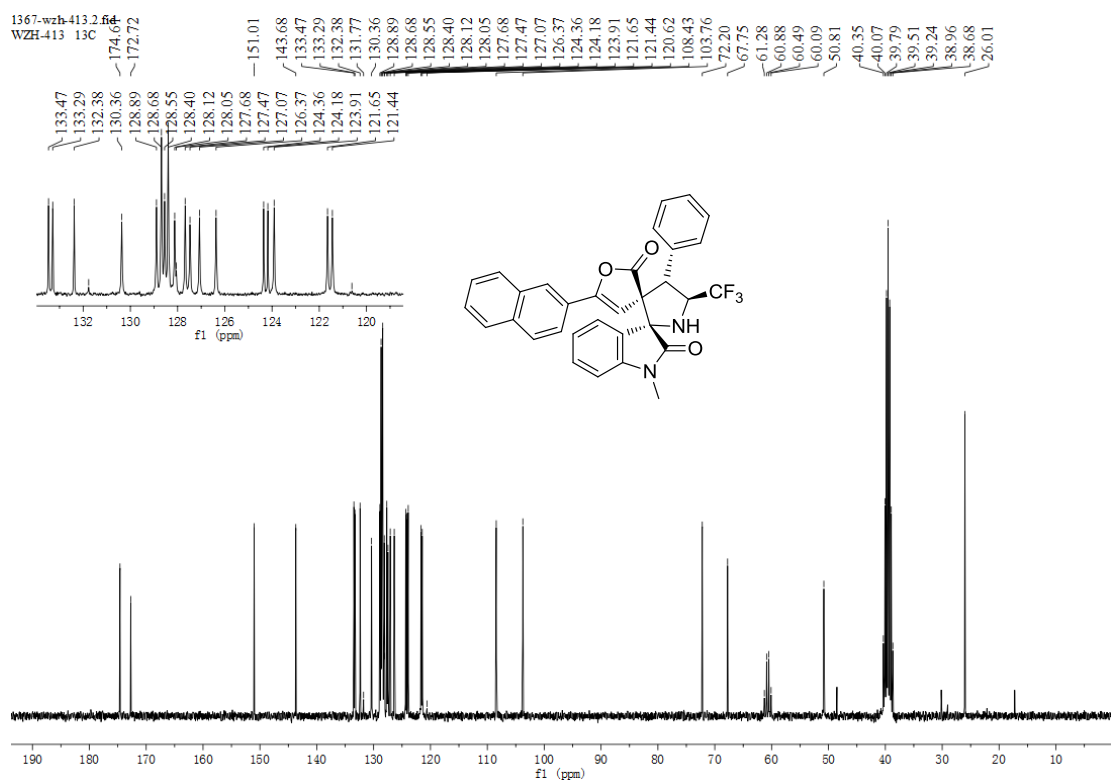
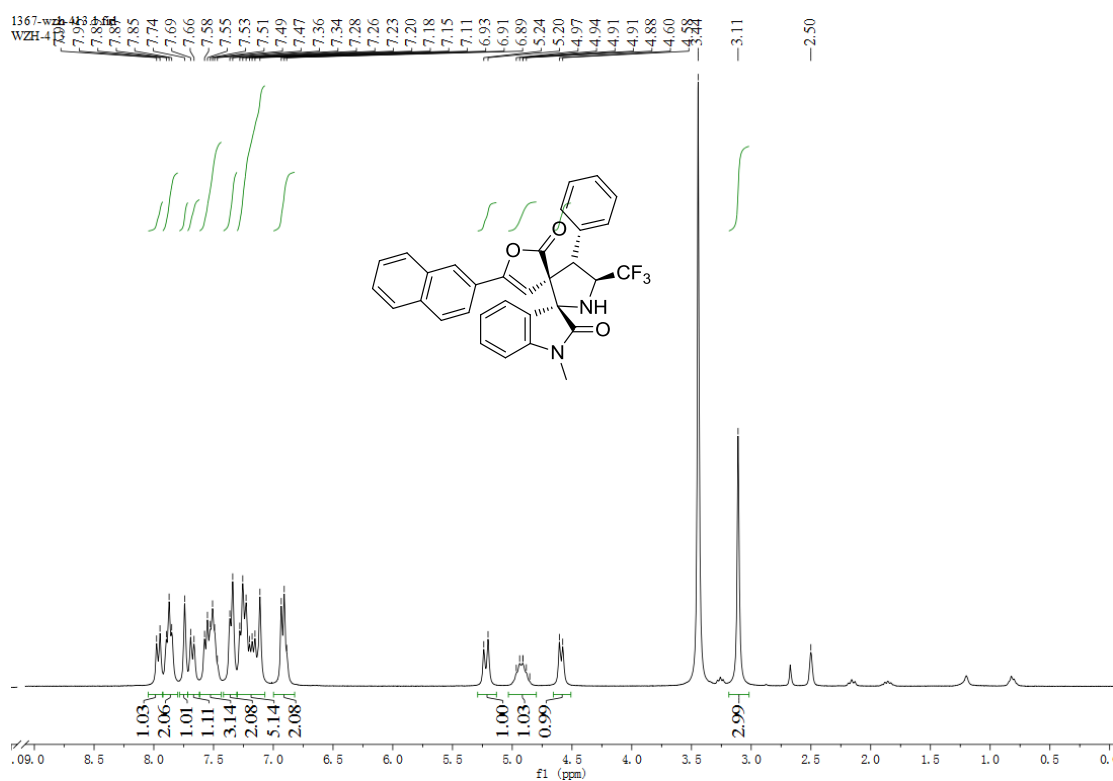
Detector
A

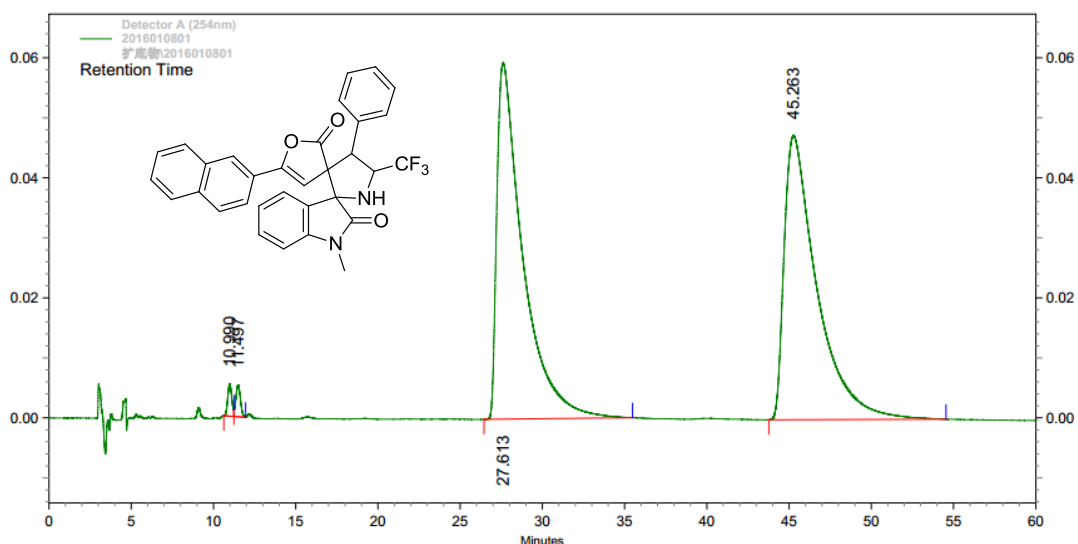
(254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.373	11032	4.38	164929	0.52
2	10.070	2662	1.06	45271	0.14
3	24.387	3017	1.20	284660	0.89
4	42.183	235203	93.37	31470280	98.45

Totals		251914	100.00	31965140	100.00
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¹H NMR, ¹³C NMR and HPLC of 3z



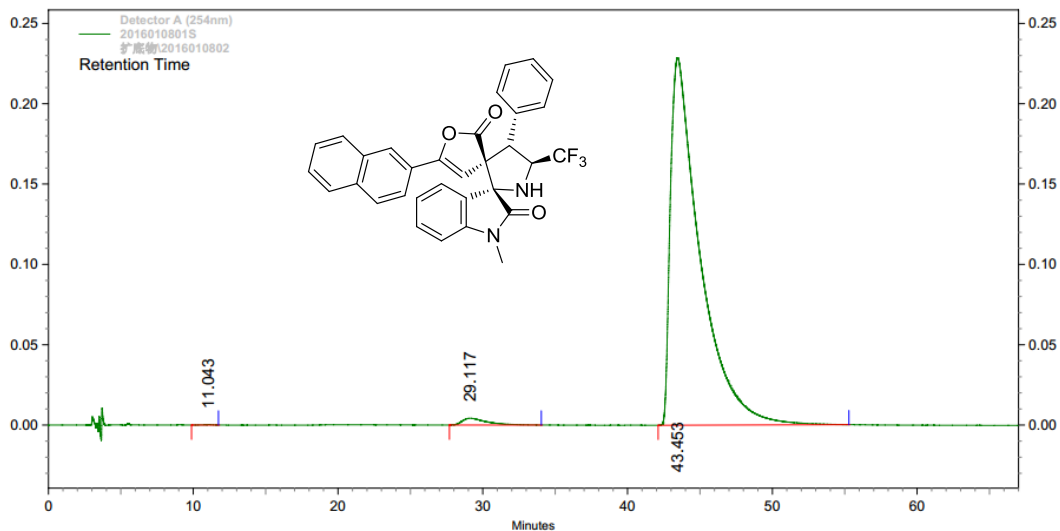


Detector
A

(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.990	5378	4.58	91970	0.70
2	11.497	5247	4.47	101038	0.76
3	27.613	59358	50.59	6483797	49.07
4	45.263	47343	40.35	6536789	49.47

Totals				
		117326	100.00	13213594
				100.00



Detector

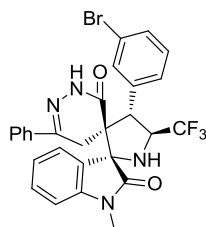
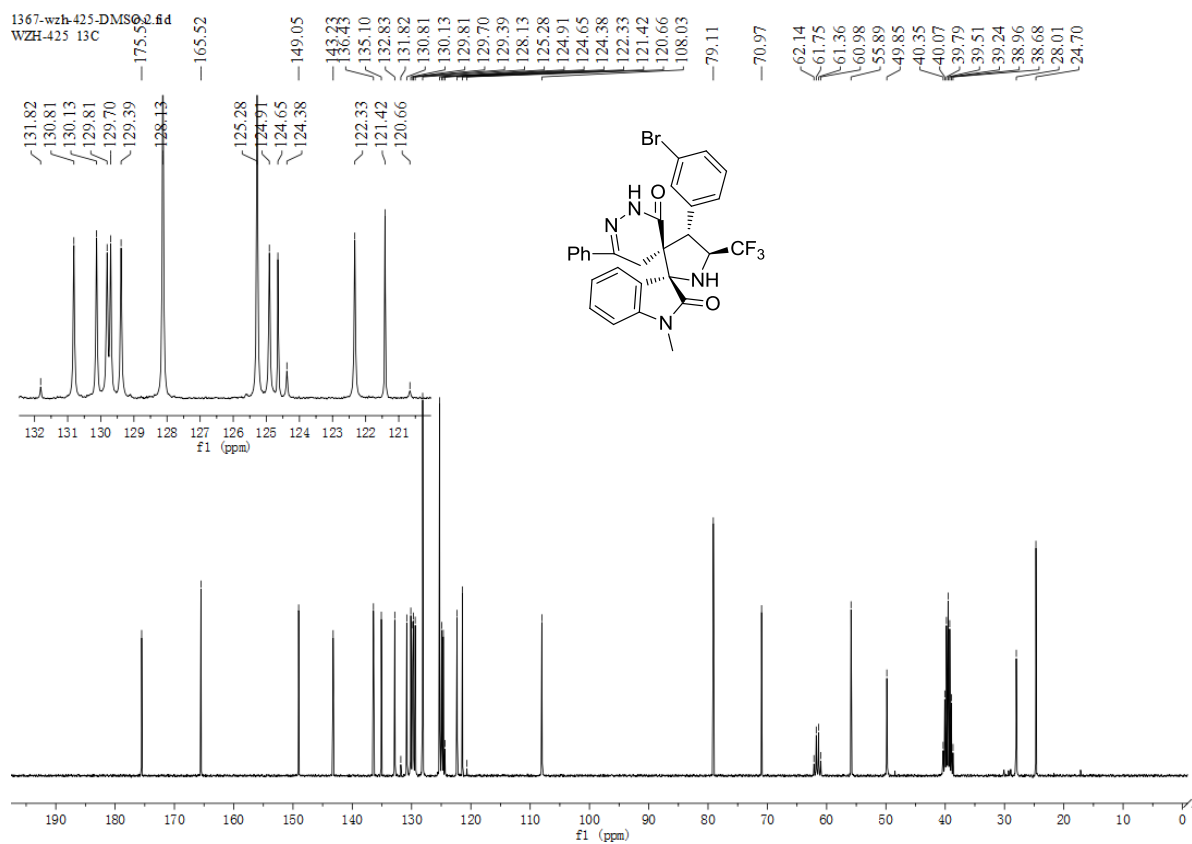
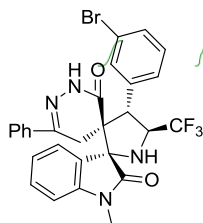
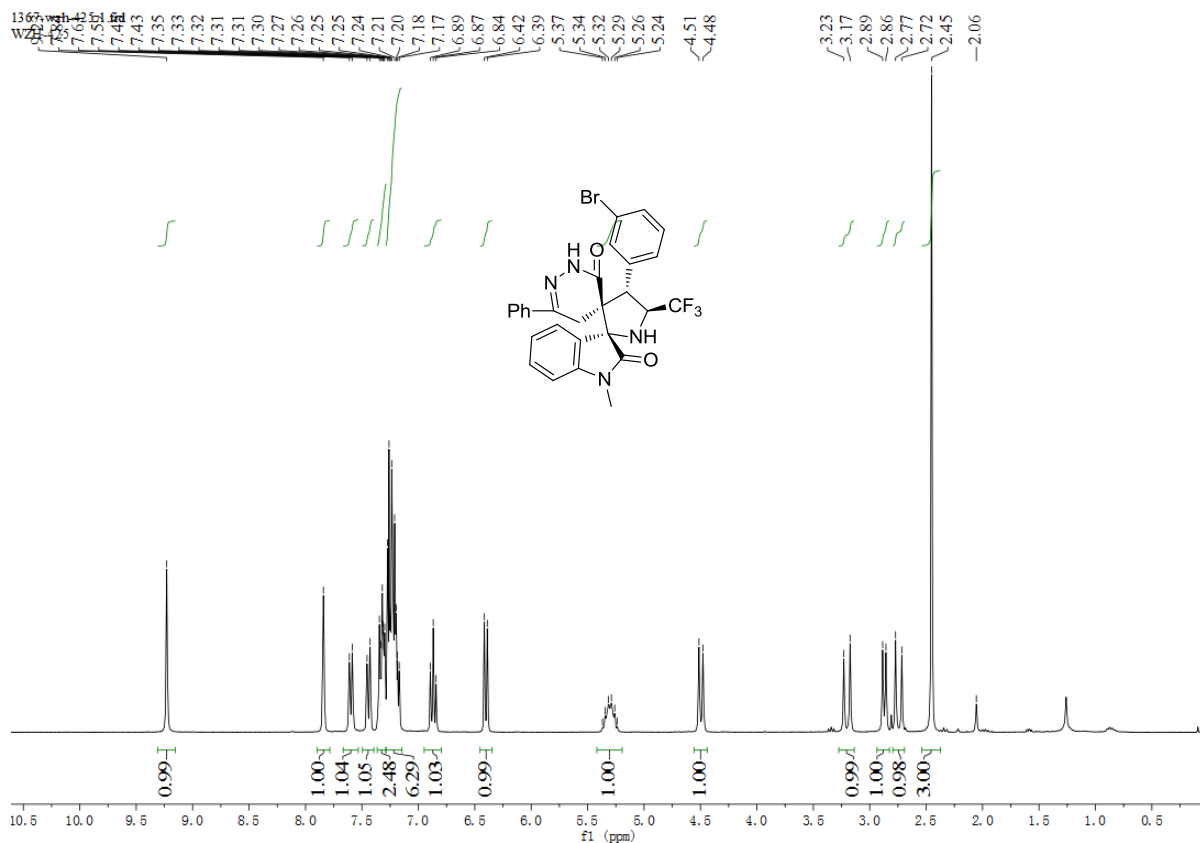
A

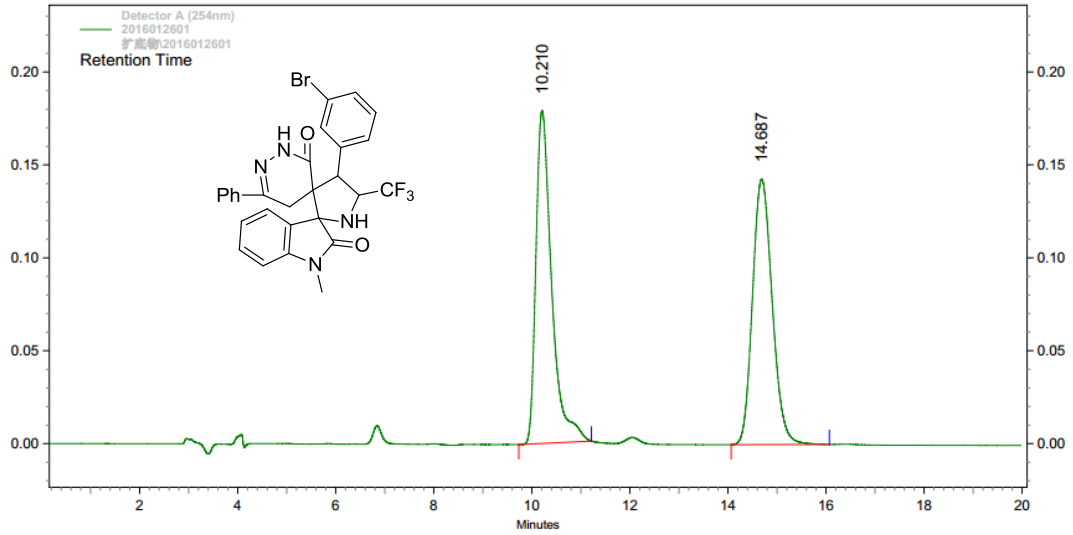
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.043	319	0.14	11376	0.03
2	29.117	4225	1.81	499828	1.52
3	43.453	228747	98.05	32445098	98.45

Totals				
		233291	100.00	32956302
				100.00

¹H NMR, ¹³C NMR and HPLC of 6

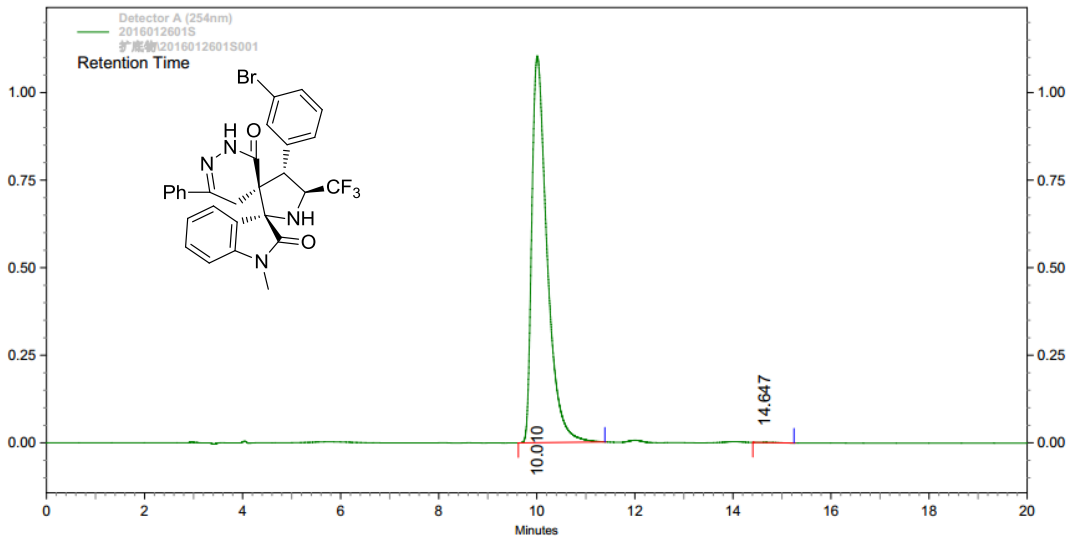




Detector
A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.210	179240	55.65	3994980	50.06
2	14.687	142824	44.35	3985438	49.94

Totals		322064	100.00	7980418	100.00
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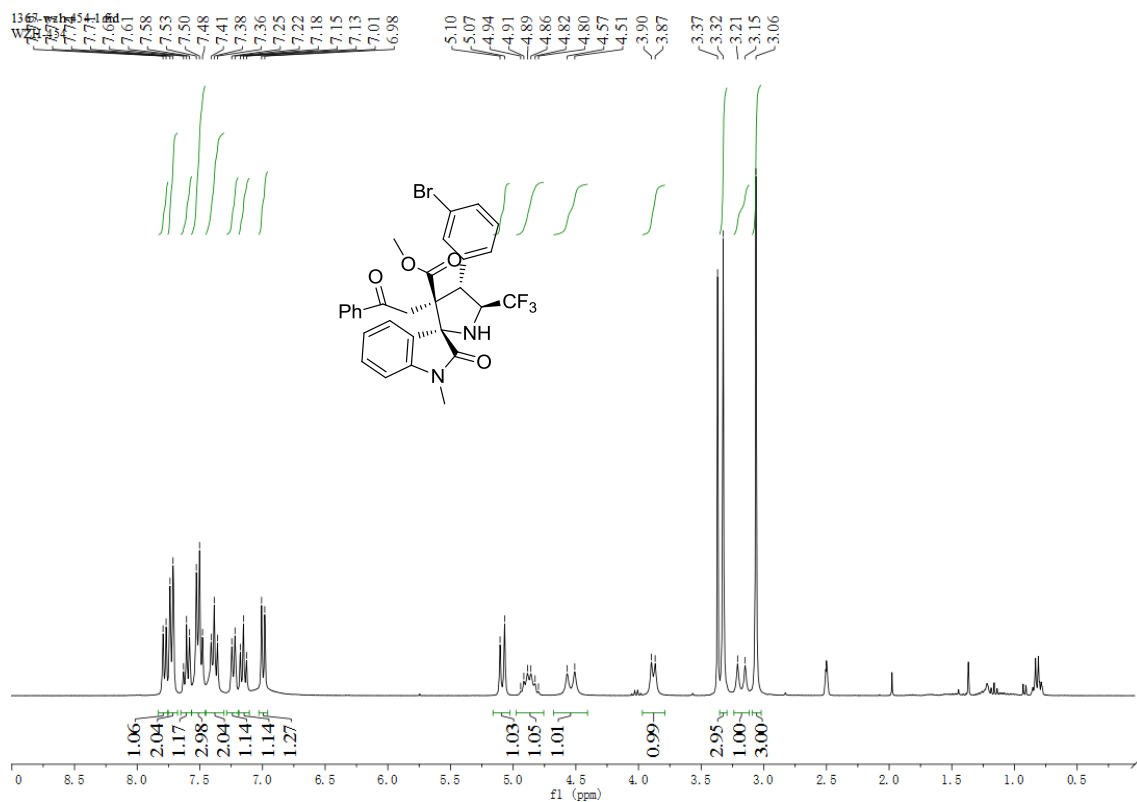


Detector
A
(254nm)

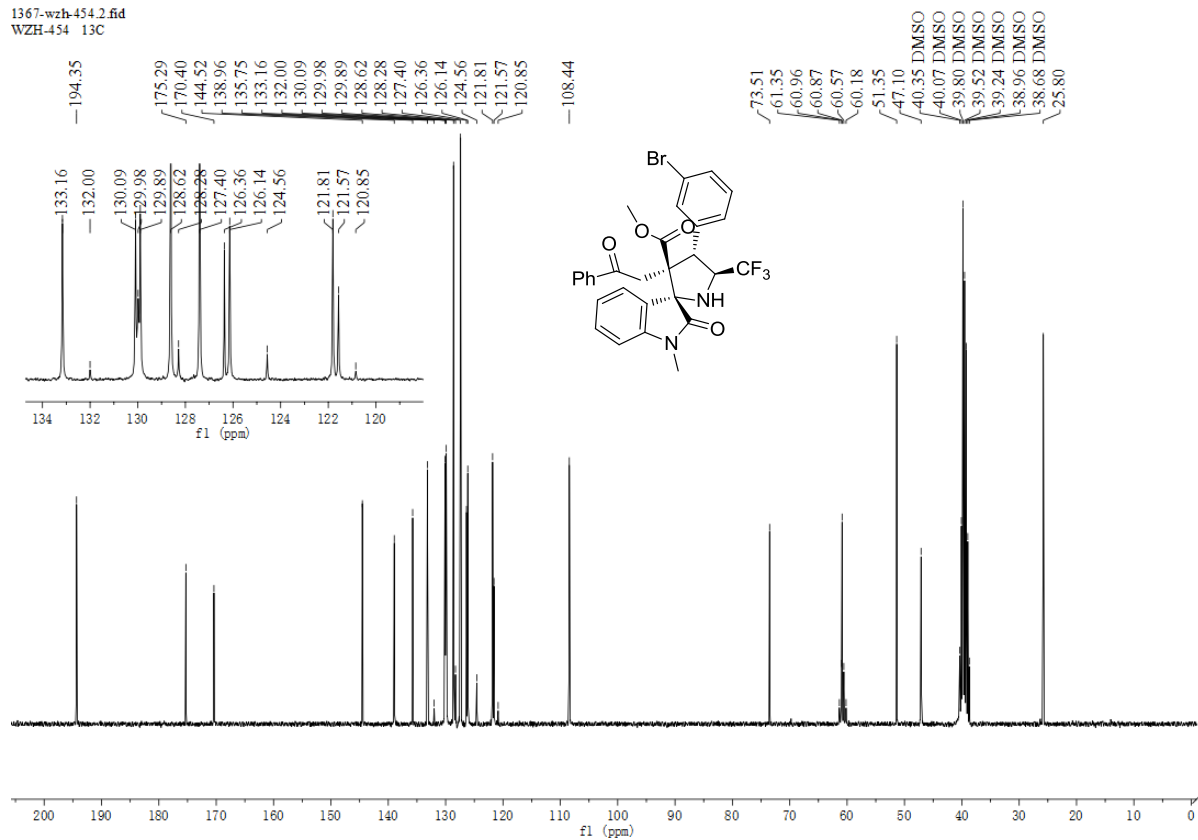
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.010	1103906	99.92	23906747	99.93
2	14.647	843	0.08	15976	0.07

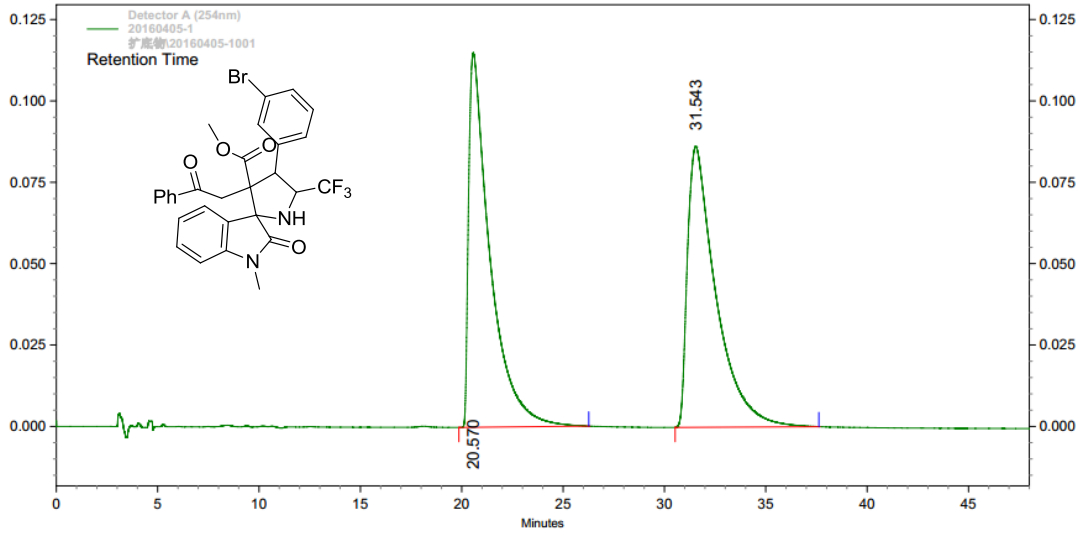
Totals		1104749	100.00	23922723	100.00
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¹H NMR, ¹³C NMR and HPLC of 4



1367-wzh-454.2.fid
 WZH-454 13C

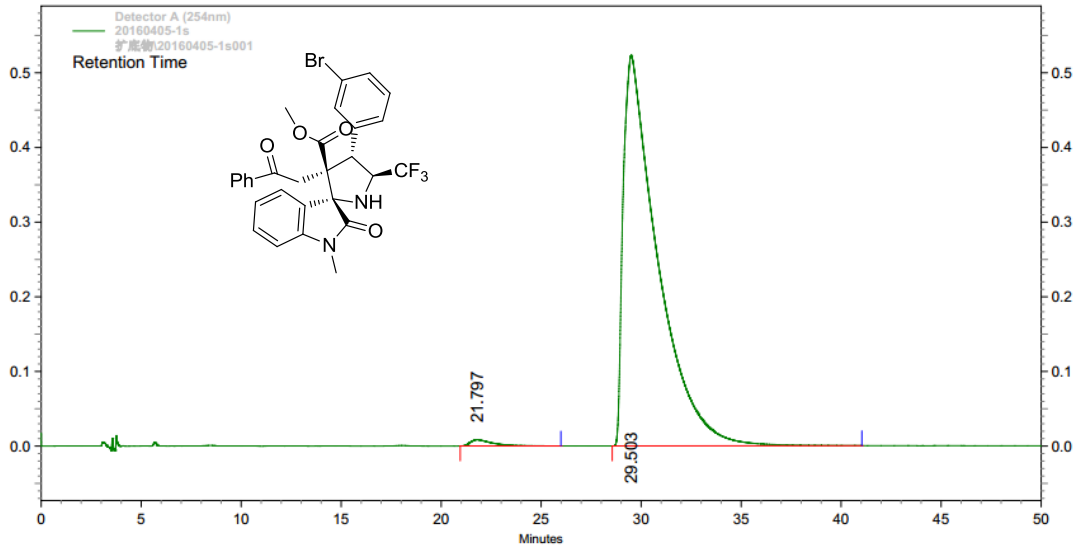




Detector A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	20.570	115048	57.14	8404657	50.01
2	31.543	86289	42.86	8402144	49.99

Totals		201337	100.00	16806801	100.00
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Detector A
(254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	21.797	8223	1.55	659597	1.04
2	29.503	523060	98.45	62507373	98.96

Totals		531283	100.00	63166970	100.00
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