Supporting Information:

Pd-Catalyzed Asymmetric Hydrogenation of Unprotected Indoles Activated by Brønsted Acids

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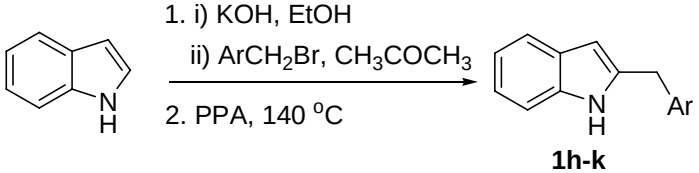
1. General and Materials

General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 spectrometers. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.23 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. TLC analysis was performed using glass-backed plates coated with 0.2 mm silica. Quantitative analysis was performed by ^{1}H NMR on Bruker DRX 400 instrument. Flash column chromatography was performed on silica gel (200-300 mesh). Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured with JASCO P-1010 polarimeter. The configuration was determined by comparison of rotation sign with the literature data or by analogue.

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. Acetone was dried with anhydrous $CaSO_4$ and distilled over $KMnO_4$. The solvents for asymmetric hydrogenation reaction were purchased without further purification.

2. Typical Procedure for the Synthesis of Indoles

Indoles **1b-f**[1a,1b] and **1o-p**[1c,1d] were synthesized according to the literature procedure. 2-Benzyl substituted indoles **1g-k** were prepared following modified known methods.[1e,1f] Procedure for the synthesis of unknown compounds**1h-k** were depicted as follows. .

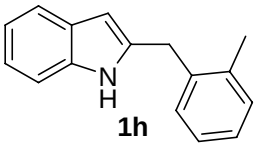


1h-k

To a solution of indole (20 mmol, 2.343 g) in ethanol (20 mL) at room temperature, KOH pellets were added (25 mmol, 1.403 g), and the mixture was stirred until total solubilization. The ethanol was completely removed in vacuum and acetone (20 mL) added followed by the benzyl bromide (20 mmol). A precipitate was formed instantly. The solid was filtered and the solution concentrated in vacuum to give *N*-benzylindole which was purified by flash chromatography.

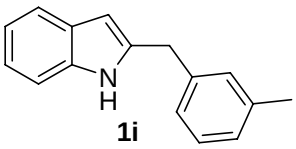
The *N*-benzylindole (4.2 mmol) was added to polyphosphoric acid (50 mL), which was prewarmed to the desired reaction temperature and vigorously stirred. Stirring and heating was continued until the starting material was consumed as indicated by TLC. Then the dark reaction mixture was cooled in an ice bath and mated carefully with ice water (40 mL). Extraction with EtOAc (3×30 mL) and washing the combined organic layers with saturated aqueous sodium bicarbonate solution and brine (30 mL each) was followed by drying over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography to give **1h-k**.

2-(2'-Methylbenzyl)indole (1h). Yellow solid, mp = 72-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 4.07 (s, 2H), 6.23 (s, 1H), 7.03-7.11 (m, 2H), 7.16-7.21 (m, 5H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.64 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 32.8, 101.1, 110.6, 119.9, 120.1, 121.3, 126.5, 127.3, 128.9, 129.7, 130.8, 136.2, 136.7, 137.1, 137.4; HRMS Calculated for $C_{16}H_{14}N$ $[M-H]^-$ 220.1126, found 220.1117.



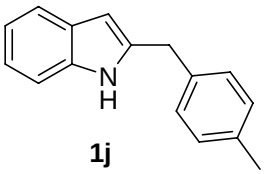
1h

2-(3'-Methylbenzyl)indole (1i). Yellow solid, mp = 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 4.08 (s, 2H), 6.32 (s, 1H), 7.05-7.12 (m, 5H), 7.19-7.23 (m, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.73 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 34.8, 101.2, 110.7, 119.9, 120.2, 121.4, 126.1, 127.7, 128.8, 129.8, 136.4, 138.1, 138.6; HRMS Calculated for $C_{16}H_{14}N$ $[M-H]^-$ 220.1126, found 220.1134.



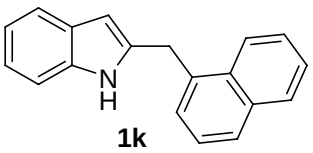
1i

2-(4'-Methylbenzyl)indole (1j). Yellow solid, mp = 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 4.05 (s, 2H), 6.29 (s, 1H), 7.03-7.13 (m, 6H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.67 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 34.5, 101.1, 110.7, 119.9, 120.2, 121.4, 128.9, 129.6, 135.6, 136.4, 136.5, 138.3; HRMS Calculated for $C_{16}H_{14}N$ $[M-H]^-$ 220.1126, found 220.1130.



1j

2-(1'-Naphthylmethyl)indole (1k). Yellow solid, mp = 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (s, 2H), 6.39 (s, 1H), 7.09-7.11 (m, 2H), 7.18-7.19 (m, 1H), 7.39-7.56 (m, 5H), 7.72 (br, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.5, 101.0, 110.7, 119.9, 120.1, 121.4, 124.1, 125.8, 126.1, 126.6, 127.3, 128.0, 128.9, 132.2, 134.2, 134.4, 136.2, 137.7; HRMS Calculated for $C_{19}H_{14}N$ $[M-H]^-$ 256.1126, found 256.1129.

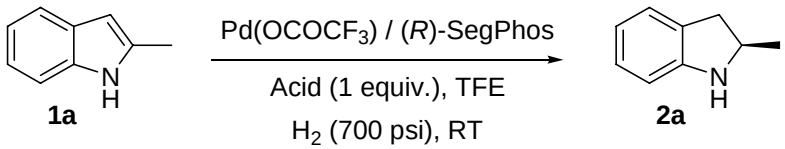


1k

3. The Effect of Acids and Ligands on the Reactivity and Enantioselectivity

The effect of various Brønsted acids on the reactivity and enantioselectivity was achieved for the asymmetric hydrogenation of simple 2-methylindole **1a** (Table 1, entries 1-10). It was found that this reaction was strongly Brønsted acid-dependent, strong acids gave full conversion and moderate enantioselectivity whereas weak acids showed poor reactivity and enantioselectivity (entries 3-6 *vs* entries 8-9). Without the addition of acid, the reaction did not occur (entry 1). L-CSA gave full conversion and the highest enantioselectivity (entry 6, 71% ee). In contrast, D-CSA with opposite configuration gave product with somewhat lower ee and 44% conversion (entry 7, 66% ee). Subequivalent L-CSA resulted in deteriorated enantioselectitvity and activity. Therefore, L-CSA was selected as the activator for further study.

Table 1. The Effect of Brønsted Acids on the Reactivity and Enantioselectivity[a]

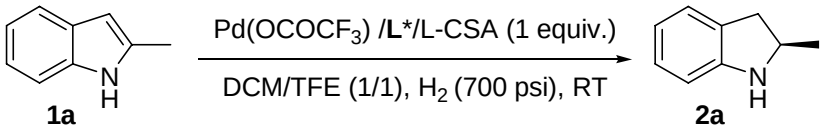


entry	acid[b]	convn. (%)[c]	ee (%)[d]
1[e]	no	<5	-
2	TfOH	61	54 (*R*)
3	$PhSO_3H$	>95	62 (*R*)
4	$TsOH{\cdot}H_2O$	>95	69 (*R*)
5	TFA	>95	8 (*R*)
6	**L-CSA**	**>95**	**71 (*R*)**
7	D-CSA	44	66 (*R*)
8	$PhCO_2H$	<5	-
9	Salicylic acid	35	4 (*R*)
10[f]	L-CSA	94	63 (*R*)

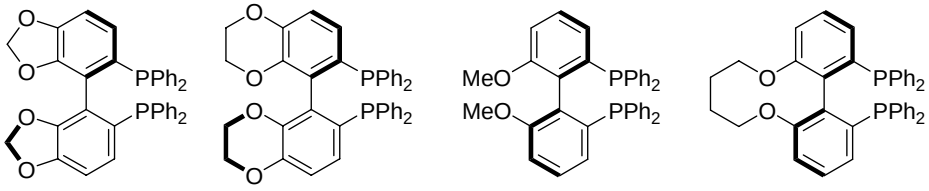
[a] Conditions: 0.25 mmol **1a**, $Pd(OCOCF_3)_2$ (2 mol %), (*R*)-SegPhos (2.4 mol %), Acid (1.0 equiv.), 3 mL TFE, 24 h, RT. [b] TfOH: Triflic acid; $PhSO_3H$: Benzenesulfonic acid; $TsOH{\cdot}H_2O$: *p*-Toluenesulfonic acid monohydrate; TFA: trifluoroacetic acid; L-CSA: L-(-)-Camphorsulfonic acid; D-CSA: D-(+)-Camphorsulfonic acid. [c] Determined by ^{1}H-NMR. [d] Determined by HPLC. [e] with no acid. [f] with 0.9 equiv. L-CSA.

Next, the effect of chiral ligands on the reactivity and enantioselectivity was examined for the asymmetric hydrogenation of simple 2-methylindole **1a**. Axially chiral bisphosphine ligands were effective, full conversions and high to excellent enantioselectivities were obtained (Table 2, entry 1-6, 84-91% ee). Ferrocene-based bisphosphine ligand (JosiPhos-type) displayed moderate activity and excellent enantioselectivity (entry 7, 80% ee). Me-DuPhos showed no activity for this transformation (entry 8). Subsequently, higher temperature was applied for the activity. At 50 ^oC, the catalyst loading could be reduced to 0.5% but with lower enantioselectivity (entry 9, 84% ee *vs* 91% ee).

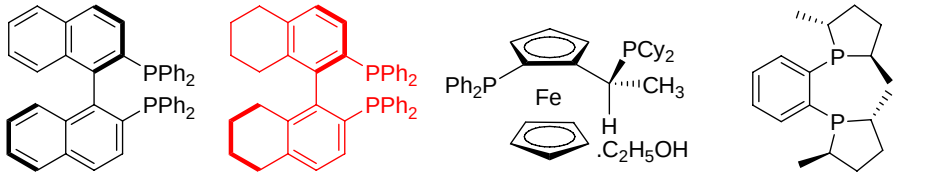
Table 2. The Effect of Chiral Ligands on the Reactivity and Enantioselectivity[a]



entry	ligand	convn. (%)[b]	ee (%)[c]
1	(*R*)-SegPhos	>95	85 (*R*)
2	(*R*)-SynPhos	>95	86 (*R*)
3	(*R*)-MeOBiPhep	>95	84 (*R*)
4	(*R*)-C4-TunePhos	>95	84 (*R*)
5	(*R*)-BINAP	>95	85 (*R*)
6	**(*R*)-H8-BINAP**	**>95**	**91 (*R*)**
7	(*R*)-(*S*)-PPF-PCy$_2$-JosiPhos	49	80 (*R*)
8	(*R*,*R*)-Me-DuPhos	<5	-
9[d]	(*R*)-H8-BINAP	>95	84 (*R*)



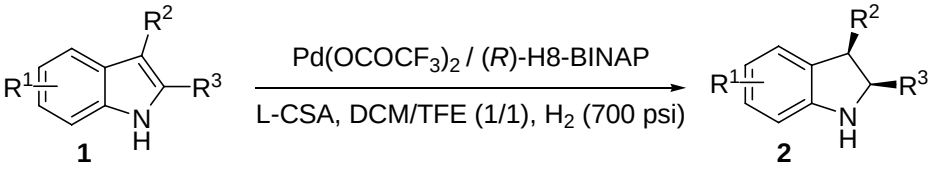
(*R*)-SegPhos (*R*)-SynPhos (*R*)-MeO-BiPhep (*R*)-C4-TunePhos



(*R*)-BINAP (*R*)-H8-BINAP (*R*)-(*S*)-PPF-PCy$_2$-JosiPhos (*R*,*R*)-Me-DuPhos

[a] Conditions: 0.25 mmol **1a**, Pd(OCOCF$_3$)$_2$ (2 mol %), Ligand (2.4 mol %), L-CSA (1.0 equiv.), 3 mL TFE, 24 h, RT. [b] Determined by ^{1}H-NMR. [c] Determined by HPLC. [d] With oil bath of 50 ^{o}C and 0.5 mol % catalyst.

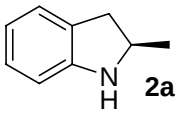
4. Typical Procedure for Pd-catalyzed Asymmetric Hydrogenation of Unprotected Indoles



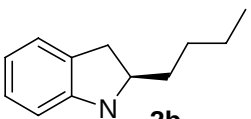
(*R*)-H8-BINAP (3.8 mg, 0.006 mmol) and $Pd(OCOCF_3)_2$ (1.7 mg, 0.005 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at rt for 1 h, then solvent was removed under vacuum to give the catalyst. In a glovebox, L-CSA (0.25 mmol) and substrate **1** (0.25 mmol) were stirred in 1 mL solvent (DCM and TFE were mixed in ratio of 1:1 before use) at room temperature for 5 min. Subsequently, the above catalyst together with 2 mL solvent was added to the reaction mixture. The hydrogenation was performed at room temperature under H_2 (700 psi) in a stainless steel autoclave for 24 h. After carefully releasing the hydrogen, the resulting mixture was concentrated under vacuum and dissolved in saturated aqueous $NaHCO_3$ (5 mL). After stirring for 10 min, the mixture was extracted with CH_2Cl_2 (3×5 mL) and dried over Na_2SO_4. After purified by silica gel chromatography using petroleum ether/EtOAc (10/1) as eluent, the enantiomeric excess of the products were determined by HPLC with chiral columns (OD-H, OJ-H or IC).

Racemates of **2** were prepared by the hydrogenation of the indoles catalyzed by $Pd(OCOCF_3)_2$/(+/-)-SegPhos in TFE or reduced by refluxing in EtOH with Sn/HCl.[2]

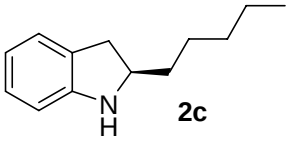
(+)-(*R*)-2-Methylindoline (2a).[3] 88% yield, 91% *ee*, $[\alpha]^{RT}_D$ = +6.96 (*c* 0.63, benzene), {Lit. $[\alpha]^{RT}_D$ = -12.2 (*c* 2.60, benzene) for (*S*)-enantiomer}[3]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (d, *J* = 6.2 Hz, 3H), 2.64 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.15 (dd, *J* = 15.4, 8.5 Hz, 1H), 3.76 (br, 1H), 3.90-4.00 (m, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 38.0, 55.4, 109.4, 118.7, 124.9, 127.4, 129.1, 151.1; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.8 mL/min), (*R*) t_1 = 9.3 min, (*S*) t_2 = 10.1 min.



(+)-(*R*)-2-Butylindoline (2b).[4] 82% yield, 93% *ee*, $[\alpha]^{RT}_D$ = +12.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 6.6 Hz, 3H), 1.36-1.40 (m, 4H), 1.63 (q, *J* = 6.2 Hz, 2H), 2.69 (dd, *J* = 15.4, 8.4 Hz, 1H), 3.14 (dd, *J* = 15.4, 8.6 Hz, 1H), 3.81-3.89 (m, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 23.0, 29.0, 36.3, 36.7, 60.3, 109.3, 118.6, 124.8, 127.4, 129.1, 151.2; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 6.5 min, t_2 = 7.9 min.

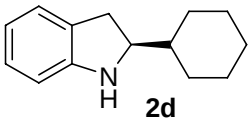


(+)-(*R*)-2-Pentylindoline (2c). 89% yield, 92% *ee*, $[\alpha]^{RT}_D$ = +15.5 (*c* 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 6.4 Hz, 3H), 1.35-1.43 (m, 6H), 1.59-1.64 (m, 2H) 2.69 (dd, *J* = 15.4, 8.5 Hz, 1H), 3.14 (dd, *J* = 15.4, 8.6 Hz, 1H), 3.83-3.89 (m, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* =



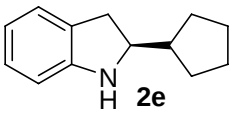
7.4 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 26.5, 32.1, 36.4, 37.0, 60.3, 109.2, 118.6, 124.8, 127.4, 129.1, 151.2; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 6.2 min, t_2 = 7.6 min; HRMS Calculated for $C_{13}H_{19}N$ $[M]^+$ 189.1517, found 189.1524.

(+)-(*R*)-2-Cyclohexanylindoline (2d).[4] White solid, mp = 61-63 °C, 90% yield, 95% *ee*, $[\alpha]^{RT}_D$ = +1.82 (*c* 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97-1.04 (m, 2H), 1.20-1.31 (m, 3H), 1.44-1.47 (m, 1H), 1.70-1.90 (m, 5H), 2.75 (dd, *J* = 15.4, 9.8 Hz, 1H), 3.07 (dd, *J* = 15.5, 8.7 Hz, 1H), 3.57 (q, *J* = 8.5 Hz, 1H), 3.80 (br, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 26.2, 26.7, 29.8, 30.3, 34.3, 44.1, 65.8, 109.0, 118.5, 124.7, 127.3, 129.3, 151.4; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.8 mL/min), t_1 = 8.0 min, t_2 = 11.9 min.



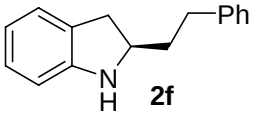
2d

(+)-(*R*)-2-Cyclopentylindoline (2e). White solid, mp = 54-57 °C, 85% yield, 95% *ee*, $[\alpha]^{RT}_D$ = +17.1 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24-1.29 (m, 2H), 1.58-1.68 (m, 4H), 1.70-1.88 (m, 2H), 1.99-2.06 (m, 1H), 2.75 (dd, *J* = 15.5, 8.9 Hz, 1H), 3.11 (dd, *J* = 15.5, 8.6 Hz, 1H), 3.66 (q, *J* = 8.7 Hz, 1H), 3.82 (br, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 25.7, 29.7, 30.4, 35.5, 46.3, 65.4, 109.1, 118.5, 124.8, 127.3, 129.3, 151.3; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 254 nm, flow rate: 0.8 mL/min), t_1 = 8.6 min, t_2 = 12.2 min; HRMS Calculated for $C_{13}H_{17}N$ $[M]^+$ 187.1361, found 187.1368.



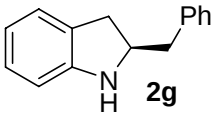
2e

(+)-(*R*)-2-Phenethylindoline (2f).[5] 89% yield, 93% *ee*, $[\alpha]^{RT}_D$ = +12.7 (*c* 1.70, $CHCl_3$), {Lit. $[\alpha]^{23}_D$ = +12.0 (*c* 0.17, $CHCl_3$)}[5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89-1.96 (m, 2H), 2.67-2.74 (m, 3H), 3.13 (dd, *J* = 15.4, 8.6 Hz, 1H), 3.80-3.88 (m, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.05(d, *J* = 7.2 Hz, 1H), 7.16-7.20 (m, 3H), 7.26-7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 33.1, 36.3, 38.6, 59.7, 109.3, 118.7, 124.8, 126.1, 127.4, 128.5, 128.6, 128.9, 141.9, 151.1; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.8 mL/min), t_1 = 11.5 min, t_2 = 14.0 min.



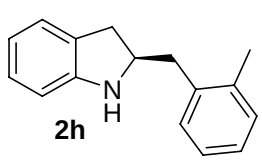
2f

(+)-(*R*)-2-Benzylindoline (2g).[4] 99% yield, 95% *ee*, $[\alpha]^{RT}_D$ = +80.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74-2.91 (m, 3H), 3.12 (dd, *J* = 15.5, 8.4 Hz, 1H), 3.79 (br, 1H), 4.01-4.09 (m, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.19-7.30 (m, 3H), 7.31-7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.1, 42.9, 61.2, 109.3, 118.7, 125.0, 126.6, 127.5, 128.5, 128.8, 129.3, 139.3, 150.7; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 10.7 min, t_2 = 12.0 min.



2g

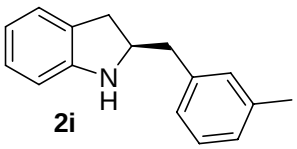
(+)-(*R*)-2-(2'-Methylbenzyl)indoline (2h). 84% yield, 94% *ee*, $[\alpha]^{RT}_D$ = +74.8 (*c* 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.82-2.91 (m, 3H), 3.77 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.80 (br, 1H), 4.08-4.13 (m, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.6



2h

Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.13-7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 36.3, 39.9, 59.8, 109.3, 118.7, 125.0, 126.3, 126.8, 127.6, 128.6, 129.9, 130.7, 136.7, 137.4, 150.8; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 9.8min, t_2 = 10.8 min; HRMS Calculated for $C_{16}H_{17}N$ $[M]^+$ 223.1361, found 223.1368.

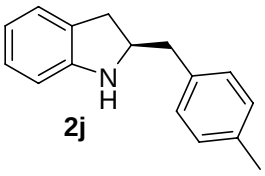
(+)-(*R*)-2-(3'-Methylbenzyl)indoline (2i). 95% yield, 94% *ee*, $[\alpha]^{RT}_D$ = +75.4 (*c* 1.60, $CHCl_3$); ^{1}H



2i

NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.78-2.91 (m, 3H), 3.16 (dd, *J* = 15.4, 8.4 Hz, 1H), 3.80 (br, 1H), 4.07-4.11 (m, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 7.00-7.11 (m, 5H), 7.24 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 36.1, 42.8, 61.2, 109.3, 118.6, 118.7, 125.0, 126.3, 127.4, 127.5, 128.7, 130.1, 138.4, 139.2, 150.7; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 8.5 min, t_2 = 9.3 min; HRMS Calculated for $C_{16}H_{17}N$ $[M]^+$ 223.1361, found 223.1369.

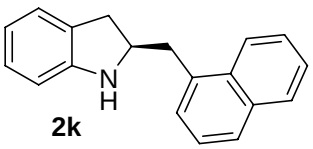
(+)-(*R*)-2-(4'-Methylbenzyl)indoline (2j). 82% yield, 93% *ee*, $[\alpha]^{RT}_D$ = +75.5 (*c* 1.50, $CHCl_3$); ^{1}H



2j

NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.77-2.90 (m, 3H), 3.14 (dd, *J* = 15.5, 8.4 Hz, 1H), 3.80 (br, 1H), 4.04-4.08 (m, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.08-7.17 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 36.1, 42.4, 61.3, 109.3, 118.7, 125.0, 127.5, 128.6, 129.2, 129.5, 129.6, 136.2, 150.8; HPLC (OD-H, elute: Hexanes / *i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 8.5 min, t_2 = 9.3 min; HRMS Calculated for $C_{16}H_{17}N$ $[M]^+$ 223.1361, found 223.1364.

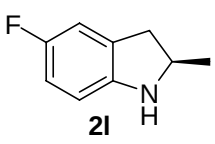
(+)-(*R*)-2-(1'-Naphthylmethyl)indoline (2k). 78% yield, 96% *ee*, $[\alpha]^{RT}_D$ = +43.5 (*c* 1.20, $CHCl_3$);



2k

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (dd, *J* = 15.5, 6.5 Hz, 1H), 3.18-3.39 (m, 3H), 3.80 (br, 1H), 4.25-4.29 (m, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 6.9 Hz, 1H), 7.44-7.54 (m, 3H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.4, 39.7, 60.3, 109.4, 118.7, 124.0, 125.0, 125.7, 125.9, 126.2, 127.3, 127.5, 127.6, 128.5, 129.0, 132.3, 134.2, 135.3, 150.6; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.8 mL/min), t_1 = 13.3 min, t_2 = 16.6 min; HRMS Calculated for $C_{19}H_{17}N$ $[M]^+$ 259.1361, found 259.1368.

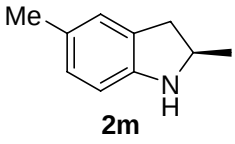
(+)-(*R*)-5-Fluoro-2-methylindoline (2l).[6] 84% yield, 88% *ee*, $[\alpha]^{RT}_D$ = +7.56 (*c* 0.80, $CHCl_3$),



2l

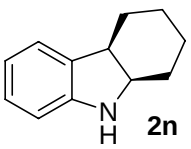
{Lit. $[\alpha]^{RT}_D$ = -10.1 (*c* 0.50, $CHCl_3$) for 99% ee of (*S*)-enantiomer }[6]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, *J* = 6.2 Hz, 3H), 2.62 (dd, *J* = 15.6, 7.8 Hz, 1H), 3.11 (dd, *J* = 15.7, 8.4 Hz, 1H), 3.60 (br, 1H), 3.96-4.00 (m, 1H), 6.47-6.51(m, 1H), 6.66-6.70 (m, 1H), 6.78-6.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 38.2, 56.1, 109.5, 112.3, 113.3, 130.0, 147.1, 158.4; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 6.5 min, t_2 = 9.1 min.

(+)-(*R*)-2,5-Dimethylindoline (2m).[7] 81% yield, 84% *ee*, $[\alpha]^{RT}_{D}$ = +12.4 (*c* 1.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (d, *J* = 6.2 Hz, 3H), 2.27 (s, 3H), 2.62 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.12 (dd, *J* = 15.4, 8.4 Hz, 1H), 3.60 (br, 1H), 3.93-4.01 (m, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 22.4, 38.0, 55.6, 109.4, 125.7, 127.7, 128.1, 129.5, 148.7; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 7.2 min, t_2 = 9.2 min.



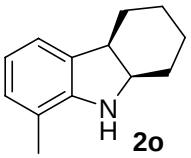
2m

(+)-(2*R*,3*R*)-*cis*-5,6,7,8,8a,9-Hexahydro-4bH-carbazole (2n).[5] 91% yield, 91% *ee*, $[\alpha]^{RT}_{D}$ = +23.4 (*c* 1.20, $CHCl_3$), {Lit. $[\alpha]^{23}_{D}$ = -20.0 (*c* 0.25, $CHCl_3$) (84% ee)}[5]; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36-1.44 (m, 3H), 1.55-1.60 (m, 2H), 1.61-1.74 (m, 1H), 1.76-1.81 (m, 2H), 3.12 (q, *J* = 6.6 Hz, 1H), 3.70 (br, 1H), 3.74 (q, *J* = 6.4 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.7, 27.1, 29.4, 41.1, 59.8, 110.3, 119.0, 123.3, 127.2, 133.7, 150.9; HPLC (IC, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 5.0 min, t_2 = 7.5 min.



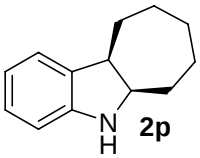
2n

(+)-(2*R*,3*R*)-*cis*-1-methyl-5,6,7,8,8a,9-hexahydro-4bH-carbazole (2o).[8] 83% yield, 96% *ee*, $[\alpha]^{RT}_{D}$ = +17.9 (*c* 0.90, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.37-1.43 (m, 3H), 1.55-1.58 (m, 2H), 1.60-1.70 (m, 1H), 1.75-1.79 (m, 2H), 2.15 (m, 3H), 3.13 (q, *J* = 6.6 Hz, 1H), 3.15 (br, 1H), 3.75 (q, *J* = 6.7 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 22.0, 22.7, 27.2, 29.7, 41.4, 59.7, 119.1, 119.6, 120.8, 128.2, 132.9, 149.5; HPLC (IC, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 4.4 min, t_2 = 4.9 min.



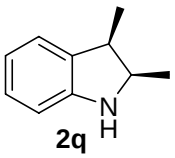
2o

(+)-(2*R*,3*R*)-*cis*-5,5a,6,7,8,9,10,10a-Octahydrocyclohepta[b]indole (2p).[5] White solid, mp = 61-64 °C, 96% yield, 90% *ee*, $[\alpha]^{RT}_{D}$ = +32.6 (*c* 1.20, $CHCl_3$), {Lit. $[\alpha]^{RT}_{D}$ = -30.0 (*c* 0.52, $CHCl_3$) (86% ee)}[5]; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33-1.43 (m, 3H), 1.70-1.91 (m, 6H), 1.94-2.00 (m, 1H), 3.48 (td, *J* = 10.6, 3.2 Hz, 1H), 3.64 (br, 1H), 4.01-4.08 (m, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.99-7.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 28.9, 31.6, 33.8, 46.9, 63.6, 108.6, 118.3, 124.3, 127.5, 133.7, 150.4; HPLC (IC, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 5.6 min, t_2 = 7.1 min.



2p

(+)-(2*R*,3*R*)-*cis*-2,3-Dimethylindoline (2q).[9] 84% yield, 92% *ee*, $[\alpha]^{RT}_{D}$ = +26.6 (*c* 0.83, $CHCl_3$), {Lit. $[\alpha]^{26}_{D}$ = +19.3 (*c* 0.30, $CHCl_3$)}[9]; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, *J* = 6.6 Hz, 3H), 1.19 (d, *J* = 7.2 Hz, 3H), 3.23-3.29 (m, 1H), 3.65 (br, 1H), 3.91-3.97 (m, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 7.00-7.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 16.5, 39.6, 58.6, 109.5, 118.9, 124.0, 127.4, 134.5, 150.3; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 16.7 min, t_2 = 20.6 min.

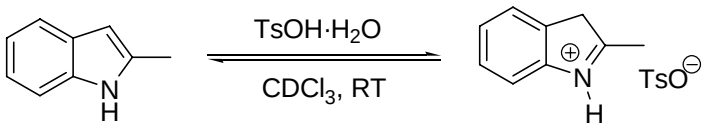


2q

5. Mechanism Study

To elucidate the mechanism of Pd-catalyzed asymmetric hydrogenation of unprotected indoles in the presence of Brønsted acid, ^{1}H-NMR and two isotopic labeling experiments were carried out.

^{1}H-NMR Study: TsOH·H_2O (48 mg, 0.25 mmol) was added to 2-methylindole (33 mg, 0.25 mmol) solution in $CDCl_3$ and stirred for 5 min at room temperature.



^{1}H-NMR analysis of the resulted yellow solution, it was showed that the signal of the 2-methyl and hydrogen at the 3-position become broad peaks and shifted to downfield, and the N-H peak and olefinic hydrogen at the 3-position of 2-methylindole disappeared rapidly (**Figure 1**). These results indicated that fast reversible process of protonation and deprotonation existed.

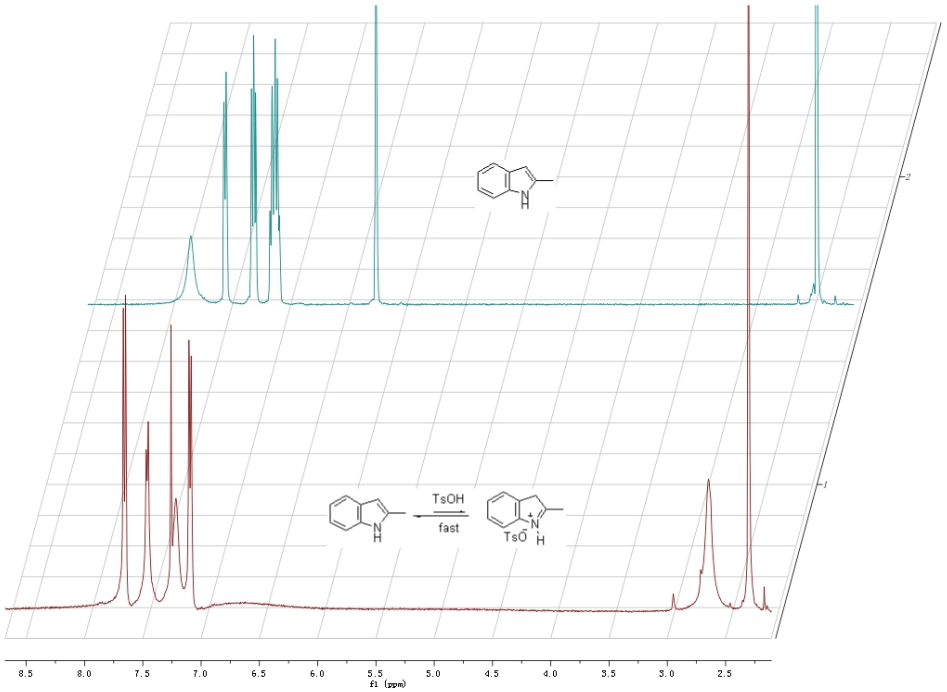
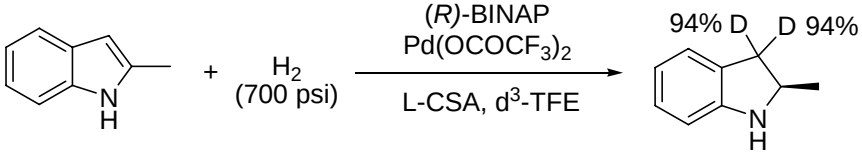


Figure 1. ^{1}H-NMR Study of TsOH and 2-Methylindole in $CDCl_3$

Asymmetric Hydrogenation of 2-Methylindole with the Deuterated L-CSA in d^3-TFE: Deuterated L-CSA was obtained by stirring d^3-TFE (1000 mg) and L-CSA (58 mg, 0.25 mmol) at room temperature in glove box for 0.5 h for sufficient Hydrogen/Deuterium exchange. Subsequently, the hydrogenation was carried out.



^{1}H-NMR analysis of the crude hydrogenated product showed that two deuterium atoms were incorporated to the 3-position (both with 94% incorporation) of hydrogenation product 2-methylindoline **2a**, which suggested that a rapid reversible process of protonation and

deprotonation existed (**Figure 2**), and the equilibrium was faster than hydrogenation. Thus, two deuterium atoms was imported to the 3-position of the 2-methylindoline before hydrogenation occurred.

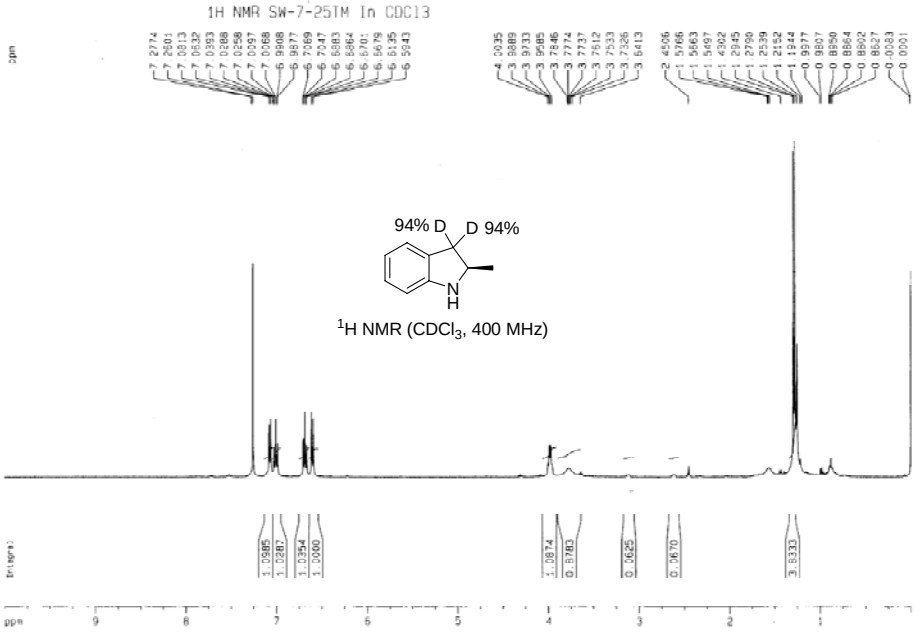


Figure 2. ^{1}H-NMR of Product 1a with d^3-TFE and L-CSA

Asymmetric Hydrogenation of 2-Methylindole with D_2: 2-Methylindole **1a** was hydrogenated in D_2 (116 psi) with the $Pd(OCOCF_3)_2$/(*R*)-BINAP/TFE condition.

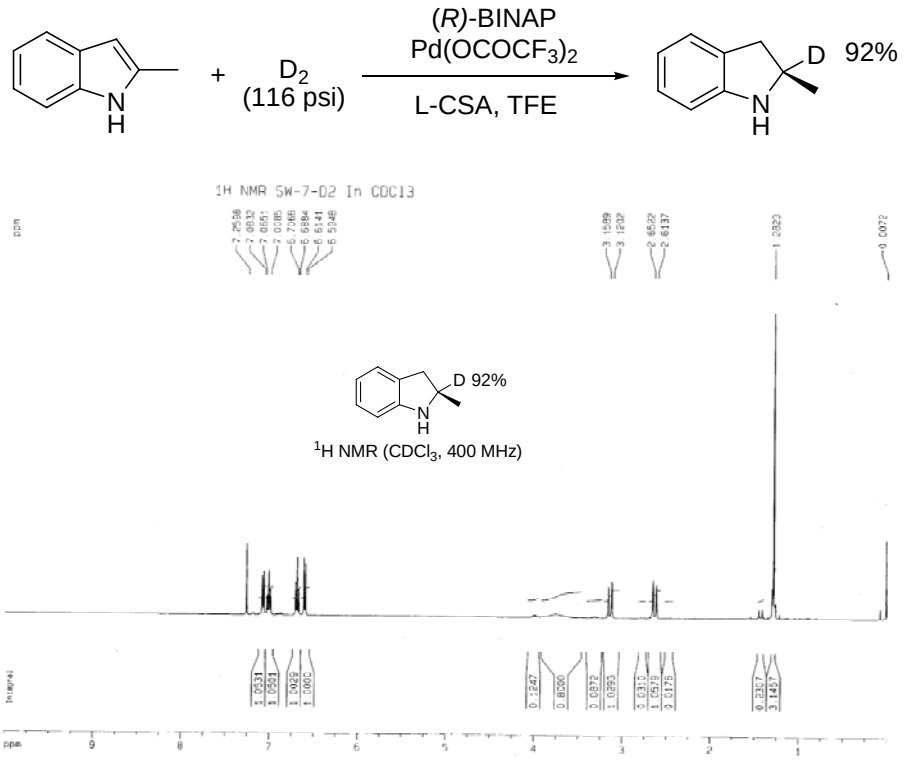


Figure 3. ^{1}H-NMR of Product 1a with D_2

2-*deuterio*-2-Methylindoline with 92% incorporation was obtained, deuterium at 3-position was not observed (**Figure 3**). These results confirmed that the simple unprotected indole can be activated by a Brønsted acid to form iminium *in situ*, which was then hydrogenated by the Pd-catalyst.

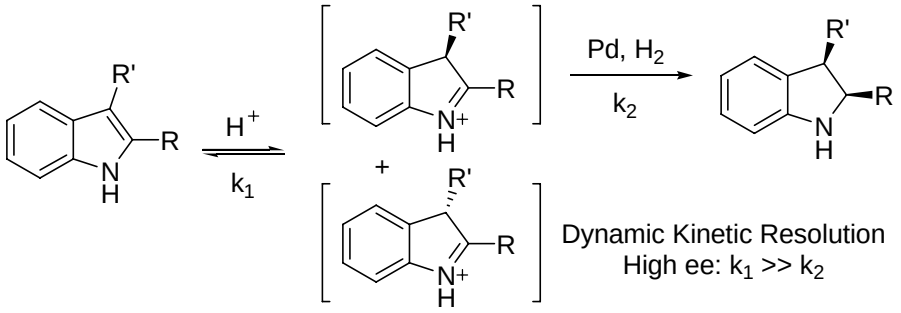


Figure 4. Mechanism of Hydrogenation of 2,3-Disubstituted Indoles

For the Pd catalyzed asymmetric hydrogenation of 2,3-disubstituted indole activated by a Brønsted acid, the mechanism was slightly different from that of 2-substituted indoles. The hydrogenation of an intermediate iminium salt of 2-substituted indole is the enantioselectivity-controlled step, while enantio-selectivity-controlled step of 2,3-disubstituted indole is the protonation of carbon-carbon double bond and the hydrogenation of iminium salt, which is in fact a dynamic kinetic resolution process (**Figure 4**). To obtain high ee, it should meet the equation of $k_1 >> k_2$. The above mechanism study indicated that rate of protonation k_1 is faster than rate of hydrogenation k_2 ($k_1 >> k_2$).

6. References

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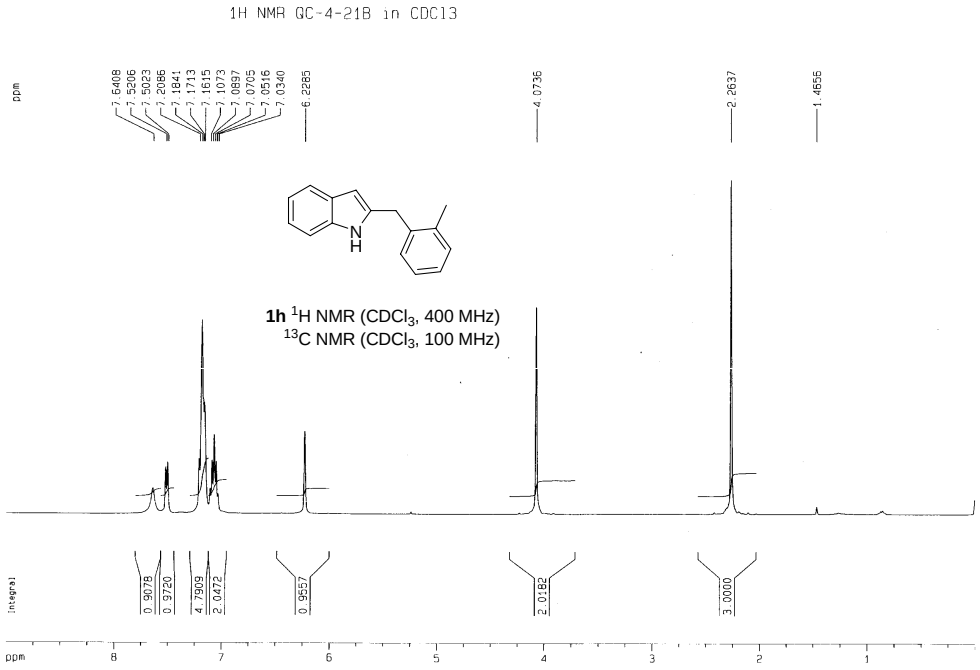
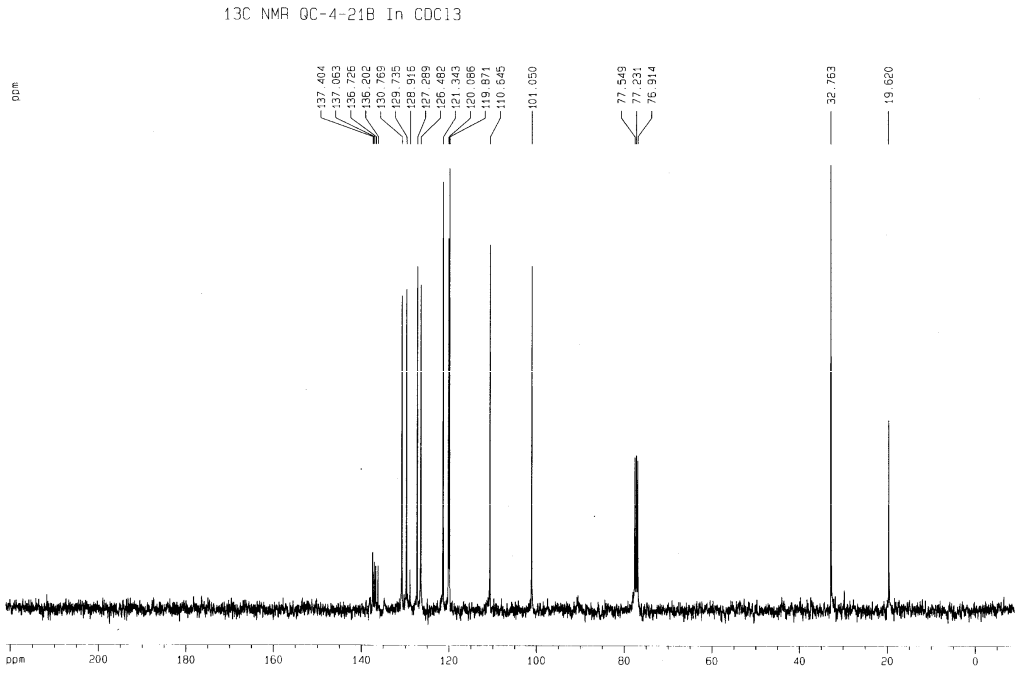
7. Copy of NMR and HRMS Spectra

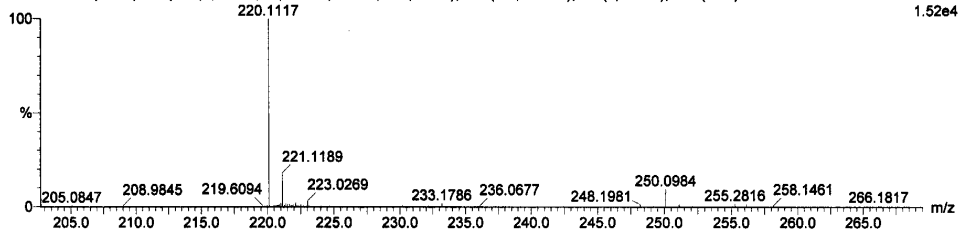




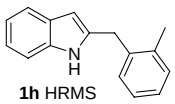
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Selected filters: None

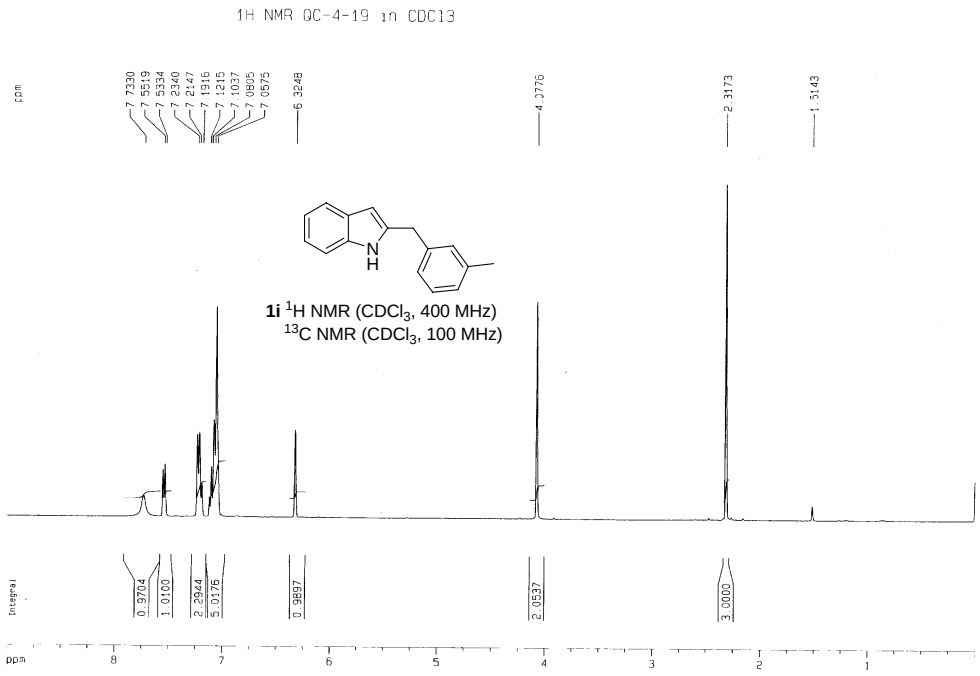
Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-60 H: 8-80 N: 0-9
QC-4-21B
10041305 30 (0.749) AM (Cen,6, 80.00, Ar,5000.0,220.11,0.70,LS 10); Sm (SG, 2x3.00); Sb (1,40.00); Cm (8:34) 1: TOF MS ES-
1.52e4



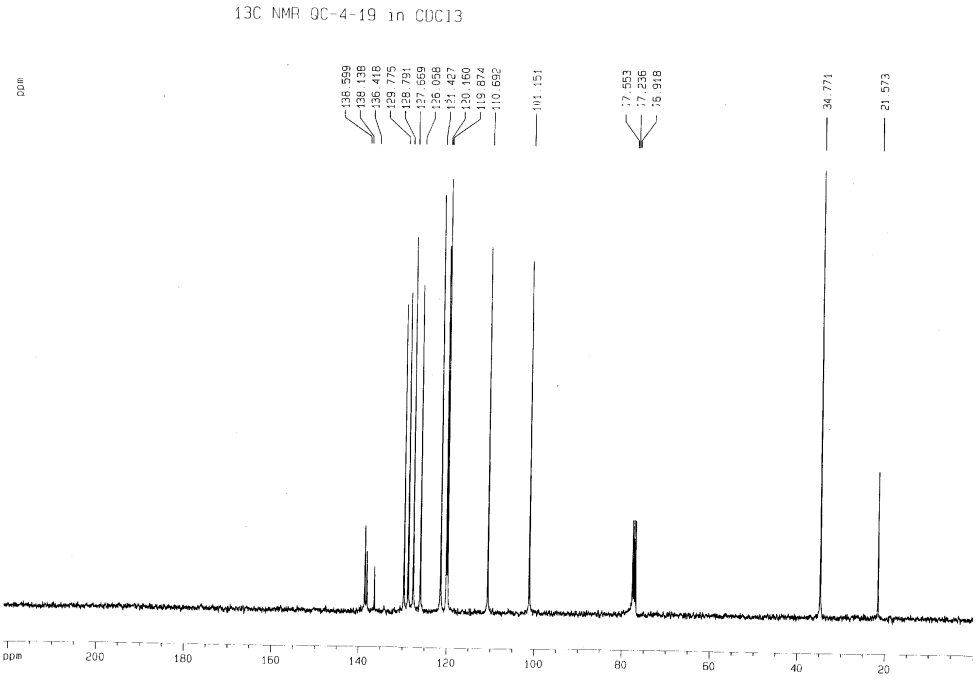
Minimum:				-1.5		
Maximum:		5.0	50.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
220.1117	220.1126	-0.9	-4.1	10.5	9.9	C16 H14 N



1h HRMS



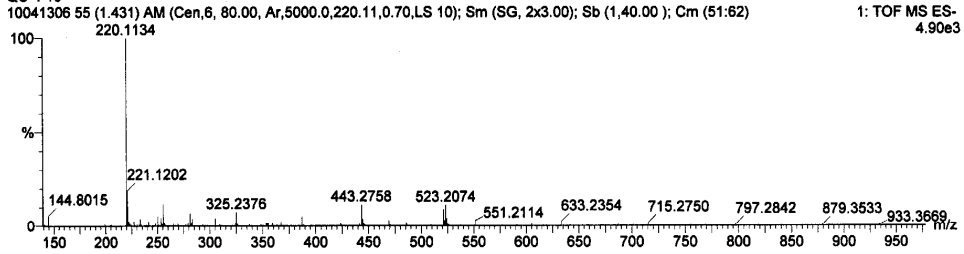
1i ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



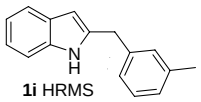
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-60 H: 8-80 N: 0-9

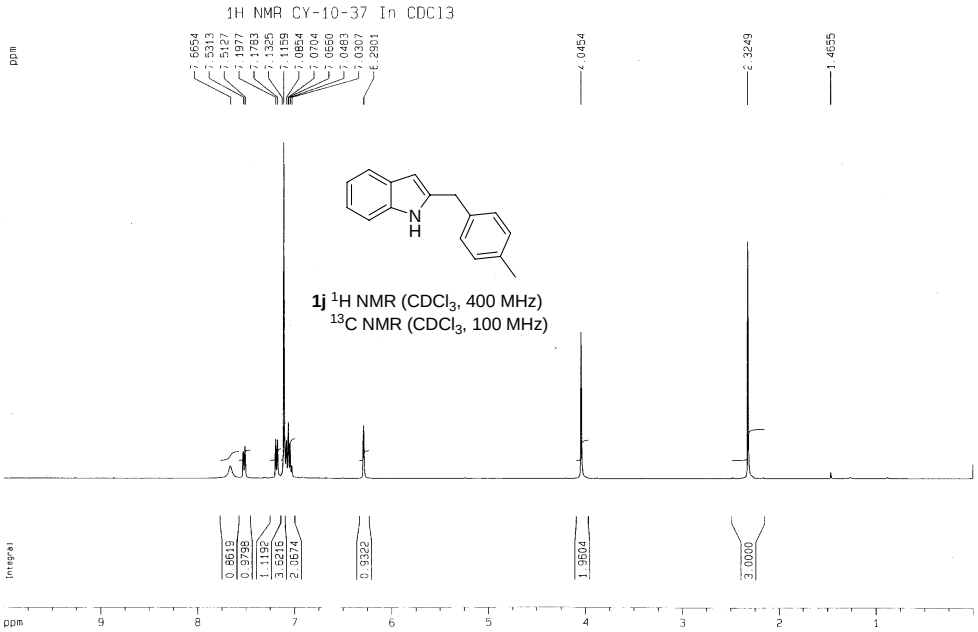
QC-4-19
10041306 55 (1.431) AM (Cen,6, 80.00, Ar,5000.0,220.11,0.70,LS 10); Sm (SG, 2x3.00); Sb (1,40.00); Cm (51:62) 1: TOF MS ES-
4.90e3



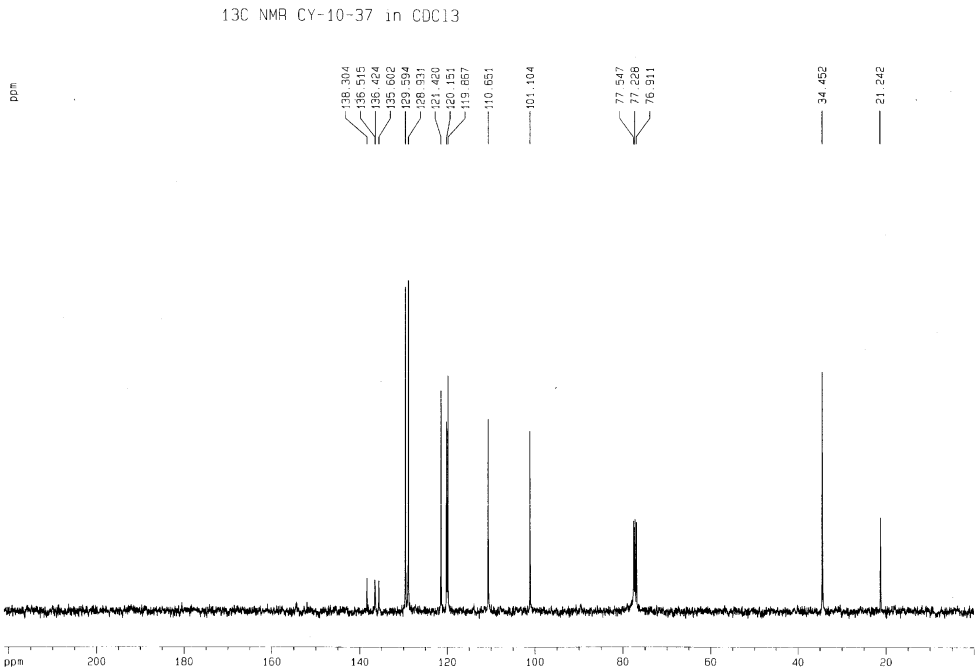
Minimum:				-1.5		
Maximum:		5.0	50.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
220.1134	220.1126	0.8	3.6	10.5	10.4	C16 H14 N



1i HRMS

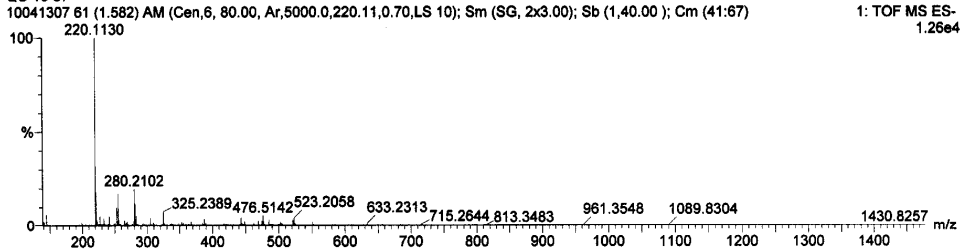


1j ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)

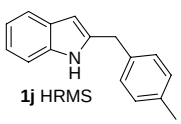


Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Selected filters: None

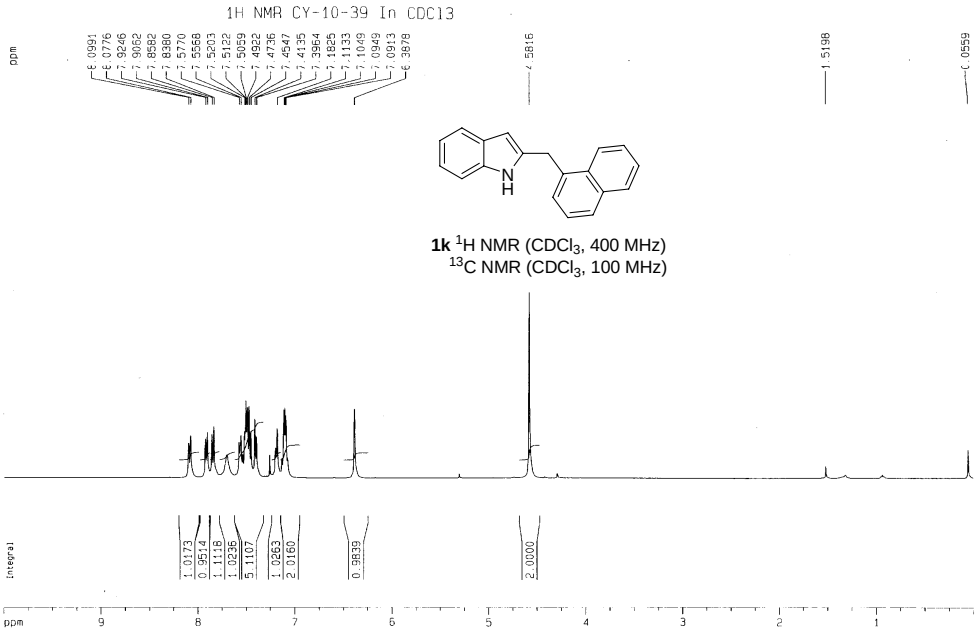
Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-60 H: 8-80 N: 0-9
QC-10-37
10041307 61 (1.582) AM (Cen,6, 80.00, Ar,5000.0,220.11,0.70,LS 10); Sm (SG, 2x3.00); Sb (1,40.00); Cm (41:67) 1: TOF MS ES- 1.26e4



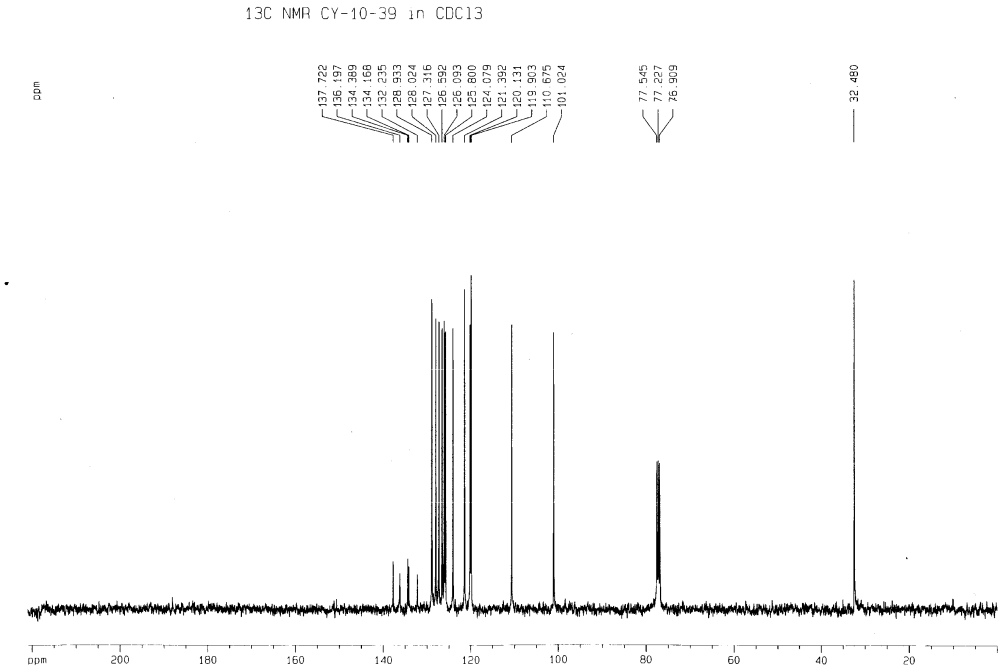
Minimum:				-1.5		
Maximum:		5.0	50.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
220.1130	220.1126	0.4	1.8	10.5	45.8	C16 H14 N



1j HRMS

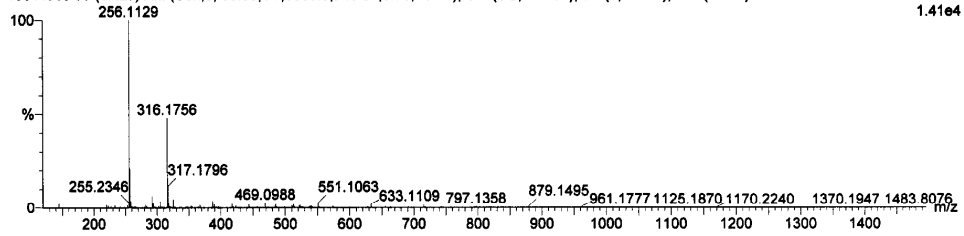


1k ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)

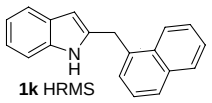


Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Selected filters: None

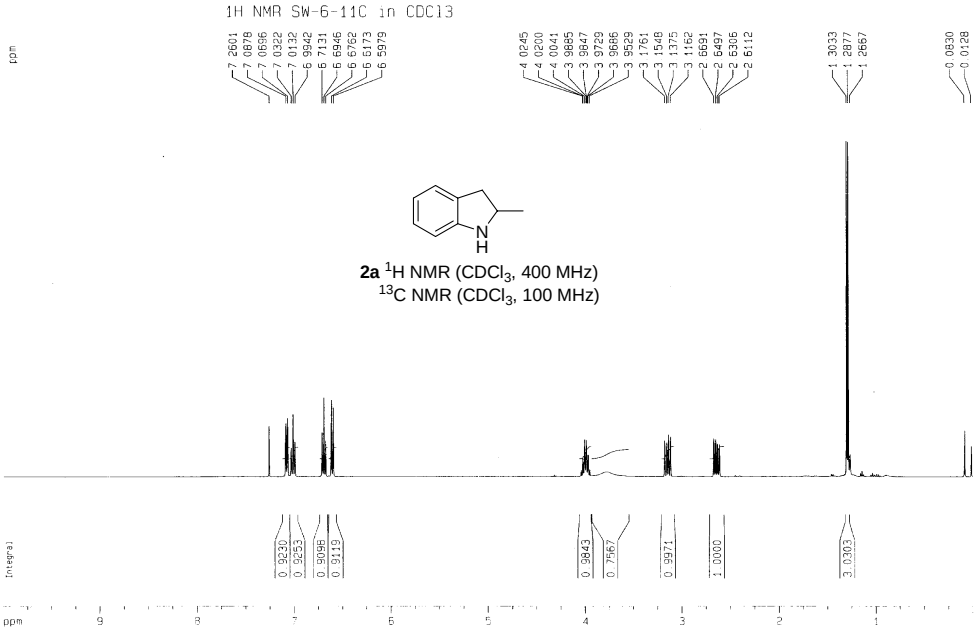
Monoisotopic Mass, Even Electron Ions
26 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-60 H: 8-80 N: 0-9
QC-10-39
10041308 55 (1.429) AM (Cen,6, 80.00, Ar,5000.0,220.07,0.70,LS 10); Sm (SG, 2x3.00); Sb (1,40.00); Cm (36:67) 1: TOF MS ES-
1.41e4



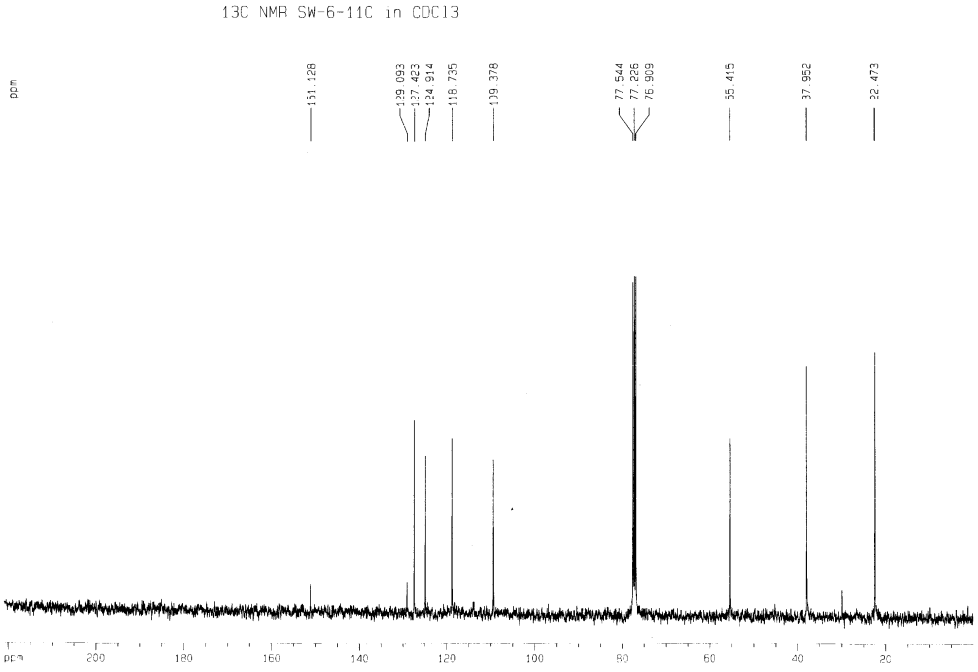
Minimum:				-1.5		
Maximum:		5.0	5.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
256.1129	256.1126	0.3	1.2	13.5	44.2	C19 H14 N

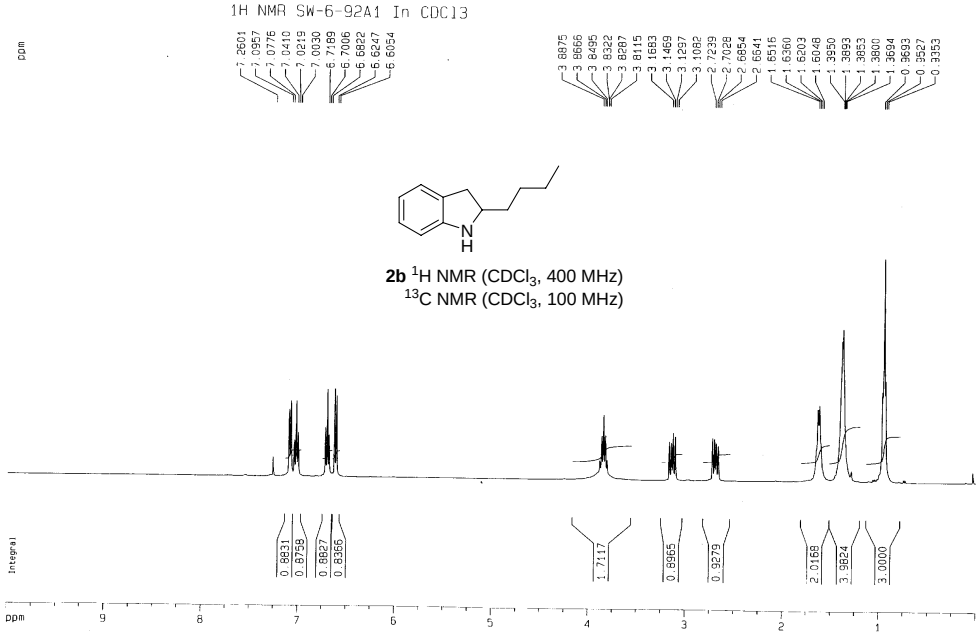


1k HRMS

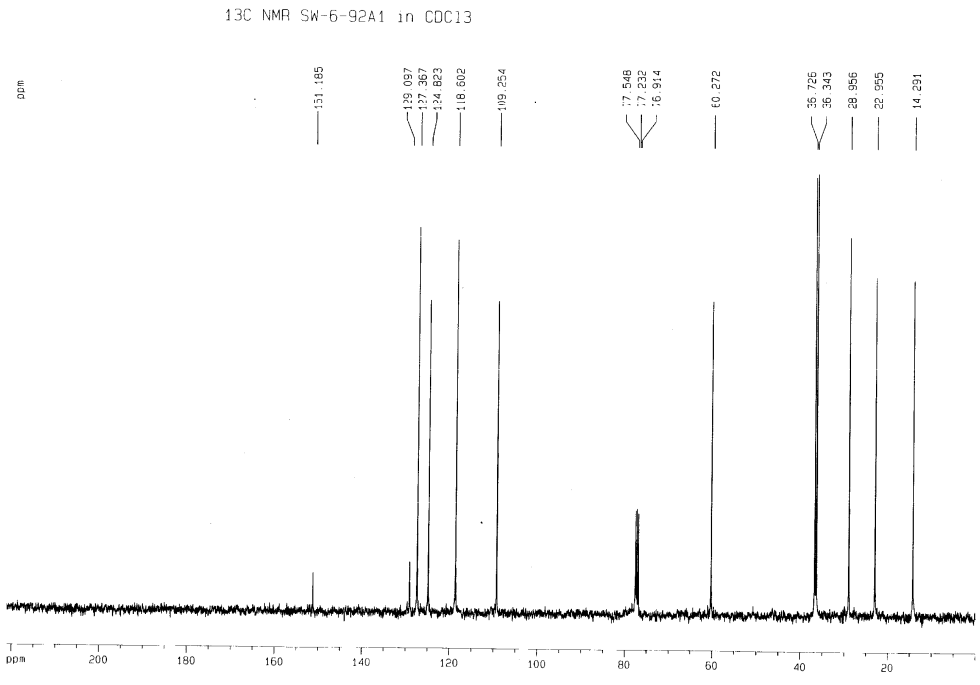


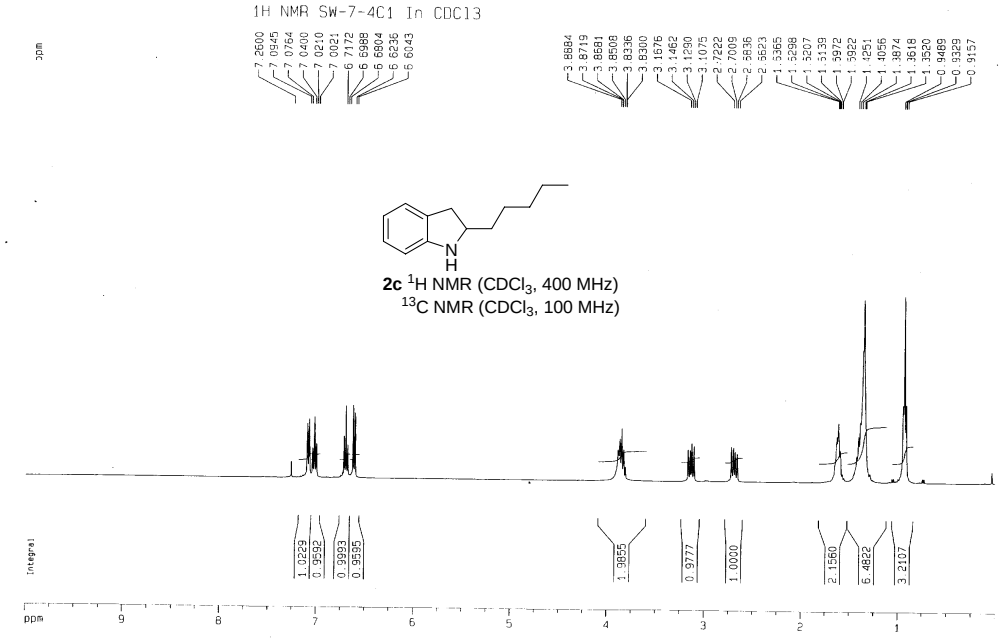
2a ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



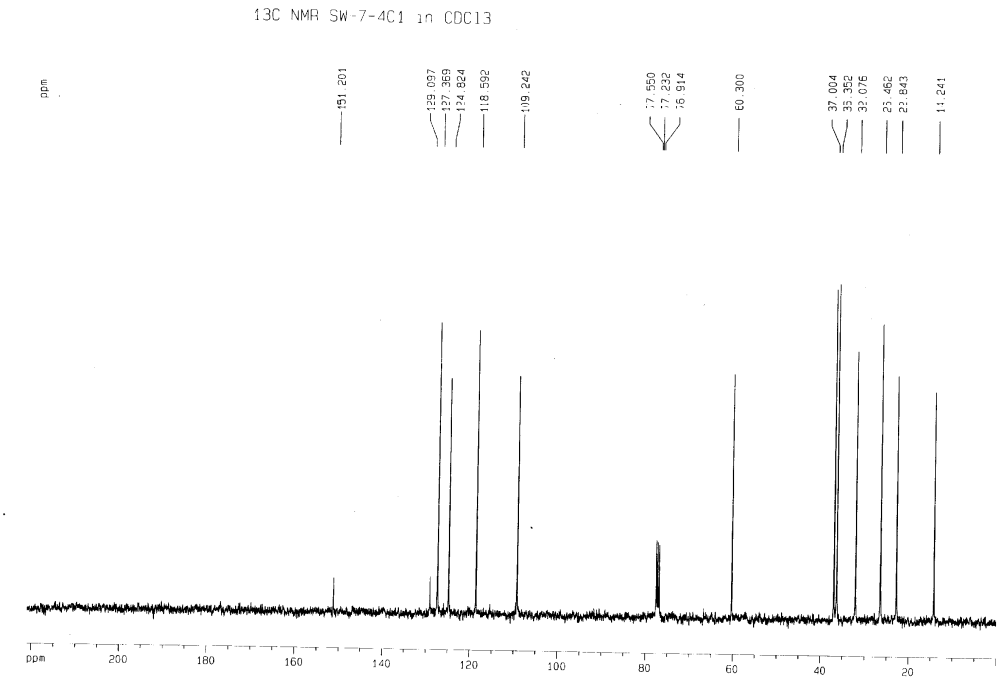


2b ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)





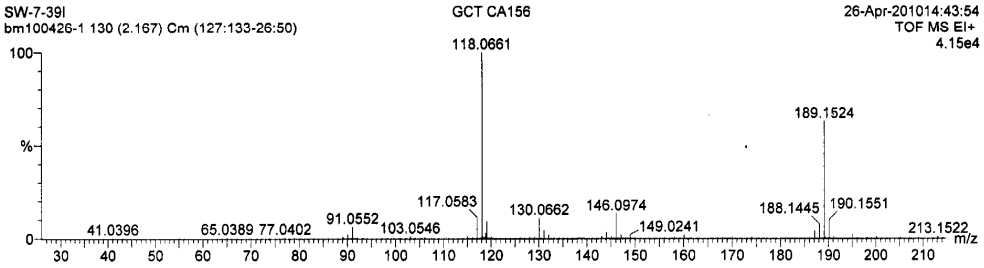
2c ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



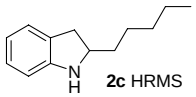
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

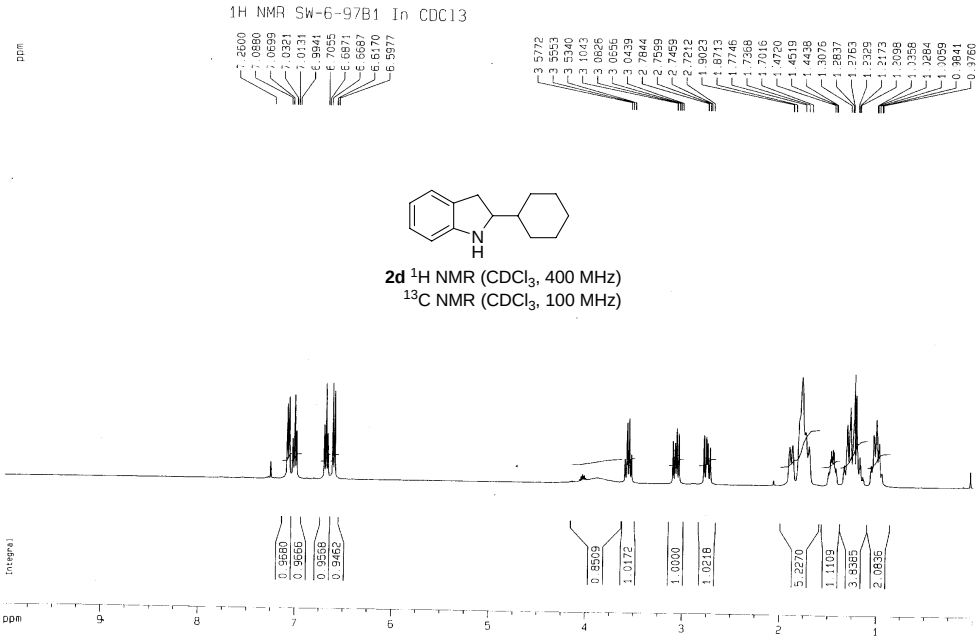
Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)



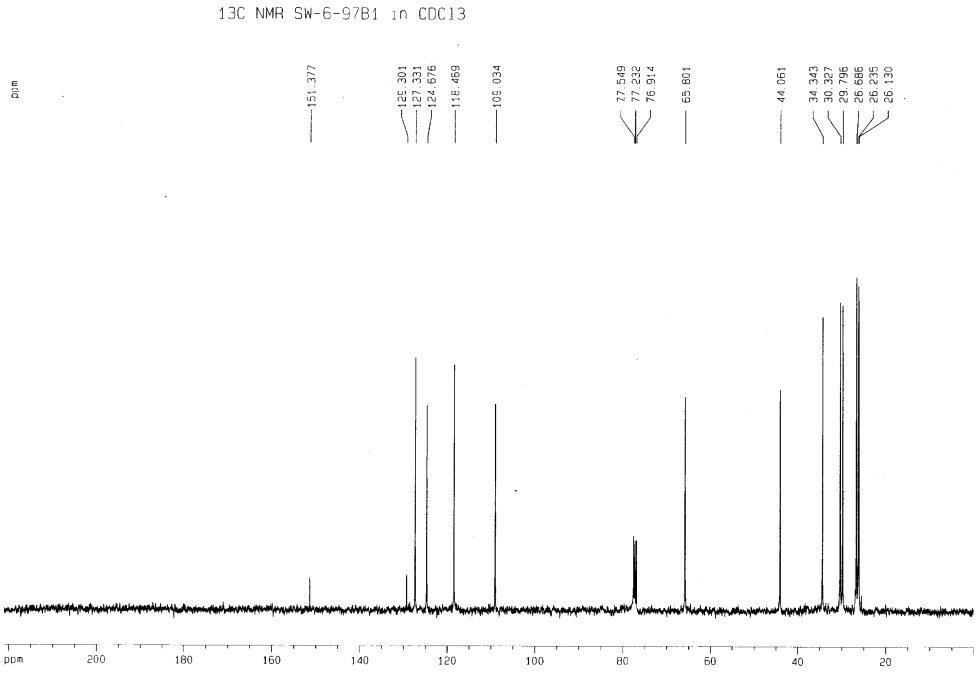
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
189.1524	189.1517	0.7	3.4	5.0	2	C13 H19 N
	189.0704	82.0	433.4	11.5	3	C15 H9
	189.0578	94.6	499.9	12.0	1	C14 H7 N

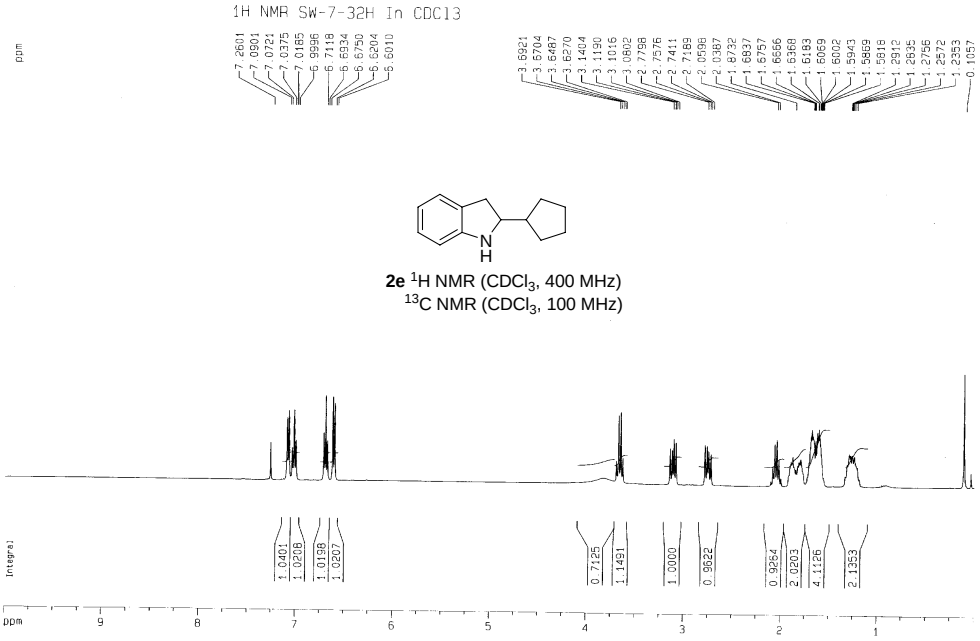


2c HRMS

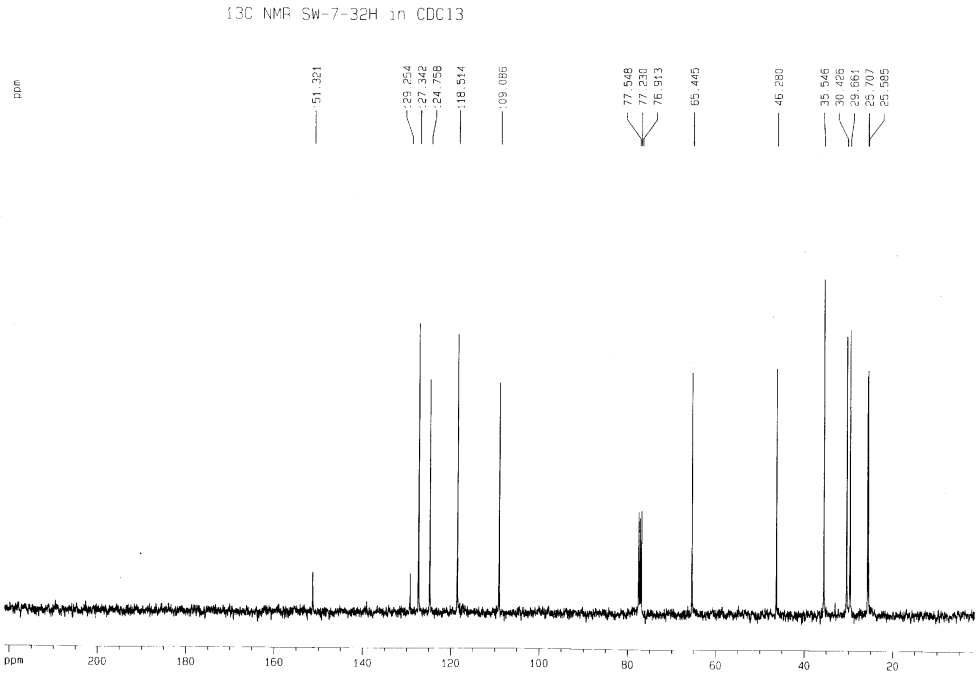


2d ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)





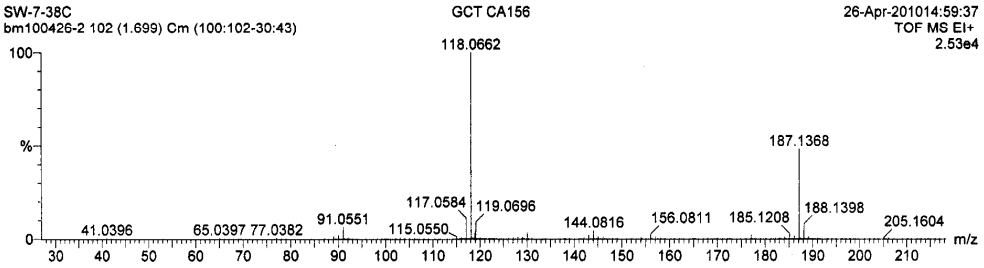
2e ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



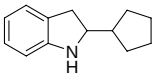
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

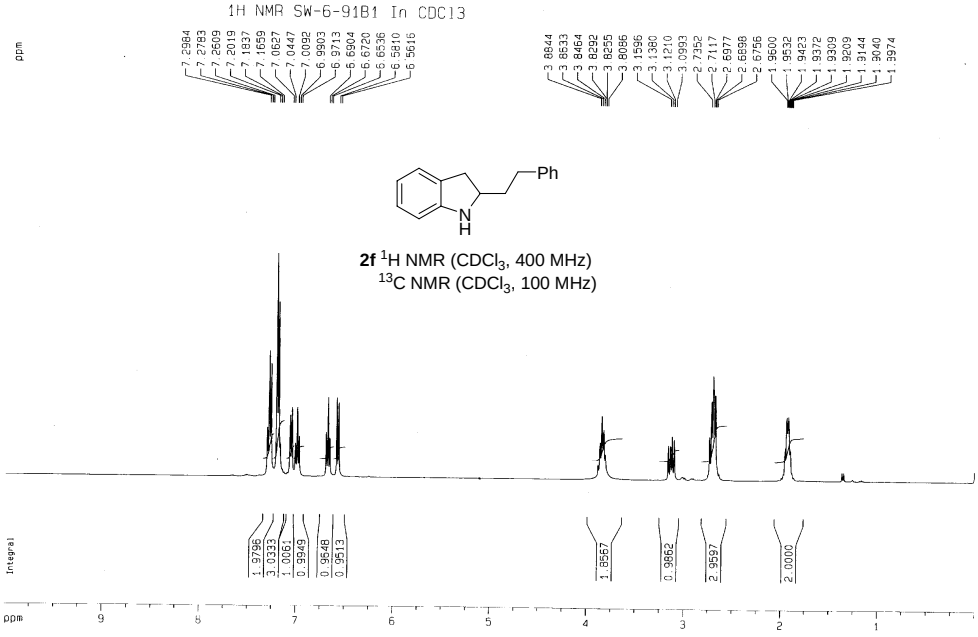
Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)



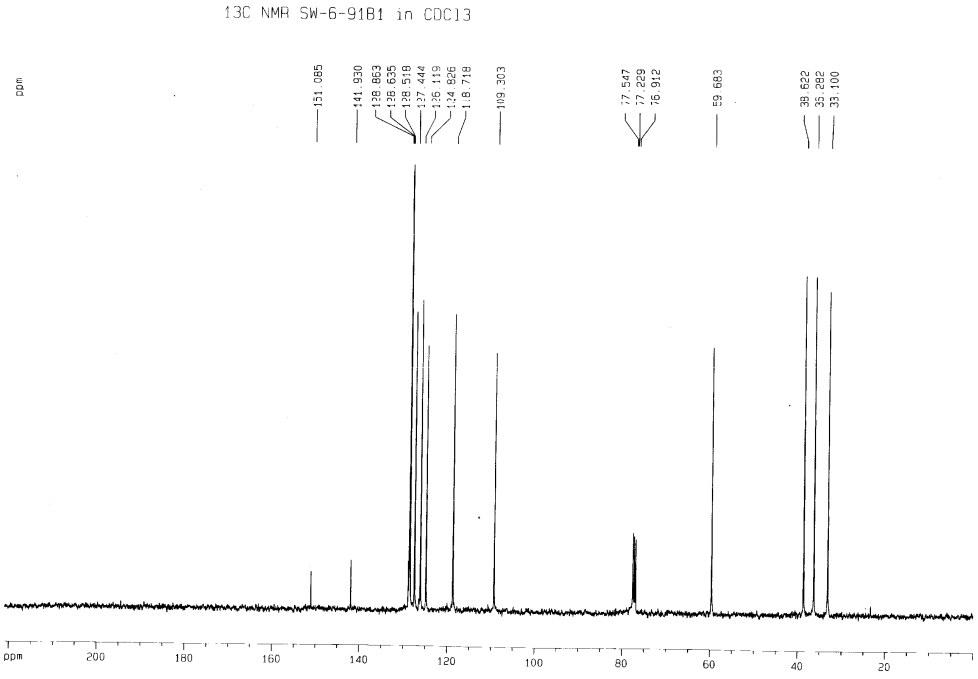
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
187.1368	187.1361	0.7	3.7	6.0	4	C13 H17 N
	187.1487	-11.9	-63.5	5.5	3	C14 H19
	187.0548	82.0	438.3	12.5	2	C15 H7
	187.0422	94.6	505.5	13.0	1	C14 H5 N

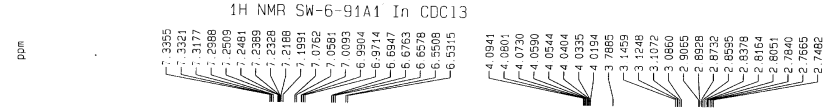


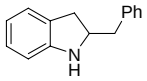
2e HRMS



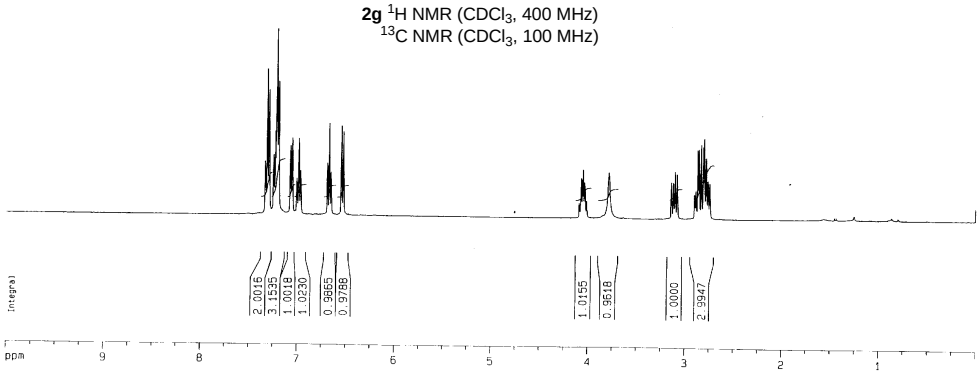
2f ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)

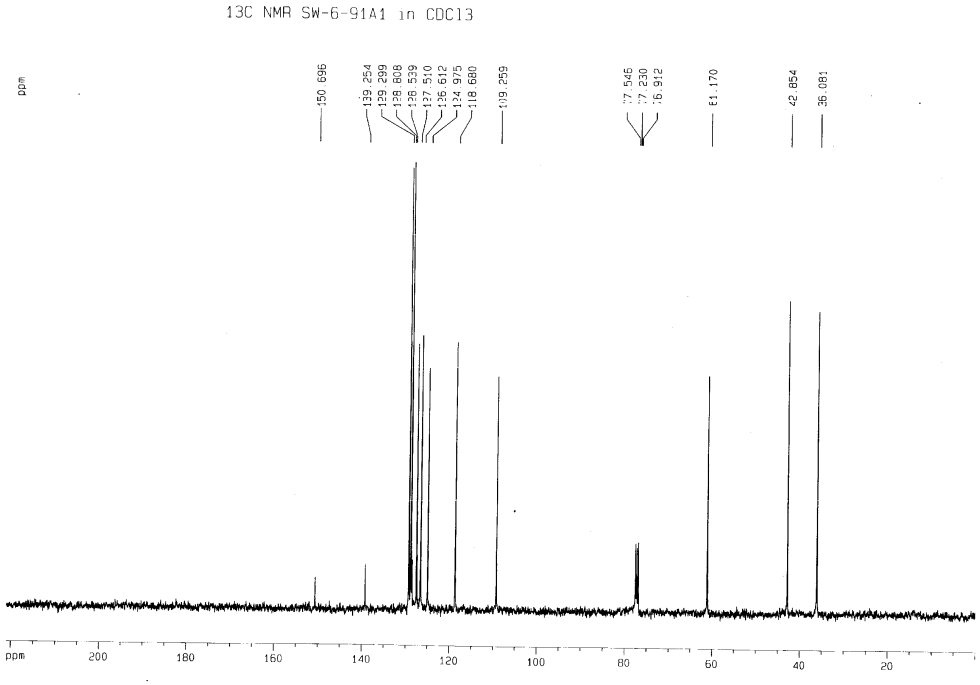


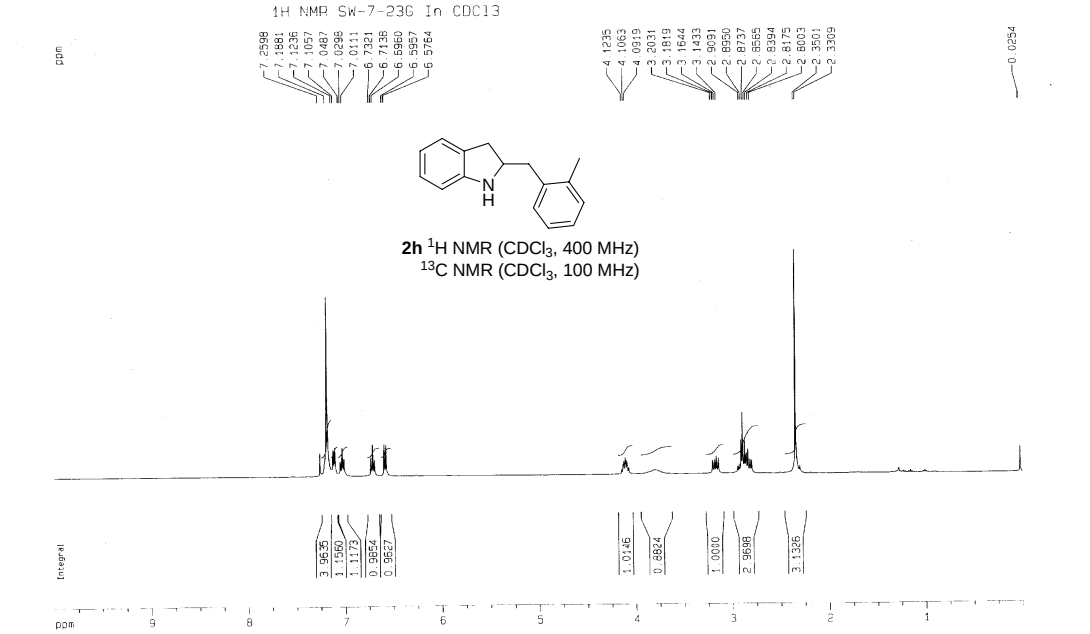




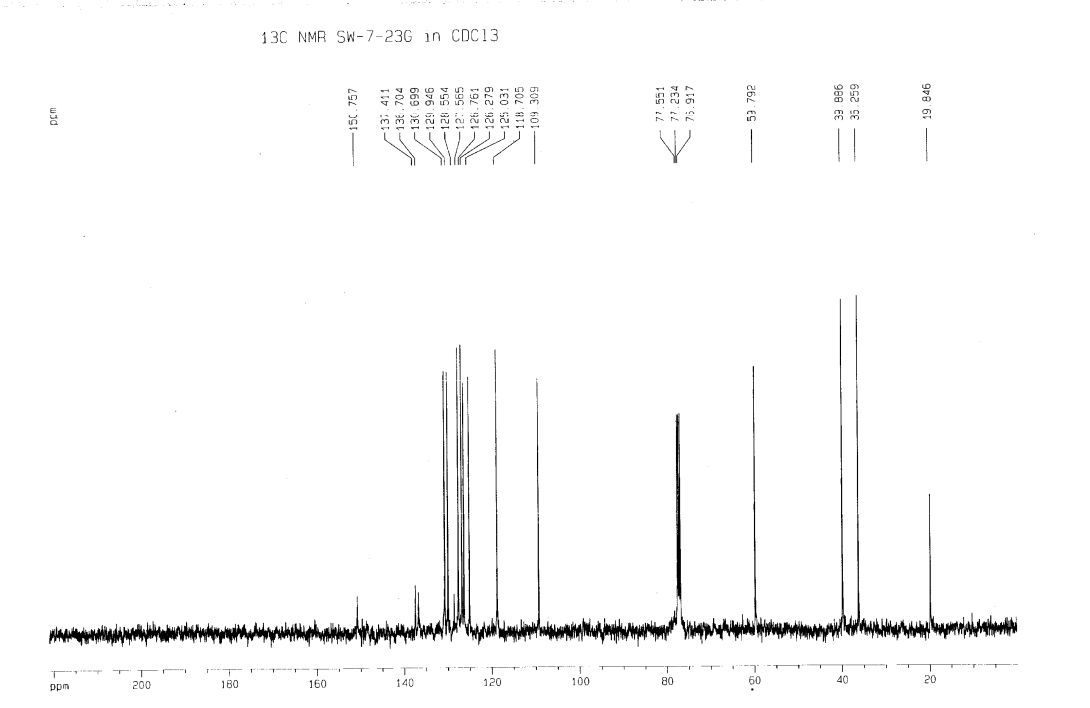
2g ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)







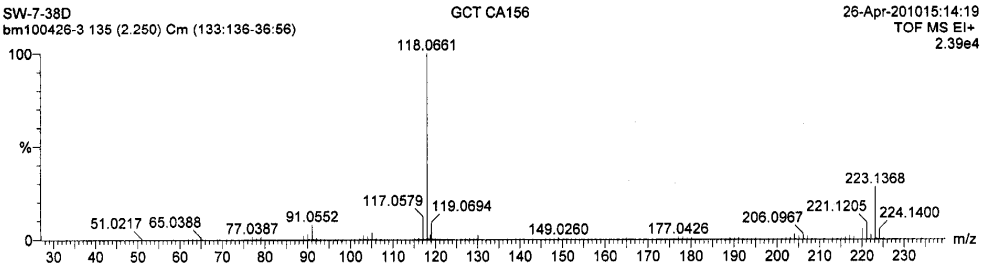
2h ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



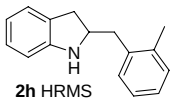
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

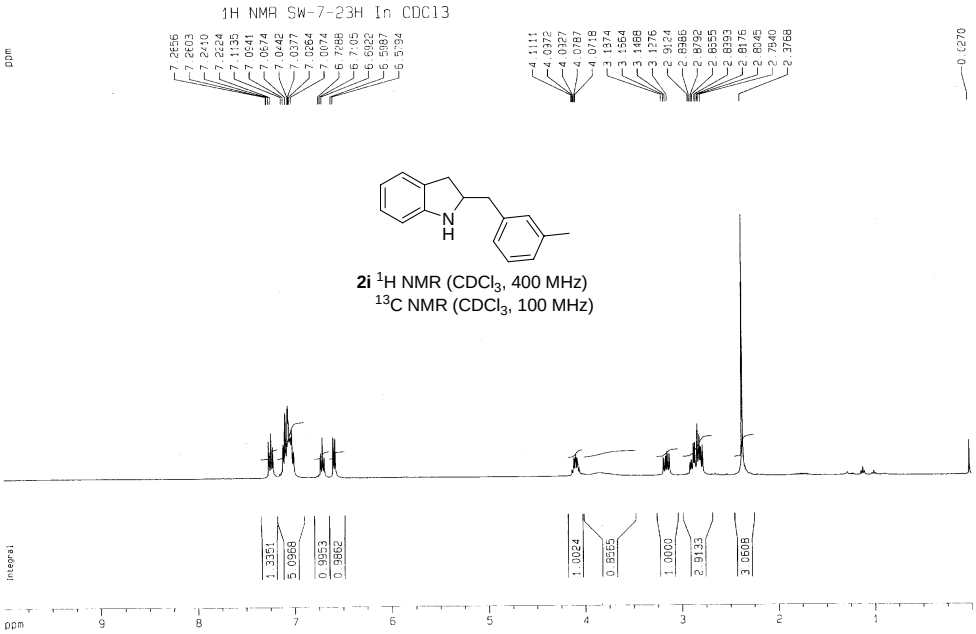
Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)



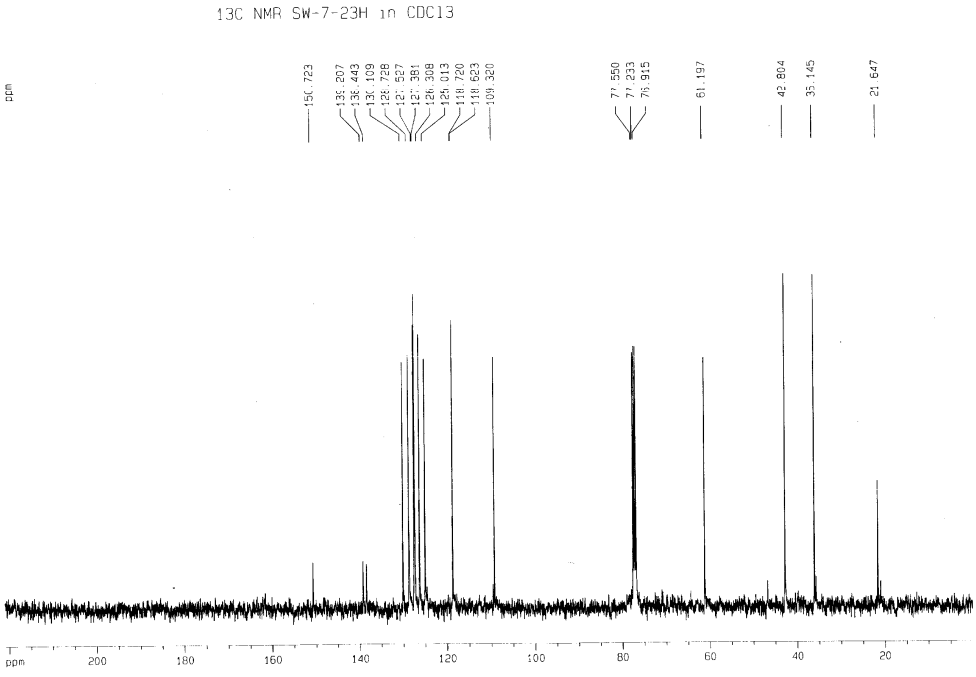
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
223.1368	223.1361	0.7	3.1	9.0	1	C16 H17 N
	223.1487	-11.9	-53.2	8.5	2	C17 H19
	223.0548	82.0	367.6	15.5	4	C18 H7
	223.0422	94.6	424.0	16.0	3	C17 H5 N



2h HRMS



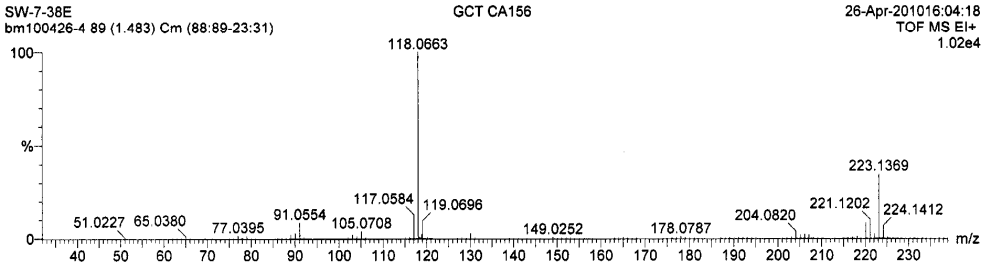
2i ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



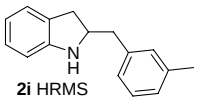
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

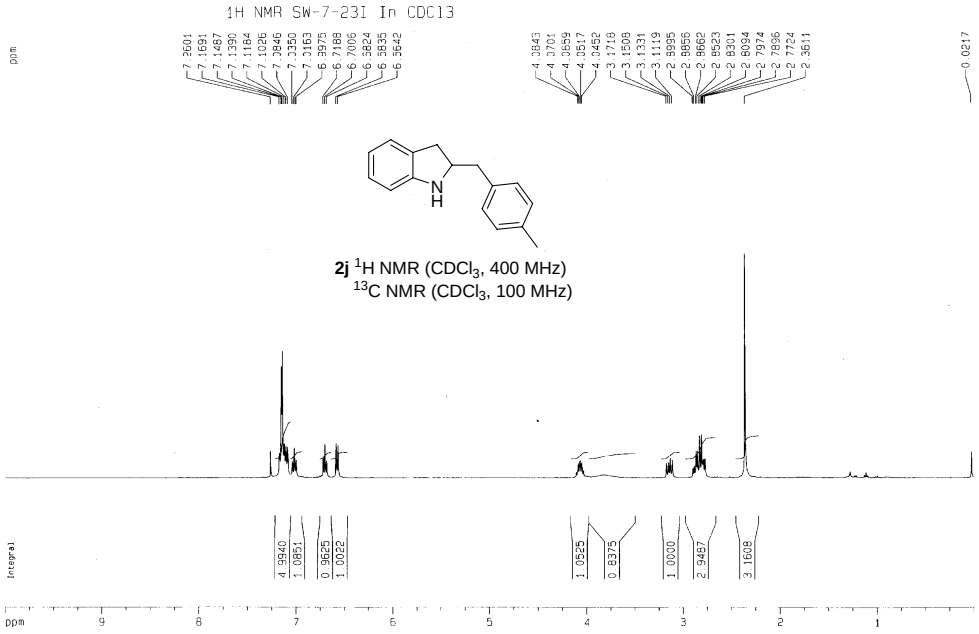
Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)



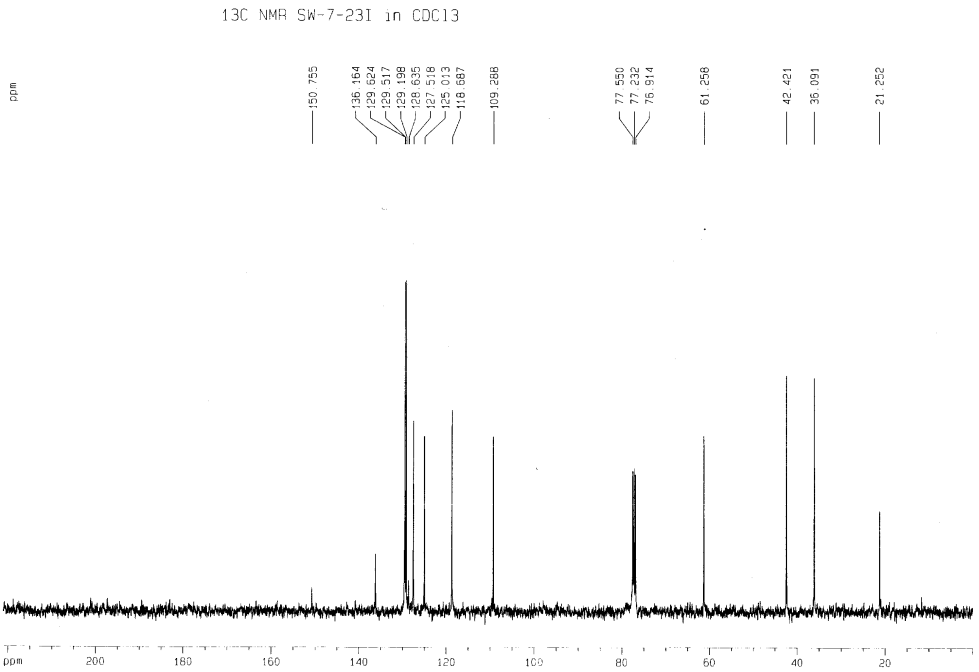
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
223.1369	223.1361	0.8	3.6	9.0	1	C16 H17 N
	223.1487	-11.8	-52.8	8.5	2	C17 H19
	223.0548	82.1	368.0	15.5	4	C18 H7
	223.0422	94.7	424.4	16.0	3	C17 H5 N



2i HRMS



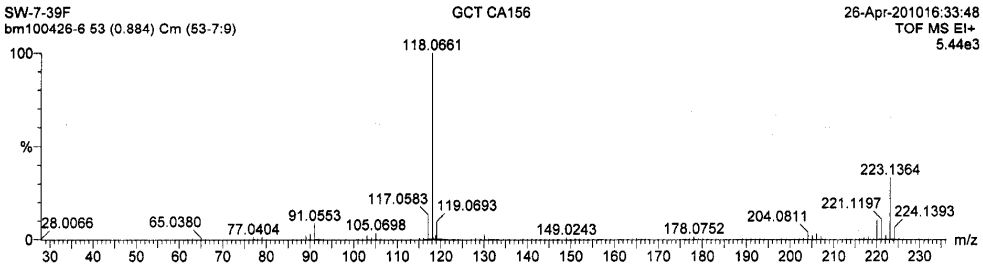
2j ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



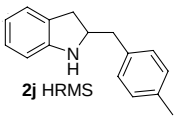
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

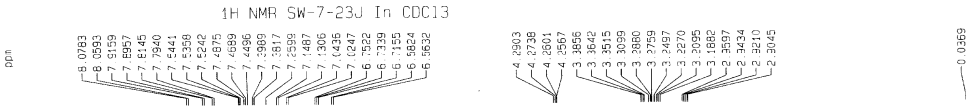
Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

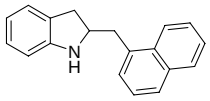


Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
223.1364	223.1361	0.3	1.3	9.0	3	C16 H17 N
	223.1487	-12.3	-55.0	8.5	1	C17 H19
	223.0548	81.6	365.8	15.5	4	C18 H7
	223.0422	94.2	422.2	16.0	2	C17 H5 N

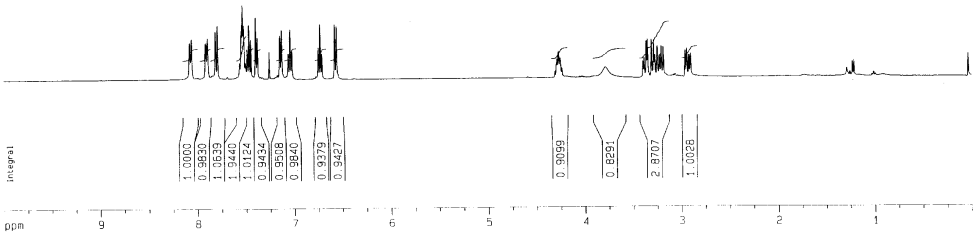


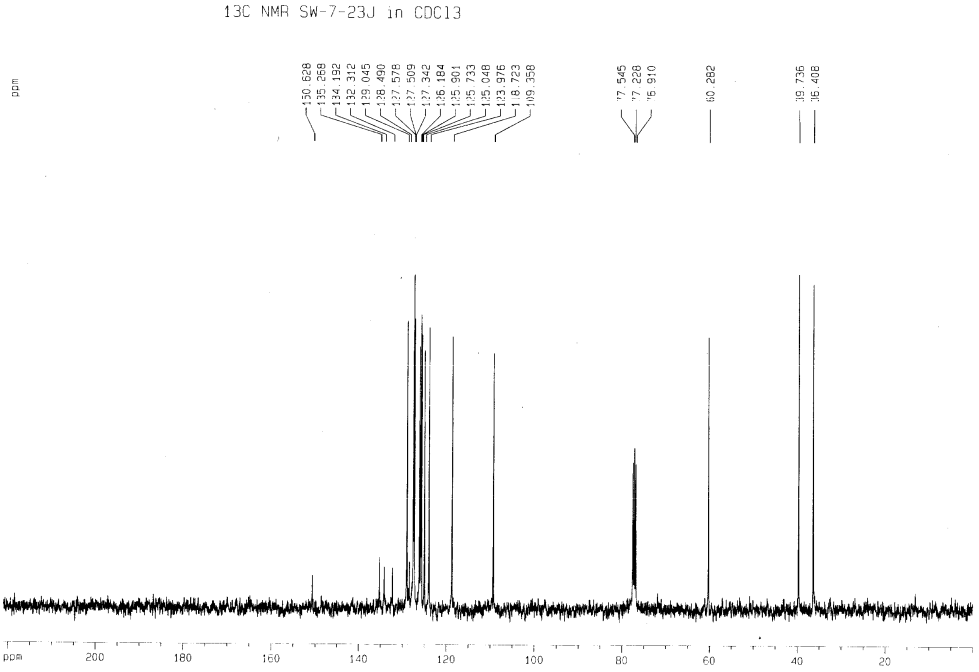
2j HRMS





2k ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)

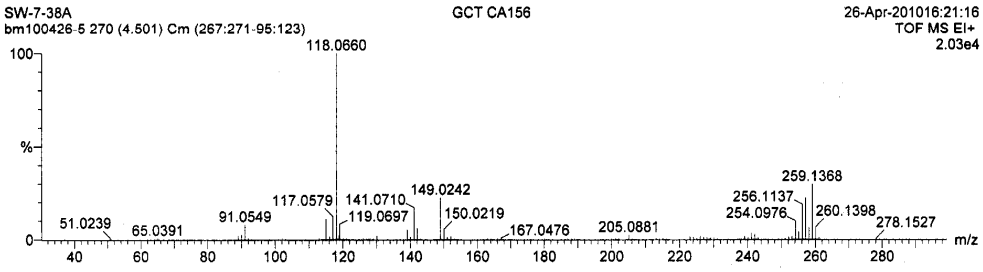




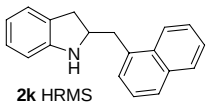
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

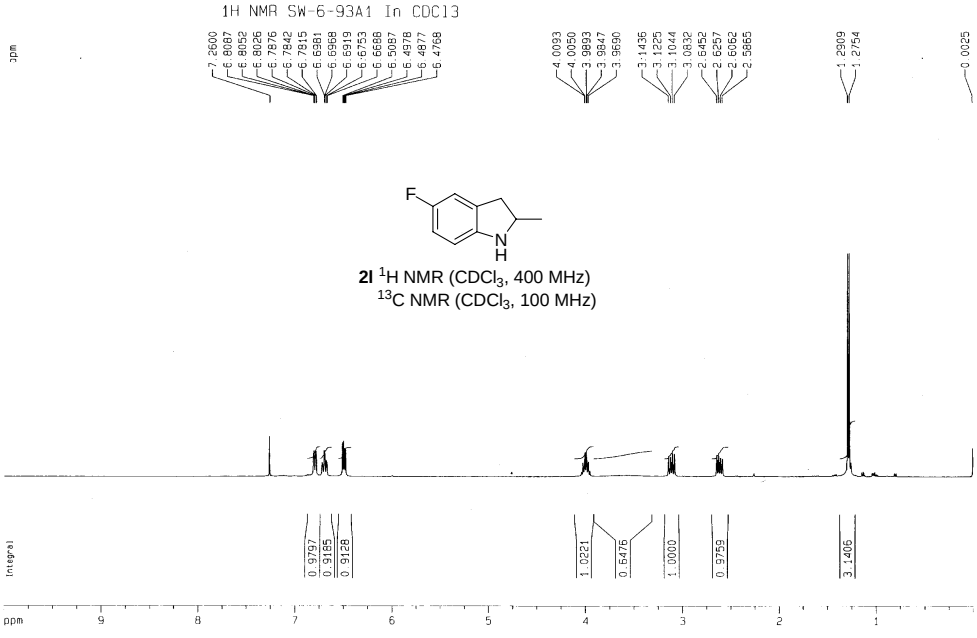
Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)



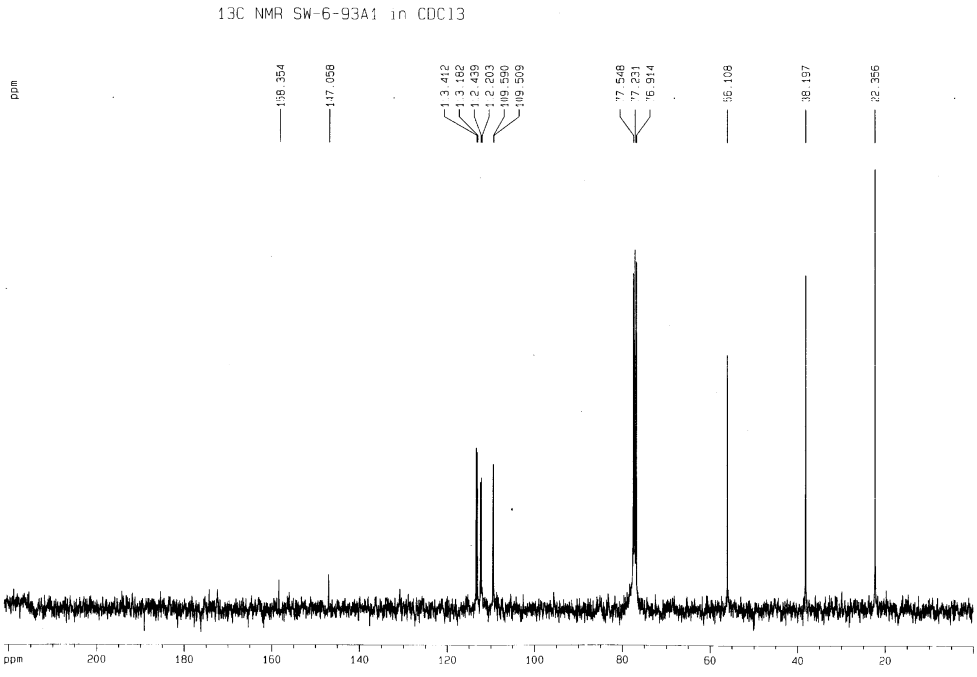
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
259.1368	259.1361	0.7	2.7	12.0	2	C19 H17 N
	259.1487	-11.9	-45.8	11.5	1	C20 H19
	259.0548	82.0	316.5	18.5	4	C21 H7
	259.0422	94.6	365.1	19.0	3	C20 H5 N

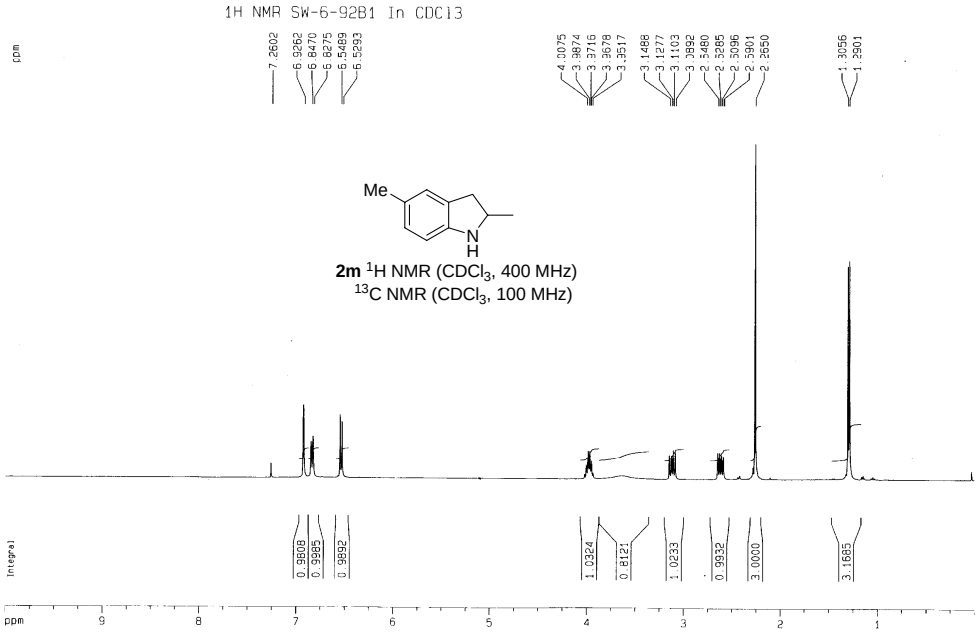


2k HRMS

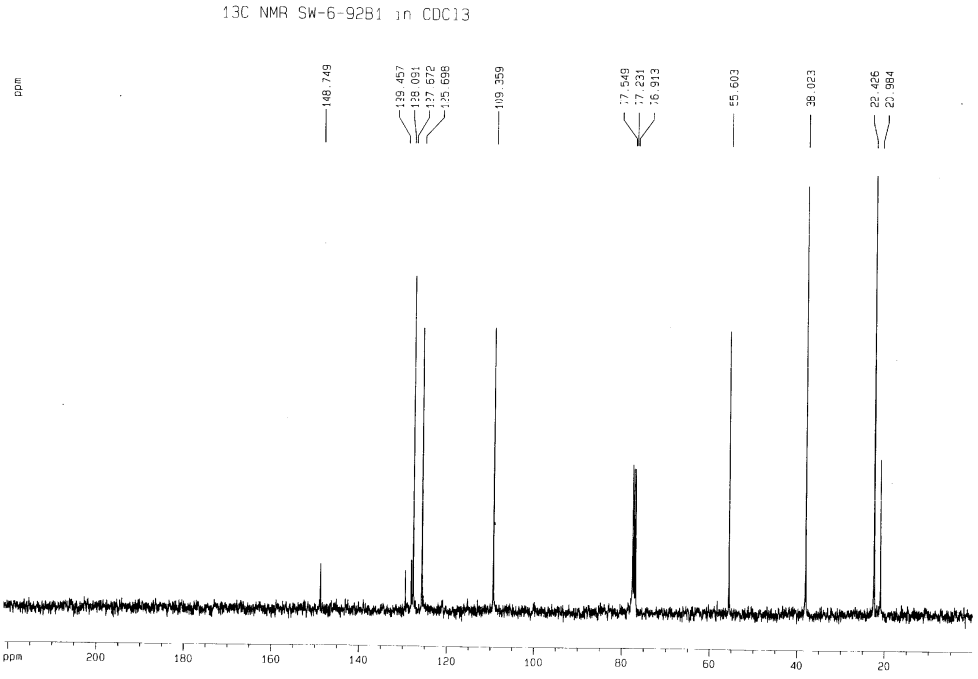


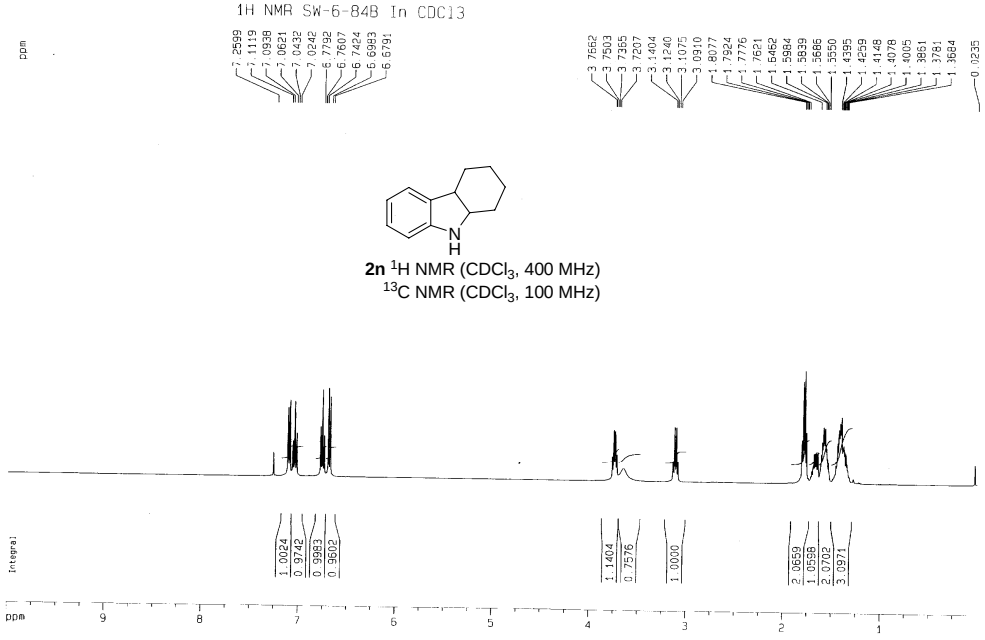
2l ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



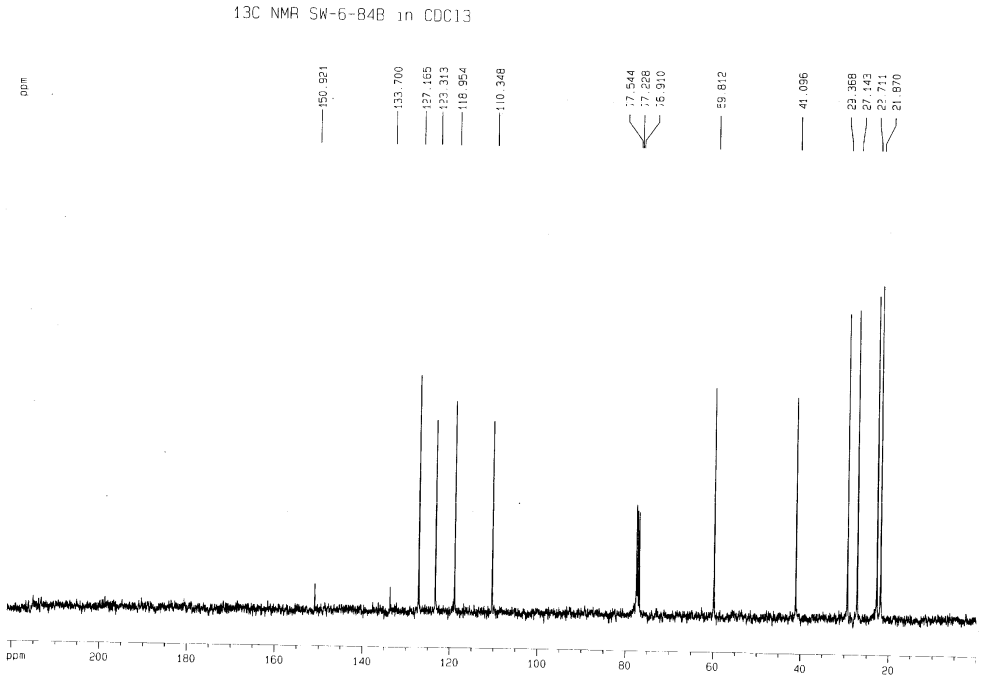


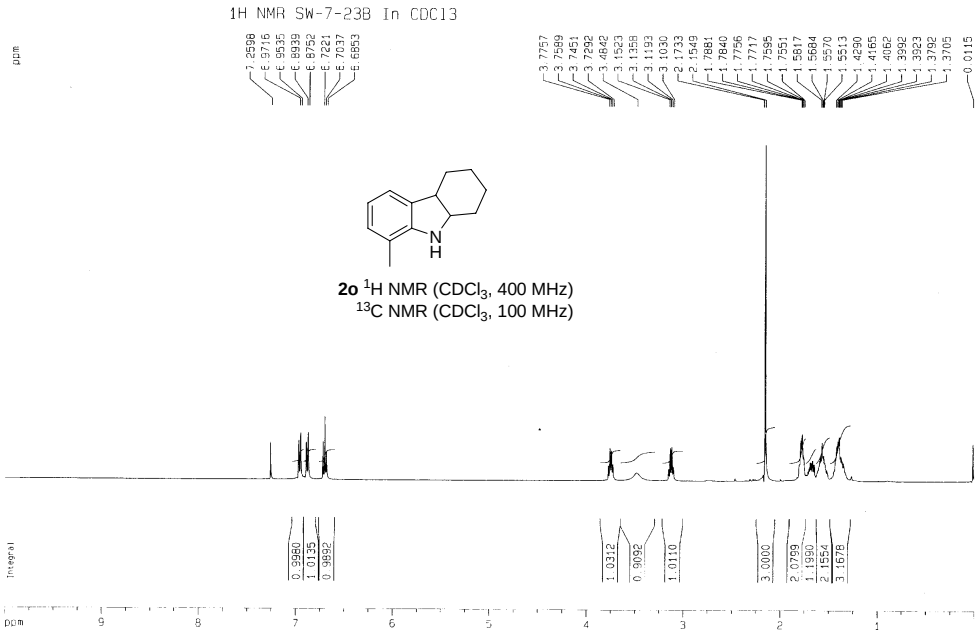
2m ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



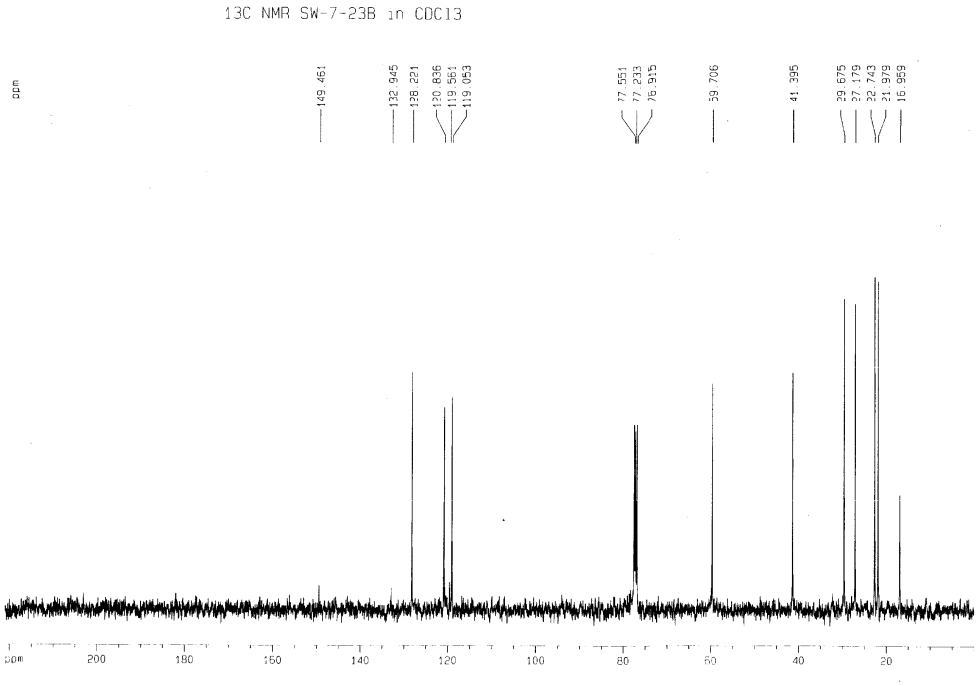


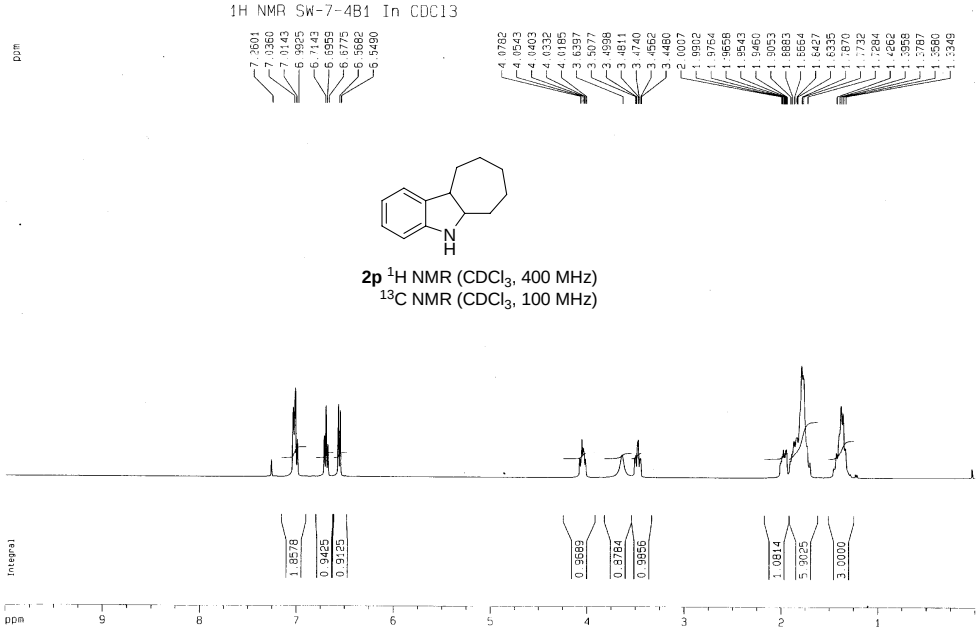
2n ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



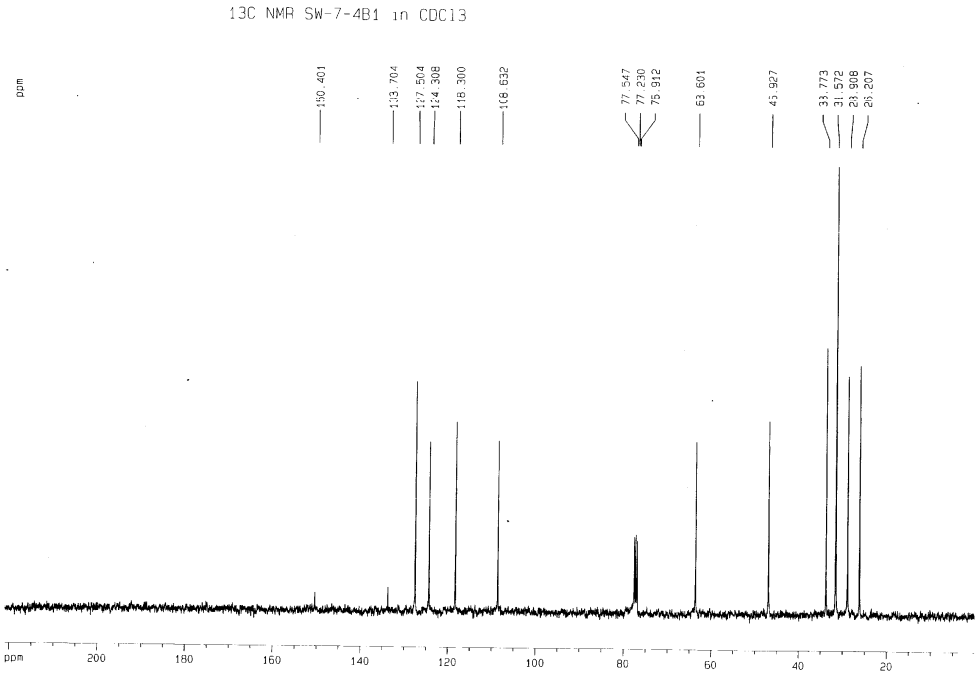


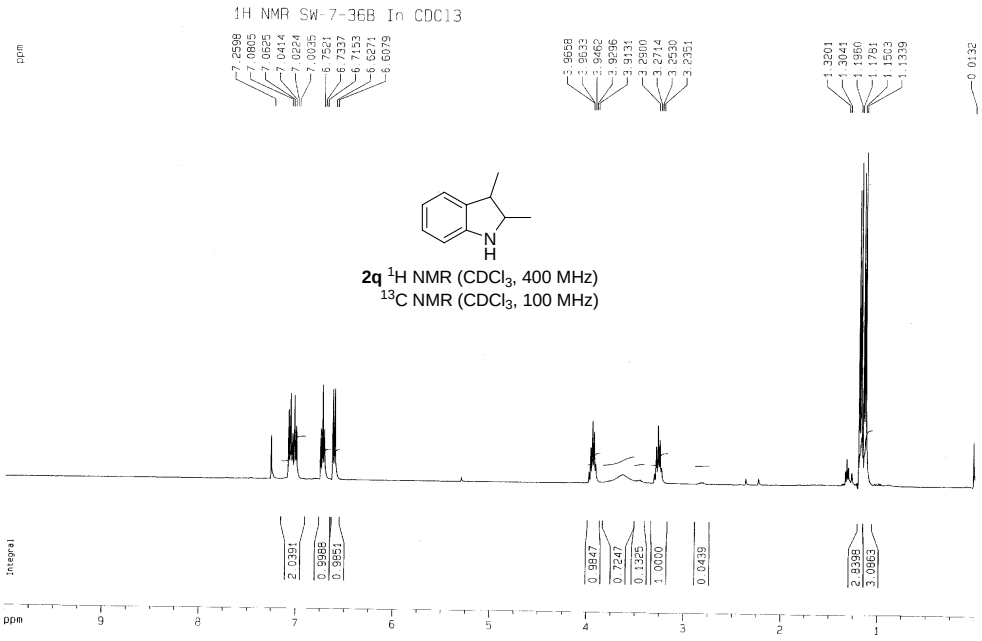
2o ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



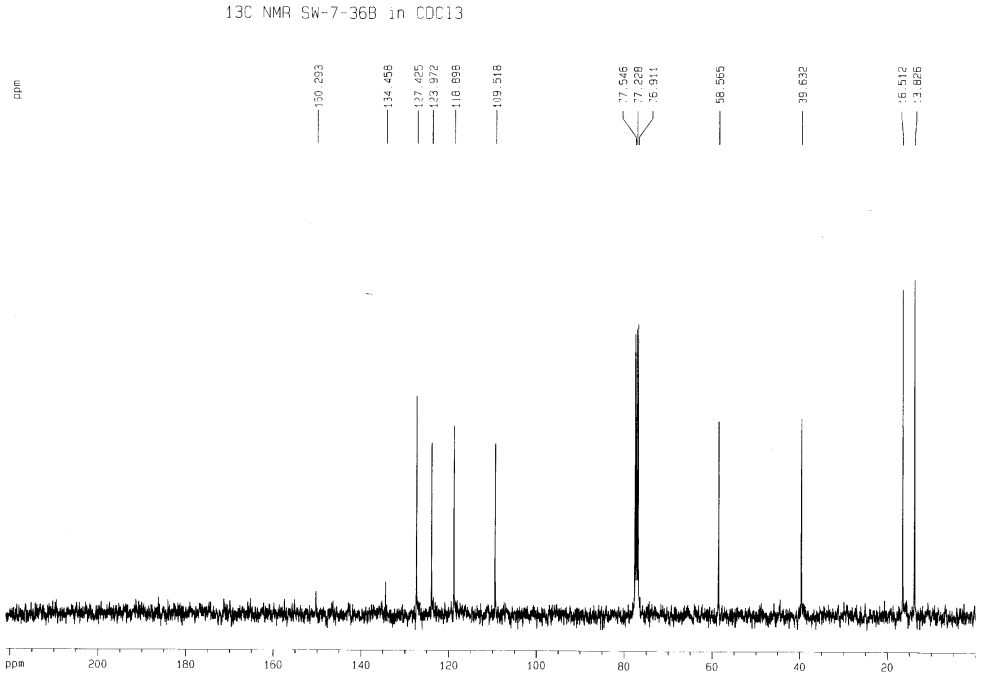


2p ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)





2q ^{1}H NMR ($CDCl_3$, 400 MHz)
^{13}C NMR ($CDCl_3$, 100 MHz)



8. Copy of HPLC for Racemic and Chiral Compounds

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008620.D Sample Name: SW-6-11C

OD-H, H/i-PrOH =97/3, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/24/2010 10:44:17 PM
Sample Name     : SW-6-11C                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/24/2010 10:48:55 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/24/2010 10:57:12 PM
                  (modified after loading)
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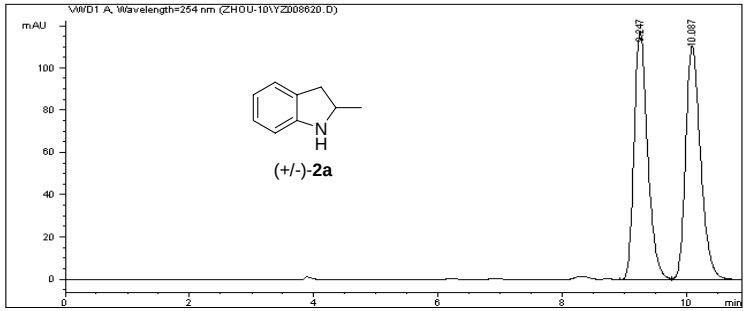

(+/-)-**2a**

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min] mAU   *s    [mAU   ]      %
----|------|----|-------|----------|----------|-------|
   1   9.247 VV    0.2323 1777.86108  117.17072  49.0494
   2  10.087 VB    0.2559 1846.76953  110.61621  50.9506

Totals :                  3624.63062  227.78693

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

Instrument 1 4/24/2010 10:57:15 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008619.D Sample Name: SW-7-35A

OD-H, H/i-PrOH =97/3, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/24/2010 10:30:13 PM
Sample Name     : SW-7-35A                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/24/2010 10:26:52 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/24/2010 10:48:52 PM
                  (modified after loading)
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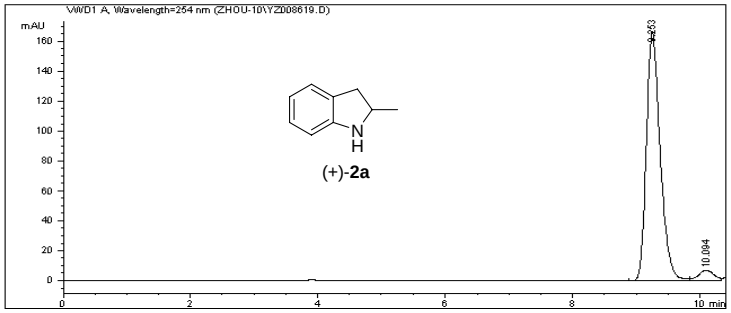

(+)-**2a**

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min] mAU   *s    [mAU   ]      %
----|------|----|-------|----------|----------|-------|
   1   9.253 VV    0.2311 2520.65015  165.94914  95.5271
   2  10.094 VV    0.2576  118.02444    6.95730   4.4729

Totals :                  2638.67459  172.90644

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

Instrument 1 4/24/2010 10:48:55 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008651.D Sample Name: SW-6-92A1
OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 11:51:49 PM
Sample Name     : SW-6-92A1                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 11:48:44 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 12:02:22 AM
                  (modified after loading)
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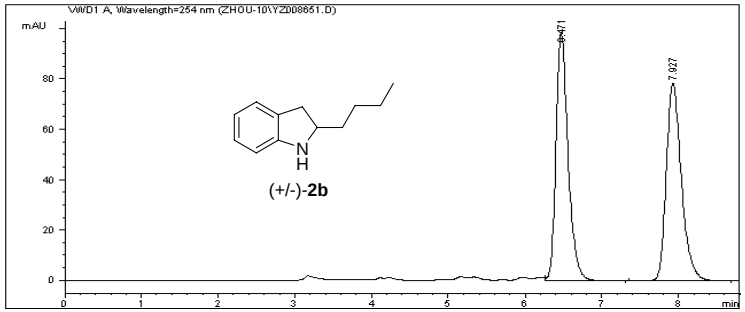

(+/-)-**2b**

```
                    Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.471 VB    0.1665 1073.27893   98.43377  50.1311
   2   7.927 BB    0.2088 1067.66406   78.20947  49.8689

Totals :                  2140.94299  176.64323

 Results obtained with enhanced integrator!

                    *** End of Report ***
```


Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008650.D Sample Name: SW-7-39H
OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 11:29:01 PM
Sample Name     : SW-7-39H                     Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 11:24:00 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 12:02:25 AM
                  (modified after loading)
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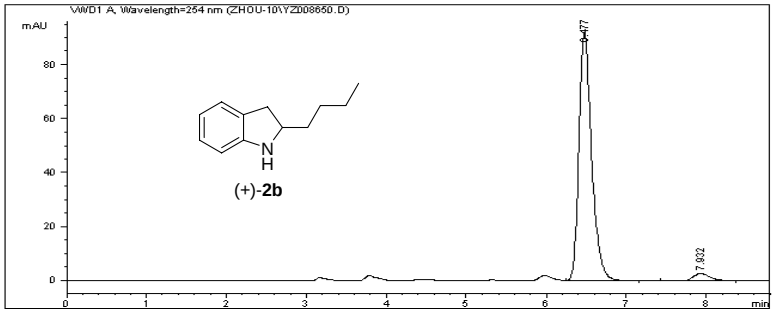

(+)-**2b**

```
                    Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.477 VB    0.1677 1011.73425   91.97246  96.2562
   2   7.932 BV    0.2179   39.34998    2.70256   3.7438

Totals :                  1051.08424   94.67502

 Results obtained with enhanced integrator!

                    *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008653.D Sample Name: SW-7-4Cl

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
==========================================================================
Injection Date  : 4/26/2010 12:25:14 AM
Sample Name     : SW-7-4Cl                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 12:21:39 AM
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Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 7:01:15 PM
                  (modified after loading)
==========================================================================
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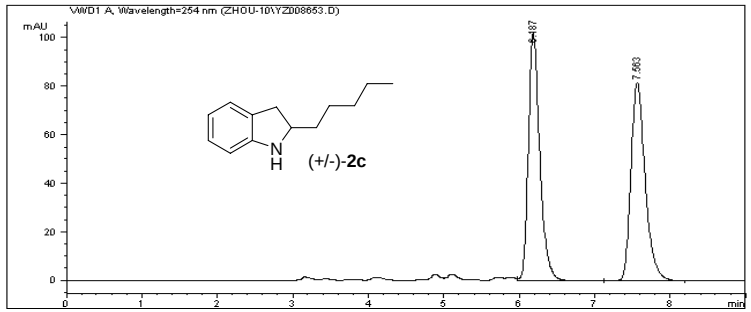


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s     [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.187 VV    0.1591 1072.82458  101.97888  50.1674
   2   7.563 VV    0.1992 1065.66626   81.45729  49.8326

Totals :                  2138.49084  183.43617

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```


Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008652.D Sample Name: SW-7-39I

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
==========================================================================
Injection Date  : 4/26/2010 12:07:51 AM
Sample Name     : SW-7-39I                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 12:02:48 AM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 7:00:57 PM
                  (modified after loading)
==========================================================================
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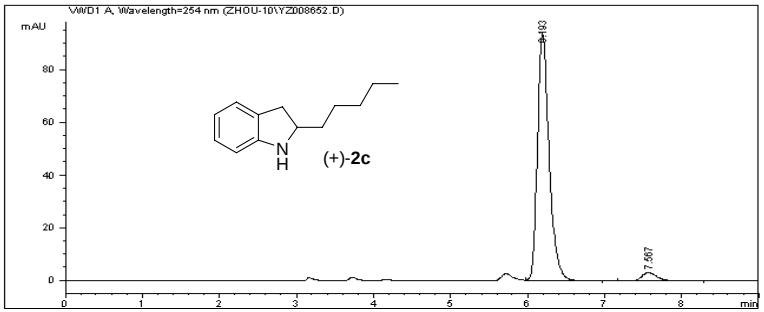


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s     [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.193 VB    0.1602  985.57794   93.97333  95.9530
   2   7.567 BB    0.2049   41.56880    3.06292   4.0470

Totals :                  1027.14674   97.03624

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008634.D Sample Name: SW-6--97B1

OD-H, H/i-PrOH =97/3, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 4:21:55 PM
Sample Name     : SW-6--97B1                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 4:17:14 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 5:52:49 PM
                  (modified after loading)
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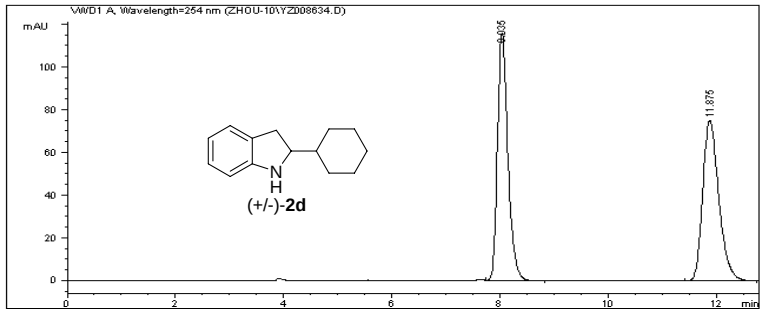

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.035	VB	0.2037	1549.07898	116.08145	50.1021
2	11.875	PV	0.3166	1542.76257	75.17569	49.8979
Totals :				3091.84155	191.25714	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008638.D Sample Name: SW-7-38B

OD-H, H/i-PrOH =97/3, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 5:31:21 PM
Sample Name     : SW-7-38B                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 4:59:47 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 5:56:18 PM
                  (modified after loading)
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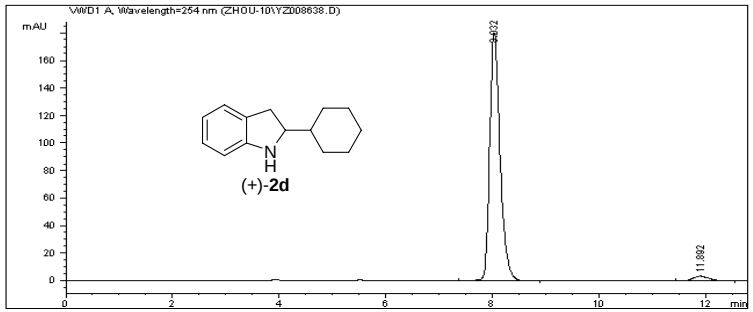

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.032	VB	0.2034	2419.27466	179.98511	97.2924
2	11.892	MM R	0.3428	67.32703	3.27377	2.7076
Totals :				2486.60168	183.25887	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008639.D Sample Name: SW-7-23E
OD-H, H/i-PrOH =97/3, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 6:00:35 PM
Sample Name     : SW-7-23E                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 5:56:39 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 6:37:51 PM
                  (modified after loading)
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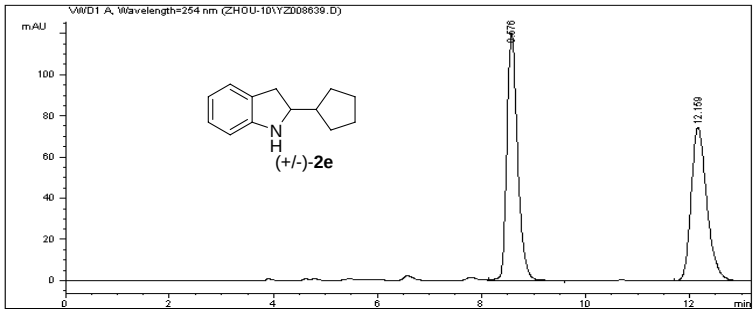

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.576	VV	0.2158	1712.58838	120.11675	52.4836
2	12.159	VV	0.3209	1550.50159	74.22321	47.5164
Totals :				3263.08997	194.33997	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008640.D Sample Name: SW-7-38C
OD-H, H/i-PrOH =97/3, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 6:22:45 PM
Sample Name     : SW-7-38C                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 6:22:18 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 6:37:54 PM
                  (modified after loading)
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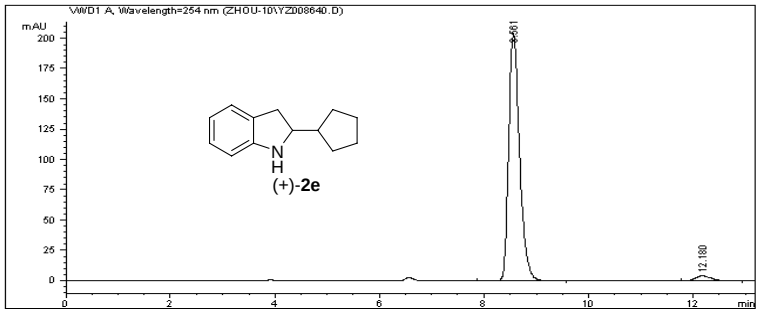

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.561	VB	0.2178	2921.91113	204.30115	97.3110
2	12.180	BB	0.3219	80.74018	3.87222	2.6890
Totals :				3002.65131	208.17336	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008689.D Sample Name: SW-7-11C

OD-H, H/i-PrOH =90/10, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 10:19:23 PM
Sample Name     : SW-7-11C                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 10:14:52 PM
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Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 10:47:39 PM
                  (modified after loading)
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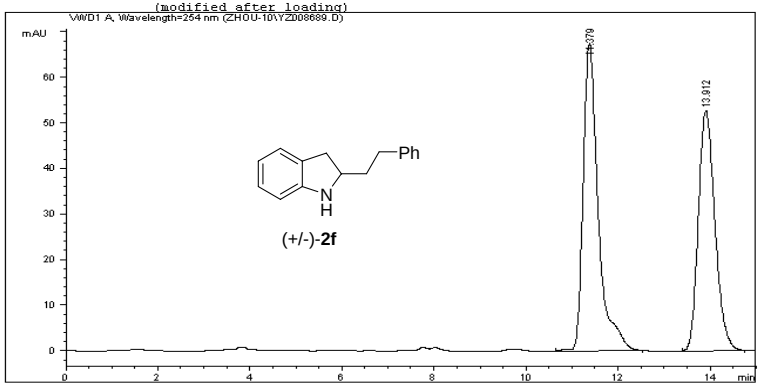

(+/-)-**2f**

```
                    Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.379 BB    0.3412 1535.80872   67.48908  53.7729
   2  13.912 BB    0.3887 1320.29248   52.63951  46.2271

Totals :                  2856.10120  120.12859

 Results obtained with enhanced integrator!

                    *** End of Report ***
```


Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008686.D Sample Name: SW-7-40R

OD-H, H/i-PrOH =90/10, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 6:24:08 PM
Sample Name     : SW-7-40R                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 5:49:27 PM
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Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 10:48:46 PM
                  (modified after loading)
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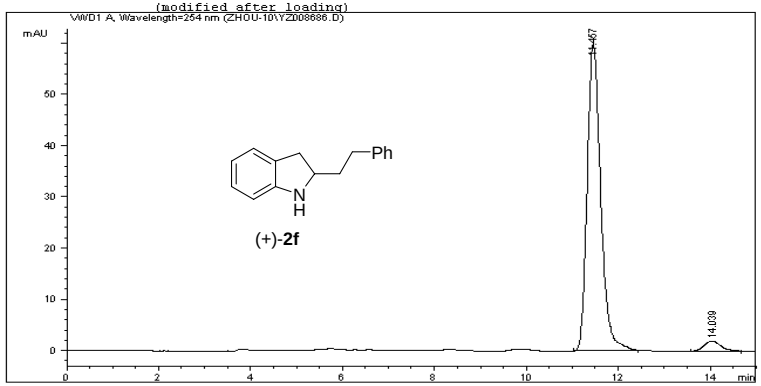


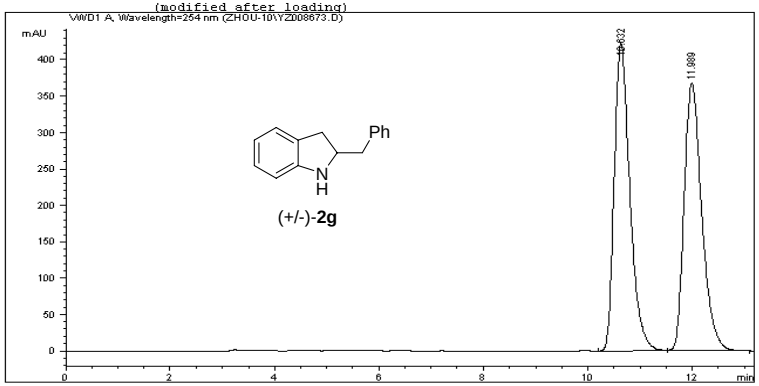
(+)-**2f**

```
                    Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.457 BB    0.3151 1230.97864   60.00121  96.2850
   2  14.039 BB    0.3741   47.49486    1.91309   3.7150

Totals :                  1278.47350   61.91430

 Results obtained with enhanced integrator!

                    *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008673.D Sample Name: SW-7-11B

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 10:23:57 AM
Sample Name     : SW-7-11B                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 10:01:51 AM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 10:45:46 AM
                  (modified after loading)
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.632 VV     0.3160 8756.19043  422.54440  50.4167
   2  11.989 VB     0.3607 8611.43848  367.51370  49.5833

Totals :                  1.73676e4   790.05811

 Results obtained with enhanced integrator!
```

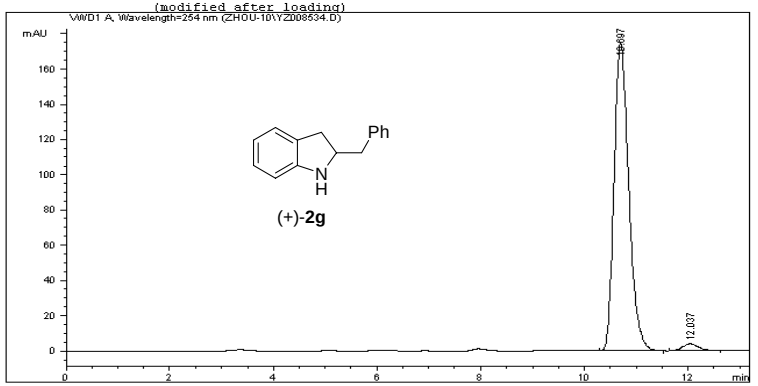
*** End of Report ***

Instrument 1 4/27/2010 10:45:48 AM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008534.D Sample Name: SW-7-39G

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/19/2010 12:36:34 AM
Sample Name     : SW-7-39G                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/19/2010 12:32:49 AM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 10:45:13 AM
                  (modified after loading)
```



Area Percent Report

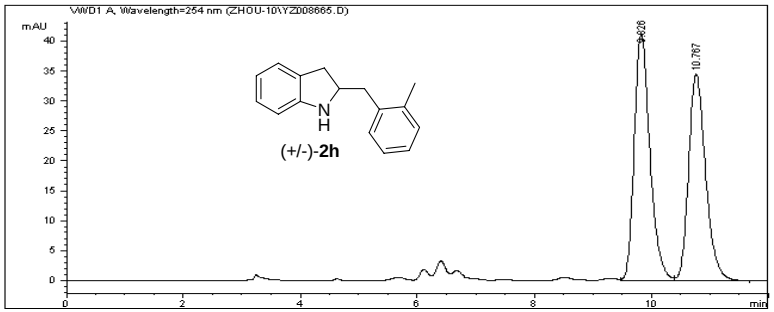
```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.697 PB     0.3019 3424.12744  174.39500  97.6928
   2  12.037 PP     0.3308   80.86794    3.82951   2.3072

Totals :                  3504.99538  178.22451

 Results obtained with enhanced integrator!
```

*** End of Report ***

Instrument 1 4/27/2010 10:45:17 AM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008665.D Sample Name: SW-7-23G
OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

Injection Date : 4/26/2010 10:57:05 PM
Sample Name : SW-7-23G Location : Vial 1
Acq. Operator :
Acq. Method : C:\HPCHEM\1\METHODS\SW.M
Last changed : 4/26/2010 10:52:04 PM
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed : 4/26/2010 11:31:59 PM
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.826	VV	0.2839	768.05121	41.31530	52.3584
2	10.767	VV	0.3125	698.85999	34.42633	47.6416
Totals :				1466.91119	75.74163	

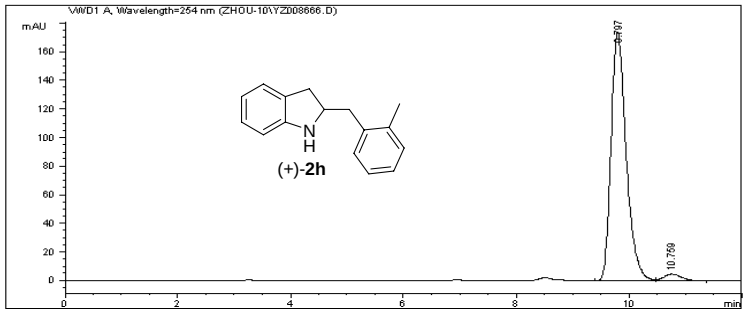
Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 4/26/2010 11:32:38 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008666.D Sample Name: SW-7-38D
OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

Injection Date : 4/26/2010 11:12:42 PM
Sample Name : SW-7-38D Location : Vial 1
Acq. Operator :
Acq. Method : C:\HPCHEM\1\METHODS\SW.M
Last changed : 4/26/2010 11:10:17 PM
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed : 4/26/2010 11:31:44 PM
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.797	VV	0.2861	3231.70166	173.23311	97.0243
2	10.759	VV	0.3224	99.11546	4.65925	2.9757
Totals :				3330.81712	177.89236	

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 4/26/2010 11:31:59 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008663.D Sample Name: SW-7-24H

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/26/2010 10:24:02 PM
Sample Name     : SW-7-24H                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 10:20:45 PM
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Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 10:51:31 PM
                  (modified after loading)
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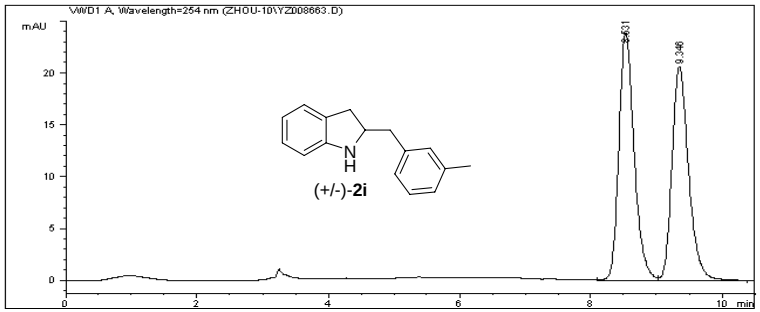

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1   8.531 VV    0.2460  384.32294   23.87985  51.4304
   2   9.346 VB    0.2676  362.94531   20.65594  48.5696

Totals :                   747.26825   44.53579

 Results obtained with enhanced integrator!
```

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008664.D Sample Name: SW-7-38E

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/26/2010 10:39:30 PM
Sample Name     : SW-7-38E                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 10:35:52 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 10:52:02 PM
                  (modified after loading)
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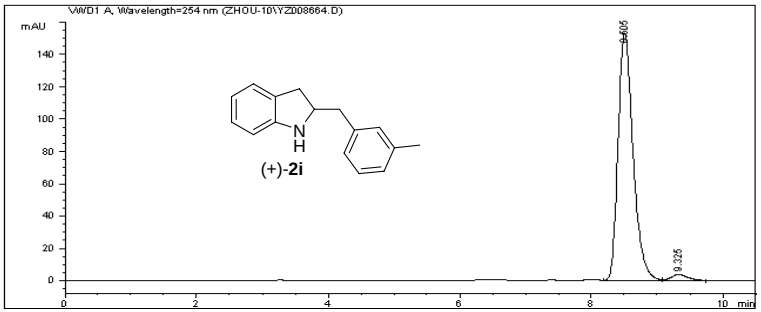


Area Percent Report

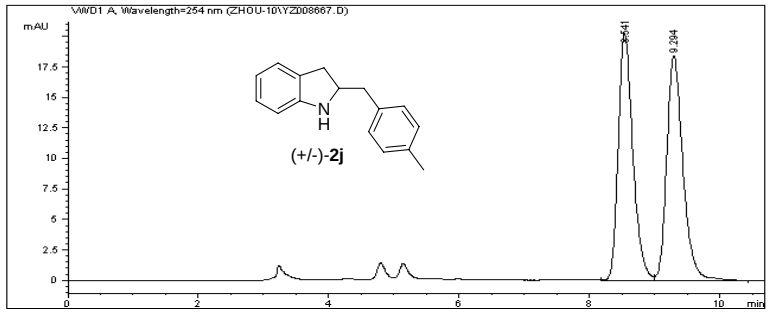
```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1   8.505 VV    0.2402 2410.26196  153.30032  97.1798
   2   9.325 VV    0.2807   69.94645    3.76668   2.8202

Totals :                  2480.20841  157.06700

 Results obtained with enhanced integrator!
```

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008667.D Sample Name: SW-7-24I

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

Injection Date	: 4/26/2010 11:37:13 PM		
Sample Name	: SW-7-24I	Location : Vial 1	
Acq. Operator	:		
Acq. Method	: C:\HPCHEM\1\METHODS\SW.M		
Last changed	: 4/26/2010 11:32:57 PM (modified after loading)		
Analysis Method	: C:\HPCHEM\1\METHODS\SW.M		
Last changed	: 4/26/2010 11:52:55 PM (modified after loading)		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.541	VV	0.2384	315.90903	20.29078	49.6497
2	9.294	VV	0.2654	320.36688	18.43404	50.3503
Totals :				636.27591	38.72482	

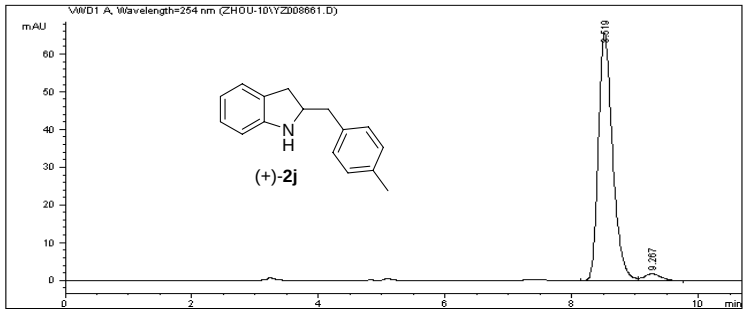
Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008661.D Sample Name: SW-7--39F

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

Injection Date	: 4/26/2010 9:45:55 PM		
Sample Name	: SW-7--39F	Location : Vial 1	
Acq. Operator	:		
Acq. Method	: C:\HPCHEM\1\METHODS\SW.M		
Last changed	: 4/26/2010 9:20:58 PM (modified after loading)		
Analysis Method	: C:\HPCHEM\1\METHODS\SW.M		
Last changed	: 4/26/2010 11:53:13 PM (modified after loading)		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.519	VV	0.2396	1028.83875	65.66262	96.6692
2	9.267	VV	0.2837	35.44900	1.85855	3.3308
Totals :				1064.28774	67.52117	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008676.D Sample Name: SW-7-24J

OD-H, H/i-PrOH =90/10, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 11:55:30 AM
Sample Name     : SW-7-24J                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 11:50:15 AM
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Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 12:16:17 PM
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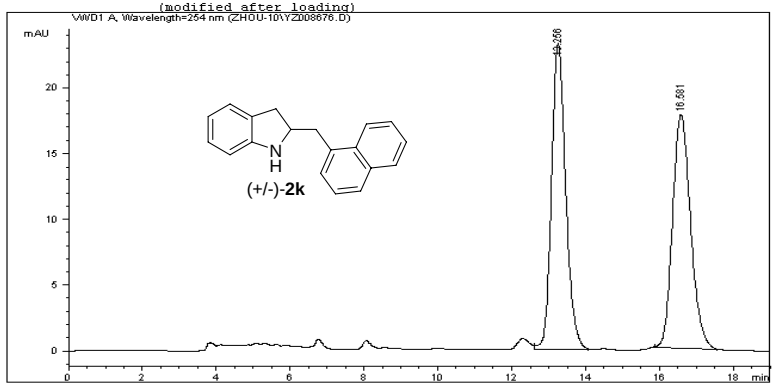

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.256	VB	0.4105	620.52875	23.24019	50.7143
2	16.581	BB	0.5284	603.04840	17.76894	49.2857
Totals :				1223.57715	41.00914	

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 4/27/2010 12:16:23 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008678.D Sample Name: SW-7-38A

OD-H, H/i-PrOH =90/10, 0.8 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 12:55:54 PM
Sample Name     : SW-7-38A                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 12:31:40 PM
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Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 1:17:59 PM
                  (modified after loading)
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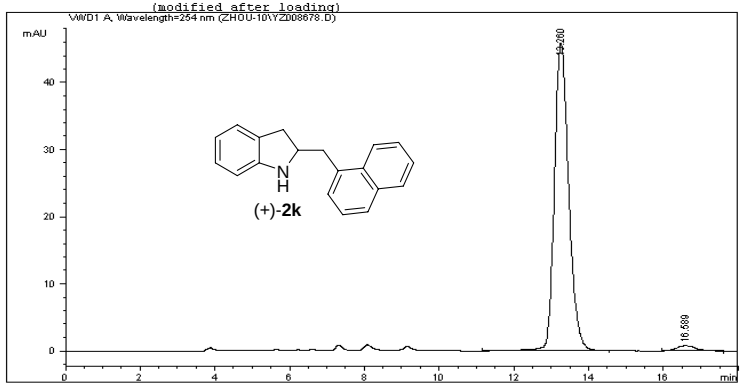

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.260	BB	0.4101	1221.06433	45.79693	97.8249
2	16.589	BB	0.5158	27.15018	7.93293e-1	2.1751
Totals :				1248.21452	46.59022	

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 4/27/2010 1:18:12 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008647.D Sample Name: SW-6-93Al
OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 10:01:32 PM
Sample Name     : SW-6-93Al                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 9:32:32 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 11:23:43 PM
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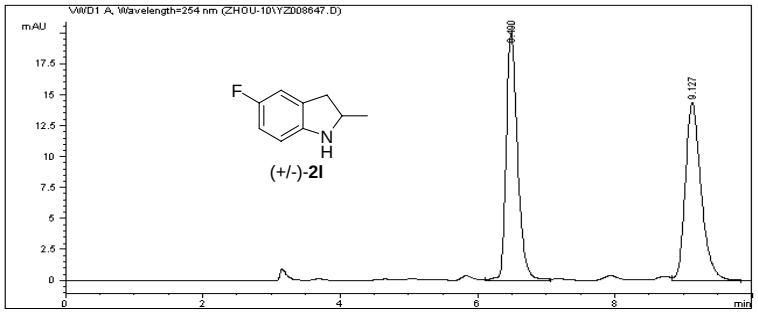


Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s     [mAU   ]     %
----|-------|----|-------|----------|----------|-------|
   1   6.490 VV    0.1725  227.99286   19.96414  49.9148
   2   9.127 VB    0.2433  228.77126   14.30935  50.0852

Totals :                   456.76411   34.27350

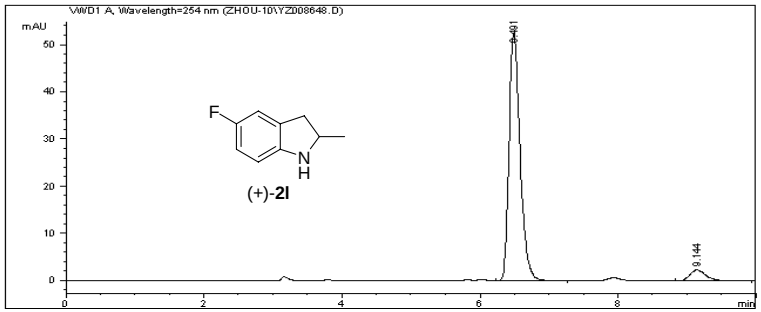
 Results obtained with enhanced integrator!
```

*** End of Report ***

Instrument 1 4/25/2010 11:24:00 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008648.D Sample Name: SW-7-39J
OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 10:49:09 PM
Sample Name     : SW-7-39J                     Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 10:58:32 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 11:23:19 PM
                  (modified after loading)
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s     [mAU   ]     %
----|-------|----|-------|----------|----------|-------|
   1   6.491 VB    0.1677  577.88287   52.49230  94.0699
   2   9.144 VB    0.2460   36.42935    2.26370   5.9301

Totals :                   614.31222   54.75600

 Results obtained with enhanced integrator!
```

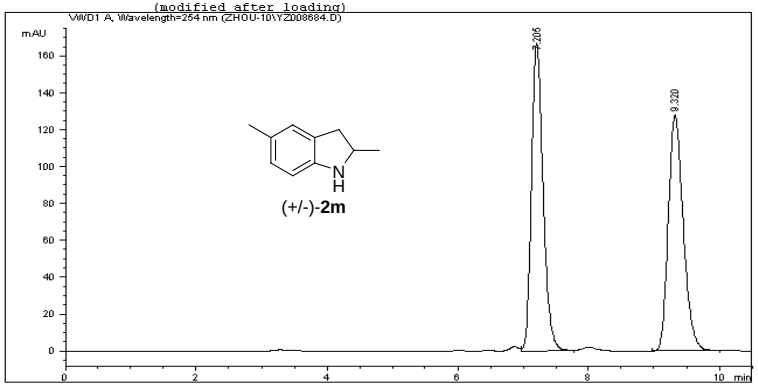
*** End of Report ***

Instrument 1 4/25/2010 11:23:42 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008684.D Sample Name: SW-6-92B1

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 5:36:59 PM
Sample Name     : SW-6-92B1                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 4:44:38 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 9:32:44 PM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.205 VB    0.1877 2038.46985  166.77177  50.1703
   2   9.320 PB    0.2444 2024.63025  127.89831  49.8297

Totals :                  4063.10010  294.67008

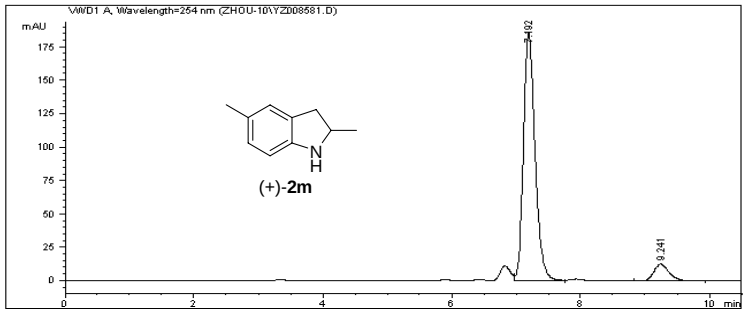
 Results obtained with enhanced integrator!

                        *** End of Report ***
```


Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008581.D Sample Name: SW-7-40P

OD-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/21/2010 11:33:20 PM
Sample Name     : SW-7-40P                     Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/21/2010 11:44:04 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/23/2010 9:15:24 PM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.192 VV    0.1912 2298.70093  185.46124  92.1186
   2   9.241 BB    0.2447  196.66985   12.30543   7.8814

Totals :                  2495.37077  197.76667

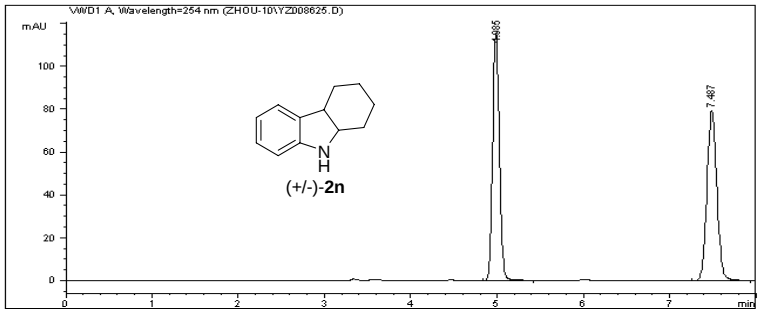
 Results obtained with enhanced integrator!

                        *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008625.D Sample Name: SW-7-11D

IC, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 1:54:48 PM
Sample Name     : SW-7-11D                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 1:30:54 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:25:58 PM
                  (modified after loading)
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.985	VV	0.0850	625.33887	115.48093	49.8515
2	7.487	VV	0.1232	629.06342	79.23167	50.1485
Totals :				1254.40228	194.71261	

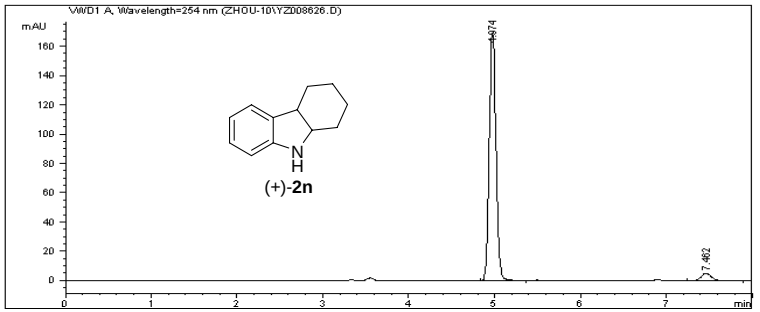
Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008626.D Sample Name: SW-7-39K

IC, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 2:10:28 PM
Sample Name     : SW-7-39K                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:05:24 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:25:33 PM
                  (modified after loading)
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.974	VV	0.0852	918.31342	169.13048	95.4348
2	7.462	VV	0.1342	43.92846	5.01747	4.5652
Totals :				962.24188	174.14795	

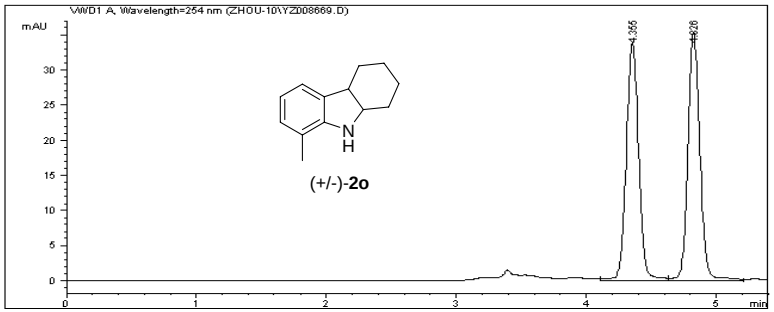
Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008669.D Sample Name: SW-7-23B

IC, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 12:22:27 AM
Sample Name     : SW-7-23B                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/26/2010 11:58:54 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/27/2010 12:48:01 AM
                  (modified after loading)
```



(+/-)-**2o**

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.355	VV	0.1039	226.62943	34.01210	49.9656
2	4.826	VV	0.0982	226.94147	35.32448	50.0344
Totals :				453.57089	69.33657	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008544.D Sample Name: SW-7-39L

IC, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/19/2010 3:50:58 PM
Sample Name     : SW-7-39L                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/19/2010 3:47:09 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/27/2010 12:49:41 AM
                  (modified after loading)
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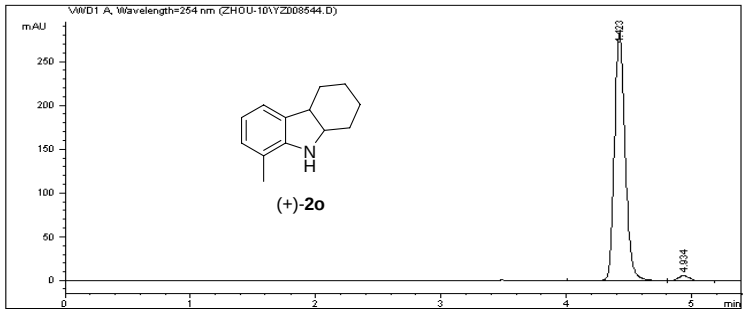


(+)-**2o**

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

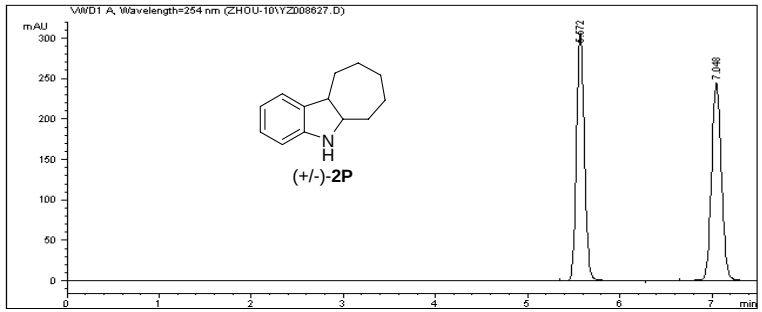
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.423	VV	0.0936	1703.24329	282.84137	97.7914
2	4.934	VV	0.0992	38.46766	5.91249	2.2086
Totals :				1741.71094	288.75386	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008627.D Sample Name: SW-7-4B1
IC, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 2:33:22 PM
Sample Name     : SW-7-4B1                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:26:02 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:55:24 PM
                  (modified after loading)
```



Area Percent Report

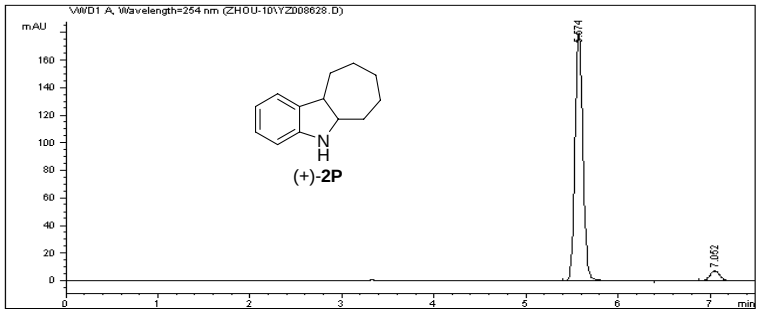
```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s     [mAU   ]      %
----|-------|----|--------|----------|----------|--------|
   1   5.572 VB    0.0913 1825.28418  306.38882  49.8947
   2   7.048 VB    0.1166 1832.98853  244.53371  50.1053

Totals :                  3658.27271  550.92253

 Results obtained with enhanced integrator!
```

*** End of Report ***

Instrument 1 4/25/2010 2:55:42 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008628.D Sample Name: SW-7-40M
IC, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/25/2010 2:43:55 PM
Sample Name     : SW-7-40M                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:43:54 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 4/25/2010 2:55:21 PM
                  (modified after loading)
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s     [mAU   ]      %
----|-------|----|--------|----------|----------|--------|
   1   5.574 VV    0.0926 1068.05249  179.84387  95.1571
   2   7.052 VB    0.1174   54.35738    7.06525   4.8429

Totals :                  1122.40987  186.90912

 Results obtained with enhanced integrator!
```

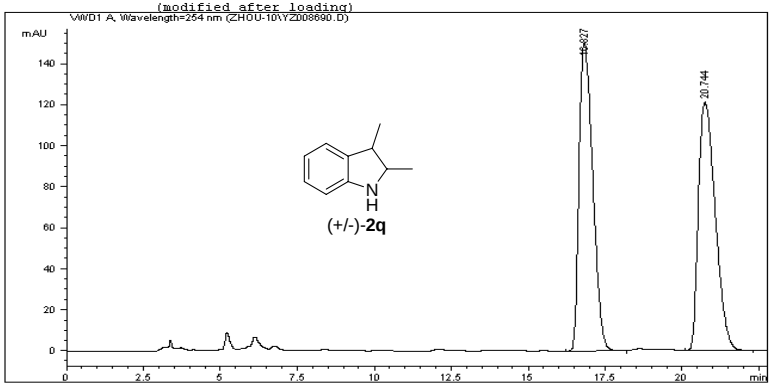
*** End of Report ***

Instrument 1 4/25/2010 2:55:23 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008690.D Sample Name: SW-7-40N+-

OJ-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 11:10:18 PM
Sample Name     : SW-7-40N+-                    Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 11:32:29 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 11:38:59 PM
                  (modified after loading)
```



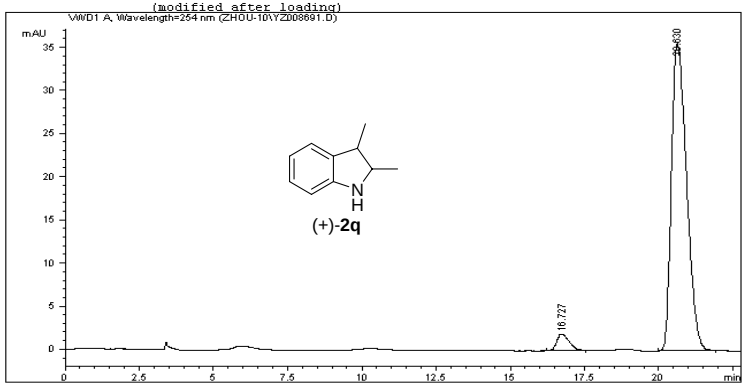
(+/-)-**2q**

```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.827 VB    0.4934 4620.73193  149.96339  50.0083
   2  20.744 VB    0.6084 4619.20117  121.02340  49.9917

Totals :                  9239.93311  270.98679

 Results obtained with enhanced integrator!

                          *** End of Report ***
```


Data File C:\HPCHEM\1\DATA\ZHOU-10\YZ008691.D Sample Name: SW-7-40N

OJ-H, H/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm

```
Injection Date  : 4/27/2010 11:36:01 PM
Sample Name     : SW-7-40N                      Location : Vial 1
Acq. Operator   :
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/27/2010 11:39:02 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/28/2010 12:00:22 AM
                  (modified after loading)
```



(+)-**2q**

```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.727 PB    0.4281   54.82727    1.90162   4.1651
   2  20.630 BB    0.5590 1261.51917   35.60186  95.8349

Totals :                  1316.34644   37.50347

 Results obtained with enhanced integrator!

                          *** End of Report ***
```