Asymmetric Assembly of 2-Oxindole and α-Angelica Lactone Units to Construct Vicinal Quaternary Chiral Centers

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Supplementary Information

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1. General Methods

NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate, acetone, ethyl ether and petroleum ether (PE) (EtOAc/PE, Acetone/PE or ethyl ether/PE). ^{1}H NMR spectra were recorded at 400 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 MHz (Varian). Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.27 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. Optical rotations were measured at 589 nm at 20 ºC. Enantiomeric excess was determined by HPLC analysis on Chiralpak AD, AS and Chiralcel OD columns. Mesitylene was distilled from CaH_2. All other chemicals were used without purification as commercially available. Catalysts **1a**–**1f**[1] were prepared according to the literature procedures. Morita−Baylis−Hillman carbonates of isatins[2] and α-angelica lactone[3] were prepared according to the literature procedures.

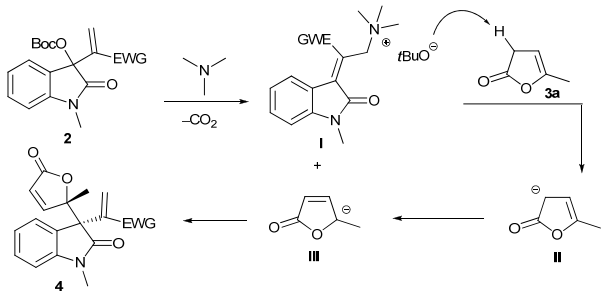
(1) (*a*) H. Waldmann, V. Khedkar, H. Dückert, M. Schürmann, I. M. Oppel and K. Kumar, *Angew. Chem., Int. Ed.* 2008, **47**, 6869; (*b*) J. Peng, X. Huang, L. Jiang, H.-L. Cui and Y.-C. Chen, *Org. Lett.*, 2011, **13**, 4584.

(2) Y. M. Chung, Y. J. Im and J. N. Kim, *Bull. Korean Chem. Soc.* 2002, **23**, 1651.

(3) J. A. Marshall, M. A. Wolf and E. M. Wallace, *J. Org. Chem.* 1997, **62**, 367.

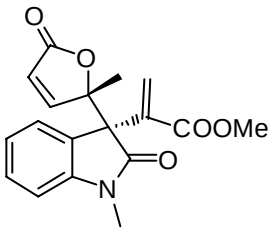
2. The proposed catalytic mechanism

As showing in the following scheme, the tertiary amine catalyst could attack the MBH carbonate **2**, which would generate the ammonium ion **I** and *t*-butoxy anion. Subsequently, the strong Brønsted base would deproton the acidic C-H of α-angelica lactone **3a**, affording the anion **II**. Then, the isomerized anion **III** would attack the electrophilic ion **I** to deliver the allylic product **4** after the elimination of the tertiary amine catalyst.

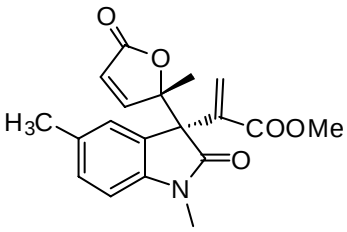


3. General procedure for assembly of MBH carbonates and α-angelica lactone

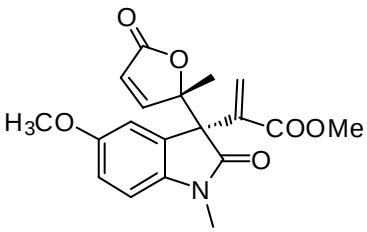
To a solution of MBH carbonate **2** (34.7 mg, 0.1 mmol), α-angelica lactone **3a** (19.6 mg, 0.2 mmol), 4Å MS (20 mg) and R-BINOL (3.0 mg) in mesitylene (0.5 mL) was added catalyst **1a** (3.2 mg, 10 mol%) at -10 °C. The mixture was kept at the temperature until the consumption of **2a**, which was monitored by TLC analysis. Purification by flash chromatography on silica gel (AcOEt/petroleum ether = 1:5) gave **4**.



4a, 80% yield; $[\alpha]_D^{20}$ = +8.5 (*c* = 0.4 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 26.532 min, t (minor) = 18.793 min,]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 5.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 5.70 (d, *J* = 5.6 Hz, 1H), 3.62 (s, 3H), 3.29 (s, 3H), 1.88 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.6, 171.6, 165.6, 157.1, 143.6, 136.9, 131.1, 129.2, 127.1, 125.0, 122.7, 122.4, 108.1, 89.7, 59.9, 52.3, 26.6, 19.1 ppm; ESI-HRMS: calcd. for $C_{18}H_{17}NO_5$+Na 350.1004, found 350.1002.

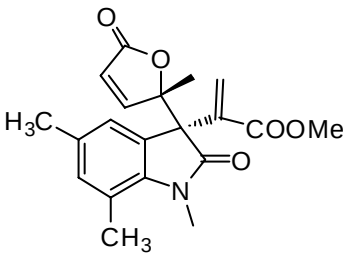


4d, 90% yield; $[\alpha]_D^{20}$ = +41.0 (*c* = 0.4 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 15.910 min, t (minor) = 8.967 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 5.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 6.82 (s, 1H), 6.74 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 5.6 Hz, 1H), 3.62 (s, 3H), 3.26 (s, 3H), 2.24 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 171.6, 165.7, 157.2, 141.1, 137.0, 132.3, 131.0, 129.5, 127.1, 125.8, 122.4, 107.8, 89.7, 60.0, 52.3, 26.6, 21.0, 19.1 ppm; ESI-HRMS: calcd. for $C_{19}H_{19}NO_5$+Na 364.1161, found 364.1156.

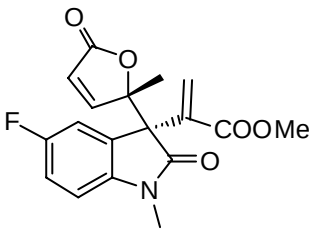


4e, 90% yield; $[\alpha]_D^{20}$ = +26.8 (*c* = 0.5 in $CHCl_3$); 89% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 18.740 min, t (minor) = 11.663 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, *J* = 5.6 Hz, 1H), 6.81 (s, 1H), 6.77 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 6.74 (s, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.70 (d, *J* = 5.6 Hz, 1H), 3.69 (s, 3H), 3.61 (s, 3H), 3.24 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C

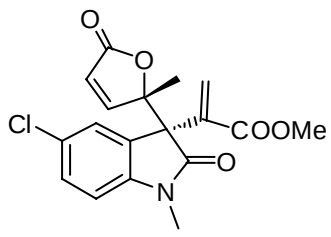
NMR (100 MHz, $CDCl_3$): δ = 175.2, 171.7, 165.6, 157.3, 155.7, 136.9, 131.2, 128.3, 122.4, 114.7, 111.3, 108.6, 89.6, 60.2, 55.7, 52.3, 26.7, 19.1 ppm; ESI-HRMS: calcd. for $C_{19}H_{19}NO_6$+Na 380.1110, found 380.1109.



4f, 88% yield; $[\alpha]_D^{20}$ = +27.2 (*c* = 0.5 in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 12.660 min, t (minor) = 6.586 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 5.6 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 2.8 Hz, 2H), 5.70 (d, *J* = 5.6 Hz, 1H), 3.63 (s, 3H), 3.52 (s, 3H), 2.49 (s, 3H), 2.18 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 171.6, 165.7, 157.3, 138.8, 137.2, 133.5, 131.9, 130.8, 127.6, 123.7, 122.3, 119.1, 89.7, 59.5, 52.2, 23.0, 20.6, 19.2, 18.8 ppm; ESI-HRMS: calcd. for $C_{20}H_{21}NO_5$+Na 378.1317, found 378.1316.

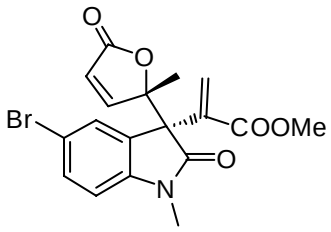


4g, 80% yield; $[\alpha]_D^{20}$ = +8.0 (*c* = 0.2 in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 13.872 min, t (minor) = 8.391 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 5.6 Hz, 1H), 6.96 (td, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.89 (dd, *J* = 8.0 Hz, 2.4Hz, 1H), 6.83 (s, 1H), 6.77 (s, 1H), 6.73 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 5.75 (d, *J* = 5.6 Hz, 1H), 3.64 (s, 3H), 3.27 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.2, 171.2, 165.5, 158.8 (d, $^1J_{C,F}$ = 240.8 Hz), 157.0, 139.6, 136.6, 131.6, 128.8 (d, $^3J_{C,F}$ = 8.4 Hz), 122.5, 115.6 (d, $^2J_{C,F}$ = 23.6 Hz), 113.2 (d, $^2J_{C,F}$ = 25.0 Hz), 108.6 (d, $^3J_{C,F}$ = 8.0 Hz), 89.4, 60.1, 52.4, 26.8, 19.2 ppm; ESI-HRMS: calcd. for $C_{18}H_{16}FNO_5$+Na 368.0910, found 368.0903.

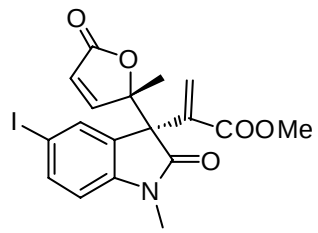


4h, 83% yield; $[\alpha]_D^{20}$ = +45.2 (*c* = 0.4 in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 28.473 min, t (minor) = 16.415 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 5.6 Hz, 1H), 6.84 (s, 1H), 6.78 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H),

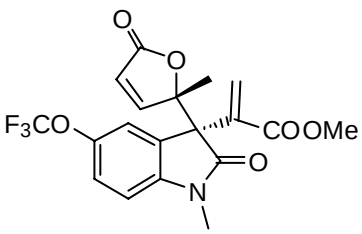
5.76 (d, *J* = 5.6 Hz, 1H), 3.64 (s, 3H), 3.27 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.2, 171.1, 165.5, 156.8, 142.2, 136.5, 131.7, 129.2, 128.8, 128.0, 125.4, 122.7, 109.0, 89.3, 52.4, 26.8, 25.3, 19.2 ppm; ESI-HRMS: calcd. for $C_{18}H_{16}ClNO_5$+Na 384.0615, found 384.0612.



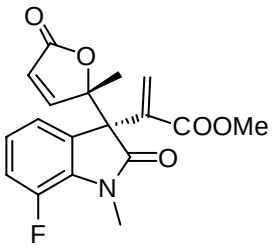
4i, 91% yield; $[\alpha]_D^{20}$ = +61.0 (*c* = 0.5 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 21.370 min, t (minor) = 11.016 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 7.03 (d, *J* = 5.6 Hz, 1H), 6.81 (s, 1H), 6.75 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.74 (d, *J* = 5.6 Hz, 1H), 3.62 (s, 3H), 3.24 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 171.1, 165.5, 156.7, 142.7, 136.5, 132.1, 131.7, 129.1, 128.1, 122.7, 115.2, 109.5, 89.2, 60.0, 52.4, 26.7, 19.1 ppm; ESI-HRMS: calcd. for $C_{18}H_{16}BrNO_5$+Na 428.0110, found 428.0112.



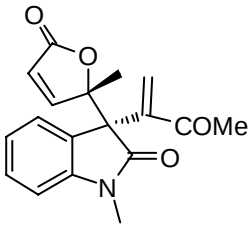
4j, 90% yield; $[\alpha]_D^{20}$ = +60.6 (*c* = 0.5 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 20.384 min, t (minor) = 10.854 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.04 (d, *J* = 5.6 Hz, 1H), 6.83 (s, 1H), 6.77 (s, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.76 (d, *J* = 5.6 Hz, 1H), 3.64 (s, 3H), 3.26 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.0, 171.1, 165.5, 156.6, 143.4, 138.1, 136.5, 133.6, 131.7, 129.3, 122.8, 110.1, 89.2, 85.0, 52.4, 26.7, 19.1 ppm; ESI-HRMS: calcd. for $C_{18}H_{16}INO_5$+Na 475.9971, found 475.9981.



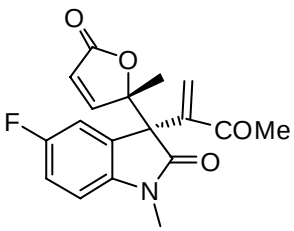
4k, 83% yield; $[\alpha]_D^{20}$ = +12.0 (*c* = 0.2 in $CHCl_3$); 86% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 15.291 min, t (minor) = 8.201 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 5.6 Hz, 1H), 7.01 (s, 1H), 6.84 (s, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 6.77 (s, 1H), 5.74 (d, *J* = 5.6 Hz, 1H), 3.63 (s, 3H), 3.28 (s, 3H), 1.85 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.3, 170.9, 165.6, 156.7, 144.4, 142.3, 136.4, 131.8, 128.7, 122.6, 122.5, 119.0, 108.5, 89.2, 60.0, 52.4, 26.8, 19.2 ppm; ESI-HRMS: calcd. for $C_{19}H_{16}F_3NO_6$+Na 434.0827, found 434.0828.



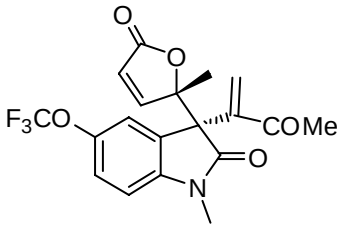
4l, 75% yield; $[\alpha]_D^{20}$ = +27.0 (*c* = 0.2 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 9.237 min, t (minor) = 7.006 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 5.6 Hz, 1H), 6.99-6.88 (m, 3H), 6.83 (s, 1H), 6.76 (s, 1H), 5.75 (d, *J* = 5.6 Hz, 1H), 3.65 (s, 3H), 3.49 (d, $J_{H,F}$ = 2.4 Hz, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.2, 171.4, 165.6, 156.9, 147.4 (d, $^1J_{C,F}$ = 242.3 Hz), 136.7, 131.5, 130.2, 129.9, 123.1 (d, $^3J_{C,F}$ = 6.4 Hz), 122.6, 120.8 (d, $^4J_{C,F}$ = 3.1 Hz), 117.2 (d, $^2J_{C,F}$ = 19.6 Hz), 89.4, 60.1, 52.4, 29.1 (d, $^4J_{C,F}$ = 6.1 Hz), 19.0 ppm; ESI-HRMS: calcd. for $C_{18}H_{16}FNO_5$+H 346.1091, found 346.1084.



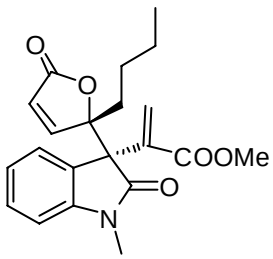
4m, 80% yield; $[\alpha]_D^{20}$ = +29.2 (*c* = 0.5 in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralcel AS, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 31.230 min, t (minor) = 21.196 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.09 (s, 1H), 7.05 (d, *J* = 5.6 Hz, 1H), 7.04 (d, *J* = 1.2 Hz, 1H), 6.91 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.68 (d, *J* = 5.6 Hz, 1H), 3.28 (s, 3H), 2.30 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 176.0, 171.6, 157.2, 146.2, 143.6, 131.3, 129.1, 127.2, 124.6, 122.5, 122.3, 108.1, 89.6, 77.2, 26.6, 25.9, 19.0 ppm; ESI-HRMS: calcd. for $C_{18}H_{17}NO_4$+Na 334.1055, found 334.1054.



4n, 73% yield; $[\alpha]_D^{20}$ = +6.5 (*c* = 0.4 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralcel AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 14.320 min, t (minor) = 10.904 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 5.6 Hz, 1H), 6.94 (td, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.81 (dd, *J* = 12.0 Hz, 2.4 Hz, 1H), 6.71 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 6.64 (s, 1H), 5.74 (d, *J* = 5.6 Hz, 1H), 3.28 (s, 3H), 2.32 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 175.7, 171.3, 158.7 (d, $^1J_{C,F}$ = 240.5 Hz), 157.0, 145.9, 139.6, 131.8, 128.9, 122.5, 115.4 (d, $^2J_{C,F}$ = 23.1 Hz), 112.8 (d, $^2J_{C,F}$ = 25.4 Hz), 108.6 (d, $^3J_{C,F}$ = 7.9 Hz), 89.3, 26.8, 25.9, 24.4, 19.1 ppm; ESI-HRMS: calcd. for $C_{18}H_{16}FNO_4$+Na 352.0961, found 352.0960.

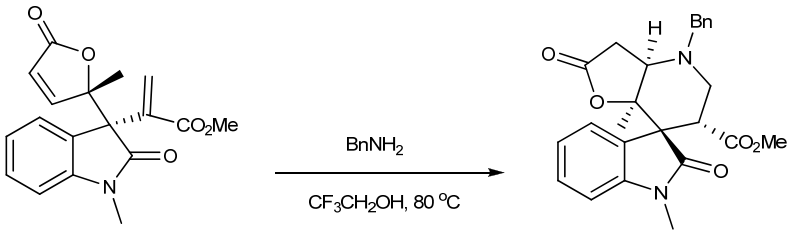


4o, 80% yield; $[\alpha]_D^{20}$ = +2.2 (*c* = 0.4 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralcel AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 11.253 min, t (minor) = 8.685 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 5.2 Hz, 1H), 7.11 (s, 1H), 7.04 (d, *J* = 5.6 Hz, 1H), 6.95 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.66 (s, 1H), 5.74 (d, *J* = 5.6 Hz, 1H), 3.30 (s, 3H), 2.32 (s, 3H), 1.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 175.8, 170.9, 156.8, 145.8, 142.3, 132.0, 128.8, 122.6, 122.3, 118.7, 108.5, 89.2, 77.2, 59.7, 26.9, 25.9, 19.1 ppm; ESI-HRMS: calcd. for $C_{19}H_{16}F_3NO_5$+Na 418.0878, found 418.0878.



4p, 70% yield; $[\alpha]_D^{20}$ = +30.4 (*c* = 0.5 in $CHCl_3$); dr = 83:17 (by ^{1}H NMR analysis); for major isomer: 80% ee, determined by HPLC analysis [Daicel Chiralcel AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.937 min, t (minor) = 5.417 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 5.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.78 (s, 1H), 6.72 (s, 1H), 5.73 (d, *J* = 5.6 Hz, 1H), 3.62 (s, 3H), 3.28 (s, 3H), 2.58-2.42 (m, 2H), 1.34-1.24 (m, 2H), 0.94-0.89 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.7, 172.1, 165.8, 155.6, 143.5, 137.0, 131.1, 129.2, 127.3, 125.0, 123.6, 122.7, 108.0, 92.4, 60.5, 52.3, 29.4, 26.6, 25.2, 22.6, 13.9 ppm; ESI-HRMS: calcd. for $C_{21}H_{23}NO_5$+Na 392.1474, found 392.1475.

Synthetic transformations of allylic product 4a

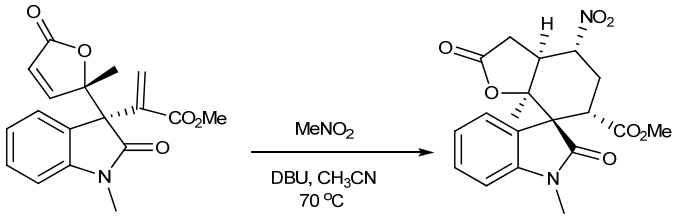


4a 90%ee

5 70% yield, 90% ee

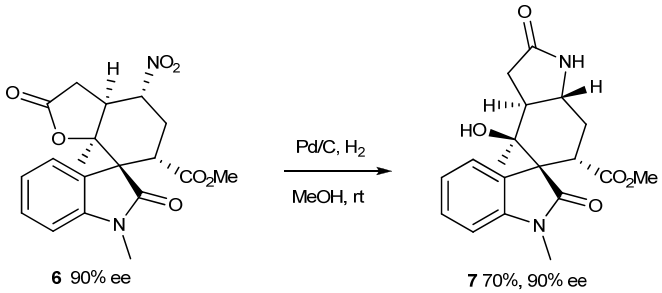
A solution of **4a** (65.4 mg, 0.20 mmol, 90% ee) and $BnNH_2$ (110 μL, 1.00 mmol) in CF_3CH_2OH (0.5mL) was stirred at 80 °C for 5 hours. Then Boc_2O (436 mg, 2.00 mmol) was added and the solution was stirred at rt until the consumption of excess $BnNH_2$. After removing the solvent, the residue was purified by flash chromatography on silica gel (PE/AcOEt = 2:1) to afford the product **5** as a colorless oil

(61.0 mg, 70% yield). $[\alpha]_D^{20}$ = -9.2 (*c* = 0.9 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel AD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 15.195 min, t (minor) = 14.046 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.2 Hz, 1H), 7.41-7.30 (m, 6H), 6.97 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.97 (d, *J* = 13.6 Hz, 1H), 3.71 (dd, *J* = 7.2 Hz, 6.0 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 3.35 (d, *J* = 5.6 Hz, 1H), 3.29 (dd, *J* = 12.4 Hz, 7.2 Hz, 1H), 3.28 (s, 3H), 3.23 (s, 3H), 3.05 (dd, *J* = 12.4 Hz, 6.0 Hz, 1H), 2.83 (d, *J* = 18.0 Hz, 1H), 2.66 (dd, *J* = 18.0 Hz, 5.6 Hz, 1H), 0.94 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 175.8, 170.9, 156.8, 145.8, 142.3, 132.0, 128.8, 122.6, 122.3, 118.7, 108.5, 89.2, 77.2, 59.7, 26.9, 25.9, 19.1 ppm; ESI-HRMS: calcd. for $C_{25}H_{26}N_2O_5$+H 435.1920, found 435.1920. The relative configuration has been established by 2D NMR and NOE analysis.



4a 90%ee — **6** 40% yield, 90% ee

A solution of **4a** (50.0 mg, 0.15 mmol, 90% ee), $MeNO_2$ (1.50 mmol, 80 μL) and DBU (0.07 mmol, 11.4 mg) in CH_3CN (0.5 mL) was refluxed until the consumption of **4a** (5 h). Then the solvent was removed in vacuum and the residue was purified by flash chromatography on silica gel (PE/AcOEt = 2:1) to give **6** as a white solid (23.0 mg, 40% yield). $[\alpha]_D^{20}$ = +5.5 (*c* = 0.9 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 26.963 min, t (minor) = 19.554 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 4.76 (m, 1H), 3.56 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 3.46 (s, 3H), 3.29 (s, 3H), 3.11 (dd, *J* = 10.8 Hz, 6.8 Hz, 1H), 2.86-2.80 (m, 2H), 2.97 (dd, *J* = 18.0 Hz, 6.8 Hz, 1H), 2.70 (d, *J* = 18.0 Hz, 1H), 1.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 172.7, 169.8, 145.0, 129.8, 126.5, 124.5, 122.7, 109.0, 86.0, 85.8, 53.3, 52.4, 42.9, 42.2, 35.4, 27.1, 26.7, 22.7 ppm; ESI-HRMS: calcd. for $C_{19}H_{20}N_2O_7$+Na 411.1168, found 411.1167. The relative configuration has been established by 2D NMR and NOE analysis.

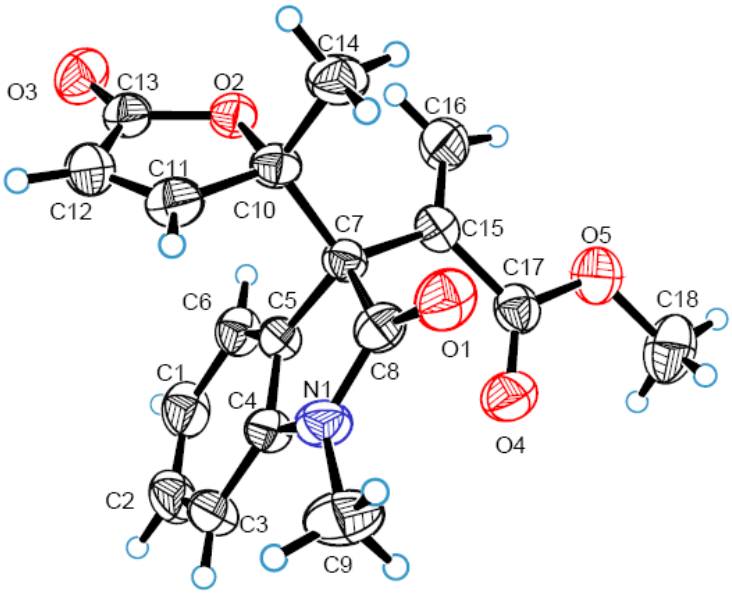


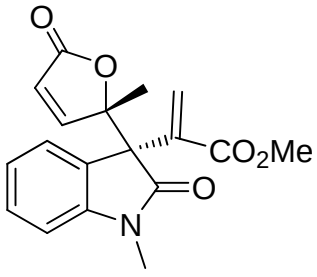
6 90% ee

7 70%, 90% ee

A solution of compound **6** (44.0 mg, 0.11 mmol, 90% ee) and Pd/C (10%, 5.0 mg) in MeOH was stirred at room temperature under H_2 atmosphere until the consumption of **6** (7 h). Then the reaction mixture was filtered and washed with methanol. The combined filtrates were evaporated in vacuum and the residue was purified by flash chromatography on silica gel (DCM/MeOH = 50:1) to give **7** as a white solid (27.5 mg, 70% yield). $[\alpha]_D^{20}$ = +16.0 (*c* = 0.1 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralcel AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 14.526 min, t (minor) = 8.835 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.88 (bs, 1H), 3.57 (dd, *J* = 14.0 Hz, 4.0 Hz, 1H), 3.41 (s, 3H), 3.27 (s, 3H), 2.92-2.84 (m, 2H), 2.71-2.58 (m, 3H), 2.35 (dt, *J* = 8.8 Hz, 4.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.3, 175.0, 171.4, 145.0, 129.2, 127.8, 124.9, 122.5, 108.5, 86.8, 60.8, 53.9, 52.0, 43.1, 40.2, 36.2, 26.6, 26.3, 21.8 ppm; ESI-HRMS: calcd. for $C_{19}H_{22}N_2O_5$+K 397.1166, found 397.1164.

4. Crystal data and structure refinement for enantiopure 4a



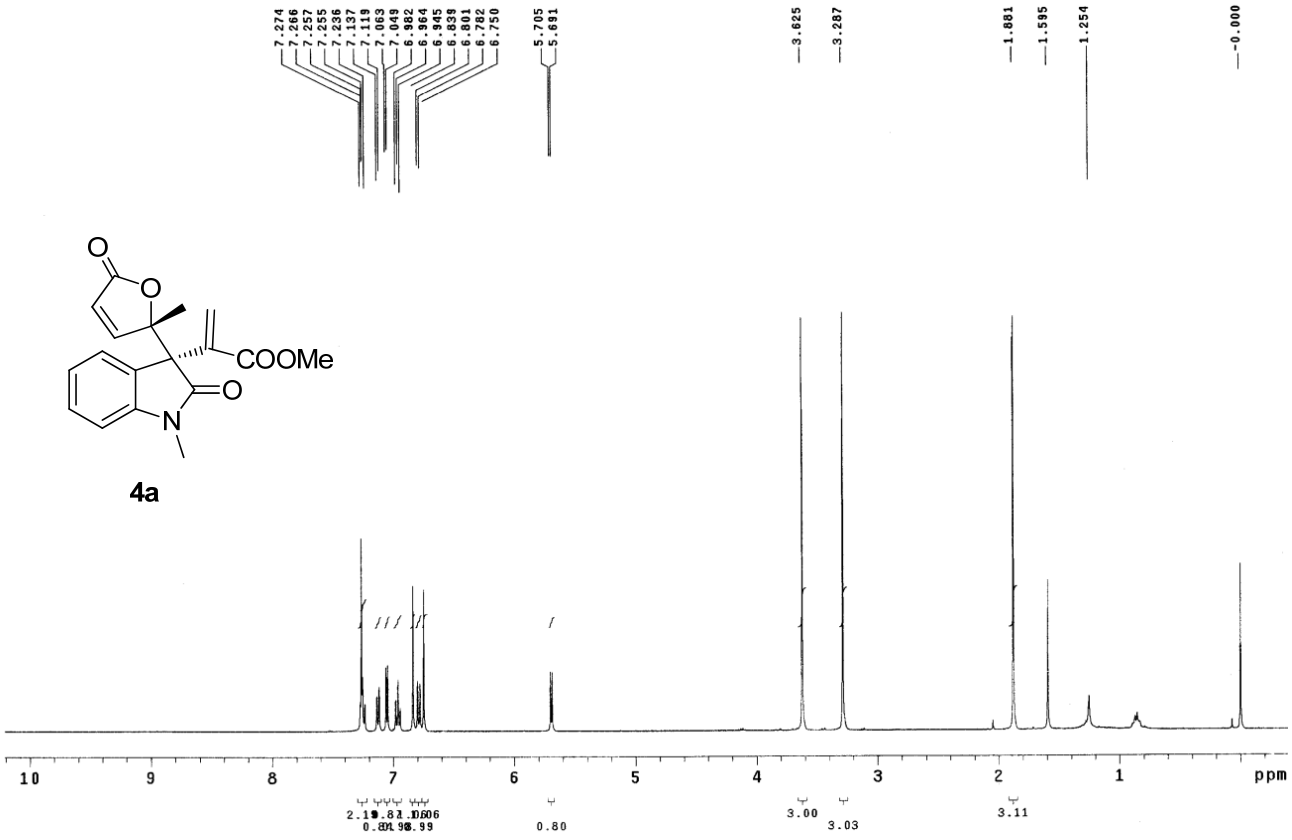


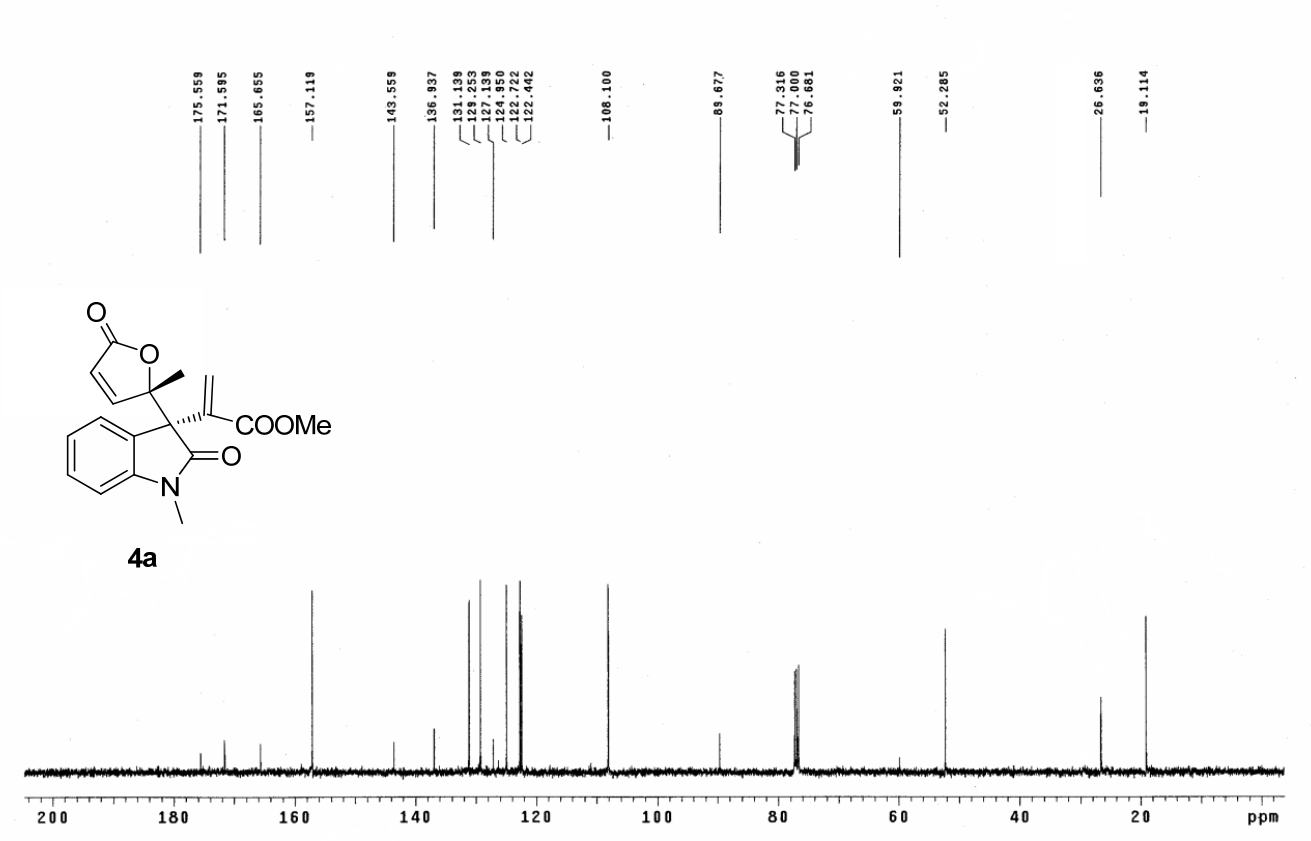
4a

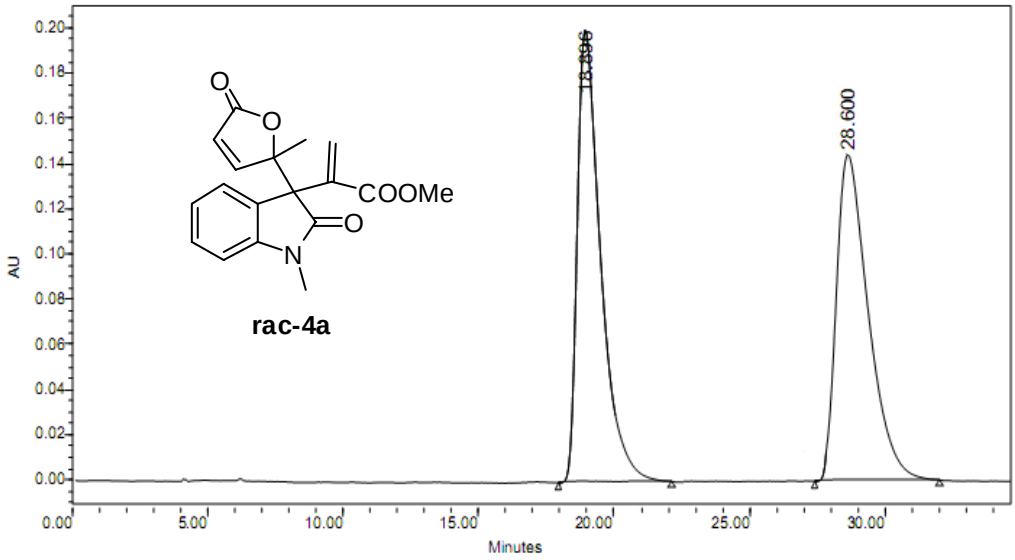
Identification code	**4a**
Empirical formula	$C_{18}H_{17}O_5N$
Formula weight	327.33
Temperature	291(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å, b/Å, c/Å	8.923(5), 12.210(5), 15.345(5)
α/°, β/°, γ/°,	90.000(5), 90.000(5), 90.000(5)
Volume/$Å^3$	1671.8(13)
Z	4
$\rho_{calc}mg/mm^3$	1.300
m/mm^{-1}	0.795
F(000)	688
Crystal size	0.40 × 0.40 × 0.32
Theta range for data collection	4.63 to 69.70°
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-18 \leq l \leq 17$
Reflections collected	14220
Independent reflections	3123[R(int) = 0.0206]

Data/restraints/parameters	3123/0/221
Goodness-of-fit on F^2	1.051
Final R indexes [I>2σ (I)]	$R_1 = 0.0283$, $wR_2 = 0.0737$
Final R indexes [all data]	$R_1 = 0.0285$, $wR_2 = 0.0740$
Largest diff. peak/hole	0.133/-0.132

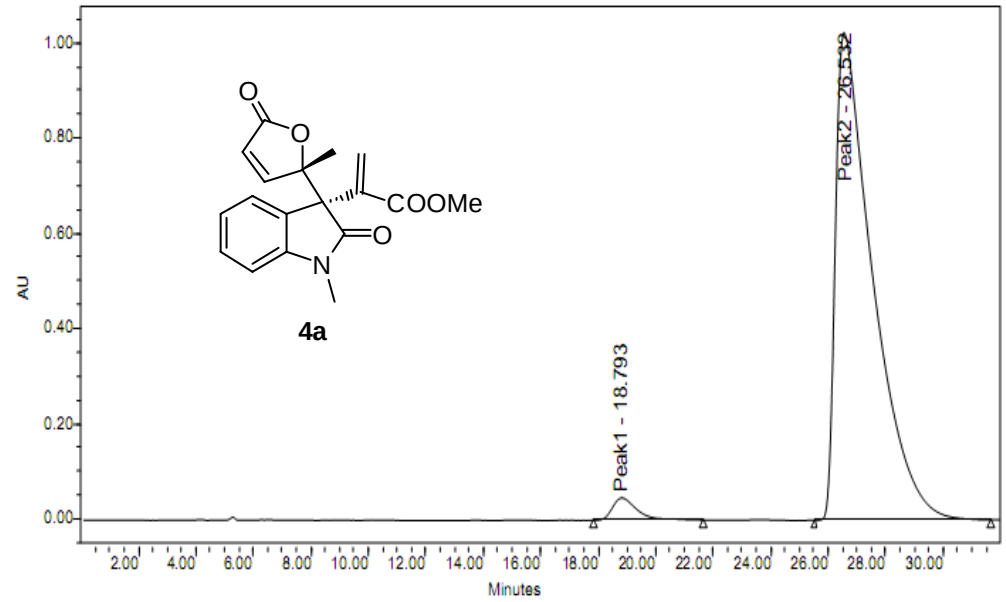
5. NMR spectra and HPLC chromatograms



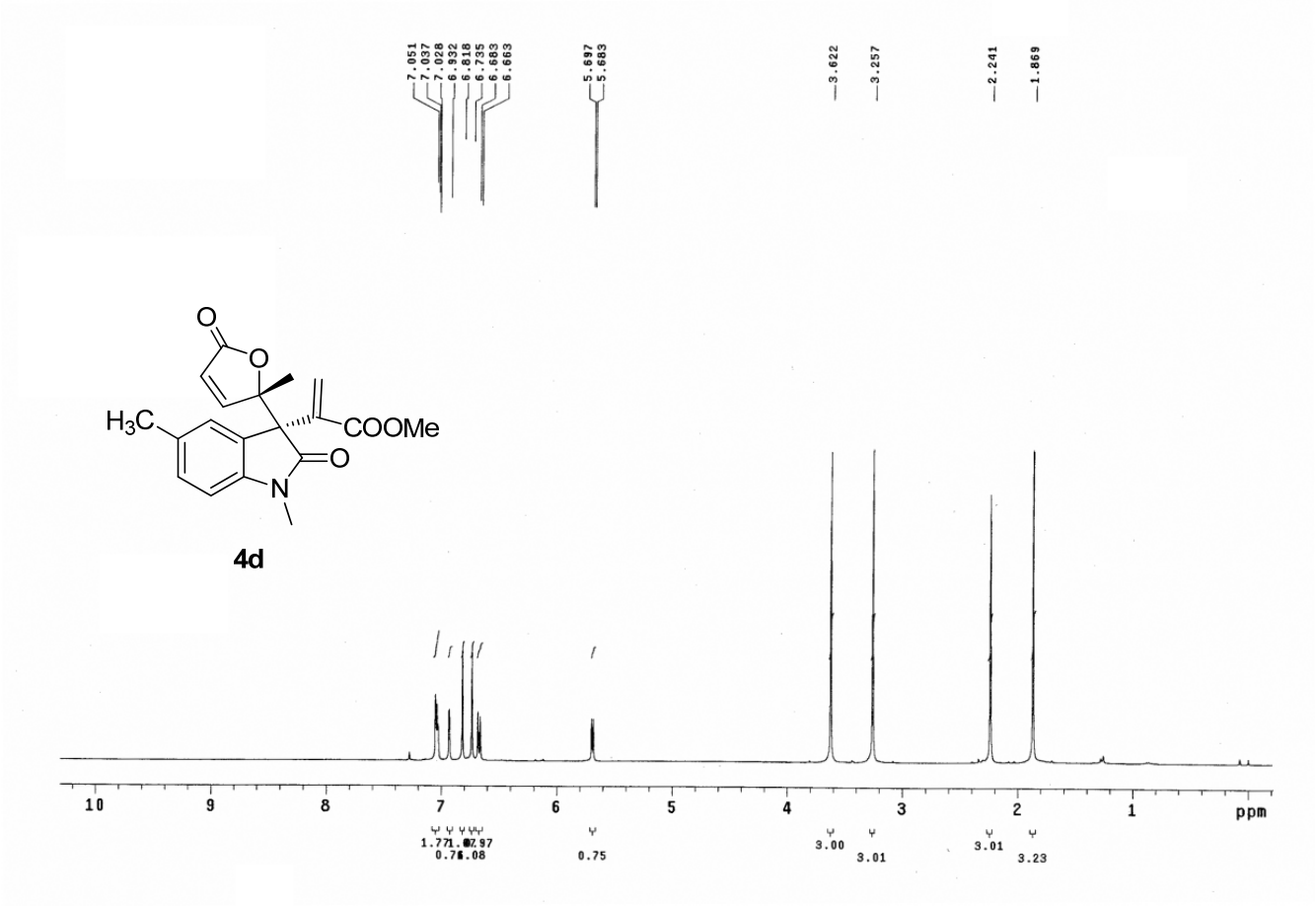




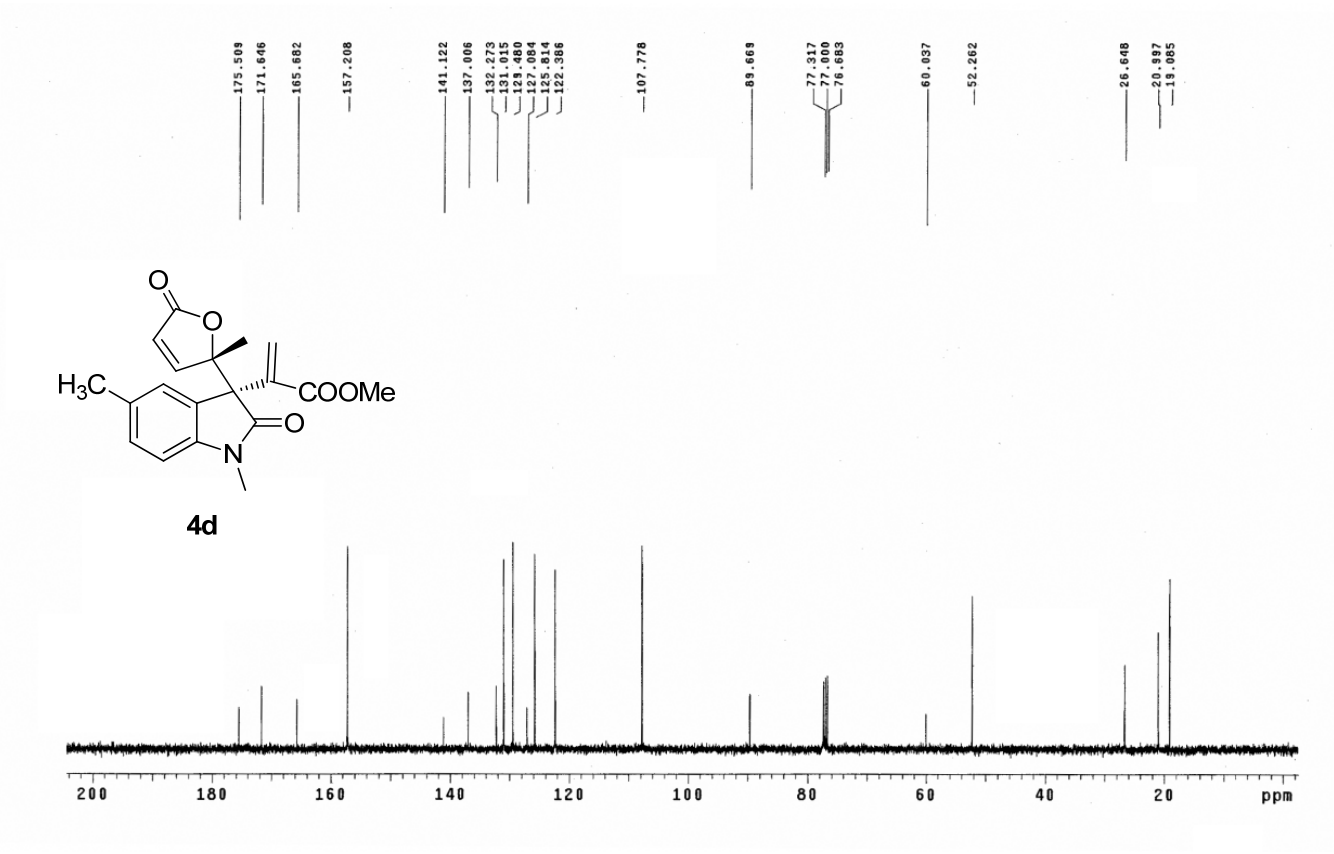
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	18.896	11673635	49.51	200015	58.08
2	28.600	11905673	50.49	144377	41.92



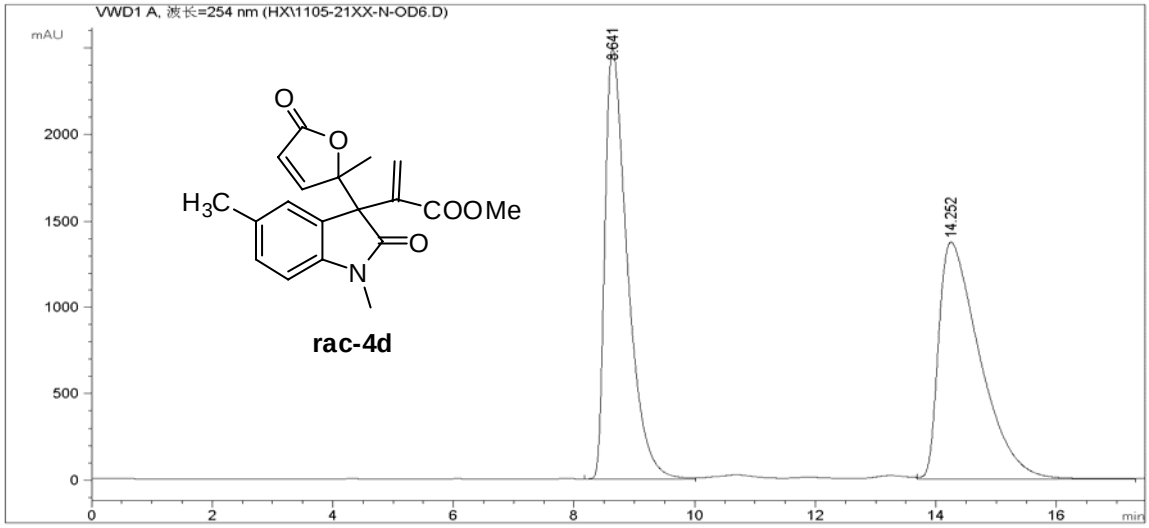
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	18.793	2832175	4.95	46418	5.07
2	26.532	54434236	95.05	868762	94.93


7.051
7.037
7.028
6.932
6.818
6.735
6.683
6.663
5.697
5.683
3.622
3.257
2.241
1.869
O
O
H3C
COOMe
O
N
10
9
8
7
6
5
4
3
2
1
ppm
1.77
1.00
2.97
0.75
3.00
3.01
3.01
3.23

4d

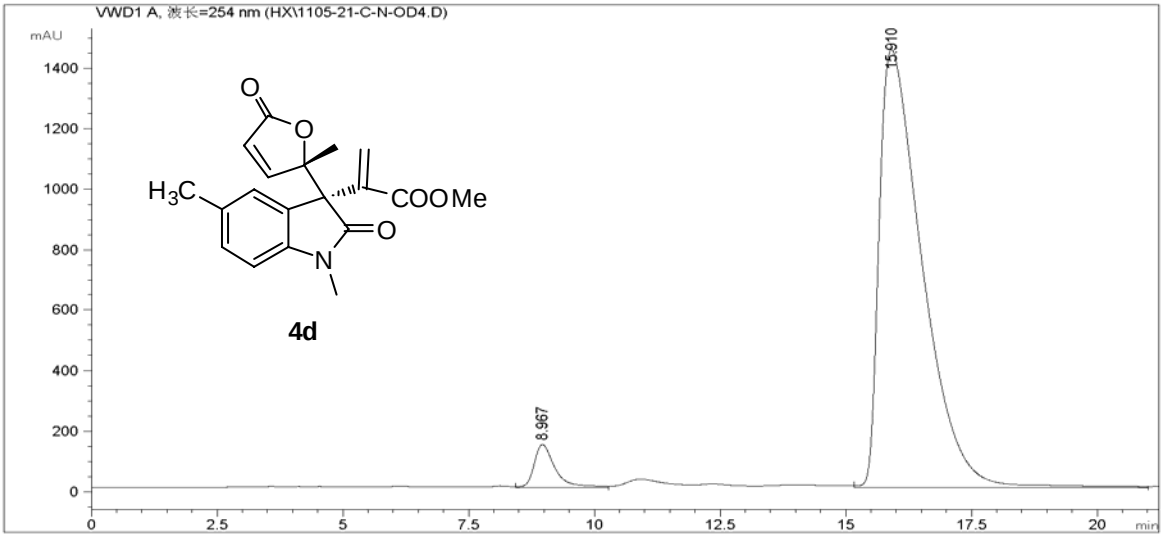

175.509
171.646
165.682
157.208
141.122
137.006
132.273
131.015
129.480
127.084
125.814
122.386
107.778
89.669
77.317
77.000
76.683
60.037
52.262
26.648
20.997
19.085
O
O
H3C
COOMe
O
N
200
180
160
140
120
100
80
60
40
20
ppm

4d



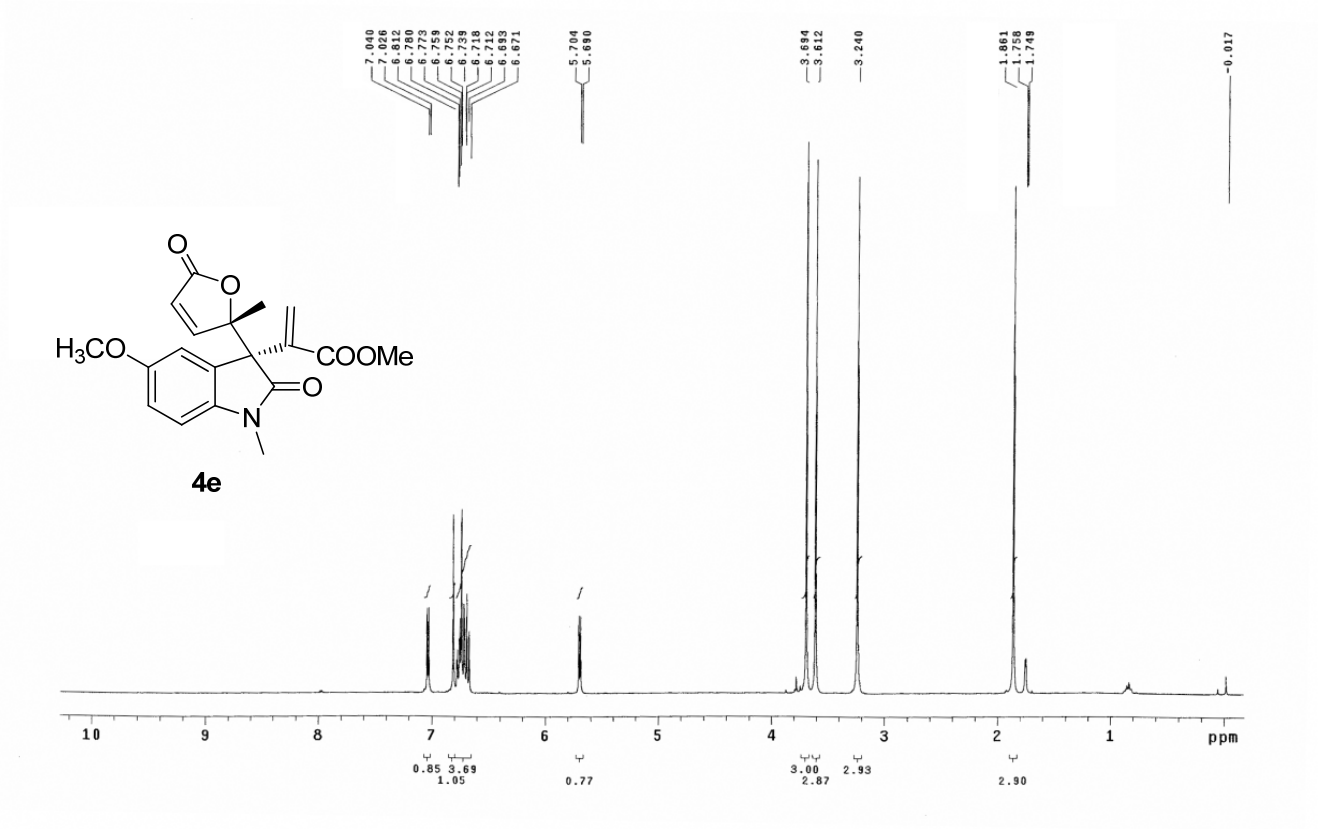
rac-4d

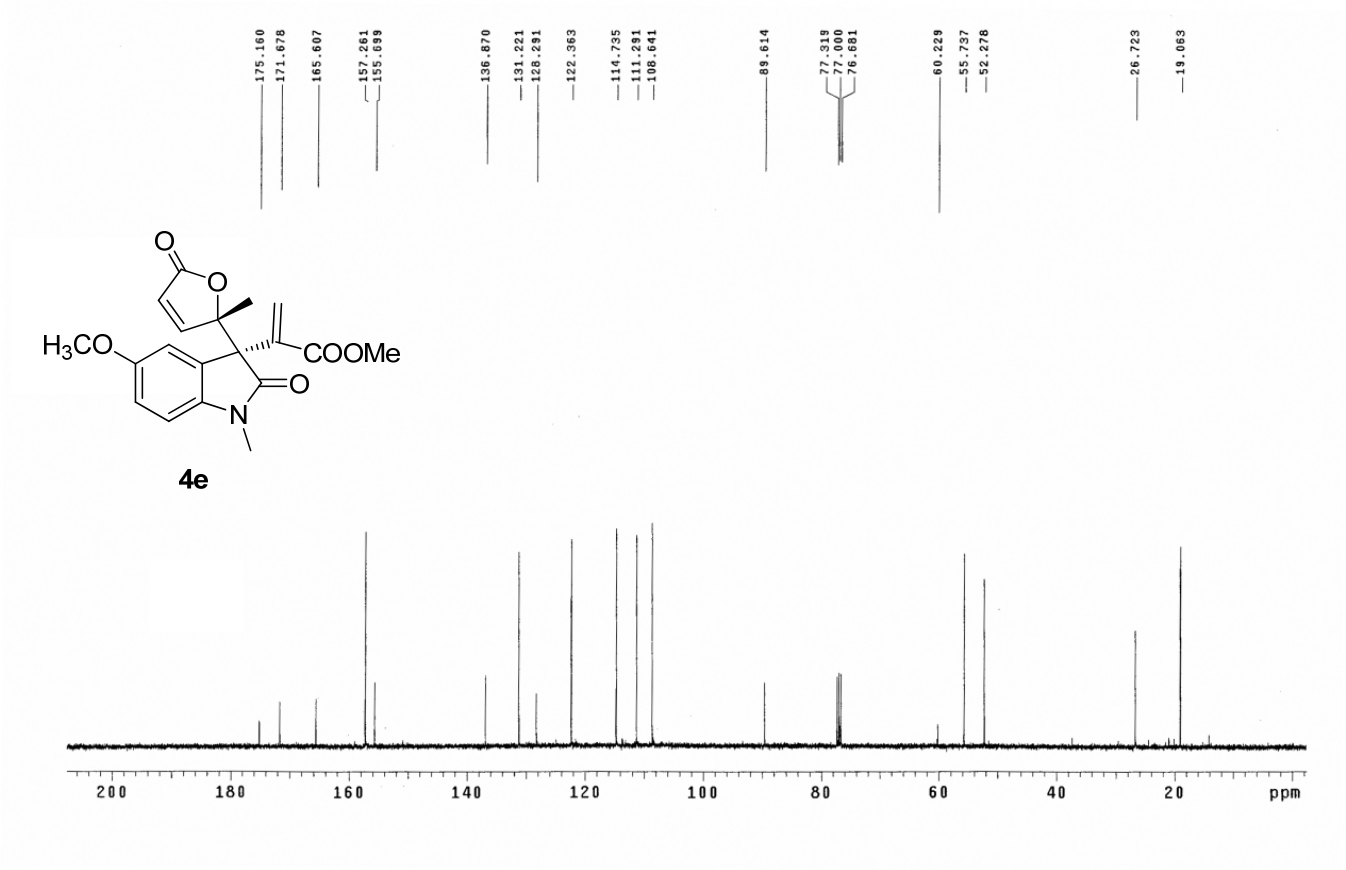
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.641	VV	0.3893	6.43025e4	2484.79736	49.7821
2	14.252	VV	0.7141	6.48655e4	1373.38098	50.2179

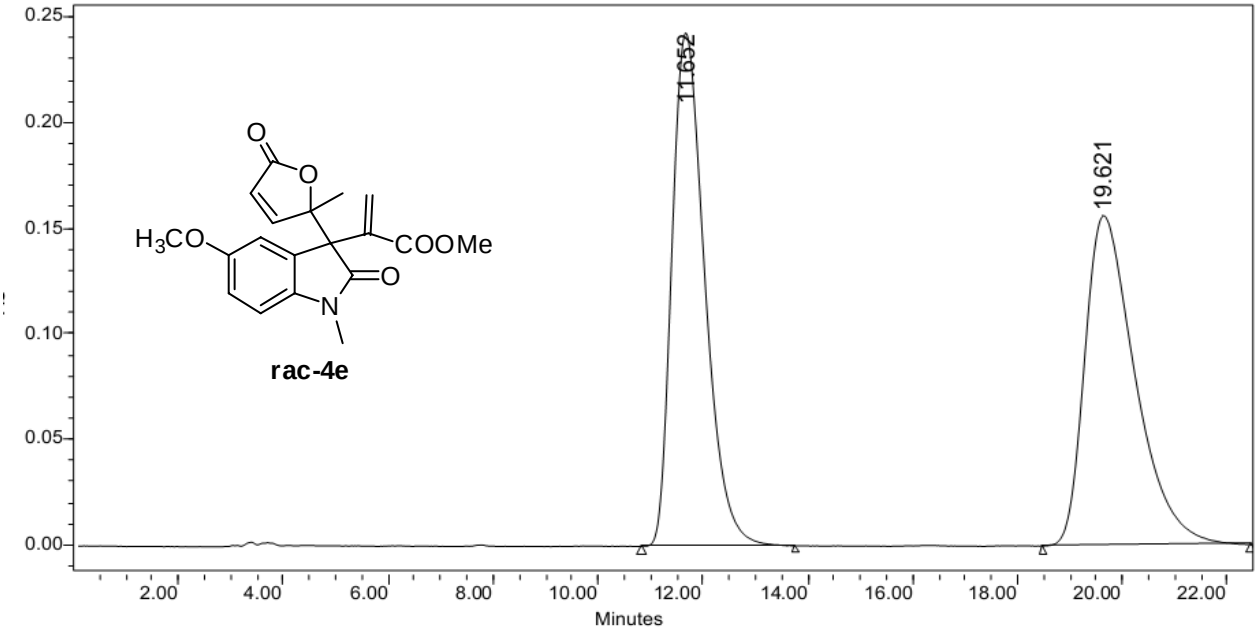


4d

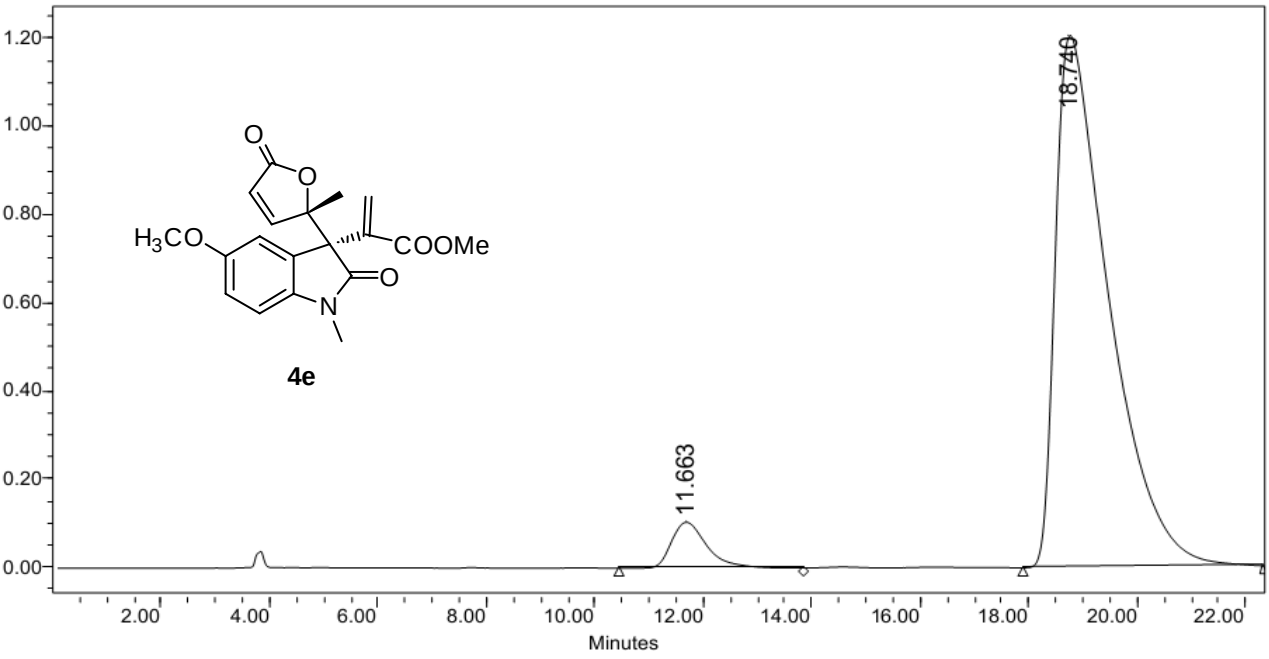
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.967	VV	0.4290	4052.00586	140.78642	4.5299
2	15.910	VB	0.8874	8.53974e4	1445.16736	95.4701


7.040
7.026
6.812
6.780
6.773
6.759
6.752
6.738
6.718
6.712
6.693
6.671
5.704
5.680
3.694
3.612
3.240
1.861
1.758
1.749
-0.017
O
O
H3CO
COOMe
O
N
4e
10
9
8
7
6
5
4
3
2
1
ppm
0.85
3.69
1.05
0.77
3.00
2.87
2.93
2.90

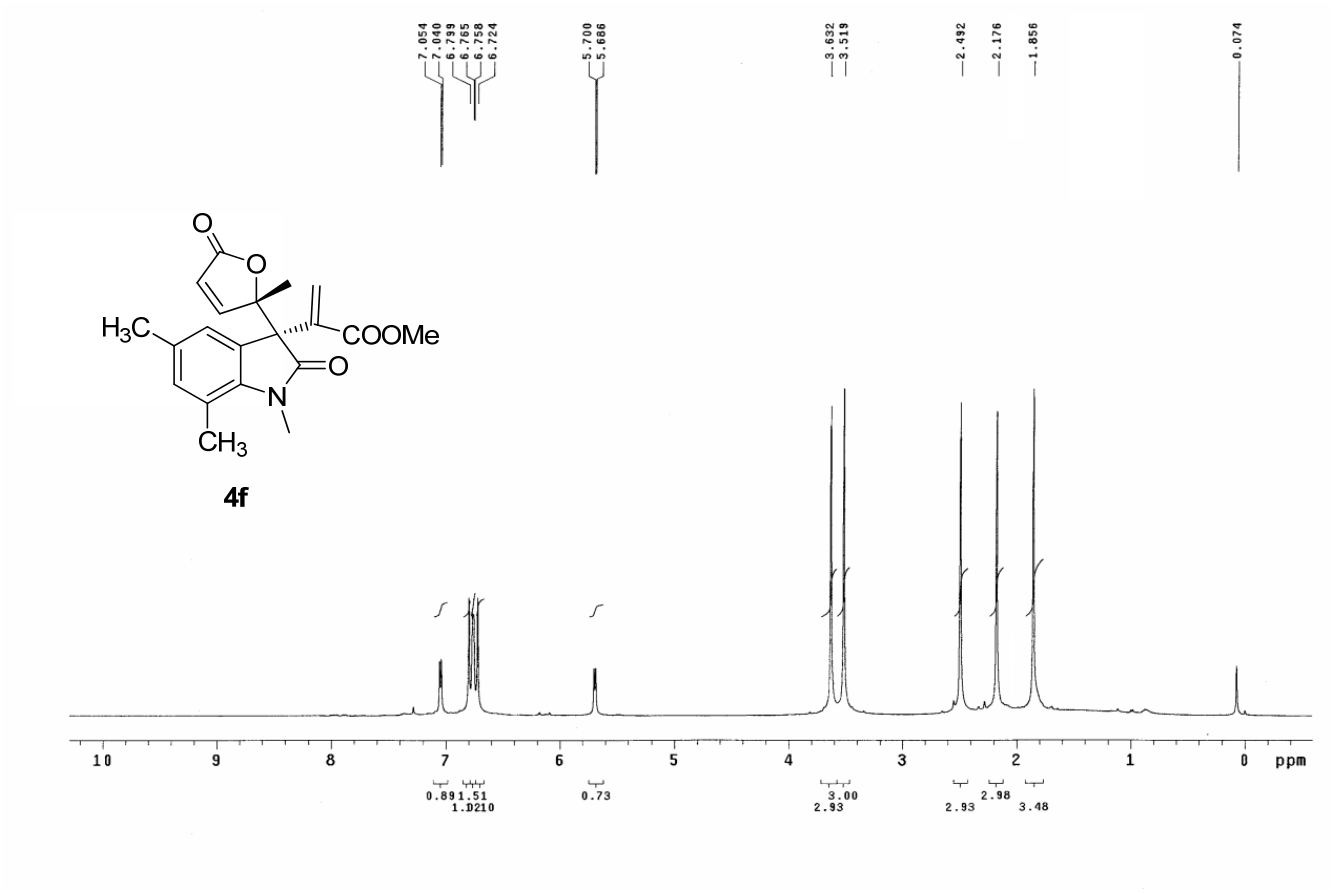

175.160
171.678
165.607
157.261
155.699
136.870
131.221
128.291
122.363
114.735
111.291
108.641
89.614
77.319
77.000
76.681
60.229
55.737
52.278
26.723
19.063
O
O
H3CO
COOMe
O
N
4e
200
180
160
140
120
100
80
60
40
20
ppm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	11.652	10586116	50.34	242936	60.86
2	19.621	10443486	49.66	156225	39.14



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	11.663	4726172	5.39	104075	7.93
2	18.740	82877032	94.61	1208366	92.07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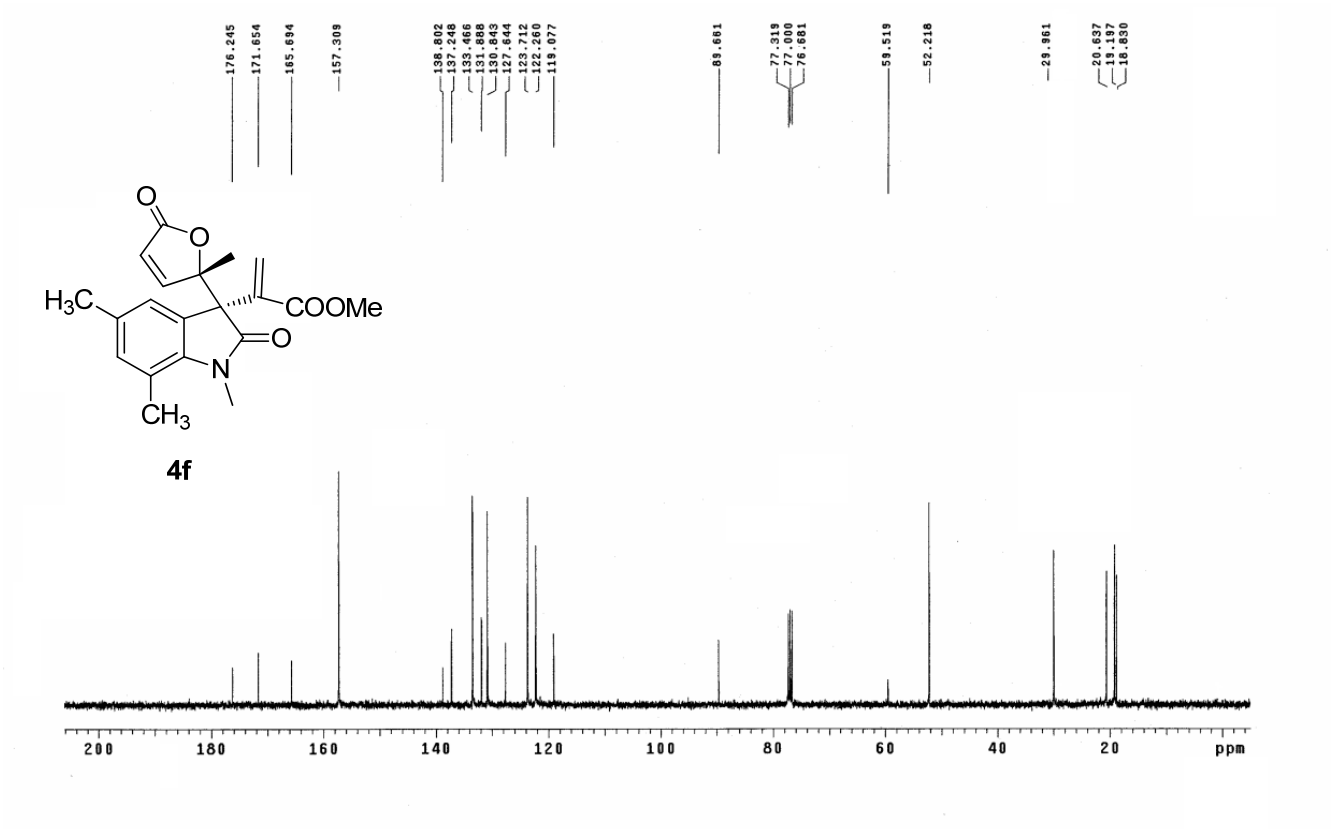
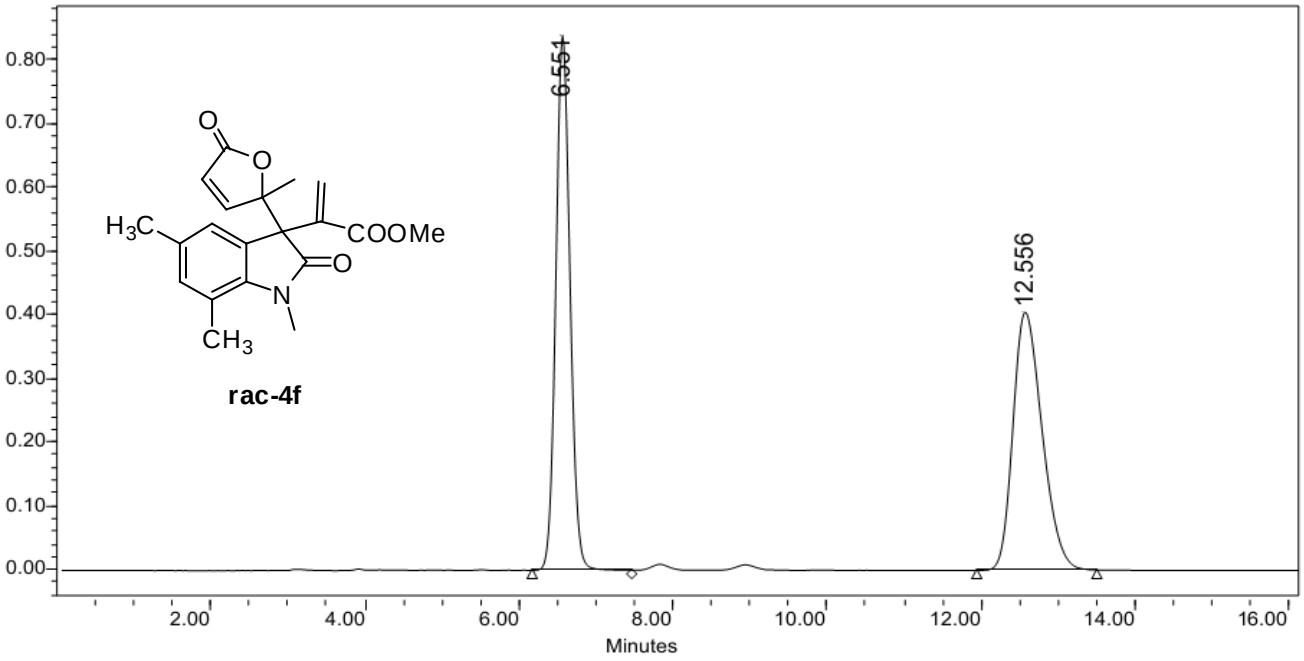
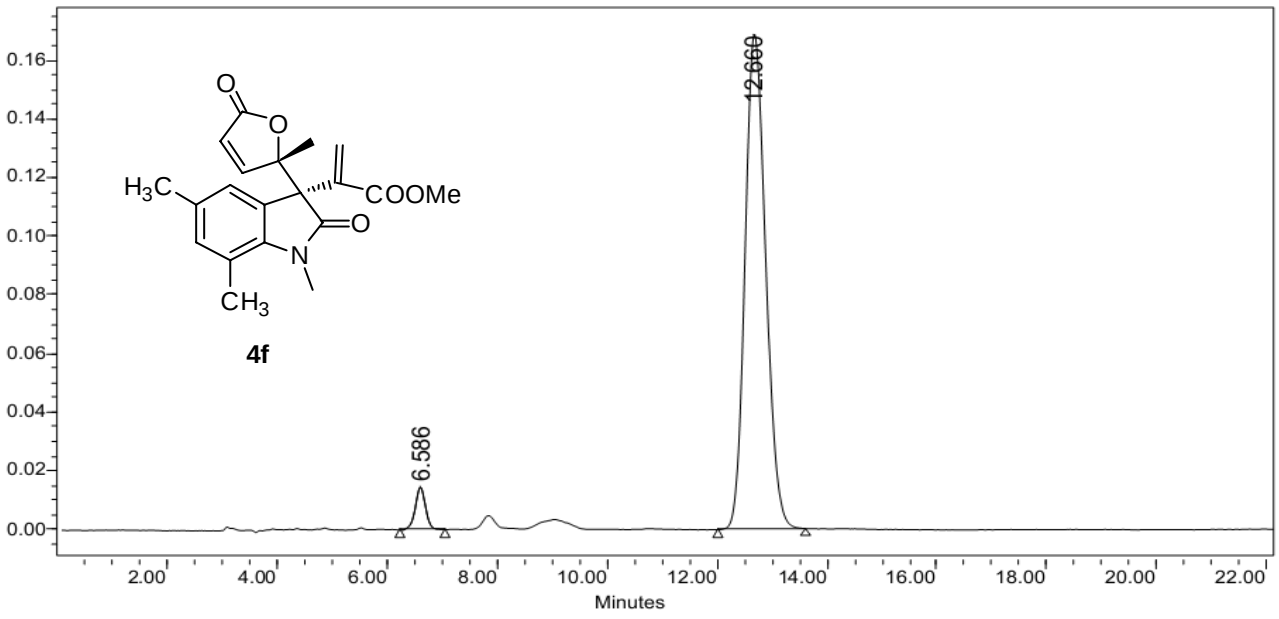
7.040
6.799
6.765
6.758
6.724
5.700
5.686
3.632
3.519
2.492
2.176
1.856
0.074
O
O
H3C
COOMe
O
N
CH3
4f
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
1.51
1.D210
0.73
3.00
2.93
2.93
2.98
3.48


176.245
171.654
165.694
157.309
138.802
137.248
133.466
131.888
130.843
127.644
123.712
122.260
119.077
89.661
77.319
77.000
76.681
59.519
52.218
29.961
20.637
19.197
18.830
O
O
H3C
COOMe
O
N
CH3
4f
200
180
160
140
120
100
80
60
40
20
ppm



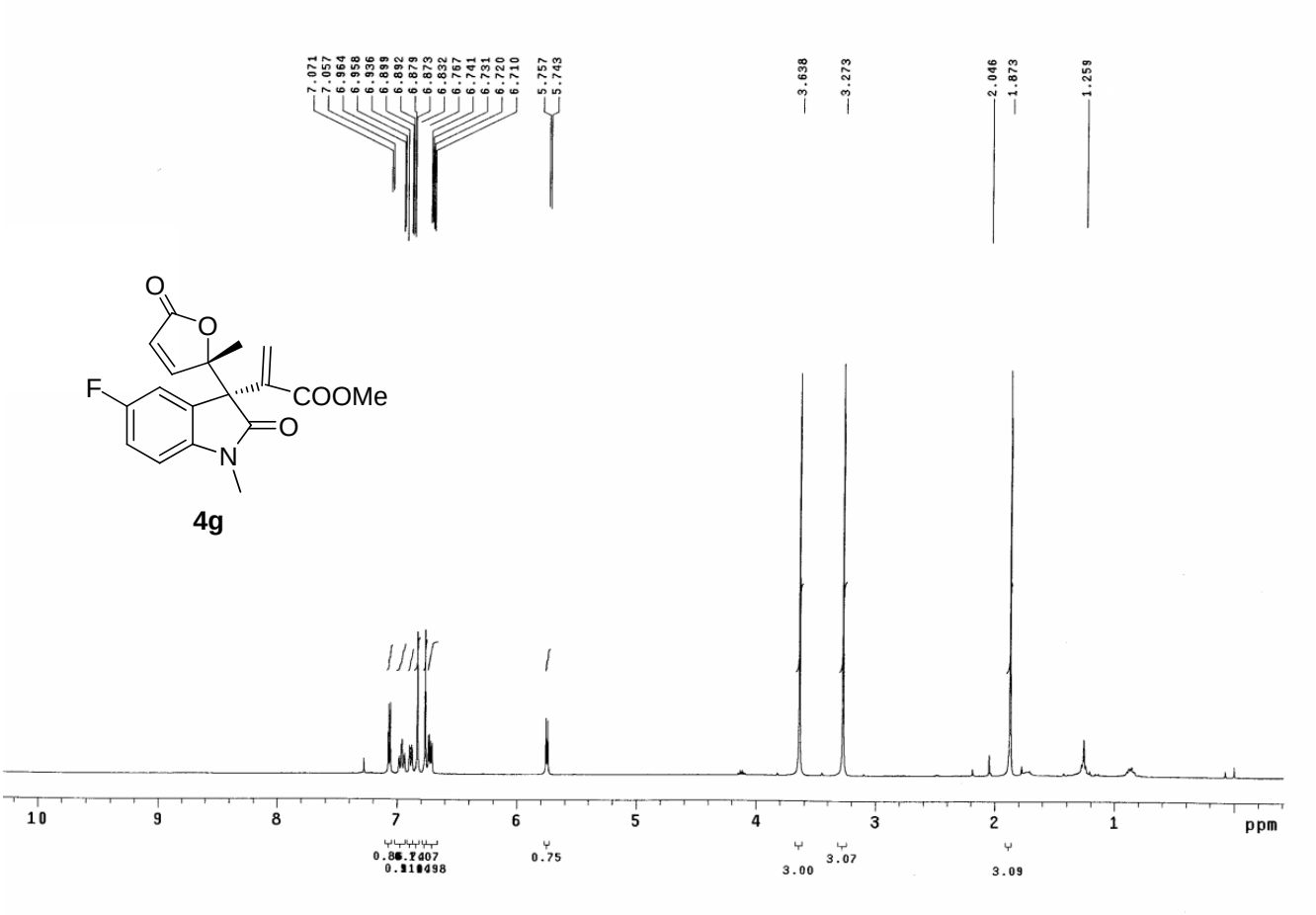
rac-4f

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.551	10716013	50.15	839477	67.45
2	12.556	10653569	49.85	405024	32.55



4f

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.586	190676	4.15	14529	7.92
2	12.660	4402915	95.85	168924	92.08


7.071
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6.958
6.936
6.899
6.892
6.879
6.873
6.832
6.767
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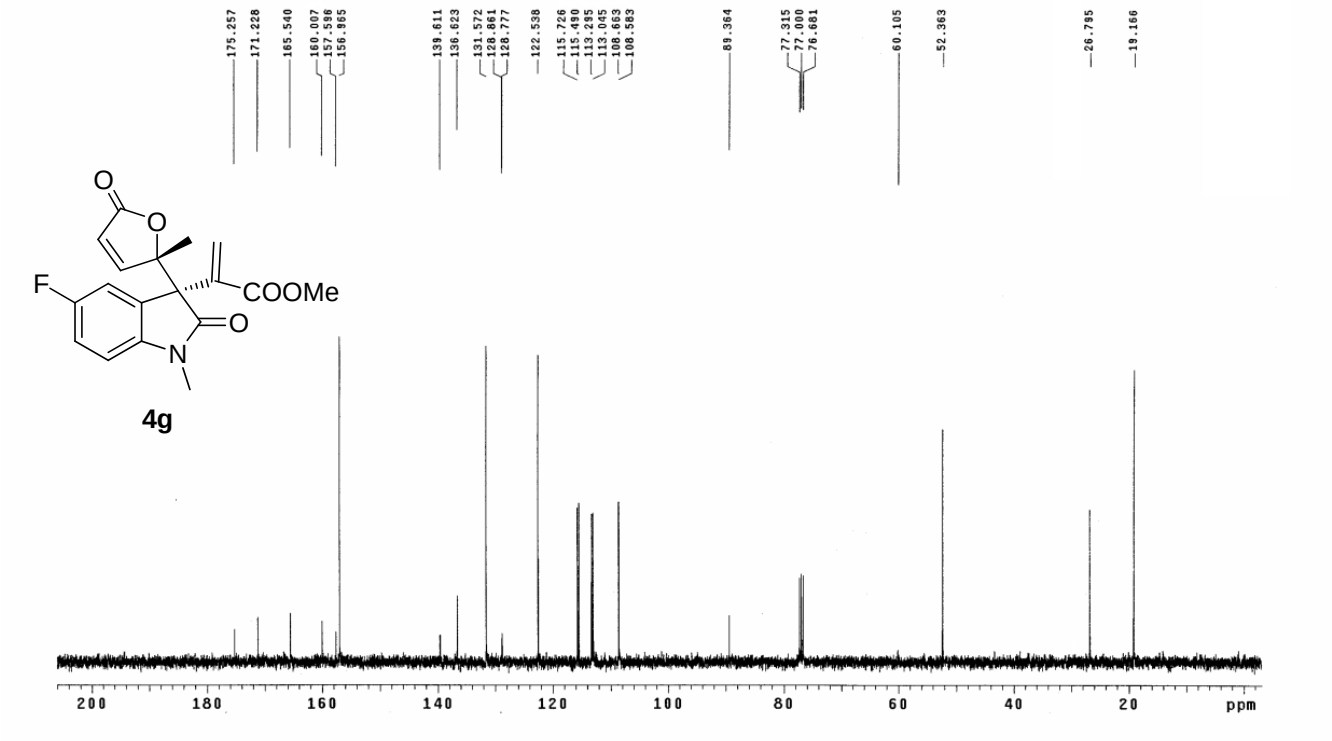
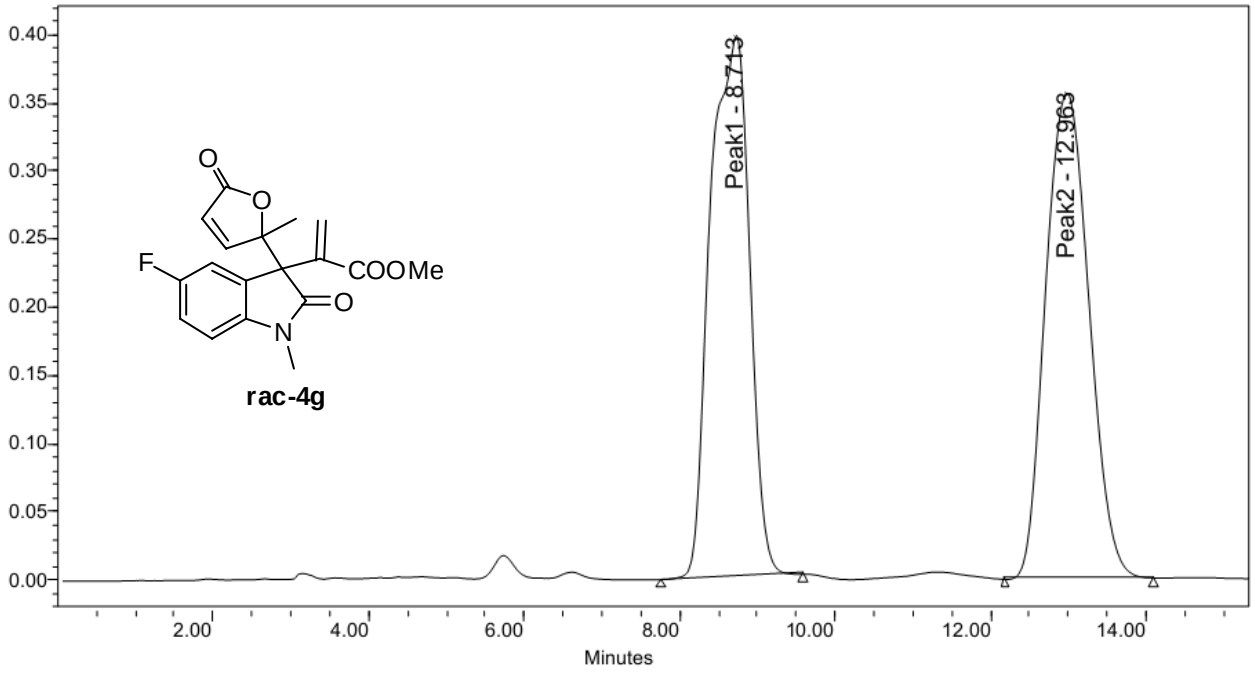
6.731
6.720
6.710
5.757
5.743
3.638
3.273
2.046
1.873
1.259
O
O
F
COOMe
O
N
10
9
8
7
6
5
4
3
2
1
ppm
0.75
3.00
3.07
3.09

4g

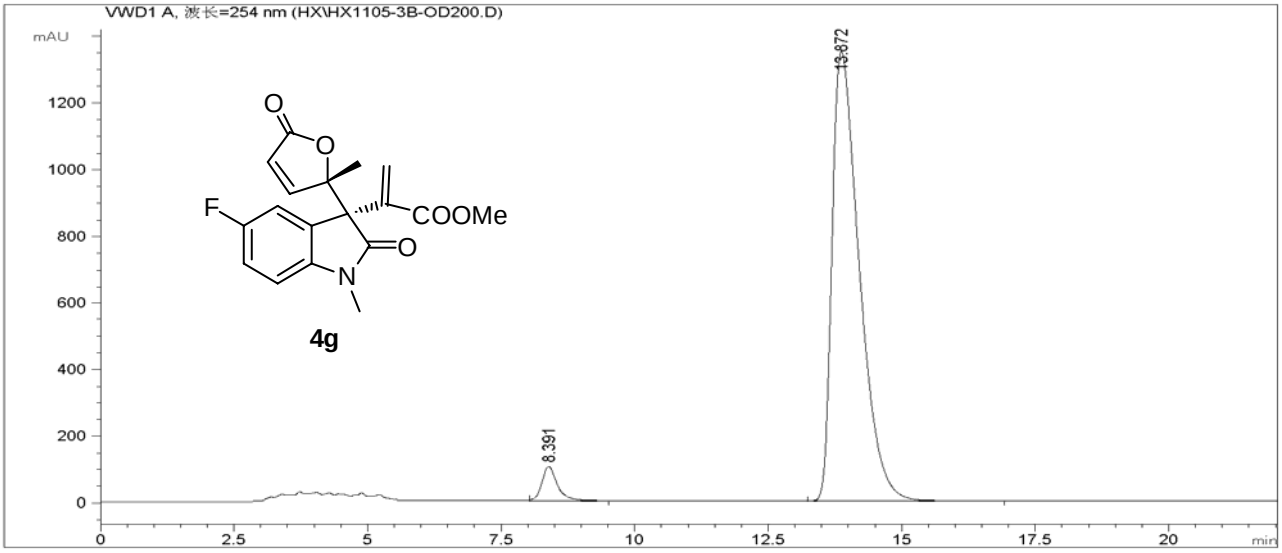

175.257
171.228
165.540
160.007
157.596
156.965
139.611
136.623
131.572
128.861
128.777
122.538
115.726
115.490
113.295
113.045
106.663
106.583
89.364
77.315
77.000
76.681
60.105
52.363
26.795
19.166
O
O
F
COOMe
O
N
200
180
160
140
120
100
80
60
40
20
ppm

4g



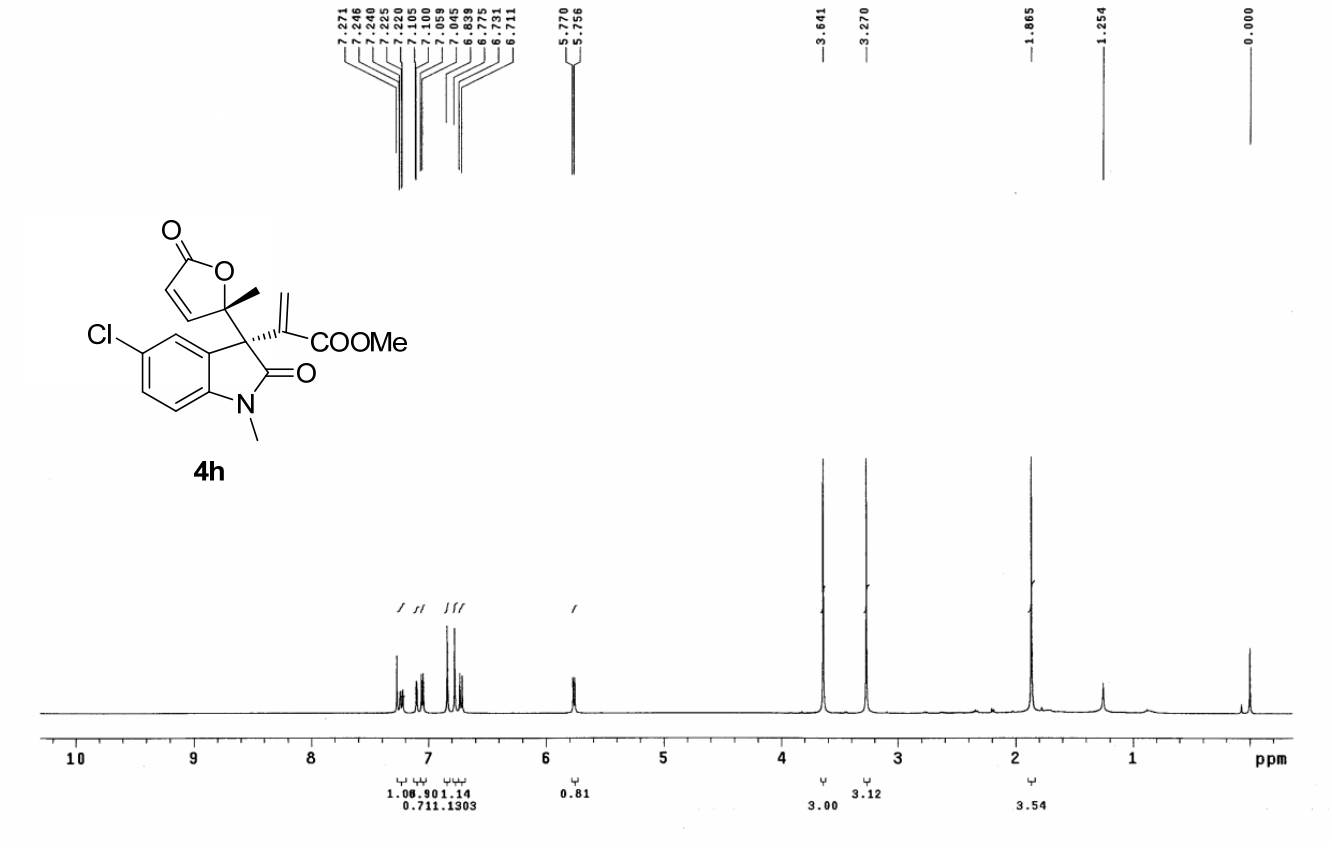
rac-4g

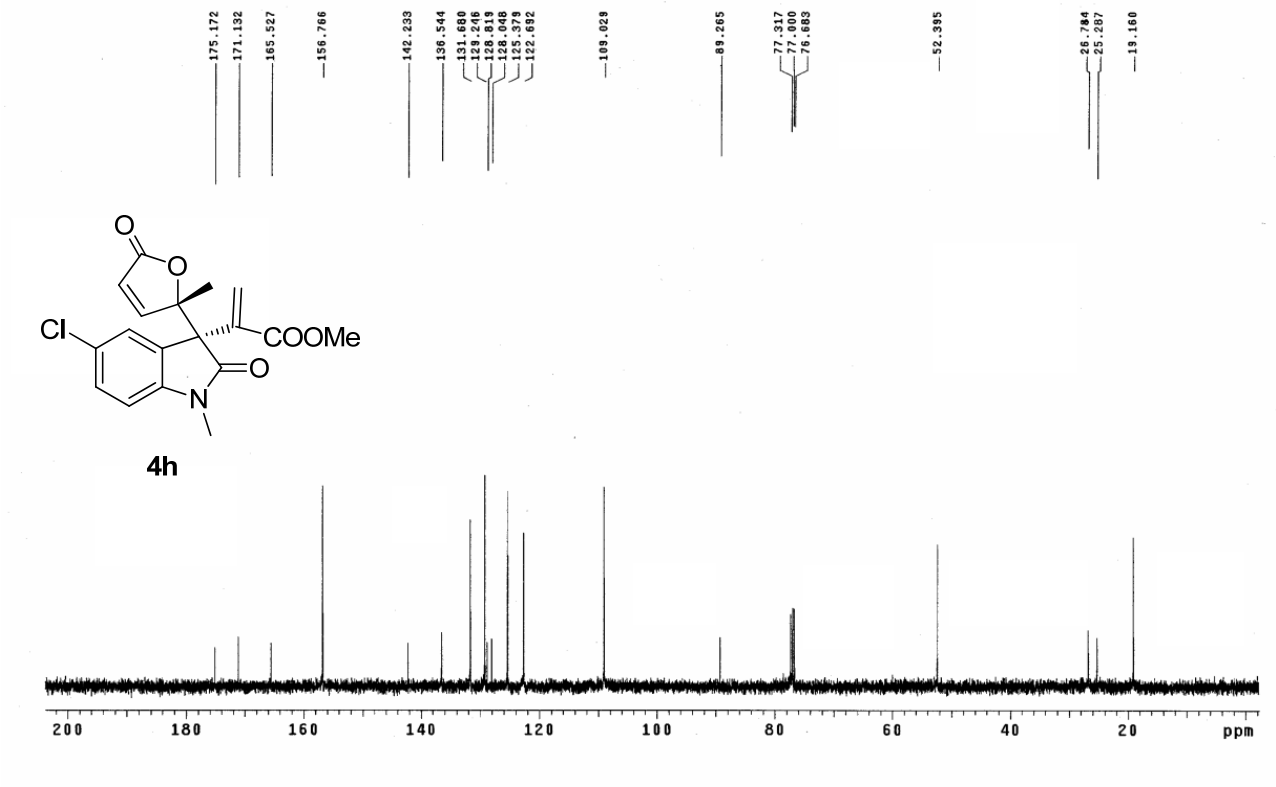
	Peak Name	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	Peak1	8.713	13922205	50.15	397190	52.70
2	Peak2	12.963	13838396	49.85	356535	47.30

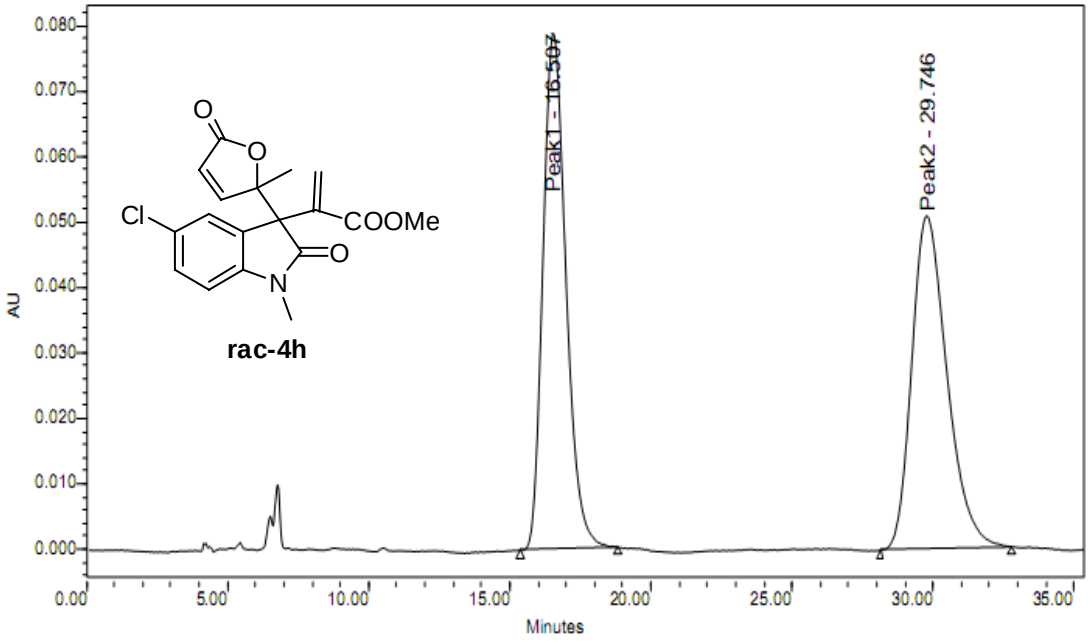


4g

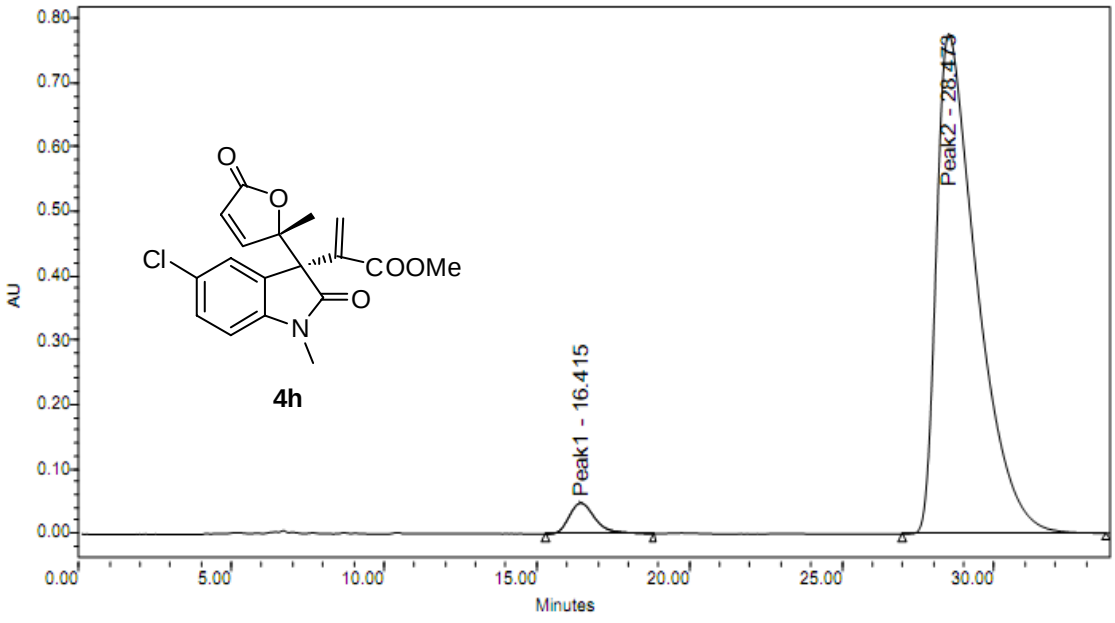
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.391	VV	0.2943	2045.96777	103.65731	4.1056
2	13.872	VB	0.5414	4.77881e4	1348.97253	95.8944


7.271
7.246
7.240
7.225
7.220
7.105
7.100
7.059
7.045
6.839
6.775
6.731
6.711
5.770
5.756
3.641
3.270
1.865
1.254
0.000
Cl
COOMe
O
N
4h
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.90
1.14
0.71
1.13
0.81
3.00
3.12
3.54

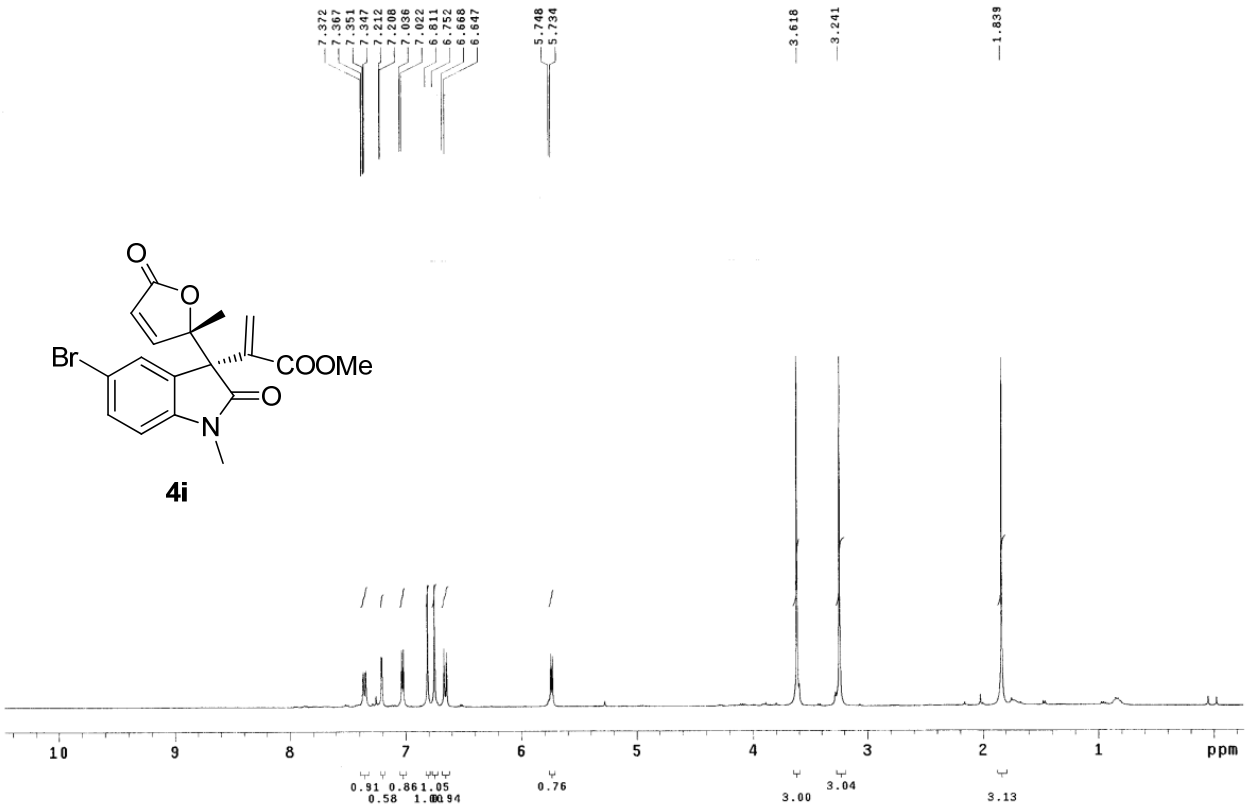

175.172
171.132
165.527
156.766
142.233
136.544
131.680
129.246
128.819
128.048
125.379
122.692
109.029
89.265
77.317
77.000
76.683
52.395
26.784
25.287
19.160
Cl
COOMe
O
N
4h
200
180
160
140
120
100
80
60
40
20
ppm



	Peak Name	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	Peak1	16.507	4468800	50.25	78909	60.78
2	Peak2	29.746	4423872	49.75	50918	39.22



	Peak Name	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	Peak1	16.415	2850288	3.83	48028	5.82
2	Peak2	28.473	71554621	96.17	777192	94.18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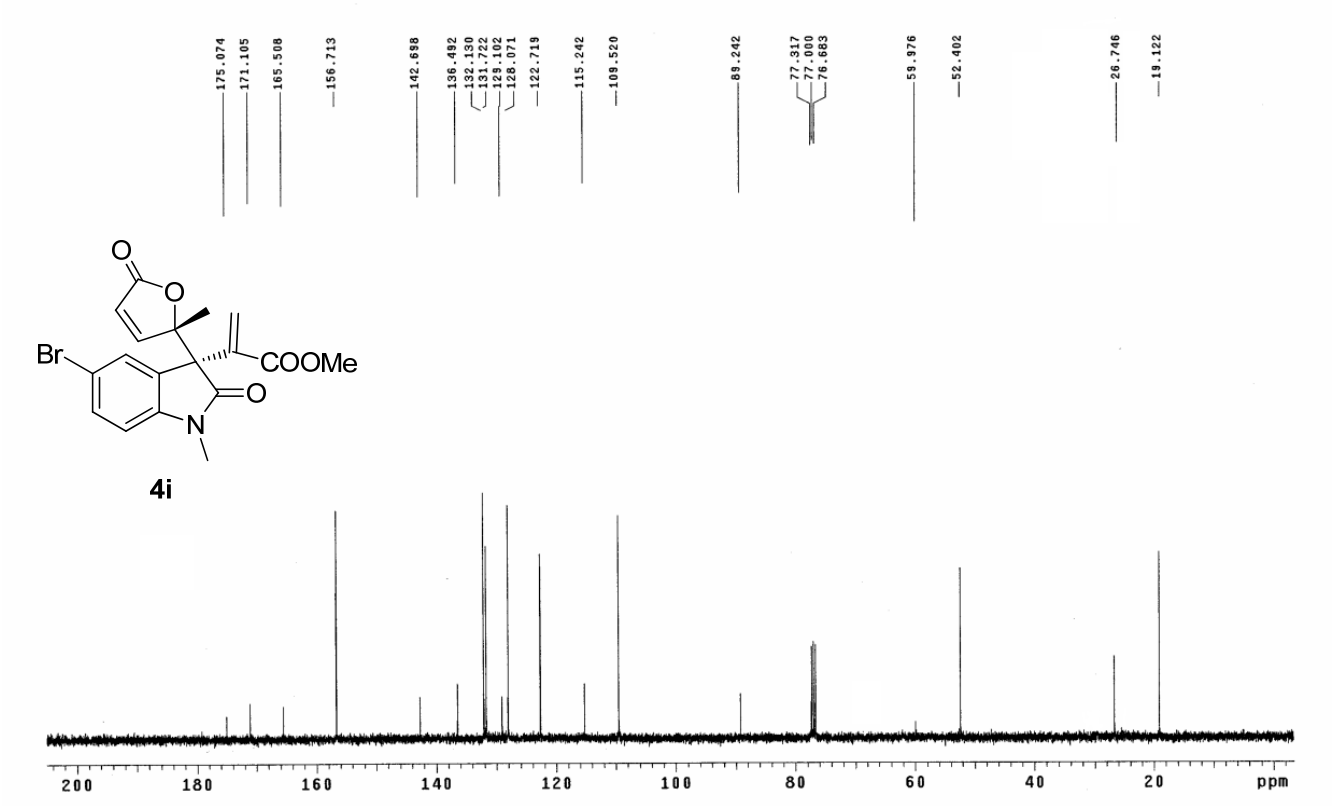
7.347
7.212
7.208
7.036
7.022
6.811
6.752
6.668
6.647
5.748
5.734
3.618
3.241
1.839
Br
COOMe
O
N
4i
10
9
8
7
6
5
4
3
2
1
ppm
0.91
0.86
1.05
0.58
1.00
0.94
0.76
3.00
3.04
3.13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156.713
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136.492
132.130
131.722
129.102
128.071
122.719
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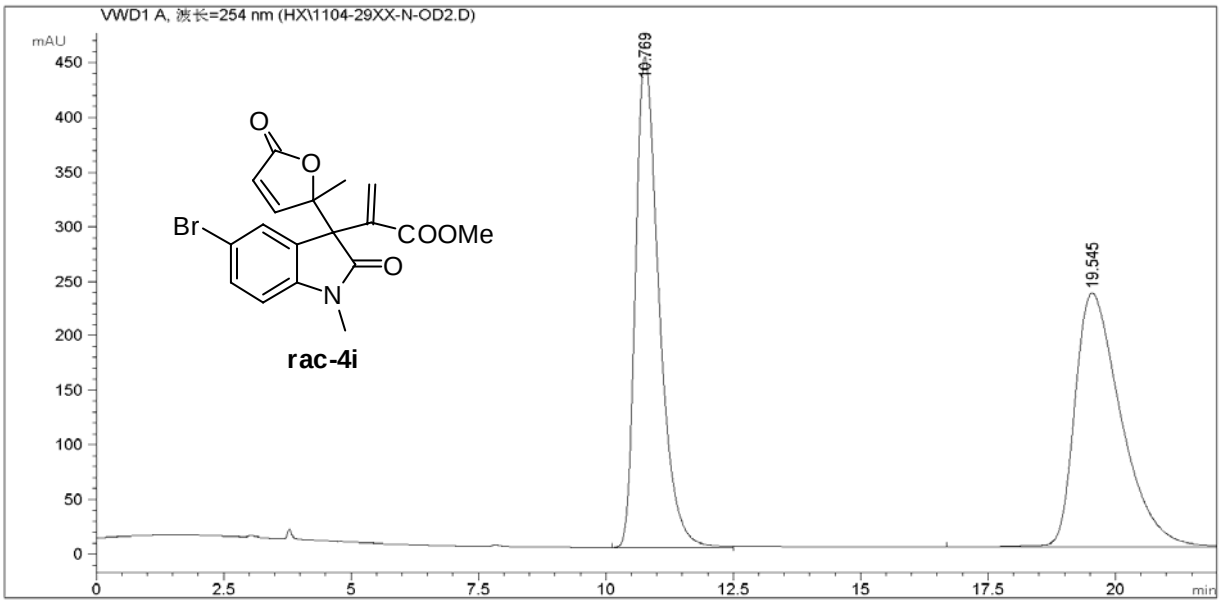
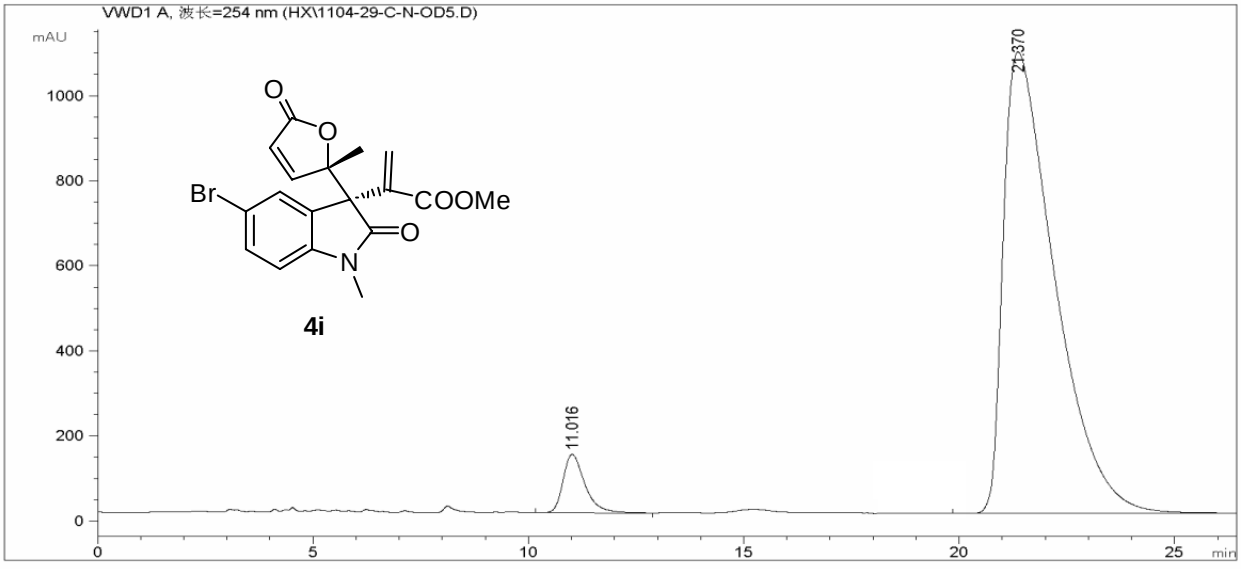
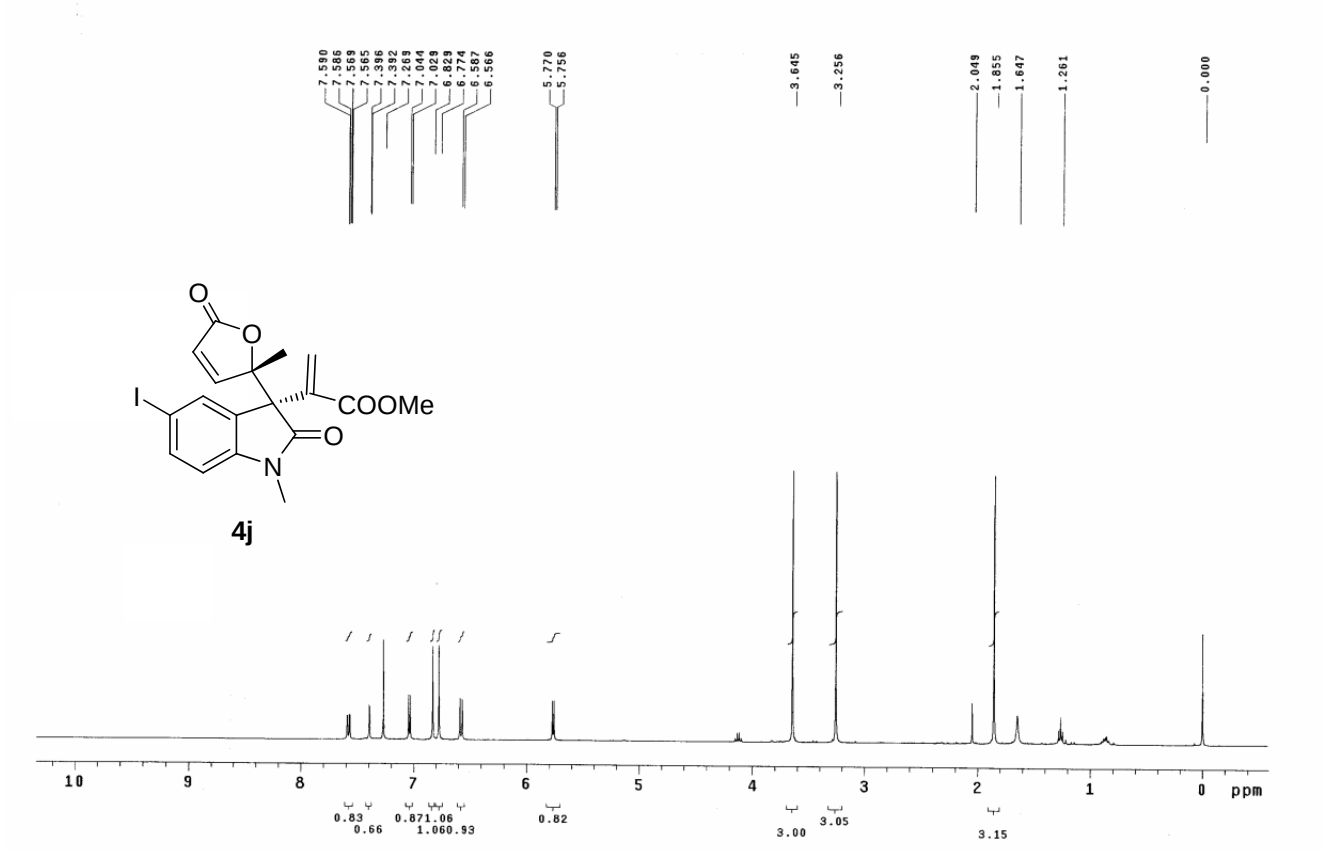
109.520
89.242
77.317
77.000
76.683
59.976
52.402
26.746
19.122
Br
COOMe
O
N
4i
200
180
160
140
120
100
80
60
40
20
ppm



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	10.769	BV	0.4900	1.43696e4	448.80643	49.5355
2	19.545	BBA	0.9543	1.46391e4	233.01639	50.4645



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	11.016	VV	0.5329	4837.74268	137.45110	5.1199
2	21.370	VBA	1.2500	8.96514e4	1084.32117	94.8801


7.590
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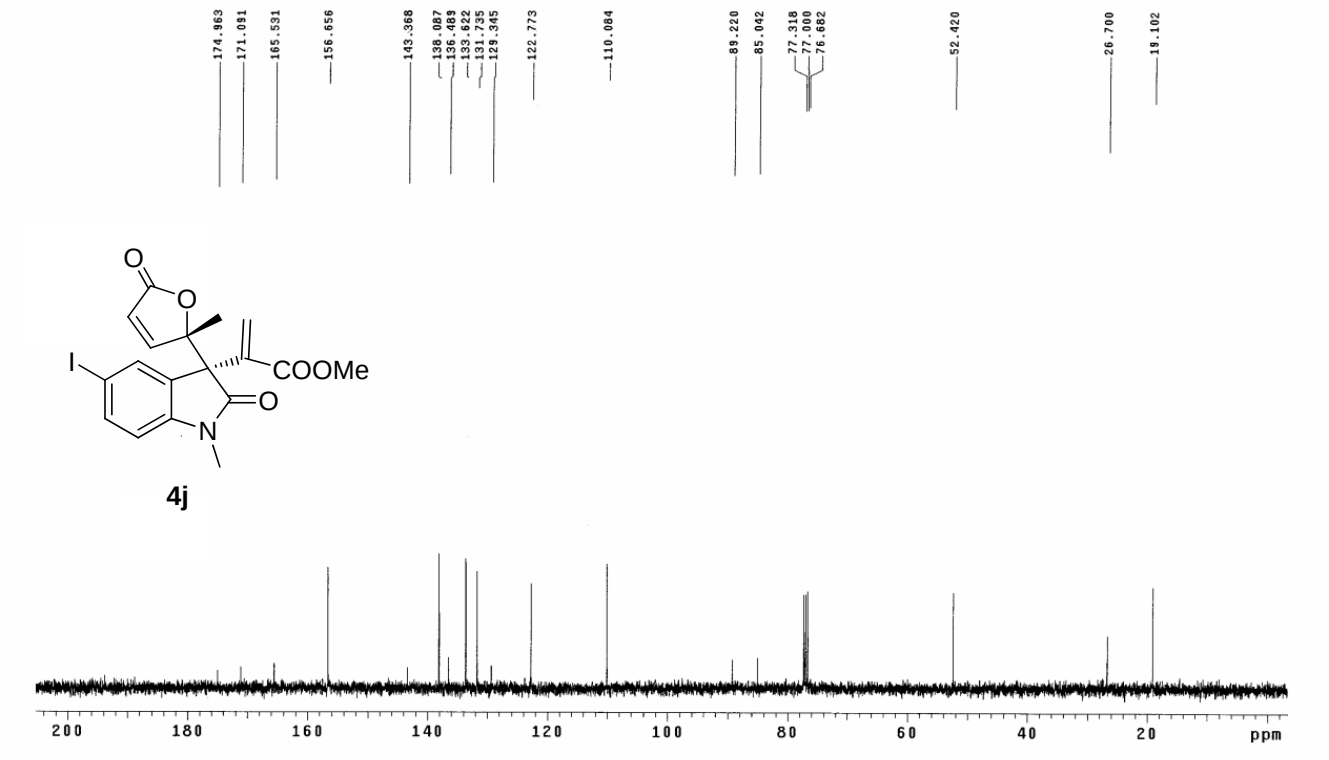
7.569
7.565
7.396
7.392
7.269
7.044
7.029
6.829
6.774
6.587
6.566
5.770
5.756
3.645
3.256
2.049
1.855
1.647
1.261
0.000
O
O
I
COOMe
O
N
4j
10
9
8
7
6
5
4
3
2
1
0
ppm
0.83
0.66
0.871.06
1.060.93
0.82
3.00
3.05
3.15


174.963
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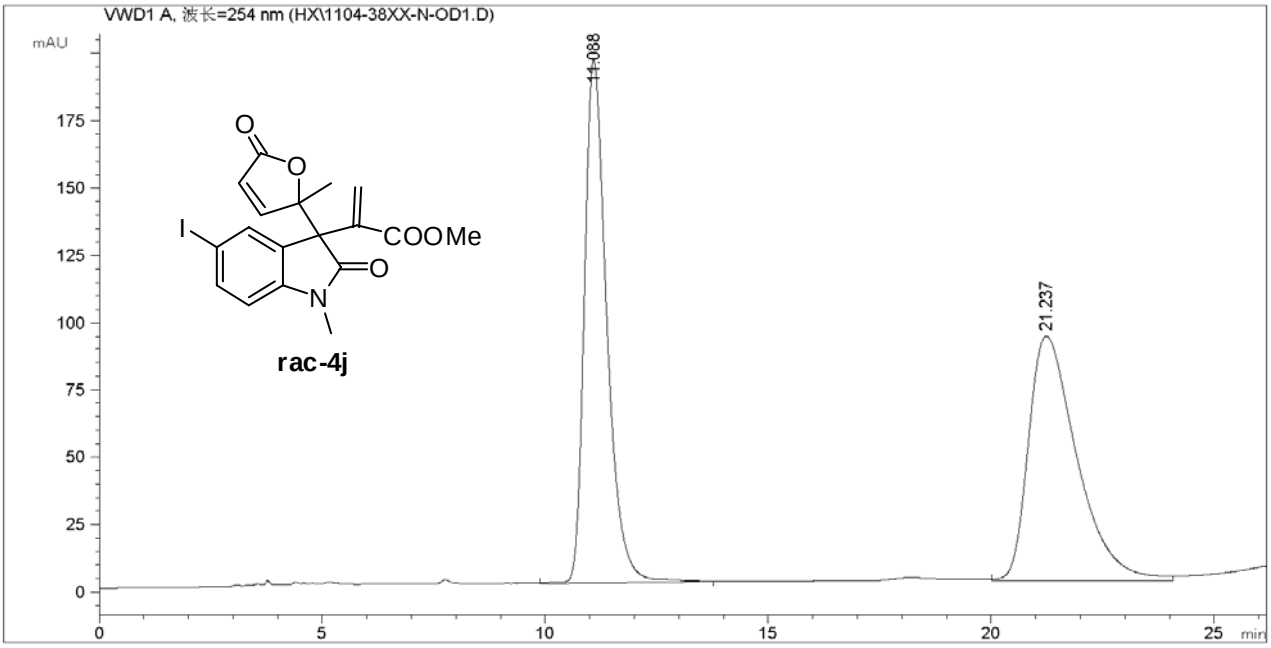
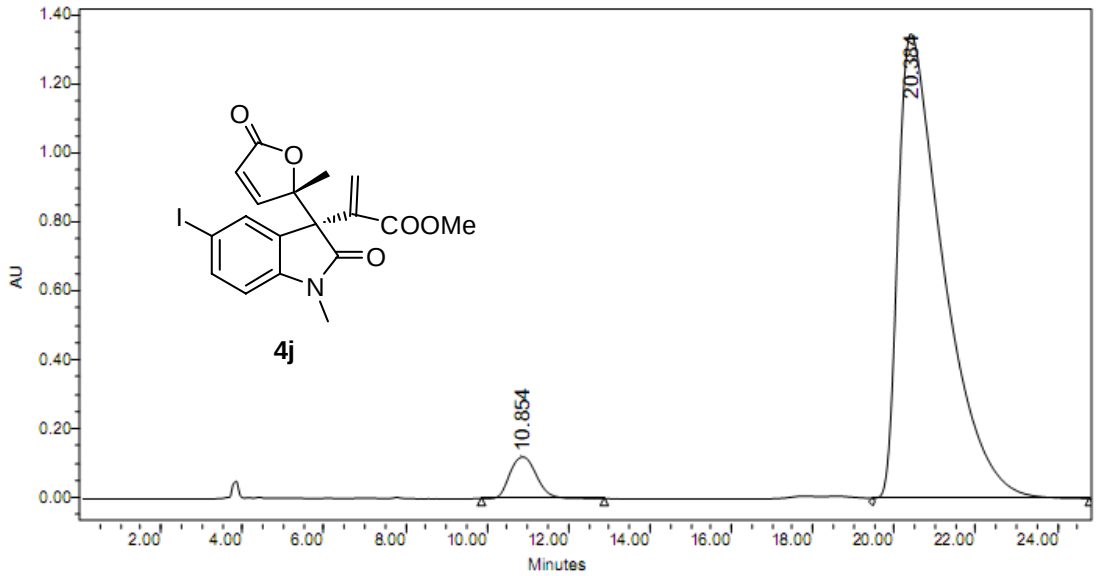
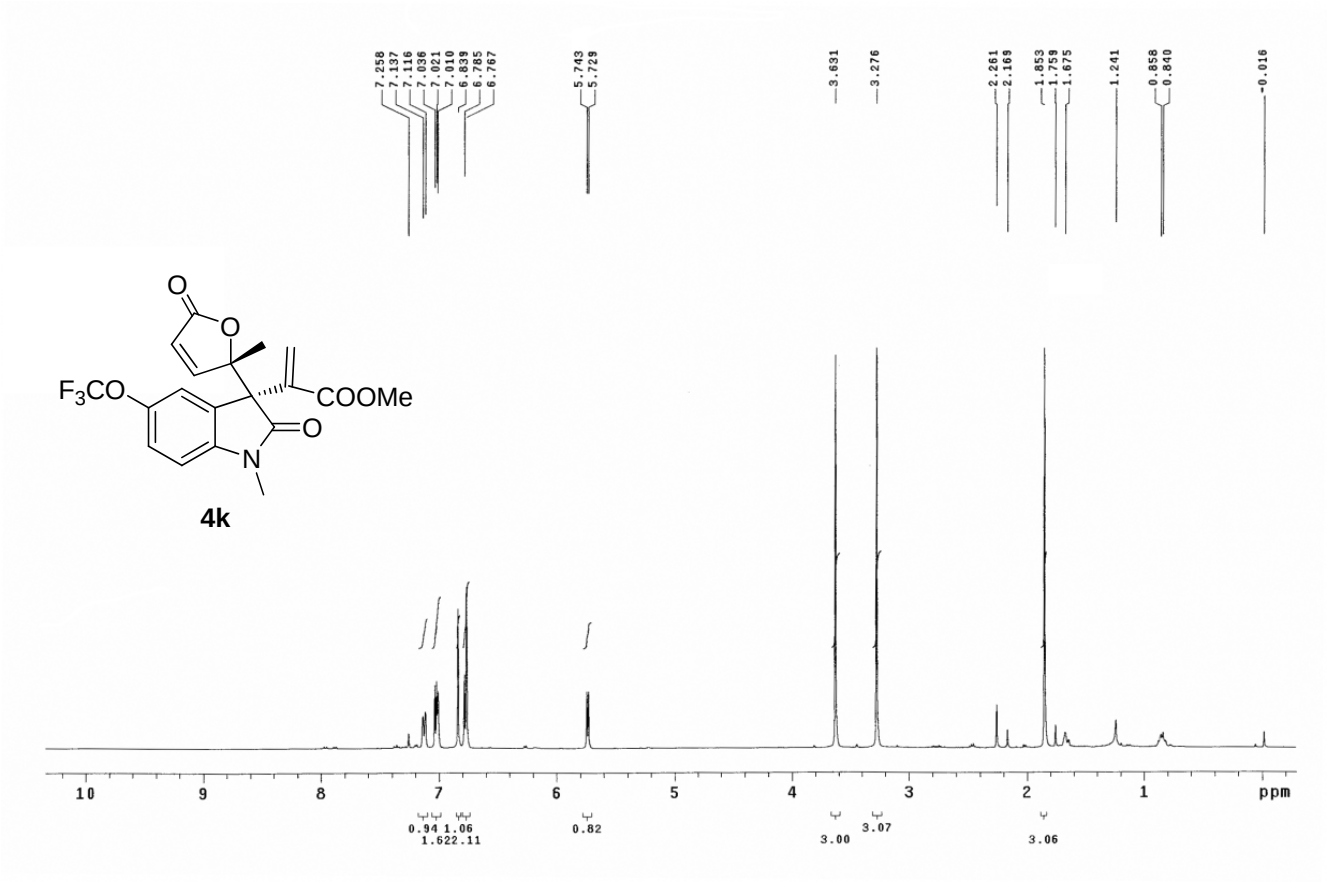
165.531
156.656
143.368
138.087
136.489
133.622
131.735
129.345
122.773
110.084
89.220
85.042
77.318
77.000
76.682
52.420
26.700
19.102
O
O
I
COOMe
O
N
4j
200
180
160
140
120
100
80
60
40
20
ppm

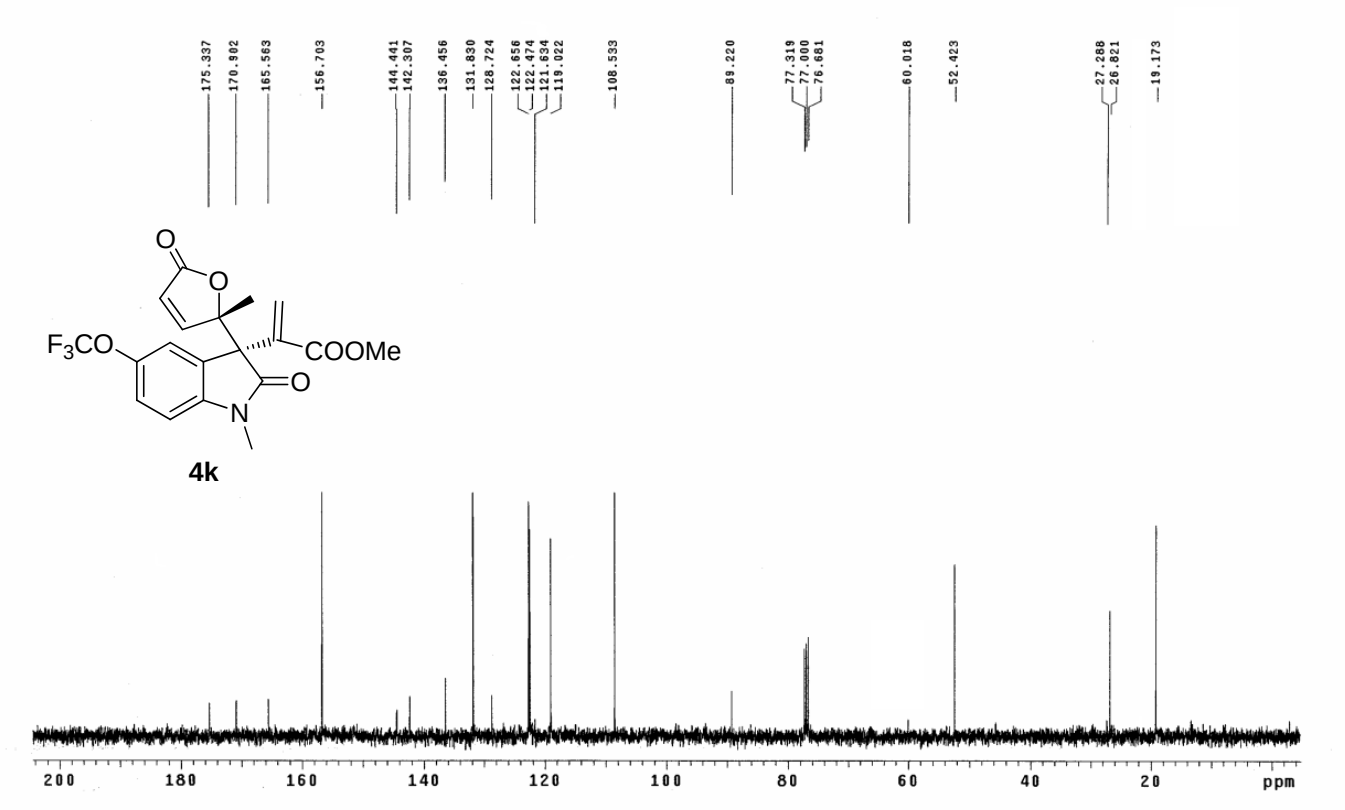


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	11.088	BB	0.5299	6786.74951	194.25641	49.7116
2	21.237	BB	1.1414	6865.48682	91.08699	50.2884



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	10.854	5542041	5.06	121024	8.24
2	20.384	103923702	94.94	1347531	91.76


7.258
7.137
7.116
7.036
7.021
7.010
6.839
6.785
6.767
5.743
5.729
3.631
3.276
2.261
2.169
1.853
1.759
1.675
1.241
0.858
0.840
-0.016
O
O
F3CO
COOMe
O
N
4k
10
9
8
7
6
5
4
3
2
1
ppm
0.94 1.06
1.622.11
0.82
3.00
3.07
3.06


175.337
170.802
165.563
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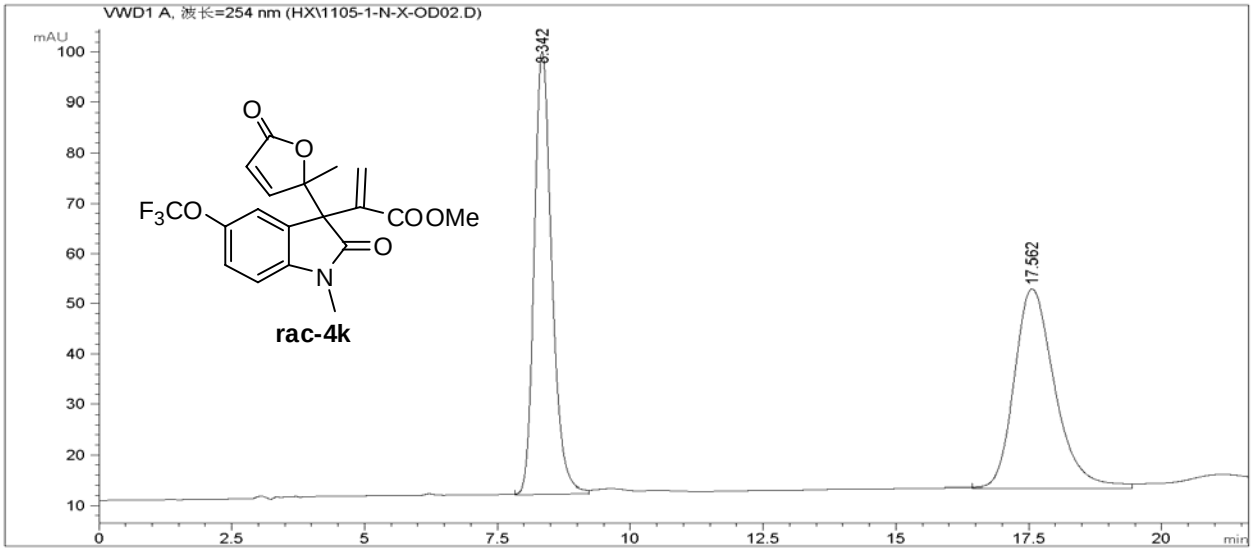
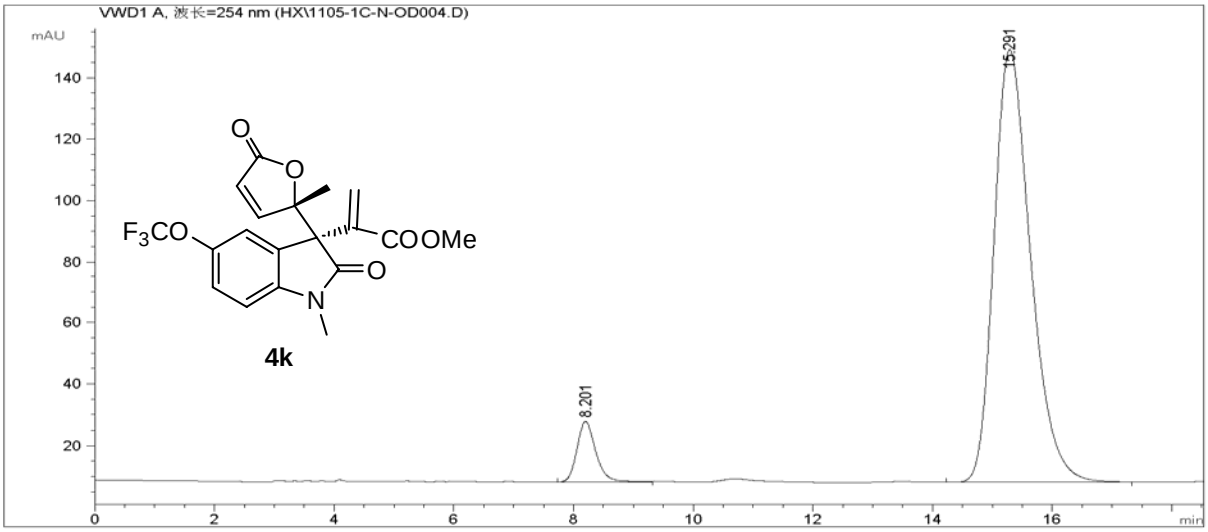
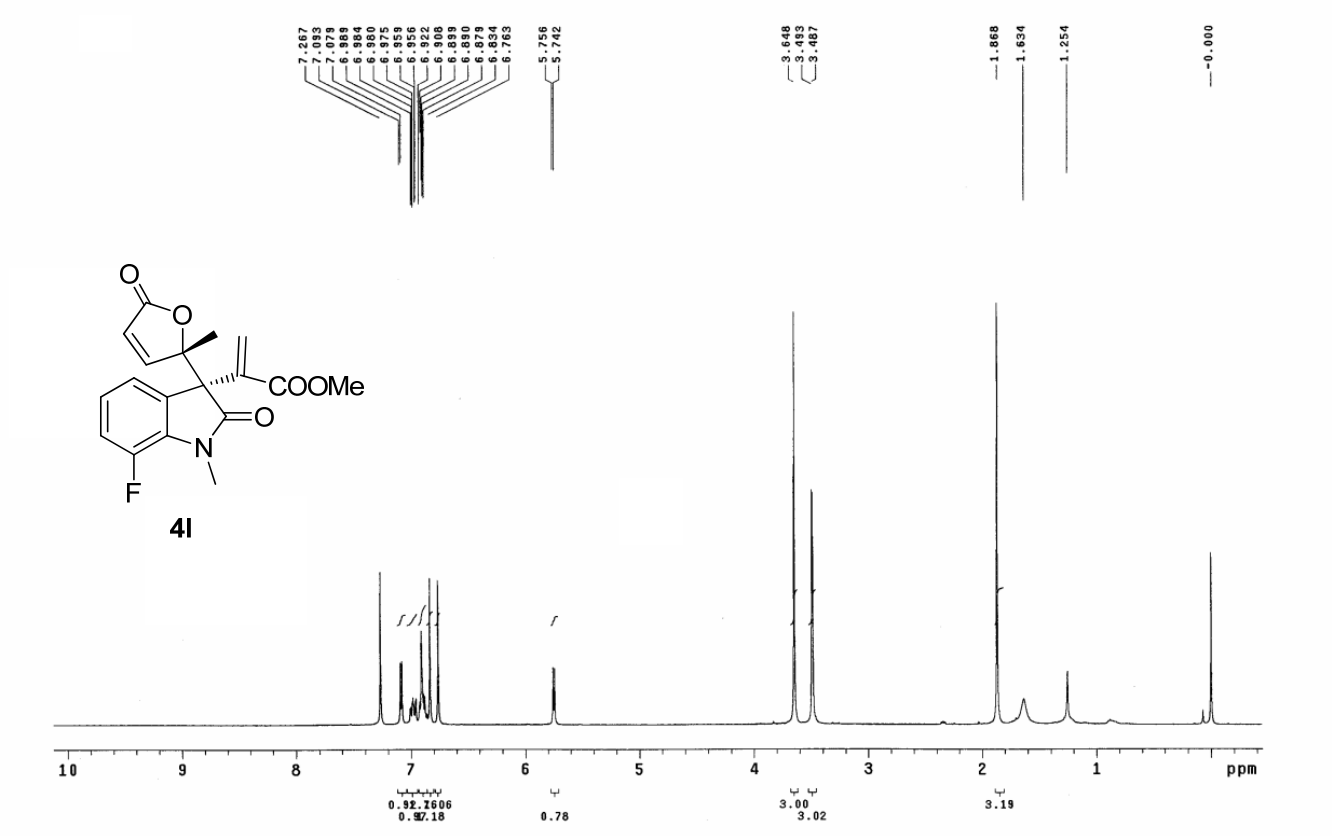
144.441
142.307
136.456
131.830
128.724
122.656
122.474
121.834
119.022
108.533
89.220
77.319
77.000
76.681
60.018
52.423
27.288
26.821
19.173
O
O
F3CO
COOMe
O
N
4k
200
180
160
140
120
100
80
60
40
20
ppm



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.342	BV	0.3509	2027.46423	87.82693	49.2600
2	17.562	BB	0.8066	2088.37720	39.65810	50.7400



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.201	BB	0.3343	433.77298	19.57243	6.7566
2	15.291	VB	0.6583	5986.25537	141.01189	93.2434


7.267
7.093
7.079
6.989
6.984
6.980
6.975
6.959
6.956
6.922
6.906
6.899
6.890
6.879
6.834
6.763
5.756
5.742
3.648
3.493
3.487
1.868
1.634
1.254
-0.000
COOMe
O
N
F
4l
10
9
8
7
6
5
4
3
2
1
ppm
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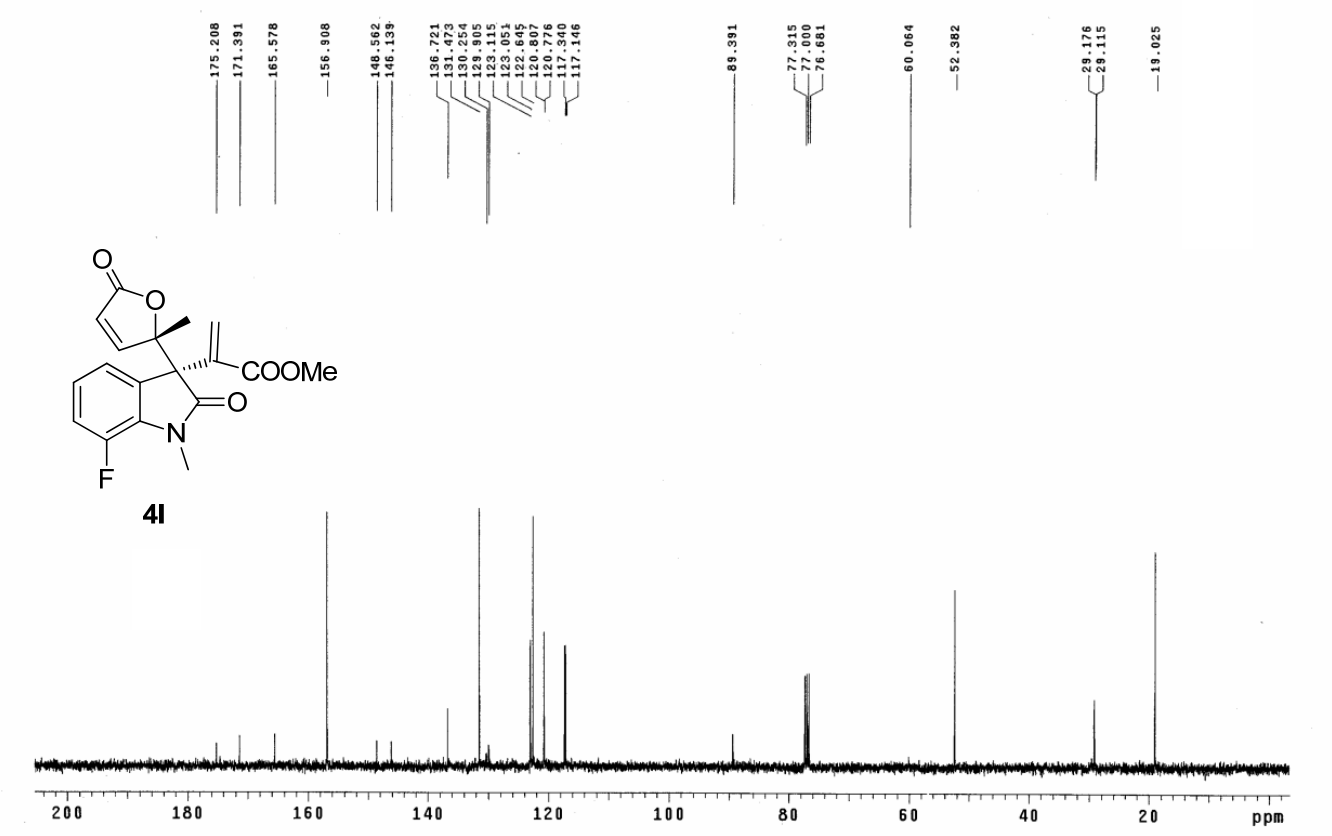
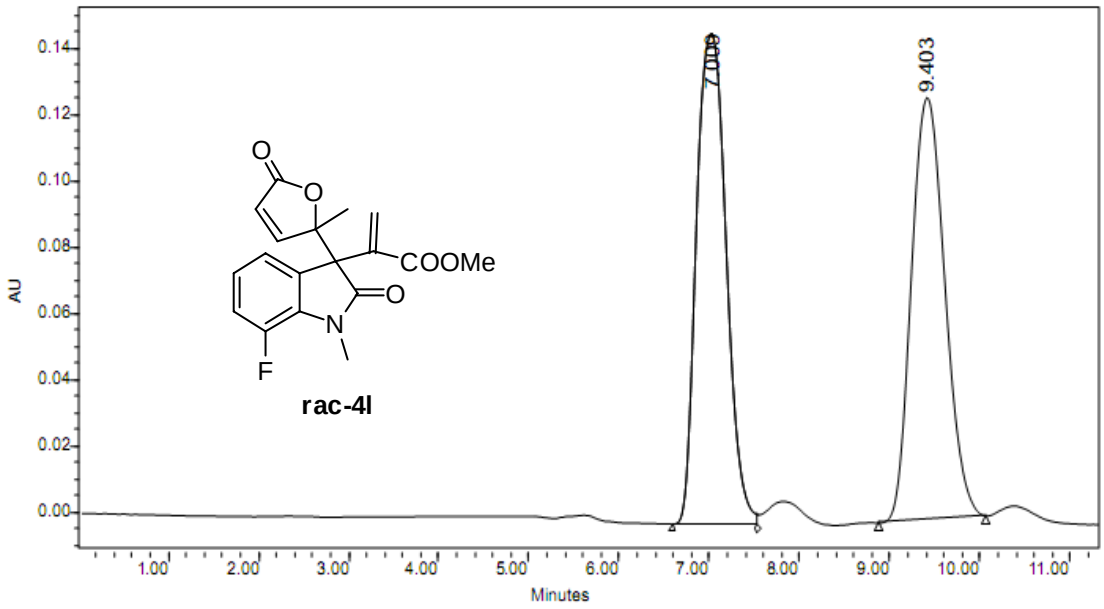
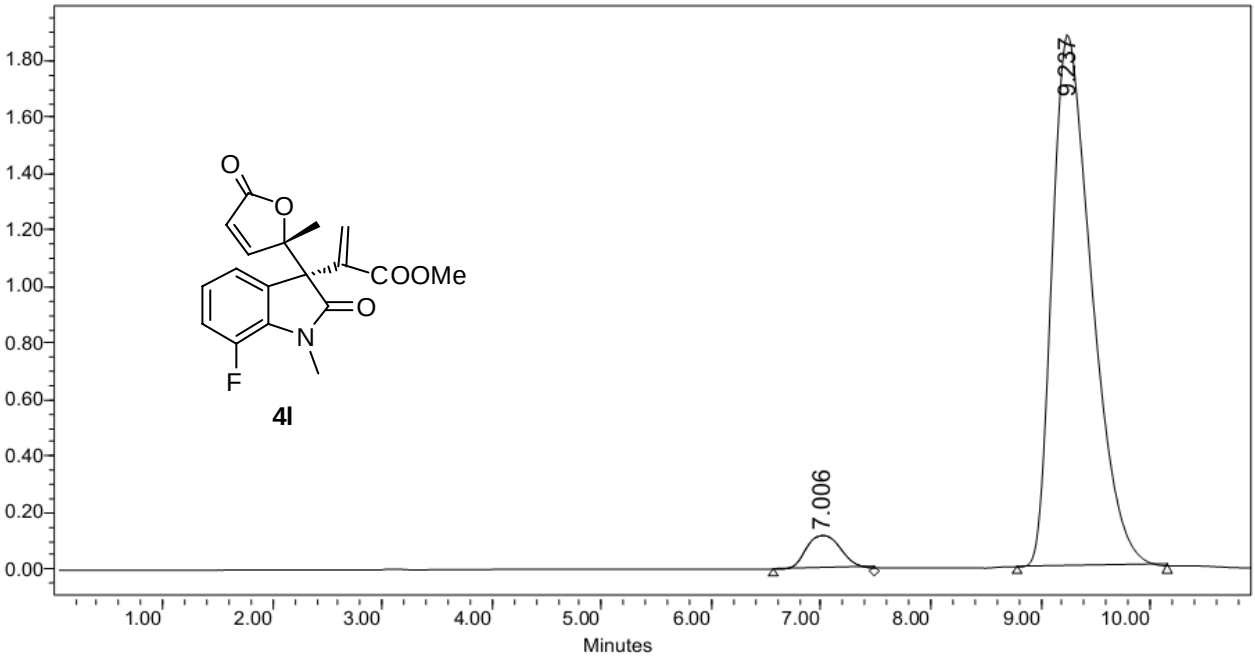
3.00
3.02
3.19


175.208
171.391
165.578
156.908
148.562
146.139
136.721
131.473
130.254
129.905
123.115
123.051
122.645
120.807
120.776
117.340
117.146
89.391
77.315
77.000
76.681
60.064
52.382
29.176
29.115
19.025
COOMe
O
N
F
4l
200
180
160
140
120
100
80
60
40
20
ppm



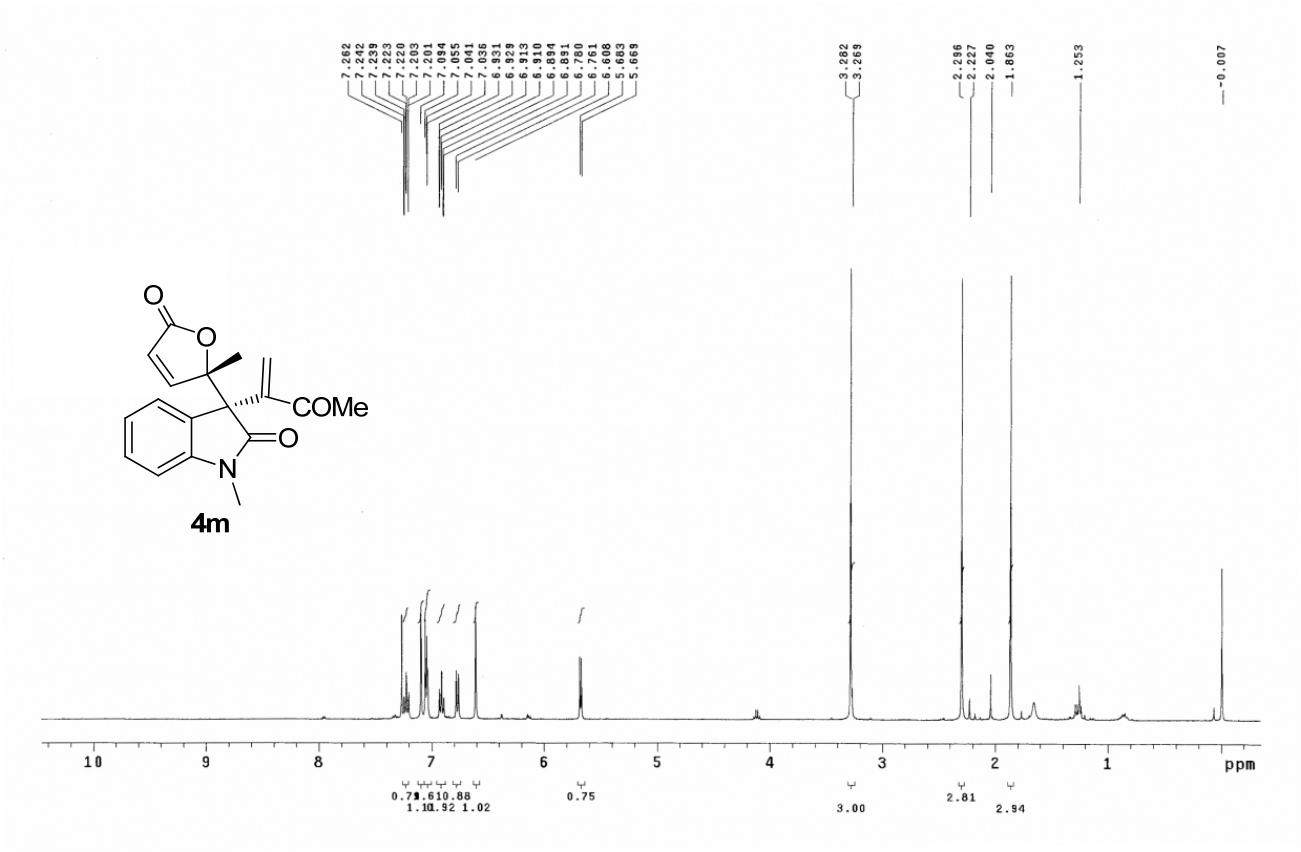
rac-4l

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.009	3395882	50.79	148287	53.77
2	9.403	3289654	49.21	127483	46.23



4l

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.006	2613011	5.23	117281	5.86
2	9.237	47320700	94.77	1884370	94.14


7.262
7.242
7.238
7.223
7.220
7.203
7.201
7.084
7.055
7.041
7.036
6.931
6.929
6.913
6.910
6.894
6.891
6.780
6.761
6.608
5.683
5.669
3.282
3.269
2.296
2.227
2.040
1.863
1.253
-0.007
O
O
COMe
O
N
4m
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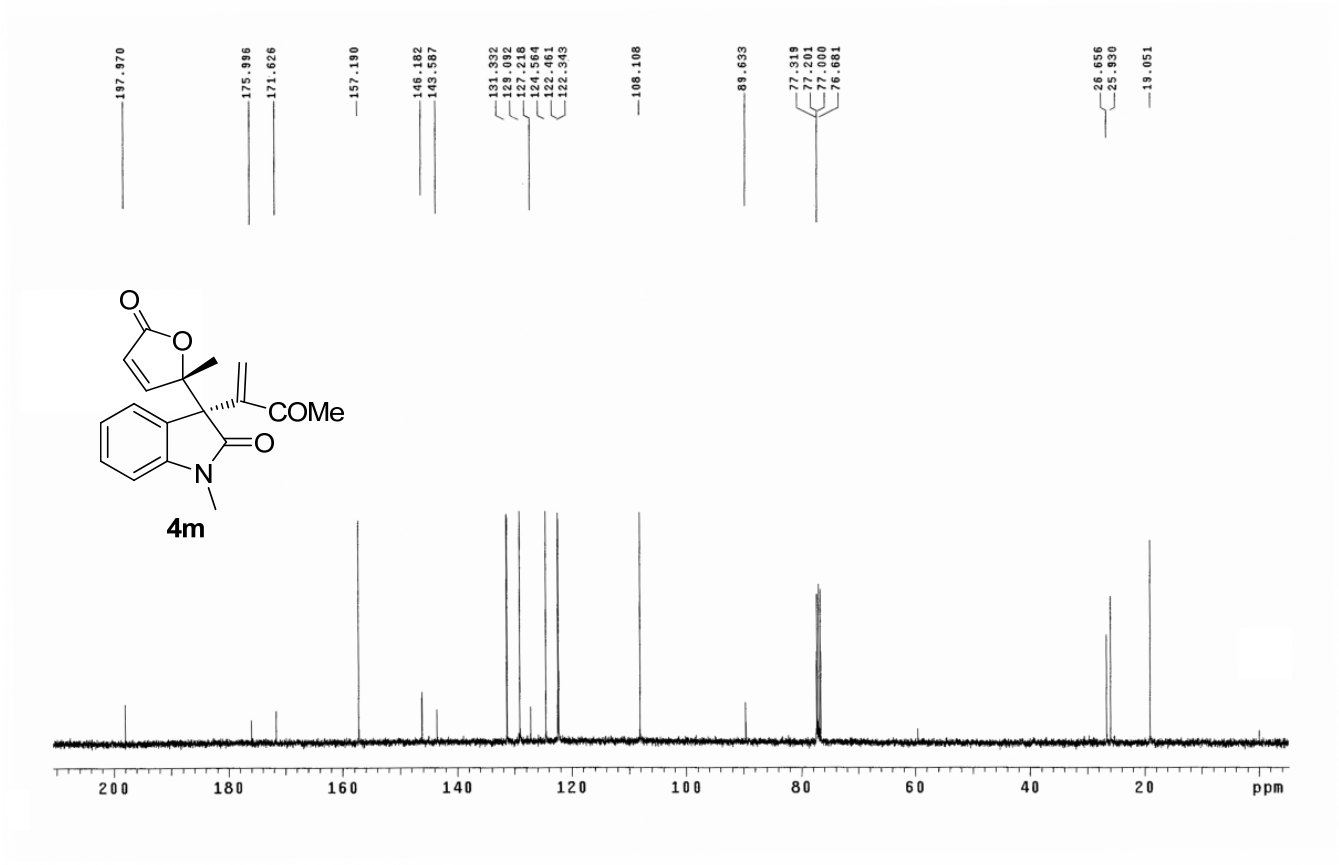
9
8
7
6
5
4
3
2
1
ppm
0.75
3.00
2.81
2.94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157.190
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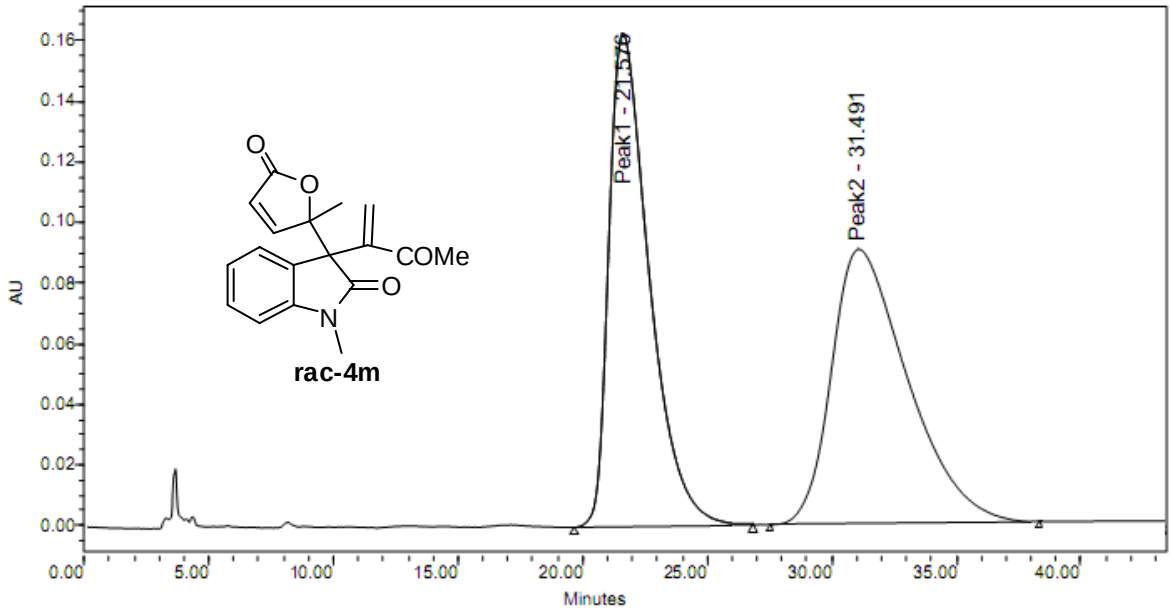
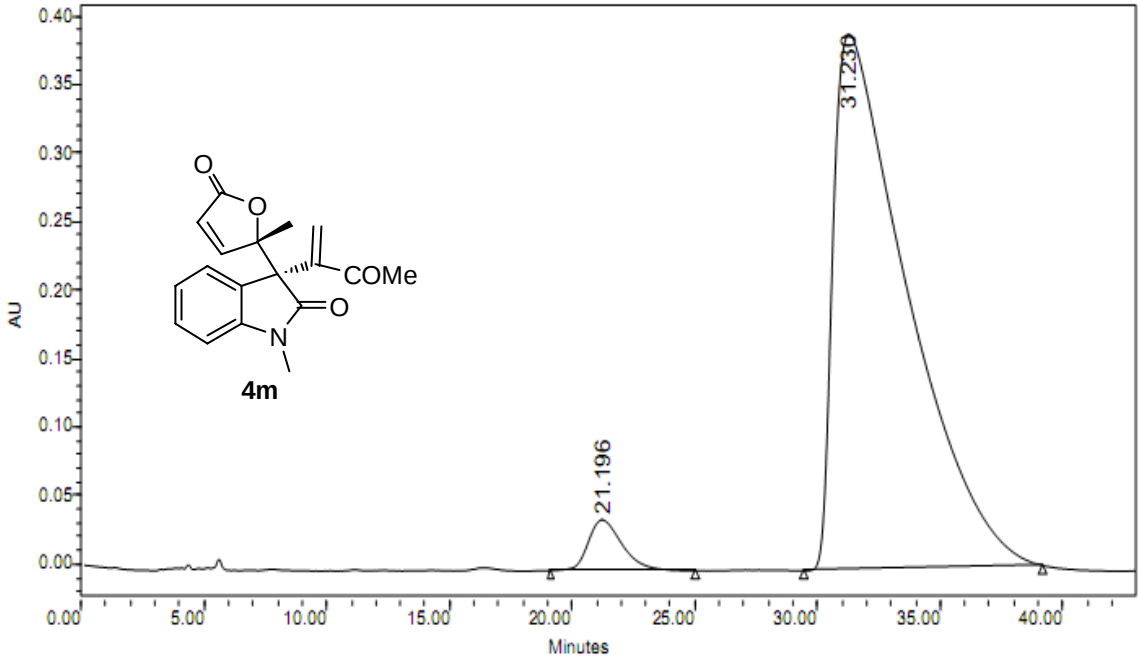
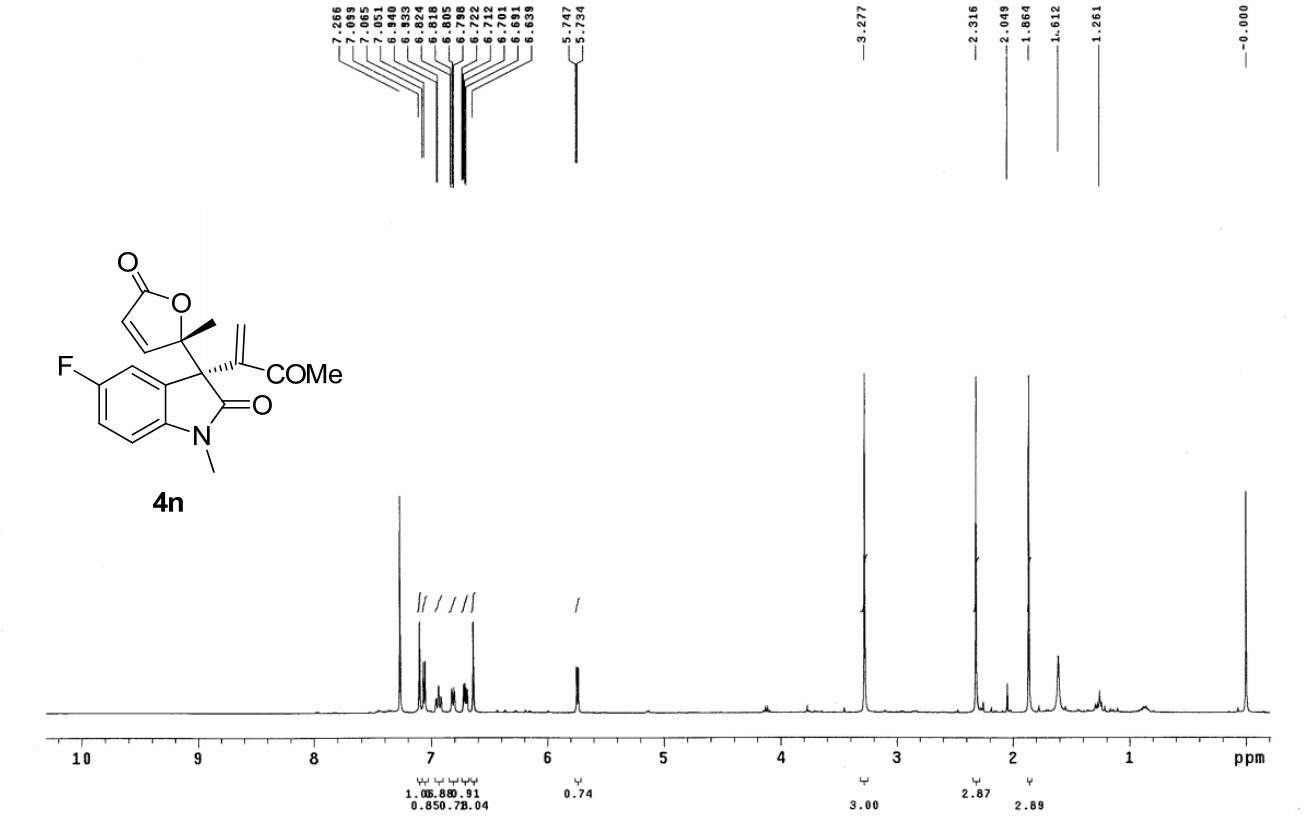
143.587
131.332
128.092
127.218
124.564
122.461
122.343
108.108
89.633
77.319
77.201
77.000
76.681
26.656
25.930
19.051
O
O
COMe
O
N
4m
200
180
160
140
120
100
80
60
40
20
ppm



	Peak Name	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	Peak1	21.576	18462292	48.77	162841	64.25
2	Peak2	31.491	19396275	51.23	90610	35.75



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	21.196	3588846	4.18	37025	8.65
2	31.230	82248507	95.82	391052	91.35


7.266
7.059
7.065
7.051
6.840
6.833
6.824
6.818
6.805
6.798
6.722
6.712
6.701
6.691
6.639
5.747
5.734
3.277
2.316
2.049
1.864
1.612
1.261
0.000
O
O
F
COMe
O
N
4n
10
9
8
7
6
5
4
3
2
1
ppm
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1.04
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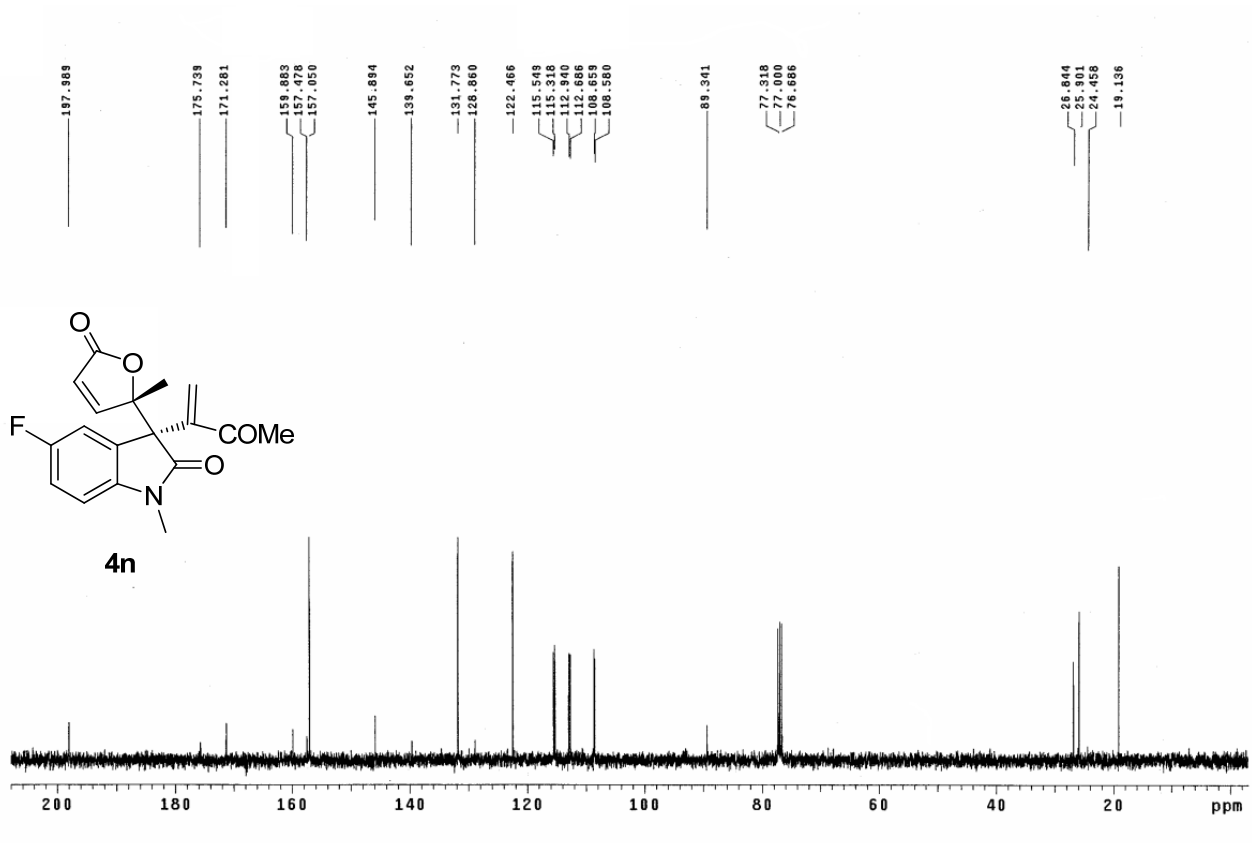
3.00
2.87
2.89


197.389
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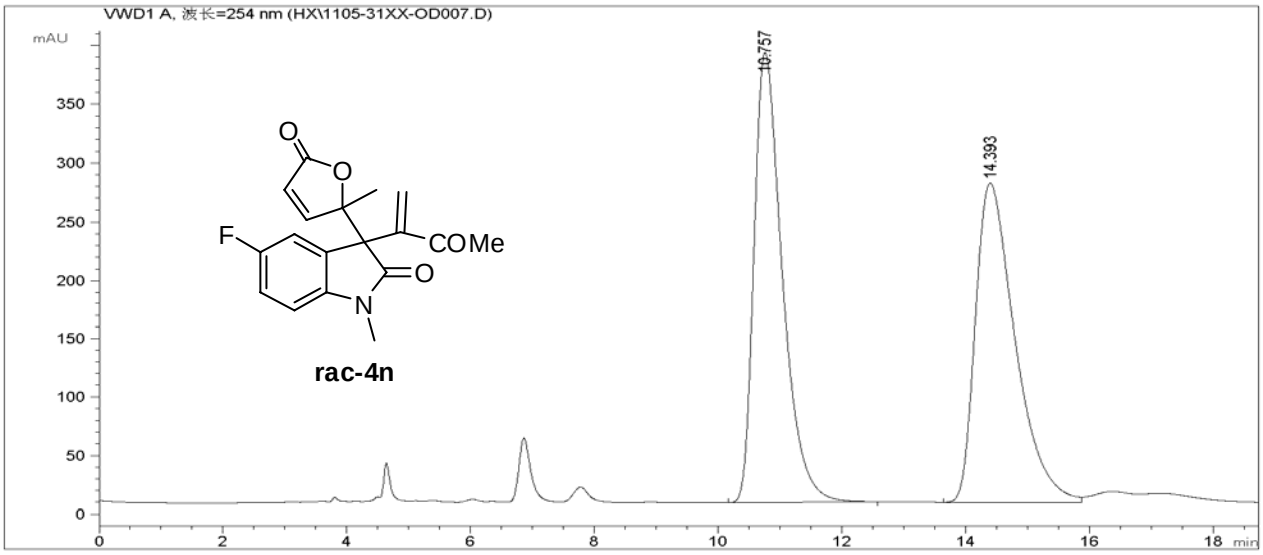
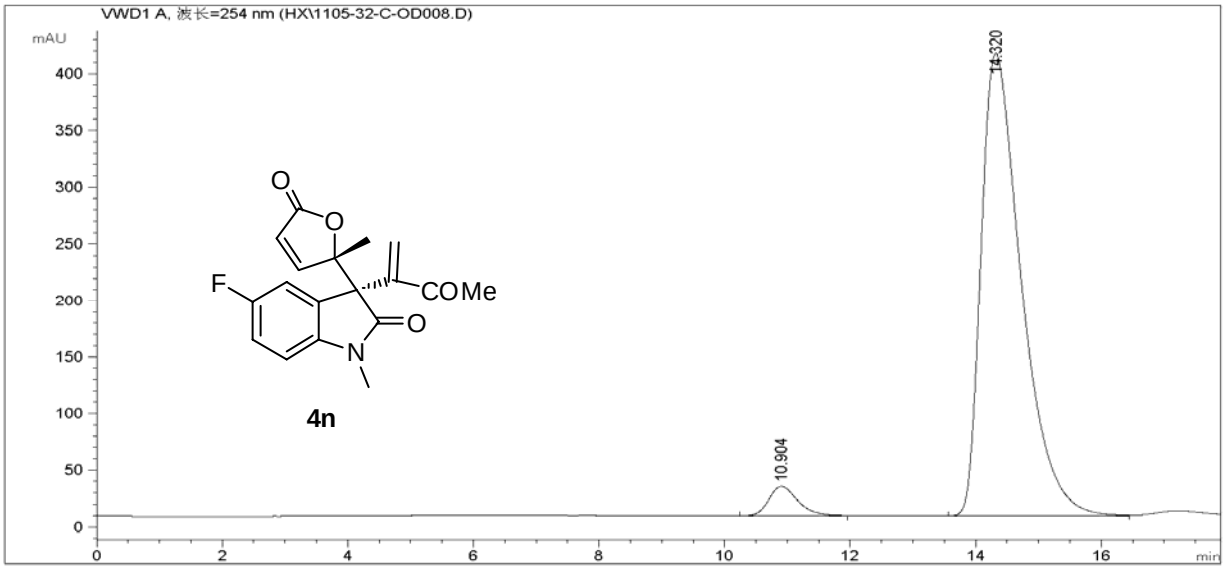
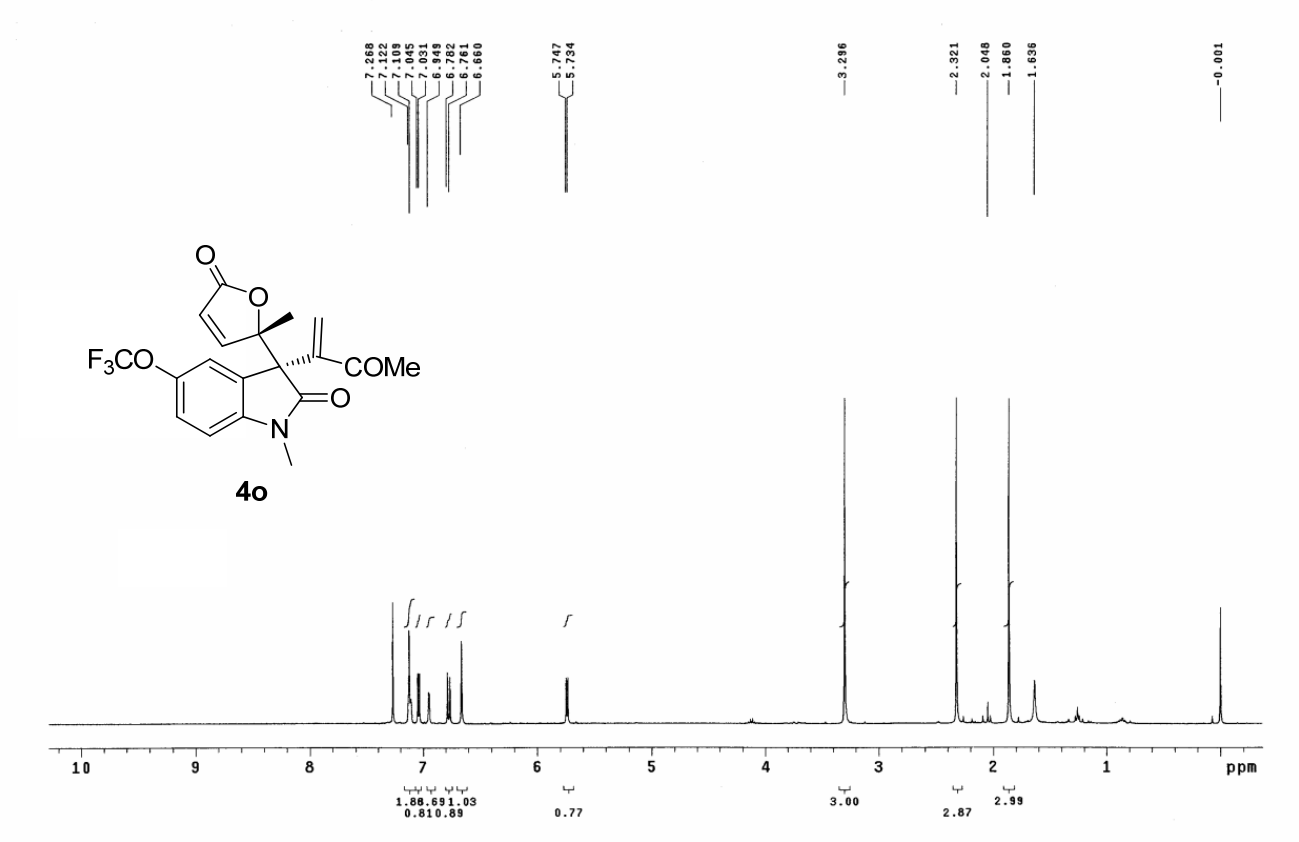
159.883
157.478
157.050
145.894
139.652
131.773
128.860
122.466
115.549
115.318
112.940
112.686
108.659
108.580
89.341
77.318
77.000
76.686
26.844
25.901
24.458
19.136
O
O
F
COMe
O
N
4n
200
180
160
140
120
100
80
60
40
20
ppm



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	10.757	BB	0.4830	1.22472e4	383.76743	50.1846
2	14.393	BV	0.6829	1.21571e4	272.87119	49.8154



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	10.904	BB	0.4860	836.00775	26.29274	4.3890
2	14.320	BB	0.6776	1.82116e4	408.28864	95.6110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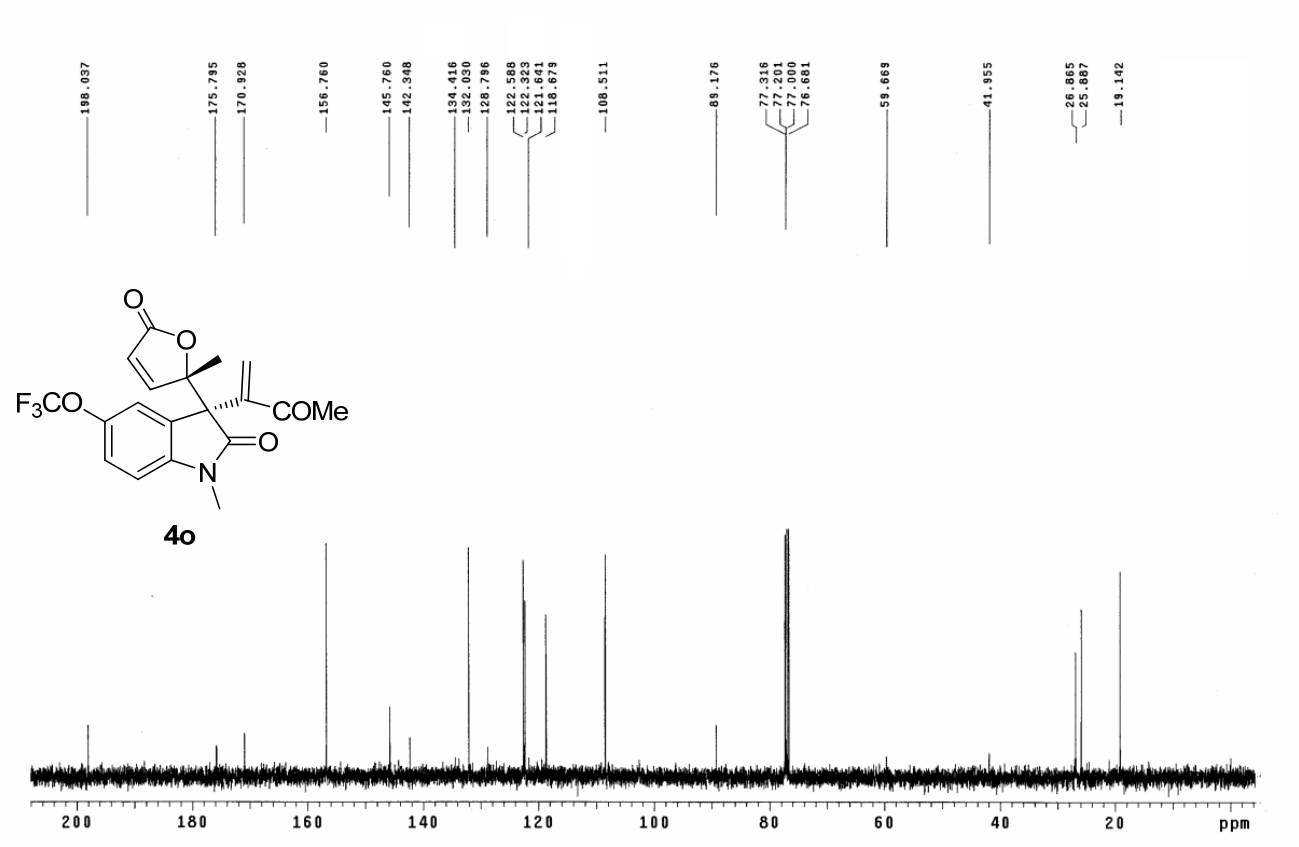
7.122
7.109
7.045
7.031
6.949
6.782
6.761
6.660
5.747
5.734
3.296
2.321
2.048
1.860
1.636
0.001
O
O
F3CO
COMe
O
N
4o
10
9
8
7
6
5
4
3
2
1
ppm
1.88
6.91
1.03
0.81
0.89
0.77
3.00
2.87
2.99


198.037
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170.928
156.760
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142.348
134.416
132.030
128.796
122.588
122.323
121.641
118.679
108.511
83.176
77.316
77.201
77.000
76.681
59.669
41.955
26.865
25.887
19.142
O
O
F3CO
COMe
O
N
4o
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180
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140
120
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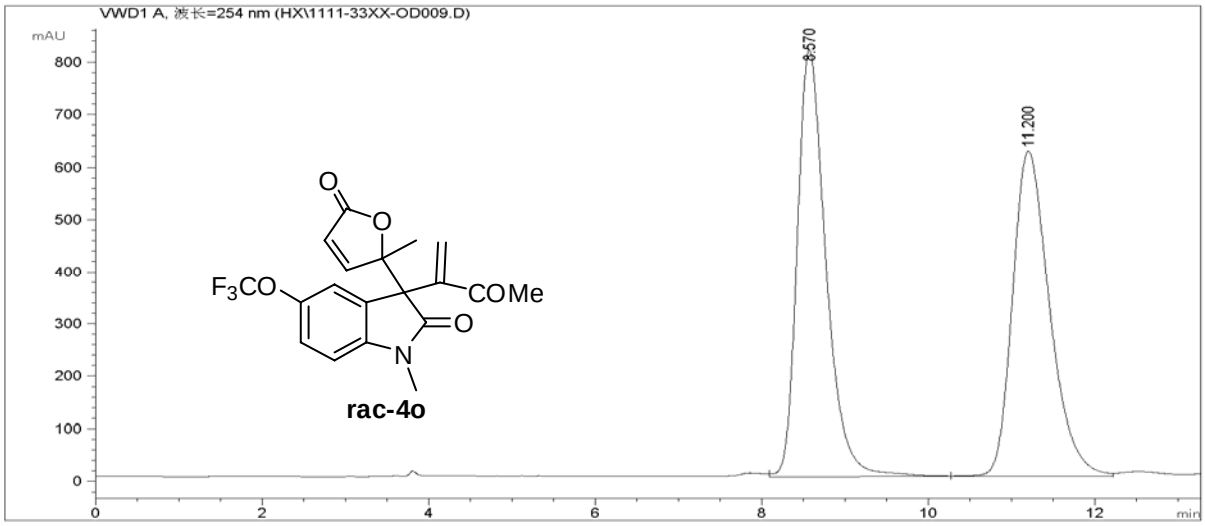
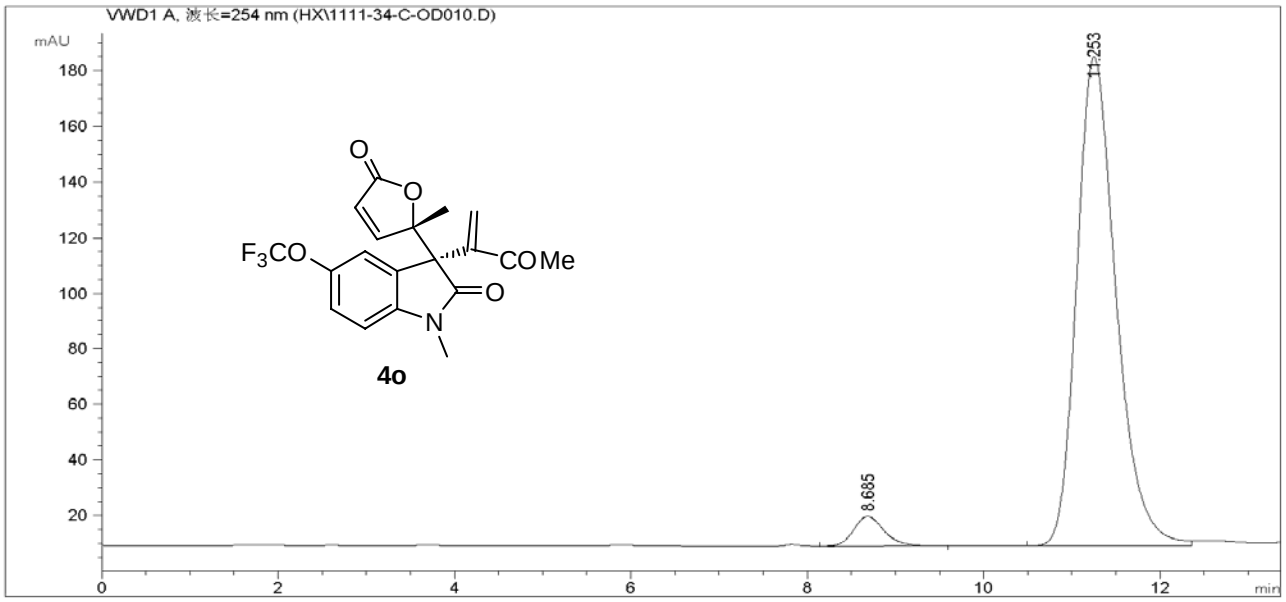
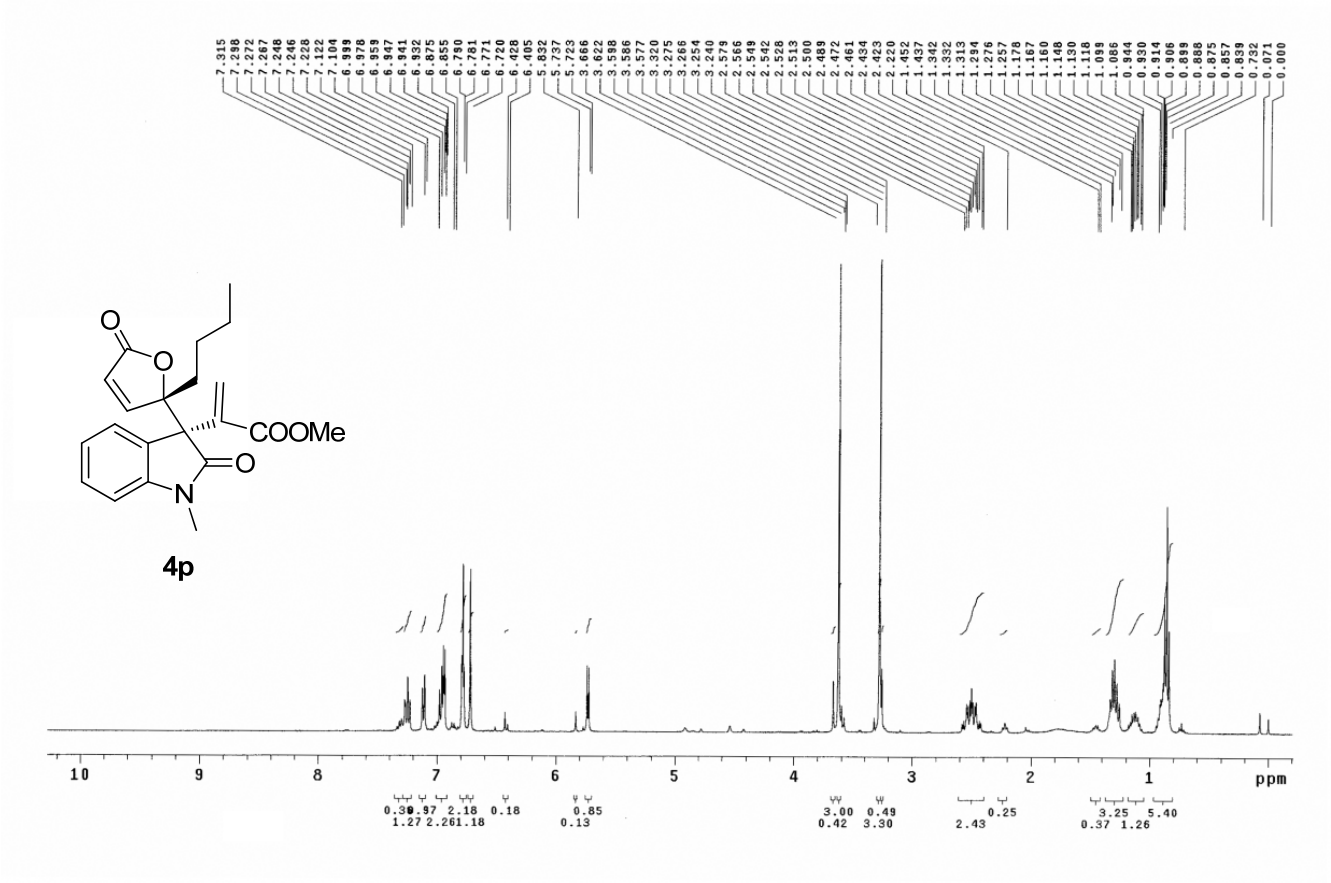
80
60
40
20
ppm

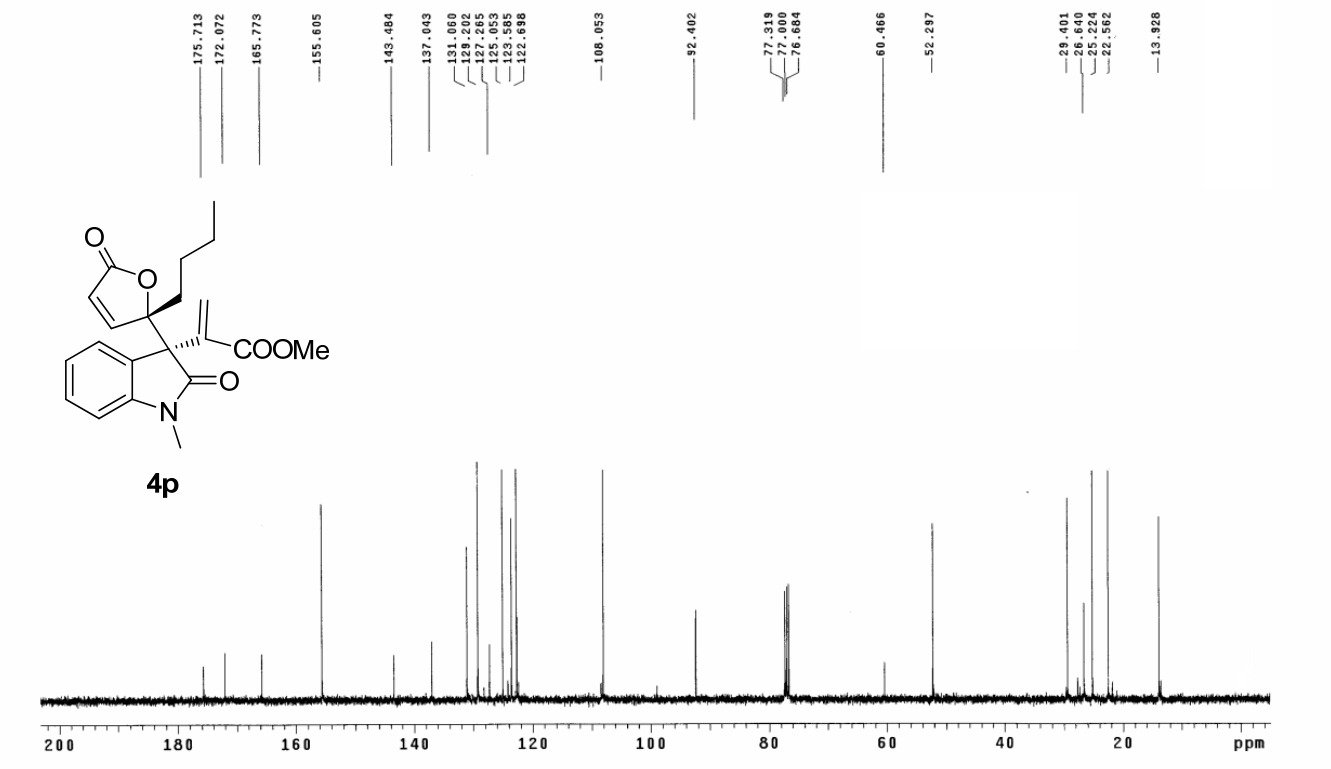


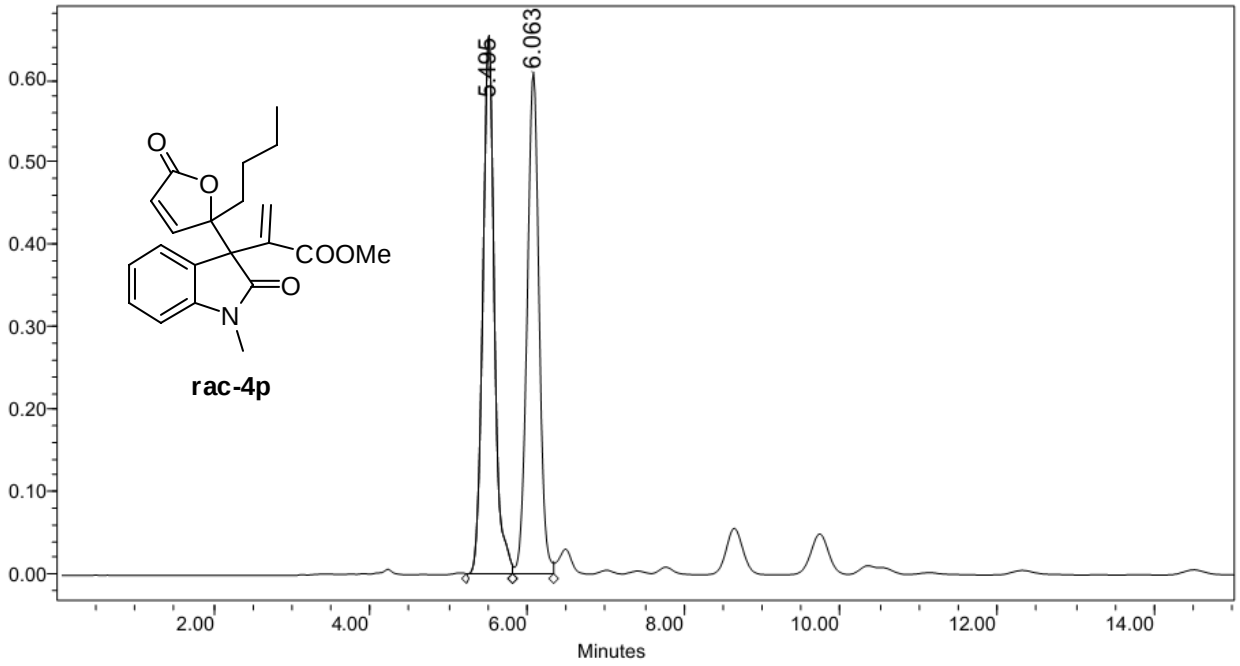
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.570	VV	0.3675	1.95446e4	814.02753	50.3948
2	11.200	VV	0.4776	1.92384e4	621.59009	49.6052



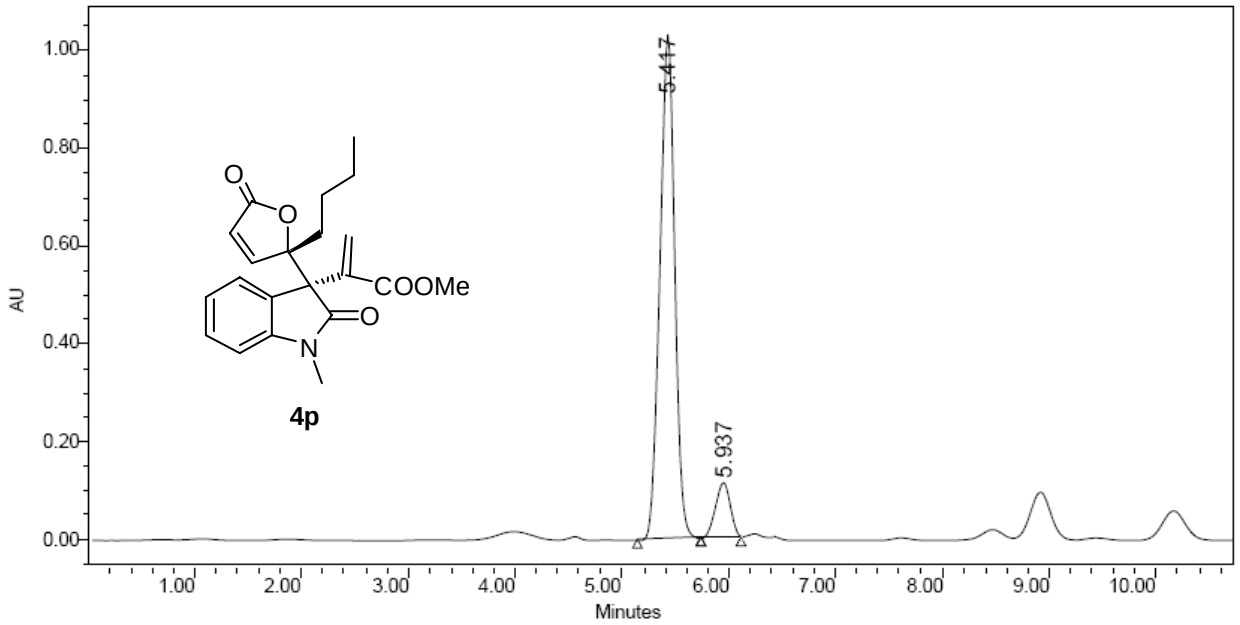
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.685	VB	0.3699	257.98065	10.65350	4.5200
2	11.253	BV	0.4723	5449.52588	175.79794	95.4800


COOMe
4p
ppm

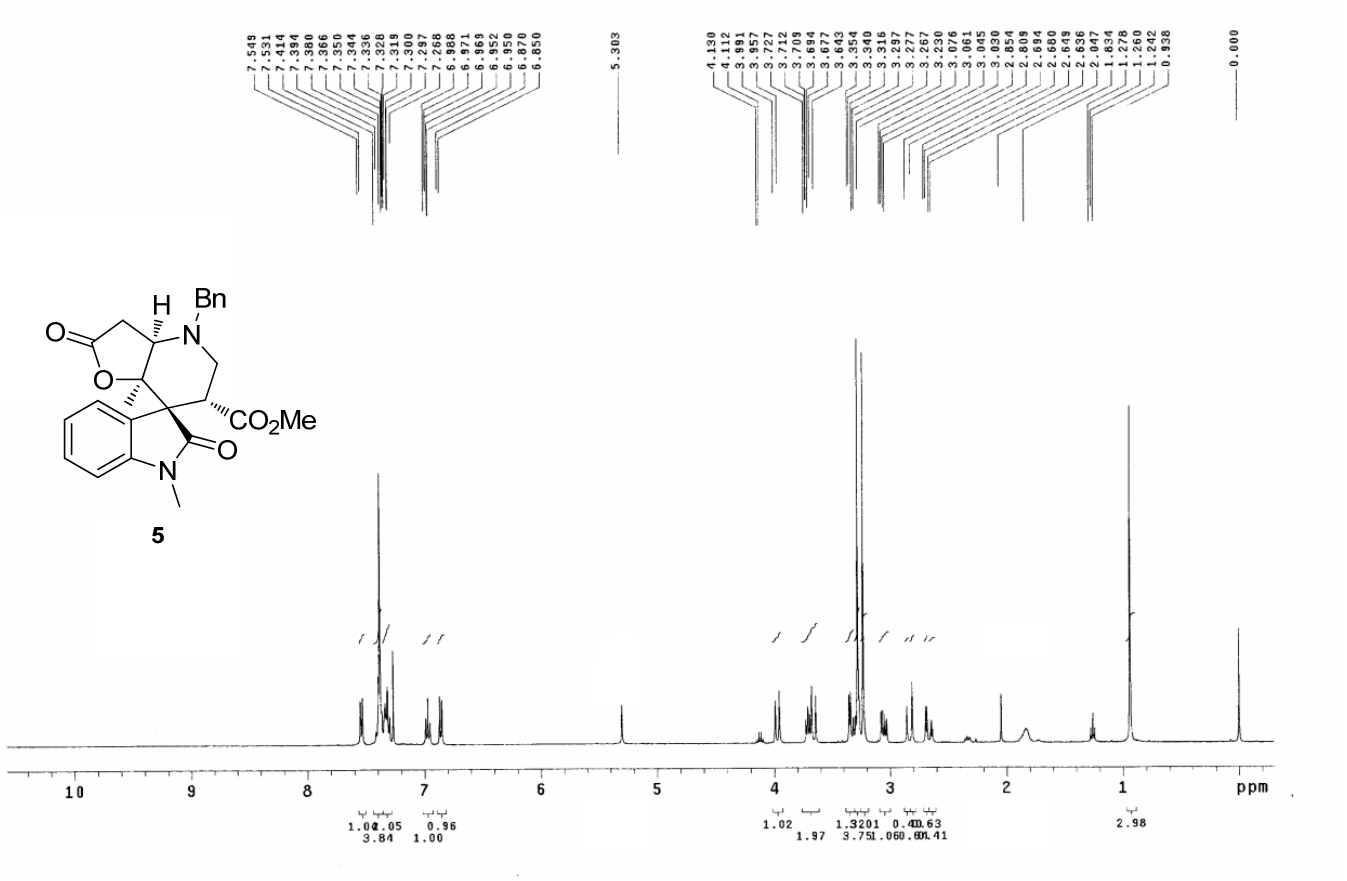

COOMe
4p
ppm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.495	6706061	50.81	656093	51.79
2	6.063	6491730	49.19	610637	48.21



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.417	9925478	89.82	1031136	90.01
2	5.937	1125530	10.18	114398	9.99


7.549
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7.394
7.380
7.366
7.350
7.344
7.336
7.328
7.319
7.300
7.297
7.268
6.988
6.971
6.969
6.952
6.950
6.870
6.850
5.303
4.130
4.112
3.991
3.957
3.727
3.712
3.709
3.694
3.677
3.643
3.354
3.340
3.316
3.297
3.277
3.267
3.230
3.076
3.061
3.045
3.030
2.854
2.809
2.694
2.680
2.649
2.636
2.047
1.834
1.278
1.260
1.242
0.938
0.000
H
Bn
N
O
O
CO2Me
O
N
5
10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.05
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1.00
1.02
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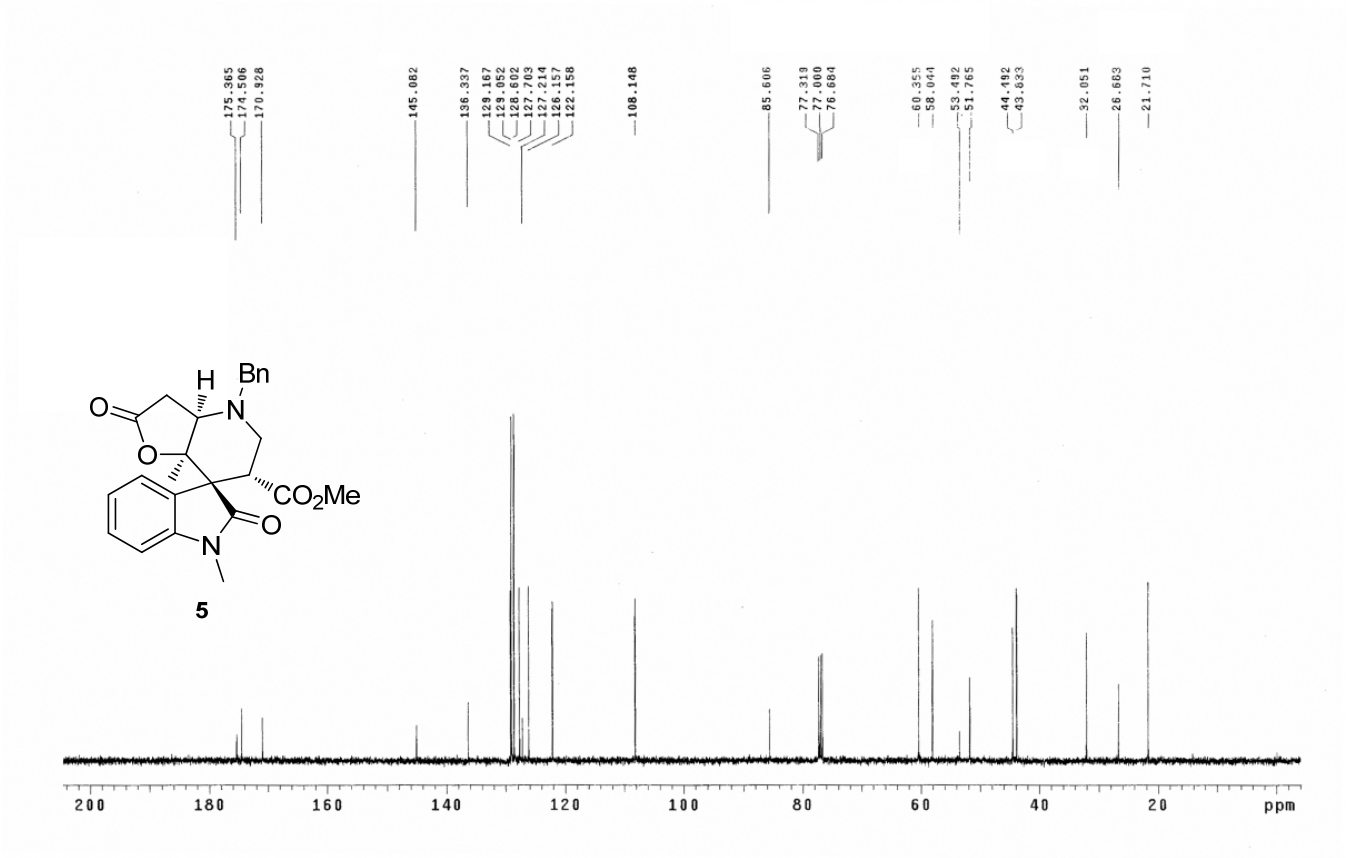
1.32
3.75
0.40
1.06
0.63
0.41
2.98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136.337
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128.602
127.703
127.214
126.157
122.158
108.148
85.606
77.318
77.000
76.684
60.355
58.044
53.492
51.765
44.192
43.633
32.051
26.663
21.710
H
Bn
N
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O
CO2Me
O
N
5
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120
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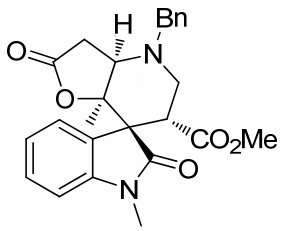
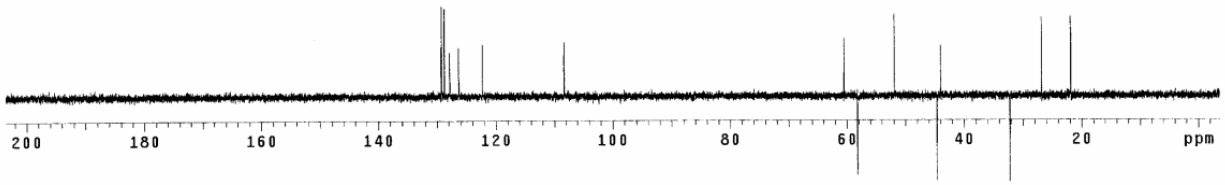
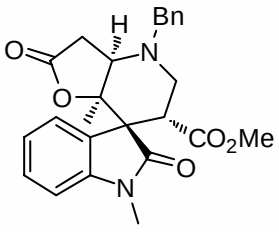
60
40
20
ppm

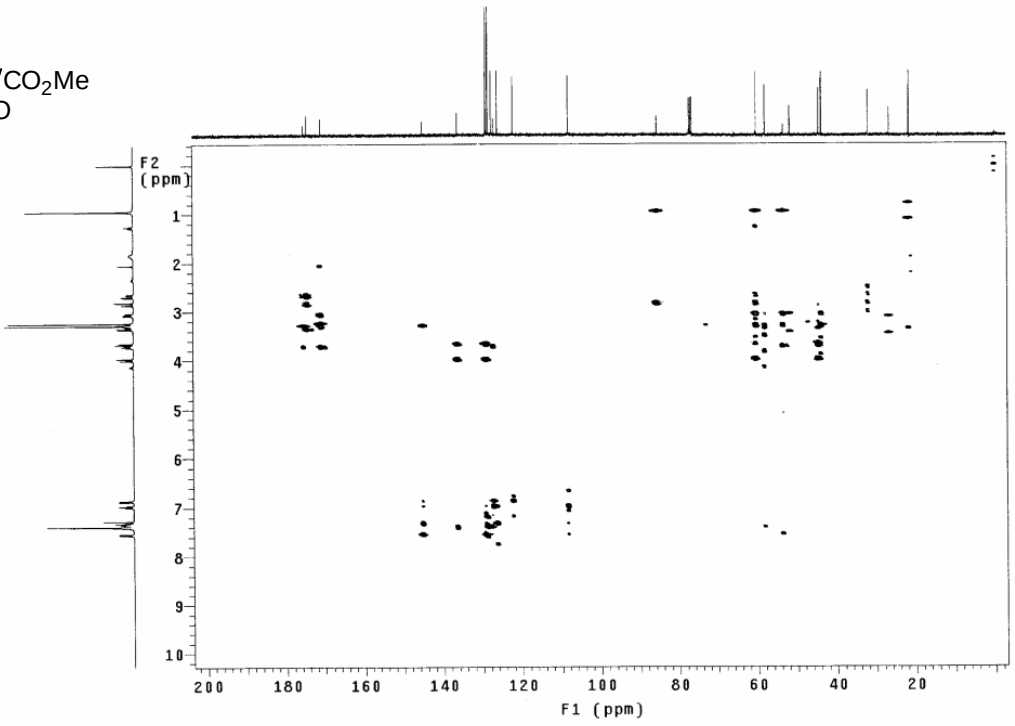


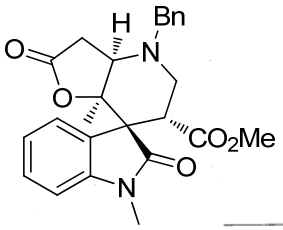
DEPT of **5**



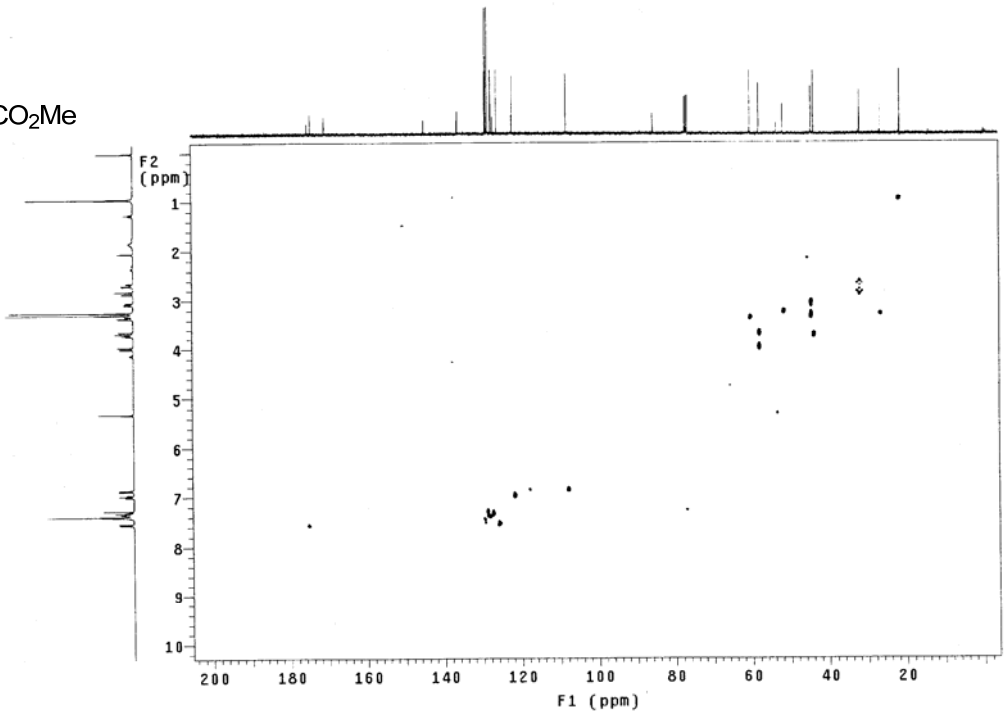


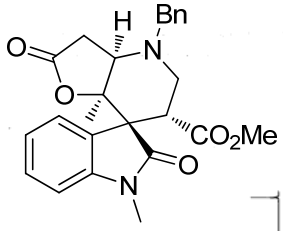
HMBC of **5**



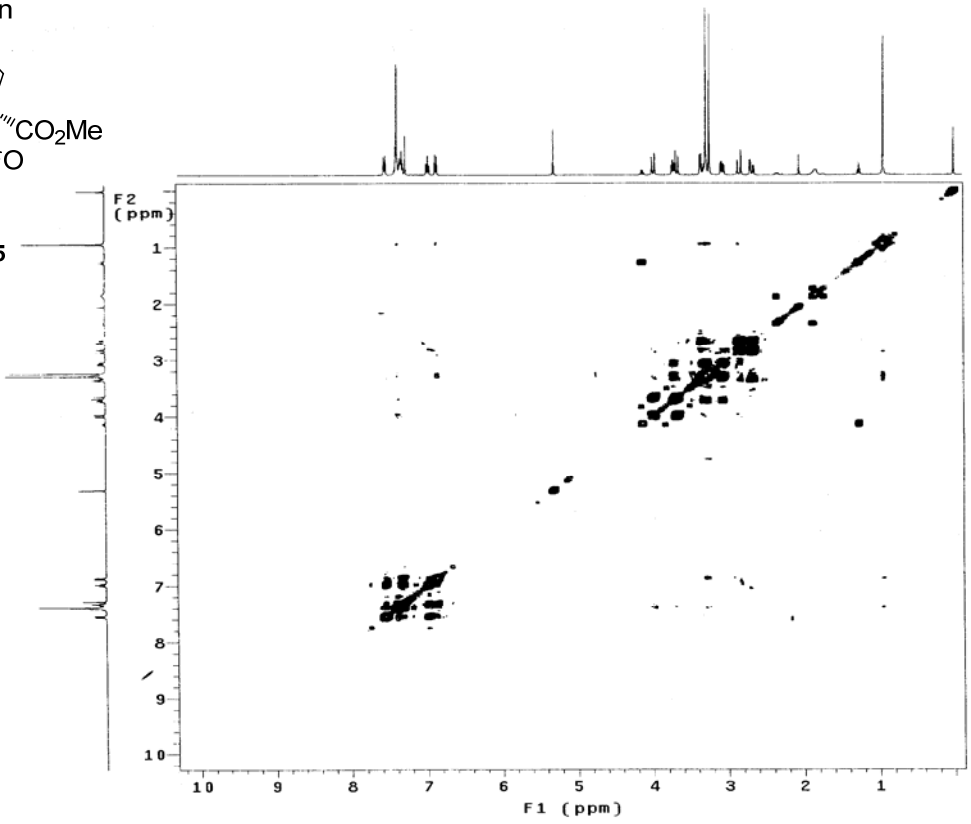


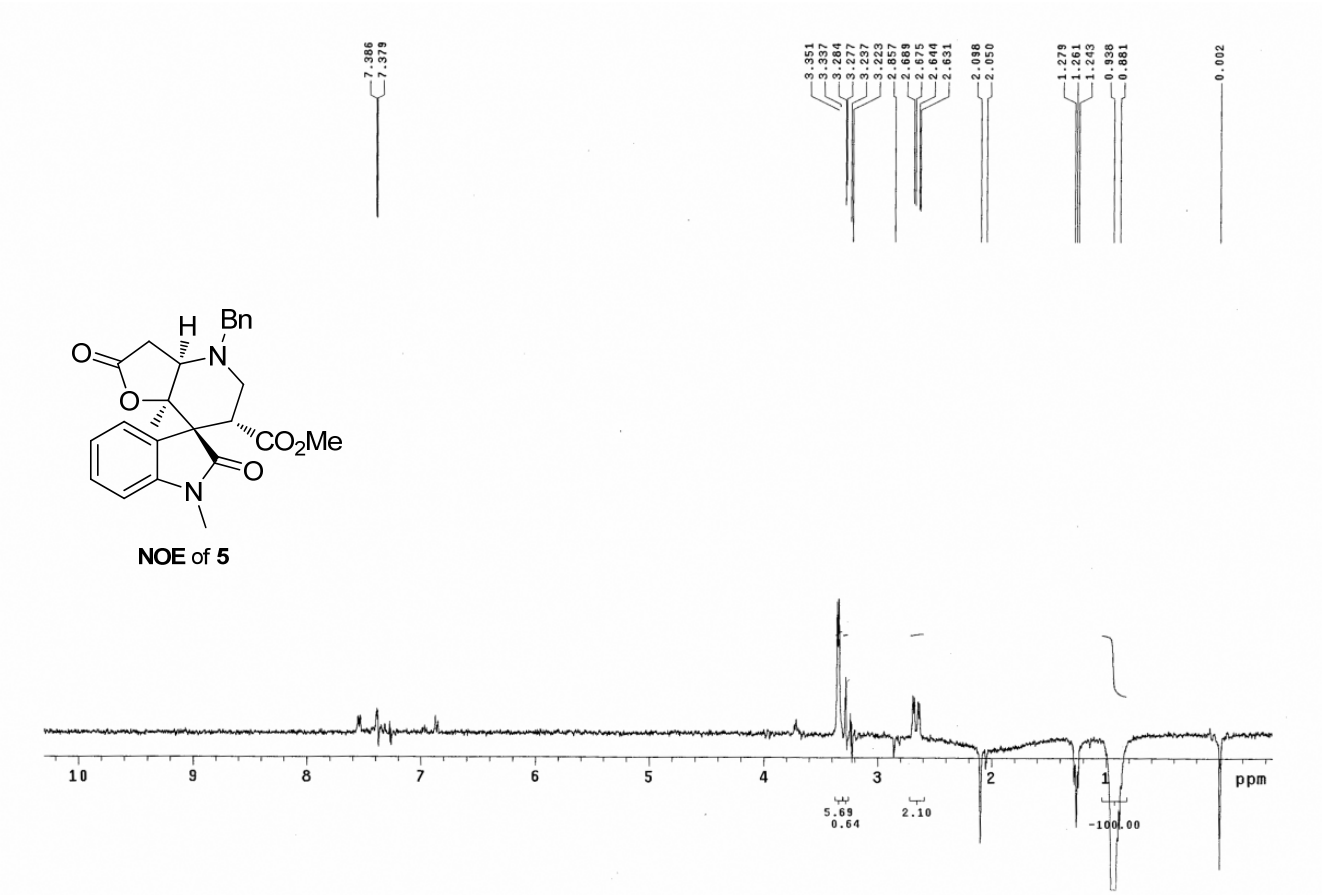
HMQC of **5**



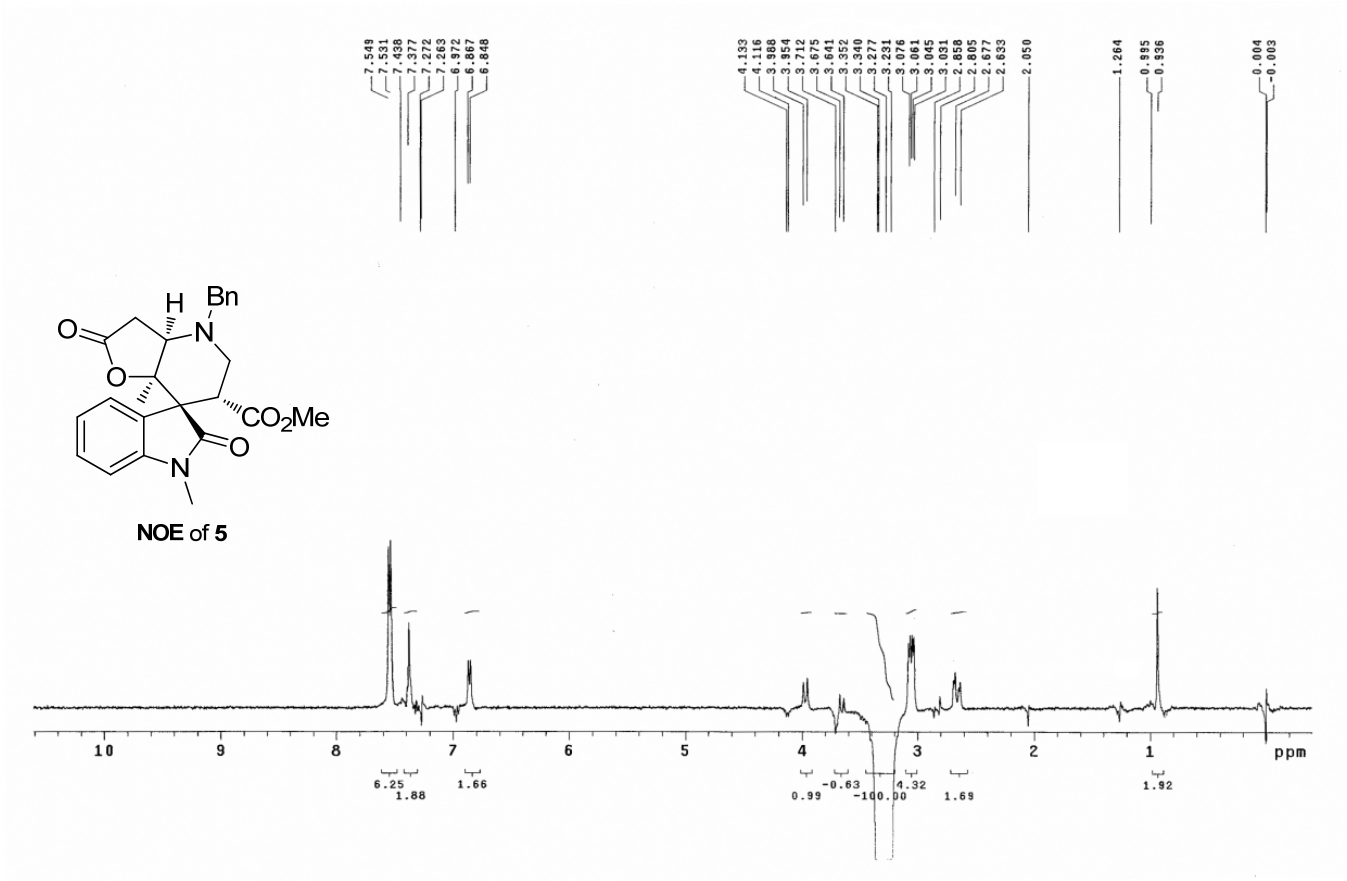


COSY of **5**

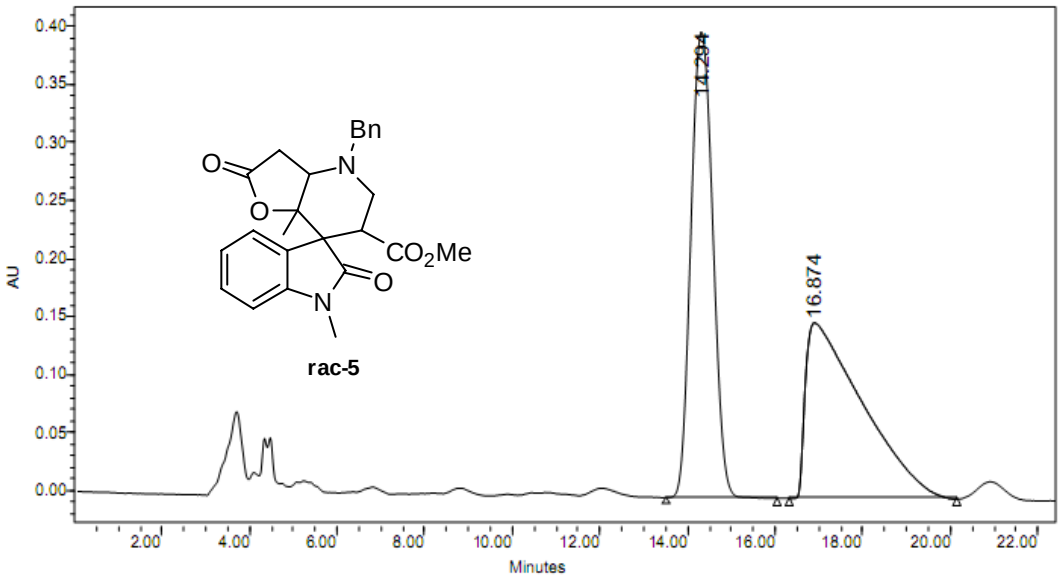




NOE of **5**

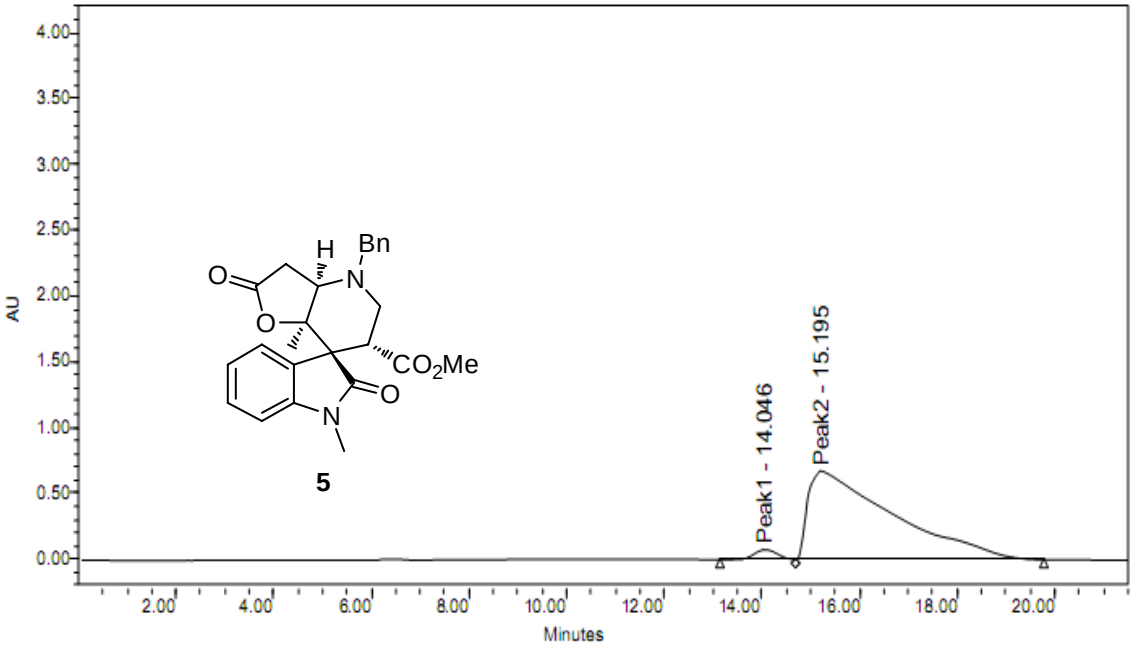


NOE of **5**



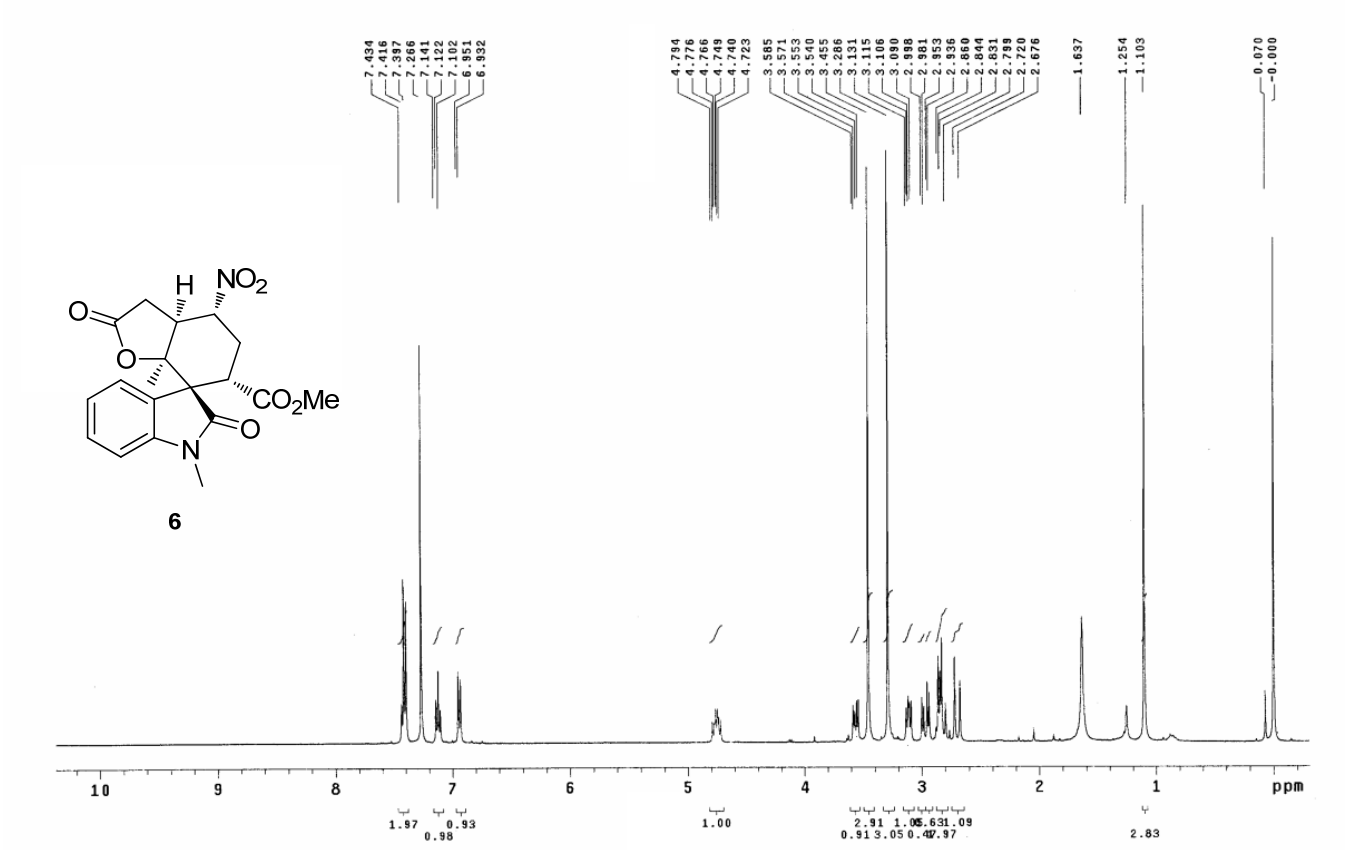
rac-5

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	14.294	13922676	50.34	401200	72.60
2	16.874	13734645	49.66	151398	27.40



5

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	14.046	2559014	4.89	75837	13.92
2	15.195	49780074	95.11	469046	86.08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7.102
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4.776
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4.749
4.740
4.723
3.585
3.571
3.553
3.540
3.455
3.286
3.131
3.115
3.106
3.090
2.998
2.981
2.953
2.936
2.860
2.844
2.831
2.799
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2.676
1.637
1.254
1.103
0.070
-0.000
H
NO2
O
O
CO2Me
O
N
6
10
9
8
7
6
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ppm
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2.91
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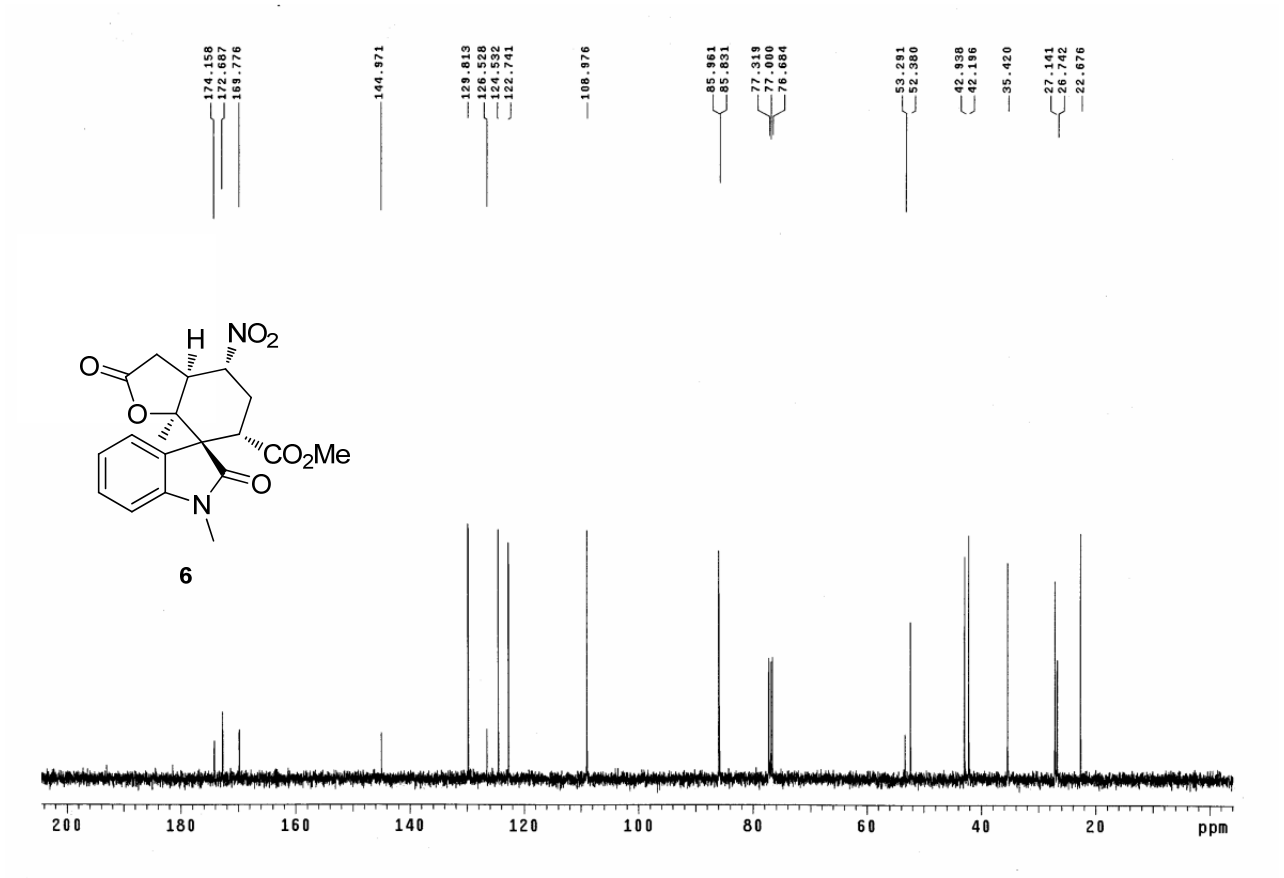
0.97
2.83


174.158
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169.776
144.971
129.813
126.528
124.532
122.741
108.976
85.961
85.831
77.319
77.000
76.684
53.291
52.980
42.938
42.196
35.420
27.141
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22.676
H
NO2
O
O
CO2Me
O
N
6
200
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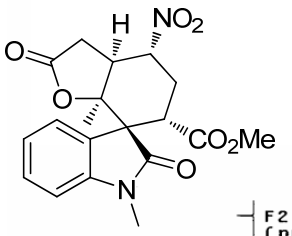
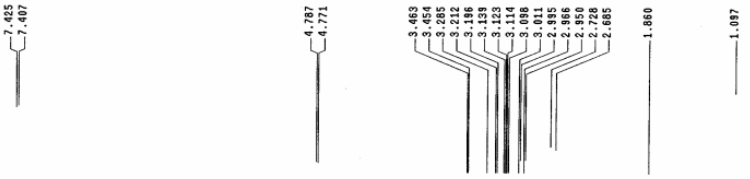
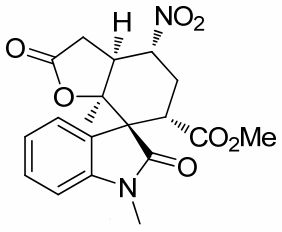
140
120
100
80
60
40
20
ppm

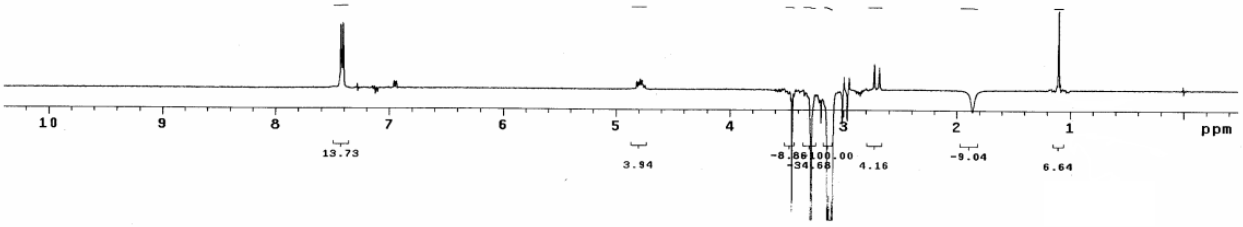


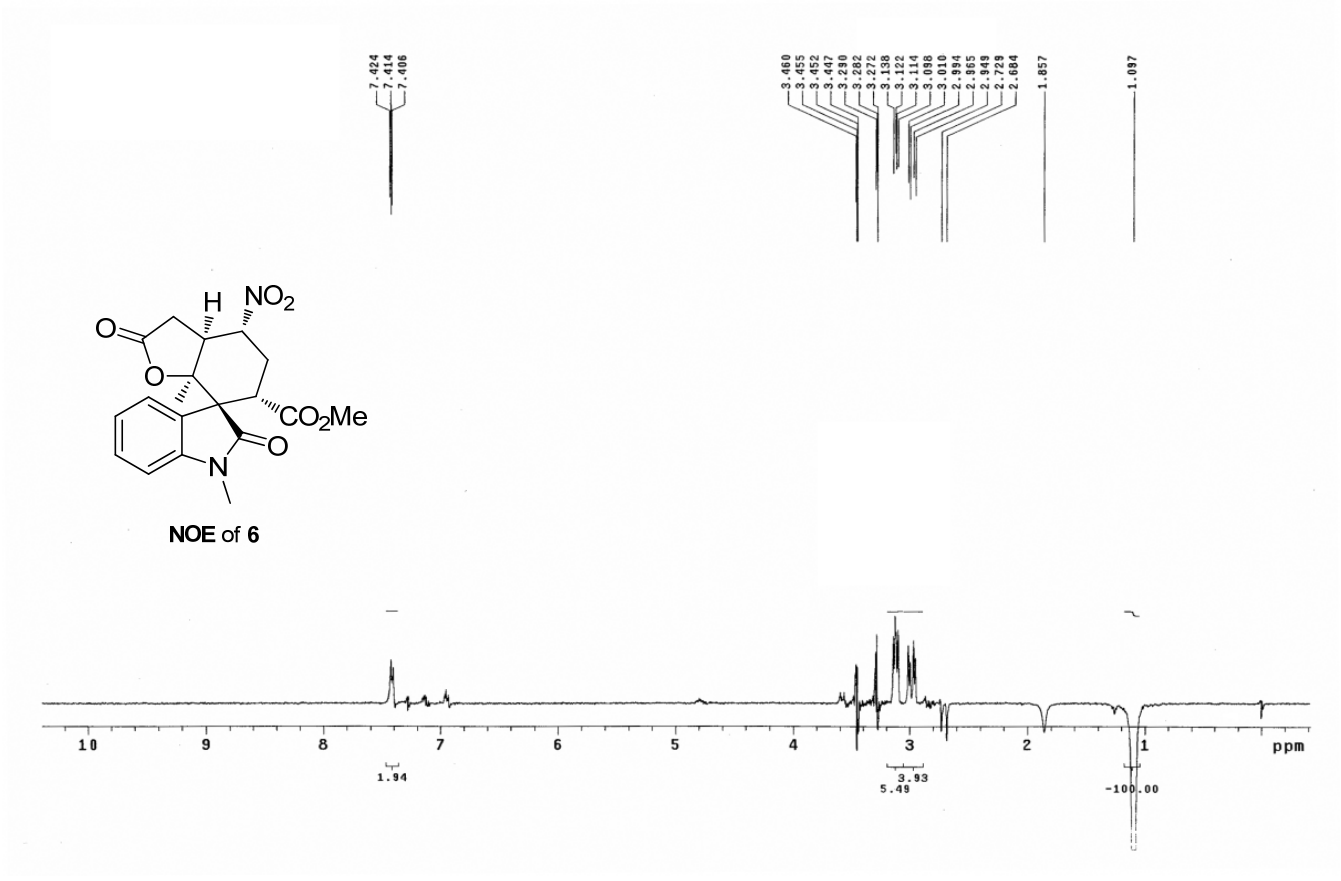
COSY of **6**



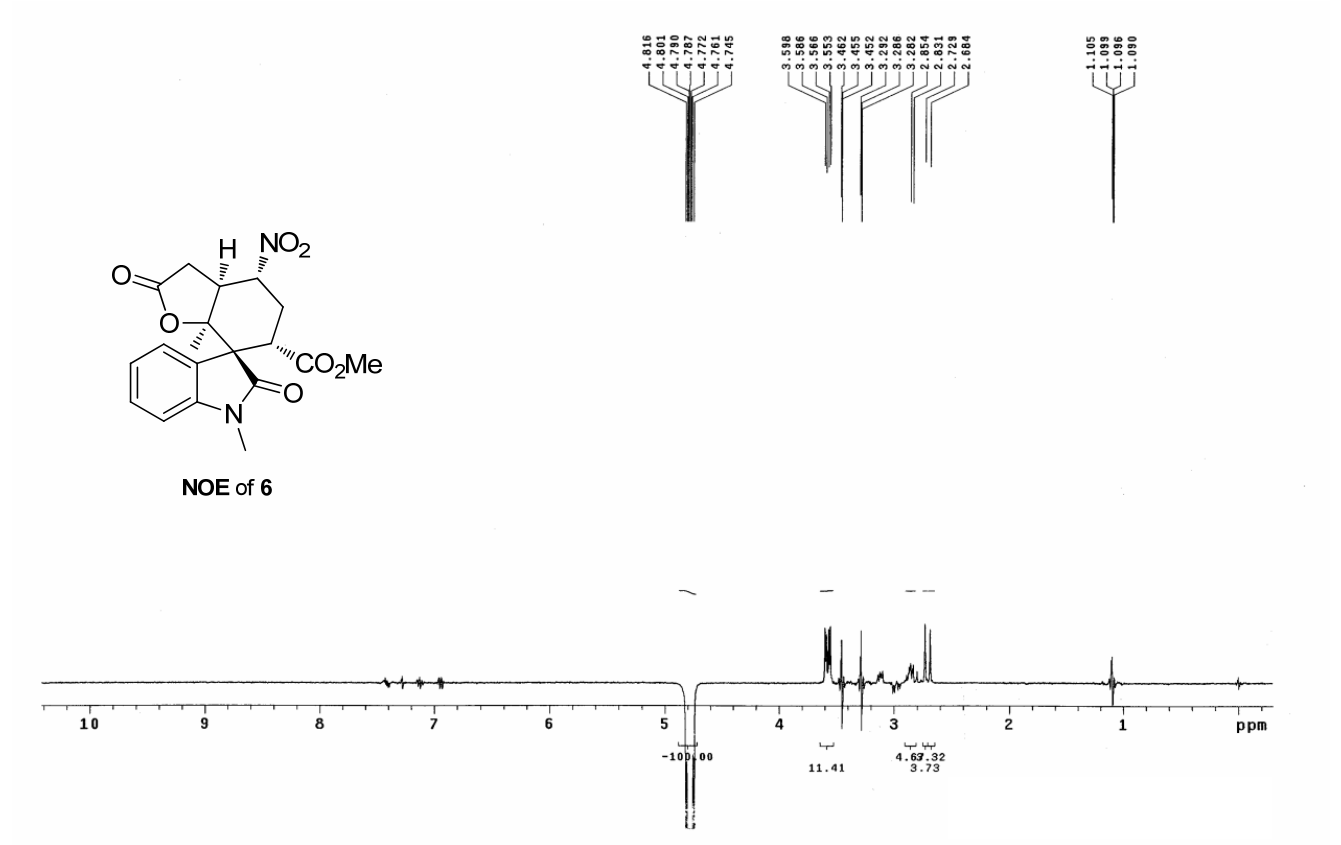


NOE of **6**

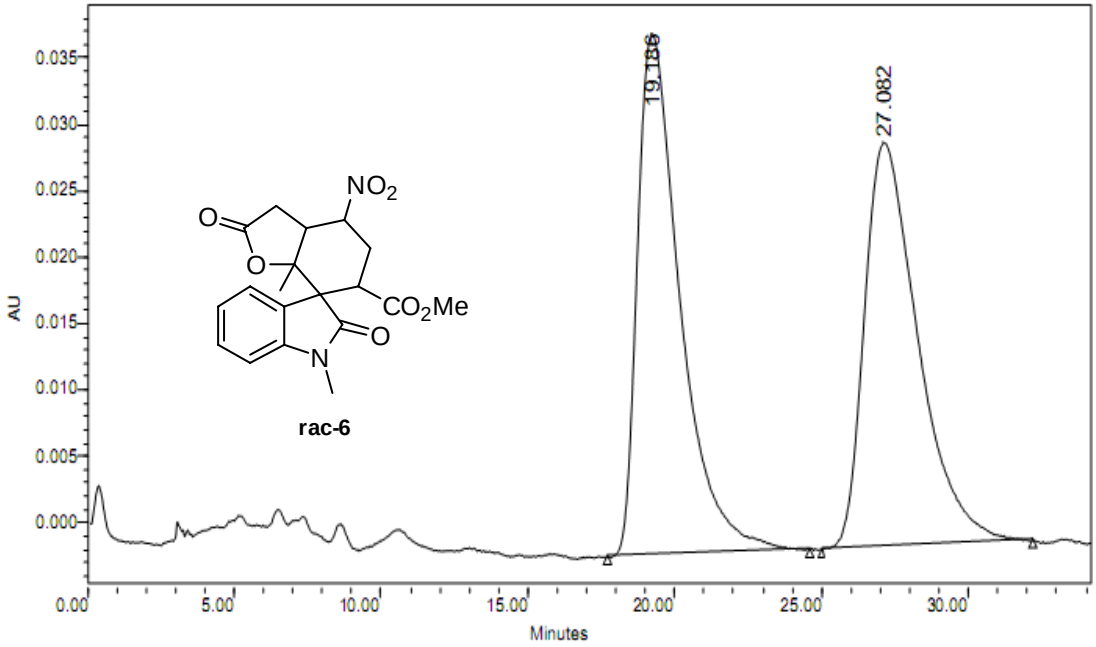




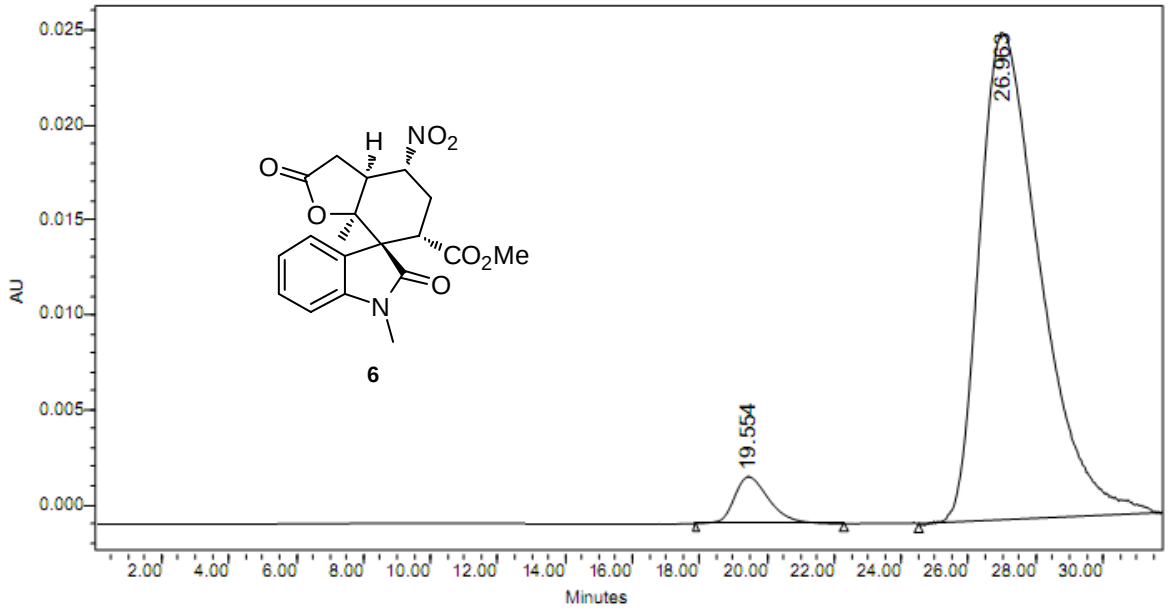
NOE of **6**



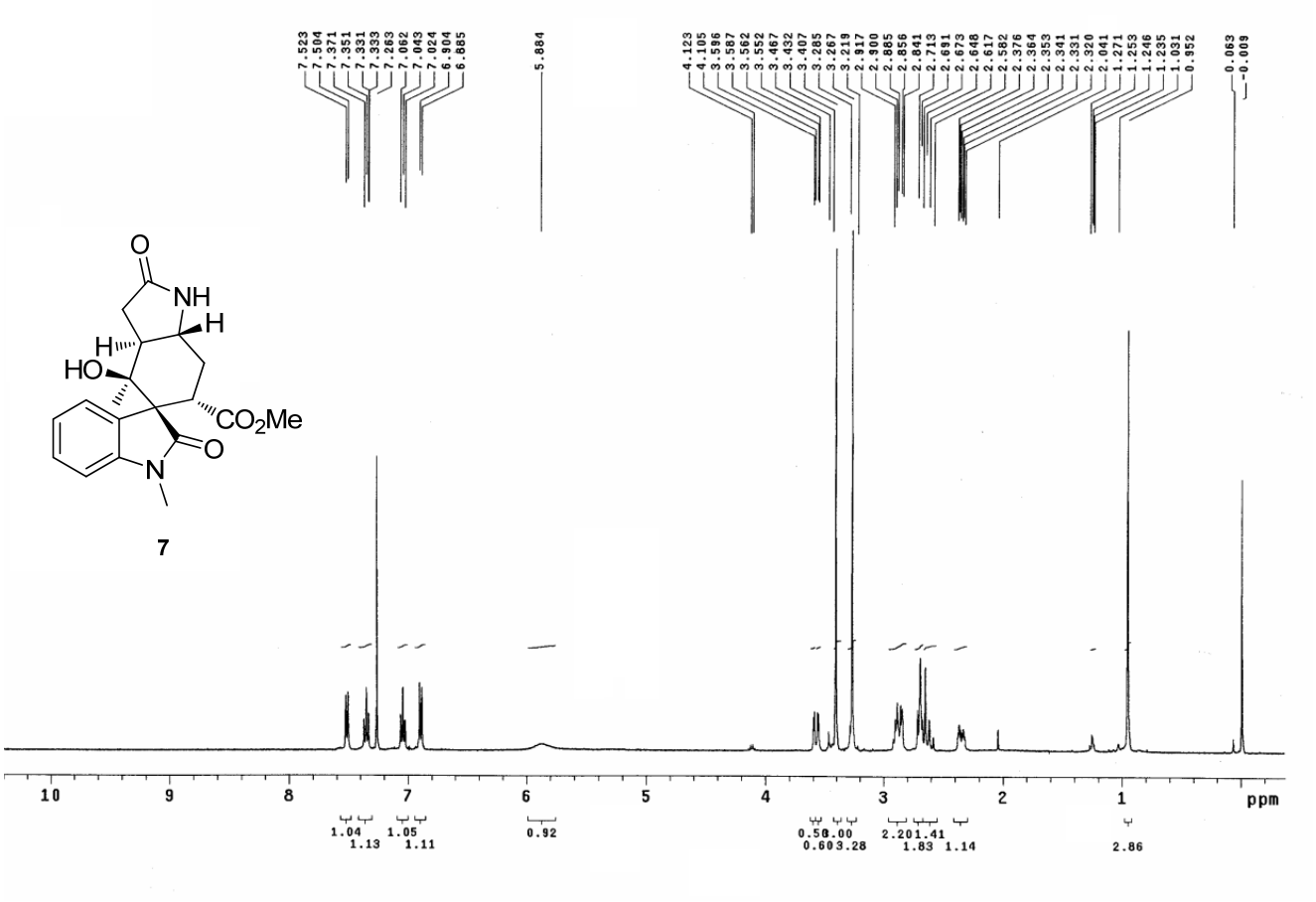
NOE of **6**



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	19.186	3962798	50.61	39268	56.33
2	27.082	3866628	49.39	30447	43.67



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	19.554	169187	4.96	1957	7.08
2	26.963	3242247	95.04	25695	92.92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7.263
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7.024
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5.884
4.123
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3.586
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3.562
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3.487
3.432
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3.285
3.267
3.219
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1.235
1.031
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-0.009
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H
HO
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CO2Me
O
O
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9
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7
6
5
4
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2
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ppm
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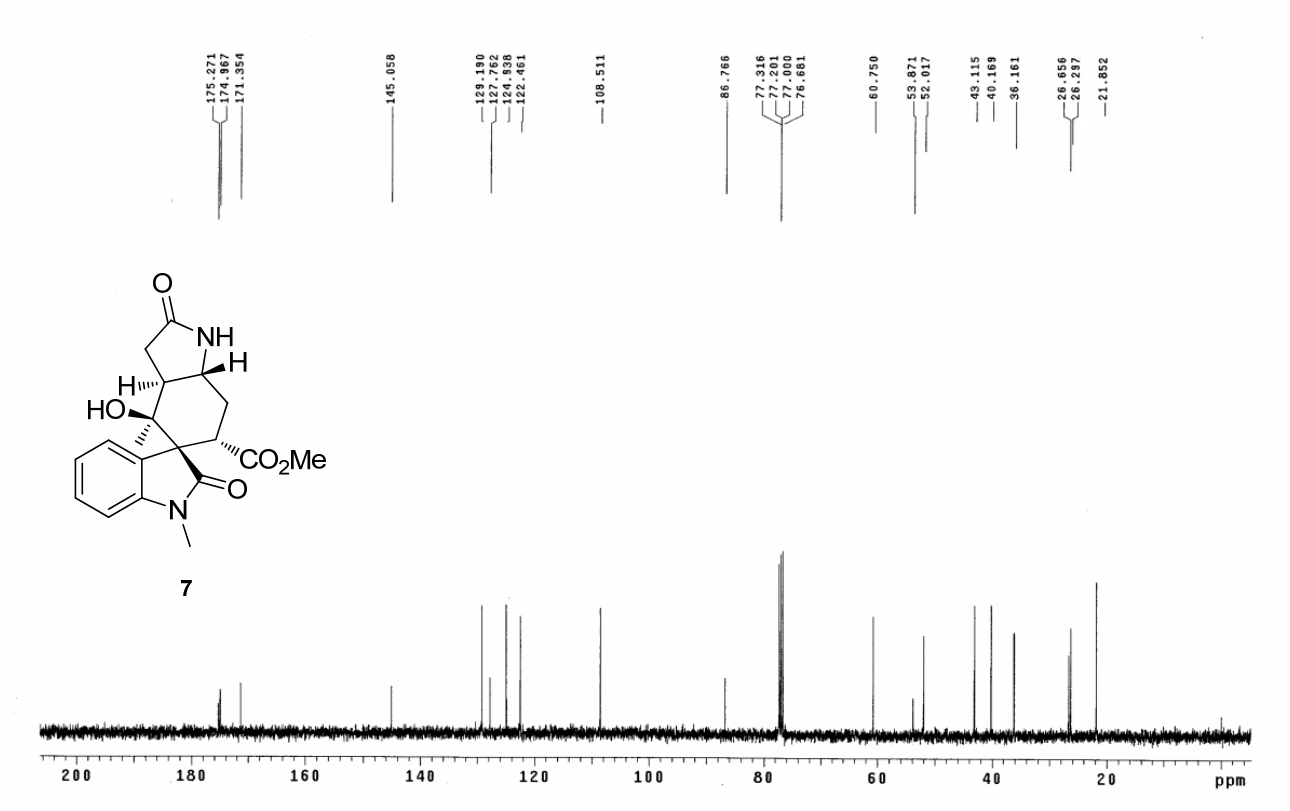
2.86


175.271
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145.058
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127.762
124.938
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86.766
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77.000
76.681
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26.656
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21.852
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HO
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CO2Me
O
O
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140
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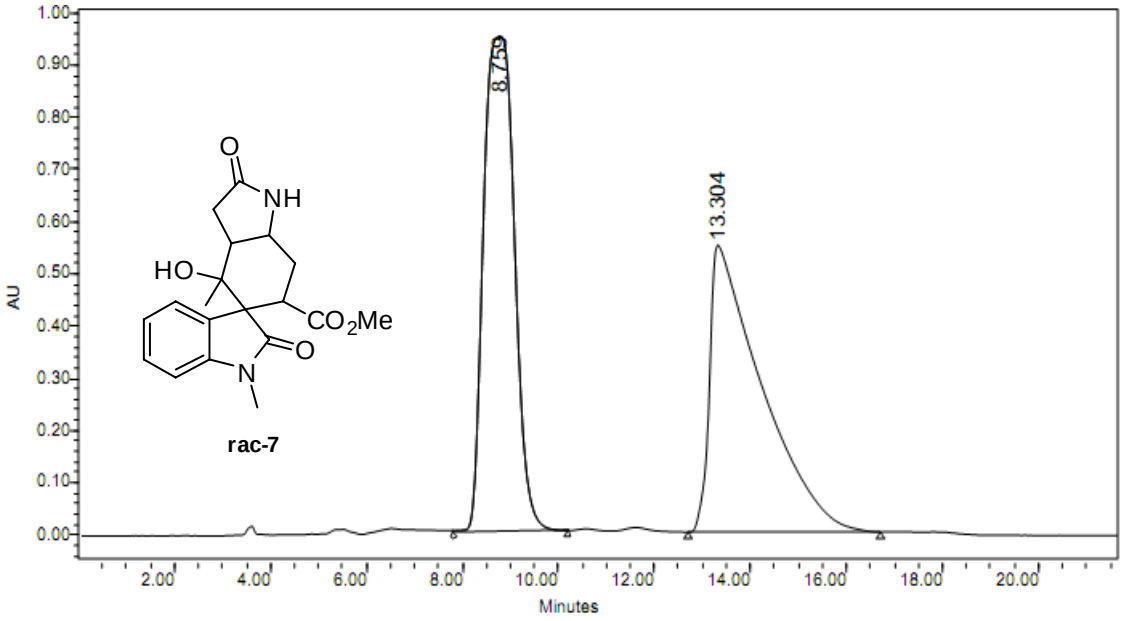
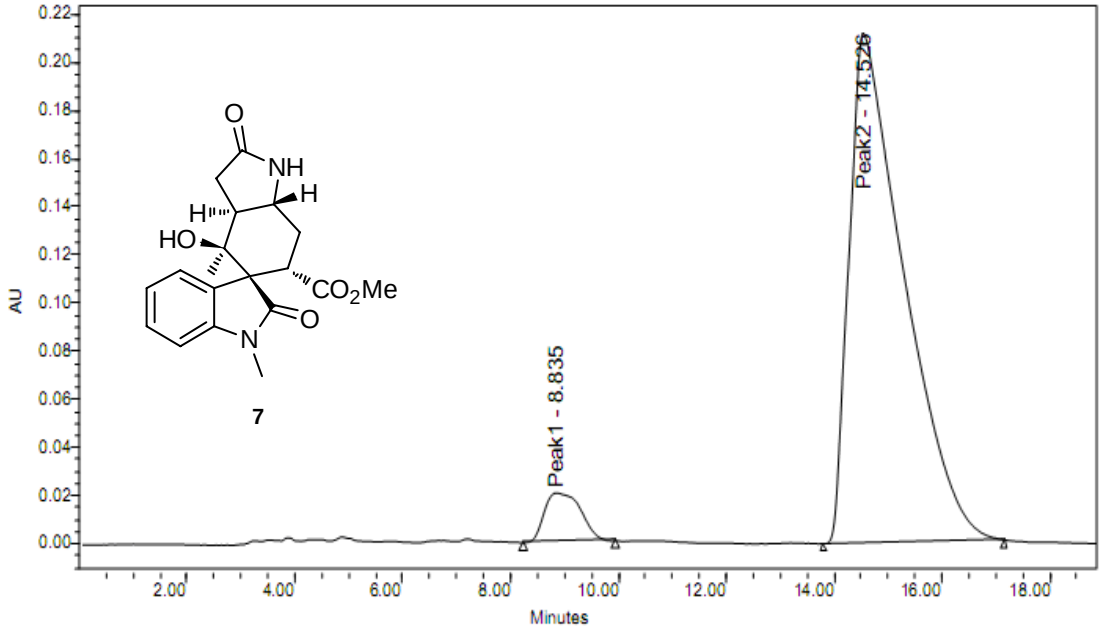
20
ppm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.759	42530400	50.63	949708	63.34
2	13.304	41478430	49.37	549686	36.66



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.835	829175	5.27	18790	8.17
2	14.526	14914555	94.73	211273	91.83