Supporting Information

Asymmetric [3+2] Cycloaddition of 3-Amino Oxindole-based Azomethine Ylides and α,β-Enones with Divergent Diastereocontrol on the Spiro[pyrrolidine-oxindoles]

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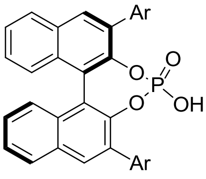
1. General Information

All reactions were carried out in Schlenk tube under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{19}F NMR spectra were recorded on a Bruker Avance II 400 MHz and Bruker Avance III 471 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance II 101 MHz or Bruker Avance III 126 MHz. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = double doublet, coupling constants in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). HRMS (ESI) was determined by a HRMS/MS instrument (LTQ Orbitrap XL TM). Enantiomeric excess values were determined by HPLC employing a chiral column on Agilent 1100 series. Optical rotations were reported as follows: $[\alpha]^{T}_{D}$(c g/100 mL, solvent). The absolute configurations of **5cfa** and **5can'** were assigned by the X-ray analysis. All the aldehydes were commercially obtained and recrystallized or distilled prior to use. 3-Amino oxindole hydrochlorides[1] and α,β-unsaturated enones[2] were prepared according to literature methods.

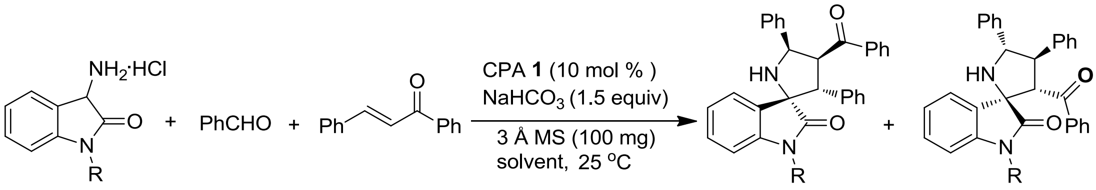
2. Screening of Optimal Reaction Conditions and Substrate Scope

Table S1. Screening of the Optimal Reaction Conditions [a]



BPA **1**

1a, Ar = 2-naphthyl
1b, Ar = $SiPh_3$
1c, Ar = 2,4,6-(i-Pr)$_3$-C_6H_2
1d, Ar = 9-phenanthryl
1e, Ar = 9-anthryl
1f, Ar = Ph
1g, Ar = 4-MeO-C_6H_4
1h, Ar = 4-Ph-C_6H_4

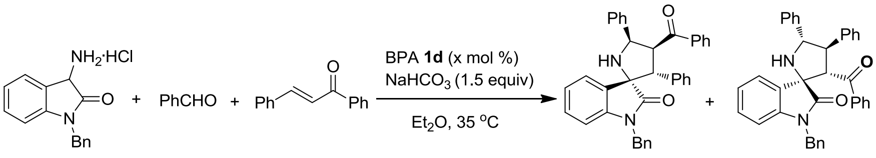


2 **3a** **4a** **5** (major) **5'** (minor)

entry	R	**1**	solvent	t (h)	yield (%)[b]	rr[c]	*ee* (%)[d]
1	Me	**1a**	CH_2Cl_2	12	99	9:1	84, 50
2	Me	**1b**	CH_2Cl_2	12	99	7:1	76, 43
3	Me	**1c**	CH_2Cl_2	12	93	10:1	77, 60
4	Me	**1d**	CH_2Cl_2	23	79	7:1	90,87
5	Me	**1e**	CH_2Cl_2	12	95	7:1	74, 65
6	Me	**1f**	CH_2Cl_2	12	99	9:1	84, 53
7	Me	**1g**	CH_2Cl_2	24	99	11:1	82, 53
8	Me	**1h**	CH_2Cl_2	24	99	7:1	76, 61
9	Me	**1d**	DCE	23	87	8:1	91, 81
10	Me	**1d**	$CHCl_3$	23	95	8:1	89, 49
11	Me	**1d**	THF	19	99	4:1	89, 14
12	Me	**1d**	Et_2O	120	80	8:1	94,80
13	Me	**1d**	MTBE	68	88	5:1	94,56
14	Me	**1d**	toluene	108	86	3:1	91,90
15[e]	Me	**1d**	Et_2O	120	80	8:1	94,80
16[e,f]	Me	**1d**	Et_2O	120	86	8:1	94,78
17[e,f]	H	**1d**	Et_2O	72	20	—	—
18[e,f]	Bn	**1d**	Et_2O	85	99	9:1	96,85

[a] The reaction was carried out on a 0.1 mmol scale, **1** (10 mol %) in 1.0 mL Et_2O, the ratio of **2**/**3a**/**4a** was 1/1.2/1.1. [b] Isolated yield. [c] The rr was determined by ^{1}H NMR of the crude reaction mixture. [d] The *ee* was determined by chiral HPLC. [e] Without 3 Å MS. [f] At 35 °C.

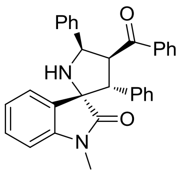
Table S2. Screening of the Catalyst Loading in the Reaction[a]



entry	x (mol%)	t (h)	yield (%)[b]	rr[c]	*ee* (%)[d]
1	10	85	99	9:1	96, 85
2	5	85	99	8:1	95, 77
3	2	85	99	7:1	94, 66
4	1	109	99	6:1	94, 51

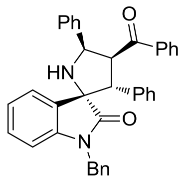
[a] The reaction was carried out on a 0.1 mmol scale, **1d** (x mol %) in 1.0 mL Et_2O, the ratio of **2c**/**3a**/**4a** was 1/1.2/1.1. [b] Isolated yield. [c]The rr was determined by ^1H NMR of the crude reaction mixture. [d]The *ee* was determined by chiral HPLC.

Scheme S1. Substrate Scope of 3-Amino Oxindole Hydrochlorides and Aldehydes.



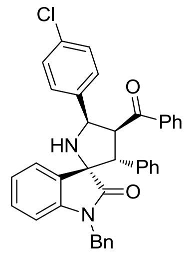
5baa

120 h, 83% yield,
8:1 rr, 94% *ee*, 80% *ee*



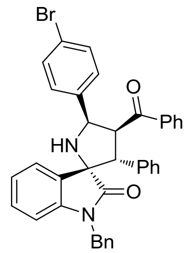
5caa

88 h, 99% yield,
9:1 rr, 96% *ee*, 85% *ee*



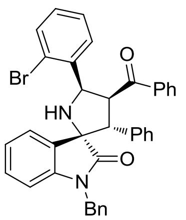
5cca

82 h, 99% yield,
9:1 rr, 97% *ee*, -



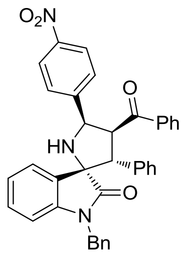
5cea

82 h, 96% yield,
8:1 rr, 96% *ee*, 92% *ee*



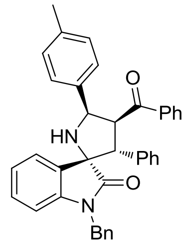
5cfa

86 h, 99% yield,
8:1 rr, 95% *ee*, 91% *ee*



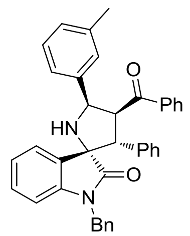
5cga

80 h, 99% yield,
5:1 rr, 99% *ee*, 94% *ee*



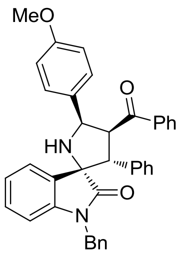
5cha

120 h, 99% yield,
10:1 rr, 95% *ee*, 82% *ee*



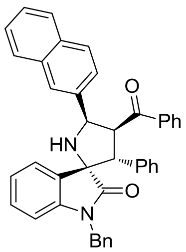
5cia

84 h, 99% yield,
9:1 rr, 94% *ee*, -



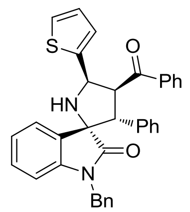
5cja

120 h, 50% yield,
11:1 rr, 90% *ee*, -



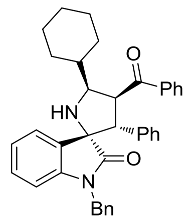
5cka

86 h, 99% yield,
16:1 rr, 98% *ee*, -



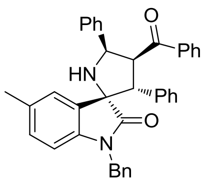
5cla

84 h, 87% yield,
> 20:1 rr, 94% ee, 82% *ee*



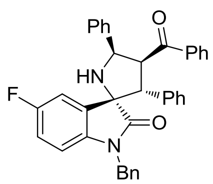
5cma

120 h, 99% yield,
3:1 rr, 56% *ee*, -



5daa

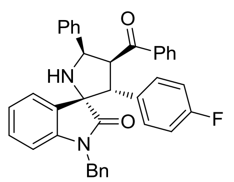
85 h, 99% yield,
4:1 rr, 92% *ee*, 81% *ee*



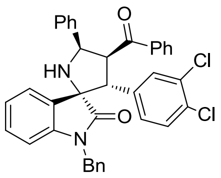
5eaa

85 h, 97% yield,
16:1 rr, 93% *ee*, 45% *ee*

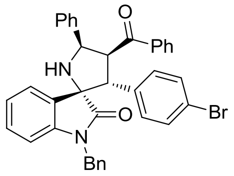
Scheme S2. Substrate Scope of α,β-Enones.



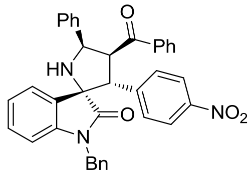
5cab
82 h, 99% yield,
8:1 rr, 95% *ee*, -



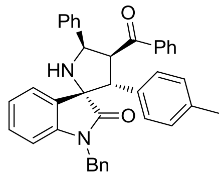
5cac
95 h, 99% yield,
4:1 rr, 95% *ee*, 81% *ee*



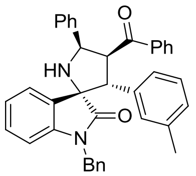
5cad
87 h, 99% yield,
6:1 rr, 96% *ee*, -



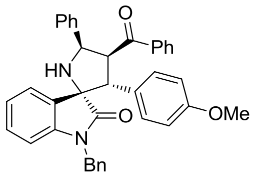
5cae
82 h, 99% yield,
4:1 rr, 97% *ee*, 74% *ee*



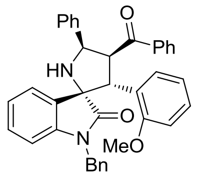
5caf
95 h, 99% yield,
10:1 rr, 96% ee, 84% *ee*



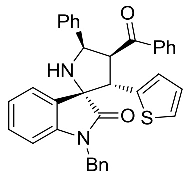
5cag
92 h, 99% yield,
10:1 rr, 94%, 82% *ee*



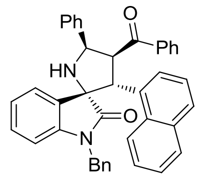
5cah
86 h, 99% yield,
16:1 rr, 95% *ee*, 85% *ee*



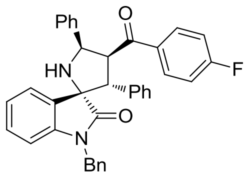
5cai
120 h, 98% yield,
8:1 rr, 91% *ee*, 47% *ee*



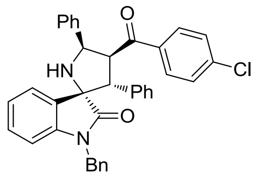
5caj
87 h, 99% yield,
16:1 rr, 94% *ee*, 68% *ee*



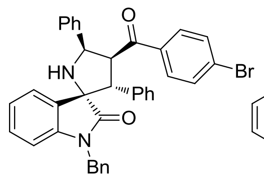
5cak
87 h, 99% yield,
12:1 rr, 95% *ee*, 67% *ee*



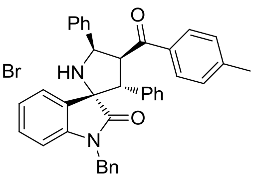
5cal
90 h, 99% yield,
7:1 rr, 96% *ee*, -



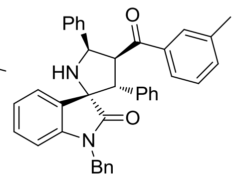
5cam
90 h, 99% yield,
6:1 rr, 95% *ee*, -



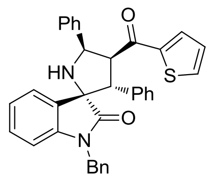
5can
87 h, 95% yield,
6:1 rr, 96% *ee*, 66% *ee*



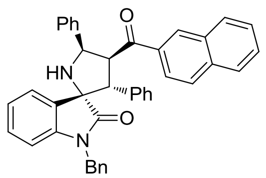
5cao
86 h, 99% yield,
10:1 rr, 96% *ee*, -



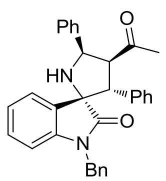
5cap
86 h, 99% yield,
8:1 rr, 95% *ee*, -



5caq
120 h, 62% yield,
5:1 rr, 91% *ee*, 64% *ee*



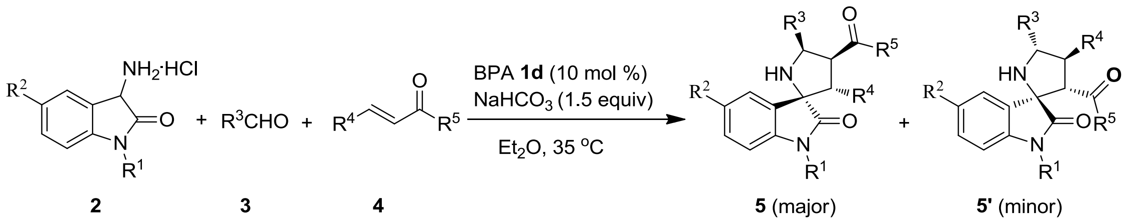
5car
120 h, 88% yield,
6:1 rr, 91% *ee*, 78% *ee*



5cas
120 h, 60% yield,
8:1 rr, 96% *ee*, 70% *ee*

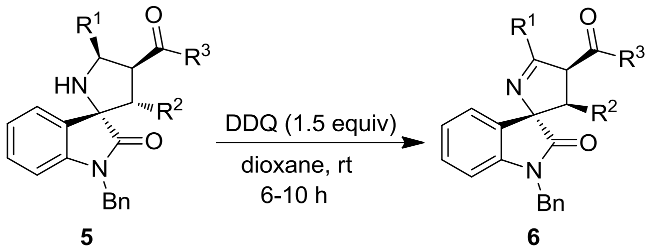
3. General Procedure for Synthesis of the Products

General Procedure for the Synthesis of Spiro[pyrrolidin-2,3'-oxindoles] (5)



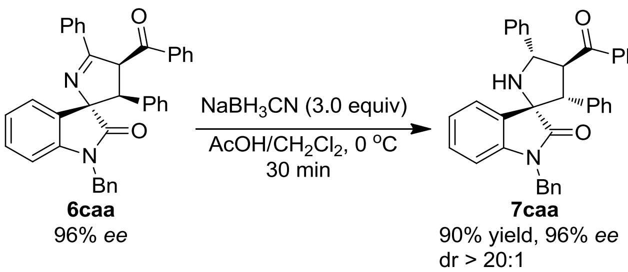
In a Schlenk tube, 3-amino oxindole hydrochloride **2** (0.2 mmol), $NaHCO_3$ (0.3 mmol), α,β-enone **4** (0.22 mmol), and catalyst (0.02 mmol) were added into Et_2O (2 mL) under a dry argon atmosphere at 35 °C. Then, aldehyde **3** (0.24 mmol) was added and the reaction solution was stirred at the same temperature. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5**.

The Method for the Synthesis of 3,4-Dihydrospiro[pyrrol-2,3'-oxindoles]



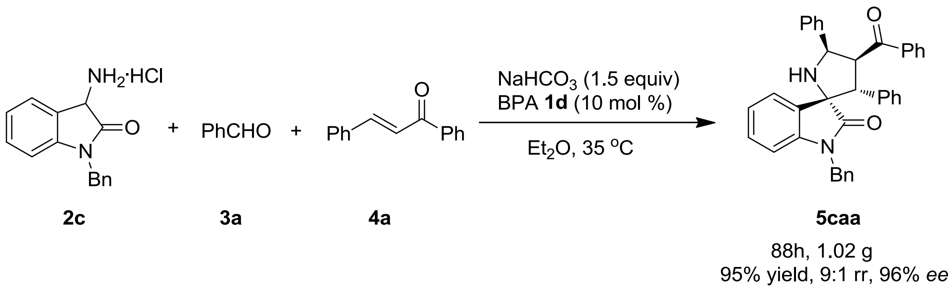
A reaction tube was charged with **5** (0.1 mmol) and dioxane (1 mL), then DDQ (0.15 mmol) was added at room temperature. The reaction was stirred until it was complete (monitored by TLC), then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/8) on silica gel to give the product **6**.

The Method for the Synthesis the Epimer of Spiro[pyrrolidin-2,3'-oxindole] (5caa) from Dihydrospiro[pyrrol-2,3'-oxindole] (7caa)



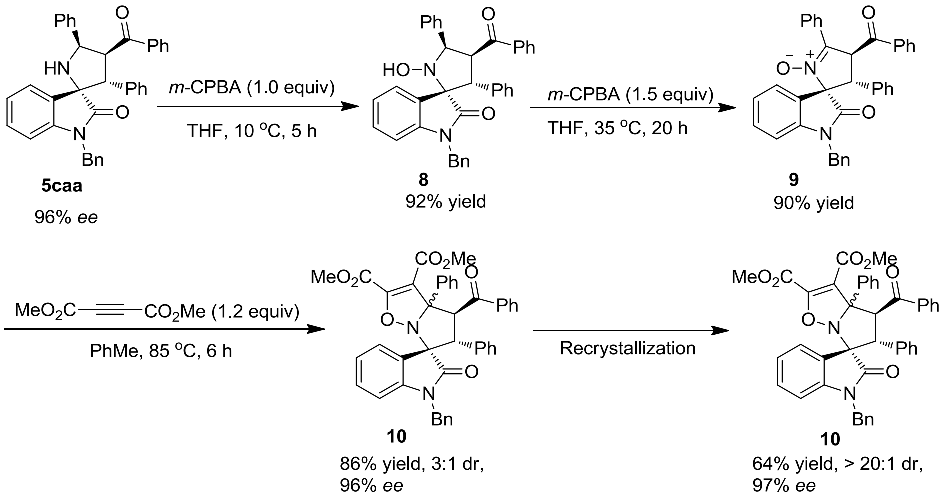
A reaction tube was charged with **6caa** (0.1 mmol) and 1 mL the mixture solvent ($AcOH/CH_2Cl_2$ = 1:1) at 0 °C, then $NaBH_3CN$ (0.3 mmol) was added at the same temperature. The reaction was stirred until it was complete (monitored by TLC), then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/8) on silica gel to give the product **7caa** with 90% (48 mg) yield.

Procedure for Gram-scale Reaction



In a Schlenk tube, 3-amino oxindole hydrochloride **2c** (2.2 mmol), BPA **1g** (0.22 mmol), chalcone **4a** (2.42 mmol) and $NaHCO_3$ (3.3 mmol) were added in Et_2O (22 mL) under an argon atmosphere at 35 °C. Then, benzaldehyde **3a** (2.64 mmol) was added and the solution was stirred at the same temperature for 65 h. The crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5caa** with 95% (1.02g) yield.

Procedure for the Synthesis of Compounds 8, 9 and 10

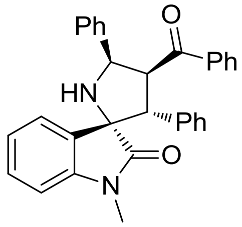


In a tube, the spiro[indoline-3,2'-pyrrolidin]-2-one **5caa** (0.2 mmol) was added in THF (2 mL) at 10 °C. Then, *m*-CPBA (0.2 mmol) was added at the same temperature and the reaction solution was stirred for 5 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/8 to 1/4) to afford product **8** with 92% (101 mg) yield.

In a tube, the spiro[indoline-3,2'-pyrrolidin]-2-one **8** (0.2 mmol) was added in THF (2 mL) at 35 °C, then *m*-CPBA (0.3 mmol) was added. The reaction mixture was stirred for 20 h. The solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/8 to 1/2) to afford product **9** with 90% (99 mg) yield.

In a tube, the nitrone derivative **9** (0.2 mmol) and dimethyl acetylenedicaroxylate (0.24 mmol) were added in toluene (2 mL) at room temperature. The reaction mixture was stirred at 85 °C for 6 h. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether =1/4) to afford product **10** with 86% (119 mg) yield, 96% *ee* and 3:1 dr. After the recrystallization of the crude product **10** through ethyl acetate and petroleum ether, almost single diastereoisomer was obtained with 64% yield, 97% *ee* and > 20:1 dr.

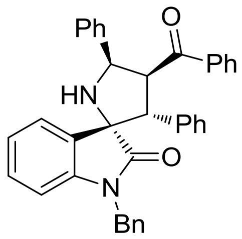
4. Characterization Datas



5baa

(2S,3R,4S,5R)-4-Benzoyl-1'-methyl-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

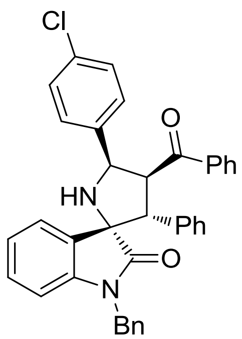
Yield: 83% (76 mg); 8:1 rr; White solid, mp: 169-171 ^{o}C, 94% *ee*. $[\alpha]_{D}^{13}$ = 44.1 (*c* 0.42, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.24 (m, 5H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.10 – 7.00 (m, 8H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.76 – 5.67 (m, 2H), 4.60 – 4.52 (m, 1H), 2.84 (s, 3H), 2.67 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 179.4, 143.7, 141.5, 137.9, 135.0, 132.8, 129.6, 129.2, 128.4, 128.3, 127.9, 127.8, 127.7, 127.4, 127.3, 127.4, 127.3, 123.5, 123.0, 107.9, 72.8, 62.2, 55.3, 52.9, 25.6; HRMS (ESI) for $C_{31}H_{27}N_2O_2$ $[M+H]^+$ calcd 459.2067, found 459.2051. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 25.9 min, t_R (minor) = 37.2 min.



5caa

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

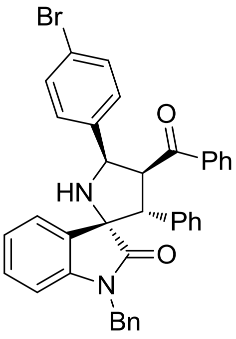
Yield: 99% (106 mg); 9:1 rr; White solid, mp: 88-90 ^{o}C, 96% *ee*. $[\alpha]_{D}^{13}$ = 92.8 (*c* 1.01, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 4H), 7.18 – 7.01 (m, 13H), 6.46 (d, *J* = 7.4 Hz, 2H), 6.34 (d, *J* = 7.6 Hz, 1H), 5.83 (t, *J* = 11.0 Hz, 1H), 5.73 (d, *J* = 10.6 Hz, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 2.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 179.4, 143.2, 141.5, 137.9, 135.2, 135.1, 132.9, 129.6, 129.4, 128.7, 128.4, 128.3, 128.2, 127.8, 127.5, 127.2, 126.5, 123.8, 123.1, 109.3, 72.6, 62.1, 54.8, 52.9, 43.5; HRMS (ESI) for $C_{37}H_{31}N_2O_2$ $[M+H]^+$ calcd 535.2380, found 535.2364. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 95 : 5, 0.8 mL/min, λ = 254 nm) t_R (major) = 18.9 min, t_R (minor) = 30.0 min.



5cca

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-5-(4-chlorophenyl)-3-phenylspiro[pyrrolidin-2,3'-oxindole]

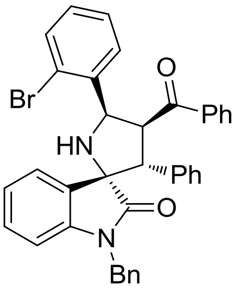
Yield: 99% (112 mg); 9:1 rr; White solid, mp: 101-103 ^{o}C, 97% *ee*. $[\alpha]_{D}^{13}$ = 72.5 (*c* 1.02, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.02 (m, 14H), 6.46 (d, *J* = 7.3 Hz, 2H), 6.35 (d, *J* = 7.6 Hz, 1H), 5.81 (t, *J* = 11.0 Hz, 1H), 5.71 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 2.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 179.3, 143.1, 140.1, 137.8, 135.0, 134.9, 133.1, 129.7, 129.4, 128.7, 128.5, 128.3, 128.1, 127.9, 127.6, 127.2, 126.5, 123.8, 123.2, 109.4, 72.5, 61.2, 54.5, 52.5, 43.5; HRMS (ESI) for $C_{37}H_{30}ClN_2O_2$ $[M+H]^+$ calcd 569.1990, found 569.1970. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 9.9 min, t_R (minor) = 20.3 min.



5cea

(2S,3R,4S,5R)-4-Benzoyl-1’-benzyl-5-(4-bromophenyl)-3-phenylspiro[pyrrolidin-2,3’-oxindole]

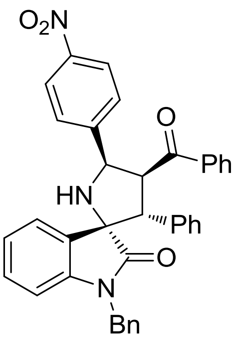
Yield: 96% (118 mg); 8:1 rr; White solid, mp: 99-101 ^{o}C, 96% *ee*. $[\alpha]_D^{13}$ = 59.1 (*c* 0.88, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.05 (m, 14H), 6.47 (d, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 7.3 Hz, 1H), 5.81 (t, *J* = 11.0 Hz, 1H), 5.70 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 179.3, 143.1, 140.6, 137.7, 135.0, 134.8, 133.1, 130.8, 130.1, 129.4, 128.7, 128.5, 128.4, 128.3, 128.1, 127.5, 127.2, 126.5, 123.8, 123.2, 121.4, 109.4, 72.5, 61.2, 54.5, 52.4, 43.5; HRMS (ESI) for $C_{37}H_{30}BrN_2O_2$ $[M+H]^+$ calcd 613.1485, found 613.1463. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 10.1 min, t_R (minor) = 21.4 min.



5cfa

(2S,3R,4S,5R)-4-Benzoyl-1’-benzyl-5-(2-bromophenyl)-3-phenylspiro[pyrrolidin-2,3’-oxindole]

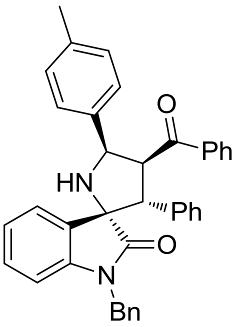
Yield: 99% (121 mg); 8:1 rr; White solid, mp: 89-91 ^{o}C, 95% *ee*. $[\alpha]_D^{13}$ = 100.6 (*c* 0.76, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.73 – 7.66 (m, 2H), 7.46 – 7.38 (m, 1H), 7.33-7.26 (m, 3H), 7.22 – 7.06 (m, 11H), 6.94 (td, *J* = 7.9, 1.7 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 2H), 6.43 – 6.31 (m, 2H), 5.72 (t, *J* = 10.3 Hz, 1H), 5.08 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 10.4 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 2.68 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 178.9, 143.1, 134.0, 137.6, 135.2, 132.8, 132.0, 130.8, 129.4, 129.3, 128.8, 128.6, 128.4, 128.3, 128.1, 127.5, 127.2, 126.5, 124.1, 124.0, 123.1, 109.2, 72.5, 60.3, 56.2, 52.1, 43.4; HRMS (ESI) for $C_{37}H_{30}BrN_2O_2$ $[M+H]^+$ calcd 613.1485, found 613.1470. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 25.2 min, t_R (minor) = 11.8 min



5cga

(2S,3R,4S,5R)-4-Benzoyl-1’-benzyl-5-(4-nitrophenyl)-3-phenylspiro[pyrrolidin-2,3’-oxindole]

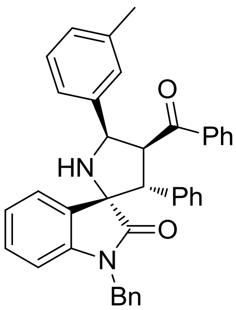
Yield: 99% (115 mg); 5:1 rr; Yellow solid, mp: 217-219 ^{o}C, 99% *ee*. $[\alpha]_D^{13}$ = 53.6 (*c* 0.79, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 6.8 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.50-7.45 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.04 (m, 10H), 6.49 (d, *J* = 7.3 Hz, 2H), 6.39 (d, *J* = 7.5 Hz, 1H), 5.96 – 5.79 (m, 2H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 11.0 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 2.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 179.2, 149.3, 147.2, 143.1, 137.5, 134.9, 134.4, 133.5, 129.6, 129.2, 129.0, 128.7, 128.5, 128.2, 128.1, 127.7, 127.2, 126.5, 123.9, 123.3, 122.9, 109.5, 72.6, 61.0, 54.5, 52.2, 43.5; HRMS (ESI) for $C_{37}H_{30}N_3O_4$ $[M+H]^+$ calcd 580.2231, found 580.2211. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 12.0 min, t_R (minor) = 48.6 min.



5cha

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-phenyl-5-(p-tolyl)spiro[pyrrolidin-2,3'-oxindole]

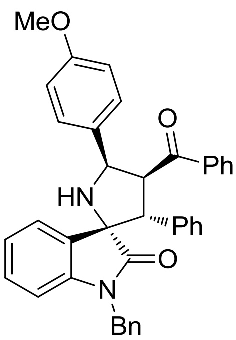
Yield: 99% (109 mg); 10:1 rr; White solid, mp: 92-94 ^{o}C, 95% *ee.* $[\alpha]_{D}^{13}$ = 84.9 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.02 (m, 12H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.46 (d, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 7.5 Hz, 1H), 5.82 (t, *J* = 11.0 Hz, 1H), 5.70 (d, *J* = 10.5 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.21 (d, *J* = 16.1 Hz, 1H), 2.68 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 179.4, 143.2, 138.5, 137.9, 137.0, 135.2, 135.1, 132.8, 129.7, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.4, 127.1, 126.5, 123.8, 123.1, 109.3, 72.6, 62.0, 54.8, 52.9, 43.5, 21.1; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ $[M+H]^+$ calcd 549.2537, found 549.2518. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 10.3 min, t_R (minor) = 20.6 min.



5cia

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-phenyl-5-(m-tolyl)spiro[pyrrolidin-2,3'-oxindole]

Yield: 99% (109 mg); 9:1 rr; White solid, mp: 88-90 ^{o}C, 94% *ee.* $[\alpha]_{D}^{13}$ = 98.6 (*c* 0.93, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.19 – 6.95 (m, 13H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 7.4 Hz, 1H), 5.81 (t, *J* = 11.0 Hz, 1H), 5.69 (d, *J* = 10.6 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.21 (d, *J* = 16.1 Hz, 1H), 2.67 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 179.4, 143.2, 141.3, 138.1, 137.2, 135.2, 135.1, 132.7, 129.7, 129.3, 128.7, 128.3, 128.2, 127.8, 127.4, 127.1, 126.5, 125.3, 123.8, 123.1, 109.3, 72.6, 62.1, 54.7, 53.0, 43.5, 21.3; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ $[M+H]^+$ calcd 549.2537, found 549.2520. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 12.0 min, t_R (minor) = 9.6 min.

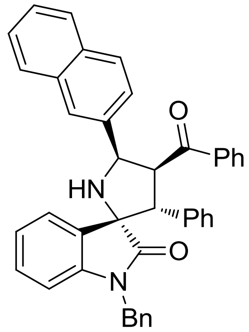


5cja

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-5-(4-methoxyphenyl)-3-phenylspiro[pyrrolidin-2,3'-oxindole]

Yield: 50% (56 mg); 11:1 rr; White solid, mp: 95-97 ^{o}C, 90% *ee.* $[\alpha]_{D}^{13}$ = 83.4 (*c* 0.41, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.04 (m, 12H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 7.2 Hz, 2H), 6.37 (d, *J* = 7.3 Hz, 1H), 5.79 (t, *J* = 10.9 Hz, 1H), 5.71 (d, *J* = 10.6 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.24 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 2.66 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 179.4, 158.8, 143.1, 137.9, 135.2, 135.1, 133.5, 132.8, 129.6, 129.4, 129.3, 128.6, 128.4, 128.3, 128.1, 127.4, 127.1, 126.5, 123.7, 123.1, 113.2, 109.3, 72.5, 61.6, 55.2, 54.7, 52.8, 43.4; HRMS (ESI) for $C_{38}H_{33}N_2O_3$ $[M+H]^+$ calcd 565.2486, found 565.2469. Enantiomeric excess was determined by

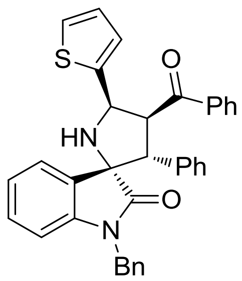
HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 9.9 min, t_R (minor) = 11.4 min.



5cka

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-5-(naphthalen-2-yl)-3-phenylspiro[pyrrolidin-2,3'-oxindole]

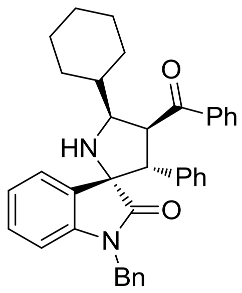
Yield: 99% (116 mg); 16:1 rr; White solid, mp: 83-85 °C, 98% *ee.* $[\alpha]_D^{13}$ = 69.9 (*c* 0.91, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 3H), 7.61 – 7.57 (m, 3H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.24 – 7.20 (m, 3H), 7.18 – 7.04 (m, 9H), 6.46 (d, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 7.6 Hz, 1H), 5.91 (d, *J* = 5.4 Hz, 2H), 5.07 (d, *J* = 16.0 Hz, 1H), 4.79 – 4.73 (m, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 179.4, 143.2, 138.9, 137.9, 135.1, 132.9, 132.8, 129.6, 129.4, 128.7, 128.5, 128.3, 128.2, 127.9, 127.6, 127.5, 127.2, 126.5, 126.2, 125.8, 125.7, 123.9, 123.2, 109.4, 72.7, 62.2, 54.8, 52.9, 43.5; HRMS (ESI) for $C_{41}H_{33}N_2O_2$ $[M+H]^+$ calcd 585.2537, found 585.2518. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 11.3 min, t_R (minor) = 18.8 min.



5cla

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-phenyl-5-(thiophen-2-yl)spiro[pyrrolidin-2,3'-oxindole]

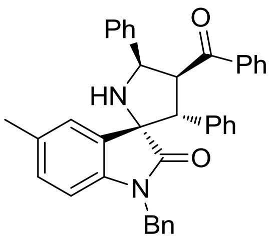
Yield: 87% (94 mg); > 20:1 rr; White solid, mp: 95-97 °C, 94% *ee.* $[\alpha]_D^{13}$ = 89.4 (*c* 0.99, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.89 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.11 (m, 5H), 7.10 – 6.99 (m, 6H), 6.66 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.45 (d, *J* = 7.3 Hz, 2H), 6.37 – 6.34 (m, 2H), 5.97 (d, *J* = 9.9 Hz, 1H), 5.88 (t, *J* = 10.8 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 2.99 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 179.3, 147.8, 143.0, 137.7, 135.0, 134.6, 133.2, 129.8, 129.4, 128.7, 128.5, 128.4, 128.0, 127.5, 127.2, 126.5, 124.9, 124.4, 124.2, 123.3, 109.3, 72.1, 57.6, 53.8, 52.2, 43.6; HRMS (ESI) for $C_{35}H_{29}N_2O_2S$ $[M+H]^+$ calcd 541.1944, found 541.1928. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 13.8 min, t_R (minor) = 16.6 min.



5cma

(2S,3R,4S,5S)-4-Benzoyl-1'-benzyl-5-cyclohexyl-3-phenylspiro[pyrrolidin-2,3'-oxindole]

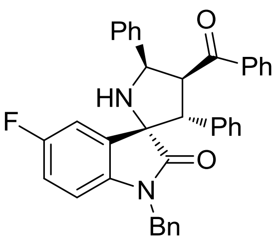
Yield: 99% (107 mg); 3:1 rr; Pale yellow solid, mp: 78-80 °C, 56% *ee.* $[\alpha]_D^{13}$ = 47.9 (*c* 0.66, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.66 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.497.45 (m, 2H), 7.17 – 7.02 (m, 8H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.43 (d, *J* = 7.3 Hz, 2H), 6.38 6.31 (m, 1H), 5.51 (t, *J* = 10.0, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.40 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.27 (d, *J* = 11.1 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 2.52 (s, 1H), 1.97 (d, *J* = 10.1 Hz, 1H), 1.75-1.70 (m, 1H), 1.57 (s, 2H), 1.45 – 1.34 (m, 3H), 1.18 – 1.00 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 179.1, 143.0, 138.1, 135.5, 135.2, 133.2, 130.5, 129.1, 128.9, 128.6, 128.3, 128.2, 127.9, 127.3, 127.1, 126.5, 123.5, 123.0, 109.1, 72.6, 64.4, 57.4, 51.4, 43.5, 40.7, 32.1, 27.8, 26.3, 26.0; HRMS (ESI) for $C_{37}H_{37}N_2O_2$ [M+H]$^+$ calcd 541.2850, found 541.2835. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 11.0 min, t_R (minor) = 7.7 min.



5daa

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-5'-methyl-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

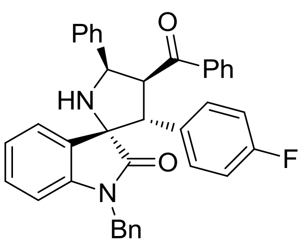
Yield: 99% (109 mg); 4:1 rr; White solid, mp: 88-90 °C, 92% *ee.* $[\alpha]_D^{13}$ = 114.3 (*c* 0.82, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.63 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.28 (m, 4H), 7.19 – 7.01 (m, 11H), 6.91 (dd, *J* = 7.9, 0.7 Hz, 1H), 6.46 (d, *J* = 7.2 Hz, 2H), 6.24 (d, *J* = 7.9 Hz, 1H), 5.81 (t, *J* = 10.9 Hz, 1H), 5.74 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 179.3, 141.5, 140.8, 137.9, 135.3, 135.2, 132.8, 132.7, 129.6, 128.6, 128.4, 128.3, 128.2, 127.8, 127.5, 127.4, 127.1, 126.5, 124.5, 109.1, 72.7, 62.2, 54.8, 52.9, 43.5, 21.3; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ [M+H]$^+$ calcd 549.2537, found 549.2519. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 13.1 min, t_R (minor) = 8.5 min.



5eaa

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-5'-fluoro-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

Yield: 97% (107 mg); 16:1 rr; White solid, mp: 104-106 °C, 92% *ee.* $[\alpha]_D^{13}$ = 84.9 (*c* 0.91, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 2H), 7.56 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.19 – 7.03 (m, 11H), 6.80 (td, *J* = 8.9, 2.6 Hz, 1H), 6.45 (d, *J* = 7.3 Hz, 2H), 6.25 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.86 – 5.70 (m, 2H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 10.7 Hz, 1H), 4.19 (d, *J* = 16.1 Hz, 1H), 2.71 (s, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 179.2, 159.7 (*J* = 242.4 Hz), 158.5, 141.2, 139.0 (*J* = 2.0 Hz), 137.8, 134.8, 132.86 (s), 131.60 (*J* = 7.5 Hz), 128.7, 128.5, 128.4, 128.3, 128.2 128.2, 127.8, 127.6, 127.3, 126.5, 115.61 (*J* = 24.2 Hz), 111.86 (*J* = 24.2 Hz), 109.98 (*J* = 7.9 Hz), 72.8, 62.0, 54.9, 52.7, 43.6 ; ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.43; HRMS (ESI) for $C_{37}H_{30}FN_2O_2$ [M+H]$^+$ calcd 553.2286, found 553.2270. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 12.1 min, t_R (minor) = 8.1 min.

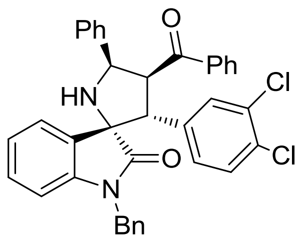


5cab

(2S,3R,4S,5R)-4-benzoyl-1'-Benzyl-3-(4-fluorophenyl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

Yield: 99% (109 mg); 8:1 rr; White solid, mp: 103-105 °C, 95% *ee.* $[\alpha]_D^{13}$ = 68.5 (*c* 1.12, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.25 (m, 4H), 7.20 – 6.99 (m, 10H), 6.72 (t, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 6.7

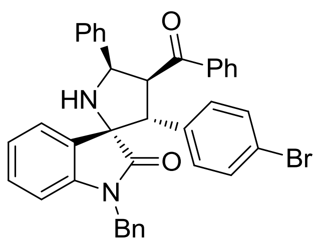
Hz, 2H), 6.45 – 6.38 (m, 1H), 5.82 – 5.67 (m, 2H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 10.6 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 2.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 179.2, 162.3 (*J* = 247.5 Hz), 161.1, 143.2, 141.3, 137.7, 135.0, 132.9, 130.9 (*J* = 3.0 Hz), 129.7 (*J* = 8.1 Hz), 129.5, 129.4, 128.6, 128.4, 128.3, 127.8, 127.5, 126.5, 123.8, 123.2, 115.4, 115.3 (*J* = 22.2 Hz), 109.3, 72.5, 62.0, 54.0, 53.0, 43.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.03; HRMS (ESI) for $C_{37}H_{30}FN_2O_2$ $[M+H]^+$ calcd 553.2286, found 553.2267. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 8.4 min, t_R (minor) = 9.7 min.



5cac

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-(3,4-dichlorophenyl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

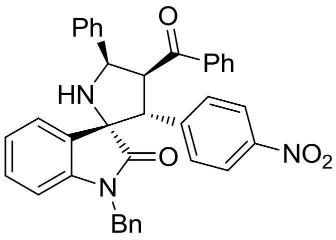
Yield: 99% (119 mg); 4:1 rr; White solid, mp: 163-165 °C, 95% *ee*. $[\alpha]_D^{13}$ = 130.6 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.74 – 7.68 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.21 – 7.14 (m, 6H), 7.10 – 7.02 (m, 4H), 6.87 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.64 – 6.62 (m, 2H), 6.52 – 6.44 (m, 1H), 5.79 – 5.60 (m, 2H), 5.08 (d, *J* = 15.8 Hz, 1H), 4.65 – 4.53 (m, 1H), 4.26 (d, *J* = 15.8 Hz, 1H), 2.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 178.9, 143.1, 141.1, 137.5, 135.8, 135.0, 133.1, 132.4, 131.6, 130.3, 130.0, 129.7, 128.9, 128.8, 128.4, 128.3, 127.8, 127.6, 127.5, 126.5, 123.7, 123.4, 109.5, 72.2, 62.0, 53.7, 53.1, 43.7; HRMS (ESI) for $C_{37}H_{29}Cl_2N_2O_2$ $[M+H]^+$ calcd 603.1601, found 603.1581. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 8.7 min, t_R (minor) = 10.2 min.



5cad

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-(4-bromophenyl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

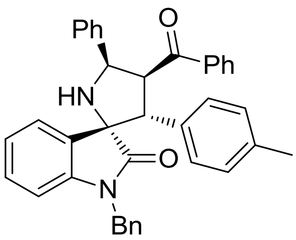
Yield: 96% (121 mg); 6:1 rr; White solid, mp: 179-181 °C, 96% *ee*. $[\alpha]_D^{13}$ = 115.5 (*c* 0.96, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.20 – 7.06 (m, 10H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.60 6.48 (m, 2H), 6.41 (d, *J* = 7.1 Hz, 1H), 5.83 – 5.66 (m, 2H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.62 (d, *J* = 10.4 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 179.1, 143.1, 141.3, 137.6, 135.0, 134.3, 133.0, 131.5, 129.9, 129.5, 129.2, 128.8, 128.4, 128.3, 128.3, 127.8, 127.6, 127.4, 126.5, 123.8, 123.3, 121.6, 109.4, 72.3, 62.0, 54.1, 52.9, 43.6; HRMS (ESI) for $C_{37}H_{30}BrN_2O_2$ $[M+H]^+$ calcd 613.1485, found 613.1475. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 8.2 min, t_R (minor) = 10.2 min.



5cae

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-(4-nitrophenyl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

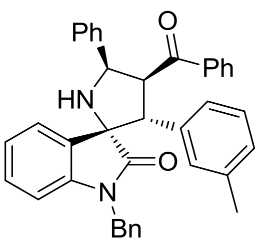
Yield: 99% (115 mg); 4:1 rr; White solid, mp: 179-181 °C, 96% *ee*. $[\alpha]_D^{13}$ = 115.5 (*c* 0.96, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 3H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.02 (m, 12H), 6.64 (d, *J* = 7.5 Hz, 2H), 6.58 – 6.49 (m, 1H), 5.885.66 (m, 2H), 4.94 (d, *J* = 15.7 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.27 (d, *J* = 15.7 Hz, 1H), 2.76 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 178.7, 147.3, 143.0, 140.9, 137.3, 135.1, 133.2, 129.9, 129.0, 128.7, 128.5, 128.3, 127.9, 127.8, 126.8, 123.8, 123.5, 123.4, 109.4, 72.2, 62.0, 54.4, 53.1, 43.6; HRMS (ESI) for $C_{37}H_{30}N_3O_4$ $[M+H]^+$ calcd 580.2231, found 580.2215. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 51.2 min, t_R (minor) = 16.1 min.



5caf

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-5-phenyl-3-(p-tolyl)spiro[pyrrolidin-2,3'-oxindole]

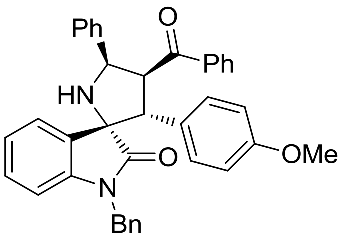
Yield: 99% (108 mg); 10:1 rr; White solid, mp: 180-182 °C, 96% *ee*. $[\alpha]_D^{13}$ = 120.6 (*c* 0.96, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.28 (m, 4H), 7.19–7.01 (m, 8H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.50 (d, *J* = 7.5 Hz, 2H), 6.35 (d, *J* = 7.6 Hz, 1H), 5.80 (t, *J* = 10.9 Hz, 1H), 5.72 (d, *J* = 10.6 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 11.3 Hz, 1H), 4.20 (d, *J* = 16.1 Hz, 1H), 2.69 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 179.5, 143.2, 141.6, 137.9, 136.9, 135.2, 132.8, 132.1, 129.7, 129.3, 129.1, 128.5, 128.4, 128.3, 128.0, 127.8, 127.5, 127.2, 126.6, 123.8, 123.1, 109.3, 72.6, 62.1, 54.5, 53.0, 43.5, 21.2; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ $[M+H]^+$ calcd 549.2537, found 549.2524. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 16.6 min, t_R (minor) = 15.7 min.



5cag

(2S,3R,4S,5R)-4-benzoyl-1'-Benzyl-5-phenyl-3-(m-tolyl)spiro[pyrrolidin-2,3'-oxindole]

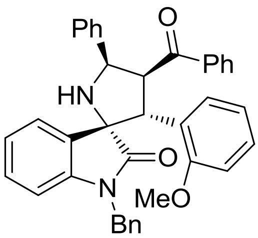
Yield: 99% (108 mg); 10:1 rr; White solid, mp: 93-95 °C, 94% *ee*. $[\alpha]_D^{13}$ = 89.9 (*c* 1.03, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.20 – 7.02 (m, 8H), 6.99 – 6.92 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.46 (d, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 7.6 Hz, 1H), 5.81 (t, *J* = 11.0 Hz, 1H), 5.73 (d, *J* = 10.6 Hz, 1H), 5.10 (d, *J* = 16.1 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.21 (d, *J* = 16.1 Hz, 1H), 2.70 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 179.5, 143.2, 141.5, 137.8, 135.2, 135.0, 132.8, 129.7, 129.3, 128.7, 128.6, 128.4, 128.3, 127.8, 127.5, 127.2, 126.4, 125.2, 123.8, 123.1, 109.3, 72.6, 62.1, 54.7, 52.8, 43.5, 21.4; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ $[M+H]^+$ calcd 549.2537, found 549.2525. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), t_R (major) = 8.3 min, t_R (minor) = 14.8 min.



5cah

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-3-(4-methoxyphenyl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

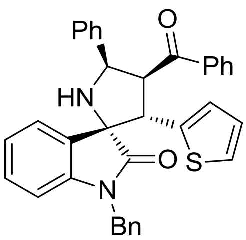
Yield: 99% (112 mg); 16:1 rr; White solid, mp: 188-190 °C, 95% *ee.* $[\alpha]_D^{13}$ = 126.3 (*c* 0.83, CH_2Cl_2); ^1H NMR (400 MHz, CDCl3) δ 7.80 (d, *J* = 7.1 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.29 (m, 4H), 7.19 – 7.02 (m, 8H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 7.5 Hz, 1H), 5.81 – 5.70 (m, 2H), 5.09 (d, *J* = 16.1 Hz, 1H), 4.63 (d, *J* = 11.2 Hz, 1H), 4.19 (d, *J* = 16.1 Hz, 1H), 3.64 (s, 3H), 2.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 179.5, 159.0, 143.2, 141.6, 137.9, 135.1, 132.9, 129.8, 129.3, 129.1, 128.5, 128.4, 128.3, 127.8, 127.5, 127.2, 127.1, 126.5, 123.8, 123.1, 113.8, 109.3, 72.6, 62.0, 55.0, 54.1, 52.9, 43.4; HRMS (ESI) for $C_{38}H_{33}N_2O_3$ $[M+H]^+$ calcd 565.2486, found 565.2473. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm), t_R (major) = 14.1 min, t_R (minor) = 16.7 min



5cai

(2S,3R,4S,5R)-4-benzoyl-1'-Benzyl-3-(2-methoxyphenyl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

Yield: 98% (111 mg); 8:1 rr; White solid, mp: 94-96 °C, 91% *ee.* $[\alpha]_D^{13}$ = 90.4 (*c* 0.73, CH_2Cl_2); ^1H NMR (400 MHz, CDCl3) δ 7.84 (d, *J* = 7.2 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.18 – 6.99 (m, 9H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 7.3 Hz, 2H), 6.32 (d, *J* = 7.7 Hz, 1H), 5.86 – 5.66 (m, 2H), 5.40 (d, *J* = 11.0 Hz, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 3.29 (s, 3H), 2.72 (s, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 198.4, 179.7, 158.4, 142.8, 141.5, 138.0, 135.3, 132.7, 129.7, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.5, 127.4, 127.1, 126.5, 125.0, 124.1, 122.4, 120.6, 110.7, 108.8, 72.5, 62.5, 55.0, 53.9, 46.2, 43.4; HRMS (ESI) for $C_{38}H_{33}N_2O_3$ $[M+H]^+$ calcd 565.2486, found 565.2674. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm), t_R (major) = 33.8 min, t_R (minor) = 38.3 min.

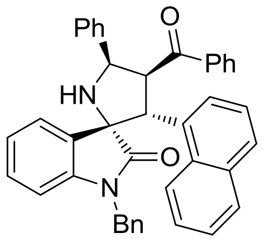


5caj

(2S,3S,4S,5R)-4-benzoyl-1'-Benzyl-5-phenyl-3-(thiophen-2-yl)spiro[pyrrolidin-2,3'-oxindole]

Yield: 99% (107 mg); 16:1 rr; White solid, mp: 103-105 °C, 94% *ee.* $[\alpha]_D^{13}$ = 70.9 (*c* 0.98, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.20 – 7.11 (m, 5H), 7.10 – 7.02 (m, 3H), 6.96 (d, *J* = 5.0 Hz, 1H), 6.74 (t, *J* = 4.4 Hz, 1H), 6.65 – 6.63 (m, 3H), 6.49– 6.46 (m, 1H), 5.78 – 5.64 (m, 2H), 5.09 (d, *J* = 15.9 Hz, 1H), 4.93 – 4.87(m, 1H), 4.29 (d, *J*

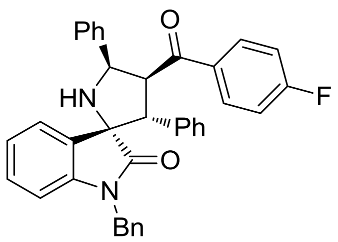
= 15.9 Hz, 1H), 2.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 179.0, 143.6, 141.1, 138.5, 137.7, 135.2, 133.0, 129.6, 129.1, 128.7, 128.5, 128.4, 128.3, 127.8, 127.6, 127.3, 126.8, 126.7, 125.2, 124.1, 123.9, 123.2, 109.3, 72.1, 61.9, 54.7, 50.2, 43.5; HRMS (ESI) for $C_{35}H_{29}N_2O_2S$ $[M+H]^+$ calcd 541.1944, found 541.1934. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm), t_R (major) = 52.8 min, t_R (minor) = 61.2 min.



5cak

(2S,3R,4S,5R)-4-benzoyl-1'-Benzyl-3-(naphthalen-1-yl)-5-phenylspiro[pyrrolidin-2,3'-oxindole]

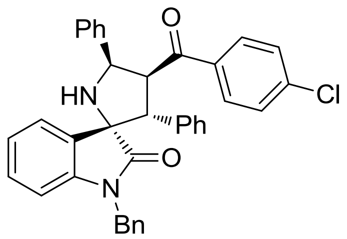
Yield: 99% (116 mg); 12:1 rr; White solid, mp: 101-103 °C, 95% *ee.* $[\alpha]^{13}_{D}$ = 21.9 (*c* 0.93, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.40– 7.34 (m, 3H), 7.30 – 7.21 (m, 5H), 7.14 – 7.02 (m, 5H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 7.7 Hz, 2H), 6.10 (d, *J* = 7.8 Hz, 1H), 5.93 (d, *J* = 9.9 Hz, 1H), 5.81 (t, *J* = 10.1 Hz, 1H), 5.74 (d, *J* = 10.2 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.15 (d, *J* = 16.1 Hz, 1H), 2.83 (s, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 198.8, 179.8, 142.9, 141.1, 137.9, 135.0, 133.8, 132.7, 132.3, 129.5, 129.3, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5, 127.1, 126.4, 125.6, 125.3 , 124.9, 124.2, 123.8, 122.8, 109.2, 73.0, 62.8, 56.1, 48.6, 43.4; HRMS (ESI) for $C_{41}H_{33}N_2O_2$ $[M+H]^+$ calcd 585.2537, found 585.2523. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column. (n-hexane:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm), t_R (major) = 18.1 min, t_R (minor) = 22.3 min.



5cal

(2S,3R,4S,5R)-1'-Benzyl-4-(4-fluorobenzoyl)-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

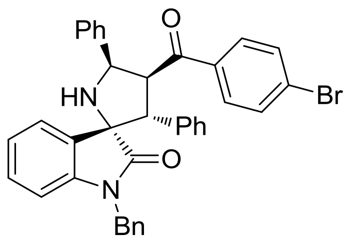
Yield: 99% (109 mg); 7:1 rr; White solid, mp: 107-109 °C, 96% *ee.* $[\alpha]^{13}_{D}$ = 82.1 (*c* 1.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.74 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.28 (d, *J* = 6.7 Hz, 2H), 7.18 – 7.02 (m, 13H), 6.97 (t, *J* = 8.5 Hz, 2H), 6.46 (d, *J* = 7.4 Hz, 2H), 6.35 (d, *J* = 7.6 Hz, 1H), 5.83 – 5.66 (m, 2H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 10.1 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 2.71 (s, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 196.5, 179.3, 165.6 (J = 255.5 Hz), 143.2, 141.3, 135.1, 134.32 (J = 2.9 Hz), 130.88 (J = 9.3 Hz), 129.5, 129.4, 128.7, 128.5, 128.4, 128.1, 127.9, 127.6, 127.6 (J = 10.1 Hz), 126.5, 123.8, 123.2, 115.5 (J = 22.2 Hz), 115.3, 109.4, 72.6, 62.1, 54.7, 52.9, 43.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -105.44; HRMS (ESI) for $C_{37}H_{30}FN_2O_2$ $[M+H]^+$ calcd 553.2286, found 553.2273. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), t_R (major) = 8.0 min, t_R (minor) = 11.4 min.



5cam

(2S,3R,4S,5R)-1'-Benzyl-4-(4-chlorobenzoyl)-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

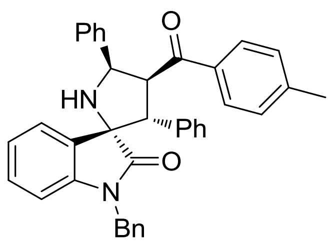
Yield: 99% (113 mg); 6:1 rr; White solid, mp: 103-105 °C, 95% *ee*. $[\alpha]_D^{13}$ = 79.2 (*c* 0.90, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 4H), 7.20 – 7.02 (m, 13H), 6.46 (d, *J* = 7.4 Hz, 2H), 6.35 (d, *J* = 7.5 Hz, 1H), 5.83 – 5.65 (m, 2H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 179.3, 143.1, 141.3, 139.2, 136.2, 135.0, 129.7, 129.4, 128.7, 128.5, 128.4, 128.0, 127.7, 127.6, 127.2, 126.5, 123.8, 123.2, 109.4, 72.6, 62.0, 54.6, 52.9, 43.5; HRMS (ESI) for $C_{37}H_{30}ClN_2O_2$ $[M+H]^+$ calcd 569.1990, found 569.1978. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), tR (major) = 8.4 min, tR (minor) = 13.7 min.



5can

(2S,3R,4S,5R)-1'-Benzyl-4-(4-bromobenzoyl)-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

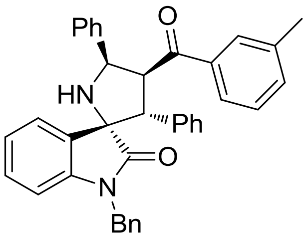
Yield: 95% (116 mg); 6:1 rr; White solid, mp: 105-107 °C, 96% *ee*. $[\alpha]_D^{13}$ = 78.2 (*c* 0.39, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.21 – 7.03 (m, 13H), 6.48 (d, *J* = 7.4 Hz, 2H), 6.37 (d, *J* = 7.6 Hz, 1H), 5.84 – 5.67 (m, 2H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.75 – 4.60 (m, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 179.3, 143.1, 141.2, 136.6, 135.0, 131.6, 129.7, 129.4, 129.3, 128.6, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6, 127.2, 126.4, 123.8, 123.2, 109.4, 72.5, 62.0, 54.6, 52.9, 43.5; HRMS (ESI) for $C_{37}H_{30}BrN_2O_2$ $[M+H]^+$ calcd 613.1485, found 613.1472. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), tR (major) = 17.9 min, tR (minor) = 24.0 min.



5cao

(2S,3R,4S,5R)-1'-Benzyl-4-(4-methylbenzoyl)-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

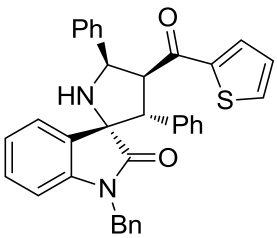
Yield: 99% (109 mg); 10:1 rr; White solid, mp: 99-101 °C, 96% *ee*. $[\alpha]_D^{13}$ = 93.6 (*c* 0.88, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.0 Hz, 2H), 7.19 – 7.00 (m, 15H), 6.45 (d, *J* = 7.4 Hz, 2H), 6.34 (d, *J* = 7.6 Hz, 1H), 5.82 (t, *J* = 11.0 Hz, 1H), 5.72 (d, *J* = 10.6 Hz, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 2.70 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 179.4, 143.7, 143.2, 141.6, 135.4, 135.2, 135.1, 129.7, 129.3, 129.1, 128.7, 128.5, 128.4, 128.1, 127.8, 127.5, 127.4, 127.2, 126.5, 123.8, 123.1, 109.3, 72.6, 62.2, 54.8, 52.6, 43.5, 21.7; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ $[M+H]^+$ calcd 549.2537, found 549.2523. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), tR (major) = 9.6 min, tR (minor) = 19.3 min.



5cap

(2S,3R,4S,5R)-1'-Benzyl-4-(3-methylbenzoyl)-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

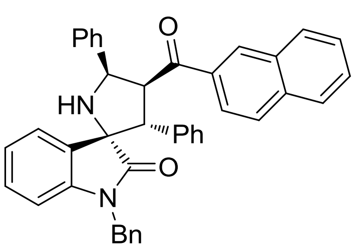
Yield: 99% (109 mg); 8:1 rr; White solid, mp: 99-101 ^{o}C, 96% *ee.* $[\alpha]_D^{13}$ = 85.6 (*c* 0.91, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.48 (s, 1H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.24 – 7.02 (m, 15H), 6.47 (d, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 7.6 Hz, 1H), 5.82 (t, *J* = 11.0 Hz, 1H), 5.73 (d, *J* = 10.6 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 179.4, 143.2, 141.6, 138.1, 138.0, 135.1, 133.6, 129.7, 129.3, 128.8, 128.7, 128.4, 128.2, 128.1, 127.9, 127.5, 127.2, 126.5, 125.6, 123.8, 123.1, 109.3, 72.6, 62.1, 54.7, 52.9, 43.5, 21.3; HRMS (ESI) for $C_{38}H_{33}N_2O_2$ $[M+H]^+$ calcd 549.2537, found 549.2525. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), tR (major) = 7.7 min, tR (minor) = 8.7 min.



5caq

(2S,3R,4S,5R)-1'-Benzyl-3,5-diphenyl-4-(thiophene-2-carbonyl)spiro[pyrrolidin-2,3'-oxindole]

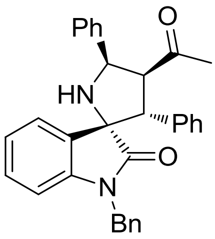
Yield: 62% (67 mg); 5:1 rr; White solid, mp: 196-198 ^{o}C, 91% *ee.* $[\alpha]_D^{13}$ = 99.6 (*c* 0.51, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 3.7 Hz, 1H), 7.47 (d, *J* = 4.9 Hz, 1H), 7.37 (d, *J* = 7.1 Hz, 2H), 7.20 – 7.03 (m, 14H), 6.46 (d, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 7.6 Hz, 1H), 5.77 (d, *J* = 10.5 Hz, 1H), 5.61 (t, *J* = 10.9 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 11.3 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 179.3, 145.6, 143.1, 141.1, 135.0, 134.9, 133.8, 132.0, 129.5, 129.4, 128.7, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.2, 126.4, 123.9, 123.2, 109.3, 72.6, 62.5, 54.6, 54.3, 43.4; HRMS (ESI) for $C_{35}H_{29}N_2O_2S$ $[M+H]^+$ calcd 541.1944, found 541.1934. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm), tR (major) = 8.9 min, tR (minor) = 10.8 min.



5car

(2S,3R,4S,5R)-4-(2-Naphthoyl)-1'-benzyl-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

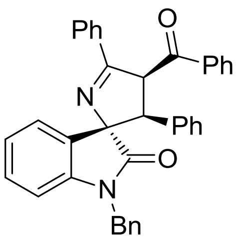
Yield: 88% (103 mg); 6:1 rr; White solid, mp: 113-115 ^{o}C, 91% *ee.* $[\alpha]_D^{13}$ = 95.0 (*c* 0.75, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.02 – 7.95 (m, 1H), 7.86 (d, *J* = 7.1 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.67 (dd, *J* = 22.6, 8.6 Hz, 2H), 7.57–7.52 (m, 2H), 7.33 – 7.27 (m, 2H), 7.20 – 7.00 (m, 13H), 6.49 (d, *J* = 7.4 Hz, 2H), 6.38 (d, *J* = 7.6 Hz, 1H), 6.02 (t, *J* = 11.1 Hz, 1H), 5.83 (d, *J* = 10.6 Hz, 1H), 5.07 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.25 (d, *J* = 16.1 Hz, 1H), 2.74 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 179.5, 143.2, 141.5, 135.5, 135.4, 135.1, 132.5, 130.0, 129.7, 129.4, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 127.2, 126.7, 126.5, 124.1, 123.9, 123.2, 109.4, 72.7, 62.2, 54.8, 52.8, 43.5; HRMS (ESI) for $C_{41}H_{33}N_2O_2$ $[M+H]^+$ calcd 585.2537, found 585.2519. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm), tR (major) = 38.7 min, tR (minor) = 45.2 min.



5cas

(2S,3R,4S,5R)-4-Acetyl-1'-benzyl-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

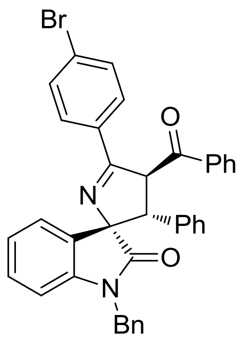
Yield: 60% (57 mg); 8:1 rr; White solid, mp: 85-87 °C, 96% *ee*. $[\alpha]_D^{13}$ = 90.5 (*c* 0.39, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.8 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 – 7.02 (m, 10H), 6.44 (d, *J* = 7.4 Hz, 2H), 6.34 (d, *J* = 7.4 Hz, 1H), 5.73 (d, *J* = 10.6 Hz, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.87 (t, *J* = 11.0 Hz, 1H), 4.44 (d, *J* = 11.4 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 2.61 (s, 1H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 179.0, 143.0, 141.6, 135.1, 135.0, 129.4, 129.3, 128.6, 128.4, 128.2, 128.1, 127.5, 127.1, 126.4, 123.7, 123.1, 109.3, 72.5, 61.2, 58.7, 54.8, 43.4, 31.5; HRMS (ESI) for $C_{32}H_{29}N_2O_2$ $[M+H]^+$ calcd 473.2224, found 473.2214. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 90:10, 0.5 mL/min, λ = 254 nm), tR (major) = 17.9 min, tR (minor) = 23.5 min.



6caa

(2S,3S,4S)-4-Benzoyl-1'-benzyl-3,5-diphenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

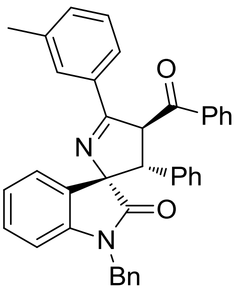
Yield: 95% (51 mg); White solid, mp: 83-85 °C, 96 % *ee*. $[\alpha]_D^{22}$ = -107.0 (*c* 0.62, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.29 (s, 1H), 7.25–7.20 (m, 4H), 7.18 – 7.10 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.46–6.43 (m, 3H), 6.37 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.43 (d, *J* = 10.8 Hz, 1H), 4.24 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 177.1, 174.1, 143.3, 136.7, 134.9, 133.9, 133.6, 133.2, 131.2, 129.7, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 127.1, 126.5, 124.4, 123.4, 109.4, 85.5, 62.2, 59.5, 43.8; HRMS (ESI) for $C_{37}H_{29}N_2O_2$ $[M+H]^+$ calcd 533.2224, found 533.2223. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 35.2 min, tR (minor) = 17.8 min.



6cea

(2S,3R,4S)-4-Benzoyl-1'-benzyl-5-(4-bromophenyl)-3-phenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

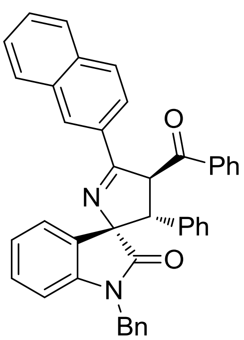
Yield: 91% (56 mg); White solid, mp: 107-109 ^{o}C, 97 % *ee.* $[\alpha]_{D}^{22}$ = -111.3 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.54 (m, 4H), 7.46 – 7.41 (m, 4H), 7.23 – 7.10 (m, 8H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.45 (d, *J* = 7.1 Hz, 3H), 6.34 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 176.2, 173.8, 143.2, 136.5, 134.8, 134.1, 133.3, 132.1, 131.8, 129.8, 129.4, 129.1, 128.7, 128.8, 128.7, 128.6, 127.2, 126.4, 125.9, 124.4, 123.4, 109.5, 85.5, 62.3, 59.3, 43.8; HRMS (ESI) for $C_{37}H_{28}BrN_2O_2$ $[M+H]^+$ calcd 613.1314, found 613.1302. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 31.0 min, tR (minor) = 36.8 min.



6cia

(2S,3R,4S)-4-Benzoyl-1'-benzyl-3-phenyl-5-(m-tolyl)-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

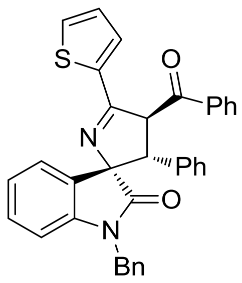
Yield: 95% (52 mg); White solid, mp: 88-90 ^{o}C, 94 % *ee.* $[\alpha]_{D}^{22}$ = -102.8 (*c* 0.51, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.67–7.65 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.22 (d, *J* = 6.9 Hz, 3H), 7.19 – 7.11 (m, 7H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.45 (d, *J* = 7.7 Hz, 3H), 6.36 (d, *J* = 10.8 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.24 (d, *J* = 16.0 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 177.3, 174.0, 143.3, 138.3, 136.9, 134.9, 133.8, 133.6, 133.1, 132.0, 129.7, 129.0, 128.7, 128.6, 128.3, 127.9, 127.1, 126.4, 125.4 124.4, 123.4, 109.4, 85.4, 62.1, 59.5, 43.8, 21.2; HRMS (ESI) for $C_{38}H_{31}N_2O_2$ $[M+H]^+$ calcd 547.2380, found 547.2365. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 24.9 min, tR (minor) = 10.5 min.



6cka

(2S,3R,4S)-4-Benzoyl-1'-benzyl-5-(naphthalen-2-yl)-3-phenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

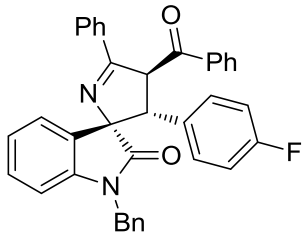
Yield: 95% (56 mg); White solid, mp: 101-103 ^{o}C, 96 % *ee.* $[\alpha]_{D}^{22}$ = -66.9 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.71– 7.69 (m, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.43 – 7.37 (m, 1H), 7.28 (s, 1H), 7.24 –7.23 (m, 2H), 7.20 – 7.17 (m, 4H), 7.12 (d, *J* = 7.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.51 (d, *J* = 10.8 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 3H), 5.12 (d, *J* = 16.0 Hz, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.26 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 177.4, 174.0, 143.3, 136.9, 134.9, 134.7, 134.0, 133.5, 132.6, 130.4, 129.8, 129.5, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.7, 127.3, 127.2, 126.6, 126.5, 124.9, 124.5, 123.8, 123.5, 109.5, 85.3, 62.1, 59.6, 43.9; HRMS (ESI) for $C_{41}H_{31}N_2O_2$ $[M+H]^+$ calcd 583.2380, found 583.2364. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 41.3 min, tR (minor) = 22.3 min.



6cla

(2S,3R,4S)-4-Benzoyl-1'-benzyl-3-phenyl-5-(thiophen-2-yl)-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

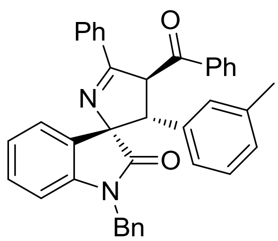
Yield: 93% (50 mg); White solid, mp: 203-205 °C, 97 % *ee*. $[\alpha]_D^{22}$ = -61.7 (*c* 0.36, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.66–7.63 (m, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 5.0 Hz, 1H), 7.23 – 7.09 (m, 8H), 7.05 (t, *J* = 6.8 Hz, 3H), 6.88 (t, *J* = 4.4 Hz, 1H), 6.42 (d, *J* = 7.4 Hz, 3H), 6.33 (d, *J* = 11.1 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.51 (d, *J* = 11.1 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 173.9, 170.5, 143.3, 134.9, 134.1, 133.3, 130.5, 129.7, 129.2, 128.9, 128.6, 128.5, 127.9, 127.6, 127.1, 126.4, 124.5, 123.4, 109.4, 85.1, 62.5, 59.2, 43.8; HRMS (ESI) for $C_{35}H_{27}N_2O_2S$ $[M+H]^+$ calcd 539.1788, found 539.1770. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 35.7 min, tR (minor) = 24.6 min.



6cab

(2S,3R,4S)-4-Benzoyl-1'-benzyl-3-(4-fluorophenyl)-5-phenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

Yield: 87% (48 mg); White solid, mp: 91-93 °C, 97 % *ee*. $[\alpha]_D^{22}$ = -154.7 (*c* 0.27, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.14 (m, 5H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.84 (t, *J* = 8.4 Hz, 2H), 6.51 (t, *J* = 6.6 Hz, 3H), 6.30 (d, *J* = 11.0 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 4.27 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 177.0, 173.9, 162.5 (*J* = 247.5 Hz), 143.3, 136.6, 134.9, 134.0, 133.1, 131.2, 130.3, 129.8, 129.5, 129.4 (*J* = 3.0 Hz), 129.1, 128.7, 128.5, 128.3, 127.4, 126.5, 124.4, 123.5, 115.5 (*J* = 22.2 Hz), 109.4, 85.3, 61.5, 59.6, 43.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.03; HRMS (ESI) for $C_{37}H_{28}FN_2O_2$ $[M+H]^+$ calcd 551.2129, found 551.2155. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 37.6 min, tR (minor) = 11.5 min.

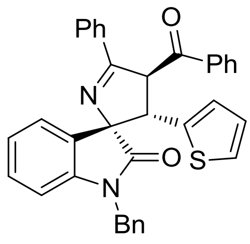


6cag

(2S,3R,4S)-4-Benzoyl-1'-benzyl-5-phenyl-3-(m-tolyl)-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

Yield: 85% (47 mg); White solid, mp: 88-90 °C, 96 % *ee*. $[\alpha]_D^{22}$ = -133.8 (*c* 0.45, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.68 – 7.61 (m, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.19 – 6.96 (m, 9H), 6.46 (d, *J* = 7.3 Hz, 3H), 6.36 (d, *J* = 10.8 Hz, 1H), 5.13 (d, *J*

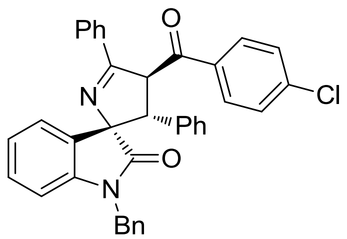
= 16.0 Hz, 1H), 4.40 (d, *J* = 10.8Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 177.1, 174.1, 143.3, 138.1, 136.8, 135.1, 133.9, 133.5, 133.3, 131.1, 129.9, 129.6, 129.3, 129.0, 128.8, 128.7, 128.5, 128.3, 127.1, 126.4, 125.7, 124.4, 123.3, 109.3, 85.4, 62.2, 59.4, 43.8, 21.3; HRMS (ESI) for $C_{38}H_{31}N_2O_2$ $[M+H]^+$ calcd 547.2380, found 547.2365. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.4 mL/min, λ = 254 nm) tR (major) = 17.4 min, tR (minor) = 13.1 min.



6caj

(2S,3S,4S)-4-Benzoyl-1'-benzyl-5-phenyl-3-(thiophen-2-yl)-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

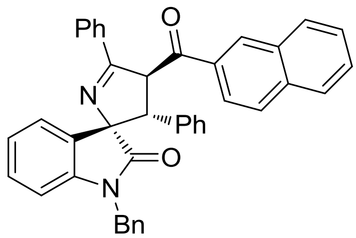
Yield: 95% (51 mg); White solid, mp: 82-84 °C, 94 % *ee*. $[\alpha]_D^{22}$ = -128.4 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.62–7.56 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.24–7.23 (m, 2H), 7.21 – 7.11 (m, 5H), 7.03 (d, *J* = 5.0 Hz, 1H), 6.87–6.86 (m, 1H), 6.80 (t, *J* = 4.3 Hz, 1H), 6.70 (d, *J* = 7.0 Hz, 2H), 6.54 (d, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 10.8 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.71 (d, *J* = 10.8 Hz, 1H), 4.37 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 176.9, 173.8, 143.7, 136.7, 136.2, 135.1, 134.1, 133.1, 131.2, 129.9, 129.4, 129.1, 128.9, 128.7, 128.5, 128.2, 127.3, 127.0, 126.8, 126.5, 124.7, 124.4, 123.5, 109.5, 84.8, 60.8, 57.2, 43.9; HRMS (ESI) for $C_{35}H_{27}N_2O_2S$ $[M+H]^+$ calcd 539.1788, found 539.1770. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 29.2 min, tR (minor) = 22.3 min.



6cam

(2S,3R,4S)-1'-Benzyl-4-(4-chlorobenzoyl)-3,5-diphenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

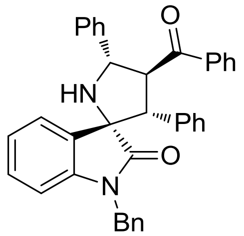
Yield: 85% (48 mg); White solid, mp: 113-115 °C, 94 % *ee*. $[\alpha]_D^{22}$ = -115.7 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.43 – 7.37 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.10 (m, 8H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.47 – 6.44 (m, 3H), 6.30 (d, *J* = 10.8 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 176.7, 174.0, 143.3, 140.6, 134.9, 133.4, 133.2, 131.2, 130.1, 129.7, 129.6, 129.4, 128.7, 128.6, 128.2, 128.1, 127.1, 126.4, 124.3, 123.4, 109.4, 85.6, 62.3, 59.5, 43.8; HRMS (ESI) for $C_{37}H_{27}ClN_2NaO_2$ $[M+Na]^+$ calcd 589.1653, found 589.1643. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 11.4 min, tR (minor) = 7.0 min.



6car

(2S,3R,4S)-4-(2-Naphthoyl)-1'-benzyl-3,5-diphenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]

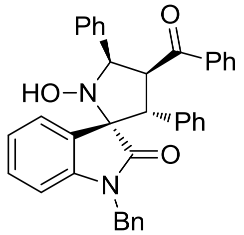
Yield: 96% (56 mg); White solid, mp: 225-227 °C, 92 % *ee*. $[\alpha]_D^{22}$ = -37.0 (*c* 0.31, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.82 (m, 3H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.62–7.53 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.24 (s, 1H), 7.20–7.11 (m, 6H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.53 (d, *J* = 10.8 Hz, 1H), 6.49–6.44 (m, 3H), 5.13 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 10.8 Hz, 1H), 4.26 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 177.2, 174.2, 143.3, 135.9, 135.0, 134.0, 133.7, 133.3, 132.5, 131.1, 129.8, 129.7, 129.1, 129.0, 128.8, 128.6, 128.3, 128.0, 127.8, 127.1, 126.5, 124.4, 124.1, 123.4, 109.4, 85.6, 62.4, 59.6, 43.8; HRMS (ESI) for $C_{41}H_{31}N_2O_2$ $[M+H]^+$ calcd 583.2380, found 583.2366. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 67.1 min, tR (minor) = 25.3 min.



7caa

(2S,3R,4S,5S)-4-Benzoyl-1'-benzyl-3,5-diphenylspiro[pyrrolidin-2,3'-oxindole]

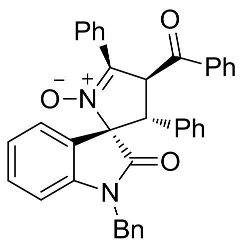
Yield: 90% (48 mg); White solid, mp: 87-89 °C, 96 % *ee.* $[\alpha]_D^{22}$= -200.0 (*c* 0.37, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2 Hz, 3H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.03 (m, 9H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.91– 6.90 (m, 2H), 6.43–6.38 (m, 3H), 5.53 (dd, *J* = 11.8, 9.9 Hz, 1H), 5.06 (d, *J* = 15.9 Hz, 1H), 5.00 – 4.90 (m, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.20 (d, *J* = 15.9 Hz, 1H), 2.74 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 178.7, 143.0, 142.0, 137.4, 135.1, 134.0, 133.1, 131.3, 129.3, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.6, 127.1, 126.5, 123.3, 123.1, 109.3, 72.3, 68.4, 60.7, 56.2, 43.8; HRMS (ESI) for $C_{37}H_{31}N_2O_2$ $[M+H]^+$ calcd 535.2380, found 535.2368. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) tR (major) = 46.1 min, tR (minor) = 12.1 min.



8

(2S,3R,4S,5R)-4-Benzoyl-1'-benzyl-1-hydroxy-3,5-diphenylspiro[pyrrol-2,3'-oxindole]

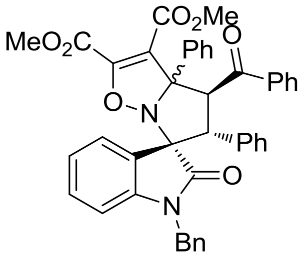
Yield: 92% (101 mg); White solid, mp: 116-118 °C, $[\alpha]_D^{13}$ = 109.6 (*c* 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.25 (m, 4H), 7.20 – 7.04 (m, 13H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.40 (d, *J* = 7.1 Hz, 1H), 5.81 – 5.71 (m, 2H), 5.07 (d, *J* = 16.1 Hz, 1H), 4.79 (d, *J* = 9.3 Hz, 1H), 4.73 (s, 1H), 4.47 (d, *J* = 16.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 175.3, 143.9, 138.8, 137.5, 135.1, 134.8, 132.7, 129.6, 129.2, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 127.4, 127.1, 126.5, 123.8, 122.9, 109.3, 78.2, 69.3, 49.8, 49.5, 43.3; HRMS (ESI) for $C_{37}H_{31}N_2O_3$ $[M+H]^+$ calcd 551.2329, found 551.2328.



9

(2S,3R,4S)-4-Benzoyl-1'-benzyl-2-oxo-3,5-diphenyl-3,4-dihydrospiro[pyrrol-2,3'-oxindole]- 1-oxide

Yield: 90% (99 mg); White solid, mp: 124-126 °C, 96% *ee*. $[\alpha]_D^{13}$ = -129.6 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.75 – 7.70 (m, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.25 (m, 6H), 7.21 – 7.17 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 2H), 6.50 – 6.45 (m, 3H), 6.37 (d, *J* = 9.5 Hz, 1H), 5.08 (d, *J* = 16.1 Hz, 1H), 4.33 (dd, *J* = 12.8, 6.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 171.3, 144.4, 144.1, 136.0, 134.4, 134.3, 131.9, 131.2, 130.8, 129.3, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 127.9, 127.3, 126.4, 124.8, 124.7, 123.9, 110.0, 87.0, 54.4, 52.7, 43.9; HRMS (ESI) for $C_{37}H_{29}N_2O_3$ $[M+H]^+$ calcd 549.2173, found 549.2168.

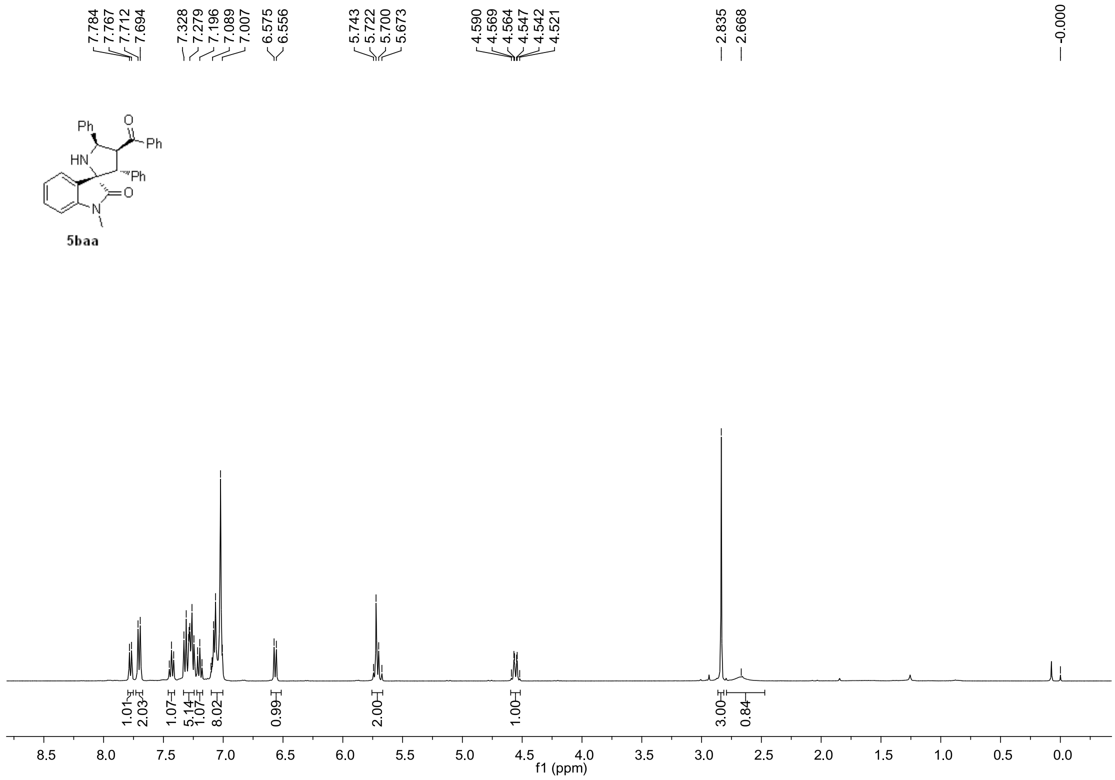


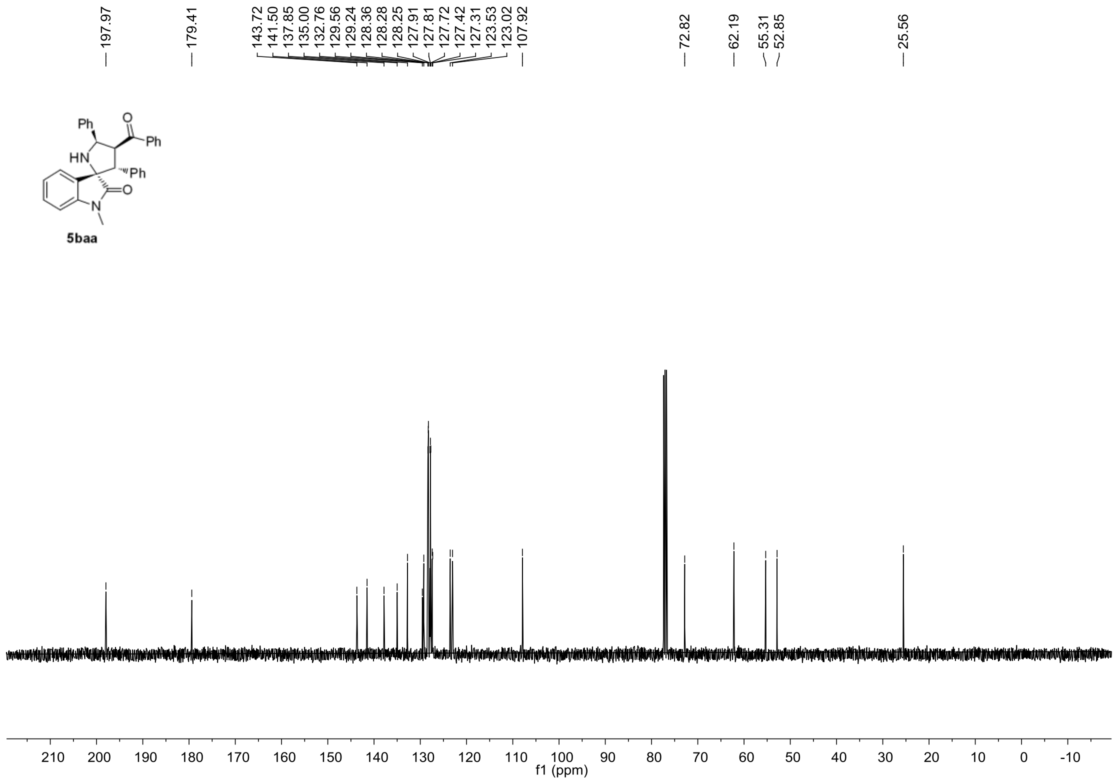
10

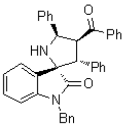
(3S,4S,5R)-Dimethyl-4-benzoyl-1'-benzyl-2-oxo-3a,5-diphenyl-4,5-dihydro-3aH-spiro[indoline-3',6-pyrrolo[1,2-b]isoxazole]-2,3-dicarboxylate

Yield: 86% (119 mg); 3:1 dr; White solid, mp: 125-127 ^{o}C, 96% *ee*. $[\alpha]_D^{13}$ = 194.0 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 14.8, 7.5 Hz, 4H), 7.80 (s, 1H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.39 – 7.25 (m, 5H), 7.19 – 6.97 (m, 10H), 6.50 (d, *J* = 6.9 Hz, 2H), 6.42 – 6.28 (m, 2H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.30 (d, *J* = 16.1 Hz, 1H), 3.95 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 173.5, 162.1, 159.2, 154.3, 143.6, 142.1, 137.8, 134.7, 133.3, 132.6, 130.2, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.2, 126.4, 123.3, 122.8, 109.7, 109.5, 85.6, 79.9, 58.1, 55.0, 53.5, 51.5, 43.6; HRMS (ESI) for $C_{43}H_{34}N_2NaO_7$ $[M+Na]^+$ calcd 713.2258, found 713.2260. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexane:i-propanol = 80:20, 0.7 mL/min, λ = 254 nm), tR (major) = 38.6 min, tR (minor) = 22.0 min.

5. Copies of ^{1}H and ^{13}C NMR Spectra



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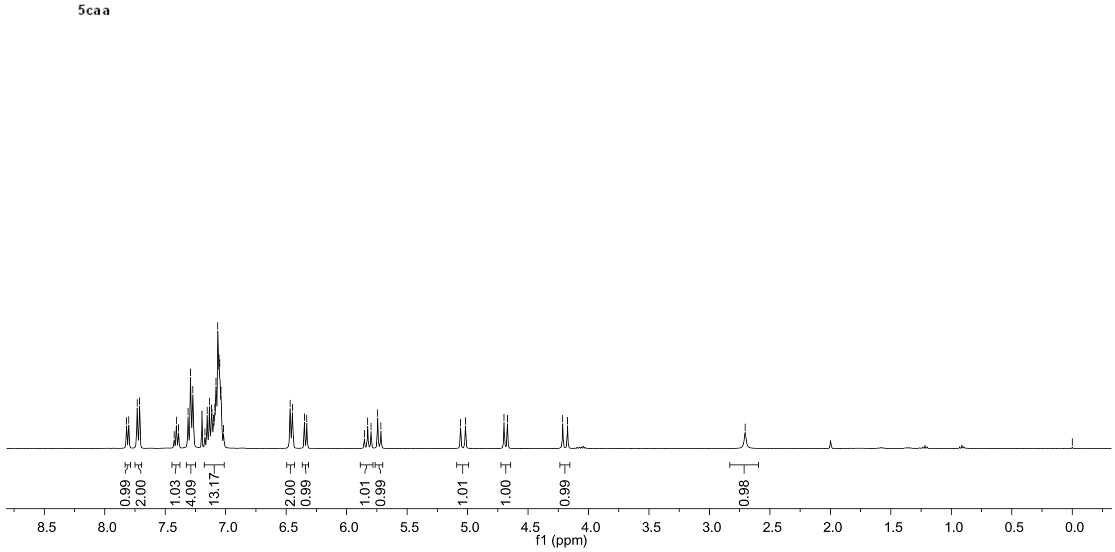
HN
O
Ph
Ph
N
O
Bn

5caa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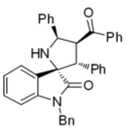
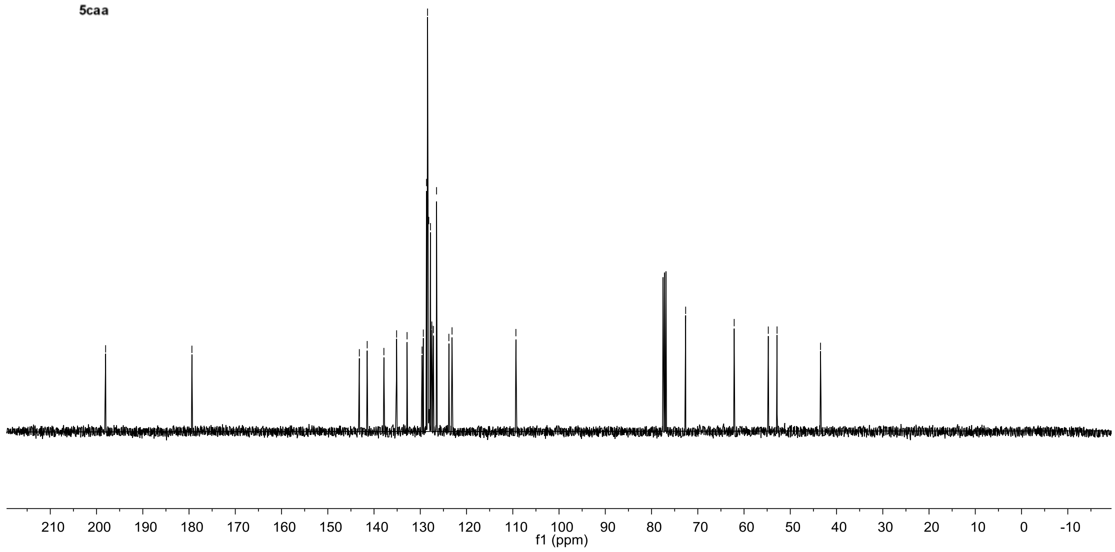
6.449
6.349
6.330
5.853
5.826
5.798
5.743
5.717
5.058
5.018
4.699
4.670
4.213
4.173
2.705
-0.000
0.99
2.00
1.03
4.09
13.17
2.00
0.99
1.01
0.99
1.01
1.00
0.99
0.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
HN
O
Ph
Ph
N
O
Bn

5caa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128.32
128.16
127.80
127.51
127.46
127.16
126.48
123.82
123.13
109.33
72.62
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54.76
52.86
43.46
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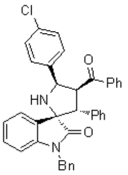
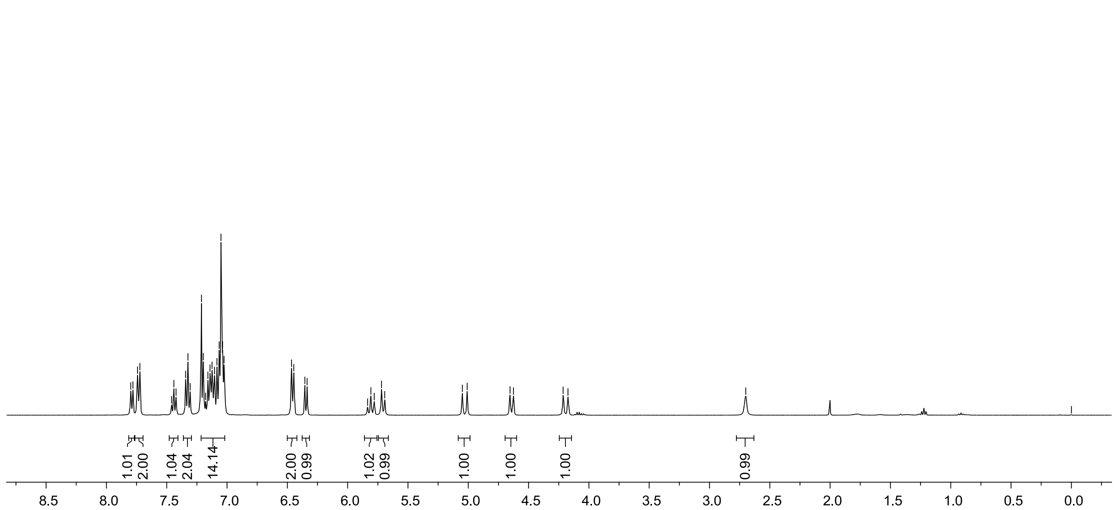
f1 (ppm)



5cca



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7.780
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7.124
7.084
7.050
7.025
6.465
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6.355
6.336
5.834
5.808
5.780
5.719
5.693
5.049
5.009
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4.625
4.213
4.173
2.700
-0.000
1.01
2.00
1.04
2.04
14.14
2.00
0.99
1.02
0.99
1.00
1.00
1.00
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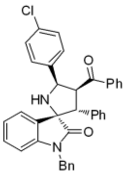

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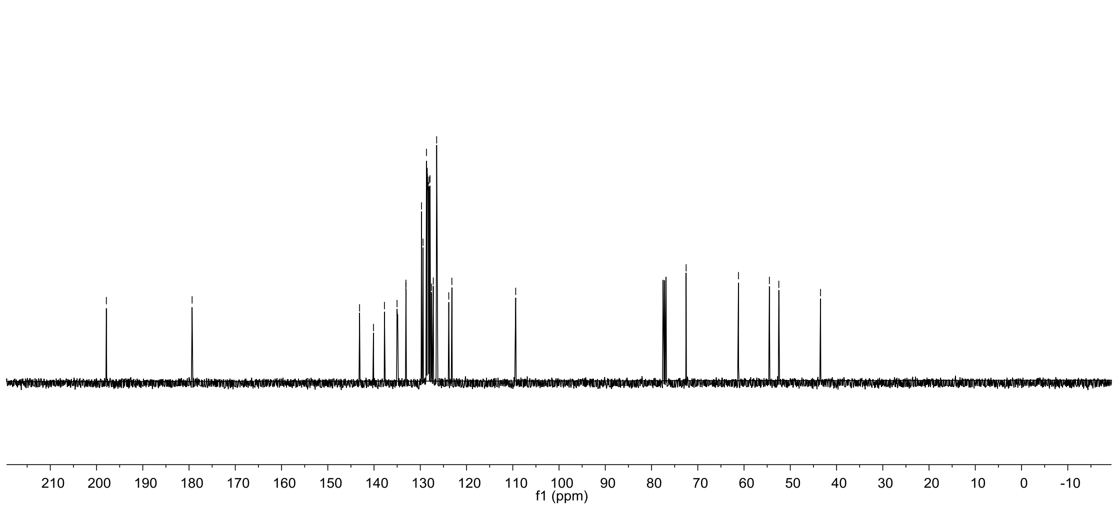

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128.12
127.89
127.55
127.19
126.46
123.84
123.17
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52.48
43.46
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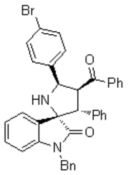
f1 (ppm)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Ph
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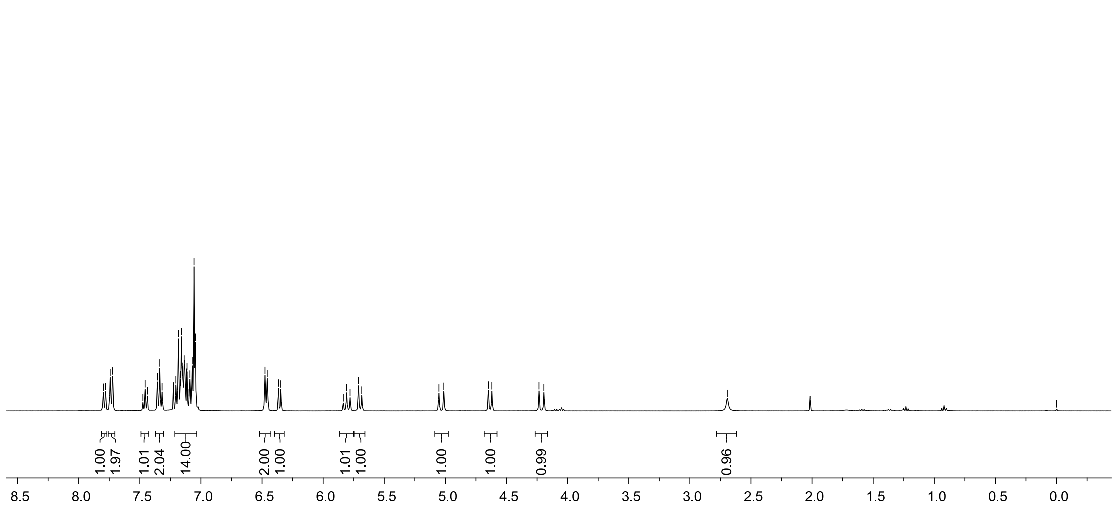
Ph
O
N
Bn

5cea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6.366
6.347
5.835
5.808
5.780
5.710
5.684
5.053
5.013
4.648
4.620
4.234
4.194
2.694
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1.00
1.97
1.01
2.04
14.00
2.00
1.00
1.01
1.00
1.00
1.00
0.99
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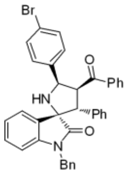
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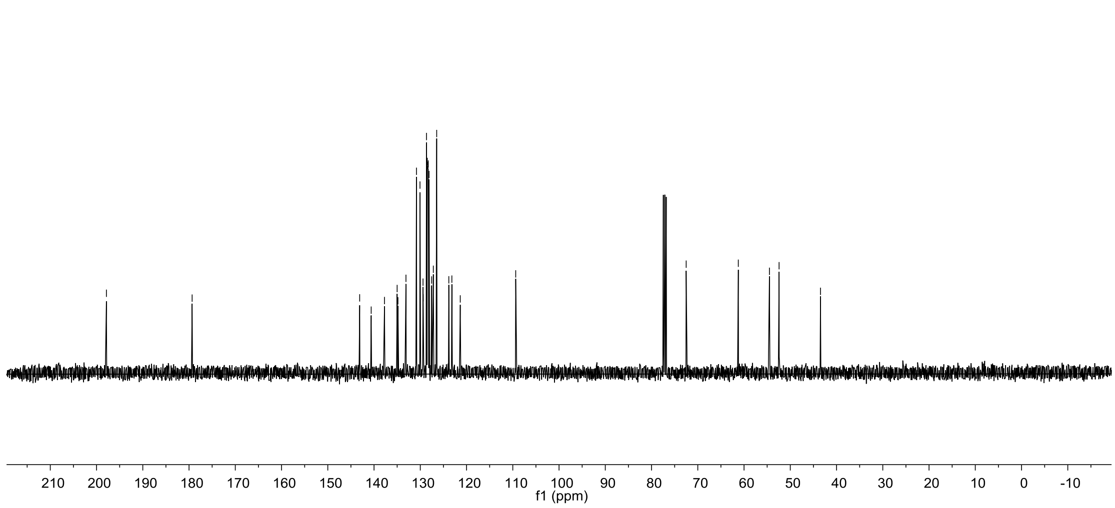
Ph
HN
Ph
O
N
Bn

5cea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128.27
128.10
127.54
127.18
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123.83
123.17
121.36
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52.42
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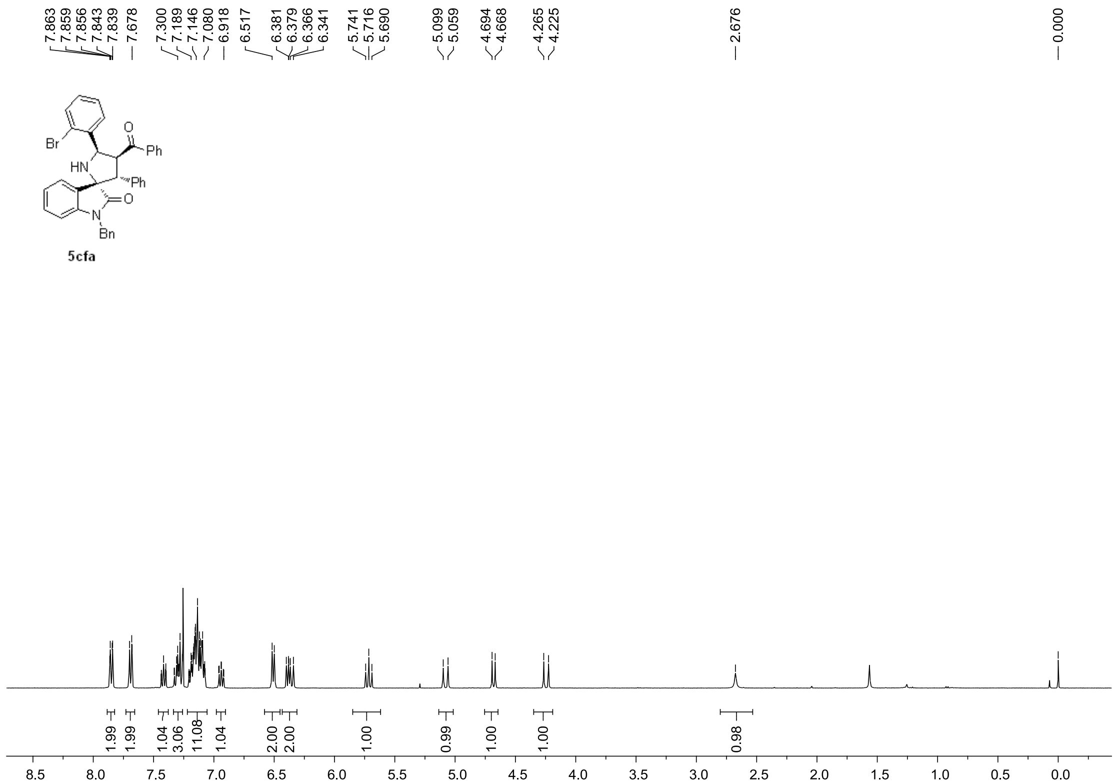
f1 (ppm)



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Br
HN
O
Ph
Ph
O
N
Bn
5cfa
1.99 1.99 1.04 3.06 11.08 1.04 2.00 2.00 1.00 0.99 1.00 1.00 0.98
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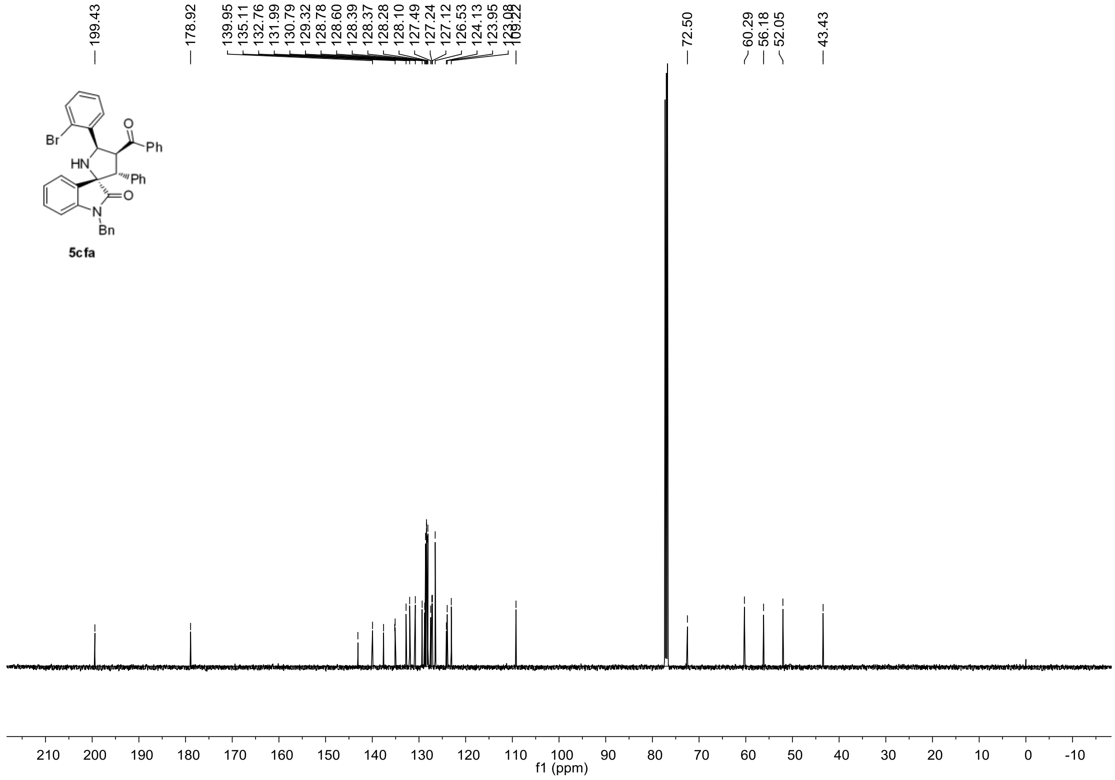

199.43 178.92 139.95 135.11 132.76 131.99 130.79 129.32 128.78 128.60 128.39 128.37 128.28 128.10 127.49 127.24 127.12 126.53 124.13 123.95 123.08 109.22 72.50 60.29 56.18 52.05 43.43
Br
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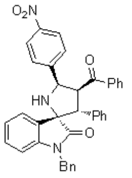
O
Ph
Ph
O
N
Bn
5cfa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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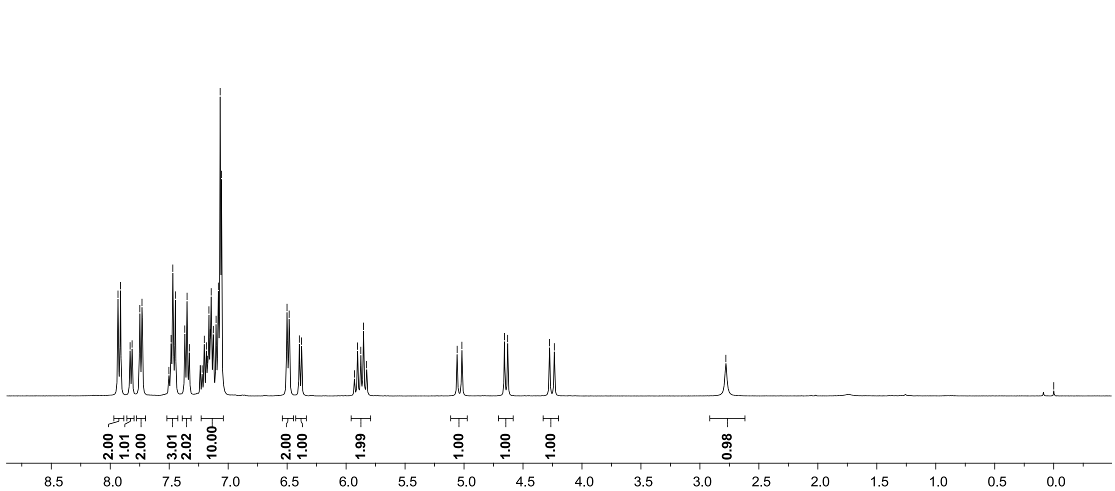

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5.930
5.903
5.875
5.853
5.826
5.058
5.018
4.658
4.630
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4.235
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1.01
2.00
3.01
2.02
10.00
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1.00
1.99
1.00
1.00
1.00
0.98
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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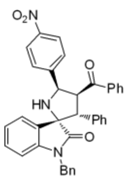
0.0



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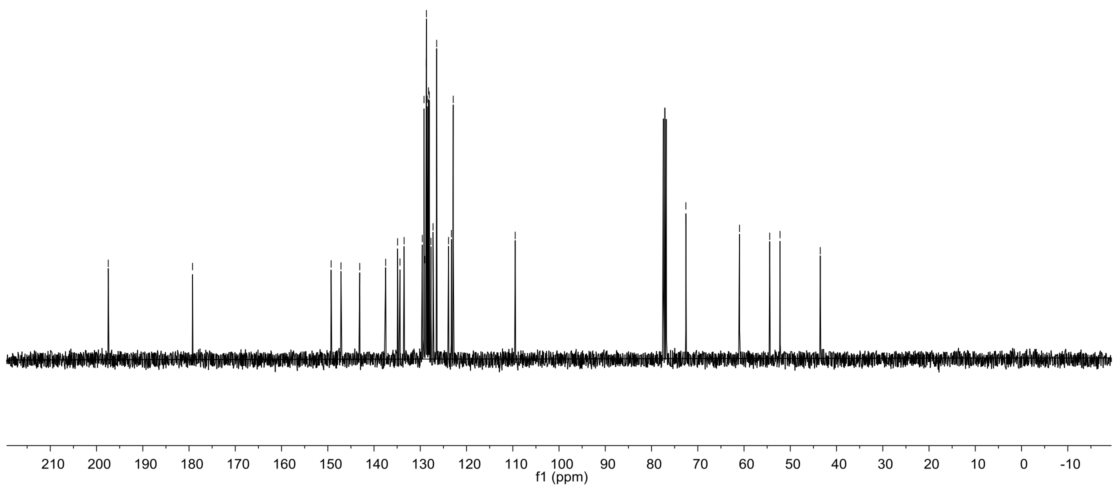

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128.50
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128.06
127.71
127.24
126.46
123.89
123.27
122.88
109.47
72.58
60.98
54.45
52.21
43.52
210
200
190
180
170
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30
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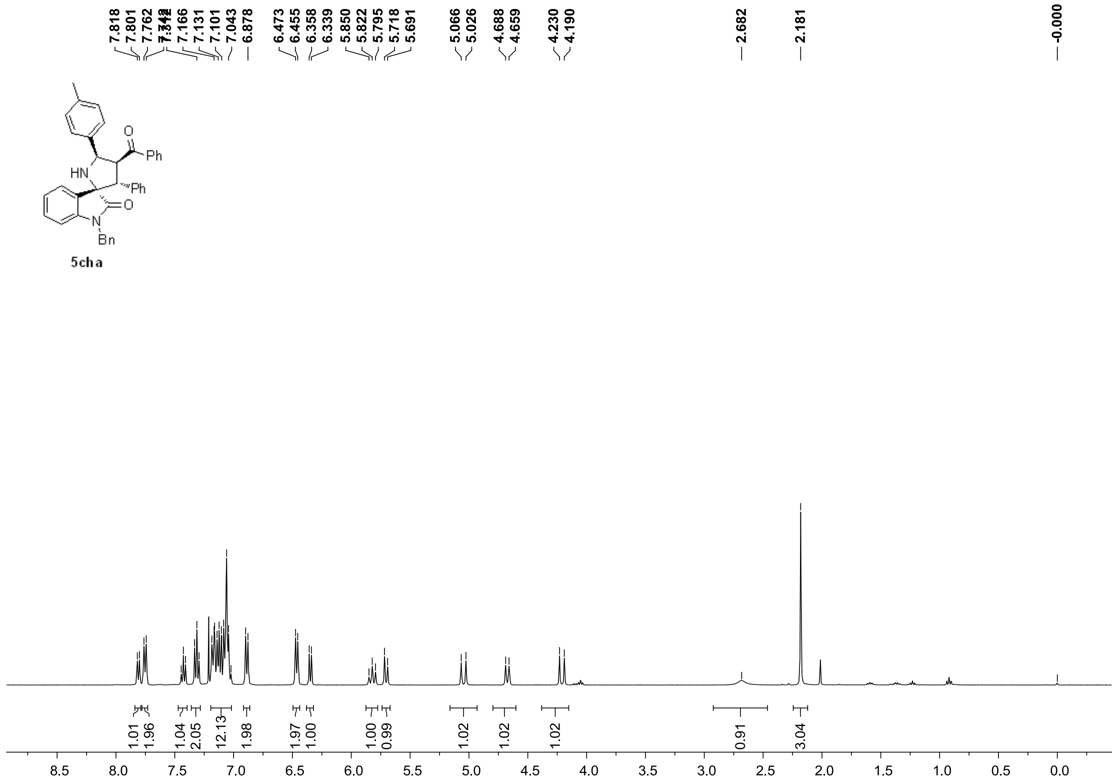
-10
f1 (ppm)



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6.339
5.850
5.822
5.795
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5.691
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4.230
4.190
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Ph
HN
Ph
O
N
Bn
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1.97
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0.99
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1.02
1.02
0.91
3.04
8.5
8.0
7.5
7.0
6.5
6.0
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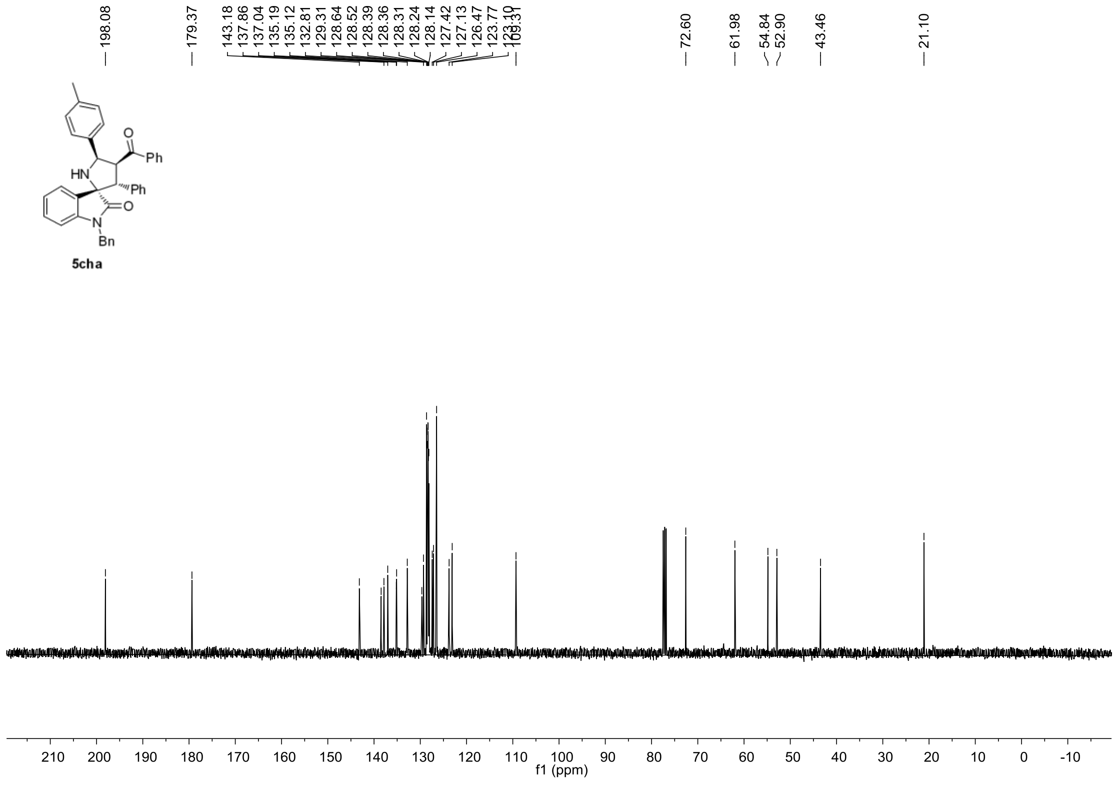

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127.42
127.13
126.47
123.77
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52.90
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21.10
O
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HN
Ph
O
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Bn
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210
200
190
180
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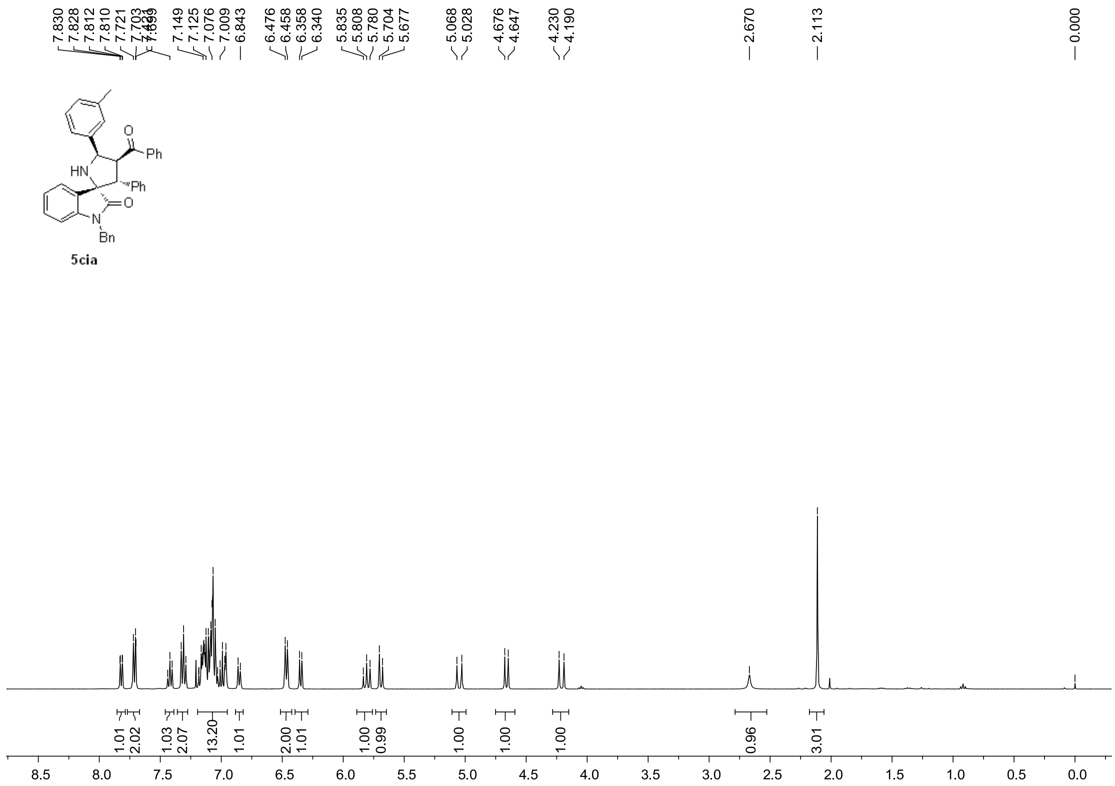
f1 (ppm)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O
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HN
Ph
O
N
Bn
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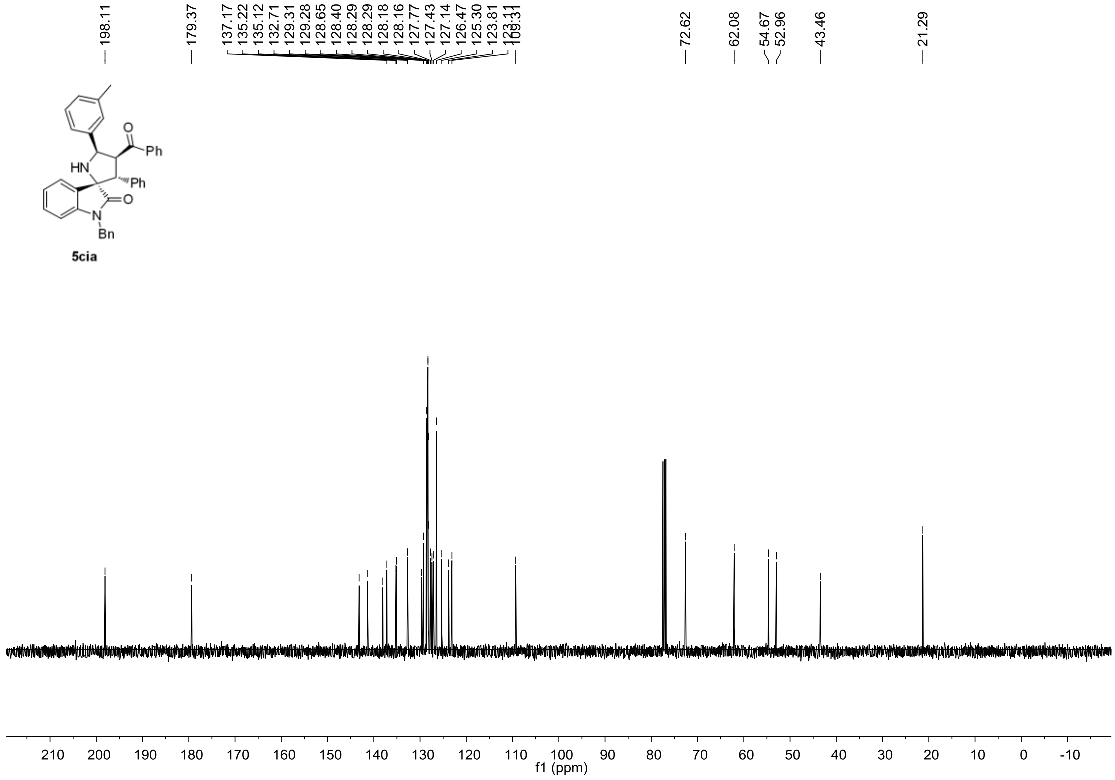
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Ph
O
N
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5cia
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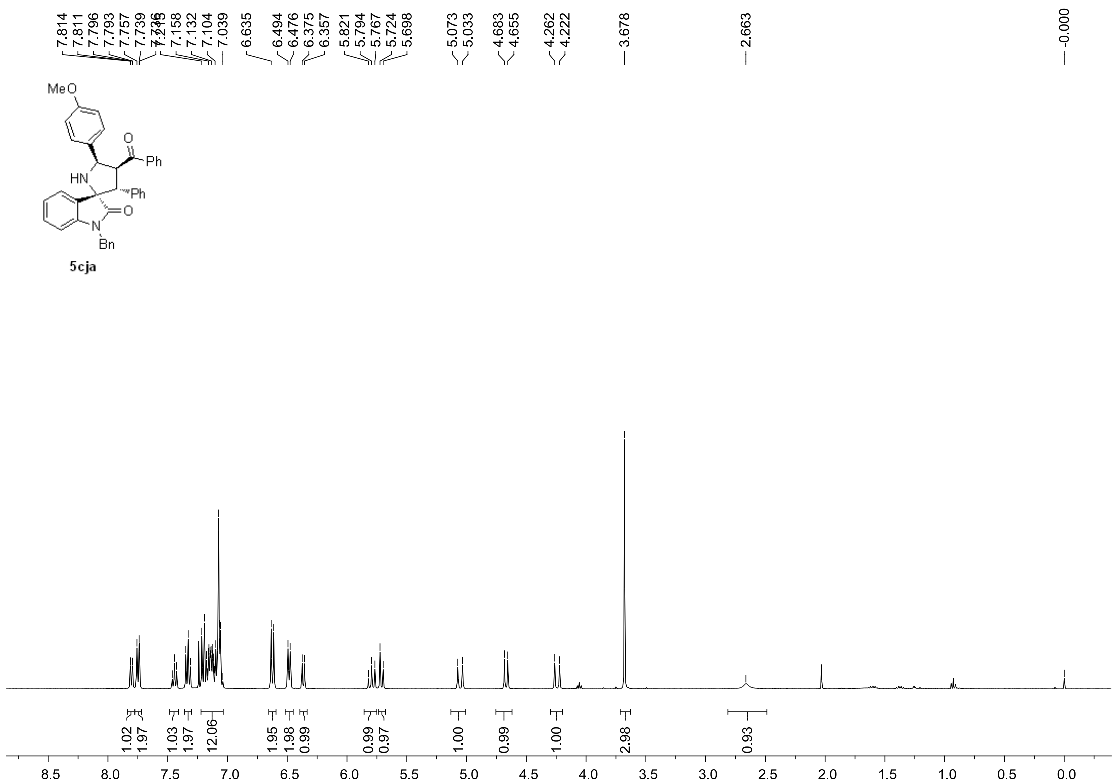
f1 (ppm)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6.476
6.375
6.357
5.821
5.794
5.767
5.724
5.698
5.073
5.033
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4.655
4.262
4.222
3.678
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MeO
O
Ph
HN
Ph
O
N
Bn
5cja
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1.03
1.97
12.06
1.95
1.98
0.99
0.99
0.97
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0.99
1.00
2.98
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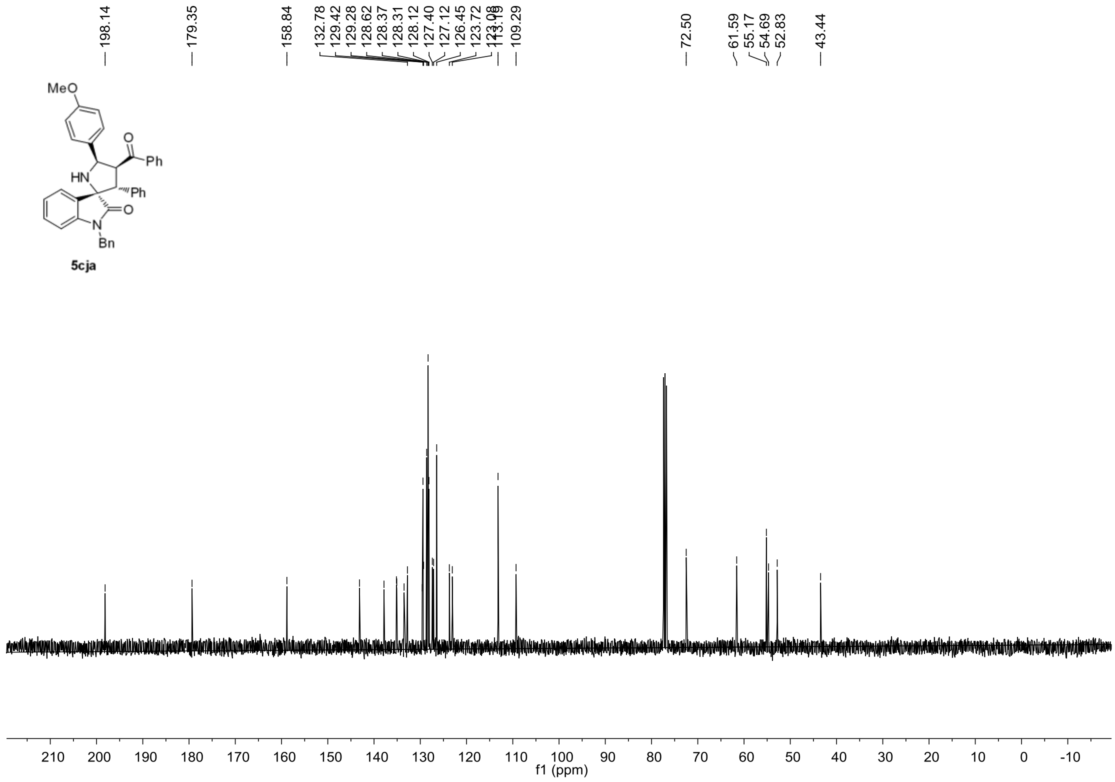
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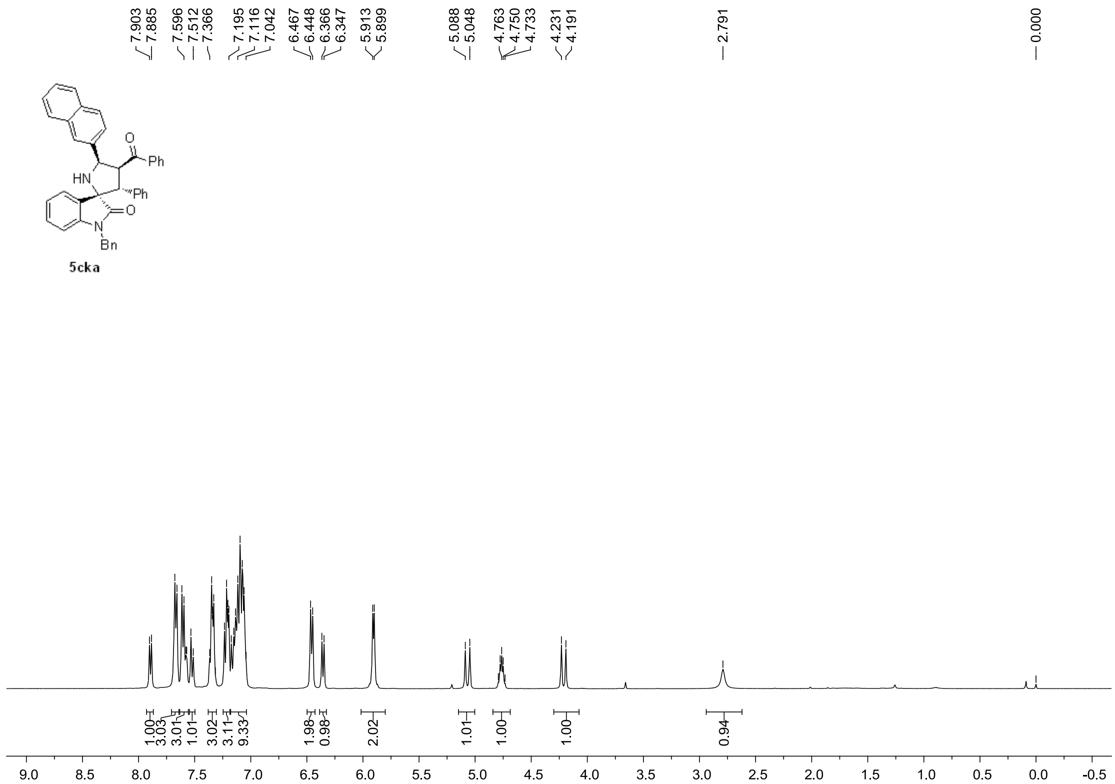
127.40
127.12
126.45
123.72
109.29
72.50
61.59
55.17
54.69
52.83
43.44
MeO
O
Ph
HN
Ph
O
N
Bn
5cja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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Ph
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1.01
3.02
3.11
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7.5
7.0
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6.0
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2.0
1.5
1.0
0.5
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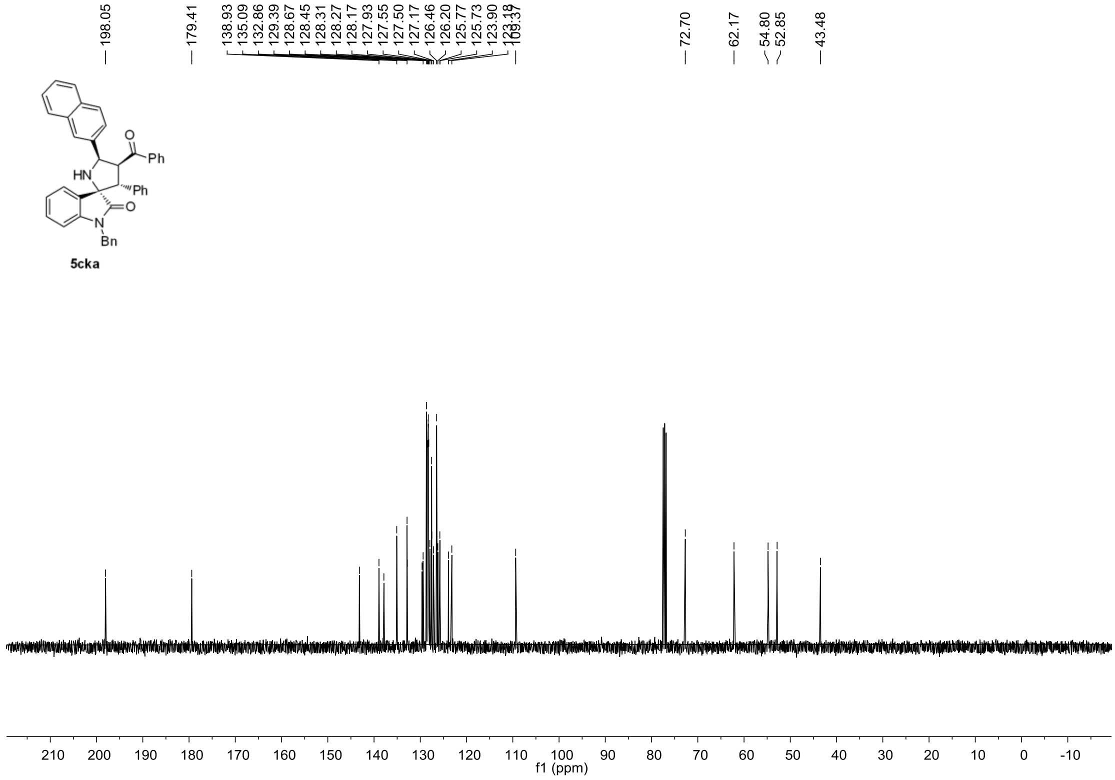
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126.20
125.77
125.73
123.90
72.70
62.17
54.80
52.85
43.48
HN
Ph
Ph
O
O
N
Bn
5cka
210
200
190
180
170
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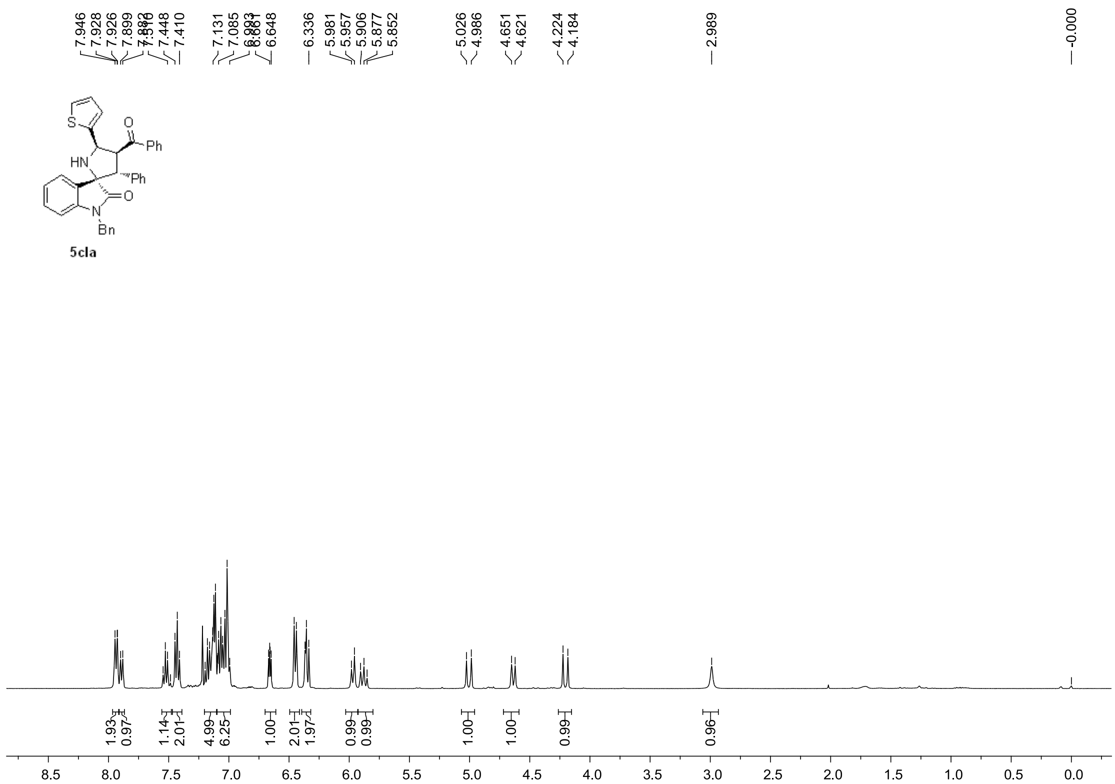
f1 (ppm)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Ph
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S
N
Bn
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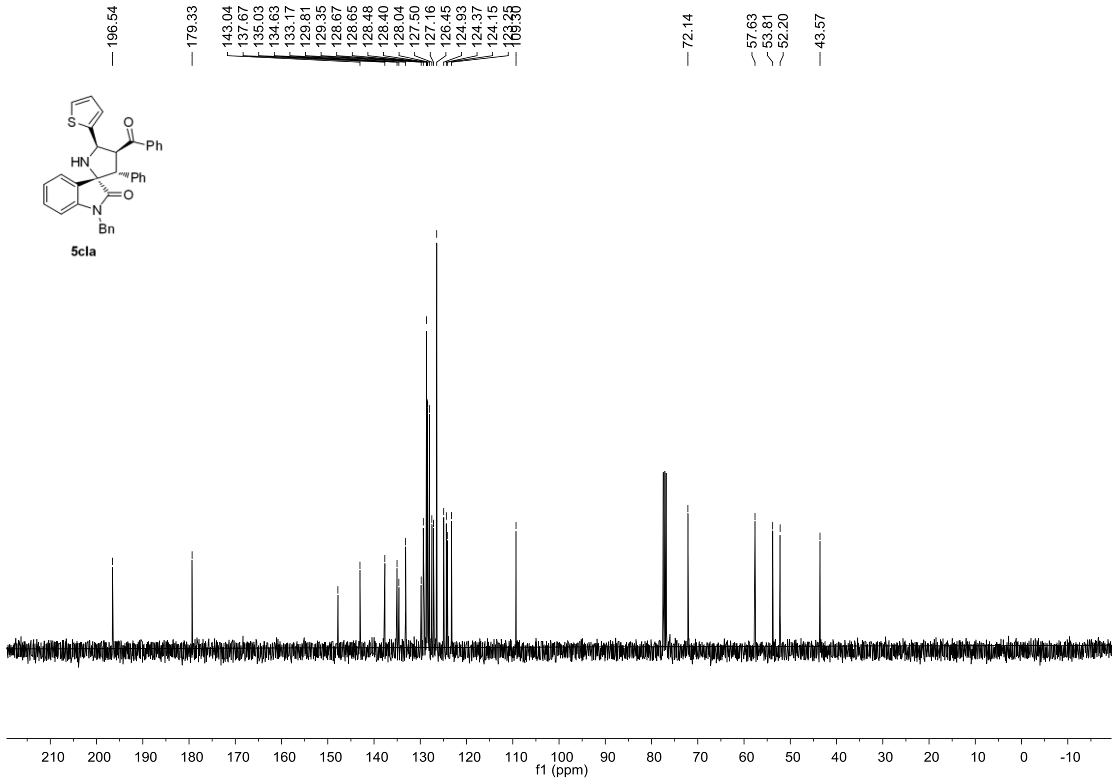
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124.15
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Ph
HN
Ph
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S
N
Bn
5cla
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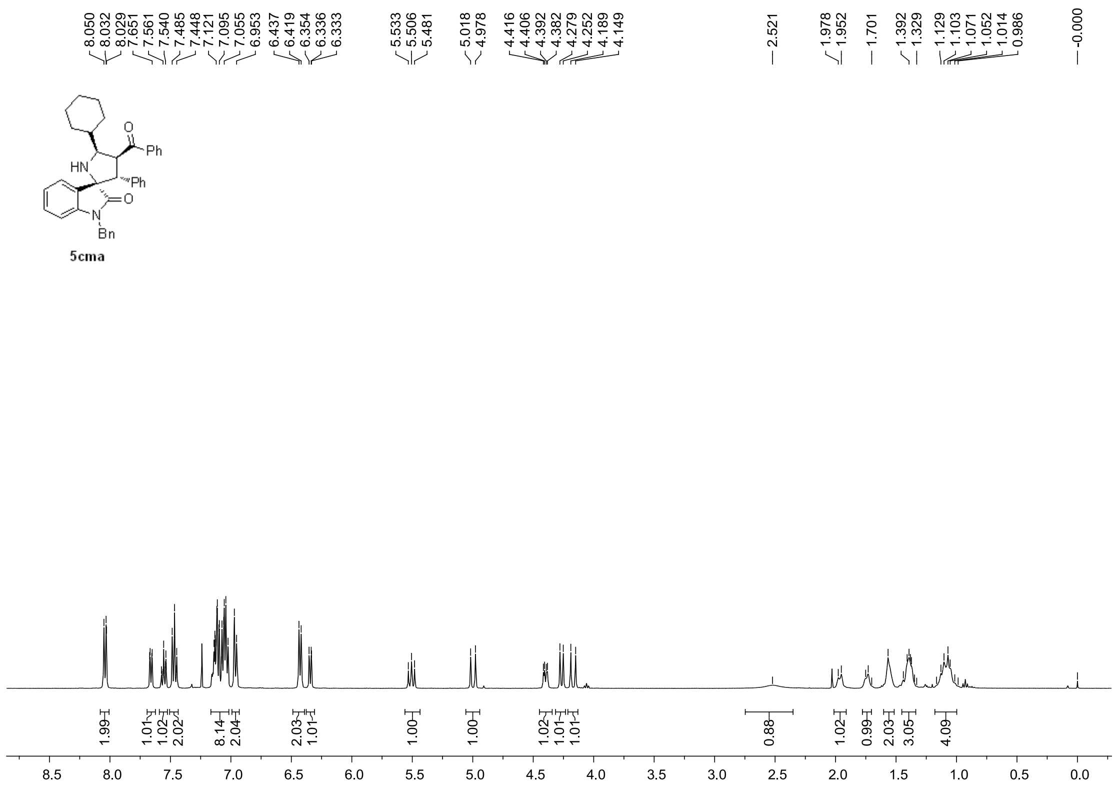
f1 (ppm)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4.416 4.406 4.392 4.382 4.279 4.252 4.189 4.149
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1.701
1.392 1.329
1.129 1.103 1.071 1.052 1.014 0.986
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Ph
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Ph
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N
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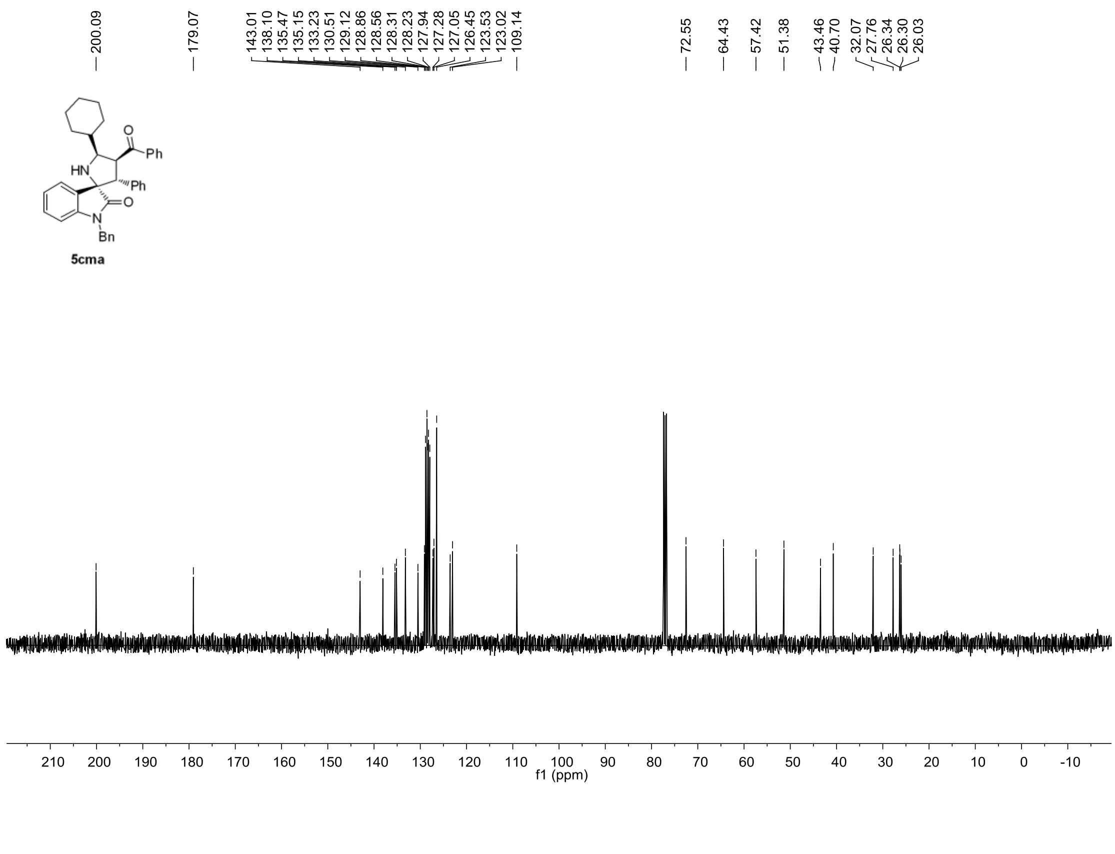
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72.55
64.43
57.42
51.38
43.46 40.70
32.07 27.76 26.34 26.30 26.03
O
Ph
HN
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O
N
Bn
5cma
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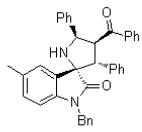
f1 (ppm)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HN
Ph
O
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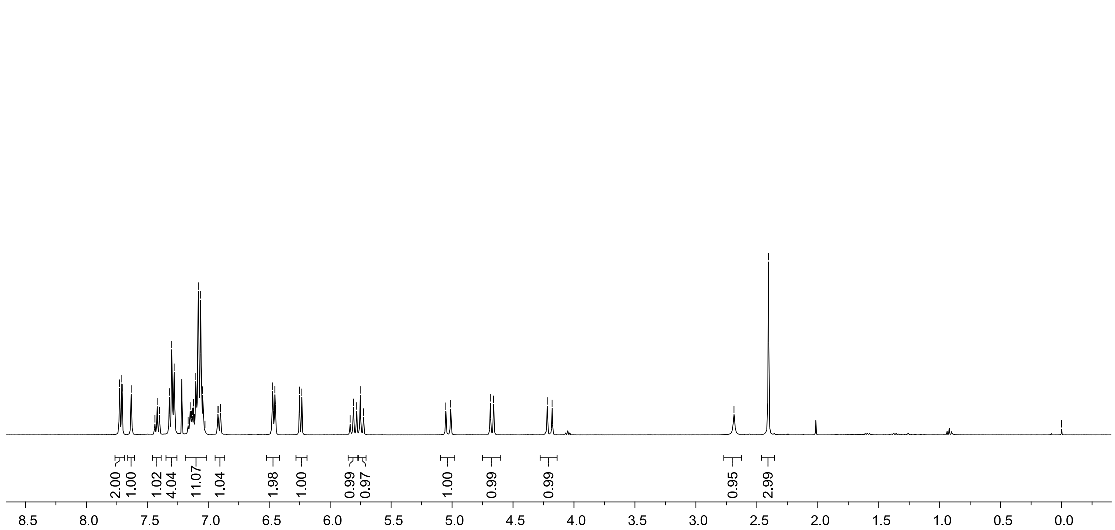
Bn

5daa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1.02
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11.07
1.04
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0.95
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7.0
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6.0
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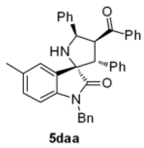
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Ph
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Ph
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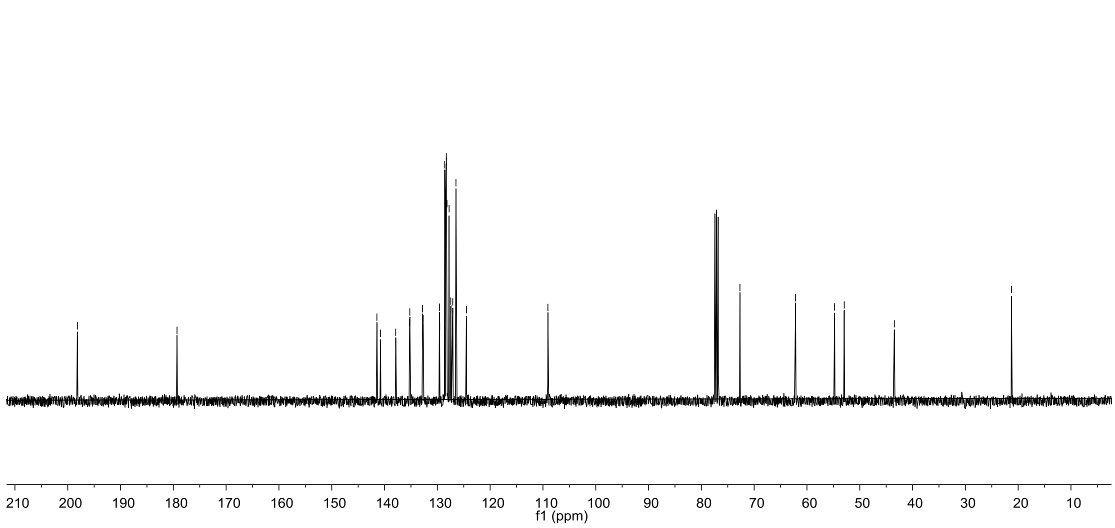
5daa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127.08
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72.69
62.17
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43.46
21.28
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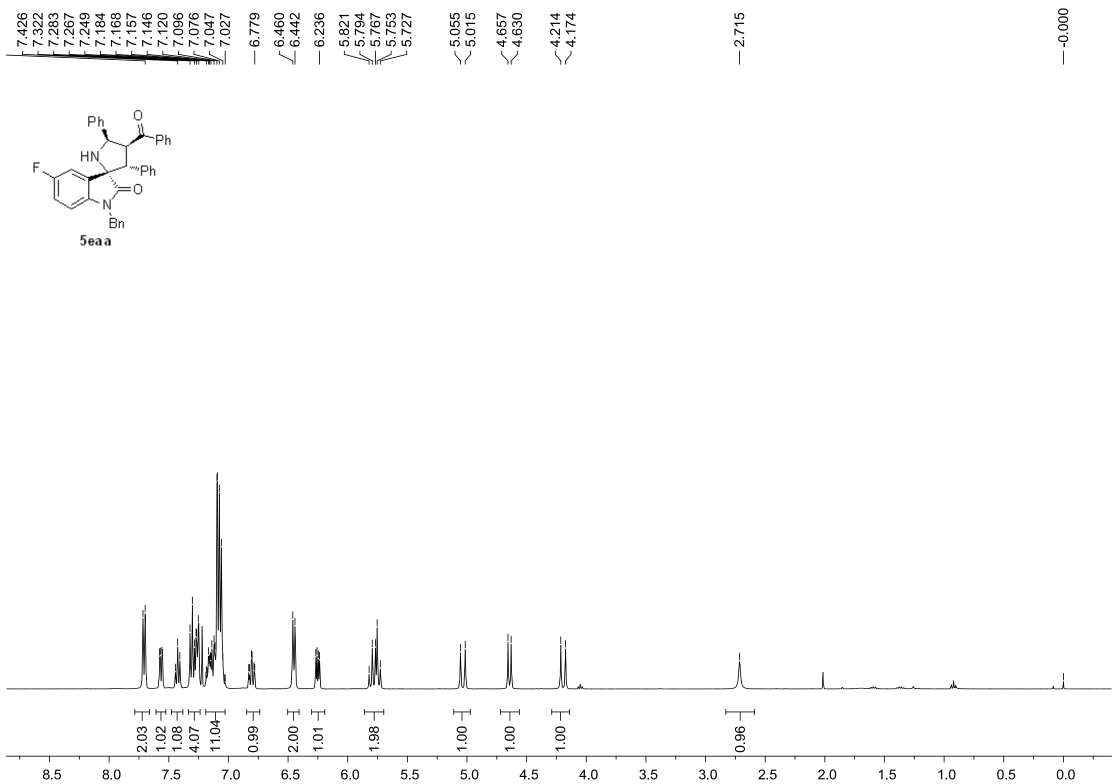
10
f1 (ppm)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7.027
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6.442
6.236
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4.630
4.214
4.174
2.715
-0.000
5eaa
2.03
1.02
1.08
4.07
11.04
0.99
2.00
1.01
1.98
1.00
1.00
1.00
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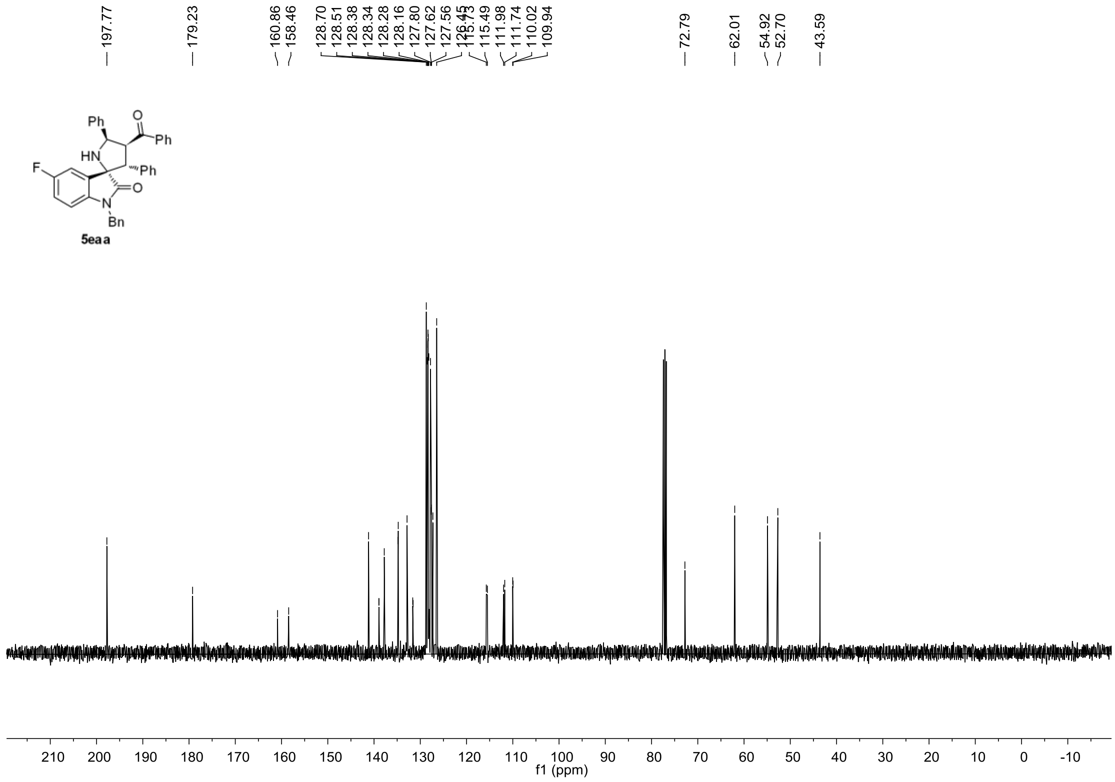
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111.74
110.02
109.94
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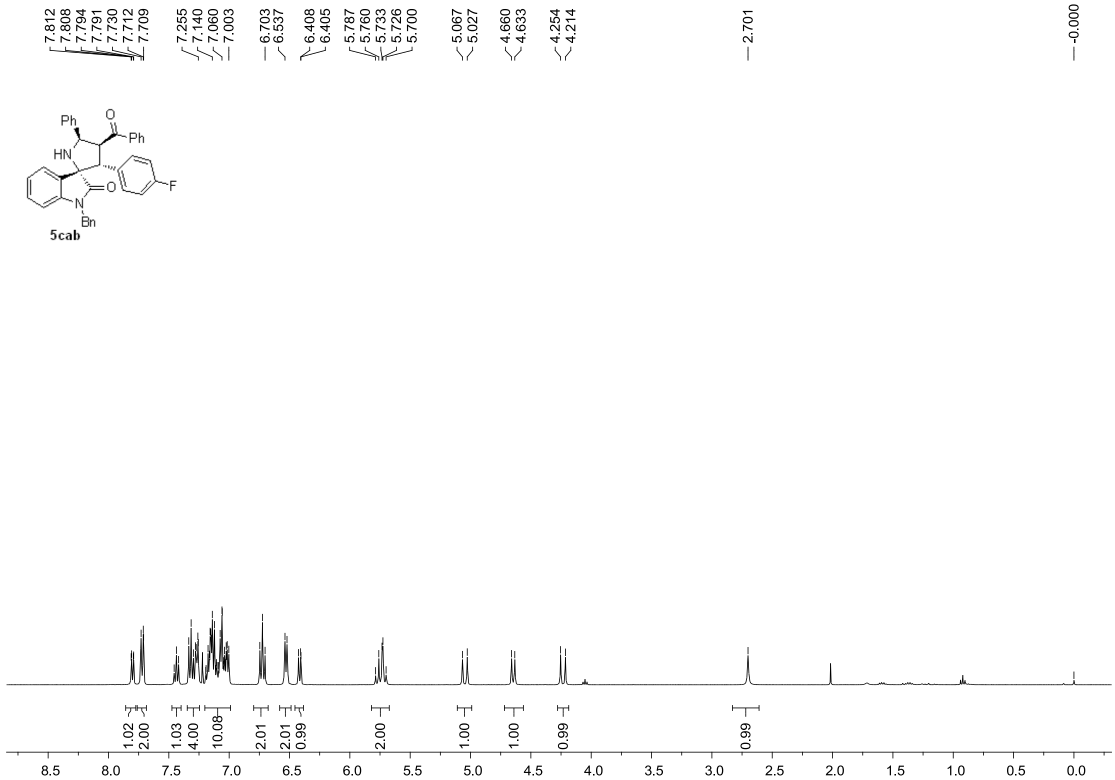
f1 (ppm)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5.760
5.733
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5.700
5.067
5.027
4.660
4.633
4.254
4.214
2.701
-0.000
Ph
O
Ph
HN
N
O
F
Bn
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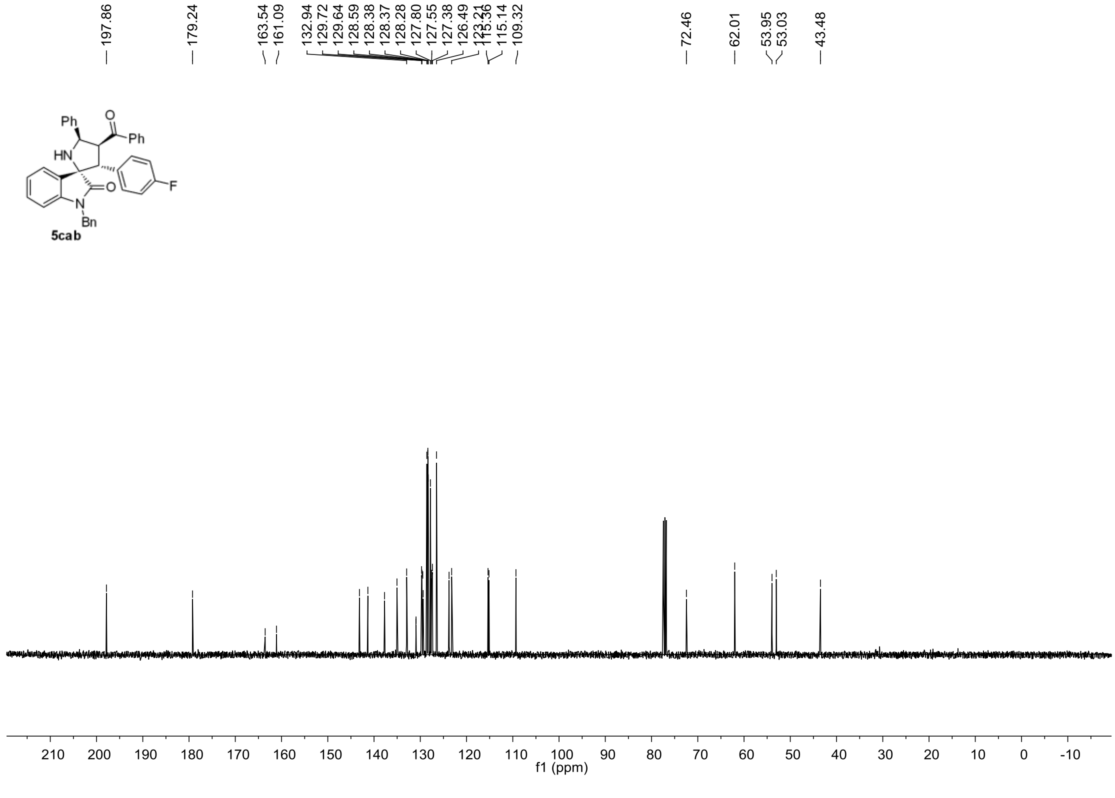
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127.38
126.49
123.21
115.36
115.14
109.32
72.46
62.01
53.95
53.03
43.48
Ph
O
Ph
HN
N
O
F
Bn
5cab
210
200
190
180
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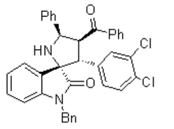
10
0
-10
f1 (ppm)



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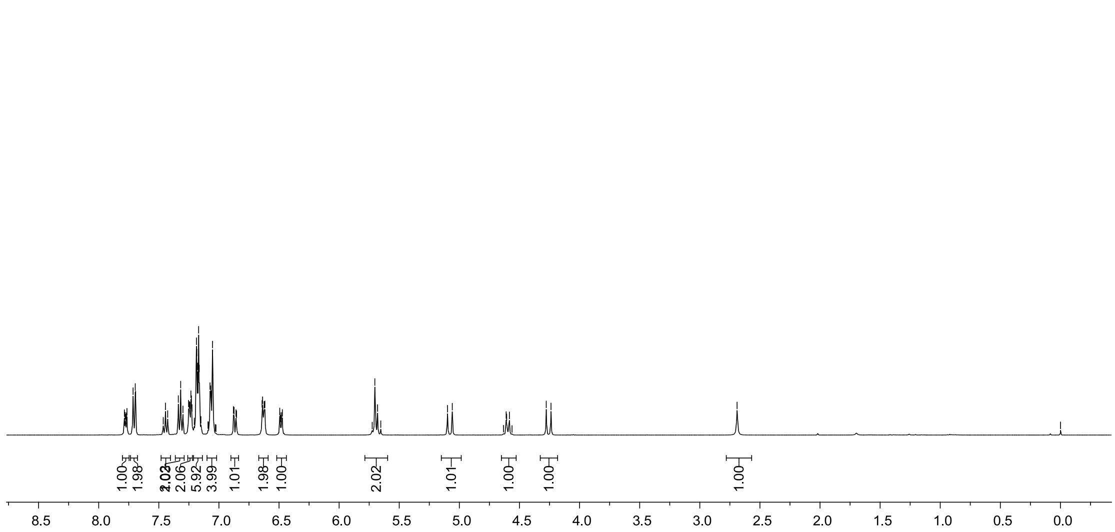

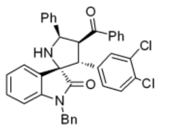

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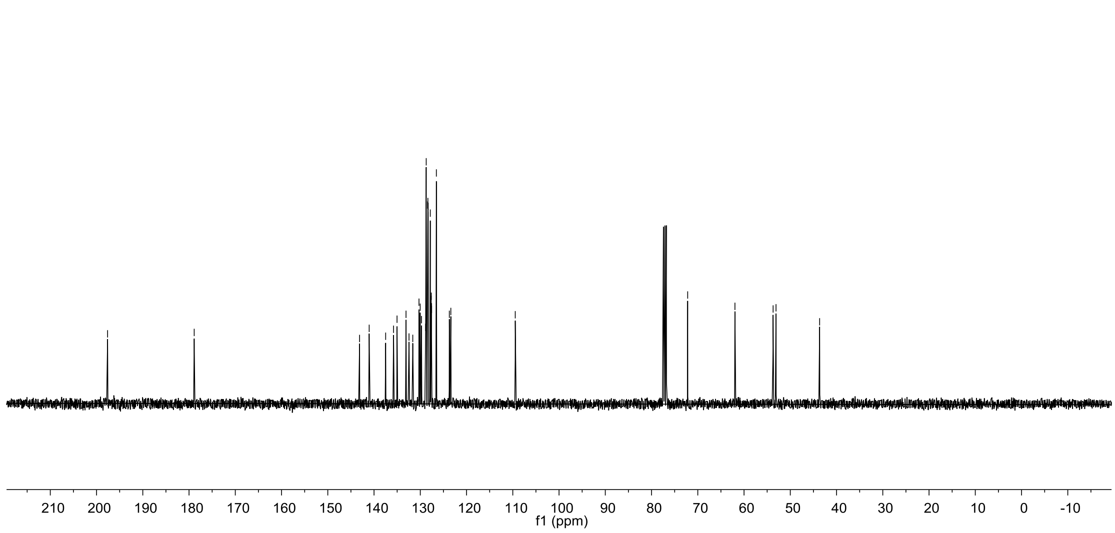

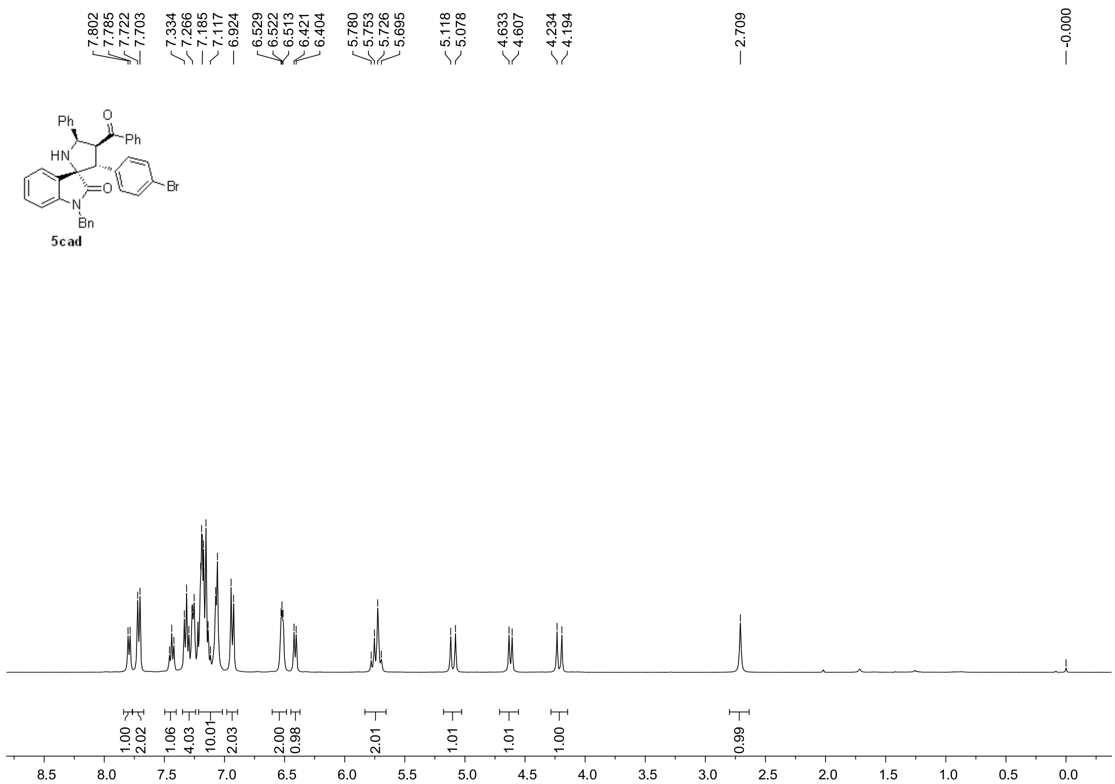

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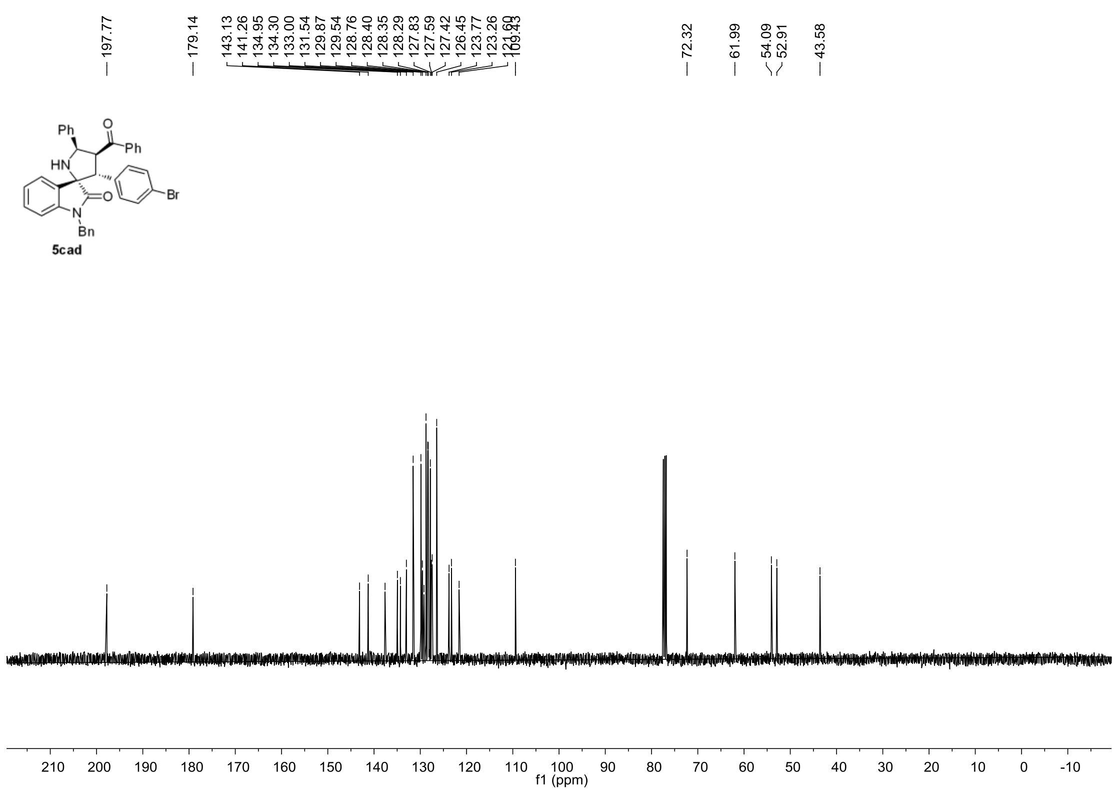

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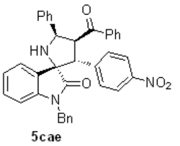

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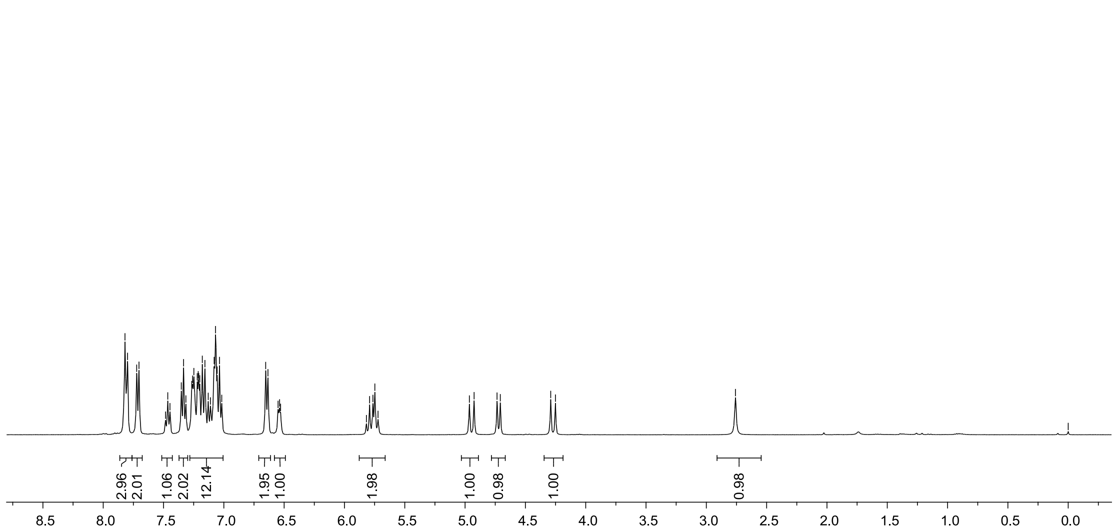

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5.748
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1.06
2.02
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1.98
1.00
0.98
1.00
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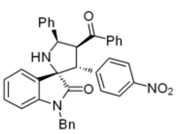

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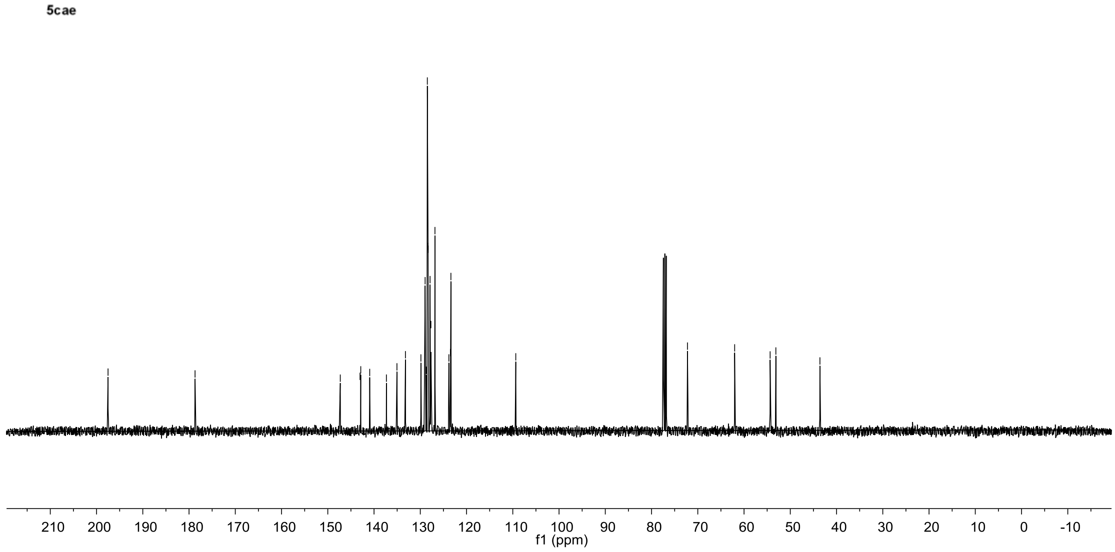

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128.28
127.89
127.70
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123.82
123.48
123.38
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53.12
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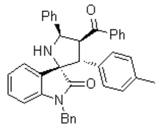
f1 (ppm)



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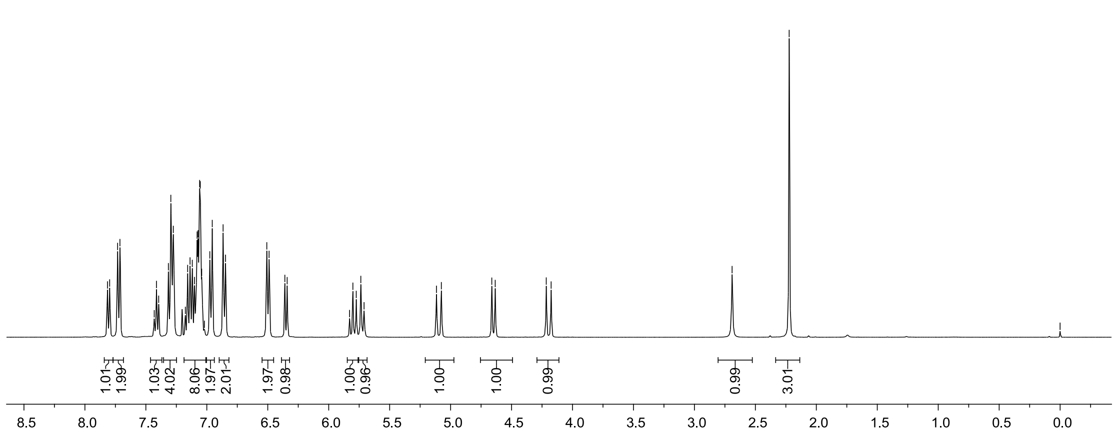
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6.341
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5.802
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5.076
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1.03
4.02
8.06
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2.01
1.97
0.98
1.00
0.96
1.00
1.00
0.99
0.99
3.01
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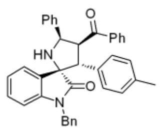

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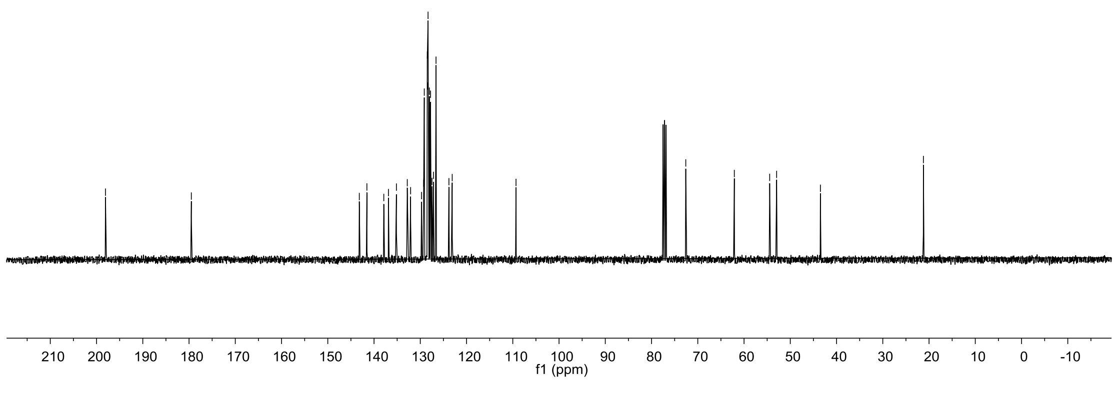
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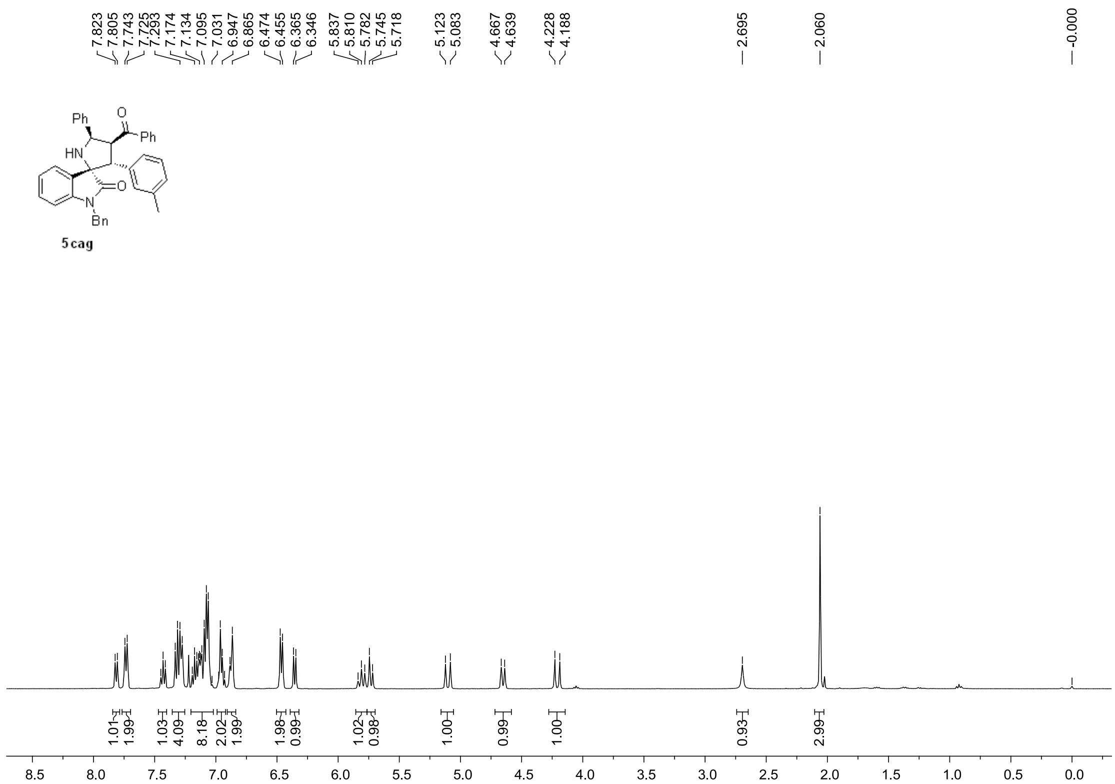
f1 (ppm)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O
Ph
HN
N
O
Bn
5cag
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1.00
0.93
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8.0
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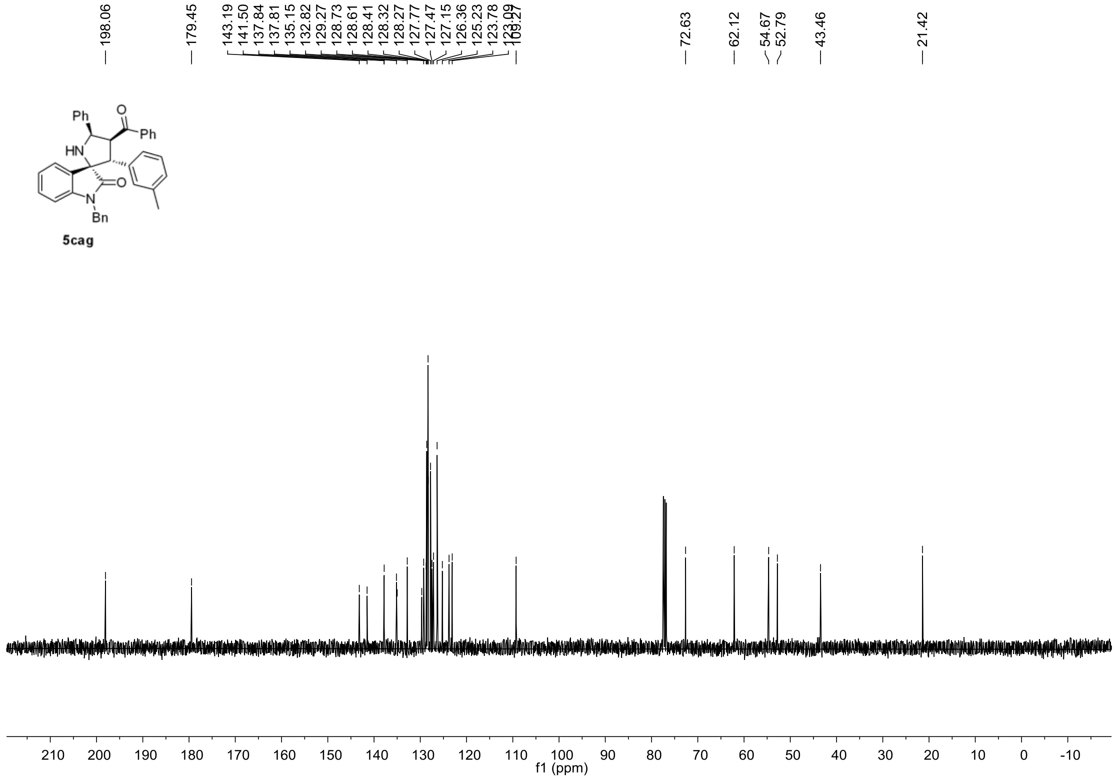
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127.47
127.15
126.36
125.23
123.78
109.27
72.63
62.12
54.67
52.79
43.46
21.42
Ph
O
Ph
HN
N
O
Bn
5cag
210
200
190
180
170
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100
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40
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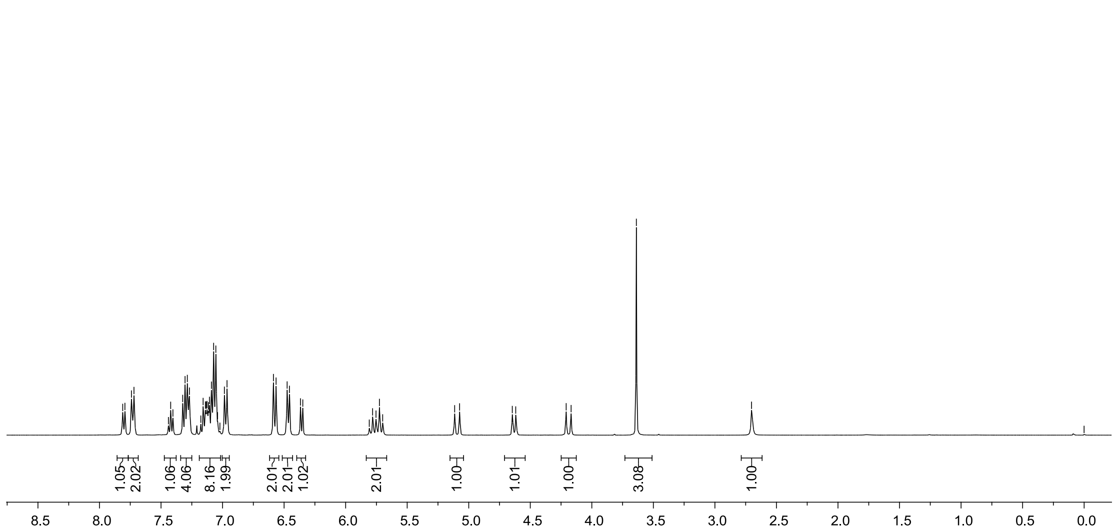
0
-10
f1 (ppm)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1.05 2.02 1.06 4.06 8.16 1.99 2.01 2.01 1.02 2.01 1.00 1.01 1.00 3.08 1.00
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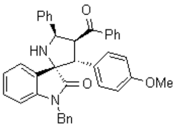
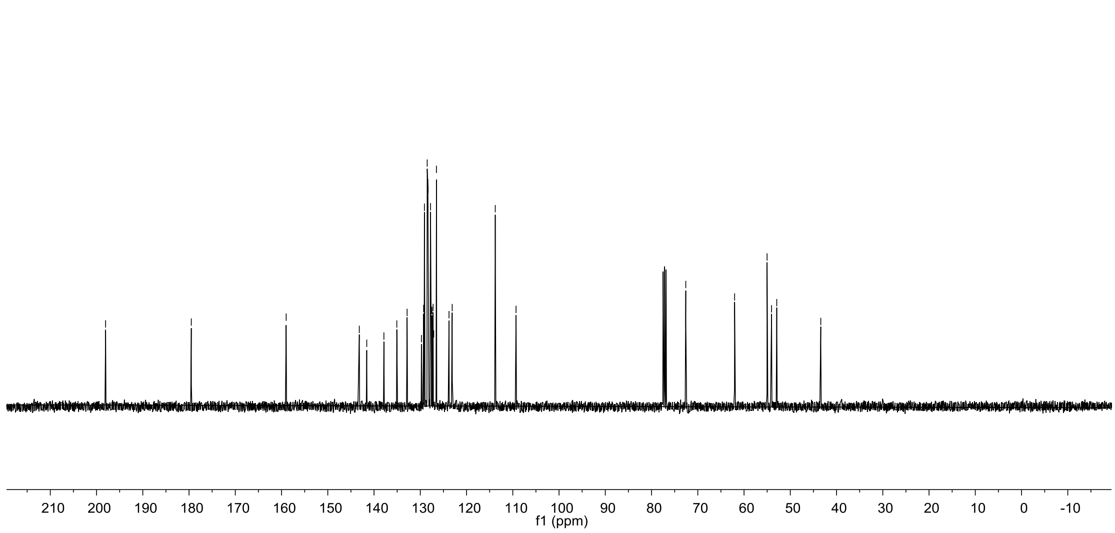

Ph
O
Ph
HN
OMe
O
N
Bn

5cah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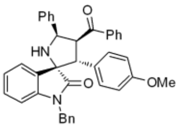
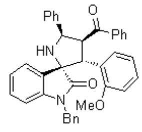
f1 (ppm)


Ph
O
Ph
HN
OMe
O
N
Bn

5cah



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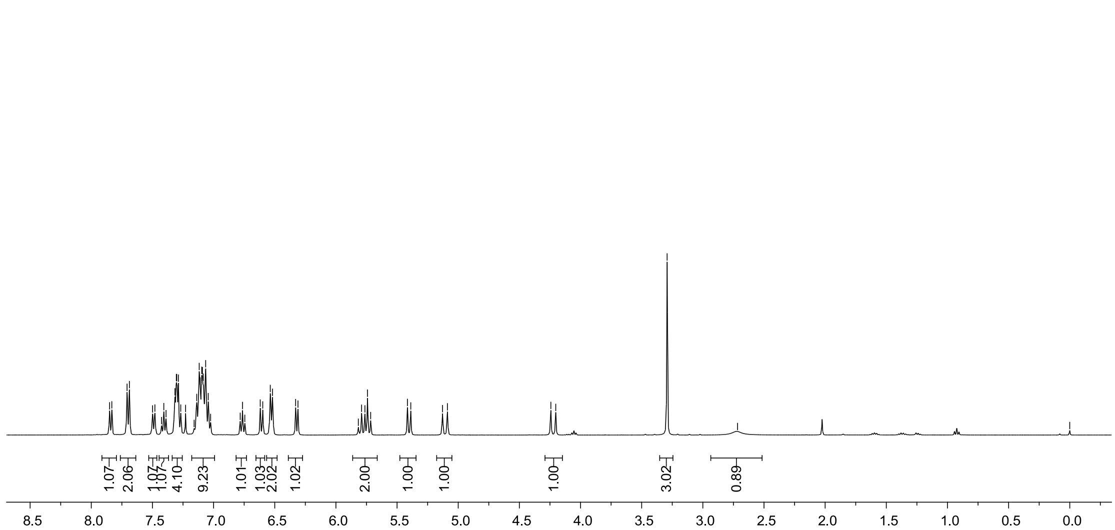

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7.024
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6.310
5.790
5.742
5.716
5.415
5.388
5.128
5.088
4.243
4.202
3.292
2.716
0.000
1.07
2.06
1.07
1.07
4.10
9.23
1.01
1.03
2.02
1.02
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1.00
1.00
1.00
3.02
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7.5
7.0
6.5
6.0
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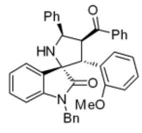

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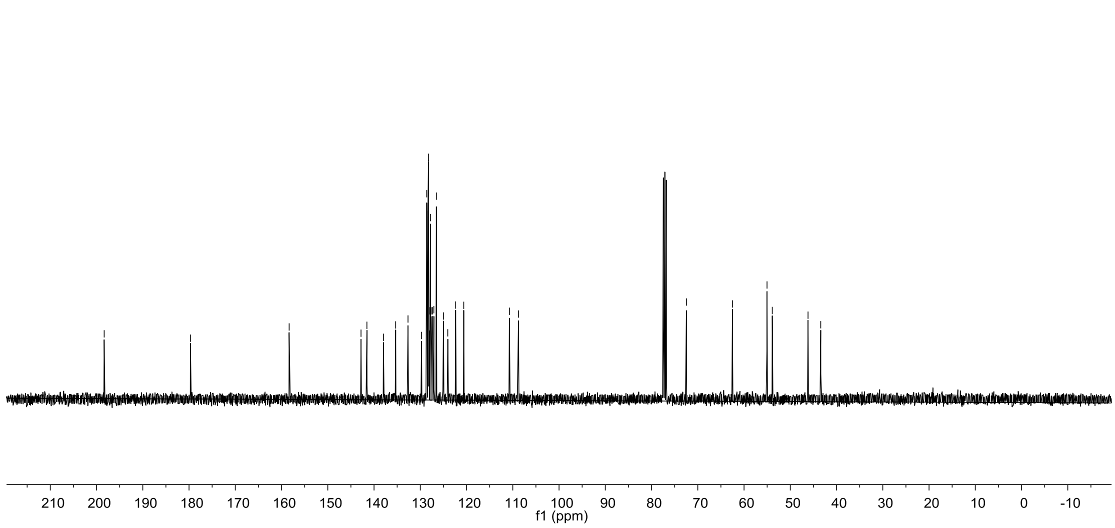

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158.35
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128.14
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127.07
126.52
122.35
120.60
110.73
108.77
72.46
62.50
55.03
53.90
46.16
43.42
210
200
190
180
170
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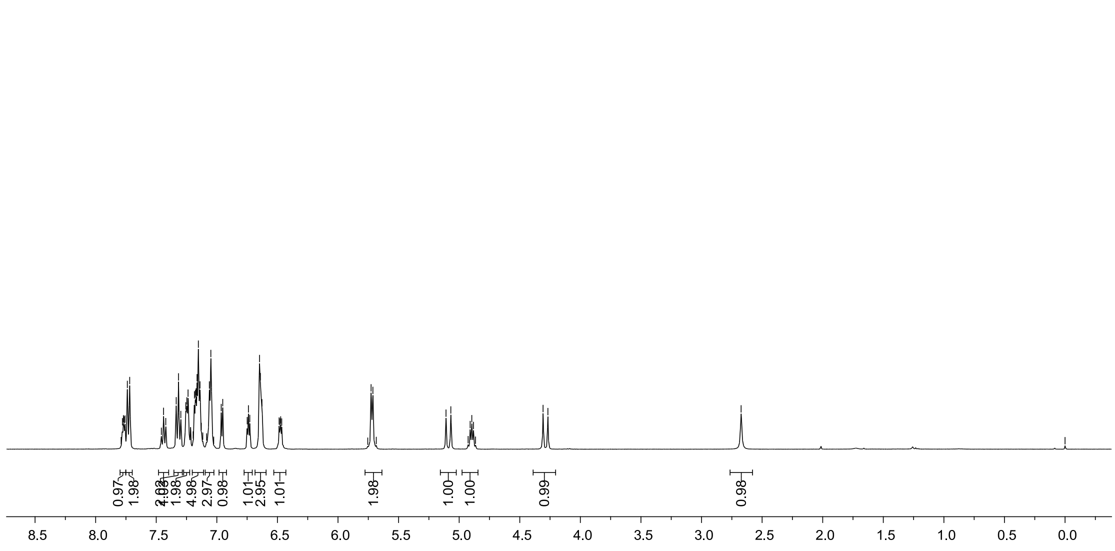
f1 (ppm)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5.727
5.712
5.684
5.109
5.069
4.896
4.882
4.865
4.308
4.268
2.673
0.000
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1.98
1.98
4.96
2.97
0.98
1.01
2.95
1.01
1.98
1.00
1.00
0.99
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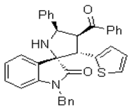
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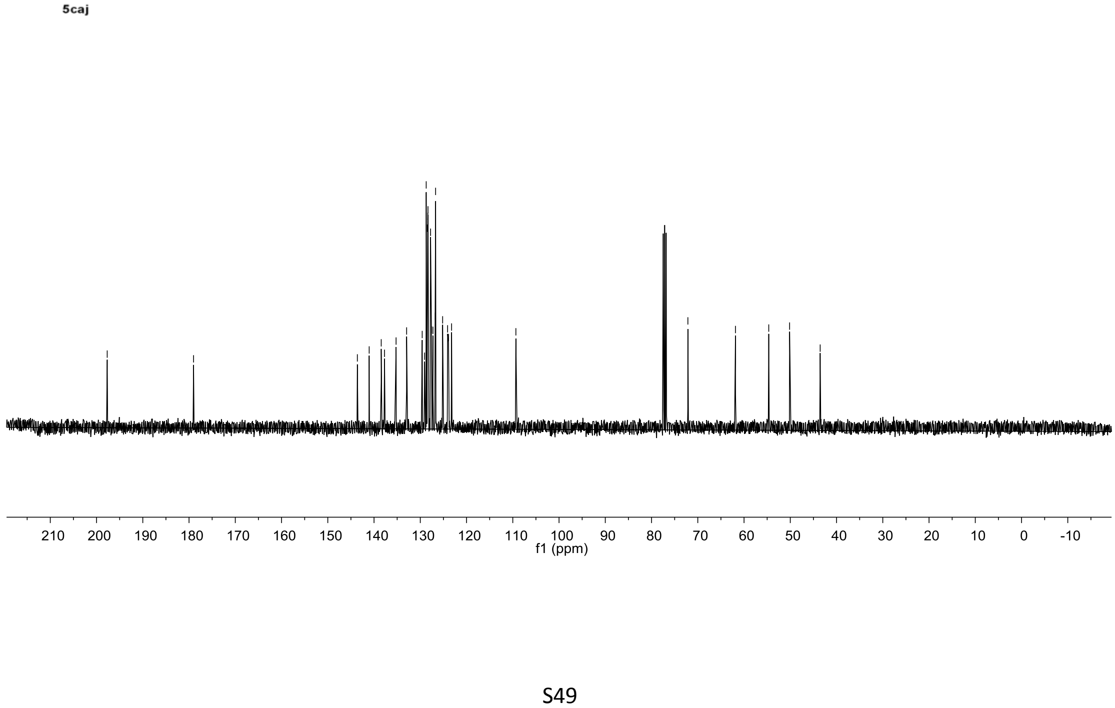
Ph
HN
S
N
O
Bn

5caj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127.58
127.27
126.75
126.69
125.17
124.09
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43.53
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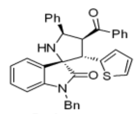
f1 (ppm)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Ph
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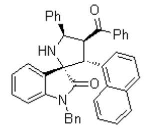
S
N
O
Bn

5caj



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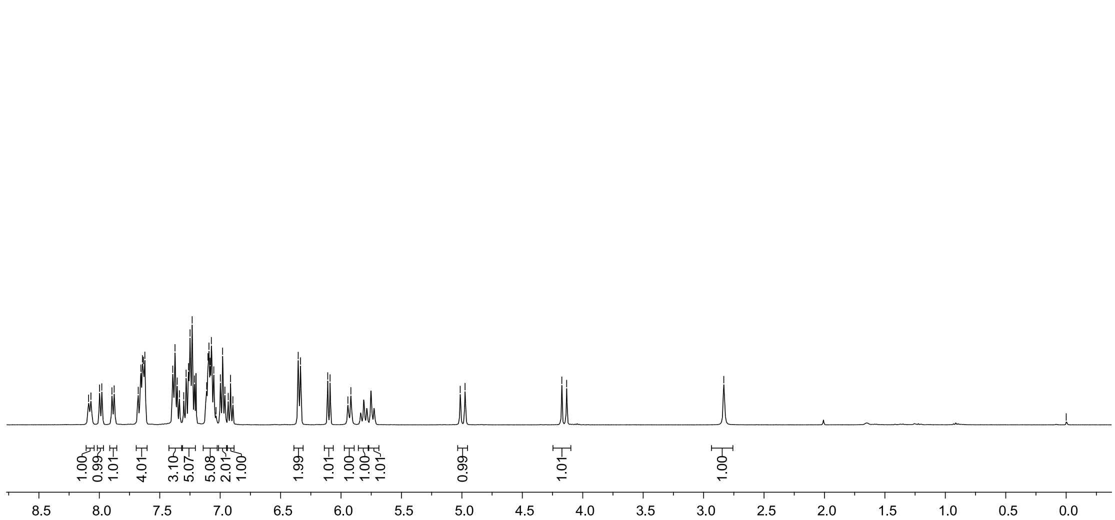

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7.249
7.112
7.083
7.034
6.961
6.895
6.354
6.335
6.091
5.943
5.919
5.014
4.974
4.173
4.133
2.833
-0.000
1.00
0.99
1.01
4.01
3.10
5.07
5.08
2.01
1.00
1.99
1.01
1.00
1.00
1.01
0.99
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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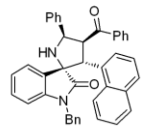
0.0



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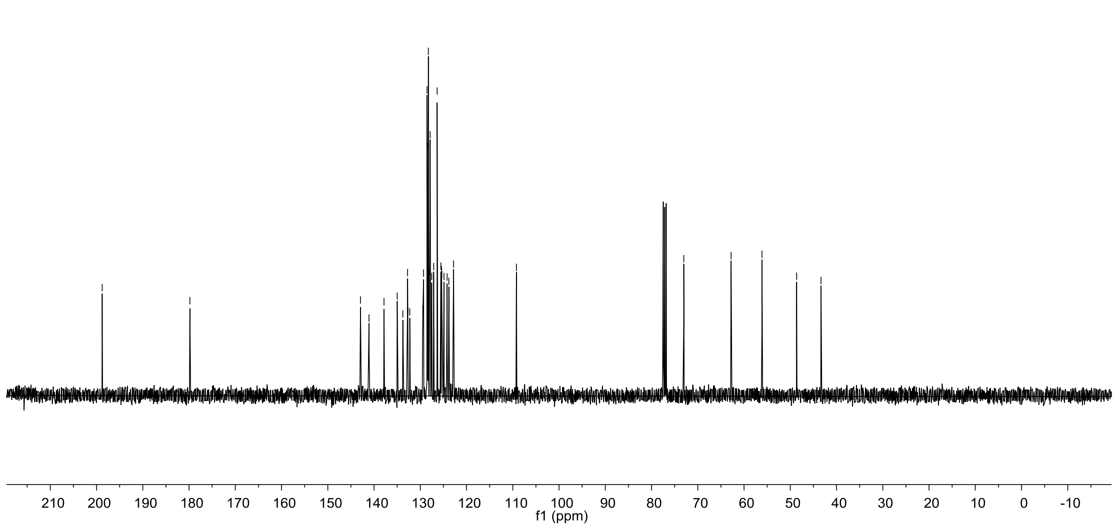

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128.43
128.26
128.24
128.00
127.86
127.53
127.10
126.35
125.55
125.39
125.34
124.87
124.20
123.83
122.81
109.22
73.03
62.80
56.12
48.63
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200
190
180
170
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120
110
100
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80
70
60
50
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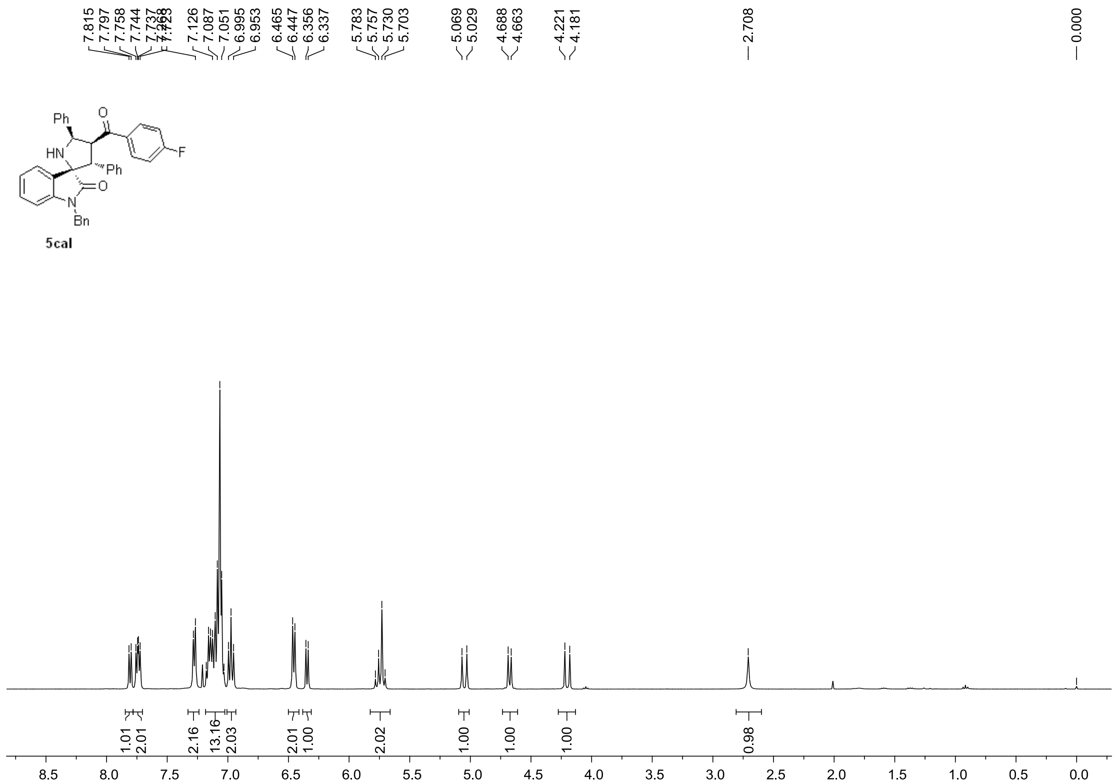
30
20
10
0
-10
f1 (ppm)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7.727
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7.087
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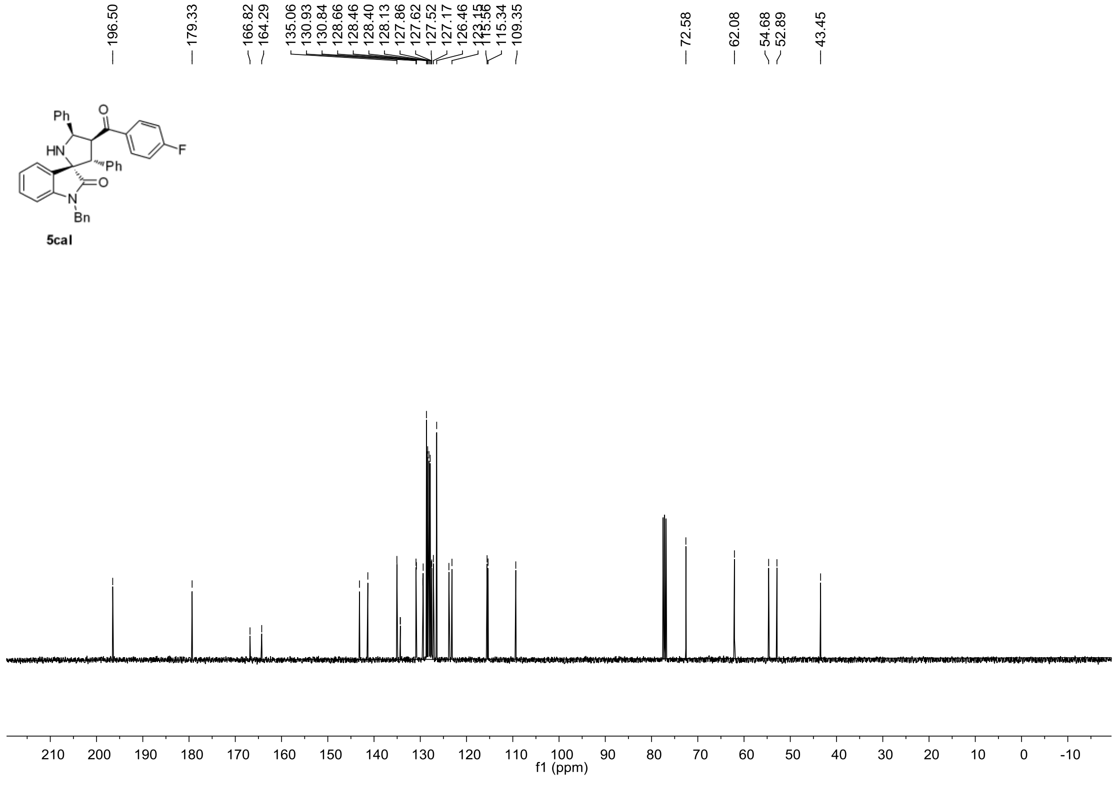
6.447
6.356
6.337
5.783
5.757
5.730
5.703
5.069
5.029
4.688
4.663
4.221
4.181
2.708
0.000
Ph
O
F
HN
Ph
O
N
Bn
5cal
1.01
2.01
2.16
13.16
2.03
2.01
1.00
2.02
1.00
1.00
1.00
0.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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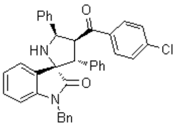
130.93
130.84
128.66
128.46
128.40
128.13
127.86
127.62
127.52
127.17
126.46
123.15
115.56
115.34
109.35
72.58
62.08
54.68
52.89
43.45
Ph
O
F
HN
Ph
O
N
Bn
5cal
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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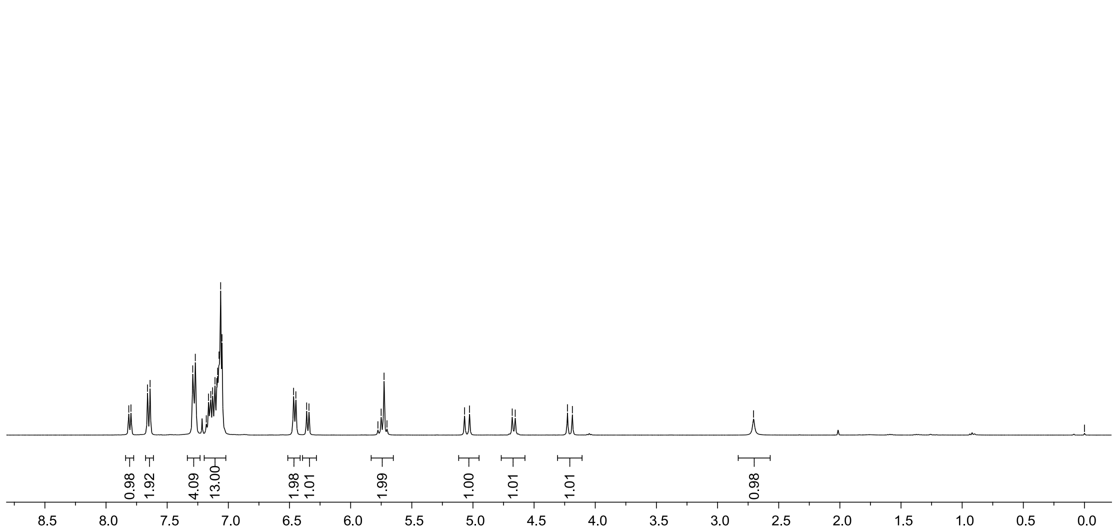
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7.095
7.076
7.052
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6.448
6.360
6.341
5.777
5.751
5.727
5.703
5.068
5.028
4.679
4.654
4.227
4.187
2.706
0.000
0.98
1.92
4.09
13.00
1.98
1.01
1.99
1.00
1.01
1.01
0.98
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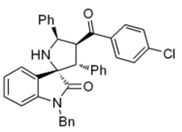
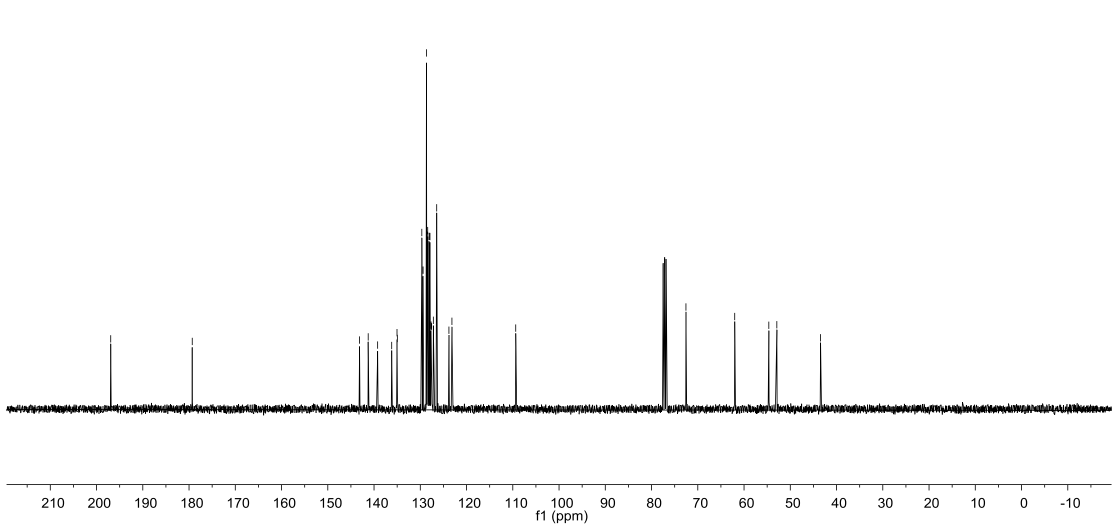


5cam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136.18
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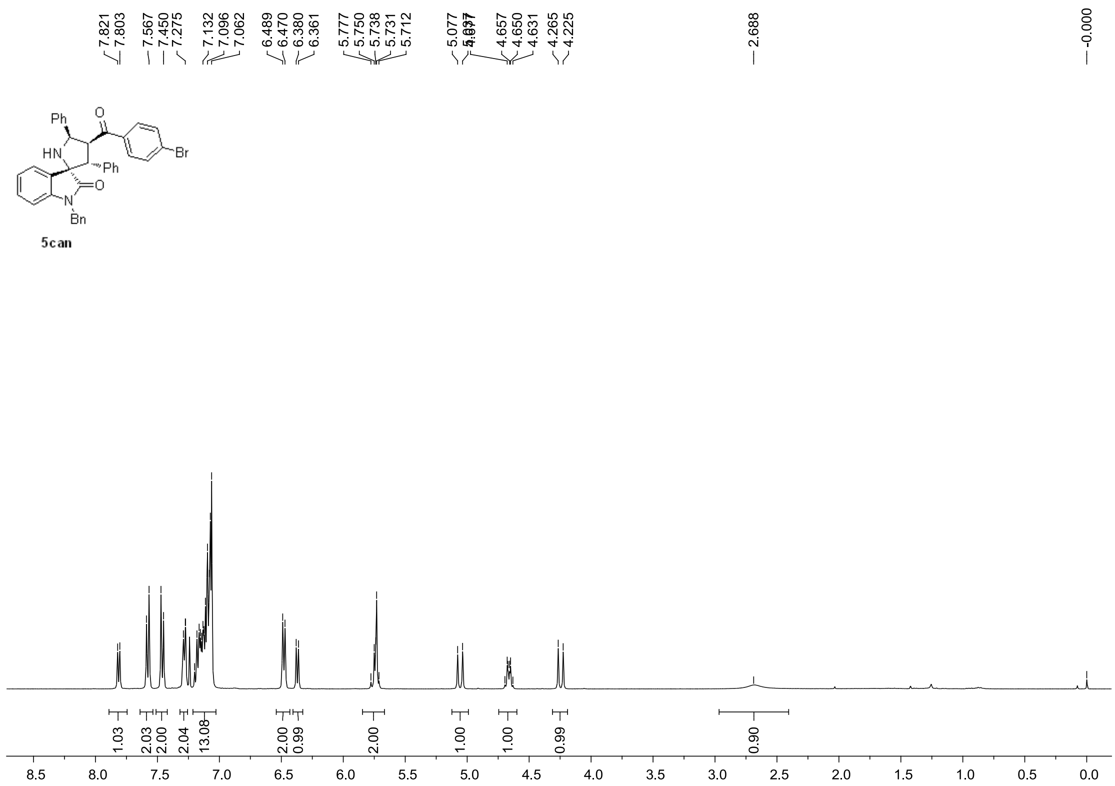
129.39
128.67
128.47
128.40
128.11
127.91
127.67
127.55
127.17
126.45
123.81
123.16
109.36
72.56
62.01
54.64
52.91
43.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.361
5.777
5.750
5.738
5.731
5.712
5.077
4.657
4.650
4.631
4.265
4.225
2.688
-0.000
Ph
O
HN
Br
Ph
O
N
Bn
5can
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2.03
2.00
2.04
13.08
2.00
0.99
2.00
1.00
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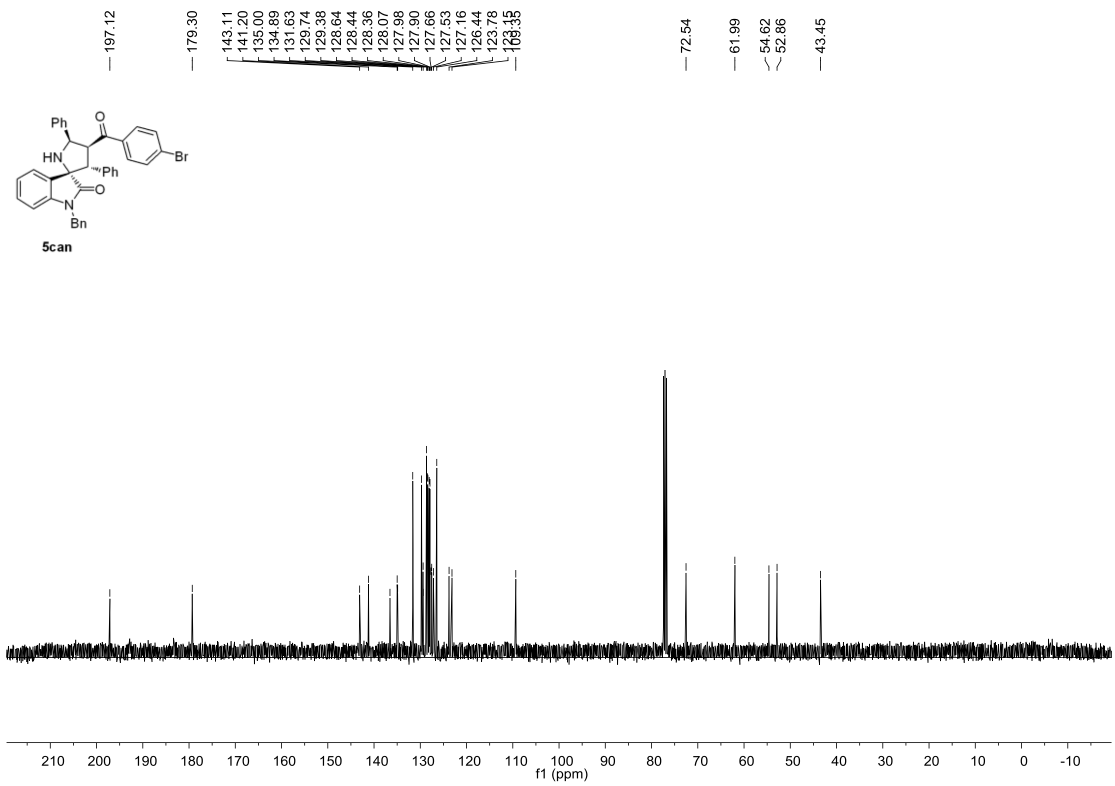
0.99
0.90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128.64
128.44
128.36
128.07
127.98
127.90
127.66
127.53
127.16
126.44
123.78
109.35
72.54
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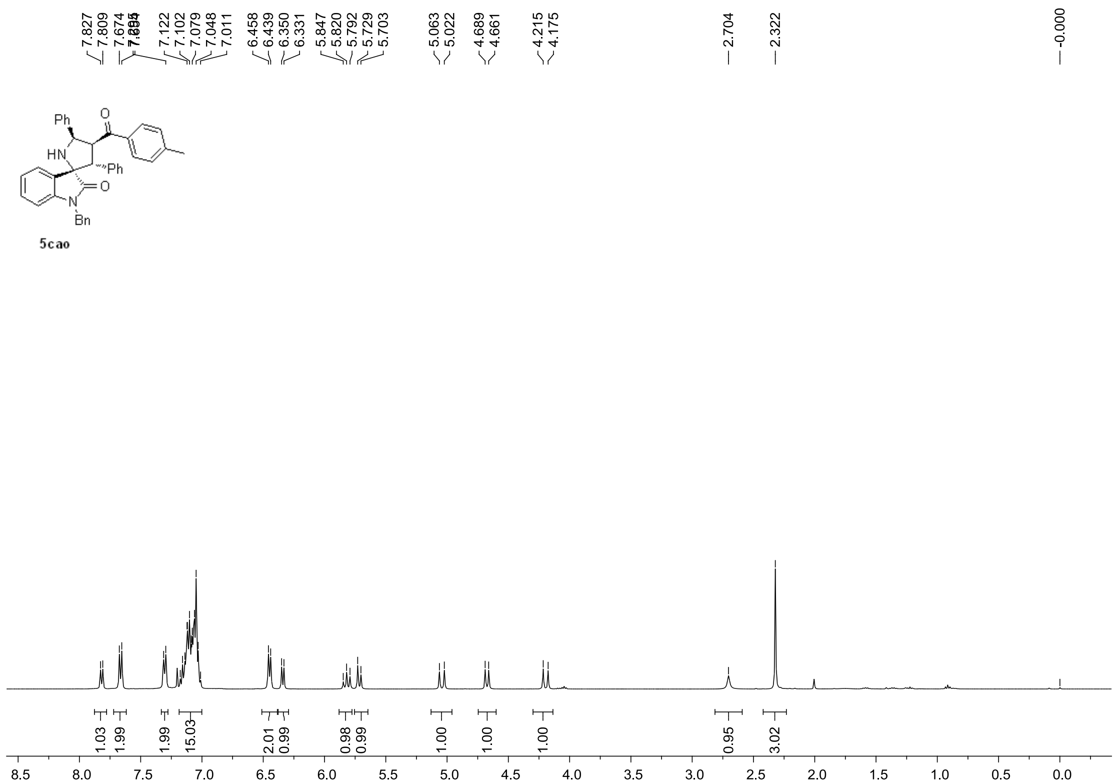
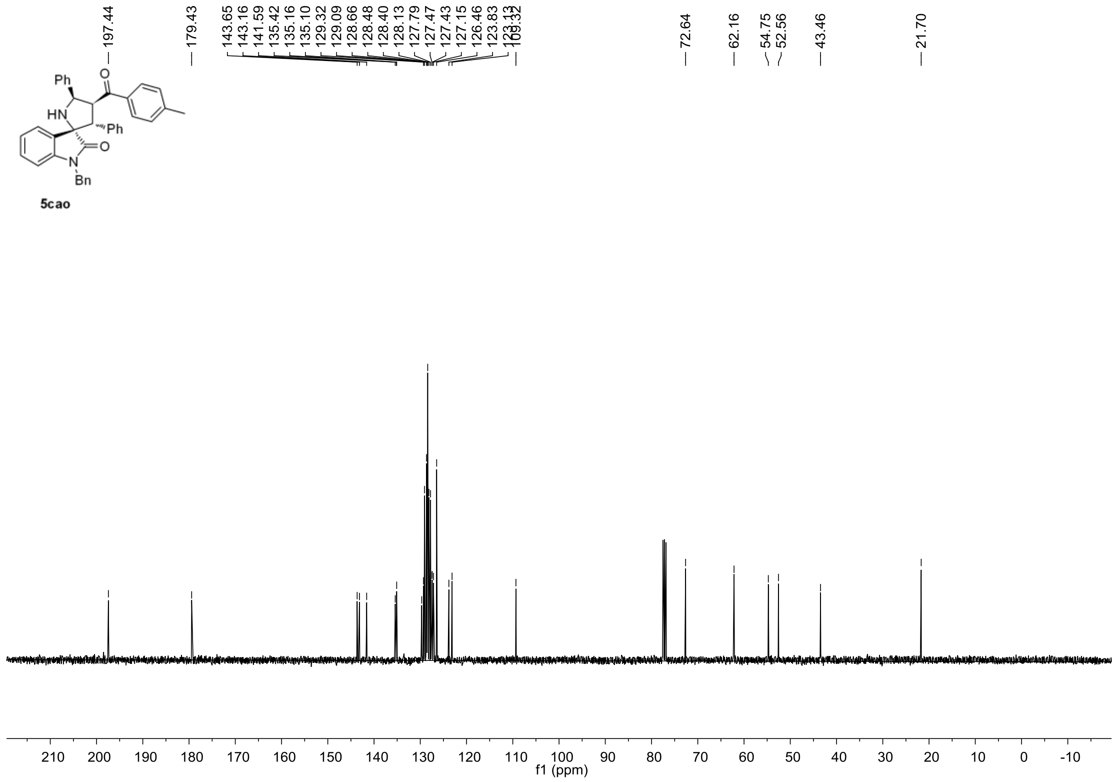
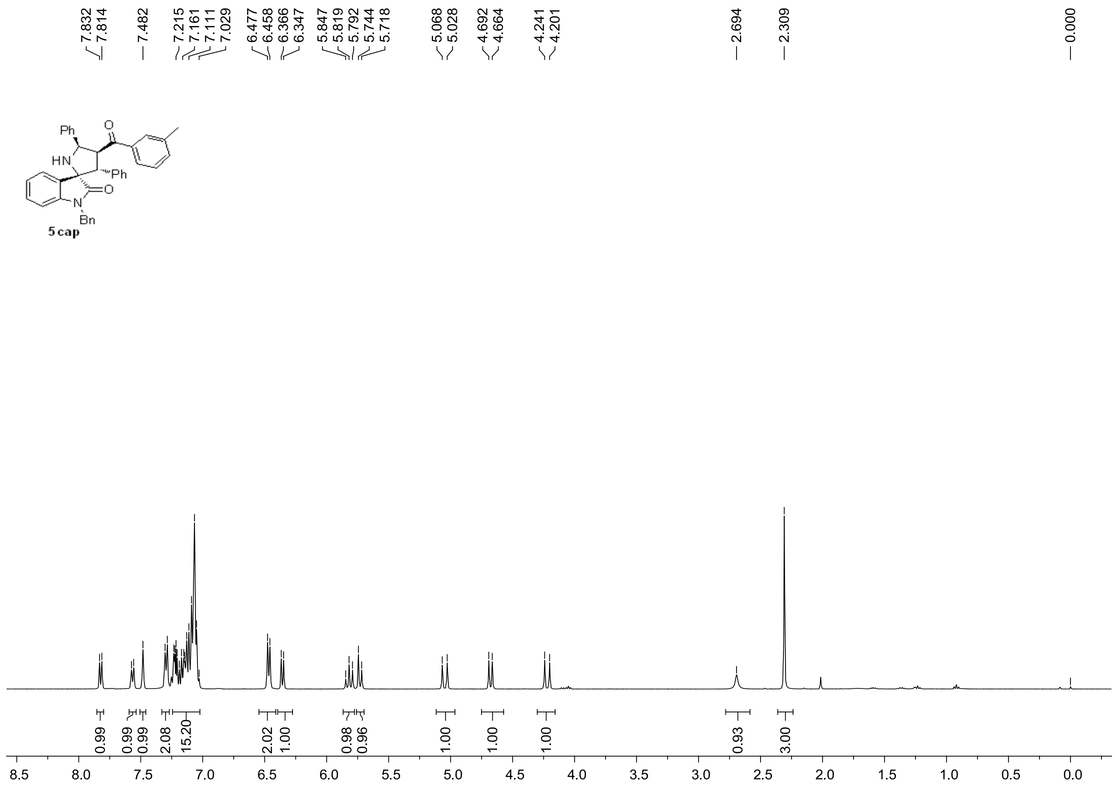
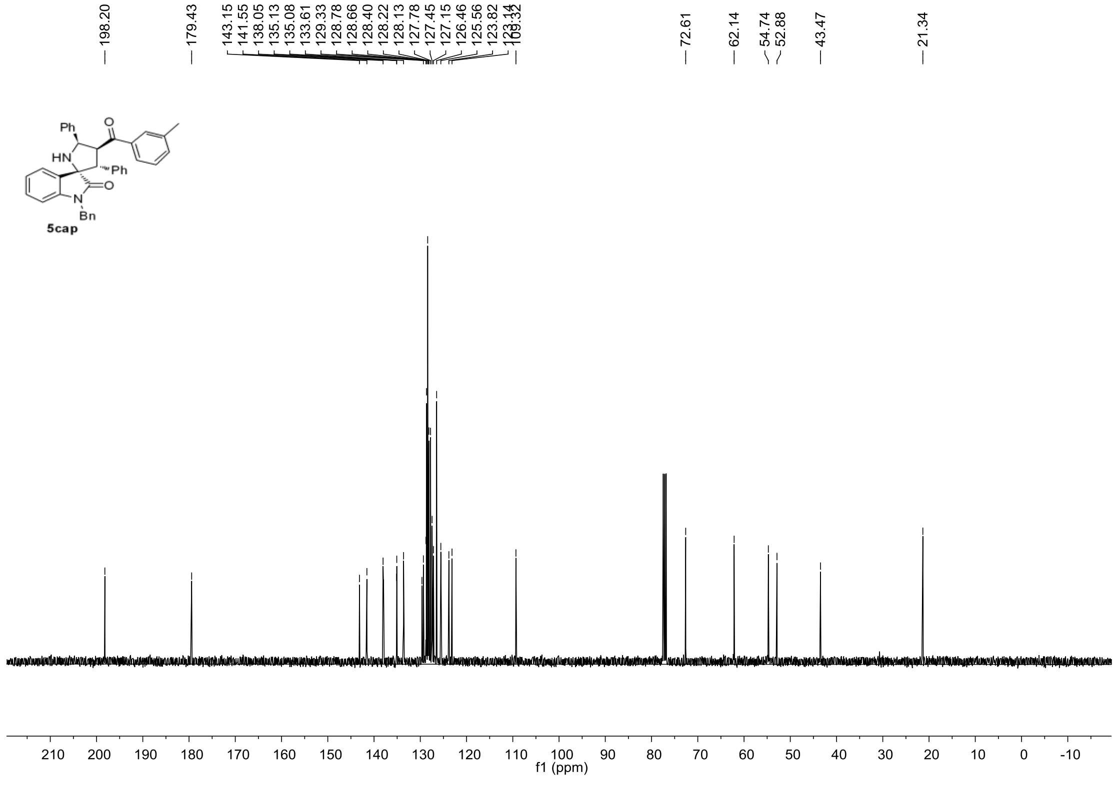
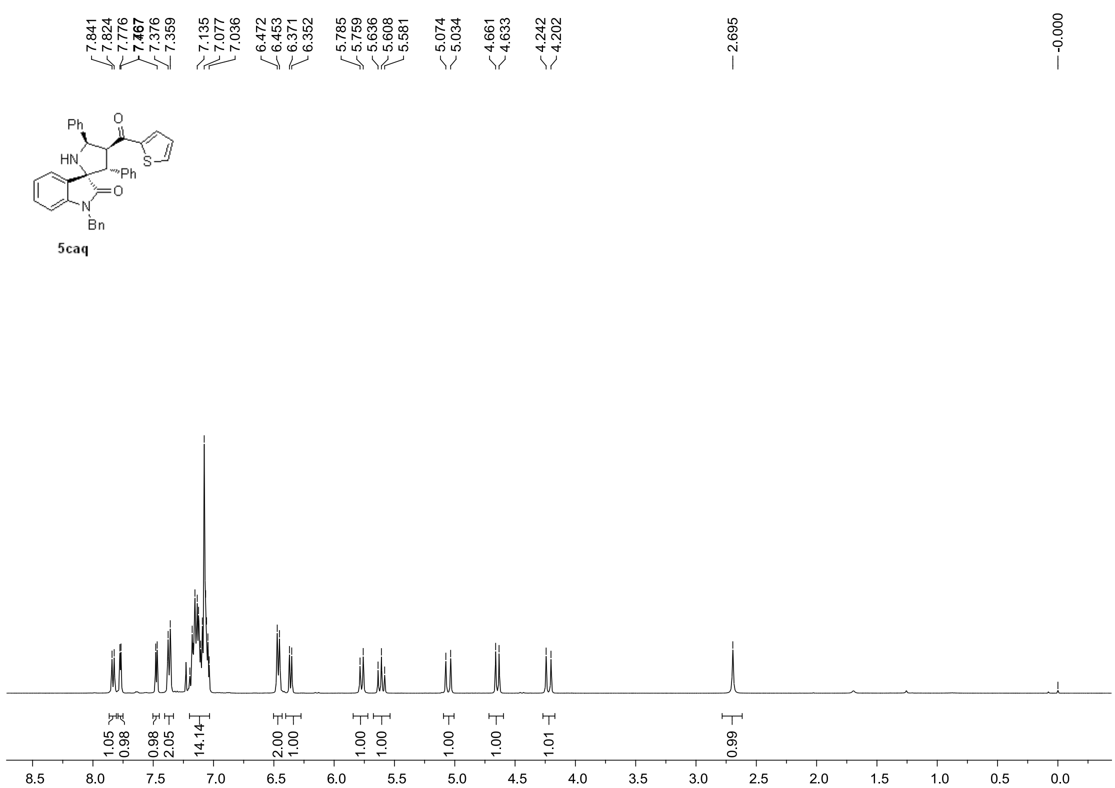
52.86
43.45
Ph
O
HN
Br
Ph
O
N
Bn
5can
f1 (ppm)

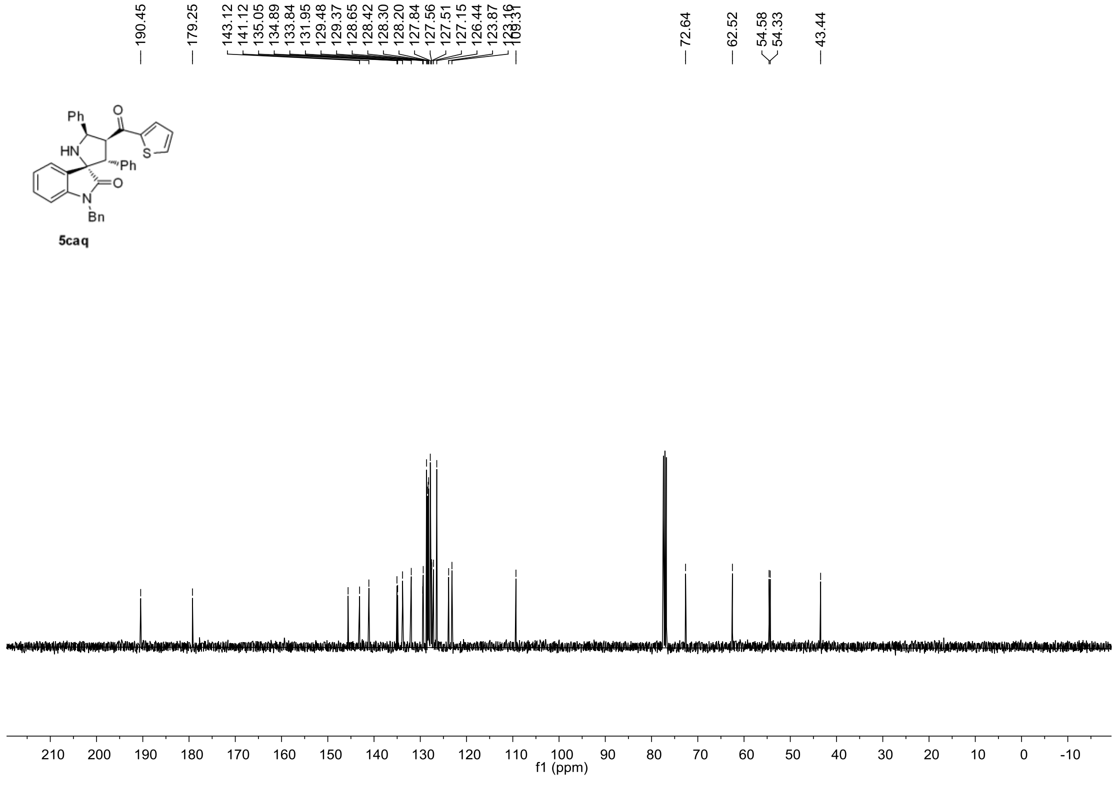


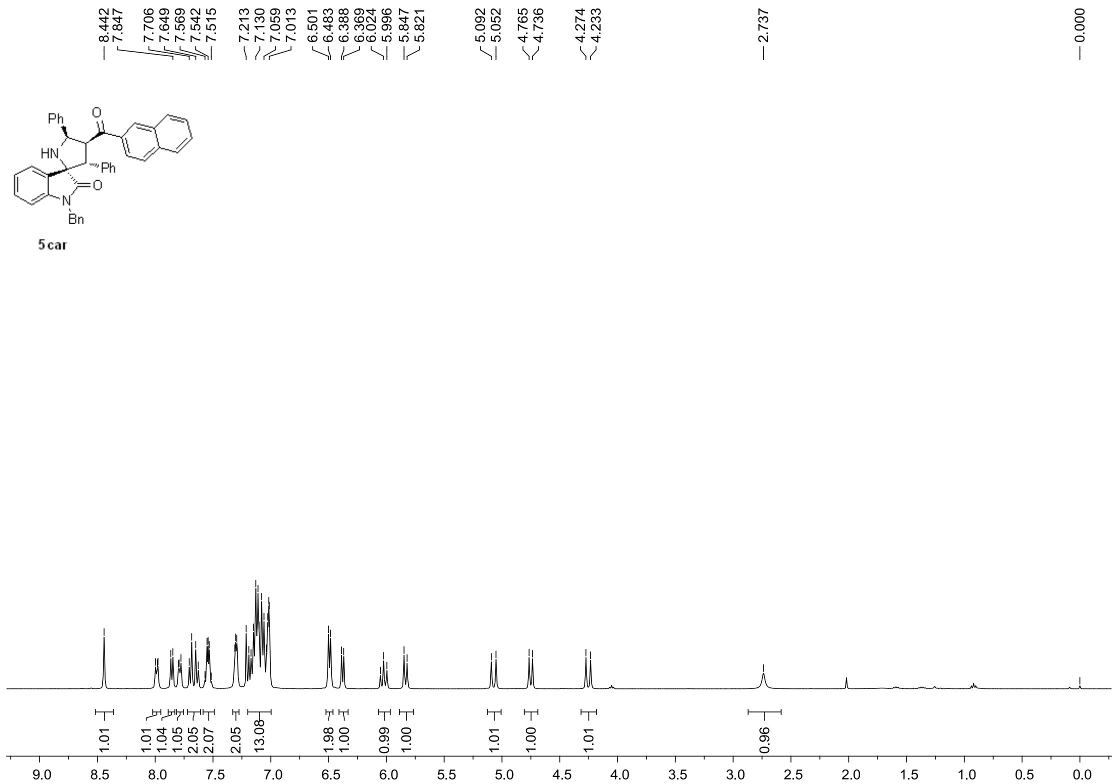








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7.059
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6.369
6.024
5.996
5.847
5.821
5.092
5.052
4.765
4.736
4.274
4.233
2.737
0.000
Ph
O
HN
Ph
N
O
Bn
5car
1.01
1.01
1.04
1.05
2.05
2.07
2.05
13.08
1.98
1.00
0.99
1.00
1.01
1.00
1.01
0.96
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7.5
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6.0
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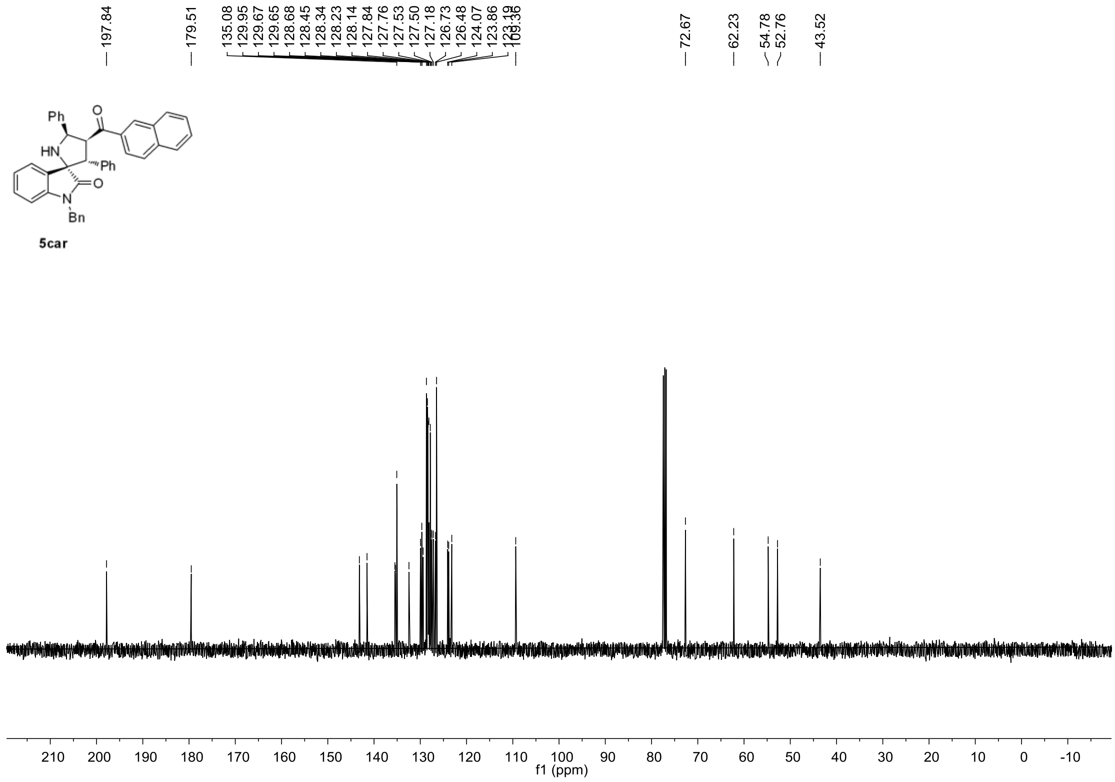
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127.53
127.50
127.18
126.73
126.48
124.07
123.86
123.19
109.36
72.67
62.23
54.78
52.76
43.52
Ph
O
HN
Ph
N
O
Bn
5car
210
200
190
180
170
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100
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30
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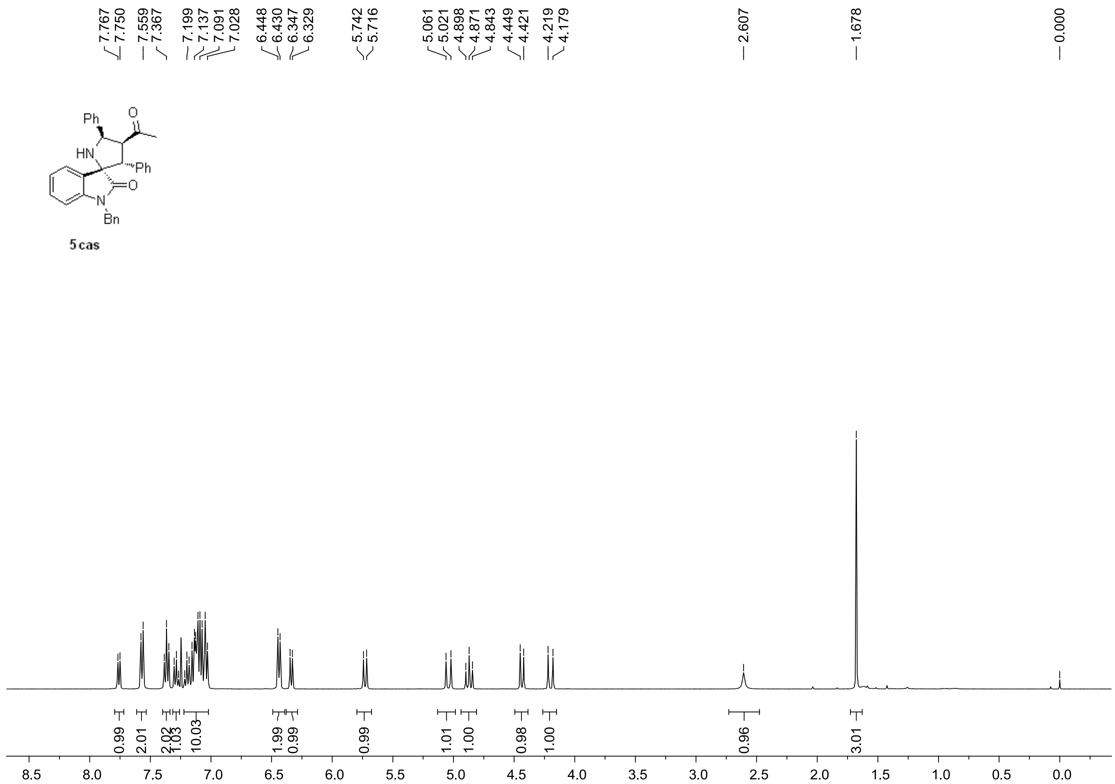
f1 (ppm)



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5.716
5.061
5.021
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4.219
4.179
2.607
1.678
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Ph
N
O
Bn
5cas
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2.01
2.02
1.03
10.03
1.99
0.99
0.99
1.01
1.00
0.98
1.00
0.96
3.01
8.5
8.0
7.5
7.0
6.5
6.0
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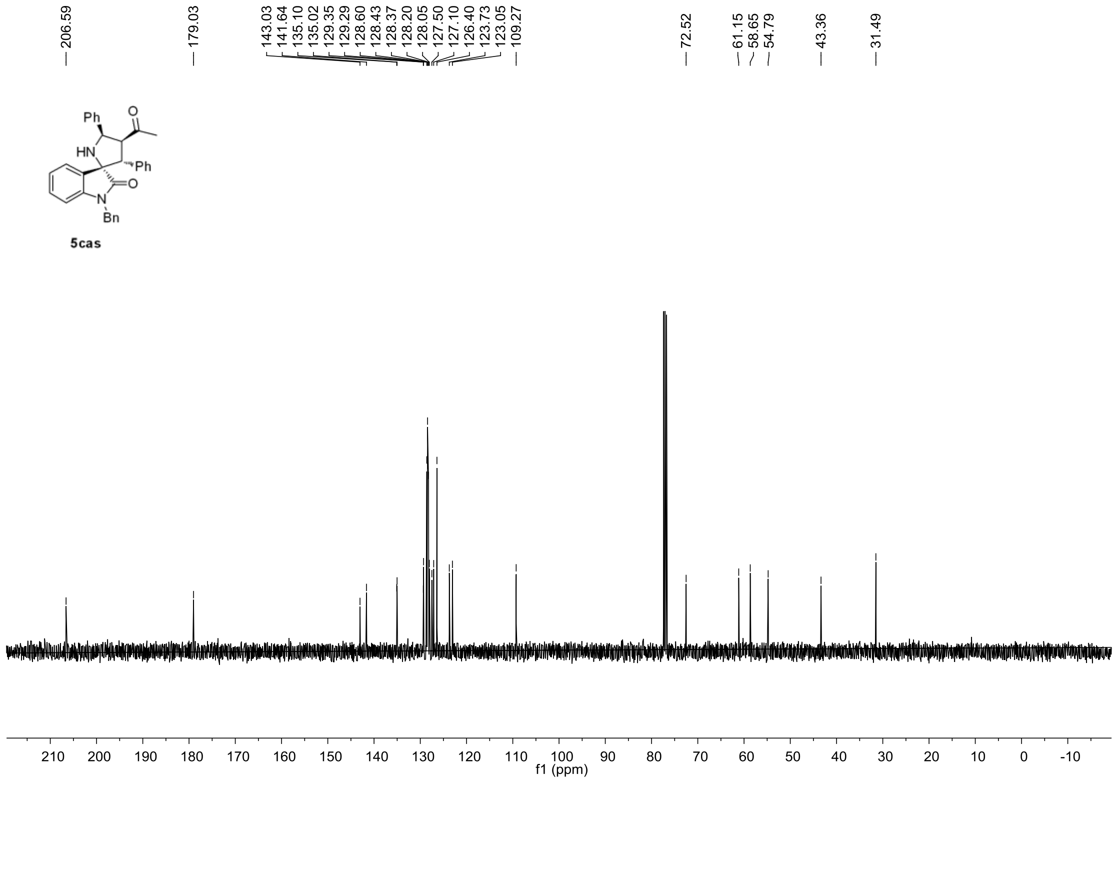

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135.02
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129.29
128.60
128.43
128.37
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128.05
127.50
127.10
126.40
123.73
123.05
109.27
72.52
61.15
58.65
54.79
43.36
31.49
Ph
HN
O
Ph
N
O
Bn
5cas
210
200
190
180
170
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100
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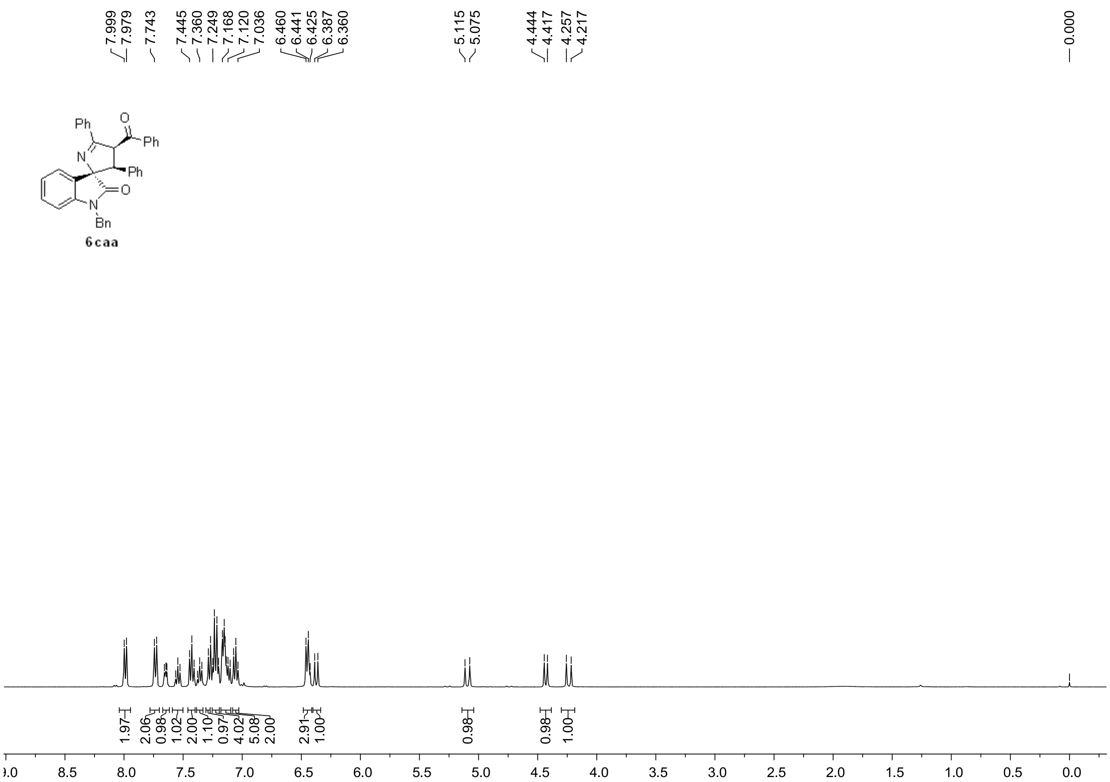
f1 (ppm)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7.120
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6.425
6.387
6.360
5.115
5.075
4.444
4.417
4.257
4.217
0.000
Ph
O
Ph
N
Ph
O
N
Bn
6caa
1.97
2.06
0.98
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2.00
1.10
0.97
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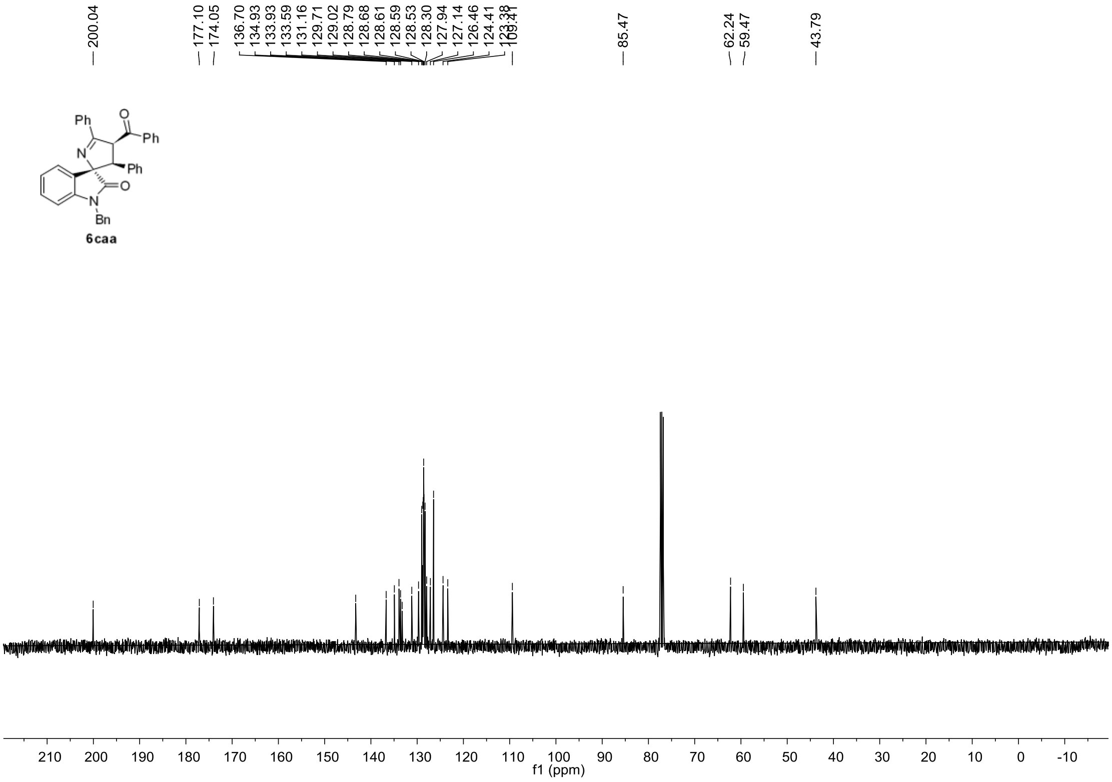
5.08
2.00
2.91
1.00
0.98
0.98
1.00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174.05
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133.93
133.59
131.16
129.71
129.02
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128.61
128.59
128.53
128.30
127.94
127.14
126.46
124.41
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59.47
43.79
Ph
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Ph
N
Ph
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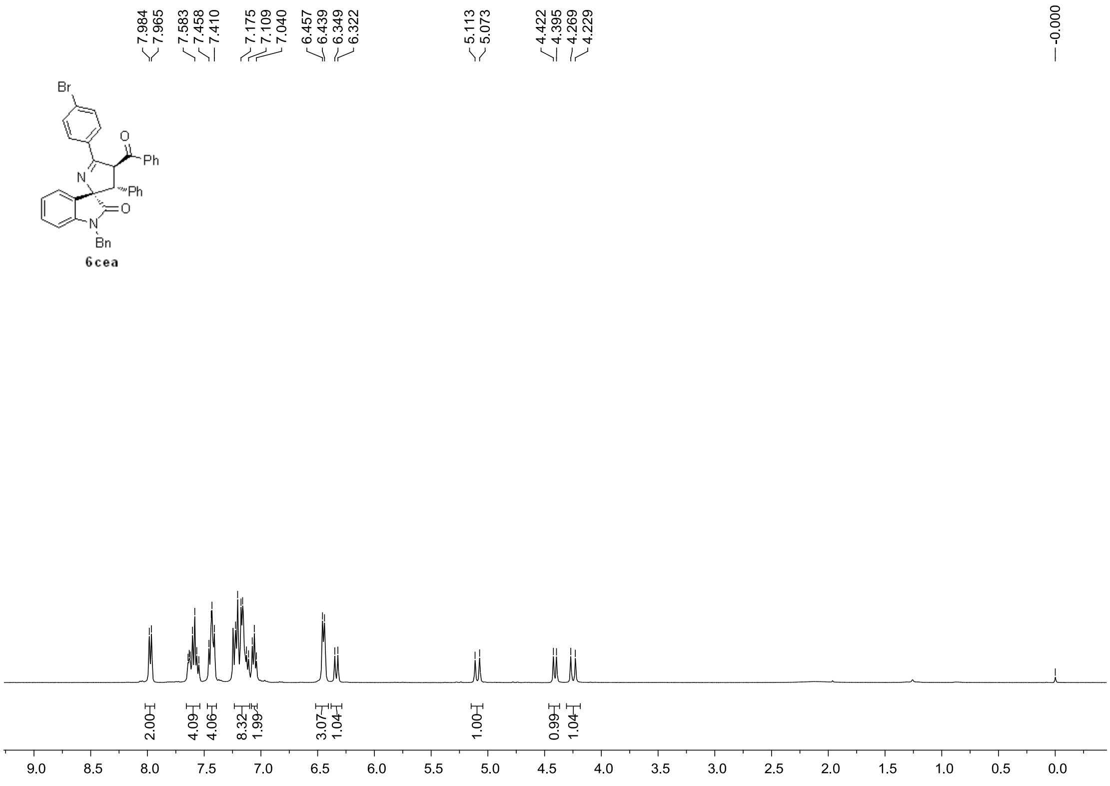
Bn
6caa
f1 (ppm)



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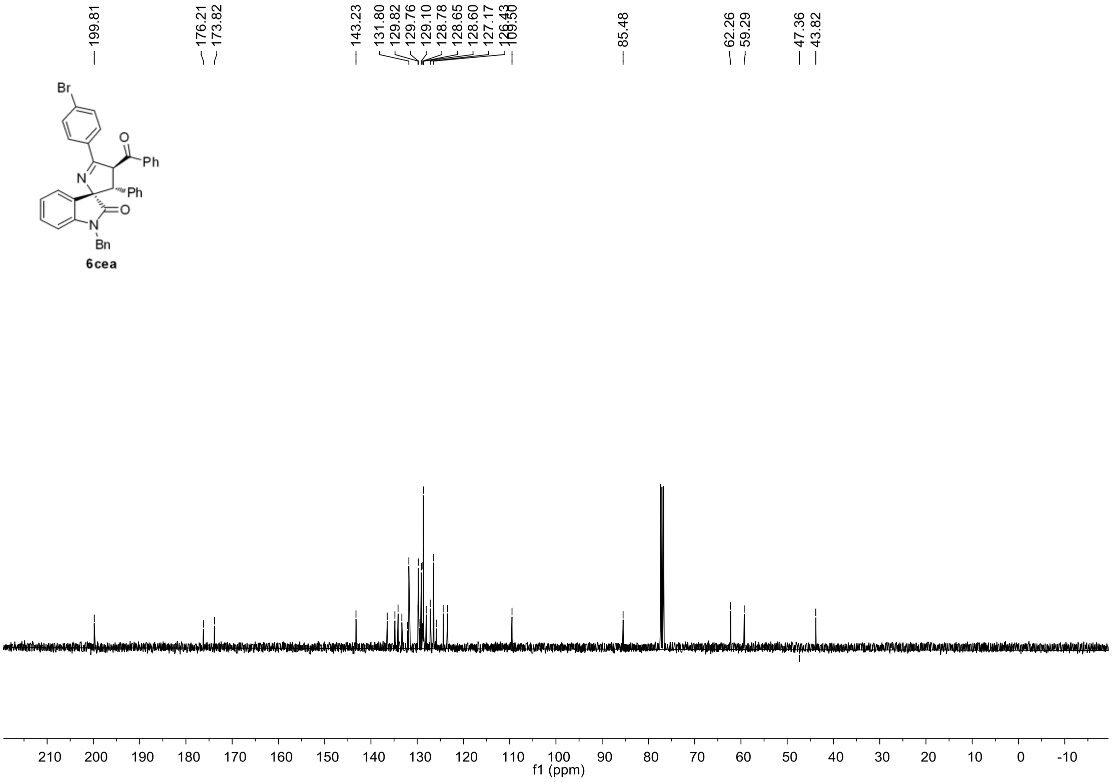

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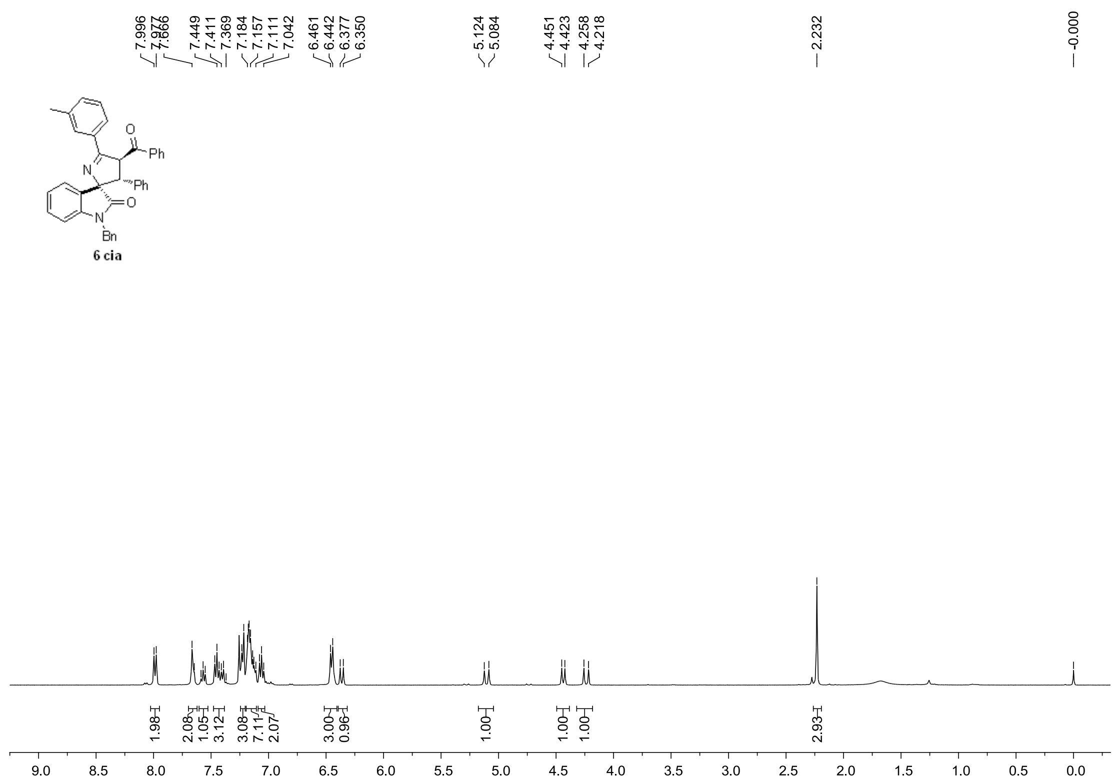
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7.157
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6.442
6.377
6.350
5.124
5.084
4.451
4.423
4.258
4.218
2.232
-0.000
O
Ph
N
Ph
O
N
Bn
6 cia
1.98
2.08
1.05
3.12
3.08
7.11
2.07
3.00
0.96
1.00
1.00
1.00
2.93
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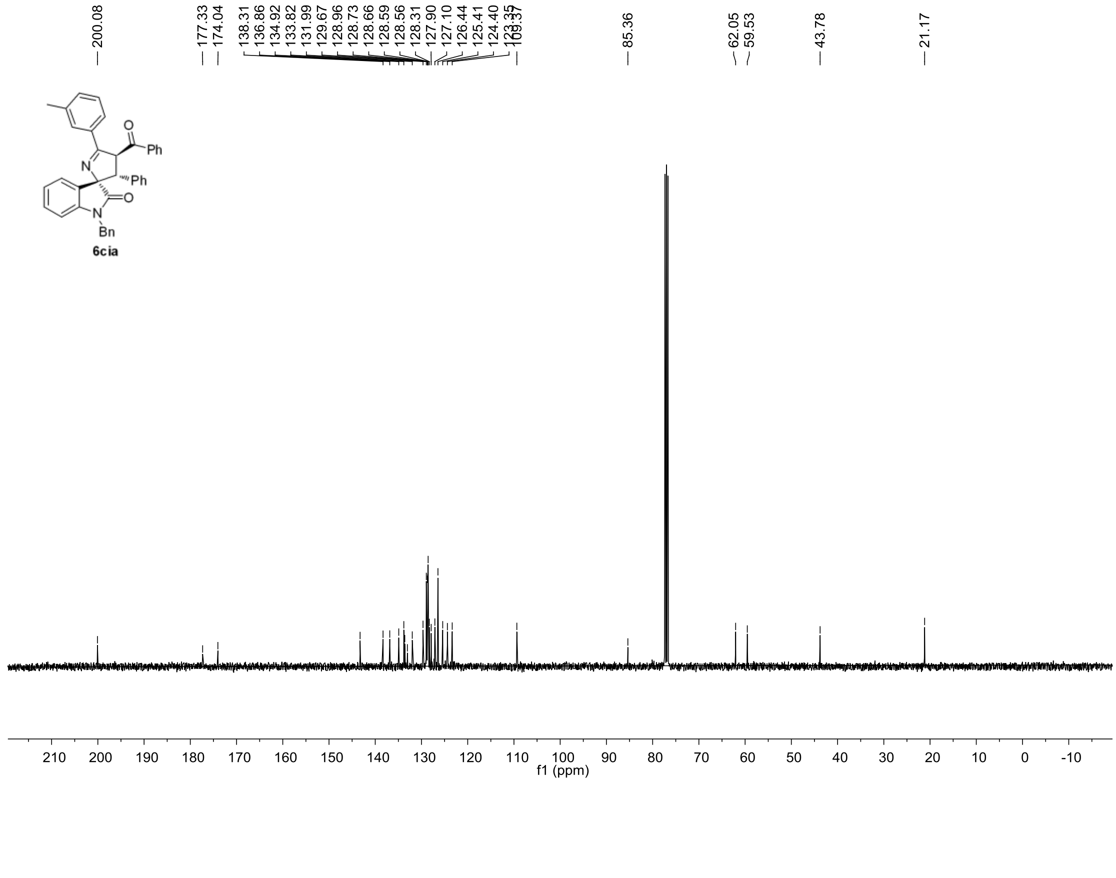
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128.56
128.31
127.90
127.10
126.44
125.41
124.40
123.35
109.37
85.36
62.05
59.53
43.78
21.17
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Ph
O
N
Bn
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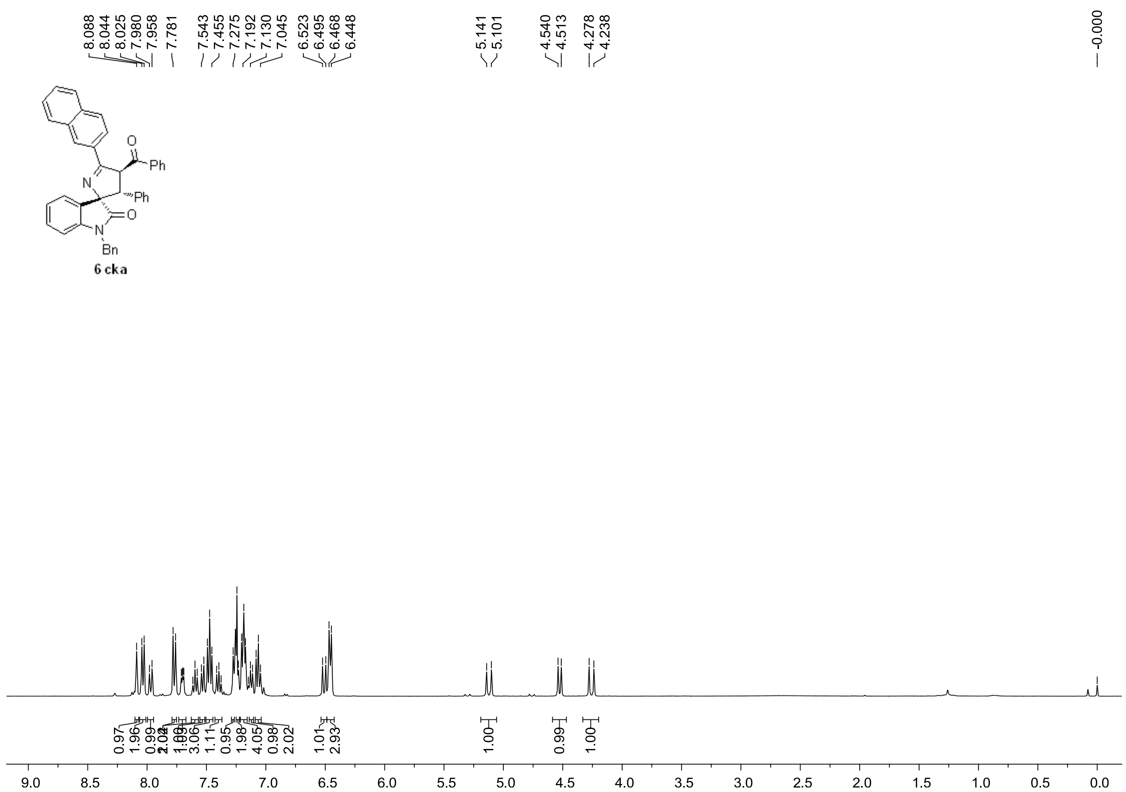
f1 (ppm)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4.238
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Ph
N
Ph
O
N
Bn
6 cka
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1.96
0.99
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3.06
1.11
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4.05
0.98
2.02
1.01
2.93
1.00
0.99
1.00
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8.0
7.5
7.0
6.5
6.0
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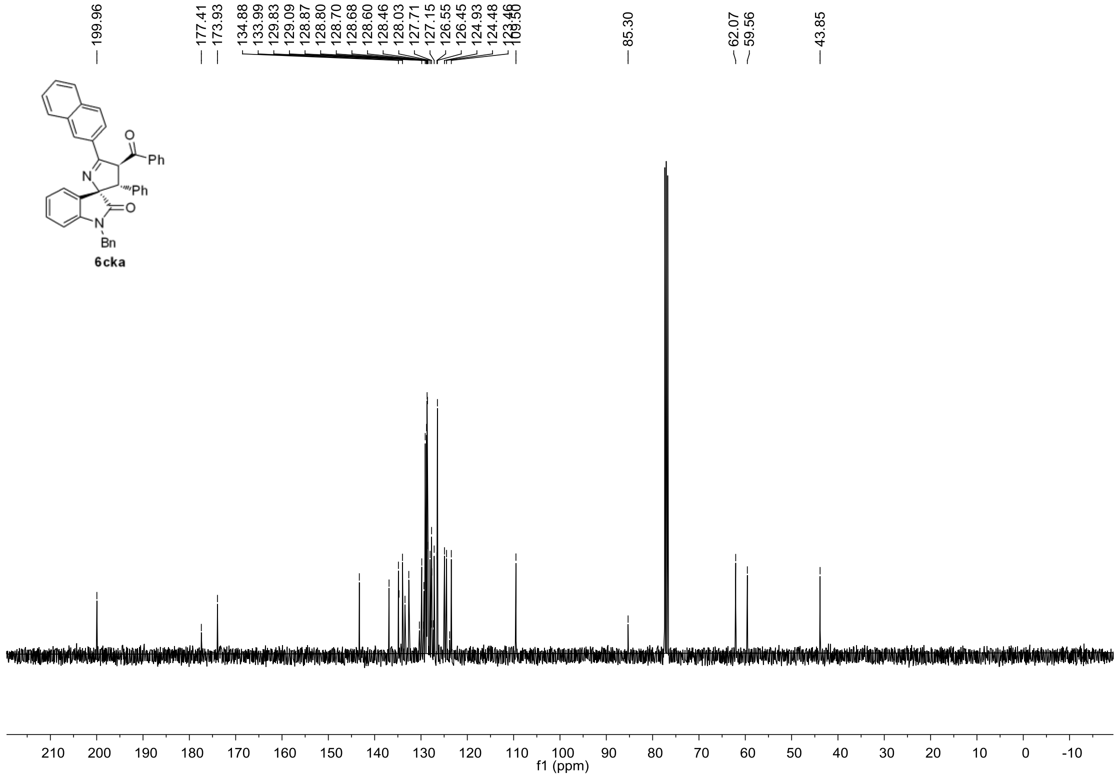
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127.71
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126.55
126.45
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124.48
123.46
109.50
85.30
62.07
59.56
43.85
O
Ph
N
Ph
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Bn
6cka
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200
190
180
170
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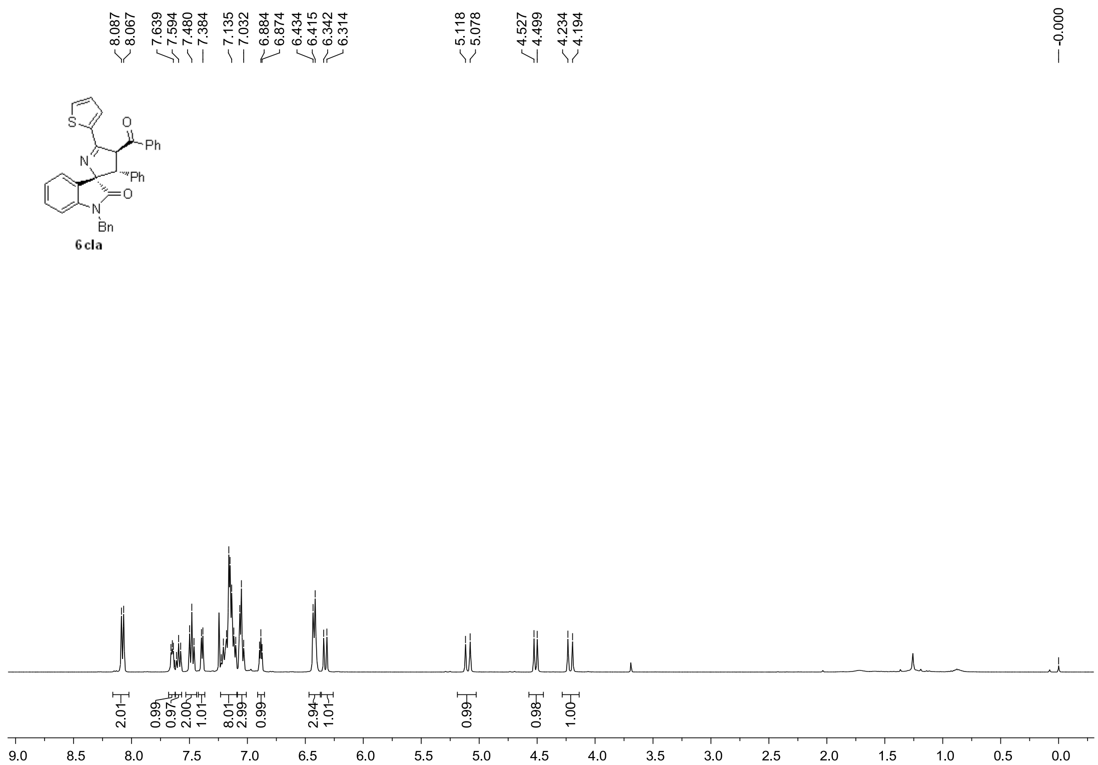
f1 (ppm)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4.194
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N
Bn
6cla
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2.00
1.01
8.01
2.99
0.99
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1.01
0.99
0.98
1.00
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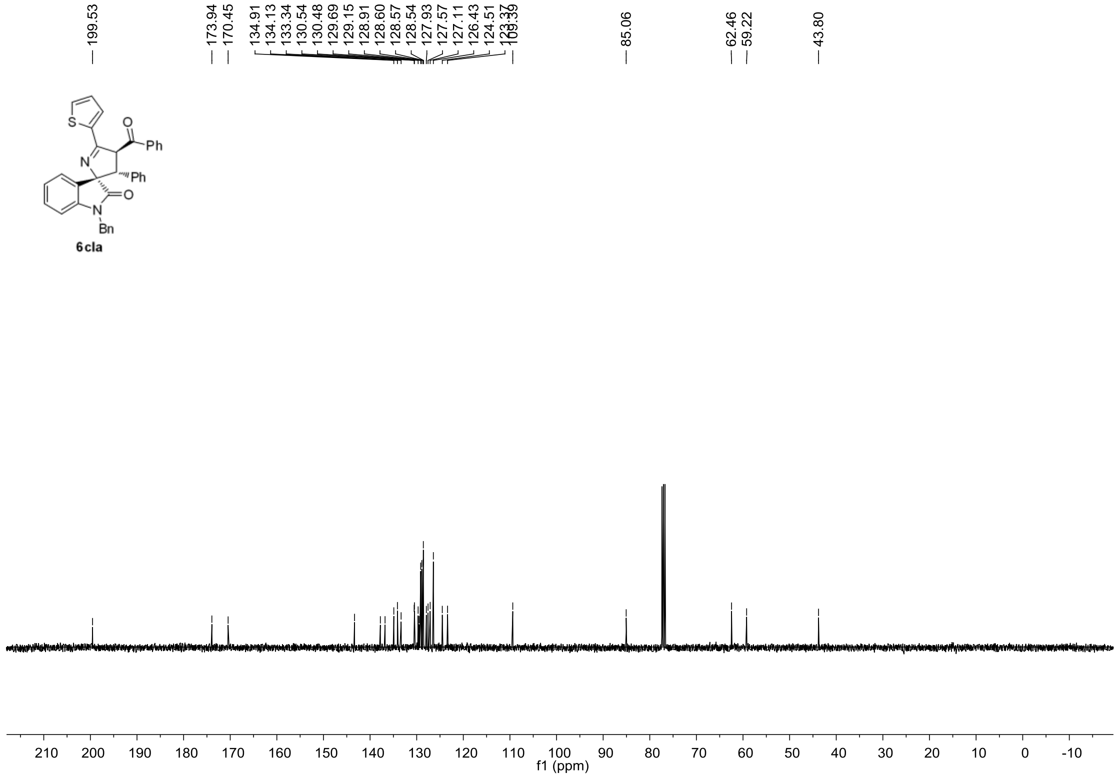
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127.57
127.11
126.43
124.51
123.37
109.39
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62.46
59.22
43.80
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N
Bn
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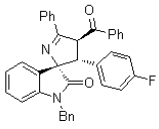
f1 (ppm)



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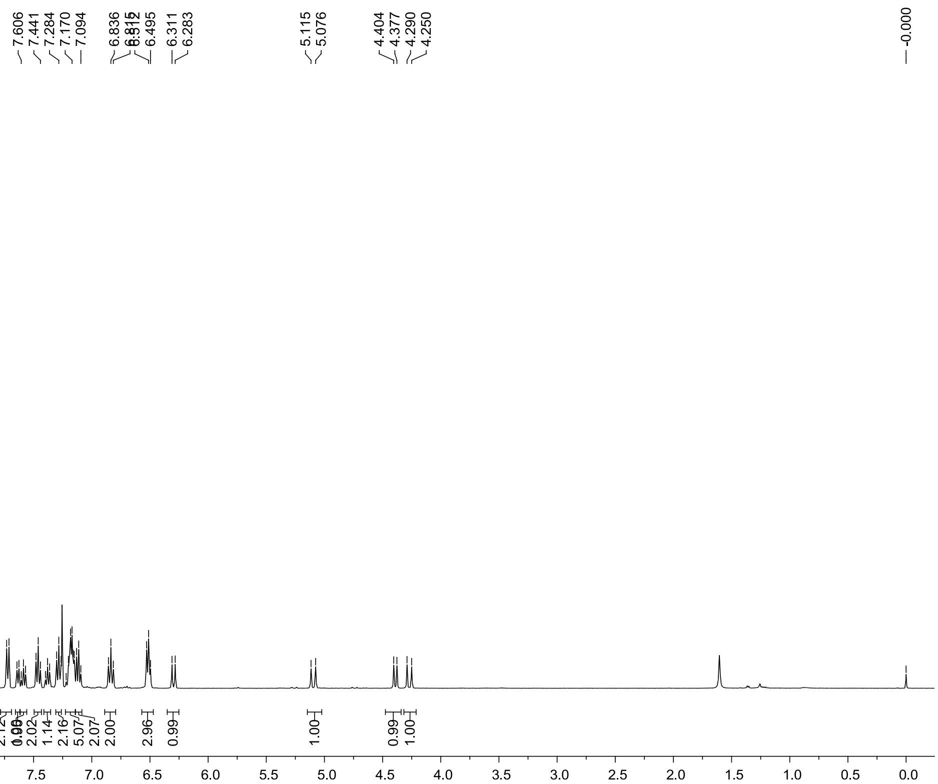

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6.311
6.283
5.115
5.076
4.404
4.377
4.290
4.250
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2.12
1.00
1.04
2.02
1.14
2.16
5.07
2.07
2.00
2.96
0.99
1.00
0.99
1.00
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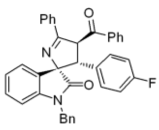

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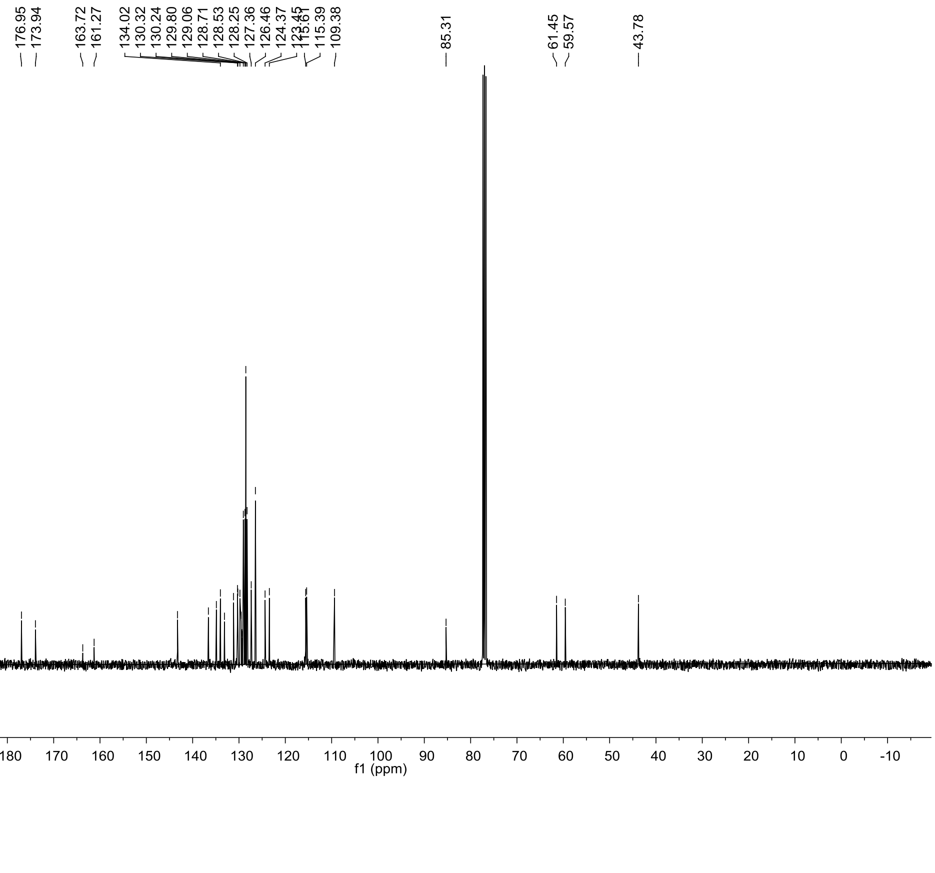

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129.06
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128.53
128.25
127.36
126.46
124.37
123.45
115.61
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61.45
59.57
43.78
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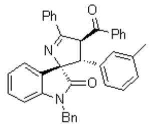
f1 (ppm)



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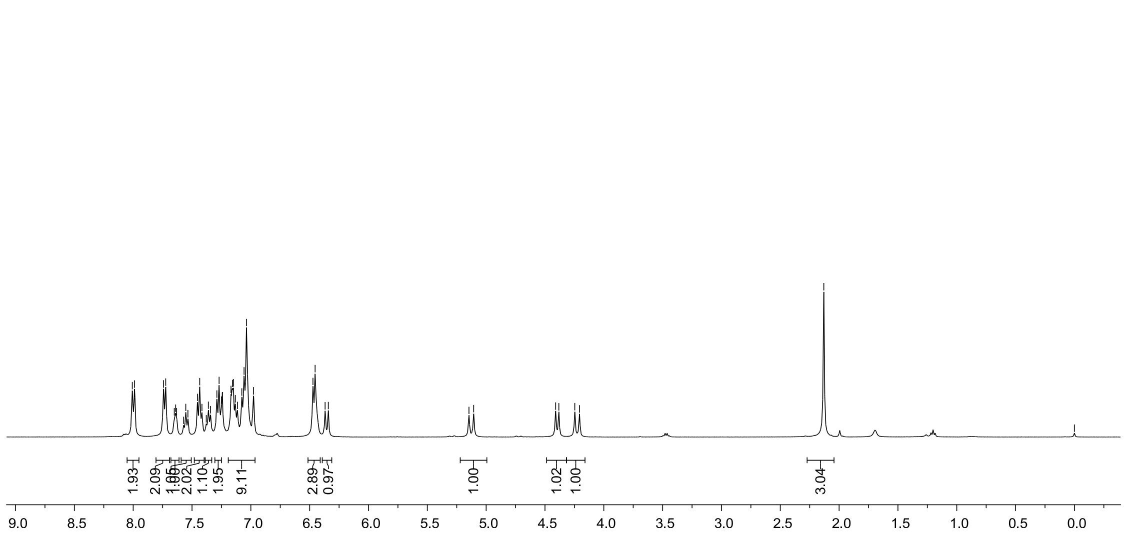

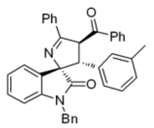

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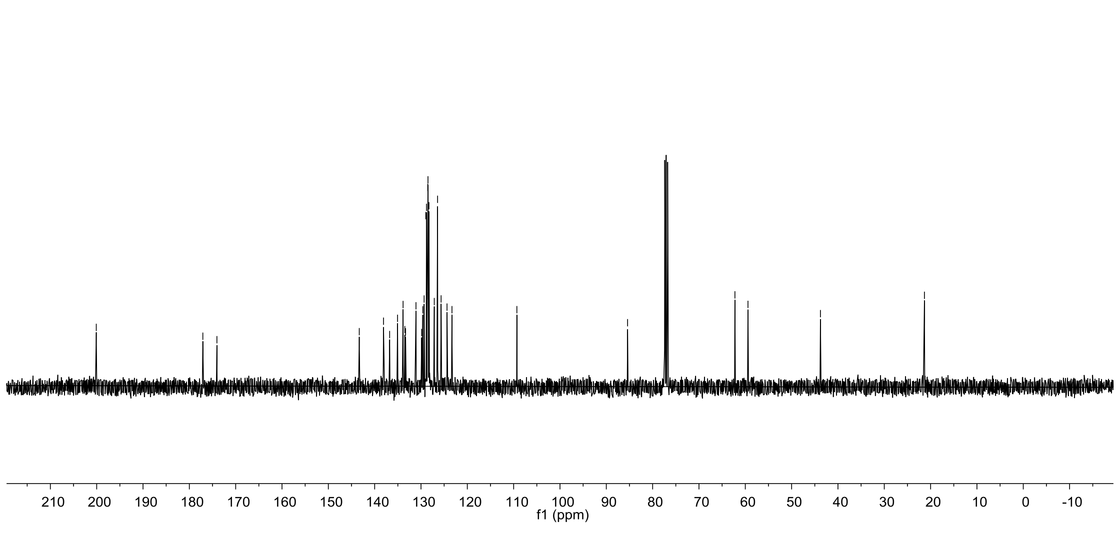

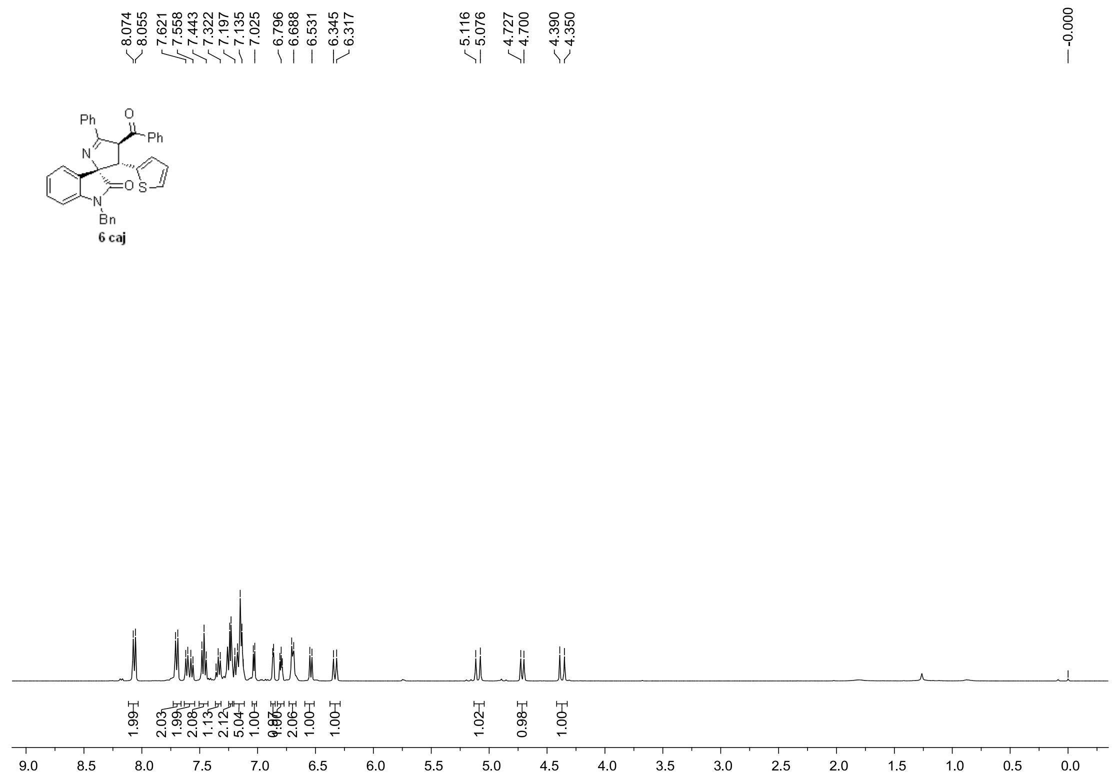
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7.135
7.025
6.796
6.688
6.531
6.345
6.317
5.116
5.076
4.727
4.700
4.390
4.350
-0.000
Ph
O
Ph
N
S
O
N
Bn
6 caj
1.99
2.03
1.99
2.08
1.13
2.12
5.04
1.00
2.06
1.00
1.00
1.02
0.98
1.00
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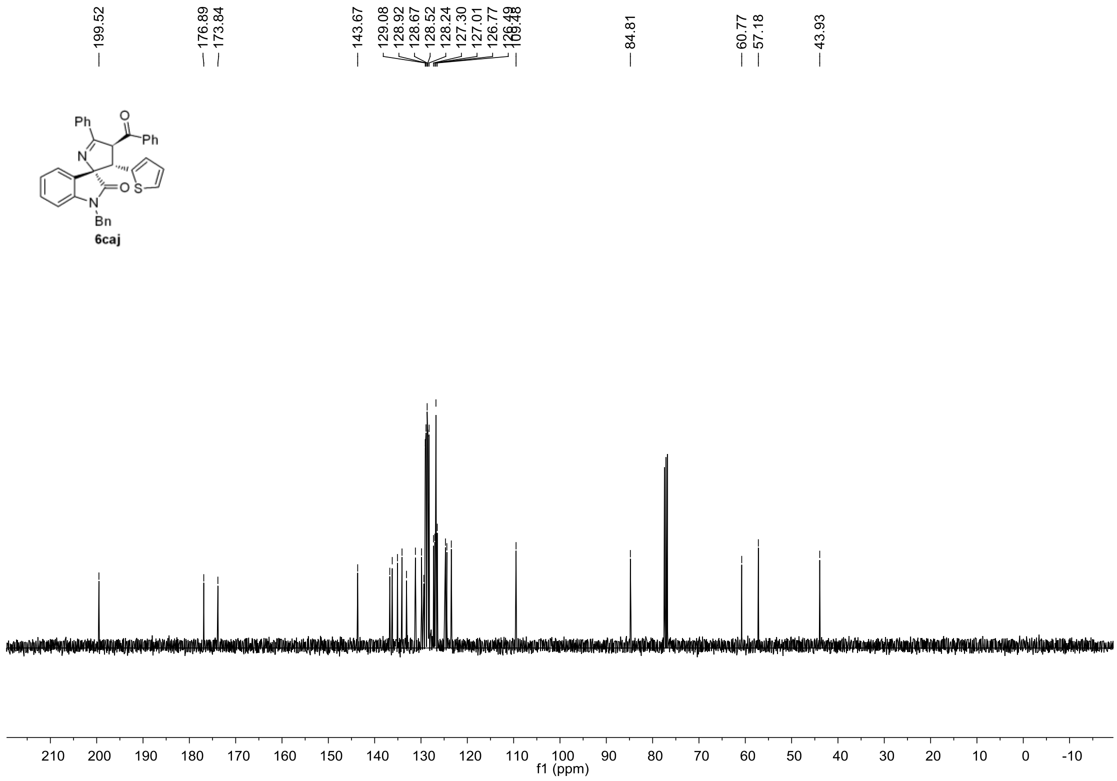
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84.81
60.77
57.18
43.93
Ph
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Ph
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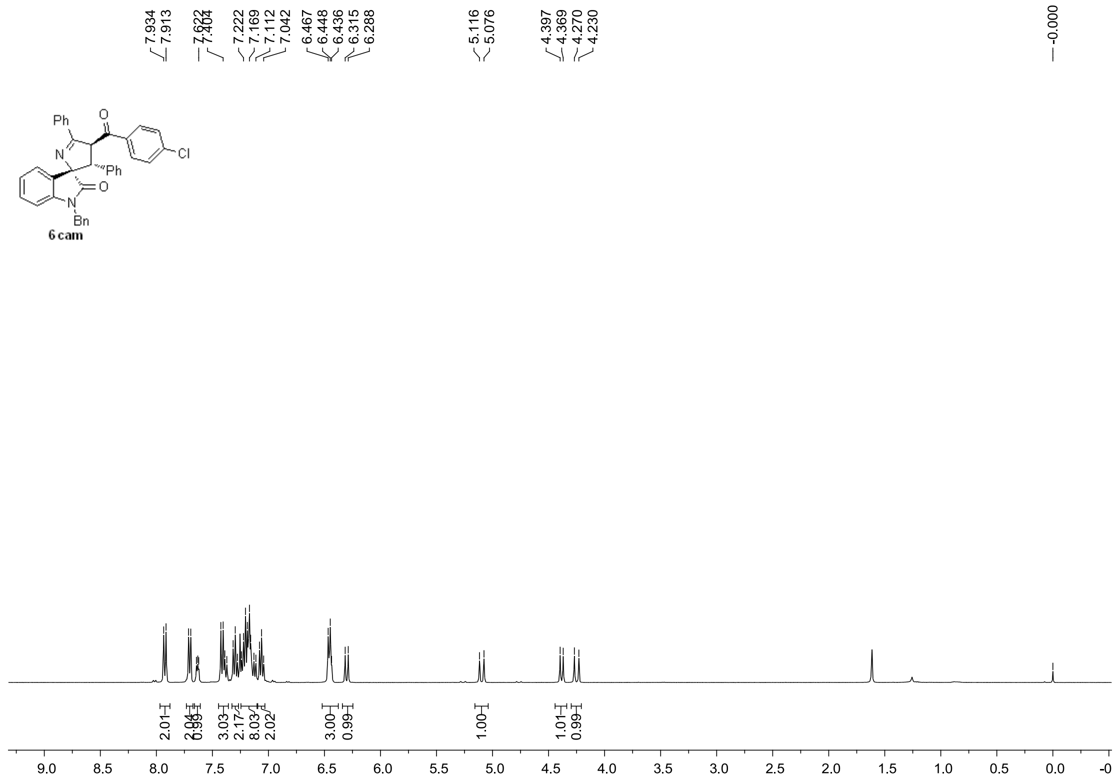
S
O
N
Bn
6caj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.315
6.288
5.116
5.076
4.397
4.369
4.270
4.230
-0.000
Ph
O
N
Ph
Cl
O
N
Bn
6cam
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2.04
0.99
3.03
2.17
8.03
2.02
3.00
0.99
1.00
1.01
0.99
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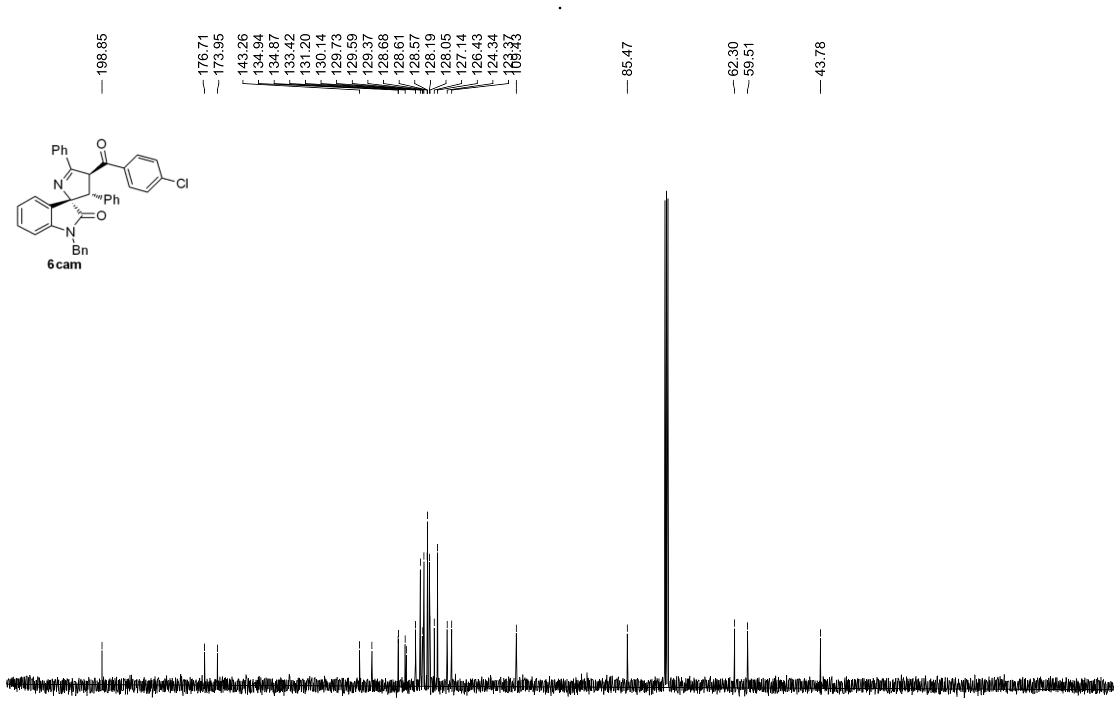
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128.68
128.61
128.57
128.19
128.05
127.14
126.43
124.34
123.37
109.43
85.47
62.30
59.51
43.78
Ph
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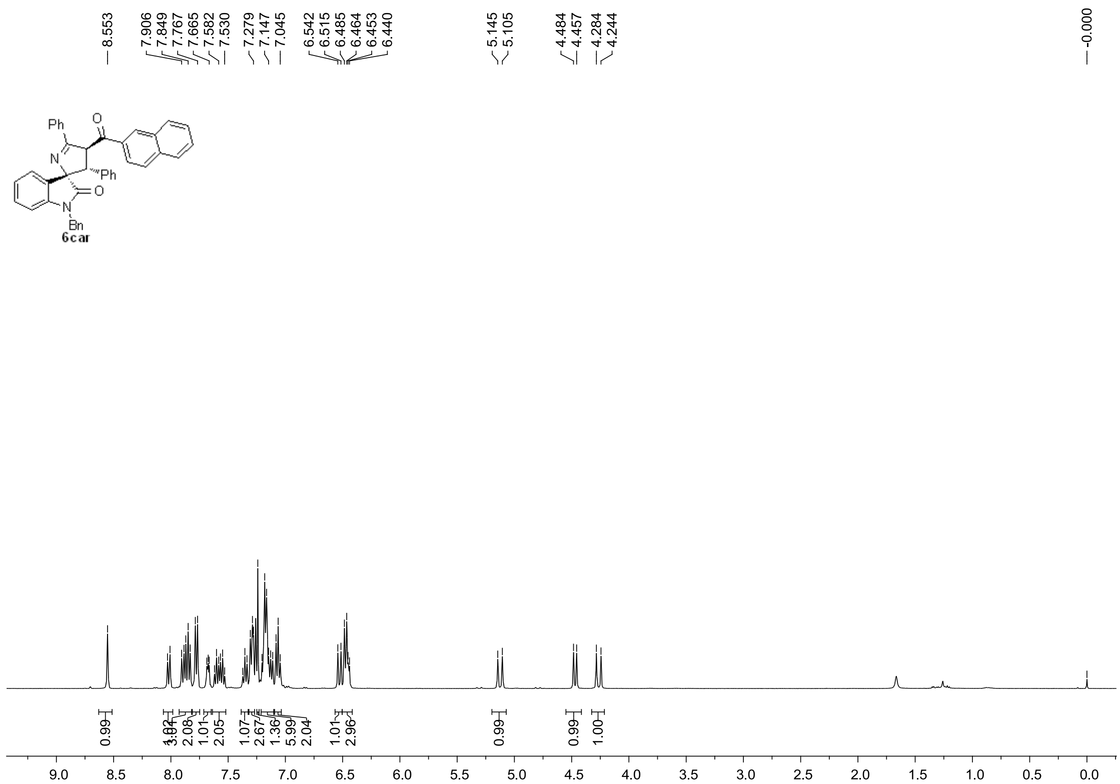
N
Ph
Cl
O
N
Bn
6cam
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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5.145
5.105
4.484
4.457
4.284
4.244
-0.000
Ph
O
N
Ph
O
N
Bn
6car
0.99
3.02
3.01
2.08
1.01
2.05
1.07
2.67
1.36
5.99
2.04
1.01
2.96
0.99
0.99
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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2.0
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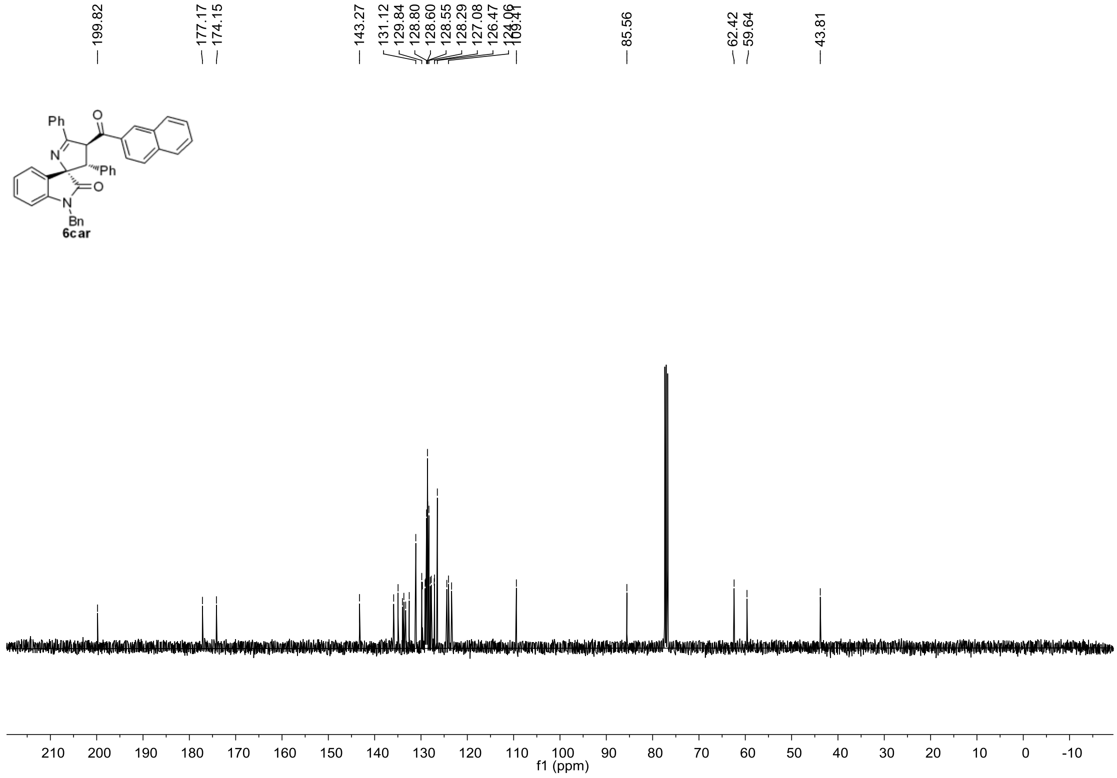
0.0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124.06
109.41
85.56
62.42
59.64
43.81
Ph
O
N
Ph
O
N
Bn
6car
210
200
190
180
170
160
150
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110
100
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80
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20
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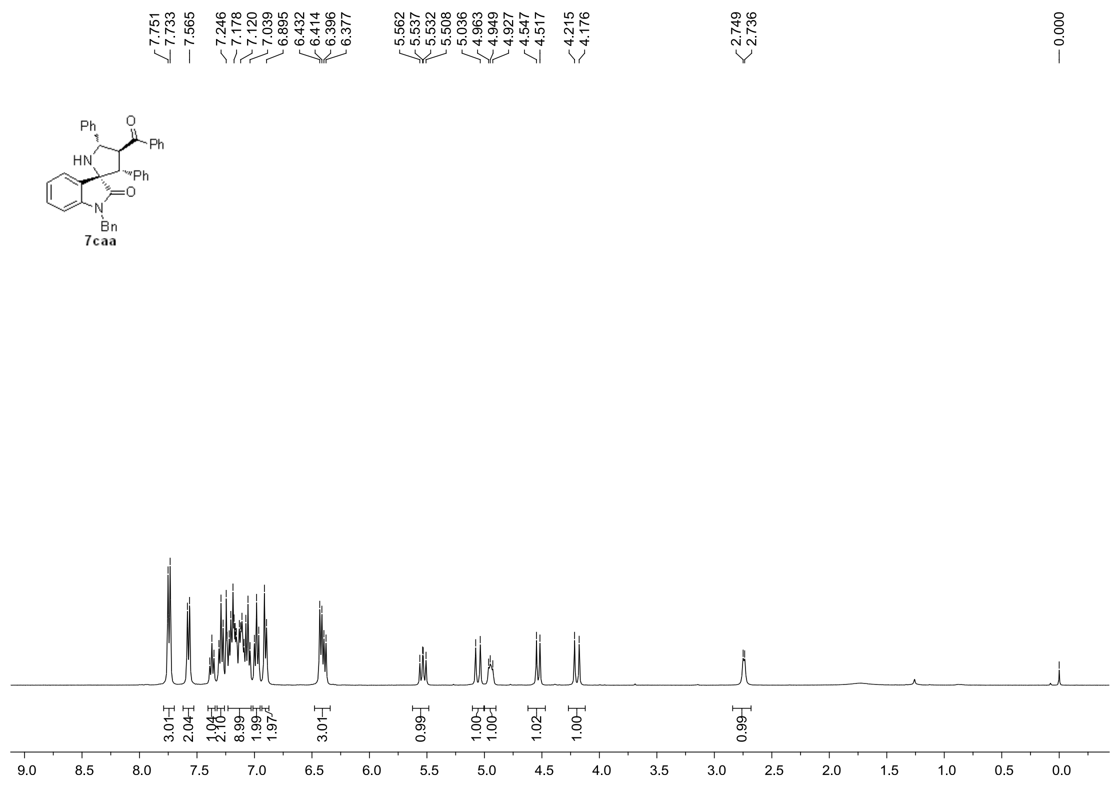
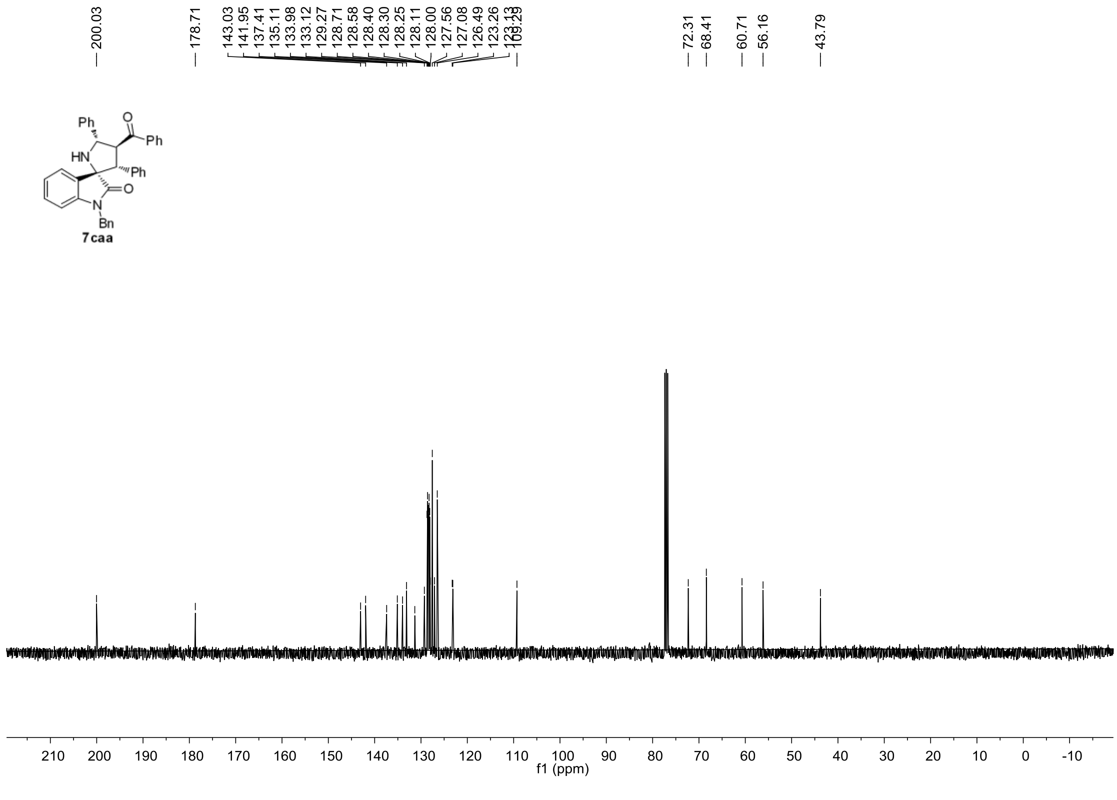
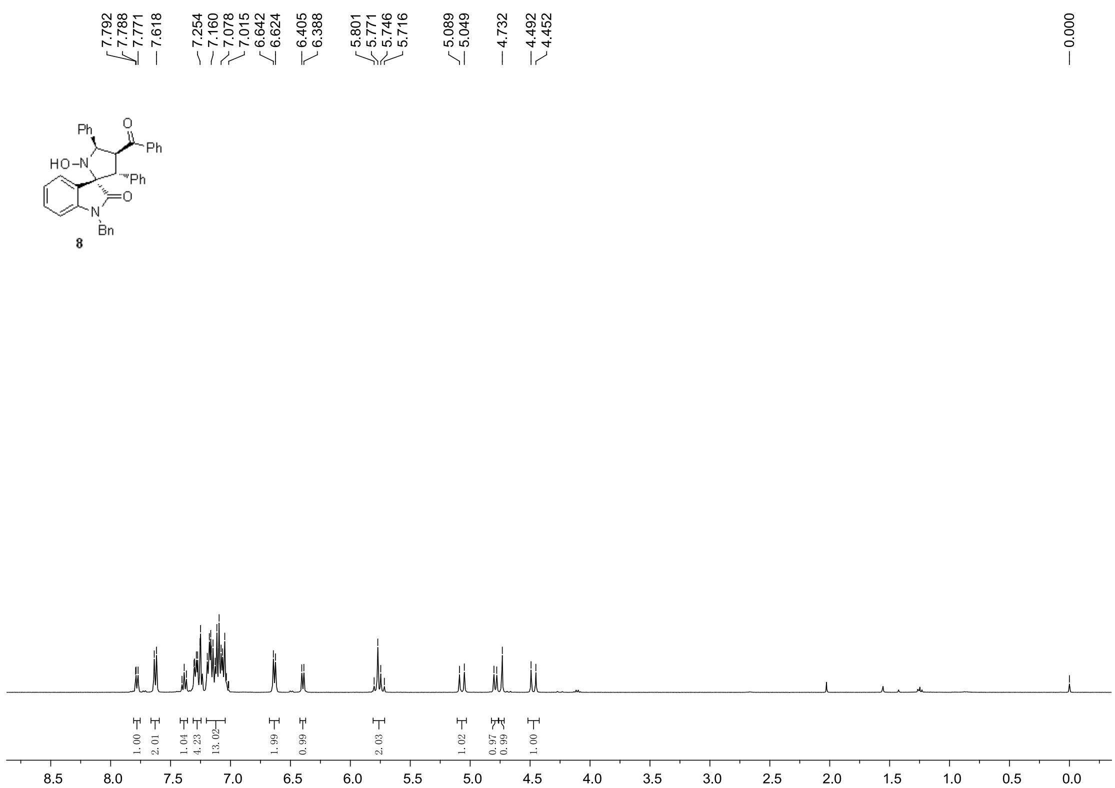
0
-10
f1 (ppm)



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5.049
4.732
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O
Ph
HO
N
Ph
O
N
Bn
8
1.00
2.01
1.04
4.23
13.02
1.99
0.99
2.03
1.02
0.97
0.99
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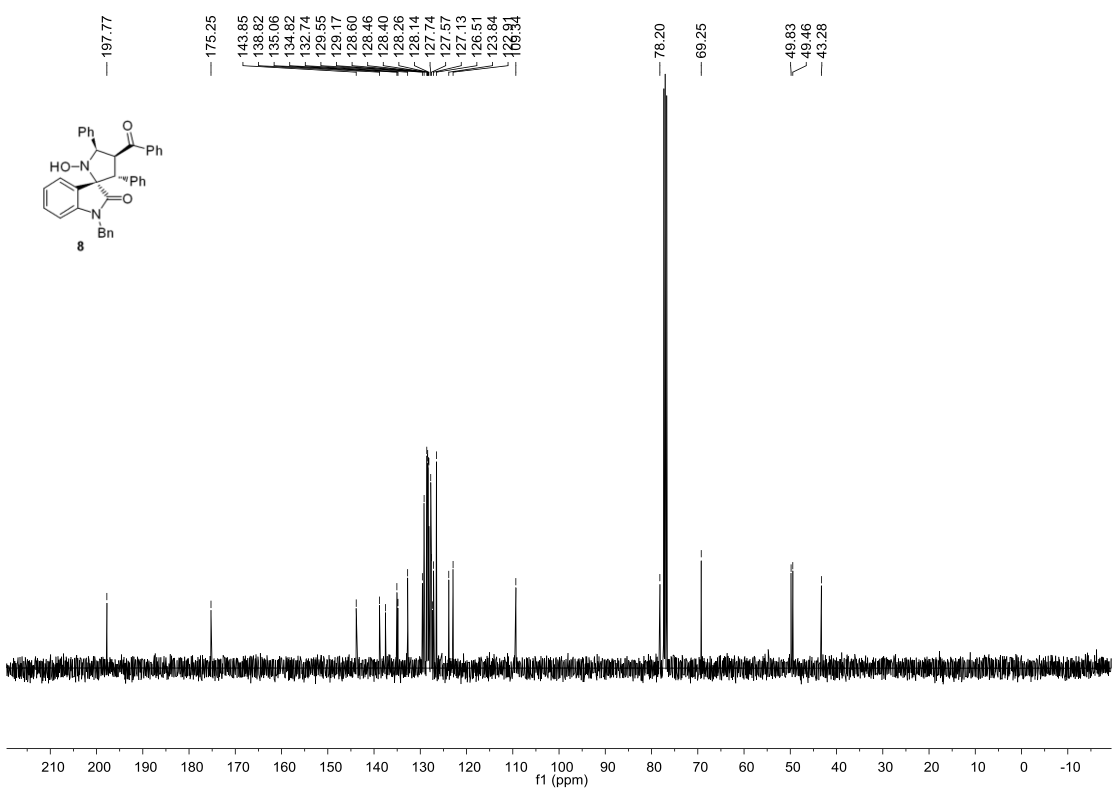
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127.74
127.57
127.13
126.51
123.84
78.20
69.25
49.83
49.46
43.28
Ph
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Ph
HO
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Ph
O
N
Bn
8
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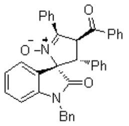
f1 (ppm)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Ph
O
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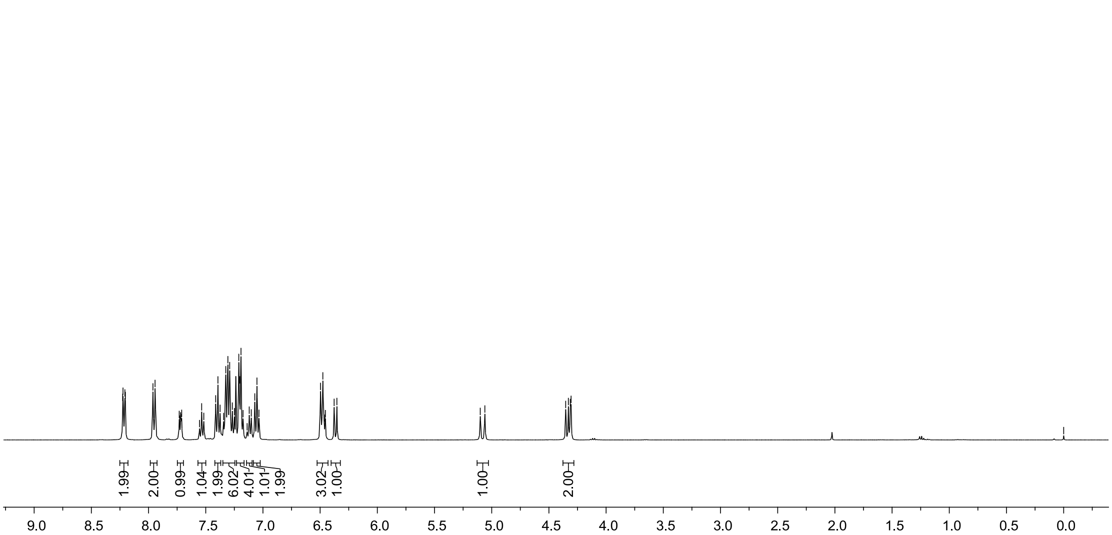
Ph
N
O
Bn

9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6.458
6.454
6.377
6.354
5.100
5.060
4.353
4.330
4.313
4.306
-0.000
1.99
2.00
0.99
1.04
1.99
6.02
4.01
1.01
1.99
3.02
1.00
1.00
2.00
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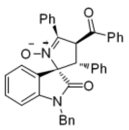
Ph
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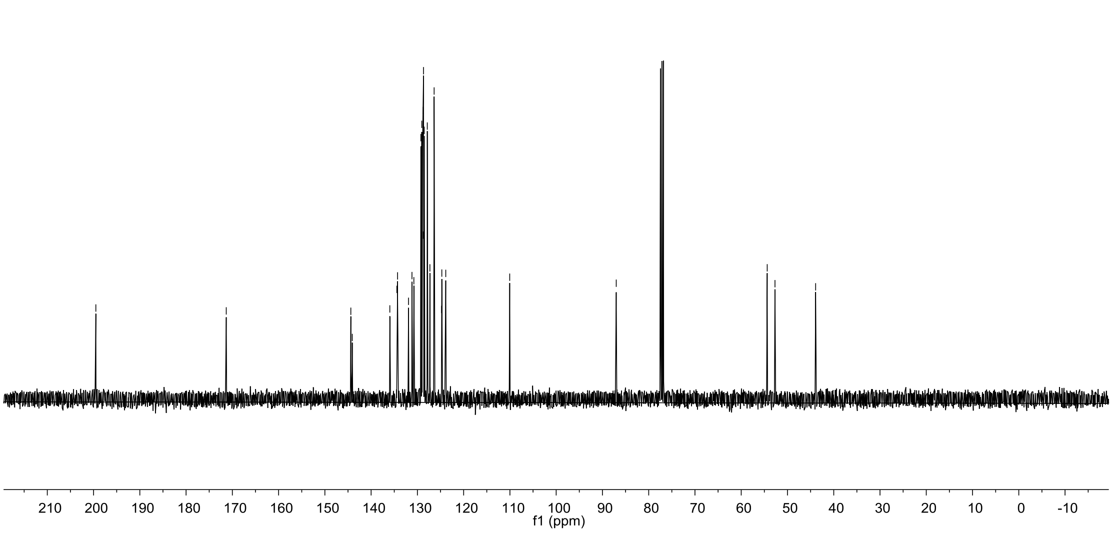
Ph
O
N
Ph
N
O
Bn

9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128.88
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54.38
52.70
43.91
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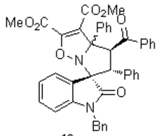
f1 (ppm)



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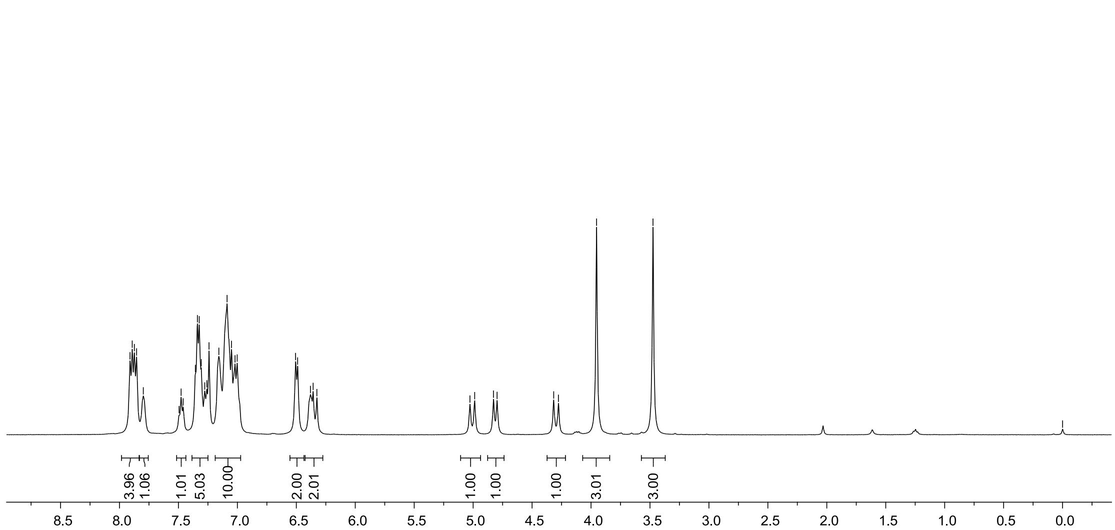

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7.157
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6.489
6.380
6.357
6.326
5.027
4.987
4.828
4.797
4.317
4.276
3.953
3.474
-0.000
3.96
1.06
1.01
5.03
10.00
2.00
2.01
1.00
1.00
1.00
3.01
3.00
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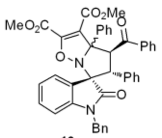

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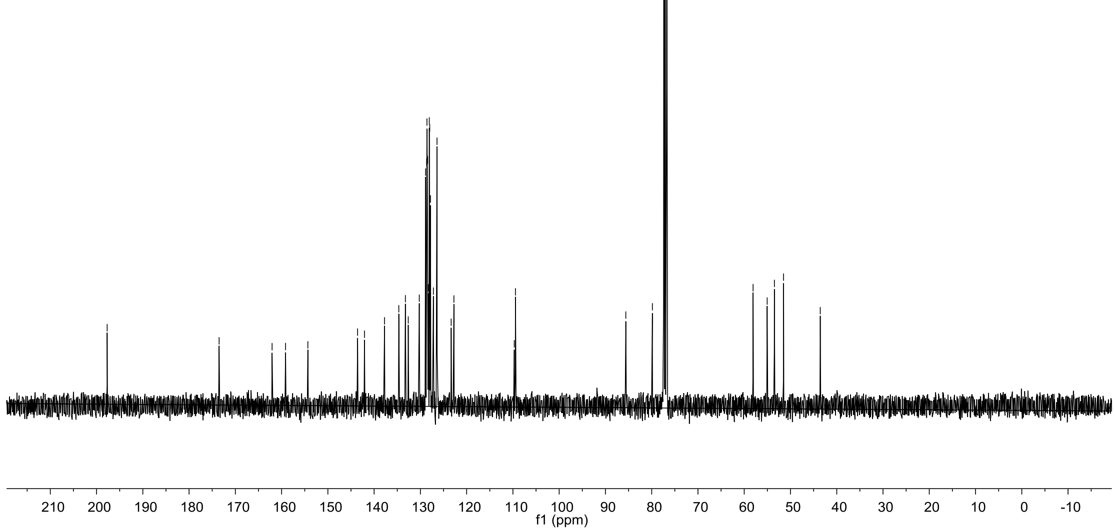

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159.15
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128.87
128.65
128.58
128.51
128.43
128.28
128.08
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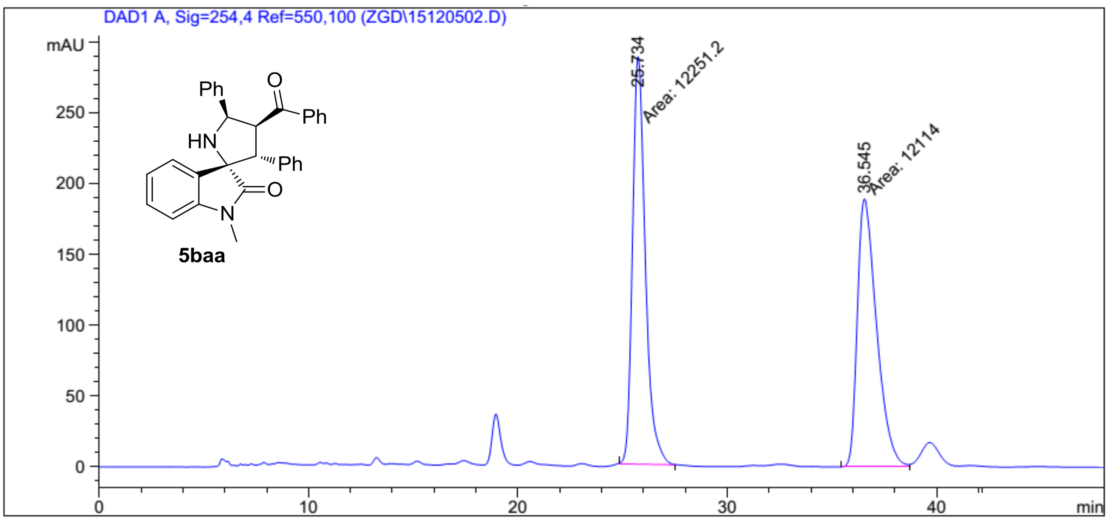
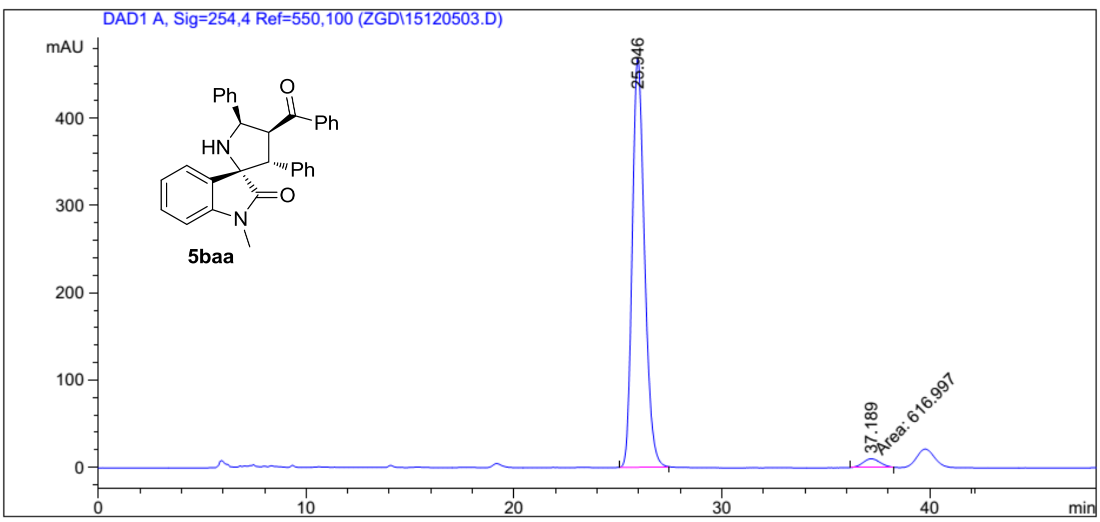
127.82
127.19
109.71
109.45
85.60
79.85
58.08
55.04
53.48
51.50
43.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

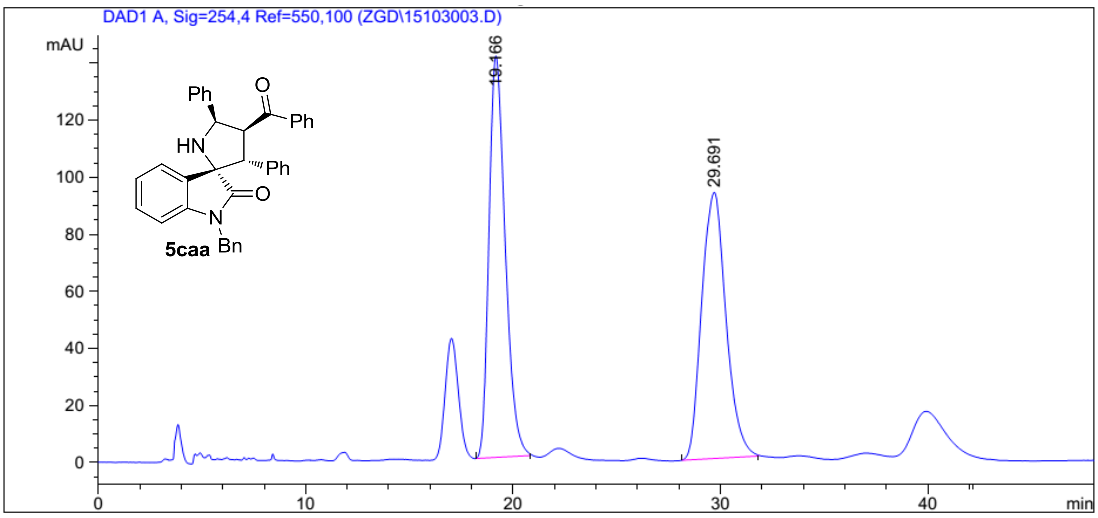
6. Copies of HPLC Chromatographs



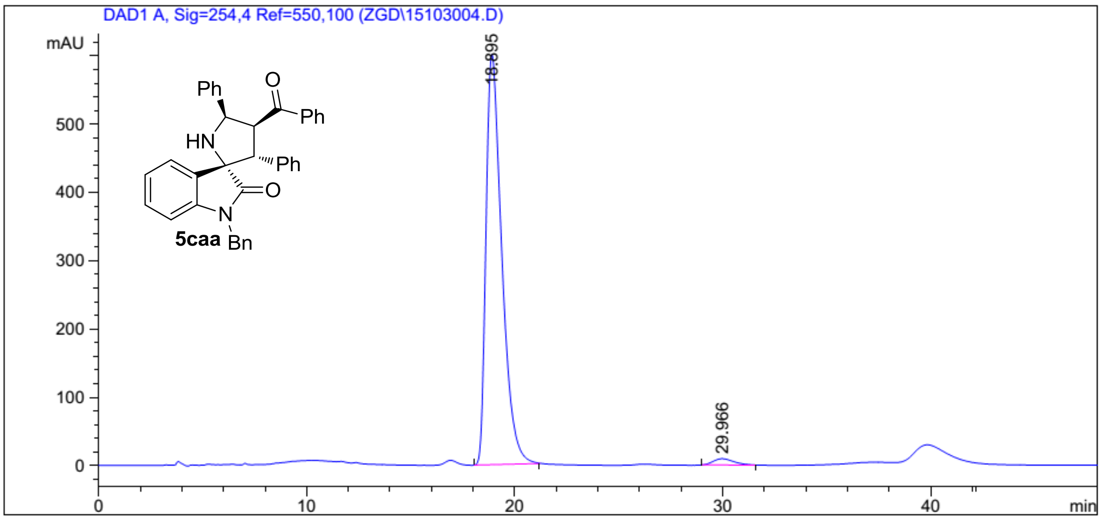
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.734	MM	0.7088	1.22512e4	288.05698	50.2815
2	36.545	MM	1.0659	1.21140e4	189.42276	49.7185



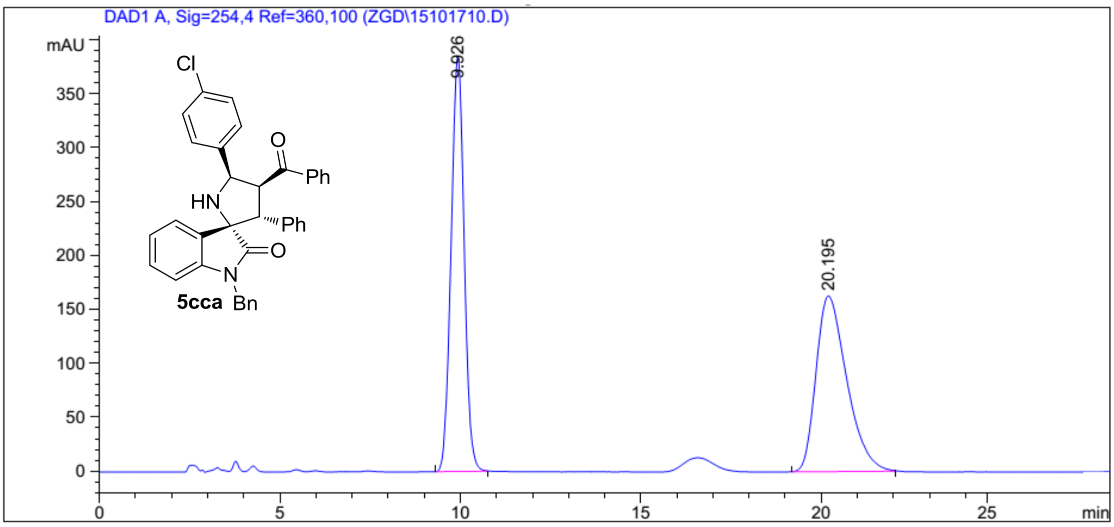
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.946	BB	0.6294	1.92566e4	468.60760	96.8954
2	37.189	MM	0.9986	616.99670	10.29777	3.1046



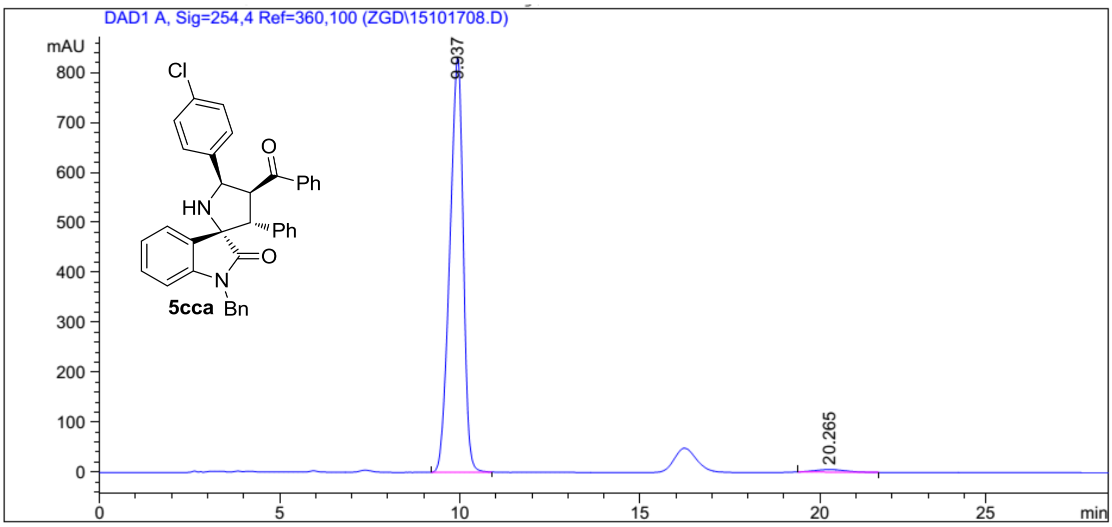
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.166	BB	0.8305	7627.00293	140.69041	50.1353
2	29.691	BB	1.1465	7585.84033	93.30399	49.8647



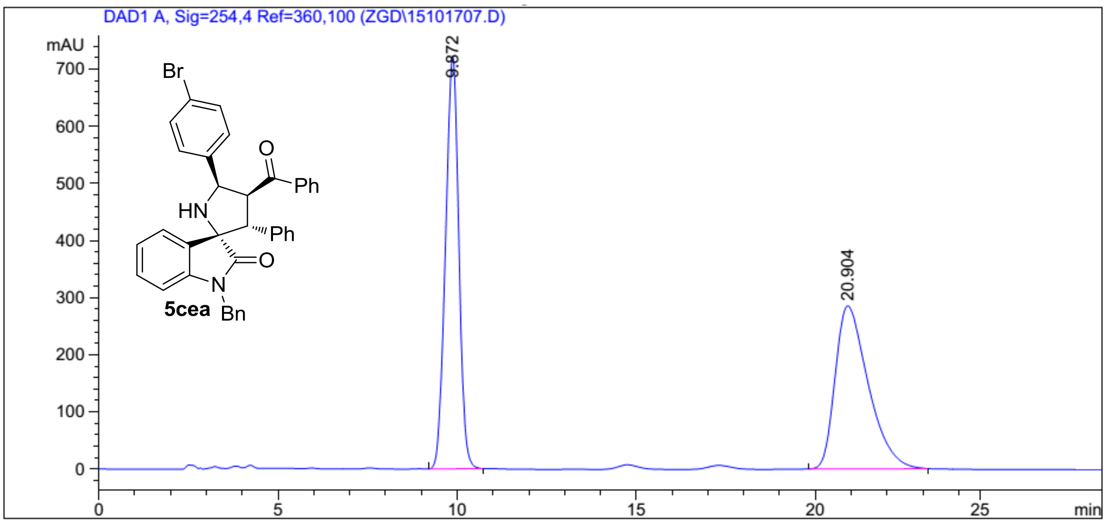
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.895	BB	0.8013	3.15767e4	600.71106	98.0143
2	29.966	BB	0.8265	639.71277	9.20799	1.9857



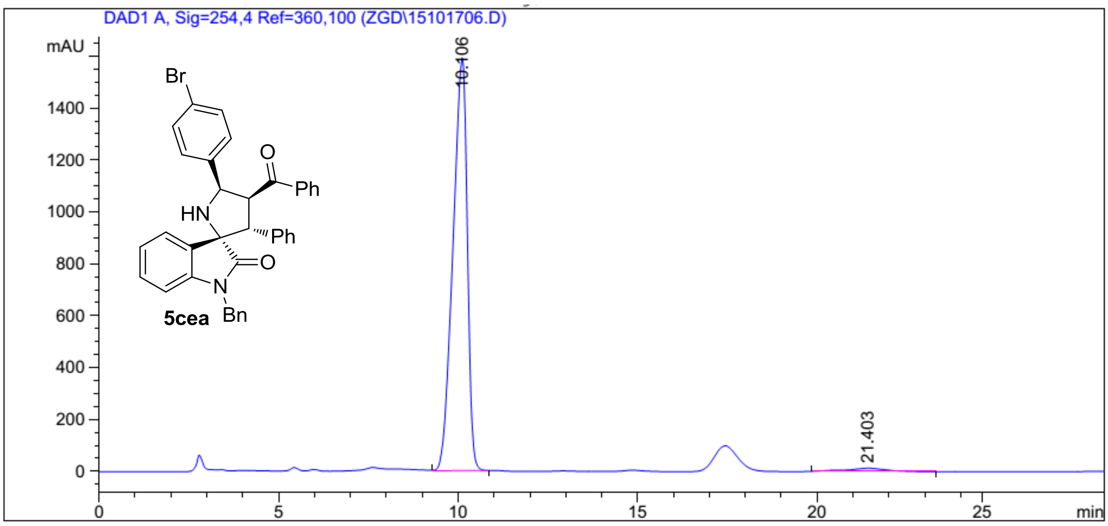
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.926	BB	0.3937	9680.09180	384.57996	50.1638
2	20.195	BB	0.8985	9616.86328	162.95447	49.8362



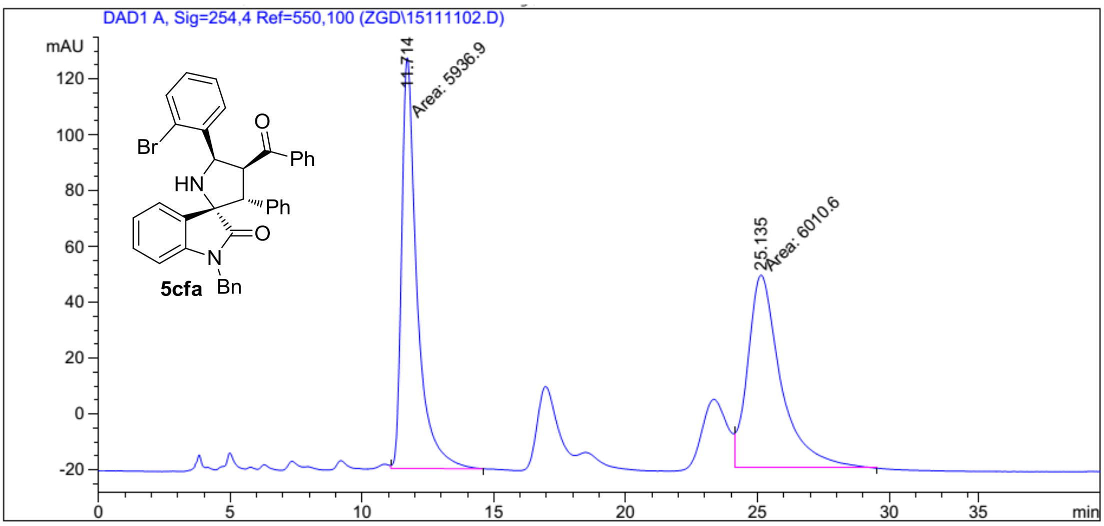
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.937	BB	0.4042	2.15008e4	830.14398	98.5715
2	20.265	BP	0.7014	311.58572	5.27269	1.4285



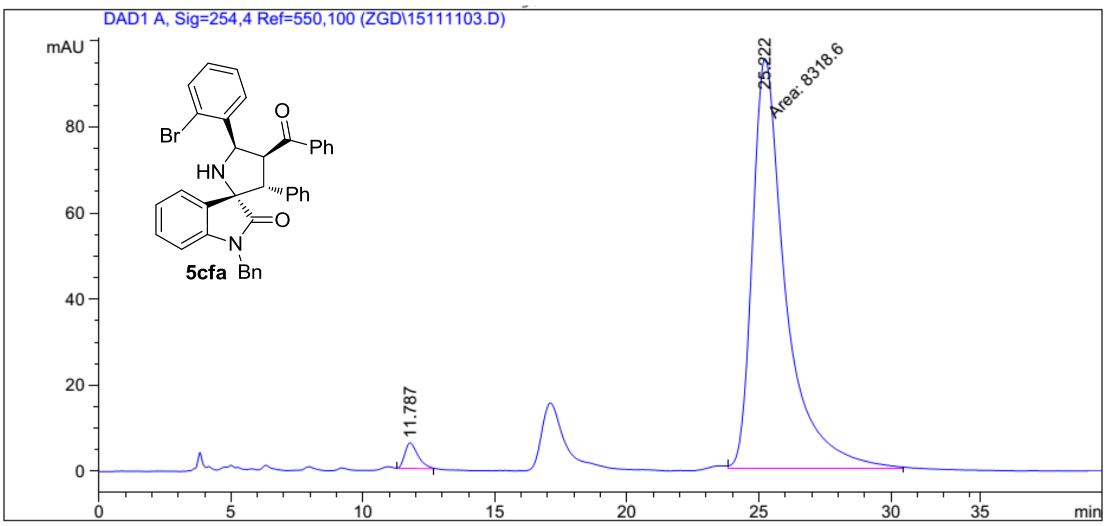
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.872	PB	0.3979	1.85618e4	722.14374	50.3451
2	20.904	BB	0.9777	1.83073e4	285.63751	49.6549



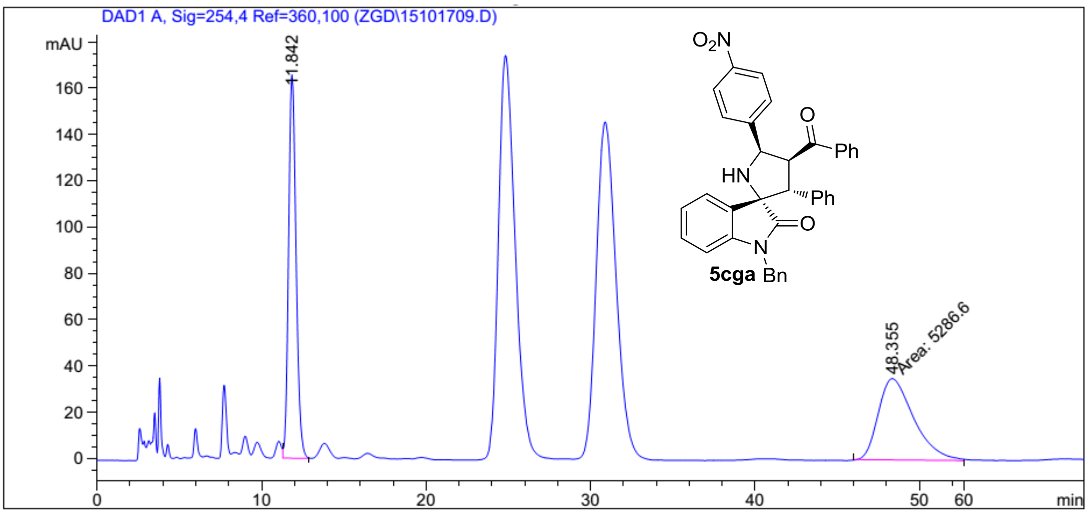
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.106	BP	0.4286	4.39886e4	1591.06213	97.7907
2	21.403	BB	0.9847	993.79193	12.70319	2.2093



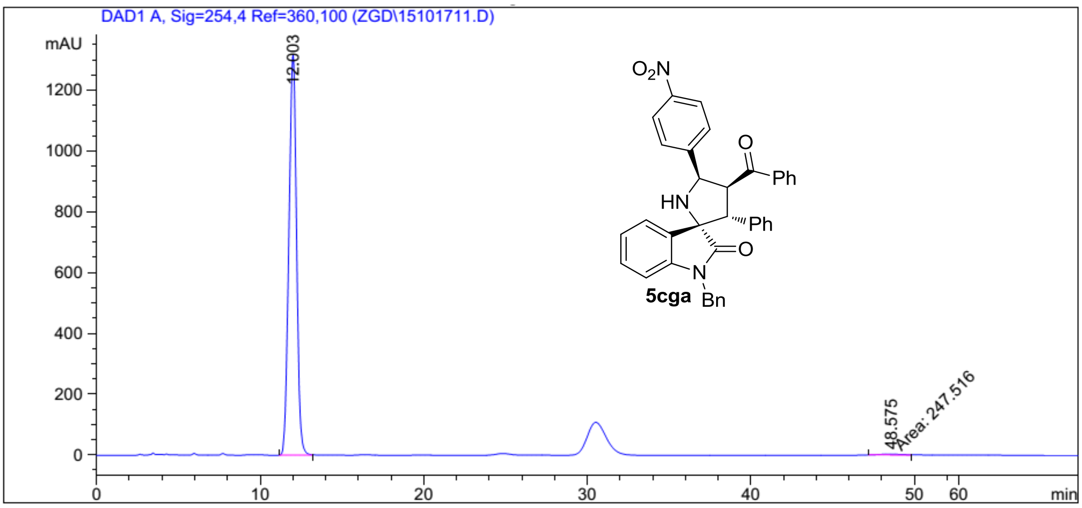
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.714	MM	0.6724	5936.89893	147.14738	49.6916
2	25.135	MM	1.4514	6010.59863	69.02276	50.3084



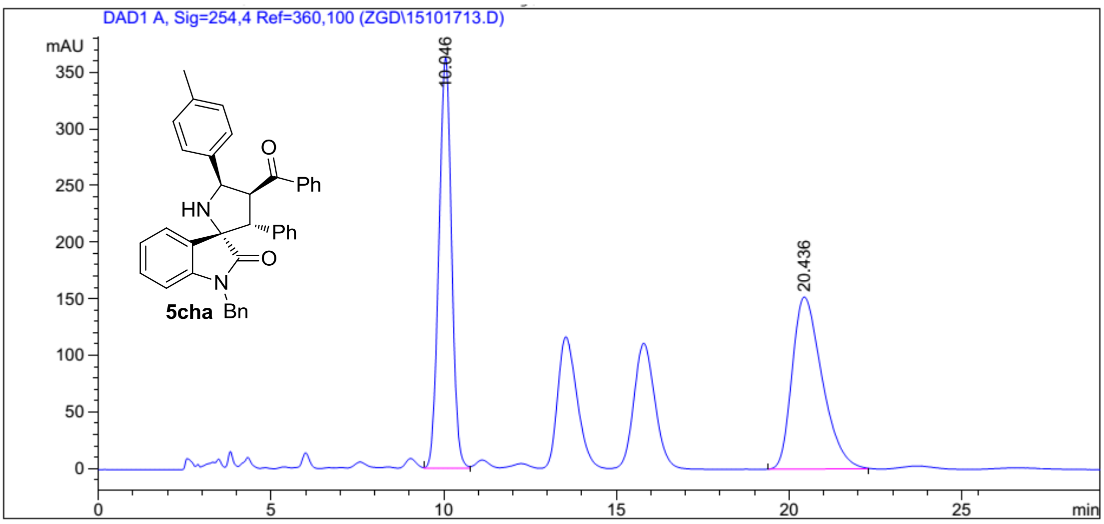
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.787	PB	0.4731	205.25452	5.94058	2.4080
2	25.222	MM	1.4563	8318.59766	95.20308	97.5920



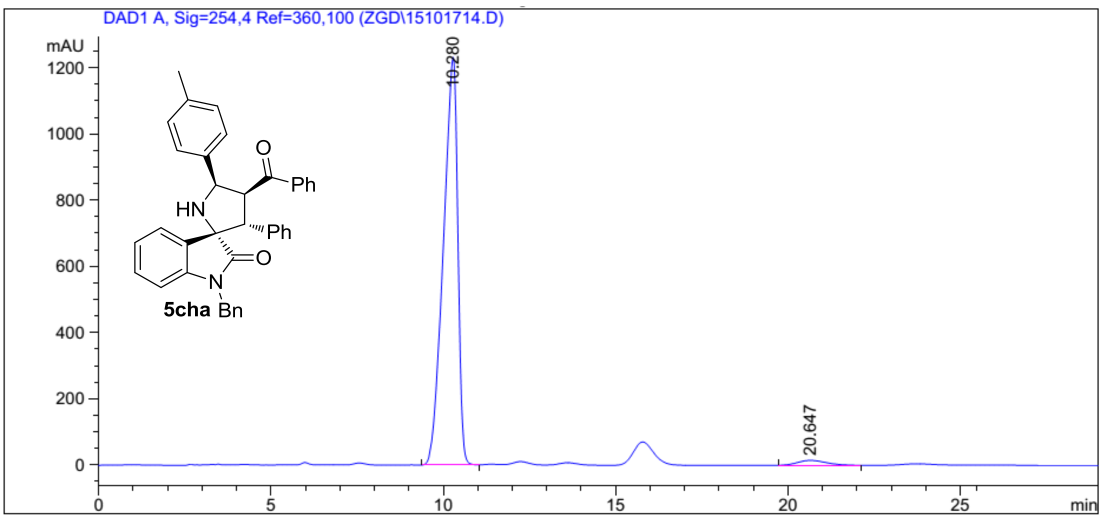
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.842	VB	0.4867	5207.52246	165.67145	49.6232
2	48.355	MM	2.5110	5286.60107	35.09027	50.3768



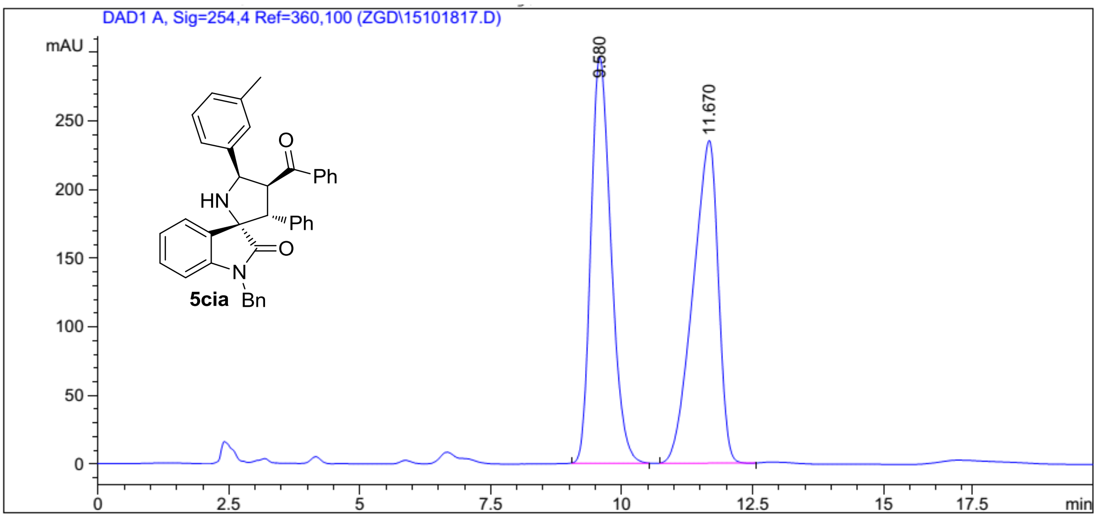
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.003	BB	0.5087	4.27485e4	1317.03369	99.4243
2	48.575	MM	1.6939	247.51628	2.43542	0.5757



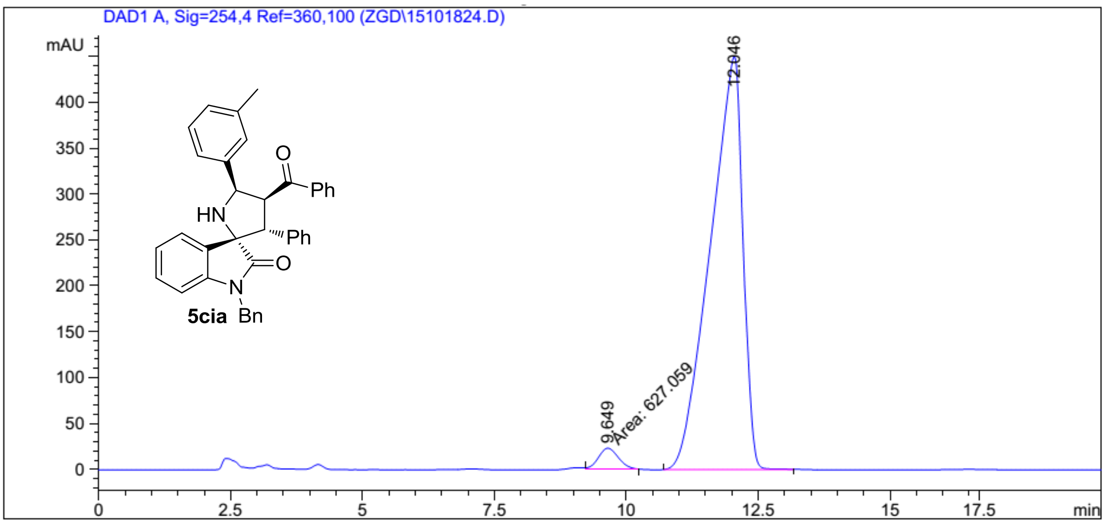
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.046	VV	0.3938	9196.17578	362.75006	50.0600
2	20.436	BB	0.9122	9174.14746	151.98752	49.9400



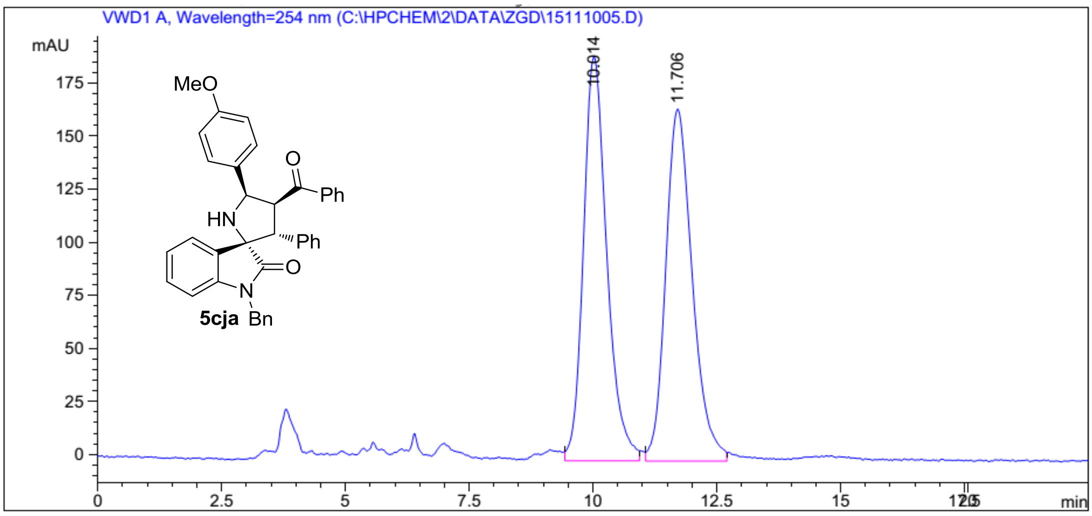
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.280	PB	0.4423	3.57188e4	1231.71362	97.5898
2	20.647	BB	0.7800	882.14044	14.95948	2.4102



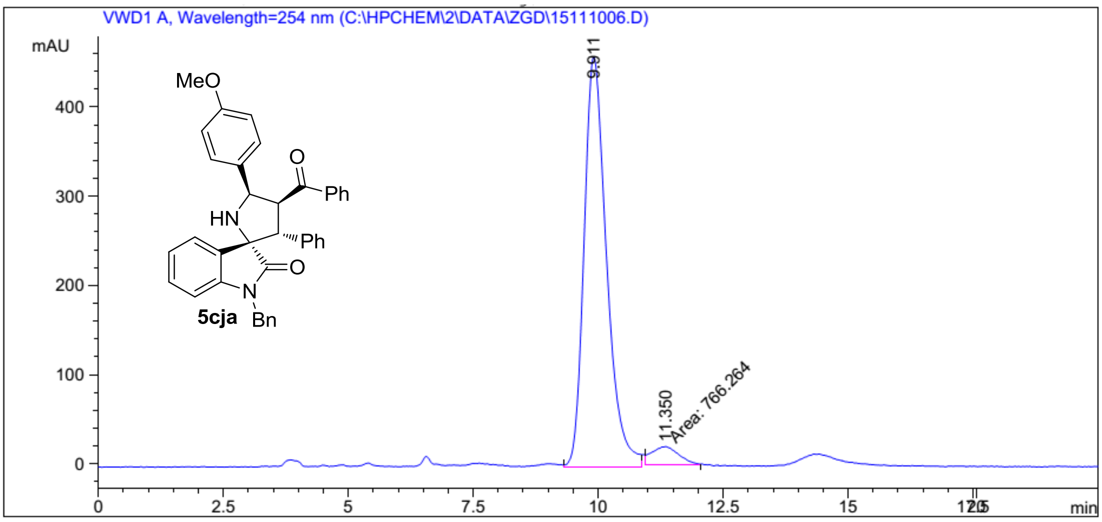
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.580	BB	0.4134	7904.74756	296.14294	50.1089
2	11.670	BP	0.5045	7870.39941	235.13507	49.8911



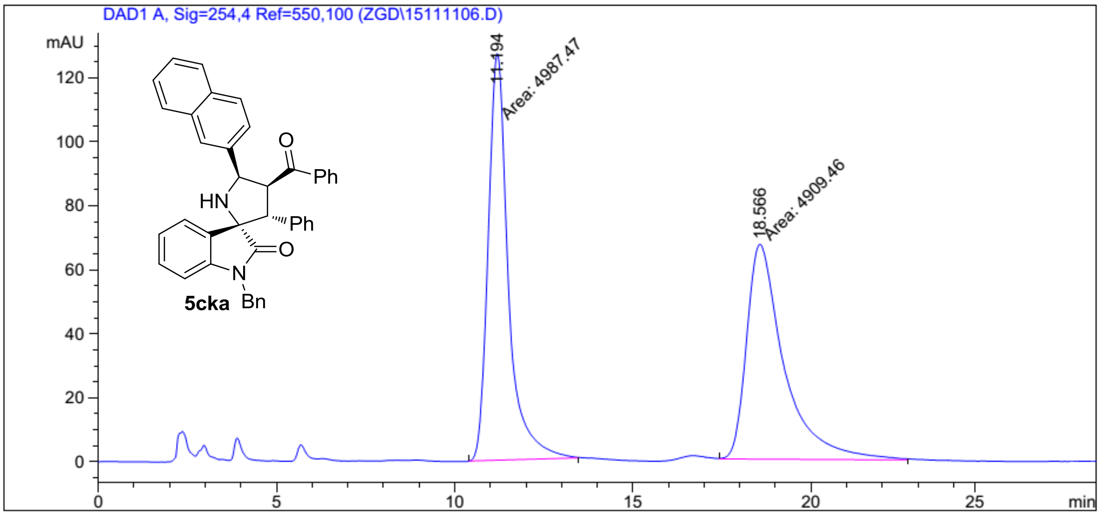
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.649	MM	0.4480	627.05890	23.33031	3.1566
2	12.046	BB	0.6006	1.92378e4	450.11816	96.8434



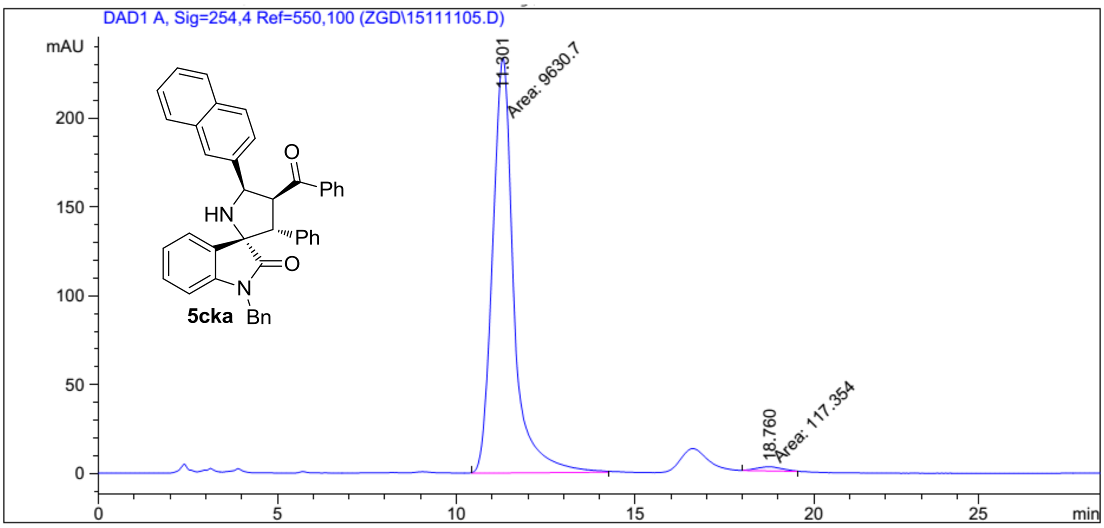
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.014	VV	0.4653	6251.10156	190.75208	50.2001
2	11.706	VV	0.5495	6201.26660	165.95999	49.7999



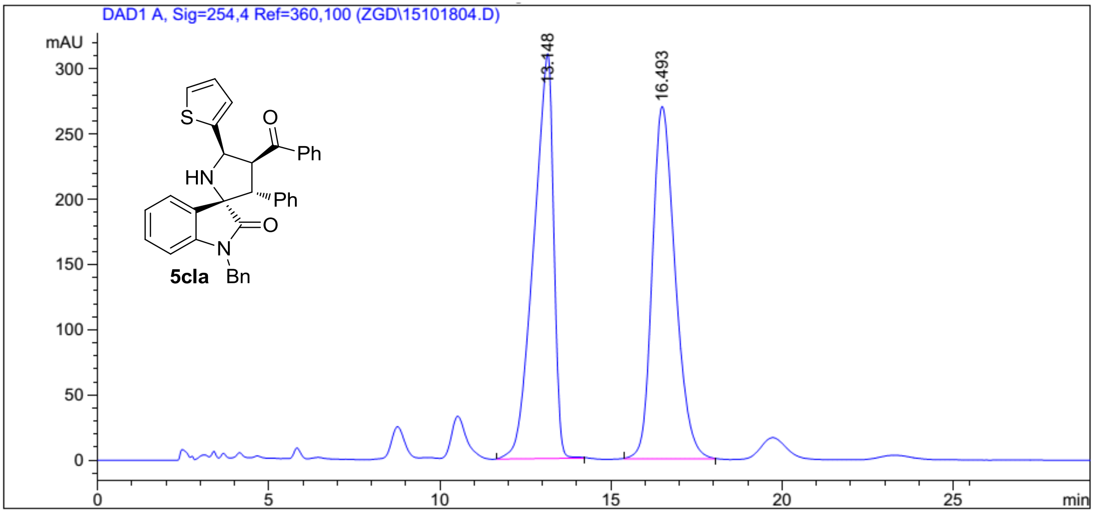
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.911	VV	0.4740	1.43898e4	460.21332	94.9442
2	11.350	MM	0.6256	766.26447	20.41512	5.0558



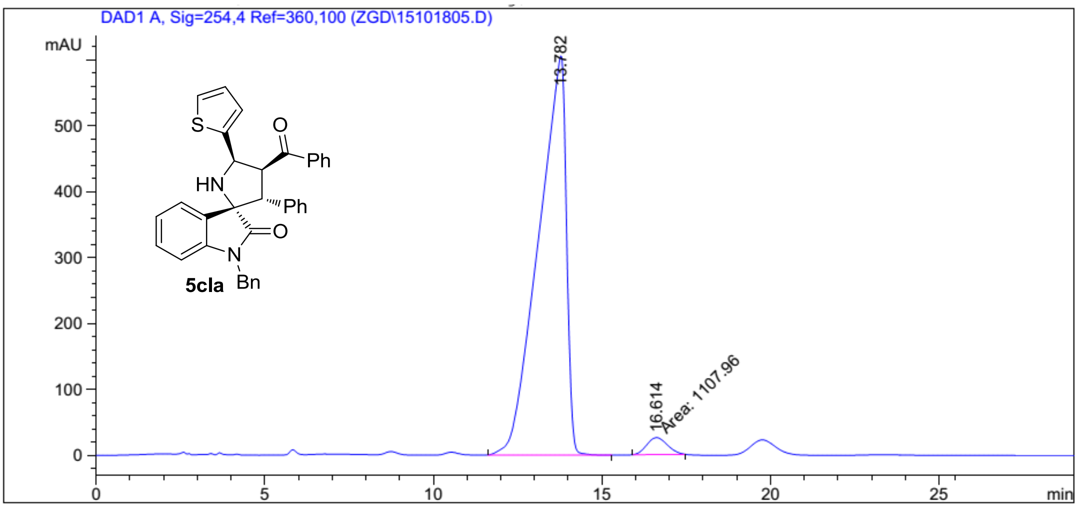
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.194	MM	0.6541	4987.47168	127.08762	50.3941
2	18.566	MM	1.2182	4909.45898	67.16957	49.6059



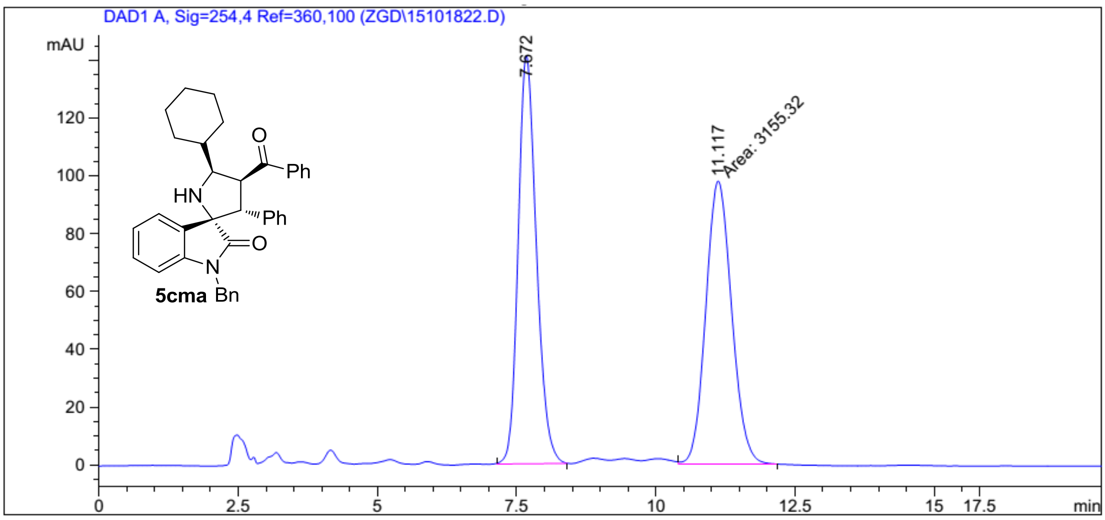
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.301	MM	0.6863	9630.69824	233.87166	98.7961
2	18.760	MM	0.8426	117.35416	2.32126	1.2039



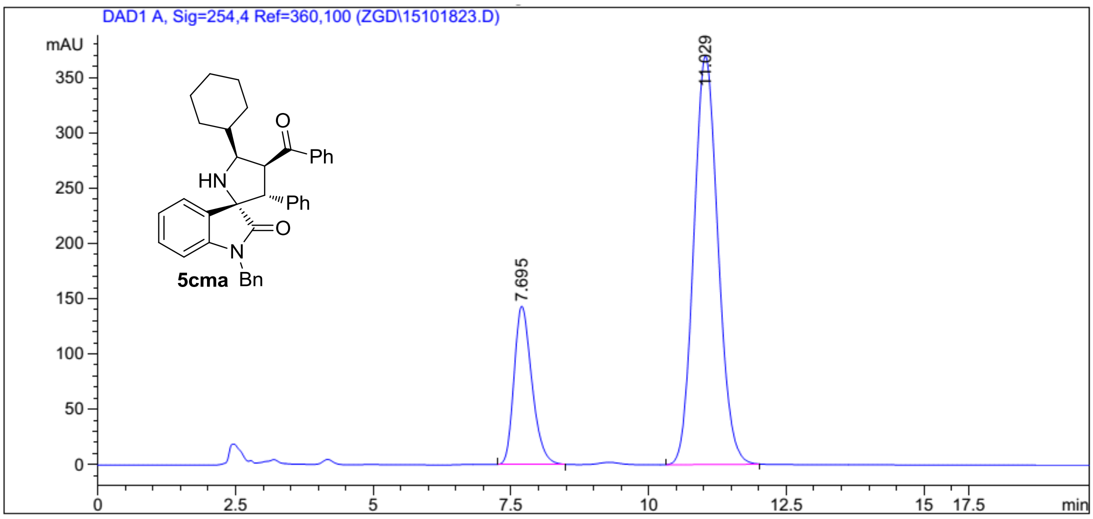
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.148	BB	0.5796	1.24951e4	310.44067	49.7524
2	16.493	BB	0.7186	1.26195e4	270.34299	50.2476



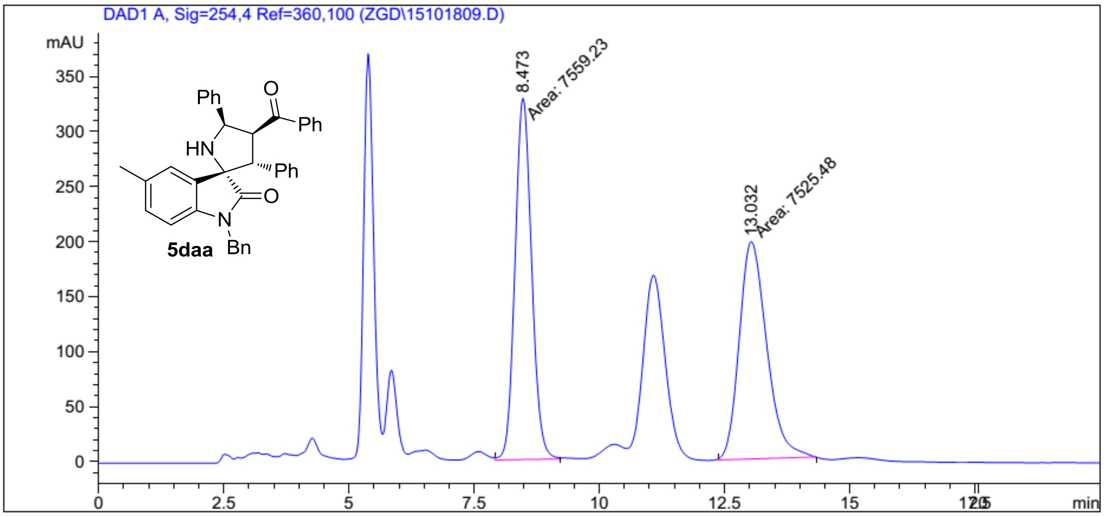
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.782	BP	0.7558	3.45835e4	606.03369	96.8957
2	16.614	MM	0.7132	1107.95984	25.89350	3.1043



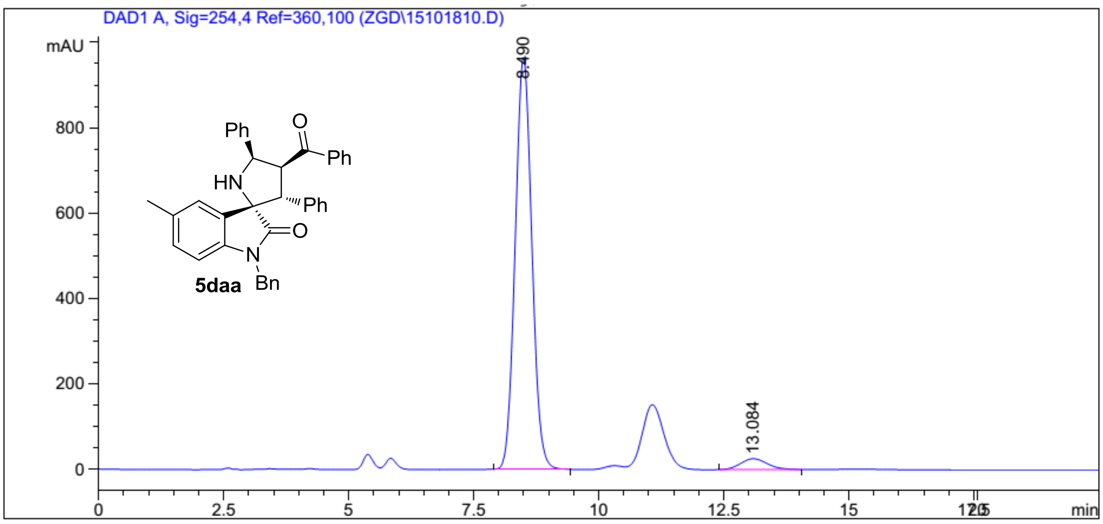
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.672	BB	0.3494	3209.51050	141.06767	50.4257
2	11.117	MM	0.5372	3155.31982	97.89326	49.5743



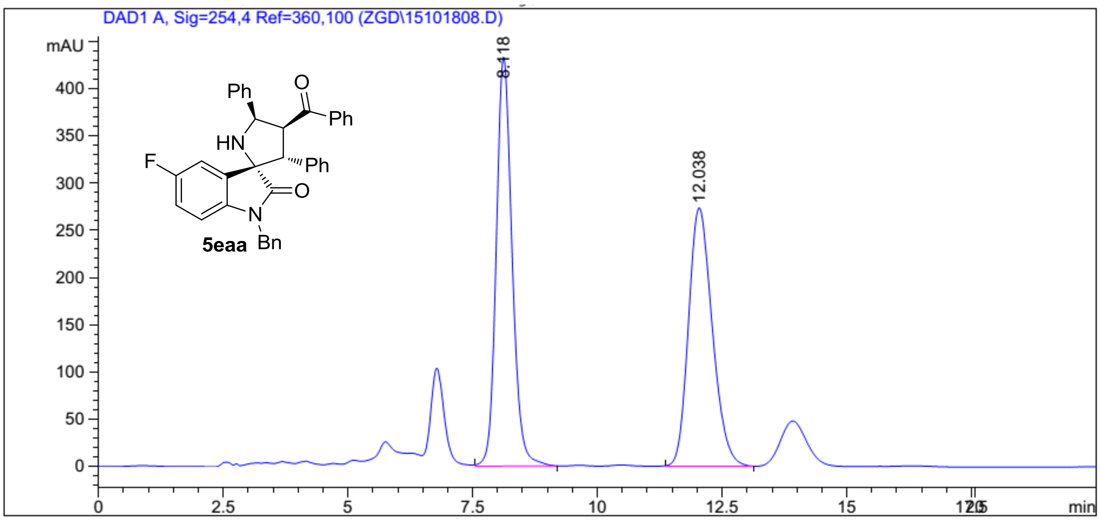
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.695	BB	0.3466	3224.80981	143.29755	22.2375
2	11.029	BB	0.4760	1.12768e4	369.52127	77.7625



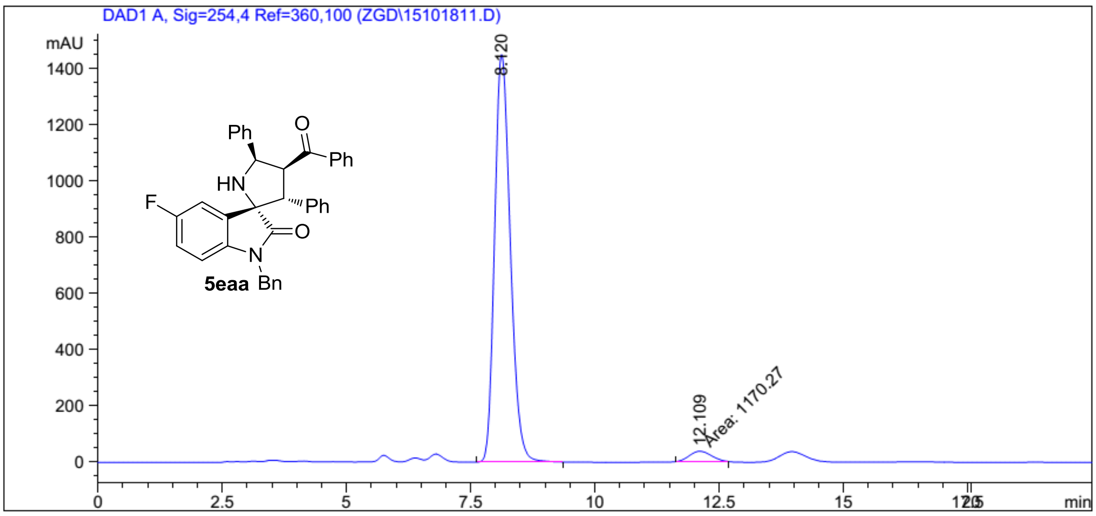
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.473	MM	0.3839	7559.23145	328.14682	50.1119
2	13.032	MM	0.6354	7525.47510	197.39442	49.8881



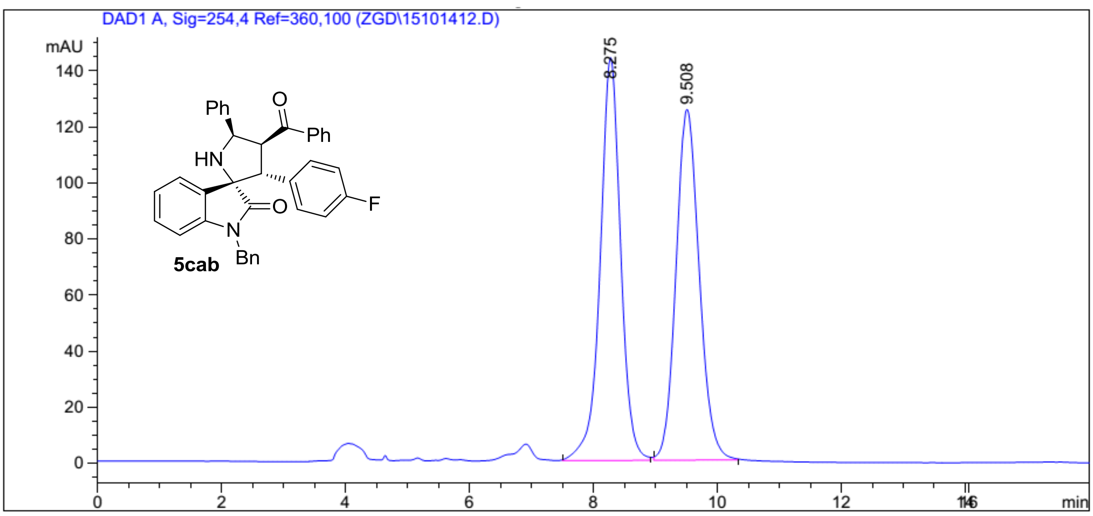
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.490	BB	0.3598	2.23181e4	965.19720	95.8887
2	13.084	BB	0.5610	956.89435	25.78032	4.1113



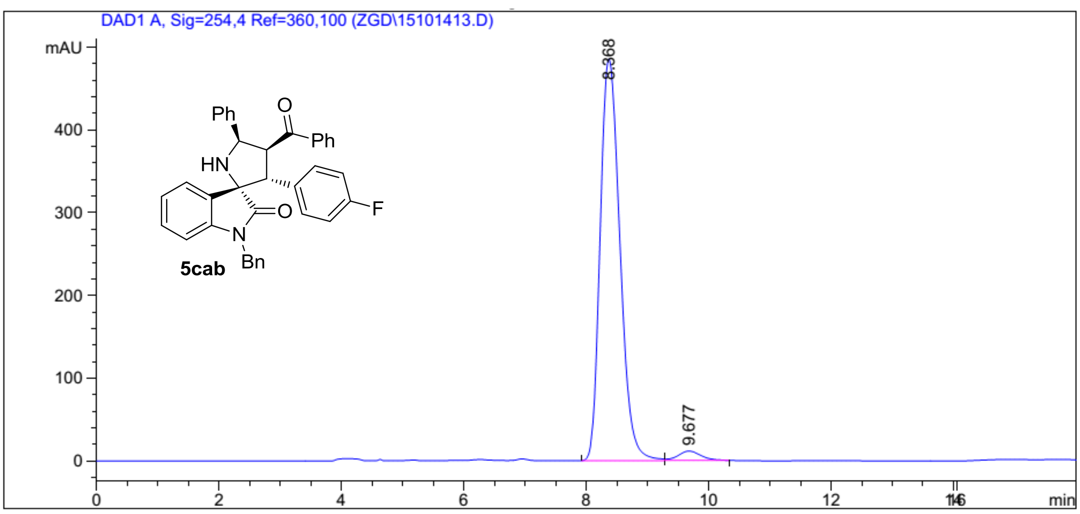
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.118	BP	0.3389	9538.70313	433.20645	51.2419
2	12.038	BB	0.5087	9076.32617	273.83630	48.7581



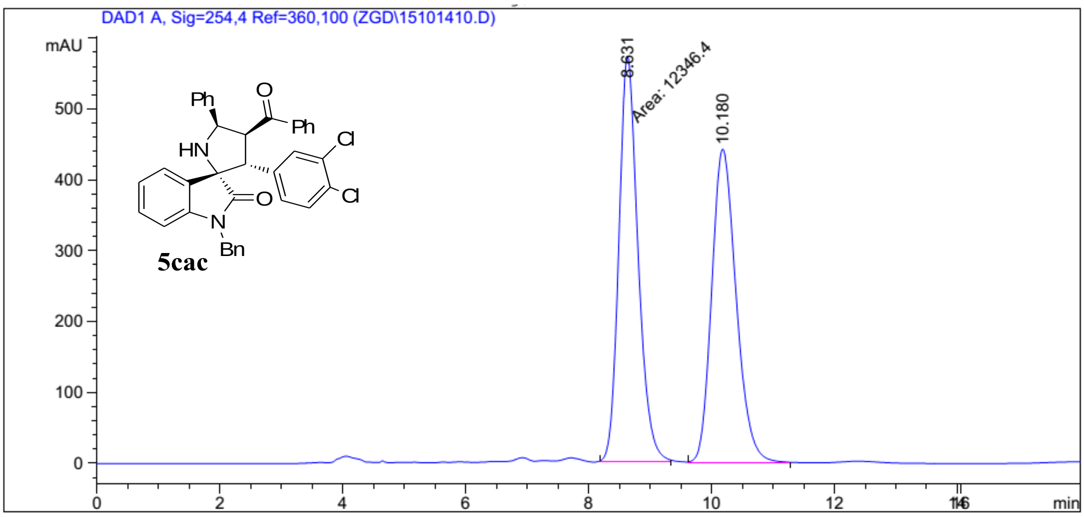
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.120	BB	0.3425	3.18931e4	1450.86829	96.4605
2	12.109	MM	0.5181	1170.26953	37.64779	3.5395



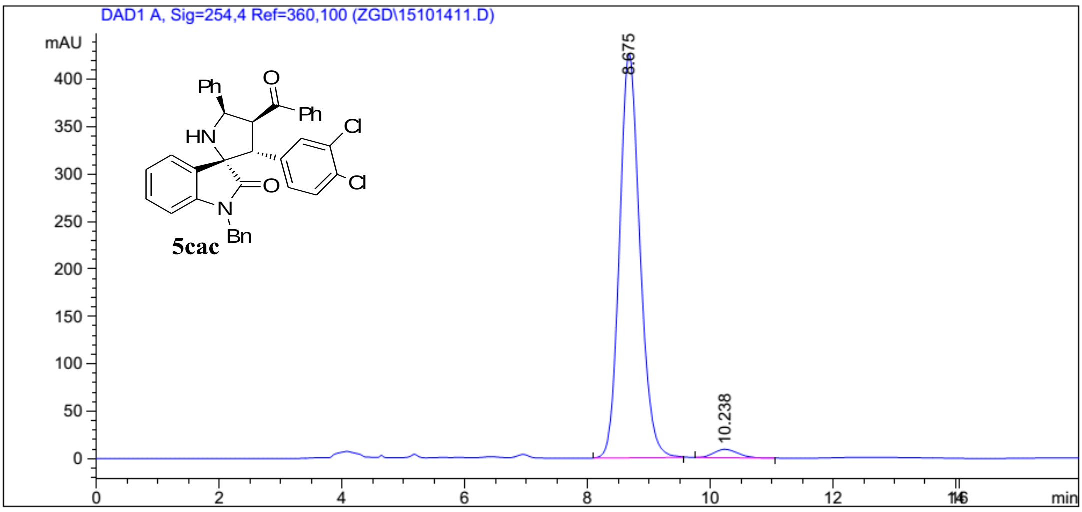
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.275	BB	0.3475	3293.38916	143.61438	50.2755
2	9.508	BB	0.4017	3257.29639	125.12472	49.7245



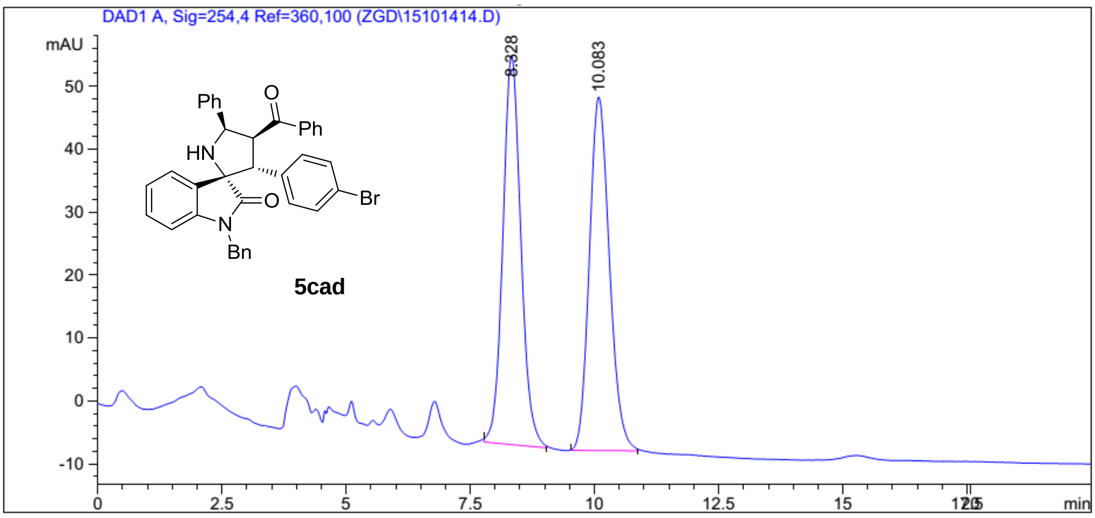
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.368	BB	0.3547	1.08399e4	485.16681	97.2857
2	9.677	BB	0.3846	302.43442	11.58504	2.7143



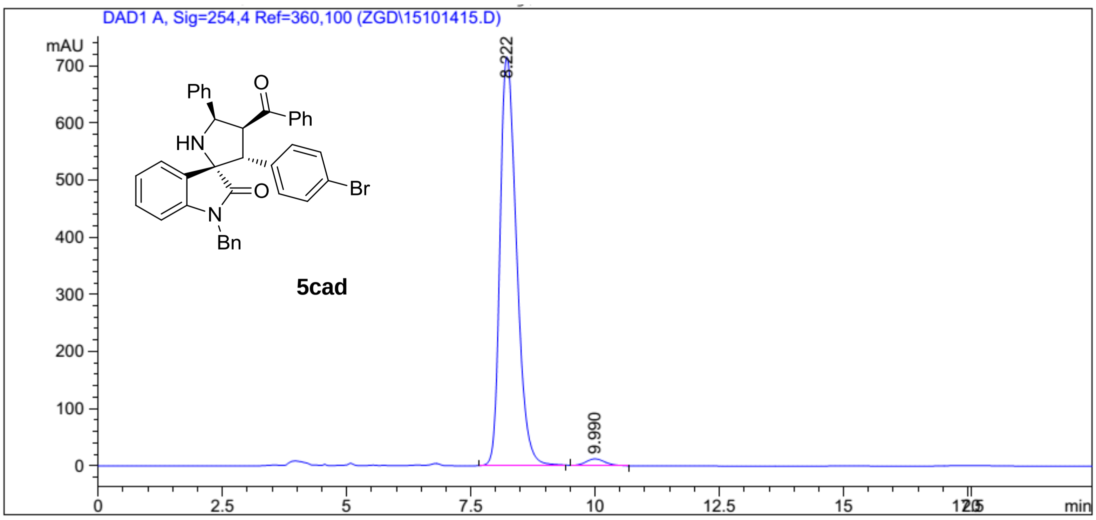
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.631	MM	0.3604	1.23464e4	570.99530	50.2770
2	10.180	BB	0.4281	1.22104e4	442.22018	49.7230



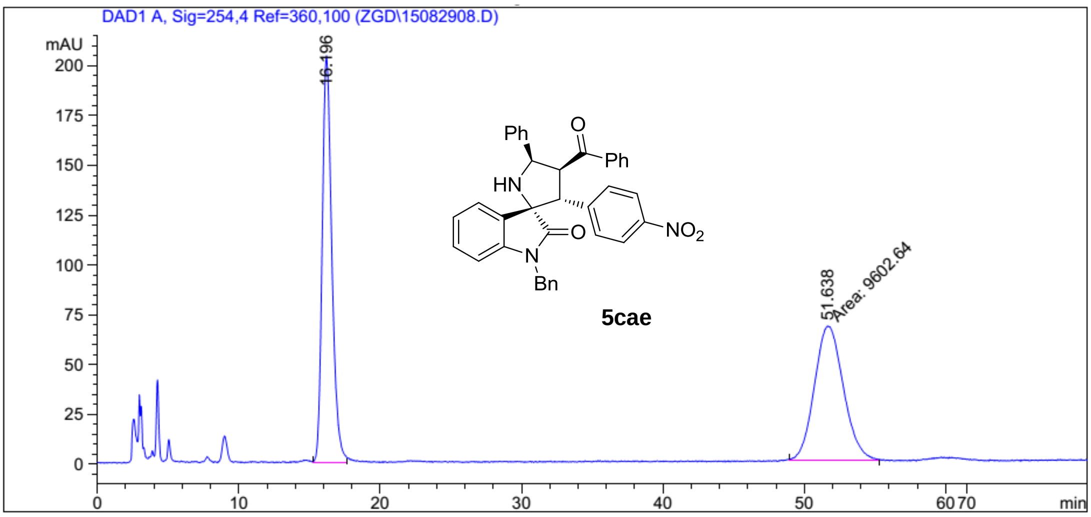
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.675	BB	0.3533	9836.23828	426.14743	97.5908
2	10.238	PB	0.4124	242.82851	8.95283	2.4092



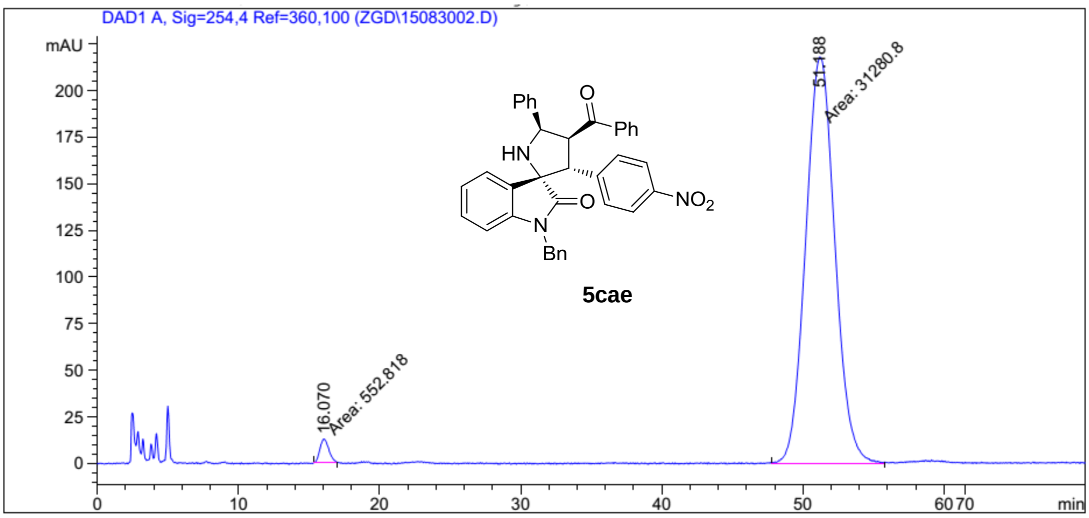
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.328	BB	0.3855	1554.01233	61.77503	49.7336
2	10.083	BB	0.4304	1570.66138	56.14819	50.2664



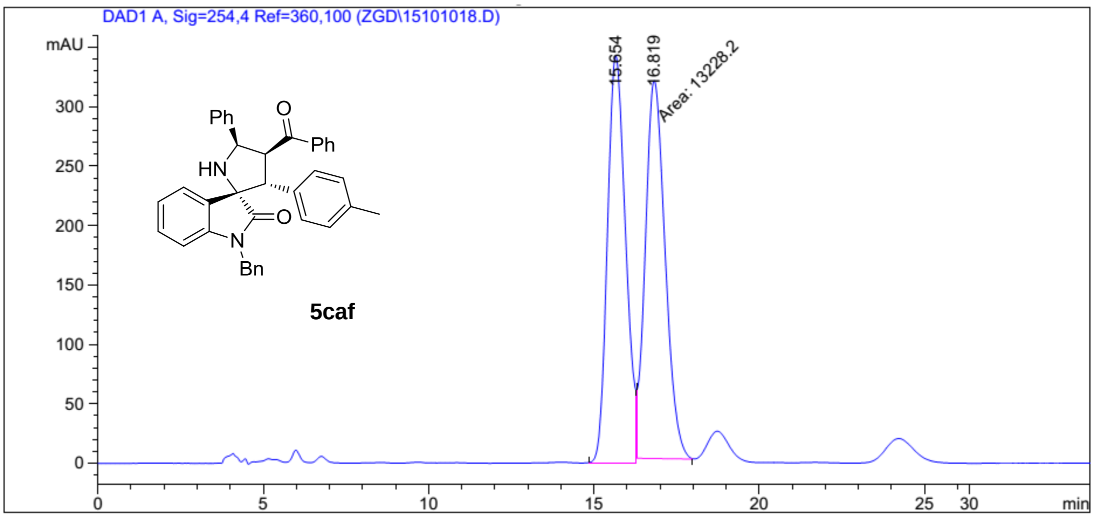
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.222	BB	0.3575	1.65253e4	715.25671	97.9588
2	9.990	BB	0.4253	344.33554	12.27229	2.0412



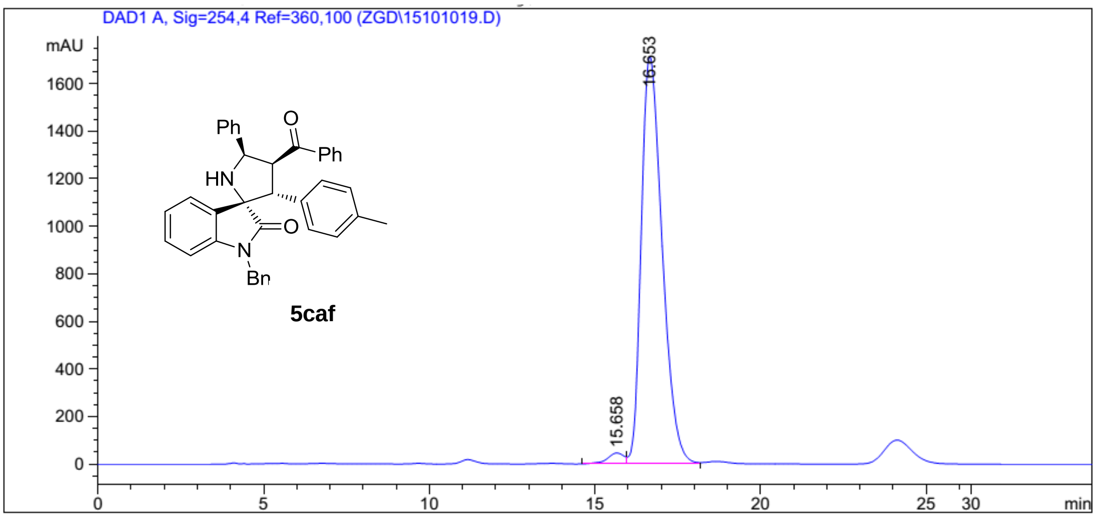
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.196	VV	0.6816	9701.27637	204.43376	50.2555
2	51.638	MM	2.3722	9602.64453	67.46654	49.7445



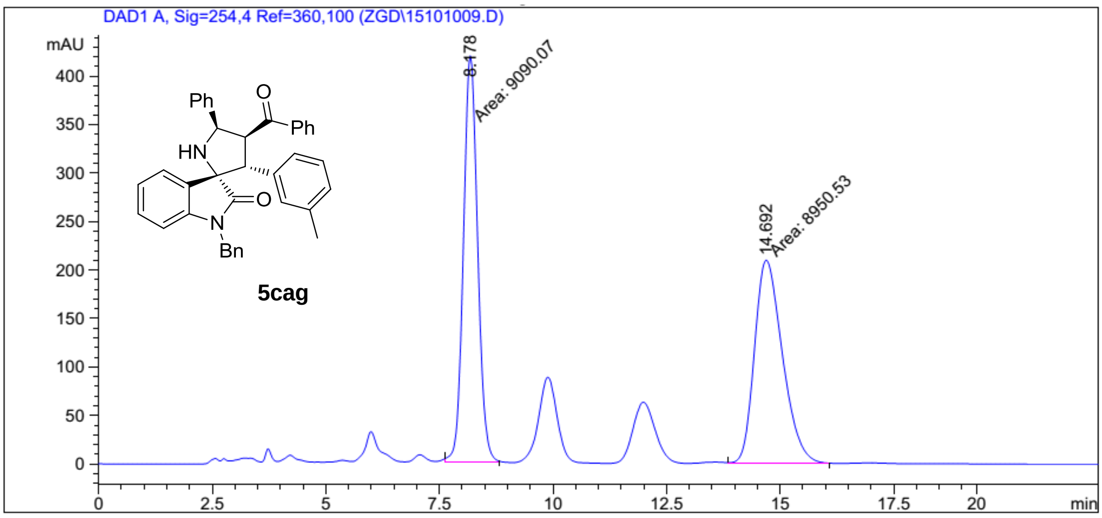
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.070	MM	0.7300	552.81787	12.62099	1.7366
2	51.188	MM	2.3919	3.12808e4	217.96635	98.2634



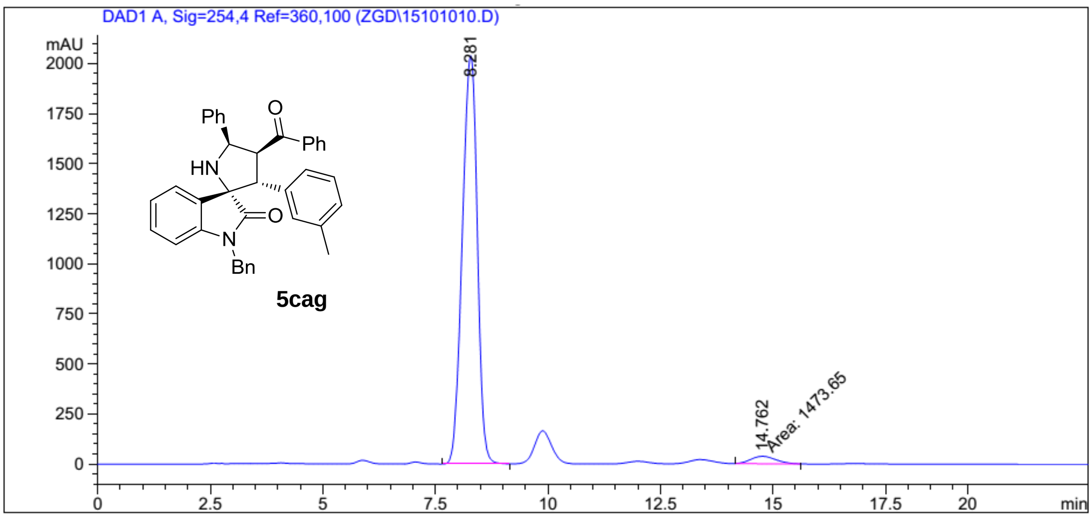
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.654	BV	0.5839	1.30903e4	342.46594	49.7379
2	16.819	MM	0.6936	1.32282e4	317.88327	50.2621



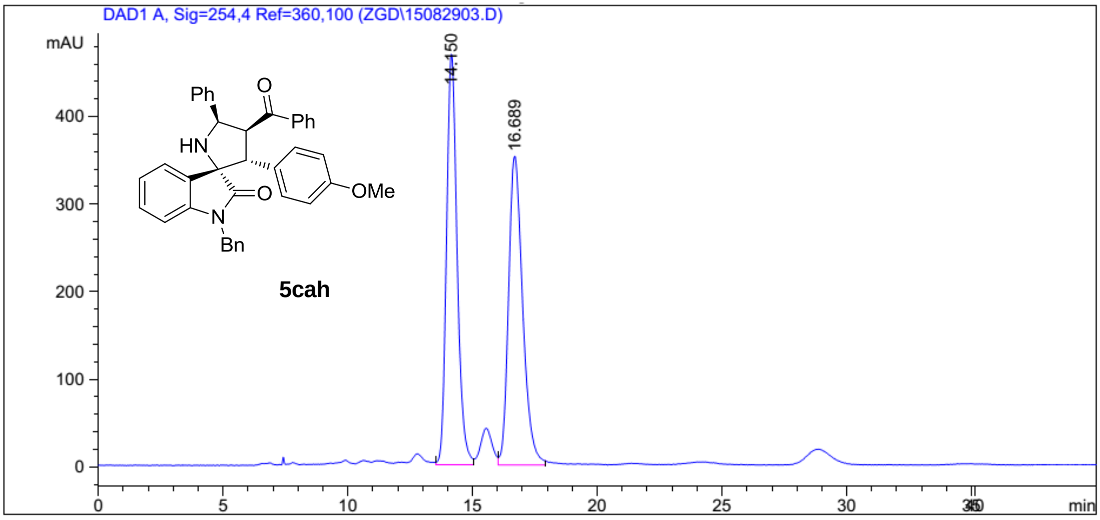
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.658	BV	0.5445	1651.06763	46.24964	2.1449
2	16.653	VB	0.6832	7.53245e4	1712.41089	97.8551



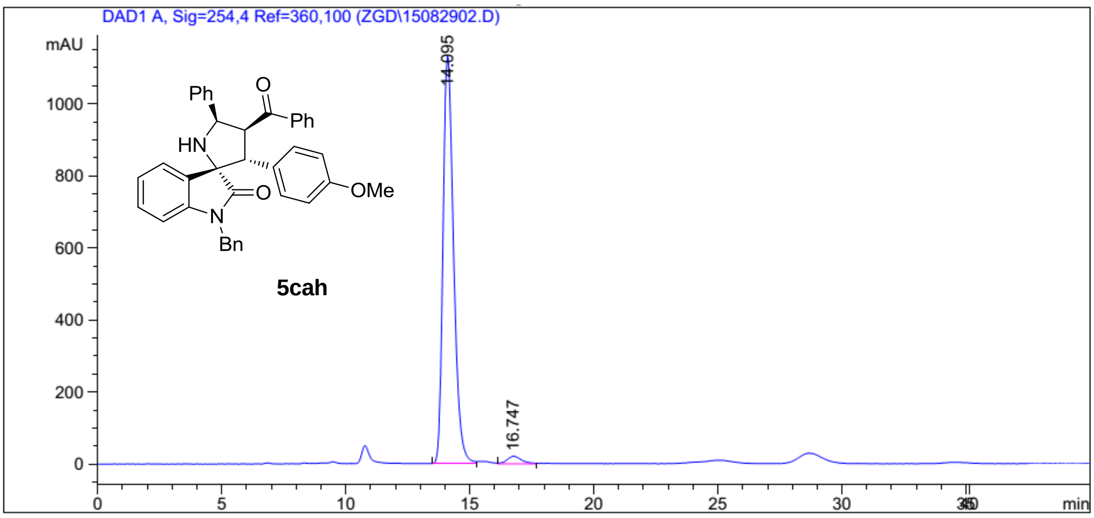
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.178	MM	0.3615	9090.06934	419.06921	50.3867
2	14.692	MM	0.7110	8950.53027	209.81055	49.6133



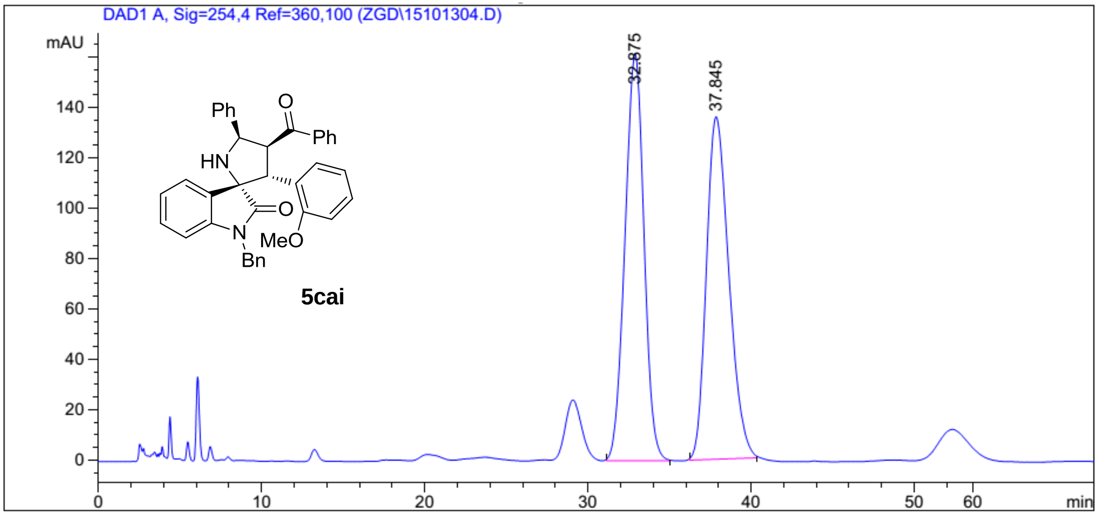
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.281	BB	0.3679	4.71816e4	2039.22205	96.9712
2	14.762	MM	0.6557	1473.64954	37.45887	3.0288



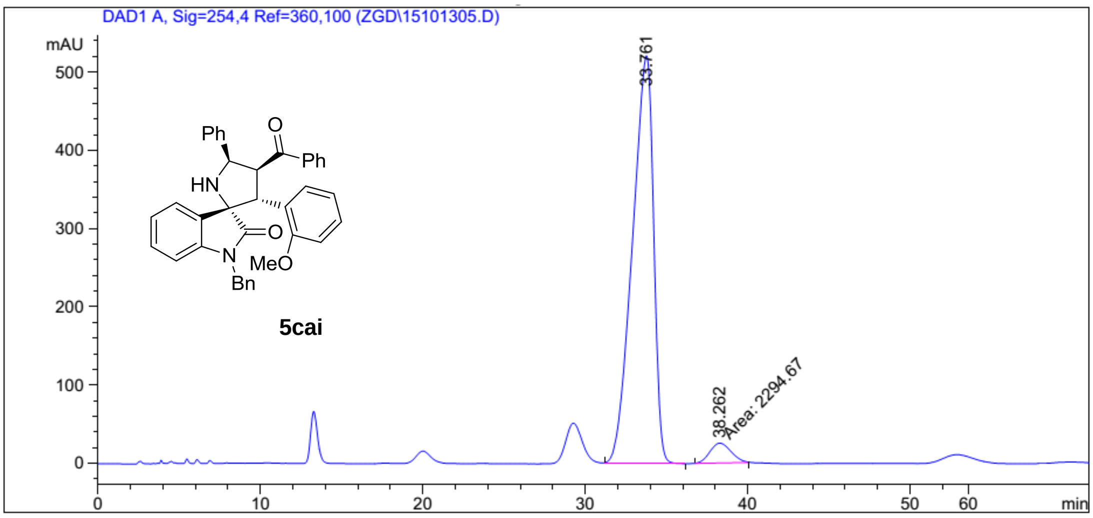
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.150	BV	0.4470	1.38768e4	469.21878	49.9979
2	16.689	VB	0.5709	1.38779e4	352.80905	50.0021



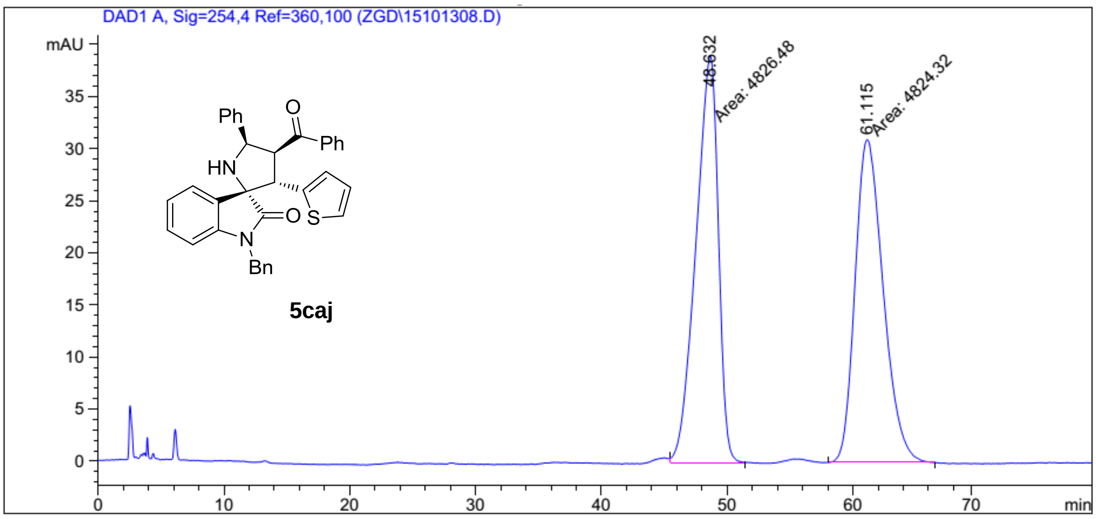
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.095	VV	0.4366	3.34455e4	1132.30127	97.4955
2	16.747	BV	0.4988	859.17212	21.11022	2.5045



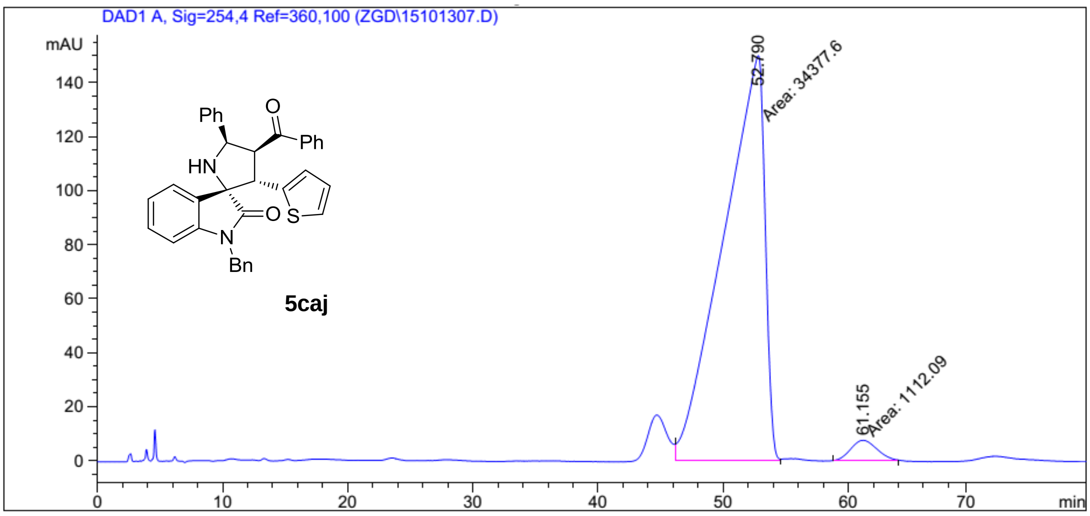
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.875	BB	1.2303	1.30733e4	161.51305	50.2110
2	37.845	BB	1.4322	1.29635e4	135.98615	49.7890



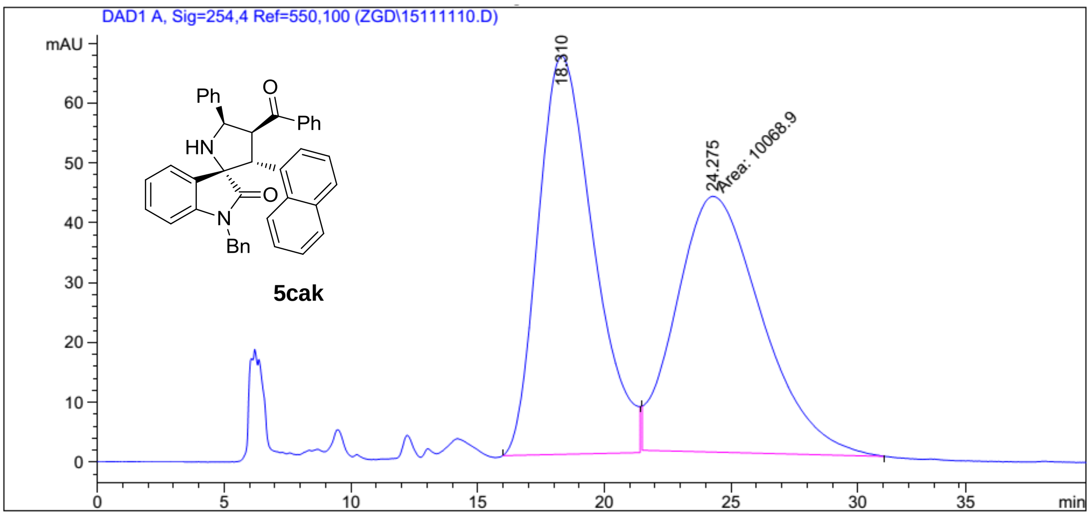
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.761	BP	1.3131	4.70526e4	521.28015	95.3500
2	38.262	MM	1.5096	2294.66772	25.33426	4.6500



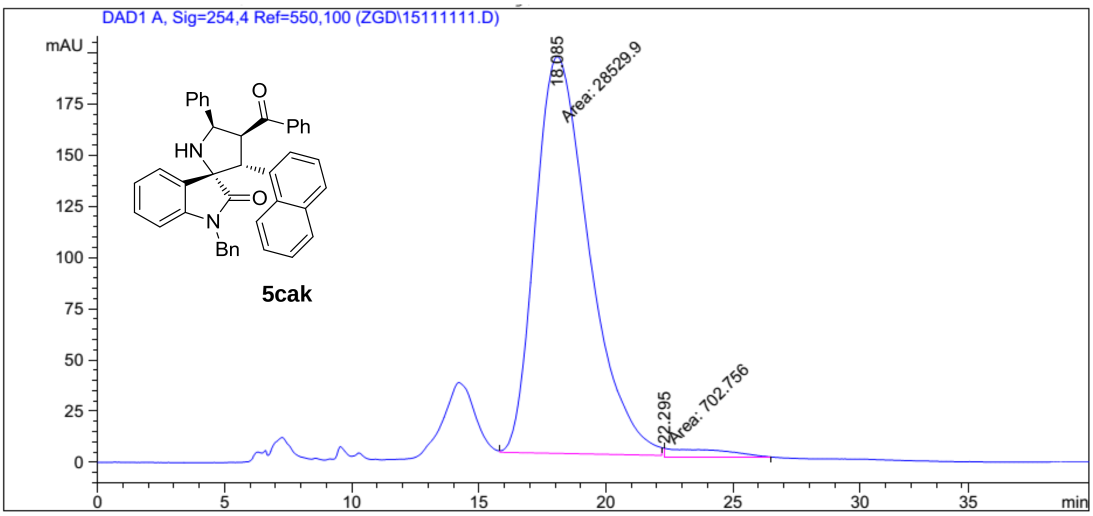
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.632	MM	2.0593	4826.48486	39.06335	50.0112
2	61.115	MM	2.5935	4824.32324	31.00210	49.9888



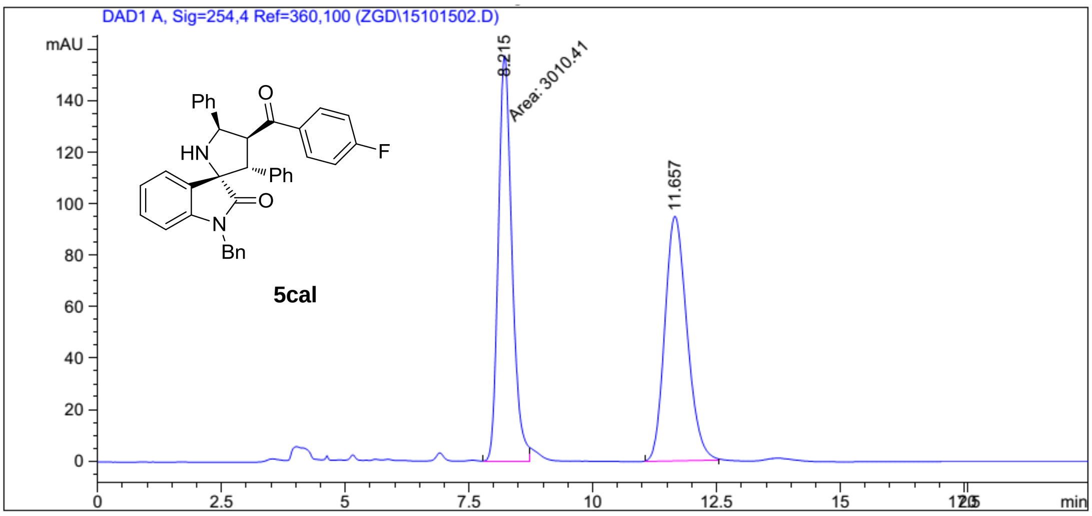
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.790	MM	3.8266	3.43776e4	149.73026	96.8664
2	61.155	MM	2.4475	1112.09363	7.57288	3.1336



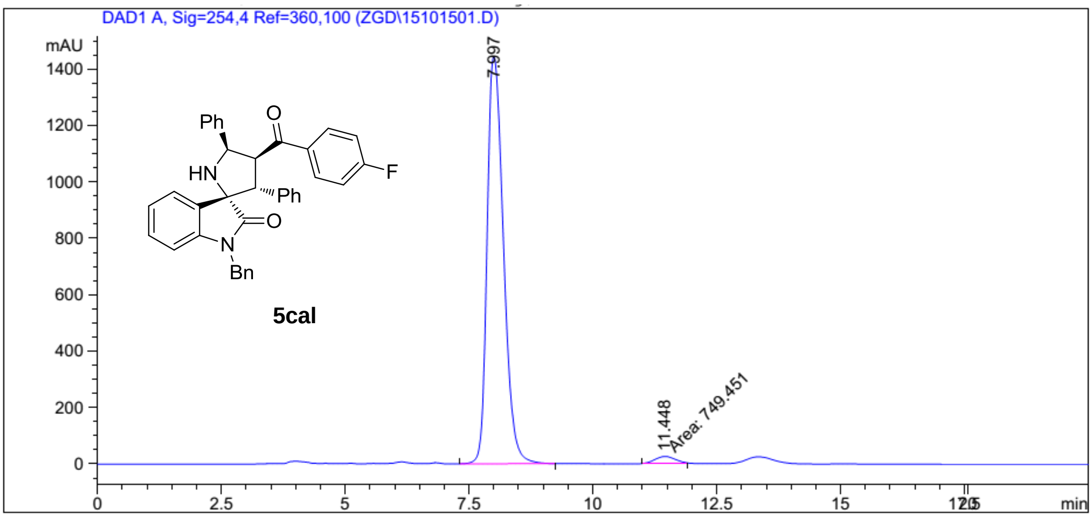
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.310	BV	1.7973	1.01300e4	66.64472	50.1513
2	24.275	MM	3.9249	1.00689e4	42.75621	49.8487



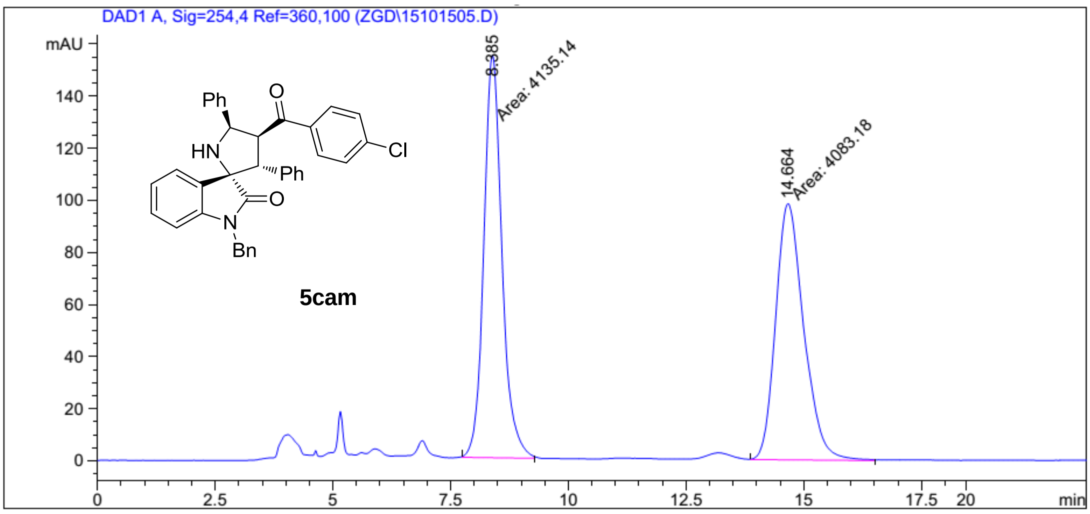
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.085	MM	2.4548	2.85299e4	193.70195	97.5960
2	22.295	MM	1.8291	702.75623	4.48607	2.4040



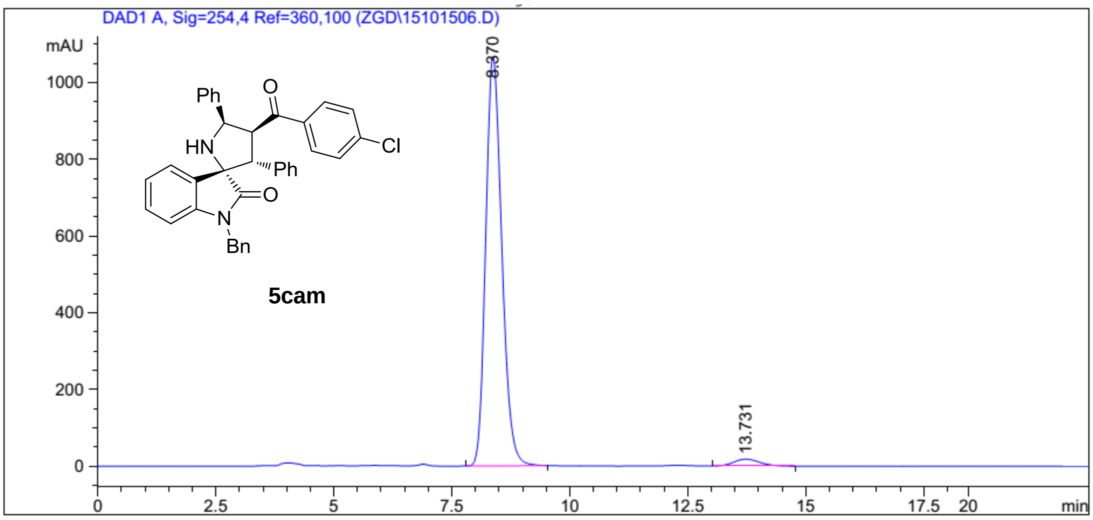
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.215	MM	0.3181	3010.41431	157.70827	50.4006
2	11.657	BB	0.4814	2962.55591	95.09804	49.5994



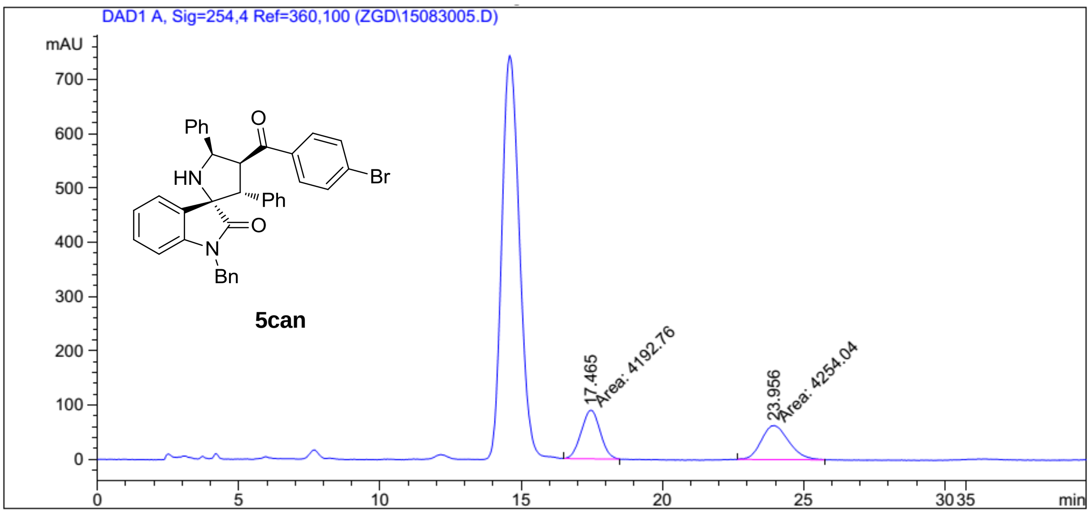
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.997	BB	0.3578	3.31282e4	1443.37195	97.7878
2	11.448	MM	0.4850	749.45135	25.75536	2.2122



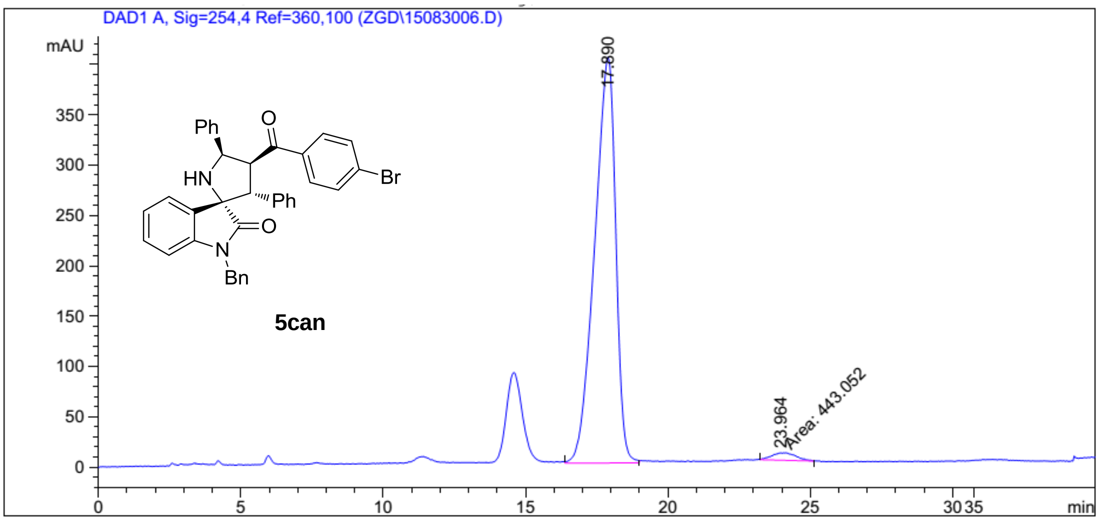
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.385	MM	0.4462	4135.14258	154.44666	50.3162
2	14.664	MM	0.6916	4083.17700	98.39610	49.6838



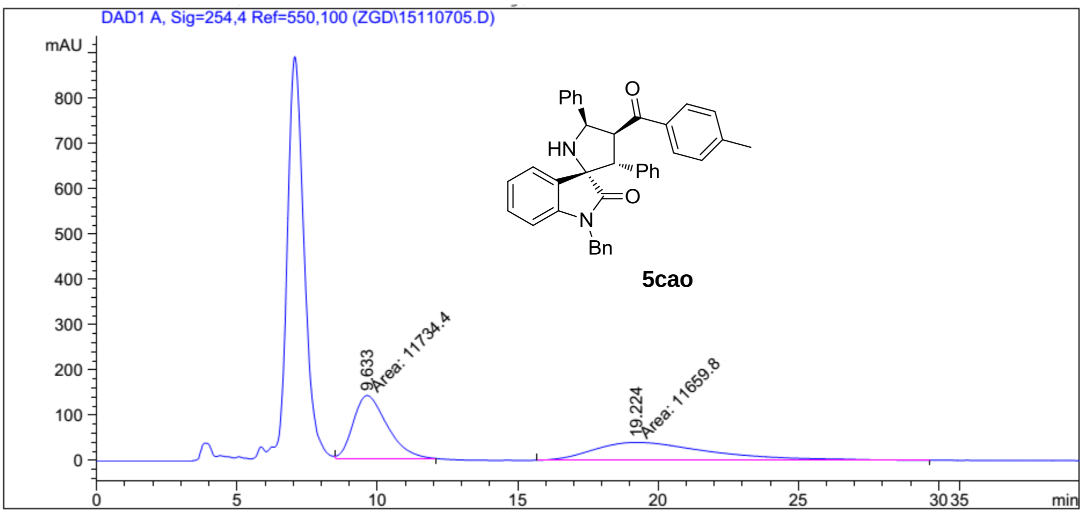
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.370	BB	0.3708	2.53006e4	1066.22498	97.2855
2	13.731	PB	0.5875	705.94049	18.48687	2.7145



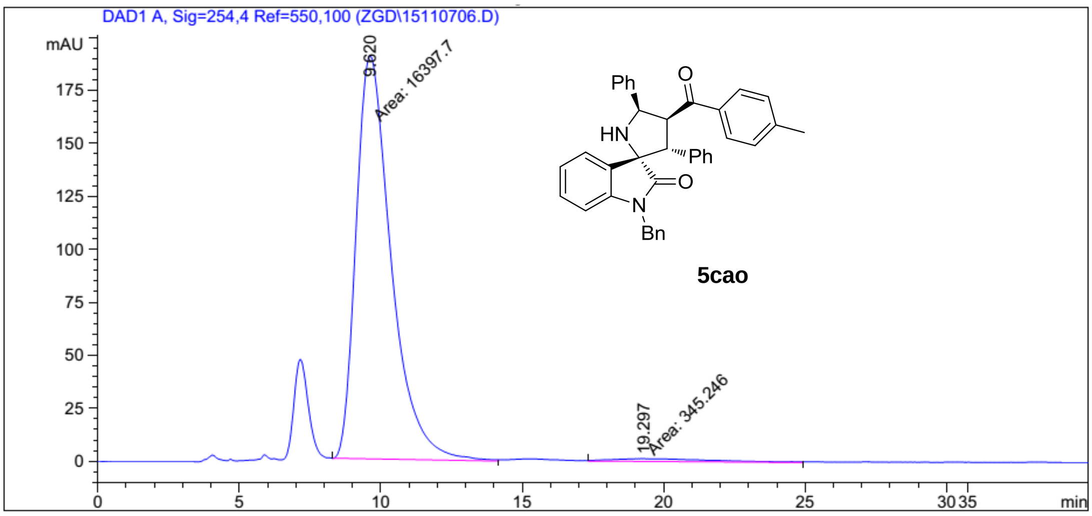
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.465	MM	0.7785	4192.76172	89.75790	49.6373
2	23.956	MM	1.1278	4254.04053	62.86657	50.3627



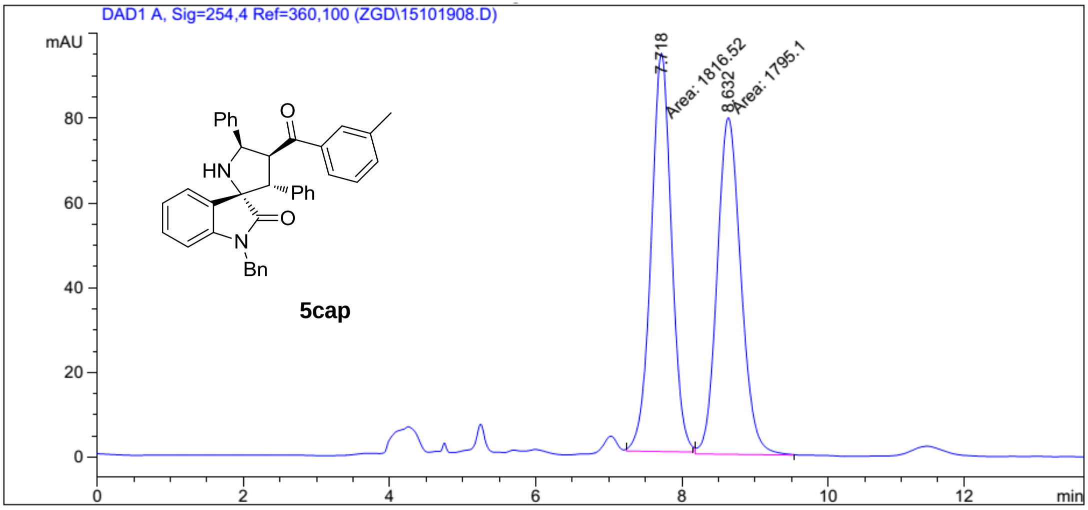
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.890	VV	0.7022	2.07389e4	403.14368	97.9084
2	23.964	MM	0.9882	443.05179	7.47270	2.0916



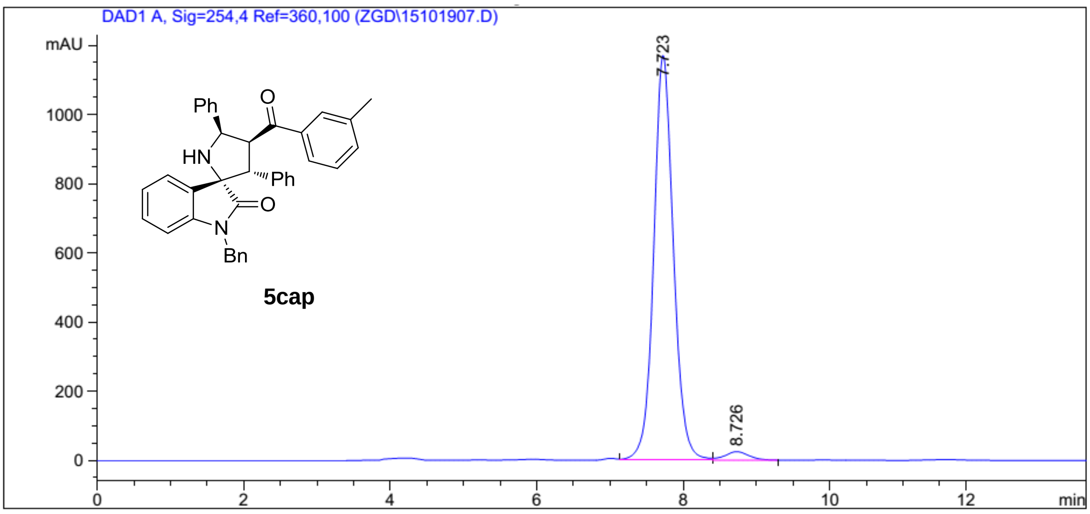
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.633	MM	1.4029	1.17344e4	139.40822	50.1595
2	19.224	MM	4.8645	1.16598e4	39.94881	49.8405



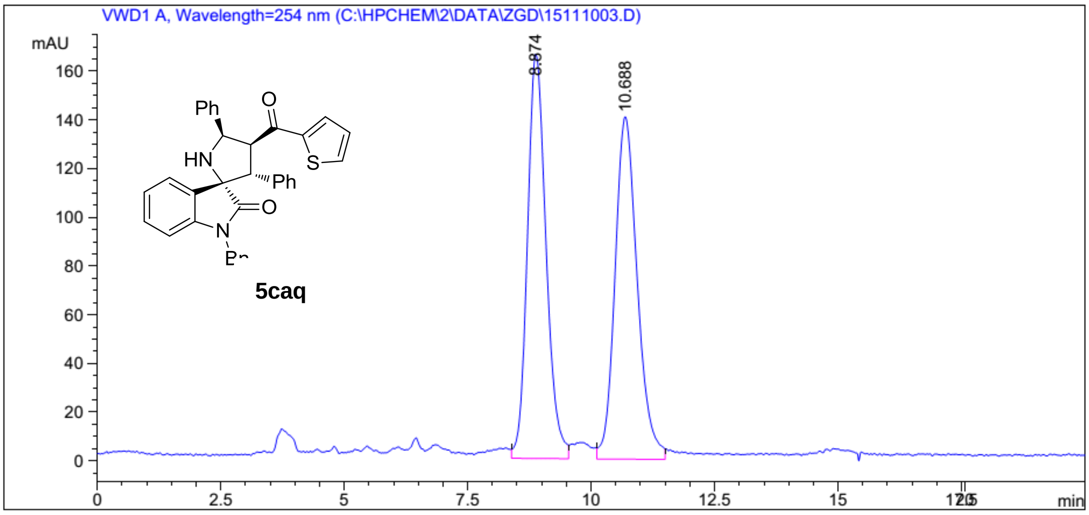
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.620	MM	1.4362	1.63977e4	190.29622	97.9380
2	19.297	MM	4.2820	345.24612	1.34379	2.0620



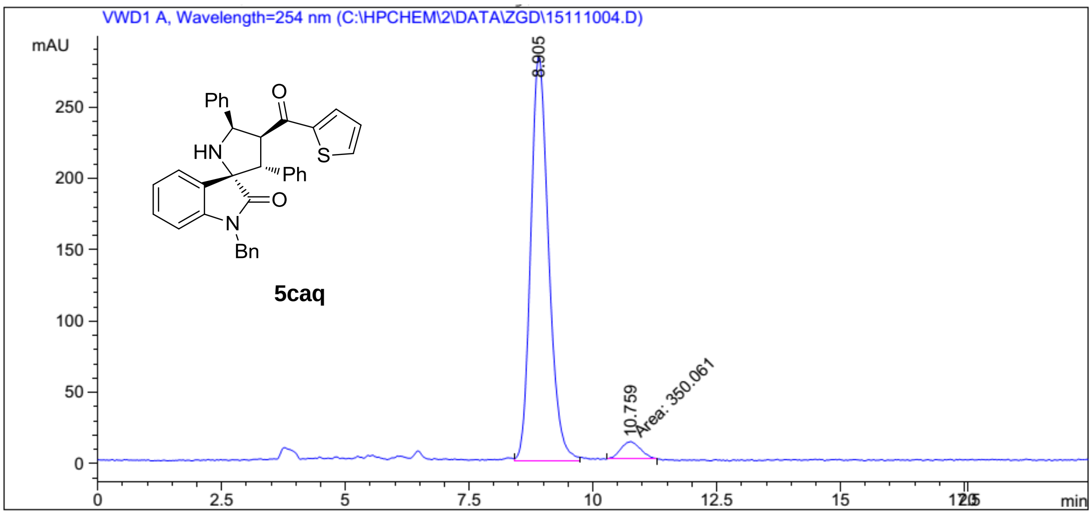
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.718	MM	0.3221	1816.51941	94.00548	50.2965
2	8.632	MM	0.3766	1795.09937	79.44741	49.7035



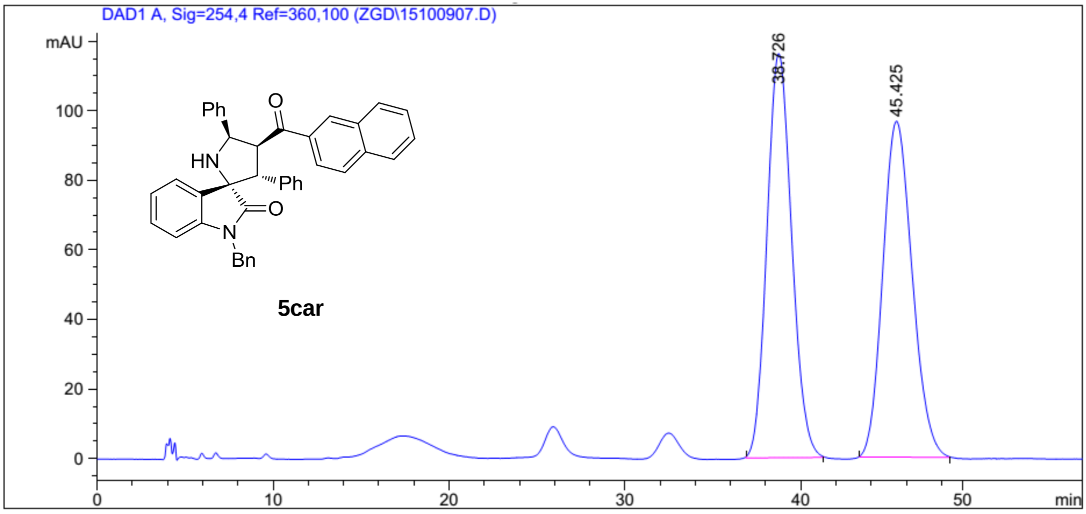
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.723	VV	0.2833	2.17970e4	1170.48218	97.4832
2	8.726	VB	0.3457	562.73822	24.89908	2.5168



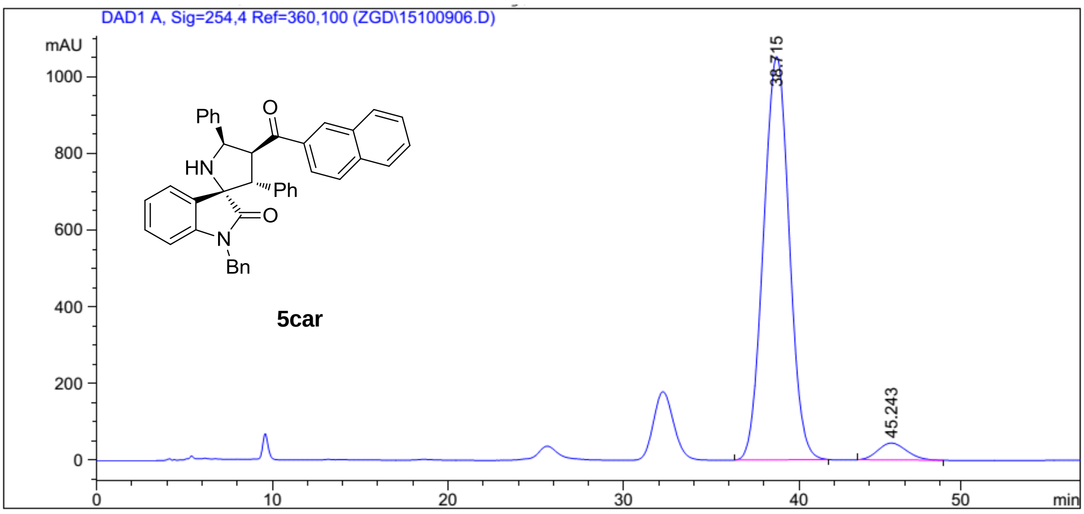
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.874	VV	0.4017	4349.05762	166.05238	49.6759
2	10.688	VV	0.4616	4405.81006	140.61810	50.3241



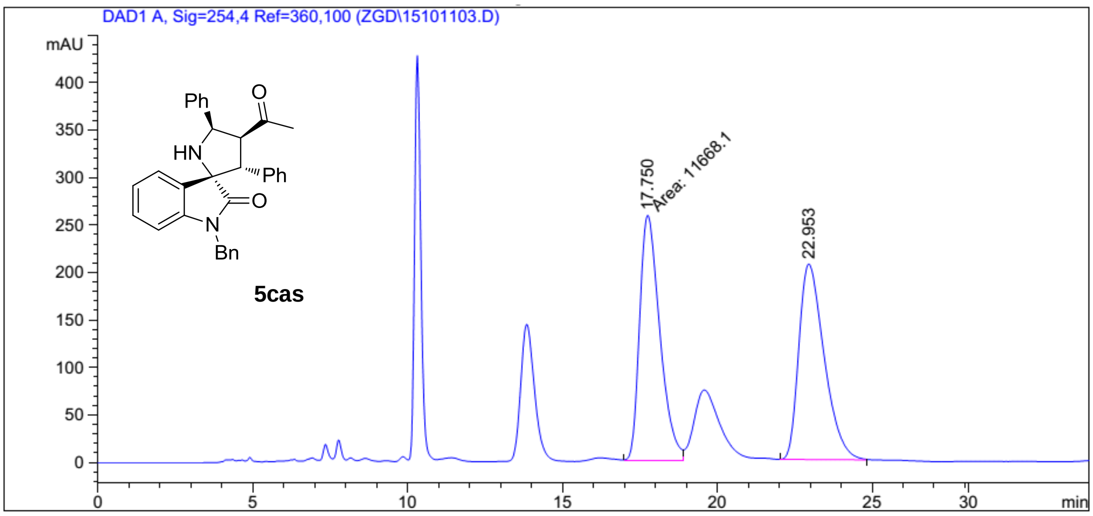
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.905	VV	0.3827	7113.14307	283.80576	95.3095
2	10.759	MM	0.4687	350.06146	12.44842	4.6905



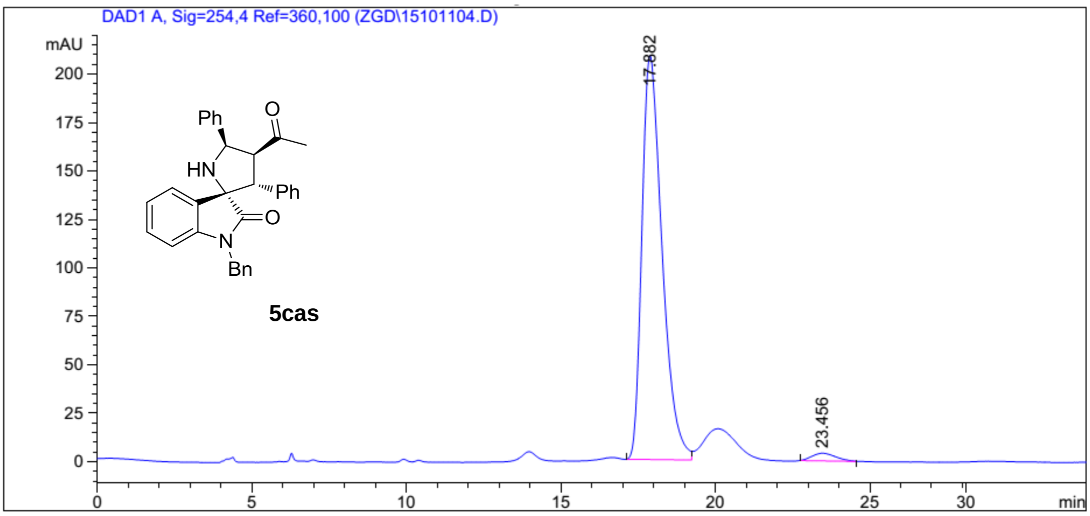
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.726	BB	1.4328	1.13376e4	116.14907	50.3218
2	45.425	BB	1.5444	1.11926e4	96.55113	49.6782



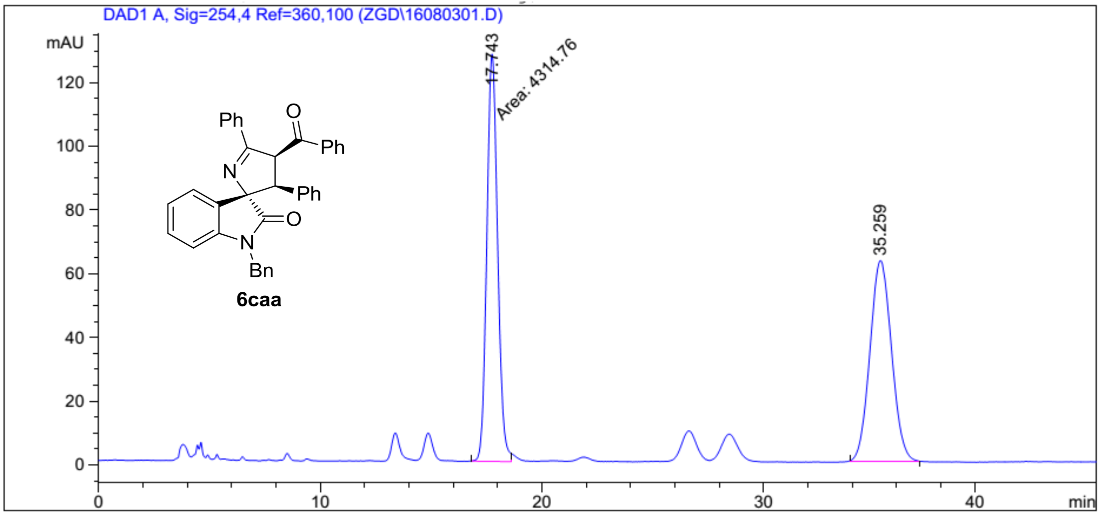
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.715	BB	1.5300	1.06937e5	1051.95215	95.4842
2	45.243	BB	1.3592	5057.40674	44.19108	4.5158



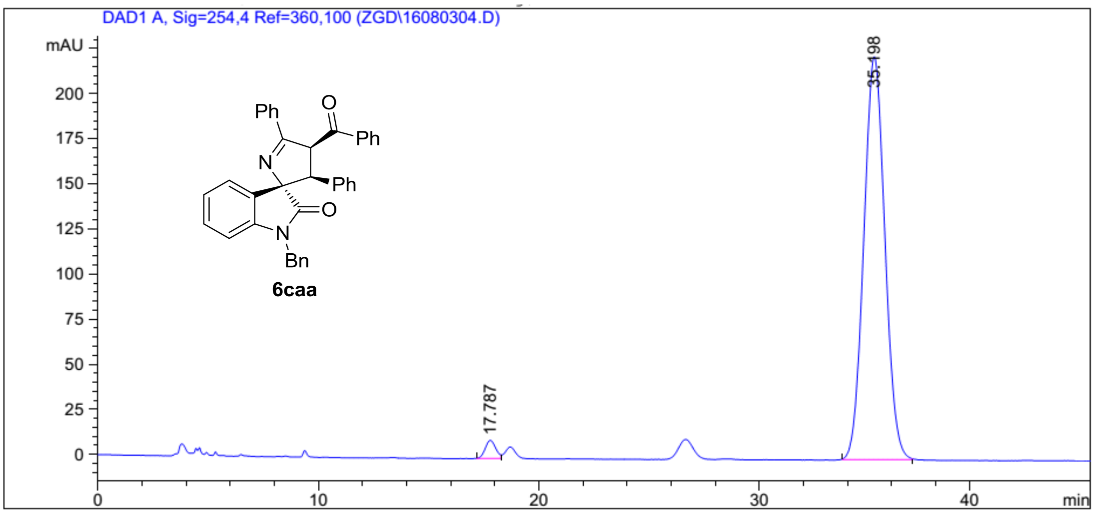
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.750	MM	0.7532	1.16681e4	258.17471	49.8762
2	22.953	PB	0.8696	1.17260e4	206.15710	50.1238



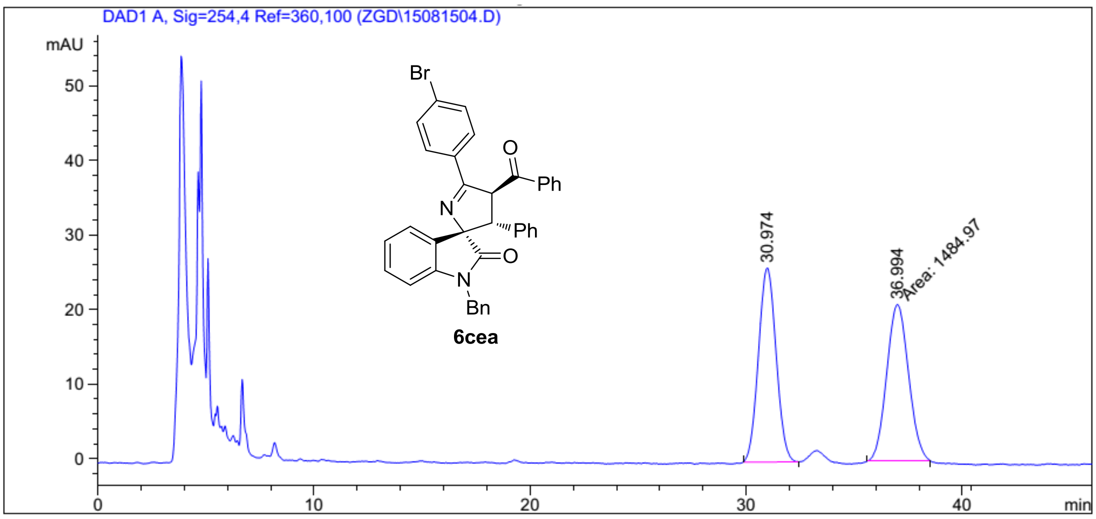
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.882	PB	0.6954	9454.20020	208.32912	97.7983
2	23.456	BB	0.6424	212.83849	3.93876	2.2017



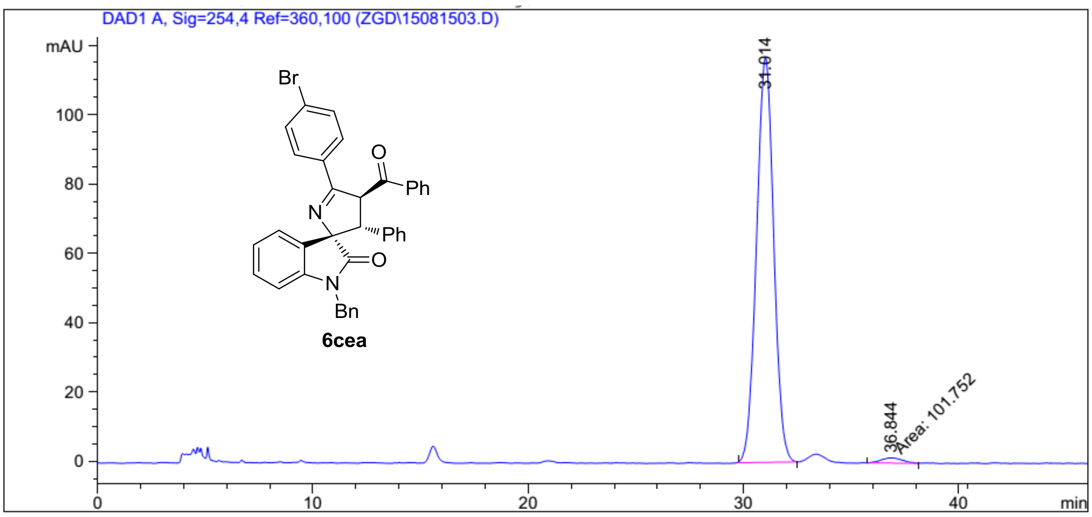
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.743	MM	0.5625	4314.76318	127.84127	50.2338
2	35.259	BB	0.9906	4274.60352	63.08243	49.7662



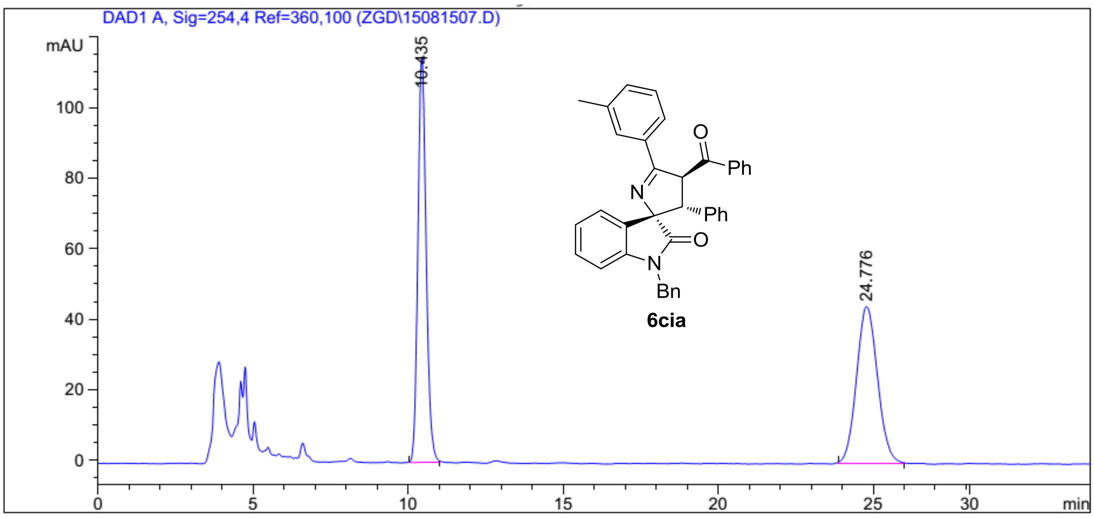
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.787	BV	0.4545	336.15051	10.09586	2.2240
2	35.198	BB	0.9942	1.47787e4	223.28596	97.7760



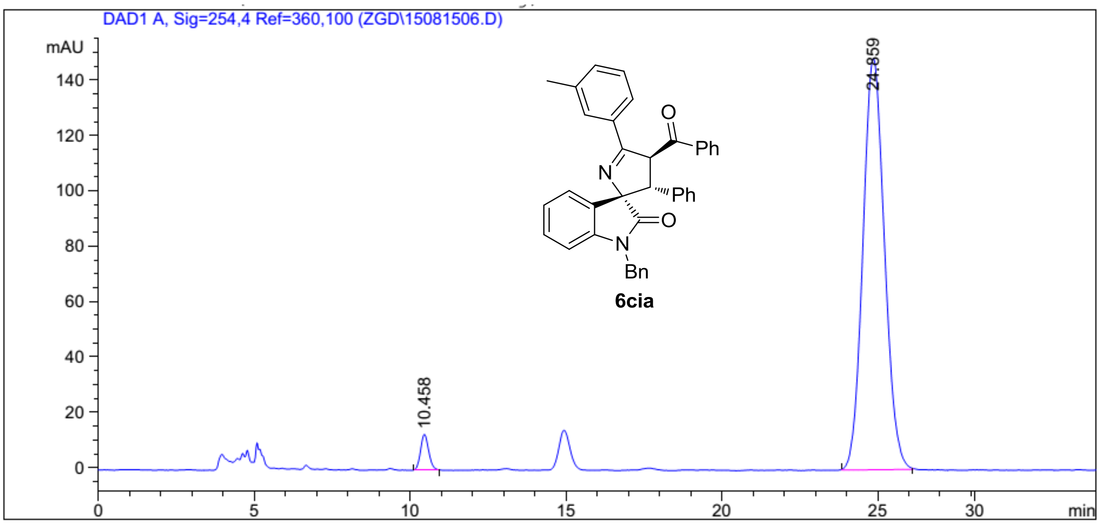
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.974	BP	0.7064	1477.86926	26.03006	49.8801
2	36.994	MM	1.1753	1484.97485	21.05734	50.1199



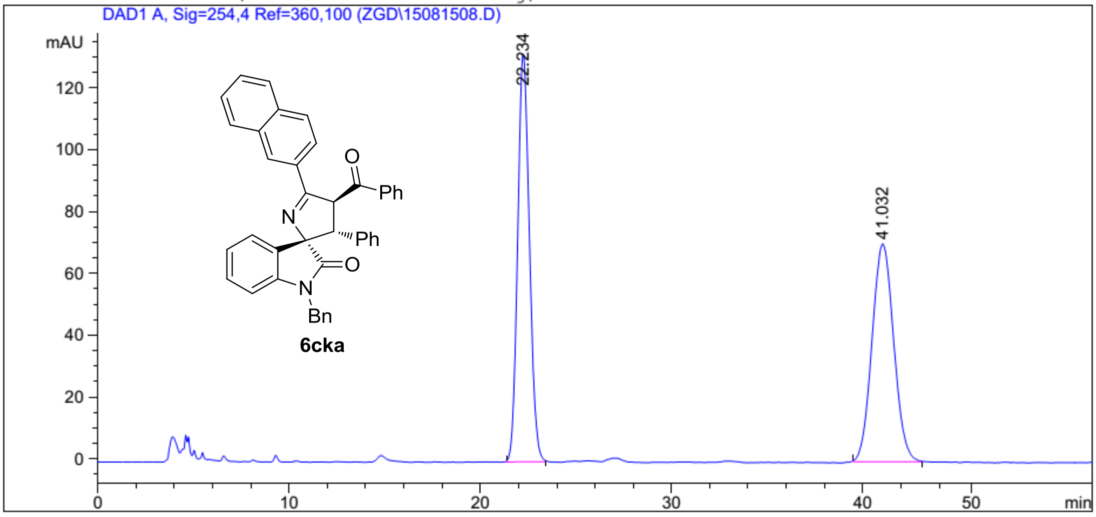
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.014	BB	0.8602	6465.37744	116.72876	98.4506
2	36.844	MM	1.1302	101.75175	1.50047	1.5494



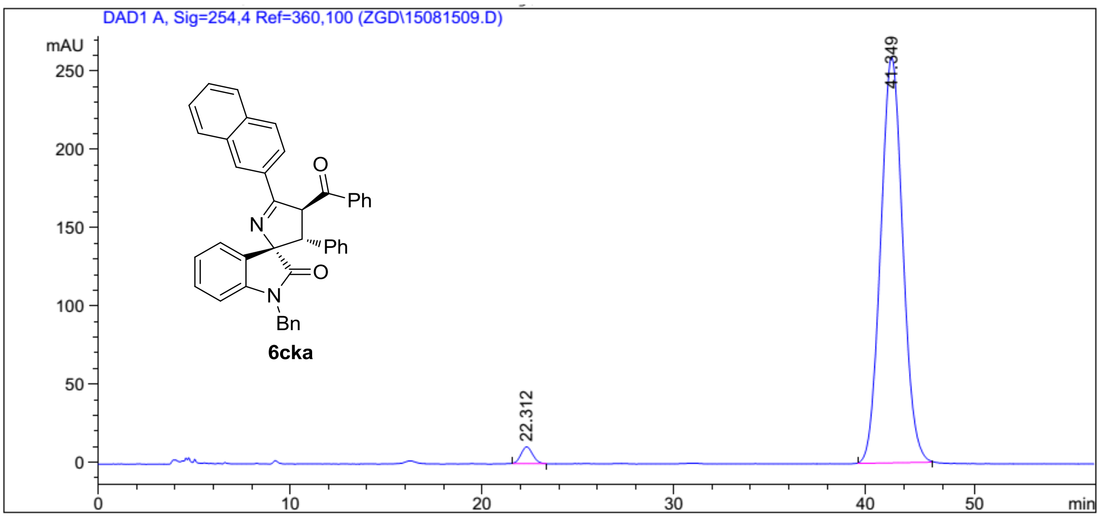
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.435	BB	0.2854	2120.74194	114.86540	50.3248
2	24.776	BB	0.7037	2093.36548	44.42717	49.6752



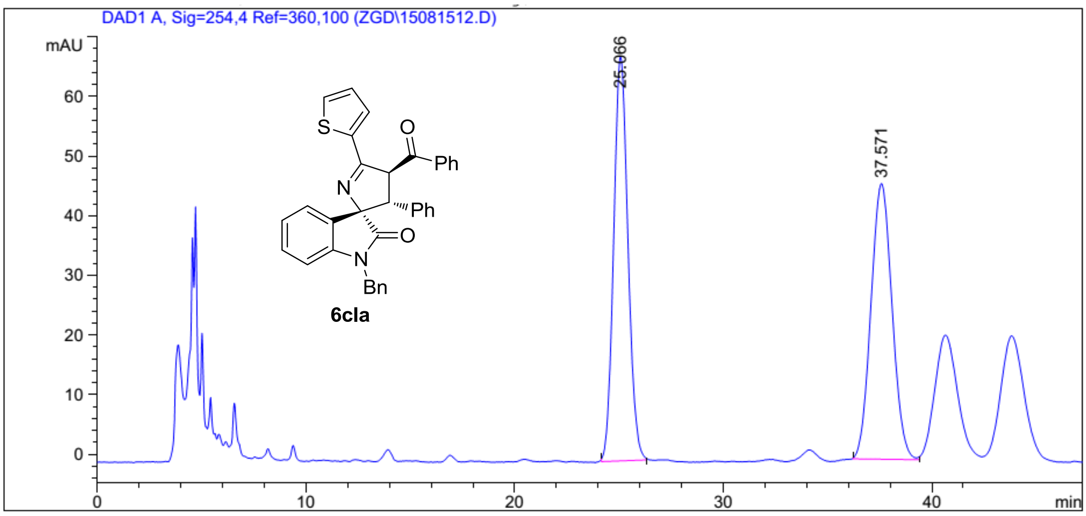
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.458	BB	0.2812	236.53937	12.94119	3.2199
2	24.859	BB	0.7447	7109.57568	148.46971	96.7801



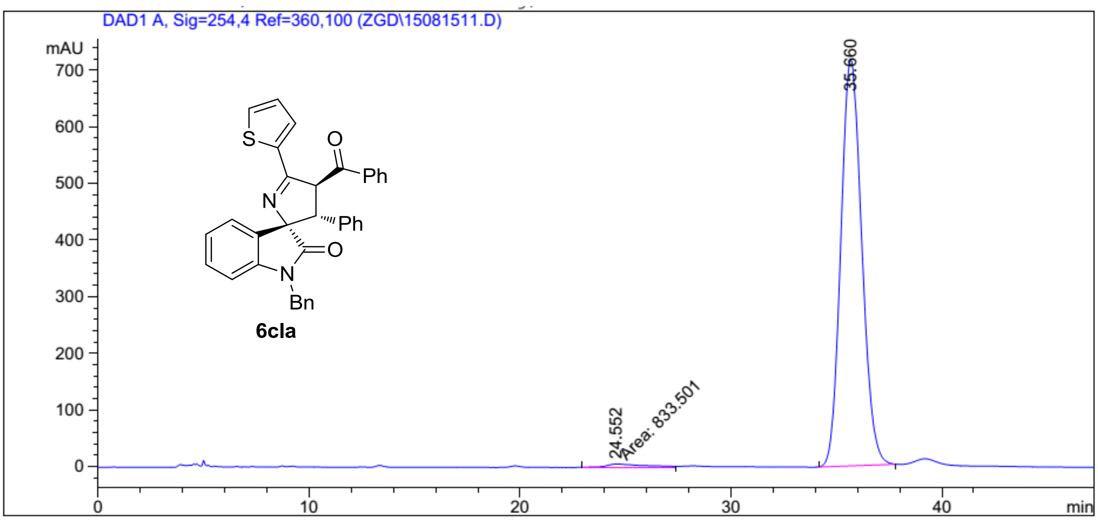
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.234	BB	0.6420	5608.98584	131.93970	50.4039
2	41.032	BB	1.1221	5519.08643	70.44077	49.5961



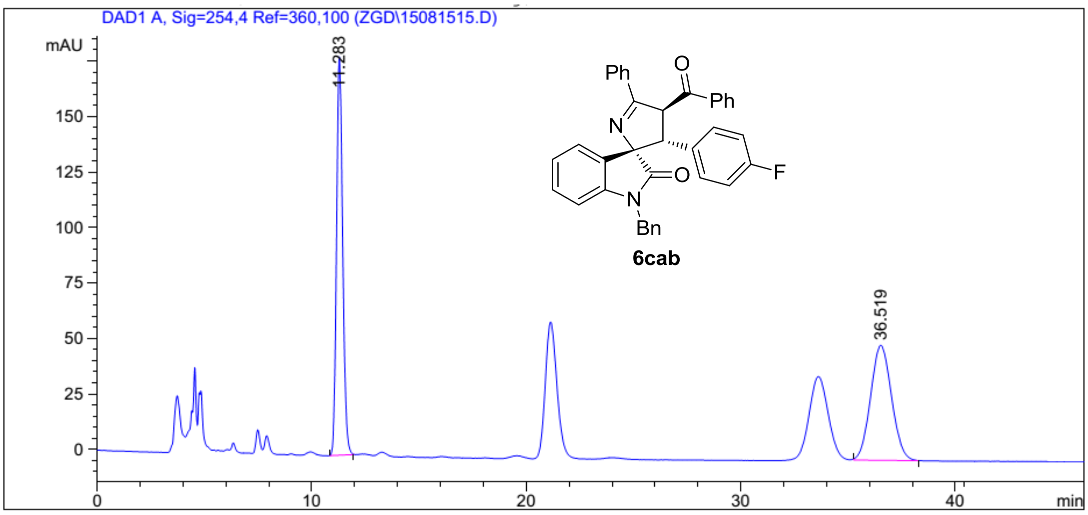
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.312	BB	0.5221	456.43323	10.73461	2.1522
2	41.349	BB	1.2013	2.07516e4	259.41739	97.8478



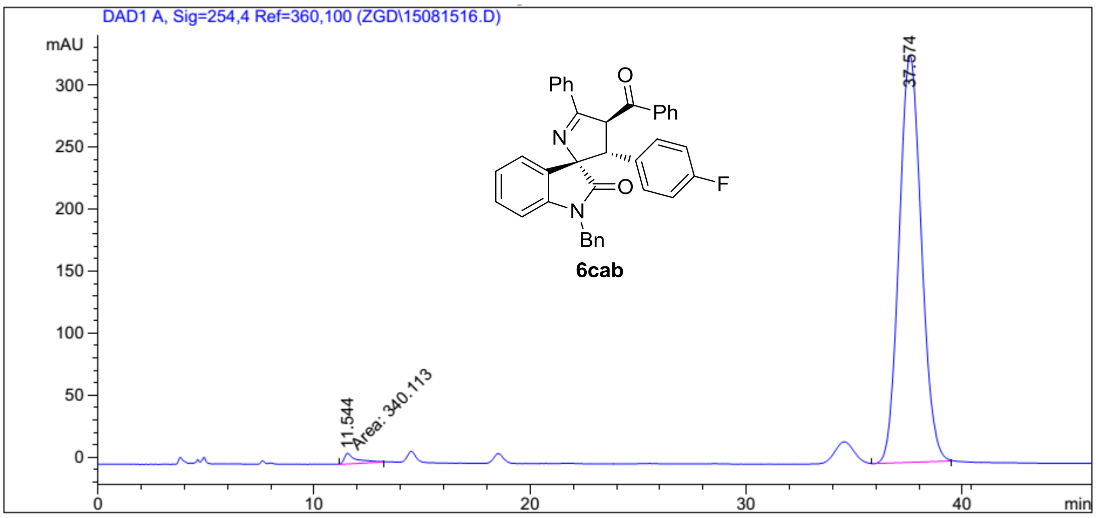
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.066	BB	0.7372	3211.65430	67.73172	49.7435
2	37.571	BB	1.0010	3244.77344	46.22058	50.2565



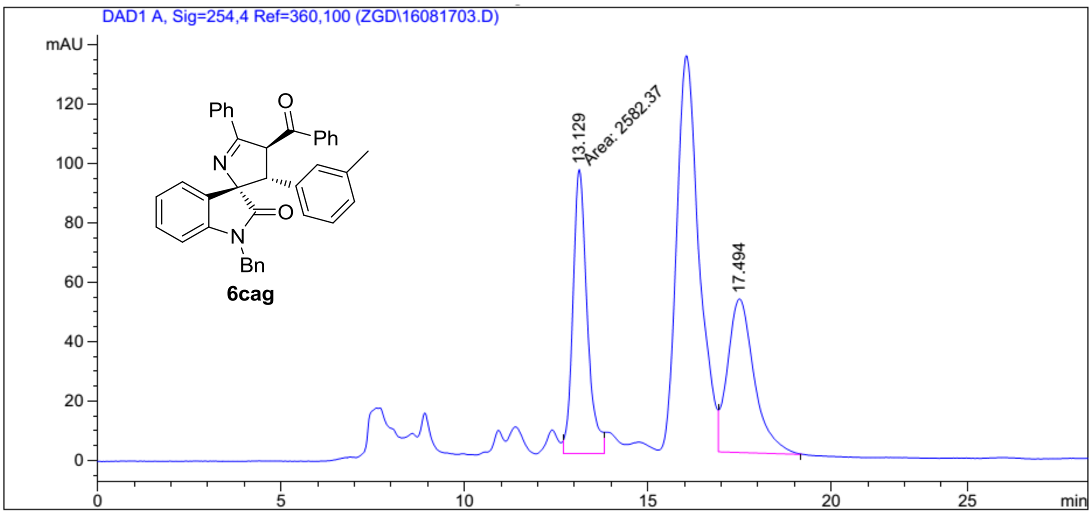
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.552	MM	2.2936	833.50128	6.05660	1.6595
2	35.660	BB	1.0593	4.93921e4	717.36469	98.3405



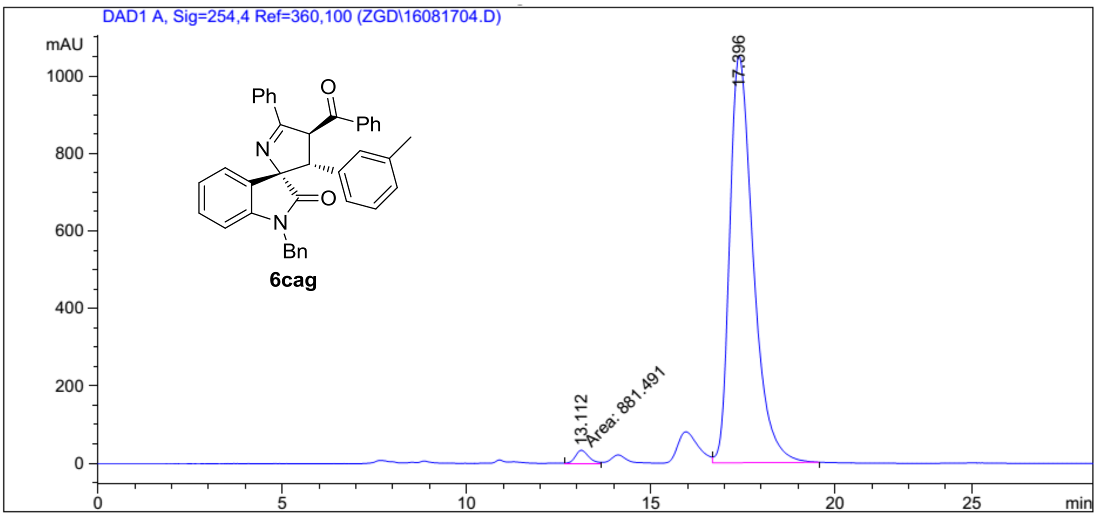
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.283	BB	0.3077	3565.22656	179.50783	50.3800
2	36.519	BB	0.9071	3511.44629	51.78307	49.6200



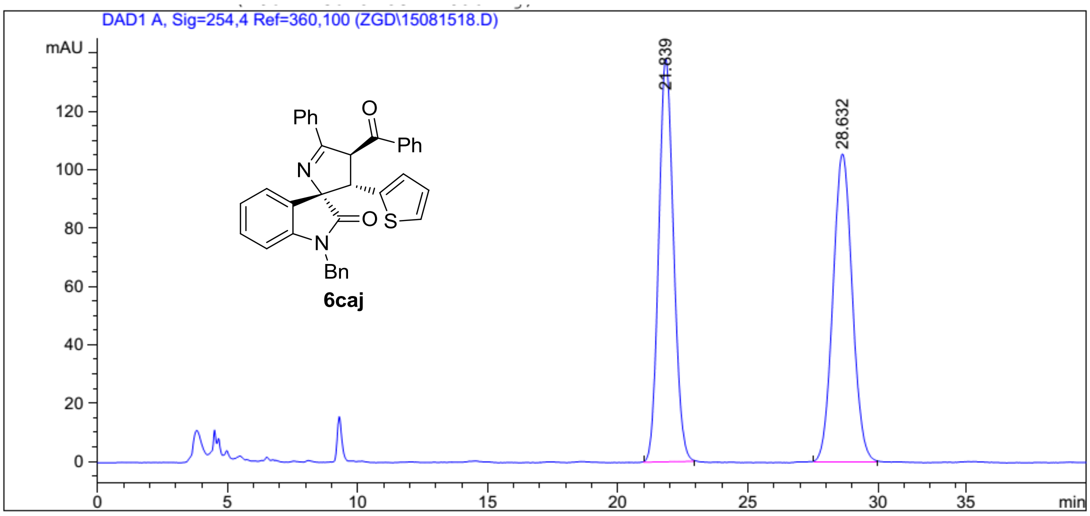
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.544	MM	0.6614	340.11255	8.57086	1.4351
2	37.574	VB	1.0882	2.33596e4	327.49554	98.5649



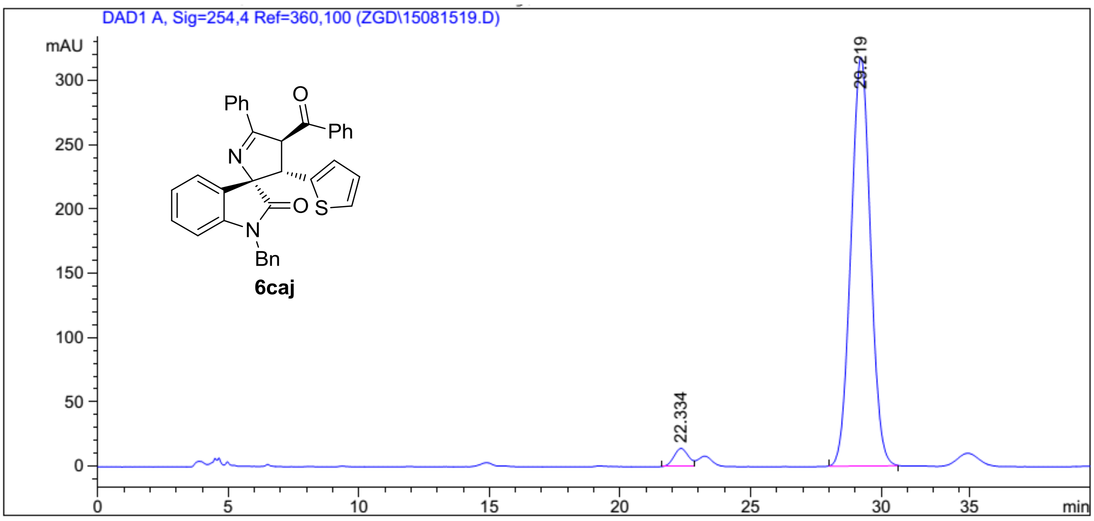
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.129	MM	0.4489	2582.37158	95.87856	49.7084
2	17.494	VB	0.7554	2612.66479	51.71620	50.2916



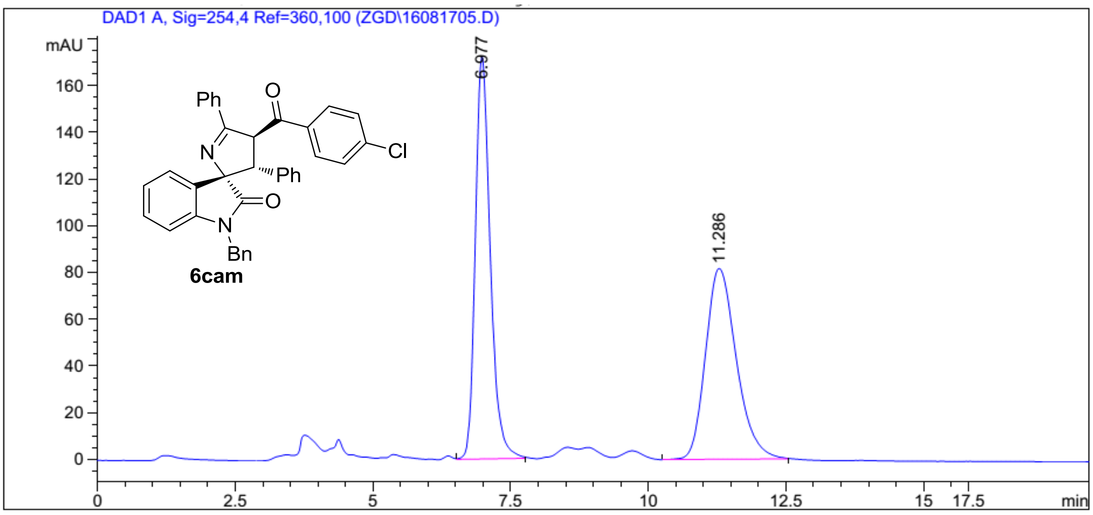
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.112	MM	0.4246	881.49060	34.60060	1.8601
2	17.396	VB	0.6624	4.65072e4	1050.66736	98.1399



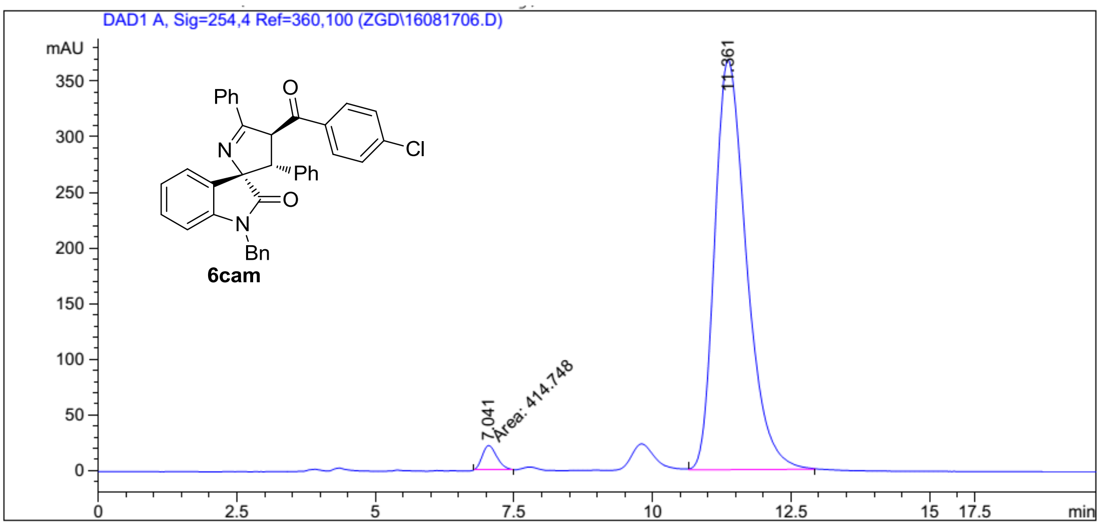
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.839	BB	0.6051	5482.60303	138.12187	50.2307
2	28.632	BB	0.7810	5432.24316	105.45042	49.7693



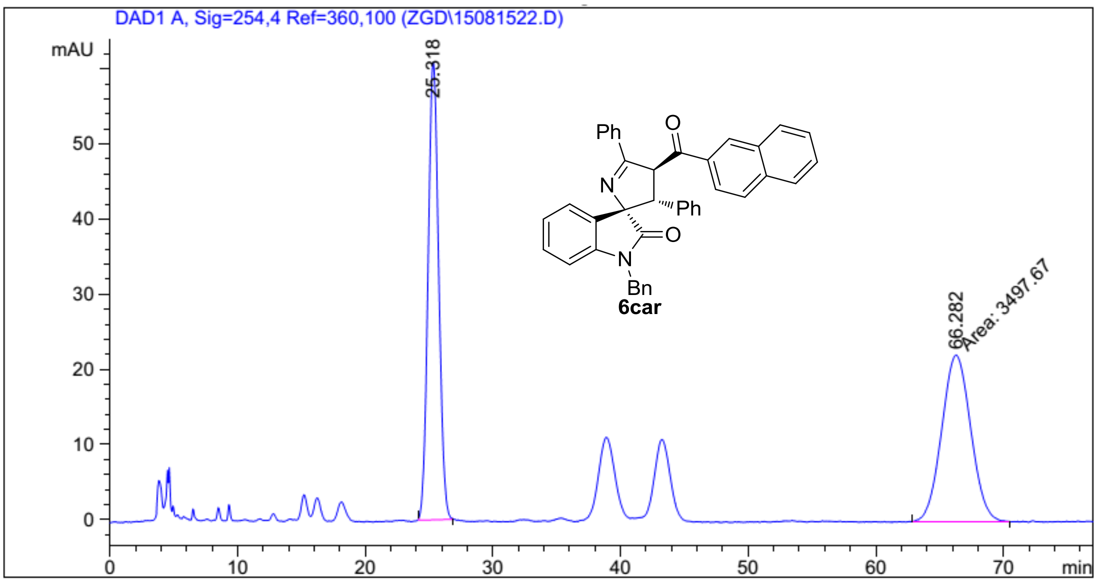
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.334	BV	0.5254	550.05890	14.09019	3.2262
2	29.219	BB	0.7955	1.64996e4	317.90234	96.7738



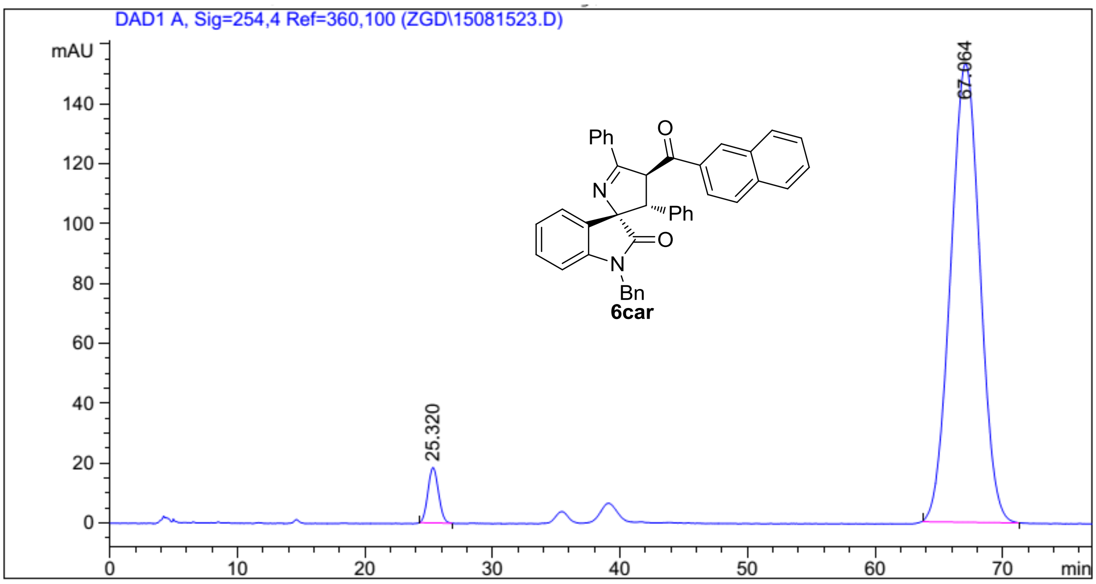
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.977	VB	0.2877	3242.33423	172.13969	50.4804
2	11.286	VB	0.5860	3180.62109	81.73486	49.5196



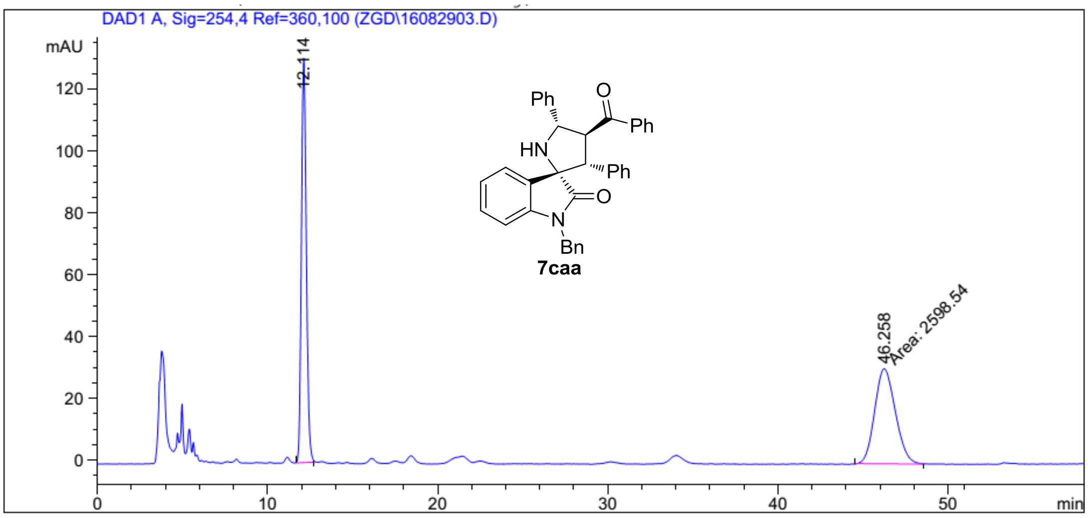
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.041	MM	0.3095	414.74768	22.33662	2.7501
2	11.361	BB	0.6105	1.46664e4	368.34241	97.2499



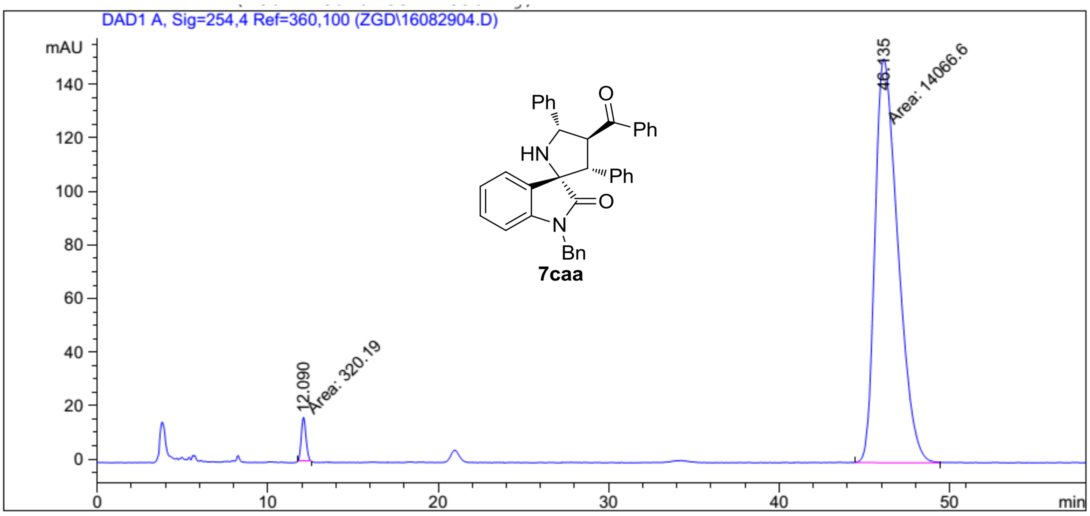
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.318	BB	0.8680	3498.10522	60.91014	50.0031
2	66.282	MM	2.6281	3497.66504	22.18159	49.9969



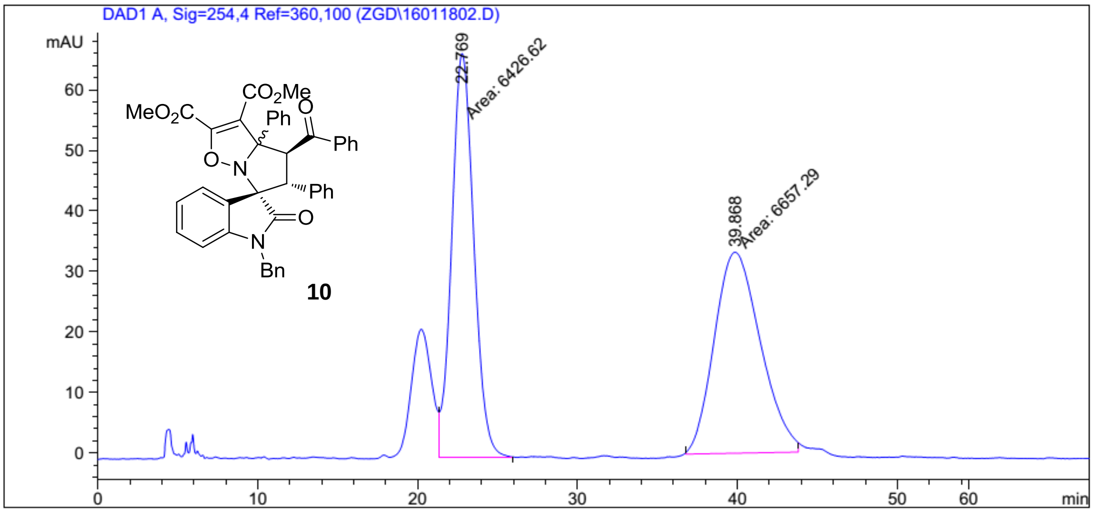
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.320	BB	0.7007	1070.86755	18.51685	4.1937
2	67.064	BB	1.8797	2.44643e4	153.14400	95.8063



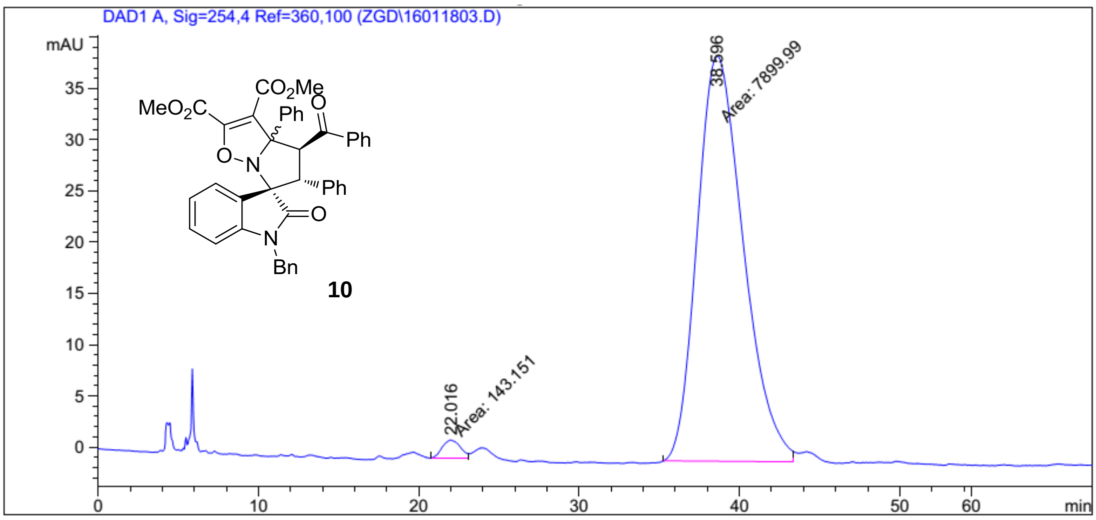
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.114	BB	0.3075	2619.51831	130.88480	50.2010
2	46.258	MM	1.4094	2598.54395	30.72837	49.7990



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.090	MM	0.3236	320.18954	16.49314	2.2256
2	46.135	MM	1.5542	1.40666e4	150.84041	97.7744



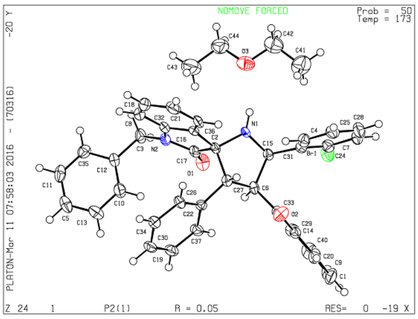
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.769	MM	1.6020	6426.61670	66.86135	49.1185
2	39.868	MM	3.3397	6657.29004	33.22295	50.8815



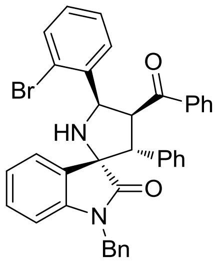
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.016	MM	1.3301	143.15051	1.79375	1.7798
2	38.596	MM	3.3293	7899.99072	39.54782	98.2202

7. Data of 5cfa and 5can’ and Proposed Stereocontrol Model

For 5cfa:



≡



5cfa

Empirical formula C41 H39 Br N2 O3

Formula weight 687.65

Temperature (K) 173(2)

Crystal system Monoclinic

Space group P2(1)

a (Å) 12.4503(7)

b (Å) 9.3115(4)

c (Å) 15.1532(8)

α(°) 90.00

β(°) 103.909(2)

γ(°) 90.00

Volume (Å ^{3}) 1705.22(15)

Z 4

Dcalcd (g cm^{3}) = 1.339

μ(mm^{-1}) = 1.247

F (000) = 716

Theta range for data collection 1.38 to 24.28

Index ranges -12<=h<=14, -10<=k<=10, -17<=l<=16

Reflections collected 11241

Independent reflections 5308 [R(int) = 0.0455]

Data/restraints/parameters 5308/1/424

GOF (on F^{2}) 1.002

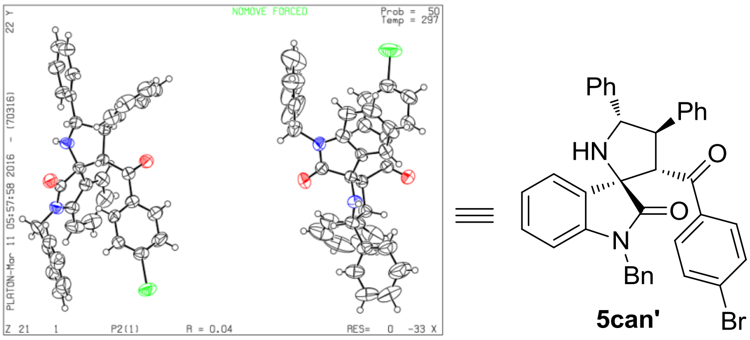
Final R indexes [I>=2σ (I)] R1 = 0.0455, wR2 = 0.0891

Final R indexes [all data] R1 = 0.0653, wR2 = 0.0956

Largest diff. peak and hole (e Å $^{-3}$) 0.501/-0.488

Flack parameter 0.036(9)

For 5can':



Empirical formula C37 H29 Br N2 O2

Formula weight 613.53

Temperature (K) 297(2)

Crystal system Monoclinic

Space group P2(1)

a (Å) 10.0039(12)

b (Å) 11.6625(13)

c (Å) 25.912(3)

α(°) 90.00

β(°) 94.479(3)

γ(°) 90.00

Volume (Å ^{3}) 3013.9(6)

Z 4

Dcalcd (g cm^3) = 1.352

μ(mm^{-1}) = 1.400

F (000) = 1264

Theta range for data collection 2.04 to 25.00

Index ranges -11<=h<=11, -13<=k<=13, -30<=l<=30

Reflections collected 49575

Independent reflections 9639 [R(int) = 0.0416]

Data/restraints/parameters 9639/1/757

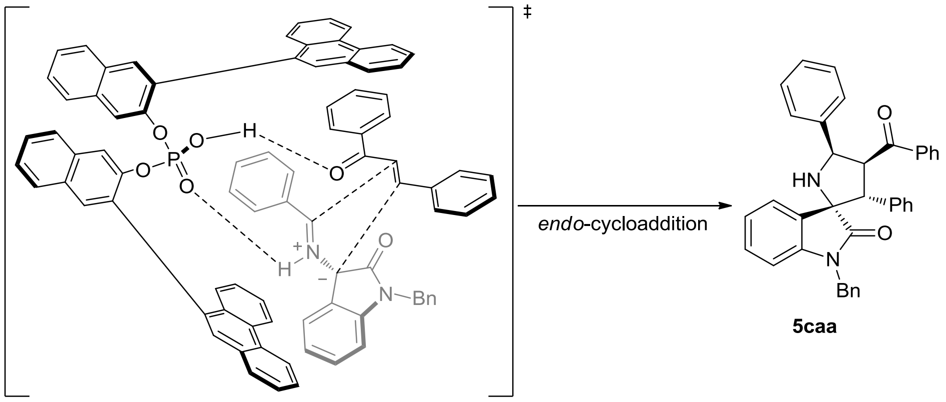
GOF (on F^2) 1.024

Final R indexes [I>=2σ (I)] R1 = 0.0424, wR2 = 0.1041

Final R indexes [all data] R1 = 0.0591, wR2 = 0.1103

Largest diff. peak and hole (e Å $^{-3}$) 0.667 / -0.653

Flack parameter 0.034(6)



5caa

Figure S1. Proposed stereocontrol model.

8. References

1. The synthesis of 3-amino oxindole hydrochloride, see: (a) Chen, W.-B.; Wu, Z.-J.; Hu, J.; Cun, L.-F.; Zhang, X.-M; Yuan, W.-C. *Org. Lett*. **2011**, *13*, 2472.
2. The synthesis of α,β-unsaturated enones, see: (a) El-Batta, A.; Jiang, C.; Zhao, W.; Anness, R.; Cooksy, A. L.; Bergdahl, M. *J. Org. Chem.* **2007**, *72*, 5244. (b) Zhang, X.; Kang, J.; Niu, P.; Wu, J.; Yu, W.; Chang, J. *J. Org. Chem.* **2014**, *79*, 10170.
3. CCDC 1463860 (**5can’**).