Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Bifunctional pyrazolone-chromone synthon directed organocatalytic double Michael cascade reaction: forging five stereocenters in structurally diverse hexahydroxanthones

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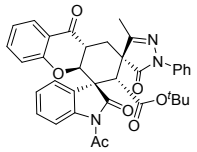
1. General experimental information

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. Chemical yields refered to pure isolated substances. 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-600 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 and 5:

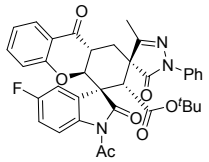
In a sealed tube equipped with a magnetic stirring bar, to the mixture of pyrazolone-chromone synthon **1** (0.10 mmol) and quinine-derived thiourea **C2** (20 mol%) in 1.0 mL of freshly distilled Et_2O was added 3-substituted methyleneoxindole **2** or methylene benzofuranone **4** (0.13 mmol). The reaction mixture was stirred in an oil bath at room temperature for 4d and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **3** or **5**, using hexane/EtOAc (10/1, v/v) as the eluent.

3. Characterization data and HPLC conditions of compounds 3 and 5:

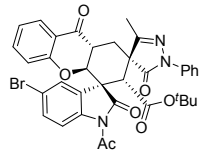


3a: White soid, m.p. 115.1-116.3 ^{o}C; 53.8 mg, yield 87%; 96% ee, >20:1 dr, $[\alpha]_D^{20}$ = +123.34 (c 0.15, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.56 min; τ_{minor} = 26.56 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.87 (s, 8H), 2.19 (s, 3H), 2.43-2.47 (m, 1H), 2.51-2.55 (m, 1H), 2.78

(s, 3H), 3.82-3.87 (m, 1H), 5.95 (d, J = 13.8 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.99-7.02 (m, 1H), 7.21-7.25 (m, 2H), 7.37-7.42 (m, 2H), 7.42-7.46 (m, 2H), 7.84-7.86 (m, 1H), 7.96 (d, J = 7.8 Hz, 2H), 8.01 (d, J = 7.8 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 25.9, 26.8, 26.9, 38.4, 52.2, 52.9, 53.5, 80.4, 83.1, 115.7, 117.8, 119.5, 120.3, 122.1, 125.4, 125.9, 126.8, 127.3, 128.0, 128.8, 129.3, 136.2, 138.1, 141.6, 160.1, 160.4, 166.0, 170.6, 175.3, 179.4, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{33}N_3NaO_7$ $[M+Na]^+$: 642.2211; Found: 642.2216.

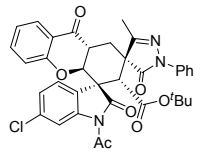


3b (C1'*S*, C2'*R*, C4'*S*, C5'*R*, C6'*S*): White soid, m.p. 121.6-122.4 °C; 47.7 mg, yield 75%; 96% ee, >20:1 dr, $[\alpha]_D^{20}$ = +110.95 (c 0.21, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.94 min; τ_{minor} = 28.95 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.93 (s, 9H), 2.19 (s, 3H), 2.43-2.52 (m, 2H), 2.77 (s, 3H), 3.80-3.86 (m, 2H), 5.91 (d, J = 13.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 7.02-7.05 (m, 1H), 7.09-7.13 (m, 1H), 7.23-7.26 (m, 1H), 7.41-7.47 (m, 3H), 7.85-7.88 (m, 2H), 7.96 (d, J = 7.8 Hz, 2H), 8.33-8.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 25.9, 26.7, 27.0, 38.3, 52.0, 52.8, 53.8, 80.3, 83.4, 114.7 (d, J_{CF} = 26.5 Hz), 115.8 (d, J_{CF} = 24.0 Hz), 117.0, 117.8, 119.4, 120.2, 122.3, 125.4, 127.3, 128.9, 129.9, 136.3, 137.6, 138.0, 159.7, 160.3, 160.5 (d, J_{CF} = 249.1 Hz), 165.8, 170.4, 175.3, 178.9, 192.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{32}FN_3NaO_7$ $[M+Na]^+$: 660.2116; Found: 660.2117.

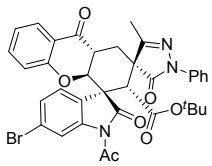


3c: White soid, m.p. 231.3-232.6 °C; 56.4 mg, yield 81%; 97% ee, >20:1 dr, $[\alpha]_D^{20}$ = +221.56 (c 0.32, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.60 min; τ_{minor} = 28.12 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.94 (s, 9H), 2.20 (s, 3H), 2.42-2.46 (m, 1H), 2.49-2.53 (m, 1H), 2.77 (s, 3H), 3.78-3.84 (m, 2H), 5.94 (d, J = 14.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 7.02-7.05 (m, 1H), 7.22-7.25 (m, 1H), 7.41-7.47 (m, 3H), 7.54-7.56 (m, 1H), 7.84-7.86 (m, 1H), 7.96-7.98 (m, 2H),

8.20-8.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.2, 25.9, 26.8, 27.0, 38.3, 52.2, 52.9, 53.5, 80.2, 83.7, 117.3, 117.8, 118.9, 119.2, 120.2, 122.3, 125.3, 127.3, 128.9, 130.0, 130.1, 132.4, 136.3, 138.0, 140.6, 159.9, 160.3, 165.8, 170.4, 175.2, 178.5, 192.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{32}BrN_3NaO_7$ $[M+Na]^+$: 720.1316; Found: 720.1316.

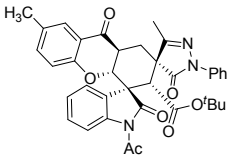


3d: White soid, m.p. 128.9-129.7 ^{o}C; 52.2 mg, yield 80%; 98% ee, >20:1 dr, $[\alpha]_D^{20}$ = +101.11 (c 0.27, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 12.22 min; τ_{minor} = 36.93 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.92 (s, 9H), 2.18 (s, 3H), 2.43-2.53 (m, 2H), 2.77 (s, 3H), 3.79-3.84 (m, 2H), 5.89 (d, *J* = 13.8 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 7.02-7.05 (m, 1H), 7.23-7.26 (m, 2H), 7.41-7.46 (m, 3H), 7.85-7.87 (m, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 8.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 25.9, 26.7, 27.0, 38.3, 52.0, 52.8, 53.4, 80.3, 83.4, 116.3, 117.8, 119.5, 120.2, 122.3, 125.5, 125.9, 126.4, 127.3, 127.9, 128.9, 135.2, 136.3, 138.0, 142.3, 159.9, 160.3, 165.9, 170.4, 175.4, 179.0, 192.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{32}ClN_3NaO_7$ $[M+Na]^+$: 676.1821; Found: 676.1823.

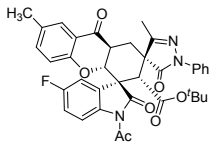


3e: White soid, m.p. 126.4-127.8 ^{o}C; 53.6 mg, yield 77%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +199.52 (c 0.21, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IF column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 14.97 min; τ_{minor} = 29.05 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.92 (s, 9H), 2.18 (s, 3H), 2.43-2.53 (m, 2H), 2.77 (s, 3H), 3.79-3.84 (m, 2H), 5.88 (d, *J* = 14.4 Hz, 1H), 6.74-6.75 (m, 1H), 7.02-7.05 (m, 1H), 7.23-7.26 (m, 1H), 7.39-7.46 (m, 4H), 7.85-7.86 (m, 1H), 7.91-7.94 (m, 3H), 8.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 25.9, 26.7, 27.0, 38.3, 52.0, 52.8, 53.4, 80.2, 83.4, 117.8, 119.0, 119.6, 120.2, 122.3, 123.2, 125.5, 127.0, 127.3, 128.2, 128.9, 136.3, 137.9, 142.5, 159.9, 160.3, 165.8, 170.4, 175.4, 178.9, 192.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{32}BrN_3NaO_7$ $[M+Na]^+$: 720.1316; Found:

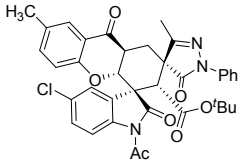
720.1316.



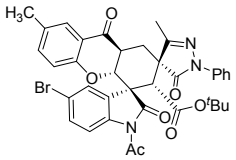
3f: White soid, m.p. 96.3-97.4 °C; 46.8 mg, yield 74%; 97% ee, >20:1 dr, $[\alpha]_D^{20}$ = +81.15 (c 0.26, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 17.58 min; τ_{minor} = 41.41 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.87 (s, 9H), 2.18 (s, 3H), 2.28 (s, 3H), 2.43-2.52 (m, 2H), 2.77 (s, 3H), 3.79-3.84 (m, 2H), 5.89 (d, *J* = 13.8 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 7.20-7.25 (m, 3H), 7.38-7.41 (m, 1H), 7.43-7.46 (m, 2H), 7.63 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 20.4, 26.0, 26.8, 26.9, 38.4, 52.2, 52.8, 53.6, 80.4, 83.0, 115.6, 117.6, 119.5, 119.8, 125.3, 125.9, 126.8, 128.1, 128.8, 129.3, 131.6, 137.2, 138.1, 141.6, 158.2, 160.4, 166.0, 170.6, 175.4, 179.4, 192.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{37}H_{35}N_3NaO_7$ $[M+Na]^+$: 656.2367; Found: 656.2365.



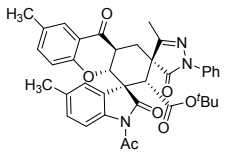
3g: White soid, m.p. 107.3-108.4 °C; 54.0 mg, yield 83%; 95% ee, >20:1 dr, $[\alpha]_D^{20}$ = +94.85 (c 0.32, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.67 min; τ_{minor} = 46.08 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.92 (s, 9H), 2.19 (s, 3H), 2.29 (s, 3H), 2.45-2.48 (m, 2H), 2.76 (s, 3H), 3.77-3.82 (m, 2H), 5.85 (d, *J* = 14.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 7.09-7.12 (m, 1H), 7.22-7.25 (m, 2H), 7.44-7.47 (m, 2H), 7.64 (s, 1H), 7.86-7.88 (m, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.32-8.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 20.4, 26.0, 26.7, 27.0, 38.3, 51.9, 52.8, 53.8, 80.3, 83.4, 114.7 (d, J_{CF} = 27.0 Hz), 115.7 (d, J_{CF} = 22.5 Hz), 116.9, 117.0, 117.6, 119.4, 119.8, 125.4, 126.8, 128.9, 130.1, 131.8, 137.3, 137.7, 138.0, 158.0, 160.4, 160.5 (d, J_{CF} = 243.0 Hz), 165.8, 170.4, 175.4, 179.0, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{37}H_{34}FN_3NaO_7$ $[M+Na]^+$: 674.2273; Found: 674.2277.



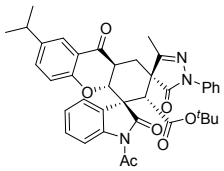
3h: White soid, m.p. 103.4-104.6 °C; 57.3 mg, yield 86%; 95% ee, >20:1 dr, $[\alpha]_D^{20}$ = +66.00 (c 0.25, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.94 min; τ_{minor} = 40.79 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.93 (s, 9H), 2.19 (s, 3H), 2.29 (s, 3H), 2.43-2.51 (m, 2H), 2.76 (s, 3H), 3.76-3.81 (m, 2H), 5.88 (d, *J* = 14.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 7.22-7.25 (m, 2H), 7.37-7.40 (m, 1H), 7.44-7.47 (m, 2H), 7.64 (s, 1H), 7.96-7.98 (m, 2H), 8.07 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 20.4, 26.0, 26.7, 27.0, 38.2, 52.0, 52.9, 53.7, 80.2, 83.6, 116.9, 117.6, 119.2, 119.8, 125.3, 126.8, 127.2, 128.9, 129.4, 129.9, 131.2, 131.8, 137.3, 138.0, 140.1, 158.0, 160.3, 165.8, 170.4, 175.3, 178.7, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{37}H_{34}ClN_3NaO_7$ $[M+Na]^+$: 690.1977; Found: 690.1981.



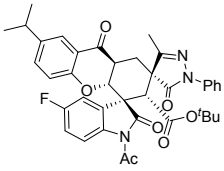
3i: White soid, m.p. 104.3-105.2 °C; 49.7 mg, yield 70%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +130.40 (c 0.25, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.92 min; τ_{minor} = 41.39 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.94 (s, 9H), 2.19 (s, 3H), 2.29 (s, 3H), 2.41-2.51 (m, 2H), 2.76 (s, 3H), 3.76-3.81 (m, 2H), 5.88 (d, *J* = 14.4 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 1H), 7.22-7.25 (m, 2H), 7.44-7.47 (m, 2H), 7.53-7.55 (m, 1H), 7.64 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.21-8.24 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 22.7, 26.0, 26.8, 27.0, 38.2, 52.1, 52.9, 53.6, 80.2, 83.6, 117.3, 117.6, 118.8, 119.2, 119.8, 125.3, 126.8, 128.9, 130.0, 130.2, 131.8, 132.3, 137.3, 138.1, 140.6, 158.0, 160.3, 165.8, 170.4, 175.2, 178.6, 192.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{37}H_{34}BrN_3NaO_7$ $[M+Na]^+$: 734.1472; Found: 734.1475.



3j: White soid, m.p. 92.3-93.5 °C; 47.2 mg, yield 73%; 90% ee, >20:1 dr, $[\alpha]_D^{20}$ = +74.29 (c 0.21, 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} = 12.69 min; τ_{minor} = 31.01 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.88 (s, 9H), 2.18 (s, 3H), 2.28 (s, 3H), 2.34 (s, 3H), 2.40-2.45 (m, 1H), 2.49-2.53 (m, 1H), 2.76 (s, 3H), 3.77-3.83 (m, 2H), 5.90 (d, *J* = 13.8 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 7.19-7.25 (m, 3H), 7.44-7.47 (m, 2H), 7.63 (s, 1H), 7.78 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 20.4, 21.4, 25.9, 26.7, 26.9, 38.4, 52.2, 53.0, 53.5, 80.3, 83.0, 115.5, 117.6, 119.3, 119.9, 125.2, 126.8, 127.2, 127.9, 128.8, 129.6, 131.5, 135.5, 137.1, 138.2, 139.2, 158.3, 160.4, 166.1, 170.5, 175.3, 179.5, 192.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{38}H_{37}N_3NaO_7$ $[M+Na]^+$: 670.2524; Found: 670.2527.

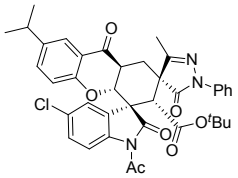


3k: White soid, m.p. 143.8-144.6 °C; 56.2 mg, yield 85%; 91% ee, >20:1 dr, $[\alpha]_D^{20}$ = +149.31 (c 0.29, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.31 min; τ_{minor} = 27.40 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.87 (s, 9H), 1.19 (s, 3H), 1.20 (s, 3H), 2.19 (s, 3H), 2.43-2.47 (m, 1H), 2.49-2.53 (m, 1H), 2.77 (s, 3H), 3.79-3.85 (m, 2H), 5.90 (d, *J* = 14.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 7.22-7.27 (m, 2H), 7.27-7.29 (m, 1H), 7.38-7.41 (m, 1H), 7.43-7.46 (m, 2H), 7.70 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 23.9, 26.0, 26.8, 26.9, 33.3, 38.4, 52.2, 52.9, 53.6, 80.4, 83.0, 115.6, 117.7, 119.5, 124.2, 125.3, 125.9, 126.8, 128.1, 128.8, 129.3, 134.9, 138.1, 141.6, 142.8, 158.4, 160.4, 166.0, 170.6, 175.3, 179.4, 192.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{39}H_{39}N_3NaO_7$ $[M+Na]^+$: 684.2680; Found: 684.2681.

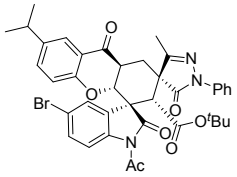


3l: White soid, m.p. 127.6-128.4 °C; 47.5 mg, yield 70%; 92% ee, >20:1 dr, $[\alpha]_D^{20}$ = +188.57 (c

0.21, 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} = 13.92 min; τ_{minor} = 41.39 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.92 (s, 9H), 1.20 (s, 3H), 1.21 (s, 3H), 2.19 (s, 3H), 2.45-2.51 (m, 2H), 2.76 (s, 3H), 2.83-2.89 (m, 1H), 3.78-3.83 (m, 2H), 5.86 (d, *J* = 14.4 Hz, 1H), 6.66 (d, *J* = 9.0 Hz, 1H), 7.09-7.12 (m, 1H), 7.22-7.25 (m, 1H), 7.29-7.31 (m, 1H), 7.43-7.46 (m, 2H), 7.70 (s, 1H), 7.85-7.87 (m, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 8.32-8.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 23.8, 23.9, 26.0, 26.7, 27.0, 33.3, 38.3, 52.0, 52.8, 53.8, 80.3, 83.4, 114.7 (d, J_{CF} = 25.5 Hz), 115.7 (d, J_{CF} = 22.5 Hz), 117.0, 117.7, 119.3, 119.9, 124.3, 125.4, 128.9, 135.0, 137.7, 138.0, 143.0, 158.3, 160.4, 160.5 (d, J_{CF} = 243.0 Hz), 165.9, 170.4, 175.3, 178.9, 192.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{39}H_{38}FN_3NaO_7$ $[M+Na]^+$: 702.2586; Found: 702.2589.

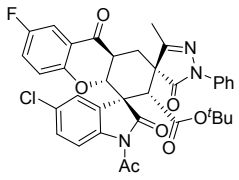


3m: White soid, m.p. 123.7-124.6 °C; 50.0 mg, yield 72%; 90% ee, >20:1 dr, $[\alpha]_D^{20}$ = +267.06 (c 0.17, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 8.76 min; τ_{minor} = 24.31 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 0.93 (s, 9H), 1.20 (s, 3H), 1.21 (s, 3H), 2.19 (s, 3H), 2.42-2.52 (m, 2H), 2.76 (s, 3H), 2.84-2.89 (m, 1H), 3.76-3.82 (m, 2H), 5.89 (d, *J* = 14.4 Hz, 1H), 6.66 (d, *J* = 9.0 Hz, 1H), 7.22-7.25 (m, 1H), 7.29-7.31 (m, 1H), 7.37-7.40 (m, 1H), 7.44-7.47 (m, 2H), 7.70 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 2H), 8.06 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.1, 23.9, 26.0, 26.7, 27.0, 33.3, 38.3, 52.1, 52.9, 53.6, 80.2, 83.6, 116.9, 117.7, 119.2, 119.9, 124.3, 125.3, 127.1, 128.9, 129.3, 129.9, 131.2, 135.0, 138.1, 140.1, 143.0, 158.3, 160.3, 165.8, 170.4, 175.3, 178.7, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{39}H_{38}ClN_3NaO_7$ $[M+Na]^+$: 718.2290; Found: 718.2293.

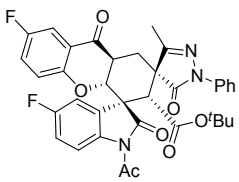


3n: White soid, m.p. 117.8-118.6 °C; 51.0 mg, yield 69%; 91% ee, >20:1 dr, $[\alpha]_D^{20}$ = +195.26 (c

0.19, 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} = 9.62 min; τ_{minor} = 26.31 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.94 (s, 9H), 1.20 (s, 3H), 1.21 (s, 3H), 2.19 (s, 3H), 2.42-2.52 (m, 2H), 2.76 (s, 3H), 2.84-2.89 (m, 1H), 3.76-3.81 (m, 2H), 5.89 (d, J = 14.4 Hz, 1H), 6.66 (d, J = 9.0 Hz, 1H), 7.22-7.25 (m, 1H), 7.28-7.31 (m, 2H), 7.44-7.47 (m, 2H), 7.53-7.55 (m, 1H), 7.70 (s, 1H), 7.97 (d, J = 7.8 Hz, 2H), 8.20 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 23.8, 23.9, 26.0, 26.8, 27.0, 33.3, 38.3, 52.1, 52.9, 53.6, 80.2, 83.6, 117.3, 117.7, 118.8, 119.1, 119.9, 124.3, 125.3, 128.9, 129.9, 130.2, 132.3, 135.0, 138.1, 140.6, 143.0, 158.2, 160.3, 165.8, 170.5, 175.2, 178.5, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{39}H_{38}BrN_3NaO_7$ $[M+Na]^+$: 762.1785; Found: 762.1789.

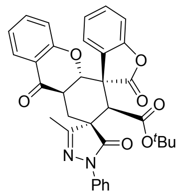


3o: White soid, m.p. 128.5-129.7 °C; 52.3 mg, yield 78%; 90% ee, >20:1 dr, $[\alpha]_D^{20}$ = +154.85 (c 0.33, CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.96 min; τ_{minor} = 20.10 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.93 (s, 9H), 2.19 (s, 3H), 2.45-2.50 (m, 2H), 2.77 (s, 3H), 3.78-3.82 (m, 2H), 5.94 (d, J = 14.4 Hz, 1H), 6.71-6.73 (m, 1H), 7.13-7.16 (m, 1H), 7.23-7.26 (m, 1H), 7.38-7.40 (m, 1H), 7.45-7.47 (m, 2H), 7.49-7.51 (m, 1H), 7.96-7.97 (m, 2H), 8.05 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 25.8, 26.7, 27.0, 38.3, 52.2, 52.9, 53.5, 80.4, 83.7, 112.3 (d, J_{CF} = 12.6 Hz), 117.0, 119.2, 119.6, 120.8, 123.7 (d, J_{CF} = 24.0 Hz), 125.4, 127.1, 128.9, 129.5, 129.6, 131.3, 138.0, 140.0, 156.2, 157.7 (d, J_{CF} = 242.4 Hz), 160.2, 165.7, 170.4, 175.2, 178.6, 191.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{31}ClFN_3NaO_7$ $[M+Na]^+$: 694.1727; Found: 694.1729.

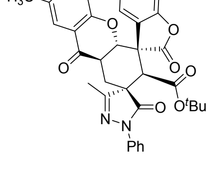


3p: White soid, m.p. 137.2-138.4 °C; 51.7 mg, yield 79%; 91% ee, >20:1 dr, $[\alpha]_D^{20}$ = +160.00 (c

0.23, 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} = 11.40 min; τ_{minor} = 21.25 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 0.93 (m, 9H), 2.19 (s, 3H), 2.45-2.48 (m, 2H), 2.77 (s, 3H), 3.81-3.83 (m, 2H), 5.91 (d, *J* = 14.4 Hz, 1H), 6.71-6.73 (m, 1H), 7.10-7.16 (m, 2H), 7.23-7.26 (m, 1H), 7.44-7.47 (m, 2H), 7.49-7.51 (m, 1H), 7.83-7.86 (m, 1H), 7.94-7.96 (m, 2H), 8.32-8.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.1, 25.9, 26.7, 27.0, 38.3, 52.1, 52.8, 53.6, 80.5, 83.5, 112.3 (d, J_{CF} = 22.5 Hz), 114.7 (d, J_{CF} = 25.5 Hz), 115.9 (d, J_{CF} = 24.0 Hz), 117.1, 119.4, 119.5, 119.6, 123.7 (d, J_{CF} = 24.0 Hz), 125.5, 128.9, 137.6, 137.9, 156.2, 157.6 (d, J_{CF} = 259.5 Hz), 160.2, 160.4 (d, J_{CF} = 238.5 Hz), 165.7, 170.4, 175.3, 178.8, 191.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{31}F_2N_3NaO_7$ $[M+Na]^+$: 678.2022; Found: 678.2025.

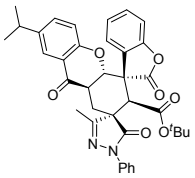


5a (C1'*S*, C2'*R*, C4'*S*, C5'*R*, C6'*S*): White solid, m.p. 150.2-151.2 °C; 37.0 mg, yield 64%; >99% ee, >20:1 dr, $[\alpha]_D^{20}$ = +59.59 (*c* 0.24 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 19.99 min; τ_{minor} = 25.03 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (s, 9H), 2.15 (s, 3H), 2.44 (d, *J* = 10.0 Hz, 1H), 3.71-3.77 (m, 1H), 3.78 (s, 1H), 5.85 (d, *J* = 14.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.96-7.00 (m, 1H), 7.15-7.23 (m, 3H), 7.36-7.44 (m, 4H), 7.80-7.83 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.1, 26.0, 26.9, 38.2, 51.6, 52.4, 52.7, 83.4, 109.9, 117.9, 119.4, 122.1, 125.0, 125.3, 126.8, 127.1, 127.7, 128.8, 129.9, 136.2, 137.9, 154.6, 159.8, 160.3, 165.7, 175.3, 177.6, 192.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{34}H_{30}N_2NaO_7$ $[M+Na]^+$: 601.1945; Found: 601.1951.

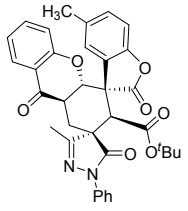


5b: White solid, m.p. 131.5-132.4 °C; 34.9 mg, yield 59%; >99% ee, >20:1 dr, $[\alpha]_D^{20}$ = +157.39 (*c* 0.17 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5

hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 25.19 min; τ_{minor} = 38.22 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.89 (s, 9H), 2.14 (s, 3H), 2.25 (s, 3H), 2.40-2.44 (m, 2H), 3.67-3.76 (m, 1H), 3.77 (s, 1H), 5.80 (d, J = 14.4 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 7.14-7.22 (m, 4H), 7.35-7.44 (m, 4H), 7.59 (s, 1H), 7.91 (d, J = 8.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.1, 20.3, 26.1, 27.0, 38.2, 51.6, 52.4, 52.8, 79.5, 83.4, 109.9, 117.7, 119.4, 119.6, 125.0, 125.3, 126.6, 126.9, 127.7, 128.8, 129.9, 131.6, 137.2, 154.6, 157.9, 160.3, 165.8, 175.3, 177.7, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{35}H_{32}N_2NaO_7$ $[M+Na]^+$: 615.2102; Found: 615.2107.

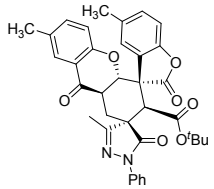


5c: White solid, m.p. 122.5-123.4 °C; 39.0 mg, yield 63%; 99% ee, >20:1 dr, $[\alpha]_D^{20}$ = +156.70 (*c* 0.24 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.38 min; τ_{minor} = 21.50 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.89 (s, 9H), 1.15 (s, 3H), 1.17 (s, 3H), 2.14 (s, 3H), 2.40-2.44 (m, 2H), 2.78-2.85 (m, 1H), 3.68-3.73 (m, 1H), 3.67 (s, 1H), 5.81 (d, J = 14.4 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H), 7.13-7.26 (m, 4H), 7.34-7.42 (m, 3H), 7.64 (d, J = 2.4 Hz, 1H), 7.89-7.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.1, 23.8, 26.1, 26.9, 33.2, 38.2, 51.6, 52.5, 52.7, 79.5, 83.4, 109.9, 117.8, 119.4, 119.7, 124.0, 124.9, 125.3, 126.9, 127.7, 128.8, 129.8, 134.9, 142.7, 154.6, 158.1, 160.3, 165.8, 175.3, 177.6, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{37}H_{36}N_2NaO_7$ $[M+Na]^+$: 643.2415; Found: 643.2418.

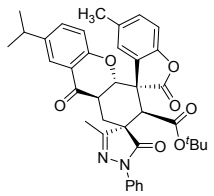


5d: White solid, m.p. 195.6-196.5 °C; 35.5 mg, yield 60%; >99% ee, >20:1 dr, $[\alpha]_D^{20}$ = +218.89 (*c* 0.17 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.32 min; τ_{minor} = 19.65 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (s, 9H), 2.14 (s, 3H), 2.31 (s, 3H), 2.43 (d, J = 9.6 Hz, 1H), 3.69-3.76 (m, 1H), 3.78 (s, 1H), 5.86 (d, J = 14.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.95-6.99 (m, 1H),

7.07 (d, J = 8.4 Hz, 1H), 7.15-7.25 (m, 2H), 7.35-7.44 (m, 3H), 7.67 (s, 1H), 7.79-7.81 (m, 1H), 7.93 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.1, 21.3, 26.0, 26.9, 38.2, 51.7, 52.6, 52.7, 79.4, 83.3, 109.6, 117.9, 119.2, 122.0, 125.2, 126.6, 127.0, 127.9, 128.8, 130.2, 134.6, 136.1, 152.5, 159.8, 160.3, 165.8, 175.2, 177.9, 192.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{35}H_{32}N_2NaO_7$ $[M+Na]^+$: 615.2102; Found: 615.2105.

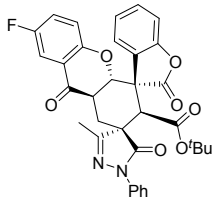


5e: White solid, m.p. 128.5-129.2 °C; 38.1 mg, yield 63%; >99% ee, >20:1 dr, $[\alpha]_D^{20}$ = +219.49 (c 0.13 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/i-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 18.41 min; τ_{minor} = 26.65 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (s, 9H), 2.14 (s, 3H), 2.24 (s, 3H), 2.31 (s, 3H), 2.41 (d, J = 9.6 Hz, 2H), 3.66-3.73 (m, 1H), 3.75 (s, 1H), 5.80 (d, J = 14.4 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.14-7.22 (m, 3H), 7.40-7.44 (m, 2H), 7.59 (s, 1H), 7.68 (s, 1H), 7.93 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.1, 20.3, 21.3, 26.1, 26.9, 38.2, 51.6, 52.6, 52.8, 79.4, 83.3, 109.6, 117.7, 119.2, 119.6, 125.2, 126.6, 126.7, 128.0, 130.1, 131.5, 134.5, 137.2, 152.5, 157.9, 160.3, 165.8, 175.2, 178.0, 192.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{34}N_2NaO_7$ $[M+Na]^+$: 629.2258; Found: 629.2252.

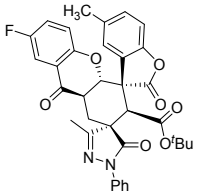


5f: White solid, m.p. 128.3-129.2 °C; 34.9 mg, yield 55%; 97% ee, >20:1 dr, $[\alpha]_D^{20}$ = +170.77 (c 0.20 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/i-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.59 min; τ_{minor} = 18.63 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (s, 9H), 1.16 (s, 3H), 1.17 (s, 3H), 2.14 (s, 3H), 2.31 (s, 3H), 2.42 (d, J = 9.6 Hz, 2H), 2.78-2.86 (m, 1H), 3.67-3.73 (m, 1H), 3.75 (s, 1H), 5.82 (d, J = 14.4 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.14-7.22 (m, 2H), 7.24-7.27 (m, 1H), 7.40-7.44 (m, 2H), 7.65-7.67 (m, 2H), 7.92-7.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.1, 21.3, 23.8,

26.1, 26.9, 33.3, 38.2, 51.7, 52.6, 52.7, 79.4, 83.3, 109.6, 117.8, 119.2, 119.7, 124.0, 125.2, 126.7, 127.9, 128.8, 130.1, 134.5, 134.9, 142.7, 152.5, 158.2, 160.3, 165.8, 175.2, 178.0, 192.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{38}H_{38}N_2NaO_7$ $[M+Na]^+$: 657.2571; Found: 657.2574.



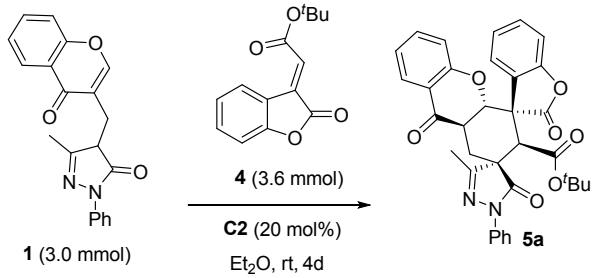
5g: White solid, m.p. 165.2-166.1 °C; 39.9 mg, yield 67%; 96% ee, >20:1 dr, $[\alpha]_D^{20}$ = +225.38 (*c* 0.19 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IF column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 22.17 min; τ_{minor} = 33.05 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 0.91 (s, 9H), 2.16 (s, 3H), 2.38-2.50 (m, 2H), 3.71-3.78 (m, 2H), 5.87 (d, *J* = 14.4 Hz, 1H), 6.72-6.75 (m, 1H), 7.10-7.14 (m, 1H), 7.17-7.27 (m, 3H), 7.37-7.48 (m, 4H), 7.91-7.93 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 13.1, 26.0, 26.9, 38.1, 51.7, 52.4, 52.6, 79.7, 83.5, 110.0, 112.0 (d, J_{CF} = 23.2 Hz), 119.4, 119.6 (d, J_{CF} = 8.3 Hz), 123.7 (d, J_{CF} = 25.1 Hz), 125.4, 127.7, 128.8, 130.0, 137.9, 154.6, 157.5 (d, J_{CF} = 242.4 Hz), 160.2, 165.6, 166.2, 175.3, 177.6, 191.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{34}H_{29}FN_2NaO_7$ $[M+Na]^+$: 619.1851; Found: 619.1848.



5h: White solid, m.p. 156.2-157.2 °C; 42.7 mg, yield 70%; 97% ee, >20:1 dr, $[\alpha]_D^{20}$ = +157.73 (*c* 0.16 CH_2Cl_2); The ee was determined by HPLC analysis using a Chiralpak IE column (96/4 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 24.99 min; τ_{minor} = 37.43 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 0.92 (s, 9H), 2.16 (s, 3H), 2.33 (s, 3H), 2.43 (d, *J* = 9.2 Hz, 2H), 3.70-3.78 (m, 2H), 5.87 (d, *J* = 14.4 Hz, 1H), 6.73-6.76 (m, 1H), 7.07-7.14 (m, 2H), 7.17-7.27 (m, 2H), 7.42-7.48 (m, 3H), 7.68 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 13.1, 21.3, 25.9, 26.9, 38.2, 51.7, 52.6, 52.7, 79.7, 83.4, 109.6, 112.1 (d, J_{CF} = 23.0 Hz), 119.3, 123.6 (d, J_{CF} = 25.2 Hz), 125.3, 126.5, 127.9, 128.8, 130.3, 134.7, 138.0, 152.5, 156.1, 157.5 (d, J_{CF} = 244.1 Hz), 160.2, 165.7, 166.2, 175.2, 177.9, 191.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{35}H_{31}FN_2NaO_7$

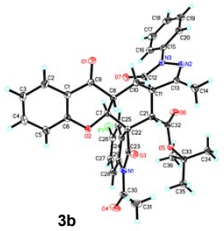
[M+Na]$^+$: 633.2008; Found: 633.2012.

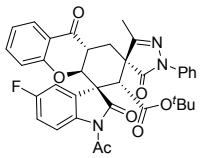
4. Gram scale synthesis of the product 5a



In a sealed tube equipped with a magnetic stirring bar, to the mixture of pyrazolone-chromone synthon **3** (3.0 mmol) and quinine-derived thiourea catalyst **C2** (20 mol%) in 60.0 mL of freshly distilled Et_2O was added methylene benzofuranone **4** (3.6 mmol). The reaction mixture was stirred at rt for 4 d and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **5a**, using hexane/EtOAc (10/1, v/v) as the eluent (1.13 g, 65%, >99% ee, >20:1 dr).

5. X-ray crystal data for compounds 3b



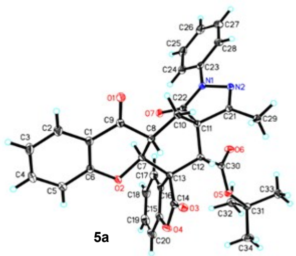


3b

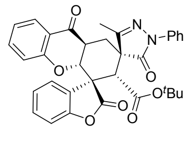
Table S1 Crystal data and structure refinement for 3b

Identification code	**3b**
Empirical formula	$C_{36}H_{32}FN_3O_7$
Formula weight	637.64
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å, b/Å, c/Å	11.74660(10), 12.2636(2), 22.7319(2)
α/°, β/°, γ/°,	90, 93.0910(10), 90.
Volume/Å^3	3269.89(7)
Z	4
ρ_{calc}g/cm^3	1.295
μ/mm^{-1}	0.783
F(000)	1336.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.892 to 147.35
Index ranges	$-14 \le h \le 10$, $-15 \le k \le 13$, $-28 \le l \le 25$
Reflections collected	33134
Independent reflections	10880 [R_{int} = 0.0240, R_{sigma} = 0.0243]
Data/restraints/parameters	10880/1/858
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0958
Final R indexes [all data]	R_1 = 0.0353, wR_2 = 0.0964
Largest diff. peak/hole / e Å^{-3}	0.36/-0.21
Flack/Hooft parameter	0.06(4)/0.06(3)

Table S2 Crystal data and structure refinement for 5a



5a



5a

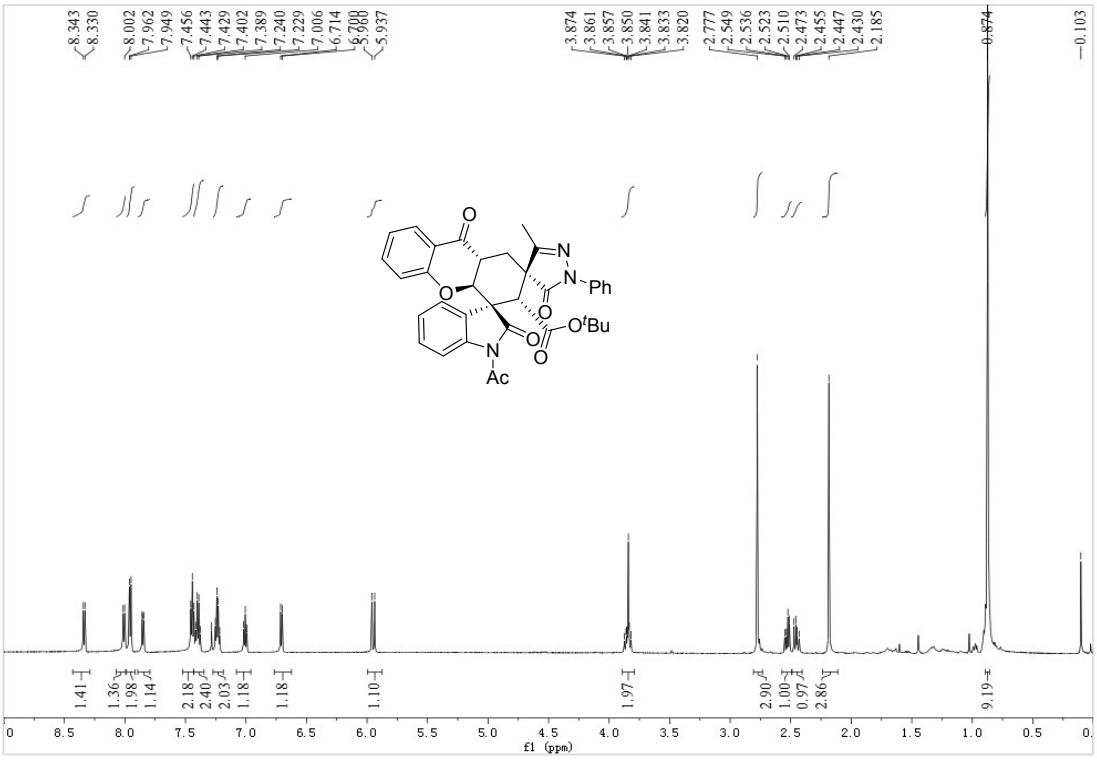
Identification code	**5a**
Empirical formula	$C_{34}H_{30}N_2O_7$
Formula weight	578.60
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å, b/Å, c/Å	9.72120(10), 10.32080(10), 28.5171(3)
α/°, β/°, γ/°,	90, 90, 90.
Volume/Å^3	2861.14(5)
Z	4
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	0.776
F(000)	1216.0
Crystal size/mm^3	0.16 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.198 to 146.98
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-35 \leq l \leq 34$
Reflections collected	37400
Independent reflections	5734 [R_{int} = 0.0370, R_{sigma} = 0.0174]
Data/restraints/parameters	5734/0/392
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0810
Final R indexes [all data]	R_1 = 0.0327, wR_2 = 0.0813
Largest diff. peak/hole / e Å^{-3}	0.15/-0.24
Flack/Hooft parameter	0.04(4)/0.06(4)

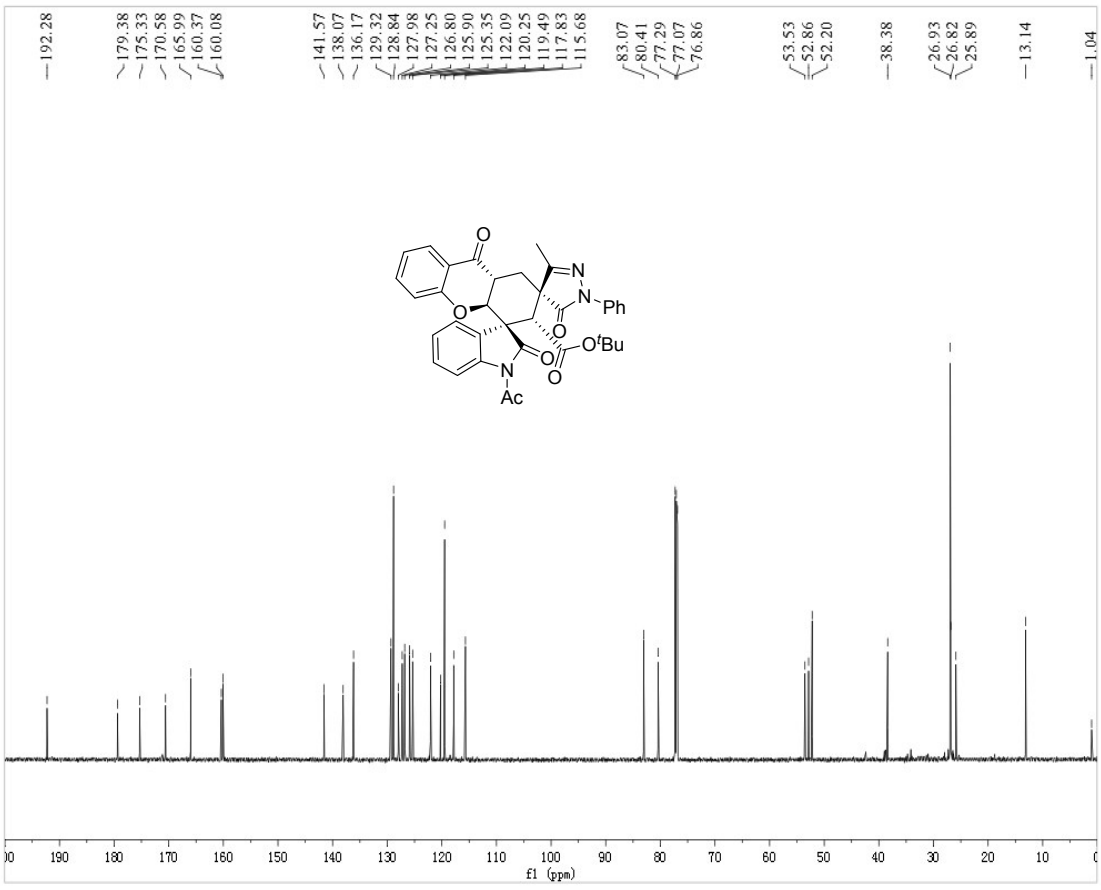
Crystal structure determination of 5a

Crystal Data for $C_{34}H_{30}N_2O_7$ (M =578.60 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.72120(10) Å, b = 10.32080(10) Å, c = 28.5171(3) Å, V = 2861.14(5) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 0.776 mm^{-1}, $Dcalc$ = 1.343 g/cm^3, 37400 reflections measured (6.198° ≤ 2Θ ≤ 146.98°), 5734 unique (R_{int} = 0.0370, R_{sigma} = 0.0174) which were used in all calculations. The final R_1 was 0.0323 (I > 2σ(I)) and wR_2 was 0.0813 (all data).

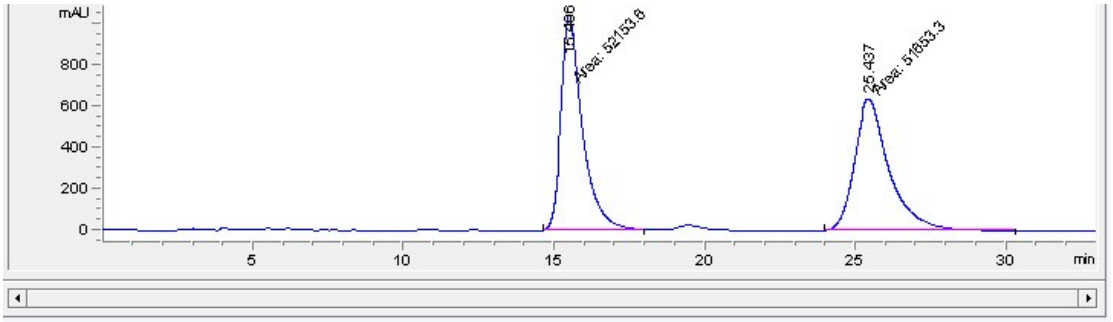
6. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds 3 and 5

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

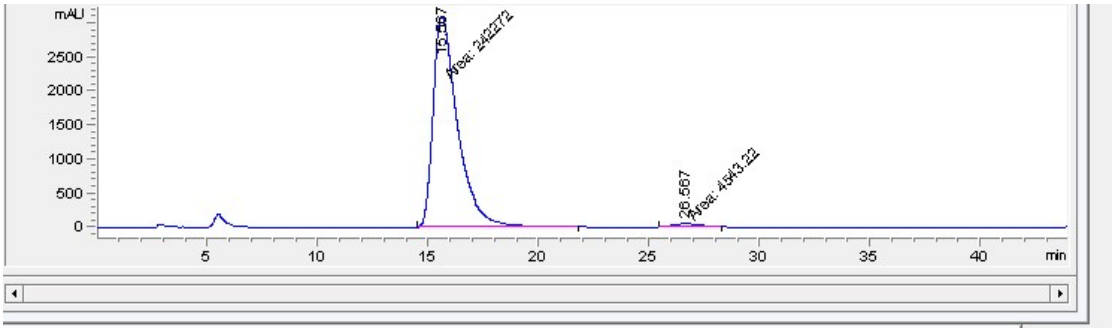




HPLC of 3a

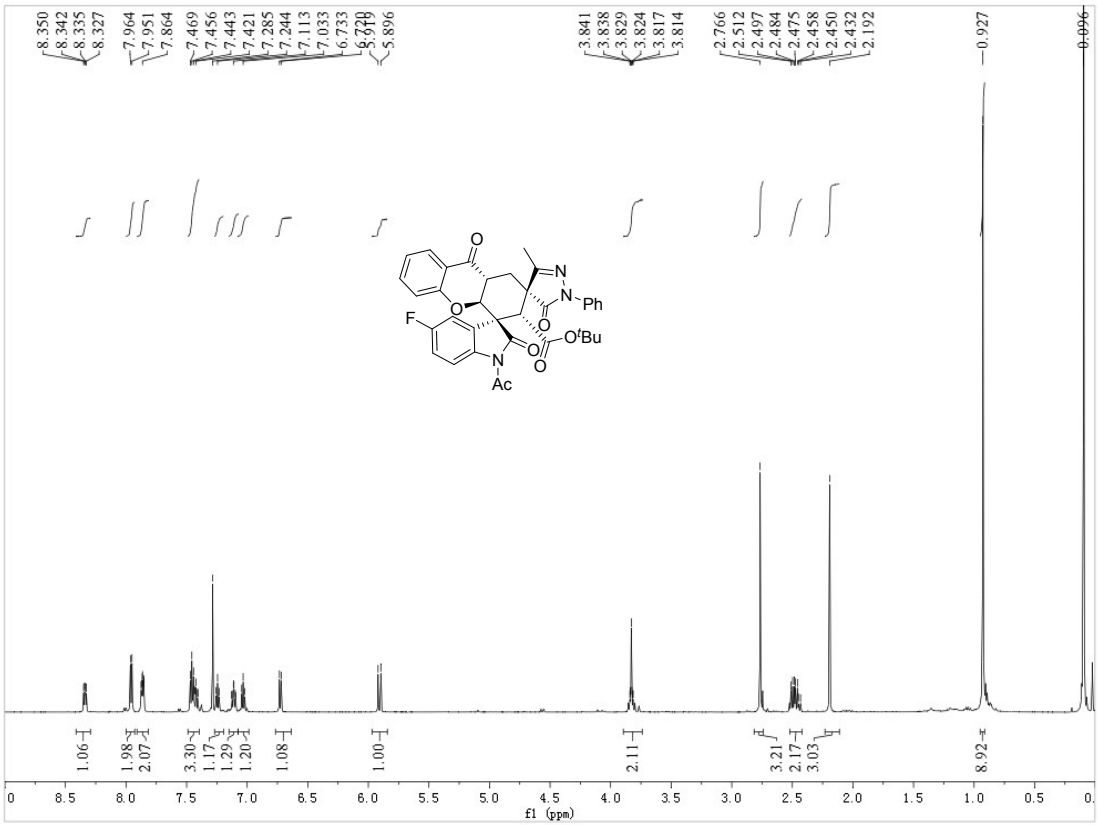


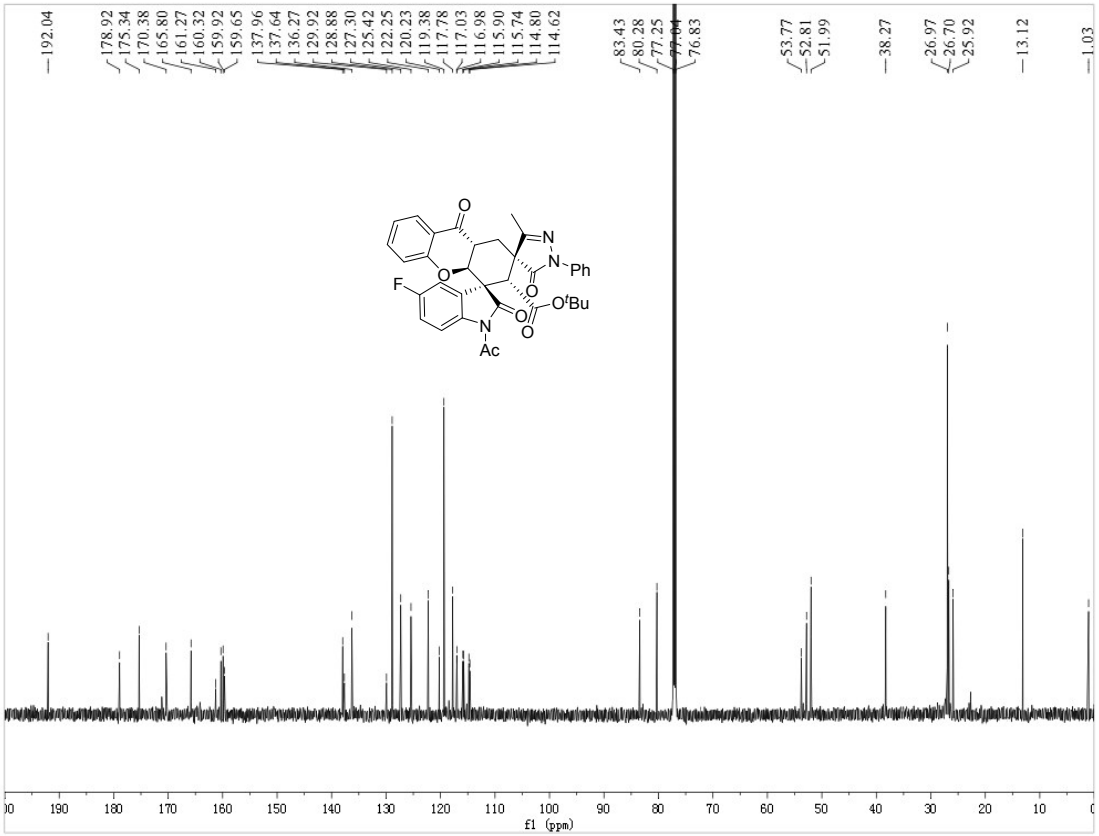
#	Time	Area	Height	Width	Area%	Symmetry
1	15.496	52153.6	1042.6	0.8337	50.241	0.617
2	25.437	51653.3	639.8	1.3456	49.759	0.698



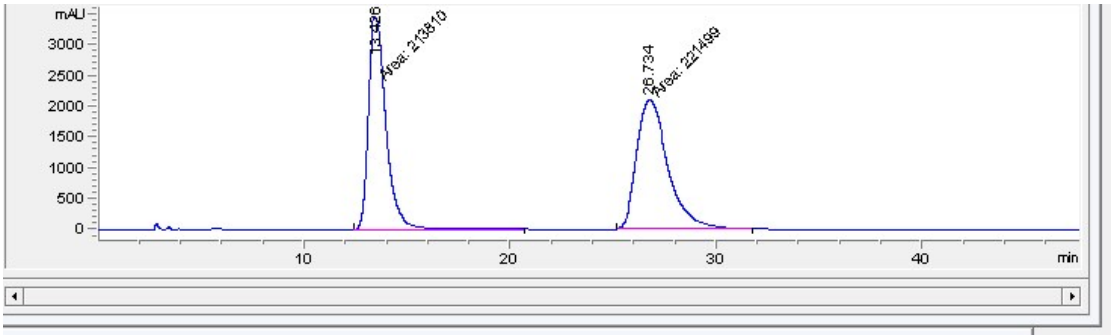
#	Time	Area	Height	Width	Area%	Symmetry
1	15.567	242272.3	3103.4	1.3011	98.159	0.505
2	26.567	4543.2	48.8	1.5529	1.841	0.736

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

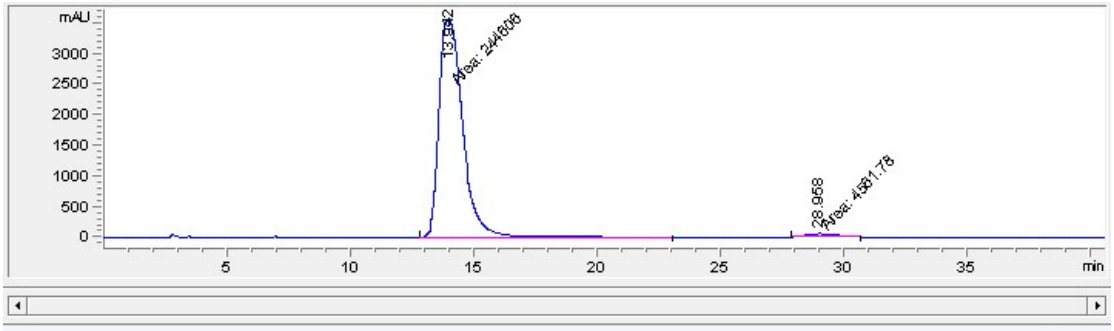




HPLC of 3b

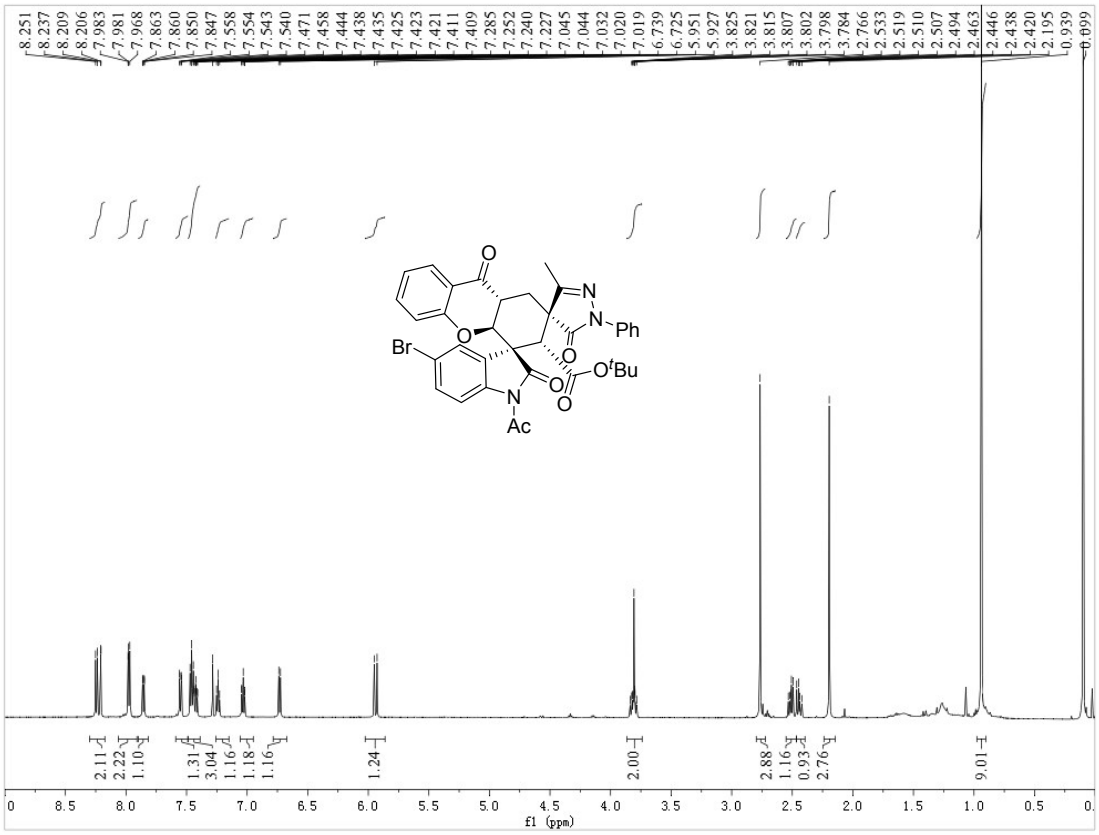


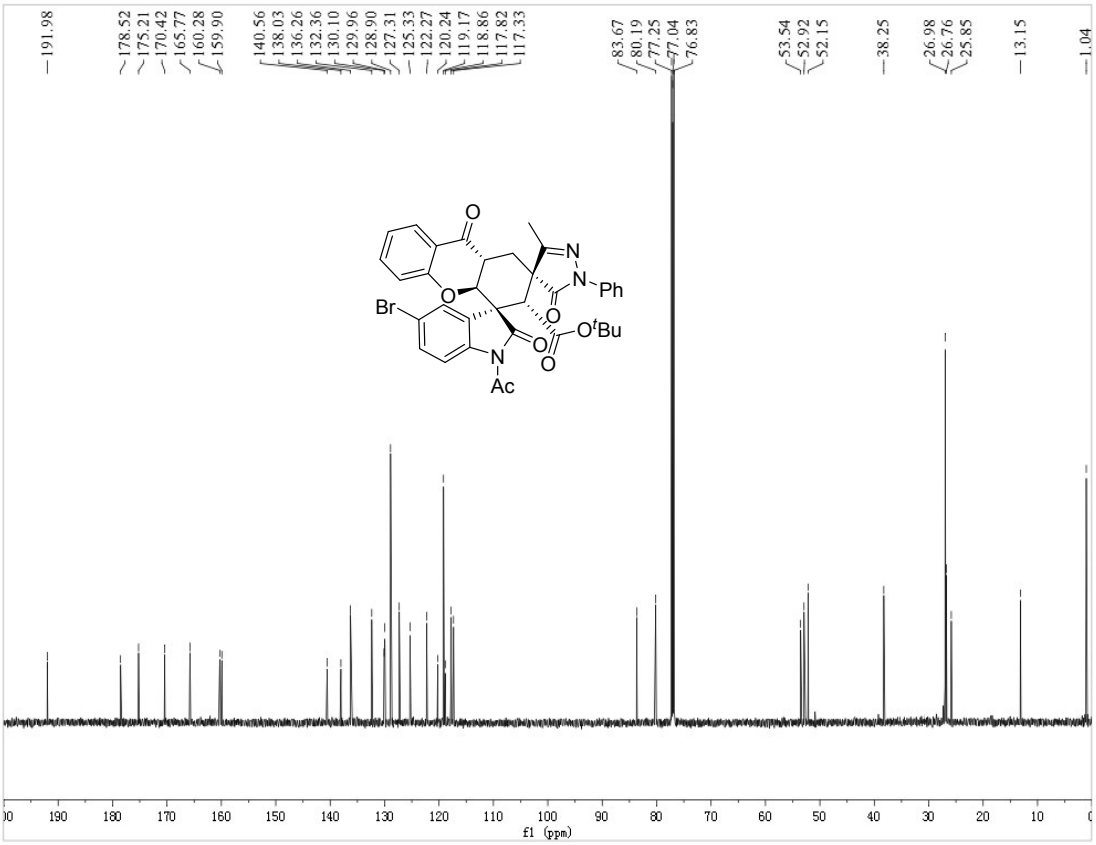
#	Time	Area	Height	Width	Area%	Symmetry
1	13.426	213809.9	3458.5	1.0304	49.117	0.65
2	26.734	221498.8	2092	1.7647	50.883	0.655



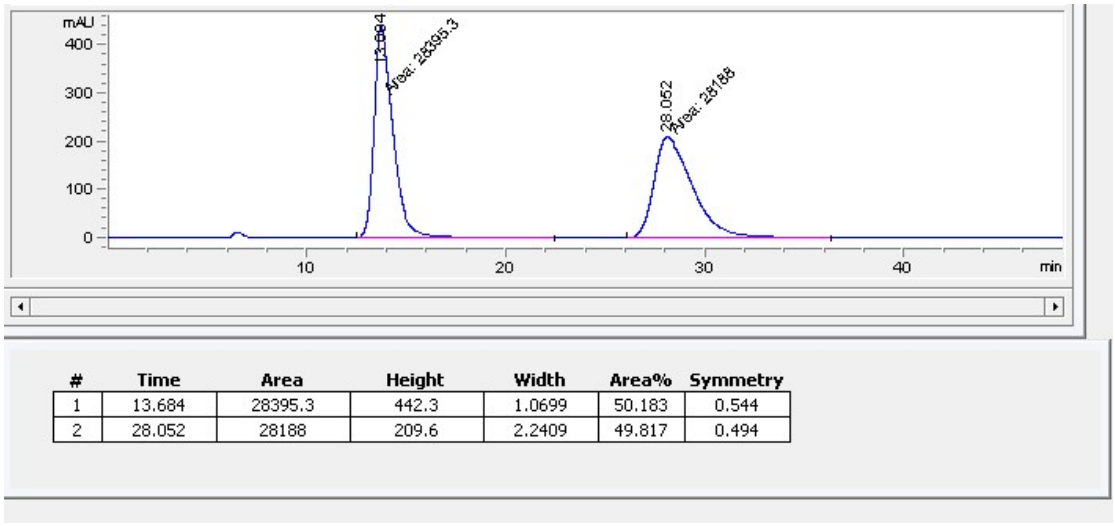
#	Time	Area	Height	Width	Area%	Symmetry
1	13.942	244606.5	3564.6	1.1437	98.169	0.549
2	28.958	4561.8	52.2	1.4577	1.831	0.746

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

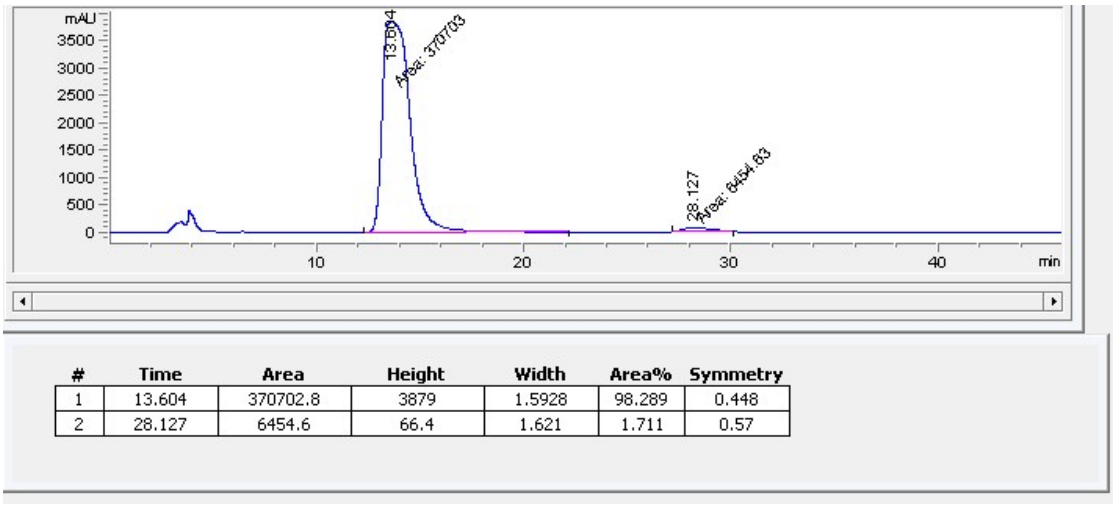




HPLC of 3c

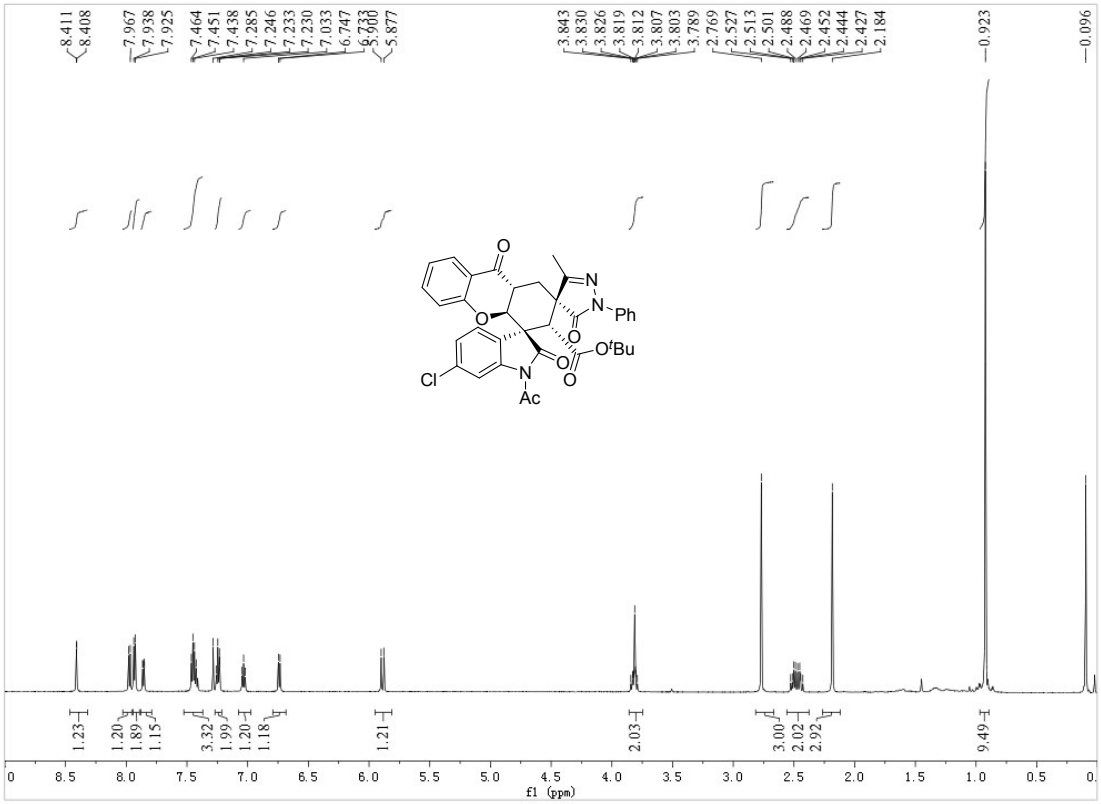


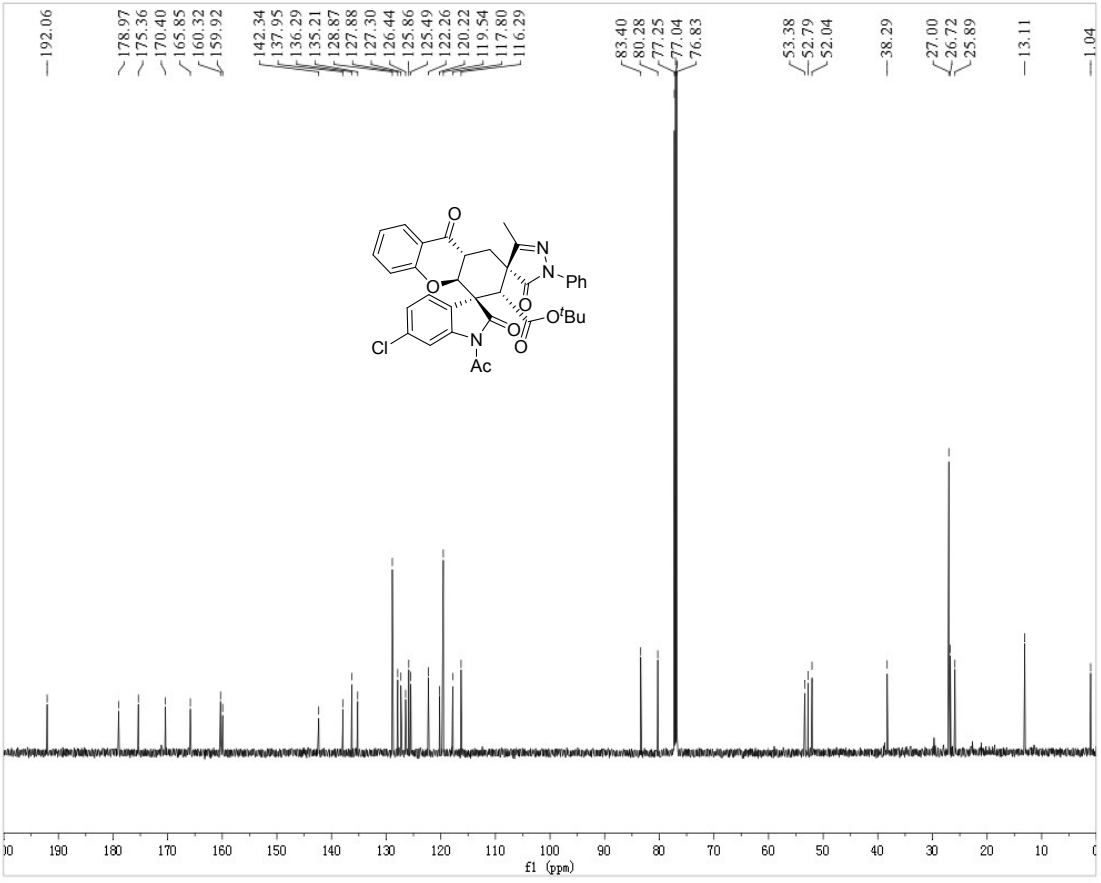
#	Time	Area	Height	Width	Area%	Symmetry
1	13.684	28395.3	442.3	1.0699	50.183	0.544
2	28.052	28188	209.6	2.2409	49.817	0.494



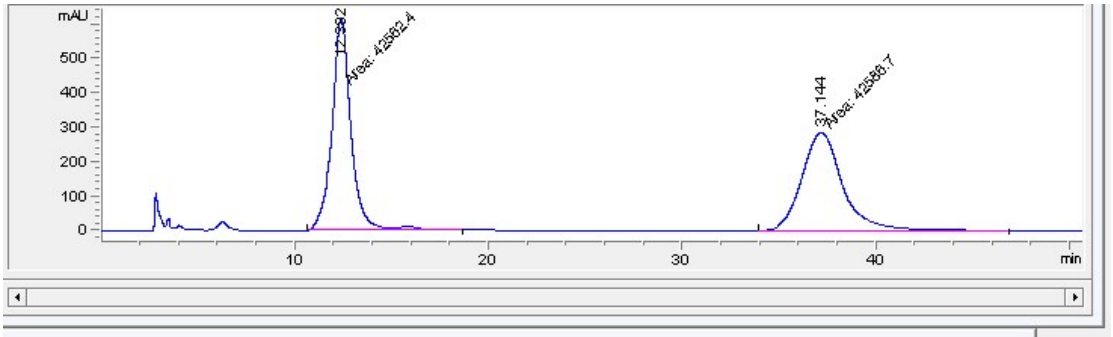
#	Time	Area	Height	Width	Area%	Symmetry
1	13.604	370702.8	3879	1.5928	98.289	0.448
2	28.127	6454.6	66.4	1.621	1.711	0.57

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

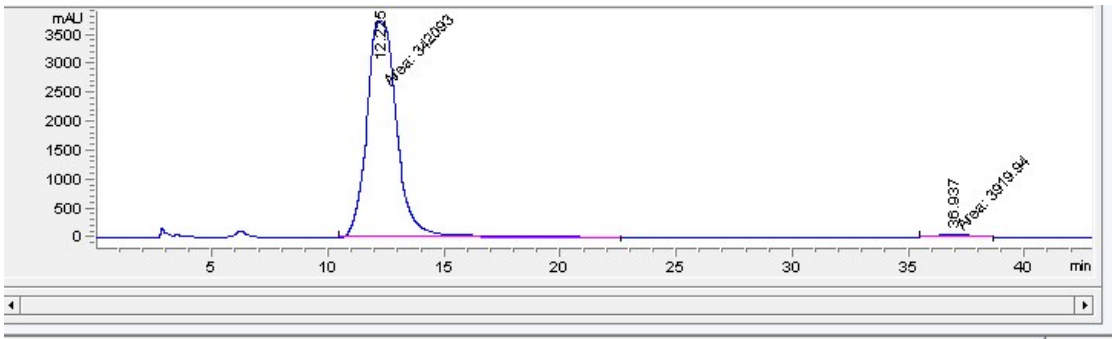




HPLC of 3d

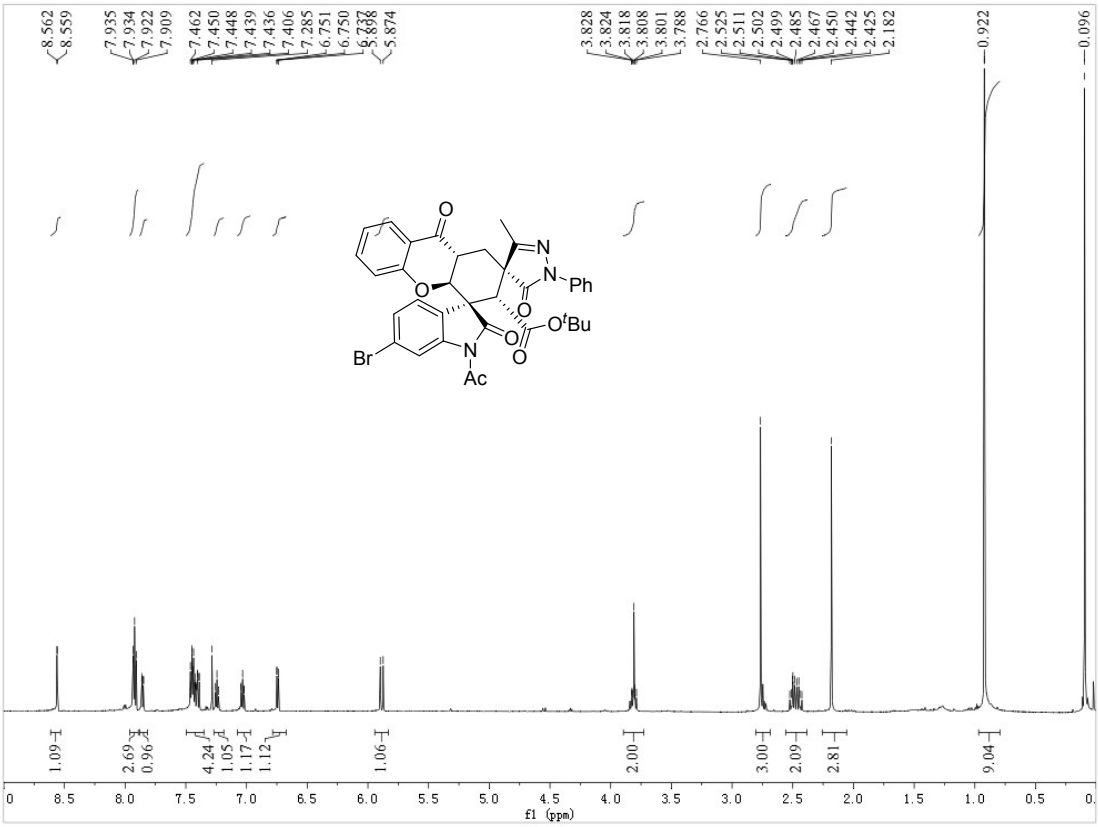


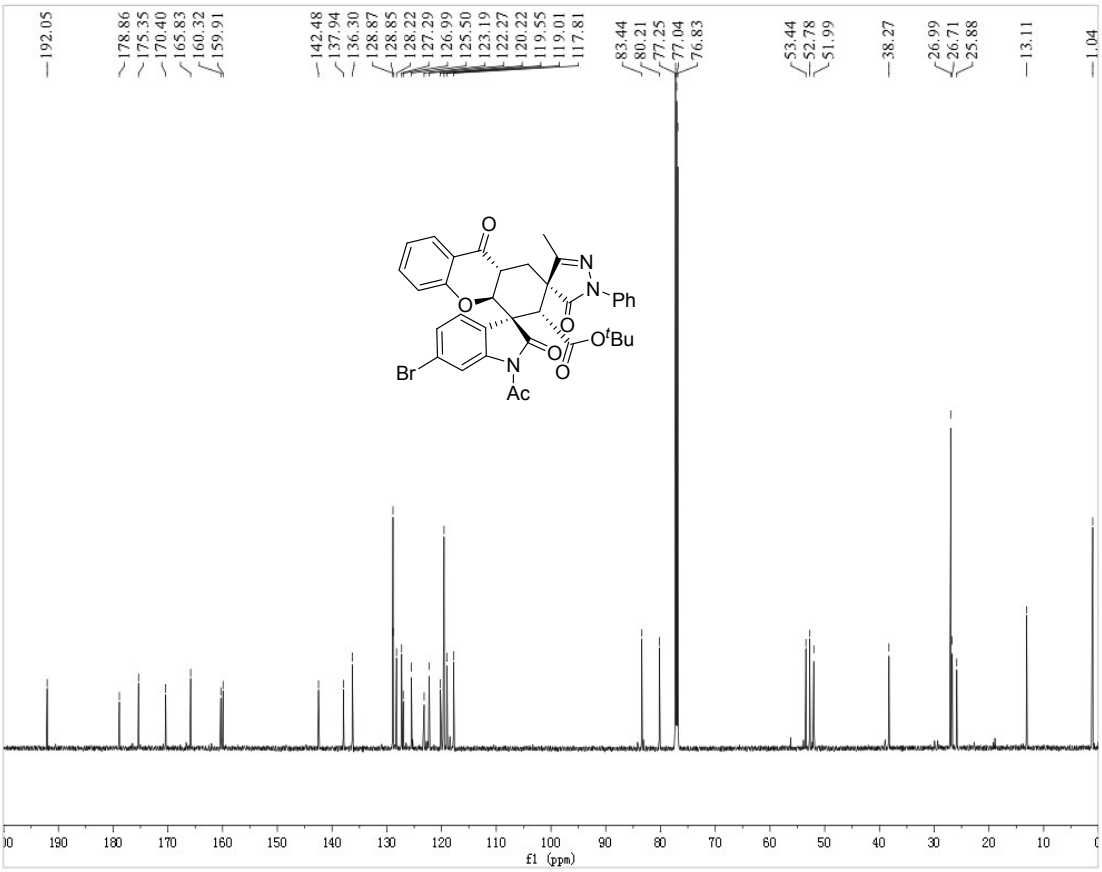
#	Time	Area	Height	Width	Area%	Symmetry
1	12.382	42562.4	616.5	1.1506	49.986	0.896
2	37.144	42586.7	285.9	2.4824	50.014	0.828



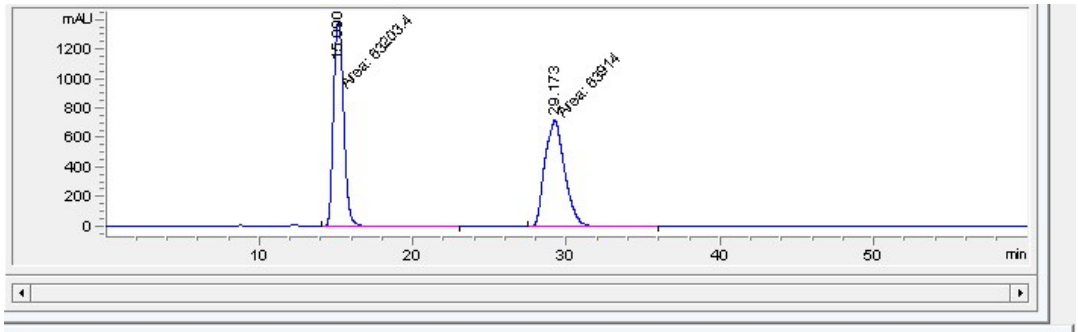
#	Time	Area	Height	Width	Area%	Symmetry
1	12.225	342093.1	3738.5	1.5251	98.867	0.764
2	36.937	3919.9	39.1	1.6696	1.133	0.785

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

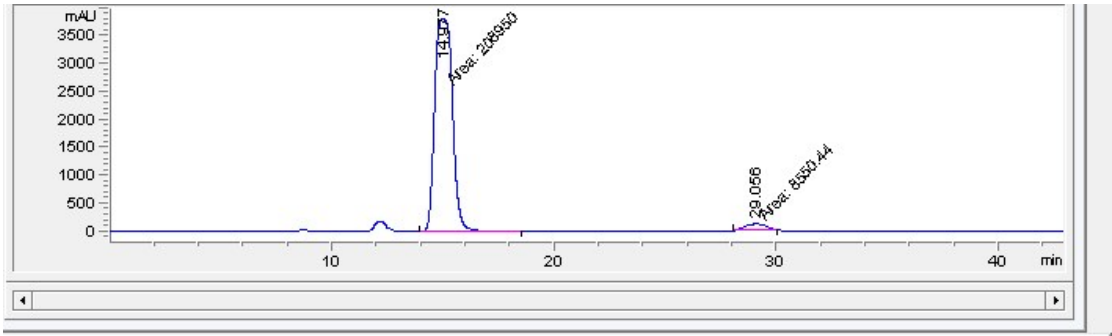




HPLC of 3e

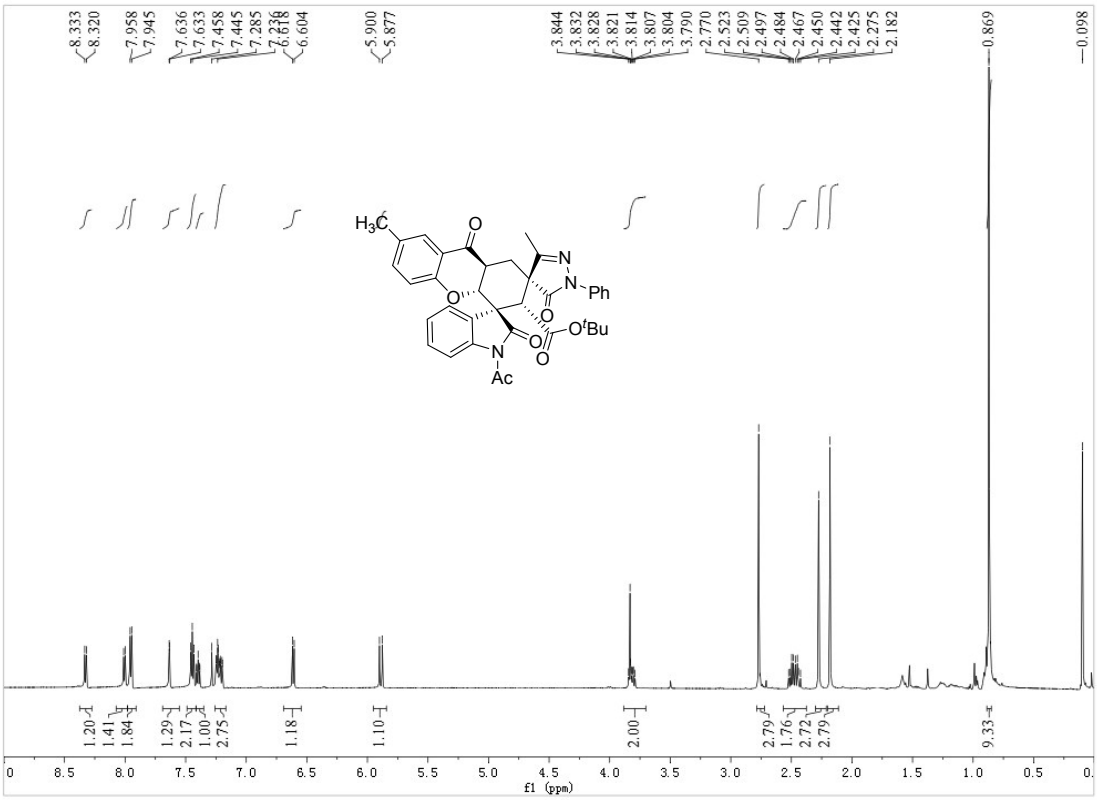


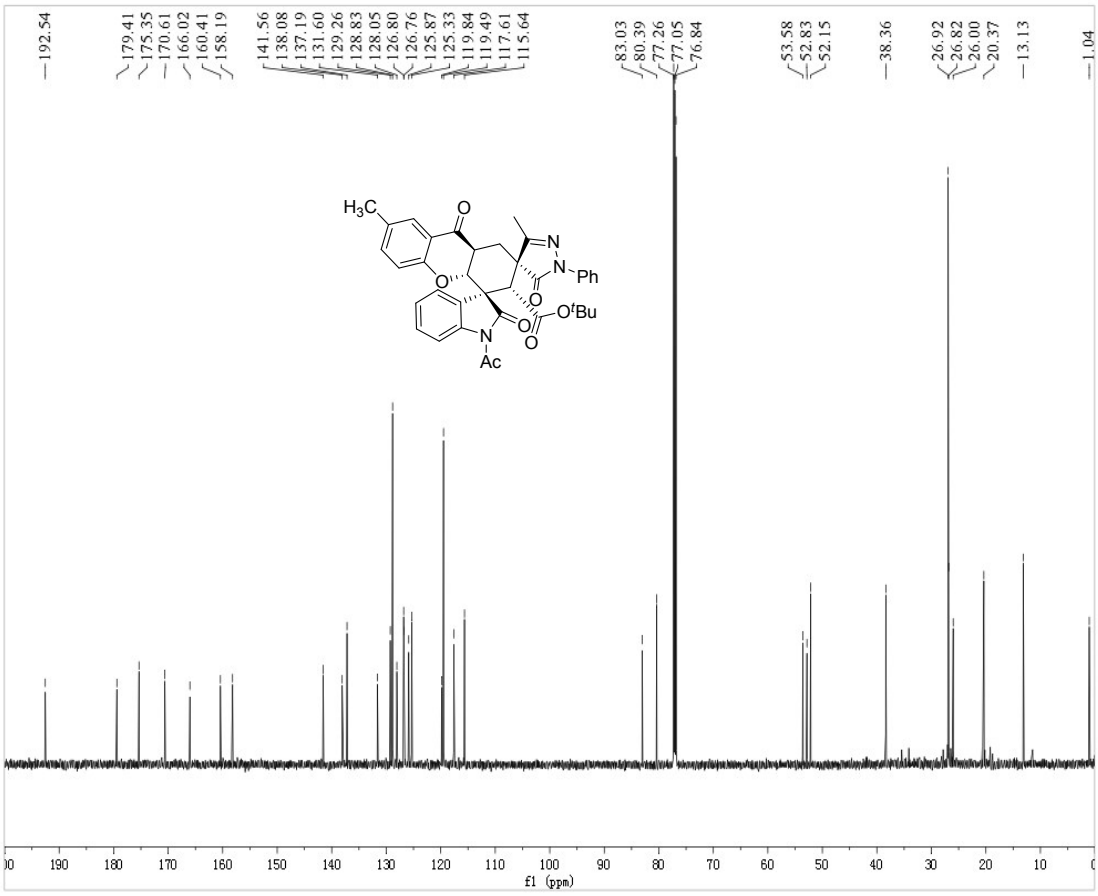
#	Time	Area	Height	Width	Area%	Symmetry
1	15.09	63203.4	1393.2	0.7561	49.721	0.88
2	29.173	63914	723.9	1.4716	50.279	0.938



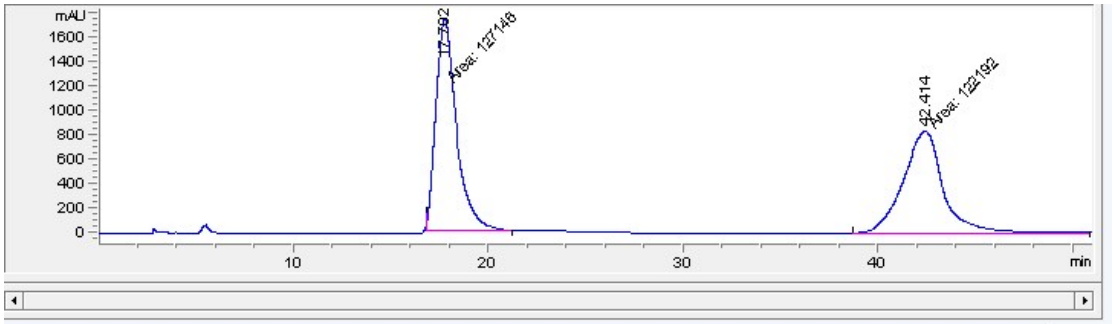
#	Time	Area	Height	Width	Area%	Symmetry
1	14.977	208950.5	3813.6	0.9132	96.069	0.826
2	29.056	8550.4	116.5	1.2232	3.931	1.177

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

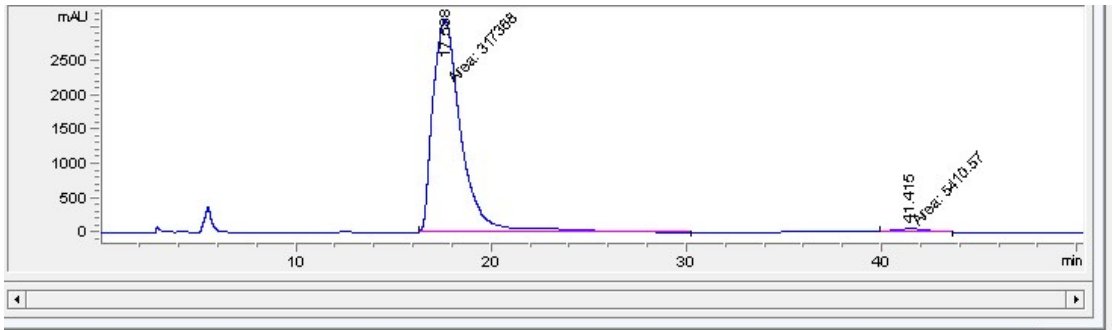




HPLC of 3f

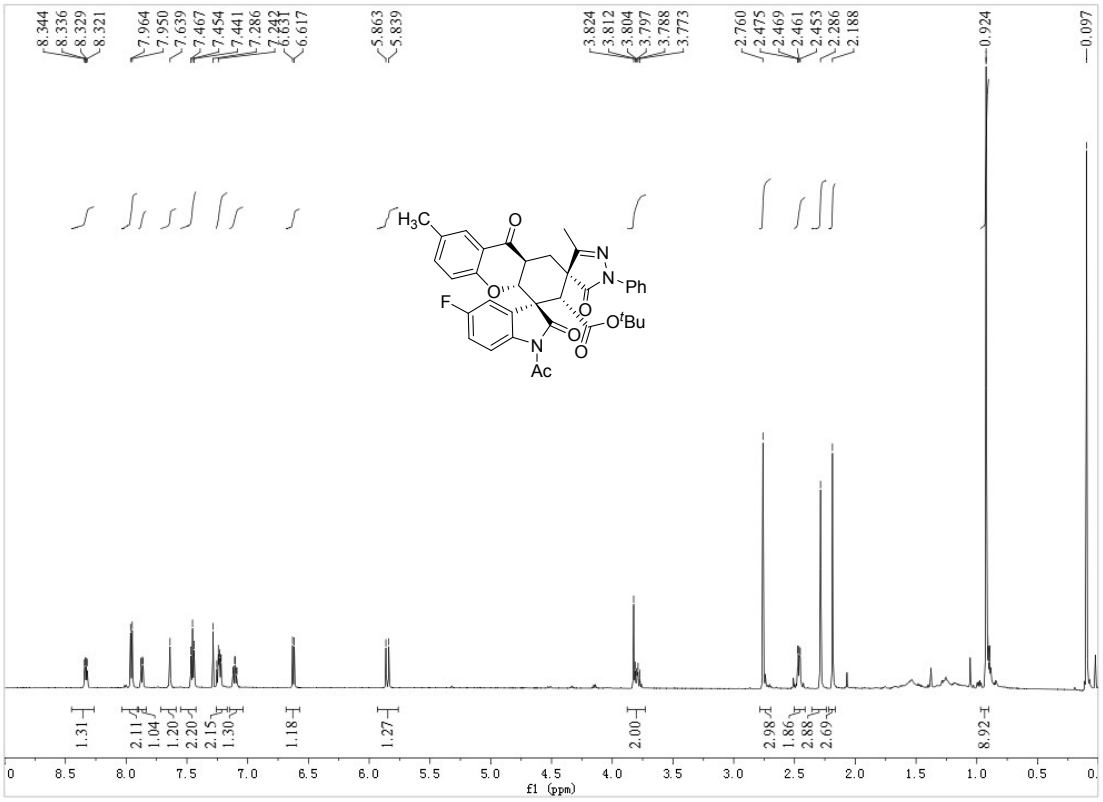


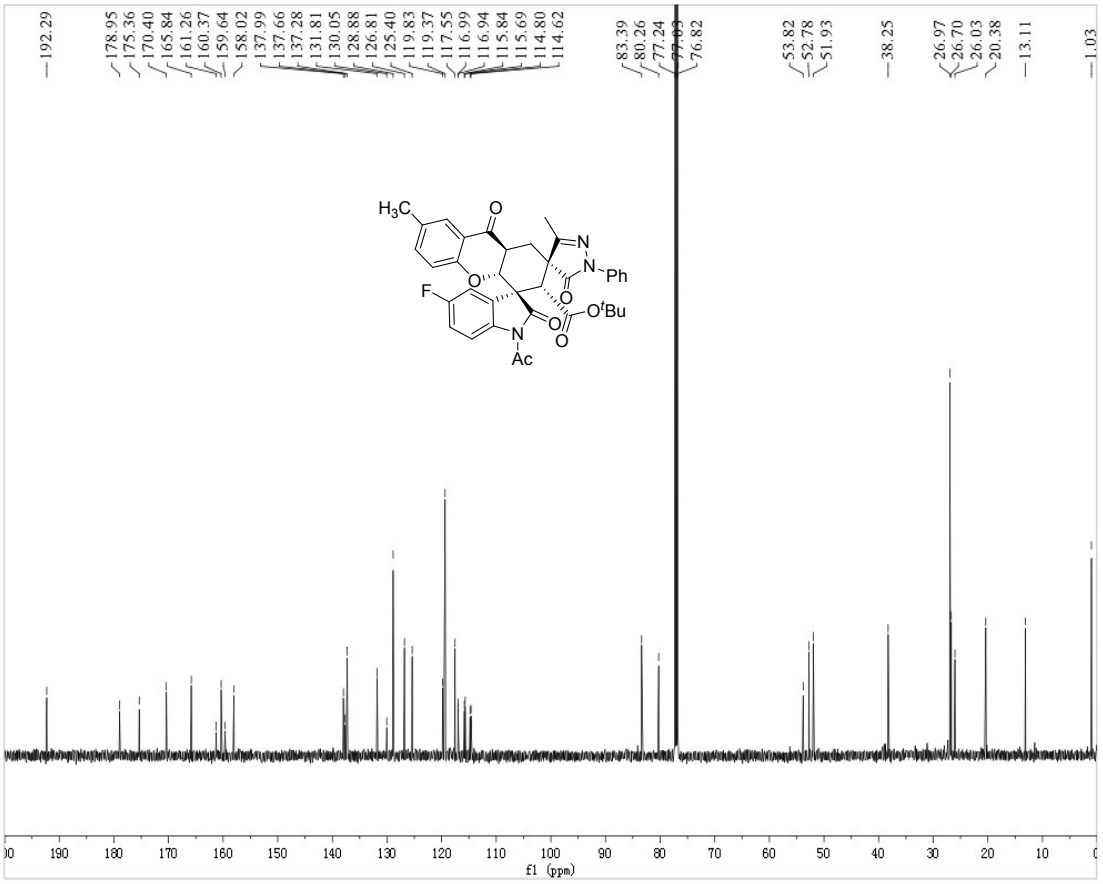
#	Time	Area	Height	Width	Area%	Symmetry
1	17.702	127146	1734.3	1.2218	50.993	0.674
2	42.414	122191.9	833.7	2.4426	49.007	1.154



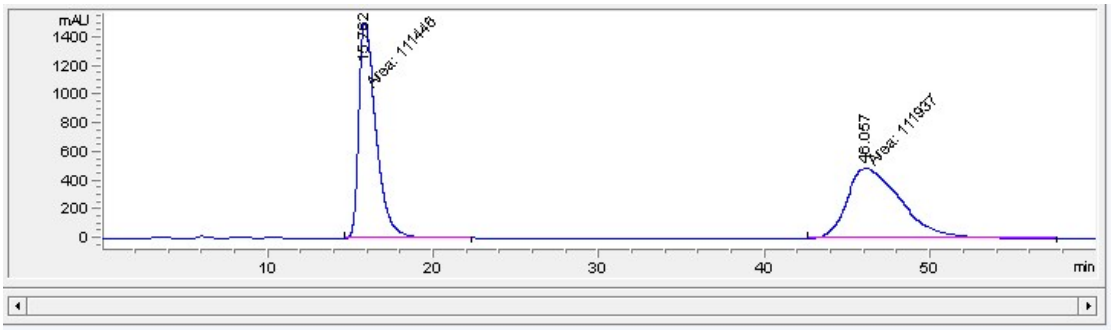
#	Time	Area	Height	Width	Area%	Symmetry
1	17.588	317367.9	3113.9	1.6986	98.324	0.684
2	41.415	5410.6	46.3	1.9475	1.676	0.913

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

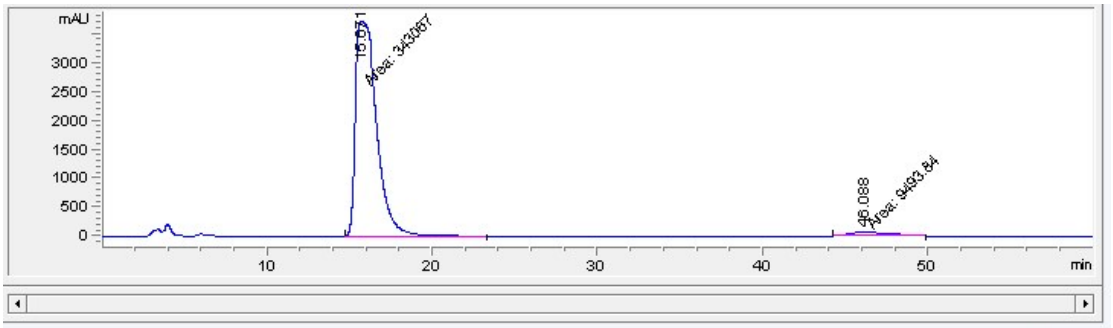




HPLC of 3g

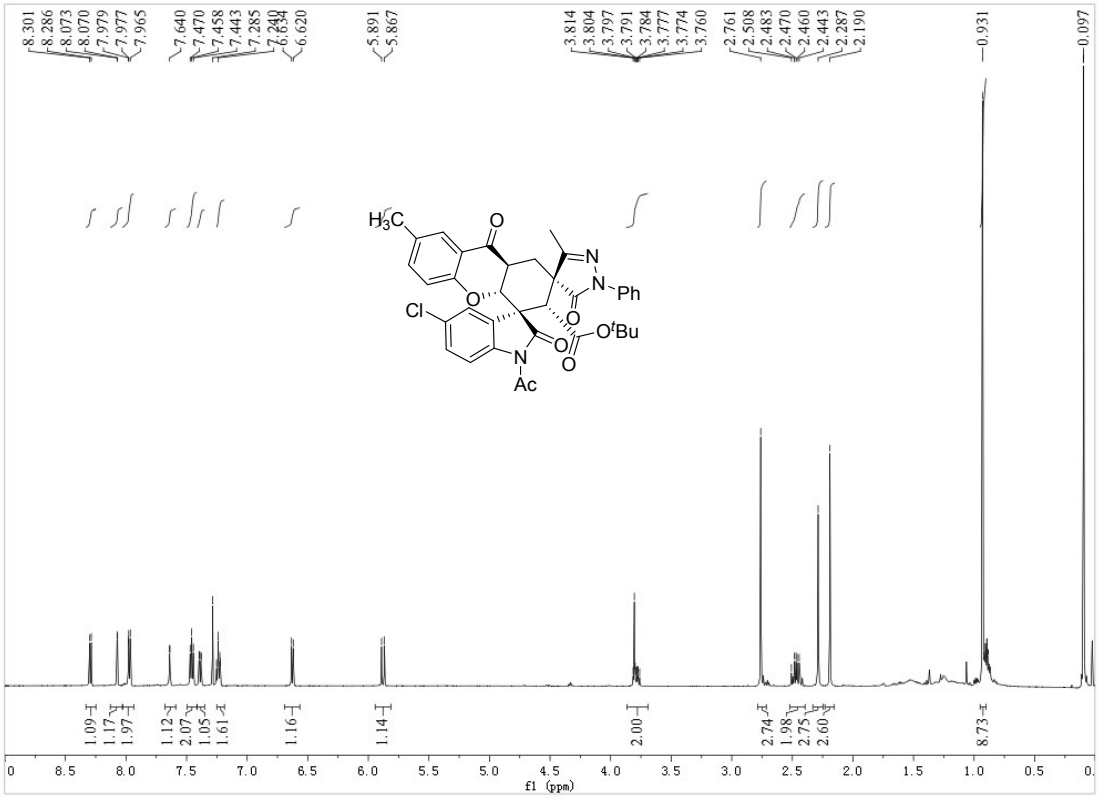


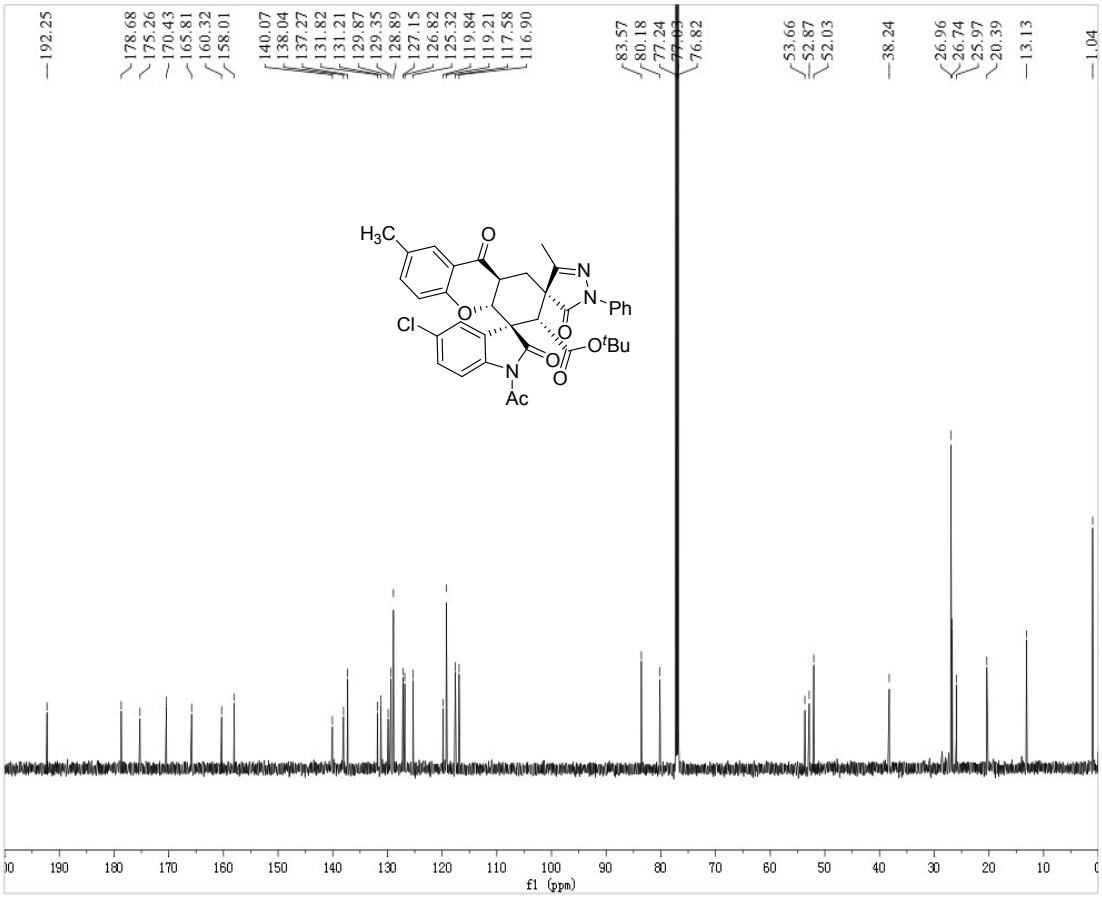
#	Time	Area	Height	Width	Area%	Symmetry
1	15.762	111445.7	1496	1.2416	49.890	0.445
2	46.057	111937.4	489	3.8155	50.110	0.52



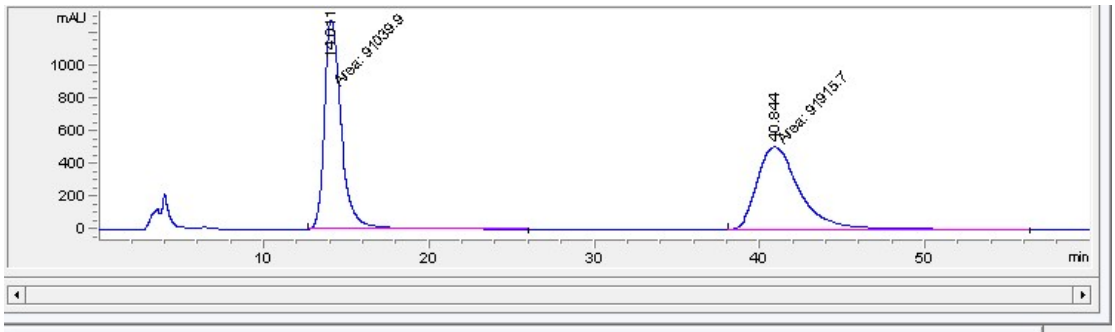
#	Time	Area	Height	Width	Area%	Symmetry
1	15.671	343066.7	3715.3	1.539	97.307	0.408
2	46.088	9493.8	55	2.8751	2.693	0.515

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

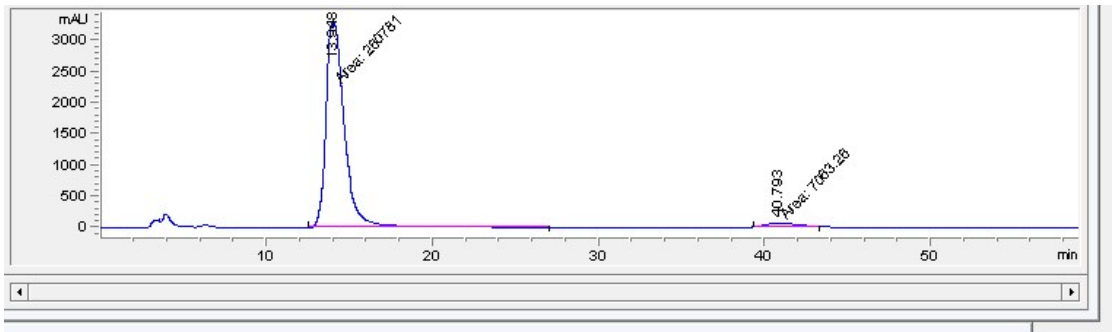




HPLC of 3h

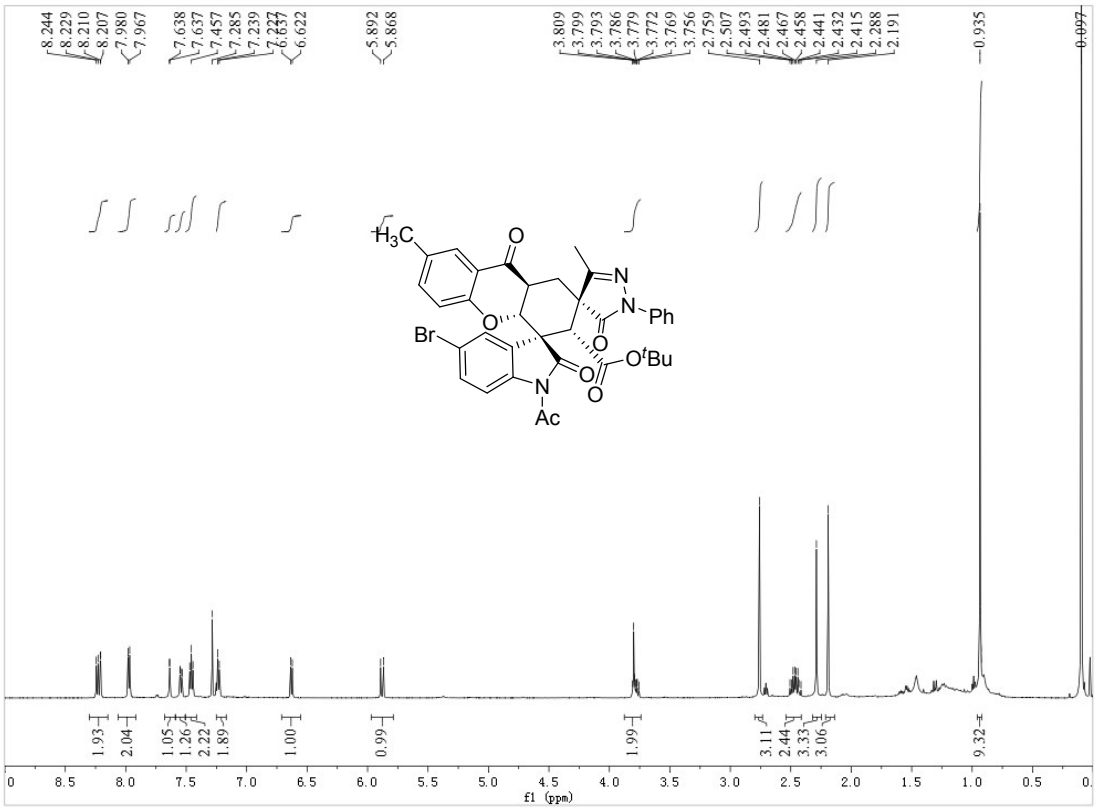


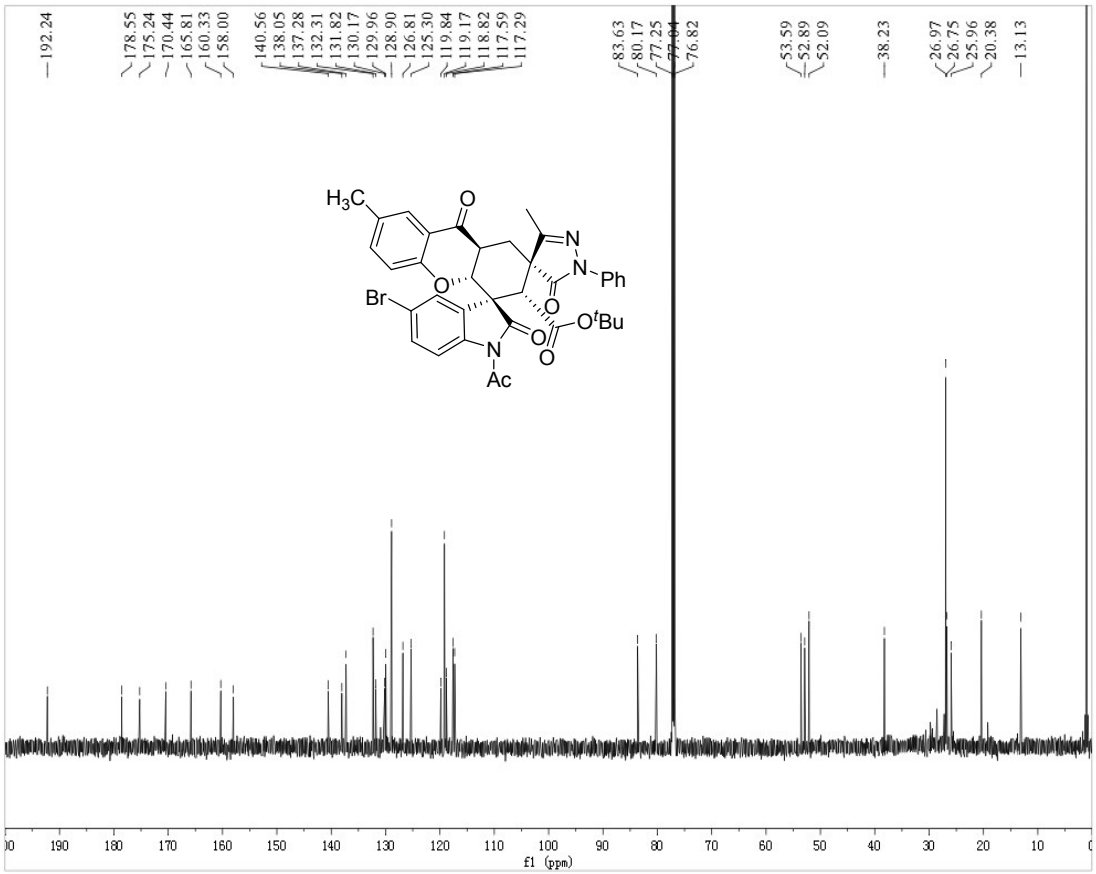
#	Time	Area	Height	Width	Area%	Symmetry
1	14.011	91039.9	1271.8	1.1931	49.761	0.6
2	40.844	91915.7	503.2	3.0444	50.239	0.618



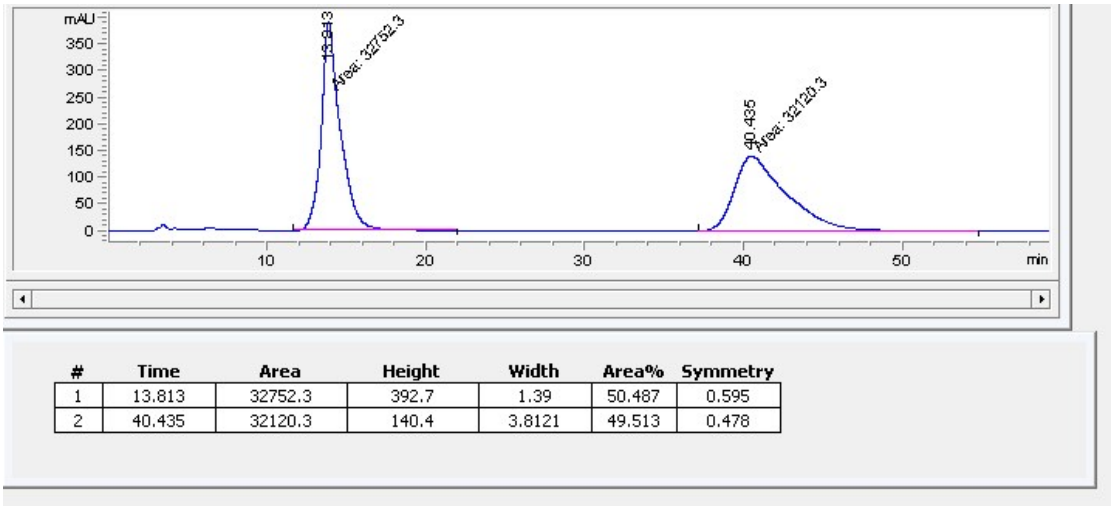
#	Time	Area	Height	Width	Area%	Symmetry
1	13.948	260781.2	3301.9	1.3163	97.363	0.562
2	40.793	7063.3	53.6	2.195	2.637	0.651

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

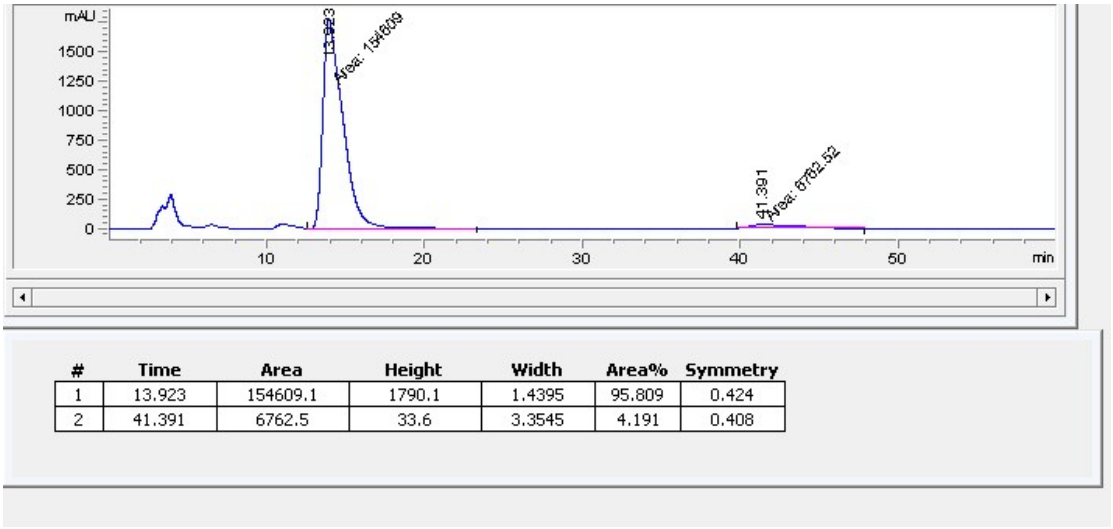




HPLC of 3i

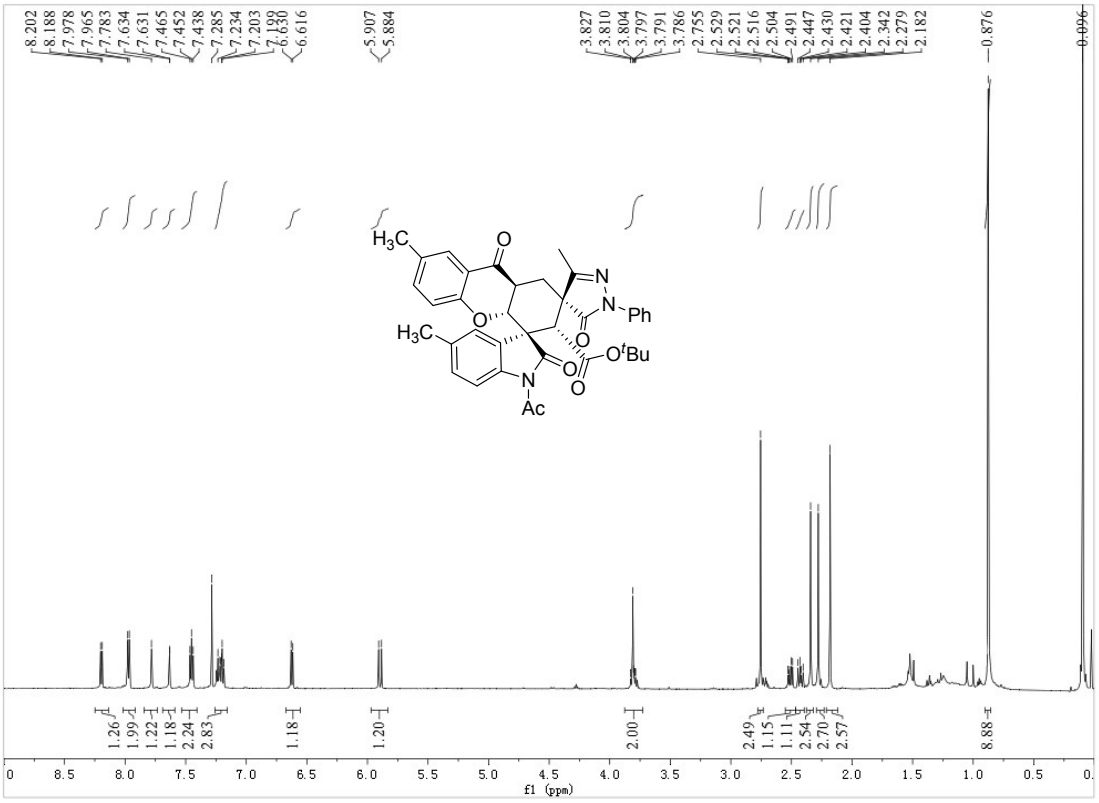


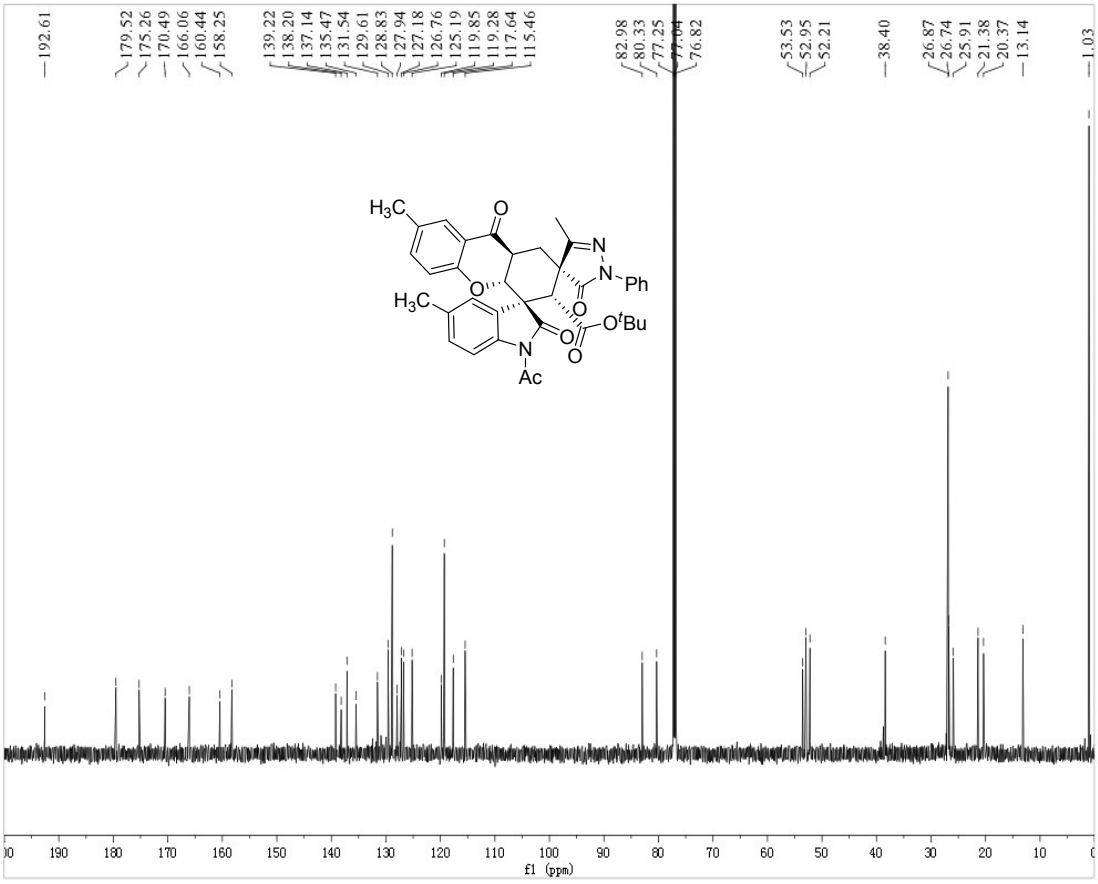
#	Time	Area	Height	Width	Area%	Symmetry
1	13.813	32752.3	392.7	1.39	50.487	0.595
2	40.435	32120.3	140.4	3.8121	49.513	0.478



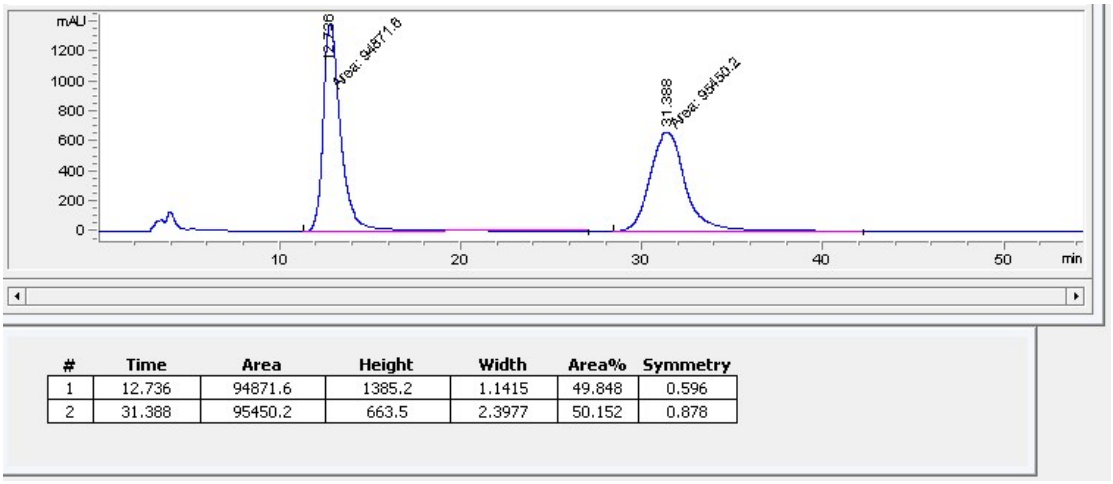
#	Time	Area	Height	Width	Area%	Symmetry
1	13.923	154609.1	1790.1	1.4395	95.809	0.424
2	41.391	6762.5	33.6	3.3545	4.191	0.408

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

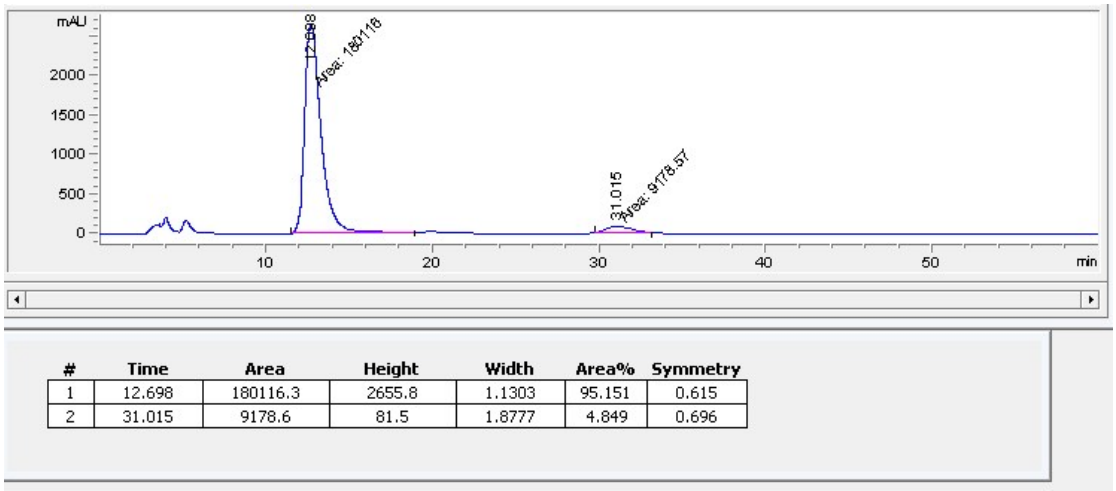




HPLC of 3j

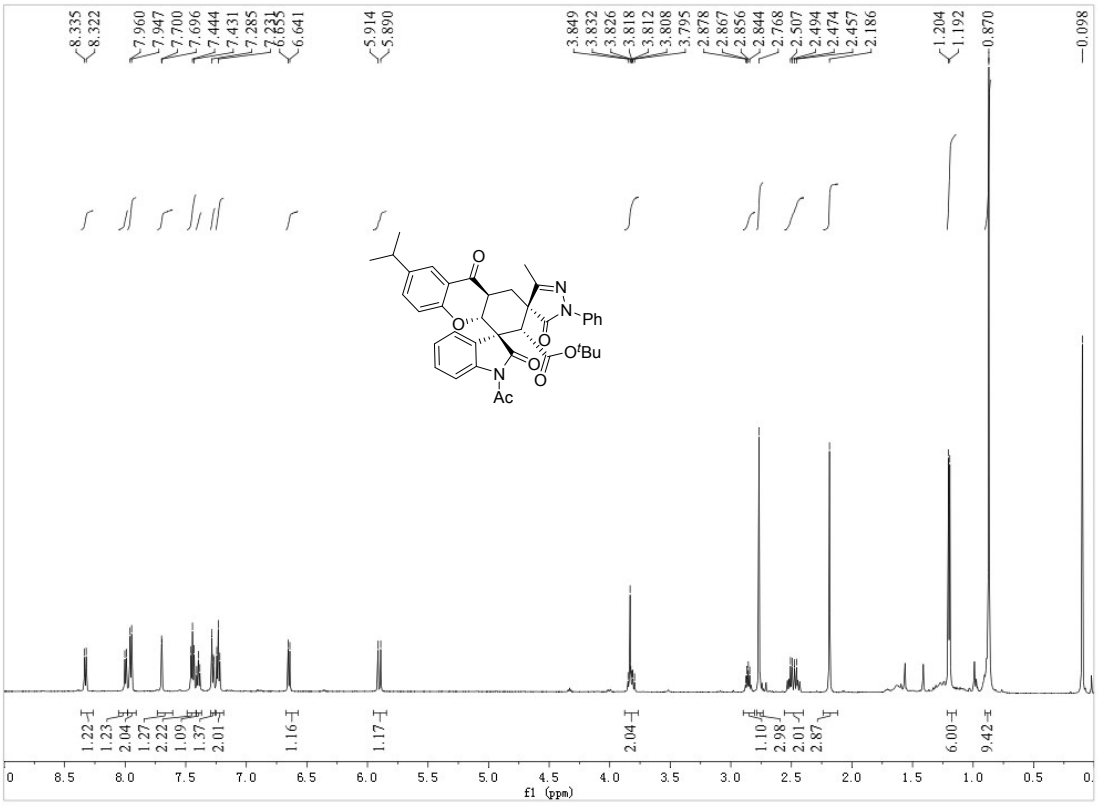


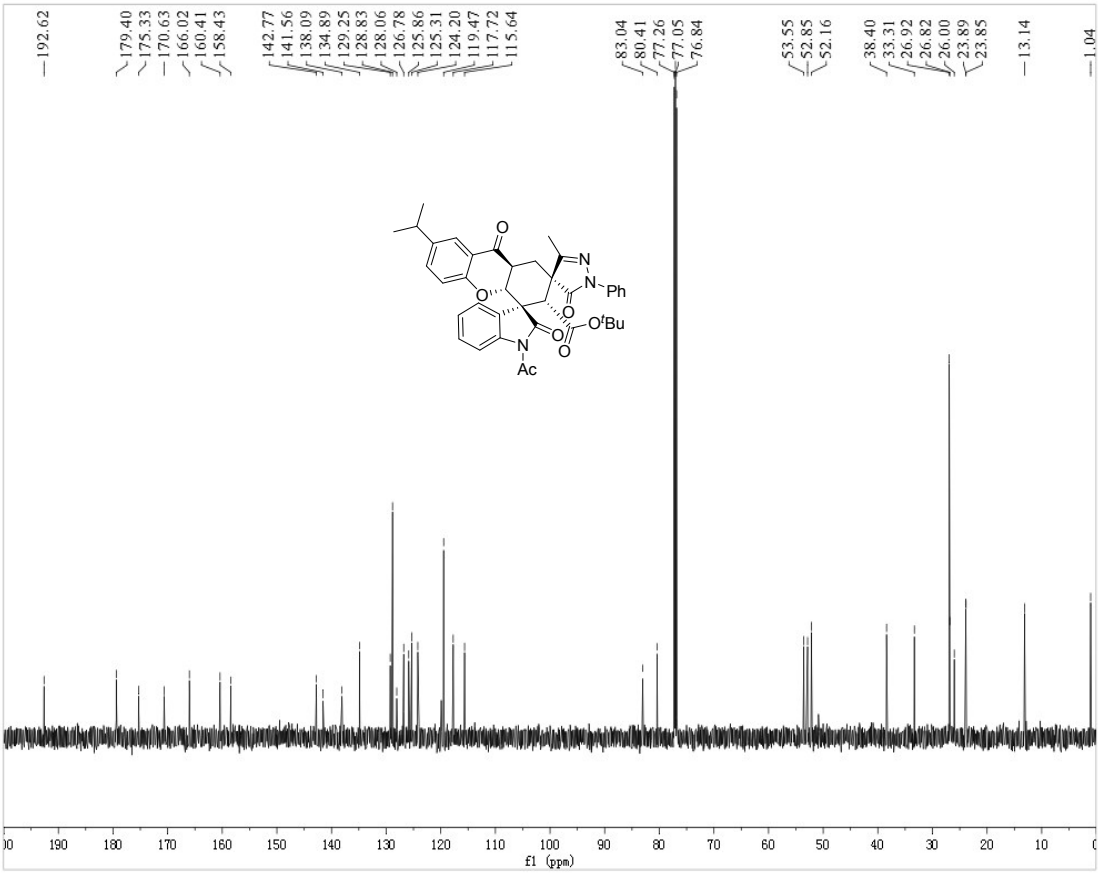
#	Time	Area	Height	Width	Area%	Symmetry
1	12.736	94871.6	1385.2	1.1415	49.848	0.596
2	31.388	95450.2	663.5	2.3977	50.152	0.878



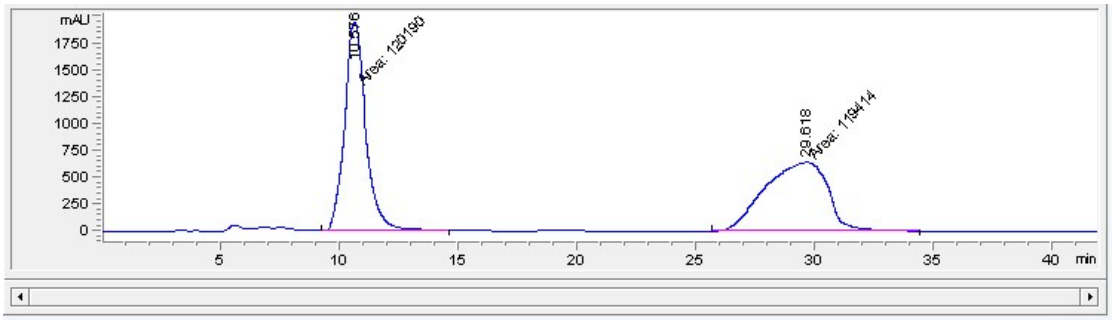
#	Time	Area	Height	Width	Area%	Symmetry
1	12.698	180116.3	2655.8	1.1303	95.151	0.615
2	31.015	9178.6	81.5	1.8777	4.849	0.696

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

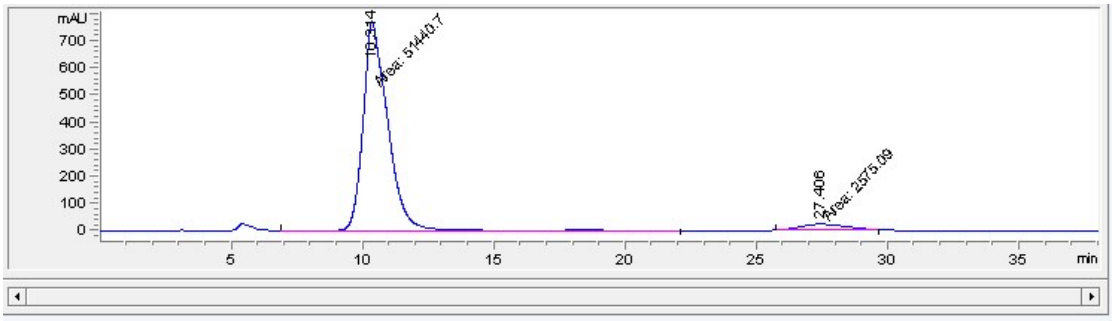




HPLC of 3k

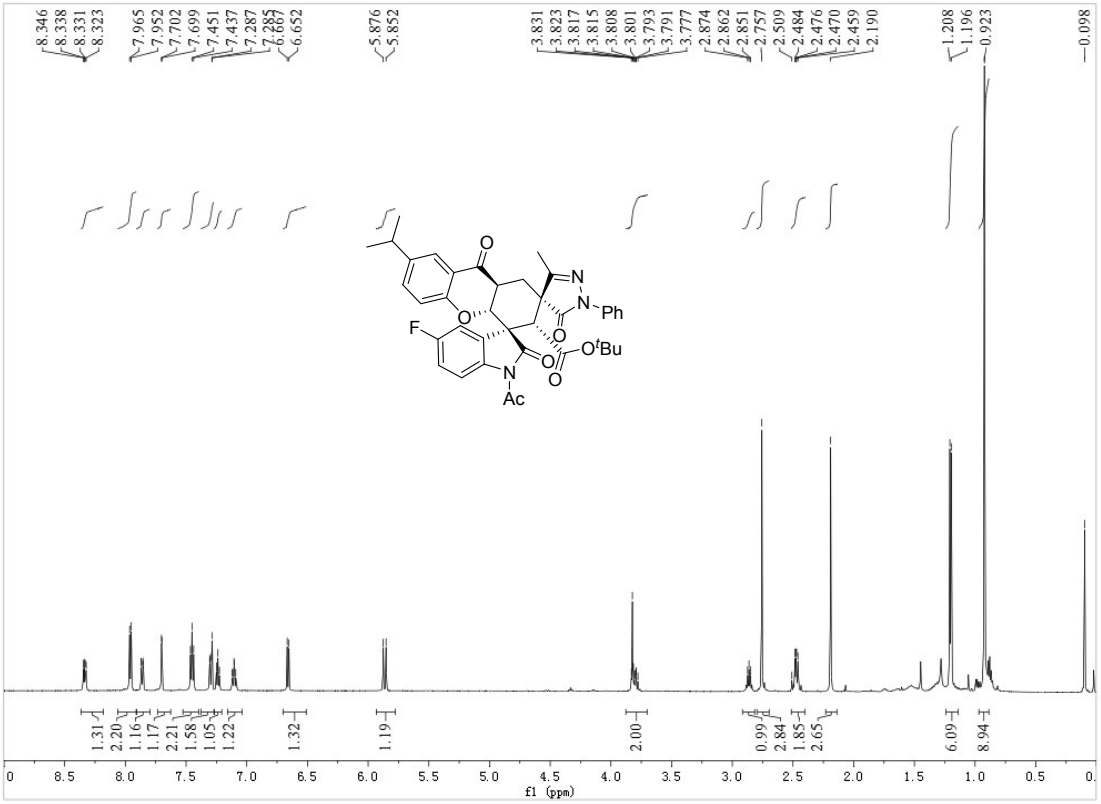


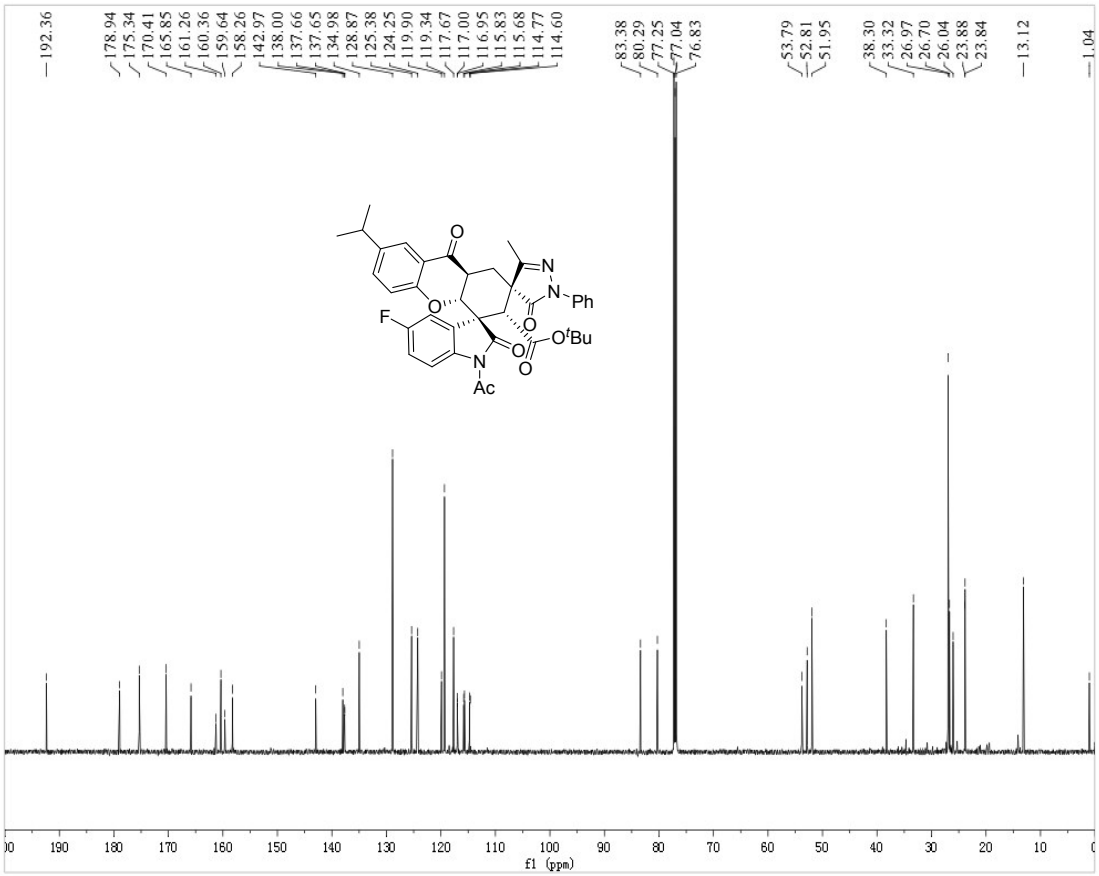
#	Time	Area	Height	Width	Area%	Symmetry
1	10.576	120189.8	1940.1	1.0325	50.162	0.777
2	29.618	119414.1	641.7	3.1017	49.838	1.755



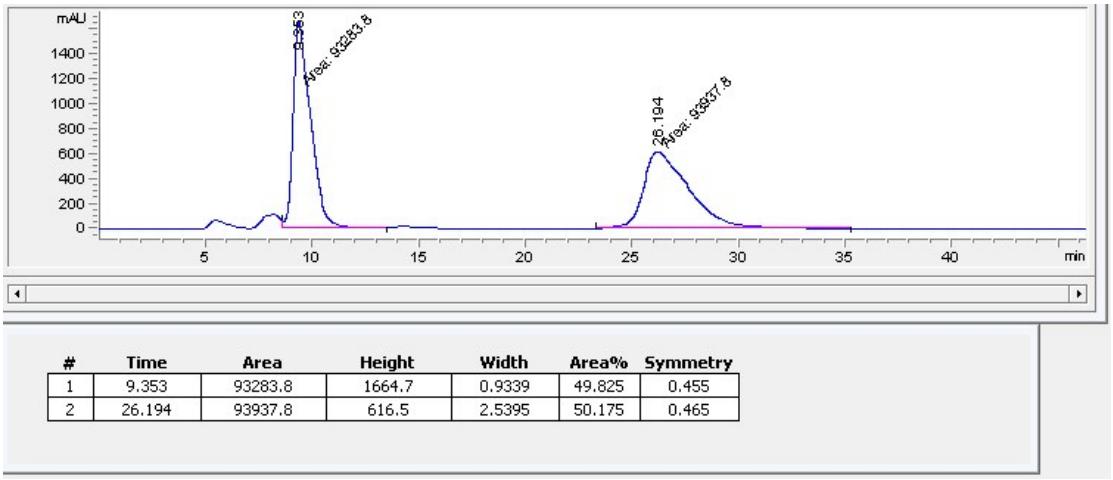
#	Time	Area	Height	Width	Area%	Symmetry
1	10.314	51440.7	775.1	1.1061	95.233	0.546
2	27.406	2575.1	21.4	2.0049	4.767	0.807

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

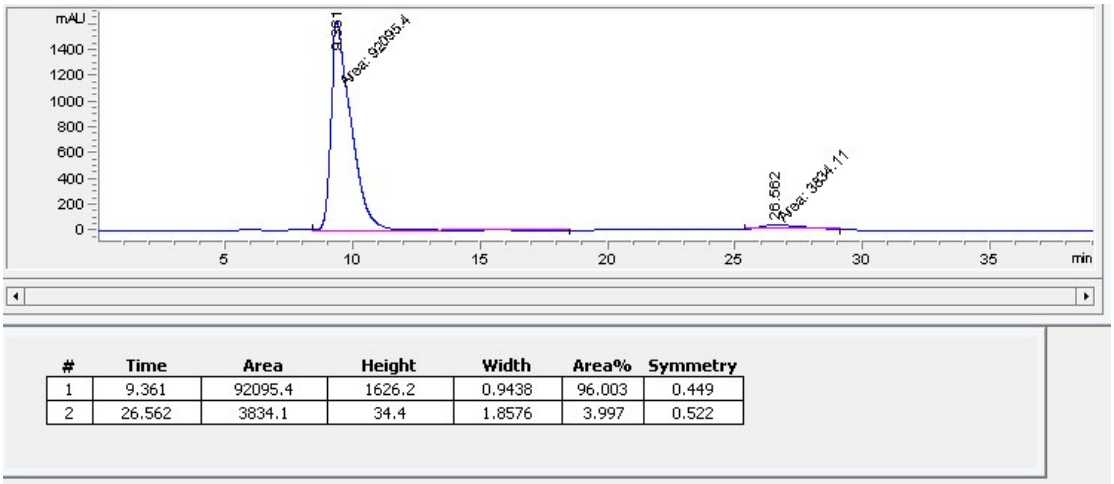




HPLC of 3l

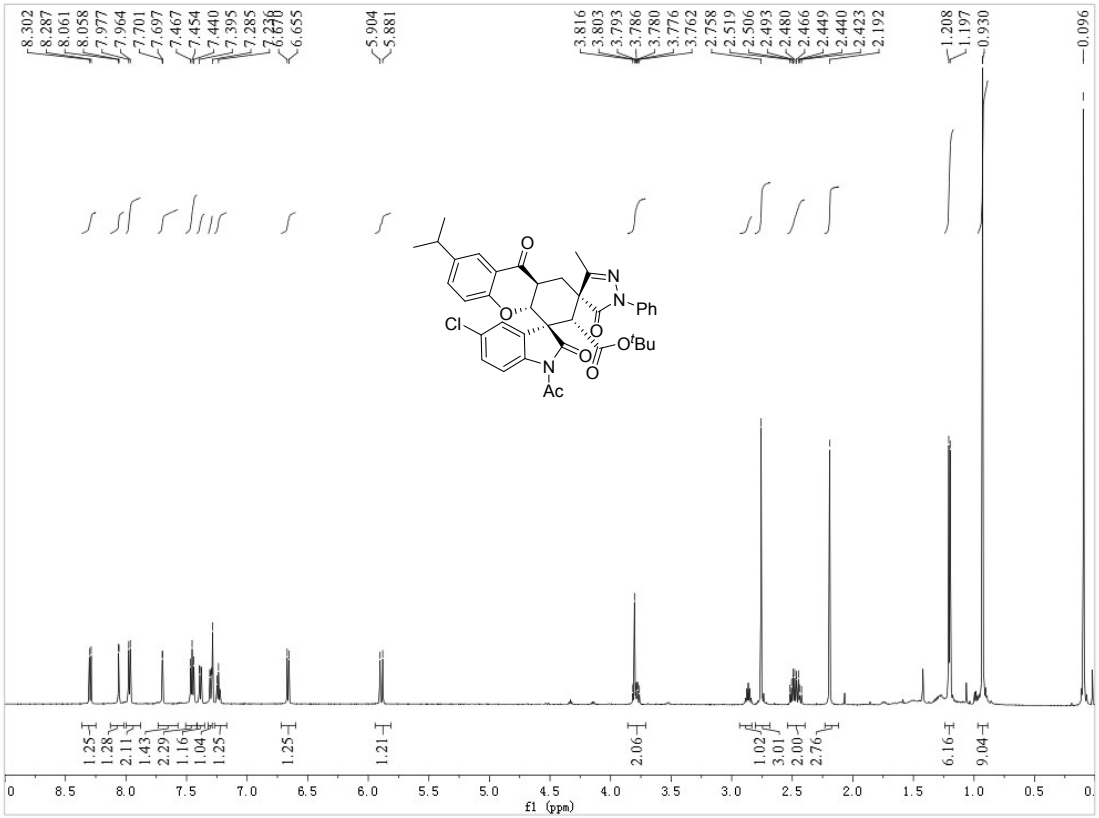


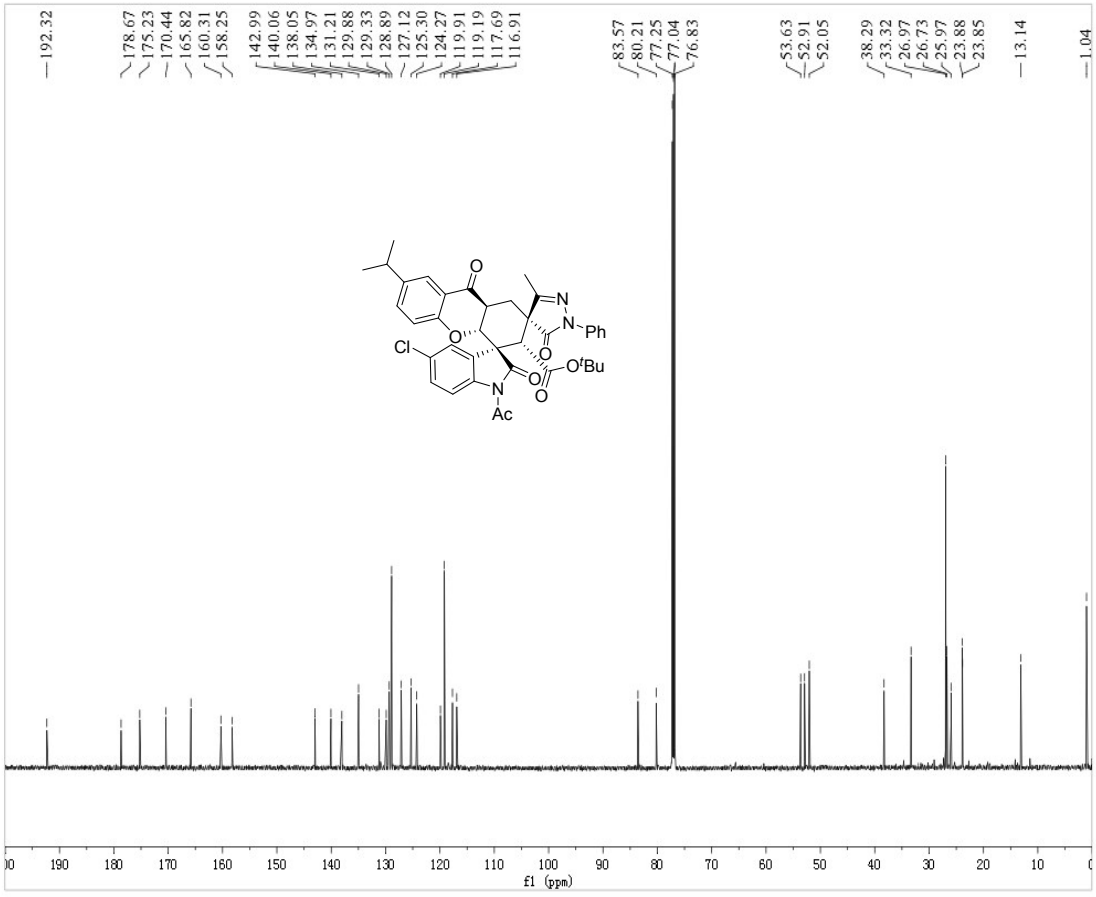
#	Time	Area	Height	Width	Area%	Symmetry
1	9.353	93283.8	1664.7	0.9339	49.825	0.455
2	26.194	93937.8	616.5	2.5395	50.175	0.465



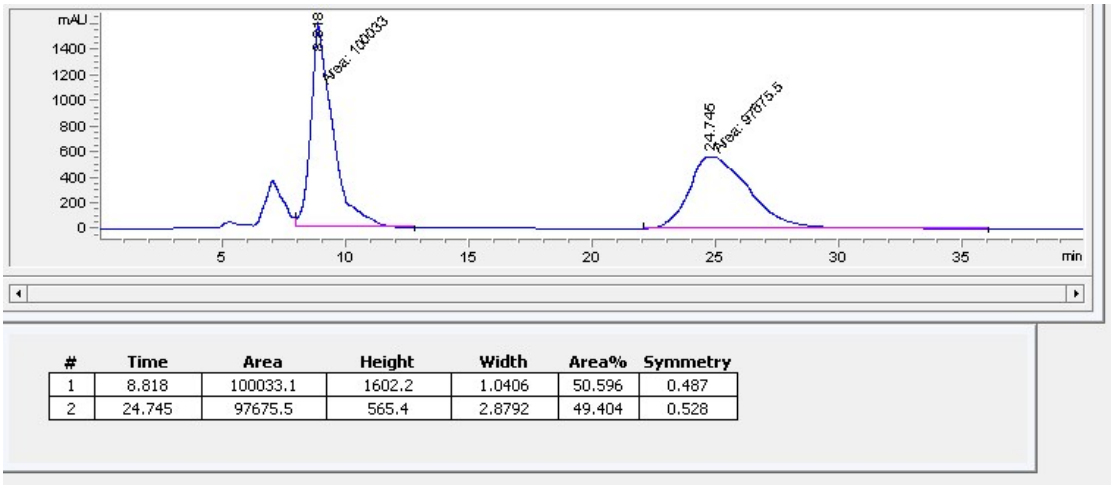
#	Time	Area	Height	Width	Area%	Symmetry
1	9.361	92095.4	1626.2	0.9438	96.003	0.449
2	26.562	3834.1	34.4	1.8576	3.997	0.522

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

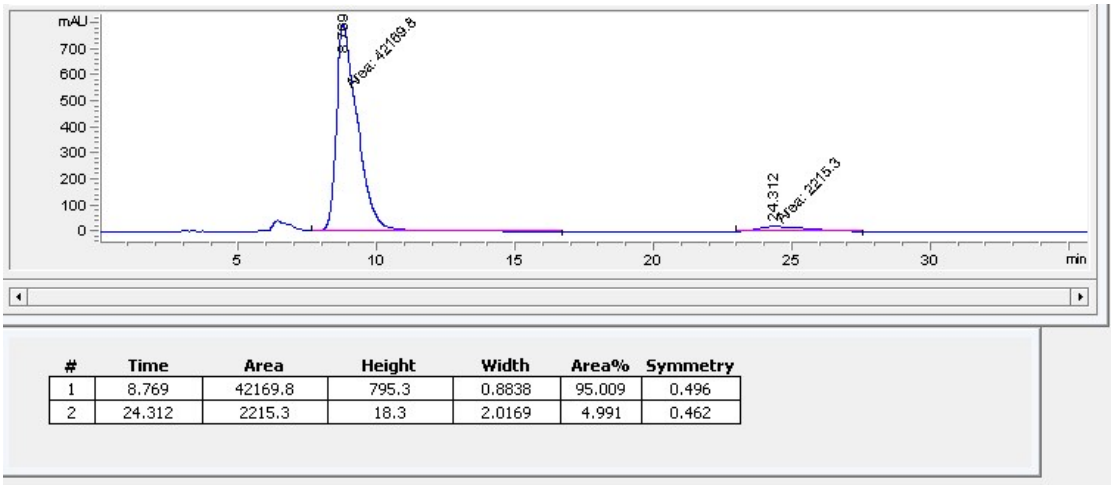




HPLC of 3m

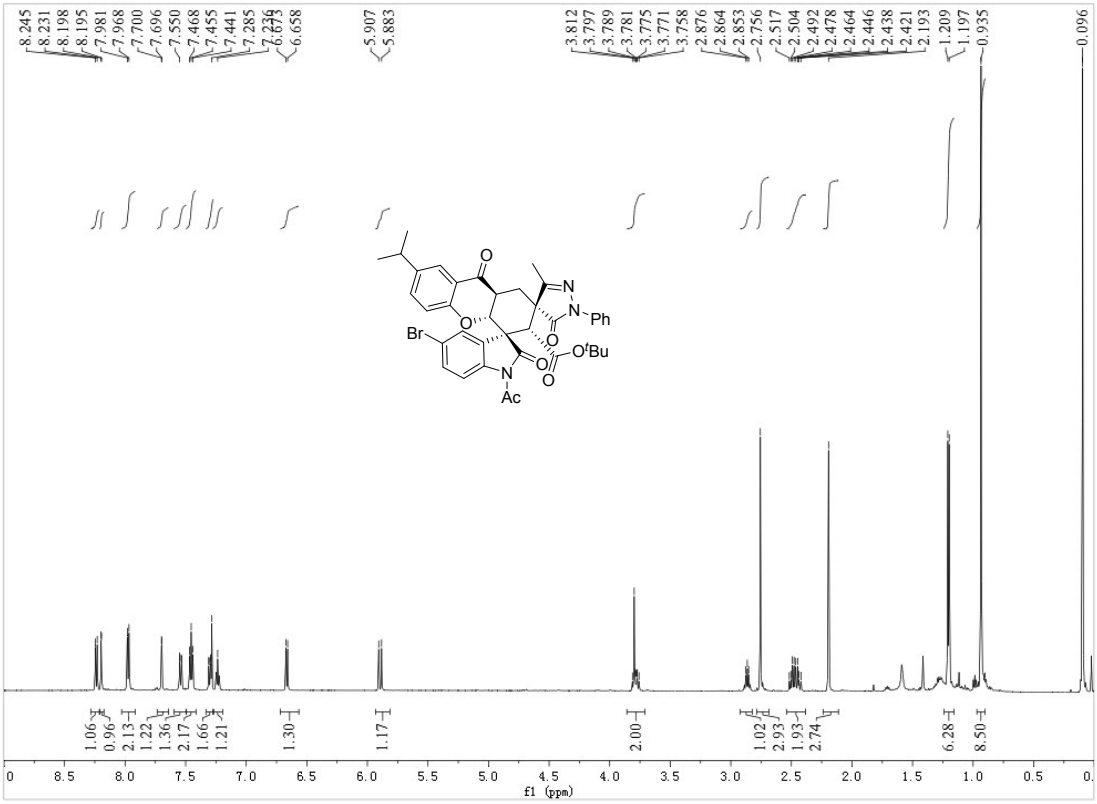


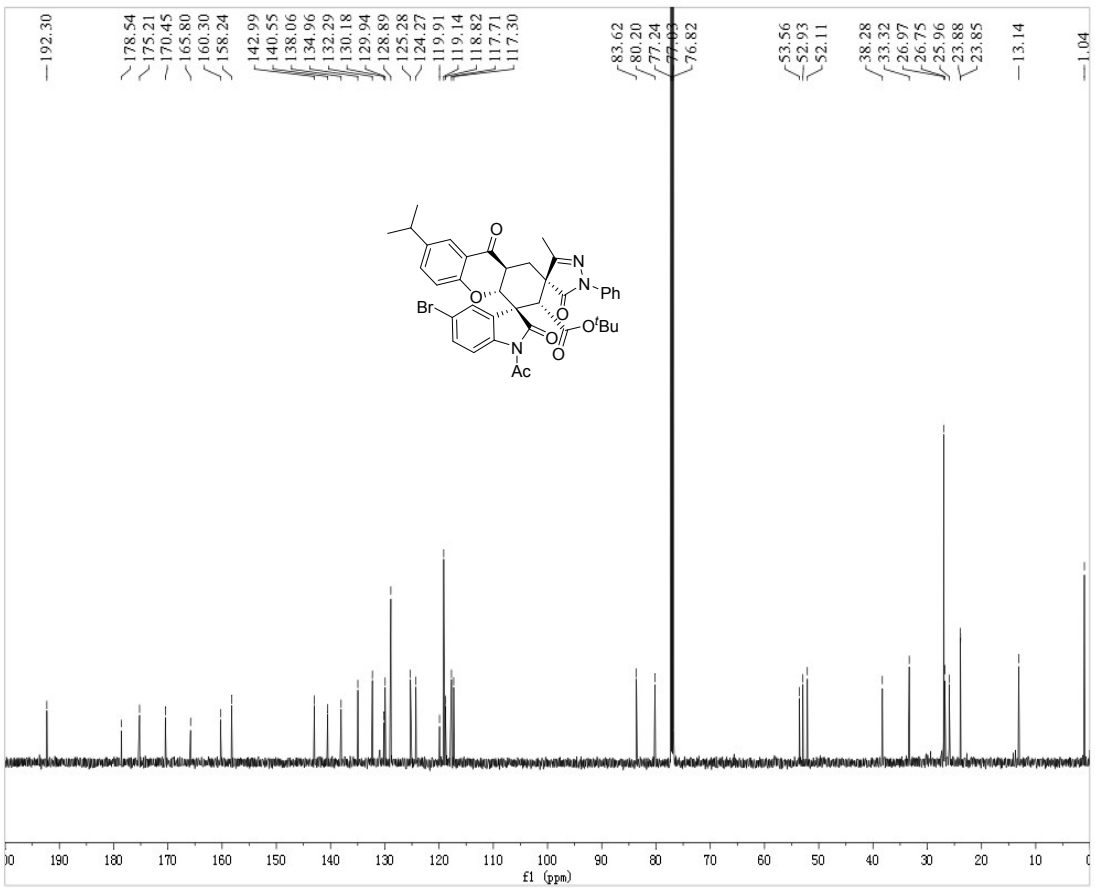
#	Time	Area	Height	Width	Area%	Symmetry
1	8.818	100033.1	1602.2	1.0406	50.596	0.487
2	24.745	97675.5	565.4	2.8792	49.404	0.528



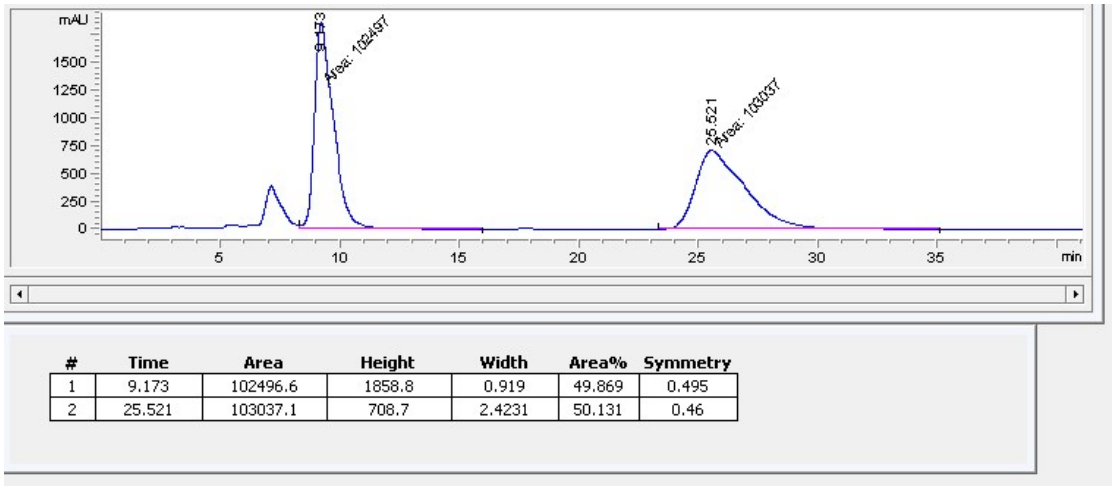
#	Time	Area	Height	Width	Area%	Symmetry
1	8.769	42169.8	795.3	0.8838	95.009	0.496
2	24.312	2215.3	18.3	2.0169	4.991	0.462

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

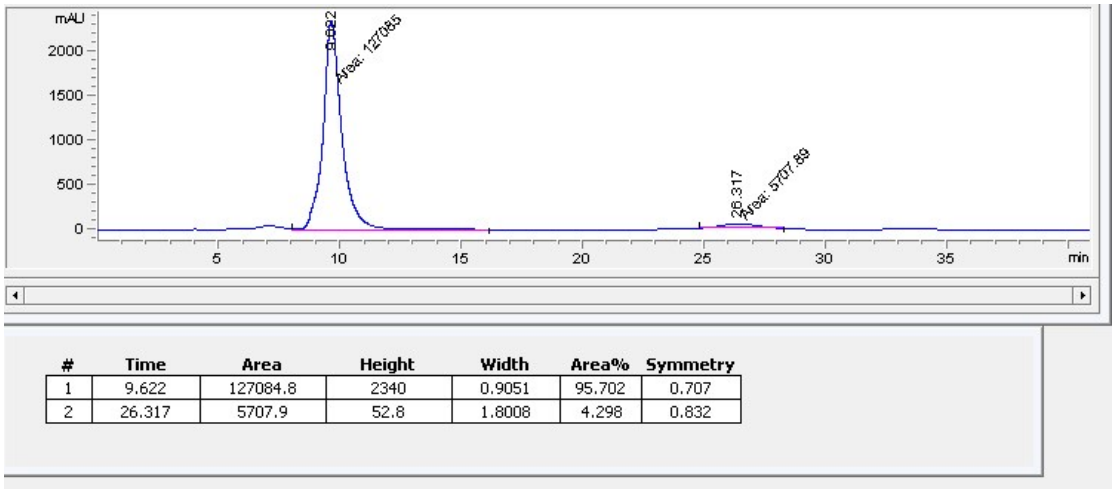




HPLC of 3n

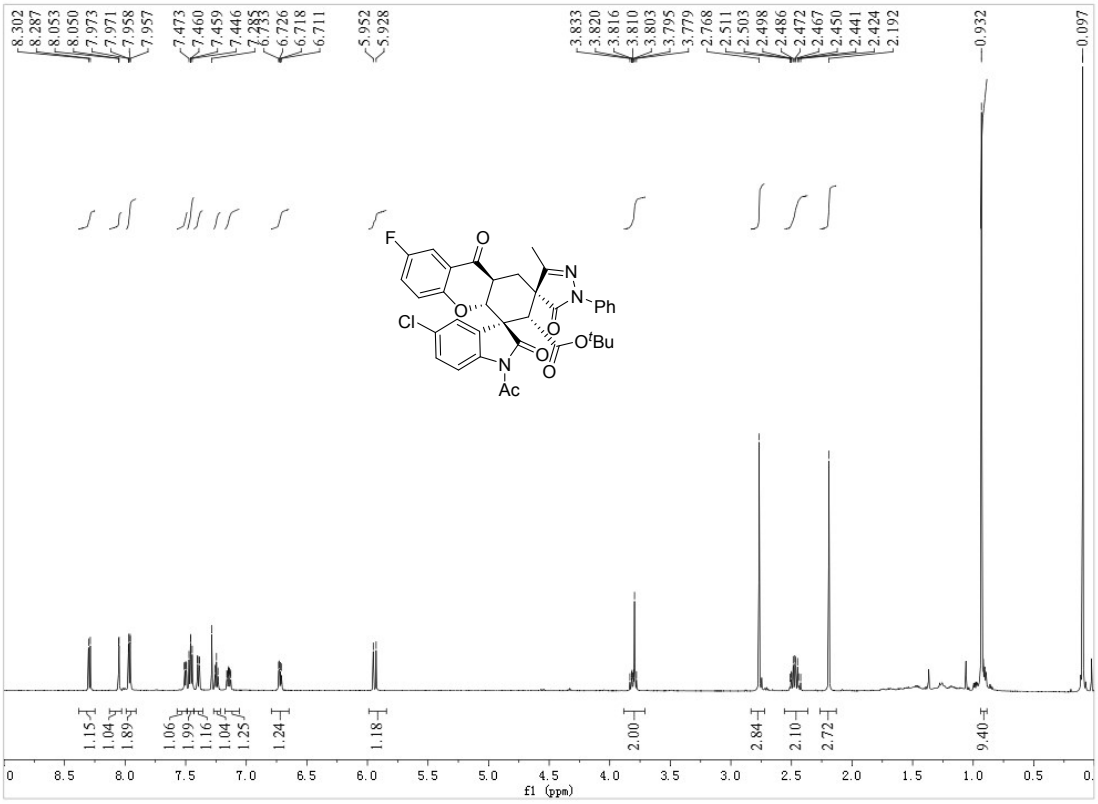


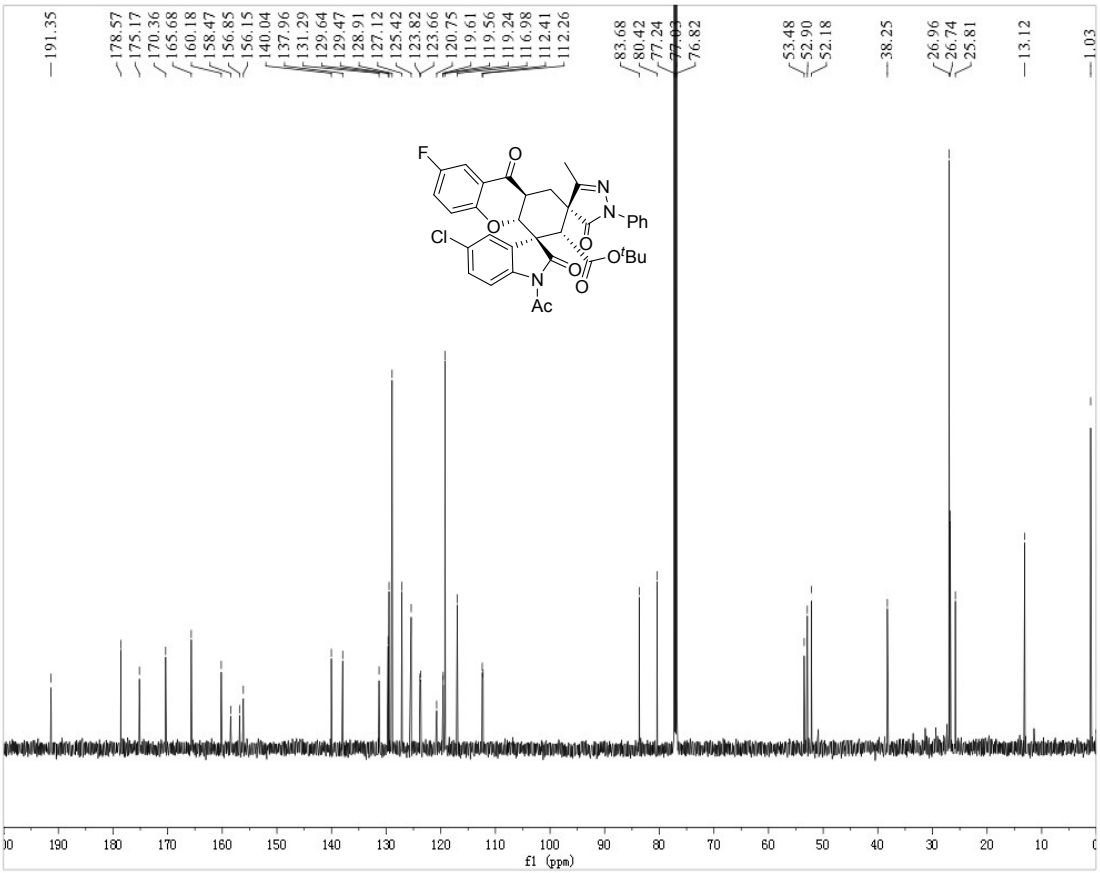
#	Time	Area	Height	Width	Area%	Symmetry
1	9.173	102496.6	1858.8	0.919	49.869	0.495
2	25.521	103037.1	708.7	2.4231	50.131	0.46



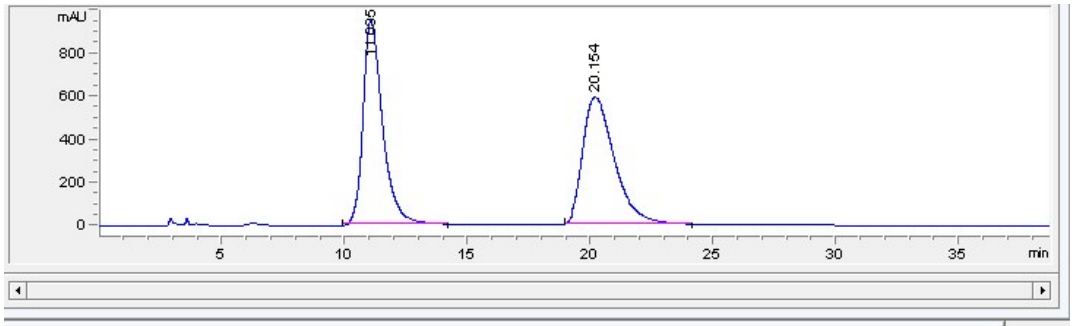
#	Time	Area	Height	Width	Area%	Symmetry
1	9.622	127084.8	2340	0.9051	95.702	0.707
2	26.317	5707.9	52.8	1.8008	4.298	0.832

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

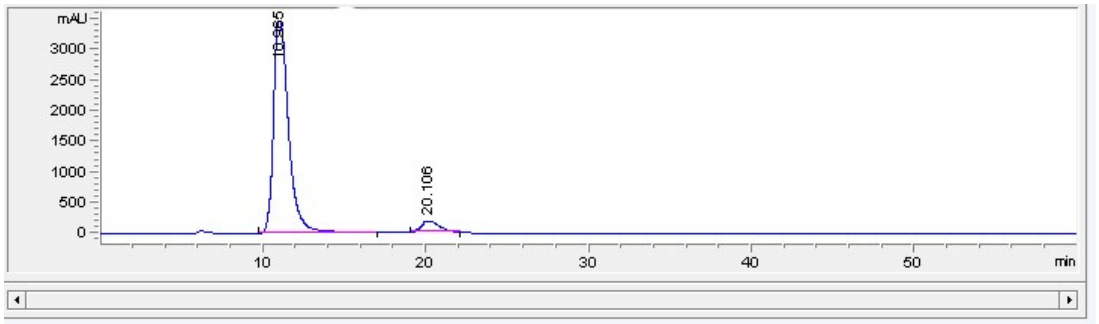




HPLC of 3o

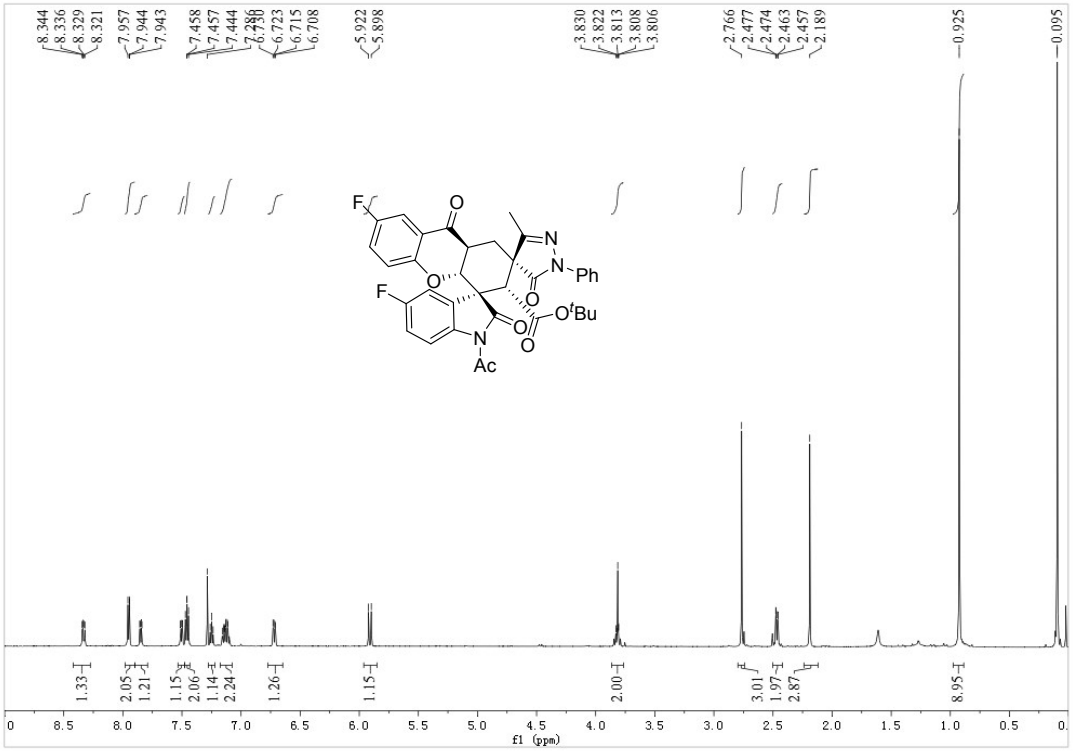


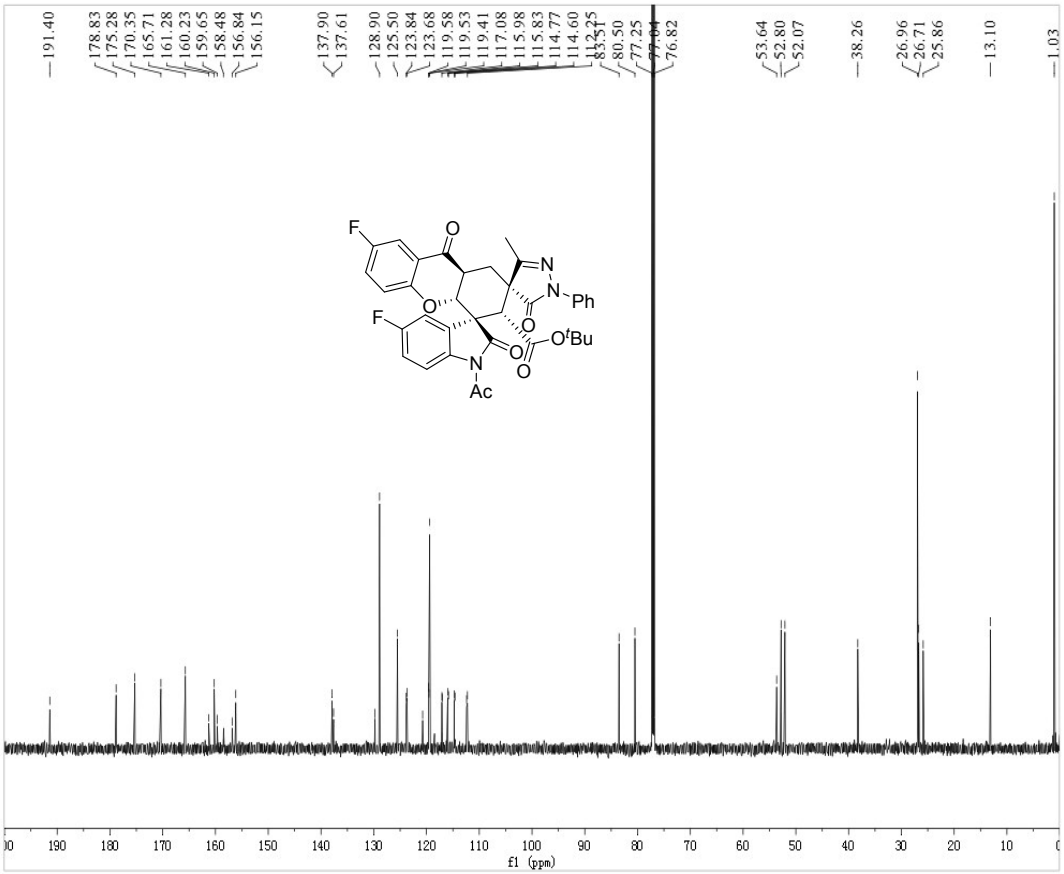
#	Time	Area	Height	Width	Area%	Symmetry
1	11.035	52763.8	945.7	0.9299	49.666	0.64
2	20.154	53472.6	588.5	1.5143	50.334	0.577



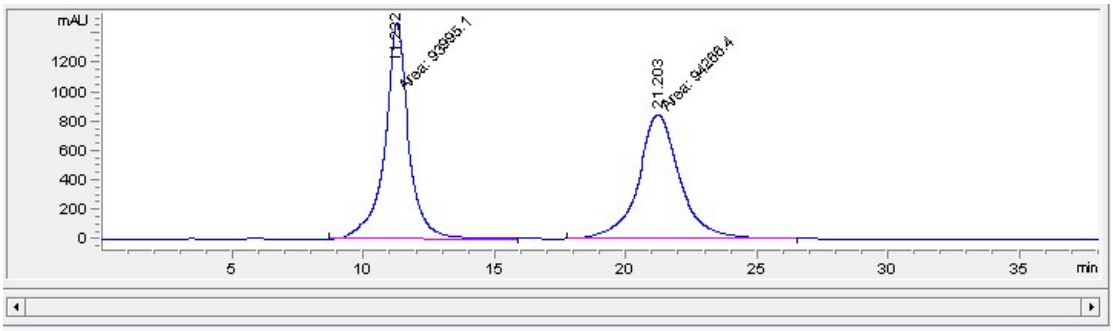
#	Time	Area	Height	Width	Area%	Symmetry
1	10.965	223326.8	3455.9	1.077	94.935	0.599
2	20.106	14166.1	177	1.3336	5.065	0.633

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

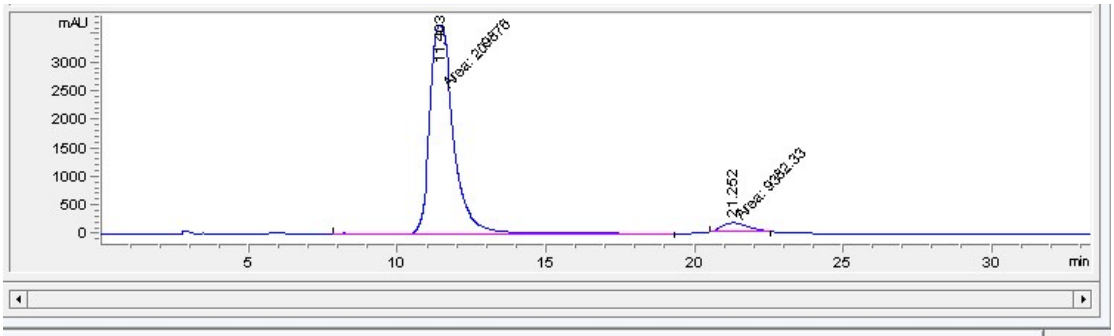




HPLC of 3p

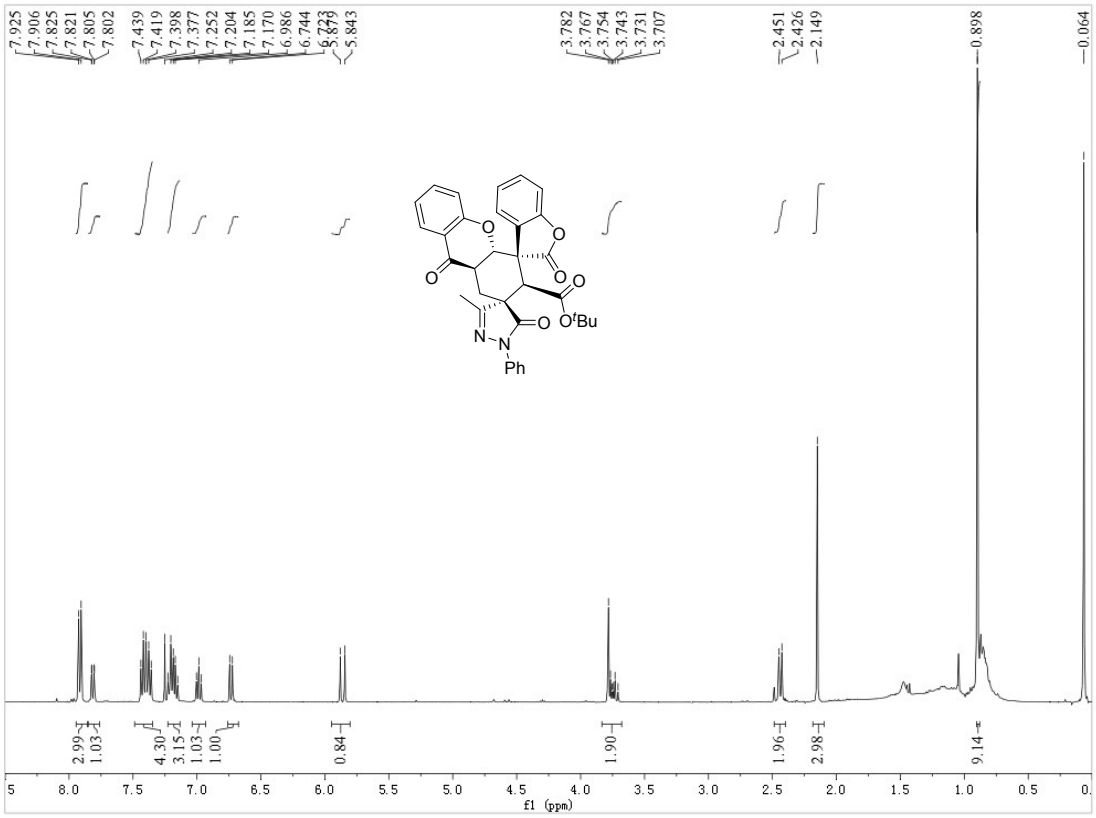


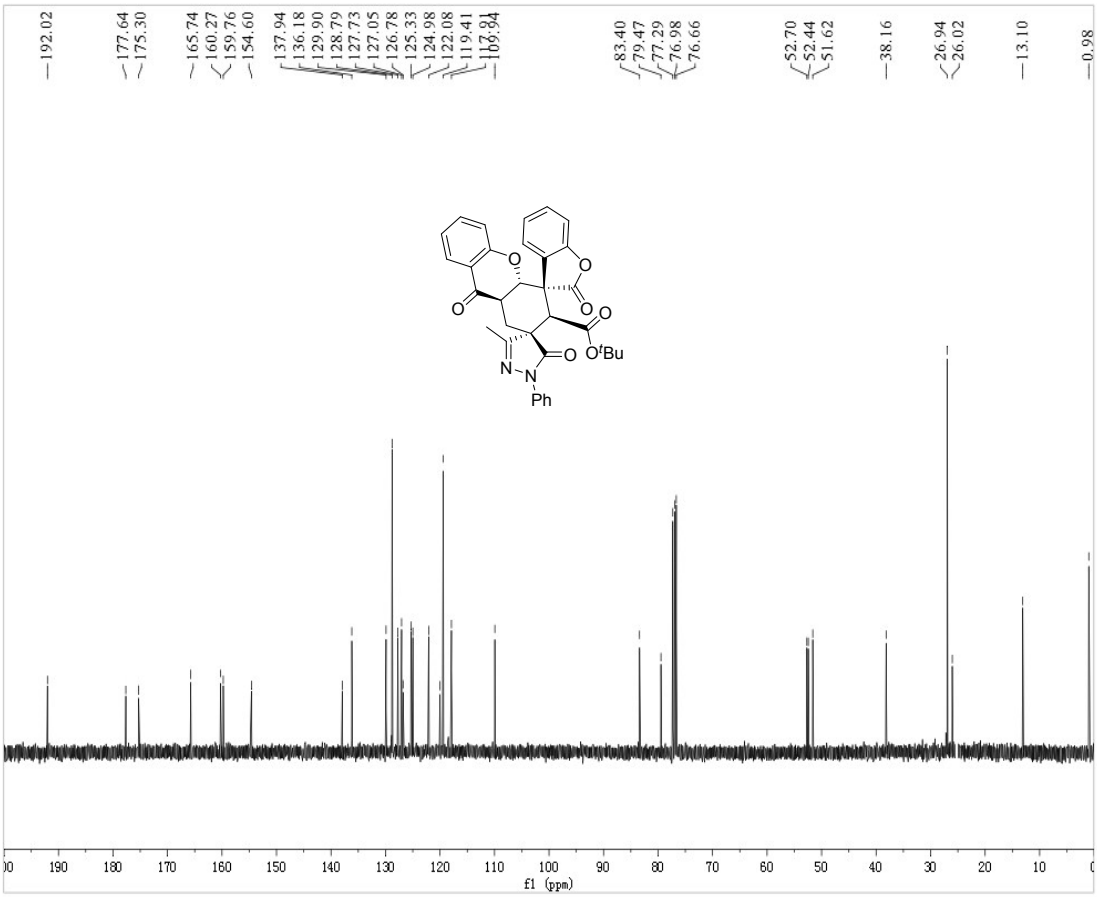
#	Time	Area	Height	Width	Area%	Symmetry
1	11.232	93995.1	1467	1.0678	49.928	0.948
2	21.203	94266.4	844.8	1.8598	50.072	0.898



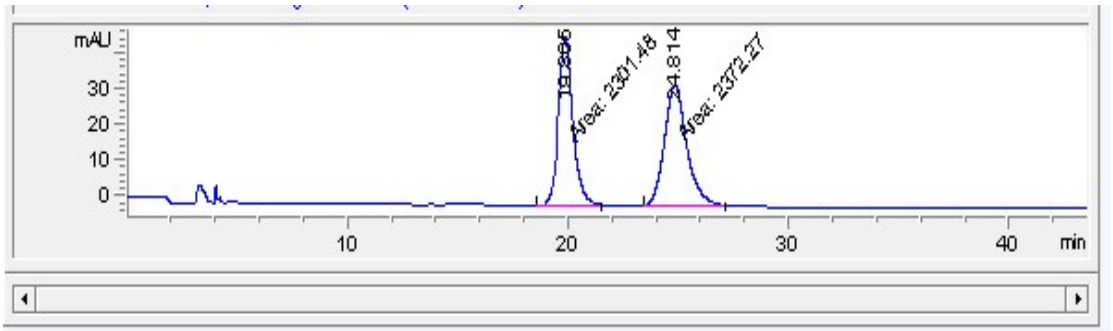
#	Time	Area	Height	Width	Area%	Symmetry
1	11.403	209875.8	3658.2	0.9562	95.721	0.662
2	21.252	9382.3	152.4	1.0263	4.279	0.681

^{1}H and ^{13}C NMR of 5a

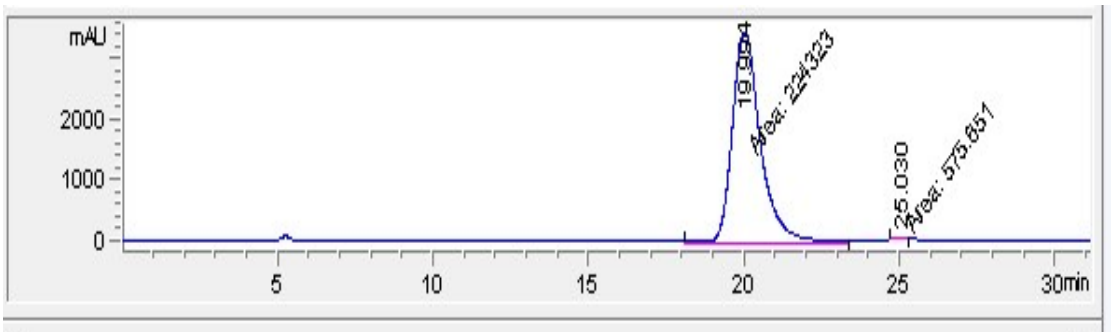




HPLC of 5a

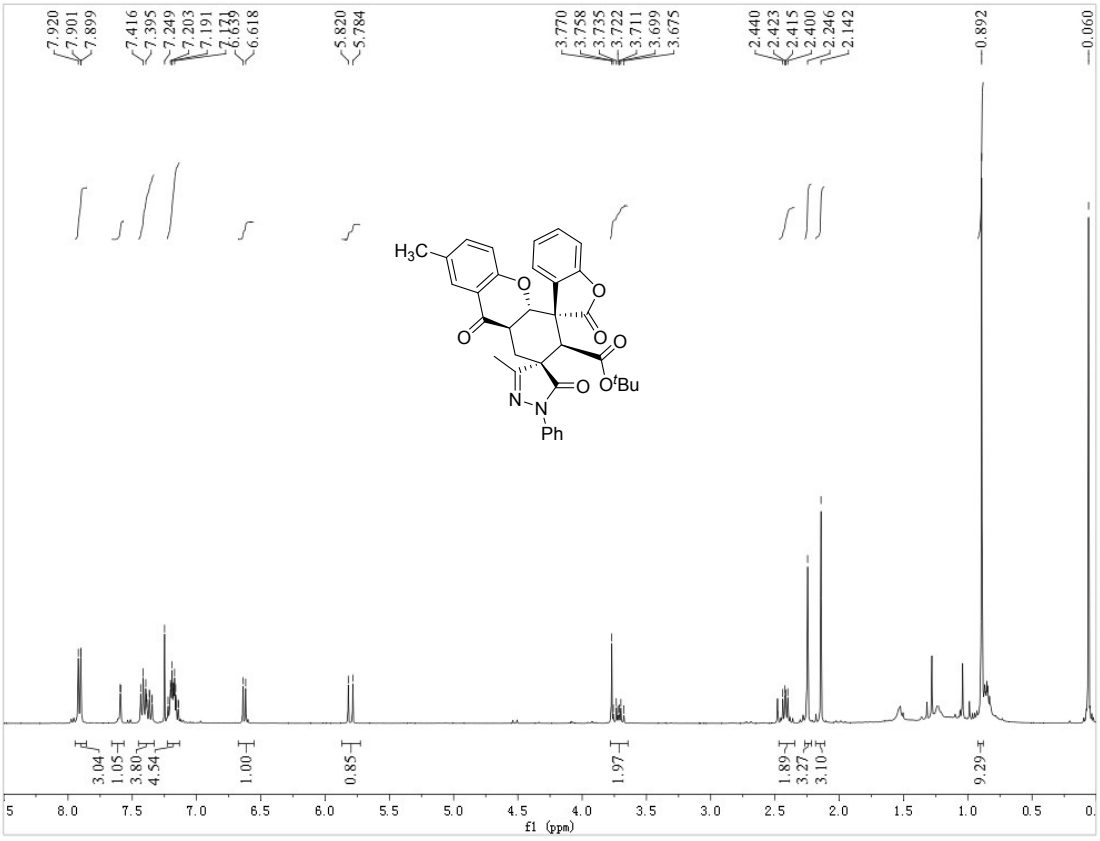


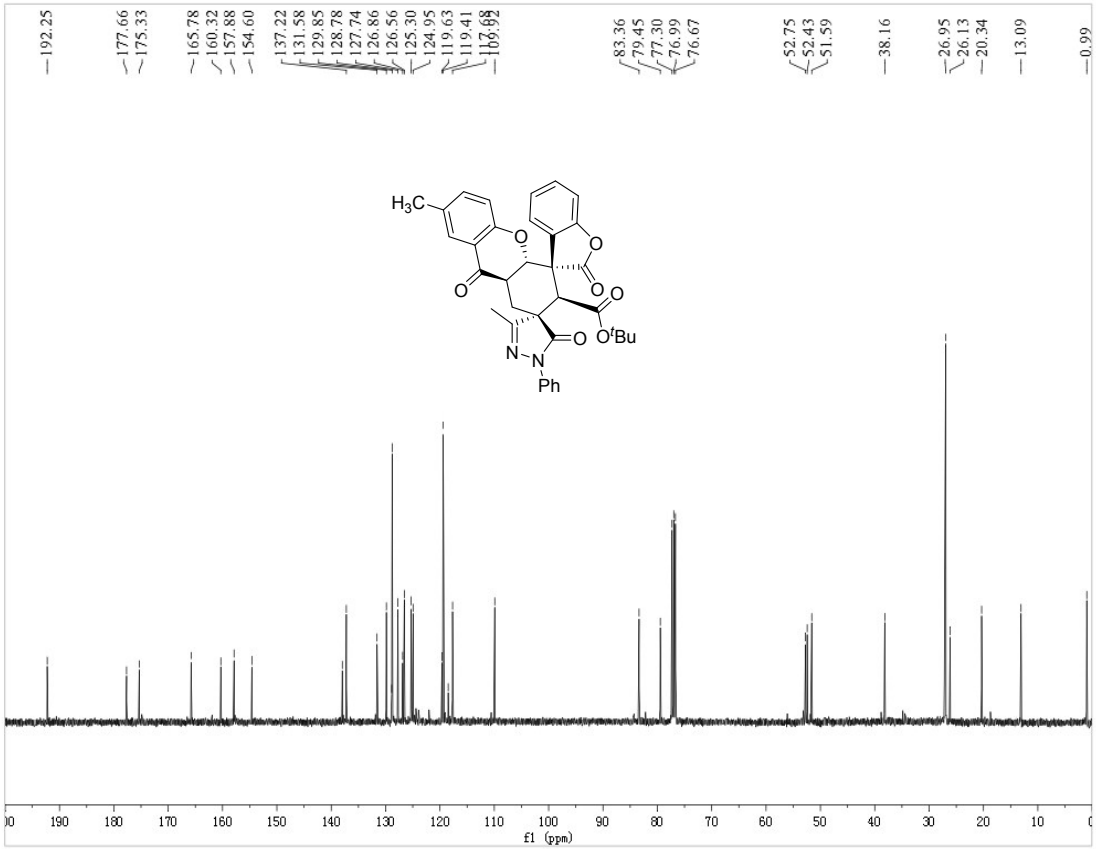
#	Time	Area	Height	Width	Area%	Symmetry
1	19.865	2301.5	47.7	0.8039	49.243	0.938
2	24.814	2372.3	34	1.1641	50.757	0.853



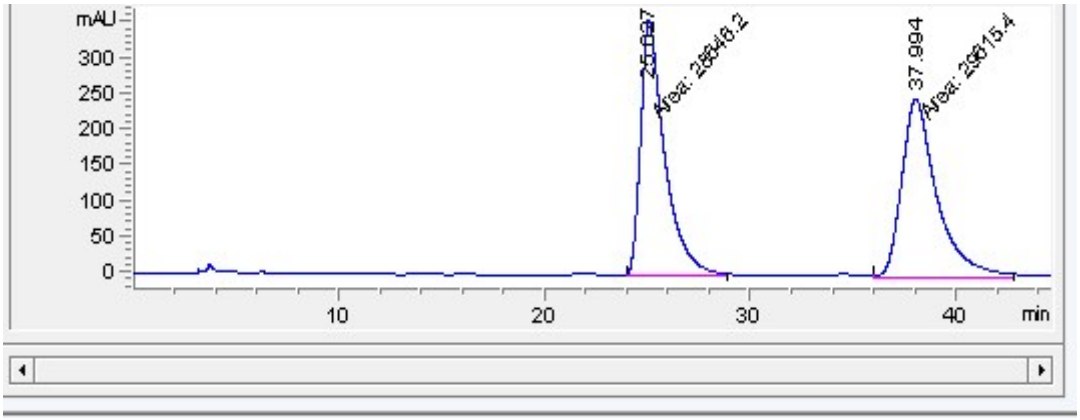
#	Time	Area	Height	Width	Area%	Symmetry
1	19.994	224322.7	3479.1	1.0746	99.744	0.758
2	25.03	575.7	15.4	0.6227	0.256	5.728

^{1}H and ^{13}C NMR of 5b

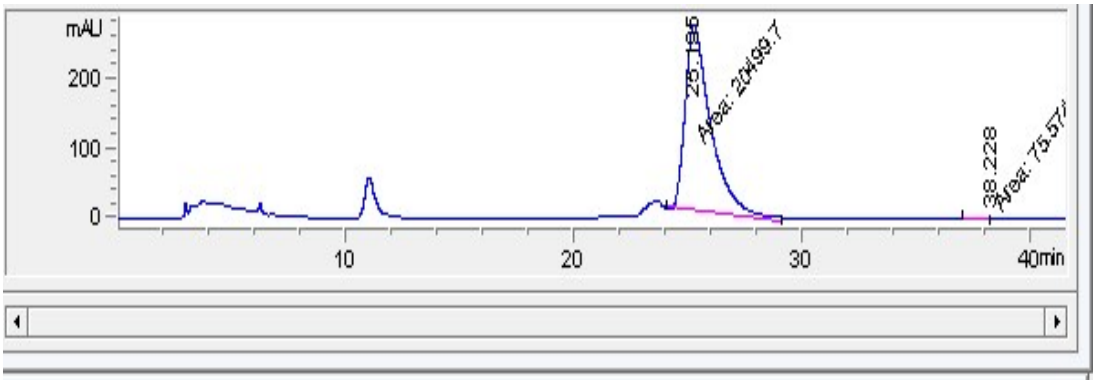




HPLC of 5b

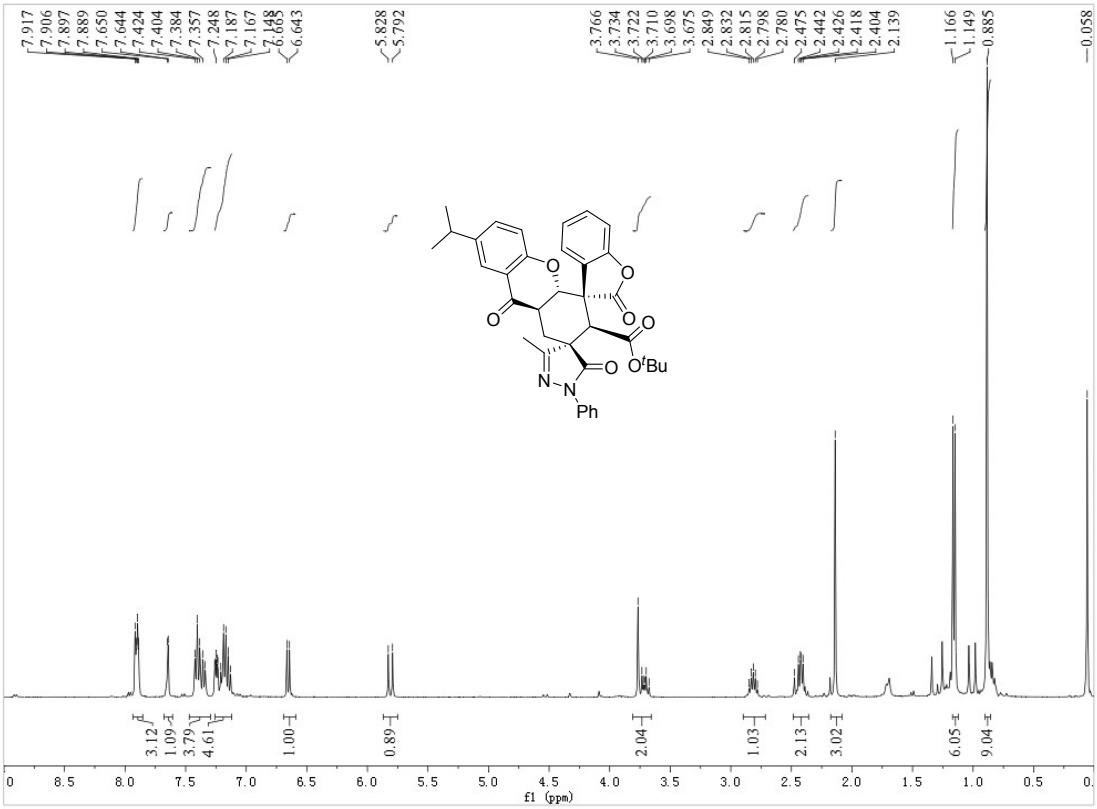


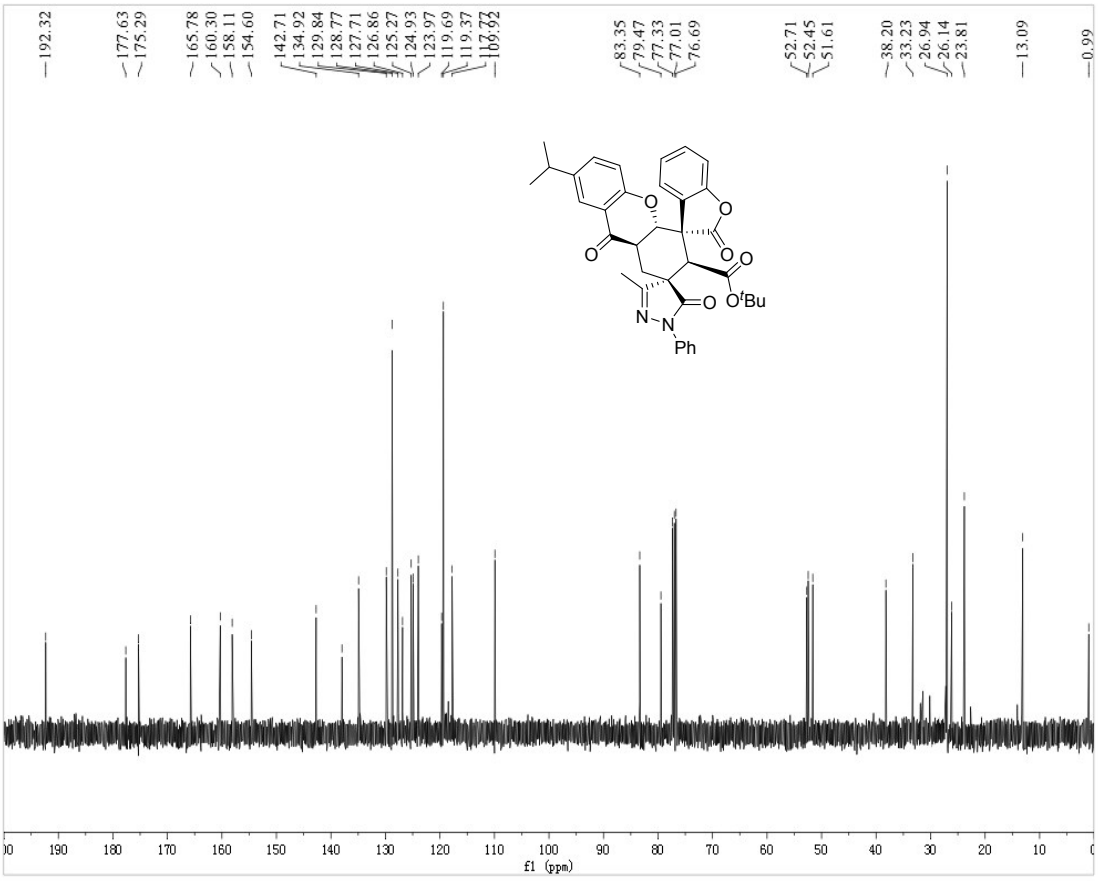
#	Time	Area	Height	Width	Area%	Symmetry
1	25.027	28646.2	357	1.3373	49.168	0.505
2	37.994	29615.4	250.5	1.9704	50.832	0.631



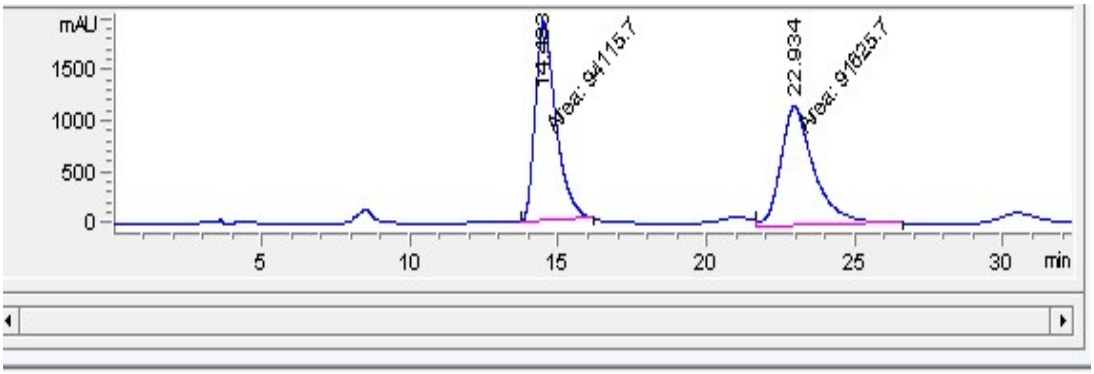
#	Time	Area	Height	Width	Area%	Symmetry
1	25.195	20499.7	264.1	1.2937	99.633	0.489
2	38.228	75.6	2.1	0.5937	0.367	0

^{1}H and ^{13}C NMR of 5c

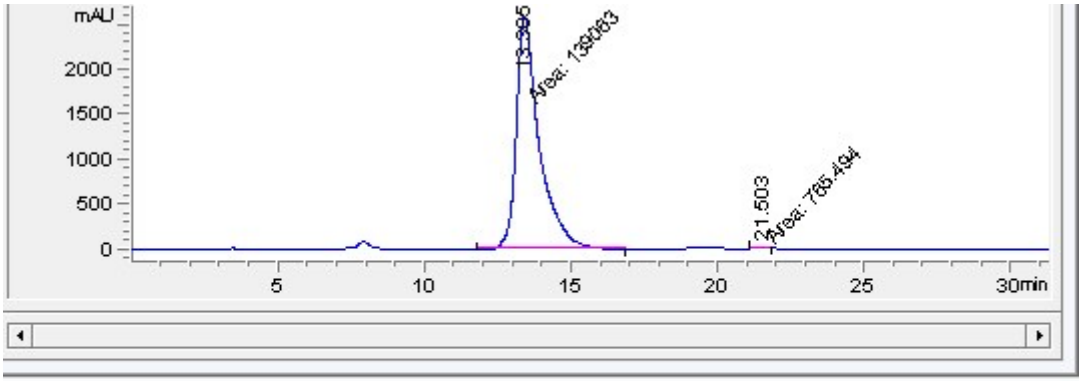




HPLC of 5c

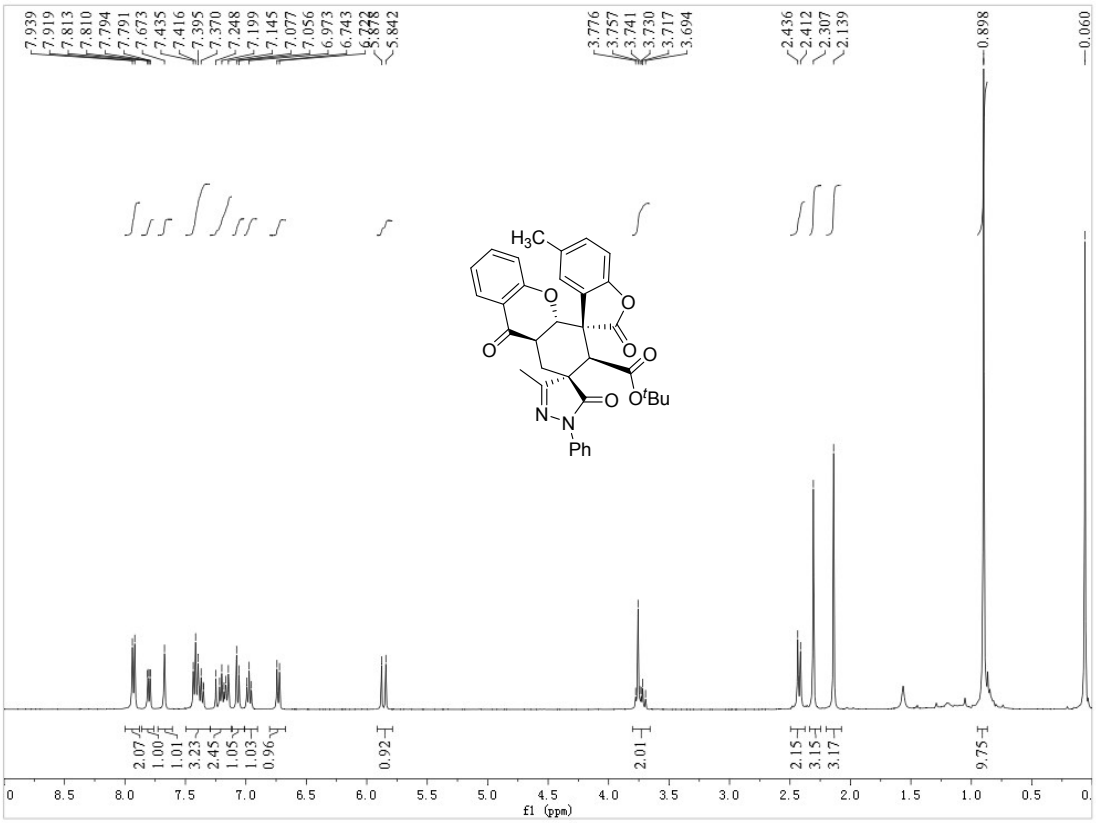


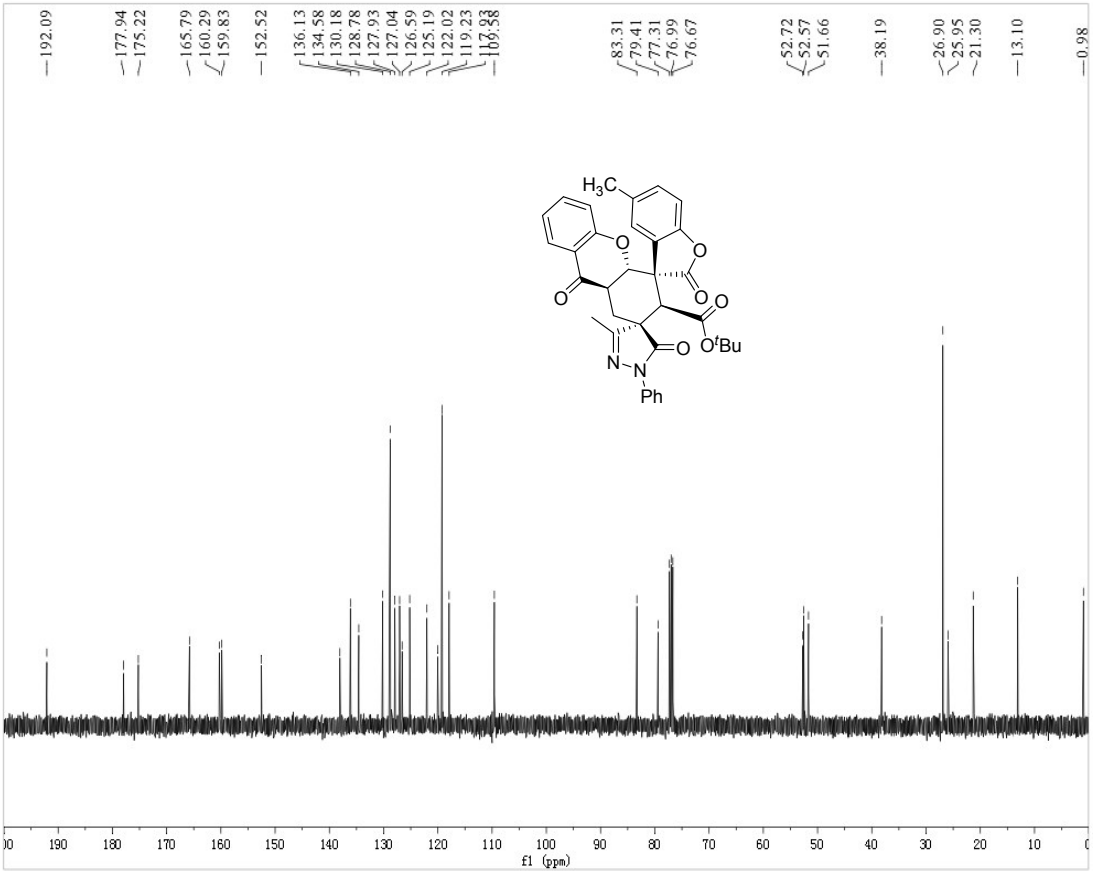
#	Time	Area	Height	Width	Area%	Symmetry
1	14.483	94115.7	1954.3	0.8027	50.670	0.634
2	22.934	91625.7	1174.7	1.3	49.330	0.648



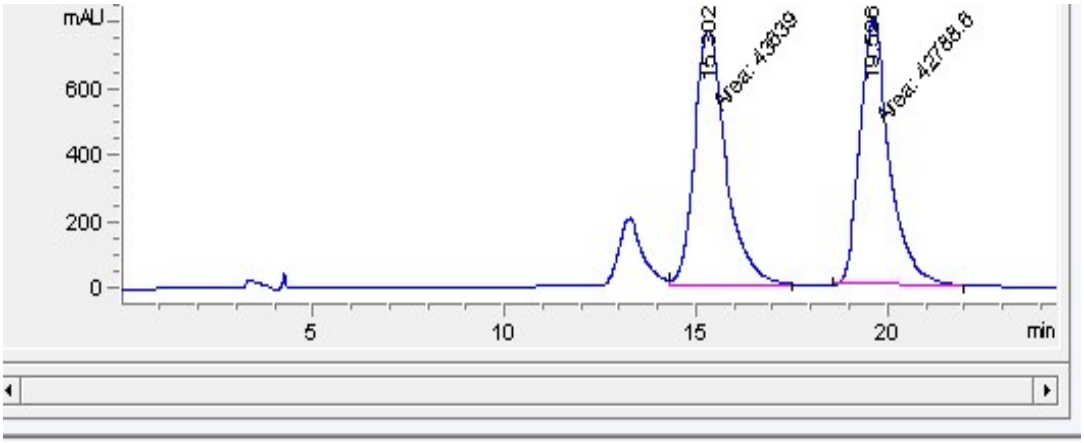
#	Time	Area	Height	Width	Area%	Symmetry
1	13.385	139062.7	2589.6	0.895	99.453	0.521
2	21.503	765.5	19.7	0.6481	0.547	1.341

^{1}H and ^{13}C NMR of 5d

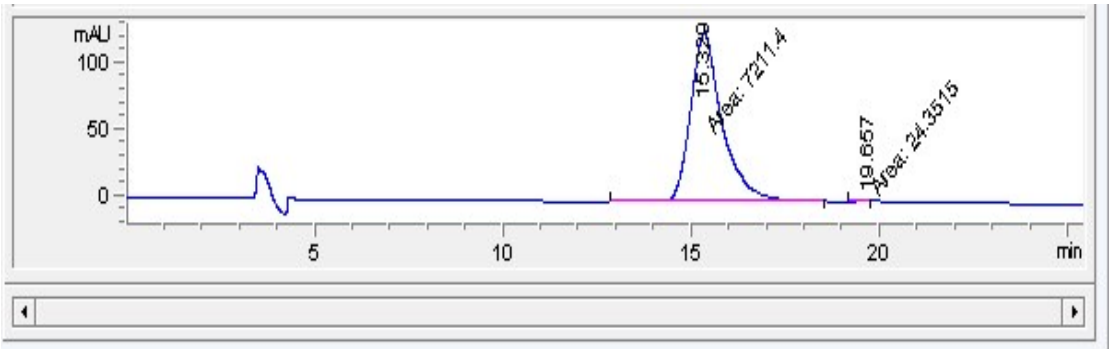




HPLC of 5d

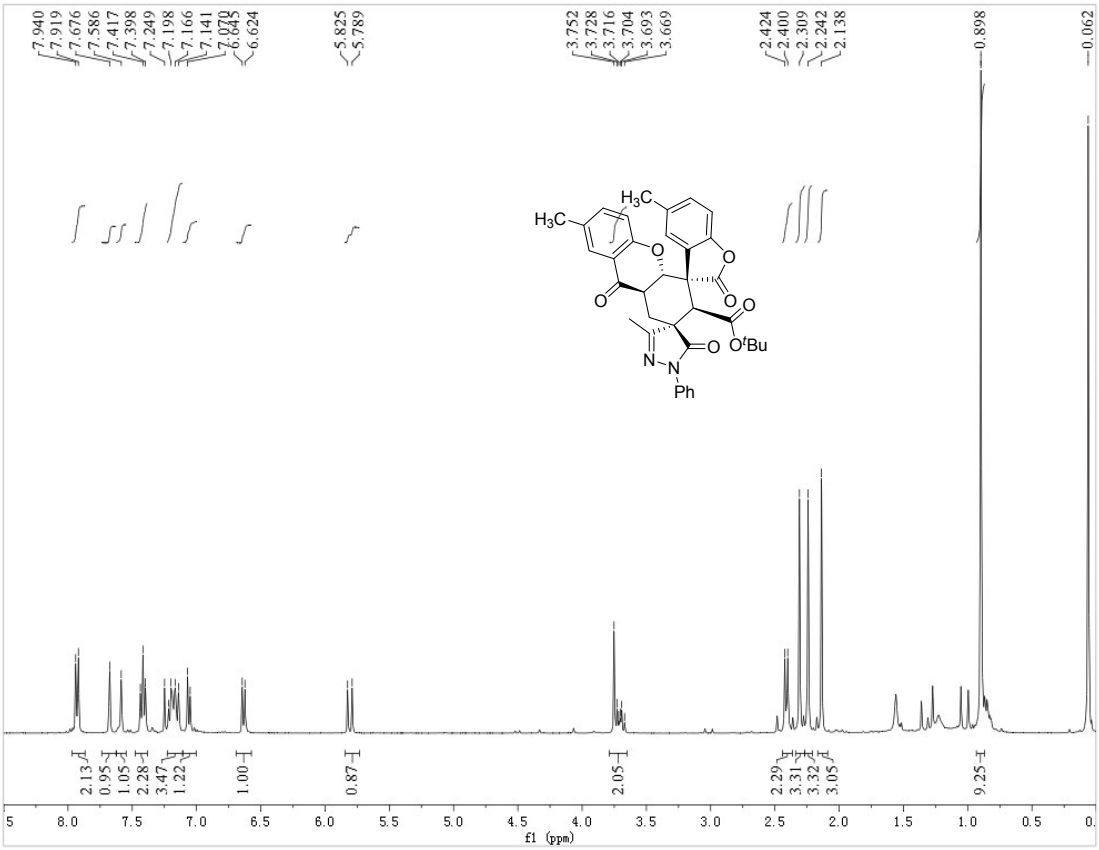


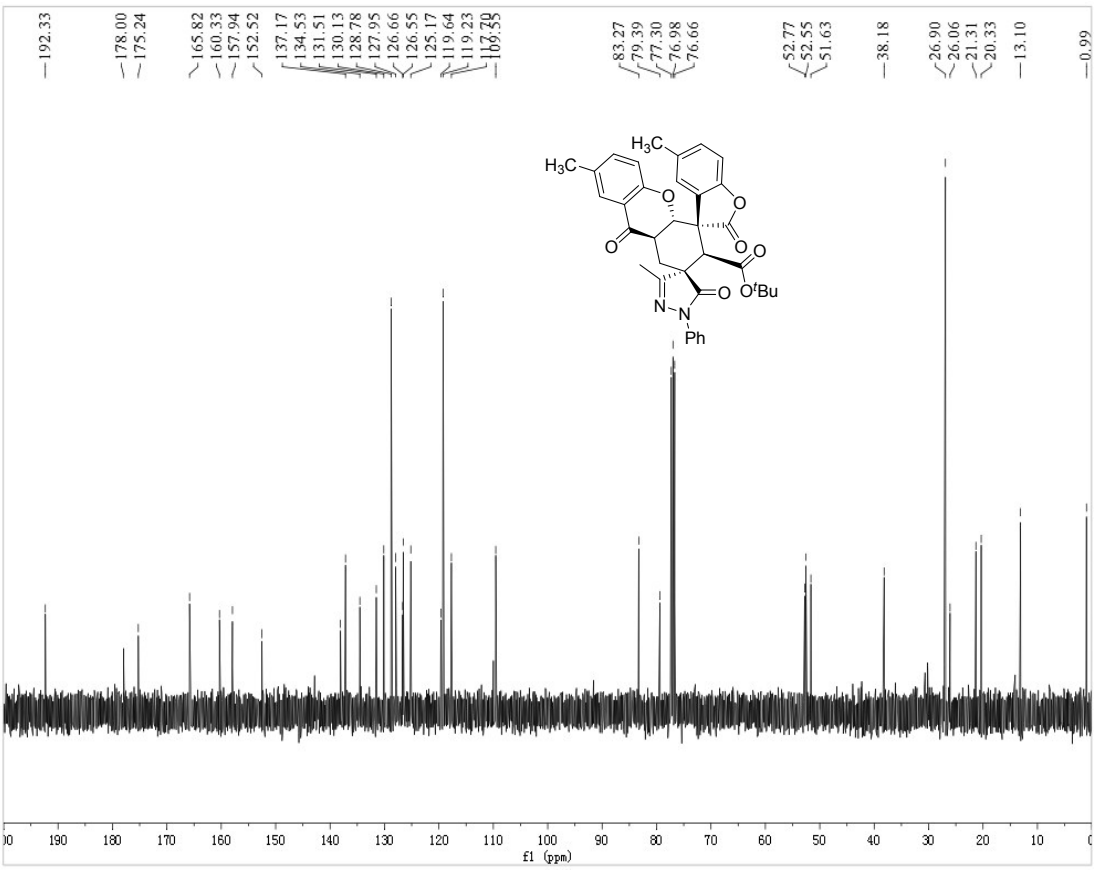
#	Time	Area	Height	Width	Area%	Symmetry
1	15.302	43639	770.4	0.9441	50.492	0.784
2	19.596	42788.6	798.8	0.8928	49.508	0.741



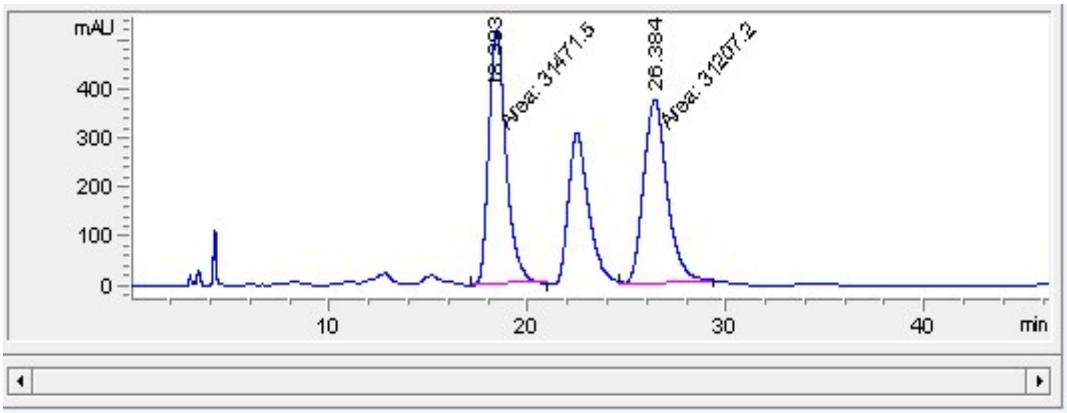
#	Time	Area	Height	Width	Area%	Symmetry
1	15.329	7211.4	127.5	0.943	99.663	0.741
2	19.657	24.4	9.6E-1	0.4209	0.337	3.543

^{1}H and ^{13}C NMR of 5e

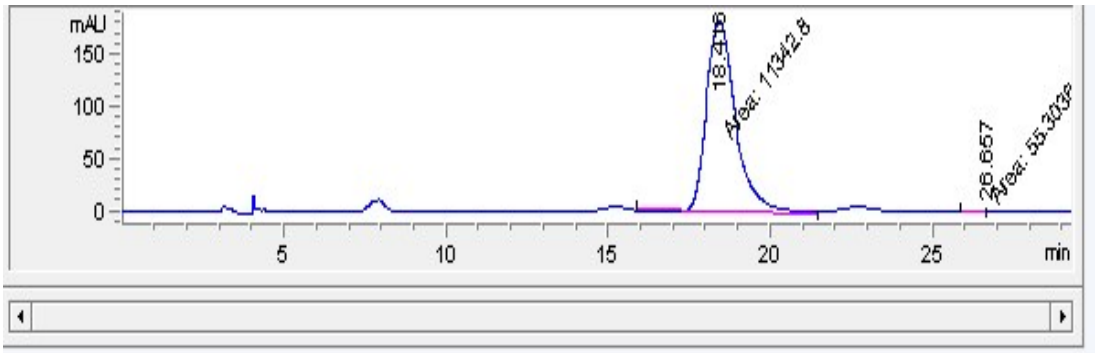




HPLC of 5e

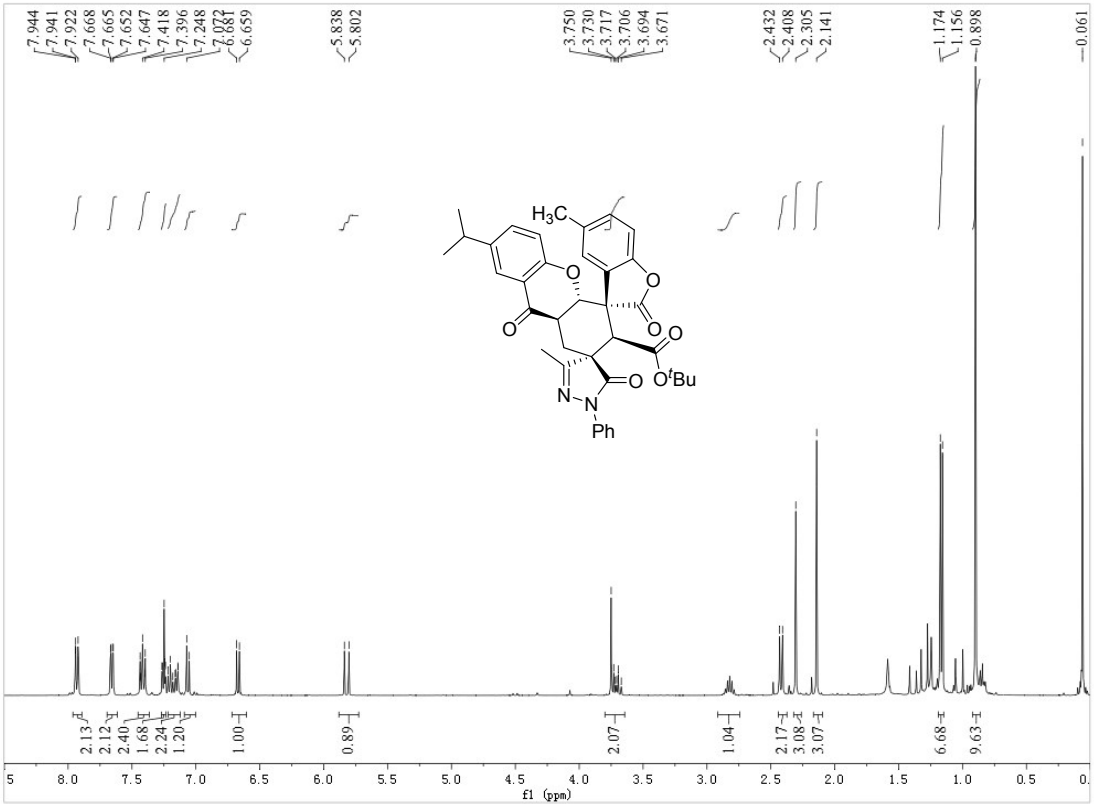


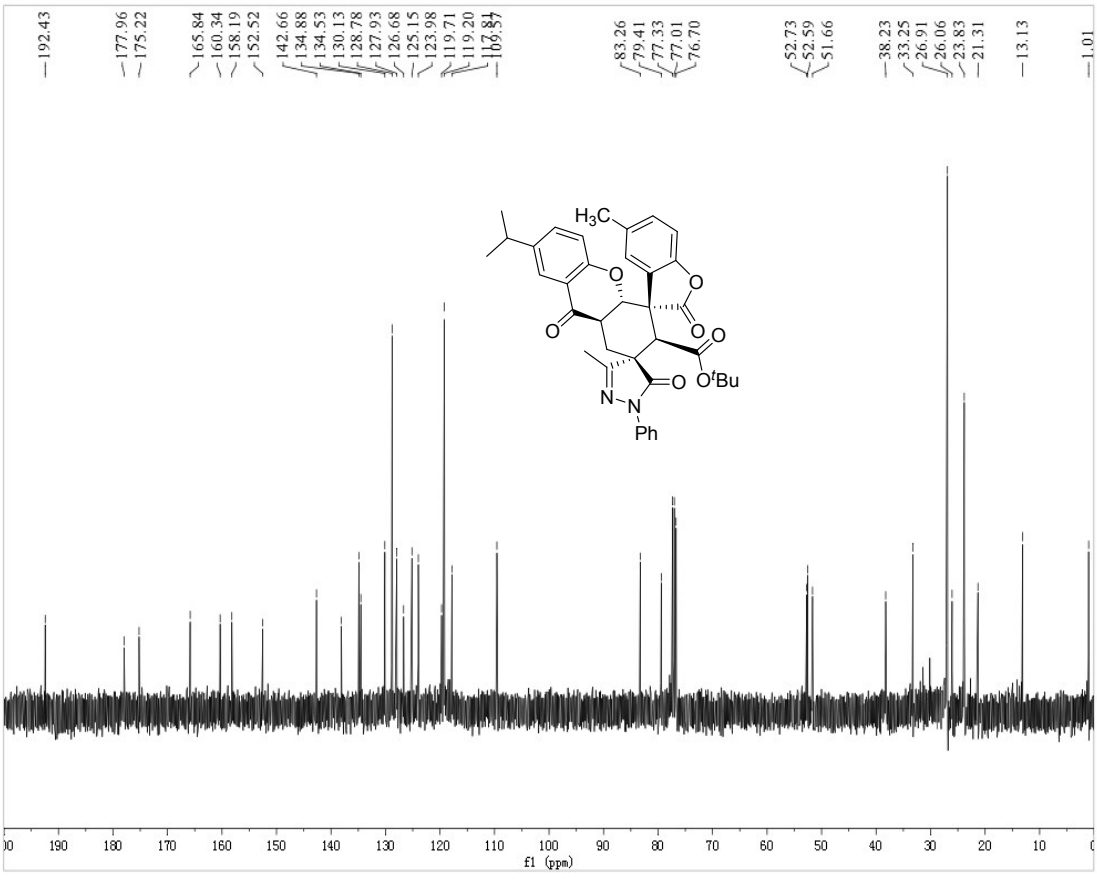
#	Time	Area	Height	Width	Area%	Symmetry
1	18.393	31471.5	520.7	1.0073	50.211	0.788
2	26.384	31207.2	375.6	1.3848	49.789	0.871



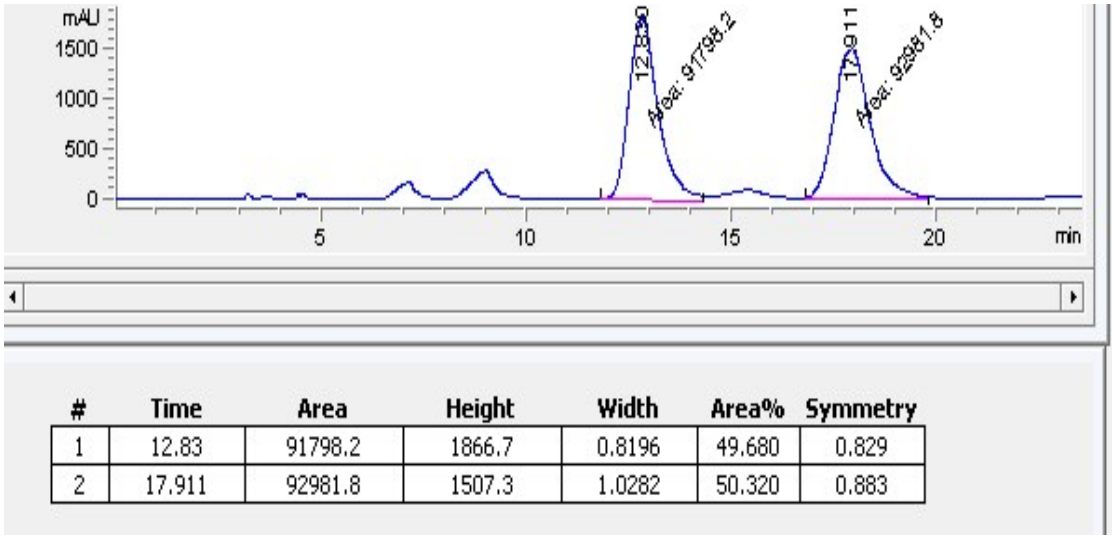
#	Time	Area	Height	Width	Area%	Symmetry
1	18.416	11342.8	182	1.0386	99.515	0.796
2	26.657	55.3	1.9	0.4969	0.485	12.087

^{1}H and ^{13}C NMR of 5f

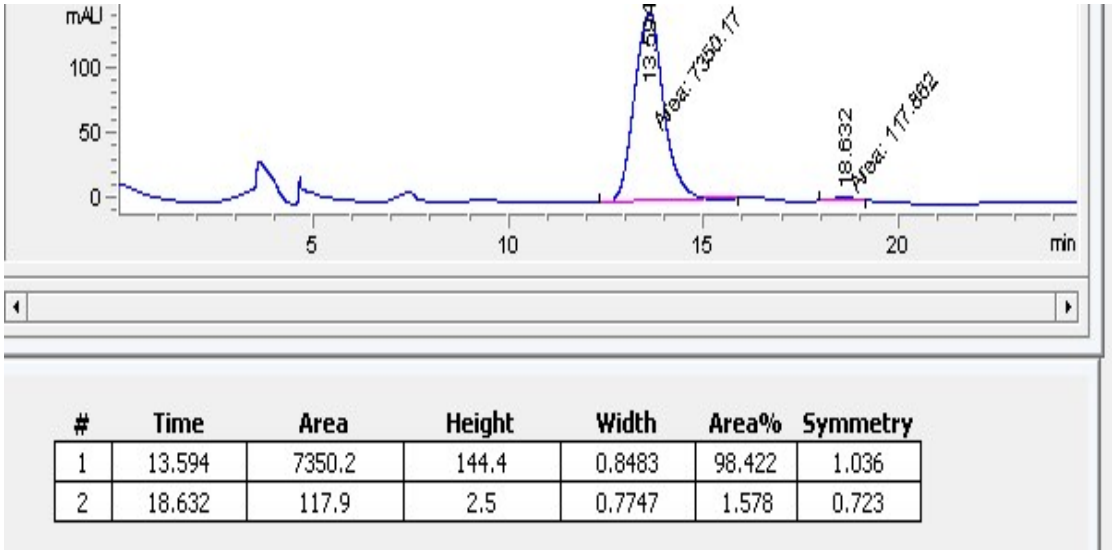




HPLC of 5f

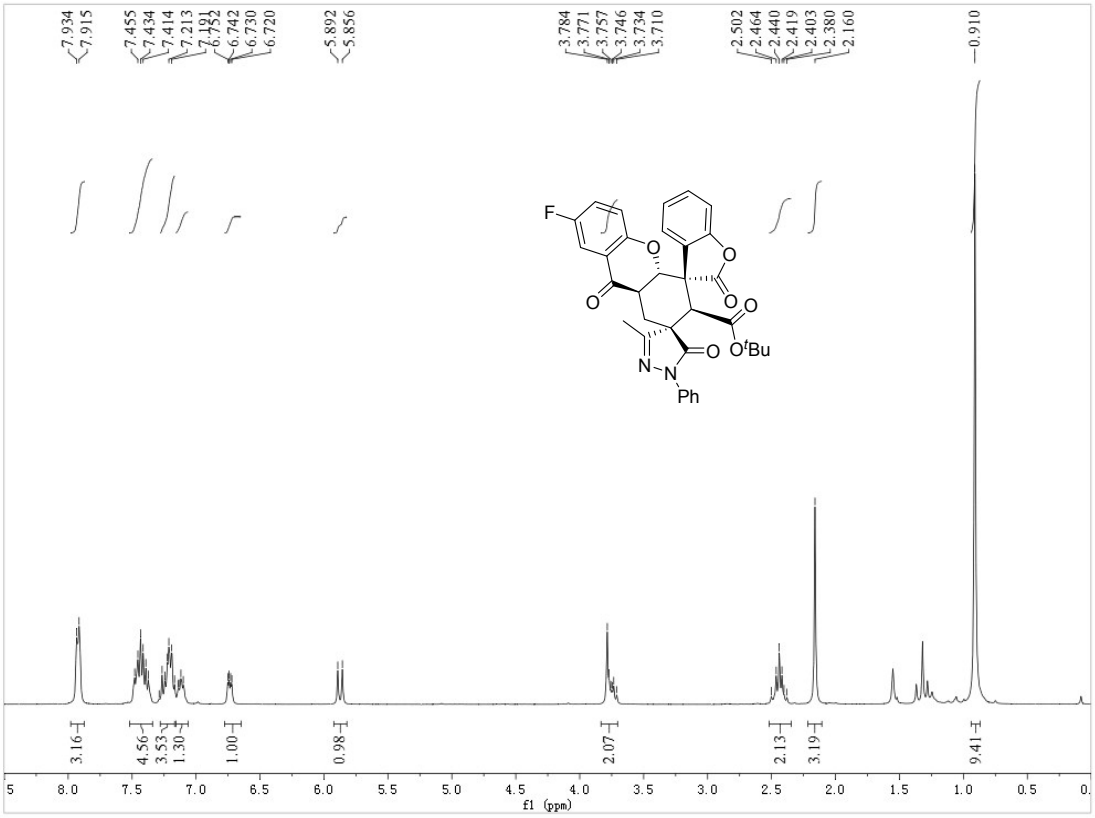


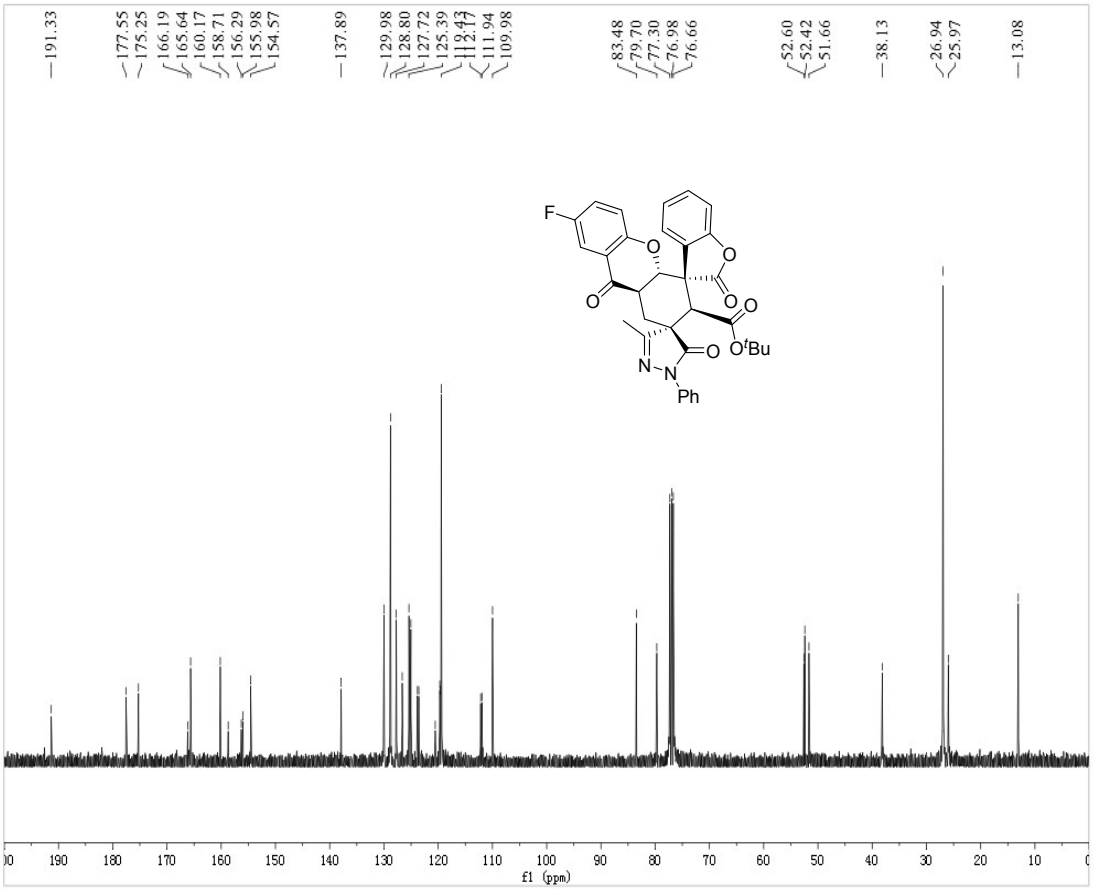
#	Time	Area	Height	Width	Area%	Symmetry
1	12.83	91798.2	1866.7	0.8196	49.680	0.829
2	17.911	92981.8	1507.3	1.0282	50.320	0.883



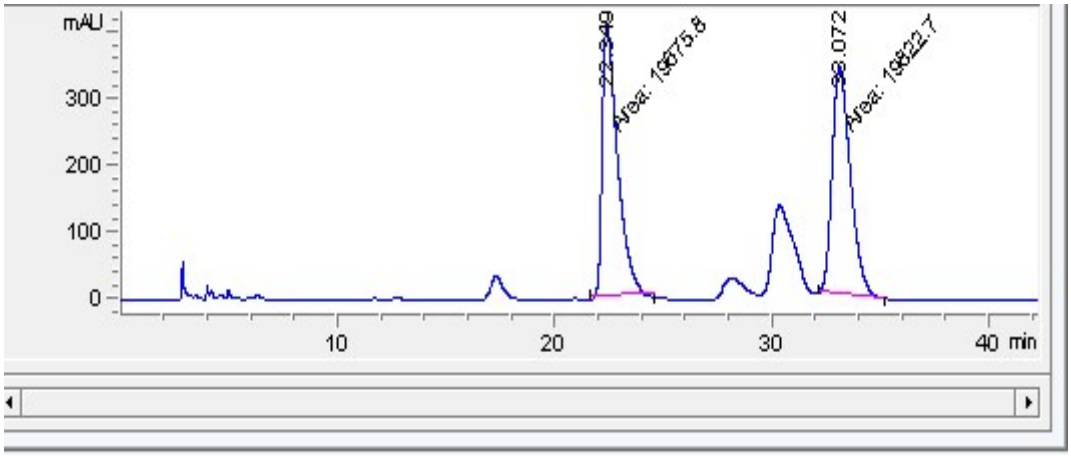
#	Time	Area	Height	Width	Area%	Symmetry
1	13.594	7350.2	144.4	0.8483	98.422	1.036
2	18.632	117.9	2.5	0.7747	1.578	0.723

^{1}H and ^{13}C NMR of 5g

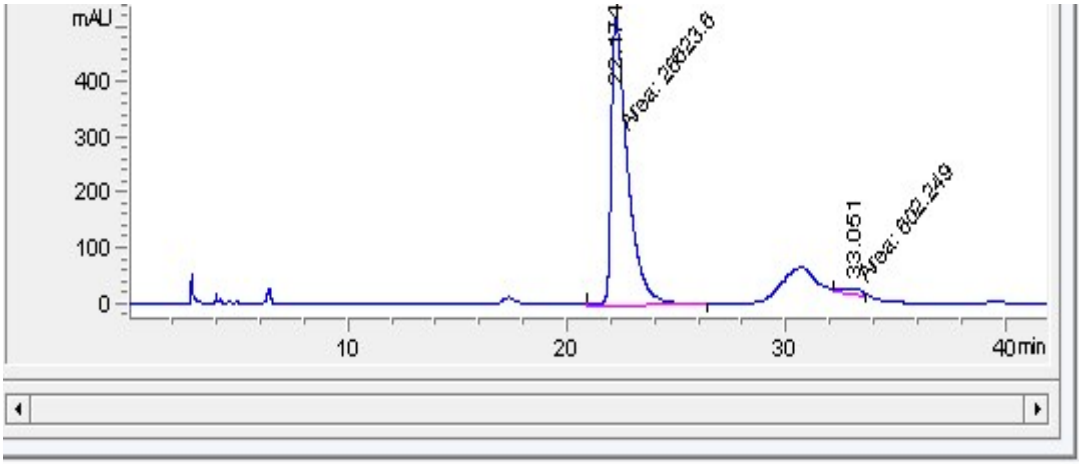




HPLC of 5g

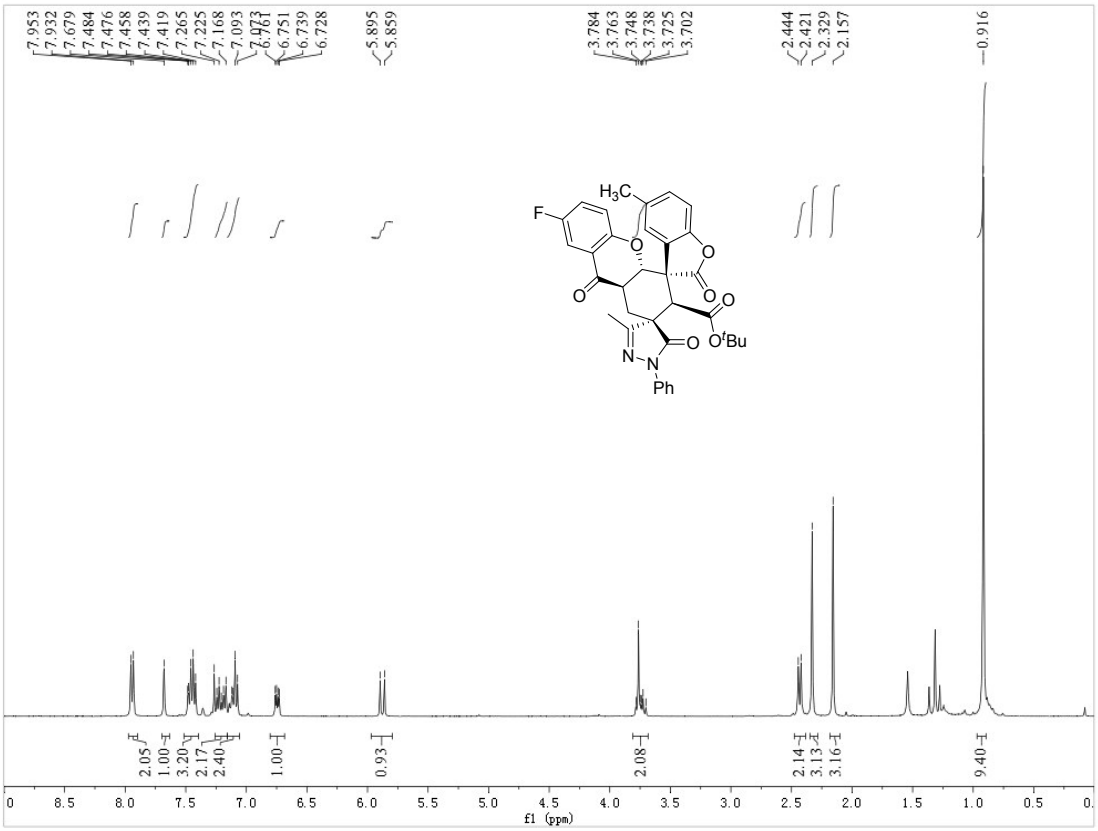


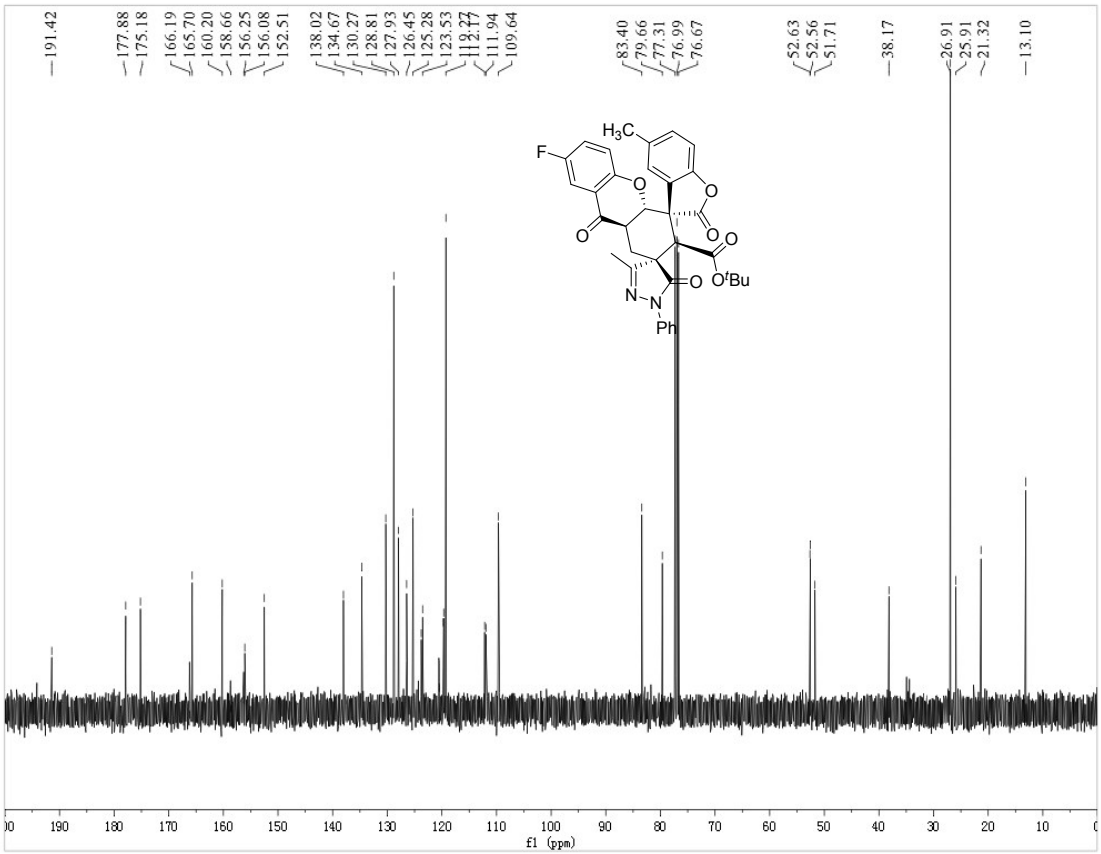
#	Time	Area	Height	Width	Area%	Symmetry
1	22.349	19675.8	410.4	0.7991	49.814	0.404
2	33.072	19822.7	342	0.9661	50.186	0.639



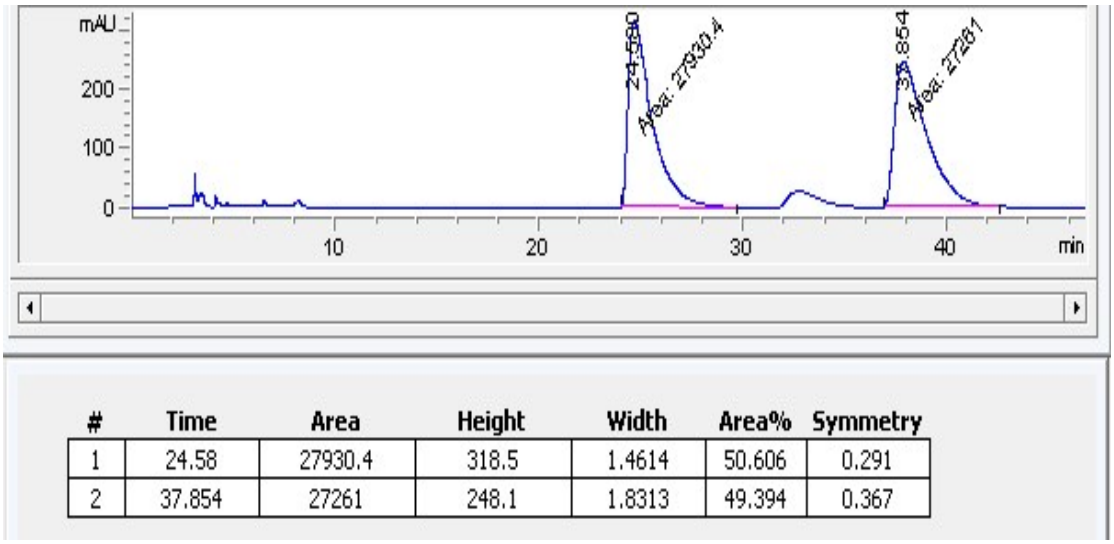
#	Time	Area	Height	Width	Area%	Symmetry
1	22.174	26623.6	517.6	0.8573	97.788	0.374
2	33.051	602.2	10.9	0.9206	2.212	1.023

^{1}H and ^{13}C NMR of 5h

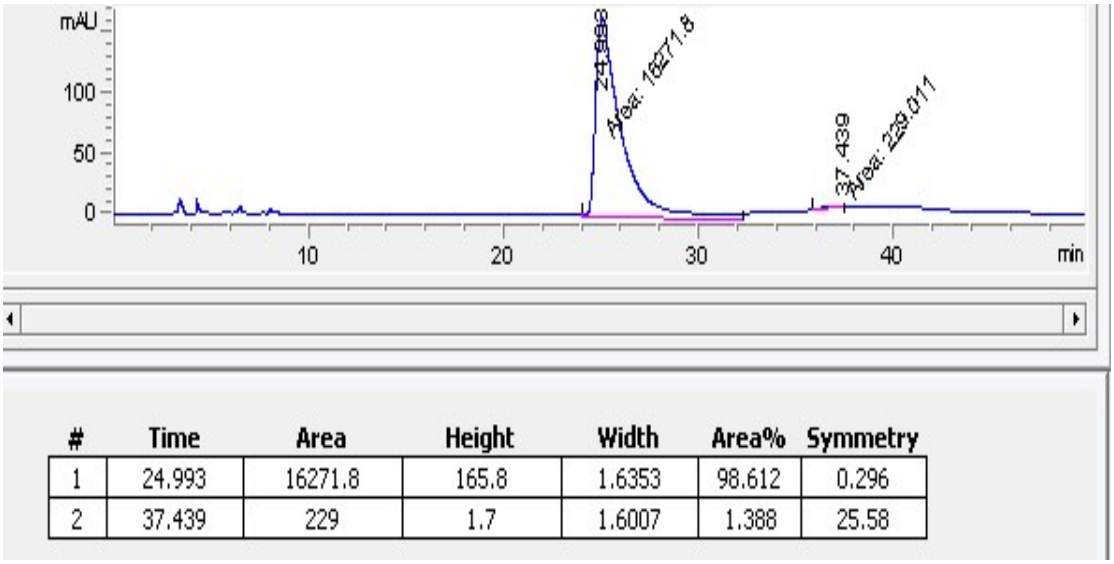




HPLC of 5h



#	Time	Area	Height	Width	Area%	Symmetry
1	24.58	27930.4	318.5	1.4614	50.606	0.291
2	37.854	27261	248.1	1.8313	49.394	0.367



#	Time	Area	Height	Width	Area%	Symmetry
1	24.993	16271.8	165.8	1.6353	98.612	0.296
2	37.439	229	1.7	1.6007	1.388	25.58