Electronic Supplementary Material (ESI) for ChemComm.

Catalytic Asymmetric Construction of Spiro[pyrrolidine-2,3'-oxindole] Scaffolds through a Chiral Phosphoric Acid-Catalyzed 1,3-Dipolar Cycloaddition Involving 3-Amino Oxindoles

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Contents

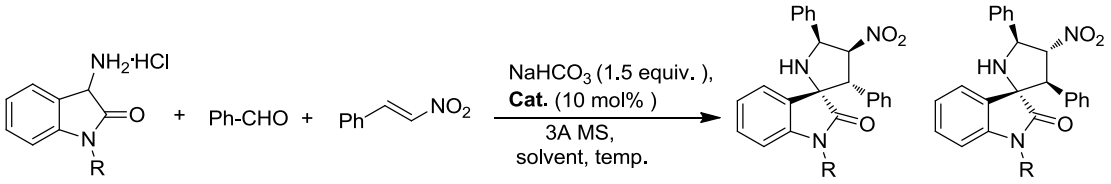
1. General information

All reactions were carried out in Schlenk tube under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{19}F NMR spectra were recorded on a Bruker Avance Ⅱ 400 MHz and Bruker Avance ⅢⅠ 471 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance Ⅱ 101 MHz or Bruker Avance ⅢⅠ 126 MHz. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = doublet doublet, coupling constants in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). HRMS (ESI) was determined by a HRMS/MS instrument (LTQ Orbitrap XL TM). Enantiomeric excess values were determined by HPLC employing a chiral column on Agilent 1100 series. Optical rotations were reported as follows: $[\alpha]_D^{18}$ (c g/100 mL, solvent). IR spectra were recorded using Nicolet-20DXB IR instrument and are reported in wavenumbers (cm^{-1}). The absolute configurations of **5s** were assigned by the X-ray analysis.

Starting materials: All the aldehydes were commercially obtained and recrystallized or distilled prior to use. 3-Amino oxindoles were prepared following the reported procedures: (1) W. B. Chen, Z. J. Wu, J. Hu., L. F. Cun, X. M. X. M Zhang and W. C. Yuan, *Org. Lett*., 2011, **13**, 2472. Nitroolefins were synthesized according to following literature procedures: (a) B. M. Trost and C. Müller, *J. Am. Chem. Soc.* 2008, **130**, 2438; (b) P. Cheng, J. J. Chen, N. Huang, R. R. Wang, Y. T. Zheng and Y. Z. Liang, *Molecules*, 2009, **14**, 3176; (c) P. Jakubec, D. M. Cockfield, P. S. Hynes, E. Cleator and D. J. Dixon, *Tetrahedron: Asymmetry*, 2011, **22**, 1147.

2. Experimental sections

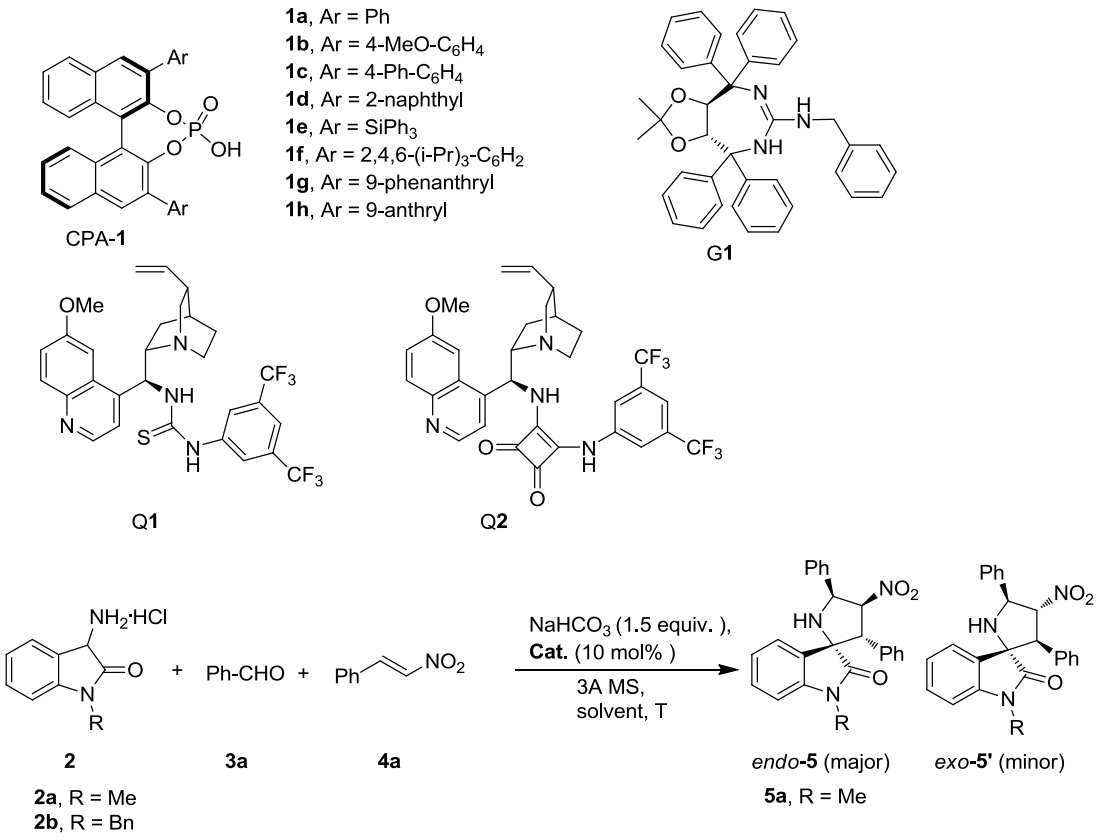
General procedure for the synthesis of spiro[indoline-3,2'-pyrrolidin]-2-one



In a Schlenk tube, 3-amino oxindole **2** (0.2 mmol) and $NaHCO_3$ (0.3 mmol) were added into solvent (2 mL) under an argon atmosphere. After the solution was stirred for 20 minutes at 25°C, 3Å MS (200 mg) was added and stirred for 20 minutes again. Then catalyst (0.02 mmol), aldehyde **3a** and nitroalkene **4a** were added to this flask in turn at the same temperature. The reaction mixture was stirred at the same temperature. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5**.

Screening of catalysts and optimization of conditions

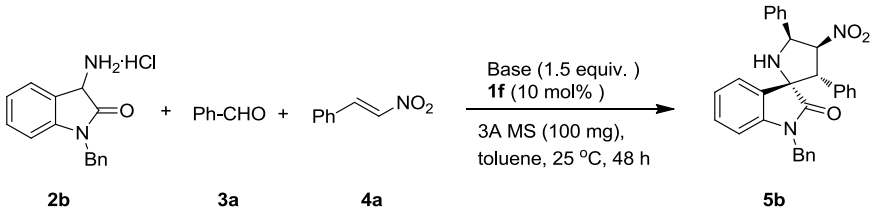
***Table 1*:** Optimization of reaction conditions.[a] CPA=chiral phosphoric acid.



Entry	R	**Cat.**	Solvent	*T* [℃]	*t* [h]	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	Me	G**1**	CH_2Cl_2	25	47	99	7 : 1	2
2	Me	Q**1**	CH_2Cl_2	25	12	98	9 : 1	-24
3	Me	Q**2**	CH_2Cl_2	25	12	96	9 : 1	-6
4	Me	**1a**	CH_2Cl_2	25	12	98	8 : 1	23
5	Me	**1b**	CH_2Cl_2	25	12	96	9 : 1	26
6	Me	**1e**	CH_2Cl_2	25	12	94	6 : 1	1
7	Me	**1f**	CH_2Cl_2	25	12	99	>20 : 1	75
8	Me	**1g**	CH_2Cl_2	25	12	96	20 : 1	67
9	Me	**1h**	CH_2Cl_2	25	12	99	12 : 1	44
10	Me	**1f**	$(CH_2Cl)_2$	25	12	99	17 : 1	65
11	Me	**1f**	$CHCl_3$	25	12	95	>20 : 1	74
12	Me	**1f**	THF	25	24	99	4 : 1	2
13	Me	**1f**	Et_2O	25	40	99	5 : 1	21
14	Me	**1f**	toluene	25	65	98	>20 : 1	89
15[e]	Me	**1f**	toluene	25	65	98	>20 : 1	89
16[e]	H	**1f**	toluene	25	144	29	>20 : 1	85
17[e]	Bn	**1f**	toluene	25	65	99	12 : 1	93
18[e]	Bn	**1f**	toluene	15	65	93	13 : 1	92
19[e]	Bn	**1f**	toluene	35	24	99	11 : 1	91
20[ef]	Bn	**1f**	toluene	25	65	99	10 : 1	90
21[eg]	Bn	**1f**	toluene	25	48	99	15 : 1	93
22[eh]	Bn	**1f**	toluene	25	65	98	12 : 1	92
23[ei]	Bn	**1f**	toluene	25	65	95	10 : 1	92
24[ej]	Bn	**1f**	toluene	25	65	82	14 : 1	90
25[ek]	Bn	**1f**	toluene	25	82	96	10 : 1	92

[a]The reaction was carried out on a 0.1 mmol scale with 3A MS (100 mg), **1** (10 mol%) in 1.0 ml solvent, the ratio of **2**/**3a**/**4a** was 1/2/1. [b]Isolated yield. [c]The dr was determined by ^{1}H NMR. [d]The *ee* was determined by HPLC. [e]The ratio of **2**/**3a**/**4a** was 1/1.2/1.1. f in the presence of 5 mol% **1f**. g in the presence of 15 mol% **1f**. [h]By using 4A MS (100 mg). [i]By using 5A MS (100 mg). [j]The reaction was performed at a 0.2 M concentration. [k]The reaction was performed at a 0.05 M concentration.

***Table 2*:** Optimization of base in the reaction [a]

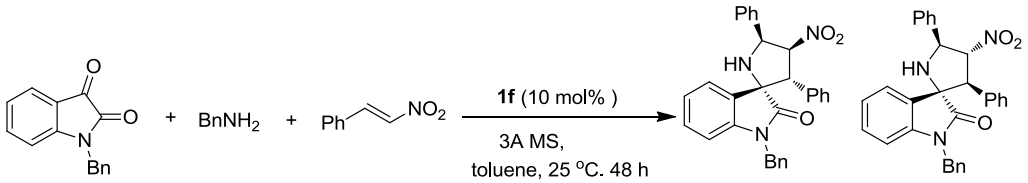


2b **3a** **4a** **5b**

Entry	Base	Yield [%]	d.r.	*ee* [%]
1	K_2HPO_4	82	11:1	89
2	$KHCO_3$	72	11:1	88
3	KF	72	12:1	88
4	Li_2CO_3	99	10:1	90

[a]The reaction was carried out on a 0.1 mmol scale with 3A MS (100 mg), **1** (10 mol%) in 1.0 ml solvent, the ratio of **2b**/**3a**/**4a** was 1/1.2/1.

Procedure for asymmetric catalytic [3+2] cycloaddition of isatin with benzylamine and nitroolefin in the presence CPA-**1f**

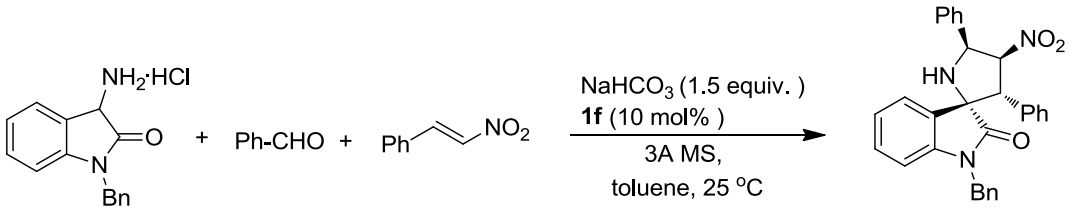


6 **7** **4a** **5 b** (endo-major) (exo-minor)

63% yield, 79% *ee*, 4:1 d.r.

In a Schlenk tube, isatin **6** (0.1 mmol) and 3Å MS (100 mg) were added in toluene (1 mL) under an argon atmosphere. After the solution was stirred for 20 minutes at 25°C, **1f** (0.01mmol), benzylamine **7** and nitroalkene **4a** were added to this flask in turn at the same temperature. The reaction mixture was stirred at the same temperature for 48 h. the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5b** with 4:1 dr and 79% *ee*, and the product was purified again by column chromatography (ethyl acetate/petroleum ether = 1/10) give 63% yield.

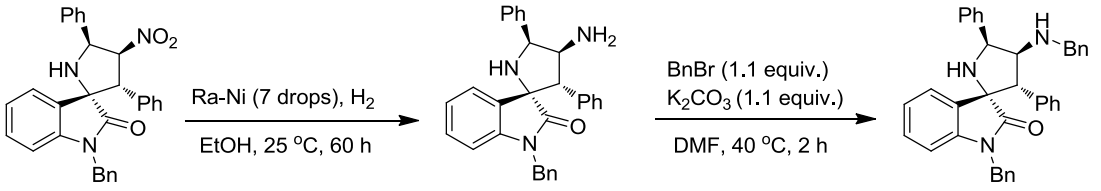
Procedure for gram-scale reactions



5b 1.05 g, 99% yield, 94% *ee,* 12:1 d.r.

In a Schlenk tube, 3-amino oxindole (2.2 mmol) and $NaHCO_3$ (3.3 mmol) were added in solvent (22 mL) under an argon atmosphere. After the solution was stirred for 20 minutes at 25 °C, 3Å MS (2.2 g) was added and stirred for 20 minutes again. Then **1f** (0.22 mmol), benzaldehyde and nitrostyrene were added to this flask in turn at the same temperature for 65 h. The crude product was purified by column chromatography on silica gel to give the product **5b**.

Procedure for the Synthesis of Compound **8** and **9**

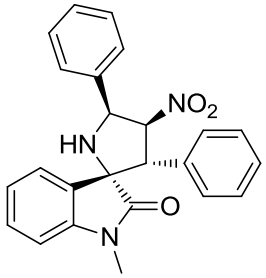


5b, 96% *ee* **8**, 88% yield **9**, 70% yield, 96% *ee*

The spiro[indoline-3,2'-pyrrolidin]-2-one **5b** (0.2 mmol, 95.1 mg) was added in EtOH (5 mL), Raney nickel (7 drops of the commercially available suspension in water) was added, and the reaction mixture was stirred at 25 °C under an H_2 balloon for 60 h. Then the mixture was filtered and washed with EtOH. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/4 to 1/2) to afford product **8** (78 mg, 88% yield).

The spiro[indoline-3,2'-pyrrolidin]-2-one **8** (0.2 mmol, 89 mg) and K_2CO_3 (0.22 mmol, 30 mg) was added in DMF (5 mL) under an argon atmosphere , then BnBr (0.22 mmol, 37.6 mg) was added. The reaction mixture was stirred 40 °C for 2 h. The reaction mixture was cooled to room temperature and quenched with ethyl acetate (5 mL) and water (5 mL). Then this solution was extracted with ethyl acetate (5×2 mL). The organic phases were washed with water (10 ml), brine (10 ml) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/10) to afford product **9** (75 mg, 70% yield).

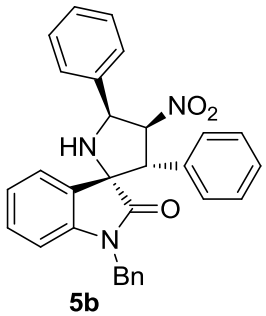
Characterization data of spiro[indoline-3,2'-pyrrolidin]-2-one



5a

(2'S,3'S,4'S,5'S)-1-methyl-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (5a)

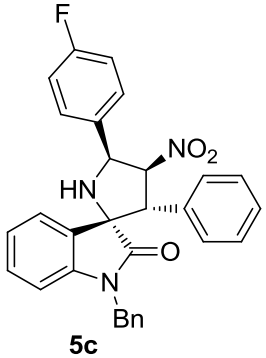
White solid, mp: 167-169 ℃, 92% ee. $[\alpha]_D^{18}$ = 11.1 (*c* 0.69, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.37–7.25 (m, 4H), 7.22 – 7.20 (m, 1H), 7.13 – 7.07 (m, 3H), 6.98 (dd, *J* = 8.0, 1.3 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.38 (t, *J* = 9.9 Hz, 1H), 5.86 (d, *J* = 9.7 Hz, 1H), 4.56 (d, *J* = 10.1 Hz, 1H), 2.79 (s, 3H), 2.59 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 143.8, 138.1, 132.1, 130.0, 128.8, 128.4, 128.3, 128.3, 127.9, 127.9, 123.8, 123.4, 108.3, 91.1, 72.0, 61.5, 56.4, 25.7; IR (thin film): 3340.0, 1704.7, 1614.4, 1552.6, 1493.4, 1470.1, 1373.0, 1350.2, 1112.2, 749.2, 699.1 cm^{-1}; HRMS (ESI) for $C_{24}H_{21}N_3O_3$ $[M+H]^+$ calcd 400.1656, found 400.1649. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes: i-propanol = 90:10, 0.8 mL/min, λ = 254 nm) t_R (major) = 21.8 min, t_R (minor) = 21.8 min.



5b

(2'S,3'S,4'S,5'S)-1-benzyl-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (5b)

White solid, mp: 97-99℃, 93% ee. $[\alpha]_D^{18}$ = 69.3 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.25 – 7.12 (m, 6H), 7.06 (t, *J* = 8.1 Hz, 4H), 6.49 – 6.42 (m, 3H), 6.38 (d, *J* = 7.3 Hz, 1H), 5.92 (dd, *J* = 9.6, 5.5 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.69 (d, *J* = 9.8 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.66 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 143.1, 137.9, 134.7, 132.2, 130.0, 128.8, 128.7, 128.4, 128.2, 127.9, 127.9, 127.3, 126.4, 124.0, 123.5, 109.6, 91.3, 71.9, 61.6, 56.2, 43.5; IR (thin film): 3332.3, 1705.4, 1614.3, 1552.9, 1490.8, 1467.4, 1454.3, 1365.6, 1176.4, 748.7, 697.7 cm^{-1}; HRMS (ESI) for $C_{30}H_{25}N_3O_3$ $[M+H]^+$ calcd 476.1969, found 476.1961. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 25.2 min, t_R (minor) = 29.5 min.

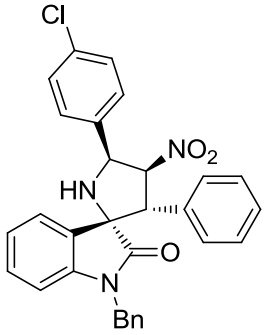


5c

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(4-fluorophenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5c)

White solid, mp:104-106℃, 93% ee. $[\alpha]_D^{18}$ = 65 (*c* 0.84, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.15 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.08 – 7.01 (m, 6H), 6.44 (dd, *J* = 11.6, 8.3 Hz, 3H), 6.38 (d, *J* = 7.2 Hz, 1H), 5.90 (dd, *J* = 9.6, 5.0 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 2.66 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR

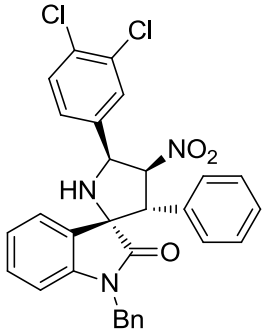
(101 MHz, $CDCl_3$) δ 178.0, 163.0(d, *J*=247.4 Hz), 143.1, 134.6, 133.7(d, *J*=3.0 Hz), 132.1, 130.1, 129.6(d, *J*=9.1 Hz), 128.9, 128.7, 128.4, 128.2, 127.7, 127.4, 126.4, 124.0, 123.5, 115.3(d, *J*=22.2 Hz) 109.7, 91.1, 71.8, 60.7, 56.0, 43.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.05; IR (thin film): 3346.2, 1704.4, 1614.7, 1552.3, 1508.2, 1467.7, 1365.8, 1223.9, 1176.2, 741.8, 697.3 cm^{-1} ;HRMS (ESI) for $C_{30}H_{24}FN_3O_3$ $[M+H]^+$ calcd 494.1874, found 494.1865. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 14.1 min, t_R (minor) = 21.2 min.



5d

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(4-chlorophenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5d)

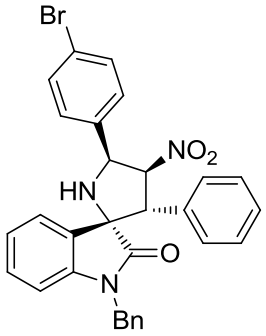
White solid, mp: 99-101℃, 97% ee. $[\alpha]_D^{18}$ = 70.7 (*c* 0.79, CH_2Cl_2);
^1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.17 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 3H), 7.06 (dd, *J* = 13.8, 7.4 Hz, 4H), 6.47 – 6.42 (m, 3H), 6.38 (d, *J* = 7.2 Hz, 1H), 5.89 (dd, *J* = 9.7, 5.2 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 9.8 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.67 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 143.1, 136.5, 134.6, 132.0, 130.1, 129.2, 128.9, 128.7, 128.6, 128.4, 128.2, 127.6, 127.4, 126.4, 124.0, 123.5, 109.7, 91.0, 71.8, 60.7, 56.0, 43.4; IR (thin film): 3347.3, 1704.2, 1615.0, 1552.5, 1490.0, 1467.4, 1365.7, 1176.4, 1088.8, 742.8, 697.2 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}ClN_3O_3$ $[M+H]^+$ calcd 510.1579, found 510.1569. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 15.3 min, t_R (minor) = 24.2 min.



5e

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(3,4-dichlorophenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5e)

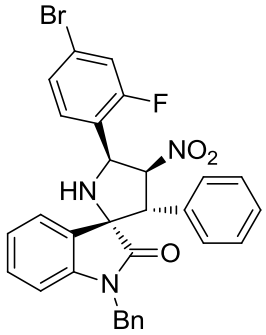
White solid, mp: 105-107℃, 96% ee. $[\alpha]_D^{18}$ = 55.2 (*c* 0.88, CH_2Cl_2);
^1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.40 (s, 2H), 7.28 – 7.18 (m, 3H), 7.14 (t, *J* = 7.7 Hz, 3H), 7.06 (dd, *J* = 15.3, 7.7 Hz, 4H), 6.48 –6.38 (m, 4H), 5.85 (dd, *J* = 9.7, 5.2 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.69 (d, *J* = 5.3 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 143.1, 138.3, 134.6, 132.8, 132.6, 131.7, 130.3, 130.2, 129.9, 128.9, 128.7, 128.5, 128.1, 127.4, 127.3, 126.4, 124.1, 123.6, 109.8, 90.8, 71.8, 60.0, 55.9, 43.5; IR (thin film): 3324.8, 1704.6, 1614.5, 1552.8, 1489.3, 1467.6, 1365.4, 1176.8, 1030.2, 742.8, 696.9 cm^{-1}; HRMS (ESI) for $C_{30}H_{23}Cl_2N_3O_3$ $[M+H]^+$ calcd 544.1189, found 544.1173. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 18.3 min, t_R (minor) = 30.1 min.



5f

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(4-bromophenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5f)

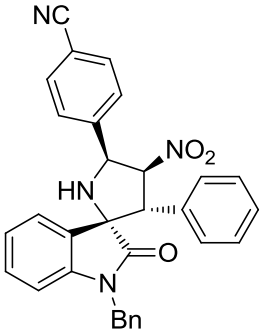
White solid, mp: 95-97℃, 97% ee. $[\alpha]_D^{18}$ = 62.7 (*c* 0.94, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.25 – 7.19 (m, 2H), 7.18 – 7.11 (m, 4H), 7.05 (dd, *J* = 14.7, 7.6 Hz, 4H), 6.48 – 6.39 (m, 3H), 6.47 – 6.41 (m, 1H), 5.86 (dd, *J* = 9.7, 5.2 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 9.8 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 2.67 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 143.1, 137.0, 134.6, 131.9, 131.5, 130.1, 129.6, 128.9, 128.7, 128.5, 128.2, 127.6, 127.4, 126.4, 124.0, 123.5, 122.9, 109.7, 91.0, 71.8, 60.8, 56.0, 43.4; IR (thin film): 3332.3, 1705.2, 1614.3, 1552.4, 1488.3, 1467.3, 1364.6, 1176.4, 1011.2, 742.8, 697.0 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}BrN_3O_3$ $[M+H]^+$ calcd 554.1074, found 544.1043; Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 16.1 min, t_R (minor) = 21.8 min.



5g

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(4-bromo-2-fluorophenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5g)

White solid, mp: 175-177℃, 95% ee. $[\alpha]_D^{18}$ = 57.3 (*c* 0.81, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.28 – 7.22 (m, 2H), 7.12-7.21 (m, *J* = 5H), 7.06 (t, *J* = 8.2 Hz, 4H), 6.44 – 6.39 (m, 4H), 6.23 (dd, *J* = 9.3, 5.6 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 9.0 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 2.59 (d, *J* = 3.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 160.4(d, *J* = 254.5 Hz), 143.2, 134.6, 132.1, 130.2, 128.9, 128.7, 128.5, 128.3, 127.6, 127.5, 127.4, 126.5, 124.3(d, *J* = 12.6 Hz), 124.0, 123.5, 122.9(d, *J* = 10.8 Hz), 119.0(d, *J* = 25.2 Hz), 109.7, 90.9, 71.9, 56.9, 55.0, 43.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.03; IR (thin film): 3339.6, 1707.9, 1614.2, 1553.3, 1486.7, 1467.7, 1363.0, 1177.1, 863.1, 744.0, 696.9 cm^{-1}; HRMS (ESI) for $C_{30}H_{23}BrFN_3O_3$ $[M+H]^+$ calcd 572.0980, found 572.0950. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 11.2 min, t_R (minor) = 15.2 min.

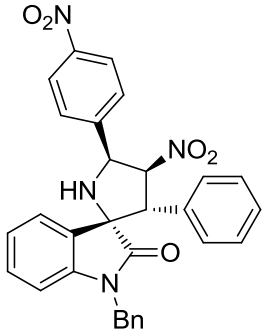


5h

4-((2'S,3'S,4'S,5'S)-1-benzyl-4'-nitro-2-oxo-3'-phenylspiro[indoline-3,2'-pyrrolidin]-5'-yl)benzonitrile (5h)

White solid, mp: 115-117 ℃, >99% ee. $[\alpha]_D^{18}$ = 61.4 (*c* 0.75, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.12 (m, 4H), 7.06 (dd, *J* = 13.8, 7.4 Hz, 4H), 6.47 – 6.37 (m, 4H), 5.89 (dd, *J* = 9.7, 5.2 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 9.8 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.67 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 143.4, 143.1, 134.5,

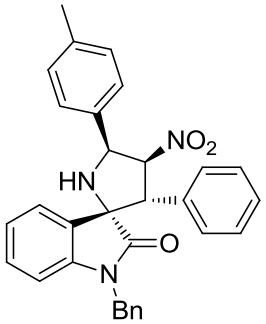
132.1, 131.6, 130.3, 128.9, 128.7, 128.7, 128.6, 128.1, 127.4, 127.3, 126.4, 124.0, 123.6, 118.6, 112.6, 109.8, 90.9, 71.9, 60.6, 55.9, 43.5; IR (thin film): 3324.8, 2229.2, 1705.1, 1614.2, 1552.7, 1495.8, 1467.6, 1366.2, 1176.9, 742.6, 697.6 cm^{-1}; HRMS (ESI) for $C_{31}H_{24}N_4O_3$ $[M+H]^+$ calcd 501.1921, found 501.1912. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 26.0 min.



5i

(2'S,3'S,4'S,5'S)-1-benzyl-4'-nitro-5'-(4-nitrophenyl)-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5i)

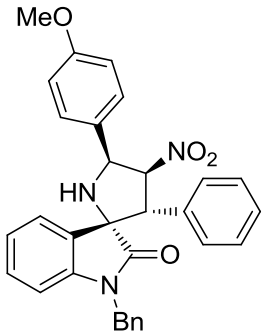
White solid, mp: 116-118℃, 98% ee. $[\alpha]_D^{18}$ = 51.3 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.84 – 7.79 (m, 3H), 7.29 – 7.23 (m, 2H), 7.21 – 7.14 (m, 4H), 7.09 – 7.05 (m, 4H), 6.54 (t, *J* = 9.9 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 2H), 6.41 (d, *J* = 7.2 Hz, 1H), 6.02 (d, *J* = 9.8 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 9.9 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 2.79 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 148.1, 145.4, 143.1, 134.5, 131.5, 130.3, 128.9, 128.8, 128.7, 128.6, 128.1, 127.4, 127.2, 126.4, 124.0, 123.6, 123.5, 109.8, 90.9, 71.9, 60.4, 56.0, 43.5; IR (thin film): 3332.3, 1704.9, 1614.2, 1552.8, 1521.9, 1467.6, 1347.2, 1176.6, 857.3, 747.7, 697.4 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}N_4O_5$ $[M+H]^+$ calcd 521.1819, found 521.1814; Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 21.2 min. t_R (minor) = 39.6 min.



5j

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(4-methoxyphenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5j)

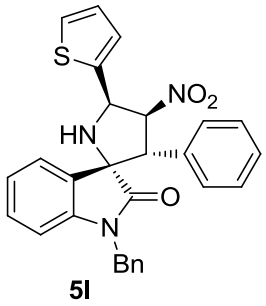
White solid; mp: 99-101℃, 90% ee. $[\alpha]_D^{18}$ = 68.7 (*c* 0.77, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 15.5, 7.1 Hz, 2H), 7.14 (dd, *J* = 14.7, 7.1 Hz, 6H), 7.05 (dd, *J* = 11.8, 4.7 Hz, 4H), 6.46 – 6.40 (m, 3H), 6.36 (d, *J* = 7.3 Hz, 1H), 5.88 (dd, *J* = 9.6, 5.4 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 9.8 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 2.63 (d, *J* = 5.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 143.1, 138.6, 134.9, 134.7, 132.3, 130.0, 129.1, 128.8, 128.7, 128.3, 128.2, 128.0, 127.8, 127.3, 126.4, 124.0, 123.4, 109.6, 91.3, 71.9, 61.5, 56.2, 43.4, 21.3; IR (thin film): 3334.5, 1705.9, 1614.3, 1552.5, 1489.1, 1467.4, 1364.3, 1176.2, 742.5, 697.0 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_3$ $[M+H]^+$ calcd 490.2125, found 490.2115. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 13.4 min. t_R (minor) = 17.0 min.



5k

(2'S,3'S,4'S,5'S)-1-benzyl-5'-(4-methoxyphenyl)-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5k)

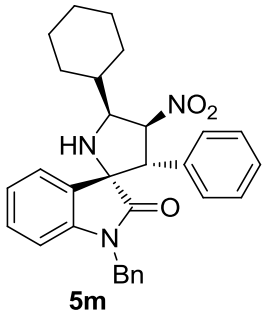
White solid, mp: 96-98℃, 99% ee. $[\alpha]_D^{18}$ = 78.3 (*c* 0.48, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.21 (m, 1H), 7.20 – 7.13 (m, 5H), 7.07 (t, *J* = 8.2 Hz, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.42 (t, *J* = 9.0 Hz, 3H), 6.40 – 6.37(m, 1H), 5.89 (d, *J* = 9.6 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.69 (d, *J* = 9.8 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 3.77 (s, 3H), 2.65 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 134.7, 132.3, 130.0, 129.0, 128.8, 128.7, 128.3, 128.2, 127.3, 126.4, 124.0, 123.4, 113.7, 109.6, 91.3, 71.8, 61.2, 56.1, 55.2, 43.4; IR (thin film): 3332.3, 1705.0, 1613.1, 1551.8, 1511.3, 1364.0, 1249.2, 1173.5, 1030.9, 743.5, 697.3 cm^{-1} ; HRMS (ESI) for $C_{31}H_{27}N_3O_4$ $[M+H]^+$ calcd 506.2074, found 506.2068. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 19.7 min. t_R (minor) = 24.5 min.



5l

(2'S,3'S,4'S,5'R)-1-benzyl-4'-nitro-3'-phenyl-5'-(thiophen-2-yl)spiro[indoline-3,2'-pyrrolidin]-2-one (5l)

White solid, mp: 93-95℃, >99% ee. $[\alpha]_D^{18}$ = 38.3 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 5.0 Hz, 1H), 7.24–7.17 (m, 2H), 7.12 (q, *J* = 7.5 Hz, 4H), 7.07 – 6.99 (m, 6H), 6.60 – 6.55 (m, 1H), 6.38 (d, *J* = 7.5 Hz, 2H), 6.34 (d, *J* = 7.6 Hz, 1H), 6.00 (dd, *J* = 9.4, 5.7 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 3.02 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.1 (s), 143.8 (d, *J* = 1.3 Hz), 143.0 (s), 134.6 (s), 131.7 (s), 130.1 (s), 128.8 (d, *J* = 15.9 Hz), 128.4 (s), 128.0 (d, *J* = 9.7 Hz), 127.5 (s), 127.3 (s), 126.4 (s), 125.8 (s), 125.4 (s), 124.3 (s), 123.6 (s), 109.7 (s), 89.4 (s), 71.4 (s), 57.0 (s), 54.6 (s), 43.5(s); IR (thin film): 3329.9, 1705.7, 1614.2, 1553.6, 1489.0, 1454.5, 1365.5, 1177.6, 796.4, 742.0, 697.1 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_4$ $[M+H]^+$ calcd 482.1533, found 482.1521.Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexanes:i-propanol = 60:40, 0.8 mL/min, λ = 254 nm) t_R (major) = 12.5 min.



5m

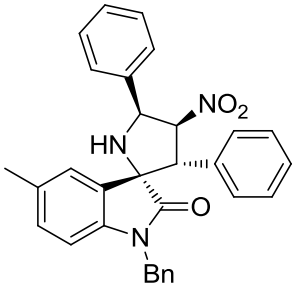
(2'S,3'S,4'S,5'S)-1-benzyl-5'-cyclohexyl-4'-nitro-3'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5m)

White solid, mp: 163-165℃, 4% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 1H), 7.26 (dd, *J* = 13.1, 5.8 Hz, 1H), 7.11-7.20 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.43 – 6.37 (m, 3H), 5.97 (t, *J* = 6.4 Hz, 1H), 5.04 (d, *J* = 15.9 Hz, 1H), 4.59 – 4.55 (m, 1H), 4.43 (d, *J* = 5.7 Hz, 1H), 4.09 (d, *J* = 15.9 Hz, 1H), 2.84 (s, 1H), 1.89 (d, *J* = 10.5 Hz, 2H), 1.73

(s, 2H), 1.66 (d, *J* = 9.0 Hz, 1H), 1.49 (d, *J* = 8.7 Hz, 1H), 1.30 – 1.17 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 143.0, 134.9, 133.9, 129.9, 128.7, 128.6, 128.5, 128.3, 128.1, 127.2, 126.5, 123.4, 123.3, 109.4, 93.8, 72.8, 67.3, 61.5, 43.4, 39.2, 31.1, 30.4, 26.2, 25.7, 25.7.

IR (thin film): 3339.8, 2926.1, 2852.7, 1712.3, 1614.1, 1547.6, 1493.8, 1468.2, 1362.8, 1175.5, 745.4, 697.0 cm^{-1}; HRMS (ESI) for $C_{30}H_{31}N_3O_3$ $[M+H]^+$ calcd 482.2438 found 482.2430. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 9.5 min. t_R (minor) = 7.9 min.

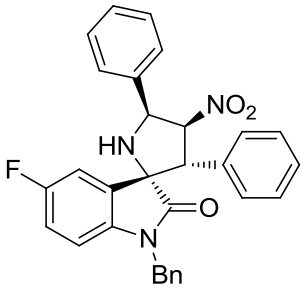


5n

(2'S,3'S,4'S,5'S)-1-benzyl-5-methyl-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (5n)

White solid, mp:118-120℃, 87% ee. $[\alpha]_D^{18}$ = 80 (*c* 0.44, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 3H), 7.40 – 7.32 (m, 3H), 7.28 – 7.23 (m, 1H), 7.18 – 7.12 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 4H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.45 (dd, *J* = 18.2, 8.5 Hz, 3H), 6.27 (d, *J* = 7.9 Hz, 1H), 5.94 (dd, *J* = 9.5, 5.0 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 9.7 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.65 (d, *J* = 5.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 140.7, 137.9, 134.8, 133.1, 132.4, 130.3, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9, 127.3, 126.4, 124.6, 109.4, 91.5, 72.0, 61.6, 56.3, 43.4, 21.3; IR (thin film): 3332.3, 1704.1, 1603.7, 1553.6, 1496.7, 1454.1, 1366.5, 1167.2, 809.7, 738.3, 697.5 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_3$ [M+H]+ calcd 490.2125 , found 490.2116. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 14.3 min, t_R (minor) = 16.3 min.



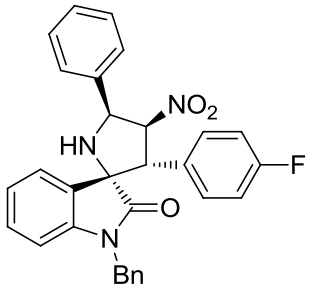
5o

(2'S,3'S,4'S,5'S)-1-benzyl-5-fluoro-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (5o)

White solid; mp: 93-95℃, 97% ee. $[\alpha]_D^{18}$ = 61 (*c* 0.67, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 3H), 7.38 – 7.26 (m, 4H), 7.16 (dd, *J* = 15.5, 7.8 Hz, 3H), 7.09 – 7.05 (m, 4H), 6.84 (td, *J* = 8.8, 2.6 Hz, 1H), 6.43 (dd, *J* = 20.3, 8.6 Hz, 3H), 6.28 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.91 (dd, *J* = 9.6, 5.1 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 9.8 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 2.67 (d, *J* = 5.3 Hz, 1H).

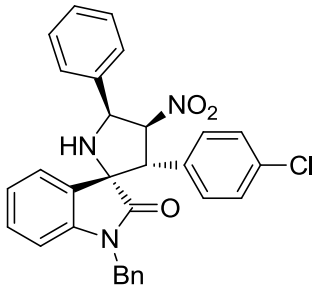
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 159.7(d, *J* = 243.4 Hz), 138.9(d, *J*=2.0 Hz), 137.6, 134.4, 131.9, 130.0(d, *J*=7.1 Hz), 128.9, 128.8, 128.6, 128.4, 128.2, 127.9, 127.5, 126.4, 116.4(d, J = 23.3 Hz), 112.1(d,J = 25.3 Hz),110.4(d,*J*=7.1 Hz), 91.0, 72.0, 72.0, 61.5, 56.3, 43.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.67; IR (thin film): 3332.3, 1707.8, 1616.0, 1555.3, 1492.6, 1366.1, 1266.7, 1172.0, 814.4, 737.9, 697.9 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}FN_3O_3$ [M+H]+ calcd 494.1874 , found 494.1857. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column.(n-hexanes:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm), t_R (major) = 44.2 min, t_R (minor) = 54.0 min.



5p

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(4-fluorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5p)

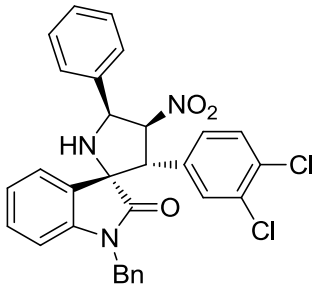
White solid, mp: 104-106℃, 91% ee. $[\alpha]_D^{18}$ = 54.4 (*c* 0.55, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.21 – 7.18 (m, 3H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.01 (dd, *J* = 8.5, 5.3 Hz, 2H), 6.81 (t, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 7.4 Hz, 2H), 6.46 – 6.38 (m, 2H), 5.90 (d, *J* = 9.2 Hz, 1H), 5.01 (d, *J* = 15.9 Hz, 1H), 4.65 (d, *J* = 9.9 Hz, 1H), 4.22 (d, *J* = 15.9 Hz, 1H), 2.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 162.8(d, *J*=248.5 Hz), 143.1, 137.8, 134.7, 130.2, 129.9(d,*J*=8.1 Hz), 128.9, 128.7, 128.4, 128.0 (d,*J*=4.0 Hz), 127.8, 127.7, 127.6, 126.5, 124.0, 123.6, 115.8(d, *J*=22.2Hz), 109.6, 91.2, 71.8, 61.4, 55.4, 43.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.31; IR (thin film): 3332.3, 1704.8, 1614.1, 1554.3, 1512.7, 1467.5, 1366.2, 1235.5, 1176.9, 751.7, 698.9 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}FN_3O_3$ $[M+H]^+$ calcd 494.1874 found 494.1866. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column. (n-hexanes:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm) t_R (major) = 35.8 min. t_R (minor) = 48.9 min.



5q

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(3,4-dichlorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5q)

White solid, mp: 115-117℃, 84% ee. $[\alpha]_D^{18}$ = 78.4 (*c* 0.62, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.21 – 7.14 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 6.5 Hz, 2H), 6.44 – 6.39 (m, 2H), 5.89 (d, *J* = 9.5 Hz, 1H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.65 (d, *J* = 9.9 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 2.67 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 143.1, 137.7, 134.6, 134.5, 130.8, 130.2, 129.5, 129.0, 128.9, 128.7, 128.4, 127.8, 127.6, 127.5, 126.4, 124.0, 123.6, 109.7, 91.0, 71.7, 61.4, 55.5, 43.5; IR (thin film): 3329.9, 1705.2, 1614.4, 1554.6, 1493.8, 1467.3, 1364.4, 1176.1, 1094.0, 751.5, 698.6 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}ClN_3O_3$ $[M+H]^+$ calcd 510.1579 found 510.1576; Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 30.2 min. t_R (minor) = 27.7 min.

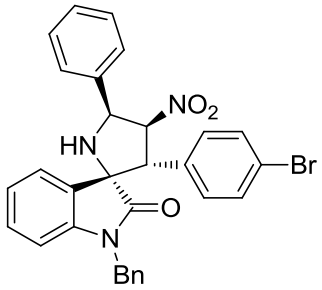


5r

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(3,4-dichlorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5r)

White solid, mp: 95-97℃, 88% ee. $[\alpha]_D^{18}$ = 74.4 (*c* 0.51, CH_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.3, 3.2 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.24 – 7.15 (m, 7H), 6.85 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.59 (d, *J* = 7.1 Hz, 2H), 6.52 (dd, *J* = 5.4, 3.2 Hz, 1H), 6.37 (t, *J* = 9.8 Hz, 1H), 5.90 – 5.88 (m, 1H), 5.06 (d, *J* = 15.8 Hz, 1H), 4.62 (d, *J* = 9.9 Hz, 1H), 4.24 (d, *J* = 15.8 Hz, 1H), 2.68 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ

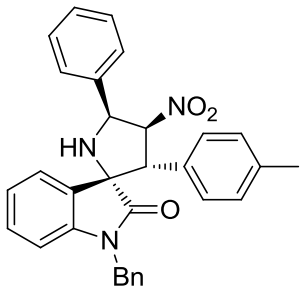
177.6, 143.1, 137.5, 134.6, 133.0, 132.8, 132.6, 130.7, 130.4, 130.0, 129.0, 128.8, 128.4, 127.8, 127.7, 127.5, 127.2, 126.5, 124.0, 123.7, 109.8, 90.8, 71.5, 61.4, 55.0, 43.6; IR (thin film): 3333.9, 1704.5, 1614.4, 1553.4, 1467.9, 1489.5, 1365.6, 1177.0, 1029.9, 750.9, 698.8 cm^{-1}; HRMS (ESI) for $C_{30}H_{23}Cl_2N_3O_3$ $[M+H]^+$ calcd 544.1189 found 544.1180. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 20.0 min. t_R (minor) = 17.3 min.



5s

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(4-bromophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5s)

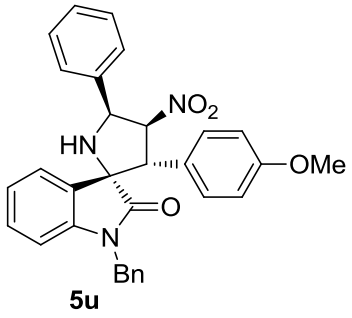
White solid, mp: 128-130℃, 86% ee. $[\alpha]_D^{18}$ = 74.3 (*c* 0.46, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.18 (m, 5H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.50 – 6.48 (m, 2H), 6.43 (dd, *J* = 18.6, 9.0 Hz, 2H), 5.91 (d, *J* = 9.6 Hz, 1H), 5.07 (d, *J* = 15.9 Hz, 1H), 4.64 (d, *J* = 9.9 Hz, 1H), 4.21 (d, *J* = 15.9 Hz, 1H), 2.68 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8 ,143.1, 137.7, 134.6, 131.9, 131.3, 130.2, 129.9, 128.9, 128.8, 128.4, 127.8, 127.6, 127.5, 126.4, 124.0, 123.6, 122.7, 109.7, 90.9, 71.7, 61.4, 55.5, 43.6; IR (thin film): 3333.9, 1705.2, 1614.2, 1553.5, 1489.9, 1467.3, 1365.9, 1176.2, 751.4, 698.2 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}BrN_3O_3$ $[M+H]^+$ calcd 554.1074 found 554.1045. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 16.1 min. t_R (minor) = 13.6 min.



5t

(2'S,3'S,4'S,5'S)-1-benzyl-4'-nitro-5'-phenyl-3'-(p-tolyl)spiro[indoline-3,2'-pyrrolidin]-2-one (5t)

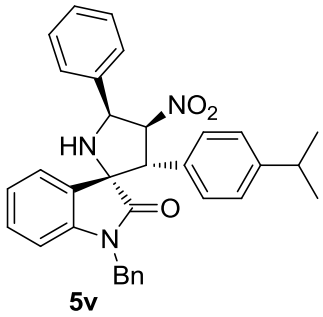
White solid, mp: 99-101℃, 94% ee. $[\alpha]_D^{18}$ = 72.6 (*c* 0.74, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.15 (dd, *J* = 15.8, 6.7 Hz, 3H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.93 (s, 4H), 6.44 (dd, *J* = 14.3, 8.7 Hz, 3H), 6.37 (d, *J* = 7.5 Hz, 1H), 5.89 (d, *J* = 9.6 Hz, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 9.8 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 2.68 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 143.2, 138.0, 138.0, 134.8, 123.0, 129.5, 129.2, 128.8, 128.5, 128.4, 128.1, 128.1, 127.9, 127.3, 126.6, 124.0, 123.4, 109.6, 91.4, 71.9, 61.5, 55.9, 43.5, 21.2; IR (thin film): 3344.0, 1705.0, 1614.8, 1553.9, 1490.3, 1467.4, 1365.9, 1177.4, 751.2, 698.9 cm^{-1} ;HRMS (ESI) for $C_{31}H_{27}N_3O_3$ $[M+H]^+$ calcd 490.2125 found 490.2118. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column. (n-hexanes:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 35.8 min. t_R (minor) = 22.1 min.



5u

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(4-methoxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5u)

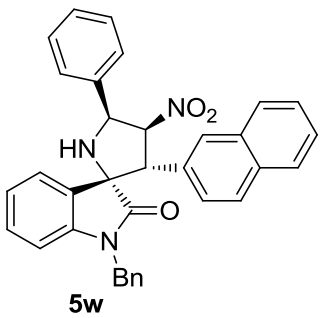
White solid, mp: 186-188℃, 97% ee. $[\alpha]_D^{18}$ = 0.768 (*c* 0.77, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.21 – 7.13 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.66 (t, *J* = 5.9 Hz, 2H), 6.46 – 6.38 (m, 4H), 5.89 (d, *J* = 9.6 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.63 (d, *J* = 9.9 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 3.70 (s, 3H), 2.66 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 159.7, 143.2, 138.0, 134.7, 130.0, 129.3, 128.8, 128.6, 128.3, 128.1, 127.9, 127.4, 126.5, 124.1, 124.0, 123.4, 114.1, 109.6, 91.4, 71.9, 61.4, 55.6, 55.1, 43.4; IR (thin film): 3325.8, 1705.8, 1613.6, 1553.0, 1515.6, 1467.1, 1364.7, 1253.1, 1180.8, 1030.2, 750.7, 698.7 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_4$ $[M+H]^+$ calcd 506.20745 found 506.2066. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexanes:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 28.1 min. t_R (minor) = 30.5 min.



5v

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(4-isopropylphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5v)

White solid, mp: 94-96℃, 92% ee. $[\alpha]_D^{18}$ = 65.8 (*c* 0.69, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.20 – 7.11 (m, 3H), 7.08 (dd, *J* = 10.0, 4.6 Hz, 2H), 7.03 – 6.98 (m, 4H), 6.59 (d, *J* = 7.3 Hz, 2H), 6.44 – 6.37 (m, 2H), 5.91 (d, *J* = 9.8 Hz, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 2.84 (hept, *J* = 6.9 Hz, 1H), 2.64 (s, 1H), 1.18 (dd, *J* = 6.9, 2.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 148.8, 143.2, 137.9, 134.9, 130.0, 129.6, 128.8, 128.6, 128.3, 128.2, 128.1, 127.9, 127.4, 126.8, 126.6, 124.0, 123.4, 109.7, 91.9, 71.8, 61.5, 56.0, 43.6, 33.6, 23.9, 23.8; IR (thin film): 3339.8, 2961.5, 1706.3, 1614.3, 1553.4, 1489.8, 1467.3, 1364.7, 1175.3, 750.4, 698.1 cm^{-1}; HRMS (ESI) for $C_{33}H_{31}N_3O_3$ $[M+H]^+$ calcd 518.2438 found 518.2430.Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexanes:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm) t_R (major) = 22.8 min. t_R (minor) = 17.2 min.

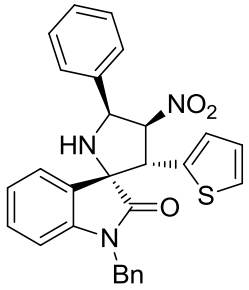


5w

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(naphthalen-2-yl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one(5w)

White solid, mp: 96-98℃, >99% ee. $[\alpha]_D^{18}$ = -58 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.67 – 7.64 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 3H), 7.35 – 7.27 (m, 2H), 7.14-7.18 (m, 2H), 7.07 – 6.99 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.36 (t, *J* = 8.2 Hz, 1H), 6.21 (d, *J* = 7.6 Hz, 2H), 6.15 (t, *J* = 7.1 Hz, 2H), 5.72 (d, *J* = 7.6 Hz, 1H), 4.93 (d, *J* =

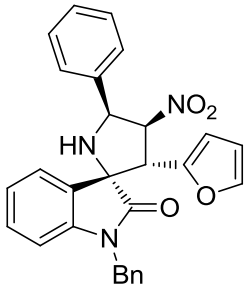
16.0 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 2.89 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 143.0, 137.2, 134.6, 133.7, 132.1, 130.0, 129.6, 128.9, 128.9, 128.6, 128.5, 128.5, 128.2, 127.6, 127.2, 126.2, 126.1, 126.0, 125.8, 125.5, 124.3, 123.2, 122.9, 109.6, 95.4, 72.4, 63.4, 51.4, 43.3; IR (thin film): 3329.9, 3062.4, 1705.2, 1614.0, 1553.2, 1489.9, 1467.7, 1364.5, 1177.0, 789.6, 750.9, 698.2 cm^{-1}; HRMS (ESI) for $C_{34}H_{27}N_3O_3$ $[M+H]^+$ calcd 526.2125 found 526.2118. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.8 mL/min, λ = 254 nm) t_R (major) = 21.8 min.



5x

(2'S,3'S,4'S,5'S)-1-benzyl-4'-nitro-5'-phenyl-3'-(thiophen-2-yl)spiro[indoline-3,2'-pyrrolidin]-2-one (5x)

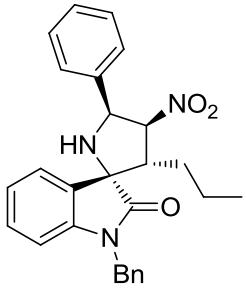
White solid, mp: 101-103℃, 96% ee. $[\alpha]_D^{18}$ = 41.5 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.7, 2.9 Hz, 1H), 7.58 (d, *J* = 6.9 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.21 – 7.19 (m, 2H), 7.17 – 7.11 (m, 3H), 7.05 (dd, *J* = 5.0, 0.9 Hz, 1H), 6.84 – 6.82 (m, 1H), 6.80 (d, *J* = 3.4 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 2H), 6.50 – 6.48 (m, 1H), 6.40 (t, *J* = 10.0 Hz, 1H), 5.86 (dd, *J* = 9.8, 5.0 Hz, 1H), 5.02 (d, *J* = 15.9 Hz, 1H), 4.89 (d, *J* = 10.1 Hz, 1H), 4.27 (d, *J* = 15.9 Hz, 1H), 2.62 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 148.8, 134.9, 129.9, 128.8, 128.6, 128.3, 128.2, 127.9, 127.4, 126.8, 126.6, 124.0, 123.4, 109.7, 91.9, 71.8, 61.5, 56.0, 43.6, 33.6, 23.9, 23.8.
IR (thin film): 3338.1, 1705.4, 1615.0, 1554.5, 1490.1, 1467.4, 1367.2, 1177.5, 750.8, 699.2 cm^{-1}
HRMS (ESI) for $C_{28}H_{23}N_3O_3S$ $[M+H]^+$ calcd 482.1533 found 482.1526. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexanes:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm) t_R (major) = 56.9 min. t_R (minor) = 42.4 min.



5y

(2'S,3'S,4'S,5'S)-1-benzyl-3'-(furan-2-yl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (5y)

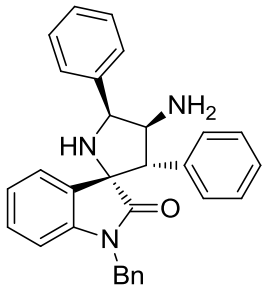
White solid, mp: 89-91℃, 96% ee. $[\alpha]_D^{18}$ = 28.9 (*c* 0.43, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.37 – 7.31 (m, 3H), 7.25 – 7.18 (m, 5H), 7.16 – 7.15 (m, 1H), 6.92 – 6.89 (m, 2H), 6.60 – 6.58 (m, 1H), 6.17 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.97 (d, *J* = 3.3 Hz, 1H), 5.88 (dd, *J* = 9.6, 4.5 Hz, 1H), 5.05 (d, *J* = 15.8 Hz, 1H), 4.79 (d, *J* = 9.4 Hz, 1H), 4.39 (d, *J* = 15.8 Hz, 1H), 2.60 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 147.4, 143.3, 142.8, 137.4, 135.1, 130.1, 128.8, 128.8, 128.3, 127.9, 127.6, 127.6, 127.1, 124.0, 123.5, 110.5, 109.5, 108.4, 90.8, 70.1, 61.4, 50.3, 43.6; IR (thin film): 3337.1, 1707.9, 1614.6, 1553.6, 1489.6, 1467.4, 1365.3, 1176.3, 744.0, 698.7 cm^{-1}; HRMS (ESI) for $C_{28}H_{23}N_3O_4$ $[M+H]^+$ calcd 466.1761 found 466.1754. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column. (n-hexanes:i-propanol = 90:10, 0.8 mL/min, λ = 254 nm), t_R (major) = 55.7 min. t_R (minor) = 37.7 min.



5z

(2'S,3'S,4'S,5'S)-1-benzyl-4'-nitro-5'-phenyl-3'-propylspiro[indoline-3,2'-pyrrolidin]-2-one (5z)

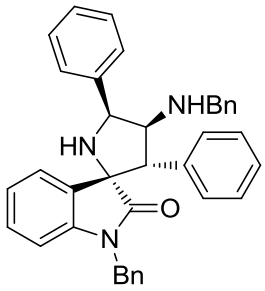
White solid, mp: 66-68℃, 93% ee. $[\alpha]_D^{18}$ = -38.6 (*c* 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.34 – 7.24 (m, 9H), 7.16 (td, *J* = 7.6, 0.9 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.78 (d, *J* = 8.7 Hz, 1H), 5.51 (dd, *J* = 8.9, 7.3 Hz, 1H), 5.05 (d, *J* = 15.5 Hz, 1H), 4.69 (d, *J* = 15.5 Hz, 1H), 3.42 (ddd, *J* = 10.0, 7.2, 5.2 Hz, 1H), 2.52 (s, 1H), 1.58 – 1.47 (m, 1H), 1.27 – 1.19 (m, 1H), 1.18 – 1.08 (m, 1H), 1.03 – 0.94 (m, 1H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 143.2, 137.0, 135.7, 129.8, 128.9, 128.8, 128.6, 128.3, 127.9, 127.5, 127.5, 124.1, 123.5, 109.3, 94.7, 70.1, 62.6, 52.5, 43.7, 31.1, 20.9, 13.9; IR (thin film) 3329.9, 2964.9, 2927.4, 1705.7, 1613.9, 1551.8, 1489.2, 1466.8, 1361.7, 1174.7, 752.0, 698.6 cm^{-1}; HRMS (ESI) for $C_{27}H_{27}N_3O_3$ $[M+H]^+$ calcd 442.2125 found 422.2118. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm), t_R (major) = 22.9 min. t_R (minor) = 24.9 min.



8

(2'S,3'S,4'S,5'S)-4'-amino-1-benzyl-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (8)

White solid, mp: 89-91℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.6 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.03 (m, 10H), 6.41 (d, *J* = 7.3 Hz, 2H), 6.31 (d, *J* = 7.6 Hz, 1H), 5.33 (d, *J* = 9.2 Hz, 1H), 5.02 (dd, *J* = 18.6, 9.9 Hz, 2H), 4.17 (d, *J* = 16.1 Hz, 1H), 3.41 (d, *J* = 11.0 Hz, 1H), 1.46 (br s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 143.0, 142.7, 135.1, 134.7, 130.5, 129.1, 128.7, 128.6, 128.6, 128.4, 128.3, 127.6, 127.4, 127.1, 126.4, 123.6, 122.9, 109.2, 71.7, 62.1, 61.5, 55.6, 43.5; IR (thin film): 3338.0, 1710.1, 1613.4, 1489.1, 1466.3, 1453.3, 1353.4, 1176.0, 740.8, 698.3 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}N_3O$ $[M+H]^+$ calcd 446.2227 found 446.2220.



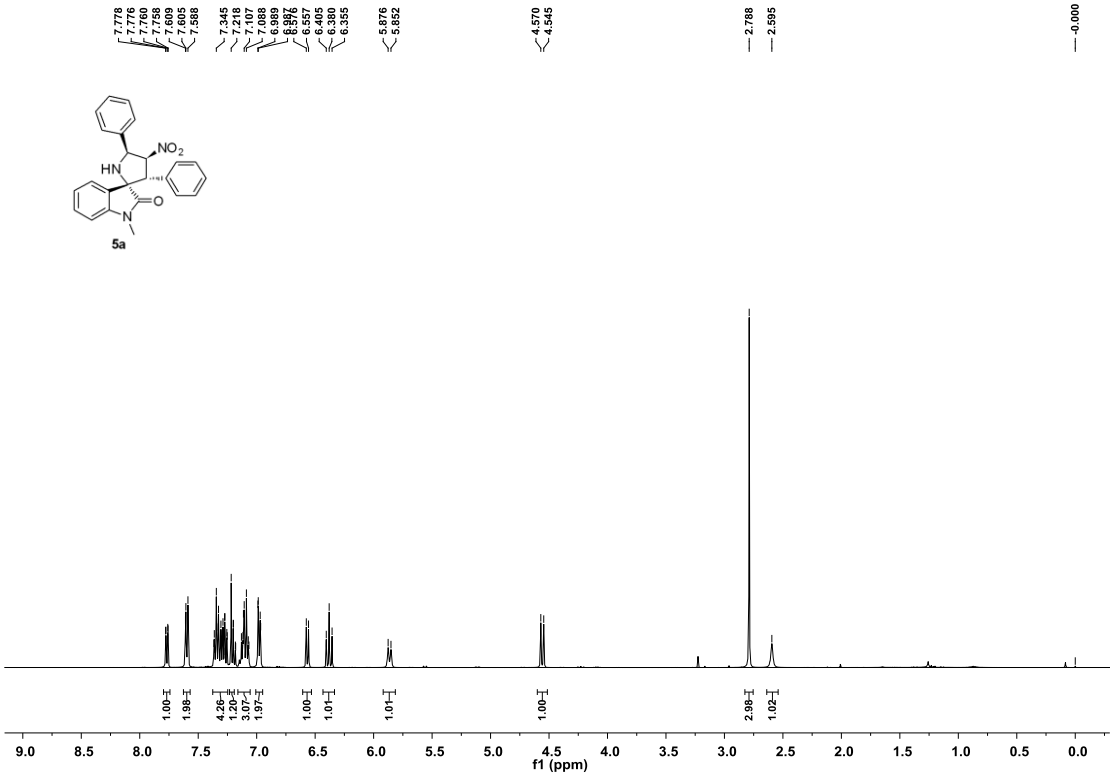
9

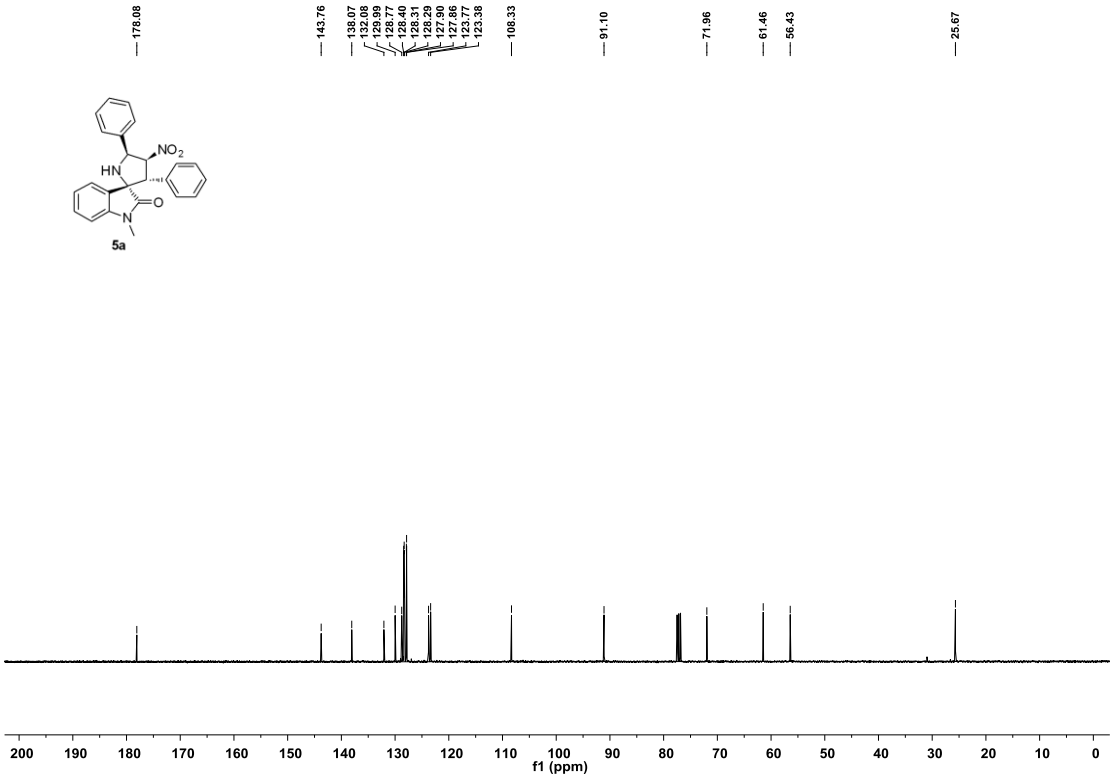
(2'S,3'S,4'S,5'S)-1-benzyl-4'-(benzylamino)-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (9)

White solid, 97% ee. mp: 67-69℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 9.0 Hz, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.23 – 7.05 (m, 12H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.82 (dd, *J* = 6.6, 2.8 Hz, 2H), 6.41 (d, *J* = 7.3 Hz, 2H), 6.30 (d, *J* = 7.3 Hz, 1H), 5.49 (d, *J* = 8.9 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.82 (dd, *J* = 10.7, 9.0 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.45 (s, 2H), 2.55 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 143.0, 142.4, 140.1, 135.2, 135.1, 130.4, 129.0, 128.9, 128.8, 128.6, 128.3, 128.3, 128.2, 128.1, 127.6, 127.3, 127.0, 126.8, 126.4, 123.6, 122.9, 109.2, 71.7, 61.8, 61.1, 60.4, 52.3, 43.4; IR (thin film): 3340.0, 2954.5, 2924.0, 1707.4, 1613.8, 1489.8, 1466.1, 1453.5, 1355.6, 1174.4, 742.0, 697.4 cm^{-1}; HRMS (ESI) for $C_{37}H_{33}N_3O$ $[M+H]^+$ calcd 536.2696 found 536.2706. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column. (n-hexanes:i-propanol = 70:30, 0.5 mL/min, λ = 254 nm) t_R (major) = 12.3 min. t_R (minor) = 14.4 min.

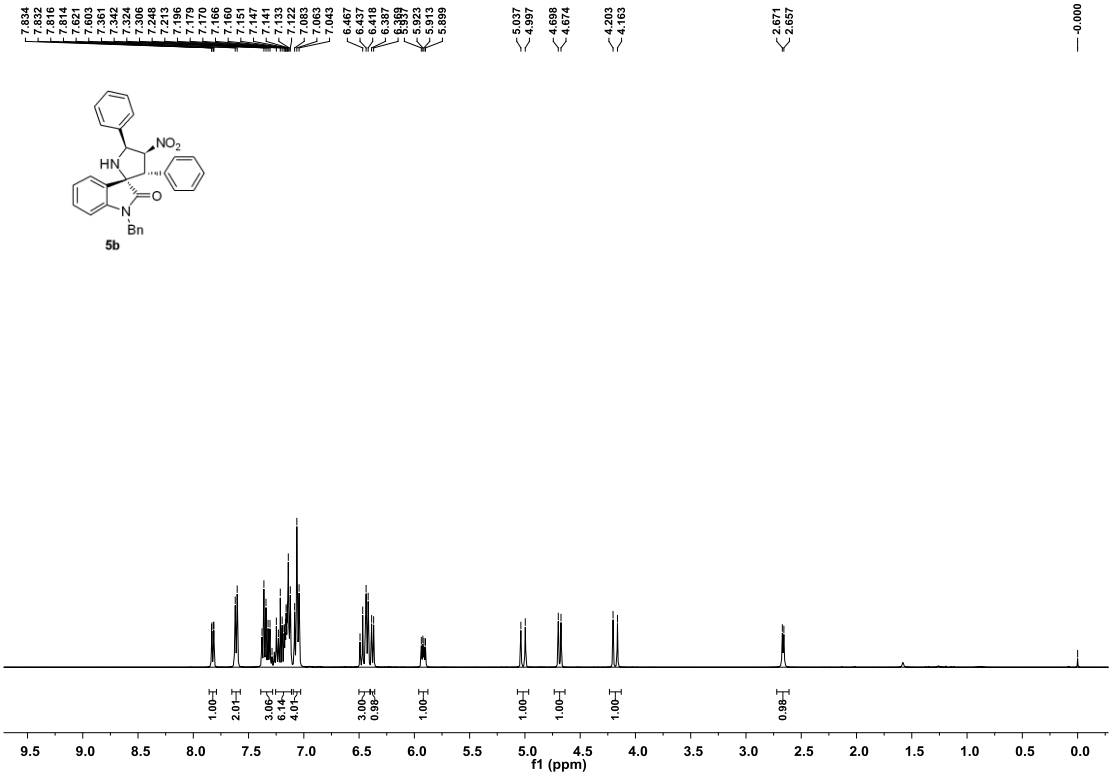
3. Copies of 1H NMR and 13C NMR spectra of the compounds

5a





5b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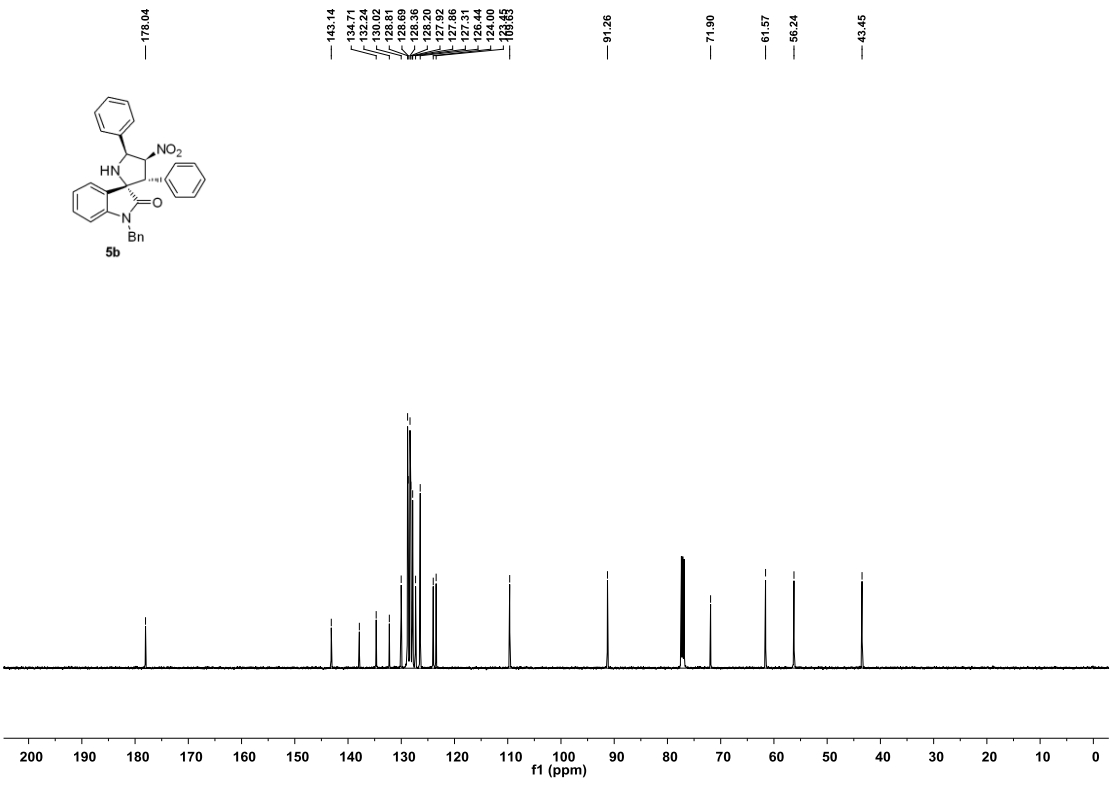
7.248
7.213
7.196
7.179
7.170
7.166
7.160
7.151
7.147
7.141
7.133
7.122
7.083
7.063
7.043
6.467
6.437
6.418
6.387
5.923
5.913
5.899
5.037
4.997
4.698
4.674
4.203
4.163
2.671
2.657
0.000
NO2
HN
O
N
Bn
5b
1.00
2.01
3.06
6.14
4.01
3.00
0.98
1.00
1.00
1.00
1.00
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.71
132.24
130.02
128.81
128.69
128.36
128.20
127.92
127.86
127.31
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124.00
123.45
109.83
91.26
71.90
61.57
56.24
43.45
NO2
HN
O
N
Bn
5b
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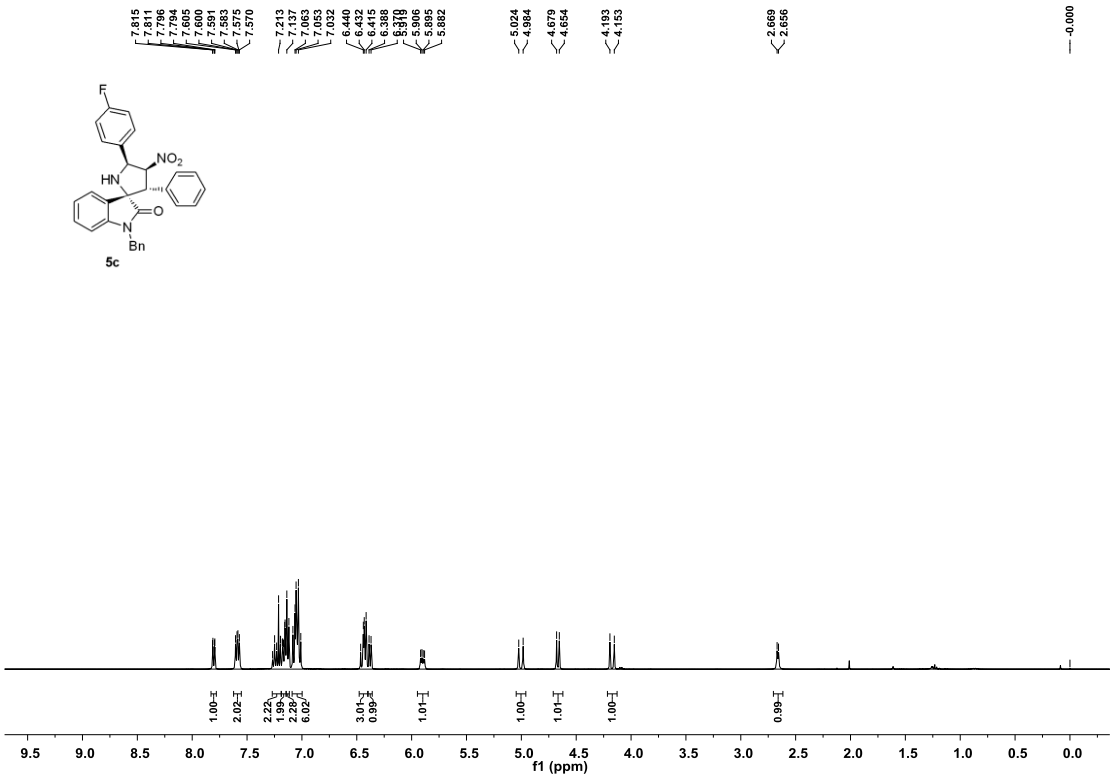
f1 (ppm)

5c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7.796
7.794
7.605
7.600
7.591
7.583
7.575
7.570
7.213
7.137
7.063
7.053
7.032
6.440
6.432
6.415
6.388
5.906
5.895
5.882
5.024
4.984
4.679
4.654
4.193
4.153
2.669
2.656
-0.000
F
NO2
HN
O
N
Bn
5c
1.00
2.02
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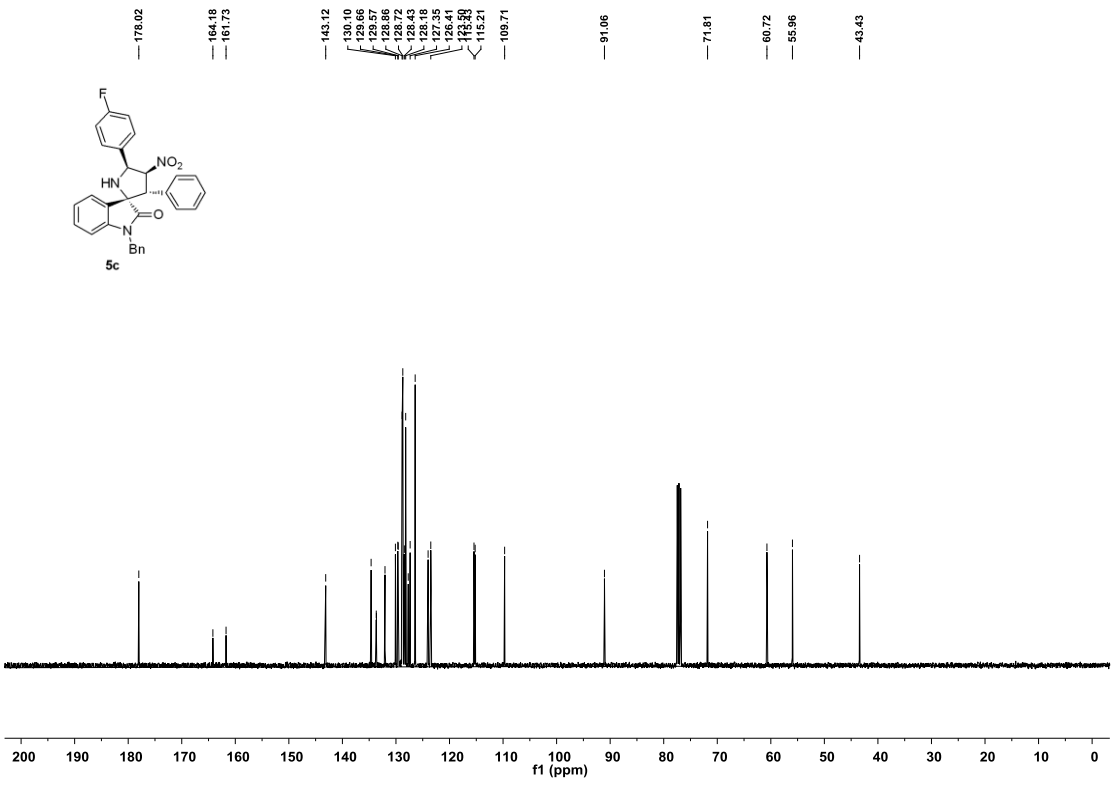
6.02
3.01
0.99
1.01
1.00
1.01
1.00
0.99
f1 (ppm)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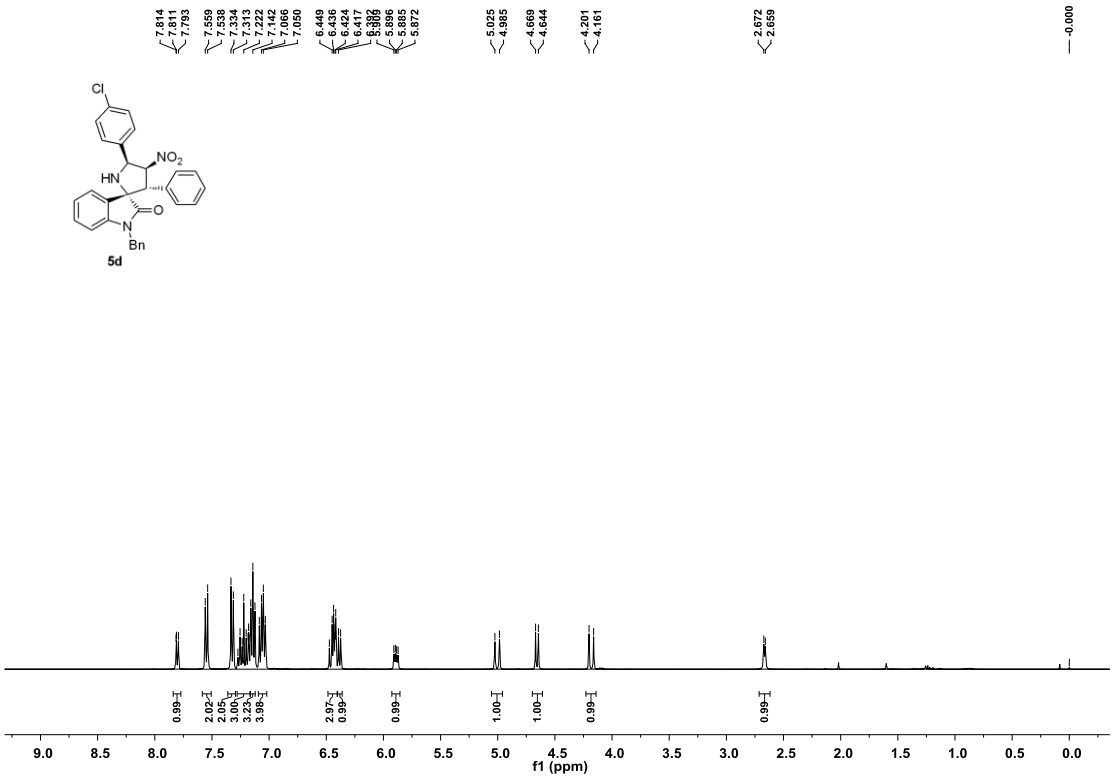
164.18
161.73
143.12
130.10
129.66
129.57
128.86
128.72
128.43
128.18
127.35
126.41
115.43
115.21
109.71
91.06
71.81
60.72
55.96
43.43
F
NO2
HN
O
N
Bn
5c
f1 (ppm)

5d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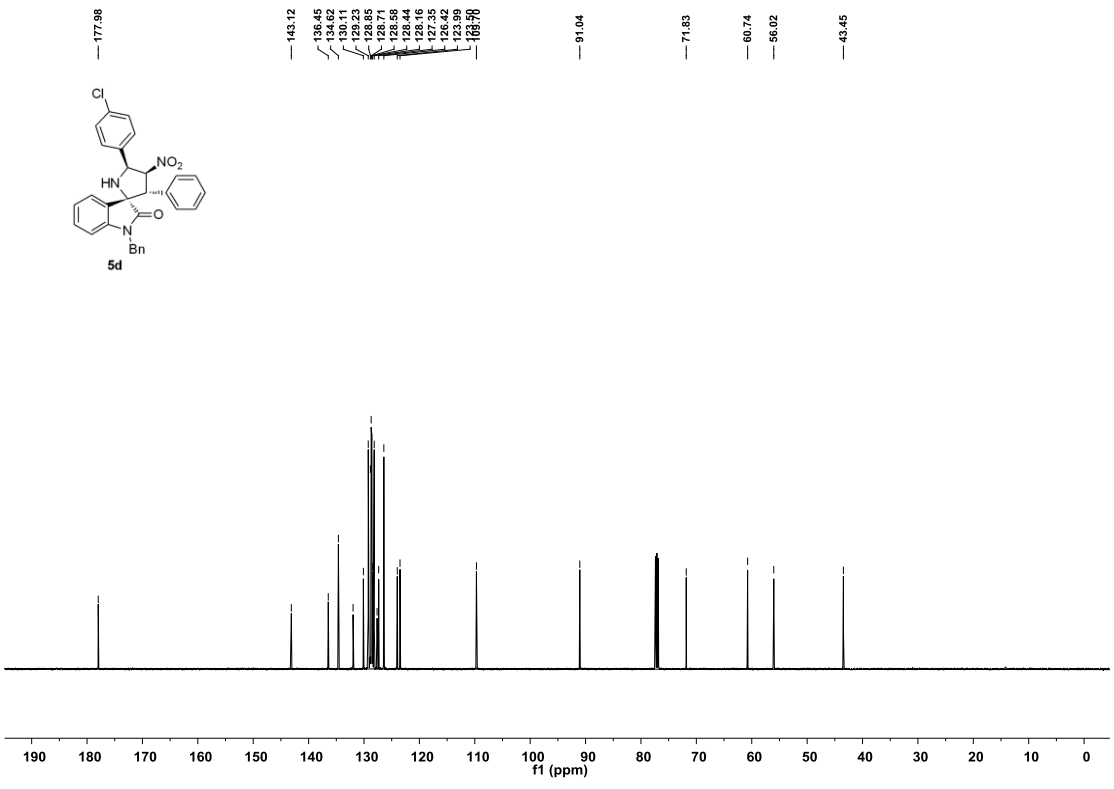
7.793
7.559
7.538
7.334
7.313
7.222
7.142
7.066
7.050
6.449
6.436
6.424
6.417
5.896
5.885
5.872
5.025
4.985
4.669
4.644
4.201
4.161
2.672
2.659
-0.000
Cl
NO2
HN
O
N
Bn
5d
0.99
2.02
2.05
3.00
3.23
3.98
2.97
0.99
0.99
1.00
1.00
0.99
0.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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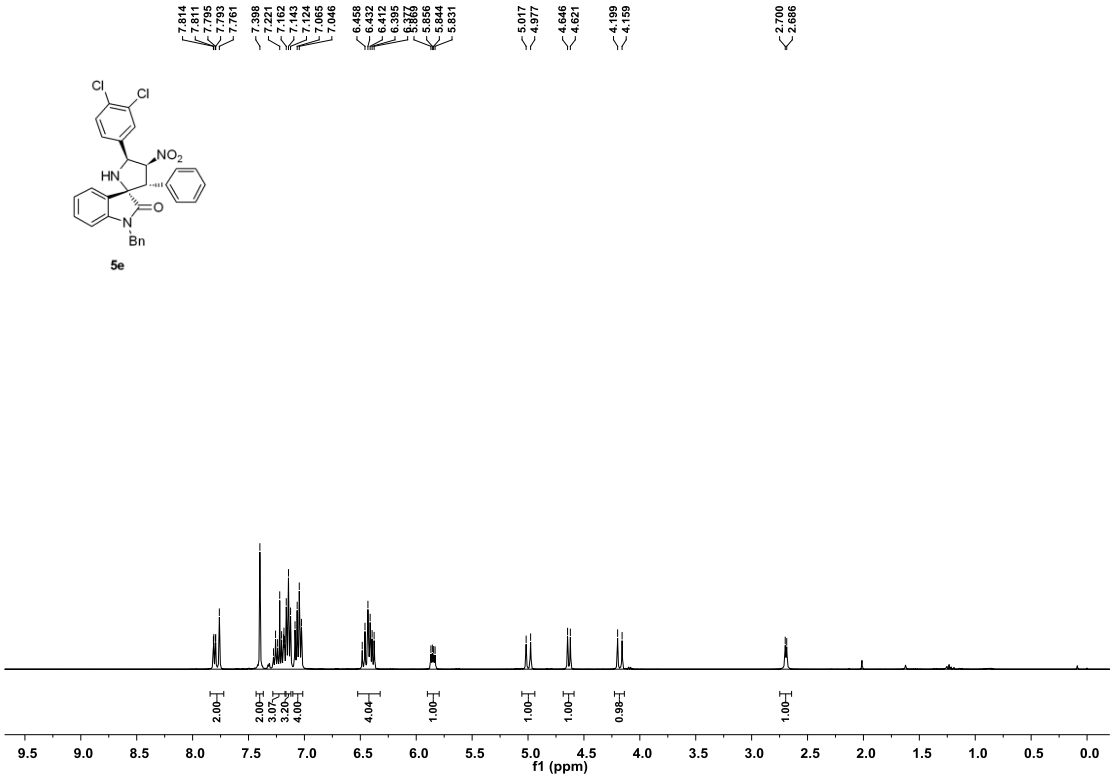
134.62
130.11
129.23
128.85
128.71
128.55
128.44
128.16
127.35
126.42
123.99
91.04
71.83
60.74
56.02
43.45
Cl
NO2
HN
O
N
Bn
5d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5e


7.814
7.811
7.795
7.793
7.761
7.398
7.221
7.162
7.143
7.124
7.065
7.046
6.458
6.432
6.412
6.395
5.856
5.844
5.831
5.017
4.977
4.646
4.621
4.199
4.159
2.700
2.686
Cl
Cl
NO2
HN
O
N
Bn
5e
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4.04
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1.00
1.00
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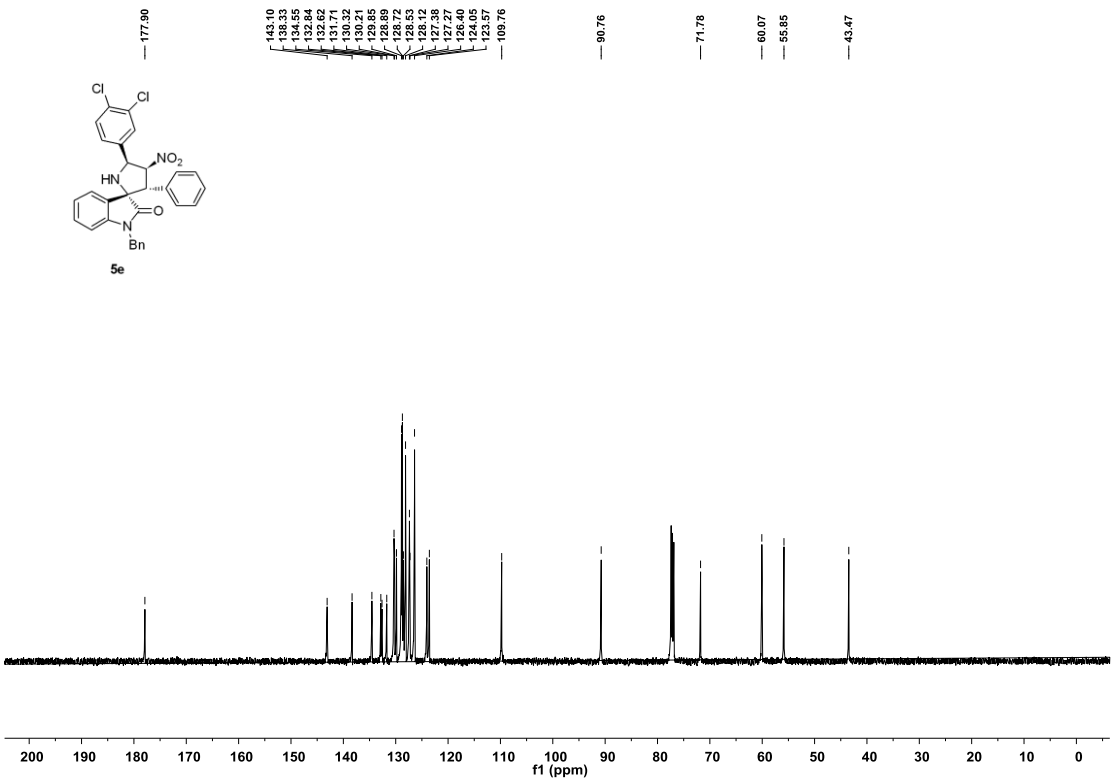
1.00
f1 (ppm)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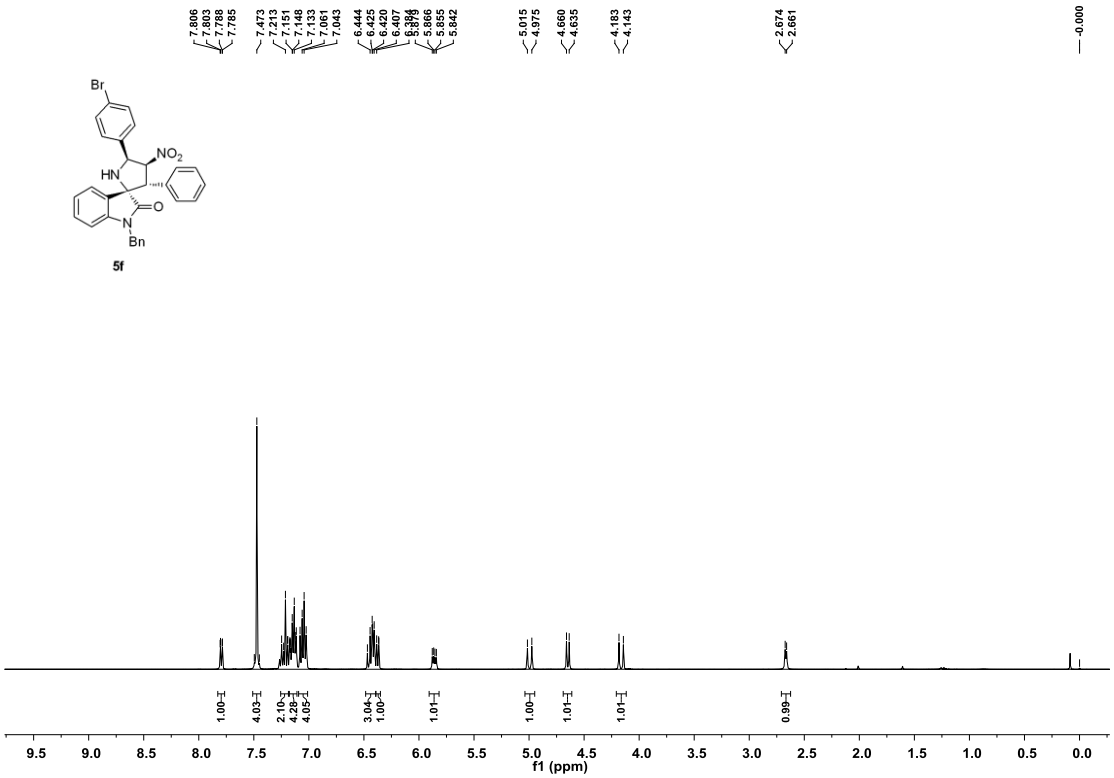
138.33
134.55
132.84
132.62
131.71
130.32
130.21
129.85
128.89
128.72
128.53
128.12
127.38
127.27
126.40
124.05
123.57
109.76
90.76
71.78
60.07
55.85
43.47
Cl
Cl
NO2
HN
O
N
Bn
5e
f1 (ppm)

5f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7.213
7.151
7.148
7.133
7.065
7.043
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6.425
6.420
6.407
5.866
5.855
5.842
5.015
4.975
4.660
4.635
4.183
4.143
2.674
2.661
0.000
Br
NO2
HN
O
N
Bn
5f
1.00
4.03
2.10
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4.05
3.04
1.00
1.01
1.00
1.01
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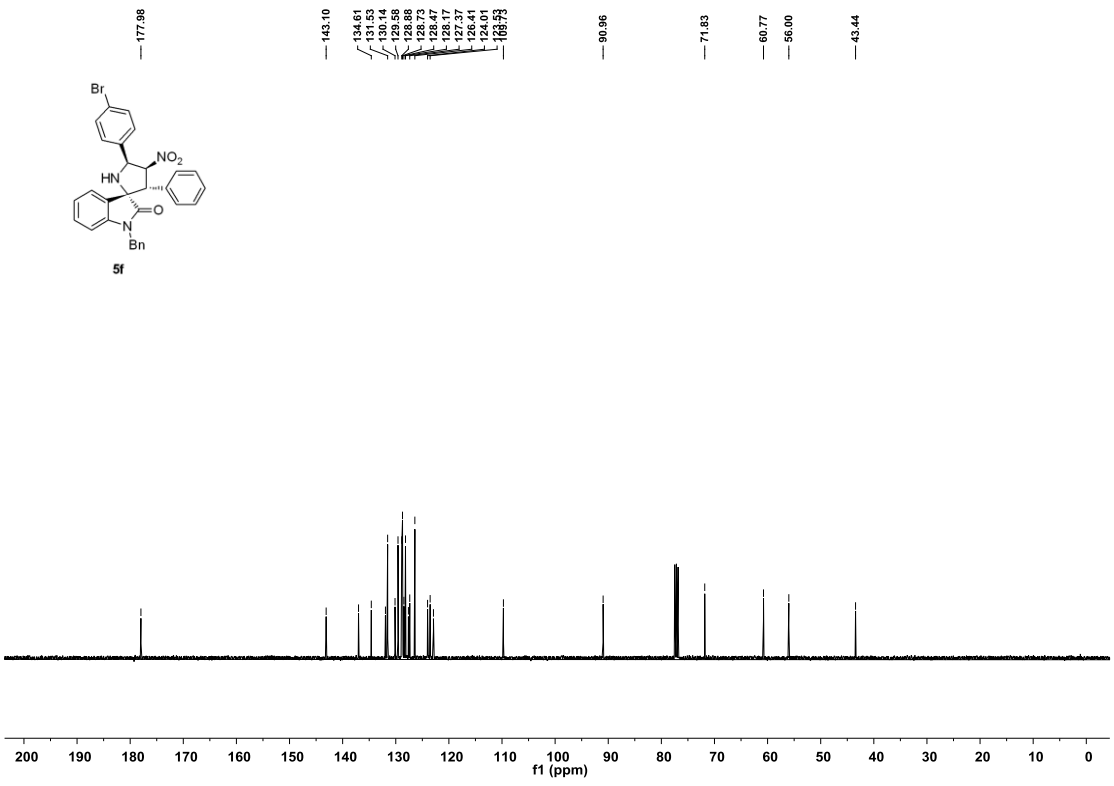
0.99
f1 (ppm)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128.73
128.47
128.17
127.37
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124.01
110.73
90.96
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60.77
56.00
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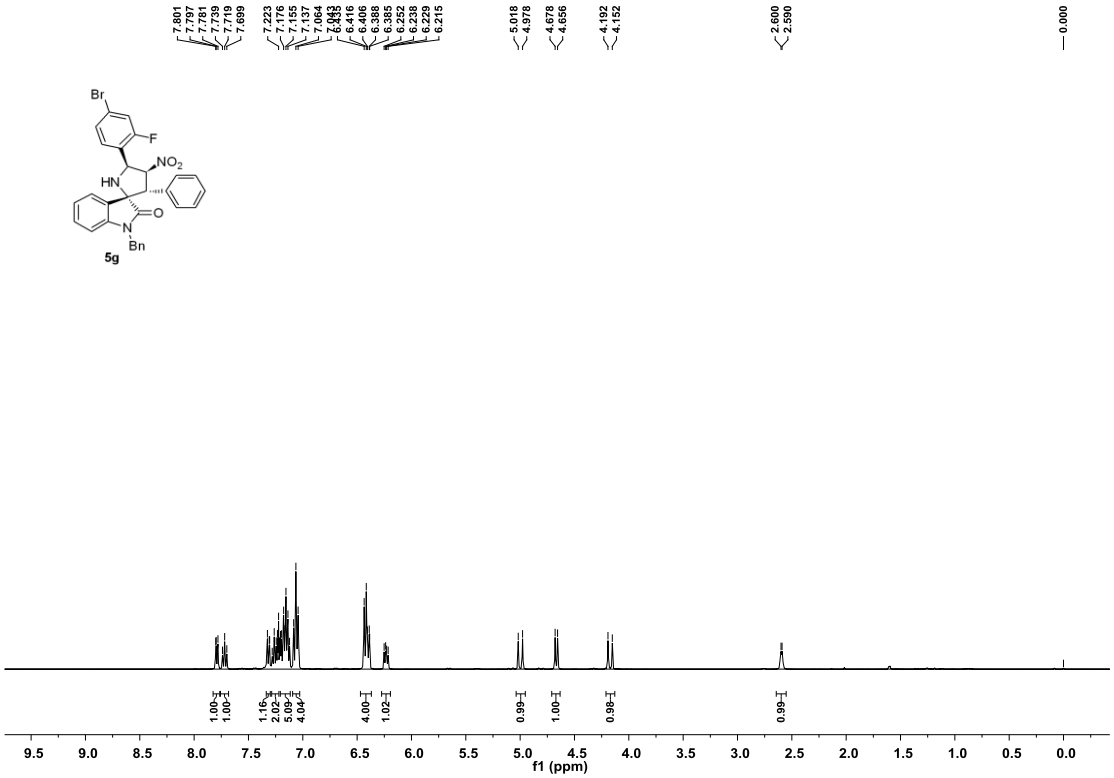
Br
NO2
HN
O
N
Bn
5f
f1 (ppm)

5g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7.176
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7.137
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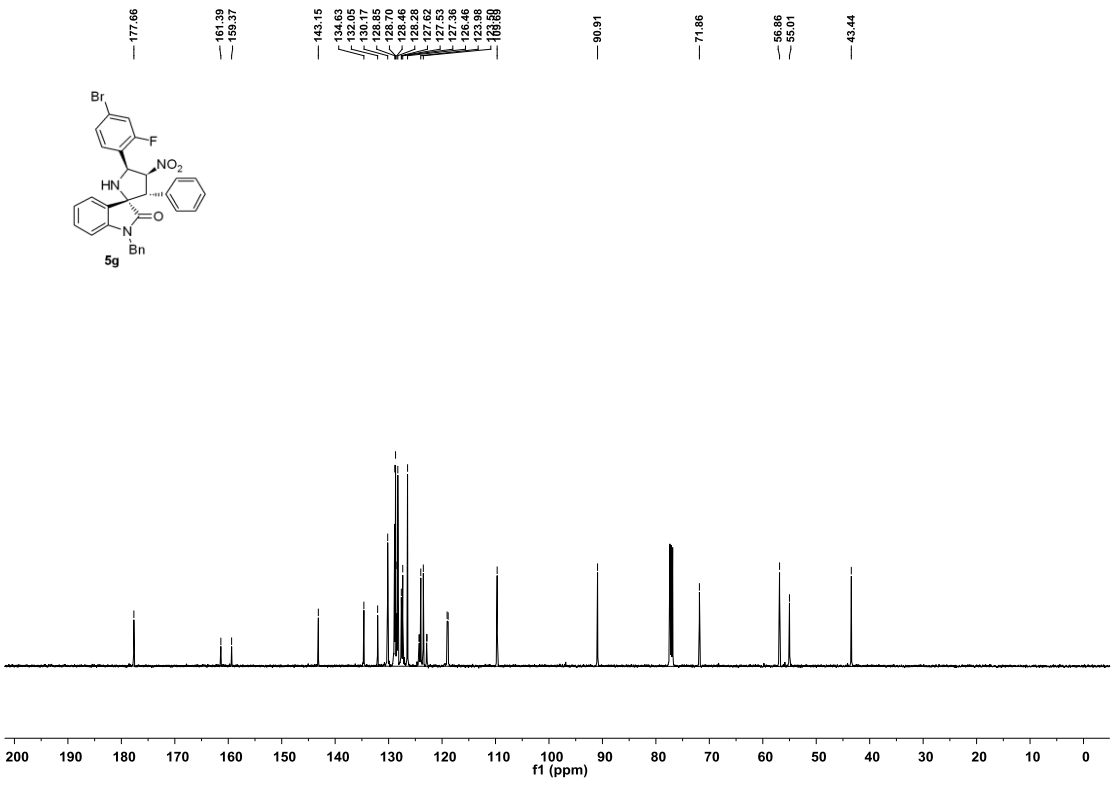
6.406
6.388
6.385
6.252
6.238
6.229
6.215
5.018
4.978
4.678
4.656
4.192
4.152
2.600
2.590
0.000
Br
F
NO2
HN
O
N
Bn
5g
1.00
1.00
1.16
2.02
5.09
4.04
4.00
1.02
0.99
1.00
0.98
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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159.37
143.15
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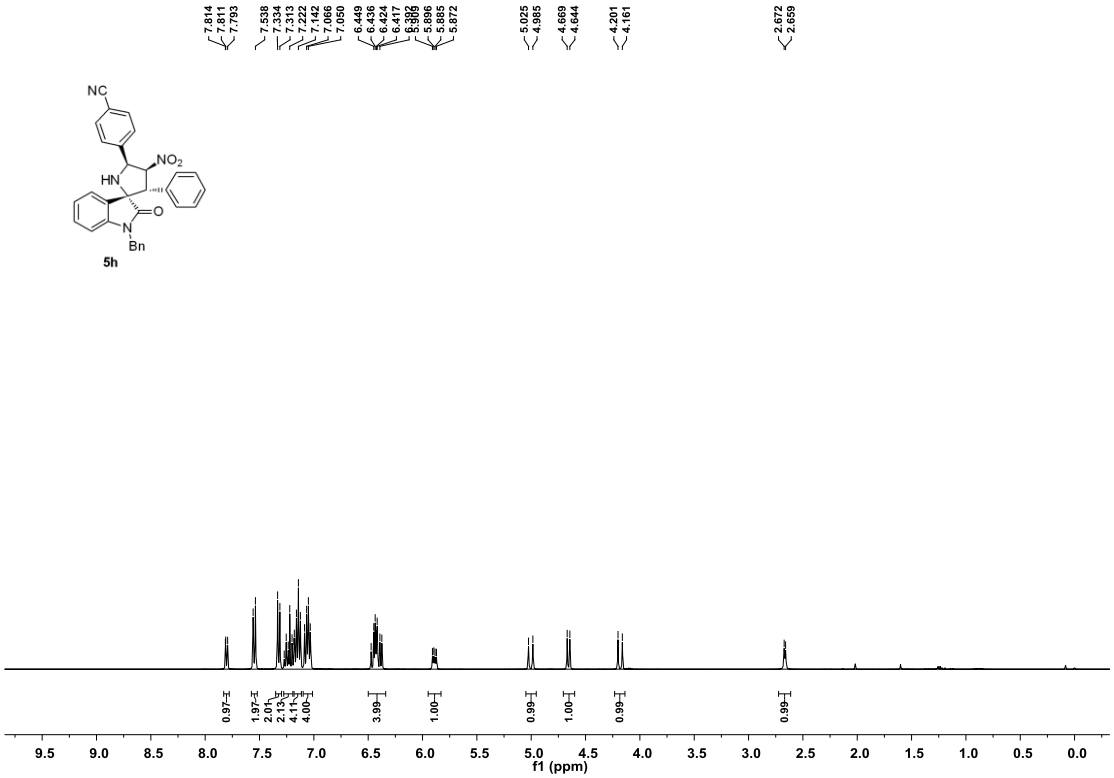
130.17
128.85
128.70
128.46
128.28
127.62
127.53
127.36
126.46
123.98
110.60
90.91
71.86
56.86
55.01
43.44
Br
F
NO2
HN
O
N
Bn
5g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5h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7.313
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7.142
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7.050
6.449
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6.417
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4.985
4.669
4.644
4.201
4.161
2.672
2.659
NC
NO2
HN
O
N
Bn
5h
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3.99
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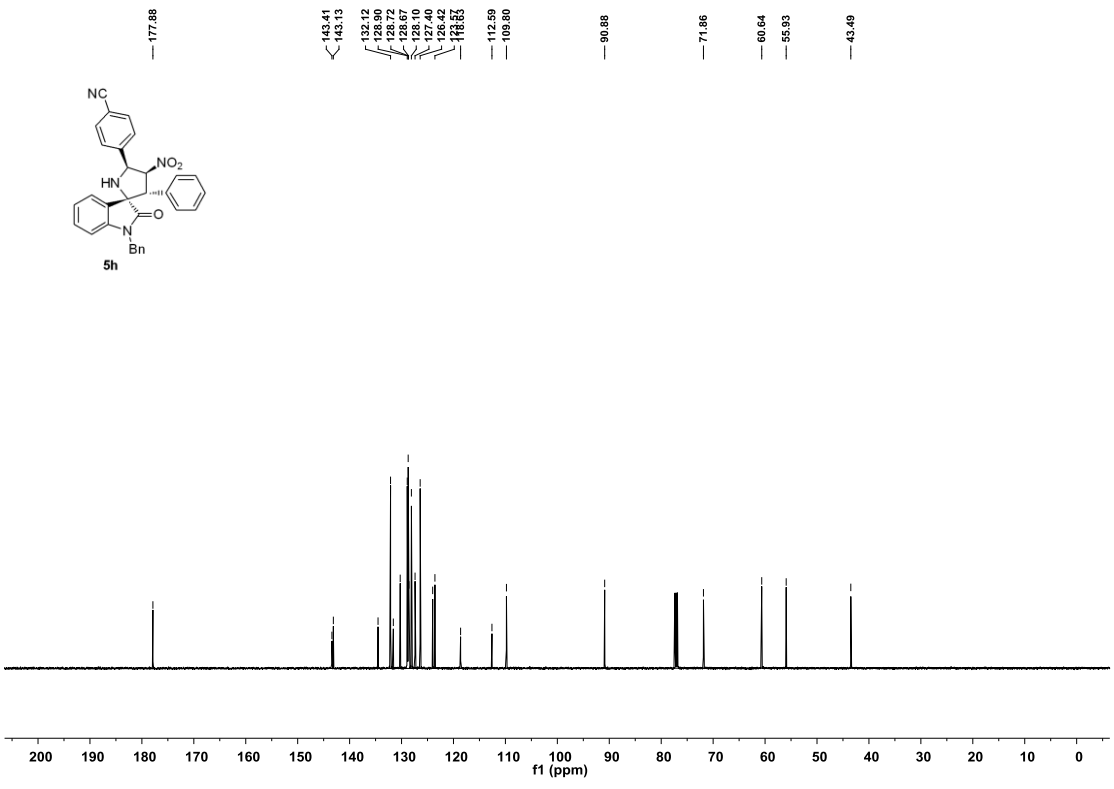
0.99
0.99
f1 (ppm)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55.93
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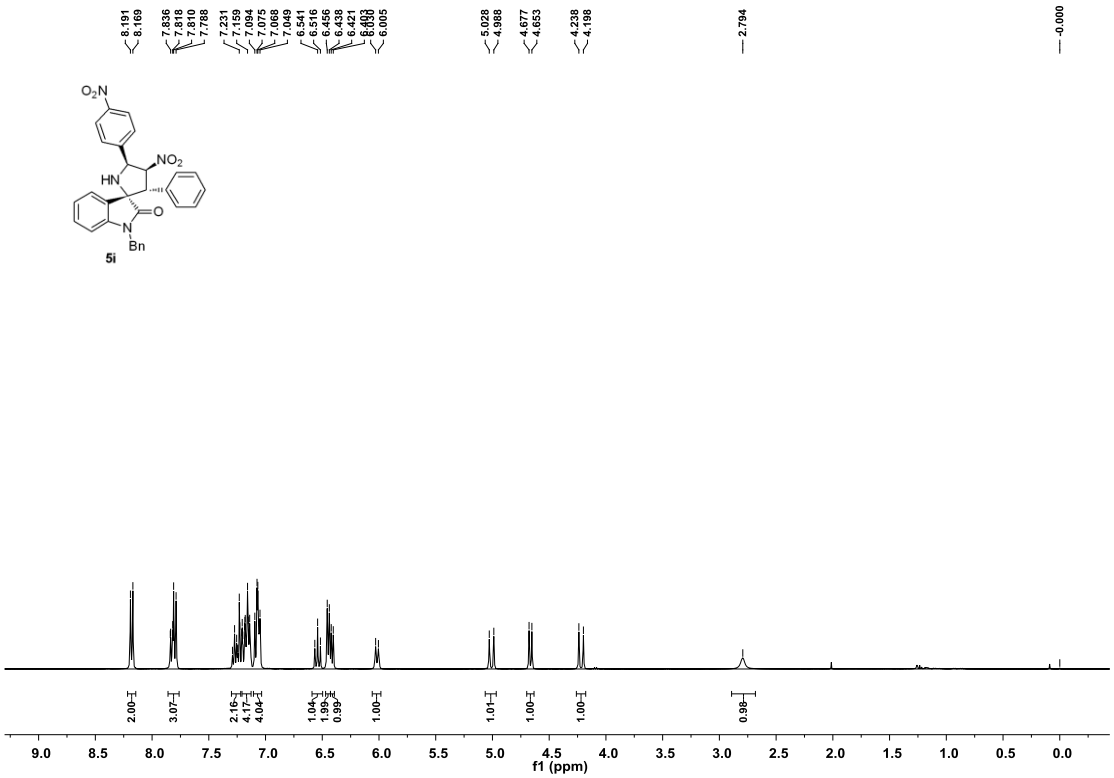
NC
NO2
HN
O
N
Bn
5h
f1 (ppm)

5i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6.516
6.456
6.438
6.421
6.030
6.005
5.028
4.988
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4.653
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4.198
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NO2
HN
O
N
Bn
5i
2.00
3.07
2.16
4.17
4.04
1.04
1.99
0.99
1.00
1.01
1.00
1.00
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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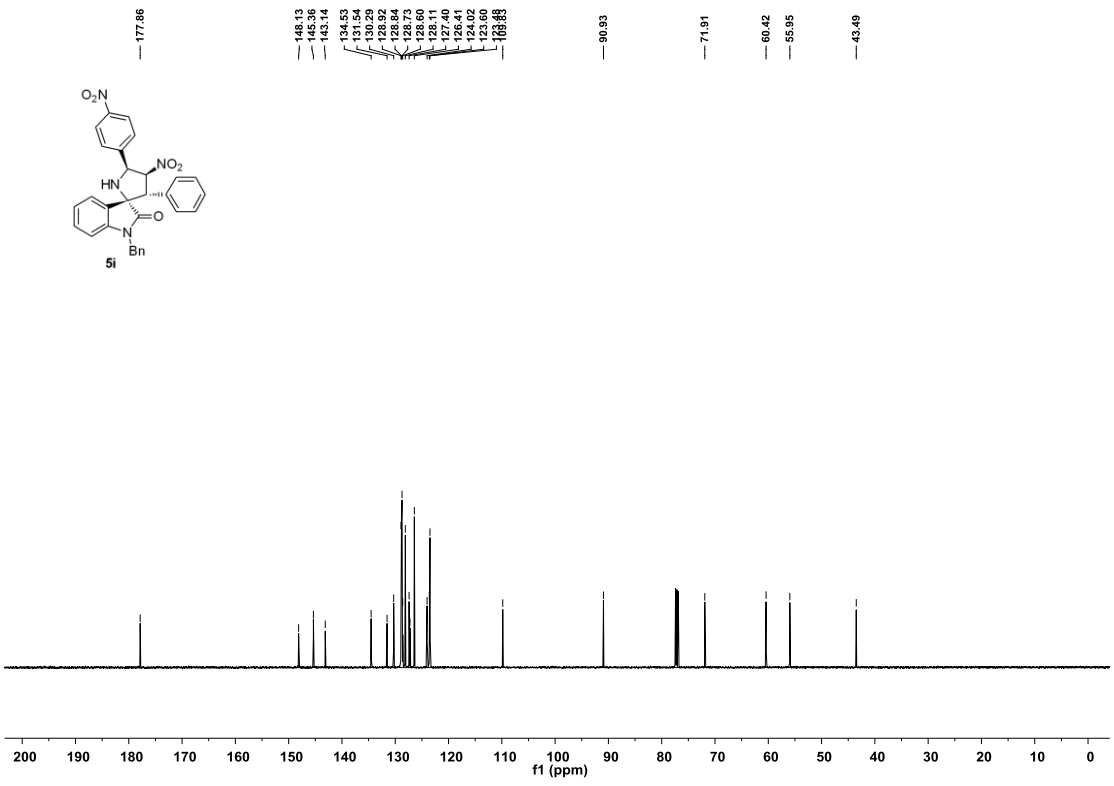
f1 (ppm)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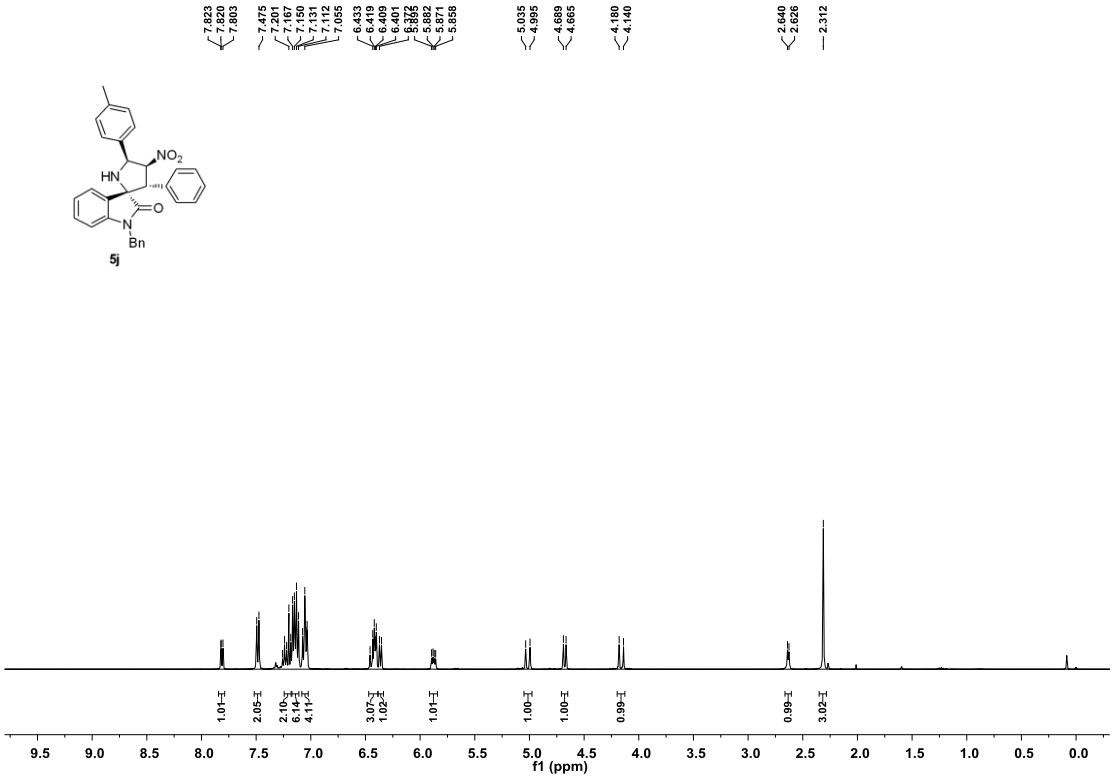
131.54
130.29
128.92
128.84
128.73
128.60
128.11
127.40
126.41
124.02
123.60
110.83
90.93
71.91
60.42
55.95
43.49
O2N
NO2
HN
O
N
Bn
5i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5j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5.035
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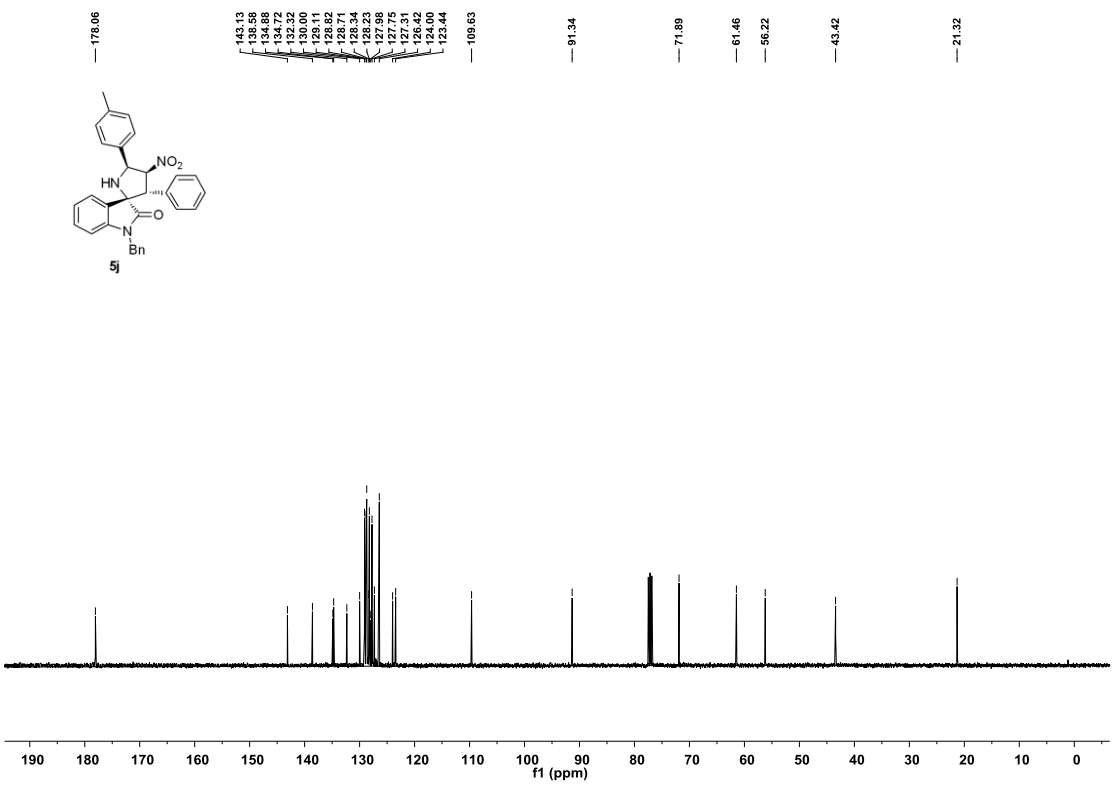
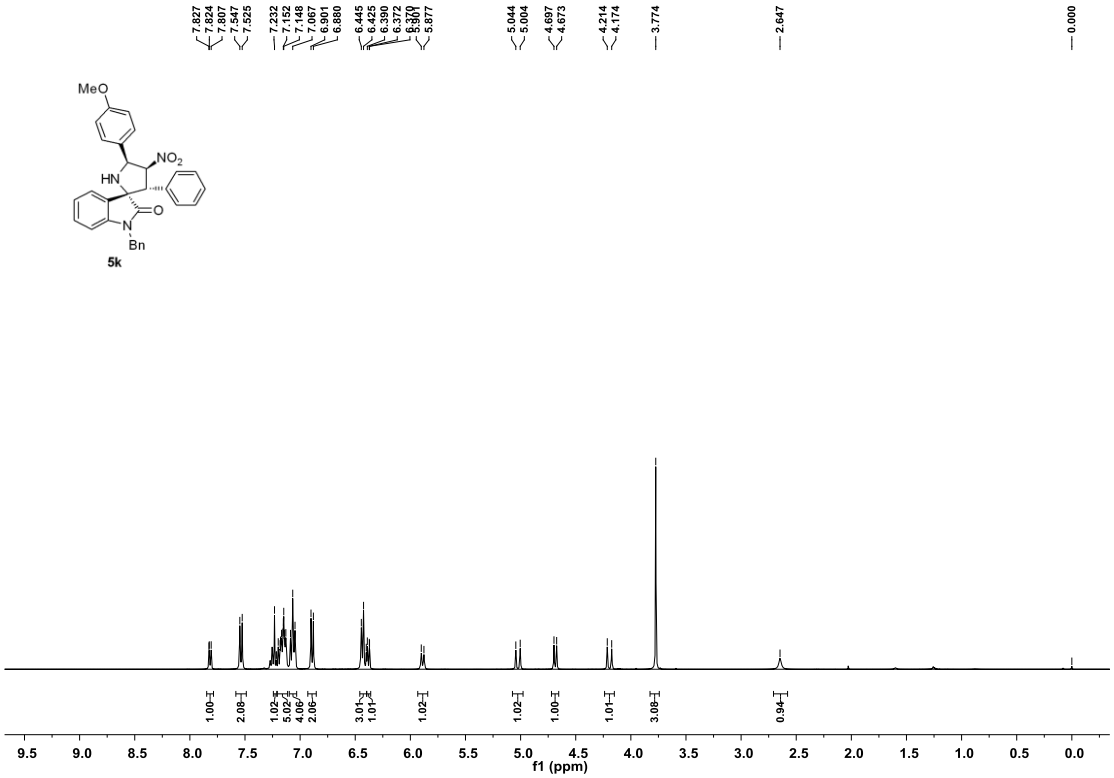
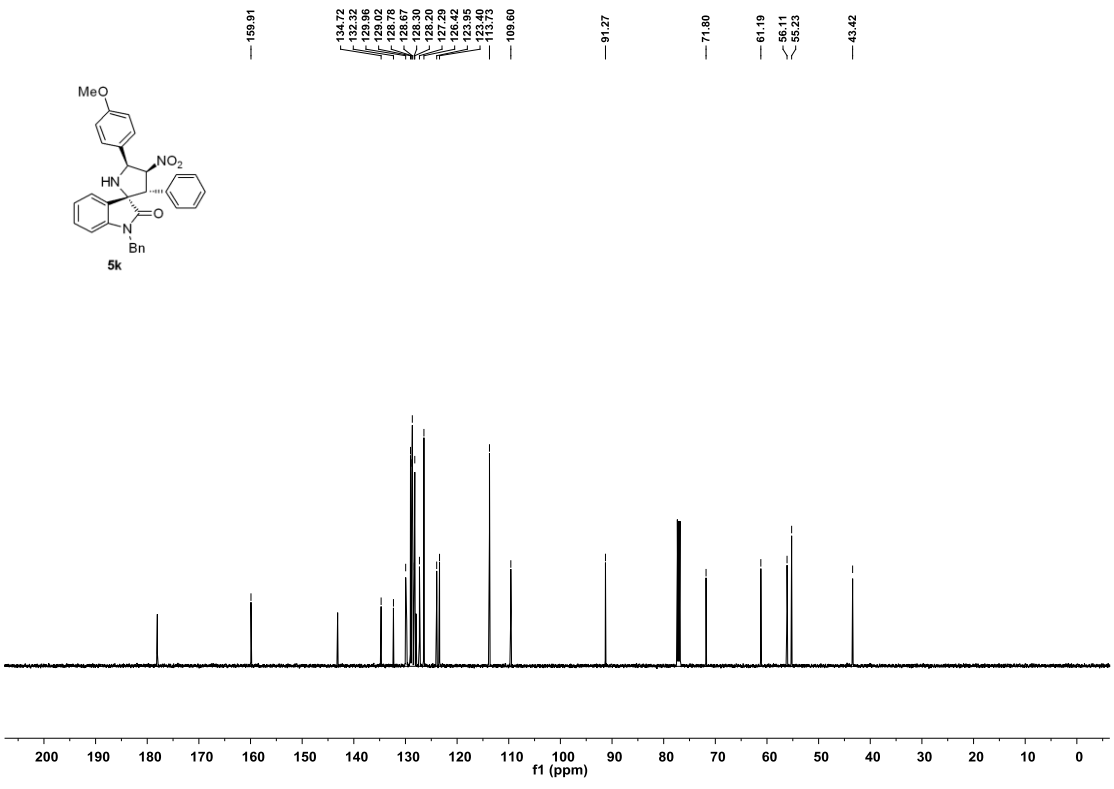
4.140
2.640
2.626
2.312
NO2
HN
O
N
Bn
5j
1.01
2.05
2.10
6.14
4.11
3.07
1.02
1.01
1.00
1.00
0.99
0.99
3.02
f1 (ppm)

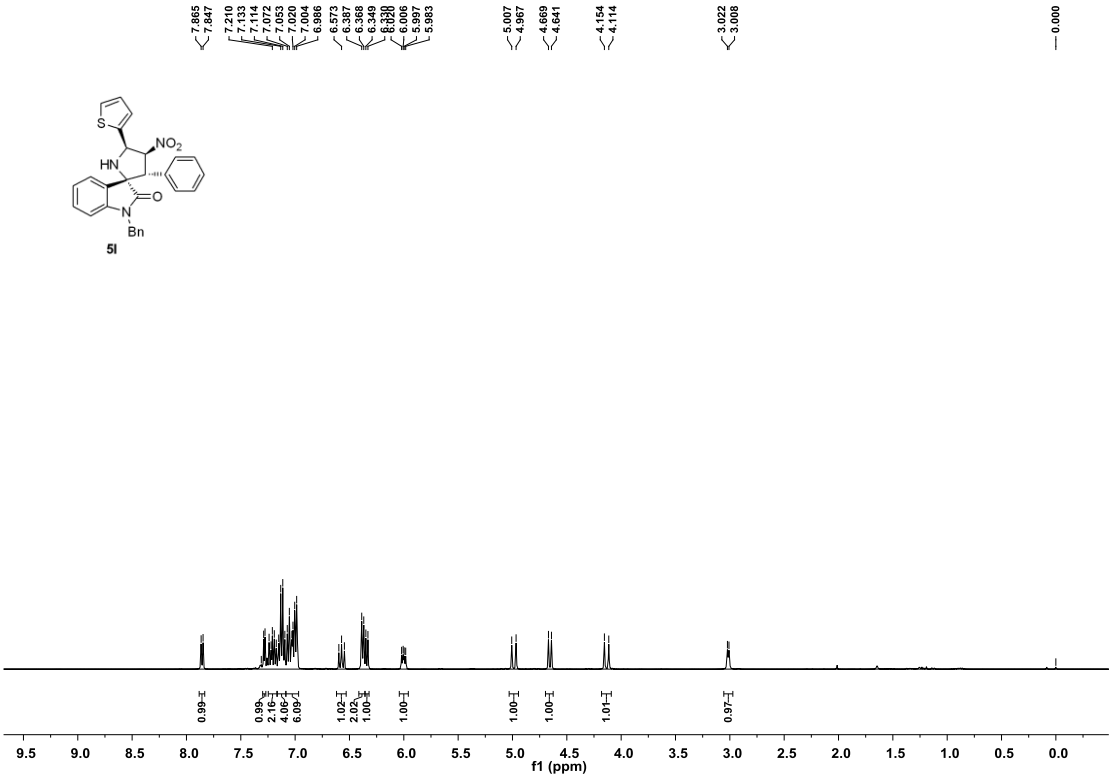

178.06
143.13
138.58
134.88
134.72
132.32
130.00
129.11
128.82
128.71
128.34
128.23
127.88
127.75
127.31
126.42
124.00
123.44
109.63
91.34
71.89
61.46
56.22
43.42
21.32
NO2
HN
O
N
Bn
5j
f1 (ppm)

5k


7.827
7.824
7.807
7.547
7.525
7.232
7.152
7.148
7.067
6.901
6.880
6.445
6.425
6.390
6.372
5.877
5.044
5.004
4.697
4.673
4.214
4.174
3.774
2.647
0.000
MeO
NO2
HN
O
N
Bn
5k
1.00
2.08
1.02
5.02
4.06
2.06
3.01
1.01
1.02
1.02
1.00
1.01
3.08
0.94
f1 (ppm)


159.91
134.72
132.32
129.86
129.02
128.78
128.67
128.30
128.20
127.29
126.42
123.95
123.40
113.73
109.60
91.27
71.80
61.19
56.11
55.23
43.42
MeO
NO2
HN
O
N
Bn
5k
f1 (ppm)

5l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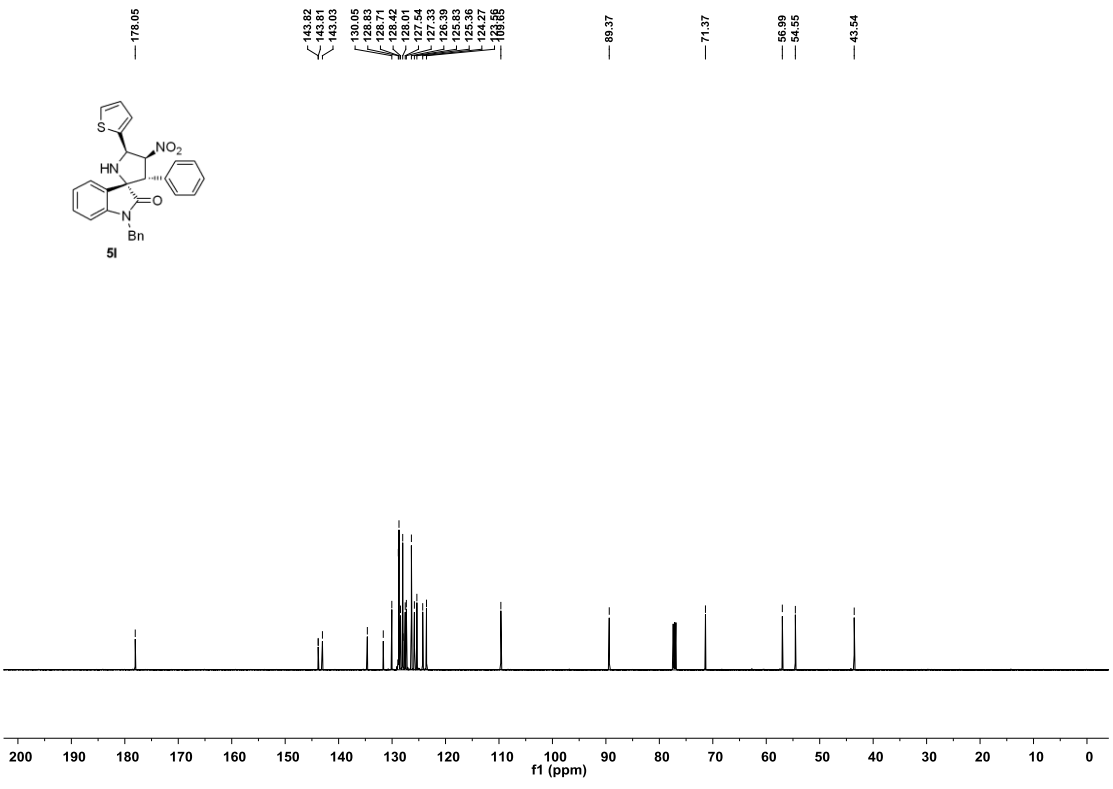
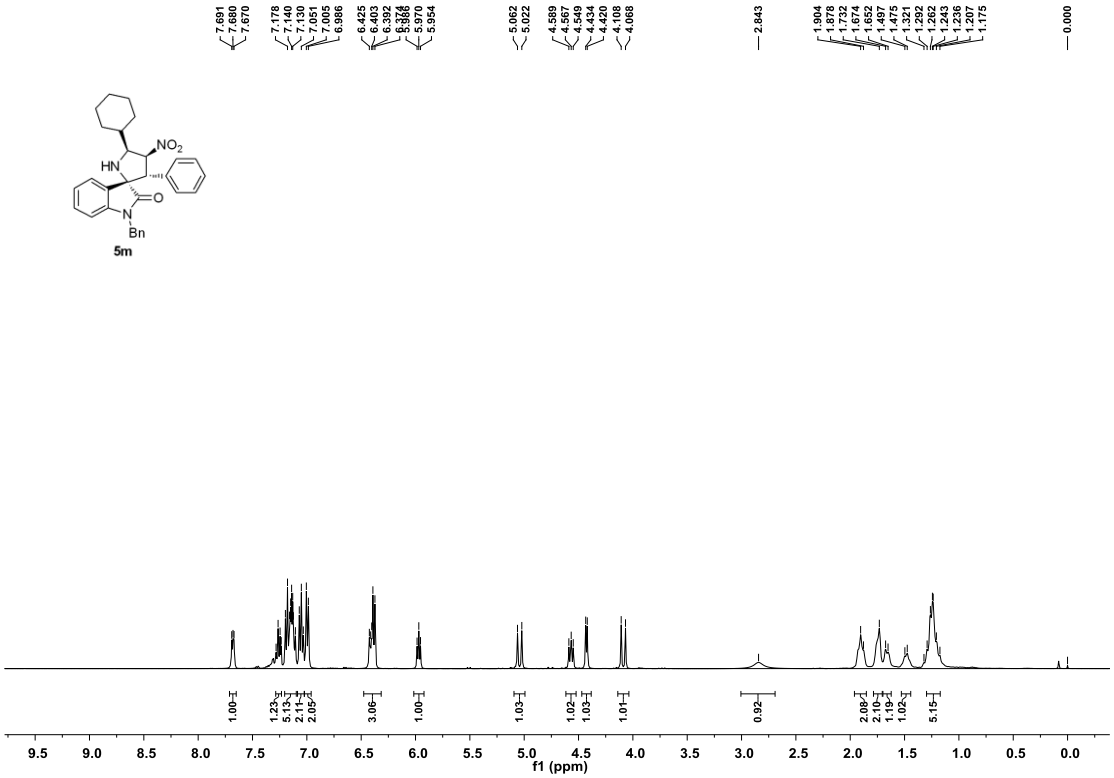
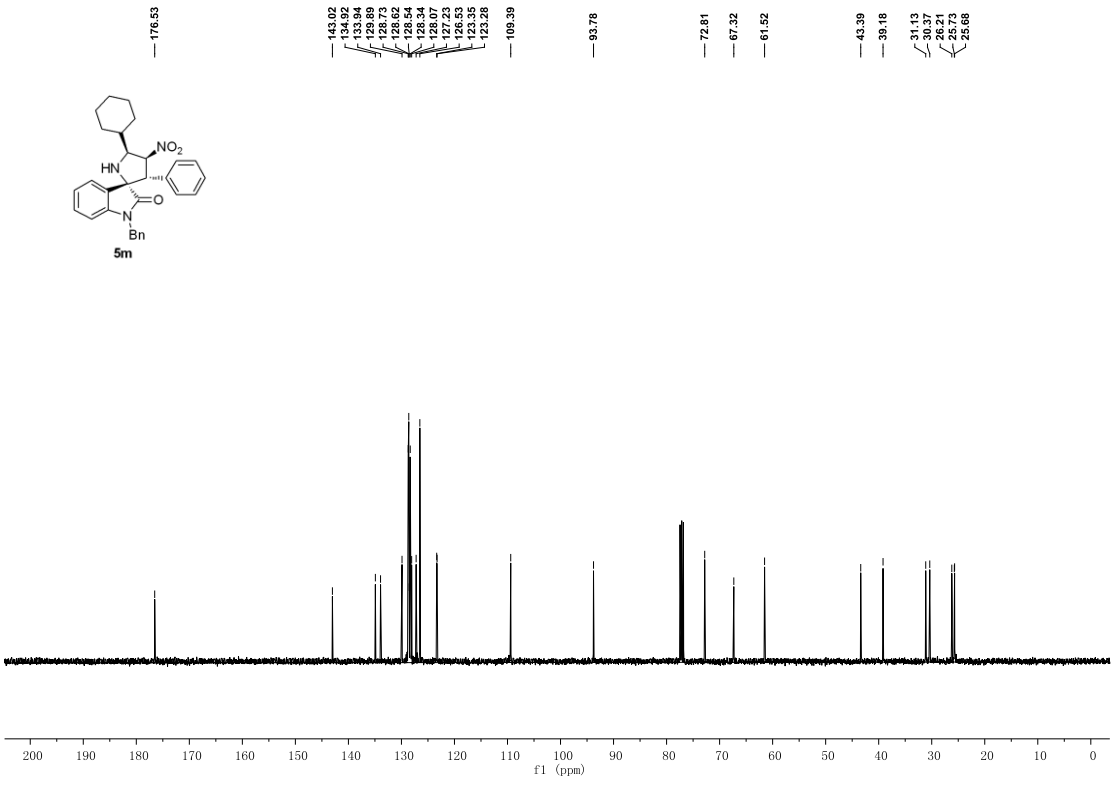
7.847
7.210
7.133
7.114
7.072
7.055
7.020
7.004
6.986
6.573
6.387
6.368
6.349
6.330
6.006
5.997
5.983
5.007
4.987
4.669
4.641
4.154
4.114
3.022
3.008
0.000
S
NO2
HN
O
N
Bn
5l
0.99
0.99
2.16
4.06
6.09
1.02
2.02
1.00
1.00
1.00
1.00
1.01
0.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

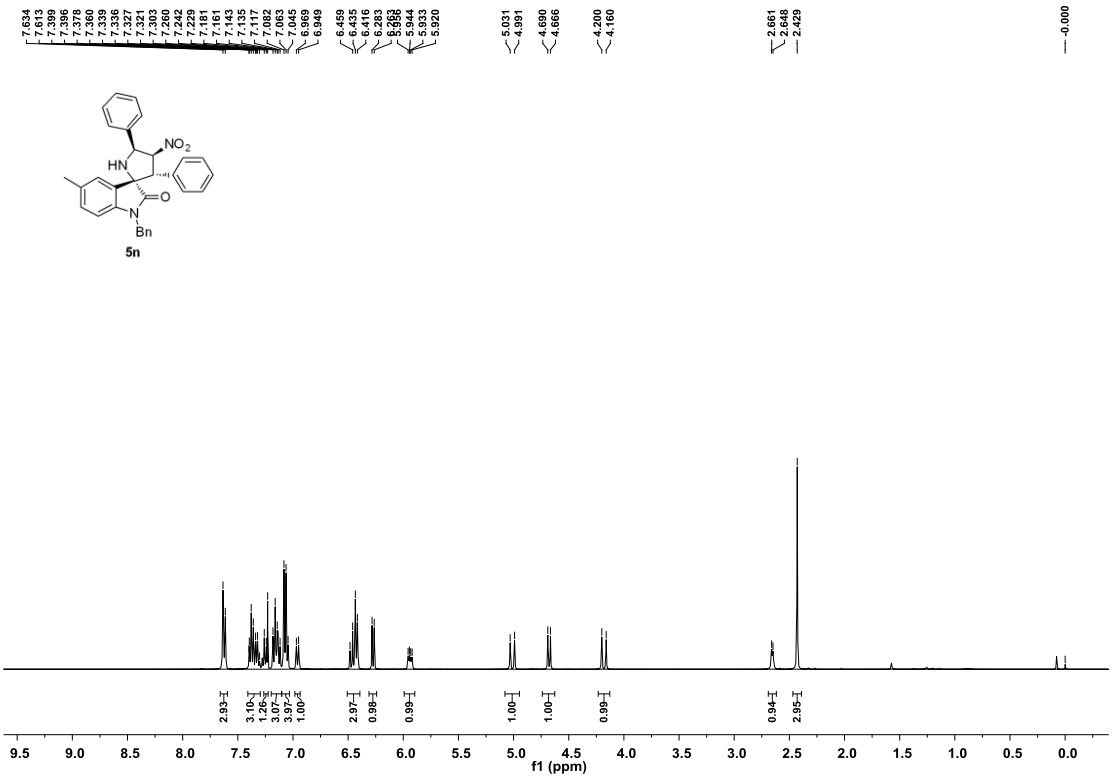

178.05
143.82
143.81
143.03
130.05
128.83
128.71
128.42
128.01
127.54
127.33
126.39
125.83
125.36
124.27
110.55
89.37
71.37
56.99
54.55
43.54
S
NO2
HN
O
N
Bn
5l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

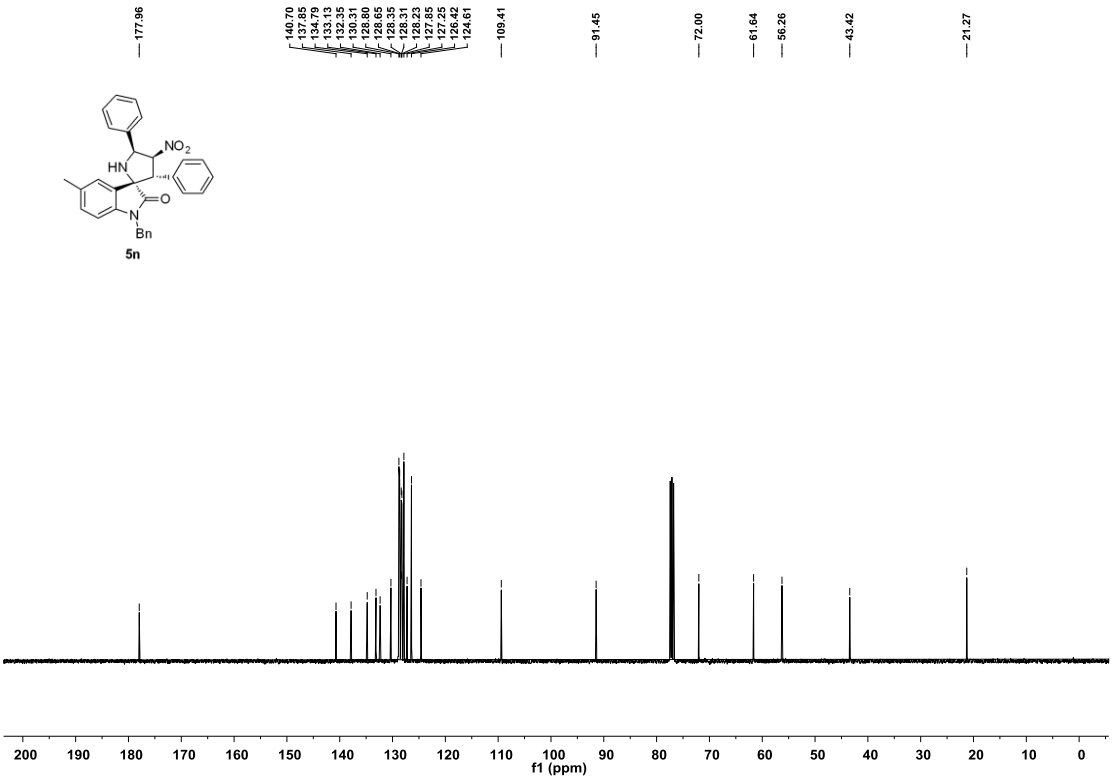
5m


7.691
7.680
7.670
7.178
7.140
7.130
7.051
7.005
6.986
6.425
6.403
6.392
5.970
5.954
5.062
5.022
4.589
4.567
4.549
4.434
4.420
4.108
4.068
2.843
1.904
1.878
1.732
1.674
1.652
1.497
1.475
1.321
1.292
1.262
1.243
1.236
1.207
1.175
0.000
NO2
HN
O
N
Bn
5m
1.00
1.23
5.13
2.11
2.05
3.06
1.00
1.03
1.02
1.03
1.01
0.92
2.08
2.10
1.19
1.02
5.15
f1 (ppm)

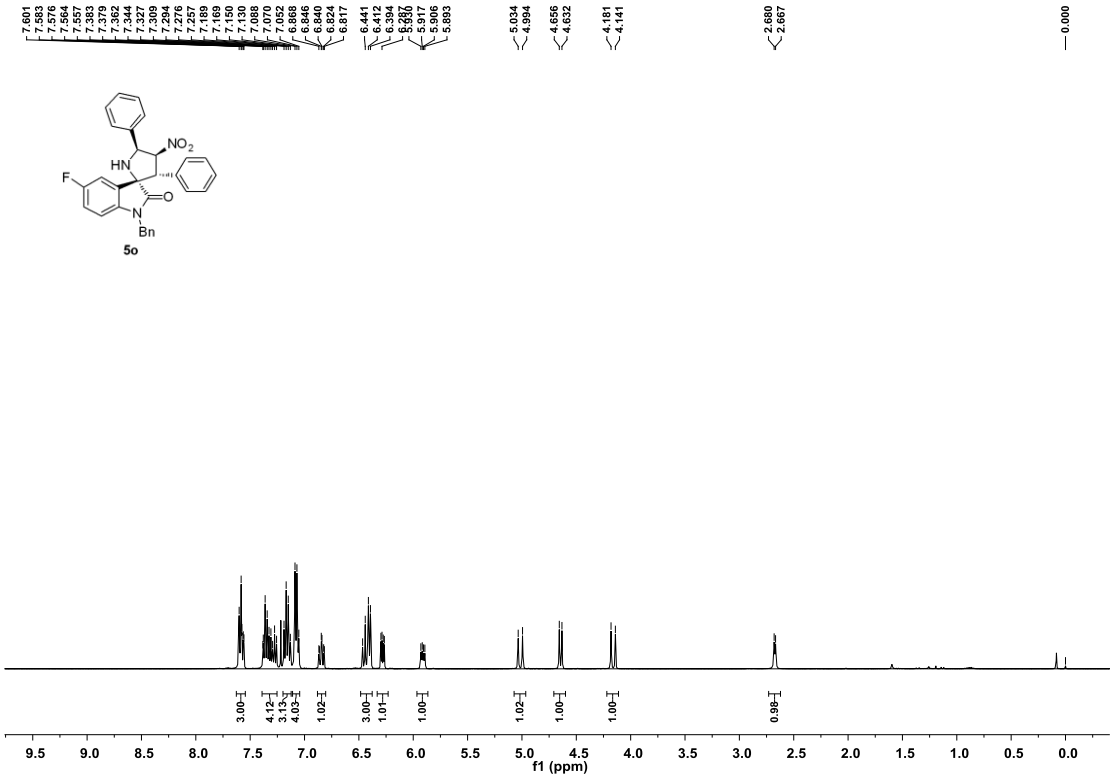

176.53
143.02
134.92
133.94
129.89
128.73
128.62
128.54
128.34
128.07
127.23
126.53
123.35
123.28
109.39
93.78
72.81
67.32
61.52
43.39
39.18
31.13
30.37
26.71
25.73
25.68
NO2
HN
O
N
Bn
5m
f1 (ppm)

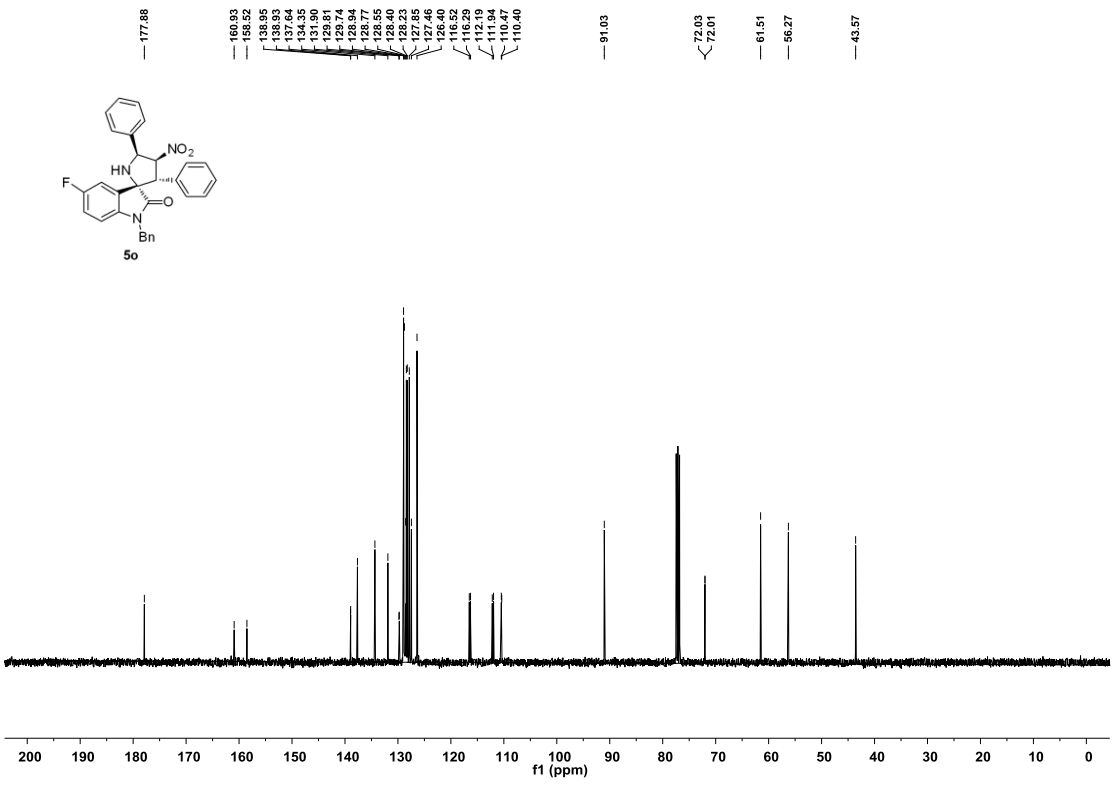
5n


7.634
7.613
7.399
7.396
7.378
7.360
7.339
7.336
7.327
7.321
7.303
7.260
7.242
7.229
7.181
7.161
7.143
7.135
7.117
7.092
7.063
7.045
6.969
6.949
6.459
6.435
6.416
6.283
5.958
5.944
5.933
5.920
5.031
4.991
4.690
4.666
4.200
4.160
2.661
2.648
2.429
-0.000
NO2
HN
O
N
Bn
5n
2.93
3.10
1.26
3.07
3.97
1.00
2.97
0.98
0.99
1.00
1.00
0.99
0.94
2.95
f1 (ppm)


177.96
140.70
137.85
134.79
133.13
132.35
130.31
129.80
128.85
128.35
128.31
128.23
127.85
127.25
126.42
124.61
109.41
91.45
72.00
61.64
56.26
43.42
21.27
NO2
HN
O
N
Bn
5n
f1 (ppm)

5o


7.601
7.583
7.576
7.564
7.557
7.383
7.379
7.362
7.344
7.327
7.309
7.294
7.276
7.257
7.189
7.169
7.150
7.130
7.098
7.070
7.052
6.868
6.846
6.840
6.824
6.817
6.441
6.412
6.394
5.917
5.906
5.893
5.034
4.994
4.656
4.632
4.181
4.141
2.680
2.667
0.000
NO2
HN
F
O
N
Bn
5o
3.00
4.12
3.13
4.03
1.02
3.00
1.01
1.00
1.02
1.00
1.00
0.98
f1 (ppm)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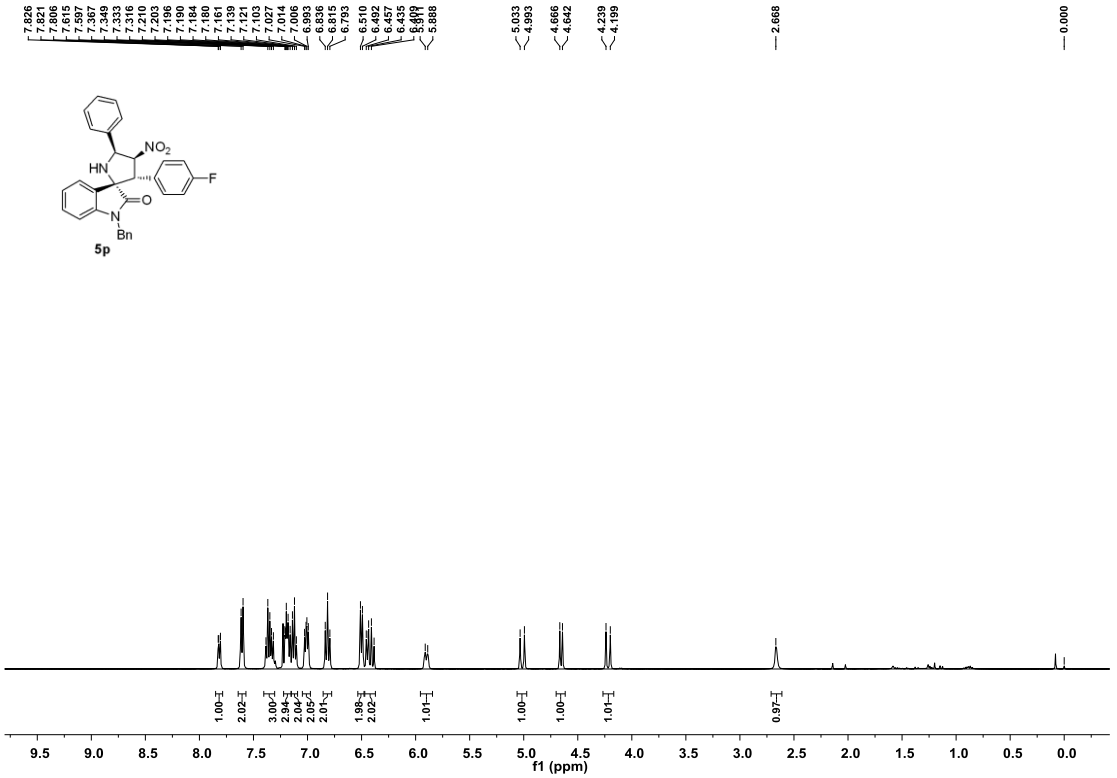
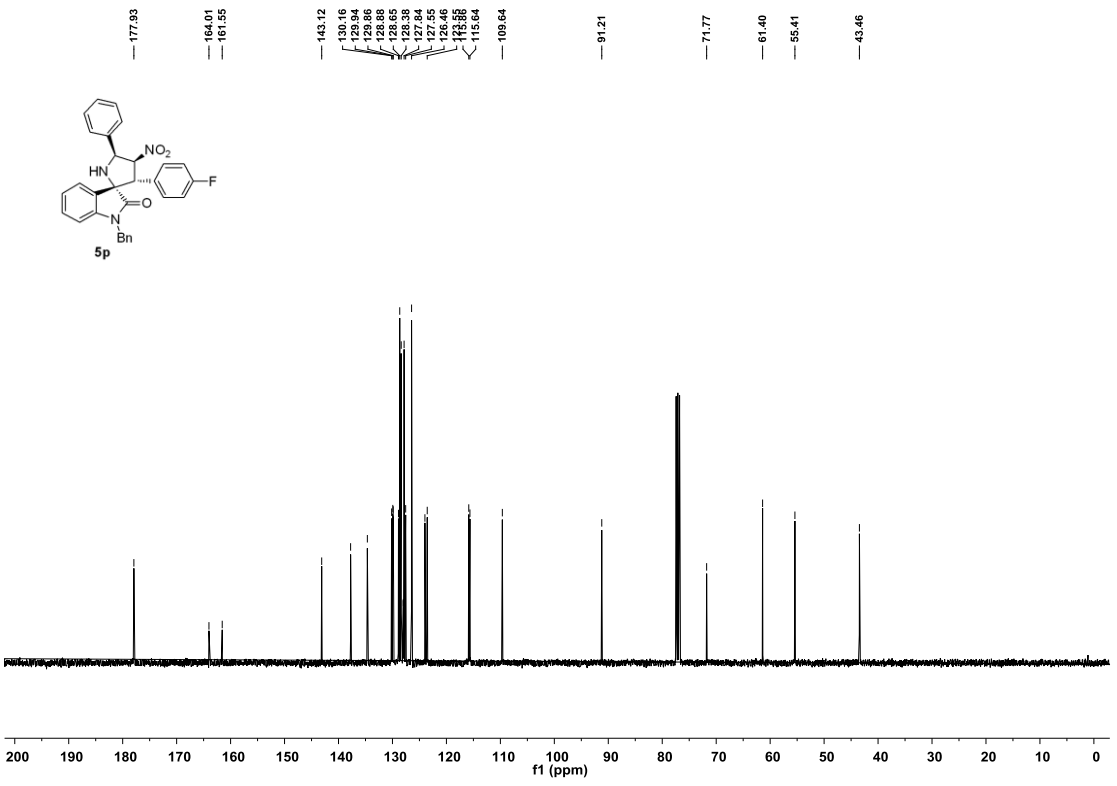
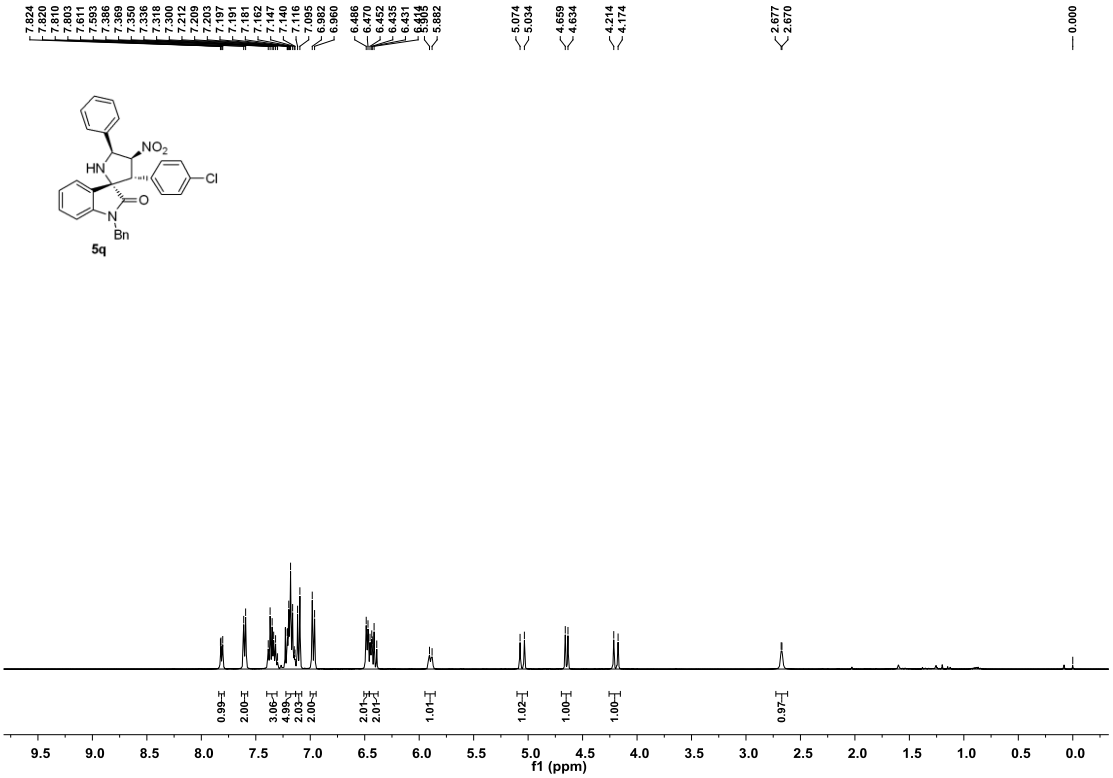
160.93
158.52
138.95
138.93
137.64
134.35
131.90
129.81
129.74
129.64
128.77
128.55
128.40
128.23
127.85
127.46
126.40
116.52
116.29
112.19
111.94
110.47
110.40
91.03
72.03
72.01
61.51
56.27
43.57
NO2
HN
F
O
N
Bn
5o
f1 (ppm)

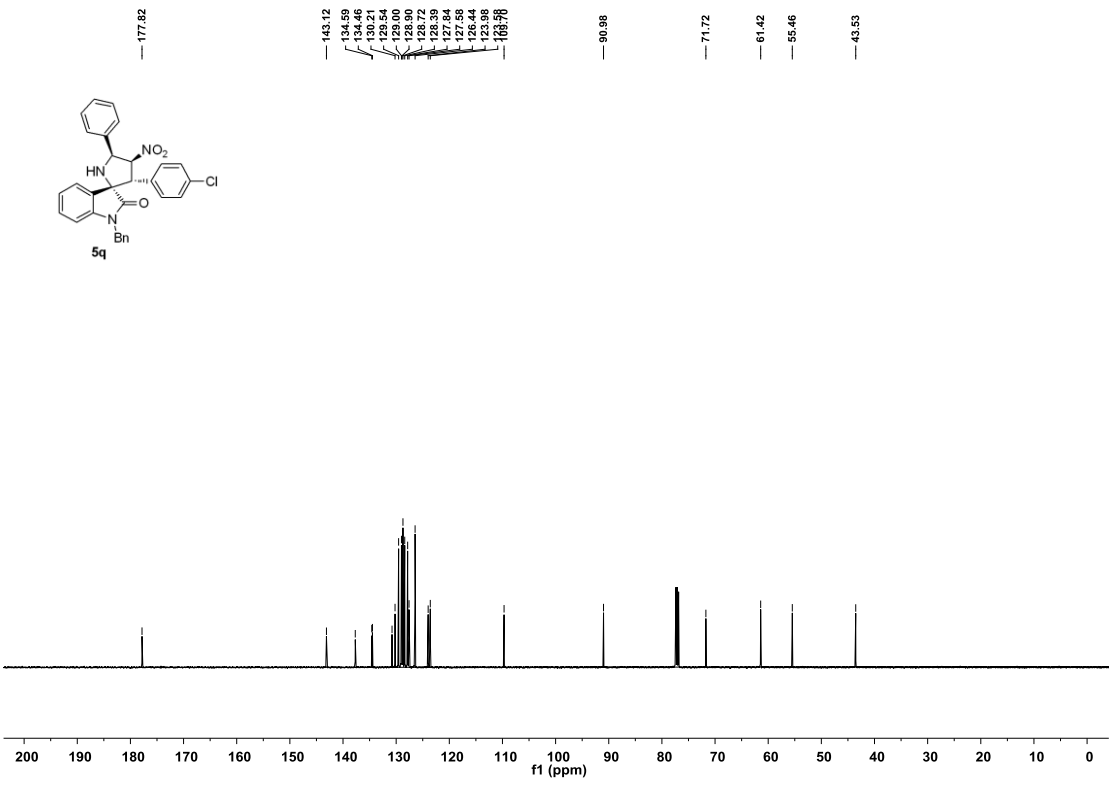
5p


7.826
7.821
7.806
7.615
7.597
7.367
7.349
7.333
7.316
7.210
7.203
7.196
7.190
7.184
7.180
7.161
7.139
7.121
7.103
7.027
7.014
7.006
6.993
6.836
6.815
6.793
6.510
6.492
6.457
6.435
5.888
5.033
4.993
4.666
4.642
4.239
4.199
2.668
0.000
NO2
HN
F
O
N
Bn
5p
1.00
2.02
3.00
2.94
2.04
2.05
2.01
1.98
2.02
1.01
1.00
1.00
1.01
0.97
f1 (ppm)

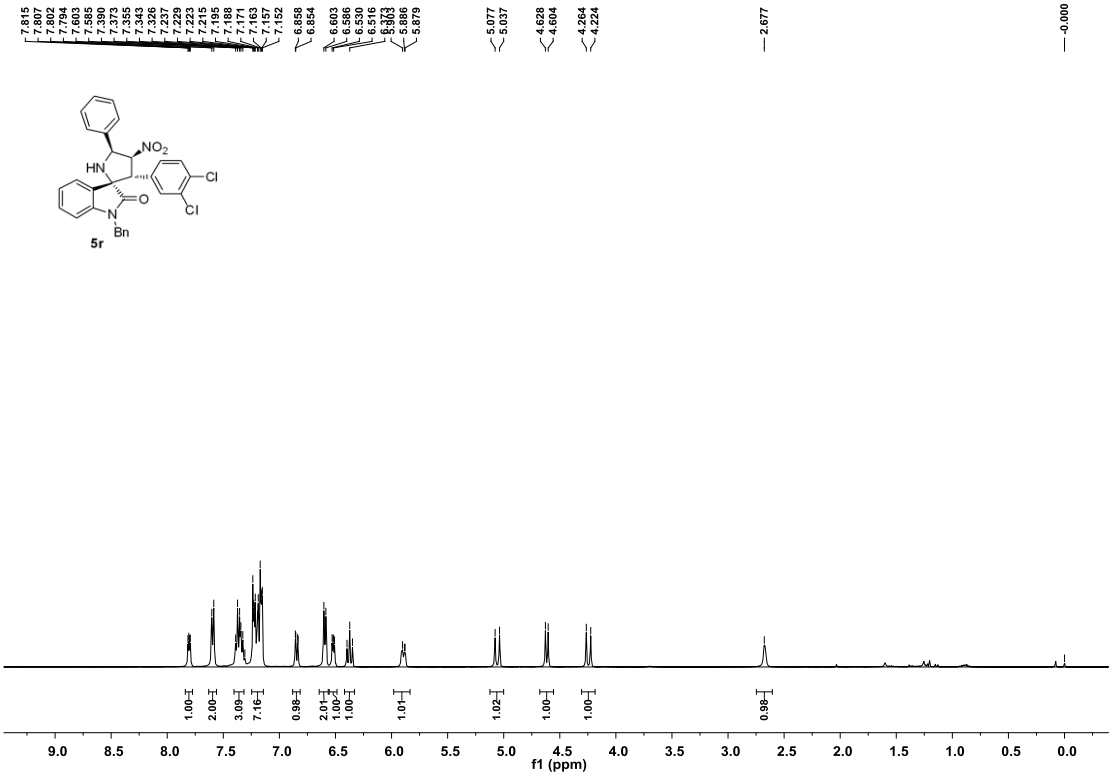

177.93
164.01
161.55
143.12
130.16
129.94
129.86
128.88
128.65
128.38
127.84
127.55
126.46
115.64
109.64
91.21
71.77
61.40
55.41
43.46
NO2
HN
F
O
N
Bn
5p
f1 (ppm)

5q


7.824
7.820
7.810
7.803
7.611
7.593
7.386
7.369
7.350
7.336
7.318
7.300
7.212
7.209
7.203
7.197
7.191
7.181
7.162
7.147
7.140
7.116
7.095
6.982
6.960
6.486
6.470
6.452
6.435
6.431
5.914
5.900
5.882
5.074
5.034
4.659
4.634
4.214
4.174
2.677
2.670
0.000
NO2
HN
Cl
O
N
Bn
5q
0.99
2.00
3.06
4.99
2.03
2.00
2.01
2.01
1.01
1.02
1.00
1.00
0.97
f1 (ppm)


177.82
143.12
134.59
134.46
130.21
129.54
129.00
128.90
128.72
128.39
127.84
127.58
126.44
123.98
110.70
90.98
71.72
61.42
55.46
43.53
NO2
HN
Cl
O
N
Bn
5q
f1 (ppm)

5r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7.802
7.794
7.603
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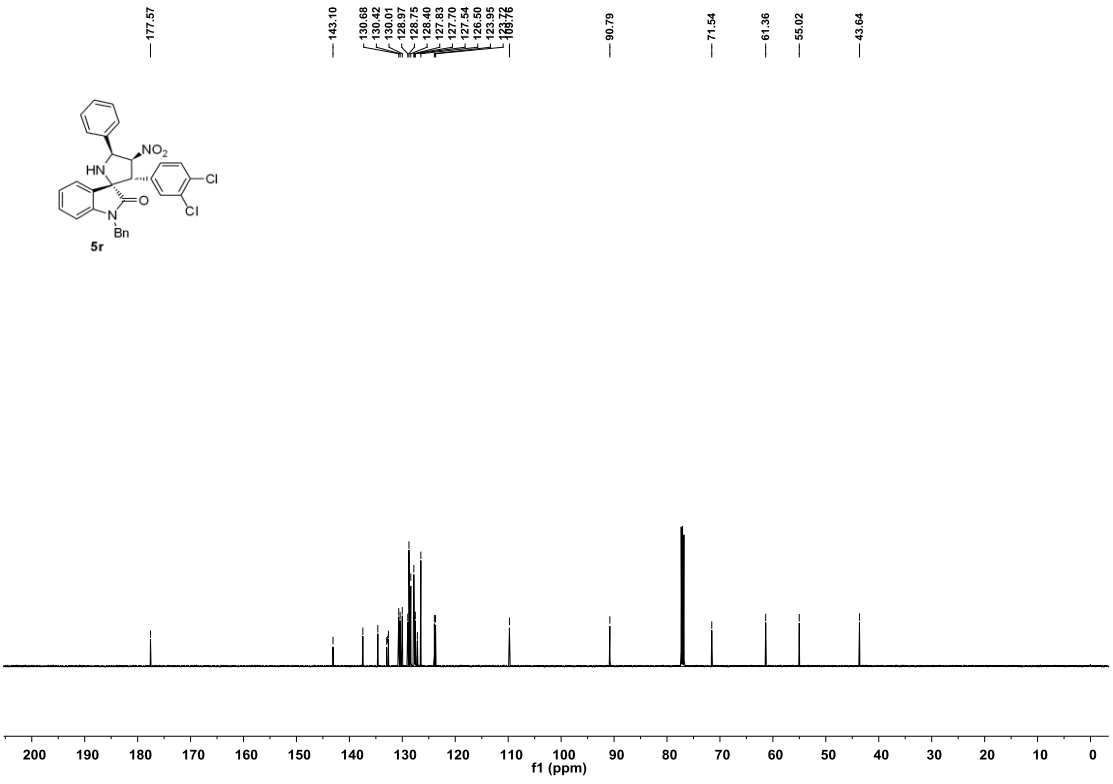
7.390
7.373
7.355
7.343
7.326
7.237
7.229
7.223
7.215
7.195
7.188
7.171
7.163
7.157
7.152
6.858
6.854
6.603
6.586
6.530
6.516
5.886
5.879
5.077
5.037
4.628
4.604
4.264
4.224
2.677
0.000
NO2
HN
Cl
Cl
O
N
Bn
5r
1.00
2.00
3.09
7.16
0.98
2.01
1.02
1.00
1.01
1.02
1.00
1.00
0.98
f1 (ppm)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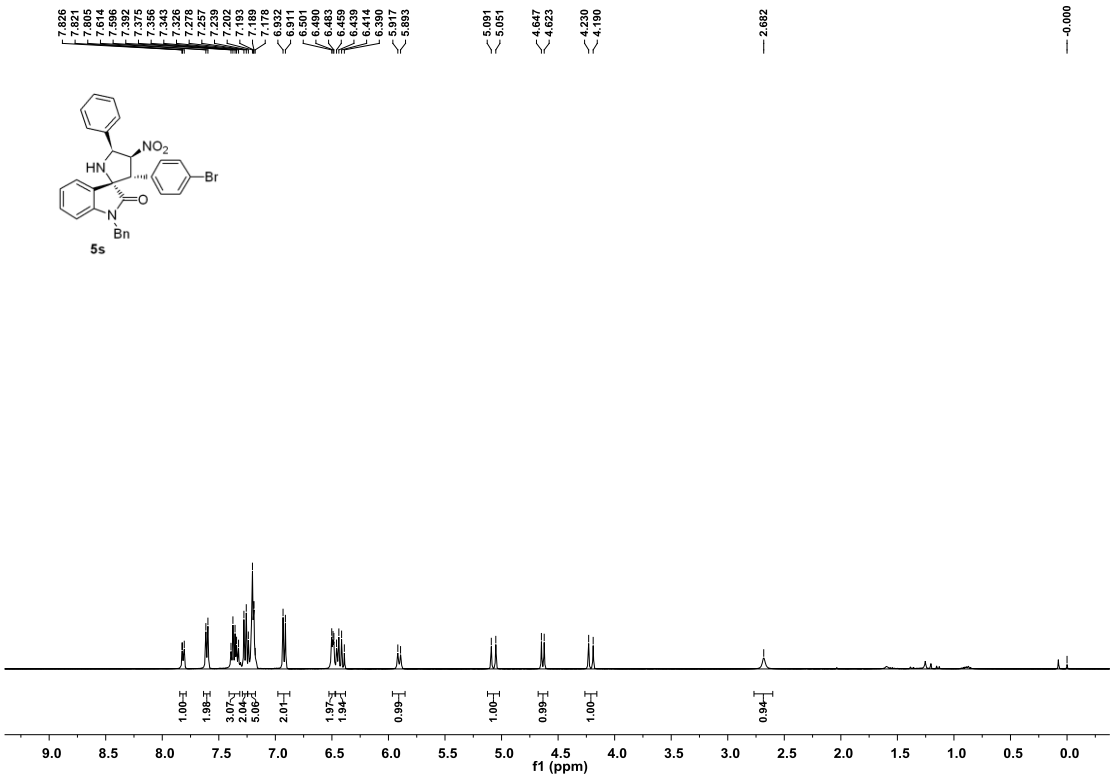
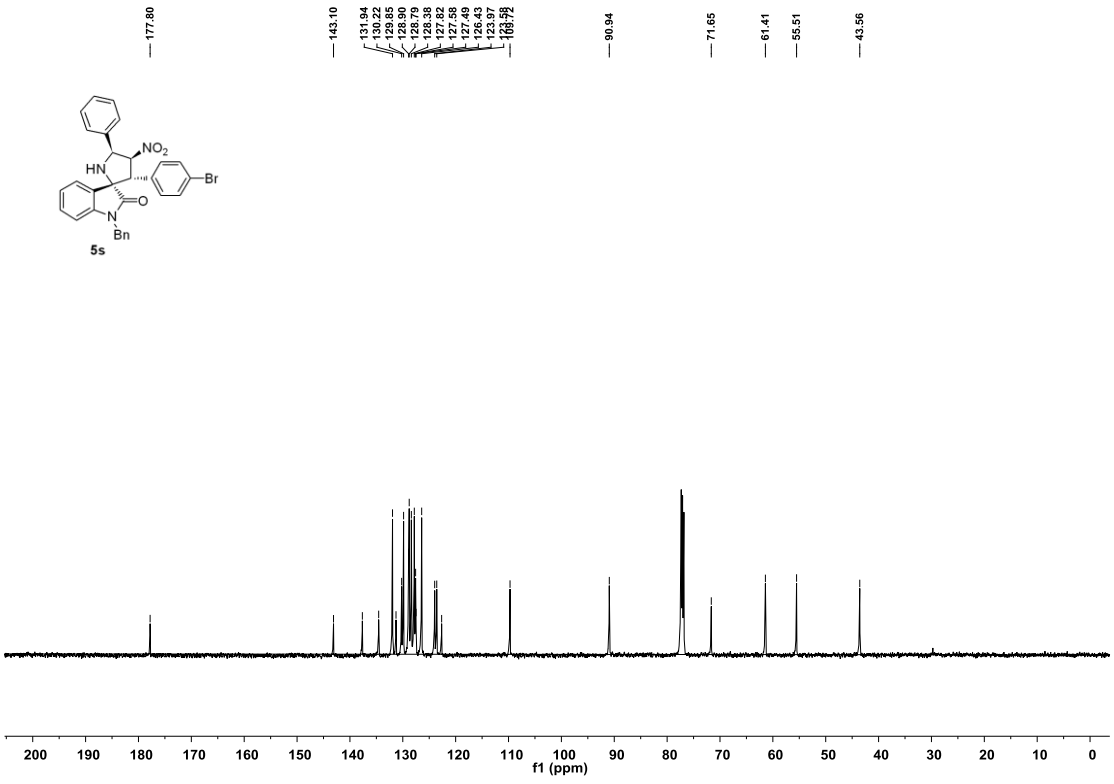
143.10
130.68
130.42
130.01
128.97
128.75
128.40
127.83
127.70
127.54
126.50
123.55
110.76
90.79
71.54
61.36
55.02
43.64
NO2
HN
Cl
Cl
O
N
Bn
5r
f1 (ppm)

5s


7.826
7.821
7.805
7.654
7.596
7.392
7.375
7.356
7.343
7.326
7.278
7.257
7.239
7.202
7.193
7.188
7.178
6.932
6.911
6.501
6.490
6.483
6.459
6.439
6.414
6.390
5.917
5.893
5.091
5.051
4.647
4.623
4.230
4.190
2.682
-0.000
NO2
HN
Br
O
N
Bn
5s
1.00
1.98
3.07
2.04
5.06
2.01
1.97
1.94
0.99
1.00
0.99
1.00
0.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.80
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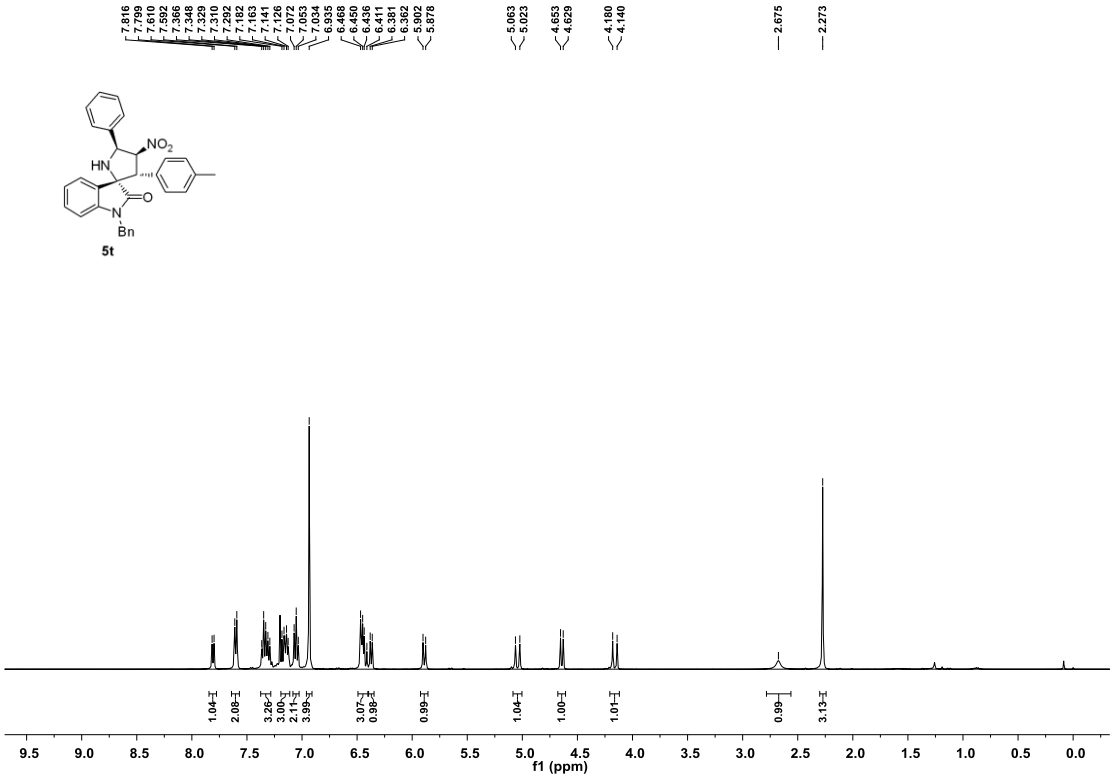
130.22
129.85
128.90
128.79
128.38
127.82
127.58
127.49
127.43
123.97
123.58
110.72
90.94
71.65
61.41
55.51
43.56
NO2
HN
Br
O
N
Bn
5s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5t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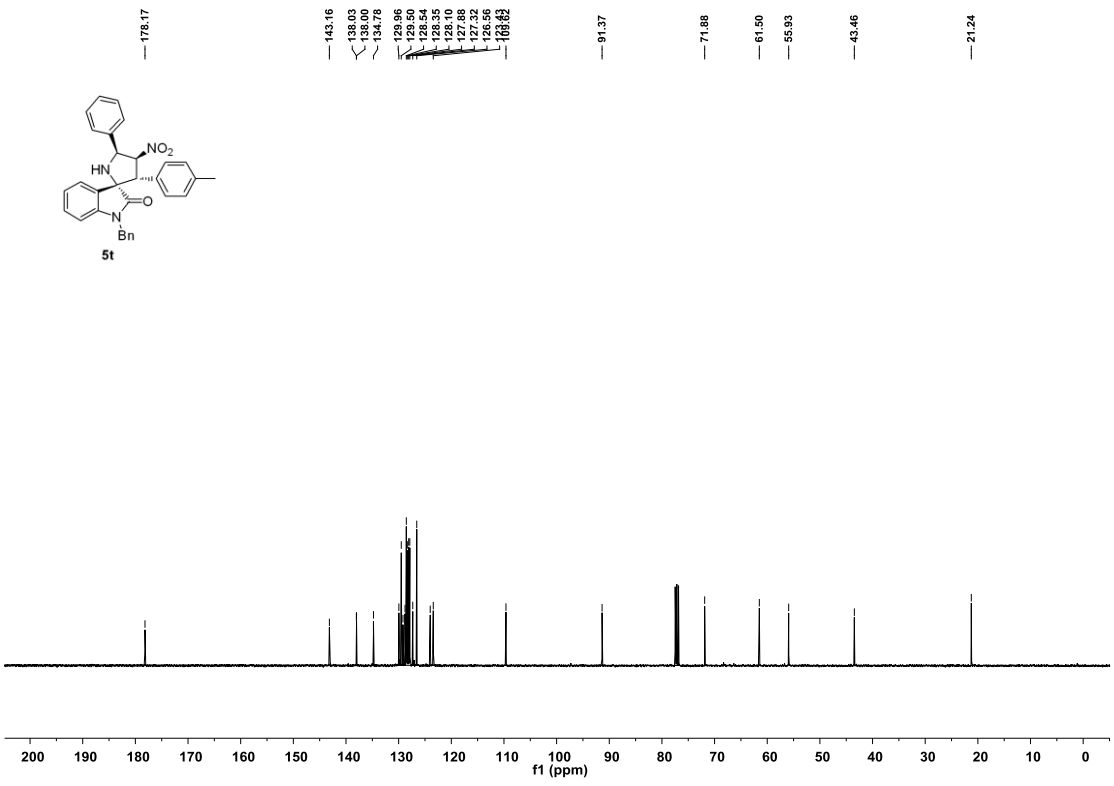
7.610
7.592
7.366
7.348
7.329
7.310
7.292
7.163
7.141
7.126
7.072
7.053
7.034
6.935
6.468
6.450
6.436
6.411
6.381
6.362
5.902
5.878
5.063
5.023
4.653
4.629
4.180
4.140
2.675
2.273
NO2
HN
O
N
Bn
5t
1.04
2.08
3.26
3.00
2.11
3.99
3.07
0.98
0.99
1.04
1.00
1.01
0.99
3.13
f1 (ppm)


178.17
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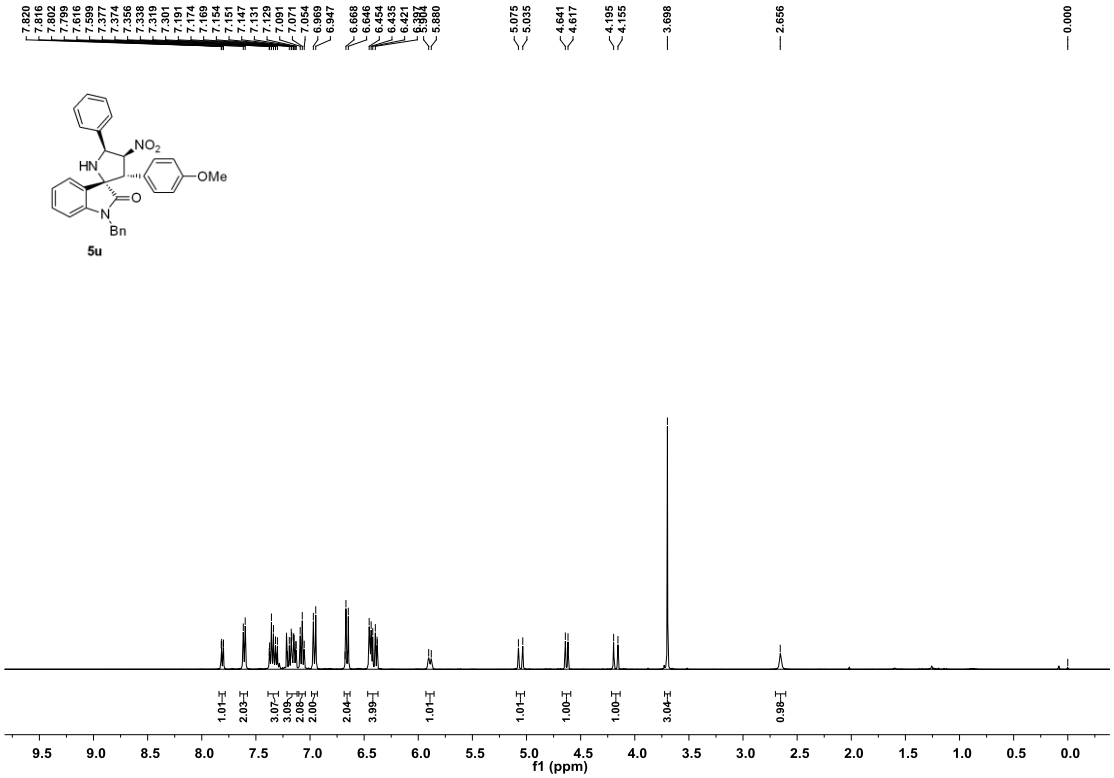
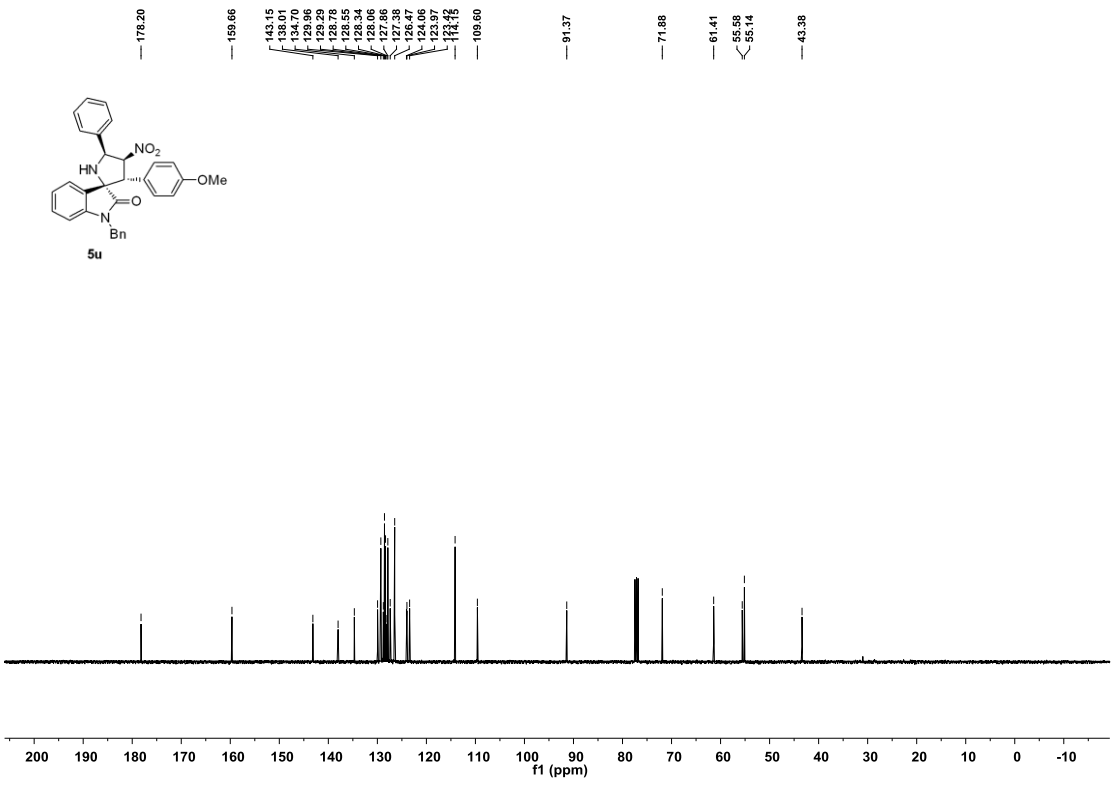
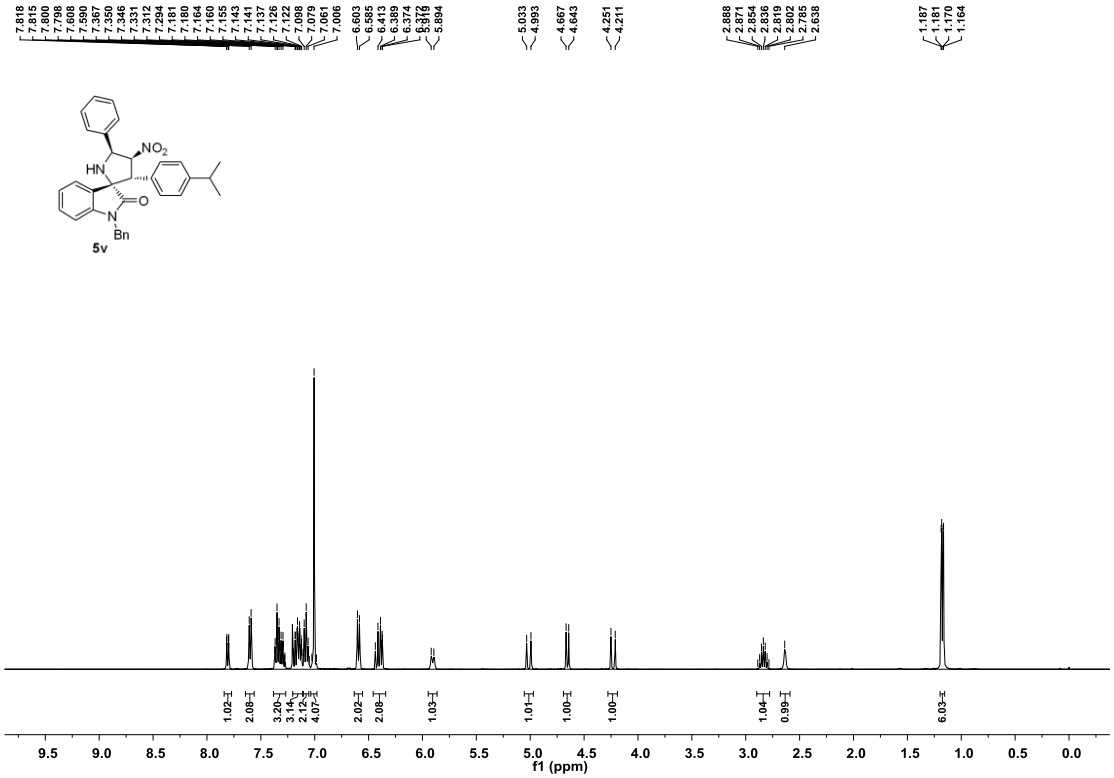
138.00
134.78
129.96
129.50
128.54
128.35
128.10
127.88
127.32
126.56
110.62
91.37
71.88
61.50
55.93
43.46
21.24
NO2
HN
O
N
Bn
5t
f1 (ppm)

5u


7.820
7.816
7.802
7.799
7.616
7.599
7.377
7.374
7.355
7.338
7.319
7.301
7.191
7.174
7.169
7.154
7.151
7.147
7.131
7.120
7.091
7.071
7.054
6.969
6.947
6.668
6.646
6.454
6.435
6.421
5.880
5.075
5.035
4.641
4.617
4.195
4.155
3.698
2.656
0.000
NO2
HN
OMe
O
N
Bn
5u
1.01
2.03
3.07
3.09
2.08
2.00
2.04
3.99
1.01
1.01
1.00
1.00
3.04
0.98
f1 (ppm)


178.20
159.66
143.15
138.01
134.70
129.96
129.29
128.78
128.55
128.34
128.06
127.86
127.38
126.47
124.06
123.97
123.42
114.15
109.60
91.37
71.88
61.41
55.58
55.14
43.38
NO2
HN
OMe
O
N
Bn
5u
f1 (ppm)

5v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7.608
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7.350
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7.331
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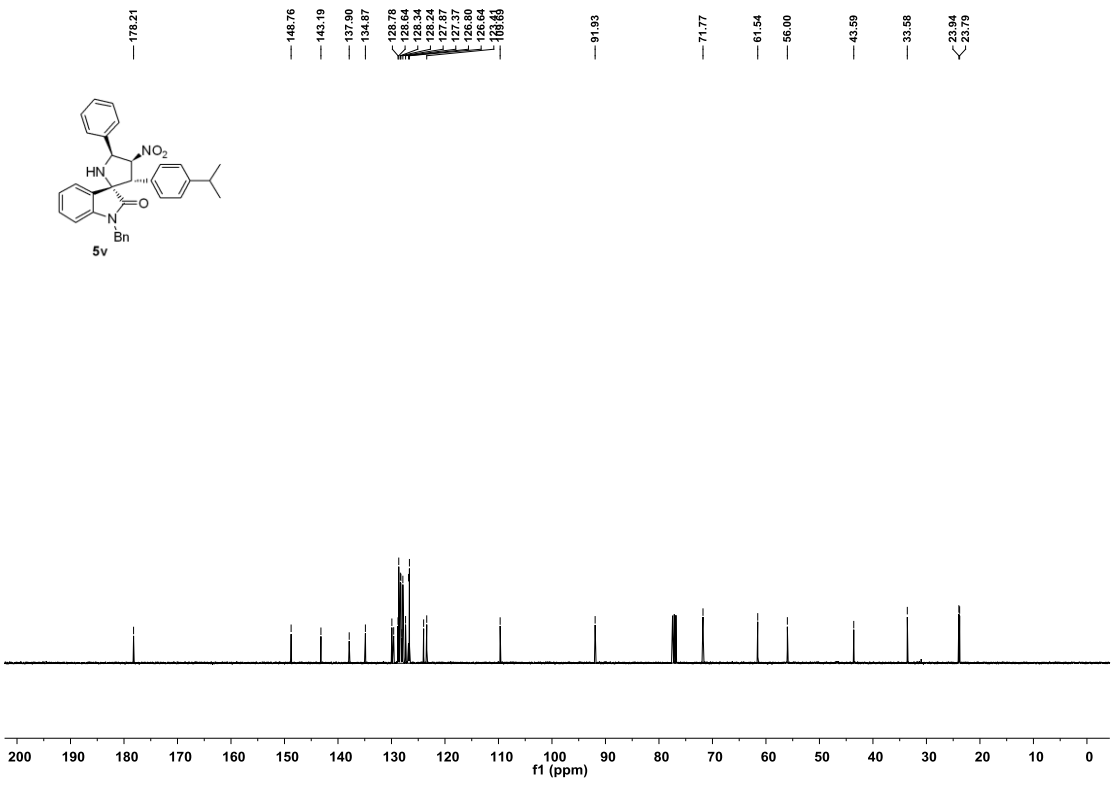
7.181
7.160
7.160
7.155
7.143
7.141
7.137
7.126
7.122
7.098
7.079
7.061
7.006
6.603
6.585
6.413
6.389
6.374
5.910
5.894
5.033
4.993
4.667
4.643
4.251
4.211
2.888
2.871
2.854
2.836
2.819
2.802
2.785
2.638
1.187
1.181
1.170
1.164
NO2
HN
O
N
Bn
5v
1.02
2.08
3.20
3.14
2.12
4.07
2.02
2.08
1.03
1.01
1.00
1.00
1.04
0.99
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.87
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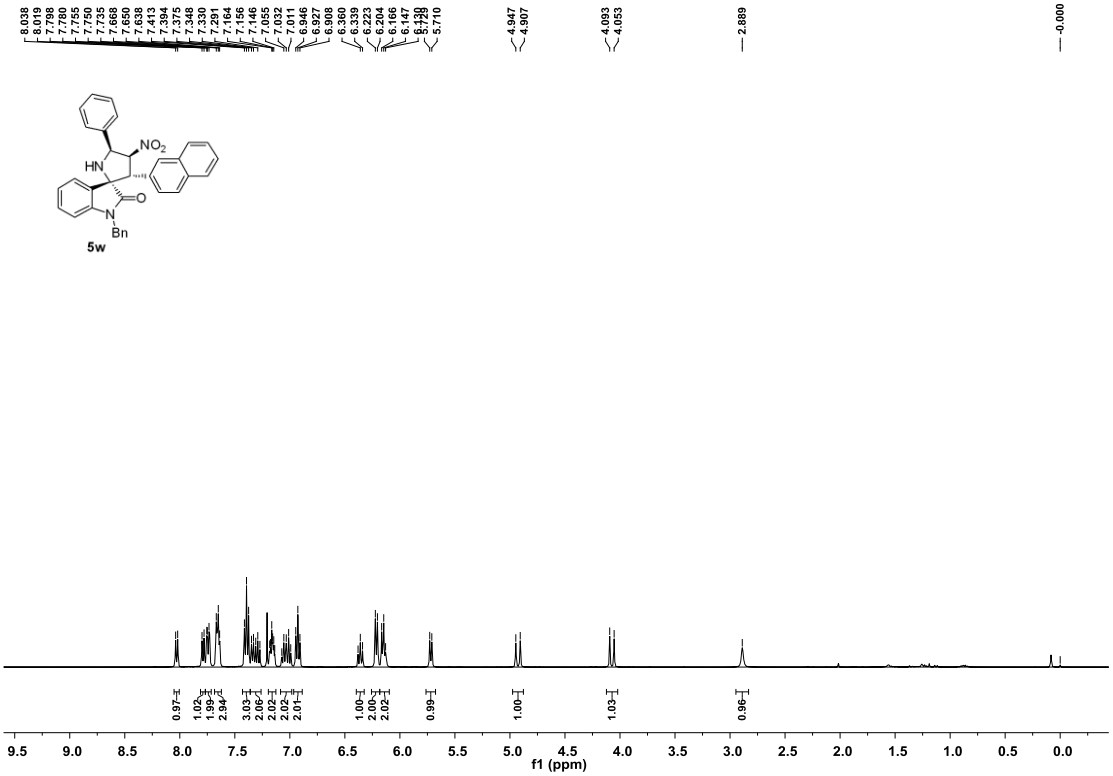
127.87
127.37
126.80
126.64
91.93
71.77
61.54
56.00
43.59
33.58
23.94
23.79
NO2
HN
O
N
Bn
5v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5w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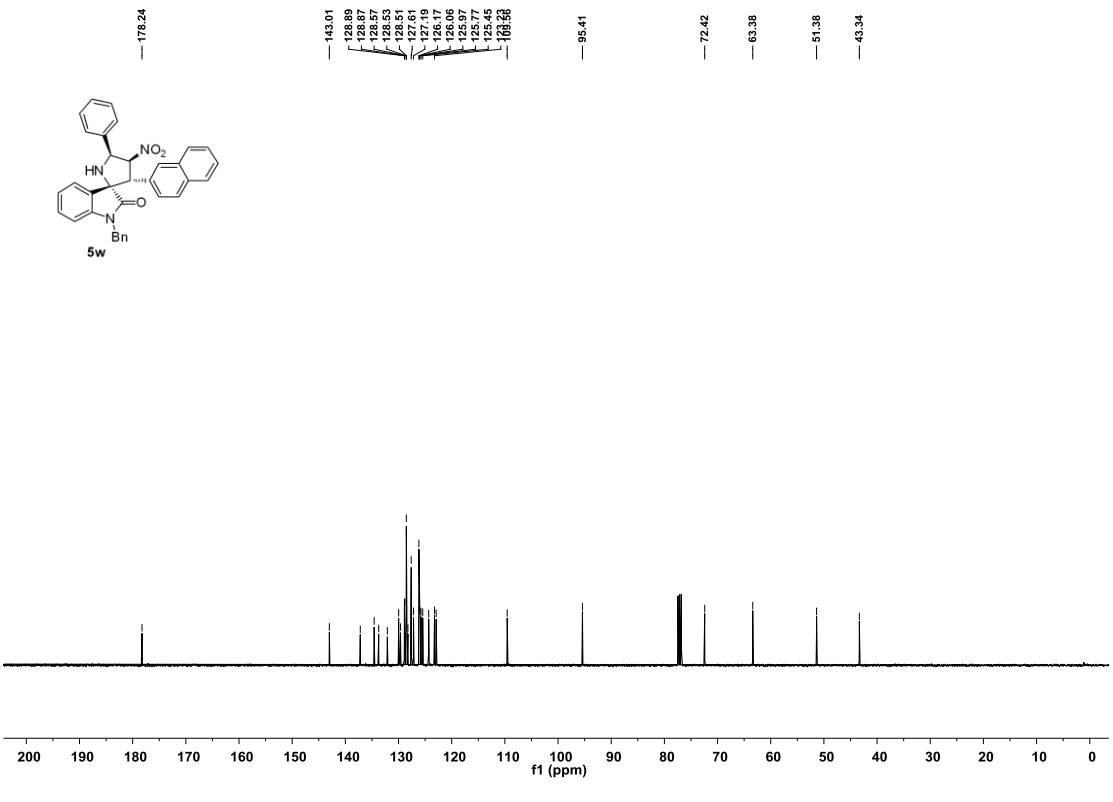
7.755
7.750
7.735
7.668
7.650
7.638
7.413
7.394
7.375
7.348
7.330
7.291
7.164
7.156
7.146
7.055
7.032
7.011
6.946
6.927
6.908
6.360
6.339
6.223
6.204
6.166
6.147
5.729
5.710
4.947
4.907
4.093
4.053
2.889
-0.000
NO2
HN
O
N
Bn
5w
0.97
1.02
1.99
2.94
3.03
2.06
2.02
2.02
2.01
1.00
2.00
2.02
0.99
1.00
1.03
0.96
f1 (ppm)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128.53
128.51
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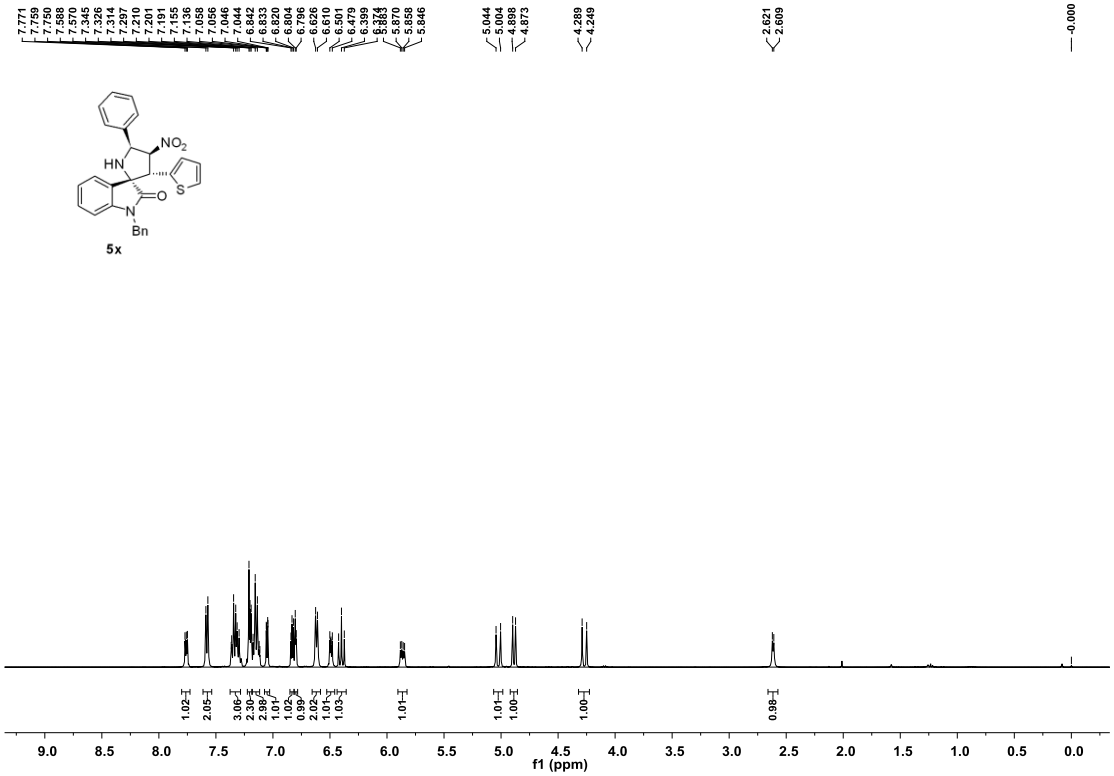
126.17
126.06
125.97
125.77
125.45
95.41
72.42
63.38
51.38
43.34
NO2
HN
O
N
Bn
5w
f1 (ppm)

5x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7.314
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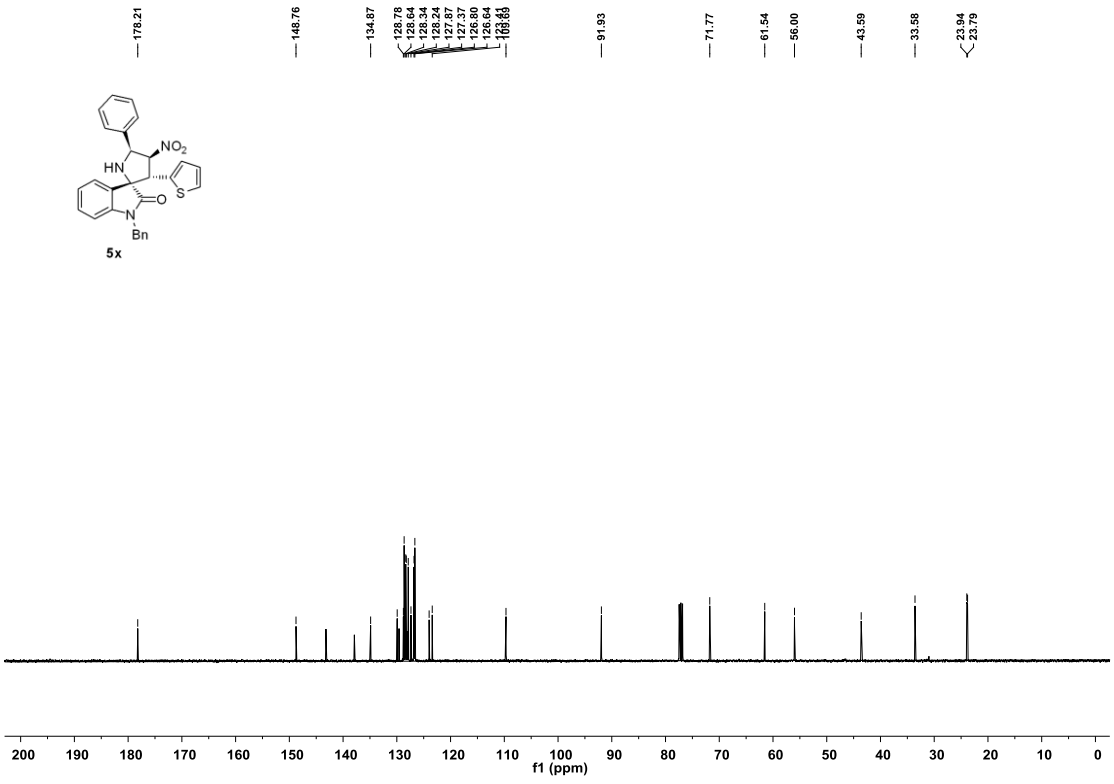
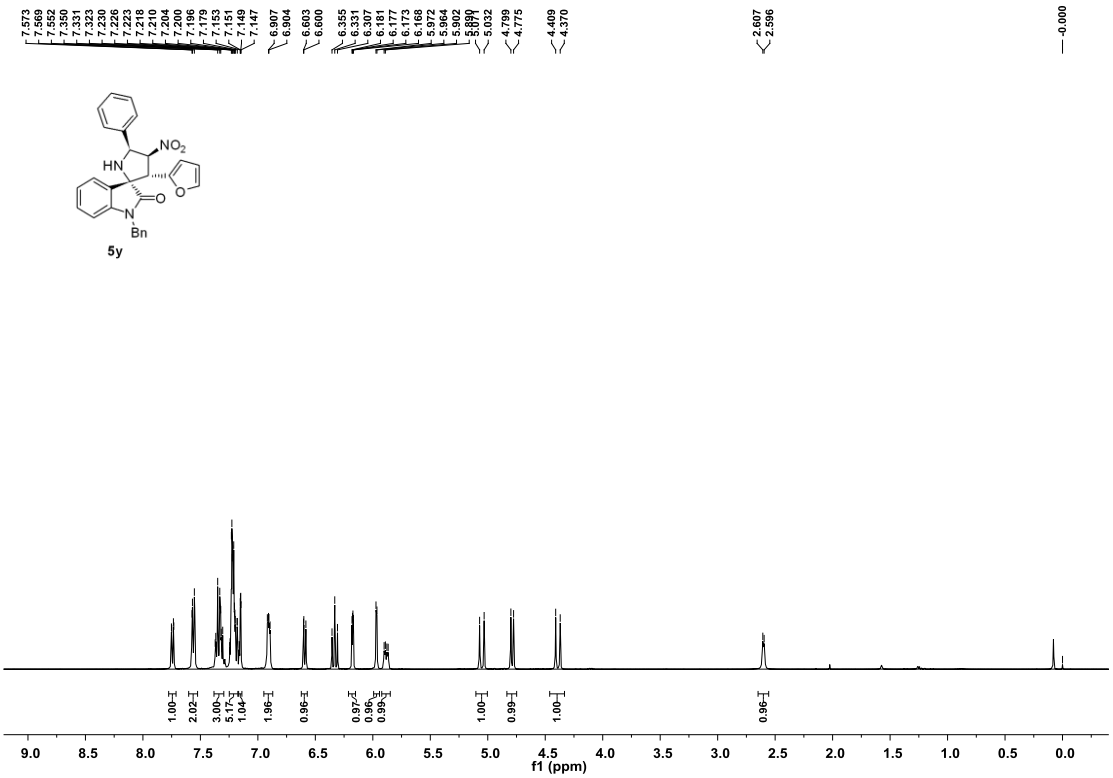
7.210
7.201
7.191
7.155
7.136
7.058
7.056
7.046
7.044
6.842
6.833
6.820
6.804
6.796
6.626
6.610
6.591
6.479
6.399
6.374
5.870
5.858
5.846
5.044
5.004
4.898
4.873
4.289
4.249
2.621
2.609
-0.000
NO2
HN
O
S
N
Bn
5x
1.02
2.05
3.06
2.30
2.98
1.01
1.02
0.99
2.02
1.01
1.03
1.01
1.01
1.00
1.00
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.21
148.76
134.87
128.78
128.64
128.34
128.24
127.87
127.37
126.80
126.64
110.69
91.93
71.77
61.54
56.00
43.59
33.58
23.94
23.79
NO2
HN
O
S
N
Bn
5x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5y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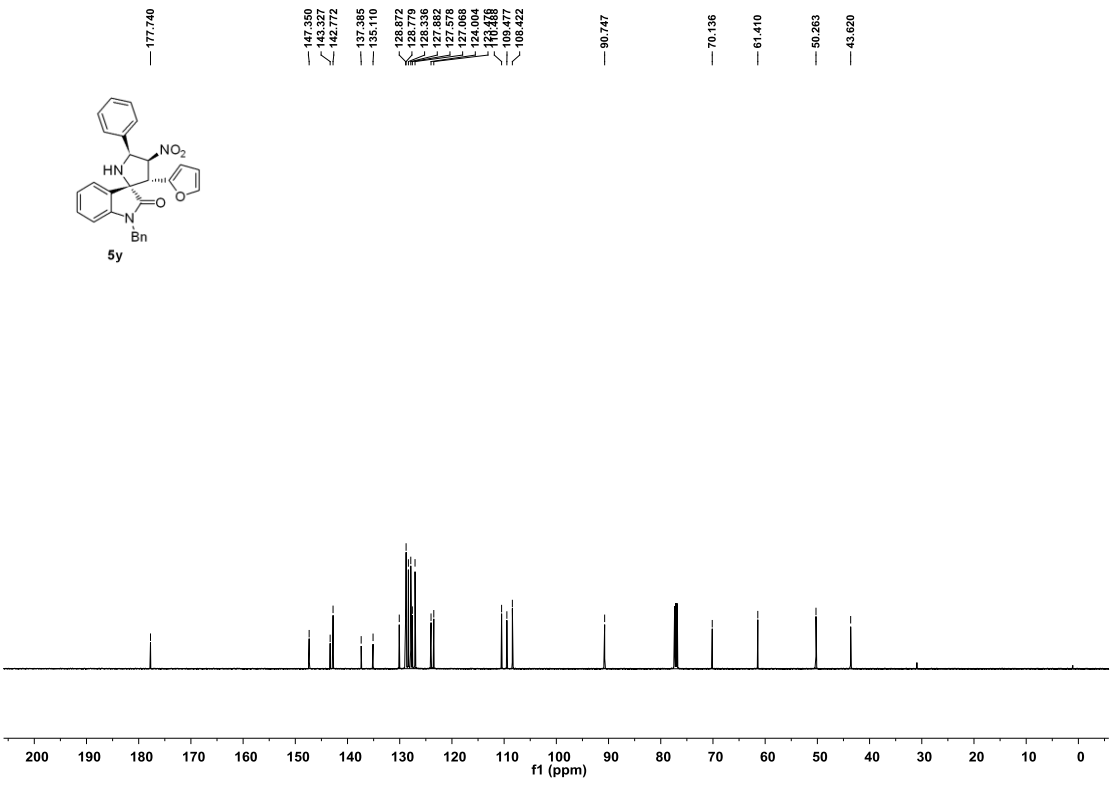
7.226
7.223
7.218
7.210
7.204
7.200
7.196
7.179
7.153
7.151
7.149
7.147
6.907
6.904
6.603
6.600
6.355
6.331
6.307
6.181
6.177
6.173
6.168
5.972
5.964
5.902
5.032
4.799
4.775
4.409
4.370
2.607
2.596
-0.000
NO2
HN
O
N
Bn
5y
1.00
2.02
3.00
5.17
1.04
1.96
0.96
0.97
0.96
0.99
1.00
0.99
1.00
0.96
f1 (ppm)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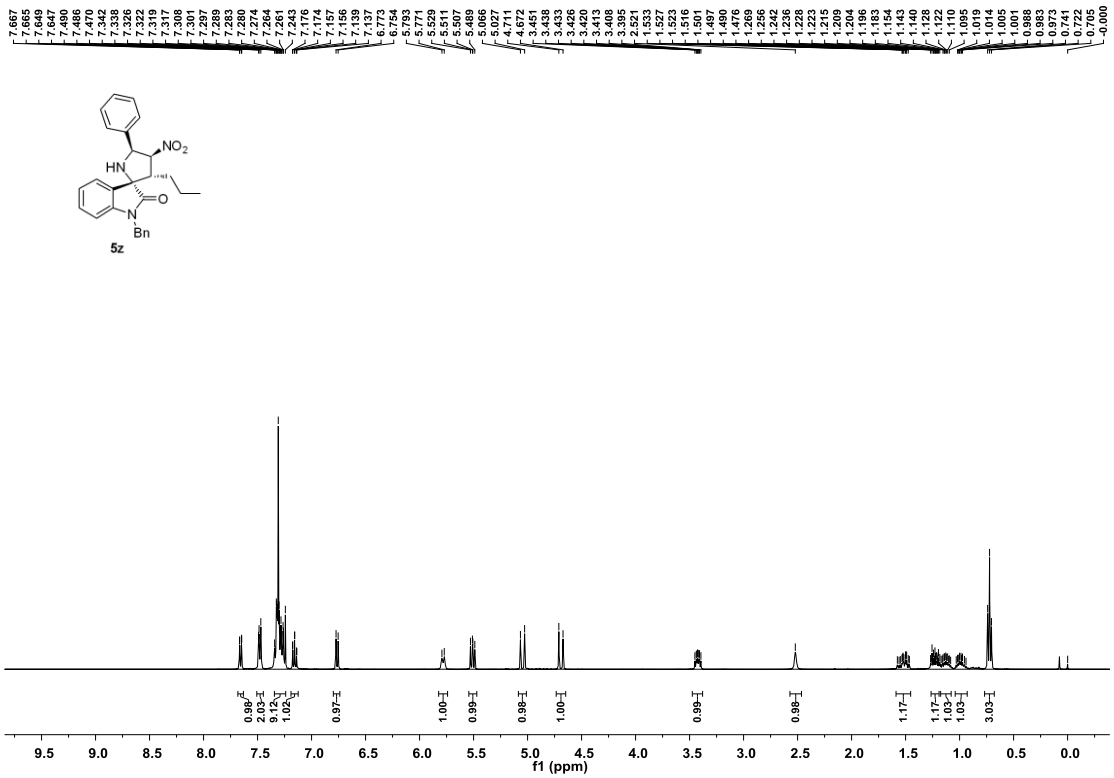
127.068
124.004
110.488
109.477
108.422
90.747
70.136
61.410
50.263
43.620
NO2
HN
O
N
Bn
5y
f1 (ppm)

5z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7.319
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7.308
7.301
7.297
7.289
7.283
7.280
7.274
7.264
7.261
7.243
7.176
7.174
7.157
7.156
7.139
7.137
6.773
6.754
5.793
5.771
5.529
5.511
5.507
5.489
5.066
5.027
4.711
4.672
4.451
3.438
3.433
3.426
3.420
3.413
3.408
3.395
2.521
1.553
1.527
1.523
1.516
1.501
1.497
1.490
1.476
1.269
1.256
1.242
1.236
1.228
1.223
1.215
1.209
1.204
1.196
1.183
1.154
1.143
1.140
1.128
1.122
1.110
1.095
1.019
1.014
1.005
1.001
0.988
0.983
0.973
0.741
0.722
0.705
-0.000
NO2
HN
O
N
Bn
5z
0.98
2.03
9.12
1.02
0.97
1.00
0.99
0.98
1.00
0.99
0.98
1.17
1.17
1.03
1.03
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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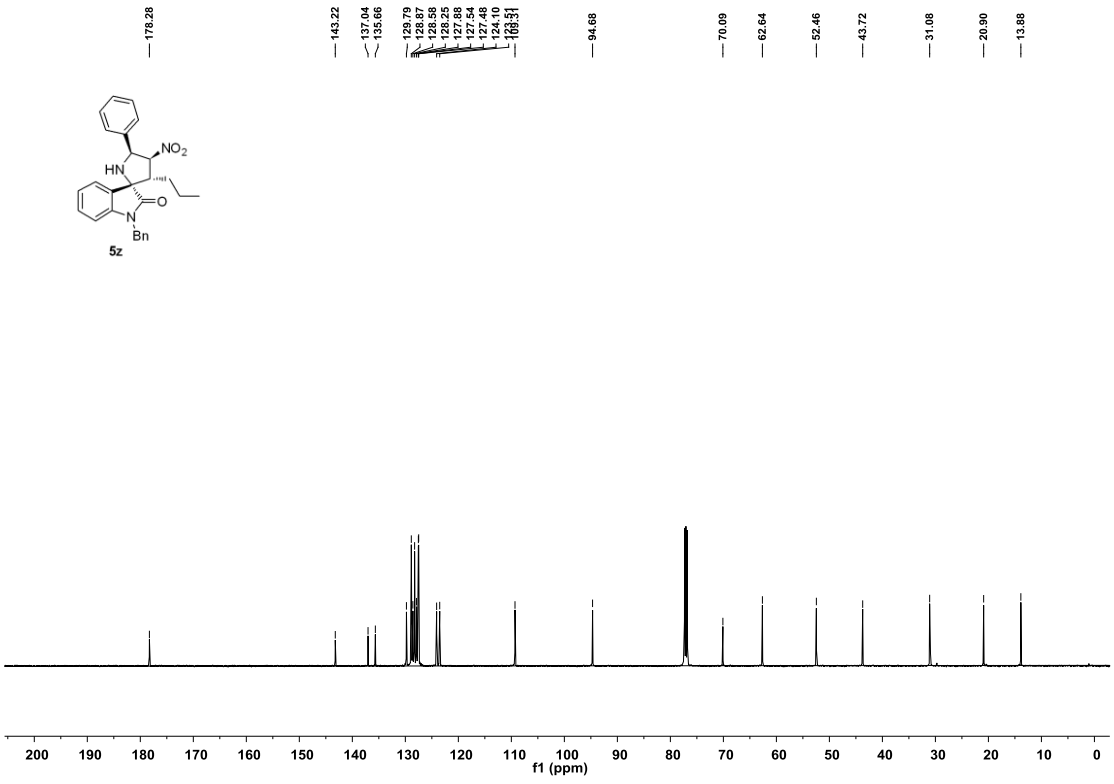
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.28
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137.04
135.66
129.79
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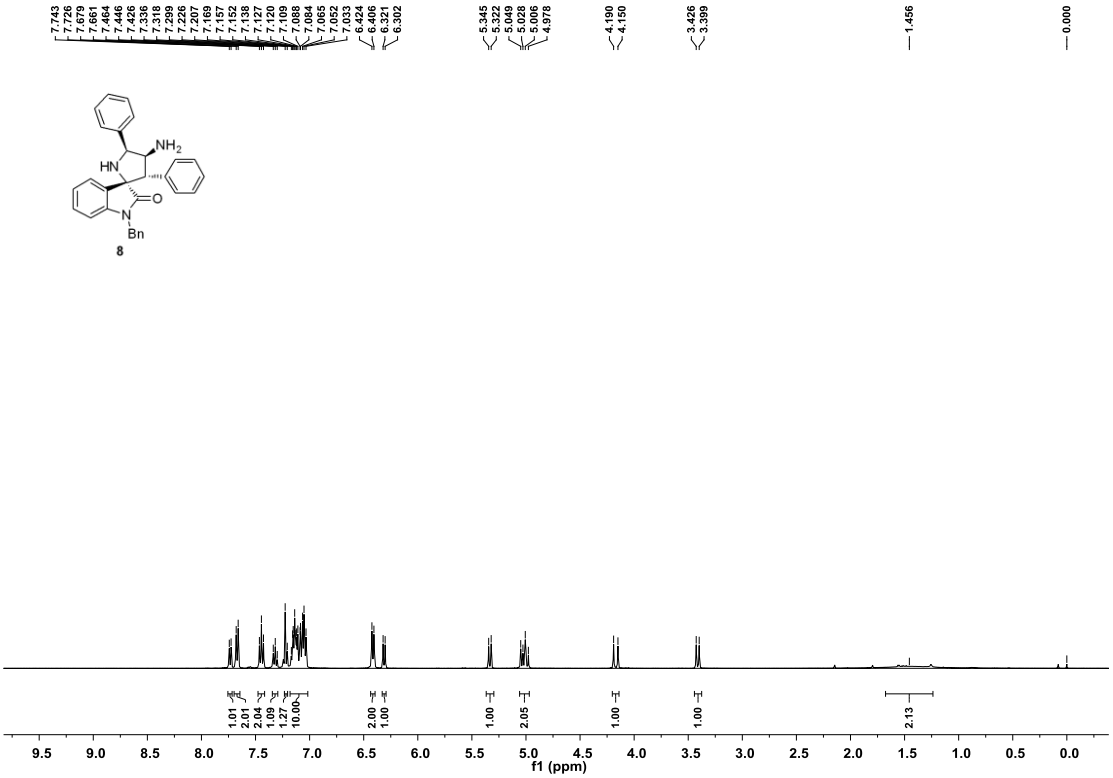
128.58
128.25
127.88
127.54
127.48
124.10
110.31
94.68
70.09
62.64
52.46
43.72
31.08
20.90
13.88
NO2
HN
O
N
Bn
5z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8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7.336
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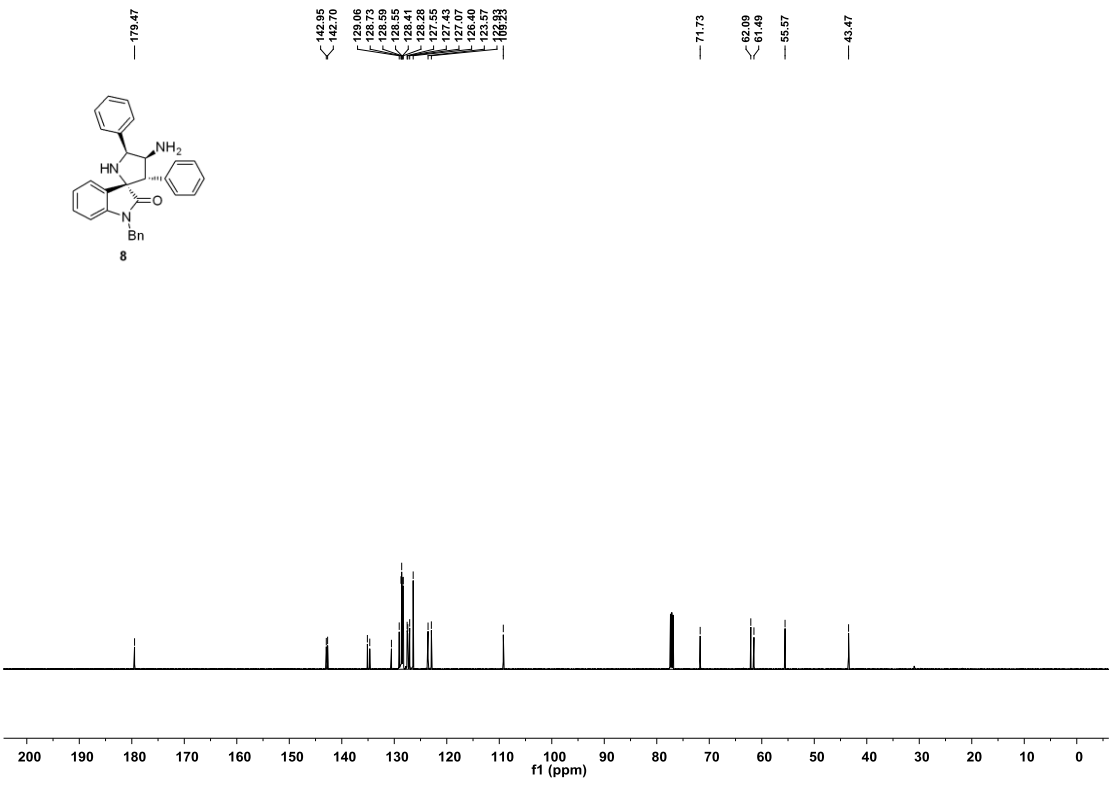
7.299
7.226
7.207
7.169
7.157
7.152
7.138
7.127
7.120
7.109
7.088
7.084
7.065
7.052
7.033
6.424
6.406
6.321
6.302
5.345
5.322
5.049
5.028
5.006
4.978
4.190
4.150
3.426
3.399
1.456
0.000
NH2
HN
O
N
Bn
8
1.01
2.01
2.04
1.09
1.27
10.00
2.00
1.00
1.00
2.05
1.00
1.00
2.13
f1 (ppm)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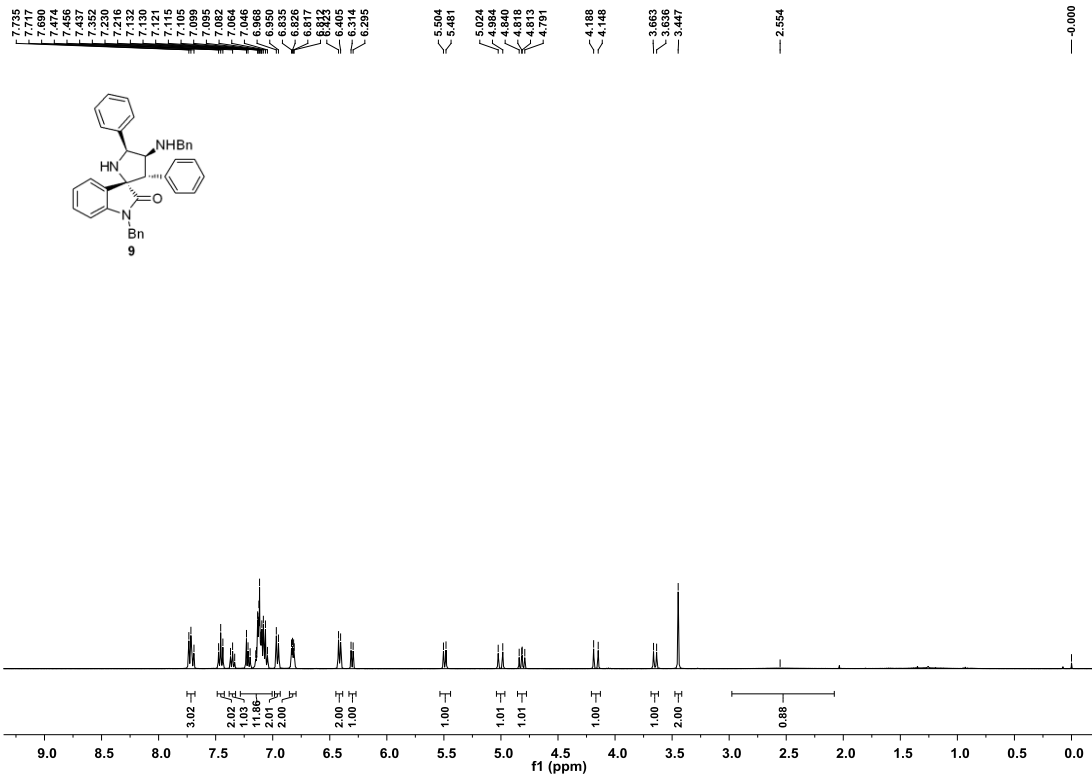
128.73
128.59
128.55
128.41
128.28
127.55
127.43
127.07
126.40
123.57
110.93
110.23
71.73
62.09
61.49
55.57
43.47
NH2
HN
O
N
Bn
8
f1 (ppm)

9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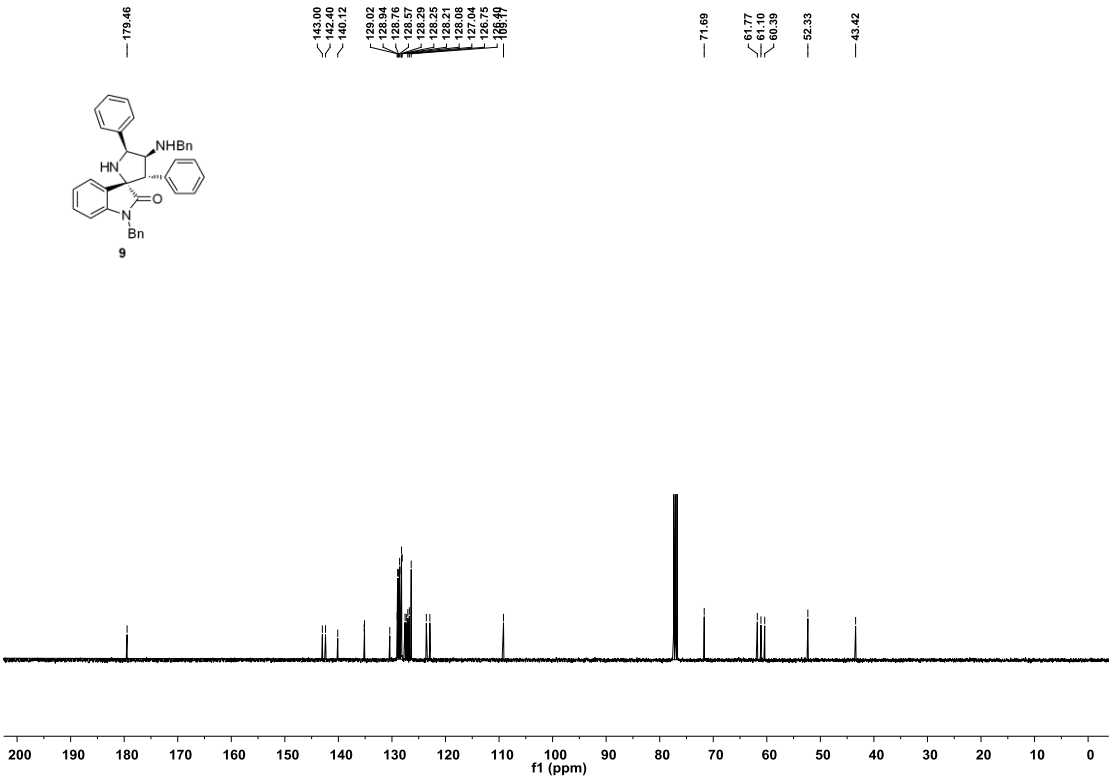
7.216
7.132
7.130
7.121
7.115
7.105
7.099
7.095
7.082
7.064
7.046
6.968
6.950
6.835
6.829
6.817
6.423
6.405
6.314
6.295
5.504
5.481
5.024
4.984
4.840
4.816
4.813
4.791
4.188
4.148
3.663
3.636
3.447
2.554
-0.000
NHBn
HN
O
N
Bn
9
3.02
2.02
1.03
11.86
2.01
2.00
2.00
1.00
1.00
1.01
1.01
1.00
1.00
2.00
0.88
f1 (ppm)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129.02
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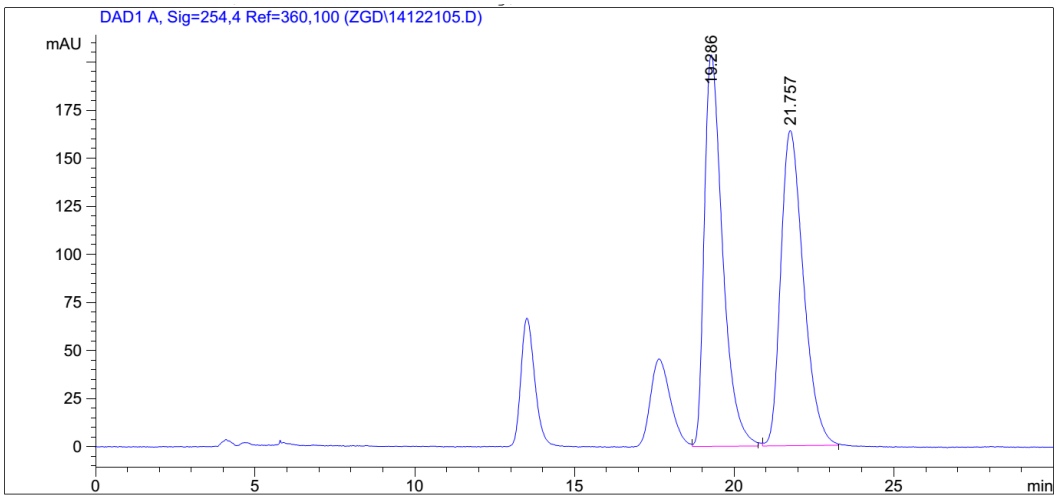
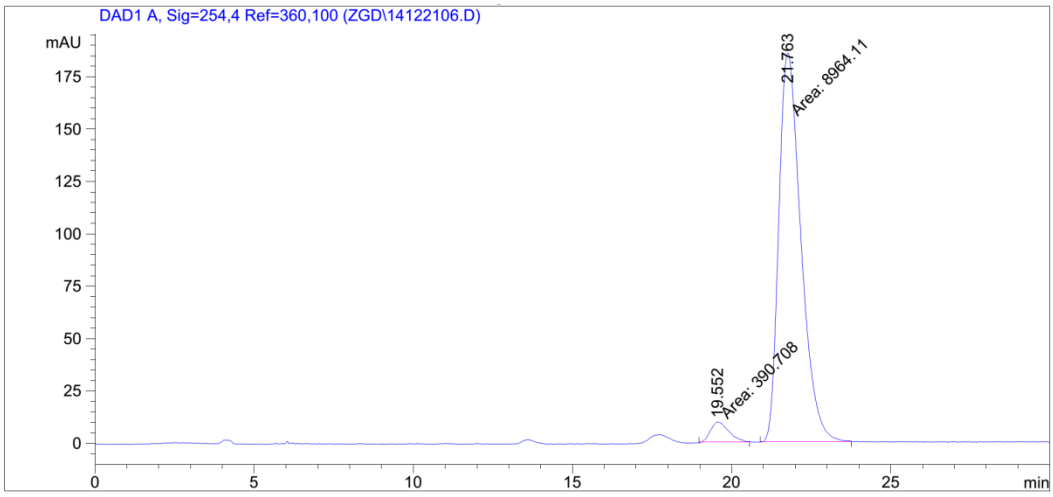
128.57
128.29
128.25
128.21
128.08
127.04
126.75
110.40
110.17
71.69
61.77
61.10
60.39
52.33
43.42
NHBn
HN
O
N
Bn
9
f1 (ppm)

4. Copies of HPLC chromatographs

HPLC Chromatographs of **5a**

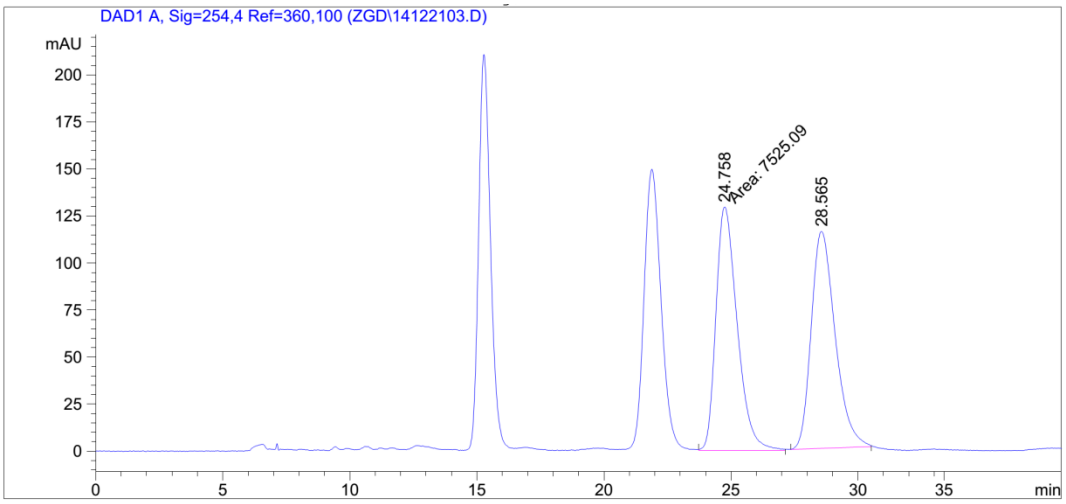


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	19.286	8134.95947	203.58200	50.0912
2	21.757	8105.33838	163.92245	49.9088

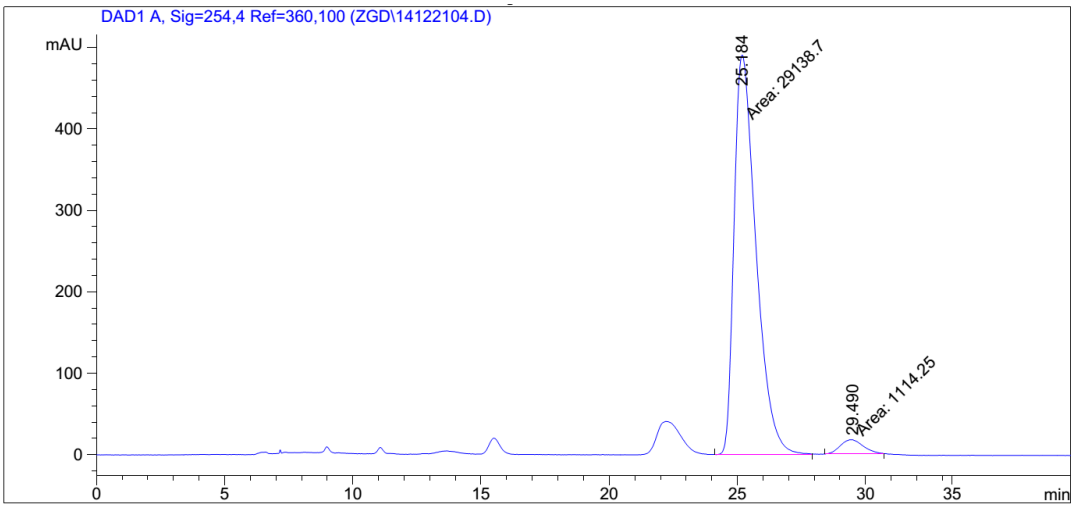


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	19.552	390.70813	9.65274	4.1765
2	21.763	8964.11426	185.40921	95.8235

HPLC Chromatographs of **5b**

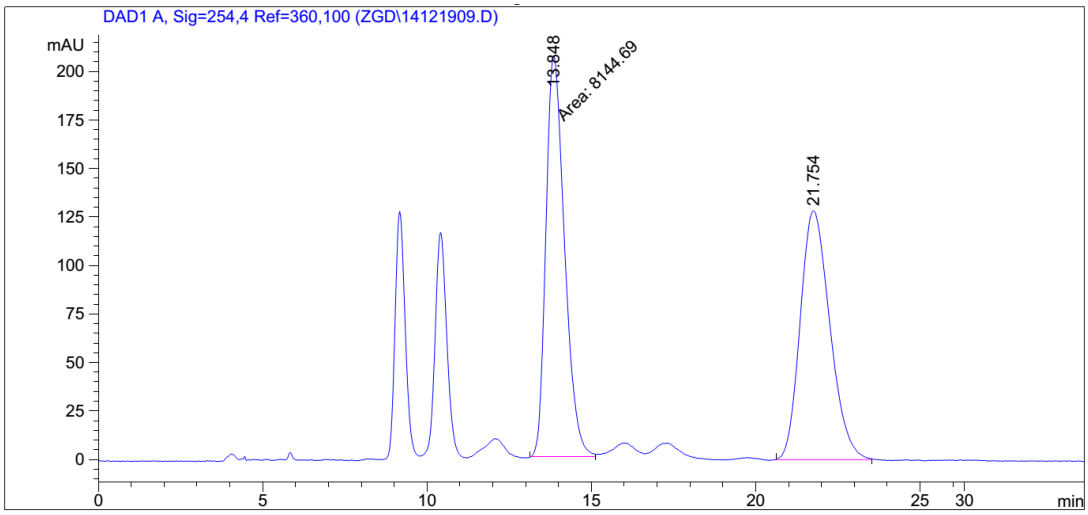


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	24.758	7525.09229	129.46397	49.9089
2	28.565	7552.57715	115.31859	50.0911

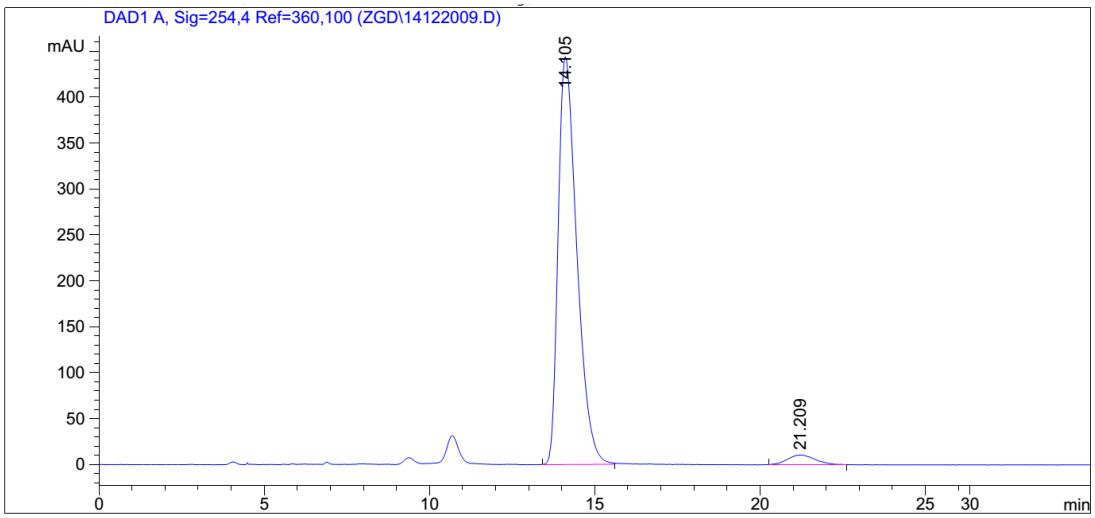


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	25.184	2.91387e4	490.88147	96.3169
2	29.490	1114.24695	17.52676	3.6831

HPLC Chromatographs of **5c**

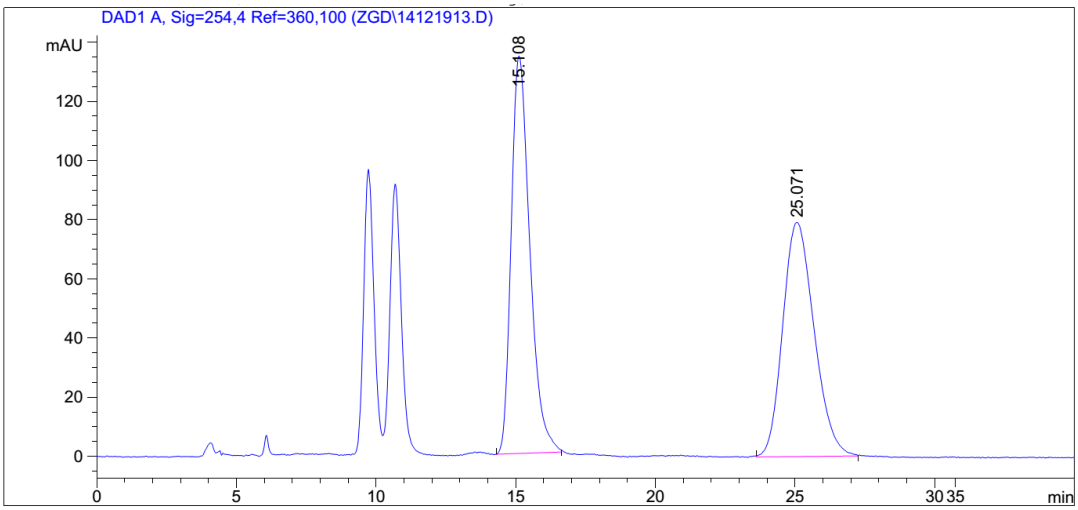


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	13.848	8144.68652	206.79213	50.2910
2	21.754	8050.42139	128.23347	49.7090

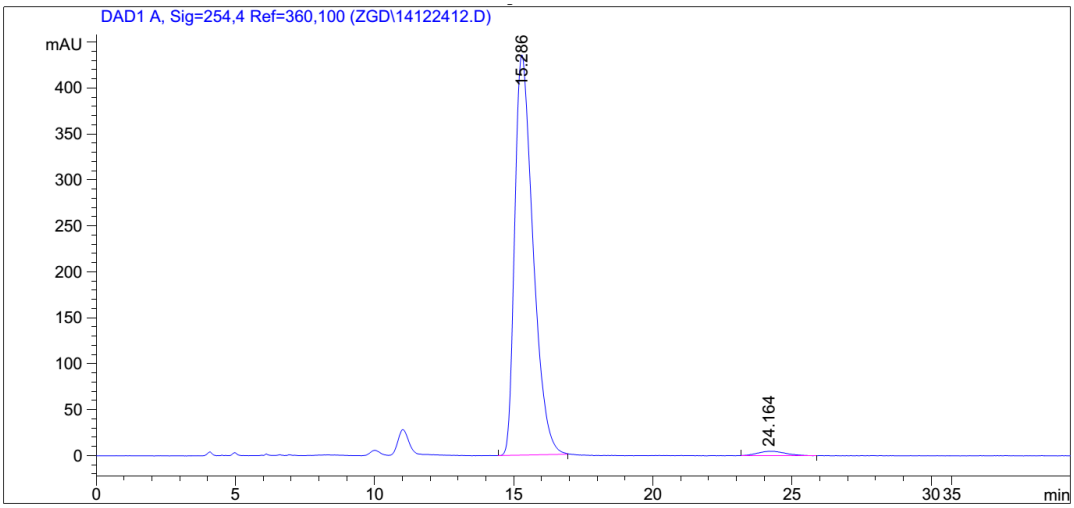


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	14.105	1.74384e4	444.03928	96.4333
2	21.209	644.98792	10.65072	3.5667

HPLC Chromatographs of **5d**

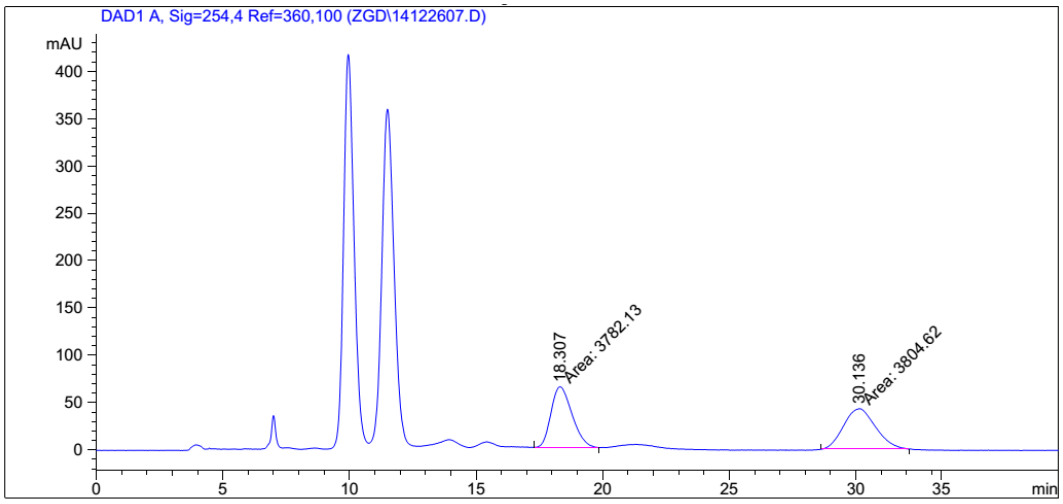


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	15.108	6214.87598	134.36545	50.1301
2	25.071	6182.60840	79.15697	49.8699

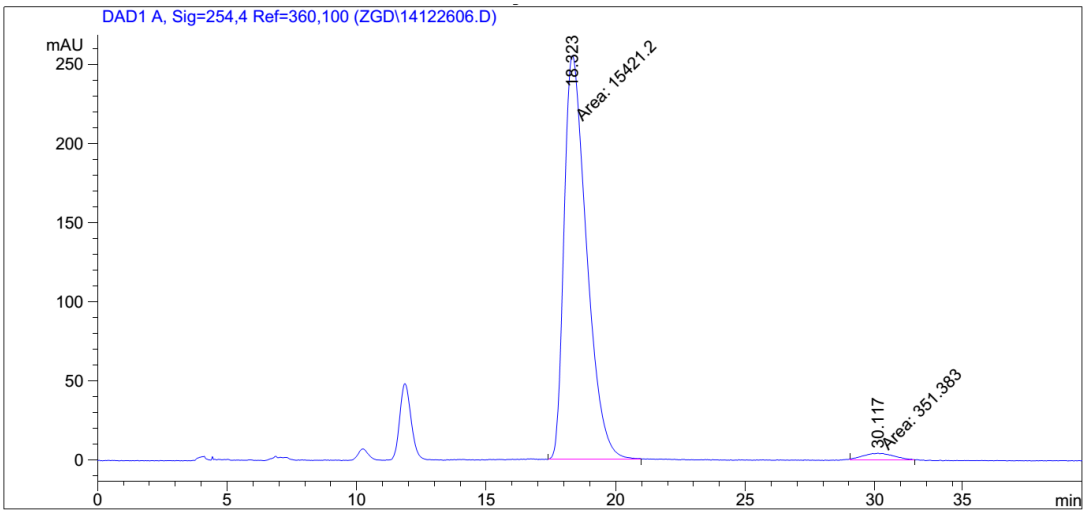


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	15.286	1.99069e4	435.32956	98.3531
2	24.164	333.34573	4.83869	1.6469

HPLC Chromatographs of **5e**

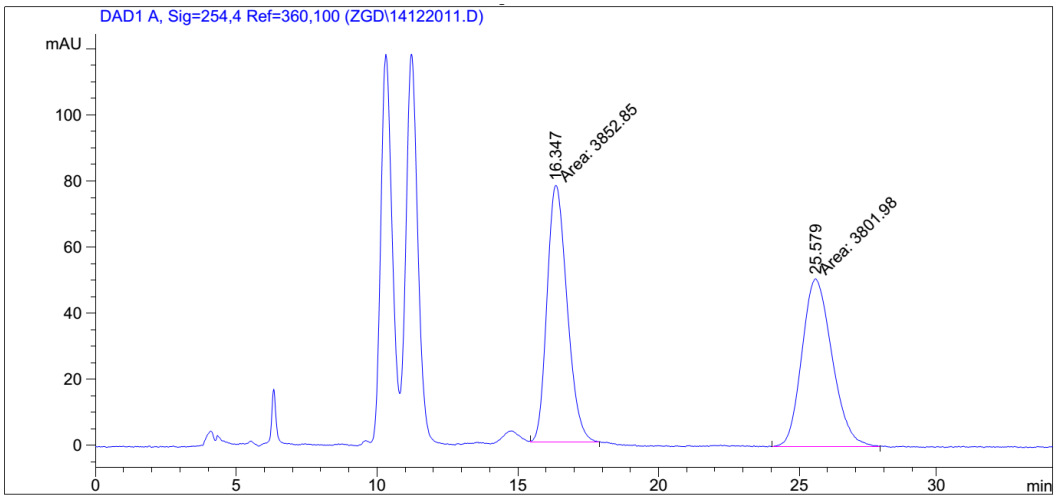


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	18.307	37682.13135	64.60121	49.8518
2	30.136	3804.62427	42.96786	50.1482

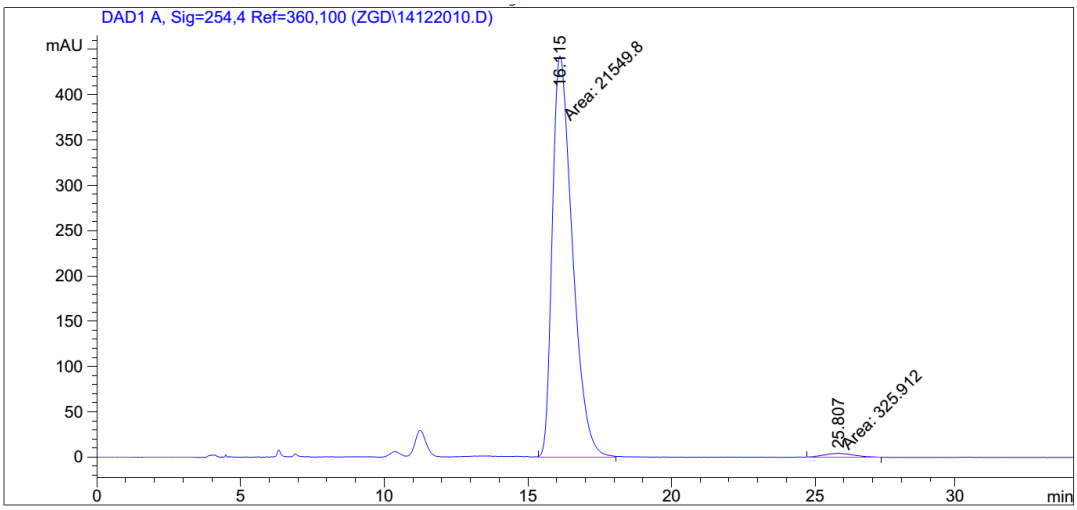


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	18.323	1.54212e4	255.18507	97.7722
2	30.117	351.38312	4.27291	2.2278

HPLC Chromatographs of **5f**

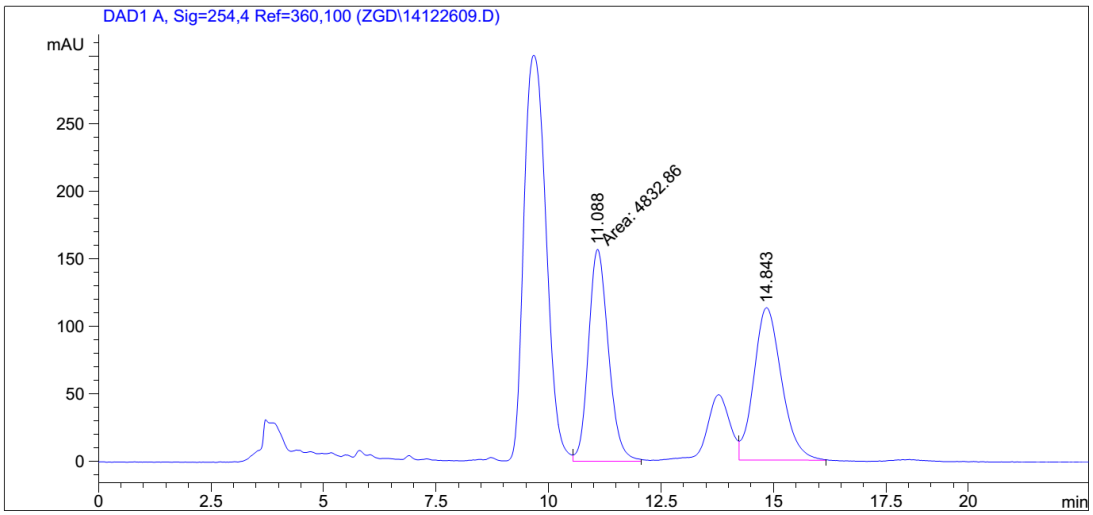


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	16.347	3852.85449	77.70826	50.3323
2	25.579	3801.98437	50.94347	49.6677

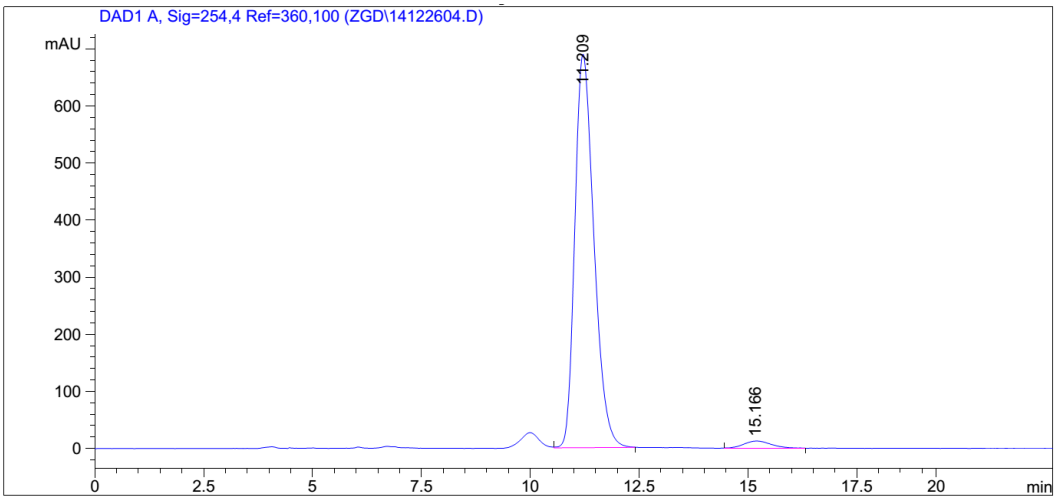


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	16.115	2.15498e4	443.30603	98.5102
2	25.807	325.91199	4.41010	1.4898

HPLC Chromatographs of **5g**

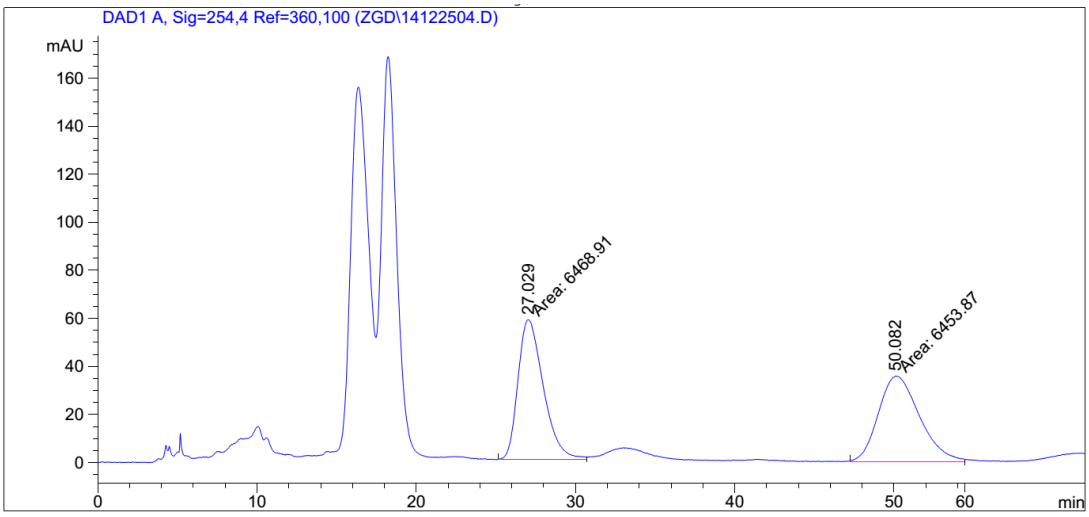


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	11.088	4832.85937	156.95360	49.9076
2	14.843	4850.75830	112.92374	50.0924

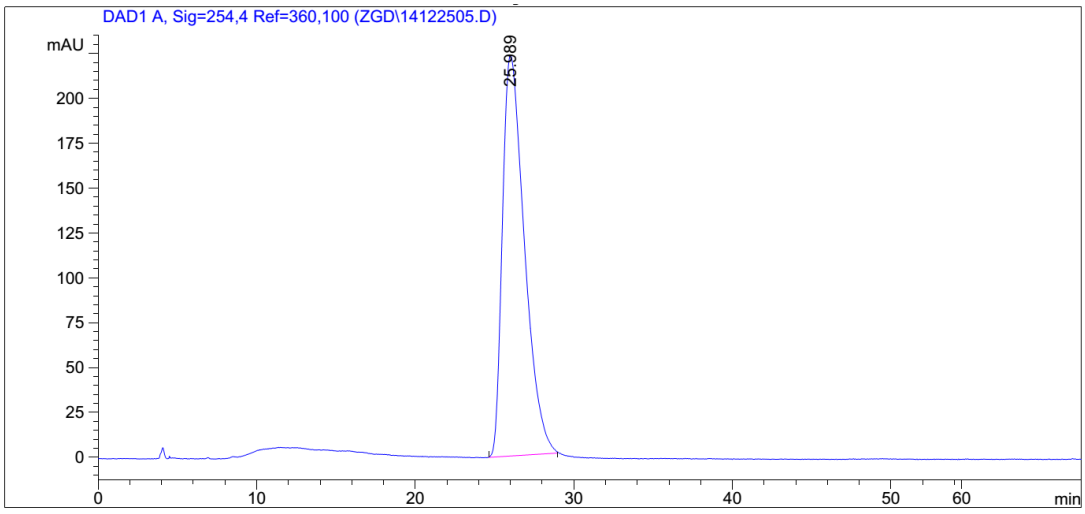


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	11.209	2.10019e4	689.25537	97.4626
2	15.166	546.77405	12.44795	2.5374

HPLC Chromatographs of **5h**

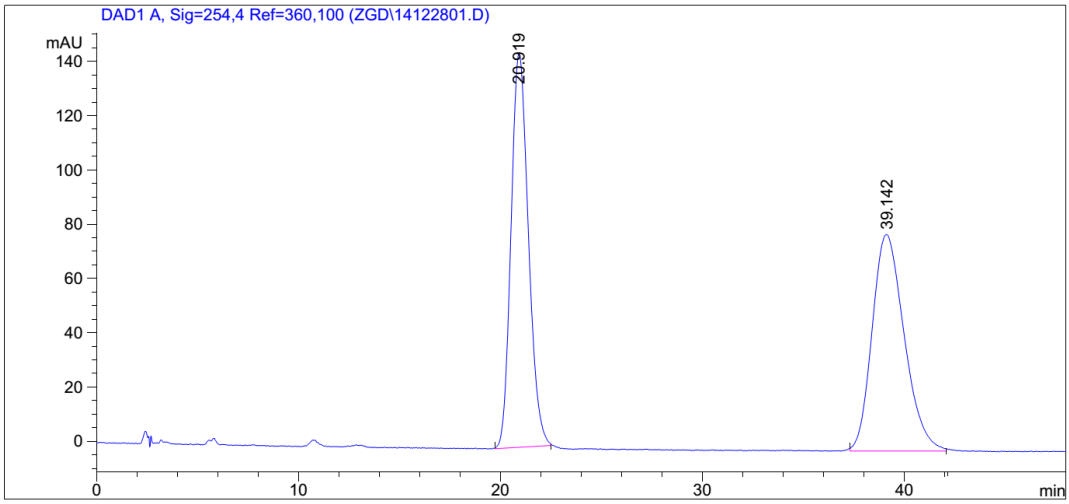


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	27.029	6468.90869	58.31380	50.0582
2	50.082	6453.87012	35.71738	49.9418

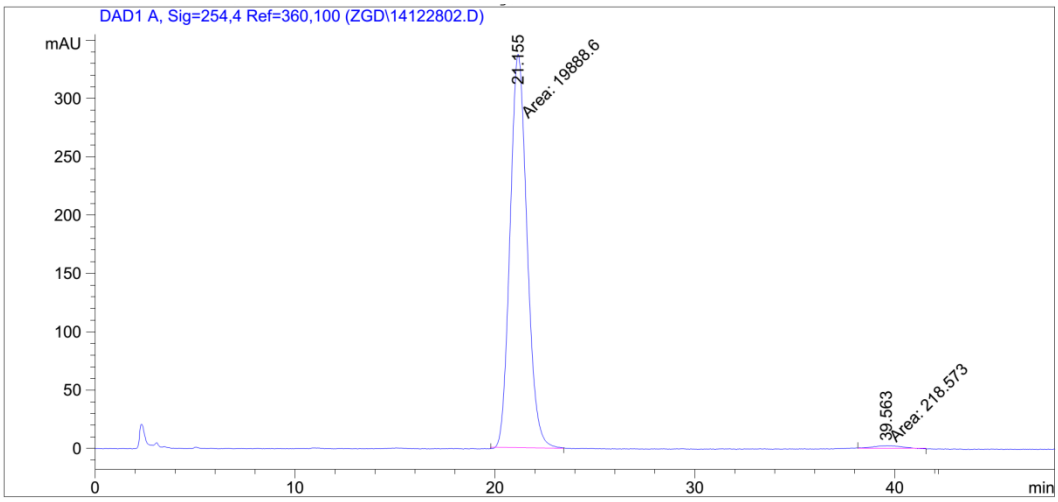


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	25.989	2.14691e4	223.24588	100

HPLC Chromatographs of **5i**

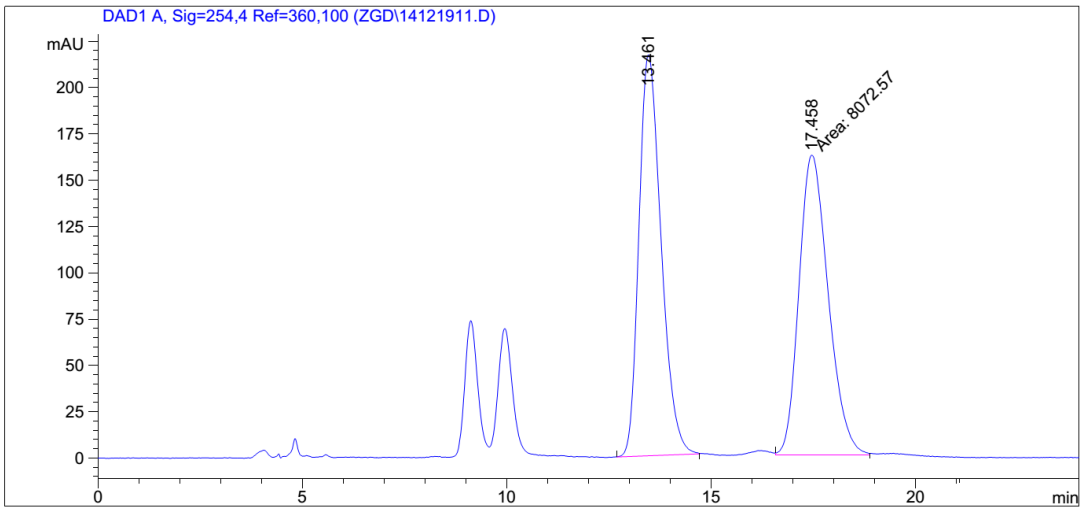


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	20.919	8653.52734	145.27211	49.5959
2	39.142	8794.53906	79.75707	50.4041

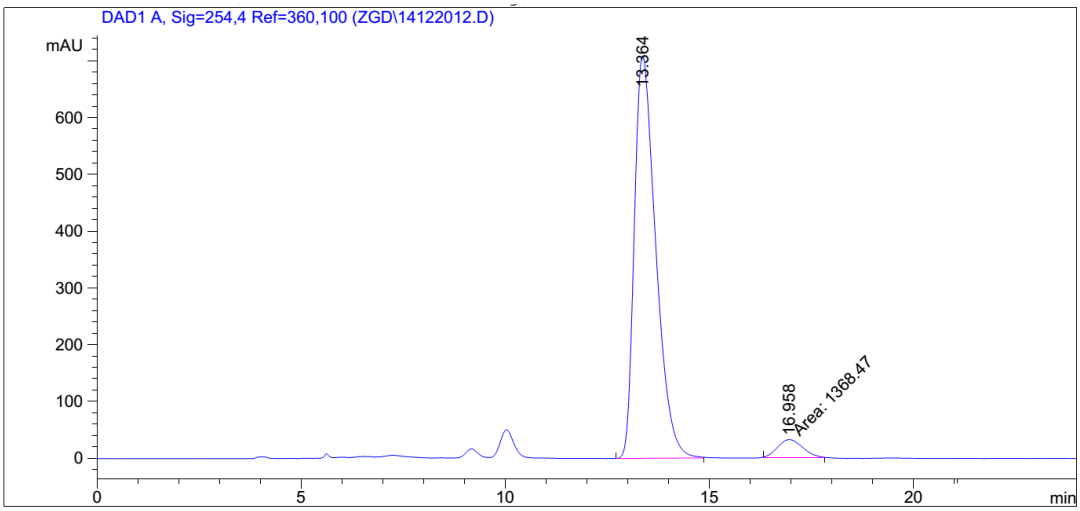


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	21.155	1.9886e4	337.31702	98.9130
2	39.563	218.57323	2.34055	1.0870

HPLC Chromatographs of **5j**

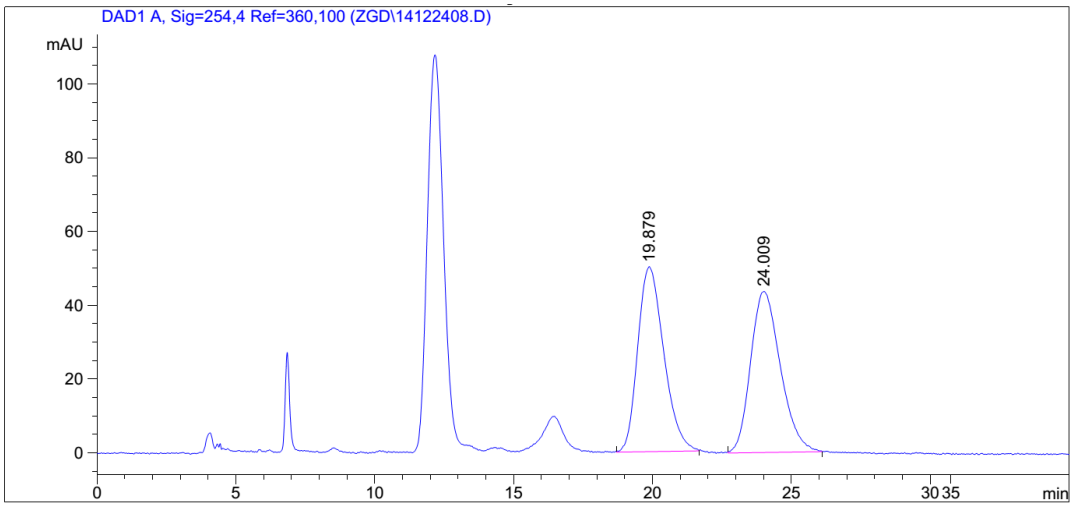


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	13.461	8172.76123	216.56232	50.3084
2	17.458	8072.56592	162.06212	49.6916

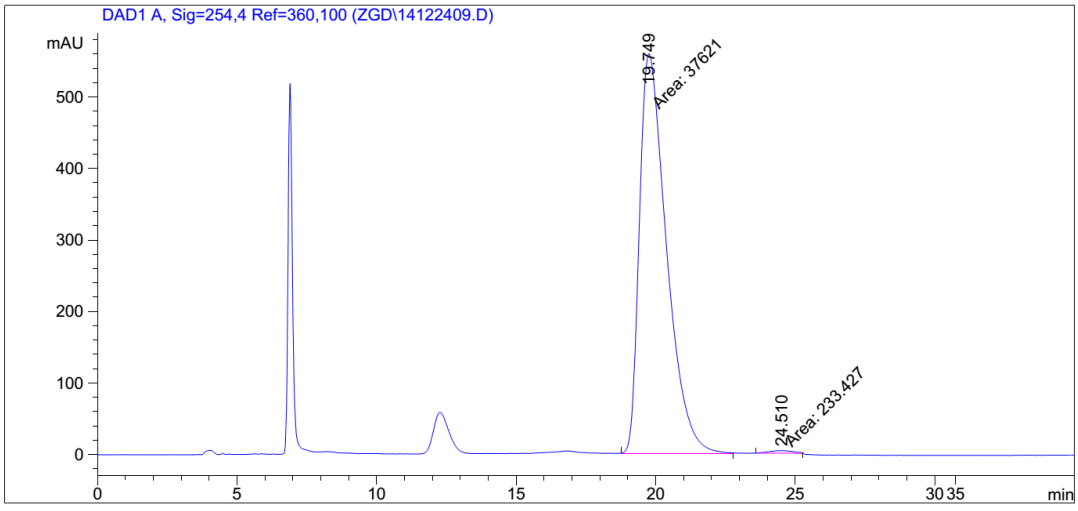


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	13.364	2.59024e4	708.85284	94.9819
2	16.958	1368.47046	31.82646	5.01818

HPLC Chromatographs of **5k**

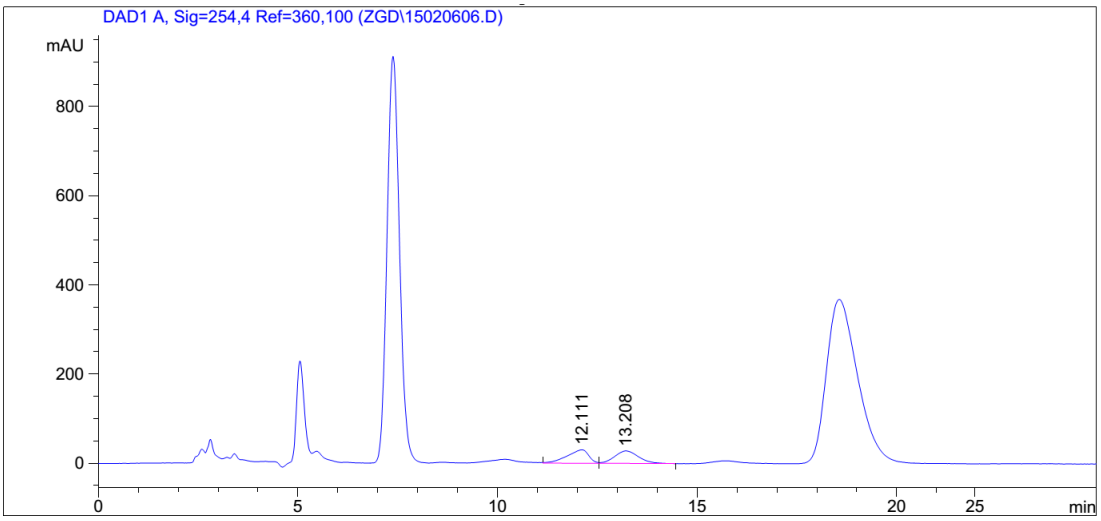


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	19.879	3271.51245	50.18114	50.1427
2	24.009	3252.89722	43.66678	49.8573

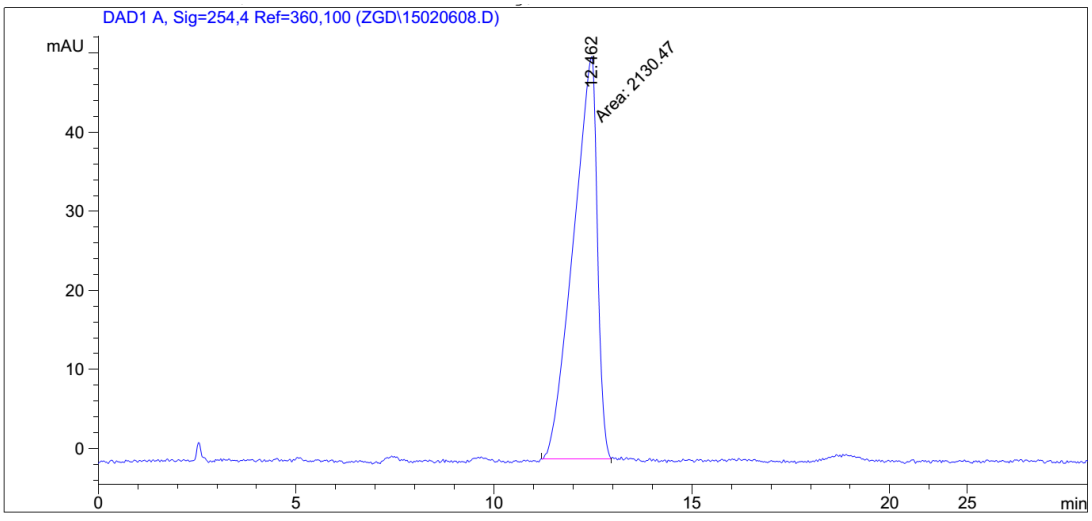


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	19.749	3.76210e4	559.19189	99.3834
2	24.510	233.42668	3.78906	0.6166

HPLC Chromatographs of **5l**

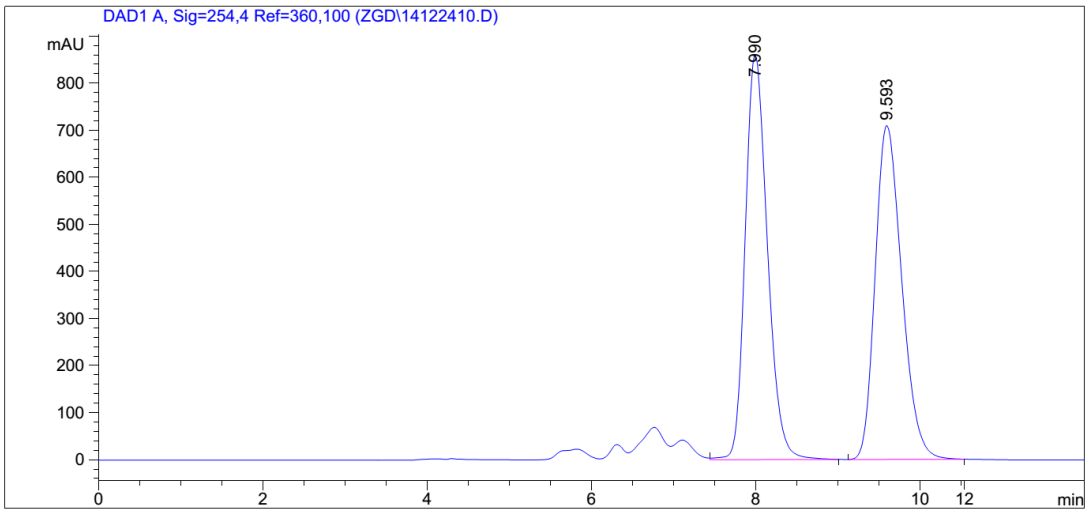


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	12.111	1156.81079	30.38846	49.3222
2	13.208	1188.60425	28.06830	50.6778

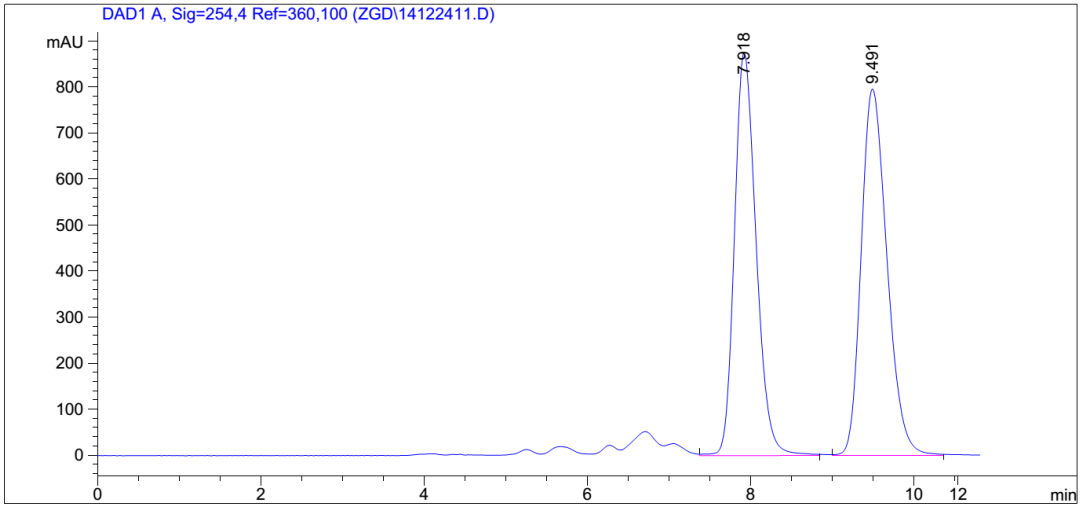


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	12.462	2130.47437	50.86459	100.0000

HPLC Chromatographs of **5m**

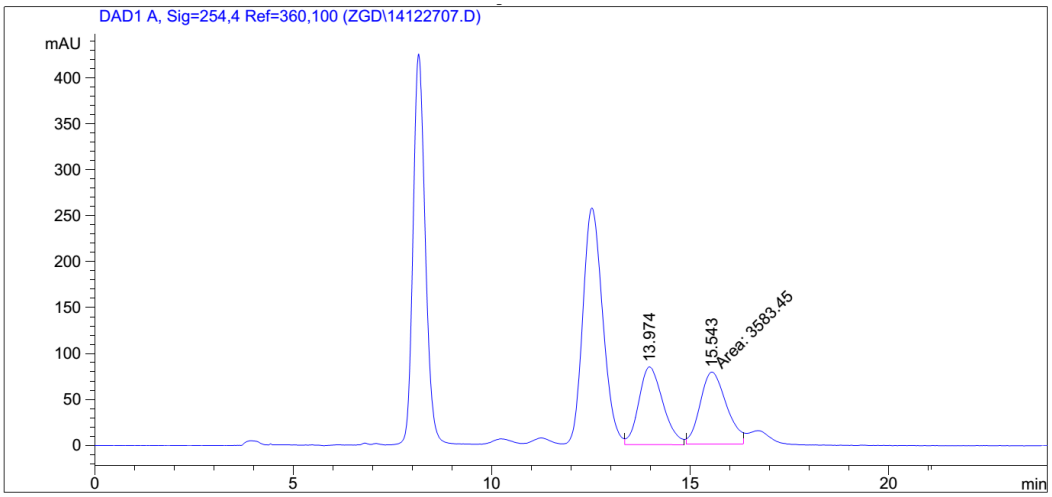


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	7.990	1.61564e4	859.98309	50.3163
2	9.593	1.59533e4	709.94983	49.6837

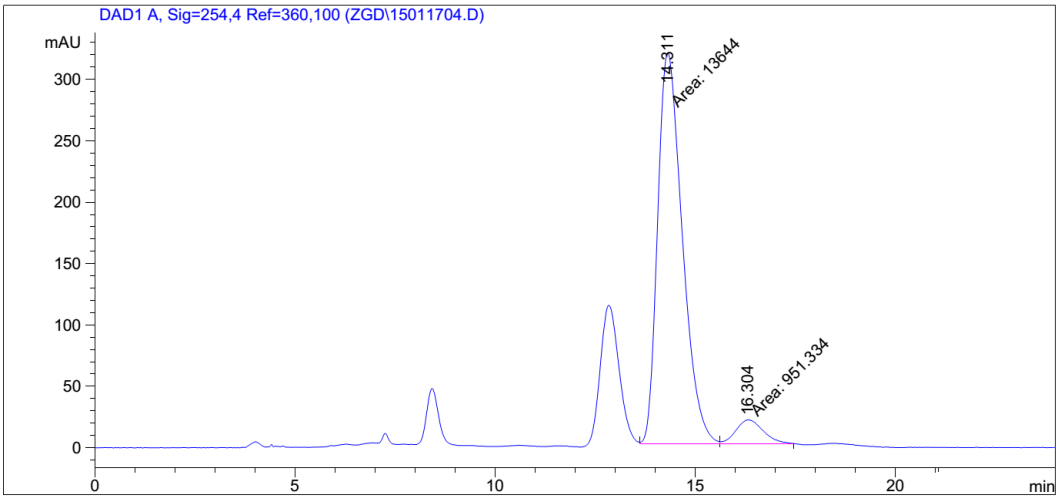


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	7.918	1.61426e4	875.02179	47.9898
2	9.491	1.74949e4	796.38147	52.0102

HPLC Chromatographs of **5n**

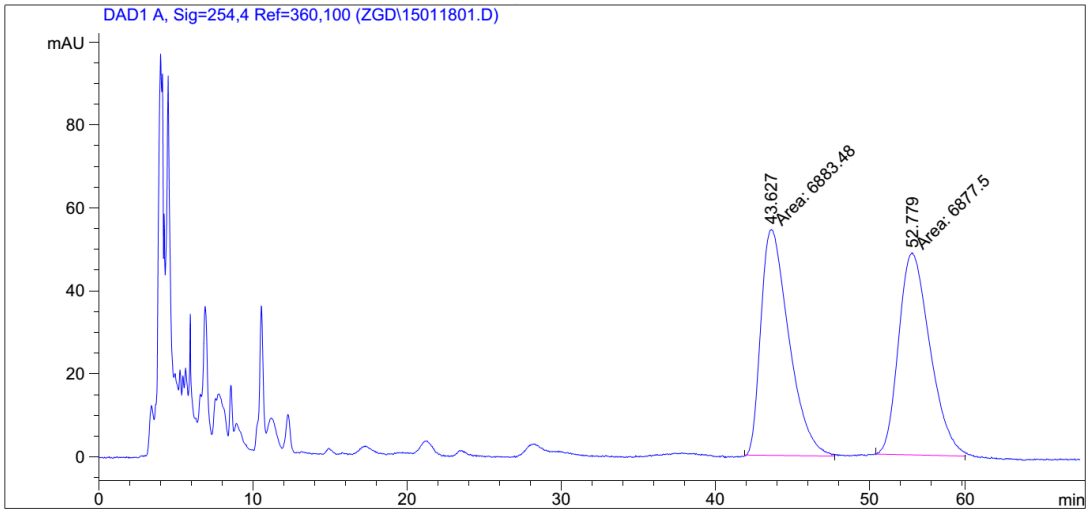


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	13.974	3583.67017	84.72951	50.0015
2	15.543	3583.45459	78.12737	49.9985

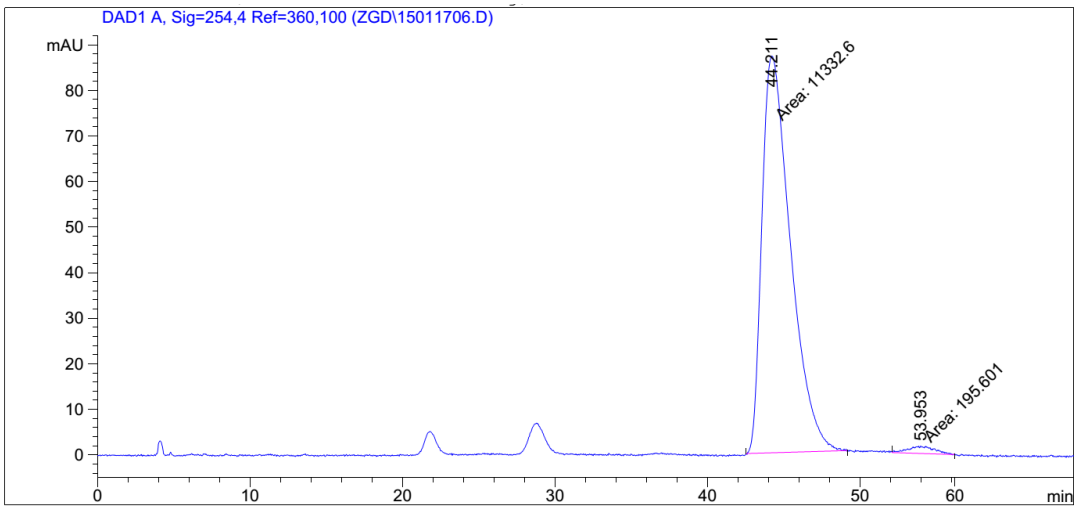


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	14.311	1.36440e4	318.66226	93.4819
2	16.304	951.33441	19.69536	6.5181

HPLC Chromatographs of **5o**

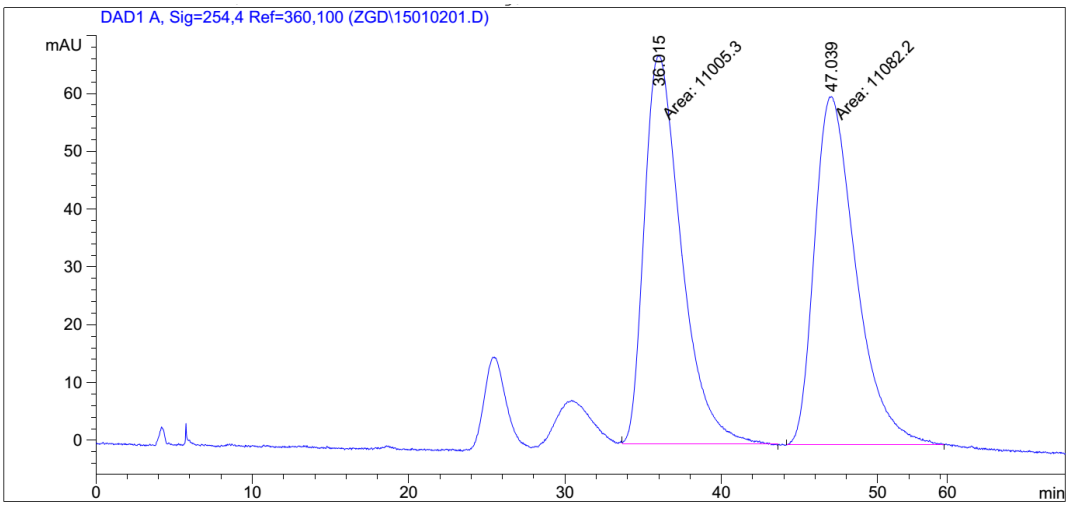


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	43.627	6883.48047	54.49902	50.0217
2	52.779	6877.49512	48.71394	49.9783

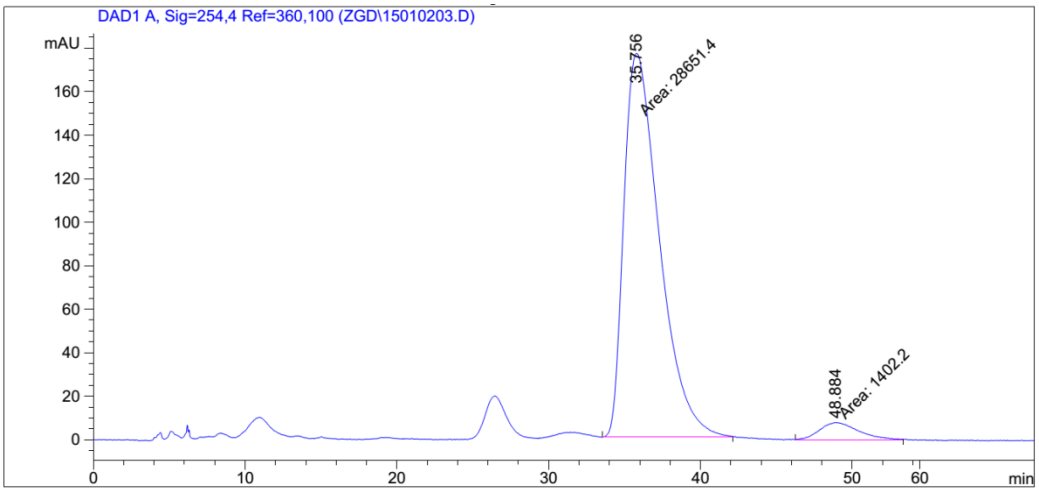


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	44.211	1.13326e4	87.12114	98.3033
2	53.953	195.60104	1.65826	1.6967

HPLC Chromatographs of **5p**

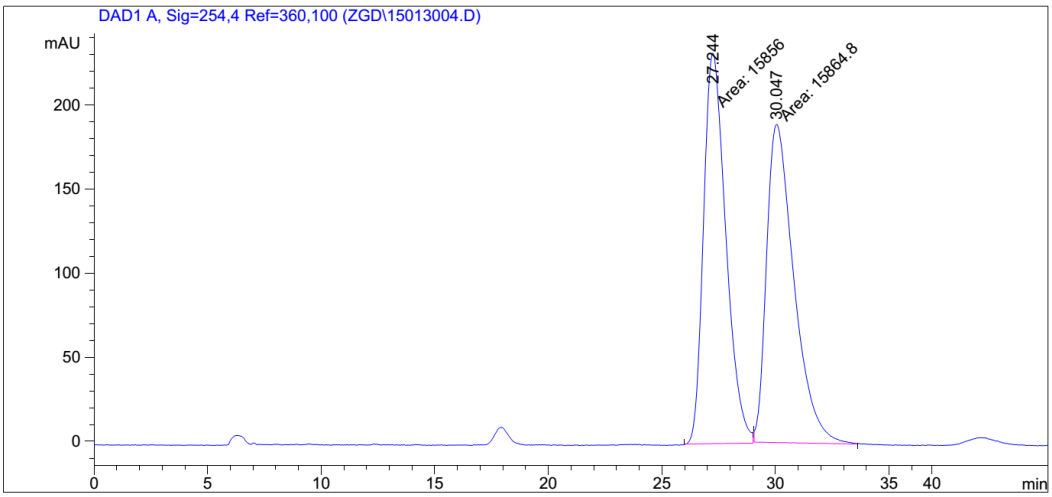


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	36.015	1.10053e4	67.14655	49.8259
2	47.039	1.10822e4	60.22472	50.1741

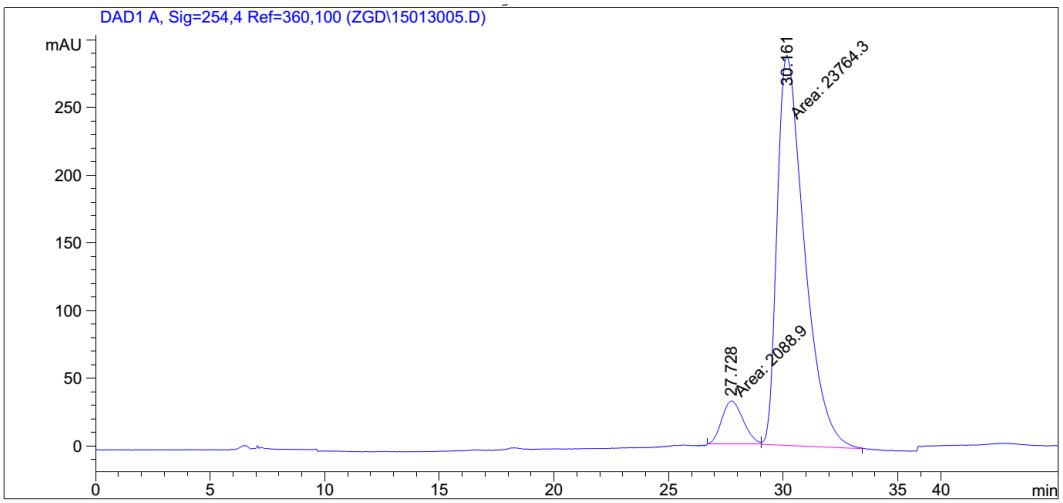


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	35.756	2.86514e4	176.34558	95.3343
2	48.884	1402.20276	7.88333	4.6657

HPLC Chromatographs of **5q**

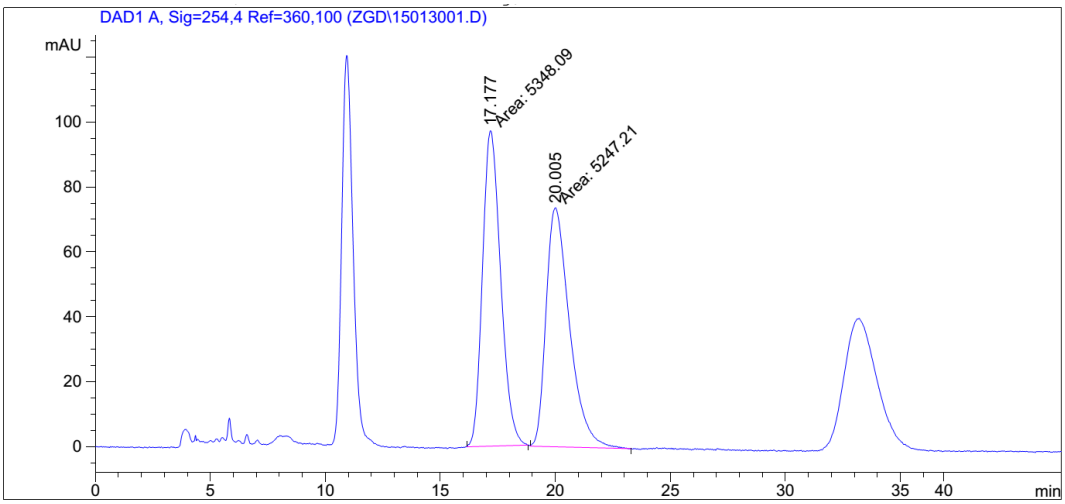


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	27.244	1.58560e4	231.96855	49.9860
2	30.047	1.58648e4	189.10829	50.0140

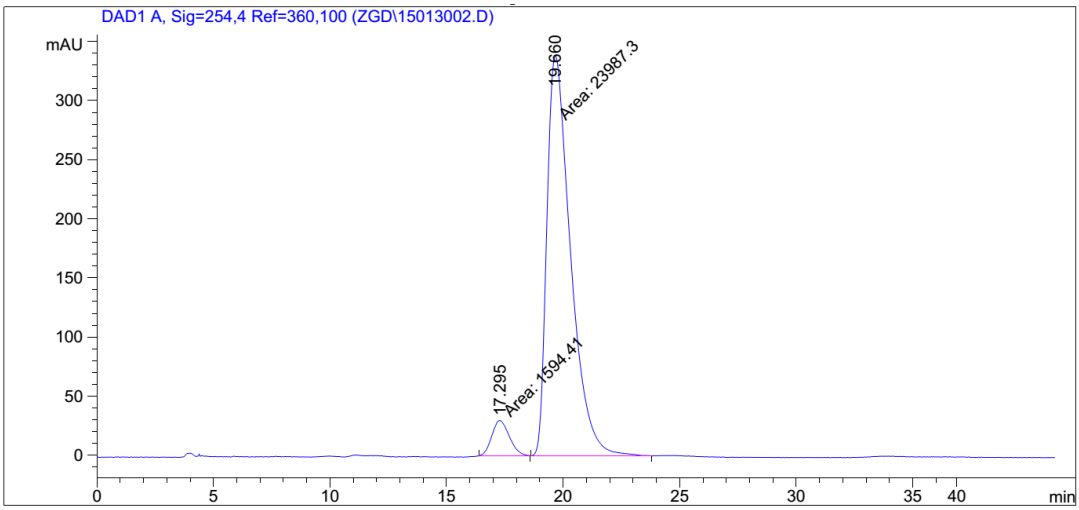


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	27.728	2088.89893	32.133.62	8.0798
2	30.161	2.37643e4	287.99234	91.9202

HPLC Chromatographs of **5r**

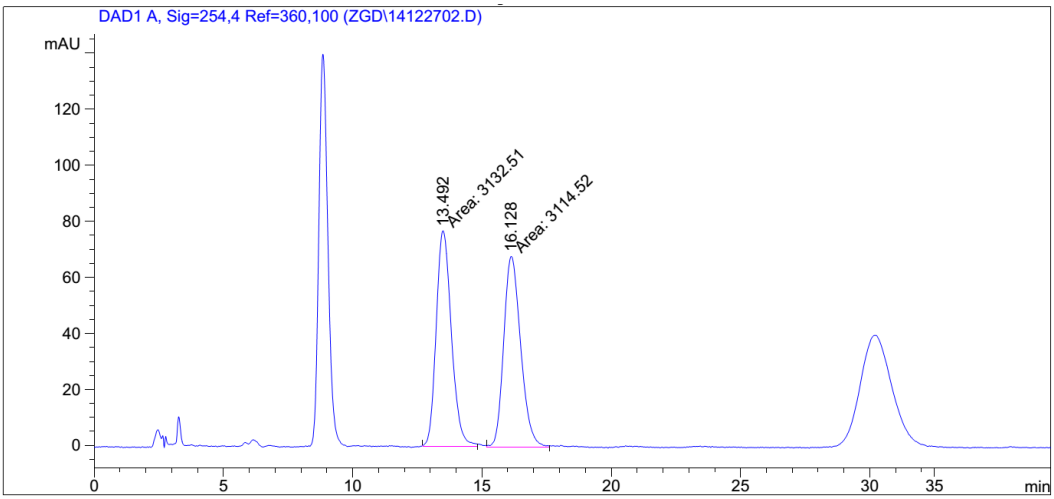


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	17.177	5348.09229	97.21286	50.4761
2	20.005	5247.20947	73.71542	49.5239

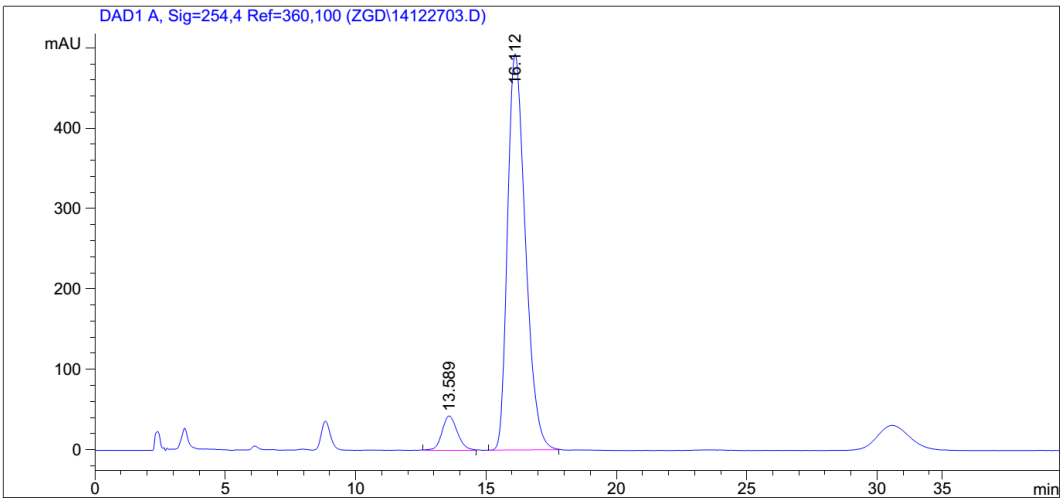


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	17.295	1594.40930	30.00825	6.2326
2	19.660	2.39873e4	339.32184	93.7674

HPLC Chromatographs of **5s**

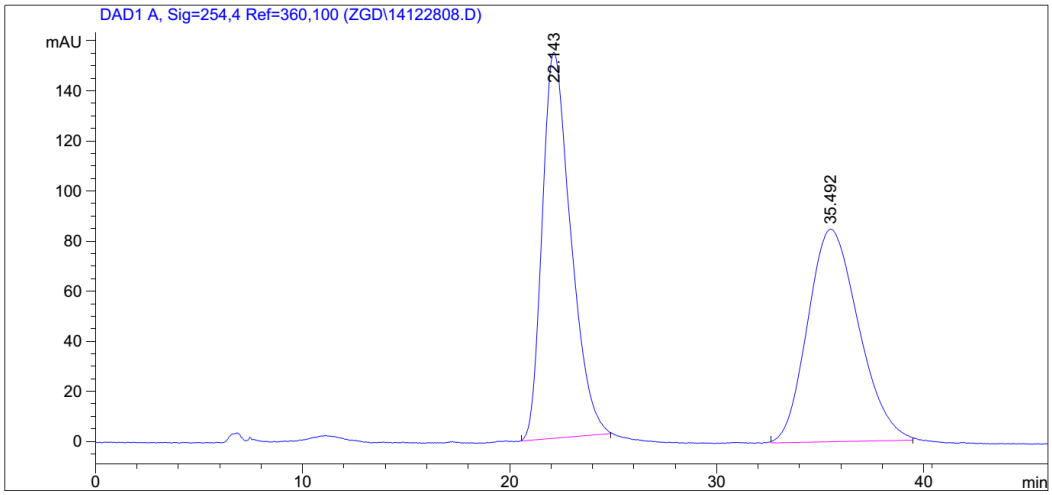


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	13.492	3132.50903	76.94271	50.1439
2	16.128	3114.52490	68.11089	49.8561

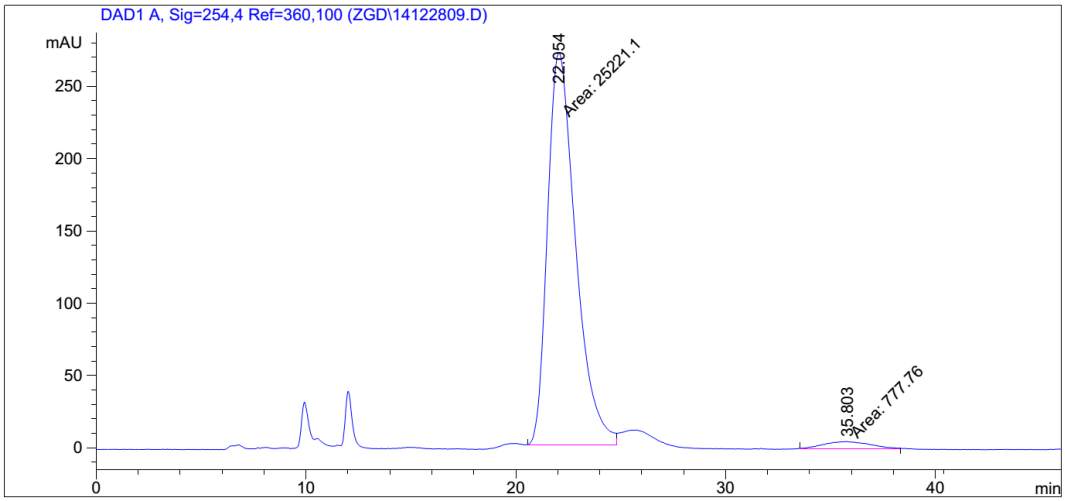


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	13.589	1730.33899	42.58423	6.8707
2	16.112	2.34539e4	492.95691	93.1293

HPLC Chromatographs of **5t**

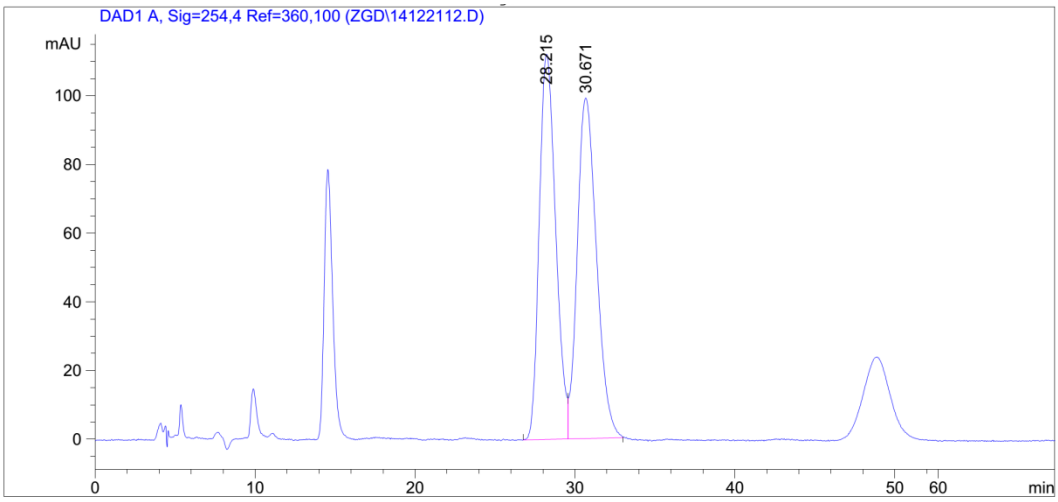


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	22.143	1.47529e4	154.08113	50.4444
2	35.492	1.44930e4	84.89651	49.5556

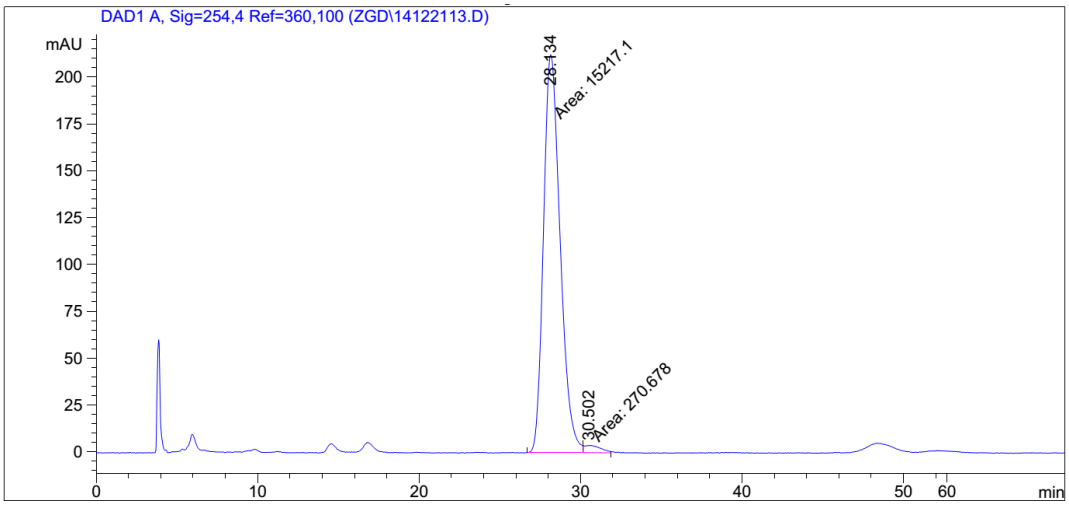


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	22.054	2.52211e4	271.01450	97.0085
2	35.803	777.75964	5.11109	2.9915

HPLC Chromatographs of **5u**

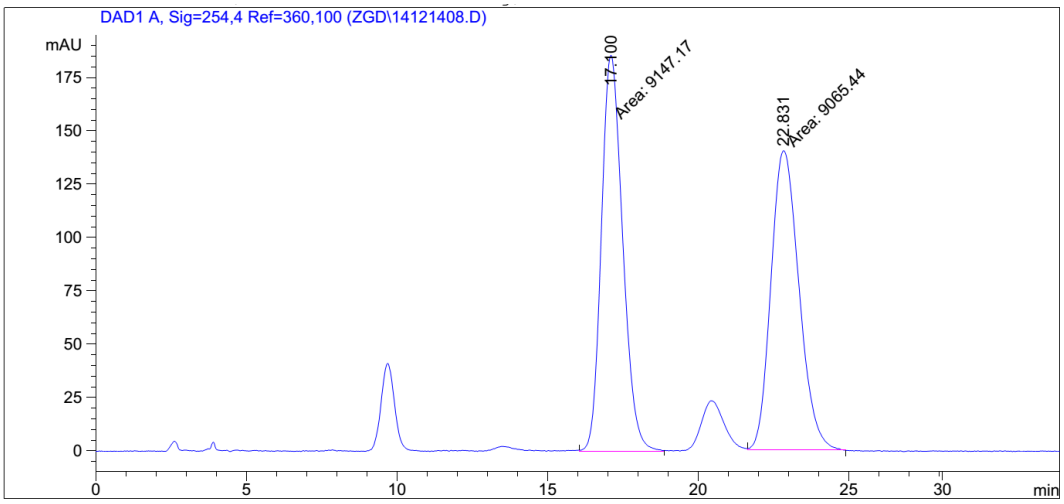


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	28.215	7996.54932	112.14704	49.0536
2	30.671	8305.11035	99.16809	50.9464

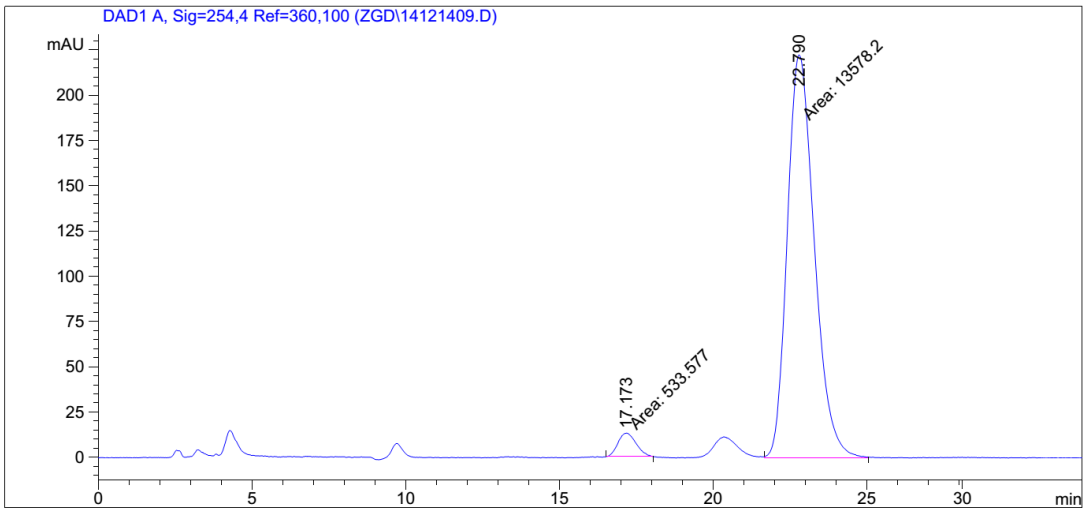


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	28.134	1.52171e4	212.35622	98.2523
2	30.502	270.67783	3.89468	1.7477

HPLC Chromatographs of **5v**

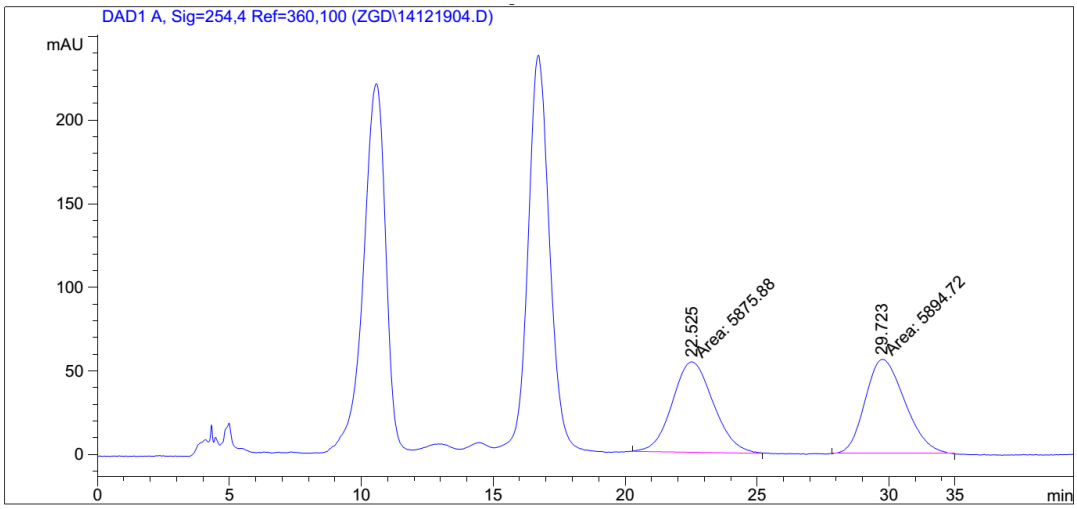


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	17.100	9147.16992	185.88162	50.2244
2	22.831	9065.44043	140.18929	49.7756

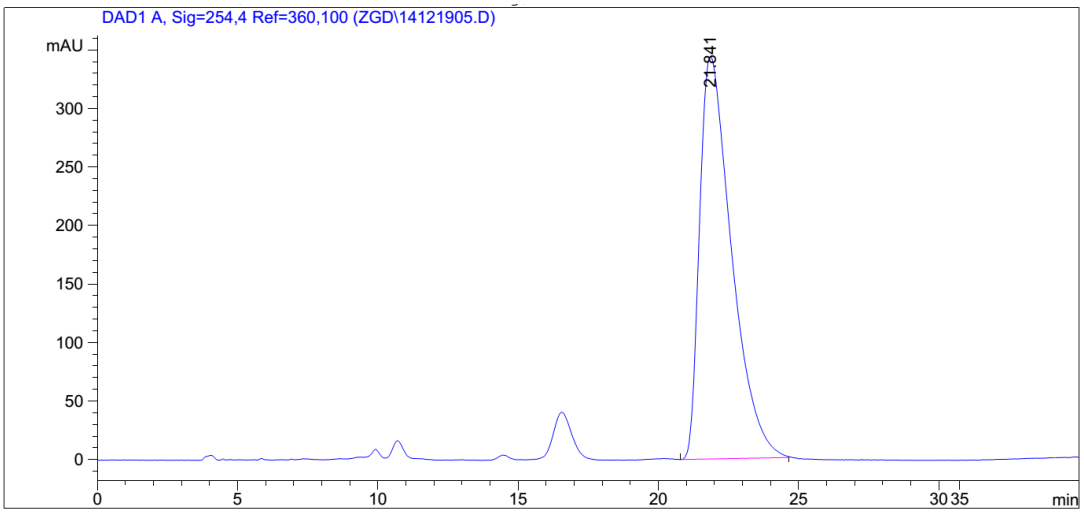


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	17.173	533.57678	13.02085	3.7811
2	22.790	1.35782e4	222.42790	96.2189

HPLC Chromatographs of **5w**

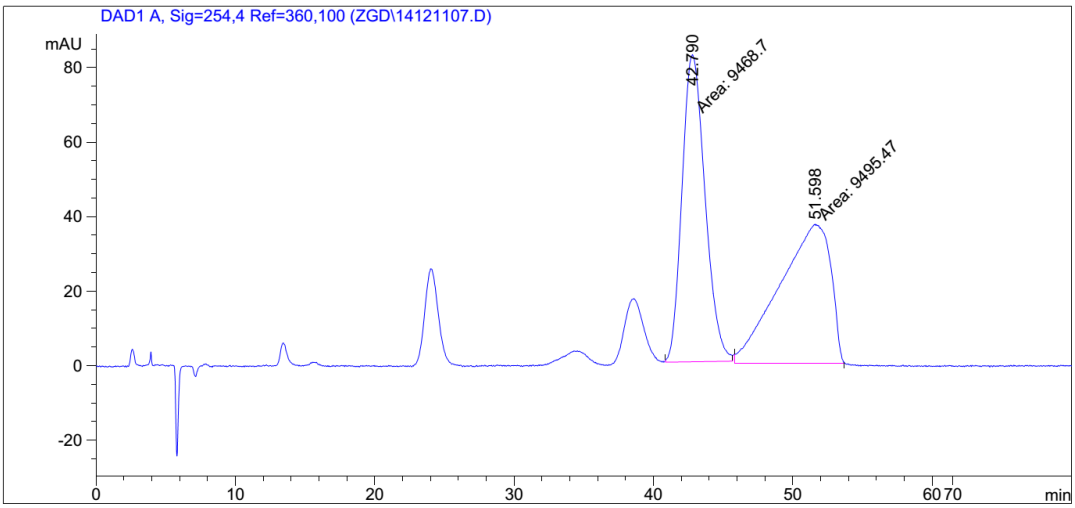


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	22.525	5875.87793	54.21181	49.9200
2	29.723	5894.72070	56.31526	50.0800

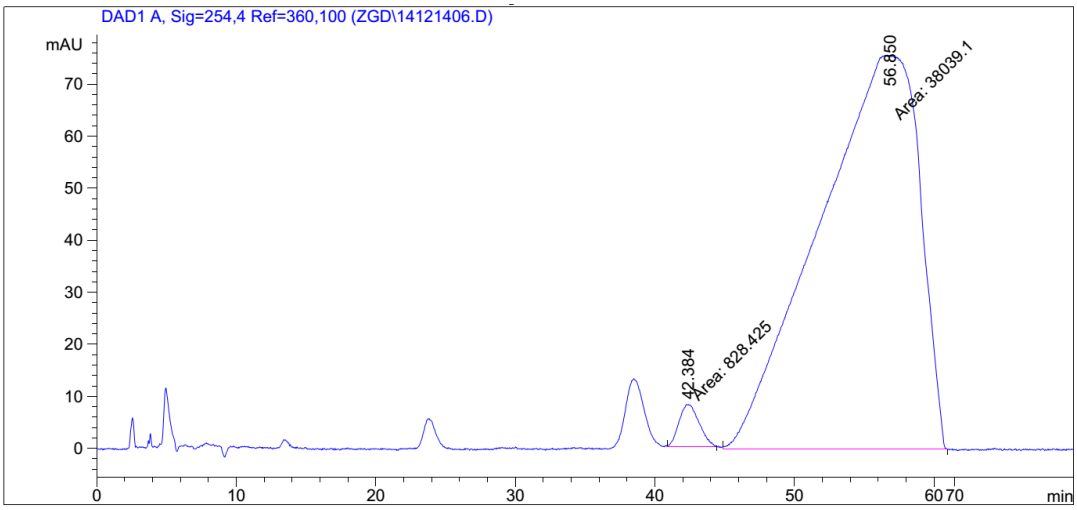


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	21.841	2.72013e4	344.12561	100.0000

HPLC Chromatographs of **5x**

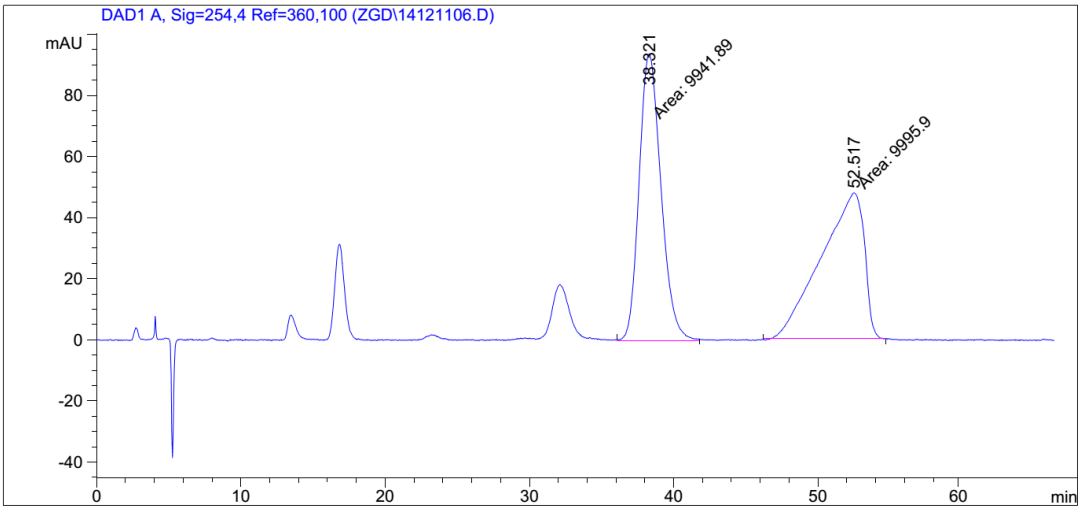


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	42.790	9468.70410	82.44812	49.9294
2	51.598	9495.47363	37.33463	50.0706

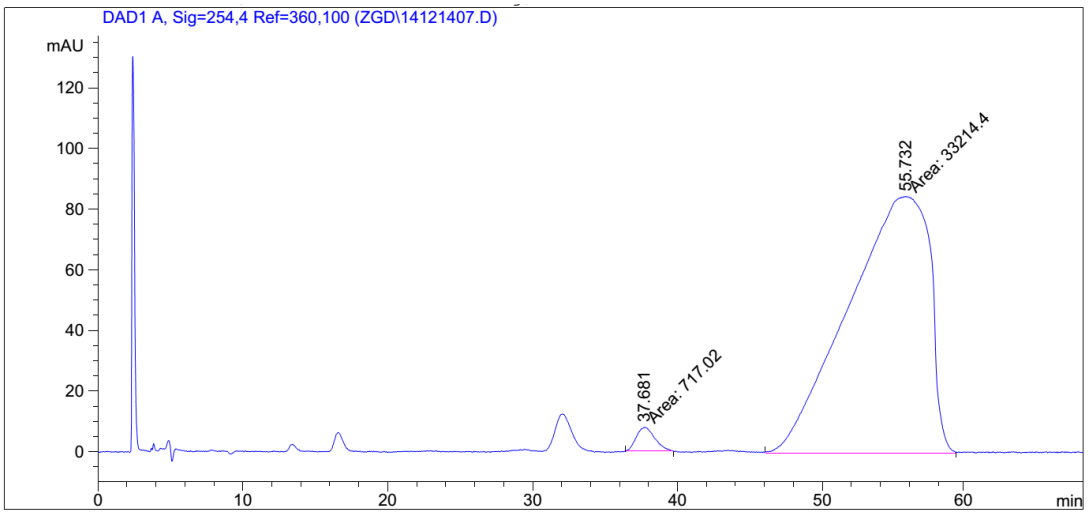


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	42.384	828.42517	8.21677	2.1314
2	56.850	3.80391e4	75.70667	97.8686

HPLC Chromatographs of **5y**

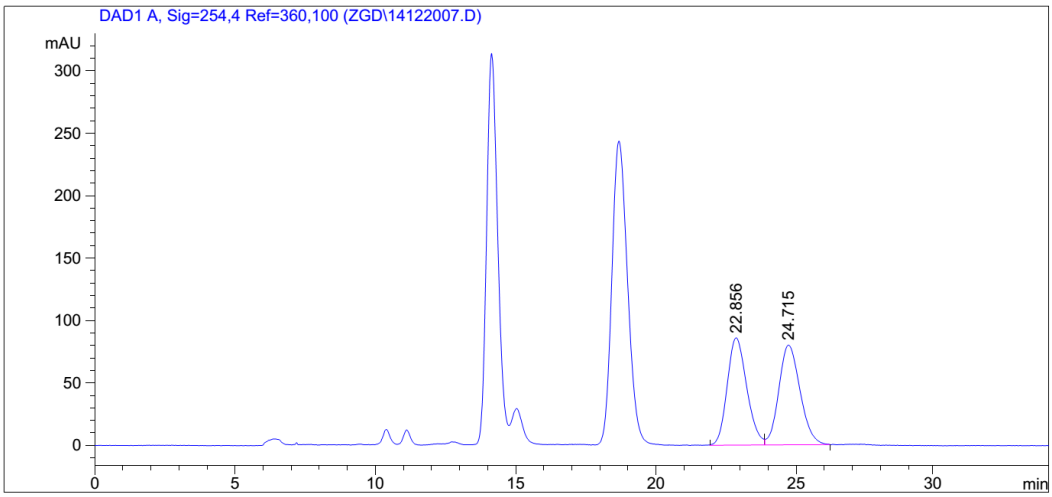


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	38.321	9941.89160	93.98986	49.8645
2	52.517	9995.90430	47.82924	50.1355

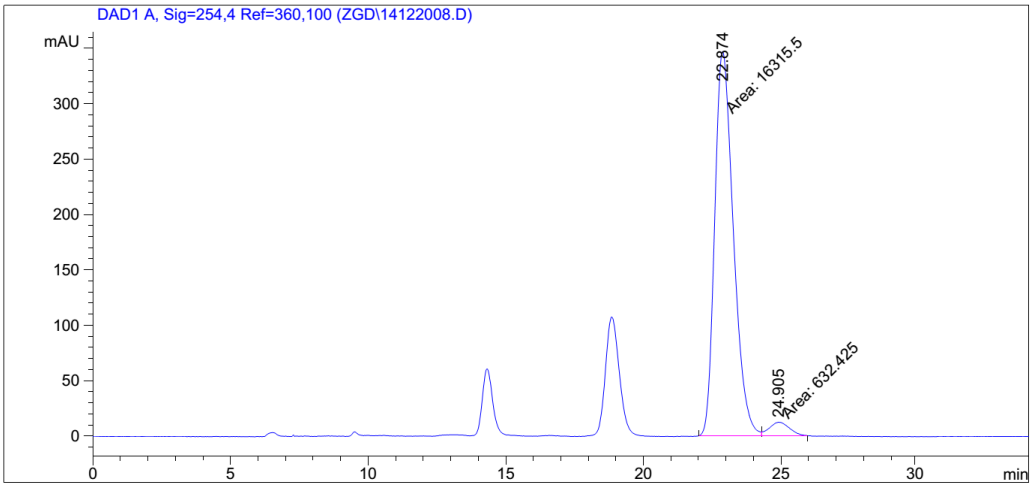


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	37.681	717.01965	7.99870	2.1131
2	55.732	3.32144e4	84.75545	97.8869

HPLC Chromatographs of **5z**

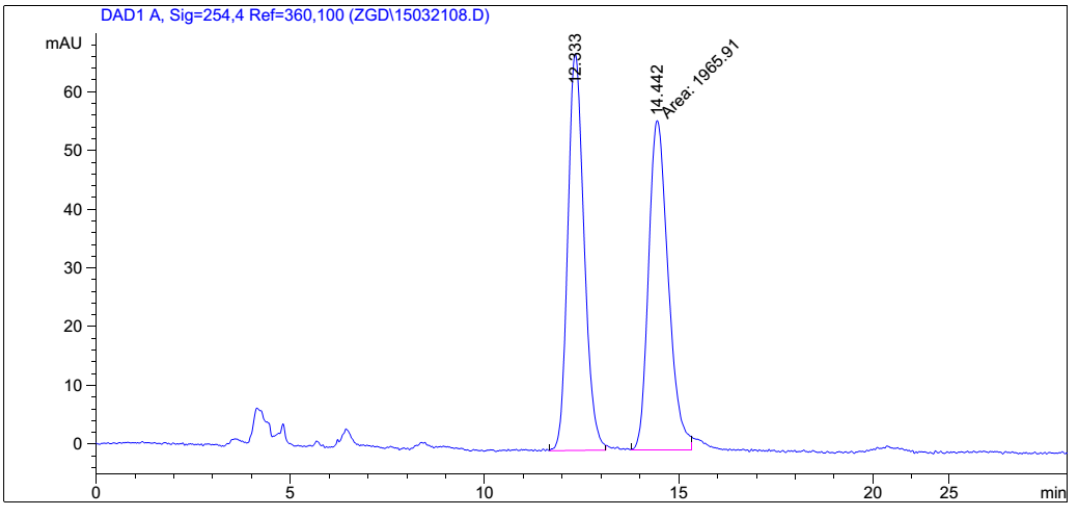


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	22.856	4173.46631	86.00167	49.7487
2	24.715	4215.62256	79.99422	50.2513

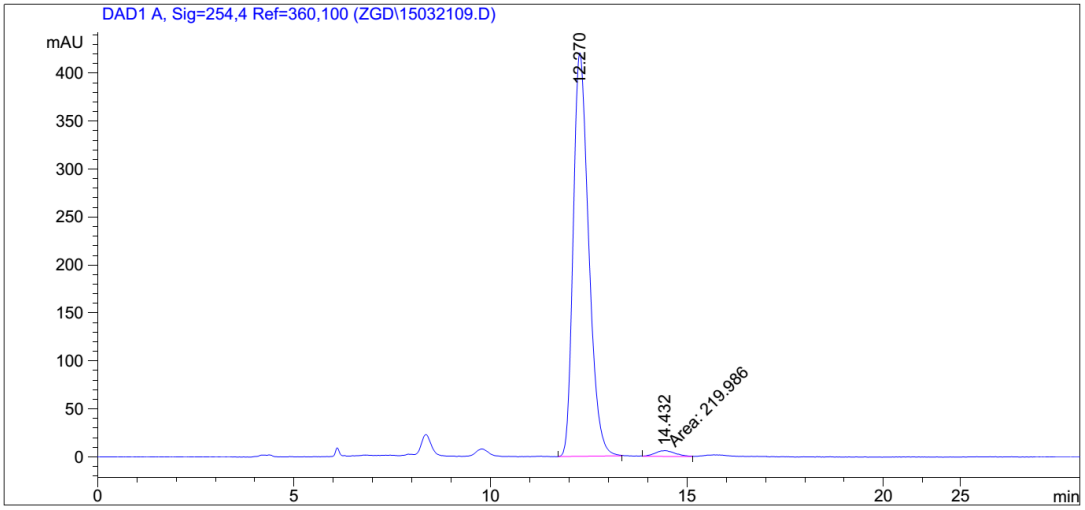


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	22.874	1.63155e4	346.73935	96.2684
2	24.905	632.42474	12.35190	3.7316

HPLC Chromatographs of **9**

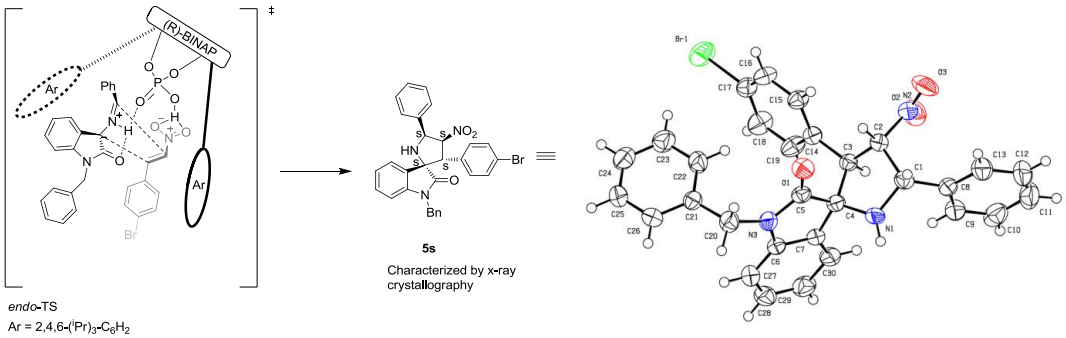


Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	12.333	1964.61816	67.50786	49.9835
2	14.442	1965.91248	56.07698	50.0165



Peak	RT (min)	Area (mAU*s)	Heighe (mAU)	% Area
1	12.270	1.15167e4	420.62274	98.1256
2	14.432	219.98599	6.13325	1.8744

5. Crystal data for 5s and the proposed transition state model for the [3+2] cycloaddition reaction.



Proposed transition state model for the [3+2] cycloaddition reaction.

Empirical formula C30 H24 Br N3 O3
Formula weight 554.43
Crystal dimensions (mm^3) 0.36×0.33×0.29
Temperature (K) 296(2)
Crystal system Orthorhombic
Space group P2(1)2(1)2(1)
a (Å) 10.8543(2)
b (Å) 13.1630(2)
c (Å) 17.7406(3)
α(°) 90.00
β(°) 90.00
γ(°) 90.00
Volume ($Å^3$) 2534.69(7)
Z 4
D_{calcd} ($g\ cm^3$) = 1.453
μ(mm^{-1}) = 1.660
F (000) = 1136
Theta range for data collection 1.93 to 24.99°
Index ranges -12<=h<=12, -14<=k<=15, -21<=l<=20
Reflections collected 13755
Independent reflections 4435 [R(int) = 0.0308]
Data/restraints/parameters 4435/0/334
GOF (on F^2) 1.000
Final R indexes [I>=2σ (I)] R1 = 0.0321, wR2 = 0.0736
Final R indexes [all data] R1 = 0.0423, wR2 = 0.0766
Largest diff. peak and hole (e $Å^{-3}$) 0.377/-0.353
Flack parameter 0.012(7)