SUPPORTING INFORMATION

Bifunctional Thiourea-modified Polymers of Intrinsic Microporosity for Enantioselective Amination of 3-Aryl-2-oxindoles in Batch and Flow Conditions.

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1. NMR (PIM-1n, Catalyst II, 6a-g, 7, 8, 9, 10, 11, 12)

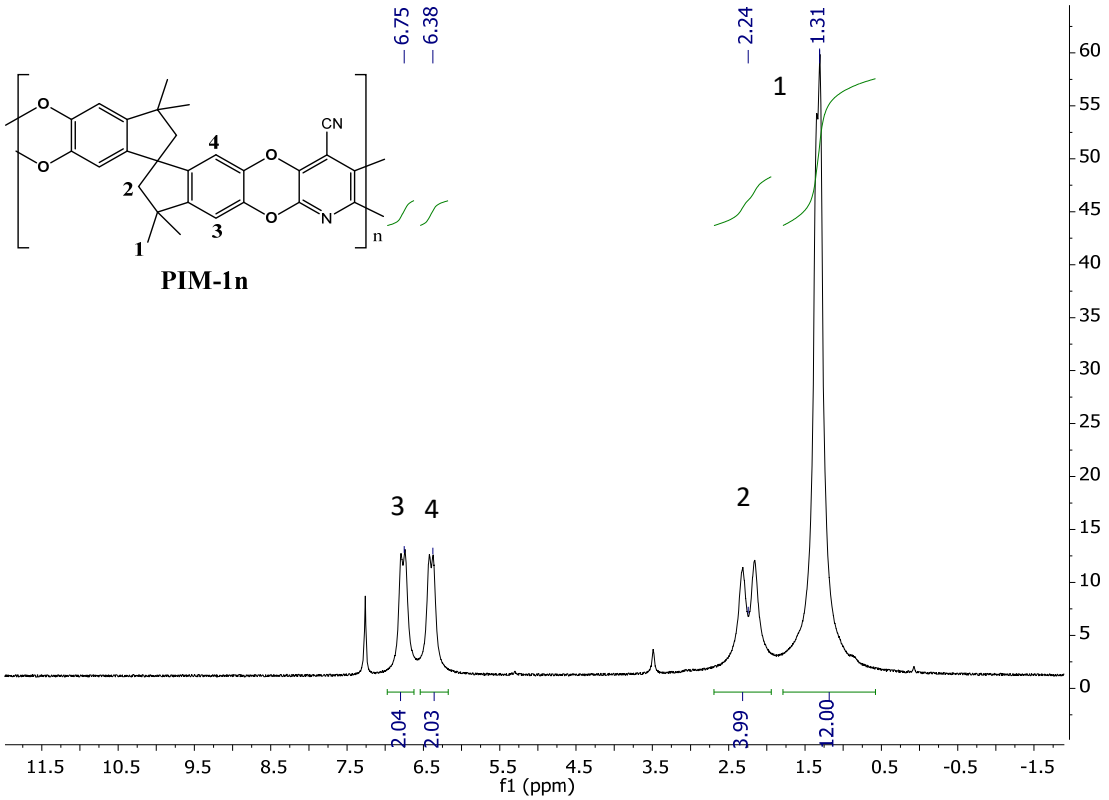


Figure S1. ^{1}H NMR spectrum of **PIM-1n** ($CDCl_3$, 400 MHz)

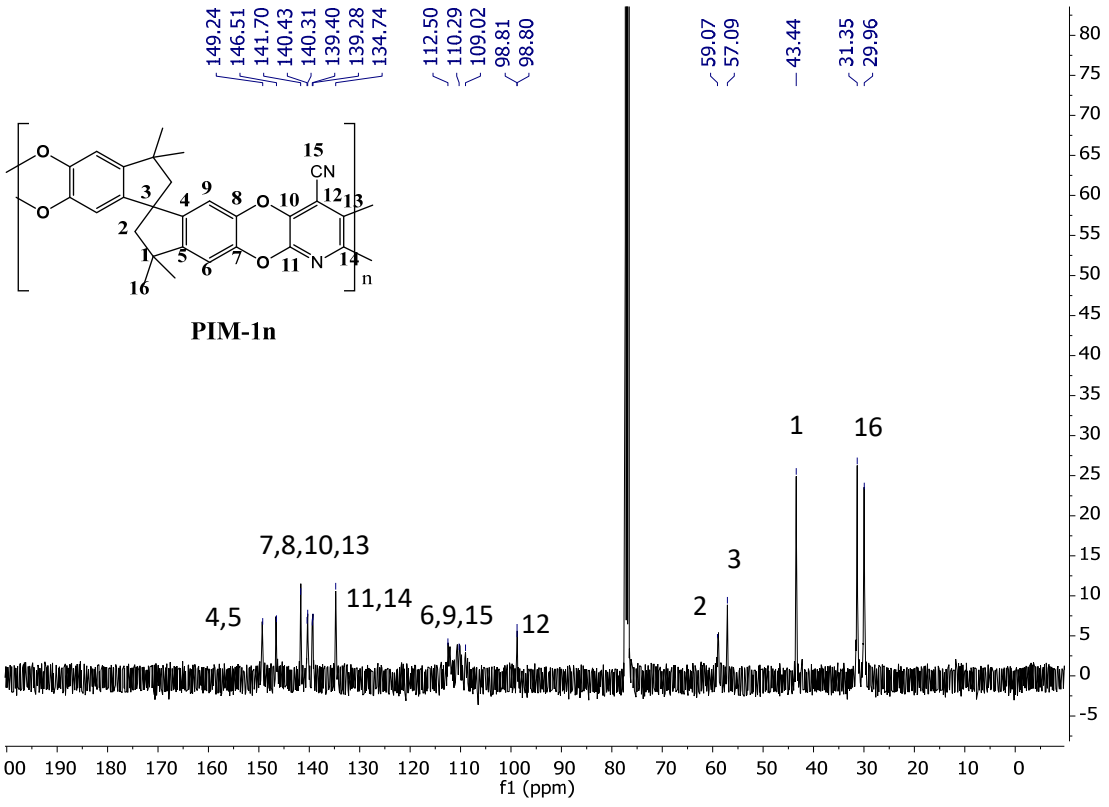


Figure S2. ^{13}C NMR spectrum of **PIM-1n** ($CDCl_3$, 100 MHz)

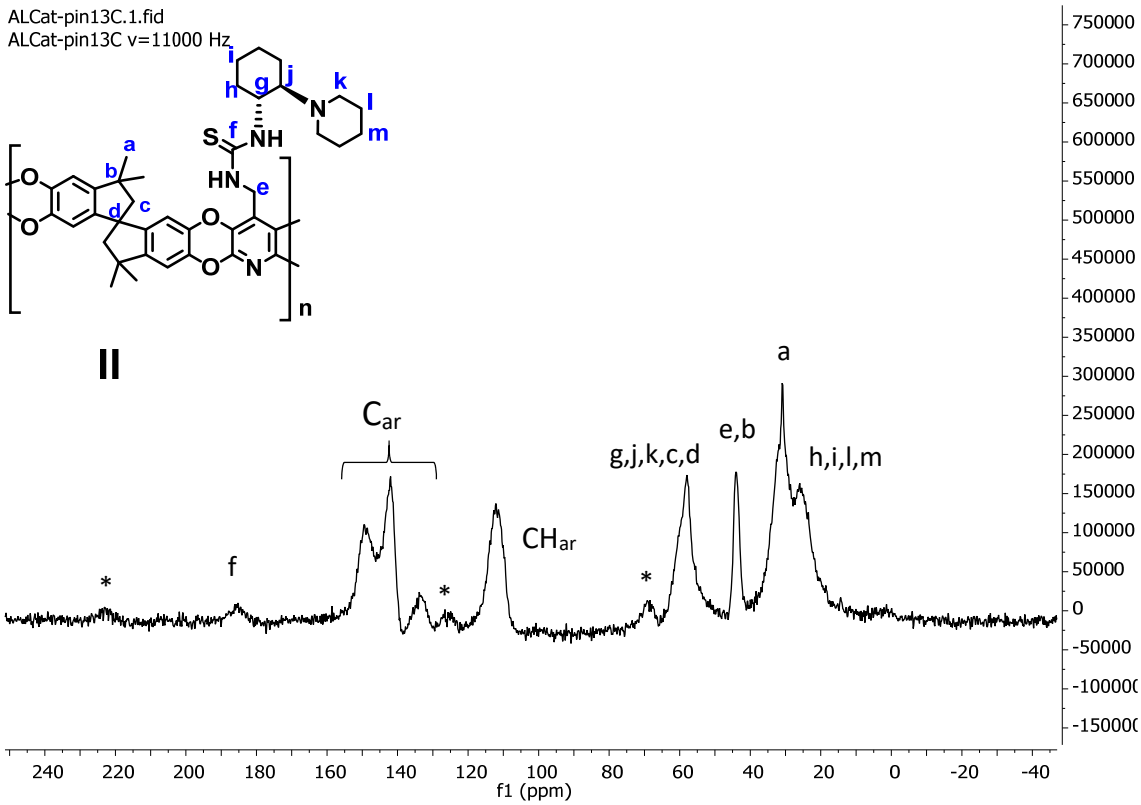


Figure S3. ^{13}C-SS CP/MAS NMR analysis of **Catalyst II**. *(rotation side bands)

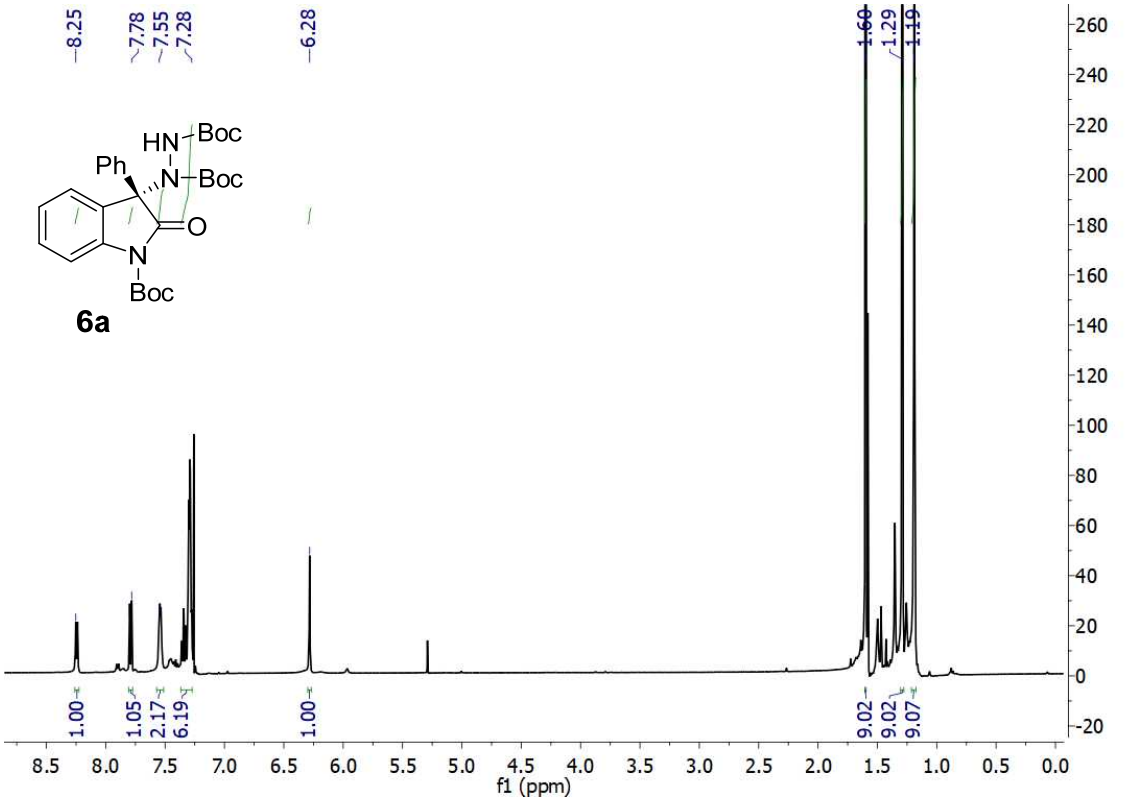


Figure S4. ^{1}H NMR spectrum of **6a** ($CDCl_3$, 500 MHz)

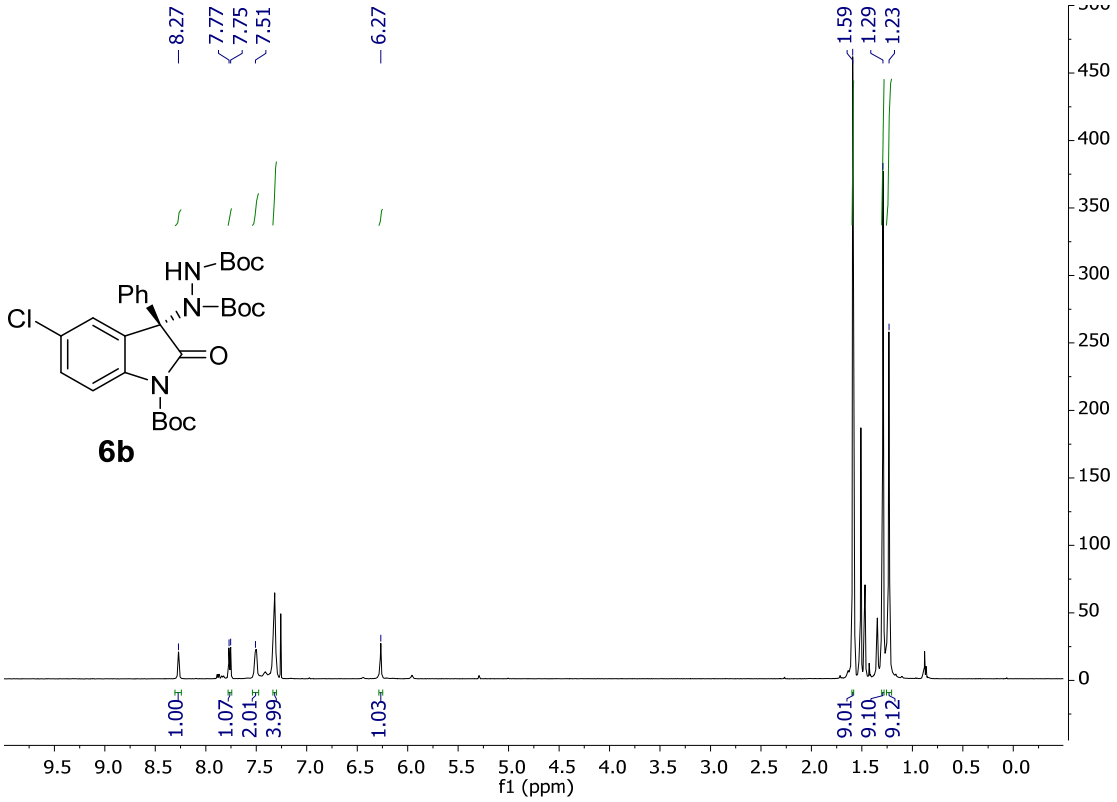


Figure S5. ^{1}H NMR spectrum of **6b** ($CDCl_3$, 400 MHz)

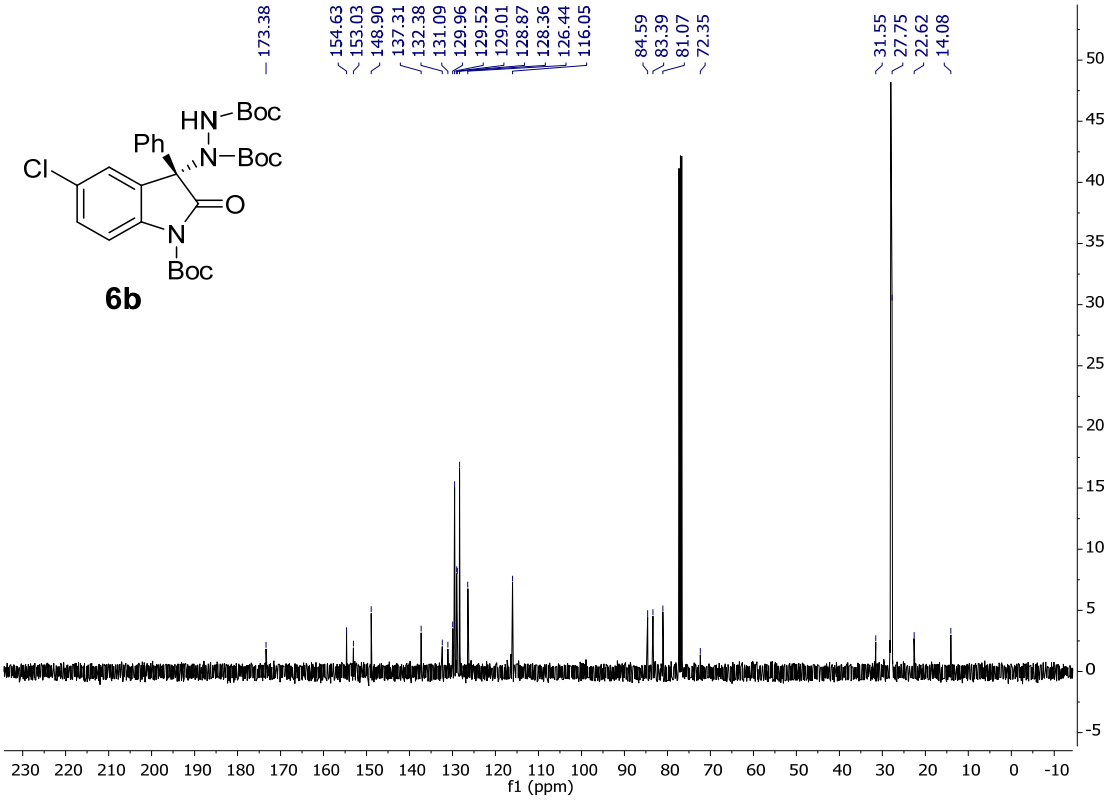


Figure S6. ^{13}C NMR spectrum of **6b** ($CDCl_3$, 100 MHz)

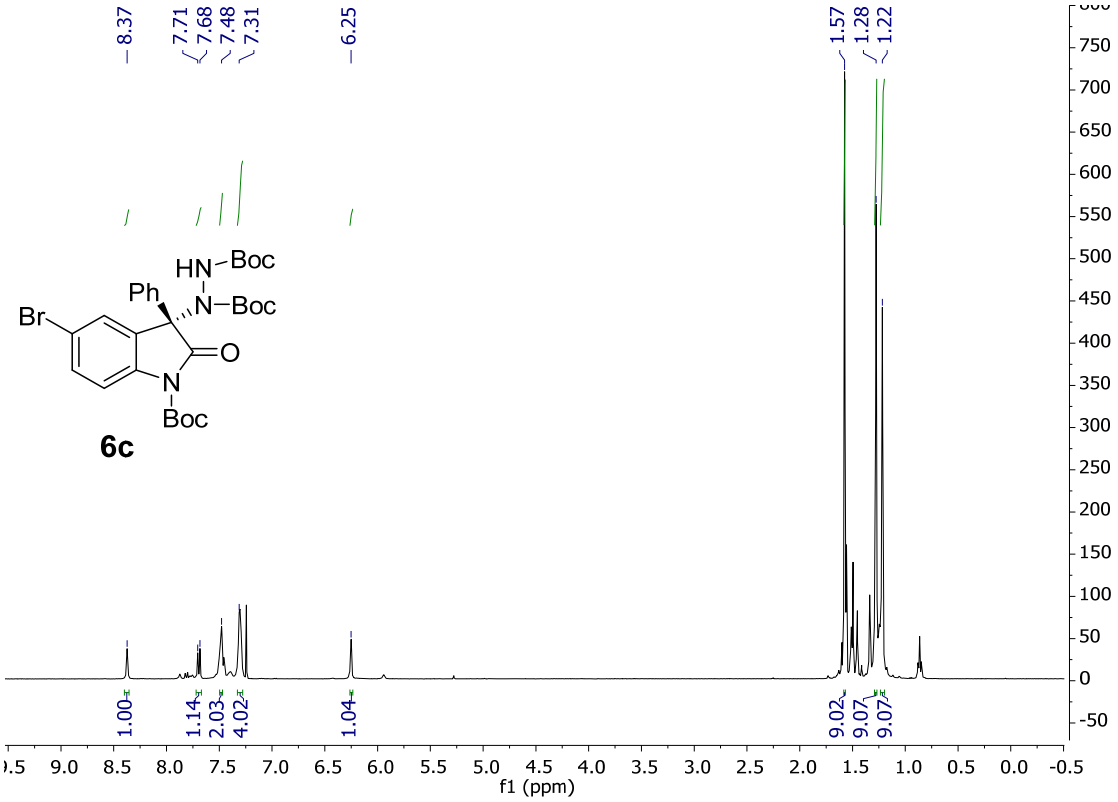


Figure S7. ^{1}H NMR spectrum of **6c** ($CDCl_3$, 400 MHz)

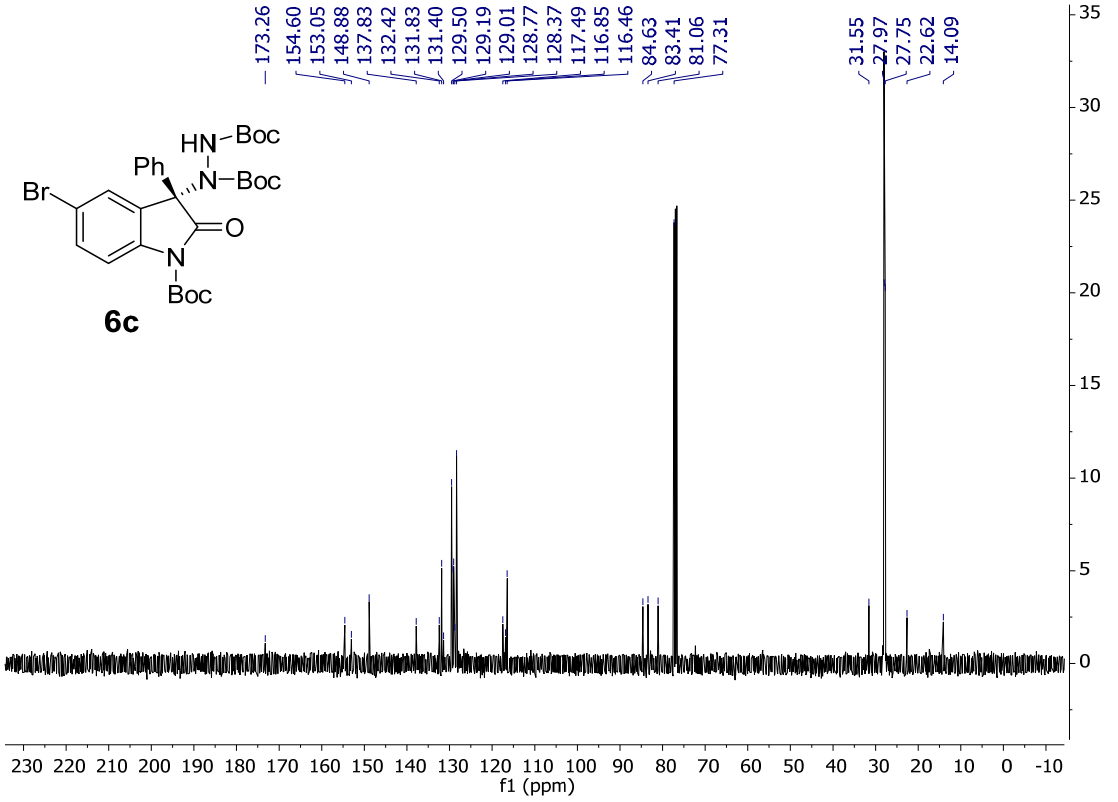


Figure S8. ^{13}C NMR spectrum of **6c** ($CDCl_3$, 100 MHz)

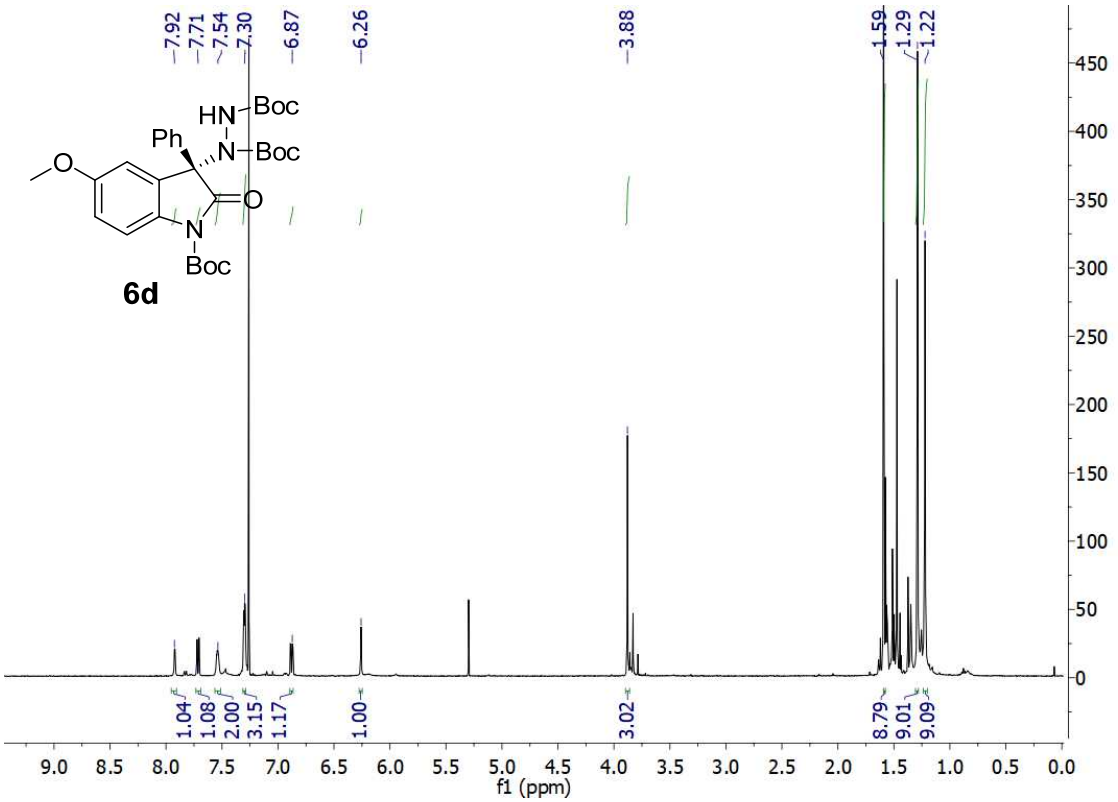


Figure S9. ^{1}H NMR spectrum of **6d** ($CDCl_3$, 500 MHz)

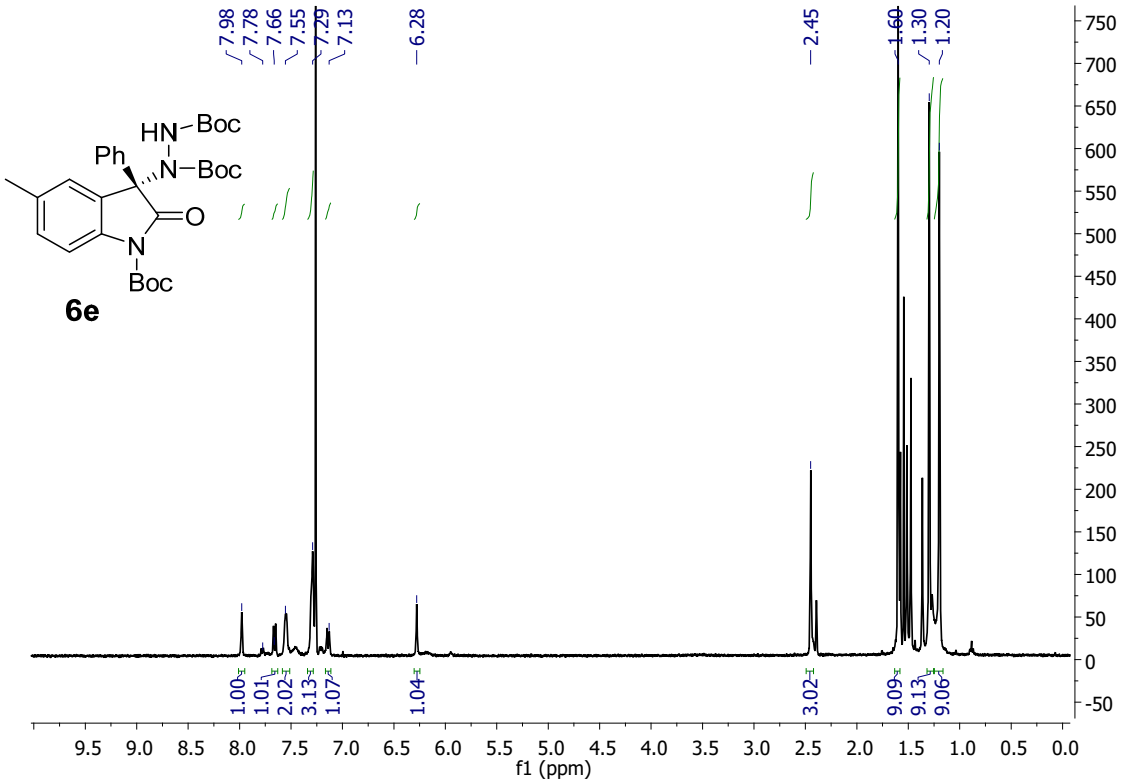


Figure S10. ^{1}H NMR spectrum of **6e** ($CDCl_3$, 400 MHz)

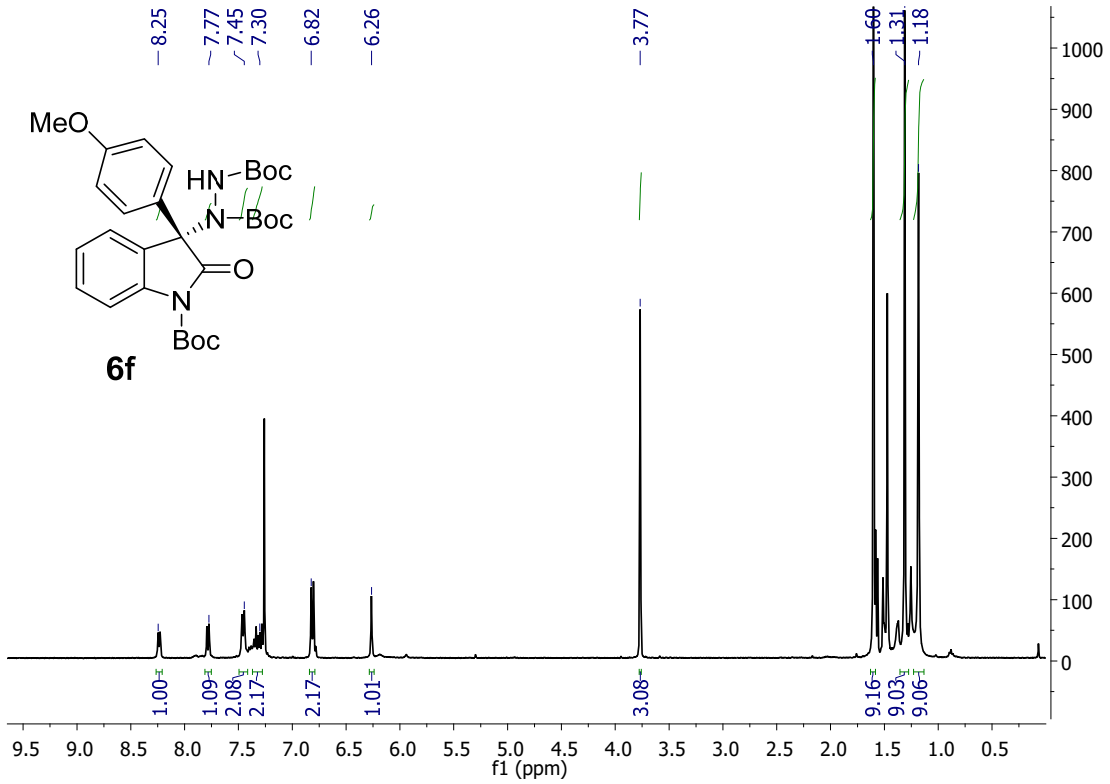


Figure S11. ^{1}H NMR spectrum of **6f** ($CDCl_3$, 400 MHz)

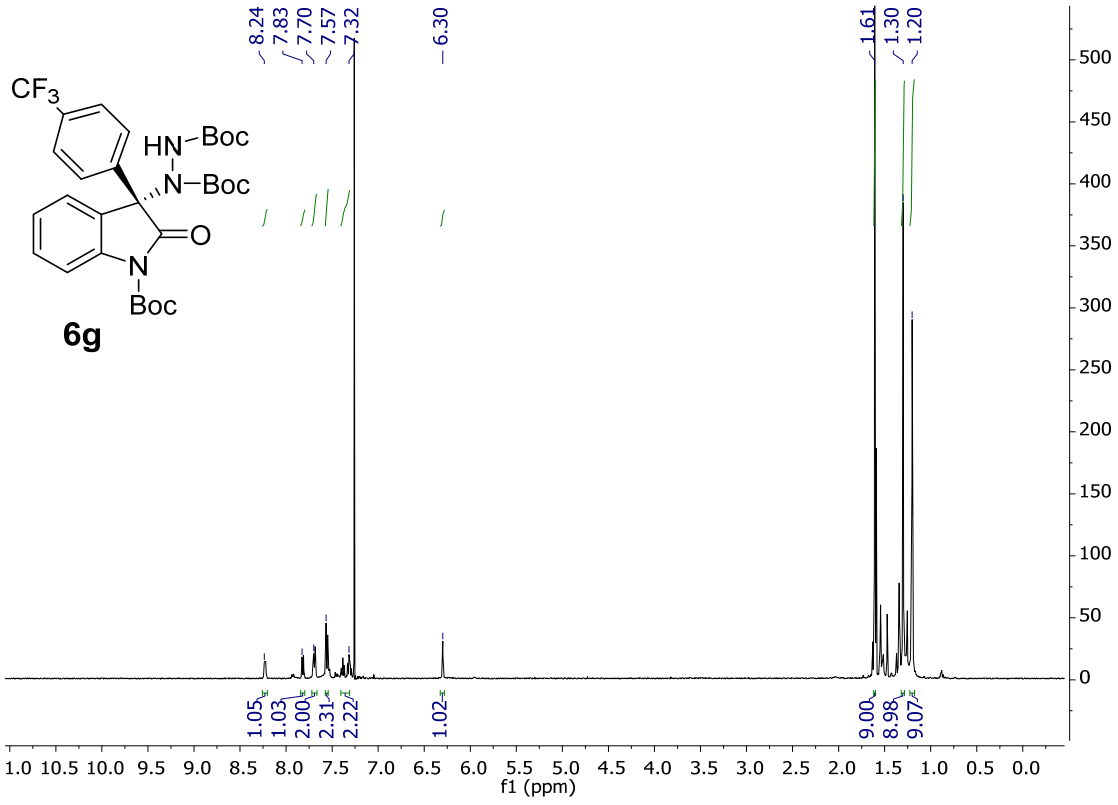


Figure S12. ^{1}H NMR spectrum of **6g** ($CDCl_3$, 400 MHz)

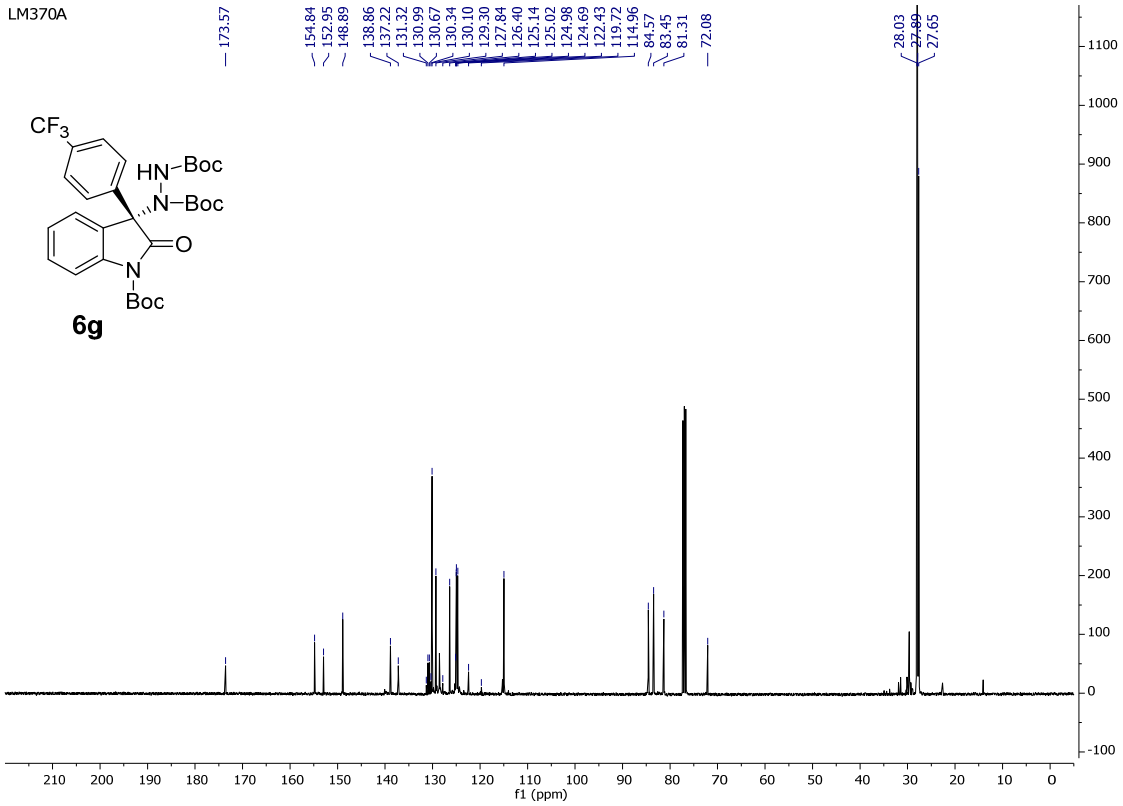


Figure S13. ^{13}C NMR spectrum of **6g** ($CDCl_3$, 100 MHz)

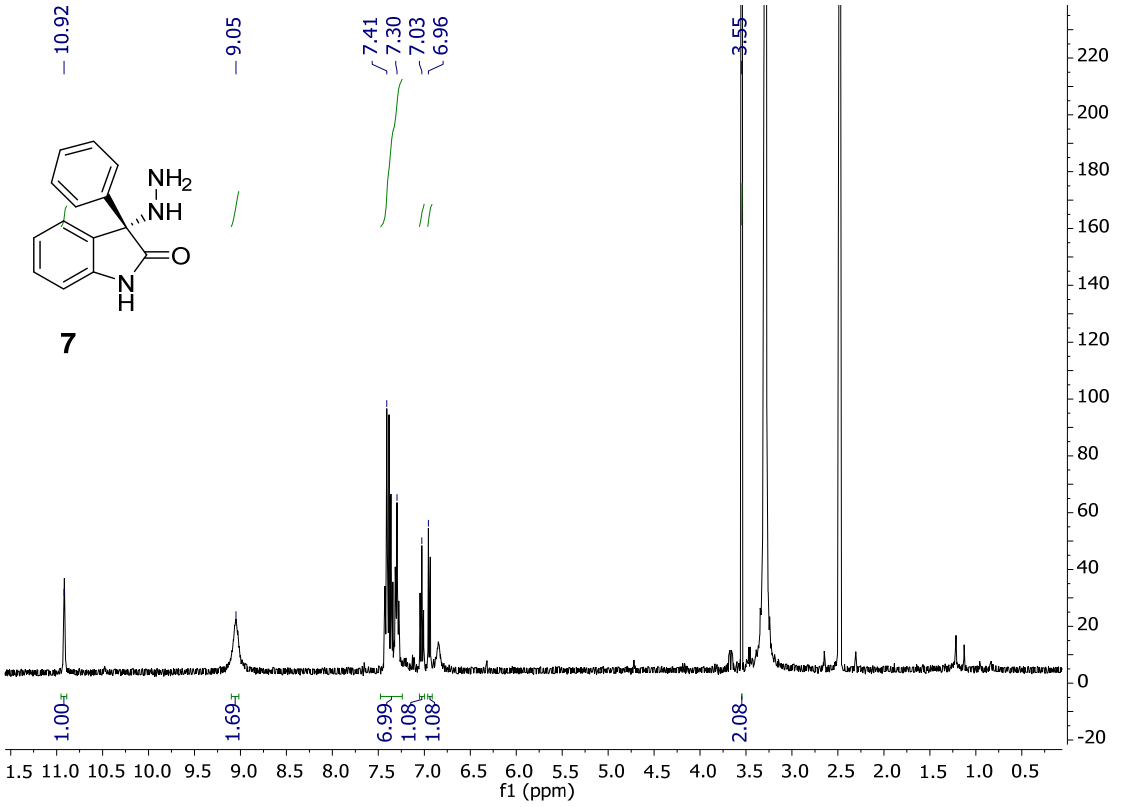


Figure S14. ^{1}H NMR spectrum of **7** (DMSO-d6, 400 MHz)

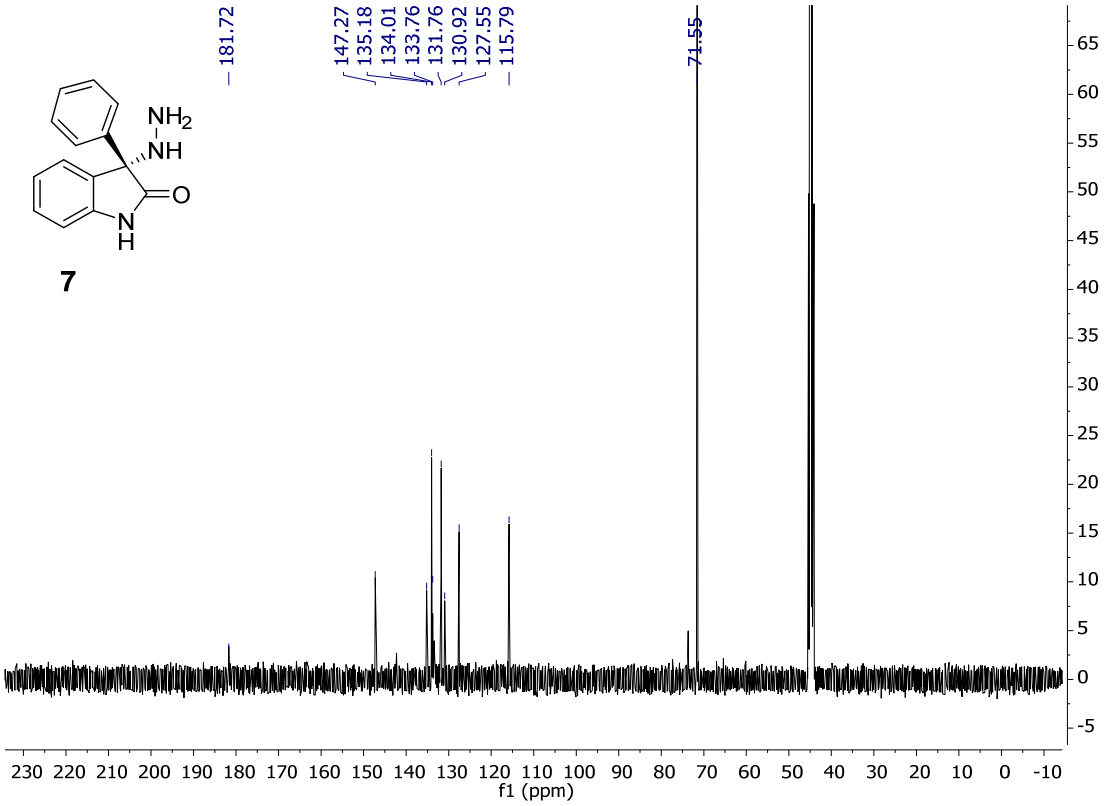


Figure S15. ^{13}C NMR spectrum of **7** (DMSO-d6, 100 MHz)

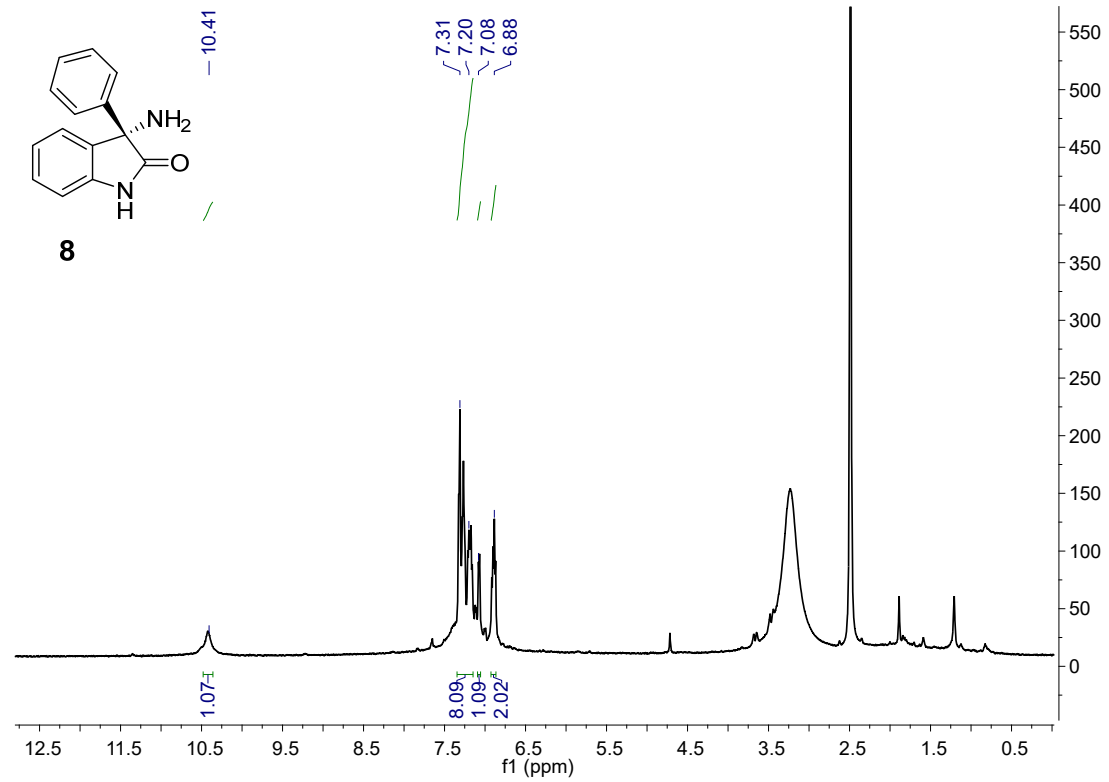


Figure S16. ^{1}H NMR spectrum of **8** (DMSO-d6, 500 MHz)

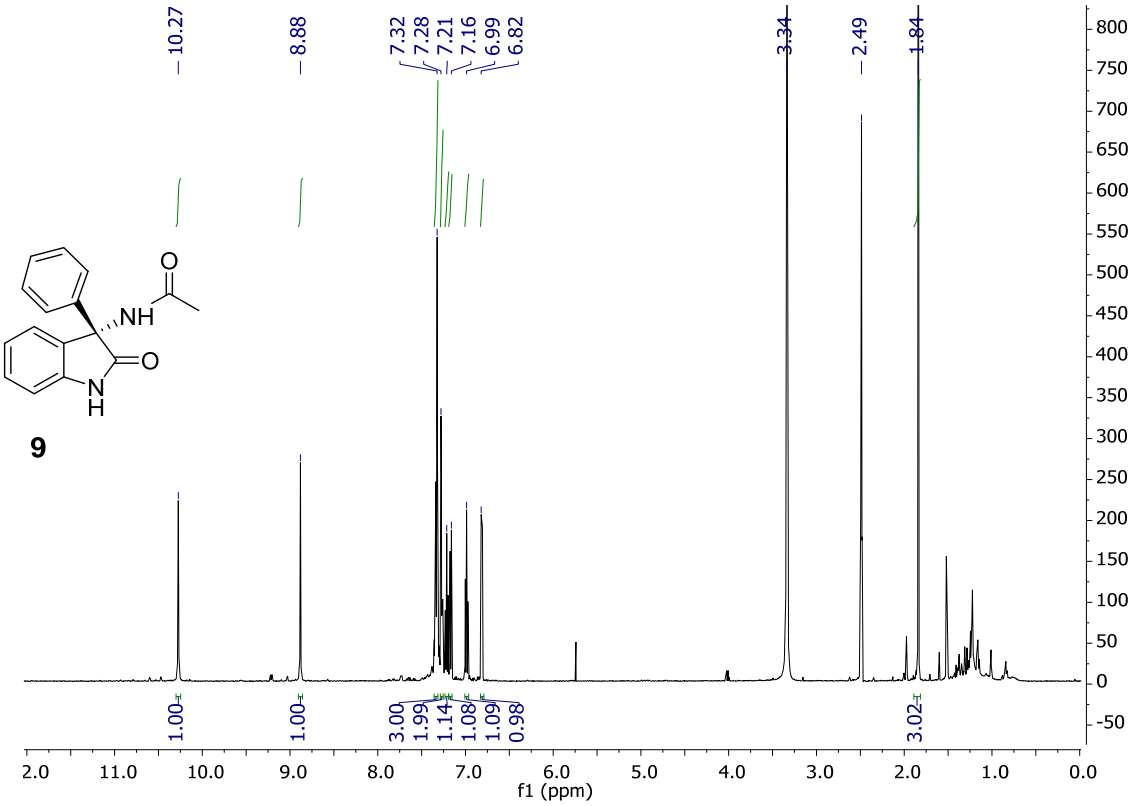


Figure S17. ^{1}H NMR spectrum of **9** (DMSO-d6, 500 MHz)

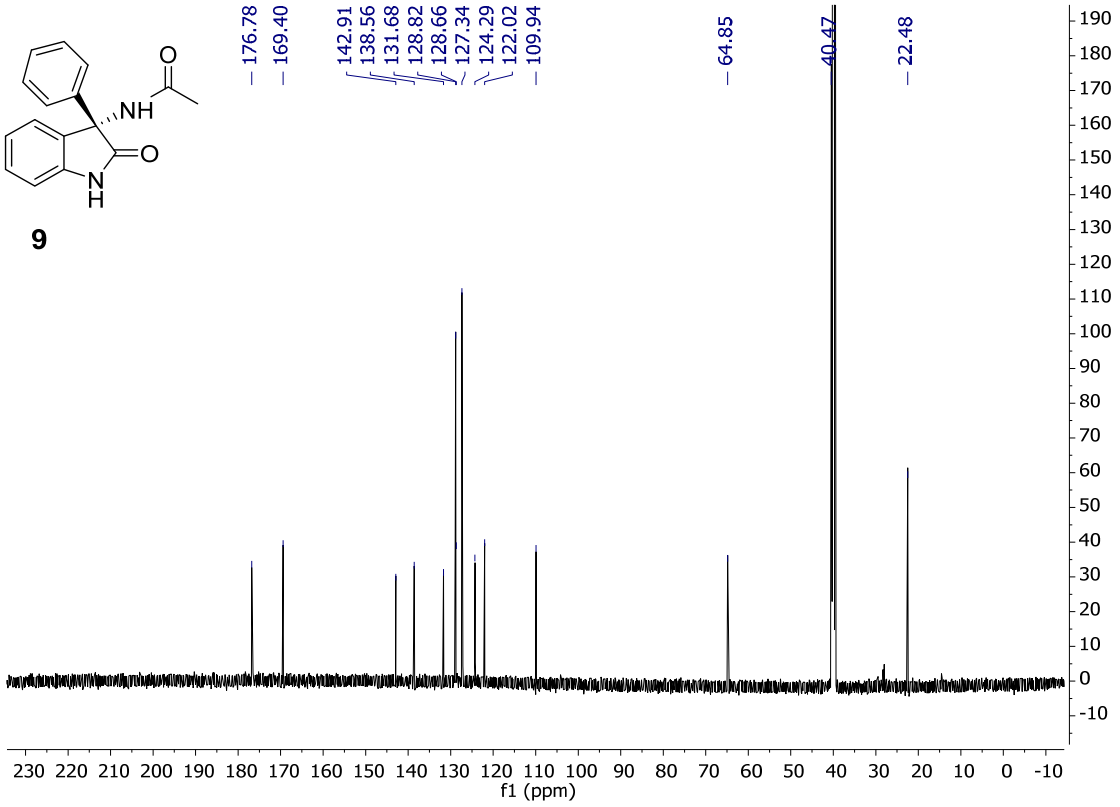


Figure S18. ^{13}C NMR spectrum of **9** (DMSO-d6, 126 MHz)

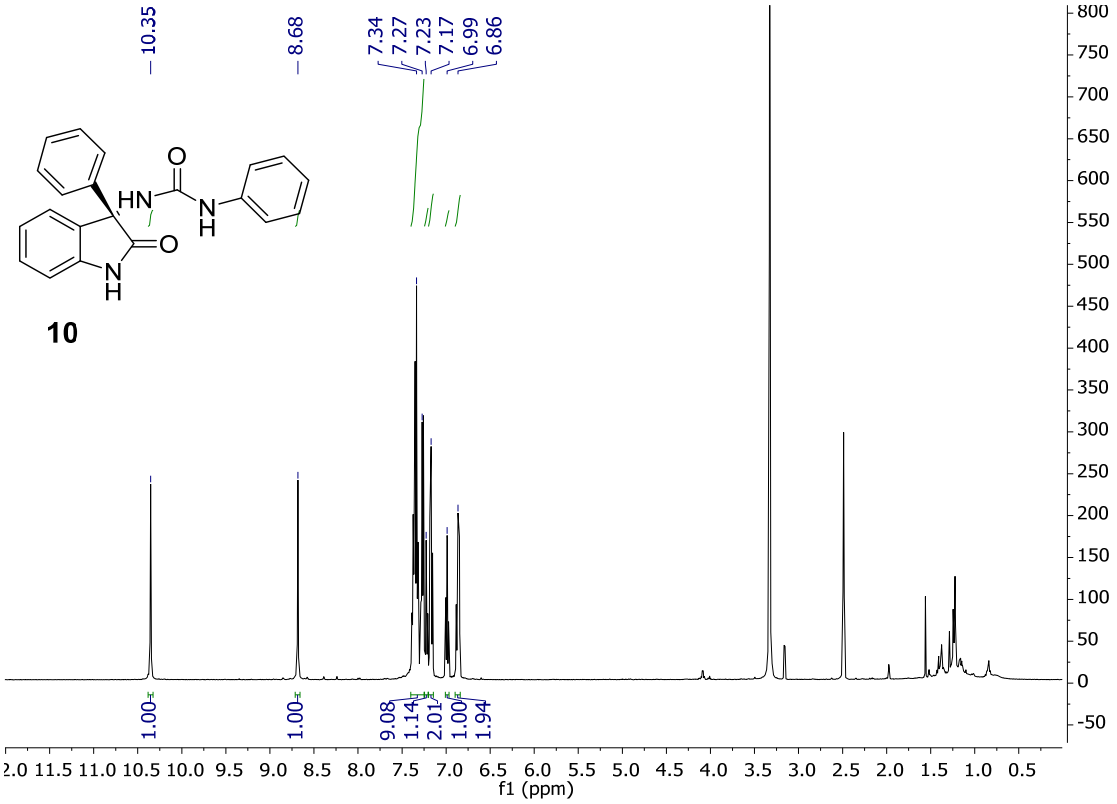


Figure S19. [1]H NMR spectrum of **10** (DMSO-d6, 500 MHz)

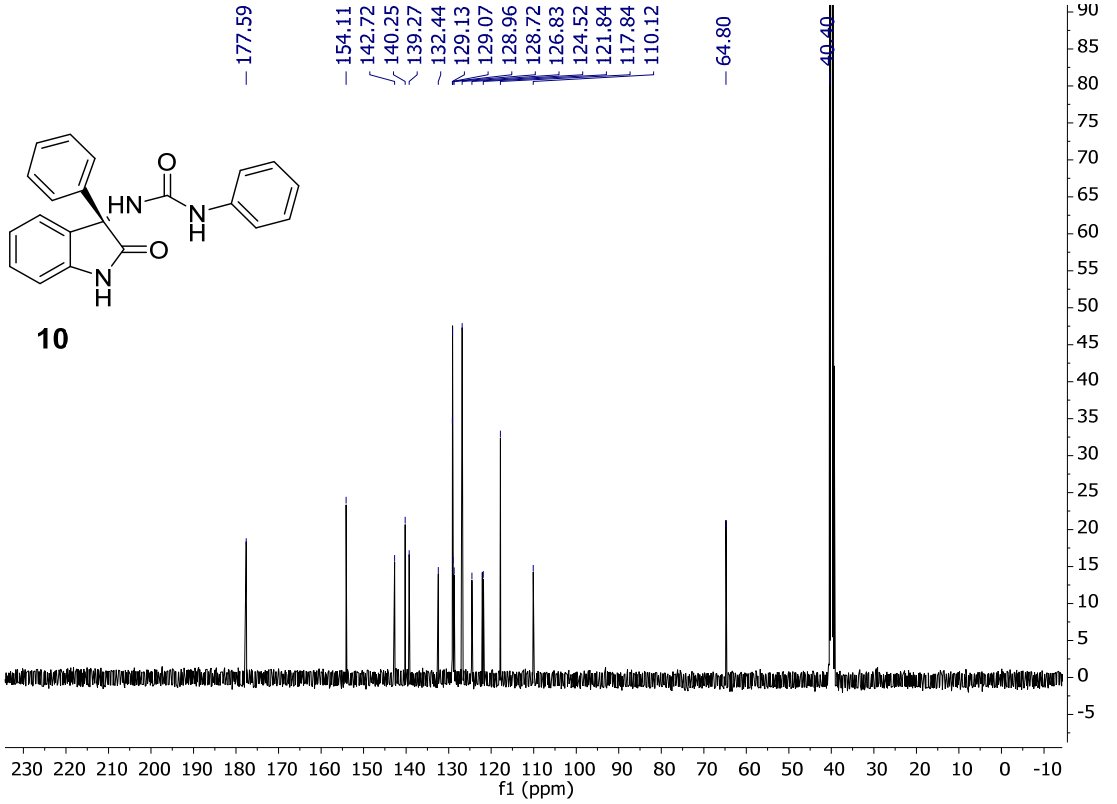


Figure S20. [13]C NMR spectrum of **10** (DMSO-d6, 100 MHz)

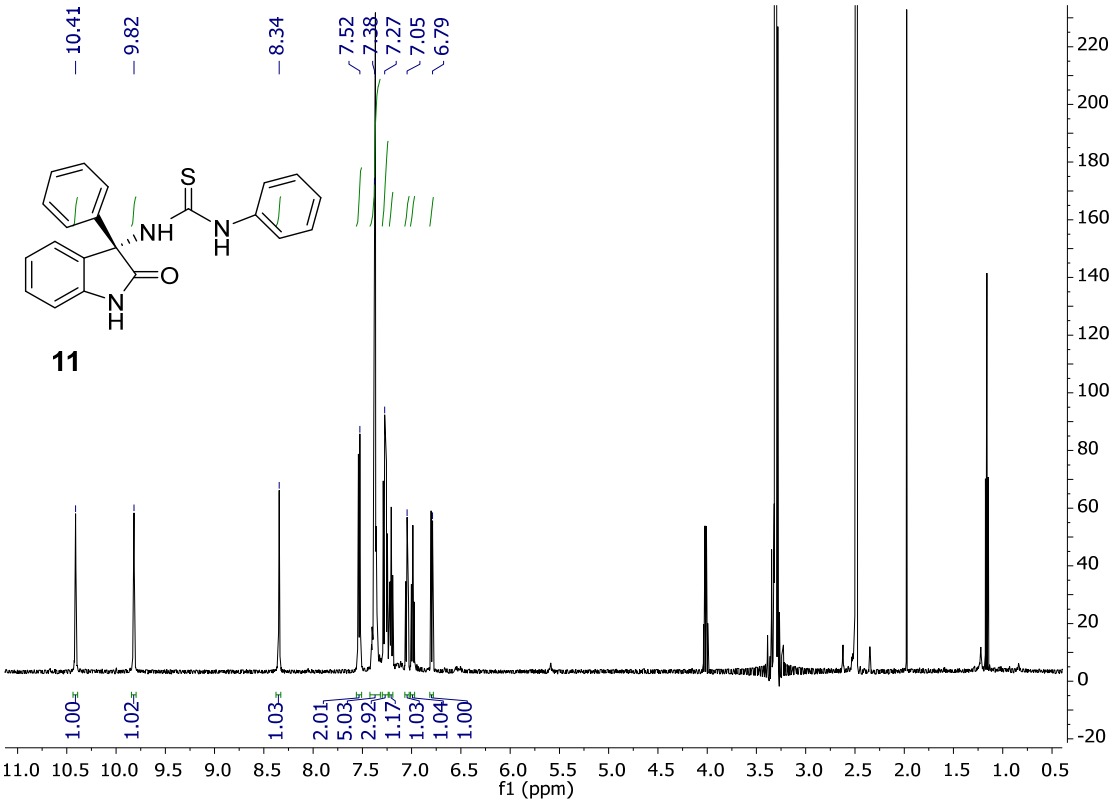


Figure S21. ^{1}H NMR spectrum of **11** (DMSO-d6, 500 MHz)

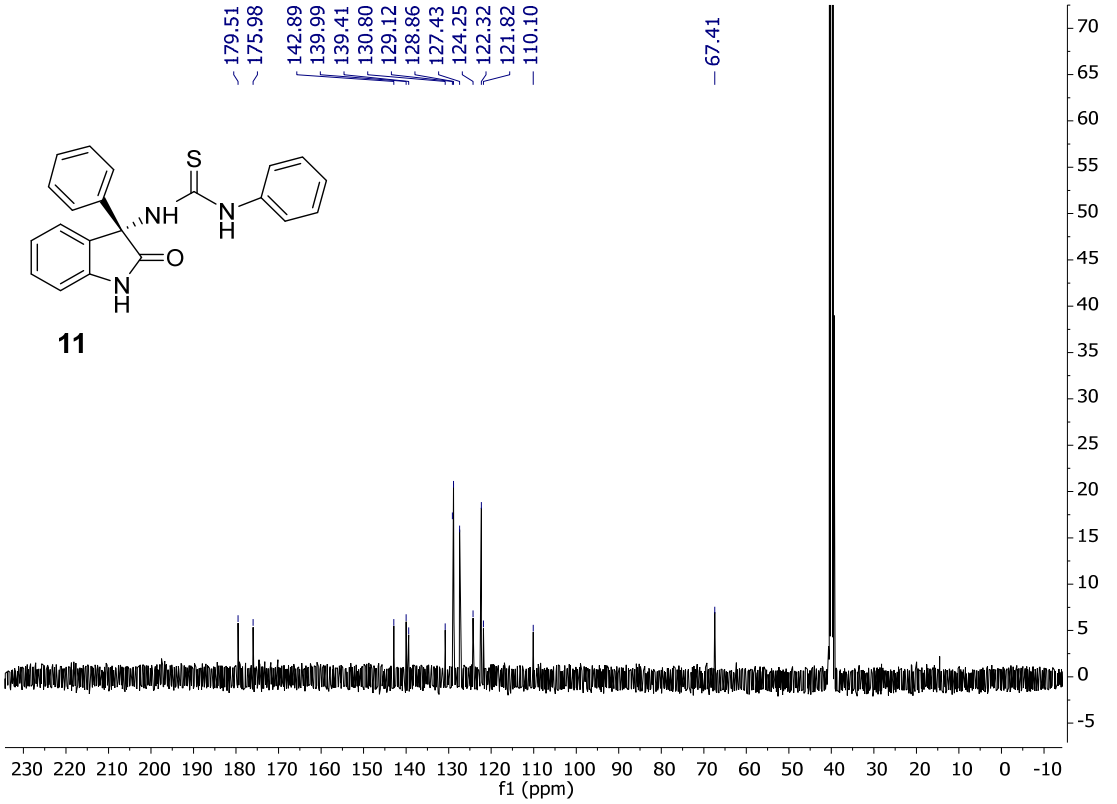


Figure S22. ^{13}C NMR spectrum of **11** (DMSO-d6, 100 MHz)

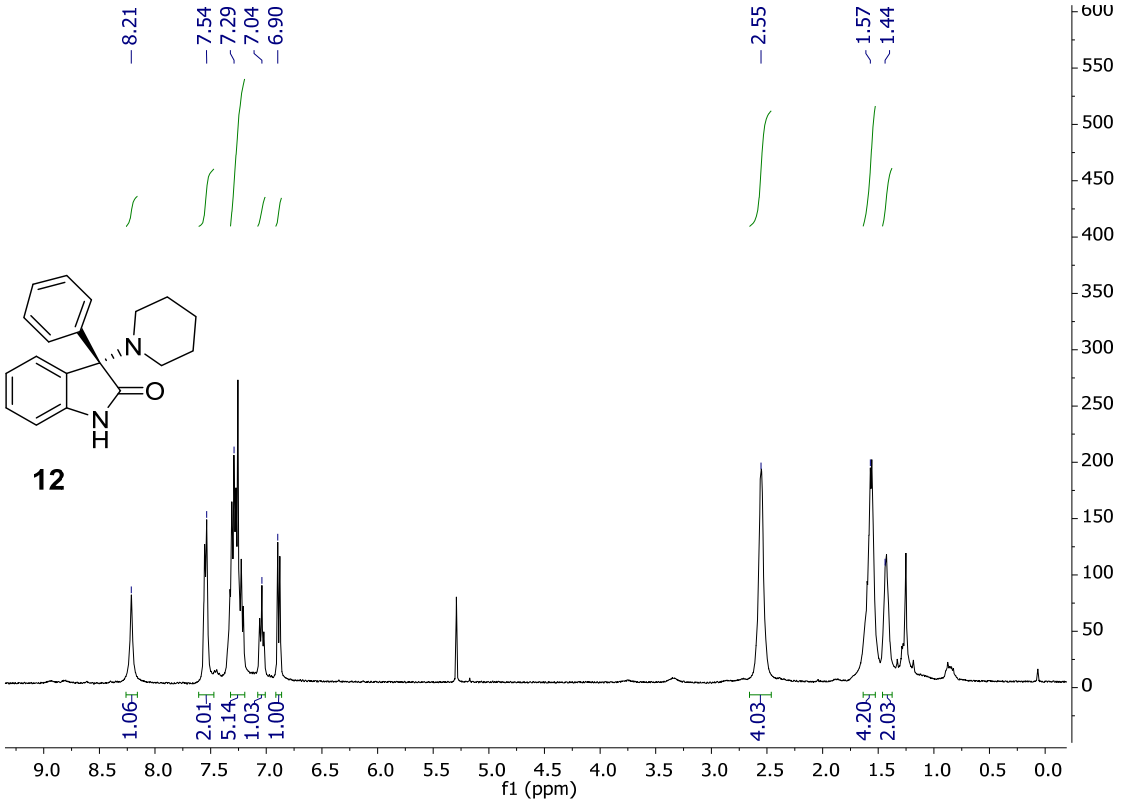


Figure S23. ^{1}H NMR spectrum of **12** ($CDCl_3$, 400 MHz)

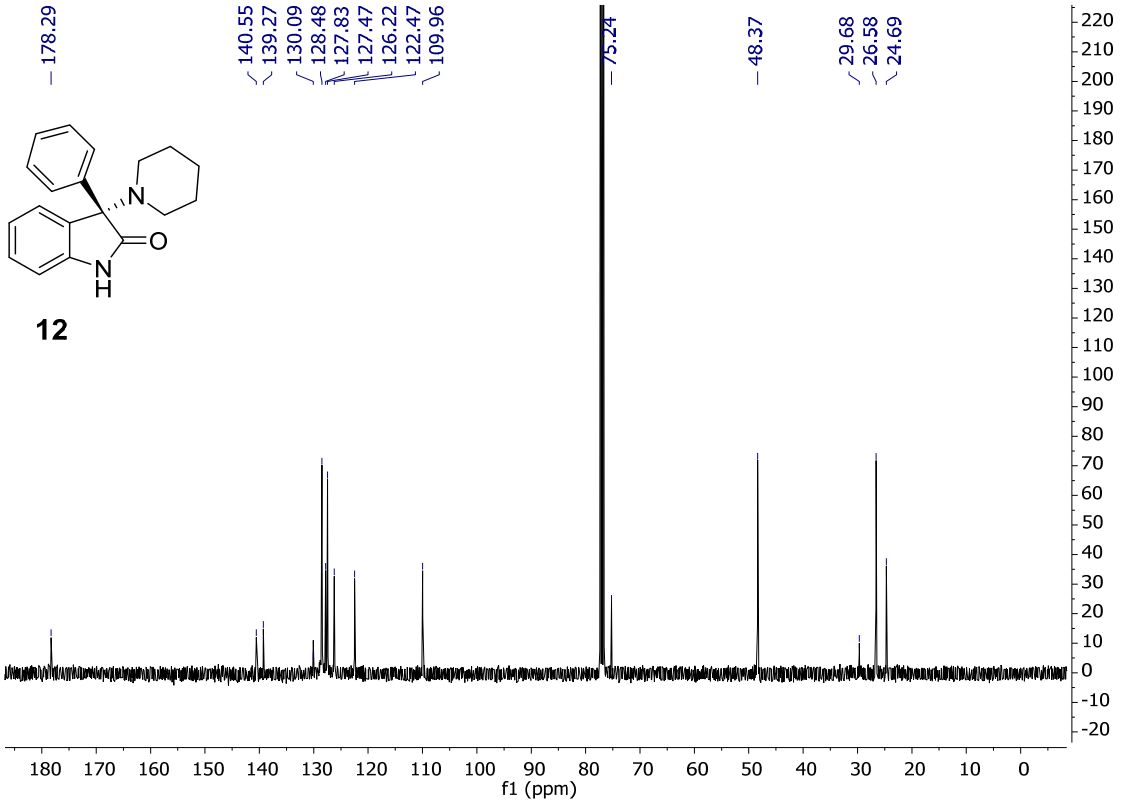


Figure S24. ^{13}C NMR spectrum of **12** ($CDCl_3$, 100 MHz)

2.-NMR spectra of crude mixtures in toluene and dicloromethane

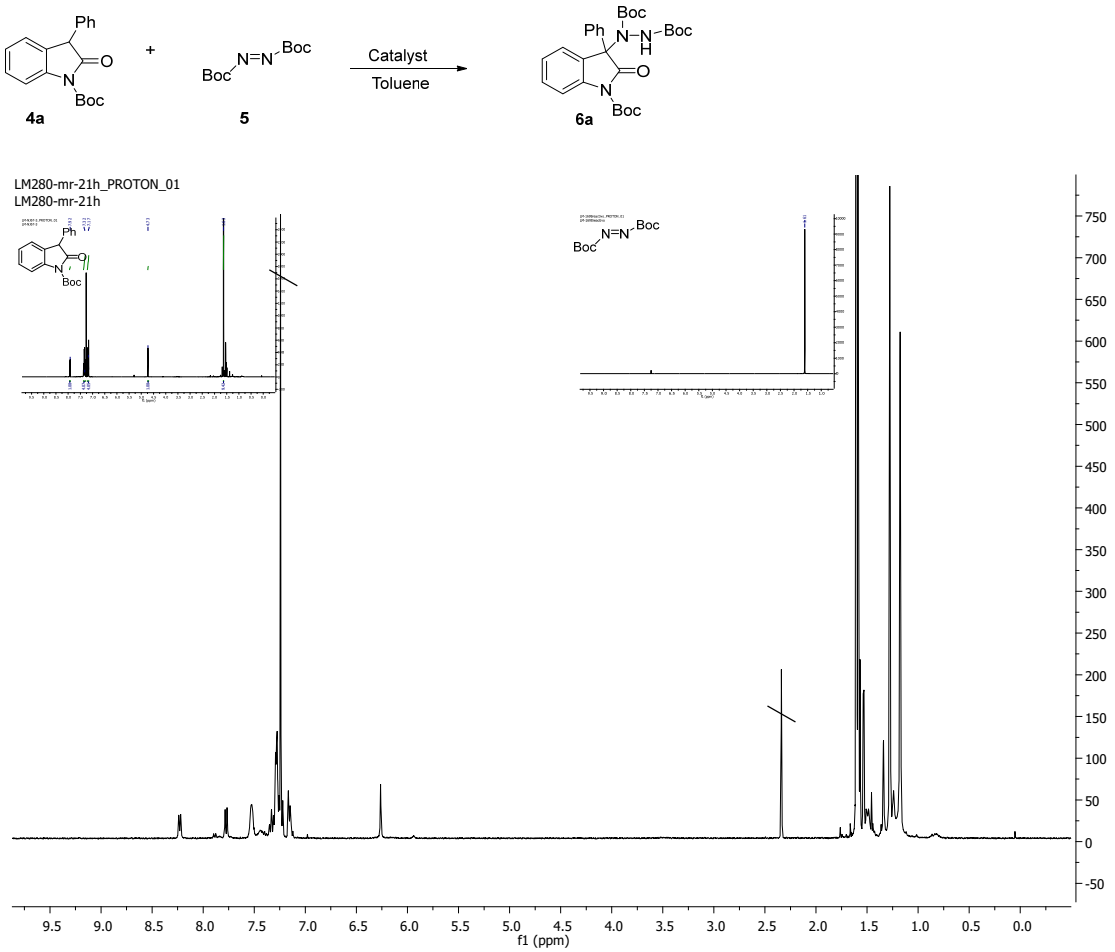


Figure S25. ^{1}H NMR spectrum of crude mixture of **6a** in toluene ($CDCl_3$, 400 MHz)

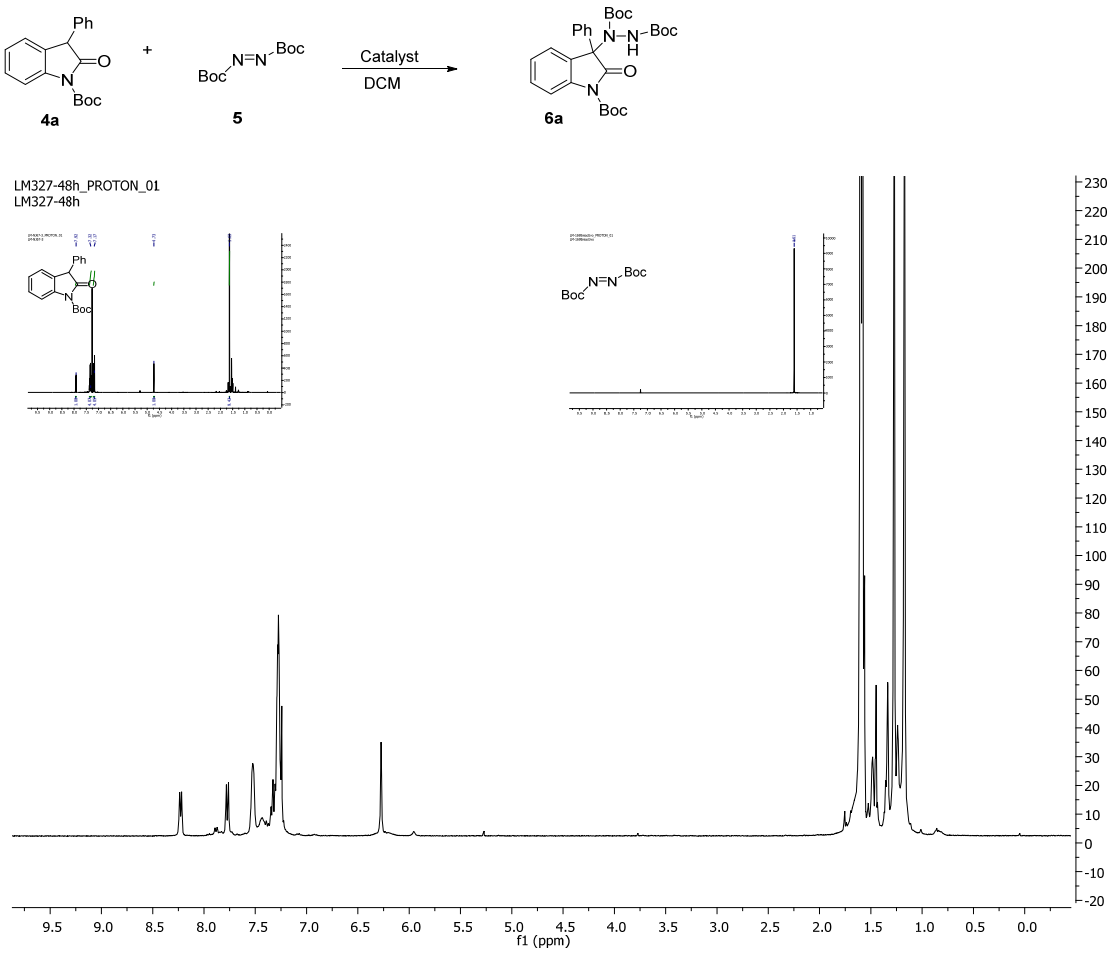


Figure S26. ^{1}H NMR spectrum of crude mixtureof **6a** in diclorometha ne ($CDCl_3$, 400 MHz)

3.- IR (PIM-1n, Amine PIM-1n and catalyst II) spectra

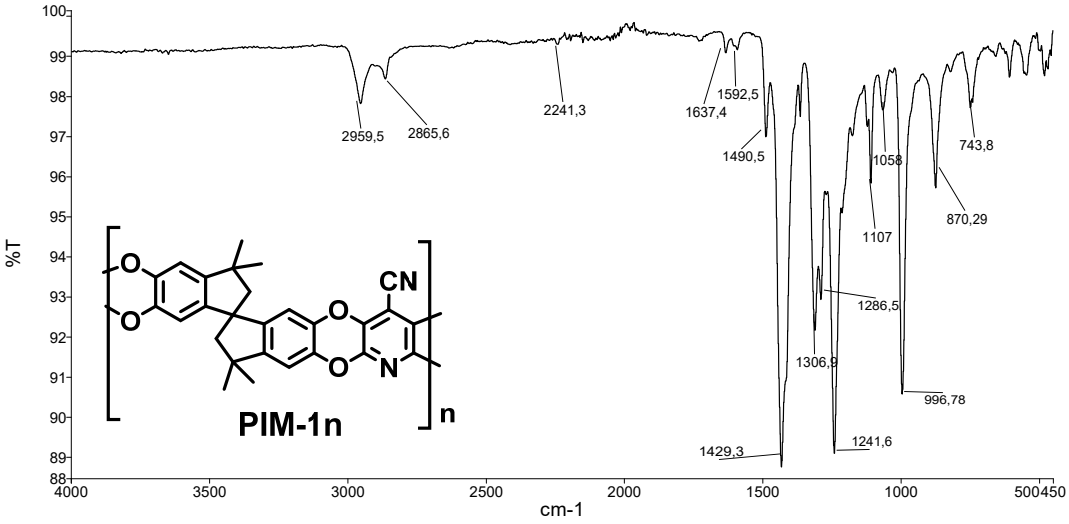


Figure S27. IR (ATR) for **PIM-1n**

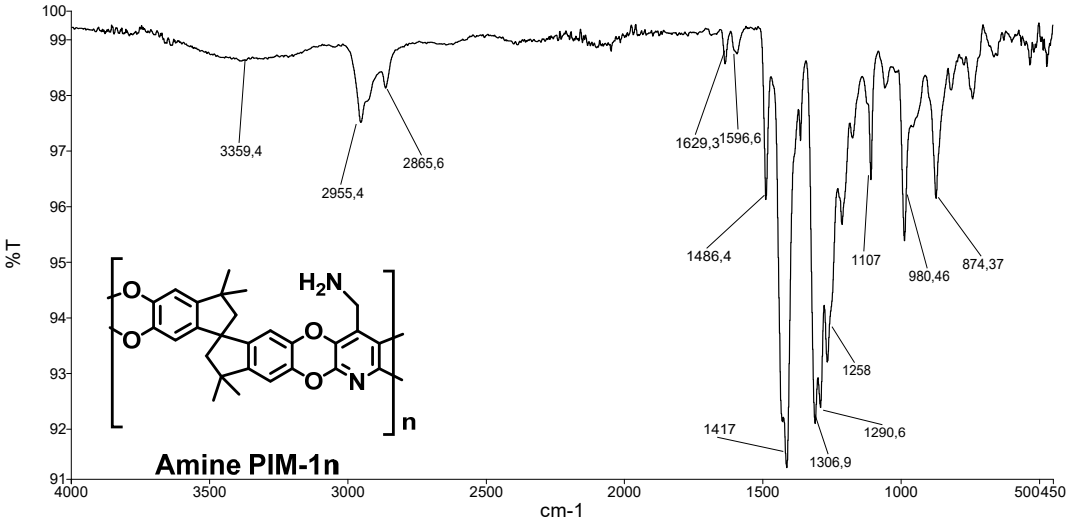


Figure S28. IR (ATR) for **Amine PIM-1n**

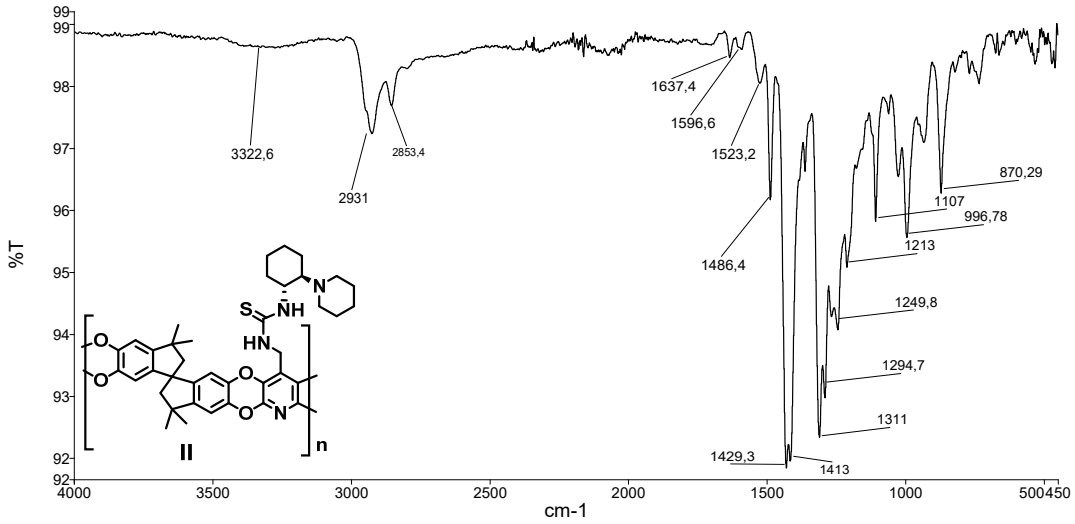


Figure S29. IR (ATR) for thiourea **II (catalyst II)**

4.- TGA analysis (PIM-1n, Amine PIM-1n, catalyst II)

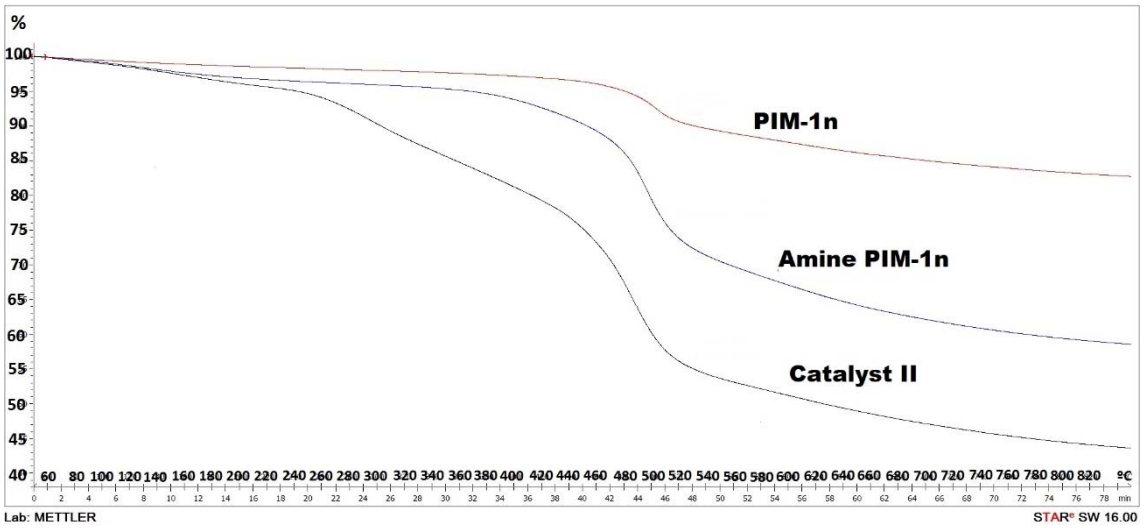


Figure S30. TGA thermograms comparison of **PIM-1n**, **Amine PIM-1n** and **catalyst II** under nitrogen atmosphere.

5.- BET analysis and SEM micrographs (Catalyst II)

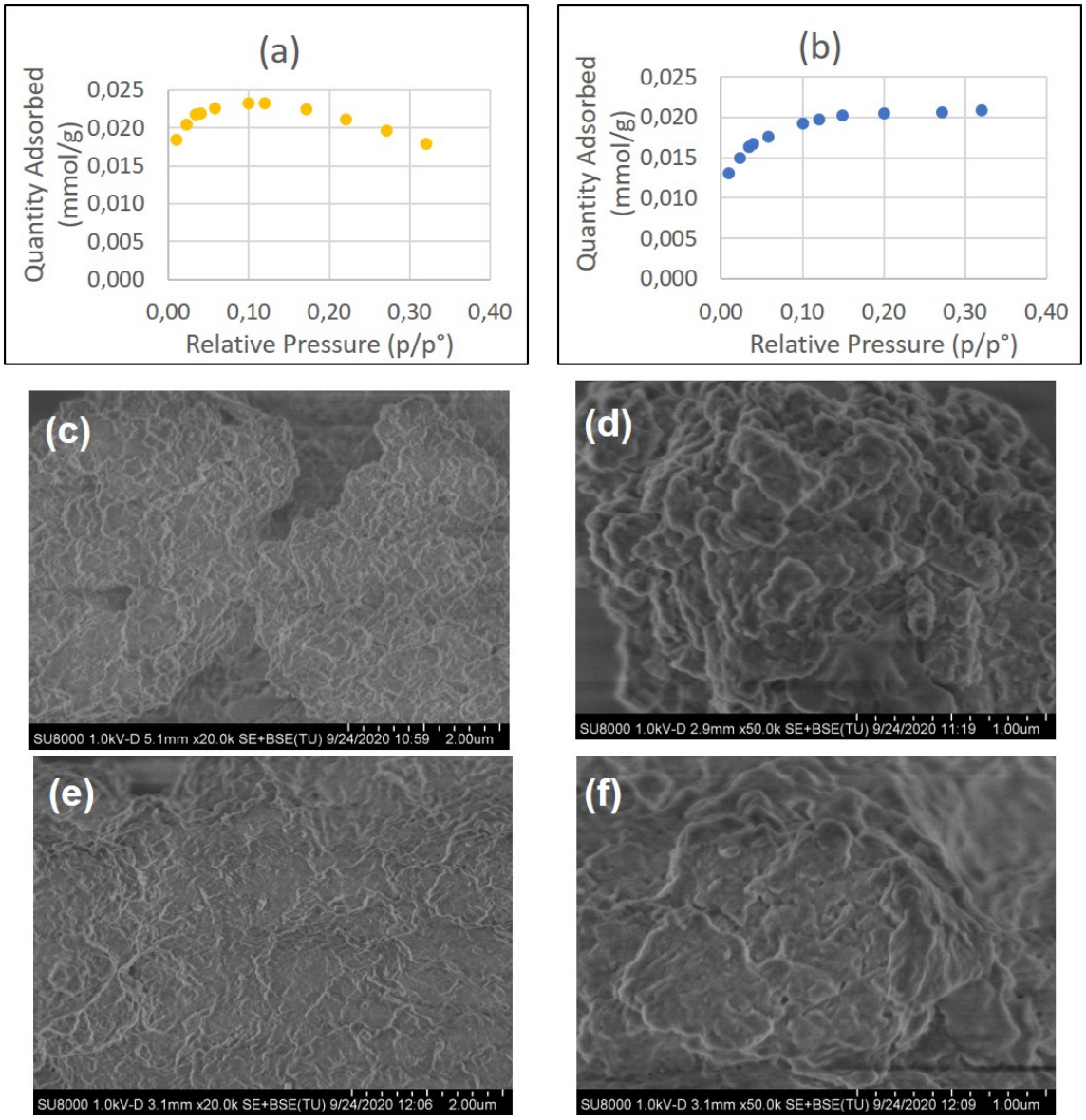
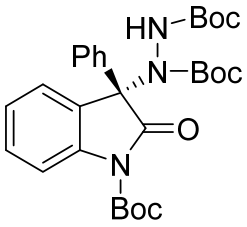
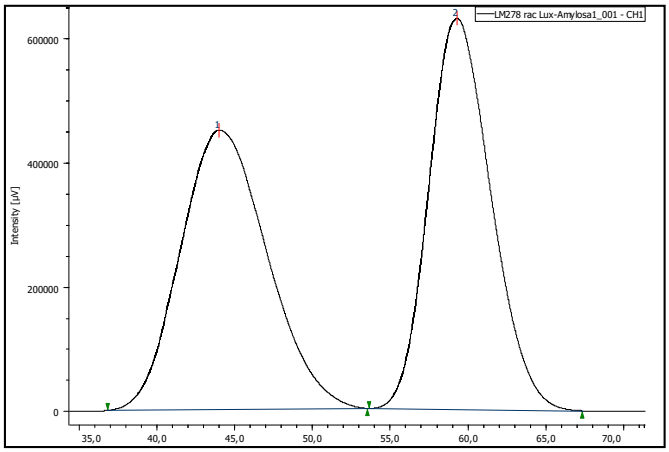


Figure S31. N_2 adsorption isotherms of the dry powder catalyst **II** before (a) and after (b) used in flow conditions. SEM micrographs of dry powder catalyst **II** before (c, d) and after (e, f) used in flow conditions.

6.- HPLC chromatograms

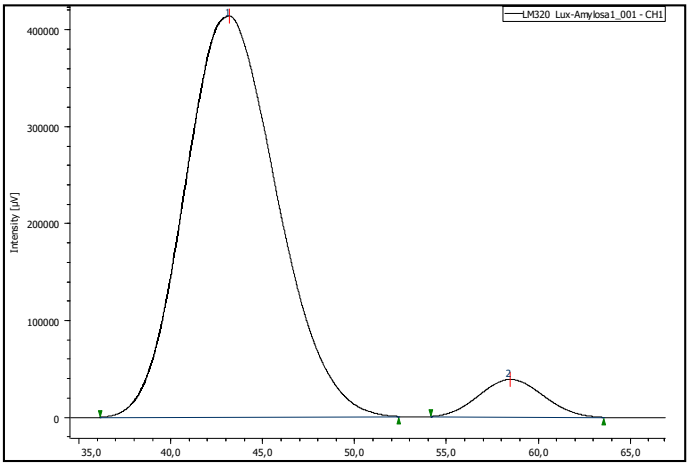
(*S*)-Di-*tert*-butyl-1-[1-(*tert*-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl]hydrazine-1,2-dicarboxylate (6a).





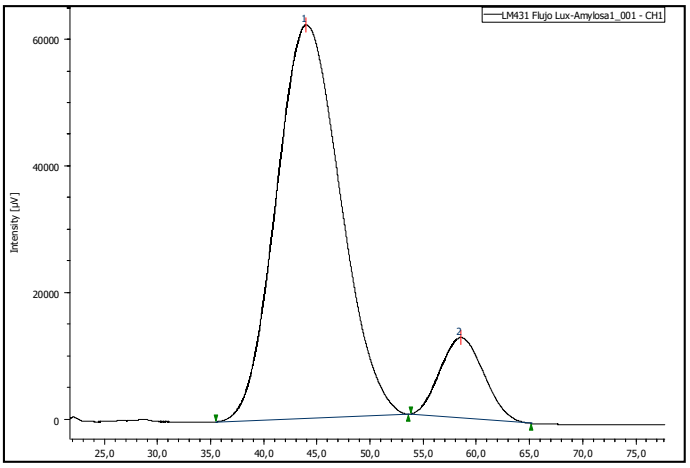
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**43,992**	174300373	449637	**49,900**	41,689	1,172
2	**59,267**	174997518	628907	**50,100**	58,311	1,168

Figure S32. HPLC profile for **6a** (racemic).



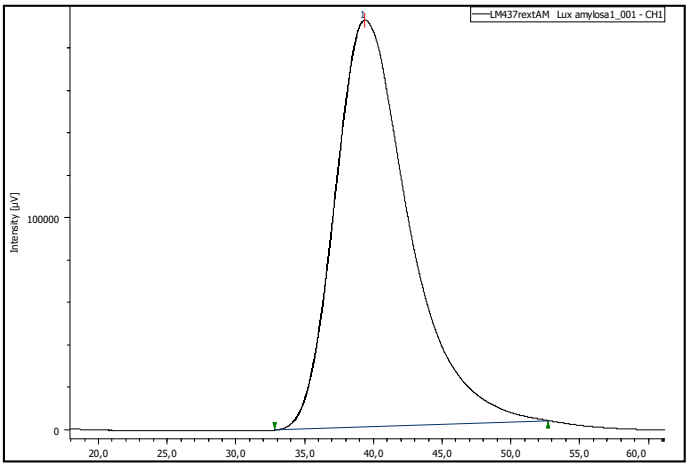
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**43,158**	144295895	412662	**93,842**	91,413	1,128
2	**58,450**	9468326	38762	**6,158**	8,587	1,057

Figure S33. HPLC profile for **6a**. Entry 8, table 1. 94:6 er.



Peak Name	tR	Area	Height	Area%	Height%	Symmetry
1	**43,933**	26002195	62001	**87,814**	83,009	1,121
2	**58,517**	3608435	12691	**12,186**	16,991	1,095

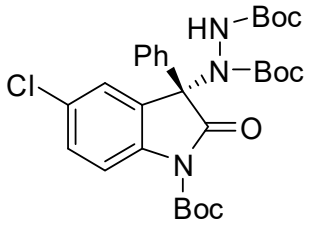
Figure S34. HPLC profile for **6a** (flow experiments). Entry 1, table 2. 88:12 er.

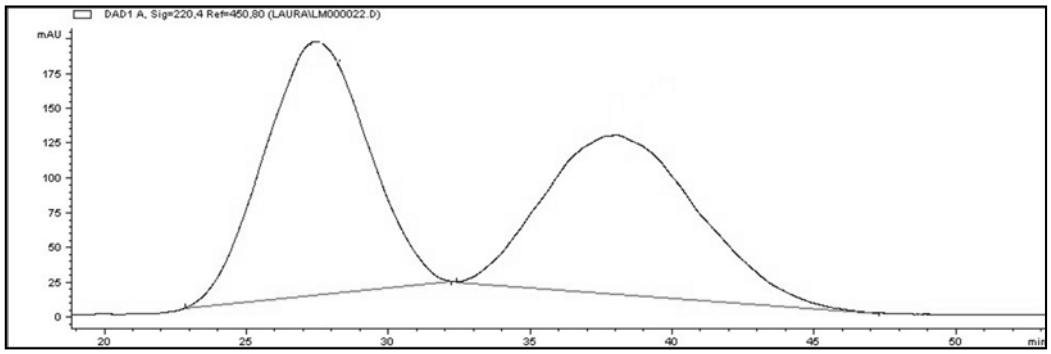


Peak Name	tR	Area	Height	Area%	Height%	Symmetry
1	**39,358**	71893883	191518	**100,000**	100,000	1,463

Figure S35. HPLC profile for **6a** after recrystallization. ≥ 98:2 er.

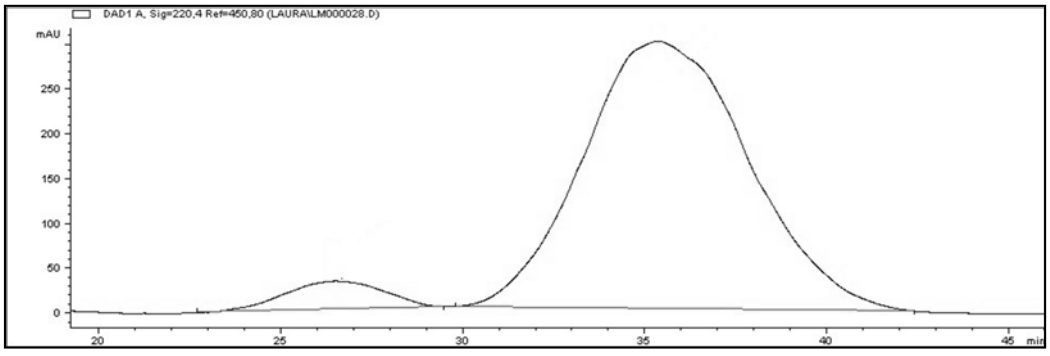
(*S*)-Di-*tert*-butyl-1-[1-(*tert*-butoxycarbonyl)-5-chloro-2-oxo-3-phenylindolin-3-yl]hydrazine-1,2-dicarboxylate (6b).





Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**27.395**	46693.1	182.9	4.2557	**51.755**	0.947
2	**38.058**	43525.9	114.7	6.3272	**48.245**	0.868

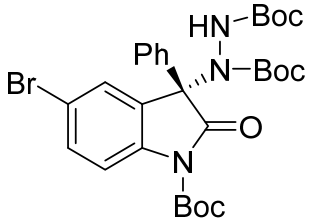
Figure S36. HPLC profile for **6b** (racemic).

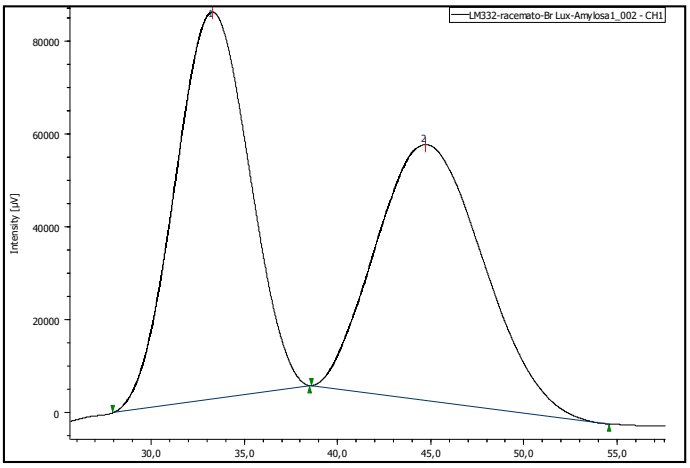


Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**26.48**	5962.5	31.4	3.1601	**5.929**	1.072
2	**35.358**	94596.8	298.8	5.2768	**94.071**	0.821

Figure S37. HPLC profile for **6b**. Table 2. 94:6 er.

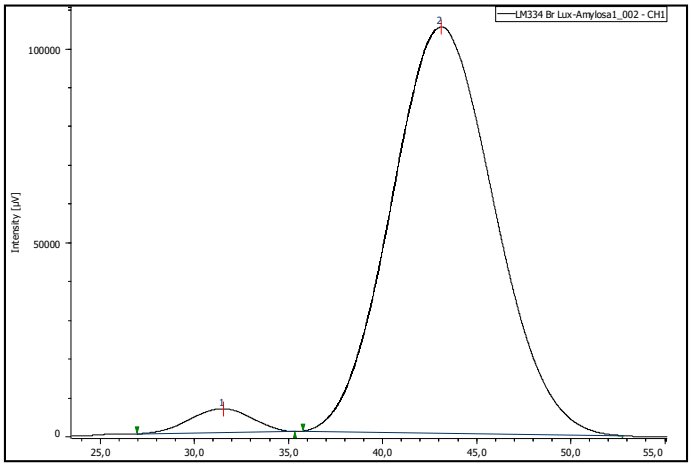
(*S*)-Di-*tert*-butyl-1-[5-bromo-1-(*tert*-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl]hydrazine-1,2-dicarboxylate (6c).





Peak Name	t_R	Area	Height	Area%	Height %	Symmetry
1	**33,275**	23004985	83155	**51,164**	60,217	1,004
2	**44,708**	21957865	54937	**48,836**	39,783	1,153

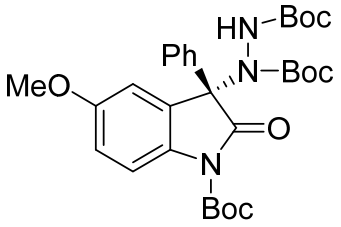
Figure S38. HPLC profile for **6c** (racemic).

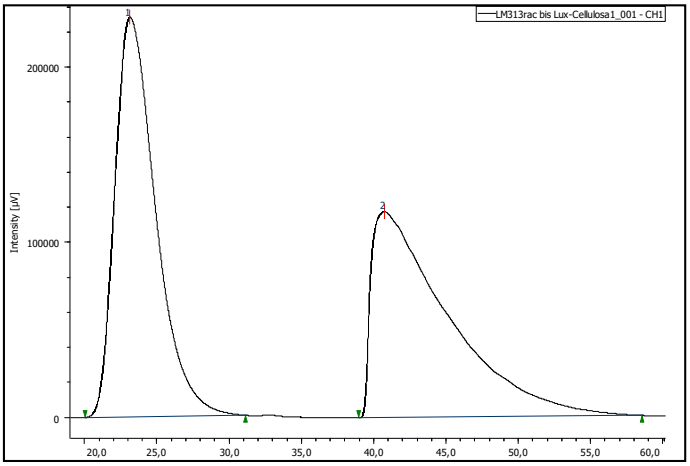


Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**31,542**	1413907	6169	**3,426**	5,573	0,919
2	**43,108**	39851860	104525	**96,574**	94,427	1,074

Figure S39. HPLC profile for **6c**. Table 2. 97:3 er.

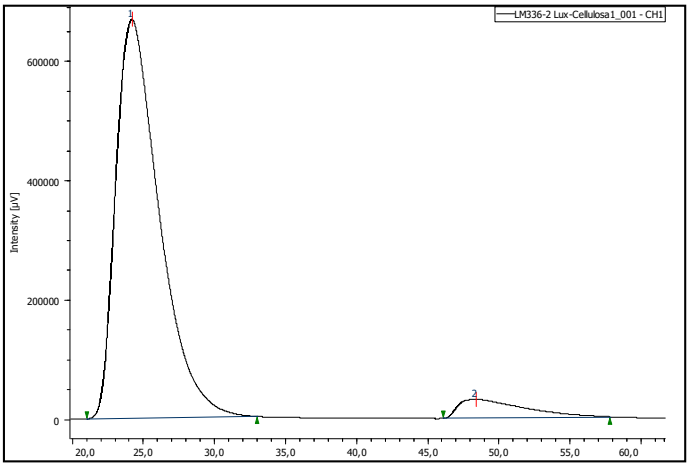
(*S*)-Di-*tert*-butyl-1-[1-(*tert*-butoxycarbonyl)-5-methoxy-2-oxo-3-phenylindolin-3-yl] hydrazine-1,2-dicarboxylate (6d).





Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**23,142**	44598008	227942	**50,739**	65,974	1,571
2	**40,692**	43298609	117559	**49,261**	34,026	5,053

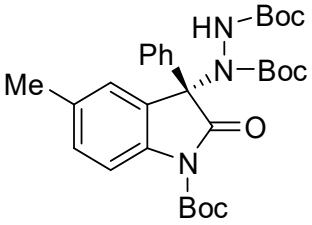
Figure S40. HPLC profile for **6d** (racemic).

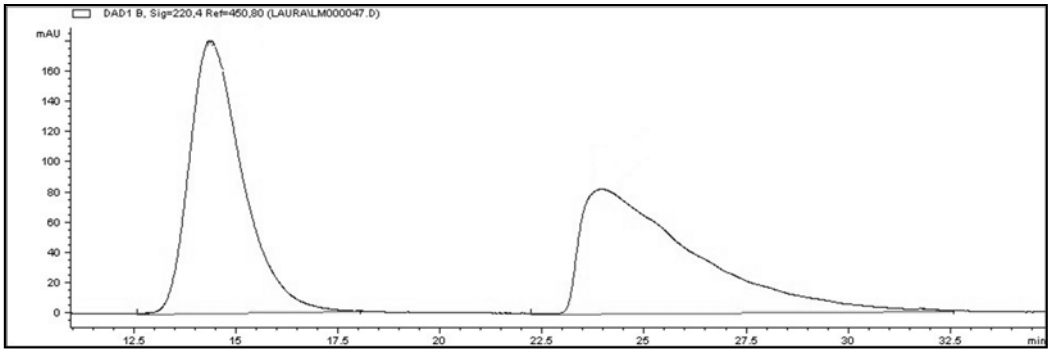


Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**24,183**	141635570	666399	**93,432**	95,487	1,672
2	**48,400**	9955985	31496	**6,568**	4,513	2,527

Figure S41. HPLC profile for **6d**. Table 2. 93:7 er.

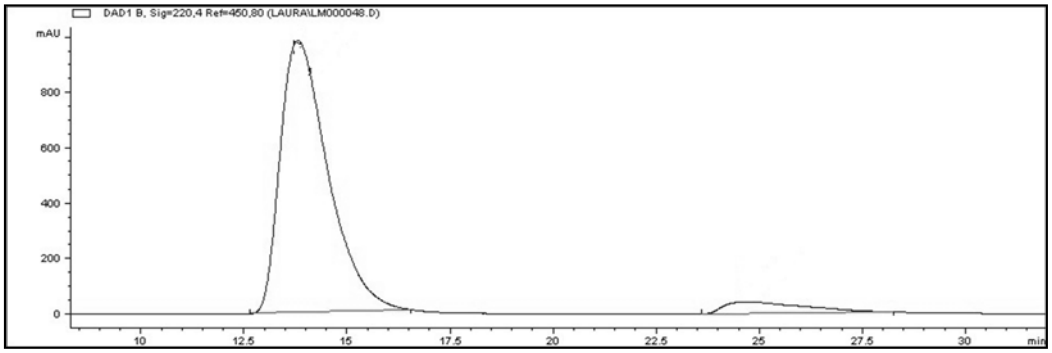
(*S*)-Di-*tert*-butyl-1-(1-(*tert*-butoxycarbonyl)-5-methyl-2-oxo-3-phenylindolin-3-yl)hydrazine-1,2-dicarboxylate (6e).





Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**14.359**	16457.3	180.9	1.5165	**50.388**	0.622
2	**23.944**	16203.7	82.8	3.2613	**49.612**	0.224

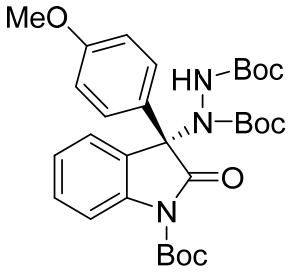
Figure S42. HPLC profile for **6e** (racemic).

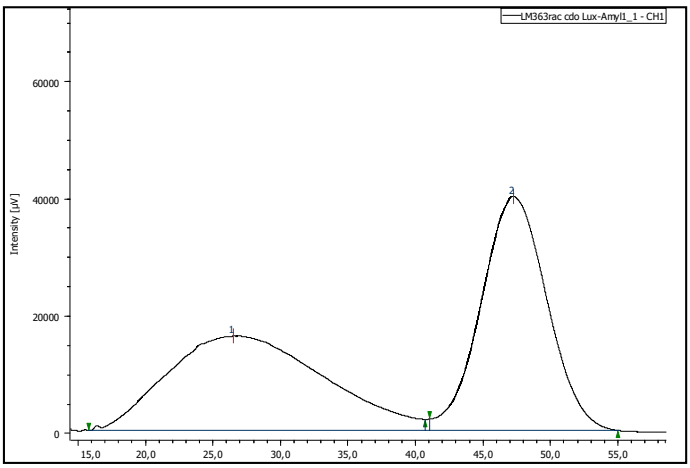


Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**13.786**	79530.5	985.2	1.3455	**92.687**	0.547
2	**24.667**	6274.6	44.4	1.6633	**7.313**	0.364

Figure S43. HPLC profile for **6e**. Table 2. 93:7 er.

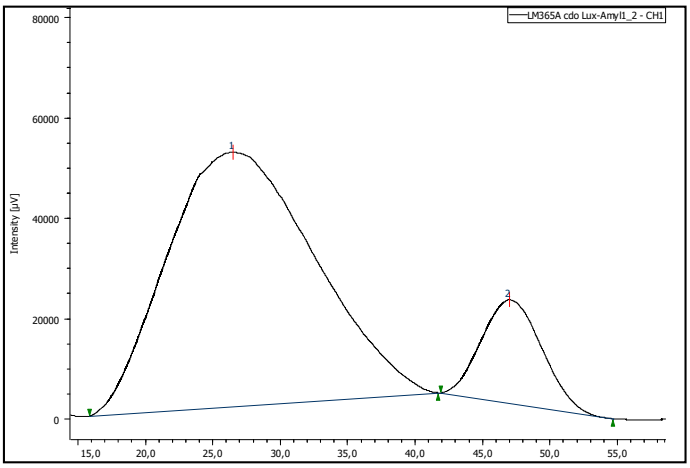
(*S*)-Di-*tert*-butyl-1-(1-(*tert*-butoxycarbonyl)-3-(4-methoxyphenyl)-2-oxoindolin-3-yl)hydrazine-1,2-dicarboxylate (6f).





Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**26,517**	13004900	16099	**49,077**	28,752	N/A
2	**47,192**	13493833	39895	**50,923**	71,248	0,973

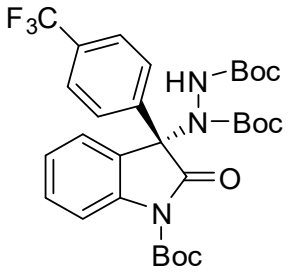
Figure S44. HPLC profile for **6f** (racemic).

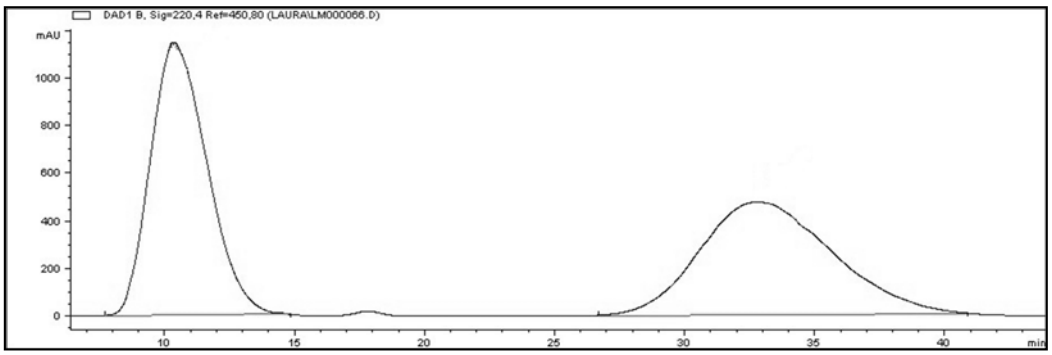


Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**26,492**	38412522	50620	**85,714**	71,110	1,211
2	**46,925**	6402293	20565	**14,286**	28,890	1,110

Figure S45. HPLC profile for **6f**. Table 2. 86:14 er.

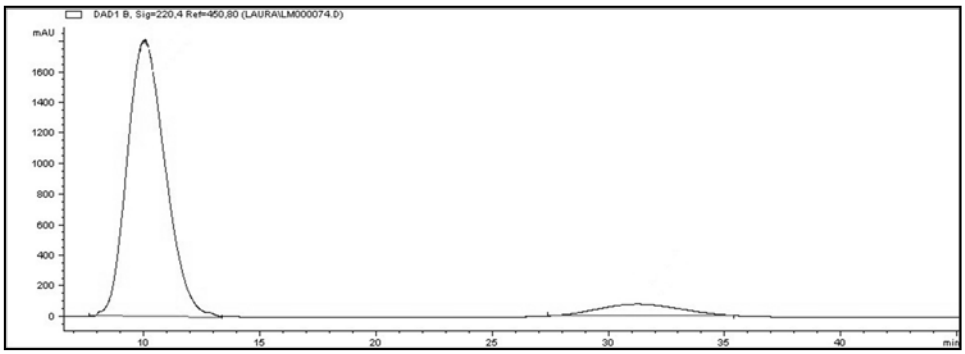
(*S*)-Di-*tert*-butyl-1-(1-(*tert*-butoxycarbonyl)-2-oxo-3-(4-(trifluoromethyl)phenyl) indolin-3-yl)hydrazine-1,2-dicarboxylate (6g).





Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**10.36**	174134.8	1150.4	2.5229	**50.345**	0.725
2	**32.843**	171750.6	477.8	5.9907	**49.655**	0.8

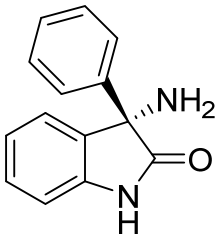
Figure S46. HPLC profile for **6g** (racemic).

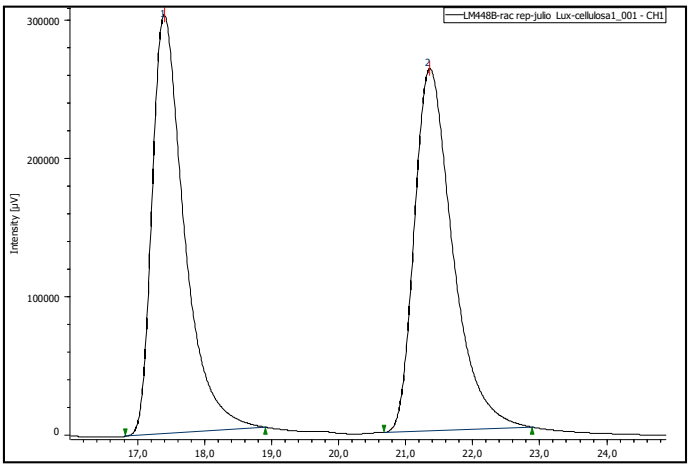


Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**9.997**	206703.9	1809.1	1.9043	**91.134**	0.722
2	**31.254**	20108.8	79.6	4.212	**8.866**	0.915

Figure S47. HPLC profile for **6g**. Table 2. 91:9 er.

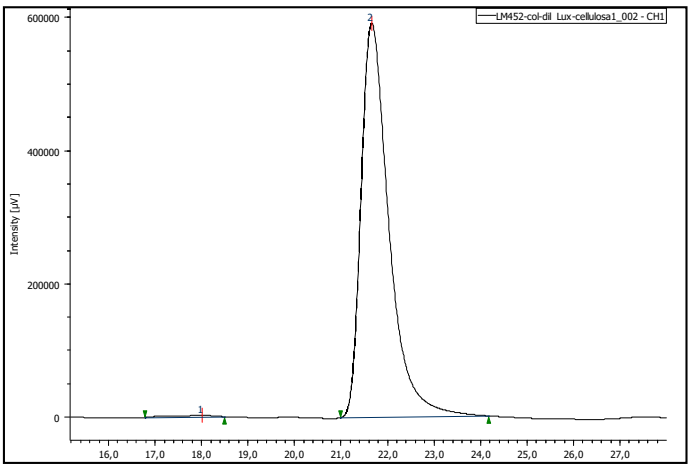
(*S*)-3-Amino-3-phenylindolin-2-one (8).





Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**17,400**	10109409	302477	**49,331**	53,617	1,680
2	**21,350**	10383581	261671	**50,669**	46,383	1,514

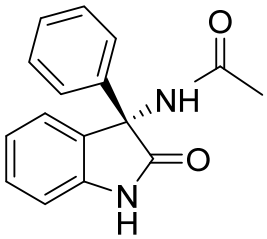
Figure S48. HPLC profile for **8** (racemic).

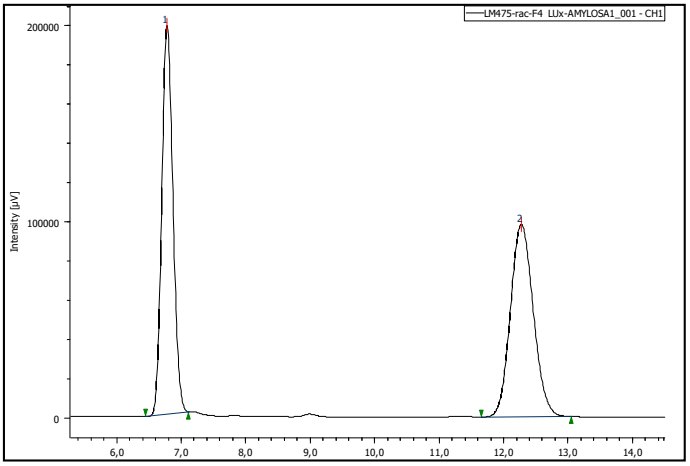


Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**18,017**	173409	2423	**0,700**	0,408	0,684
2	**21,650**	24615475	591128	**99,300**	99,592	1,620

Figure S49. HPLC profile for **8**. 99:1 er.

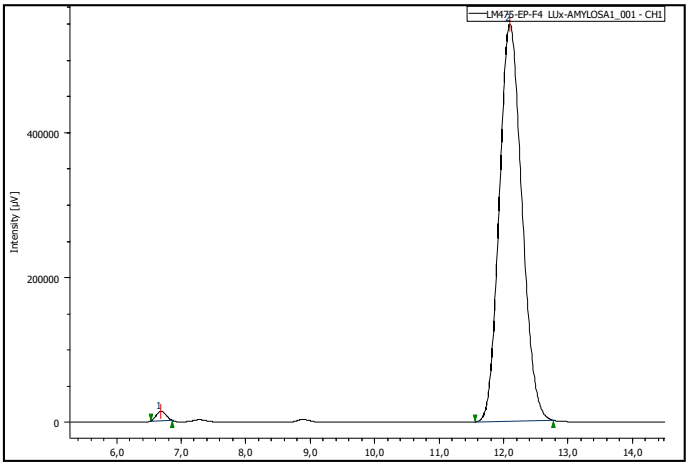
(*S*)-*N*-(2-Oxo-3-phenylindolin-3-yl)acetamide (9).





Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**6,783**	2370162	197352	**49,610**	66,883	1,083
2	**12,267**	2407380	97719	**50,390**	33,117	1,100

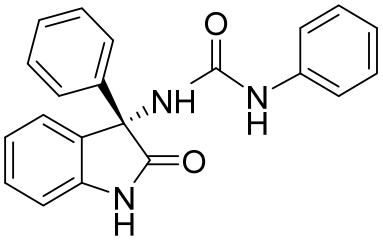
Figure S50. HPLC profile for **9** (racemic).

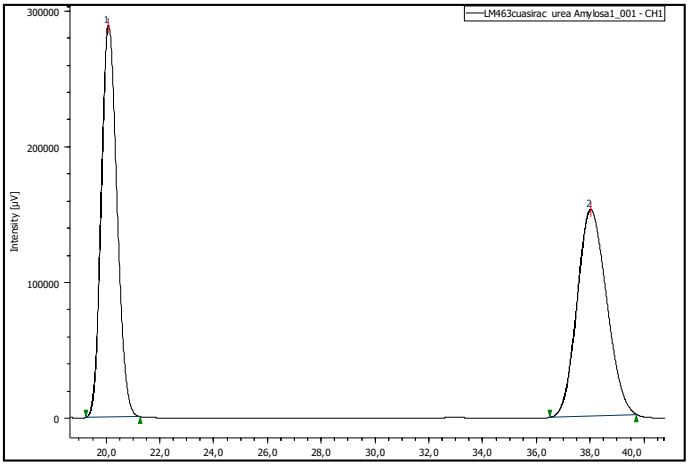


Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**6,683**	137192	13085	**1,018**	2,335	1,059
2	**12,092**	13341103	547398	**98,982**	97,665	1,122

Figure S51. HPLC profile for **9**. 99:1 er.

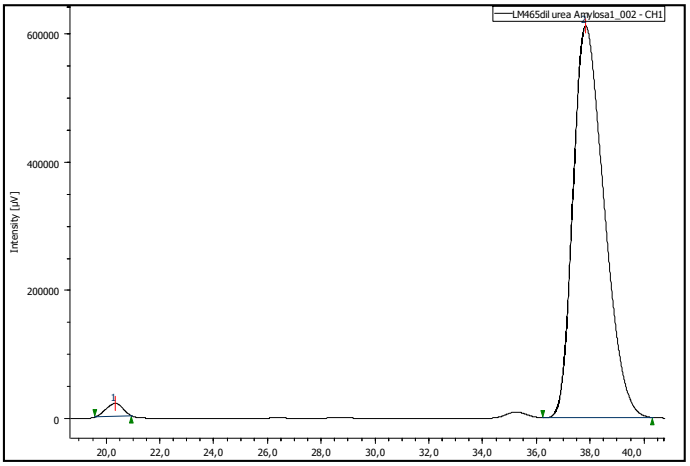
(*S*)-1-(2-Oxo-3-phenylindolin-3-yl)-3-phenylurea (10).





Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**20,092**	11682793	288021	**50,273**	65,501	1,142
2	**37,992**	11556092	151701	**49,727**	34,499	1,120

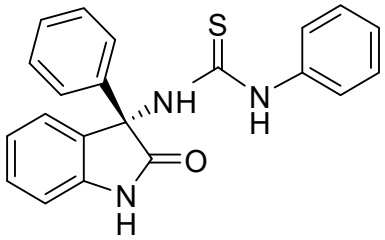
Figure S52. HPLC profile for **10** (racemic).

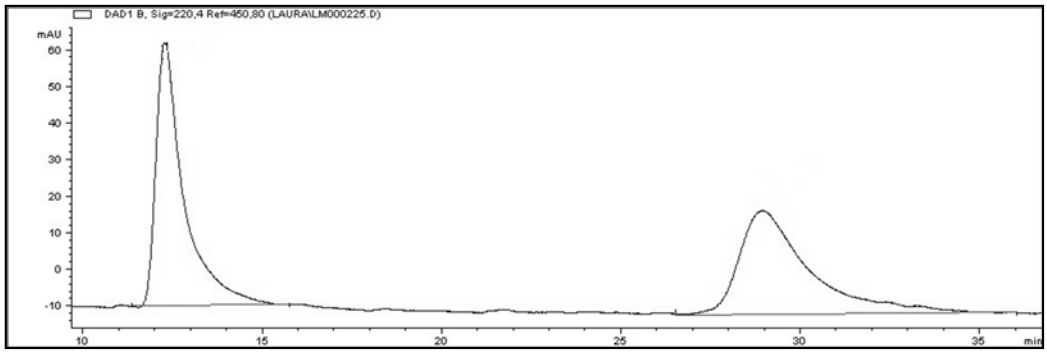


Peak Name	t_R	Area	Height	Area%	Height%	Symmetry
1	**20,342**	867306	20198	**1,749**	3,204	0,905
2	**37,800**	48720274	610210	**98,251**	96,796	1,347

Figure S53. HPLC profile for **10**. 98:2 er.

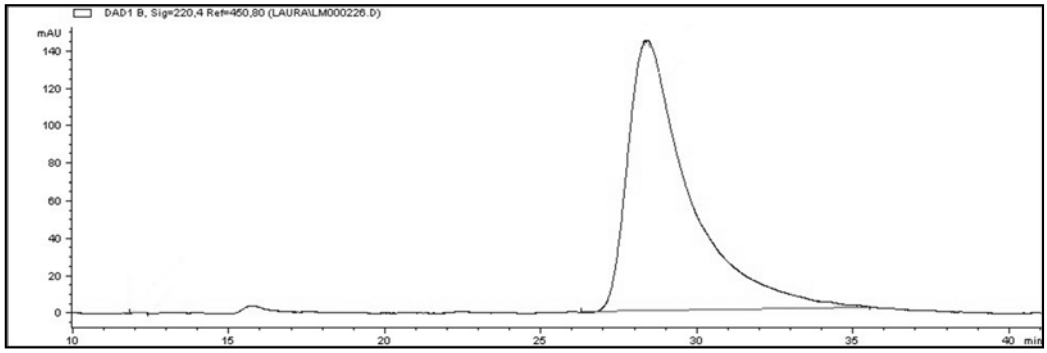
(*S*)-1-(2-Oxo-3-phenylindolin-3-yl)-3-phenylthiourea (11).





Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**12.273**	3922.5	72.4	0.9027	**49.933**	0.447
2	**28.949**	3933	28.6	2.2942	**50.067**	0.498

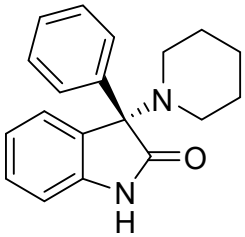
Figure S54. HPLC profile for **11** (racemic).

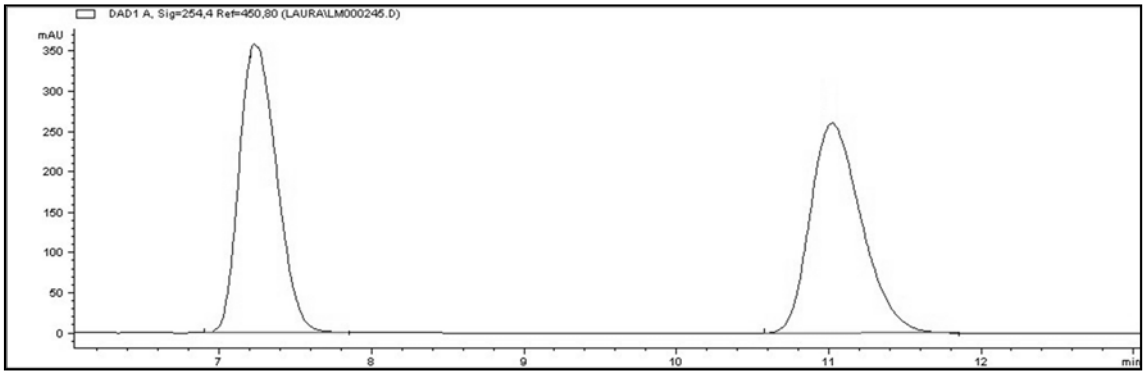


Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**12.100**	9.2	4.7E-1	0.3262	**0.046**	0.956
2	**28.378**	19863.2	144.8	2.2858	**99.954**	0.431

Figure S55. HPLC profile for **11**. 99:1 er.

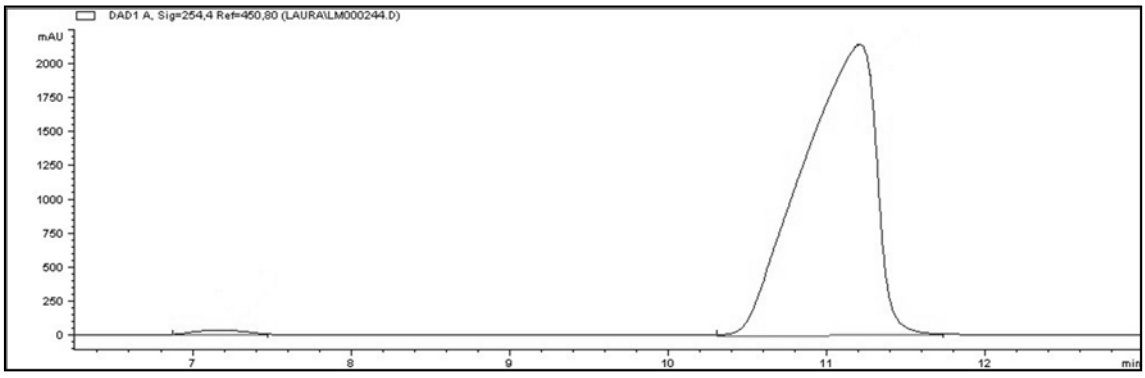
(*S*)-3-Phenyl-3-(piperidin-1-yl)indolin-2-one (12).





Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**7.232**	6095.7	360	0.2711	**49.930**	0.723
2	**11.019**	6112.8	260.4	0.3666	**50.070**	0.71

Figure S56. HPLC profile for **12** (racemic).



Peak Name	t_R	Area	Height	Width	Area%	Symmetry
1	**7.163**	834.5	34.8	0.3996	**1.195**	0.879
2	**11.204**	69020.5	2151.1	0.5348	**98.805**	3.001

Figure S57. HPLC profile for **12**. 99:1 er.