Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Asymmetric Normal-Electron-Demand Aza-Diels–Alder Reaction via Trienamine Catalysis

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Supplementary Information

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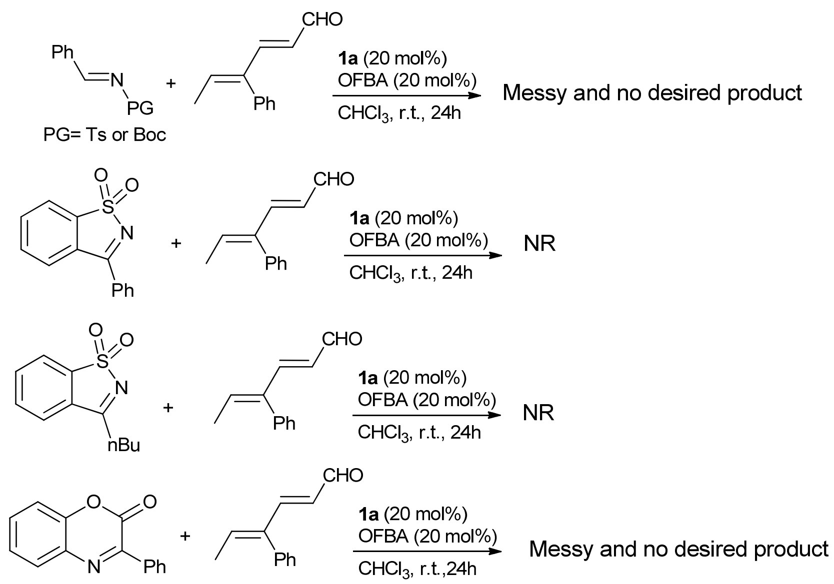
1. General Methods

TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether or acetone/petroleum ether). NMR spectra were recorded with tetramethylsilane as the internal standard. ^{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 = 7.26 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 IA, IB, IC, AD and Chiralcel OD columns. THF was distilled from sodium. All other chemicals were used without purification as commercially available. Toluene, THF, ethyl acetate (EA), petroleum ether (PE), methylene chloride (DCM) and MeCN were freshly distilled before use. 2,4-Dienals[1] and secondary amine catalysts[2] **1** were synthesized according to the literature procedures.

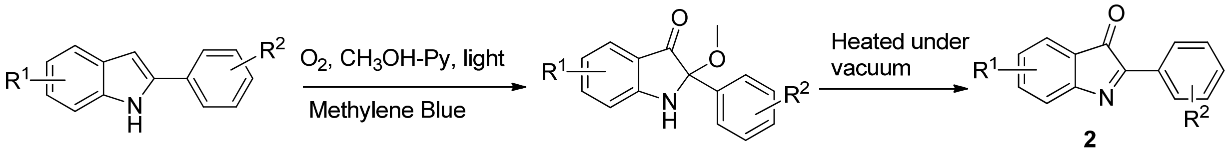
1. Z.-J. Jia, Q. Zhou, Q.-Q. Zhou, P.-Q. Chen and Y.-C. Chen, *Angew. Chem., Int. Ed.,* 2011, **123**, 8797.

2. (*a*) M. Marigo, T. C. Wabnitz, D. Fielenbach and K. A. Jørgensen, *Angew. Chem., Int. Ed.,* 2005, **44**, 794; (*b*) Y. Hayashi, H. Gotoh, T. Hayashi and M. Shoji, *Angew. Chem., Int. Ed.,* 2005, **44**, 4212; (*c*) Y.-K. Liu, C. Ma, K. Jiang, T.-Y. Liu and Y.-C. Chen, *Org. Lett.,* 2009, **11**, 2848; (*d*) J.-L. Li, S.-L. Zhou, P.-Q. Chen, L. Dong, T.-Y. Liu and Y.-C. Chen, *Chem. Sci.,* 2012, **3**, 1879.

2. Exploration of more imine substrates in aza-Diels−Alder reaction



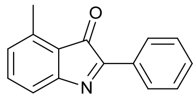
3. Preparation of 2-aryl-*3H*-indol-3-ones



2-Aryl-*3H*-indol-3-ones could be conveniently prepared according to the literature procedure.[3]

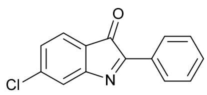
3. K.-Q. Ling, *Synth. Commun.* 1995, **23**, 3831.

For some selected ^{1}H NMR data:



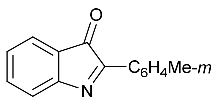
2b

Red solid (m.p. = 159.9-161.2 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.38-8.36 (m, 1H), 7.53-7.46 (m, 3H), 7.41-7.37 (m, 2H), 7.26-7.23 (m, 1H), 7.06-7.02 (m, 1H), 2.66 (s, 3H) ppm.



2e

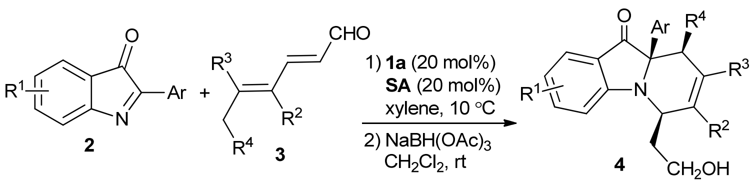
Red solid (m.p. = 128.0-131.1 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.38 (d, J = 7.6 Hz, 2H), 7.59-7.55 (m, 1H), 7.52-7.49 (m, 3H), 7.42 (s, 1H), 7.26-7.25 (m, 1H) ppm.



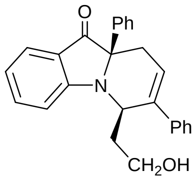
2h

Red solid (m.p. = 172.6-172.9 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.21-8.19 (m, 2H), 7.57-7.53 (m, 2H), 7.44-7.35 (m, 3H), 7.29-7.25 (m, 1H), 2.44 (s, 3H) ppm.

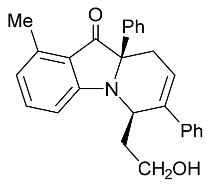
4. General procedure for asymmetric aza-Diels–Alder and reduction reactions



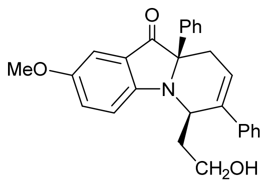
The reaction was performed with 2-aryl-*3H*-indol-3-one **2** (0.1 mmol), 2,4-dienal **3** (0.12 mmol), catalyst **1a** (0.02 mmol) and salicylic acid (0.02 mmol) in xylene (0.5 mL) at 10 °C for a specified reaction time. After completion, the DA adduct was isolated by flash chromatography, and dissolved in dichloromethane (0.5 mL). Sodium triacetoxyborohydride (0.3 mmol) were added sequentially and the resulting mixture was stirred at room temperature for 12 hours. The mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the alcohol product **4.**



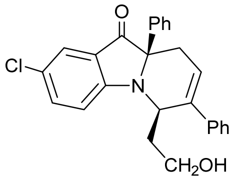
4a yellow oil; 94% yield; $[\alpha]_D^{20}$ = -135.0 (*c* = 5.5 in $CHCl_3$); 92% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 5.84 min, t (minor) = 7.22 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.69 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.35-7.21 (m, 11H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.18-6.16 (m, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 3.54 (dt, *J* = 14.0, 2.8 Hz, 1H), 3.42-3.38 (m, 1H), 3.23 (dd, *J* = 18.4, 6.0 Hz, 1H), 2.59-2.53 (m, 1H), 1.46-1.39 (m, 1H), 0.78-070 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 203.7, 162.1, 141.6, 139.5, 138.8, 137.9, 128.5, 128.0, 127.5, 127.3, 126.4, 125.6, 121.5, 117.9, 121.6, 117.7, 109.8, 67.7, 58.8, 51.7, 35.0, 28.0 ppm; ESI-HRMS: calcd. for $C_{26}H_{23}NO_2$+Na^+ 404.1621, found 404.1627.



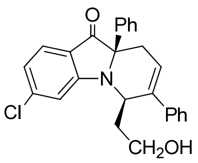
4b yellow oil; 77% yield; $[\alpha]_D^{20}$ = -135.0 (*c* = 5.5 in $CHCl_3$); 83% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 5.14 min, t (minor) = 6.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.42 (t, *J* = 8.0 Hz, 1H), 7.35-7.23 (m, 10H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.17 (t, *J* = 2.8 Hz, 1H), 5.05 (d, *J* = 7.2 Hz, 1H), 3.60-3.55 (m, 1H), 3.46-3.41 (m, 1H), 3.22 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.63-2.58 (m, 4H), 1.48-1.40 (m, 1H), 0.90-0.77 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 204.1, 162.7, 141.6, 141.2, 139.6, 139.4, 137.1, 131.3, 128.6, 128.5, 127.9, 127.5, 127.3, 126.4, 121.6, 119.6, 116.0, 106.9, 67.6, 59.1, 51.8, 35.2, 28.3, 18.5 ppm; ESI-HRMS: calcd. for $C_{27}H_{25}NO_2$+Na^+ 418.1778, found 418.1779.



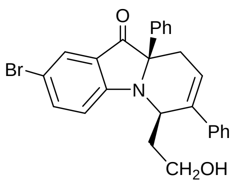
4c yellow oil; 97% yield; $[\alpha]_D^{20}$ = -216.9 (*c* = 12.2 in $CHCl_3$); 90% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 20.40 min, t (minor) = 11.80 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.35-7.23 (m,12H) , 7.12 (d, *J* = 2.4 Hz, 1H), 6.19-6.17 (*m*, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 3.80 (s, 3H), 3.62-3.56 (m, 1H), 3.48-3.43 (m, 1H), 3.21(dd, *J* = 18.4, 6.4 Hz, 1H), 2.54 (dt, *J* = 18.0, 2.8 Hz, 1H), 1.50-1.44 (m, 1H), 0.90-0.83 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 203.8, 158.5, 152.6, 141.8, 139.5, 139.2, 128.7, 128.6, 128.5, 127.9 127.5, 127.1, 126.3, 121.3, 117.6, 111.5, 105.1, 68.5, 58.9, 55.8, 52.3, 34.9, 28.5 ppm; ESI-HRMS: calcd. for $C_{27}H_{25}NO_3$+Na^+ 434.1732, found 434.1730.



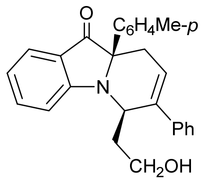
4d yellow oil; 74% yield; $[\alpha]_D^{20}$ = -170.6 (*c* = 10.5 in $CHCl_3$); 85% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 18.09 min, t (minor) = 21.40 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.36-7.23 (m,11H) , 6.19-6.18 (m, 1H), 5.05 (d, *J* = 9.8 Hz, 1H), 3.54 (dt, *J* = 10.4, 2.8 Hz, 1H), 3.46-3.41 (m, 1H), 3.24 (dd, *J* = 19.2, 5.6 Hz, 1H), 2.54 (dt, *J* = 18.0, 2.4 Hz, 1H), 1.47-1.40(m, 1H), 0.78-0.72 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 160.4, 141.5, 139.3, 138.4, 137.8, 128.7, 128.6, 128.2, 127.6 127.1, 126.4, 124.6, 123.0, 121.3, 118.6, 111.2, 68.2, 58.6, 51.8, 34.7, 28.0 ppm; ESI-HRMS: calcd. for $C_{26}H_{22}ClNO_2$+Na^+ 438.1231, found 438.1233.



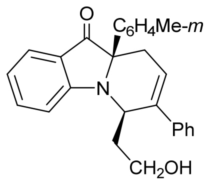
4e yellow oil; 76% yield; $[\alpha]_D^{20}$ = -40.3 (*c* = 3.3 in $CHCl_3$); 84% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 5.44 min, t (minor) = 7.43 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 4.4 Hz, 1H), 7.36-7.23 (m, 11H), 6.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.19-6.18 (m, 1H), 5.02 (d, *J* = 9.6 Hz, 1H), 3.52 (dt, *J* = 10.4, 3.2 Hz, 1H), 3.44-3.40 (m, 1H), 3.25 (dd, *J* = 18.0, 5.6 Hz, 1H), 2.54 (dd, *J* = 13.2, 3.2 Hz, 1H), 1.47-1.40 (m, 1H), 0.73-0.67 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 162.2, 144.6, 141.4, 139.3, 138.4, 128.7, 128.6, 128.2, 127.7, 127.2, 126.5, 126.4, 121.4, 118.7, 116.2, 109.8, 68.2, 58.6, 51.8, 34.7, 28.0 ppm; ESI-HRMS: calcd. for $C_{26}H_{22}ClNO_2$+Na^+ 438.1231, found 438.1235.



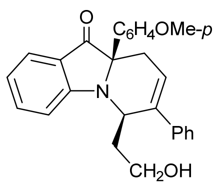
4f yellow oil; 82% yield; $[\alpha]_D^{20}$ = -225.0 (*c* = 9.5 in $CHCl_3$); 85% *ee*, determined by HPLC analysis [Chiralpak IA, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 20.40 min, t (minor) = 11.79 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.35-7.20 (m, 11H), 6.19-6.18 (m, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 3.52-3.47 (m, 1H), 3.43-3.40 (m, 1H), 3.23 (dd, *J* = 19.2, 6.4 Hz, 1H), 2.54 (d, *J* = 18.0 Hz , 1H), 1.48-1.39 (m, 1H), 0.76-0.69 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 160.6, 141.5, 140.3, 139.3, 138.4, 128.7, 128.6, 128.2, 127.8 127.7, 127.2, 126.4, 121.4, 119.3, 111.6, 109.8, 68.2, 58.7, 51.8, 34.9, 28.0 ppm; ESI-HRMS: calcd. for $C_{26}H_{22}BrNO_2$+Na^+ 482.0727, found 4382.0733.



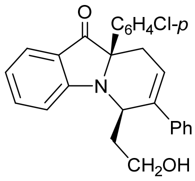
4g yellow oil; 69% yield; $[\alpha]_D^{20}$ = -32.9 (*c* = 1.6 in $CHCl_3$); 89% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 5.08 min, t (minor) = 6.90 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.2 Hz, 1H), 7.57-7.53 (m, 1H), 7.32-7.22 (m, 6H), 7.14-7.05 (m, 4H), 6.83-6.79 (m, 1H), 6.17-6.16 (m, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 3.57-3.51 (m, 1H), 3.43-3.38 (m, 1H), 3.20 (dd, *J* = 18.0, 6.4 Hz, 1H), 2.54 (dt, *J* = 18.0, 2.4 Hz, 1H), 2.28 (s, 3H), 1.46-1.39 (m, 1H), 0.83-0.76 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.8, 162.0, 141.5, 139.5, 137.8, 137.7, 135.6, 129.2, 128.5, 127.4 127.1, 126.4, 125.5, 121.5, 117.7, 117.6, 119.7, 67.5, 58.8, 51.6, 35.0, 28.1, 21.0 ppm; ESI-HRMS: calcd. for $C_{27}H_{25}NO_2$+Na^+ 418.1778, found 418.1784.



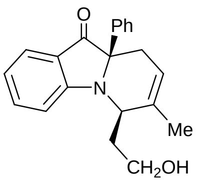
4h 72% yield; $[\alpha]_D^{20}$ = -236.4 (*c* = 9.4 in $CHCl_3$); 87% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 5.85 min, t (minor) = 7.92 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.35-7.25 (m, 6H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.08-7.03 (m, 3H), 6.84-6.80 (m, 1H), 6.18-6.16 (m, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 3.59-3.54 (m, 1H), 3.46-3.41 (m, 1H), 3.23 (dd, *J* = 18.4, 6.4 Hz, 1H), 2.56 (d, *J* = 18.4 Hz, 1H), 2.04 (s, 3H), 1.47-1.40 (m, 1H), 0.84-0.77 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.8, 162.1, 141.5, 139.5, 138.6, 138.2, 137.9, 128.8, 128.6 128.4, 127.8, 127.5, 126.4, 125.6, 124.3, 121.6 117.8, 117.7, 109.7, 67.7, 58.9, 51.7, 35.0, 28.1, 21.5 ppm; ESI-HRMS: calcd. for $C_{27}H_{25}NO_2$+Na^+ 418.1778, found 418.1784.



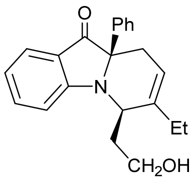
4i yellow oil; 84% yield; $[\alpha]_D^{20}$ = -151 (*c* = 5.4 in $CHCl_3$); 91% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 15.56 min, t (minor) = 13.48 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz ,1H), 7.35-7.24 (m, 6H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.83-6.75 (m, 3H), 6.17-6.16 (m, 1H), 5.06 (d, *J* = 6.8 Hz, 1H), 3.76 (s, 1H), 3.57-3.52 (m, 1H), 3.45-3.43 (m, 1H), 3.18 (dd, *J* = 18.0 , 6.0 Hz, 1H), 2.54 (d, *J* = 18.0 Hz, 1H), 1.47-1.41 (m, 1H), 0.85-0.78 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.9, 161.9, 159.2, 141.6, 140.0, 137.9, 130.7, 128.6, 128.5, 127.5, 126.5, 125.6, 121.5, 117.8, 117.6, 113.9, 109.7, 67.3, 58.9, 55.2, 51.6, 35.0, 28.3 ppm; ESI-HRMS: calcd. for $C_{27}H_{25}NO_3$+H^+ 412.1907, found 412.1913.



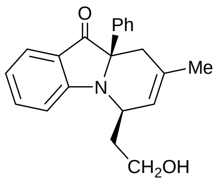
4j yellow oil; 82% yield; $[\alpha]_D^{20}$ = -170.6 (*c* = 10.5 in $CHCl_3$); 84% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 6.90 min, t (minor) = 10/15 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 4.0 Hz, 1H), 7.61-7.56 (m ,1H), 7.36-7.19 (m,10H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.16-6.15 (m, 1H), 5.08 (d, *J* = 7.2 Hz, 1H), 3.57-3.53 (m, 1H), 3.48-3.43 (m, 1H), 3.17 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.60-2.55 (m, 1H), 1.51-1.43 (m, 1H), 0.87-0.77 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 162.2, 141.9, 139.4, 138.1, 137.6, 133.9, 128.8, 128.6, 127.7, 126.4 125.7, 121.1, 118.3, 117.6, 110.0, 67.2, 58.8, 51.8, 35.2, 28.2 ppm; ESI-HRMS: calcd. for $C_{26}H_{22}ClNO_2$+H^+ 416.1412, found 416.1411.



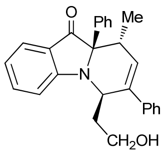
4k yellow oil; 72% yield; $[\alpha]_D^{20}$ = -394 (*c* = 13 in $CHCl_3$); 90% *ee*, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 8.83 min, t (minor) = 13.47 min] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.6 Hz, 1H), 7.54-7.49 (m,1H), 7.26-7.24 (m, 3H), 7.19-7.17 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 5.75 (d, *J* = 4.0 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 3.60-3.52 (m, 2H), 3.03 (dd, *J* = 17.6, 6.0 Hz, 1H), 2.34 (dd, *J* = 17.6, 6.0 Hz, 1H), 1.75-1.69 (m, 4H), 0.81-0.73 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.9, 161.8, 138.8, 137.7, 135.9, 128.5, 127.9, 127.5, 125.6, 118.6, 117.6, 117.5, 109.5, 67.9, 59.0, 53.9, 34.4, 27.6, 21.1 ppm; ESI-HRMS: calcd. for $C_{21}H_{21}NO_2$+Na^+ 342.1465, found 342.1471.



4l yellow oil; 81% yield; $[\alpha]_D^{20}$ = -102 (*c* = 3 in $CHCl_3$); 92% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 4.31 min, t (minor) = 4.63 min] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.6 Hz, 1H), 7.53-7.49 (m, 1H), 7.26-7.17 (m, 5H), 7.10 (d, *J* = 6.4 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 5.76-5.74 (m, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 3.61-4.00 (m, 2H), 3.05 (dd, *J* = 17.2, 4.2 Hz, 1H), 2.40-2.35 (m, 1H), 2.14-1.98 (m, 2H), 1.73-1.66 (m, 1H), 1. 26 (t, *J* = 6.4 Hz, 3H), 0.80-0.73 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0, 161.9, 141.6, 139.0, 137.7, 128.5, 127.9, 127.4, 125.6, 117.6, 117.6, 116.7, 109.6, 68.2, 59.1, 52.6, 34.3, 27.6, 26.9, 12.2 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}NO_2$+Na^+ 356.1621, found 3356.1625.

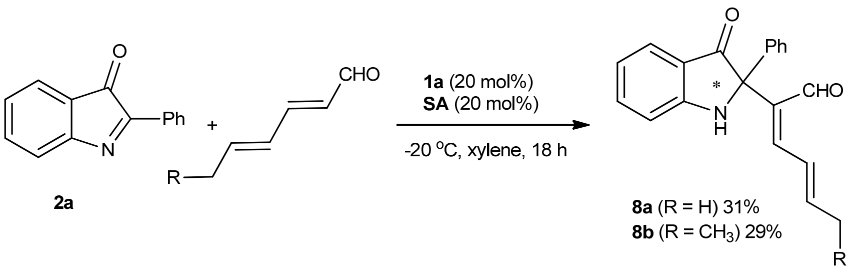


4m yellow oil; 69% yield; $[\alpha]_D^{20}$ = -70 (*c* = 4.5 in $CHCl_3$); 80% *ee*, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.28 min, t (minor) = 13.25 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.65 (d, *J* = 7.6 Hz, 1H), 7.54-7.40 (m, 1H), 7.26-7.25 (m,3H), 7.14-7.08 (m, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 5.46 (d, *J* = 1.2 Hz, 1H), 4.44-4.43 (m, 1H), 3.65-3.60 (m, 2H), 2.90 (d, *J* = 17.2 Hz, 1H), 2.23 (d, *J* = 16.8 Hz, 1H), 1. 9 (s, 3H), 1.51-1.44 (m, 1H), 1.20-1.14 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 203.2, 161.7, 138.7, 137.8, 130.4, 128.5, 127.8, 126.9, 125.6, 123.6, 117.8, 117.5, 109.5, 68.9, 59.0, 50.8, 37.6, 32.2, 23.3 ppm; ESI-HRMS: calcd. for $C_{21}H_{21}NO_2$+Na^+ 342.1465, found 342.1470.



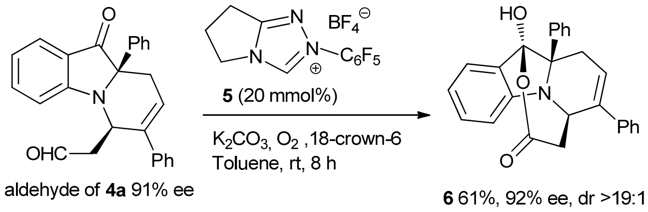
4n yellow oil; 77% yield; $[\alpha]_D^{20}$ = -150.5 (*c* = 6.5 in $CHCl_3$); 71% *ee*, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 4.73 min, t (minor) = 5.53 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.54-7.48 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.14 (m, 9H), 6.74 (t, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 7.6 Hz, 1H), 5.15 (d, *J* = 8.0 Hz, 1H), 3.56-3.48 (m, 2H), 3.35-3.29 (m, 1H), 2.66-2.58 (m, 1H), 2.01-2.00 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 200.4, 158.9, 141.8, 140.2, 139.9, 137.1, 128.6, 128.6, 127.9, 127.7, 127.4, 126.5, 125.6, 125.5, 121.3, 117.5, 110.3, 59.7, 52.9, 36.2, 36.1, 29.7, 15.8 ppm; ESI-HRMS: calcd. for $C_{27}H_{25}NO_2$+Na^+ 418.1778, found 418.1781.

5. Aza-Baylis-Hillman-type pathway of simple 2,4-hexadienal or 2,4-heptadienal

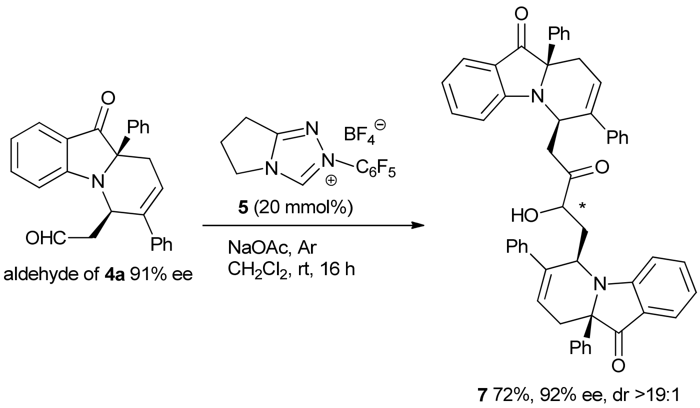


2-Phenyl-*3H*-indol-3-ones **2a** was tested in the reactions of simple 2,4-hexadienal or 2,4-heptadienal in xylene. The desired aza-Diels–Alder cycloadducts were not obtained, but the aza-Baylis–Hillman-type products **8** were observed at lower -20 °C but with yield. The isolated products are not very stable.

6. Synthetic transformations of cycloadduct



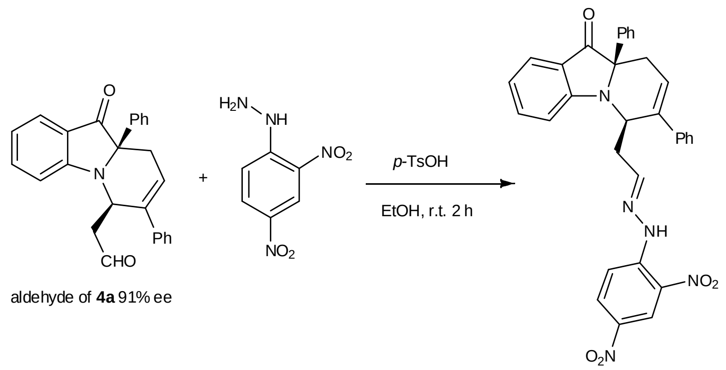
Salt **5** (0.04 mmol, 16 mg), K_2CO_3 (0.04 mmol, 5.5 mg), 18-crown-6 (0.04 mmol, 10 mg) were added to a solution of aldehyde of **4a** (0.2 mmol, 76 mg) in toluene (0.5 mL), and the mixture was stirred at room temperature under O_2 atmosphere. After 8 hours, the solvent was concentrated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford hemiacetal **6** as a yellow oil; (48.3 mg, 61% yield); $[\alpha]_D^{20}$ = -135.0 (*c* = 3.2 in $CHCl_3$); 92% *ee*, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 6.26 min, t (minor) = 10.89 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (t, *J* = 3.6 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.35-7.26 (m, 11H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.22-6.20 (m, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 3.24 (dd, *J* = 18.8, 2.8 Hz, 1H), 2.61 (d, *J* = 18.0 Hz, 1H), 2.16 (dd, *J* = 16.8, 2.8 Hz, 1H), 1.83 (dd, *J* = 16.4, 10.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 176.1, 160.1, 140.0, 138.5, 138.2, 137.6, 128.8, 128.3, 128.0, 127.4, 127.3, 126.4, 125.6, 122.6, 118.6, 118.0, 110.7, 67.9, 52.5, 37.4, 28.1 ppm; ESI-HRMS: calcd. for $C_{26}H_{21}NO_3+Na^+$ 418.1414, found 418.1418.



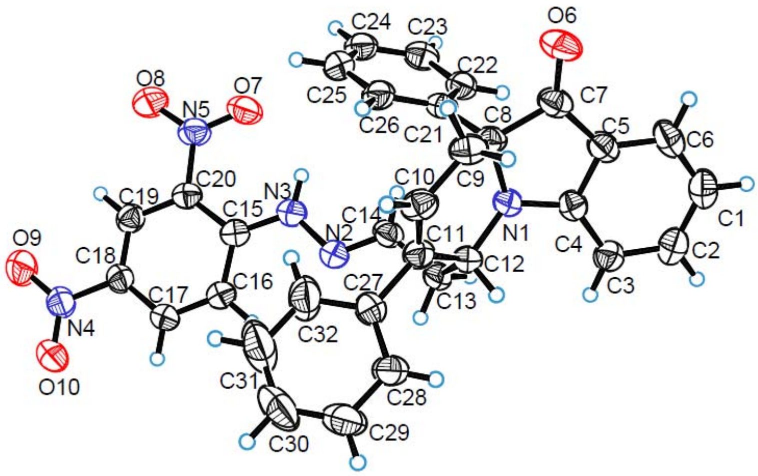
Salt **5** (0.04 mmol, 16 mg), NaOAc (0.04 mmol, 3.3 mg) were added to a solution of aldehyde of **4a** (0.2 mmol, 76 mg) in DCM (0.5 mL), and the mixture was stirred at room temperature under Ar atmosphere. After 8 hours, the solvent was concentrated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford **7** as a yellow oil; (55 mg, 72% yield); $[\alpha]_D^{20}$ = -155.0 (*c* = 3.5 in $CHCl_3$); 92% *ee*, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 7.50 min, t (minor) = 11.07 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.55 (m, 3H), 7.55-7.50 (m, 2H), 7.50-7.24 (m,11H), 6.95-6.78

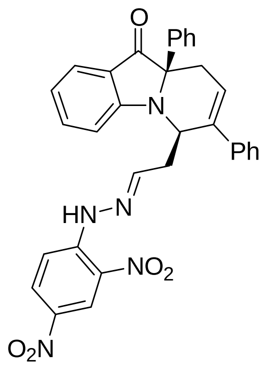
(m, 8H), 6.63-6.54 (m, 4H), 6.30-6.25 (m, 2H), 5.19 (d, J = 9.6 Hz, 1H), 5.06 (d, J = 10.4 Hz, 1H), 3.57-3.55 (m, 2H), 3.12 (td, J = 17.6, 6.4 Hz, 2H), 2.59-2.49 (m, 2H), 1.59-1.51 (m, 1H), 1.29-1.22 (m, 1H), 0.78 (t, J = 12.0 Hz, 1H), 0.11-0.05 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 203.6, 203.0, 161.8, 161.1, 140.2, 139.6, 139.1, 138.6, 138.2, 138.0, 137.8, 137.2, 129.0, 128.8, 128.3, 128.0, 127.9, 127.9, 126.9, 126.6, 126.0, 125.7, 125.4, 122.3, 121.5, 118.5, 118.3, 117.9, 117.6, 111.6, 110.5, 73.0, 67.5, 67.0, 51.6, 49.7, 39.9, 28.0, 27.9 ppm; ESI-HRMS: calcd. for $C_{52}H_{42}N_2O_4+Na^+$ 781.3038, found 781.3043. *We tried to conduct esterification of the newly generated OH group with Mosher's acid in order to determine its absolute configuration. Unfortunately, the corresponding ester could not be produced under diverse reaction conditions, probably due to the crowded structure and the effect of the adjacent carbonyl group.*

7. Crystal data and structure refinement for enantiopure 2,4-dinitrobenzenehydrazone of aldehyde of product 4a



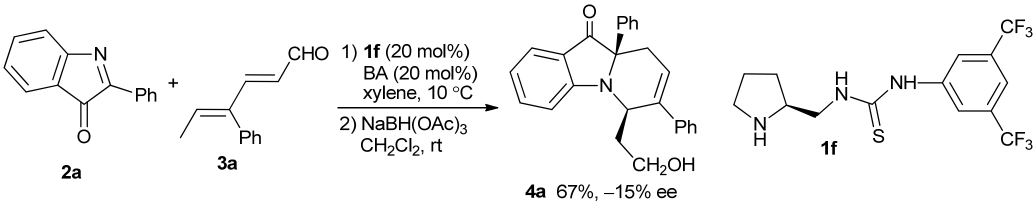
Aldehyde of **4a** (0.1 mmol, 91% ee), 2,4-dinitrobenzenehydrazine (0.11 mmol) and 4-toluene sulfonic acid (0.01 mmol) were stirred in EtOH (2 mL) at room temperature for 2 hour. After completion, the product was isolated by flash chromatography as a yellow solid (45.2 mg, 82% yield). The obtained 2,4-dinitrobenzenehydrazone was slowly crystallized from a solution of Et_2O/*n*-hexane (1:2) at room temperature to give the optically pure crystals suitable X-ray analysis. (m.p. = 194.5-196.2 ℃); $[\alpha]_D^{20}$ = -45.0 (c = 1.5 in $CHCl_3$); ≥99.5% *ee*, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t = 15.89 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.55 (s, 1H), 9.09 (s, 1H), 8.23 (dd, J = 9.6, 2.4 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 9.6 Hz, 1H), 7.62-7.58 (m, 1H), 7.39-7.26 (m, 9H), 6.90 (d, J = 8.4 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.65 (t, J = 6.4 Hz, 1H), 6.27-6.25 (m, 1H), 5.06-5.04 (m, 1H), 4.12 (q, J = 7.2 Hz, 1H), 3.30 (dd, J = 19.6, 6.0 Hz, 1H), 2.60-2.56 (m, 1H), 2.43-2.37 (m, 1H), 2.21-2.14 (m, 1H) ppm; ESI-HRMS: calcd. for $C_{32}H_{25}N_5O_5+Na^+$ 582.1748, found 582.1755.





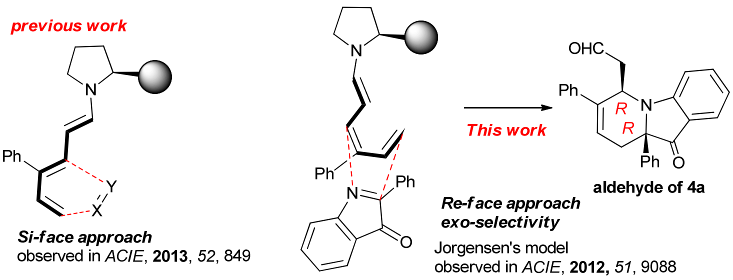
Identification code	**4a**
Formula sum	C32 H25 N5 O5
Formula weight	559.57 g/mol
Crystal system	triclinic
Space-group	P 1 (1)
Cell parameters	a=7.9810(2) Å b=8.9970(2) Å c=19.1833(5) Å
	α=78.855(2)° β=84.930(2)° γ=88.715(2)°
Cell ratio	a/b=0.8871 b/c=0.4690 c/a=2.4036
Cell volume	1346.17(6) Å3
Z	2
Calc. density	1.38041 g/cm3
RAll	0.0361
Pearson code	aP134
Formula type	N5O5P25Q32
Wyckoff sequence	a134

Based on the absolute configuration of the cycloadduct, it was found that inversed enantioselectivity was observed in comparison with our previous work (*Angew. Chem., Int. Ed.*, 2013, **52**, 948). We further checked the trienamine catalysis in literatures. In fact, the Jørgensen group reported a similar enantioselectivity in amine **1a**-catalysed DA reaction of 2,4-dienals and 3-cyanochromones, though the ee values was only fair (*Angew. Chem., Int. Ed.*, 2012, **51**, 9088). We further tested our reaction with a bifunctional catalyst **1f**. As outlined in the following scheme, the enantioselectivity was low but inversed in comparison with that of amine **1a**, also in accordance to that observed in Jørgensen's paper.

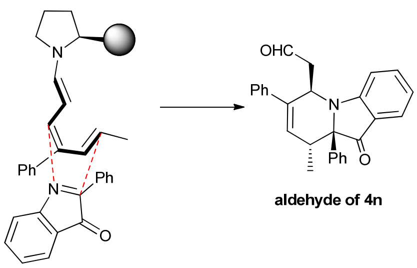


Therefore, as stated in Jørgensen's paper, "*the obtained results suggest that the mechanism(s) of trienamine-mediated reactions can be a rather complex issue and might be highly dependent on the structure of the starting dienal*", **and the dienophiles used**.

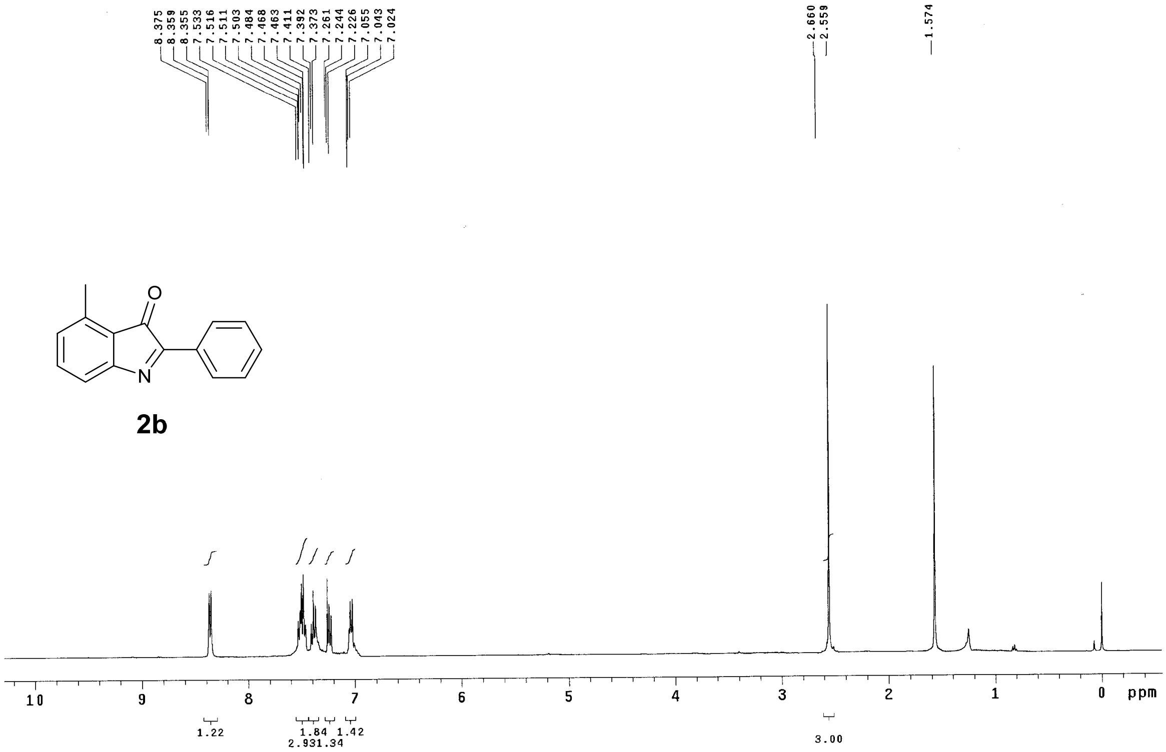
A proposed catalytic transition state was outlined in the following scheme based on the absolute configuration of cycloadduct **4a** and Jørgensen's model.



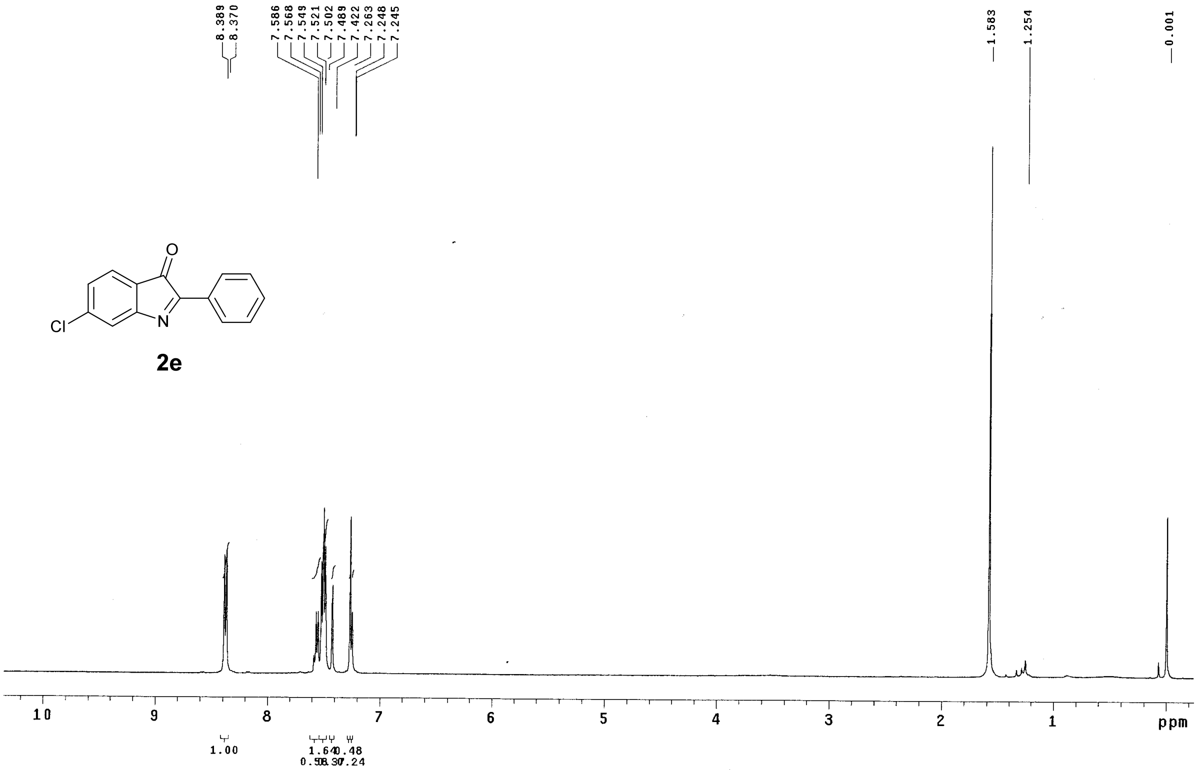
In addition, we further analyzed the structure of cycloadduct **4n**. The chiral center adjacent to methyl group was established by NOE study. It was also in fine accordance to that observed in Jørgensen's paper. The proposed transition state for the generation of aldehyde of **4n** was outlined in the following scheme.



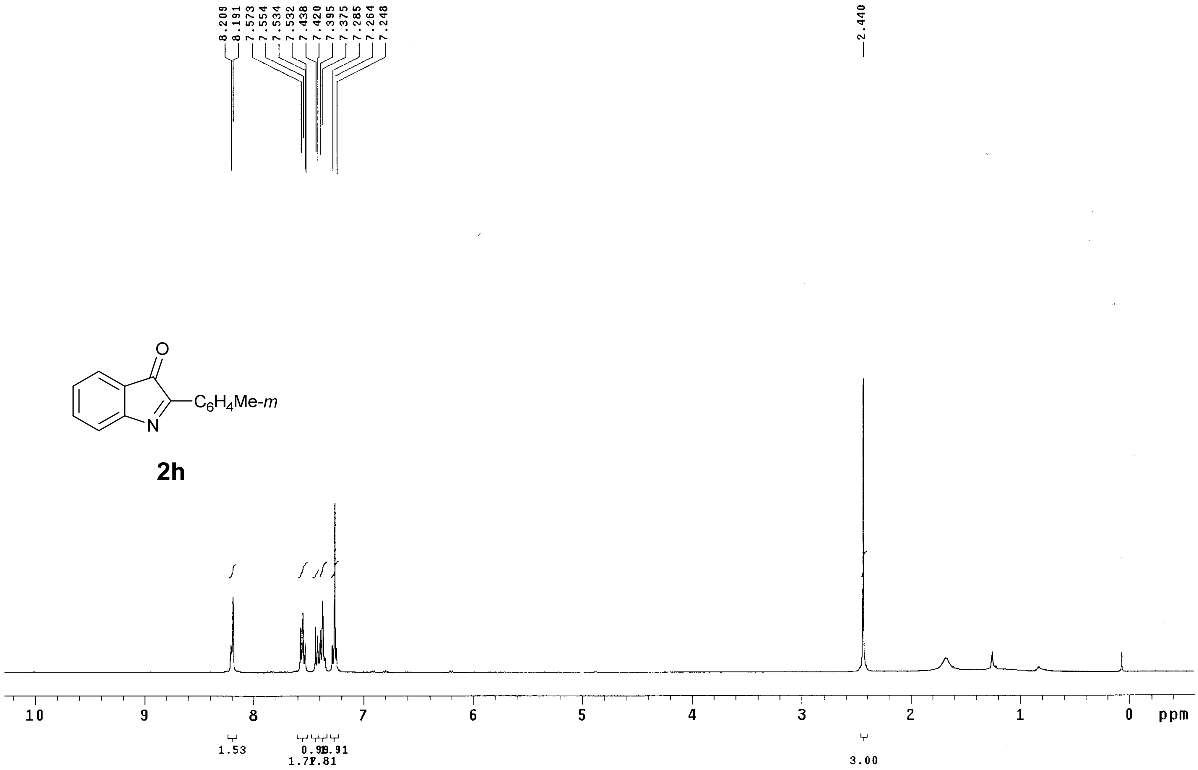
8. NMR spectra and HPLC chromatograms



2b



2e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7.534
7.532
7.438
7.420
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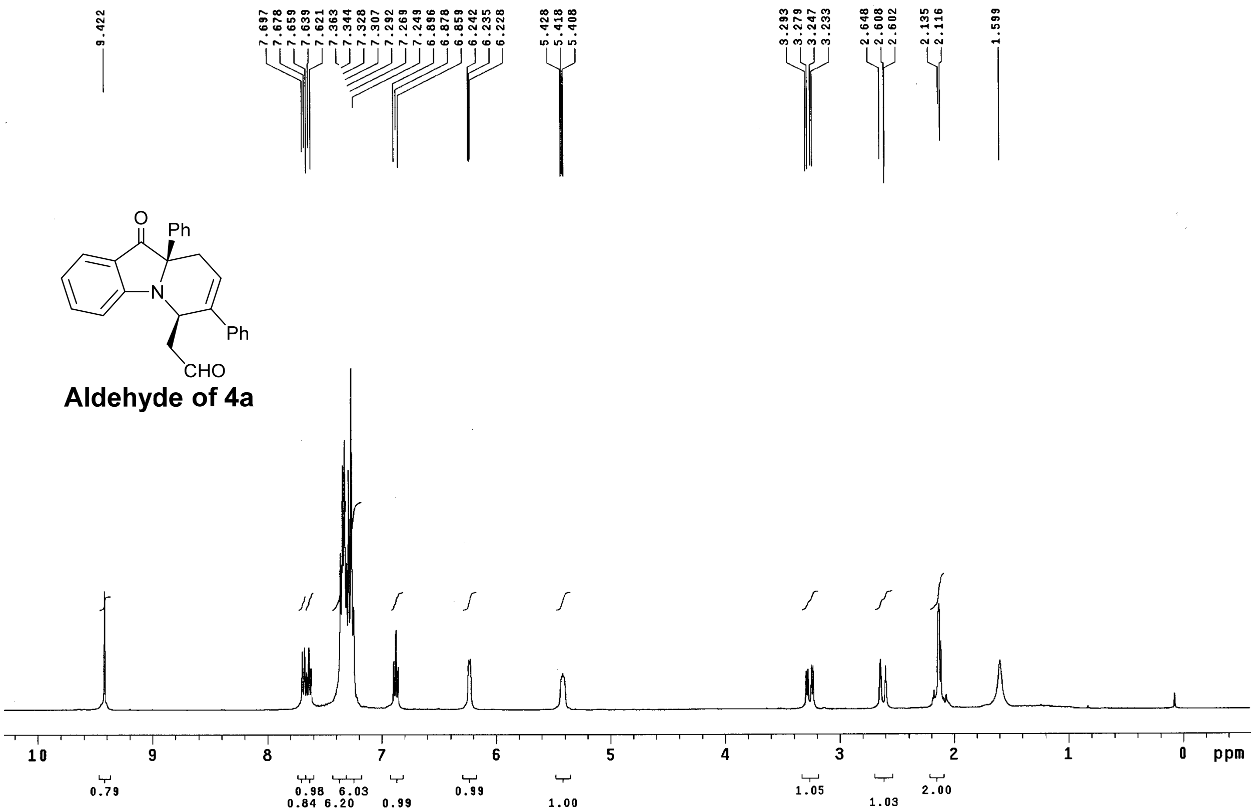
7.375
7.285
7.264
7.248
2.440
O
N
C_6H_4Me-*m*
2h
10
9
8
7
6
5
4
3
2
1
0
ppm
1.53
3.00


9.422
7.697 7.678 7.659 7.639 7.621 7.363 7.344 7.328 7.307 7.292 7.269 7.249 6.896 6.878 6.859 6.242 6.235 6.228
5.428 5.418 5.408
3.293 3.279 3.247 3.233
2.648 2.608 2.602
2.135 2.116
1.599
O
Ph
N
Ph
CHO
Aldehyde of 4a
10 9 8 7 6 5 4 3 2 1 0 ppm
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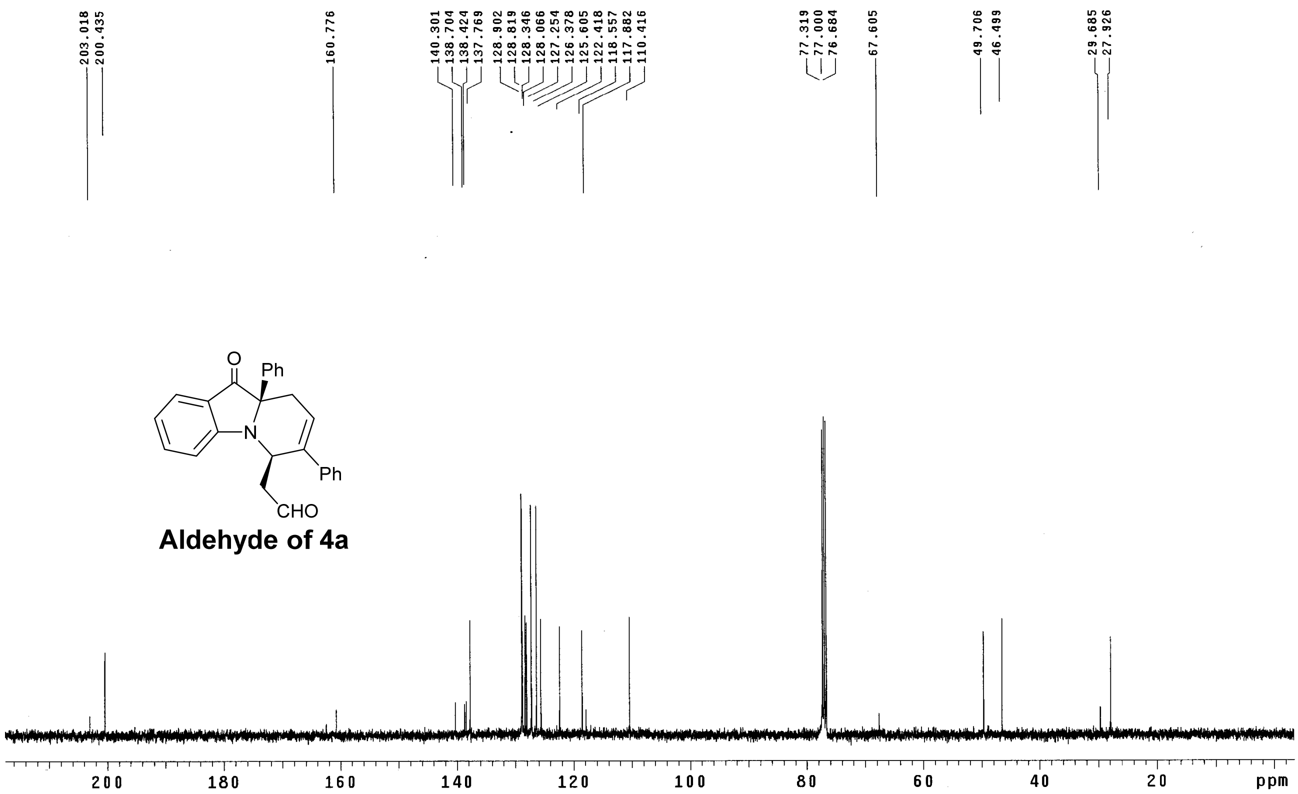
0.98 6.03
0.84 6.20
0.99
0.99
1.00
1.05
1.03
2.00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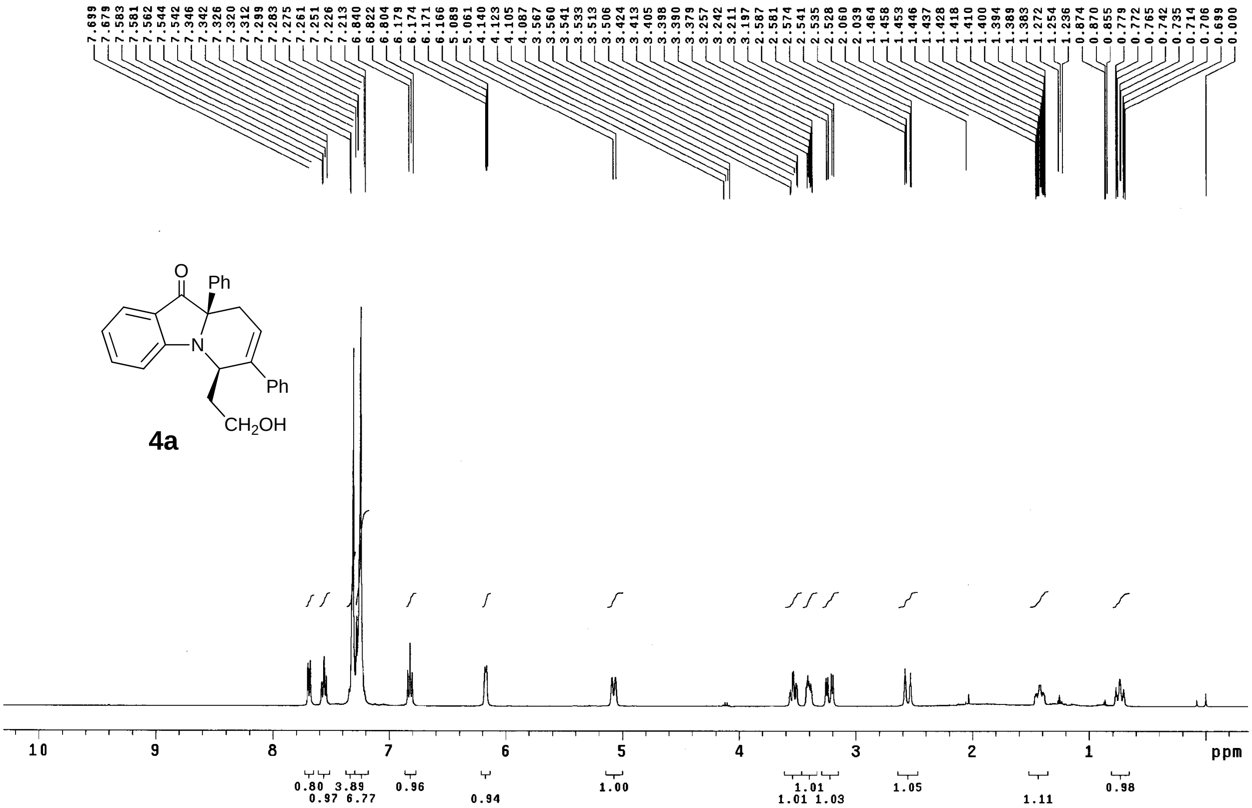
140.301 138.704 138.424 137.769 128.902 128.819 128.346 128.066 127.254 126.378 125.605 122.418 118.557 117.882 110.416
77.319 77.000 76.684
67.605
49.706 46.499
29.685 27.926
O
Ph
N
Ph
CHO
Aldehyde of 4a
200 180 160 140 120 100 80 60 40 20 ppm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7.283
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2.060
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1.383
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0.772
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0.742
0.735
0.714
0.706
0.699
0.000
O
Ph
N
Ph
CH2OH
4a
10
9
8
7
6
5
4
3
2
1
ppm
0.80
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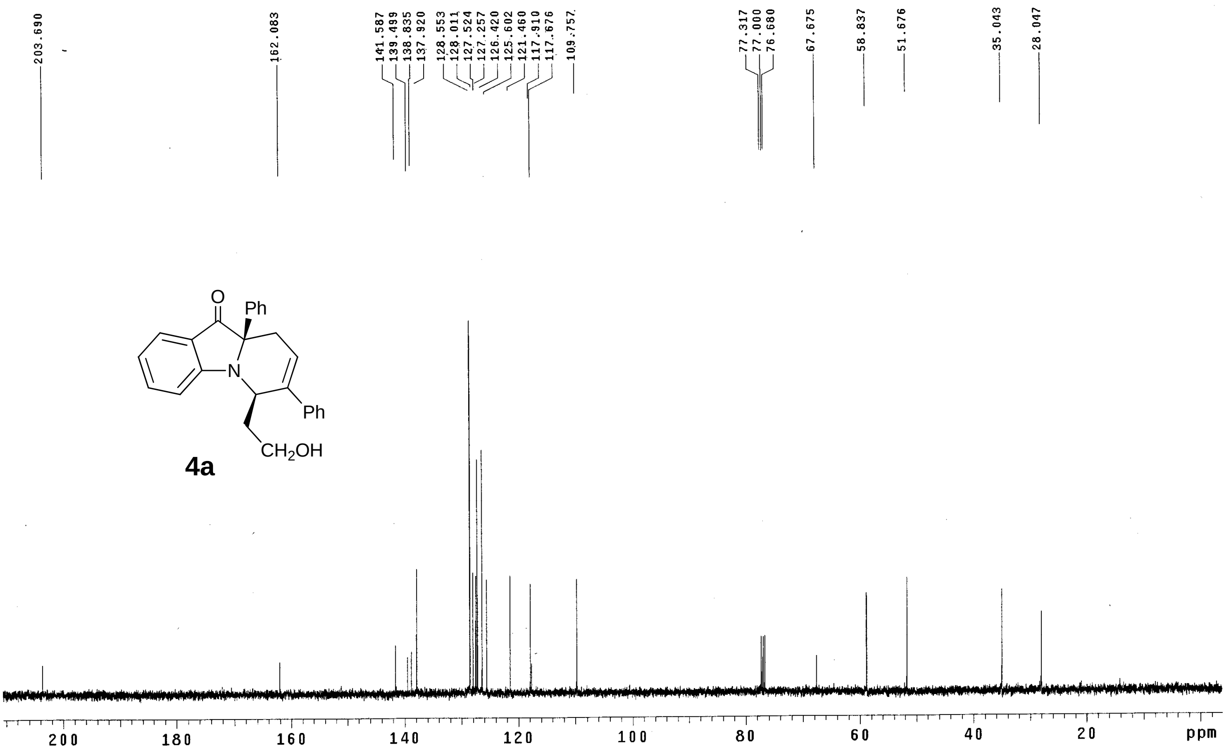
0.96
0.94
1.00
1.01
1.01
1.03
1.05
1.11
0.98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127.257
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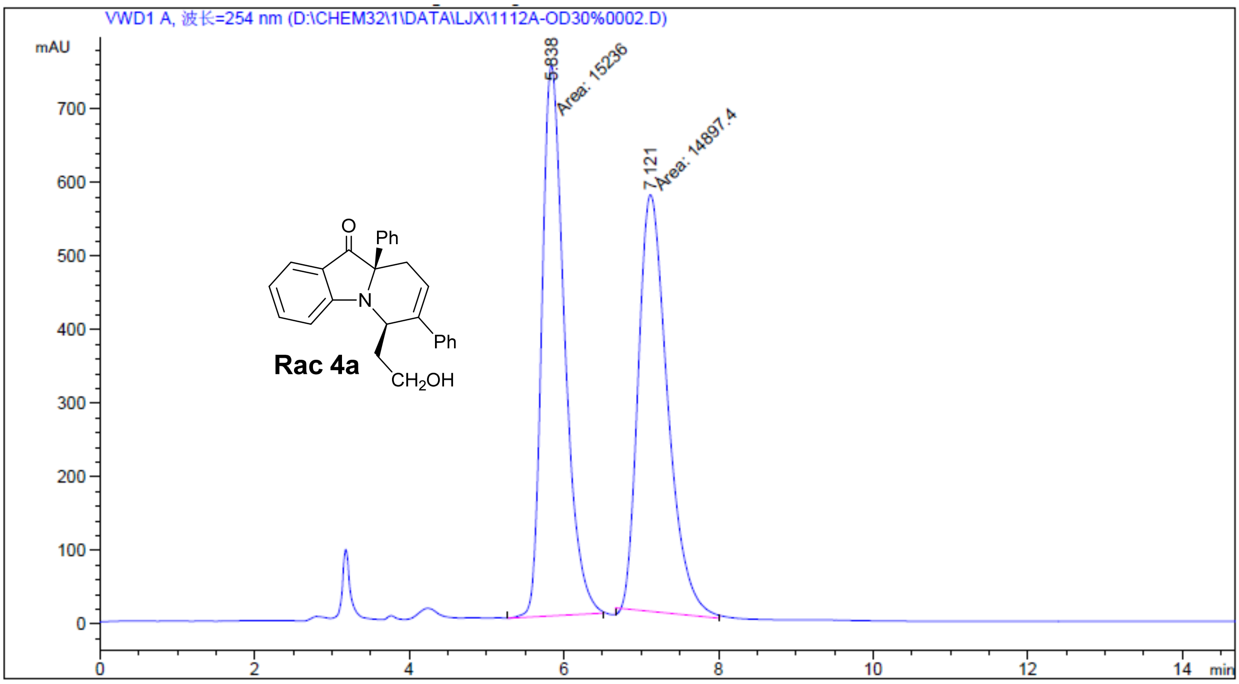
117.910
117.676
109.757
77.317
77.000
76.680
67.675
58.837
51.676
35.043
28.047
O
Ph
N
Ph
CH2OH
4a
200
180
160
140
120
100
80
60
40
20
ppm



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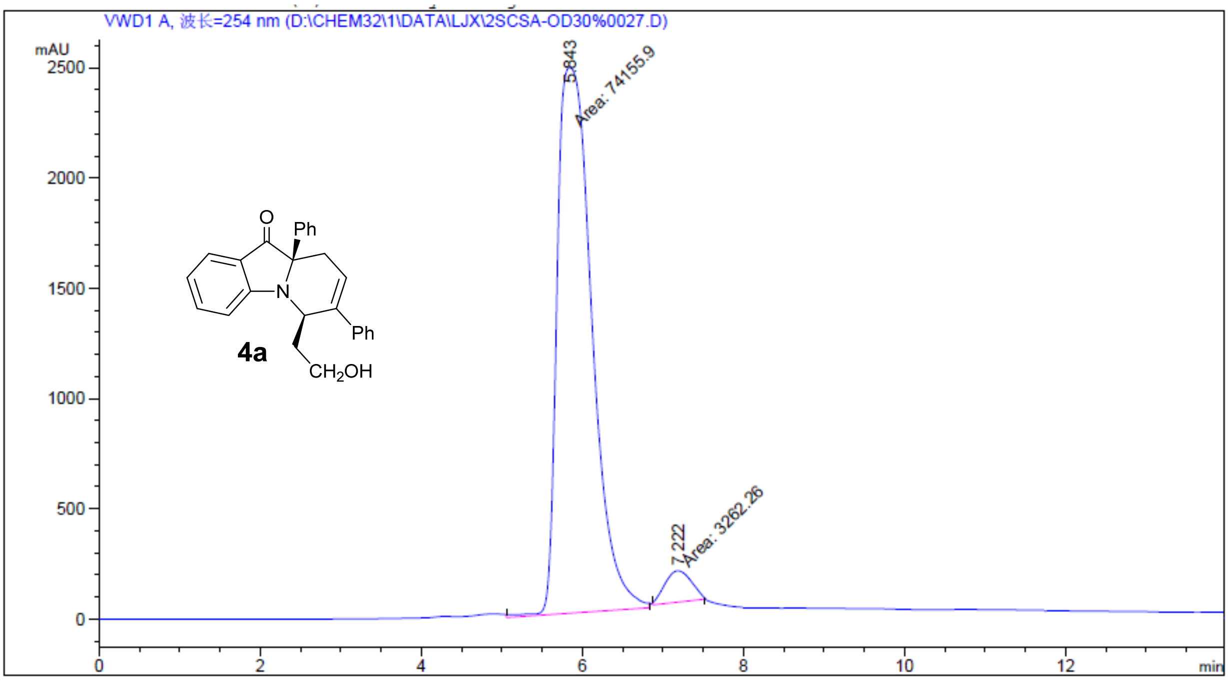
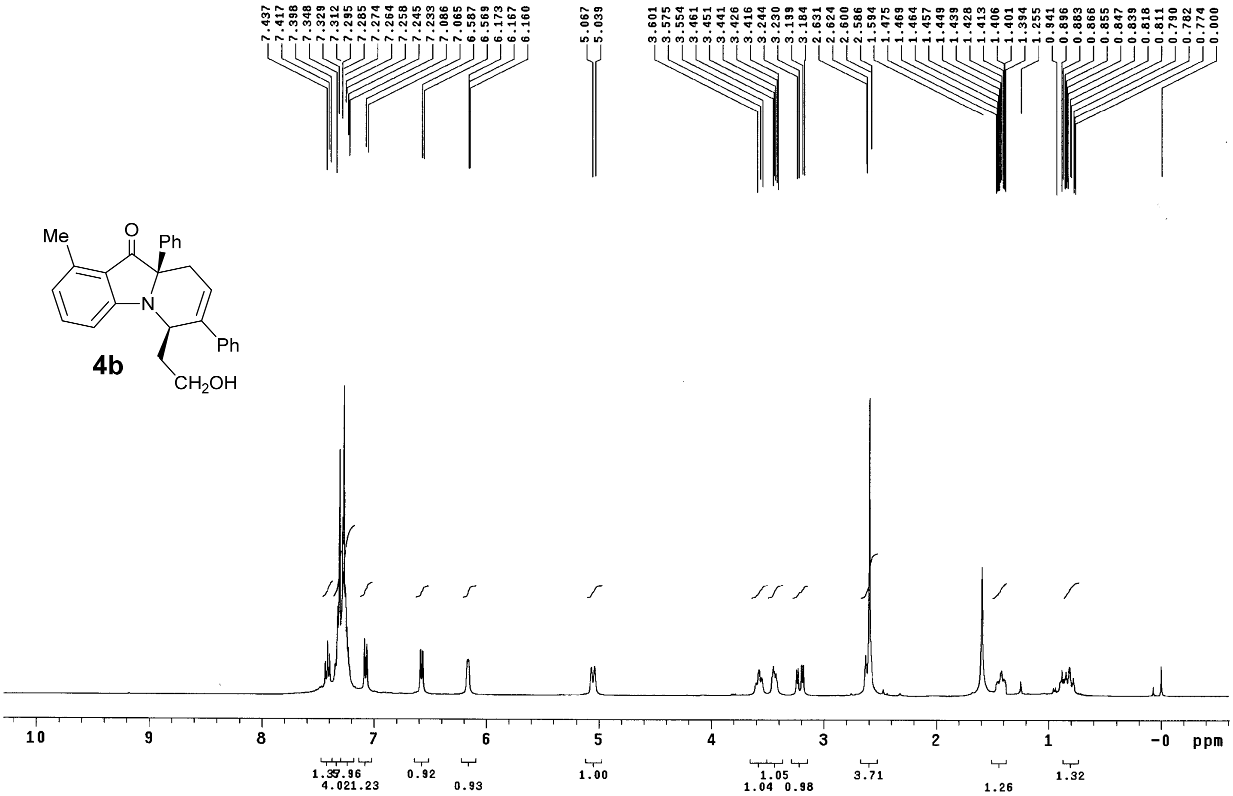
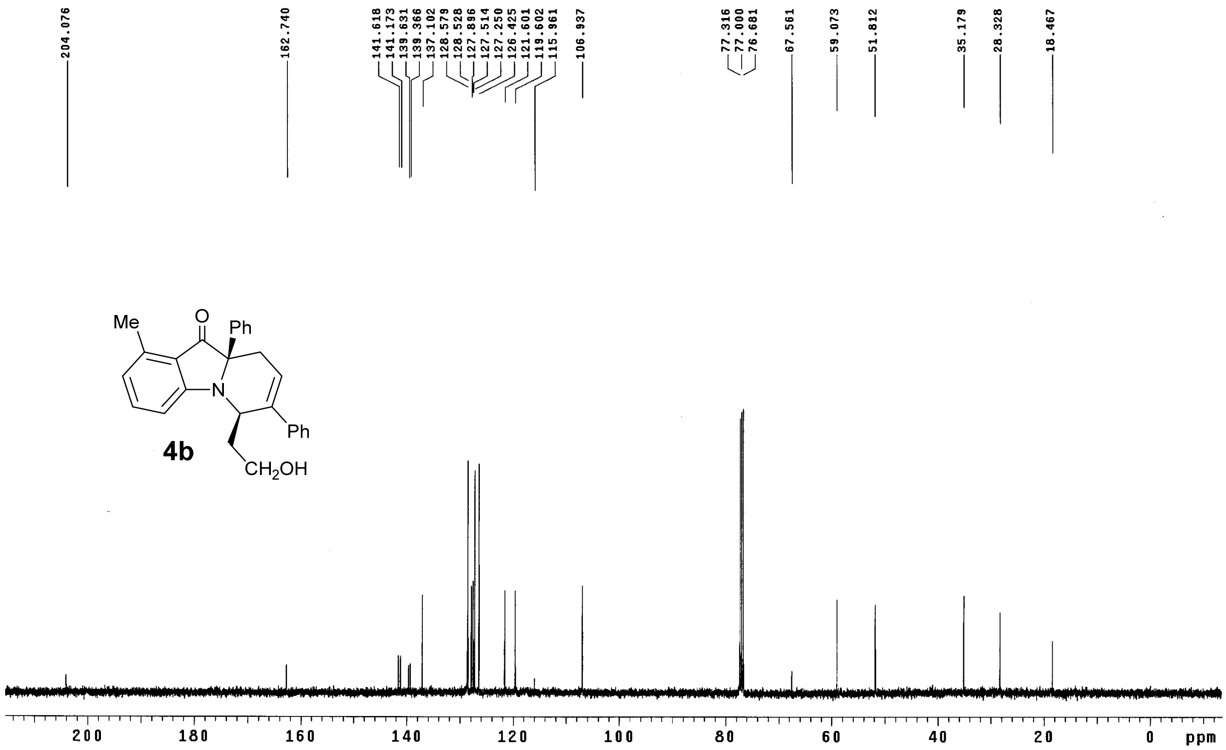
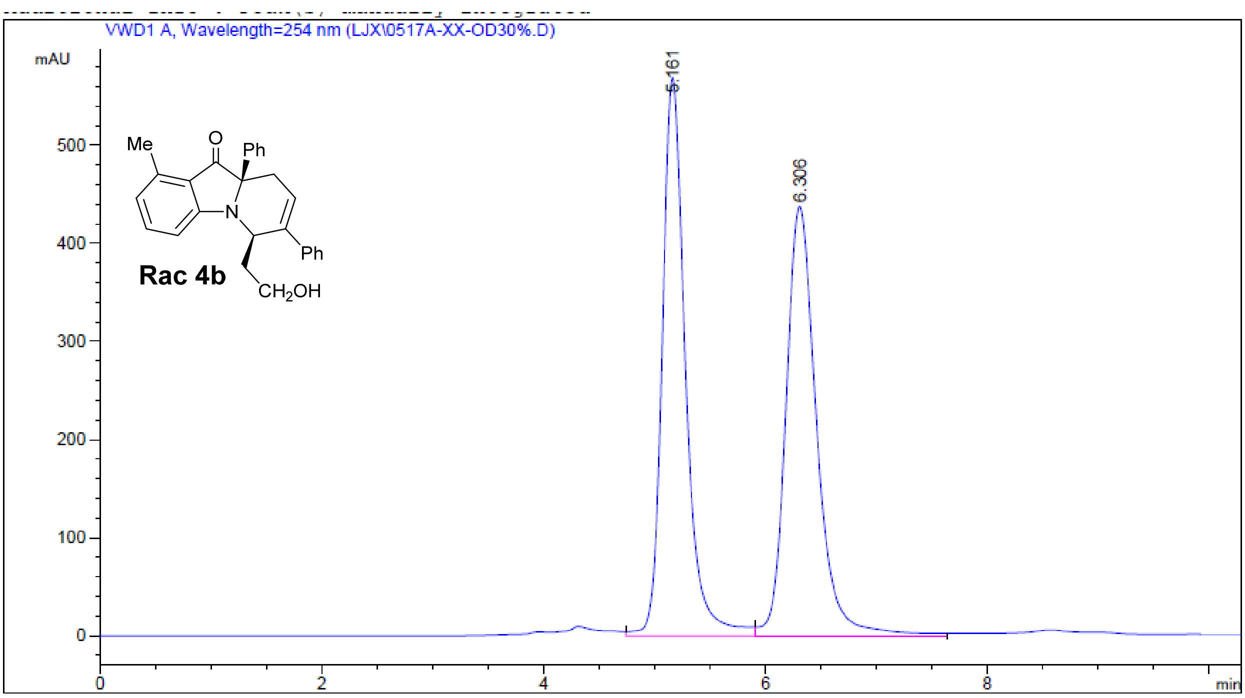
2	7.121	MM	0.4382	1.48974e4	566.56335	49.4381



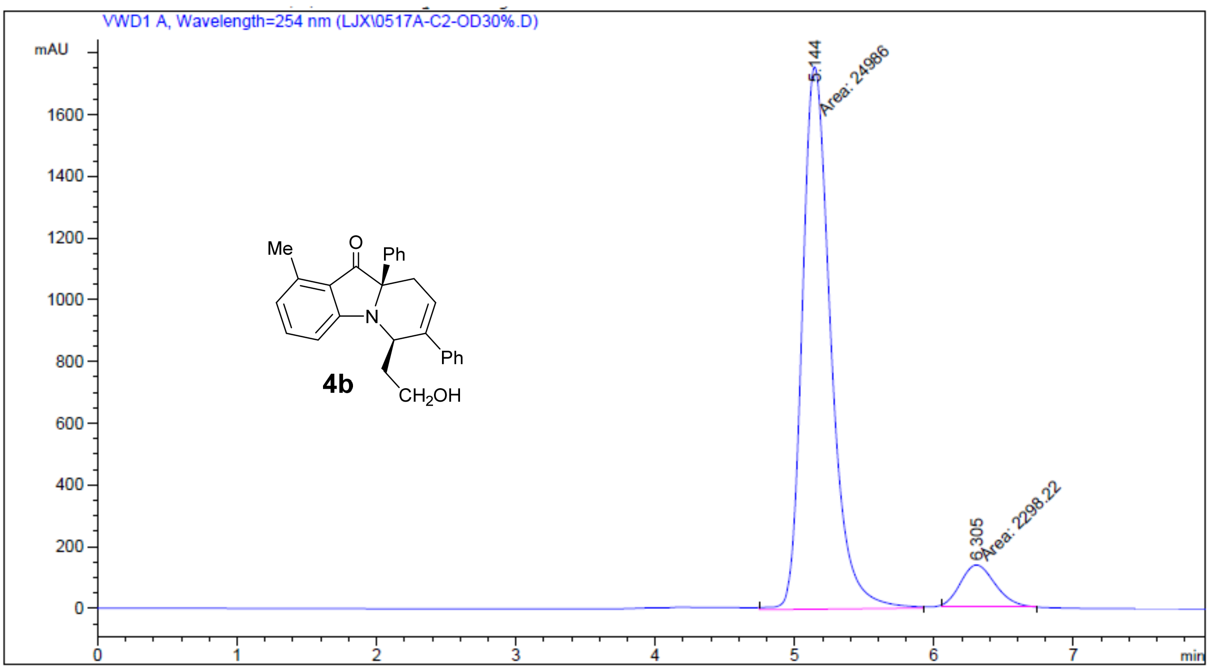
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.843	MM	0.4993	7.41559e4	2475.50293	95.7862
2	7.222	MM	0.3817	3262.26221	142.43834	4.2138



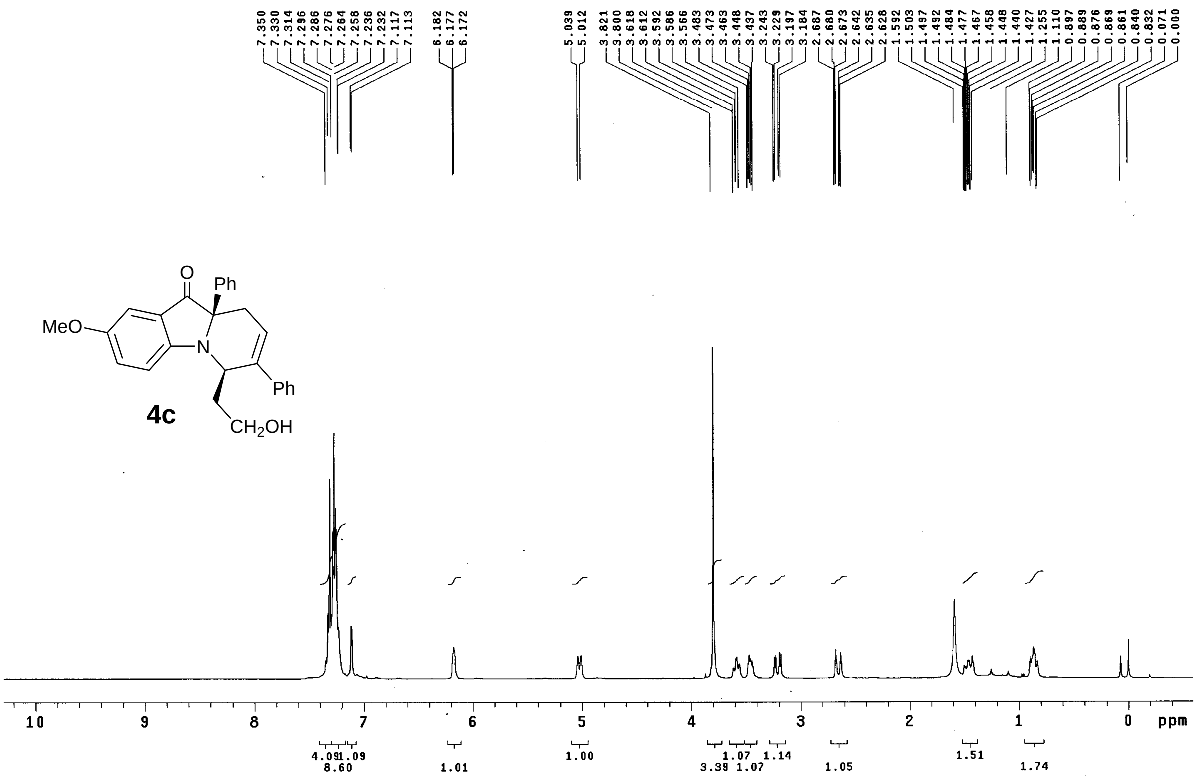


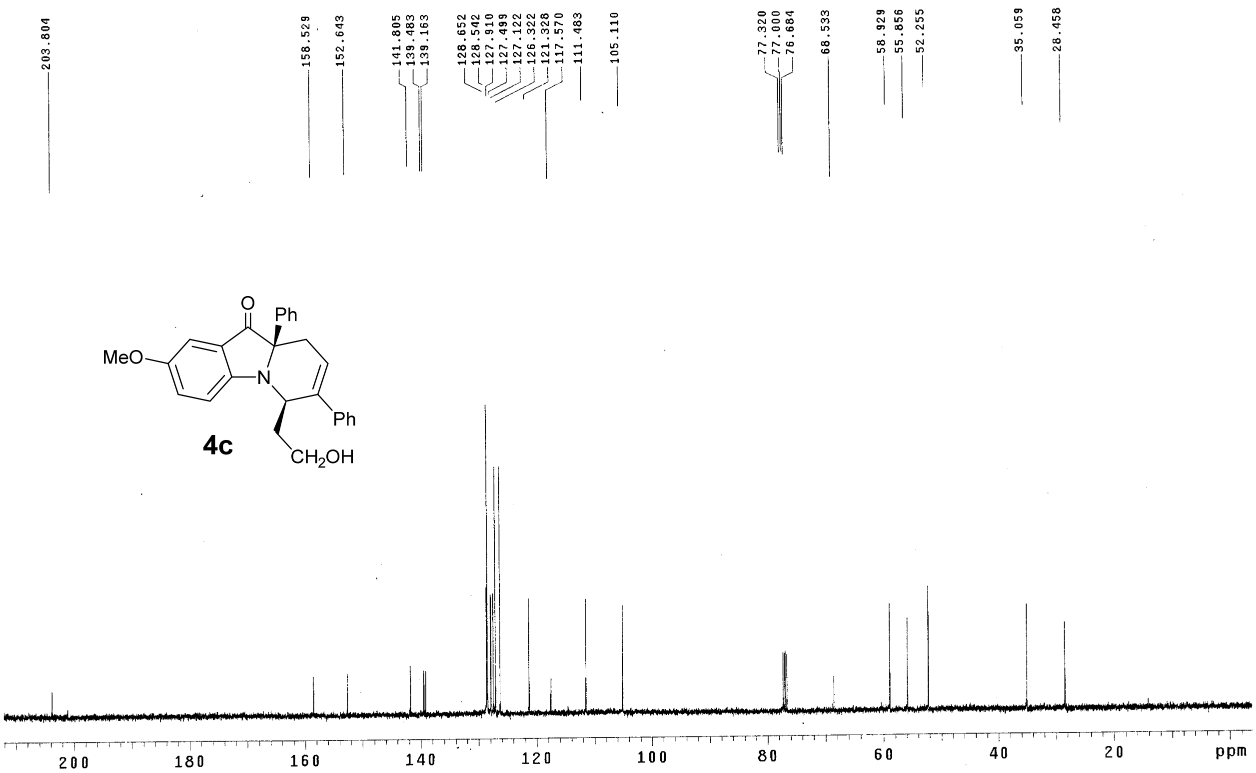


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.161	VV	0.2171	8315.78906	568.87433	49.6560
2	6.306	VB	0.2946	8431.02051	437.77109	50.3440



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.144	MM	0.2365	2.49860e4	1761.01086	91.5768
2	6.305	MM	0.2849	2298.21533	134.45268	8.4232


MeO
Ph
Ph
4c
CH2OH
ppm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127.910
127.499
127.122
126.322
121.328
117.570
111.483
105.110
77.320
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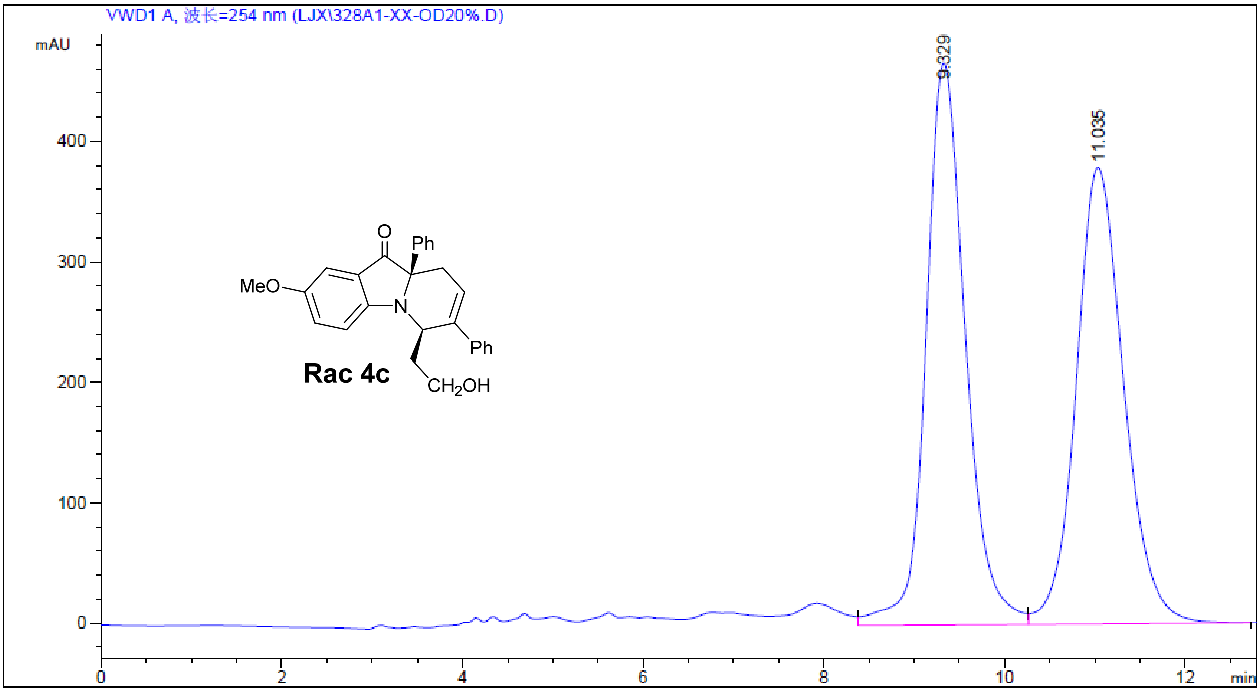
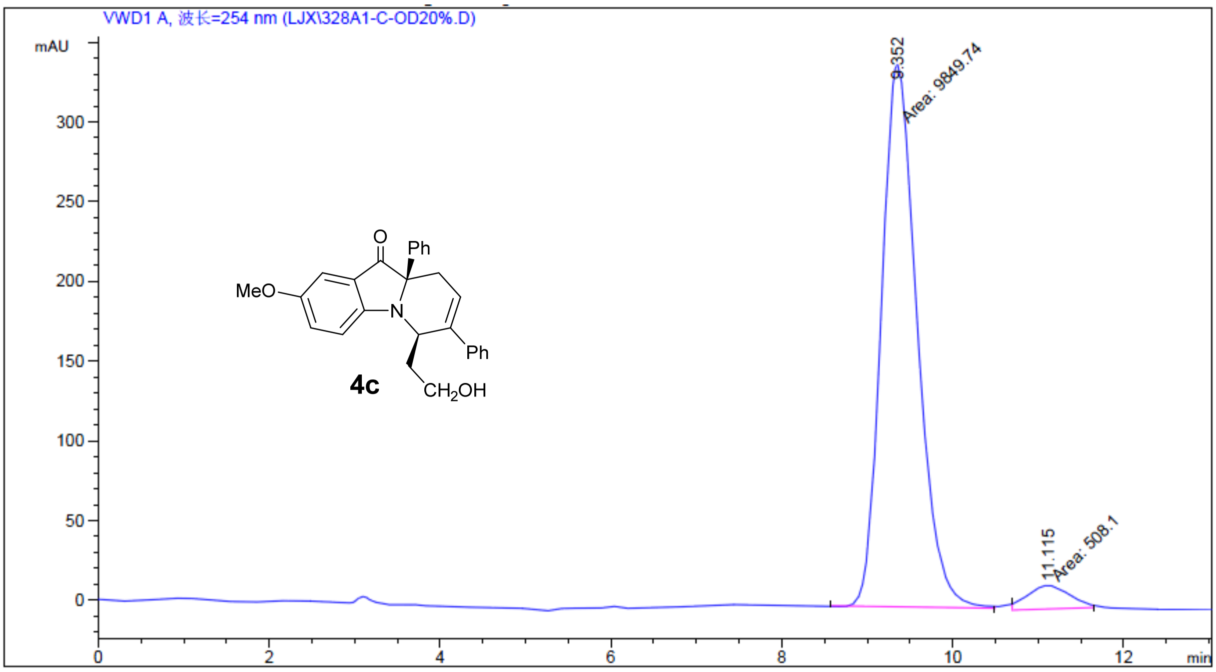
Ph
Ph
4c
CH2OH
ppm



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.329	VV	0.4668	1.42392e4	466.44348	50.5905
2	11.035	VBA	0.5564	1.39068e4	378.88132	49.4095



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.352	MM	0.4822	9849.74316	340.46234	95.0945
2	11.115	MM	0.5715	508.09952	14.81728	4.9055

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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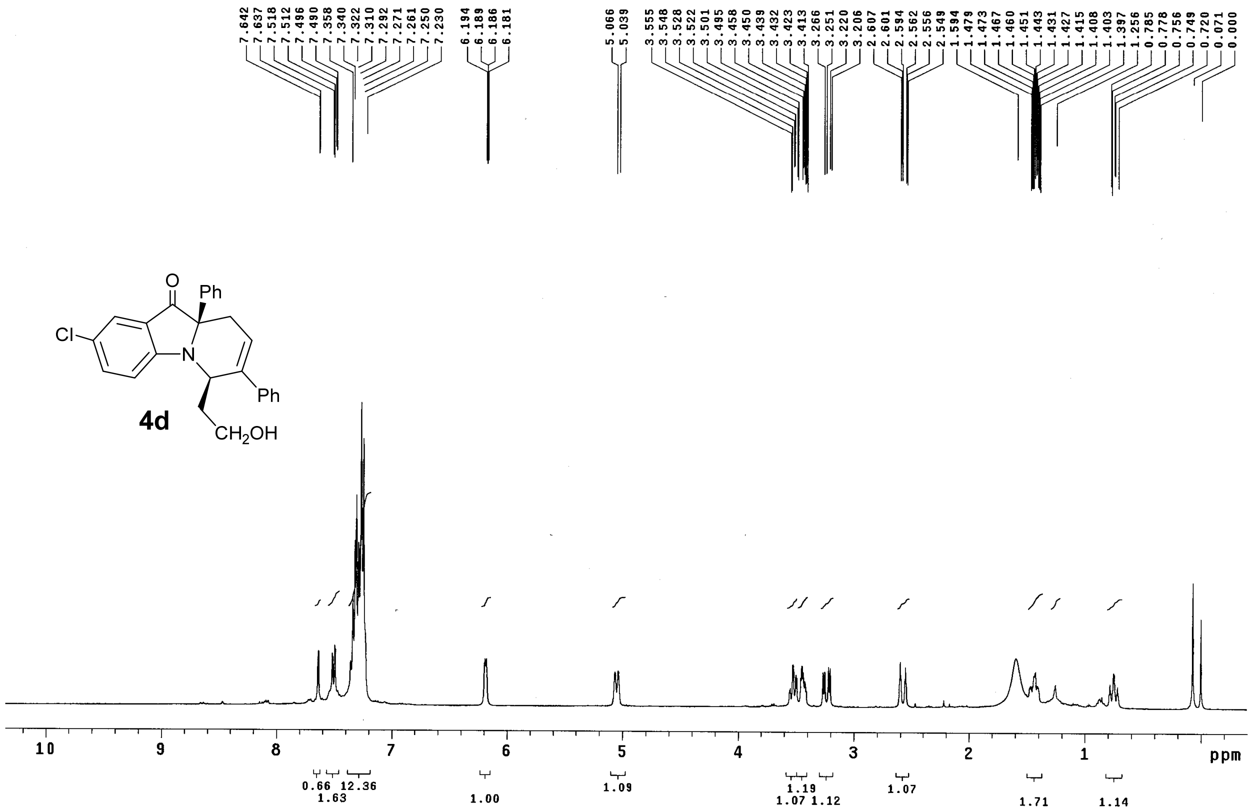
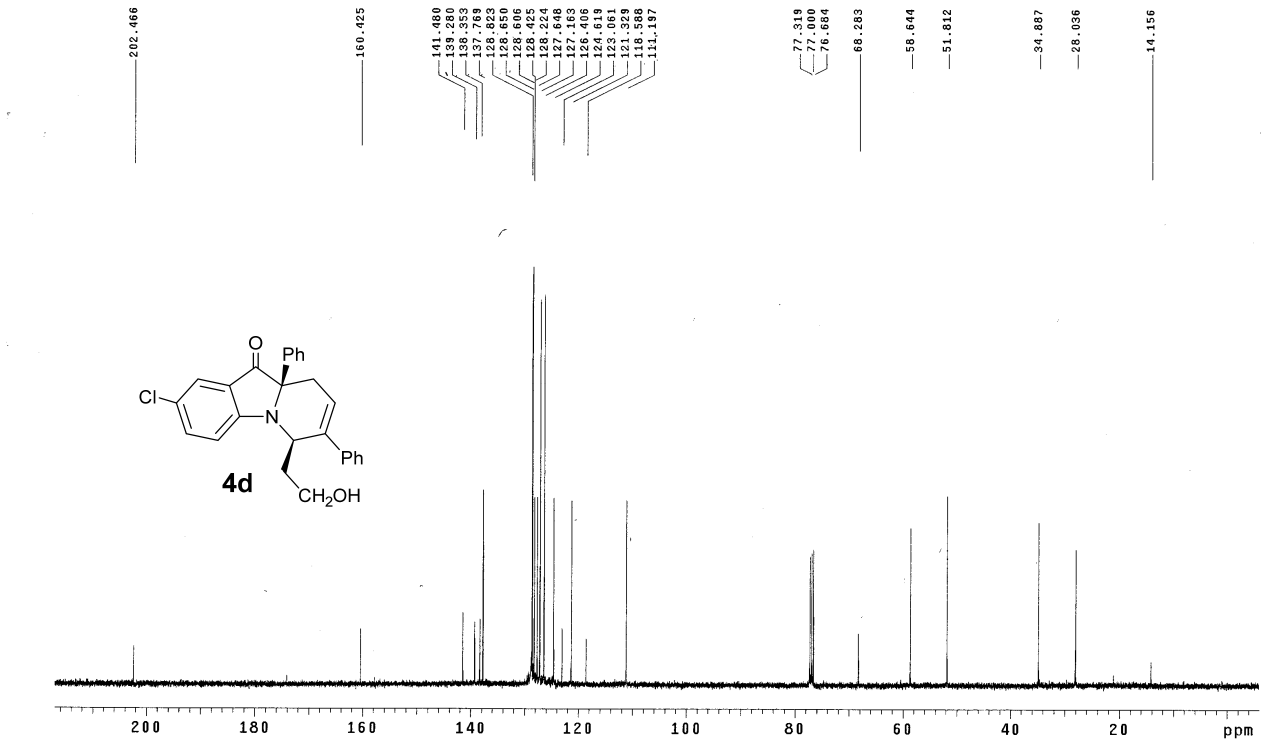
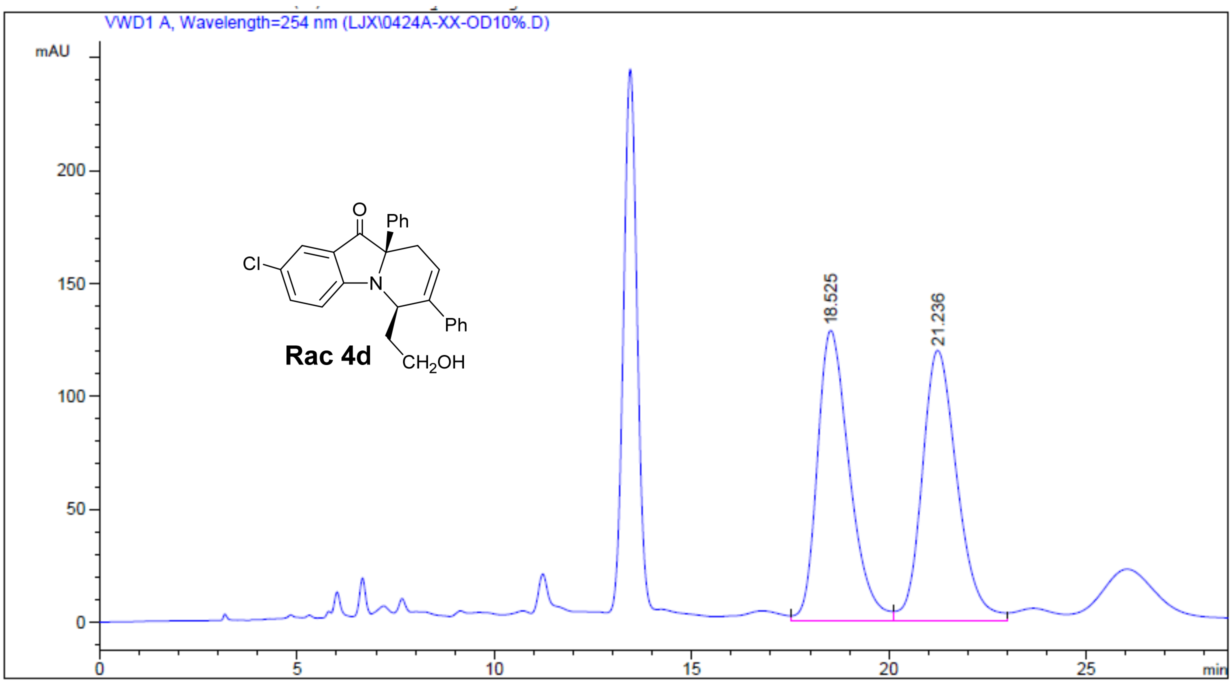
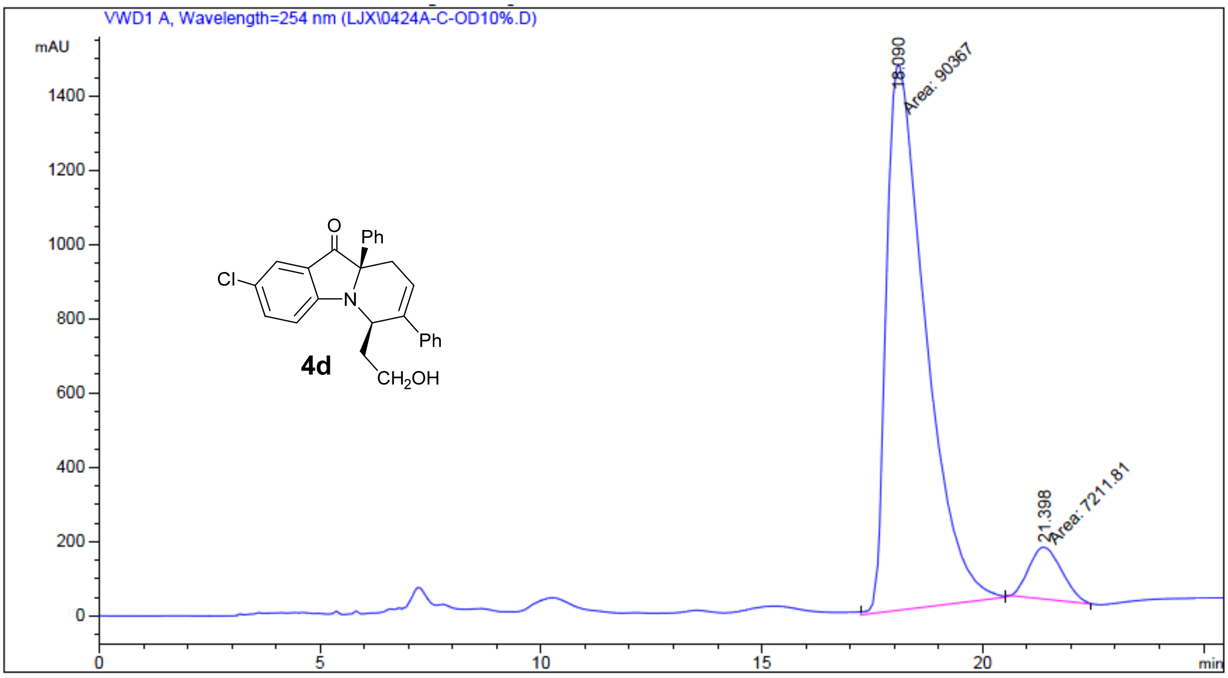




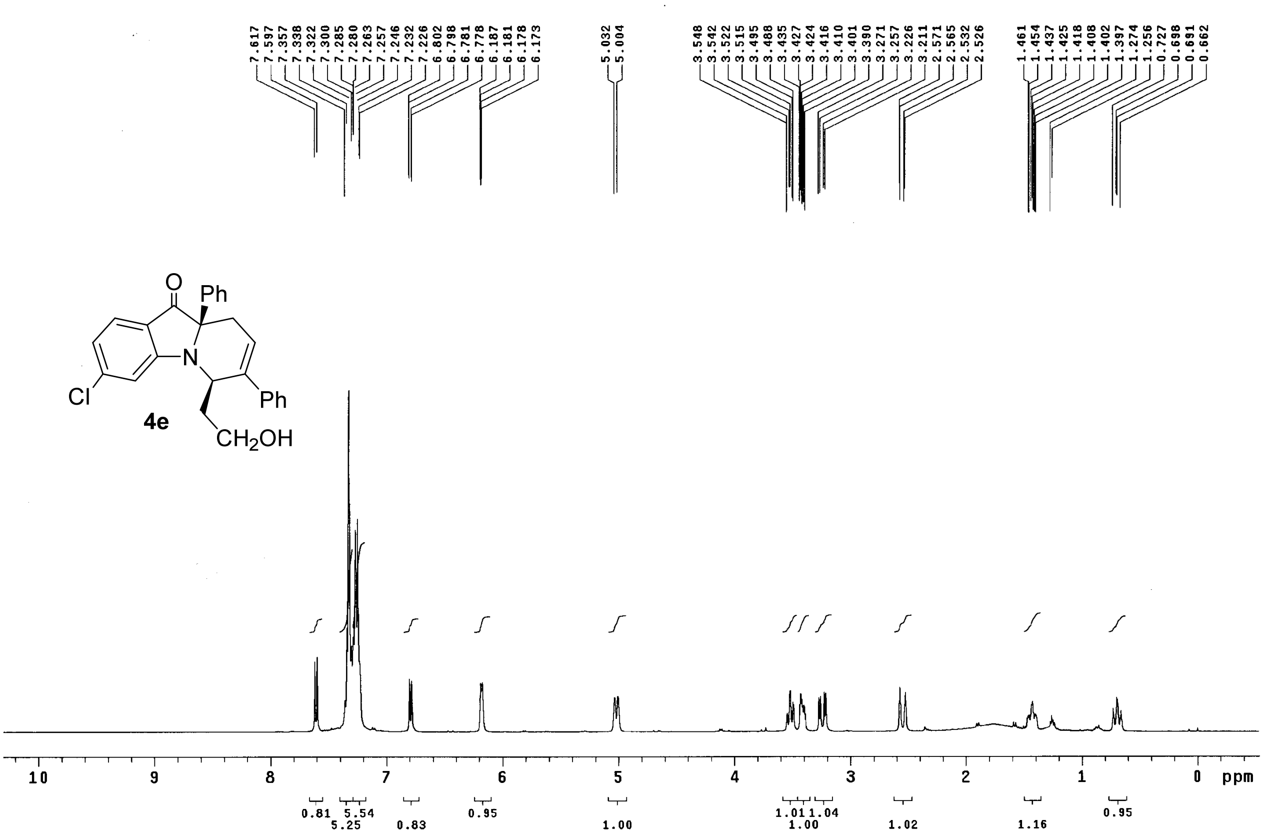


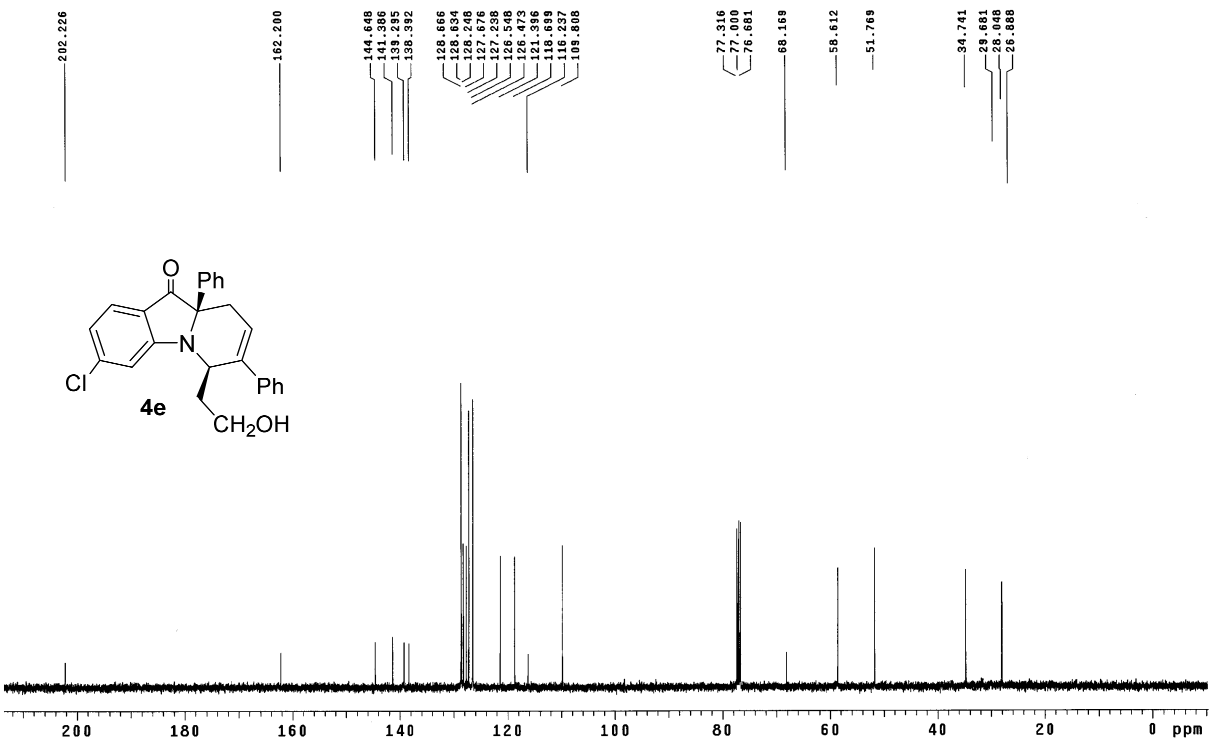
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.525	VV	0.8696	7267.92627	128.48488	49.6119
2	21.236	VV	0.9465	7381.64648	119.71524	50.3881

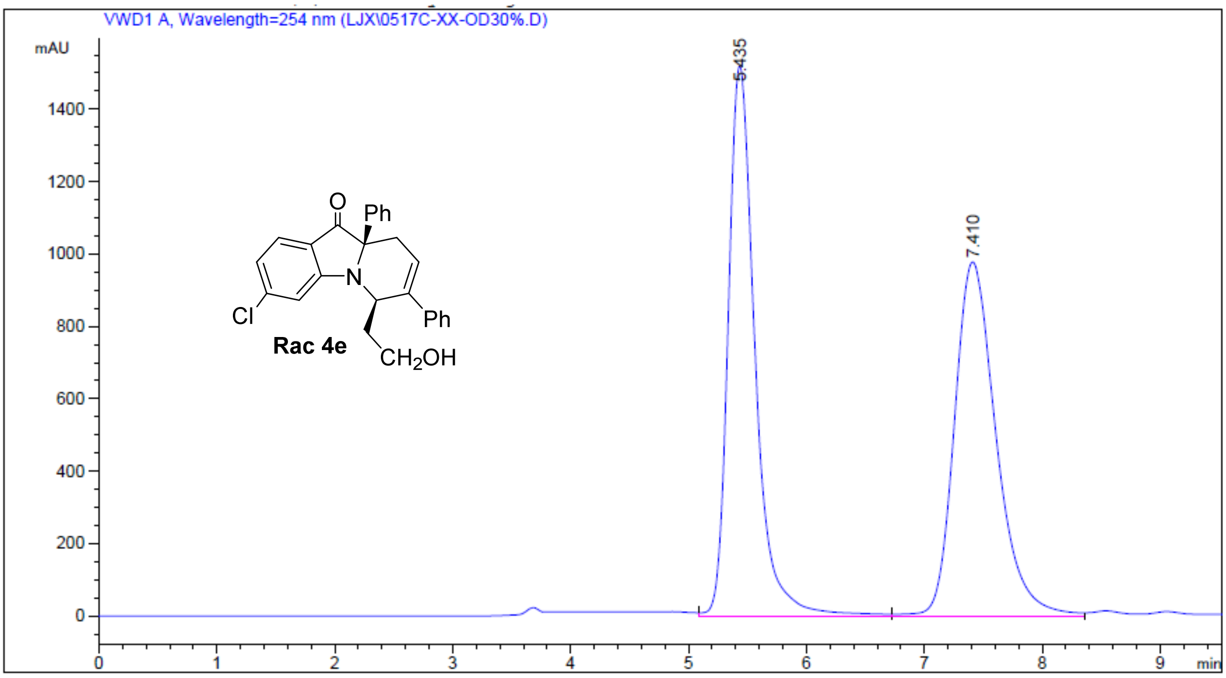


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.090	MM	1.0246	9.03670e4	1469.96179	92.6092
2	21.398	MM	0.8614	7211.80615	139.54285	7.3908

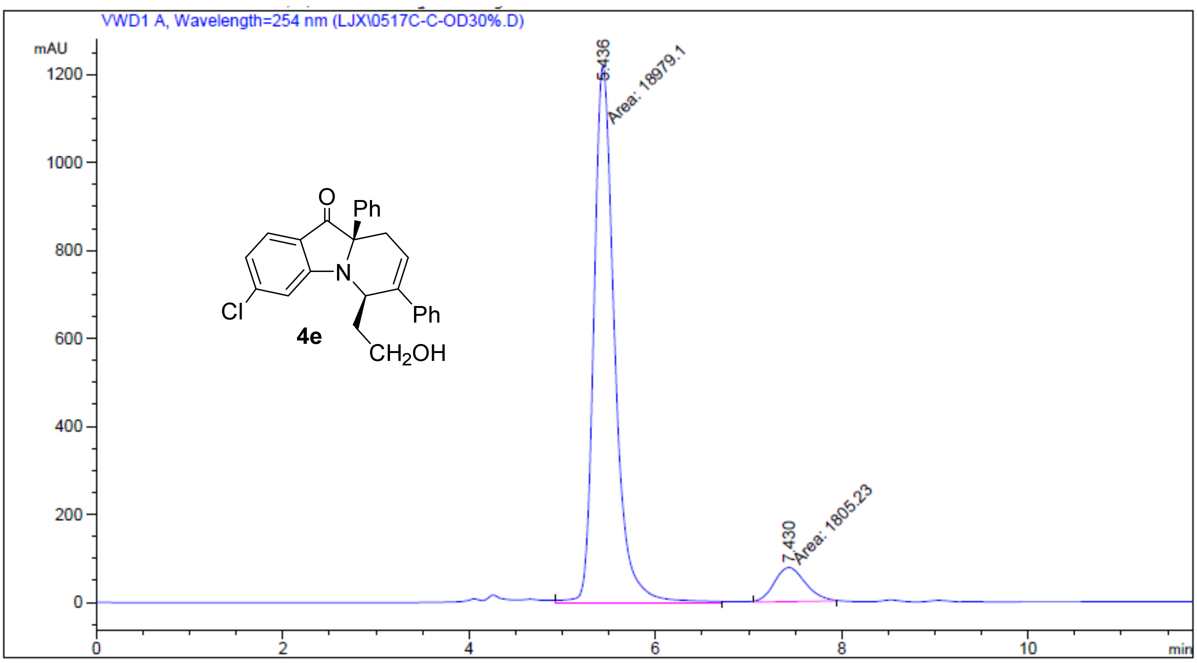
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



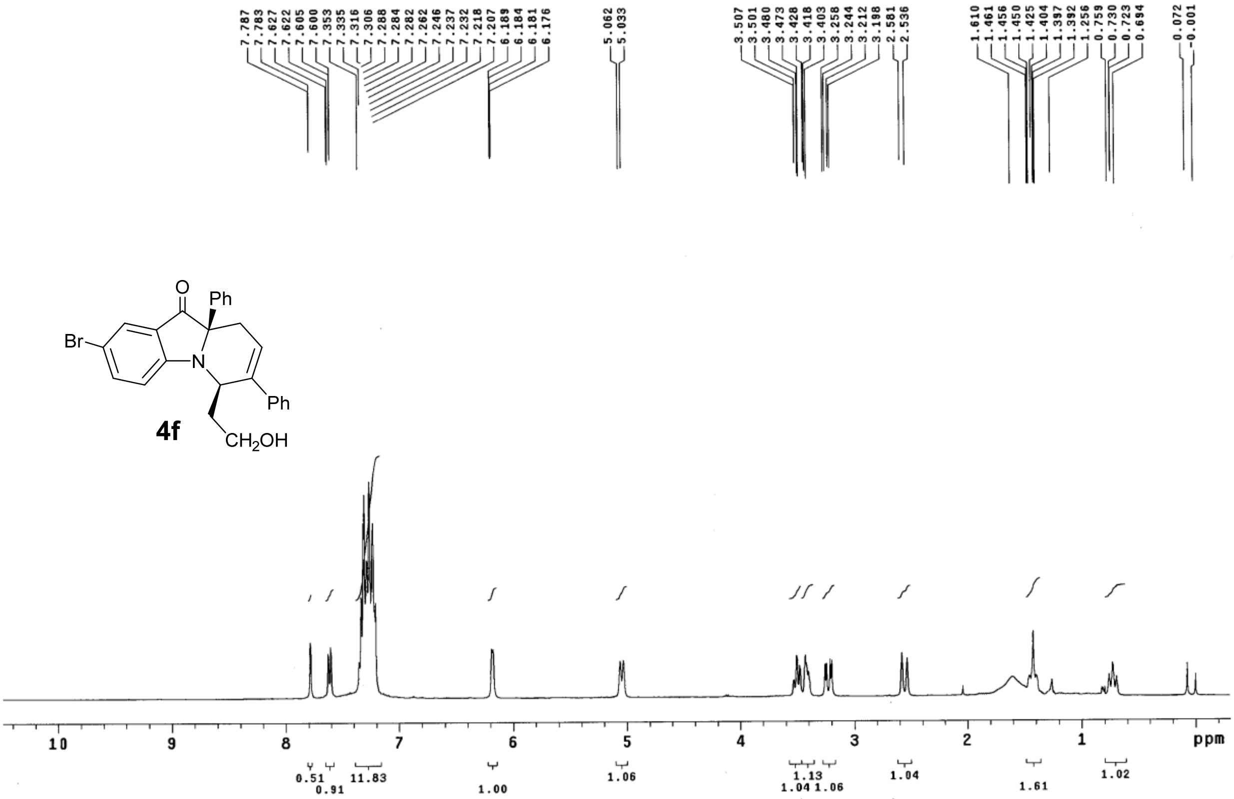




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.435	VV	0.2432	2.40536e4	1516.95422	50.0204
2	7.410	VV	0.3799	2.40340e4	978.01581	49.9796



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.436	MM	0.2585	1.89791e4	1223.78418	91.3145
2	7.430	MM	0.3871	1805.22900	77.72024	8.6855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7.282
7.262
7.246
7.237
7.232
7.218
7.207
6.189
6.184
6.181
6.176
5.062
5.033
3.507
3.501
3.480
3.473
3.428
3.418
3.403
3.258
3.244
3.212
3.198
2.581
2.536
1.610
1.461
1.456
1.450
1.425
1.404
1.397
1.392
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0.730
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0.072
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Ph
Br
N
Ph
4f
CH2OH
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9
8
7
6
5
4
3
2
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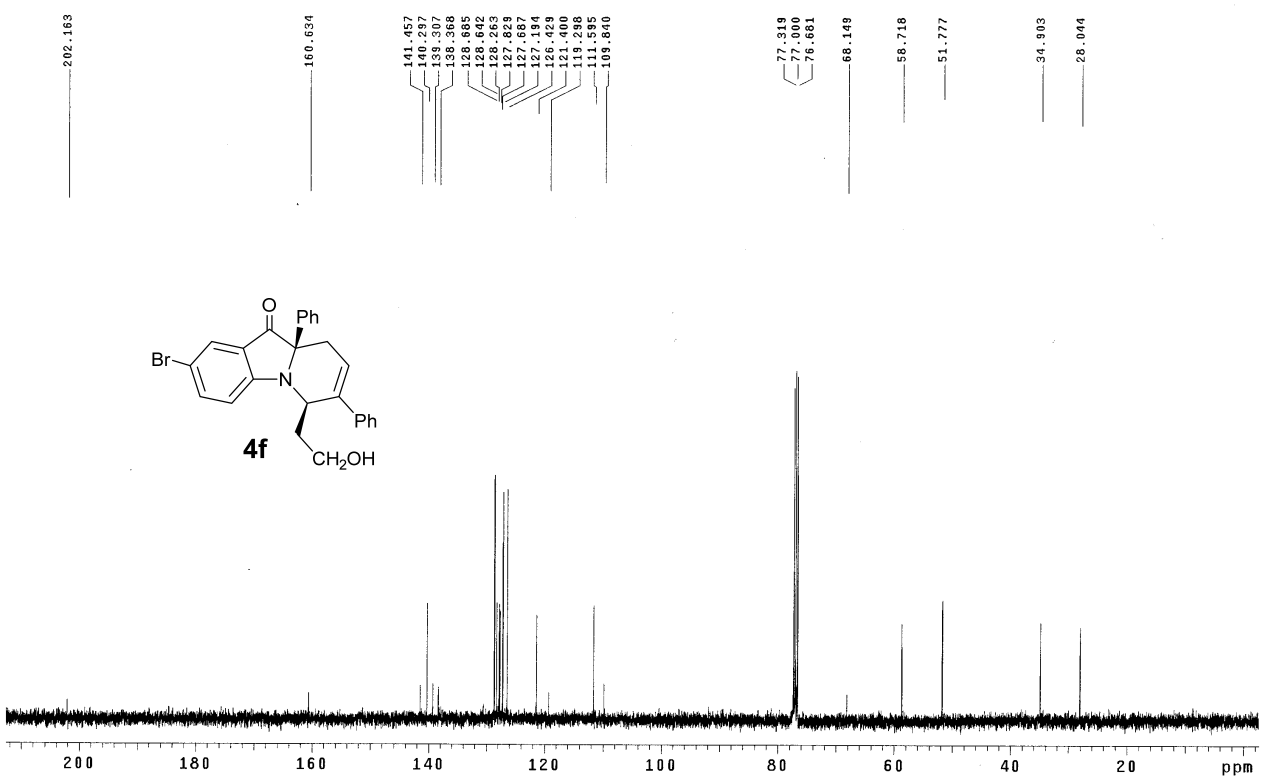
1.02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68.149
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51.777
34.903
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Ph
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140
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80
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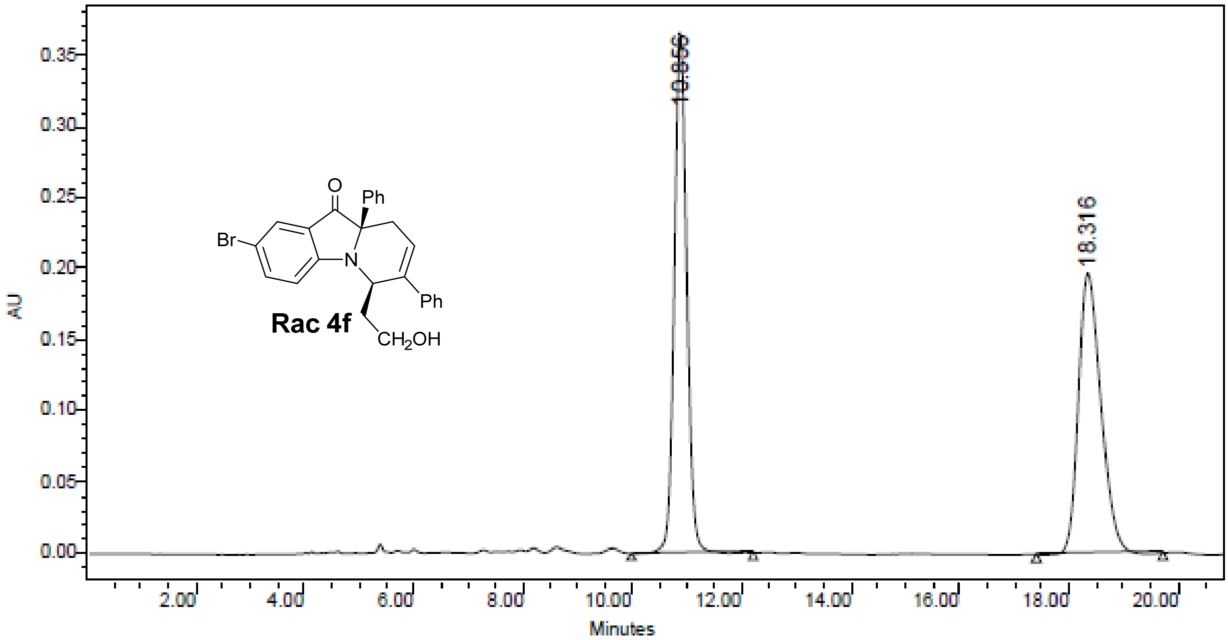
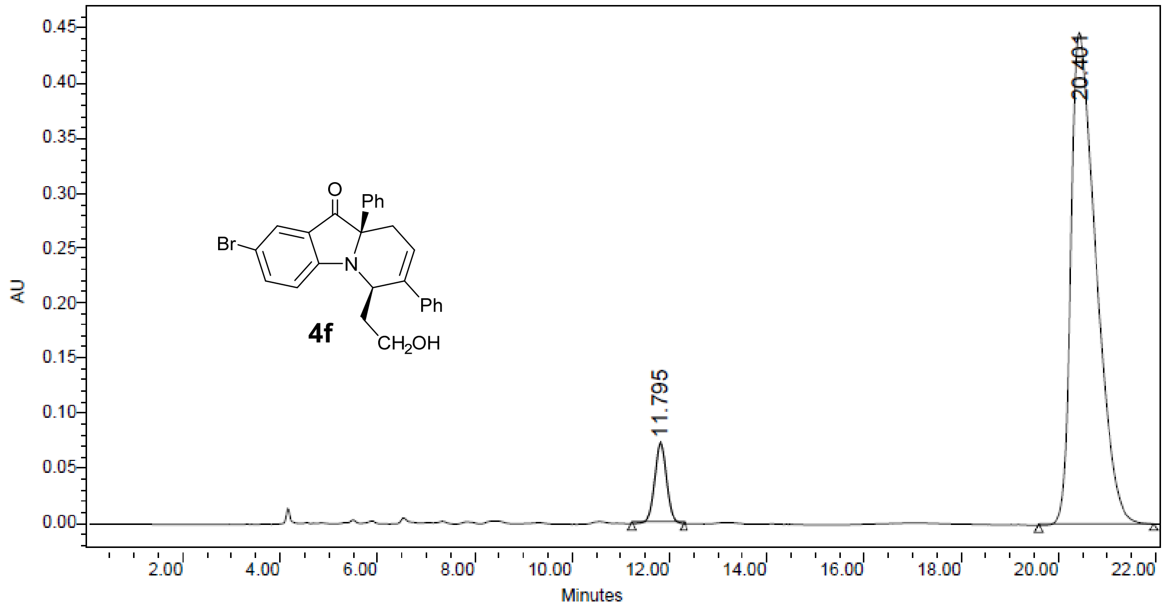
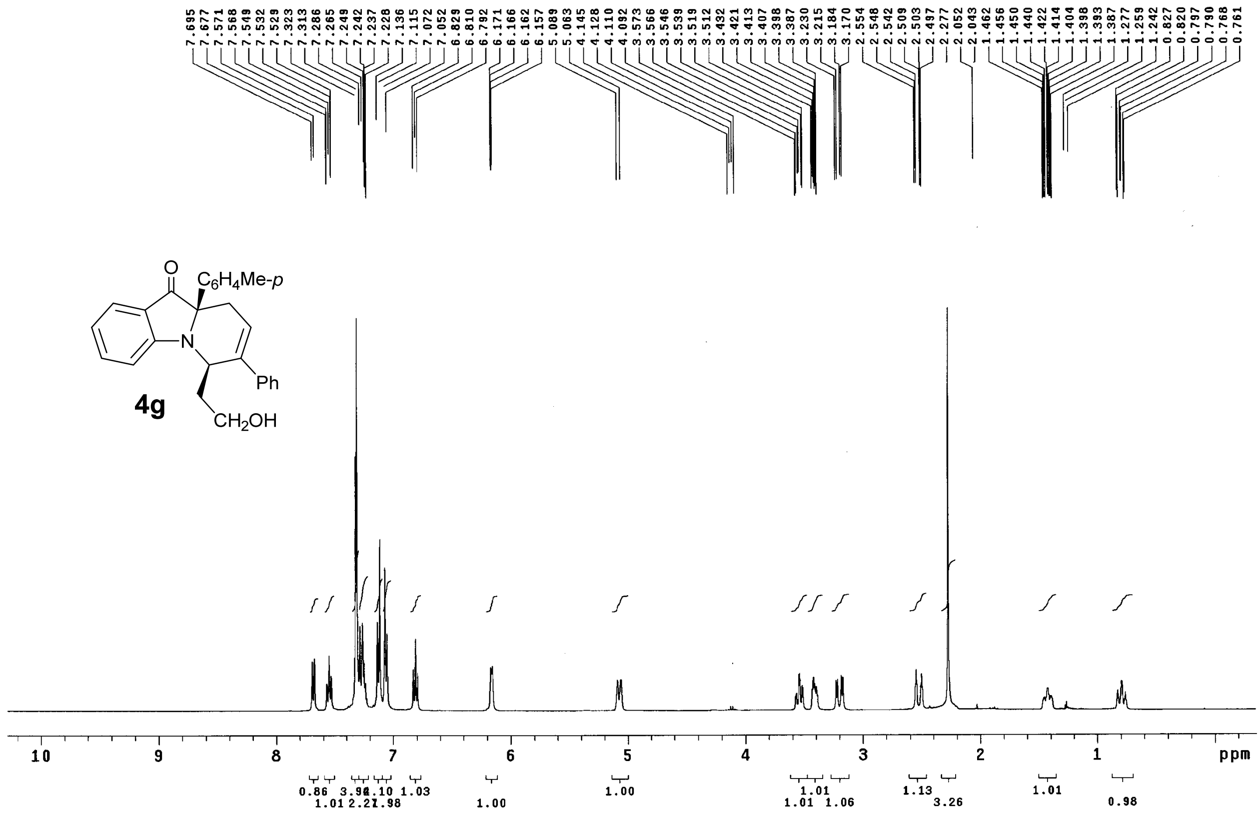
20
ppm



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.856	5825590	50.70	366221	64.96
2	18.316	5663931	49.30	197578	35.04



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	11.795	1266658	7.33	73556	14.10
2	20.401	16015380	92.67	448027	85.90


O
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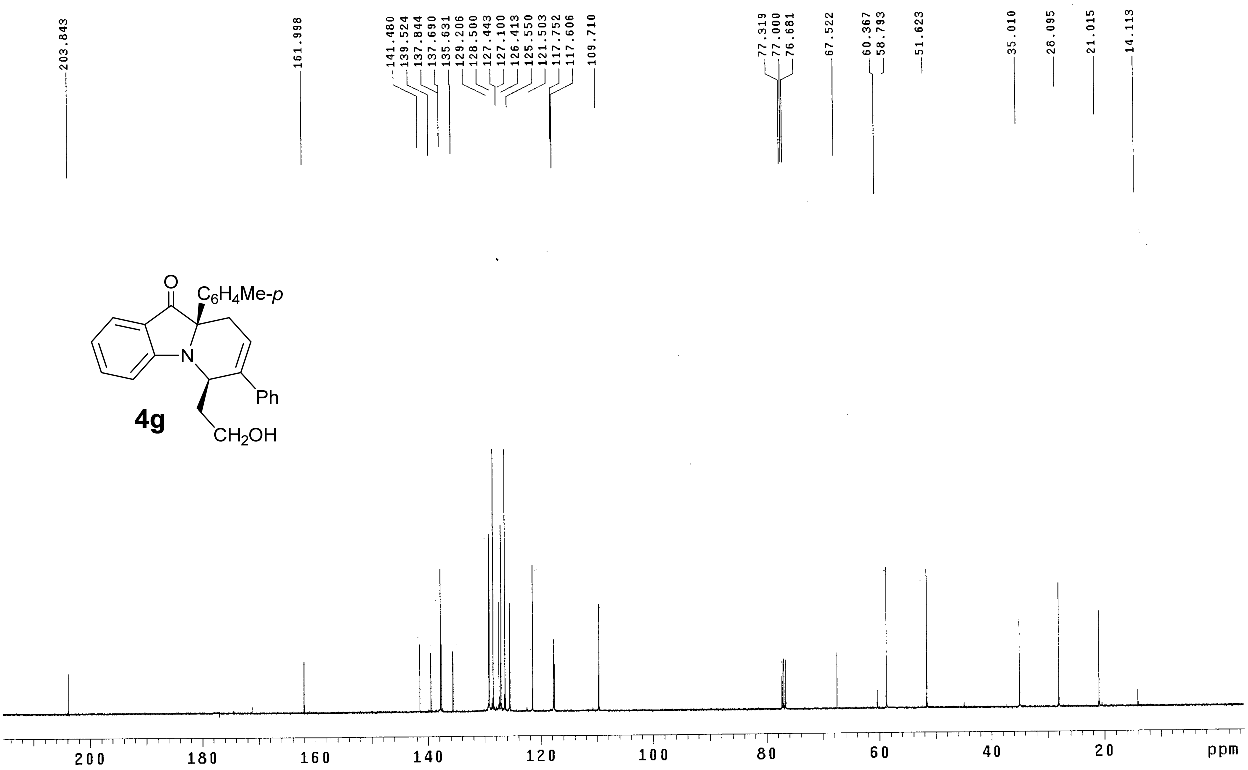
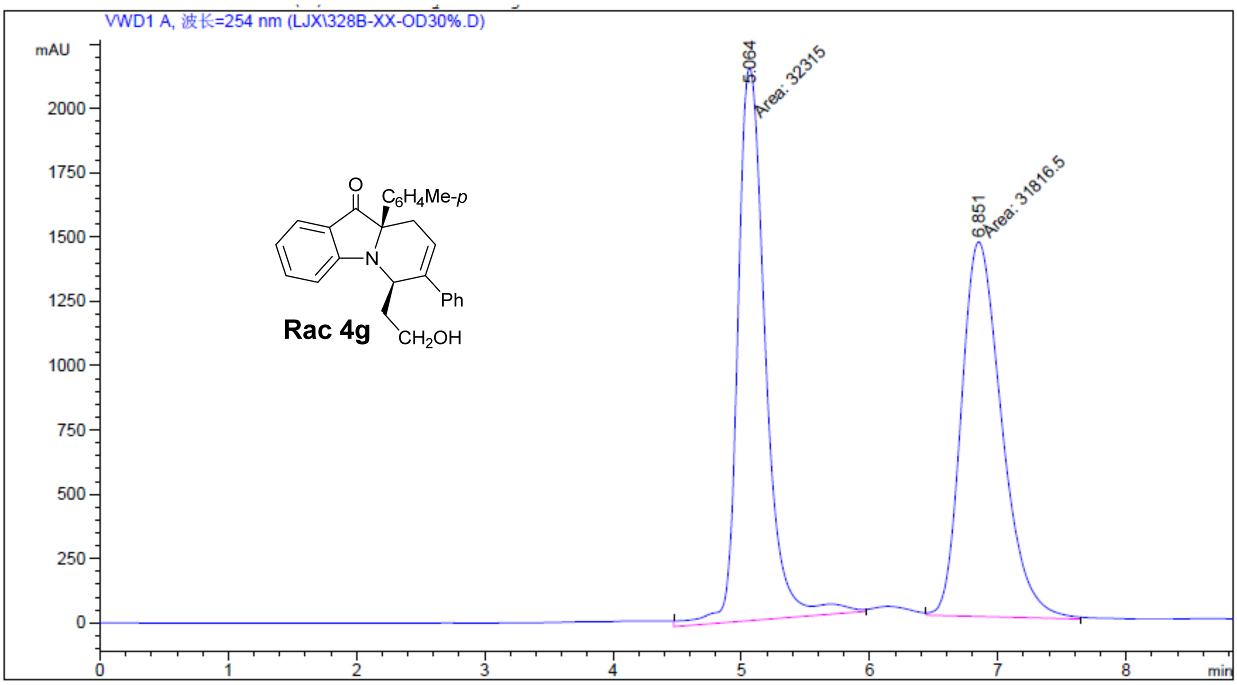
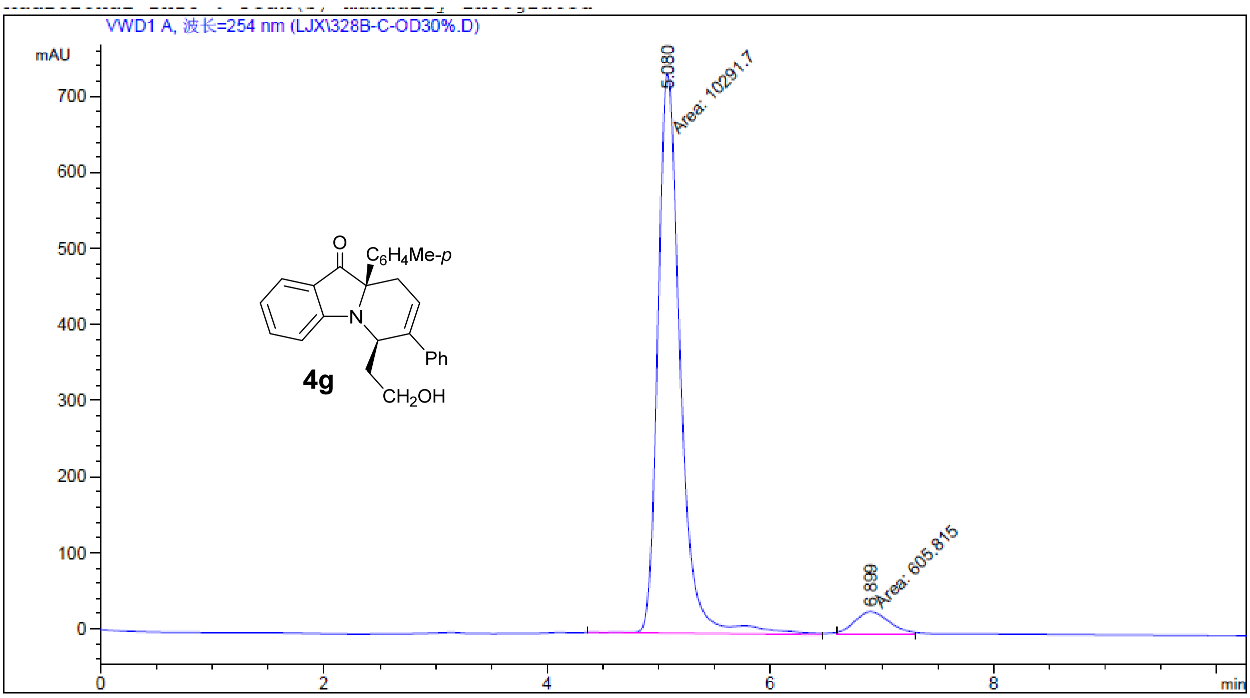
N
Ph
4g
CH2OH
ppm

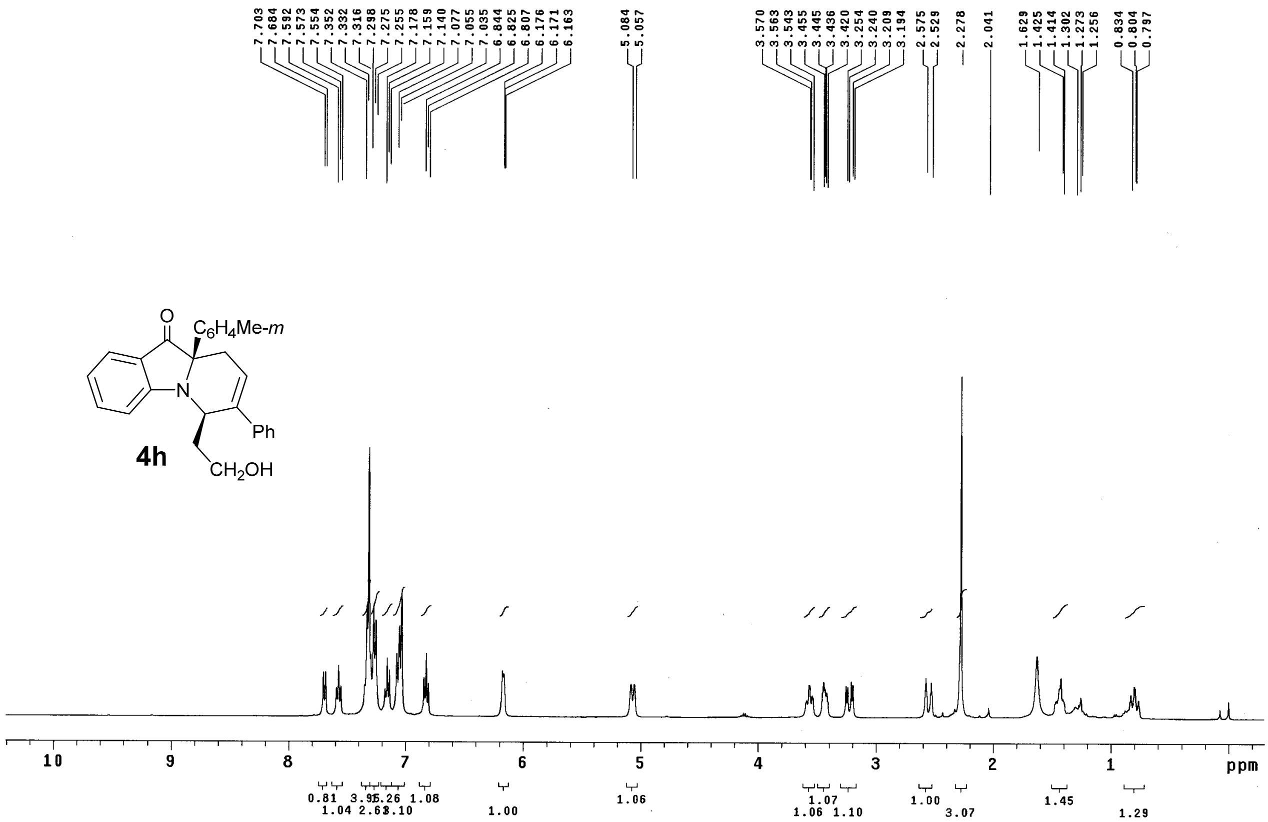

O
C6H4Me-p
N
Ph
4g
CH2OH
ppm



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.064	MM	0.2501	3.23150e4	2153.51611	50.3887
2	6.851	MM	0.3640	3.18165e4	1456.90430	49.6113



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.080	MM	0.2323	1.02917e4	738.35883	94.4408
2	6.899	MM	0.3528	605.81543	28.61869	5.5592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7.275
7.255
7.178
7.159
7.140
7.077
7.055
7.035
6.844
6.825
6.807
6.176
6.171
6.163
5.084
5.057
3.570
3.563
3.543
3.455
3.445
3.436
3.420
3.254
3.240
3.224
3.209
3.194
2.575
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1.629
1.425
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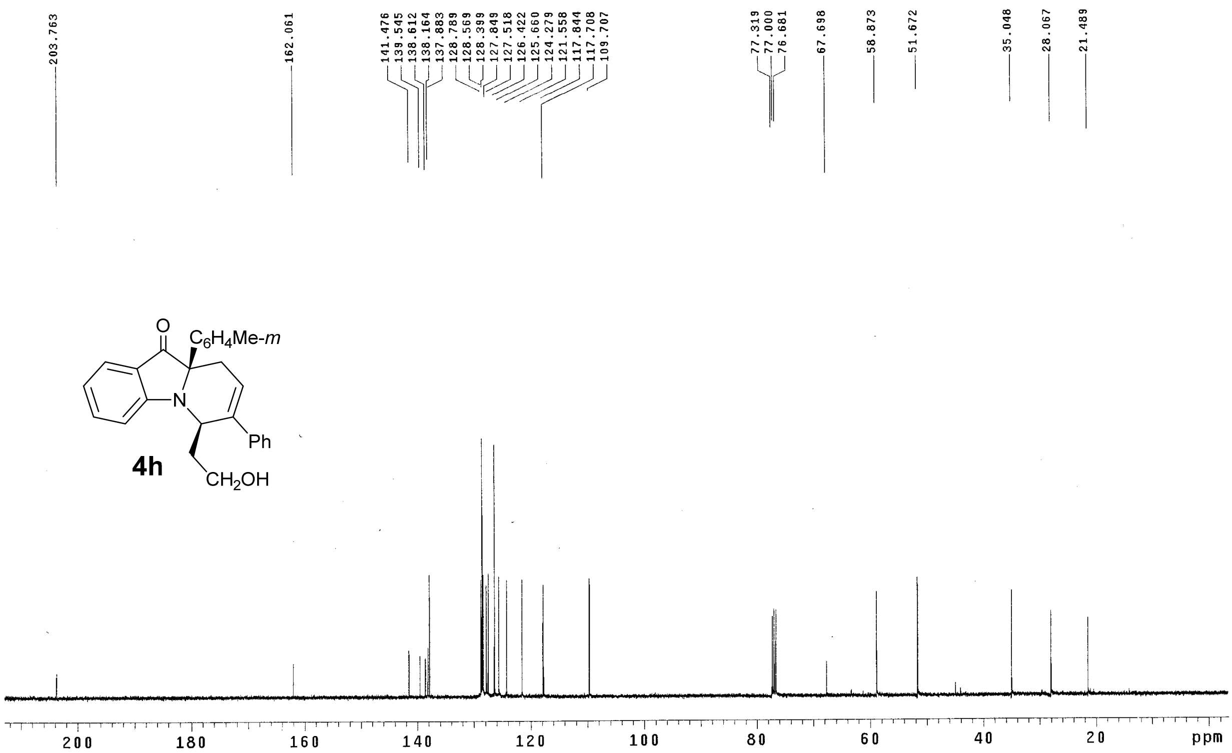
C6H4Me-m
Ph
4h
CH2OH
ppm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117.708
109.707
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77.000
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51.672
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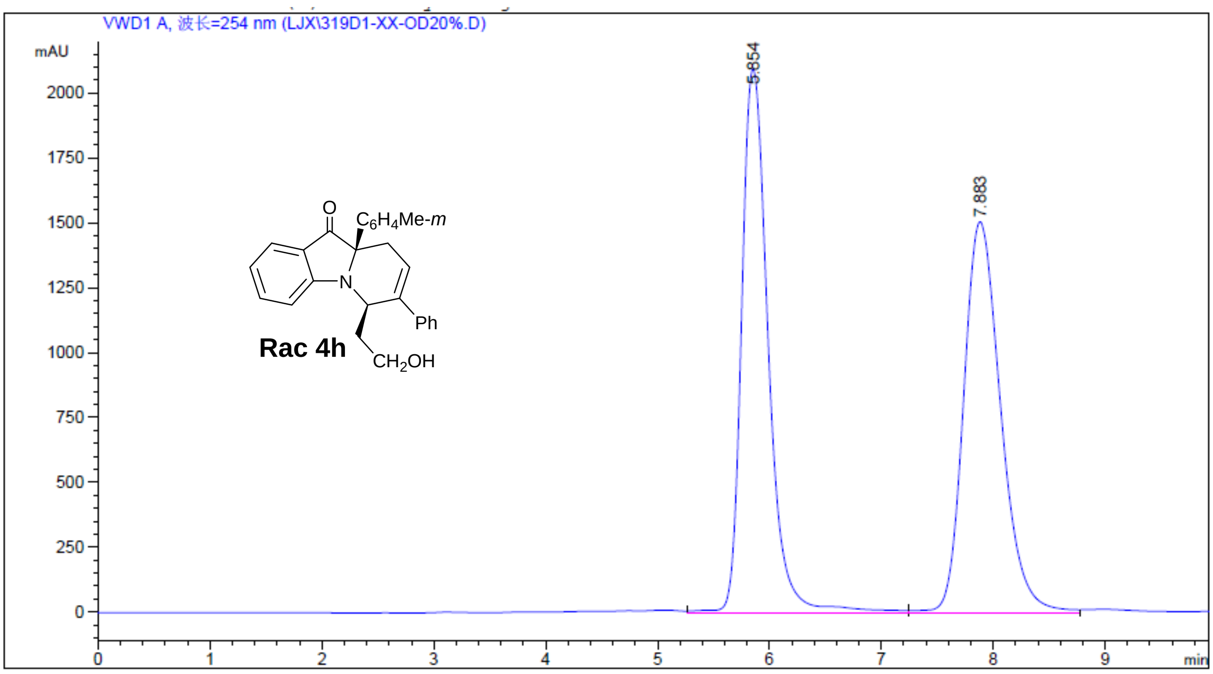
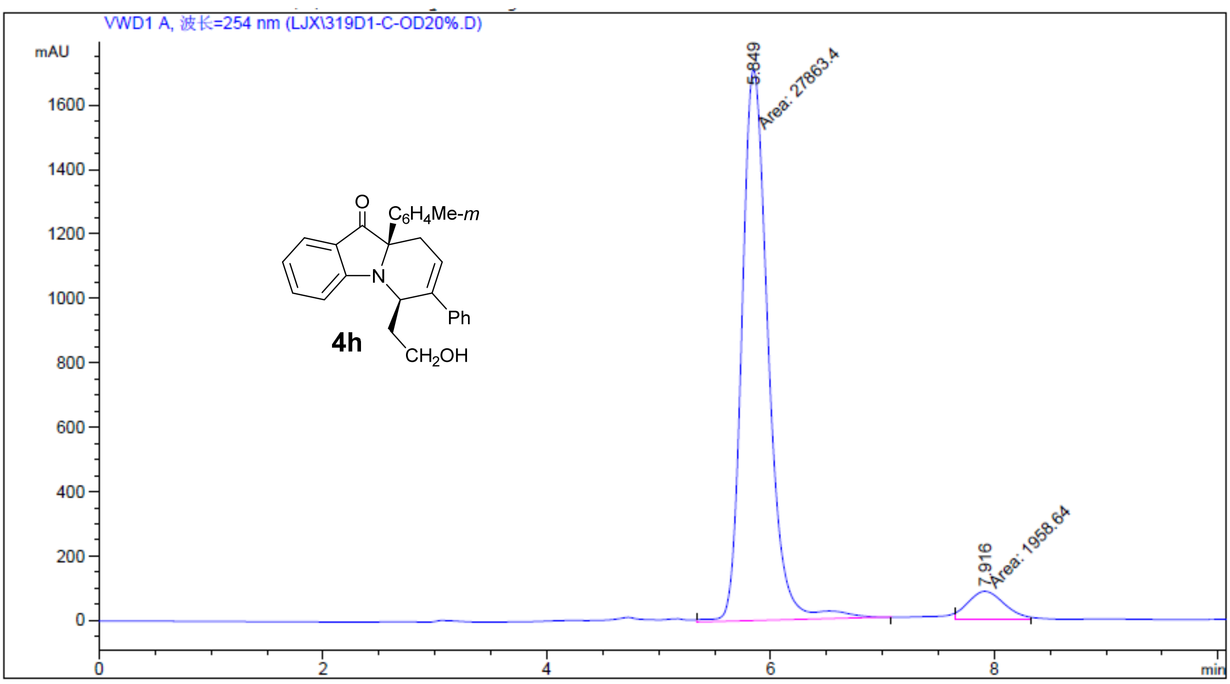
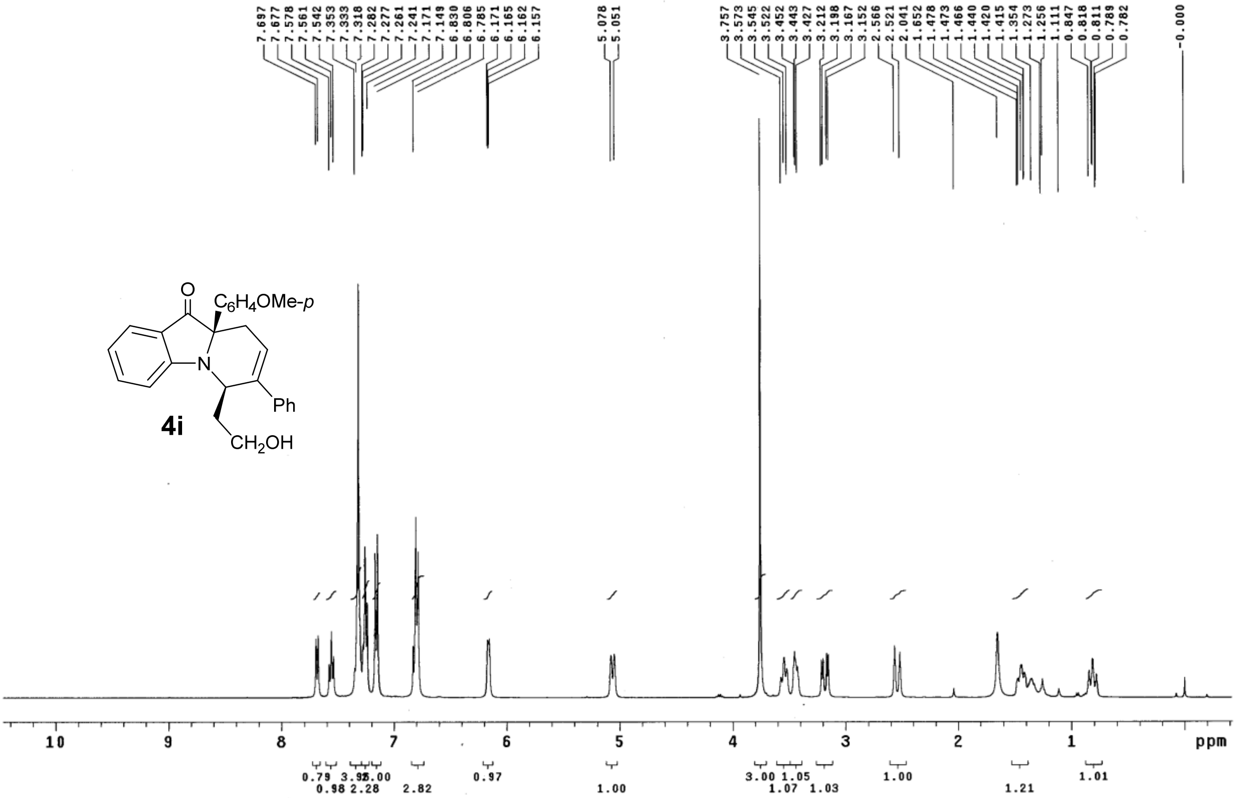
21.489
C6H4Me-m
Ph
4h
CH2OH
ppm



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.854	VV	0.2581	3.48319e4	2094.17139	50.0799
2	7.883	VV	0.3563	3.47207e4	1505.95435	49.9201



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.849	MM	0.2712	2.78634e4	1712.60889	93.4322
2	7.916	MM	0.3767	1958.63770	86.64683	6.5678


O
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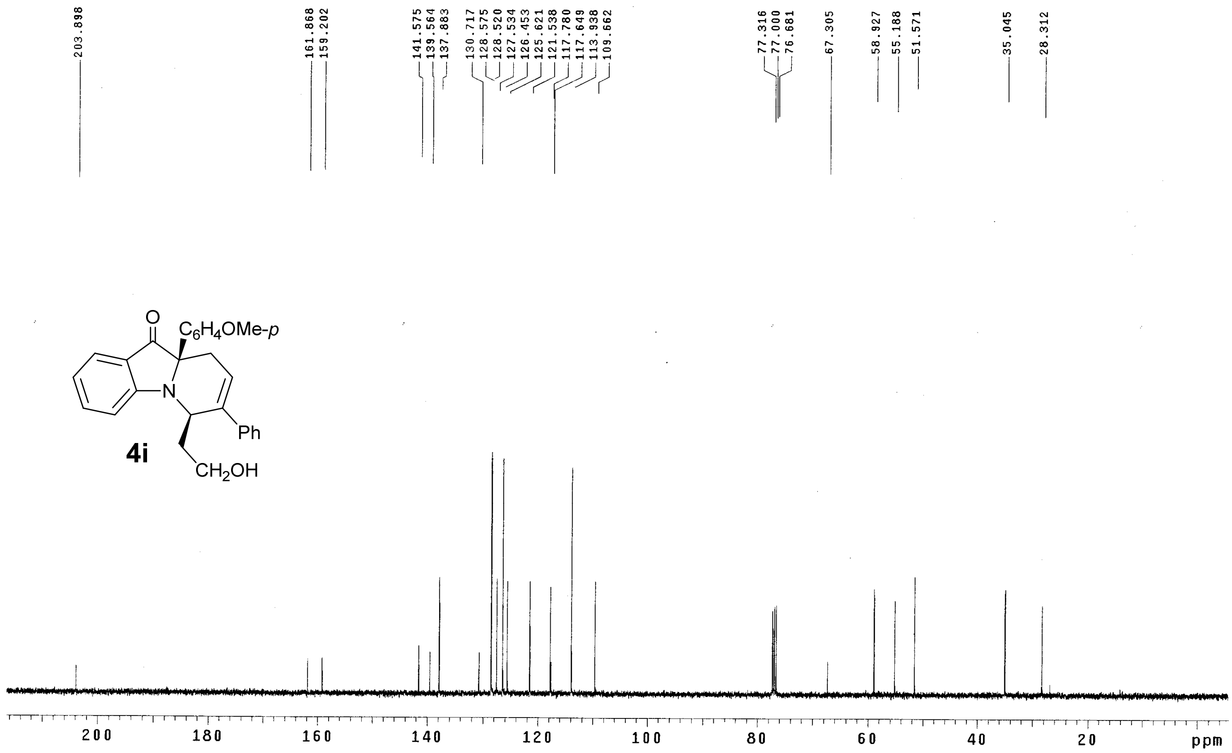
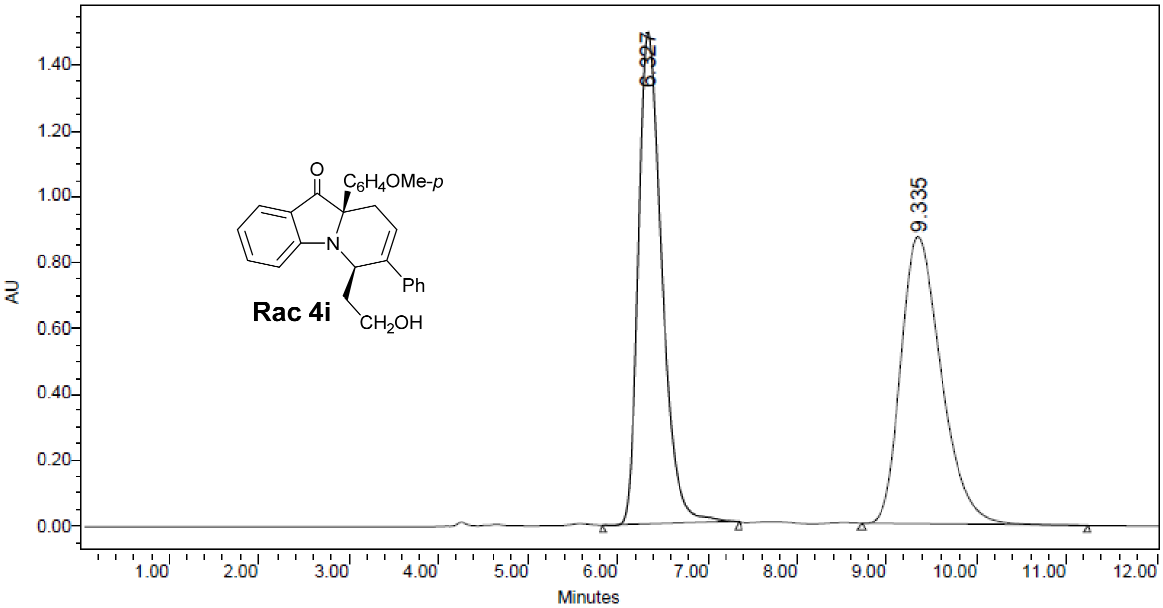
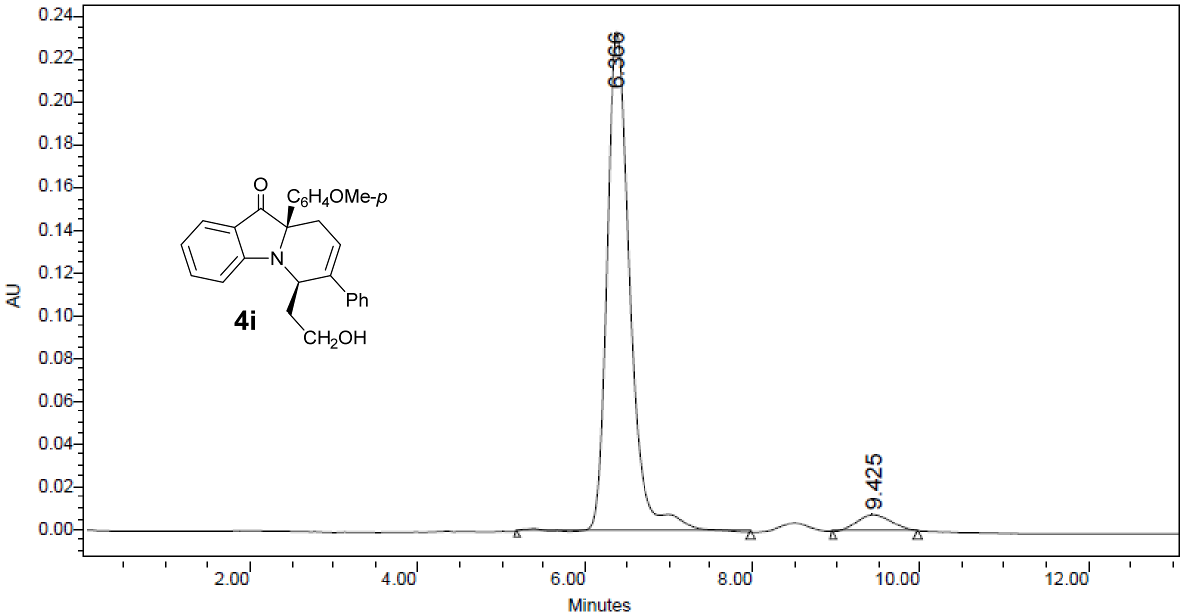
N
Ph
4i
CH_2OH
ppm

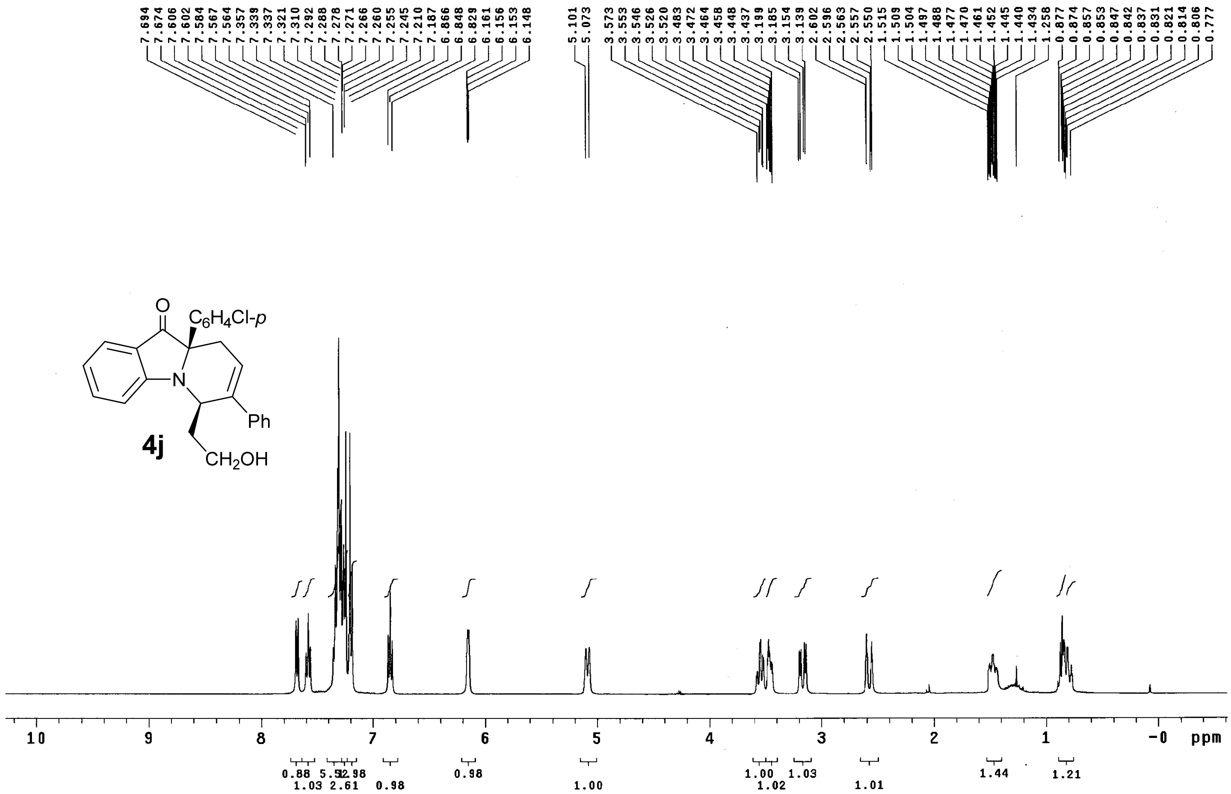

O
C_6H_4OMe-*p*
N
Ph
4i
CH_2OH
ppm

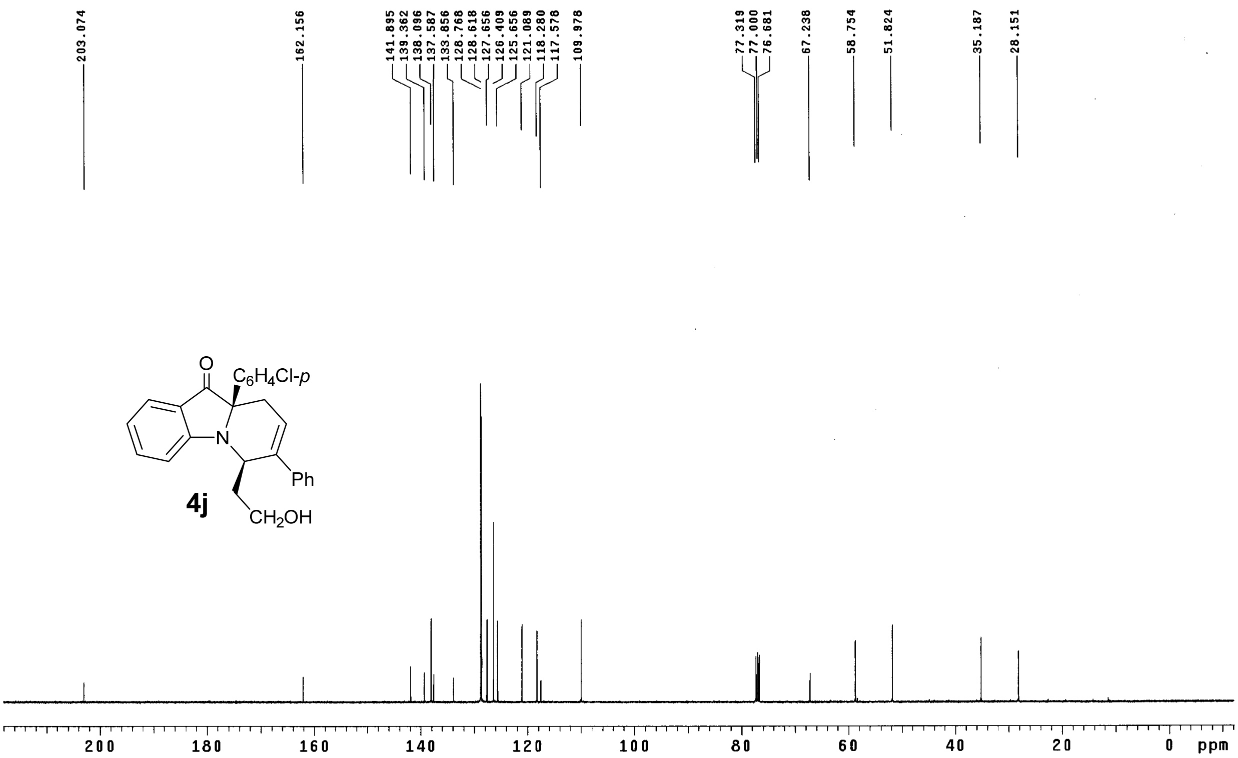


	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.327	27347437	49.96	1498022	63.17
2	9.335	27395366	50.04	873386	36.83



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.366	4483729	95.25	233415	96.80
2	9.425	223645	4.75	7722	3.20


7.694 7.674 7.606 7.602 7.584 7.567 7.564 7.357 7.339 7.337 7.321 7.310 7.292 7.288 7.278 7.271 7.266 7.260 7.255 7.245 7.210 7.187 6.866 6.848 6.829 6.161 6.156 6.153 6.148
5.101 5.073 3.573 3.553 3.546 3.526 3.520 3.483 3.472 3.464 3.458 3.448 3.437 3.199 3.185 3.154 3.139 2.602 2.596 2.563 2.557 2.550 1.515 1.509 1.504 1.497 1.488 1.477 1.470 1.461 1.452 1.445 1.440 1.434 1.258 0.877 0.874 0.857 0.853 0.847 0.842 0.837 0.831 0.821 0.814 0.806 0.777
O
C6H4Cl-p
N
Ph
4j
CH2OH
10 9 8 7 6 5 4 3 2 1 -0 ppm
0.88 1.03 5.52 2.61 2.98 0.98 0.98 1.00 1.00 1.02 1.03 1.01 1.44 1.21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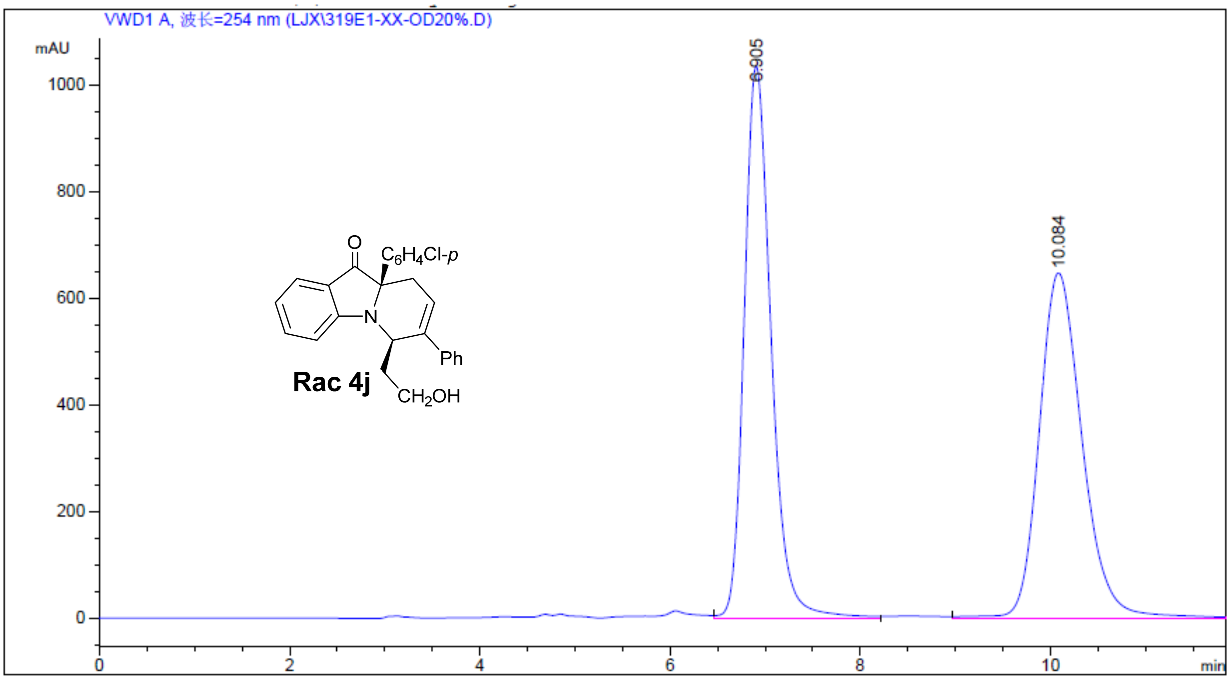
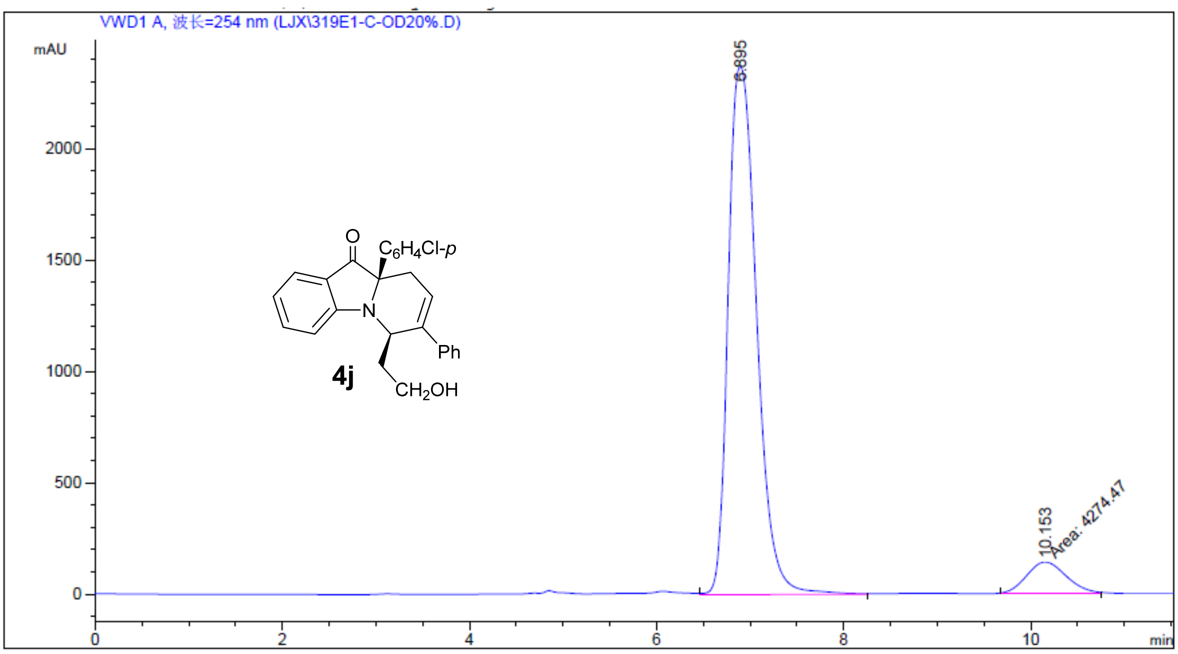
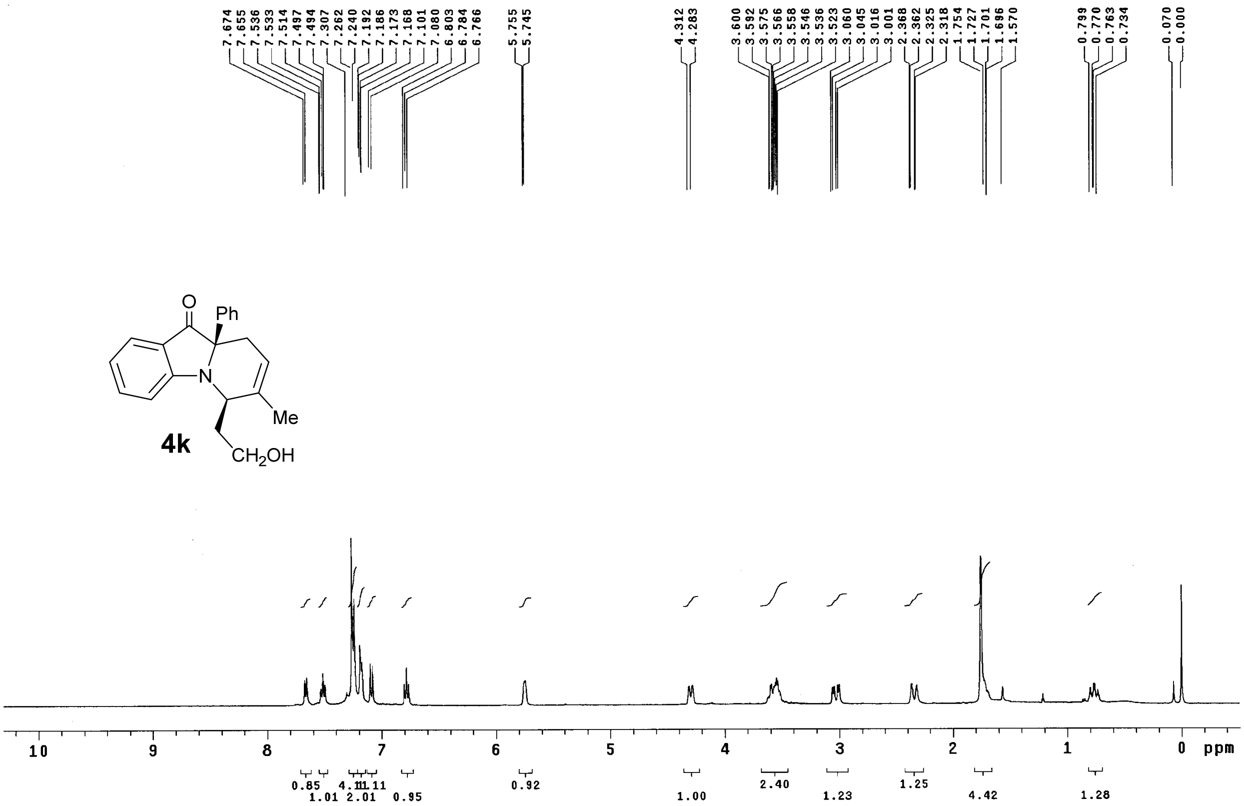
77.319 77.000 76.681 67.238 58.754 51.824 35.187 28.151
O
C6H4Cl-p
N
Ph
4j
CH2OH
200 180 160 140 120 100 80 60 40 20 0 ppm



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.905	VV	0.2997	2.03781e4	1034.72144	50.0381
2	10.084	VBA	0.4832	2.03470e4	647.36127	49.9619



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.895	VV	0.3337	5.00457e4	2369.77637	92.1310
2	10.153	MM	0.4991	4274.47412	142.74429	7.8690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O
Ph
N
Me
4k
CH2OH
10
9
8
7
6
5
4
3
2
1
0
ppm
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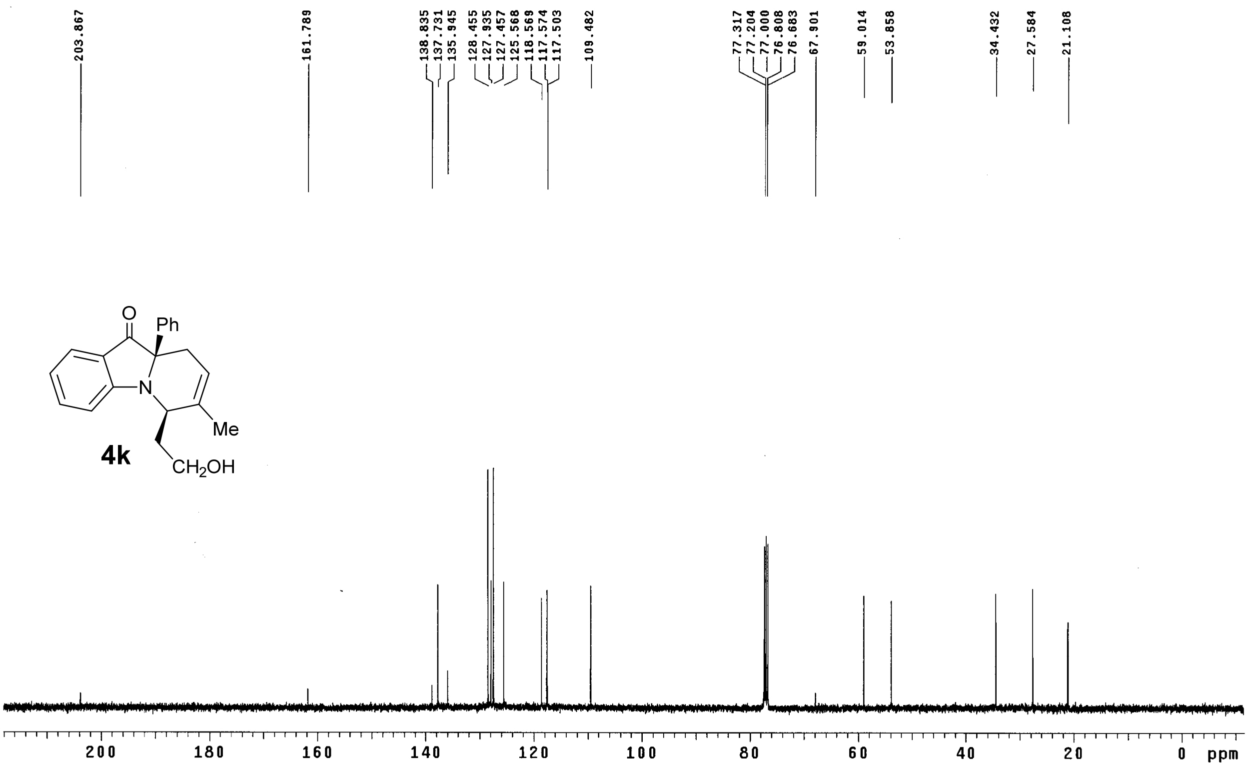
1.28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76.683
67.901
59.014
53.858
34.432
27.584
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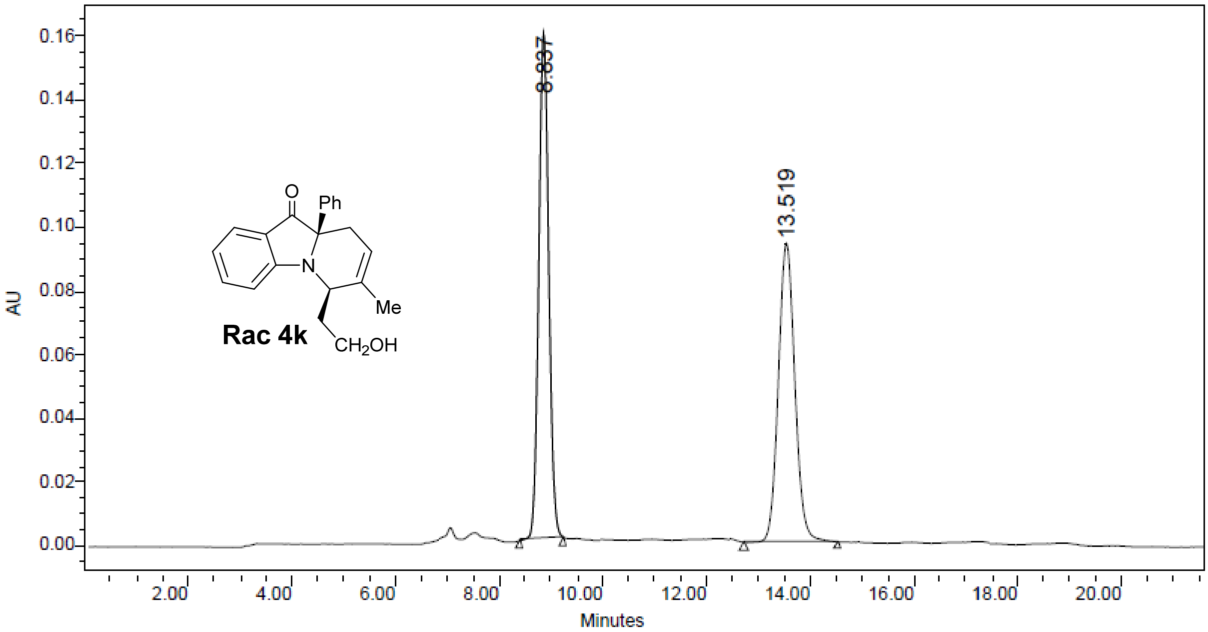
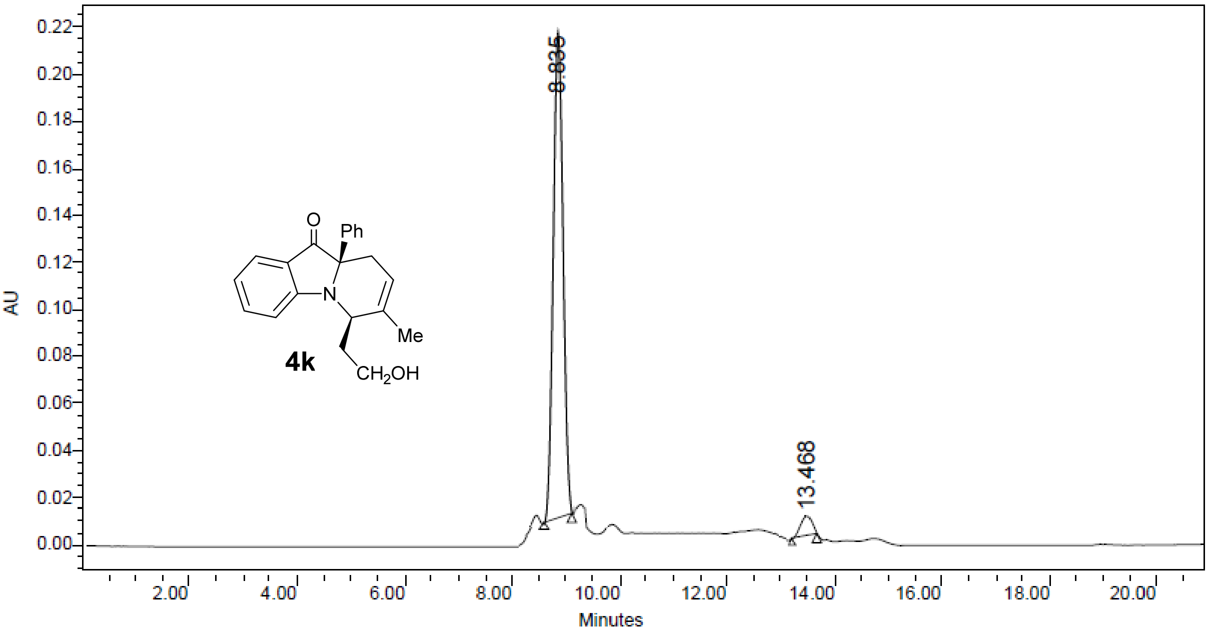
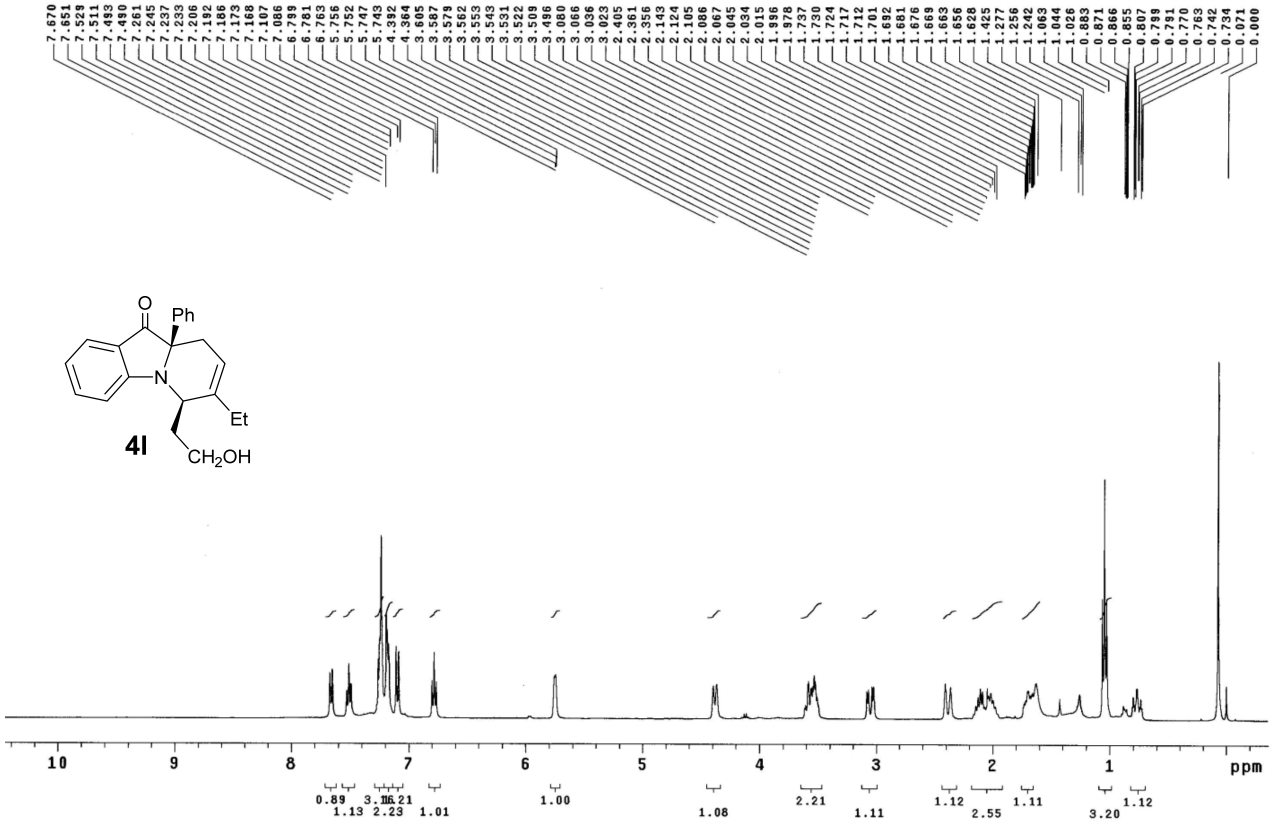
ppm

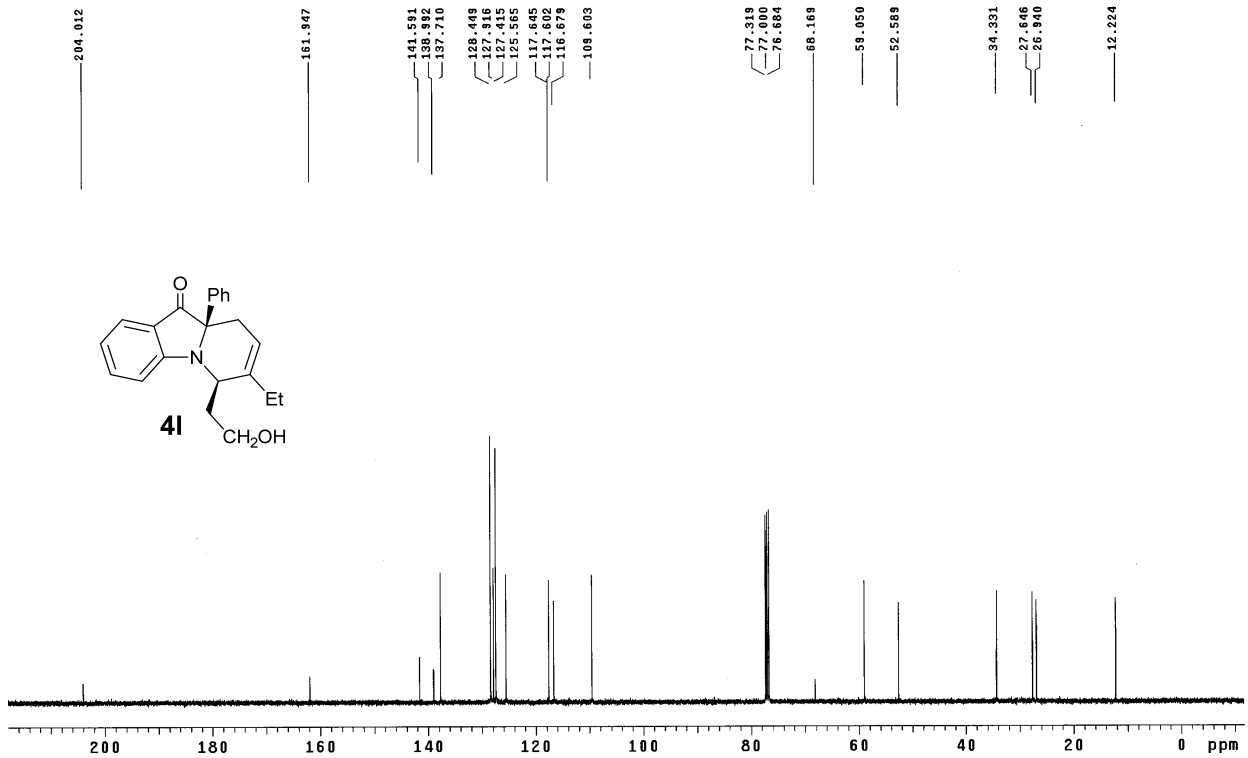


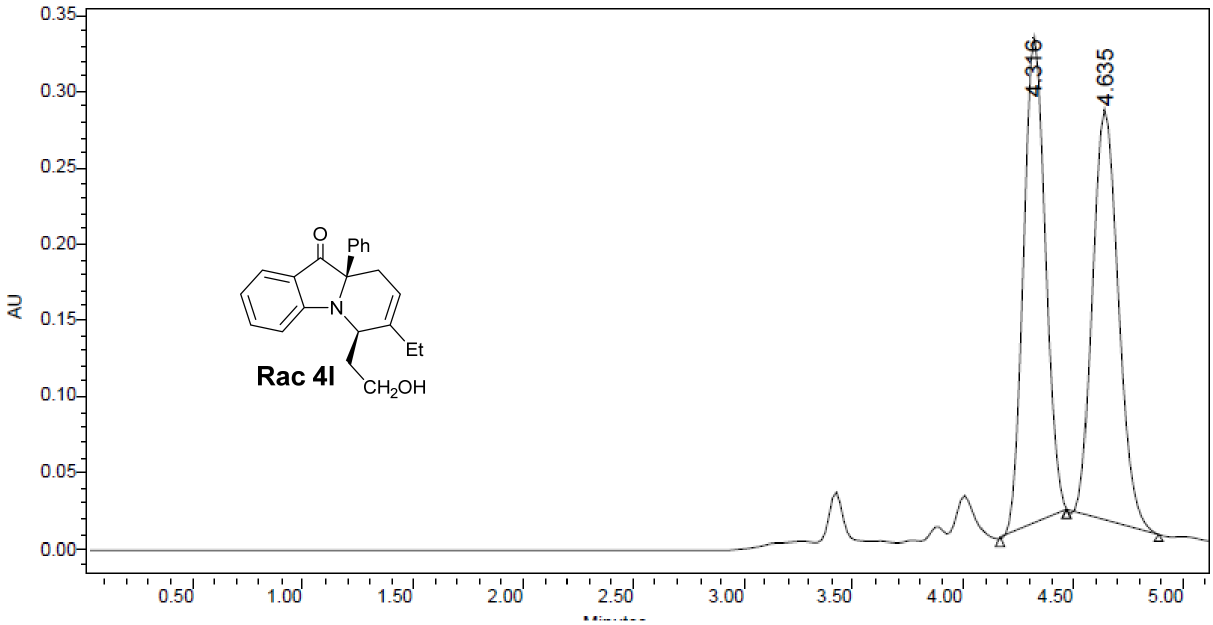
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	8.837	2145527	50.64	158793	62.88
2	13.519	2091497	49.36	93746	37.12



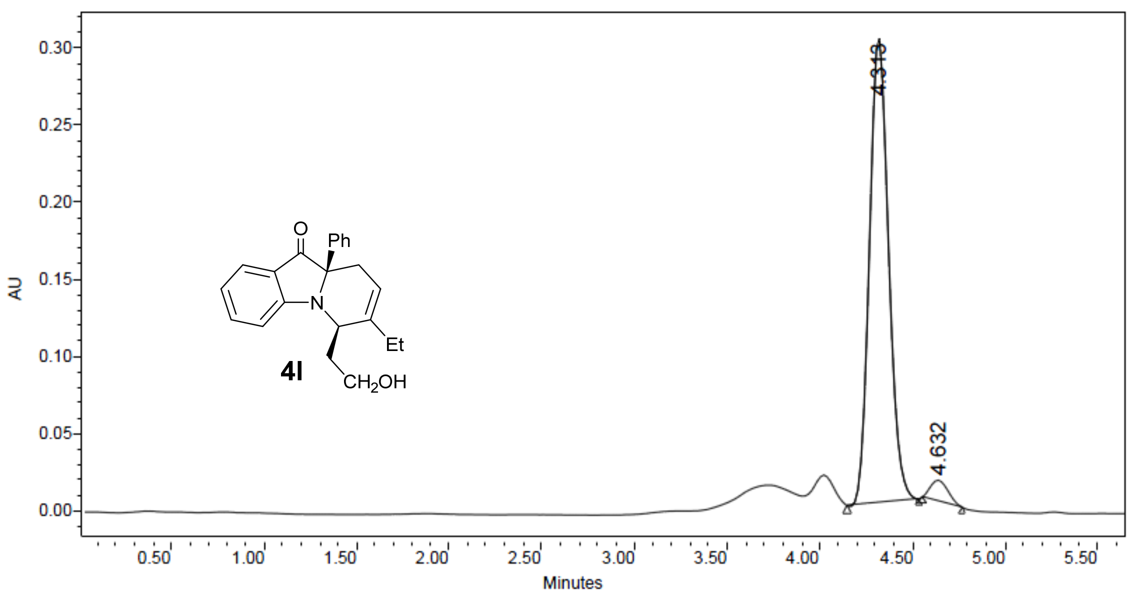
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	8.835	2635873	95.27	206306	95.97
2	13.468	130766	4.73	8654	4.03


O
Ph
N
Et
4l
CH2OH
ppm

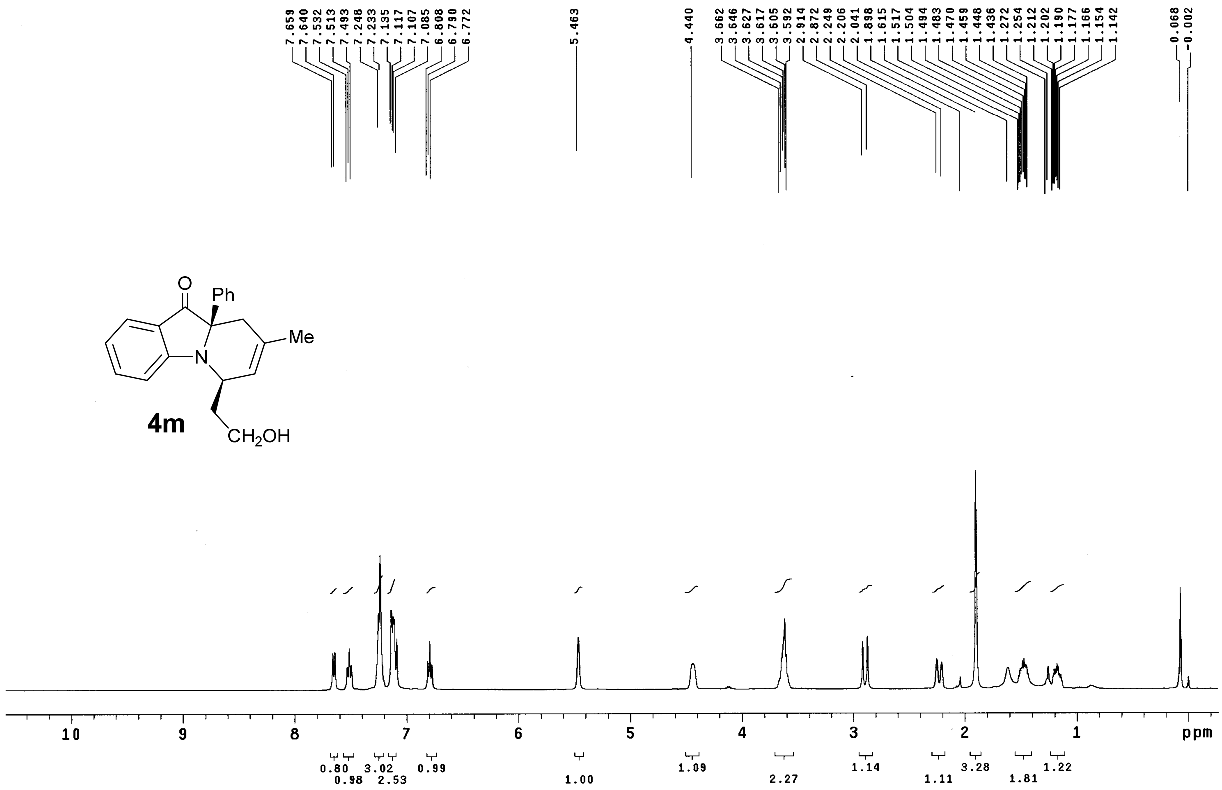

204.012
161.947
141.591
138.992
137.710
128.449
127.916
127.415
125.565
117.645
117.602
116.679
109.603
77.319
77.000
76.684
68.169
59.050
52.589
34.331
27.646
26.940
12.224
O
Ph
N
Et
4l
CH2OH
ppm

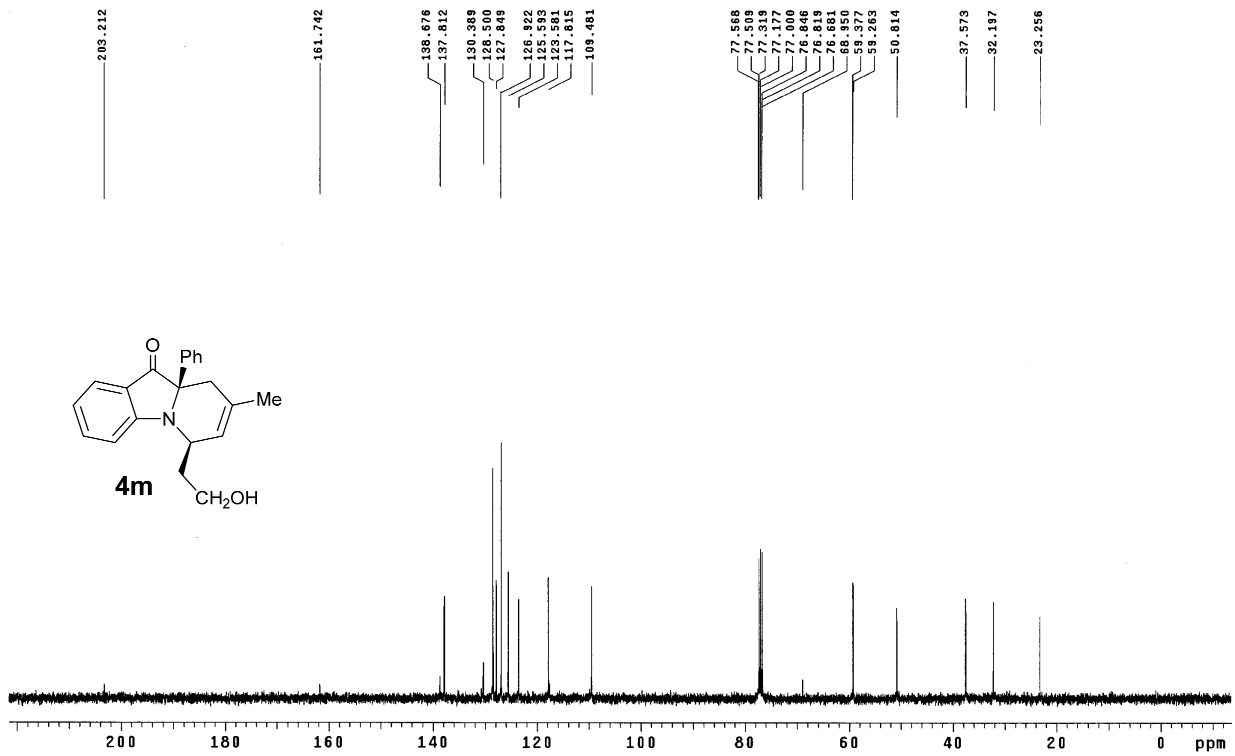


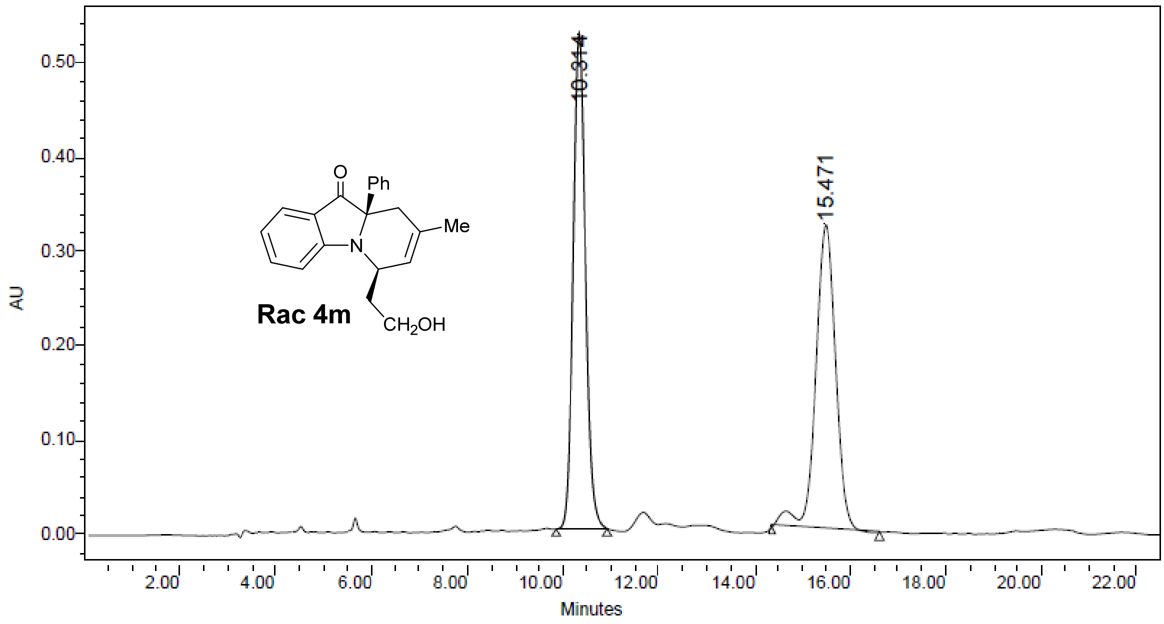
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	4.316	2239871	50.32	319116	54.21
2	4.635	2211620	49.68	269556	45.79



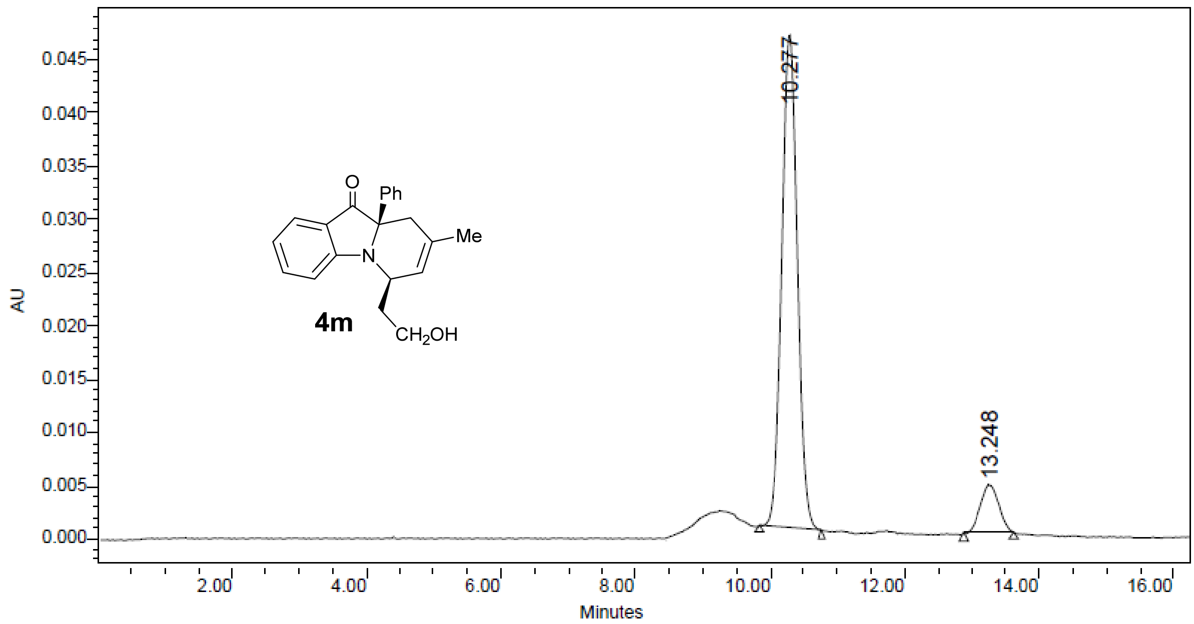
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	4.313	2163495	95.99	300624	95.71
2	4.632	90312	4.01	13467	4.29


7.659
7.640
7.532
7.513
7.493
7.248
7.233
7.135
7.117
7.107
7.085
6.808
6.790
6.772
5.463
4.440
3.662
3.646
3.627
3.617
3.605
3.592
2.914
2.872
2.249
2.206
2.041
1.898
1.615
1.517
1.504
1.494
1.483
1.470
1.459
1.448
1.436
1.272
1.254
1.212
1.202
1.190
1.177
1.166
1.154
1.142
0.068
-0.002
O
Ph
Me
N
4m
CH2OH
10 9 8 7 6 5 4 3 2 1 ppm
0.80 0.98 3.02 2.53 0.99
1.00
1.09
2.27
1.14
1.11 3.28
1.81 1.22

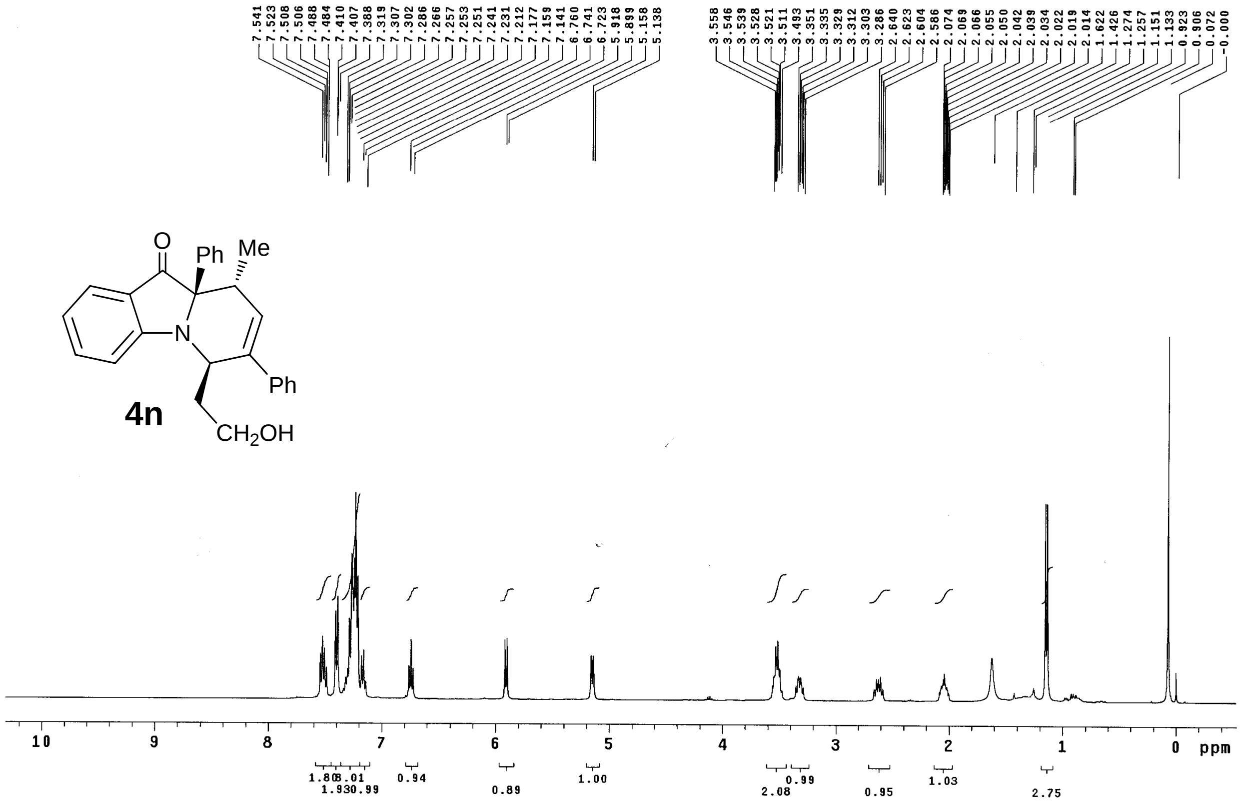

203.212
161.742
138.676
137.812
130.389
128.500
127.849
126.922
125.593
123.581
117.815
109.481
77.568
77.509
77.319
77.177
77.000
76.846
76.819
76.681
68.950
59.377
59.263
50.814
37.573
32.197
23.256
O
Ph
Me
N
4m
CH2OH
200 180 160 140 120 100 80 60 40 20 0 ppm

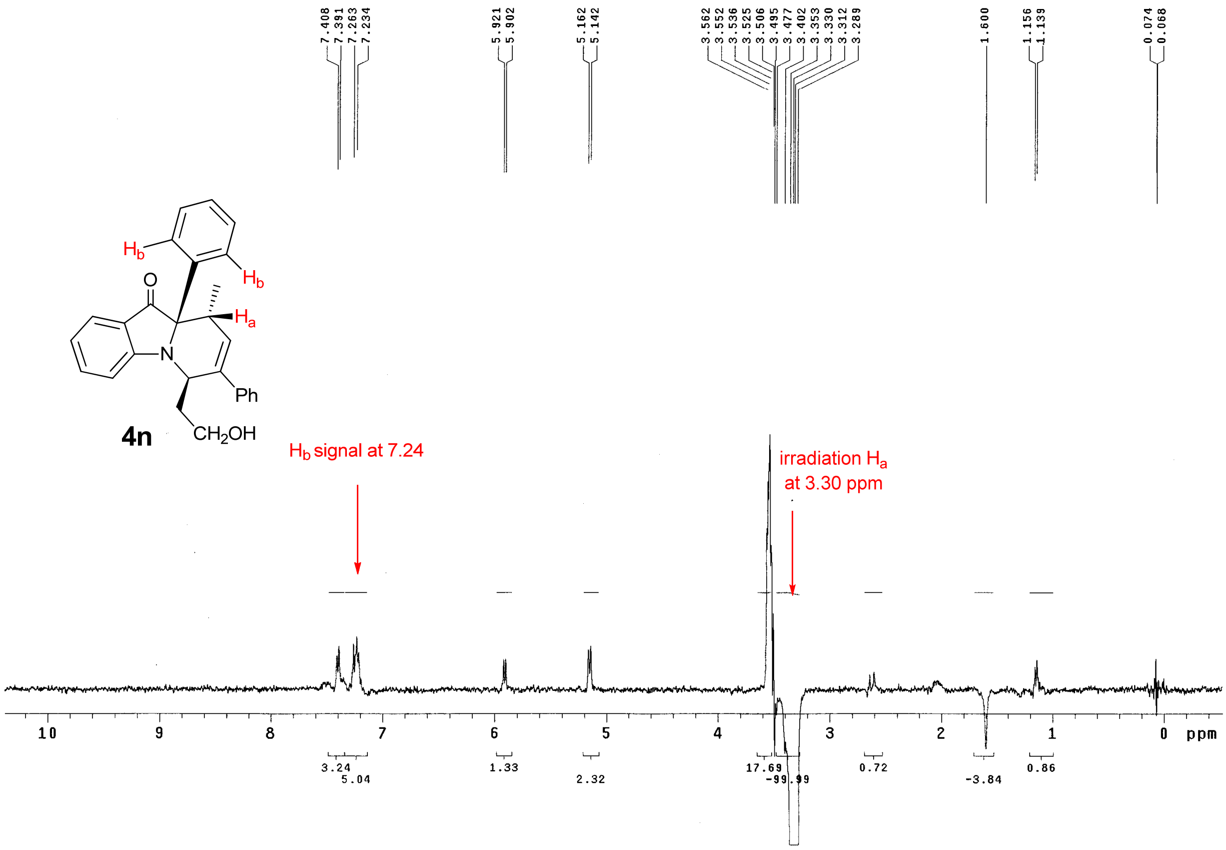


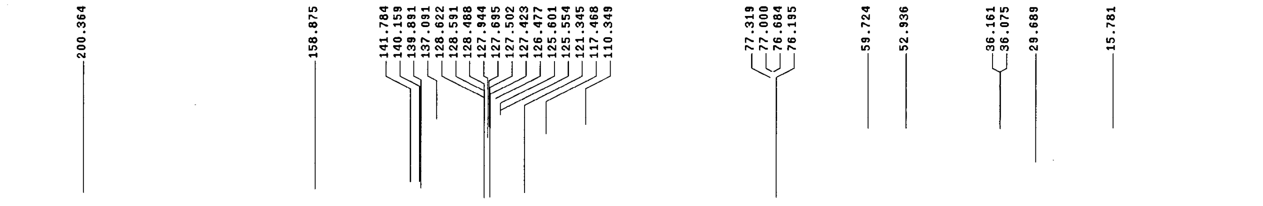
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.314	9338787	49.84	525338	61.97
2	15.471	9396908	50.16	322382	38.03

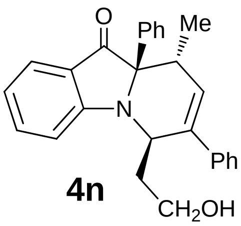


	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.277	744804	89.40	46391	91.09
2	13.248	88344	10.60	4540	8.91

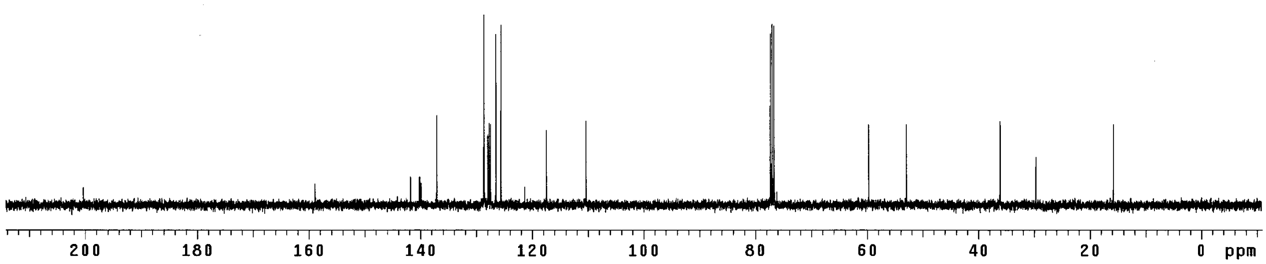

4n
Ph
Me
Ph
CH2OH
ppm

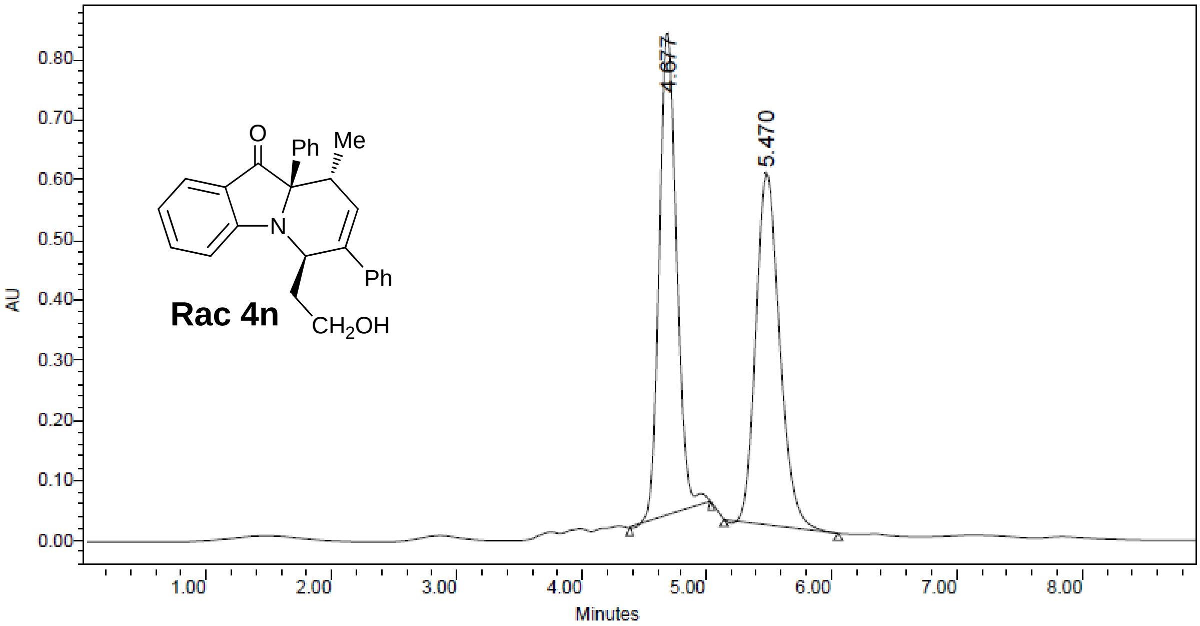

4n
Hb
Ha
Ph
CH2OH
Hb signal at 7.24
irradiation Ha at 3.30 ppm
ppm



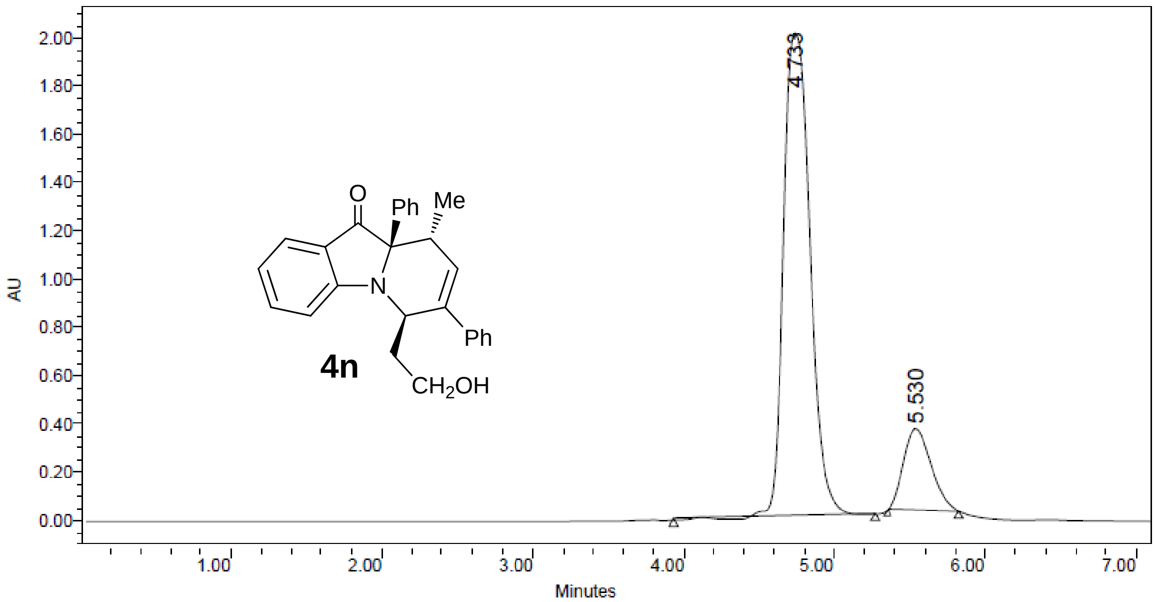


4n

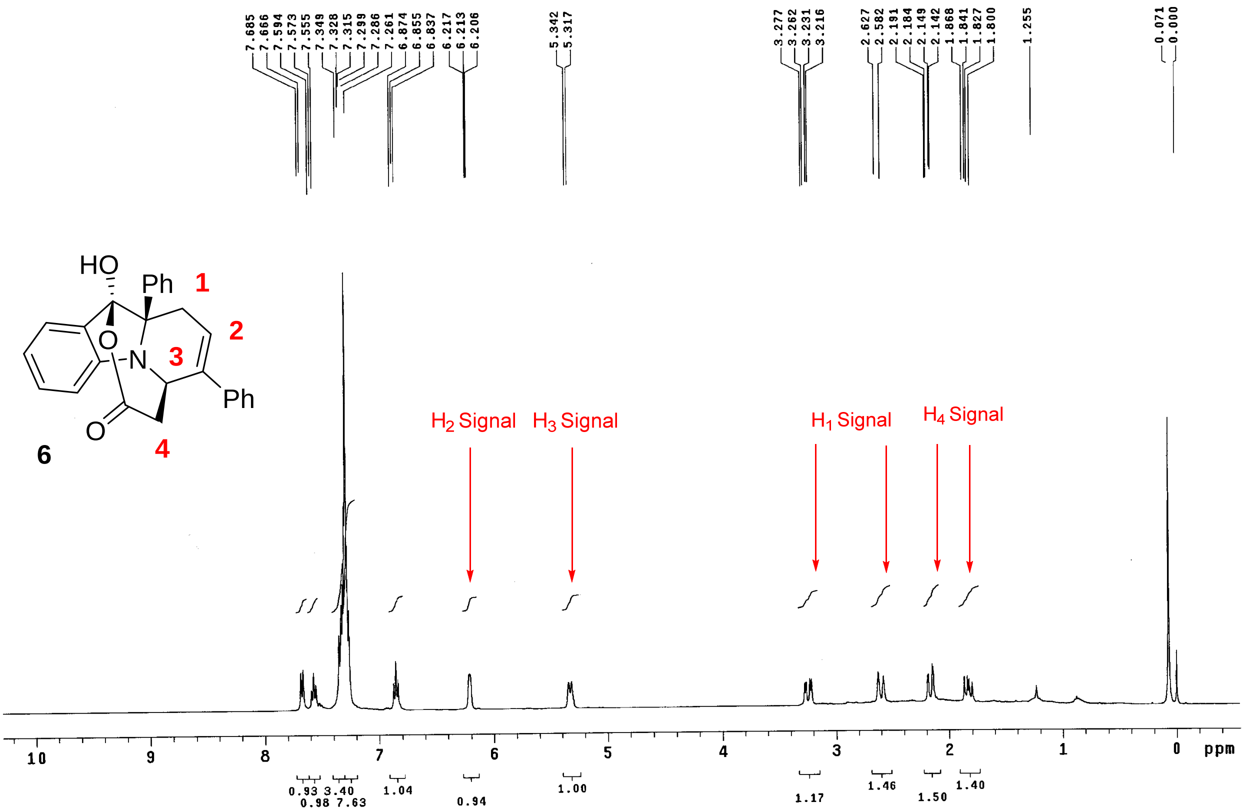


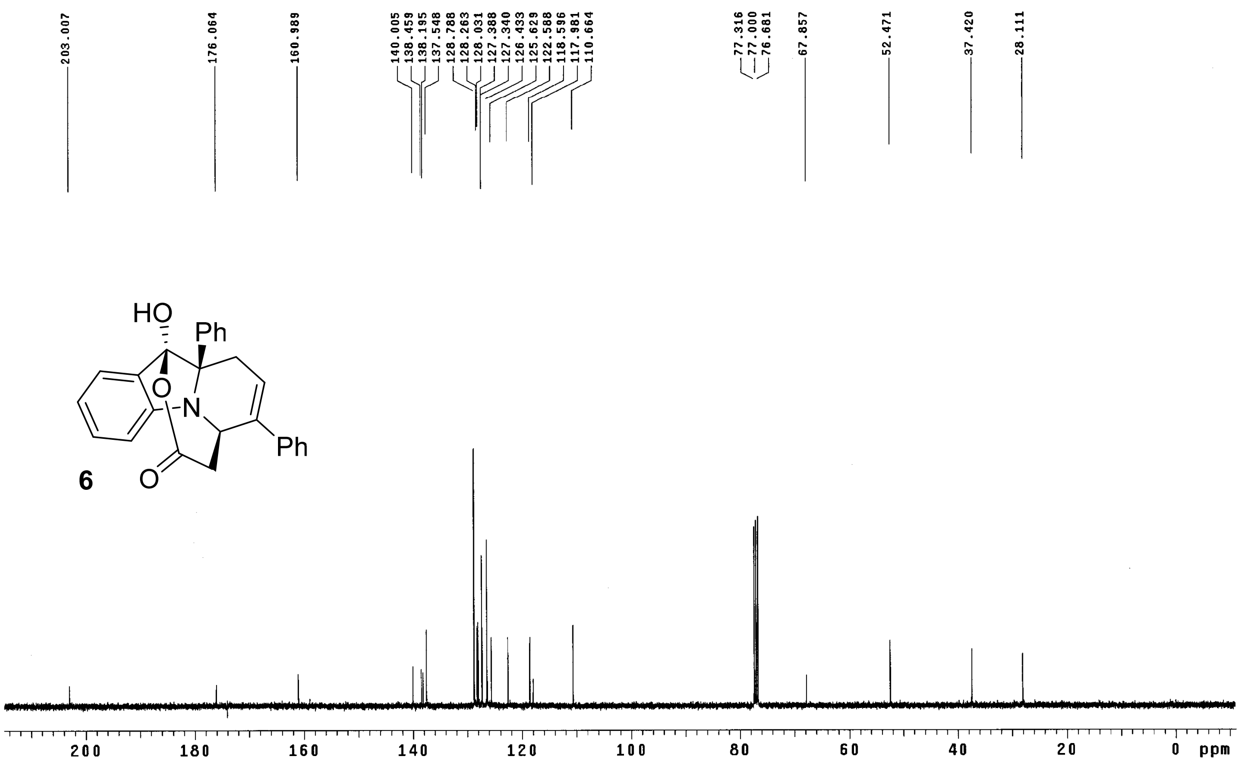


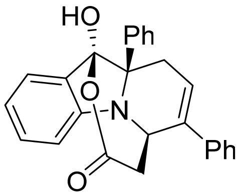
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	4.677	8031162	50.56	807404	57.98
2	5.470	7852380	49.44	585228	42.02



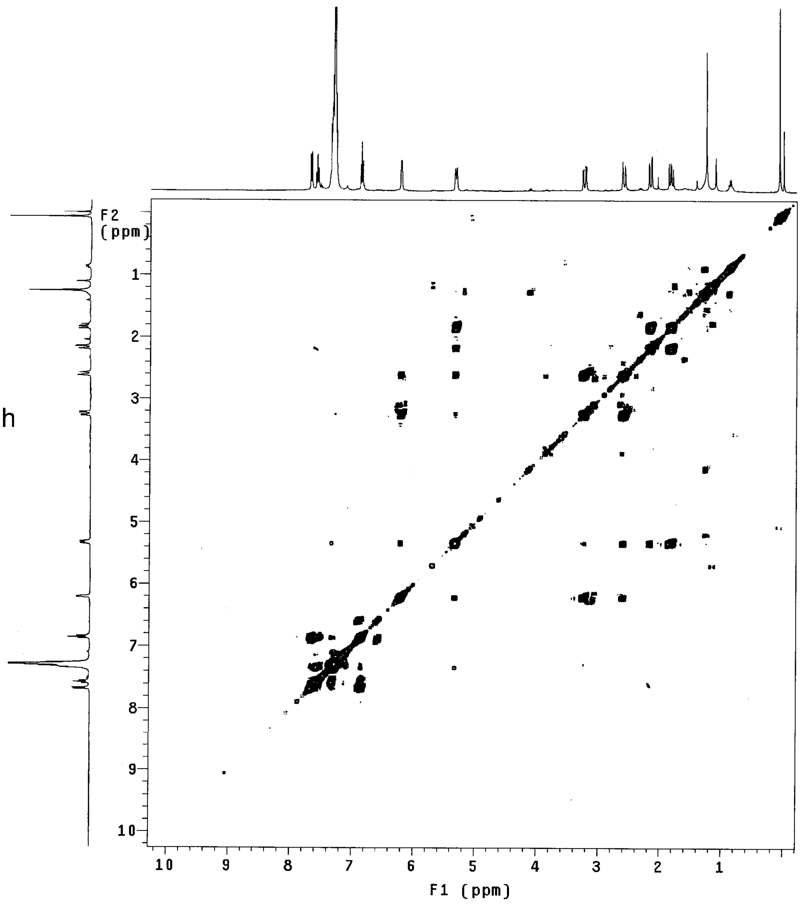
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	4.733	24589540	85.05	2005893	85.58
2	5.530	4321534	14.95	337946	14.42

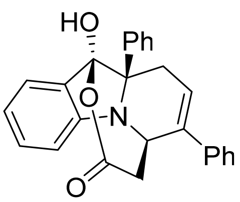

7.685
7.666
7.594
7.573
7.555
7.349
7.328
7.315
7.299
7.286
7.261
6.874
6.855
6.837
6.217
6.213
6.206
5.342
5.317
3.277
3.262
3.231
3.216
2.627
2.582
2.191
2.184
2.149
2.142
1.868
1.841
1.827
1.800
1.255
0.071
0.000
HO
Ph
1
2
O
N
3
Ph
O
6
4
H2 Signal
H3 Signal
H1 Signal
H4 Signal
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
3.40
0.98
7.63
1.04
0.94
1.00
1.17
1.46
1.50
1.40


203.007
176.064
160.989
140.005
138.459
138.195
137.548
128.788
128.263
128.031
127.388
127.340
126.433
125.629
122.588
118.596
117.981
110.664
77.316
77.000
76.681
67.857
52.471
37.420
28.111
HO
Ph
O
N
Ph
6
O
200
180
160
140
120
100
80
60
40
20
0
ppm

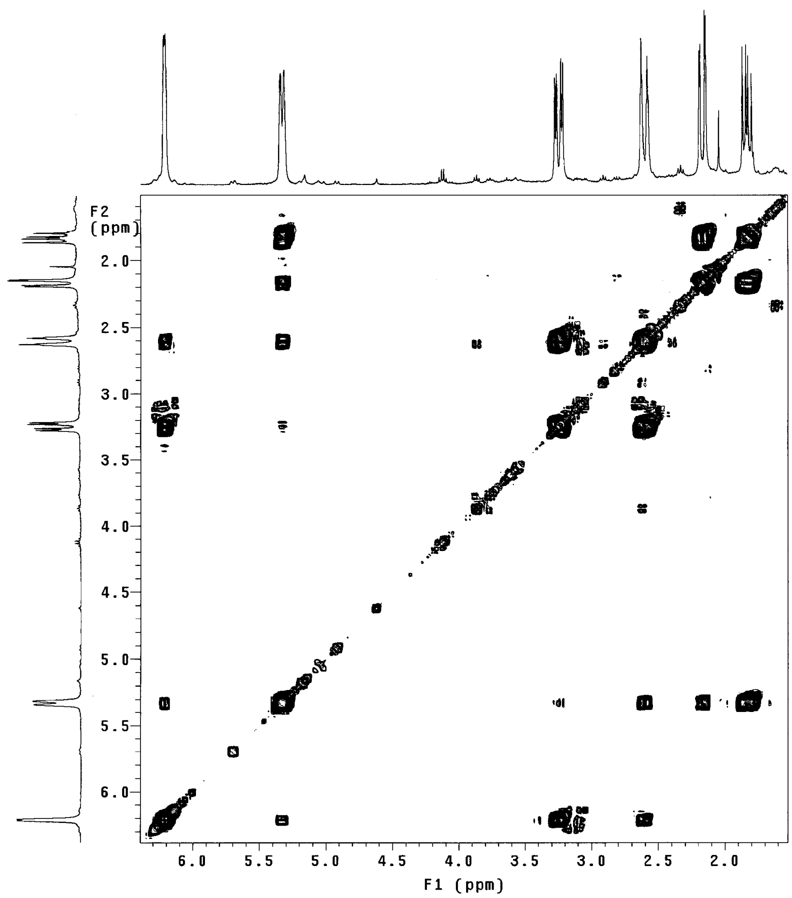


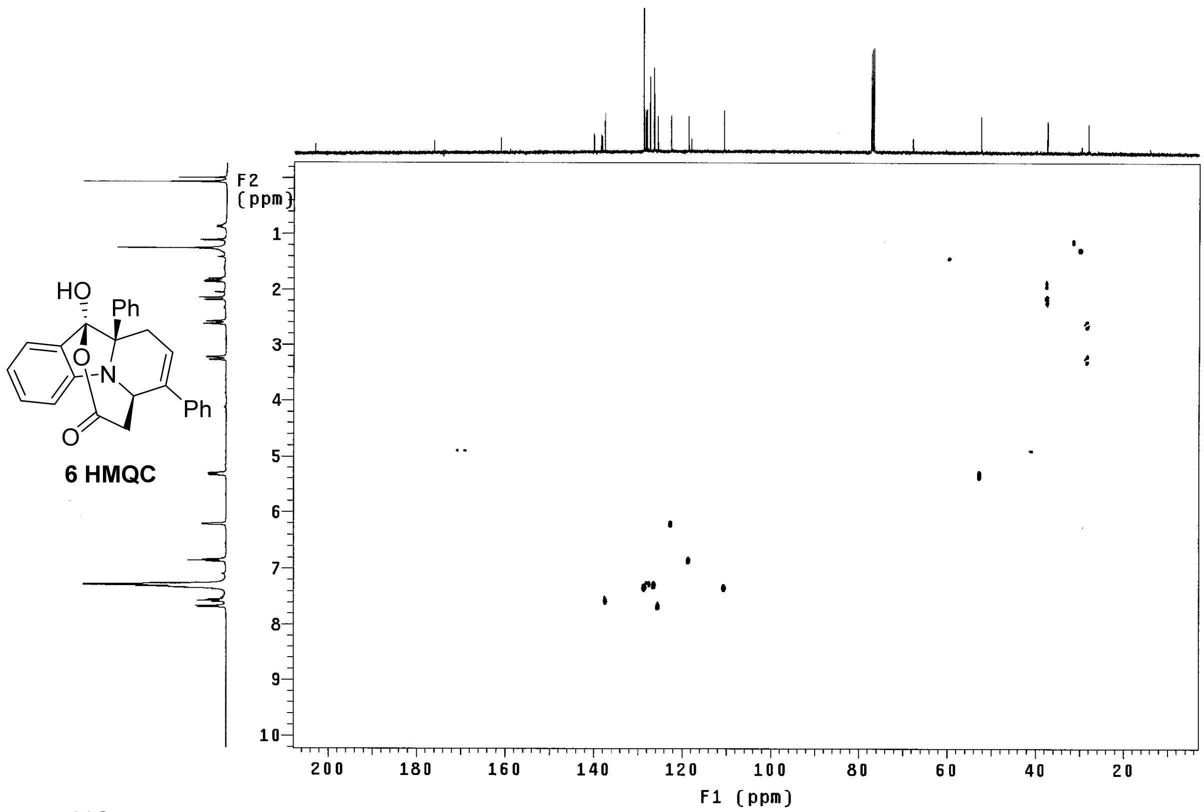
6 H-H cosy

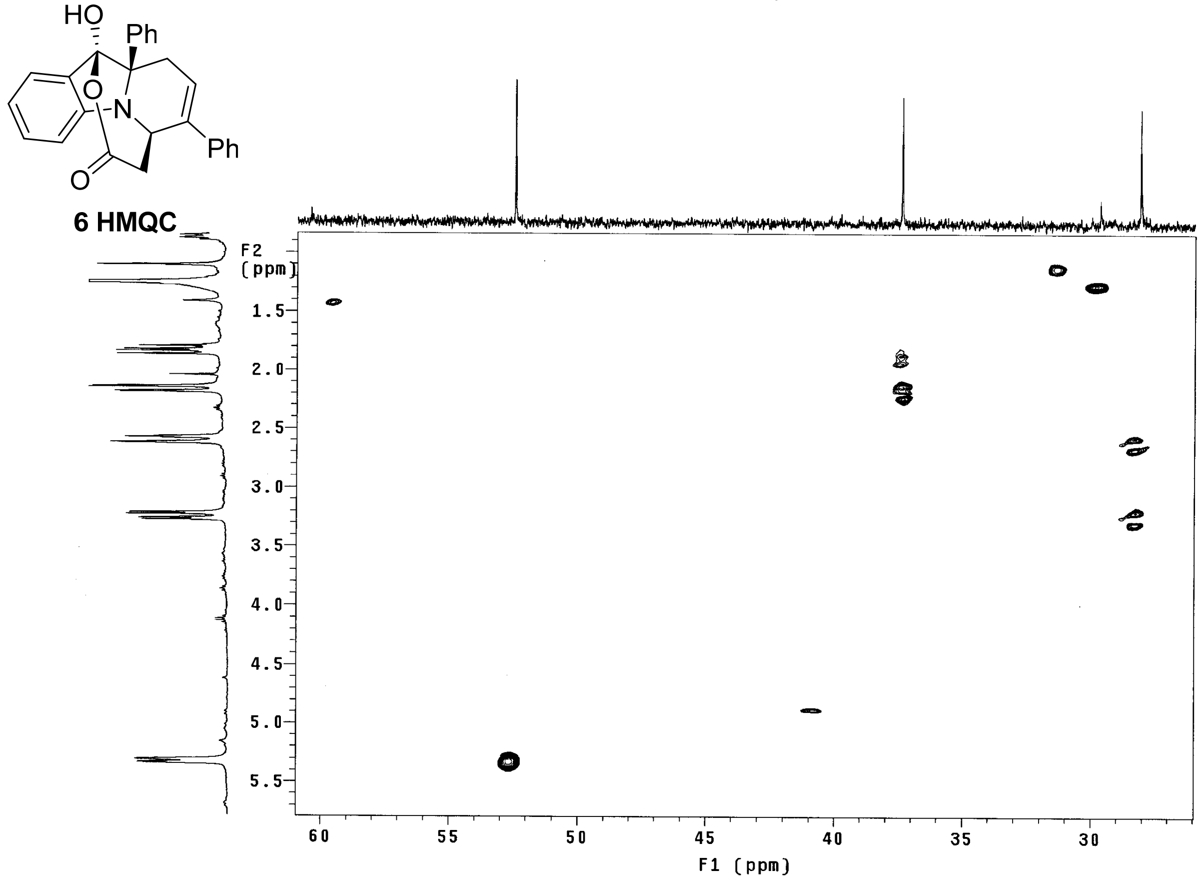


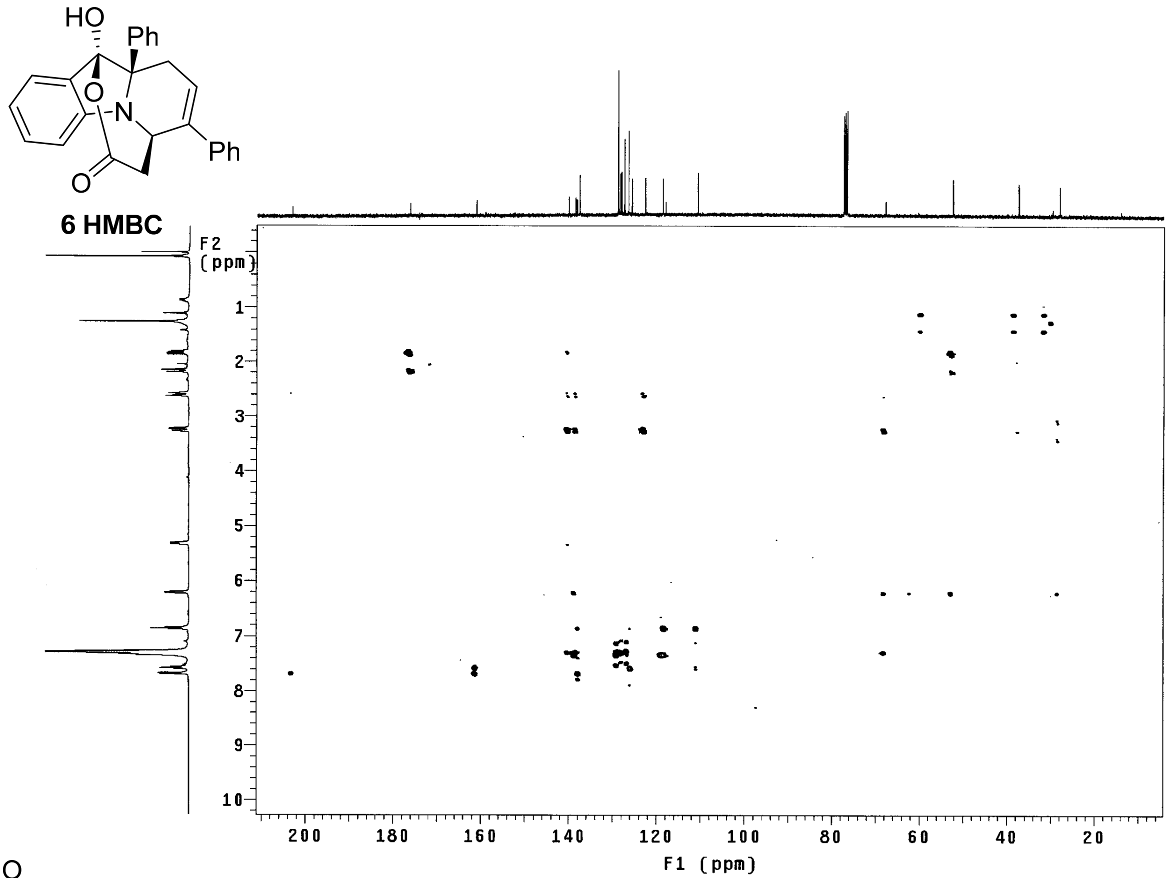


6 H-H cosy

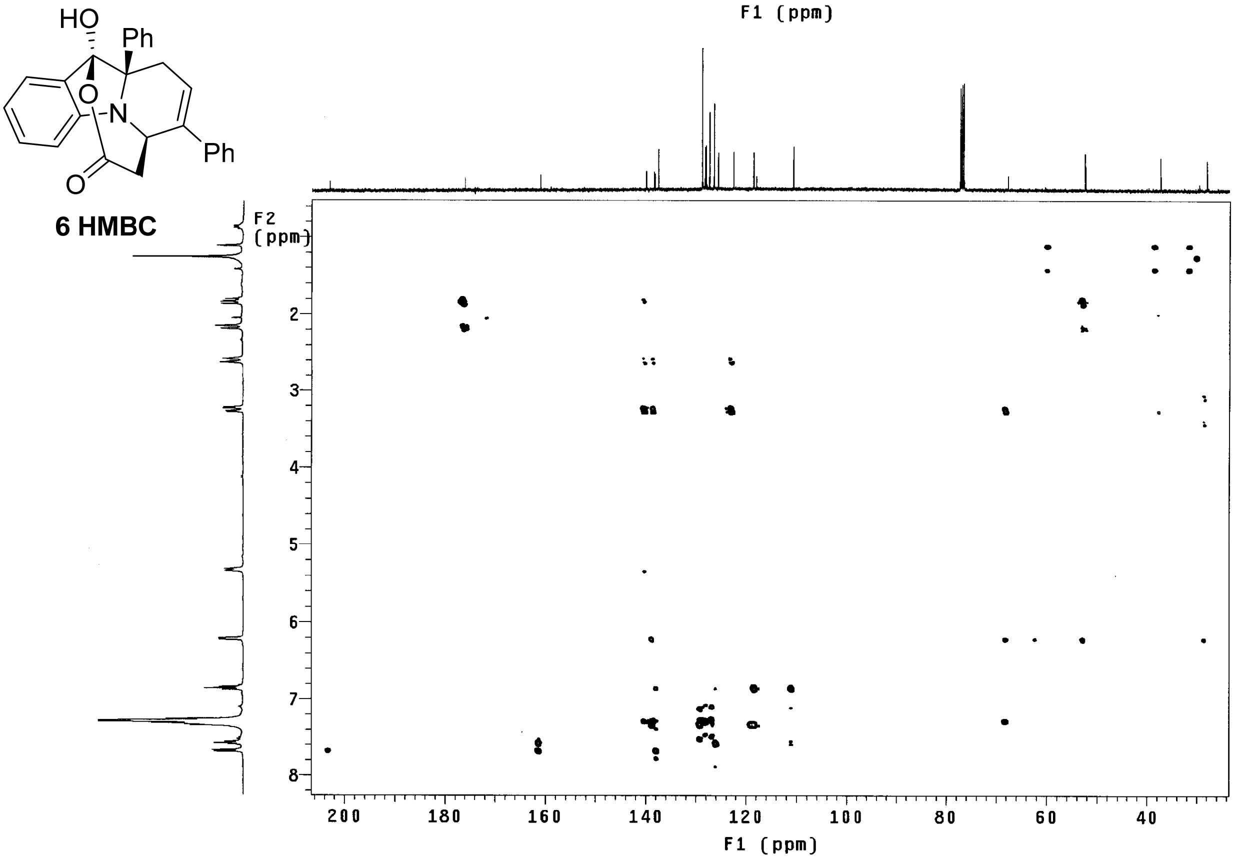



HO
Ph
O
N
Ph
O
6 HMQC
F2 (ppm)
1
2
3
4
5
6
7
8
9
10
200
180
160
140
120
100
80
60
40
20
F1 (ppm)

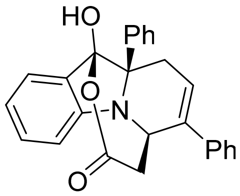

HO
Ph
O
N
Ph
O
6 HMQC
F2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
60
55
50
45
40
35
30
F1 (ppm)


HO
Ph
O
N
Ph
O
F2 (ppm)
1
2
3
4
5
6
7
8
9
10
200
180
160
140
120
100
80
60
40
20
F1 (ppm)

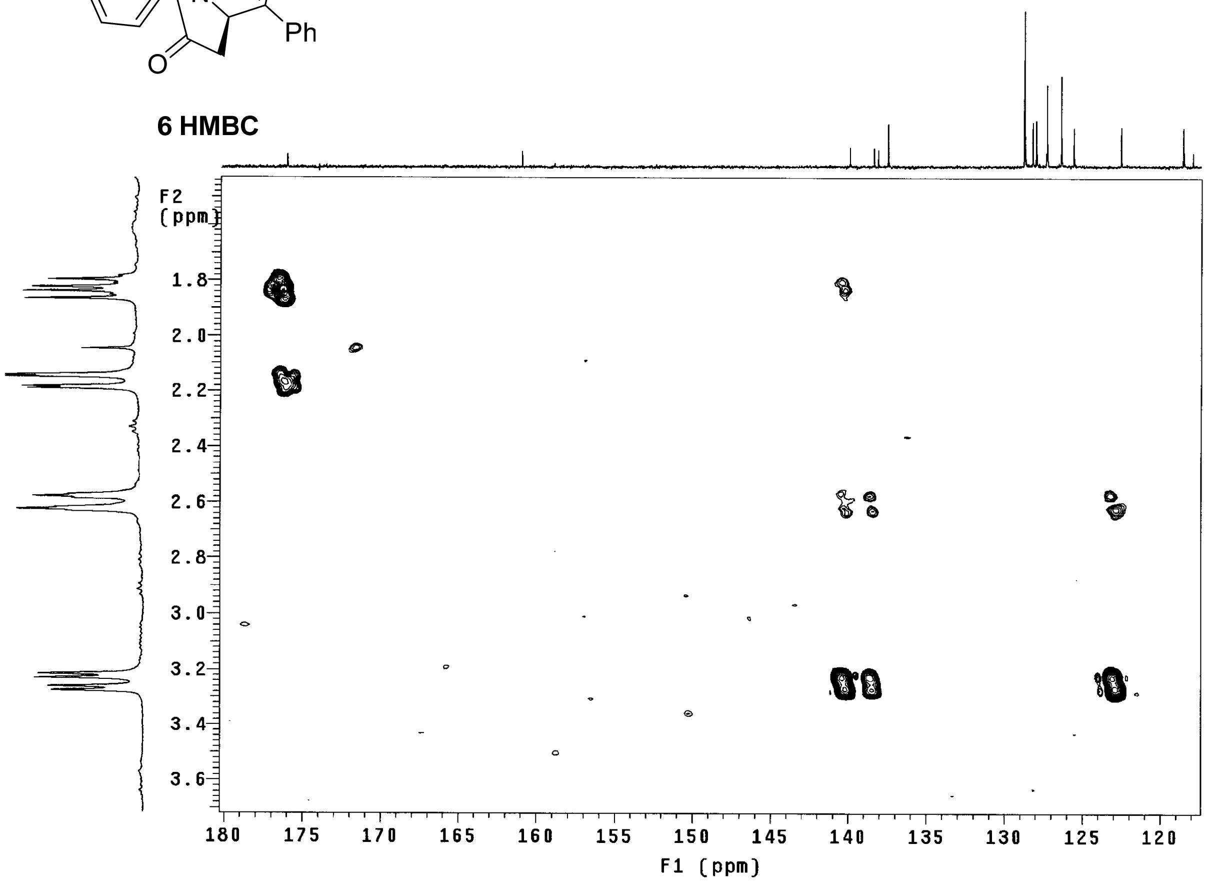
6 HMBC

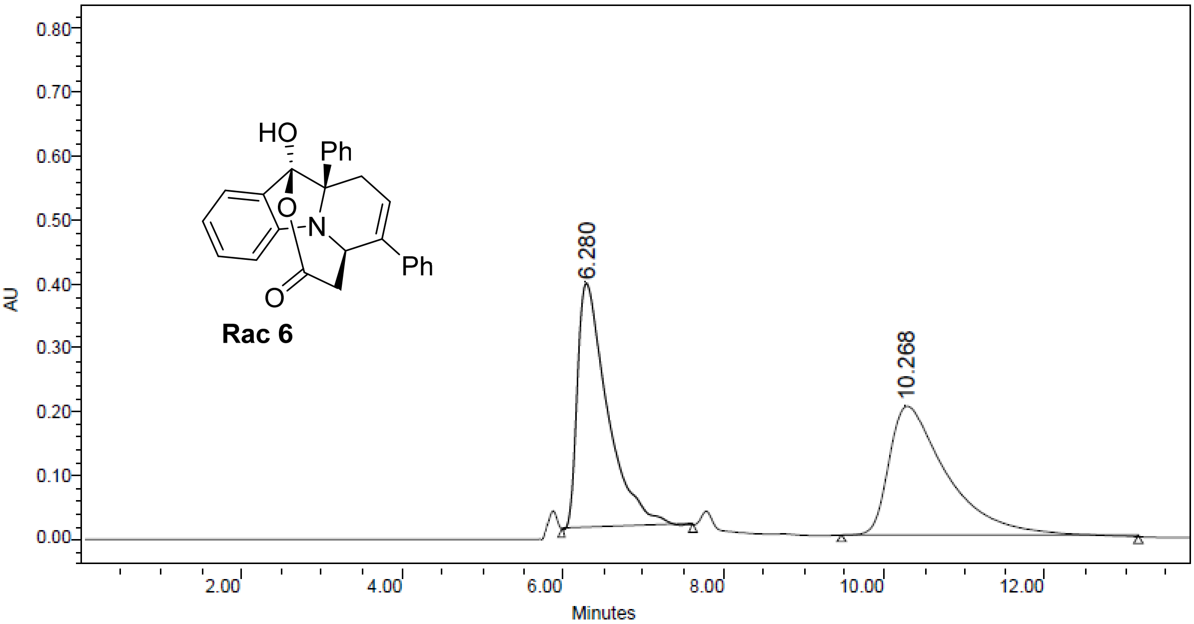

HO
Ph
O
N
Ph
O
F2 (ppm)
2
3
4
5
6
7
8
200
180
160
140
120
100
80
60
40
F1 (ppm)

6 HMBC

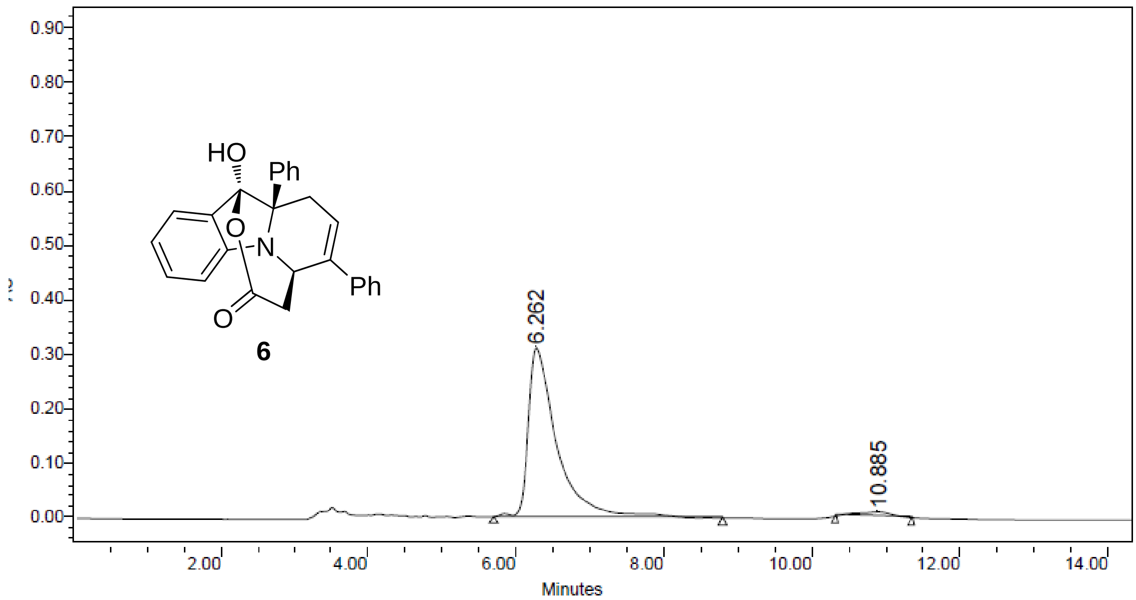

HO
Ph
O
N
Ph
O

6 HMBC

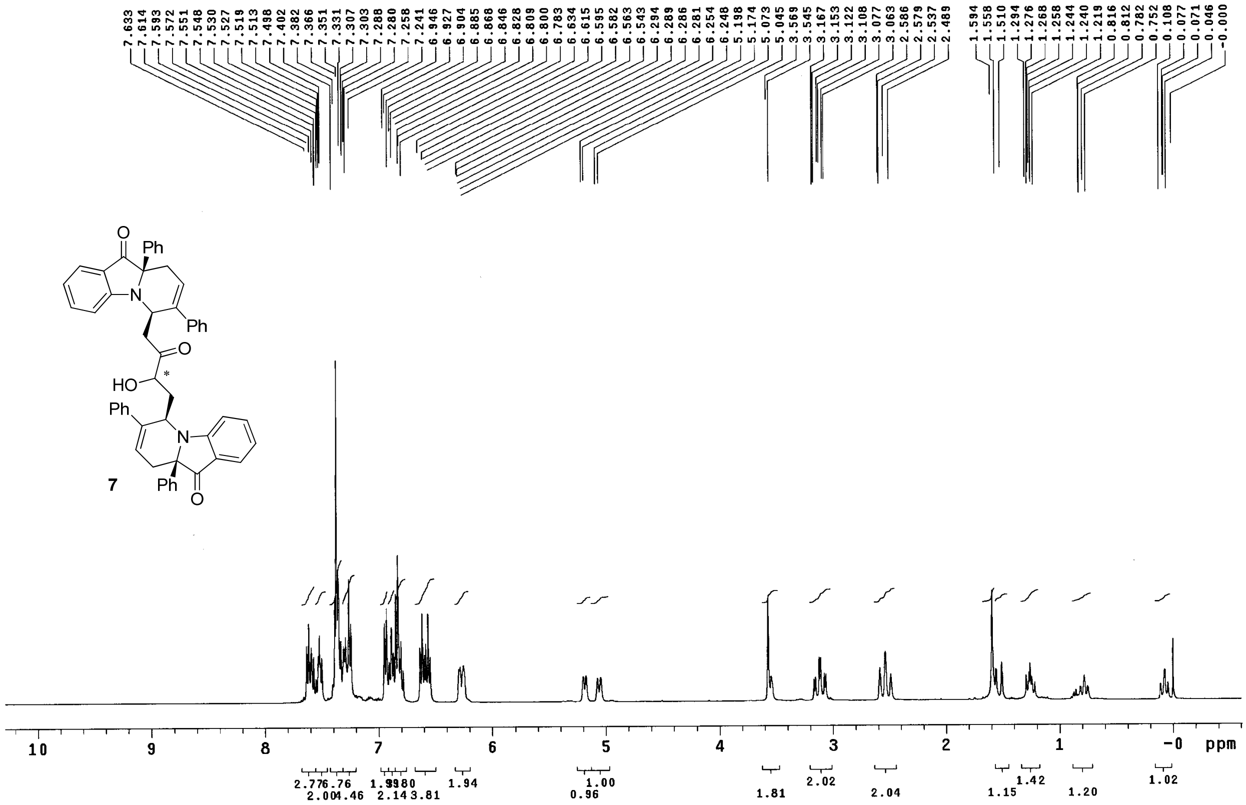

F2 (ppm)
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
180
175
170
165
160
155
150
145
140
135
130
125
120
F1 (ppm)

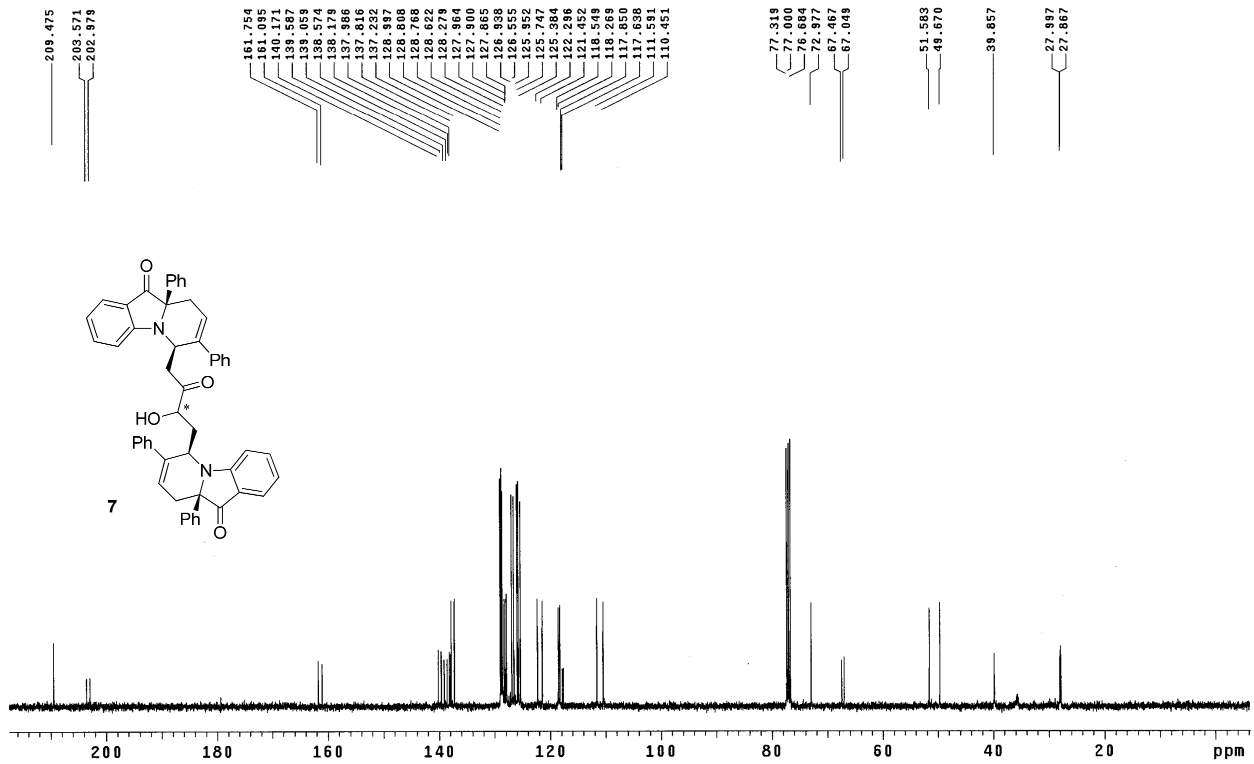


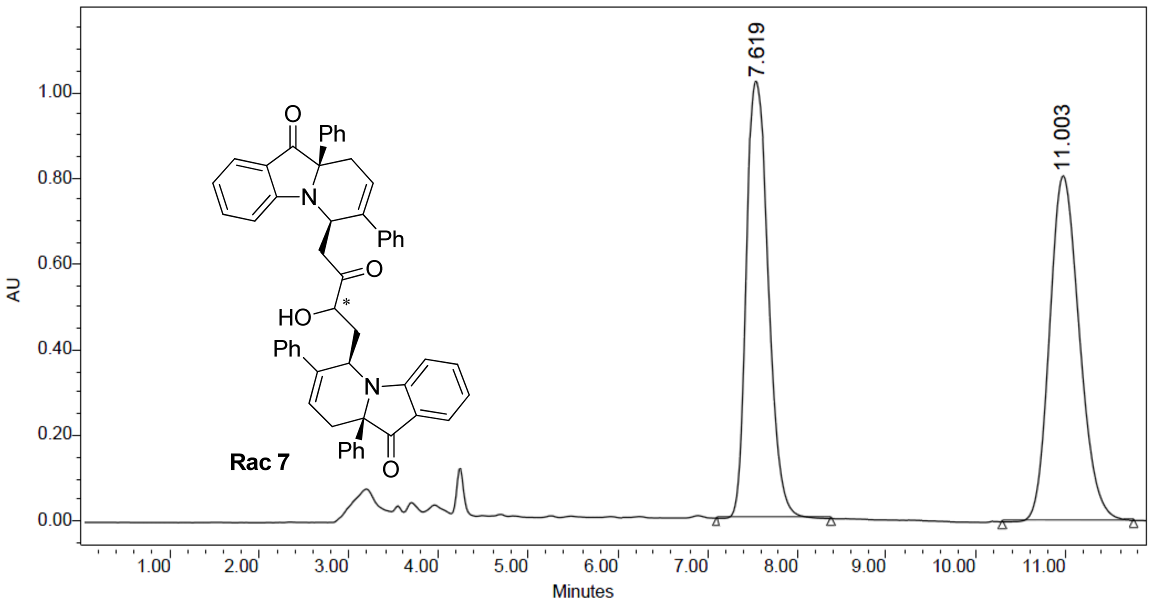
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.280	10050952	49.37	385070	65.52
2	10.268	10306502	50.63	202680	34.48



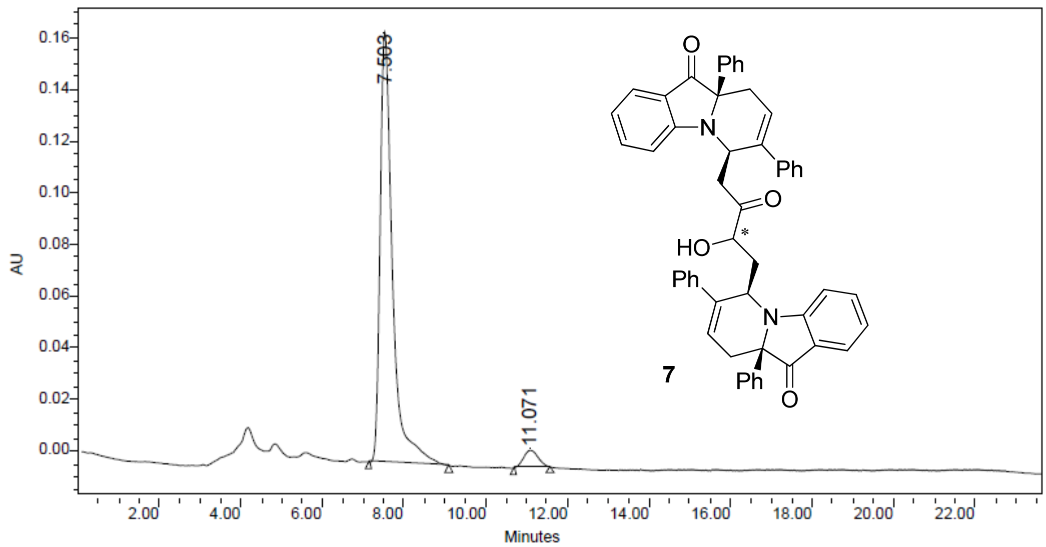
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.262	8373584	96.45	311004	97.12
2	10.885	307769	3.55	9224	2.88


7.633
7.614
7.593
7.572
7.551
7.548
7.530
7.527
7.519
7.513
7.498
7.402
7.382
7.366
7.351
7.331
7.307
7.303
7.288
7.280
7.258
7.241
6.946
6.927
6.904
6.885
6.868
6.846
6.828
6.809
6.800
6.783
6.634
6.615
6.595
6.582
6.563
6.543
6.294
6.289
6.286
6.281
6.254
6.248
5.198
5.174
5.073
5.045
3.569
3.545
3.167
3.153
3.122
3.108
3.077
3.063
2.586
2.579
2.537
2.489
1.594
1.558
1.510
1.294
1.276
1.268
1.258
1.244
1.240
1.219
0.816
0.812
0.782
0.752
0.108
0.077
0.071
0.046
-0.000
O
Ph
N
Ph
O
HO
*
Ph
N
Ph
O
7
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.77
6.76
2.00
4.46
1.99
1.80
2.14
3.81
1.94
1.00
0.96
1.81
2.02
2.04
1.15
1.42
1.20
1.02

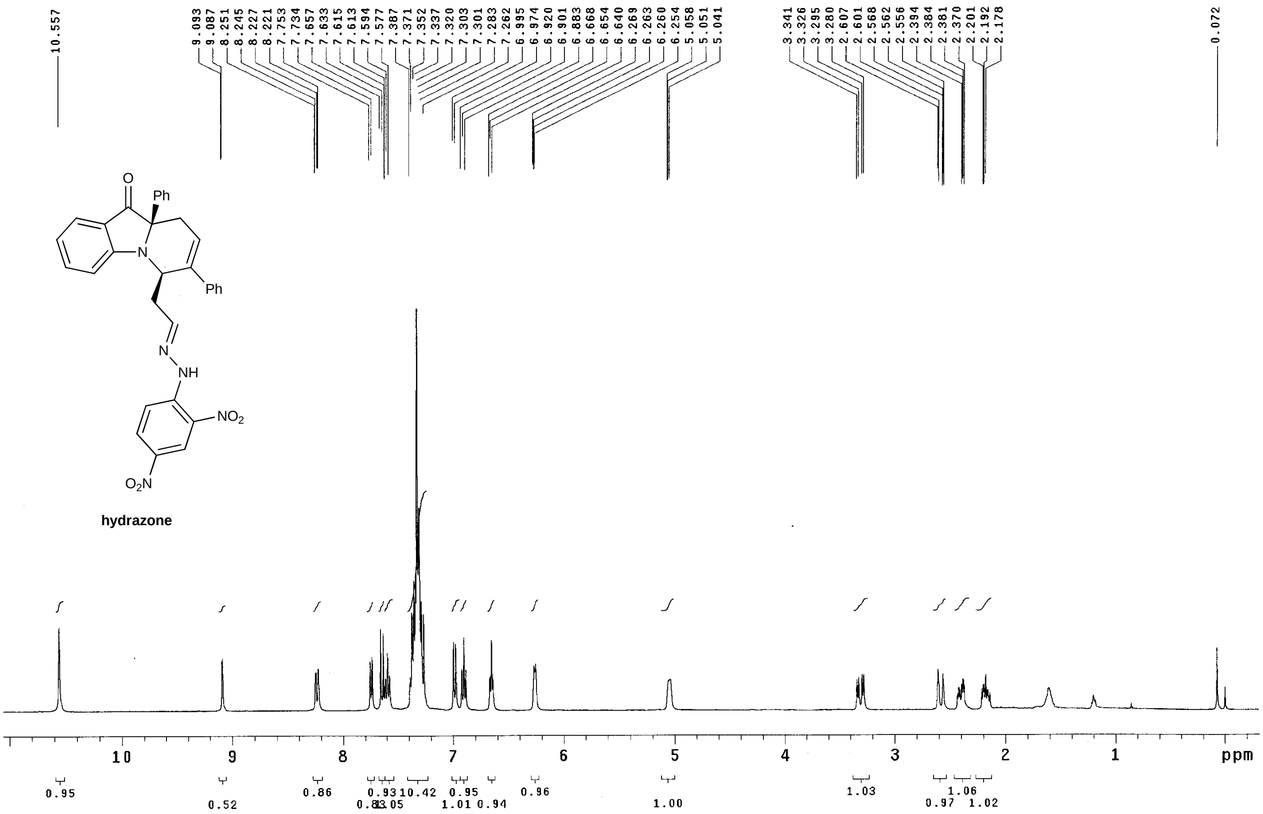

209.475
203.571
202.979
161.754
161.095
140.171
139.587
139.059
138.574
138.179
137.986
137.816
137.232
128.997
128.808
128.768
128.622
128.279
127.964
127.900
127.865
126.938
126.555
125.952
125.747
125.384
122.296
121.452
118.549
118.269
117.850
117.638
111.591
110.451
77.319
77.000
76.684
72.977
67.467
67.049
51.583
49.670
39.857
27.997
27.867
O
Ph
N
Ph
O
HO
*
Ph
N
Ph
O
7
200
180
160
140
120
100
80
60
40
20
ppm

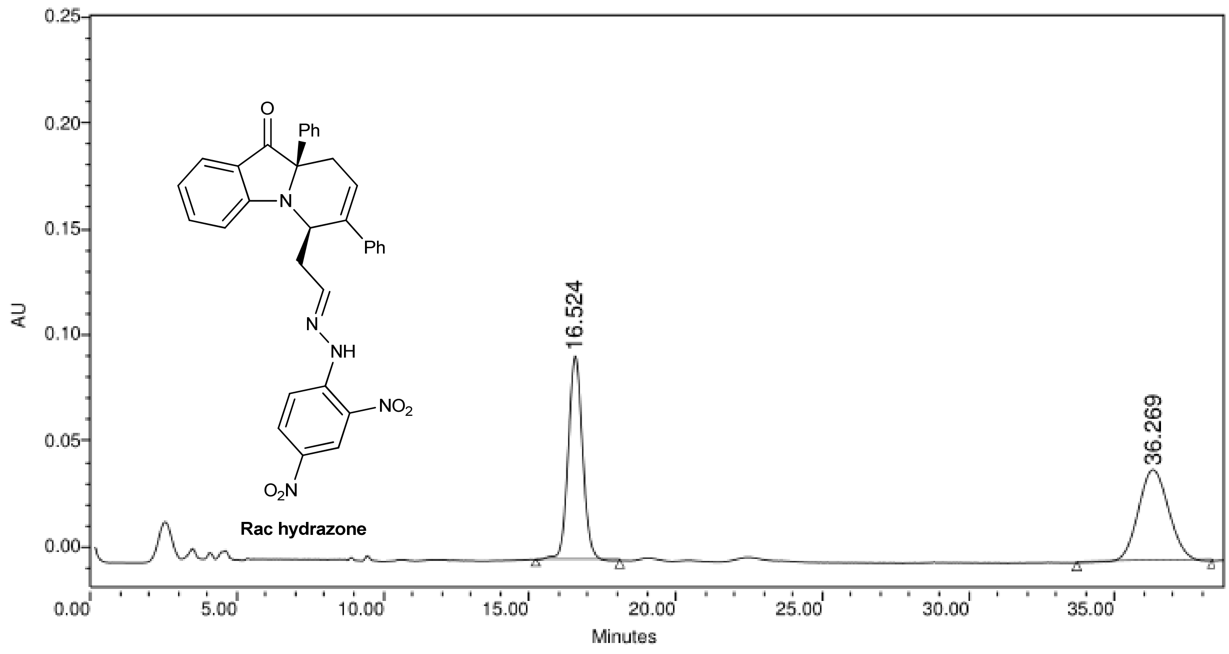


	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.619	18078874	49.04	1038811	56.30
2	11.003	18788824	50.96	806345	43.70

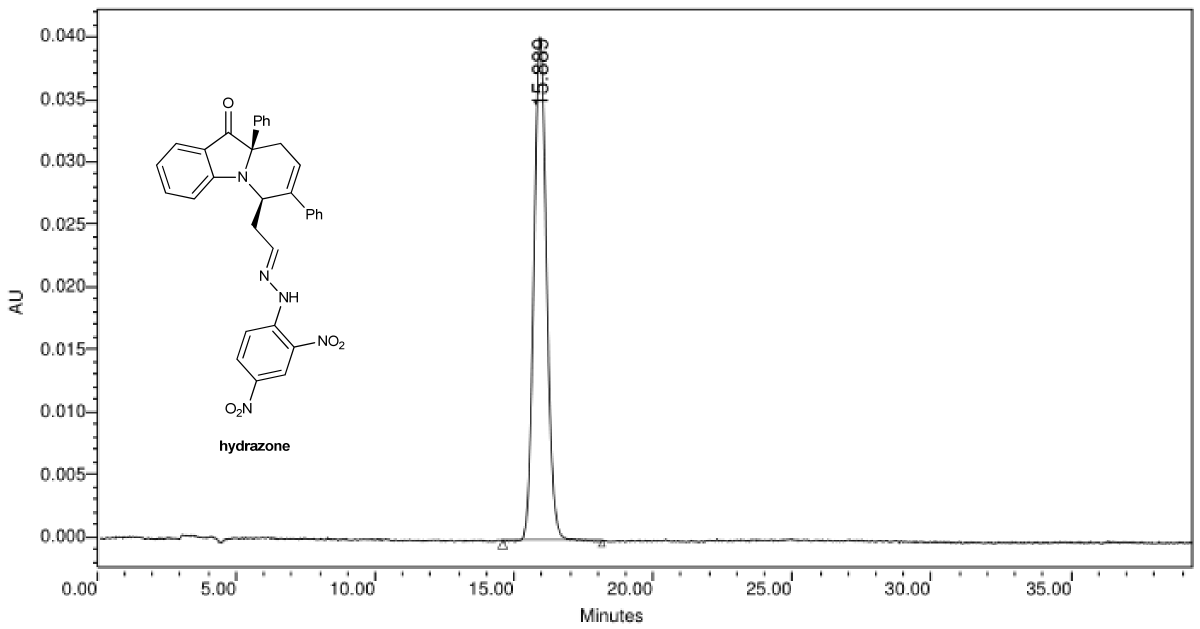


	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.503	3542566	95.98	166901	96.40
2	11.071	148353	4.02	6229	3.60

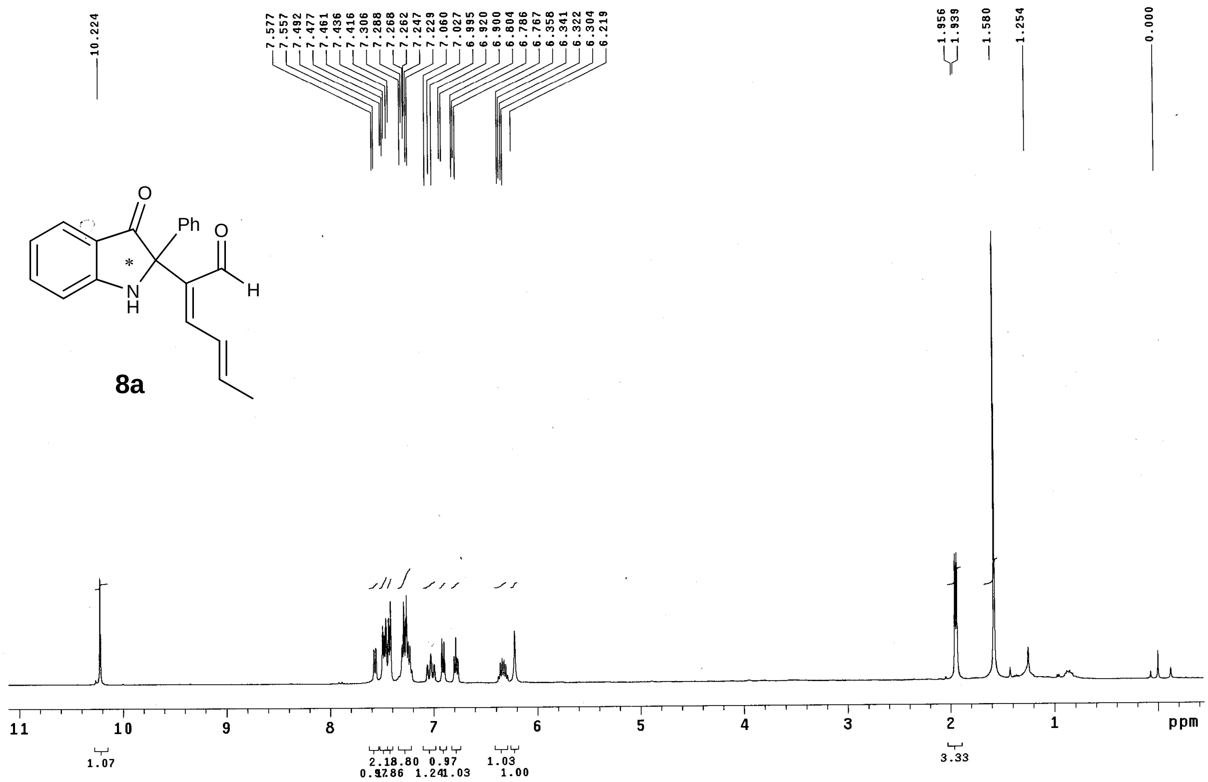




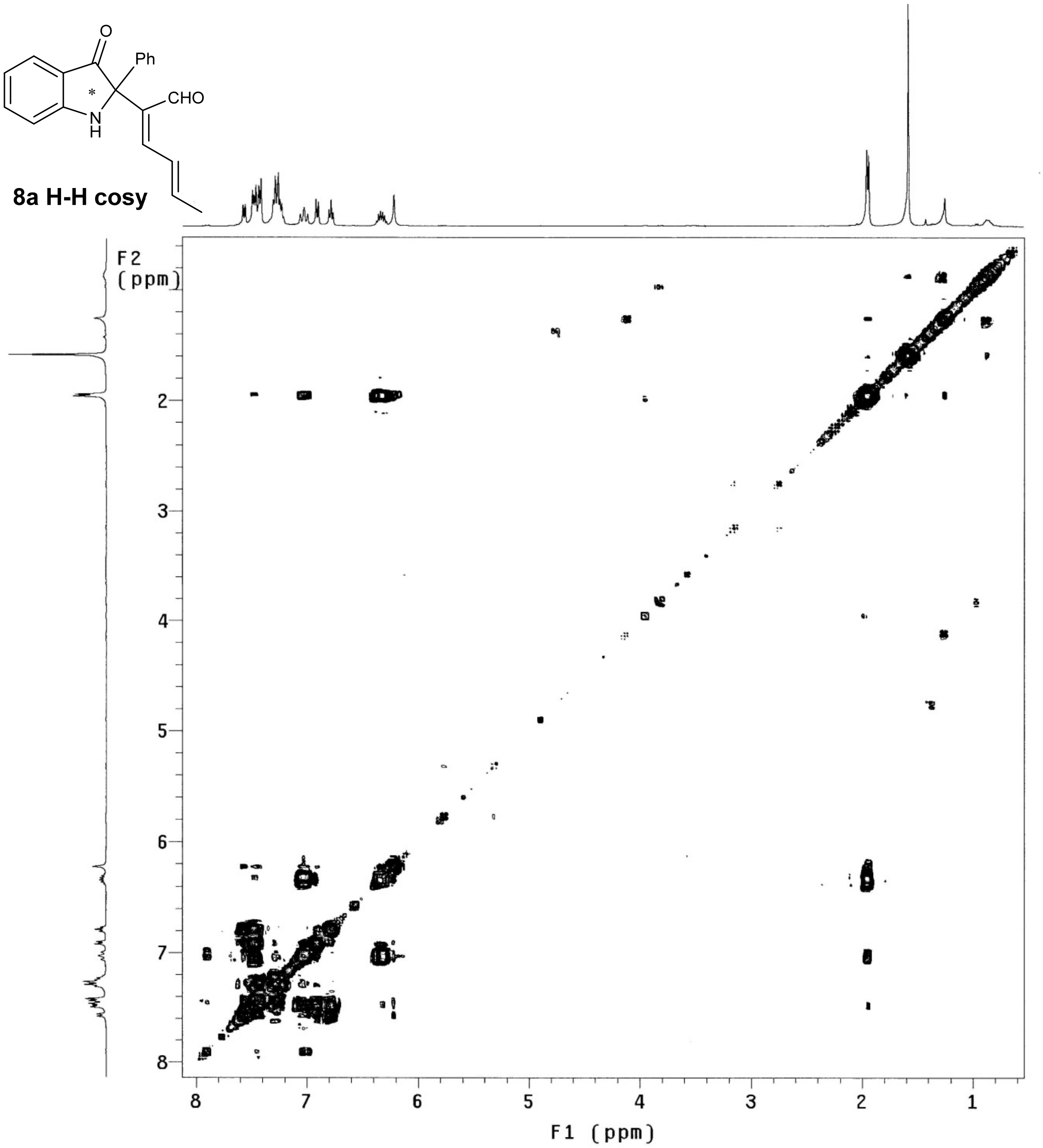
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.524	3305448	50.95	96197	68.95
2	36.269	3182010	49.05	43327	31.05

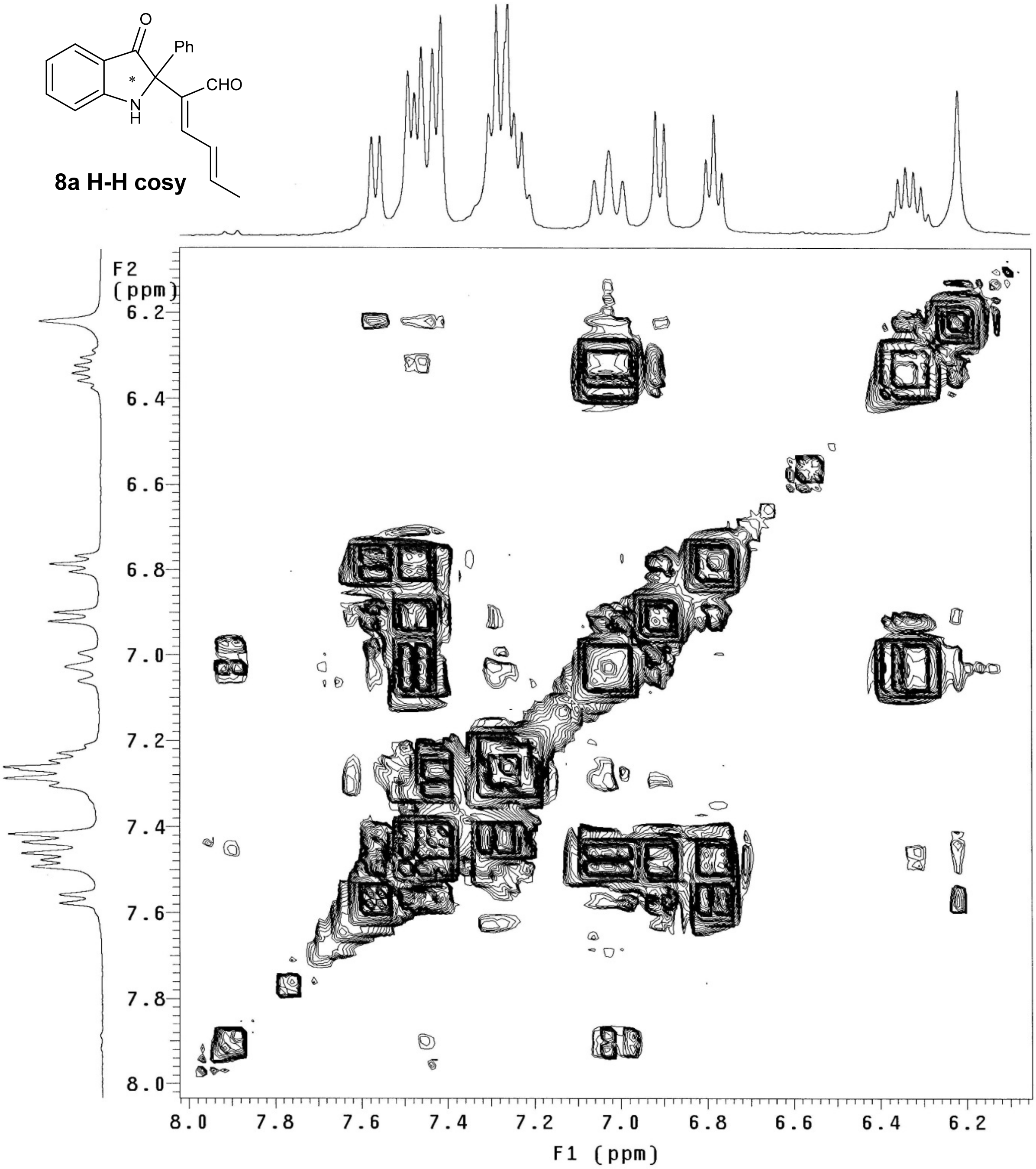


	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.889	1278774	100.00	40282	100.00

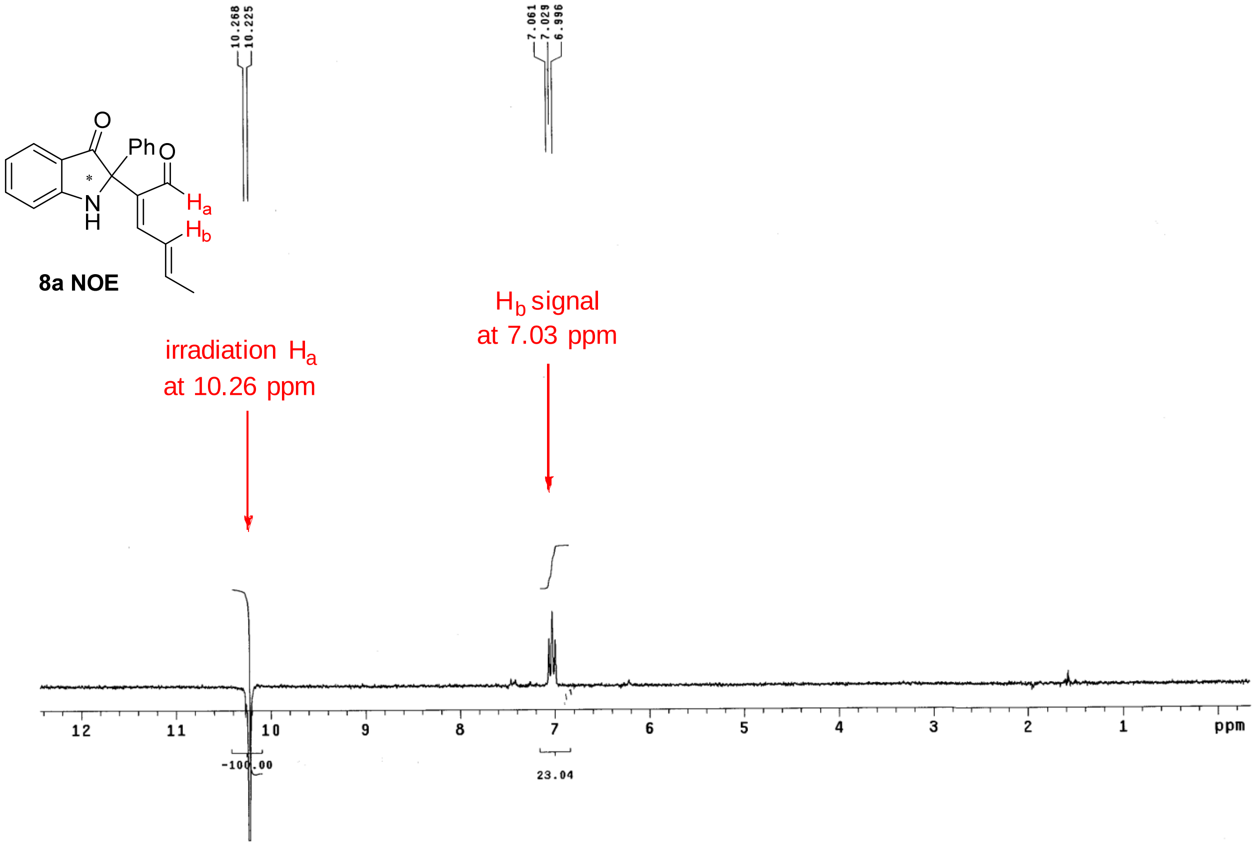

8a
Ph
O
H
N
H
11
10
9
8
7
6
5
4
3
2
1
ppm

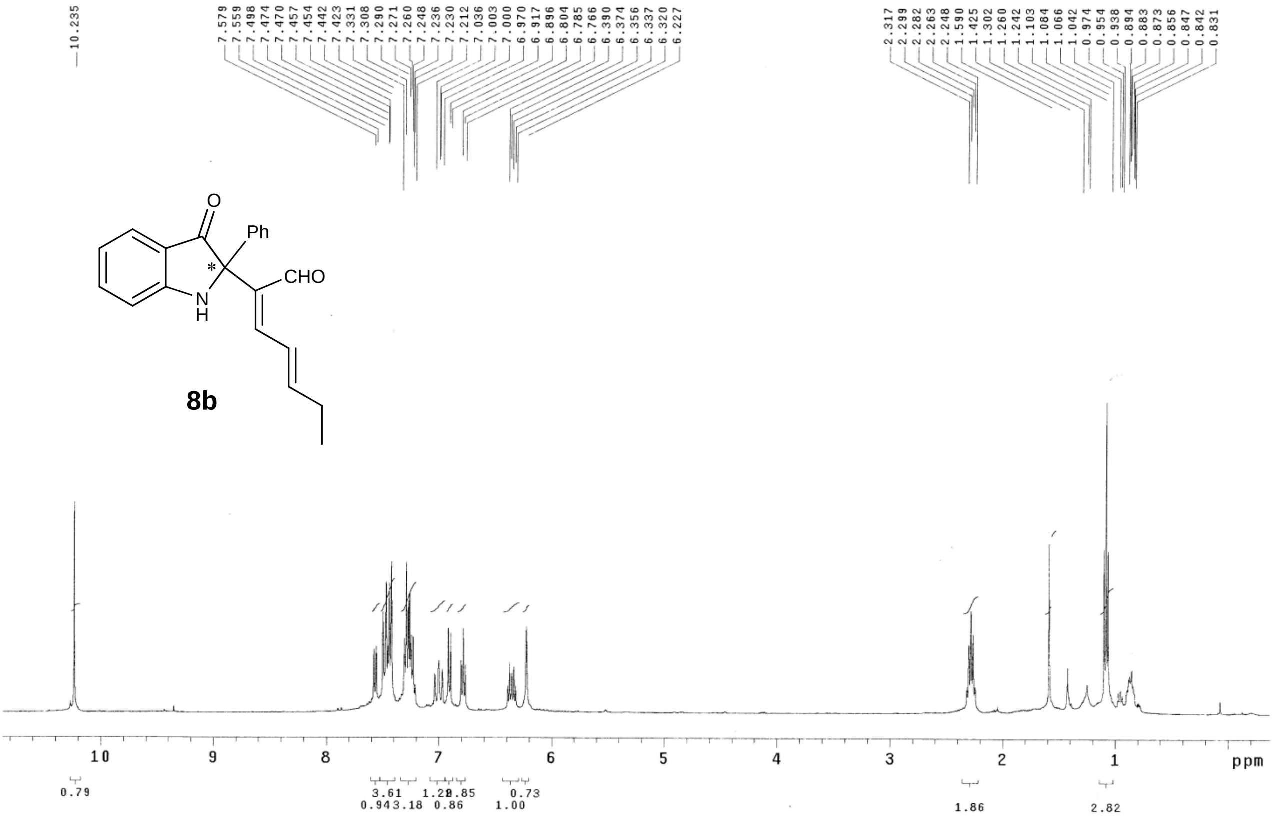
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry





8a H-H cosy


8a NOE
Ha
Hb
irradiation Ha at 10.26 ppm
Hb signal at 7.03 ppm
-100.00
23.04
ppm


8b
CHO
Ph
ppm