Asymmetric iminium ion catalysis-enabled cascade cycloaddition reaction of chromone-oxindole synthon with enal: construction of spirooxindole-hexahydroxanthone framework

Wen-Hui Zhang,[a] Yan-you Zhou,[a] Xue-Wen He,[a] Yi Gong,[a] Xiong-Li Liu,*[a] and Ying Zhou[b]

[a] Guizhou Engineering Center for Innovative Traditional Chinese Medicine and Ethnic Medicine, Guizhou University, Guiyang, 550025

[b] College of Pharmaceutical Sciences, Guizhou University of Traditional Chinese Medicine, Guiyang, 550025

E-mail: xlliu1@gzu.edu.cn (X.-L. Liu)

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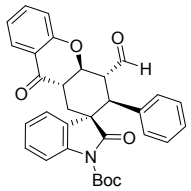
1. General experimental information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. The ee values were determined by chiral HPLC analysis. The d.r. values were determined by ^{1}H-NMR analysis. ^{1}H and ^{13}CNMR spectra were obtained using a Bruker DPX-500 spectrometer. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Optical rotations were measured with a polarimer with the solvent indicated. Melting points were measured on an electrothermal digital melting point apparatus.

2. Typical experimental procedures for catalytic asymmetric synthesis of compounds 3：

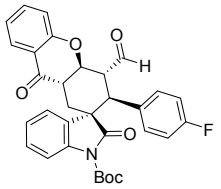
In a tube equipped with a magnetic stirring bar, to the mixture of chromone-oxindole synthon **1** (0.10 mmol) and diarylprolinol trimethylsilyl ether **C3** (20 mol%) in 1.0 mL of toluene was added enal **2** (0.15 mmol). The reaction mixture was stirred at room temperature for 2d, and then added DABCO·6H_2O (20 mol%), was stirred at room temperature for 5d, and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **3**, using hexane/EtOAc (10/1, v/v) as the eluent.

3. Characterization data and HPLC conditions of compounds 3:

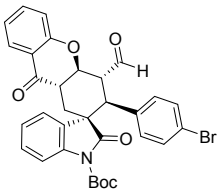


3a: White solid, m.p. 136.4-138.2 ^{o}C; Yield 57%; 95% ee, >20:1 dr, $[\alpha]_D^{20}$ = +60.10 (*c* 0.8, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.04 min; τ_{minor} = 34.08 min); ^{1}H NMR

($CDCl_3$, 500 MHz) δ: 1.56 (s, 9H), 1.96-2.03 (m, 1H), 2.59-2.64 (m, 1H), 3.23 (d, J = 14.5 Hz, 1H), 4.00-4.08 (m, 1H), 4.64-4.75 (m, 2H), 6.91-6.93 (m, 2H), 6.96-7.07 (m, 5H), 7.16-7.18 (m, 2H), 7.27-7.30 (m, 1H), 7.43-7.51 (m, 2H), 7.86-7.89 (m, 1H), 9.72 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 28.1, 31.5, 42.8, 50.8, 51.4, 52.6, 79.8, 84.5, 114.9, 118.0, 120.8, 121.9, 122.4, 124.6, 127.1, 128.1, 128.2, 128.8, 129.7, 134.3, 136.2, 138.9, 148.5, 160.8, 176.7, 192.8, 202.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{29}NNaO_6$ $[M+Na]^+$: 546.1887; Found: 546.1893.

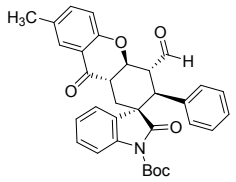


3b: White solid, m.p. 108.2-109.9 °C; Yield 54%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +60.42 (*c* 2.1, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.59 min; τ_{minor} = 23.92 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.57 (s, 9H), 1.95-2.02 (m, 1H), 2.59-2.64 (m, 1H), 3.25 (d, J = 15.0 Hz, 1H), 3.98-4.05 (m, 1H), 4.58-4.73 (m, 2H), 6.69-6.73 (m, 2H), 6.88-6.90 (m, 2H), 6.96-6.98 (m, 1H), 7.03-7.07 (m, 1H), 7.17-7.20 (m, 2H), 7.27-7.29 (m, 1H), 7.46-7.51 (m, 2H), 7.86-7.88 (m, 1H), 9.74 (d, J = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 28.0, 31.3, 42.7, 49.6, 51.3, 52.6, 79.7, 84.6, 115.0, 115.1 (d, J_{CF} = 21.2 Hz), 117.8, 120.6, 122.1 (d, J_{CF} = 29.0 Hz), 124.6, 127.0, 128.9, 129.4, 130.2, 136.1, 138.8, 148.3, 160.6, 161.6 (d, J_{CF} = 246.0 Hz), 176.5, 192.5, 201.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}FNNaO_6$ $[M+Na]^+$: 564.1793; Found: 564.1798.

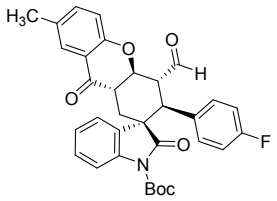


3c: White solid, m.p. 119.8-120.9 °C; Yield 55%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +40.84 (*c* 1.8, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 11.40 min; τ_{minor} = 24.21 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.58 (s, 9H), 1.94-2.01 (m, 1H), 2.59-2.64 (m, 1H), 3.24 (d, J = 15.0 Hz, 1H), 3.97-4.04 (m, 1 H), 4.59-4.71 (m, 2H), 6.80 (d, J = 9.5 Hz, 2H), 6.97 (d, J = 10.0 Hz, 1H),

7.03-7.07 (m, 1H), 7.14-7.21 (m, 4H), 7.27-7.29 (m, 1H), 7.46-7.50 (m, 2H), 7.86-7.88 (m, 1H), 9.76 (d, J = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 28.0, 31.5, 42.7, 49.7, 51.2, 52.4, 79.8, 84.7, 115.0, 117.8, 120.6, 121.9, 122.1, 122.2, 124.6, 127.0, 128.9, 129.3, 130.1, 131.3, 133.6, 136.2, 138.8, 148.2, 160.5, 176.5, 192.4, 201.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}BrNNaO_6$ $[M+Na]^+$: 624.0992; Found: 624.0993.

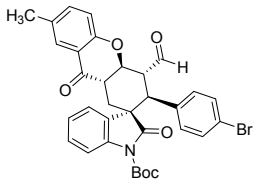


3d: White solid, m.p. 102.5-104.1 °C; Yield 57%; 93% ee, >20:1 dr, $[\alpha]_D^{20}$ = +140.40 (*c* 2.2, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 7.42 min; τ_{minor} = 12.21 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.51 (s, 9H), 1.89-1.95 (m, 1H), 2.25 (s, 3H), 2.53-2.56 (m, 1H), 3.17 (d, J = 11.5 Hz, 1H), 3.94-3.95 (m, 1H), 4.60-4.62 (m, 2H), 6.80-6.85 (m, 3H), 6.95-6.99 (m, 3H), 7.10-7.12 (m, 2H), 7.19-7.25 (m, 2H), 7.37-7.39 (m, 1H), 7.60 (s, 1H), 9.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.5, 28.1, 31.5, 42.8, 50.6, 51.4, 52.6, 79.8, 84.4, 114.8, 117.6, 120.3, 122.3, 124.5, 126.6, 127.9, 128.1, 128.7, 129.7, 131.3, 134.3, 137.2, 138.8, 148.5, 158.8, 176.7, 192.9, 202.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{33}H_{31}NNaO_6$ $[M+Na]^+$: 560.2044; Found: 560.2047.

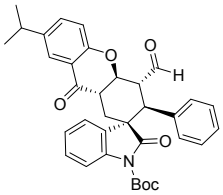


3e: White solid, m.p. 114.1-115.9 °C; Yield 57%; 96% ee, >20:1 dr, $[\alpha]_D^{20}$ = +60.02 (*c* 1.2, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 16.78 min; τ_{minor} = 21.36 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.51 (s, 9H), 1.87-1.94 (m, 1H), 2.25 (s, 3H), 2.53-2.57 (m, 1H), 3.19 (d, J = 15.0 Hz, 1H), 3.89-3.96 (m, 1H), 4.51-4.62 (m, 2H), 6.62-6.67 (m, 2H), 6.79-6.83 (m, 3H), 7.11-7.14 (m, 2H), 7.21-7.25 (m, 2H), 7.39-7.42 (m, 1H), 7.59 (s, 1H), 9.68 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.4, 28.0, 31.4, 42.7, 49.5, 51.4, 52.7, 79.8, 84.6, 114.9 (d, J_{CF} = 21.4 Hz), 115.2, 117.6, 120.2, 122.2, 124.6, 126.6, 128.8, 129.5, 130.2, 130.3, 131.4, 137.2, 138.8,

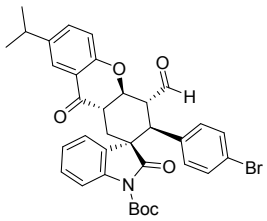
148.3, 158.7, 161.6 (d, J_{CF} = 246.2 Hz), 176.5, 192.7, 202.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{33}H_{30}FNNaO_6$ $[M+Na]^+$: 578.1949; Found: 578.1951.



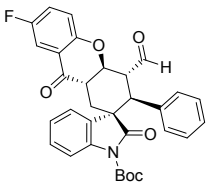
3f: White solid, m.p. 110.2-112.1 °C; Yield 56%; 91% ee, 10:1 dr, $[\alpha]_D^{20}$ = +170.33 (*c* 2.2, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 18.90 min; τ_{minor} = 24.60 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.52 (s, 9H), 1.87-1.92 (m, 1H), 2.53-2.56 (m, 1H), 3.18 (d, *J* = 11.5 Hz, 1H), 3.90-3.92 (m, 1H), 4.56-4.58 (m, 2H), 6.72-6.74 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 7.07-7.13 (m, 4H), 7.19-7.25 (m, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.59 (s, 1H), 9.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 20.5, 28.1, 31.6, 42.8, 49.6, 51.2, 52.5, 79.9, 84.7, 115.0, 117.6, 120.3, 122.1, 122.2, 124.7, 126.6, 129.0, 129.4, 130.2, 131.3, 131.5, 133.7, 137.3, 138.8, 148.3, 158.7, 176.5, 192.7, 202.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{33}H_{30}BrNNaO_6$ $[M+Na]^+$: 638.1149; Found: 638.1155.



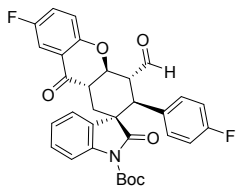
3g: White solid, m.p. 128.4-129.7 °C; Yield 42%; 93% ee, >20:1 dr, $[\alpha]_D^{20}$ = +27.98 (*c* 0.34, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 16.22 min; τ_{minor} = 36.25 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.23 (s, 3H), 1.25 (s, 3H), 1.57 (s, 9H), 1.95-2.02 (m, 1H), 2.61-2.66 (m, 1H), 2.86-2.93 (m, 1H), 3.24 (d, J = 14.5 Hz, 1H), 3.99-4.06 (m, 1H), 4.66-4.73 (m, 2H), 6.90-6.96 (m, 3H), 7.00-7.08 (m, 3H), 7.17-7.19 (m, 2H), 7.29-7.31 (m, 1H), 7.37-7.40 (m, 1H), 7.44-7.46 (m, 1H), 7.73 (s, 1H), 9.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 24.0, 28.2, 31.6, 33.4, 42.9, 50.7, 51.4, 52.6, 79.9, 84.5, 114.9, 117.8, 120.4, 122.4, 124.1, 124.6, 128.0, 128.2, 128.8, 129.7, 134.4, 135.0, 138.9, 142.5, 148.6, 159.1, 176.8, 193.1, 202.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{35}H_{35}NNaO_6$ $[M+Na]^+$: 588.2357; Found: 588.2362.



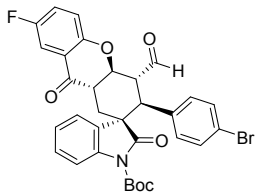
3h: White solid, m.p. 129.7-131.6 °C; Yield 40%; 93% ee, >20:1 dr, $[\alpha]_D^{20}$ = +40.80 (*c* 0.60, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (98/2 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 45.00 min; τ_{minor} = 109.77 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.22 (s, 3H), 1.24 (s, 3H), 1.58 (s, 9H), 1.93-2.00 (m, 1H), 2.60-2.65 (m, 1H), 2.86-2.93 (m, 1H), 3.25 (d, *J* = 14.5 Hz, 1H), 3.96-4.02 (m, 1H), 4.58-4.68 (m, 2H), 6.80 (d, *J* = 9.5 Hz, 2H), 6.91 (d, *J* = 10.5 Hz, 1H), 7.14-7.21 (m, 4H), 7.28-7.30 (m, 1H), 7.37-7.40 (m, 1H), 7.46-7.49 (m, 1H), 7.72 (d, *J* = 3.0 Hz, 1H), 9.76 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 24.0, 28.1, 31.6, 33.4, 42.8, 49.7, 51.3, 52.6, 80.0, 84.8, 115.1, 117.8, 120.4, 122.1, 122.3, 124.1, 124.8, 129.0, 129.4, 130.3, 131.4, 133.8, 135.0, 138.9, 142.6, 148.4, 159.0, 176.6, 192.9, 202.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{35}H_{34}BrNNaO_6$ $[M+Na]^+$: 666.1462; Found: 666.1467.



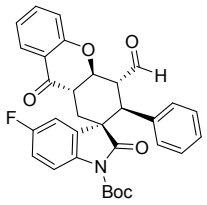
3i: White solid, m.p. 101.9-103.3 °C; Yield 52%; 96% ee, >20:1 dr, $[\alpha]_D^{20}$ = +80.42 (*c* 1.5, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.60 min; τ_{minor} = 20.28 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.50 (s, 9H), 1.89-1.96 (m, 1H), 2.53-2.57 (m, 1H), 3.15 (d, *J* = 15.0 Hz, 1H), 3.93-4.00 (m, 1H), 4.56-4.68 (m, 2H), 6.85-6.91 (m, 3H), 6.93-7.02 (m, 3H), 7.10-7.16 (m, 3H), 7.20-7.23 (m, 1H), 7.37-7.39 (m, 1H), 7.44-7.47 (m, 1H), 9.64 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.0, 31.3, 42.7, 50.7, 51.2, 52.4, 79.8, 84.4, 112.0 (d, J_{CF} = 23.1 Hz), 114.8, 119.5, 119.6, 121.1, 122.2, 123.6 (d, J_{CF} = 24.2 Hz), 124.5, 128.0, 128.2, 128.8, 129.4, 134.0, 138.8, 148.4, 156.2, 157.5 (d, J_{CF} = 213.8 Hz), 176.6, 201.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}FNNaO_6$ $[M+Na]^+$: 564.1793; Found: 564.1798.



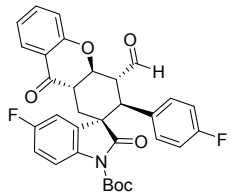
3j: White solid, m.p. 122.1-123.2 °C; Yield 56%; 95% ee, >20:1 dr, $[\alpha]_D^{20}$ = +50.35 (*c* 1.6, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 14.80 min; τ_{minor} = 18.01 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.51 (s, 9H), 1.87-1.94 (m, 1H), 2.53-2.58 (m, 1H), 3.16 (d, *J* = 15.0 Hz, 1H), 3.91-3.98 (m, 1H), 4.52-4.65 (m, 2H), 6.63-6.67 (m, 2H), 6.83-6.85 (m, 2H), 6.88-6.91 (m, 1H), 7.12-7.16 (m, 3H), 7.19-7.22 (m, 2H), 7.40-7.42 (m, 1H), 7.44-7.47 (m, 1H), 9.66 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.0, 31.2, 42.6, 49.7, 51.3, 52.5, 79.9, 84.7, 112.0 (d, J_{CF} = 24.0 Hz), 115.0 (d, J_{CF} = 20.4 Hz), 115.2 (d, J_{CF} = 22.7 Hz), 119.5, 119.6, 122.2, 123.6 (d, J_{CF} = 25.0 Hz), 124.6, 128.9, 129.2, 138.8, 148.3, 156.2, 157.4 (d, J_{CF} = 241.0 Hz), 162.2 (d, J_{CF} = 246.2 Hz), 176.5, 191.8, 201.7; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -113.57, -120.58; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}F_2NNaO_6$ $[M+Na]^+$: 582.1699; Found: 582.1704.



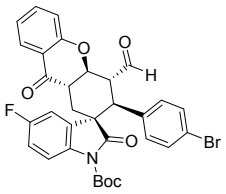
3k: White solid, m.p. 92.3-93.4 °C; Yield 62%; 96% ee, >20:1 dr, $[\alpha]_D^{20}$ = +30.62 (*c* 2.8, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.72 min; τ_{minor} = 20.37 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.63 (s, 9H), 1.99-2.04 (m, 1H), 2.64-2.68 (m, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 4.01-4.07 (m, 1H), 4.64-4.75 (m, 2H), 6.85-6.86 (m, 2H), 6.99-7.02 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.23-7.29 (m, 3H), 7.31-7.33 (m, 1H), 7.52-7.57 (m, 2H), 9.78 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.0, 31.4, 42.6, 49.7, 51.1, 52.3, 80.0, 84.8, 112.0, 112.2, 115.1, 119.5, 119.6, 121.1, 122.1 (d, J_{CF} = 23.8 Hz), 123.7 (d, J_{CF} = 25.1 Hz), 124.7, 129.0, 129.1, 131.3, 133.4, 138.8, 148.2, 156.8, 157.5 (d, J_{CF} = 241.3 Hz), 176.5, 191.7, 201.7; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -120.51; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}BrFNNaO_6$ $[M+Na]^+$: 642.0898; Found: 642.0893.



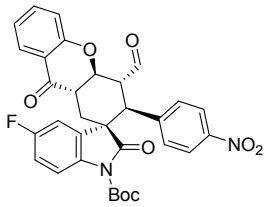
3l: White solid, m.p. 133.5-135.1 °C; Yield 60%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +50.05 (*c* 1.4, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 16.27 min; τ_{minor} = 32.42 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.50 (s, 9H), 1.85-1.90 (m, 1H), 2.54-2.58 (m, 1H), 3.12 (d, *J* = 11.5 Hz, 1H), 3.92-3.98 (m, 1H), 4.55-4.66 (m, 2H), 6.79-6.82 (m, 1H), 6.87-6.89 (m, 3H), 6.95-7.02 (m, 4H), 7.14-7.17 (m, 1H), 7.37-7.40 (m, 1H), 7.44-7.46 (m, 1H), 9.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.1, 31.4, 42.7, 50.7, 51.7, 52.5, 79.7, 84.7, 110.0 (d, J_{CF} = 24.2 Hz), 115.4 (d, J_{CF} = 22.4 Hz), 116.4, 118.0, 120.7, 122.0, 127.1, 128.3, 128.4, 131.6, 134.1, 134.7, 136.3, 148.5, 159.5 (d, J_{CF} = 246.1 Hz), 160.7, 161.1, 176.2, 192.6, 201.9; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -116.94; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}FNNaO_6$ $[M+Na]^+$: 564.1793; Found: 564.1797.



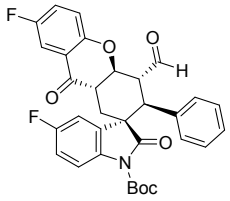
3m: White solid, m.p. 114.8-116.2 °C; Yield 59%; 95% ee, >20:1 dr, $[\alpha]_D^{20}$ = +50.71 (*c* 0.80, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.93 min; τ_{minor} = 29.65 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.58 (s, 9H), 1.90-1.97 (m, 1H), 2.61-2.66 (m, 1H), 3.22 (d, *J* = 15.0 Hz, 1H), 3.97-4.05 (m, 1H), 4.60-4.71 (m, 2H), 6.73-6.78 (m, 2H), 6.88-7.09 (m, 6H), 7.47-7.53 (m, 2H), 7.87-7.89 (m, 1H), 9.75 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.0, 31.3, 42.6, 49.6, 51.6, 52.6, 79.7, 84.8, 109.8 (d, J_{CF} = 25.4 Hz), 115.3 (d, J_{CF} = 22.3 Hz), 115.5 (d, J_{CF} = 23.1 Hz), 116.4 (d, J_{CF} = 8.1 Hz), 116.5, 117.8, 120.6, 122.0, 127.1, 130.0, 134.7, 136.2, 148.2, 158.5, 159.8 (d, J_{CF} = 214.3 Hz), 160.5, 161.3, 161.7 (d, J_{CF} = 245.0 Hz), 176.1, 192.3, 201.7; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -113.31, -116.64; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}F_2NNaO_6$ $[M+Na]^+$: 582.1699; Found: 582.17004.



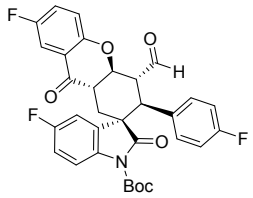
3n: White solid, m.p. 105.1-106.8 °C; Yield 56%; >99% ee, 9:1 dr, $[\alpha]_D^{20}$ = +210.10 (*c* 2.30, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 18.00 min; τ_{minor} = 24.41 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.61 (s, 9H), 1.94-1.98 (m, 1H), 2.64-2.67 (m, 1H), 3.24 (d, *J* = 10.0 Hz, 1H), 4.00-4.05 (m, 1H), 4.62-4.72 (m, 2H), 6.86-6.87 (m, 2H), 6.92-6.96 (m, 1H), 7.00 (d, *J* = 7.0 Hz, 1H), 7.04-7.06 (m, 1H), 7.08-7.10 (m, 1H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.51-7.55 (m, 2H), 7.89-7.91 (m, 1H), 9.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.1, 31.5, 42.6, 49.6, 51.5, 52.4, 79.7, 85.0, 109.8 (d, J_{CF} = 20.0 Hz), 115.6 (d, J_{CF} = 20.5 Hz), 116.6, 117.9, 120.6, 122.0, 122.3, 127.1, 131.5, 132.4, 133.4, 134.7, 136.3, 148.2, 160.0 (d, J_{CF} = 202.5 Hz), 160.5, 176.0, 192.2, 201.6; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -116.55; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}BrFNNaO_6$ $[M+Na]^+$: 642.0898; Found: 642.0895.



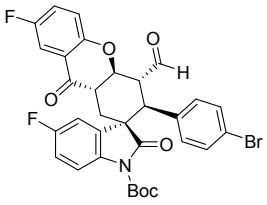
3o: White solid, m.p. 101.2-102.7 °C; Yield 40%; 93% ee, 18:1 dr, $[\alpha]_D^{20}$ = +18.31 (*c* 1.00, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 22.36 min; τ_{minor} = 42.42 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.50 (s, 9H), 1.87-1.94 (m, 1H), 2.57-2.62 (m, 1H), 3.35 (d, *J* = 11.6 Hz, 1H), 3.93-4.00 (m, 1H), 4.55-4.64 (m, 2H), 6.83-6.88 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.00-7.03 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.39-7.48 (m, 2H), 7.80-7.87 (m, 3H), 9.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 27.0, 28.7, 41.6, 48.4, 50.4, 51.3, 79.0, 84.3, 108.8 (d, J_{CF} = 24.1 Hz), 114.9 (d, J_{CF} = 22.4 Hz), 115.6, 115.7, 116.8, 119.6, 121.2, 122.3, 126.1, 128.5, 129.7, 129.8, 133.5, 135.4, 141.3, 146.4, 147.0, 159.0 (d, J_{CF} = 244.3 Hz), 159.4, 174.7, 190.9, 200.3; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -115.97; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}FN_2NaO_8$ $[M+Na]^+$: 609.1644; Found: 609.1649.



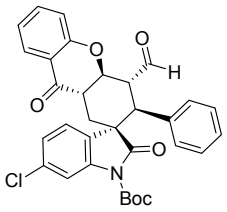
3p: White solid, m.p. 116.6-118.2 °C; Yield 55%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +70.14 (*c* 3.3, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 12.76 min; τ_{minor} = 17.61 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.50 (s, 9H), 1.85-1.90 (m, 1H), 2.54-2.58 (m, 1H), 3.12 (d, J = 11.5 Hz, 1H), 3.92-3.98 (m, 1H), 4.55-4.66 (m, 2H), 6.79-6.82 (m, 1H), 6.87-6.89 (m, 3H), 6.95-7.02 (m, 4H), 7.14-7.17 (m, 1H), 7.37-7.40 (m, 1H), 7.44-7.46 (m, 1H), 9.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.0, 31.2, 42.6, 50.7, 51.5, 52.3, 79.8, 84.7, 109.8 (d, J_{CF} = 25.0 Hz), 112.1 (d, J_{CF} = 23.8 Hz), 115.4 (d, J_{CF} = 22.5 Hz), 116.3, 116.4, 119.5, 119.6, 121.1, 123.7 (d, J_{CF} = 25.1 Hz), 128.2, 128.4, 133.8, 148.3, 156.9, 157.5 (d, J_{CF} = 241.3 Hz), 159.9 (d, J_{CF} = 242.5 Hz), 176.2, 191.8, 201.6; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -116.84, -120.59; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}F_2NNaO_6$ $[M+Na]^+$: 582.1699; Found: 582.17004.



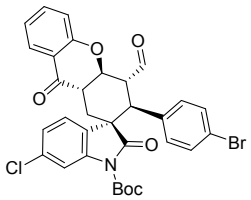
3q: White solid, m.p. 109.3-110.7 °C; Yield 56%; 93% ee, >20:1 dr, $[\alpha]_D^{20}$ = +20.61 (*c* 1.2, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.53 min; τ_{minor} = 17.95 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.51 (s, 9H), 1.82-1.89 (m, 1H), 2.54-2.58 (m, 1H), 3.14 (d, *J* = 15.0 Hz, 1H), 3.89-3.97 (m, 1H), 4.50-4.63 (m, 2H), 6.67-6.71 (m, 2H), 6.81-6.91 (m, 4H), 6.93-6.96 (m, 1H), 7.14-7.18 (m, 1H), 7.40-7.47 (m, 2H), 9.65 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.0, 31.2, 42.5, 49.6, 51.5, 52.4, 79.8, 84.9, 109.7 (d, J_{CF} = 24.2 Hz), 112.1 (d, J_{CF} = 23.4 Hz), 115.3 (d, J_{CF} = 22.5 Hz), 115.6 (d, J_{CF} = 20.1 Hz), 116.4, 116.5, 119.5, 119.6, 121.1, 123.7 (d, J_{CF} = 24.4 Hz), 129.8, 148.2, 157.7 (d, J_{CF} = 245.1 Hz), 159.6 (d, J_{CF} = 225.4 Hz), 162.3 (d, J_{CF} = 228.3 Hz), 176.1, 191.6, 201.5; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -113.16, -116.55, -120.43; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{26}F_3NNaO_6$ $[M+Na]^+$: 600.1604; Found: 600.1598.



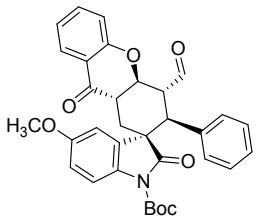
3r: White solid, m.p. 102.8-104.2 °C; Yield 58%; 97% ee, 15:1 dr, $[\alpha]_D^{20}$ = +40.74 (*c* 2.00, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.24 min; τ_{minor} = 19.73 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.52 (s, 9H), 1.83-1.88 (m, 1H), 2.54-2.57 (m, 1H), 3.12 (d, *J* = 11.5 Hz, 1H), 3.89-3.94 (m, 1H), 4.52-4.61 (m, 2H), 6.76-6.78 (m, 2H), 6.84-6.95 (m, 3H), 7.12-7.19 (m, 3H), 7.41-7.46 (m, 2H), 9.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.1, 31.4, 42.6, 49.7, 51.4, 52.3, 79.9, 85.0, 109.8 (d, J_{CF} = 25.1 Hz), 112.2 (d, J_{CF} = 22.5 Hz), 115.7 (d, J_{CF} = 22.5 Hz), 116.6, 116.7, 119.6, 122.4, 123.8 (d, J_{CF} = 25.4 Hz), 131.6, 133.2, 134.7, 148.2, 156.8, 157.5 (d, J_{CF} = 241.3 Hz), 160.0 (d, J_{CF} = 243.8 Hz), 176.0, 191.5, 201.4; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*: -116.46, -120.37; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{26}BrF_2NNaO_6$ $[M+Na]^+$: 660.0804; Found: 660.0810.



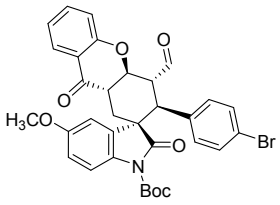
3s: White solid, m.p. 118.7-120.0 °C; Yield 47%; 93% ee, >20:1 dr, $[\alpha]_D^{20}$ = +45.03 (*c* 0.25, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (97/3 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 43.44 min; τ_{minor} = 96.47 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.58 (s, 9H), 1.93-2.00 (m, 1H), 2.58-2.63 (m, 1H), 3.20 (d, *J* = 14.5 Hz, 1H), 3.98-4.05 (m, 1H), 4.65-4.74 (m, 2H), 6.93-6.94 (m, 2H), 6.98 (d, *J* = 10.5 Hz, 1H), 7.04-7.11 (m, 4H), 7.17-7.23 (m, 2H), 7.48-7.54 (m, 2H), 7.87-7.89 (m, 1H), 9.73 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 28.1, 31.5, 42.7, 50.6, 51.3, 52.5, 79.7, 85.1, 115.7, 118.0, 120.7, 122.0, 123.3, 124.7, 127.1, 128.2, 128.3, 128.4, 128.5, 129.1, 134.1, 134.5, 136.3, 139.8, 148.3, 160.7, 176.2, 192.7, 202.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}ClNNaO_6$ $[M+Na]^+$: 580.1497; Found: 580.1501.



3t: White solid, m.p. 132.4-133.6 °C; Yield 56%; 93% ee, >20:1 dr, $[\alpha]_D^{20}$ = +54.57 (*c* 0.73, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 31.69 min; τ_{minor} = 73.49 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.51 (s, 9H), 1.84-1.91 (m, 1H), 2.50-2.55 (m, 1H), 3.16 (d, J = 14.5 Hz, 1H), 3.87-3.94 (m, 1H), 4.50-4.62 (m, 2H), 6.74 (d, J = 10.0 Hz, 1H), 6.89 (d, J = 10.5 Hz, 1H), 6.96-7.00 (m, 1H), 7.09-7.15 (m, 4H), 7.40-7.45 (m, 1H), 7.50 (s, 1H), 7.78-7.80 (m, 1H), 9.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 27.0, 30.5, 41.6, 48.5, 50.0, 51.4, 78.7, 84.2, 114.8, 116.8, 119.6, 121.0, 121.3, 122.1, 123.7, 126.0, 126.8, 129.1, 130.5, 132.4, 133.6, 135.2, 138.6, 147.0, 159.5, 174.9, 191.2, 200.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{27}BrClNNaO_6$ $[M+Na]^+$: 658.0602; Found: 658.0607.

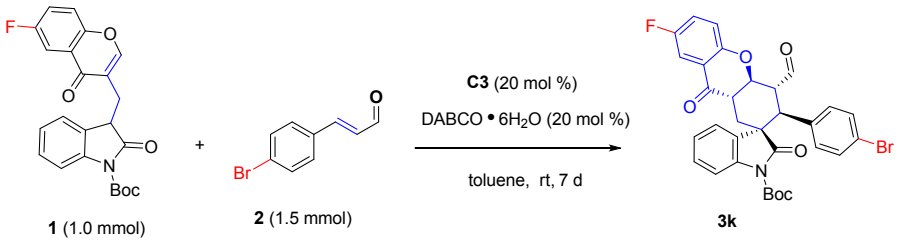


3u: White solid, m.p. 98.5-99.7 °C; Yield 34%; 94% ee, >20:1 dr, $[\alpha]_D^{20}$ = +20.47 (*c* 0.57, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 57.04 min; τ_{minor} = 74.99 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.50 (s, 9H), 1.87-1.93 (m, 1H), 2.53-2.58 (m, 1H), 3.15 (d, *J* = 14.5 Hz, 1H), 3.76 (s, 3H), 3.94-4.01 (m, 1H), 4.60-4.69 (m, 2H), 6.61-6.64 (m, 1H), 6.77 (d, *J* = 3.0 Hz, 1H), 6.88-6.92 (m, 3H), 6.95-7.01 (m, 4H), 7.31 (d, *J* = 11.0 Hz, 1H), 7.41-7.45 (m, 1H), 7.80-7.82 (m, 1H), 9.67 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 27.1, 28.7, 41.7, 49.6, 50.6, 51.5, 54.7, 78.7, 83.2, 107.4, 112.5, 114.8, 116.8, 119.7, 120.8, 126.0, 127.0, 127.2, 127.5, 129.9, 131.2, 133.2, 135.1, 147.5, 156.0, 159.7, 175.6, 191.7, 201.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{33}H_{31}NNaO_7$ $[M+Na]^+$: 576.1993; Found: 576.1989.



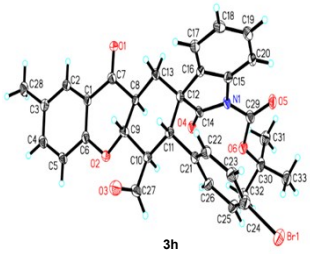
3v: White solid, m.p. 93.7-94.9 °C; Yield 41%; 97% ee, >20:1 dr, $[\alpha]_D^{20}$ = +10.67 (*c* 0.77, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 62.24 min; τ_{minor} = 76.19 min); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.51 (s, 9H), 1.84-1.91 (m, 1H), 2.52-2.57 (m, 1H), 3.15 (d, *J* = 15.0 Hz, 1H), 3.75 (s, 3H), 3.90-3.97 (m, 1H), 4.53-4.64 (m, 2H), 6.64-6.67 (m, 1H), 6.75-6.78 (m, 3H), 6.91 (d, *J* = 10.0 Hz, 1H), 6.95-7.01 (m, 1H), 7.11 (d, *J* = 11.0 Hz, 2H), 7.33 (d, *J* = 11.0 Hz, 1H), 7.41-7.45 (m, 1H), 7.80-7.82 (m, 1H), 9.69 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 27.0, 30.5, 41.7, 48.7, 50.4, 51.5, 54.7, 78.8, 83.5, 107.5, 112.6, 115.1, 116.8, 119.7, 120.9, 121.1, 126.0, 129.1, 129.6, 130.3, 131.1, 132.6, 135.2, 147.3, 156.0, 159.6, 175.5, 191.4, 200.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{33}H_{30}BrNNaO_7$ $[M+Na]^+$: 654.1098; Found: 654.11002.

4. Large-scale synthesis of product 3k



In a tube equipped with a magnetic stirring bar, to the mixture of chromone-oxindole synthon **1** (1.0 mmol) and diarylprolinol trimethylsilyl ether **C3** (20 mol%) in 10 mL of toluene was added enal **2** (1.5 mmol). The reaction mixture was stirred at room temperature for 2 d, and then added DABCO·$6H_2O$ (20 mol%), was stirred at room temperature for 5 d, and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **3k**, using hexane/EtOAc (10/1, v/v) as the eluent (0.29 g, 47%, 95% ee, >20:1 dr).

5. X-Ray Crystal Data for Compound 3h



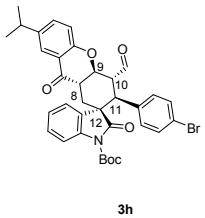
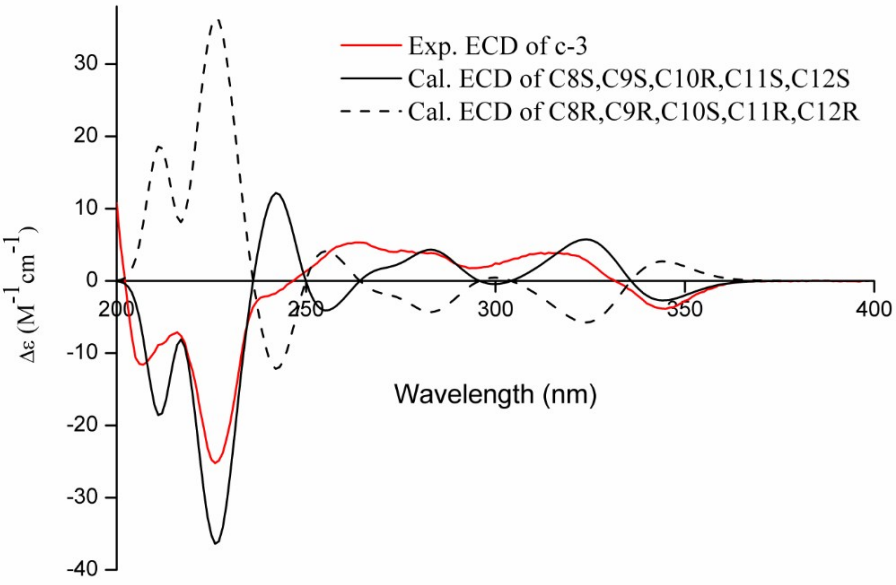


Table S1 Crystal data and structure refinement for 3h

Identification code	**3h**
Empirical formula	$C_{33}H_{30}BrNO_6$
Formula weight	616.49
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å, b/Å, c/Å	8.1114(12), 35.404(3), 9.9824(15)
α/°, β/°, γ/°,	90, 104.195(16), 90.
Volume/Å^3	2779.1(7)
Z	4
ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	2.416
F(000)	1272.0
Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.992 to 147.55
Index ranges	-9 ≤ h ≤ 5, -43 ≤ k ≤ 40, -11 ≤ l ≤ 12
Reflections collected	10494
Independent reflections	5417 [R_{int} = 0.0895, R_{sigma} = 0.1324]
Data/restraints/parameters	5417/0/374
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0809, wR_2 = 0.1684
Final R indexes [all data]	R_1 = 0.1422, wR_2 = 0.2052
Largest diff. peak/hole / e Å^{-3}	0.63/-1.05

Crystal Data for $C_{33}H_{30}BrNO_6$ (*M* =616.49 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 8.1114(12) Å, *b* = 35.404(3) Å, *c* = 9.9824(15) Å, *β* = 104.195(16)°, *V* = 2779.1(7) Å^3, *Z* = 4, *T* = 100.00(10) K, μ(CuKα) = 2.416 mm^{-1}, *Dcalc* = 1.473 g/cm^3, 10494 reflections measured (4.992° ≤ 2Θ ≤ 147.55°), 5417 unique (R_{int} = 0.0895, R_{sigma} = 0.1324) which were used in all calculations. The final R_1 was 0.0809 (I > 2σ(I)) and wR_2 was 0.2052 (all data).

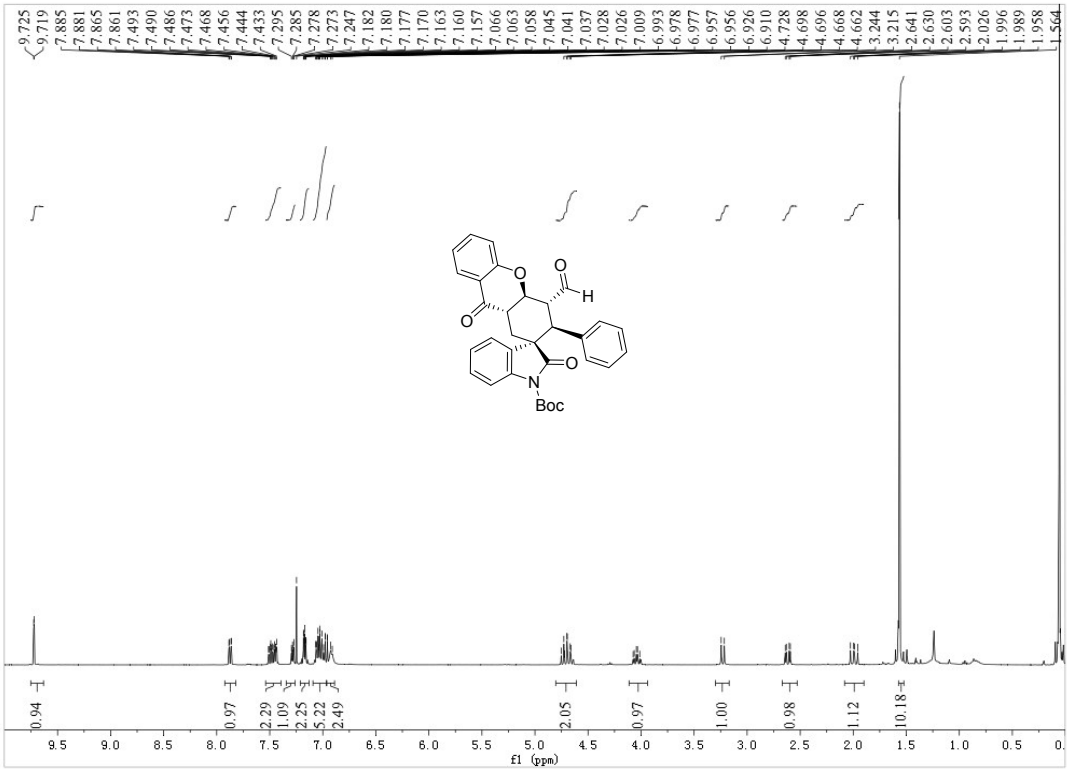
6. Assignment of the absolute configuration of 3h by the quantum chemical calculation of electronic circular dichroism (ECD)

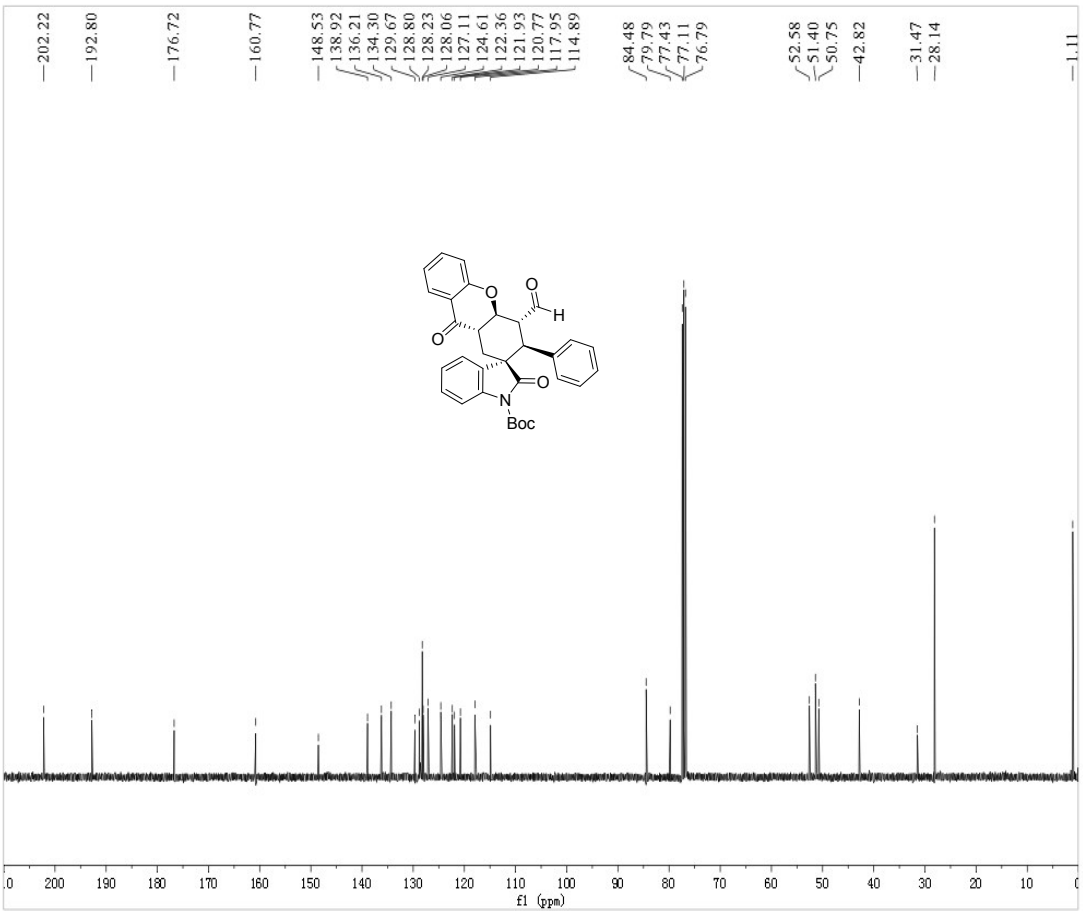


The experimental ECD spectrum of compound chiral **3h**

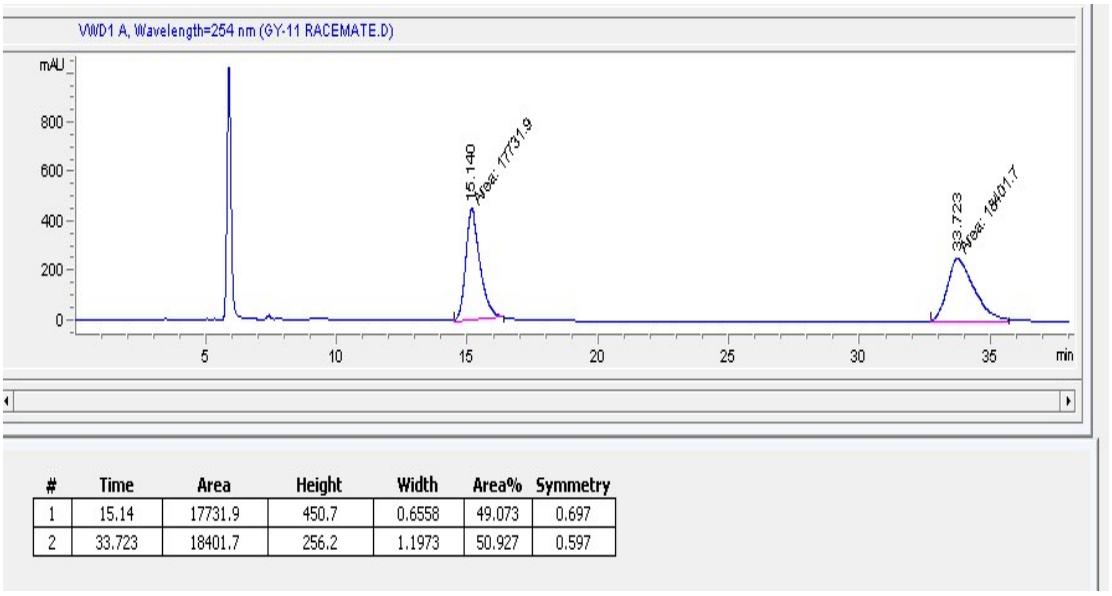
7. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds 3

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

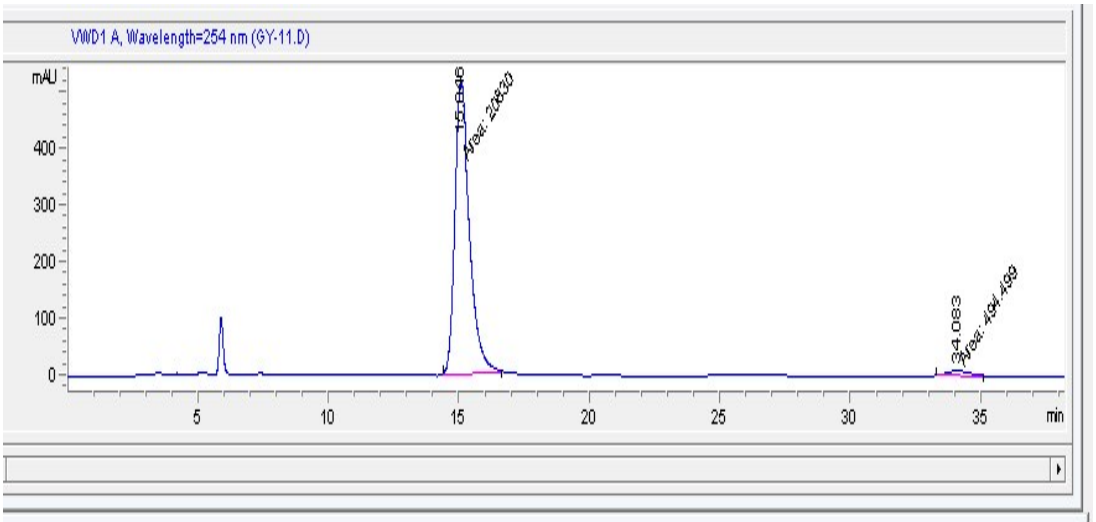




HPLC of 3a

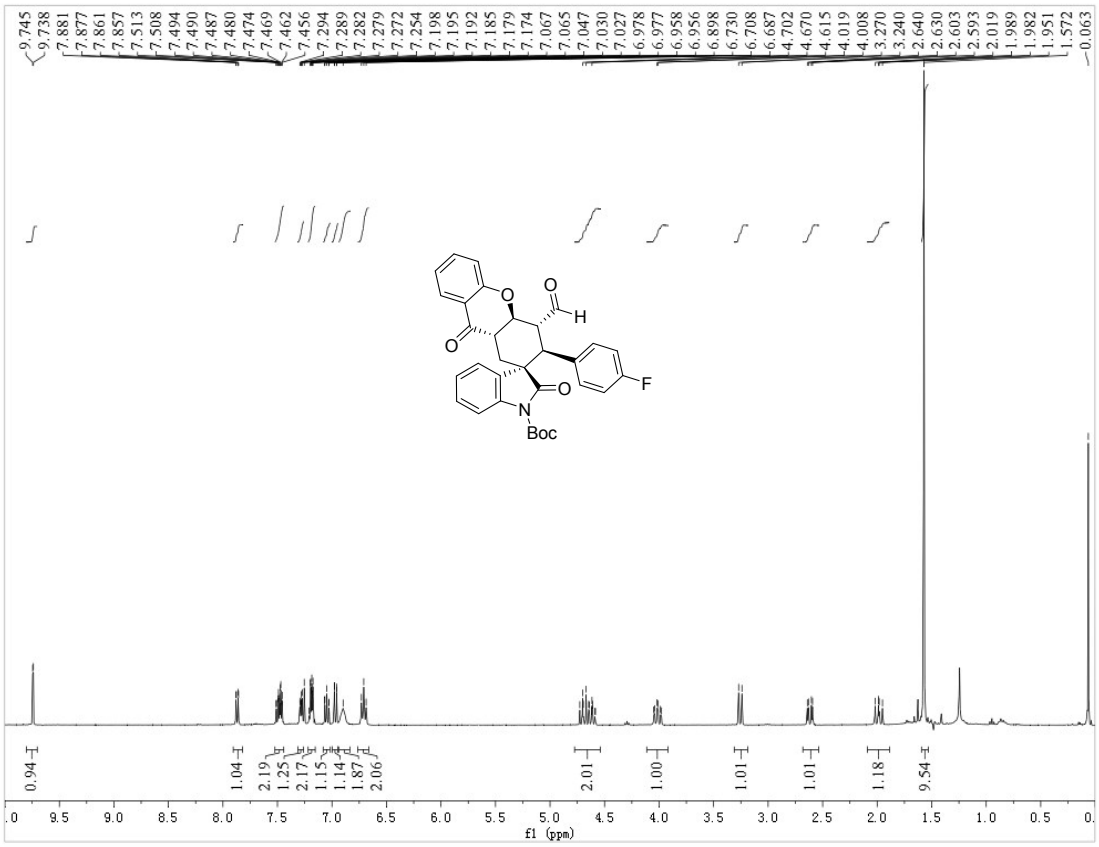


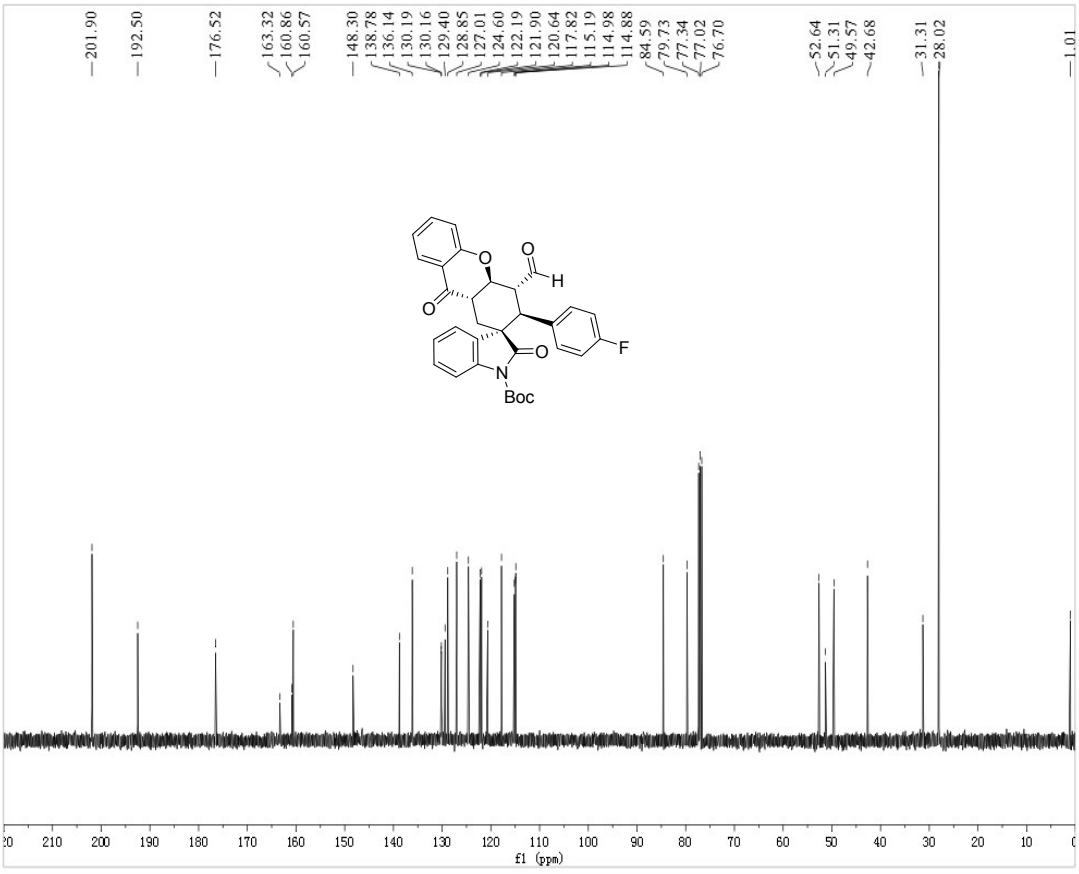
#	Time	Area	Height	Width	Area%	Symmetry
1	15.14	17731.9	450.7	0.6558	49.073	0.697
2	33.723	18401.7	256.2	1.1973	50.927	0.597



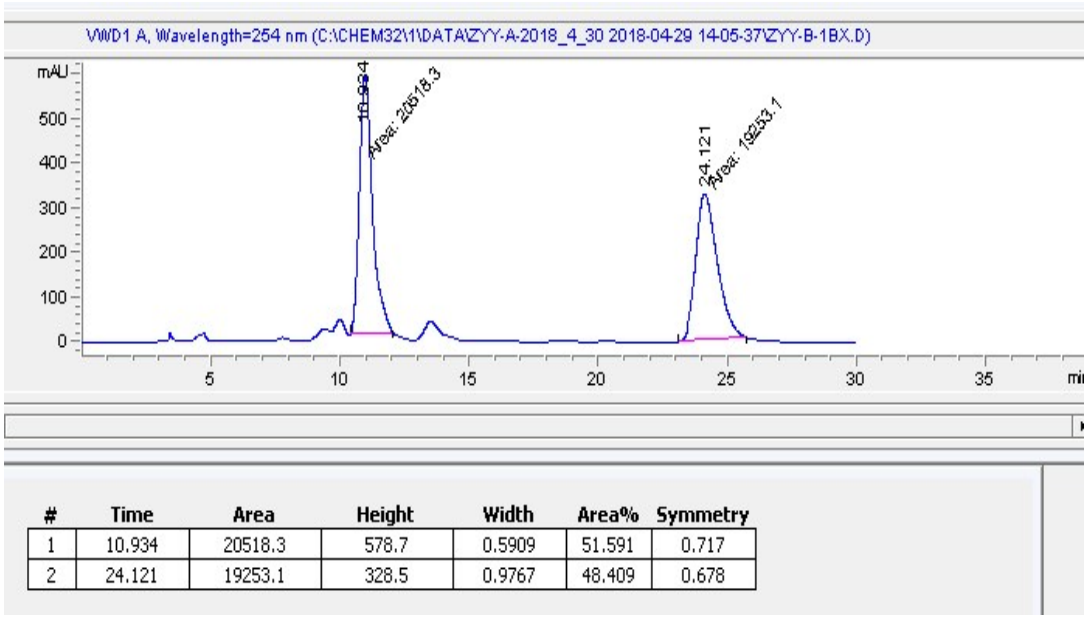
#	Time	Area	Height	Width	Area%	Symmetry
1	15.046	20830	518.3	0.6699	97.681	0.64
2	34.083	494.5	8.3	0.9887	2.319	0.607

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

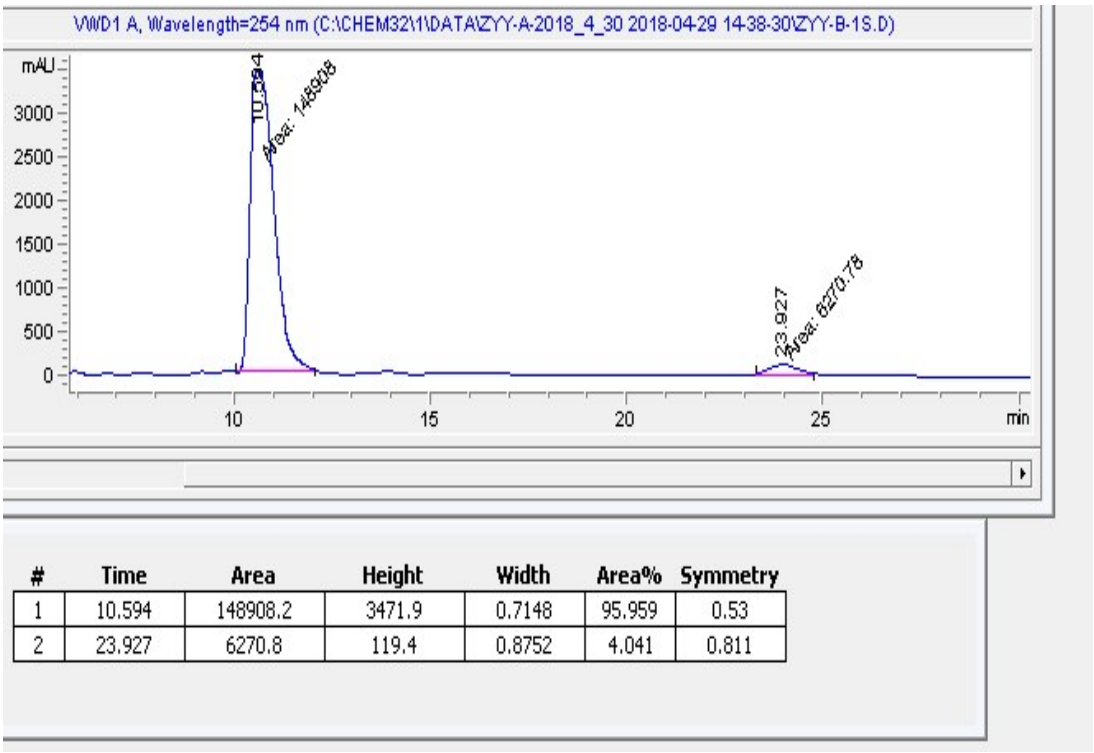




HPLC of 3b

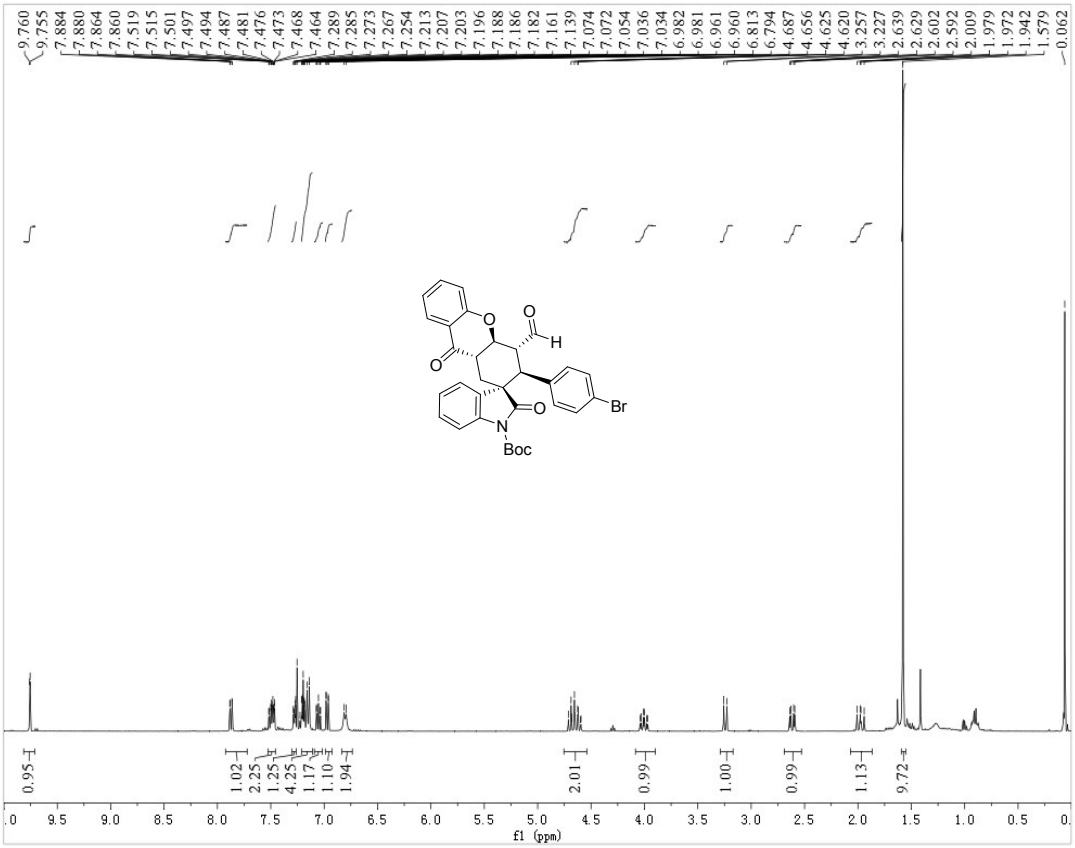


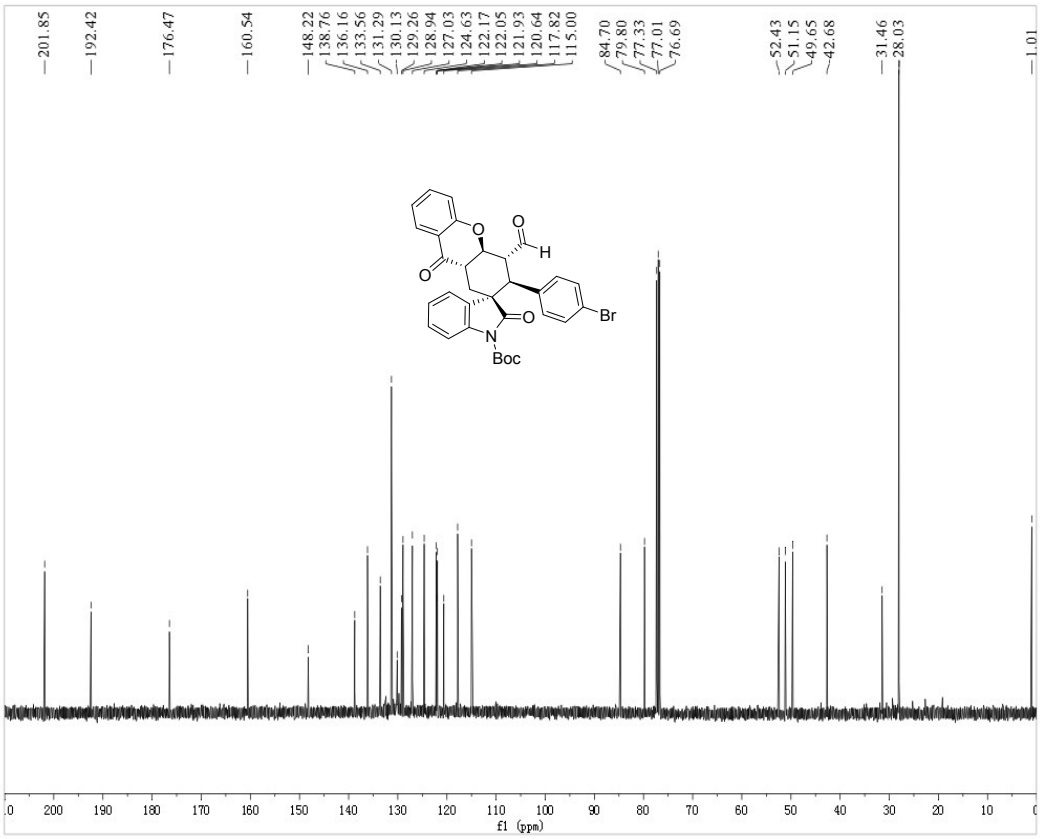
#	Time	Area	Height	Width	Area%	Symmetry
1	10.934	20518.3	578.7	0.5909	51.591	0.717
2	24.121	19253.1	328.5	0.9767	48.409	0.678



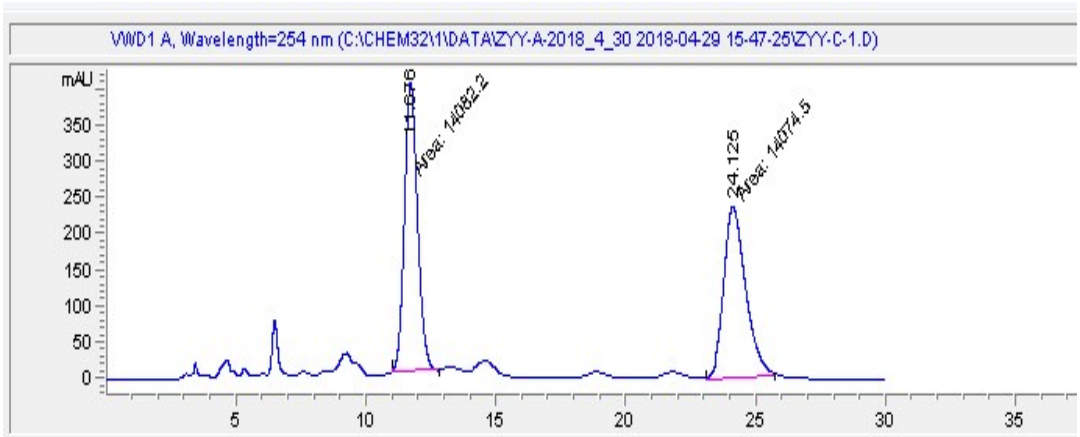
#	Time	Area	Height	Width	Area%	Symmetry
1	10.594	148908.2	3471.9	0.7148	95.959	0.53
2	23.927	6270.8	119.4	0.8752	4.041	0.811

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

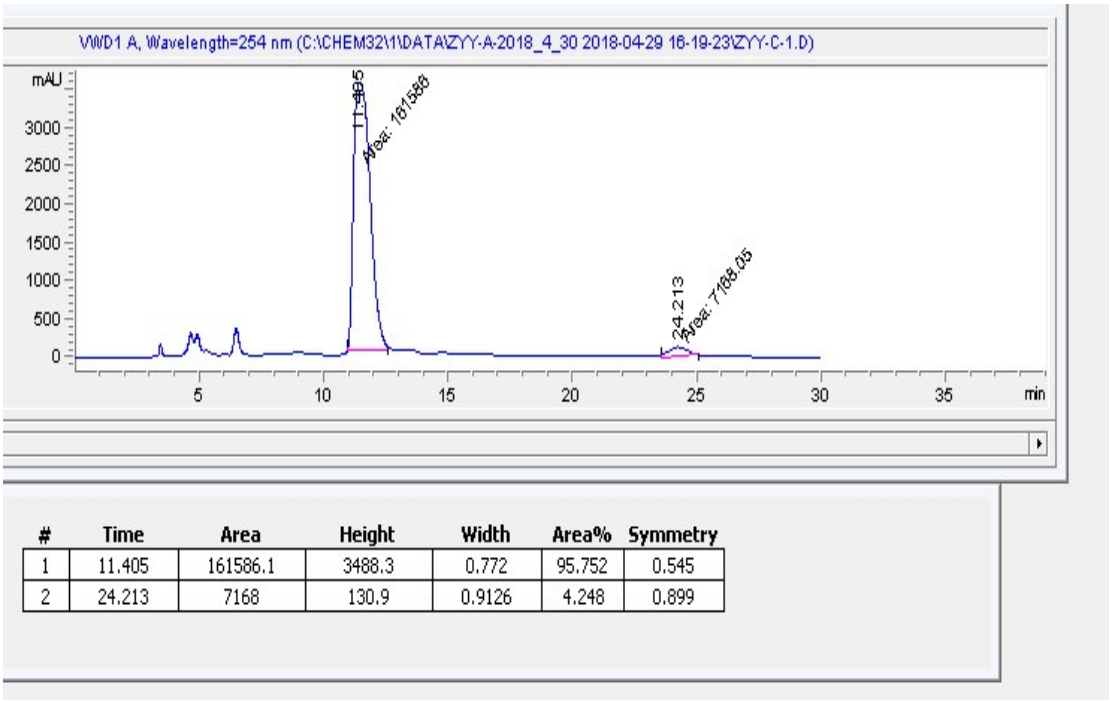




HPLC of 3c

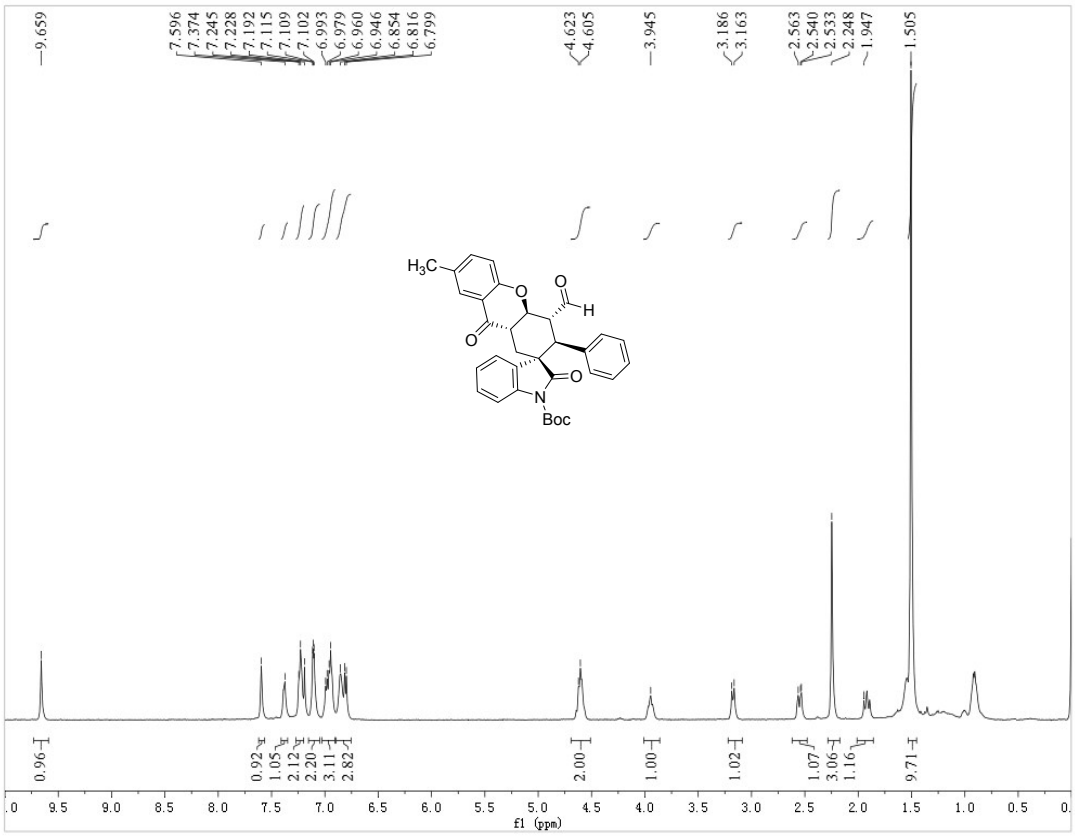


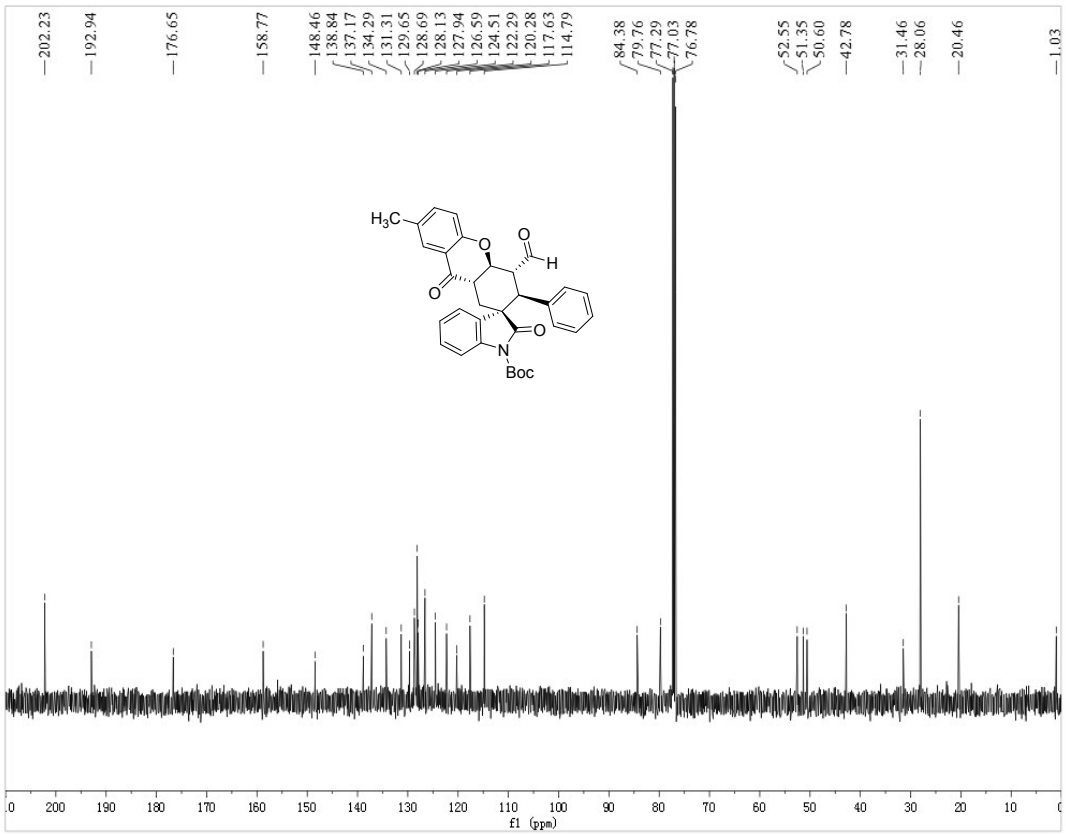
#	Time	Area	Height	Width	Area%	Symmetry
1	11.676	14082.2	400.4	0.5862	50.014	0.856
2	24.125	14074.5	236.9	0.9904	49.986	0.718



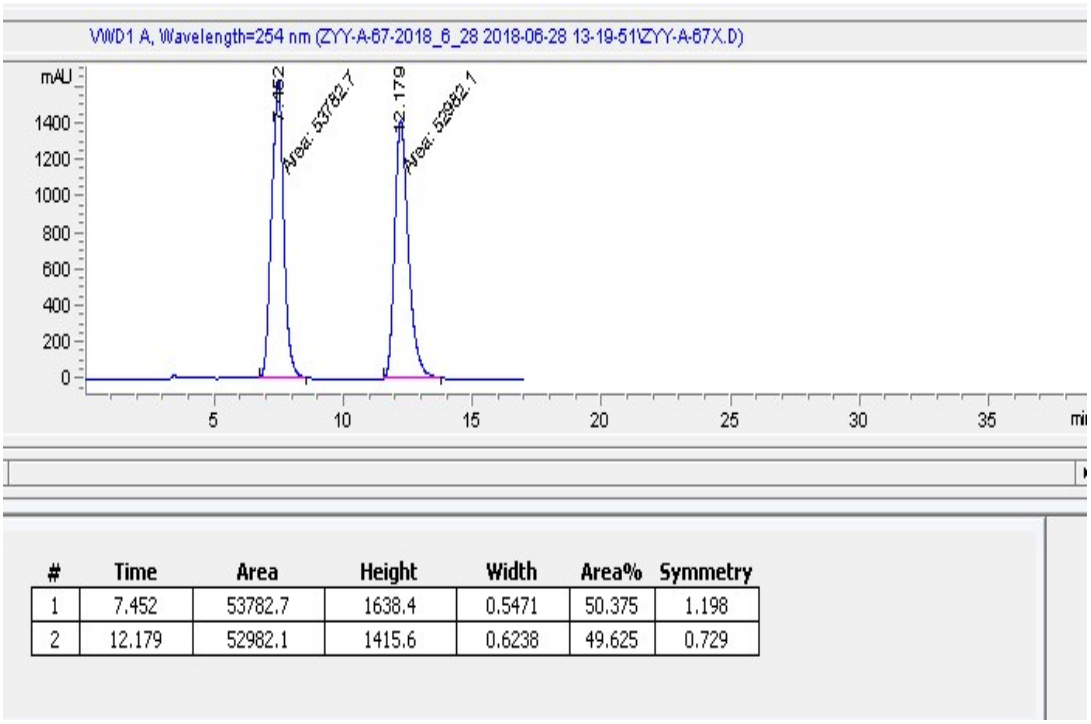
#	Time	Area	Height	Width	Area%	Symmetry
1	11.405	161586.1	3488.3	0.772	95.752	0.545
2	24.213	7168	130.9	0.9126	4.248	0.899

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

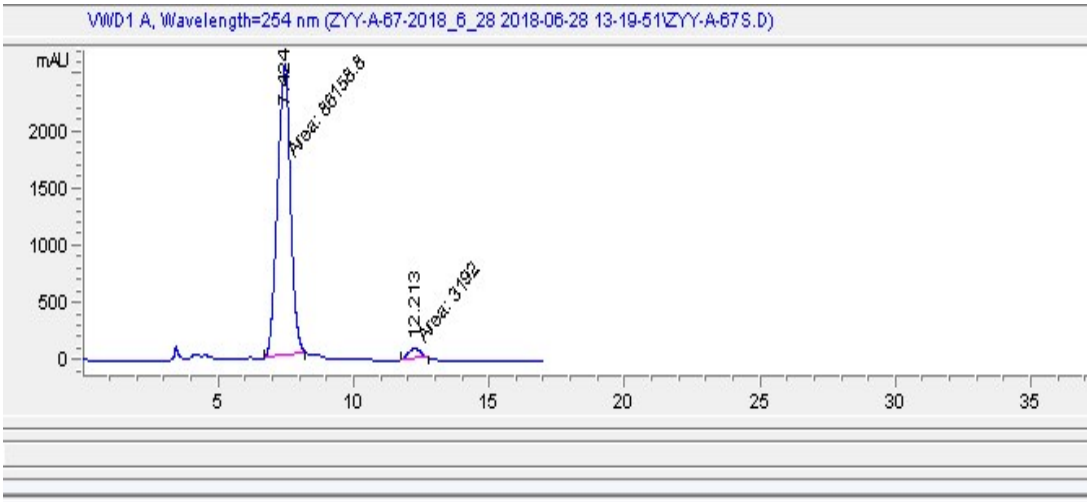




HPLC of 3d

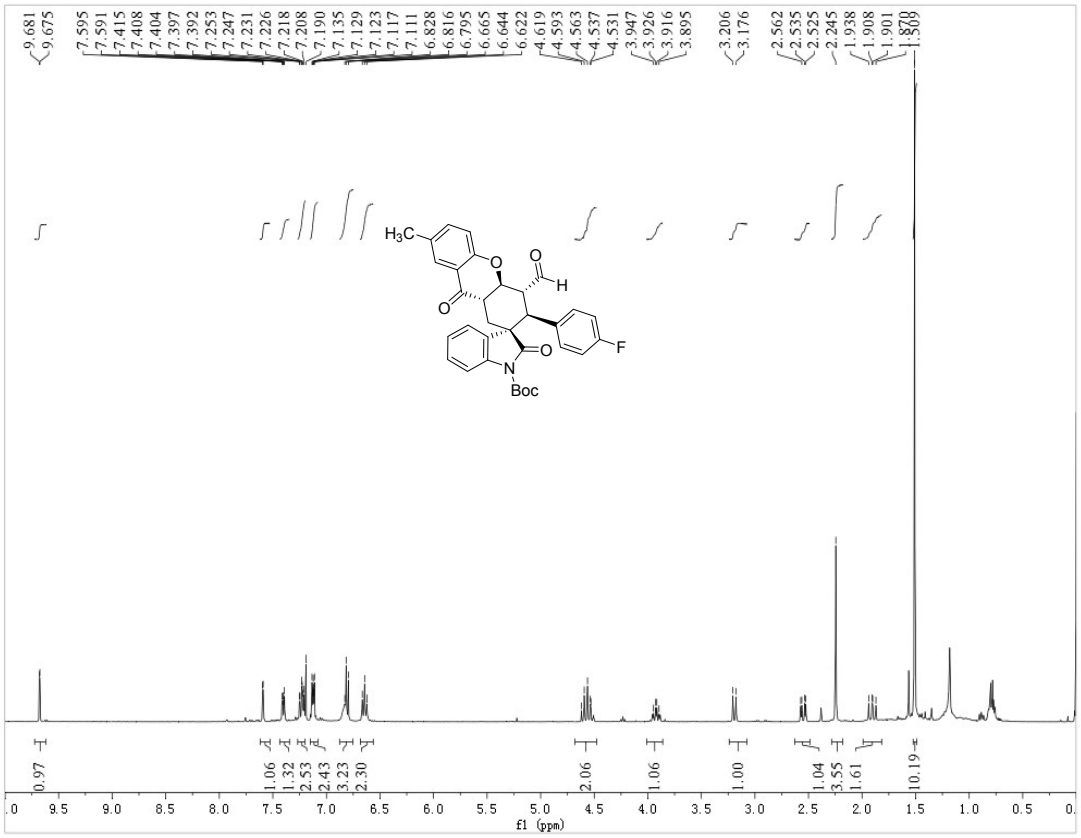


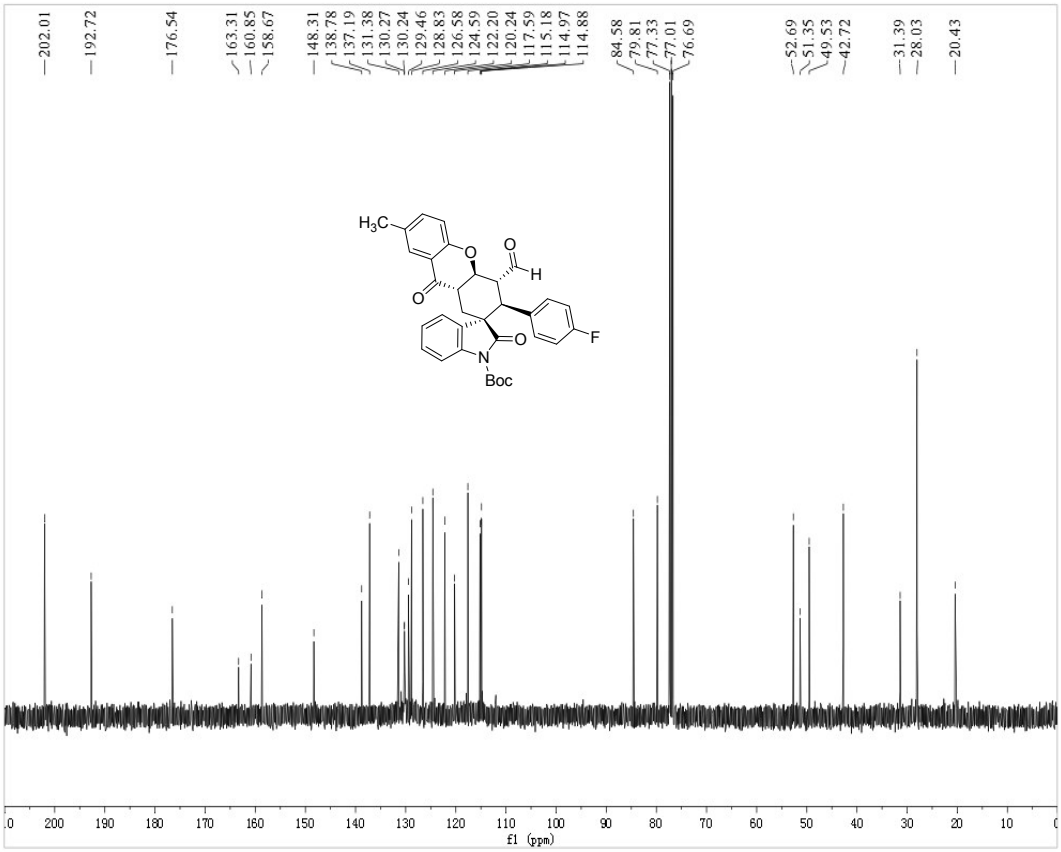
#	Time	Area	Height	Width	Area%	Symmetry
1	7.452	53782.7	1638.4	0.5471	50.375	1.198
2	12.179	52982.1	1415.6	0.6238	49.625	0.729



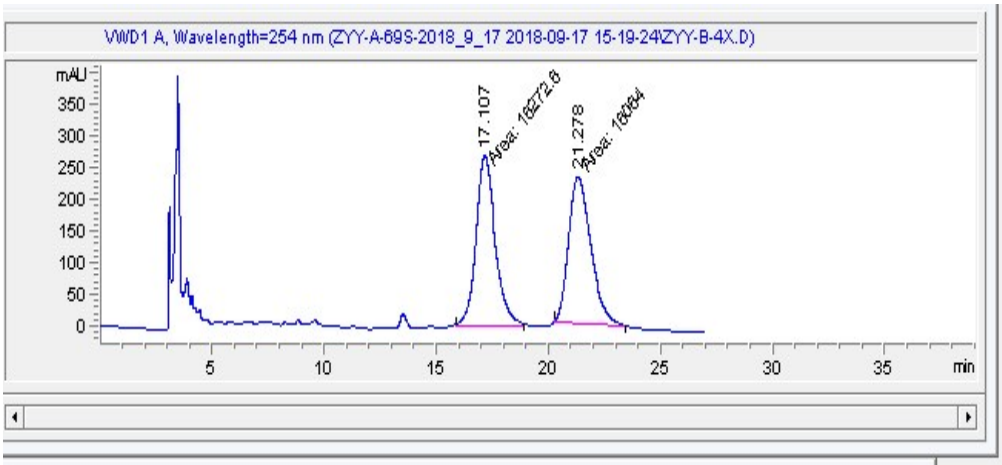
#	Time	Area	Height	Width	Area%	Symmetry
1	7.424	86158.8	2557.3	0.5615	96.428	1.246
2	12.213	3192	99.7	0.5334	3.572	1.054

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

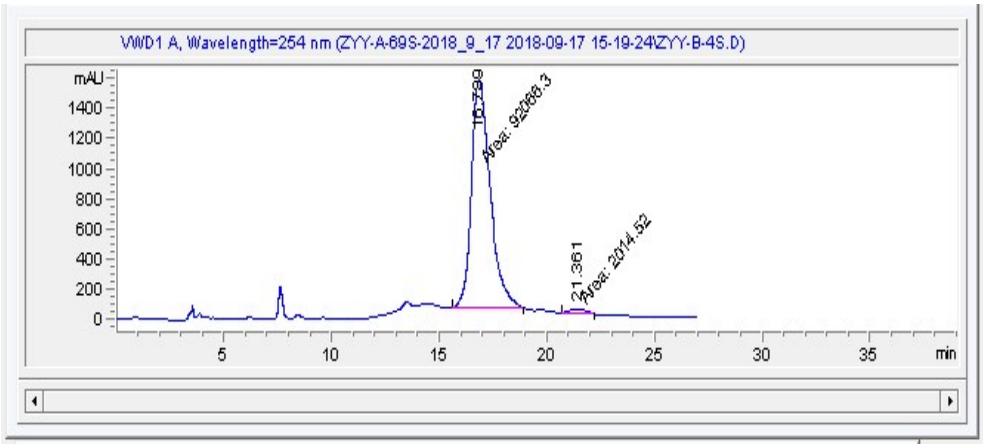




HPLC of 3e

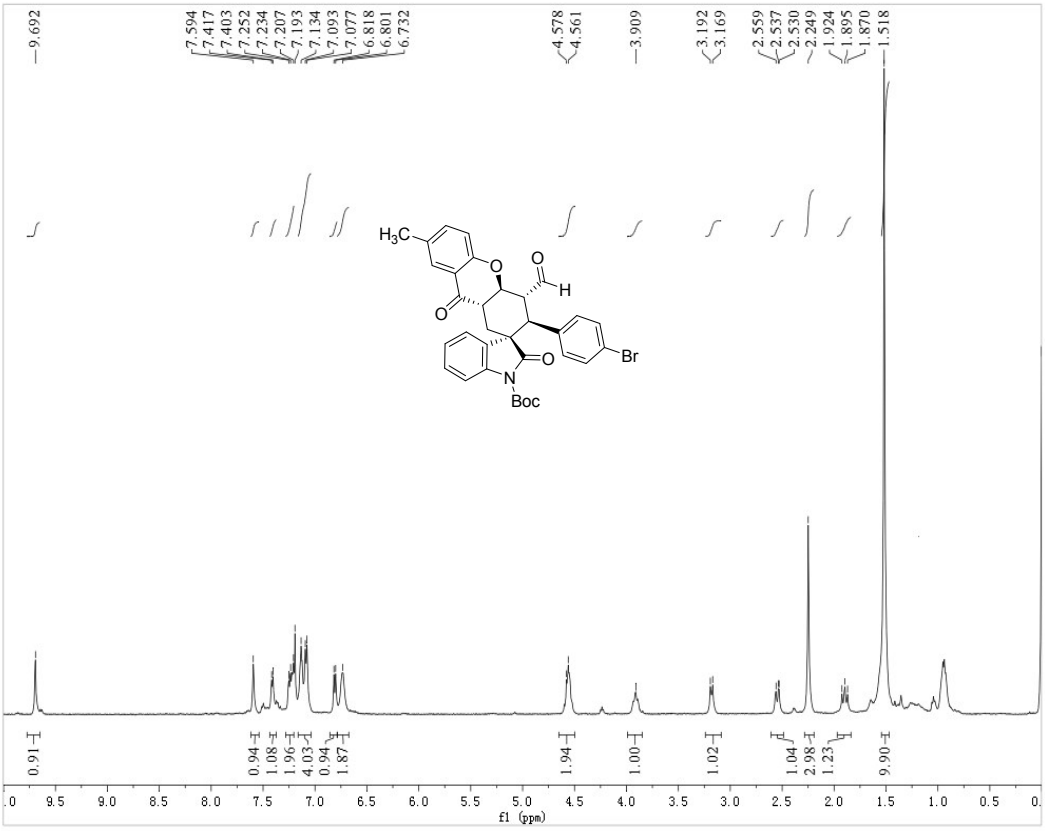


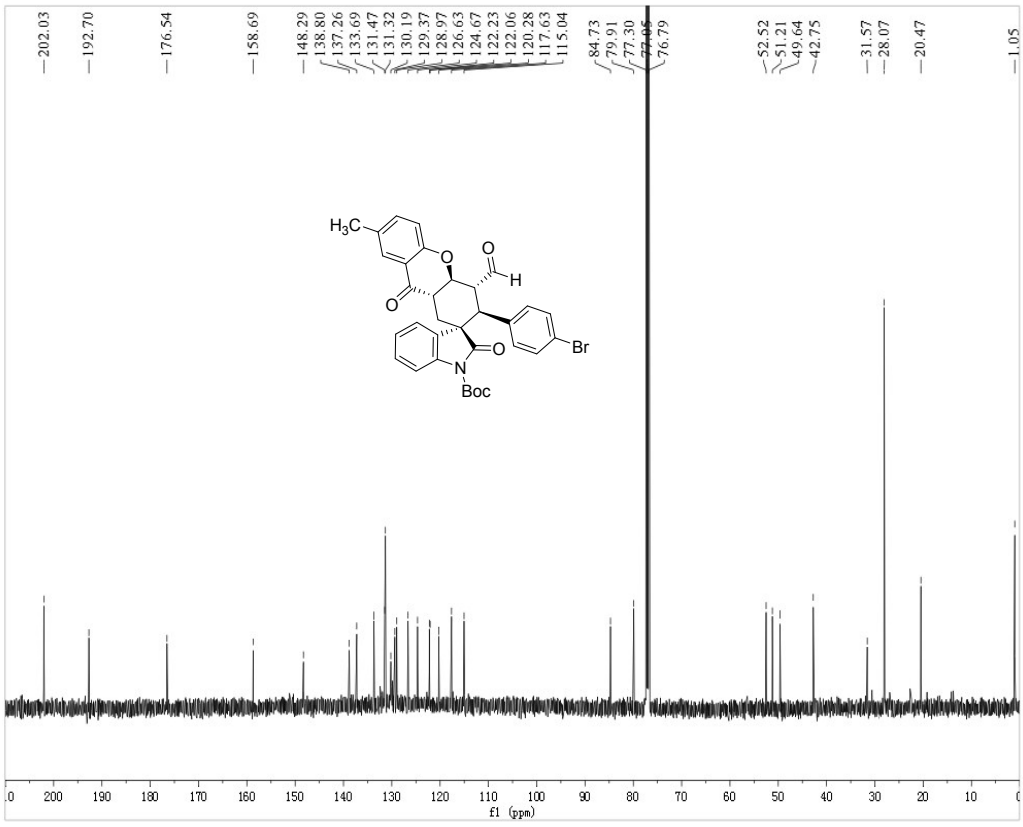
#	Time	Area	Height	Width	Area%	Symmetry
1	17.107	16272.6	268.8	1.009	50.323	0.757
2	21.278	16064	233.5	1.1464	49.677	0.696



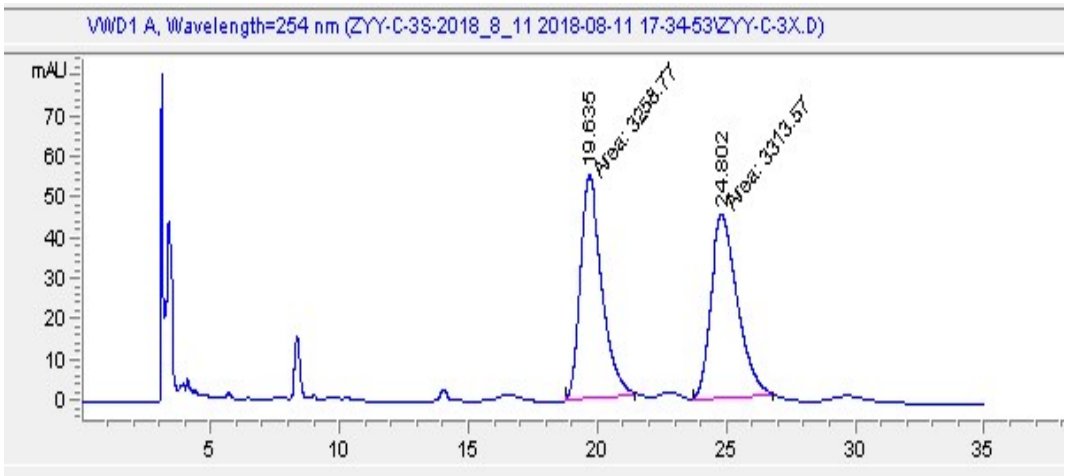
#	Time	Area	Height	Width	Area%	Symmetry
1	16.789	92066.3	1515.5	1.0125	97.859	0.621
2	21.361	2014.5	36.1	0.9296	2.141	0.752

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

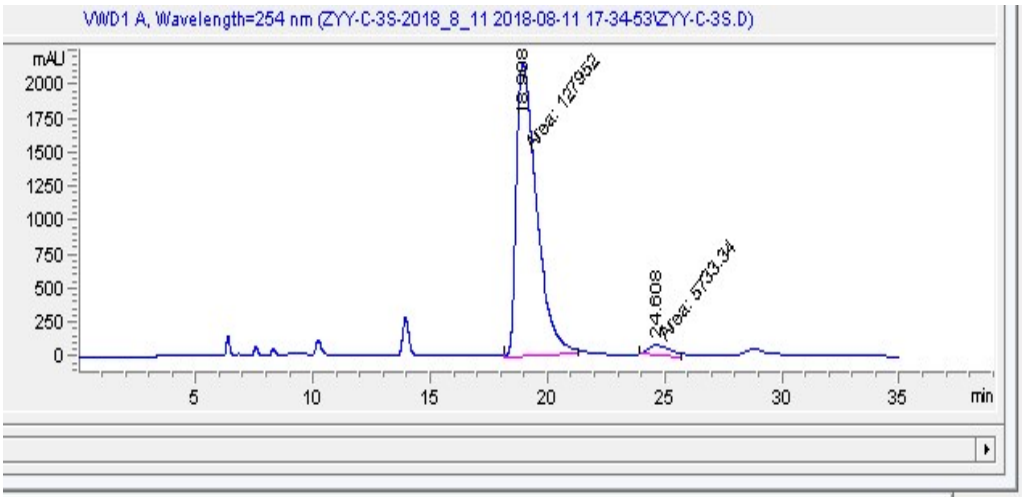




HPLC of 3f

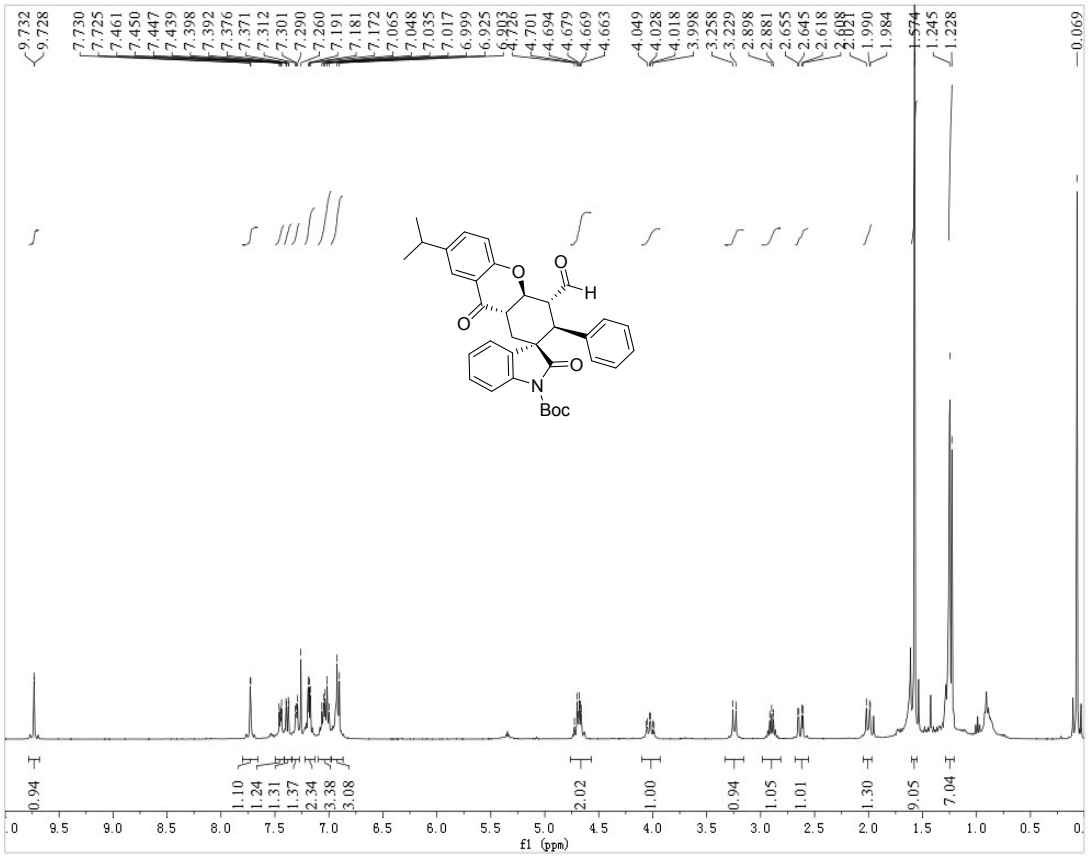


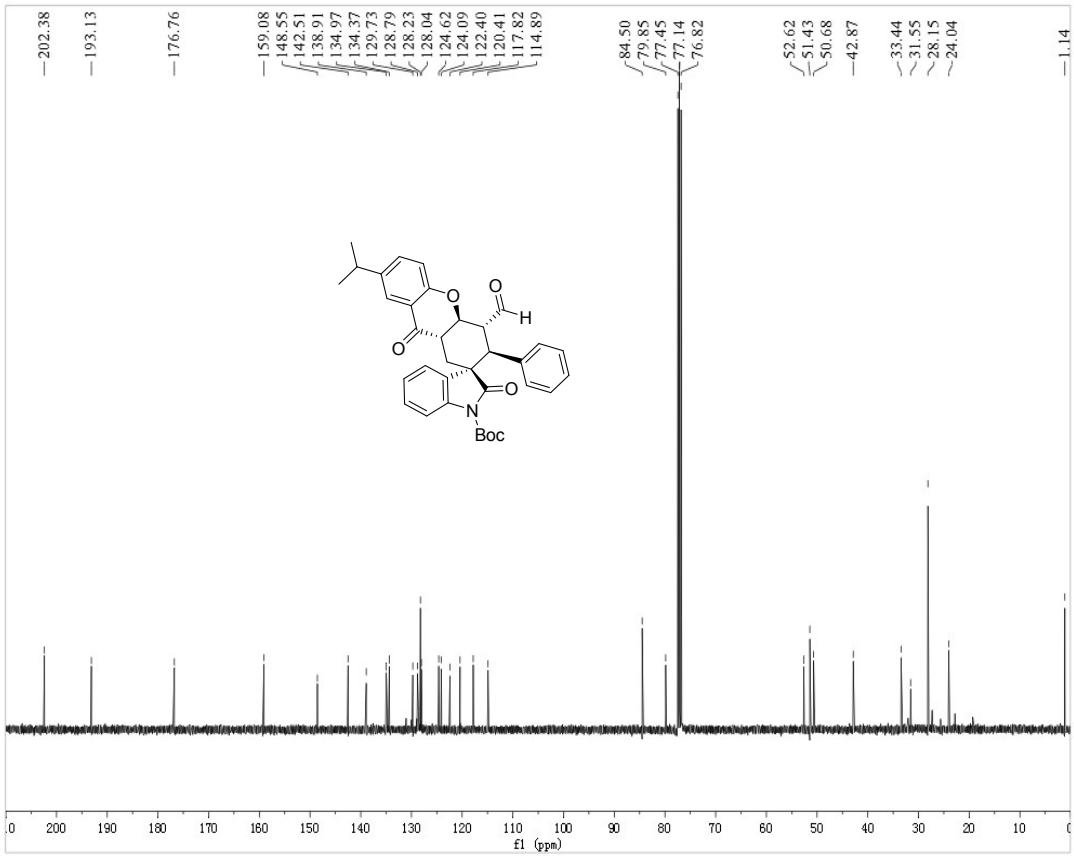
#	Time	Area	Height	Width	Area%	Symmetry
1	19.635	3258.8	54.7	0.9922	49.583	0.664
2	24.802	3313.6	45.2	1.2208	50.417	0.707



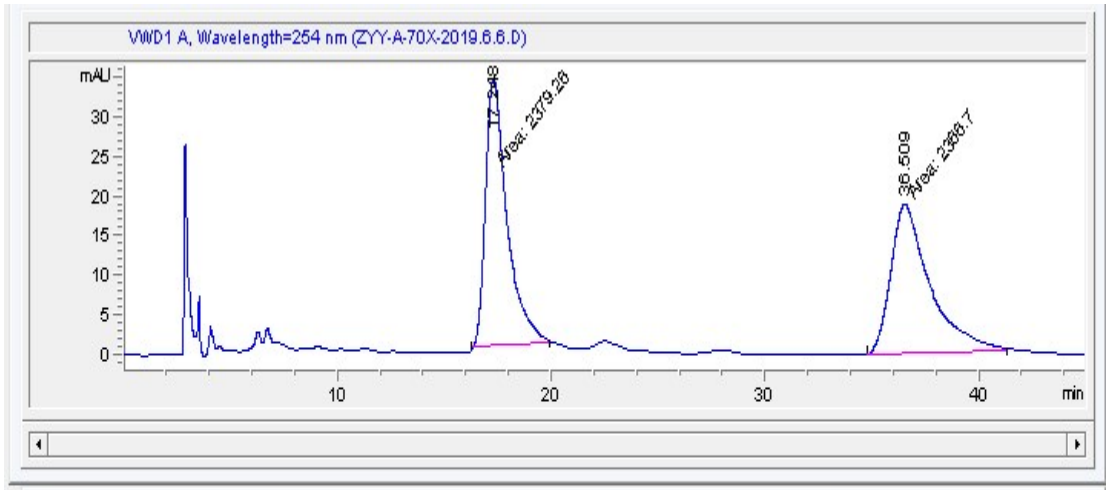
#	Time	Area	Height	Width	Area%	Symmetry
1	18.908	127952.5	2160.7	0.987	95.711	0.448
2	24.608	5733.3	79.8	1.1973	4.289	0.599

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

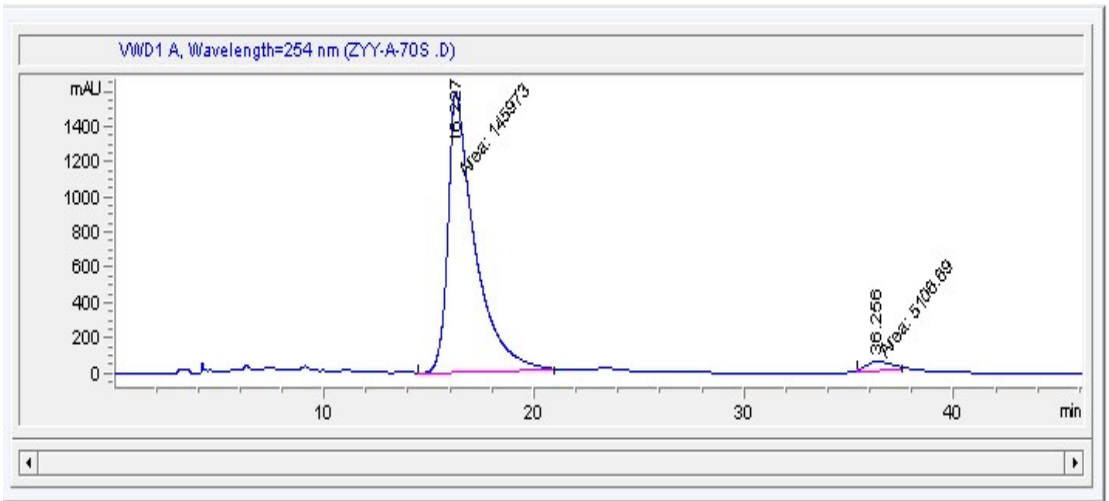




HPLC of 3g

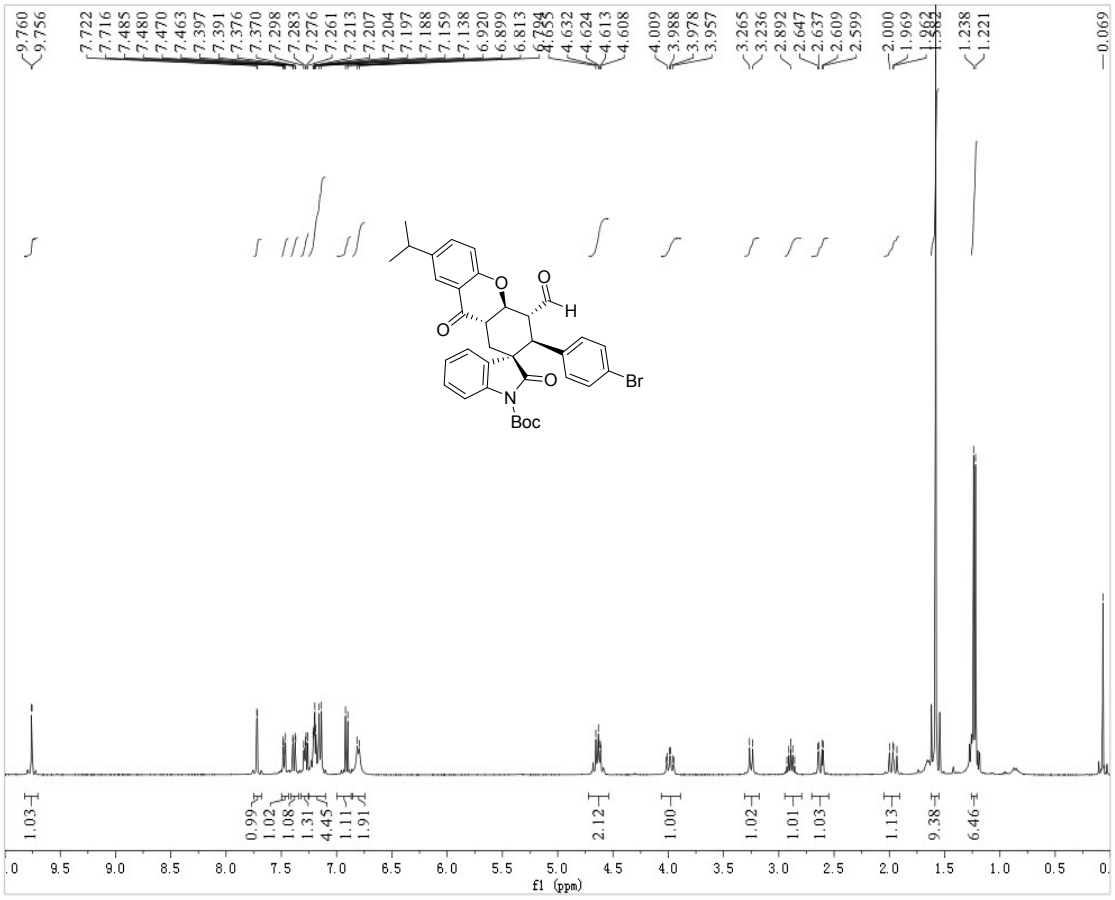


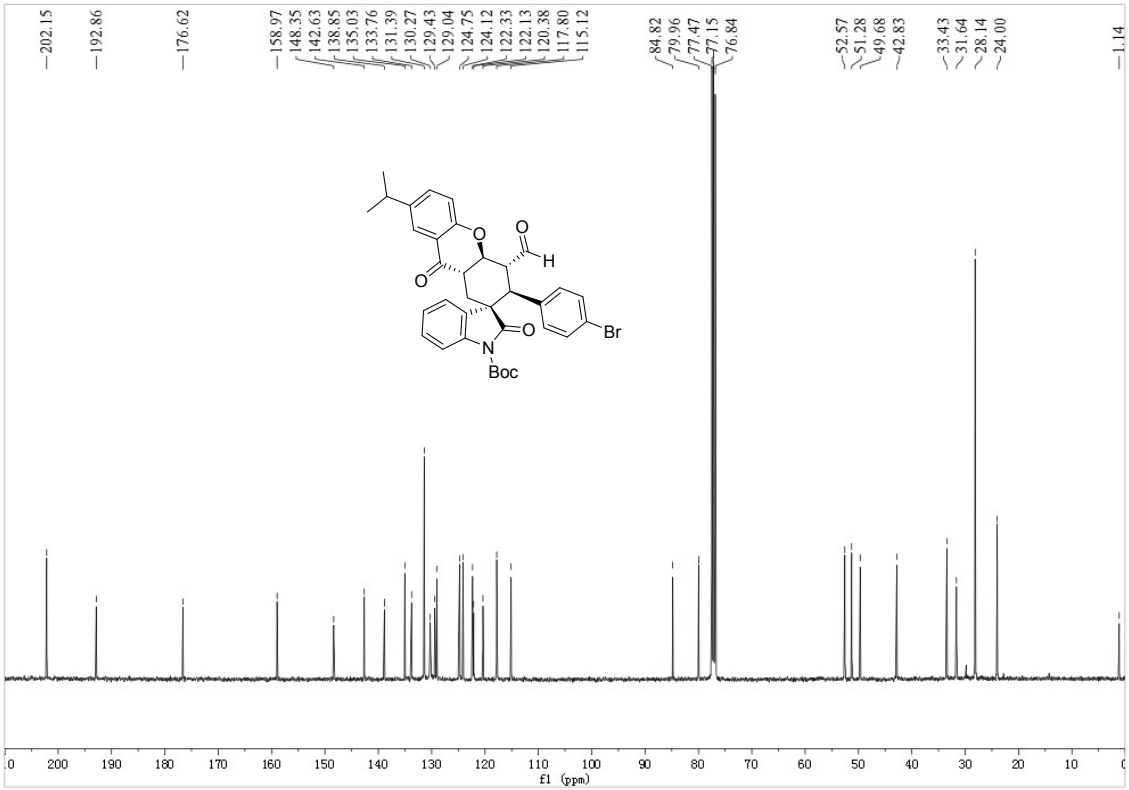
#	Time	Area	Height	Width	Area%	Symmetry
1	17.248	2379.3	33.9	1.1711	50.132	0.536
2	36.509	2366.7	18.8	2.0951	49.868	0.541



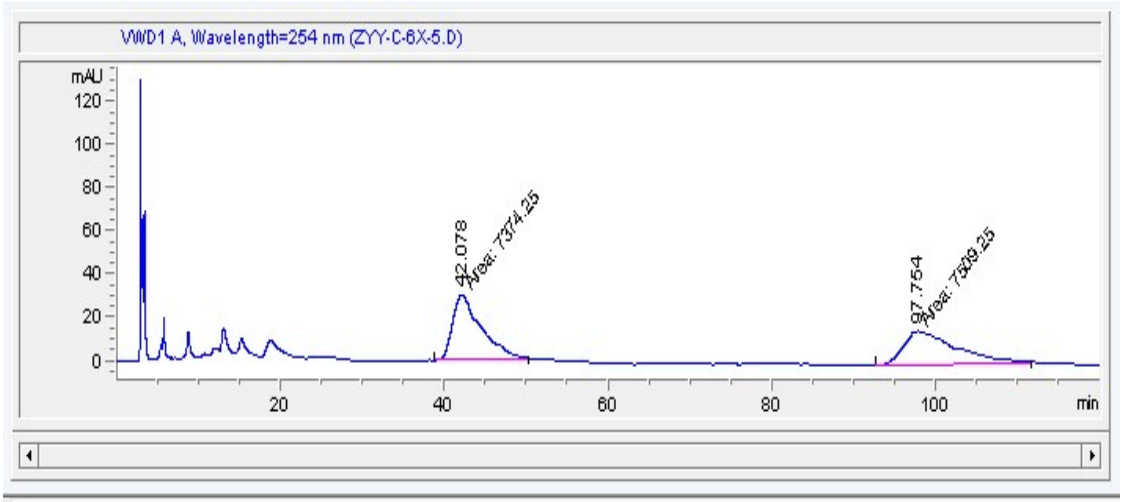
#	Time	Area	Height	Width	Area%	Symmetry
1	16.227	145972.9	1608.6	1.5124	96.620	0.393
2	36.256	5106.7	59.9	1.4211	3.380	0.798

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

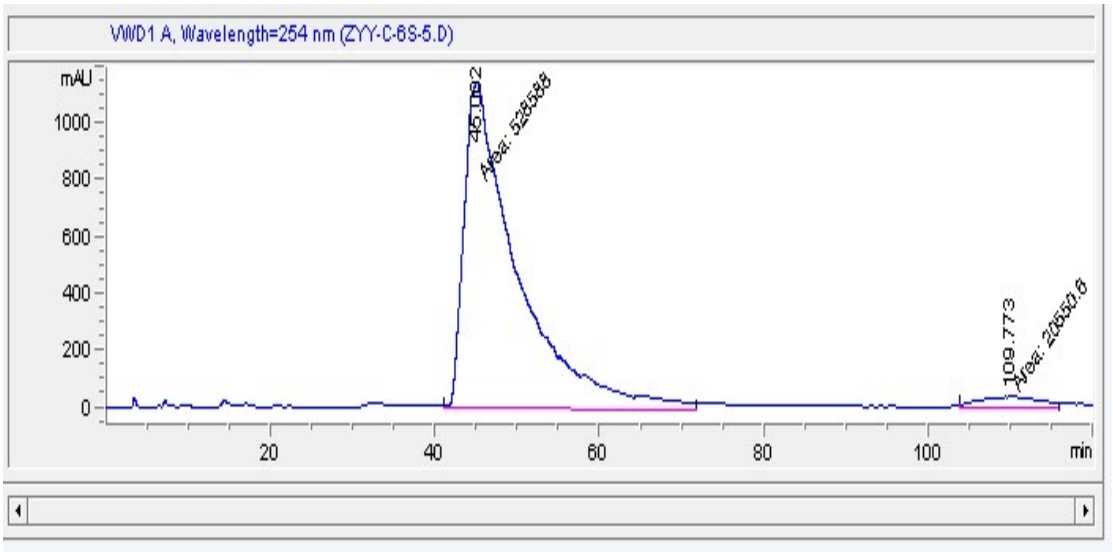




HPLC of 3h

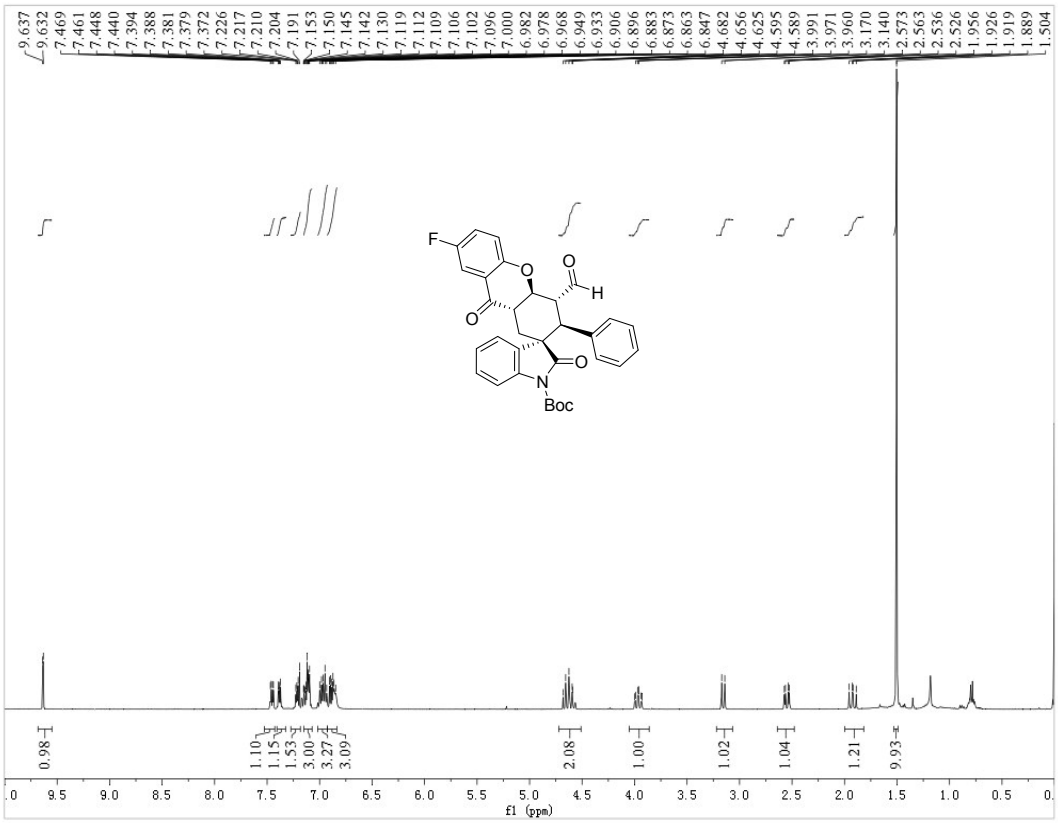


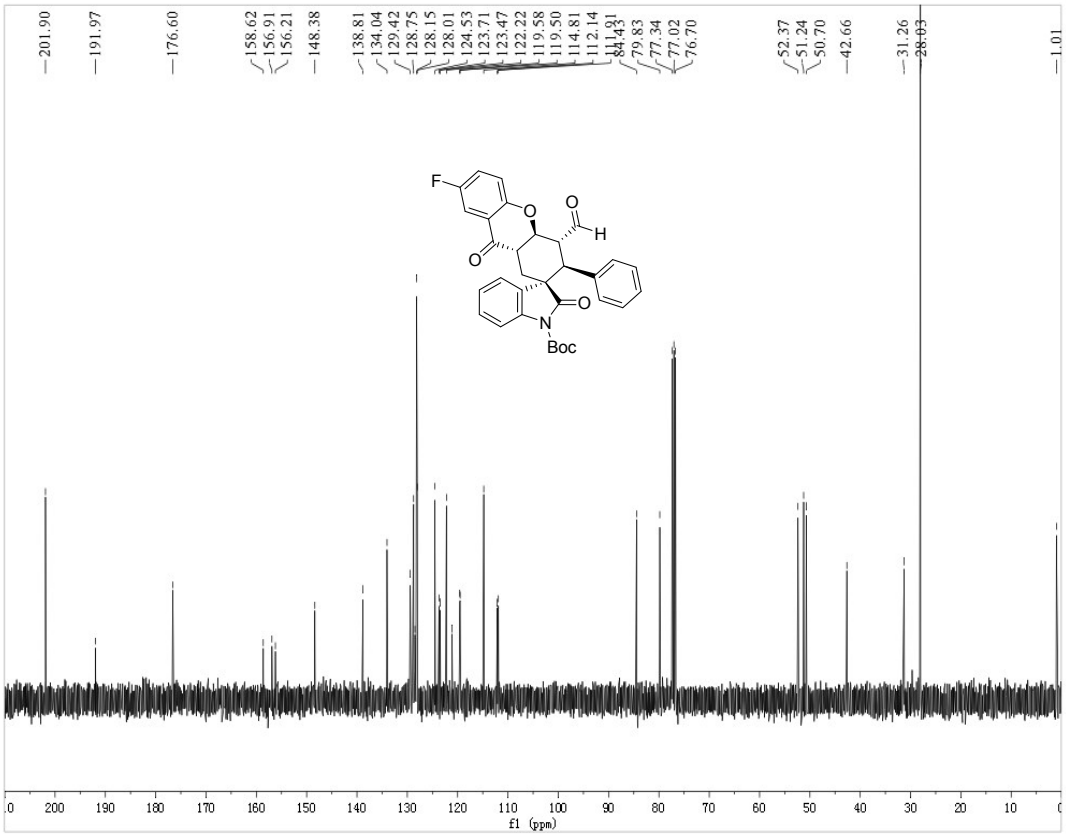
#	Time	Area	Height	Width	Area%	Symmetry
1	42.078	7374.3	30.4	4.0438	49.546	0.45
2	97.754	7509.3	16	7.8073	50.454	0.385



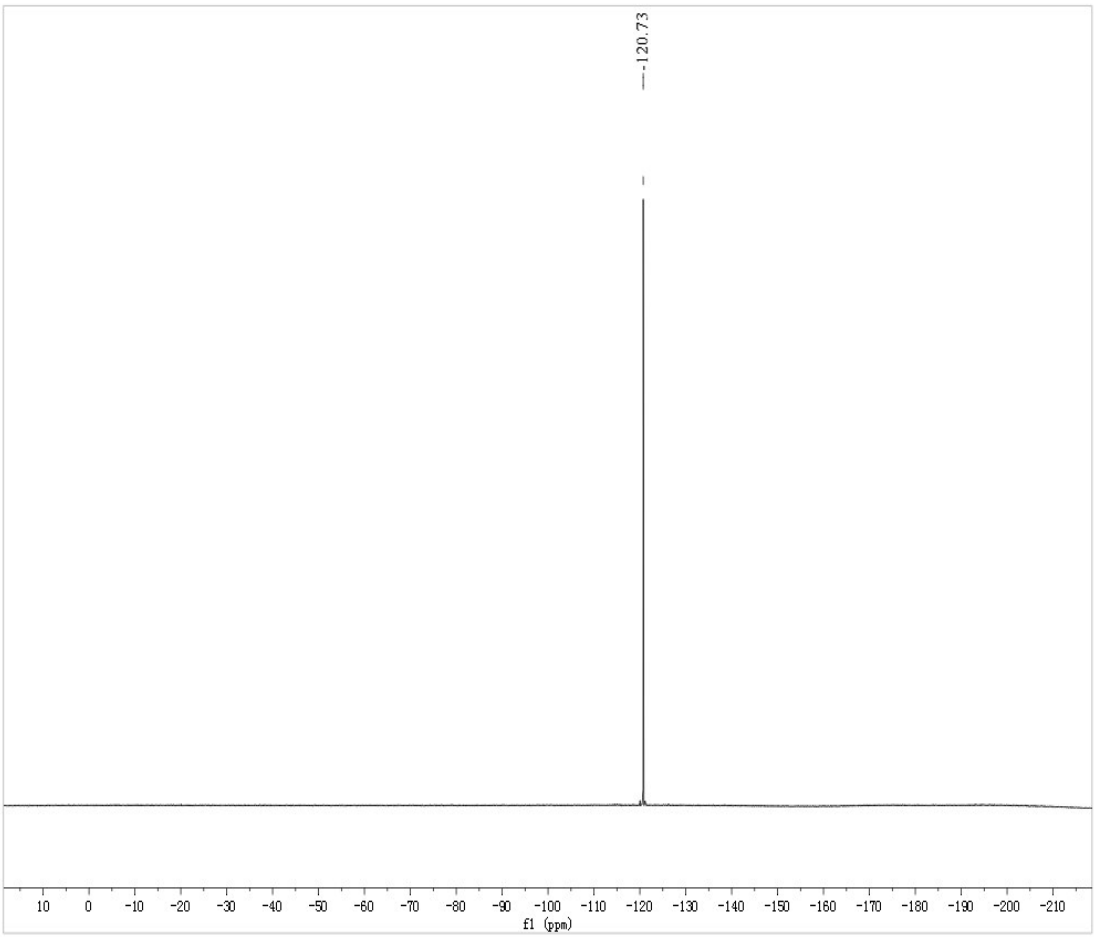
#	Time	Area	Height	Width	Area%	Symmetry
1	45.002	528587.7	1154.7	7.6296	96.258	0.296
2	109.773	20550.6	41.4	8.2671	3.742	1.007

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

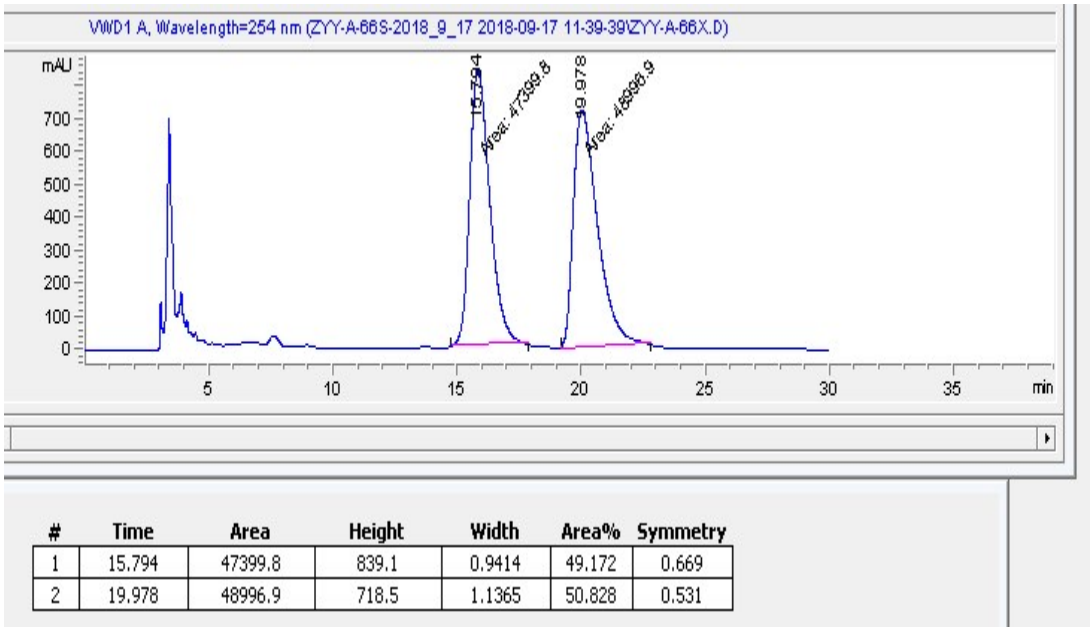




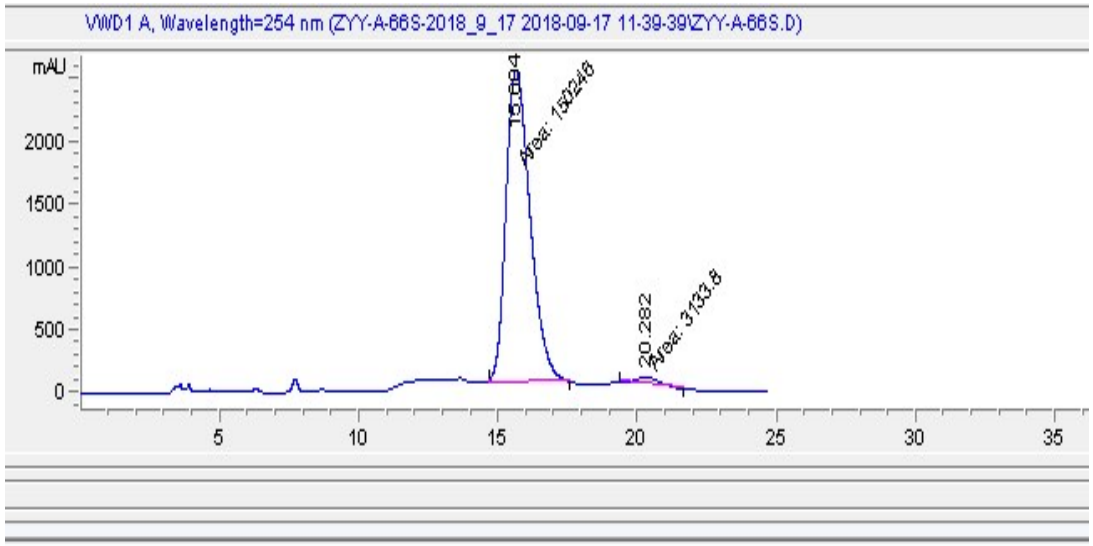
^{19}F NMR of 3i


-120.73
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3i

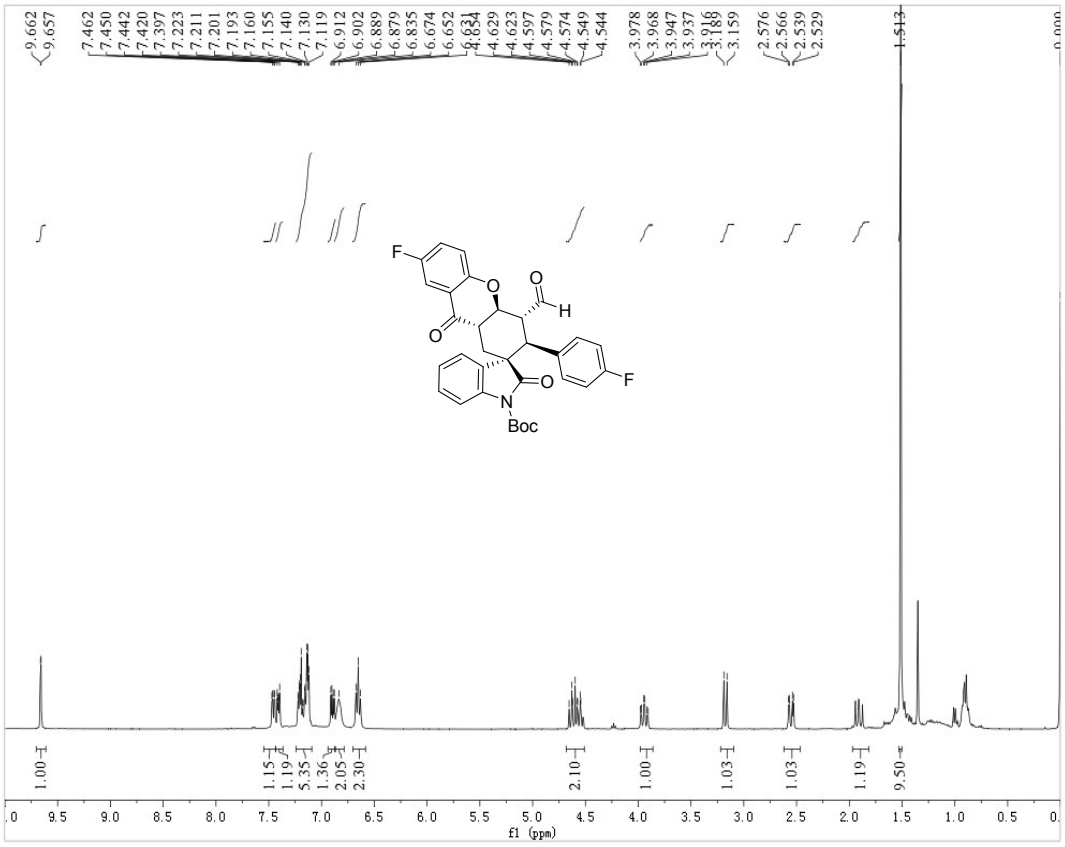


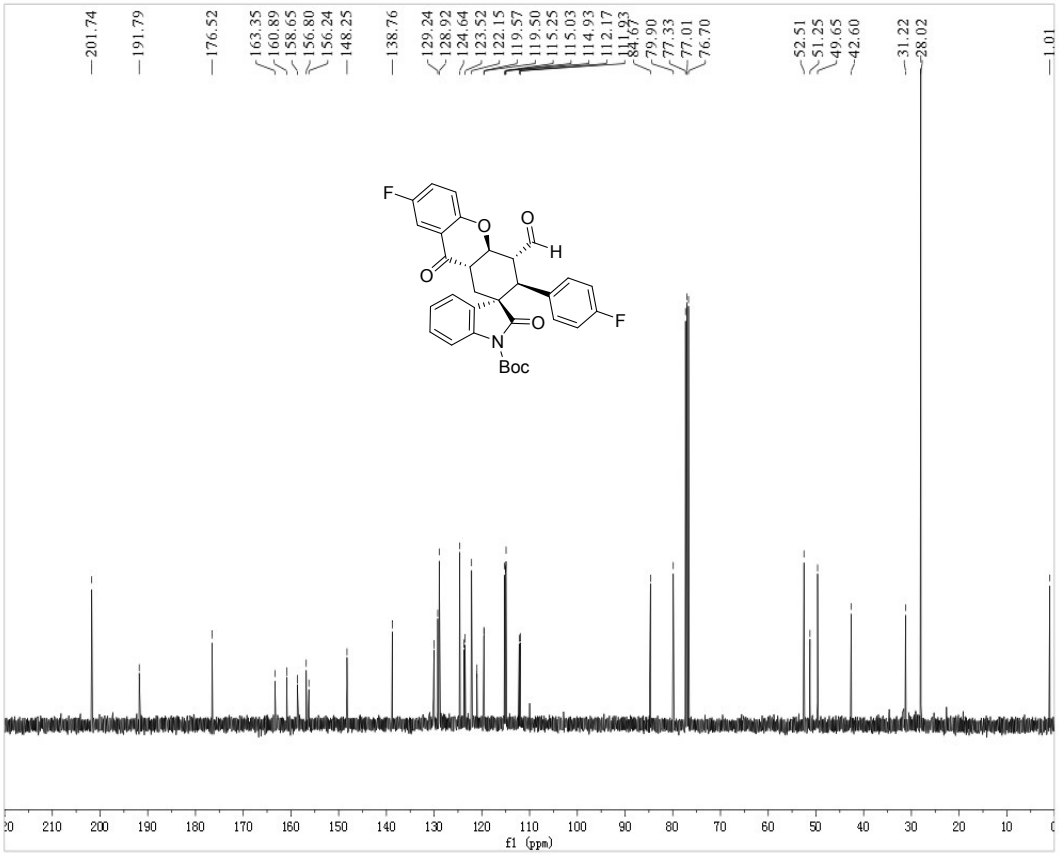
#	Time	Area	Height	Width	Area%	Symmetry
1	15.794	47399.8	839.1	0.9414	49.172	0.669
2	19.978	48996.9	718.5	1.1365	50.828	0.531



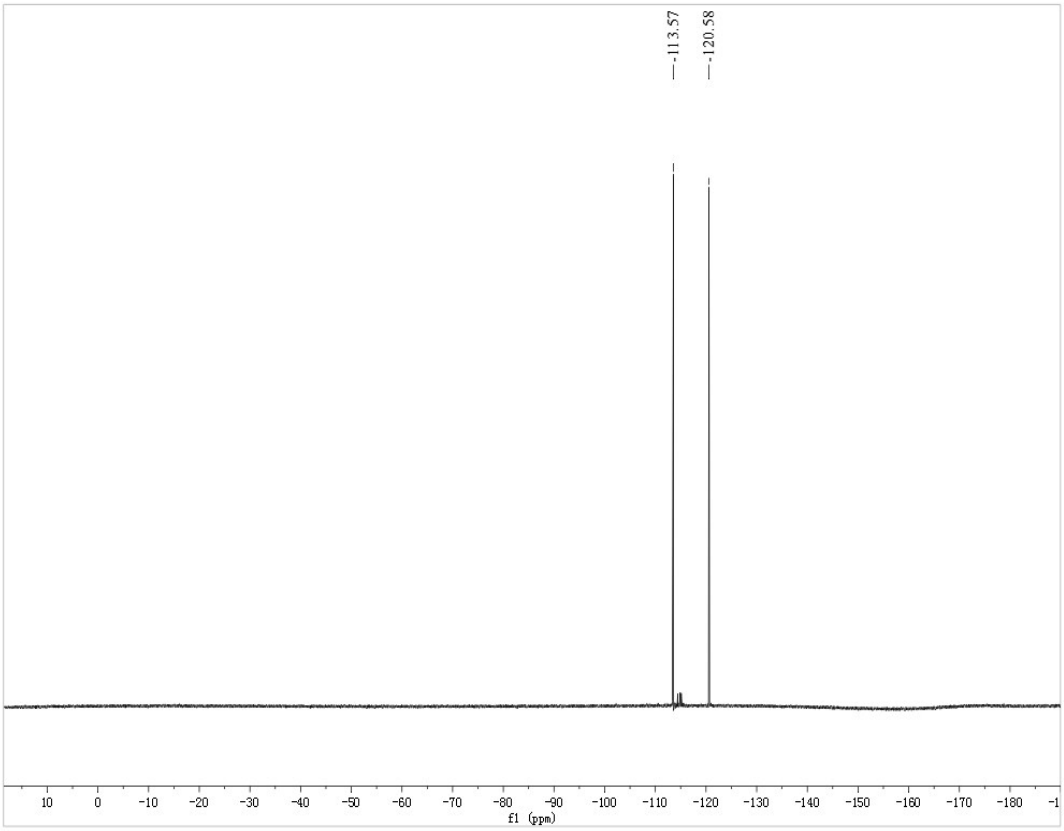
#	Time	Area	Height	Width	Area%	Symmetry
1	15.604	150245.6	2485.8	1.0074	97.957	0.706
2	20.282	3133.8	57.3	0.9112	2.043	0.631

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

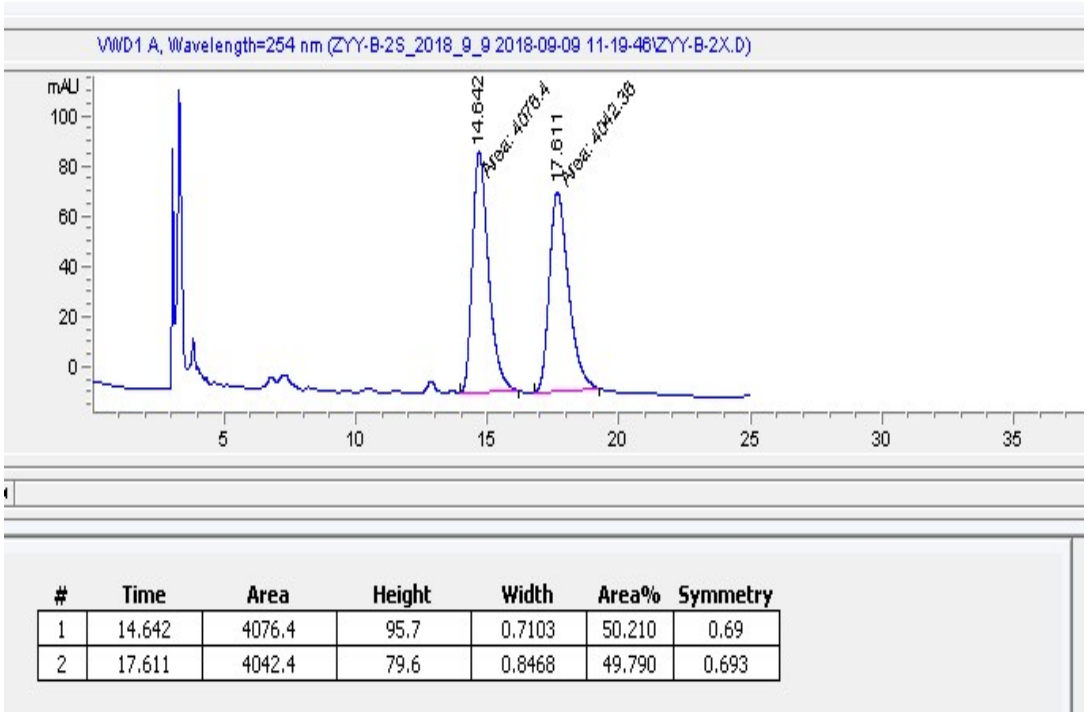




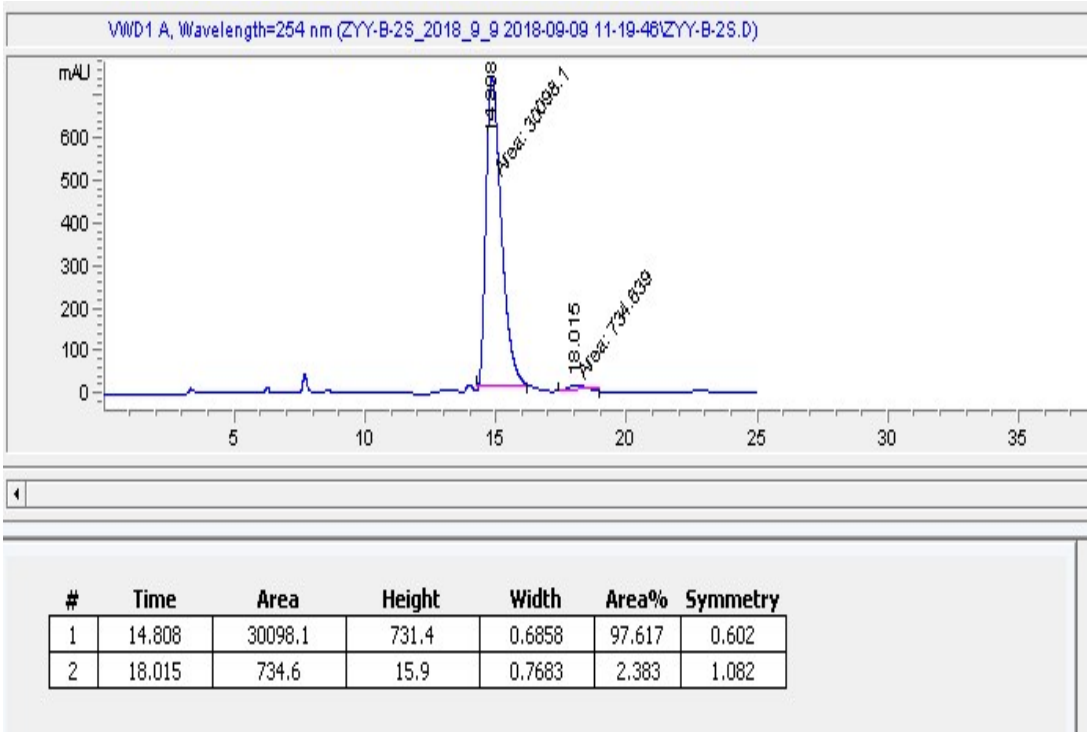
^{19}F NMR of 3j


-113.57
-120.58
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

HPLC of 3j

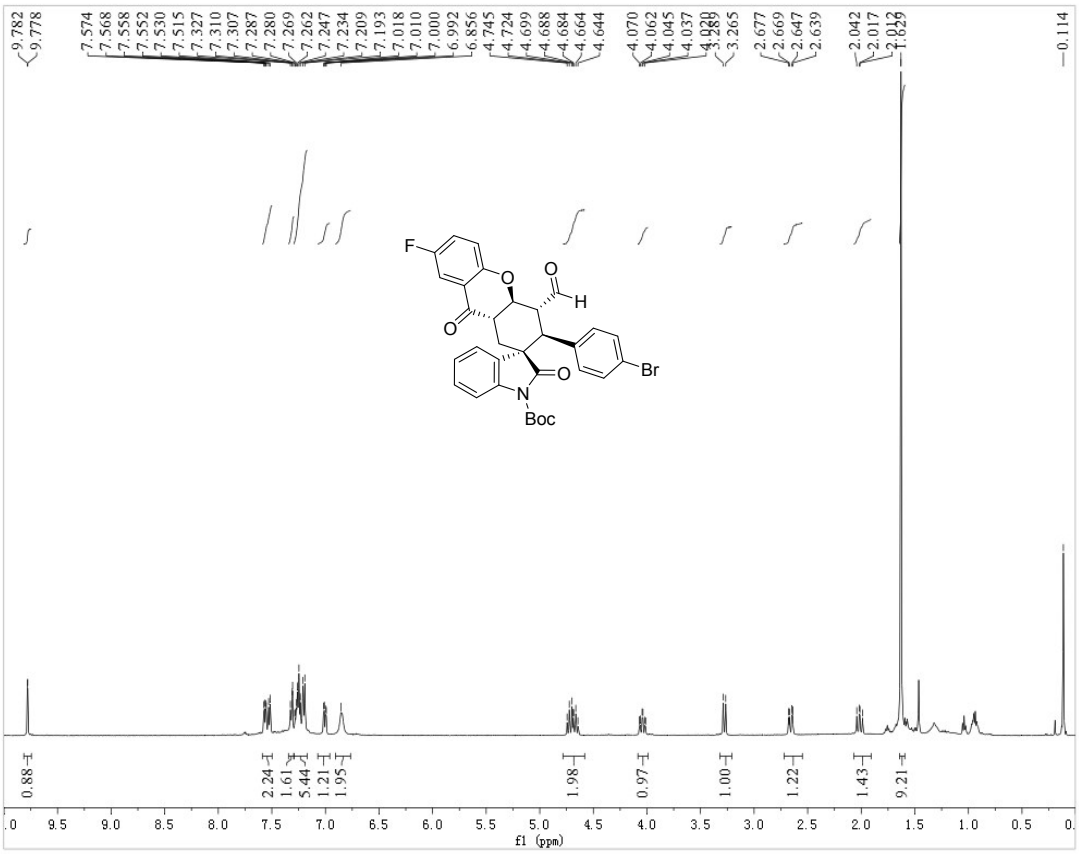


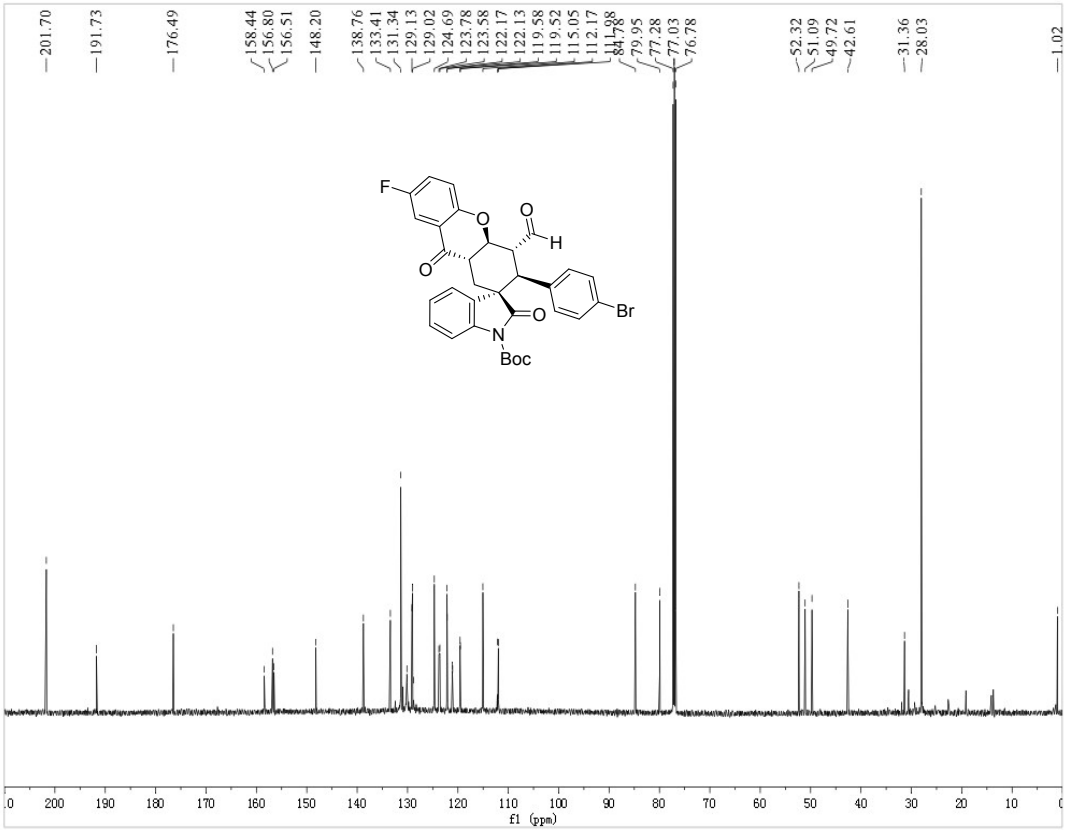
#	Time	Area	Height	Width	Area%	Symmetry
1	14.642	4076.4	95.7	0.7103	50.210	0.69
2	17.611	4042.4	79.6	0.8468	49.790	0.693



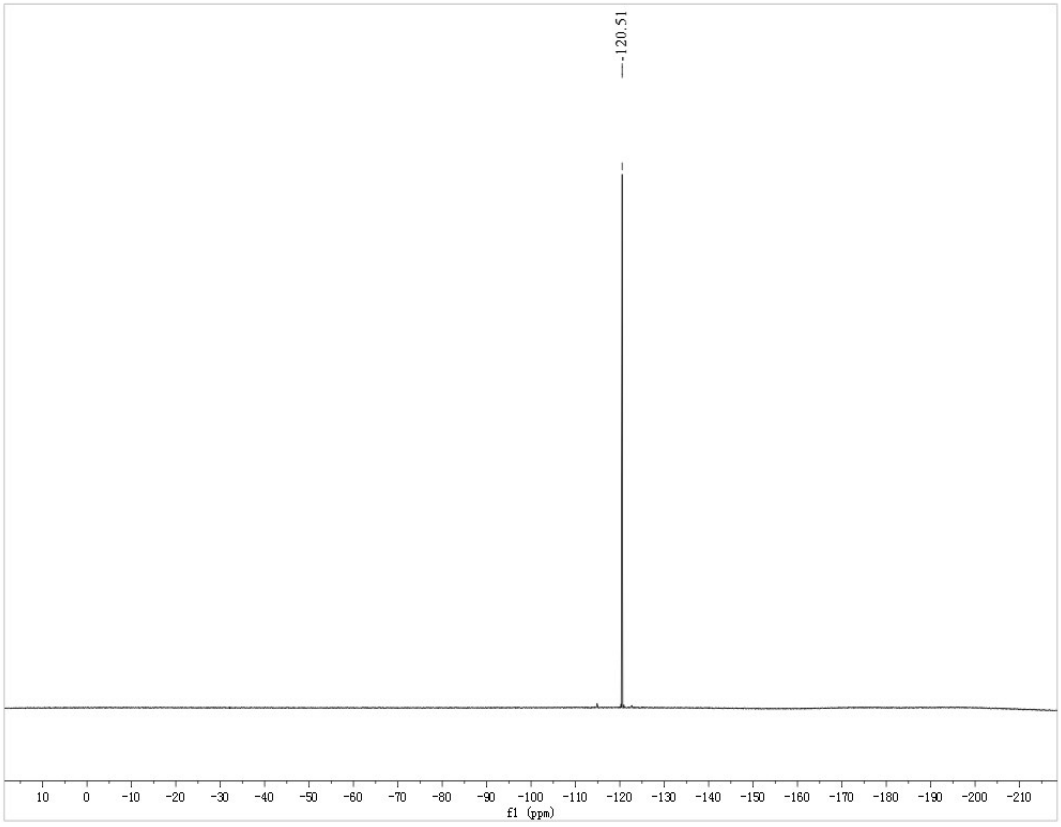
#	Time	Area	Height	Width	Area%	Symmetry
1	14.808	30098.1	731.4	0.6858	97.617	0.602
2	18.015	734.6	15.9	0.7683	2.383	1.082

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

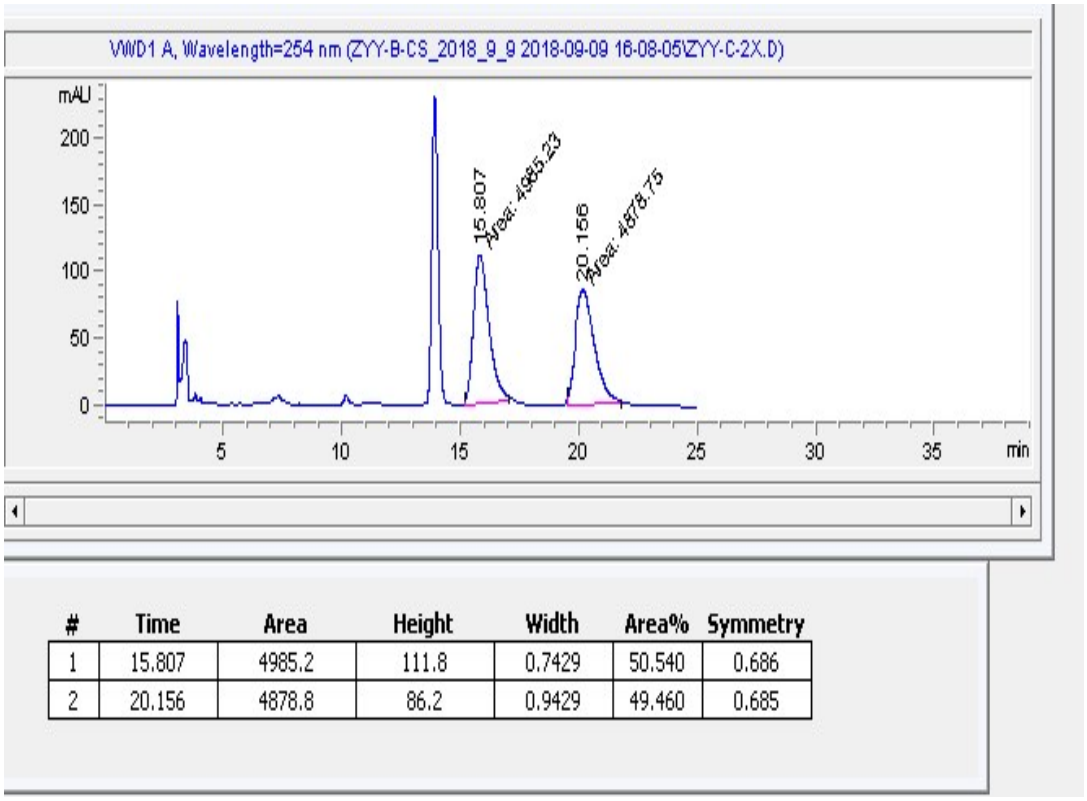




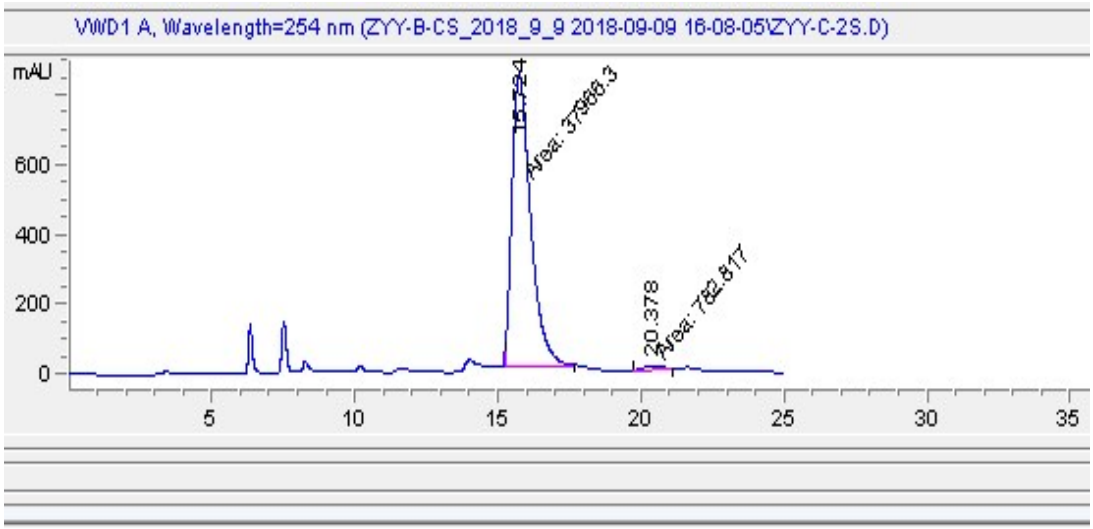
^{19}F NMR of 3k


-120.51
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3k

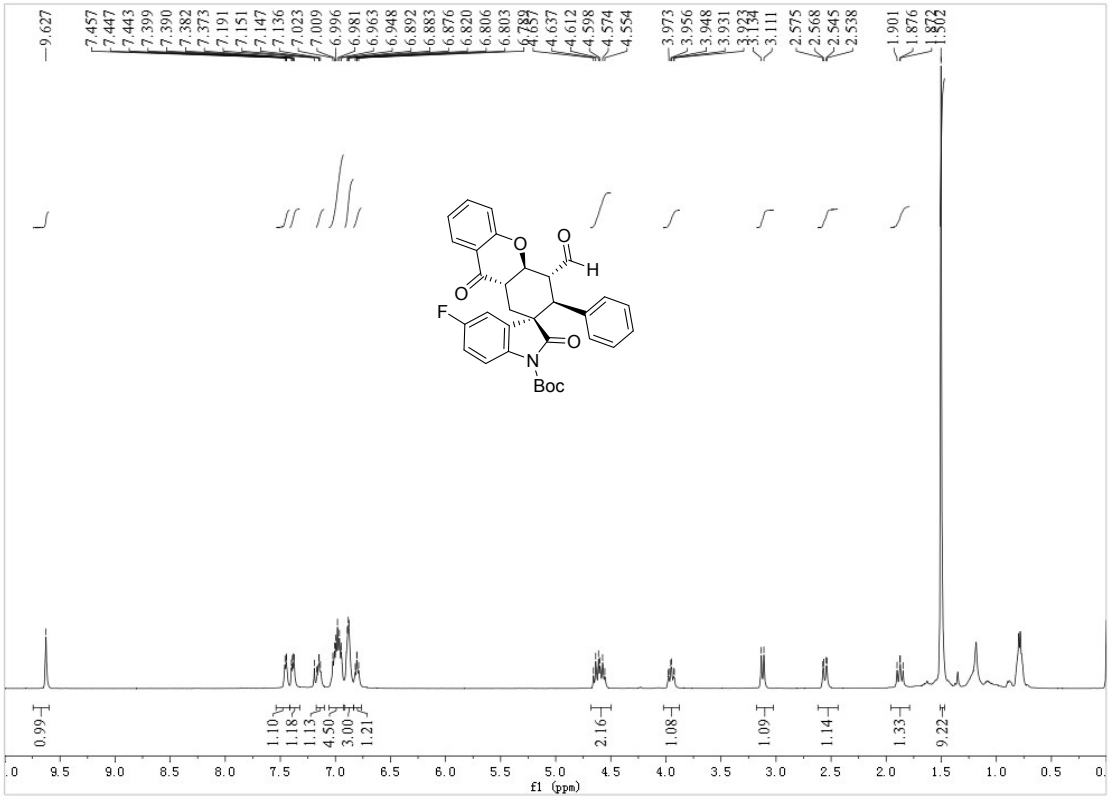


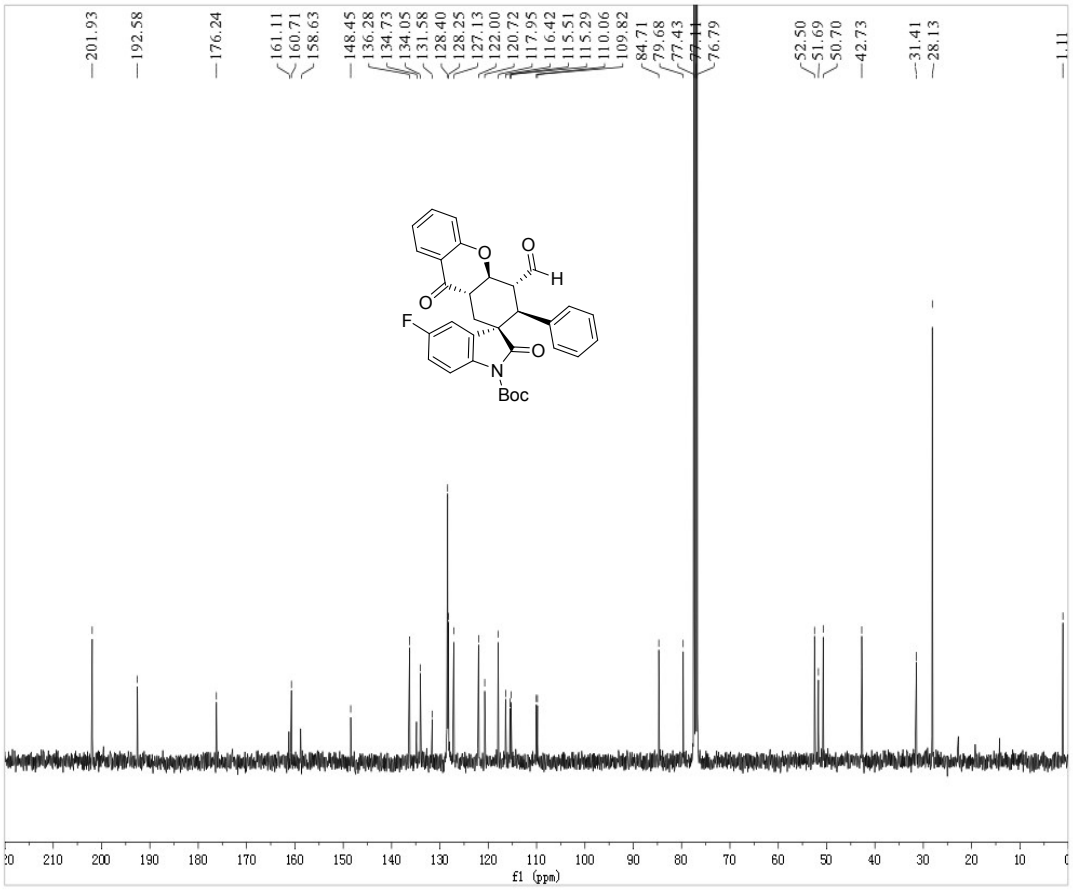
#	Time	Area	Height	Width	Area%	Symmetry
1	15.807	4985.2	111.8	0.7429	50.540	0.686
2	20.156	4878.8	86.2	0.9429	49.460	0.685



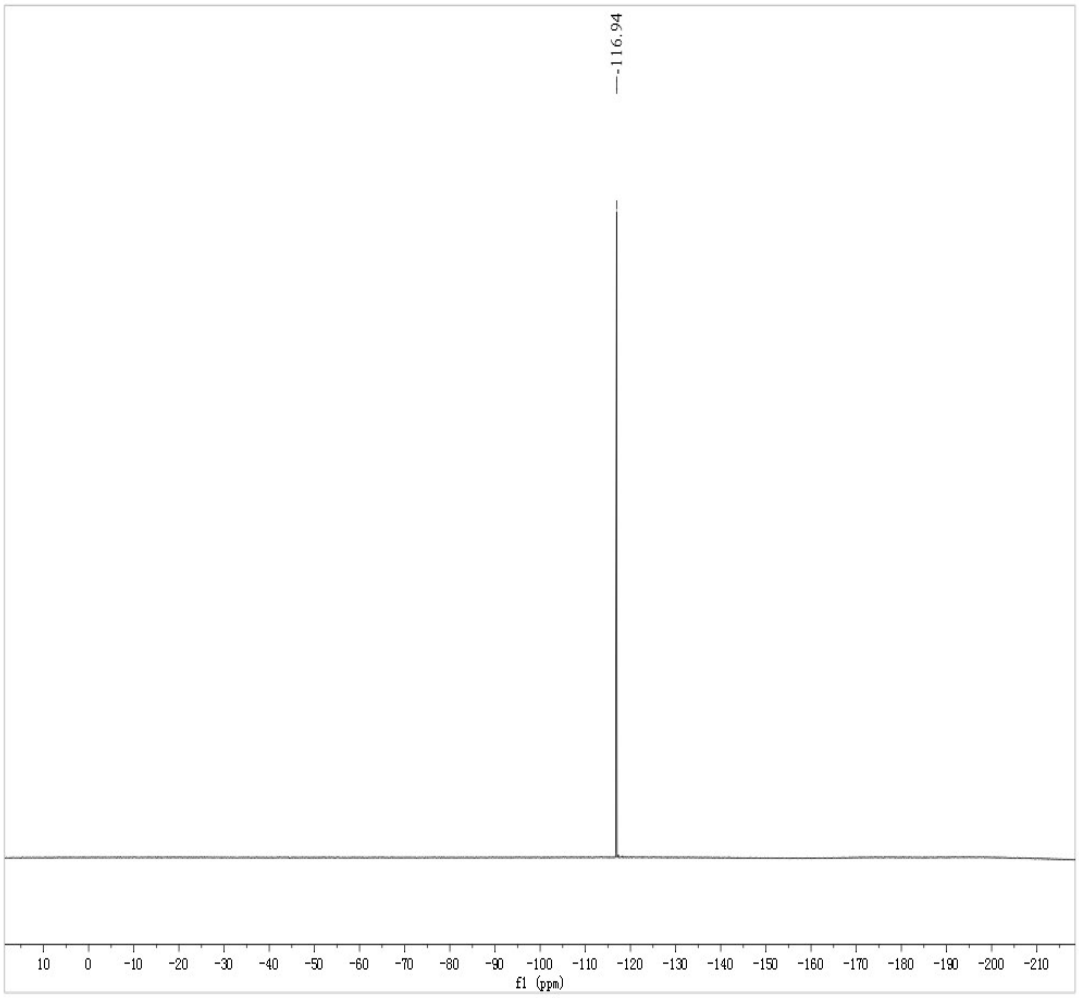
#	Time	Area	Height	Width	Area%	Symmetry
1	15.724	37966.3	844	0.7497	97.980	0.583
2	20.378	782.8	14.6	0.8923	2.020	1.142

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

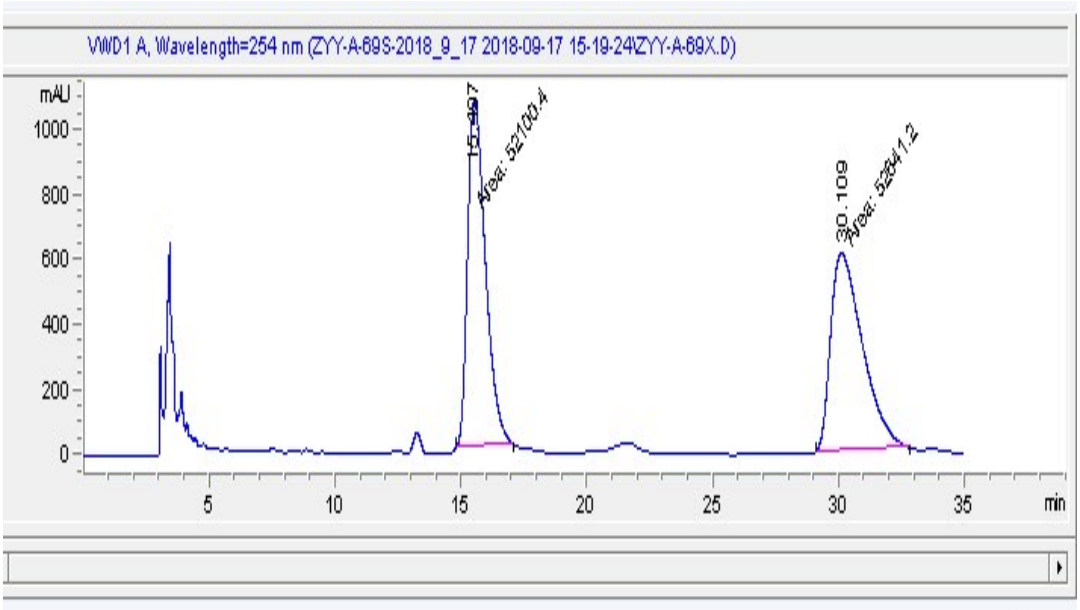




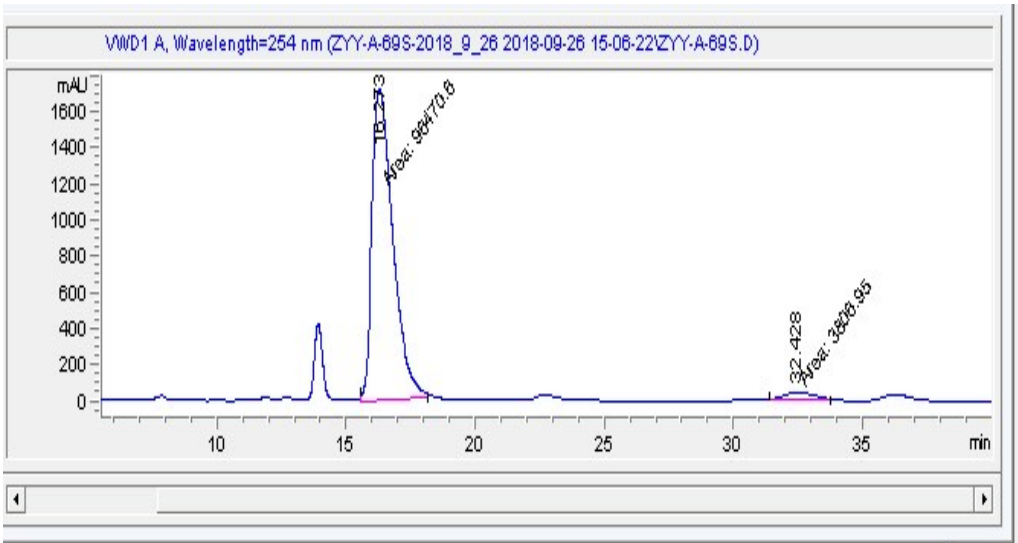
^{19}F NMR of 3l


-116.94
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3l

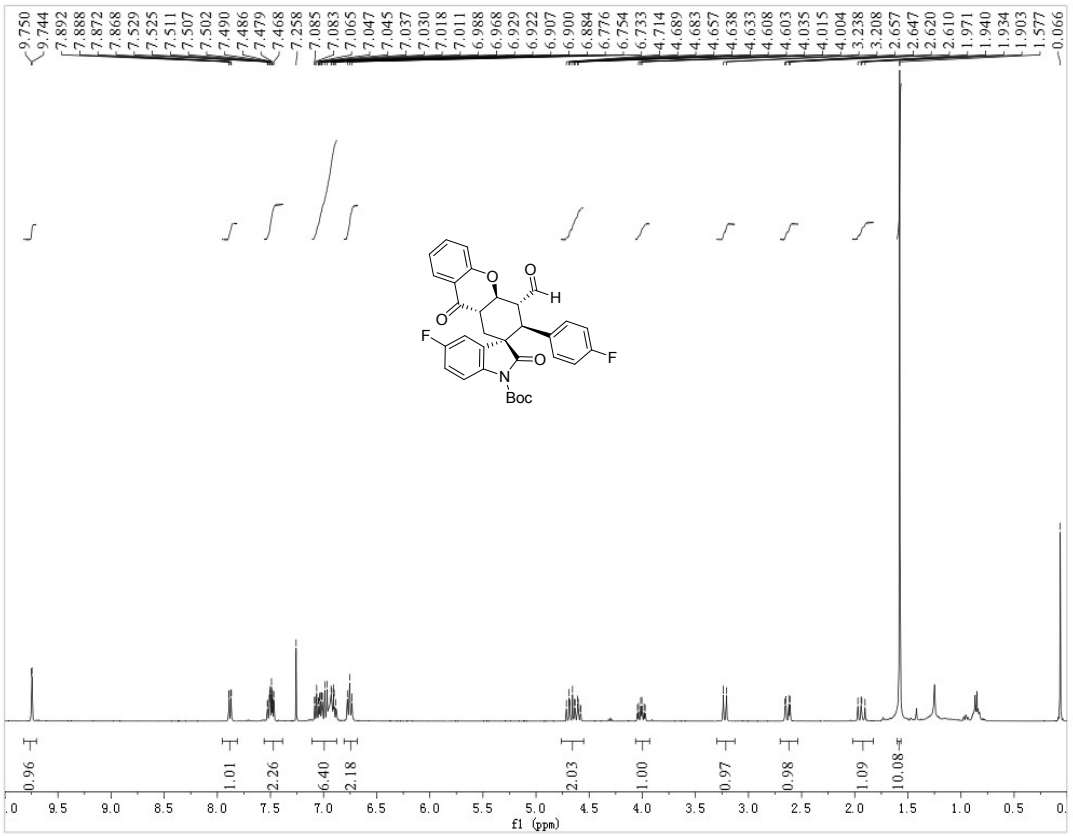


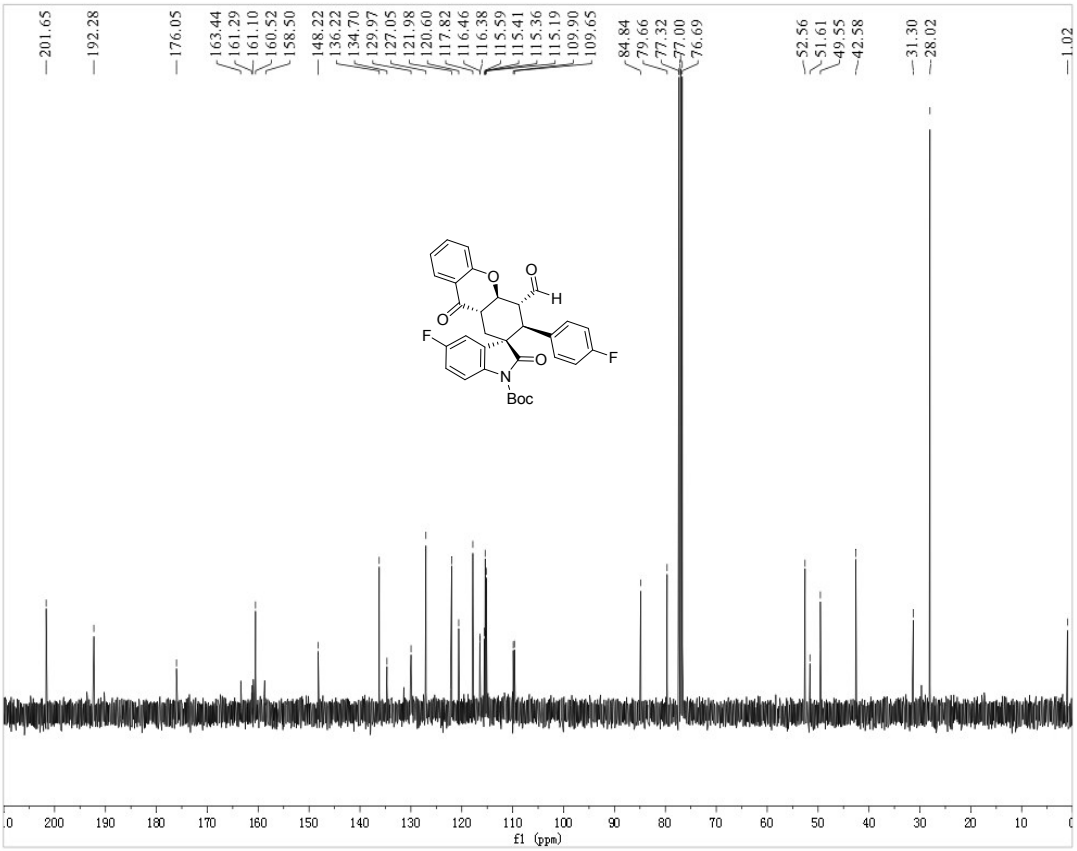
#	Time	Area	Height	Width	Area%	Symmetry
1	15.497	52100.4	1066.7	0.814	49.742	0.611
2	30.109	52641.2	604.9	1.4505	50.258	0.502



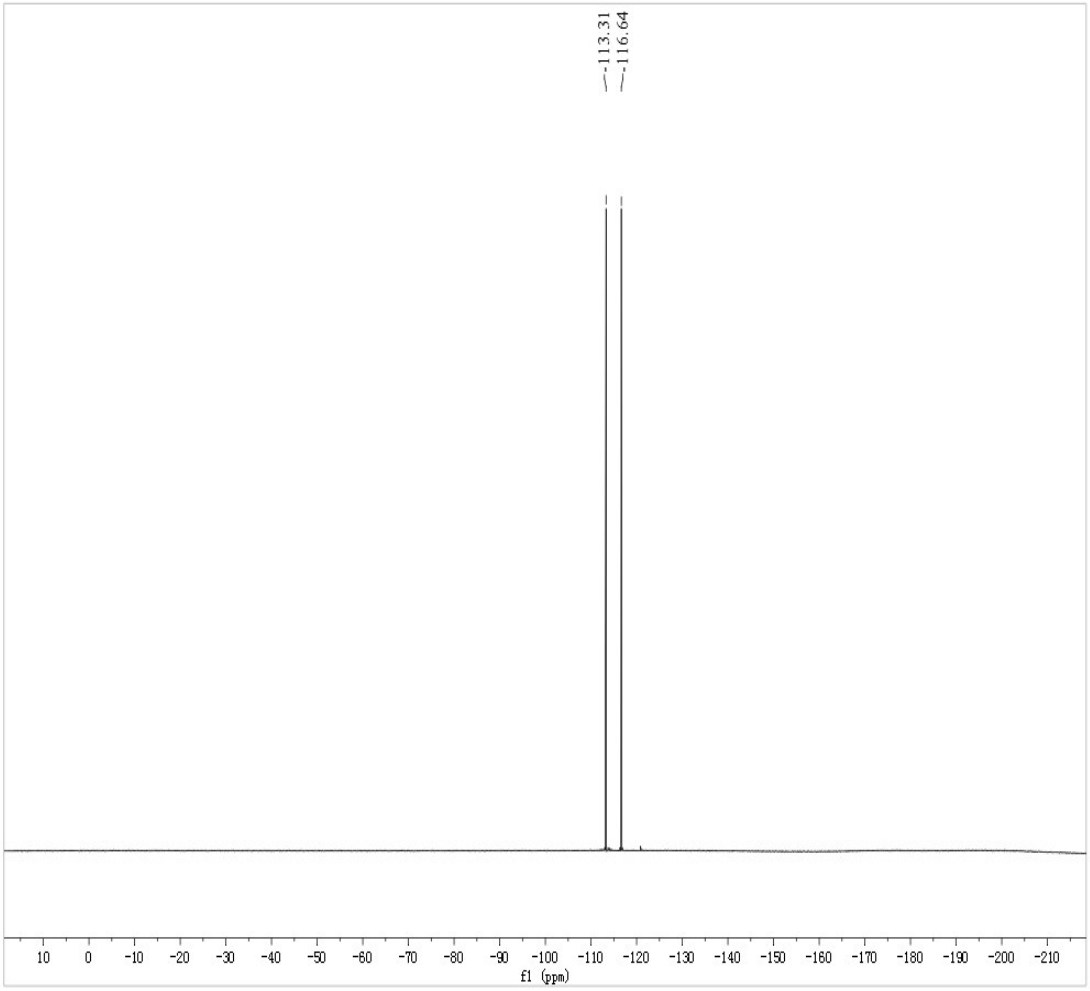
#	Time	Area	Height	Width	Area%	Symmetry
1	16.273	96470.6	1721.1	0.9342	96.204	0.565
2	32.428	3807	44.7	1.4206	3.796	0.717

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

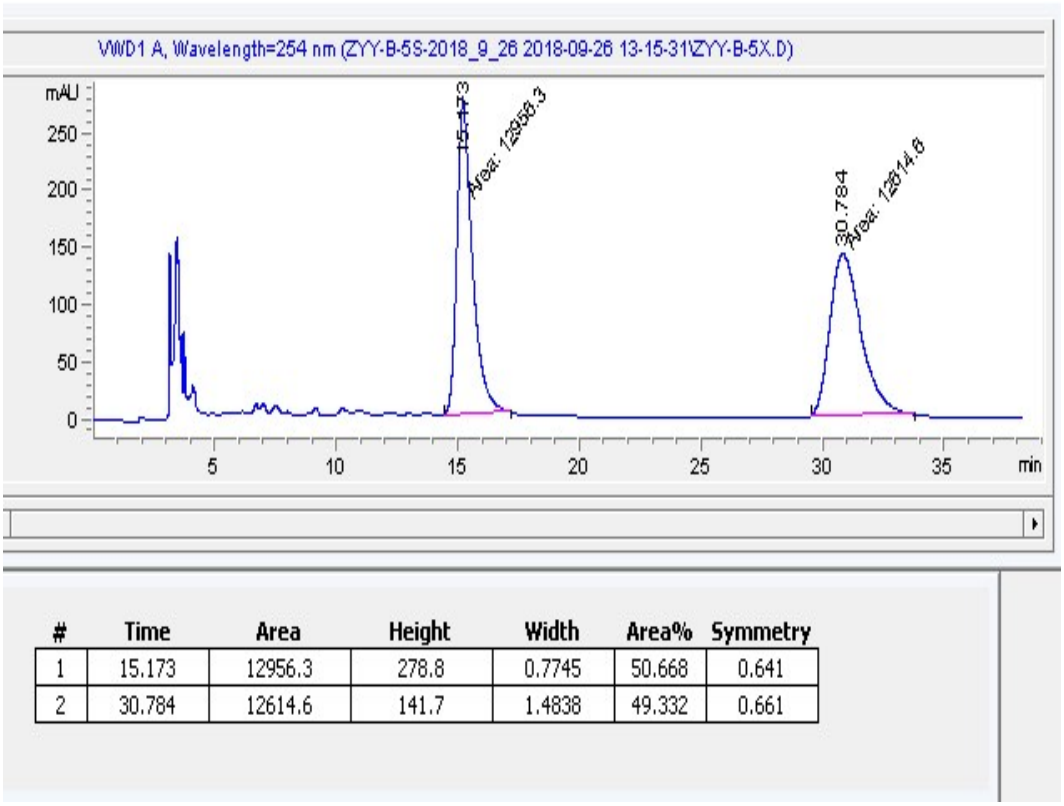




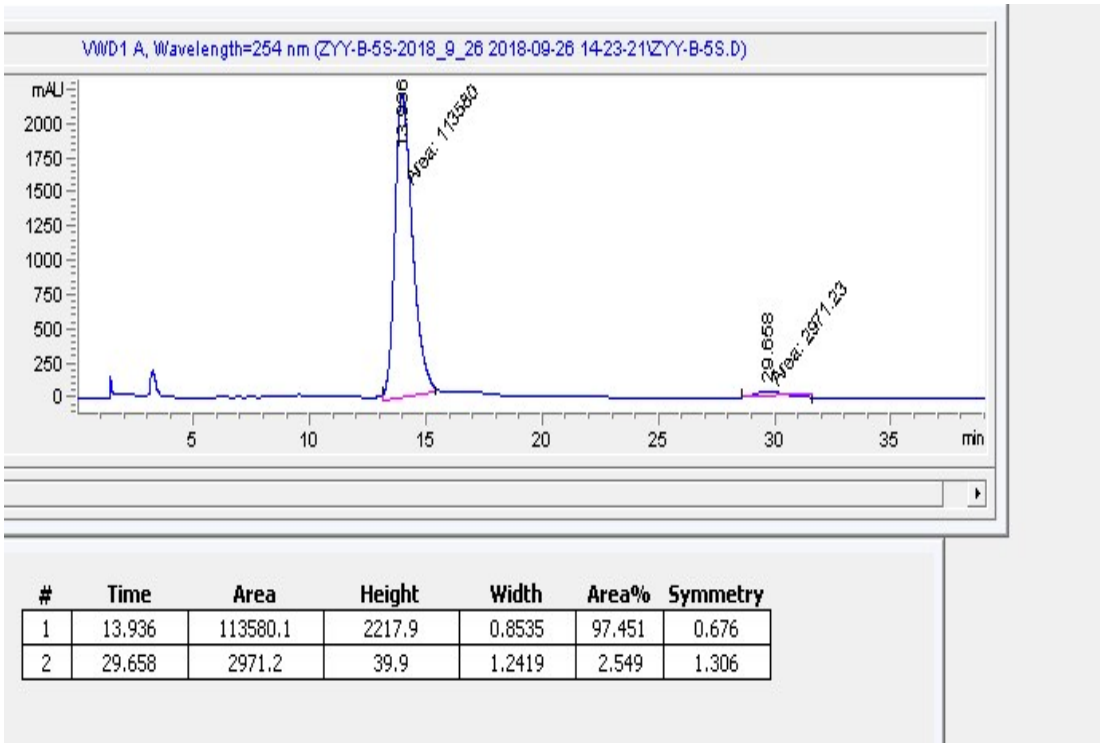
^{19}F NMR of 3m


-113.31
-116.64
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3m

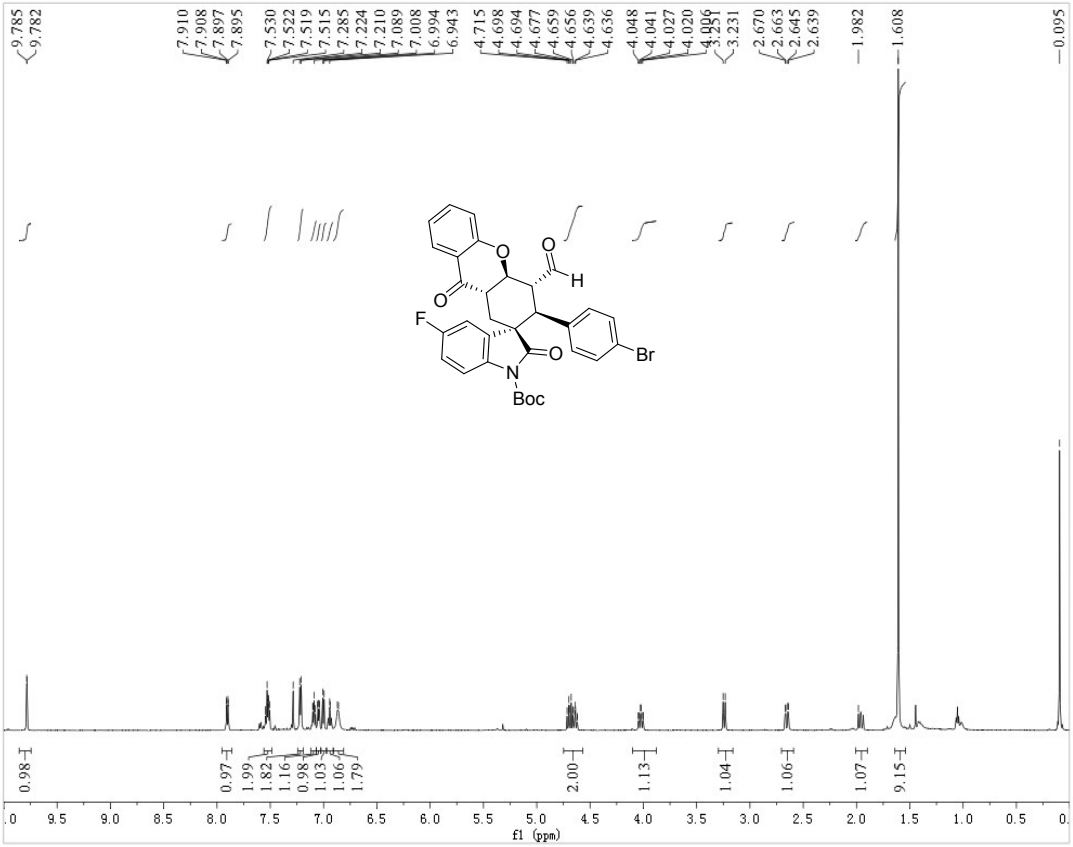


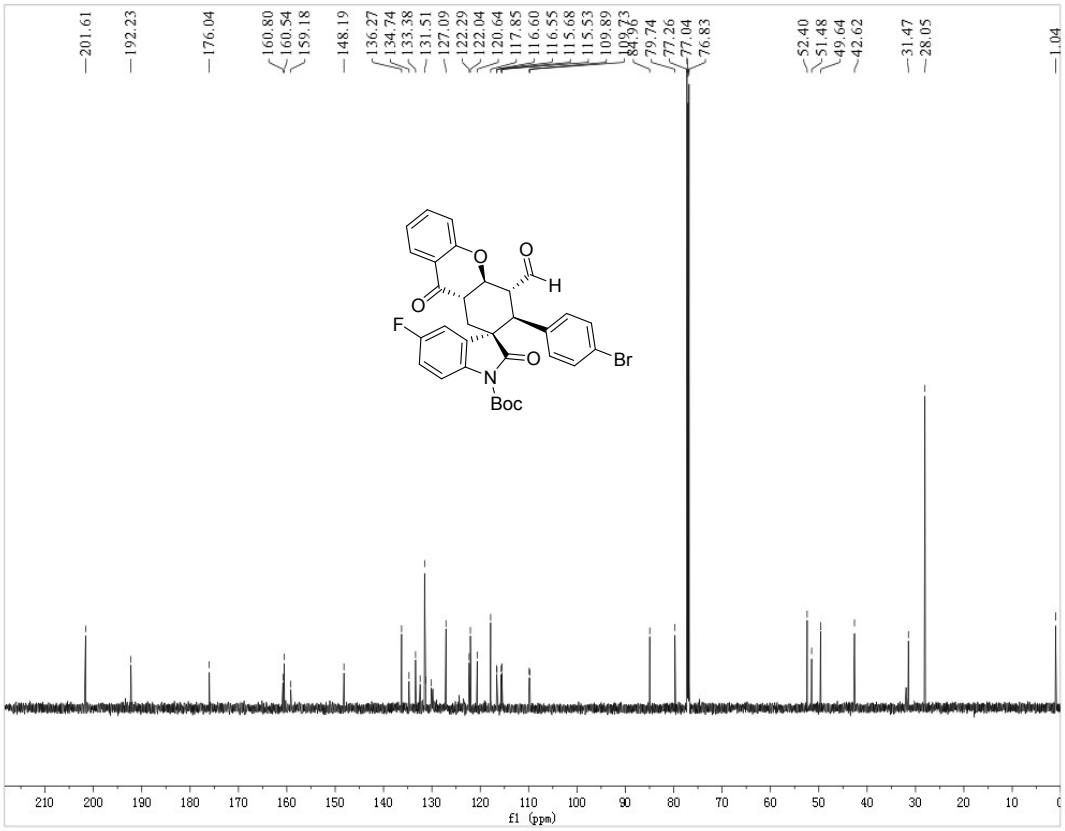
#	Time	Area	Height	Width	Area%	Symmetry
1	15.173	12956.3	278.8	0.7745	50.668	0.641
2	30.784	12614.6	141.7	1.4838	49.332	0.661



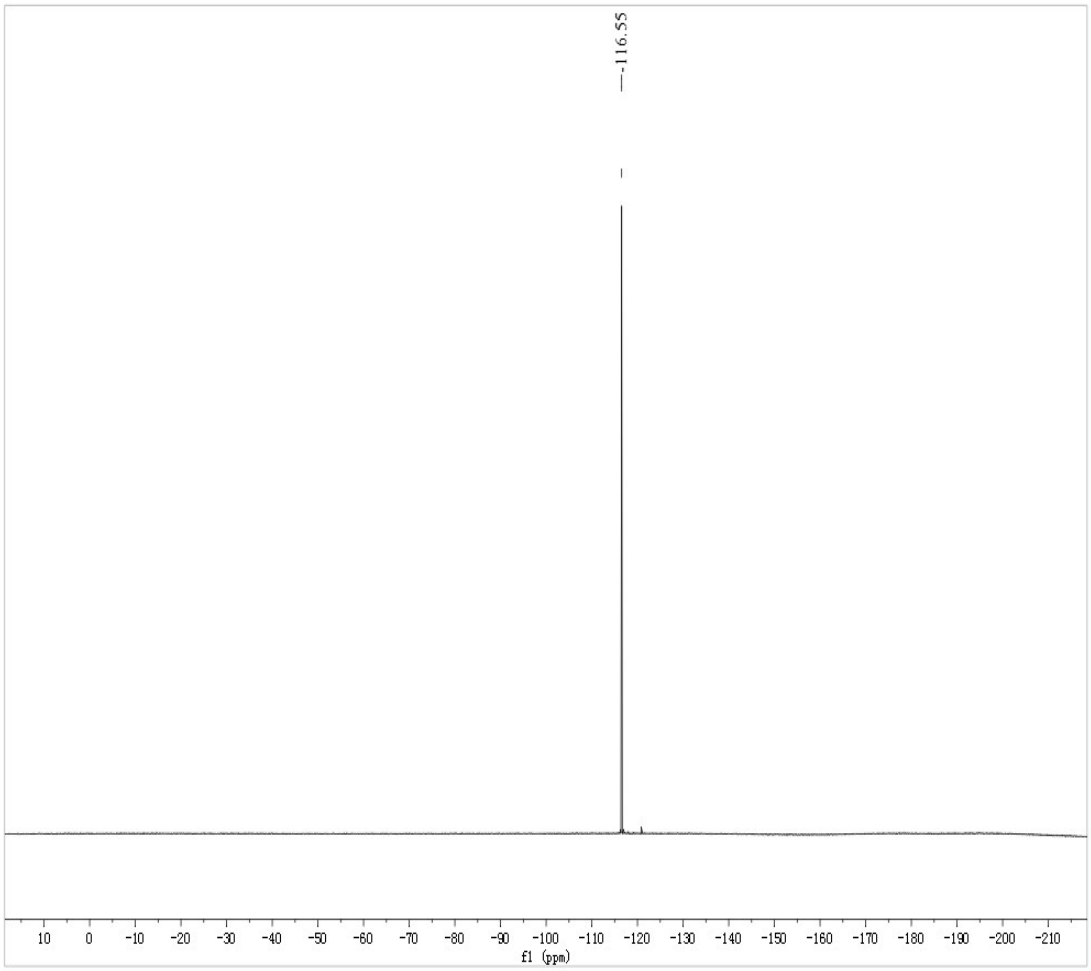
#	Time	Area	Height	Width	Area%	Symmetry
1	13.936	113580.1	2217.9	0.8535	97.451	0.676
2	29.658	2971.2	39.9	1.2419	2.549	1.306

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

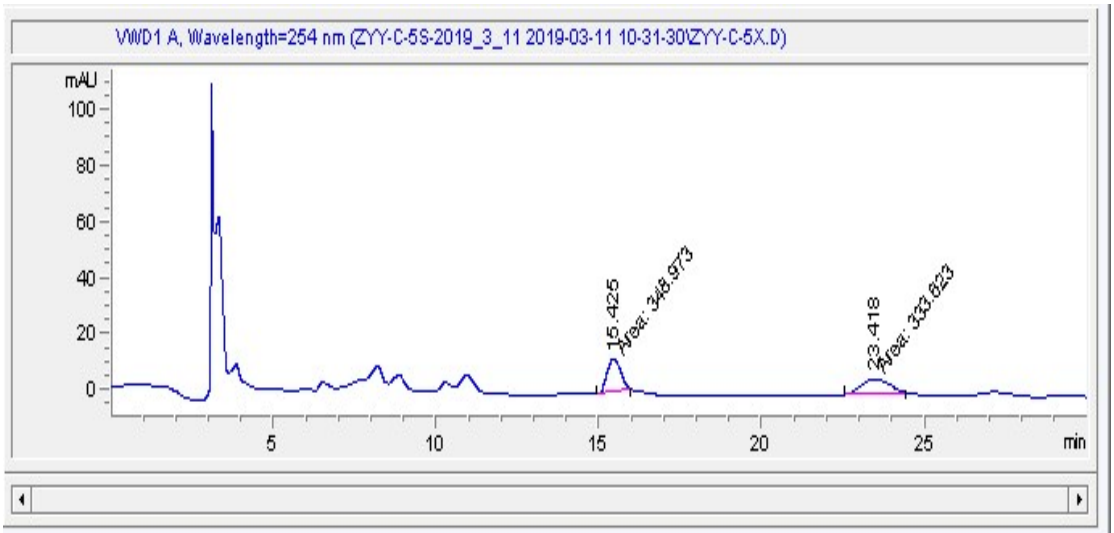




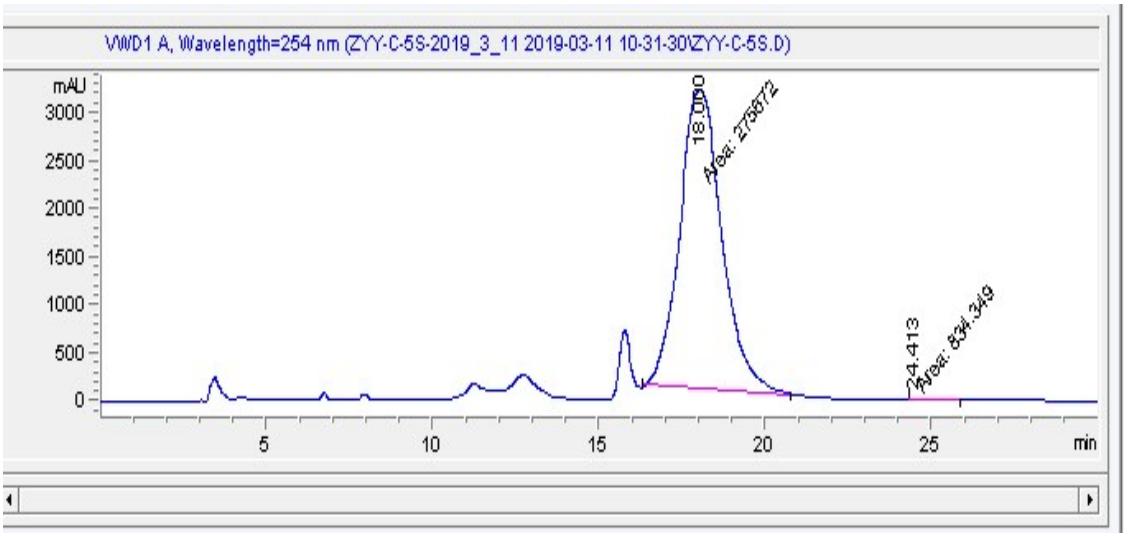
^{19}F NMR of 3n


-116.55
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3n

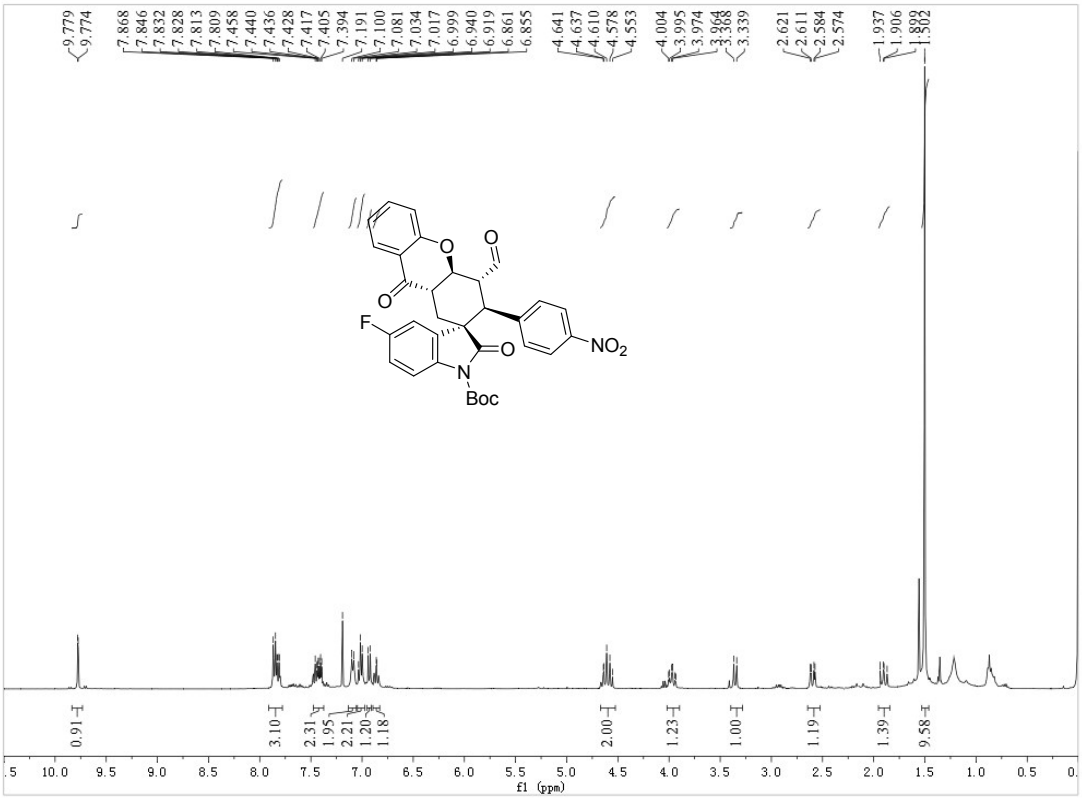


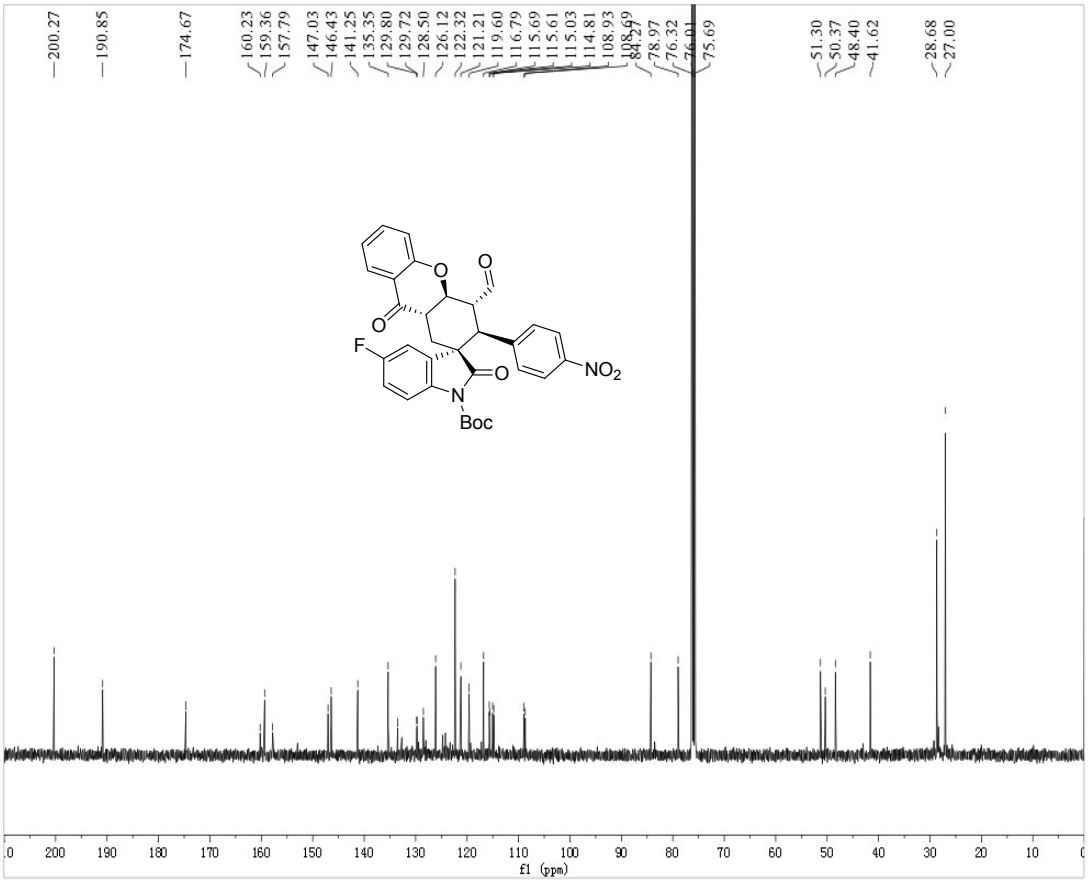
#	Time	Area	Height	Width	Area%	Symmetry
1	15.425	349	11.8	0.4911	51.124	0.87
2	23.418	333.6	5.3	1.0542	48.876	0.799



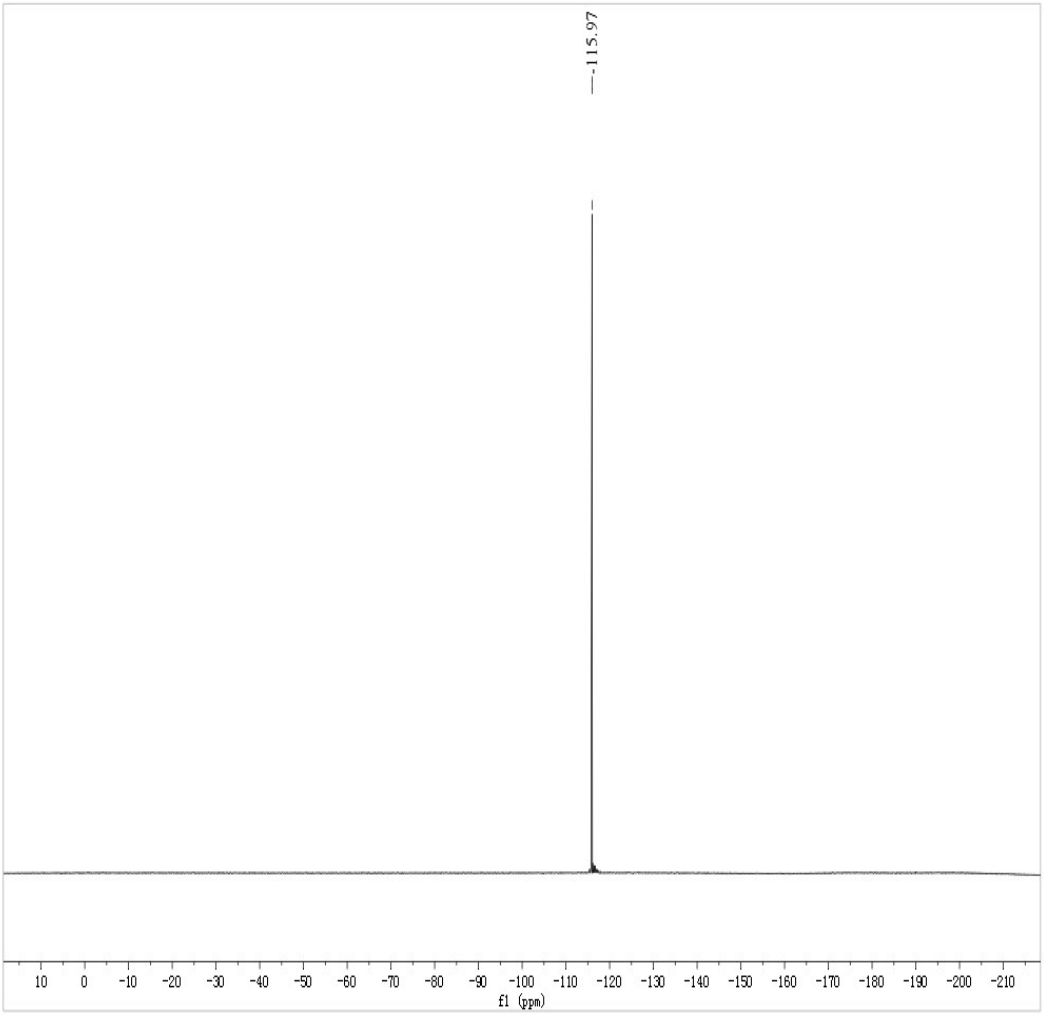
#	Time	Area	Height	Width	Area%	Symmetry
1	18	275672.1	3111.5	1.4766	99.698	0.825
2	24.413	834.3	13.4	1.0365	0.302	2.56E-2

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

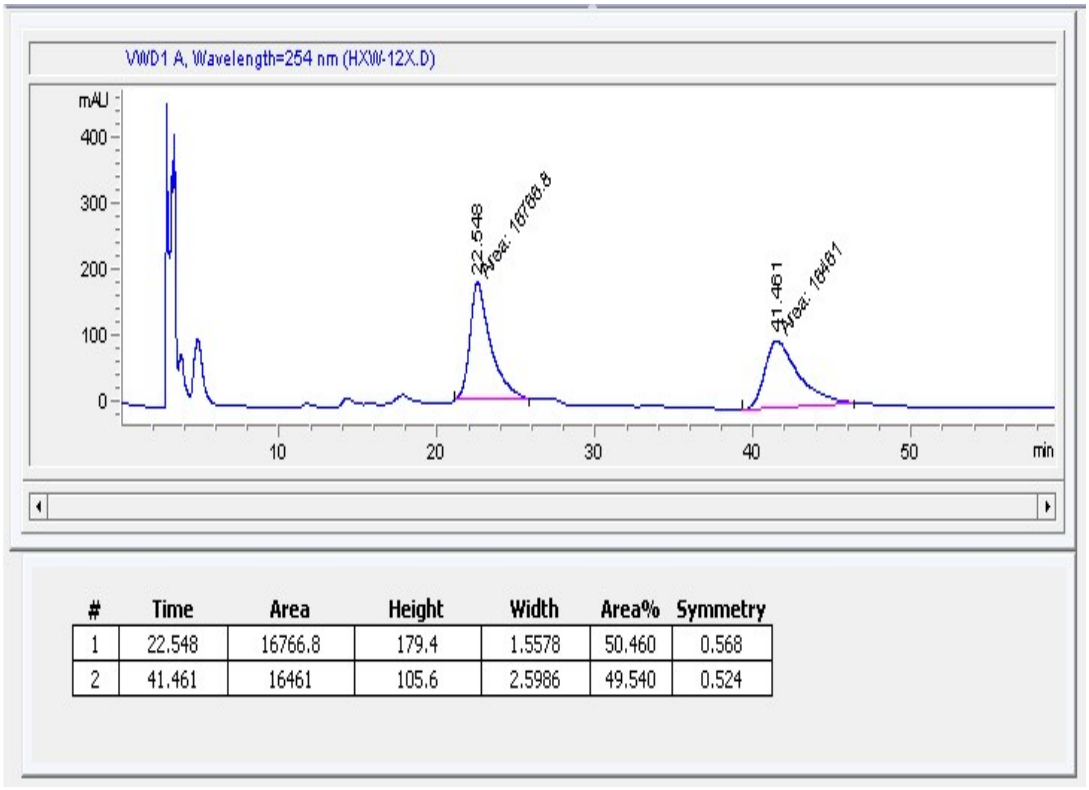




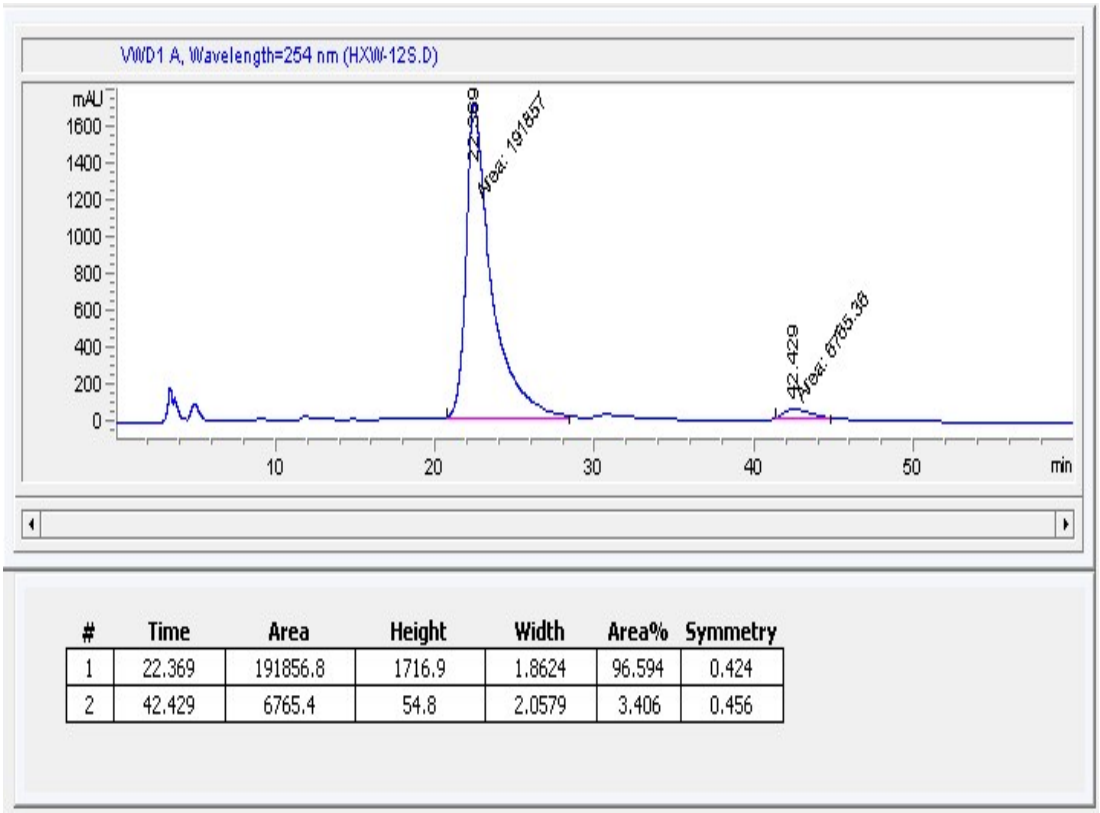
^{19}F NMR of 3o


-115.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3o

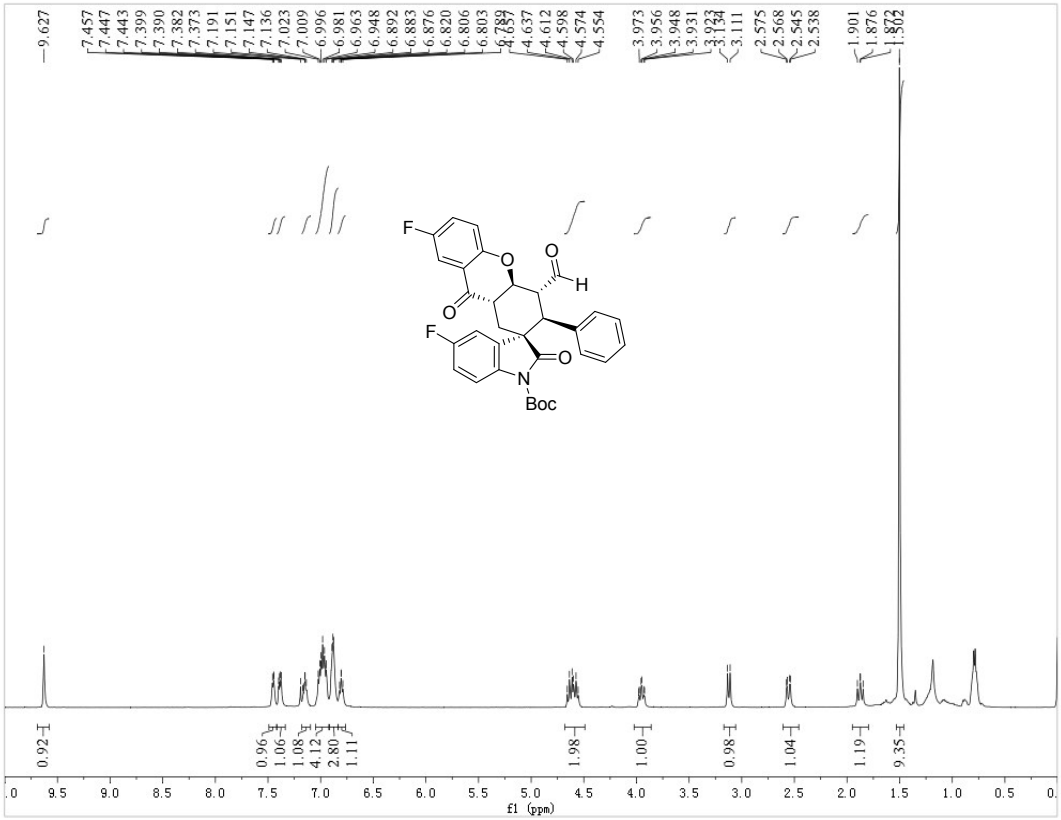


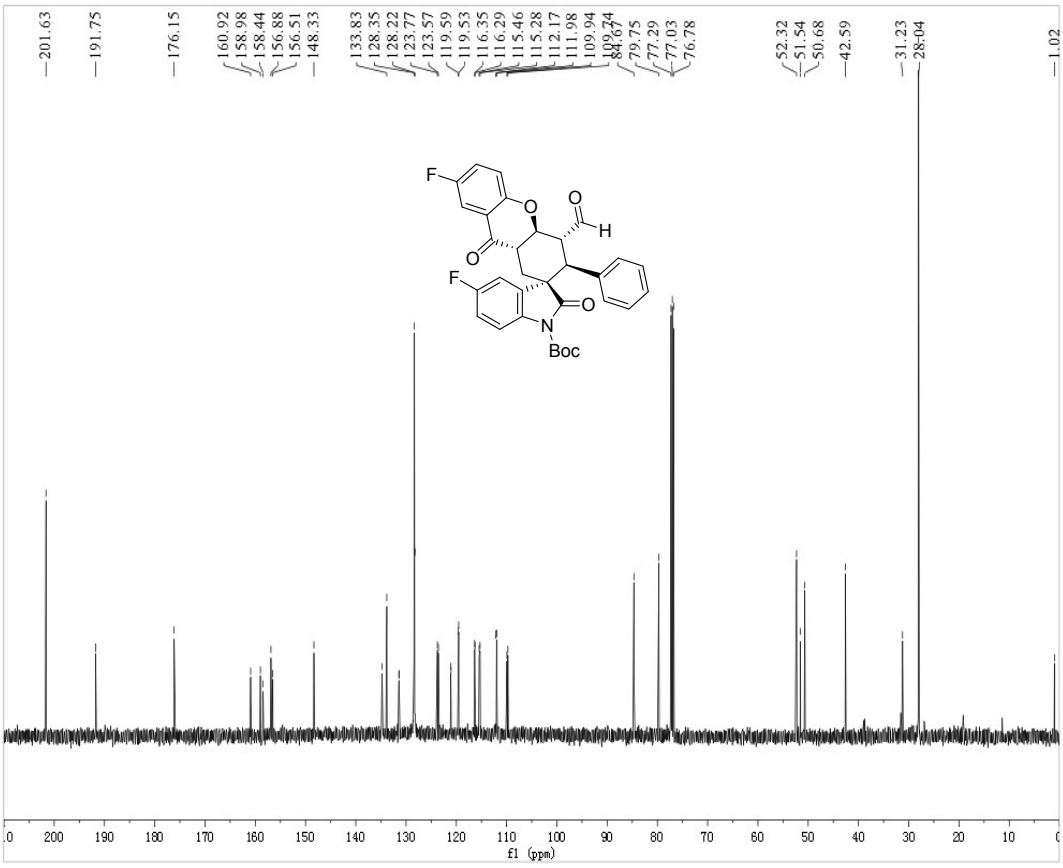
#	Time	Area	Height	Width	Area%	Symmetry
1	22.548	16766.8	179.4	1.5578	50.460	0.568
2	41.461	16461	105.6	2.5986	49.540	0.524



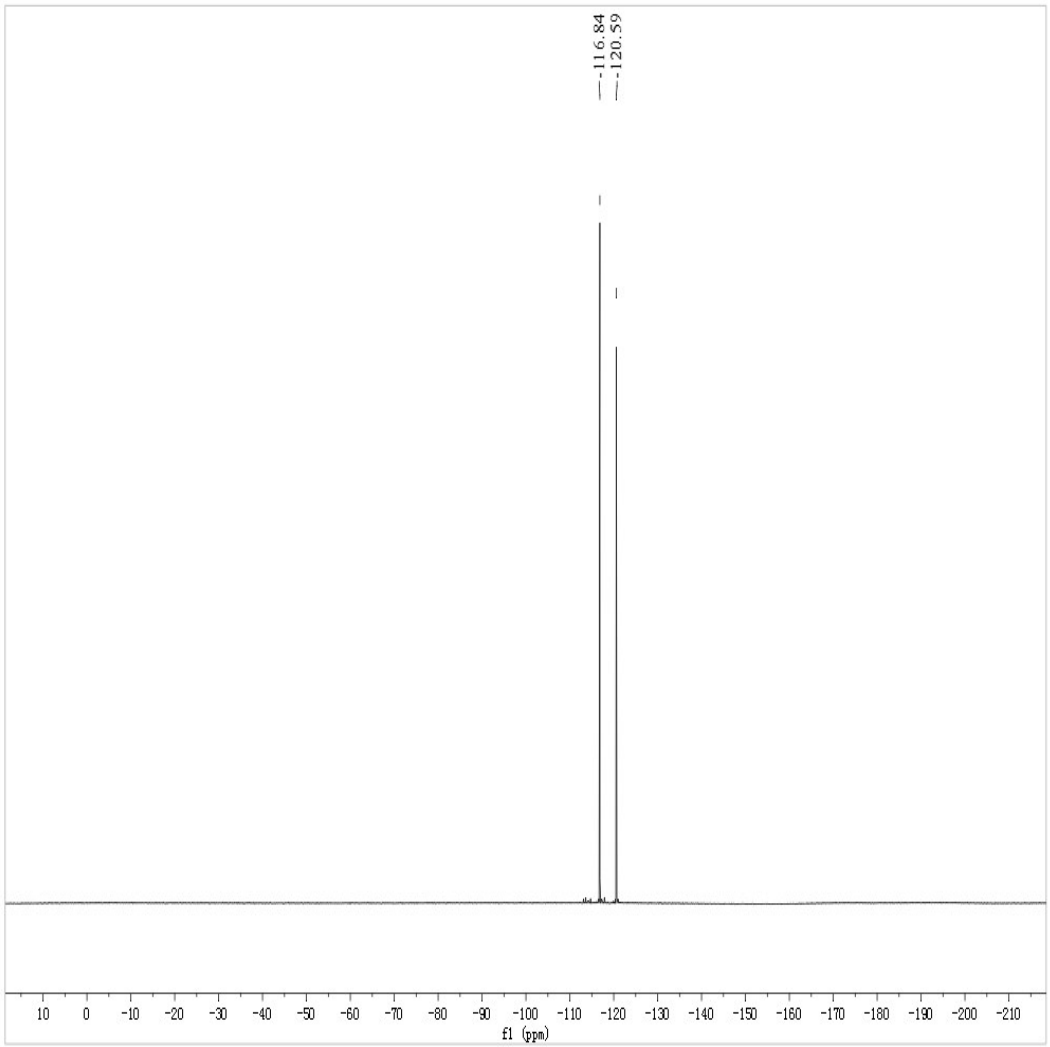
#	Time	Area	Height	Width	Area%	Symmetry
1	22.369	191856.8	1716.9	1.8624	96.594	0.424
2	42.429	6765.4	54.8	2.0579	3.406	0.456

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





^{19}F NMR of 3p


-116.84
-120.59
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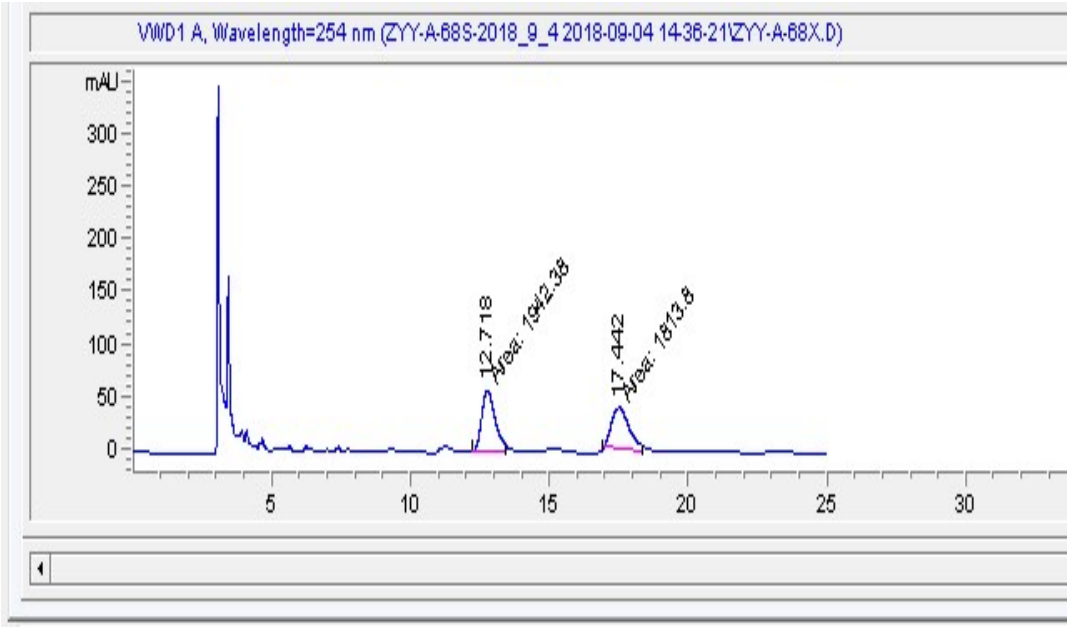
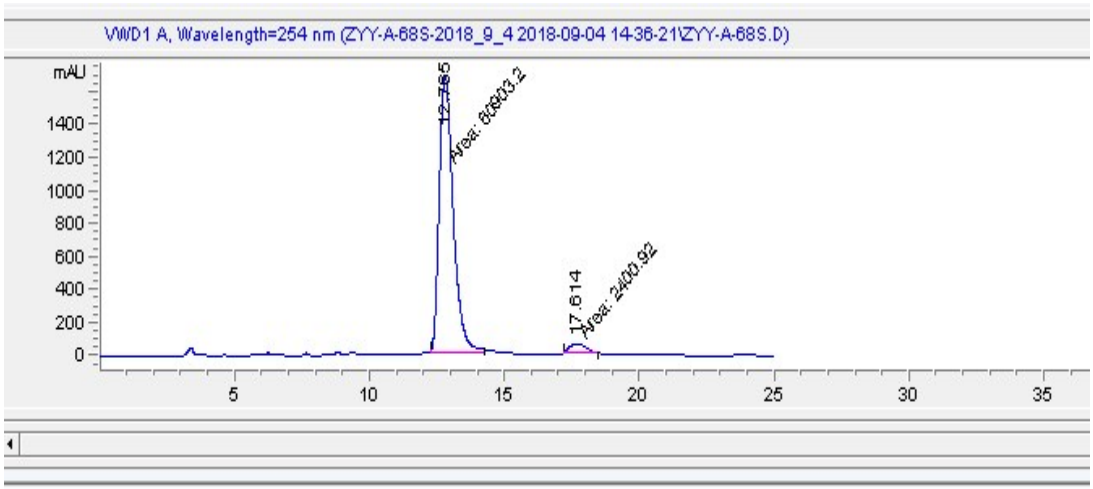
f1 (ppm)

HPLC of 3p

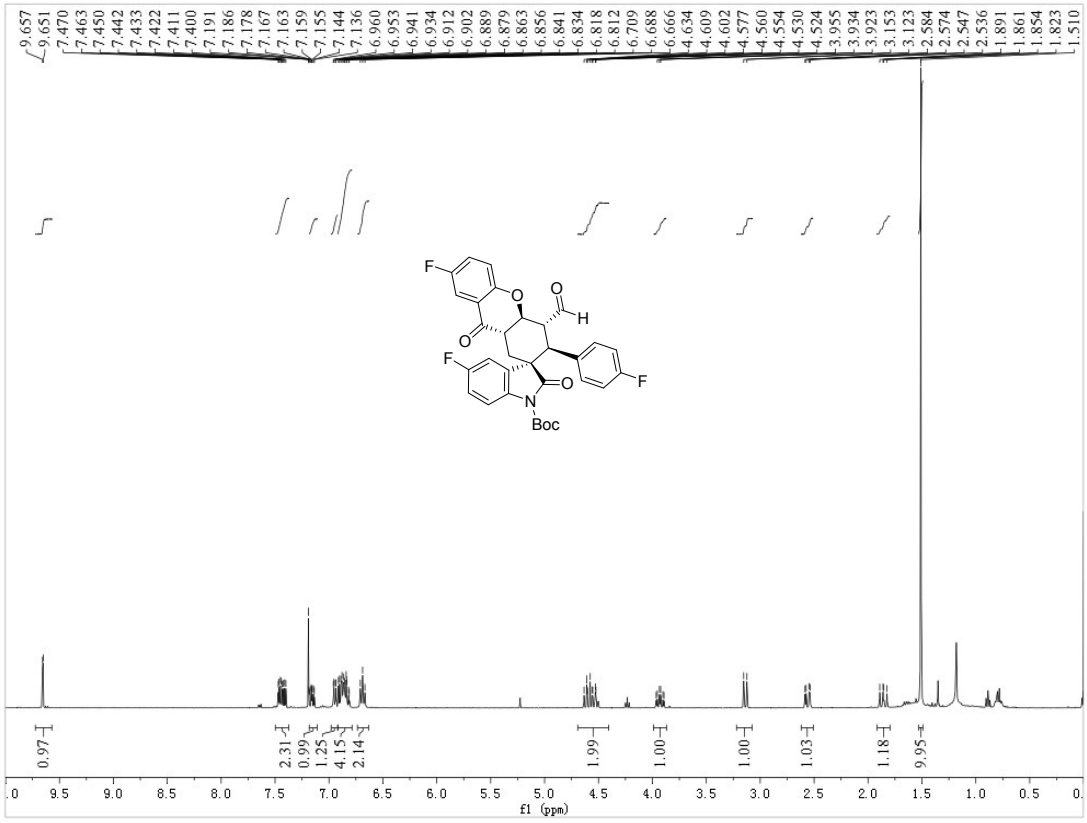


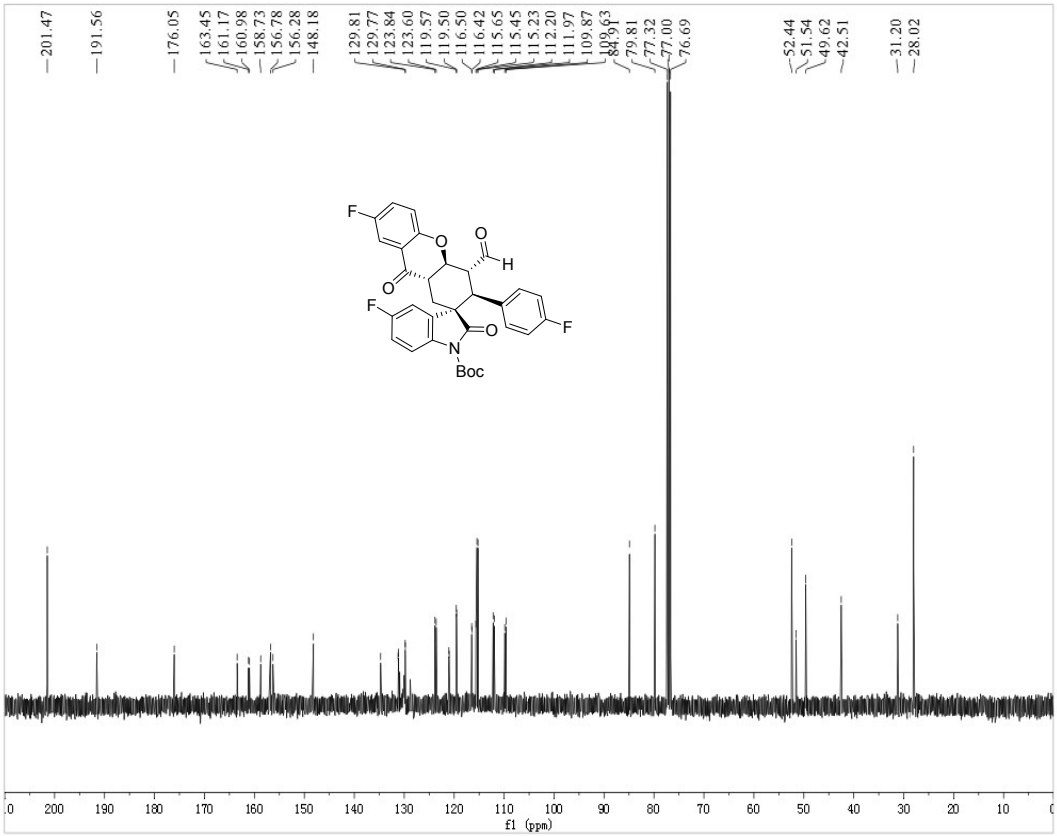
#	Time	Area	Height	Width	Area%	Symmetry
1	12.718	1942.4	58.5	0.5534	51.712	0.691
2	17.442	1813.8	40.5	0.7469	48.288	0.654



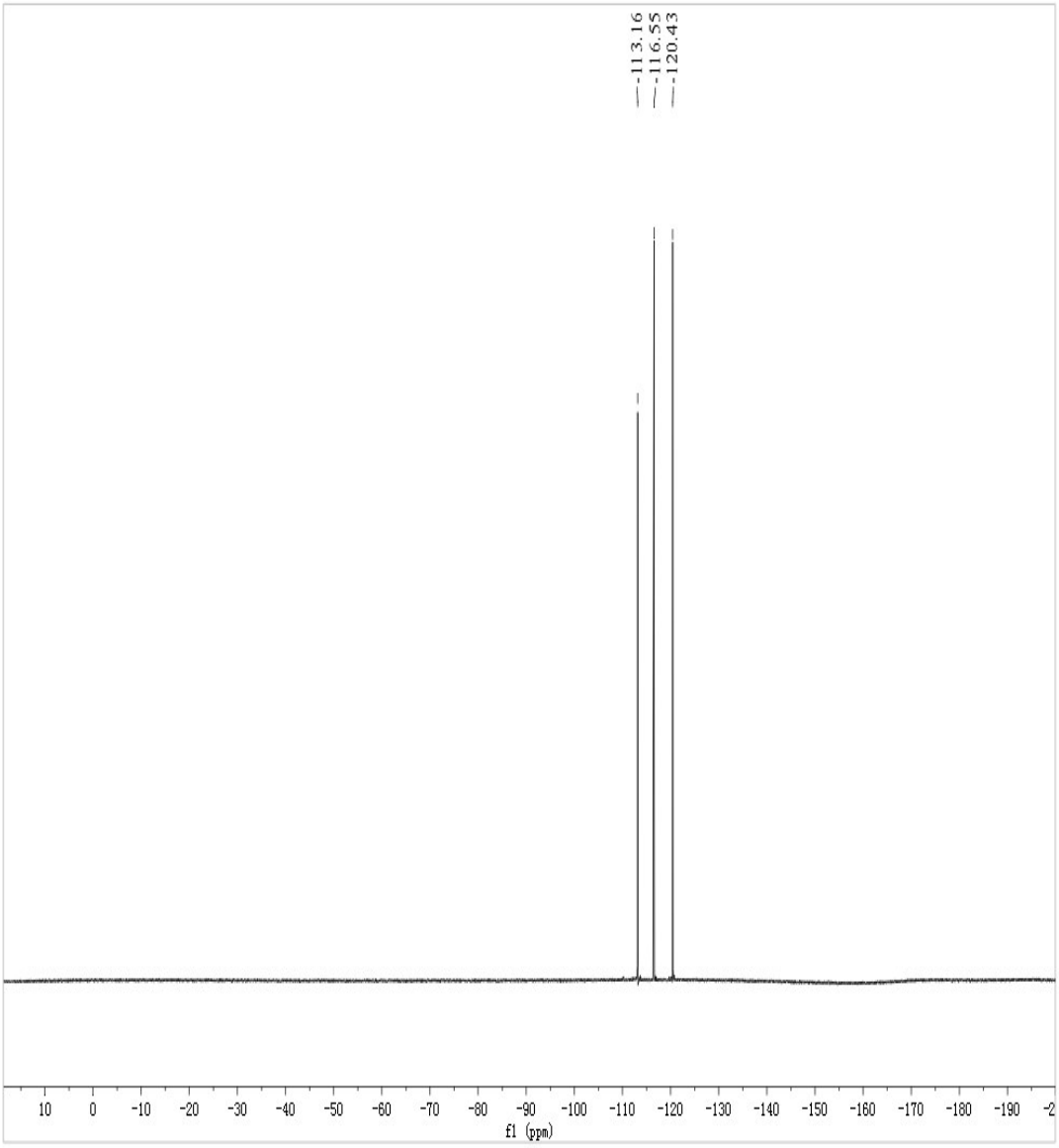
#	Time	Area	Height	Width	Area%	Symmetry
1	12.765	60903.2	1686.7	0.6018	96.207	0.703
2	17.614	2400.9	60.2	0.6653	3.793	0.837

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

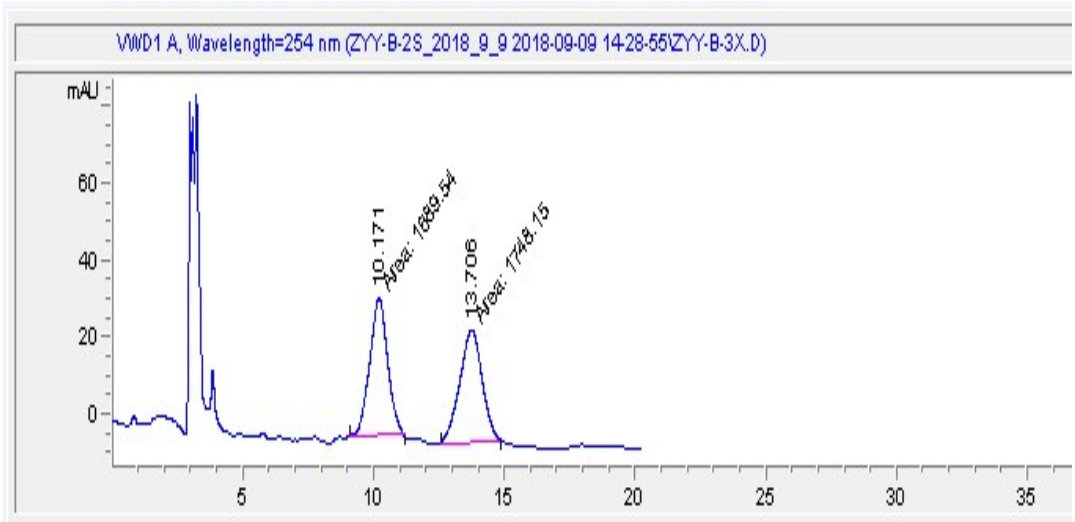




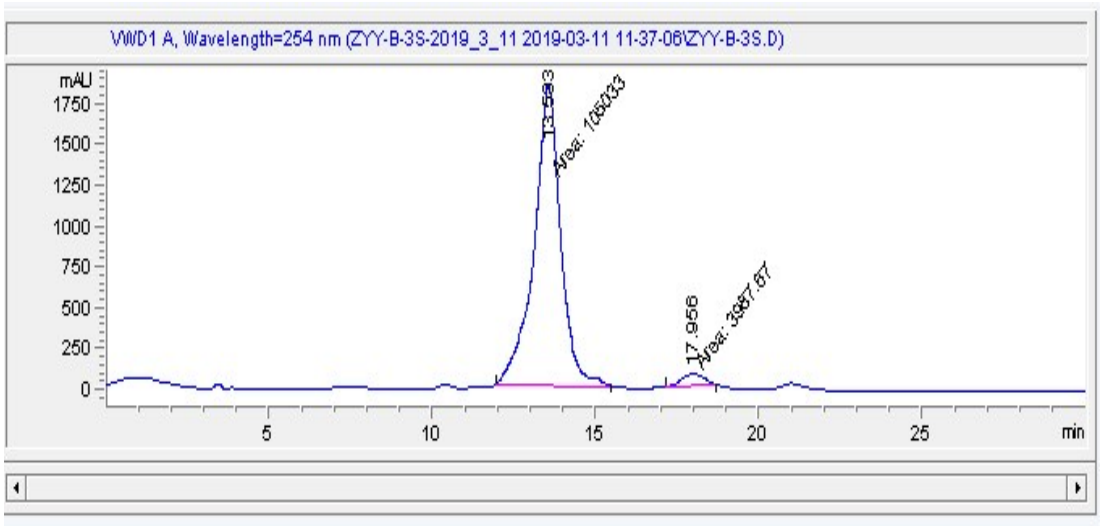
^{19}F NMR of 3q


-113.16
-116.55
-120.43
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

HPLC of 3q

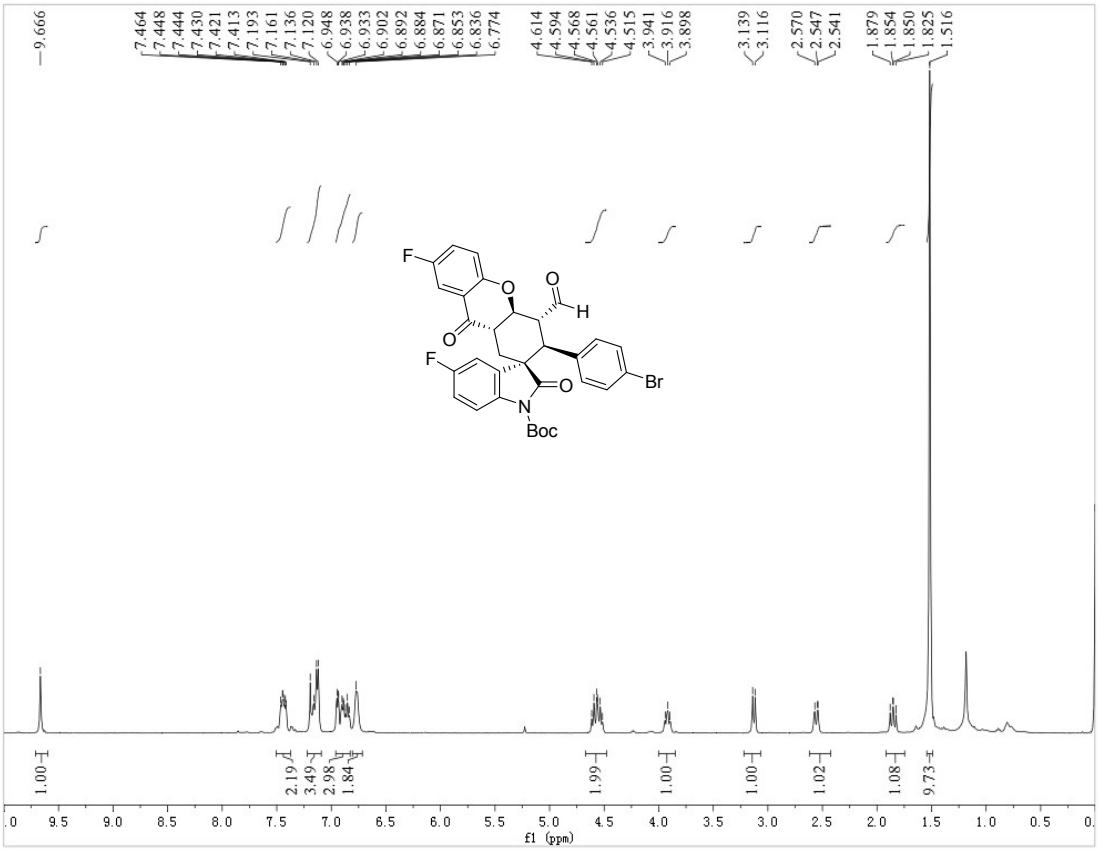


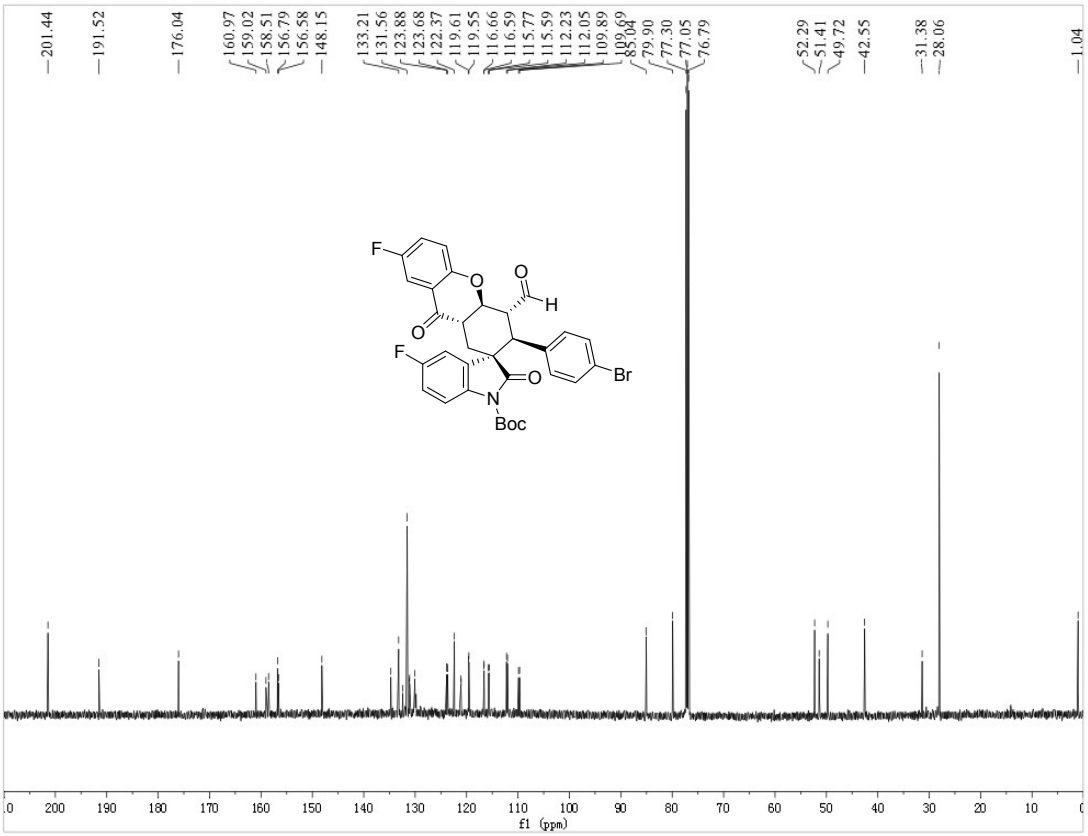
#	Time	Area	Height	Width	Area%	Symmetry
1	10.171	1689.5	35.8	0.7876	49.147	1.062
2	13.706	1748.2	29.2	0.9978	50.853	1.107



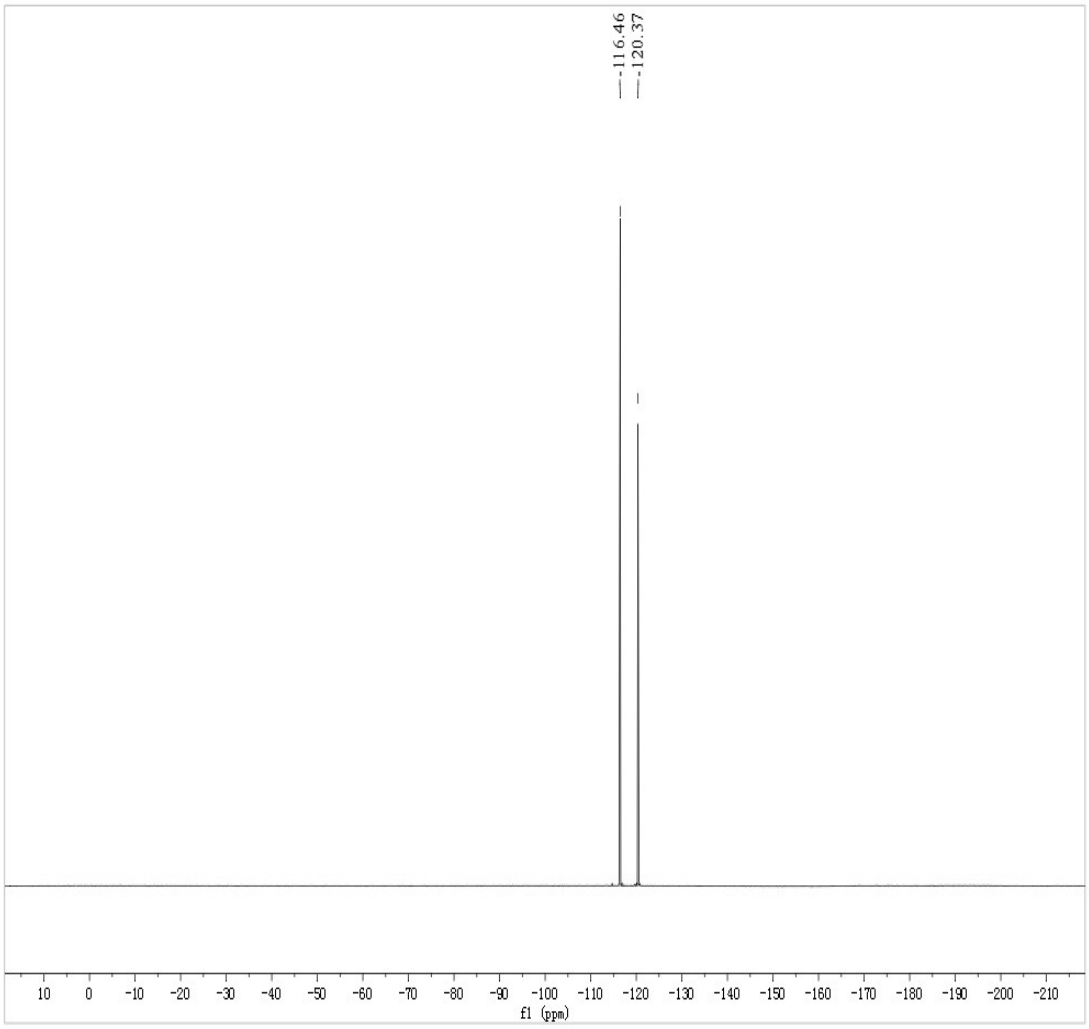
#	Time	Area	Height	Width	Area%	Symmetry
1	13.533	105033.3	1843.8	0.9494	96.342	1.156
2	17.956	3987.7	75.7	0.8776	3.658	1.016

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

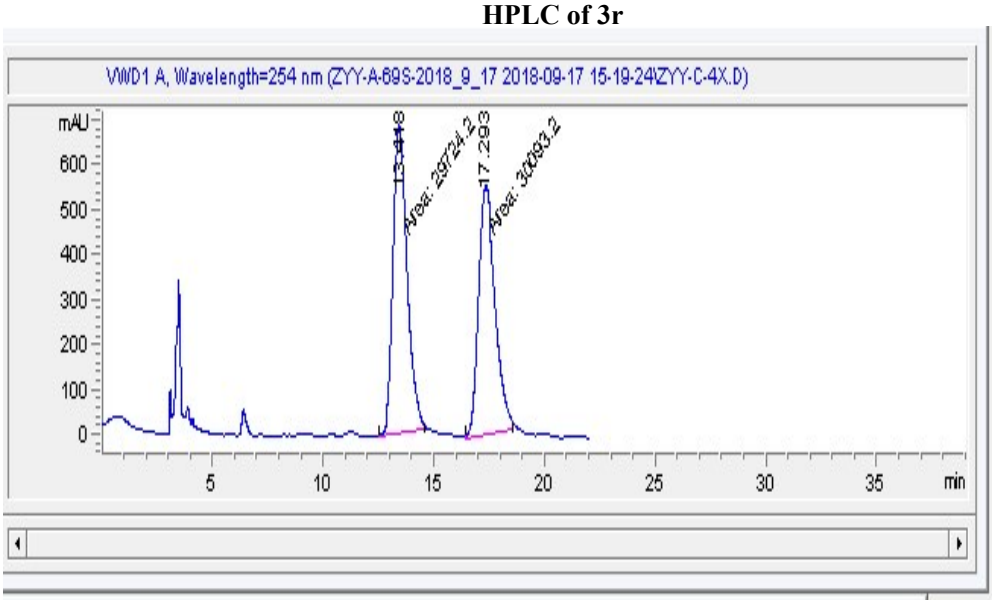




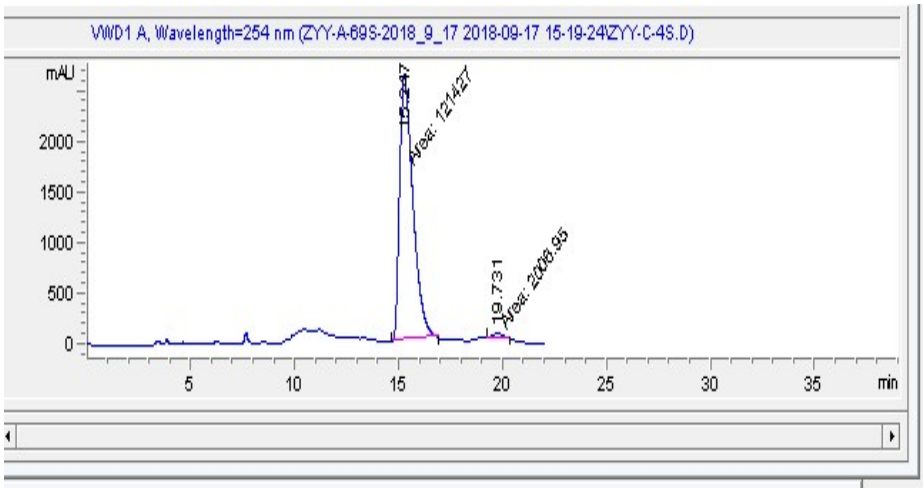
^{19}F NMR of 3r


-116.46
-120.37
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HPLC of 3r

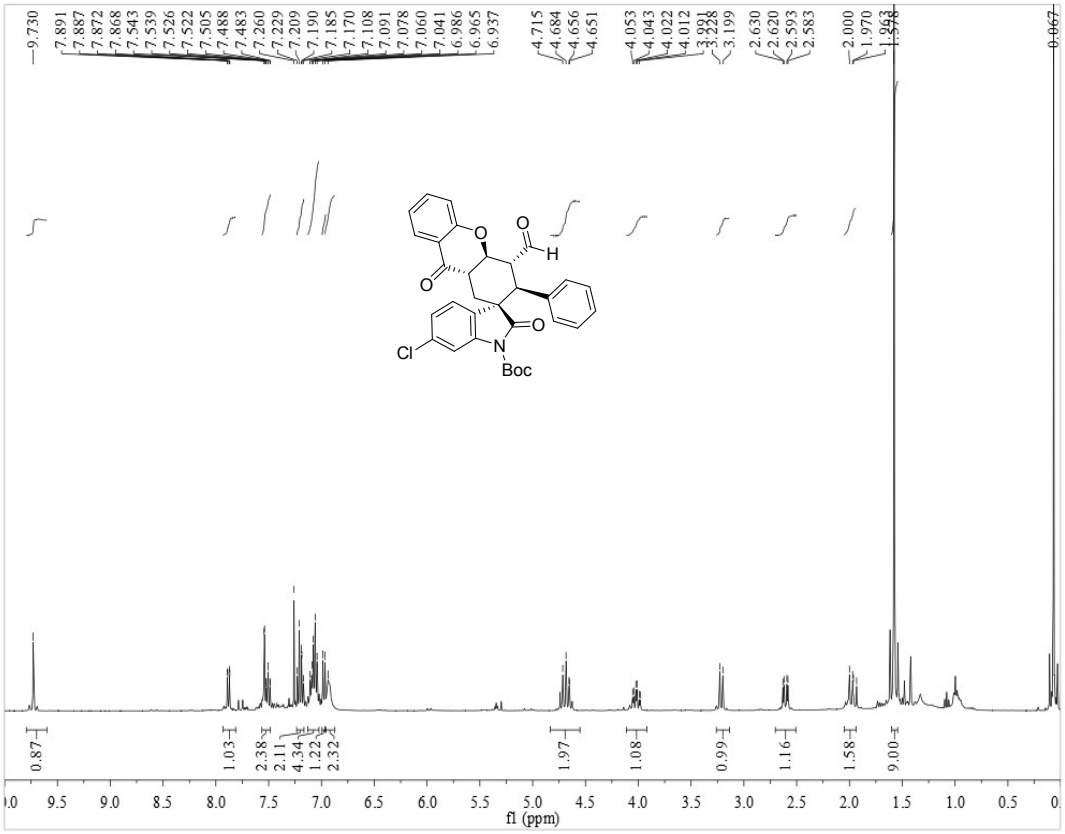


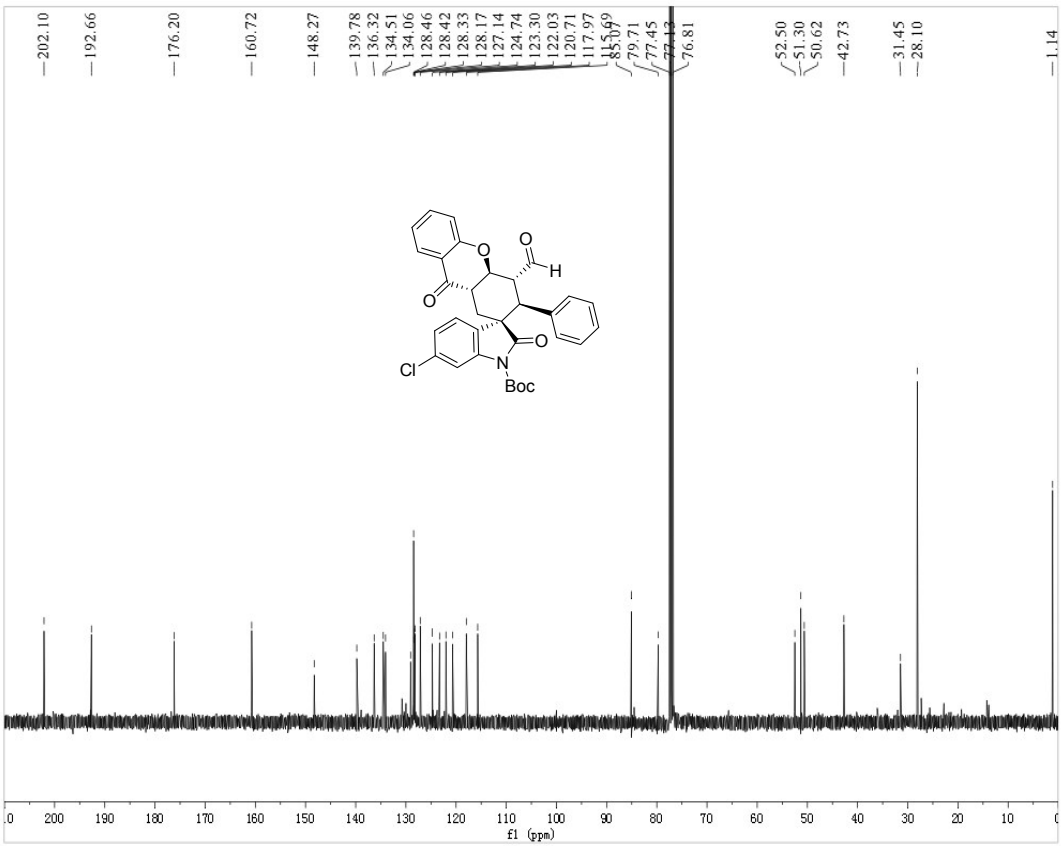
#	Time	Area	Height	Width	Area%	Symmetry
1	13.418	29724.2	685.4	0.7228	49.692	0.759
2	17.293	30093.2	557.3	0.9	50.308	0.694



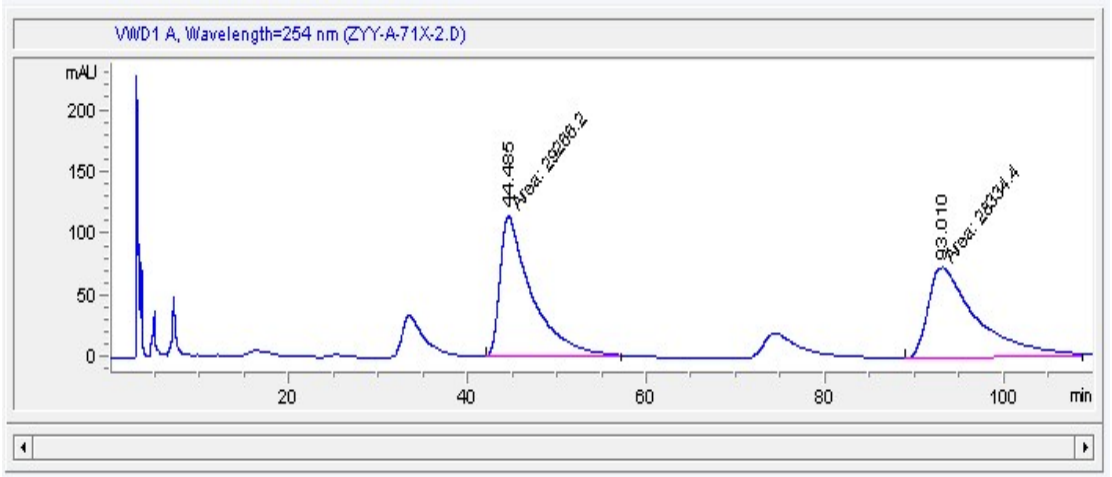
#	Time	Area	Height	Width	Area%	Symmetry
1	15.247	121427	2602.3	0.7777	98.374	0.584
2	19.731	2007	50.6	0.6606	1.626	0.788

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

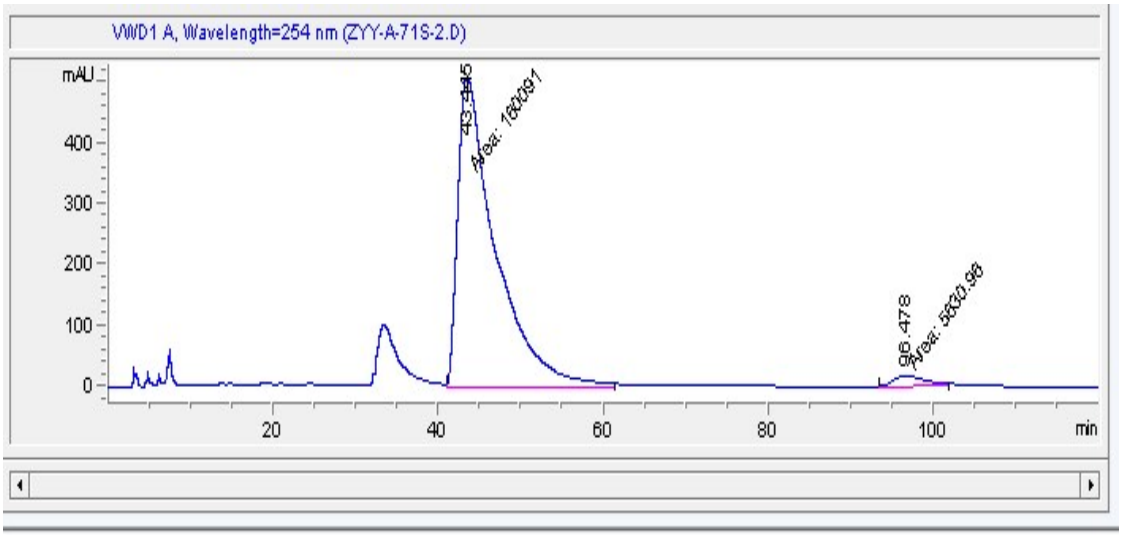




HPLC of 3s

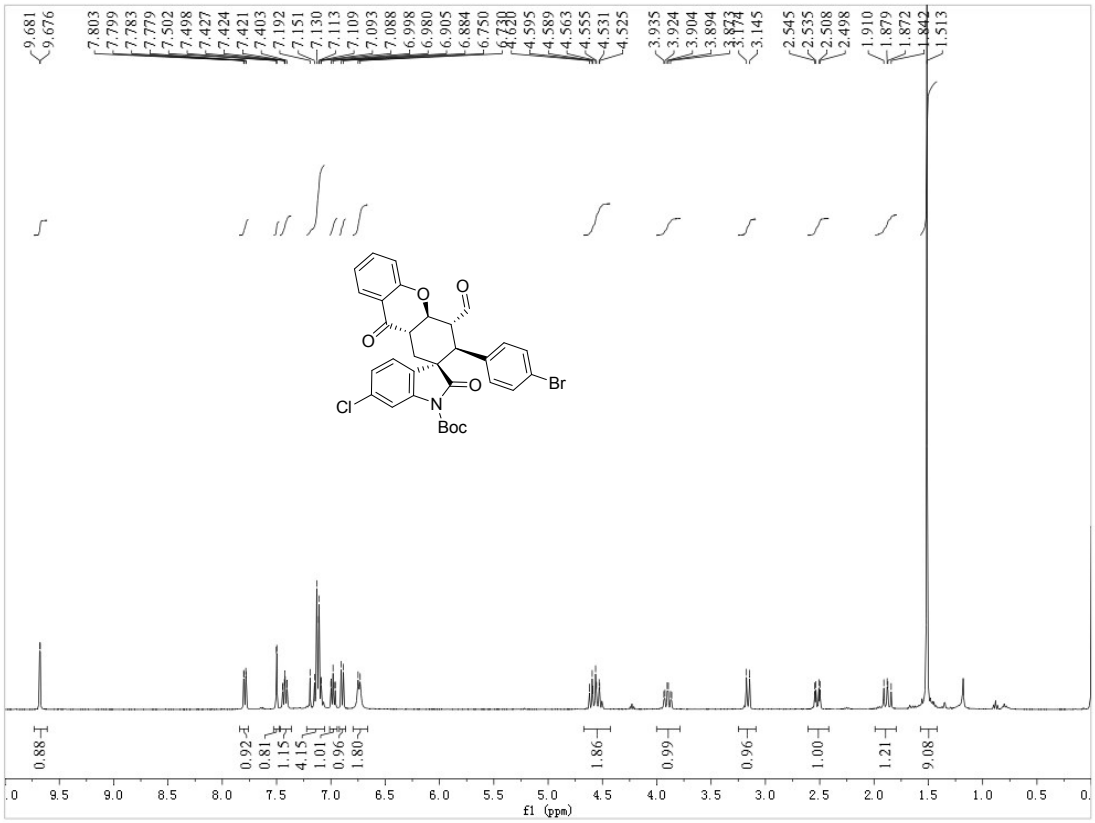


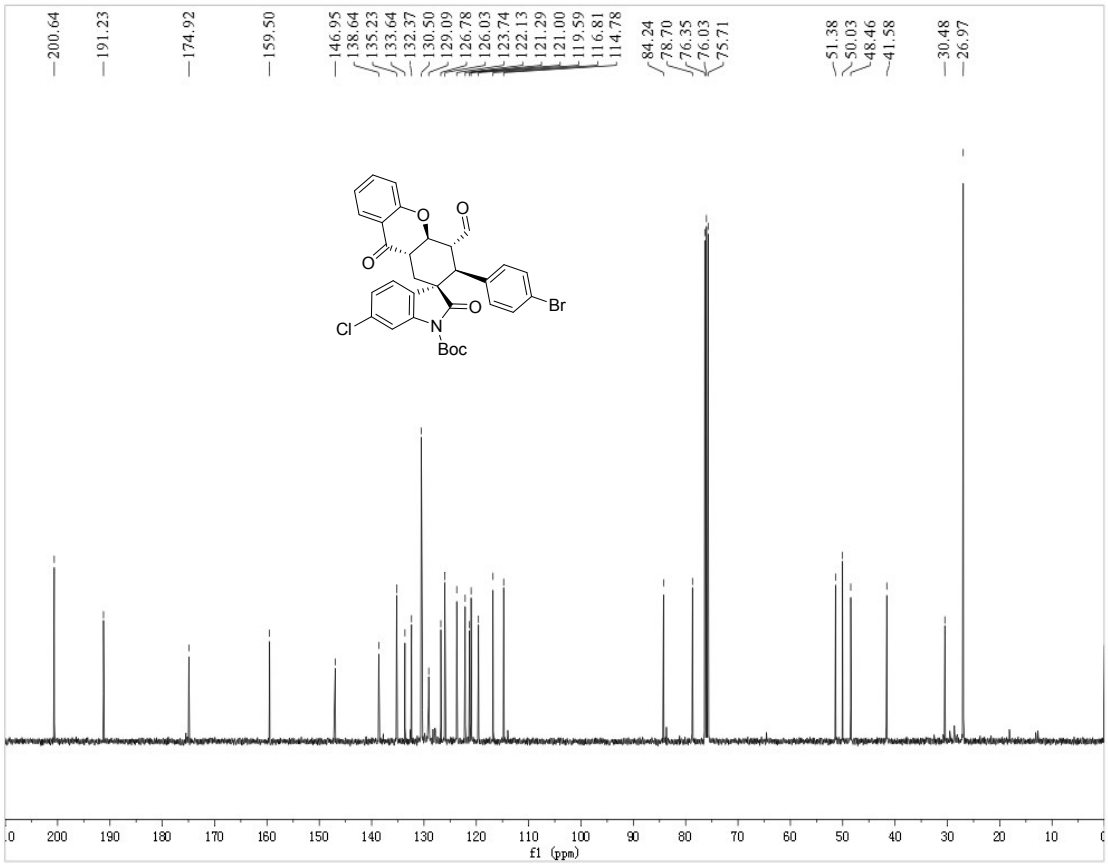
#	Time	Area	Height	Width	Area%	Symmetry
1	44.485	29266.2	113.7	4.2892	50.809	0.352
2	93.01	28334.4	73.4	6.4343	49.191	0.38



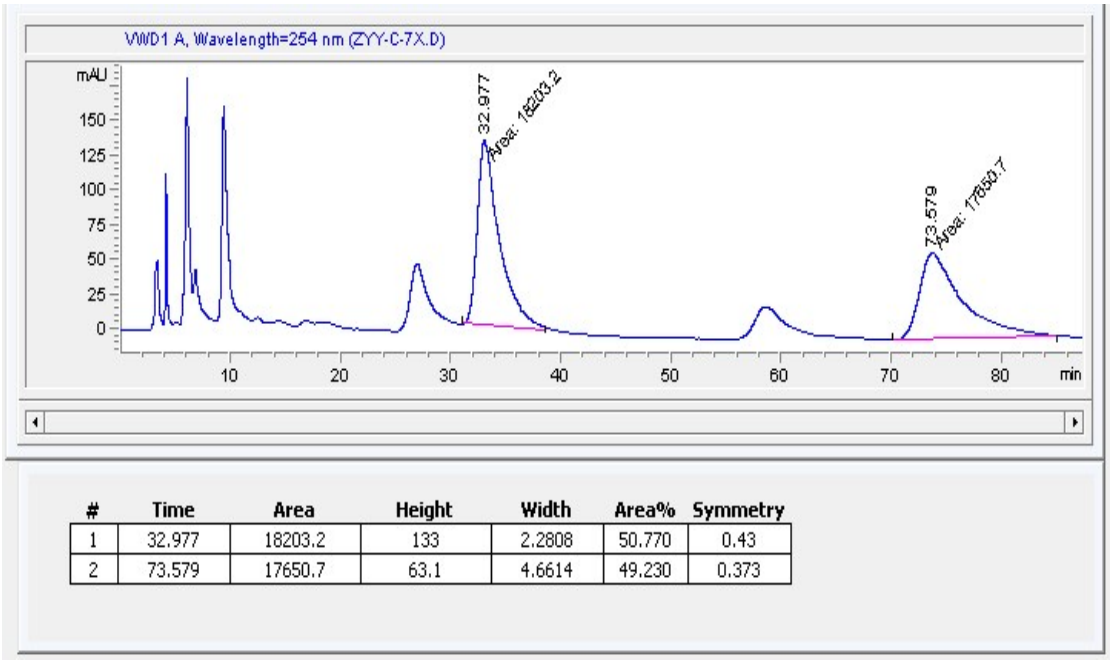
#	Time	Area	Height	Width	Area%	Symmetry
1	43.445	160091.3	507.1	5.2618	96.602	0.312
2	96.478	5631	18.9	4.9571	3.398	0.575

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

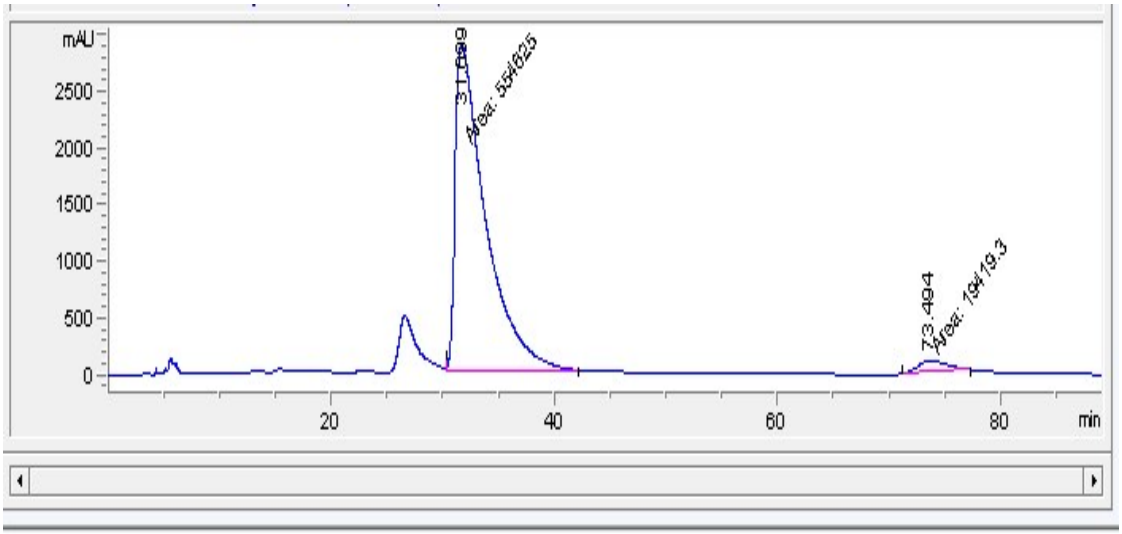




HPLC of 3t

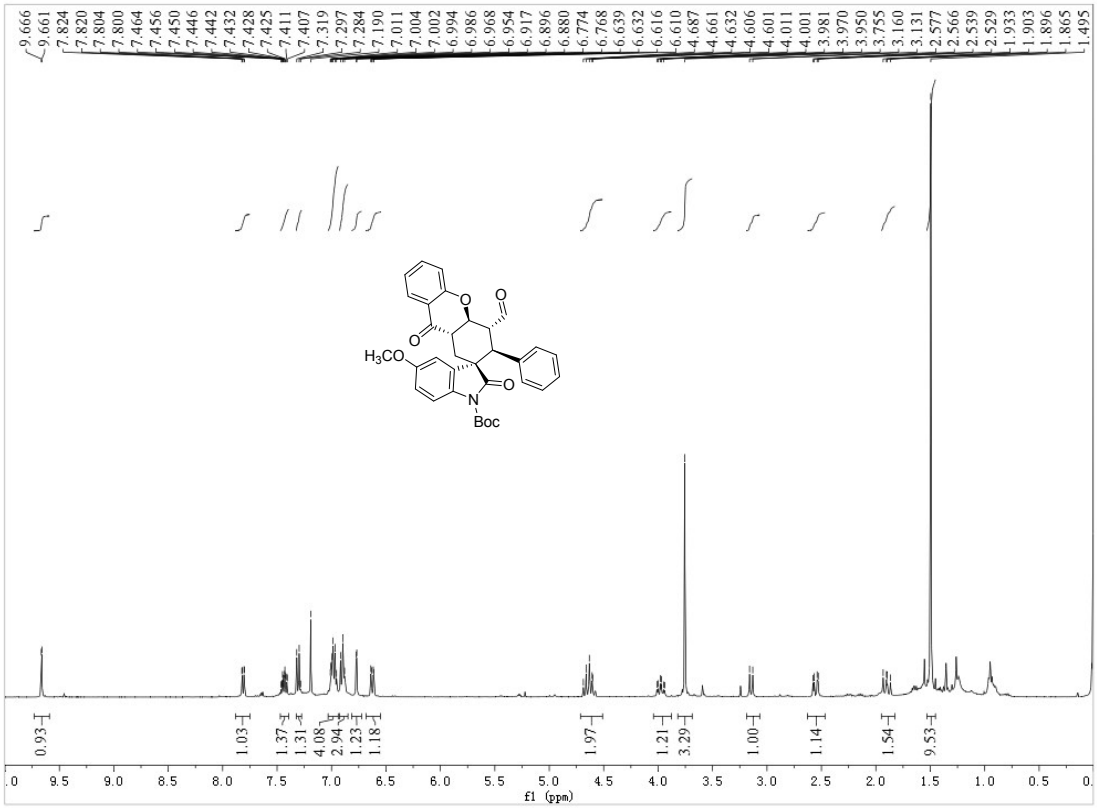


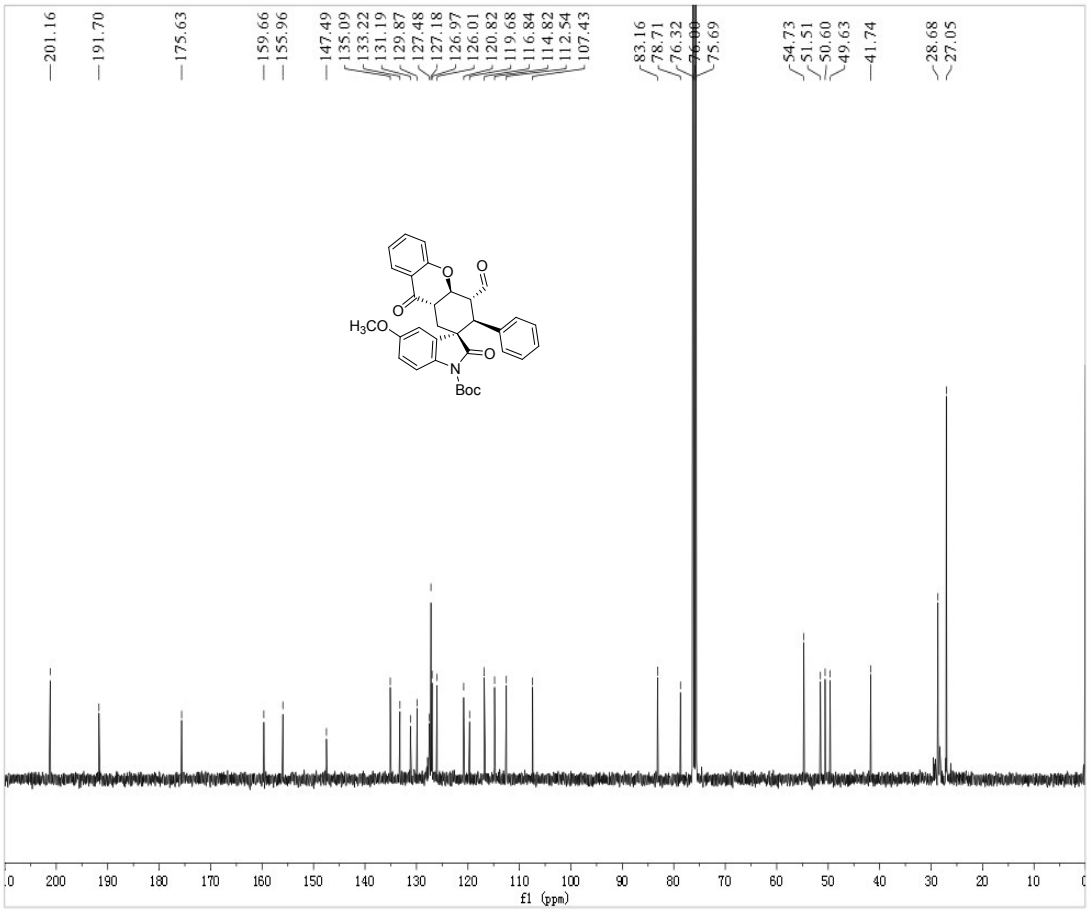
#	Time	Area	Height	Width	Area%	Symmetry
1	32.977	18203.2	133	2.2808	50.770	0.43
2	73.579	17650.7	63.1	4.6614	49.230	0.373



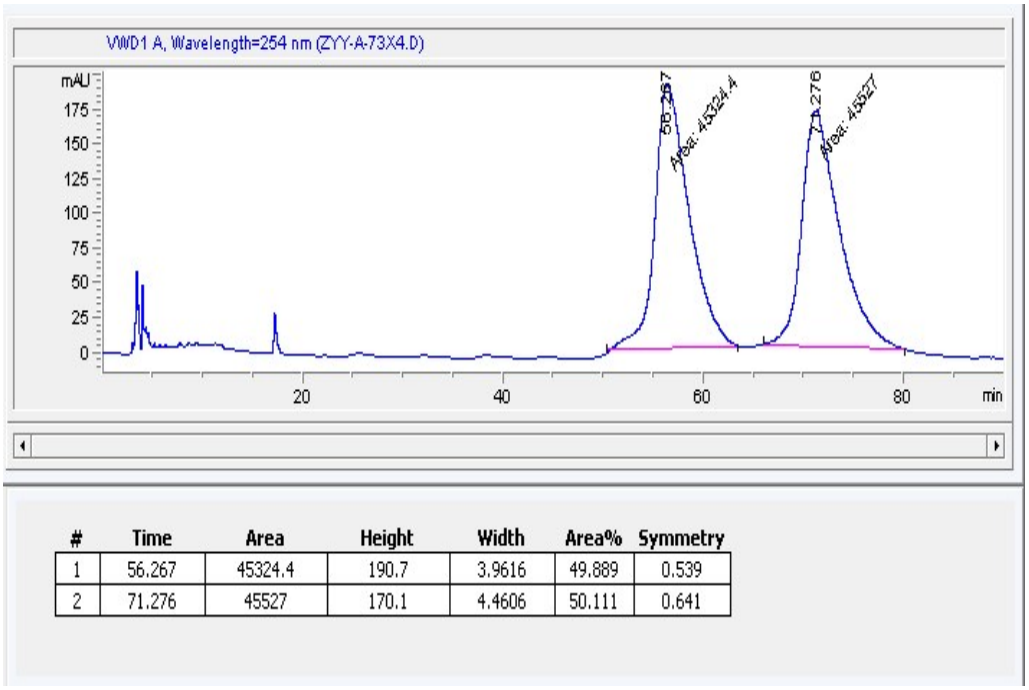
#	Time	Area	Height	Width	Area%	Symmetry
1	31.699	554625.3	2910.2	3.1763	96.617	0.285
2	73.494	19419.3	103.3	3.1335	3.383	0.596

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

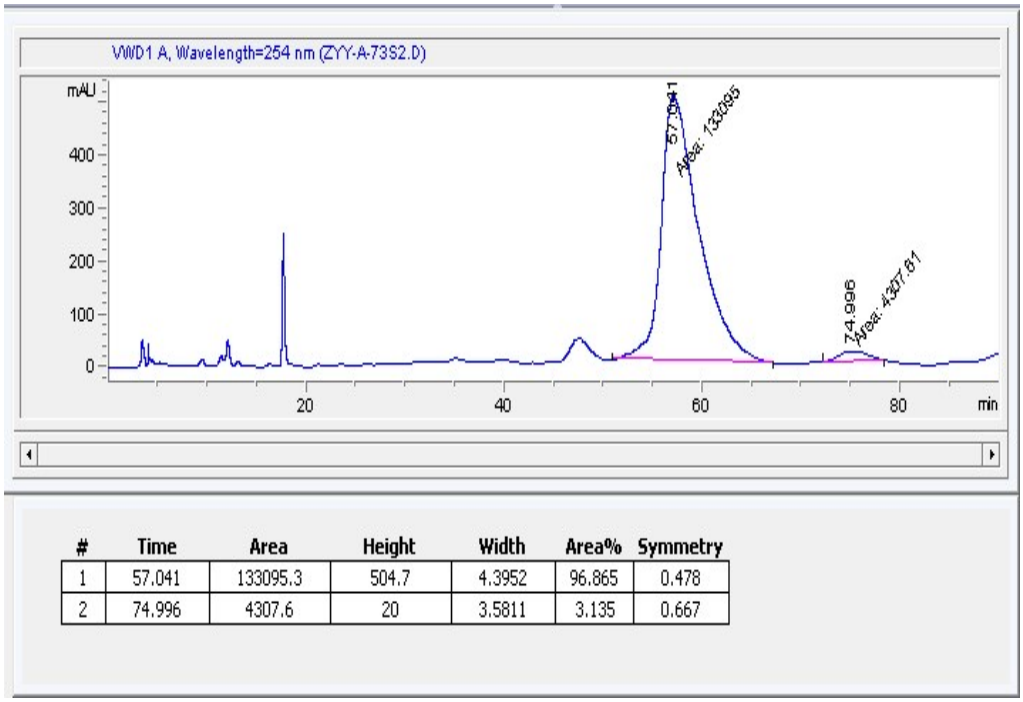




HPLC of 3u

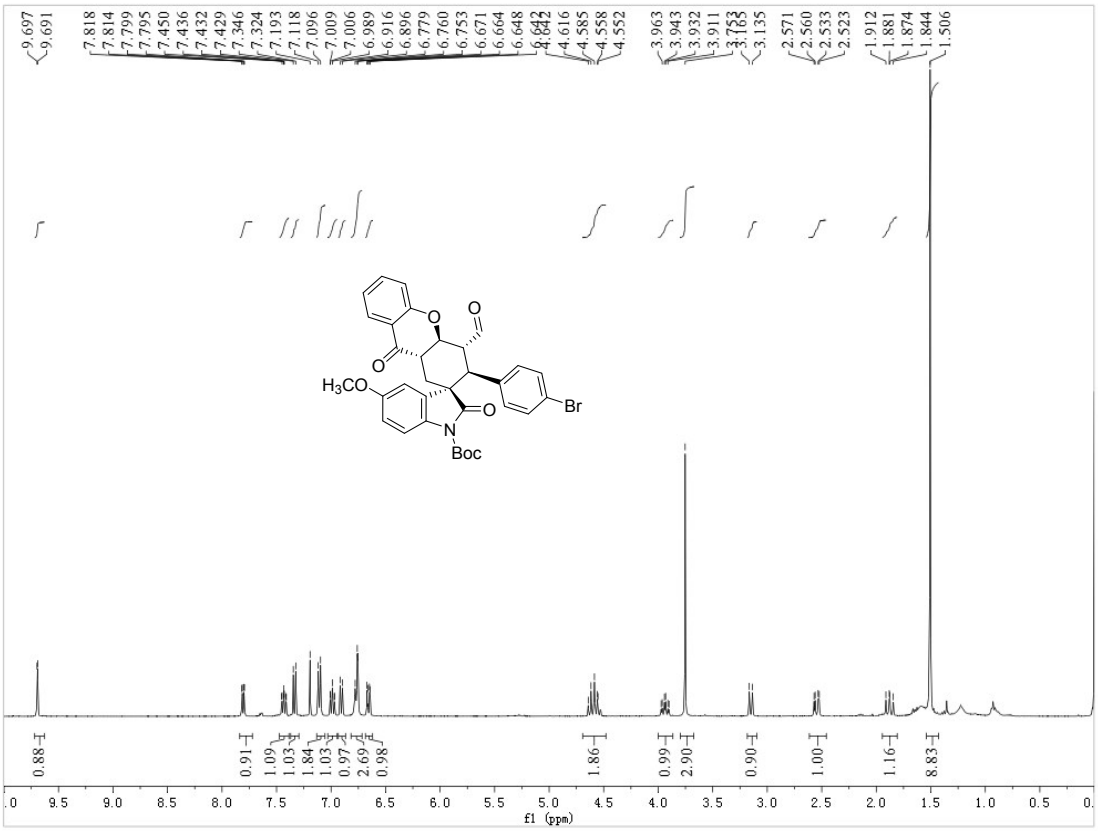


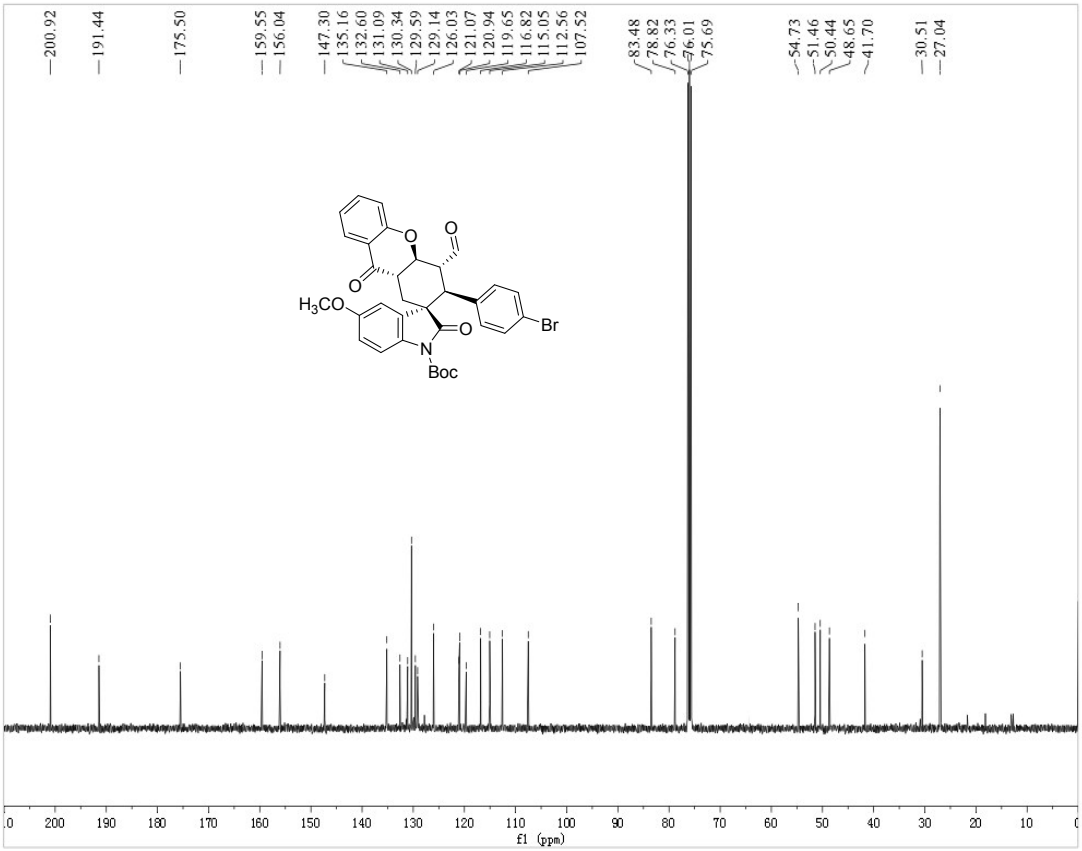
#	Time	Area	Height	Width	Area%	Symmetry
1	56.267	45324.4	190.7	3.9616	49.889	0.539
2	71.276	45527	170.1	4.4606	50.111	0.641



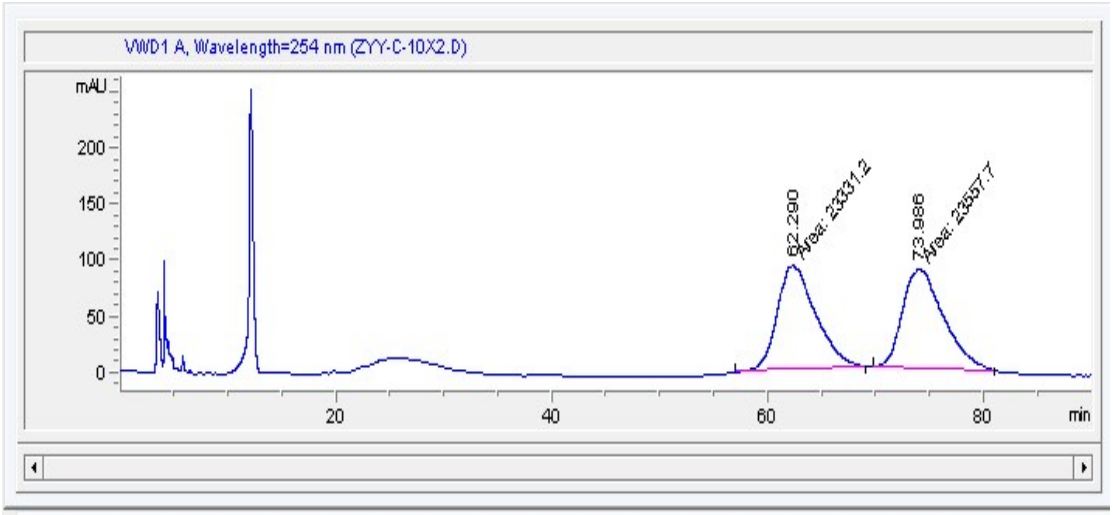
#	Time	Area	Height	Width	Area%	Symmetry
1	57.041	133095.3	504.7	4.3952	96.865	0.478
2	74.996	4307.6	20	3.5811	3.135	0.667

^{1}H and ^{13}C NMR of 3v

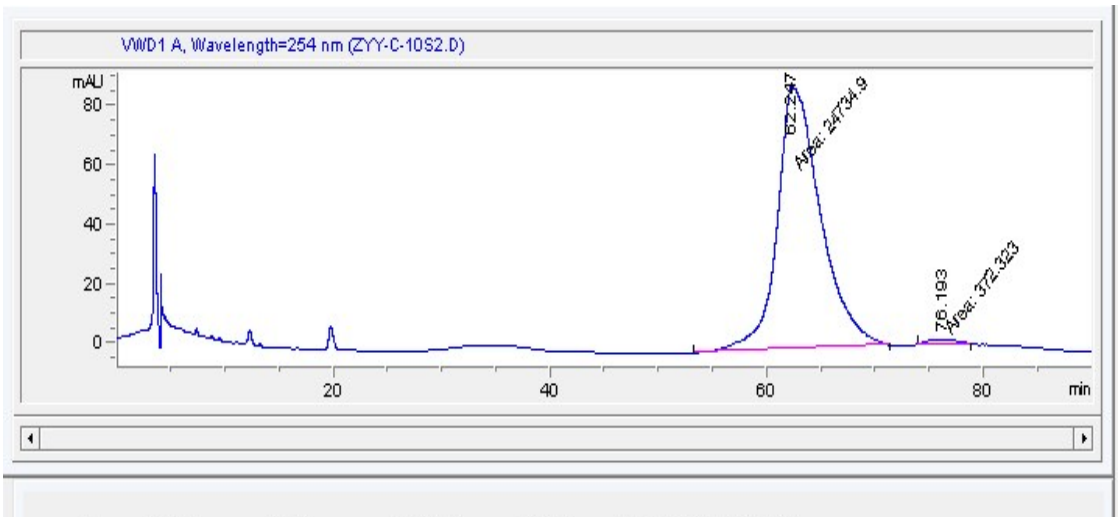




HPLC of 3v



#	Time	Area	Height	Width	Area%	Symmetry
1	62.29	23331.2	93.5	4.1586	49.758	0.717
2	73.986	23557.7	88.6	4.4333	50.242	0.637



#	Time	Area	Height	Width	Area%	Symmetry
1	62.247	24734.9	89	4.6307	98.517	0.541
2	76.193	372.3	1.9	3.273	1.483	1.118