Supporting Information

Asymmetric Synthesis of Pyrrolo[1,2-a]indoles via Bifunctional Tertiary Amine Catalyzed [3+2] Annulation of 2-Nitrovinylindoles with Azlactones

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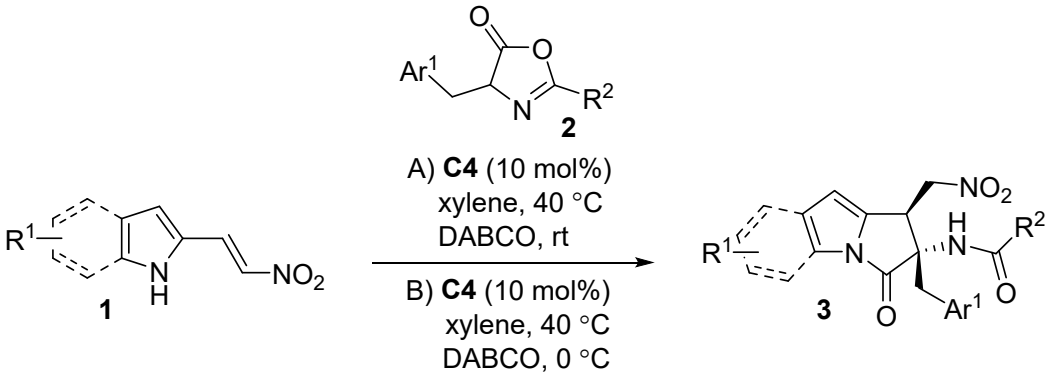
1. General Information

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H-NMR spectra were recorded at 400 MHz, ^{13}C-NMR spectra were recorded at 100 MHz. Chemical shifts were reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) or $(CD_3)_2SO$ (δ = 2.50 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) or $(CD_3)_2SO$ resonance (δ = 39.52 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. Enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H Column (4.6 mm×250 mmL), Chiralpak AS-H Column (4.6 mm×250 mmL), Chiralpak IB N-5 Column (4.6 mm×250 mmL), Chiralpak OD-H Column (4.6 mm×250 mmL). UV detection was monitored at 254 nm. TLC was performed on glass-backed silica plates. UV light was used to visualize products. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether or MeOH/DCM. Unless otherwise noted, commercial reagents were used as received and all reactions were carried out directly in air atmosphere. Nitroolefin indole compounds (**1a-1l, 1a-Me, 4a-4c, 7a**)[1] and azelactones (**2a-2t**)[2] were synthesized according to reported procedures.

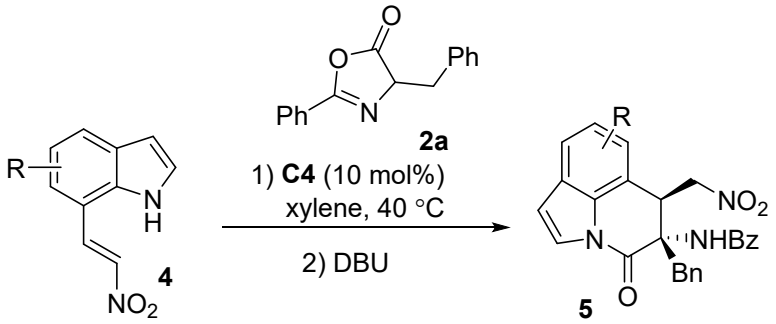
2. General procedure for the [3+2] or [4+2] Annulation of 2-Nitrovinyl indoles or 7-Nitrovinyl indoles with Azlactones



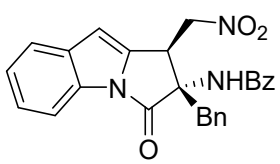
General procedure A: In a 10 mL reaction tube, 2-nitroolefin indole **1** (0.1 mmol, 1.0 eq), azlactones **2** (0.12 mmol, 1.2 eq) and catalyst **C4** (10 mol%) were dissolved in xylene (1.0 mL), the reaction mixture was stirred for 12-24 h at 40 ℃ and monitored by TLC. Upon consumption, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for

further cyclization during 2-12 h. After the reaction was completed, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford the pure chiral product **3**.

General procedure B: In a 10 mL reaction tube, 2-nitroolefin indole **1** (0.1 mmol, 1.0 eq), azlactones **2** (0.12 mmol, 1.2 eq) and catalyst **C4** (10 mol%) were dissolved in xylene (1.0 mL), the mixture was stirred for 12-24 h at 40 ℃ and monitored by TLC. After full-conversion, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/20) to afford the pure chiral product **3′**. Subsequently, the obtained **3′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 2-12 h. After the reaction was completed, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford the pure chiral product **3**.

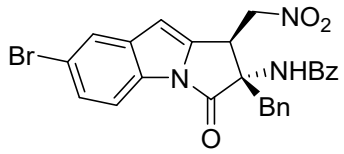


General procedure C: In a 10 mL reaction tube, 7-nitroolefin indole **4** (0.1 mmol, 1.0 eq), azlactones **2** (0.12 mmol, 1.2 eq) and catalyst **C4** (10 mol%) were dissolved in xylene (1.0 mL), the mixture was stirred for 12-24 h at 40 ℃ and monitored by TLC. After full-conversion, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/20) to afford the pure chiral product **5′**. Subsequently, the obtained **5′** was dissolved in DCM (1.0 mL), then DBU (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 2-12 h. After the reaction was completed, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford the pure chiral product **5**.

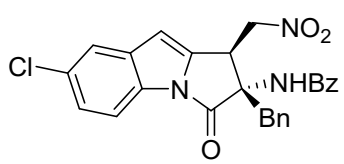


Synthesis of 3a (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, product **3a′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3a′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 6 h. After the reaction

was completed, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford product **3a** as a white solid (31.1 mg, 71% yield). M.p = 96-100 °C; $[\alpha]_D^{20}$ = -28.2 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 90% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 21.04 min, t (major) = 9.96 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.83 – 7.77 (m, 2H), 7.58 – 7.49 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 3H), 7.21 – 7.13 (m, 1H), 7.09 – 7.00 (m, 4H), 6.97 – 6.91 (m, 2H), 6.56 (dd, *J* = 2.1, 0.9 Hz, 1H), 4.56 (dd, *J* = 12.2, 10.3 Hz, 1H), 4.45 – 4.34 (m, 2H), 3.04 (d, *J* = 13.5 Hz, 1H), 2.91 (d, *J* = 13.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.55, 162.39, 136.87, 133.79, 132.59, 131.15, 130.29, 129.12, 128.39, 128.23, 127.92, 127.84, 124.53, 122.91, 121.00, 120.39, 111.39, 105.50, 76.38, 75.87, 43.70, 42.61 ppm; ESI-HRMS: calcd for $C_{26}H_{21}N_3O_4$ + Na^+ 462.1424, found 462.1416.

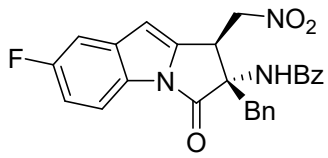


Synthesis of 3b (procedure A): (*E*)-5-bromo-2-(2-nitrovinyl)-1*H*-indole **1b** (26.7 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3b** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a light brown solid (36.3 mg, 70% yield). M.p = 86-90 °C; $[\alpha]_D^{20}$ = -20.0 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 80% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 21.92 min, t (major) = 9.09 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.58 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.38 (q, *J* = 8.0, 7.6 Hz, 3H), 7.21 – 7.07 (m, 3H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.68 (s, 1H), 6.19 (s, 1H), 5.67 (dd, *J* = 13.4, 5.5 Hz, 1H), 4.87 (dd, *J* = 13.4, 9.0 Hz, 1H), 4.78 – 4.71 (m, 1H), 3.50 (d, *J* = 13.8 Hz, 1H), 2.89 (d, *J* = 13.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.36, 168.05, 139.78, 136.15, 132.98, 132.67, 132.51, 130.26, 129.30, 128.99, 128.70, 128.24, 127.76, 127.27, 124.28, 118.43, 115.25, 101.98, 74.14, 68.04, 42.32, 38.58 ppm; ESI-HRMS: calcd for $C_{26}H_{20}BrN_3O_4$ + H^+ 518.0710, found 518.0714.

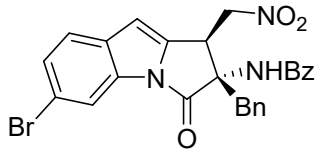


Synthesis of 3c (procedure A): (*E*)-5-chloro-2-(2-nitrovinyl)-1*H*-indole **1c** (22.2 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene

(1.0 mL) and stirred at 40 °C for 12 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3c** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a milky white solid (32.6 mg, 69% yield). M.p = 90-93 ℃; $[\alpha]_D^{20}$ = +9.4 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 82% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 20.12 min, t (major) = 8.45 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (s, 1H), 7.94 – 7.86 (m, 3H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.58 – 7.52 (m, 2H), 7.37 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.13 – 7.09 (m, 3H), 6.40 (d, *J* = 2.1 Hz, 1H), 5.36 (qd, *J* = 14.7, 7.1 Hz, 2H), 4.74 (ddd, *J* = 8.1, 5.9, 1.9 Hz, 1H), 3.40 (d, *J* = 14.2 Hz, 1H), 3.10 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.69, 166.91, 140.69, 135.06, 133.86, 132.93, 132.16, 130.07, 128.56, 128.50, 128.37, 127.82, 127.75, 127.07, 123.89, 120.78, 114.11, 100.44, 72.64, 67.91, 40.55, 37.81 ppm; ESI-HRMS: calcd for $C_{26}H_{20}ClN_3O_4$ + Na^+ 496.1035, found 496.1040.

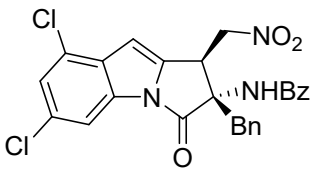


Synthesis of 3d (procedure A): (*E*)-5-fluoro-2-(2-nitrovinyl)-1*H*-indole **1d** (20.6 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3d** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (28.8 mg, 63% yield). M.p = 86-91 ℃; $[\alpha]_D^{20}$ = -19.3 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 87% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 16.75 min, t (major) = 8.07 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (s, 1H), 7.95 – 7.86 (m, 3H), 7.65 – 7.60 (m, 1H), 7.56 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.44 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.14 – 7.08 (m, 3H), 6.40 (d, *J* = 1.8 Hz, 1H), 5.36 (qd, *J* = 14.7, 7.1 Hz, 2H), 4.75 (ddd, *J* = 8.1, 6.0, 1.9 Hz, 1H), 3.41 (d, *J* = 14.3 Hz, 1H), 3.10 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.57, 166.91, 140.95, 134.90, 134.80, 133.91, 132.99, 132.15, 130.08, 128.50, 127.81, 127.75, 127.05, 126.70, 113.95, 111.70, 107.15, 100.88, 72.68, 67.85, 40.59, 37.86 ppm; ESI-HRMS: calcd for $C_{26}H_{20}FN_3O_4$ + Na^+ 480.1330, found 480.1332.

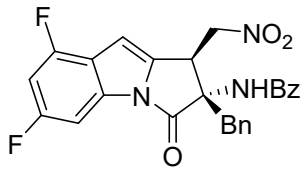


Synthesis of 3e (procedure A): (*E*)-6-bromo-2-(2-nitrovinyl)-1*H*-indole

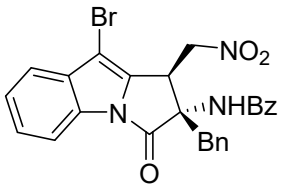
1e (26.7 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 20 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3e** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a pale yellow solid (42.4 mg, 82% yield). M.p = 203-206 ℃; $[\alpha]_D^{20}$ = -0.7 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 83% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 29.25 min, t (major) = 8.58 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (s, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.66 – 7.52 (m, 4H), 7.47 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.16 – 7.11 (m, 3H), 6.44 (d, *J* = 1.9, 0.7 Hz, 1H), 5.36 (qd, *J* = 14.8, 7.1 Hz, 2H), 4.72 (ddd, *J* = 8.0, 5.9, 1.9 Hz, 1H), 3.40 (d, *J* = 15.2 Hz, 1H), 3.09 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.72, 166.92, 139.74, 133.90, 132.90, 132.77, 132.18, 130.66, 130.14, 128.52, 127.85, 127.75, 127.07, 127.03, 123.08, 116.23, 115.33, 100.83, 72.65, 67.90, 40.67, 37.73 ppm; ESI-HRMS: calcd for $C_{26}H_{20}BrN_3O_4$ + H^+ 518.0710, found 518.0716.



Synthesis of 3f (procedure A): (*E*)-4,6-dichloro-2-(2-nitrovinyl)-1*H*-indole **1f** (25.7 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 15 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3f** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (41.1 mg, 81% yield). M.p = 70-73 ℃; $[\alpha]_D^{20}$ = -11.6 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 83% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 40.93 min, t (major) = 36.58 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.20 (s, 1H), 7.92 (d, 2H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.23 – 7.17 (m, 2H), 7.16 – 7.10 (m, 3H), 6.50 (d, *J* = 2.0 Hz, 1H), 5.47 (dd, *J* = 15.0, 7.8 Hz, 1H), 5.34 (dd, *J* = 15.0, 6.0 Hz, 1H), 4.85 – 4.74 (m, 1H), 3.41 (d, *J* = 14.3 Hz, 1H), 3.12 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.78, 167.00, 141.16, 133.75, 132.79, 132.21, 130.80, 130.52, 130.18, 128.75, 128.50, 127.84, 127.77, 127.07, 125.42, 123.73, 111.72, 98.65, 72.30, 68.03, 40.64, 37.54 ppm; ESI-HRMS: calcd for $C_{26}H_{19}Cl_2N_3O_4$ + H^+ 508.0825, found 508.0830.

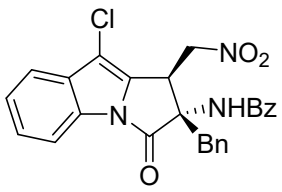


Synthesis of 3g (procedure A): (*E*)-4,6-difluoro-2-(2-nitrovinyl)-1*H*-indole **1g** (22.4 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 14 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3g** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a pale yellow solid (25.1 mg, 53% yield). M.p = 93-95 °C; $[\alpha]_D^{20}$ = -13.2 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 75% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 8.43 min, t (major) = 7.06 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.19 (s, 1H), 7.95 – 7.90 (m, 2H), 7.65 – 7.60 (m, 1H), 7.58 – 7.51 (m, 3H), 7.24 (td, *J* = 10.3, 2.2 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.14 – 7.09 (m, 3H), 6.47 (d, *J* = 1.9 Hz, 1H), 5.42 (dd, *J* = 14.9, 7.7 Hz, 1H), 5.34 (dd, *J* = 15.0, 6.1 Hz, 1H), 4.80 – 4.73 (m, 1H), 3.40 (d, *J* = 14.3 Hz, 1H), 3.14 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.91, 166.96, 139.84, 139.81, 133.67, 132.85, 132.17, 131.23, 130.95, 130.09, 128.54, 128.49, 128.45, 127.88, 127.82, 127.77, 127.07, 96.01, 72.37, 68.17, 40.39, 37.67 ppm; ESI-HRMS: calcd for $C_{26}H_{19}F_2N_3O_4$ + Na^+ 498.1236, found 498.1240.

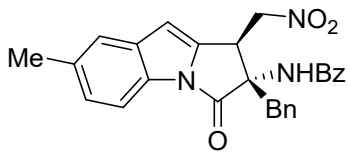


Synthesis of 3h (procedure A): (*E*)-3-bromo-2-(2-nitrovinyl)-1*H*-indole **1h** (26.7 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 17 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3h** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a pale yellow solid (41.9 mg, 81% yield). M.p = 168-171 °C; $[\alpha]_D^{20}$ = -20.7 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 92% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 15.70 min, t (major) = 7.25 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.21 (s, 1H), 7.98 – 7.91 (m, 3H), 7.66 – 7.61 (m, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.16 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.09 – 7.02 (m, 3H), 5.47 (d, *J* = 6.6 Hz, 2H), 4.94 (t, *J* = 6.5 Hz, 1H), 3.42 (d, 1H), 3.24 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.51, 167.08, 135.18, 133.50, 132.84, 132.23, 132.10, 129.87, 129.53, 128.52, 127.82, 127.76, 127.13, 125.54, 124.90, 119.01, 113.12, 89.97,

70.98, 68.52, 40.15, 37.91 ppm; ESI-HRMS: calcd for $C_{26}H_{20}BrN_3O_4$ + H^+ 518.0710, found 518.0708.

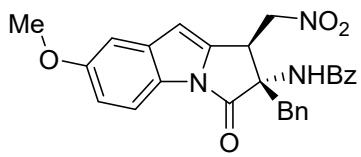


Synthesis of 3i (procedure A): (*E*)-3-chloro-2-(2-nitrovinyl)-1*H*-indole **1i** (22.2 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 17 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **3i** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a pale yellow solid (34.5 mg, 78% yield). M.p = 143-148 ℃; $[\alpha]_D^{20}$ = +0.3 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 83% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 15.25 min, t (major) = 6.55 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.18 (s, 1H), 7.97 – 7.92 (m, 3H), 7.66 – 7.60 (m, 1H), 7.58 – 7.53 (m, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.39 (m, 1H), 7.20 – 7.13 (m, 2H), 7.09 – 7.04 (m, 3H), 5.46 (d, *J* = 6.8 Hz, 2H), 4.96 (t, *J* = 6.7 Hz, 1H), 3.40 (d, *J* = 14.3 Hz, 1H), 3.22 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.39, 167.04, 133.51, 133.14, 132.81, 132.17, 130.58, 129.87, 129.00, 128.46, 127.75, 127.72, 127.08, 125.52, 124.80, 118.08, 113.17, 103.79, 71.08, 68.39, 40.02, 37.81 ppm; ESI-HRMS: calcd for $C_{26}H_{20}ClN_3O_4$ + Na^+ 496.1035, found 496.1031.

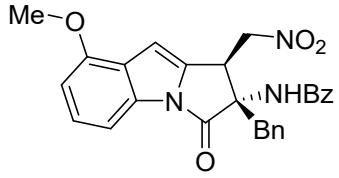


Synthesis of 3j (procedure B): (*E*)-5-methyl-2-(2-nitrovinyl)-1*H*-indole **1j** (20.2 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, product **3j′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3j′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3j** as a yellow solid (37.1 mg, 82% yield). M.p = 73-76 ℃; $[\alpha]_D^{20}$ = -12.2 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 90% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 14.86 min, t (major) = 19.10 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.06 (s, 1H), 7.91 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.55 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.38 (s,

1H), 7.19 – 7.13 (m, 3H), 7.11 (q, *J* = 3.2 Hz, 3H), 6.30 (d, *J* = 1.8 Hz, 1H), 5.34 (h, *J* = 8.3 Hz, 2H), 4.72 (ddd, *J* = 8.1, 6.2, 1.9 Hz, 1H), 3.40 (d, *J* = 14.2 Hz, 1H), 3.06 (d, *J* = 14.2 Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.52, 166.82, 139.04, 134.05, 133.89, 133.16, 133.08, 132.08, 130.06, 128.47, 128.32, 127.81, 127.72, 127.00, 125.08, 121.03, 112.48, 100.53, 72.83, 67.87, 40.58, 37.97, 21.24 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_4$ + Na^+ 476.1581, found 476.1577.

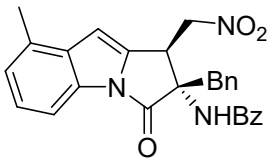


Synthesis of 3k (procedure B): (*E*)-5-methoxy-2-(2-nitrovinyl)-1*H*-indole **1k** (21.8 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 24 h. Upon workup, product **3k′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3k′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3k** as a yellow solid (35.1 mg, 75% yield). M.p = 83-87 ℃; $[\alpha]_D^{20}$ = -10.8 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 96% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 13.00 min, t (major) = 26.02 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.05 (s, 1H), 7.95 – 7.88 (m, 2H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.20 – 7.14 (m, 2H), 7.14 – 7.09 (m, 4H), 6.94 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.31 (d, *J* = 1.8 Hz, 1H), 5.34 (h, *J* = 8.2 Hz, 2H), 4.71 (ddd, *J* = 8.1, 6.1, 1.9 Hz, 1H), 3.79 (s, 3H), 3.40 (d, *J* = 14.2 Hz, 1H), 3.07 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.31, 166.81, 156.49, 139.71, 134.80, 134.04, 133.09, 132.07, 130.05, 128.46, 127.80, 127.71, 126.99, 124.71, 113.42, 112.22, 104.23, 100.80, 72.81, 67.76, 55.40, 40.59, 38.00 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_5$ + Na^+ 492.1530, found 492.1537.

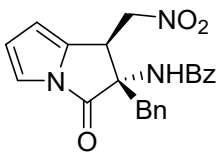


Synthesis of 3l (procedure B): (*E*)-4-methoxy-2-(2-nitrovinyl)-1*H*-indole **1l** (21.8 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 20 h. Upon workup, product **3l′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3l′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0

℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3l** as a yellow solid (31.4 mg, 63% yield). M.p = 73-75 ℃; $[\alpha]_D^{20}$ = +2.8 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 77% ee, determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 14.54 min, t (major) = 26.04 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.09 (s, 1H), 7.95 – 7.87 (m, 2H), 7.65 – 7.59 (m, 1H), 7.59 – 7.46 (m, 3H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.20 – 7.09 (m, 5H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.37 (d, 1H), 5.39 (dd, *J* = 14.6, 8.0 Hz, 1H), 5.30 (dd, *J* = 14.6, 6.3 Hz, 1H), 4.72 (ddd, *J* = 8.1, 6.3, 2.0 Hz, 1H), 3.89 (s, 3H), 3.40 (d, *J* = 14.2 Hz, 1H), 3.05 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.83, 166.85, 152.33, 137.35, 134.07, 133.04, 132.10, 131.13, 130.10, 128.48, 127.81, 127.72, 126.99, 125.26, 123.00, 105.93, 105.12, 97.71, 72.77, 67.97, 55.43, 40.57, 37.84 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_5$ + Na^+ 492.1530, found 492.1526.

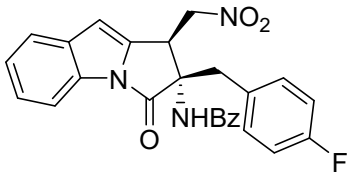


Synthesis of 3m (procedure B): (*E*)-4-methyl-2-(2-nitrovinyl)-1*H*-indole **1m** (20.2 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, product **3m** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3m′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3m** as a yellow solid (34.7 mg, 73% yield). M.p = 88-93 ℃; $[\alpha]_D^{20}$ = -12.2 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 77% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 16.83 min, t (major) = 14.73 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.06 (s, 1H), 7.91 (dt, J = 7.2, 1.4 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.24 (t, J = 7.7 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.15 – 7.09 (m, 4H), 6.44 (d, J = 2.1 Hz, 1H), 5.41 – 5.29 (m, 2H), 4.75 (td, J = 6.1, 3.1 Hz, 1H), 3.42 (d, J = 14.2 Hz, 1H), 3.05 (d, J = 14.2 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.66, 166.84, 138.40, 134.13, 133.09, 133.06, 132.07, 130.16, 130.11, 129.84, 128.46, 127.79, 127.70, 126.95, 124.44, 123.97, 110.42, 99.31, 72.84, 67.85, 40.68, 37.87, 18.20 ppm; ESI-HRMS: calcd for $C_{27}H_{25}N_3O_4$ + Na^+ 476.1581, found 476.1590.



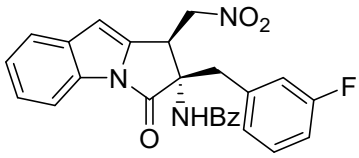
Synthesis of 3n (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-pyrrole **1n** (13.8 mg,

0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 13 h. Upon workup, product **3n′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3n′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3n** as a yellow solid (35.7 mg, 92% yield). M.p = 90-93 ℃; $[\alpha]_D^{20}$ = -7.7 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 57% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 10.07 min, t (major) = 7.67 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (s, 1H), 7.92 – 7.80 (m, 2H), 7.57 – 7.47 (m, 3H), 7.21 – 7.16 (m, 5H), 7.07 (dd, *J* = 3.2, 1.1 Hz, 1H), 6.30 (t, *J* = 3.1 Hz, 1H), 5.75 (dd, *J* = 3.1, 1.5 Hz, 1H), 4.98 (dd, *J* = 14.9, 5.9 Hz, 1H), 4.63 (dd, *J* = 15.0, 9.2 Hz, 1H), 4.30 (ddd, *J* = 9.4, 5.8, 1.3 Hz, 1H), 3.38 (d, *J* = 6.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.81, 168.03, 134.34, 133.11, 132.48, 132.09, 129.94, 128.34, 127.77, 127.64, 127.49, 118.55, 111.79, 104.76, 74.08, 67.92, 42.52, 38.41 ppm; ESI-HRMS: calcd for $C_{22}H_{19}N_3O_4$ + Na^+ 412.1268, found 412.1264.

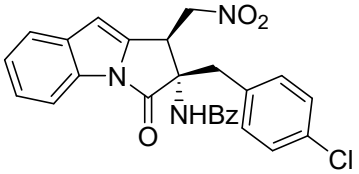


Synthesis of 3o (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-(4-fluorobenzyl)-2-phenyloxazol-5(4*H*)-one **2b** (32.2 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 13 h. Upon workup, product **3o′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3o′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3o** as a yellow solid (33.3 mg, 73% yield). M.p = 91-99 ℃; $[\alpha]_D^{20}$ = +12.0 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 60% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 8.13 min, t (major) = 8.99 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.11 (s, 1H), 7.93 – 7.86 (m, 3H), 7.65 – 7.60 (m, 2H), 7.58 – 7.53 (m, 2H), 7.38 – 7.28 (m, 2H), 7.23 (s, 4H), 6.47 (dd, *J* = 1.9, 0.7 Hz, 1H), 5.41 (dd, *J* = 14.7, 8.1 Hz, 1H), 5.30 (dd, *J* = 14.8, 6.1 Hz, 1H), 4.73 (ddd, *J* = 8.1, 6.1, 1.9 Hz, 1H), 3.39 (d, *J* = 14.2 Hz, 1H), 3.04 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.15, 166.97, 138.81, 133.63, 133.45, 133.01, 132.12, 132.07, 131.75, 130.09,

128.49, 127.71, 127.692, 124.14, 123.94, 121.22, 112.91, 101.07, 72.75, 67.64, 40.82, 36.78 ppm; ESI-HRMS: calcd for $C_{26}H_{20}FN_3O_4$ + K^+ 496.1069, found 496.1070.

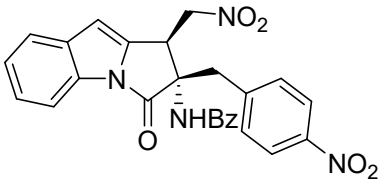


Synthesis of 3p (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-(3-fluorobenzyl)-2-phenyloxazol-5(4*H*)-one **2c** (32.2 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, product **3p′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3p′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3p** as a yellow solid (35.1 mg, 77% yield). M.p = 102-105 ℃; $[\alpha]_D^{20}$ = -7.8 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 91% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.12 min, t (major) = 14.09 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.15 (s, 1H), 7.94 – 7.86 (m, 3H), 7.66 – 7.60 (m, 2H), 7.59 – 7.52 (m, 2H), 7.32 (pd, *J* = 7.3, 1.5 Hz, 2H), 7.19 (td, *J* = 8.0, 6.3 Hz, 1H), 7.11 – 6.93 (m, 3H), 6.46 (d, *J* = 1.8 Hz, 1H), 5.41 (dd, *J* = 14.7, 8.1 Hz, 1H), 5.31 (dd, *J* = 14.7, 6.2 Hz, 1H), 4.75 (ddd, *J* = 8.1, 6.2, 1.9 Hz, 1H), 3.41 (d, *J* = 14.8 Hz, 1H), 3.10 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.30, 166.96, 138.80, 137.12, 133.63, 133.01, 132.14, 130.11, 129.59, 128.51, 127.71, 126.53, 124.15, 123.96, 121.23, 116.98, 113.90, 112.87, 101.01, 72.76, 67.76, 40.75, 37.14 ppm; ESI-HRMS: calcd for $C_{26}H_{20}FN_3O_4$ + H^+ 458.1511, found 458.1543.

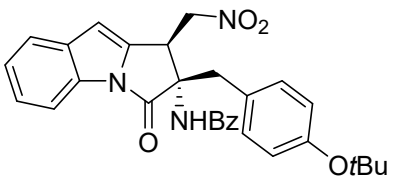


Synthesis of 3q (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-(4-chlorobenzyl)-2-phenyloxazol-5(4*H*)-one **2d** (34.2 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 19 h. Upon workup, product **3q′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3q′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3q** as a yellow solid (34.5 mg, 73% yield). M.p = 95-96 ℃; $[\alpha]_D^{20}$ = -7.3 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 92% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) =

14.19 min, t (major) = 20.96 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.10 (s, 1H), 7.95 – 7.85 (m, 3H), 7.65 – 7.60 (m, 2H), 7.55 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 7.01 – 6.93 (m, 2H), 6.45 (d, *J* = 1.9 Hz, 1H), 5.41 (dd, *J* = 14.7, 8.1 Hz, 1H), 5.31 (dd, *J* = 14.7, 6.1 Hz, 1H), 4.74 (ddd, *J* = 8.1, 6.0, 1.9 Hz, 1H), 3.38 (d, *J* = 14.3 Hz, 1H), 3.06 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.35, 166.94, 138.87, 133.61, 133.03, 132.12, 132.04, 130.42, 130.10, 128.48, 127.71, 124.11, 123.92, 121.20, 114.60, 114.38, 112.88, 100.94, 72.77, 67.74, 40.69, 36.73 ppm; ESI-HRMS: calcd for $C_{26}H_{20}ClN_3O_4$ + Na^+ 496.1035, found 496.1040.

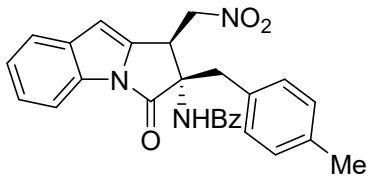


Synthesis of 3r (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-(4-nitrobenzyl)-2-phenyloxazol-5(4*H*)-one **2e** (35.5 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 20 h. Upon workup, product **3q′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3r′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 °C for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3r** as a yellow solid (39.2 mg, 81% yield). M.p = 87-90 °C; $[\alpha]_D^{20}$ = +27.4 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 91% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 29.16 min, t (major) = 11.48 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (s, 1H), 8.08 – 8.04 (m, 2H), 7.94 – 7.90 (m, 1H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.58 – 7.50 (m, 7H), 7.37 – 7.31 (m, 2H), 6.30 (d, *J* = 1.3 Hz, 1H), 5.17 (dd, *J* = 15.1, 5.9 Hz, 1H), 4.74 (dd, *J* = 8.5, 6.8 Hz, 1H), 4.48 (ddd, *J* = 9.0, 5.9, 1.6 Hz, 1H), 3.64 – 3.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.08, 167.14, 146.88, 141.56, 138.87, 134.00, 132.96, 132.29, 131.73, 129.88, 128.46, 127.87, 124.38, 123.89, 123.38, 121.23, 113.10, 101.06, 73.88, 67.97, 41.80, 38.64 ppm; ESI-HRMS: calcd for $C_{26}H_{20}N_4O_6$ + Na^+ 507.1275, found 507.1274.

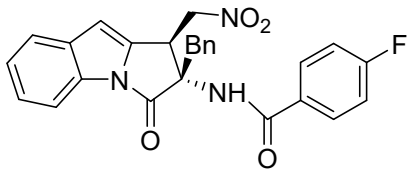


Synthesis of 3s (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-(4-(*tert*-butoxy)benzyl)-2-phenyloxazol-5(4*H*)-one **2f** (38.7 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 20 h. Upon workup, product **3s′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether =

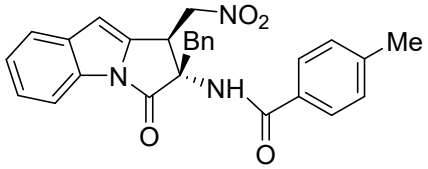
1/20). Subsequently, **3s′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3s** as a yellow solid (38.3 mg, 75% yield). M.p = 87-90 ℃; $[\alpha]_D^{20}$ = -36.8 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 92% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.40 min, t (major) = 19.95 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.09 (s, 1H), 7.95 – 7.91 (m, 2H), 7.87 (d, *J* = 7.9, 1.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.57 – 7.48 (m, 3H), 7.27 (dtd, *J* = 26.5, 7.4, 1.2 Hz, 2H), 7.07 – 6.98 (m, 2H), 6.61 – 6.53 (m, 2H), 6.26 (d, *J* = 1.9, 0.7 Hz, 1H), 5.37 (d, *J* = 7.0 Hz, 2H), 4.77 (td, *J* = 6.9, 2.0 Hz, 1H), 3.30 (d, *J* = 14.3 Hz, 1H), 3.19 (d, *J* = 14.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.43, 166.80, 153.92, 139.02, 133.53, 133.09, 132.06, 130.37, 130.09, 128.44, 127.96, 127.78, 123.96, 123.81, 123.13, 121.07, 112.73, 100.21, 77.72, 72.81, 68.46, 39.82, 39.73, 37.51, 28.30 ppm; ESI-HRMS: calcd for $C_{30}H_{29}N_3O_5$ + H^+ 512.2180, found 512.2184.



Synthesis of 3t (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-(4-methylbenzyl)-2-phenyloxazol-5(4*H*)-one **2g** (31.8 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 20 h. Upon workup, product **3t′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3t′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3t** as a yellow solid (37.6 mg, 83% yield). M.p = 88-96 ℃; $[\alpha]_D^{20}$ = -11.8 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 90% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.80 min, t (major) = 12.39 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.04 (s, 1H), 7.94 – 7.87 (m, 3H), 7.66 – 7.58 (m, 2H), 7.58 – 7.51 (m, 2H), 7.38 – 7.27 (m, 2H), 7.08 – 7.02 (m, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.40 (d, 1H), 5.33 (qd, 2H), 4.73 (ddd, *J* = 8.1, 6.1, 1.9 Hz, 1H), 3.38 (s, 1H), 3.02 (d, *J* = 14.3 Hz, 1H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.76, 166.83, 138.99, 136.05, 133.64, 133.06, 132.09, 130.93, 130.11, 129.95, 128.48, 128.43, 127.72, 124.08, 123.90, 121.19, 112.87, 100.80, 72.84, 67.84, 40.61, 37.57, 20.55 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_4$ + Na^+ 476.1581, found 476.1583.

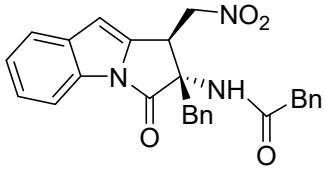


Synthesis of 3u (procedure A): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-benzyl-2-(4-fluorophenyl)oxazol-5(4*H*)-one **2h** (32.2 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, the reaction mixture was removed to room temperature added DABCO (2.7 mg, 30 mol%) for further cyclization during 5 h. After the reaction was completed, product **3u** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (37.9 mg, 83% yield). M.p = 95-100 ℃; $[\alpha]_D^{20}$ = -19.7 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 90% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 22.29 min, t (major) = 7.49 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (s, 1H), 8.03 – 7.97 (m, 2H), 7.89 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.59 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.26 (m, 2H), 7.20 – 7.14 (m, 2H), 7.12 – 7.07 (m, 3H), 6.39 (d, *J* = 1.9 Hz, 1H), 5.35 (dq, 2H), 4.74 (ddd, *J* = 8.1, 6.1, 1.9 Hz, 1H), 3.40 (d, *J* = 14.3 Hz, 1H), 3.08 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.68, 165.80, 138.91, 133.97, 133.61, 130.54, 130.45, 130.06, 129.57, 127.79, 127.00, 124.09, 123.90, 121.19, 115.60, 115.38, 112.84, 100.81, 72.78, 67.97, 40.52, 37.92 ppm; ESI-HRMS: calcd for $C_{26}H_{20}FN_3O_4$ + Na^+ 480.1330, found 480.1327.

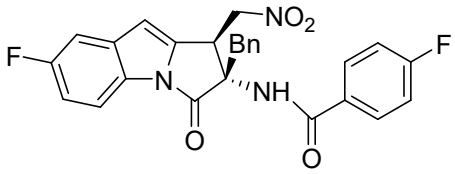


Synthesis of 3v (procedure A): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 4-benzyl-2-(p-tolyl)oxazol-5(4*H*)-one **2i** (31.8 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 5 h. After the reaction was completed, product **3v** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (35.7 mg, 79% yield). M.p = 85-88 ℃; $[\alpha]_D^{20}$ = -23.9 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 92% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 30.16 min, t (major) = 11.72 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.98 (s, 1H), 7.89 (d, *J* = 7.7, 1.3 Hz, 1H), 7.82 (d, 2H), 7.59 (d, 1H), 7.39 – 7.25 (m, 4H), 7.19 – 7.14 (m, 2H), 7.13 – 7.07 (m, 3H), 6.38 (d, 1H), 5.35 (dq, *J* = 8.3 Hz, 2H), 4.72 (ddd, *J* = 8.0, 6.1, 1.9 Hz, 1H), 3.40 (d, *J* = 14.2 Hz, 1H), 3.07 (d, *J* = 14.2 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.79, 166.68, 142.16, 138.95, 134.04, 133.60, 130.23, 130.11, 130.08, 128.99, 127.78, 127.74, 126.98, 124.06, 123.88, 121.18, 112.84,

100.70, 72.86, 67.87, 40.66, 37.90, 21.06 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_4$ + Na^+ 476.1581, found 476.1574.

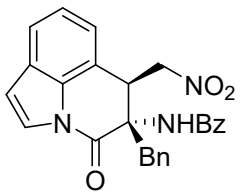


Synthesis of 3w (procedure B): (*E*)-2-(2-nitrovinyl)-1*H*-indole **1a** (18.8 mg, 0.1 mmol), 2,4-dibenzyloxazol-5(4*H*)-one **2j** (31.8 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, product **3w′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20). Subsequently, **3w′** was dissolved in DCM (1.0 mL), then DABCO (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 12 h. After the reaction was completed, the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to afford product **3w** as a yellow solid (28.5 mg, 63% yield). M.p = 84-88 ℃; $[\alpha]_D^{20}$ = +2.1 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 91% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.99 min, t (major) = 7.69 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (s, 1H), 7.84 (d, *J* = 7.8, 1.3 Hz, 1H), 7.54 (d, *J* = 7.1, 1.5 Hz, 1H), 7.33 – 7.20 (m, 8H), 7.12 – 7.02 (m, 5H), 6.31 (d, *J* = 1.8 Hz, 1H), 5.31 (d, 2H), 4.57 (td, *J* = 7.1, 1.9 Hz, 1H), 3.60 (s, 2H), 3.21 (d, *J* = 14.3 Hz, 1H), 3.06 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.87, 167.94, 138.82, 135.56, 133.64, 133.59, 129.98, 129.91, 129.09, 128.22, 127.77, 127.02, 126.49, 124.07, 123.85, 121.13, 112.78, 100.56, 72.90, 67.60, 41.36, 40.50, 37.98 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_4$ + H^+ 454.1761, found 454.1760.

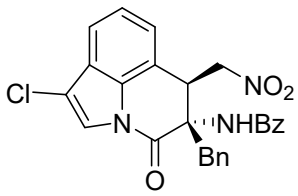


Synthesis of 3x (procedure A): (*E*)-5-fluoro-2-(2-nitrovinyl)-1*H*-indole **1d** (20.6 mg, 0.1 mmol), 4-benzyl-2-(4-fluorophenyl)oxazol-5(4*H*)-one **2h** (32.2 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 16 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 5 h. After the reaction was completed, product **3x** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (36.1 mg, 76% yield). M.p = 91-93 ℃; $[\alpha]_D^{20}$ = -13.8 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 90% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 27.04 min, t (major) = 8.23 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (s, 1H), 8.04 – 7.93 (m, 2H), 7.87 (dd, *J* = 8.8, 4.6 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.21 – 7.13 (m, 3H), 7.12 – 7.07 (m, 3H), 6.39 (d, *J* = 1.9

Hz, 1H), 5.35 (qd, *J* = 14.7, 7.0 Hz, 2H), 4.72 (ddd, *J* = 8.0, 6.0, 1.9 Hz, 1H), 3.38 (d, *J* = 14.2 Hz, 1H), 3.10 (d, *J* = 14.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.51, 165.79, 140.87, 134.85, 133.78, 130.50, 130.42, 129.98, 129.48, 127.75, 127.00, 126.64, 115.55, 115.34, 113.88, 111.64, 107.09, 100.83, 72.61, 67.88, 40.47, 37.85 ppm; ESI-HRMS: calcd for $C_{26}H_{19}F_2N_3O_4$ + Na^+ 498.1236, found 498.1243.

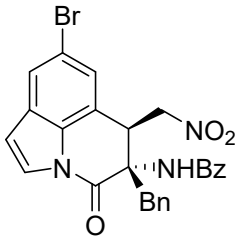


Synthesis of 5a (procedure C): (*E*)-7-(2-nitrovinyl)-1*H*-indole **4a** (18.8 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. After full-conversion, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/20) to afford the pure chiral product **5a′**. Subsequently, the obtained **5a′** was dissolved in DCM (1.0 mL), then DBU (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 2 h. After the reaction was completed, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford the pure chiral product **5a** as a pale yellow solid (31.6 mg, 72% yield). M.p = 86-88 ℃; $[\alpha]_D^{20}$ = +20.6 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 77% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 21.35 min, t (major) = 10.35 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (s, 1H), 7.94 – 7.89 (m, 2H), 7.67 (d, *J* = 3.6 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.54 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.40 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.95 – 6.89 (m, 3H), 6.81 – 6.76 (m, 3H), 5.70 (dd, *J* = 14.6, 8.0 Hz, 1H), 5.46 (dd, *J* = 14.6, 3.5 Hz, 1H), 5.30 (dd, *J* = 8.1, 3.4 Hz, 1H), 3.20 (d, *J* = 14.1 Hz, 1H), 3.00 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.02, 164.20, 133.71, 133.26, 132.65, 131.85, 129.34, 128.37, 127.70, 127.31, 127.22, 126.78, 123.72, 122.14, 120.39, 119.69, 118.95, 110.69, 74.26, 64.36, 40.55, 38.61 ppm; ESI-HRMS: calcd for $C_{26}H_{21}N_3O_4$ + Na^+ 462.1424, found 462.1427.



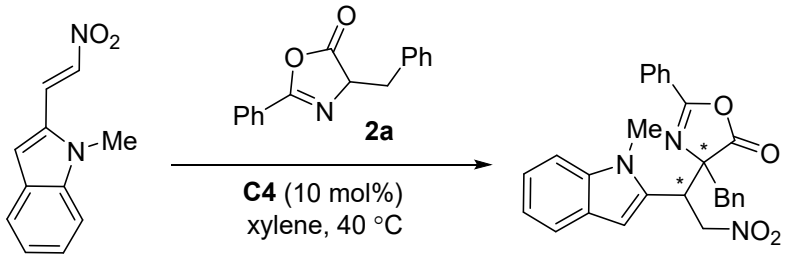
Synthesis of 5b (procedure C): (*E*)-3-chloro-7-(2-nitrovinyl)-1*H*-indole **4b** (22.2 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. After full-conversion, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/20) to afford the pure chiral product **5b′**. Subsequently, the obtained **5b′** was dissolved in DCM (1.0 mL), then DBU (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 2 h. After the reaction was completed, the

residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford the pure chiral product **5b** as a pale yellow solid (34.5 mg, 73% yield). M.p = 86-90 ℃; $[\alpha]_D^{20}$ = +1.0 (*c* = 26.0 in $CHCl_3$); >19:1 dr, 86% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 28.81 min, t (major) = 10.09 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.03 (s, 1H), 7.96 – 7.88 (m, 3H), 7.65 – 7.59 (m, 1H), 7.54 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.35 – 7.22 (m, 2H), 7.14 (dt, *J* = 7.3, 1.3 Hz, 1H), 6.94 – 6.85 (m, 3H), 6.83 – 6.77 (m, 2H), 5.75 (dd, *J* = 14.7, 7.8 Hz, 1H), 5.49 (dd, *J* = 14.7, 3.6 Hz, 1H), 5.33 – 5.26 (m, 1H), 3.19 (d, *J* = 14.1 Hz, 1H), 3.09 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.10, 163.91, 133.54, 132.78, 131.93, 131.75, 129.30, 128.38, 127.73, 127.20, 126.84, 124.48, 124.45, 120.86, 120.29, 119.03, 116.89, 114.82, 74.08, 64.05, 40.27, 39.00 ppm; ESI-HRMS: calcd for $C_{26}H_{20}ClN_3O_4$ + Na^+ 496.1035, found 496.1044.

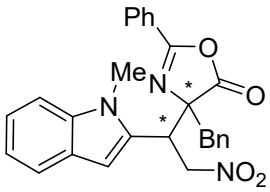


Synthesis of 5c (procedure C): (*E*)-5-bromo-7-(2-nitrovinyl)-1*H*-indole **4c** (26.7 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. After full-conversion, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/20) to afford the pure chiral product **5c′**. Subsequently, the obtained **5c′** was dissolved in DCM (1.0 mL), then DBU (2.7 mg, 30 mol%) was added to the reaction mixture and stirred at 0 ℃ for 2 h. After the reaction was completed, the residue was purified by flash chromatography (EtOAc/petroleum ether = 1/10) to afford the pure chiral product **5c** as a pale yellow solid (41.9 mg, 81% yield). M.p = 96-99 ℃; $[\alpha]_D^{20}$ = 29.6 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 53% ee, determined by HPLC analysis [Daicel chiralpak AS-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 22.94 mbin, t (major) = 40.24 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (s, 1H), 7.92 – 7.88 (m, 2H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.57 – 7.51 (m, 2H), 7.23 (t, *J* = 1.6 Hz, 1H), 6.95 – 6.87 (m, 3H), 6.82 – 6.77 (m, 2H), 6.75 (d, *J* = 3.6 Hz, 1H), 5.80 (dd, *J* = 14.7, 7.3 Hz, 1H), 5.47 (dd, *J* = 14.8, 3.9 Hz, 1H), 5.29 (dt, *J* = 7.1, 2.6 Hz, 1H), 3.19 (d, *J* = 14.1 Hz, 1H), 3.07 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.12, 164.23, 133.54, 132.85, 131.93, 131.54, 129.32, 128.90, 128.39, 127.70, 127.26, 126.94, 123.46, 122.45, 122.23, 121.73, 115.91, 110.11, 73.74, 64.17, 40.27, 38.83 ppm; ESI-HRMS: calcd for $C_{26}H_{20}BrN_3O_4$ + Na^+ 540.0529, found 540.0530.

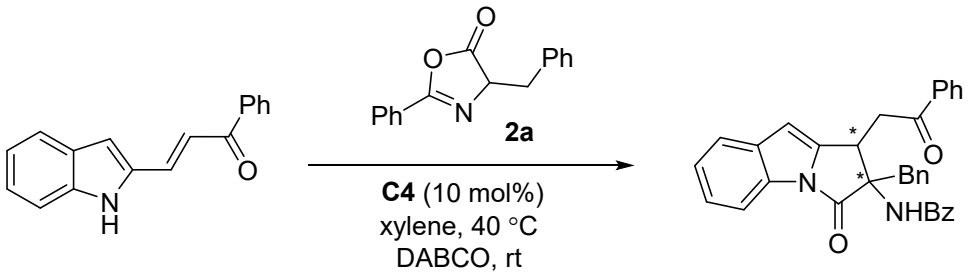
3. Asymmetric [3+2] cyclization reactions of other types of functionalized indoles



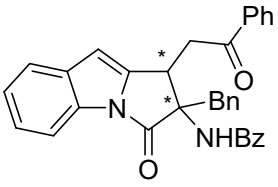
1a-Me 6a'



Synthesis of 6a′: (*E*)-1-methyl-2-(2-nitrovinyl)-1*H*-indole **1a-Me** (20.2 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12 mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. Upon workup, product **6a′** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/15) as a yellow solid (32.1 mg, 73% yield). M.p = 73-76 °C; $[\alpha]_D^{20}$ = +2.7 (*c* = 1.0 in $CHCl_3$); dr = 3:1, 53% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 12.97 min, t (major) = 10.60 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.67 (m, 2H), 7.57 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.26 (d, *J* = 3.5 Hz, 2H), 7.19 – 7.10 (m, 7H), 6.67 (s, 1H), 5.06 – 4.99 (m, 1H), 4.90 (dd, *J* = 14.0, 4.4 Hz, 1H), 4.52 (dd, *J* = 10.9, 4.5 Hz, 1H), 3.85 (s, 3H), 3.18 (d, *J* = 13.1 Hz, 1H), 3.12 (d, *J* = 13.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 177.01, 158.96, 136.29, 134.55, 133.10, 132.54, 129.59, 128.42, 127.48, 126.77, 126.68, 126.01, 123.82, 120.85, 119.53, 118.74, 109.15, 98.43, 75.72, 74.55, 29.09, 25.75, 24.19 ppm; ESI-HRMS: calcd for $C_{27}H_{23}N_3O_4$ + H^+ 454.1761, found 454.1884.



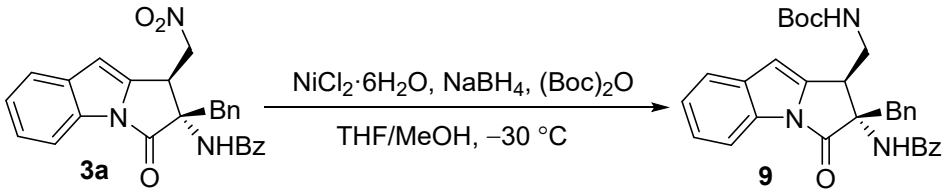
7a 8a

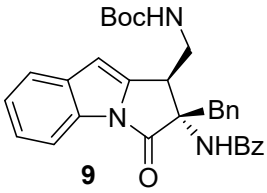


Synthesis of 8a: (*E*)-3-(1*H*-indol-2-yl)-1-phenylprop-2-en-1-one **7a** (24.7 mg, 0.1 mmol), 4-benzyl-2-phenyloxazol-5(4*H*)-one **2a** (30.1 mg, 0.12

mmol), **C4** (6.3 mg, 10 mol%) were dissolved in xylene (1.0 mL) and stirred at 40 °C for 12 h. Upon workup, the reaction mixture was removed to room temperature and added DABCO (2.7 mg, 30 mol%) for further cyclization during 6 h. After the reaction was completed, product **8a** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a pale yellow solid (21.4 mg, 43% yield). M.p = 77-79 °C; >19:1 dr, 0% ee, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.87 – 7.80 (m, 2H), 7.77 – 7.67 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.30 (m, 6H), 7.29 – 7.27 (m, 1H), 7.09 – 6.99 (m, 5H), 6.95 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.31 (d, *J* = 2.0 Hz, 1H), 4.34 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.67 (dd, *J* = 17.2, 9.3 Hz, 1H), 3.48 (dd, *J* = 17.2, 3.8 Hz, 1H), 3.18 (d, *J* = 13.4 Hz, 1H), 3.07 (d, *J* = 13.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.04, 179.51, 161.20, 136.65, 136.36, 133.78, 133.53, 133.02, 130.39, 128.87, 128.83, 128.78, 128.75, 128.69, 128.27, 128.14, 128.06, 127.50, 125.33, 122.00, 120.47, 119.79, 111.21, 102.69, 42.00, 40.99, 39.46 ppm; ESI-HRMS: calcd for $C_{33}H_{26}N_2O_3$ + H^+ 499.2016, found 499.2023.

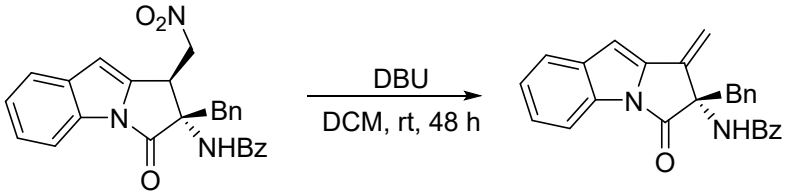
4. Synthetic transformations



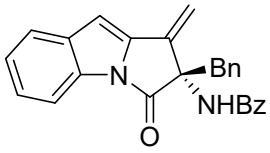


Synthesis of 9: Compound **3a** (43.9 mg, 0.10 mmol) was dissolved in THF/MeOH (2.0 mL, v/v 1:1) and cooled down to -30 °C. Then $NiCl_2·6H_2O$ (47.4 mg, 0.20 mmol) was added and stirred for 5 minutes, thereafter $NaBH_4$ (22.7 mg, 0.6 mmol) was added slowly and stirred for 10 minutes, then followed by the addition of $(Boc)_2O$ (32.7 mg, 0.15 mmol) the reaction mixture was carried out at -30 °C for 24 h and . monitored by TLC. After completion, the reaction mixture was quenched with saturated NH_4Cl and extracted with DCM (3 × 5 mL). The combined organic layers was dried over anhydrous Na_2SO_4, then filtered and concentrated under reduced pressure to afford the residue which was purified by by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give product **9** as a white solid (44.7 mg, 88% yield). M.p = 94-96 °C; $[\alpha]_D^{20}$ = +20.2 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 90% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-

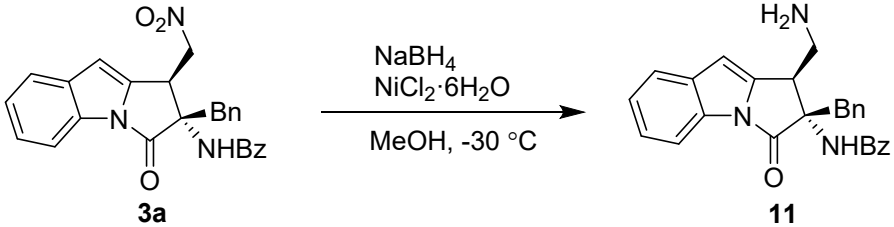
PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 6.77 min, t (major) = 10.93 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.90 (s, 1H), 7.93 – 7.85 (m,3H), 7.61 (t, J = 7.3 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.33 – 7.23 (m, 3H), 7.22 – 7.14 (m, 2H), 7.06 (p, J = 3.7 Hz, 3H), 6.37 (d, J = 1.9 Hz, 1H), 4.13 (t, J = 7.3 Hz, 1H), 3.66 (dd, J = 11.1, 5.9 Hz, 2H), 3.42 (d, J = 14.1 Hz, 1H), 3.07 (d, J = 14.1 Hz, 1H), 1.36 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.89, 166.22, 155.69, 141.79, 134.49, 133.90, 133.34, 131.85, 130.15, 130.10, 129.98, 128.34, 127.61, 127.56, 126.69, 123.74, 123.28, 120.73, 112.70, 99.59, 77.98, 67.97, 42.82, 37.82, 28.15 ppm; ESI-HRMS: calcd for $C_{31}H_{31}N_3O_4$ + Na^+ 532.2207, found 532.2208.



3a **10**

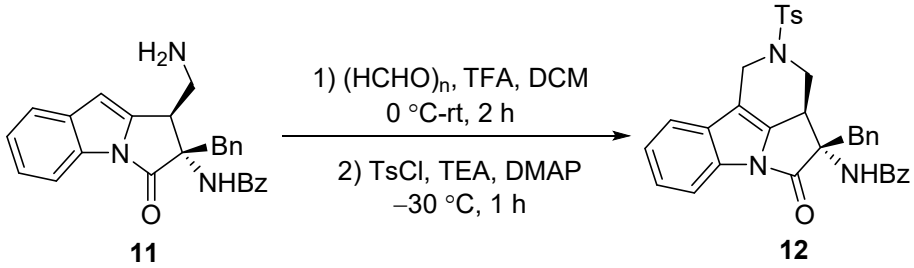


Synthesis of 10: Compound **3a** (43.9 mg, 0.1 mmol) was dissolved in DCM (2 mL), DBU (38.0 mg, 0.25 mmol) was added and the solution was stirred at room temperature for 48 h. After the reaction was completed, product **10** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (24.7 mg, 63% yield). M.p = 92-96 ℃; $[\alpha]_D^{20}$ = +26.0 (c = 1.0 in $CHCl_3$); >19:1 dr, 89% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, n-hexane/i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 6.31 min, t (major) = 7.37 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (s, 1H), 7.87 (dd, 3H), 7.59 (dd, J = 8.3, 6.3 Hz, 1H), 7.50 (t, 3H), 7.27 (t, 1H), 7.22 (t, 1H), 7.13 – 7.06 (m, 2H), 7.04 – 6.94 (m, 3H), 6.56 (s, 1H), 5.84 (s, 1H), 5.55 (s, 1H), 3.42 (dd, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.99, 166.40, 140.54, 139.36, 134.55, 133.52, 133.33, 132.39, 130.54, 130.37, 128.86, 128.21, 128.11, 127.50, 124.65, 124.52, 121.93, 113.49, 109.33, 98.49, 68.75, 42.74 ppm; ESI-HRMS: calcd for $C_{26}H_{20}N_2O_2$ + Na^+ 415.1417, found 415.1424.

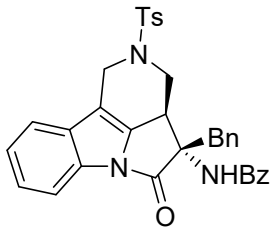


3a **11**

Synthesis of 11: Compound **3a** (43.9 mg, 0.10 mmol) was dissolved in 2 mL of MeOH, the reaction was cooled down to -30 ℃. $NiCl_2 \cdot 6H_2O$ (47.4 mg, 0.20 mmol) was added and stirred for 5 minutes, then $NaBH_4$ (22.7 mg, 0.6 mmol) was added slowly, then the reaction was carried out at -30 ℃ for 30 minutes. The reaction was monitored by TLC and was completed, then quenched with saturated NH_4Cl, the reaction was concentrated under reduced pressure, and extracted with DCM (3 × 5 mL). Product **11** was obtained by flash chromatography on silica gel (MeOH/DCM = 1/50) as a white solid (33.1 mg, 81% yield).



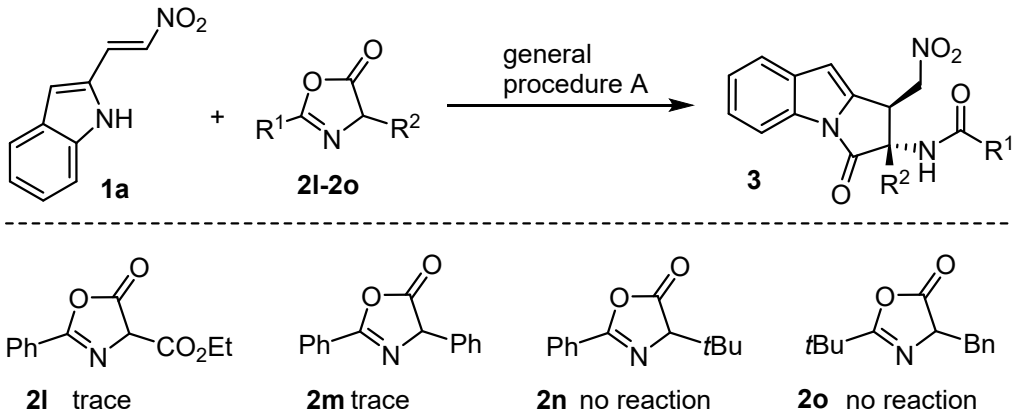
11 **12**



Synthesis of 12: Compound 11 (20.4 mg, 0.05 mmol) and $(HCHO)_n$ (1.8 mg, 0.06 mmol) were dissolved in DCM (1 mL), the reaction was cooled down at 0 ℃, and TFA (5.7 mg, 0.05 mmol) was slowly added dropwise, the reaction was stirred at room temperature for 2 h. After the reaction was completed, the reaction was extracted with DCM (3 × 5 mL), then the filtrate was concentrated under reduced pressure, obtain the product of the closing ring. The product was dissolved in dry DCM and cooled down at -30 ℃, then TEA (7.6 mg, 0.075 mmol) and DMAP (1.3 mg, 20 mol%) were added, and Ts-Cl (6.6 mg, 0.06 mmol) was added slowly, and the solution was reacted and stirred at -30 ℃ for 1h, and after the reaction was completed, product **12** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) as a white solid (20.1 mg, 70% yield). M.p = 103-105 ℃; $[\alpha]_D^{20}$ = -24.2 (*c* = 1.0 in $CHCl_3$); >19:1 dr, 89% ee, determined by HPLC analysis [Daicel chiralpak IB N-5, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (minor) = 12.58 min, t (major) = 13.99 min]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.98 (s, 1H), 7.69 (t, *J* = 8.1 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (q, *J* = 7.7 Hz, 3H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.14 (h, *J* = 5.1 Hz, 4H), 7.07 – 6.99 (m, 3H), 4.59 (d, *J* = 13.9 Hz, 1H), 3.93 (dd, *J* = 12.9, 2.4 Hz, 1H), 3.84 (d, *J* = 13.9 Hz, 1H), 3.72 (d, *J* = 4.0 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 3.01 (dd, *J* = 12.8, 4.2 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.52, 159.22, 143.44, 136.38, 133.79, 132.93, 132.47, 130.10, 129.84, 128.92, 128.63, 127.93,

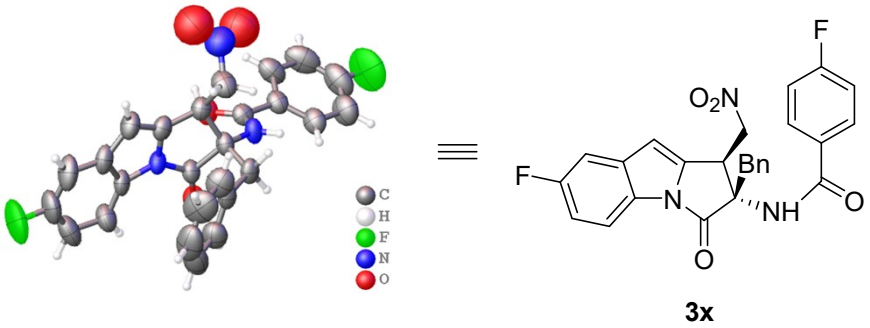
127.64, 127.24, 127.18, 125.59, 124.35, 121.76, 118.91, 117.68, 111.54, 107.38, 77.33, 45.73, 42.59, 41.67, 31.10, 20.92 ppm; ESI-HRMS: calcd for $C_{34}H_{29}N_3O_4S$ + Na^+ 598.1771, found 598.1777.

5. Failed trials of other azlactones under the optimized conditions



6. Crystal data for enantiopure cycloadducts 3x

Crystallization of 3x: The pure product **3x** (25 mg) was dissolved in the mixture solvent of *n*-hexane and dichloromethane (2 mL, 3:1, v/v) in a 10 mL vial. Then, the solution was allowed for slow evaporation to afford the crystal of **3x** in a good quality for the crystallography analysis.



Identification code	**3x**
Empirical formula	$C_{26}H_{19}F_2N_3O_4$
Formula weight	475.45
Temperature/K	200.0
Crystal system	monoclinic
Space group	$P2_1$

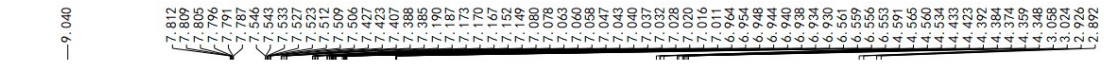
a/Å	12.0073(5)
b/Å	24.9718(10)
c/Å	17.9593(8)
α/°	90
β/°	108.3510(10)
γ/°	90
Volume/Å^3	5111.1(4)
Z	8
ρ_{calc}g/cm^3	1.401
μ/mm^{-1}	0.255
F(000)	2218.0
Crystal size/mm^3	0.39 × 0.33 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.928 to 54.984
Index ranges	-15 ≤ h ≤ 15, -32 ≤ k ≤ 32, -23 ≤ l ≤ 23
Reflections collected	69498
Independent reflections	23175 [R_{int} = 0.0643, R_{sigma} = 0.0661]
Data/restraints/parameters	23175/145/1341
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0795, wR_2 = 0.2088
Final R indexes [all data]	R_1 = 0.1316, wR_2 = 0.2516
Largest diff. peak/hole / e Å^{-3}	0.38/-0.53
Flack parameter	0.06(5)

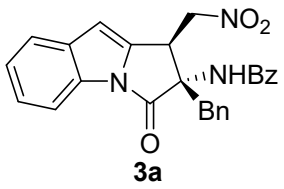
References

[1] Justin M. Lopchuk, Gordon W. Gribble; *Heterocycles.* **2011**, *82*, 1617-1631.

[2] Amanda C. de Mello, Patricia B. Momo, Antonio C. B. Burtoloso, and Giovanni W. Amarante. *J. Org. Chem.* **2018**, *83*, 11399-11406.

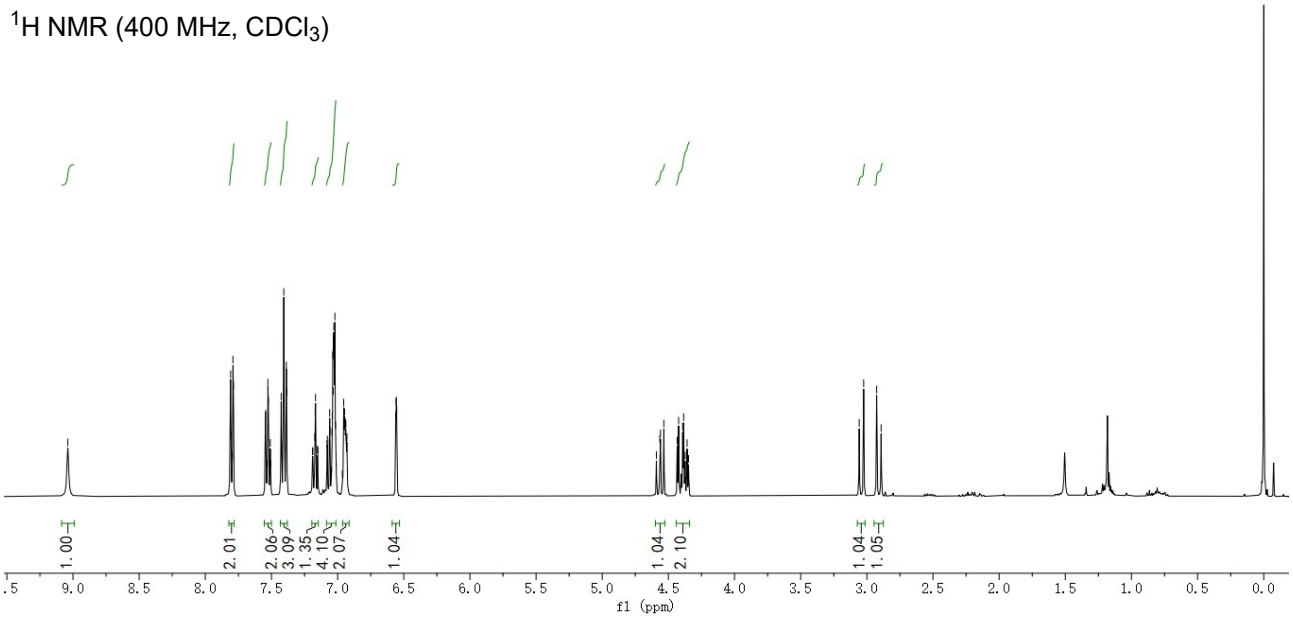
7. NMR spectra and HPLC chromatograms

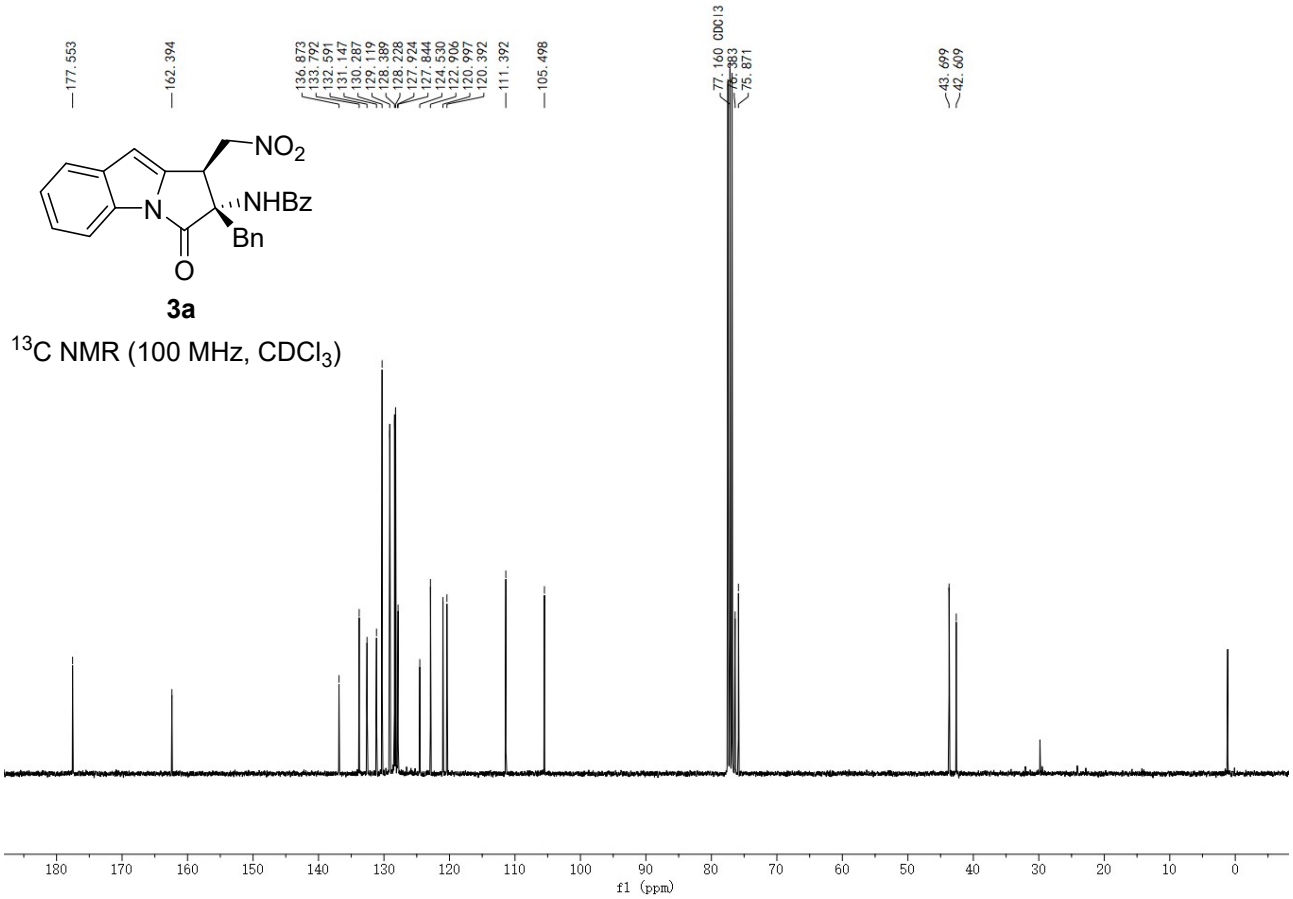


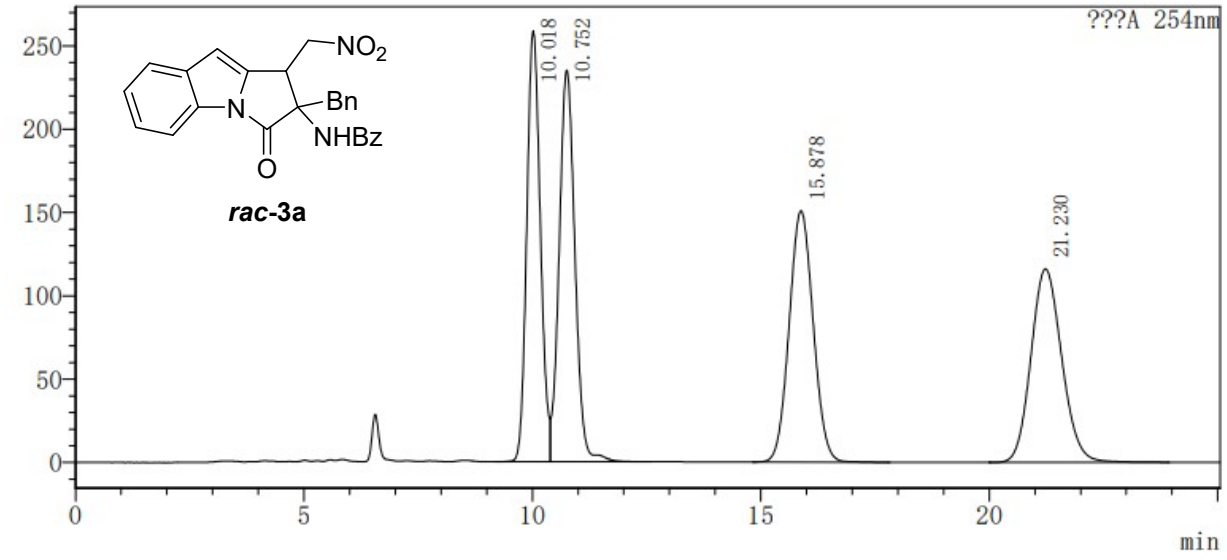


3a

^{1}H NMR (400 MHz, $CDCl_3$)







Peak#	Ret. Time	Area	Height	Area%	Height%
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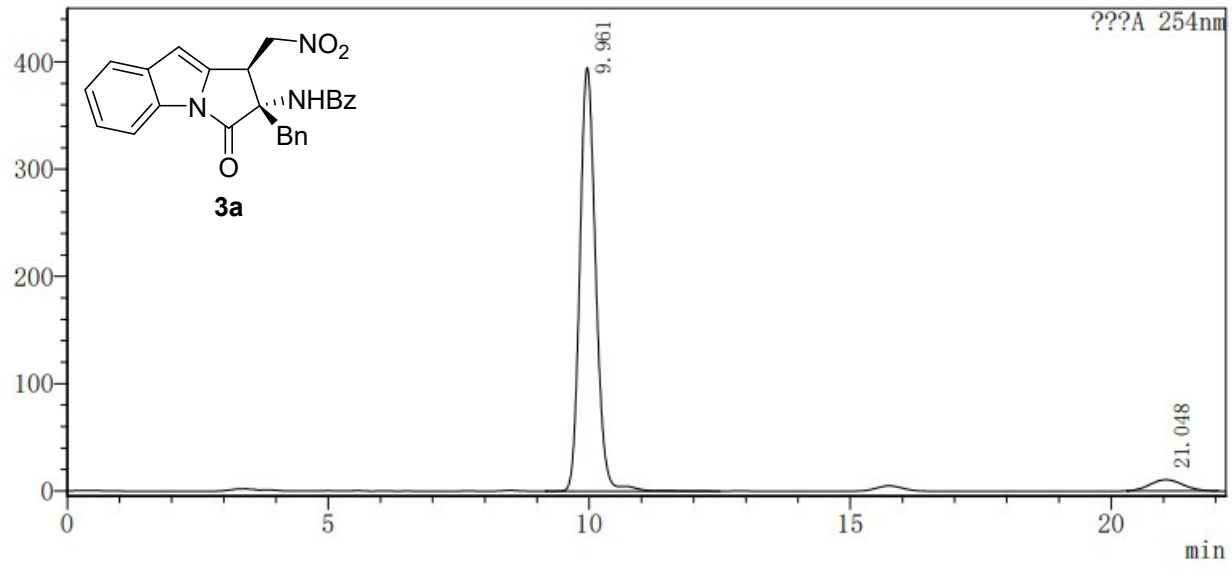
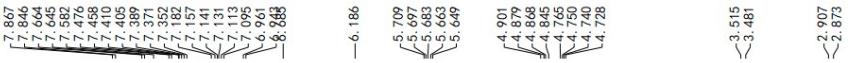
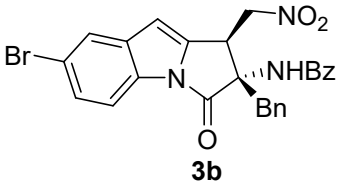
2	10.752	5645295	235063	25.718	30.904
3	15.878	5525579	150827	25.173	19.829
4	21.230	5437407	116110	24.771	15.265
Total		21950743	760630	100.000	100.000

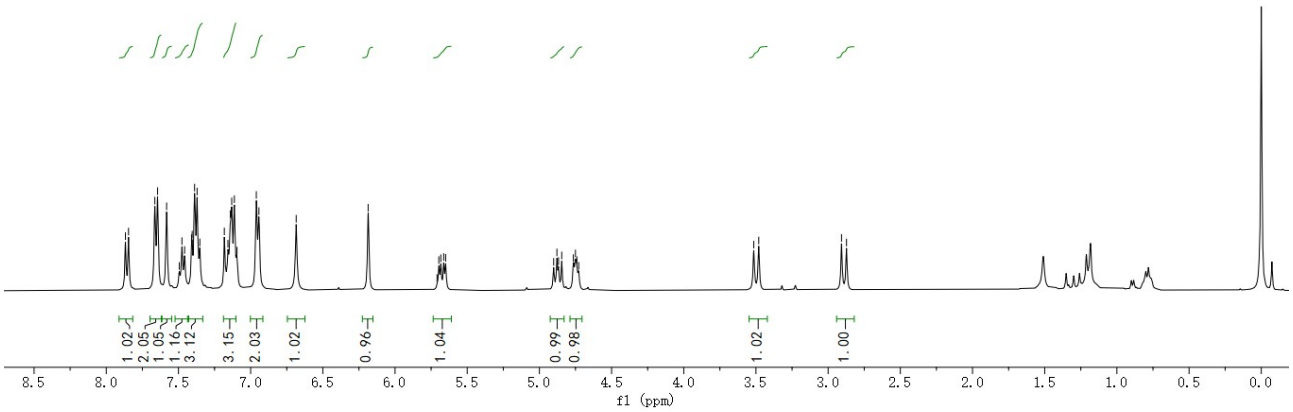


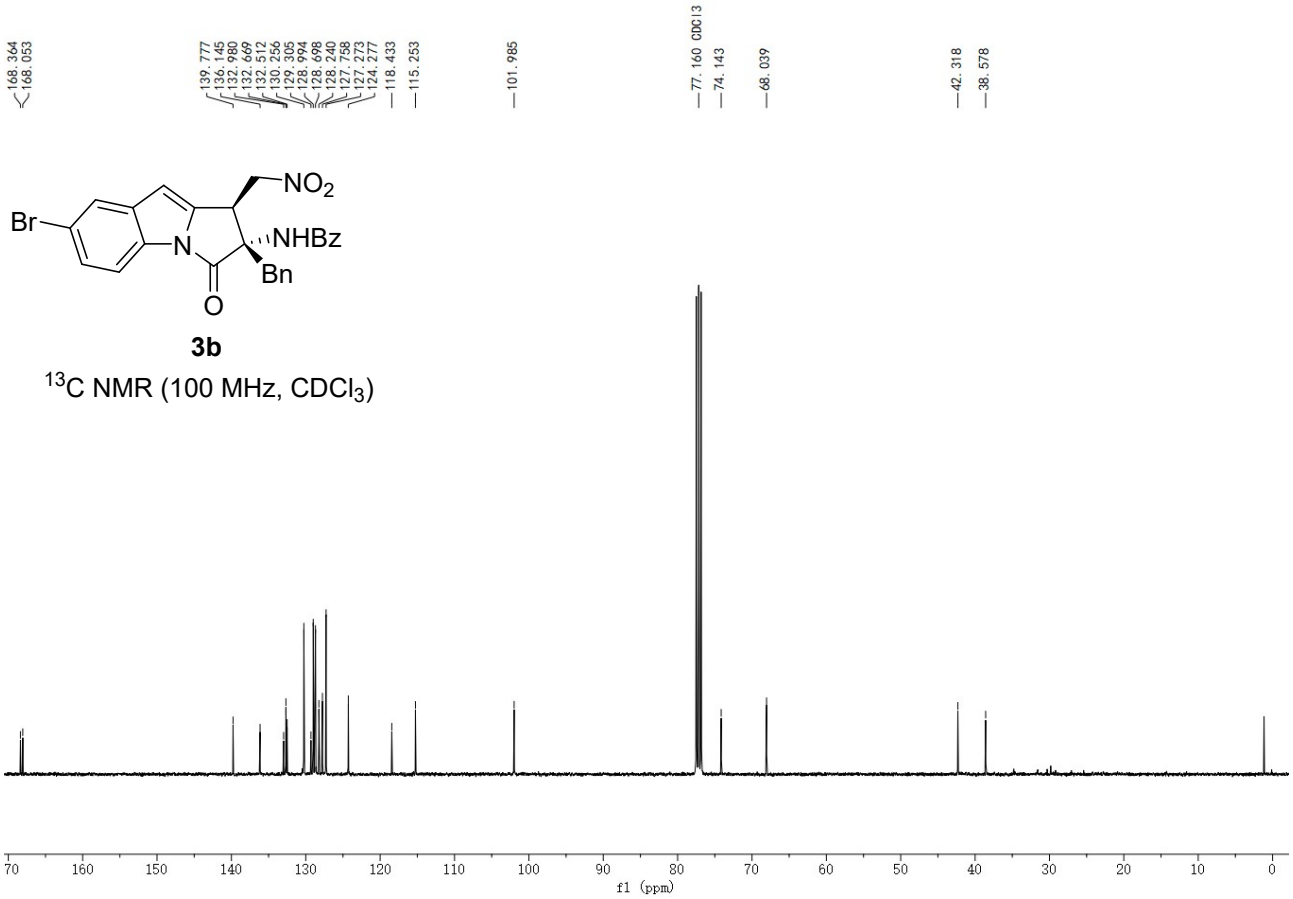
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.961	8333629	395084	94.788	97.423
2	21.048	458218	10451	5.212	2.577
Total		8791847	405535	100.000	100.000





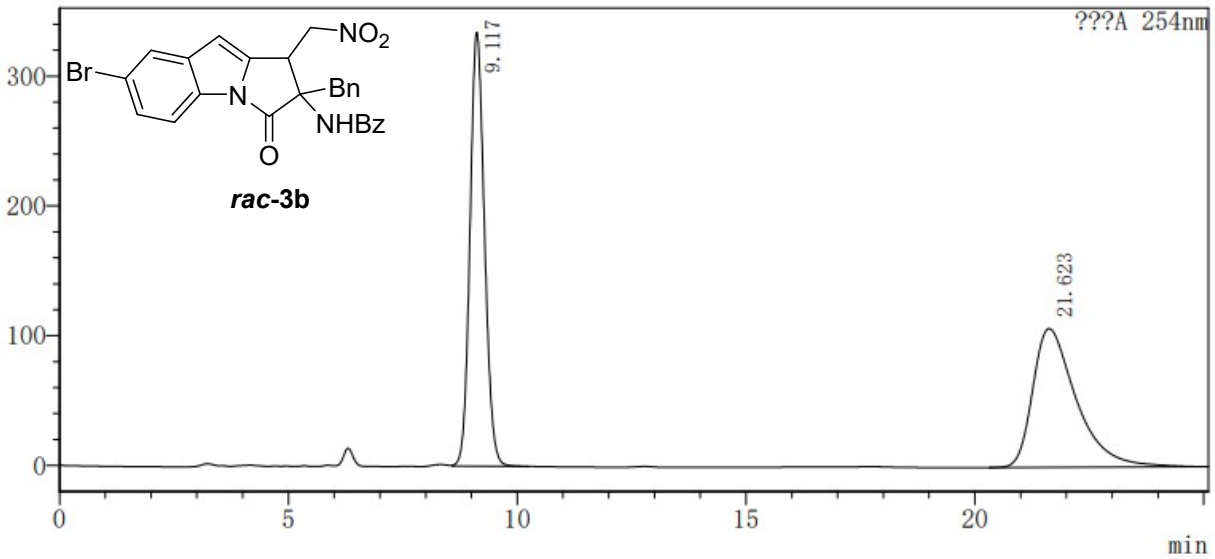
^{1}H NMR (400 MHz, $CDCl_3$)





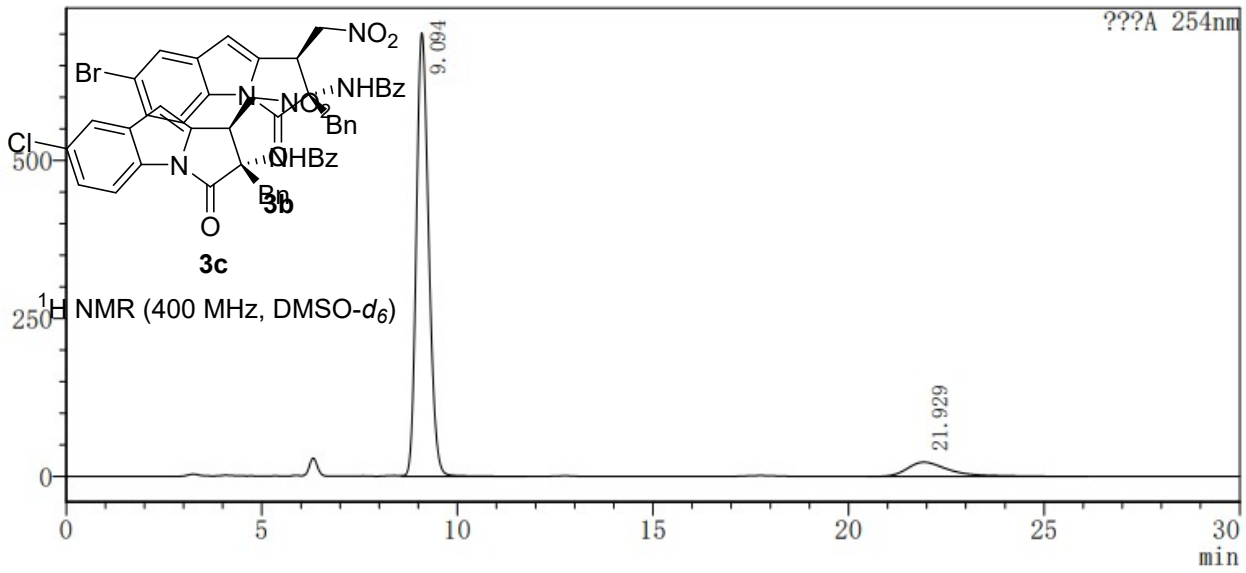
3b

^{13}C NMR (100 MHz, $CDCl_3$)

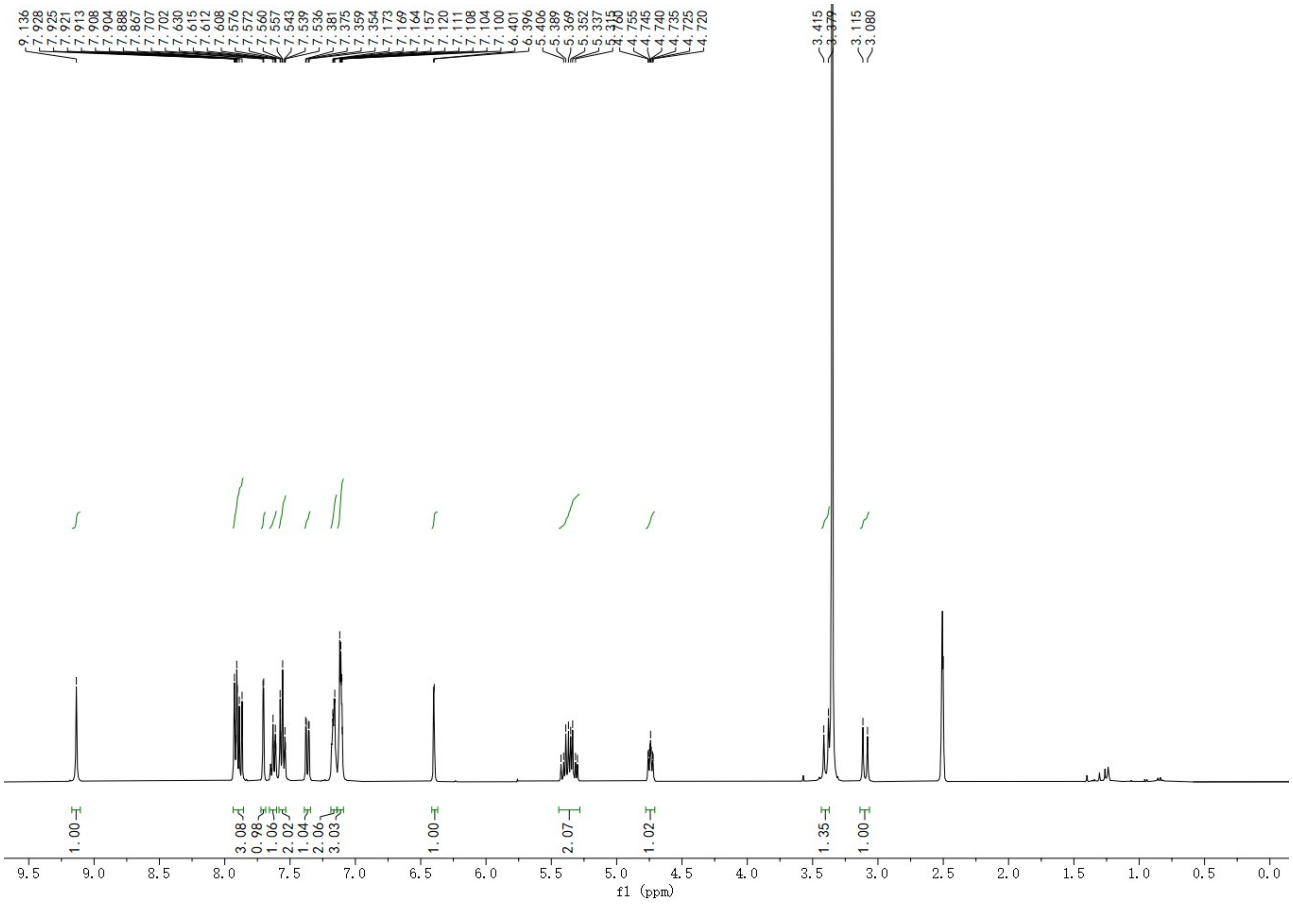


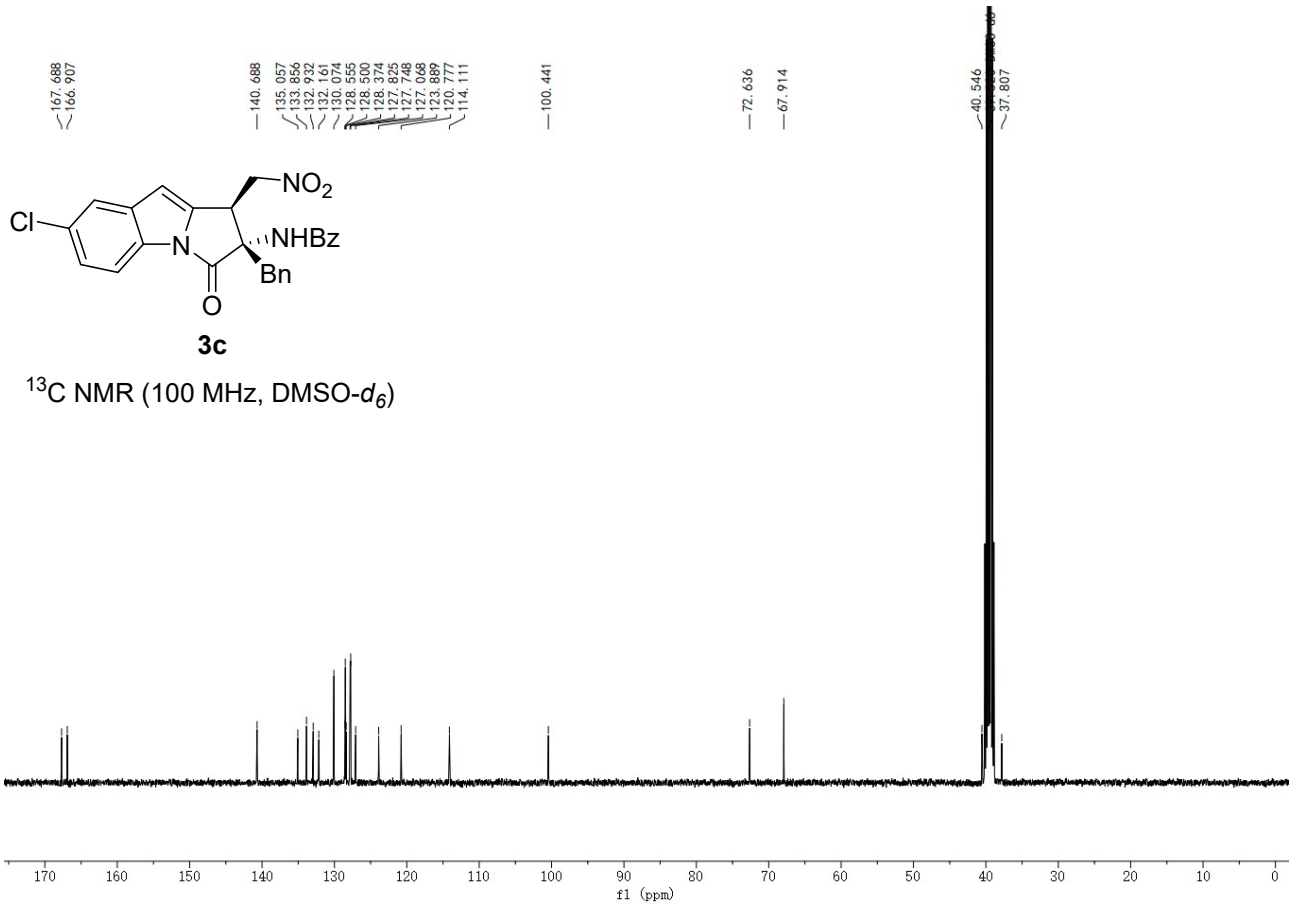
***rac*-3b**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.117	7374473	334211	50.985	75.765
2	21.623	7089563	106905	49.015	24.235
Total		14464036	441116	100.000	100.000



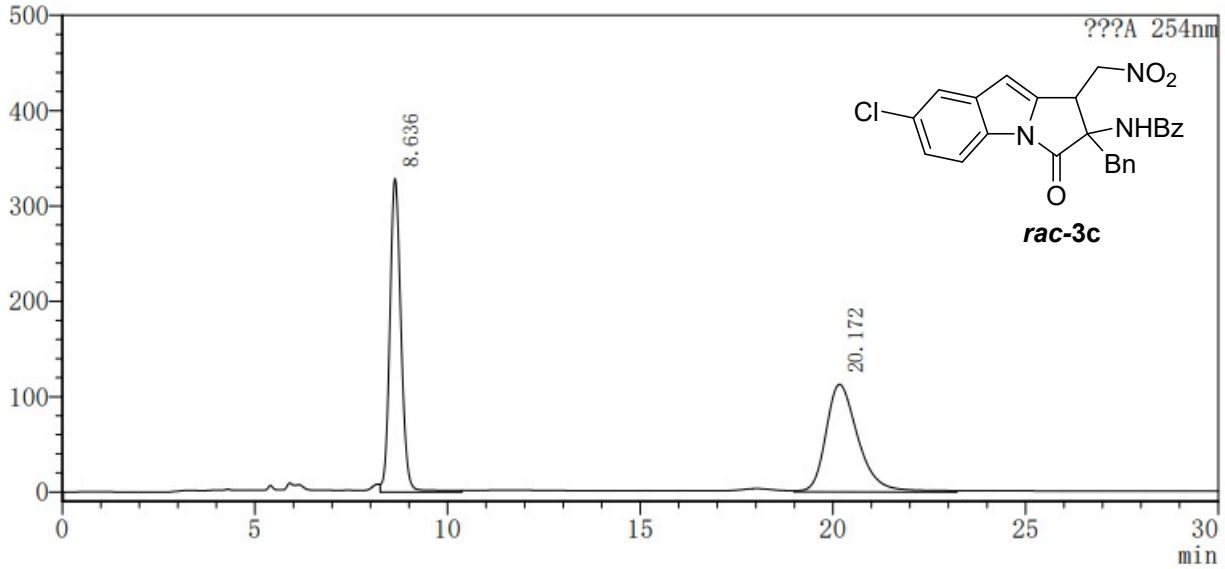
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.094	15406142	701734	90.180	96.890
2	21.929	1677695	22527	9.820	3.110
Total		17083837	724261	100.000	100.000





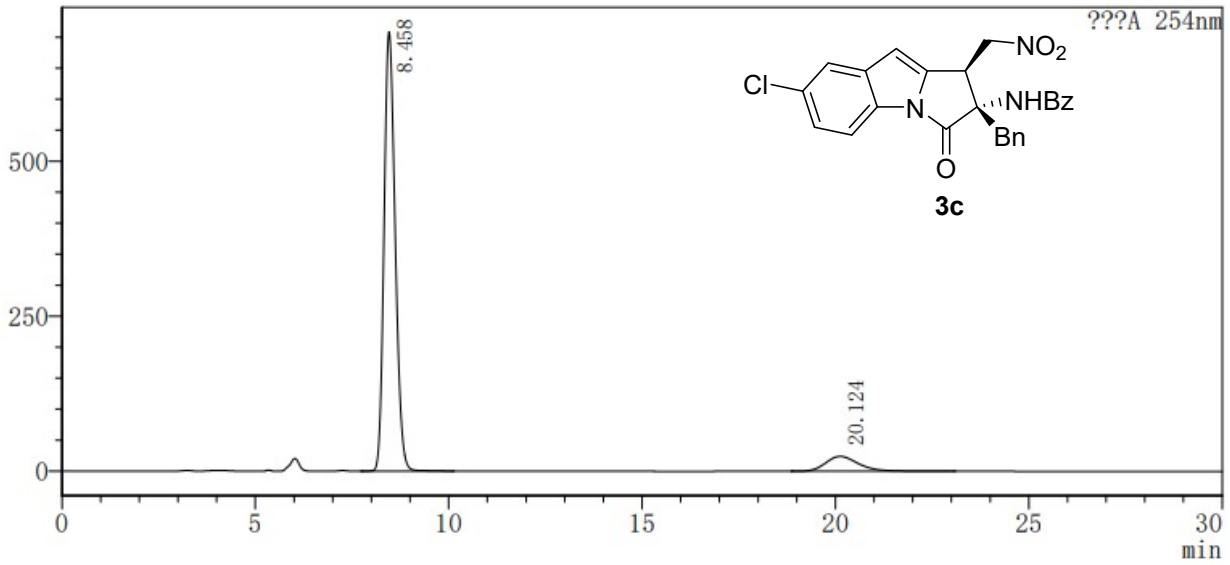
3c

^{13}C NMR (100 MHz, DMSO-d_6)



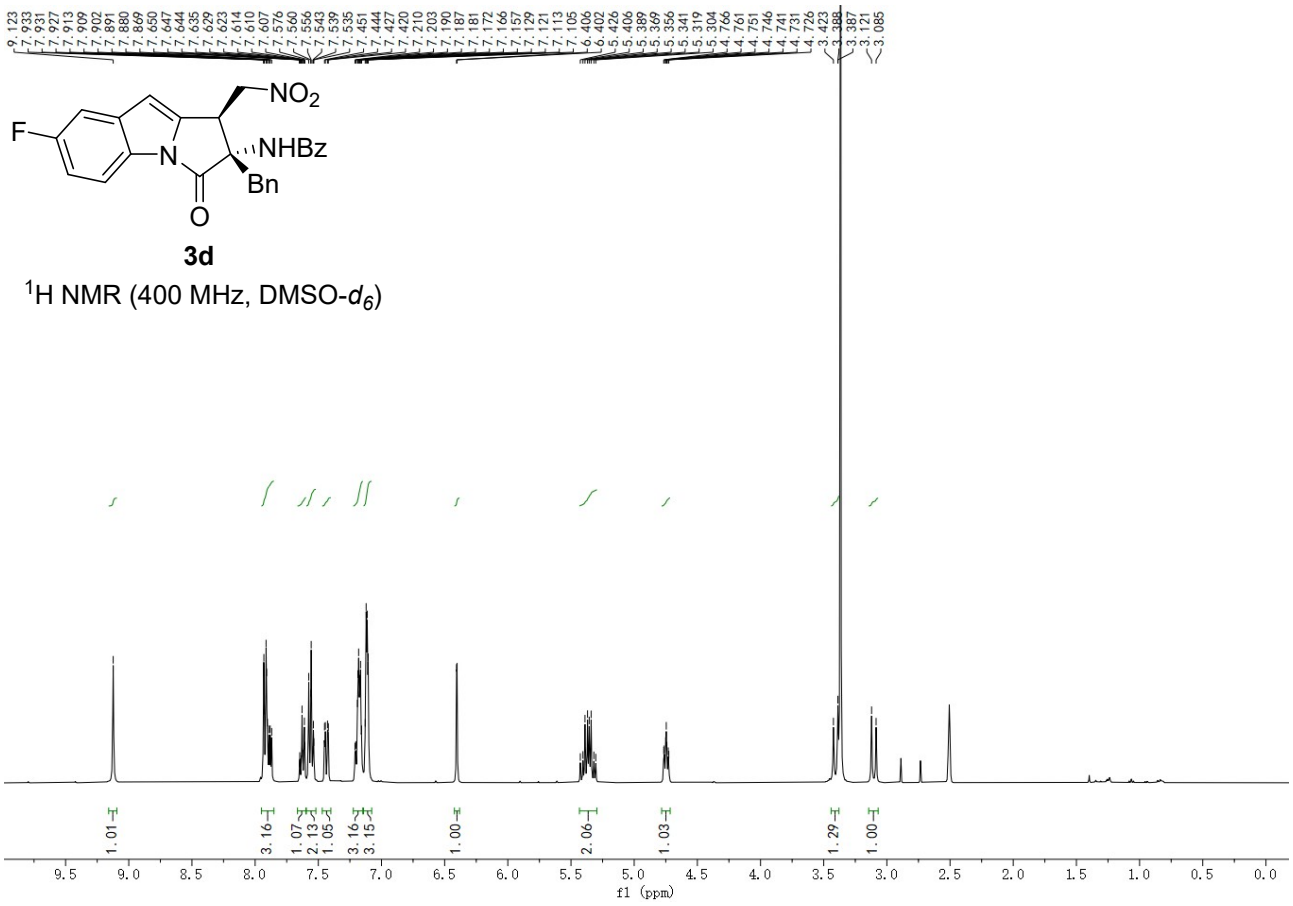
***rac*-3c**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.636	6651875	328801	50.225	74.490
2	20.172	6592227	112602	49.775	25.510
Total		13244102	441403	100.000	100.000



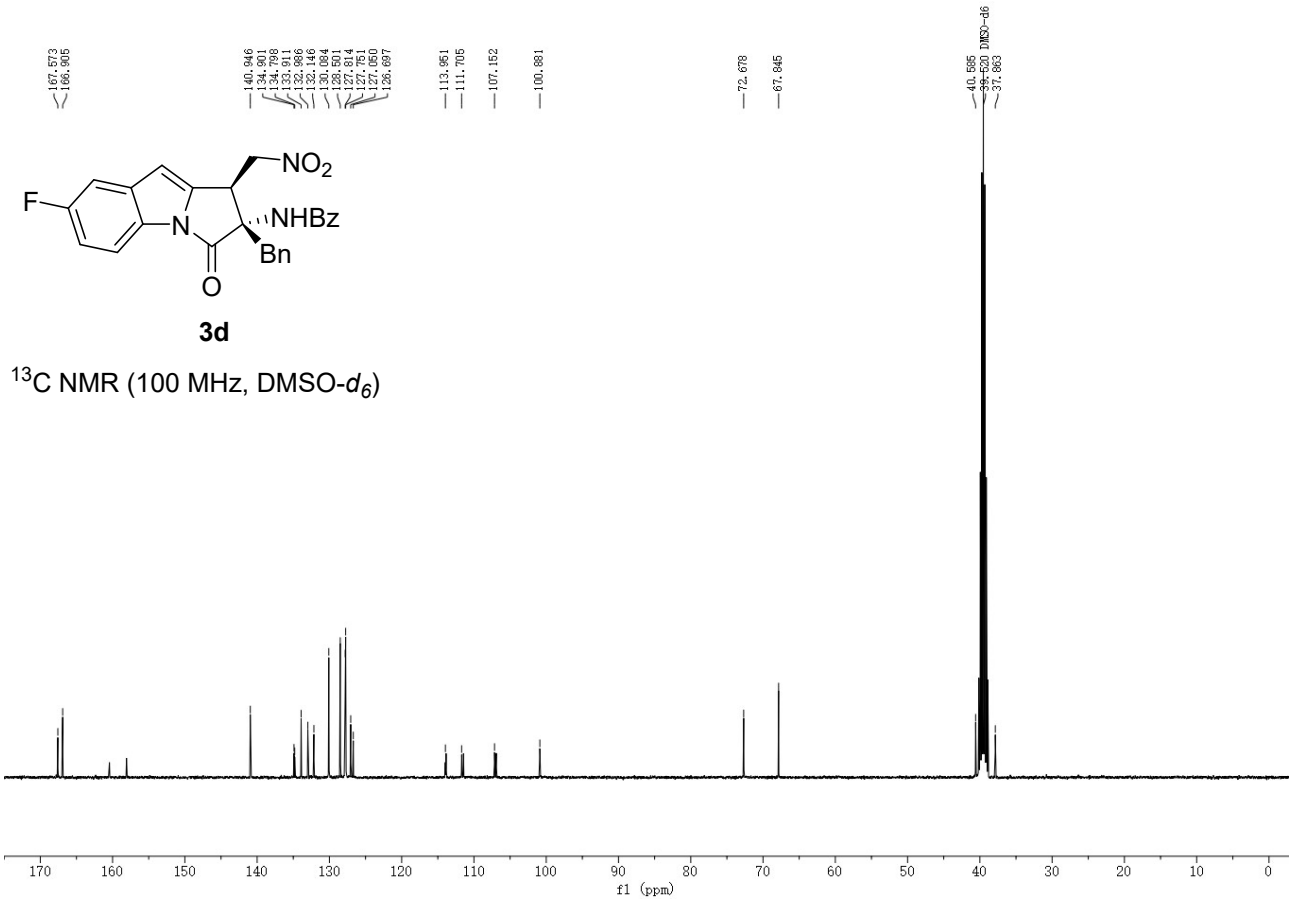
3c

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.458	14181311	708452	90.808	96.715
2	20.124	1435523	24064	9.192	3.285
Total		15616834	732516	100.000	100.000



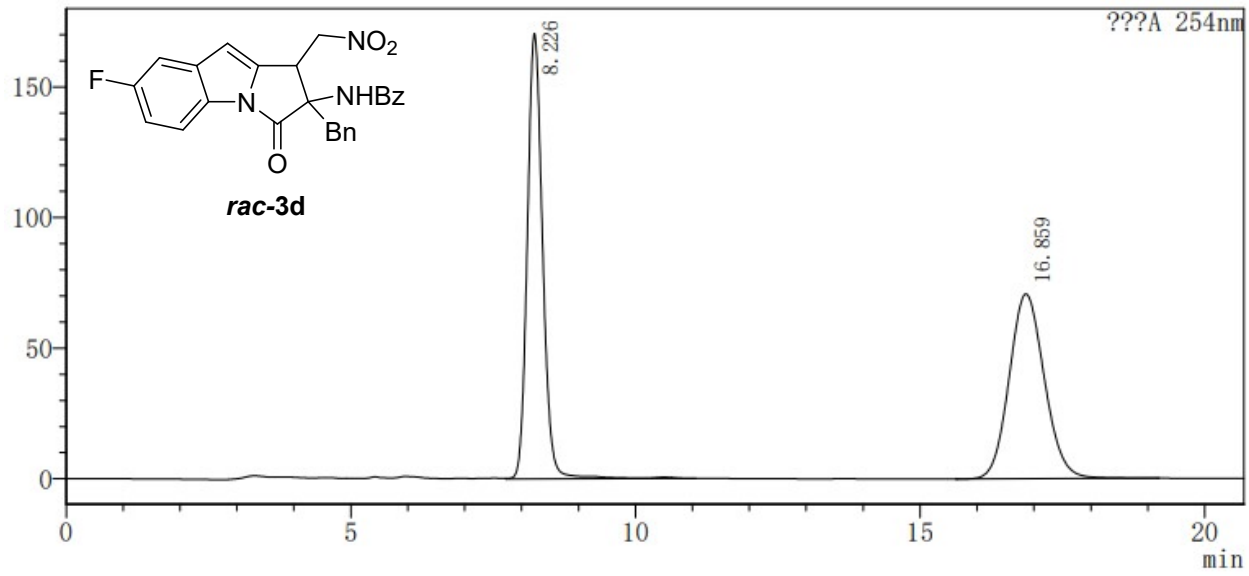
3d

^{1}H NMR (400 MHz, DMSO-d_6)



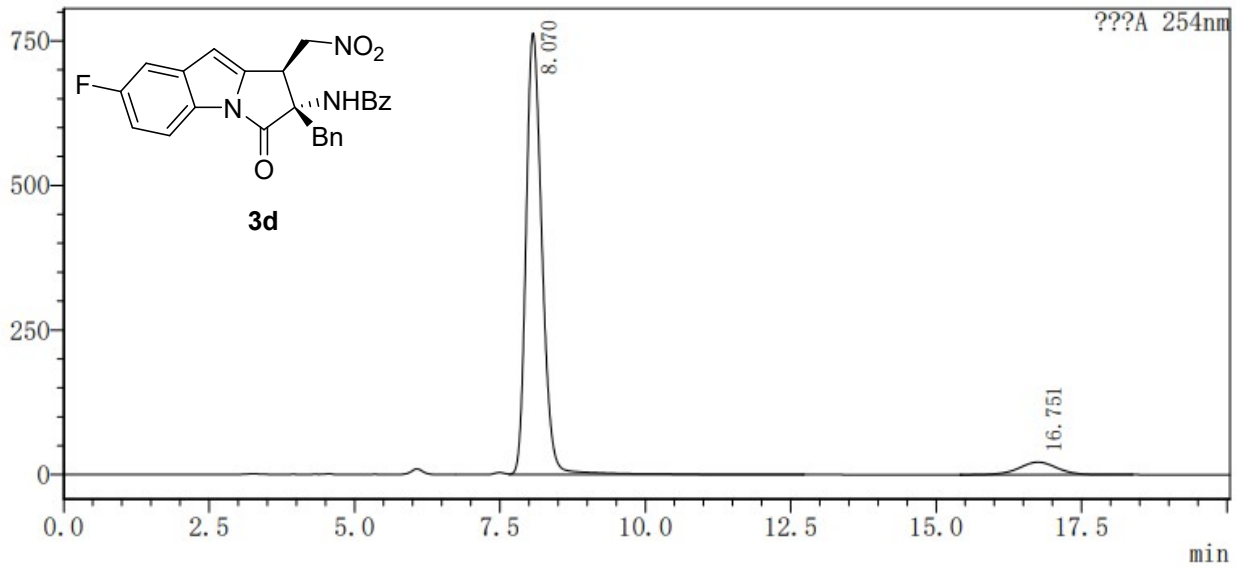
3d

^{13}C NMR (100 MHz, DMSO-d_6)



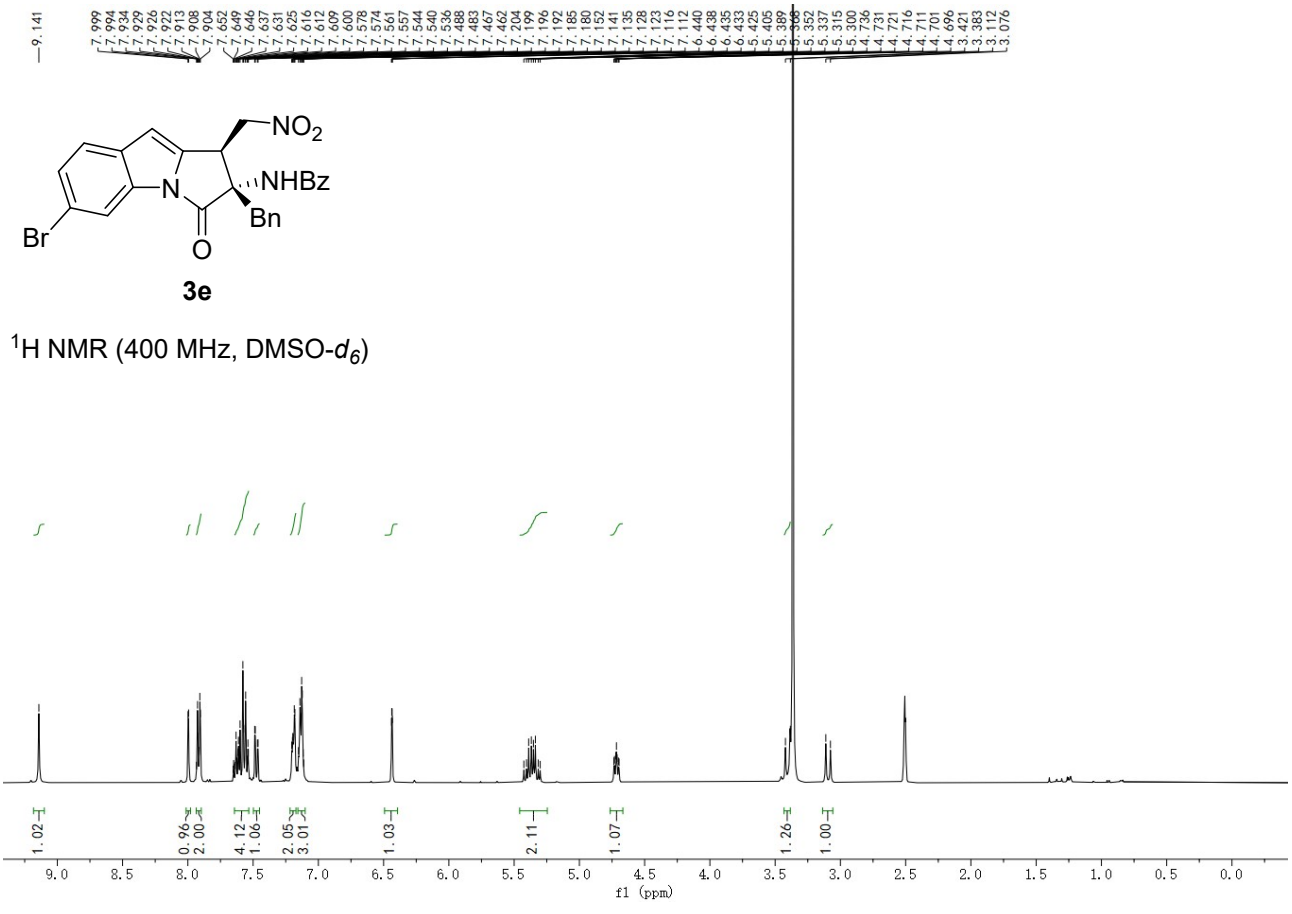
***rac*-3d**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.226	3197538	170440	51.160	70.668
2	16.859	3052509	70745	48.840	29.332
Total		6250047	241185	100.000	100.000



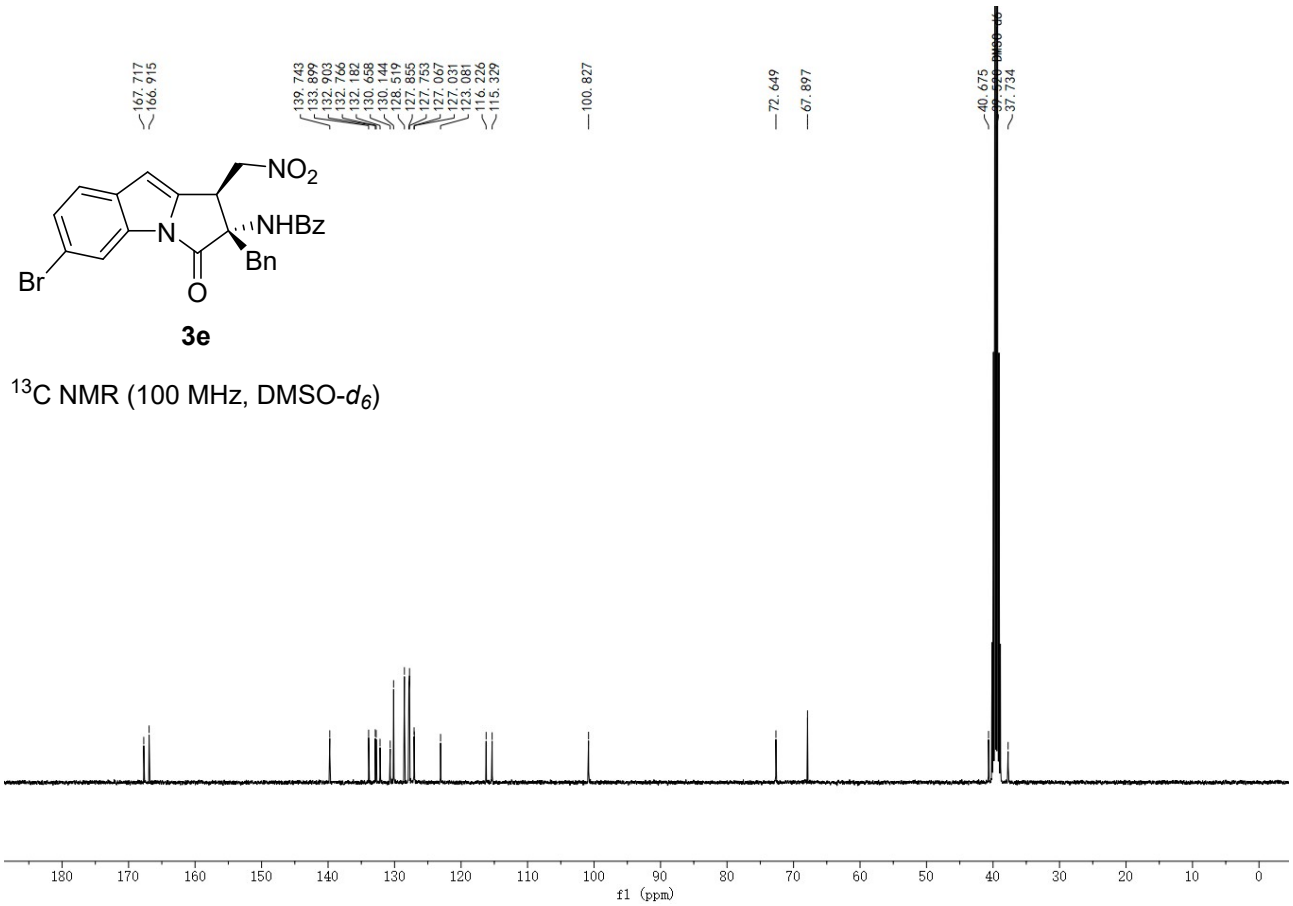
3d

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.070	14606354	763318	93.675	97.241
2	16.751	986287	21653	6.325	2.759
Total		15592642	784972	100.000	100.000



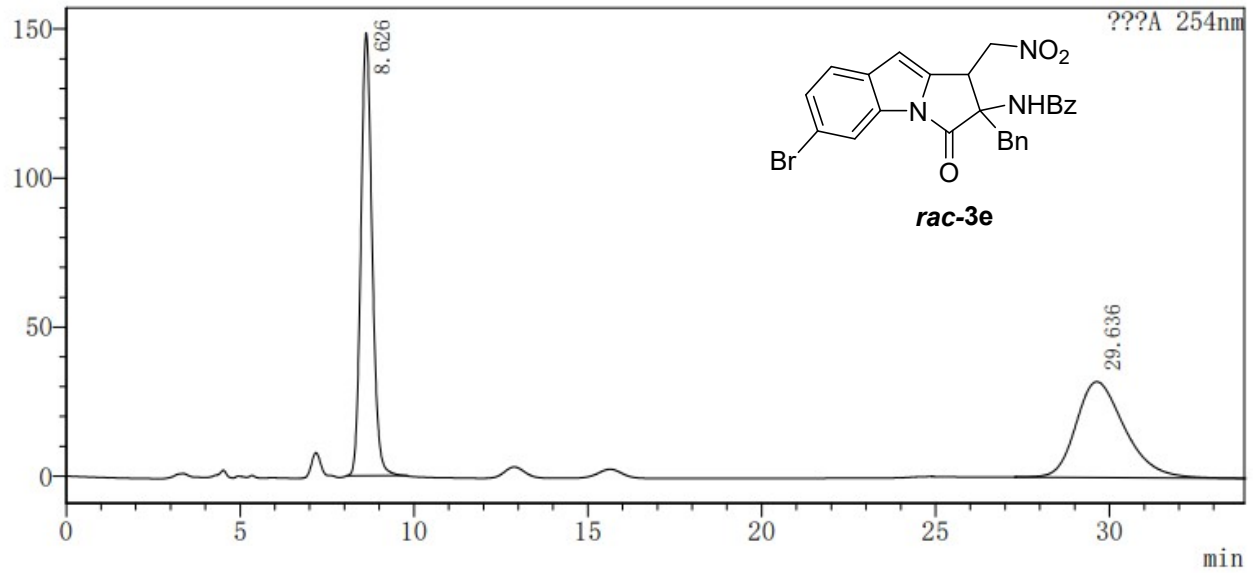
3e

^{1}H NMR (400 MHz, DMSO-d_6)



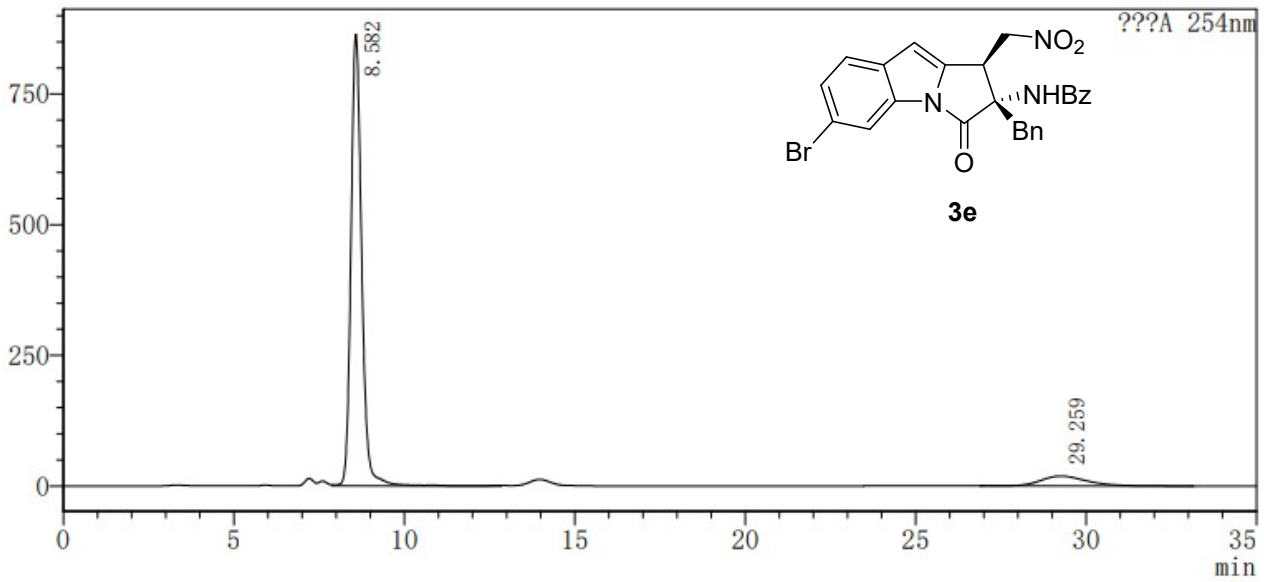
3e

^{13}C NMR (100 MHz, DMSO-d_6)



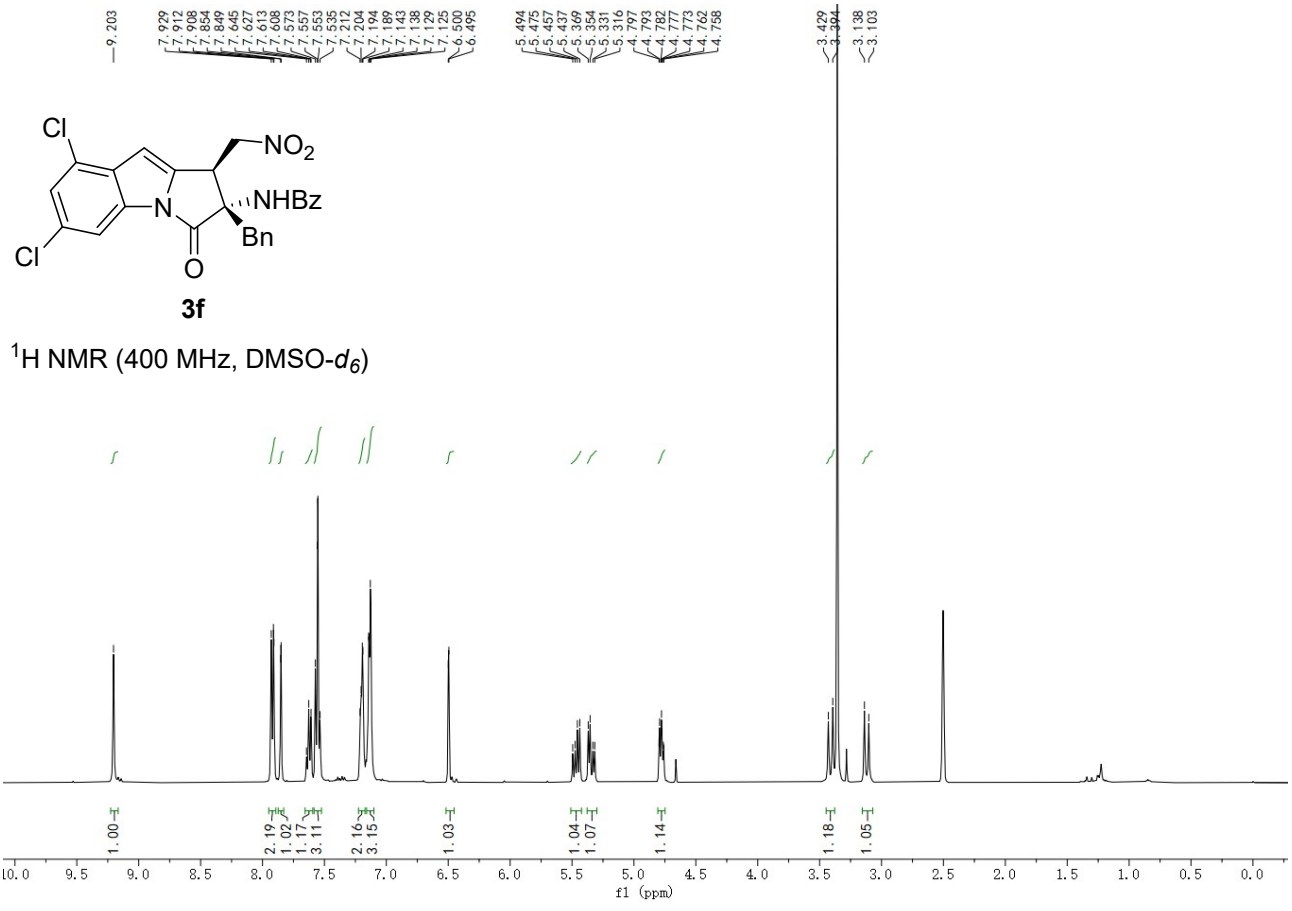
***rac*-3e**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.626	3325131	148523	51.550	82.232
2	29.636	3125134	32091	48.450	17.768
Total		6450265	180614	100.000	100.000



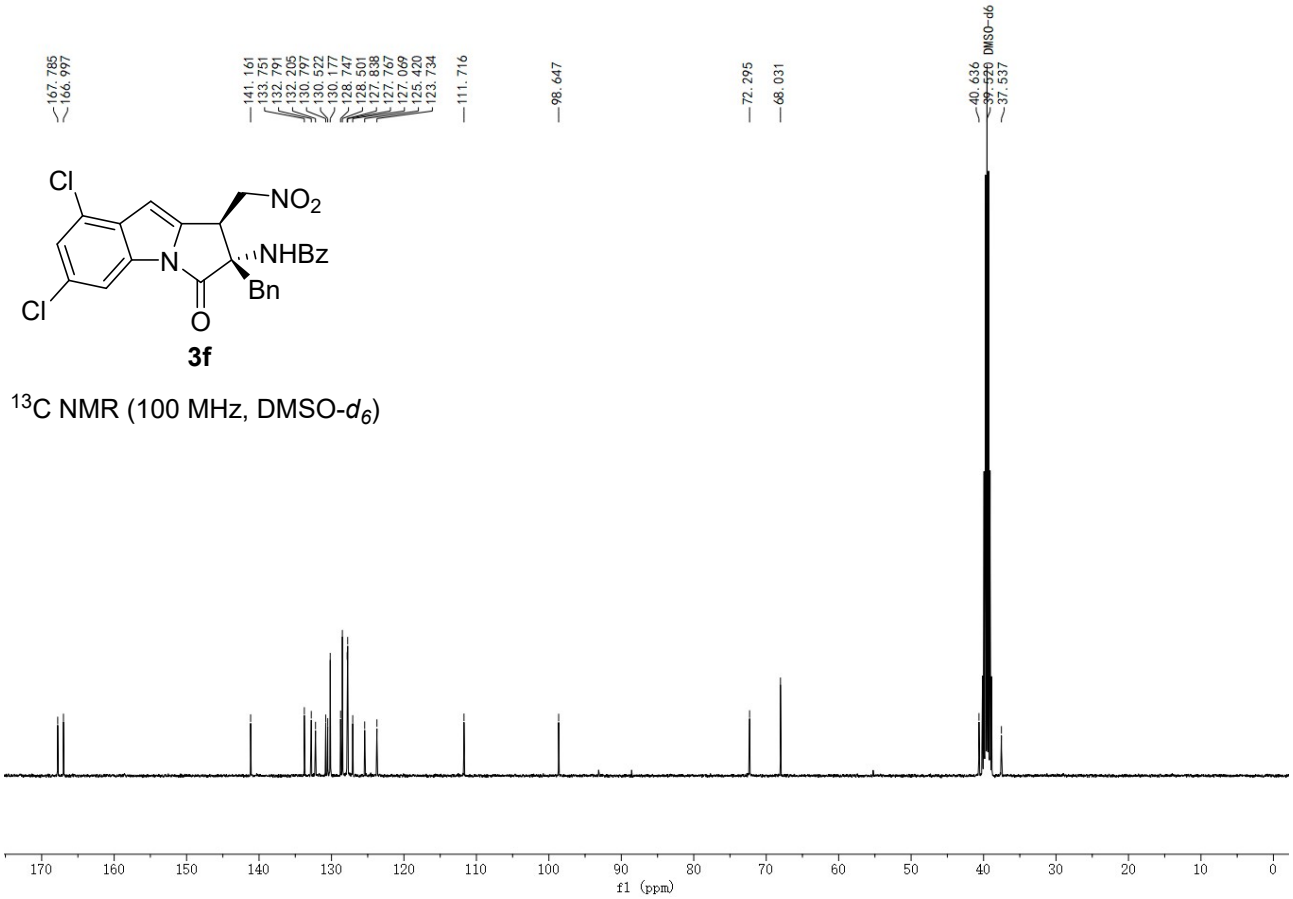
3e

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.582	18980136	864008	91.460	97.862
2	29.259	1772344	18876	8.540	2.138
Total		20752480	882884	100.000	100.000



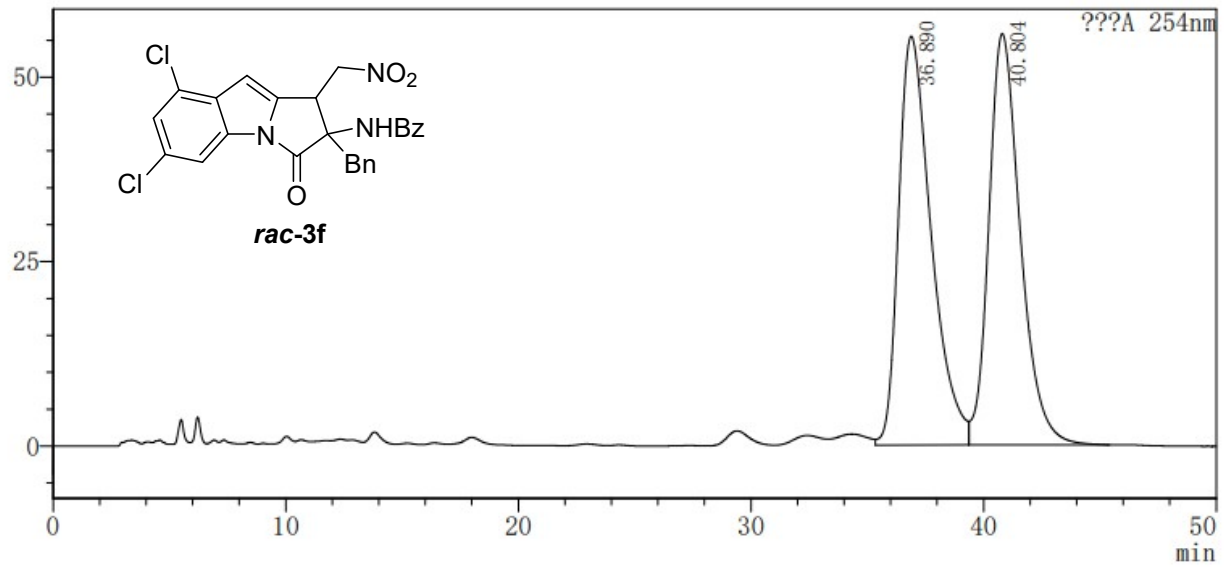
3f

^{1}H NMR (400 MHz, DMSO-d_6)



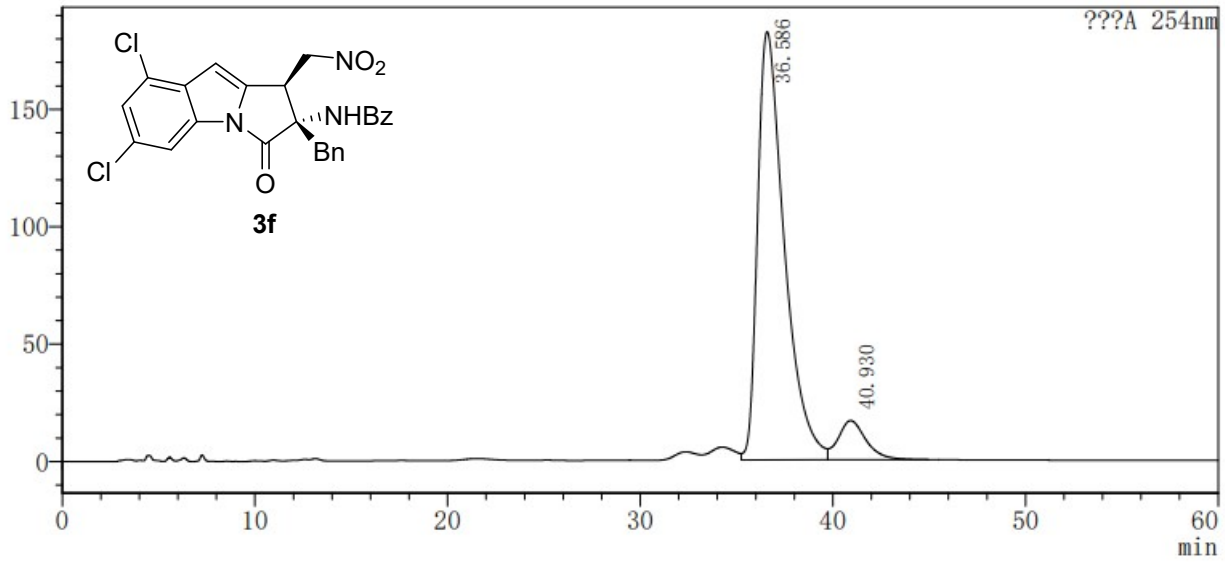
3f

^{13}C NMR (100 MHz, DMSO-d_6)



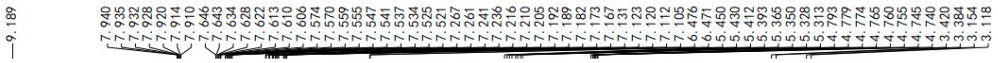
***rac*-3f**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	36.890	5405214	55397	50.744	49.854
2	40.804	5246772	55720	49.256	50.146
Total		10651987	111117	100.000	100.000



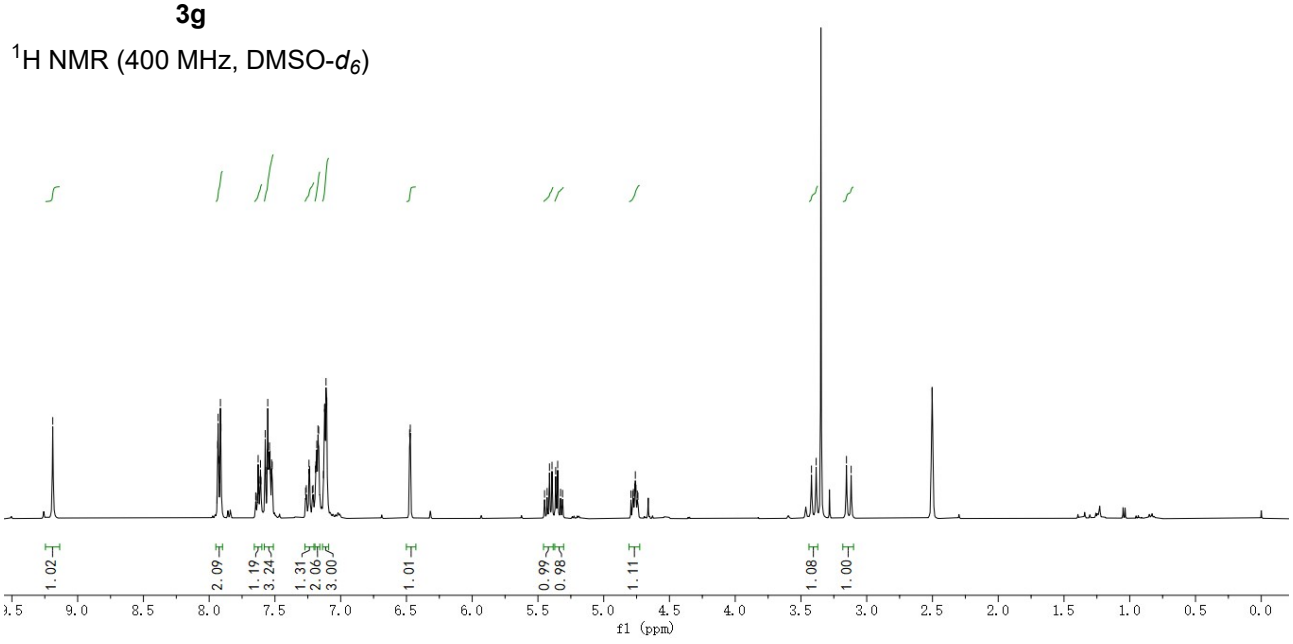
3f

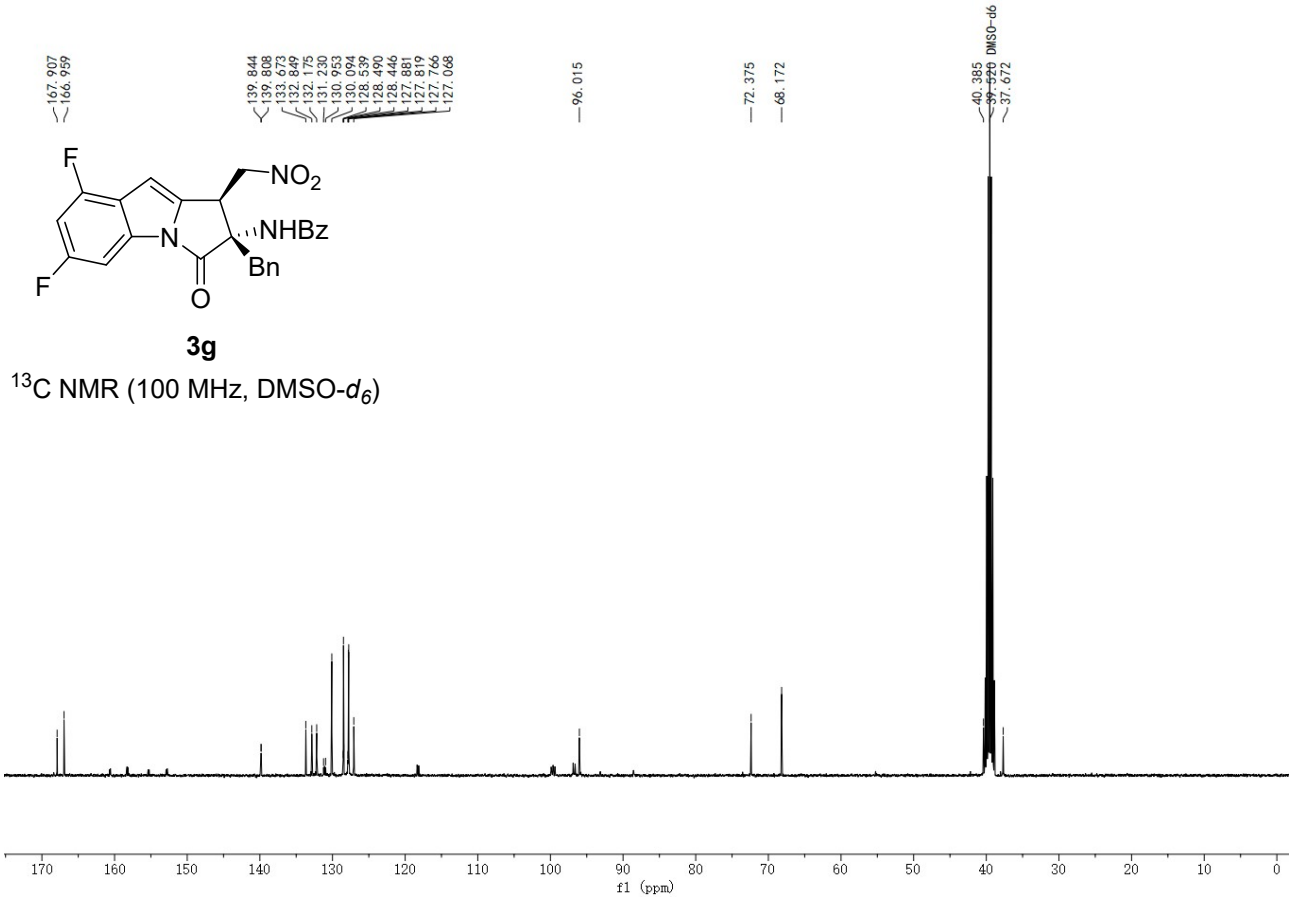
Peak#	Ret. Time	Area	Height	Area%	Height%
1	36.586	17629978	182441	91.293	91.616
2	40.930	1681371	16695	8.707	8.384
Total		19311348	199137	100.000	100.000



3g

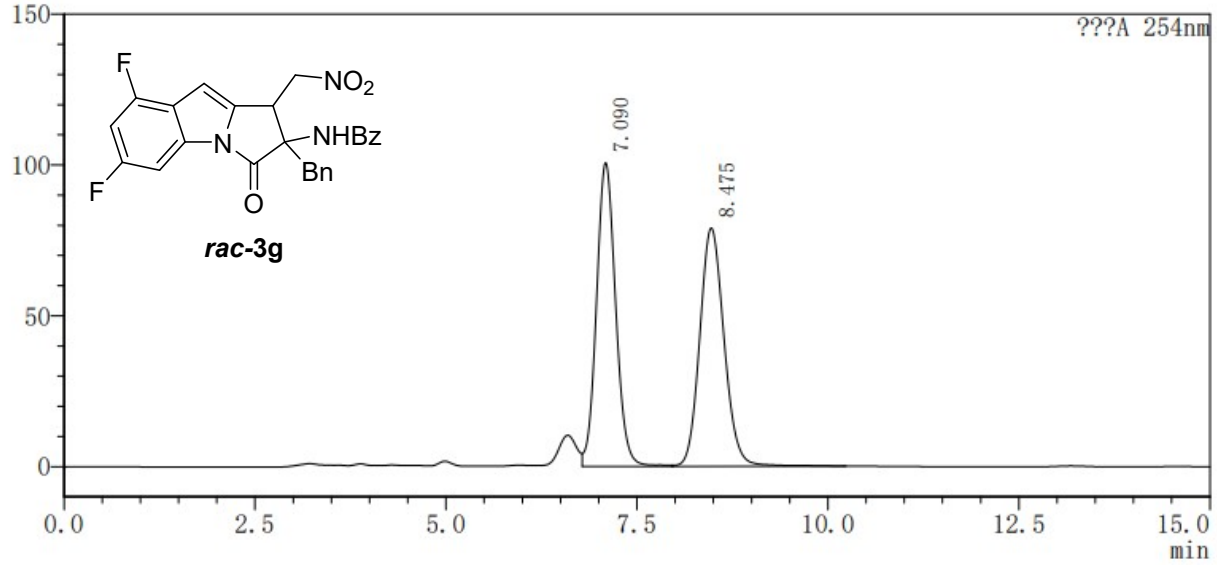
^{1}H NMR (400 MHz, DMSO-d_6)





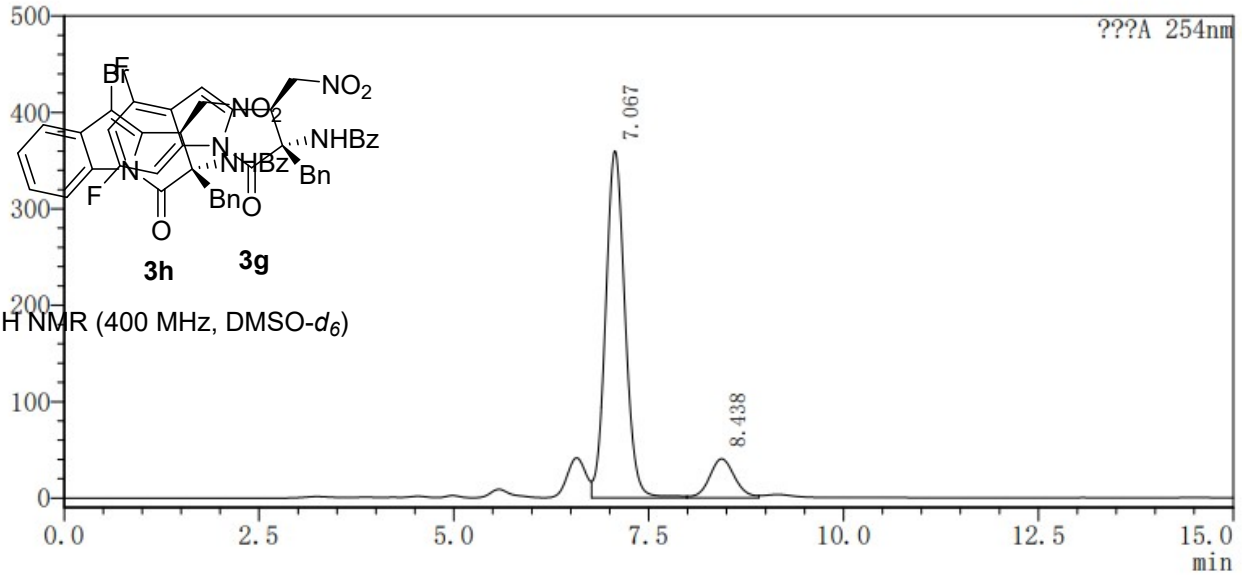
3g

^{13}C NMR (100 MHz, DMSO-d_6)



***rac*-3g**

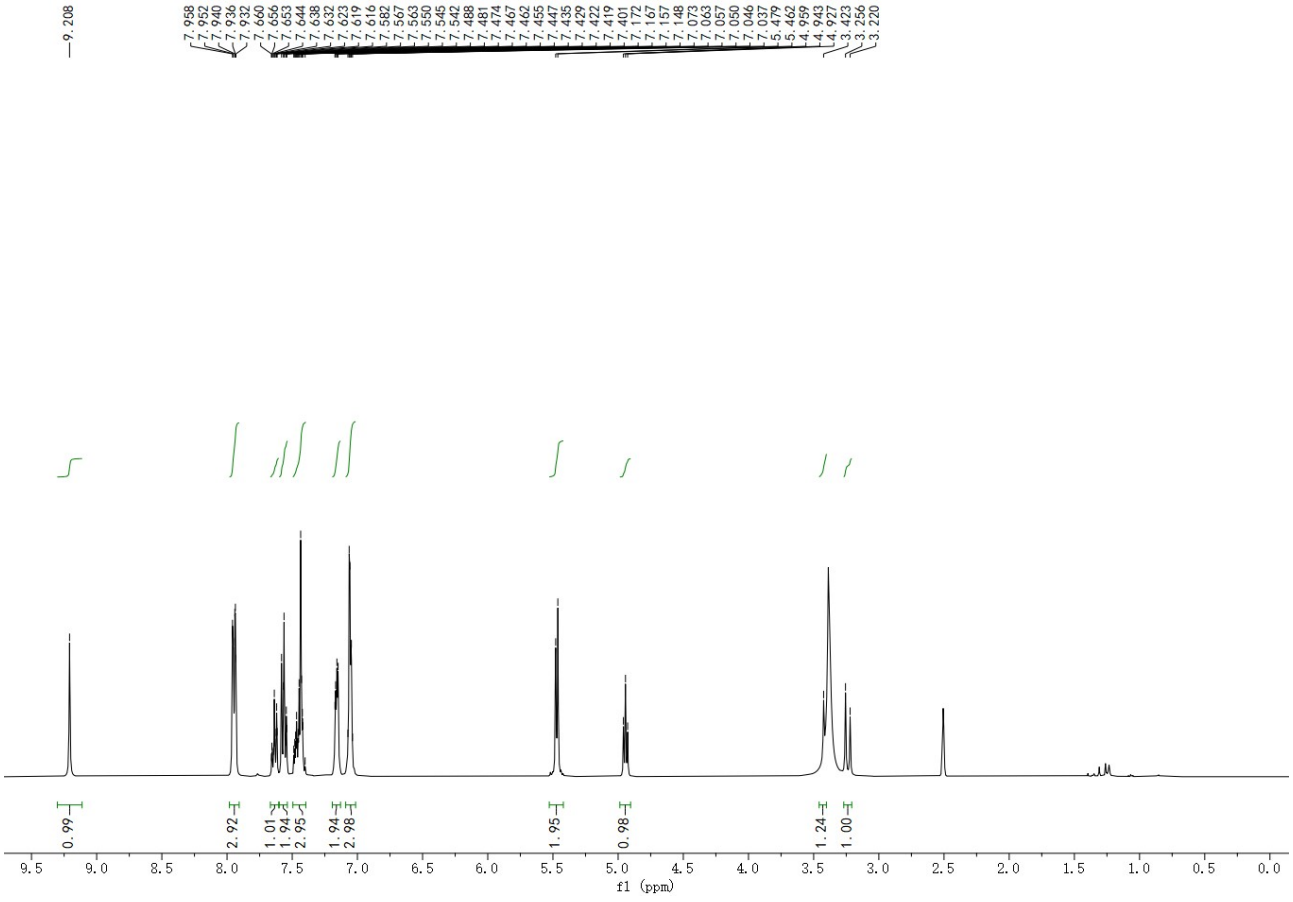
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.090	1757626	100746	50.073	56.028
2	8.475	1752505	79069	49.927	43.972
Total		3510130	179814	100.000	100.000

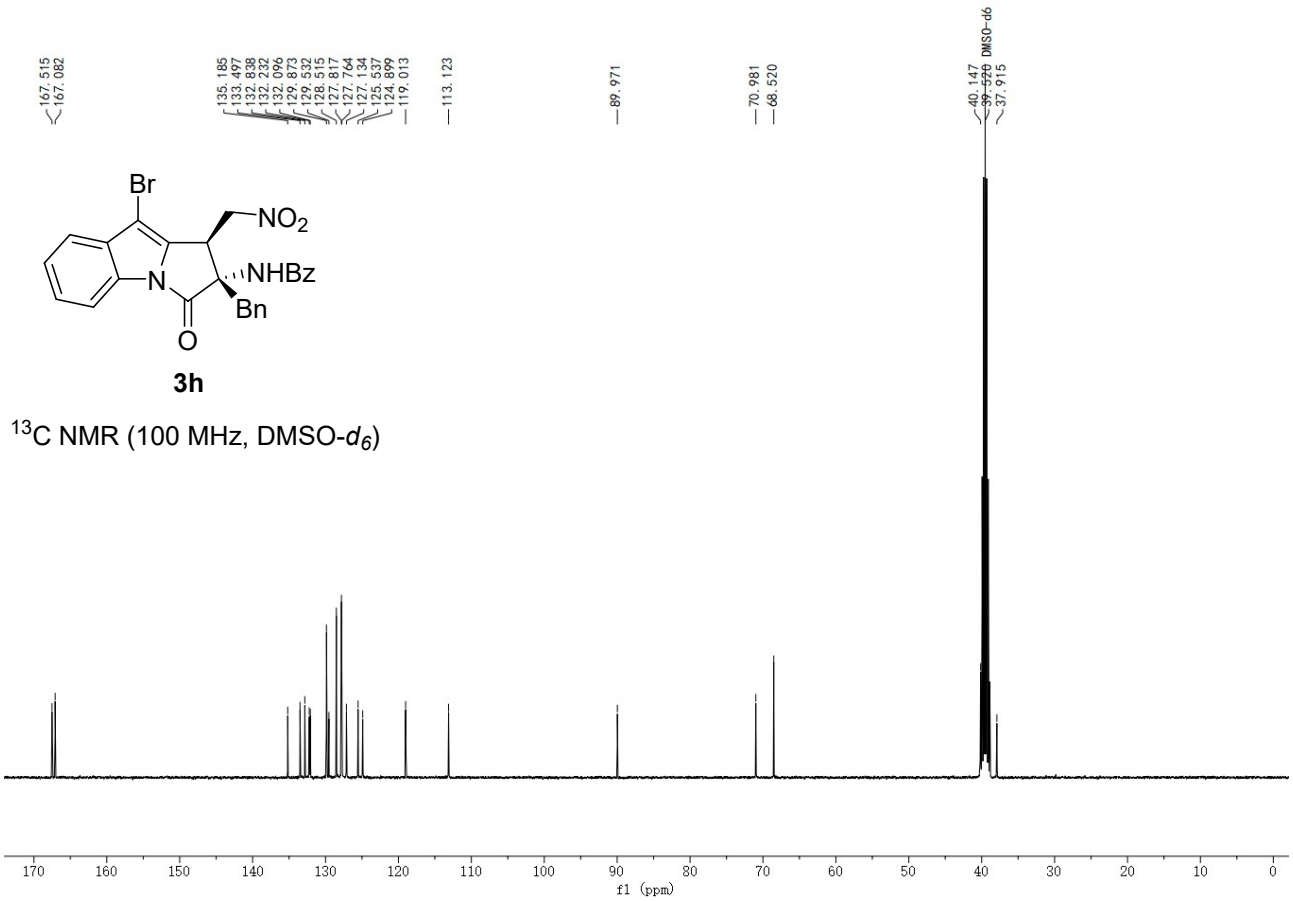


3h **3g**

^{1}H NMR (400 MHz, DMSO-d_6)

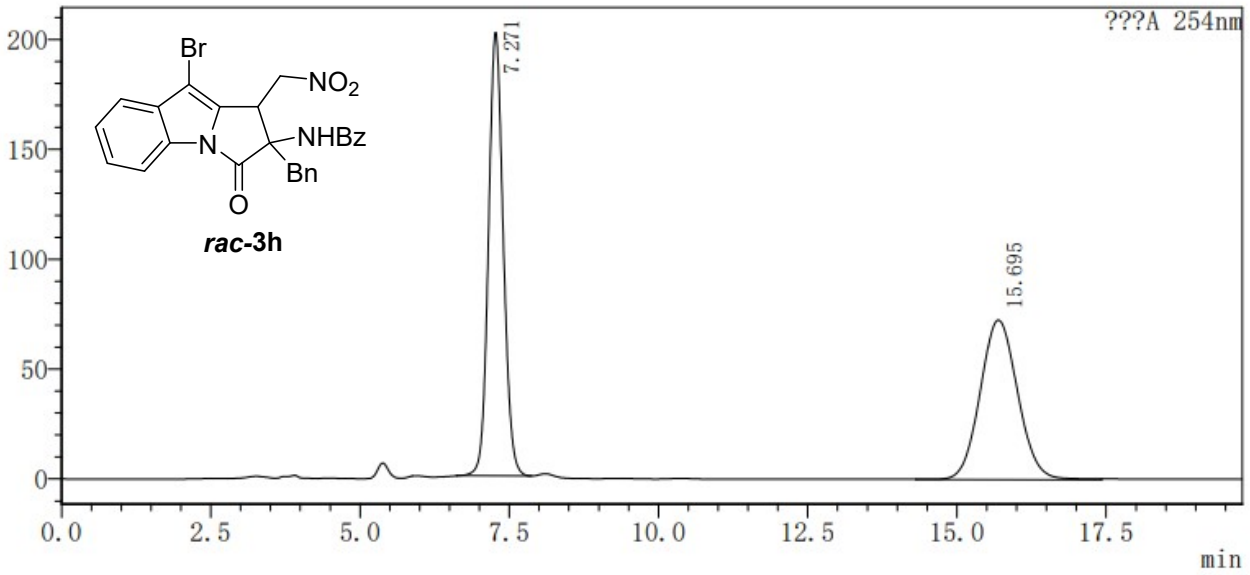
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.067	6235478	360113	87.190	89.876
2	8.438	916139	40564	12.810	10.124
Total		7151616	400677	100.000	100.000





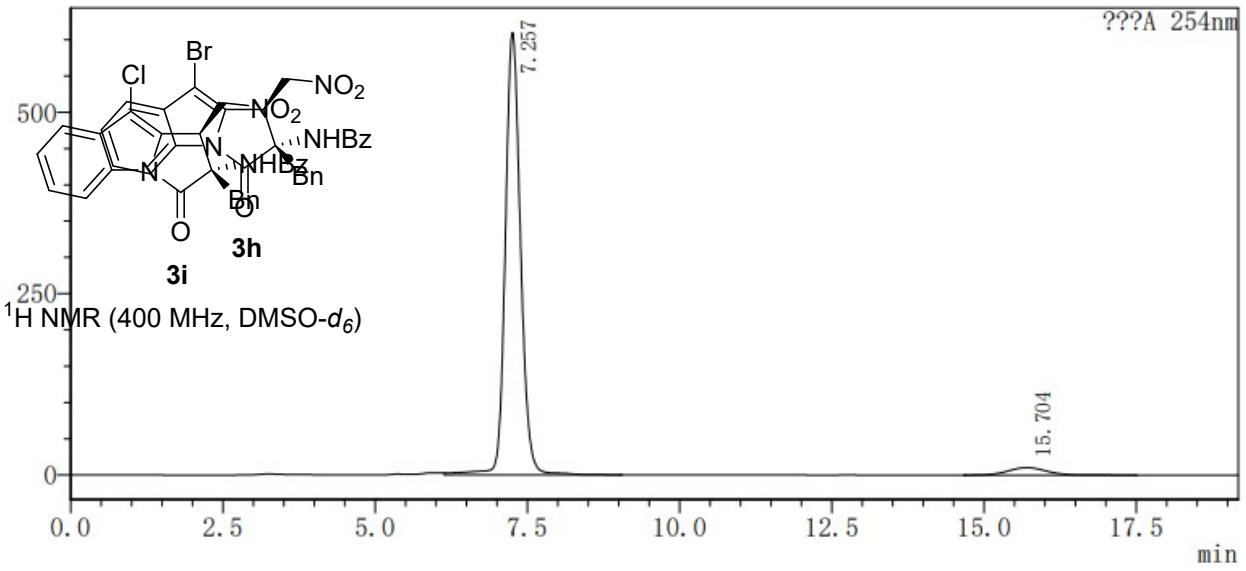
3h

^{13}C NMR (100 MHz, DMSO-d_6)



***rac*-3h**

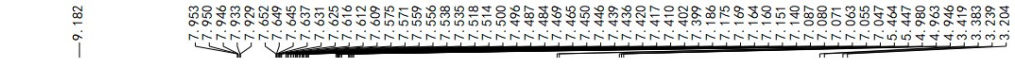
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.271	3482425	201736	52.189	73.525
2	15.695	3190284	72642	47.811	26.475
Total		6672709	274379	100.000	100.000

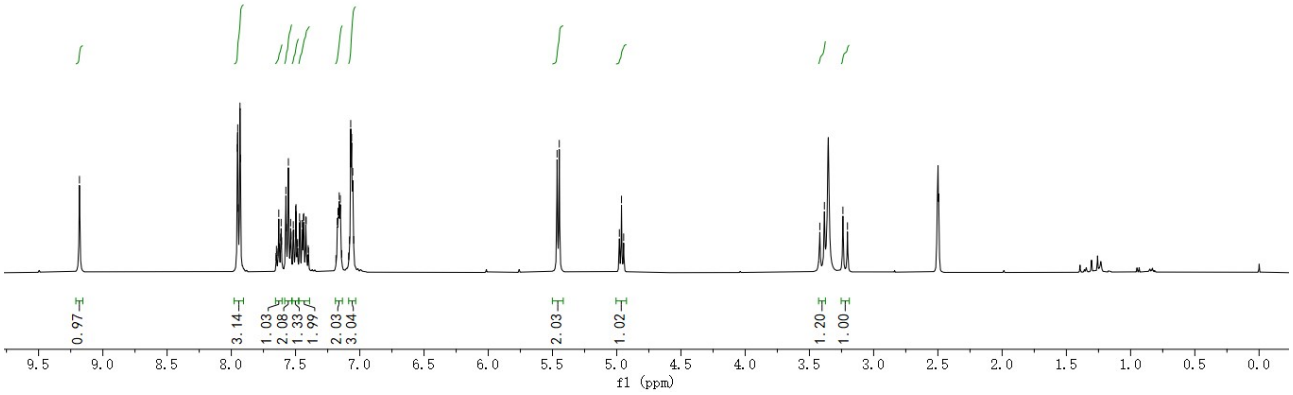


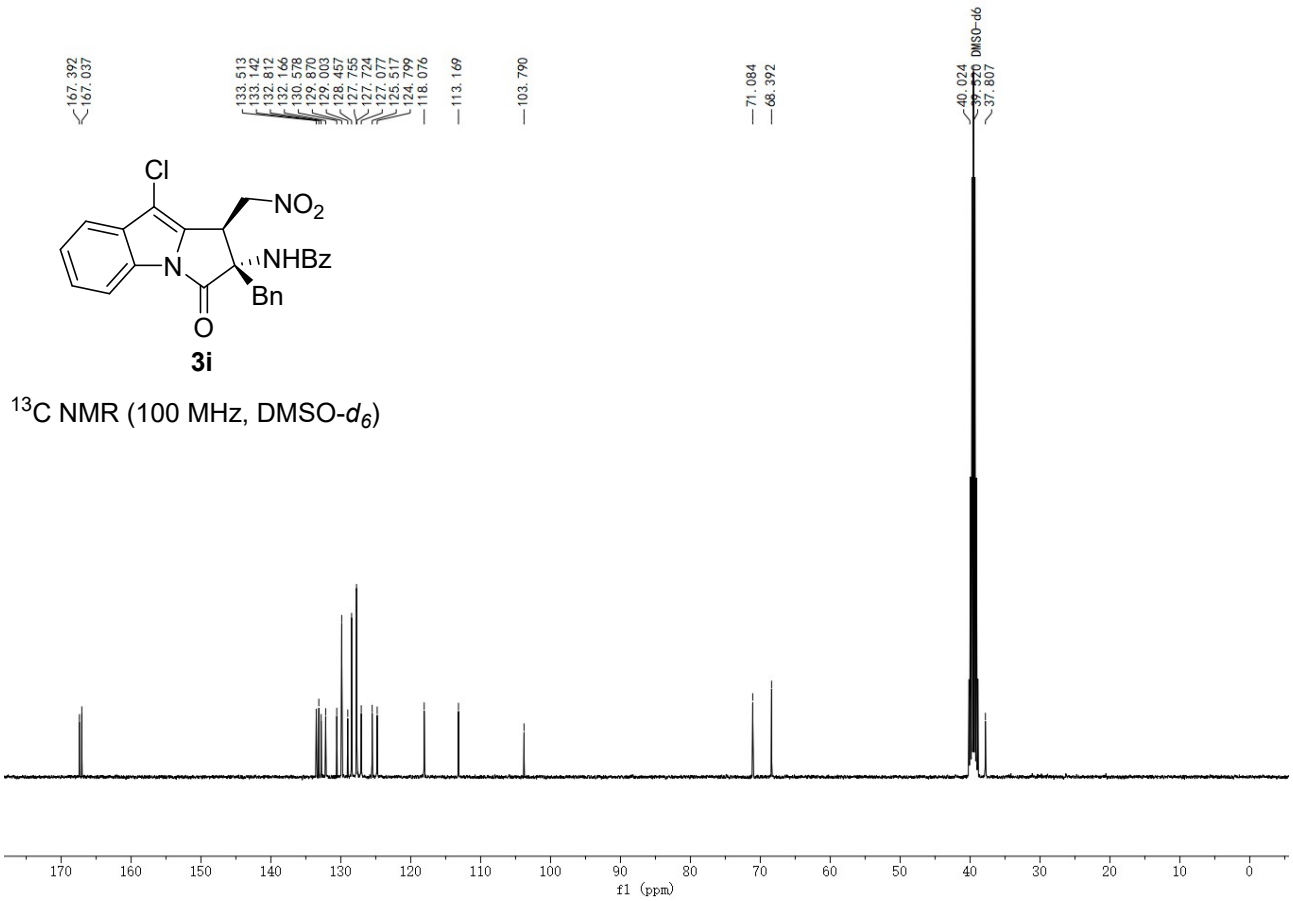
3i **3h**

^{1}H NMR (400 MHz, DMSO-d_6)

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.257	10663626	609506	95.961	98.346
2	15.704	448884	10249	4.039	1.654
Total		11112510	619755	100.000	100.000

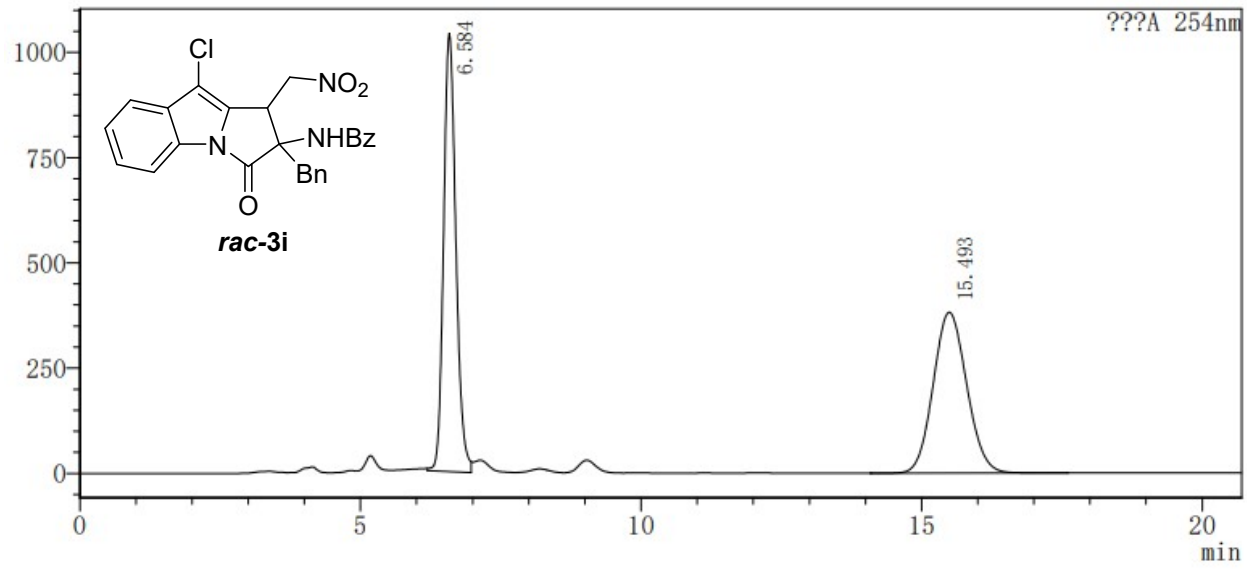






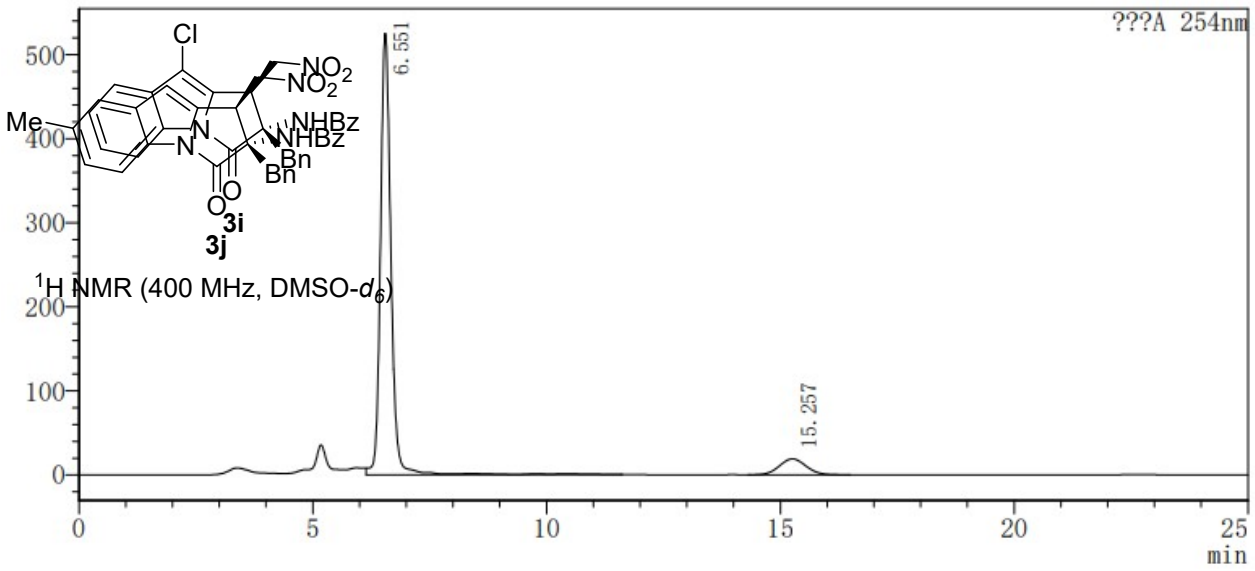
3i

^{13}C NMR (100 MHz, DMSO-d_6)



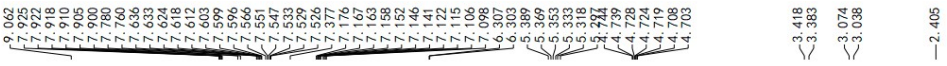
***rac*-3i**

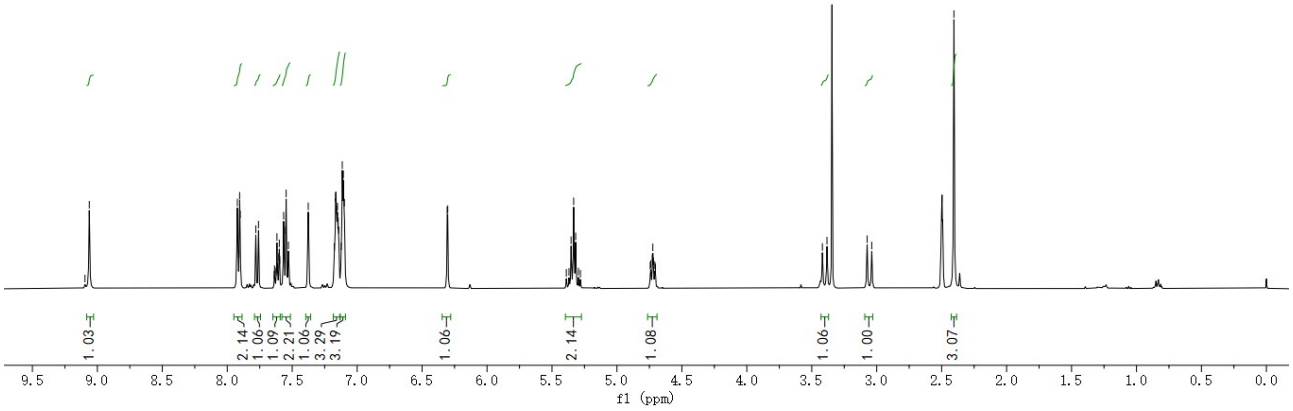
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.584	15818411	1040873	49.861	73.140
2	15.493	15906326	382258	50.139	26.860
Total		31724736	1423131	100.000	100.000

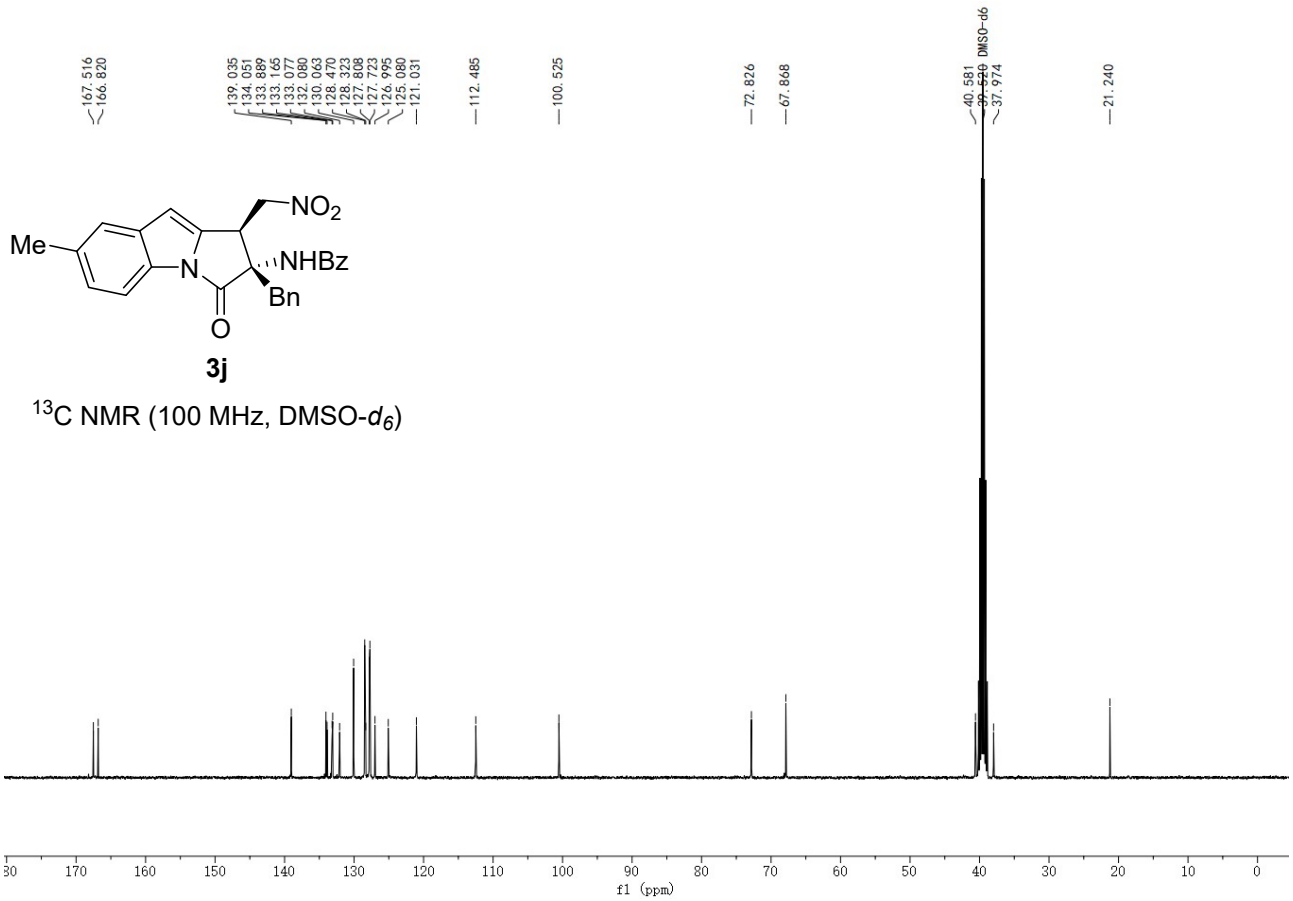


^{1}H NMR (400 MHz, DMSO-d_6)

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.551	8270088	525103	91.699	96.526
2	15.257	748628	18897	8.301	3.474
Total		9018717	544000	100.000	100.000

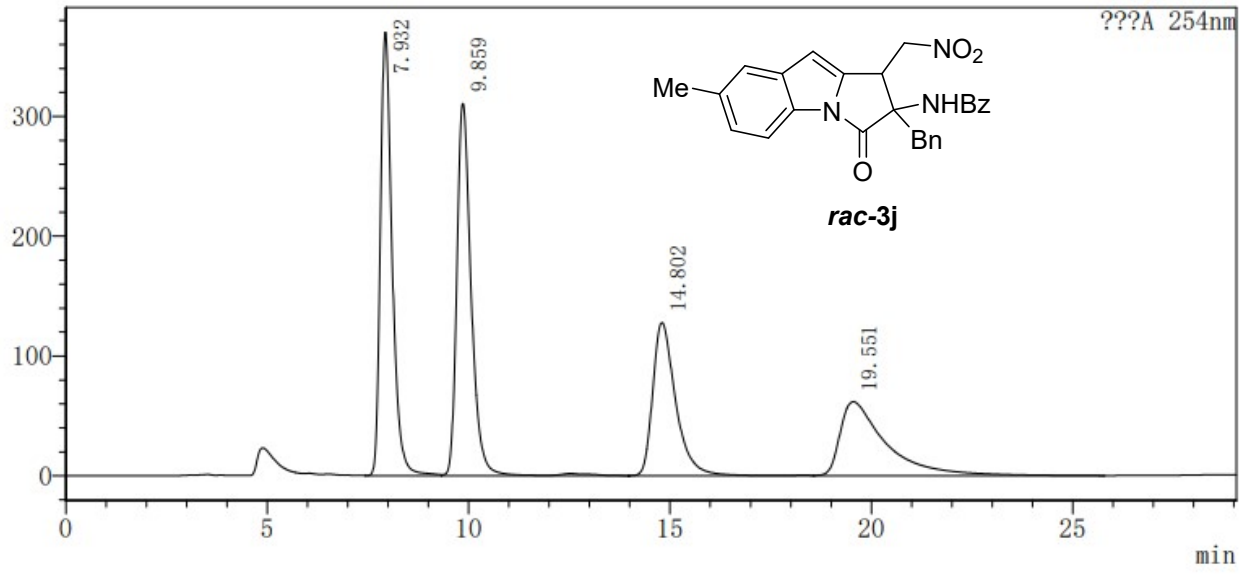






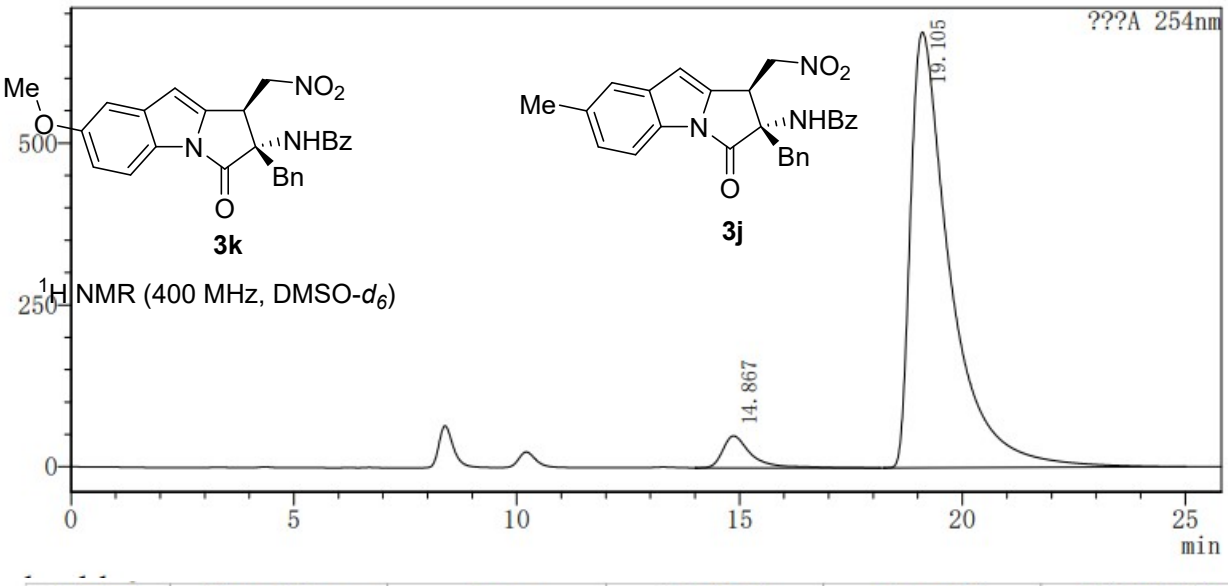
3j

^{13}C NMR (100 MHz, DMSO-d_6)



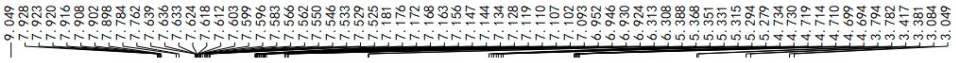
***rac*-3j**

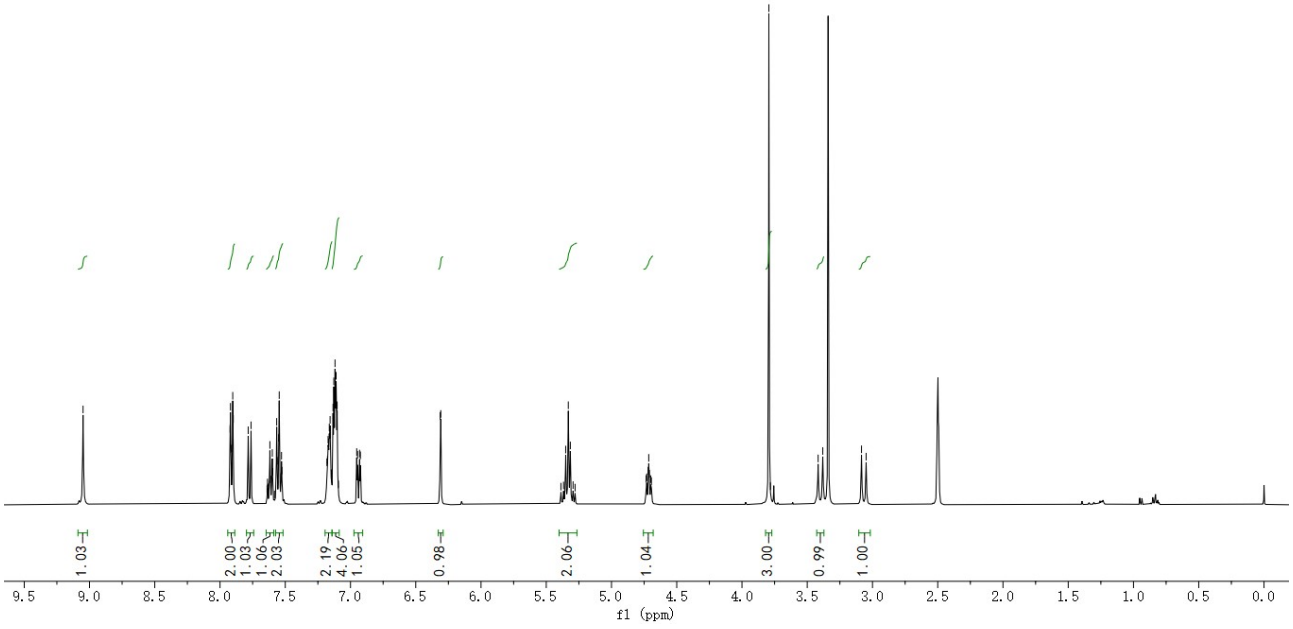
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.932	7541182	370201	29.884	42.528
2	9.859	7727972	310760	30.624	35.700
3	14.802	5071759	127784	20.098	14.680
4	19.551	4893791	61737	19.393	7.092
Total		25234703	870482	100.000	100.000

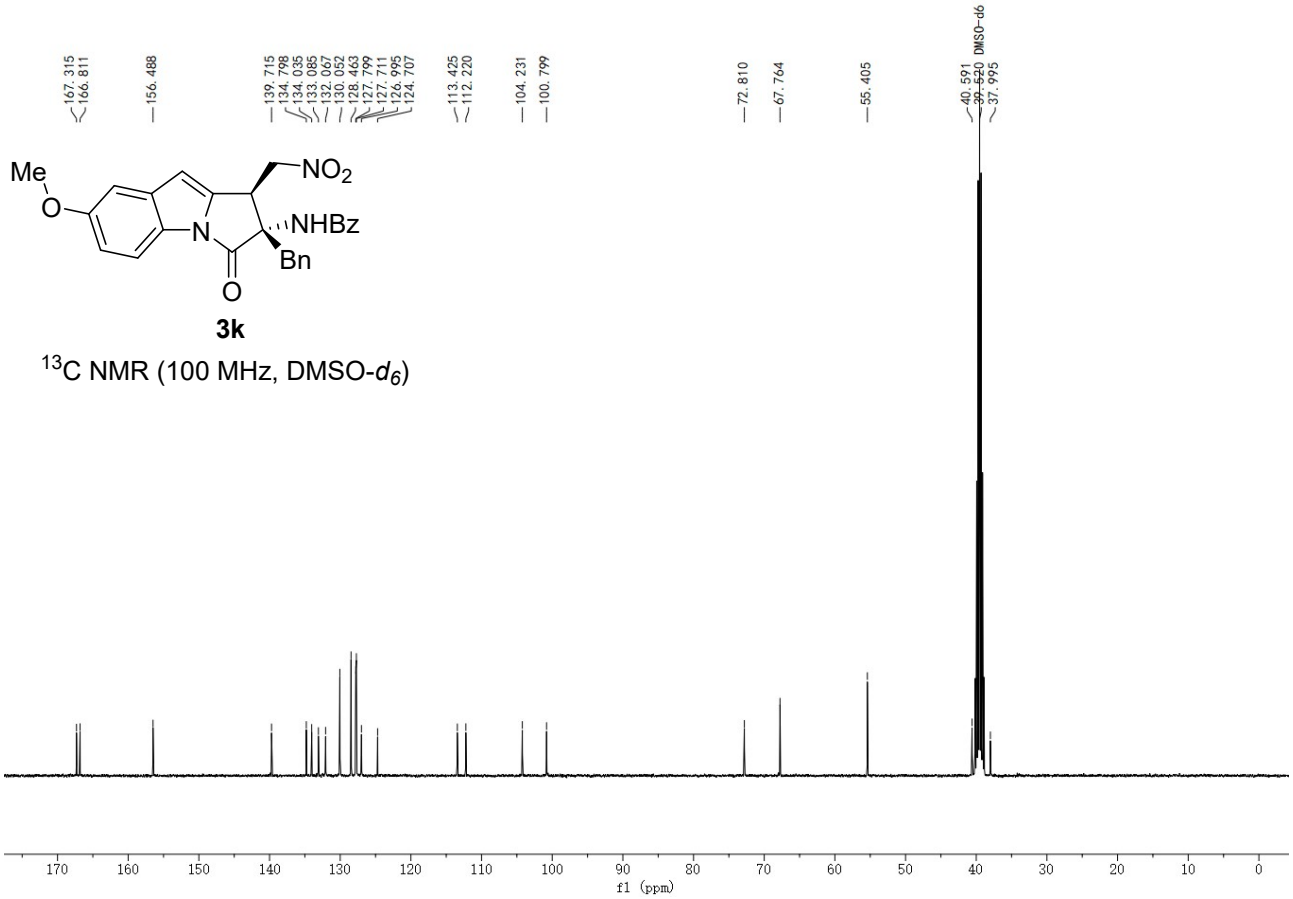


^{1}H NMR (400 MHz, DMSO-d_6)

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.867	2188817	49373	5.002	6.836
2	19.105	41569543	672841	94.998	93.164
Total		43758359	722215	100.000	100.000

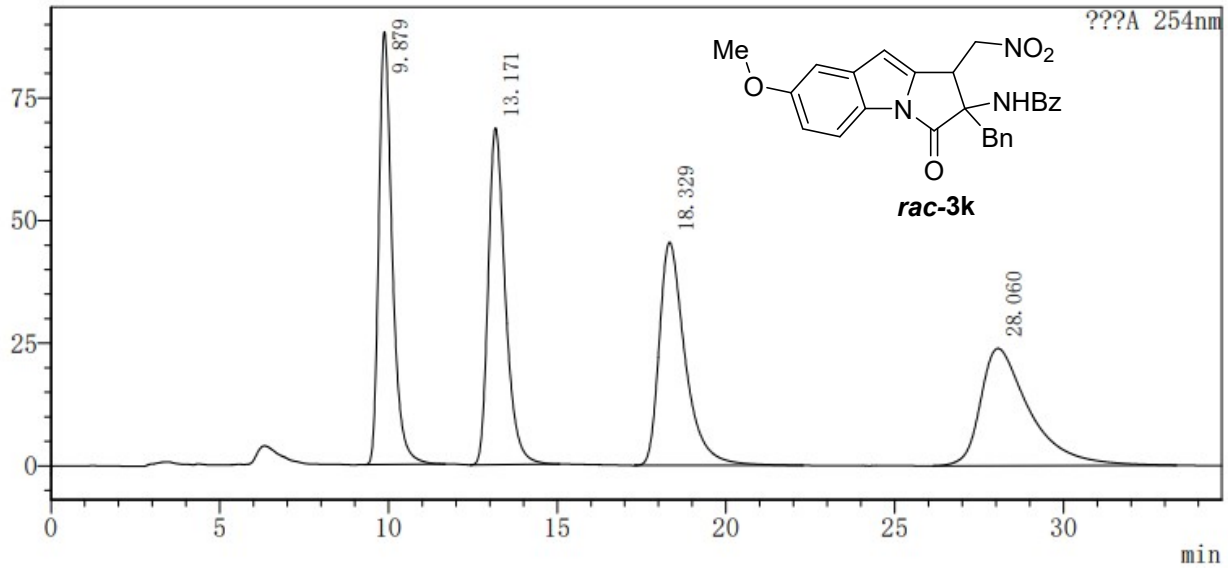






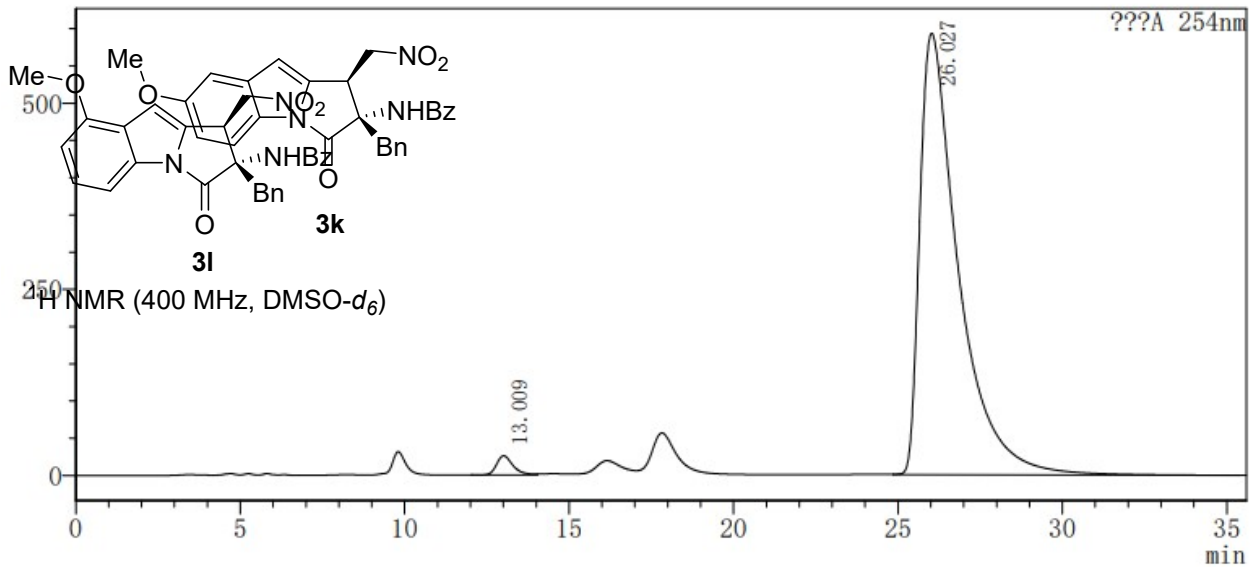
3k

^{13}C NMR (100 MHz, DMSO-d_6)



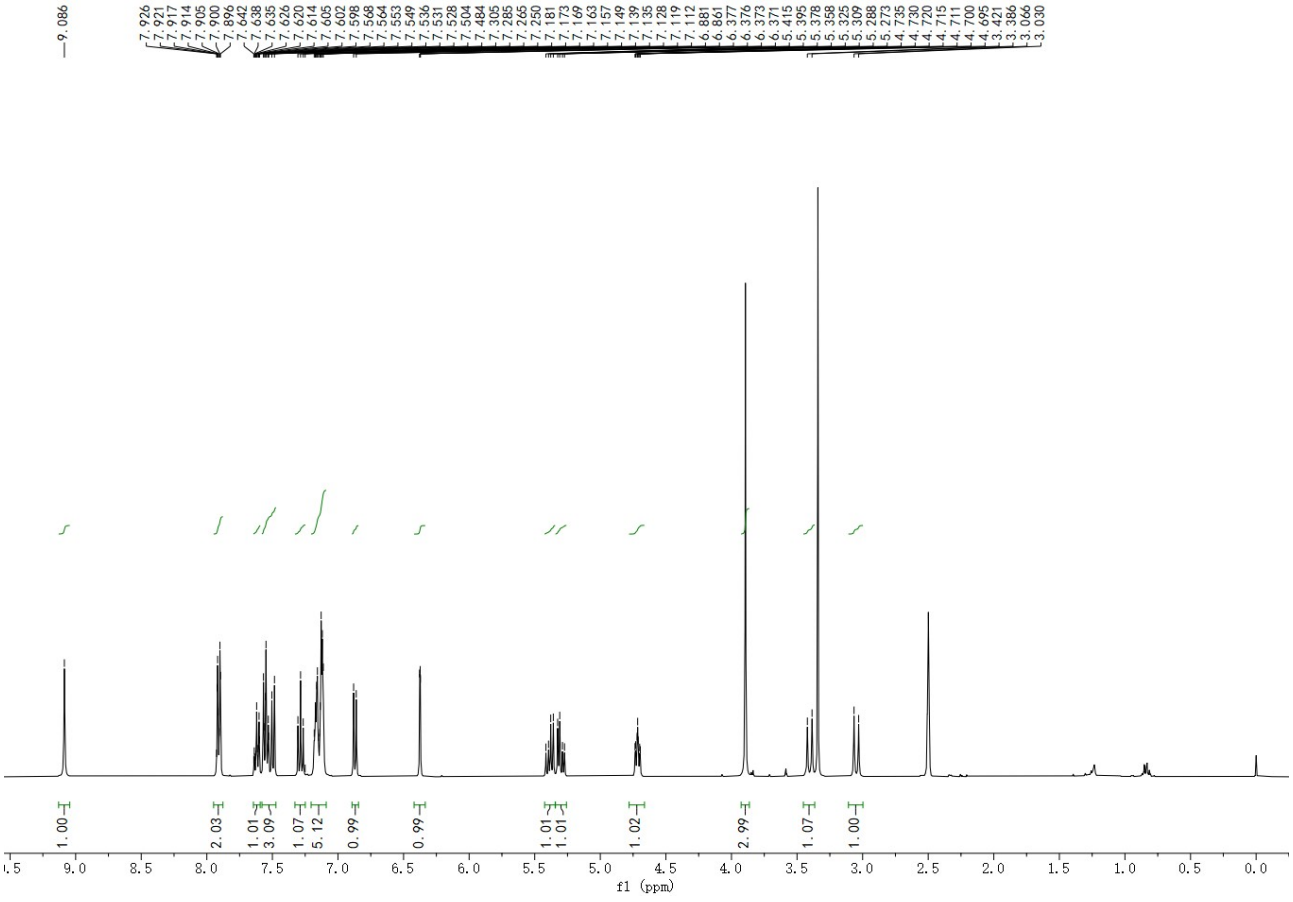
***rac*-3k**

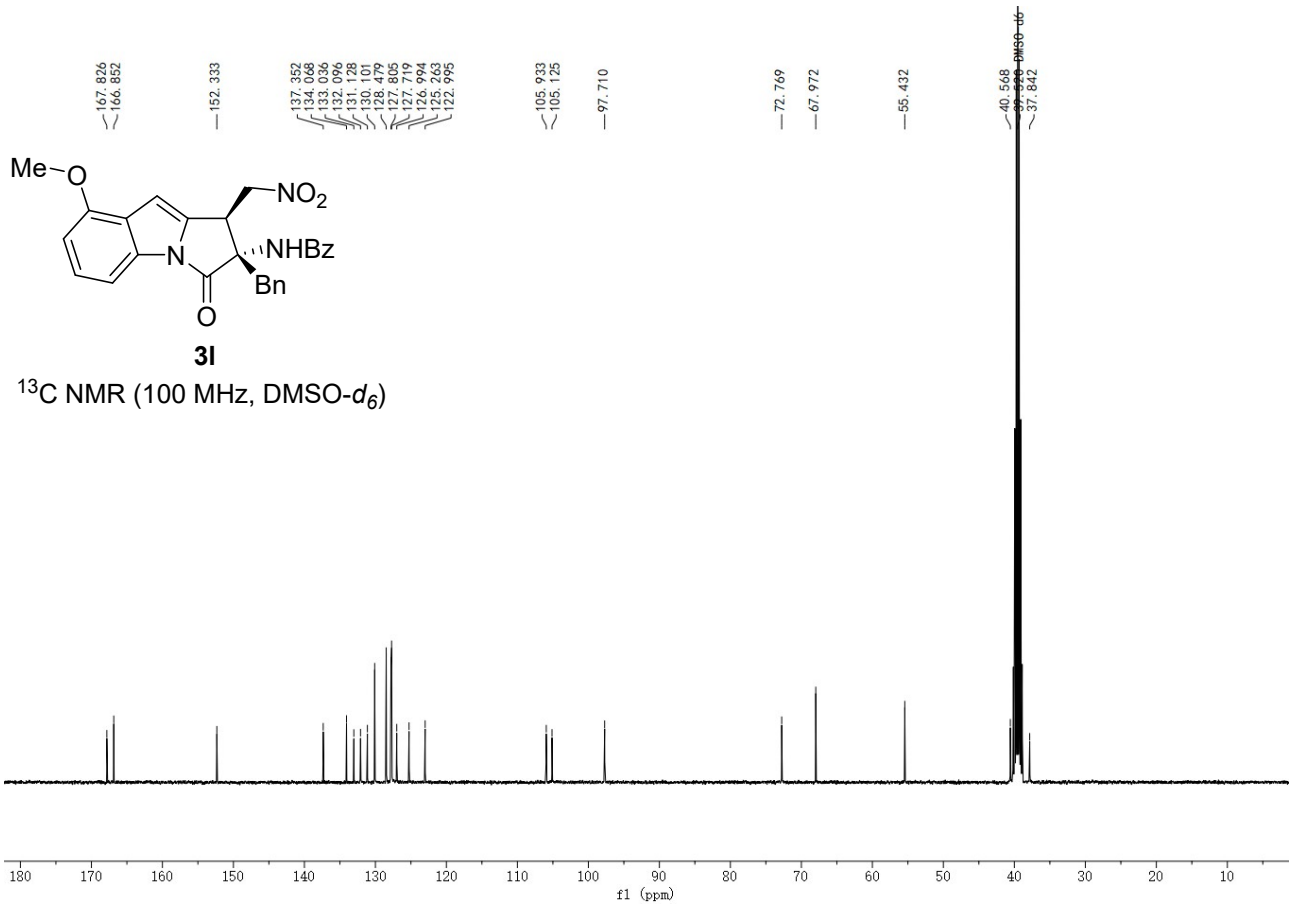
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.879	2437509	88205	25.101	38.982
2	13.171	2421916	68651	24.941	30.340
3	18.329	2433534	45505	25.061	20.111
4	28.060	2417673	23909	24.897	10.566
Total		9710632	226269	100.000	100.000



^{1}H NMR (400 MHz, DMSO-d_6)

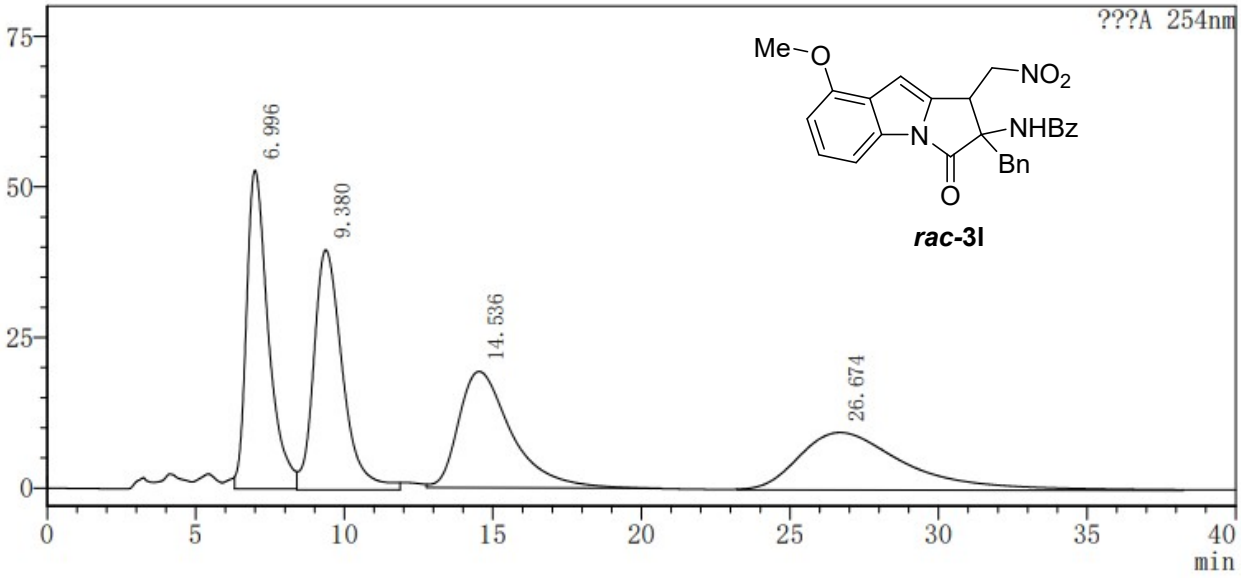
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.009	912080	25906	1.845	4.187
2	26.027	48516223	592810	98.155	95.813
Total		49428303	618717	100.000	100.000





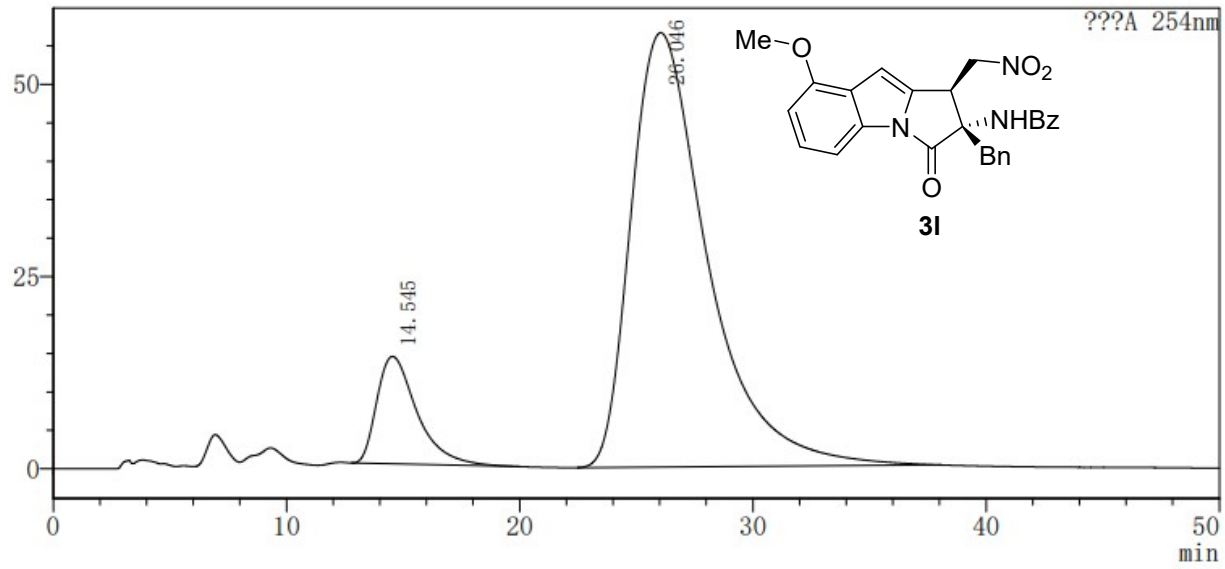
3l

^{13}C NMR (100 MHz, DMSO-d_6)

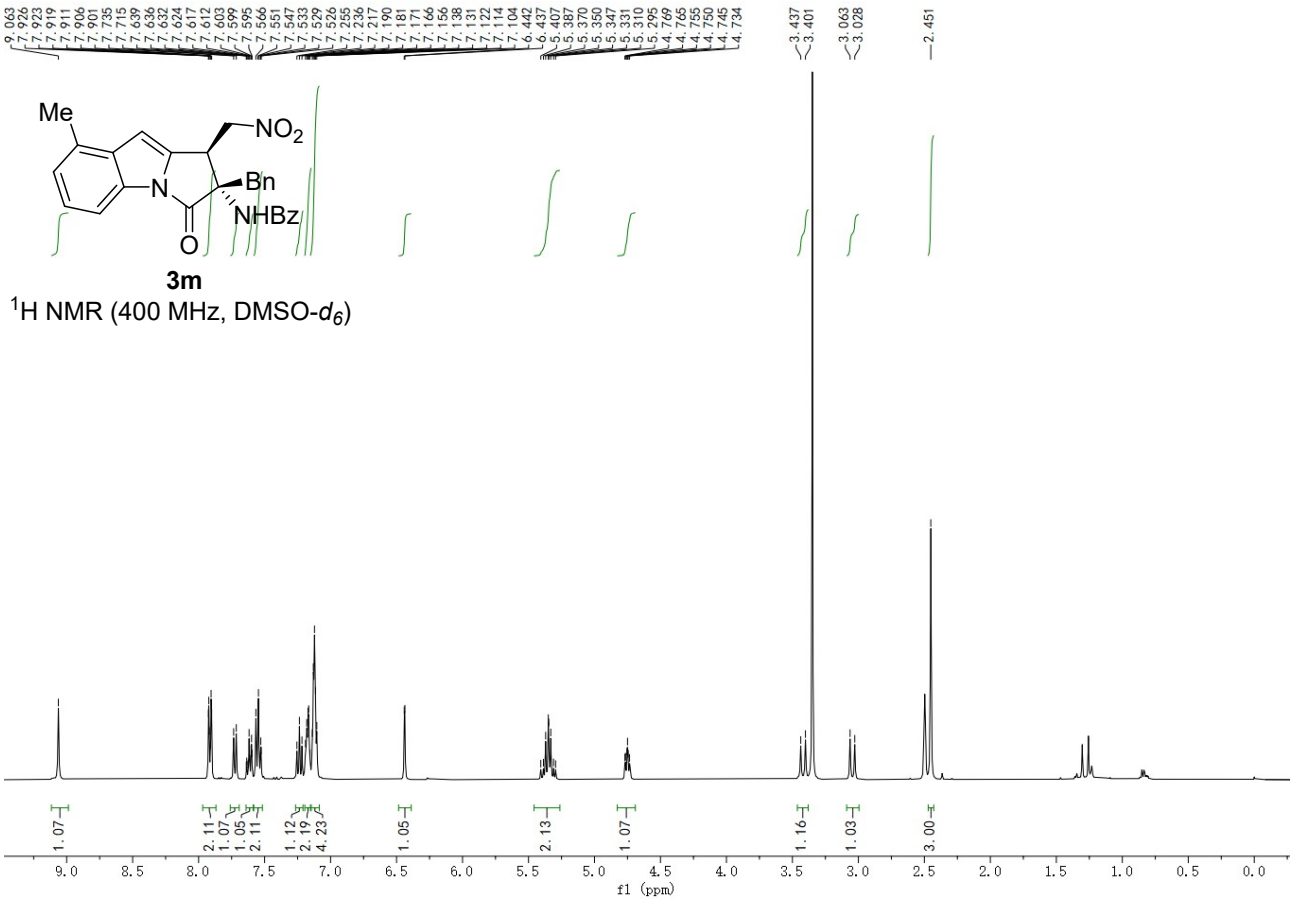


***rac*-3l**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.996	2700511	52920	26.652	43.545
2	9.380	2680103	39811	26.451	32.758
3	14.536	2373661	19281	23.426	15.865
4	26.674	2378161	9517	23.471	7.831
Total		10132435	121528	100.000	100.000

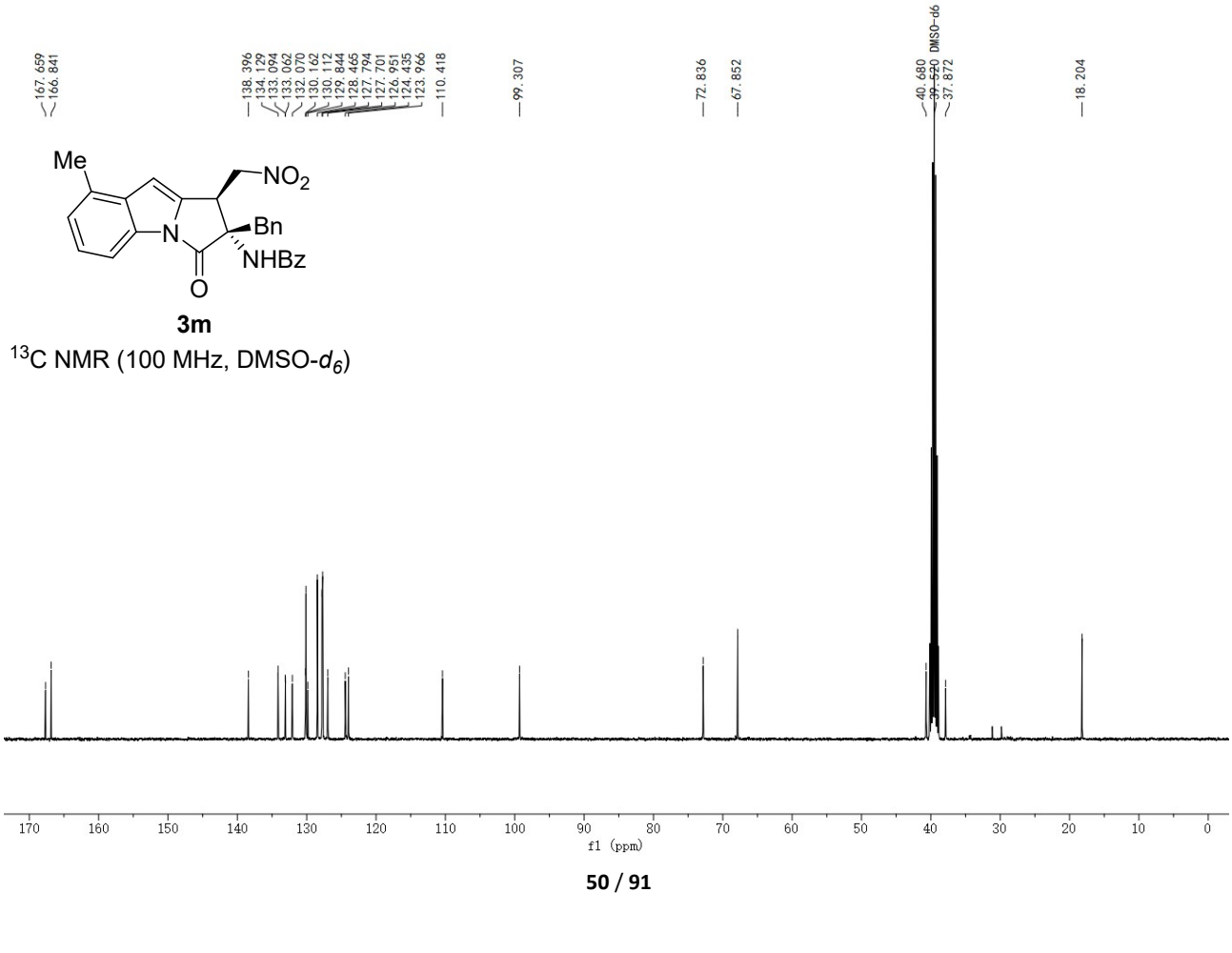


Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.545	1675133	13968	11.488	19.827
2	26.046	12906780	56481	88.512	80.173
Total		14581913	70449	100.000	100.000



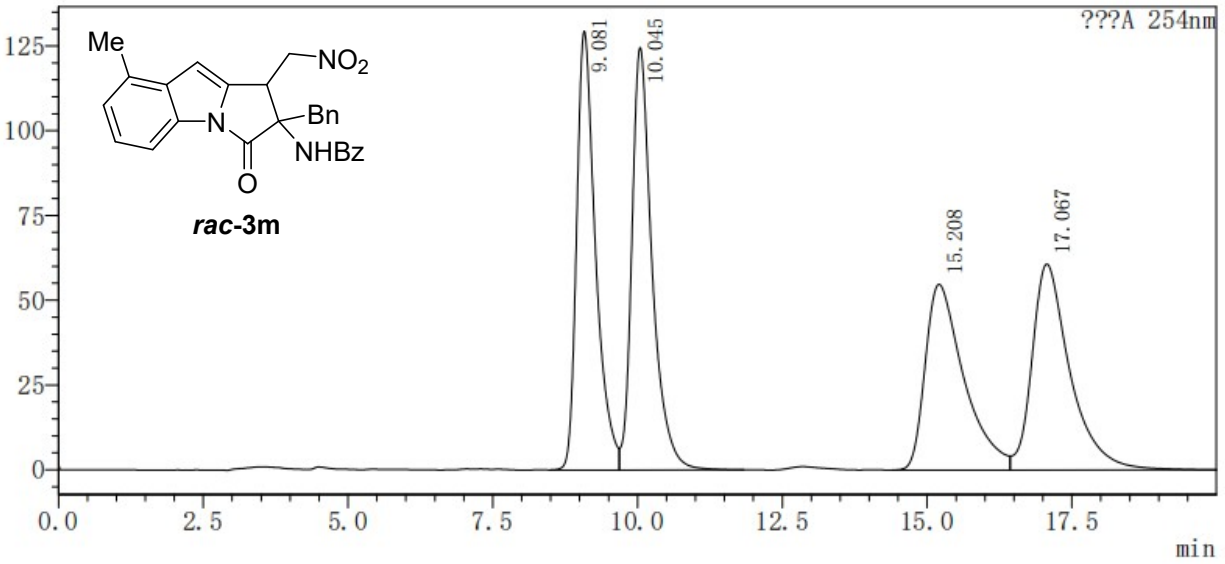
3m

^{1}H NMR (400 MHz, DMSO-d_6)

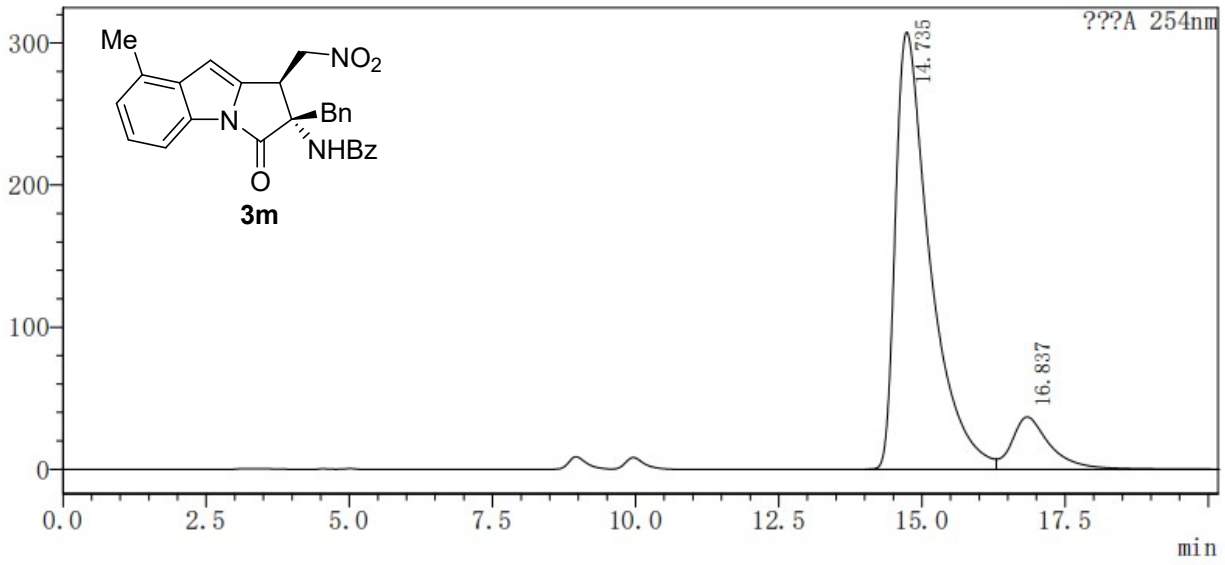


3m

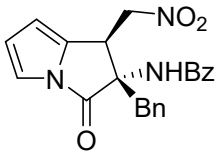
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.081	2937392	129402	26.001	35.021
2	10.045	3041186	124594	26.920	33.720
3	15.208	2544878	54755	22.527	14.819
4	17.067	2773711	60748	24.552	16.441
Total		11297167	369499	100.000	100.000

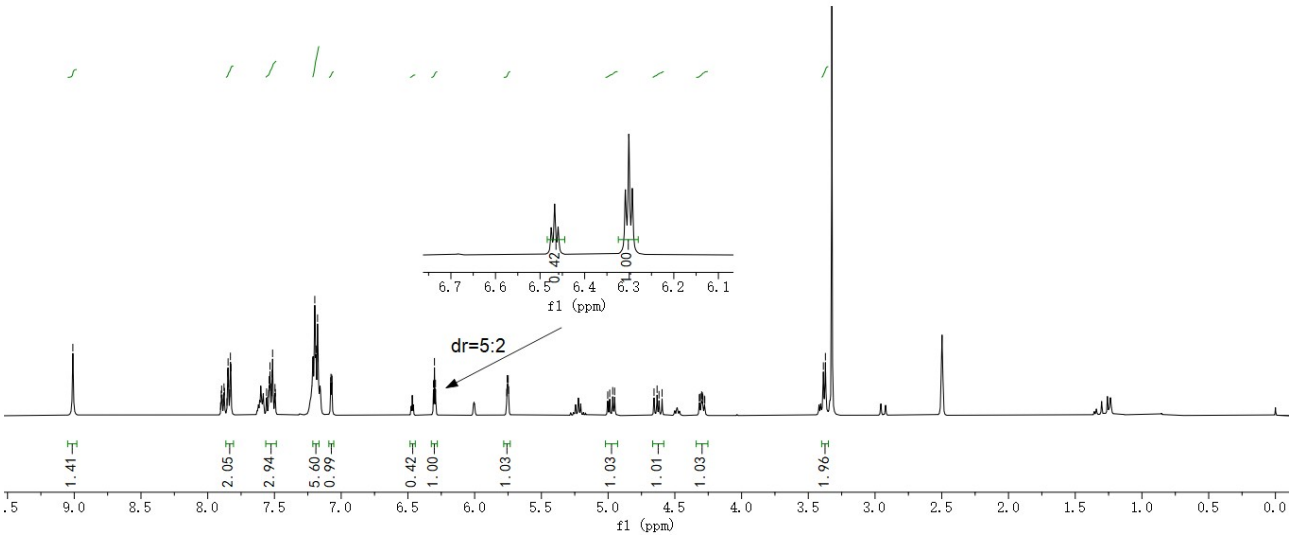


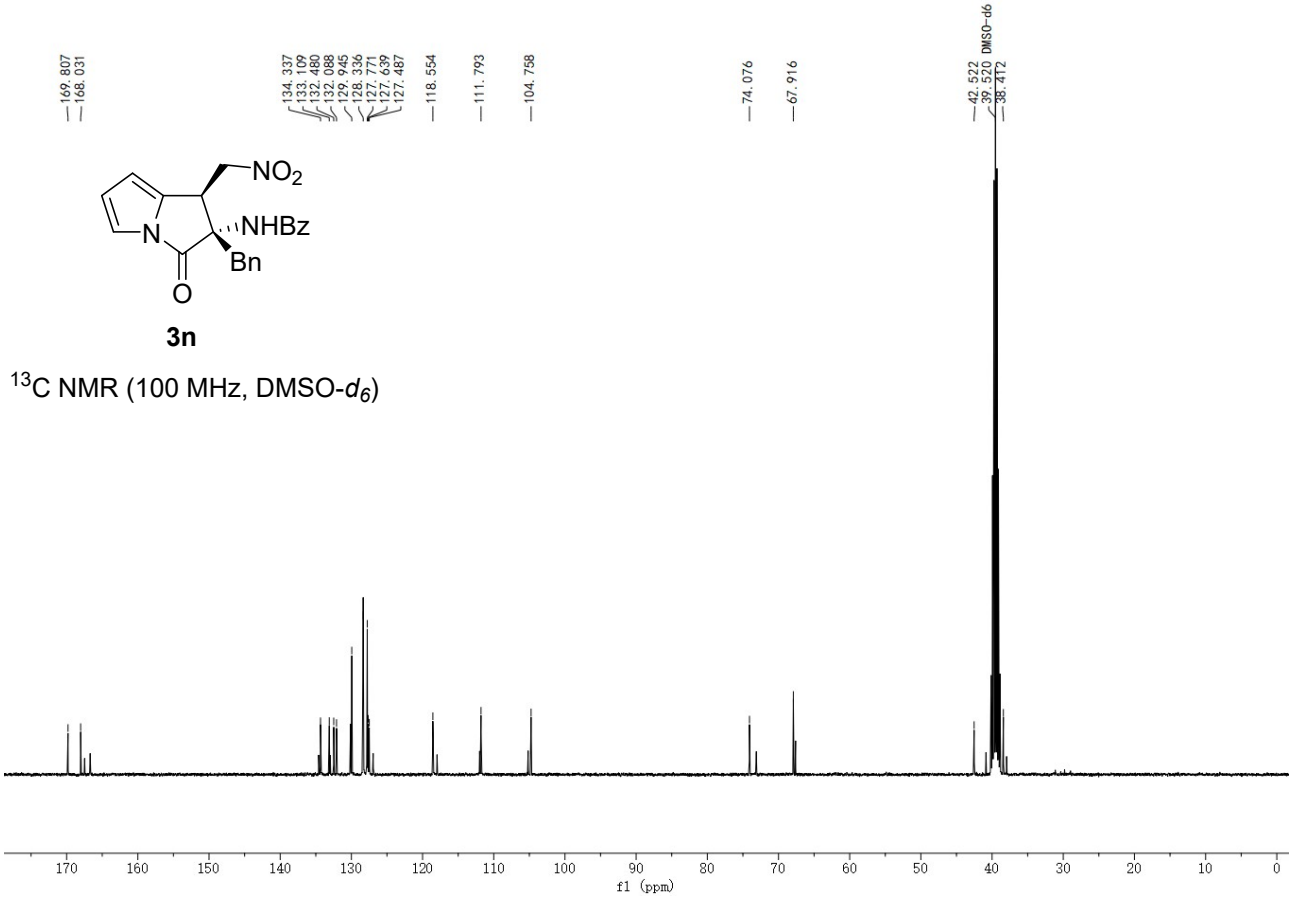
Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.735	12928410	307740	88.254	89.313
2	16.837	1720734	36822	11.746	10.687
Total		14649143	344562	100.000	100.000



3n

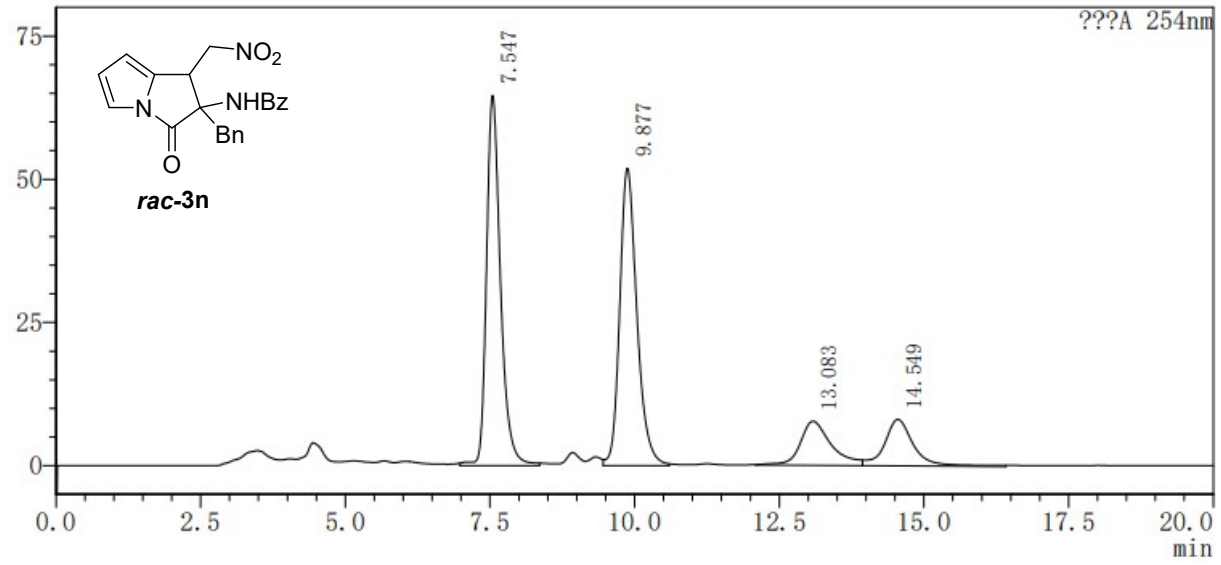
^{1}H NMR (400 MHz, DMSO-d_6)



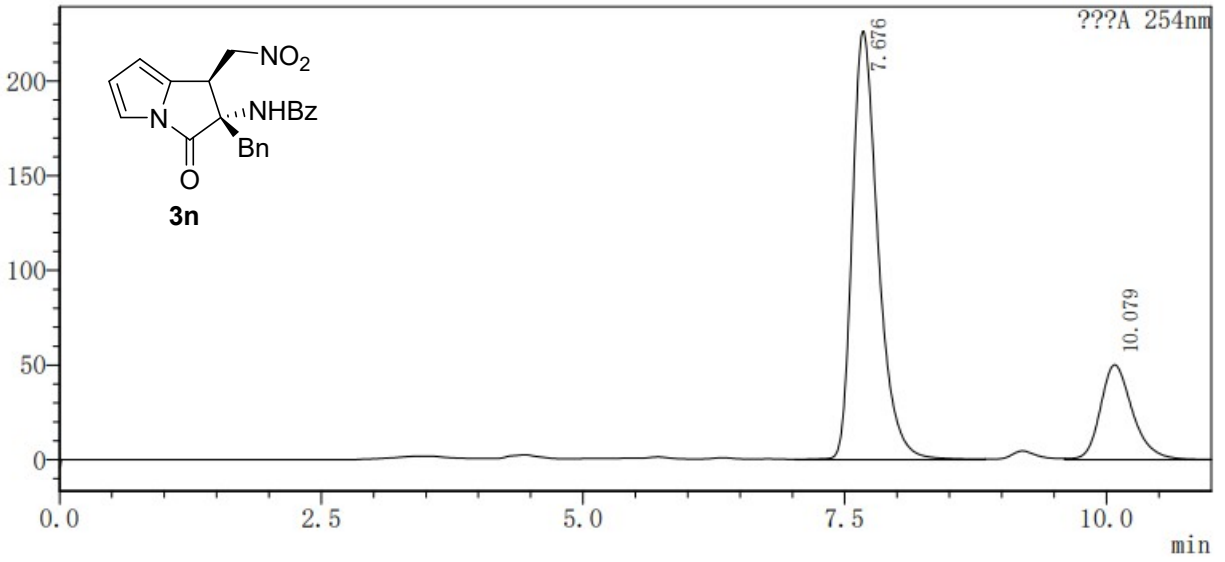


3n

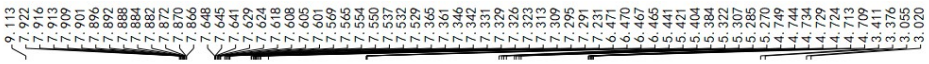
^{13}C NMR (100 MHz, DMSO-d_6)

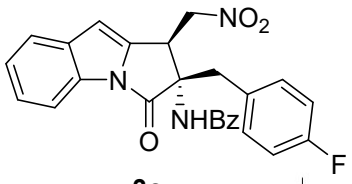


Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.547	1088138	64625	39.969	48.831
2	9.877	1064666	51916	39.107	39.228
3	13.083	286680	7700	10.530	5.819
4	14.549	282966	8102	10.394	6.122
Total		2722451	132344	100.000	100.000



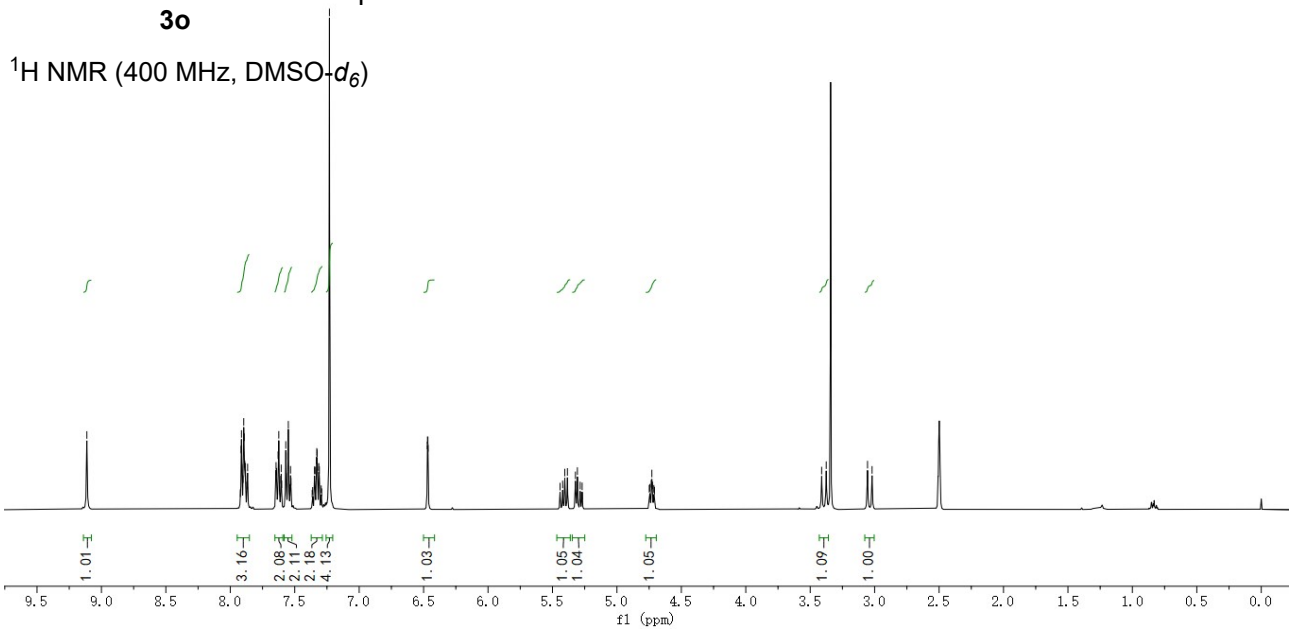
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.676	3888855	226385	78.335	81.887
2	10.079	1075515	50075	21.665	18.113
Total		4964371	276460	100.000	100.000

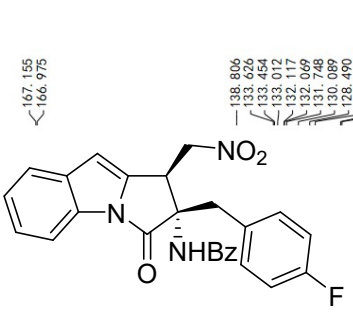




3o

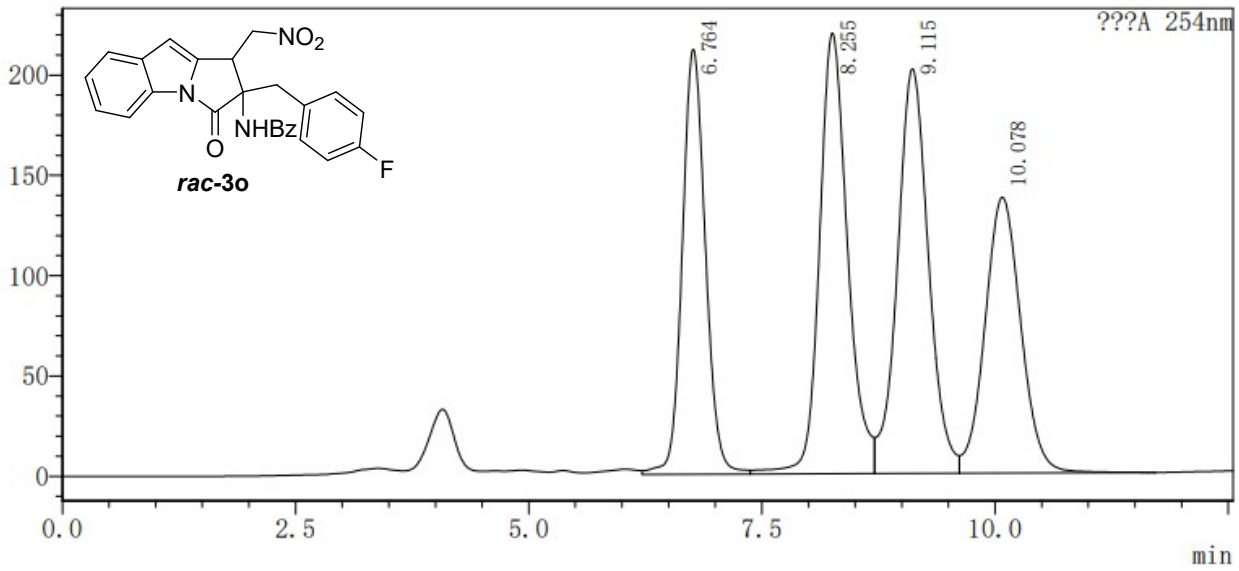
^{1}H NMR (400 MHz, DMSO-d_6)



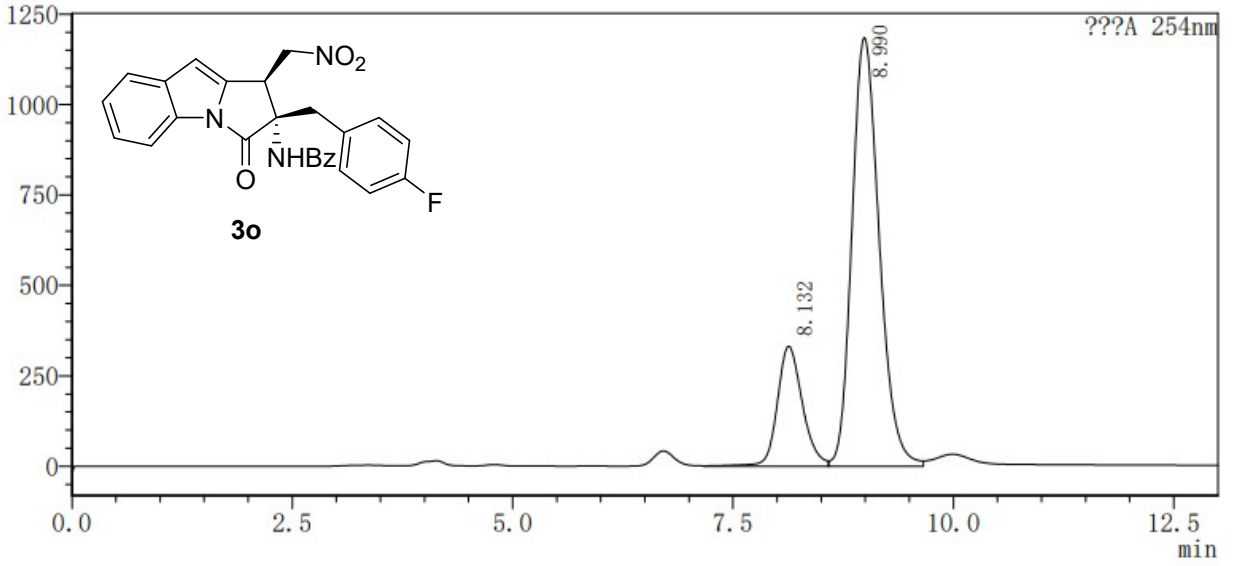


3o

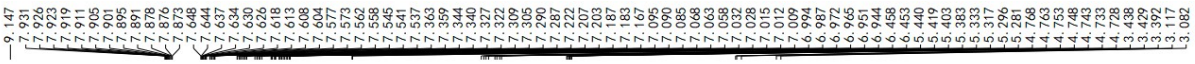
^{13}C NMR (100 MHz, DMSO-d_6)

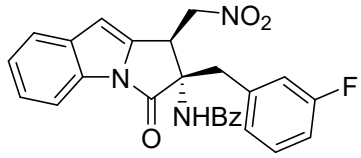


Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.764	3662934	211970	22.043	27.493
2	8.255	4613816	219688	27.765	28.494
3	9.115	4660447	201820	28.046	26.177
4	10.078	3680014	137507	22.146	17.835
Total		16617210	770985	100.000	100.000



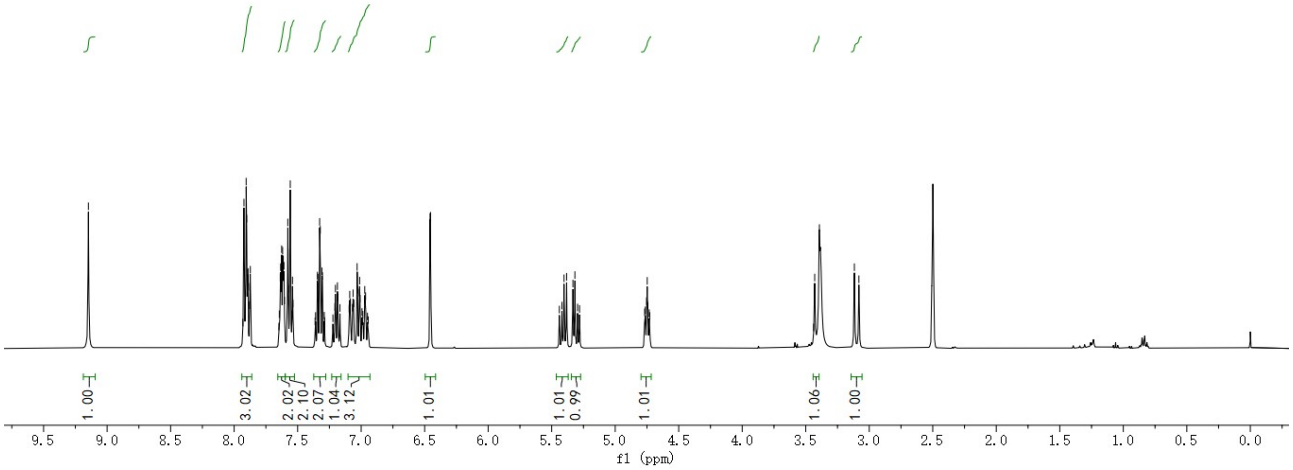
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.132	6593203	331851	20.498	21.875
2	8.990	25571534	1185162	79.502	78.125
Total		32164737	1517014	100.000	100.000

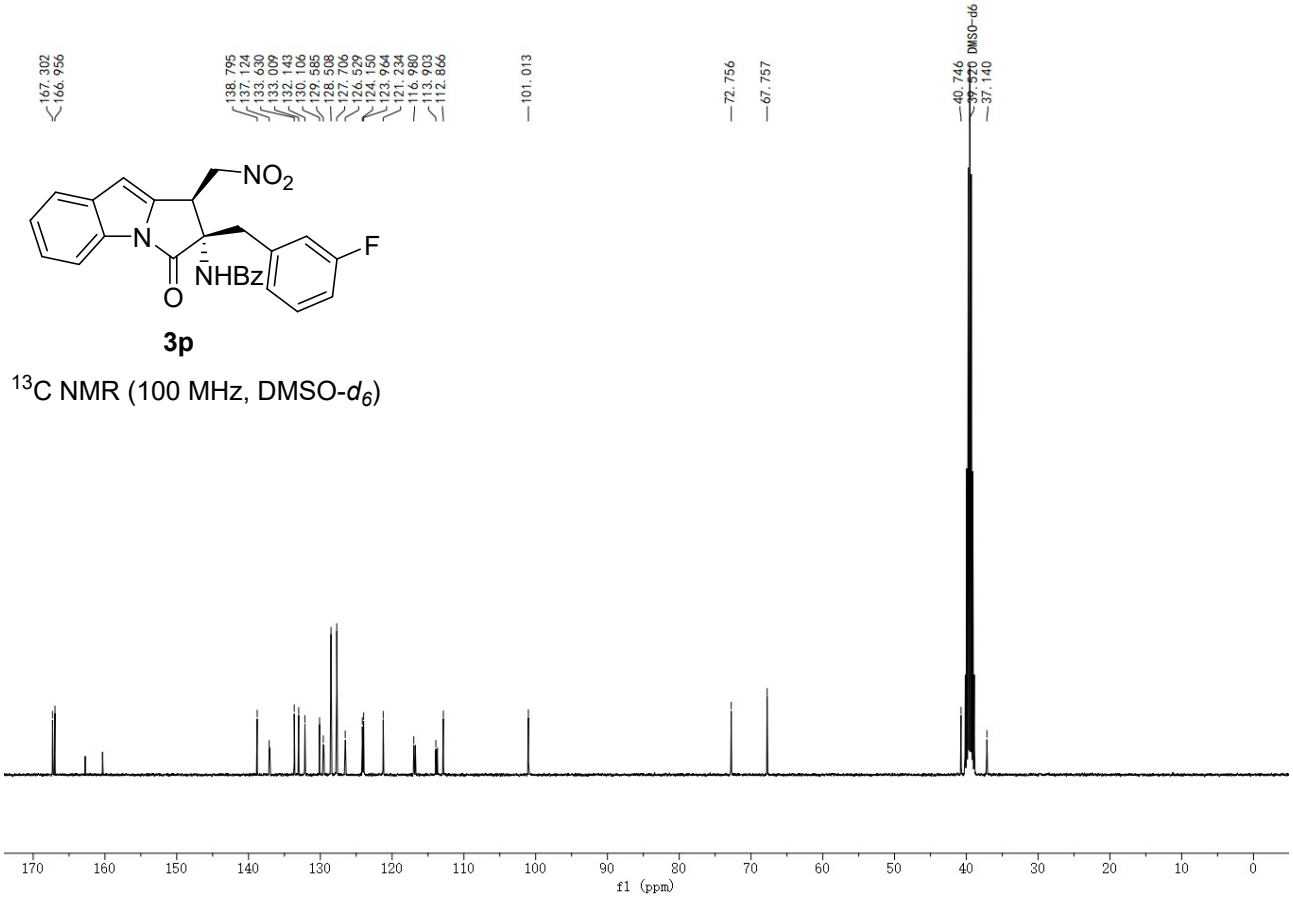




3p

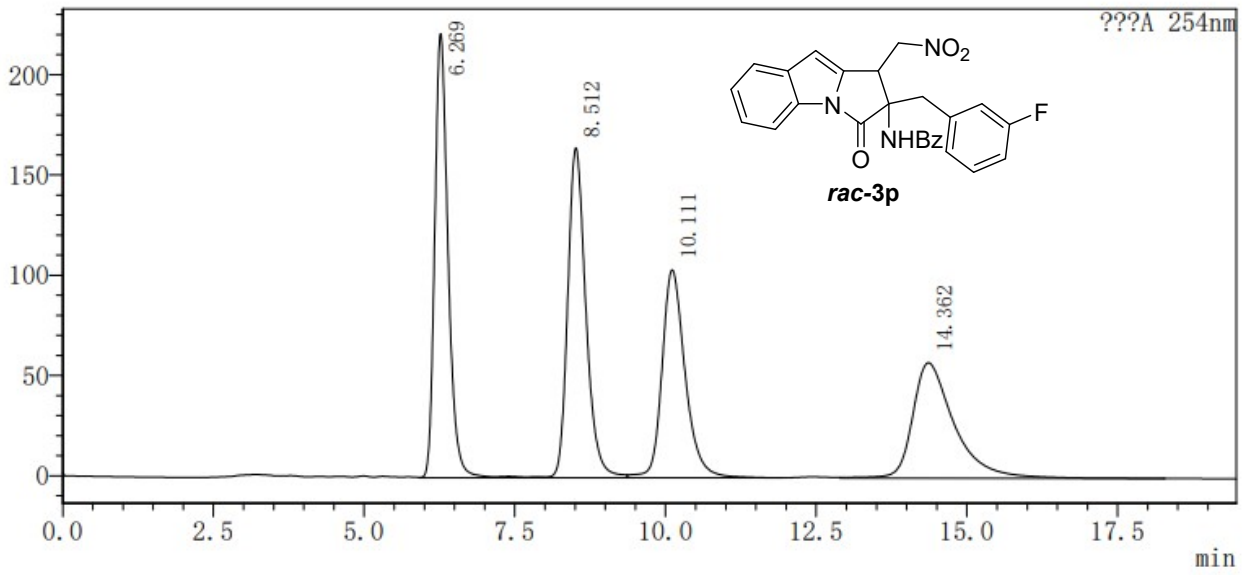
^{1}H NMR (400 MHz, DMSO-d_6)



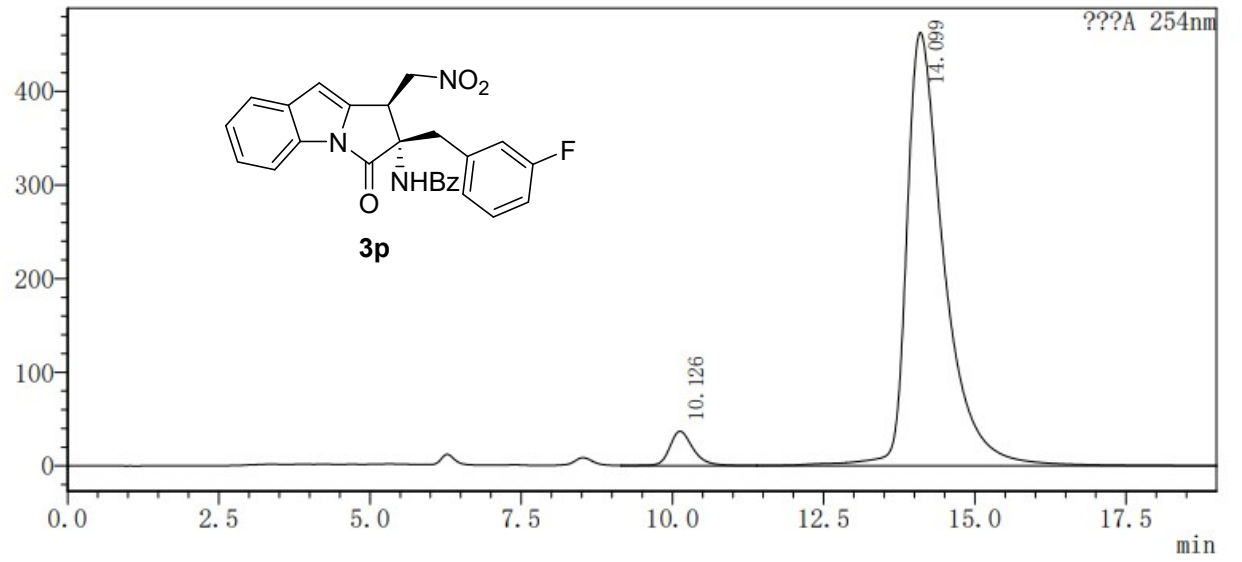


3p

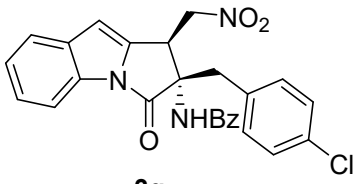
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.269	3421760	221321	27.596	40.463
2	8.512	3439577	164480	27.740	30.071
3	10.111	2776075	103691	22.389	18.957
4	14.362	2761945	57485	22.275	10.510
Total		12399357	546976	100.000	100.000

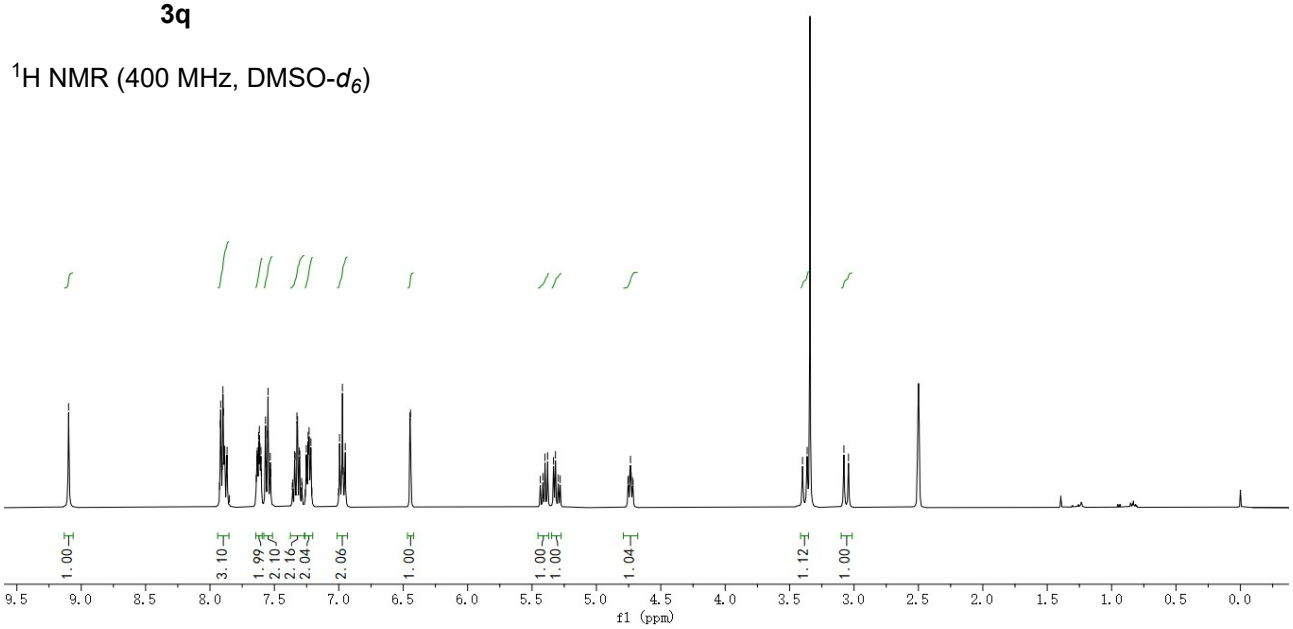


Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.126	1017347	36920	4.856	7.386
2	14.099	19931836	462948	95.144	92.614
Total		20949183	499868	100.000	100.000



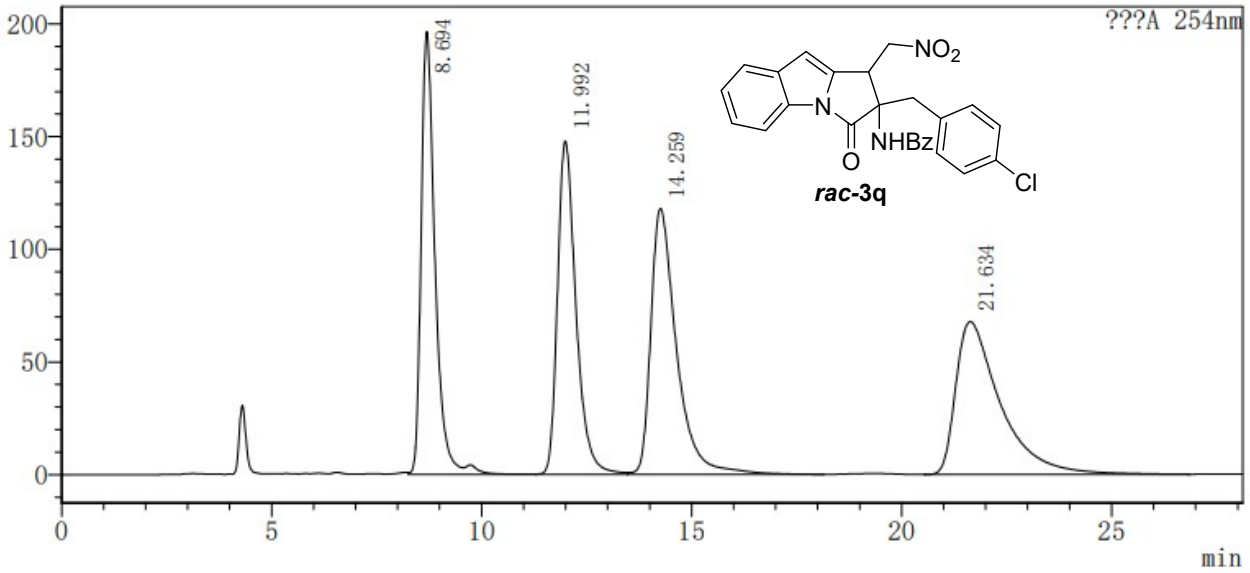
3q

^{1}H NMR (400 MHz, DMSO-d_6)

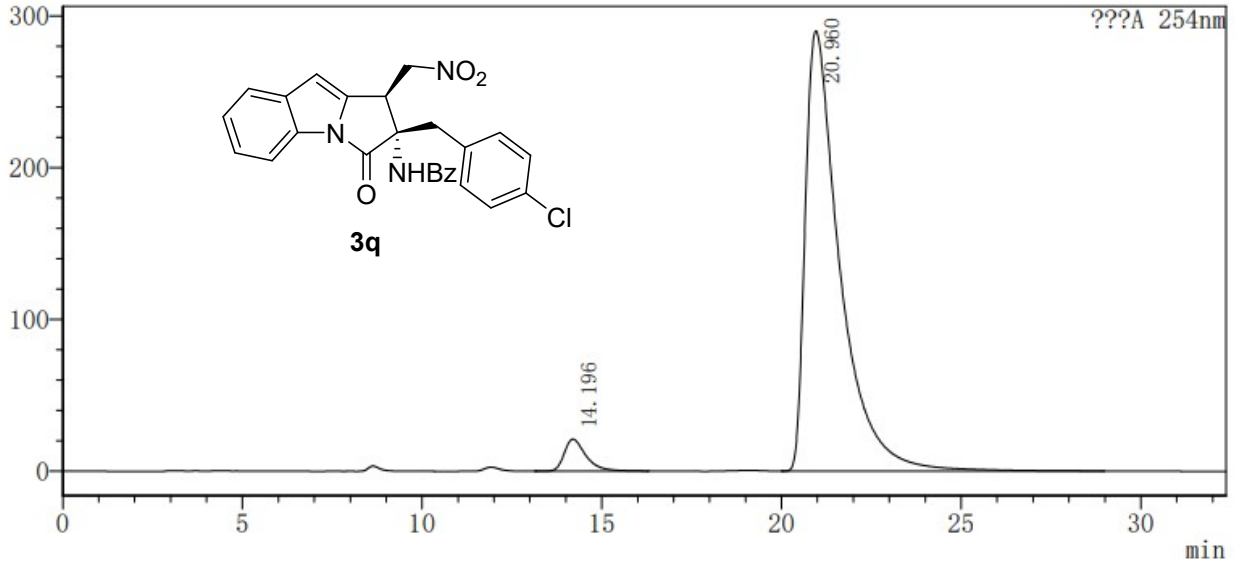


3q

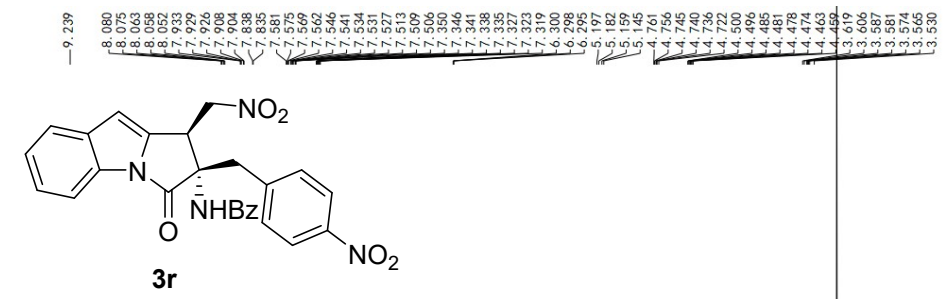
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.694	4551701	196545	23.819	37.052
2	11.992	4530298	148069	23.707	27.914
3	14.259	5023050	117992	26.286	22.244
4	21.634	5004315	67845	26.188	12.790
Total		19109364	530450	100.000	100.000

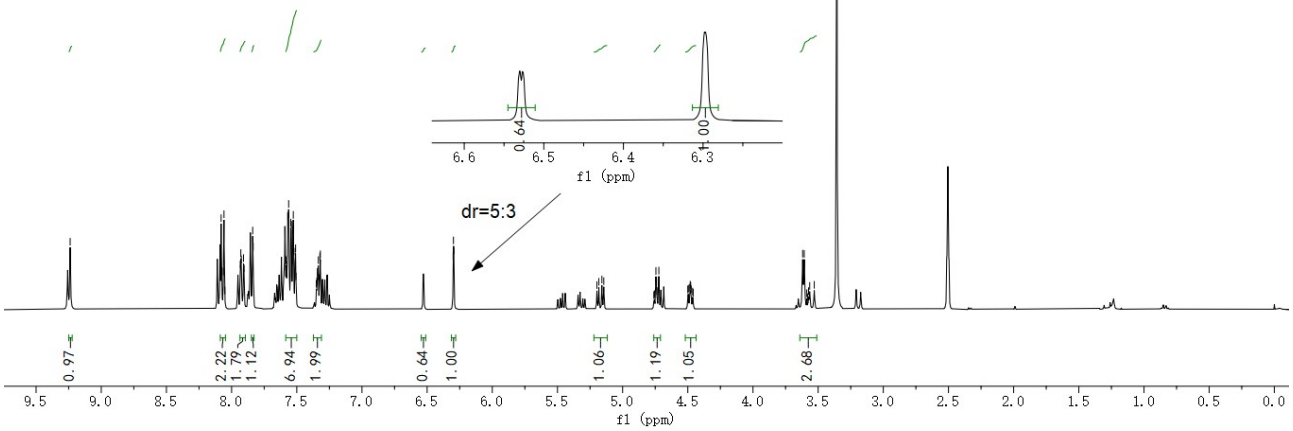


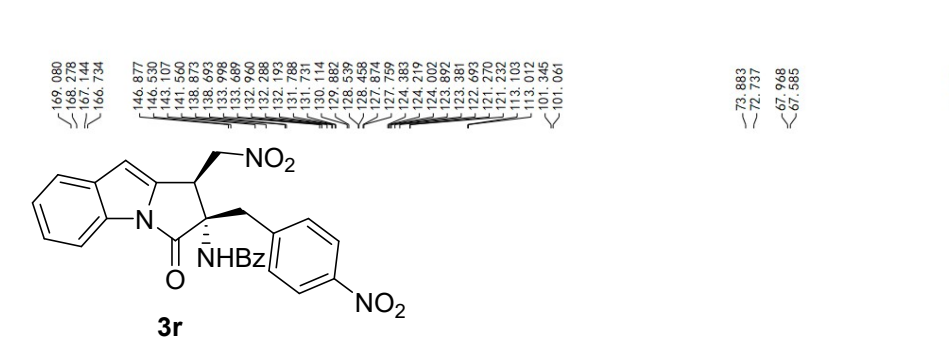
Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.196	884907	21076	4.343	6.771
2	20.960	19491190	290199	95.657	93.229
Total		20376096	311275	100.000	100.000



3r

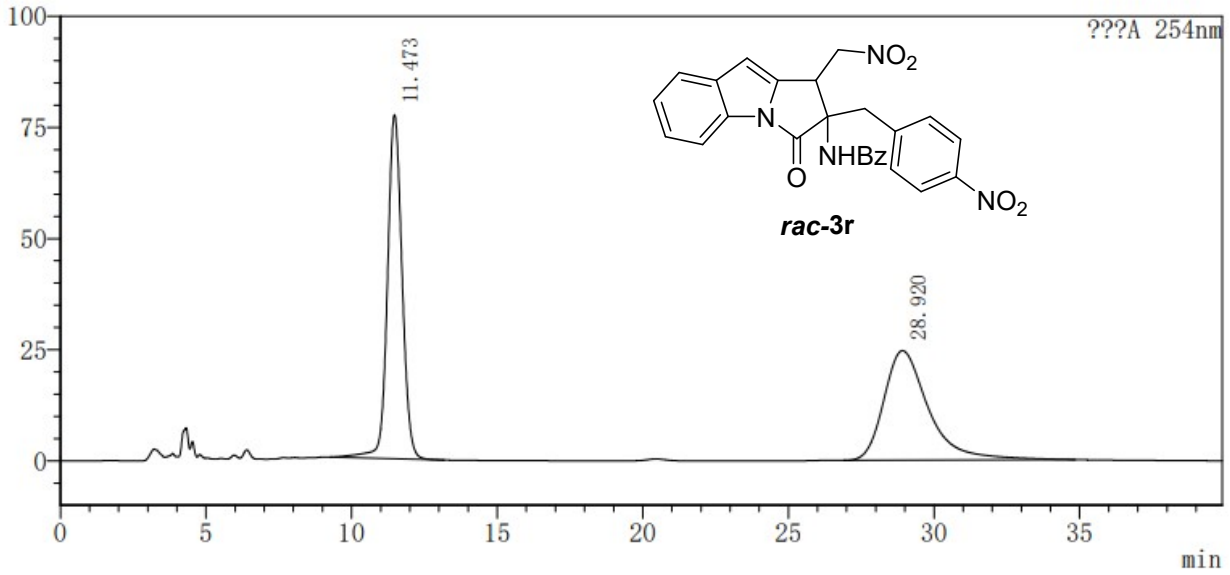
^{1}H NMR (400 MHz, DMSO-d_6)



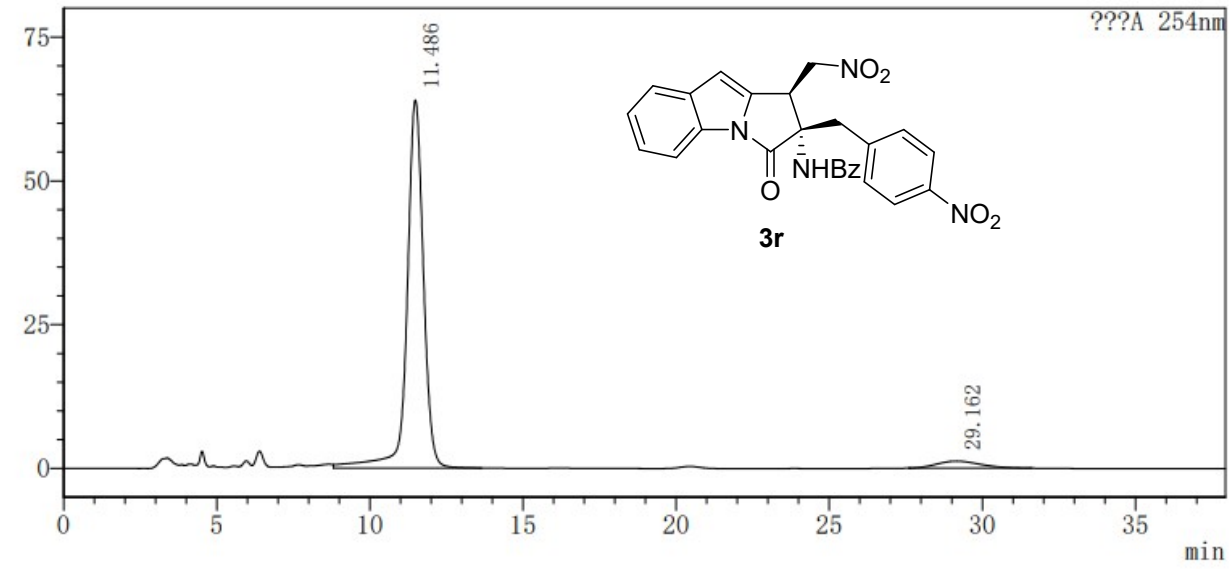


3r

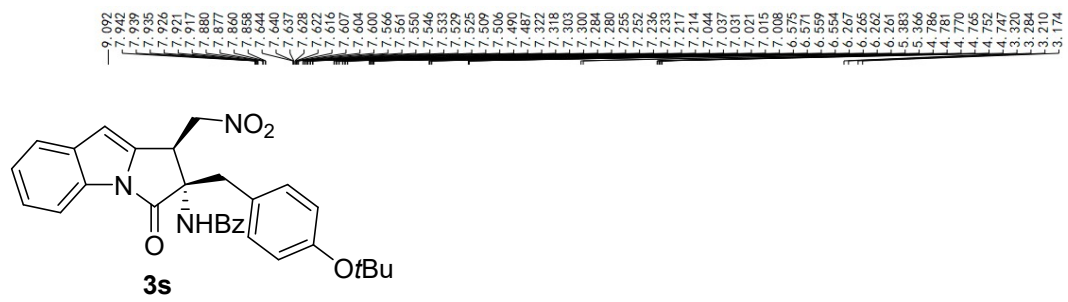
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.473	2707098	77418	50.794	75.854
2	28.920	2622509	24643	49.206	24.146
Total		5329607	102061	100.000	100.000

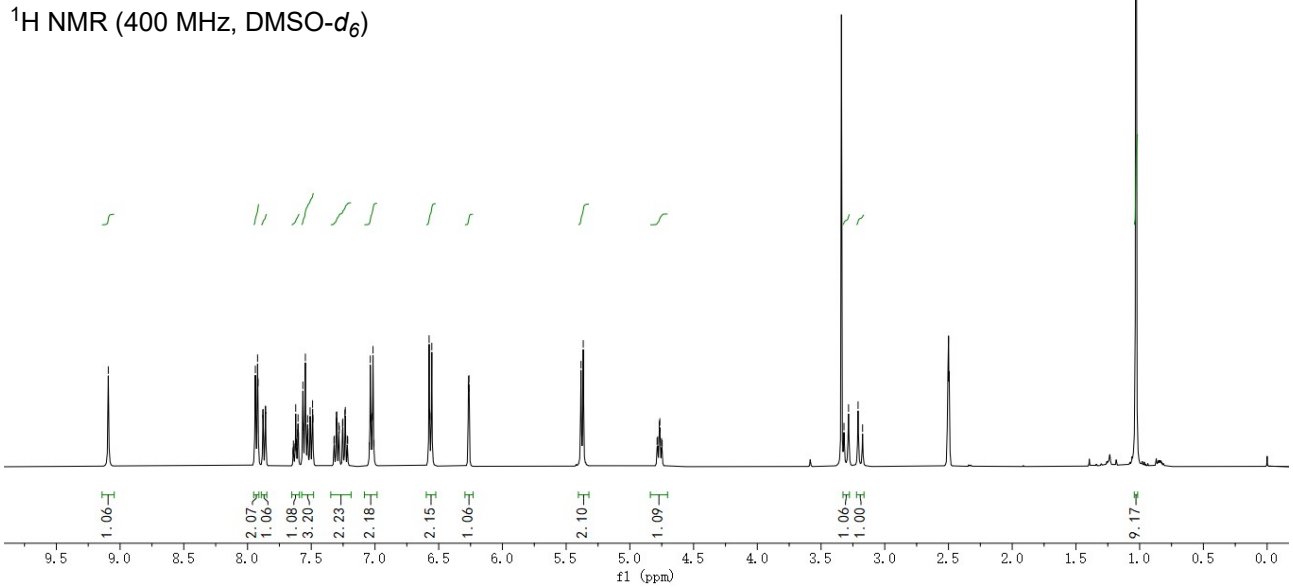


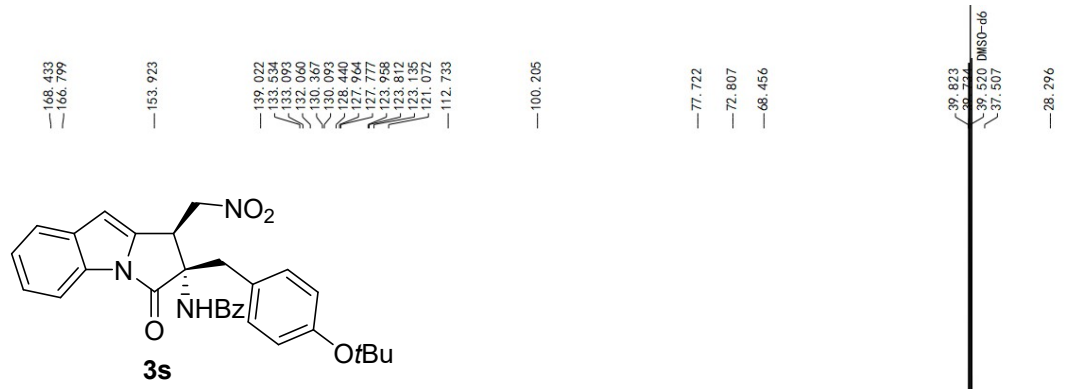
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.486	2387259	64003	95.166	98.130
2	29.162	121257	1219	4.834	1.870
Total		2508515	65222	100.000	100.000



3s

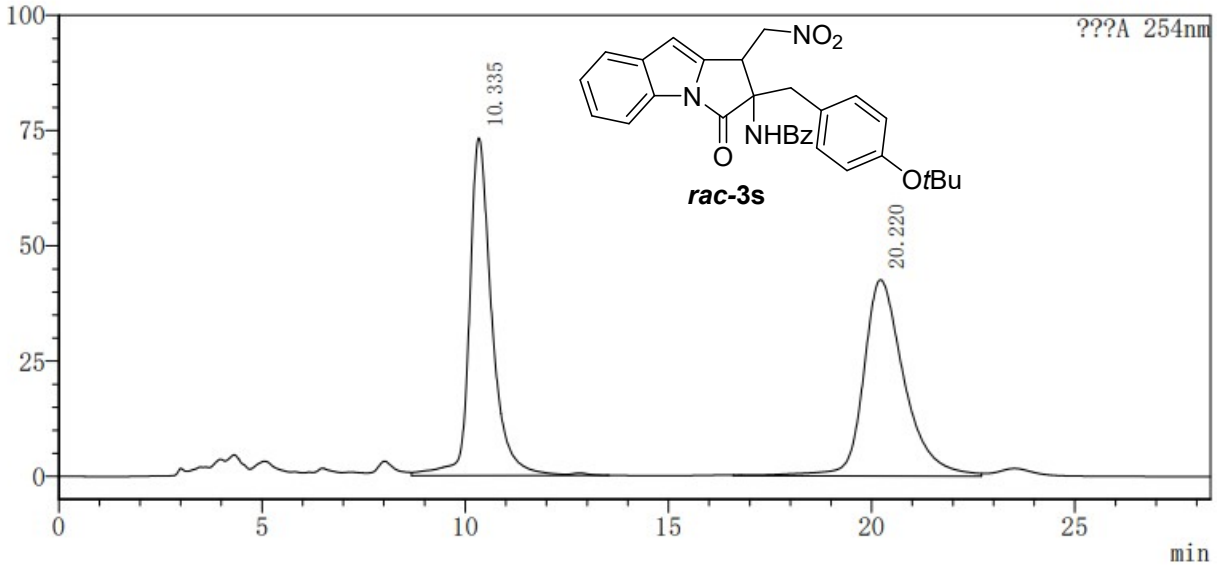
^{1}H NMR (400 MHz, DMSO-d_6)



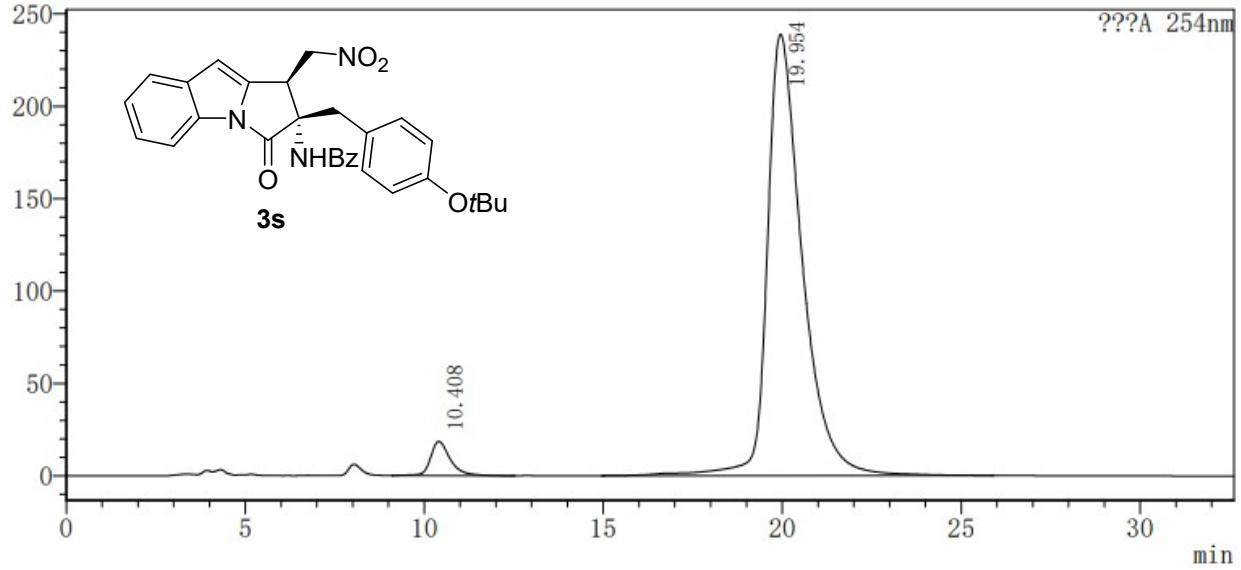


3s

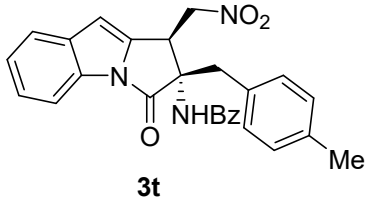
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.335	2818033	73243	48.572	63.238
2	20.220	2983762	42578	51.428	36.762
Total		5801795	115821	100.000	100.000

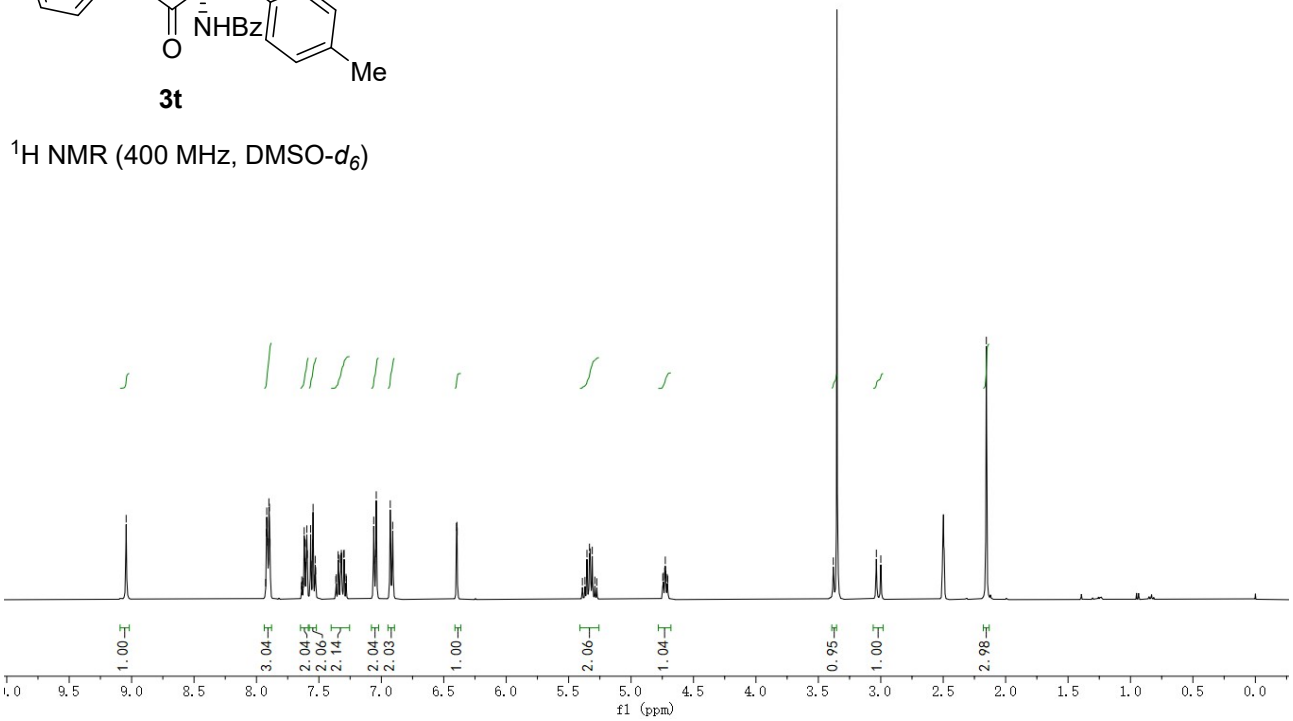


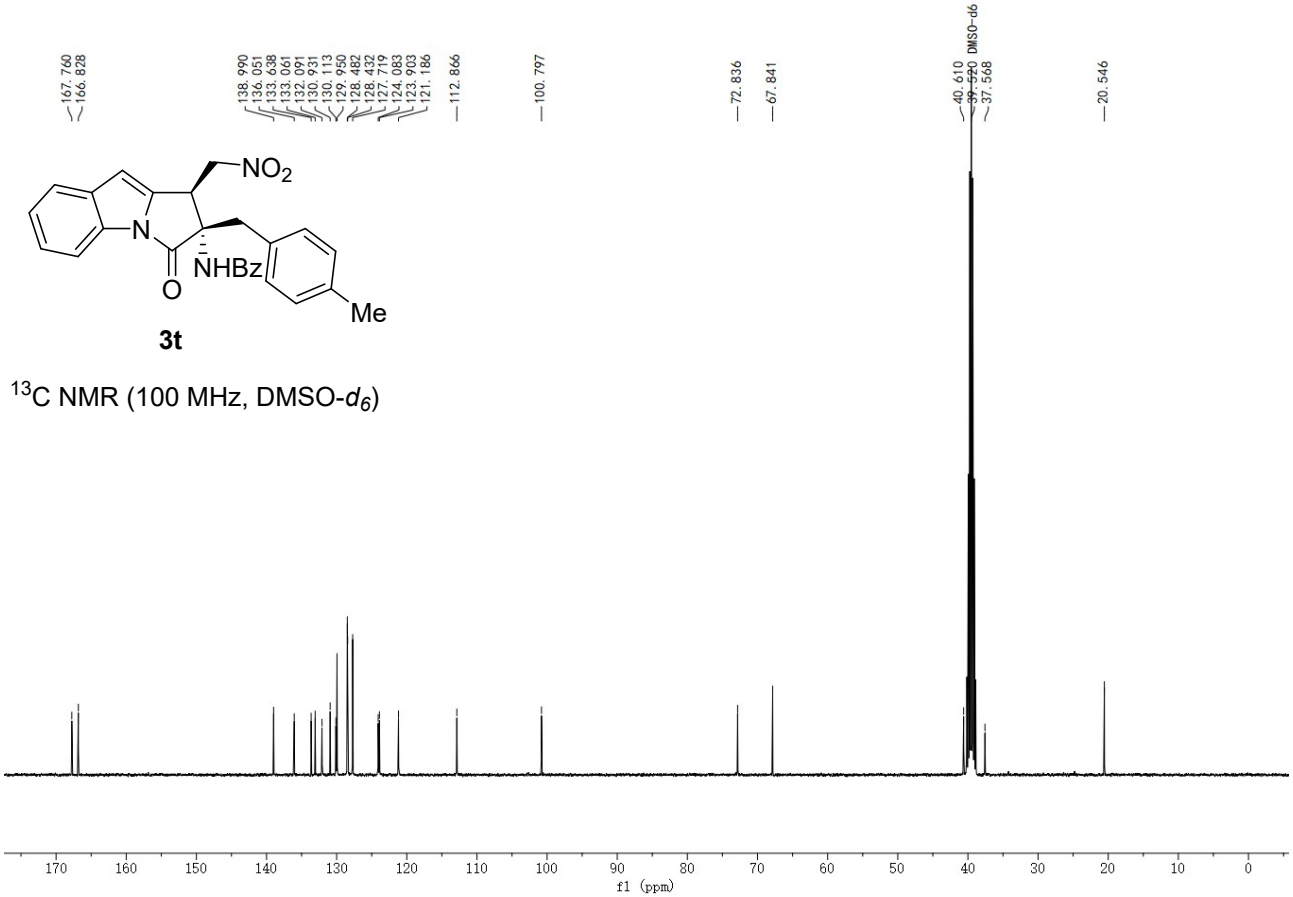
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.408	704026	18494	4.148	7.187
2	19.954	16268316	238844	95.852	92.813
Total		16972342	257338	100.000	100.000



3t

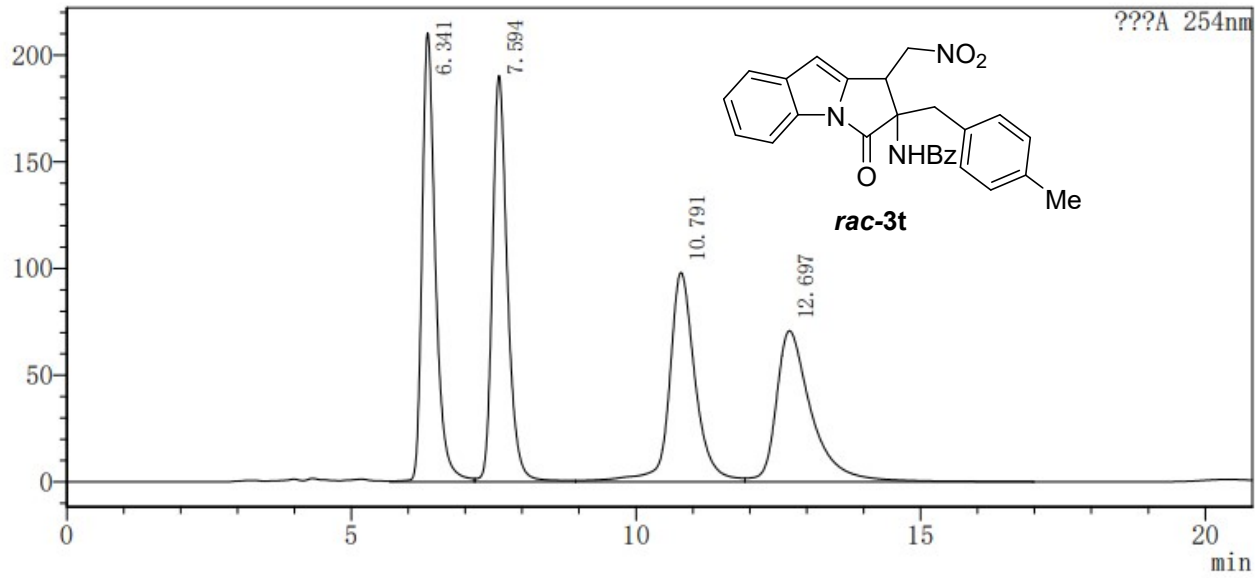
^{1}H NMR (400 MHz, DMSO-d_6)



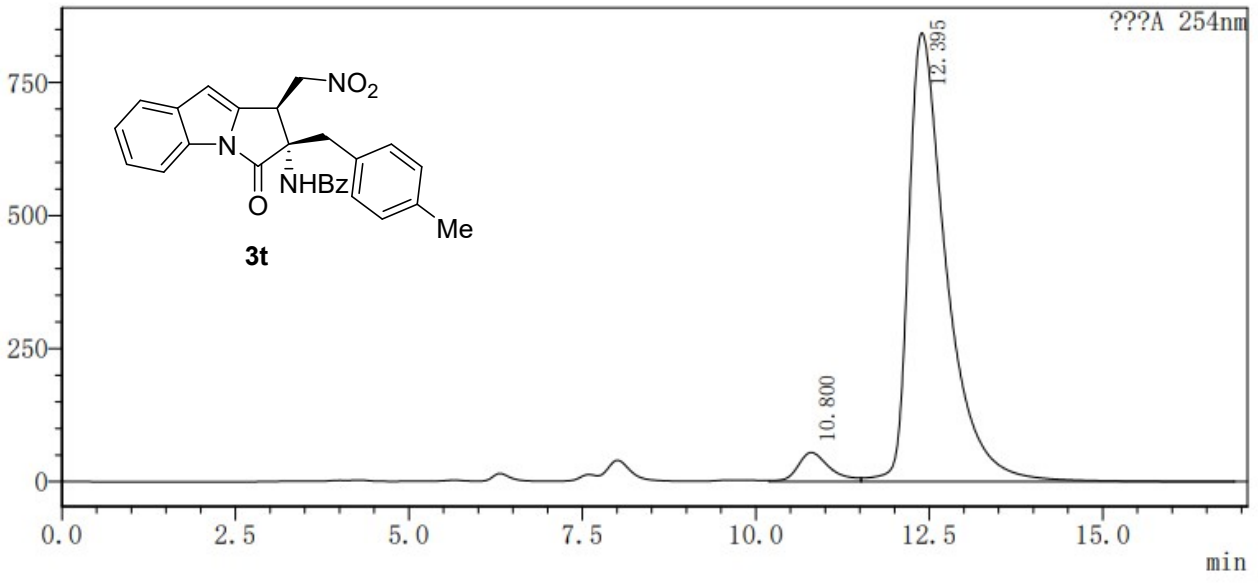


3t

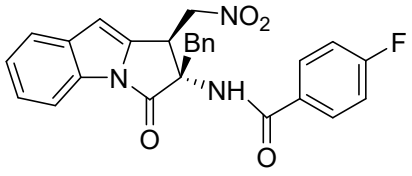
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.341	3434587	210420	26.283	36.943
2	7.594	3492961	190328	26.730	33.416
3	10.791	3103730	98116	23.751	17.226
4	12.697	3036347	70715	23.236	12.415
Total		13067624	569580	100.000	100.000

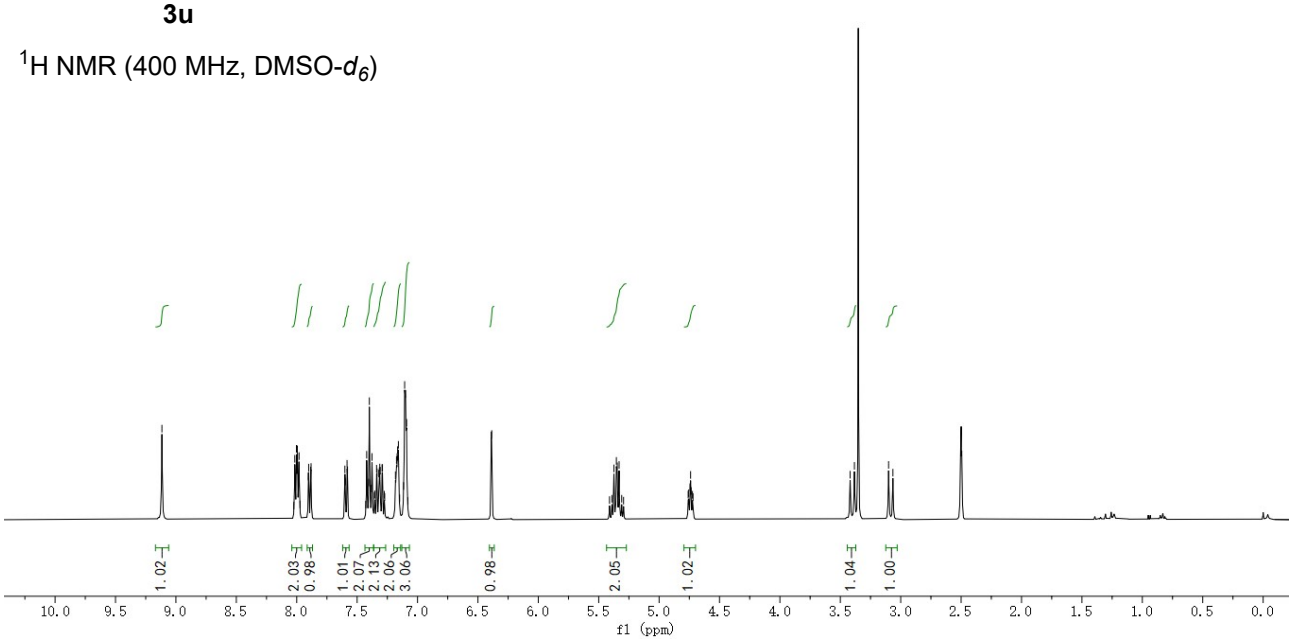


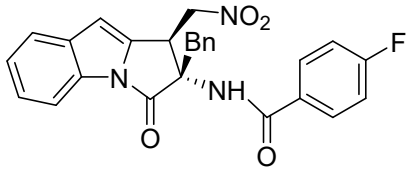
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.800	1754433	54781	5.180	6.100
2	12.395	32112540	843260	94.820	93.900
Total		33866973	898042	100.000	100.000



3u

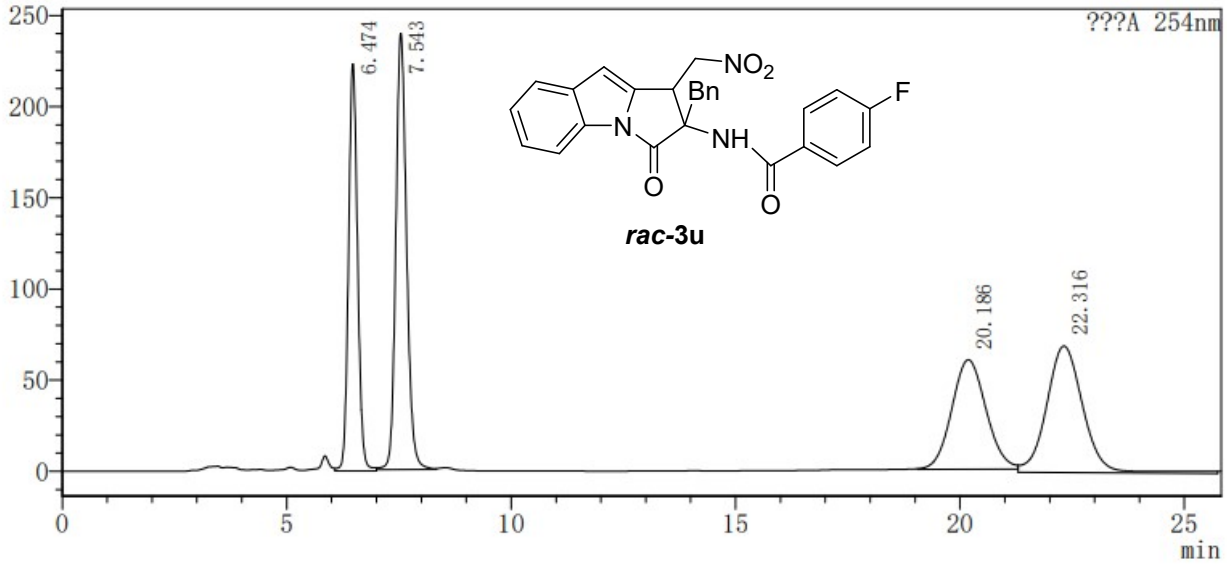
^{1}H NMR (400 MHz, DMSO-d_6)





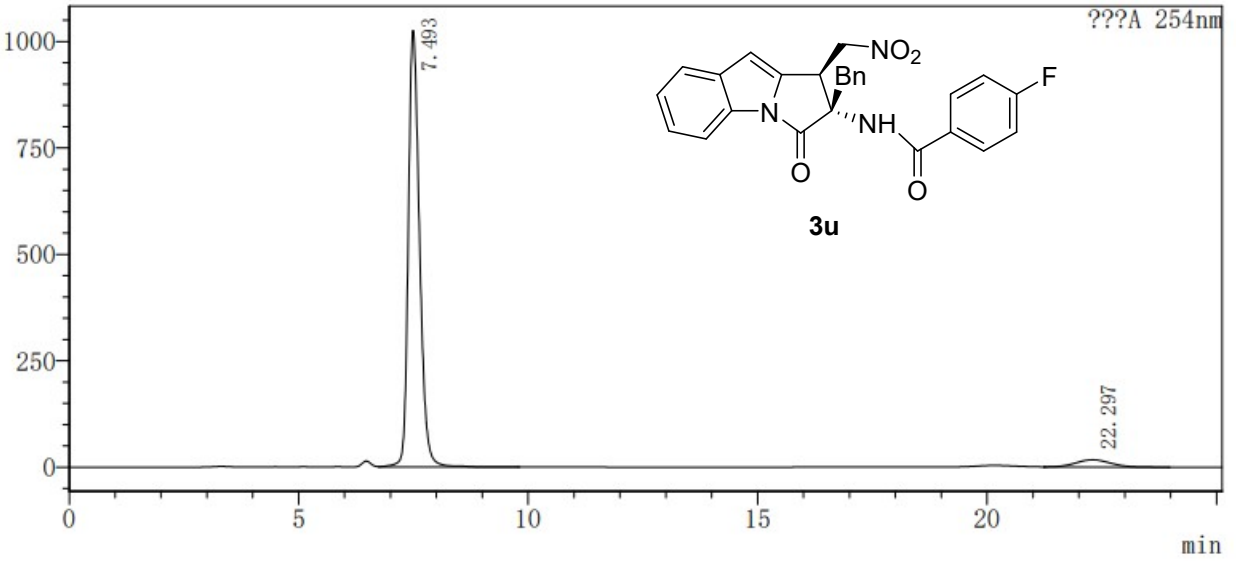
3u

^{13}C NMR (100 MHz, DMSO-d_6)



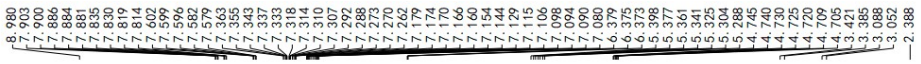
***rac*-3u**

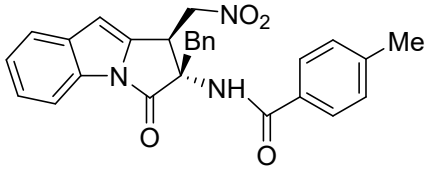
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.474	3142260	223408	22.067	37.743
2	7.543	3969932	239165	27.879	40.405
3	20.186	3177470	59964	22.314	10.130
4	22.316	3950185	69384	27.740	11.722
Total		14239847	591920	100.000	100.000



3u

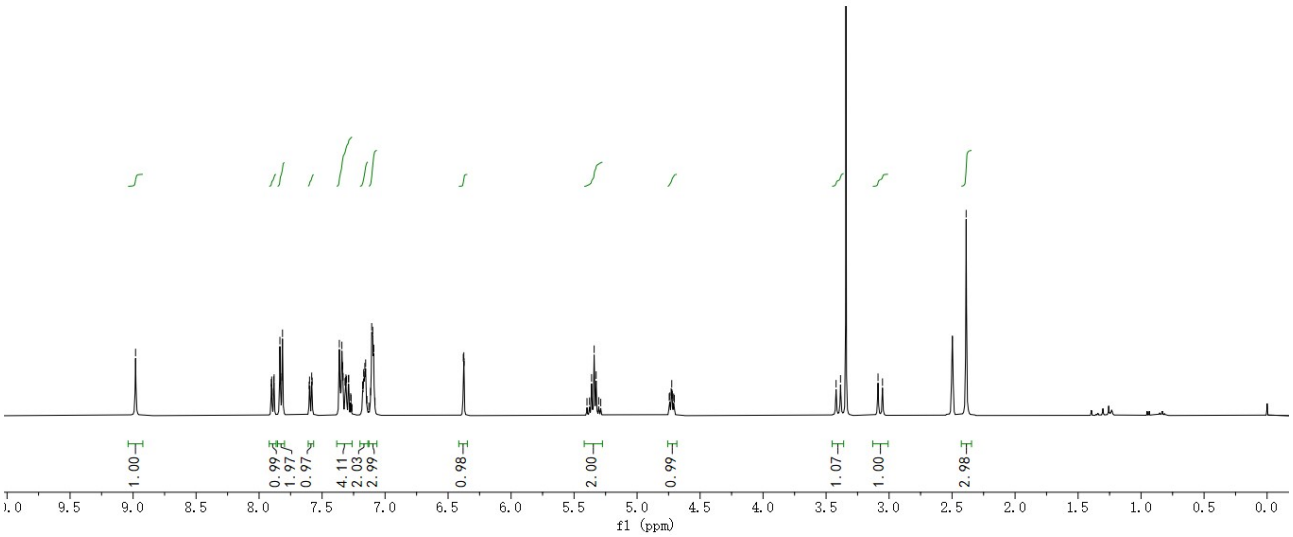
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.493	17514245	1025937	94.951	98.340
2	22.297	931253	17316	5.049	1.660
Total		18445498	1043253	100.000	100.000

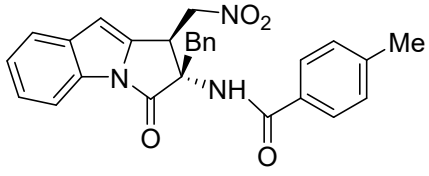




3v

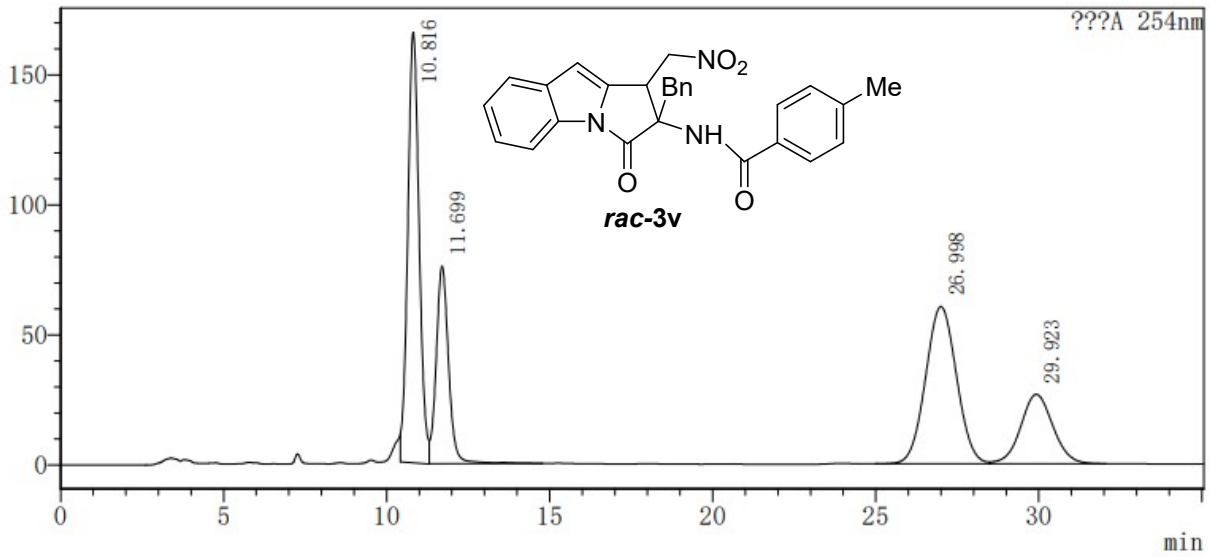
^{1}H NMR (400 MHz, DMSO-d_6)



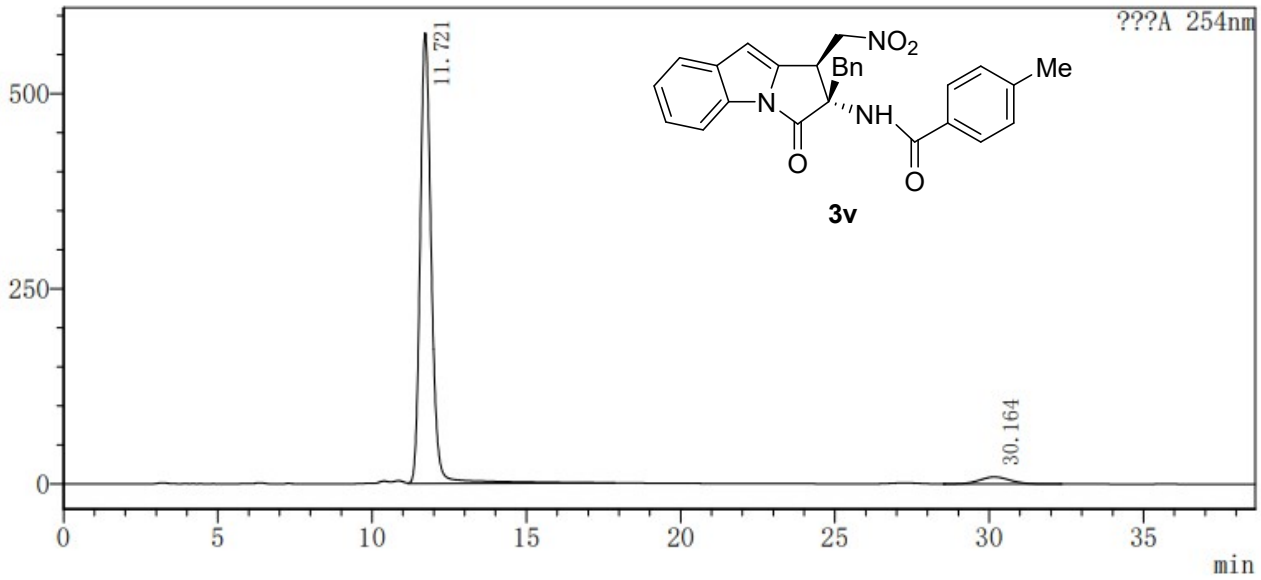


3v

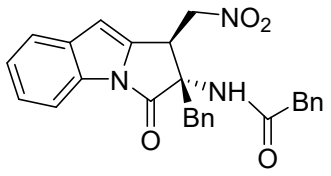
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.816	4003573	165578	33.848	50.382
2	11.699	2006533	75956	16.964	23.112
3	26.998	3984560	60455	33.688	18.395
4	29.923	1833260	26655	15.499	8.111
Total		11827925	328644	100.000	100.000

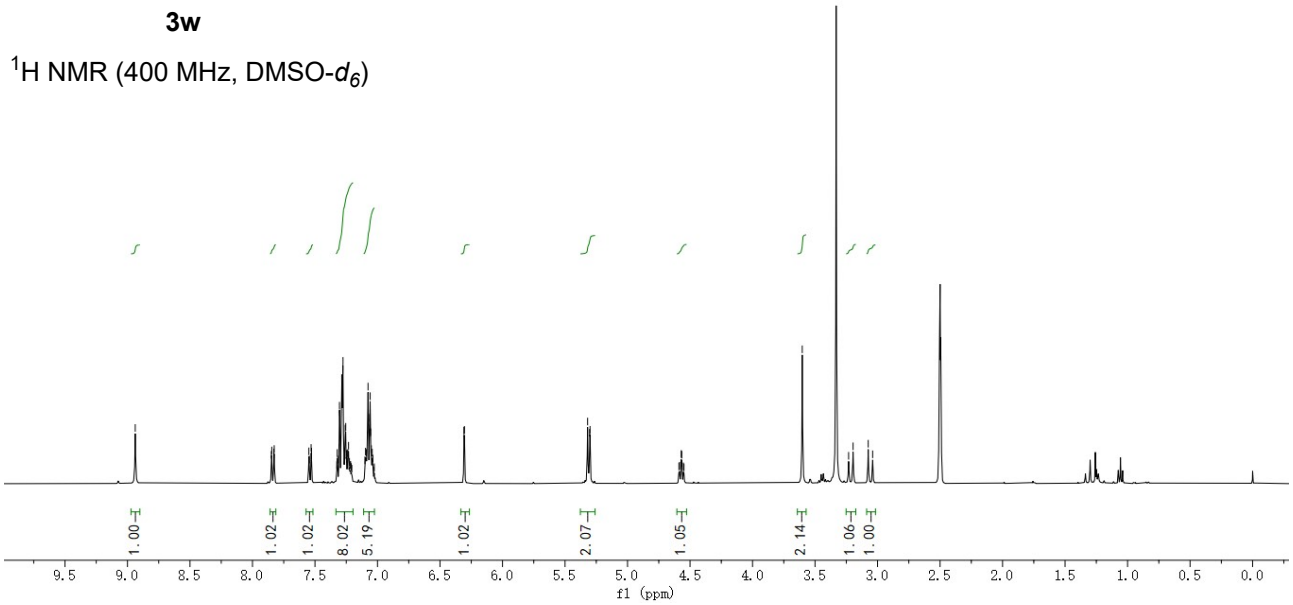


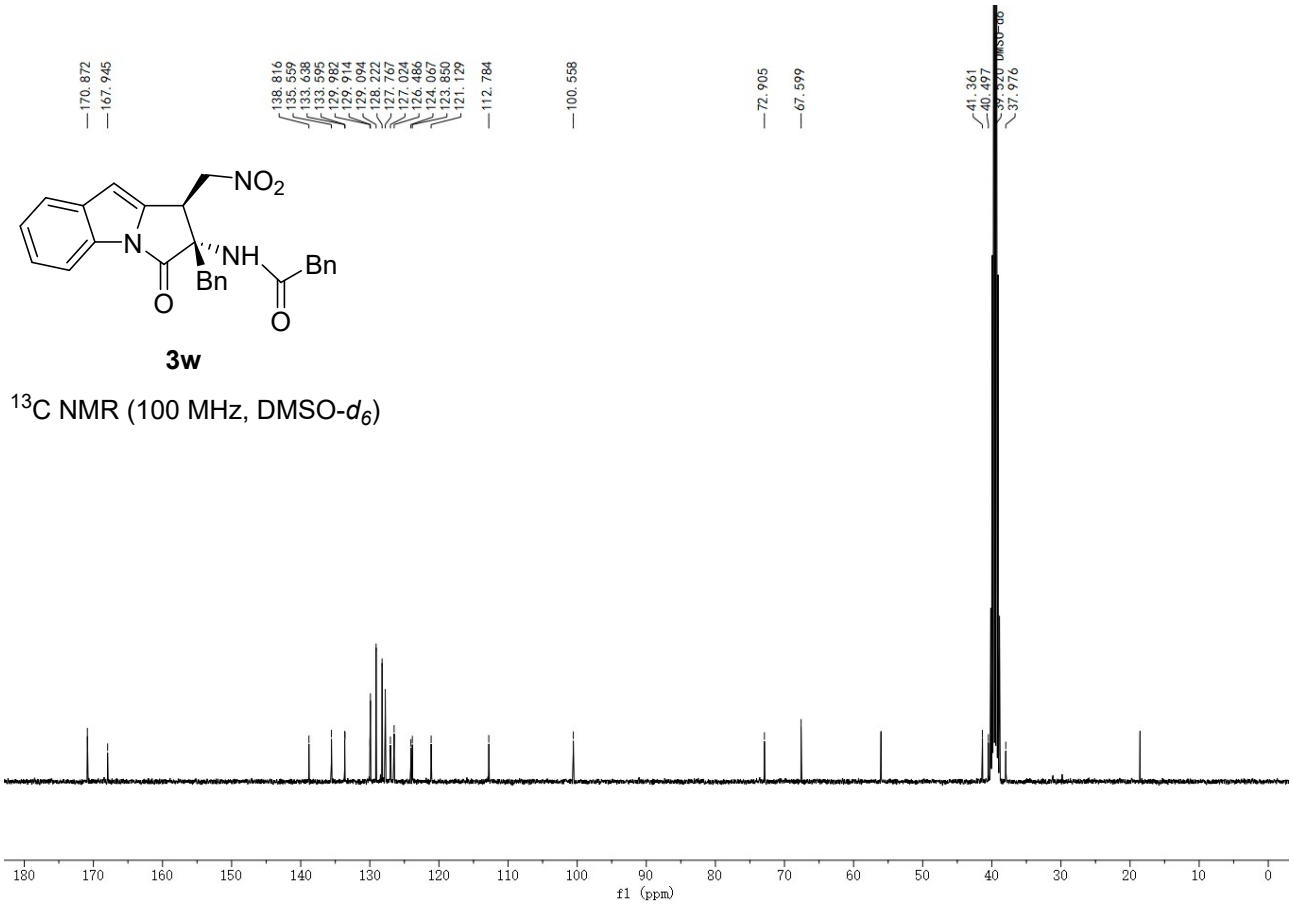
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.721	14661565	577531	95.962	98.474
2	30.164	616935	8952	4.038	1.526
Total		15278500	586483	100.000	100.000



3w

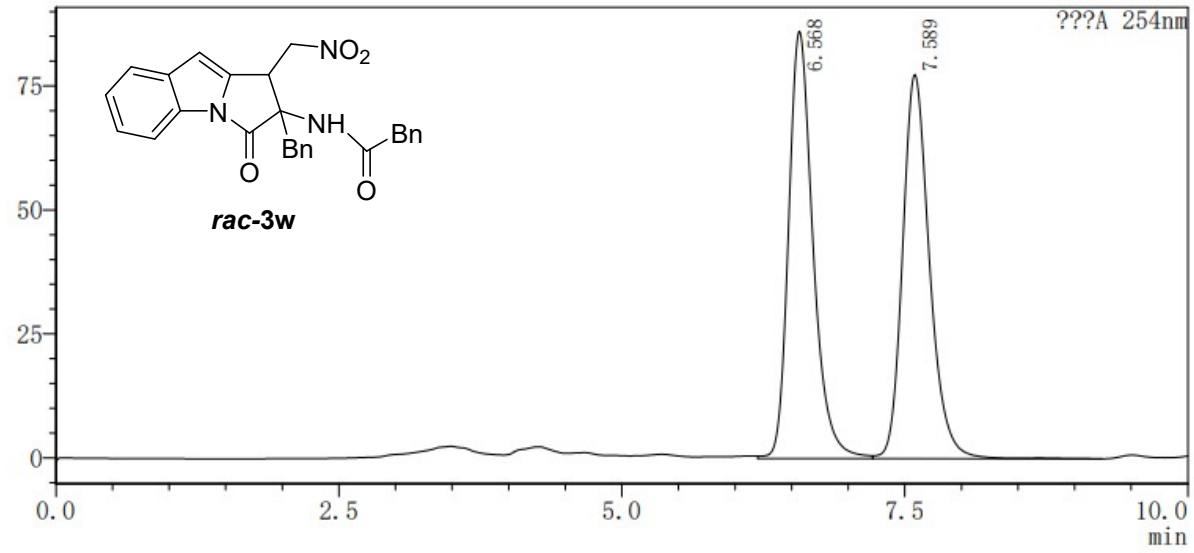
^{1}H NMR (400 MHz, DMSO-d_6)



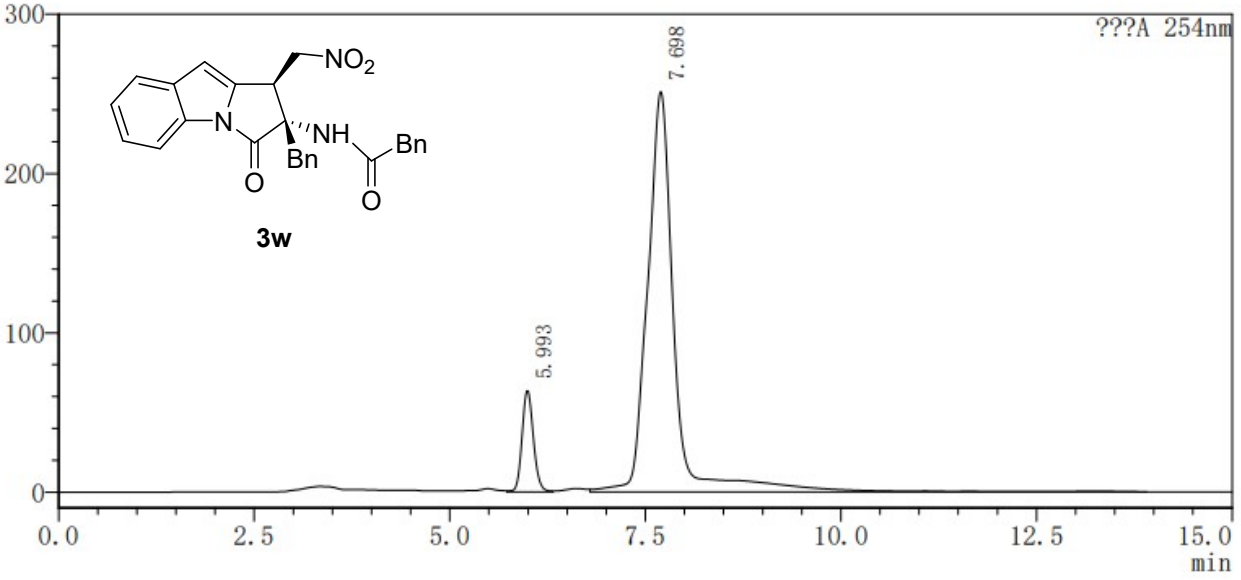


3w

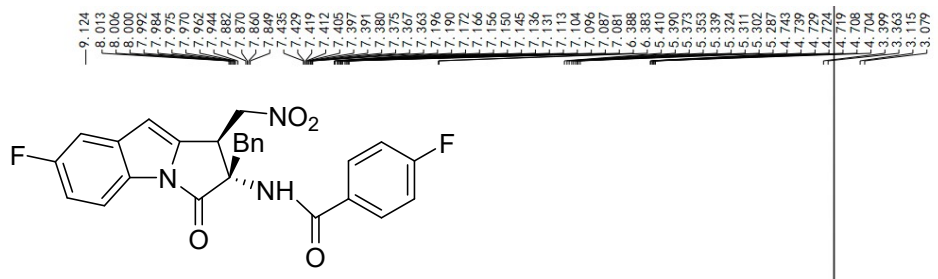
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.568	1296409	86180	50.238	52.673
2	7.589	1284149	77435	49.762	47.327
Total		2580557	163615	100.000	100.000

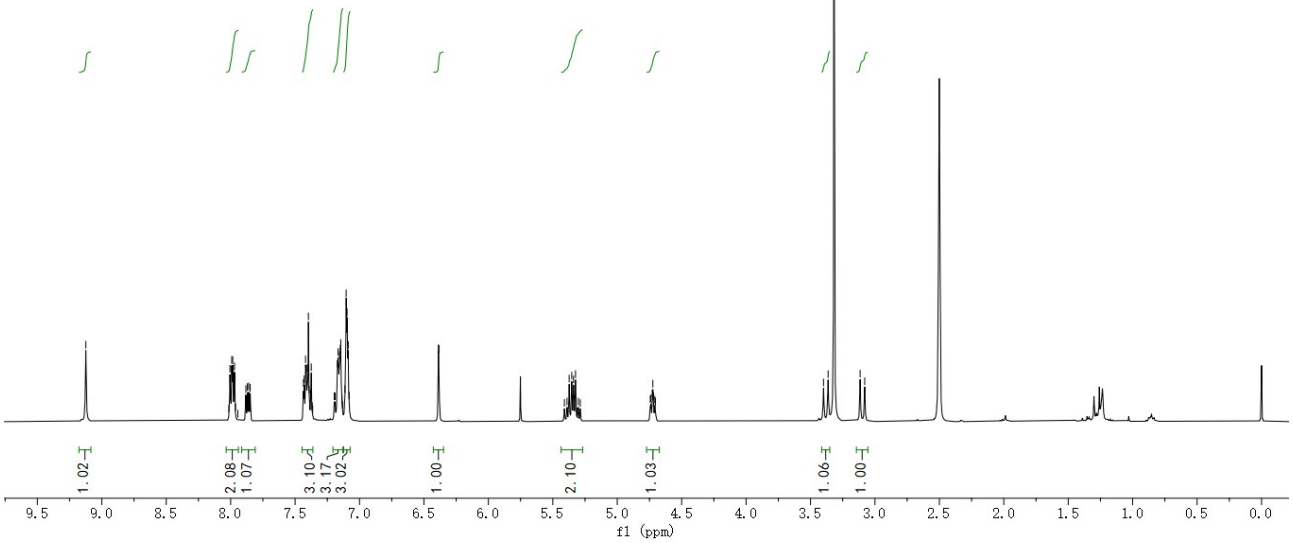


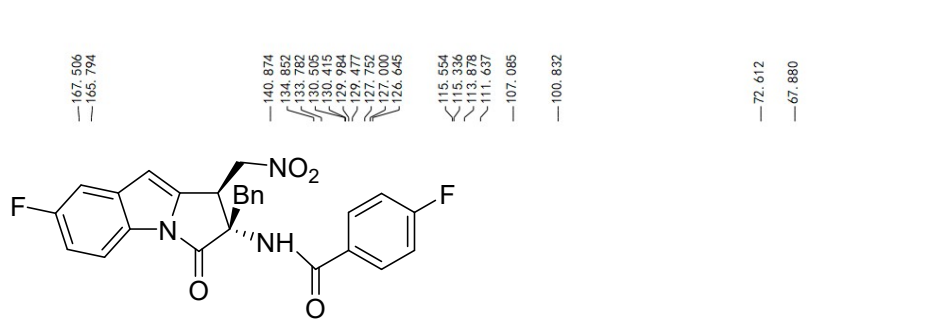
Peak#	Ret. Time	Area	Height	Area%	Height%
1	5.993	630799	63539	9.535	20.177
2	7.698	5985153	251370	90.465	79.823
Total		6615952	314909	100.000	100.000



3x

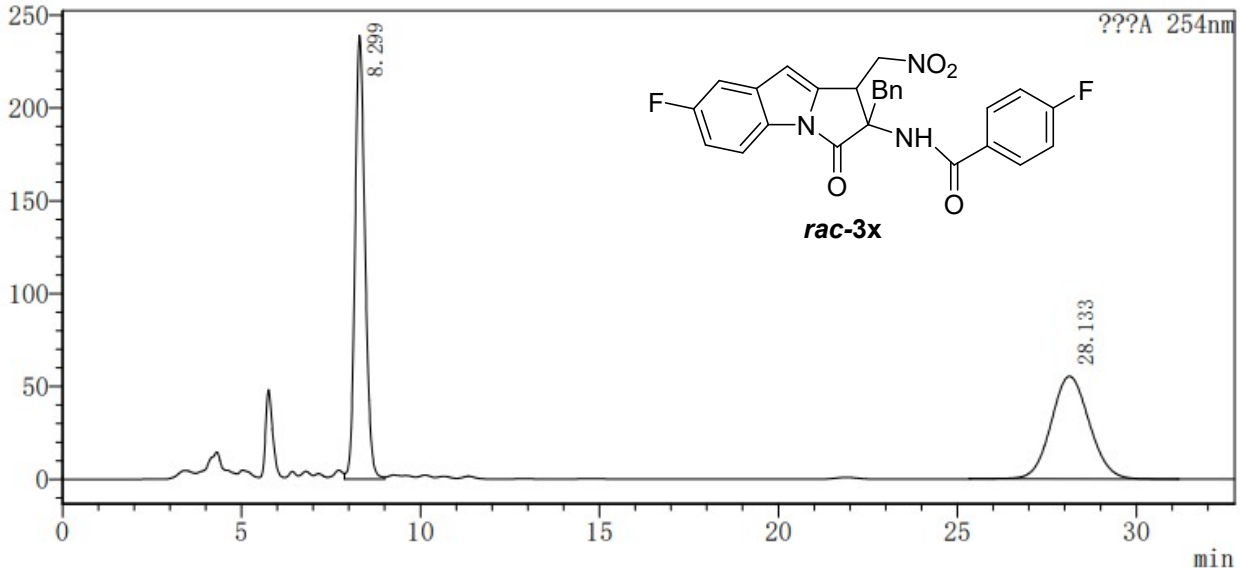
^{1}H NMR (400 MHz, DMSO-d_6)





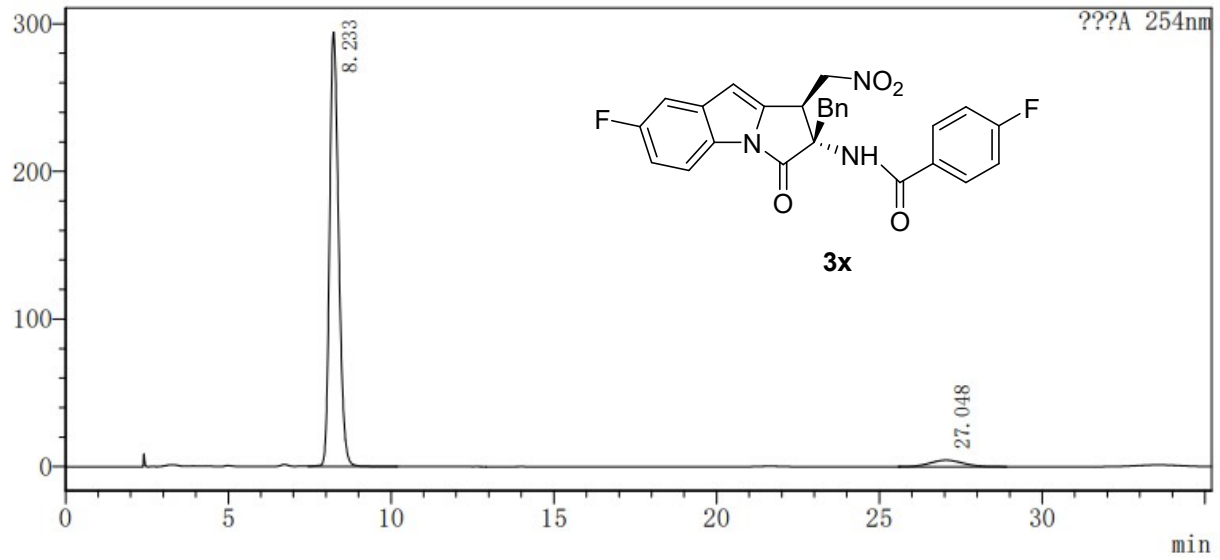
3x

^{13}C NMR (100 MHz, DMSO-d_6)



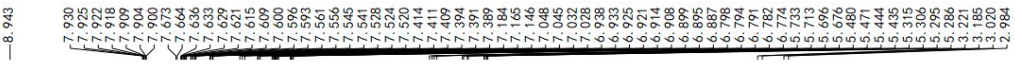
rac-3x

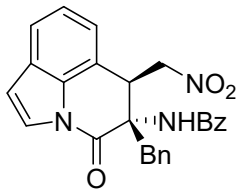
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.299	4626549	238918	52.919	81.189
2	28.133	4116109	55356	47.081	18.811
Total		8742658	294274	100.000	100.000



3x

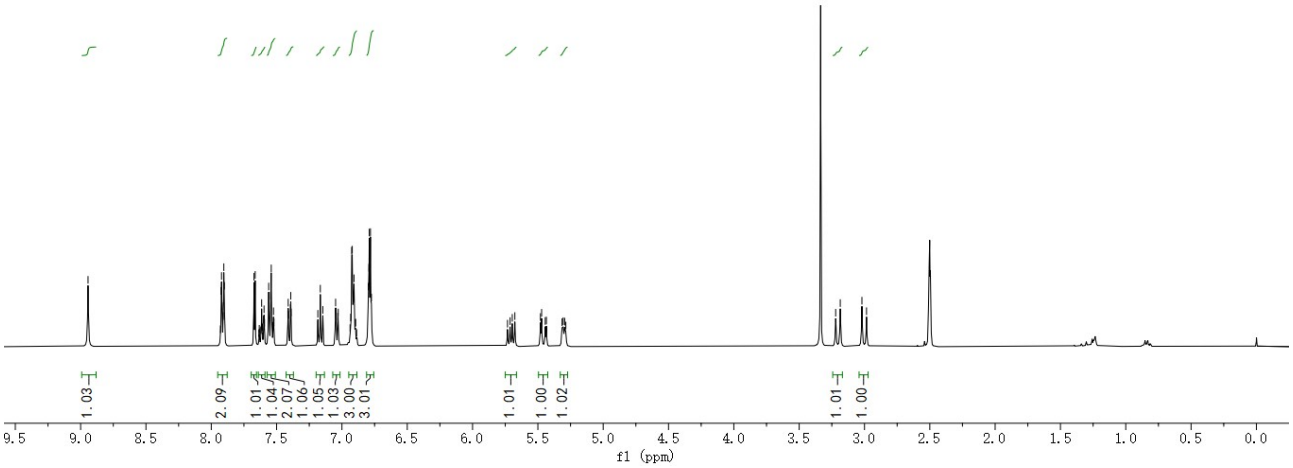
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.233	5689704	294208	94.892	98.534
2	27.048	306279	4376	5.108	1.466
Total		5995983	298584	100.000	100.000

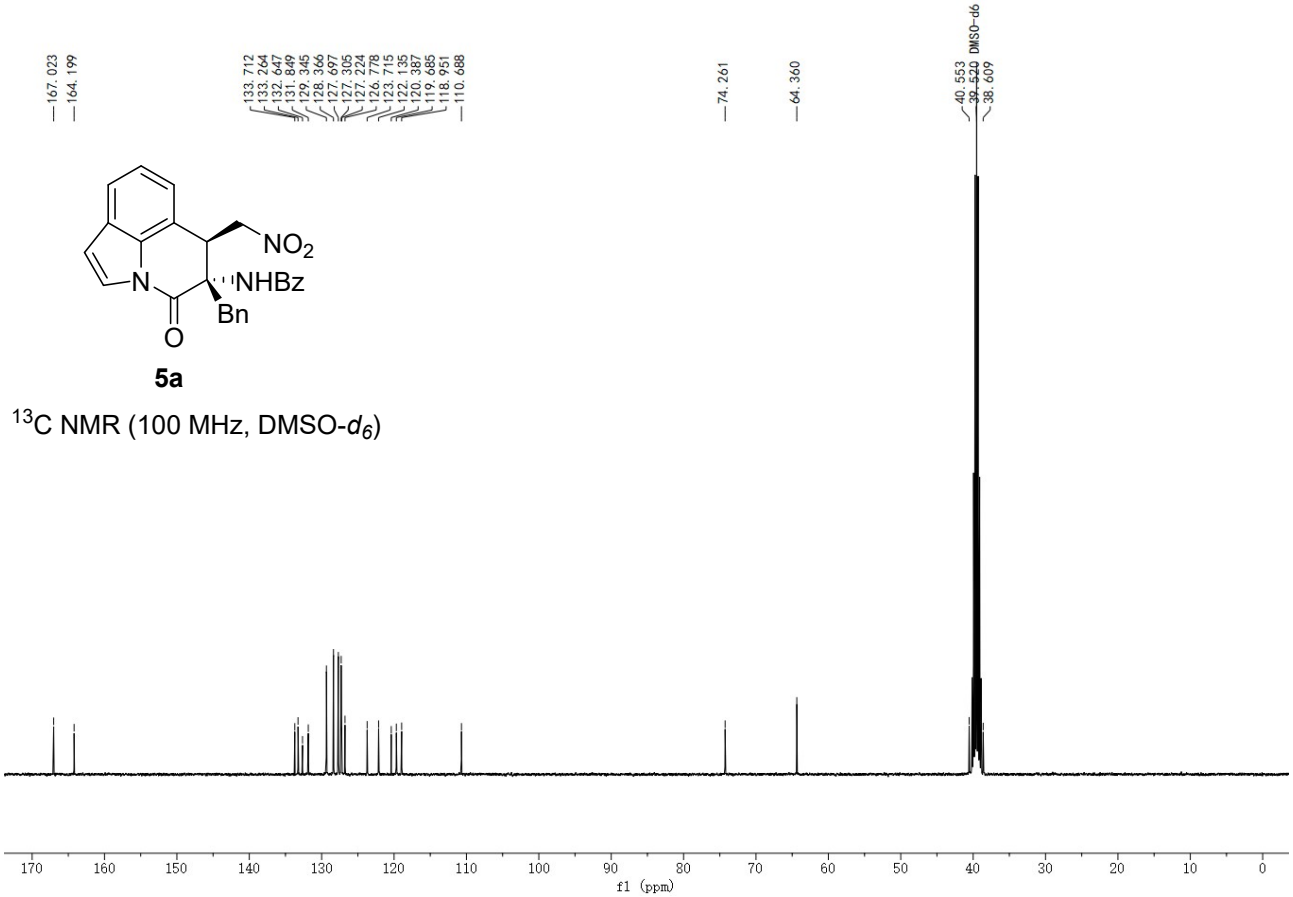




5a

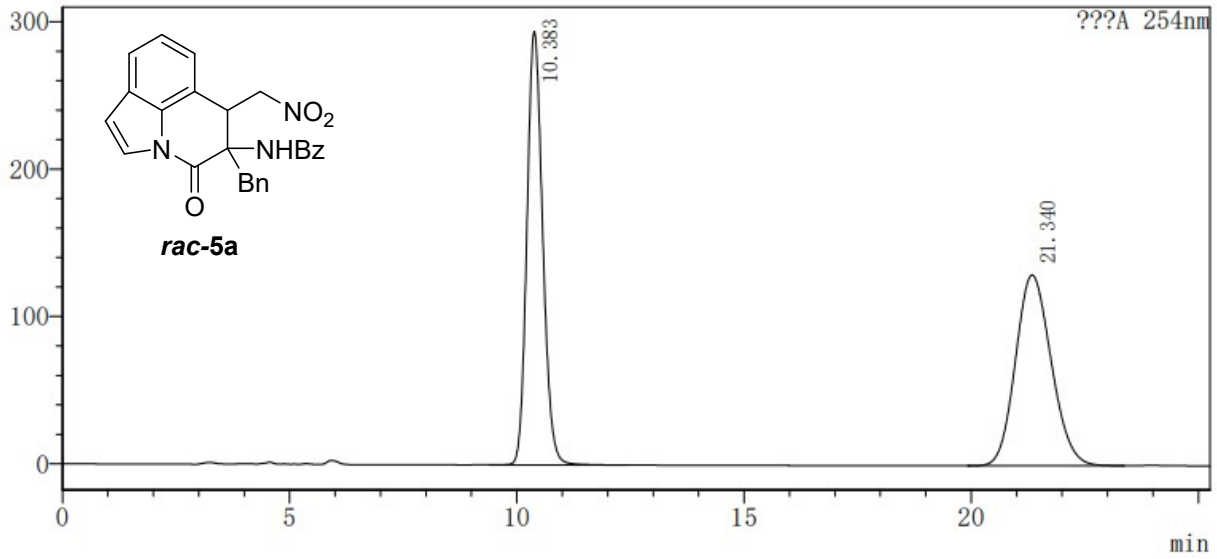
^{1}H NMR (400 MHz, DMSO-d_6)





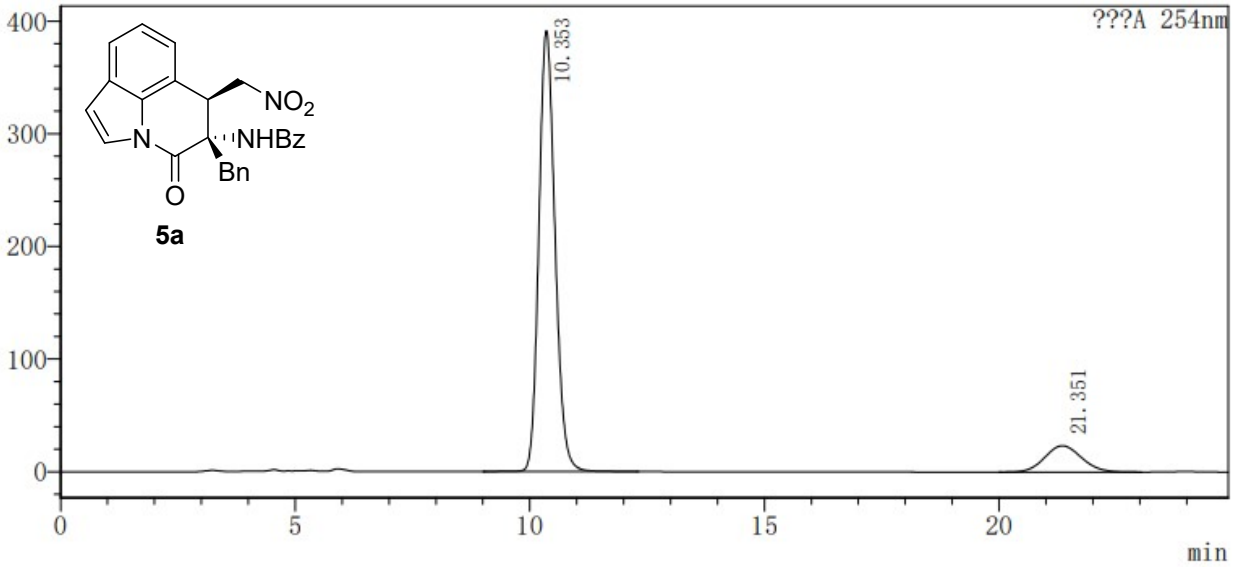
5a

^{13}C NMR (100 MHz, DMSO-d_6)



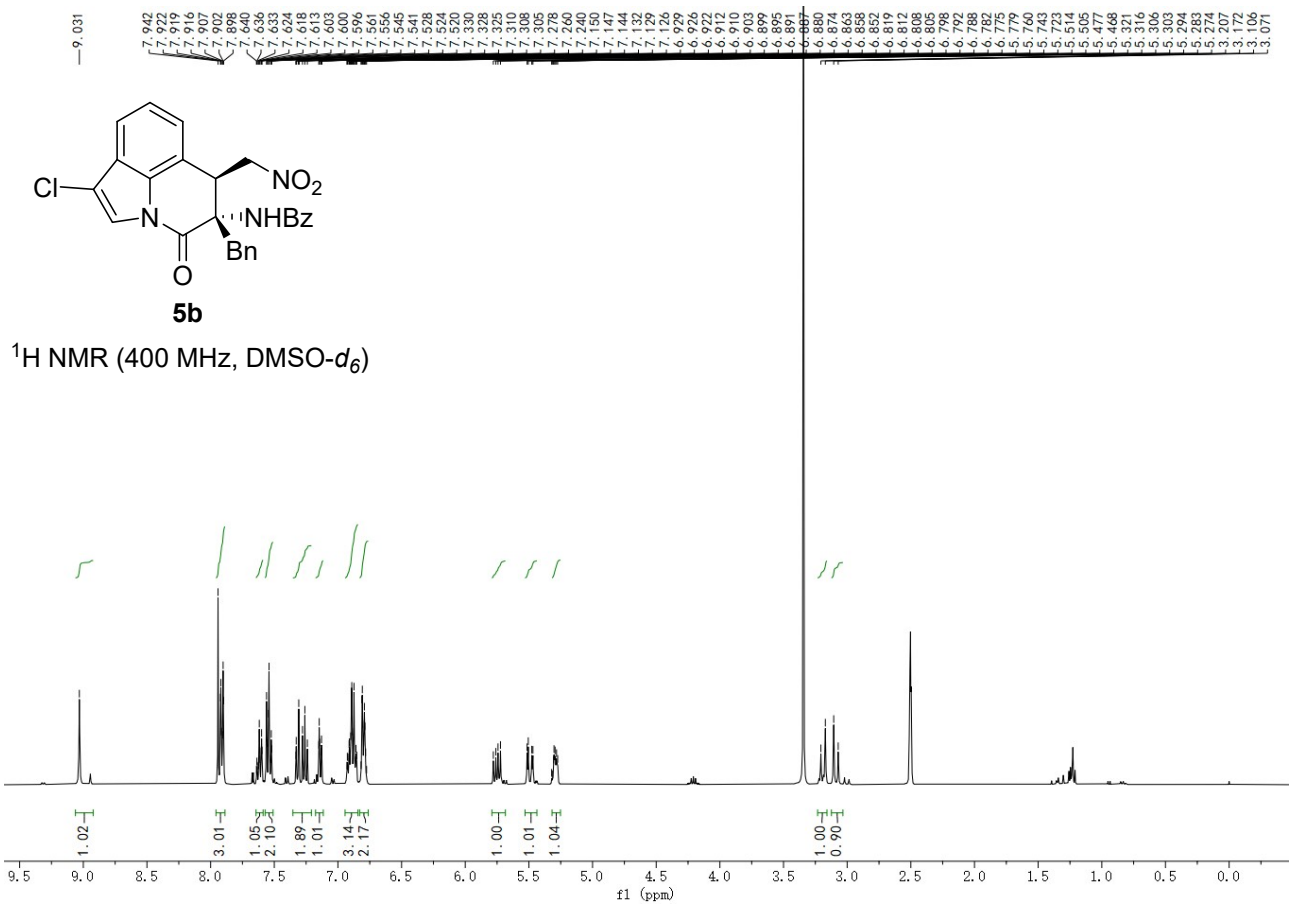
rac-**5a**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.383	7101706	294320	50.111	69.451
2	21.340	7070344	129458	49.889	30.549
Total		14172050	423778	100.000	100.000



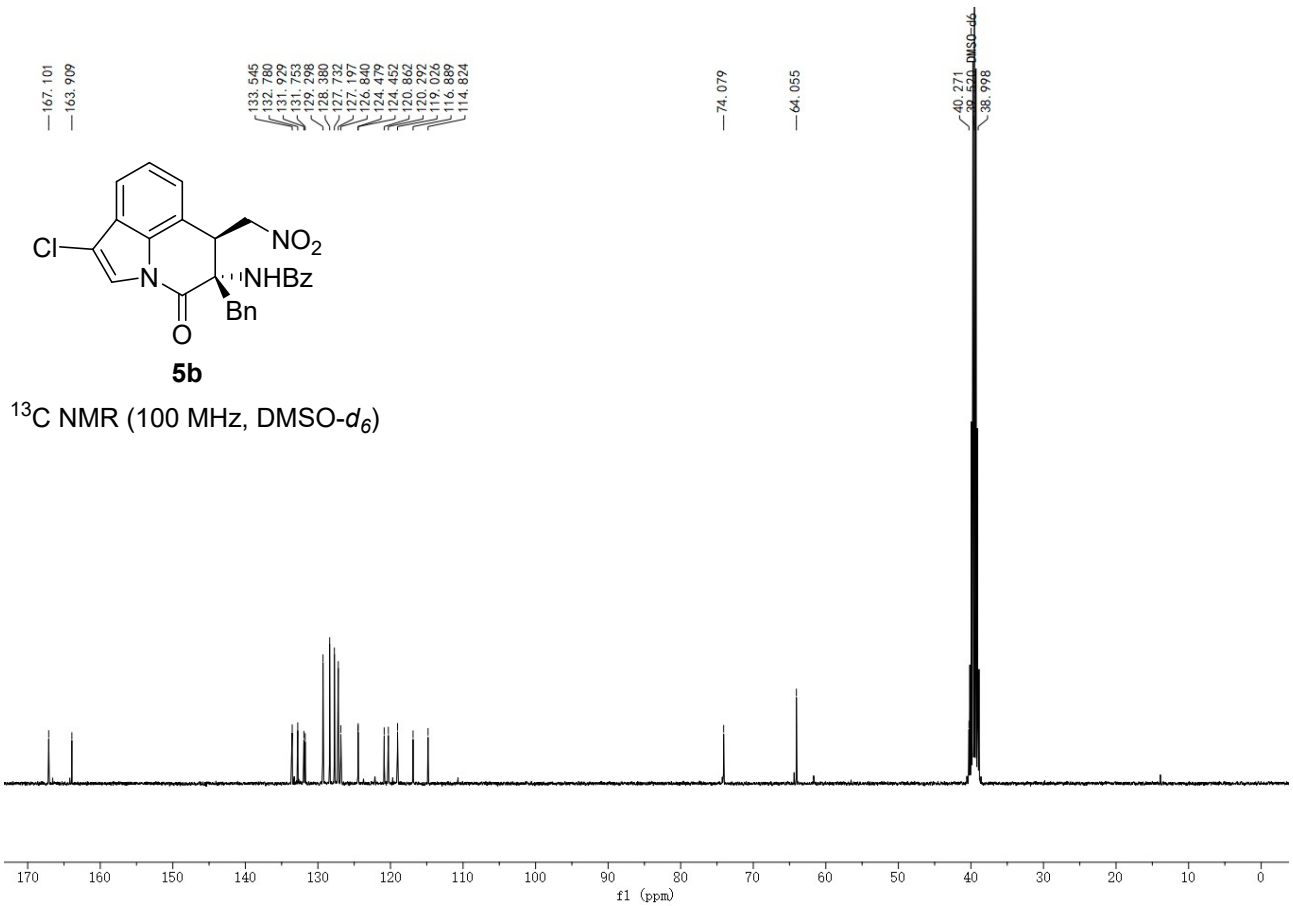
5a

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.353	9416586	391370	88.132	94.380
2	21.351	1268044	23304	11.868	5.620
Total		10684631	414674	100.000	100.000



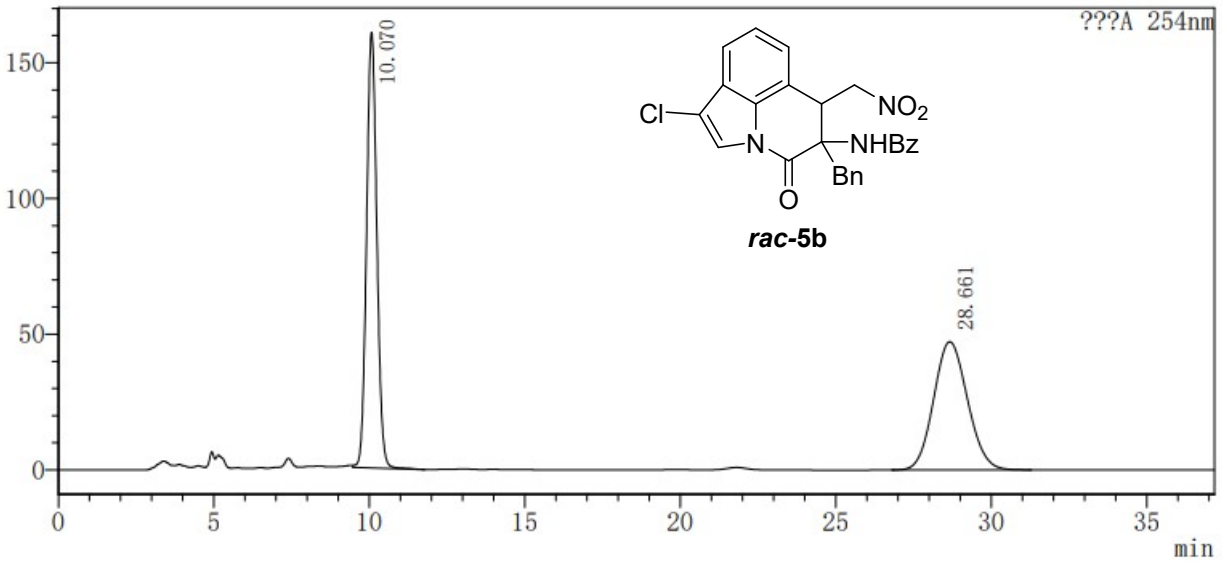
5b

^{1}H NMR (400 MHz, DMSO-d_6)



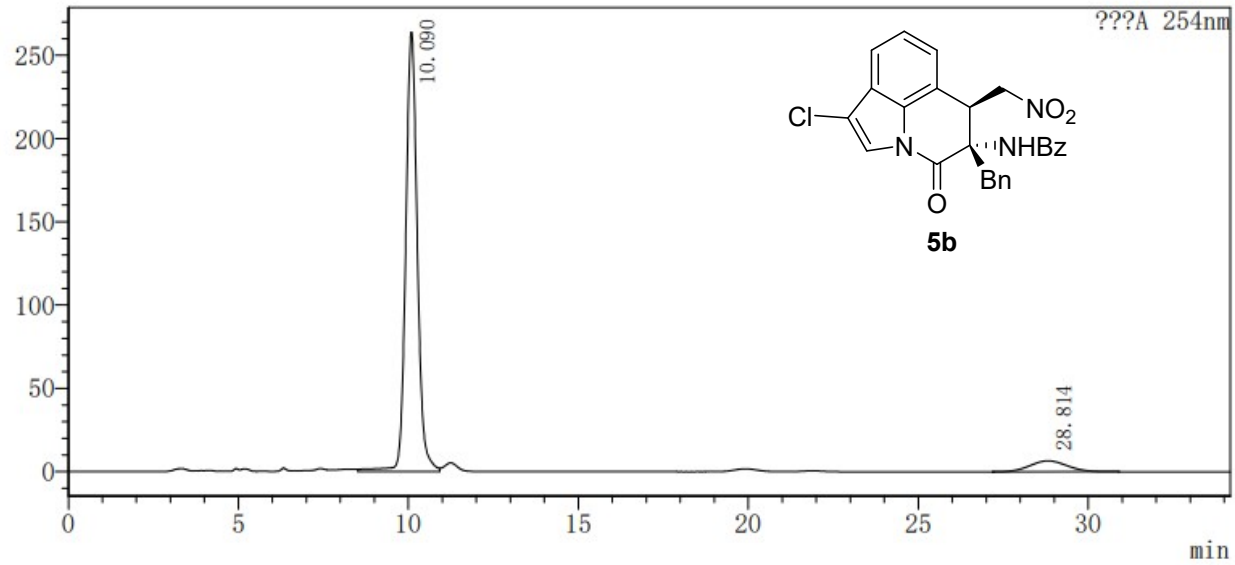
5b

^{13}C NMR (100 MHz, DMSO-d_6)



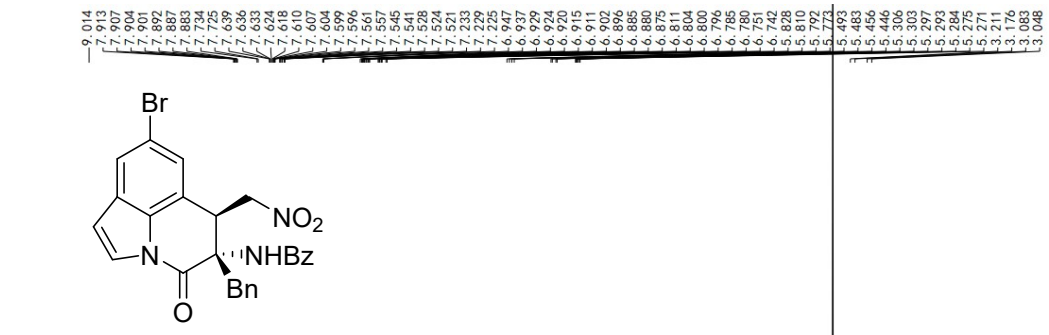
***rac*-5b**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.070	3685782	160452	50.826	77.263
2	28.661	3565999	47217	49.174	22.737
Total		7251780	207668	100.000	100.000



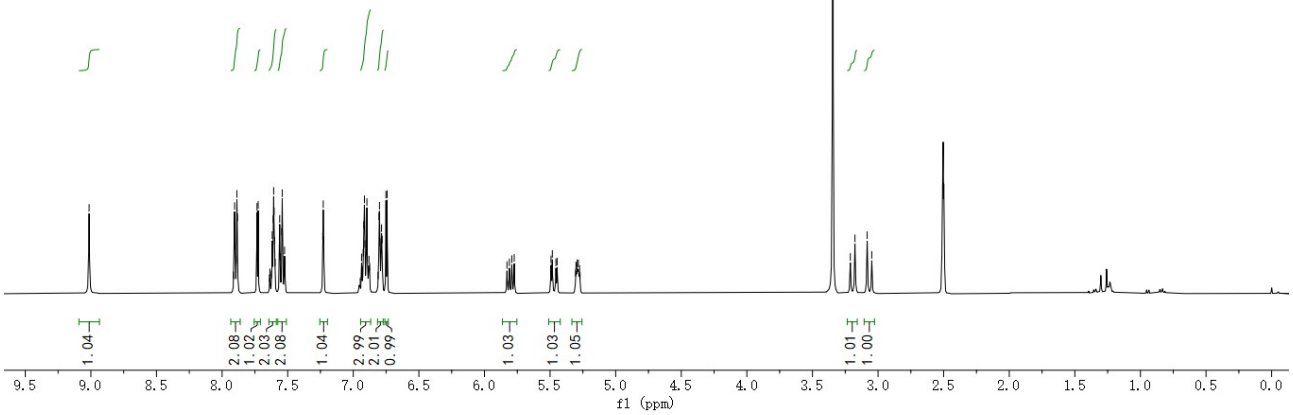
5b

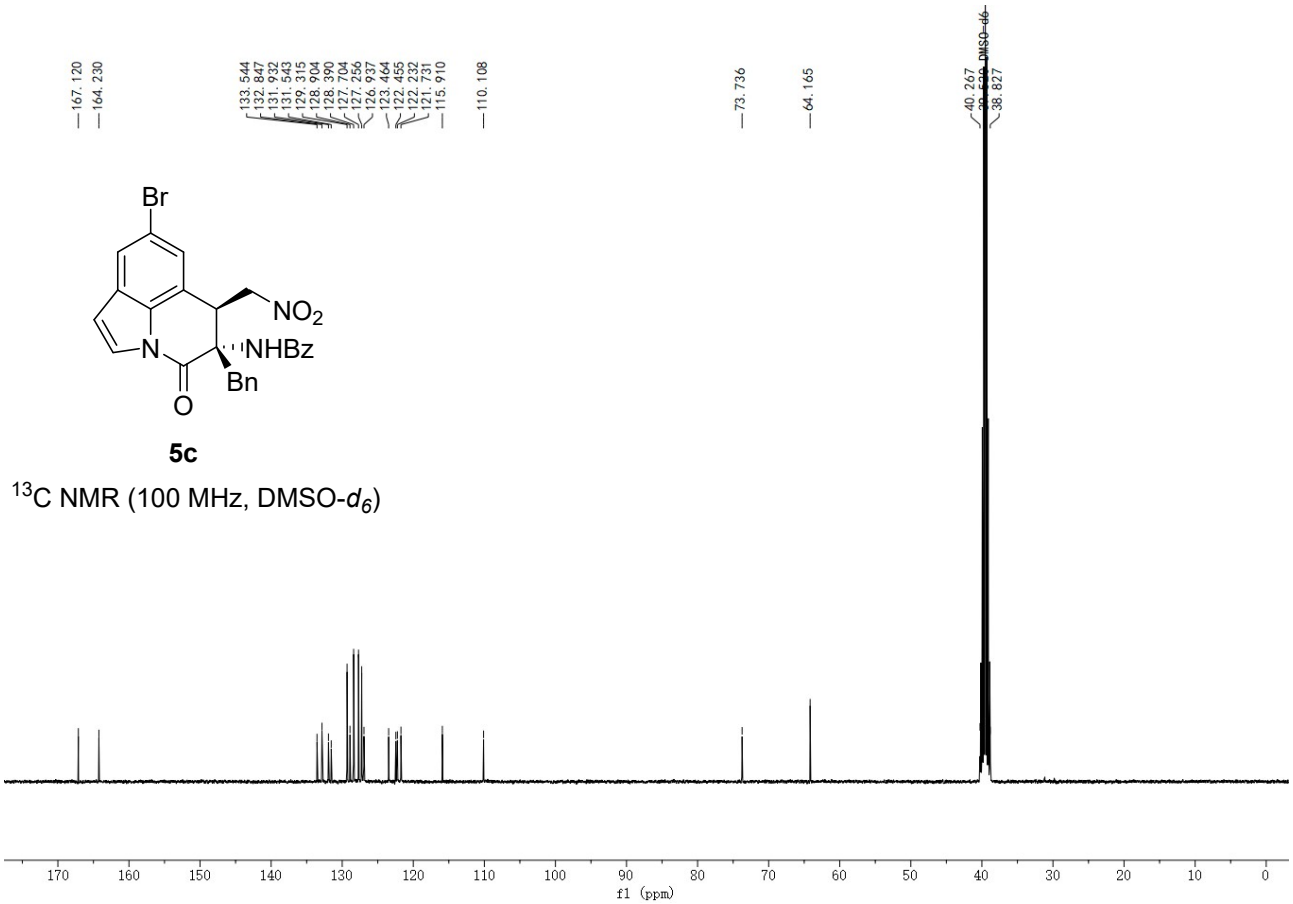
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.090	6277568	263849	92.693	97.586
2	28.814	494893	6528	7.307	2.414
Total		6772461	270377	100.000	100.000



5c

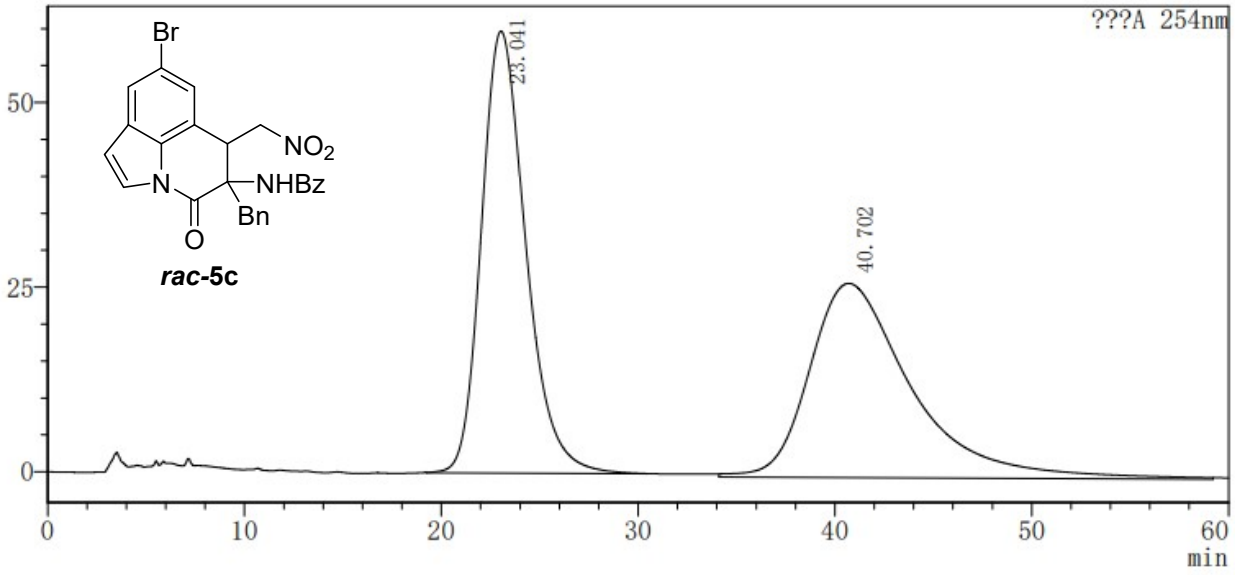
^{1}H NMR (400 MHz, DMSO-d_6)



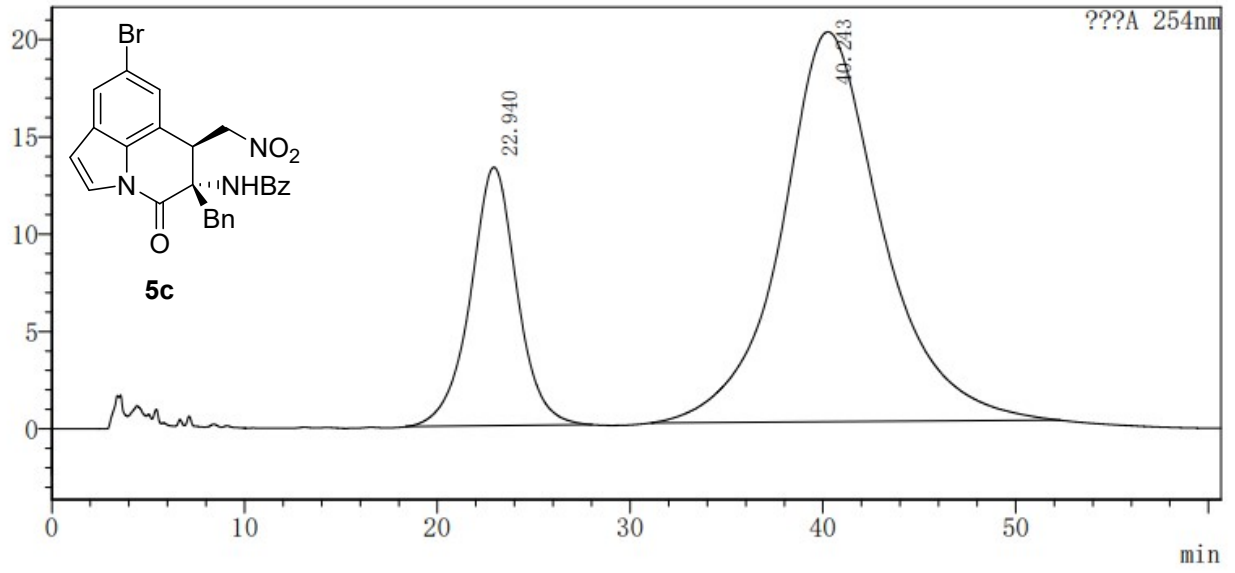


5c

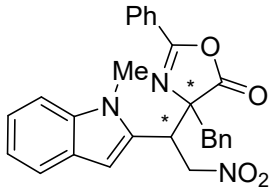
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.041	9385210	59819	49.707	69.468
2	40.702	9496008	26291	50.293	30.532
Total		18881217	86109	100.000	100.000

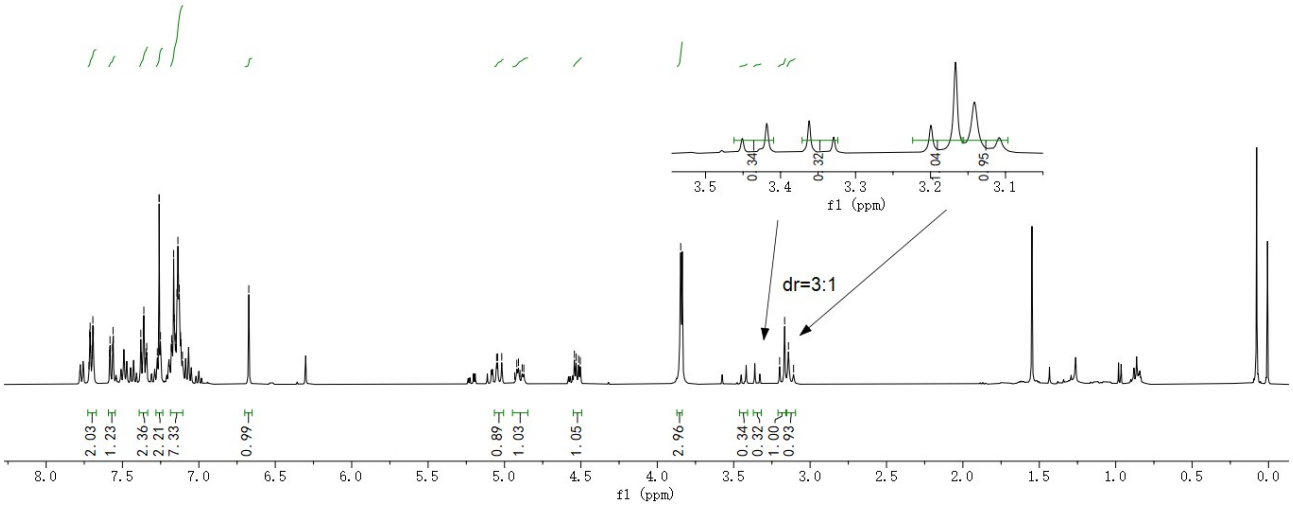


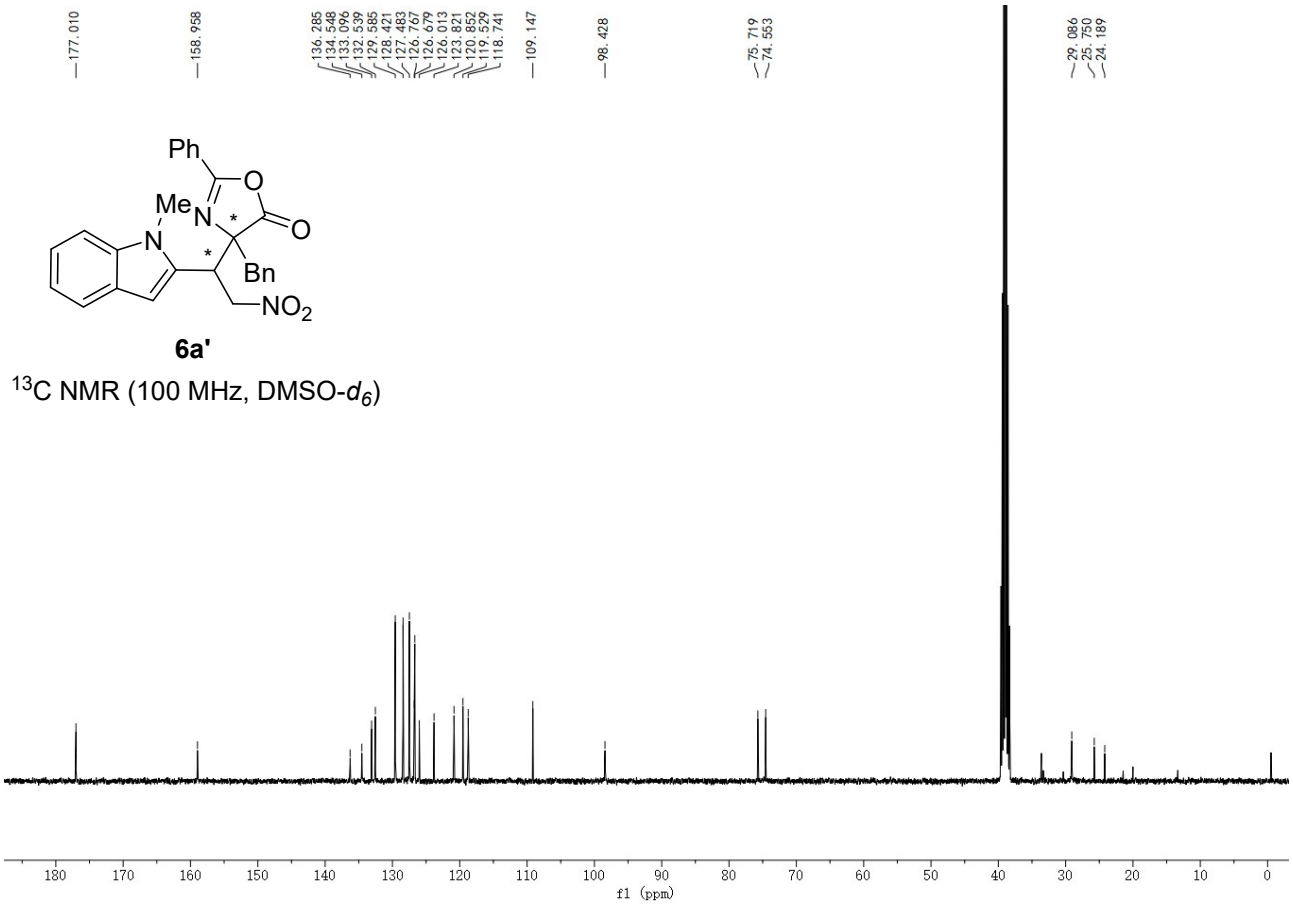
Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.940	2235851	13280	23.449	39.868
2	40.243	7298972	20030	76.551	60.132
Total		9534824	33310	100.000	100.000



6a'

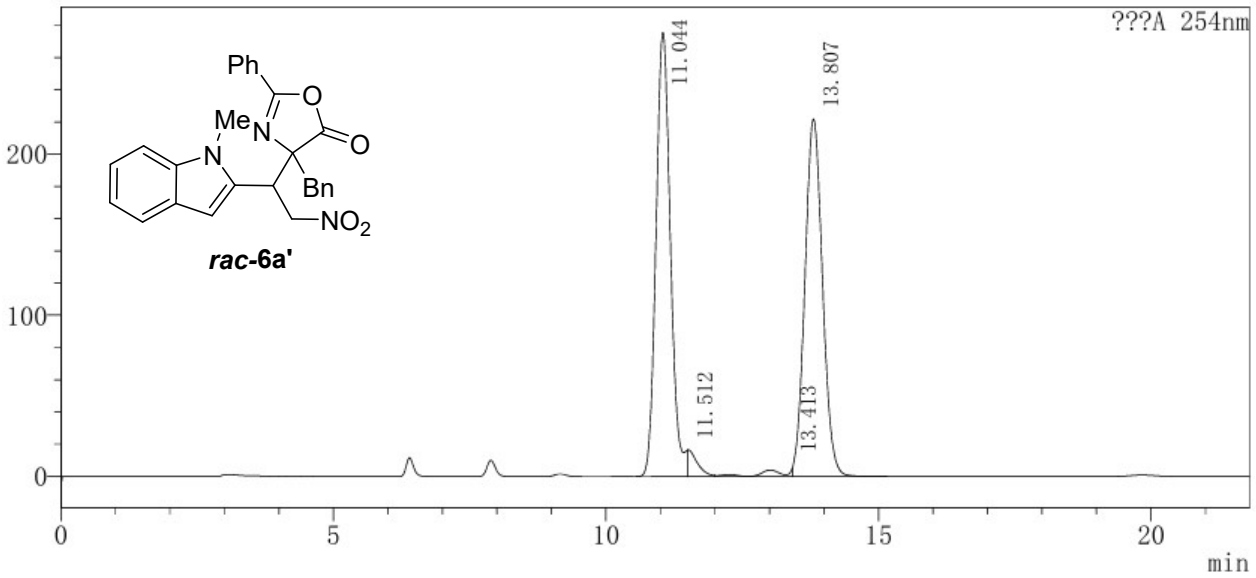
^{1}H NMR (400 MHz, $CDCl_3$)





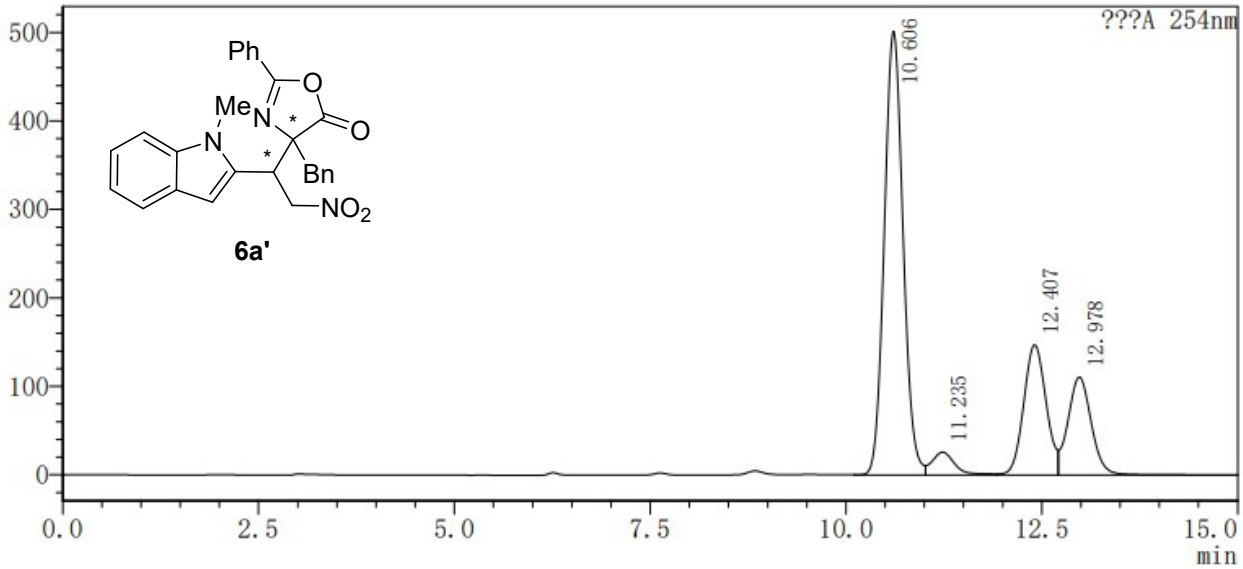
6a'

^{13}C NMR (100 MHz, DMSO-d_6)



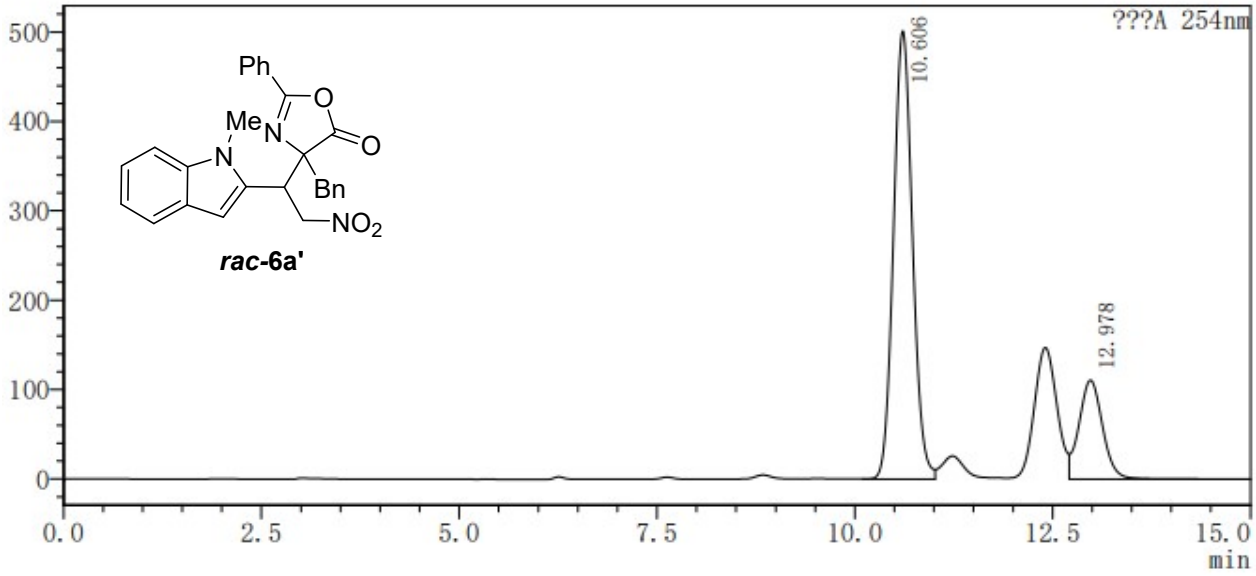
***rac*-6a'**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.044	5085196	275772	48.952	53.192
2	11.512	195067	16376	1.878	3.159
3	13.413	125099	4355	1.204	0.840
4	13.807	4982759	221940	47.966	42.809
Total		10388120	518443	100.000	100.000



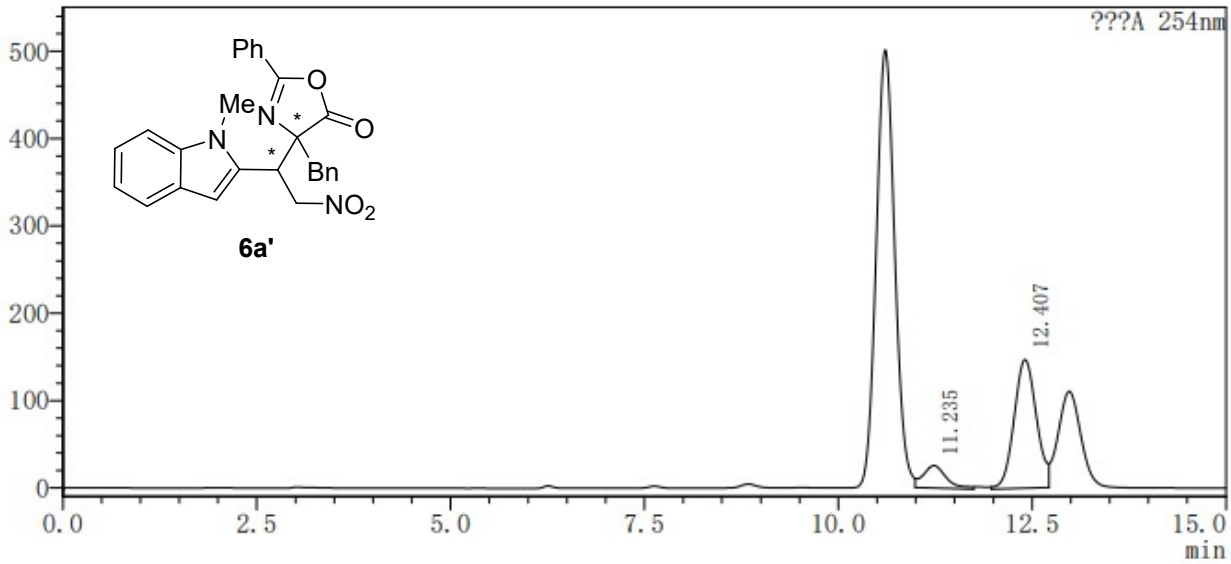
6a'

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.606	8369745	501534	59.145	63.855
2	11.235	531733	25868	3.757	3.293
3	12.407	2940676	147248	20.780	18.747
4	12.978	2309177	110780	16.318	14.104
Total		14151331	785431	100.000	100.000



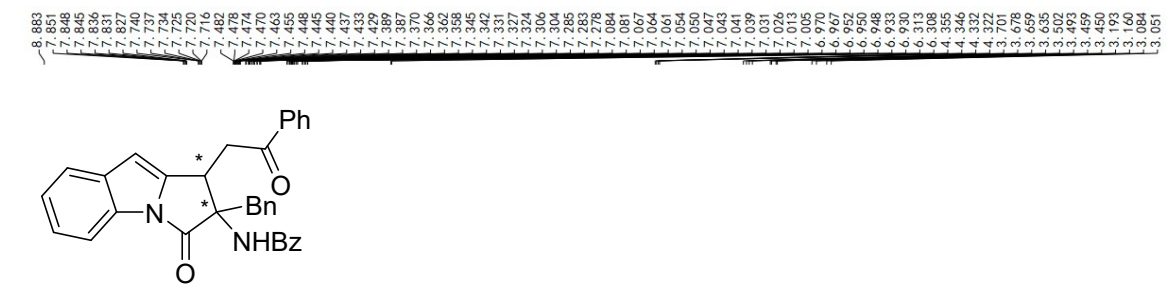
***rac*-6a'**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.606	8369745	501534	78.376	81.908
2	12.978	2309177	110780	21.624	18.092
Total		10678922	612314	100.000	100.000



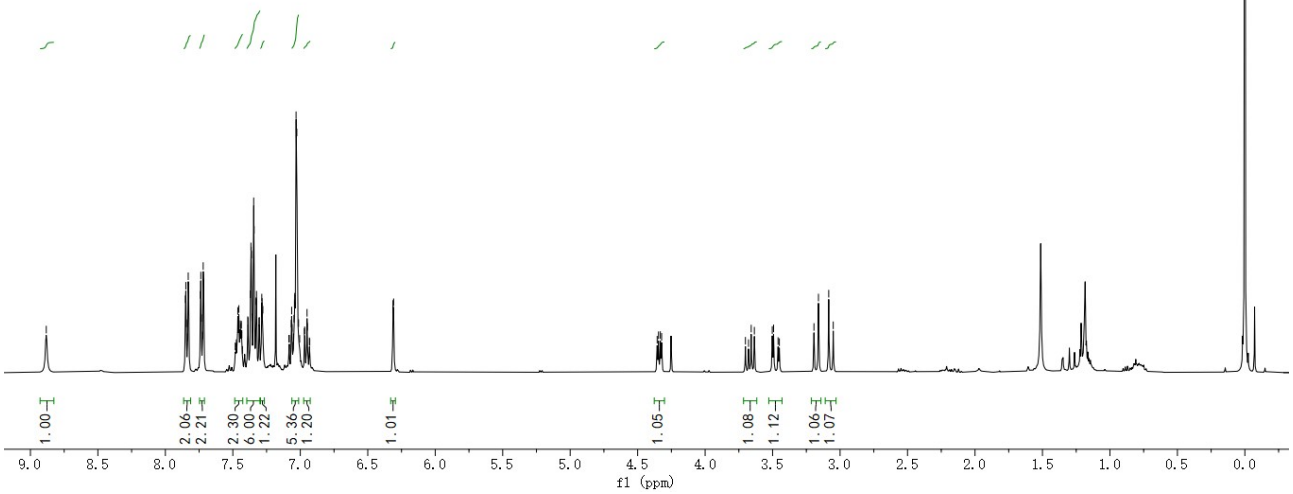
6a'

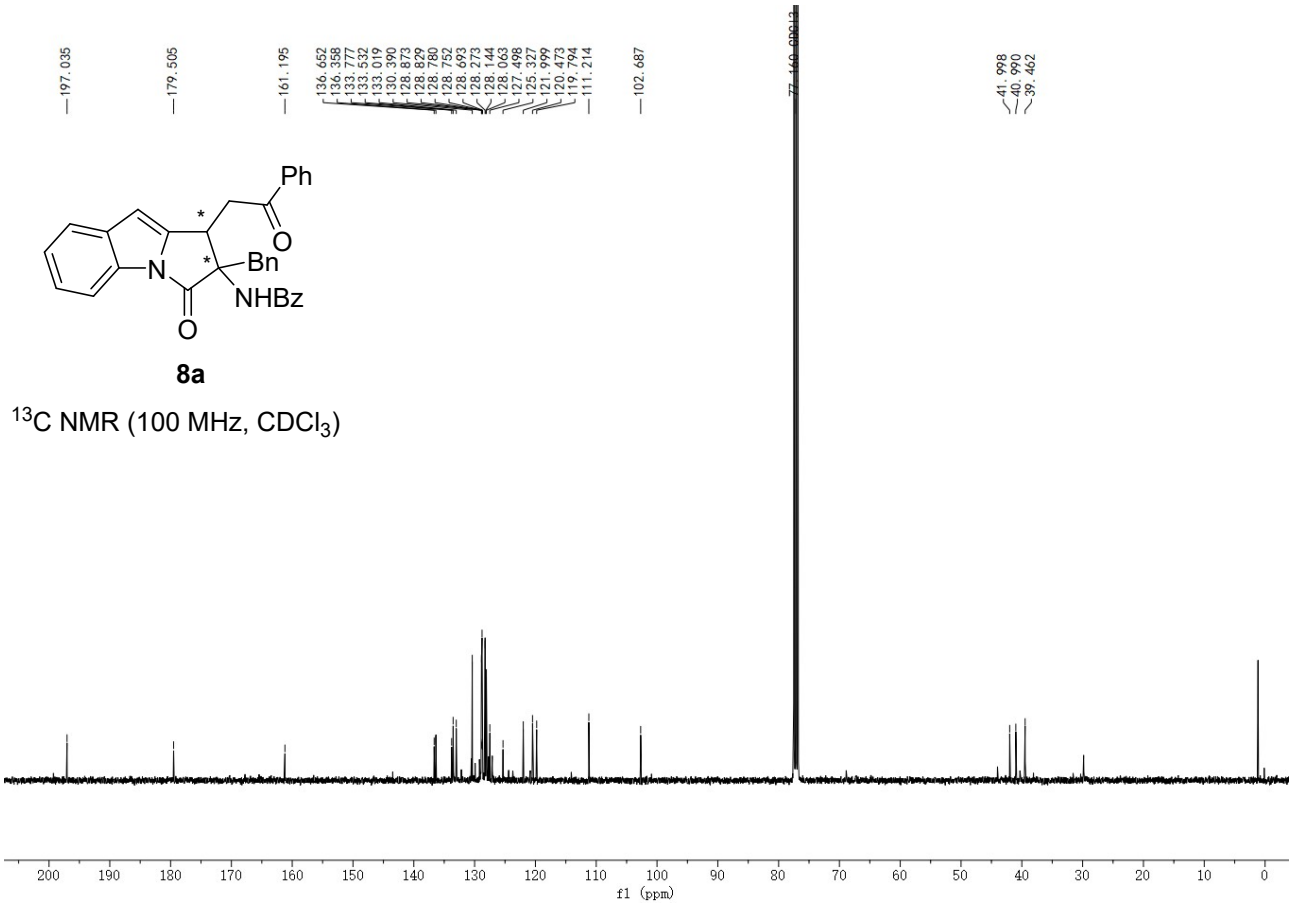
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.235	542935	25730	15.500	14.871
2	12.407	2959757	147292	84.500	85.129
Total		3502692	173022	100.000	100.000



8a

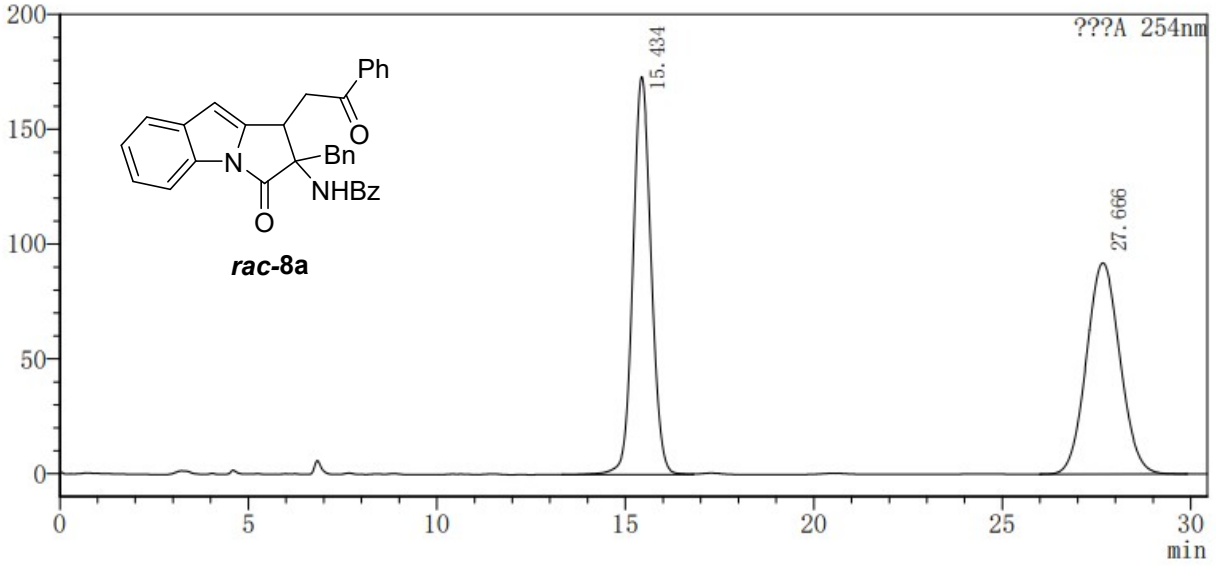
^{1}H NMR (400 MHz, $CDCl_3$)



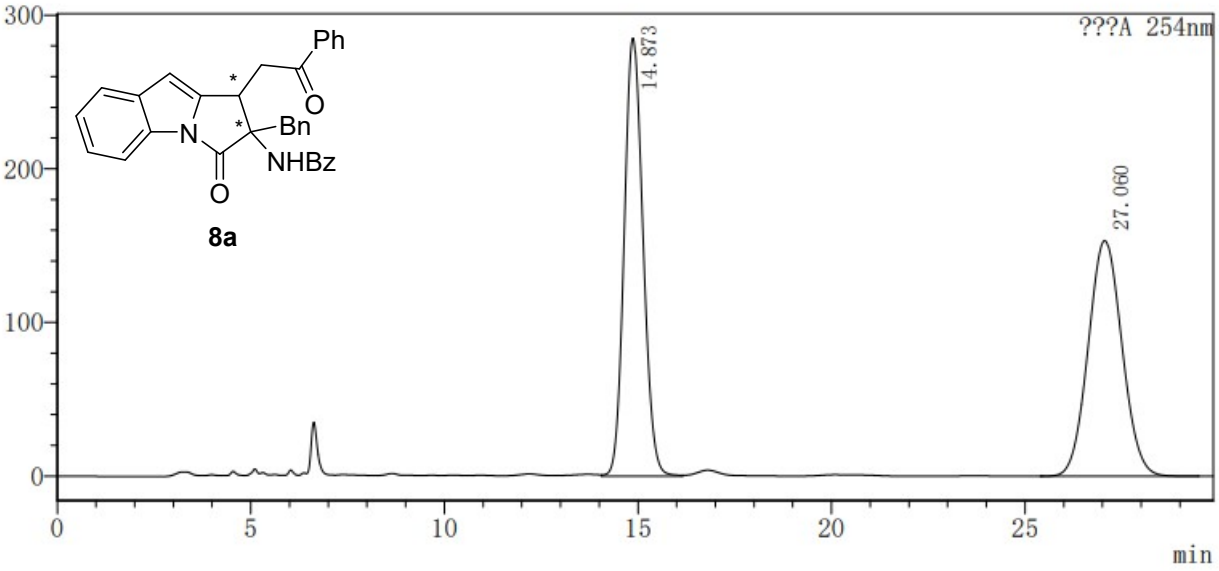


8a

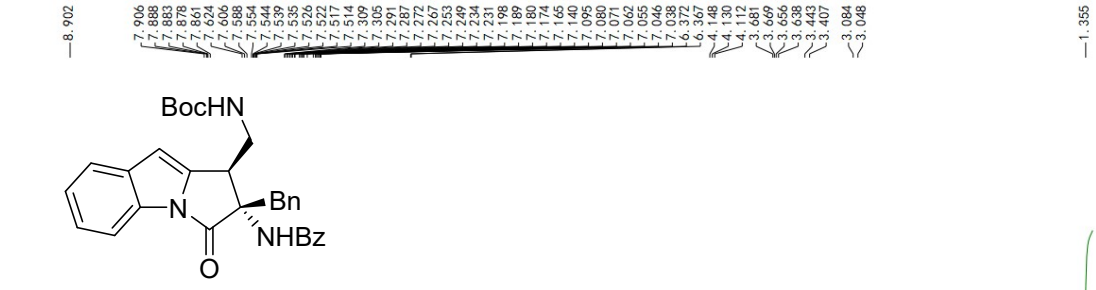
^{13}C NMR (100 MHz, $CDCl_3$)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.434	5822430	173242	50.614	65.324
2	27.666	5681104	91963	49.386	34.676
Total		11503534	265206	100.000	100.000

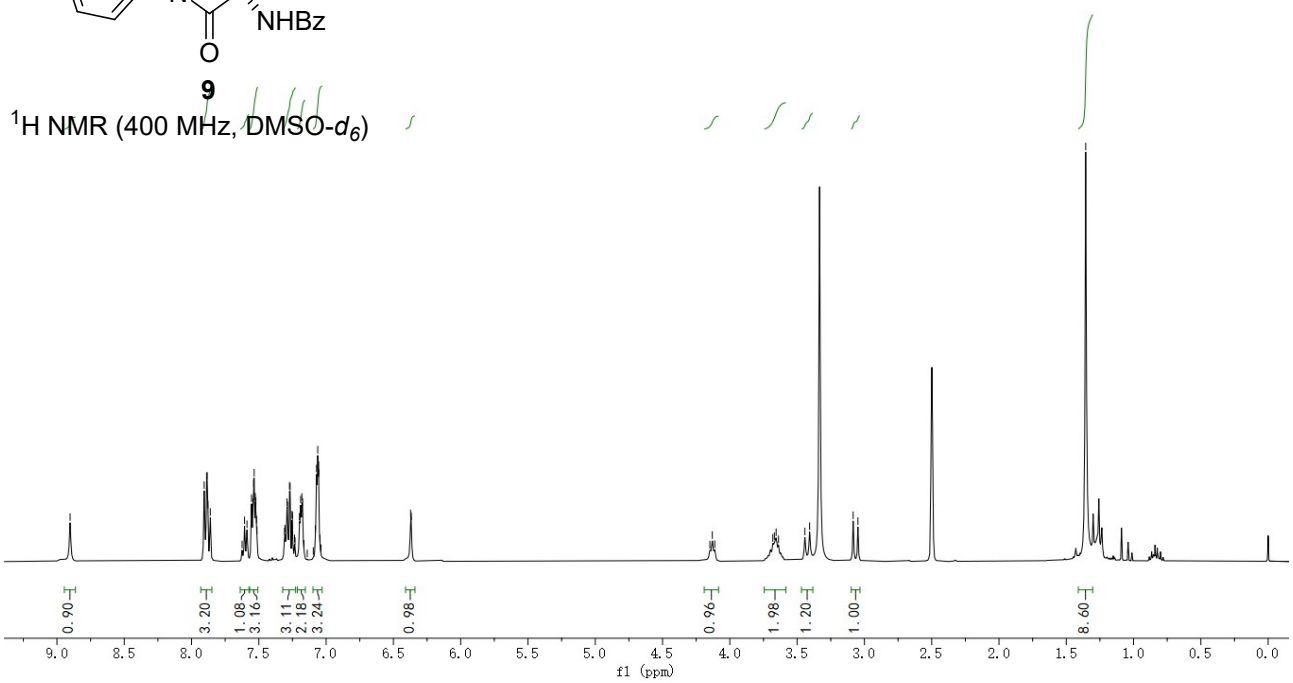


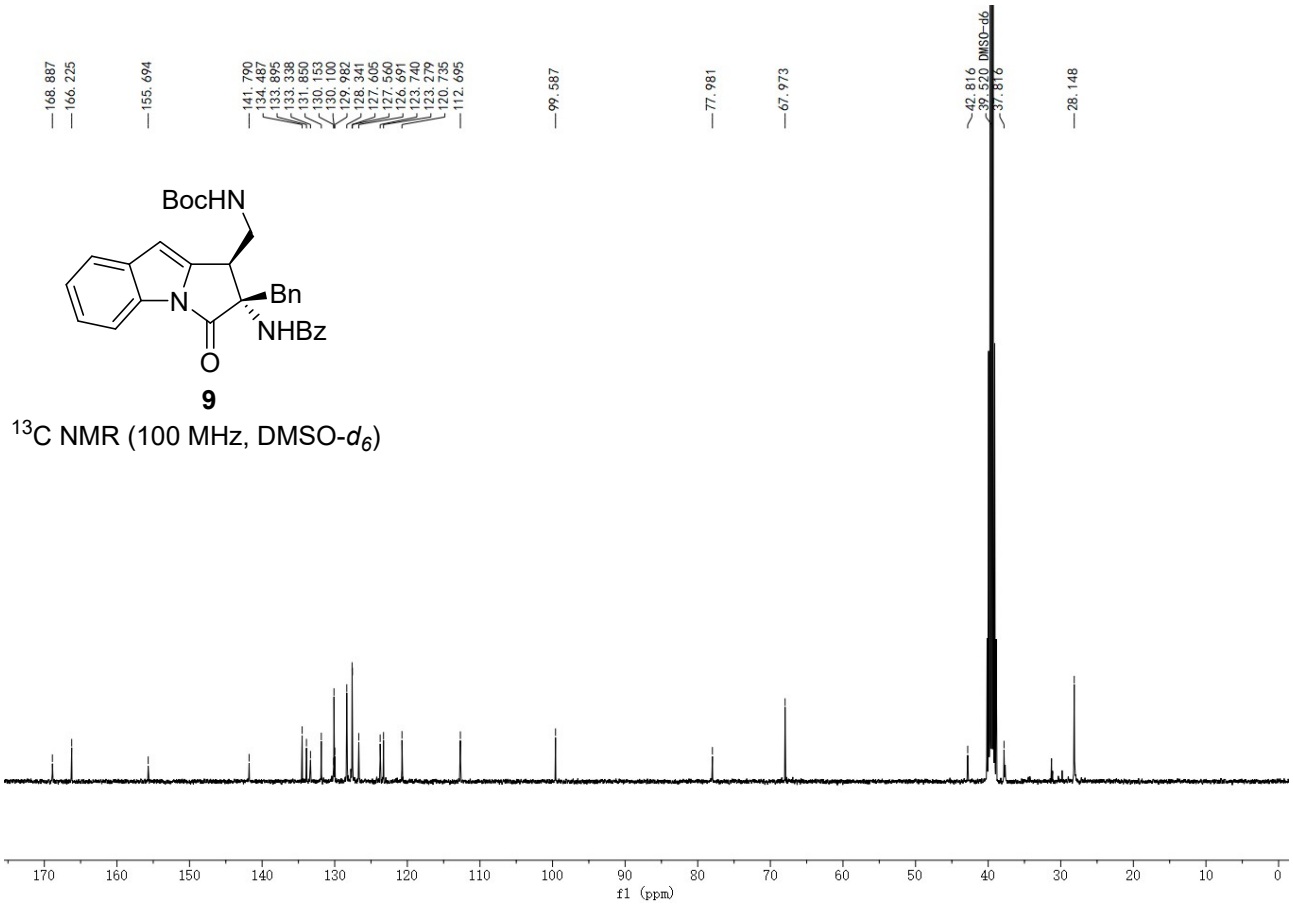
Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.873	9556465	285023	50.637	65.016
2	27.060	9315944	153367	49.363	34.984
Total		18872409	438390	100.000	100.000



9

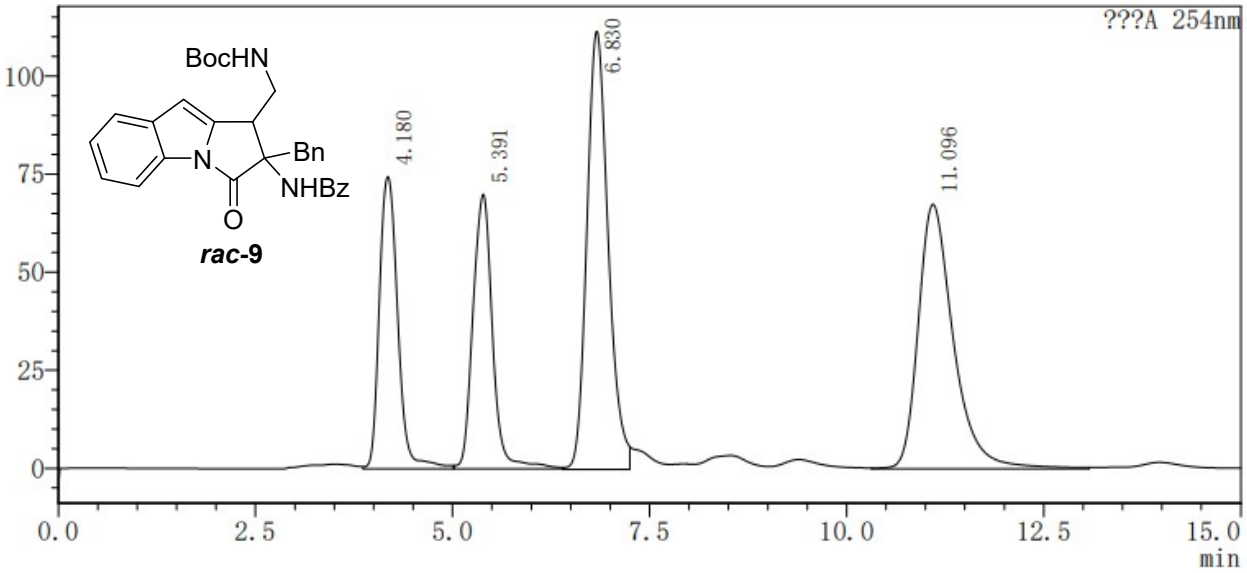
^{1}H NMR (400 MHz, DMSO-d_6)



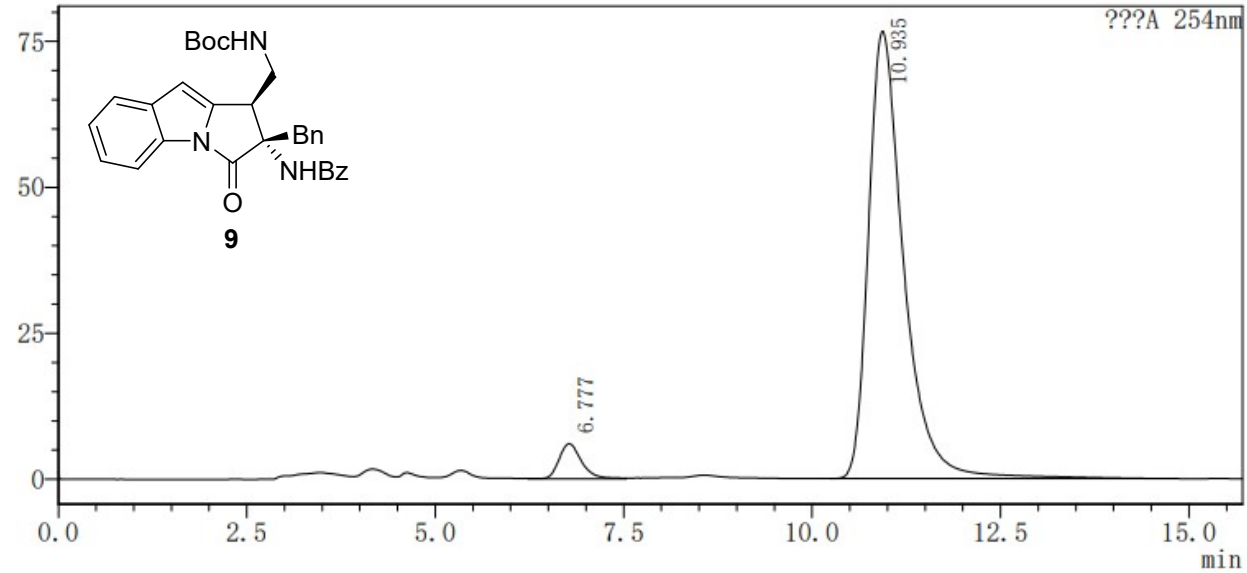


9

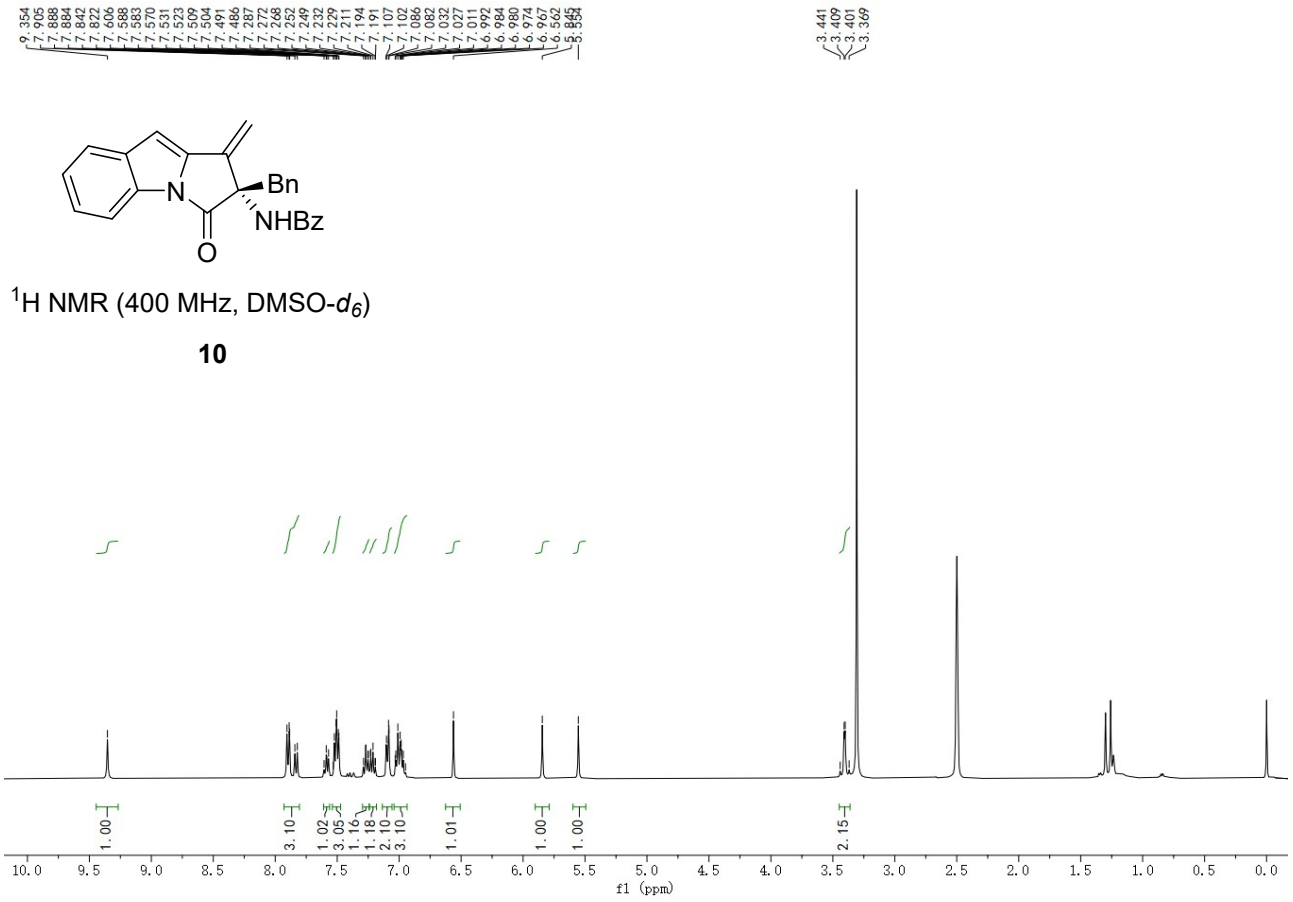
^{13}C NMR (100 MHz, DMSO-d_6)



Peak#	Ret. Time	Area	Height	Area%	Height%
1	4.180	1214175	74464	18.330	23.012
2	5.391	1209858	69987	18.265	21.628
3	6.830	2105876	111745	31.792	34.533
4	11.096	2094108	67391	31.614	20.826
Total		6624018	323586	100.000	100.000

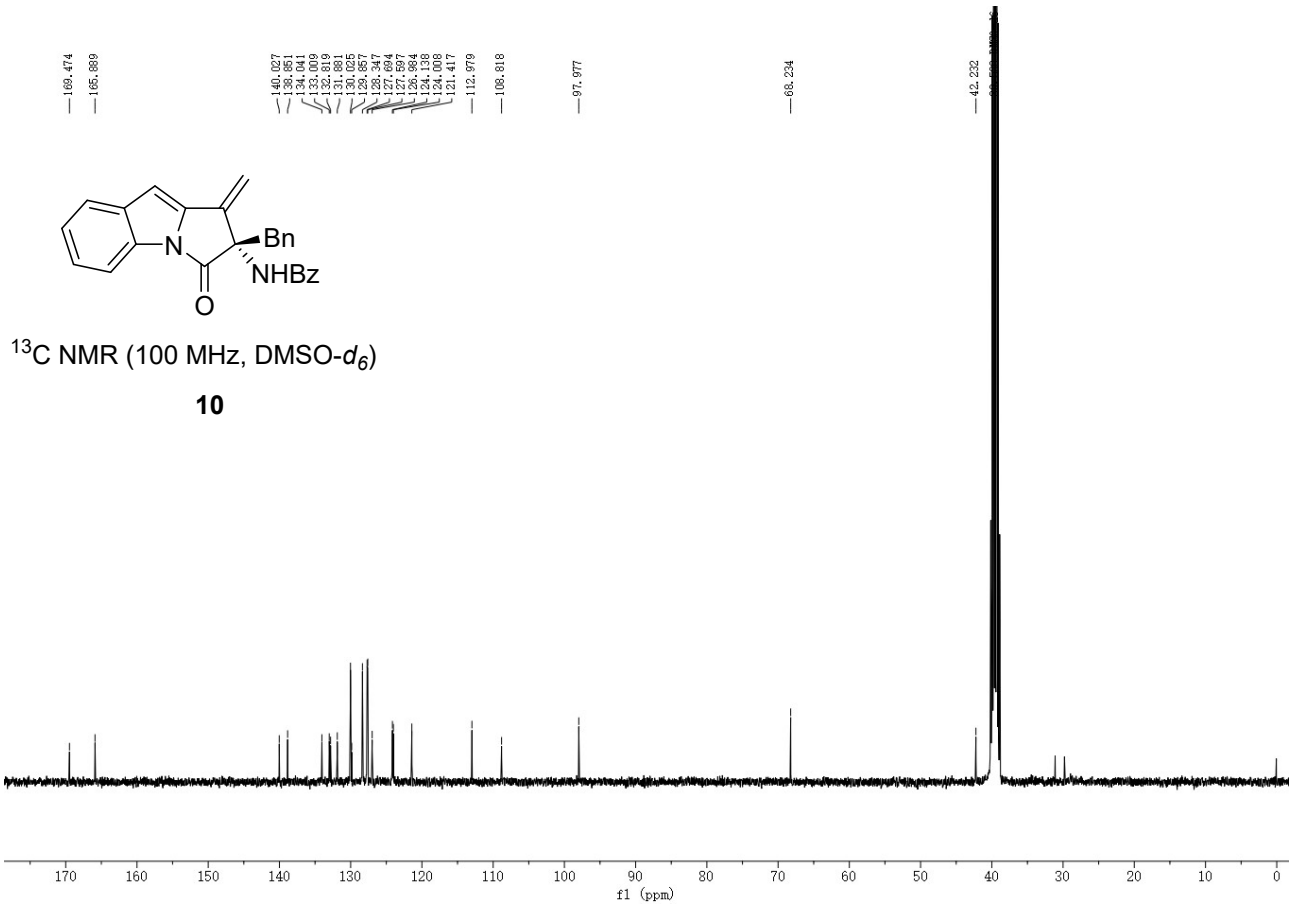


Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.777	125816	6022	4.790	7.286
2	10.935	2500869	76635	95.210	92.714
Total		2626685	82657	100.000	100.000



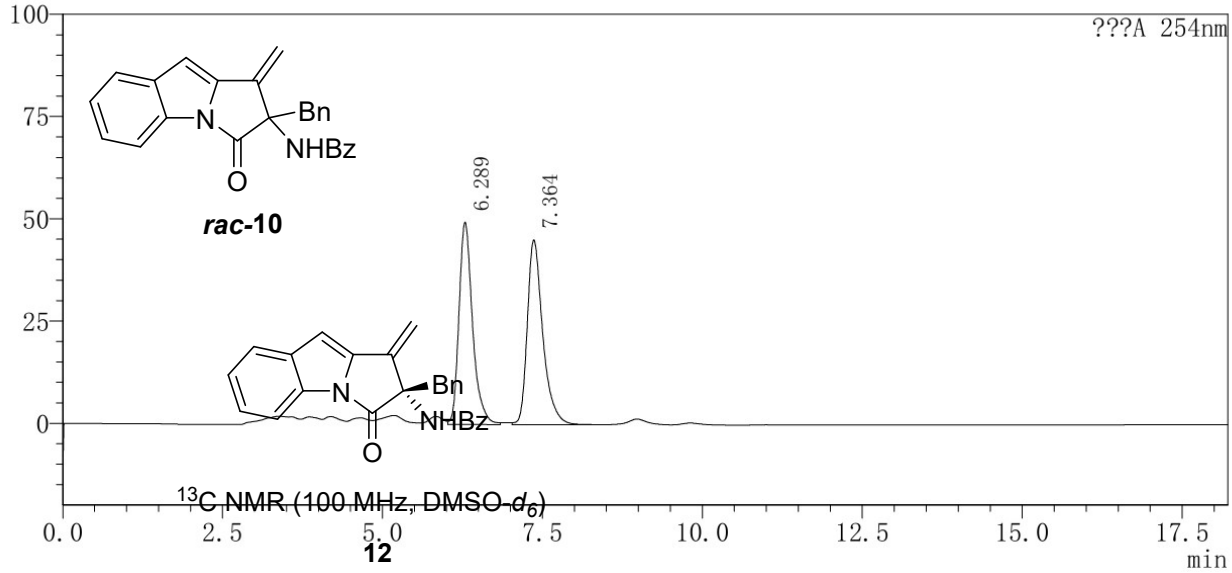
^{1}H NMR (400 MHz, DMSO-d_6)

10



^{13}C NMR (100 MHz, DMSO-d_6)

10

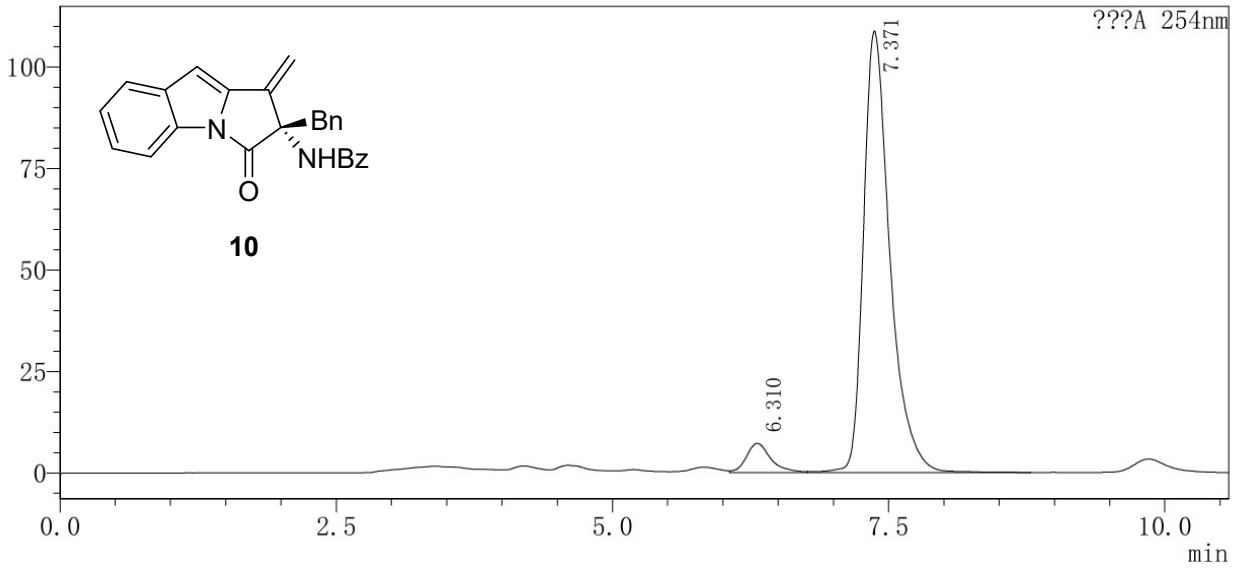


***rac*-10**

^{13}C NMR (100 MHz, DMSO-d_6)

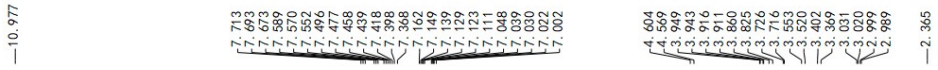
12

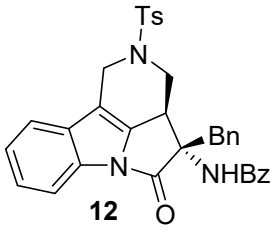
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.289	730343	49500	48.982	52.306
2	7.364	760708	45135	51.018	47.694
Total		1491050	94635	100.000	100.000



10

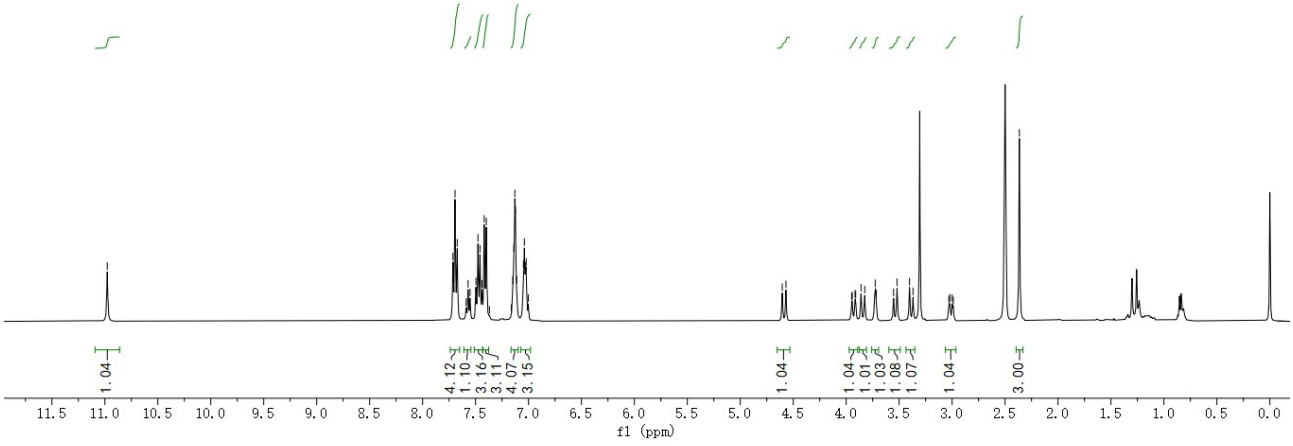
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.310	110504	7166	5.749	6.186
2	7.371	1811606	108688	94.251	93.814
Total		1922110	115854	100.000	100.000

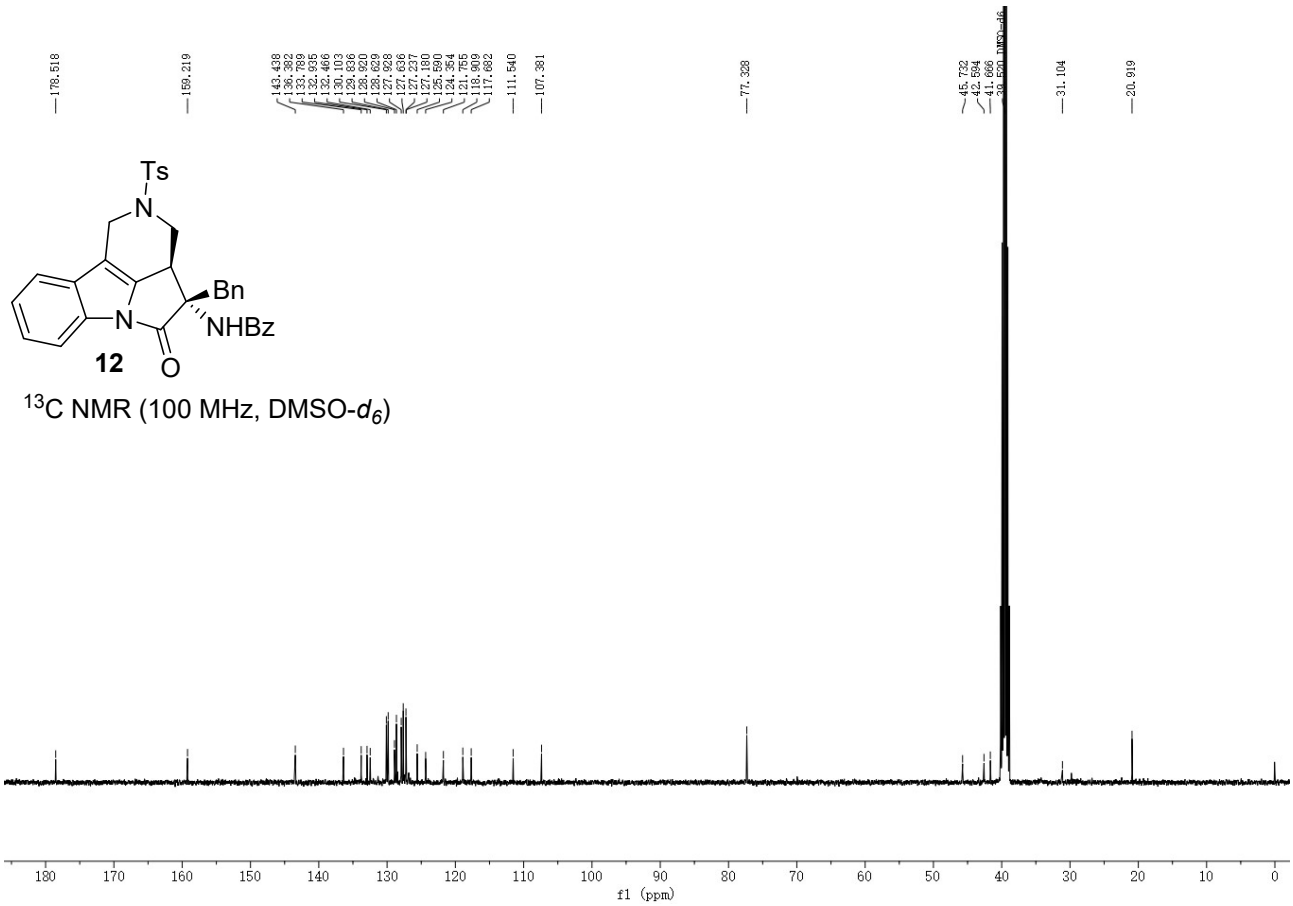




12

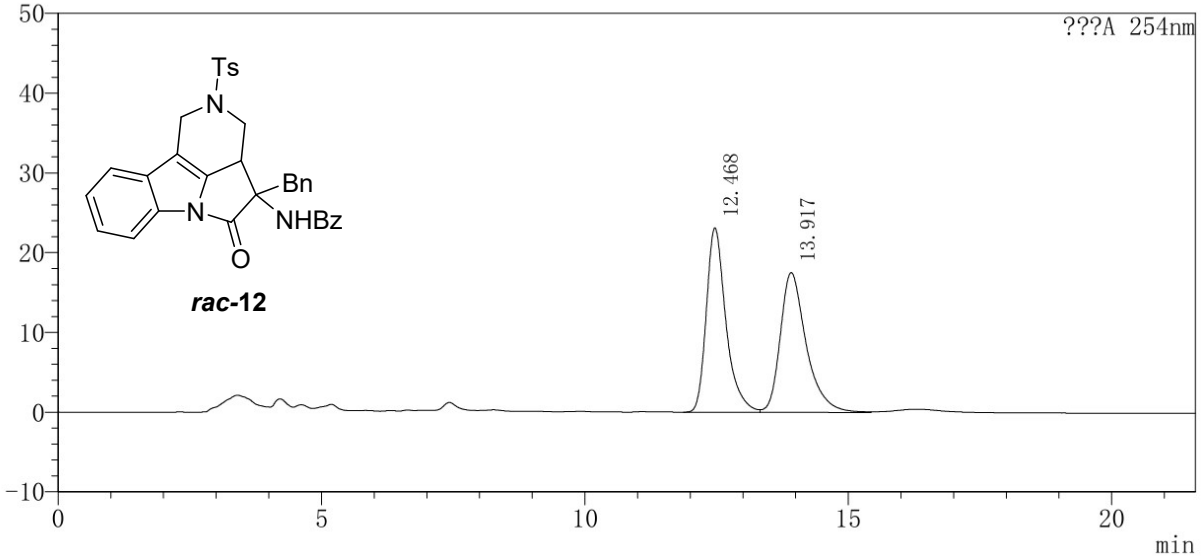
^{1}H NMR (400 MHz, DMSO-d_6)





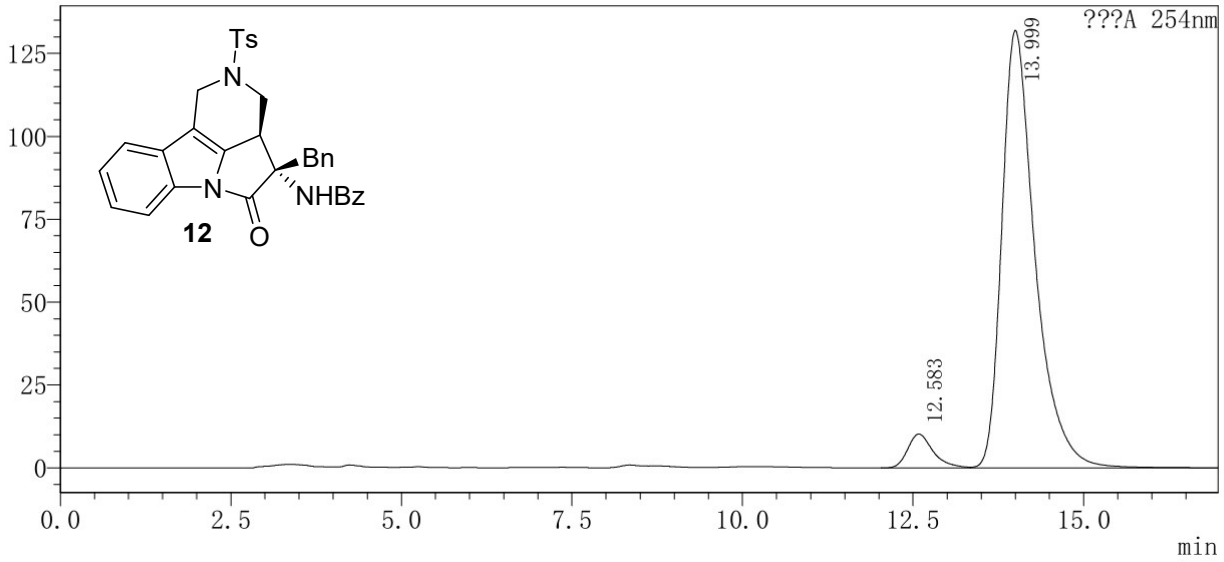
12

^{13}C NMR (100 MHz, DMSO-d_6)



***rac*-12**

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.468	599871	23115	49.971	56.870
2	13.917	600564	17530	50.029	43.130
Total		1200434	40646	100.000	100.000



Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.583	266301	10217	5.622	7.185
2	13.999	4470429	131976	94.378	92.815
Total		4736730	142192	100.000	100.000