

Supplementary Information for:

**Rhodium/diene-catalyzed asymmetric arylation of *N*-sulfonyl
indolylimines: a new access to highly optically active α -aryl
3-indolyl-methanamines**

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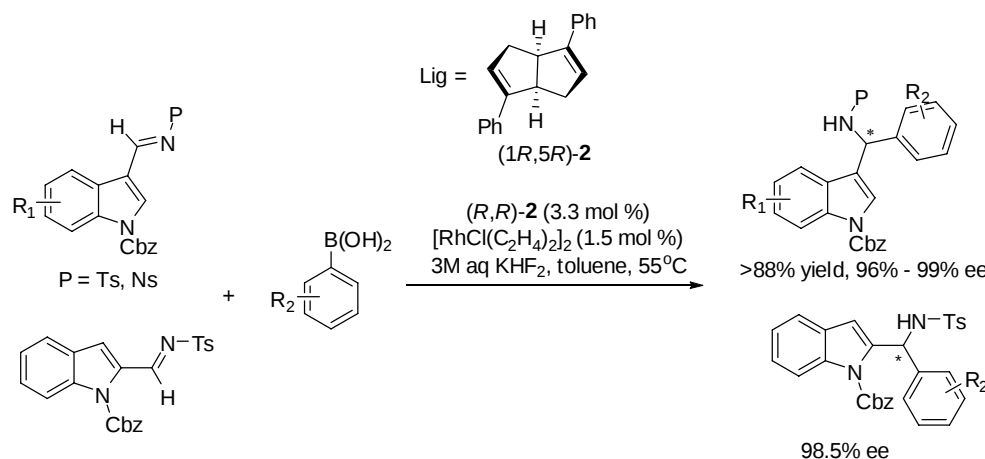
1. General

NMR spectra were recorded on a Varian spectrometer (300 MHz for ^1H , and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform- d (δ 77.05) or DMSO- d (δ 39.50) for ^{13}C NMR. HPLC was performed on a JASCO 2000 instrument by using Daicel columns.

Chiral diene ligand **2** was prepared according to the reported procedures¹.

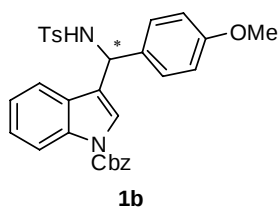
- (a) Z.-Q. Wang, C.-G. Feng, M.-H. Xu, and G.-Q. Lin, *J. Am. Chem. Soc.* 2007, **129**, 5336; (b) C.-G. Feng, Z.-Q. Wang, P. Tian, M.-H. Xu and G.-Q. Lin, *Chem. Asian J.* 2008, **3**, 1511.

2. General Procedure for the Catalytic Asymmetric Arylation of Indolylimines with arylboronic acids.



Under nitrogen atmosphere, to a Schlenk flask charged with arylboronic acid (ArB(OH)_2 , 0.5 mmol), $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (1.5 mg, 0.0075 mmol, 3 mol%), chiral diene ligand (R,R) -**2** (2.2 mg, 0.0085 mmol, 3.3 mol%) was added 1 mL of toluene. The mixture was heated to 55°C and stirred for 30 min. 3-indolylimine (0.25 mmol), toluene (1 mL) and 3M KHF_2 solution (0.25 mL, 0.75 mmol) was added sequentially. After the mixture was stirred at 55°C for 5h, 10 mL of 0.2 N HCl was added to quench the reaction. The mixture was extracted with EtOAc and washed with brine, the combined organic phases were dried and concentrated. The residue was purified by silica gel column chromatography to afford the desired indolyl methanamine product **1**.

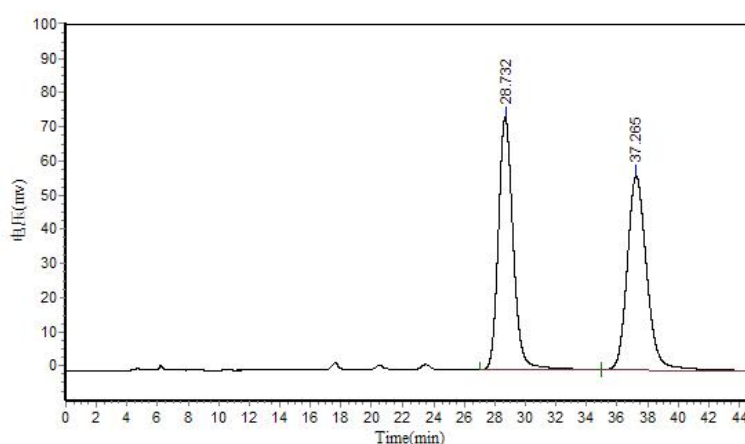
3. Characterization Data and HPLC of the Obtained Enantioenriched Indolyl-methanamines 1b-1s and 7.



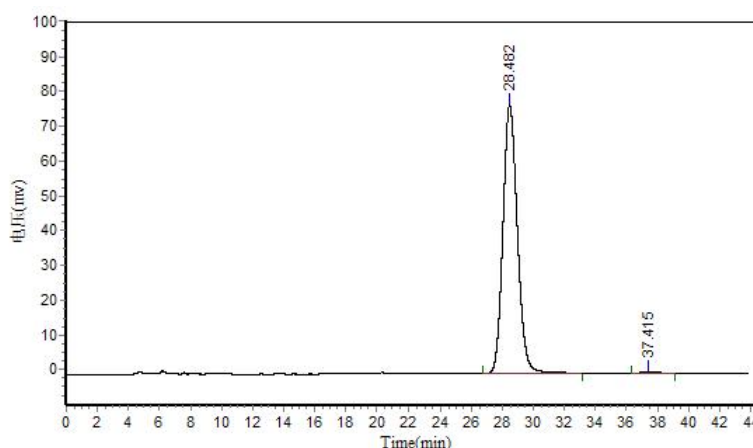
^1H NMR (300 MHz, CDCl_3): δ 2.30 (s, 3H), 3.75 (s, 3H), 4.99 (d, J = 8.1 Hz, 1H), 5.42 (s, 2H), 5.72 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 9 Hz, 2H), 7.00-7.18 (m, 6H), 7.27 (m, 2H), 7.39-7.52 (m, 7H), 8.08 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 20.76, 53.23, 55.00, 68.35, 113.51, 114.50, 119.97, 122.20, 122.76, 123.26, 124.63, 126.31, 128.15, 128.40, 128.58, 128.65, 128.79, 131.98, 134.99, 135.31, 138.40, 141.93,

149.98, 158.37; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_5\text{S}_1$: 539.1646; Found: 539.1667.

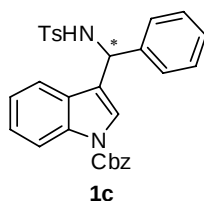
HPLC: 99% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 60:40; flow = 0.7 mL/min; Retention time: t (maj) = 28.5 min, t (min) = 37.4 min.



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.732	74042.125	5055455.000	49.7400
2		37.265	56971.836	5108304.500	50.2600
Total			131013.961	10163759.500	100.0000



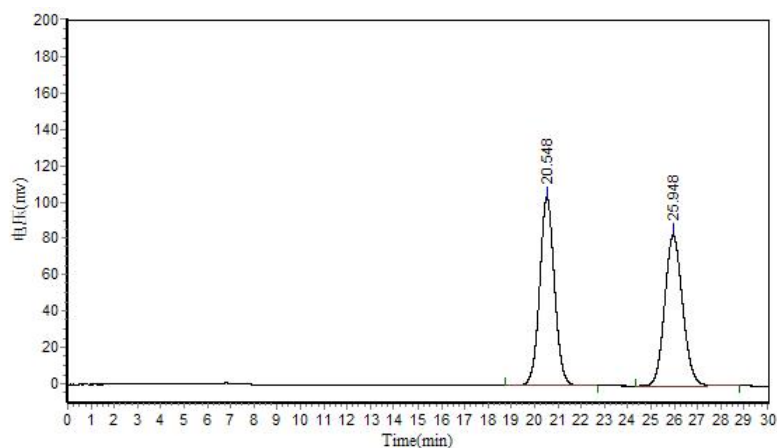
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.482	77193.898	5008505.000	99.3210
2		37.415	375.232	34241.301	0.6790
Total			77569.130	5042746.301	100.0000



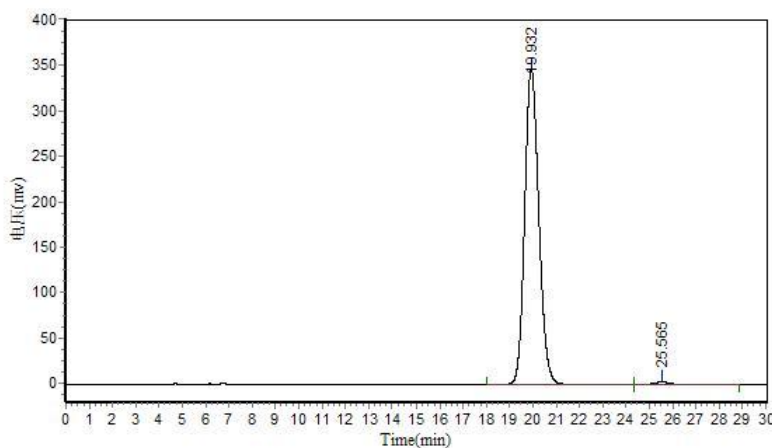
^1H NMR (300 MHz, CDCl_3): δ 2.27 (s, 3H), 5.38 (s, 2H), 5.65 (d, $J = 7.8$ Hz, 1H), 5.81 (d, $J = 8.1$ Hz, 1H), 6.93 (d, $J = 8.1$ Hz, 2H), 7.10 (m, 1H), 7.20-7.29 (m, 7H), 7.39-7.50 (m, 7H), 8.05 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.39, 54.74, 68.83, 115.34, 119.83, 121.12, 123.14, 124.44, 125.02, 127.12, 127.20, 127.93, 128.11, 128.56, 128.65, 128.81, 128.84, 129.15, 135.00, 135.94, 137.27, 138.93, 143.21, 150.57; HRMS (ESI):

m/z Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}_4\text{S}_1$: 509.1541; Found: 509.1555.

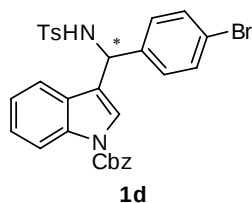
HPLC: 98% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 60:40; flow = 0.7 mL/min; Retention time: t (maj) = 19.9 min, t (min) = 25.6 min.



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.548	103613.703	4581164.500	50.8220
2		25.948	82608.914	4432965.500	49.1780
Total			186222.617	9014130.000	100.0000



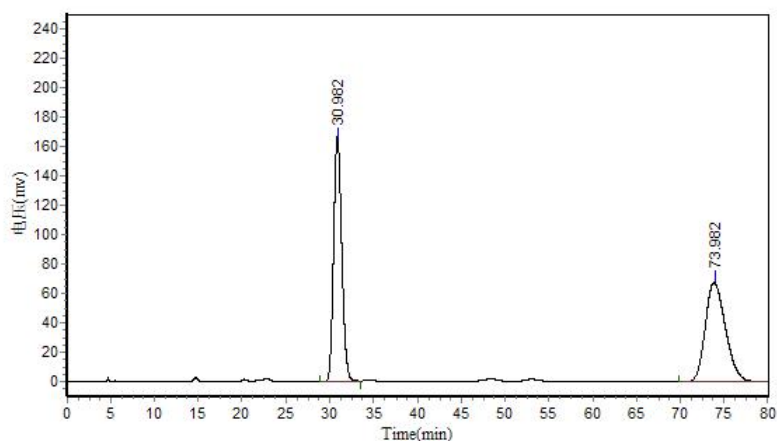
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.932	347971.406	14650066.000	98.8620
2		25.565	3074.563	168631.078	1.1380
Total			351045.969	14818697.078	100.0000



^1H NMR (300 MHz, CDCl_3): δ 2.32 (s, 3H), 5.11 (d, $J = 7.2$ Hz, 1H), 5.41 (s, 2H), 5.73 (d, $J = 7.2$ Hz, 1H), 7.01-7.50 (m, 16H), 8.08 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.42, 54.16, 68.92, 115.42, 119.67, 120.52, 121.94, 123.28, 124.46, 125.23, 127.08, 127.82, 128.59, 128.83, 128.89, 128.98, 129.24, 131.71, 134.91, 135.91, 137.11, 137.96, 143.48, 150.50; HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{24}\text{BrN}_2\text{O}_4\text{S}_1$: 587.0646;

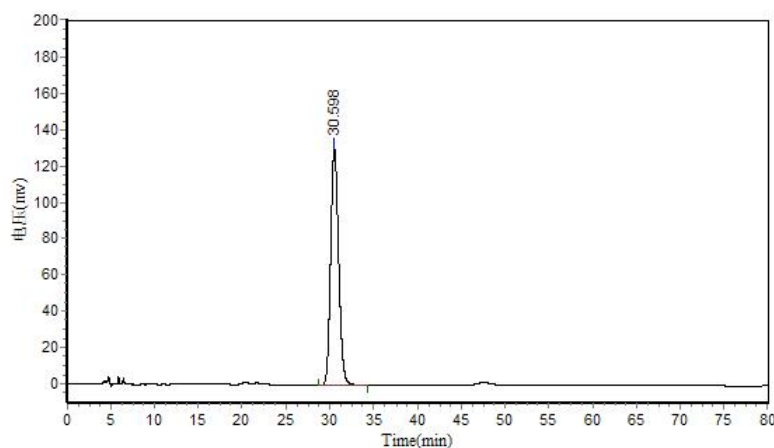
Found: 587.0669.

HPLC: >99% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 60:40; flow = 0.7 mL/min; Retention time: t (maj) = 31.0 min, t (min) = 74.0 min.



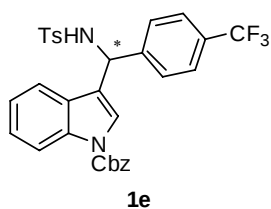
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.982	166246.109	10835320.000	49.9775
2		73.982	67597.539	10845085.000	50.0225
Total			233843.648	21680405.000	100.0000



Results

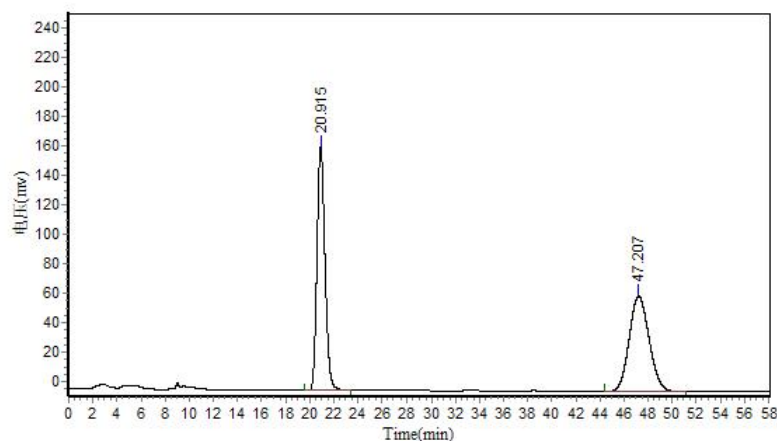
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.598	129631.055	8243733.000	100.0000
Total			129631.055	8243733.000	100.0000



^1H NMR (300 MHz, CDCl_3): δ 2.29 (s, 3H), 5.26 (d, $J = 7.5$ Hz, 1H), 5.40 (s, 2H), 5.84 (d, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 7.15 (m, 3H), 7.24-7.33 (m, 3H), 7.39-7.48 (m, 8H), 8.08 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 20.65, 53.23, 68.44, 114.58, 119.89, 121.13, 122.90, 123.57, 124.85, 125.05, 126.37, 127.88, 127.98, 128.39, 128.51, 128.58, 128.62, 128.82, 134.94, 135.24, 137.97, 142.15, 144.41,

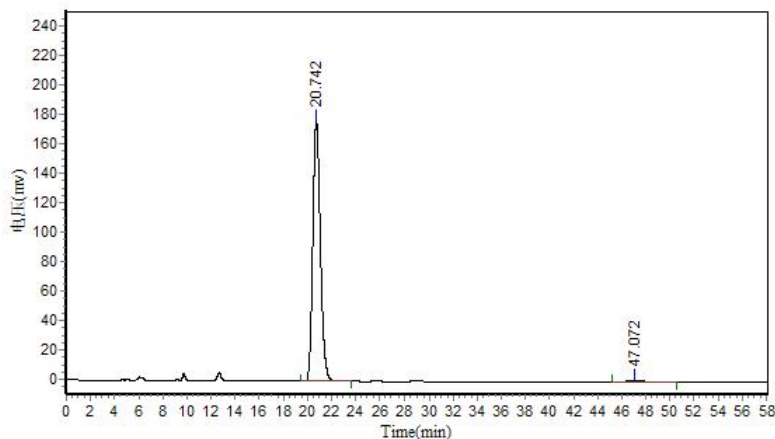
149.92; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_4\text{S}_1$: 577.1381; Found: 577.1402.

HPLC: 99% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; n -hexane / i -propanol = 60:40; flow = 0.7 mL/min; Retention time: t (maj) = 20.9 min, t (min) = 47.3 min.



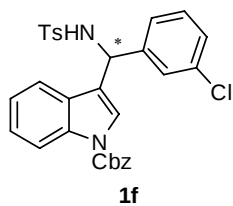
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.915	165654.313	7671645.500	50.5251
2		47.207	64943.180	7512181.500	49.4749
Total			230597.492	15183827.000	100.0000



Results

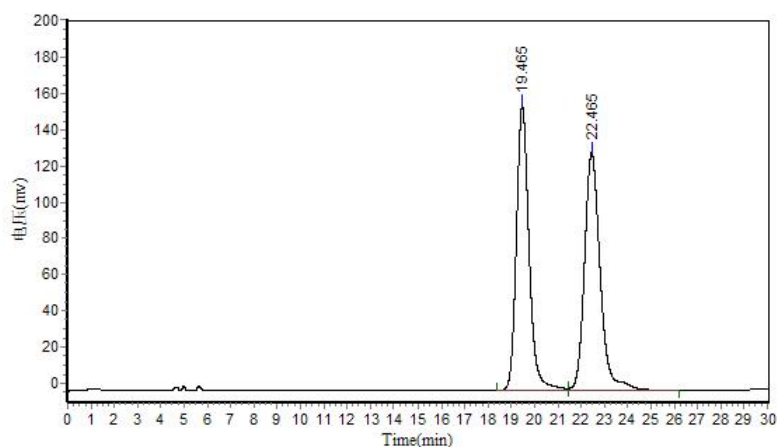
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.742	177262.547	7757339.000	99.4303
2		47.072	430.926	44445.137	0.5697
Total			177693.473	7801784.137	100.0000



^1H NMR (300 MHz, CDCl_3): δ 2.32 (s, 3H), 5.16 (d, $J = 7.8$ Hz, 1H), 5.41 (s, 2H), 5.74 (d, $J = 7.8$ Hz, 1H), 7.02-7.51 (m, 16H), 8.08 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.41, 54.21, 68.93, 115.42, 119.65, 120.51, 123.30, 124.49, 125.23, 125.41, 127.07, 127.40, 127.83, 128.06, 128.57, 128.82, 128.88, 129.27, 129.90, 134.54, 134.91, 135.90, 137.05, 140.90, 143.51, 150.51; HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{24}\text{Cl}_1\text{N}_2\text{O}_4\text{S}_1$:

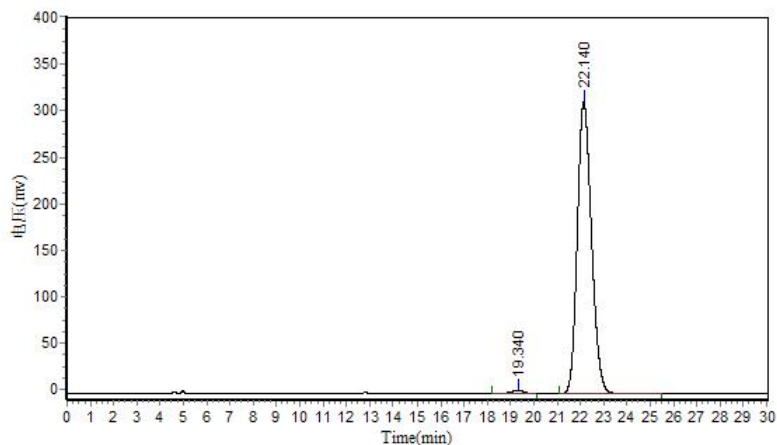
543.1151; Found: 543.1177.

HPLC: 98%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =70:30; flow = 0.7 mL/min; Retention time: t (min) = 19.3 min, t (maj) = 22.1 min.



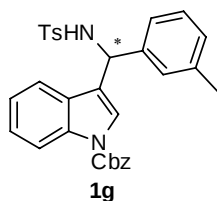
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.465	156453.000	5938213.000	49.1331
2		22.465	130918.695	6147756.000	50.8669
Total			287371.695	12085969.000	100.0000



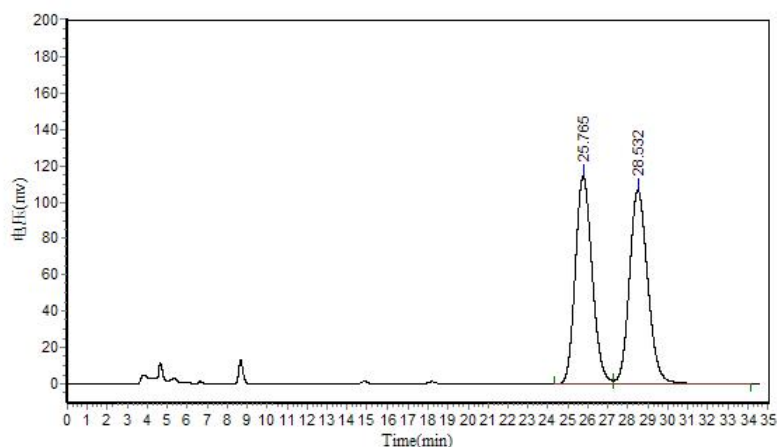
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.340	3793.413	154008.484	1.1471
2		22.140	313470.563	13271913.000	98.8529
Total			317263.975	13425921.484	100.0000



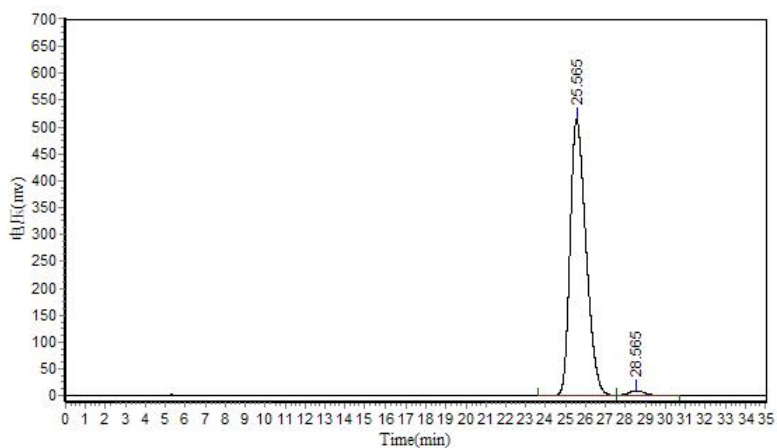
^1H NMR (300 MHz, CDCl_3): δ 2.20 (s, 3H), 2.30 (s, 3H), 5.05 (d, $J = 7.8$ Hz, 1H), 5.41 (s, 2H), 5.73 (d, $J = 7.8$ Hz, 1H), 6.90-7.02 (m, 5H) 7.09-7.13 (m, 2H), 7.20-7.29 (m, 3H), 7.40-7.51 (m, 6H), 8.08 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.25, 21.36, 54.70, 68.74, 115.22, 119.82, 121.14, 123.05, 124.17, 124.91, 127.05, 127.80, 128.10, 128.49, 128.54, 128.61, 128.76, 129.03, 134.92, 137.13, 138.24, 138.62, 143.09, 150.55; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ 1: 523.1697; Found: 523.1699.

HPLC: 96% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 60:40; flow = 0.7 mL/min; Retention time: t (maj) = 25.6 min, t (min) = 28.6 min.



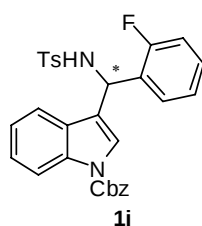
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.765	114512.195	6729014.000	49.4471
2		28.532	106968.445	6879497.500	50.5529
Total			221480.641	13608511.500	100.0000



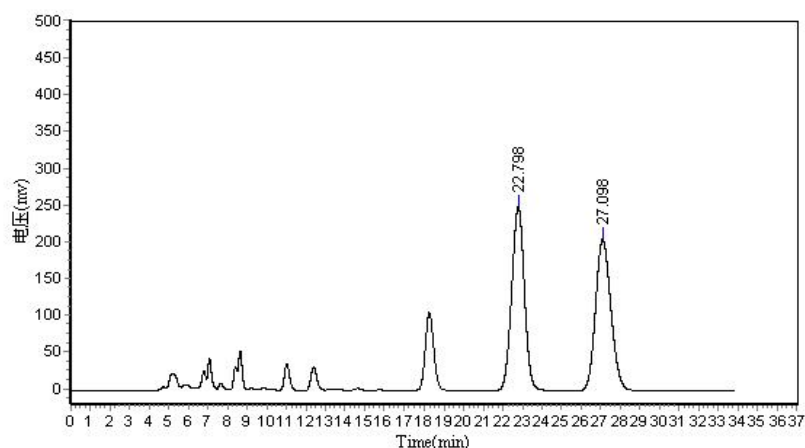
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.565	514144.375	28520058.000	98.0285
2		28.565	9367.223	573566.250	1.9714
Total			523511.598	29093624.250	100.0000

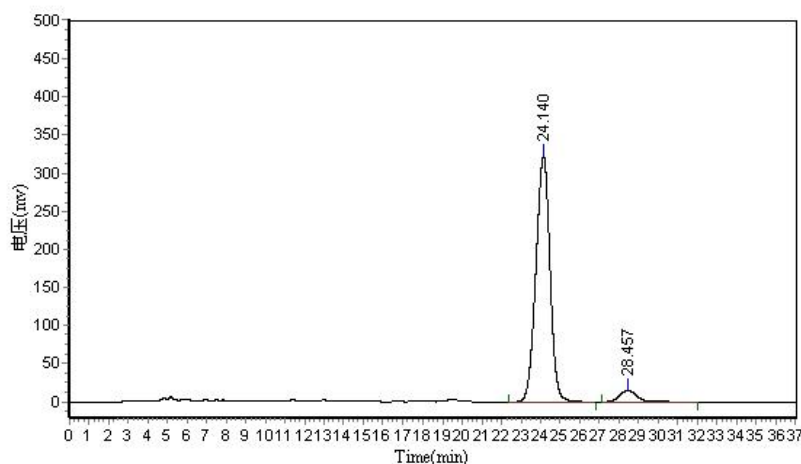


^1H NMR (300 MHz, CDCl_3): δ 2.31 (s, 3H), 5.39 (s, 2H), 6.01 (d, $J = 8.4$ Hz, 1H), 6.87 (t, $J = 8.4$ Hz, 1H), 6.92-7.04 (m, 3H), 7.15-7.21 (m, 3H), 7.24-7.32 (m, 2H), 7.38-7.46 (m, 6H), 7.55 (d, $J = 7.8$ Hz, 2H), 8.08 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.64, 53.90, 68.40, 114.54, 119.90, 121.63, 122.83, 123.56, 124.72, 125.24, 125.83, 125.99, 126.15, 126.31, 127.37, 127.73, 127.93, 128.13, 128.41, 128.58, 128.65, 128.72, 132.11, 132.46, 134.99, 135.29, 137.12, 138.20, 142.02, 149.98; HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{25}\text{F}_1\text{N}_2\text{Na}_1\text{O}_4\text{S}_1$: 551.1411; Found: 551.1430.

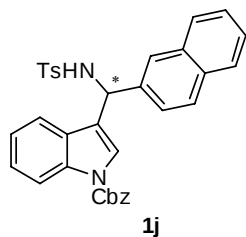
HPLC: 89% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 70:30; flow = 0.7 mL/min; Retention time: $t(\text{maj}) = 24.1$ min, $t(\text{min}) = 28.5$ min.



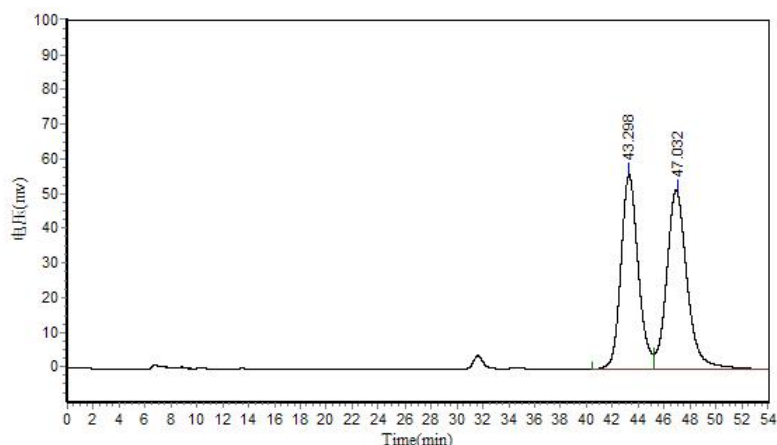
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.798	250684.078	11414850.000	50.1231
2		27.098	206242.453	11358780.000	49.8769
Total			456926.531	22773630.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.140	322833.000	16123127.000	94.4745
2		28.457	15387.827	942991.188	5.5255
Total			338220.827	17066118.188	100.0000

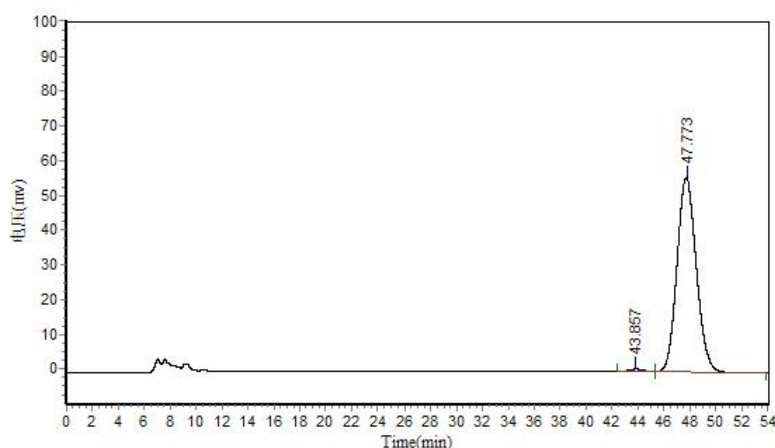


^1H NMR (300 MHz, CDCl_3): δ 2.18 (s, 3H), 5.13 (d, $J = 7.8$ Hz, 1H), 5.41 (s, 2H), 5.94 (d, $J = 7.8$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 2H) 7.09 (m, 1H), 7.24-7.30 (m, 5H), 7.39-7.50 (m, 8H), 7.56 (s, 1H), 7.63 (m, 2H), 7.68 (d, $J = 8.7$ Hz, 1H), 7.76 (m, 1H), 8.10 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 20.64, 53.90, 68.40, 114.54, 119.90, 121.63, 122.83, 123.56, 124.72, 125.24, 125.83, 125.99, 126.15, 126.31, 127.37, 127.73, 127.93, 128.13, 128.41, 128.58, 128.65, 128.72, 132.11, 132.46, 134.99, 135.29, 137.12, 138.20, 142.02, 149.98; HRMS (ESI): m/z Calcd for $\text{C}_{34}\text{H}_{27}\text{N}_2\text{O}_4\text{S}_1$: 559.1697; Found: 559.1720 .
HPLC: 98%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (min) = 43.8 min, t (maj) = 47.7 min.



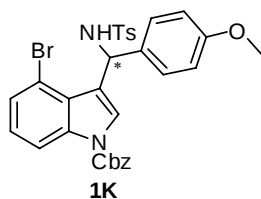
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.298	56083.387	5212191.500	47.6221
2		47.032	51683.961	5732715.500	52.3779
Total			107767.348	10944907.000	100.0000



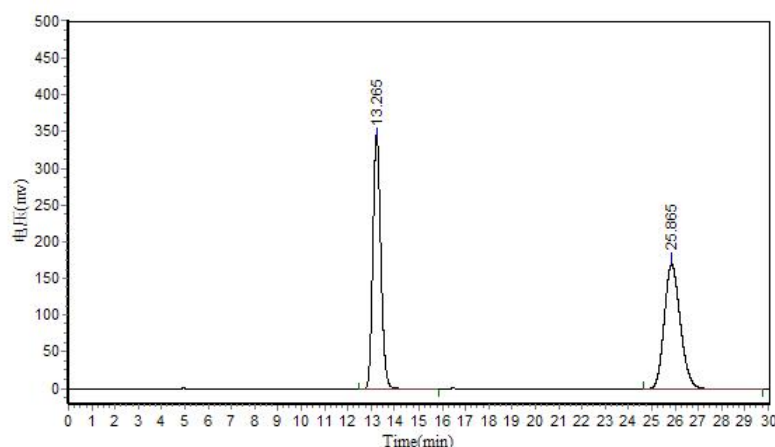
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.857	835.138	75263.742	1.2770
2		47.773	56065.949	5818677.000	98.7230
Total			56901.088	5893940.742	100.0000



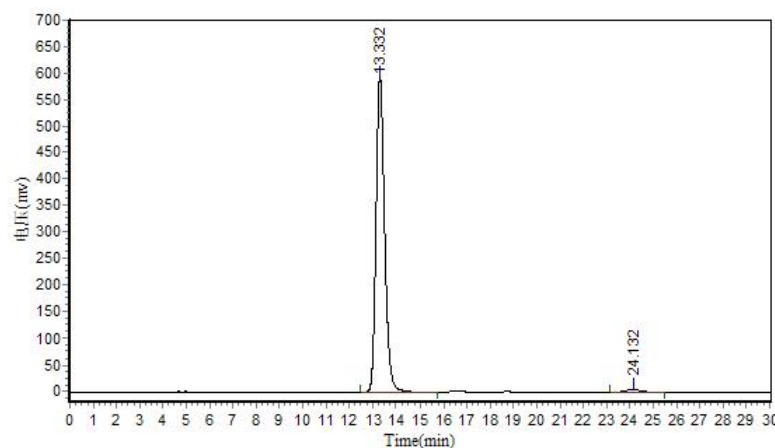
^1H NMR (300 MHz, CDCl_3): δ 1.57 (s, 3H), 2.23 (br, 1H), 3.74 (s, 3H), 5.44 (AB, $J_1 = 18.3$ Hz, $J_2 = 6.3$ Hz, 2H), 6.23 (br, 1H), 6.73 (d, $J = 8.1$ Hz, 2H), 6.99 (m, 2H), 7.10 (t, $J = 8.1$ Hz, 1H), 7.28 (d, $J = 8.1$ Hz, 1H), 7.41-7.56 (m, 7H), 8.14 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.27, 53.75, 55.19, 69.12, 113.81, 114.36, 125.67, 126.99, 127.13, 127.76, 128.78, 128.85, 129.01, 132.05, 134.68, 137.20, 149.90, 159.12; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{27}\text{Br}_1\text{N}_2\text{Na}_1\text{O}_5\text{S}_1$: 641.0716; Found: 641.0732.

HPLC: 97%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 60:40; flow = 0.7 mL/min; Retention time: t (maj) = 13.3 min, t (min) = 24.1 min.



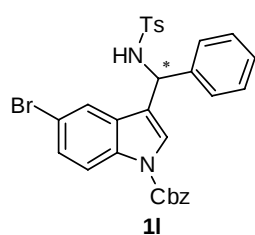
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.265	344728.844	8301529.000	50.1632
2		25.865	169760.016	8247517.500	49.8368
Total			514488.859	16549046.500	100.0000



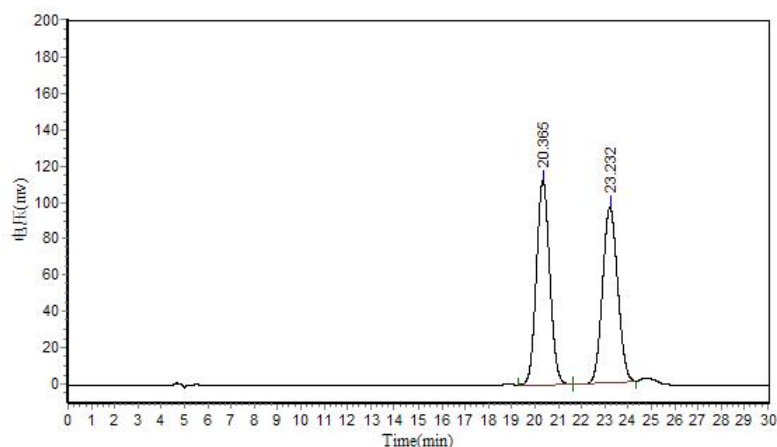
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.332	595568.313	15215435.000	98.5323
2		24.132	5067.792	226645.453	1.4677
Total			600636.104	15442080.453	100.0000

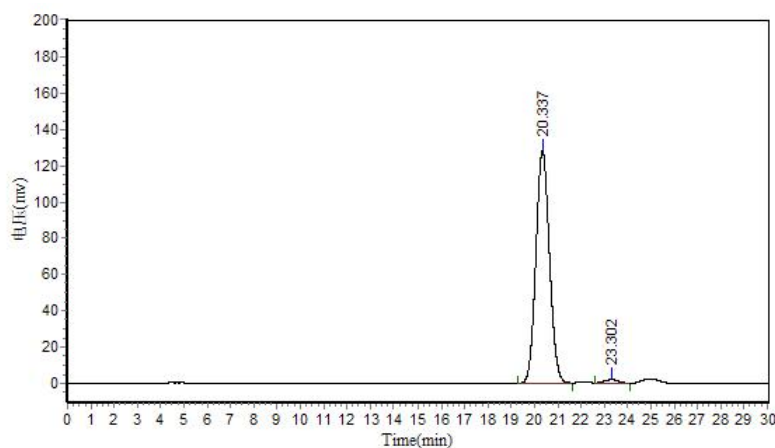


^1H NMR (300 MHz, CDCl_3): δ 2.32 (s, 3H), 5.06 (d, $J = 6.9$ Hz, 1H), 5.40 (s, 2H), 5.68 (d, $J = 6.9$ Hz, 1H), 7.05 (d, $J = 8.1$ Hz, 1H), 7.14-7.26 (m, 6H), 7.30 (s, 1H), 7.34 (d, 1H), 7.39-7.46 (m, 4H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.47, 54.49, 69.12, 116.57, 116.74, 120.52, 122.36, 125.65, 127.11, 127.91, 128.18, 128.66, 128.83, 128.85, 128.97, 129.33, 129.87, 134.62, 134.73, 137.02, 138.72, 143.44, 150.26; HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{24}\text{Br}_1\text{N}_2\text{O}_4\text{S}_1$: 587.0646; Found: 587.0645.

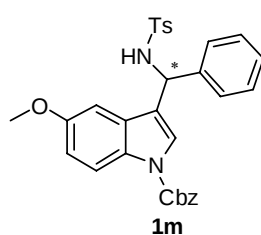
HPLC: 98%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 20.4 min, t (min) = 23.2 min.



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.365	112565.805	4531406.000	49.7488
2		23.232	98128.242	4577173.500	50.2512
Total			210694.047	9108579.500	100.0000

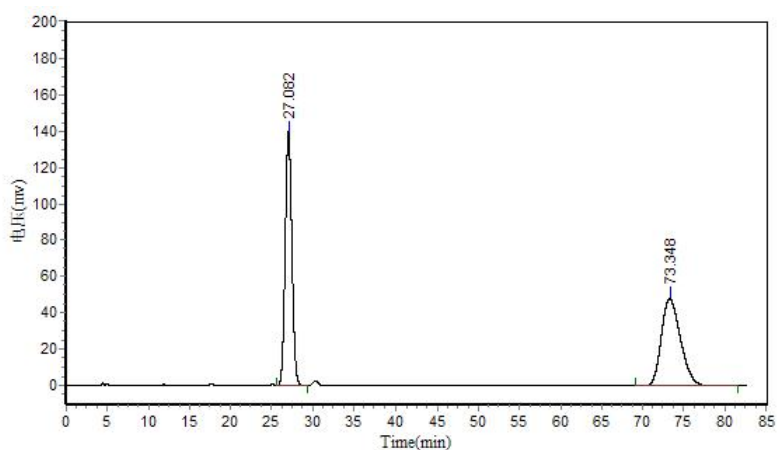


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.337	128283.563	5204307.000	98.1623
2		23.302	2122.953	97430.266	1.8377
Total			130406.515	5301737.266	100.0000



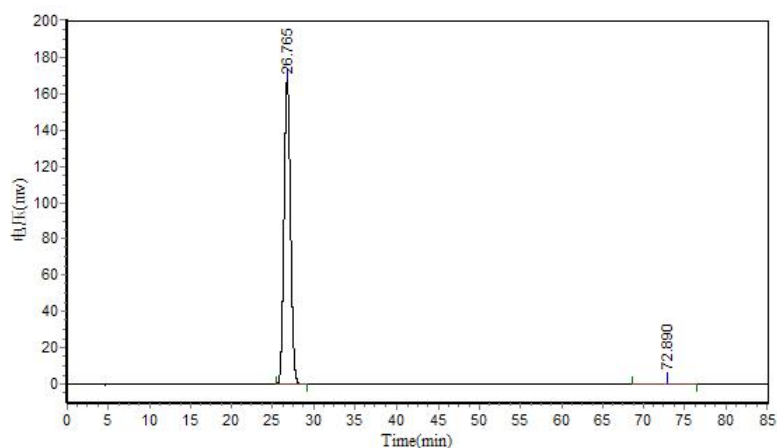
^1H NMR (300 MHz, CDCl_3): δ 2.29 (s, 3H), 3.72 (s, 3H), 5.16 (d, J = 7.8 Hz, 1H), 5.38 (s, 2H), 5.75 (d, J = 7.8 Hz, 1H), 6.73 (s, 1H), 6.87 (d, J = 8.7 Hz, 1H), 6.99 (d, J = 8.1 Hz, 2H), 7.16-7.26 (m, 6H), 7.37-7.46 (m, 6H), 7.50 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.38, 54.70, 55.64, 68.73, 102.63, 113.68, 116.04, 120.95, 125.03, 126.45, 127.06, 127.17, 127.88, 128.52, 128.62, 128.79, 129.07, 129.14, 130.49, 135.06, 137.30, 138.85, 143.19, 150.51, 156.10; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_5\text{S}_1$: 539.1646; Found: 539.1663.

HPLC: 98%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 27.1 min, t (min) = 73.3 min.



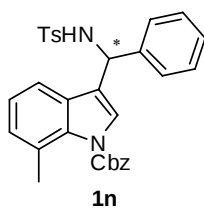
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.082	139448.828	7917050.000	50.2751
2		73.348	48107.617	7830419.000	49.7249
Total			187556.445	15747469.000	100.0000



Results

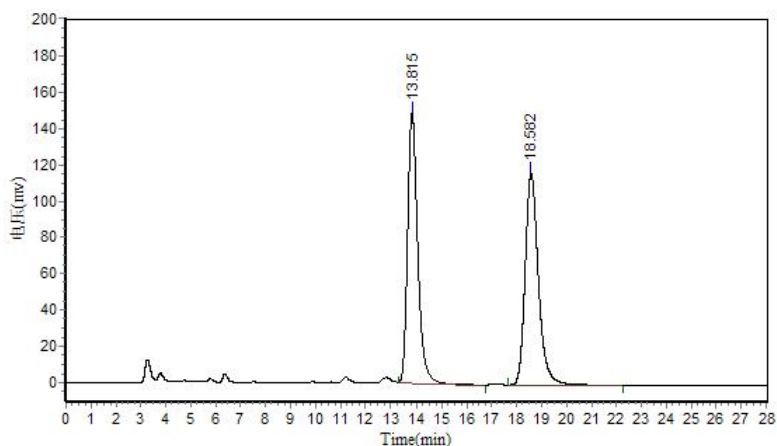
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.765	168192.875	9276557.000	99.0048
2		72.890	615.182	93250.758	0.9952
Total			168808.057	9369807.758	100.0000



^1H NMR (300 MHz, CDCl_3): δ 2.30 (s, 3H), 2.55 (s, 3H), 5.13 (d, $J = 7.8$ Hz, 1H), 5.34 (s, 2H), 5.77 (d, $J = 7.8$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 2H) 6.99-7.08 (m, 3H), 7.15-7.26 (m, 6H), 7.36-7.50 (m, 4H), 7.48 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.33, 22.13, 54.55, 68.83, 117.34, 120.57, 123.52, 125.58, 126.63, 127.01, 127.16, 127.78, 128.40, 128.52, 128.72, 129.04, 129.44, 134.94, 135.38, 137.19, 138.93, 143.06, 150.33; HRMS (ESI):

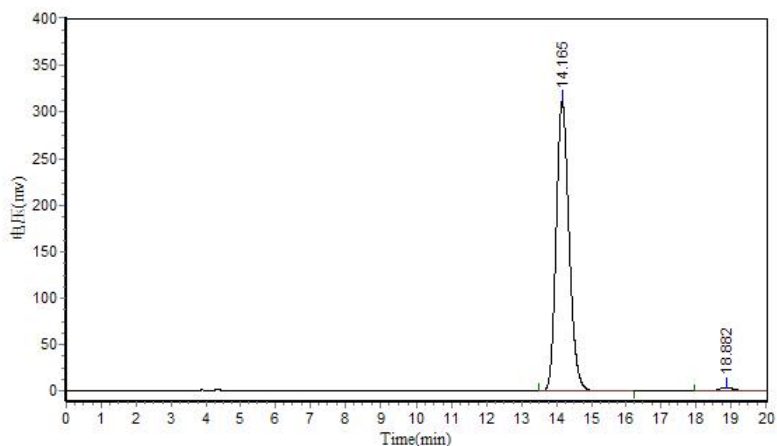
m/z Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2 \text{Na}_1\text{O}_4\text{S}_1$: 547.1662; Found: 547.1654.

HPLC: 97%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 14.2 min, t (min) = 18.9 min.



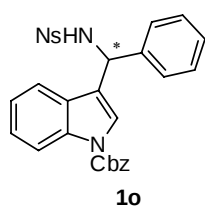
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.815	148883.781	4211180.000	49.5842
2		18.582	116214.805	4281812.000	50.4158
Total			265098.586	8492992.000	100.0000



Results

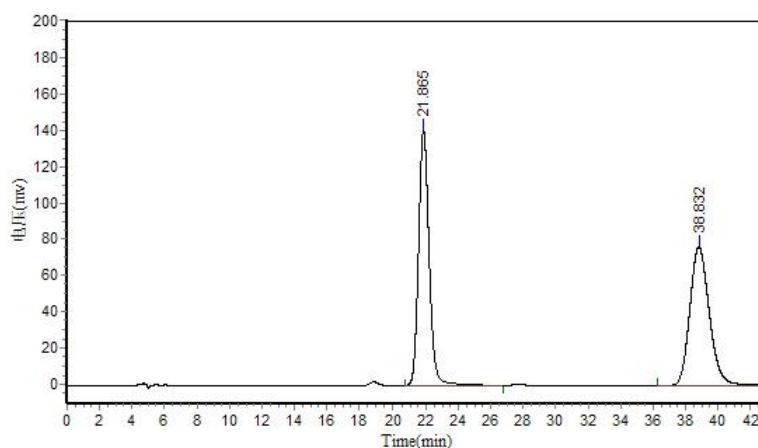
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.165	311396.781	7988925.500	98.3152
2		18.882	4071.000	136906.500	1.6848
Total			315467.781	8125832.000	100.0000



^1H NMR (300 MHz, CDCl_3): δ 5.40 (s, 2H), 5.52 (d, $J = 7.8$ Hz, 1H), 5.93 (d, $J = 7.8$ Hz, 1H), 7.15-7.32 (m, 7H), 7.37-7.47 (m, 6H), 7.66 (d, $J = 8.7$ Hz, 2H), 7.20 (d, $J = 8.7$ Hz, 2H), 8.02 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 53.91, 68.47, 114.51, 120.03, 121.44, 122.87, 123.58, 124.83, 127.17, 127.42, 127.86, 128.24, 128.33, 128.57, 128.63, 134.91, 135.20, 139.16, 146.55, 148.79, 149.91; HRMS (ESI): m/z Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_3\text{O}_6\text{S}_1$:

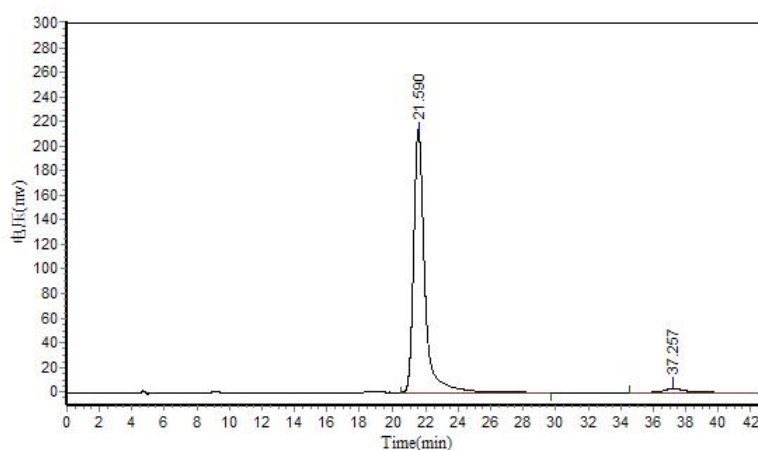
540.1235; Found: 540.1221 .

HPLC: 95%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 21.6 min, t (min) = 37.9 min.



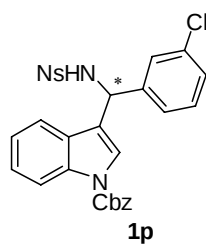
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.865	140268.797	6381585.500	49.7041
2		38.832	76476.016	6457556.500	50.2959
Total			216744.813	12839142.000	100.0000



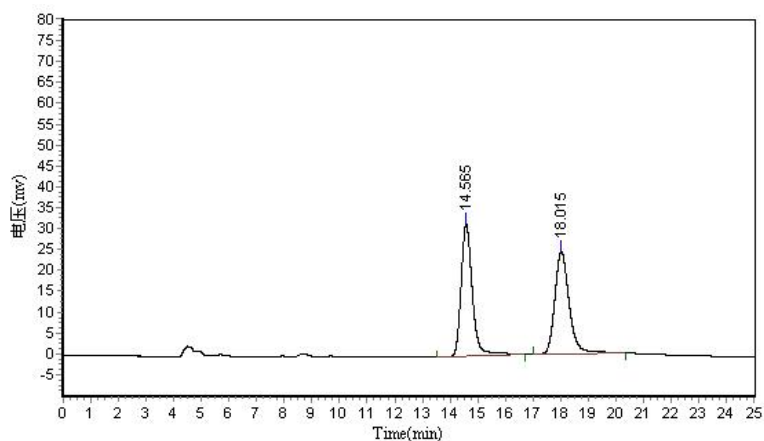
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.590	212645.813	10174735.000	97.3775
2		37.257	3199.221	274022.000	2.6225
Total			215845.034	10448757.000	100.0000

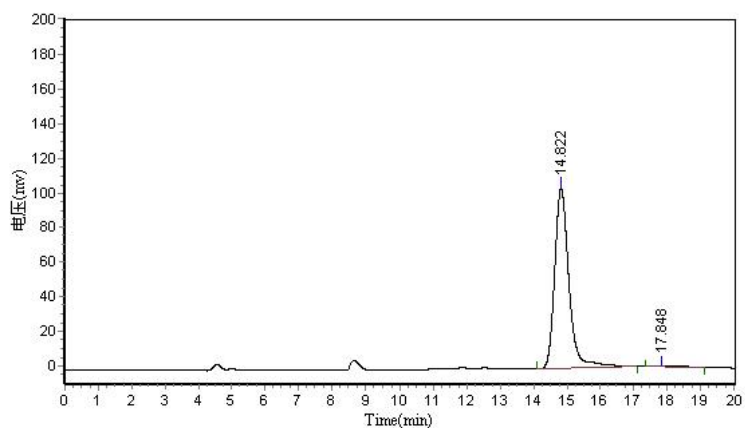


^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): δ 5.42 (s, 2H), 5.90 (d, $J = 9.3$ Hz, 1H), 7.14-7.30 (m, 6H), 7.33-7.50 (m, 7H), 7.75 (d, $J = 8.7$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 8.7$ Hz, 2H), 9.17 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 53.28, 68.53, 114.59, 119.99, 120.89, 122.97, 123.69, 124.97, 125.99, 126.98, 127.40, 127.67, 127.90, 128.36, 128.60, 128.64, 130.27, 132.91, 134.92, 135.20, 141.51, 146.32, 148.92, 149.91.

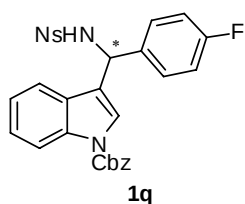
HPLC: 97%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 14.8 min, t (min) = 17.9 min.



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.565	31538.797	890769.000	50.2311
2		18.015	24421.012	882572.813	49.7689
Total			55959.809	1773341.813	100.0000

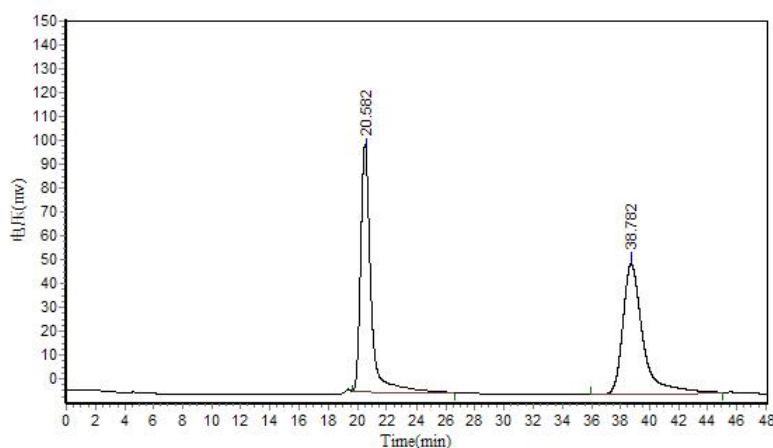


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.822	103816.594	3089683.750	98.6260
2		17.848	598.983	43043.301	1.3740
Total			104415.576	3132727.051	100.0000



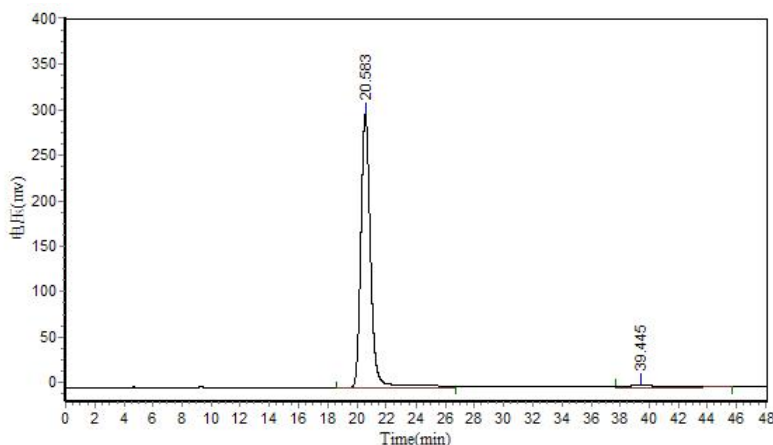
^1H NMR (300 MHz, CDCl_3): δ 5.41 (s, 2H), 5.43 (d, $J = 7.5$ Hz, 1H), 5.92 (d, $J = 7.5$ Hz, 1H), 6.93 (t, $J = 7.8$ Hz, 2H), 7.14-7.33 (m, 5H), 7.40-7.48 (m, 5H), 7.69 (d, $J = 9.0$ Hz, 2H), 7.97 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 53.18, 68.49, 114.54, 114.91, 115.13, 120.02, 121.32, 122.90, 123.66, 124.89, 127.76, 127.89, 128.35, 128.59, 128.64, 129.23, 129.32, 134.93, 135.20, 135.48, 146.48, 148.86, 149.90, 160.11, 162.53; HRMS (ESI): m/z Calcd for $\text{C}_{29}\text{H}_{21}\text{F}_1\text{N}_3\text{O}_6\text{S}_1$: 558.1141; Found: 558.1163.

HPLC: 95%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 20.6 min, t (min) = 39.4 min.



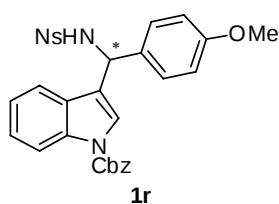
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.582	103813.875	5437901.500	50.4832
2		38.782	54643.148	5333802.000	49.5168
Total			158457.023	10771703.500	100.0000



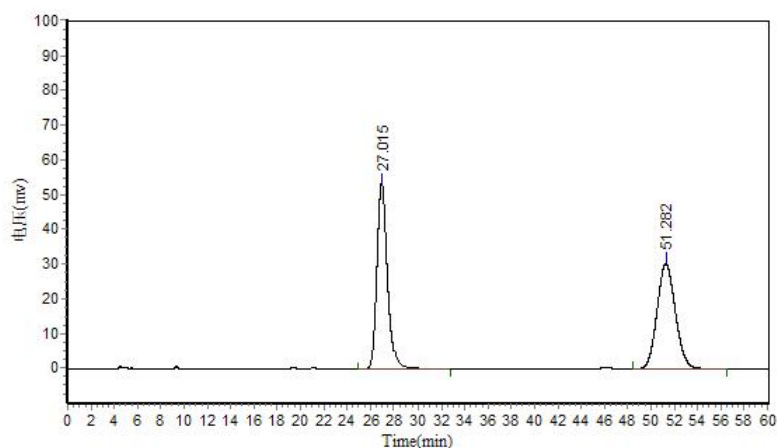
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.583	301426.969	14387653.000	97.4997
2		39.445	2704.162	368960.250	2.5003
Total			304131.130	14756613.250	100.0000

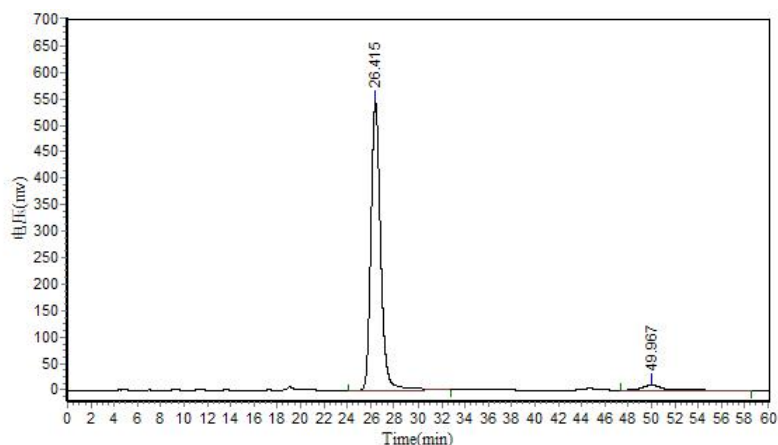


^1H NMR (300 MHz, CDCl_3): δ 3.73 (s, 3H), 5.44 (s, 2H), 5.47 (d, J = 7.8 Hz, 1H), 5.86 (d, J = 7.8 Hz, 1H), 6.70 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 7.13-7.46 (m, 9H), 7.66 (d, J = 7.5 Hz, 2H), 7.93 (d, J = 7.5 Hz, 2H), 8.02 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 53.58, 55.00, 68.48, 113.57, 114.54, 120.11, 121.76, 122.88, 123.41, 123.60, 124.84, 127.91, 128.37, 128.52, 128.61, 128.66, 131.12, 134.98, 135.25, 146.67, 148.79, 149.97, 158.54; HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_3\text{O}_7\text{S}_1$: 570.1340; Found: 570.1368.

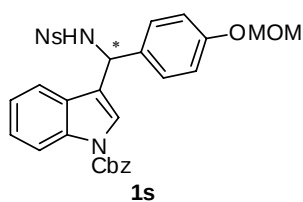
HPLC: 94%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 26.4 min, t (min) = 50.0 min.



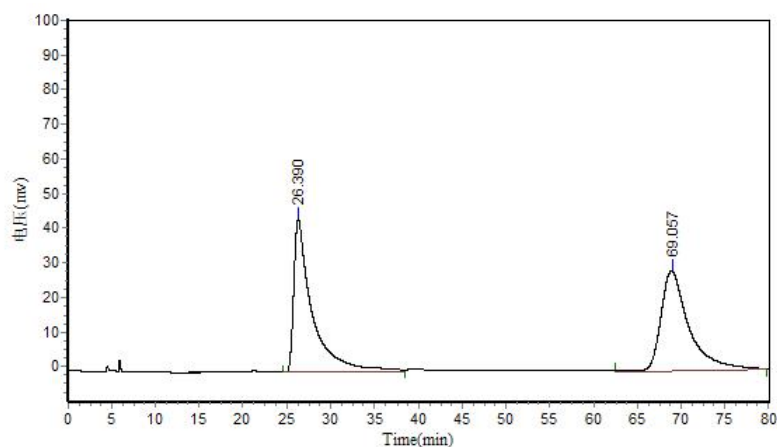
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.015	53416.684	3332644.000	50.0278
2		51.282	30190.563	3328940.000	49.9722
Total			83607.246	6661584.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.415	542736.500	31450546.000	96.8852
2		49.967	9116.074	1011130.750	3.1148
Total			551852.574	32461676.750	100.0000

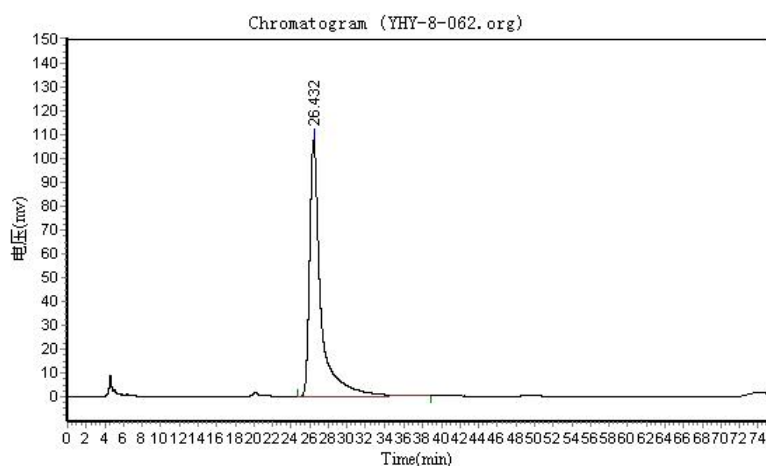


^1H NMR (300 MHz, CDCl_3): δ 3.46 (s, 3H), 5.11 (s, 2H), 5.41 (s, 2H), 5.45 (d, $J = 7.8$ Hz, 1H), 5.88 (d, $J = 7.8$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 7.16-7.45 (m, 9H), 7.68 (d, $J = 8.7$ Hz, 2H), 7.95 (d, $J = 8.7$ Hz, 2H), 8.03 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 54.74, 56.07, 69.12, 94.41, 115.48, 116.44, 119.84, 120.47, 123.36, 123.46, 124.54, 125.39, 127.88, 128.16, 128.53, 128.65, 128.85, 128.94, 129.07, 129.54, 131.12, 134.79, 135.80, 146.07, 149.55, 150.22, 157.27; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{26}\text{N}_3\text{O}_8\text{S}_1$: 600.1446; Found: 600.1435
HPLC: 99%ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol =60:40; flow = 0.7 mL/min; Retention time: t (maj) = 26.3 min, t (min) = 69.1 min



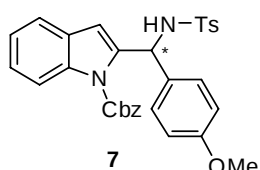
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.390	44149.453	6480526.000	50.9737
2		69.057	28532.068	6232933.000	49.0263
Total			72681.521	12713459.000	100.0000



Results

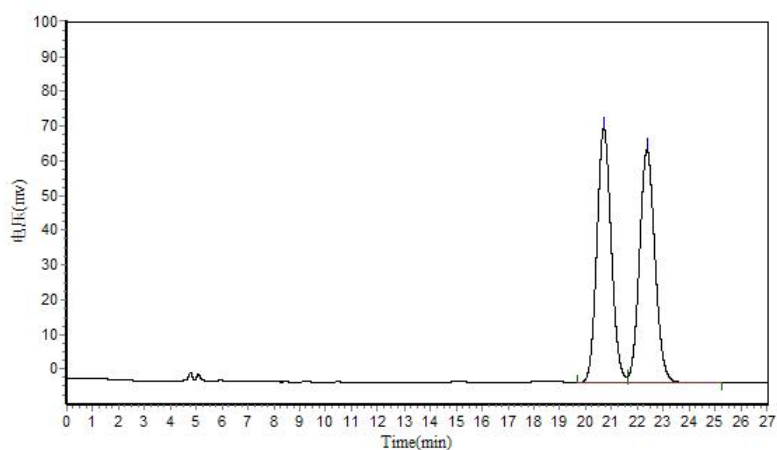
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.432	107439.758	9045296.000	100.0000
Total			107439.758	9045296.000	100.0000



^1H NMR (300 MHz, CDCl_3): δ 2.13 (s, 3H), 3.76 (s, 2H), 5.22 (dd, J = 12 and 8.4 Hz, 2H), 6.09 (d, J = 9.3 Hz, 1H), 6.61 (s, 1H), 6.72 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 7.18-7.24 (m, 2H), 7.30-7.33 (m, 2H), 7.38-7.47 (m, 5H), 7.83 (d, J = 9.3 Hz, 1H);

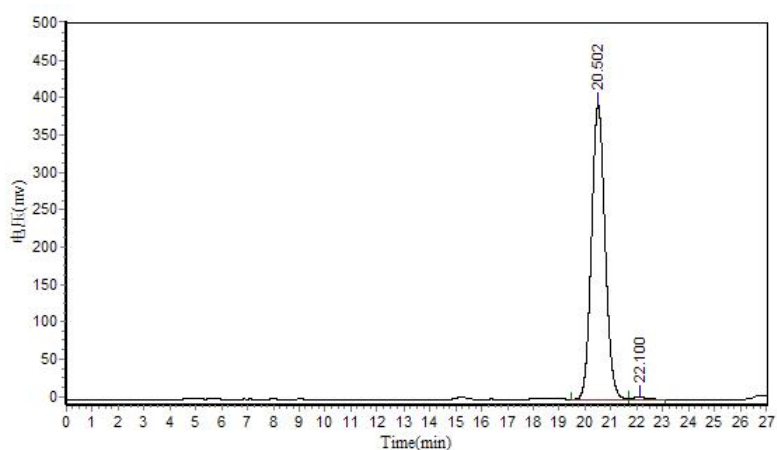
^{13}C NMR (100 MHz, CDCl_3): δ 21.1, 55.1, 56.0, 65.2, 69.0, 113.6, 115.6, 120.7, 123.3, 124.7, 126.6, 126.8, 127.5, 128.3, 128.4, 128.70, 128.75, 128.8, 128.9, 131.1, 134.4, 136.6, 137.3, 142.9, 151.1, 158.7; HRMS (ESI): m/z Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{Na}_1\text{O}_5\text{S}_1$: 563.1611; Found: 568.1878.

HPLC: 98.5% ee. Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 70:30; flow = 0.7 mL/min; Retention time: t (maj) = 20.5 min, t (min) = 22.1 min.



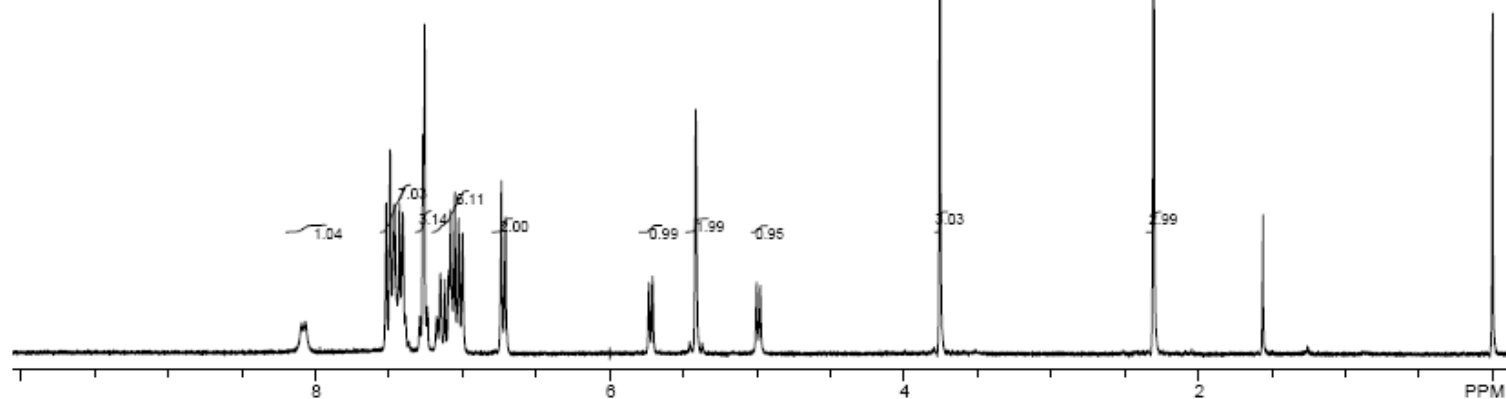
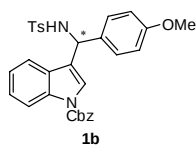
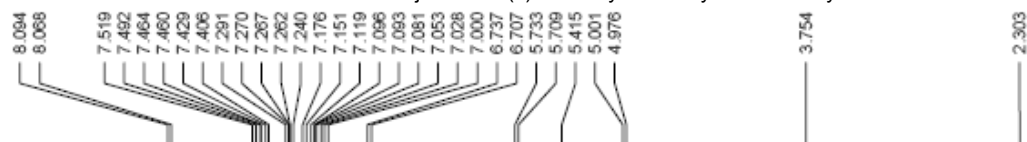
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.707	73276.352	2832710.250	50.2360
2		22.373	67226.531	2806095.000	49.7640
Total			140502.883	5638805.250	100.0000

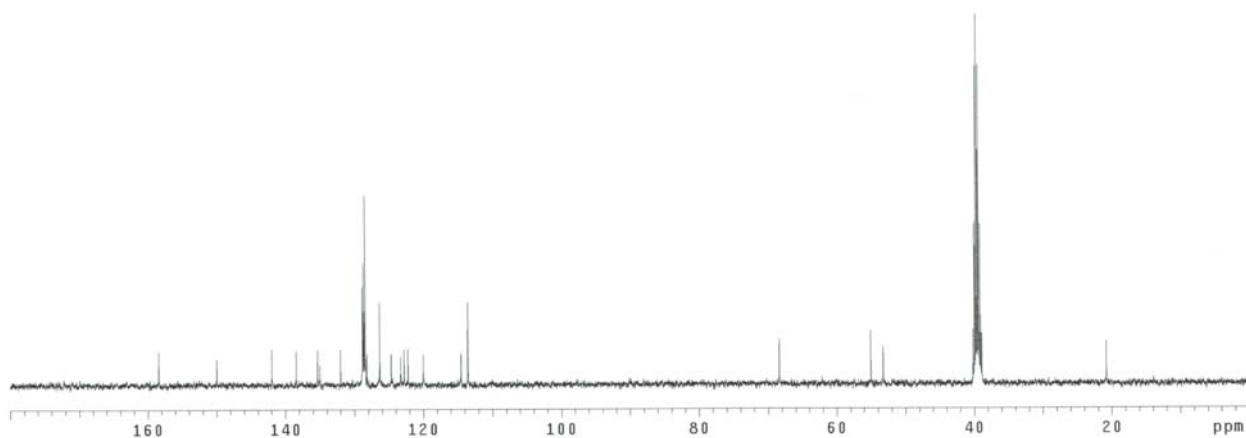
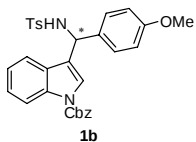


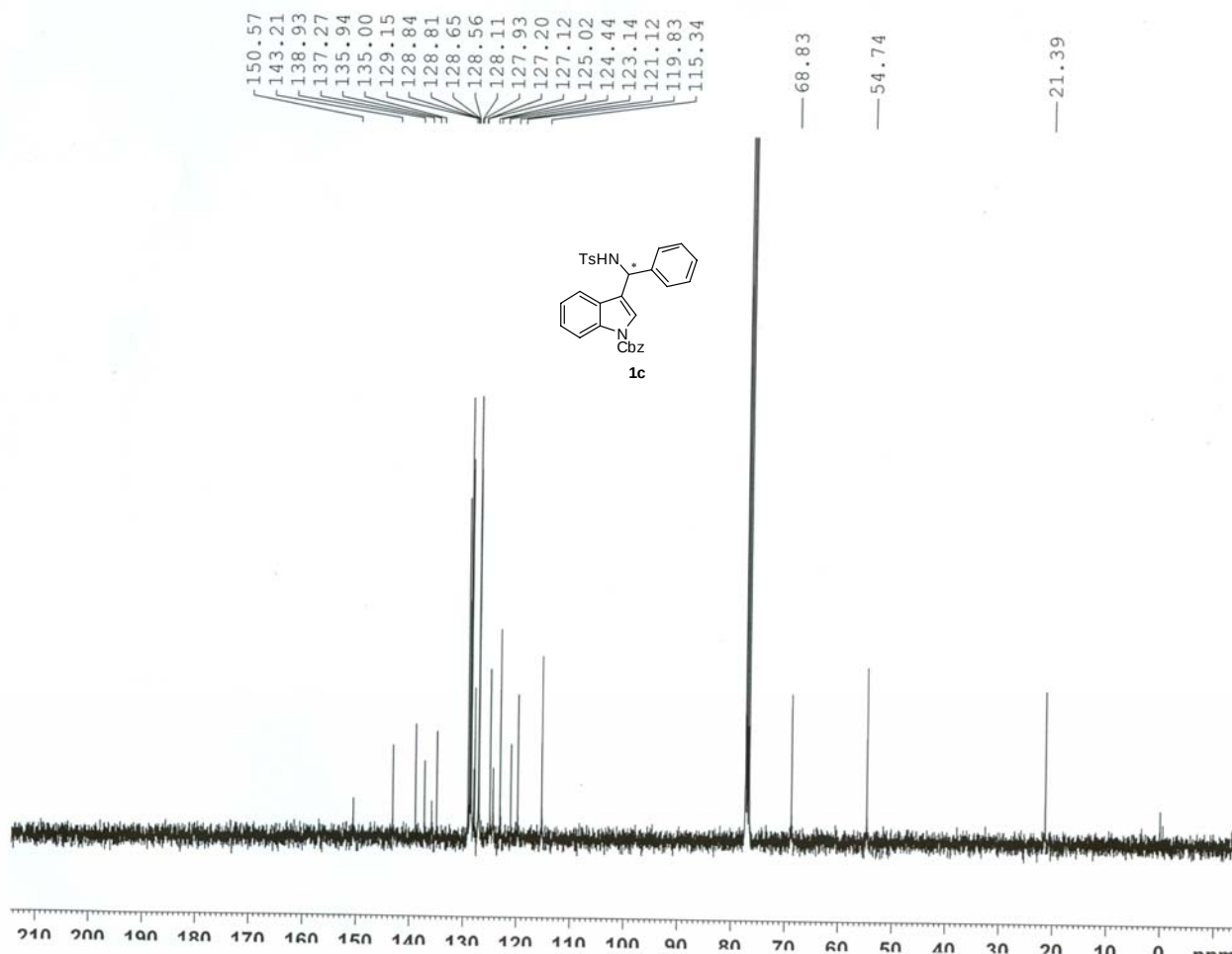
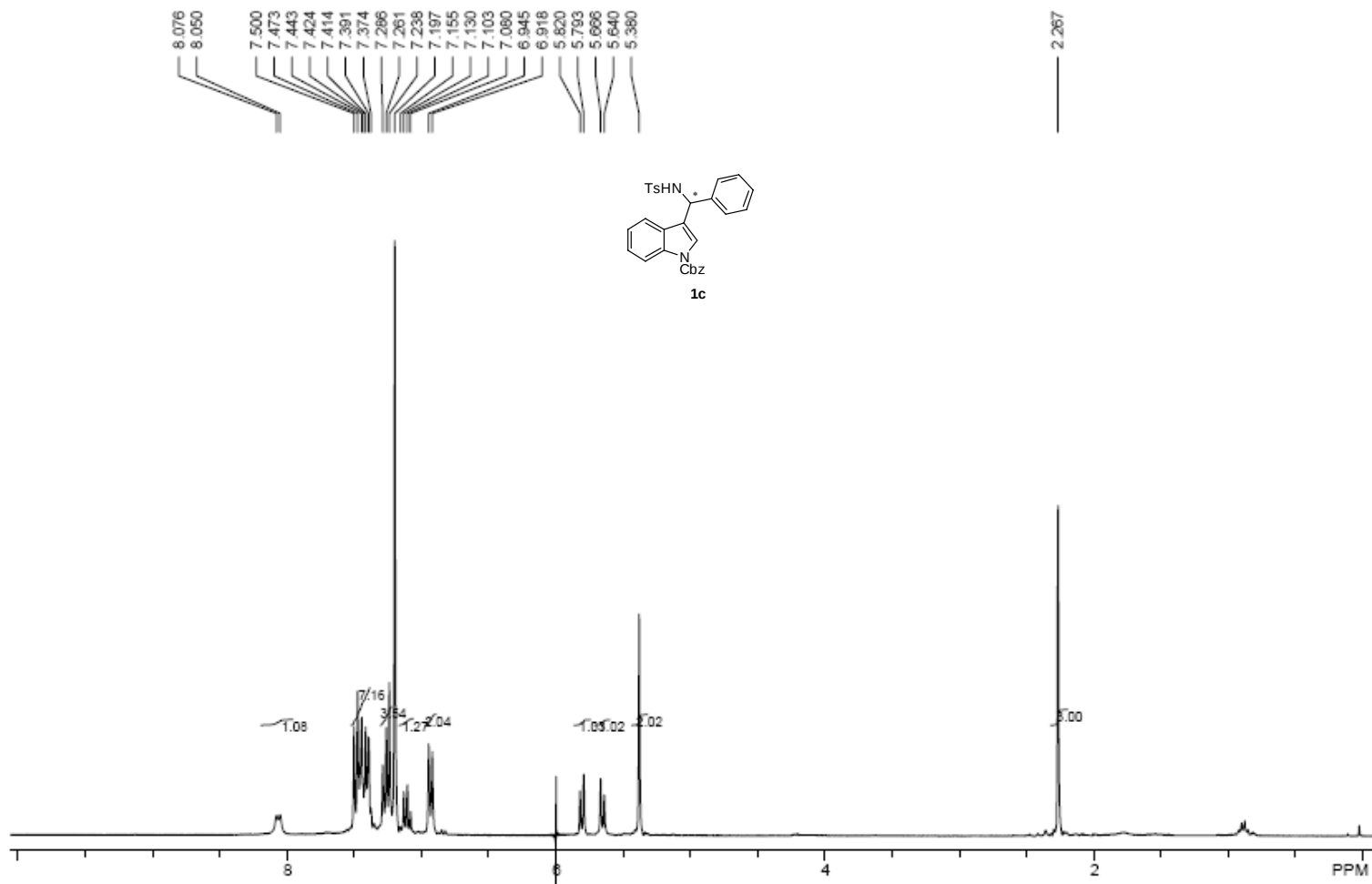
Results

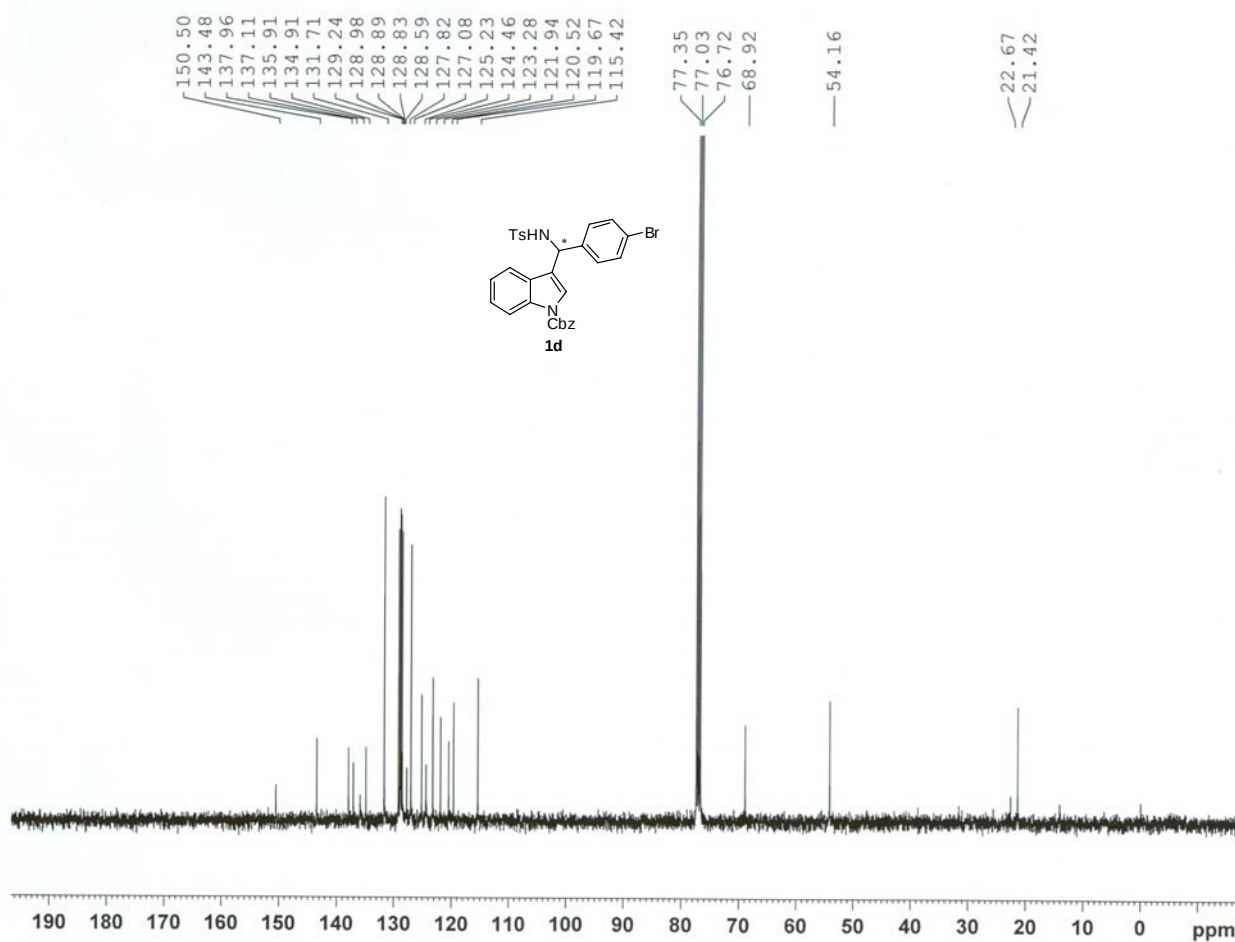
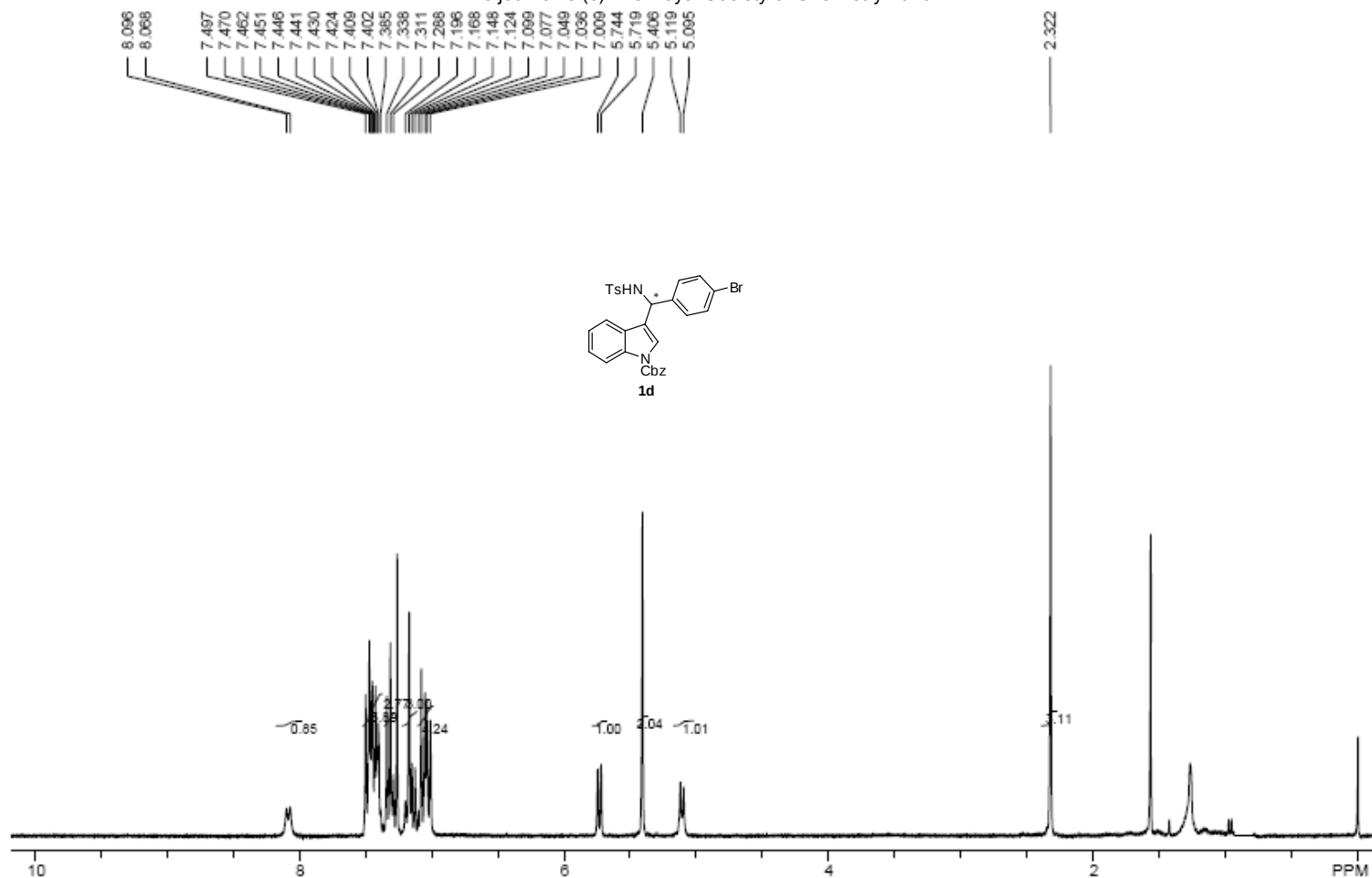
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.502	394046.219	14355149.000	99.2465
2		22.100	2785.628	108991.469	0.7535
Total			396831.847	14464140.469	100.0000

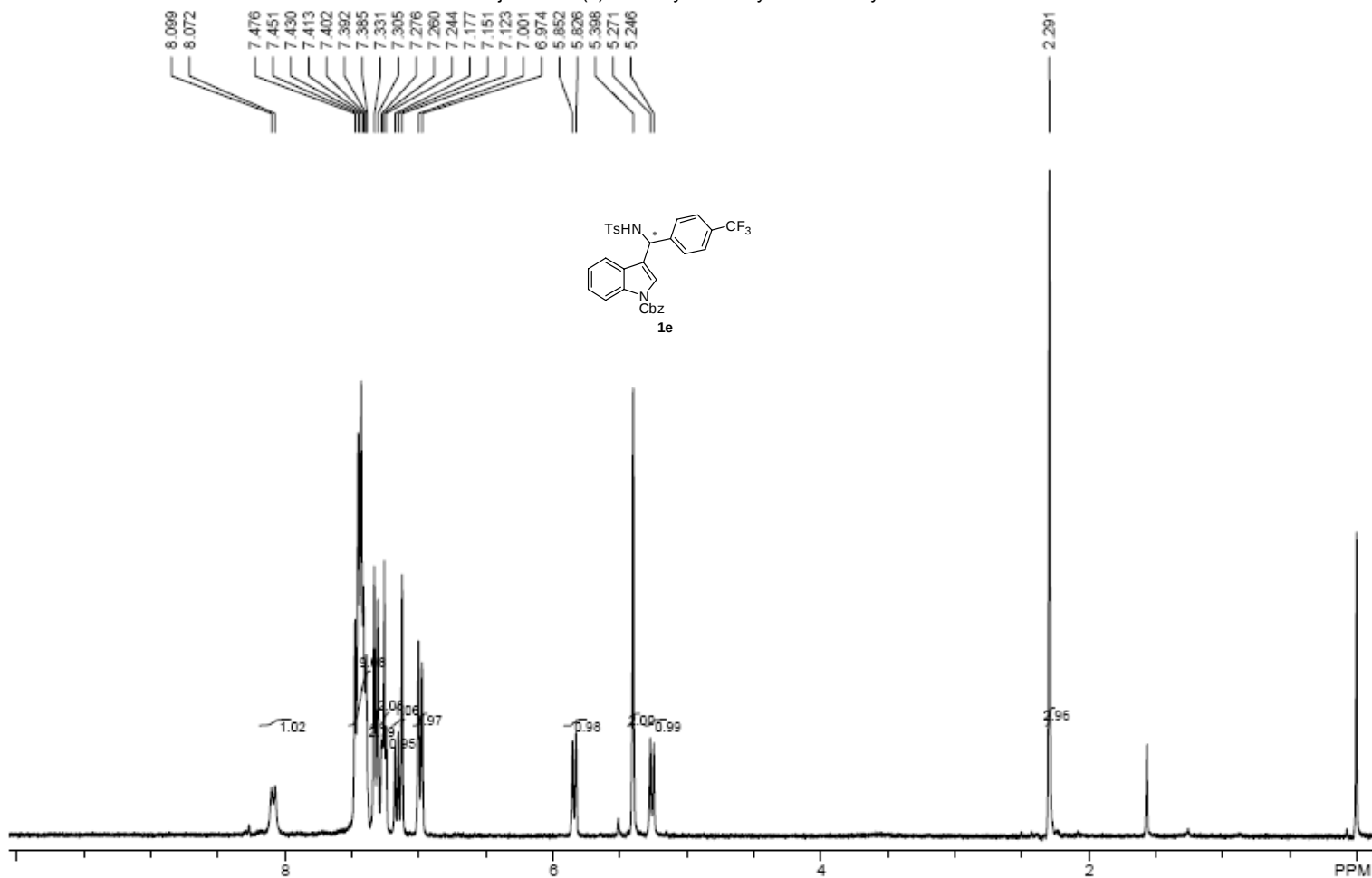


YHY-8-04 DMSO 13C-BB Apr 14 2010

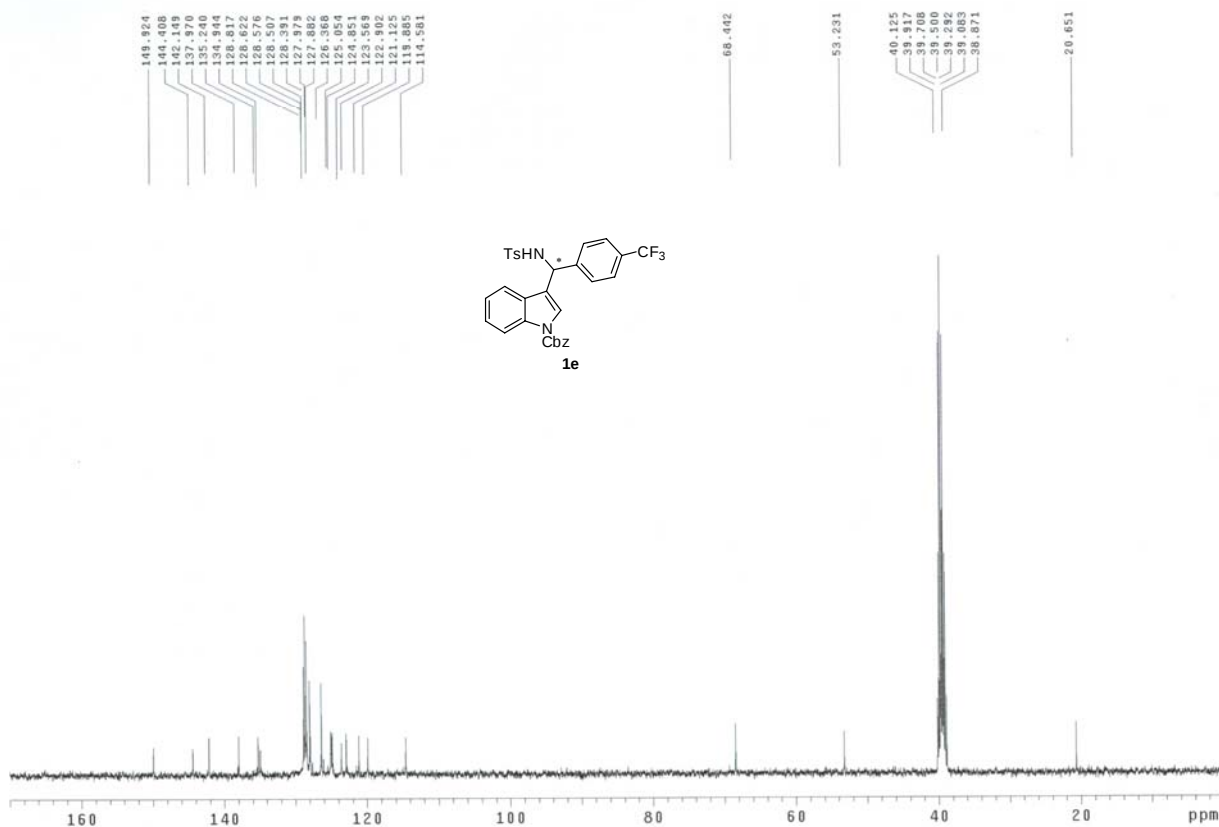


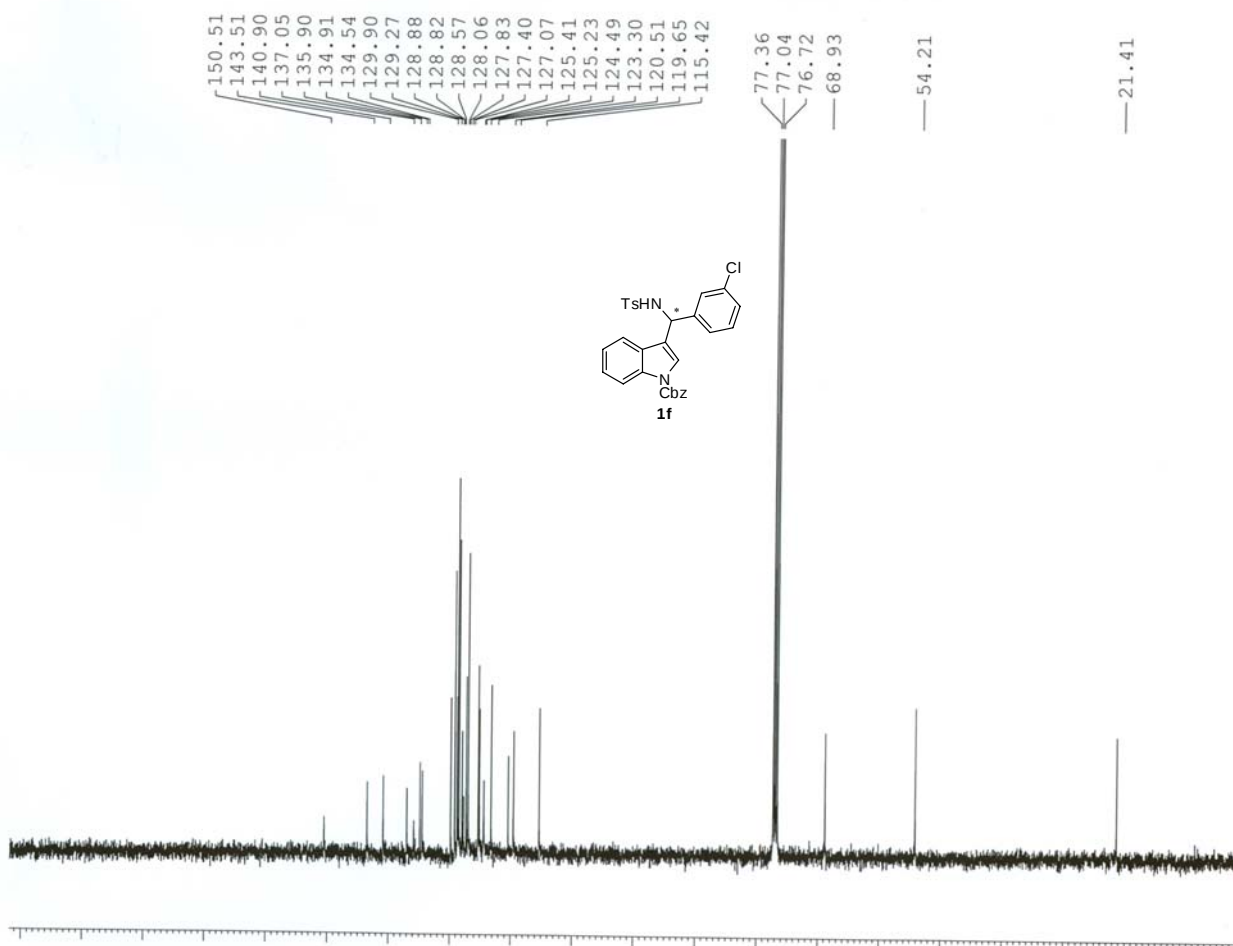
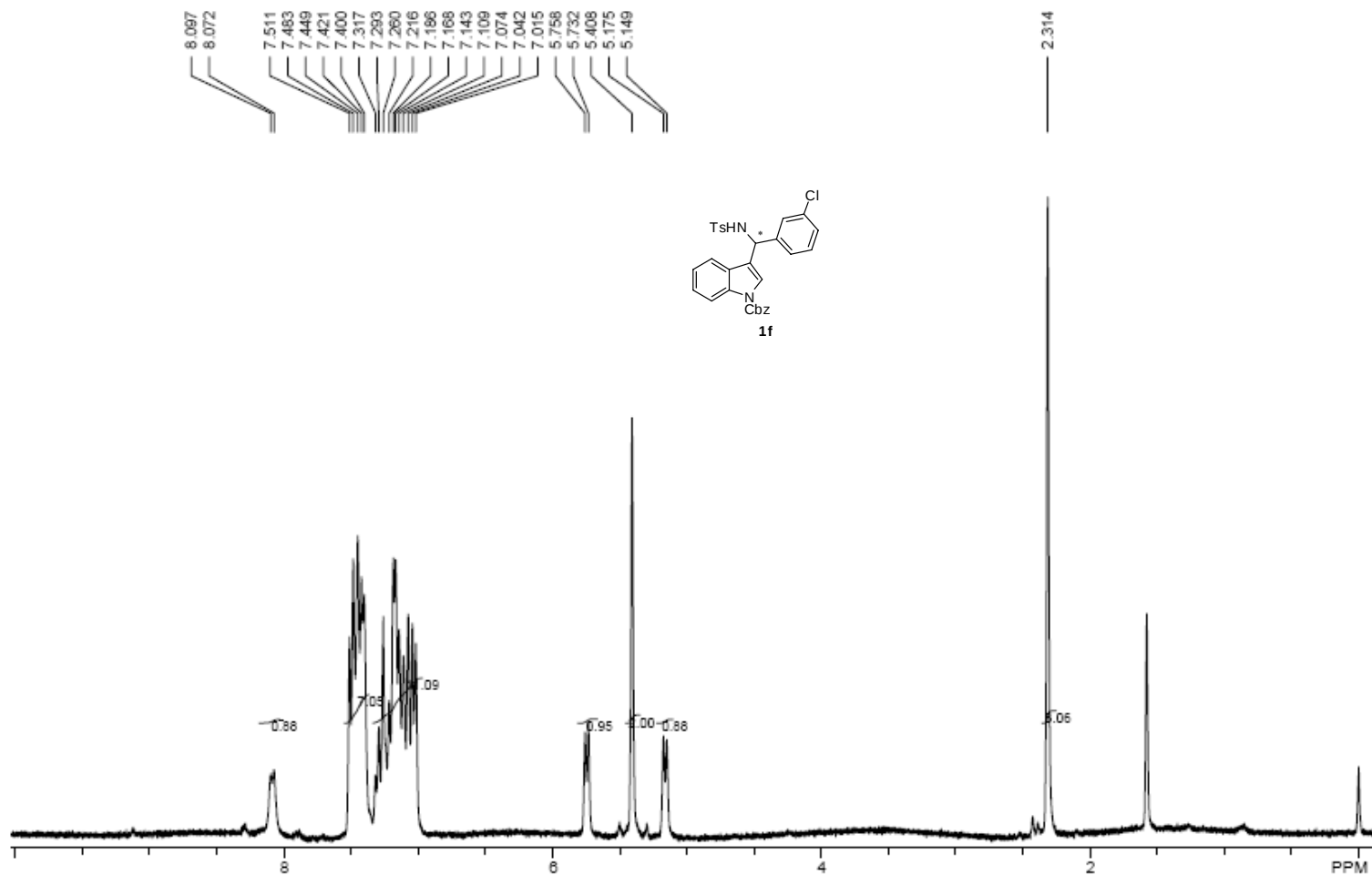


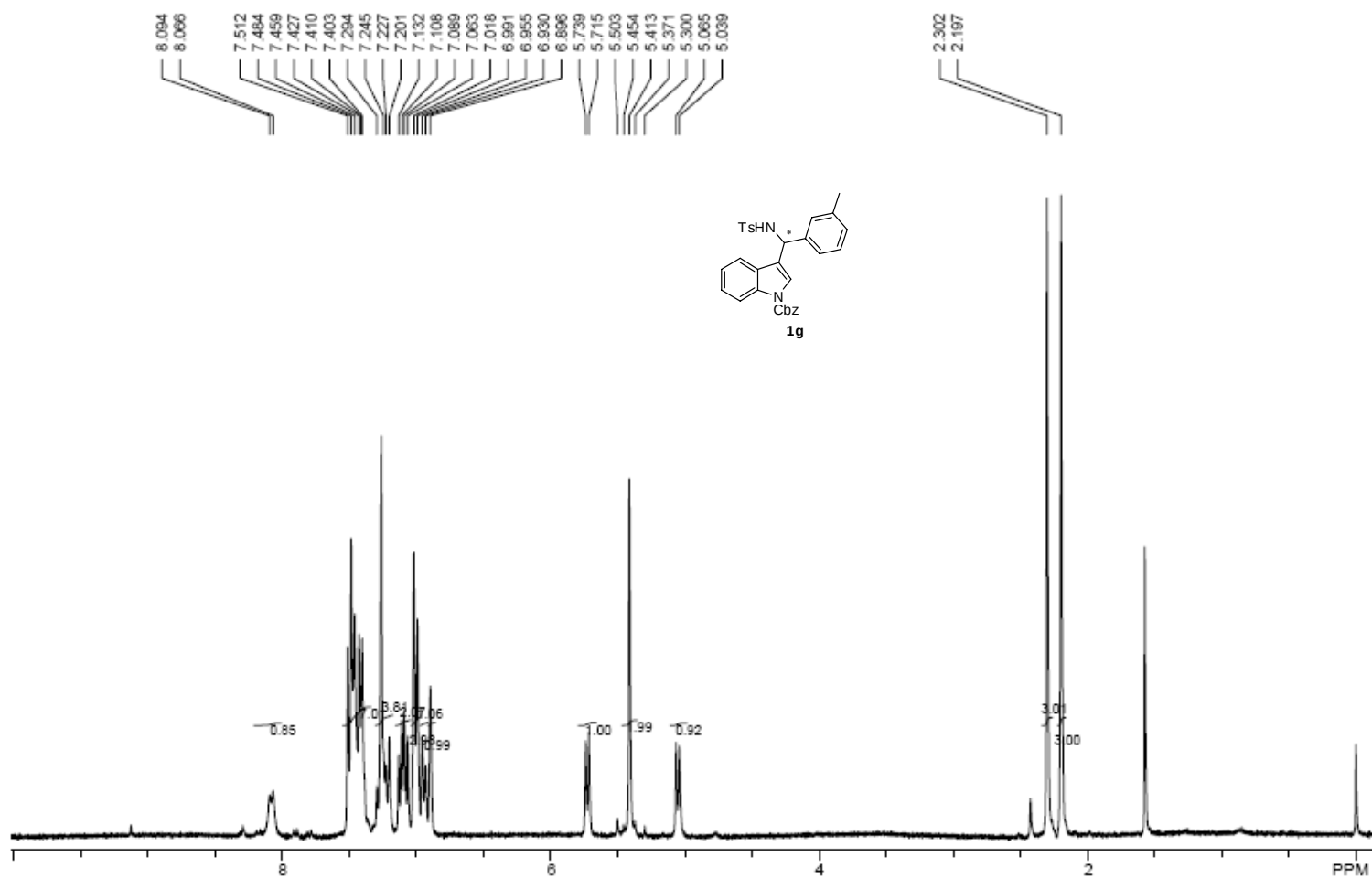




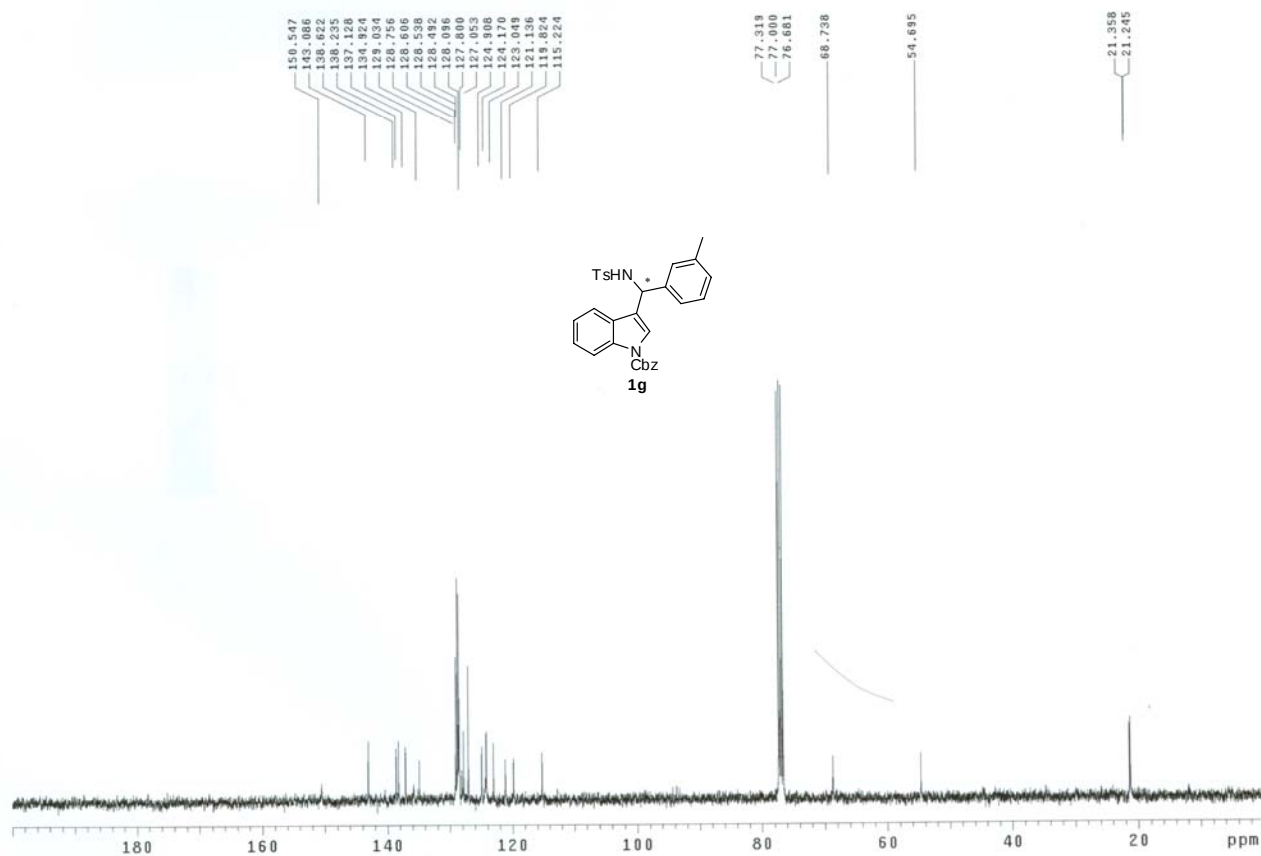
YHY-8-040 DMSO 13C-BB Apr 14 2010

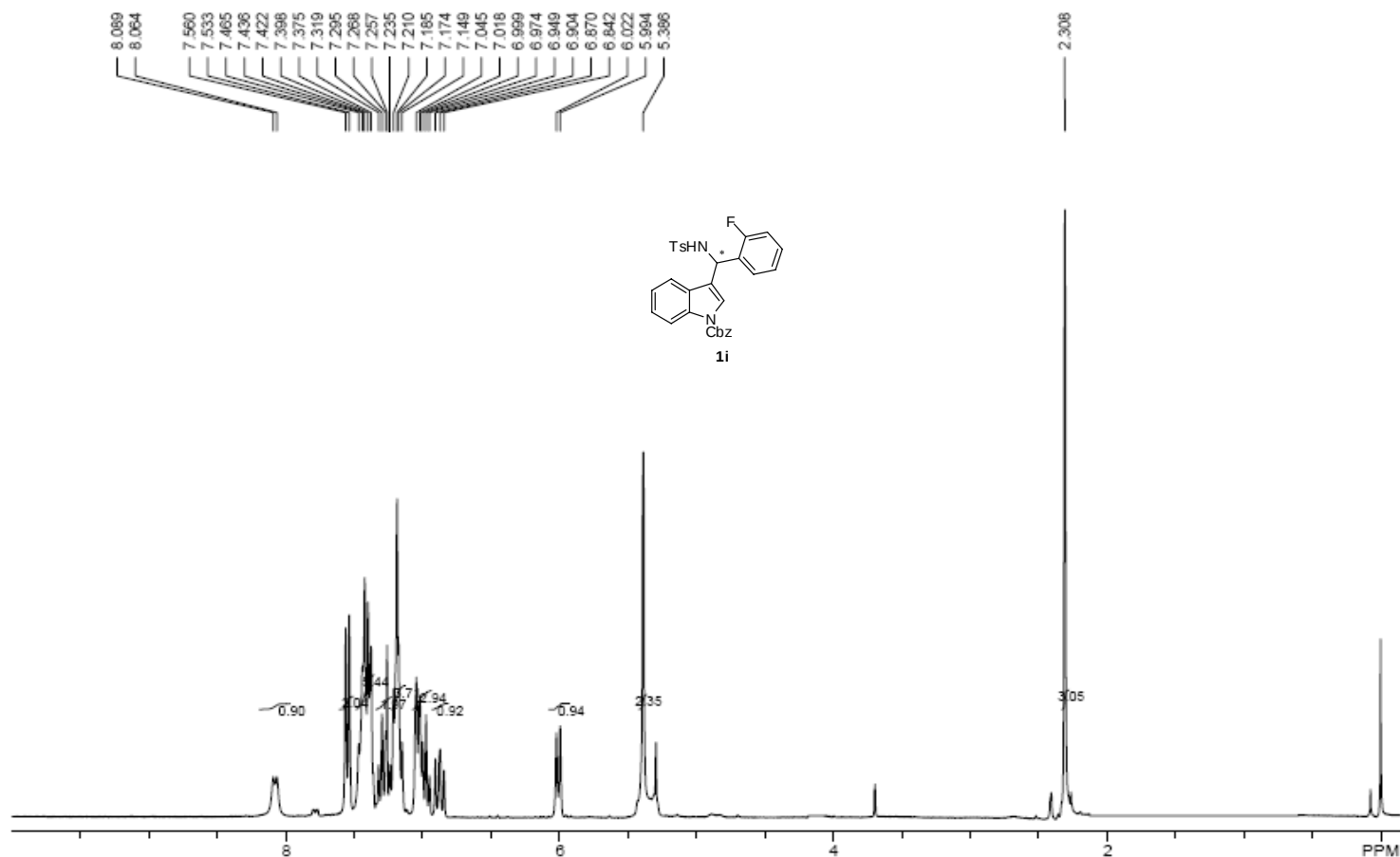




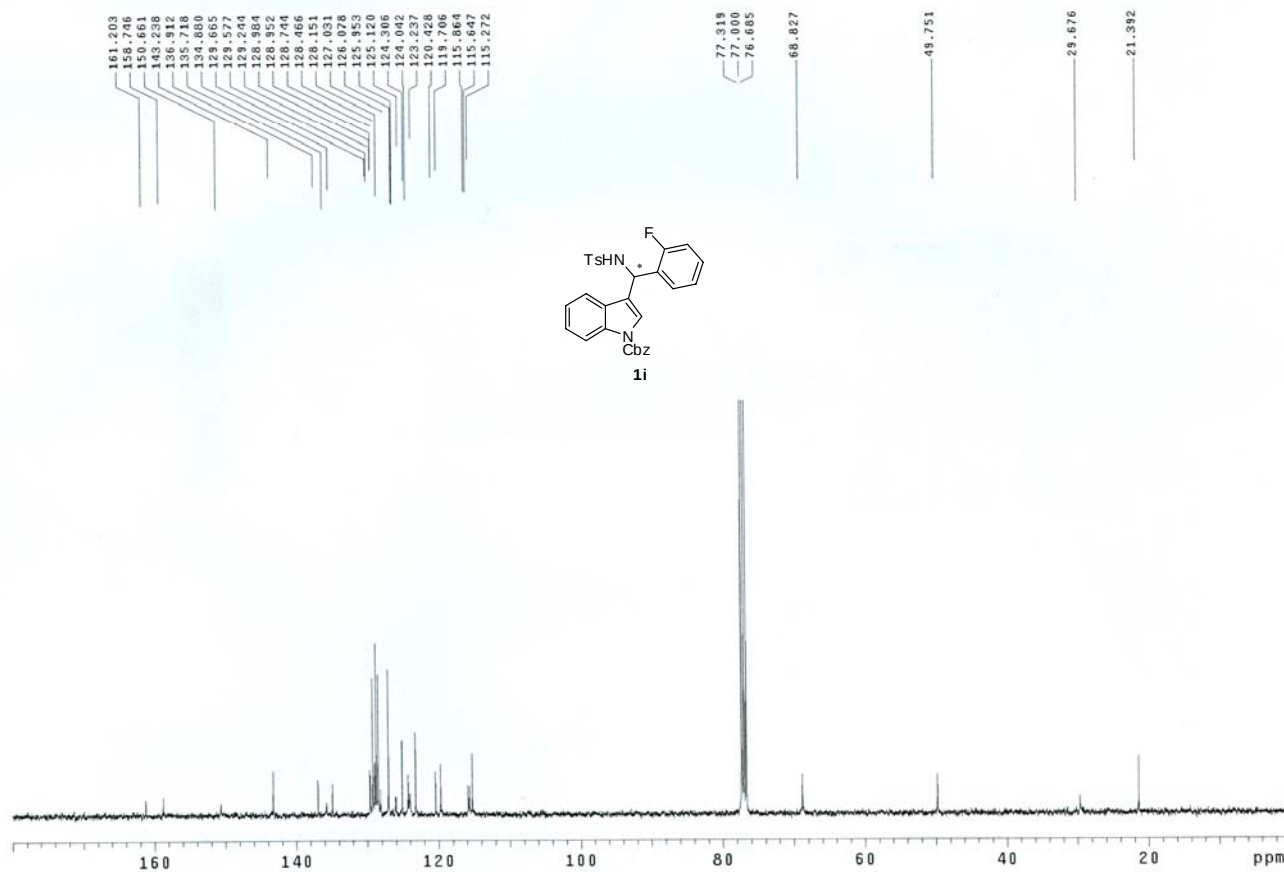


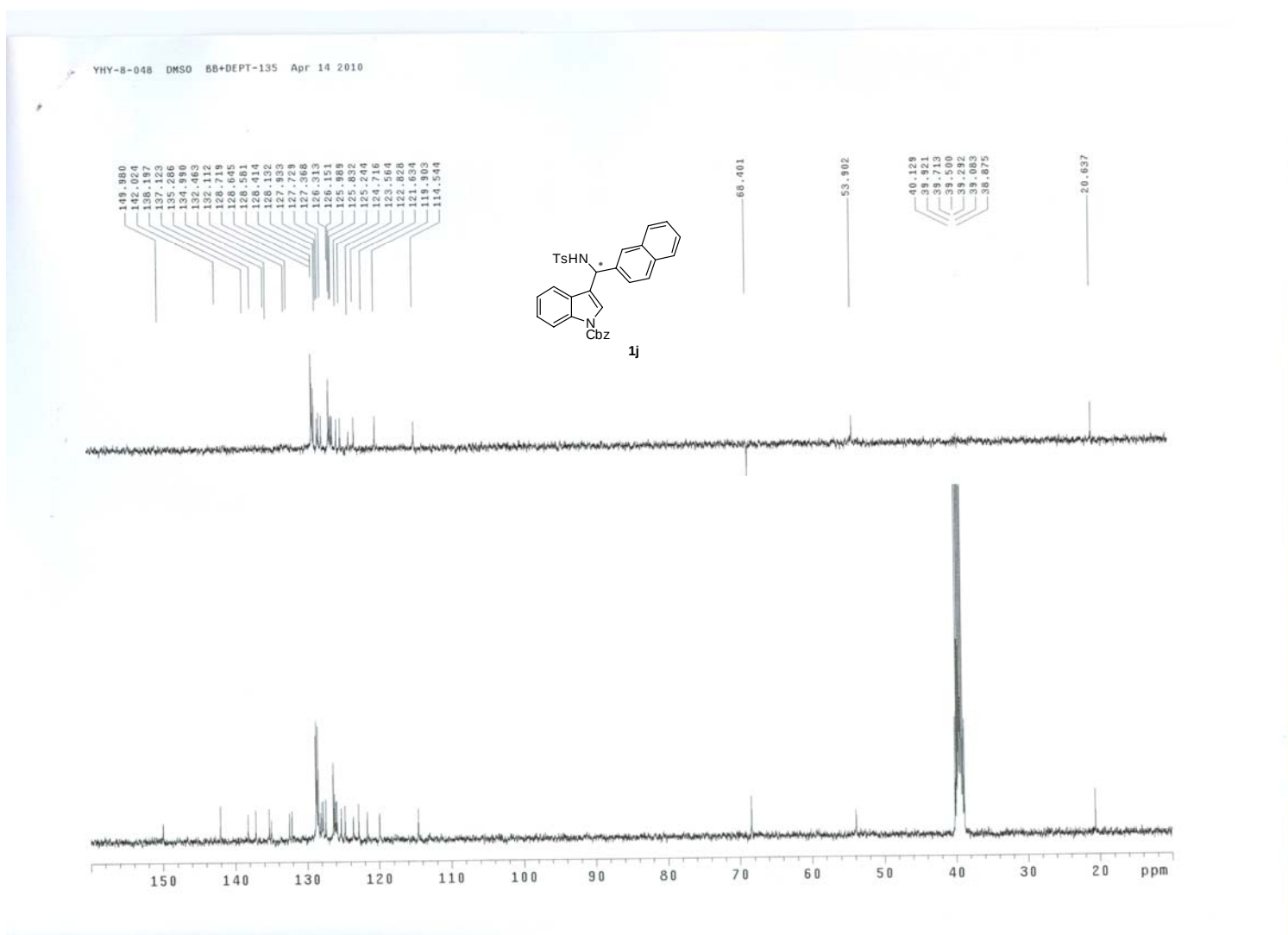
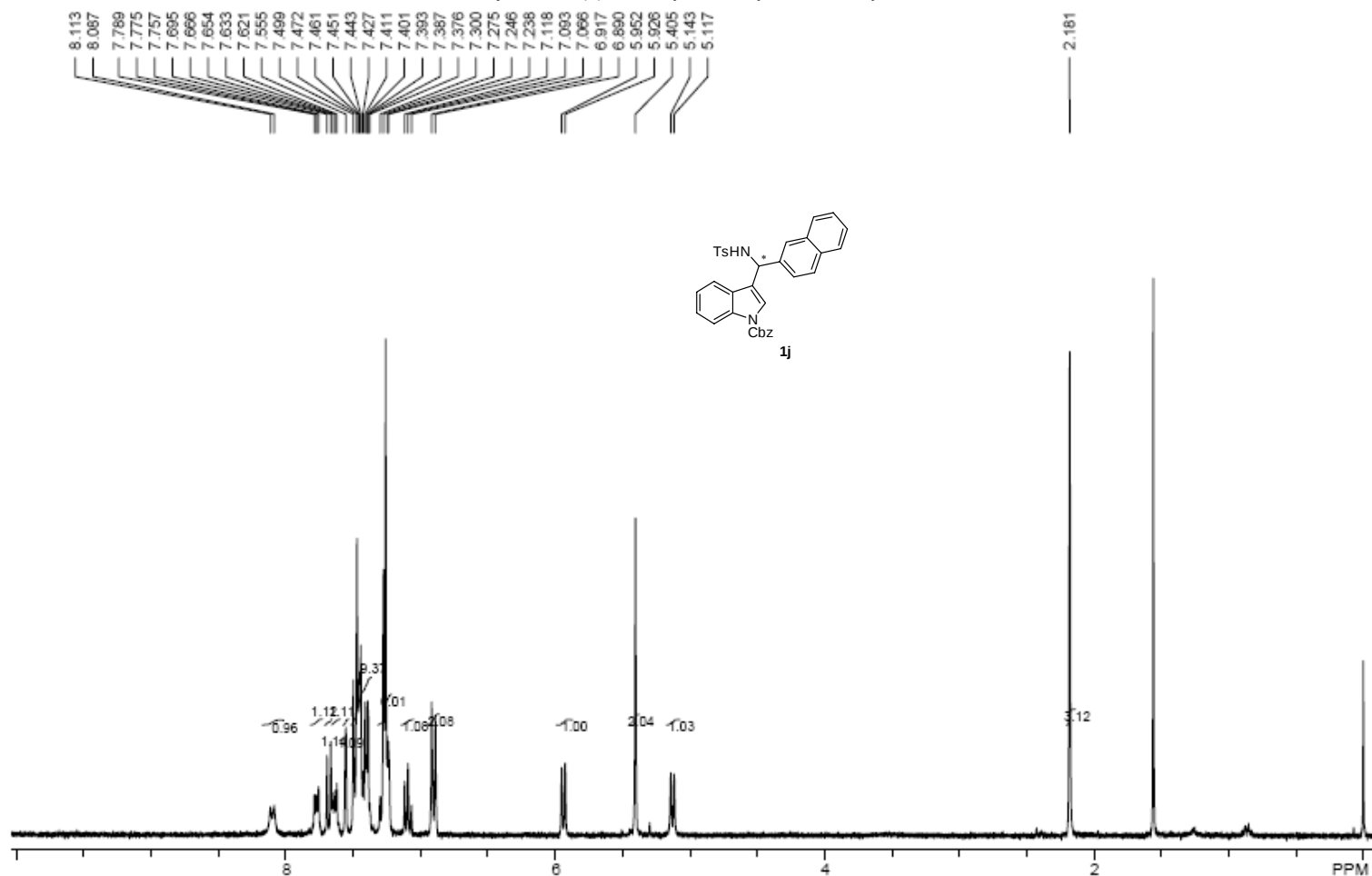
YHY-8-054 CDCl₃ 13C-BB 100416

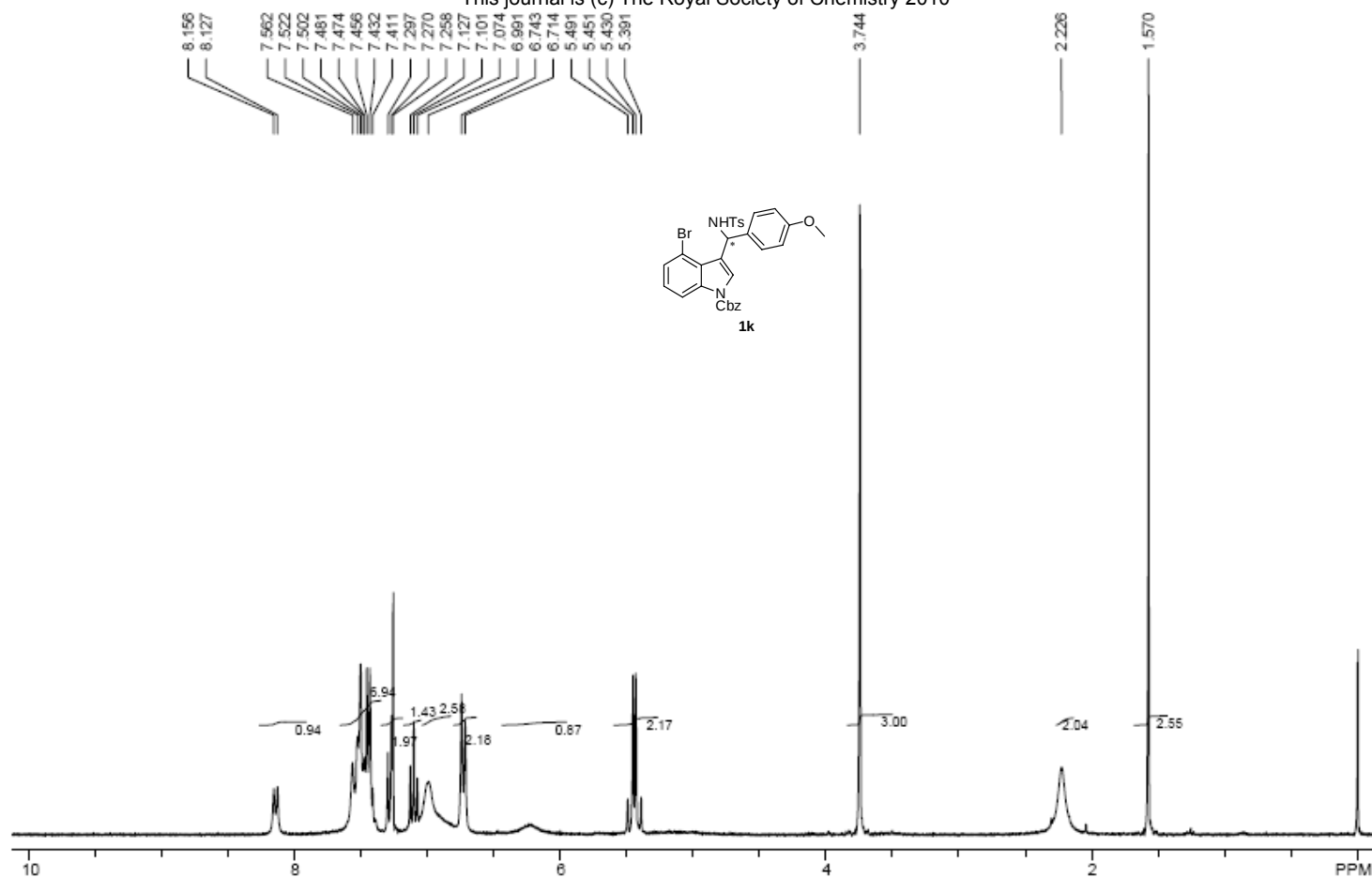




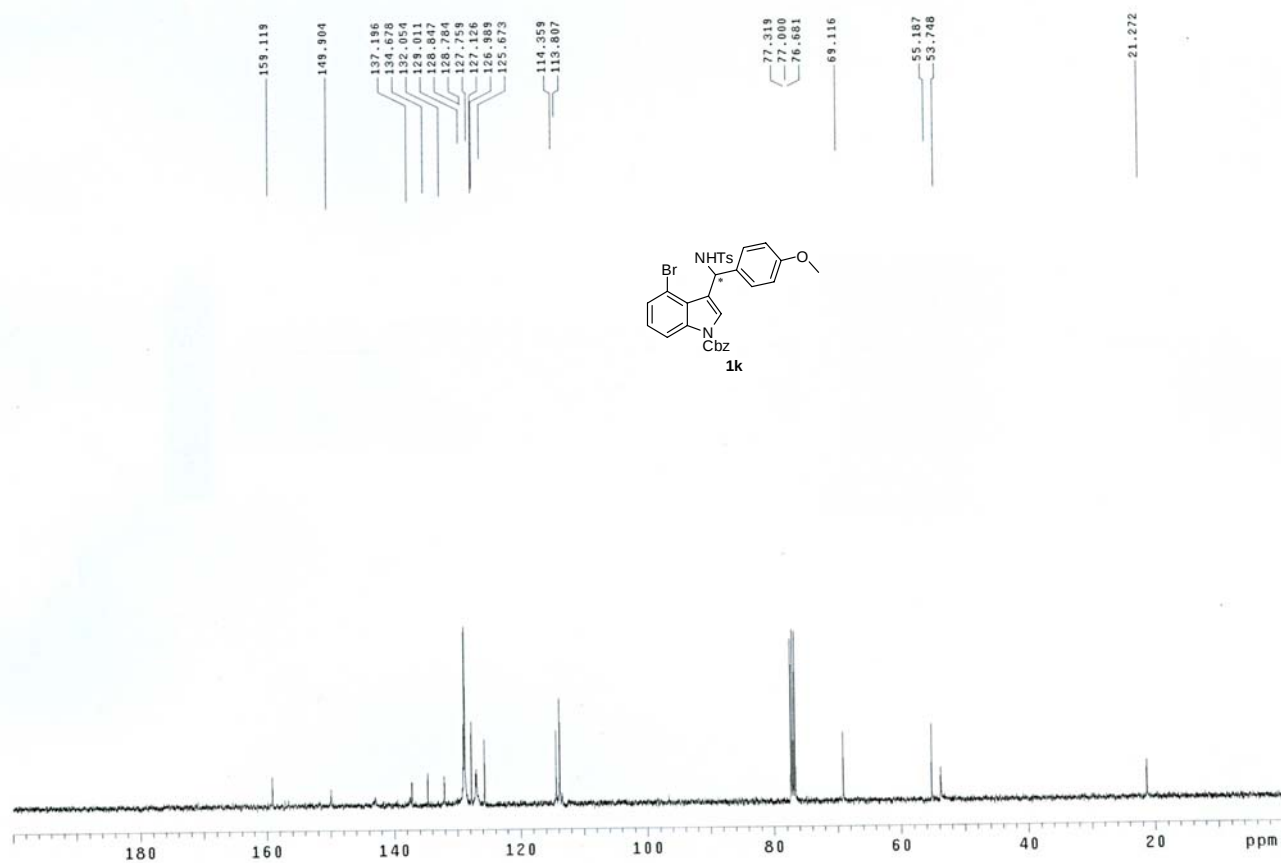
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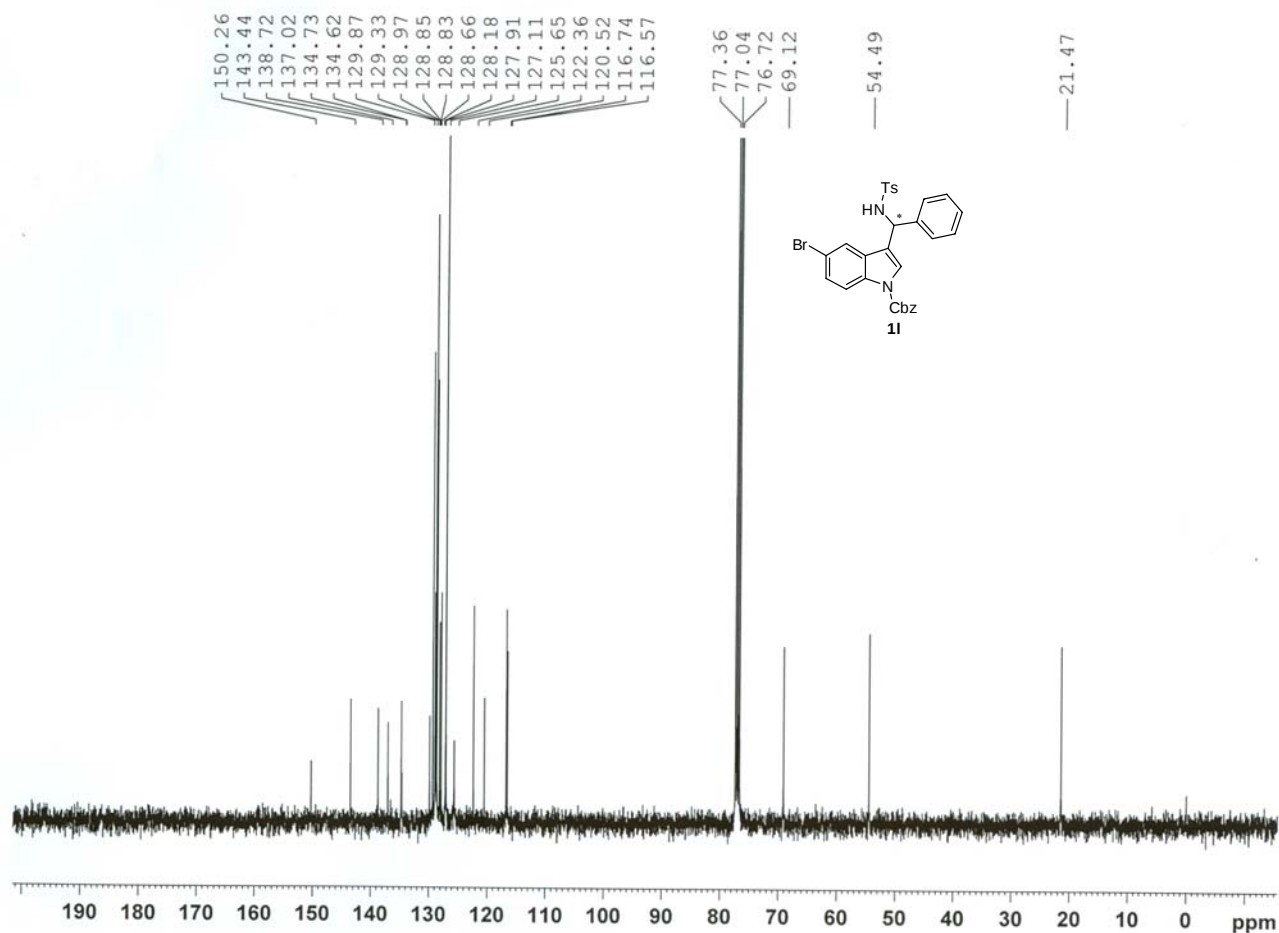
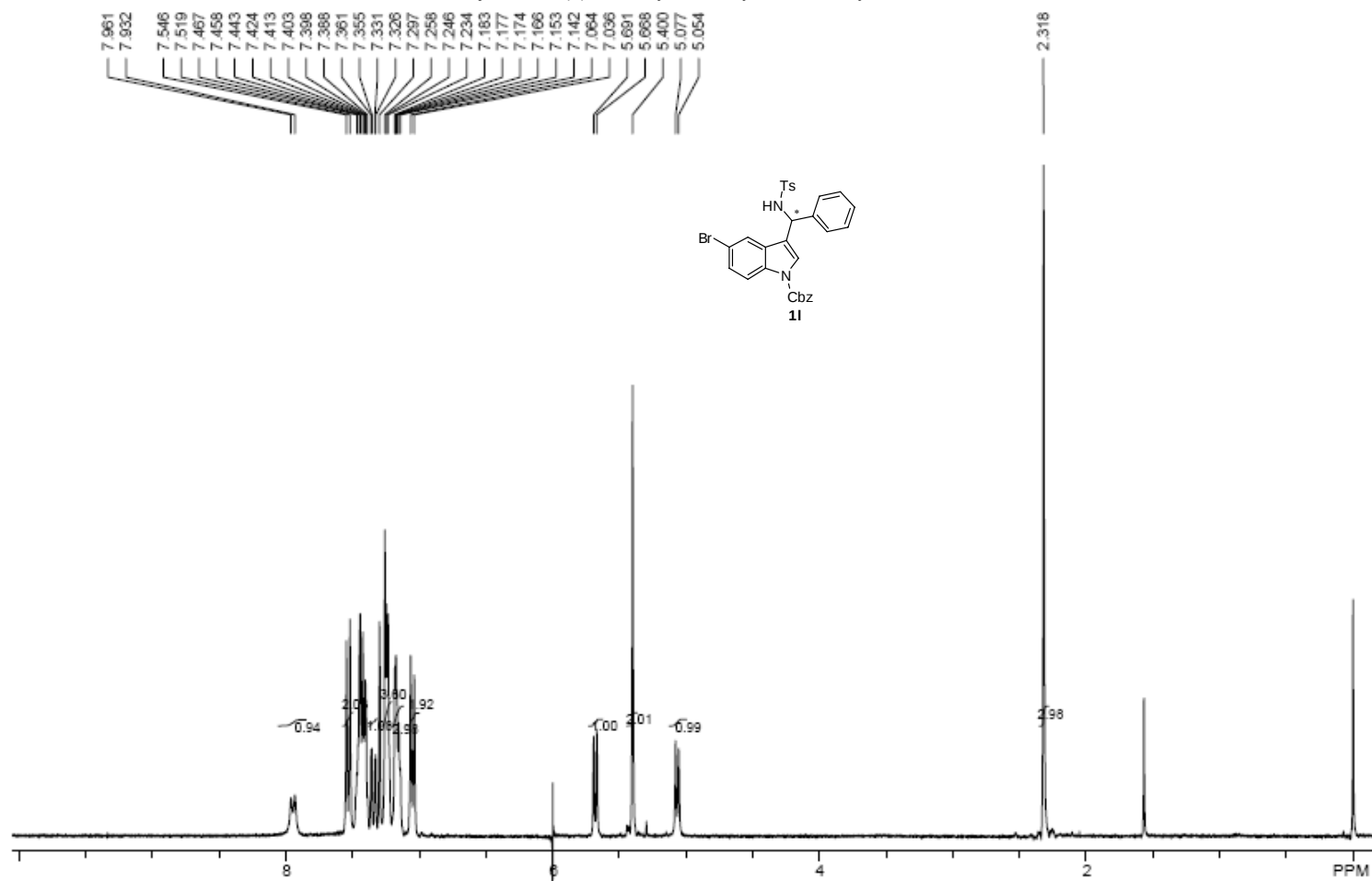


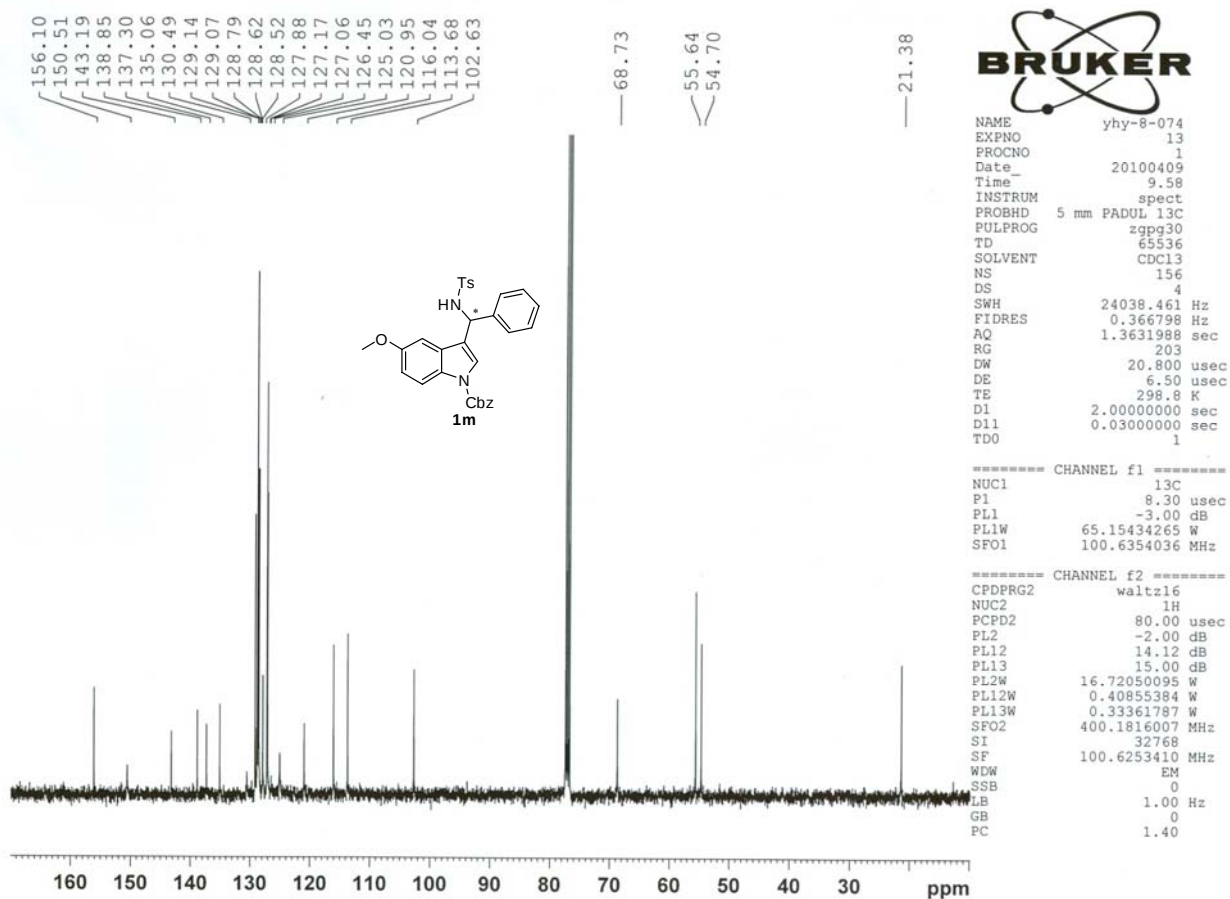
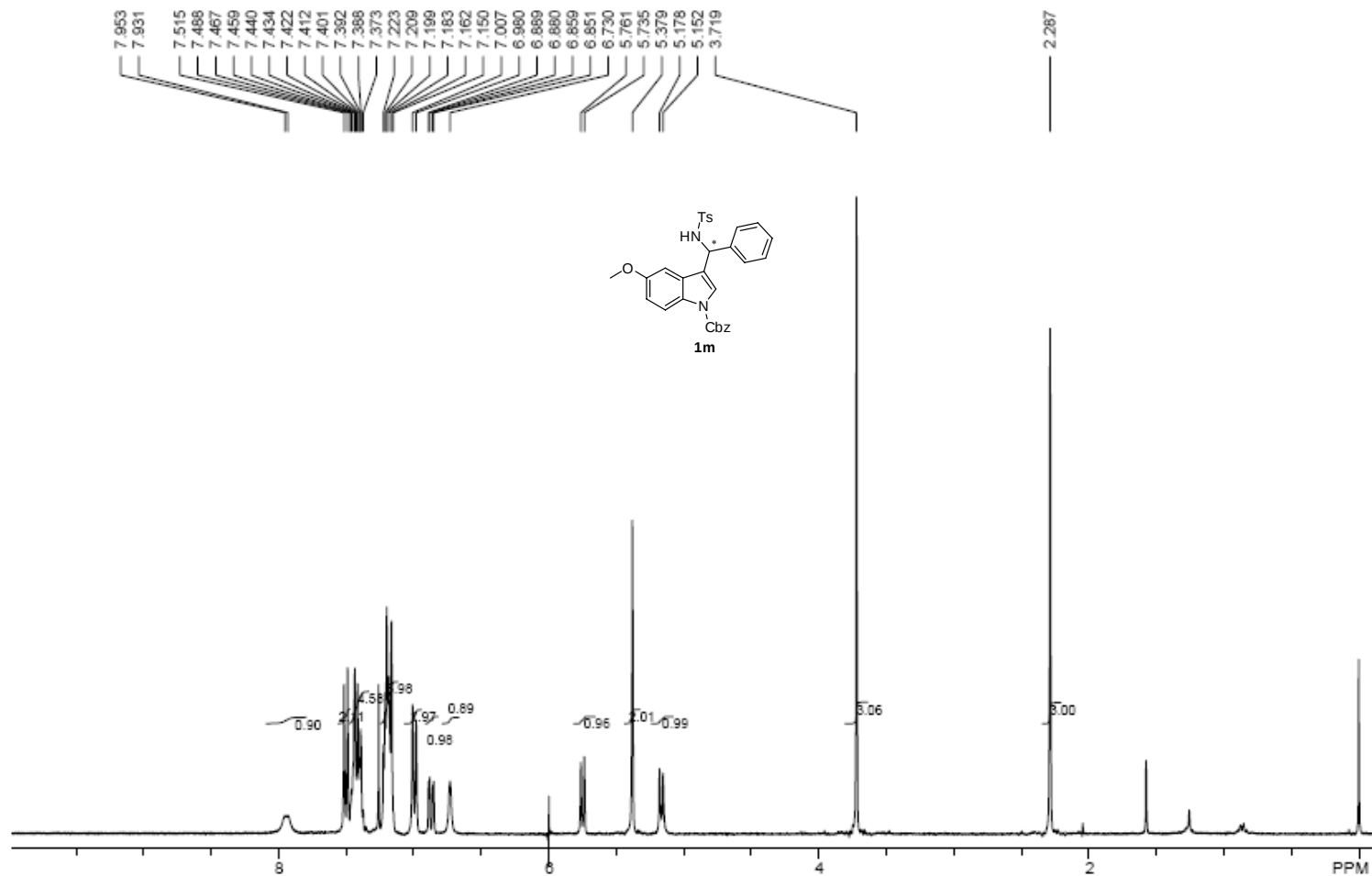


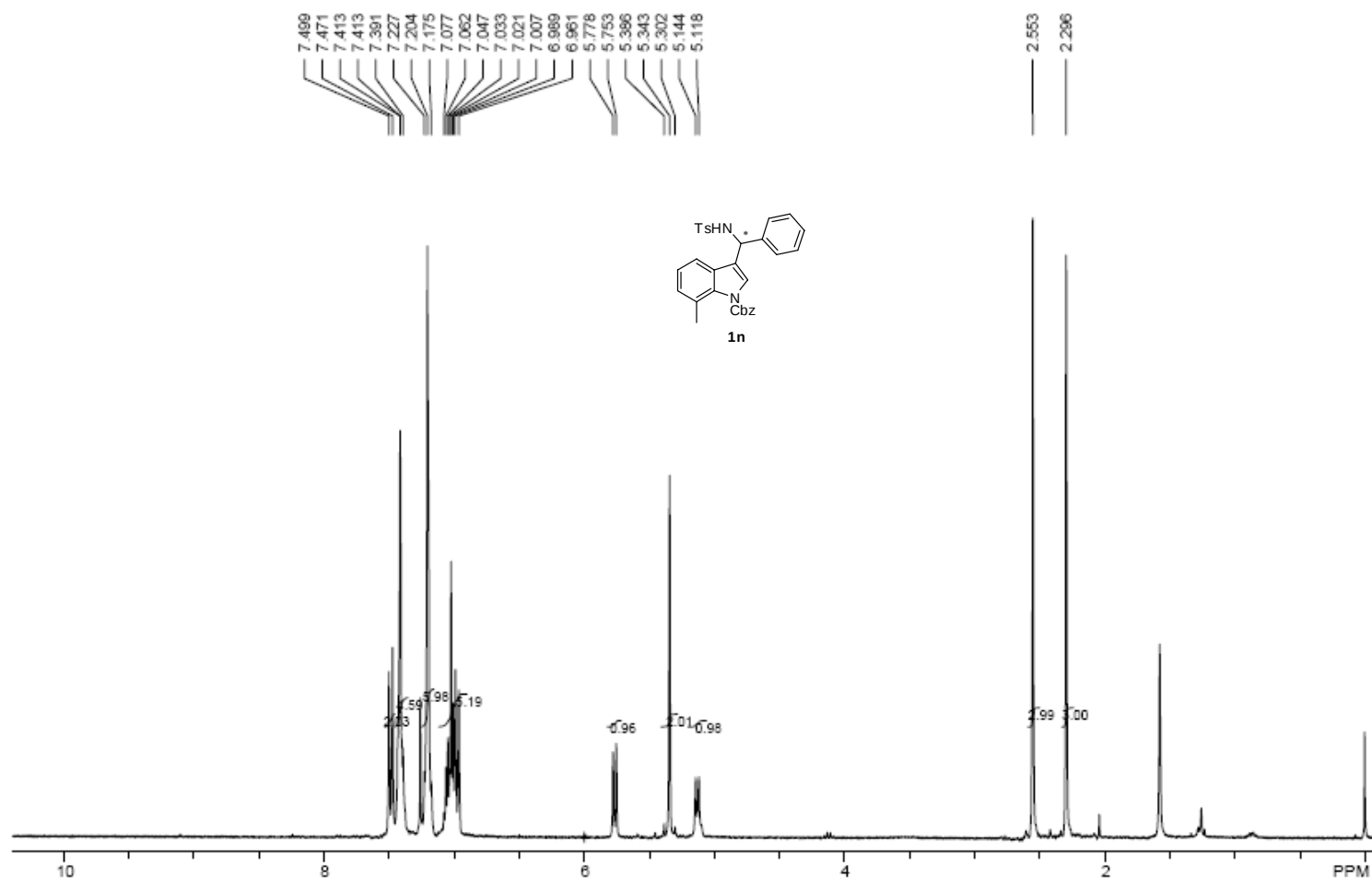


YHY-9-039 CDC13 13C BB Jul 6 2010

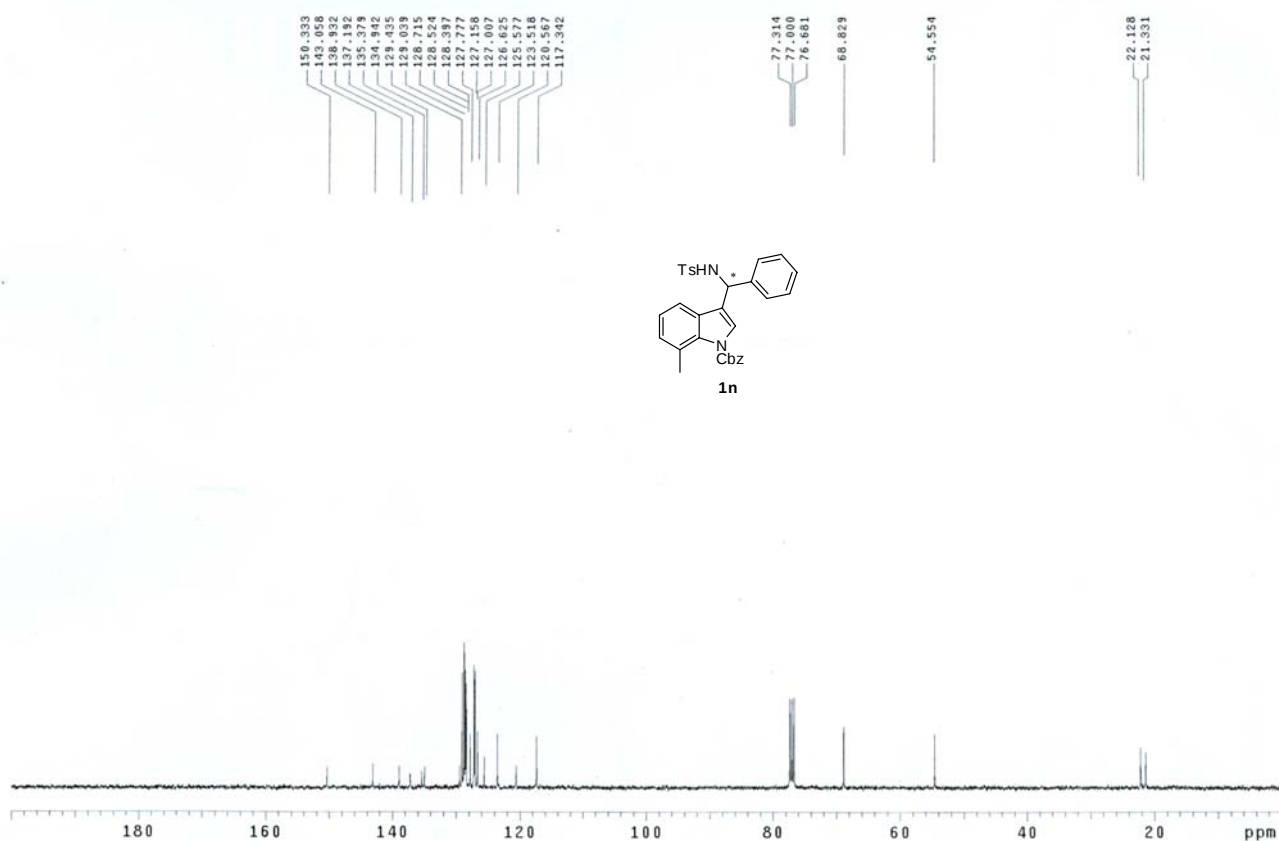


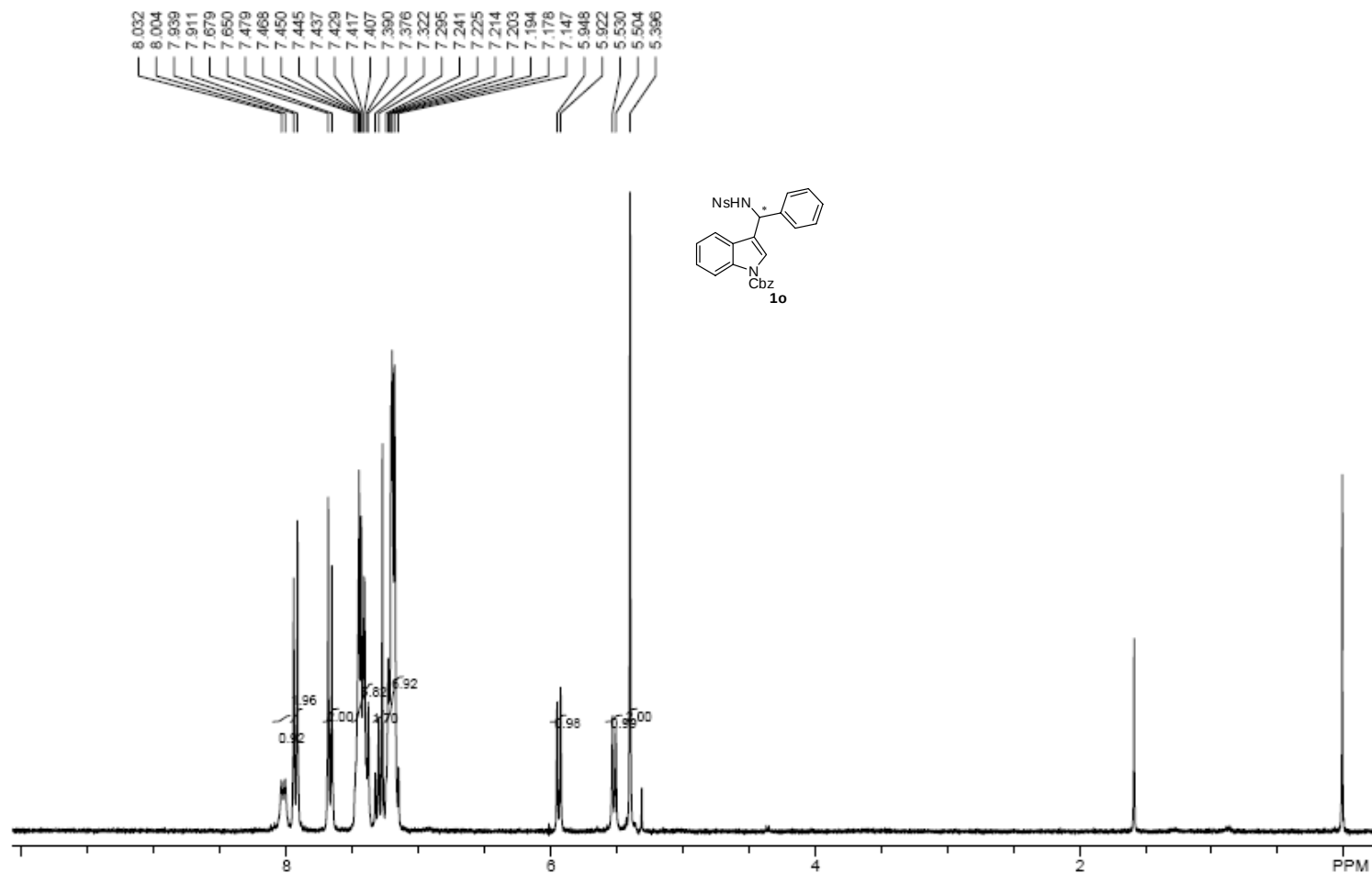




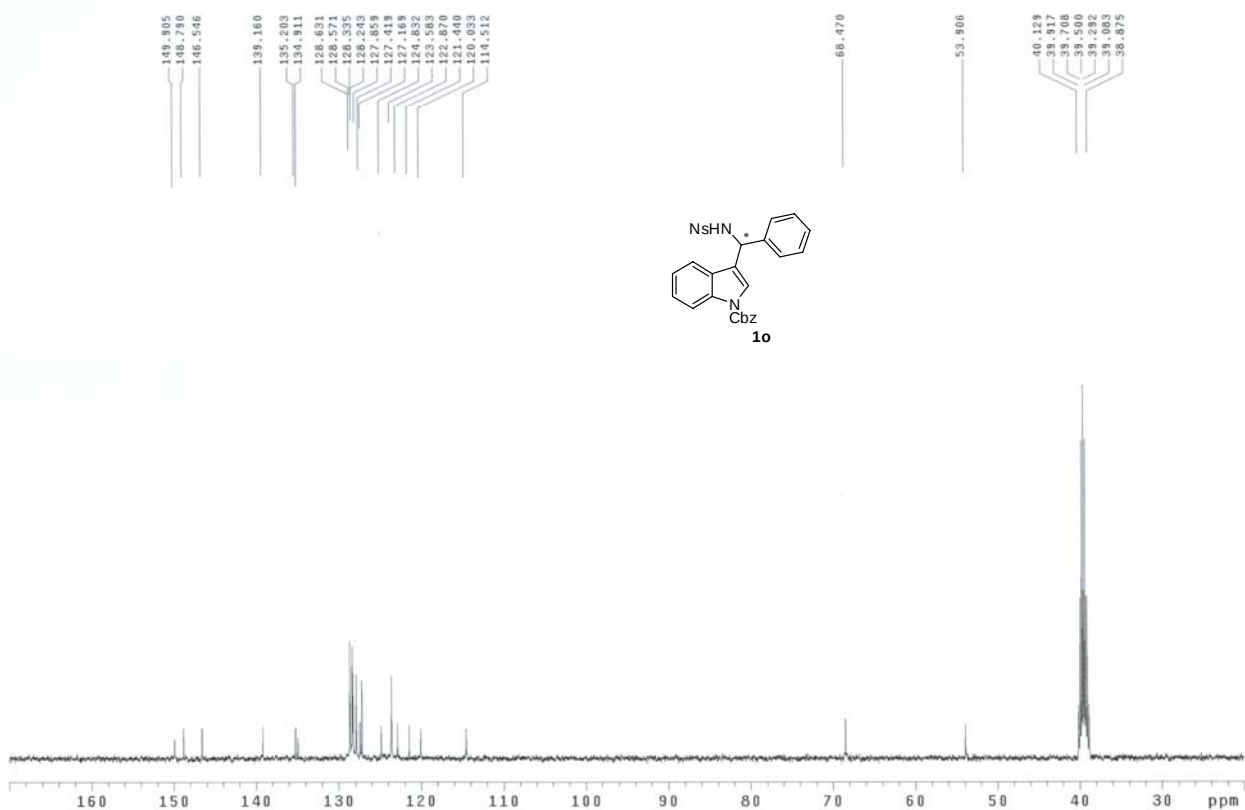


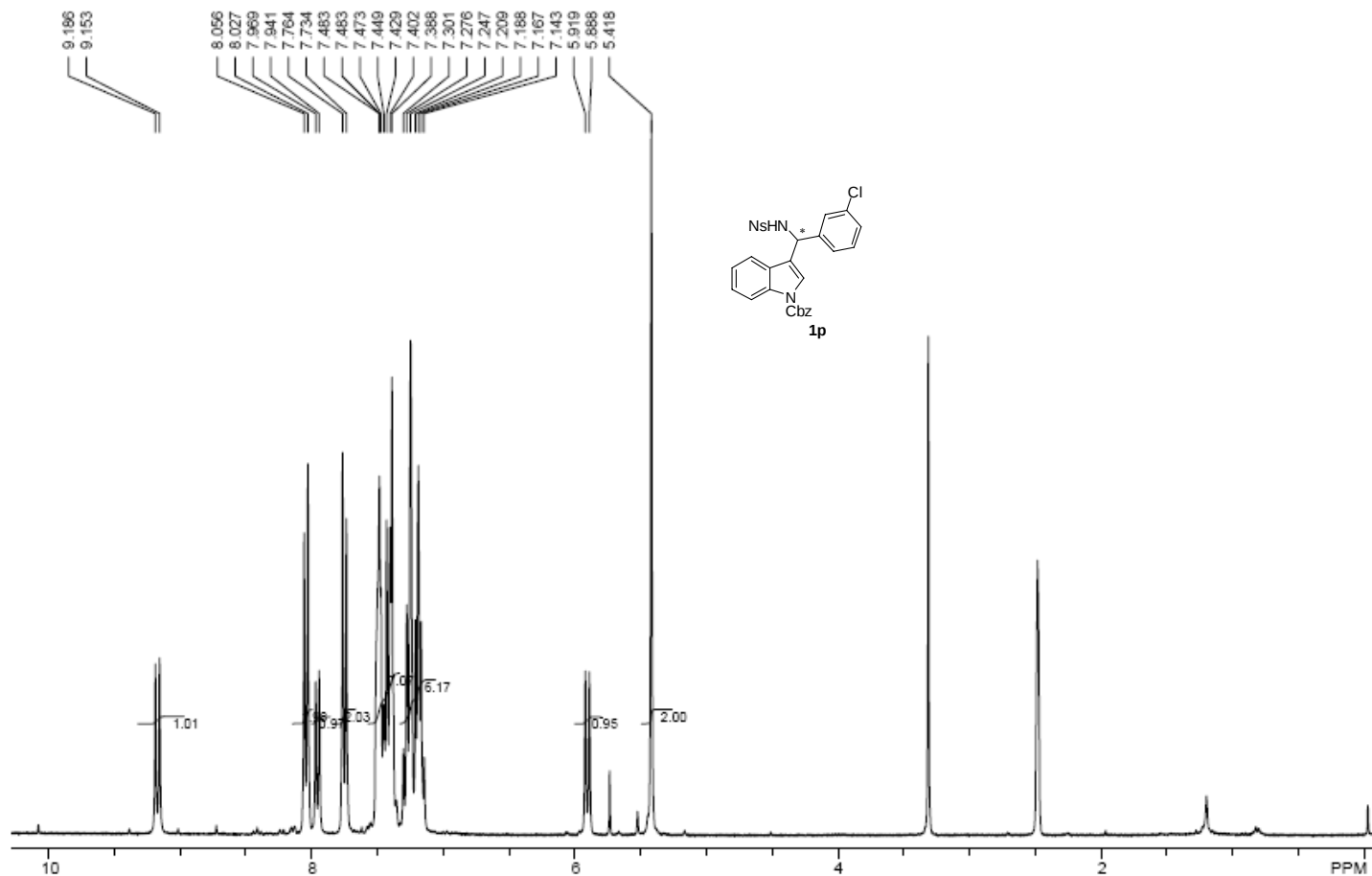
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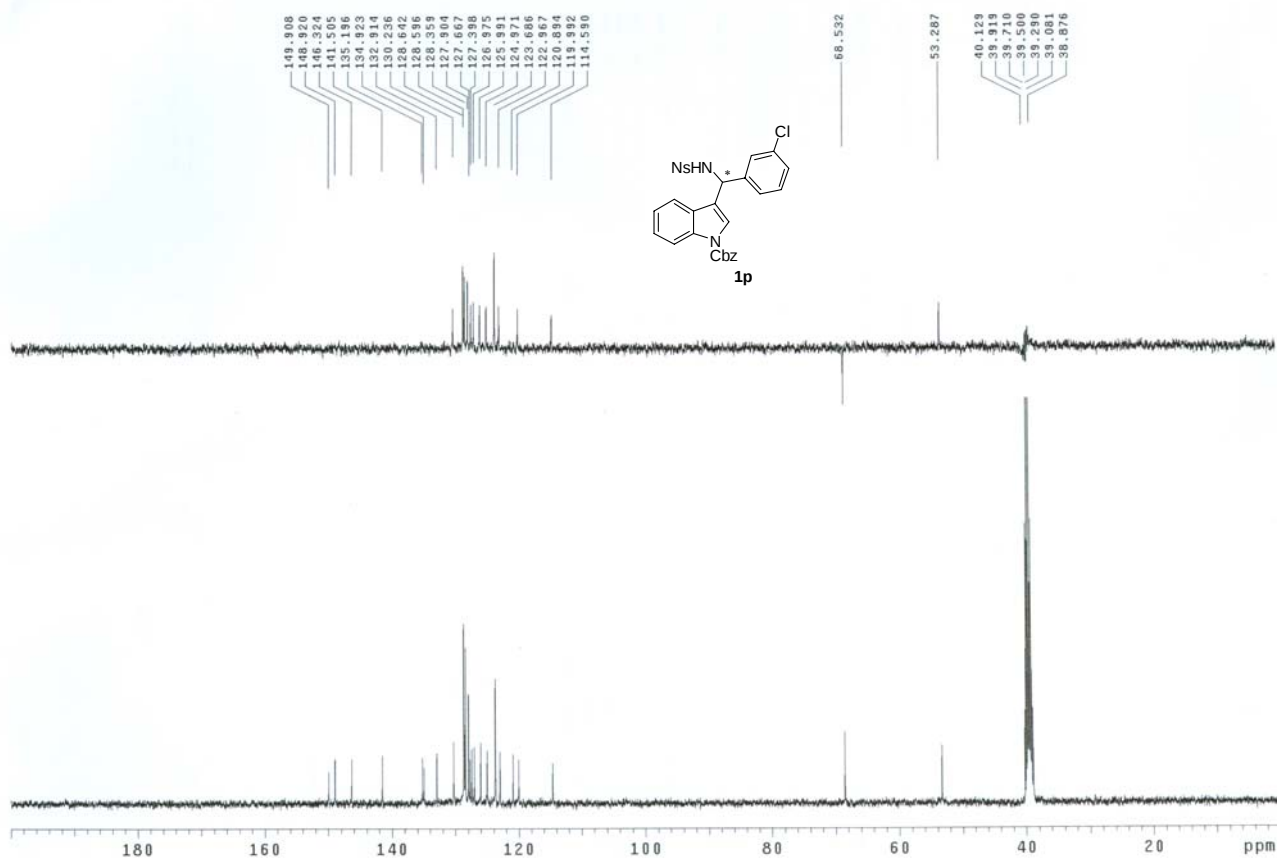


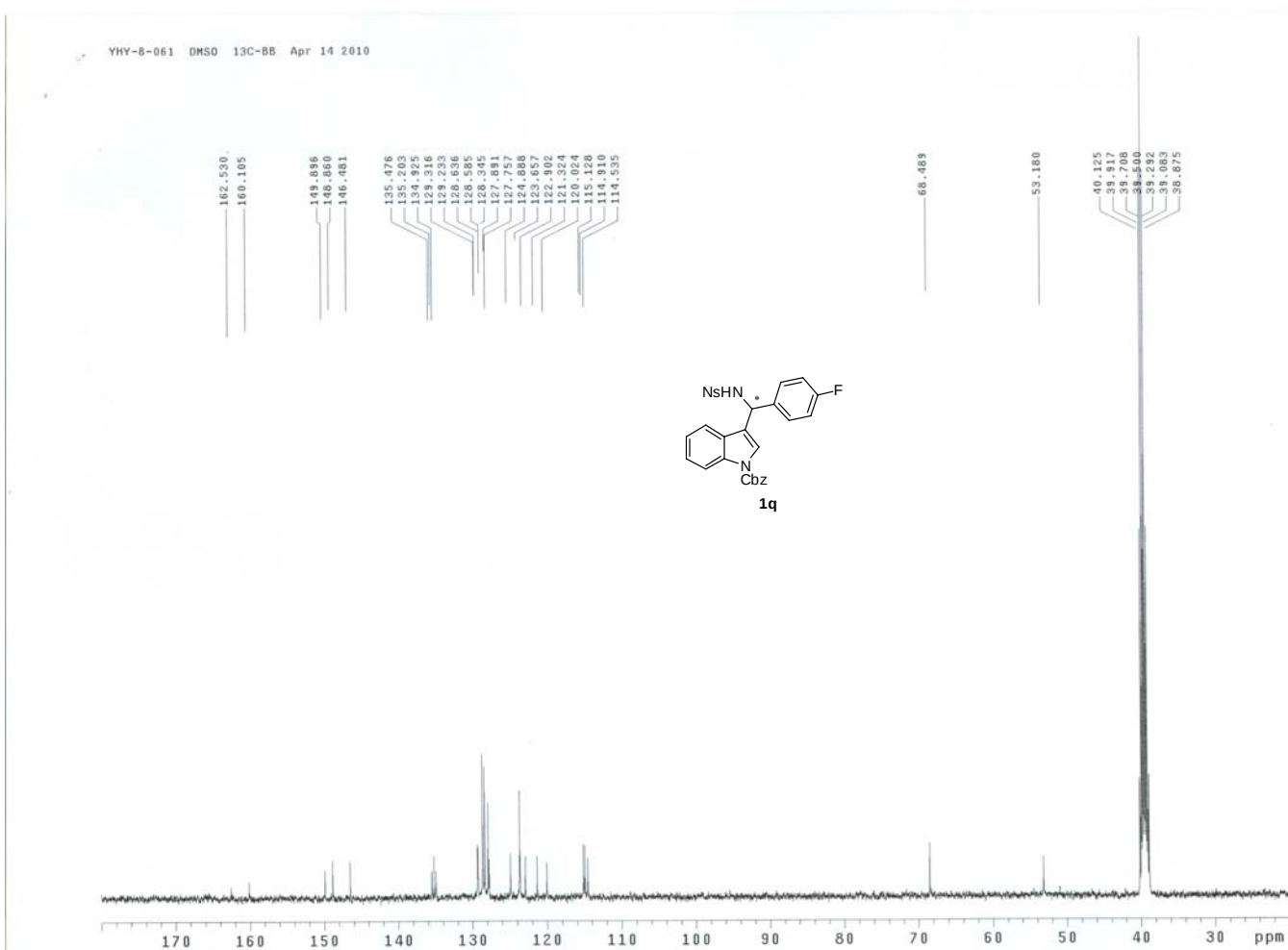
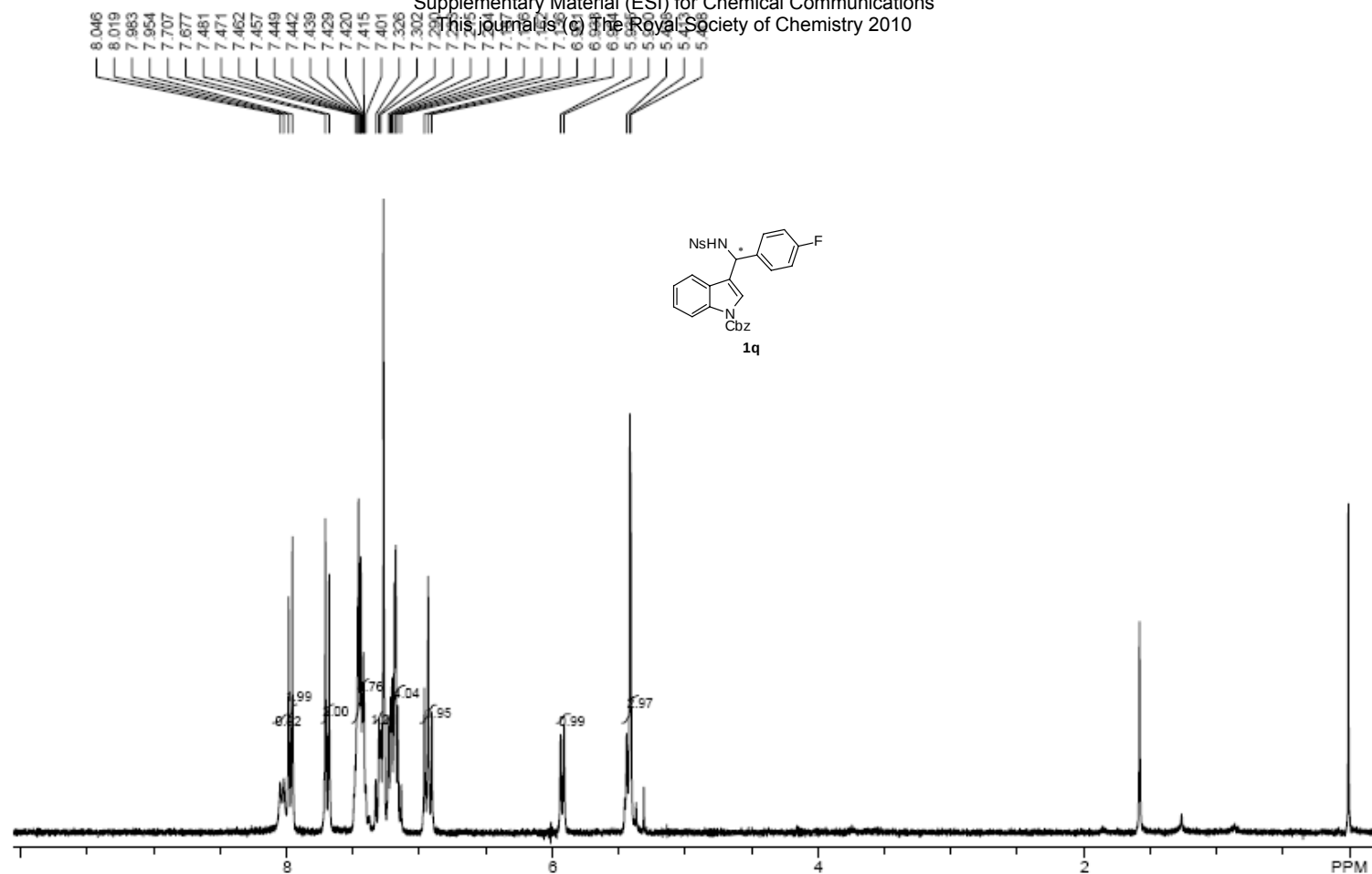
YHY-8-063 DMSO 13C-BB Apr 14 2010

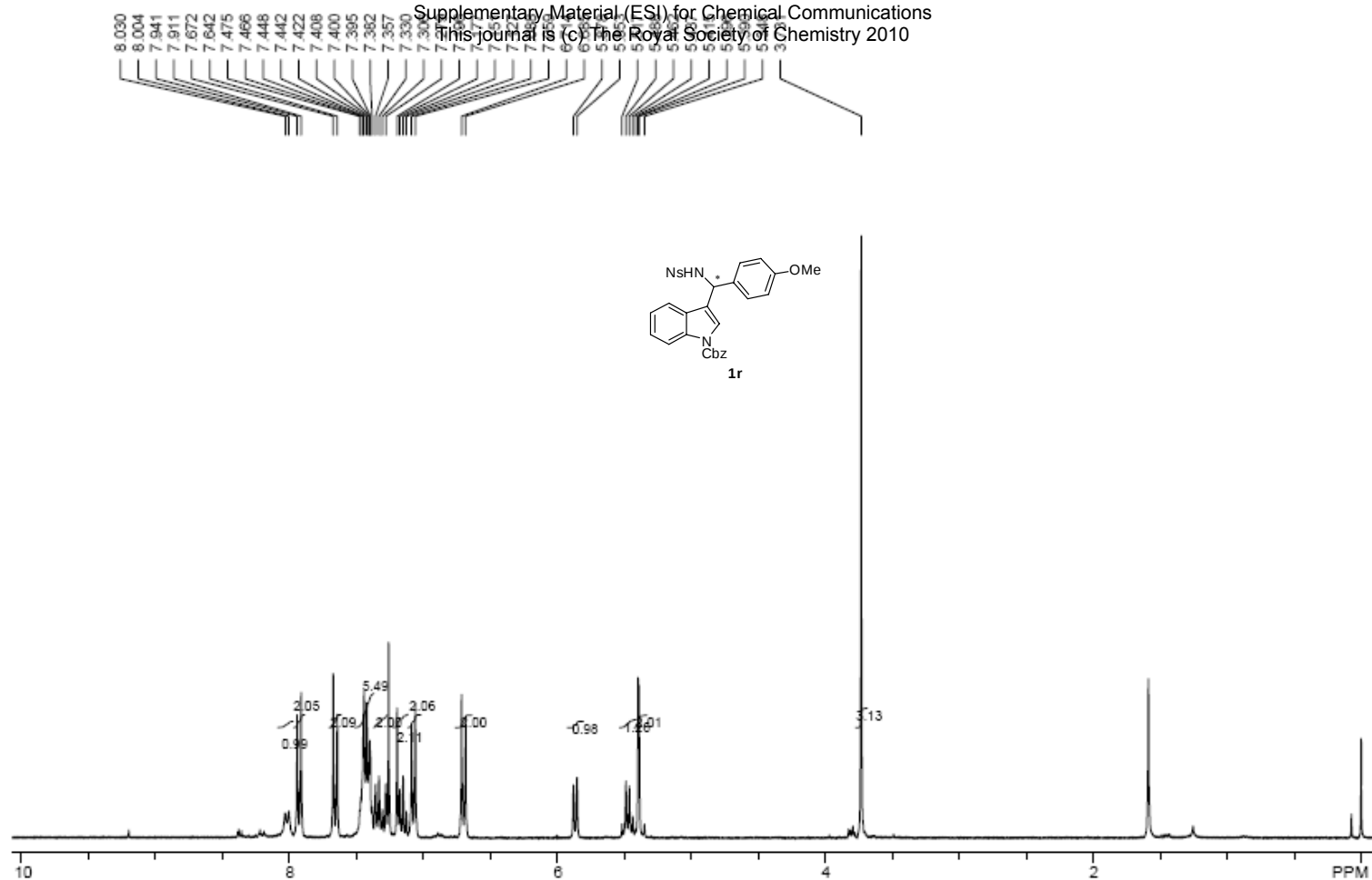




YHY-9-028 DMSO-d6 BB+DEPT-135 Sep 13 2010







YHY-8-053 DMSO 13C-BB Apr 14 2010

