Electronic Supplementary Information (ESI)

Copper/Guanidine-Catalyzed Asymmetric Alkynylation of Isatin-Derived Ketimines

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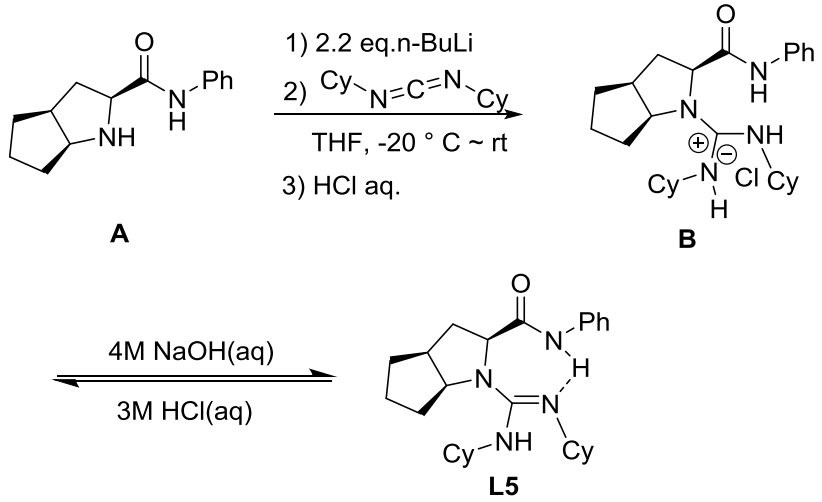
Table of contents

(A) General

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the etramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis in comparison with the authentic racemates. Details of the chiral column is as follows: Daicel Chiralcel IA [Amylose tris(3,5-dimethylphenylcarbamate) immobilized on 5μm/3μm silica support], IB [Cellulose tris(3,5-dimethylphenylcarbamate) immobilized on 5μm/3μm silica support], and IC [Cellulose tris(3,5-dichlorophenylcarbamate) immobilized on 5μm/3μm silica support]. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 ml, in solvent). CD spectra (MeOH as the solvent) were determined by Chirascan CD which was purchased from applied photophysics Ltd. HRMS was recorded on a commercial apparatus (ESI source). All the solvents were purified by usual methods before use. All alkynes were commercial available. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

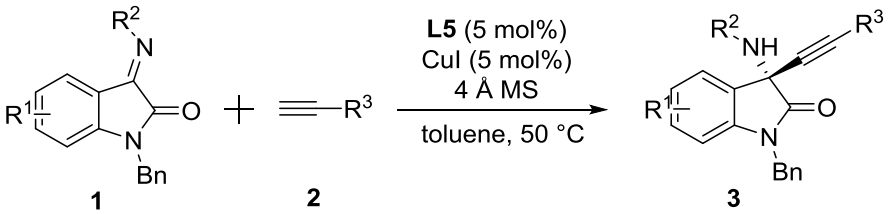
(B) Typical procedure for guanidine preparation



2.5 M *n*-BuLi in *n*-hexane (2.2 eq., 11.0 mmol) was injected into a solution of **A** (4.0 mmol) in THF (40 mL) dropwise over 10 mins under nitrogen atmosphere at −20 ℃ with well stirring. After additional 10 mins, a solution of *N*,*N*-dicyclohexylcarbodiimide (1.2 eq., 4.8 mmol) in 10 mL of THF was added dropwise within 10 mins. The reaction was allowed to warm to room temperature and detected by TLC. After 12 h, the mixture was evaporated under reduced pressure to get rid of THF, and the pH value of the mixture was brought into the range of 0–1 by the addition of 3 M HCl. The aqueous phase was extracted with CH_2Cl_2 (5 × 30 mL). The combined organic phase was washed with 3M HCl in brine, dried over anhydrous Na_2SO_4 and evaporated in vacuum, and purified through flash chromatograph on silica gel to produce guanidium salt. The obtained white foam can be recrystallized in CH_2Cl_2 and diethyl ether to get a single crystal. Then, guanidium salt

in CH_2Cl_2 (16 mL) was added 4 M NaOH (15 mL) and stirred until the basification was finished (10 mins). The pH value of the mixture was kept in the range of 11–12. The aqueous phase was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic phase was washed with 4 M NaOH, dried over anhydrous Na_2SO_4 and evaporated in vacuum. Finally, a white solid was obtained. Then it was dissolved in CH_2Cl_2 and filtration through Celite to remove the silicone gel, concentrate to get a kind of white foam (56% yield). For other guanidine catalysts, this synthesis method could be applied.

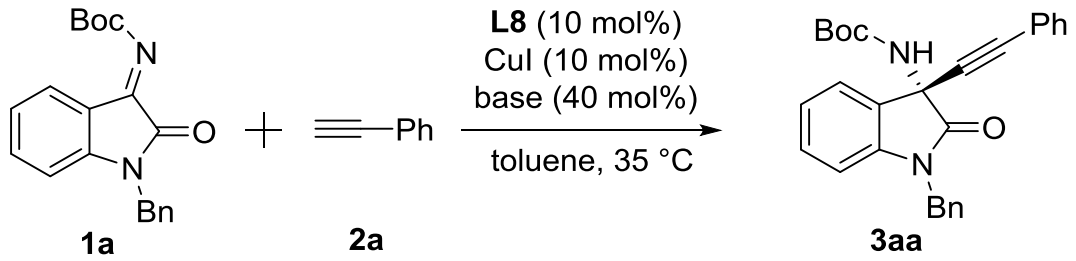
(C) General procedure for the catalytic asymmetric reaction



A mixture of CuI (5 mol%), guanidine **L5** (5 mol%), 4 Å MS (40 mg) and **1** (0.1 mmol) was weighted into a test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2** (0.11 mmol). The resulting mixture was stirred for 4 days at 50 ℃ and the product **3** was purified by flash chromatography.

(D) Optimization of the reaction conditions

Table 1: **Screen of the base**[a]

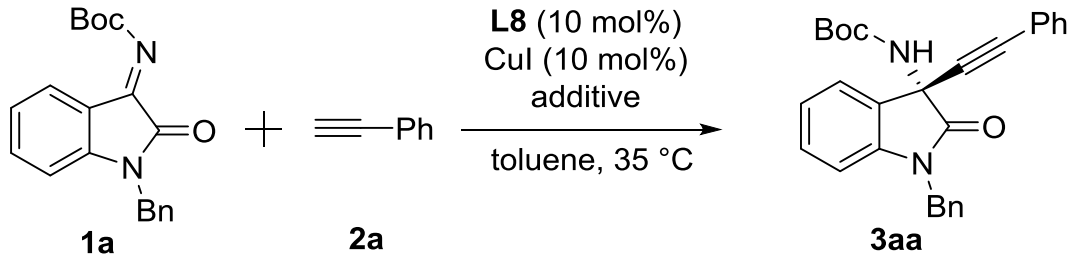


entry	base	yield of **3aa** [%][b]	*ee* of **3aa** [%][c]
1	--	17	87
2	NaI	Trace	/
3	CsF	Trace	/
4	PhCOONa	8	86
5	DABCO	Trace	/
6	Et_3N	7	80
7	iPr_2NEt	5	85
8	$CyNH_2$	7	84
9	pyridine	9	83
10	DMAP	20	75
11	piperidine	3	87
12	pyrrole	8	83

13	DBU	5	13
14	TBAF	Trace	/
15	KF	12	87
16	MeONa	Trace	/
17	NaOAc	11	86

[a] Unless specified, all reactions were performed with CuI/**L8** (10 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.11 mmol), base (40 mol%) in toluene (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table 2: **Screen of the reaction additive**[a]

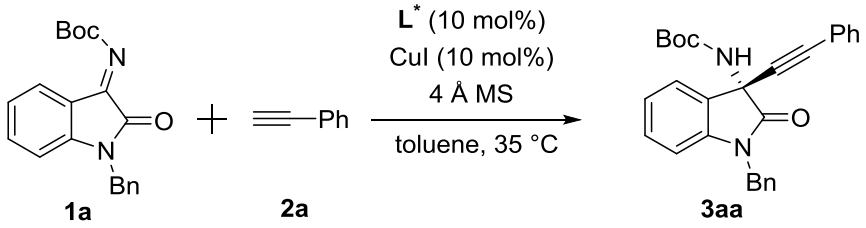


1a **2a** **3aa**

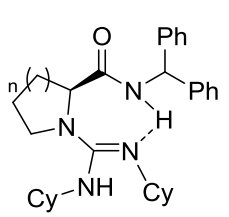
entry	additive	yield of **3aa** [%][b]	*ee* of **3aa** [%][c]
1	3 Å MS	14	86
2	4 Å MS	14	87
3	5 Å MS	14	86

[a] Unless specified, all reactions were performed with CuI/**L8** (10 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.11 mmol), additive (20 mg) in toluene (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

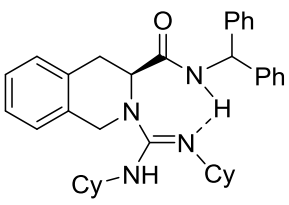
Table 3: **Screen of chiral guanidines**[a]



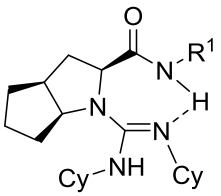
1a **2a** **3aa**



L1 n = 1
L2 n = 2



L3



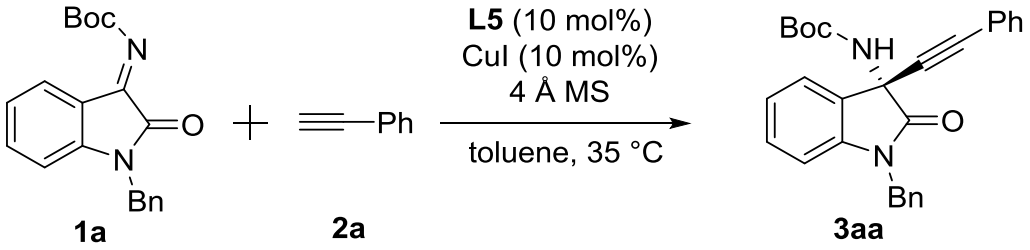
L4 R^1 = $CHPh_2$
L5 R^1 = Ph
L6 R^1 = 2,6-*i*-$Pr_2C_6H_3$
L7 R^1 = 4-*i*-PrC_6H_4
L8 R^1 = 1-adamantyl

entry	**L***	yield of **3aa** [%][b]	*ee* of **3aa** [%][c]
1	**L1**	6	60
2	**L2**	trace	/

3	**L3**	trace	/
4	**L4**	10	73
5	**L5**	32	96
6	**L6**	3	37
7	**L7**	32	94
9	**L8**	14	87

[a] Unless specified, all reactions were performed with CuI/**L*** (10 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.11 mmol), 4 Å MS (20 mg) in toluene (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table 4: **Screen of the amount of additive**[a]

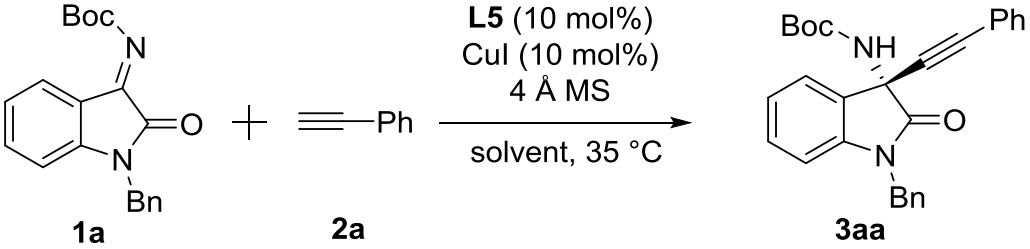


1a **2a** **3aa**

entry	4 Å MS	yield of **3aa** [%][b]	*ee* of **3aa** [%][c]
1	20 mg	32	96
2	40 mg	43	96
3	60 mg	30	96
4	80 mg	27	96
5	100 mg	23	96

[a] Unless specified, all reactions were performed with CuI/**L5** (10 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.11 mmol), 4 Å MS in toluene (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table 5: **Screen of the reaction solvents**[a]

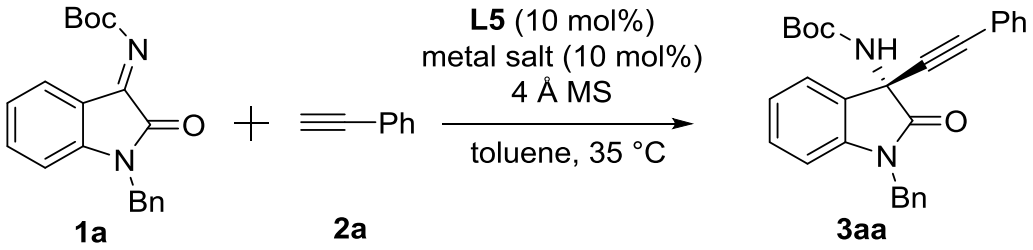


1a **2a** **3aa**

entry	solvent	yield of **3aa** [%][b]	*ee* of **3aa** [%][c]
1	Toluene	43	96
2	THF	trace	/
3	Et_2O	12	88
4	CH_2Cl_2	2	80
5	CH_3CN	trace	/
6	EtOAc	trace	/

[a] Unless specified, all reactions were performed with CuI/**L5** (10 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.11 mmol) and 4 Å MS (40 mg) in solvent (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

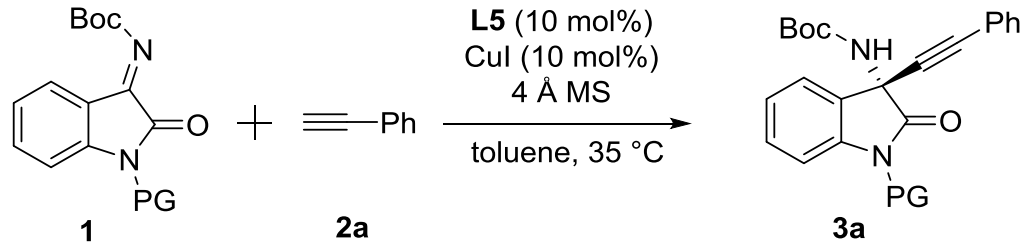
Table 6: **Screen of chiral guanidine L5 with different metal salts**[a]



entry	metal salt	yield of **3aa** [%][b]	*ee* of **3aa** [%][c]
1	CuCl	trace	/
2	CuBr	20	92
3	CuI	43	96
4	$CuBr{\cdot}SMe_2$	15	92
5	$(CuOTf)_2{\cdot}C_6H_6$	trace	/
6	$CuPF_6{\cdot}4CH_3CN$	34	28

[a] Unless specified, all reactions were performed with metal salt/**L5** (10 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.11 mmol) and 4 Å MS (40 mg) in toluene (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

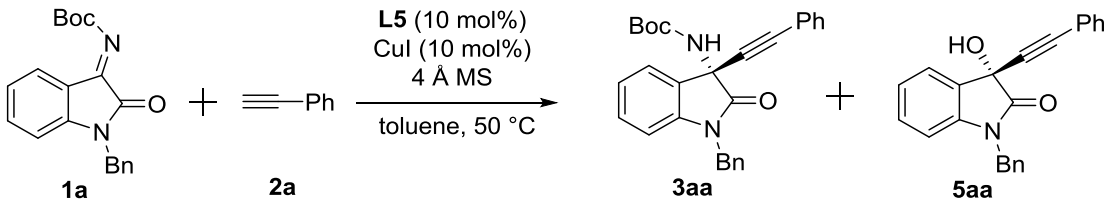
Table 7: **Screen of the *N*- protected group of isatin-derived ketimine**[a]



entry	PG	yield of **3** [%][b]	*ee* of **3** [%][c]
1	H	trace	/
2	Me	14	94
3	Bn	43	96
5	Ts	trace	/
6	Boc	trace	/

[a] Unless specified, all reactions were performed with CuI/**L5** (10 mol%, 1:1), **1** (0.10 mmol), **2a** (0.11 mmol) and 4 Å MS (40 mg) in toluene (0.5 mL) at 35 °C for 2 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

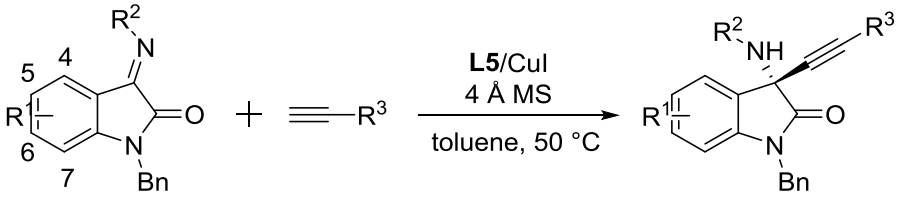
Table 8: **The effect of 4 Å MS**



entry	4 Å MS	water	yield of **3aa** [%][b]	yield of **5aa** [%][b]	*ee* of **3aa** [%][c]	*ee* of **5aa** [%][c]
1	40 mg	--	83	trace	95	/
2	40 mg	3 ul	83	trace	95	/
3	--	--	53	32	95	3
5	--	3 ul	41	49	94	3

[a] Unless specified, all reactions were performed with CuI/**L5** (10 mol%, 1:1), **1** (0.10 mmol), **2a** (0.11 mmol) and 4 Å MS (40 mg) in toluene (0.5 mL) at 50 °C for 3 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

***Table 9:*Full list of the products**



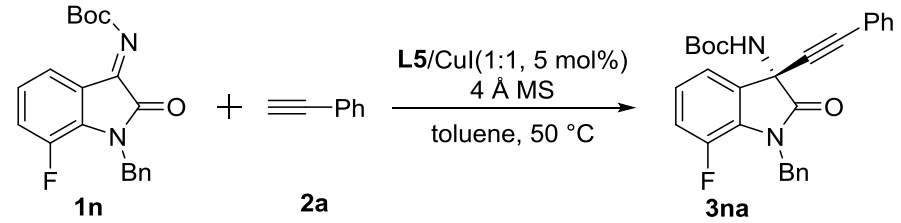
1 **2** **3**

entry	**1**: R^1	**1**: R^2	**2**: R^3	yield of **3** [%][d]	*ee* of **3** [%][e]
1[a]	**1a**: H	Boc	**2a**: C_6H_5	83 (**3aa**)	95
2[a]	**1b**: H	Cbz	**2a**: C_6H_5	85 (**3ba**)	91
3[a]	**1c**: H	CO_2Et	**2a**: C_6H_5	77 (**3ca**)	91
4[a]	**1d**: 5-F	Boc	**2a**: C_6H_5	95 (**3da**)	94
5[a]	**1e**: 5-Cl	Boc	**2a**: C_6H_5	91 (**3ea**)	92
6[a]	**1f**: 5-Br	Boc	**2a**: C_6H_5	95 (**3fa**)	93
7[a]	**1g**: 5-I	Boc	**2a**: C_6H_5	94 (**3ga**)	93
8[b]	**1h**: 5-Me	Boc	**2a**: C_6H_5	89 (**3ha**)	95
9[a]	**1i**: 5-OMe	Boc	**2a**: C_6H_5	93 (**3ia**)	95
10[a]	**1j**: 5-OCF_3	Boc	**2a**: C_6H_5	90 (**3ja**)	91
11[a]	**1k**: 6-F	Boc	**2a**: C_6H_5	78 (**3ka**)	95
12[a]	**1l**: 6-Cl	Boc	**2a**: C_6H_5	88 (**3la**)	93(*S*)
13[a]	**1m**: 6-Br	Boc	**2a**: C_6H_5	87 (**3ma**)	93
14[a]	**1n**: 7-F	Boc	**2a**: C_6H_5	91 (**3na**)	95
15[a]	**1o**: 7-Cl	Boc	**2a**: C_6H_5	88 (**3oa**)	95
16[a]	**1p**: 7-Br	Boc	**2a**: C_6H_5	89 (**3pa**)	95
17[a]	**1q**: 7-I	Boc	**2a**: C_6H_5	86 (**3qa**)	95
18[a]	**1r**: 7-CF_3	Boc	**2a**: C_6H_5	95 (**3ra**)	95
19[a]	**1s**: 7-OCF_3	Boc	**2a**: C_6H_5	90 (**3sa**)	95
20[b]	**1t**: 7-Me	Boc	**2a**: C_6H_5	76 (**3ta**)	93q
21[a]	**1n**: 7-F	Boc	**2b**: 3-FC_6H_4	88 (**3nb**)	96
22[a]	**1n**: 7-F	Boc	**2c**: 4-FC_6H_4	80 (**3nc**)	95
23[a]	**1n**: 7-F	Boc	**2d**: 3-ClC_6H_4	90 (**3nd**)	95
24[a]	**1n**: 7-F	Boc	**2e**: 3-MeC_6H_4	73 (**3ne**)	94
25[a]	**1n**: 7-F	Boc	**2f**: 4-MeC_6H_4	88 (**3nf**)	93
26[b]	**1n**: 7-F	Boc	**2g**: 3-$MeOC_6H_4$	74 (**3ng**)	94
27[b]	**1n**: 7-F	Boc	**2h**: 4-$MeOC_6H_4$	69 (**3nh**)	94

28[b]	**1n**: 7-F	Boc	**2i**: 	69 (**3ni**)	94
29[b]	**1n**: 7-F	Boc	**2j**: 	60 (**3nj**)	86
30[b]	**1n**: 7-F	Boc	**2k**: CH_2OCOPh	50 (**3nk**)	95
31[b]	**1n**: 7-F	Boc	**2l**: CH_2OtBu	77 (**3nl**)	95
32[b]	**1n**: 7-F	Boc	**2m**: CH_2NHBoc	92 (**3nm**)	89
33[c]	**1n**: 7-F	Boc	**2n**: TMS	62 (**3nn**)	91

[a] Unless otherwise noted, all reactions were carried out with **L5** (5 mol%), CuI (5 mol%), **1** (0.10 mmol), **2** (0.11 mmol) and 4 Å MS (40 mg) in toluene (0.5 mL) at 50 °C for 4 days. [b] **L5**/CuI (1/1, 10 mol%) at 50 °C for 4 days. [c] **L5**/CuI (1/1, 20 mol%) at 70 °C for 4 days. [d] Isolated yield. [e] Determined by chiral HPLC.

(E) Scaled-Up version of the reaction

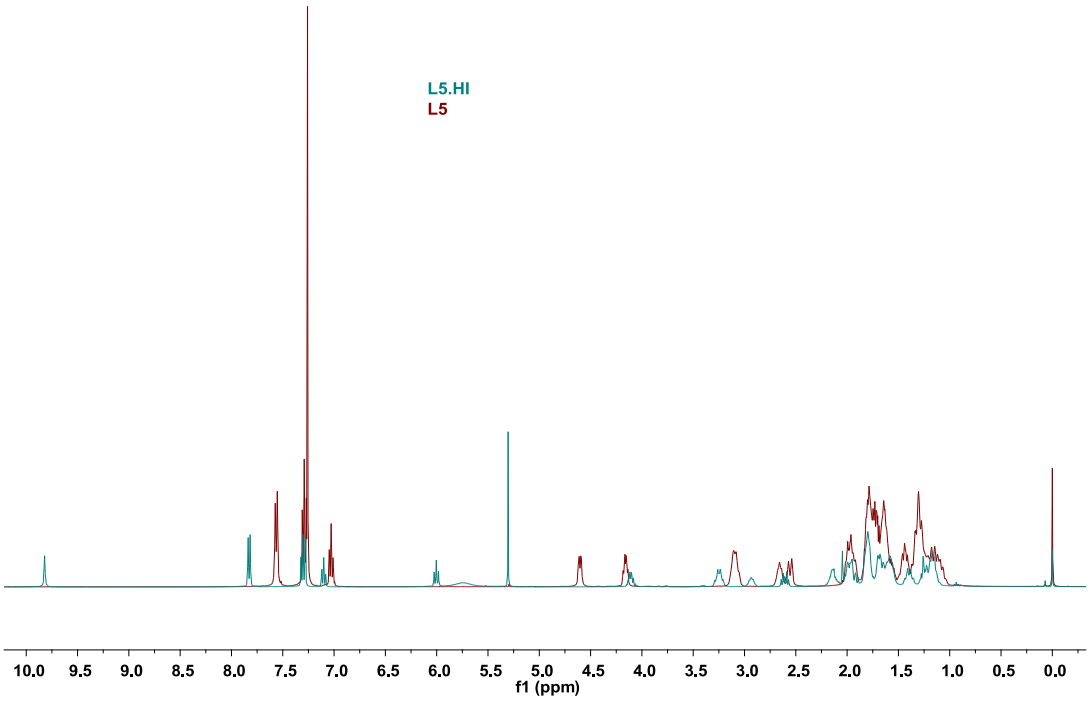


5.0 mmol, 1.77 g 5.5 mmol, 0.6 mL 2.06 g
90% yield, 95% ee

A mixture of CuI (0.25 mmol, 5 mol%), guanidine **L5** (0.25 mmol, 5 mol%), 4 Å MS (2.0 g) and **1n** (5 mmol) was weighted into a test tube. After removing air in vacuum and filling with N_2, 25.0 mL of toluene was added and the mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (5.5 mmol). The mixture was stirred for 4 days at 50 ℃. Then the mixture was filtration through Celite to remove the 4 Å MS and evaporated in vacuum, finally purified through flash chromatograph on silica gel to get **3na**.

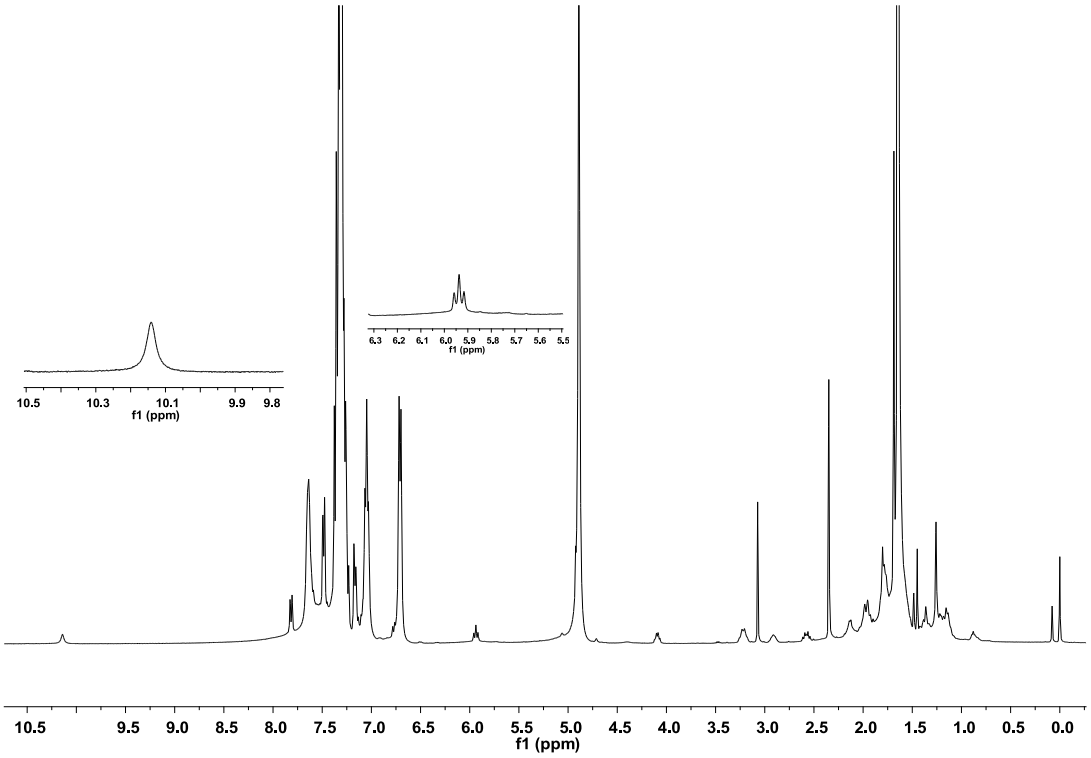
(F) NMR study

1, **L5**·HI/**L5**



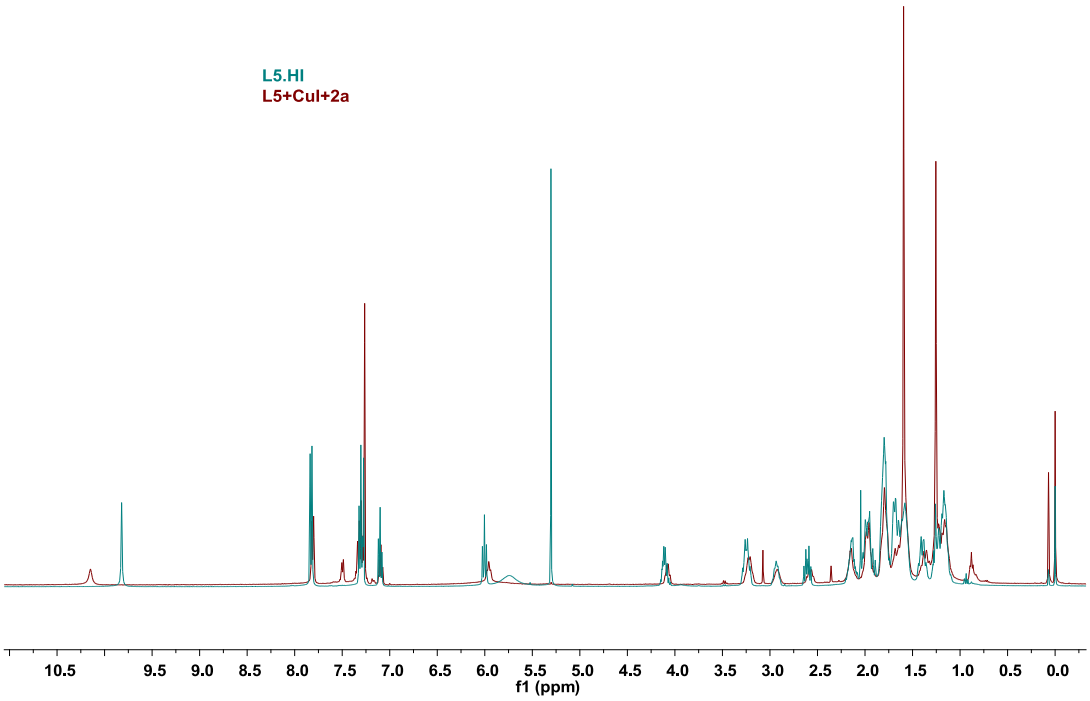
2, **L5** : CuI : **1a** : **2a** = 0.01 mmol : 0.01 mmol : 0.1 mmol : 0.1 mmol

A mixture of CuI (0.01 mmol, 10 mol%), guanidine **L5** (0.01 mmol, 10 mol%), and **1a** (0.1 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.1 mmol). The resulting mixture was stirred for 1 hour at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, $CDCl_3$ was added for ^1H NMR analysis.



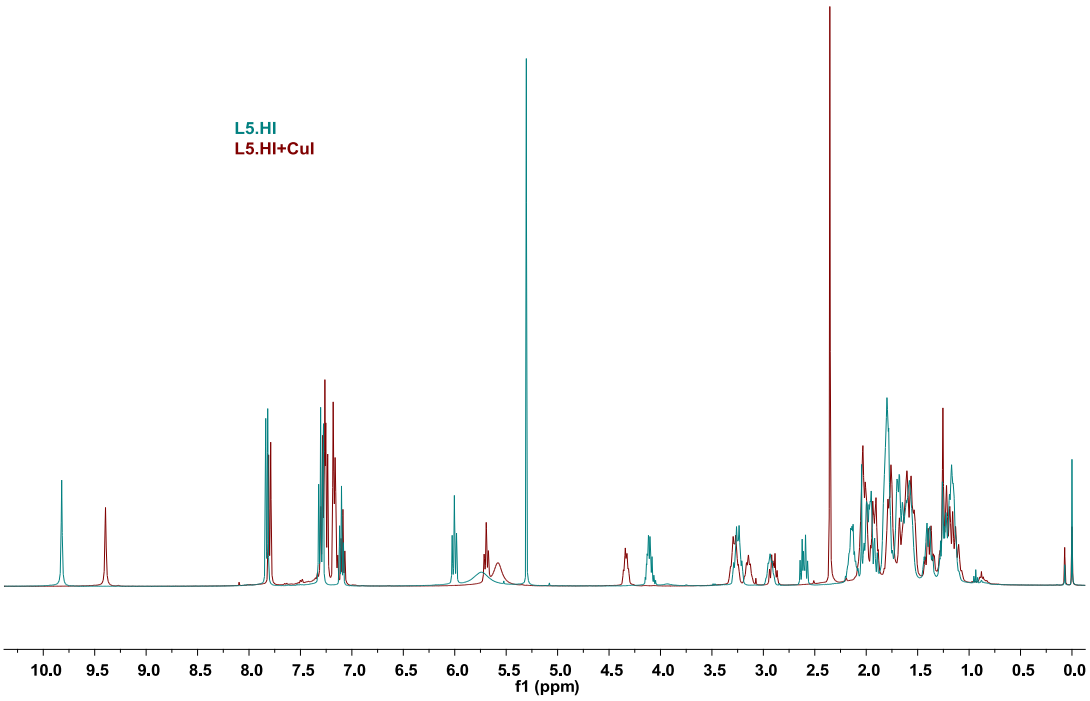
3, **L5** : CuI : **2a** = 1 : 1 : 1

A mixture of CuI (0.1 mmol) and guanidine **L5** (0.1 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.1 mmol). The resulting mixture was stirred for 1 hour at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, $CDCl_3$ was added for ^1H NMR analysis.



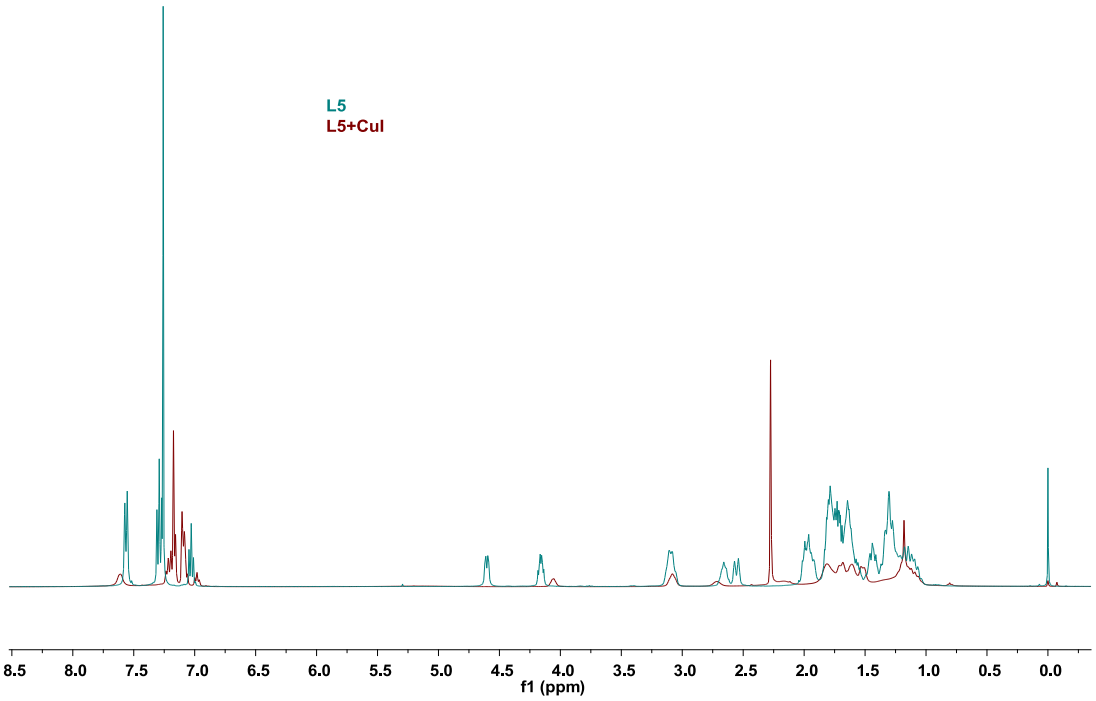
4, **L5**·HI : CuI = 1:1

A mixture of CuI (0.1 mmol) and guanidium salt **L5**·HI (0.1 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, $CDCl_3$ was added for ^1H NMR analysis.

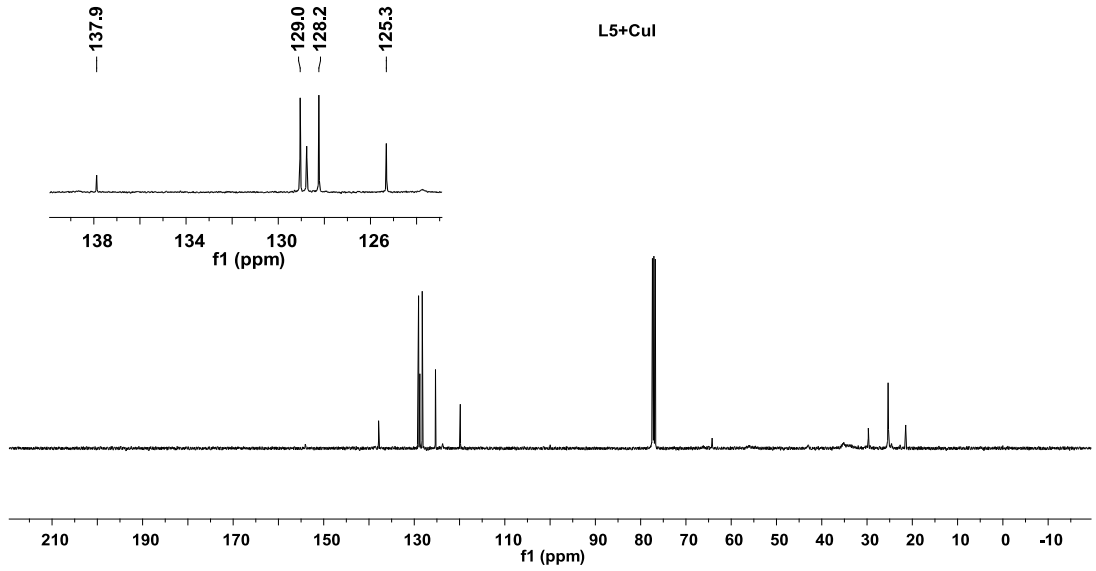


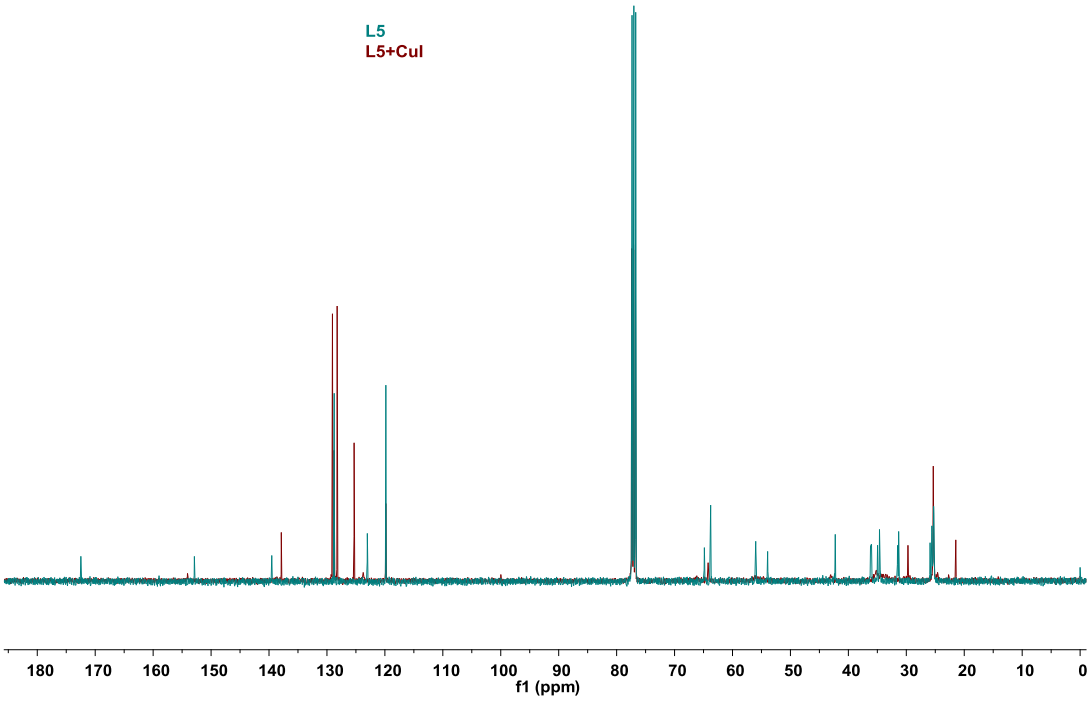
5, **L5** : CuI = 1:1

A mixture of CuI (0.1 mmol) and guanidine **L5** (0.1 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, $CDCl_3$ was added for ^1H NMR analysis.



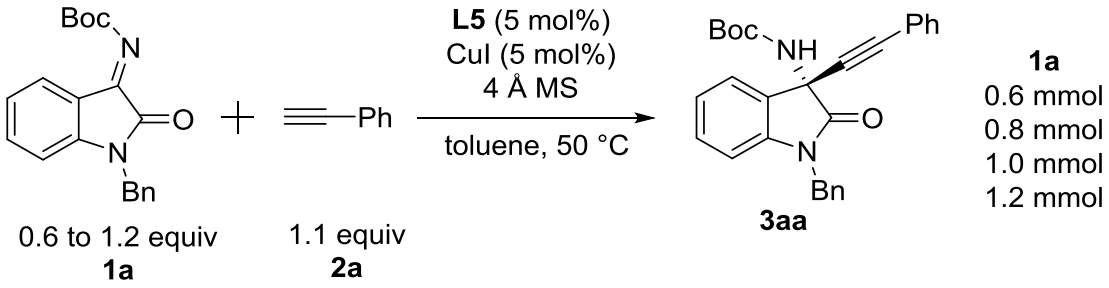
^{13}C NMR: 137.9, 129.0, 128.2, 125.3, 26.2 for toluene



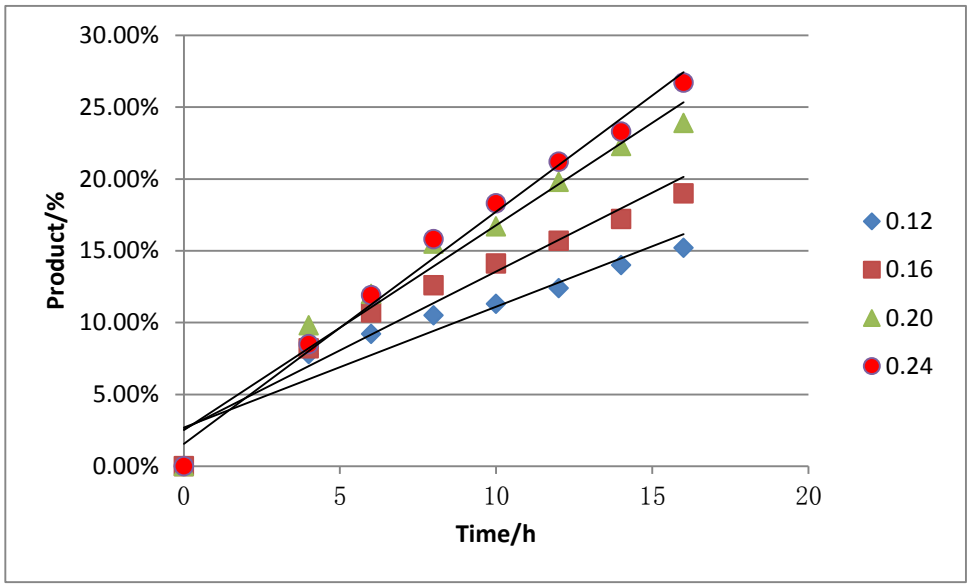


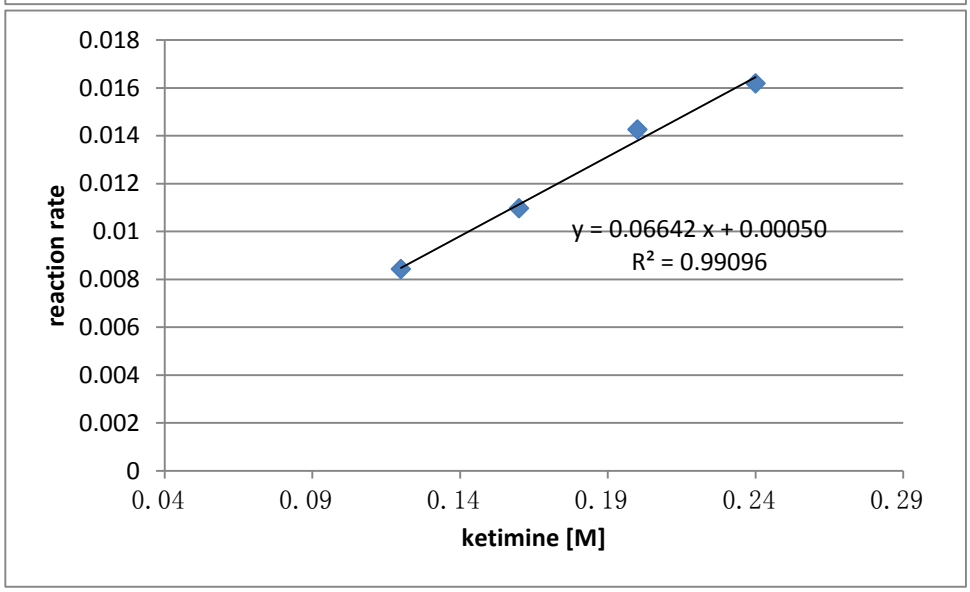
(G) Kinetic Studies

1, Dependence of the reaction rate on the concentration of **1a**



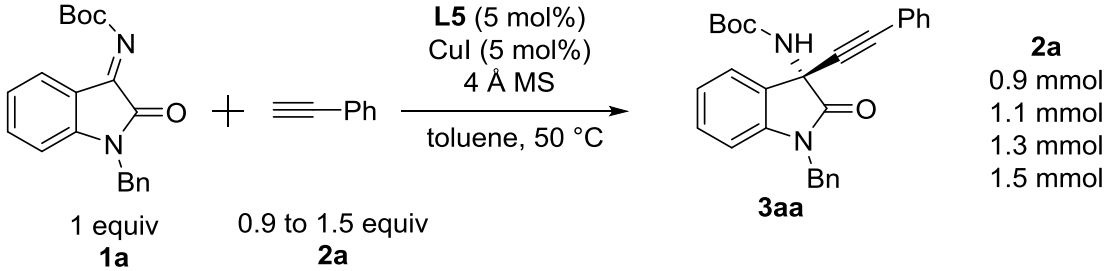
A mixture of CuI (5 mol%), guanidine **L5** (5 mol%), 4 Å MS (40 mg) and **1a** (x mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.11 mmol). The resulting mixture was stirred for the indicated time at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, the product yield of **3aa** was confirmed by ^{1}H NMR using dimethyl terephthalate as an internal standard. Kinetic profiles of different initial concentration of **1a** (from 0.6 equiv to 1.2 equiv). The plot of k_{obs} *vs* **1a** displayed a liner relationship in **1a**, which indicates a first-order kinetic dependence on **1a**.





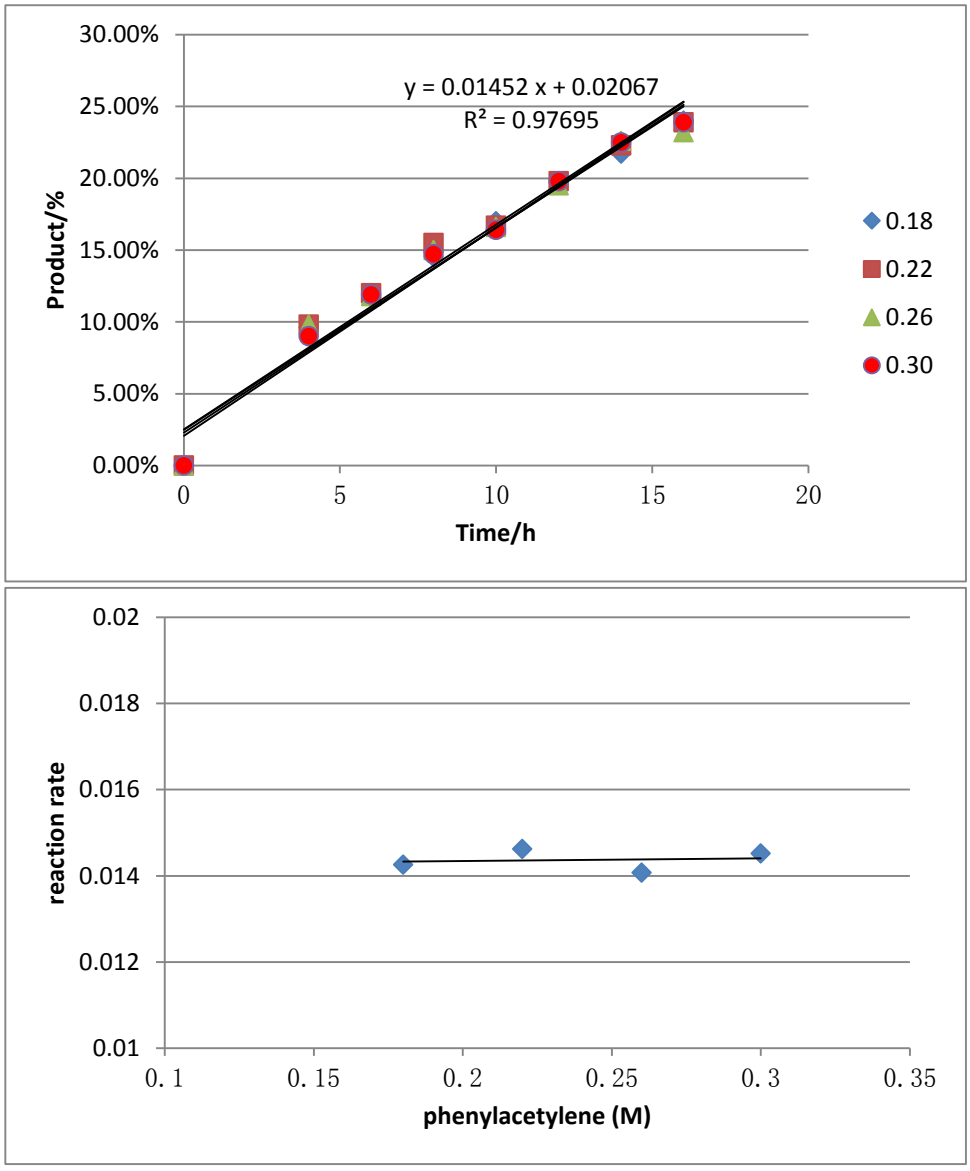
1a (M)	reaction rate
0.12	0.00842
0.16	0.01097
0.20	0.01426
0.24	0.01618

2, Dependence of the reaction rate on the concentration of **2a**



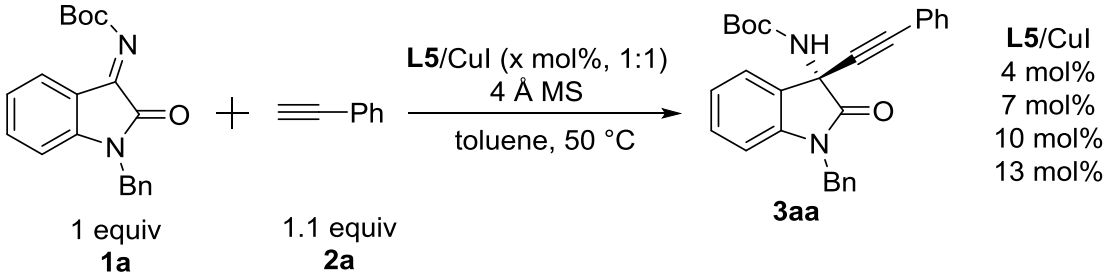
A mixture of CuI (5 mol%), guanidine **L5** (5 mol%), 4 Å MS (40 mg) and **1a** (0.10 mmol) was

weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (x mmol). The resulting mixture was stirred for the indicated time at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, the product yield of **3aa** was confirmed by ^{1}H NMR using dimethyl terephthalate as an internal standard. Kinetic profiles of different initial concentration of **2a** (from 0.9 equiv to 1.5 equiv). The plot of k_{obs} *vs* **2a** displayed a liner relationship in **2a**, which indicates a zero-order kinetic dependence on **1a**.

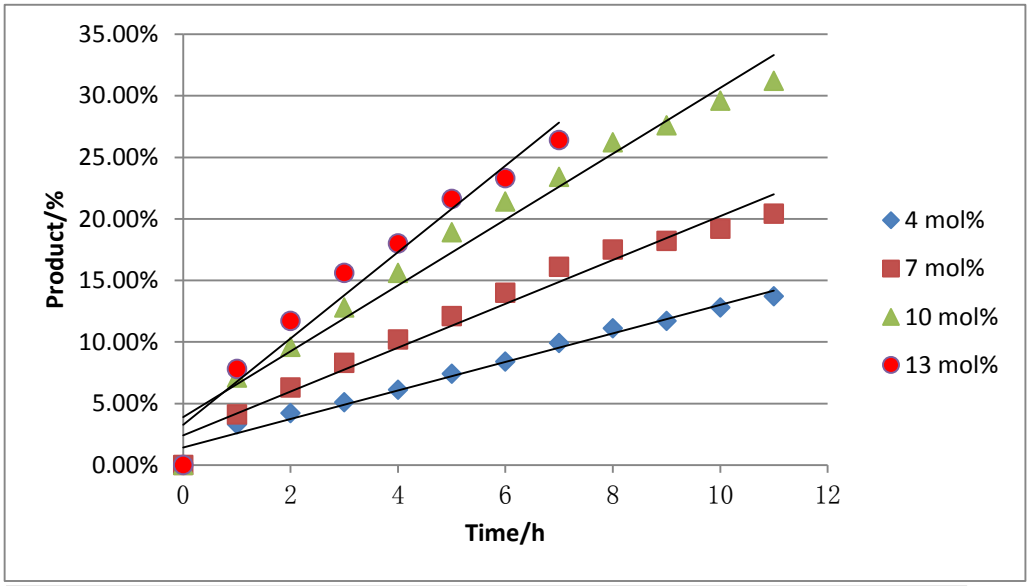


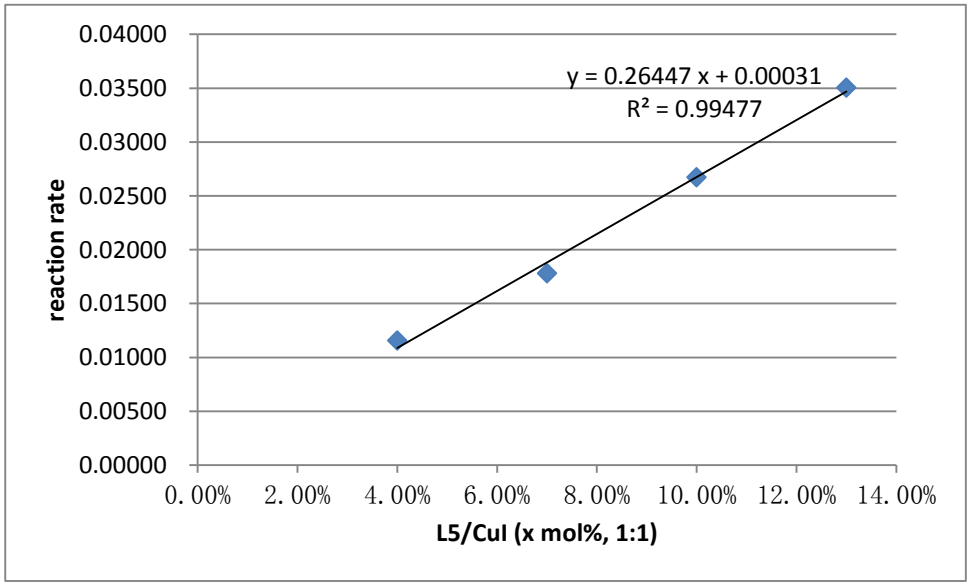
2a (M)	reaction rate
0.18	0.01426
0.22	0.01462
0.26	0.01407
0.30	0.01452

3, Dependence of the reaction rate on the concentration of **L5**/CuI



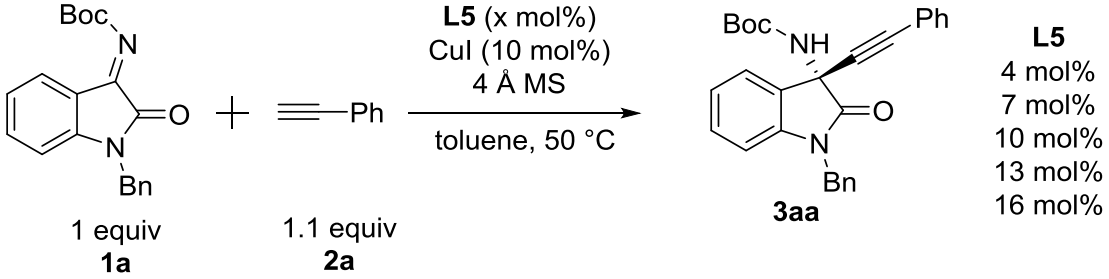
A mixture of guanidine **L5**/CuI (x mol%, 1:1), 4 Å MS (40 mg) and **1a** (0.10 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.11 mmol). The resulting mixture was stirred for the indicated time at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, the product yield of **3aa** was confirmed by ^{1}H NMR using dimethyl terephthalate as an internal standard. Kinetic profiles of different initial concentration of **L5**/CuI (from 4 mol% to 13 mol%). The plot of k_{obs} *vs* **L5**/CuI displayed a liner relationship in **L5**/CuI, which indicates a first-order kinetic dependence on **L5**/CuI.



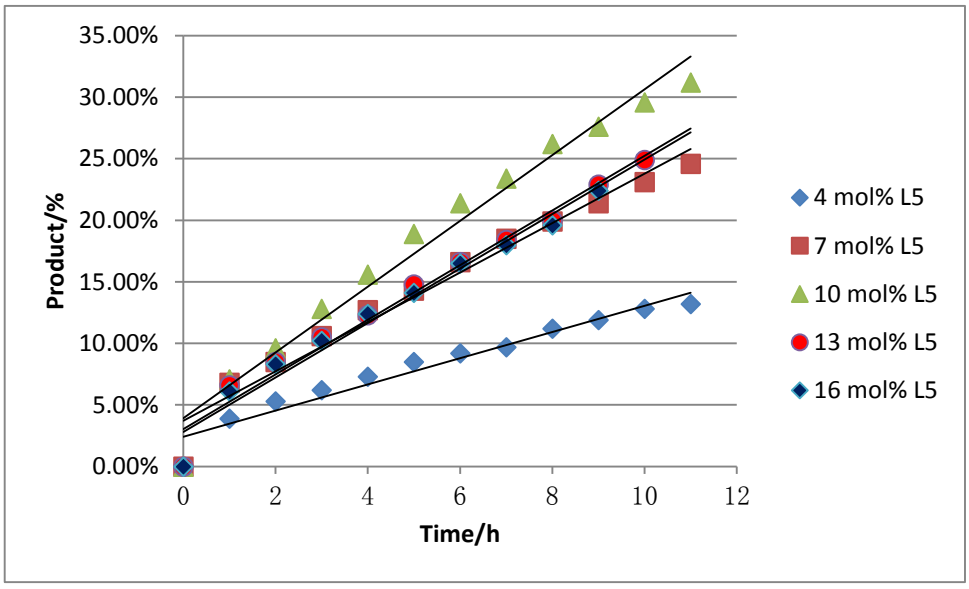


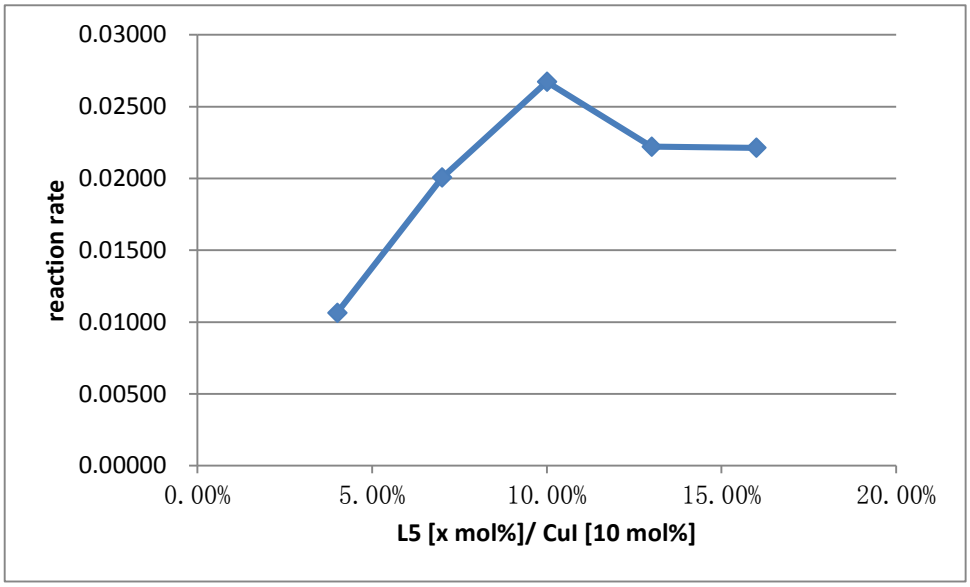
L5/CuI [x mol%, 1:1]	reaction rate
4 mol%	0.01158
7 mol %	0.01780
10 mol%	0.02673
13 mol%	0.03505

4, Dependence of the reaction rate on the concentration of **L5**



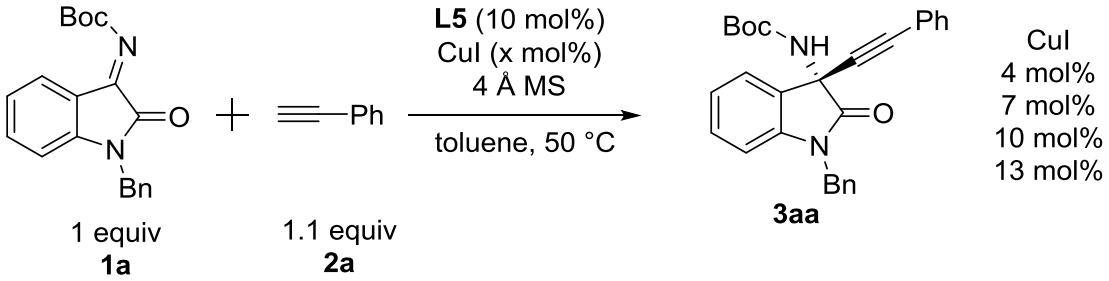
A mixture of CuI (10 mol%), guanidine **L5** (x mol%), 4 Å MS (40 mg) and **1a** (0.10 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.11 mmol). The resulting mixture was stirred for the indicated time at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, the product yield of **3aa** was confirmed by ^{1}H NMR using dimethyl terephthalate as an internal standard. Kinetic profiles of different initial concentration of **L5** (from 4 mol% to 16 mol%). The plot of k_{obs} *vs* **L5** displayed a nonliner relationship in **L5**, which indicates a fractional-order kinetic dependence on **L5**.



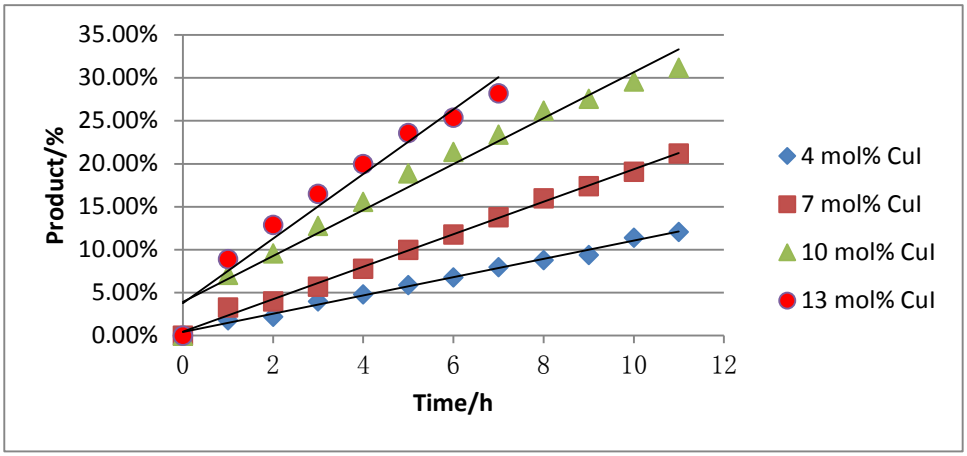


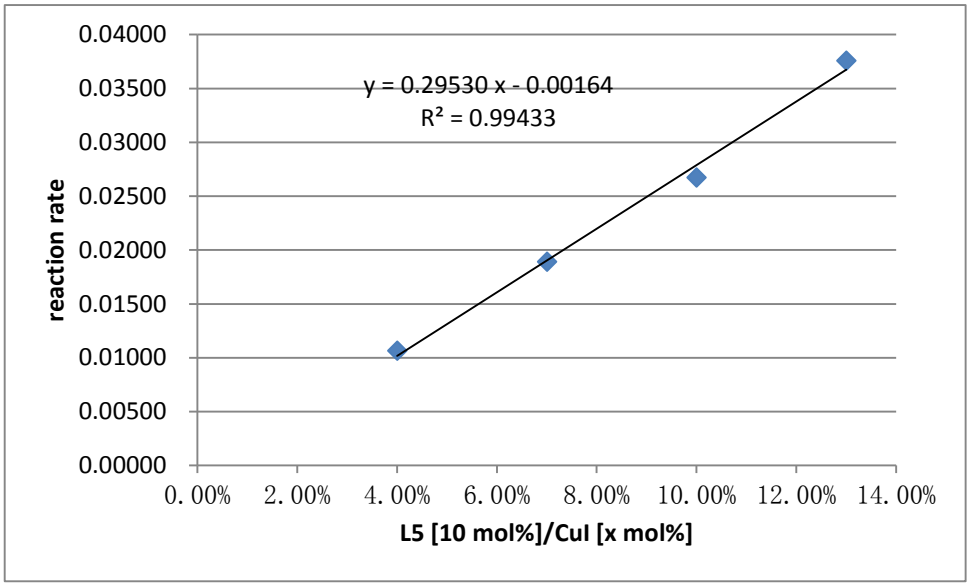
L5 [x mol%]	reaction rate
4 mol%	0.01064
7 mol %	0.02006
10 mol%	0.02673
13 mol%	0.02221
16 mol%	0.02213

5, Dependence of the reaction rate on the concentration of CuI



A mixture of CuI (x mol%), guanidine **L5** (10 mol%), 4 Å MS (40 mg) and **1a** (0.10 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.11 mmol). The resulting mixture was stirred for the indicated time at 50 ℃. Pass the reaction solution through Celite, eluting with dichloromethane. After removing dichloromethane, the product yield of **3aa** was confirmed by ^{1}H NMR using dimethyl terephthalate as an internal standard. Kinetic profiles of different initial concentration of CuI (from 4 mol% to 13 mol%). The plot of k_{obs} *vs* CuI displayed a liner relationship in CuI, which indicates a first-order kinetic dependence on CuI.

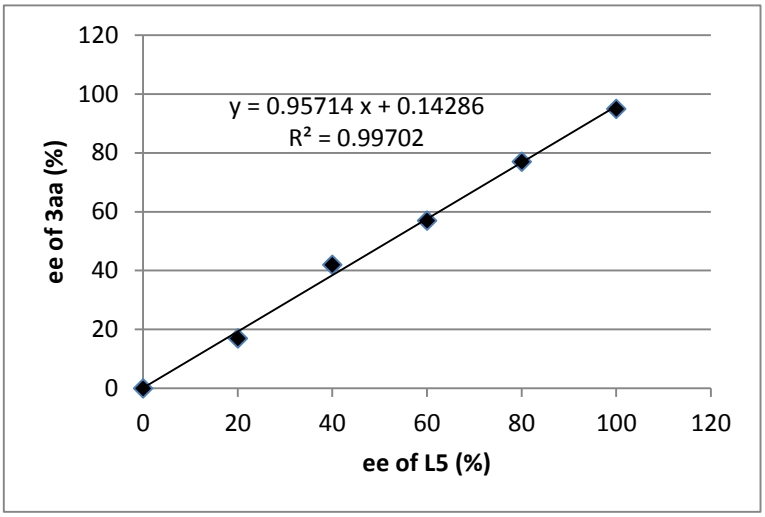




CuI [x mol%]	reaction rate
4 mol%	0.01064
7 mol %	0.01890
10 mol%	0.02673
13 mol%	0.03756

(H) Nonlinear effect experiment

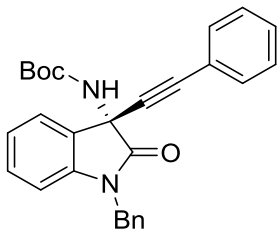
A mixture of guanidine **L5**/CuI (10 mol%, 1:1), 4 Å MS (40 mg) and **1a** (0.10 mmol) was weighted into a dry test tube. After removing air in vacuum and filling with N_2, 0.5 mL of toluene was added. The mixture was stirred at 50 ℃ for 30 min, followed by the additions of alkyne **2a** (0.11 mmol). The resulting mixture was stirred for 3 days at 50 ℃ and the product **3aa** was purified by flash chromatography.



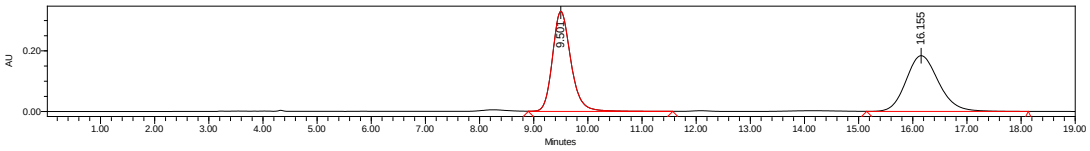
entry	ee of **L5** [%]	ee of **3aa** [%]
1	0	0
2	20	17
3	40	42
4	60	57
5	80	77
6	100	95

(I) Spectral characterization data and HPLC conditions for products

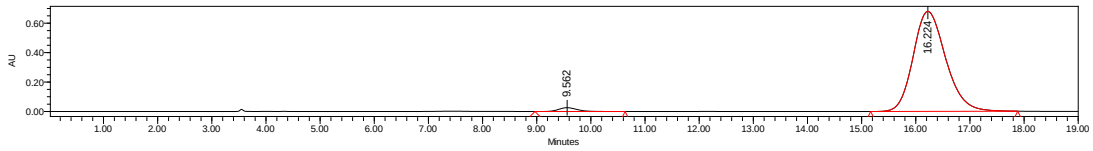
***tert*-butyl (S)-(1-benzyl-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3aa)**



White solid; m.p. 108-110 ℃; 83% yield, 95% *ee*. $[\alpha]_D^{25}$ = +29.9 (c = 1.800 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.6 min (minor), 16.2 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.13 (m, 12H), 7.06 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 5.77 (s, 1H), 5.28 - 4.62 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.2, 142.1, 135.5, 132.1, 129.4, 129.1, 128.8, 128.3, 127.6, 127.2, 123.3, 123.3, 121.4, 109.7, 85.1, 83.9, 81.0, 56.8, 44.4, 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{26}N_2NaO_3^+$ ([M + Na]$^+$) = 461.1836, Found 461.1835.

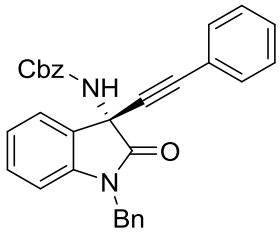


	Retention Time	Area	% Area
1	9.501	7768972	50.25
2	16.155	7691588	49.75

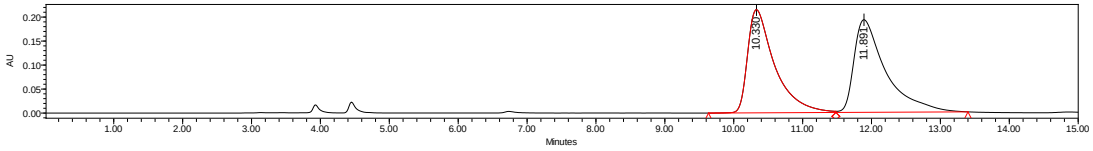


	Retention Time	Area	% Area
1	9.562	623907	2.15
2	16.224	28391952	97.85

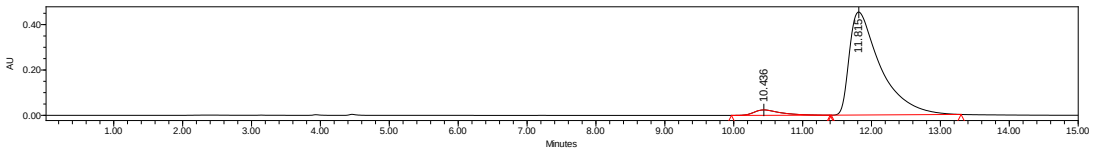
benzyl (S)-(1-benzyl-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ba)



White solid; m.p. 62-64 ℃; 85% yield, 91% *ee*. $[\alpha]_D^{25}$ = +25.4 (c = 0.350 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.4 min (minor), 11.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.16 (m, 17H), 7.08 (dd, J = 11.0, 4.1 Hz, 1H), 6.66 (d, J = 7.1 Hz, 1H), 6.00 (s, 1H), 5.03 (d, J = 14.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 153.8, 142.3, 135.3, 132.1, 129.7, 129.2, 128.8, 128.5, 128.3, 128.3, 128.2, 127.6, 127.2, 123.5, 121.3, 109.9, 85.4, 83.4, 67.4, 56.8, 44.53. HRMS (ESI-TOF) calcd for $C_{31}H_{24}N_2NaO_3^+$ ([M+Na]$^+$) = 495.1680, Found 495.1680.

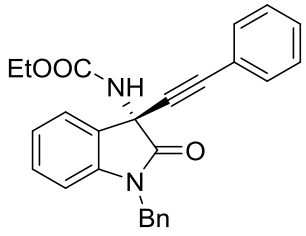


	Retention Time	Area	% Area
1	10.330	5848316	48.65
2	11.891	6172207	51.35



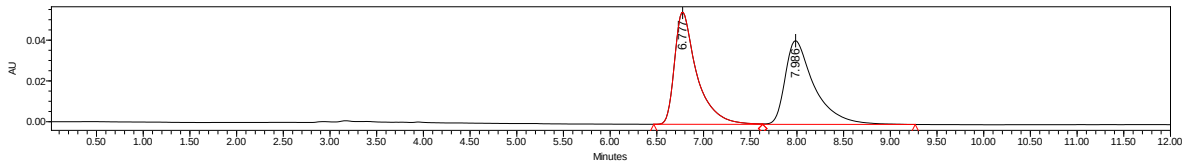
	Retention Time	Area	% Area
1	10.436	645307	4.33
2	11.815	14248359	95.67

ethyl (S)-(1-benzyl-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ca)

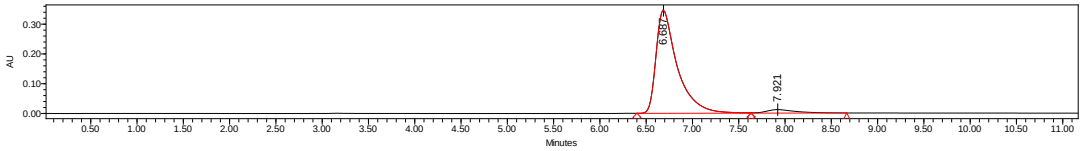


White solid; m.p. 84-96 ℃; 77% yield, 91% *ee*. $[\alpha]_D^{26}$ = +26.3 (c = 1.274 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.7 min (major), 7.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.15 (m, 13H), 7.07 (td, J = 7.6, 0.9 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 5.92 (s, 1H), 5.01 (q, J = 16.0 Hz, 2H), 4.07 (d, J = 7.1 Hz, 2H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 154.1, 142.3, 135.4, 132.1, 129.6,

129.2, 128.8, 128.3, 127.6, 127.2, 123.4, 121.3, 109.8, 85.3, 83.6, 61.6, 56.7, 44.6, 14.4. HRMS (ESI-TOF) calcd for $C_{28}H_{26}N_2NaO_3^+$ ([M+Na]$^+$) = 461.1836, Found 461.1835.

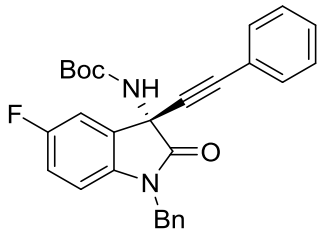


	Retention Time	Area	% Area
1	6.777	906877	50.54
2	7.986	887512	49.46

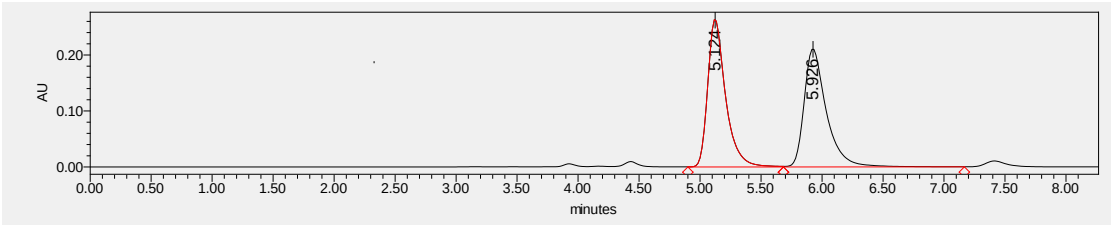


	Retention Time	Area	% Area
1	6.687	5521789	95.53
2	7.921	258655	4.47

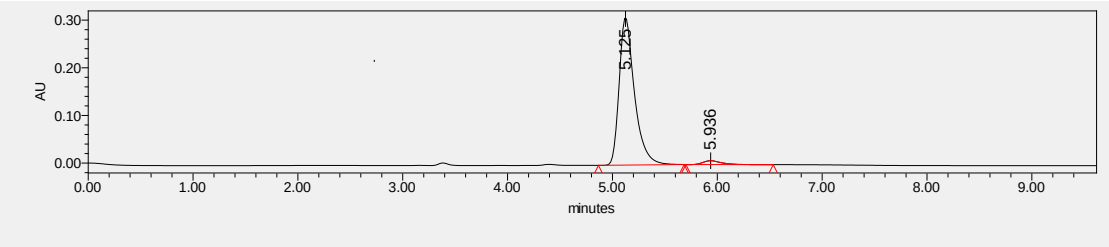
tert-butyl (S)-(1-benzyl-5-fluoro-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3da)



White solid; m.p. 66-68 ℃; 95% yield, 94% *ee*. $[\alpha]_D^{23}$ = +27.8 (c = 0.854 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.1 min (major), 5.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.34 – 7.20 (m, 7H), 6.88 (td, J = 8.9, 2.5 Hz, 1H), 6.59 (dd, J = 8.5, 4.0 Hz, 1H), 5.77 (s, 1H), 5.02 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7 , 159.6 (d, J = 242.4 Hz, 1C), 153.3, 138.0 (d, J = 2.0 Hz, 1C), 135.2, 132.1, 129.3 , 128.8, 128.3, 127.7, 127.2, 121.2, 115.7 (d, J = 23.2Hz, 1C), 111.4 (d, J = 25.2 Hz, 2C), 110.4 (d, J = 8.0 Hz, 1C), 85.6, 83.2, 81.3, 56.8, 44.6 , 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{25}FN_2NaO_3^+$ ([M+Na]$^+$) = 479.1742, Found 479.1746.

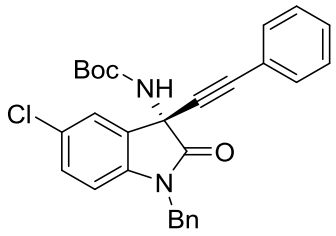


	Retention Time	Area	% Area
1	5.124	2682449	50.13
2	5.926	2668513	49.87

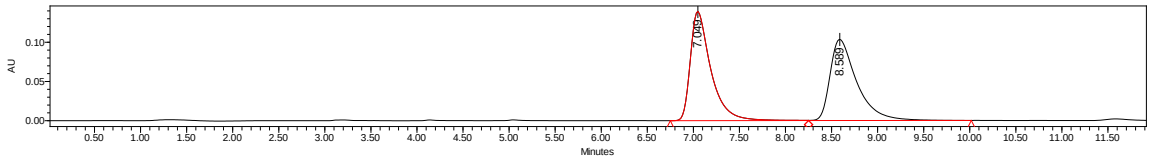


	Retention Time	Area	% Area
1	5.125	3145177	96.98
2	5.936	98023	3.02

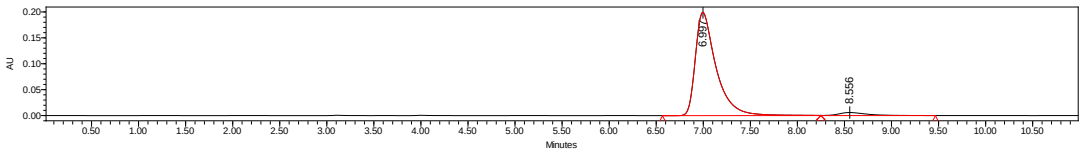
tert-butyl (S)-(1-benzyl-5-chloro-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ea)



White solid; m.p. 138-140 ℃; 91% yield, 92% *ee*. $[\alpha]_D^{22}$ = +102.5 (c = 0.866 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.0 min (major), 8.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 11H), 7.15 (dd, J = 8.3, 1.9 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.76 (s, 1H), 5.01 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 153.2, 140.7, 135.0, 132.1, 129.4, 129.3, 128.9, 128.7, 128.3, 127.8, 127.2 , 123.8, 121.1, 110.7 , 85.7, 83.0 , 81.3, 56.6, 44.6, 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{25}^{34.9689}ClN_2NaO_3^+$ ([M+Na]$^+$) = 495.1446, Found 495.1448, calcd for $C_{28}H_{25}^{36.9659}ClN_2NaO_3^+$ ([M+Na]$^+$) = 497.1417, Found 497.1427.

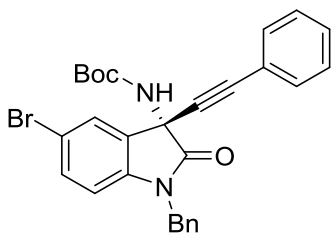


	Retention Time	Area	% Area
1	7.049	2144874	50.74
2	8.589	2082402	49.26



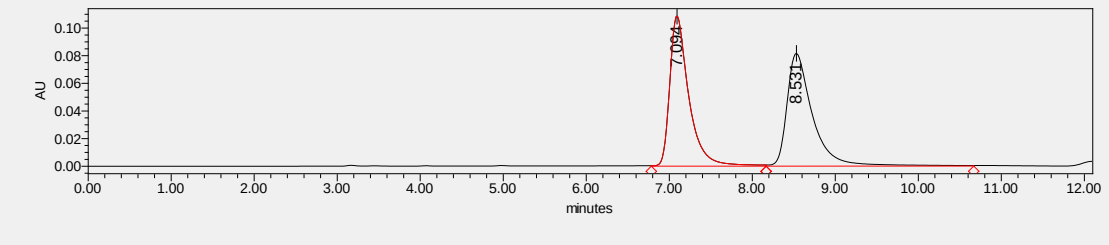
	Retention Time	Area	% Area
1	6.997	3045909	96.08
2	8.556	124131	3.92

tert-butyl (S)-(1-benzyl-5-bromo-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3fa)

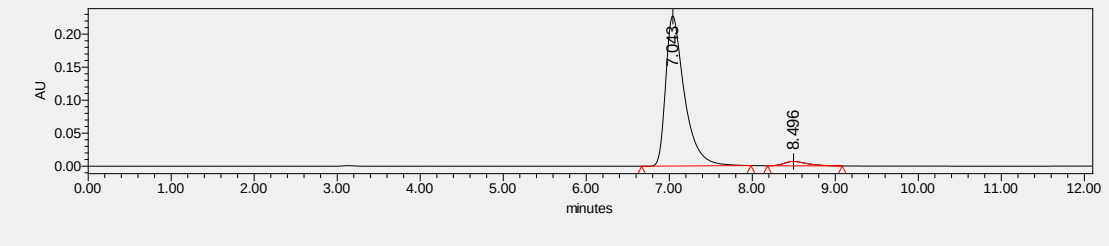


White solid; m.p. 58-60 ℃; 95% yield, 93% *ee*. $[\alpha]_D^{23}$ = +106.1 (c = 0.984in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.0 min (major), 8.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.44 – 7.26 (m, 11H),

6.55 (d, J = 8.4 Hz, 1H), 5.76 (s, 1H), 5.00 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 153.2, 141.2, 135.0, 132.2, 129.3, 128.9, 128.3, 127.8, 127.2, 126.5, 121.1, 116.0, 111.2 85.7 , 83.0 , 81.4 , 56. 6, 44.5, 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{25}{}^{78.9183}BrN_2NaO_3^+$ ($[M+Na]^+$) = 539.0941, Found 539.0941, calcd for $C_{28}H_{25}{}^{80.9163}BrN_2NaO_3^+$ ($[M+Na]^+$) = 541.0921, Found 541.0914.

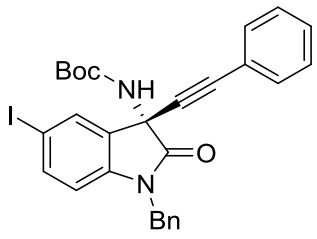


	Retention Time	Area	% Area
1	7.094	1733963	49.76
2	8.531	1750492	50.24

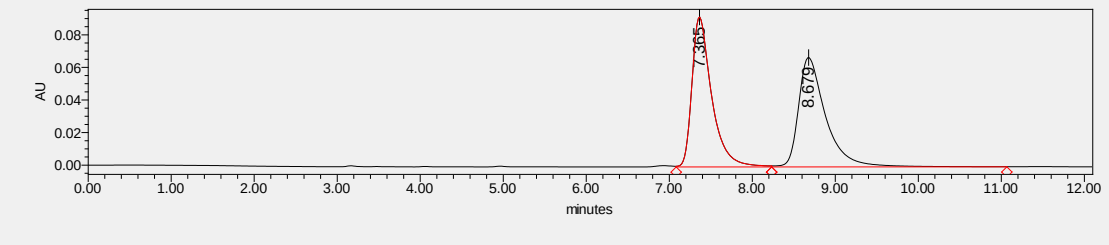


	Retention Time	Area	% Area
1	7.043	3563016	96.53
2	8.496	128023	3.47

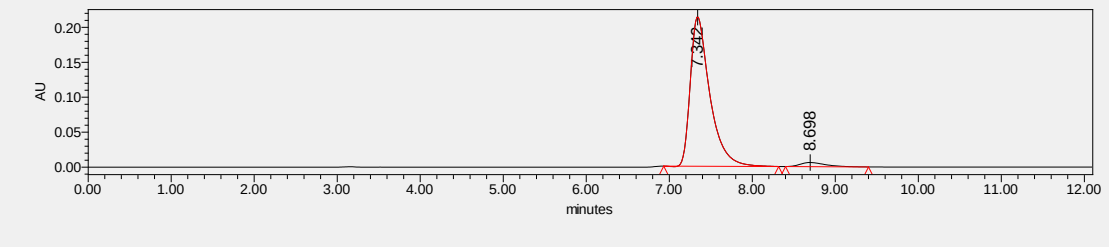
tert-butyl (S)-(1-benzyl-5-iodo-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ga)



White solid; m.p. 124-126 ℃; 94% yield, 93% *ee*. $[\alpha]_D^{23}$ = +106.1 (c = 0.984 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.3 min (major), 8.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 1.6 Hz, 1H), 7.51 – 7.26 (m, 12H), 6.45 (d, J = 8.0 Hz, 1H), 5.75 (s, 1H), 4.99 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 153.2, 141.9, 138.2, 135.0, 132.1, 132.0 , 129.3, 128.9, 128.3, 127.8, 127.2, 121.1, 111.8, 85.7, 83.1, 81.4, 56.4, 44.5 , 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{25}IN_2NaO_3^+$ ($[M+Na]^+$) = 587.0803, Found 587.0804.

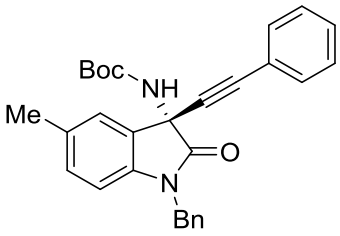


	Retention Time	Area	% Area
1	7.365	1518400	49.87
2	8.679	1526463	50.13

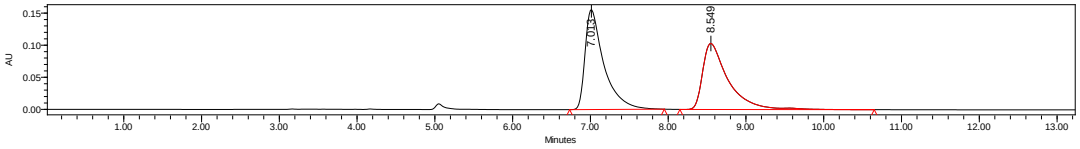


	Retention Time	Area	% Area
1	7.342	3497876	96.57
2	8.698	124212	3.43

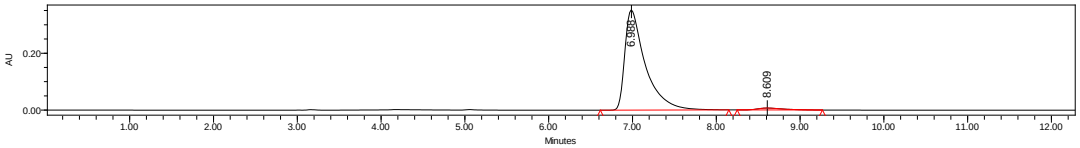
tert-butyl (S)-(1-benzyl-5-methyl-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ha)



White solid; m.p. 144-146 ℃; 89% yield, 95% *ee*. $[\alpha]_D^{23}$ = +73.8 (c = 0.692 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.0 min (major), 8.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.33 – 7.21 (m, 7H), 6.98 (d, J = 7.9 Hz, 1H), 6.57 (d, J = 7.9 Hz, 1H), 5.72 (s, 1H), 5.03 (s, 2H), 2.31 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.3, 139.7, 135.6, 133.0, 132.1, 129.7, 129.0, 128.8, 128.3, 127.5, 127.2, 124.1, 121.5, 109.4, 85.0, 84.1, 81.0, 56.8, 44.4, 28.2, 21.1. HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_2NaO_3^+$ ([M+Na]$^+$) = 475.1993, Found 475.2000.

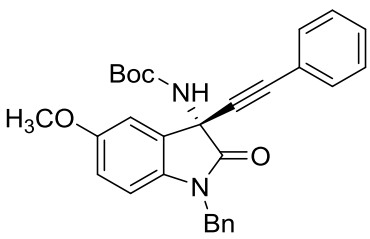


	Retention Time	Area	% Area
1	7.013	2608296	52.70
2	8.549	2341031	47.30



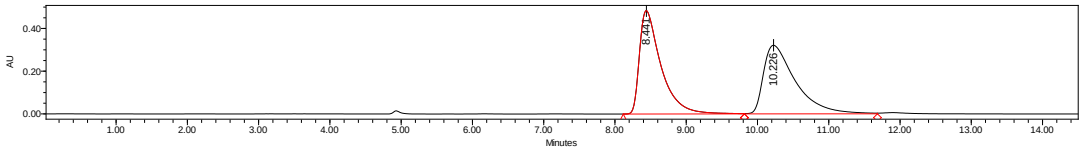
	Retention Time	Area	% Area
1	6.988	5968145	97.68
2	8.609	141669	2.32

tert-butyl (S)-(1-benzyl-5-methoxy-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ia)

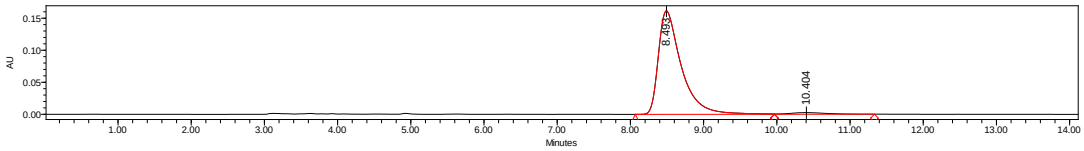


White solid; m.p. 64-66 ℃; 93% yield, 95% *ee*. $[\alpha]_D^{21}$ = +81.5 (c = 0.882 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.5 min (major), 10.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 4H), 7.35 – 7.22

(m, 6H), 7.11 (d, J = 2.5 Hz, 1H), 6.71 (dd, J = 8.5, 2.5 Hz, 1H), 6.58 (d, J = 8.5 Hz, 1H), 5.73 (s, 1H), 5.03 (s, 2H), 3.76 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 156.5, 153.3, 135.5, 135.4, 132.1, 129.1, 128.8, 128.3, 127.6, 127.2, 121.4, 113.9, 110.2, 85.2, 83.9, 81.0, 57.0, 55.8, 44.5, 28.2. HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_2NaO_4^+$ ([M+Na]$^+$) = 491.1942, Found 491.1941.

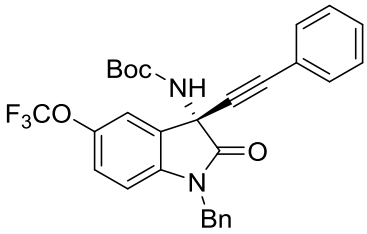


	Retention Time	Area	% Area
1	8.441	10137857	50.27
2	10.226	10028655	49.73

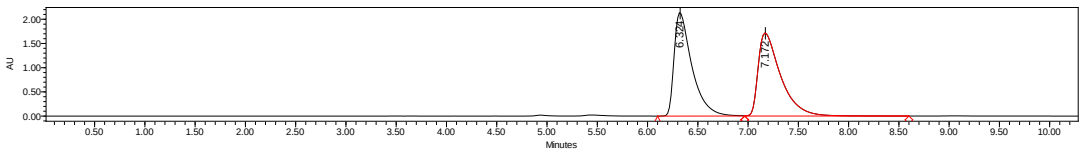


	Retention Time	Area	% Area
1	8.493	3514694	97.43
2	10.404	92622	2.57

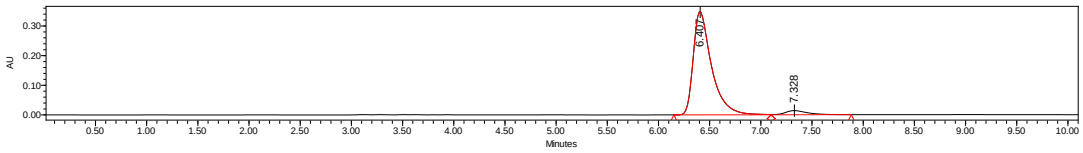
tert-butyl (S)-(1-benzyl-2-oxo-3-(phenylethynyl)-5-(trifluoromethoxy)indolin-3-yl)carbamate (3ja)



White solid; m.p. 74-76 ℃; 90% yield, 91% *ee*. $[\alpha]_D^{21}$ = +39.8 (c = 0.944 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.4 min (major), 7.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.26 (m, , 11H), 7.06 (d, J = 8.3 Hz, 1H), 6.67 (d, J = 8.5 Hz, 1H), 5.76 (s, 1H), 5.09 - 4.93 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 153.2, 145.3 (m, 1C), 140.8, 135.0, 132.1 , 129.3, 128.9, 128.3, 127.8, 127.2, 122.4, 121.1, 117.2 , 110.2, 85.8, 82.9, 81.4, 56.7, 44.6, 28.1. HRMS (ESI-TOF) calcd for $C_{29}H_{25}F_3N_2NaO_4^+$ ([M+Na]$^+$) = 545.1659, Found 545.1662.

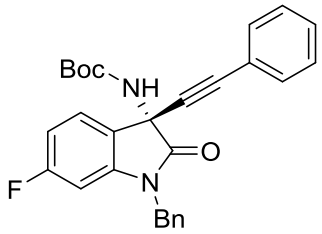


	Retention Time	Area	% Area
1	6.324	26320362	49.71
2	7.172	26630495	50.29

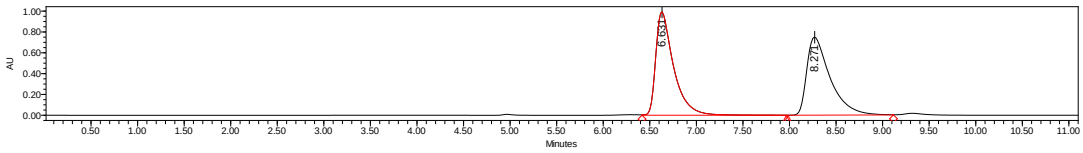


	Retention Time	Area	% Area
1	6.407	4314851	95.38
2	7.328	209157	4.62

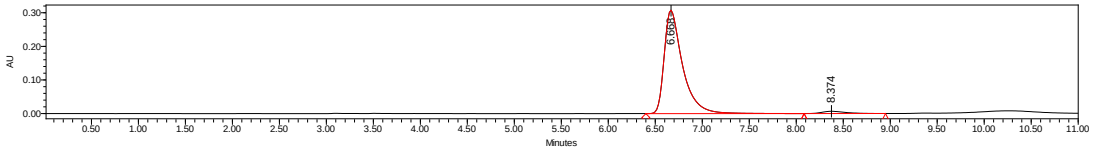
tert-butyl (S)-(1-benzyl-6-fluoro-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ka)



White solid; m.p. 140-142 ℃; 78% yield, 95% *ee*. $[\alpha]_D^{21}$ = +28.6 (c = 0.714 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.7 min (major), 8.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.38 (m, 5H), 7.36 – 7.24 (m, 6H), 6.81 – 6.68 (m, 1H), 6.42 (dd, J = 8.8, 1.5 Hz, 1H), 5.73 (s, 1H), 5.05 - 4.92 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 163.5 (d, J = 247.4 Hz, 1C), , 153.2, 143.7 (d, J = 12.1 Hz, 1C), 135.0, 132.0, 129.2, 128.9, 128.3 , 127.8, 127.2, 124.5 (d, J = 10.1 Hz, 1C), 121.3, 109.5 (d, J = 22.2 Hz, 2C),), 98.6 (d, J = 27.3 Hz, 1C), 85.3, 83.5, 81.2, 56.3, 44.6, 28.1. HRMS (ESI-TOF) calcd for $C_{29}H_{25}FN_2NaO_4^+$ ([M+Na]$^+$) = 479.1742, Found 479.1742.

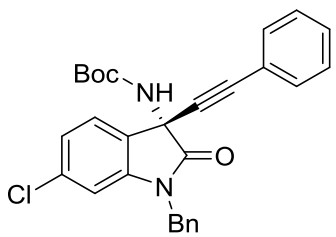


	Retention Time	Area	% Area
1	6.631	13155938	50.34
2	8.271	12977338	49.66



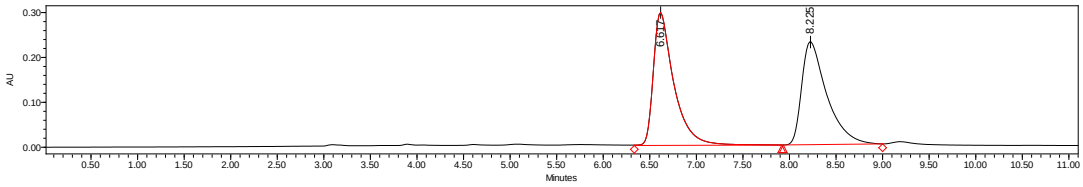
	Retention Time	Area	% Area
1	6.668	4154063	97.38
2	8.374	111909	2.62

tert-butyl (S)-(1-benzyl-6-chloro-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3la)

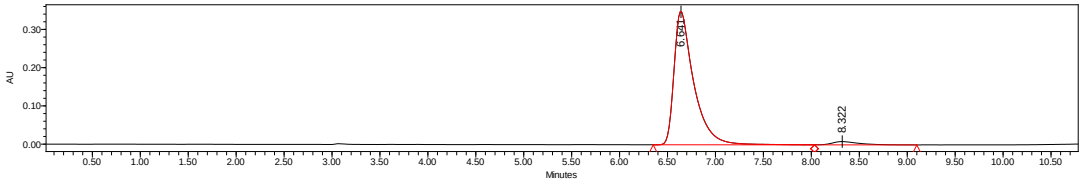


White solid; m.p. 170-172 ℃; 88% yield, 93% *ee*. $[\alpha]_D^{20}$ = +21.1 (c = 0.838 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.6 min (major), 8.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 11H), 7.05 (dd, J = 8.0, 1.7 Hz,

1H), 6.68 (d, J = 1.3 Hz, 1H), 5.74 (s, 1H), 5.20 – 4.81 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.2, 135.1, 134.9, 132.0, 129.2, 128.9, 128.3, 127.8, 127.2, 124.2, 123.3, 121.2, 110.3, 85.5, 83.2, 81.3, 56.3, 44.6, 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{25}{}^{34.9689}ClN_2NaO_3^+$ ($[M+Na]^+$) = 495.1446, Found 495.1453, calcd for $C_{28}H_{25}{}^{36.9659}ClN_2NaO_3^+$ ($[M+Na]^+$) = 497.1417, Found 495.1456.

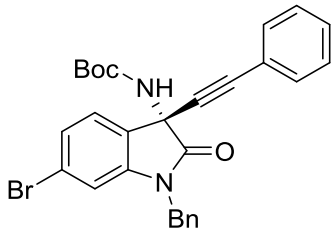


	Retention Time	Area	% Area
1	6.617	4523399	51.34
2	8.225	4287535	48.66

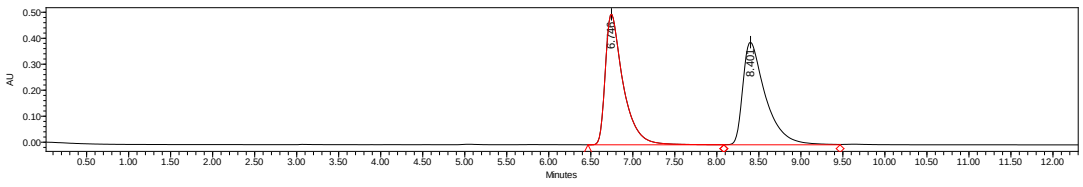


	Retention Time	Area	% Area
1	6.641	4973102	96.82
2	8.322	163148	3.18

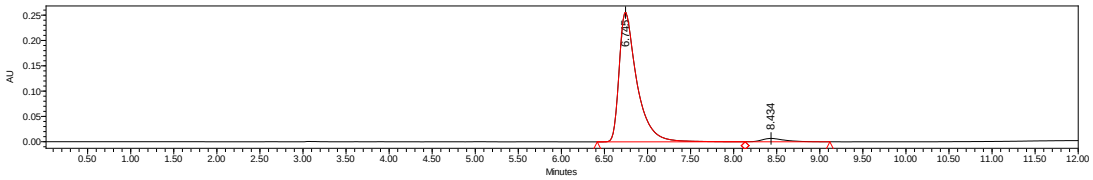
tert-butyl (S)-(1-benzyl-6-bromo-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ma)



White solid; m.p. 162-164 ℃; 87% yield, 93% *ee*. $[\alpha]_D^{20}$ = +17.6 (c = 0.900 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.7 min (major), 8.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.26 (m, 11H), 7.21 (dd, J = 7.9, 1.6 Hz, 1H), 6.83 (d, J = 1.0 Hz, 1H), 5.73 (s, 1H), 5.14 – 4.79 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 153.2, 143.4, 134.9, 132.0, 129.3, 128.9, 128.3, 127.8, 127.2, 126.3, 124.5, 123.0, 121.2, 113.0, 85.5, 83.1, 81.3, 56.4, 44.5, 28.2. HRMS (ESI-TOF) calcd for $C_{28}H_{25}{}^{78.9183}BrN_2NaO_3^+$ ($[M+Na]^+$) = 539.0941, Found 539.0943, calcd for $C_{28}H_{25}{}^{80.9163}BrN_2NaO_3^+$ ($[M+Na]^+$) = 541.0921, Found 541.0914.

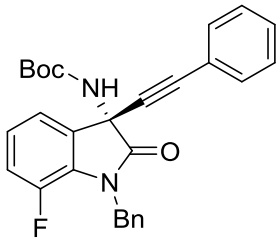


	Retention Time	Area	% Area
1	6.746	7404177	50.03
2	8.401	7395885	49.97

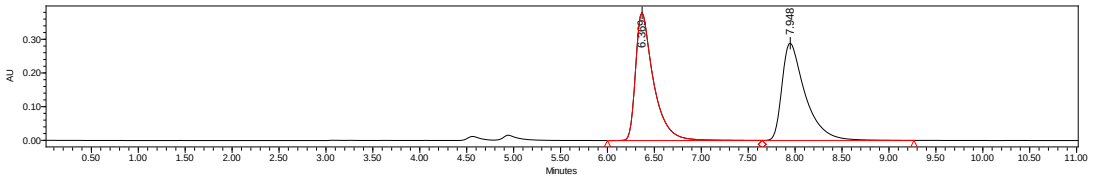


	Retention Time	Area	% Area
1	6.745	3655365	96.74
2	8.434	123124	3.26

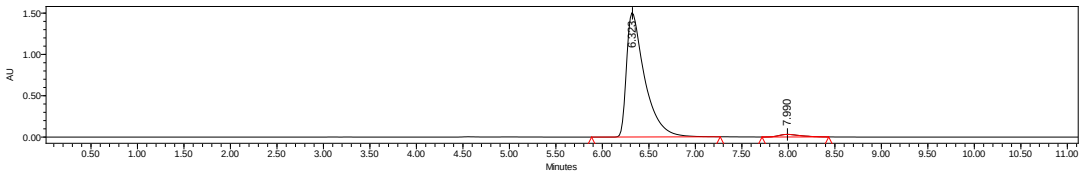
***tert*-butyl (S)-(1-benzyl-7-fluoro-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3na)**



White solid; m.p. 120-122 ℃; 91% yield, 95% *ee*. $[\alpha]_D^{24}$ = +26.8 (c = 0.834 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.3 min (major), 8.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.37 (m, 4H), 7.35 – 7.24 (m, 7H), 7.04 – 6.92 (m, 2H), 5.76 (s, 1H), 5.25 - 4.97 m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 , 153.2, 147.6 (d, J = 246.4 Hz, 1C), 136.8, 132.0, 129.3, 128.8 (d, J = 9.1 Hz, 1C), 128.5, 128.3, 127.5, 127.4, 124.0 (d, J = 6.1 Hz, 1C), 121.2, 119.0 (d, J = 3.0 Hz, 1C), 117.6 (d, J = 19.1 Hz, 2C), 85.6, 83.2, 81.3, 56.8, 46.1, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{25}FN_2NaO_3^+$ ([M+Na]$^+$) = 479.1742, Found 479.1749.

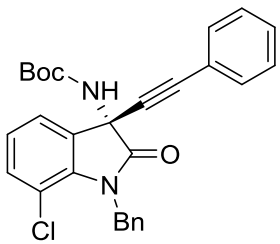


	Retention Time	Area	% Area
1	6.369	5010445	50.27
2	7.948	4957241	49.73



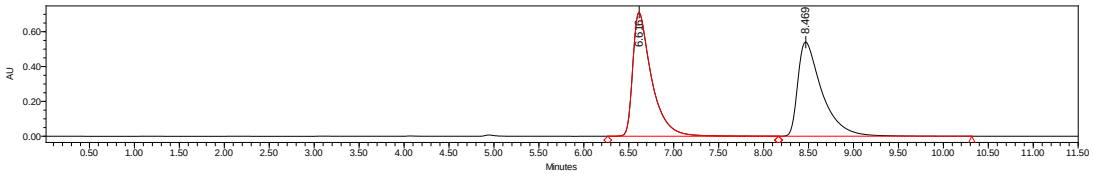
	Retention Time	Area	% Area
1	6.323	20350295	97.63
2	7.990	494168	2.37

***tert*-butyl (S)-(1-benzyl-7-chloro-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3oa)**

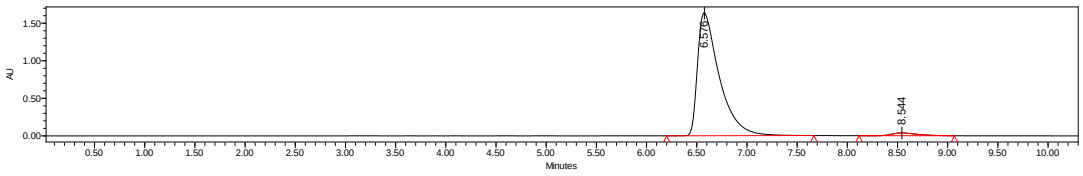


White solid; m.p. 168-170 ℃; 88% yield, 95% *ee*. $[\alpha]_D^{25}$ = –32.3 (c = 0.910 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.6 min (major), 8.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.14 (m, 12H), 7.01 (t, J = 7.8 Hz, 1H), 5.78 (s, 1H),

5.42 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 153.2, 138.2, 137.4, 132.0,132.0, 129.3, 128.5, 128.6, 127.1, 126.5, 124.3, 121.8, 121.1, 115.9, 85.7, 83.3, 81.4, 56.4, 45.6, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{25}{}^{34.9689}ClN_2NaO_3^+$ ([M+Na]$^+$) = 495.1446, Found 495.1454, calcd for $C_{28}H_{25}{}^{36.9659}ClN_2NaO_3^+$ ([M+Na]$^+$) = 497.1417, Found 495.1463.

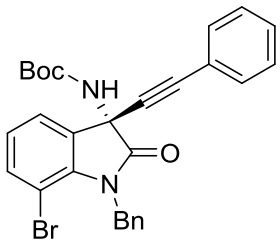


	Retention Time	Area	% Area
1	6.616	10324044	50.60
2	8.469	10081145	49.40

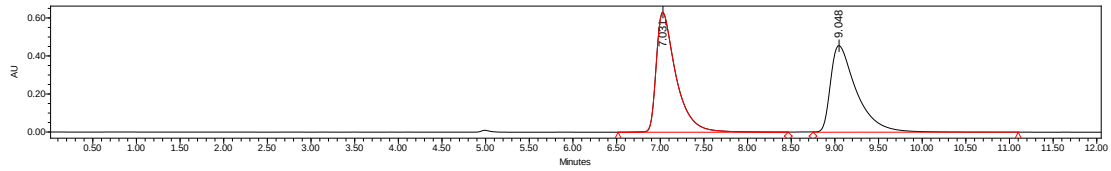


	Retention Time	Area	% Area
1	6.576	24665070	97.42
2	8.544	654062	2.58

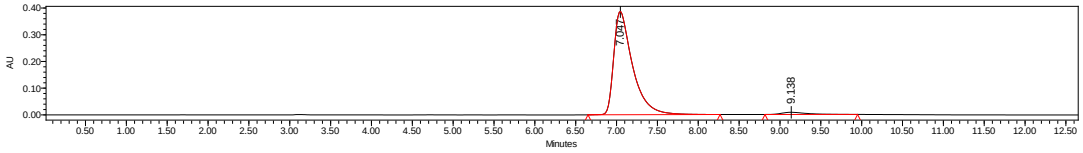
***tert*-butyl (S)-(1-benzyl-7-bromo-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3pa)**



White solid; m.p. 188-190 ℃; 89% yield, 95% *ee*. $[\alpha]_D^{24}$ = –47.6 (c = 0.930 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.0 min (major), 9.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.18 (m, 12H), 7.00 – 6.91 (m, 1H), 5.78 (s, 1H), 5.47 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 153.2, 139.68, 137.33, 135.35, 132.04, 129.31, 128.54, 128.35, 127.01, 126.4, 124.6, 122.3, 121.1, 102.9, 85.7, 83.3, 81.4, 56.4, 45.2, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{25}{}^{78.9183}BrN_2NaO_3^+$ ([M+Na]$^+$) = 539.0941, Found 539.0945, calcd for $C_{28}H_{25}{}^{80.9163}BrN_2NaO_3^+$ ([M+Na]$^+$) = 541.0921, Found 541.0935.

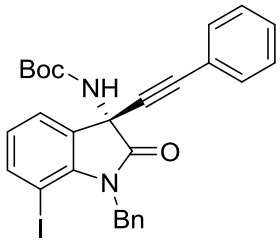


	Retention Time	Area	% Area
1	7.031	9898302	51.34
2	9.048	9381204	48.66

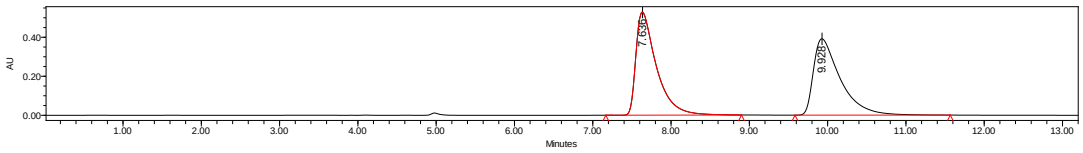


	Retention Time	Area	% Area
1	7.047	6176417	97.24
2	9.138	175287	2.76

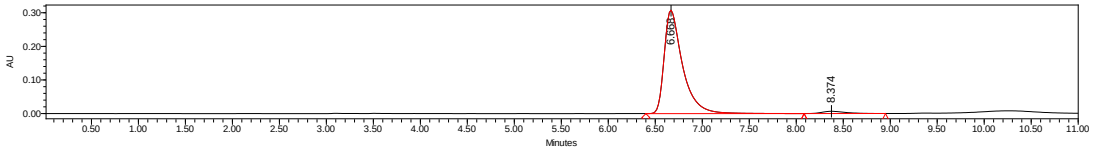
tert-butyl (S)-(1-benzyl-7-iodo-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3qa)



White solid; m.p. 180-182 ℃; 86% yield, 95% *ee*. $[\alpha]_D^{23}$ = –75.0 (c = 0.978 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.6 min (major), 10.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.1, 1.0 Hz, 1H), 7.47 (dd, J = 7.3, 1.2 Hz, 1H), 7.40 – 7.21 (m, 10H), 6.82 (t, J = 7.7 Hz, 1H), 5.77 (s, 1H), 5.50 (q, J = 17.0 Hz, 2H), 1.35 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 153.1, 142.6, 142.4, 137.1, 132.0, 129.3, 128.6, 128.4, 127.0, 126.3, 125.2, 123.1, 121.1, 85.7, 83.4, 81.3, 72.3, 56.1, 44.5, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{25}IN_2NaO_3^+$ ([M+Na]$^+$) = 587.0803, Found 587.0803.

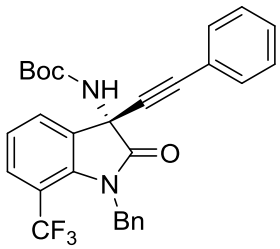


	Retention Time	Area	% Area
1	7.636	9600647	50.74
2	9.928	9319238	49.26



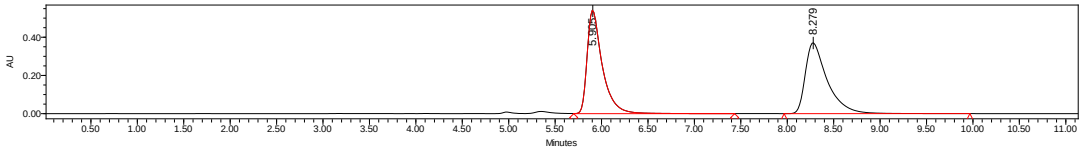
	Retention Time	Area	% Area
1	7.634	6179327	97.42
2	10.010	163661	2.58

tert-butyl (S)-(1-benzyl-2-oxo-3-(phenylethynyl)-7-(trifluoromethyl)indolin-3-yl)carbamate (3ra)

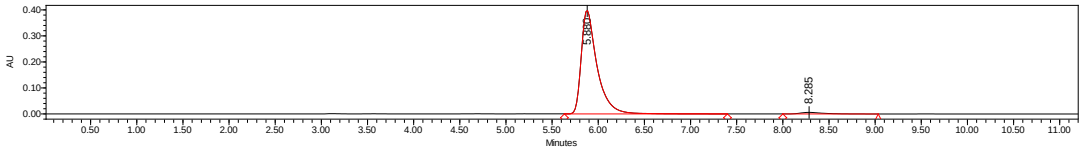


White solid; m.p. 123-125 ℃; 95% yield, 95% *ee*. $[\alpha]_D^{23}$ = –25.6 (c = 0.796 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.9 min (major), 8.3 min (minor). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.73 – 7.67 (m, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.42 – 7.16 (m, 11H), 5.79 (s, 1H), 5.51 – 4.98 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 153.1, 140.3, 136.2, 132.0, 129.4, 128.4, 128.4, 127.6, 126.9, 125.7, 124.6 , 122.9 121.9, 121.0 , 113.0, 85.8, 83.1, 81.5, 55.3, 46.2, 28.1. HRMS (ESI-TOF) calcd for $C_{29}H_{25}F_3N_2NaO_3^+$ ($[M+Na]^+$) = 529.1710, Found 529.1714.

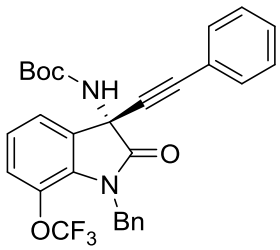


	Retention Time	Area	% Area
1	5.905	6135171	50.24
2	8.279	6076244	49.76

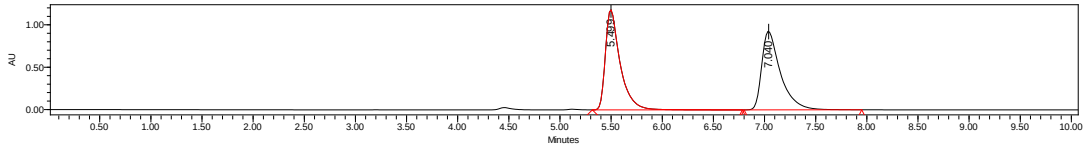


	Retention Time	Area	% Area
1	5.880	4715786	97.88
2	8.285	102284	2.12

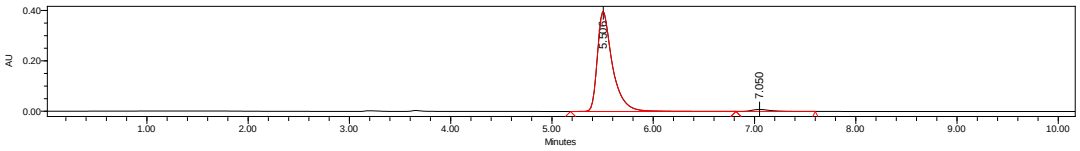
tert-butyl (S)-(1-benzyl-2-oxo-3-(phenylethynyl)-7-(trifluoromethoxy)indolin-3-yl)carbamate (3sa)



White solid; m.p. 90-92 ℃; 90% yield, 95% *ee*. $[\alpha]_D^{23}$ = +10.5 (c = 0.956 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.5 min (major), 7.0 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.05 (m, 13H), 5.77 (s, 1H), 5.19 (s, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 153.2, 136.4, 133.678 (m, 1C), 133.0, 132.1, 129.3, 128.5, 128.4, 127.3, 126.7, 123.9, 121.4, 121.1, 119.2, 85.7, 83.2, 81.4, 56.5, 45.9, 28.1. HRMS (ESI-TOF) calcd for $C_{29}H_{25}F_3N_2NaO_4^+$ ($[M+Na]^+$) = 545.1659, Found 545.1666.

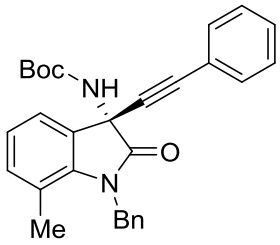


	Retention Time	Area	% Area
1	5.499	11794482	50.10
2	7.040	11749541	49.90

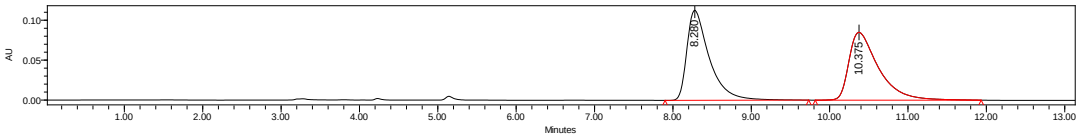


	Retention Time	Area	% Area
1	5.506	4081272	97.51
2	7.050	104005	2.49

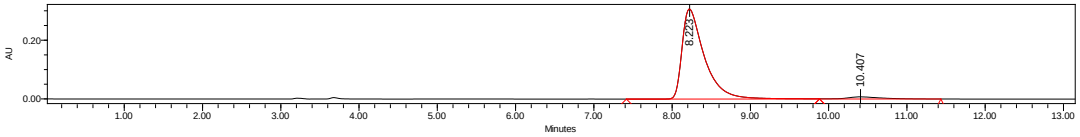
tert-butyl (S)-(1-benzyl-7-methyl-2-oxo-3-(phenylethynyl)indolin-3-yl)carbamate (3ta)



White solid; m.p. 173-175 ℃; 89% yield, 95% *ee*. $[\alpha]_D^{24}$ = –21.7 (c = 0.600 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.2 min (major), 10.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 11H), 7.04 – 6.94 (m, 2H), 5.76 (s, 1H), 5.45 - 4.99 (m, 2H), 2.25 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 153.2, 140.1, 137.5, 133.4, 132.0, 129.1, 128.9, 128.3, 127.2, 125.8, 123.4, 121.5, 121.2, 120.3, 85.1, 84.2, 81.0, 56.4, 45.8, 28.2, 18.8. HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_2NaO_3^+$ ($[M+Na]^+$) = 475.1993, Found 475.1996.

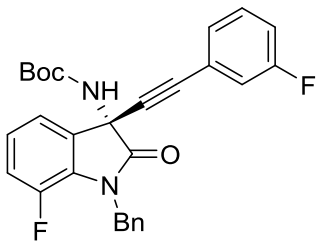


	Retention Time	Area	% Area
1	8.280	2241500	50.17
2	10.375	2226038	49.83



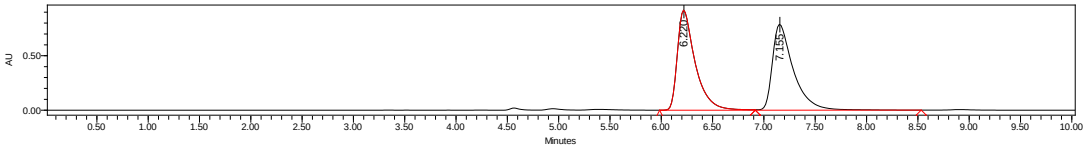
	Retention Time	Area	% Area
1	8.223	6076148	96.41
2	10.407	226344	3.59

tert-butyl (S)-(1-benzyl-7-fluoro-3-((3-fluorophenyl)ethynyl)-2-oxoindolin-3-yl)carbamate (3nb)

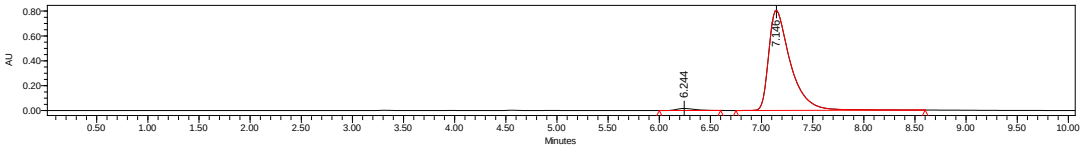


White solid; m.p. 104-106 ℃; 88% yield, 96% *ee*. $[\alpha]_D^{19}$ = +24.4 (c = 0.840 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.2 min (minor), 7.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.19 - 7.13 (m, 1H), 7.11 – 6.93 (m, 4H), 5.76 (s, 1H), 5.31 - 4.94 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 162.2 (d, J

= 247.4 Hz, 1C), 153.2, 147.6 (d, J = 245.4 Hz, 1C), 136.7, 130.0 (d, J = 9.1 Hz, 1C), 128.9 (d, J = 9.1 Hz, 1C), 128.6, 127.9 (d, J = 3.0 Hz, 1C), 127.6, 127.4, 124.1 (d, J = 6.1 Hz, 1C), 123.0 (d, J = 9.1 Hz, 1C), 119.1 (d, J = 4.0 Hz, 1C), 118.9 (d, J = 23.2 Hz, 1C), 117.8 (d, J = 20.2 Hz, 1C), 116.7 (d, J = 21.2 Hz, 2C), 84.2, 84.2, 81.4, 56.7, 46.1, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{24}F_2N_2NaO_3^+$ ([M+Na]$^+$) = 497.1648, Found 497.1655.

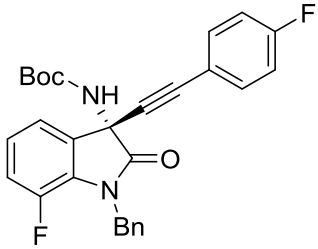


	Retention Time	Area	% Area
1	6.220	11078215	49.83
2	7.155	11155103	50.17

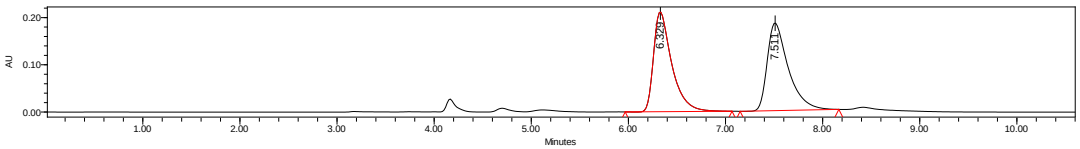


	Retention Time	Area	% Area
1	6.244	204518	1.70
2	7.146	11826693	98.30

tert-butyl (S)-(1-benzyl-7-fluoro-3-((4-fluorophenyl)ethynyl)-2-oxoindolin-3-yl)carbamate (3nc)

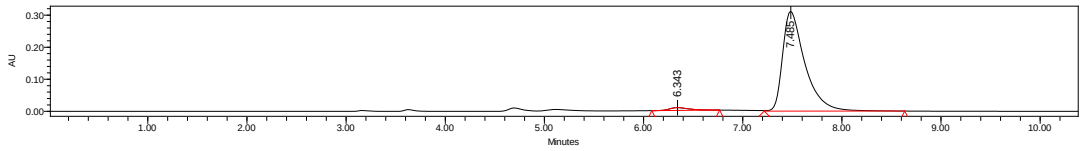


White solid; m.p. 66-68 ℃; 80% yield, 95% *ee*. $[\alpha]_D^{19}$ = +27.4 (c = 0.762 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.3 min (minor), 7.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.21 (m, 8H), 7.09 – 6.87 (m, 4H), 5.75 (s, 1H), 5.33 - 4.84 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 163.0 (d, J = 252.5 Hz, 1C), 153.2, 147.6 (d, J = 245.4 Hz, 1C), 136.7, 134.1 (d, J = 9.1 Hz, 1C), 128.8 (d, J = 9.1 Hz, 1C), 128.5, 127.5, 127.4, 124.0 (d, J = 7.1 Hz, 1C), 119.0 (d, J = 3.0 Hz, 1C), 117.7 (d, J = 19.2 Hz, 2C), 117.3 (d, J = 3.0 Hz, 1C), 115.7 (d, J = 22.2 Hz, 2C), 84.5, 83.1, 81.3, 56.8, 46.1, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{24}F_2N_2NaO_3^+$ ([M+Na]$^+$) = 497.1648, Found 497.1648.



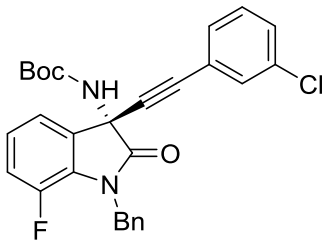
	Retention Time	Area	% Area
1	6.329	2745654	49.59

2	7.511	2790993	50.41

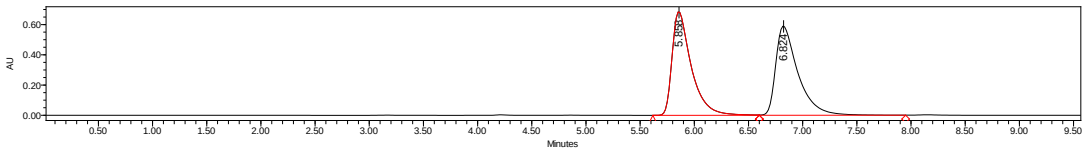


	Retention Time	Area	% Area
1	6.343	122880	2.46
2	7.485	4864322	97.54

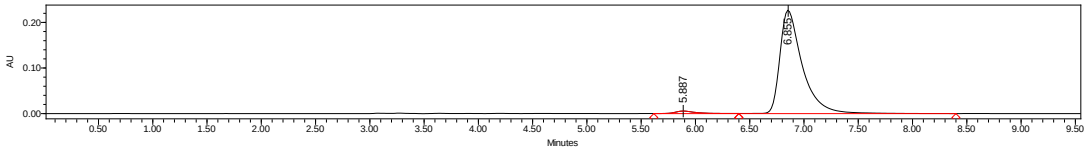
tert-butyl (S)-(1-benzyl-3-((3-chlorophenyl)ethynyl)-7-fluoro-2-oxoindolin-3-yl)carbamate (3nd)



White solid; m.p. 118-120 ℃; 90% yield, 95% *ee*. $[\alpha]_D^{21}$ = +21.7 (c = 0.888 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.9 min (minor), 6.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.33 – 7.18 (m, 7H), 7.08 – 6.90 (m, 2H), 5.76 (s, 1H), 5.28 - 4.89 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 153.2, 147.6 (d, J = 246.4 Hz, 1C), 136.7, 134.2, 131.9, 129.6, 129.6, 128.8 (d, J = 9.1 Hz, 1C), 128.6, 127.6, 127.4, 124.1 (d, J = 6.1 Hz, 1C), 122.9, 119.1 (d, J = 3.1 Hz, 1C), 117.8 (d, J = 19.1 Hz, 2C), 84.5, 84.1, 81.4, 56.7 , 46.1 , 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{24}{}^{34.9689}ClFN_2NaO_3^+$ ($[M+Na]^+$) = 513.1352, Found 513.1360, calcd for $C_{28}H_{24}{}^{36.9659}ClFN_2NaO_3^+$ ($[M+Na]^+$) = 515.1323, Found 515.1348.

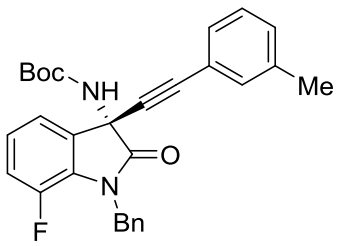


	Retention Time	Area	% Area
1	5.858	8404681	49.98
2	6.824	8410166	50.02



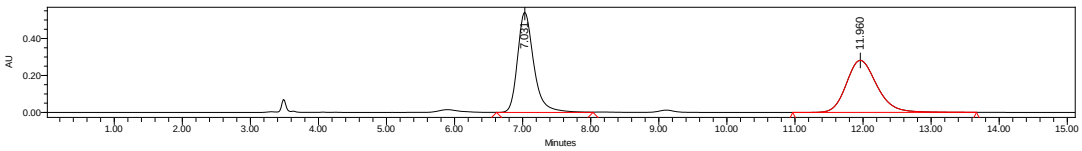
	Retention Time	Area	% Area
1	5.887	74801	2.25
2	6.855	3256533	97.75

tert-butyl (S)-(1-benzyl-7-fluoro-2-oxo-3-(m-tolylethynyl)indolin-3-yl)carbamate (3ne)

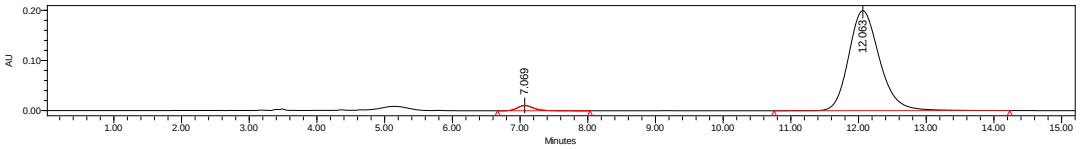


White solid; m.p. 68-70 ℃; 73% yield, 94% *ee*. $[\alpha]_D^{24}$ = +27.6 (c = 0.680 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC,

n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.1 min (minor), 12.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 2H), 7.34 – 7.11 (m, 9H), 7.06 - 6.91 (m, 2H), 5.73 (s, 1H), 5.32 - 4.86 (m, 2H), 2.29 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 153.2, 147.6 (d, J =245.4 Hz, 1C), 138.0, 136.8, 132.6, 130.1, 129.1, 128.8 (d, J = 9.1 Hz, 1C), 128.5, 128.2, 127.5, 127.4, 124.0 (d, J = 7.0 Hz, 1C), 121.0 119.0 (d, J = 3.0 Hz,1C), 117.6 (d, J = 20.2 Hz, 2C), 85.8, 82.9, 81.2, 56.8, 46.0, 28.1, 21.1. HRMS (ESI-TOF) calcd for $C_{29}H_{27}F_2N_2NaO_3^+$ ([M+Na]$^+$) = 493.1898, Found 493.1909.

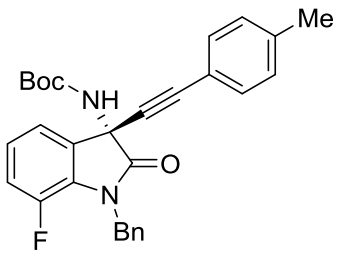


	Retention Time	Area	% Area
1	7.031	8995493	50.67
2	11.960	8756655	49.33

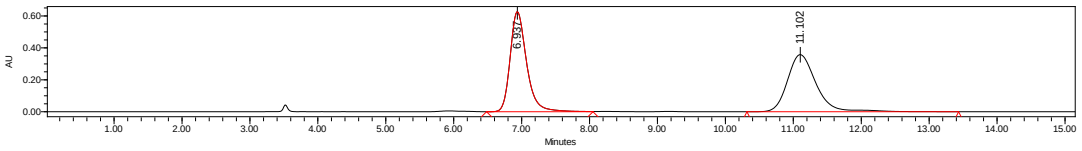


	Retention Time	Area	% Area
1	7.069	180118	2.77
2	12.063	6321414	97.23

tert-butyl (S)-(1-benzyl-7-fluoro-2-oxo-3-(p-tolylethynyl)indolin-3-yl)carbamate (3nf)

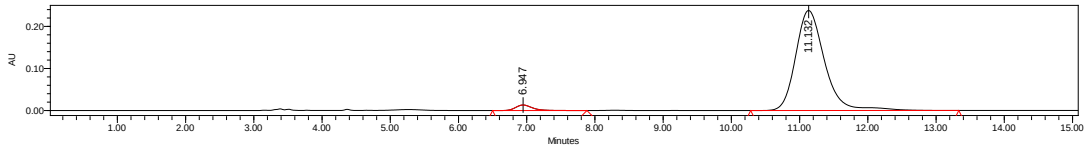


White solid; m.p. 63-65 ℃; 88% yield, 93% *ee*. $[\alpha]_D^{22}$ = +26.9 (c = 0.834 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.9 min (minor), 11.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.32 - 7.19 (m, 6H), 7.08 (d, J = 7.9 Hz, 2H), 7.04 – 6.91 (m, 2H), 5.74 (s, 1H), 5.31 - 4.93 (m, 2H), 2.32 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 153.2, 147.6 (d, J = 246.44 Hz, 1C), 139.5, 136.8, 131.9, 129.1, 128.8 (d, J = 9.1 Hz,1C), 128.5, 127.5, 127.4, 124.0 (d, J = 6.1 Hz, 1C), 119.0 (d, J = 3.0 Hz,1C), 118.1 , 117.5 (d, J = 20.2 Hz, 2C), 85.8, 82.6, 81.2, 56.8, 46.0, 28.1 , 21.5. HRMS (ESI-TOF) calcd for $C_{29}H_{27}F_2N_2NaO_3^+$ ([M+Na]$^+$) = 493.1898, Found 493.1902.



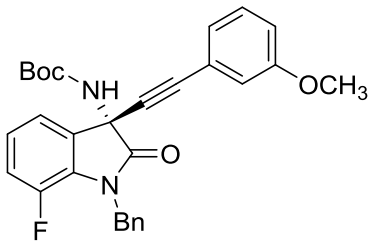
	Retention Time	Area	% Area

1	6.937	10538229	50.20
2	11.102	10454088	49.80

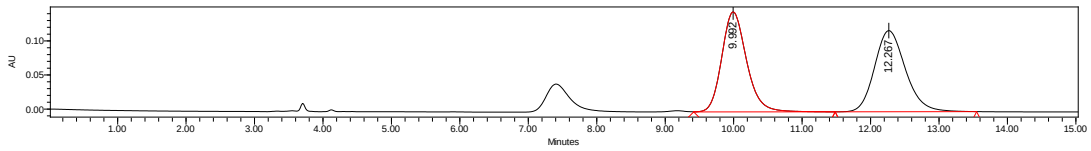


	Retention Time	Area	% Area
1	6.947	228403	3.15
2	11.132	7013443	96.85

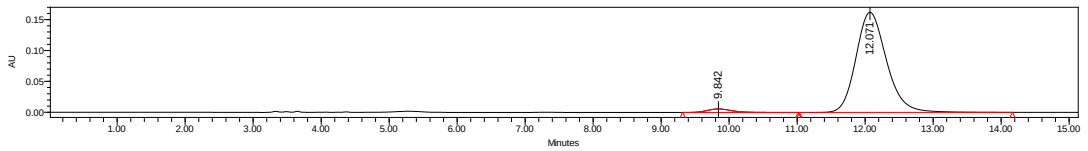
tert-butyl (S)-(1-benzyl-7-fluoro-3-((3-methoxyphenyl)ethynyl)-2-oxoindolin-3-yl)carbamate (3ng)



White solid; m.p. 54-56 ℃; 74% yield, 94% *ee*. $[\alpha]_D^{19}$ = +25.1 (c = 0.716 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.8 min (minor), 12.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 2H), 7.34 – 7.14 (m, 5H), 7.06 – 6.83 (m, 5H), 5.76 (s, 1H), 5.30 - 4.84 (m, 2H), 3.76 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 159.2, 153.2, 147.6 (d, J = 246.4 Hz, 1C), 136.6, 129.4, 128.8 (d, J = 10.1 Hz, 1C), 128.5, 127.5, 127.4, 124.6, 124.0 (d, J = 6.1 Hz, 1C), 122.1, 119.1 (d, J = 3.1 Hz, 1C), 117.6 (d, J = 20.2 Hz, 2C), 116.6, 116.1, 85.5, 83.0, 81.3, 56.8, 55.3, 46.1, 28.1. HRMS (ESI-TOF) calcd for $C_{29}H_{27}F_2N_2NaO_4^+$ ([M+Na]$^+$) = 509.1848, Found 509.1852.

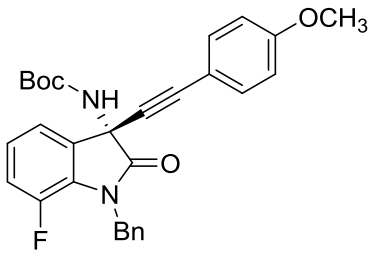


	Retention Time	Area	% Area
1	9.992	3694031	49.71
2	12.267	3736878	50.29

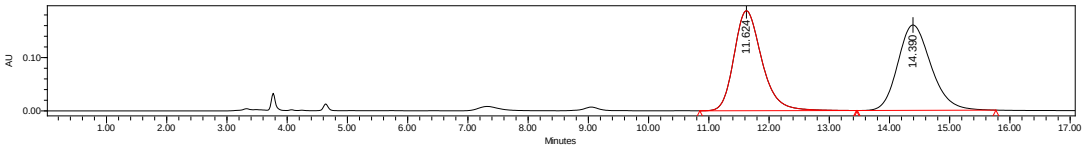


	Retention Time	Area	% Area
1	9.842	140506	2.70
2	12.071	5064596	97.30

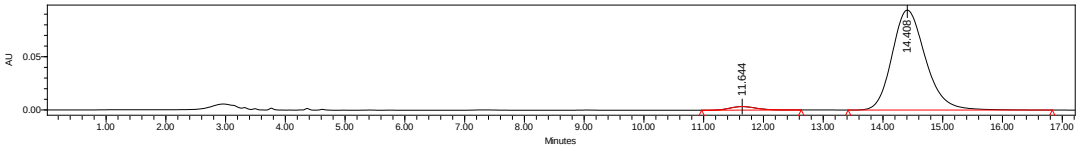
tert-butyl (S)-(1-benzyl-7-fluoro-3-((4-methoxyphenyl)ethynyl)-2-oxoindolin-3-yl)carbamate (3nh)



White solid; m.p. 70-72 ℃; 69% yield, 94% *ee*. $[\alpha]_D^{19}$ = +30.1 (c = 0.674 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.6 min (minor), 14.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.35 – 7.20 (m, 6H), 7.05 – 6.90 (m, 2H), 6.79 (d, J = 8.7 Hz, 2H), 5.76 (s, 1H), 5.33 - 4.87 (m, 2H), 3.78 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 160.3, 153.2, 148.6 (d, J = 246.4 Hz, 1C), 136.8, 133.6, 128.8 (d, J = 9.1 Hz, 1C), 128.5, 127.4 (d, J = 11.1 Hz, 1C), 124.0 (d, J = 6.1 Hz, 1C), 119.0 (d, J = 3.0 Hz, 1C), 117.5 (d, J = 19.2 Hz, 2C), 113.9, 113.2, 85.7, 82.0, 81.2, 56.9, 55.3, 46.0, 28.1. HRMS (ESI-TOF) calcd for $C_{29}H_{27}F_2N_2NaO_4^+$ ([M+Na]$^+$) = 509.1848, Found 509.1856.

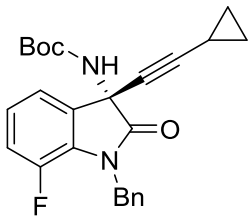


	Retention Time	Area	% Area
1	11.624	5993863	49.49
2	14.390	6117845	50.51

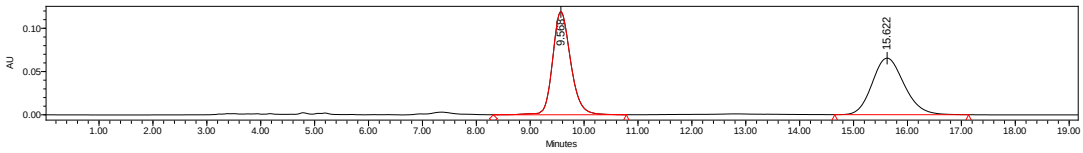


	Retention Time	Area	% Area
1	11.644	103896	2.77
2	14.408	3647923	97.23

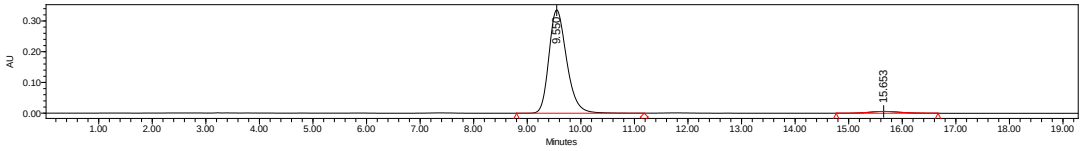
tert-butyl (S)-(1-benzyl-3-(cyclopropylethynyl)-7-fluoro-2-oxoindolin-3-yl)carbamate (3ni)



White solid; m.p. 92-94 ℃; 69% yield, 94% *ee*. $[\alpha]_D^{24}$ = +25.5 (c = 0.584 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.5 min (major), 15.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.4 Hz, 2H), 7.33 – 7.21 (m, 3H), 7.15 (d, J = 7.3 Hz, 1H), 7.04 – 6.83 (m, 2H), 5.57 (s, 1H), 5.31 - 4.75 (m, 2H), 1.51 – 1.01 (m, 10H), 0.83 – 0.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 153.6, 148.0 (d, J = 245.4 Hz, 1C), 137.4, 129.2 (d, J = 3.0 Hz, 1C), 129.0, 128.0, 127.9, 124.4 (d, J = 6.1 Hz, 1C), 119.3 (d, J = 3.0 Hz, 1C), 117.9 (d, J = 20.2 Hz, 2C), 90.5, 81.6, 70.3, 56.9, 46.5, 28.6, 9.0, 0.00. HRMS (ESI-TOF) calcd for $C_{25}H_{25}FN_2NaO_3^+$ ([M+Na]$^+$) = 443.1741, Found 443.1737.

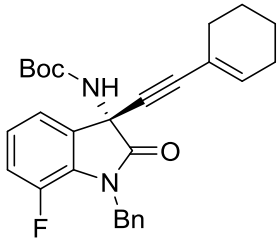


	Retention Time	Area	% Area
1	9.568	2769067	50.64
2	15.622	2698944	49.36

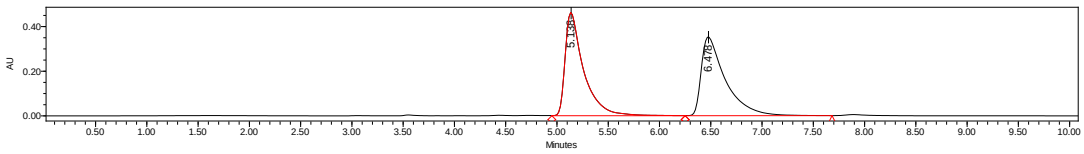


	Retention Time	Area	% Area
1	9.550	7723272	96.96
2	15.653	242540	3.04

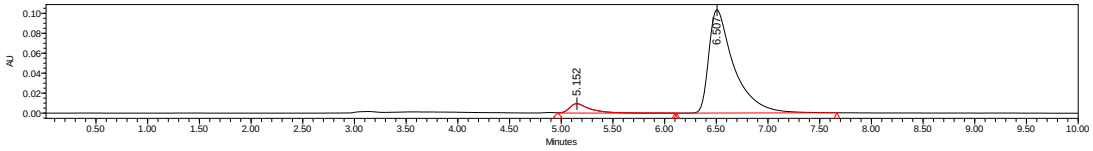
tert-butyl (S)-(1-benzyl-3-(cyclohex-1-en-1-ylethynyl)-7-fluoro-2-oxoindolin-3-yl)carbamate (3nj)



White solid; m.p. 56-58 ℃; 60% yield, 86% *ee*. $[\alpha]_D^{19}$ = +20.9 (c = 0.962 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.1 min (minor), 6.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.34 - 7.21 (m, 3H), 7.18 (d, J = 7.1 Hz, 1H), 7.04 – 6.83 (m, 2H), 6.23 - 6.02 (m, 1H), 5.62 (s, 1H), 5.30 - 4.80 (m, 2H), 2.04 (s, 4H), 1.60 - 1.02 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.1, 147.5 (d, J = 245.4 Hz, 1C), 137.5, 136.8, 128.7 (d, J = 9.1 Hz, 1C), 128.5, 127.4, 127.3, 123.9 (d, J = 6.1 Hz, 1C), 119.2, 118.8 (d, J = 2.0 Hz, 1C), 117.4 (d, J = 19.2 Hz, 1C), 87.4, 81.1, 80.6, 56.7, 46.0, 28.6, 28.1, 25.6, 22.0, 21.3. HRMS (ESI-TOF) calcd for $C_{28}H_{29}FN_2NaO_3^+$ ($[M+Na]^+$) = 483.2054, Found 483.2050.

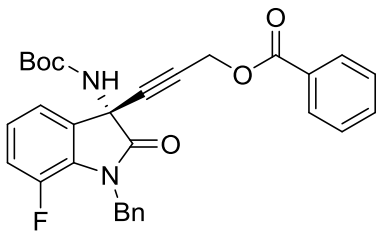


	Retention Time	Area	% Area
1	5.138	5772963	50.12
2	6.478	5744604	49.88

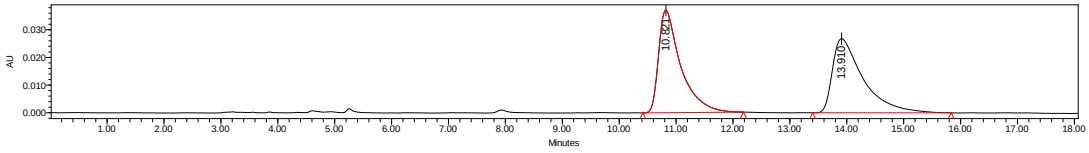


	Retention Time	Area	% Area
1	5.152	131550	7.02
2	6.507	1742282	92.98

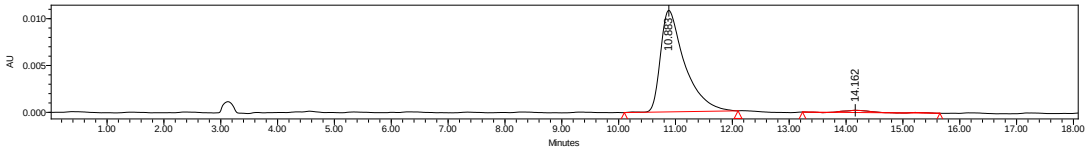
(S)-3-(1-benzyl-3-((tert-butoxycarbonyl)amino)-7-fluoro-2-oxoindolin-3-yl)prop-2-yn-1-yl benzoate (3nk)



White solid; m.p. 54-56 ℃; 50% yield, 95% *ee*. $[\alpha]_D^{19}$ = +13.2 (c = 0.508 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.9 min (major), 14.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 2H), 7.32 - 7.54 (m, 1H), 7.51 – 7.36 (m, 4H), 7.33 - 7.17 (m, 4H), 6.99 (dd, J = 11.3, 8.7 Hz, 2H), 5.68 (s, 1H), 5.26 - 4.97 (m, 2H), 4.90 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 165.6, 153.1, 147.5 (d, J = 246.4 Hz, 1C), 136.6, 133.4, 129.9, 129.2, 128.9 (d, J = 9.1 Hz, 1C), 128.5, 128.5, 127.5, 127.4, 124.1 (d, J = 7.1 Hz, 1C), 119.2 (d, J = 3.0 Hz, 1C), 117.8 (d, J = 20.2 Hz, 2C), 81.4, 81.0, 80.0, 56.2, 52.3, 46.2, 28.1. HRMS (ESI-TOF) calcd for $C_{30}H_{27}FN_2NaO_5^+$ ([M+Na]$^+$) = 537.1796, Found 537.1794.

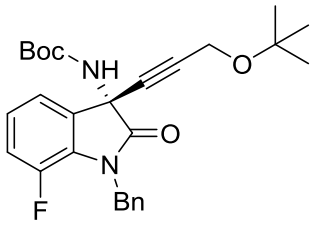


	Retention Time	Area	% Area
1	10.821	997440	49.89
2	13.910	1001796	50.11



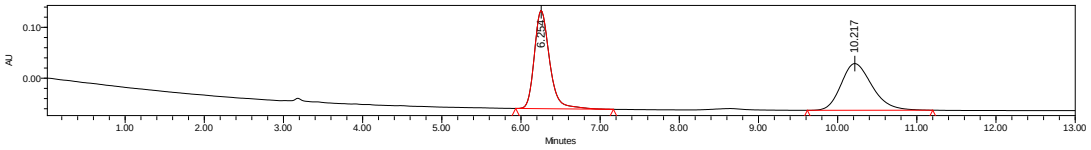
	Retention Time	Area	% Area
1	10.883	319911	97.27
2	14.162	8965	2.73

***tert*-butyl(S)-(1-benzyl-3-(3-(tert-butoxy)prop-1-yn-1-yl)-7-fluoro-2-oxoindolin-3-yl)carbamate (3nl)**

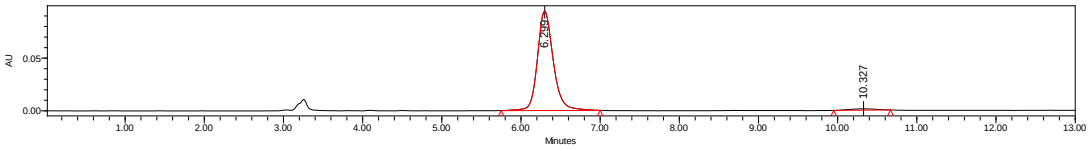


White solid; m.p. 68-70 ℃; 77% yield, 95% *ee*. $[\alpha]_D^{19}$ = +15.3 (c = 0.564 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.2 min (major), 10.2 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 2H), 7.34 – 7.15 (m, 4H), 7.03 – 6.89 (m, 2H), 5.66 (s, 1H), 5.28 - 4.89 (m, 2H), 4.16 – 3.97 (m, 2H),

1.46 -1.07 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 153.1, 147.5 (d, J = 245.4 Hz, 1C), 136.7, 128.8 (d, J = 9.1 Hz, 1C), 128.5, 127.5, 127.4, 123.9 (d, J = 7.1 Hz, 1C), 119.1 (d, J = 3.0 Hz, 1C), 117.5 (d, J = 19.2 Hz, 2C), 84.2, 81.2, 78.8, 74.8, 56.3, 50.5, 46.0, 27.1, 27.5. HRMS (ESI-TOF) calcd for $C_{27}H_{31}FN_2NaO_4^+$ ([M+Na]$^+$) = 487.2060, Found 487.2155.

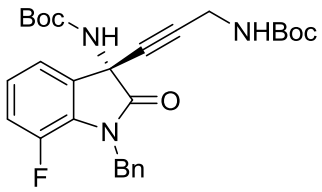


	Retention Time	Area	% Area
1	6.254	2584810	50.85
2	10.217	2498457	49.15

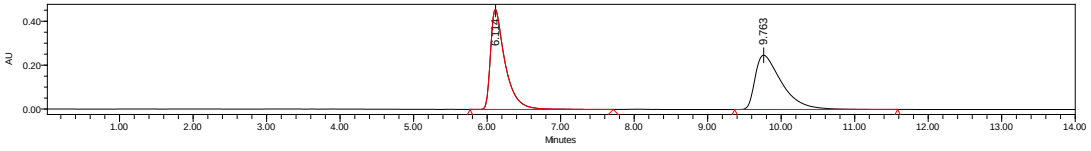


	Retention Time	Area	% Area
1	6.299	1305806	97.85
2	10.327	28726	2.15

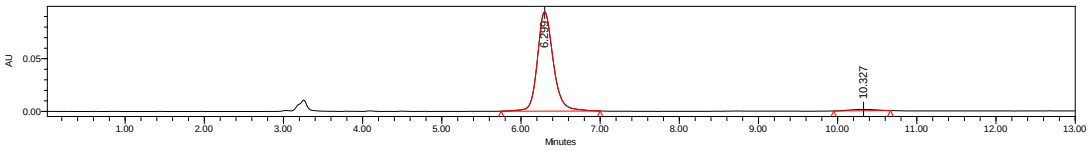
tert-butyl(S)-(1-benzyl-3-(3-((tert-butoxycarbonyl)amino)prop-1-yn-1-yl)-7-fluoro-2-oxoindolin-3-yl)carbamate (3nm)



White solid; m.p. 112-114 ℃; 92% yield, 89% *ee*. $[\alpha]_D^{20}$ = +12.2 (c = 0.718 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.1 min (major), 9.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.34 – 7.23 (m, 3H), 7.18 (dd, J = 7.0, 1.4 Hz, 1H), 7.04 – 6.91 (m, 2H), 5.75 (s, 1H), 5.11 (s, 2H), 4.73 (s, 1H), 3.91 (d, J = 3.7 Hz, 2H), 1.47 – 1.21 (m, 17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 155.1, 153.2, 147.5 (d, J = 246.4 Hz, 1C), 136.6, 128.8 (d, J = 9.1 Hz, 1C), 128.5, 127.5, 127.4, 124.0 (d, J = 6.1 Hz, 1C), 119.0 (d, J = 3.0 Hz, 1C), 117.6 (d, J = 20.2 Hz, 2C), 82.4, 81.3, 80.2, 56.2, 46.1, 30.5, 28.3, 28.1. HRMS (ESI-TOF) calcd for $C_{28}H_{32}FN_3NaO_5^+$ ([M+Na]$^+$) = 532.2218, Found 532.2211.

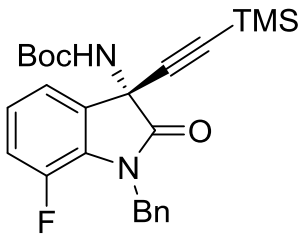


	Retention Time	Area	% Area
1	6.114	6270714	50.28
2	9.763	6201688	49.72

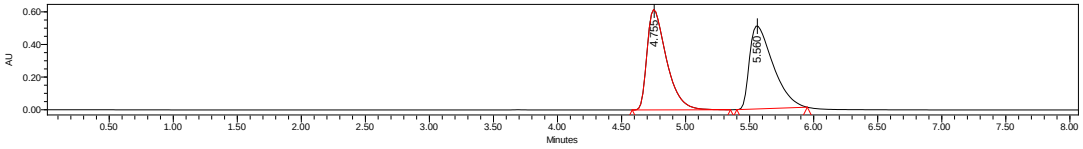


	Retention Time	Area	% Area
1	6.157	942473	94.53
2	9.952	54526	5.47

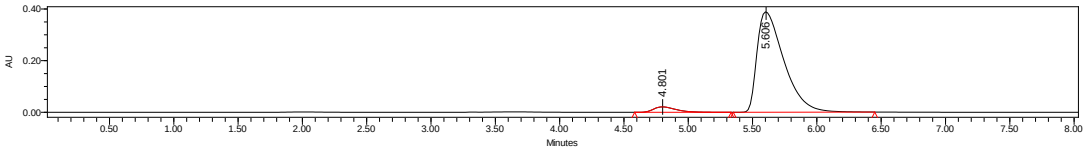
tert-butyl (_R_)-(1-benzyl-7-fluoro-2-oxo-3-((trimethylsilyl)ethynyl)indolin-3-yl)carbamate (3nn)



Colorless oil; 62% yield, 91% *ee*. $[\alpha]_D^{18}$ = +27.1 (c = 1.684 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.8 min (minor), 5.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.34 – 7.21 (m, 3H), 7.24 – 7.14 (m, 1H), 7.05 – 6.90 (m, 2H), 5.66 (s, 1H), 5.31 – 4.87 (m, 2H), 1.34 (s, 9H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.5, 147.9 (d, J = 245.4 Hz, 1C), 137.2, 129.2 (d, J = 9.2 Hz, 1C), 128.9, 127.8 (d, J = 22.2 Hz, 1C), 124.4 (d, J = 6.3 Hz, 1C), 119.3 (d, J = 3.1 Hz, 1C), 118.0 (d, J = 19.5 Hz, 1C), 99.0, 91.8, 81.6, 57.4, 46.3, 28.5, -0.0. HRMS (ESI-TOF) calcd for $C_{25}H_{29}FN_2NaO_3Si^+$ ([M+Na]$^+$) = 475.1824, Found 475.1828.

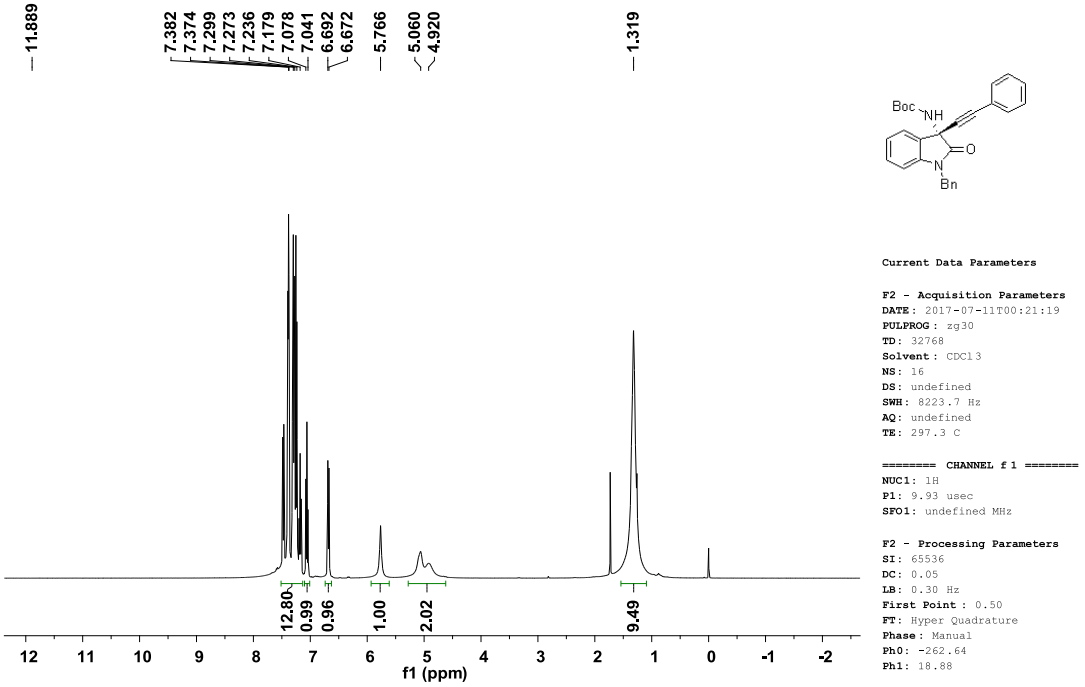


	Retention Time	Area	% Area
1	4.755	6470303	49.87
2	5.560	6503904	50.13

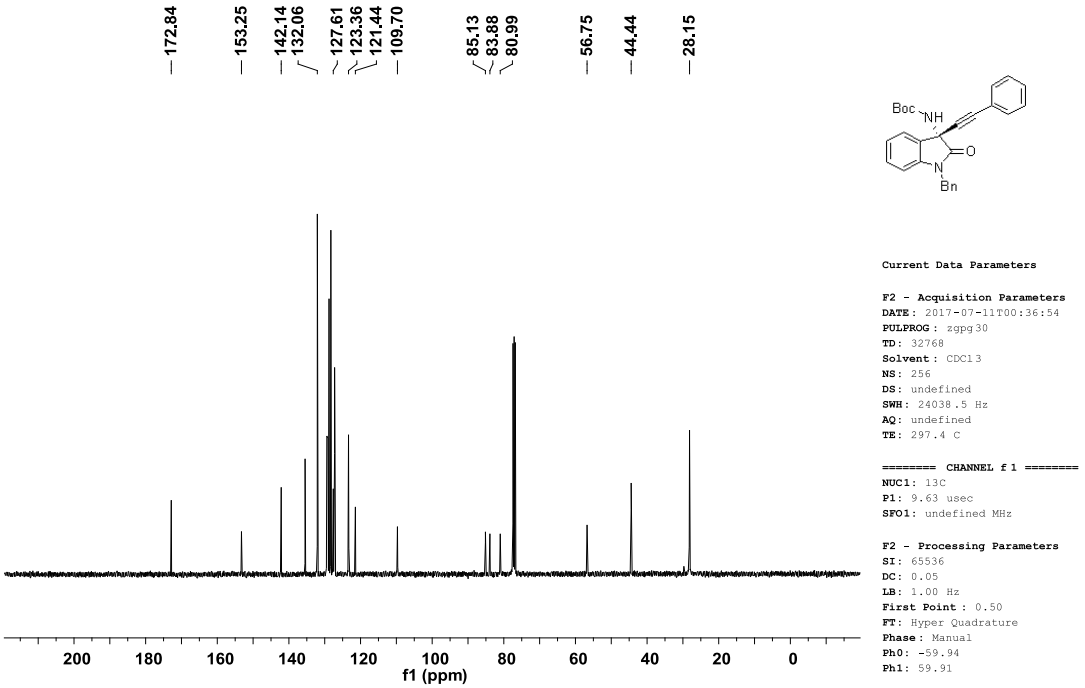


	Retention Time	Area	% Area
1	4.801	255555	4.33
2	5.606	5644547	95.67

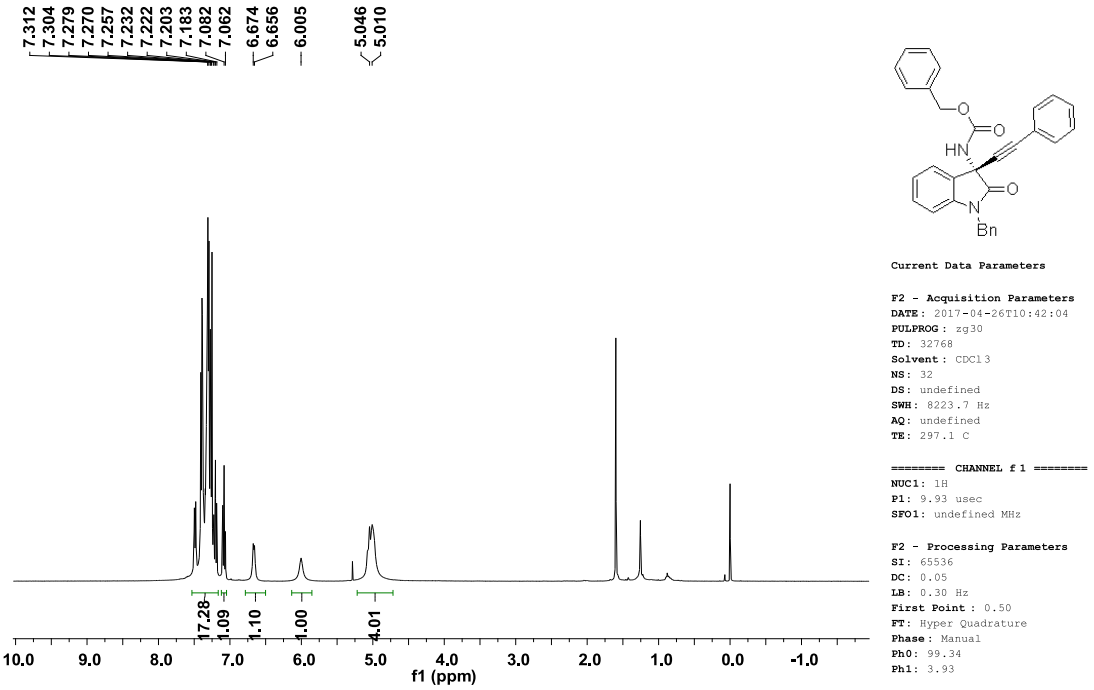
(J) Copies of NMR spectra



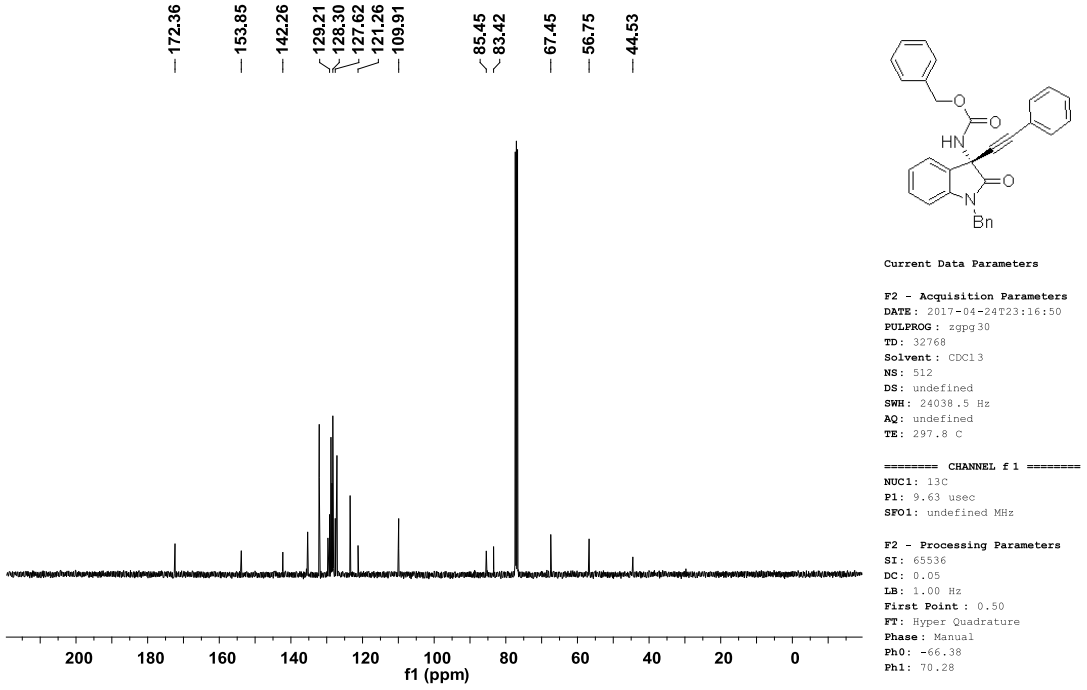
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.13 (m, 12H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 5.77 (s, 1H), 5.28 - 4.62 (m, 2H), 1.32 (s, 9H).



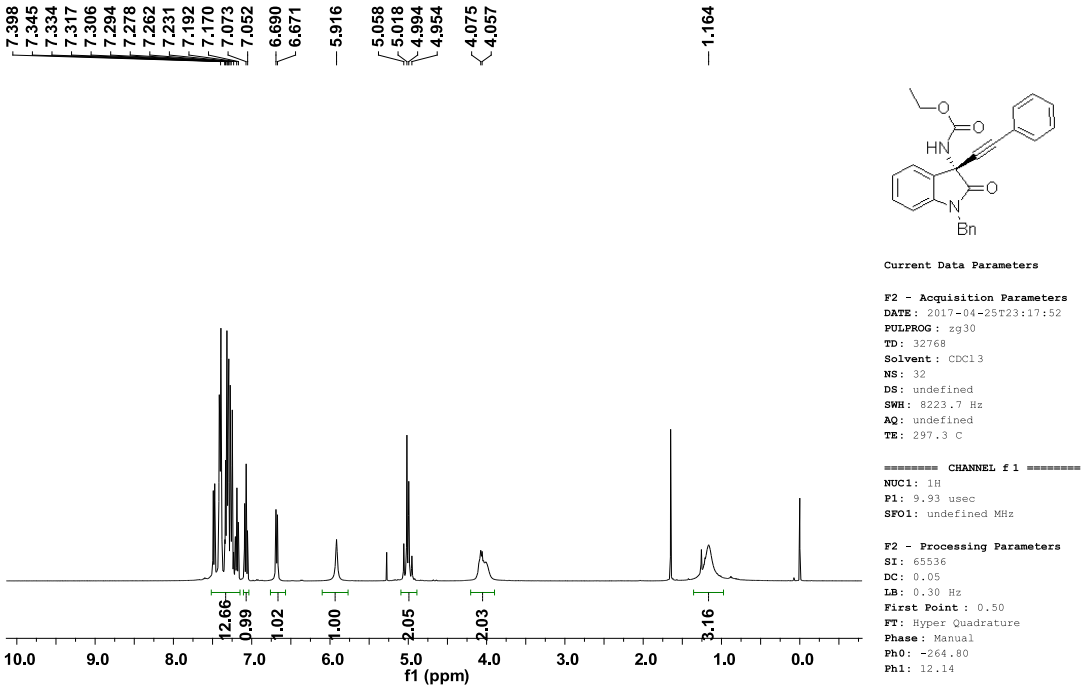
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.84, 153.25, 142.14, 135.48, 132.06, 129.42, 129.11, 128.80, 128.29, 127.61, 127.24, 123.33, 123.29, 121.44, 109.70, 85.13, 83.88, 80.99, 56.75, 44.44, 28.15.



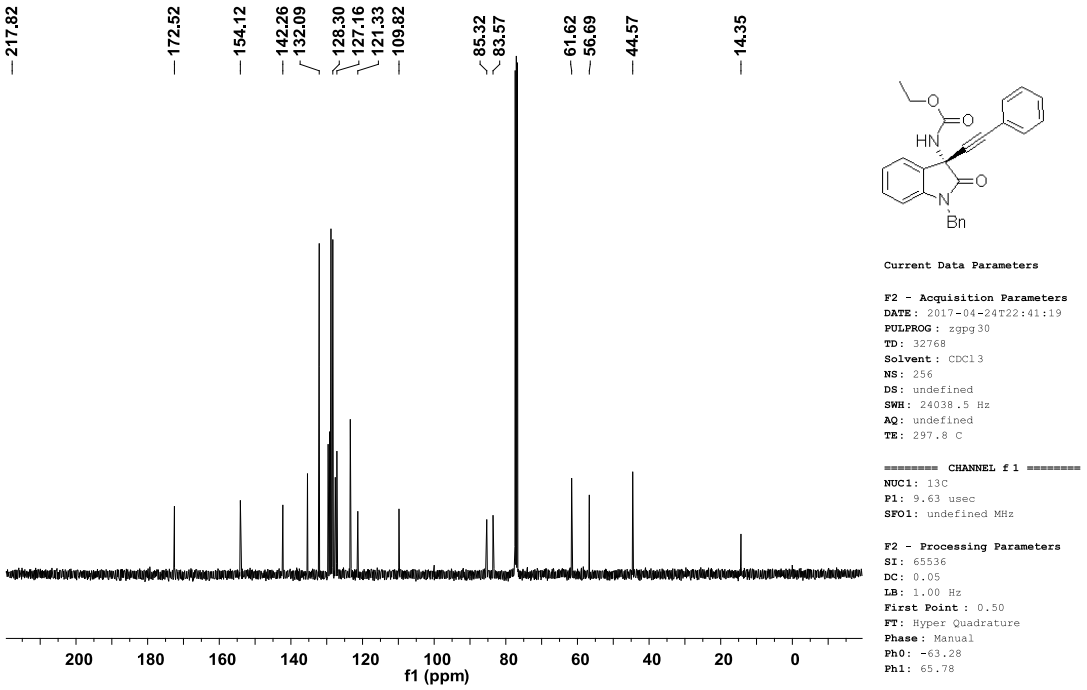
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.16 (m, 17H), 7.08 (dd, *J* = 11.0, 4.1 Hz, 1H), 6.66 (d, *J* = 7.1 Hz, 1H), 6.00 (s, 1H), 5.03 (d, *J* = 14.3 Hz, 4H).



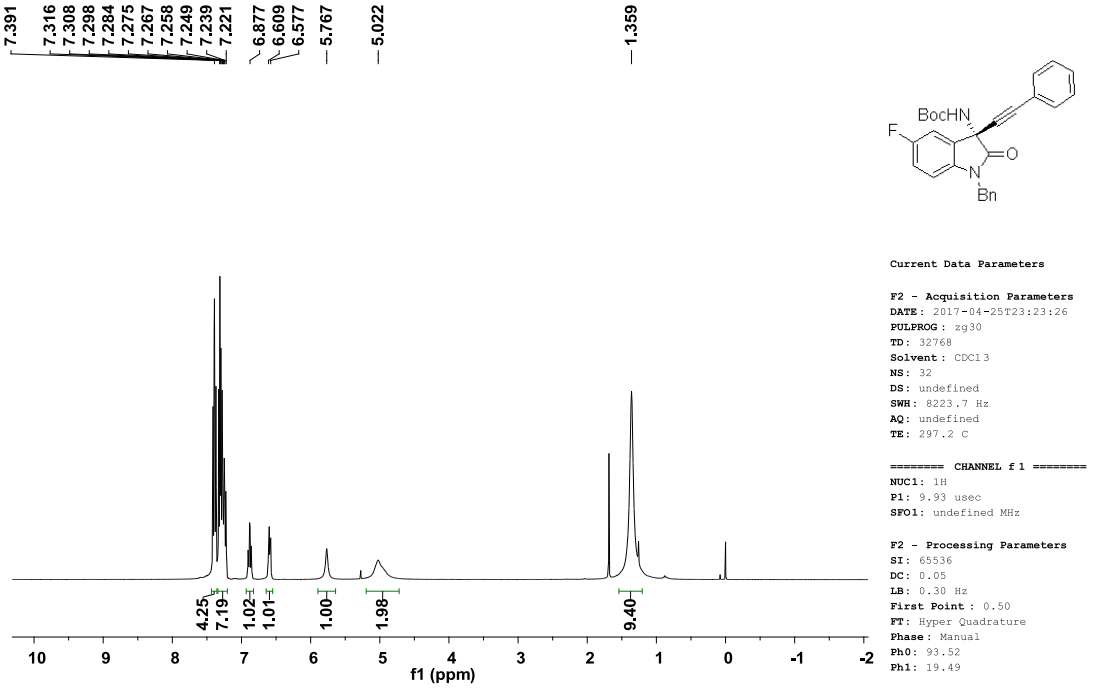
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.36, 153.85, 142.26, 135.32, 132.09, 129.67, 129.21, 128.82, 128.53, 128.30, 128.26, 128.17, 127.62, 127.15, 123.47, 121.26, 109.91, 85.45, 83.42, 67.45, 56.75, 44.53.



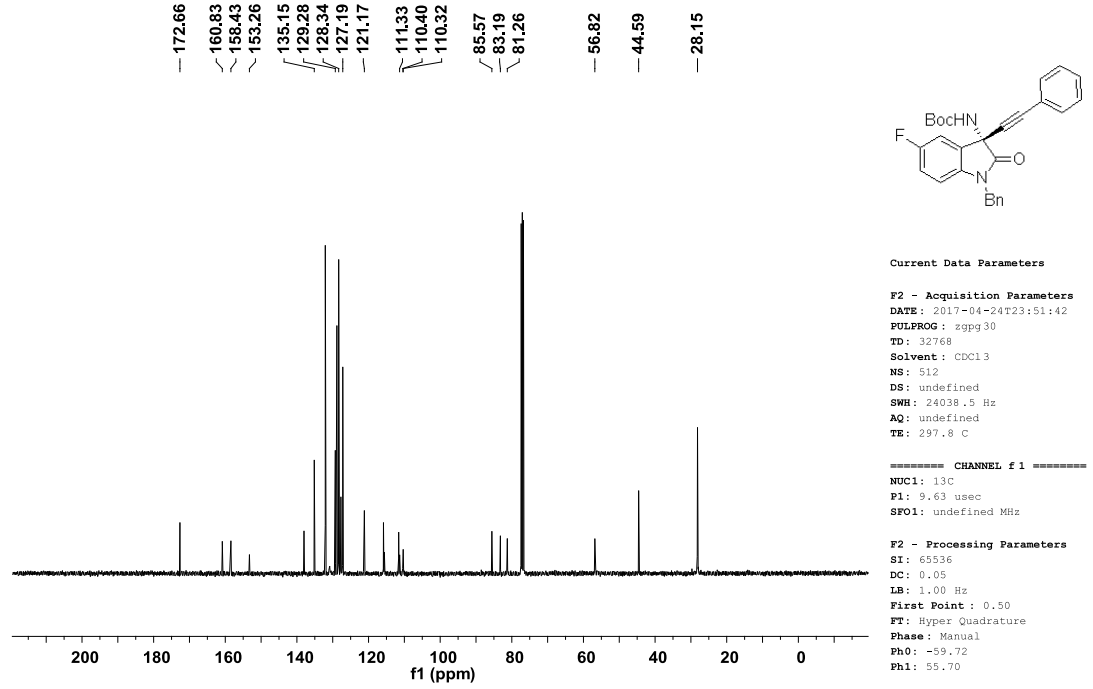
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.15 (m, 13H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 5.92 (s, 1H), 5.01 (q, *J* = 16.0 Hz, 2H), 4.07 (d, *J* = 7.1 Hz, 2H), 1.16 (s, 3H).



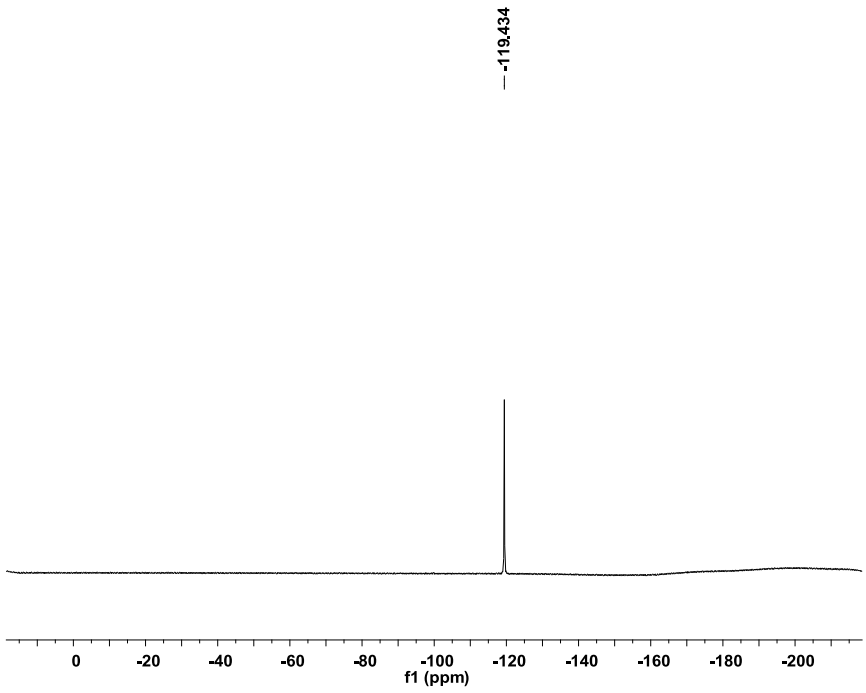
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.52, 154.12, 142.26, 135.37, 132.09, 129.61, 129.18, 128.82, 128.30, 127.61, 127.16, 123.42, 121.33, 109.82, 85.32, 83.57, 61.62, 56.69, 44.57, 14.35.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.36 (m, 4H), 7.34 – 7.20 (m, 7H), 6.88 (td, *J* = 8.9, 2.5 Hz, 1H), 6.59 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.77 (s, 1H), 1.36 (s, 9H).



^{13}C NMR (101 MHz, CDCl$_3$) δ 172.66 , 159.63 (d, J = 242.4 Hz, 1C), 153.26, 138.01 (d, *J* = 2.0 Hz, 1C), 135.15, 132.08, 129.28 , 128.84, 128.34, 127.72, 127.19, 121.17, 115.71 (d, J = 23.2Hz, 2C), 111.45 (d, J = 25.2 Hz, 1C), 110.36 (d, *J* = 8.0 Hz, 1C), 85.57, 83.19, 81.26, 56.82, 44.59 , 28.15 .



Current Data Parameters

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Solvent: CDCl3
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DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 297.6 C

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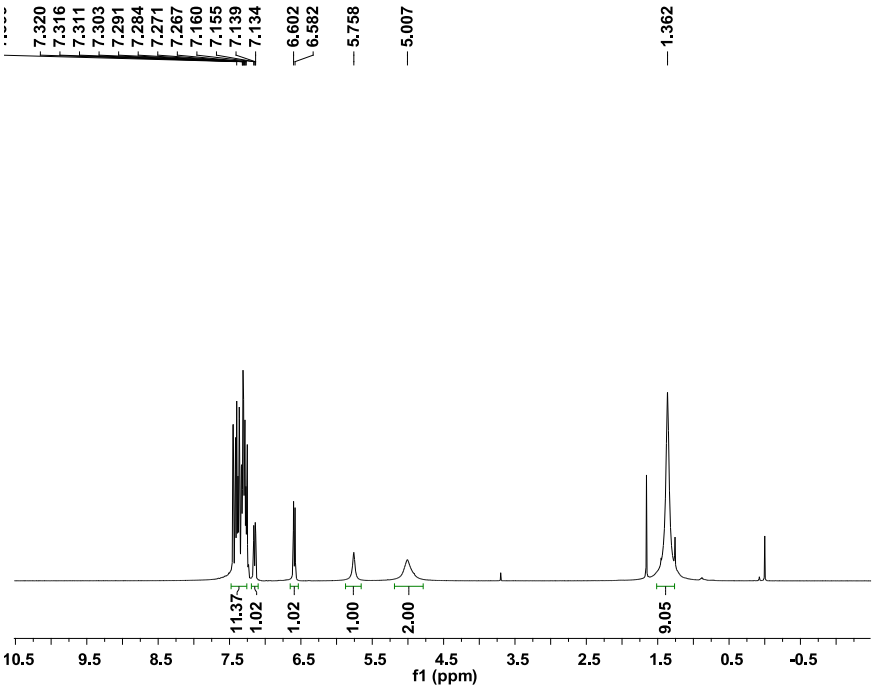
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -8.78
Ph1: 0.00

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.43.



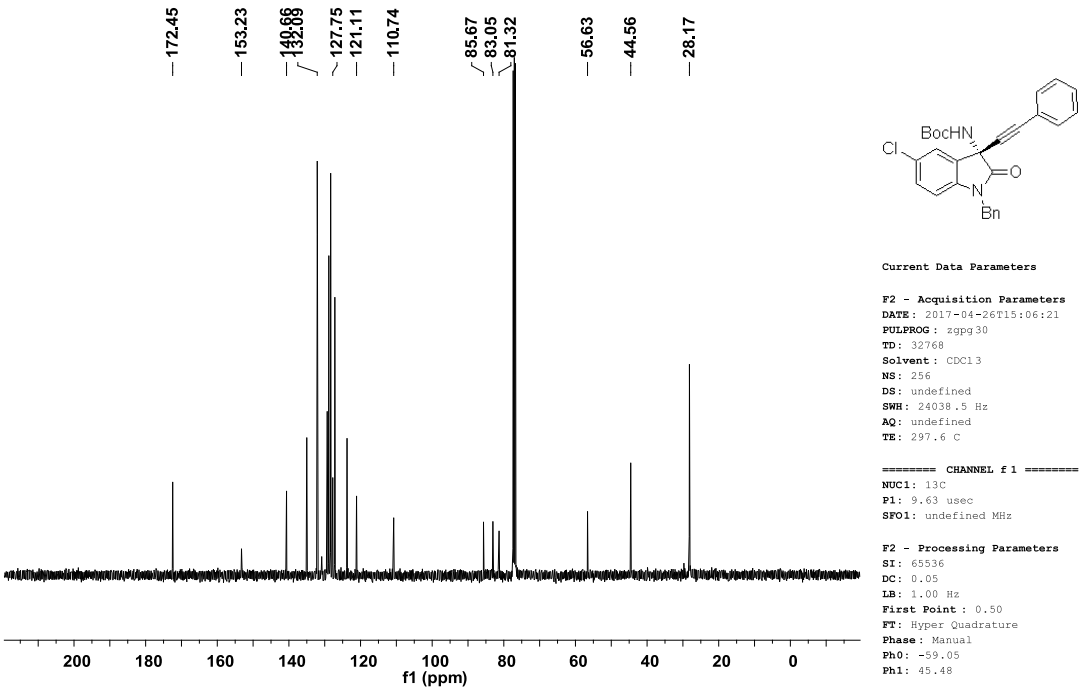
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-04-26T14:50:48
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.3 C

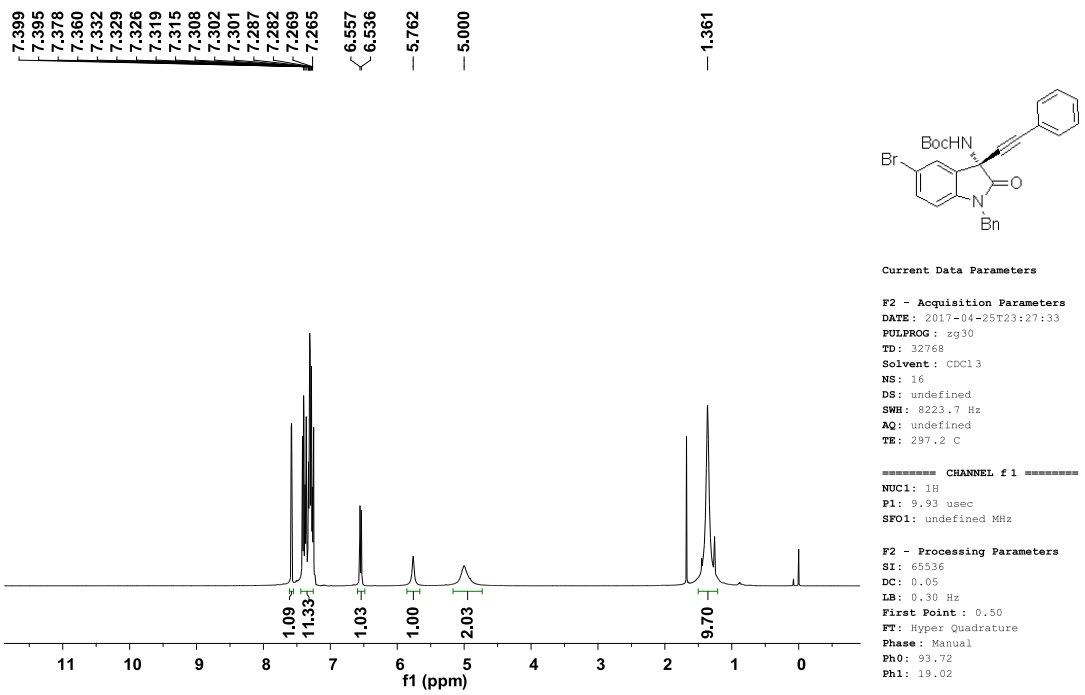
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.41
Ph1: 18.17

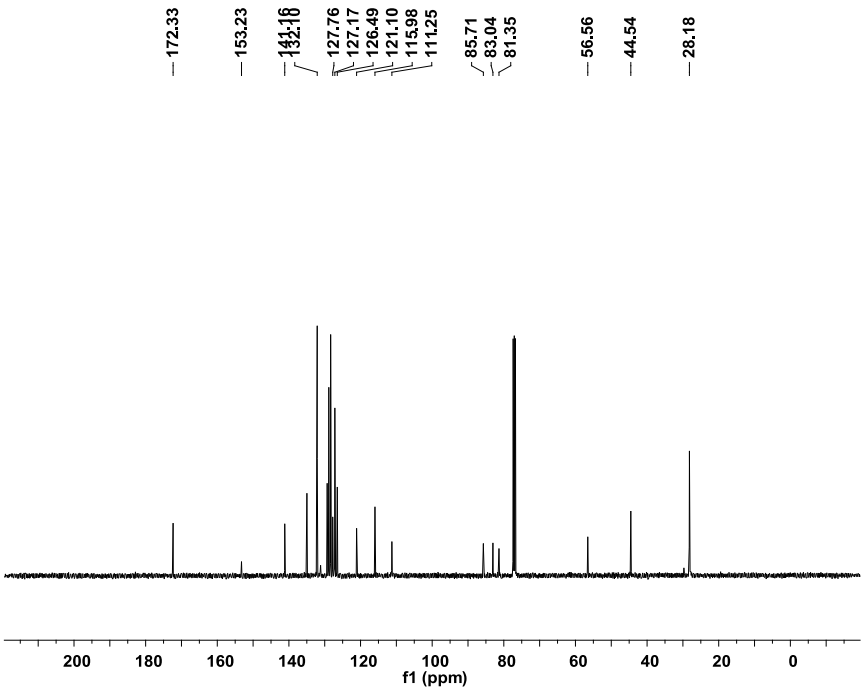
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 11H), 7.15 (dd, J = 8.3, 1.9 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.76 (s, 1H), 5.01 (s, 2H), 1.36 (s, 9H).



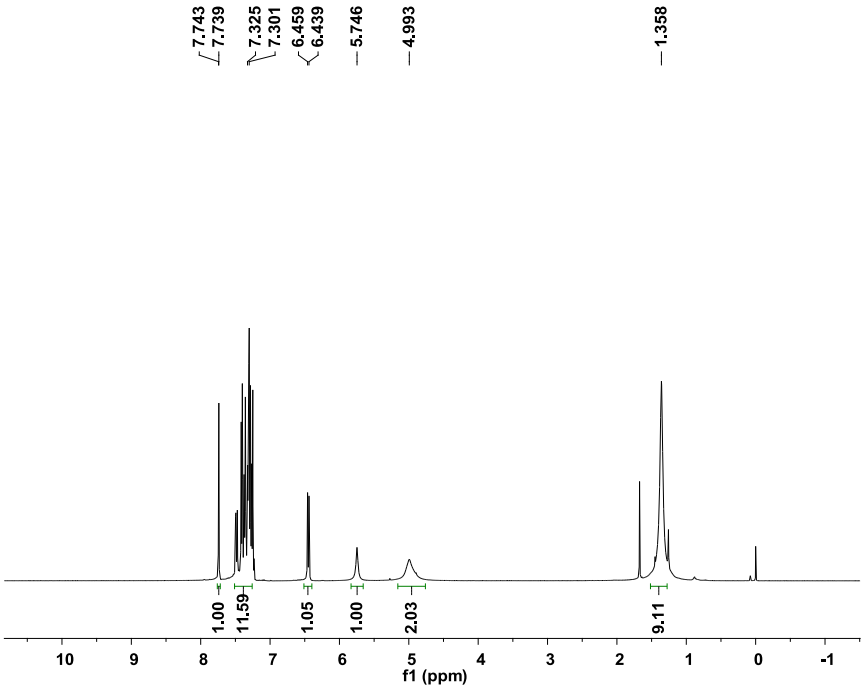
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.45, 153.23, 140.66, 135.01, 132.09, 129.35, 129.31, 128.86, 128.70, 128.34, 127.75, 127.18 , 123.77, 121.11, 110.74 , 85.67, 83.05 , 81.32, 56.63, 44.56, 28.17.



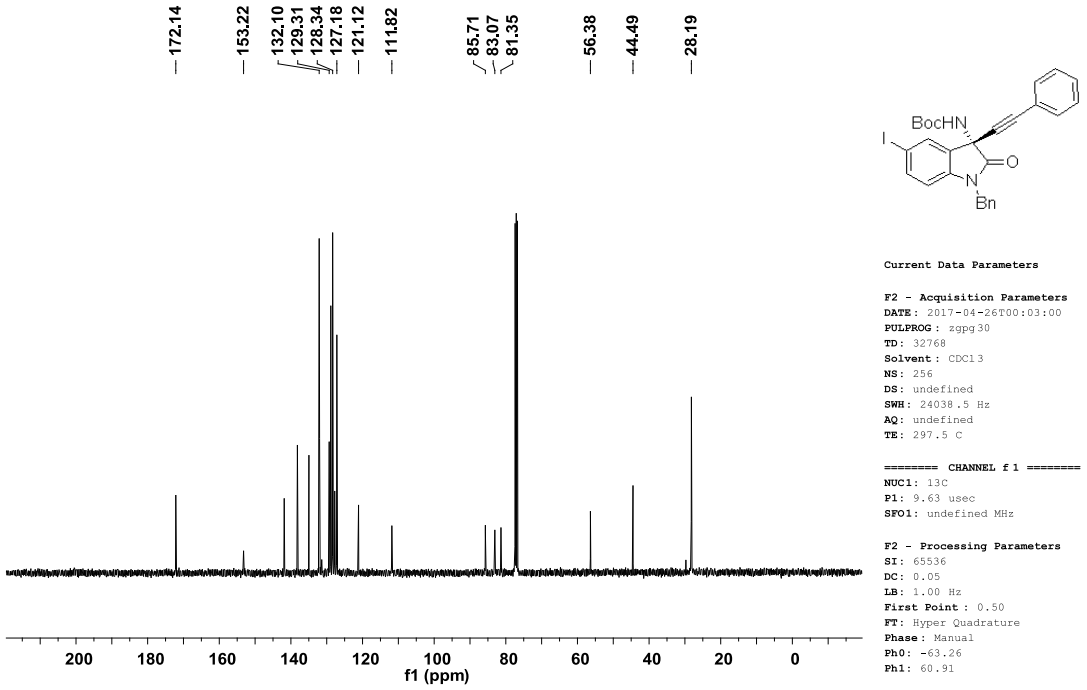
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.44 – 7.26 (m, 11H), 6.55 (d, J = 8.4 Hz, 1H), 5.76 (s, 1H), 5.00 (s, 2H), 1.36 (s, 9H).



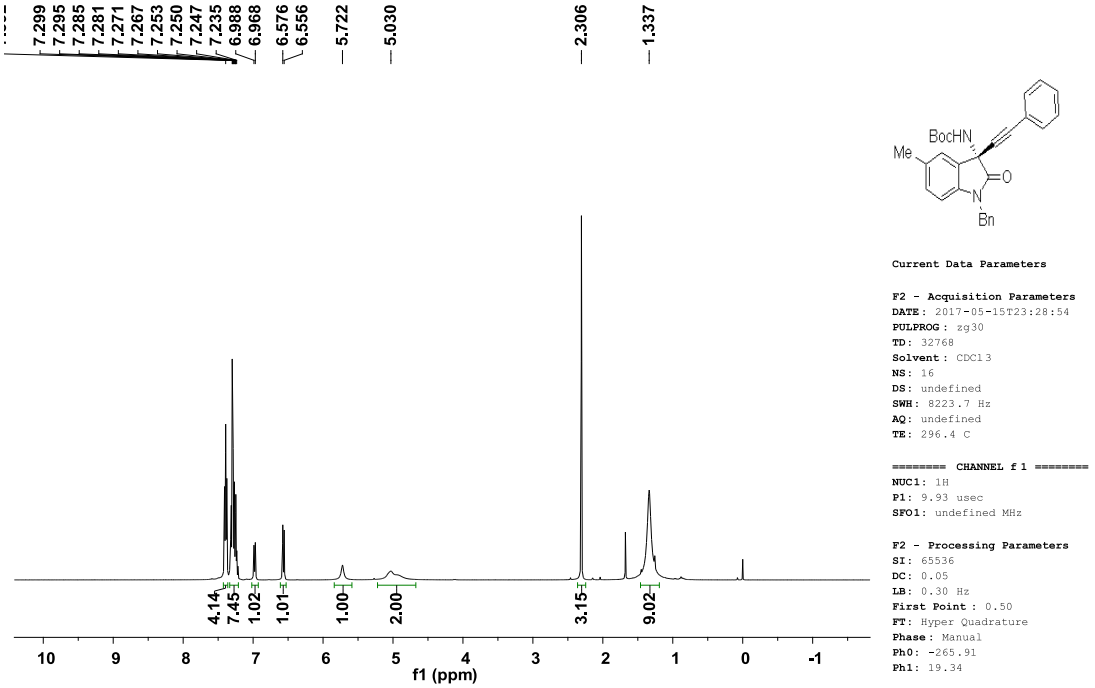
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.33, 153.23, 141.16, 134.98, 132.17, 129.32, 128.86, 128.34, 127.76, 127.17, 126.49, 121.10, 115.98, 111.25 85.71 , 83.04 , 81.35 , 56.56, 44.54, 28.18.



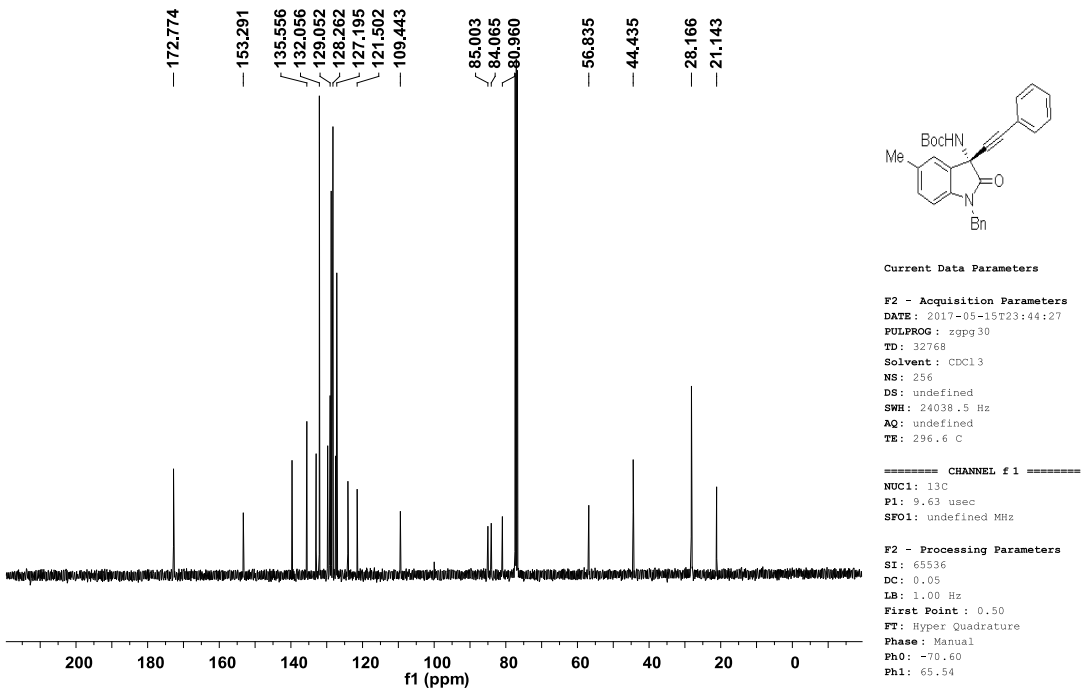
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 1.6 Hz, 1H), 7.51 – 7.26 (m, 12H), 6.45 (d, J = 8.0 Hz, 1H), 5.75 (s, 1H), 4.99 (s, 2H), 1.36 (s, 9H).



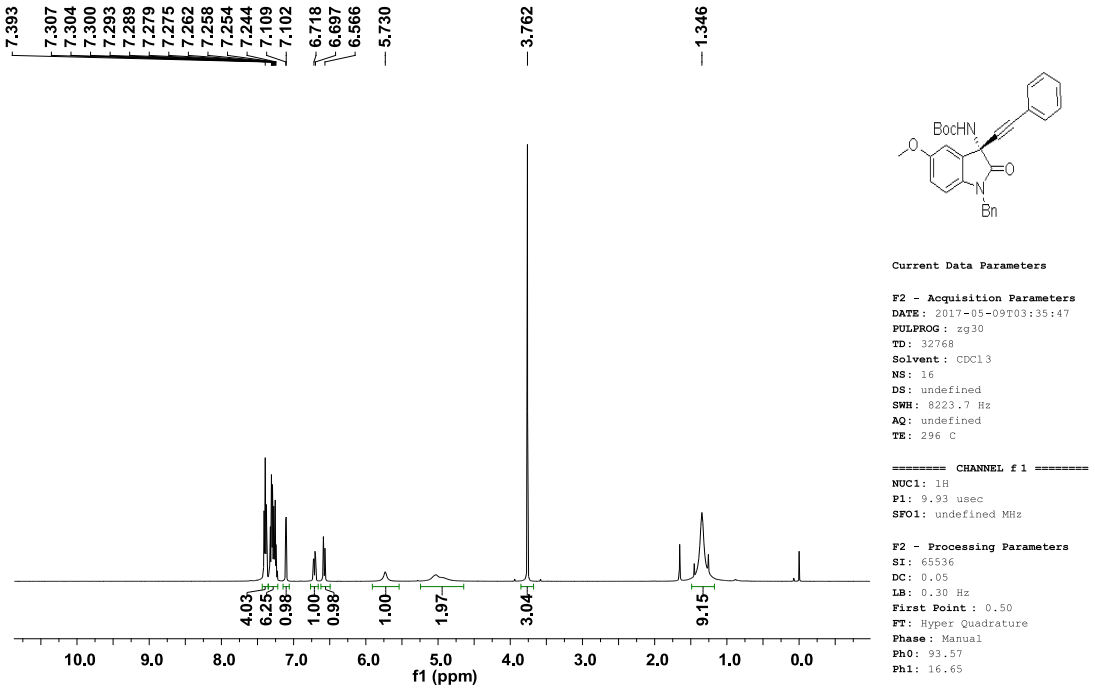
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.14, 153.22, 141.87, 138.19, 134.97, 132.10, 131.99 , 129.31, 128.86, 128.34, 127.76, 127.18, 121.12, 111.82, 85.71, 83.07, 81.35, 56.38, 44.49 , 28.19.



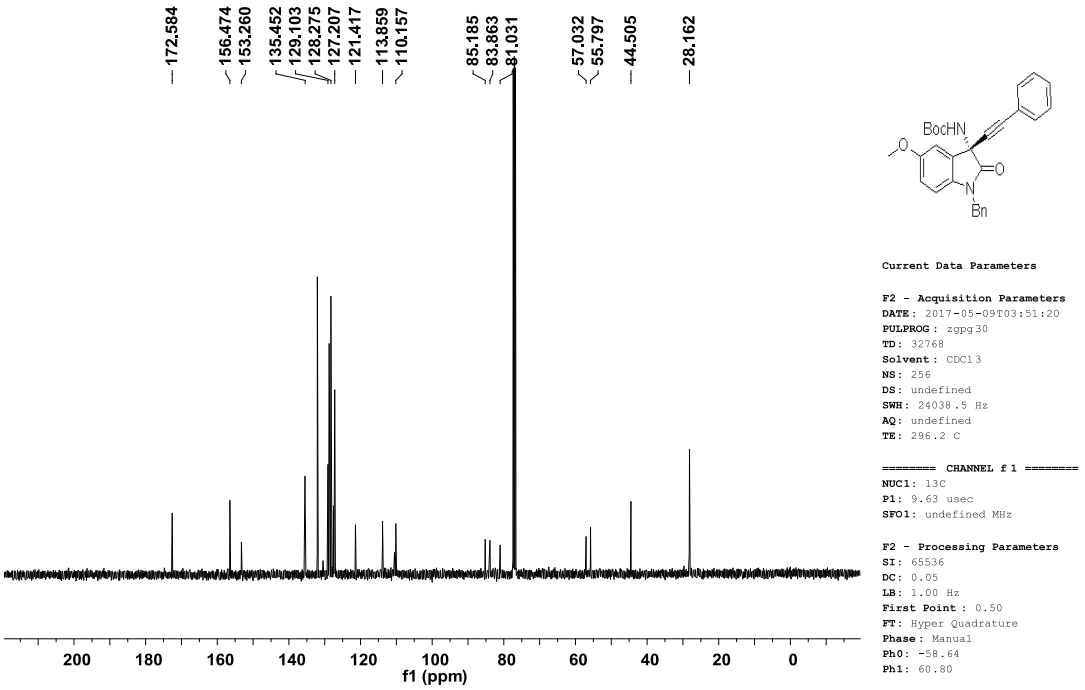
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.36 (m, 4H), 7.33 – 7.21 (m, 7H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.72 (s, 1H), 5.03 (s, 2H), 2.31 (s, 3H), 1.34 (s, 9H).



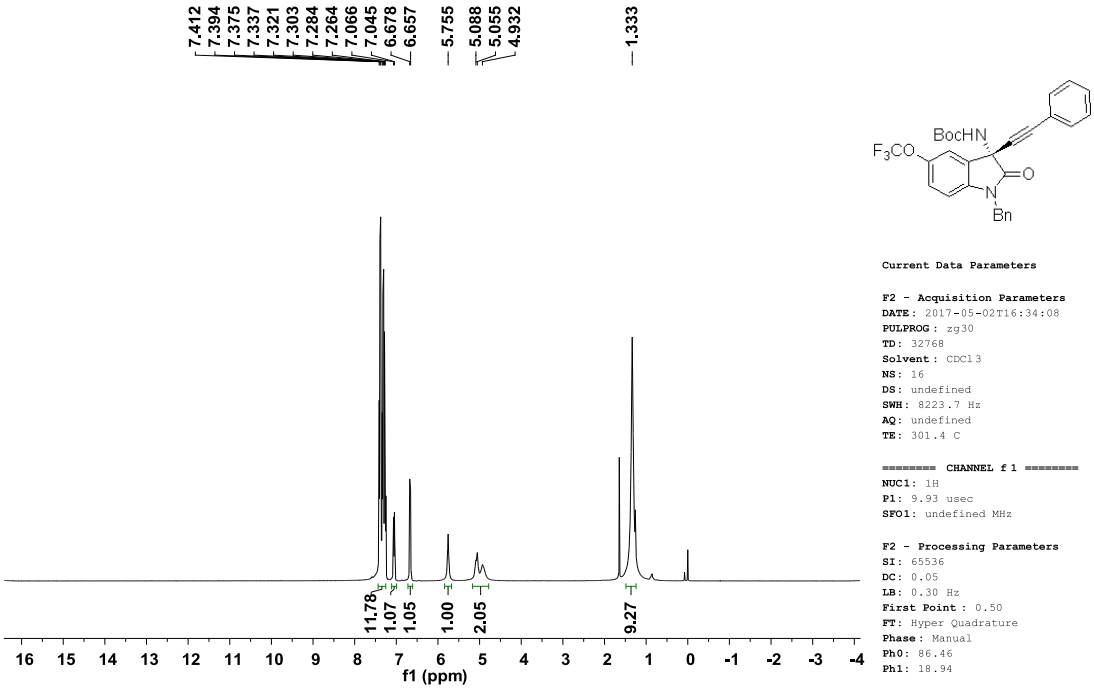
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.77, 153.29, 139.69, 135.56, 132.96, 132.06, 129.74, 129.05, 128.75, 128.26, 127.54, 127.19, 124.09, 121.50, 109.44, 85.00, 84.06, 80.96, 56.84, 44.43, 28.17, 21.14.



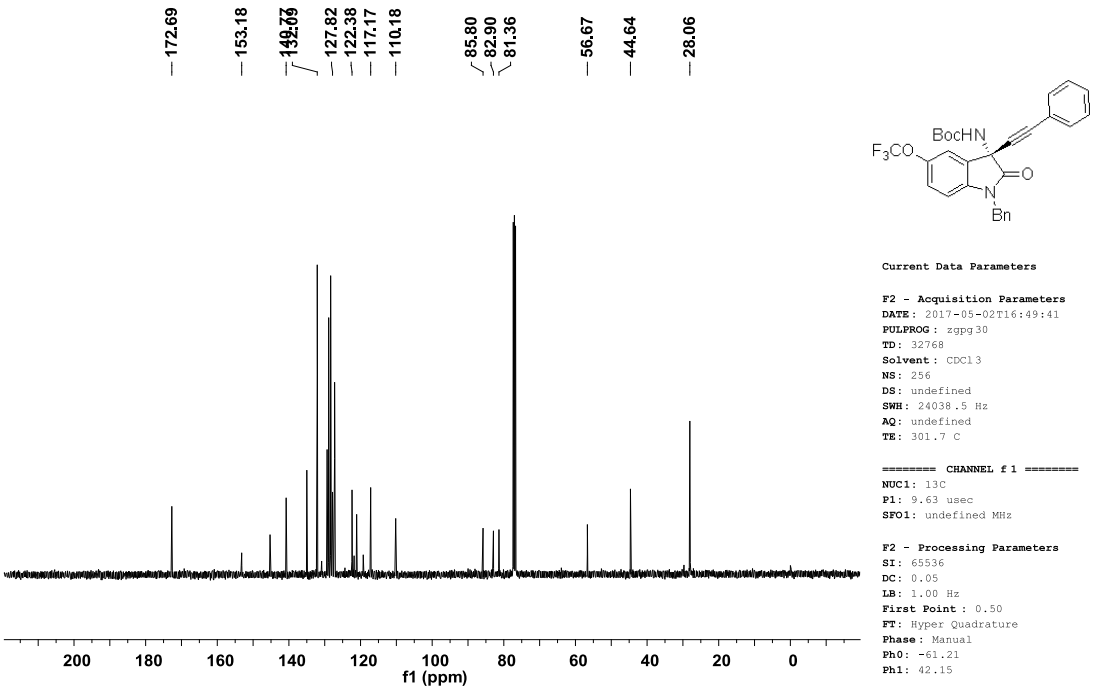
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.35 (m, 4H), 7.35 – 7.22 (m, 6H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 5.73 (s, 1H), 5.03 (s, 2H), 3.76 (s, 3H), 1.35 (s, 9H).



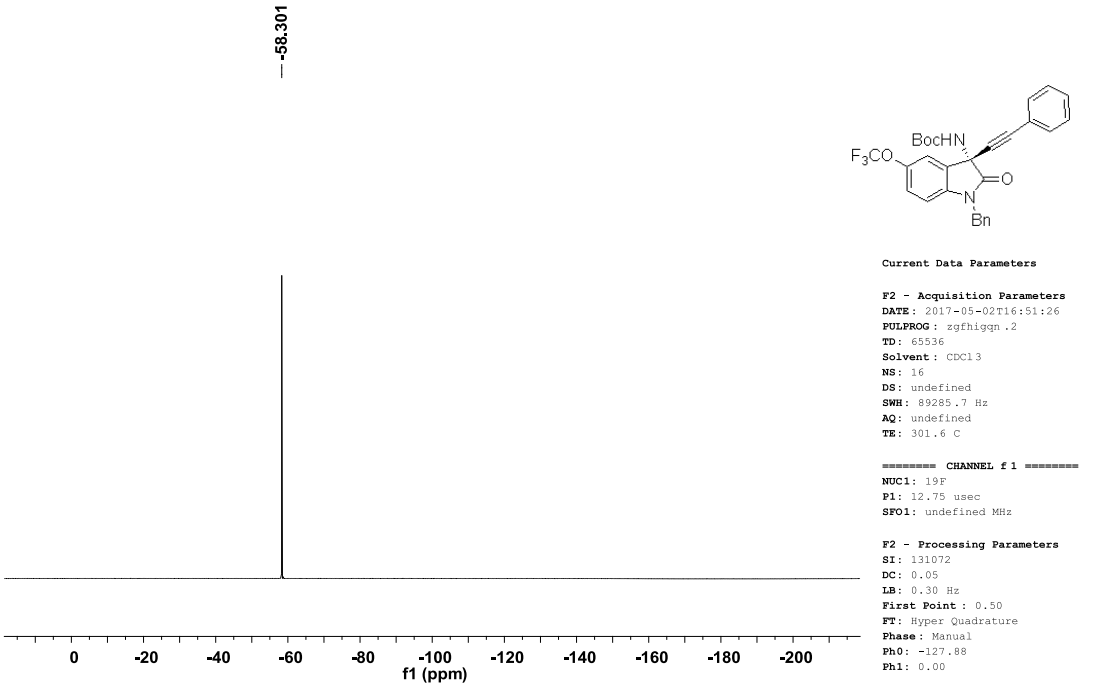
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.58, 156.47, 153.26, 135.51, 135.45, 132.06, 129.10, 128.76, 128.27, 127.56, 127.21, 121.42, 113.86, 110.16, 85.19, 83.86, 81.03, 57.03, 55.80, 44.50, 28.16.



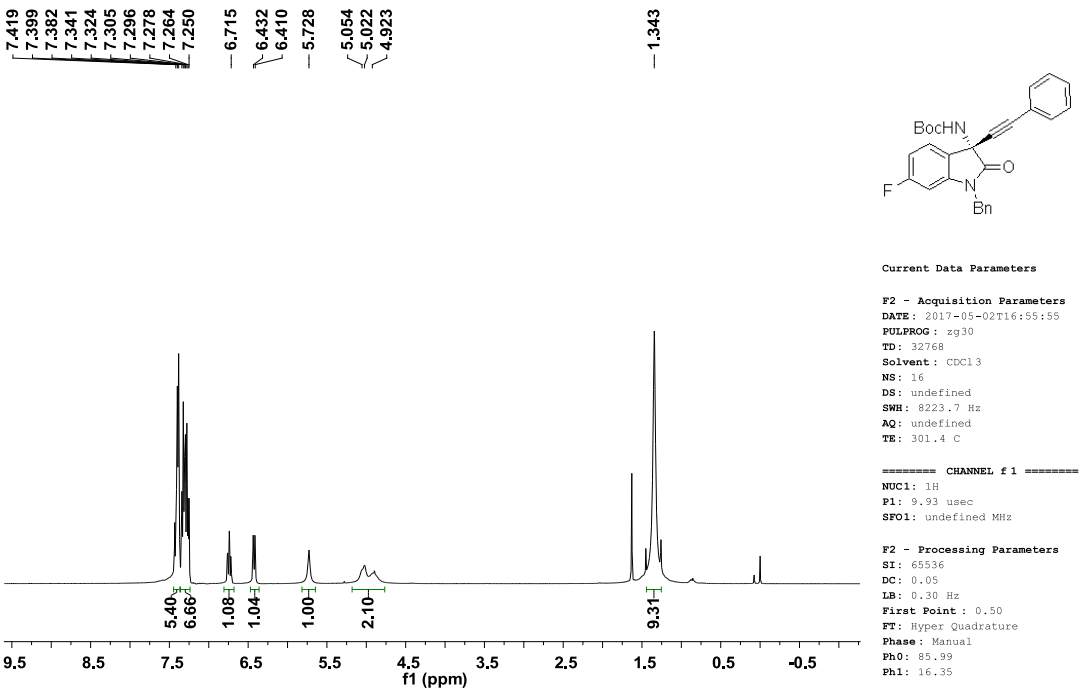
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 - 7.26 (m, , 11H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.76 (s, 1H), 5.09 - 4.93 (m, 2H), 1.33 (s, 9H).



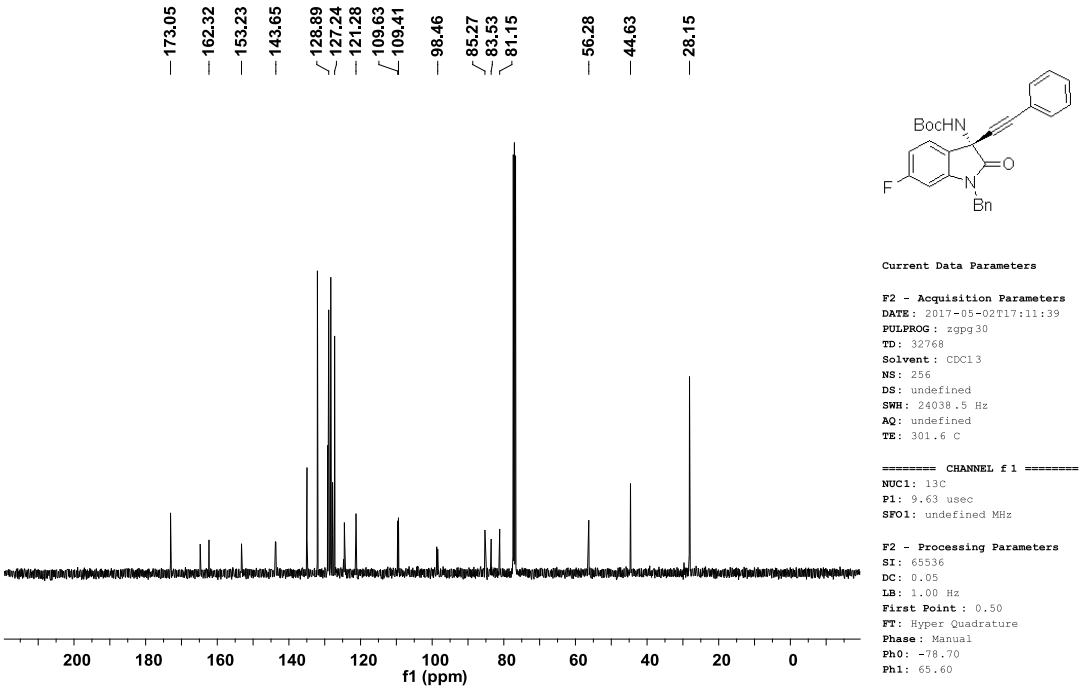
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.69, 153.18, 145.27 (m, 1C), 140.77, 135.00, 132.09 , 129.34, 128.89, 128.34, 127.82, 127.24, 122.38, 121.09, 117.17 , 110.18, 85.80, 82.90, 81.36, 56.67, 44.64, 28.06.



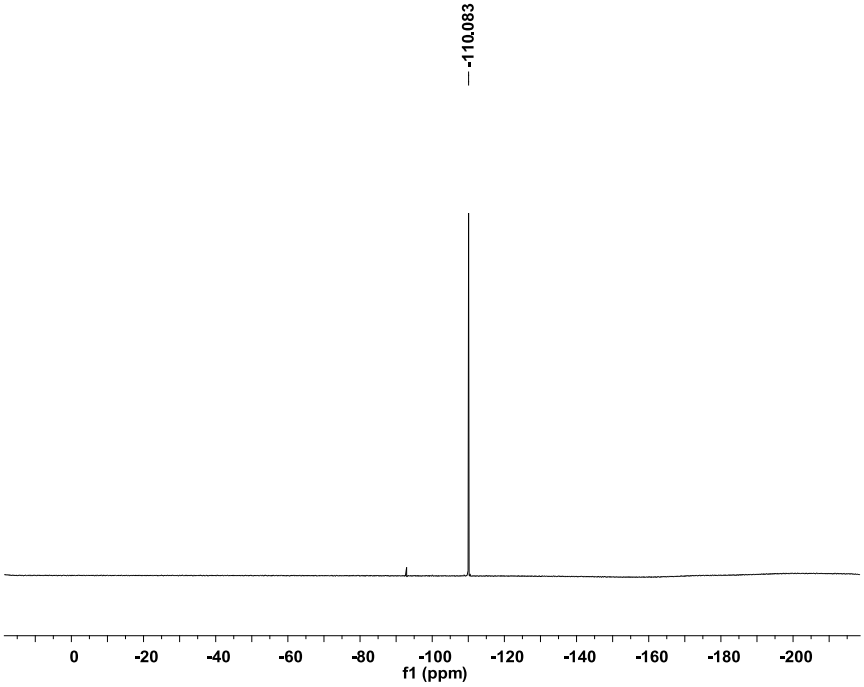
^{19}F NMR(376MHz, CDCl$_3$) δ -58.30.

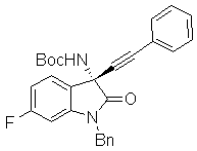


^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 - 7.38 (m, 5H), 7.36 – 7.24 (m, 6H), 6.81 – 6.68 (m, 1H), 6.42 (dd, *J* = 8.8, 1.5 Hz, 1H), 5.73 (s, 1H), 5.05 - 4.92 (m, 2H), 1.34 (s, 9H).



^{13}C NMR (101 MHz, CDCl$_3$) δ 173.05, 163.54 (d, *J* = 247.4 Hz, 1C), , 153.23, 143.71 (d, *J* = 12.1 Hz, 1C), 134.95, 132.04, 129.20, 128.89, 128.31 , 127.81, 127.24, 124.47 (d, *J* = 10.1 Hz, 1C), 121.28, 109.52 (d, *J* = 22.2 Hz, 2C),), 98.59 (d, *J* = 27.3 Hz, 1C), 85.27, 83.53, 81.15, 56.28, 44.63, 28.15.





Current Data Parameters

F2 - Acquisition Parameters
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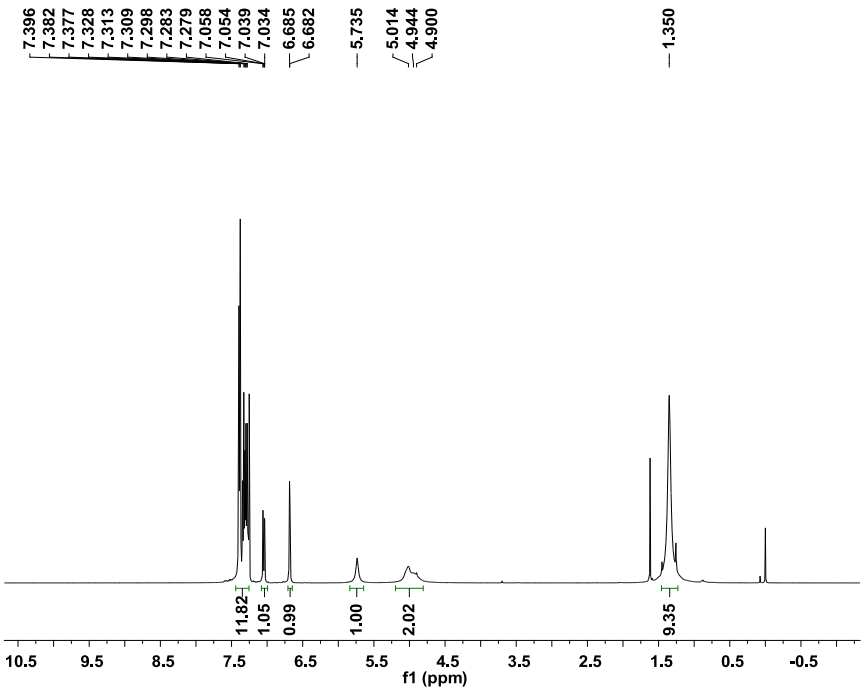
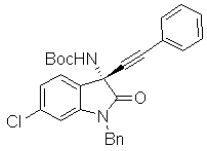
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 301.4 C

======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -30.41
Ph1: 0.00

^{19}F NMR (376 MHz, CDCl$_3$) δ -110.08.





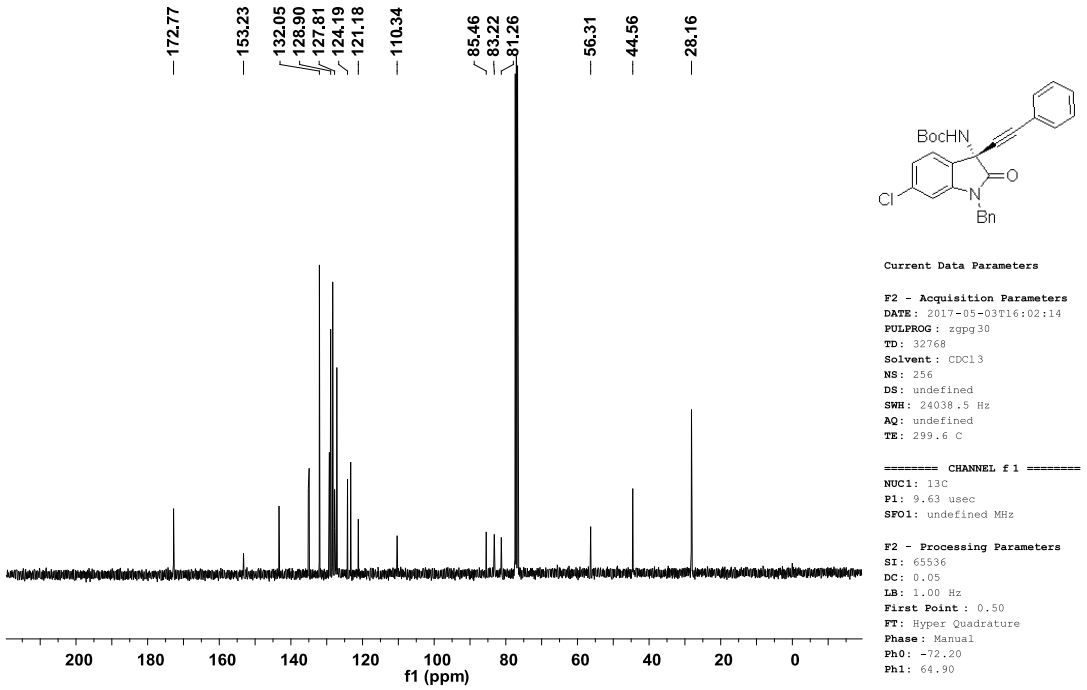
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-05-03T15:46:41
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.1 C

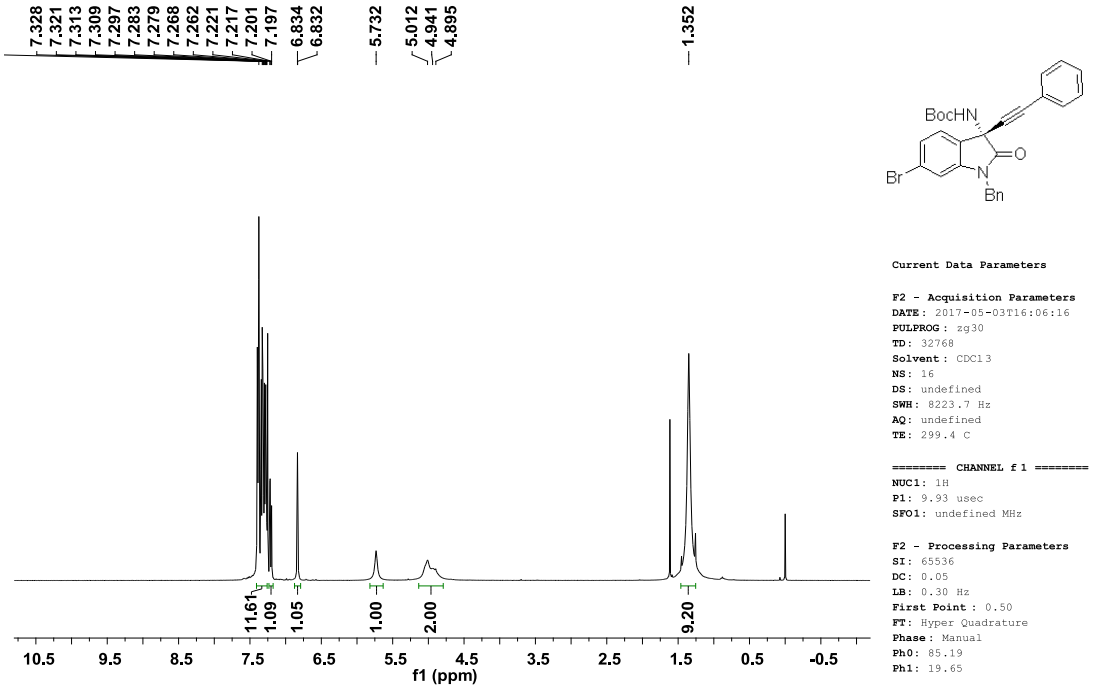
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 87.23
Ph1: 18.55

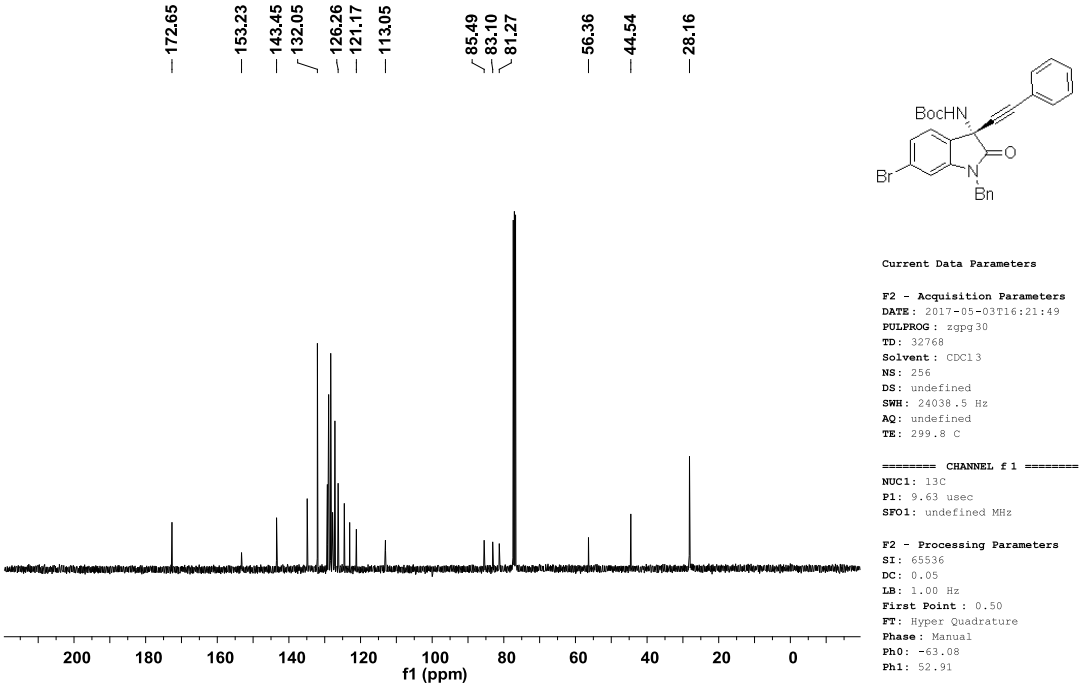
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.25 (m, 11H), 7.05 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.68 (d, *J* = 1.3 Hz, 1H), 5.74 (s, 1H), 5.20 – 4.81 (m, 2H), 1.35 (s, 9H).



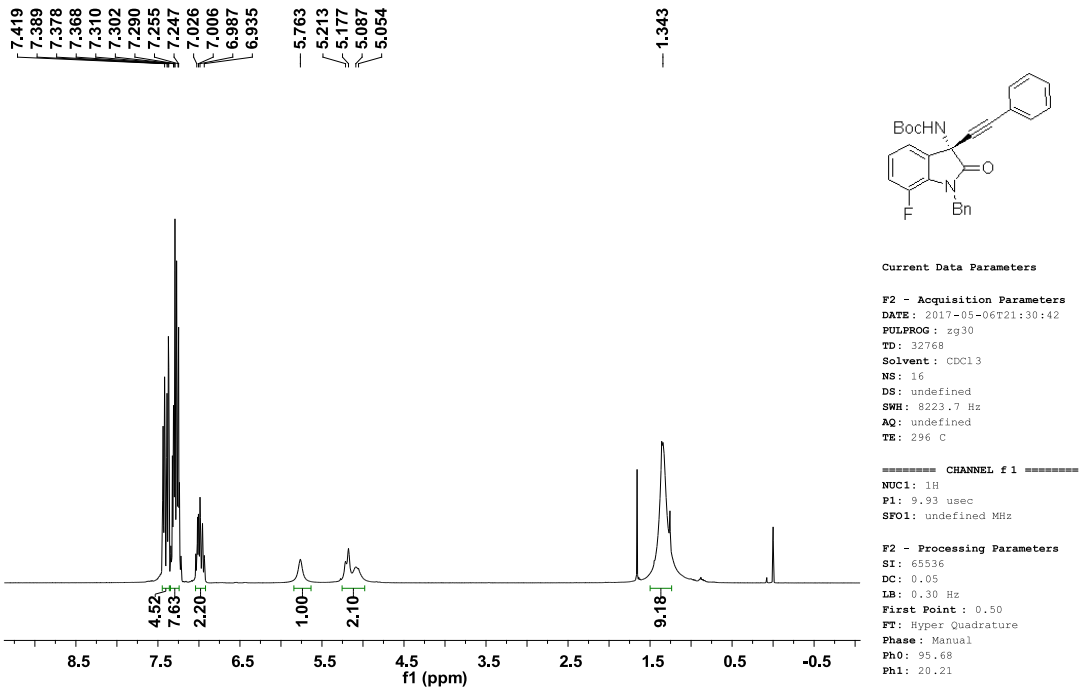
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.77, 153.23, 135.14, 134.91, 132.05, 129.25, 128.90, 128.32, 127.81, 127.17, 124.19, 123.31, 121.18, 110.34, 85.46, 83.22, 81.26, 56.31, 44.56, 28.16.



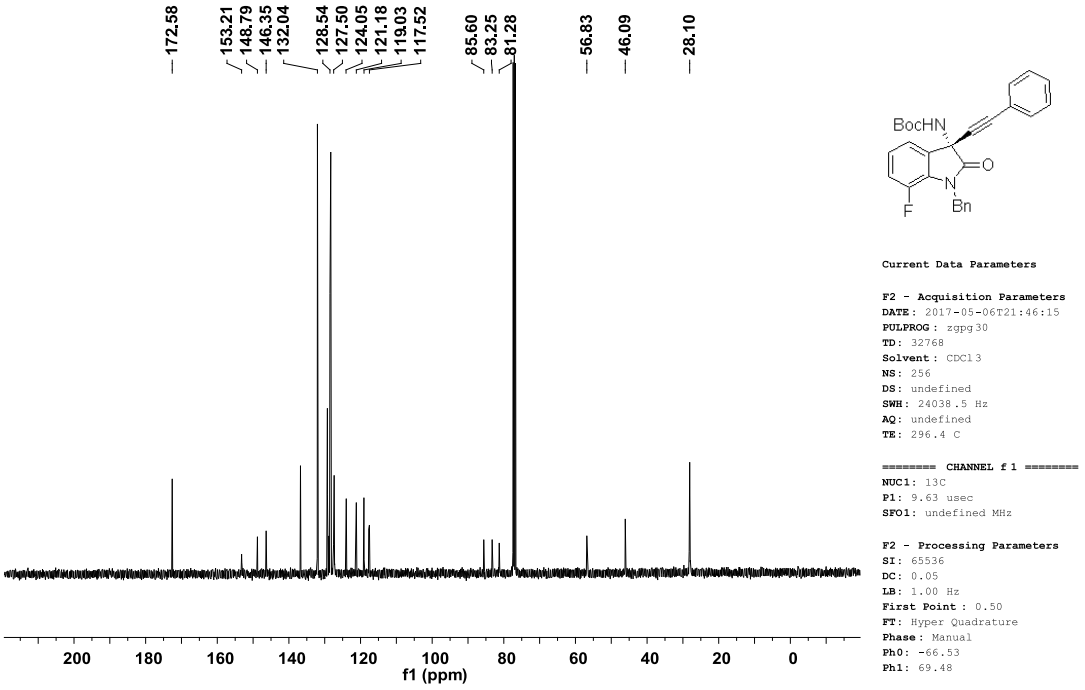
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.26 (m, 11H), 7.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.83 (d, *J* = 1.0 Hz, 1H), 5.73 (s, 1H), 5.14 – 4.79 (m, 2H), 1.35 (s, 9H).



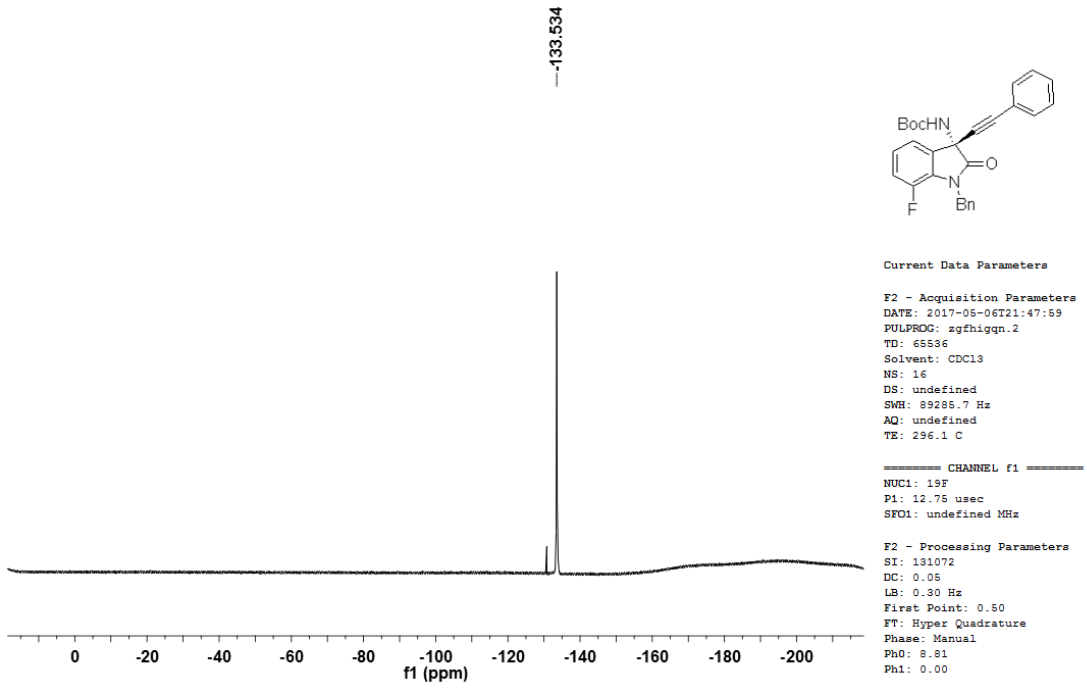
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.65, 153.23, 143.45, 134.89, 132.05, 129.26, 128.90, 128.33, 127.81, 127.16, 126.26, 124.53, 123.03, 121.17, 113.05, 85.49, 83.10, 81.27, 56.36, 44.54, 28.16.



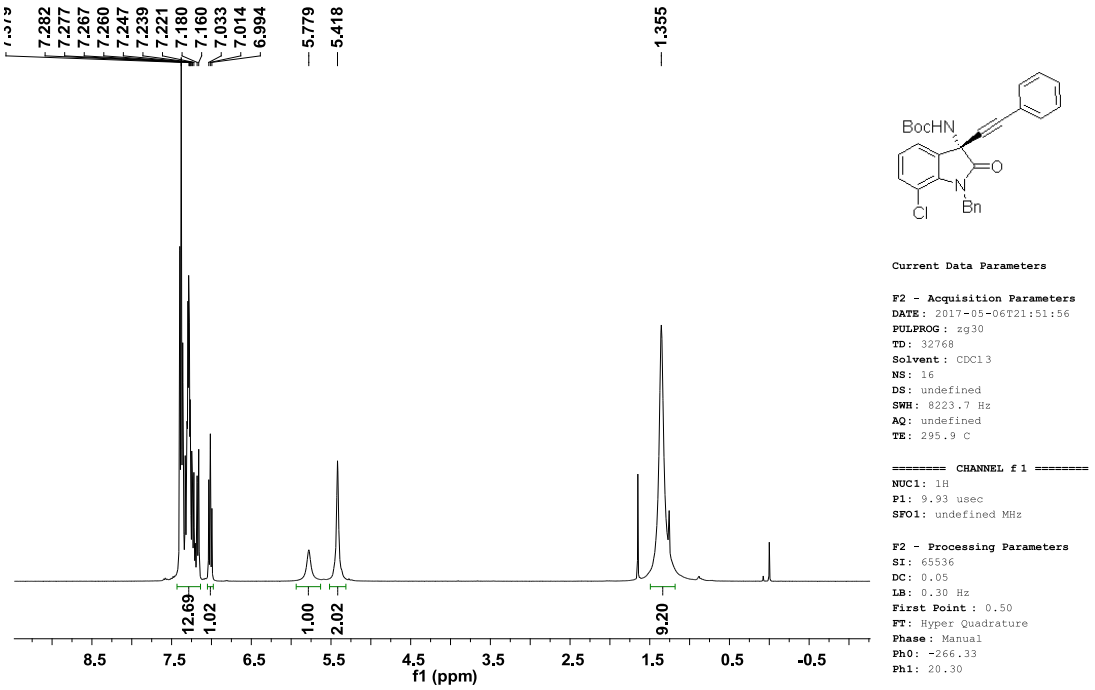
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 - 7.37 (m, 4H), 7.35 – 7.24 (m, 7H), 7.04 – 6.92 (m, 2H), 5.76 (s, 1H), 5.25 - 4.97 m, 2H), 1.34 (s, 9H).



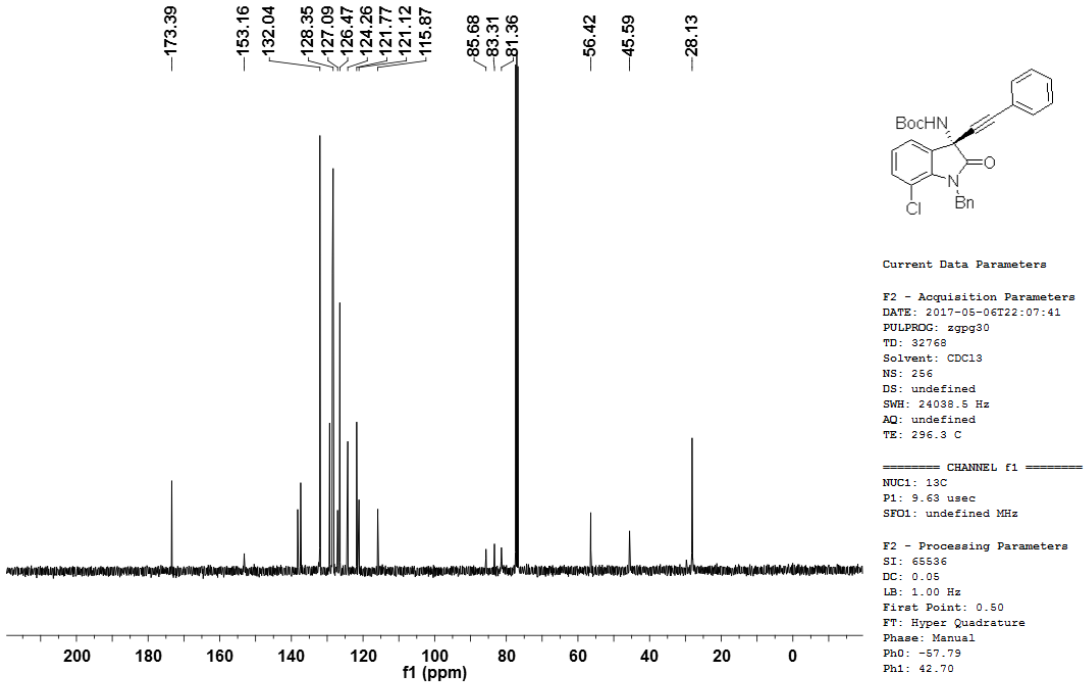
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.58 , 153.21, 147.57 (d, J = 246.4 Hz, 1C), 136.77, 132.04, 129.26, 128.84 (d, J = 9.1 Hz, 1C), 128.54, 128.32, 127.50, 127.37, 124.02 (d, J = 6.1 Hz, 1C), 121.18, 119.05 (d, J = 3.0 Hz, 1C), 117.62 (d, J = 19.1 Hz, 2C), 85.60, 83.25, 81.28, 56.83, 46.09, 28.10.



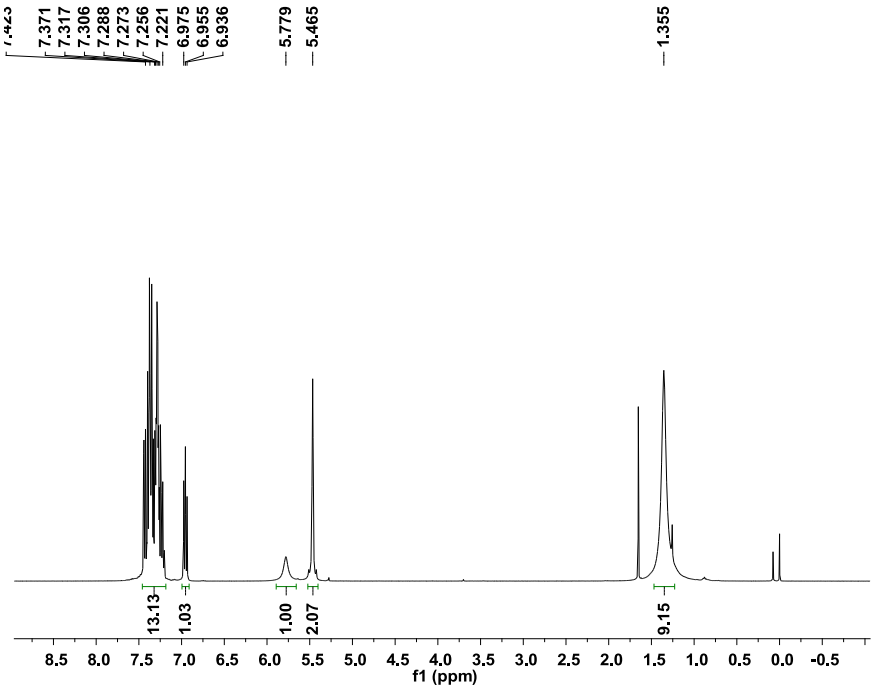
^{19}F NMR (376 MHz, CDCl$_3$) δ -133.53.



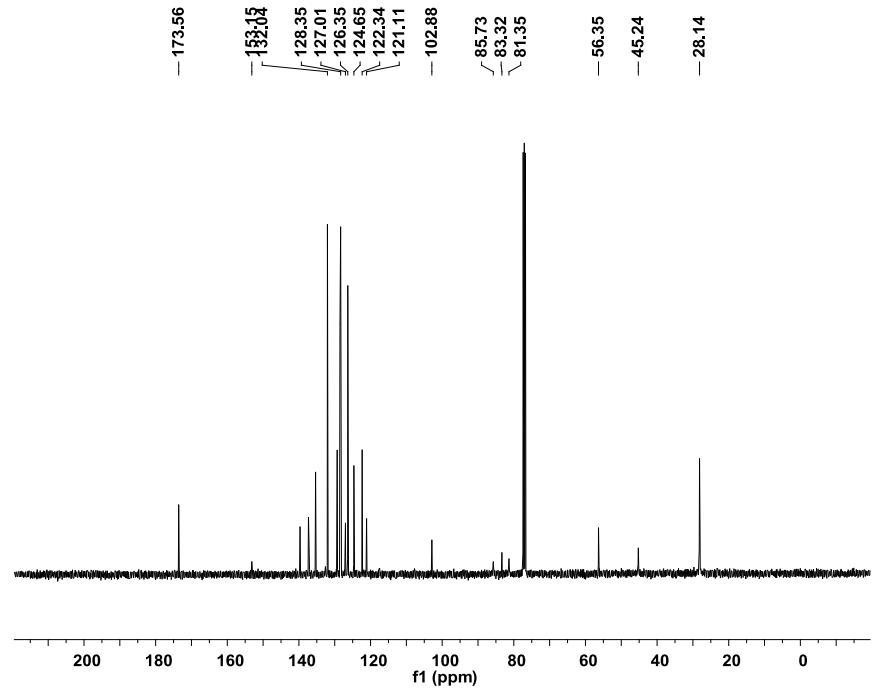
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.14 (m, 12H), 7.01 (t, J = 7.8 Hz, 1H), 5.78 (s, 1H), 5.42 (s, 2H), 1.35 (s, 9H).



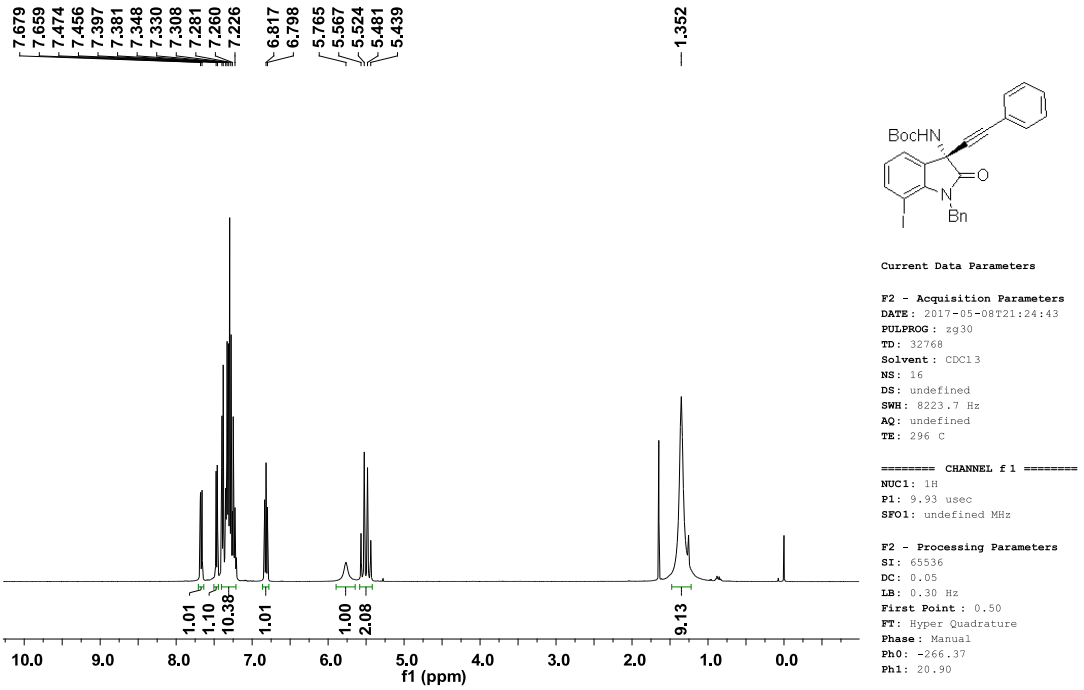
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.39, 153.16, 138.24, 137.40, 132.04,131.98, 129.31, 128.54, 128.35, 127.09, 126.47, 124.26, 121.77, 121.12, 115.87, 85.68, 83.31, 81.36, 56.42, 45.59, 28.13.



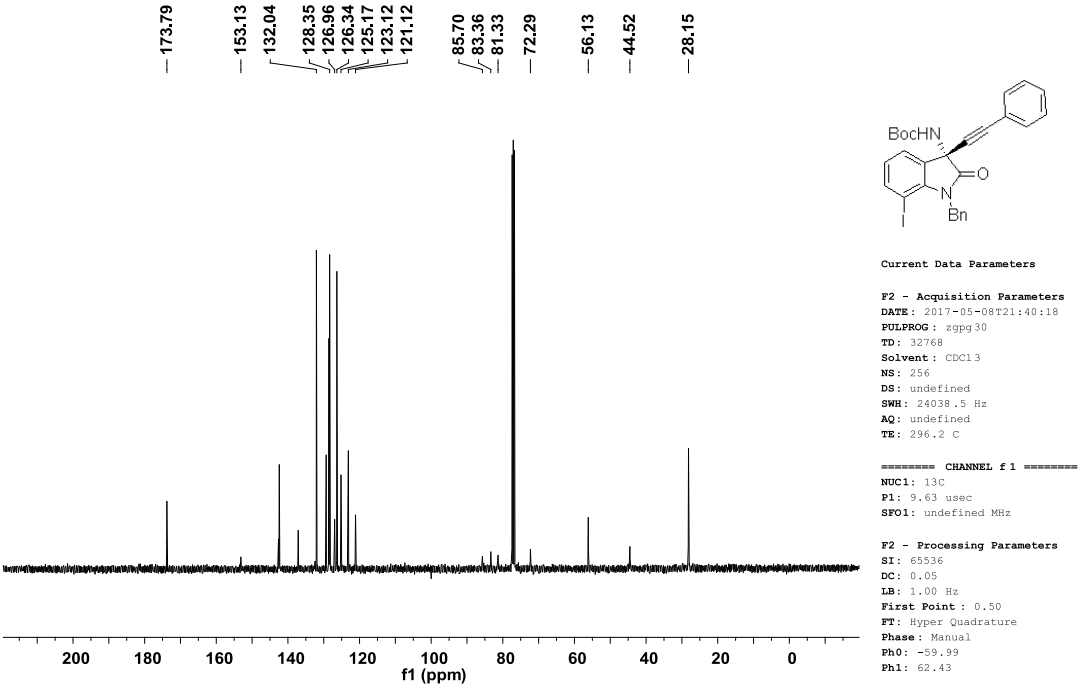
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 – 7.18 (m, 12H), 7.00 – 6.91 (m, 1H), 5.78 (s, 1H), 5.47 (s, 2H), 1.35 (s, 9H).



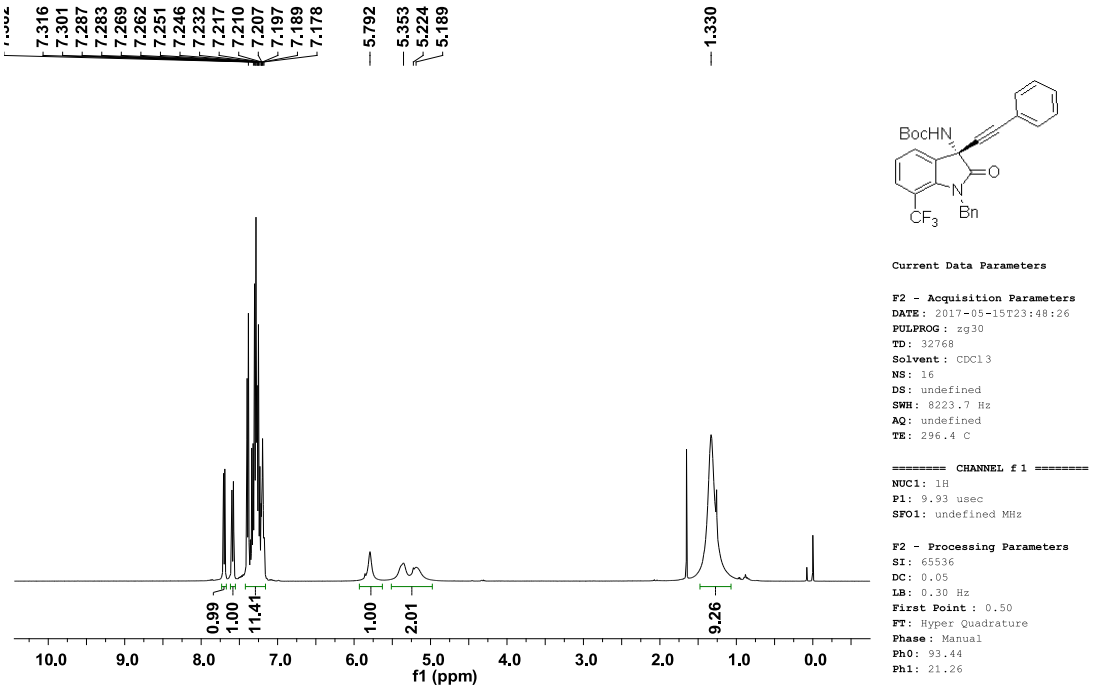
^{13}C NMR (101 MHz, CDCl$_3$) δ 173.56, 153.15, 139.68, 137.33, 135.35, 132.04, 129.31, 128.54, 128.35, 127.01, 126.35, 124.65, 122.34, 121.11, 102.88, 85.73, 83.32, 81.35, 56.35, 45.24, 28.14.



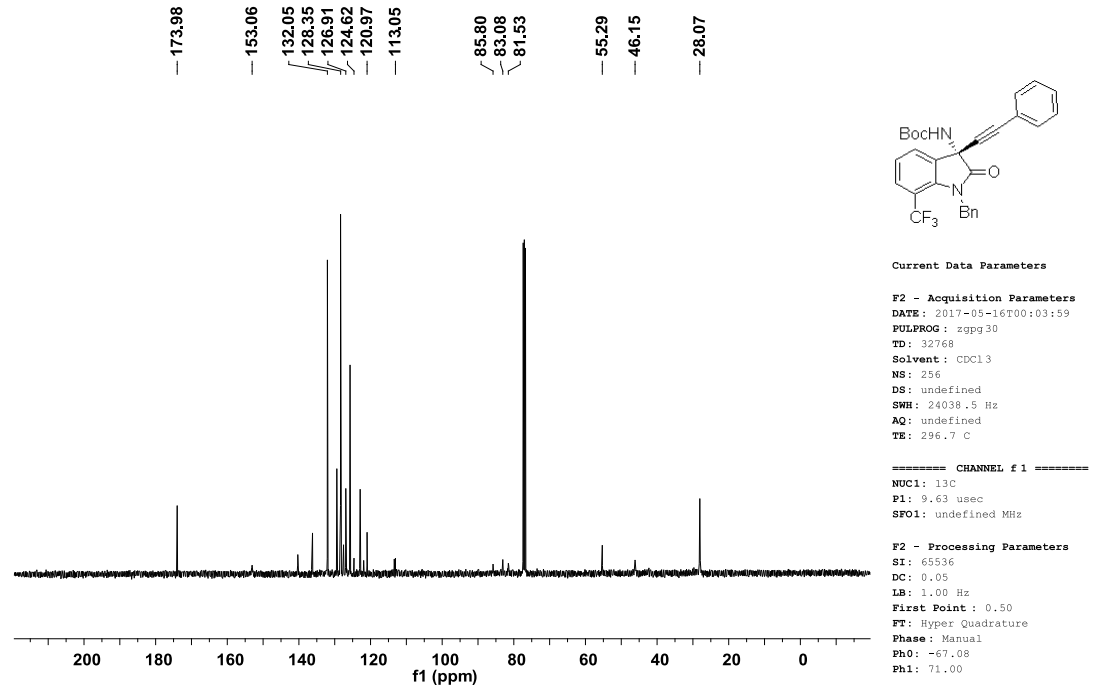
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.1, 1.0 Hz, 1H), 7.47 (dd, J = 7.3, 1.2 Hz, 1H), 7.40 – 7.21 (m, 10H), 6.82 (t, J = 7.7 Hz, 1H), 5.77 (s, 1H), 5.50 (q, J = 17.0 Hz, 2H), 1.35 (s, 9H).



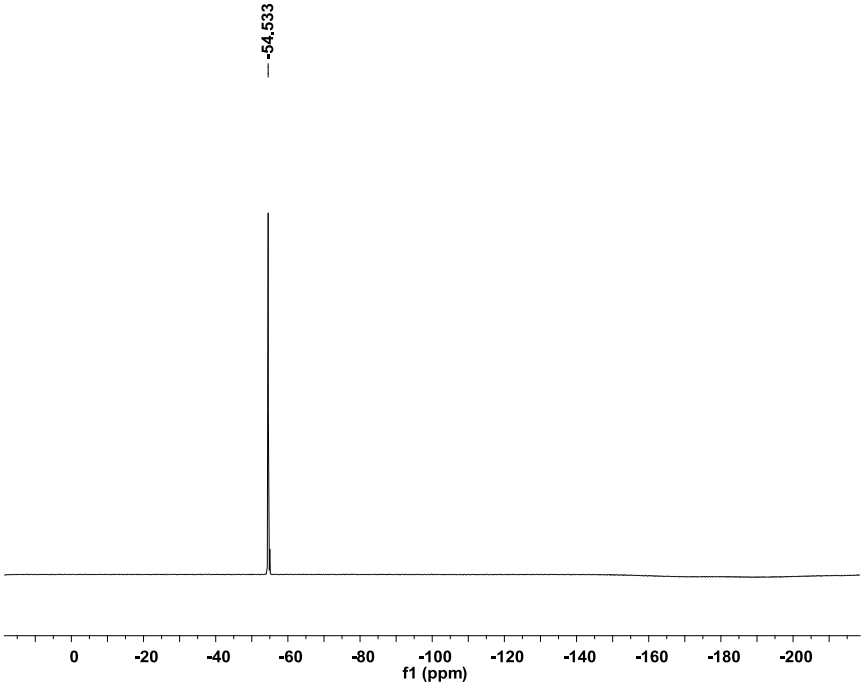
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.79, 153.13, 142.61, 142.41, 137.12, 132.04, 129.31, 128.57, 128.35, 126.96, 126.34, 125.17, 123.12, 121.12, 85.70, 83.36, 81.33, 72.29, 56.13, 44.52, 28.15.

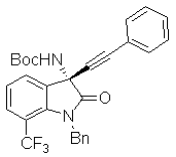


^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.67 (m, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.16 (m, 11H), 5.79 (s, 1H), 5.51 – 4.98 (m, 2H), 1.33 (s, 9H).



^{13}C NMR (101 MHz, CDCl$_3$) δ 173.98, 153.06, 140.31, 136.20, 132.05, 129.41, 128.37, 128.35, 127.60, 126.91, 125.72, 124.62 , 122.90, 121.91, 120.97 , 113.05, 85.80, 83.08, 81.53, 55.29, 46.15, 28.07.





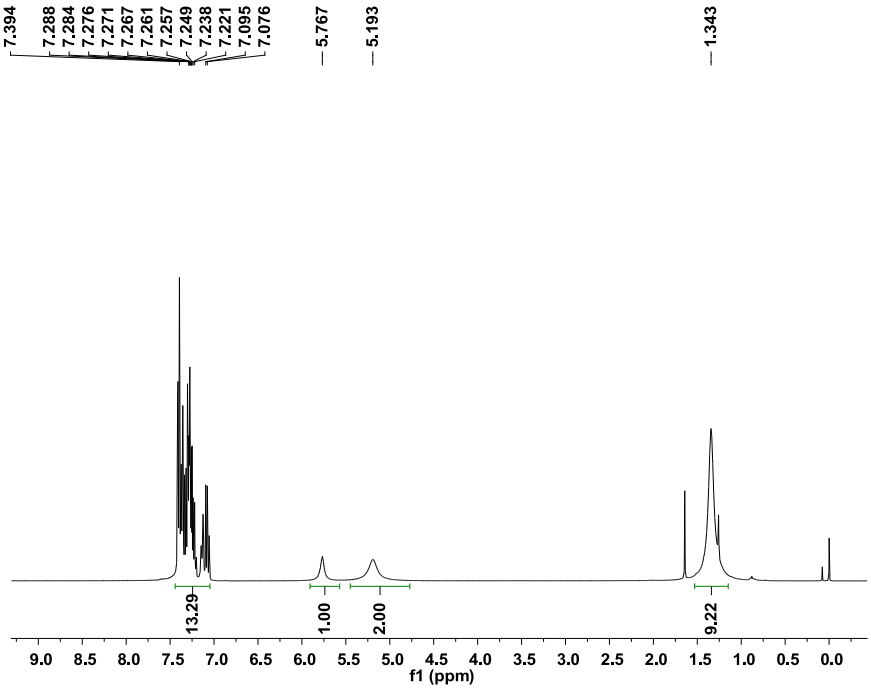
Current Data Parameters

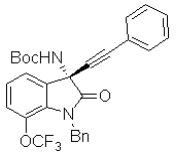
F2 - Acquisition Parameters
DATE: 2017-05-16T00:05:27
PULPROG: zgflqn
TD: 65536
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 296.5 C

======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -132.63
Ph1: 0.00

^{19}F NMR(376MHz, CDCl) δ -54.53.





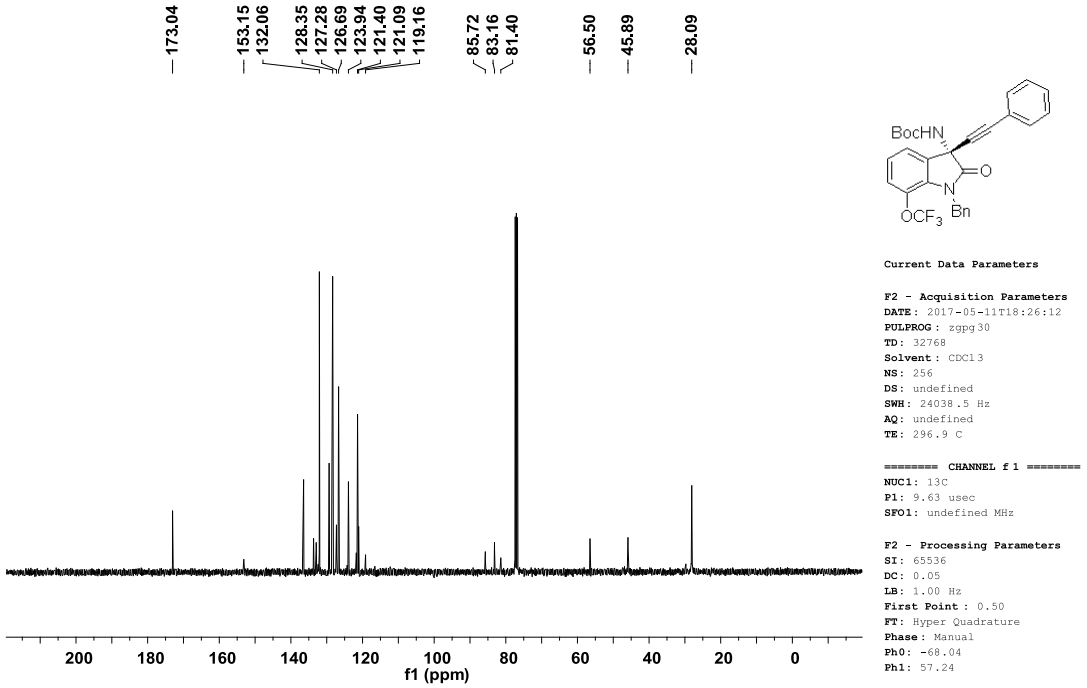
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-05-11T18:10:37
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.6 C

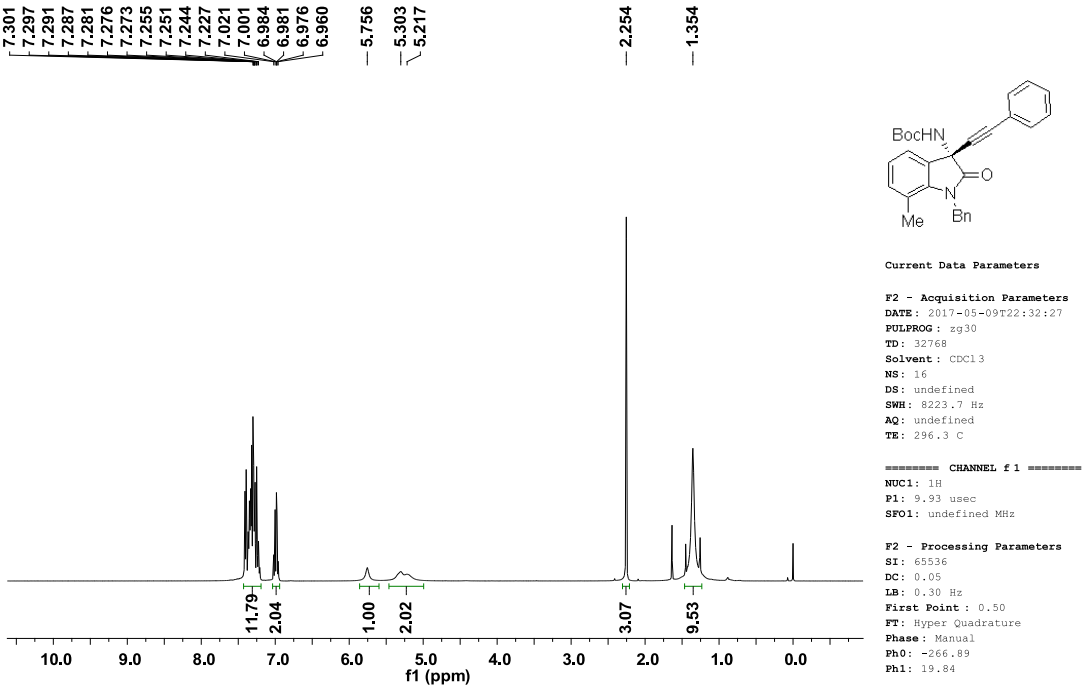
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -267.76
Ph1: 21.98

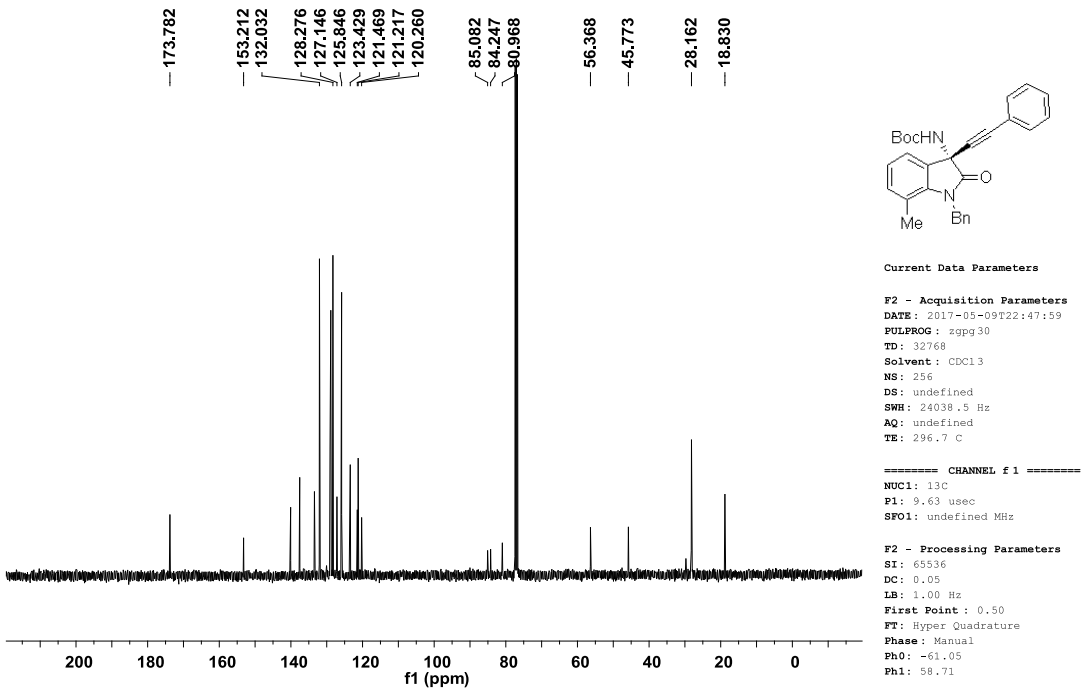
^{1}H NMR(400MHz, CDCl) δ 7.44– 7.05 (m, 13H), 5.77 (s, 1H), 5.19 (s, 2H), 1.34 (s, 9H).



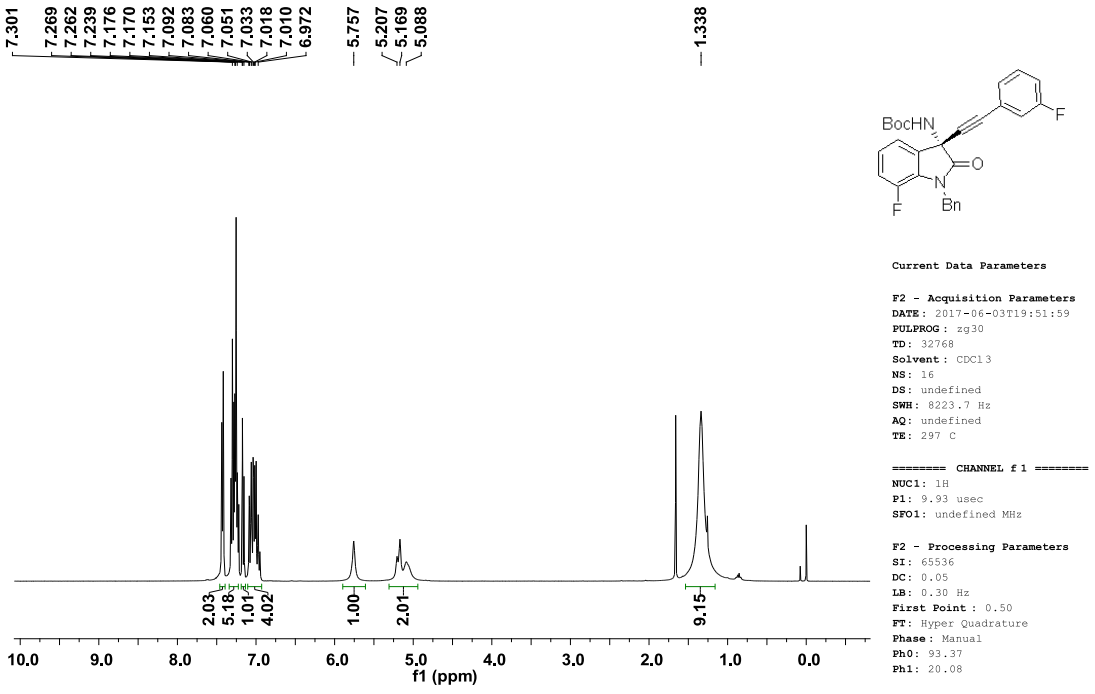
^{13}C NMR (101 MHz, CDCl$_3$) δ 173.04, 153.15, 136.45, 133.68 (m, 1C), 132.94, 132.06, 129.33, 128.47, 128.35, 127.28, 126.69, 123.94, 121.40, 121.09, 119.16, 85.72, 83.16, 81.40, 56.50, 45.89, 28.09.



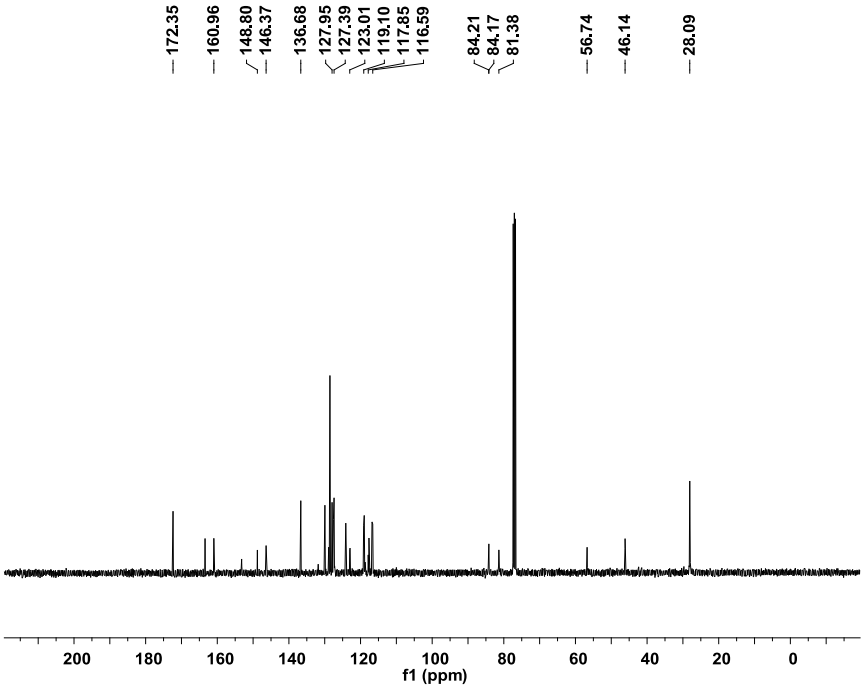
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.19 (m, 11H), 7.04 – 6.94 (m, 2H), 5.76 (s, 1H), 5.45 - 4.99 (m, 2H), 2.25 (s, 3H), 1.35 (s, 9H).



^{13}C NMR (101 MHz, CDCl$_3$) δ 173.78, 153.21, 140.07, 137.54, 133.43, 132.03, 129.08, 128.86, 128.28, 127.15, 125.85, 123.43, 121.47, 121.22, 120.26, 85.08, 84.25, 80.97, 56.37, 45.77, 28.16, 18.83.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 7.4 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.19 - 7.13 (m, 1H), 7.11 – 6.93 (m, 4H), 5.76 (s, 1H), 5.31 - 4.94 (m, 2H), 1.34 (s, 9H).



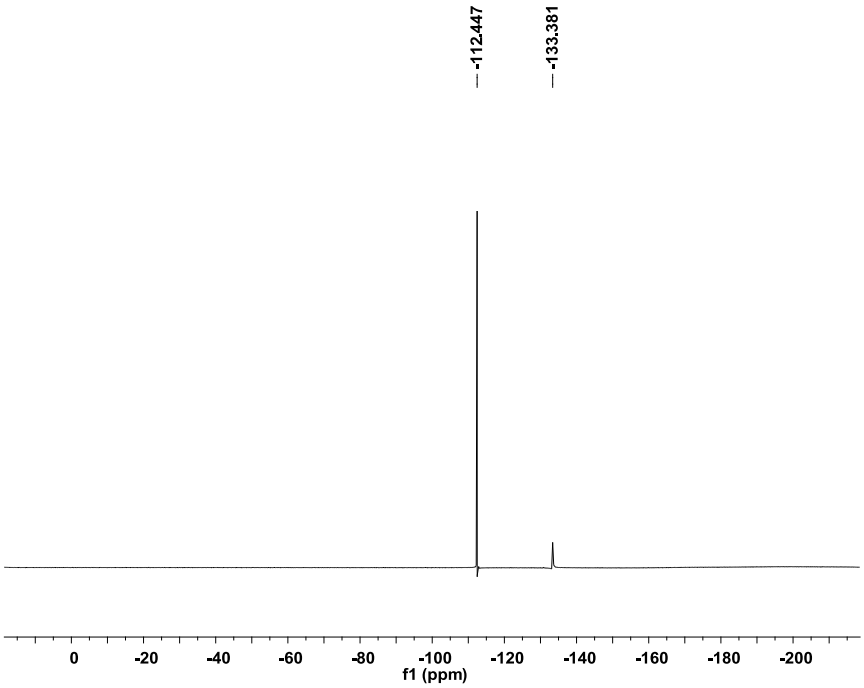
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-06-03T20:07:31
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.2 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -57.60
Ph1: 56.67

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.35, 162.18 (d, J = 247.4 Hz, 1C), 153.20, 147.58 (d, J = 245.4 Hz, 1C), 136.68, 130.00 (d, J = 9.1 Hz, 1C), 128.86 (d, J = 9.1 Hz, 1C), 128.55, 127.94 (d, J = 3.0 Hz, 1C), 127.57, 127.39, 124.09 (d, J = 6.1 Hz, 1C), 122.97 (d, J = 9.1 Hz, 1C), 119.12 (d, J = 4.0 Hz, 1C), 118.86 (d, J = 23.2 Hz, 1C), 117.75 (d, J = 20.2 Hz, 1C), 116.70 (d, J = 21.2 Hz, 2C), 84.21, 84.17, 81.38, 56.74, 46.14, 28.09.



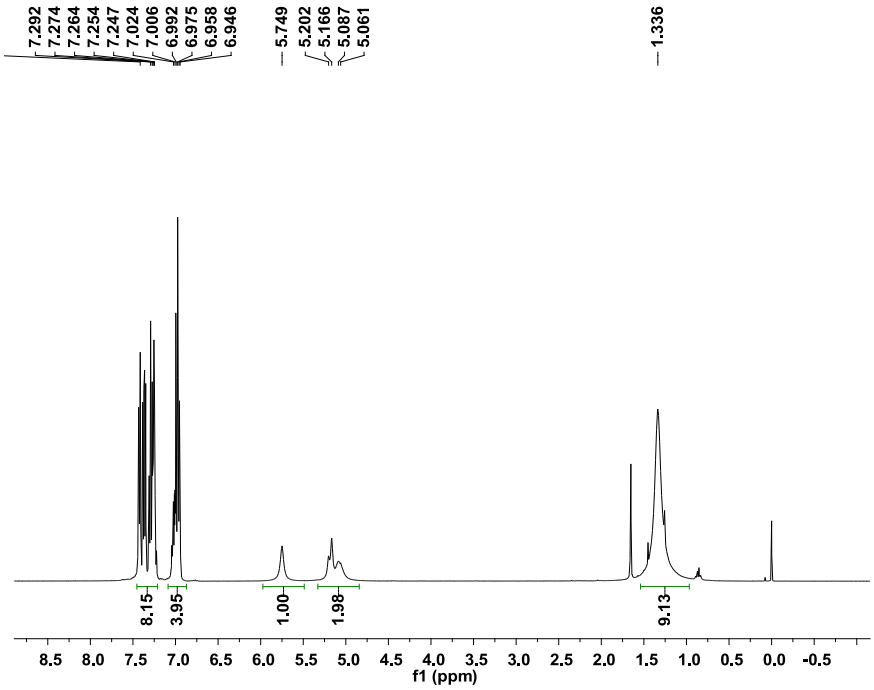
Current Data Parameters

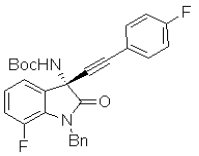
F2 - Acquisition Parameters
DATE: 2017-06-03T20:09:14
PULPROG: zgfhigqn.2
TD: 65536
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 297.1 C

======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -6.72
Ph1: 0.00

^{19}F NMR (376 MHz, CDCl$_3$) δ -112.45, -133.38.





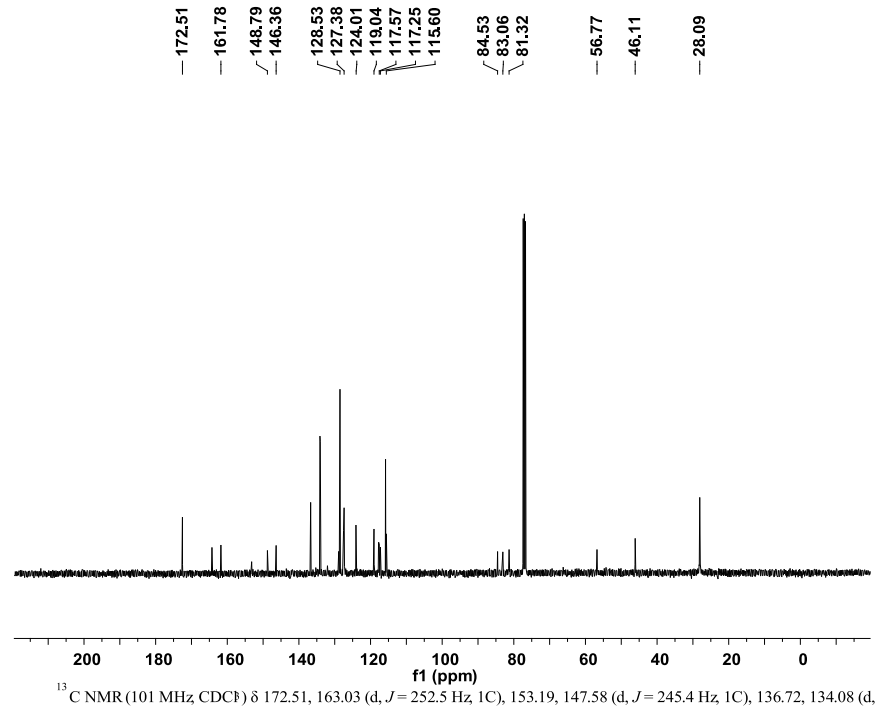
Current Data Parameters

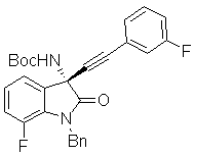
F2 - Acquisition Parameters
DATE: 2017-06-05T10:02:58
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.8 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.32
Ph1: 20.54

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.21 (m, 8H), 7.09 – 6.87 (m, 4H), 5.75 (s, 1H), 5.33 - 4.84 (m, 2H), 1.34 (s, 9H).





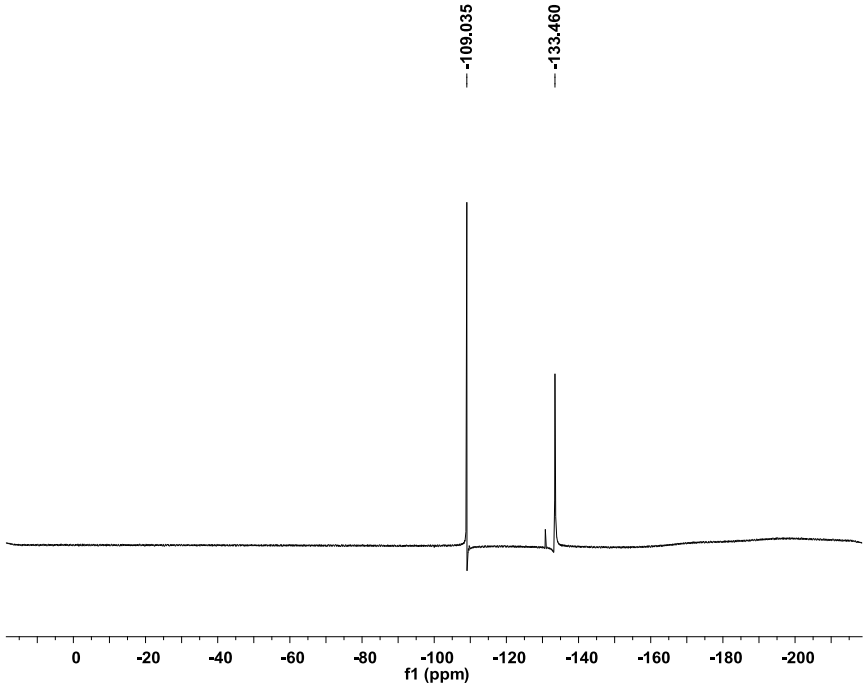
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-06-05T10:18:30
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.1 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -62.71
Ph1: 58.18

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.51, 163.03 (d, J = 252.5 Hz, 1C), 153.19, 147.58 (d, J = 245.4 Hz, 1C), 136.72, 134.08 (d, J = 9.1 Hz, 1C), 128.84 (d, J = 9.1 Hz, 1C), 128.53, 127.53, 127.38, 124.04 (d, J = 7.1 Hz, 1C), 119.05 (d, J = 3.0 Hz, 1C), 117.67 (d, J = 19.2 Hz, 2C), 117.27 (d, J = 3.0 Hz, 1C), 115.71 (d, J = 22.2 Hz, 2C), 84.53, 83.06, 81.32, 56.77, 46.11, 28.09.



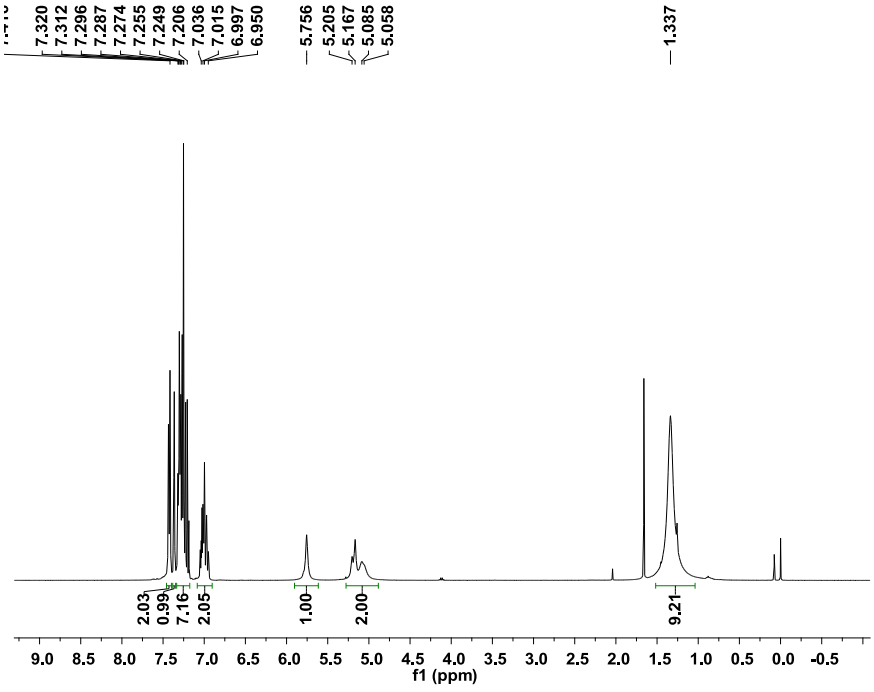
Current Data Parameters

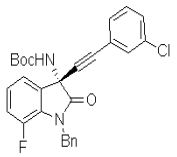
F2 - Acquisition Parameters
DATE: 2017-06-05T10:20:16
PULPROG: zgfhigqn.2
TD: 65536
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 296.9 C

======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -0.54
Ph1: 0.00

^{19}F NMR (376 MHz, CDCl$_3$) δ -109.04, -133.46.





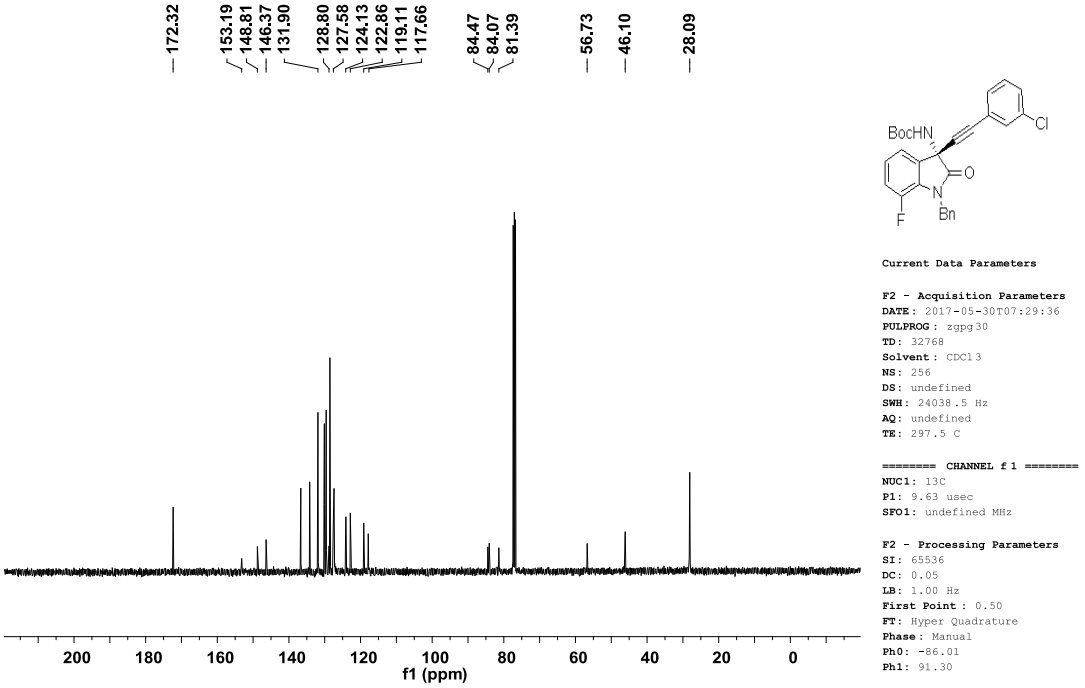
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-05-30T07:14:03
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.3 C

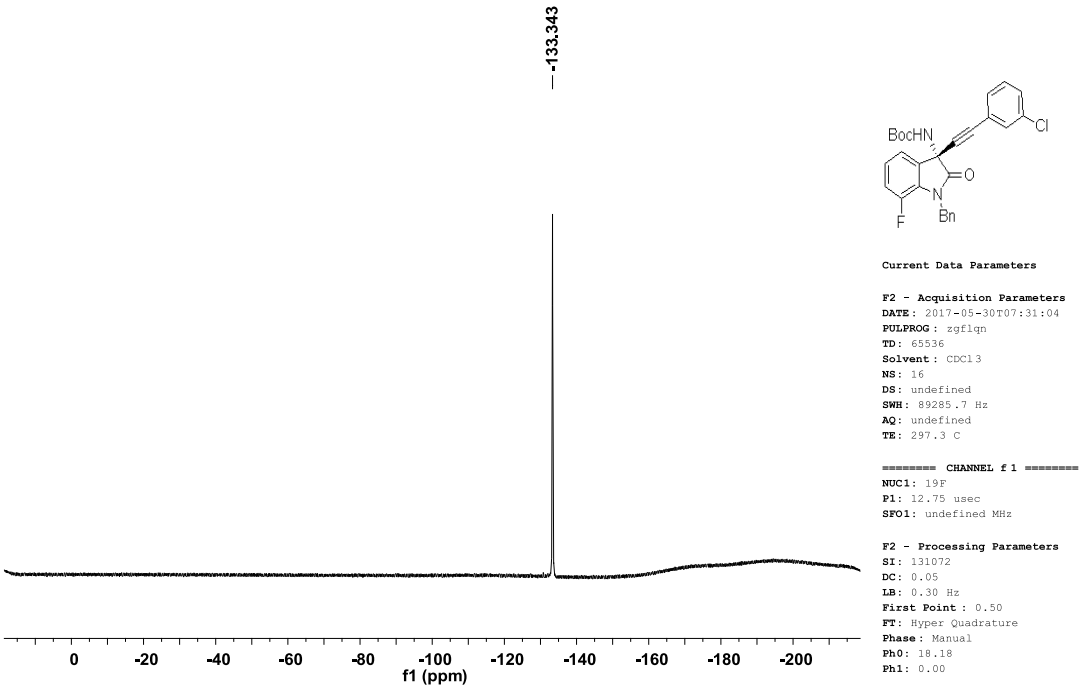
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 94.72
Ph1: 20.23

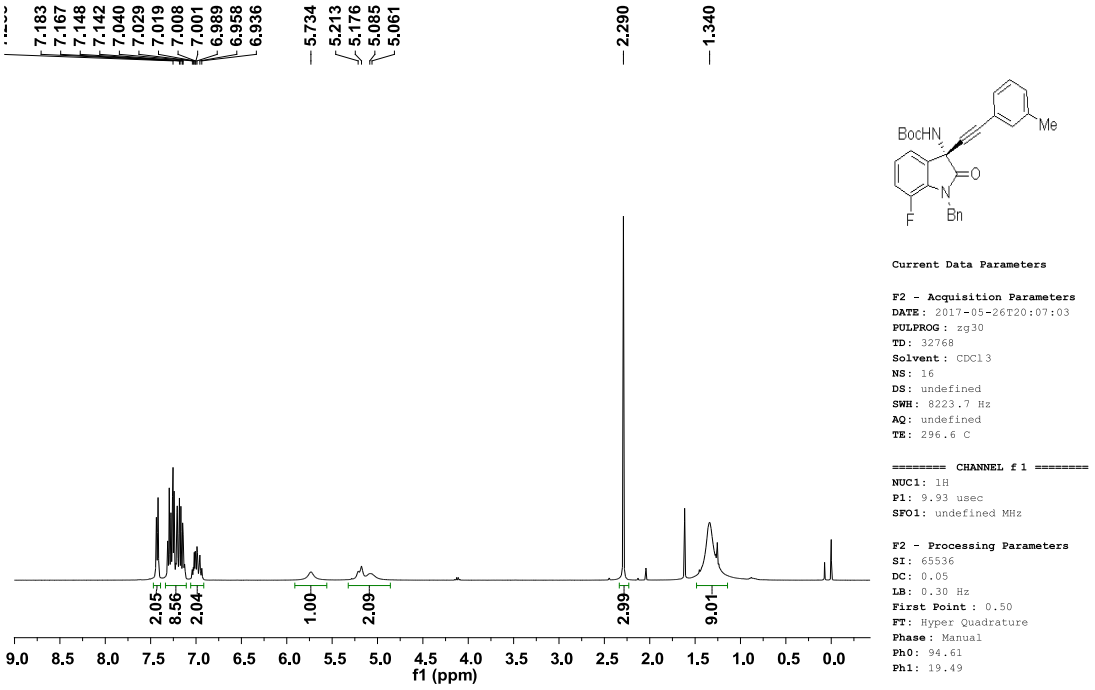
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.33 – 7.18 (m, 7H), 7.08 – 6.90 (m, 2H), 5.76 (s, 1H), 5.28 - 4.89 (m, 2H), 1.34 (s, 9H).



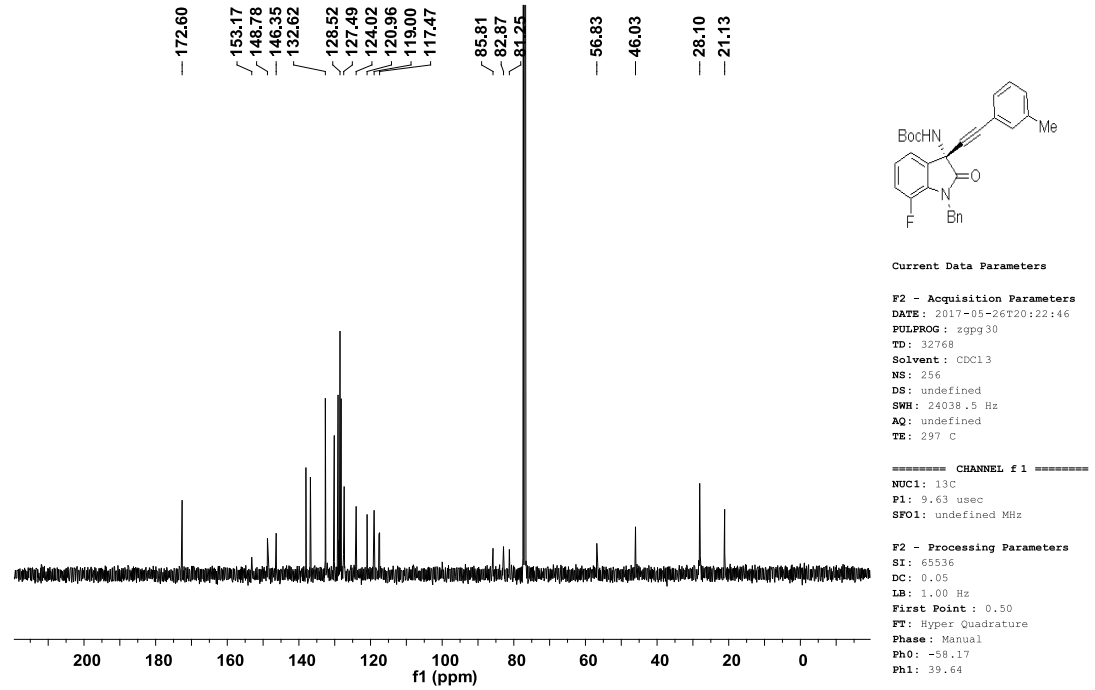
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.32, 153.19, 147.59 (d, J = 246.4 Hz, 1C), 136.68, 134.20, 131.90, 129.59, 129.56, 128.85 (d, J = 9.1 Hz, 1C), 128.56, 127.58, 127.40, 124.10 (d, J = 6.1 Hz, 1C), 122.86, 119.12 (d, J = 3.1 Hz, 1C), 117.76 (d, J = 19.1 Hz, 2C), 84.47, 84.07, 81.39, 56.73 , 46.10 , 28.09.



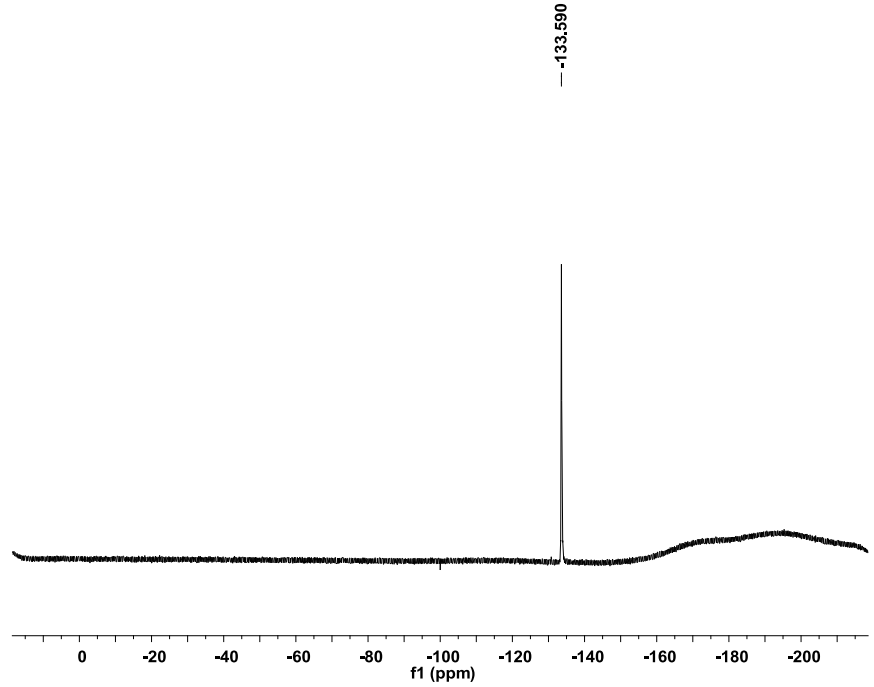
^{19}F NMR (376 MHz, CDCl$_3$) δ -133.34.



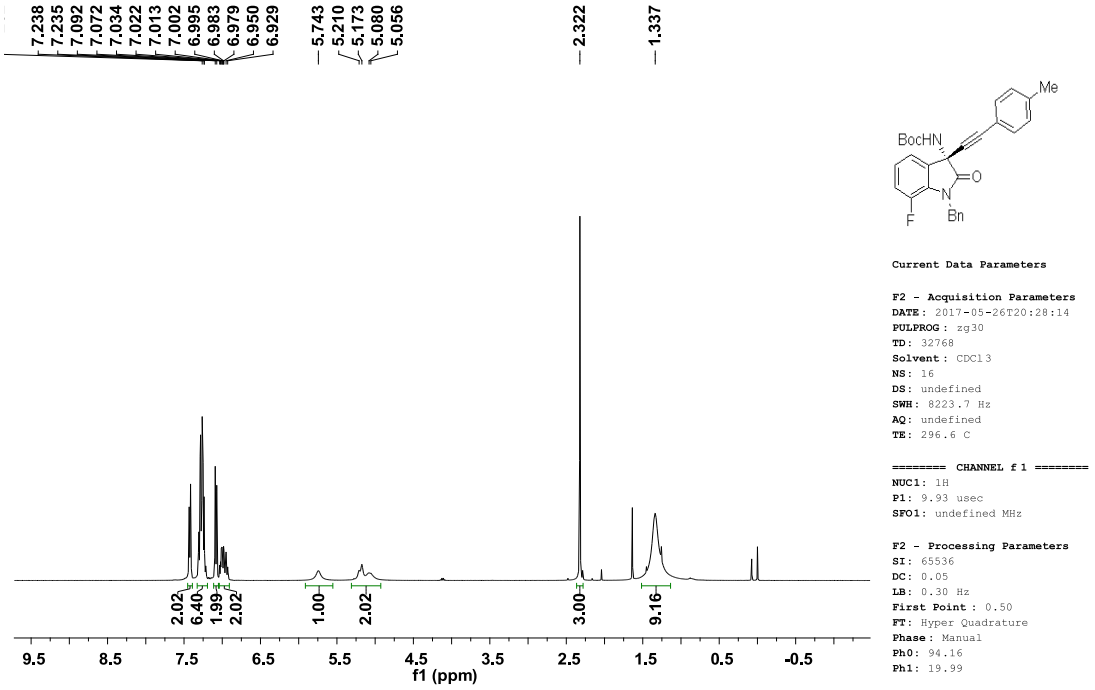
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.11 (m, 9H), 7.06 - 6.91 (m, 2H), 5.73 (s, 1H), 5.32 - 4.86 (m, 2H), 2.29 (s, 3H), 1.34 (s, 9H).



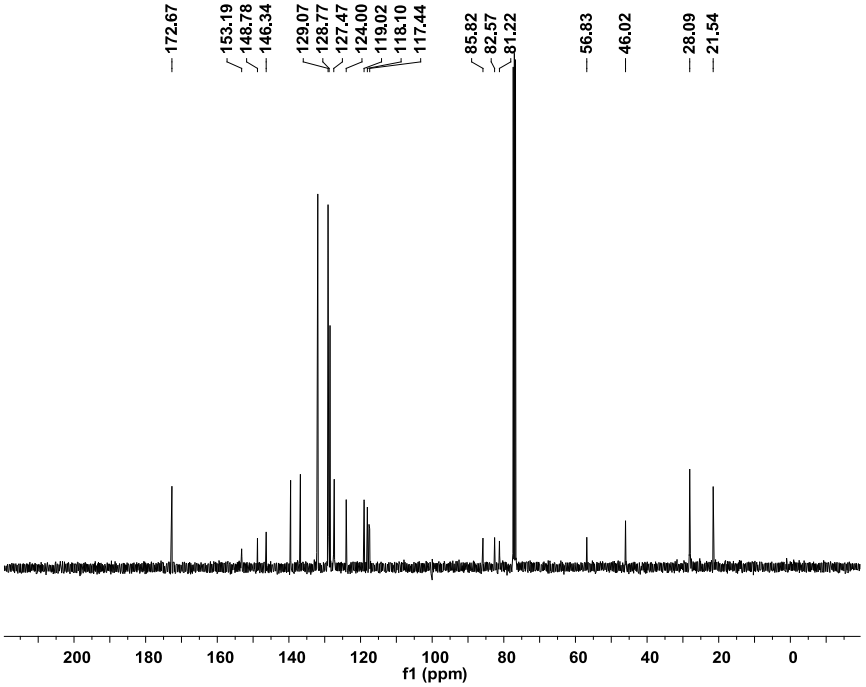
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.60, 153.17, 147.56 (d, *J* =245.4 Hz, 1C), 138.04, 136.79, 132.62, 130.13, 129.07, 128.82 (d, *J* = 9.1 Hz, 1C), 128.52, 128.20, 127.49, 127.37, 123.98 (d, *J* = 7.0 Hz, 1C), 120.96, 119.01 (d, *J* = 3.0 Hz,1C), 117.57 (d, *J* = 20.2 Hz, 2C), 85.81, 82.87, 81.25, 56.83, 46.03, 28.10, 21.13 .



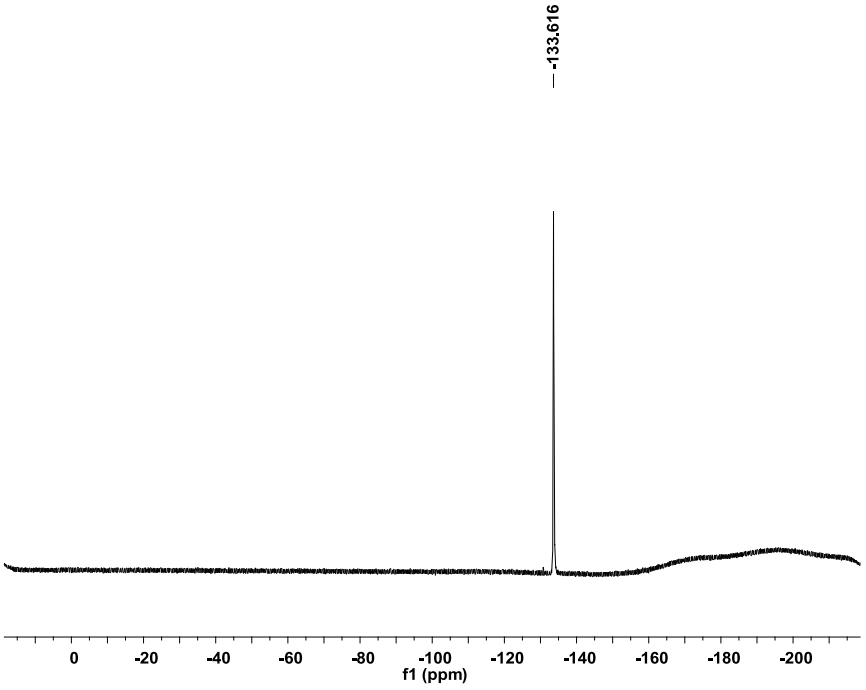
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.59.



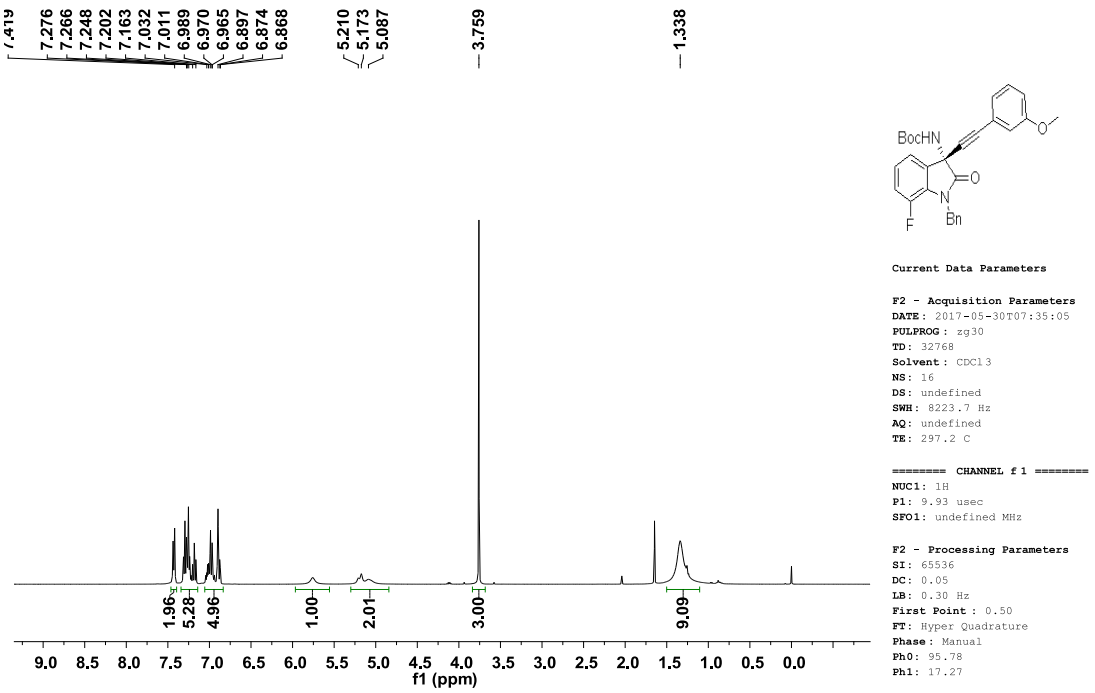
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.32 - 7.19 (m, 6H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.91 (m, 2H), 5.74 (s, 1H), 5.31 - 4.93 (m, 2H), 2.32 (s, 3H), 1.34 (s, 9H).



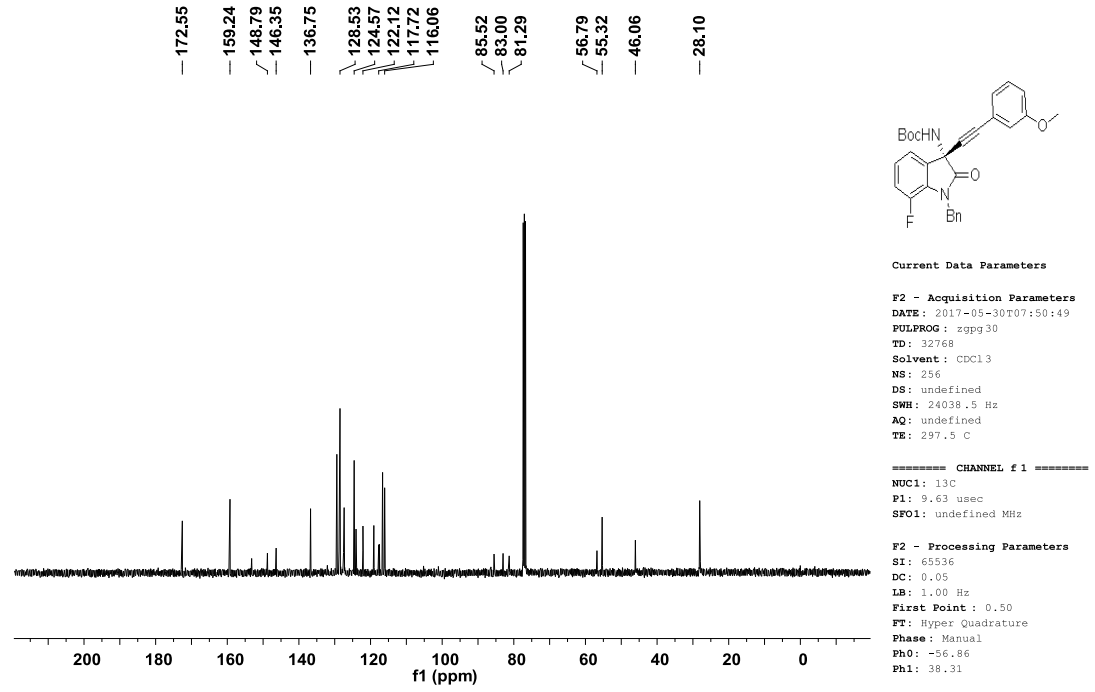
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.67, 153.19, 147.56 (d, J = 246.44 Hz, 1C), 139.52, 136.80, 131.94, 129.07, 128.82 (d, J = 9.1 Hz,1C), 128.52, 127.47, 127.35, 123.97 (d, J = 6.1 Hz, 1C), 119.01 (d, J = 3.0 Hz,1C), 118.10 , 117.54 (d, J = 20.2 Hz, 2C), 85.82, 82.57, 81.22, 56.83, 46.02, 28.09 , 21.54.



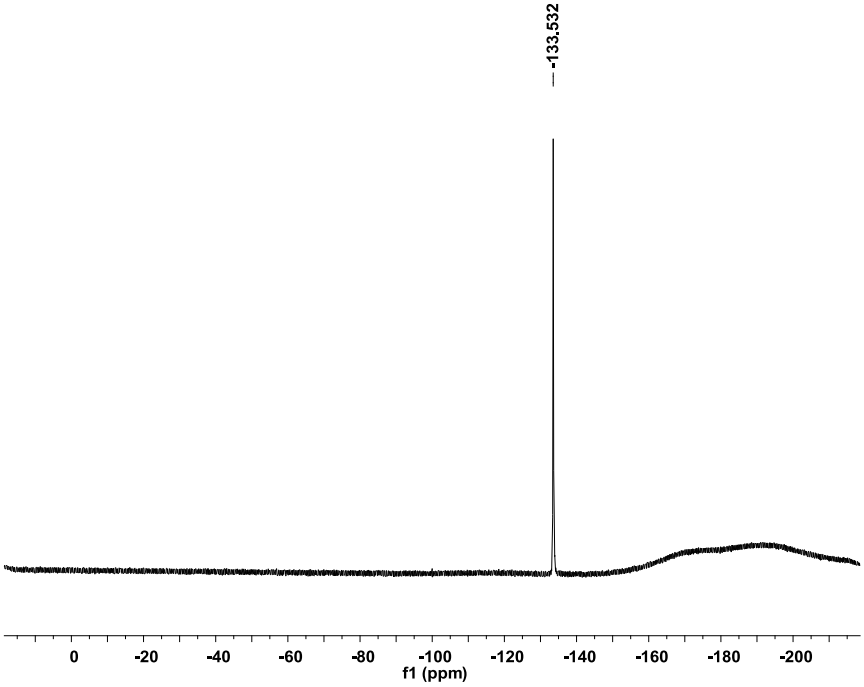
^{19}F NMR (376 MHz, CDCl$_3$) δ -133.62.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 7.4 Hz, 2H), 7.34 – 7.14 (m, 5H), 7.06 – 6.83 (m, 5H), 5.76 (s, 1H), 5.30 - 4.84 (m, 2H), 3.76 (s, 3H), 1.34 (s, 9H).



^{13}C NMR (101 MHz, CDCl$_3$) δ 172.55, 159.24, 153.19, 147.57 (d, J = 246.4 Hz, 1C), 136.75, 129.41, 128.85 (d, J = 10.1 Hz, 1C), 128.53, 127.51, 127.37, 124.57, 124.02 (d, J = 6.1 Hz, 1C), 122.12, 119.06 (d, J = 3.1 Hz, 1C), 117.62 (d, J = 20.2 Hz, 2C), 116.64, 116.06, 85.52, 83.00, 81.29, 56.79, 55.32, 46.06, 28.10.



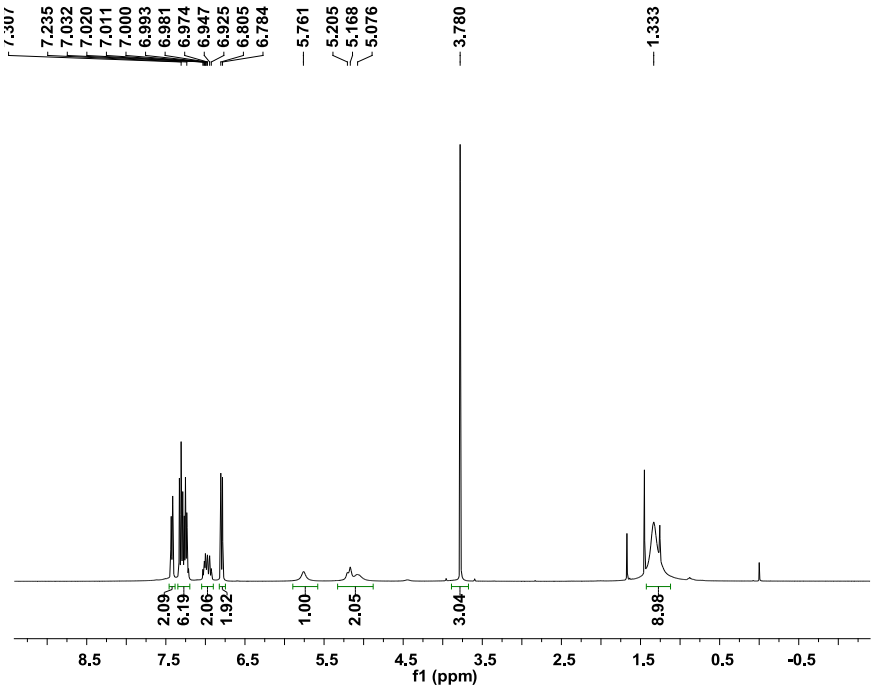
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-05-30T07:52:20
PULPROG: zgflqn
TD: 65536
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 297.3 C

======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -65.51
Ph1: 118.98

^{19}F NMR (376 MHz, CDCl$_3$) δ -133.53.



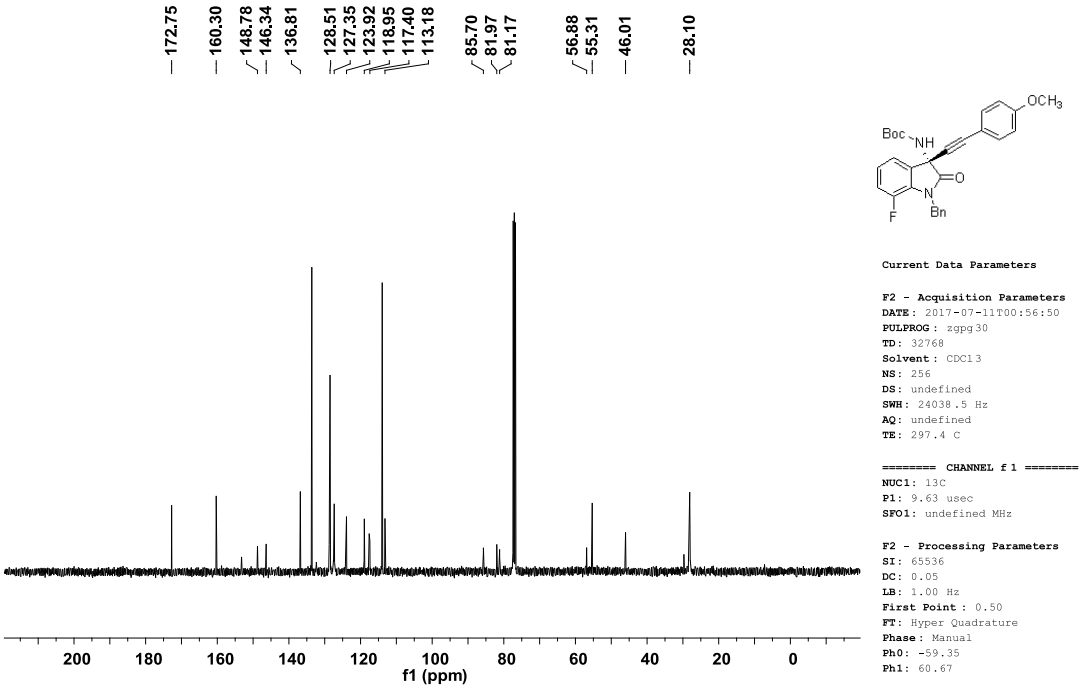
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-07-11T00:41:17
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.2 C

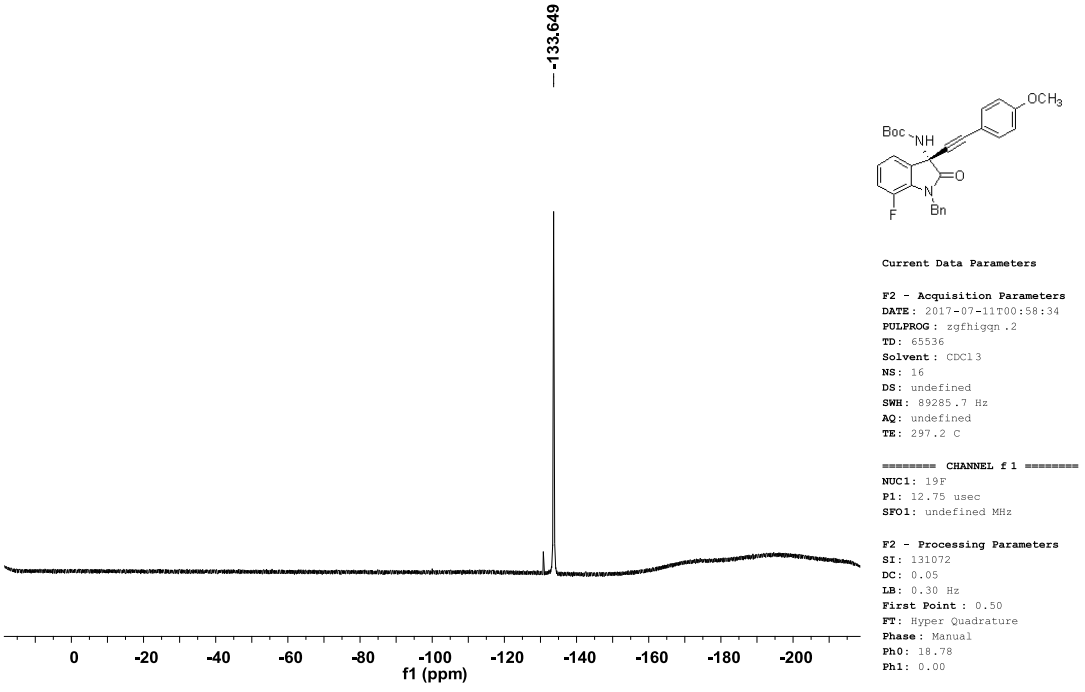
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 101.04
Ph1: 10.86

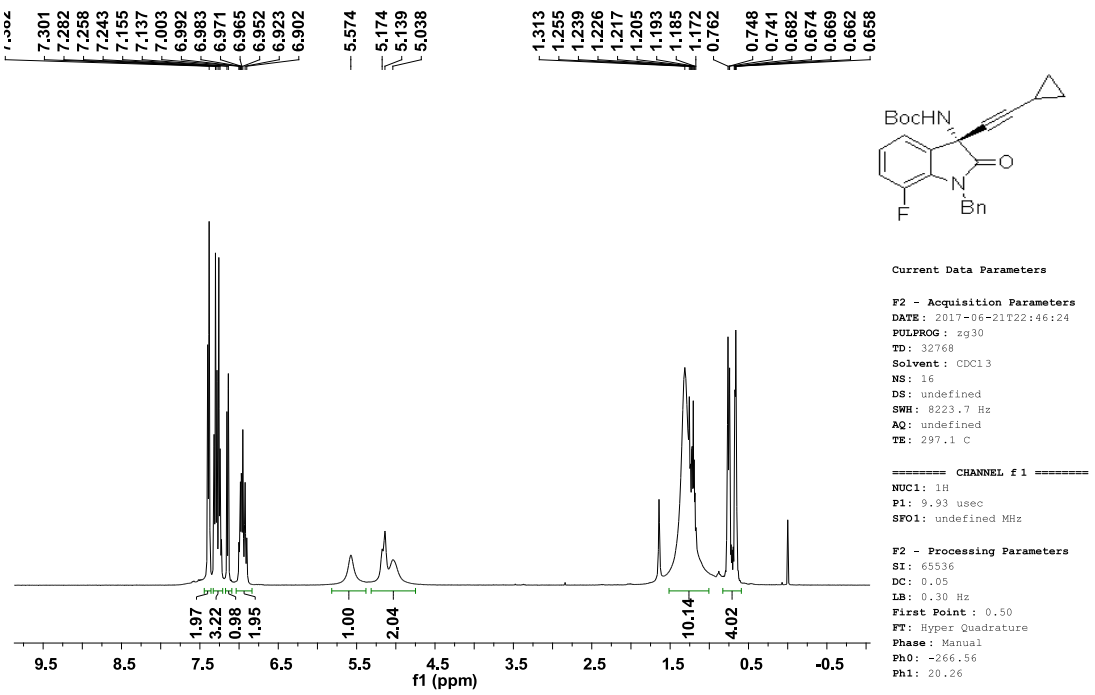
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.20 (m, 6H), 7.05 – 6.90 (m, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.76 (s, 1H), 5.33 - 4.87 (m, 2H), 3.78 (s, 3H), 1.33 (s, 9H).



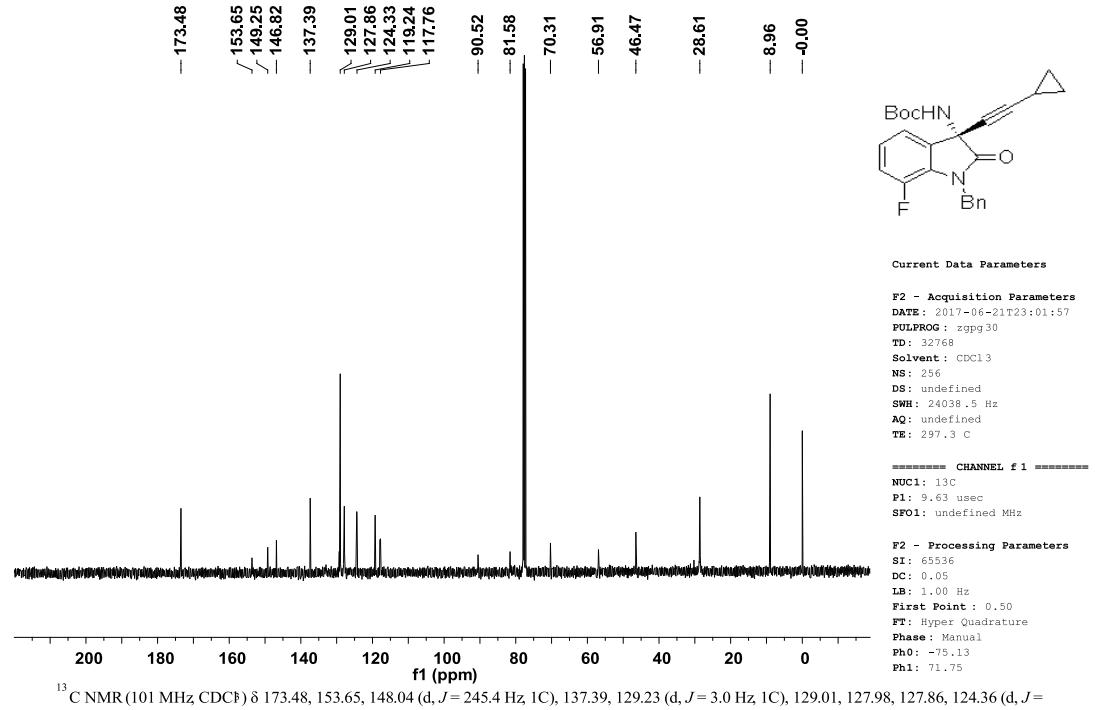
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.75, 160.30, 153.22, 148.56 (d, J = 246.4 Hz, 1C), 136.81, 133.61, 128.80 (d, J = 9.1 Hz, 1C), 128.51, 127.41 (d, J = 11.1 Hz, 1C), 123.95 (d, J = 6.1 Hz, 1C), 118.96 (d, J = 3.0 Hz, 1C), 117.49 (d, J = 19.2 Hz, 2C), 113.94, 113.18, 85.70, 81.97, 81.17, 56.88, 55.31, 46.01, 28.10.



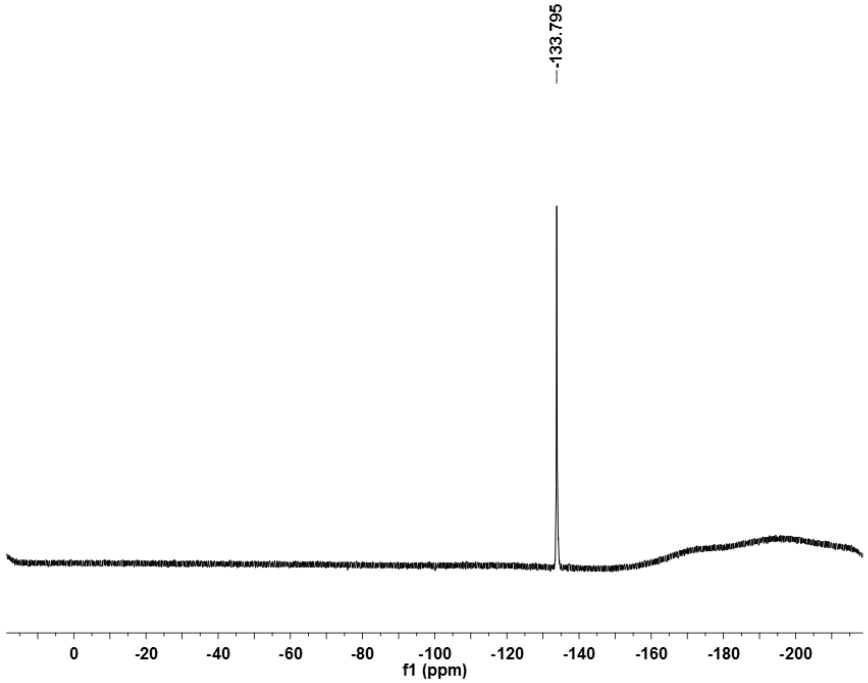
^{19}F NMR (376 MHz, CDCl$_3$) δ -133.65.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.21 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.04 – 6.83 (m, 2H), 5.57 (s, 1H), 5.31 - 4.75 (m, 2H), 1.51 – 1.01 (m, 10H), 0.83 – 0.59 (m, 4H).



^{13}C NMR (101 MHz, CDCl$_3$) δ 173.48, 153.65, 148.04 (d, *J* = 245.4 Hz, 1C), 137.39, 129.23 (d, *J* = 3.0 Hz, 1C), 129.01, 127.98, 127.86, 124.36 (d, *J* = 6.1 Hz, 1C), 119.26 (d, *J* = 3.0 Hz, 1C), 117.86 (d, *J* = 20.2 Hz, 2C), 90.52, 81.58, 70.31, 56.91, 46.47, 28.61, 8.96, 0.00.



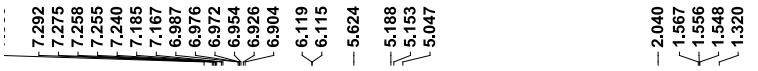
Current Data Parameters

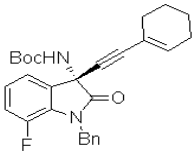
F2 - Acquisition Parameters
DATE: 2017-06-21T23:03:47
PULPROG: zgfhiqqn.2
TD: 65536
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 297.2 C

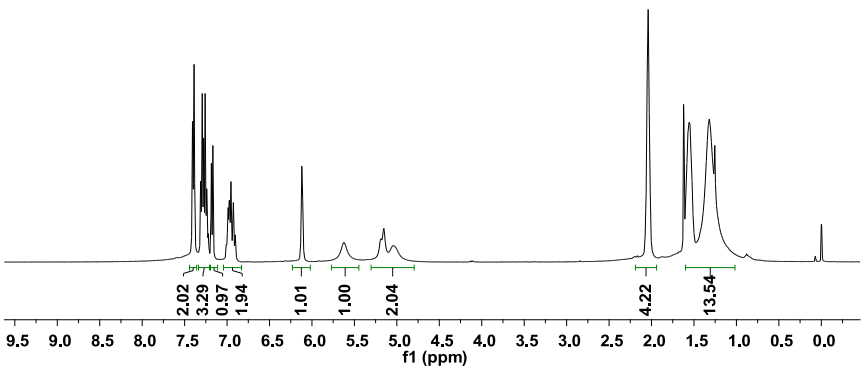
======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 12.92
Ph1: 0.00

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.79.







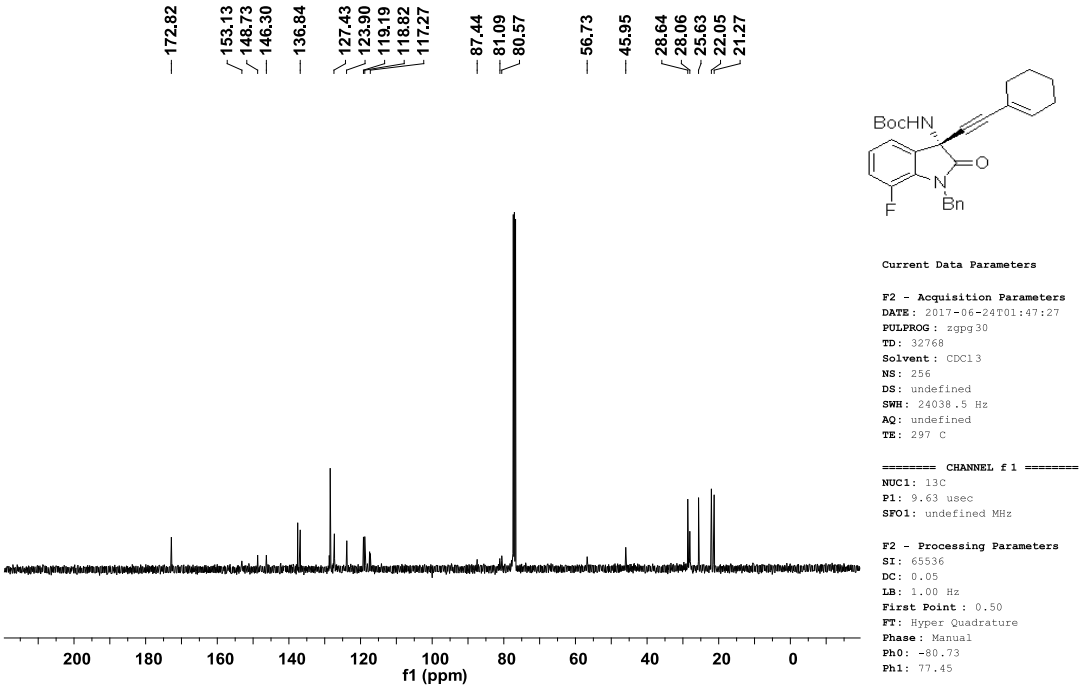
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-06-24T01:31:48
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.7 C

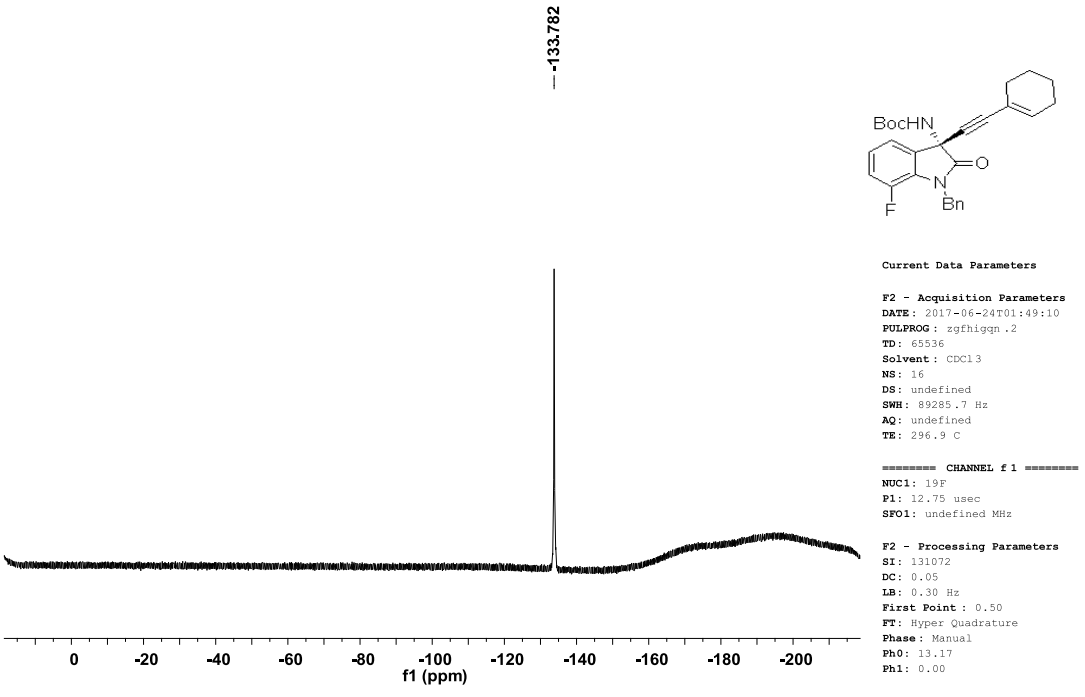
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 98.07
Ph1: 13.62

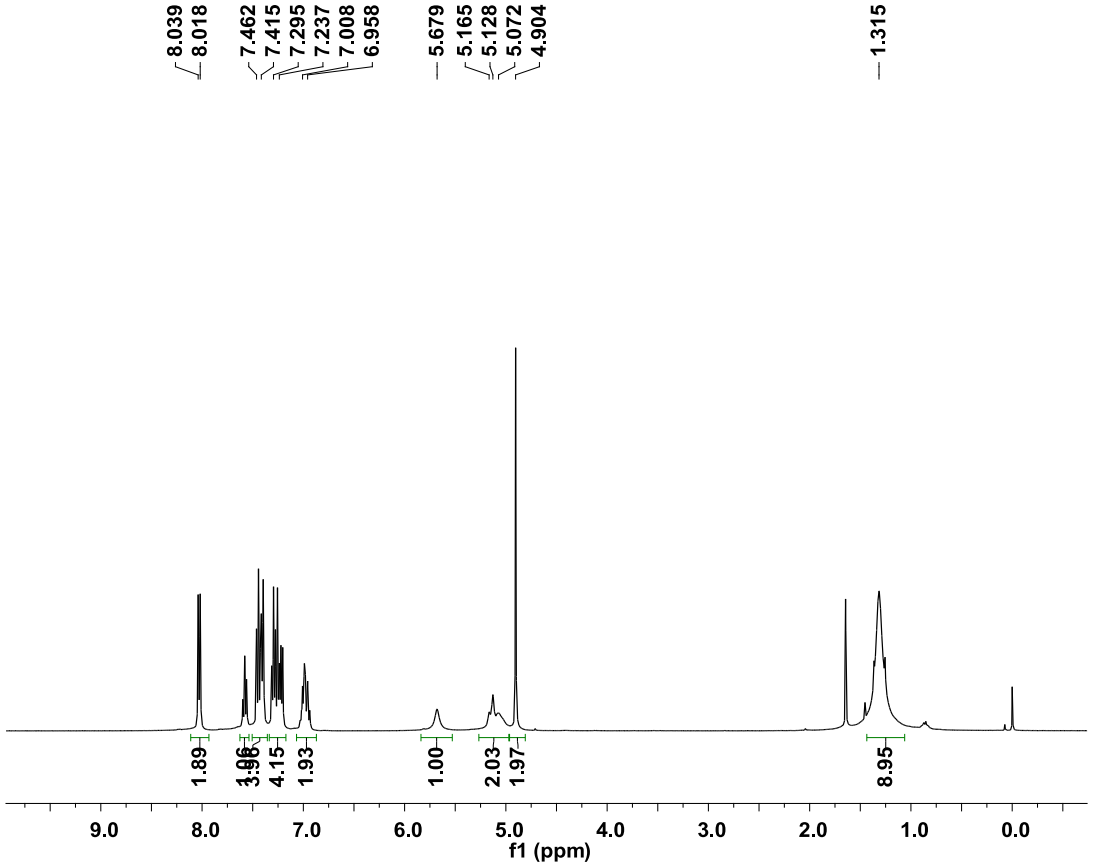
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.34 - 7.21 (m, 3H), 7.18 (d, J = 7.1 Hz, 1H), 7.04 – 6.83 (m, 2H), 6.23 - 6.02 (m, 1H), 5.62 (s, 1H), 5.30 - 4.80 (m, 2H), 2.04 (s, 4H), 1.60 - 1.02 (m, 13H).

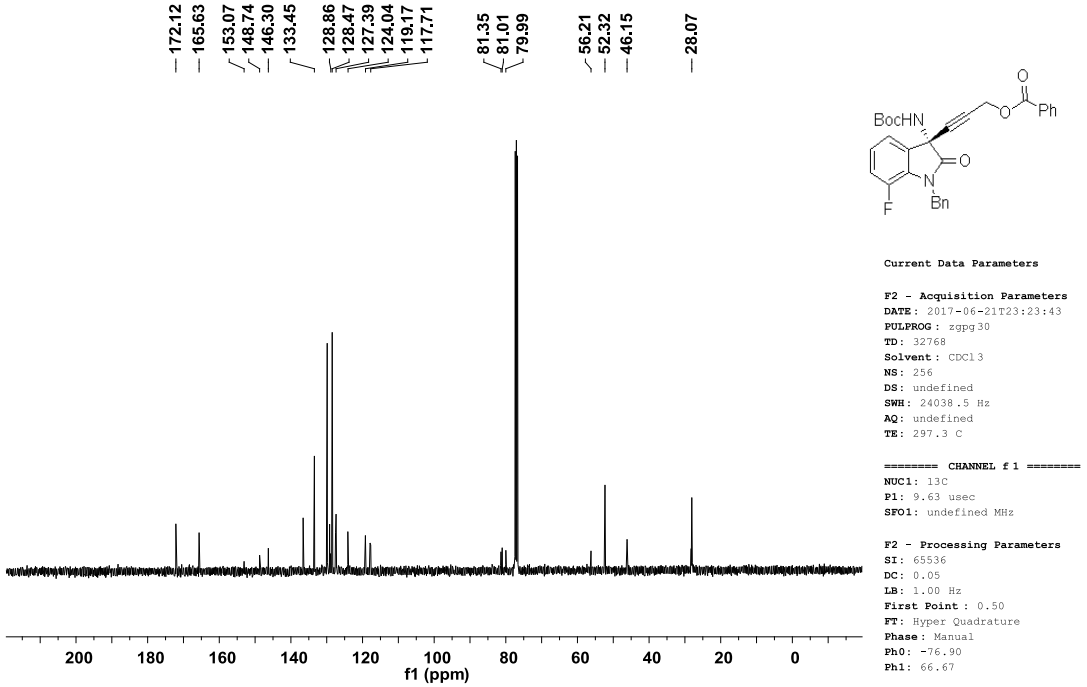


^{13}C NMR (101 MHz, $CDCl_3$) δ 172.82, 153.13, 147.52 (d, J = 245.4 Hz, 1C), 137.54, 136.84, 128.70 (d, J = 9.1 Hz, 1C), 128.47, 127.43, 127.31, 123.87 (d, J = 6.1 Hz, 1C), 119.19, 118.83 (d, J = 2.0 Hz, 1C), 117.37 (d, J = 19.2 Hz, 1C), 87.44, 81.09, 80.57, 56.73, 45.95, 28.64, 28.06, 25.63, 22.05, 21.27.



^{19}F NMR (376 MHz, $CDCl_3$) δ -133.78.





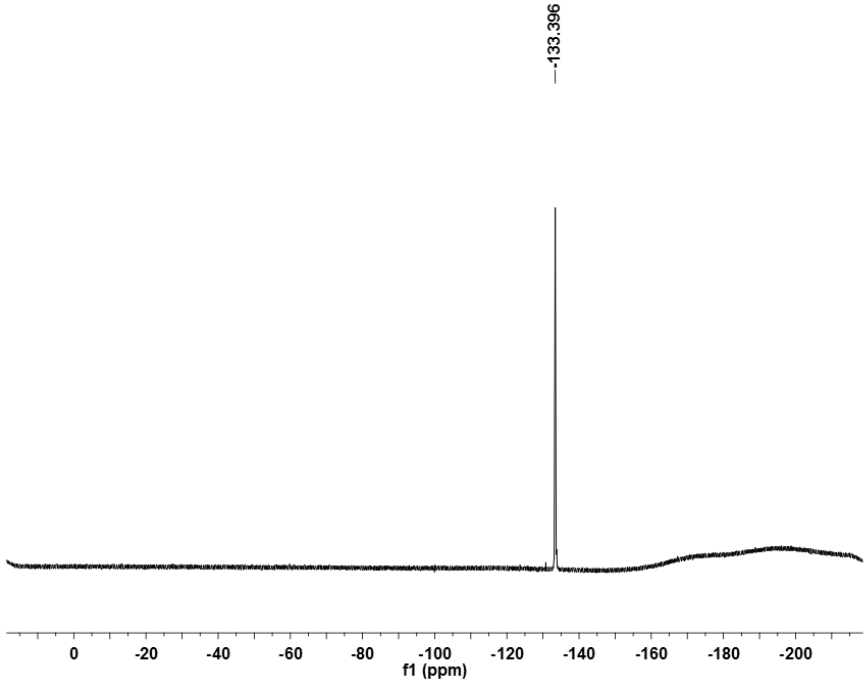
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-06-21T23:23:43
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.3 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -76.90
Ph1: 66.67

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.12, 165.63, 153.07, 147.52 (d, J = 246.4 Hz, 1C), 136.59, 133.45, 129.87, 129.20, 128.91 (d, J = 9.1 Hz, 1C), 128.53, 128.47, 127.53, 127.39, 124.07 (d, J = 7.1 Hz, 1C), 119.19 (d, J = 3.0 Hz, 1C), 117.81 (d, J = 20.2 Hz, 2C), 81.35, 81.01, 79.99, 56.21, 52.32, 46.15, 28.07
.



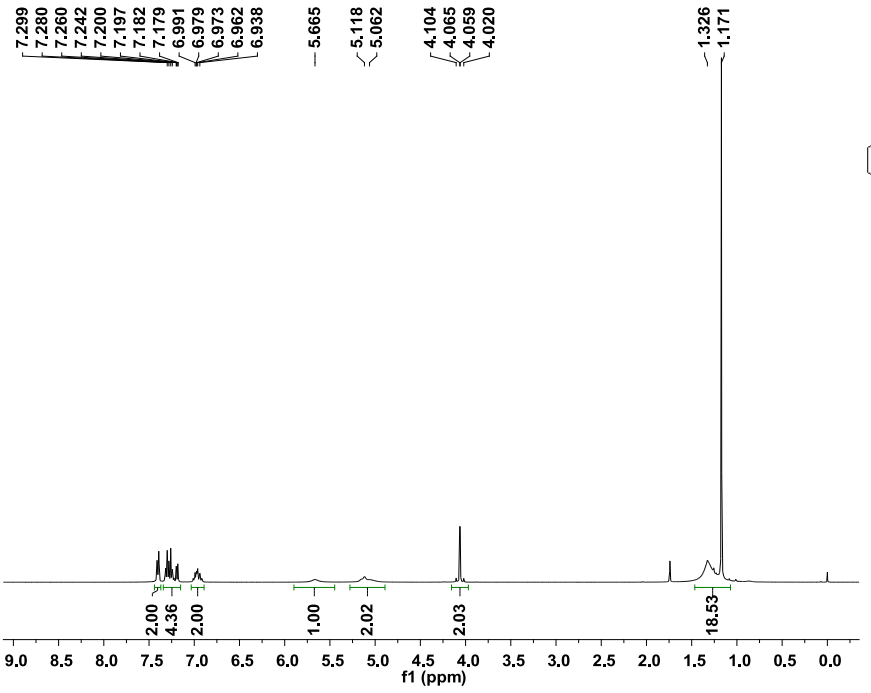
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-06-21T23:25:28
PULPROG: zgfhiqqn.2
TD: 65536
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 89285.7 Hz
AQ: undefined
TE: 297.1 C

======== CHANNEL f1 ========
NUC1: 19F
P1: 12.75 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 131072
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 13.67
Ph1: 0.00

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.40 .



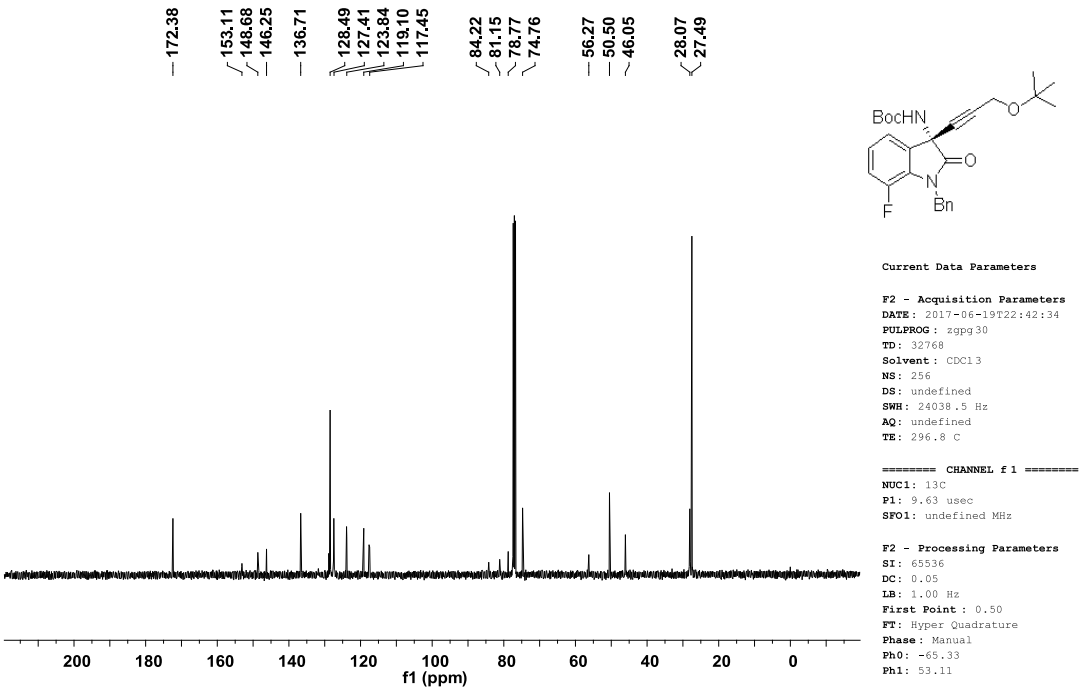
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2017-06-19T22:26:49
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.6 C

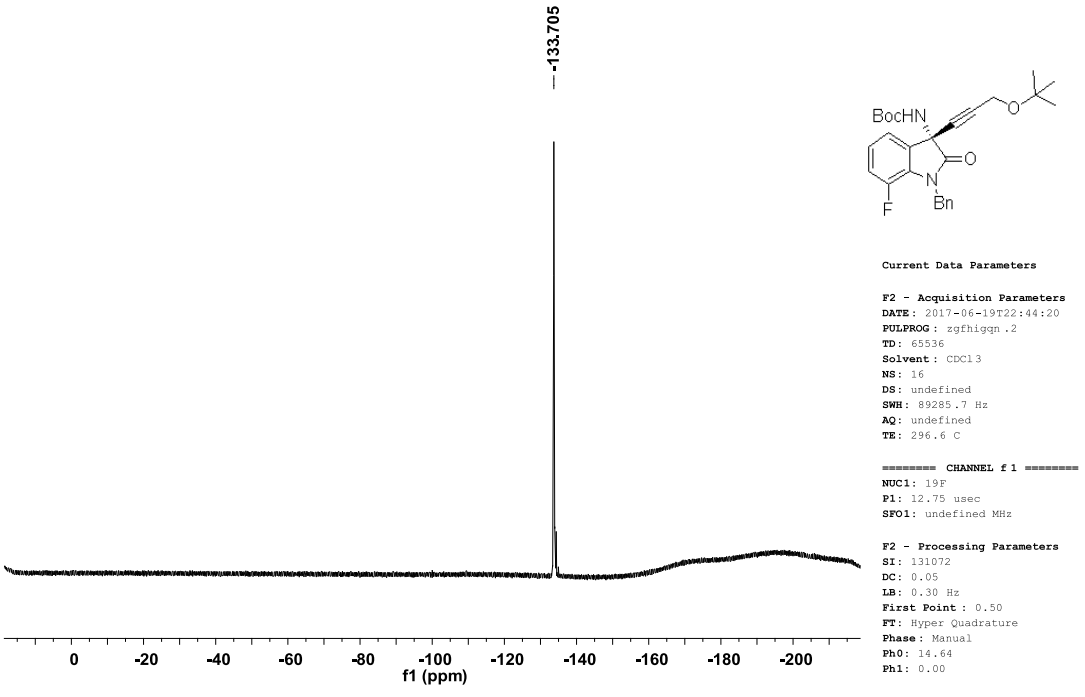
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -263.97
Ph1: 21.21

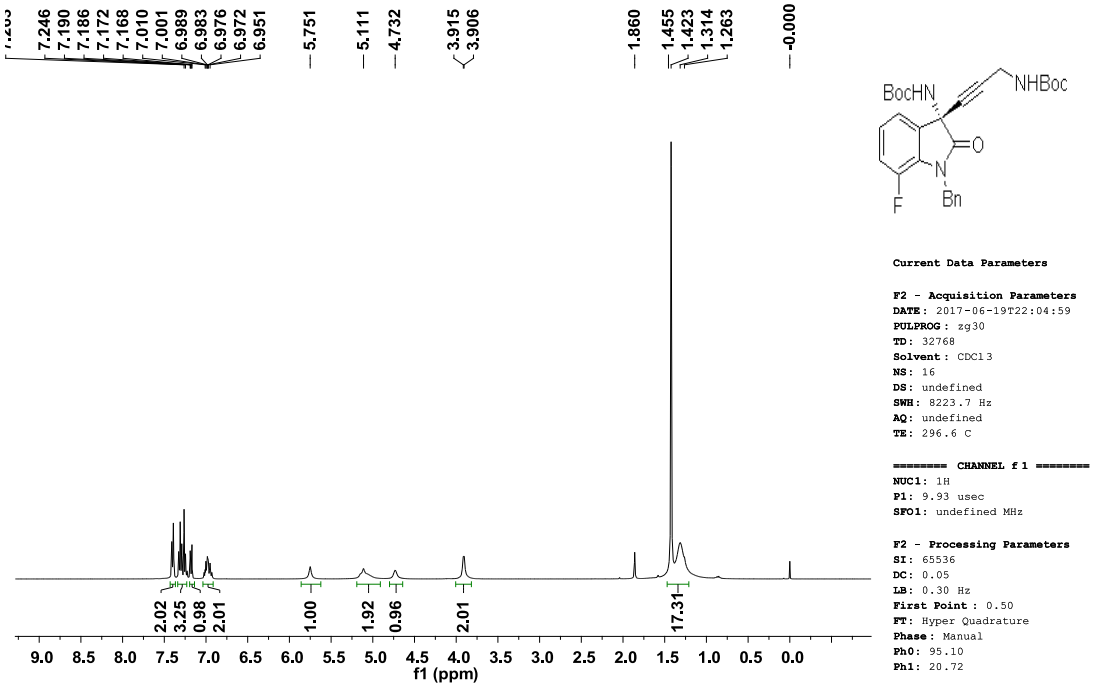
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 2H), 7.34 – 7.15 (m, 4H), 7.03 – 6.89 (m, 2H), 5.66 (s, 1H), 5.28 - 4.89 (m, 2H), 4.16 – 3.97 (m, 2H), 1.46 -1.07 (m, 18H).



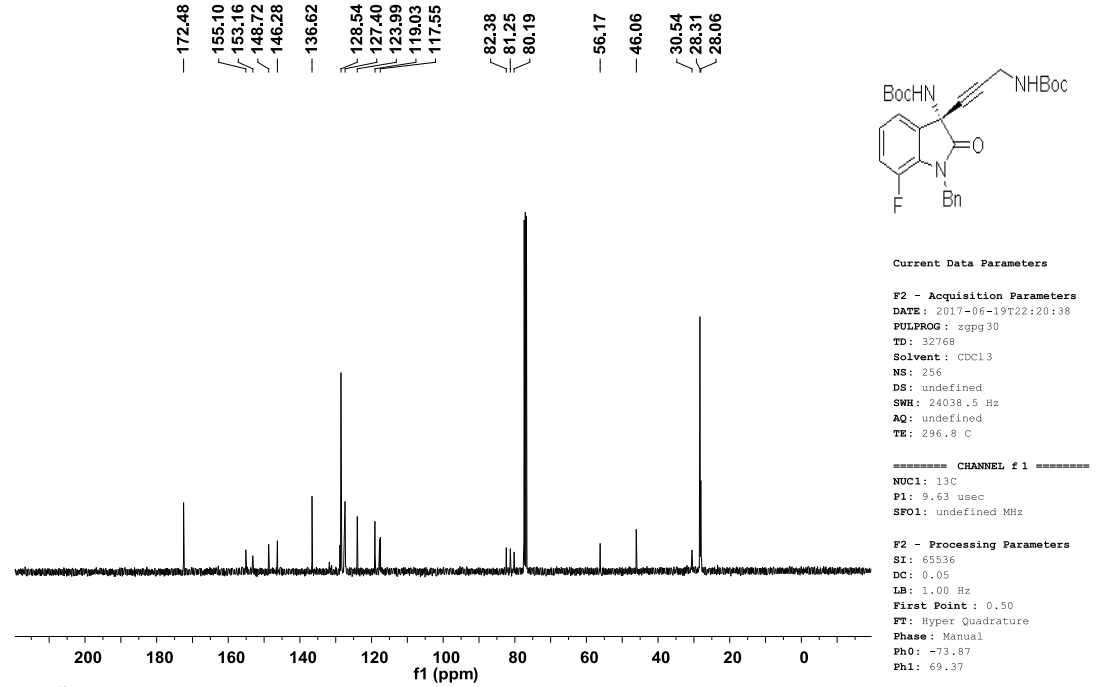
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.38, 153.11, 147.46 (d, J = 245.4 Hz, 1C), 136.71, 128.84 (d, J = 9.1 Hz, 1C), 128.49, 127.46, 127.41, 123.88 (d, J = 7.1 Hz, 1C), 119.11 (d, J = 3.0 Hz, 1C), 117.54 (d, J = 19.2 Hz, 2C), 84.22, 81.15, 78.77, 74.76, 56.27, 50.50, 46.05, 27.07, 27.49.



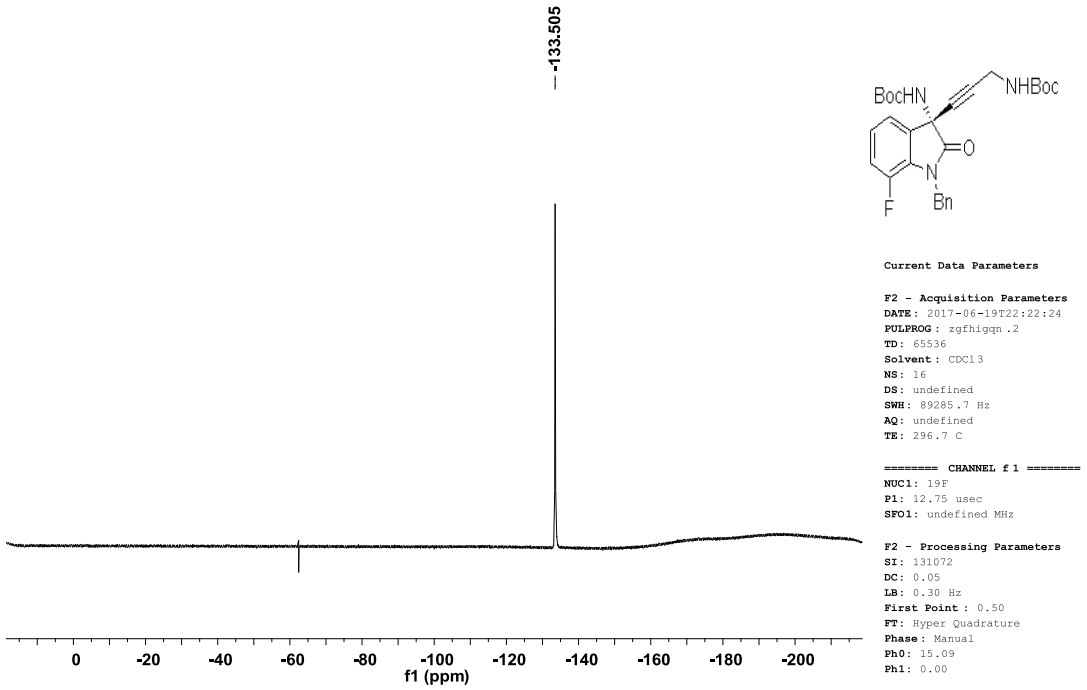
^{19}F NMR (376 MHz, CDCl$_3$) δ -133.71.



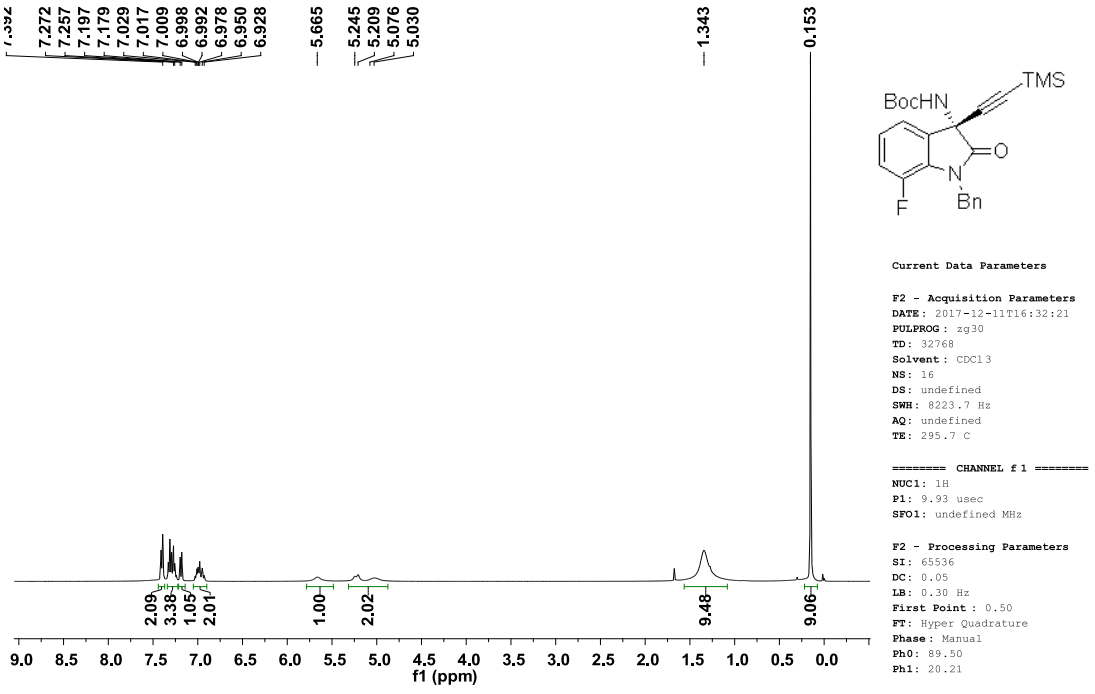
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.23 (m, 3H), 7.18 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.04 – 6.91 (m, 2H), 5.75 (s, 1H), 5.11 (s, 2H), 4.73 (s, 1H), 3.91 (d, *J* = 3.7 Hz, 2H), 1.47 – 1.21 (m, 17H).



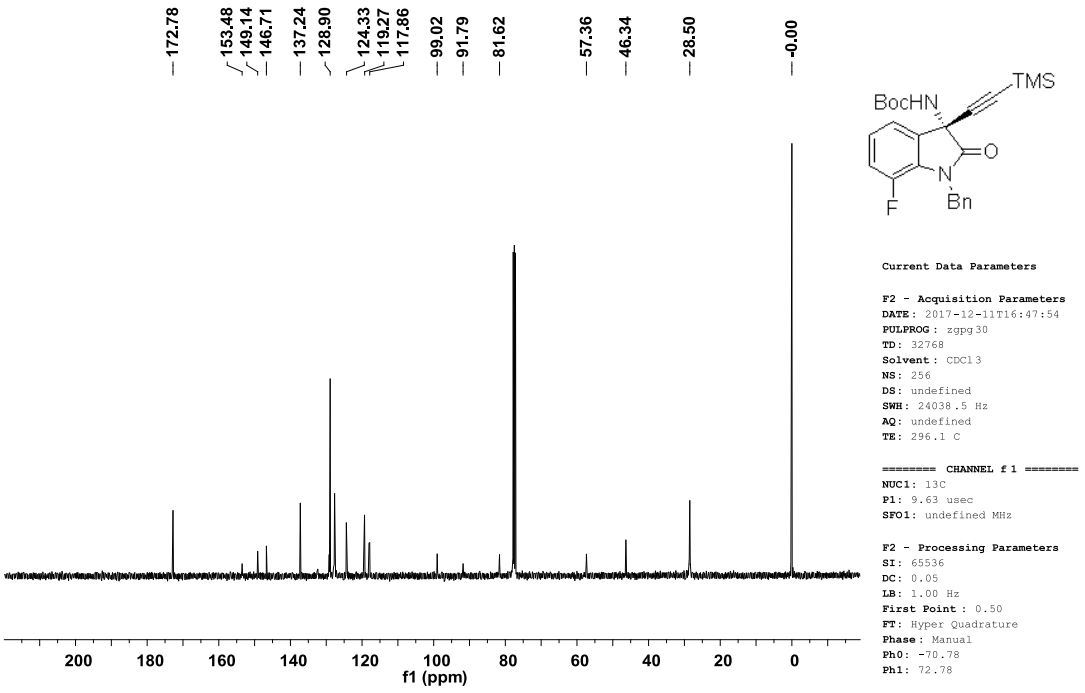
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.48, 155.10, 153.16, 147.50 (d, *J* = 246.4 Hz, 1C), 136.62, 128.80 (d, *J* = 9.1 Hz, 1C), 128.54, 127.53, 127.40, 124.02 (d, *J* = 6.1 Hz, 1C), 119.04 (d, *J* = 3.0 Hz, 1C), 117.65 (d, *J* = 20.2 Hz, 2C), 82.38, 81.25, 80.19, 56.17, 46.06, 30.54, 28.31, 28.06.



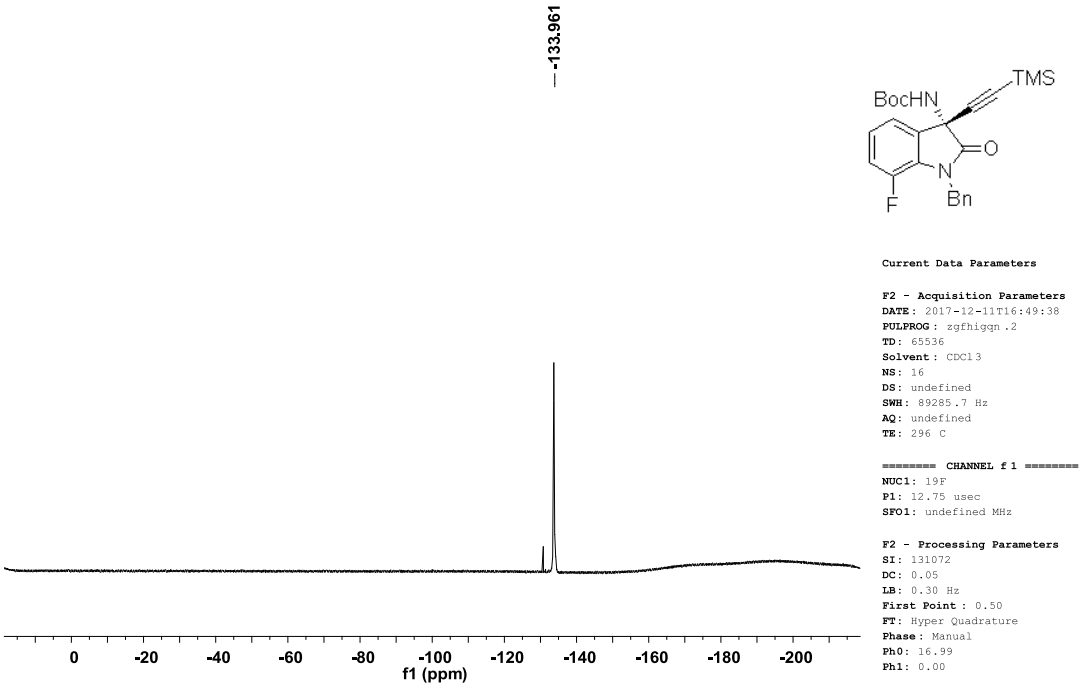
^{19}F NMR (376 MHz, CDCl$_3$) δ -133.51.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44– 7.37 (m, 2H), 7.34 – 7.21 (m, 3H), 7.24-7.14 (m, 1H), 7.05 – 6.90 (m, 2H), 5.66 (s, 1H), 5.31-4.87 (m, 2H), 1.34 (s, 9H), 0.15 (s, 9H).

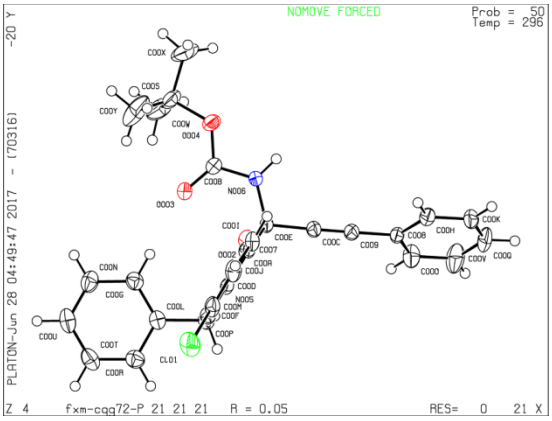


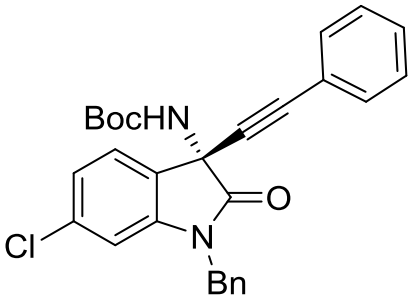
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.78, 153.48, 147.92 (d, J = 245.4 Hz, 1C), 137.24, 129.23 (d, J = 9.2 Hz, 1C), 128.90, 127.78 (d, J = 22.2 Hz, 1C), 124.36 (d, J = 6.3 Hz, 1C), 119.29 (d, J = 3.1 Hz, 1C), 117.96 (d, J = 19.5 Hz, 1C), 99.02, 91.79, 81.62, 57.36, 46.34, 28.50, -0.00.



^{19}F NMR (376 MHz, CDCl$_3$) δ -133.96.

(K) X-ray datas for 3la

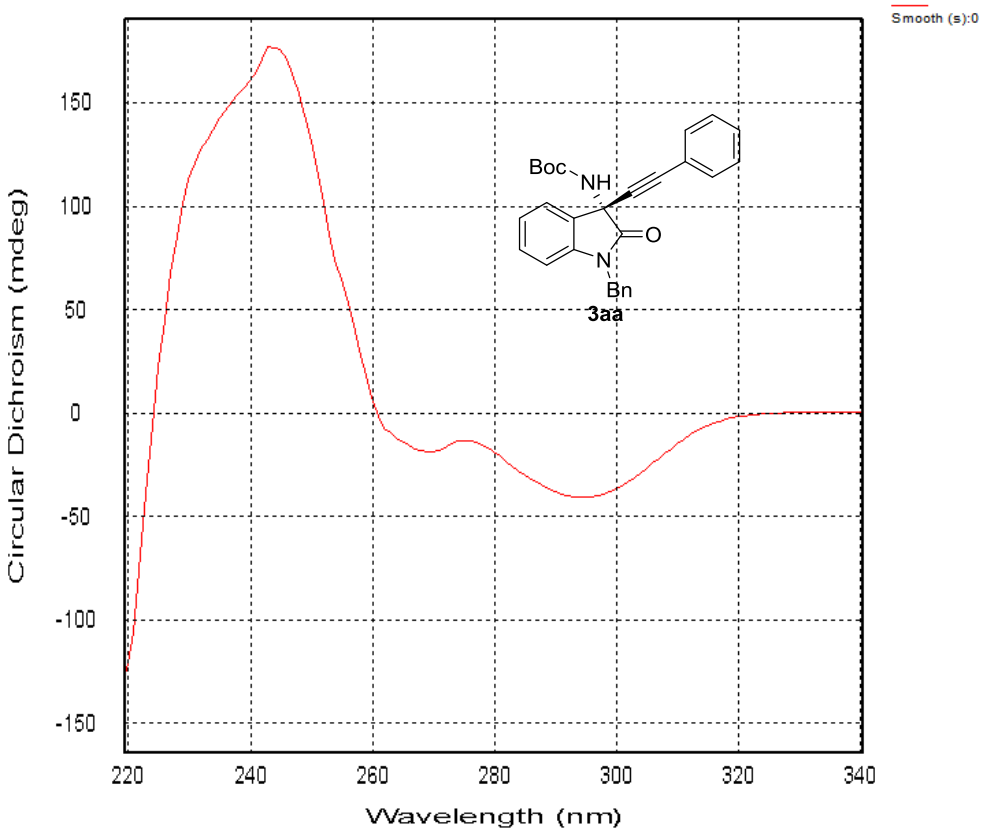


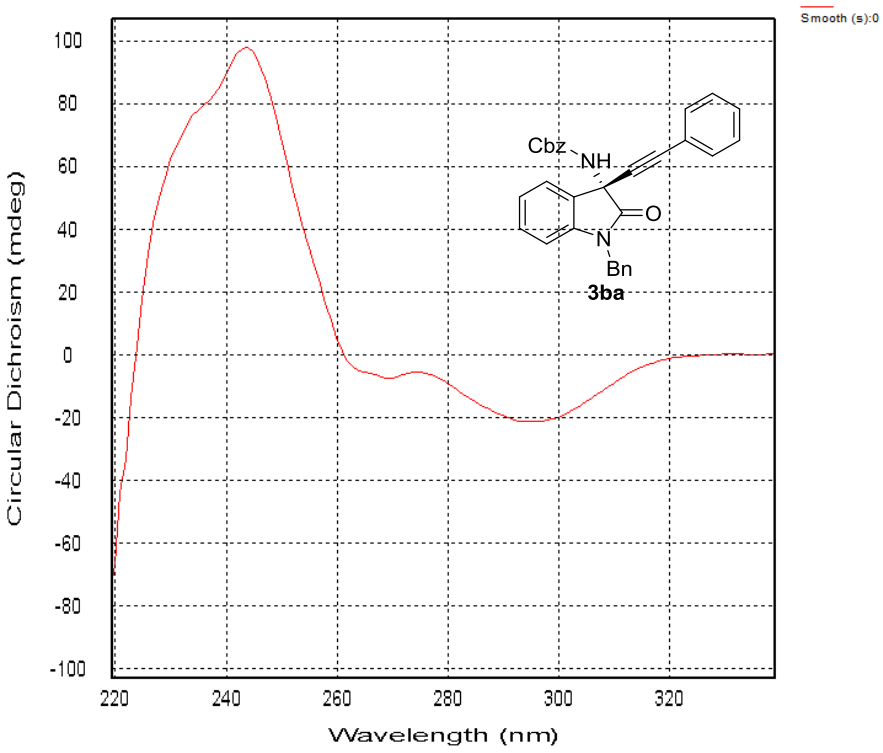


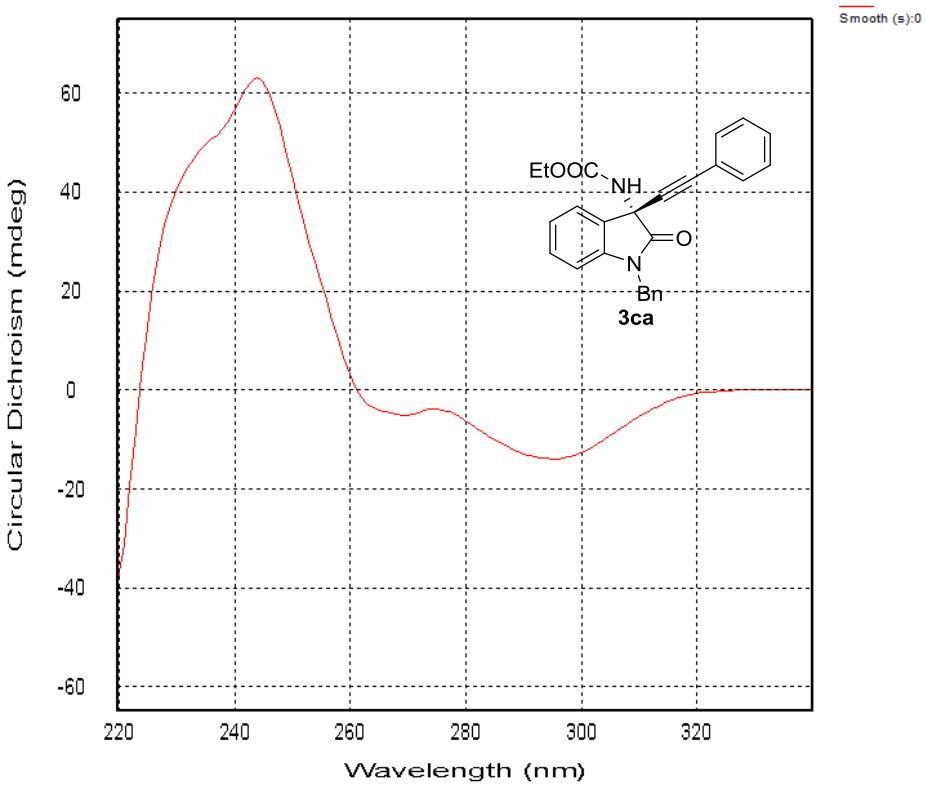
Empirical formula	$C_{27}H_{25}ClN_3O_3$
Formula weight	474.95
Temperature/K	296.31(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.5916(2)
b/Å	14.4910(4)
c/Å	14.7866(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2483.77(10)
Z	4
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	1.629
F(000)	996.0
Crystal size/mm^3	0.55 ×0.5 ×0.4
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.696 to 145.646
Index ranges	$-12 \le h \le 14$, $-12 \le k \le 17$, $-18 \le l \le 18$
Reflections collected	14531
Independent reflections	4857 [R_{int} = 0.0278, R_{sigma} = 0.0244]
Data/restraints/parameters	4857/0/310
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1191
Largest diff. peak/hole / e Å^{-3}	0.30/-0.35
Flack parameter	-0.001(6)

CCDC 1560532 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

(L) Copies of CD spectra



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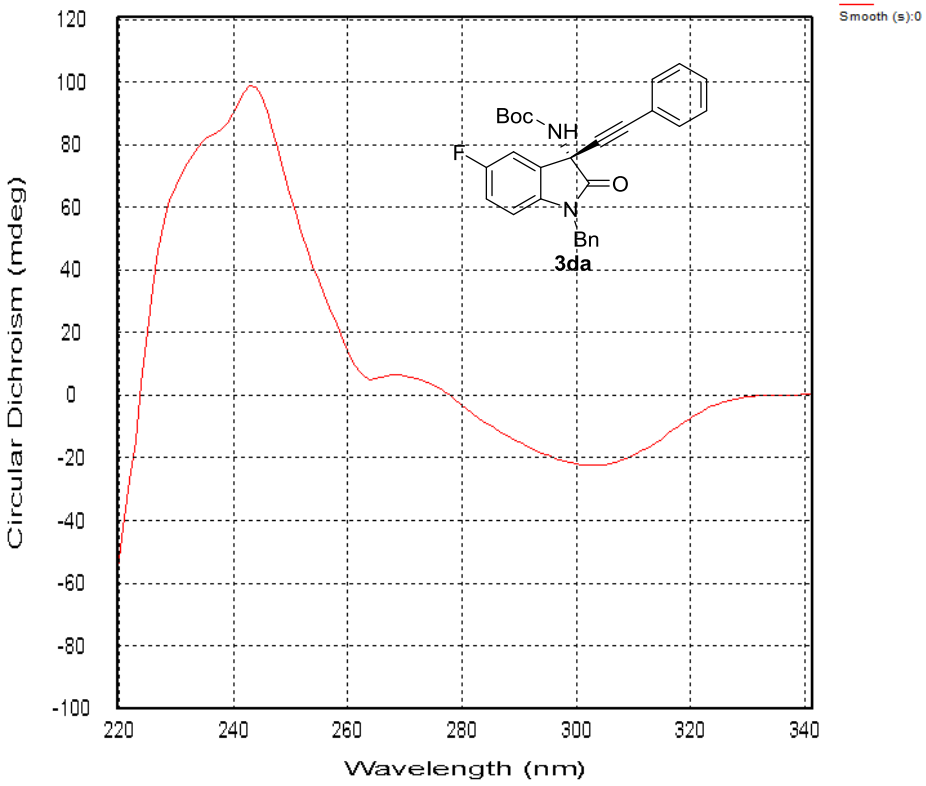
O
N
Bn
3ca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Wavelength (nm)
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F
O
N
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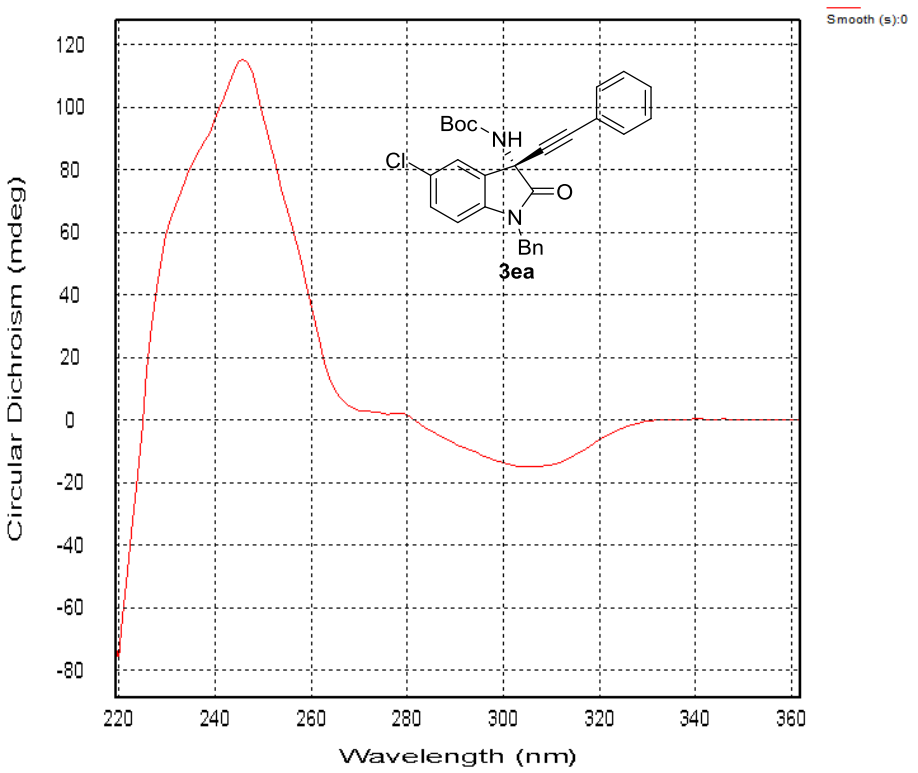
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340
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Wavelength (nm)
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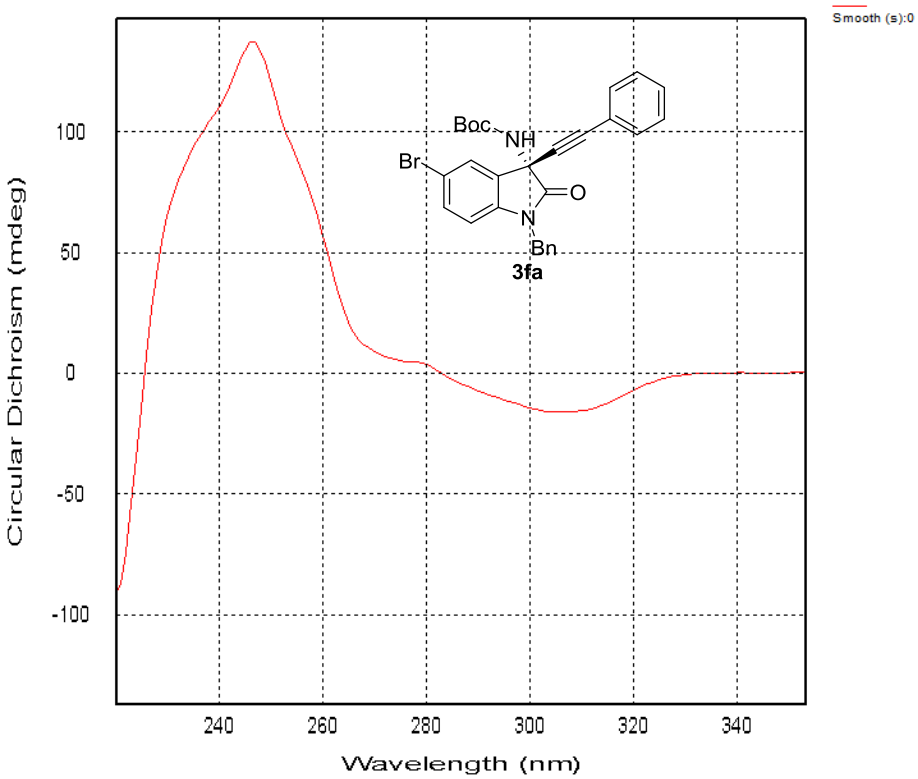
Cl
O
N
Bn
3ea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O
N
Bn
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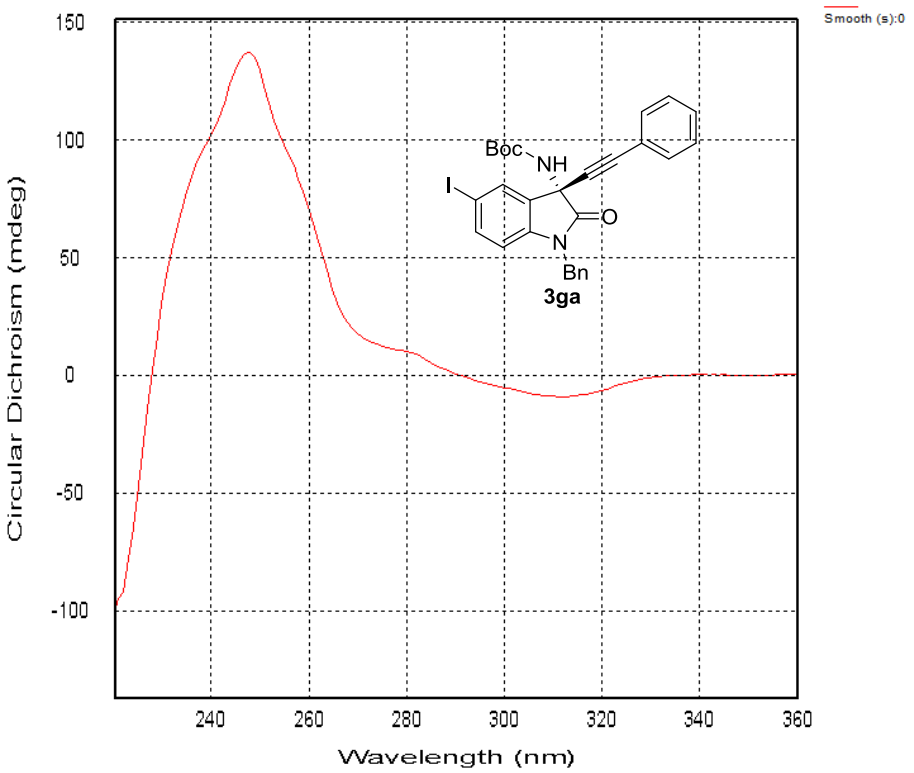
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Wavelength (nm)
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I
O
N
Bn
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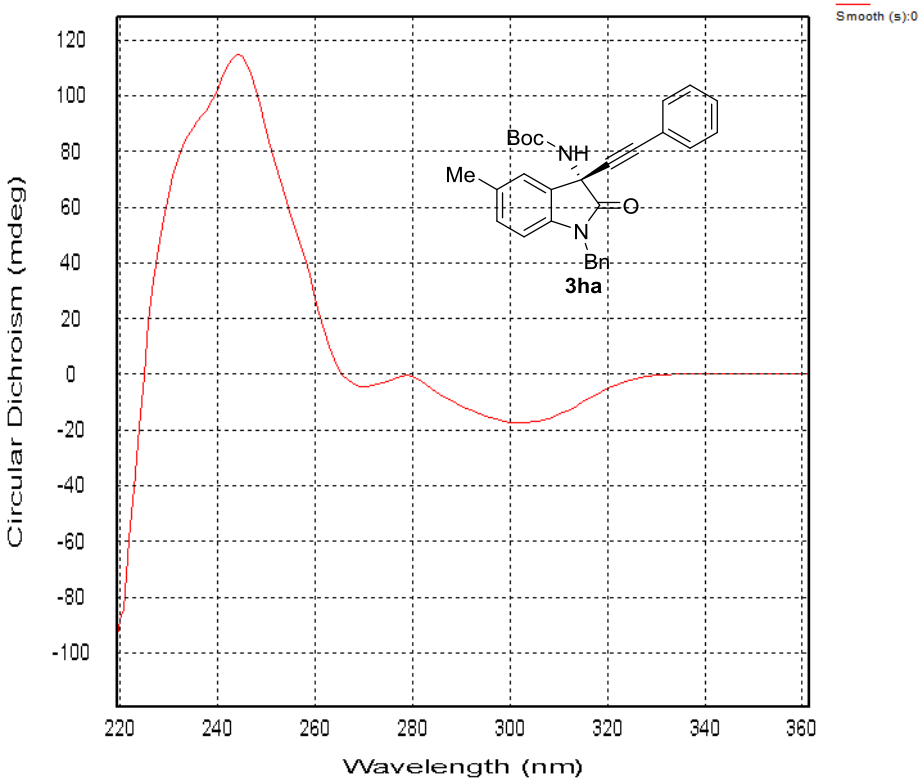
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O
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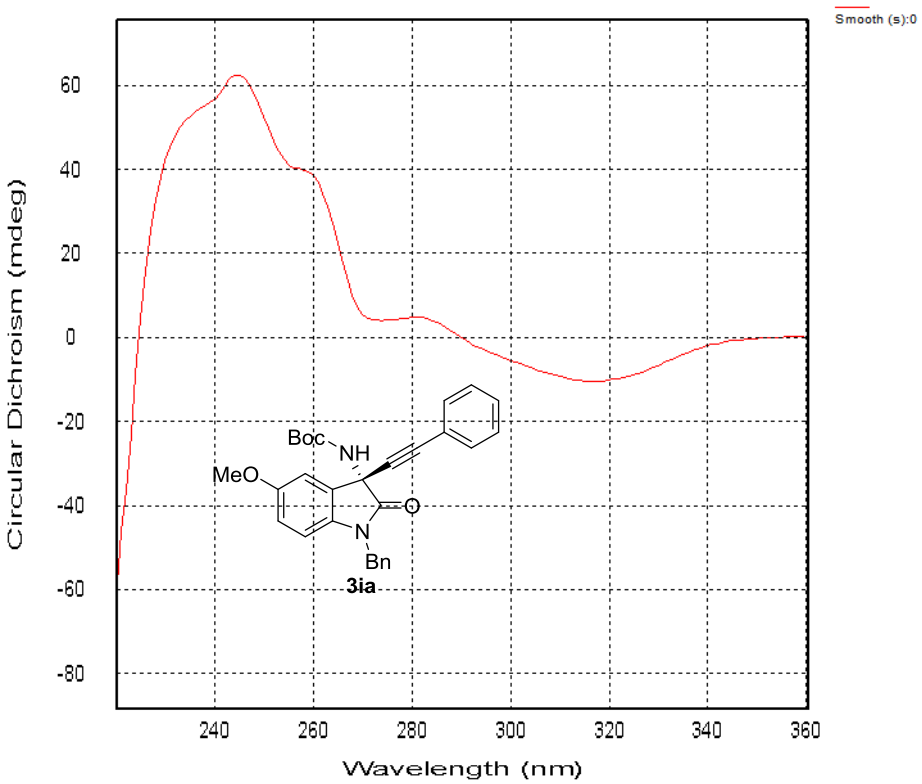
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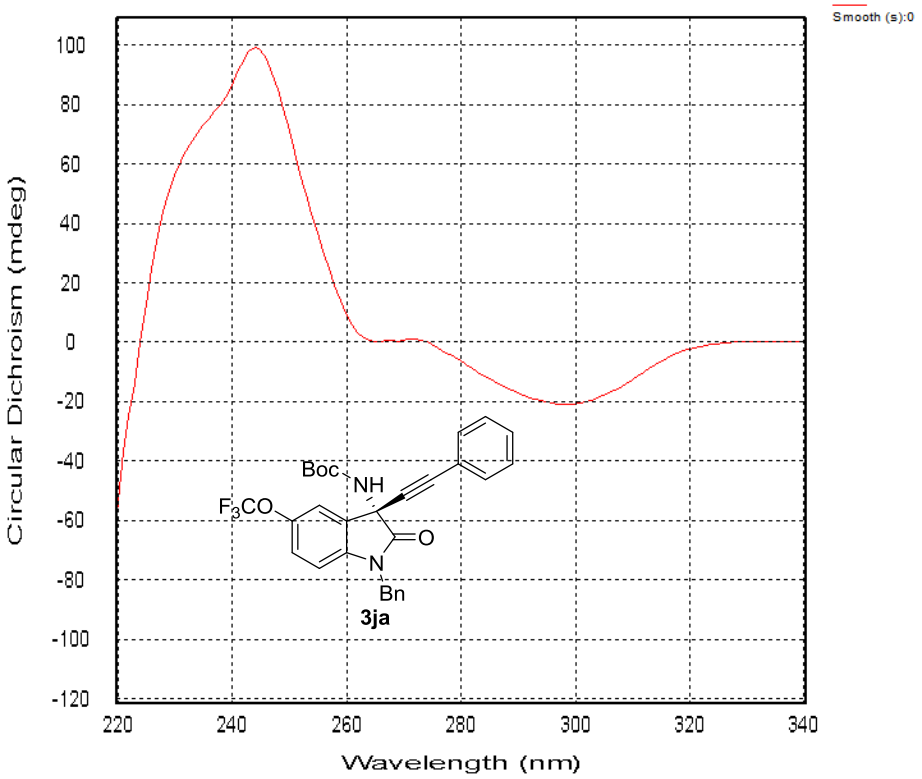
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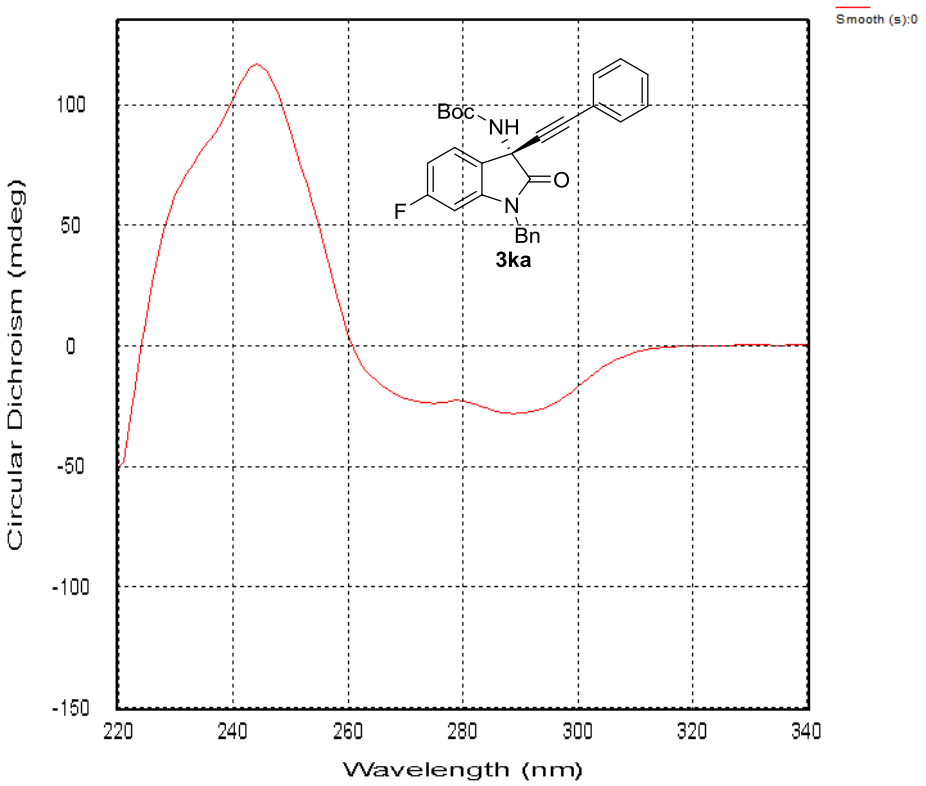
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F
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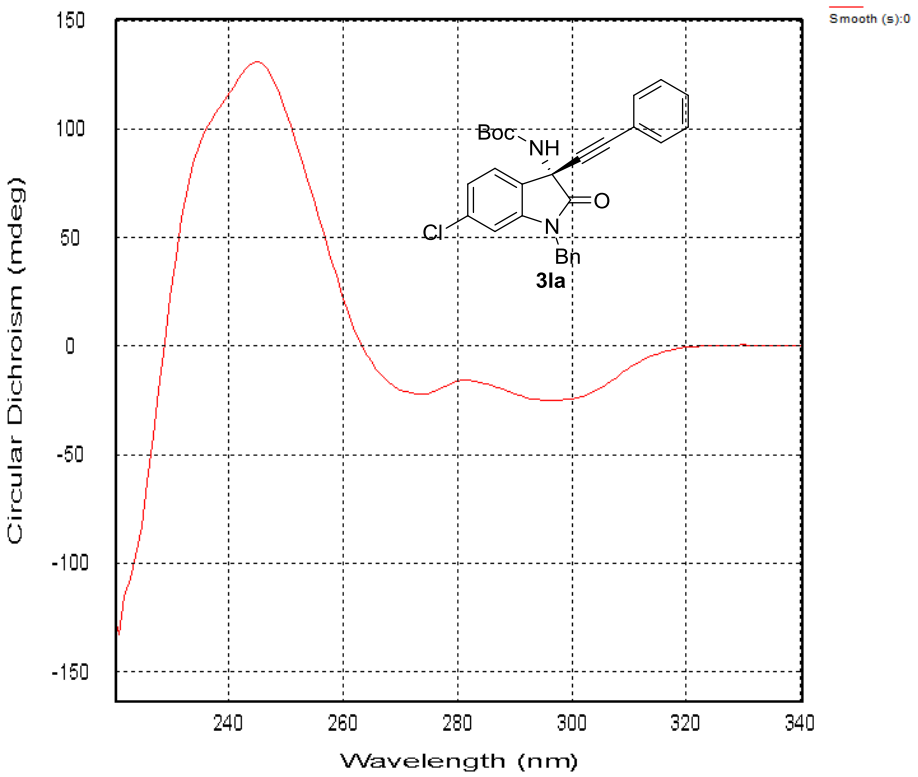
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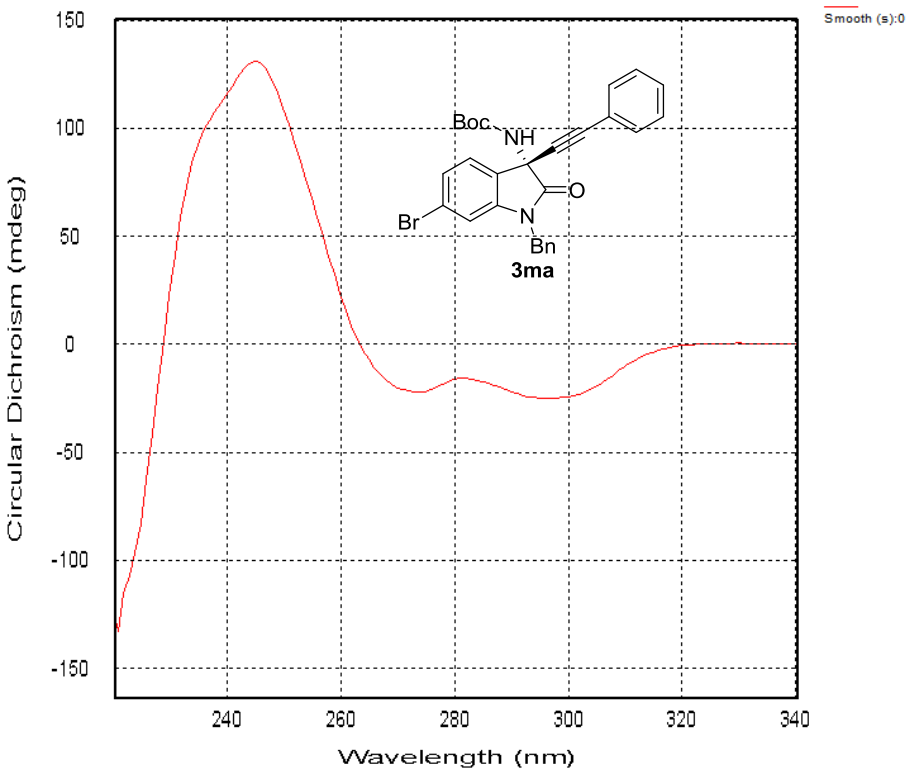
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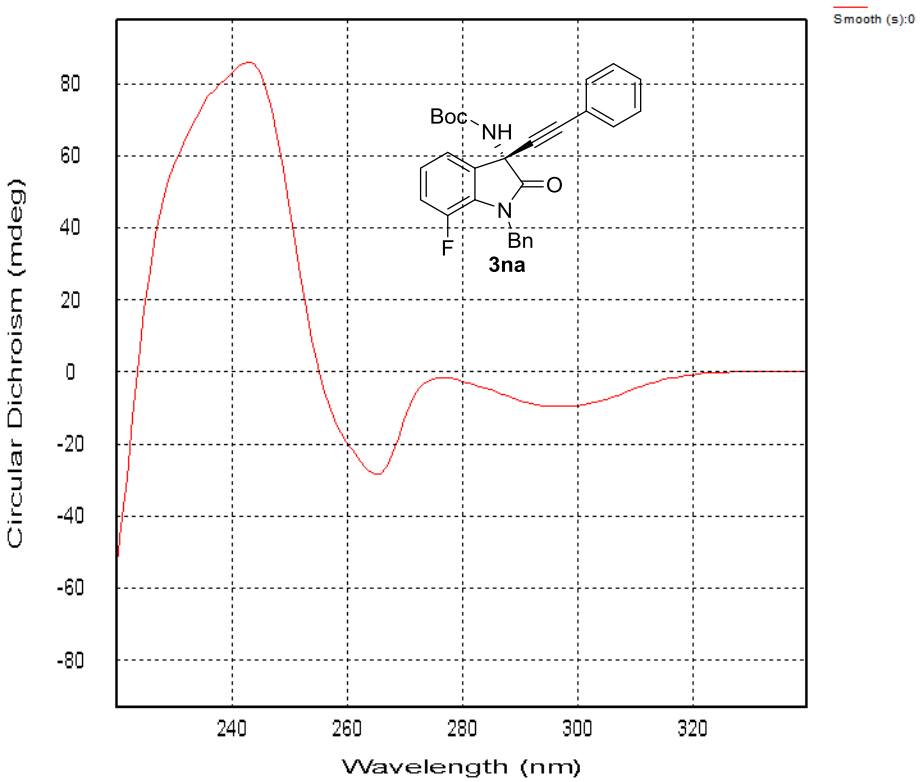
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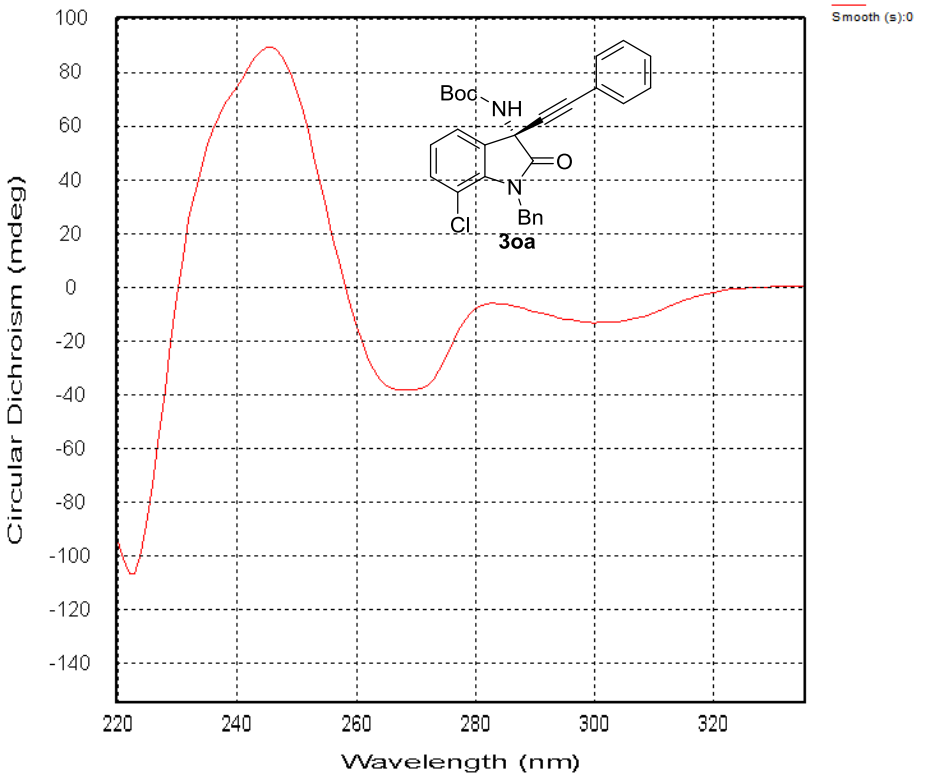
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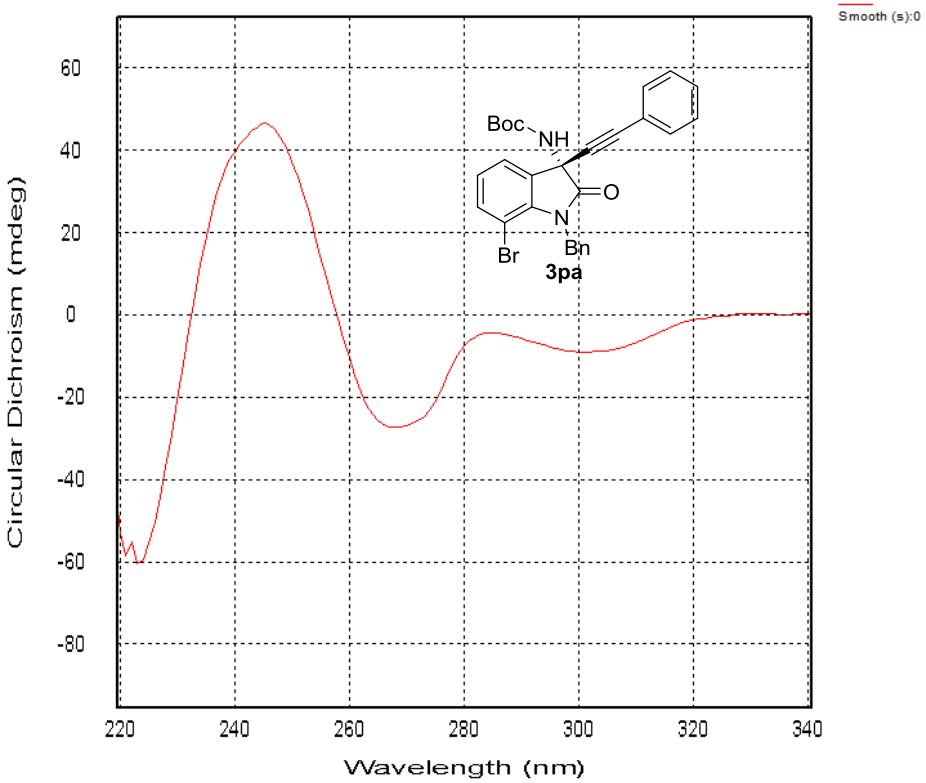
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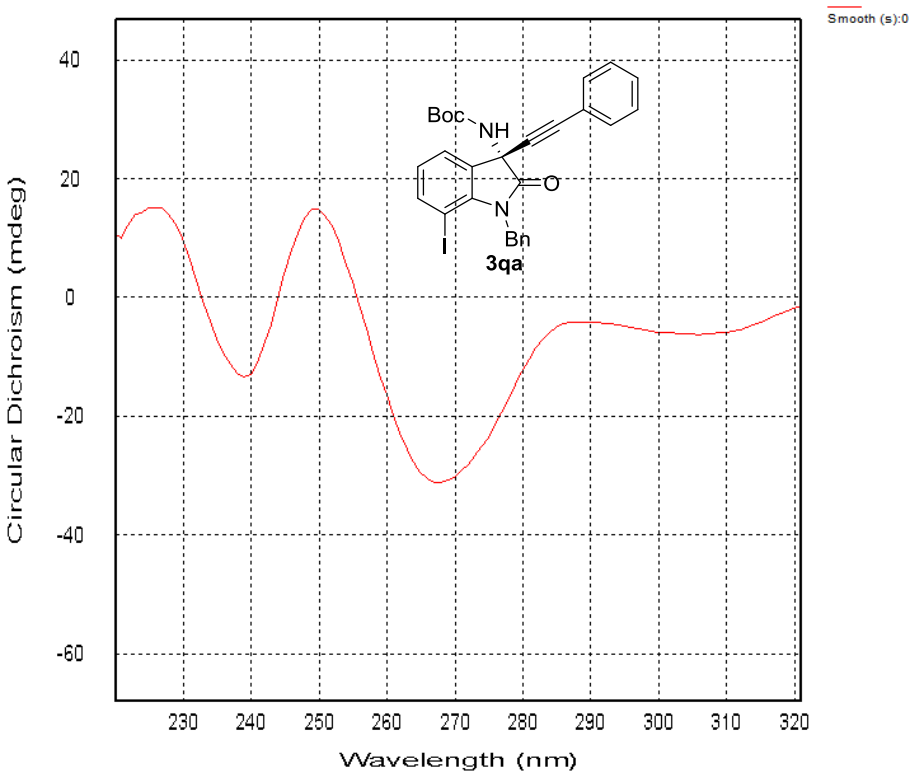
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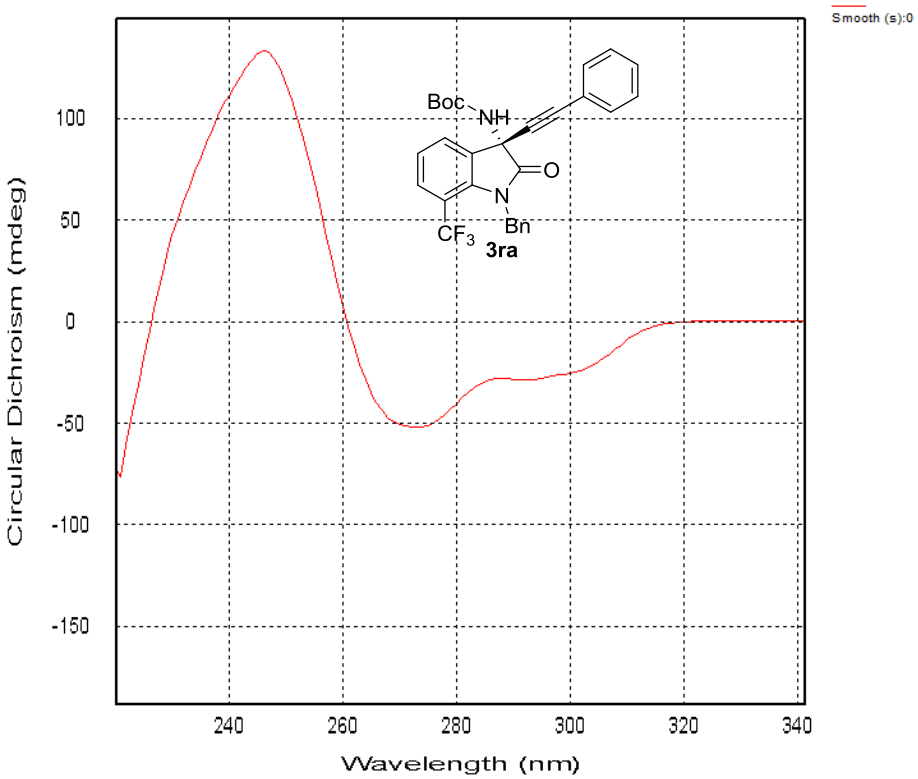
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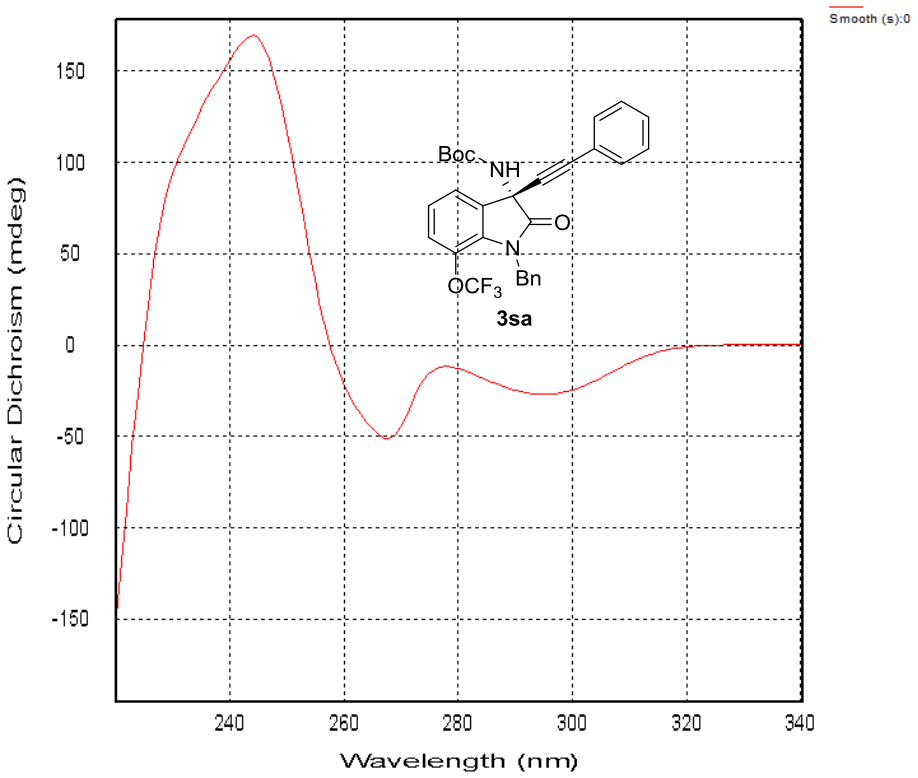
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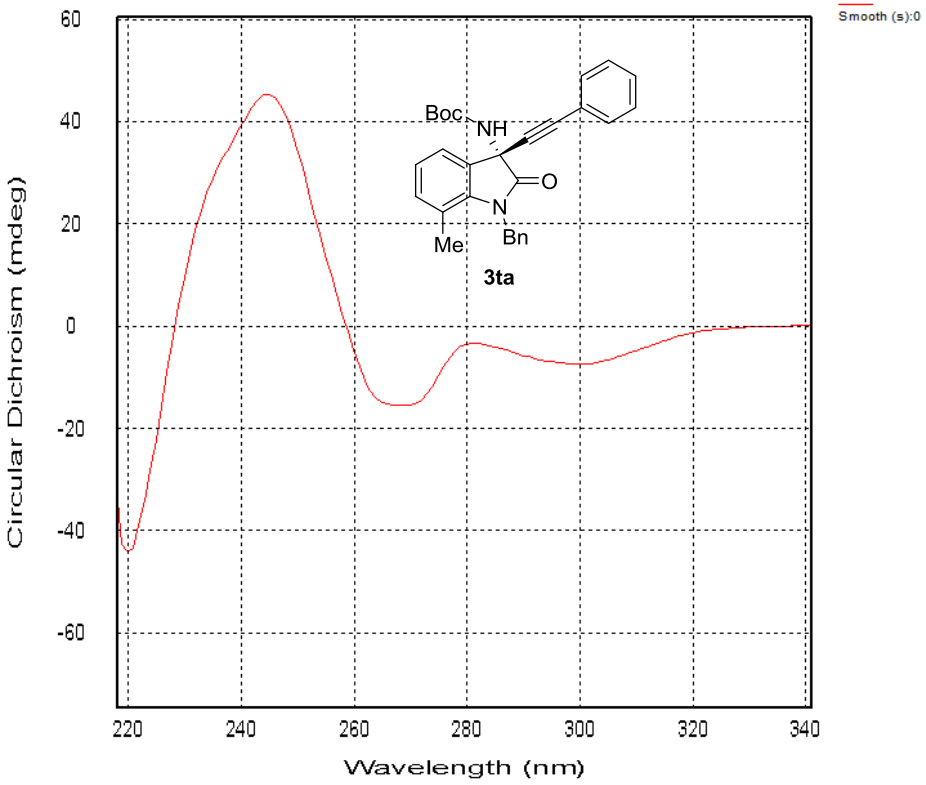
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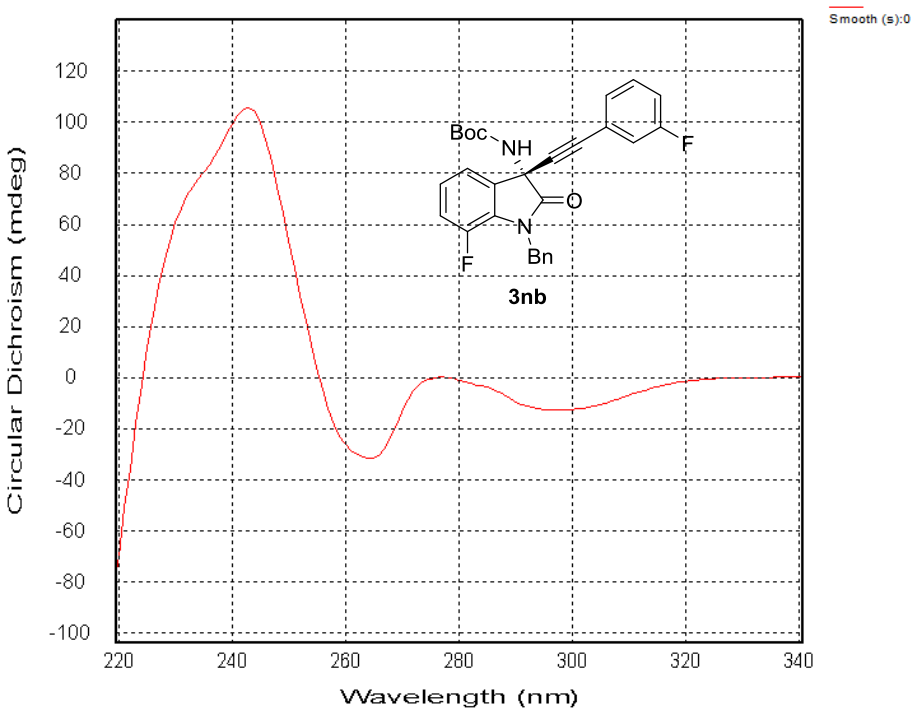
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Wavelength (nm)
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NH
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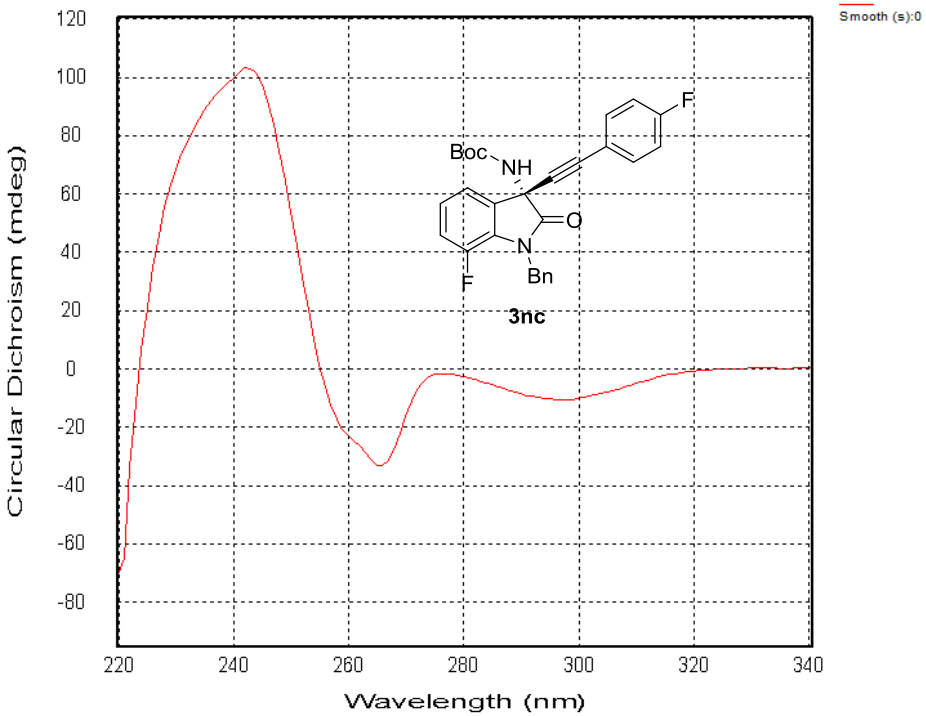
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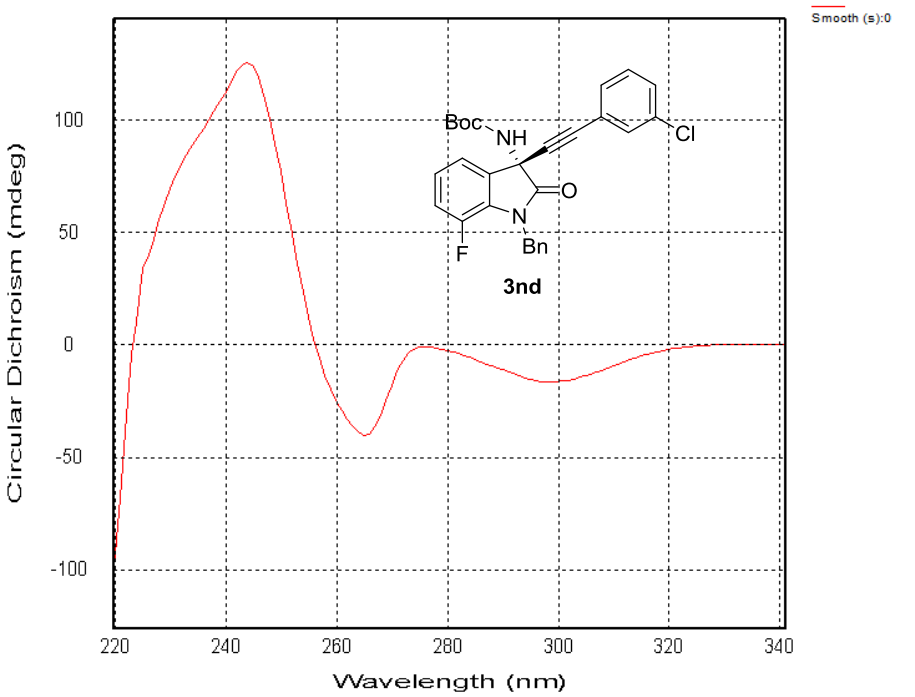
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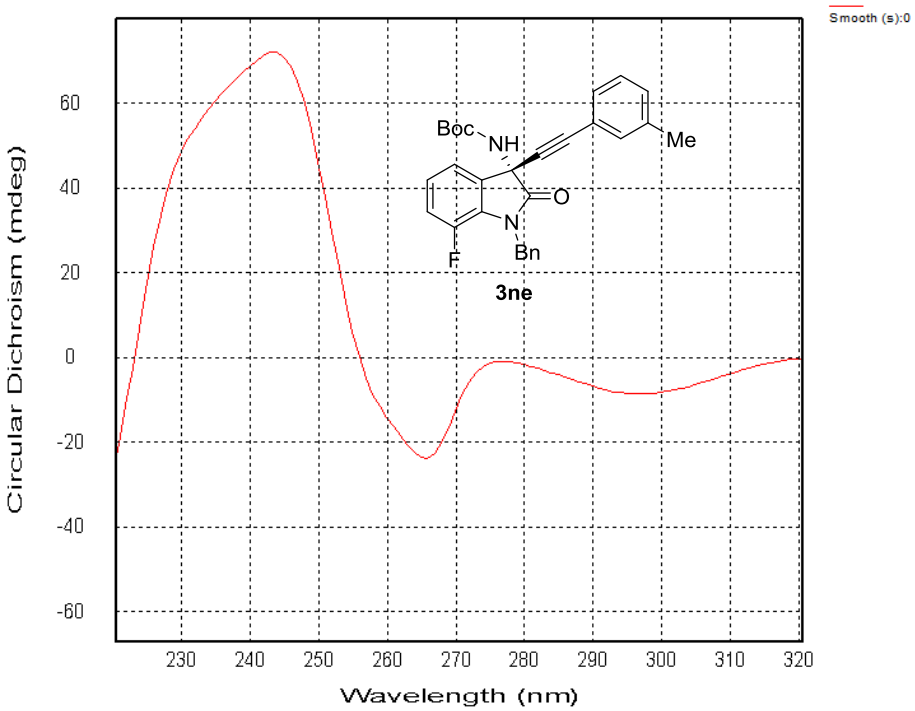
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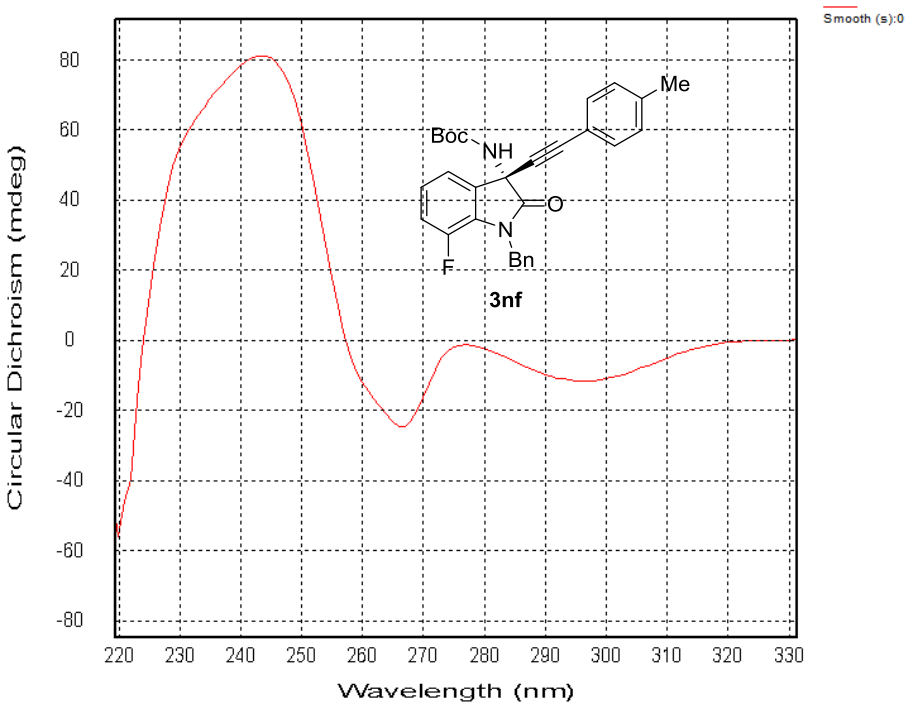
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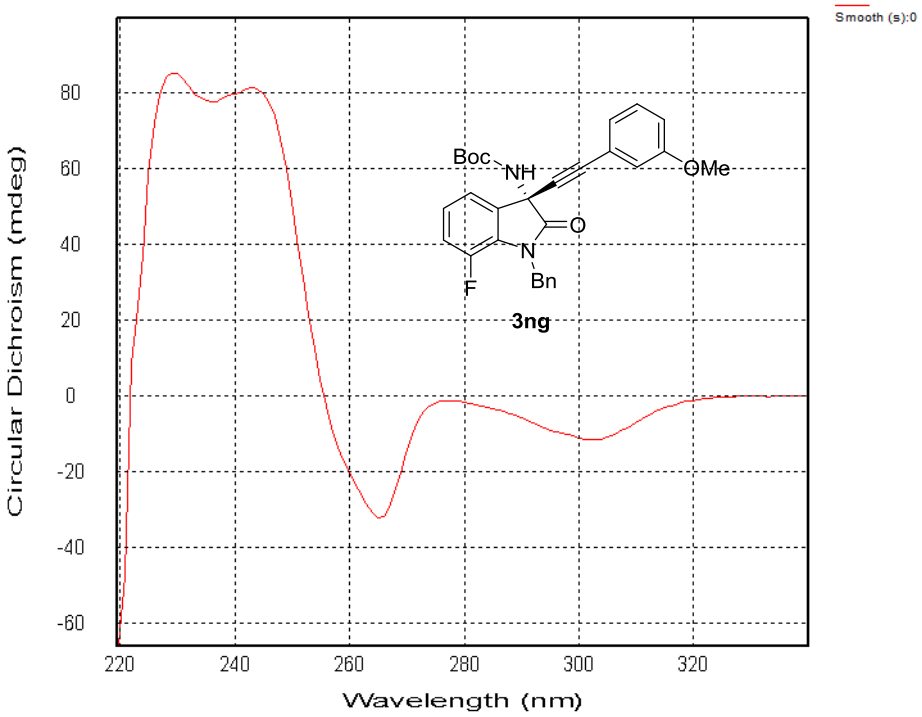
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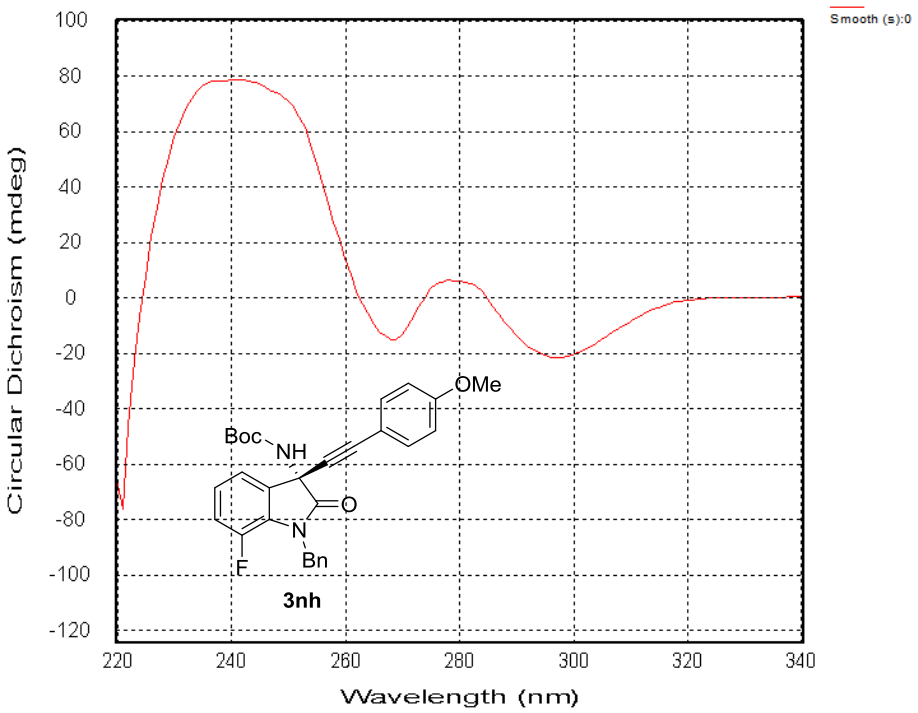
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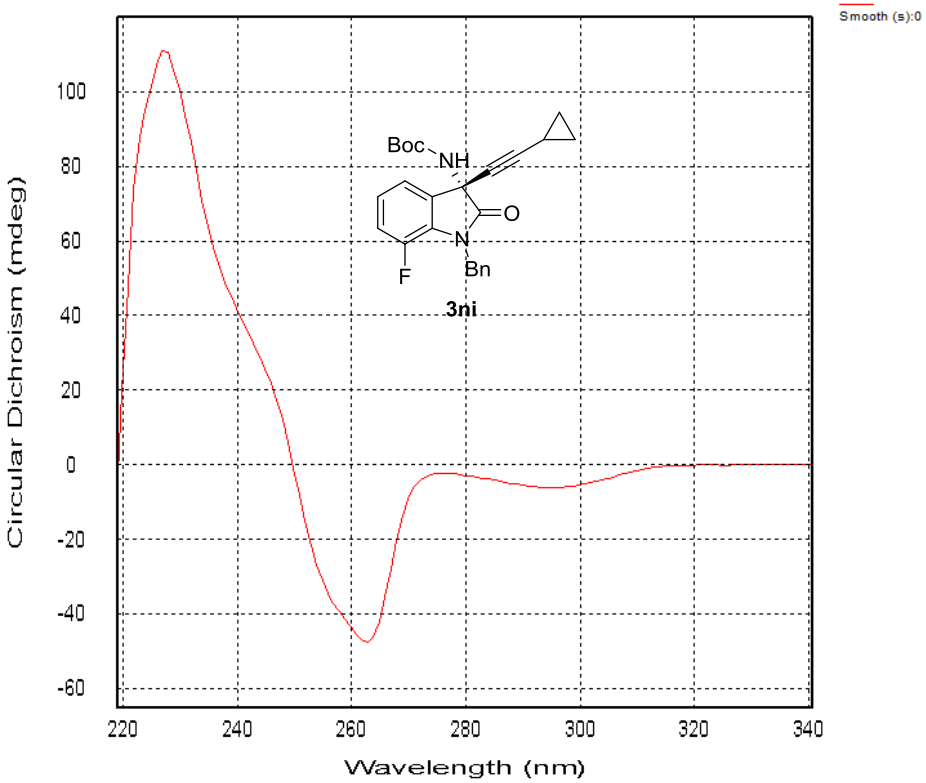
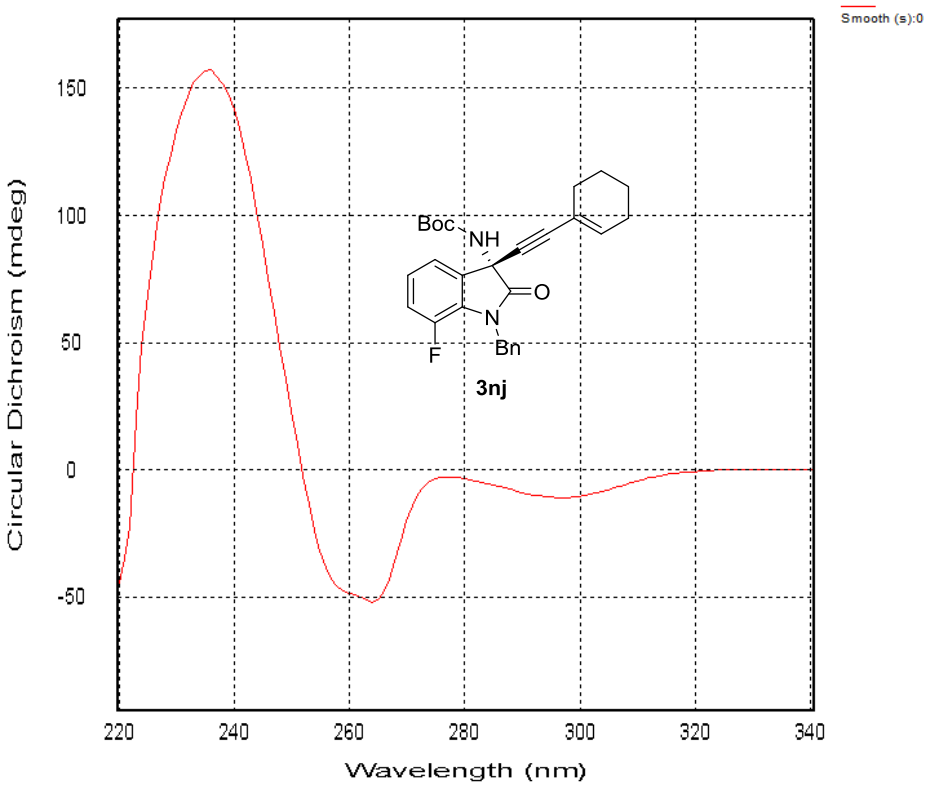
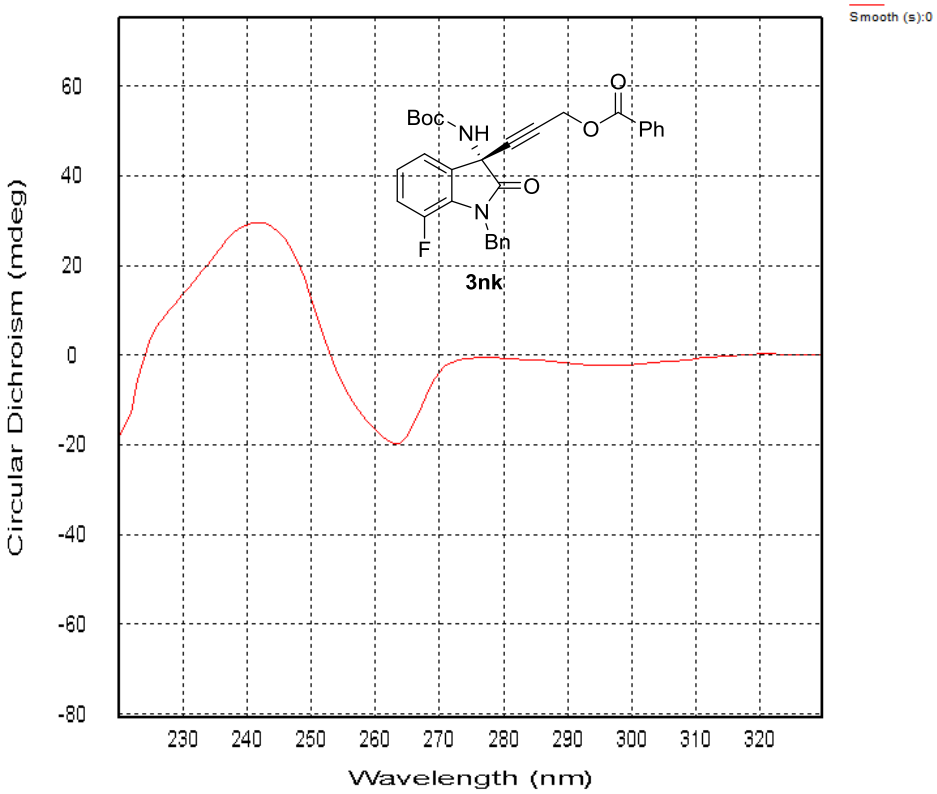
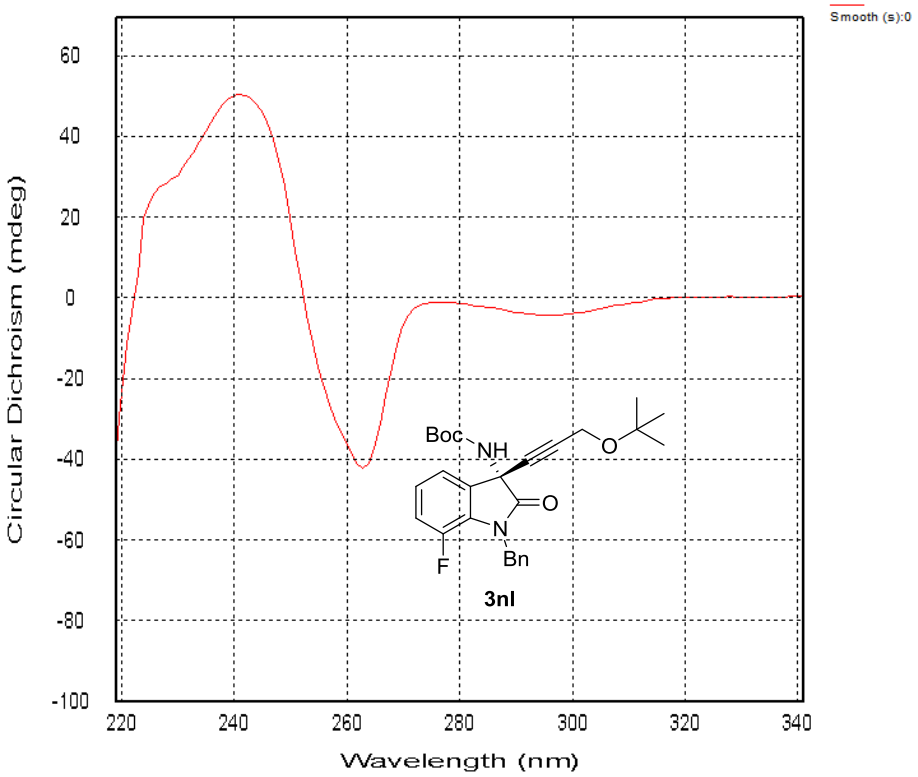
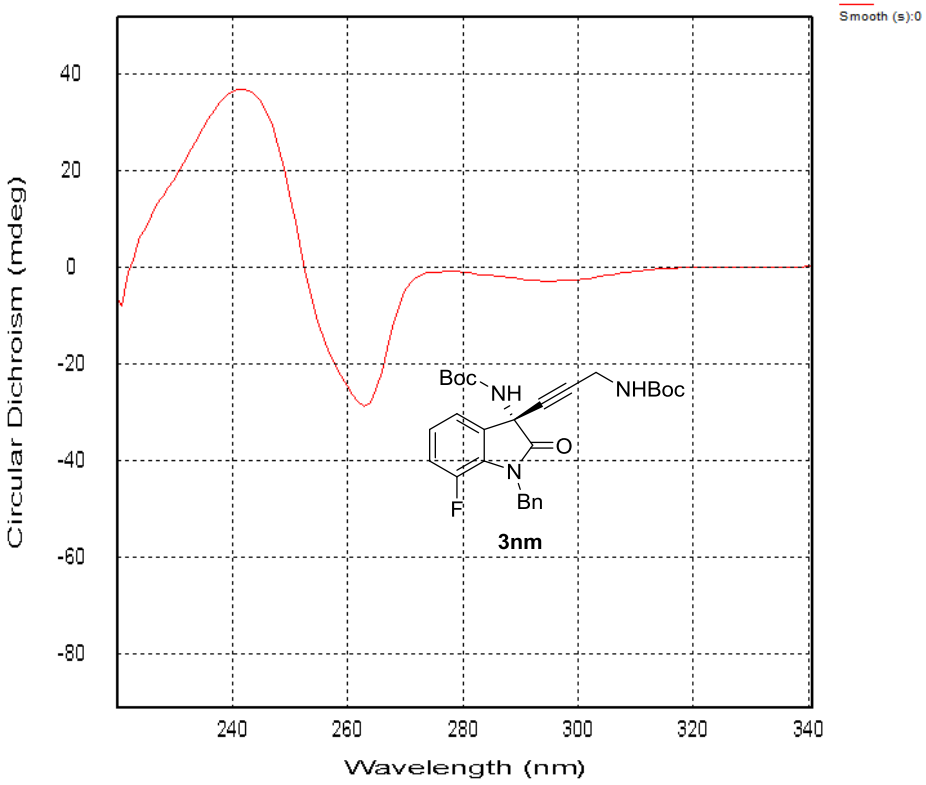
-80
-100
-120
220
240
260
280
300
320
340
Wavelength (nm)
OMe
Boc
NH
O
N
Bn
F
3nh


Smooth (s):0
Circular Dichroism (mdeg)
100
80
60
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
Wavelength (nm)
Boc
NH
O
N
Bn
F
3ni


Smooth (s):0
Circular Dichroism (mdeg)
150
100
50
0
-50
220
240
260
280
300
320
340
Wavelength (nm)
Boc
NH
O
N
Bn
F
3nj


Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Boc
NH
O
O
Ph
O
N
Bn
F
3nk





(M) References

[1] (a) Z. P. Yu, X. H. Liu, L. Zhou, L. L. Lin, X. M. Feng, *Angew.Chem. Int. Ed.* **2009**,

48, 5195. (b) S. X. Dong, X. H. Liu, Y. L. Zhang, L. L. Lin, X. M. Feng, *Org. Lett.* **2011**, *13*, 5060.