Supplemental material for:

Enantioselective Construction of Vicinal All-Carbon Quaternary Centers via Catalytic Double Asymmetric Decarboxylative Allylation

Santanu Ghosh, Subhajit Bhunia, Badrinath N. Kakde, Subhadip De, and Alakesh Bisai*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhauri, Indore By-Pass Road, Bhopal, MP- 462 066, India.
E-Mail: alakesh@iiserb.ac.in

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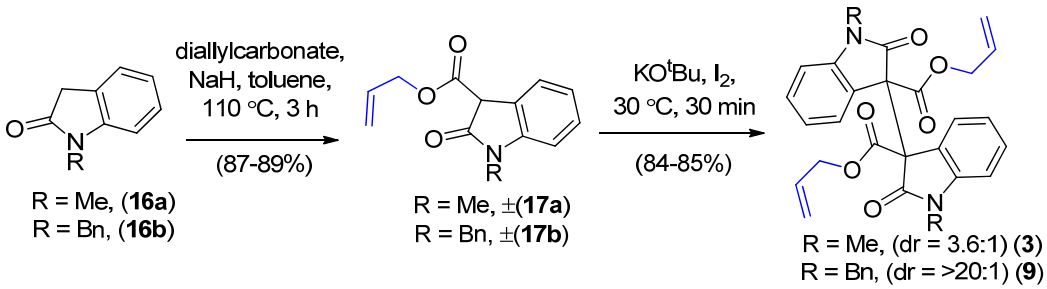
Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2), toluene, and benzene were distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperature. Thin layer chromatography was performed using silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silicagel of particle size 100-200 mesh was used for flash chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (AN ISO 9001:2000) and are uncorrected. ^1H and ^{13}C NMR spectra were recorded 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$) signal (δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) and Low-Resolution Mass Spectrometry (LRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. Optical rotations were measured on an Autopol I automatic polarimeter, Rudolph research analytical. Enantiomeric excess was determined by chiral HPLC analysis performed on PerkinElmer Technologies and Agilent Technologies HPLC system with Daicel Chiralpak AD-H and Daicel Chiralpak IB column.

General Procedure for the synthesis of bis-esters ±(3 and 9):



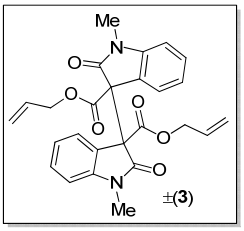
Step 1:

An oven-dried round-bottom flask under argon atmosphere was charged with 5.44 g (136.05 mmol; 4.0 equiv) of NaH (60% suspension in mineral oil) in toluene (40 mL) at room temperature. After 15 minutes of stirring, the solution of compound **16** (34.01 mmol; 1.0 equiv) and diallylcarbonate (9.76 mL, 68.03 mmol; 2.0 equiv) in 40 mL toluene was added to the reaction mixture drop wise at room temperature. The reaction mixture was stirred at room temperature for another 15 minutes then it was placed on an oil-bath maintaining the temperature 110 ºC and stirring continued for another 3 h at same temperature. Upon completion of the reaction (monitoring by TLC), the reaction was cooled to 0 ºC and 3 mL of glacial acetic acid was added drop wise to the reaction mixture and stirring was continued for 1 h. Then, the reaction mixture was filtered through celite-bed and the filtrate was evaporated under vacuum to dryness. The crude product was washed with water (2 X 100 mL) and extracted with EtOAc (2 X 150 mL). The organic layer was concentrated to dryness in rotary evaporator under reduced pressure.

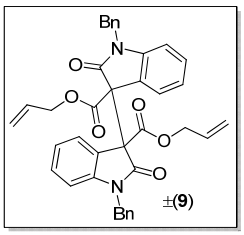
Step 2:

In an oven-dried round-bottom flask, crude compound ±(**17**) (1.0 equiv) was taken in dry THF (60 mL) at room temperature. To this reaction mixture KO^{t}Bu (4.58 g, 40.81 mmol; 1.2 equiv.) was added in one portion. After 5 minutes of stirring at same temperature, molecular iodine (10.36 g, 40.81 mmol, 1.2 equiv) was added and stirring was continued for 30 minutes (TLC showed complete consumption of starting materials). The reaction mixture was diluted with 150 mL of EtOAc and then treated with 15 mL saturated aqueous sodium thiosulfate solution at room temperature. The whole reaction

mixture was taken in a separatory funnel and extracted with ethyl acetate (100 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. Finally, the crude products were purified by flash chromatography (3:2 hexanes/EtOAc) to afford product ±(**3**) and ±(**9**). These products were recrystallized from dichloromethane and hexane to afford white solids.

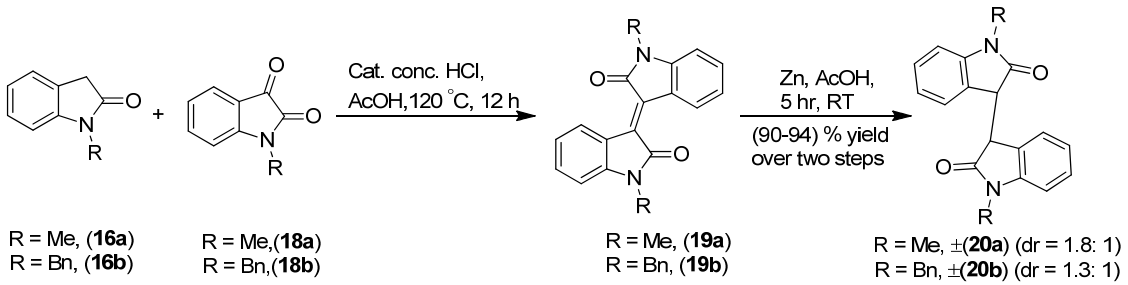


(±)-Diallyl 1,1'-dimethyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-dicarboxylate ±(3): 5.9 g (76% yield over two steps) of ±(**3**) as a white solid. R_f = 0.24 (30% EtOAc in hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$, spectrum of 3.6:1 dr) δ 7.32-7.24 (m, 2H for major + 4H for minor diastereomers), 7.18-7.14 (m, 2H for major diastereomer), 6.89 (t, *J* = 7.6 Hz, 2H for major + 2H for minor diasteromers), 6.74 (d, *J* = 7.8 Hz, 2H for minor diastereomer), 6.56 (d, *J* = 7.8 Hz, 2H for major diastereomer), 5.87-5.78 (m, 2H for major + 2H for minor diastereomers), 5.2-5.11 (m, 4H for major + 4H for minor diastereomers), 4.72-4.59 (m, 4H for major + 4H for minor diasteromers), 3.11 (s, 6H for major diastereomer), 3.05 (s, 6H for minor diastereomer); **^{13}C-NMR** (100 MHz, $CDCl_3$, spectrum contains approximately 3.6:1 diastereomers) δ 170.7, 170.2, 166.7, 166.1, 144.7, 144.0, 131.5, 131.4, 130.1, 129.7, 126.2, 126.1, 123.6, 123.2, 122.1, 122.07, 118.3, 118.0, 108.1, 107.8, 66.7, 66.6, 61.8, 26.5, 26.47; **IR** (film) υ_{max} 2925, 1744, 1731, 1609, 1493, 1471, 1372, 1349, 1263, 1227, 1133, 1089, 1028, 934, 755 cm^{-1}; **HRMS** (ESI) m/z 461.1726 $[M+H]^+$; calculated for $[C_{26}H_{24}N_2O_6 + H]^+$: 461.1707; **MP** 122–124 °C.



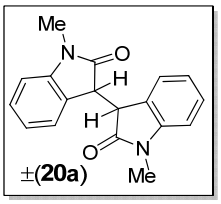
(±)-1,1'-Dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-dicarboxylate ±(**9**): 5.0 g (73% yield over two steps) of ±(**9**) as a white solid. R_f = 0.3 (30% EtOAc in hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.24-7.18 (m, 10H), 7.11 (t, *J* = 7.7 Hz, 2H), 6.85 (t, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 7.8 Hz, 2H), 5.83-5.74 (m, 2H), 5.16-5.11 (m, 4H), 5.01 (d, *J* = 15.7 Hz, 2H), 4.72-4.61 (m, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 170.4, 166.4, 143.5, 135.3, 131.3, 129.6, 128.6, 127.5, 127.4, 126.9, 124.2, 122.3, 118.2, 109.0, 66.6, 61.8, 44.1; **IR** (film) υ_{max} 2929, 1746, 1732, 1605, 1467, 1364, 1217, 1170, 752 cm^{-1}; **HRMS** (ESI) m/z 613.2352 $[M+H]^+$; calculated for $[C_{38}H_{32}N_2O_6 + H]^+$: 613.2333; **MP** 132–135 °C.

General Procedure for the synthesis of dihydroisoindigo ±(20a and **20b):**[1]



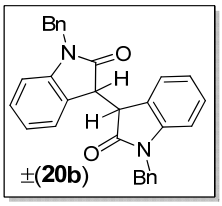
References:

[1] J J. T. Link, L. E. Overman, *J. Am. Chem. Soc.* **1996**, *118*, 8166.



(±)-1,1'-Dimethyl-[3,3'-biindoline]-2,2'-dione ±(**20a**)**:** 9.0 g (90% yield) of ±(**20a**) as a white solid. R_f = 0.25 (20% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$, spectrum of 1.8:1 dr) δ 7.23-7.19 (m, 2H for major diastereomer), 7.05-7.01 (m, 2H for minor diastereomer), 6.87-6.81 (m, 2H for major + 2H for minor diastereomer), 6.74-6.68 (m, 4H for major + 2H for minor diastereomer), 6.60 (d, *J* = 7.8 Hz, 2H for minor diastereomer), 4.21 (s, 2H for minor diastereomer), 4.10 (s, 2H for major diastereomer), 3.20 (s, 6H for minor diastereomer), 3.03 (s, 6H for major diastereomer); **^{13}C-NMR** (100 MHz, $CDCl_3$, spectrum of 1.8:1 dr) δ 175.9, 174.7, 145.0, 144.2, 128.8, 128.4, 125.9,

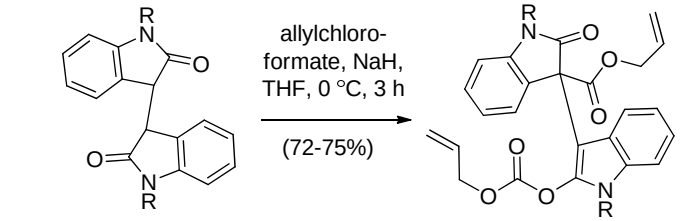
124.8, 123.3, 123.29, 122.4, 122.3, 108.3, 108.0, 46.2, 46.1, 26.3, 26.2; **IR** (film) υ_{max} 3057, 2934, 2889, 1714, 1613, 1494, 1471, 1421, 1376, 1350, 1267, 1127, 1092, 1021, 751, 734 cm^{-1}; **HRMS** (ESI) m/z 293.1299 $[M+H]^+$; calculated for $[C_{18}H_{16}N_2O_2 + H]^+$: 293.1285; **MP** 184–186 °C.



±(**20b**)

(±)-1,1'-Dibenzyl-[3,3'-biindoline]-2,2'-dione ±(20b): 9.4 g (94% yield) of ±(**20b**) as a yellow gel. R_f = 0.32 (20% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$, spectrum of 1.3:1 dr) δ 7.27-7.24 (m, 4H), 7.14-7.09 (m, 10H), 7.04-7.02 (m, 6H), 6.79 (t, *J* = 7.4 Hz, 2H), 6.72-6.68 (m, 4H), 6.57 (t, *J* = 7.4 Hz, 4H), 4.92-4.91 (m, 2H for minor diastereomer), 4.88-4.86 (m, 2H for major diastereomer), 4.66 (d, *J* = 15.8 Hz, 4H for minor diastereomer), 4.29 (d, *J* = 19.7 Hz, 4H for major diastereomer); **^{13}C-NMR** (100 MHz, $CDCl_3$, spectrum contains approximately 1.3:1 diastereomer) δ 175.9, 174.8, 144.2, 143.5, 135.6, 128.8, 128.7, 128.6, 128.4, 127.9, 127.8, 128.4, 127.2, 125.8, 124.8, 124.1, 123.7, 122.5, 122.4, 109.5, 108.9, 46.3, 46.1, 44.1, 43.9; **IR** (film) υ_{max} 3060, 3034, 2925, 1714, 1696, 1615, 1487, 1469, 1381, 1361, 1266, 1178, 1103, 1081, 1030, 1012, 936, 919, 876, 846, 751, 728, 697 cm^{-1}; **HRMS** (ESI) m/z 445.1913 $[M+H]^+$; calculated for $[C_{30}H_{24}N_2O_2 + H]^+$: 445.1911.

General Procedure for the synthesis of ester-carbonates ±(11 and 12):

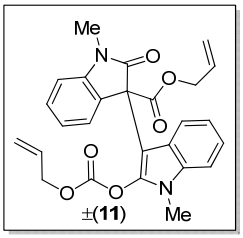


R = Me, ±(**20a**) (dr = 1.8: 1)
R = Bn, ±(**20b**) (dr = 1.3: 1)

R = Me, ±(**11**)
R = Bn, ±(**12**)

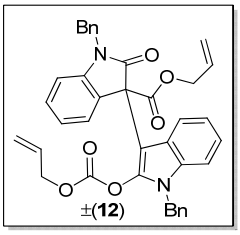
In an oven-dried round-bottom flask, the dihydroisoindigo ±(**20**) (17.12 mmol; 1.0 equiv) was taken in dry THF (15 mL) under inert atmosphere and the reaction vessel

was cooled to 0 ºC. To this reaction mixture NaH (60% suspension in mineral oil, 1.5 g, 37.67 mmol; 2.2 equiv) was added portion-wise and it was stirred for 5 min. Then allyl chloroformate (4.0 mL; 37.67 mmol; 2.2 equiv) was added very slowly drop-wise over a period of 20 minutes to the reaction mixture at 0 ºC. Then the reaction mixture was stirred for another 2 h. Upon completion of the reactions the reaction mixture was quenched with ice-water (100 mL) and then diluted with 150 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with ethyl acetate (100 mL X 2). The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. Finally, the crude products were purified by flash chromatography using (15-20) % EtOAc/hexane as eluent to afford product ±(**11** and **12**). These products were recrystallized from diethylether and hexane to afford reddish solid of ±(**11**) and ±(**12**).



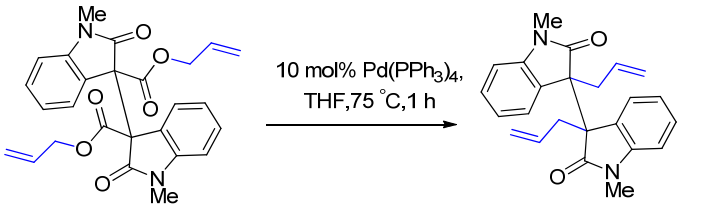
±(**11**)

(±)-Allyl 3-(2-(((allyloxy)carbonyl)oxy)-1-methyl-1H-indol-3-yl)-1-methyl-2-oxoindoline-3-carboxylate ±(**11**): 5.9 g (75% yield) of ±(**11**) as a red solid. R_f = 0.45 (20% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.24-7.15 (m, 2H), 7.09-6.98 (m, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.94-5.78 (m, 2H), 5.38-5.29 (m, 2H), 5.22-5.13 (m, 2H), 4.76-4.72 (m, 1H), 4.66-4.49 (m, 3H), 3.52 (s, 3H), 3.23 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 172.5, 168.5, 151.5, 144.4, 140.0, 132.5, 131.4, 130.7, 129.5, 126.6, 126.0, 124.2, 122.6, 122.0, 120.3, 120.27, 119.8, 118.5, 109.2, 108.2, 95.9, 70.0, 66.7, 58.3, 28.4, 26.6; **IR** (film) υ_{max} 2923, 1777, 1771, 1746, 1608, 1470, 1367, 1346, 1223, 1130, 1089, 1055, 993, 942, 910, 740 cm^{-1}; **HRMS** (ESI) m/z 461.1728 $[M+H]^+$; calculated for $[C_{26}H_{24}N_2O_6 + H]^+$: 461.1707; **MP** 139–141 ˚C.



(±)-Allyl 3-(2-(((allyloxy)carbonyl)oxy)-1-benzyl-1H-indol-3-yl)-1-benzyl-2-oxoindoline-3-carboxylate ±(12): 4.9 g (72% yield) of ±(**12**) as a red solid. R_f = 0.5 (20% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.1 Hz, 1H), 7.37-7.36 (m, 2H), 7.31-7.2 (m, 8H), 7.16-7.12 (m, 4H), 7.09-7.02 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.88-5.79 (m, 1H), 5.72-5.62 (m, 1H), 5.22-5.14 (m, 7H), 4.77-4.65 (m, 3H), 4.30-4.25 (m, 1H), 4.17-4.10 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 172.7, 168.6, 151.2, 143.7, 139.8, 136.4, 135.6, 132.3, 131.3, 130.5, 129.4, 128.7, 128.68, 127.55, 127.52, 127.4, 126.8, 126.2, 125.9, 124.8, 122.6, 122.3, 120.9, 120.6, 119.6, 118.8, 109.9, 109.2, 96.2, 69.8, 66.8, 58.6, 46.1, 44.2; **IR** (film) υ_{max} 2925, 2855, 1778, 1746, 1728, 1608, 1487, 1468, 1453, 1359, 1229, 1211, 991, 914, 912, 736 cm^{-1}; **HRMS** (ESI) m/z 613.2352 $[M+H]^+$; calculated for $[C_{38}H_{32}N_2O_6 + H]^+$: 613.2333; **MP** 75–77 °C.

Double stereoablative process for the synthesis of (± and *meso*)-4:



3 *(±:meso = 3.6:1 dr)* ***4*** *(±:meso = 6.6:1 dr)*

3,3'-Diallyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (4): In an oven-dried sealed tube under argon atmosphere, bis-ester (± and *meso*) **3** (0.13 mmol; 1.0 equiv) was dissolved in dry degassed (4 mL) THF. After that 10 mol% of $Pd(PPh_3)_4$ was added to that reaction mixture. Then the reaction mixture was placed over an oil bath mentioning temperature 75 ºC for 1 h. After full consumption of starting material (monitored by TLC) the reaction mixture was concentrated and purified by column chromatography (4 :1

hexanes/EtOAc) to afford 43 mg of **4** (90% yield) as white crystalline solid. R_f 0.65 (20% EtOAc in hexanes). **4** (± : *meso* = 6.6:1) was determined by ^{1}H NMR analysis of crude reaction mixture. Enantiomeric separation was performed *via* HPLC analysis using a Chiralpak AD-H column; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R (1st enantiomer) = 9.41 min, t_R (2nd enantiomer) = 13.12 min.

Catalytic Enantioselective double decarboxylative allylations:

[Optimization using *N*-methyl bis-esters as substrate]:

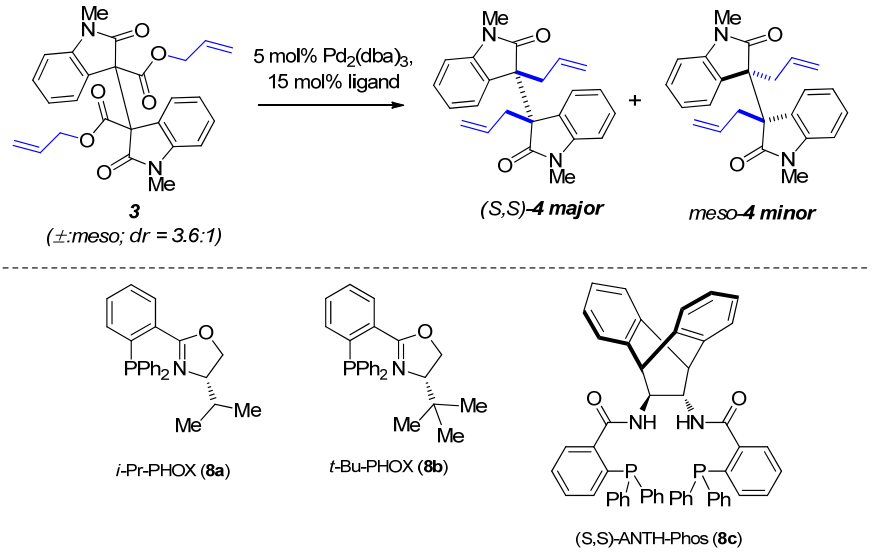
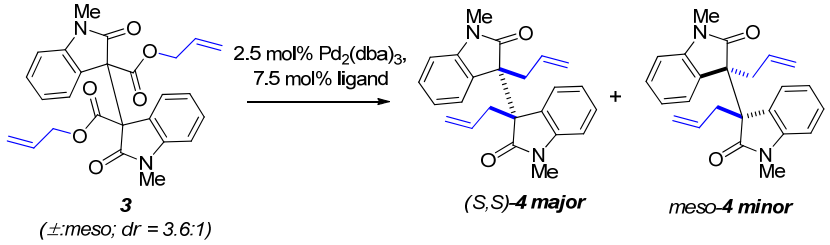


Table: 1

Entry[a]	Catalyst	Ligand	Solvent	Temp (°C)	Time	Yield (%)[b]	ee (%)	dr
1	5 mol %	**8c** (15 mol%)	toluene	30	15 h	73	74	7:1
2	5 mol %	**8c** (15 mol%)	DCE	30	24 h	c	–	--
3	5 mol %	**8c** (15 mol%)	CH_2Cl_2	30	24 h	c	–	--
4	5 mol %	**8c** (15 mol%)	DEE	30	12 h	91	75	7.6:1
5	5 mol %	**8c** (15 mol%)	THF	30	24 h	c	–	--
6	5 mol %	**8c** (15 mol%)	DME	30	24 h	c	–	--
7	5 mol %	**8a** (15 mol%)	toluene	30	36h	74	-19	7.1:1
8	5 mol %	**8a** (15 mol%)	DEE	30	15 h	92	-16	11.3:1
9	5 mol %	**8b** (15 mol%)	toluene	30	48 h	78	-5	7:1
10	5 mol %	**8b** (15 mol%)	DEE	30	14 h	89	-19	8.2:1

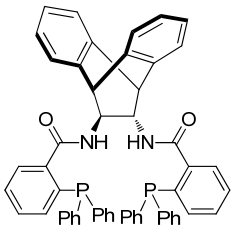
[a]Reactions were carried out on a 0.065 mmol of substrate in 3 mL of solvent in a sealed tube for specified time, unless otherwise stated. [b]Isolated yield after column chromatography. [c]Starting material was recovered in 72-80 %.



3
(±:meso; dr = 3.6:1)

*(S,S)-**4 major***

*meso-**4 minor***



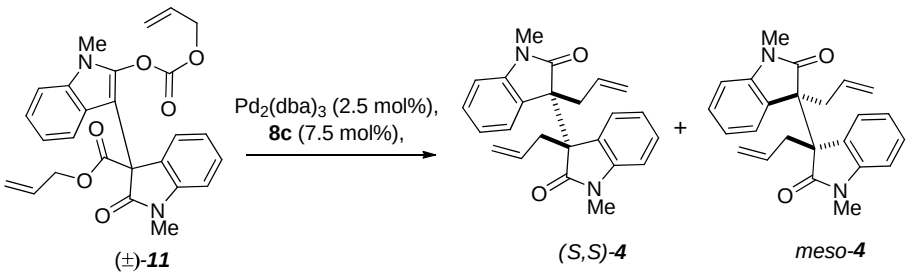
(S,S)-ANTH-Phos (**8c**)

Table: 2

Entry[a]	Catalyst	Ligand **(8c)**	Solvent	Temp (°C)	Time	Yield (%)[b]	ee (%)	dr
1	2.5 mol %	7.5 mol%	toluene	30	16 h	72	71	7.3:1
2	2.5 mol %	7.5 mol%	DEE	30	16 h	90	83	6.5:1
3	2.5 mol %	7.5 mol%	toluene	0	18 h	75	95	19.8:1
4	2.5 mol %	7.5 mol%	DEE	0	12 h	89	91	16.2:1
5	**2.5 mol %**	**7.5 mol%**	**DEE**	**-10**	**18 h**	**88**	**97**	**17:1**

[a]Reactions were carried out on a 0.065 mmol of substrate in 3 mL of solvent in a sealed tube for specified time, unless otherwise stated. [b]Isolated yield after column chromatography.

Scope using *N*-methyl ester-carbonates:



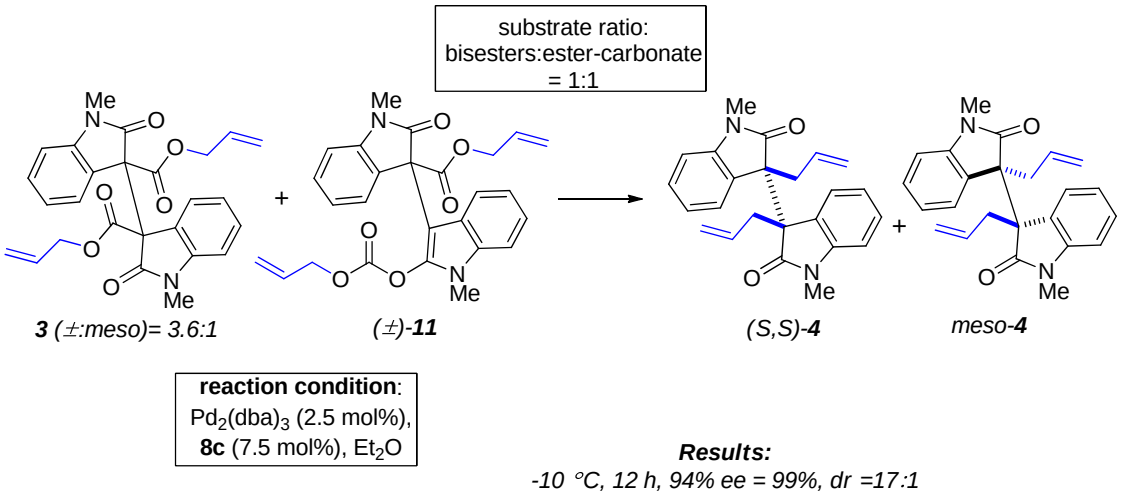
(±)-***11***

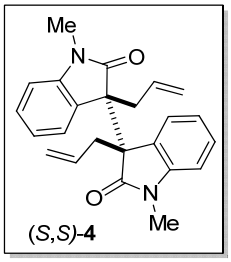
*(S,S)-**4***

*meso-**4***

Et_2O, -10 °C, 12 h, 92%: ee = 98%, dr = 15.9:1

Scope using (1:1) mixture of *N*-methyl bis-esters-(3) and ester-carbonates-(11):

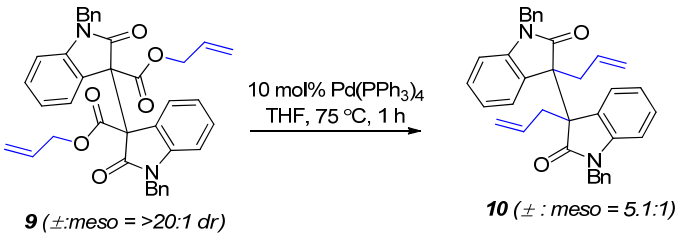




(3*S*,3'*S*)-3,3'-Diallyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (***S***,***S***)**-4:** In an oven-dried sealed tube, solvent (1.5 mL) was degassed by using nitrogen balloon at room temperature over a period of 10 minutes. 2.5 mol% of $Pd_2(dba)_3$ and 7.5 mol% ligand (**8c**) were added to it and stirred for 20 minutes until greenish color persisted. Then the reaction mixture was cooled to specified temperature and then bis-ester (± and *meso*) **3** (0.065 mmol; 1.0 equiv) was dissolved in degassed (1.5 mL) of corresponding solvent then the solution was added drop wise to the complex solution. The reaction mixture was stirred for specified time at same temperature. After complete consumption of starting material (monitored by TLC) the reaction mixture was concentrated and purified by column chromatography (4 :1 hexanes/EtOAc) to afford 21 mg (88% yield) of (***S***,***S***)**-4** as white crystalline solid. R_f = 0.65 (20% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 6.98-6.91 (m, 4H), 6.77-6.73 (m, 2H), 6.33 (d, *J* = 7.8 Hz, 2H), 5.02-4.89 (m, 4H), 4.69-4.66 (m, 2H), 3.59-3.54 (m, 2H), 2.99 (s, 6H), 2.96-2.94 (m, 2H); **^{13}C-NMR** (100

MHz, $CDCl_3$) δ 176.9, 143.3, 132.5, 128.2, 128.1, 123.4, 121.6, 118.8, 107.2, 55.9, 33.2, 25.6; **IR** (film) υ_{max} 2926, 2852, 1705, 1693, 1610, 1374, 1354, 1124, 922, 759 cm^{-1}; **HRMS** (ESI) m/z 373.1924 $[M+H]^+$; calculated for $[C_{24}H_{24}N_2O_2 + H]^+$: 373.1911; **MP** 217–220 °C; Enantiomeric excess of pure compound was determined *via* HPLC analysis using a Chiralpak AD-H column; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R major = 9.62 min, t_R minor = 13.45 min. $[\alpha]_D^{27.0}$ = –244 (c = 0.40, $CHCl_3$, for 97% ee).

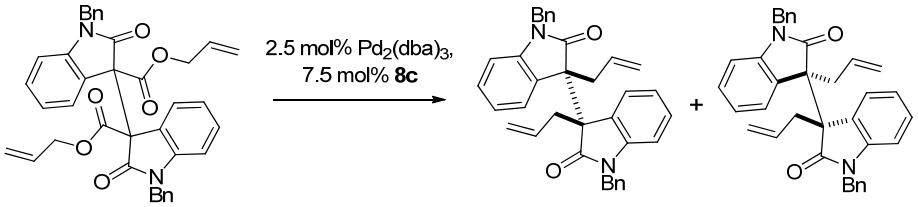
Procedure for the synthesis of (± and *meso*)-10:



9 *(±:meso = >20:1 dr)* ***10*** *(± : meso = 5.1:1)*

3,3'-diallyl-1,1'-dibenzyl-[3,3'-biindoline]-2,2'-dione 10: In an oven-dried sealed tube, bis-ester (± and *meso*) **9** (60 mg, 0.1 mmol; 1.0 equiv was dissolved in dry degassed (4 mL) of THF. After that 10 mol% of $Pd(PPh_3)_4$ was added to that reaction mixture. Then the reaction mixture was placed over an oil bath mentioning temperature 75 ºC for 1 h. After full consumption of starting material (monitored by TLC) the reaction mixture was concentrated and purified by column chromatography (10-15)% hexanes/EtOAc to afford 44 mg of **10** (86 % yield) as white crystalline solid. R_f = 0.71 (20% EtOAc in hexanes). **10** (± : *meso* = 5.1:1) was determined by ^1H NMR analysis of crude reaction mixture. Enantiomeric separation was performed *via* HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 98/2; flow rate: 1.0 mL/min; detection: at 238 nm): t_R (1st enantiomer) = 12.40 min, t_R (2nd enantiomer) = 15.20 min.

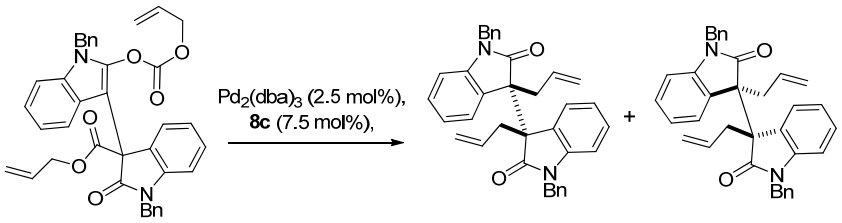
Scope using *N*-benzyl bis-esters:



9 *(±* : *meso* = > *20:1)* *(S,S)-**10*** *meso-**10***

Et_2O, 0 °C, 12 h, 90% : ee = >99%, dr = 9.4:1

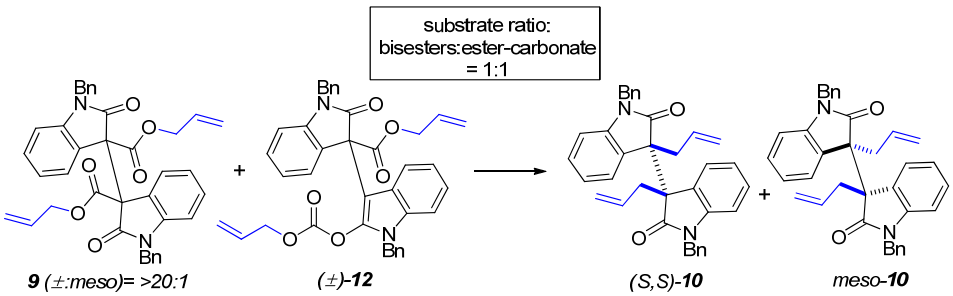
Scope using *N*-benzyl ester-carbonates:



*(±)-**12*** *(S,S)-**10*** *meso-**10***

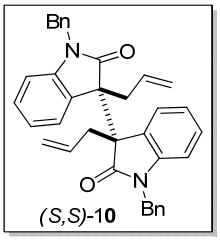
Et_2O, 0°C, 12 h, 83%: ee = 97%, dr = 8.6:1

Scope using (1:1) mixture of *N*-benzyl bis-esters (9) and ester-carbonates (12):



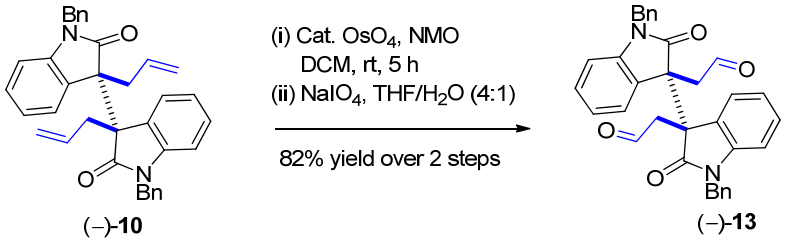
9 *(±:meso)= >20:1* *(±)-**12*** *(S,S)-**10*** *meso-**10***

Results:
0 °C, 12 h, 91% ee = 96%, dr = 9.0:1

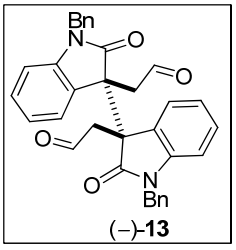


(3*S*,3'*S*)-3,3'-diallyl-1,1'-dibenzyl-[3,3'-biindoline]-2,2'-dione (–)-**10:** In an oven-dried sealed tube, Et_2O (2 mL) was degassed by using nitrogen balloon at room temperature over a period of 10 minutes. 2.5 mol% of $Pd_2(dba)_3$ and 7.5 mol% ligand (**8c**) were added to it and stirred for 20 minutes until greenish color persisted. After that the complex solution was cooled to 0 ºC. Then bis-ester (± and *meso*) **9** (60mg, 0.1 mmol; 1.0 equiv) was dissolved in degassed (2 mL) of Et_2O and the solution was added drop wise to the complex solution. The reaction mixture was stirred for specified time at same temperature. After full consumption of starting material (monitored by TLC) the reaction mixture was concentrated and purified by column chromatography (10-15)% hexanes/EtOAc to afford 47 mg (90% yield) of (***S***,***S***)-**10** as white solid. R_f = 0.71 (20% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 6H), 7.21-7.19 (m, 4H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.90 (td, *J* = 7.7, 0.8 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 2H), 6.34 (d, *J* = 7.8 Hz, 2H), 5.10 (d, *J* = 15.6 Hz, 2H), 5.06-5.02 (m, 4H), 4.78 (t, *J* = 6.0 Hz, 2H), 4.46 (d, *J* = 15.6 Hz, 2H), 3.73 (dd, *J* = 14.5, 3.4 Hz, 2H), 3.12-3.07 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 177.1, 142.7, 135.5, 132.5, 128.6, 128.2, 128.0, 127.6, 127.5, 124.0, 121.9, 119.2, 108.4, 55.7, 43.7, 34.1; **IR** (film) υ_{max} 3075, 2977, 2919, 2848, 1703, 1698, 1467, 1368, 1357, 1221, 1178, 1113, 995, 919, 754, 697 cm^{-1}; **HRMS** (ESI) m/z 525.2523 $[M+H]^+$; calculated for $[C_{36}H_{32}N_2O_2 + H]^+$: 525.2537; **MP** 223–226 °C; Enantiometric excess of pure compound was determined *via* HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 98/2; flow rate: 1.0 mL/min; detection: at 238 nm): t_R major = 11.93 min, t_R minor = 15.38 min. $[\alpha]_D^{27.4}$ = –268 (*c* = 0.36, $CHCl_3$). Reported: B. M. Trost, M. Osipov, *Angew. Chem., Int. Ed.* **2013**, *52*, 9176.; $[\alpha]_D^{22}$ = –296 (*c* = 1.08, CH_2Cl_2).

General Procedure for the synthesis of bis-aldehyde (–)-13:



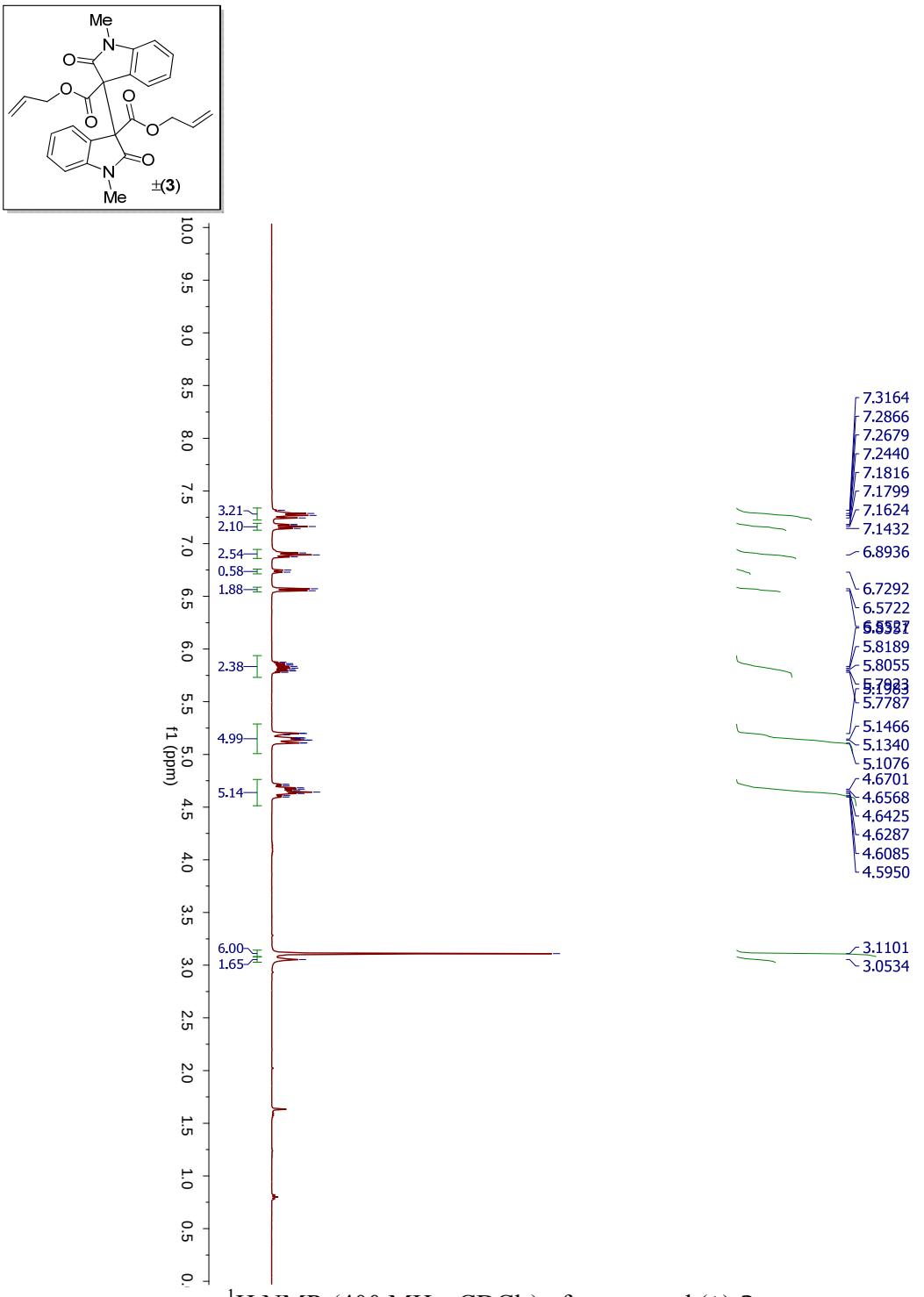
N-methyl morpholine-*N*-oxide (111 mg, 0.95 mmol; 5.0 equiv) and OsO_4 (0.1 mL, 4% solution in water) was added to a stirred solution of compound (–)-**10** (0.20 mmol; 1.0 equiv) in CH_2Cl_2 (7 mL) at room temperature. Then the reaction mixture was stirred for 5 h at same temperature. Upon completion of starting material (monitored by TLC) the reaction mixture was quenched with saturated Na_2SO_3 (1 mL) and extracted with CH_2Cl_2 (3 X 50 mL). The extracted organic layer was concentrated under reduced pressure. The crude material was directly dissolved in 10 mL THF : H_2O (4:1) mixture. Then to that reaction mixture, $NaIO_4$ (202 mg, 0.95 mmol; 5.0 equiv) was added at 0 °C and stirred for 1 h. The reaction mixture was diluted with EtOAc (50 mL) and partitioned by adding water. The extracted organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was washed with ether (2 X 5 mL) to afford compound (–)-**13,** as a white solid.



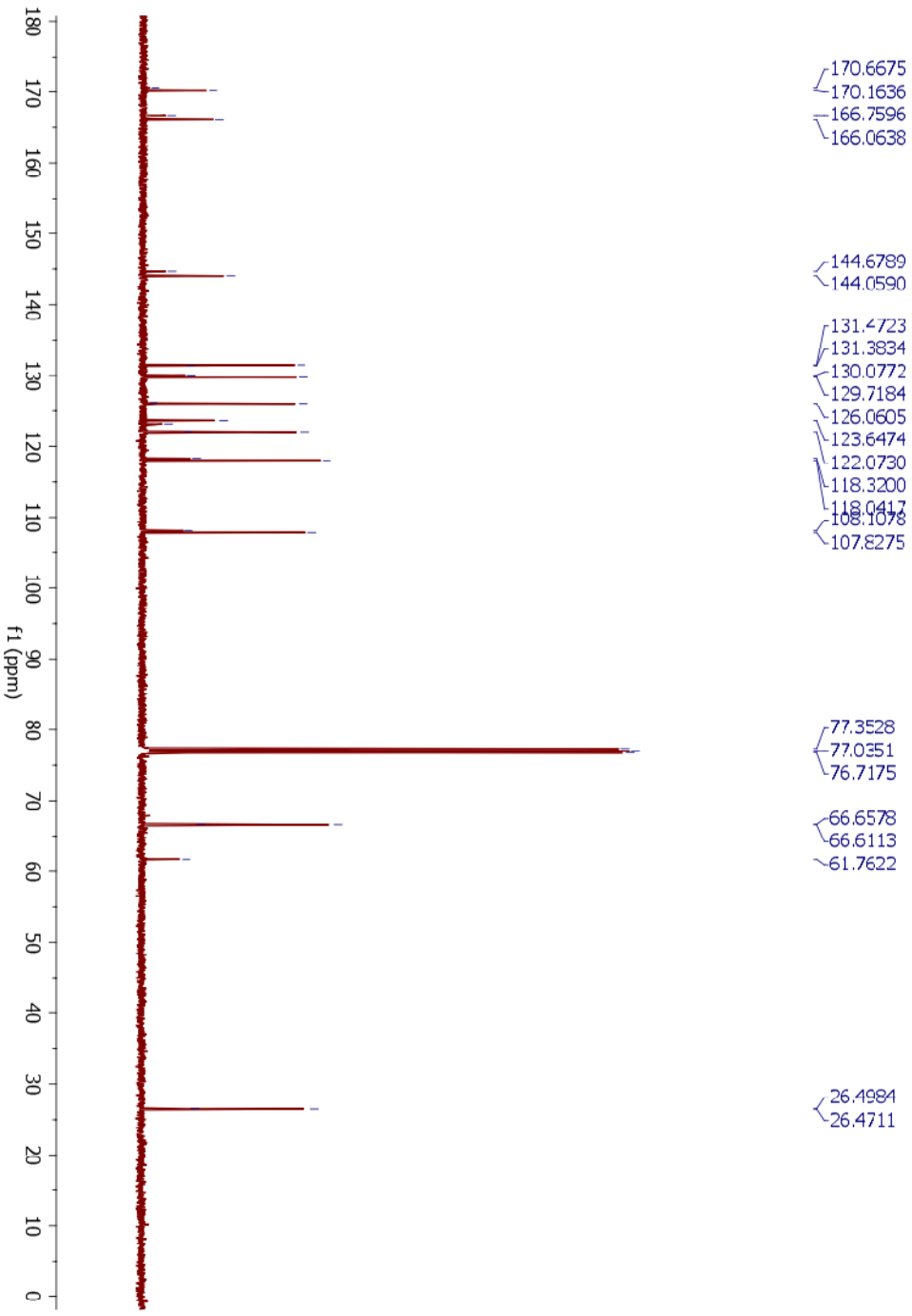
2,2'-((3*S*,3'*S*)-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)diacetaldehyde (–)-13: 82mg (82% yield) as a white solid. R_f = 0.45 (50% EtOAc in hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.37 (s, 2H), 7.33-7.24 (m, 10H), 6.91 (t, *J* = 7.6 Hz, 4H), 6.55 (t, *J* = 7.5 Hz, 2H), 6.34 (d, *J* = 7.7 Hz, 2H), 4.46 (d, *J* = 15.7 Hz, 2H), 4.29 (dd, *J* = 17.6, 1.1

Hz, 2H), 3.35 (d, *J* = 17.7 Hz, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 197.6, 176.6, 143.1, 135.2, 128.8, 128.7, 127.7, 126.3, 123.0, 122.0, 108.9, 51.4, 44.3, 43.6; **IR** (film) υ_{max} 2923, 2852, 1711, 1704, 1613, 1488, 1469, 1384, 1363, 1178, 911, 755 cm^{-1}; **HRMS** (ESI) m/z 551.1935 $[M+Na]^+$; calculated for $[C_{34}H_{28}N_2O_4 + Na]^+$: 551.1941; **MP** 215–218 °C; $[\alpha]_D^{26.9} = -143$ (*c* = 0.4095, $CHCl_3$). Reported: R. Liu, J. Zhang, *Org. Lett.* **2013**, *15*, 2266 $[\alpha]_D^{20.0} = -131.1$ (*c* = 0.30, $CHCl_3$).

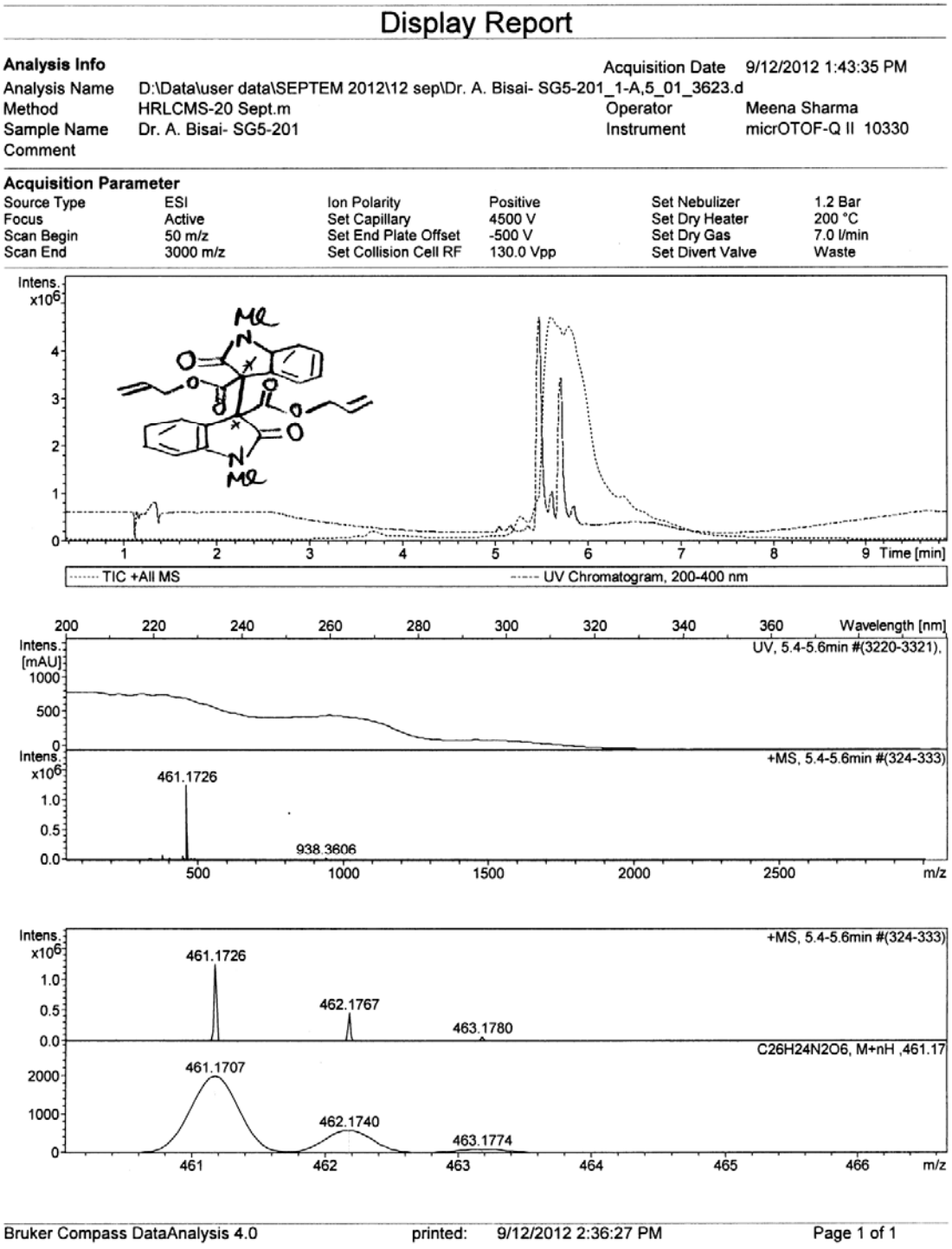
Spectral Graphics



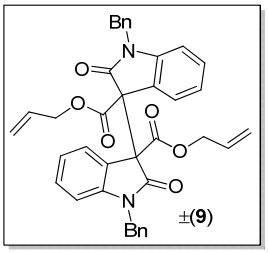
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**3**

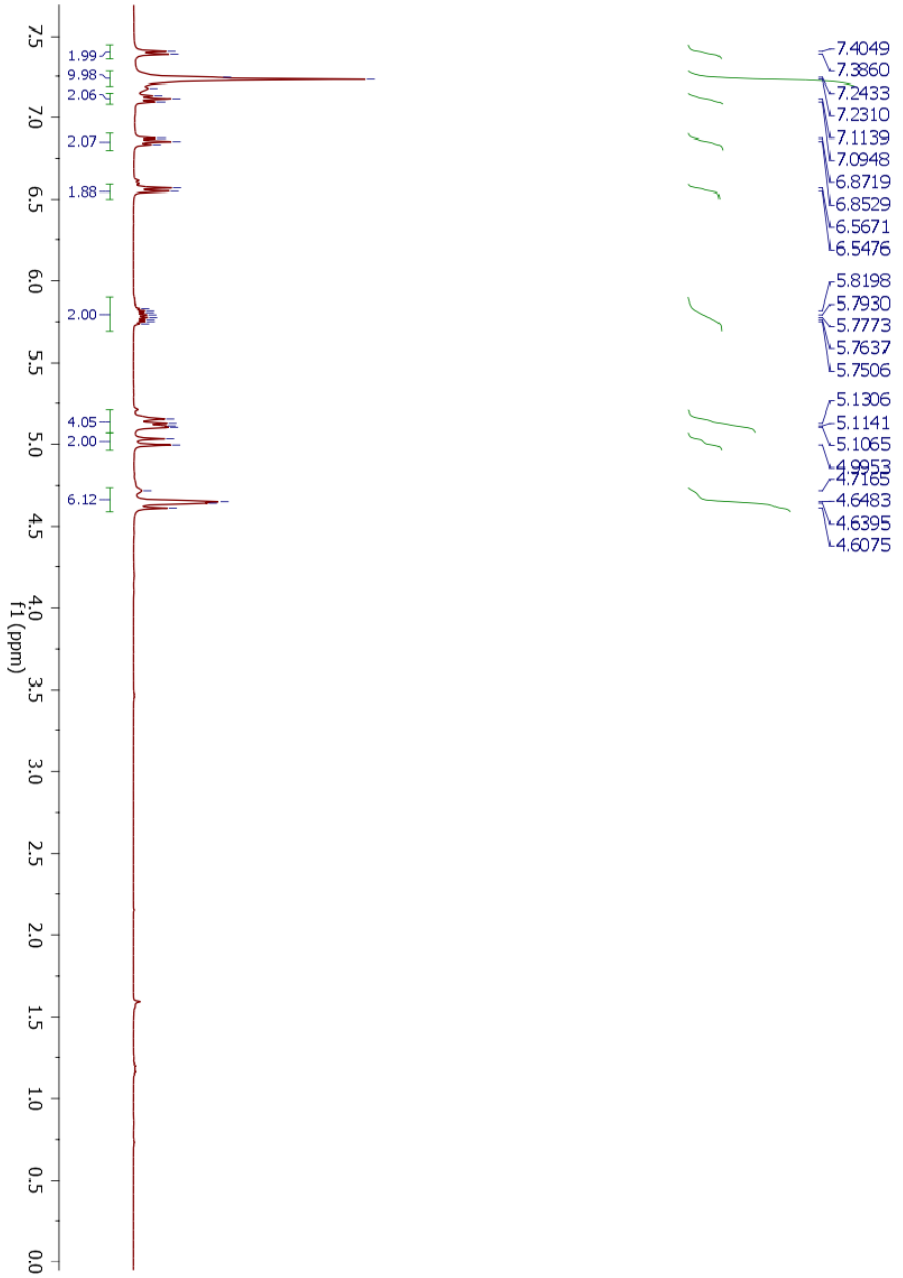


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**3**

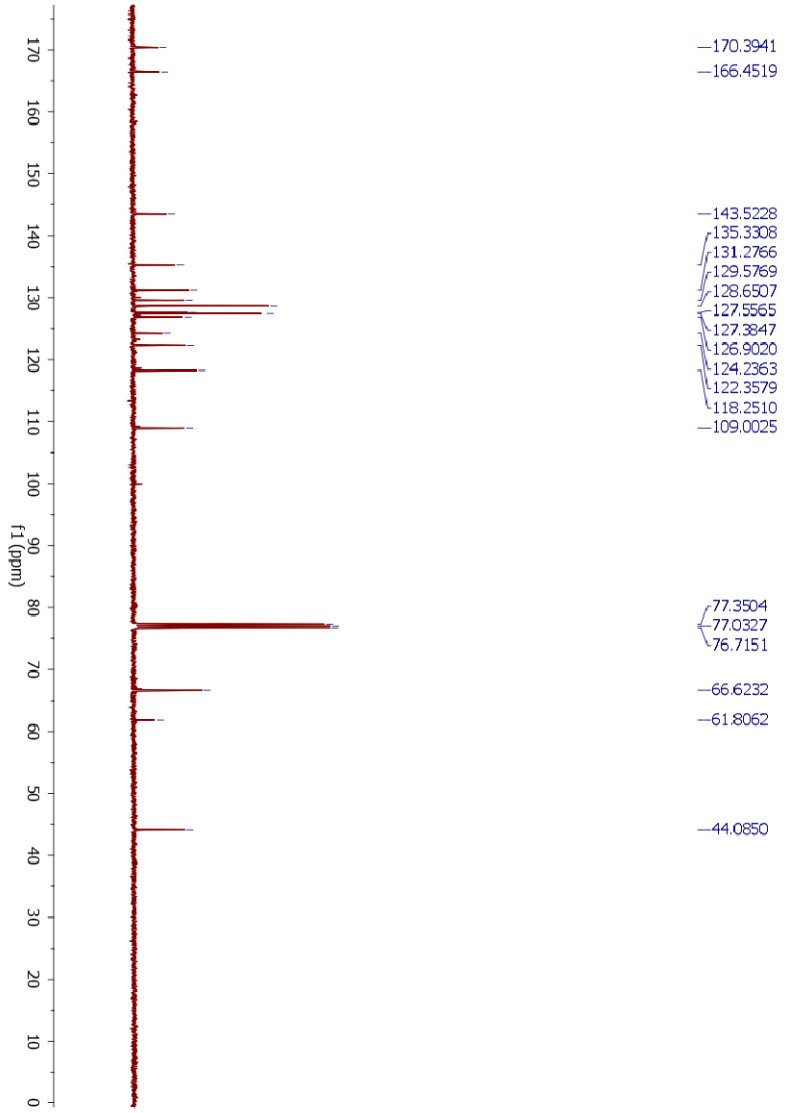


Scanned copy of mass spectrum of (±)-**3**

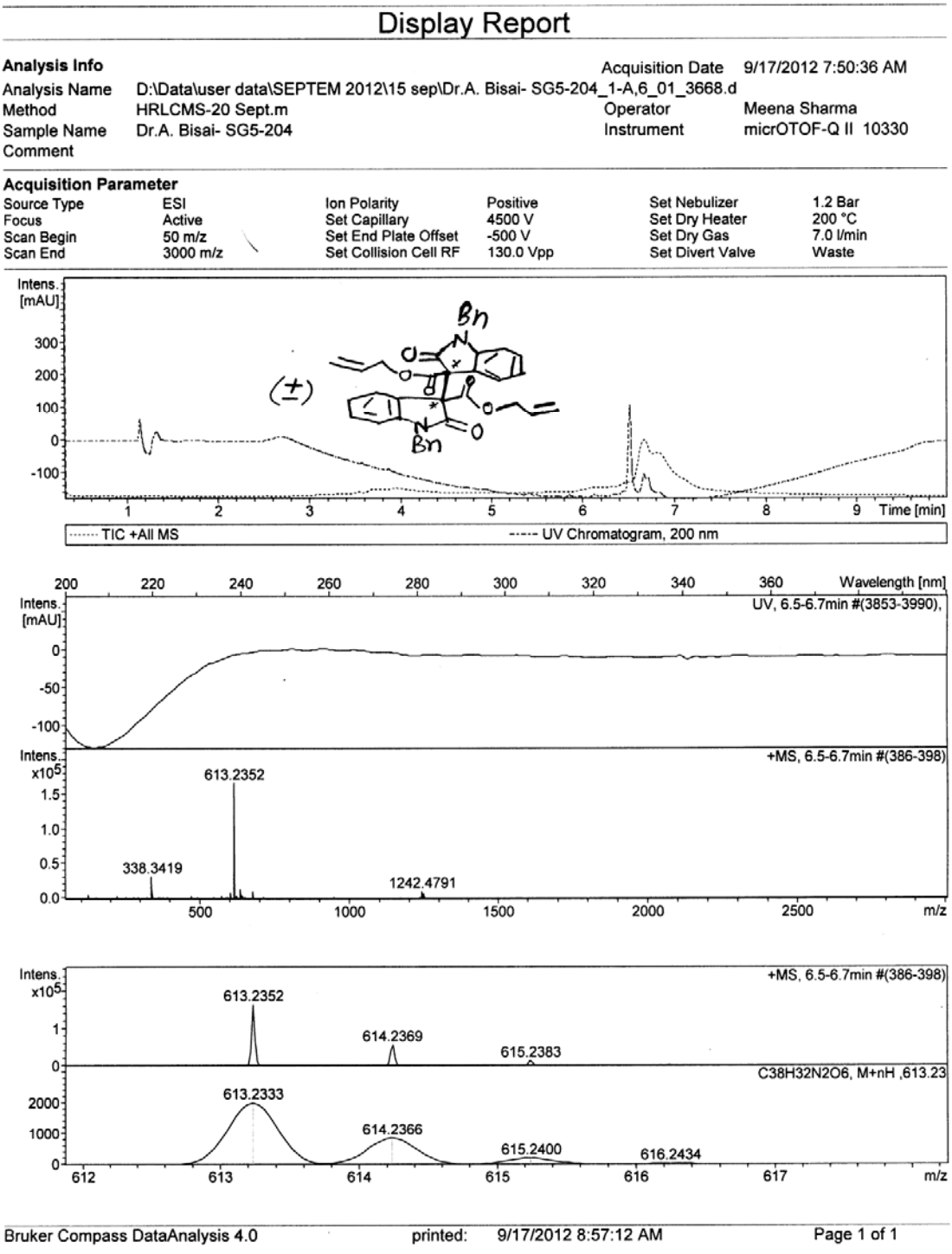




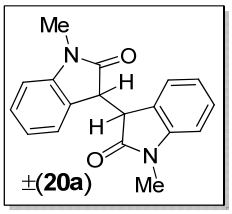
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**9**

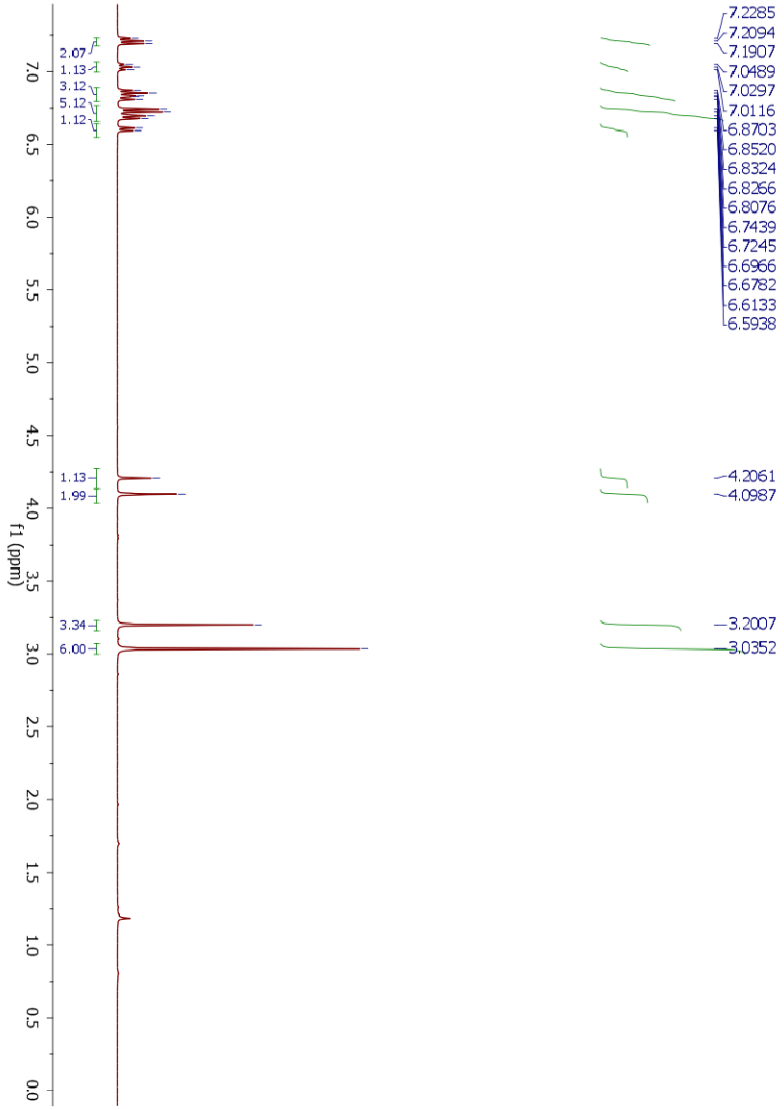


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**9**

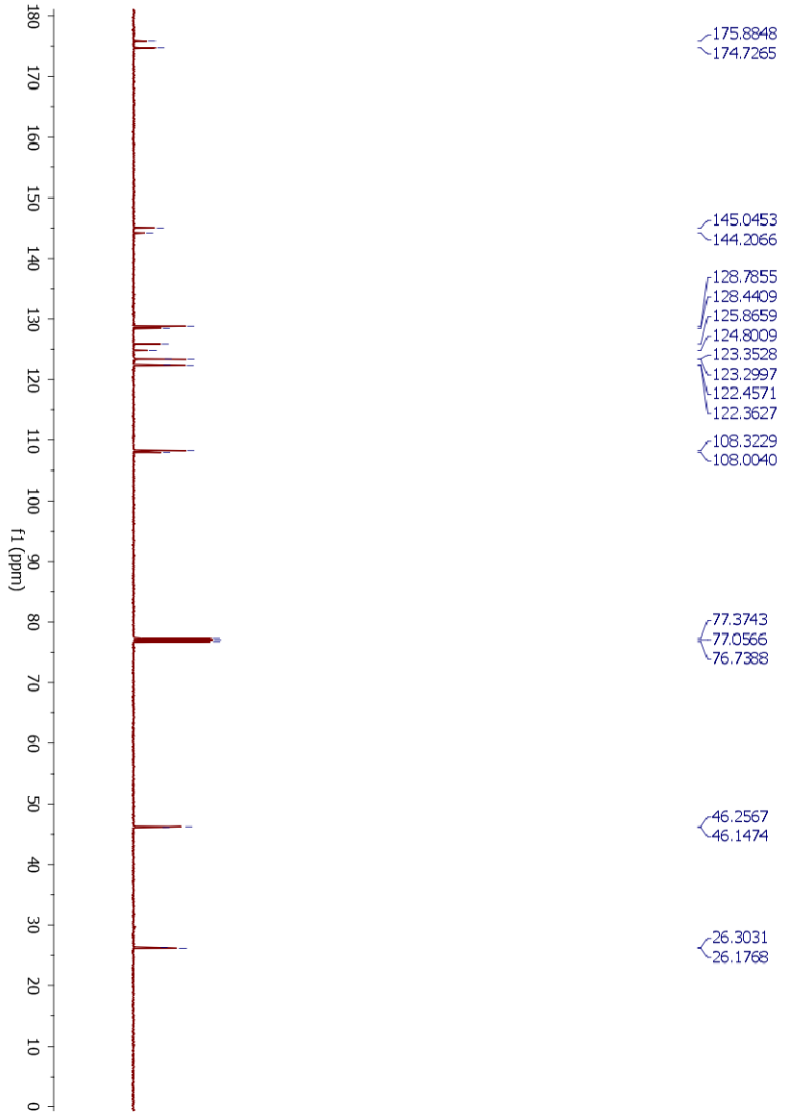


Scanned copy of mass spectrum of (±)-**9**

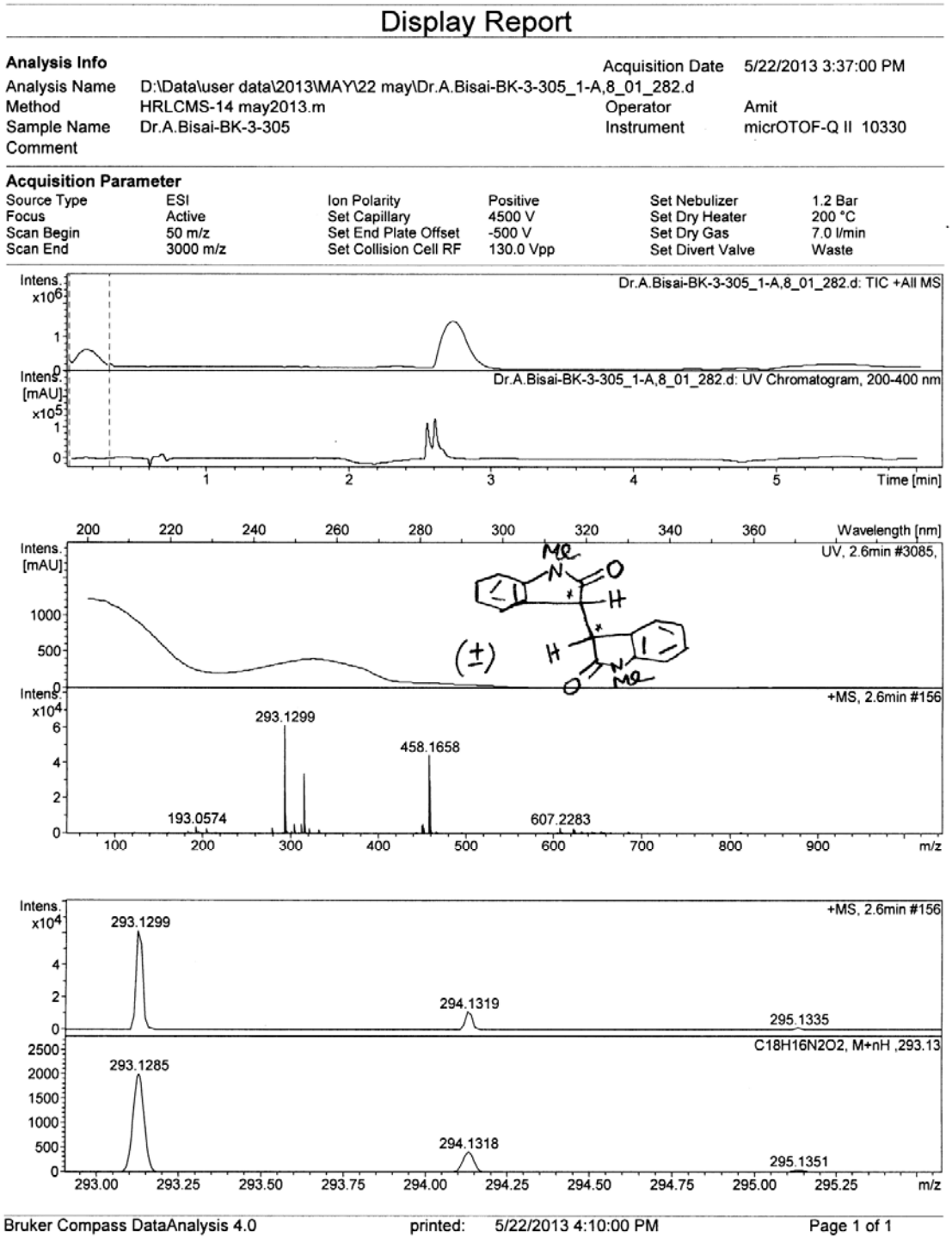




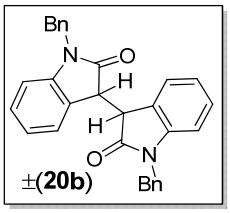
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20a**

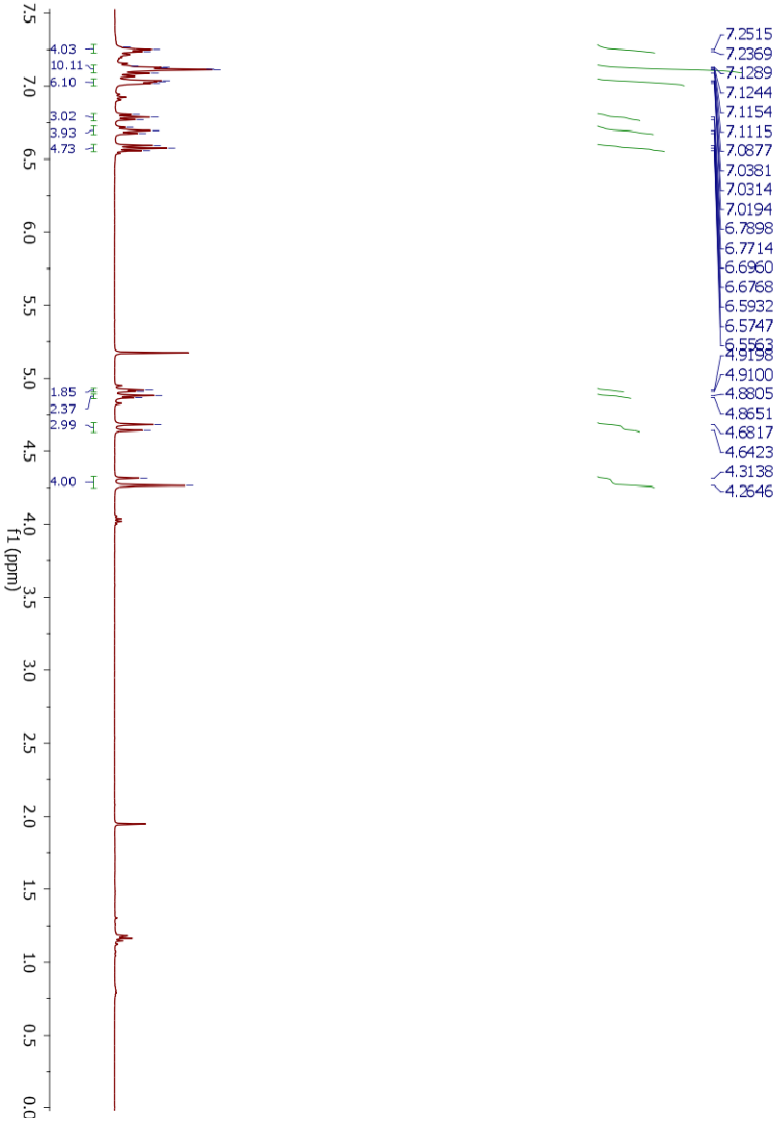


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20a**

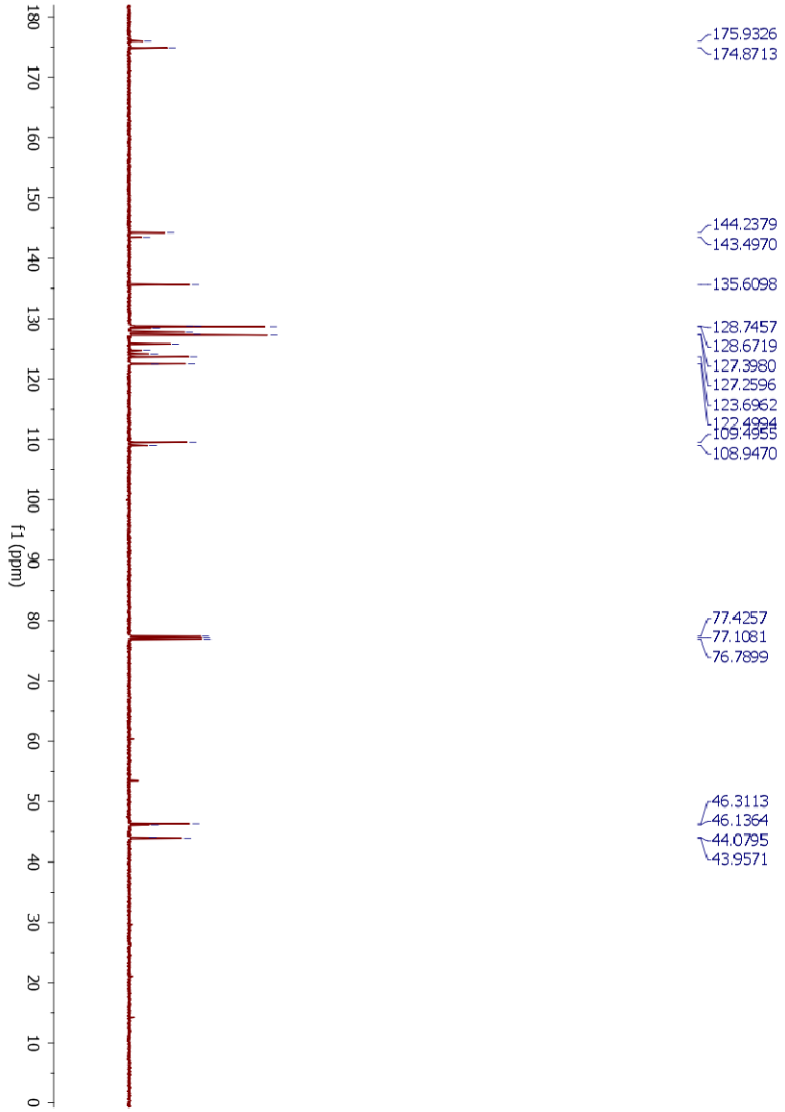


Scanned copy of mass spectrum of (±)-**20a**

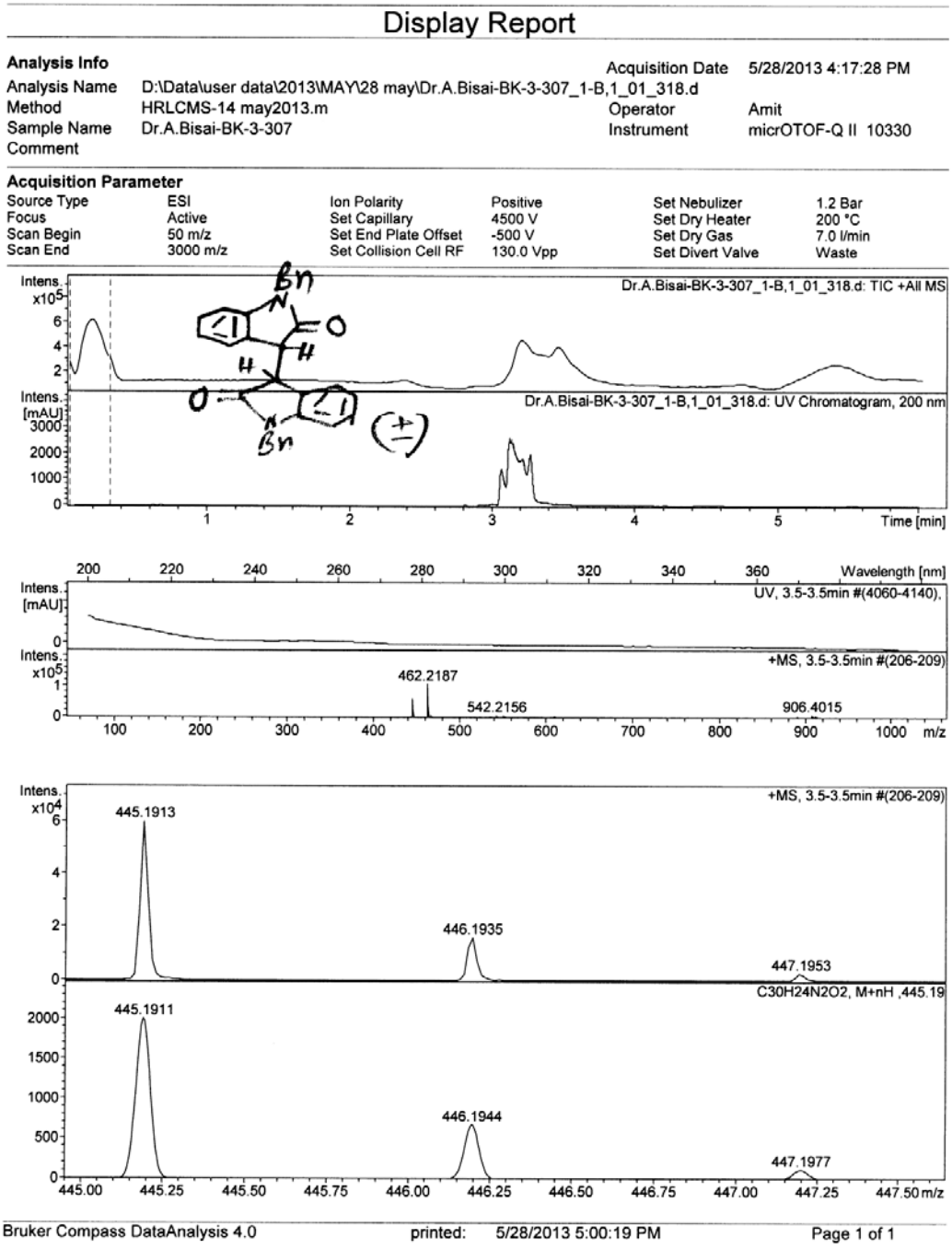




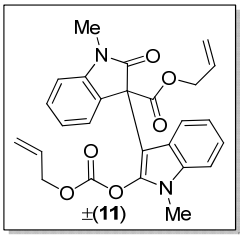
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20b**



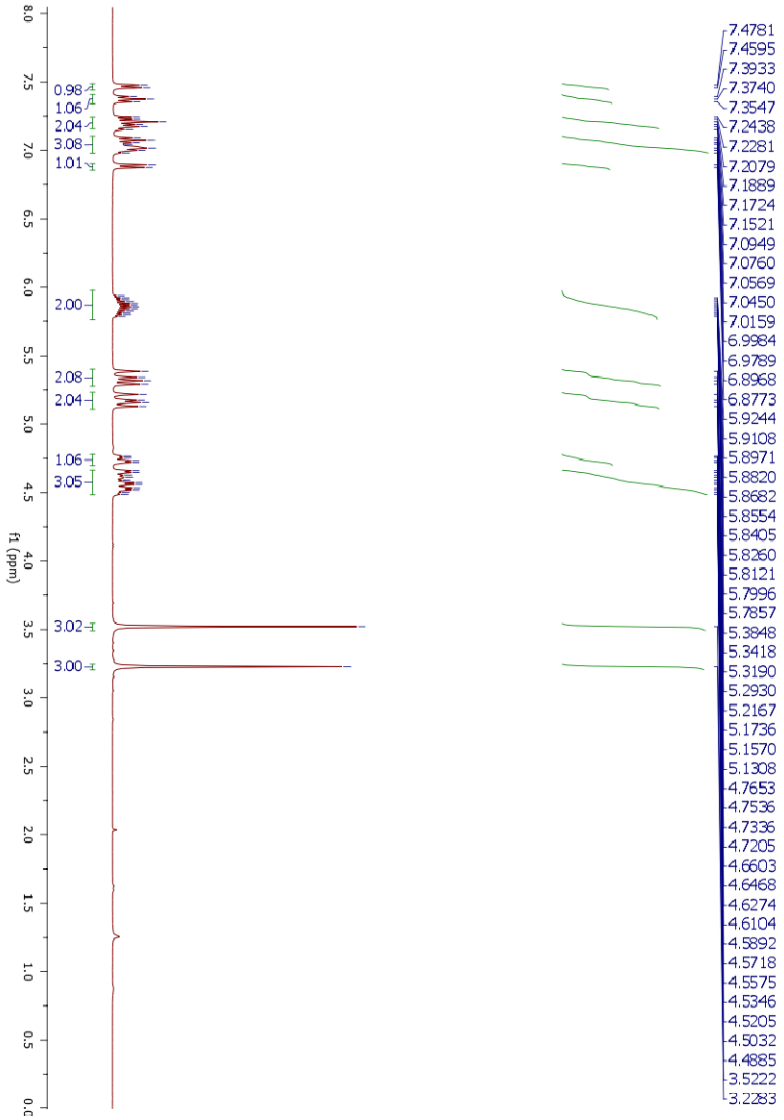
^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20b**



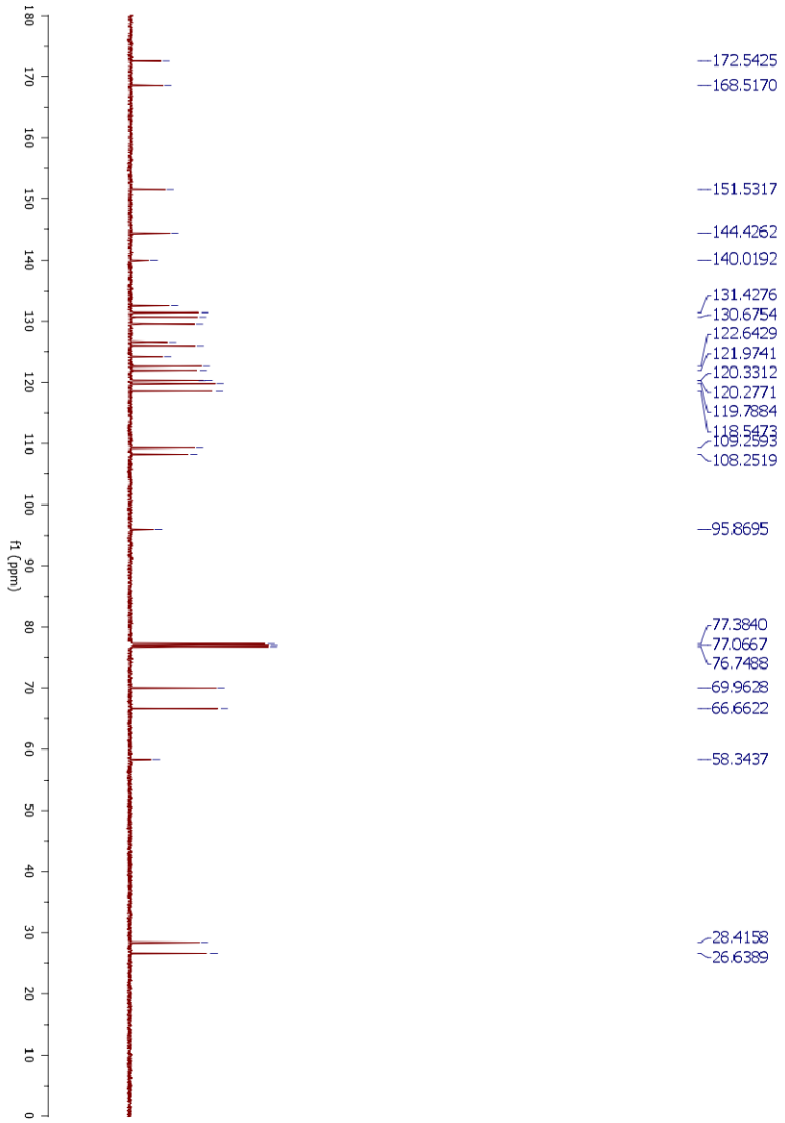
Scanned copy of mass spectrum of (±)-**20b**



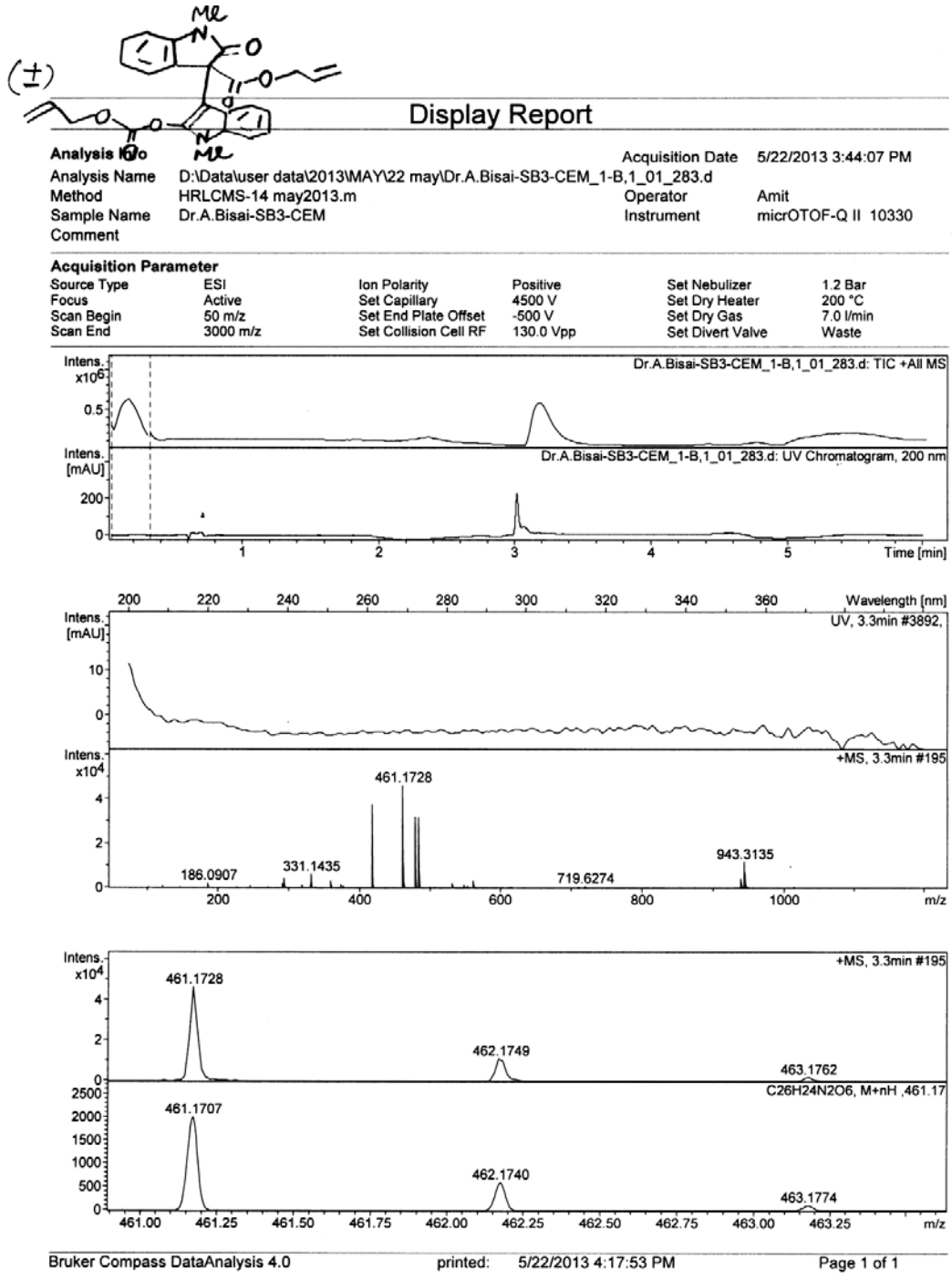
±(**11**)



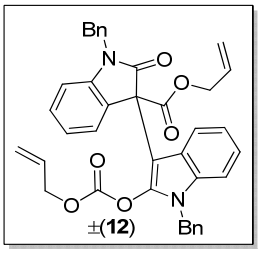
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**11**

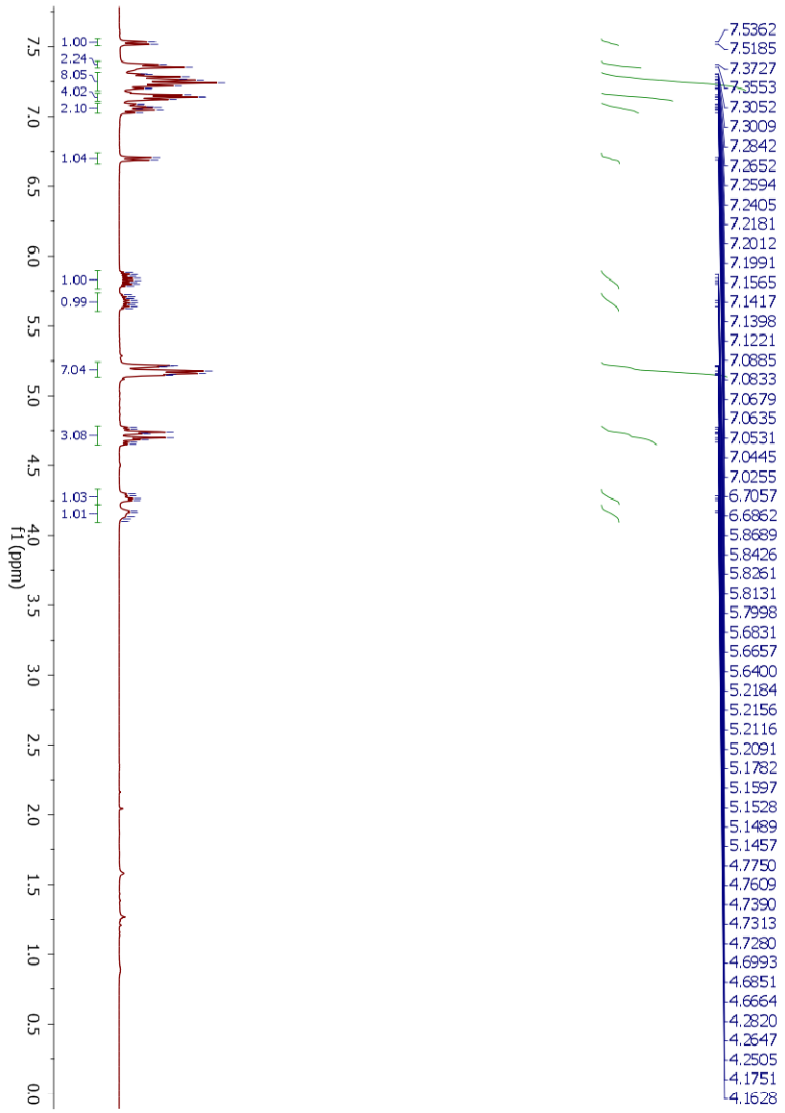


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**11**

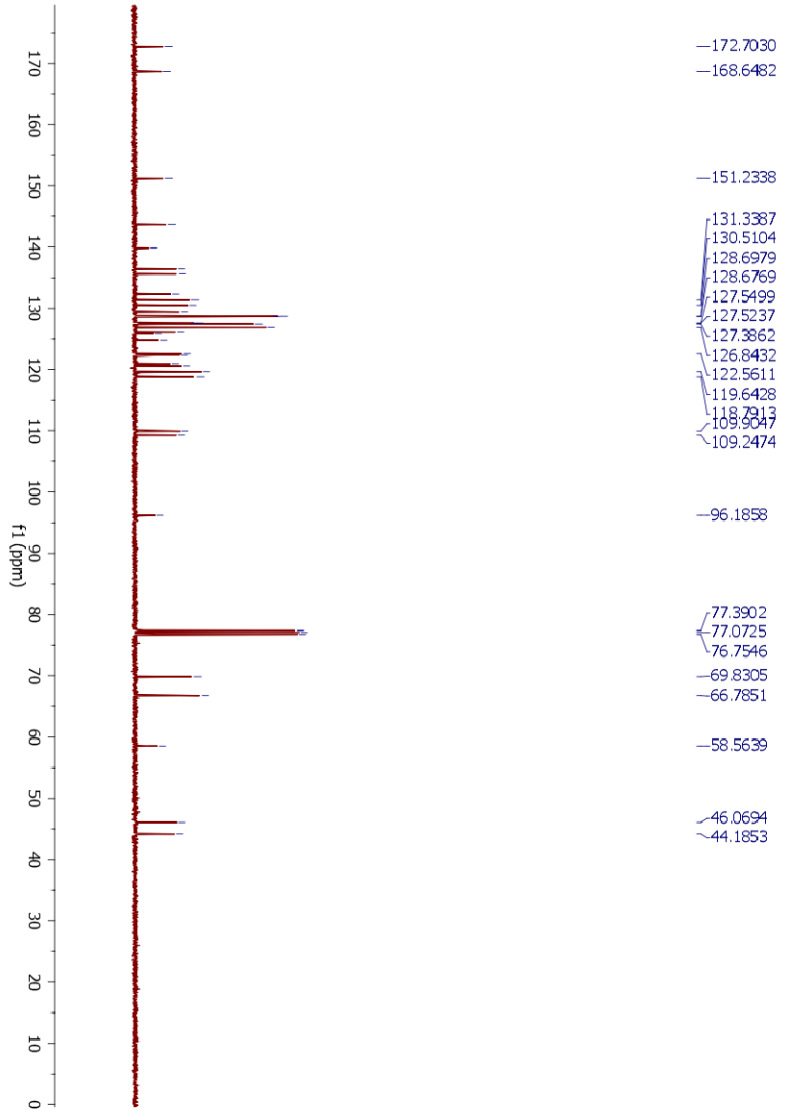


Scanned copy of mass spectrum of (±)-**11**

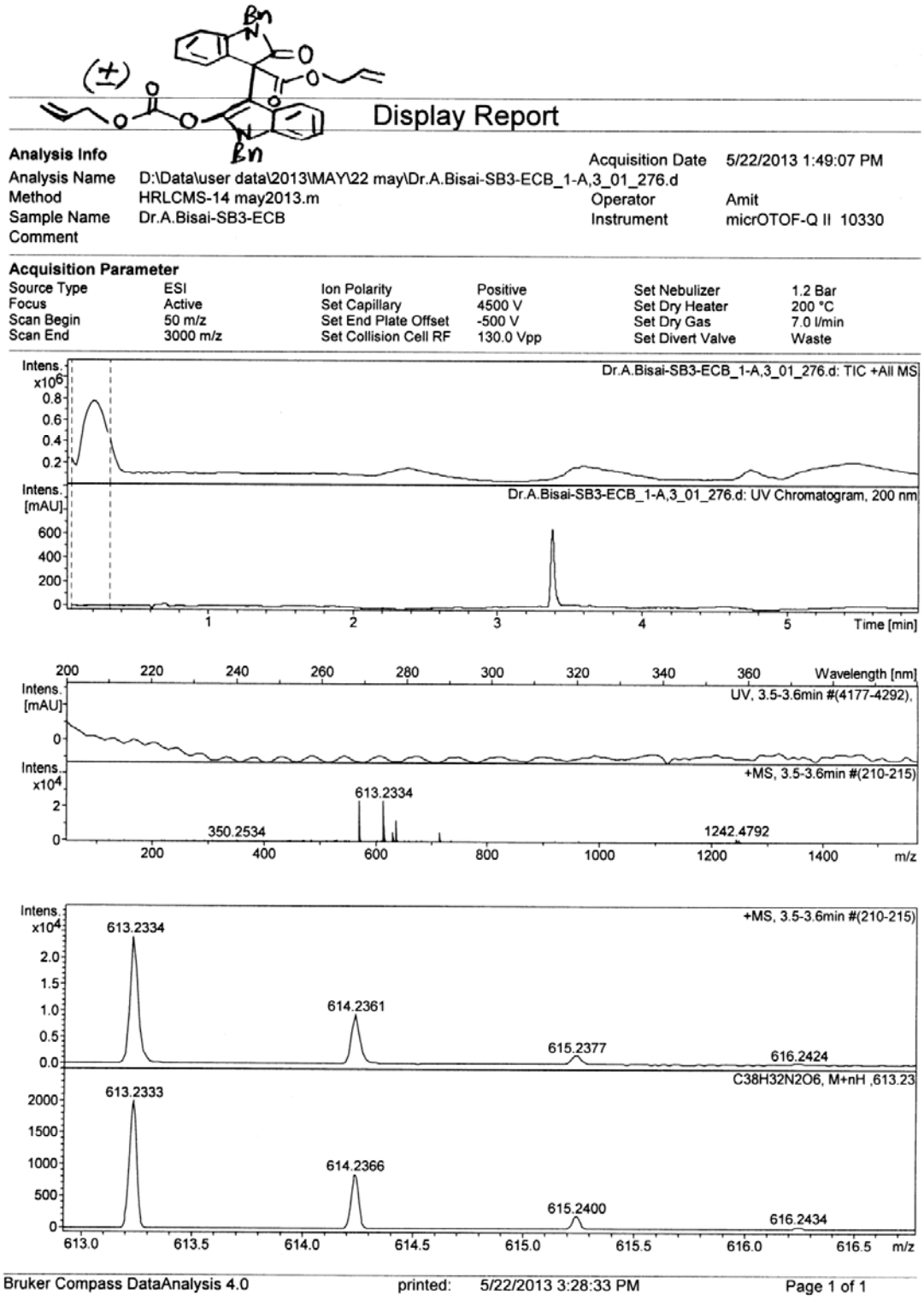




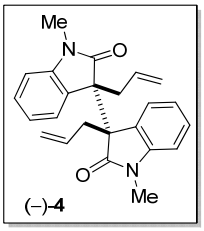
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**12**

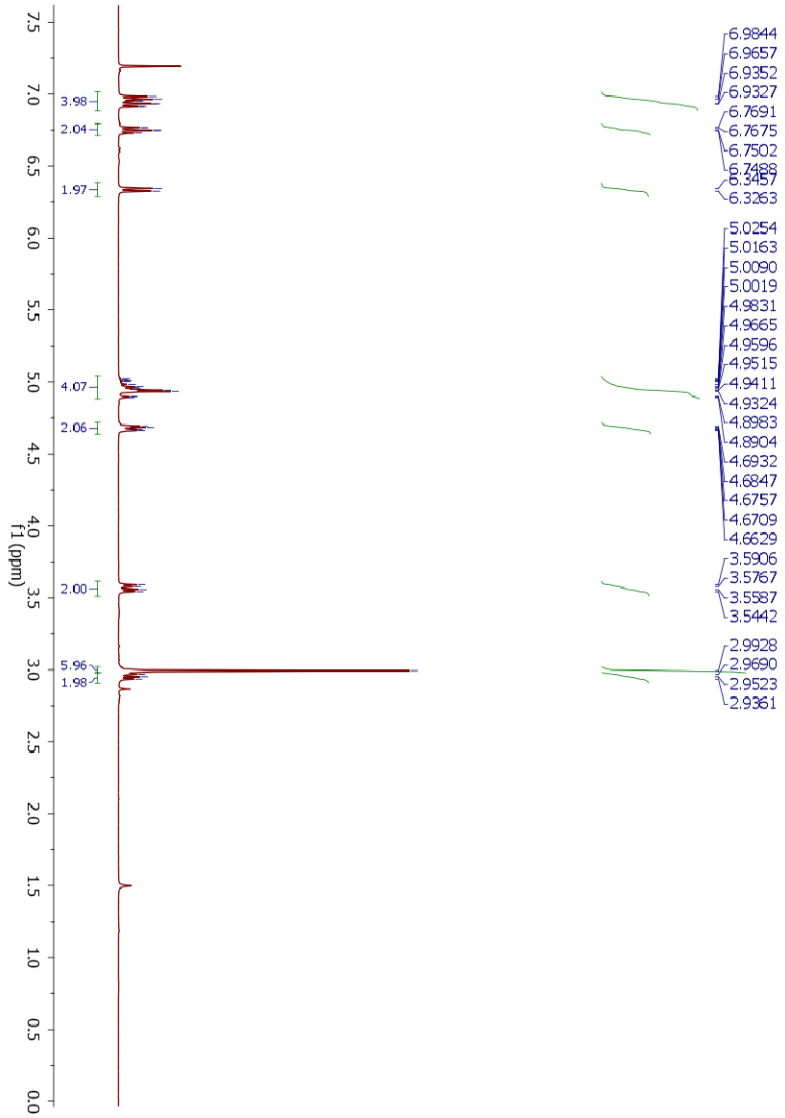


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**12**

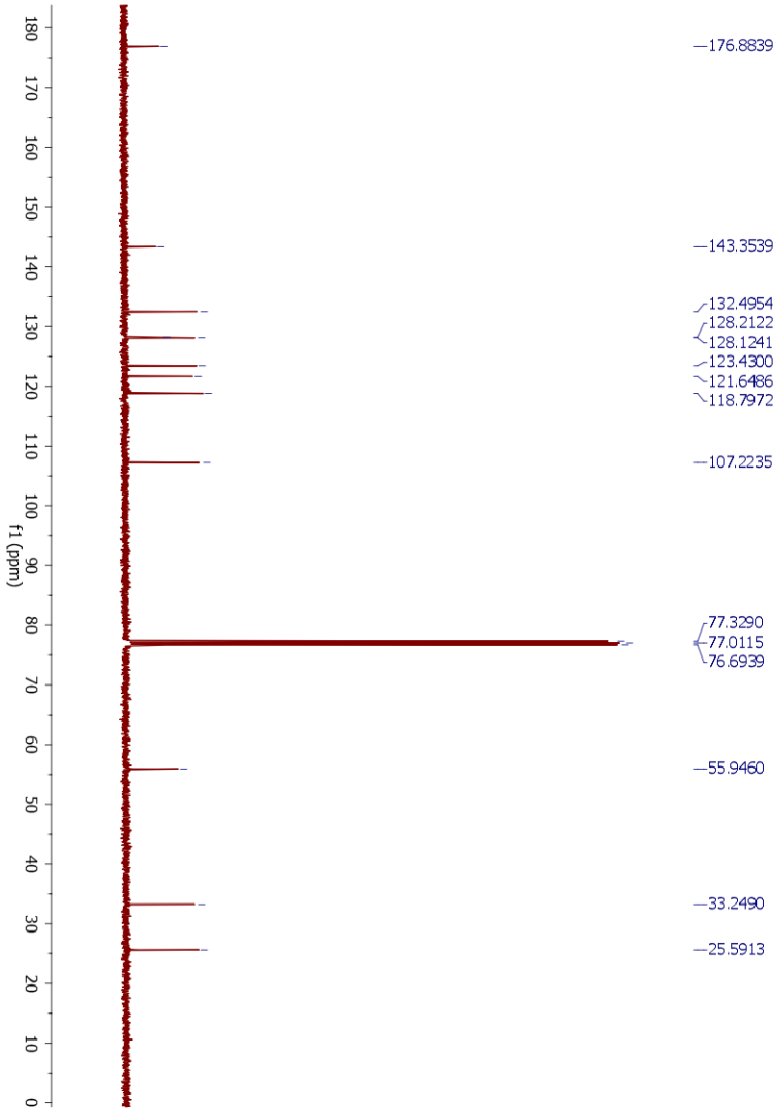


Scanned copy of mass spectrum of (±)-**12**

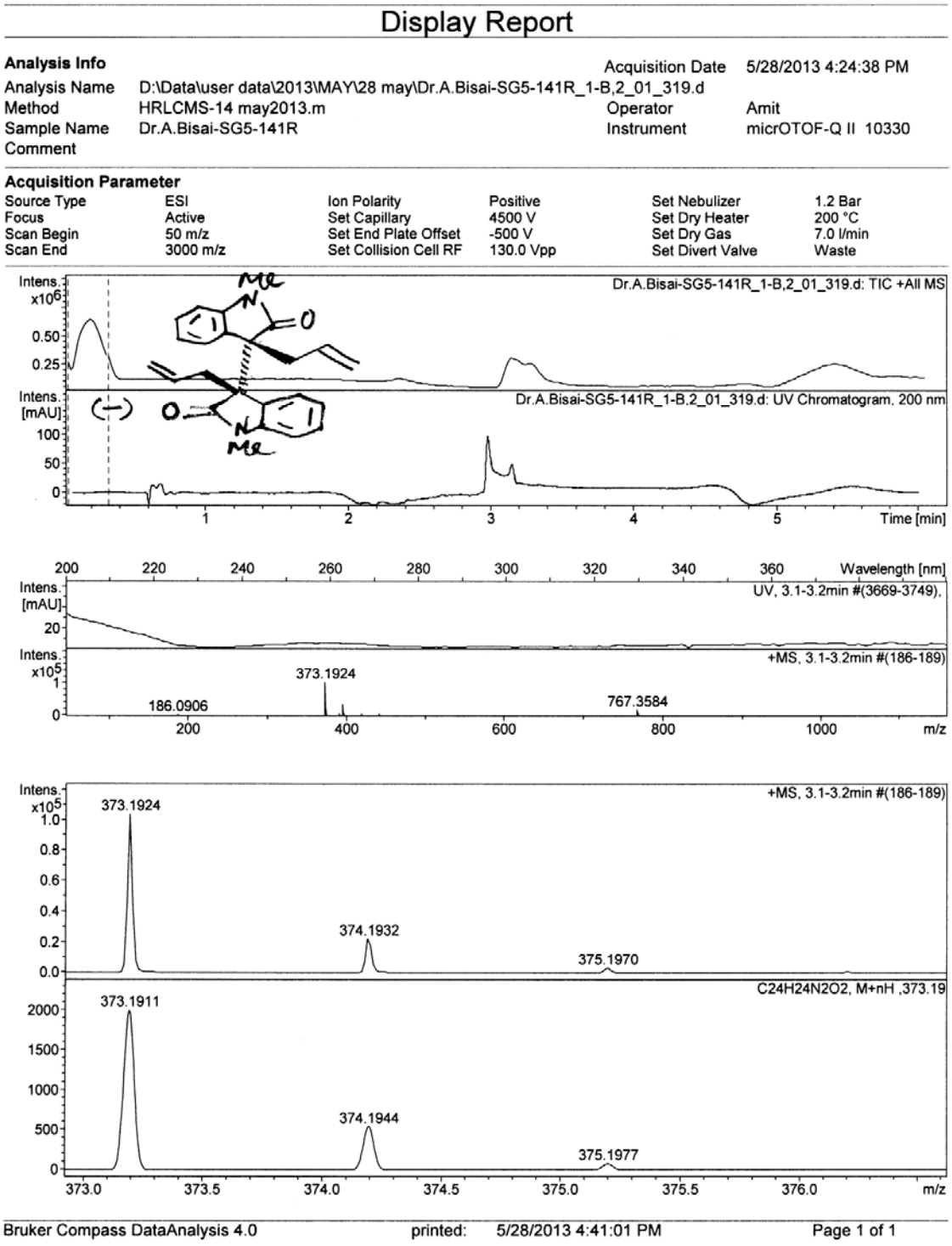




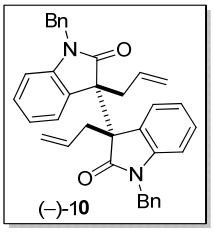
^{1}H NMR (400 MHz, $CDCl_3$) of compound (–)-**4**

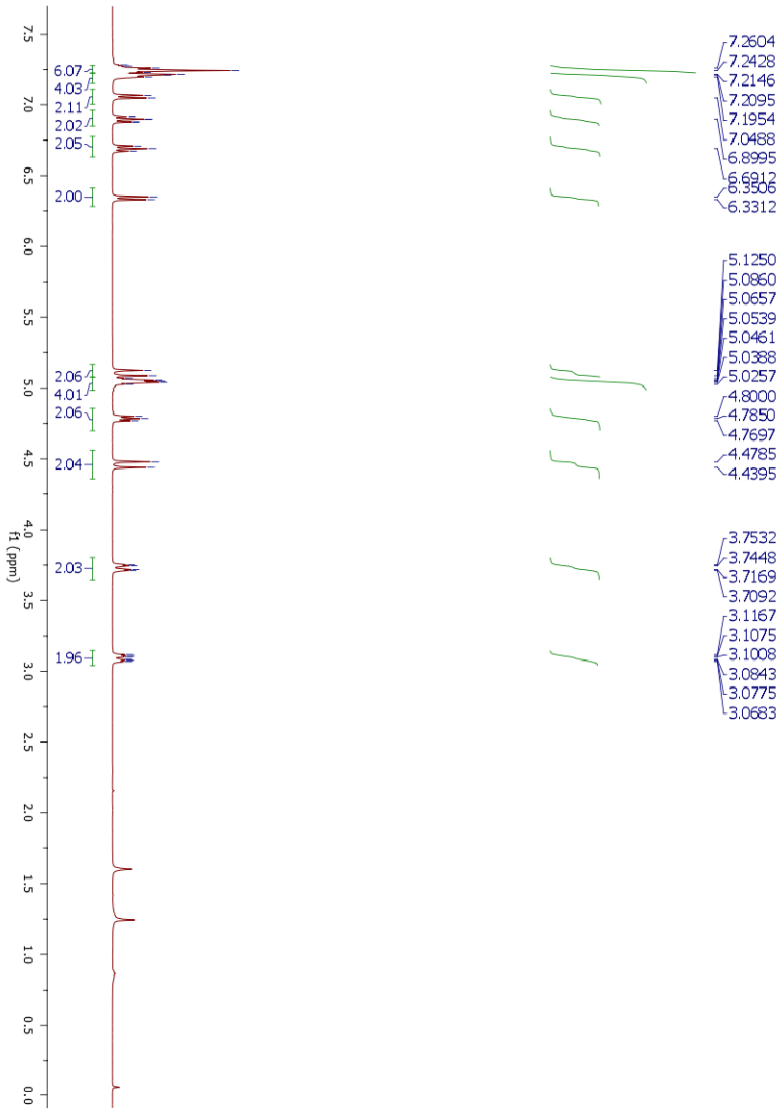


^{13}C NMR (100 MHz, $CDCl_3$) of compound (−)-**4**

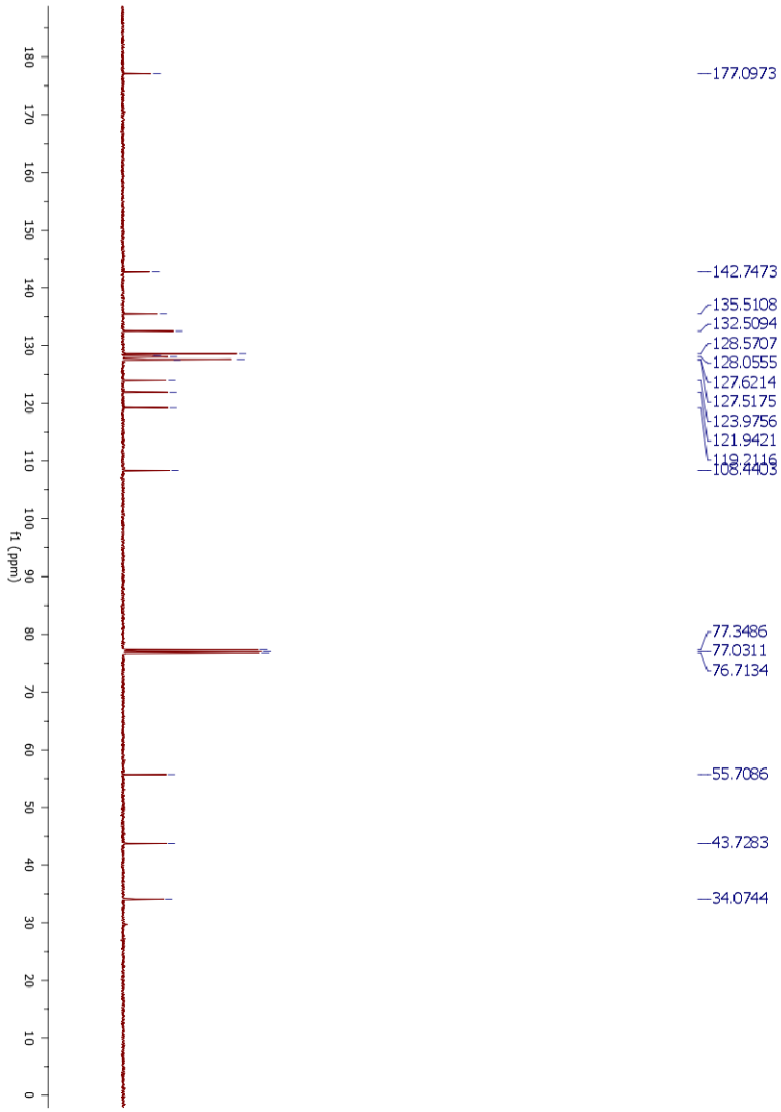


Scanned copy of mass spectrum of (–)-**4**

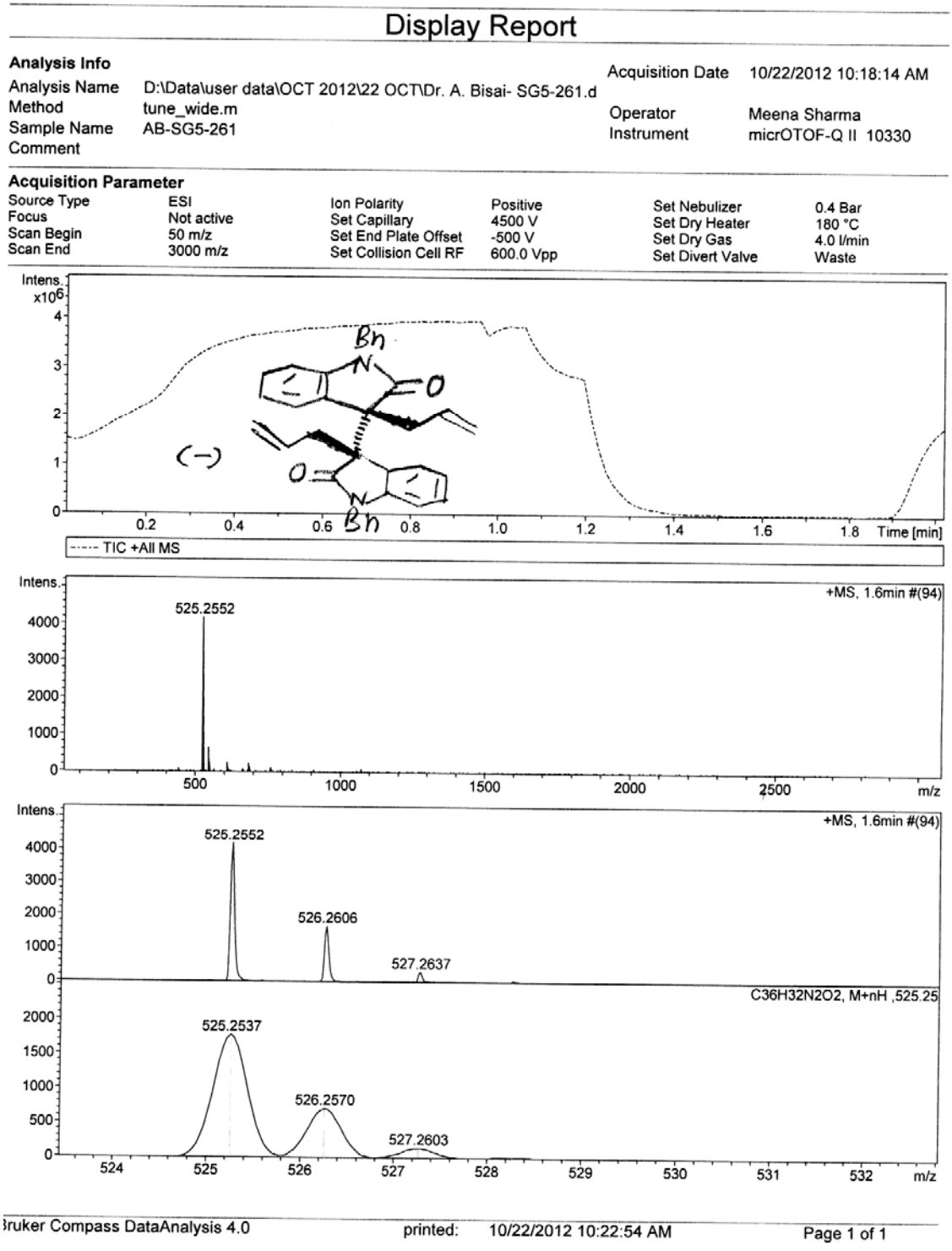




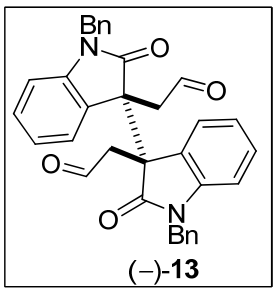
^{1}H NMR (400 MHz, $CDCl_3$) compound (–)-**10**



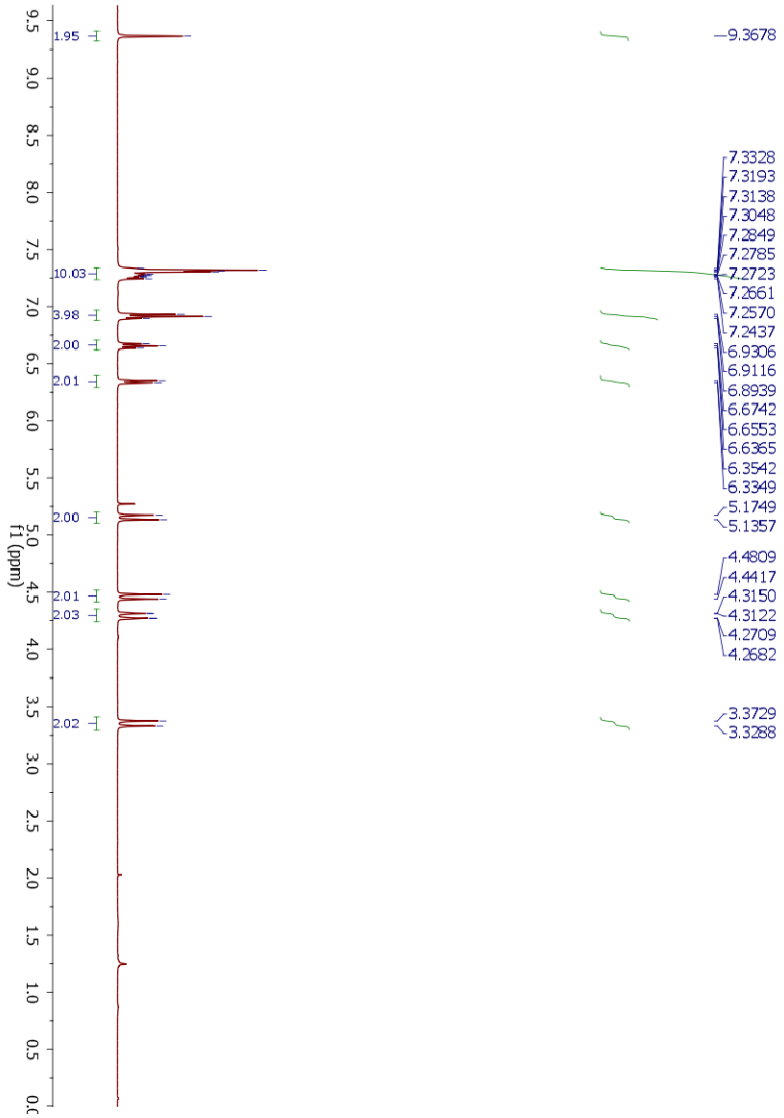
^{13}C NMR (100 MHz, $CDCl_3$) of compound (–)-**10**



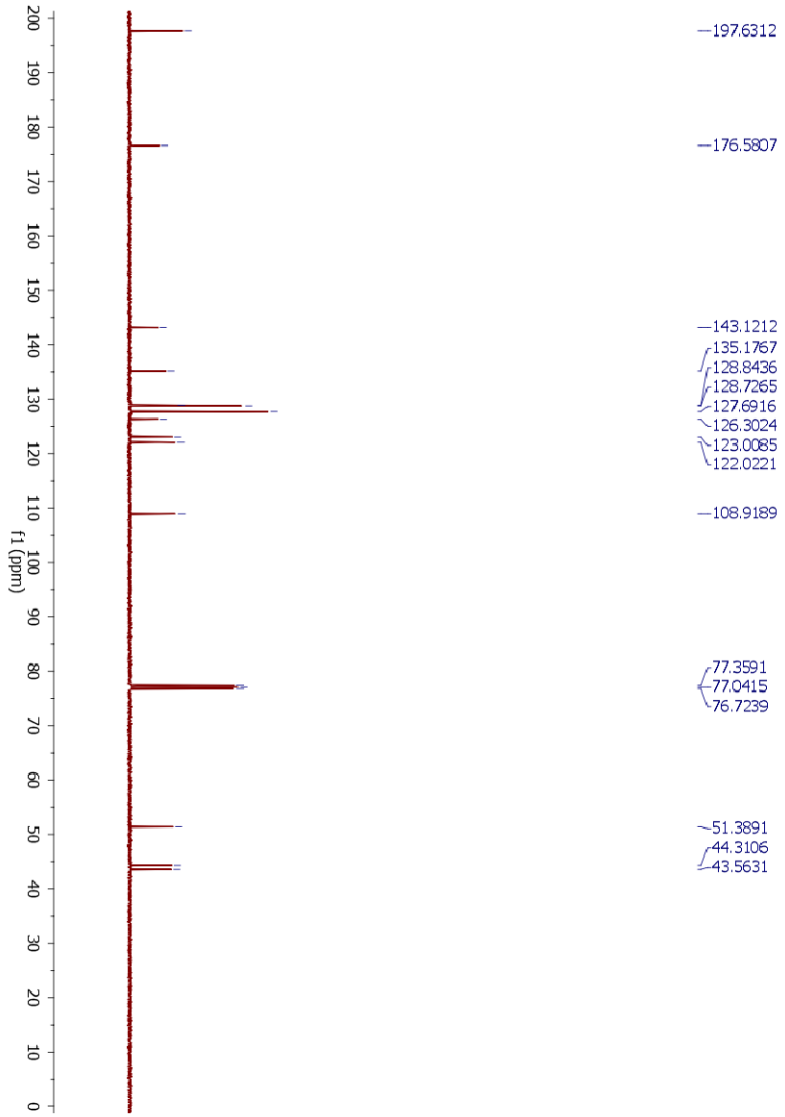
Scanned copy of mass spectrum of (–)-**10**



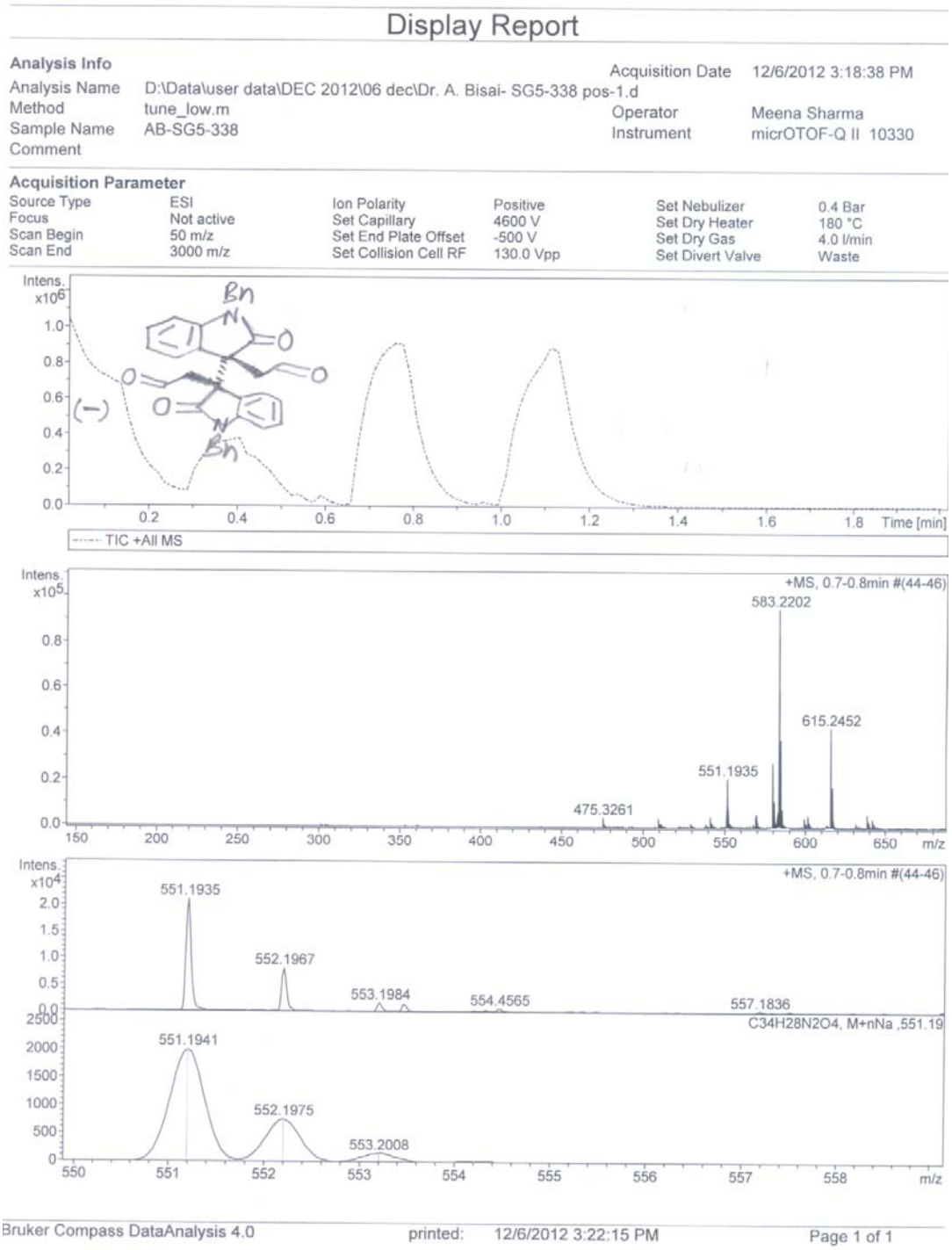
(–)-**13**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (**–**)-**13**



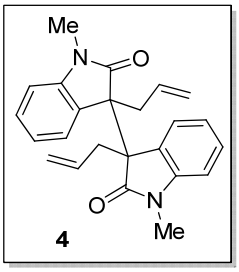
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**–**)-**13**



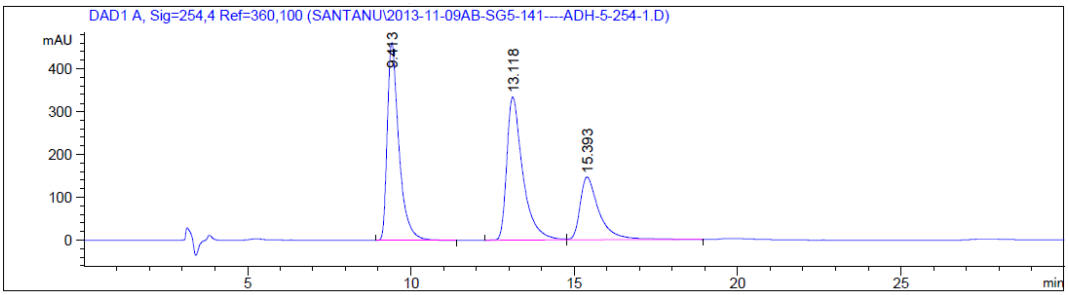
Scanned copy of mass spectrum of (–)-**13**

HPLC data

HPLC data of (4) (Racemic + *meso*)

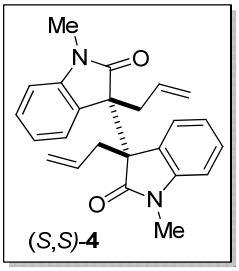



```
Data File C:\CHEM32\1\DATA\SANTANU\2013-11-09AB-SG5-141----ADH-5-254-1.D
Sample Name: AB-SG5-141----ADH-5-254-1

======================================================================
Acq. Operator   : ABGROUP
Sample Operator : ABGROUP
Acq. Instrument : HPLC 1260                    Location : Vial 1
Injection Date  : 11/9/2013 11:14:28 PM
                                             Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\SANTANU\5-254-1-30.M
```

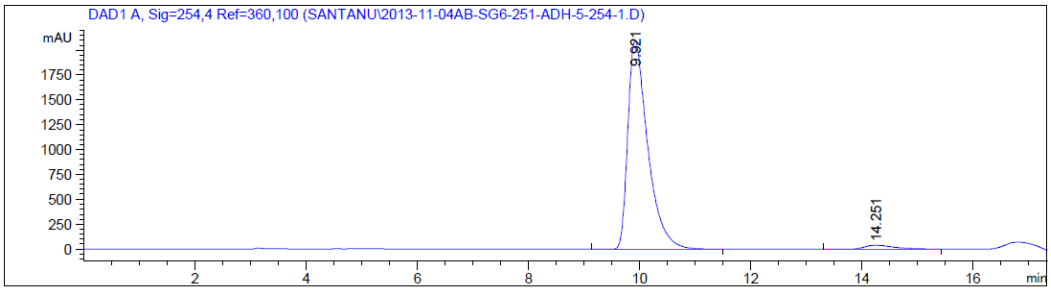



```
                      Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.413 BB    0.3668 1.13446e4   461.48209  39.4791
   2  13.118 BV    0.5046 1.13592e4   334.13837  39.5301
   3  15.393 VB    0.5985 6031.81689  147.07269  20.9908

Totals :                  2.87356e4   942.69315

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

HPLC data of (–)-4:




```
Data File C:\CHEM32\1\DATA\SANTANU\2013-11-04AB-SG6-251-ADH-5-254-1.D
Sample Name: AB-SG6-251-ADH-5-254-1

=====================================================================
Acq. Operator   : ABGROUP
                                                  Location : Vial 1
Injection Date  : 11/4/2013 12:59:07 PM
Acq. Method     : 5-254-1-30.M
Analysis Method : C:\CHEM32\1\METHODS\SUBHADIP\2-254-1-30.M
```

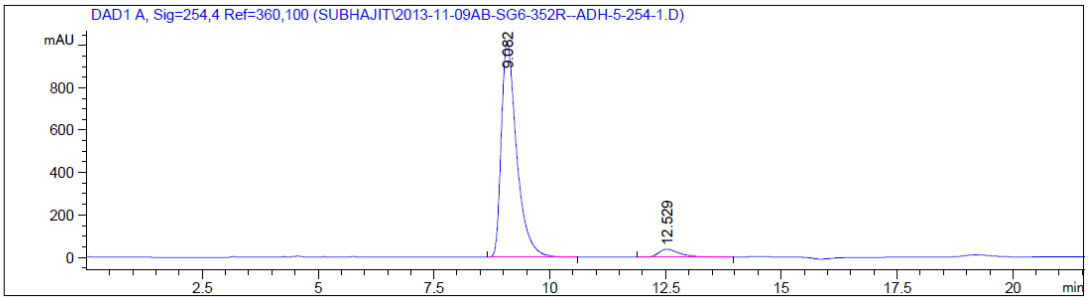



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.921 BB    0.3745 5.22215e4  2096.95898  97.2639
   2  14.251 BB    0.5566 1469.02771   39.62108   2.7361

Totals :                  5.36905e4  2136.58006

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

Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, toluene, 0 °C, 18 h, **95% ee**

HPLC data of (–)-4:

```
Data File C:\CHEM32\1\DATA\SUBHAJIT\2013-11-09AB-SG6-352R--ADH-5-254-1.D
Sample Name: AB-SG6-352R--ADH-5-254-1

=====================================================================
Acq. Operator   : ABGROUP
                                                  Location : Vial 1
Injection Date  : 11/9/2013 12:04:20 PM
Acq. Method     : 5-254-1-30.M
Analysis Method : C:\CHEM32\1\METHODS\SANTANU\5-254-1-30.M
```

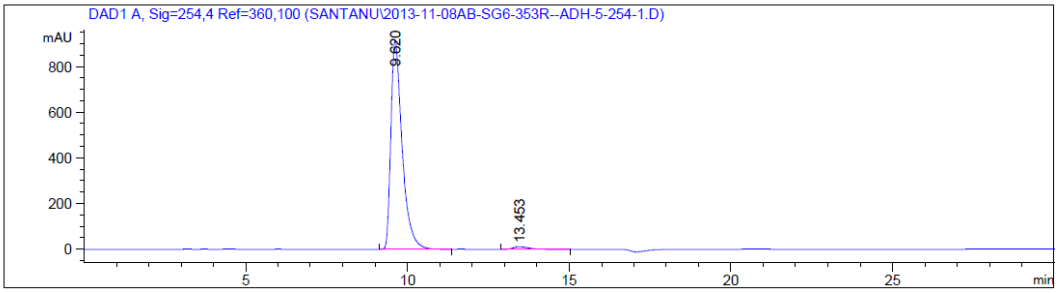



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.082 BB    0.3441 2.33086e4  1014.13007  95.1532
   2  12.529 BB    0.4798 1187.25696   37.25249   4.8468

Totals :                  2.44959e4  1051.38256


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

Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, 0 °C, 12 h, **91% ee**

HPLC data of (–)-4:

```
Data File C:\CHEM32\1\DATA\SANTANU\2013-11-08AB-SG6-353R--ADH-5-254-1.D
Sample Name: AB-SG6-353R--ADH-5-254-1

======================================================================
Acq. Operator   : ABGROUP
Sample Operator : ABGROUP
Acq. Instrument : HPLC 1260                    Location : Vial 1
Injection Date  : 11/8/2013 8:02:07 PM
                                               Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\SANTANU\5-254-1-30.M
```

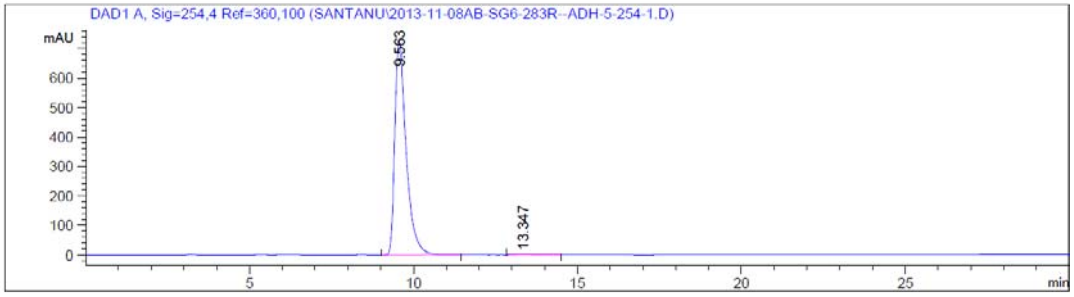



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.620 BB    0.3668 2.21210e4   912.56805  98.2939
   2  13.453 BB    0.5111  383.96362   11.22294   1.7061

Totals :                  2.25050e4   923.79099


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

Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, -10 °C, 18 h, **97% ee**

HPLC data of (–)-4 using (1:1) mixture of *N*-methyl bis-esters 3 and ester-carbonate 11 as starting material:

```
Data File C:\CHEM32\1\DATA\SANTANU\2013-11-08AB-SG6-283R--ADH-5-254-1.D
Sample Name: AB-SG6-283R--ADH-5-254-1

=====================================================================
Acq. Operator   : ABGROUP
Sample Operator : ABGROUP
Acq. Instrument : HPLC 1260                    Location : Vial 1
Injection Date  : 11/8/2013 6:52:21 PM
                                               Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\SANTANU\5-254-1-30.M
```

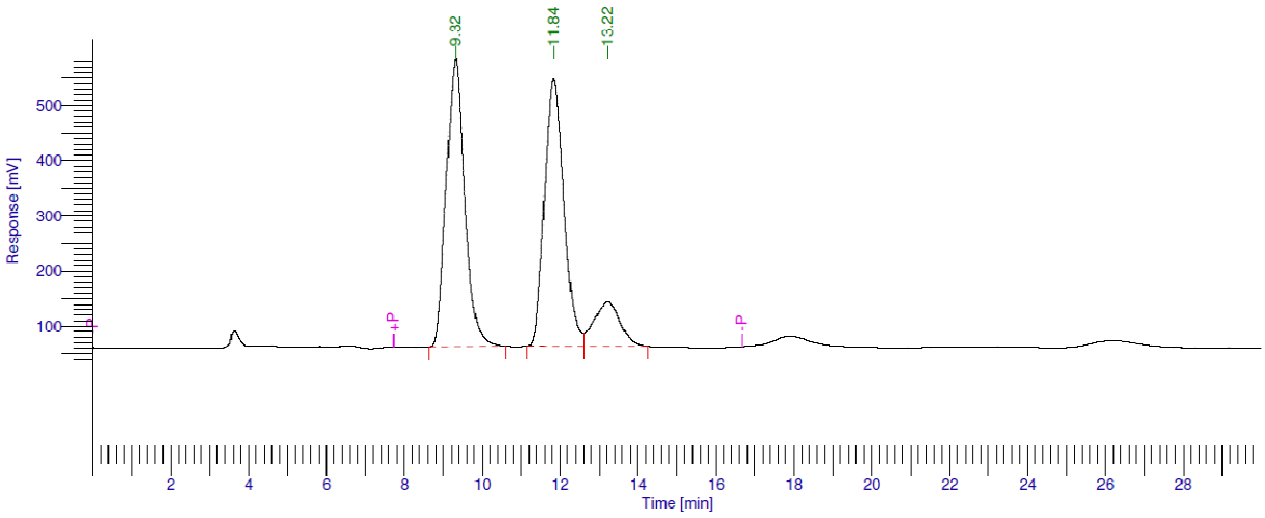



```
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.563 BV    0.3598 1.74208e4   726.42047  99.5407
   2  13.347 BV    0.5148   80.38264    2.39939   0.4593

Totals :                  1.75012e4   728.81986

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

Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, -10 °C, 18 h, **>99% ee**

Software Version	: 6.3.2.0646	Date	: 2/27/2013 12:16:57 PM
Sample Name	:	Data Acquisition Time	: 9/8/2012 8:35:04 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : C:\HPLC\Data\santanu\SG5-141-ADH-5%,30 MIN, FLOW 1.rst
Sequence File : C:\PerlExe\TcWS\Ver6.3.2\Examples\SG5-141-ADH-5%,30 MIN, FLOW 1.seq



SG 5 -141 REPORT

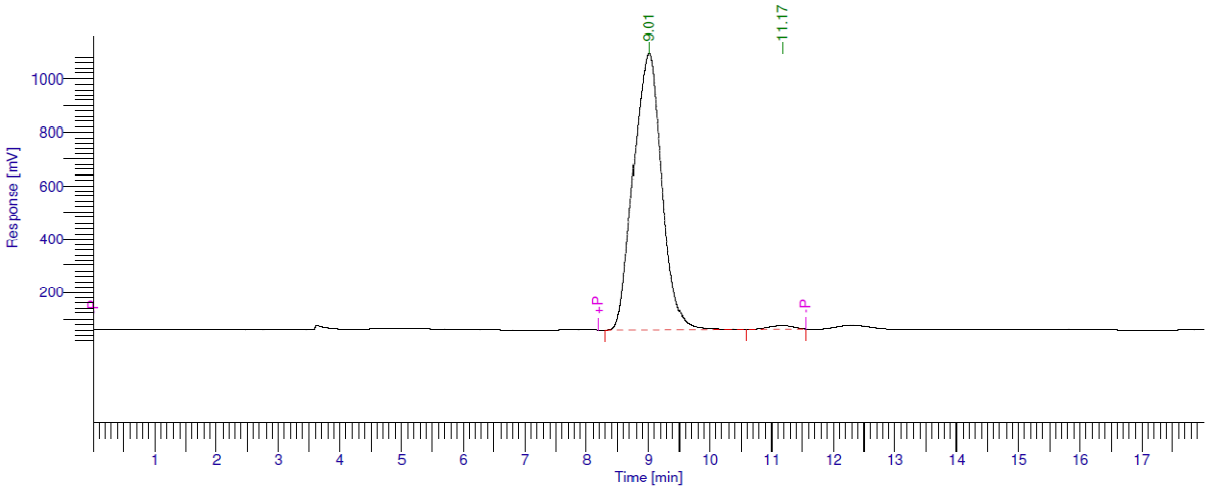
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.322	17120958.46	520826.67	45.51
2		11.838	16768603.58	483271.96	44.57
3		13.224	3729451.36	80683.96	9.91
			37619013.40	1.08e+06	100.00

HPLC data of (**4**) (Racemic + *meso*)

HPLC data of (–)-4 using (±) ester-carbonate 11 as starting material:

Software Version	: 6.3.2.0646	Date	: 7/18/2013 2:57:13 PM
Sample Name	:	Data Acquisition Time	: 11/3/2012 5:56:56 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : C:\HPLC\Data\santanu\SG5-287-ADH-5%-1-FLOW-238_001.rst
Sequence File : C:\PenExe\TcWS\Ver6.3.2\Examples\SG5-287-ADH-5%-1-FLOW-238.seq

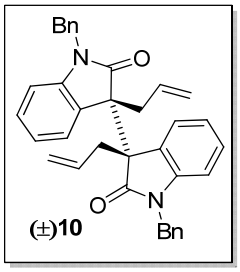


PEAK AREA

Peak #	Component Name	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		32970303.34	1.03e+06	98.89	98.89
2		371329.09	13714.31	1.11	1.11
		33341632.44	1.05e+06	100.00	100.00

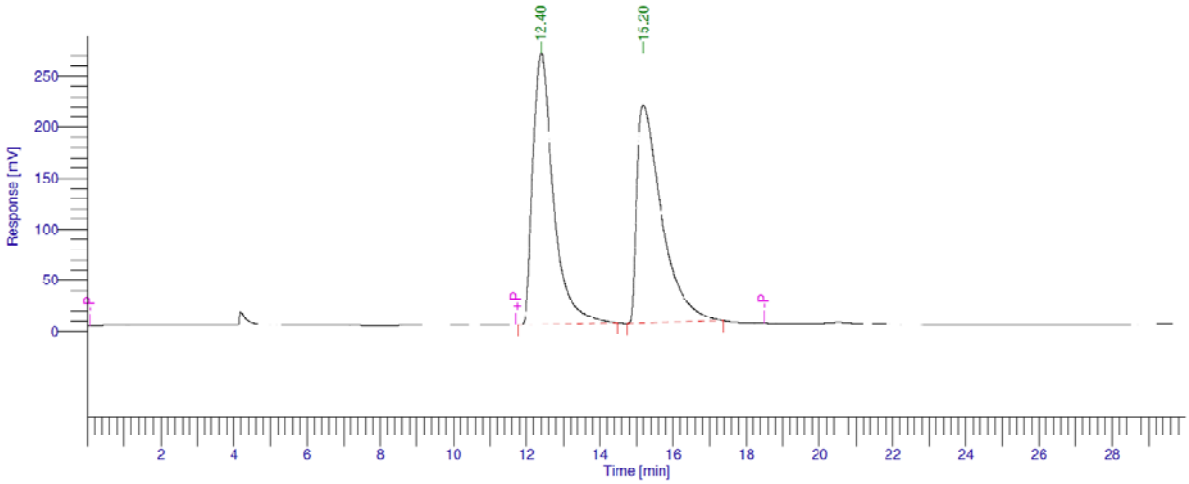
Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, -10 °C, 12 h, **98% ee**

HPLC data of (±)-10



Software Version	: 6.3.2.0646	Date	: 9/3/2013 10:34:09 AM
Sample Name	:	Data Acquisition Time	: 9/1/2013 1:17:06 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

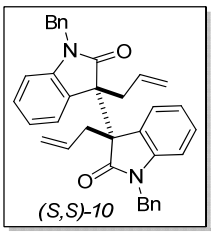
Result File : C:\HPLC\Data\santanu\SG5-261-1-9-13.rst
Sequence File : C:\PenExe\TcWS\Ver6.3.2\Examples\SG5-261-1-9-13.seq



PEAK REPORT

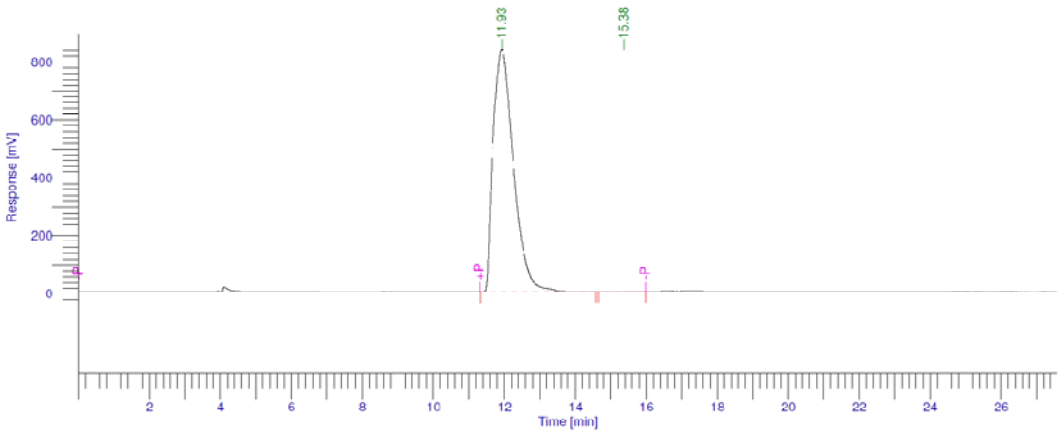
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.401	10239253.63	264918.02	50.40
2		15.197	10075055.14	213007.55	49.60
			20314308.77	477925.57	100.00

HPLC-data of (–)-10 by using (± and *meso*) bis-esters 9 as starting material



Software Version	: 6.3.2.0646	Date	: 9/3/2013 10:45:16 AM
Sample Name	:	Data Acquisition Time	: 9/2/2013 7.11.19 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : C:\HPLC\Data\santanu\SG6-240RR-IB-2-238-1-30.rst
Sequence File : C:\PenExe\TcWS\Ver6.3.2\Examples\SG6-240RR-IB-2-238-1-30.seq



PEAK REPORT

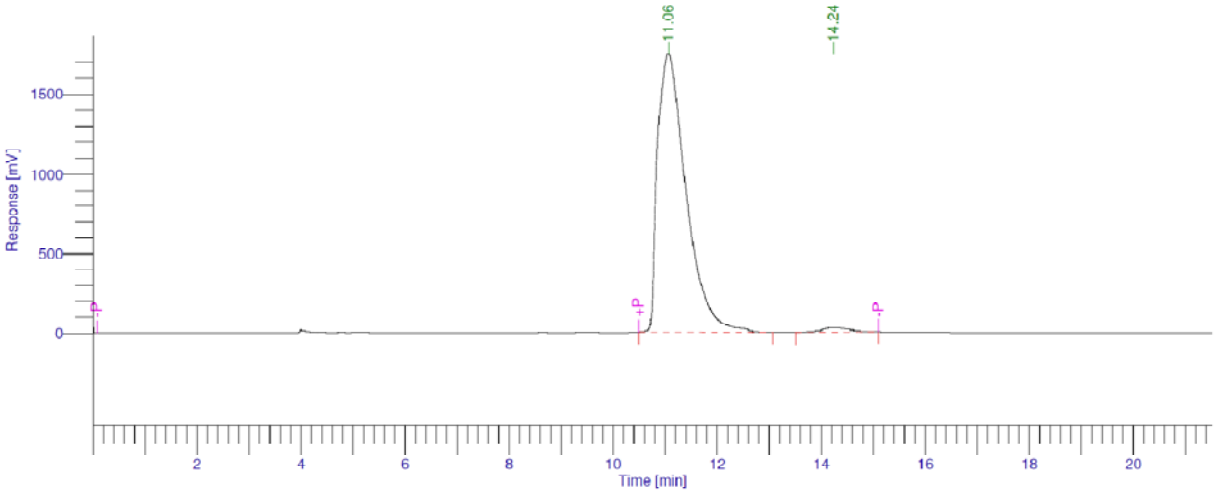
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.929	33431913.30	836515.61	99.94
2		15.377	20461.02	578.67	0.06
			33452374.32	837094.28	100.00

Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, 0 °C, 12 h, **>99% ee**

HPLC data of (–)-10 using (±) ester-carbonate 12 as starting material

Software Version	: 6.3.2.0646	Date	: 9/3/2013 9:43:12 PM
Sample Name	:	Data Acquisition Time	: 9/3/2013 9:20:39 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File :
Sequence File : C:\PenExe\TcWS\Ver6.3.2\Examples\SG6-241IB.seq



PEAK REPORT

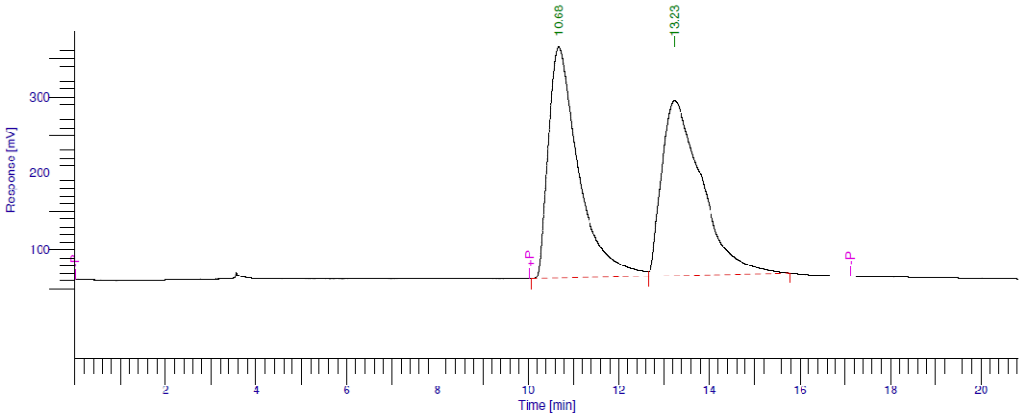
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.060	65962623.09	1.74e+06	98.45
2		14.236	1037433.84	27898.15	1.55
			67000056.93	1.77e+06	100.00

Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, 0 °C, 12 h, **97% ee**

HPLC data of (±)-10

Software Version	: 6.3.2.0646	Date	: 11/27/2013 12:25:03 AM
Sample Name	:	Data Acquisition Time	: 11/26/2013 10:07:40 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : C:\HPLC\Data\santanu\SG5-261-RACEMIC2.rst
Sequence File : C:\PenExe\TcWS\Ver6.3.2\Examples\SG5-261-RACEMIC2.seq



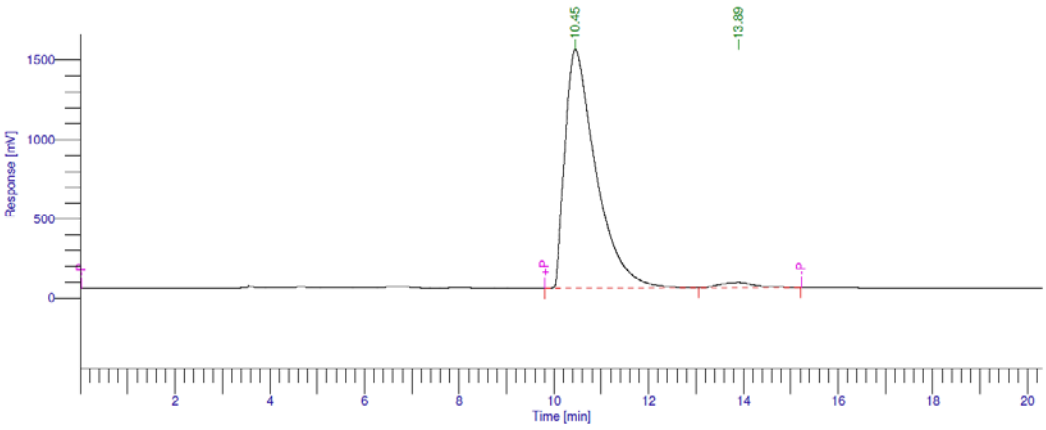
PEAK REPORT

Peak #	Component Name	Time [min]	Area [µV·s]	Height [µV]	Area [%]
1		10.679	14015768.65	302314.24	50.13
2		13.232	13940614.27	228893.93	49.87
			27956382.93	531208.17	100.00

HPLC data of (–)-10 using (1:1) mixture of bis-esters 9 and ester-carbonate 12 as starting material

Software Version	: 6.3.2.0646	Date	: 11/26/2013 10:53:14 PM
Sample Name	:	Data Acquisition Time	: 11/26/2013 10:31:10 PM
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: iiser
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : C:\HPLC\Data\santanu\SG7-27-IB-2-238.rst
Sequence File : C:\PenExe\TcWS\Ver6.3.2\Examples\SG7-27-IB-2-238.seq

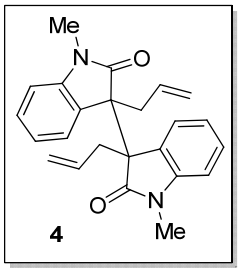


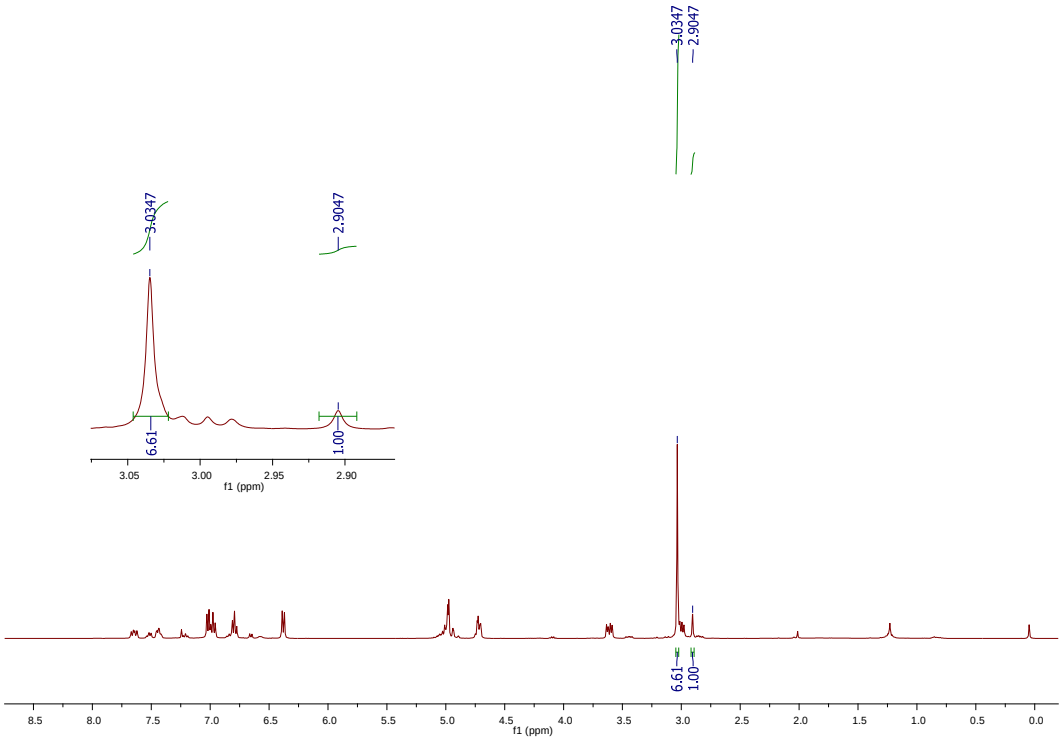
PEAK REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		10.451	68356141.57	1.51e+06	97.69
2		13.891	1614006.69	31797.64	2.31
			69970148.25	1.54e+06	100.00

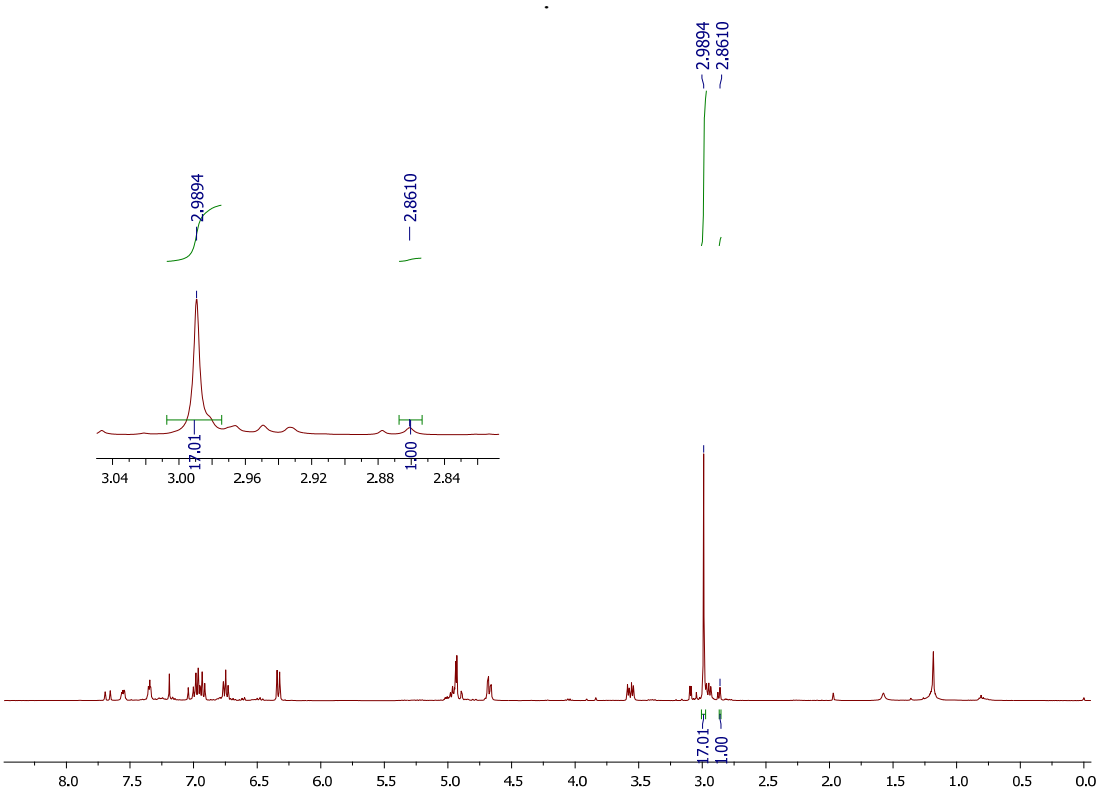
Condition: 2.5 mol% $Pd_2(dba)_3$, 7.5 mol% **8c**, Et_2O, 0 °C, 12 h, **96% ee**

Determination of diastereomeric ratio of (4) from ^{1}H-NMR of crude reaction mixture



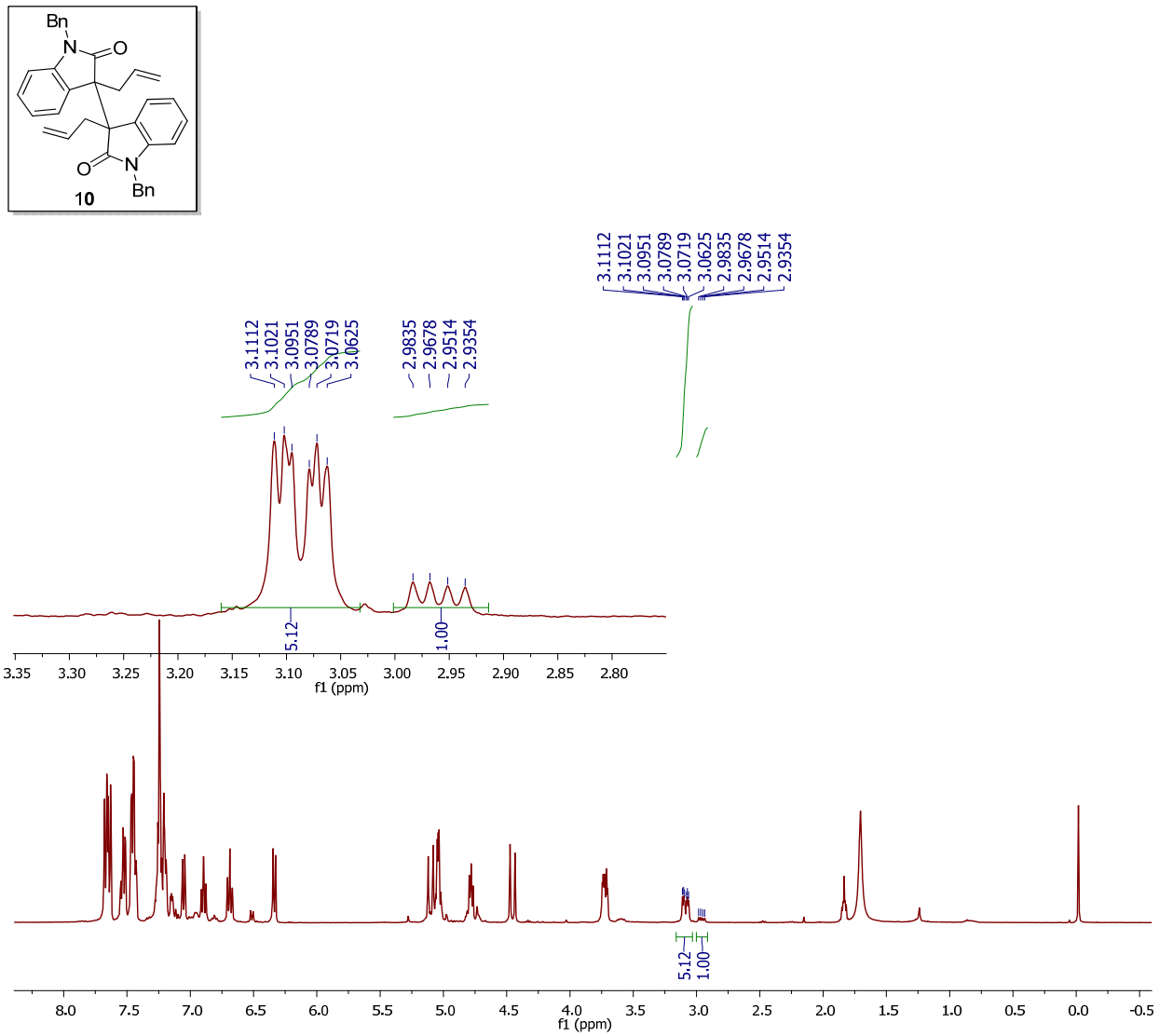


400 MHz ^{1}H-NMR ($CDCl_3$) of crude **4** [racemic + *meso*]

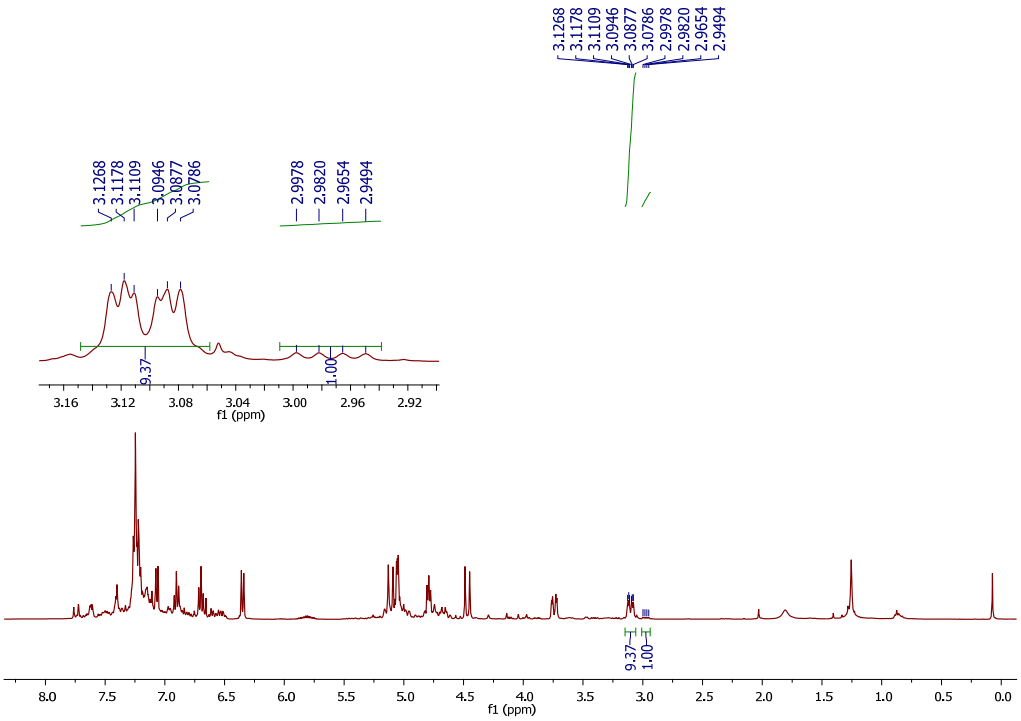


400 MHz ^{1}H-NMR ($CDCl_3$) of crude **4** [entry 5, Table 2]

Determination of diastereomeric ratio of (10) from ^{1}H-NMR of crude reaction mixture:



400 MHz ^{1}H-NMR ($CDCl_3$) of **10** (racemic + *meso*)



400 MHz ^{1}H-NMR ($CDCl_3$) of crude (**10**) [Diethylether as a solvent, 0 °C and **8c** as ligand]