Electronic Supplementary Infomation

Organocatalytic asymmetric allylic alkylation of 2-methyl-3-nitroindoles: a route to direct enantioselective functionalization of indole C(sp^3)-H Bonds

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1. General Experimental Details.

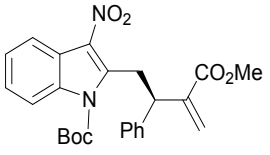
All commercially available reagents were used without further purification unless otherwise stated. All reaction solvents were purified before use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a commercial instrument at 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz. The proton signal for residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ77.0 resonance of $CHCl_3$. Coupling constants are reported in Hz. Optical rotations were recorded on an RUDOLPH/Autopol IV polarimeter. Melting points were determined on a BUCHI B-545 melting point apparatus and are uncorrected. High resolution mass spectra were recorded on a commercial high resolution mass spectrometer Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid). Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel, typically using a 50-100:1 weight ratio of silica gel to crude product. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel chiral columns on JASCO with a UV-4075 detector. The HPLC spectra of racemic mixtures were synthesized using DABCO as a catalyst. Catalyst **4a** was purchased from Biosynth Carbosynth. Catalysts **4b-g** were purchased from Shanghai Chiral bio-compound Co., Ltd. 3-Nitro-2-methylindoles **1**[1] and MBH carbonates **2**[2] were prepared according to literature procedures.

2. General Procedure for the Synthesis of 3 and 5

To a solution of MBH carbonates **2** (0.1 mmol) and catalyst **4f** (0.015 mmol) in anhydrous CH_2Cl_2 was added 3-Nitro-2-methylindoles **1** (0.15 mmol) at room temperature. The reaction mixture was stirred at room temperature for 48 h. After completion of the reaction, the reaction solution was concentrated in vacuum and the crude was purified by silica gel flash chromatography (Hexanes/EA 10:1 to 5:1) to afford the pure products. The enantiomeric ratio was determined by HPLC on a chiral stationary phase.

3. Characterization Data

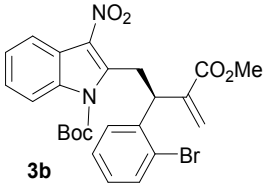
***tert*-Butyl (*R*)-2-(3-(methoxycarbonyl)-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3a).**



3a

Yellow oil; Yield : 72%; $[\alpha]_D^{30}$: −83.7 (*c* = 1.00, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.14 (m, 1H), 8.04 – 8.00 (m, 1H), 7.38 – 7.35 (m, 2H), 7.17 – (m, 3H), 7.09 – 7.06 (m, 2H), 6.39 (s, 1H), 5.86 (s, 1H), 4.41 – 4.22 (m, 3H), 3.51 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 149.1, 142.7, 142.1, 140.4, 133.9, 128.4, 127.6, 127.0, 125.9, 125.2, 125.0, 121.3, 120.6, 114.9, 86.9, 51.9, 45.9, 30.9, 28.0; HRMS (ESI): cacld for $C_{25}H_{26}N_2O_6Na$ $[M+Na]^+$: 473.1683; found: 473.1682; HPLC analysis: *er* = 92:8 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.8 mL/min, λ = 220 nm; t_{minor} = 5.23 min, t_{major} = 5.72 min.

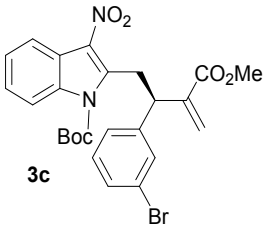
***tert*-Butyl (*S*)-2-(2-(2-bromophenyl)-3-(methoxycarbonyl)but-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3b).**



3b

Yellow solid; Yield : 88%; $[\alpha]_D^{30}$: −67.7 (*c* = 1.55, CH_2Cl_2); mp: 115-116℃; ^1H NMR (400 MHz, $CDCl_3$): 8.12 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.20 (m, 5H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.43 (s, 1H), 5.80 (s, 1H), 4.96 – 4.88 (m, 1H), 4.40 – 4.29 (m, 1H), 4.21 (dd, *J* = 12.9, 5.9 Hz, 1H), 3.47 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 149.2, 142.1, 141.2, 139.5, 134.2, 132.6, 132.2, 129.0, 128.4, 127.5, 126.0, 125.6, 125.0, 124.9, 121.4, 120.4, 115.4, 86.8, 51.8, 43.9, 30.5, 28.0 ; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6NaBr$ $[M+Na]^+$: 551.0788; found: 551.0788; HPLC analysis: *er* = 95:5 on an IF column: hexane/*i*-PrOH = 80:20, flow rate = 0.8 mL/min, λ = 220 nm; t_{major} = 12.38 min, t_{minor} = 13.03 min.

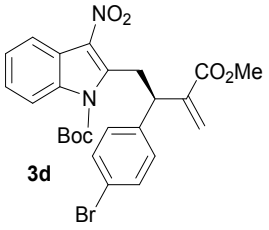
***tert*-Butyl (*R*)-2-(2-(3-bromophenyl)-3-(methoxycarbonyl)but-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3c).**



3c

Yellow solid; Yield : 79%; $[\alpha]_D^{30}$: −97.3 (*c* = 2.09, CH_2Cl_2); mp: 122-123℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.99 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.37 (dd, *J* = 6.1, 3.1 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.07 – 6.91 (m, 2H), 6.40 (s, 1H), 5.84 (s, 1H), 4.39 – 4.16 (m, 3H), 3.51 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 148.7, 142.7, 142.0, 141.1, 133.5, 131.7, 130.3, 129.8, 129.5, 126.1, 125.7, 125.5, 124.8, 122.1, 120.9, 120.3, 114.7, 86.8, 51.6, 45.3, 30.4, 27.6; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6NaBr$ $[M+Na]^+$: 551.0788; found: 551.0783; HPLC analysis: *er* = 92:8 on an AS-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{minor} = 11.35 min, t_{major} = 14.70 min.

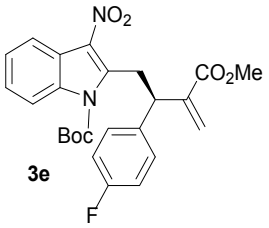
***tert*-Butyl (*R*)-2-(2-(4-bromophenyl)-3-(methoxycarbonyl)but-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3d).**



3d

Yellow solid; Yield : 78%; $[\alpha]_D^{30}$: −132.6 (*c* = 1.72, CH_2Cl_2); mp: 116-117℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.97 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.36 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.39 (s, 1H), 5.84 (s, 1H), 4.39 – 4.25 (m, 2H), 4.20 – 4.19 (m, 1H), 3.51 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4, 149.0, 142.5, 141.7, 139.6, 133.8, 131.9, 131.4, 129.4, 126.1, 125.4, 125.1, 121.2, 120.8, 120.6, 115.0, 87.0, 51.9, 45.5, 30.6, 27.9; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6NaBr$ $[M+Na]^+$: 551.0788; found: 551.0780; HPLC analysis: *er* = 95.5:4.5 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 9.96 min, t_{minor} = 10.95 min.

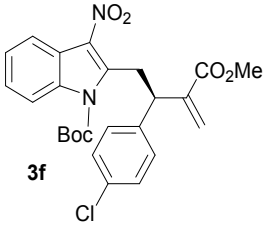
***tert*-Butyl (*R*)-2-(2-(4-fluorophenyl)-3-(methoxycarbonyl)but-3-en-1-yl)- 3-nitro-1*H*-indole-1-carboxylate (3e).**



3e

Yellow oil; Yield : 72%; $[\alpha]_D^{30}$: −31.1 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 6.2, 3.0 Hz, 1H), 7.99 (dd, J = 6.1, 3.3 Hz, 1H), 7.42 – 7.28 (m, 2H),7.03 –7.00 (m, 2H), 6.82 (t, J = 8.7 Hz, 2H), 6.38 (s, 1H), 5.85 (s, 1H), 4.41 – 4.24 (m, 2H), 4.21–4.14 (m, 1H), 3.51 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 161.7 (d, *J* = 246 Hz), 149.1, 142.6, 142.1, 136.1, 133.9, 132.0,129.6 (d, *J* = 8.3 Hz), 129.2 (d, *J* = 8.0 Hz), 126.0, 125.6, 125.1, 125.1, 121.3, 120.7, 115.5, 115.3, 115.1, 115.0, 87.0, 51.9, 45.3, 30.9, 28.0; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6NaF$ $[M+Na]^+$: 491.1589; found: 491.1584; HPLC analysis: *er* = 94:6 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 8.97 min, t_{minor} = 10.23 min.

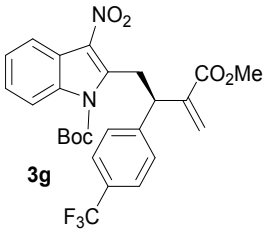
***tert*-Butyl (*R*)-2-(2-(4-chlorophenyl)-3-(methoxycarbonyl)but-3-en-1-yl)- 3-nitro-1*H*-indole-1-carboxylate (3f).**



3f

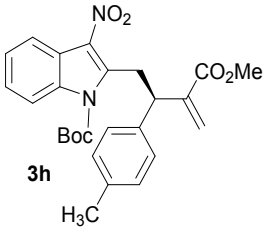
Yellow oil; Yield : 75%; $[\alpha]_D^{30}$: −65.6 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.11 (m, 1H), 8.04 – 7.90 (m, 1H), 7.43 – 7.32 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.39 (s, 1H), 5.85 (s, 1H), 4.42 – 4.26 (m, 2H), 4.25 – 4.12 (m, 1H), 3.51 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 149.0, 142.5, 141.8, 139.1, 133.9, 132.7, 131.9, 129.0, 128.7, 128.5, 126.1, 125.3, 125.1, 121.3, 120.7, 115.0, 87.0, 51.9, 45.5, 30.7, 28.0; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6Na^{35}Cl$ $[M+Na]^+$: 507.1293; found:507.1296; HPLC analysis: *er* = 96:4 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 9.61 min, t_{minor} = 10.72 min.

***tert*-Butyl (*R*)-2-(3-(methoxycarbonyl)-2-(4-(trifluoromethyl)phenyl)- but-3-en-1-yl)-3-nitro-*1H*-indole-1-carboxylate (3g).**



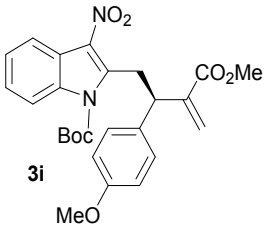
Yellow solid; Yield : 75%; $[\alpha]_D^{30}$: −99.8 (*c* = 1.30, CH_2Cl_2); mp: 128-129℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.19 (m, 1H), 7.99 – 7.97 (m, 1H), 7.50 – 7.33 (m, 4H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.45 (s, 1H), 5.91 (s, 1H), 4.48 – 4.44 (m, 1H), 4.39 – 4.26 (m, 2H), 3.54 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 149.1, 144.82, 142.4, 141.4, 133.8, 132.0, 128.8 (q, *J* = 32.0 Hz), 128.1, 126.1, 125.8, 125.3 (d, *J* = 4.0 Hz), 125.2, 121.2, 120.7, 115.0, 87.1, 52.0, 45.9, 30.6, 27.9; HRMS (ESI): cacld for $C_{26}H_{25}N_2O_6NaF_3$ $[M+Na]^+$: 541.1557; found: 541.1548; HPLC analysis: *er* = 98:2 on an IC column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 13.44 min, t_{minor} = 13.99 min.

***tert*-Butyl (*R*)-2-(3-(methoxycarbonyl)-2-(p-tolyl)but-3-en-1-yl)-3-nitro- 1*H*-indole-1-carboxylate (3h).**



Yellow oil; Yield : 71%; $[\alpha]_D^{30}$: −89.3 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.16 (m, 1H), 8.03 – 8.01 (m, 1H), 7.40 – 7.35 (m, 2H), 6.97 (s, 4H), 6.36 (s, 1H), 5.84 (s, 1H), 4.38 – 4.22 (m, 3H), 3.50 (s, 3H), 2.25 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 149.1, 142.9, 142.3, 137.4, 136.4, 133.9, 131.9, 129.1, 127.5, 125.9, 125.0, 121.3, 120.6, 114.9, 86.8, 51.8, 45.5, 30.9, 27.9, 21.0; HRMS (ESI): cacld for $C_{26}H_{28}N_2ONa$ $[M+Na]^+$: 487.1839; found: 487.1833; HPLC analysis: *er* = 96:4 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 254 nm; t_{major} = 8.42 min, t_{minor} = 9.60 min.

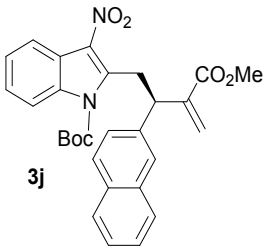
***tert*-Butyl (*R*)-2-(3-(methoxycarbonyl)-2-(4-methoxyphenyl)but-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3i).**



3i

Yellow oil; Yield : 60%; $[\alpha]_D^{30}$: −87.1 (*c* = 1.00, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.15 (m, 1H), 8.03 – 8.00 (m, 1H), 7.39 – 7.35 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.35 (s, 1H), 5.83 (s, 1H), 4.36 – 4.20 (m, 3H), 3.72 (s, 3H), 3.51 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.4, 149.1, 142.9, 142.4, 133.9, 132.4, 131.9, 128.6, 125.9, 125.0, 124.7, 121.3, 120.6, 114.9, 113.7, 86.8, 55.1, 51.8, 45.2, 30.9, 27.9; HRMS (ESI): cacld for $C_{26}H_{28}N_2O_7Na$ $[M+Na]^+$: 503.1789; found: 503.1789; HPLC analysis: *er* = 93:7 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 254 nm; t_{major} = 9.99 min, t_{minor} = 11.50 min.

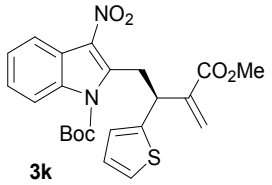
***tert*-Butyl (*R*)-2-(3-(methoxycarbonyl)-2-(naphthalen-2-yl)but-3-en-1-yl)- 3-nitro-1*H*-indole-1-carboxylate (3j).**



3j

Yellow soild; Yield : 88%; $[\alpha]_D^{30}$: −136.4 (*c* = 1.00, CH_2Cl_2); mp: 126-127℃; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 – 8.17 (m, 1H), 7.99 – 7.98 (m, 1H), 7.74 – 7.66 (m, 3H), 7.59 (s, 1H), 7.42 – 7.37 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.43 (s, 1H), 5.90 (s, 1H), 4.61 (t, *J* = 7.7 Hz, 1H), 4.43 – 4.41 (m, 2H), 3.48 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 149.0, 142.9, 142.1, 138.2, 133.9, 133.3, 132.4, 128.0, 127.8, 127.5, 126.2, 126.1, 125.9, 125.6 125.0, 121.3, 120.6, 114.9, 86.9, 51.9, 45.9, 30.9, 27.8; HRMS (ESI): cacld for $C_{29}H_{28}N_2O_6Na$ $[M+Na]^+$: 523.1840; found: 523.1844; HPLC analysis: *er* = 92:8 on an AS-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{minor} = 11.96 min, t_{major} = 13.38 min.

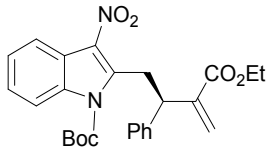
***tert*-Butyl (*S*)-2-(3-(methoxycarbonyl)-2-(thiophen-2-yl)but-3-en-1-yl)- 3-nitro-1*H*-indole-1-carboxylate (3k).**



3k

Yellow solid; Yield : 99%; $[\alpha]_D^{30}$: −53.8 (*c* = 1.00, CH_2Cl_2); mp: 128-129℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.20 (m, 1H), 8.06 – 8.04 (m, 1H), 7.40 – 7.38 (m, 2H), 7.10 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.86 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 6.35 (s, 1H), 5.87 (s, 1H), 4.73 (t, *J* = 7.9 Hz, 1H), 4.36 (d, *J* = 7.9 Hz, 2H), 3.50 (s, 3H), 1.70 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 149.1, 144.4, 142.0, 141.8, 134.0, 132.1, 126.8, 126.2, 126.1, 125.1, 124.8, 124.2, 121.3, 120.6, 115.1, 87.0, 51.9, 40.9, 32.0, 28.0; HRMS (ESI): cacld for $C_{23}H_{24}N_2O_6NaS$ $[M+Na]^+$: 479.1247; found: 479.1238; HPLC analysis: *er* = 89:11 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 8.94 min, t_{minor} = 9.84 min.

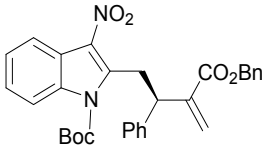
***tert*-Butyl (*R*)-2-(3-(ethoxycarbonyl)-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3l).**



3l

Yellow oil; Yield : 45%; $[\alpha]_D^{30}$: −65.2 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.10 (m, 1H), 8.02 –8.00 (m, 1H), 7.39 – 7.31 (m, 2H), 7.16 – 7.11(m, 3H), 7.06 –7.04 (m, 2H), 6.37 (s, 1H), 5.81 (s, 1H), 4.40 – 4.19 (m, 3H), 3.98 – 3.85 (m, 2H), 1.66 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 149.1, 142.7, 142.5, 140.6, 134.0, 132.0, 128.3, 127.7, 126.9, 125.9, 125.0, 124.9, 121.3, 120.6, 115.0, 86.9, 60.8, 45.9, 30.9, 28.0, 13.8; HRMS (ESI): cacld for $C_{26}H_{28}N_2O_6Na$ $[M+Na]^+$: 487.1840; found: 487.1847; HPLC analysis: *er* = 88:12% on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.8 mL/min, λ = 220 nm; t_{major} = 4.94 min, t_{minor} = 5.41 min.

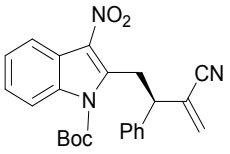
***tert*-Butyl (*R*)-2-(3-((benzyloxy)carbonyl)-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (3m).**



3m

Yellow oil; Yield : 64%; $[\alpha]_D^{30}$: −56.5 (*c* = 1.67, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.11 (m, 1H), 8.04 – 7.99 (m, 1H), 7.41 – 7.34 (m, 2H), 7.28 – 7.23 (m, 3H), 7.17 – 7.12 (m, 3H), 7.12 – 7.07 (m, 2H), 7.06 – 7.01 (m, 2H), 6.46 (s, 1H), 5.90 (s, 1H), 4.97 (d, *J* = 12.5 Hz, 1H), 4.91 (d, *J* = 12.5 Hz, 1H), 4.44 – 4.33 (m, 2H), 4.26–4.21 (m, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 149.1, 142.6, 142.1, 140.3, 135.6, 133.9, 132.0, 128.5, 128.0, 127.9, 127.7, 126.9, 125.9, 125.4, 125.0, 121.3, 120.6, 115.0, 86.9, 66.5, 46.0, 30.8, 27.9; HRMS (ESI): cacld for $C_{31}H_{30}N_2O_6Na$ $[M+Na]^+$: 549.1996; found: 549.1987; HPLC analysis: *er* = 82.5:17.5 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.8 mL/min, λ = 220 nm; t_{major} = 6.26 min, t_{minor} = 8.24 min.

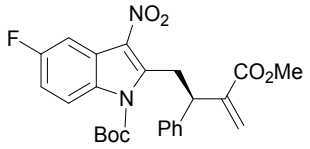
***tert*-Butyl (*R*)-2-(3-cyano-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole- 1-carboxylate (3n).**



3n

Yellow solid; Yield : 70%; $[\alpha]_D^{30}$: 0.60 (*c* = 1.00, CH_2Cl_2); mp: 122-123℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.15 (m, 1H), 8.01 – 7.91 (m, 1H), 7.44 – 7.33 (m, 2H), 7.29 – 7.21 (m, 3H), 7.17 (dd, *J* = 7.5, 1.9 Hz, 2H), 5.95 (s, 1H), 5.81 (d, *J* = 1.2 Hz, 1H), 4.44 – 4.28 (m, 2H), 4.04 (t, *J* = 7.7 Hz, 1H), 1.71 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 141.6, 138.1, 133.8, 132.1, 130.8, 128.9, 128.0, 127.6, 126.2, 125.6, 125.2, 121.2, 120.7, 117.7, 115.1, 87.4, 49.8, 30.5, 28.0; HRMS (ESI): cacld for $C_{24}H_{23}N_3O_4Na$ $[M]^+$: 440.1581; found: 440.1581; HPLC analysis: *er* = 64:36 on an IG column: hexane/*i*-PrOH = 80:20, flow rate = 0.8 mL/min, λ = 220 nm; t_{minor} = 11.50 min, t_{major} = 13.23 min.

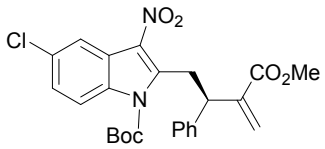
***tert*-Butyl (*R*)-5-fluoro-2-(3-(methoxycarbonyl)-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (5a).**



5a

Yellow solid; Yield : 57%; $[\alpha]_D^{30}$: −84.9 (*c* = 1.00, CH_2Cl_2); mp: 129-130℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 9.3, 4.5 Hz, 1H), 7.83 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.17 – 7.05 (m, 6H), 6.39 (s, 1H), 5.85 (s, 1H), 4.40 – 4.32 (m, 2H), 4.24 – 4.21 (m, 1H), 3.51 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 160.4 (d, *J* = 243 Hz), 148.81 (s), 144.1, 142.0, 140.2, 130.2, 128.4, 127.6, 127.0, 125.2, 122.3 (d, *J* = 11.4 Hz), 116.4 (d, *J* = 9.1 Hz), 114.0 (d, *J* = 25.3 Hz), 106.47 (d, *J* = 26.9 Hz), 87.3, 51.9, 45.9, 31.0, 27.9; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6NaF$ $[M+Na]^+$: 491.1589; found: 491.1579; HPLC analysis: *er* = 94:6 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 8.49 min, t_{minor} = 9.16 min.

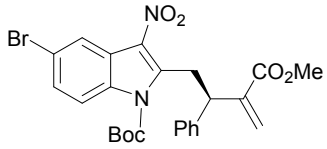
***tert*-Butyl (*R*)-5-chloro-2-(3-(methoxycarbonyl)-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (5b).**



5b

Yellow oil; Yield : 44%; $[\alpha]_D^{30}$: −71.6 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.33 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.17 – 7.14 (m, 3H), 7.06 – 7.04 (m, 2H), 6.39 (s, 1H), 5.85 (s, 1H), 4.39 – 4.31 (m, 2H), 4.23 – 4.19 (m, 1H), 3.52 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 148.7, 143.8, 142.1, 140.2, 132.3, 131.2, 131.1, 128.4, 127.6, 127.1, 126.3, 125.2, 122.4, 120.2, 116.2, 87.5, 51.9, 45.9, 30.9, 27.9; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6NaCl$ $[M+Na]^+$: 507.1293; found: 507.1286; HPLC analysis: *er* = 97.5:2.5 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 8.85 min, t_{minor} = 9.31 min.

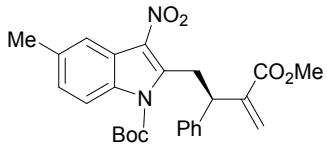
***tert*-Butyl (*R*)-5-bromo-2-(3-(methoxycarbonyl)-2-phenylbut-3-en-1-yl)-3-nitro-1*H*-indole-1-carboxylate (5c).**



5c

Yellow oil; Yield : 56%; $[\alpha]_D^{30}$: −71.7 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.46 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.18 – 7.14 (m, 3H), 7.05 – 7.03 (m, 2H), 6.39 (s, 1H), 5.85 (s, 1H), 4.38 – 4.30 (m, 2H), 4.22 – 4.16 (m, 1H), 3.52 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 148.7, 143.7, 142.0, 140.1, 132.6, 131.0, 129.0, 128.4, 127.6, 127.0, 125.2, 123.1, 122.8, 118.7, 116.5, 87.5, 51.9, 45.9, 30.9, 27.9; HRMS (ESI): cacld for $C_{25}H_{25}N_2O_6Na^{79}Br$ $[M+Na]^+$: 551.0788; found: 551.0778; HPLC analysis: *er* = 96:4 on an AS-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{minor} = 9.93 min, t_{major} = 10.96 min.

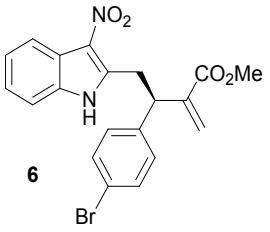
***tert*-Butyl (*R*)-2-(3-(methoxycarbonyl)-2-phenylbut-3-en-1-yl)-5-methyl-3-nitro-1*H*-indole-1-carboxylate (5d).**



5d

White solid; Yield : 47%; $[\alpha]_D^{30}$: −75.7 (*c* = 1.00, CH_2Cl_2); mp: 53-54℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.09 (s, 1H), 7.17 – 7.14 (m, 3H), 7.05 – 7.03 (m, 2H), 6.41 (s, 1H), 5.87 (s, 1H), 4.44 – 4.37 (m, 2H), 4.27 – 4.23 (m, 1H), 3.54 (s, 3H), 2.70 (s, 3H), 1.71 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 148.2, 147.3, 147.0, 141.9, 140.0, 131.3, 131.0, 130.5, 128.5, 127.6, 127.2, 125.3, 124.4, 123.5, 112.9, 88.4, 52.0, 45.9, 31.1, 27.9, 20.9; HRMS (FAB): cacld for $C_{26}H_{28}N_2O_6$ $[M]^+$: 464.1947; found: 464.1947; HPLC analysis: *er* = 94:6 on an AS-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{minor} = 14.48 min, t_{major} = 15.70 min.

Methyl (*R*)-3-(4-bromophenyl)-2-methylene-4-(3-nitro-1*H*-indol-2-yl)butanoate (6)



6

To a solution of **3d** (53 mg, 0.1 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was added TFA (0.10 mL) at room temperature overnight. After completion of the reaction, the reaction solution was neutralized with saturated $NaHCO_{3(aq)}$ and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated. The crude was purified by silica gel flash chromatography (Hexanes/EA 5:1 to 2:1) to afford the pure product **6** (36 mg).

Yellow solid; Yield : 84%; $[\alpha]_D^{30}$: −116.4 (*c* = 1.20, CH_2Cl_2); mp: 53-54℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.21 (m, 5H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 5.80 (s, 1H), 4.52 (t, *J* = 7.9 Hz, 1H), 3.97 (dd, *J* = 14.3, 7.7 Hz, 1H), 3.73 (dd, *J* = 14.3, 8.1 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 142.7, 141.3, 139.8, 132.8, 131.8, 129.3, 126.8, 126.4, 124.6, 124.0, 121.4, 121.1, 120.7, 111.7, 52.3, 45.1, 32.9; HRMS (ESI): cacld for $C_{20}H_{17}N_2O_4{}^{79}BrNa[M+Na]^+$: 451.0263; found: 451.0266; HPLC analysis: *er* = 96:4 on an AD-H column: hexane/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm; t_{major} = 15.91 min, t_{minor} = 16.85 min.

4. Computational methods

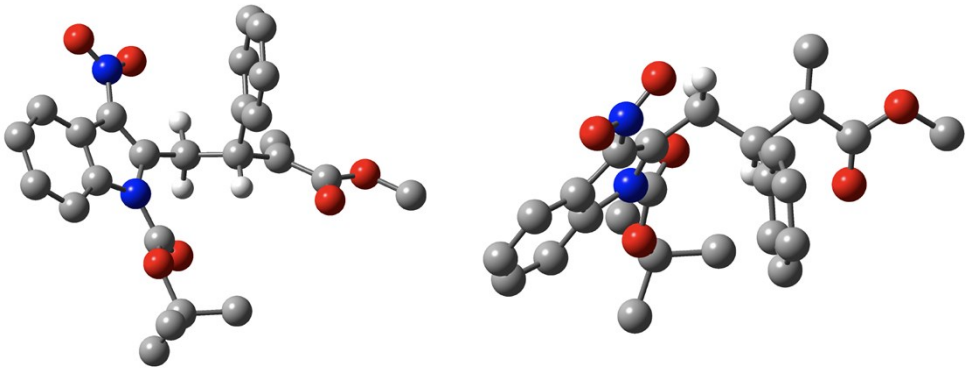
All Kohn-Sham DFT calculations were performed by Gaussian09 suite of ab initio

program[3]. All geometries were fully optimized by using a hybrid functional B3LYP[4-5] and 6-31g(d) basis set and applied for harmonic vibrational frequency calculations to confirm the minima under 298 K. In the conformation analysis, the species in *R* and *S* form with lowest energy were selected for further study. TD-DFT calculations were carried out to obtain the electronic circular dichroism (ECD) spectra. Two functional/basis sets CAM-B3LYP[4]/TZVP[7,8] and wB97XD[9]/6-311+g(d,p) were applied in the calculations for comparison. Computational solvent effect has been carried out with the polarizable conductor calculation model (CPCM)[10-11] for MeCN (ε = 37.5). The ECD data were analyzed by the program SpecDis.[12] The σ-value of 0.4 eV was applied for spectrometric correction.

Table S1. Relative energies for compound **3a** and **3d**.

3a		**3d**	
Conformation	**ΔΔ*G* (kcal mol□¹)**	**Conformation**	**ΔΔ*G* (kcal mol□¹)**
*R*1	0	*R*1	0
*R*2	2.43	*R*2	2.23
*R*3	3.02	*R*3	2.89
*R*4	1.96	*R*4	0.89
*R*5	0.54	*R*5	0.15
*R*6	1.79	*R*6	1.31
*R*7	3.60	*R*7	3.56
*R*8	4.05	*R*8	4.36
Conformation	**ΔΔ*G* (kcal mol□¹)**	**Conformation**	**ΔΔ*G* (kcal mol□¹)**
*S*1	0	*S*1	0
*S*2	3.70	*S*2	3.38
*S*3	1.78	*S*3	1.96
*S*4	4.27	*S*4	3.89
*S*5	1.79	*S*5	1.81
*S*6	3.88	*S*6	4.05
*S*7	2.79	*S*7	3.46
*S*8	2.92	*S*8	3.10

(A)



(B)

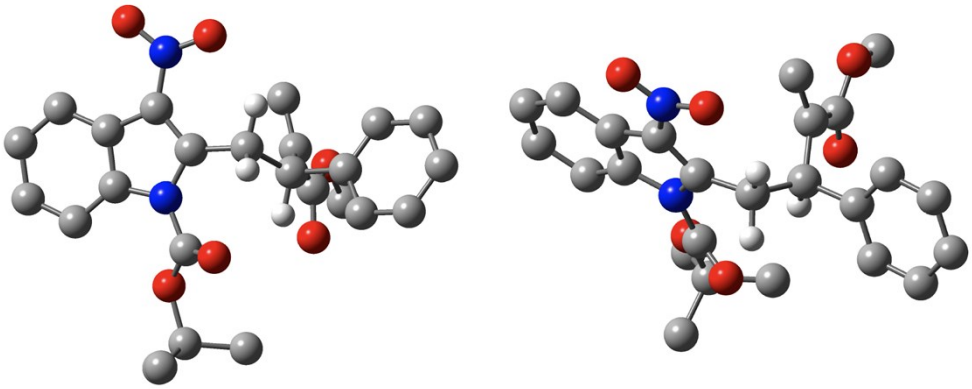


Figure S1. Two views of DFT-optimized geometries of (A) **3a**-*R*1 and (B) **3a**-*S*1. Some hydrogen atoms are omitted for clarity.

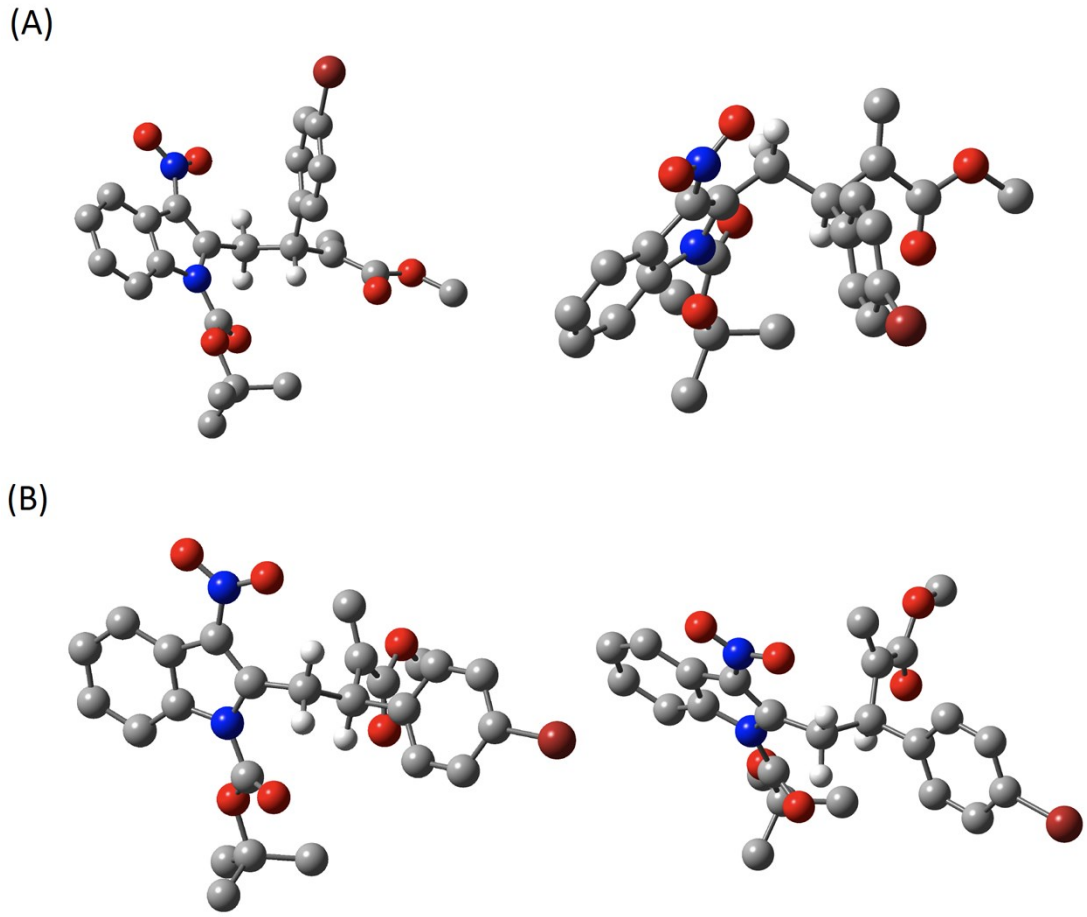


Figure S2. Two views of DFT-optimized geometries of (A) **3d**-*R*1 and (B) **3d**-*S*1. Some hydrogen atoms are omitted for clarity.

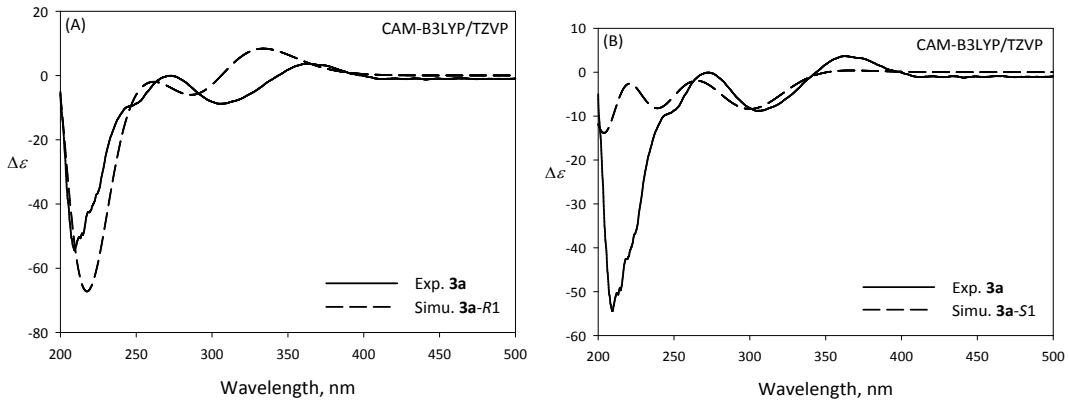


Figure S3. Experimental and calculated ECD spectra of (A) **3a**-*R*1 and (B) **3a**-*S*1 at CAM-B3LYP/TZVP level.

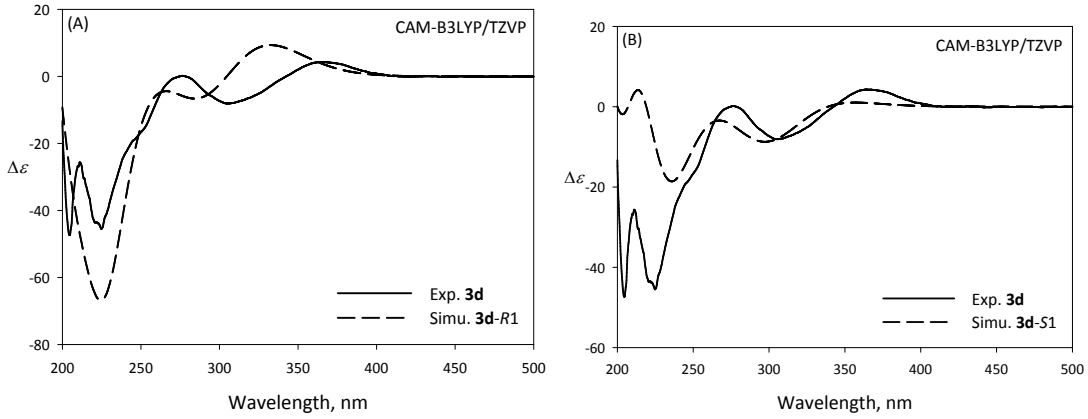


Figure S4. Experimental and calculated ECD spectra of (A) **3d**-*R*1 and (B) **3d**-*S*1 at CAM-B3LYP/TZVP level.

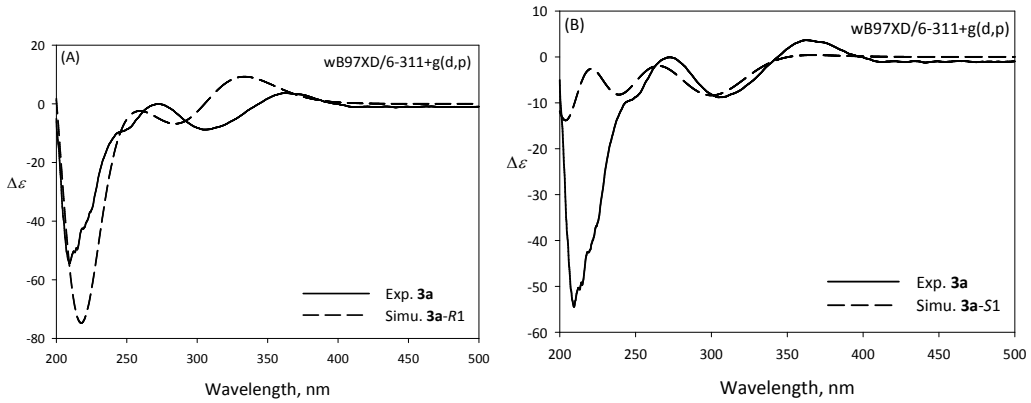


Figure S5. Experimental and calculated ECD spectra of (A) **3a**-*R*1 and (B) **3a**-*S*1 at wB97XD/6-311+g(d,p) level.

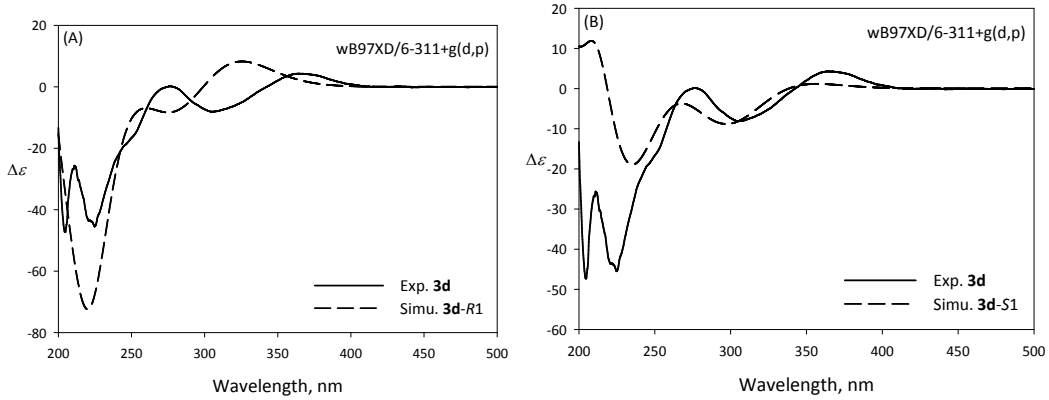


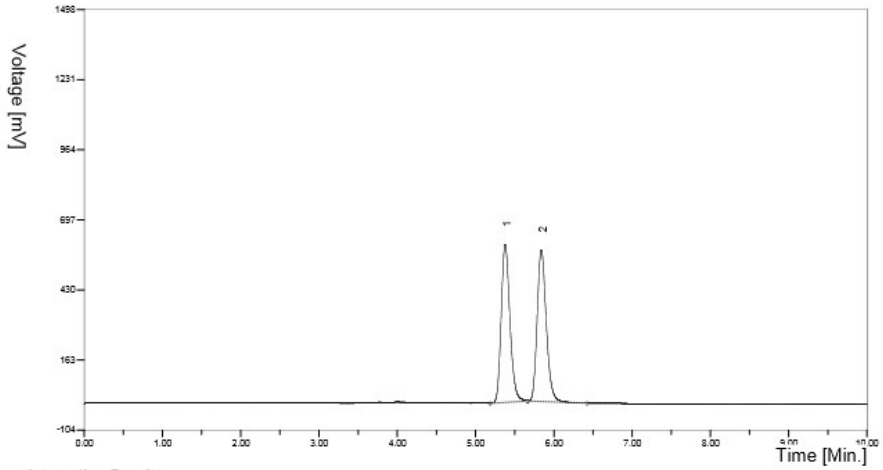
Figure S6. Experimental and calculated ECD spectra of (A) **3d**-*R*1 and (B) **3d**-*S*1 at wB97XD/6-311+g(d,p) level.

5. References

1. X.-F. Ding, W.-L. Yang, J. Mao, C.-X. Cao and W.-P. Deng, *Org. Lett.,* 2019, **21**, 5514−5518.
2. S. Kayal and S. Mukherjee, *Org. Lett.,* 2017, **19**, 4944−4947.
3. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc. Wallingford, CT, 2009.
4. C.-T. Lee, W.-T. Yang and R. G. Parr, *Phys. Rev. B*, **1988**, *37*, 785-789.
5. A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652.
6. T. Yanai, D. Tew and N. Handy, *Chem. Phys. Lett.*, **2004**, *393*, 51-57.
7. A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, **1992**, *97*, 2571-2577.
8. A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, **1994**, *100*, 5829-5835.
9. J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615-6620.
10. V. Barone and M. Cossi, *J. Phys. Chem. A*, **1998**, *102*, 1995-2001.
11. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, **2003**, *24*, 669-681.
12. T. Bruhn, A. Schaumlöffel, Y. Hemberger, SpecDis version 1.63, University of Wuerzburg, Germany, **2015**.

6. Copies of HPLC Spectra of Racemic and Chiral Products

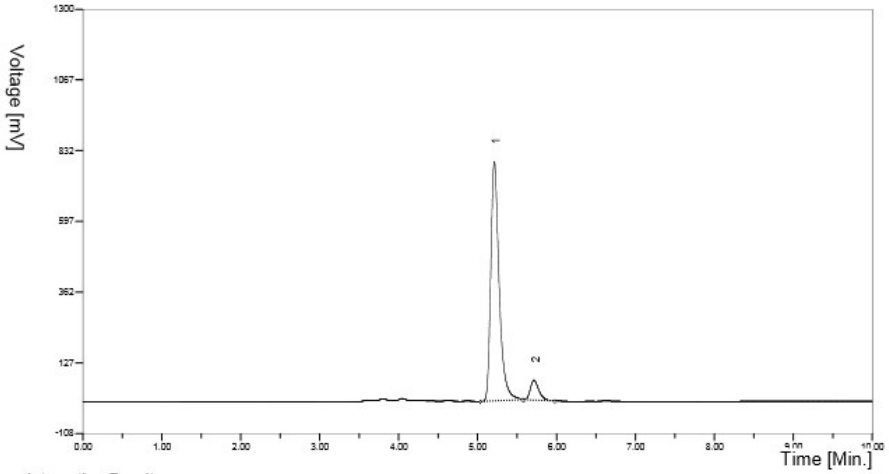
***Rac*-3a**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	5.38	4658.94	49.9524
2	5.84	4667.82	50.0476
Total		9326.76	100

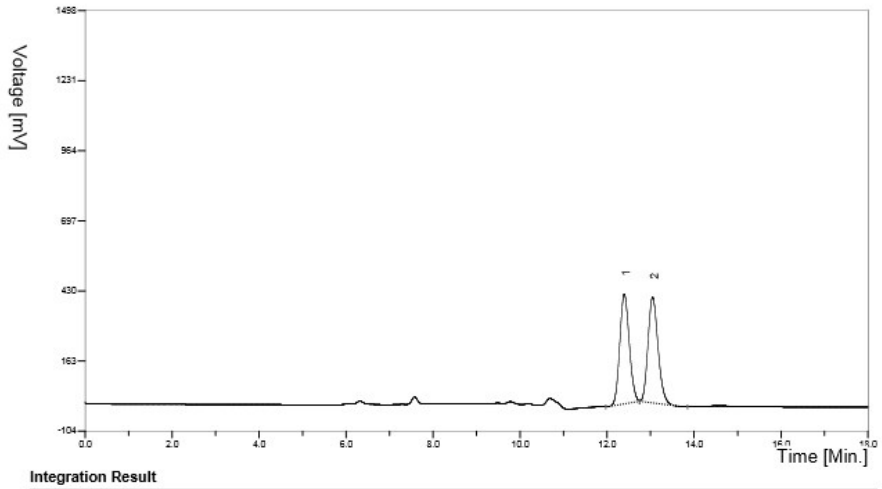
3a



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	5.21	793.56	5829.04	92.1667
2	5.71	65.96	495.41	7.8333
Total		859.52	6324.45	100

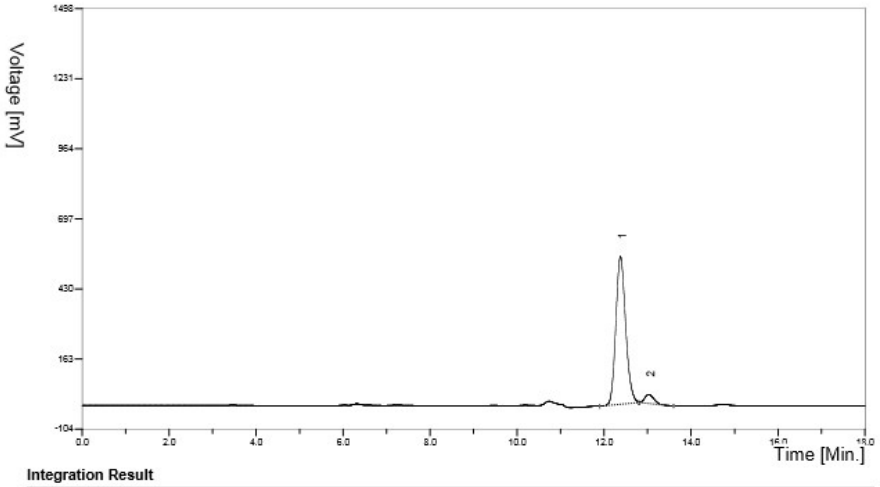
***Rac*-3b**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.40	6322.45	49.7191
2	13.05	6393.89	50.2809
Total		12716.34	100

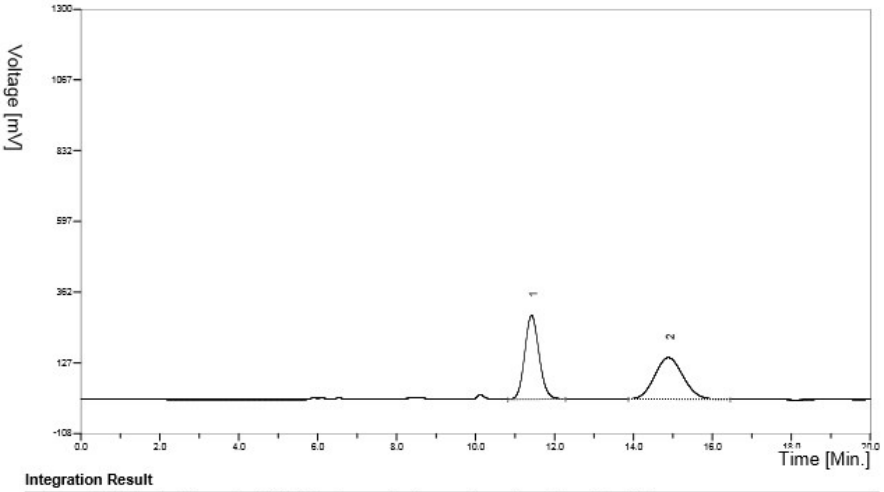
3b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.38	8795.27	95.3046
2	13.03	433.32	4.6954
Total		9228.58	100

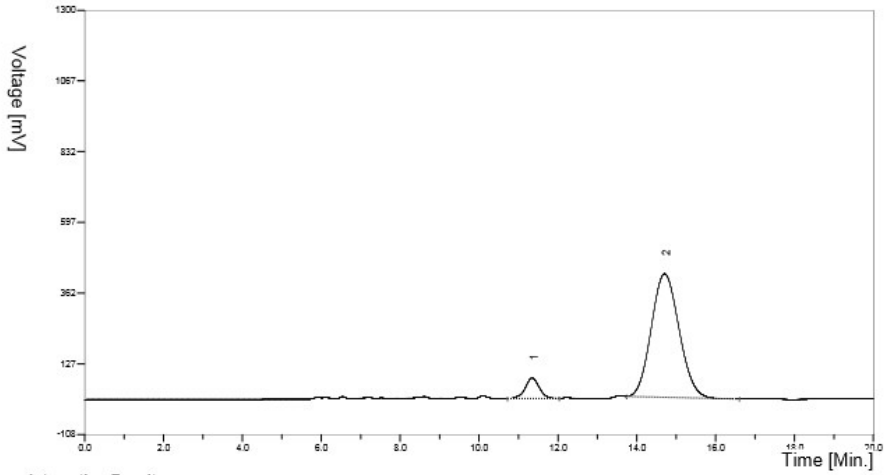
***Rac*-3c**



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	11.42	278.65	7017.56	50.3905
2	14.88	137.77	6908.80	49.6095
Total		416.42	13926.37	100

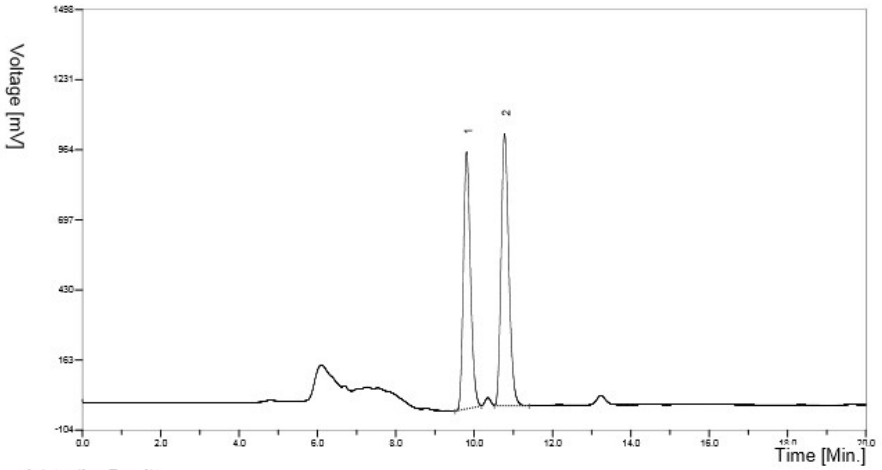
3c



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	11.35	68.01	1704.13	7.8228
2	14.70	410.21	20080.09	92.1772
Total		478.23	21784.21	100

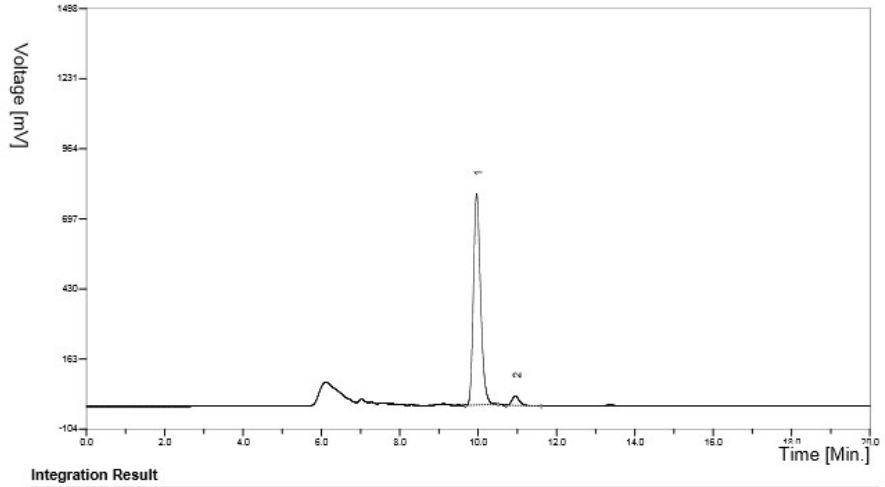
***Rac*-3d**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.81	12315.48	46.5684
2	10.78	14130.50	53.4316
Total		26445.99	100

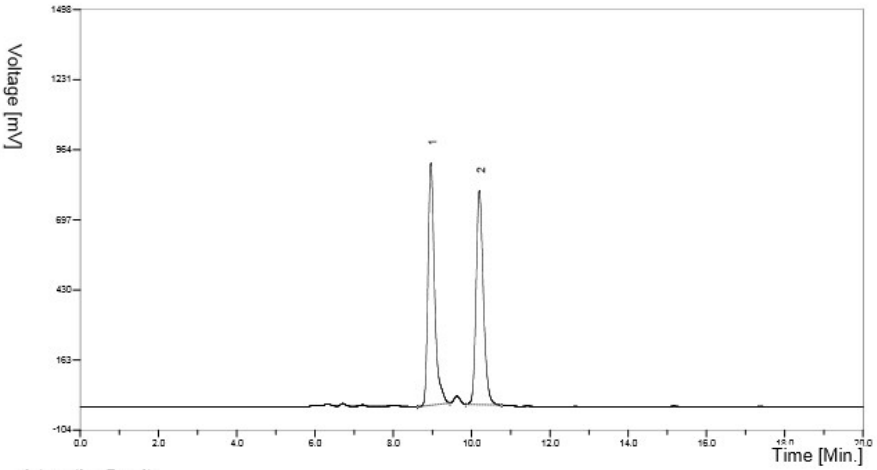
3d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.96	10204.27	95.5303
2	10.95	477.44	4.4697
Total		10681.71	100

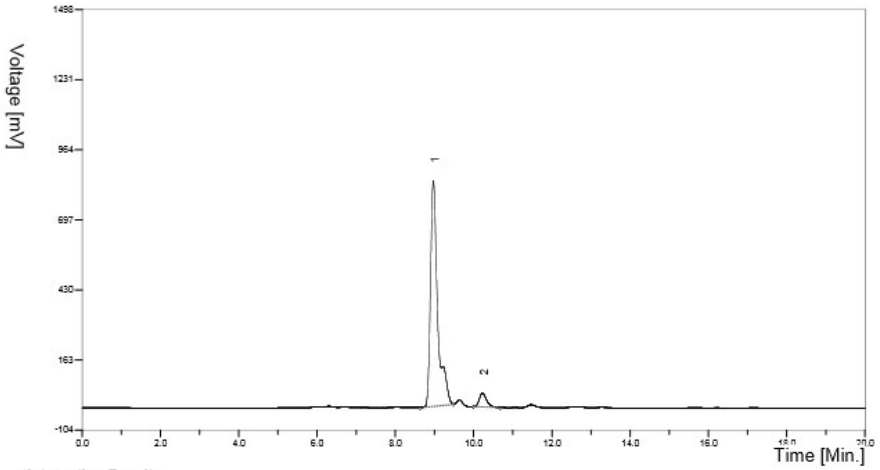
***Rac*-3e**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.96	10775.37	50.6565
2	10.20	10496.05	49.3435
Total		21271.42	100

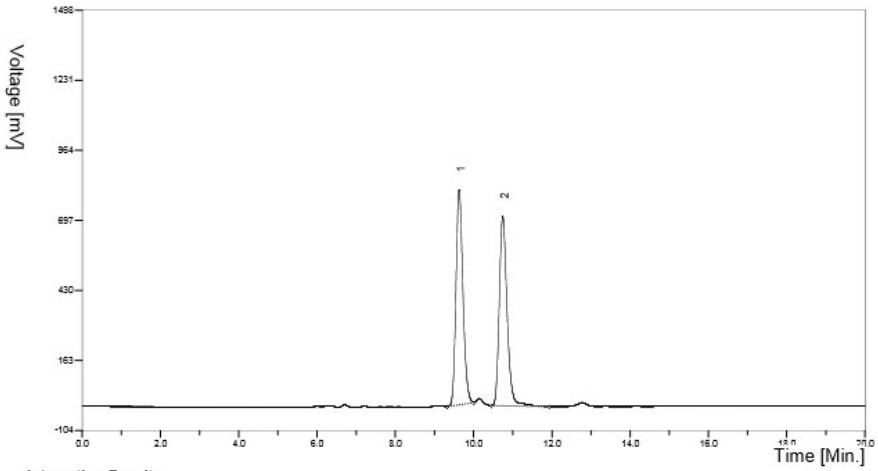
3e



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.97	10942.83	94.1322
2	10.23	682.14	5.8678
Total		11624.97	100

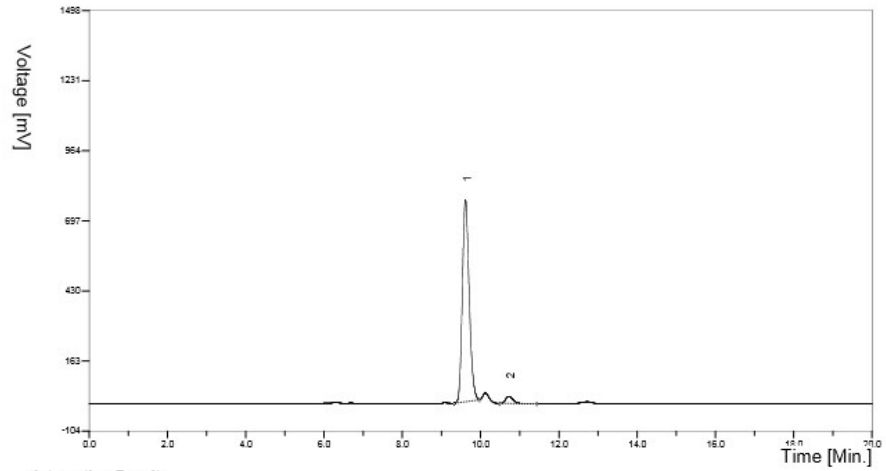
***Rac*-3f**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.63	10090.53	50.1342
2	10.75	10036.51	49.8658
Total		20127.04	100

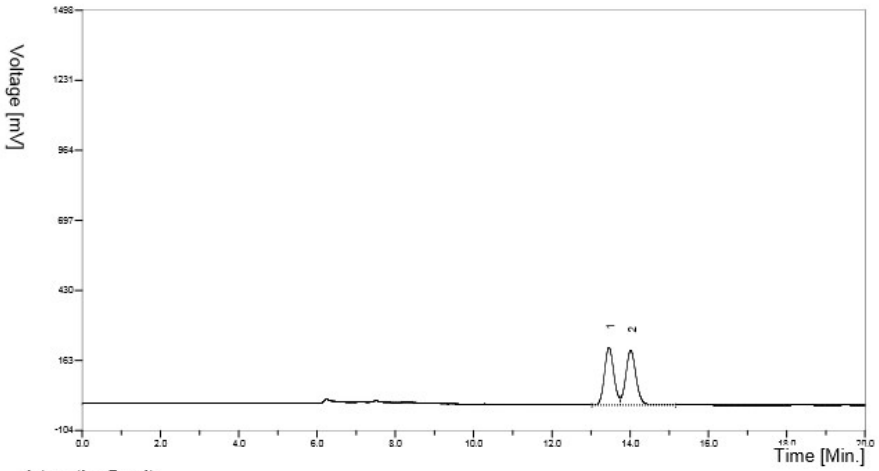
3f



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.61	9286.83	96.1525
2	10.72	371.61	3.8475
Total		9658.44	100

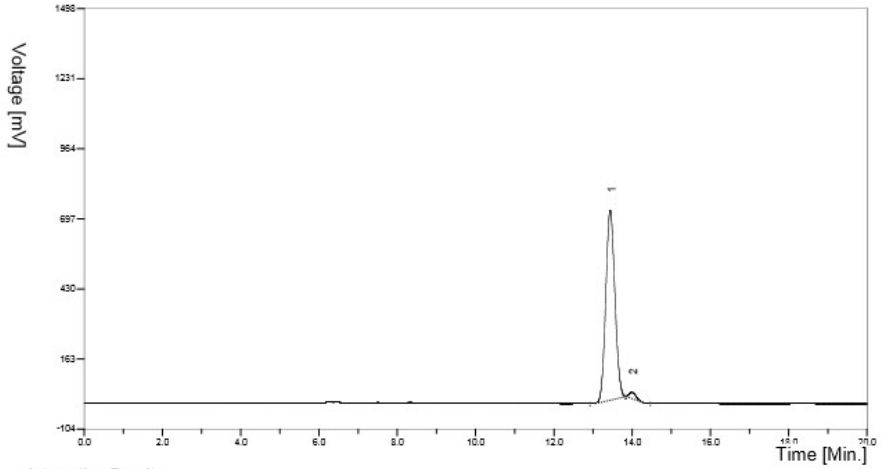
***Rac*-3g**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	13.46	3652.37	49.1994
2	14.01	3771.23	50.8006
Total		7423.60	100

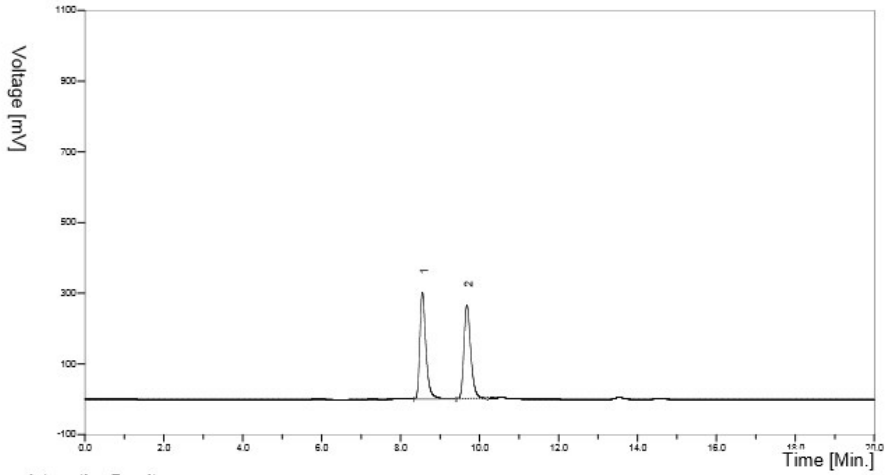
3g



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	13.44	11581.87	98.1907
2	13.99	213.42	1.8093
Total		11795.29	100

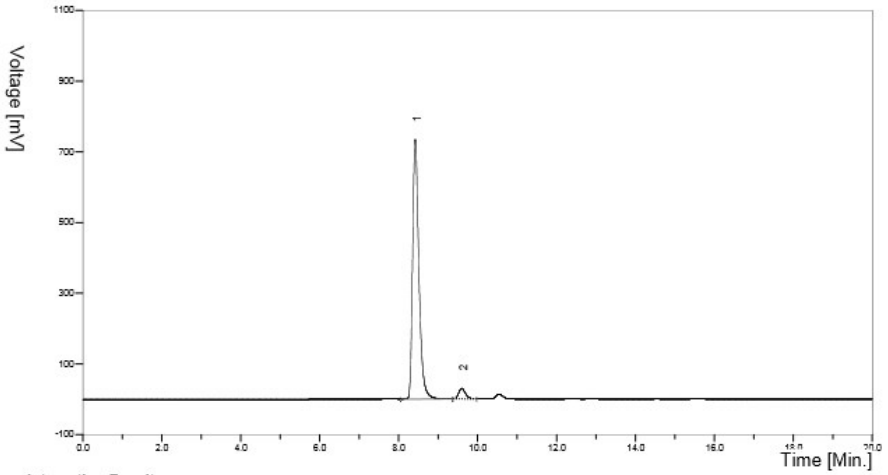
***Rac*-3h**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.55	3205.79	50.4750
2	9.68	3145.45	49.5250
Total		6351.24	100

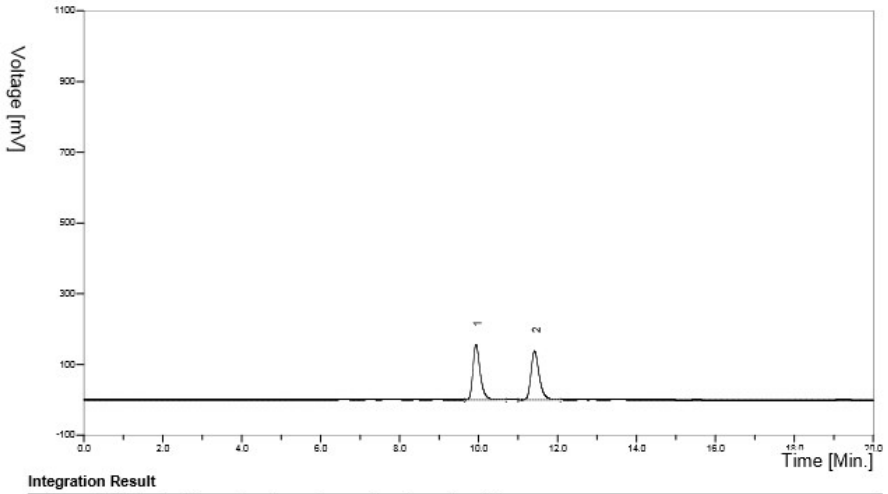
3h



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.42	8123.05	95.8118
2	9.60	355.08	4.1882
Total		8478.13	100

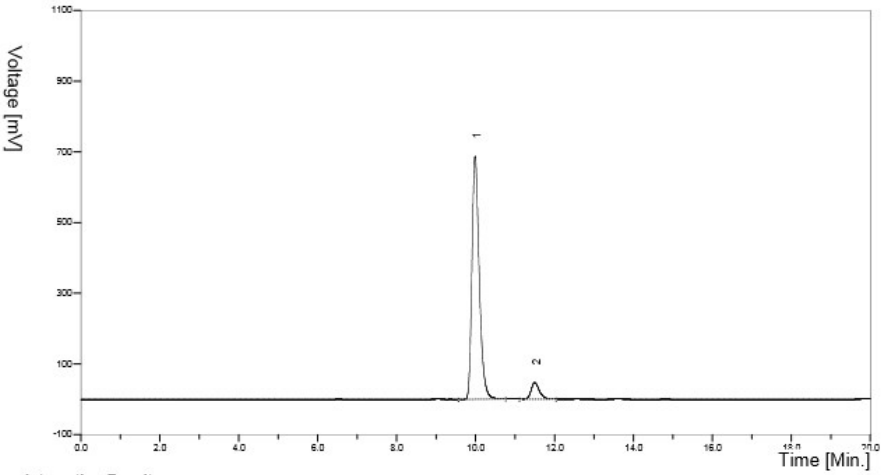
***Rac*-3i**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.94	1993.02	50.1726
2	11.42	1979.31	49.8274
Total		3972.33	100

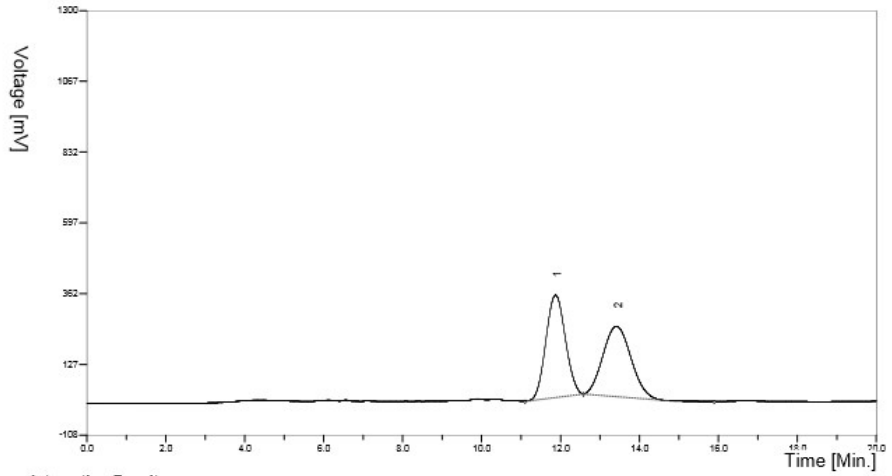
3i



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.99	8821.70	92.9306
2	11.50	671.09	7.0694
Total		9492.79	100

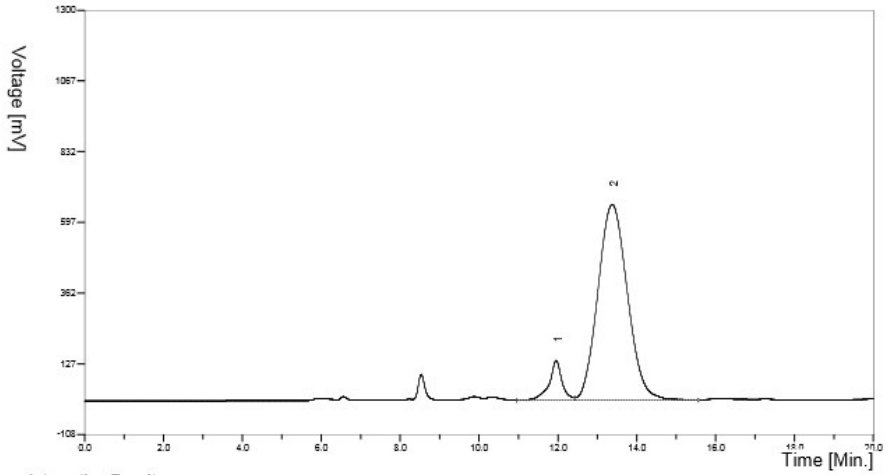
***Rac*-3j**



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	11.87	339.78	11648.79	51.6393
2	13.42	231.17	10909.23	48.3607
Total		570.95	22558.02	100

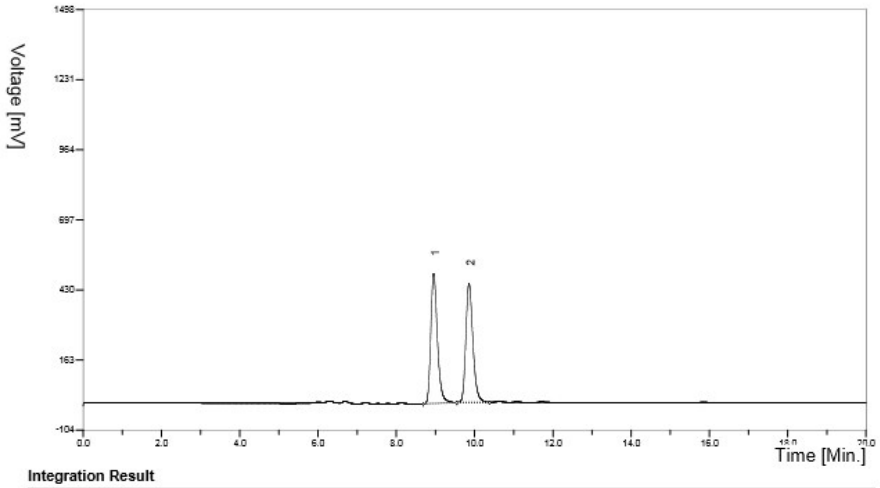
3j



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	11.96	131.75	2953.79	8.0586
2	13.38	649.52	33700.08	91.9414
Total		781.27	36653.87	100

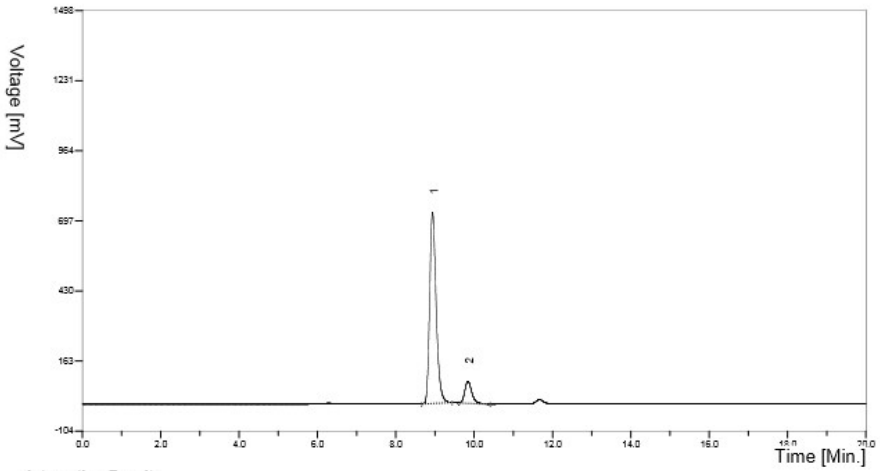
***Rac*-3k**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.95	5791.37	50.5738
2	9.86	5659.94	49.4262
Total		11451.31	100

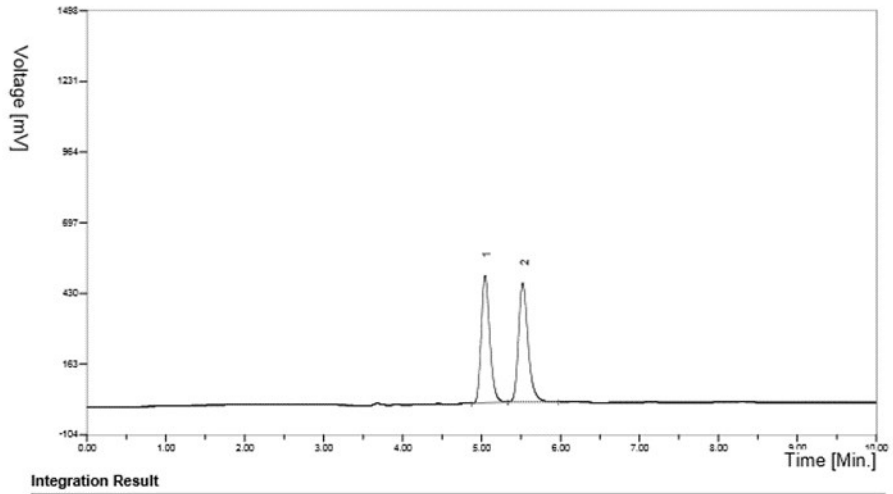
3k



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.94	8360.85	88.9481
2	9.84	1038.85	11.0519
Total		9399.70	100

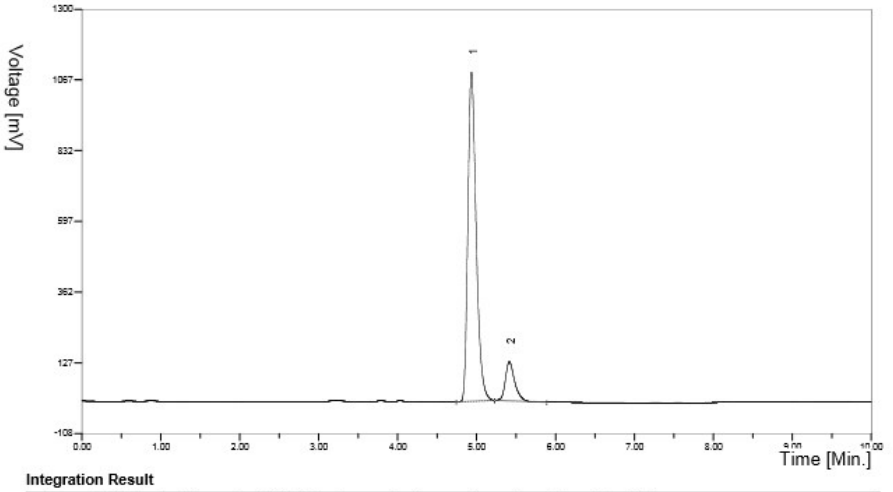
***Rac*-3l**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	5.05	3619.89	49.0979
2	5.52	3752.91	50.9021
Total		7372.79	100

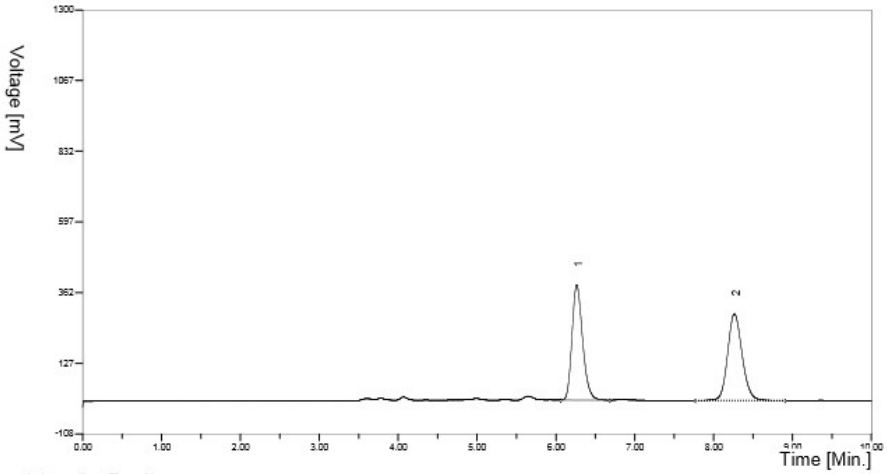
3l



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	4.94	1091.30	7941.54	88.1970
2	5.42	129.68	1062.78	11.8030
Total		1220.98	9004.32	100

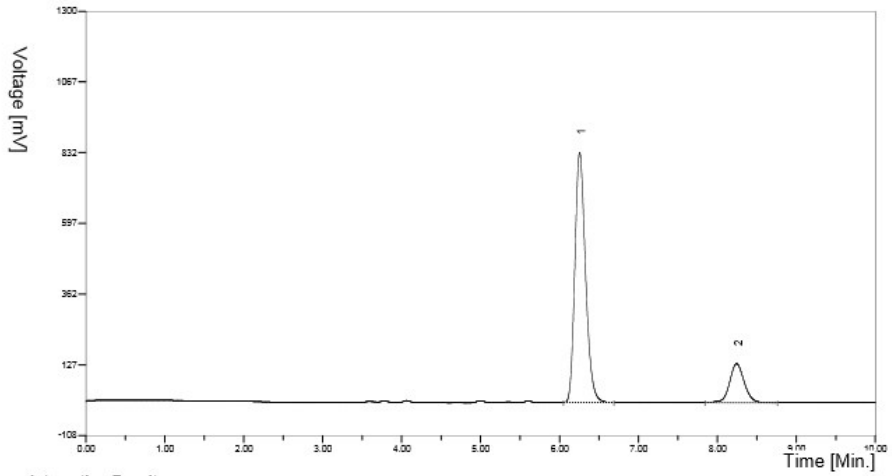
***Rac*-3m**



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	6.26	382.44	3596.07	49.3979
2	8.26	288.32	3683.73	50.6021
Total		670.75	7279.79	100

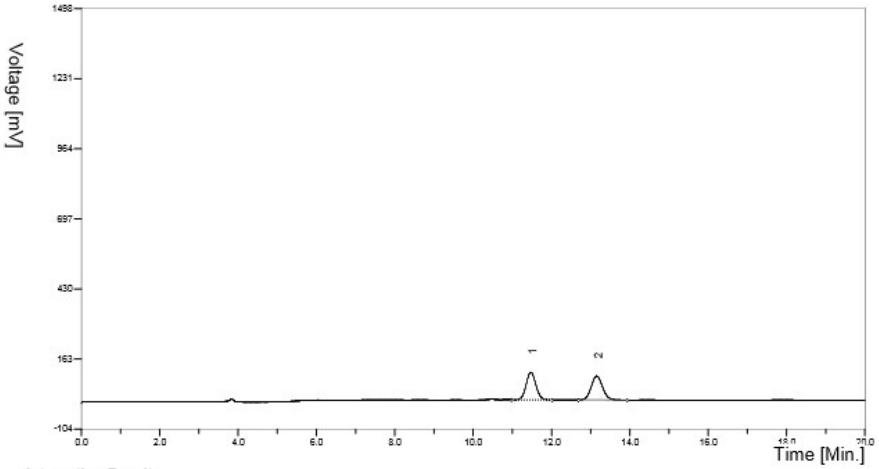
3m



Integration Result

#	Ret. Time(min)	Peak Height(mv)	Area(mv.sec)	Area Percentage(%)
1	6.26	829.73	7784.59	82.4872
2	8.24	129.15	1652.75	17.5128
Total		958.88	9437.34	100

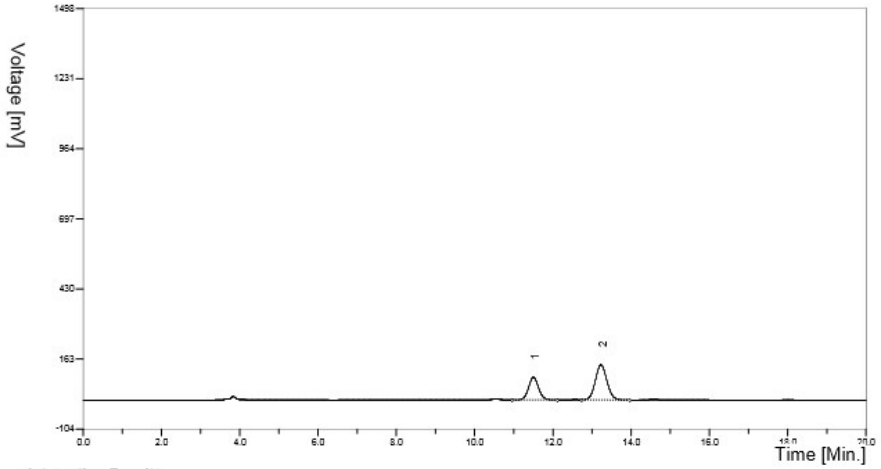
***Rac*-3n**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	11.47	1801.51	49.7436
2	13.15	1820.08	50.2564
Total		3621.58	100

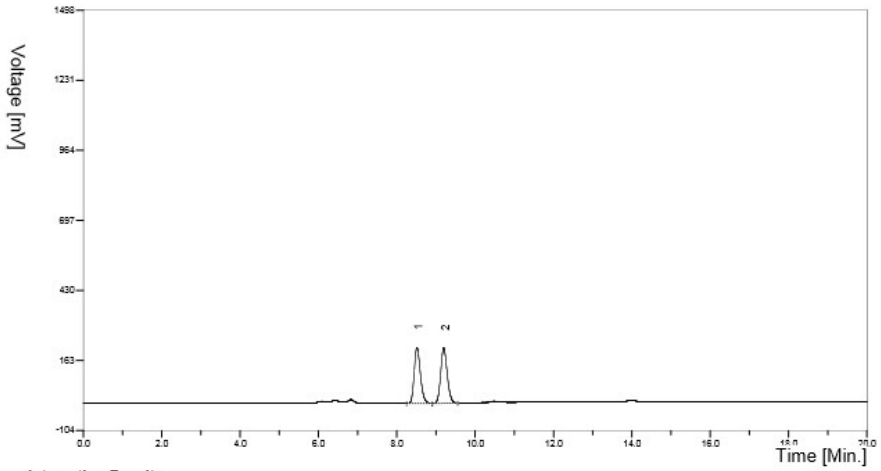
3n



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	11.50	1510.71	35.6788
2	13.23	2723.49	64.3212
Total		4234.20	100

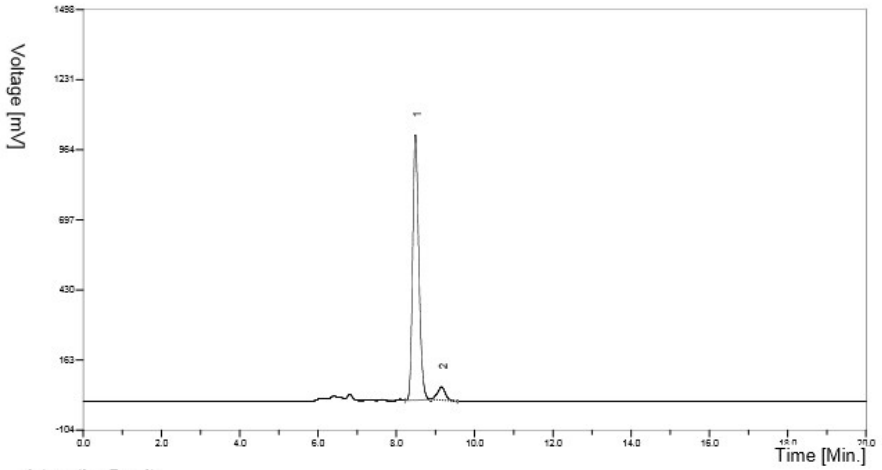
***Rac*-5a**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.52	2325.80	49.0189
2	9.20	2418.90	50.9811
Total		4744.70	100

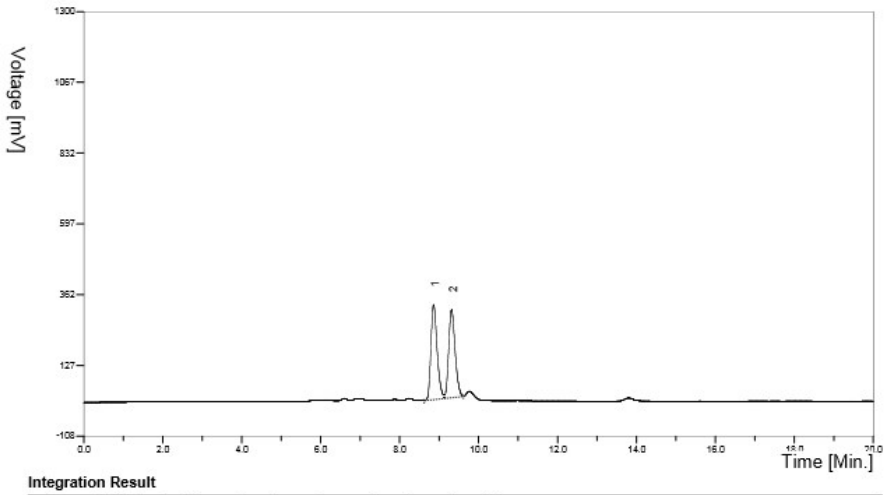
5a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.49	11059.43	94.0314
2	9.16	701.99	5.9686
Total		11761.43	100

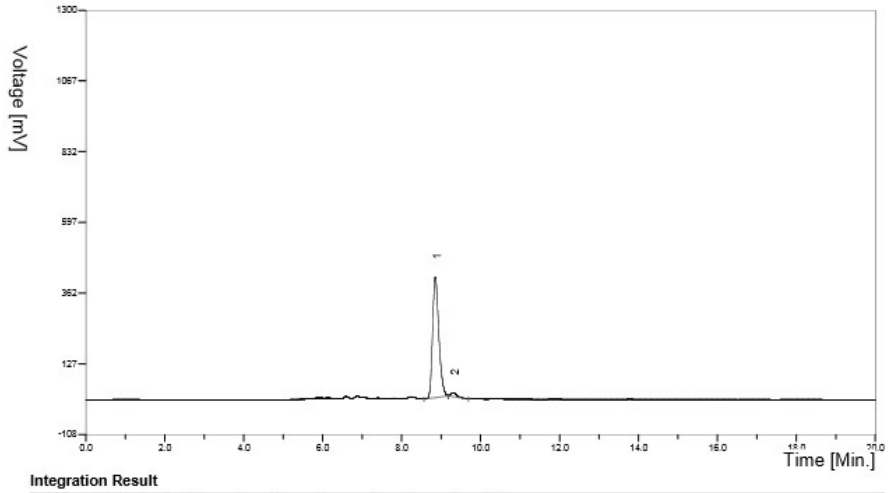
***Rac*-5b**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.86	3443.85	50.9988
2	9.32	3308.95	49.0012
Total		6752.81	100

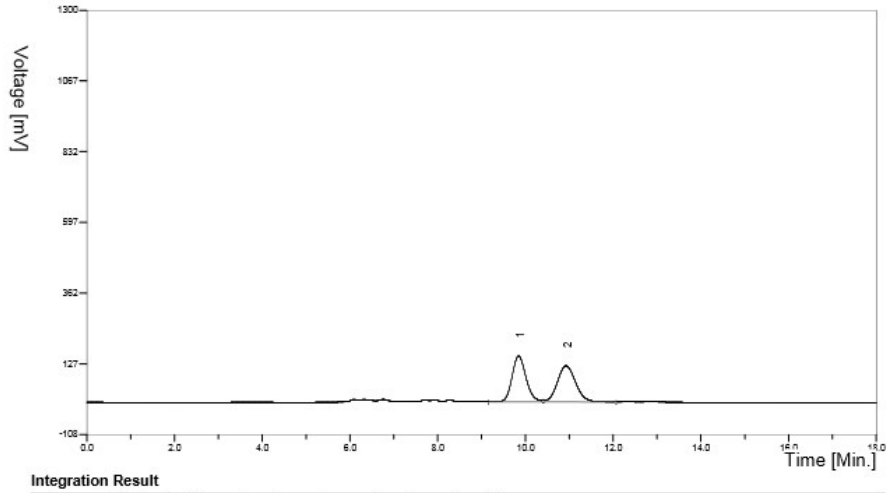
5b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.85	4393.57	97.3516
2	9.31	119.52	2.6484
Total		4513.09	100

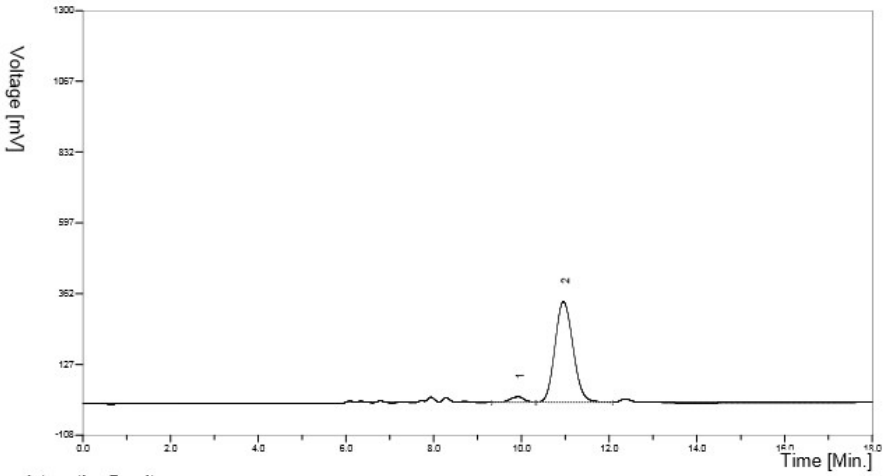
***Rac*-5c**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.84	3355.94	49.2198
2	10.93	3462.33	50.7802
Total		6818.28	100

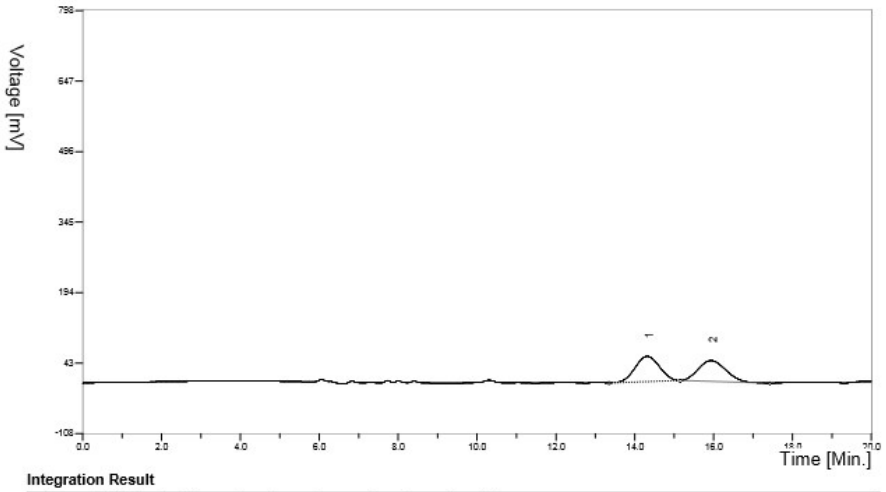
5c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.93	391.38	3.9371
2	10.96	9549.31	96.0629
Total		9940.69	100

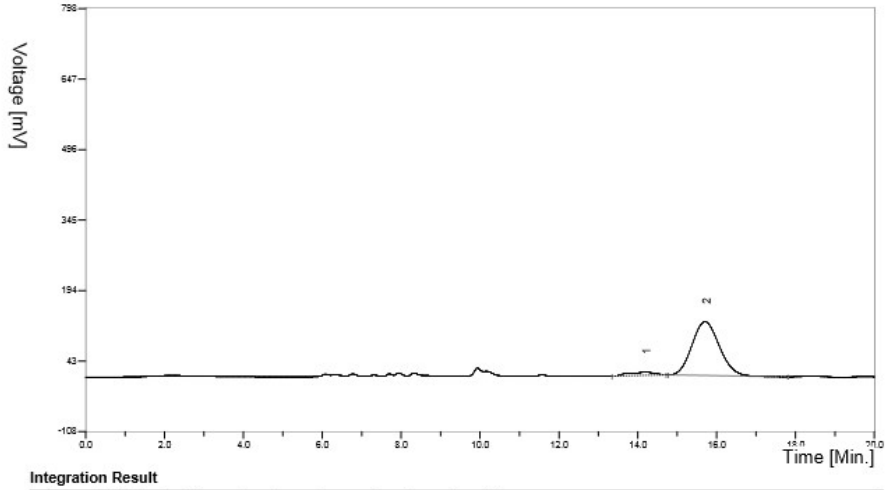
***Rac*-5d**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	14.32	2317.98	51.8815
2	15.94	2149.86	48.1185
Total		4467.84	100

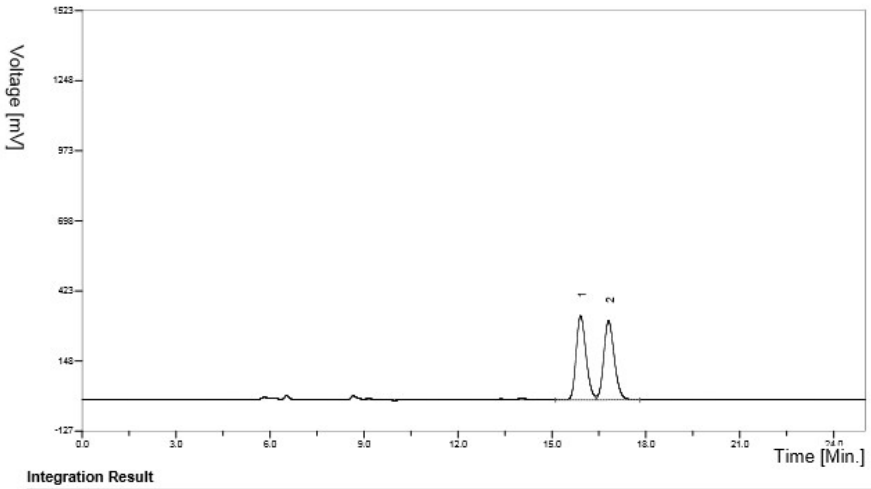
5d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	14.18	316.76	5.4109
2	15.70	5537.36	94.5891
Total		5854.13	100

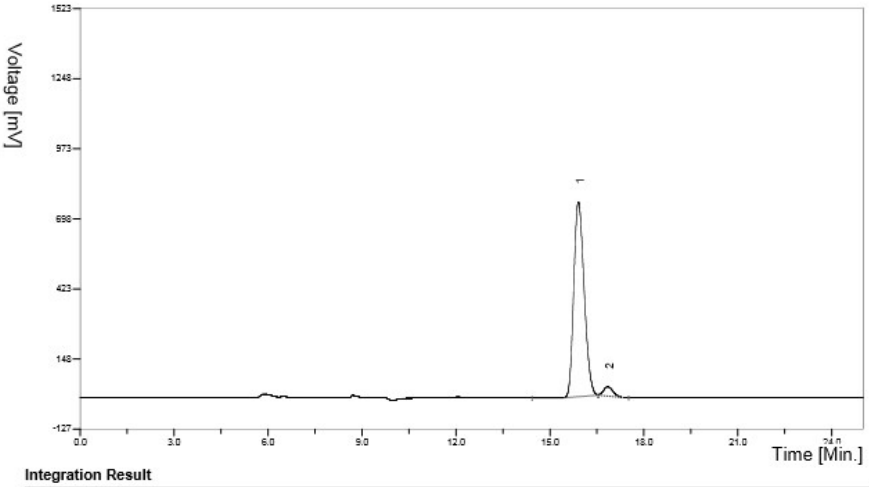
***Rac*-6**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	15.92	7198.87	49.9173
2	16.81	7222.74	50.0827
Total		14421.61	100

6



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	15.91	17337.35	95.8916
2	16.85	742.80	4.1084
Total		18080.15	100