catalysts

Supplementary Material: Asymmetric Hydrogenation of 1-aryl Substituted-3,4-dihydroisoquinolines with Iridium Catalysts Bearing Different Phosphorus-based Ligands

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Table S1. Preliminary screening with L1-L7.

Entry	Ligand	Additive	Substrate	Solvent	Conversion %[b]	e.e.(*S* %) [b]
1	**L1**-*R*	DCDMH	1a	toluene	43	12
2	**L1**-*R*	NBS	3a	toluene	46	21
3	**L1**-*R*	NBS	8a	toluene	41	11
4	**L2**-*R*	DCDMH	1a	toluene	21	30
5	**L2**-*R*	NBS	3a	toluene	12	25
6	**L2**-*R*	NBS	8a	toluene	11	-
7	**L3**-RR_{ax}	DCDMH	1a	toluene	38	33
8	**L3**-RR_{ax}	NBS	3a	toluene	22	31
9	**L3**-RR_{ax}	NBS	8a	toluene	8	-
10	**L4**-*R*	NBS	1a	THF	68	55
11	**L4**-*R*[a]	DCDMH	1a	toluene	44	61
12	**L4**-*R*	H_3PO_4	1a	toluene	65	51
13	**L4**-*R*	H_3PO_4	1a	CH_2Cl_2	99	67
14	**L4**-*R*	H_3PO_4	2a	CH_2Cl_2	99	69
15	**L4**-*R*	H_3PO_4	3a	CH_2Cl_2	99	89
16	**L4**-*R*	H_3PO_4	8a	CH_2Cl_2	99	40
17	**L5**-SSS_{ax}	DCDMH	1a	toluene	60	52
18	**L5**-SSS_{ax}	H_3PO_4	1a	toluene	45	47
19	**L5**-SSS_{ax}	H_3PO_4	1a	CH_2Cl_2	66	53
20	**L5**-SSS_{ax}	H_3PO_4	6a	CH_2Cl_2	43	72
21	**L5**-SSS_{ax}	H_3PO_4	8a	CH_2Cl_2	60	75
22	**L6**-RR_{ax}	NBS	3a	toluene	72	22
23	**L6**-RR_{ax}	NBS	8a	toluene	10	28
24	**L6**-RR_{ax}	H_3PO_4	1a	toluene	5	20
25	**L6**-RR_{ax}	H_3PO_4	1a	CH_2Cl_2	22	23
26	**L6**-RR_{ax}	H_3PO_4	8a	CH_2Cl_2	14	27
27	**L7**-$SR_{ax}R_{ax}$	NBS	3a	toluene	44	27
28	**L7**-$SR_{ax}R_{ax}$	NBS	8a	toluene	38	12
29	**L7**-$SR_{ax}R_{ax}$	H_3PO_4	1a	toluene	12	-
30	**L7**-$SR_{ax}R_{ax}$	H_3PO_4	1a	CH_2Cl_2	15	22
31	**L7**-$SR_{ax}R_{ax}$	H_3PO_4	8a	CH_2Cl_2	35	10

Reactions were conducted using 1 mol % iridium complex in solvent with additive (catalyst:additive = 1:10) at 20°C and 20 atm of H_2 pressure for 12 h; DCDMH=1,3-dichloro-5,5-dimethyl-hydantoin. [a] Reaction was conducted using 0.4 mol % iridium complex. [b] Conversion was determined by ^{1}H-NMR while enantiomeric excess was determined by HPLC equipped with chiral column (Chiralcel OD-H).

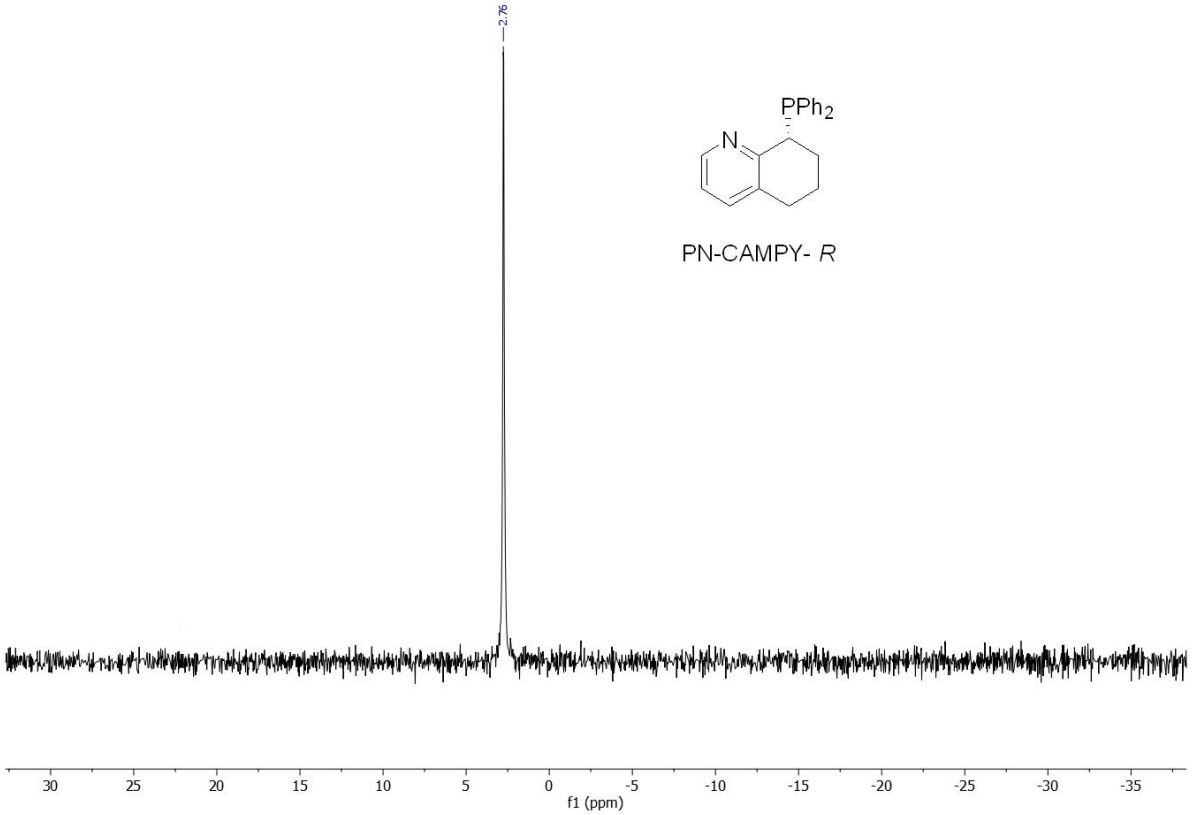

Figure S1. ^{31}P-NMR spectrum of ligand L1.

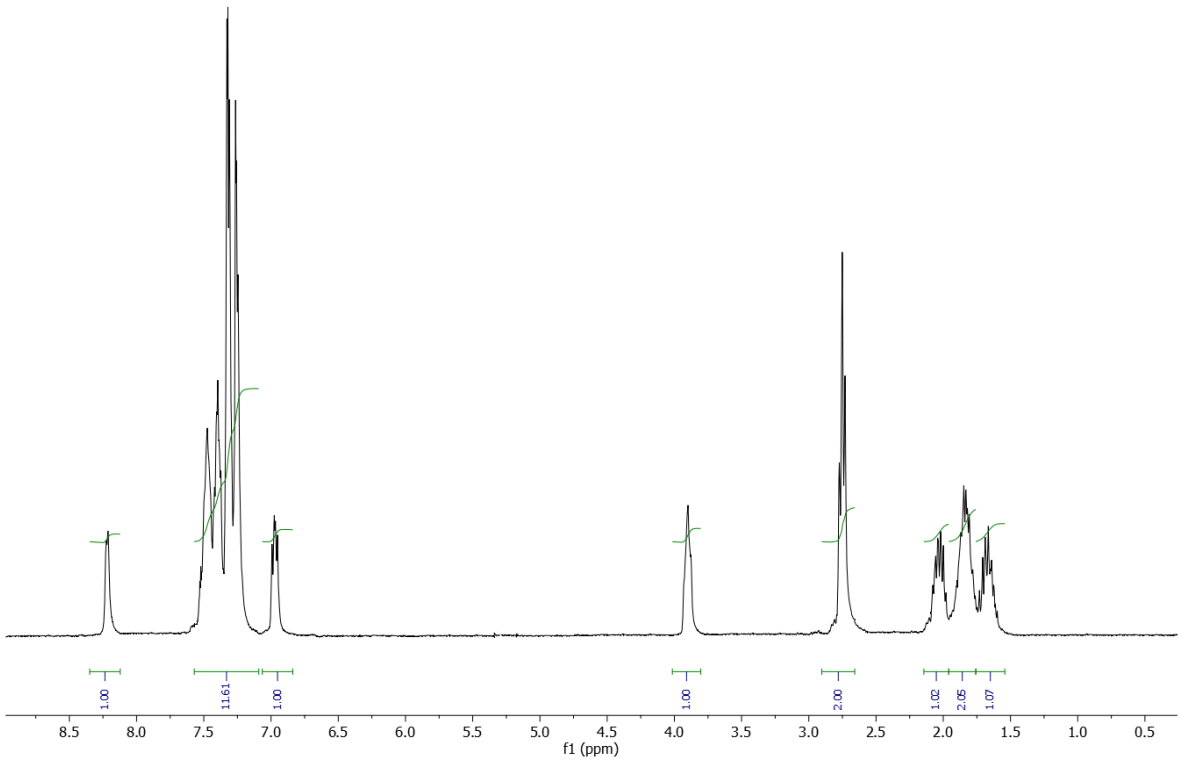

Figure S2. ^{1}H- NMR spectrum of ligand L1. ^{13}C-NMR and HPLC spectra.

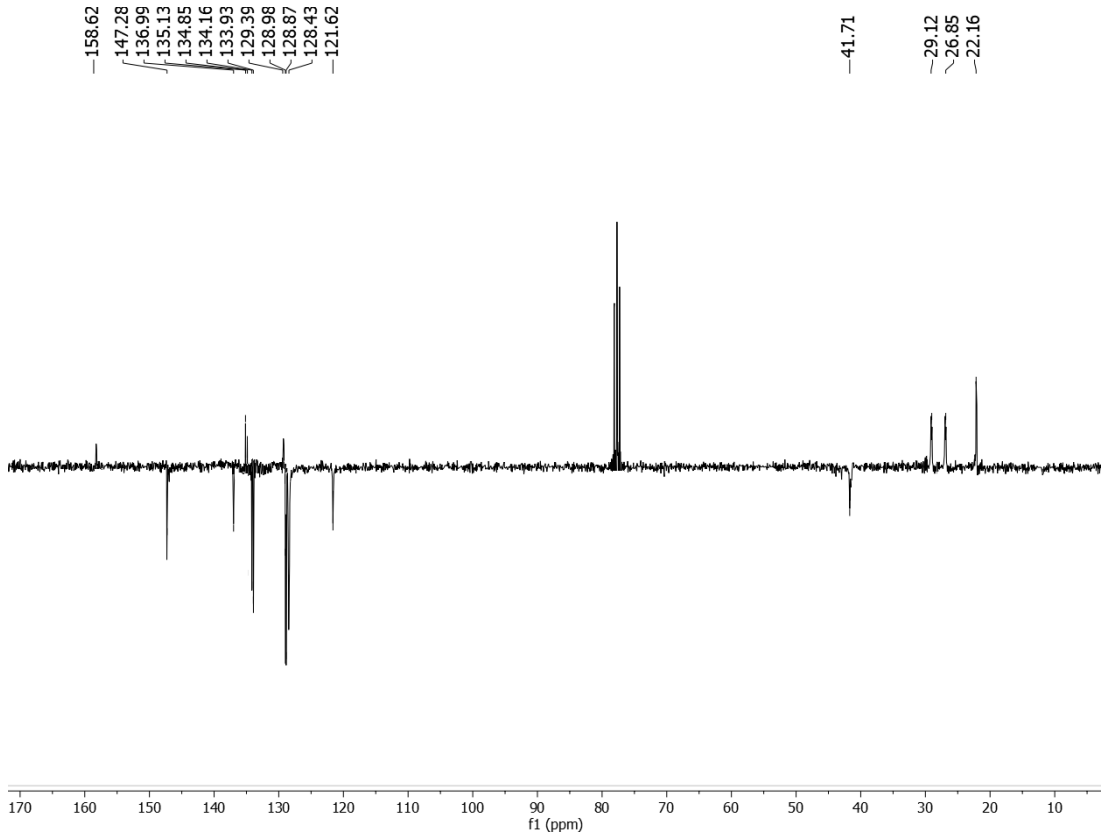

Figure S3. ^{13}C-NMR spectrum of ligand L1.

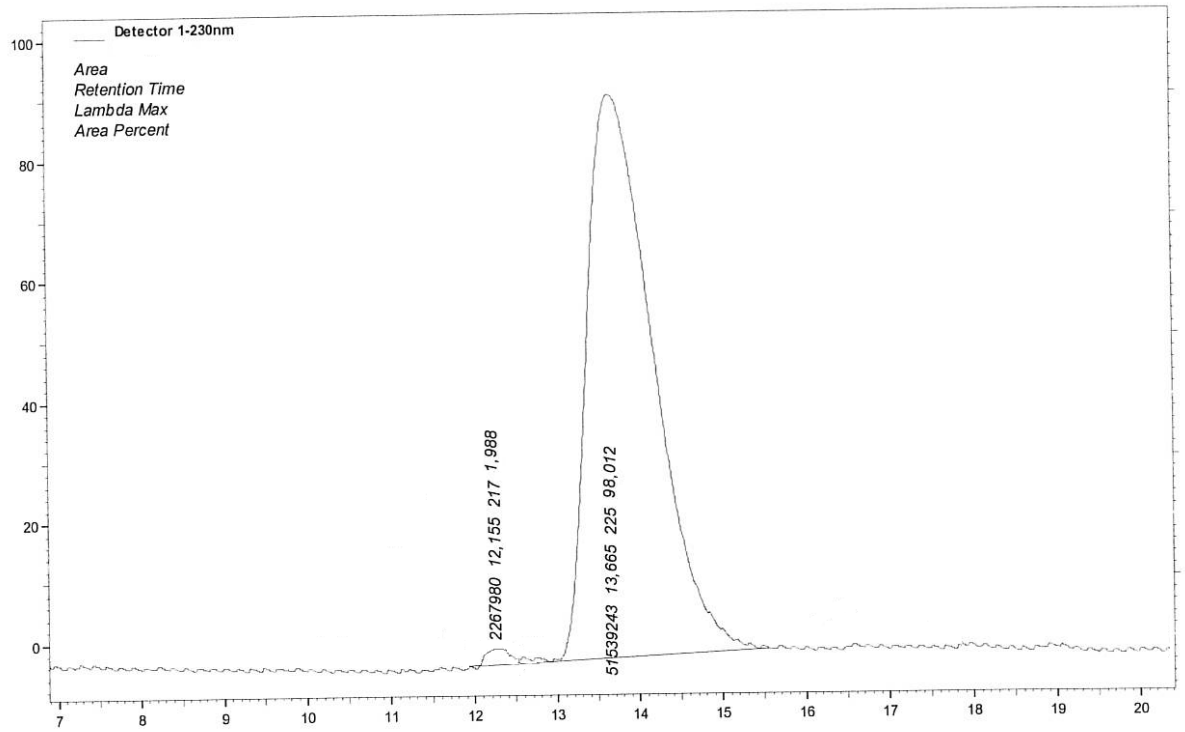

Figure S4. HPLC spectrum of ligand L1. HPLC analysis to confirm 96 % e.e. of (*R*)-L-**1** starting from (*S*)-5,6,7,8-tetrahydroquinolin-ol. Chiralpak OJ-H; eluent: 2-propanol/hexane=10/90, Flow=0.6 mL/min, λ=220 nm, (*S*)-isomer: 12.1 min, (*R*)-isomer: 13.6 min.

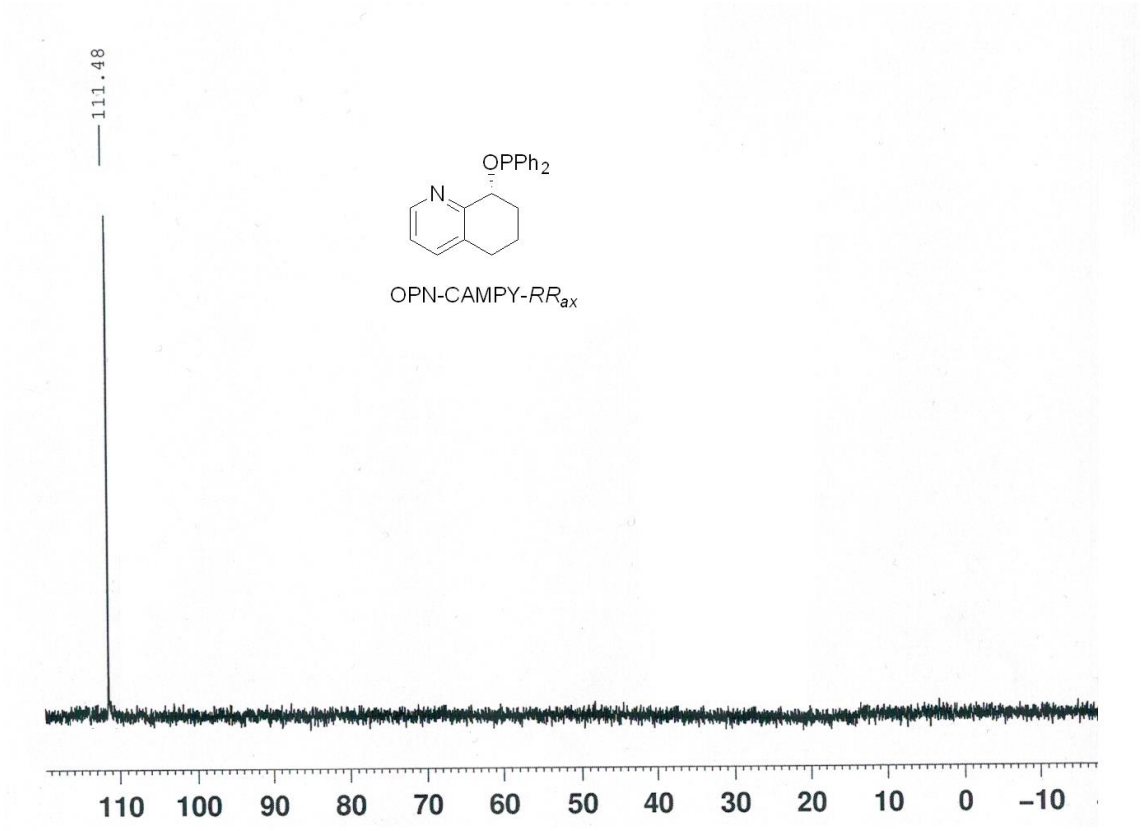

Figure S5. ^{31}P-NMR spectrum of ligand L2.[1].

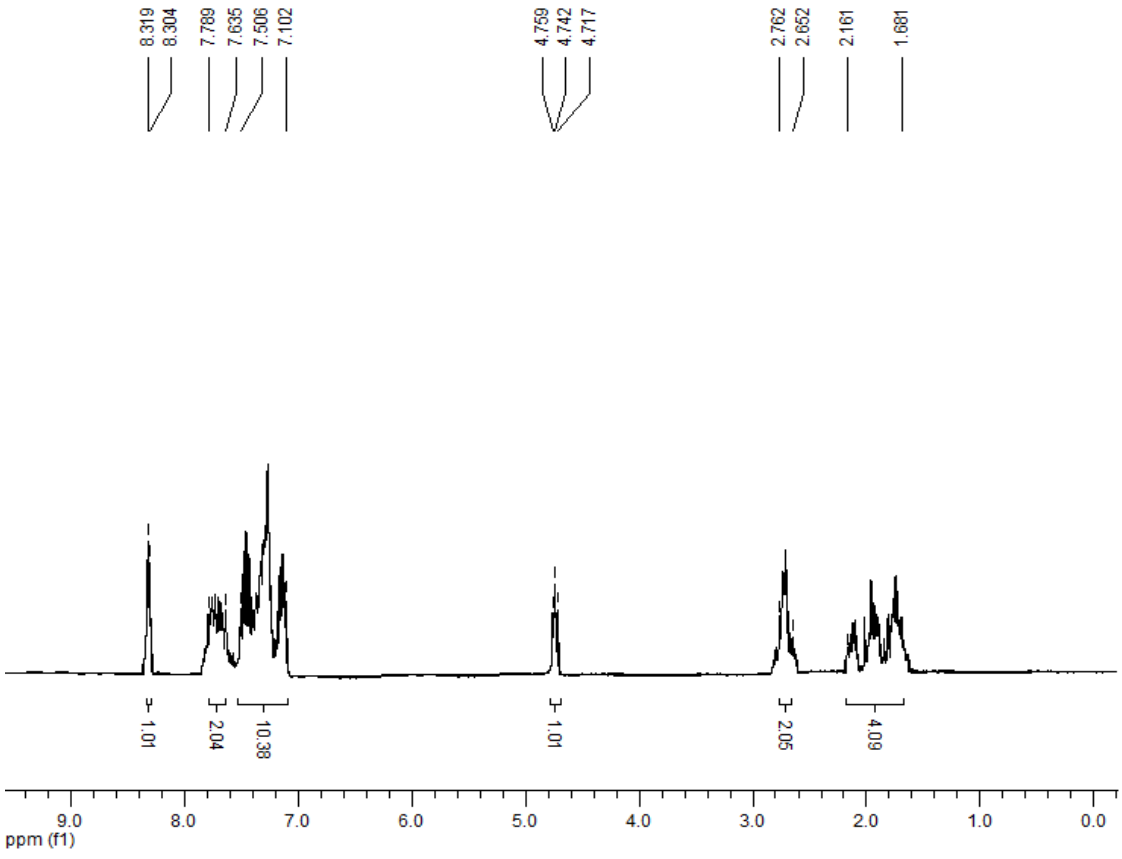

Figure S6. ^{1}H-NMR spectrum of ligand L2.

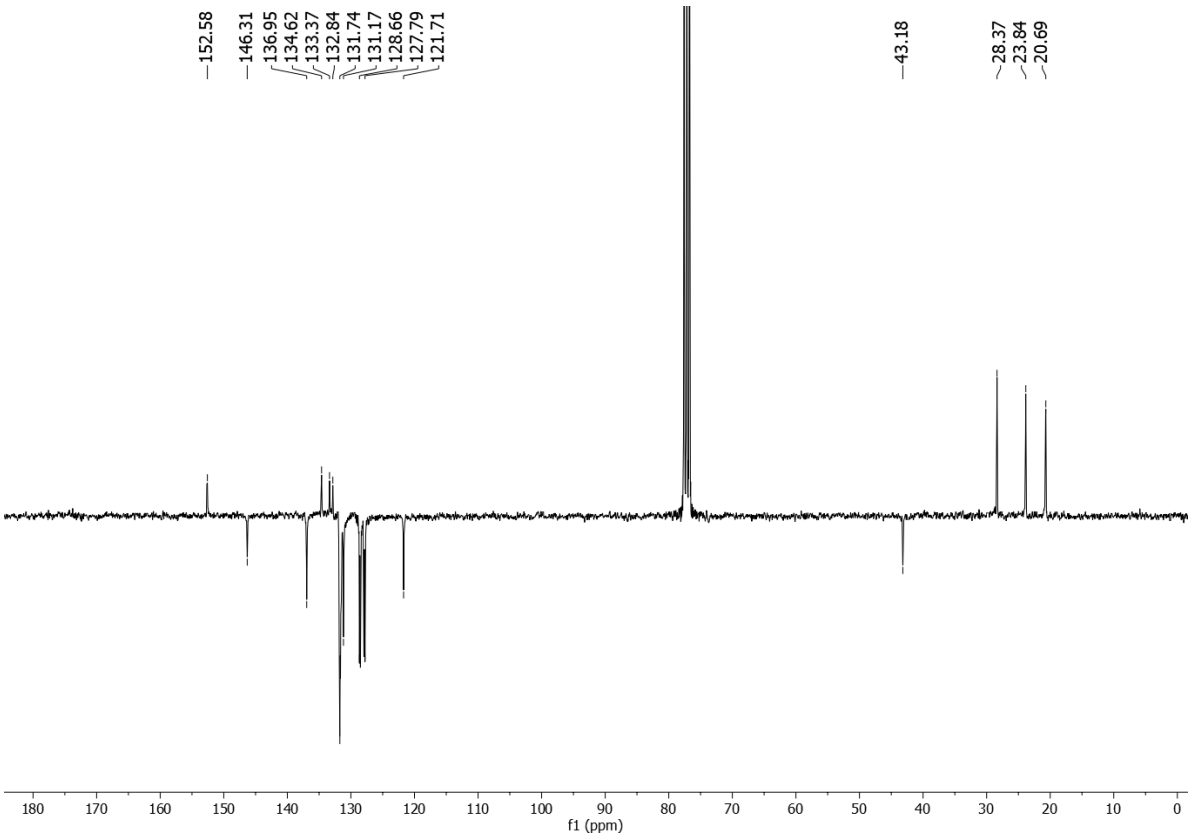

Figure S7. ^{13}C-NMR spectrum of ligand L2.

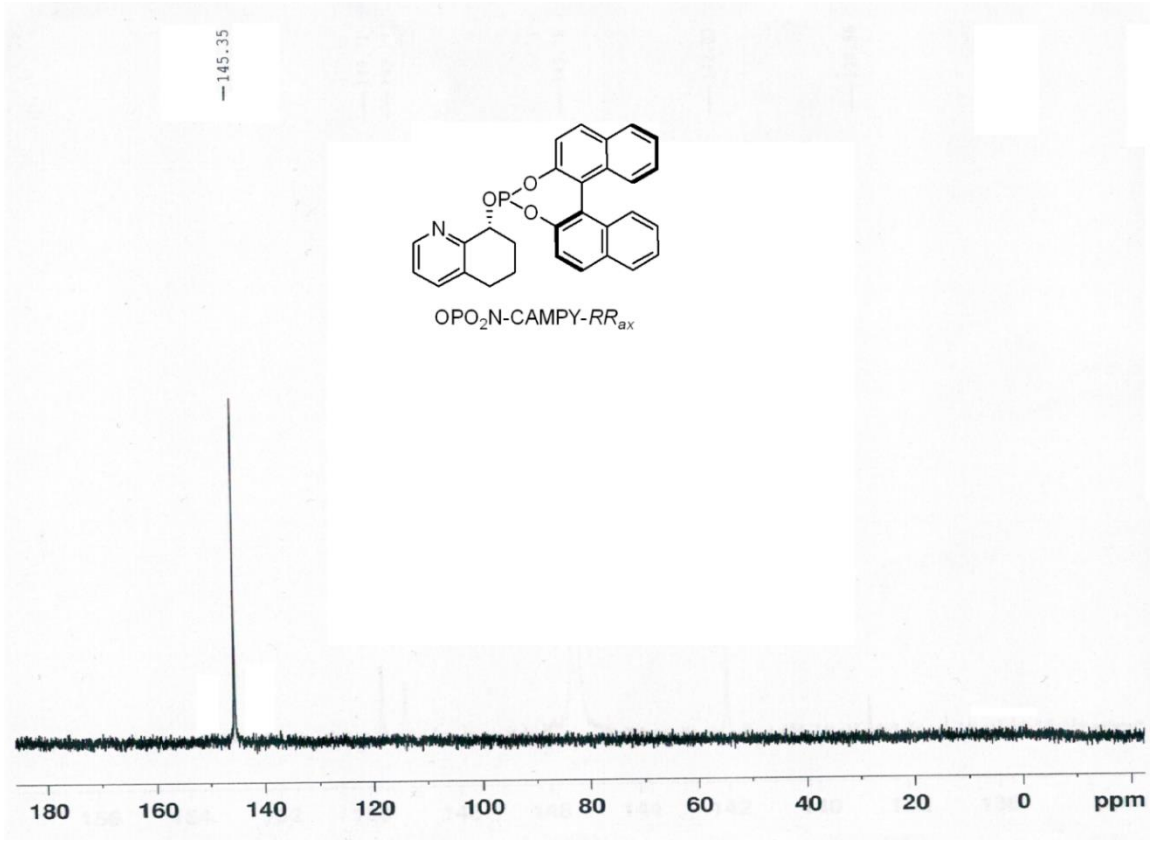

Figure S8. ^{31}P-NMR spectrum of ligand L3.

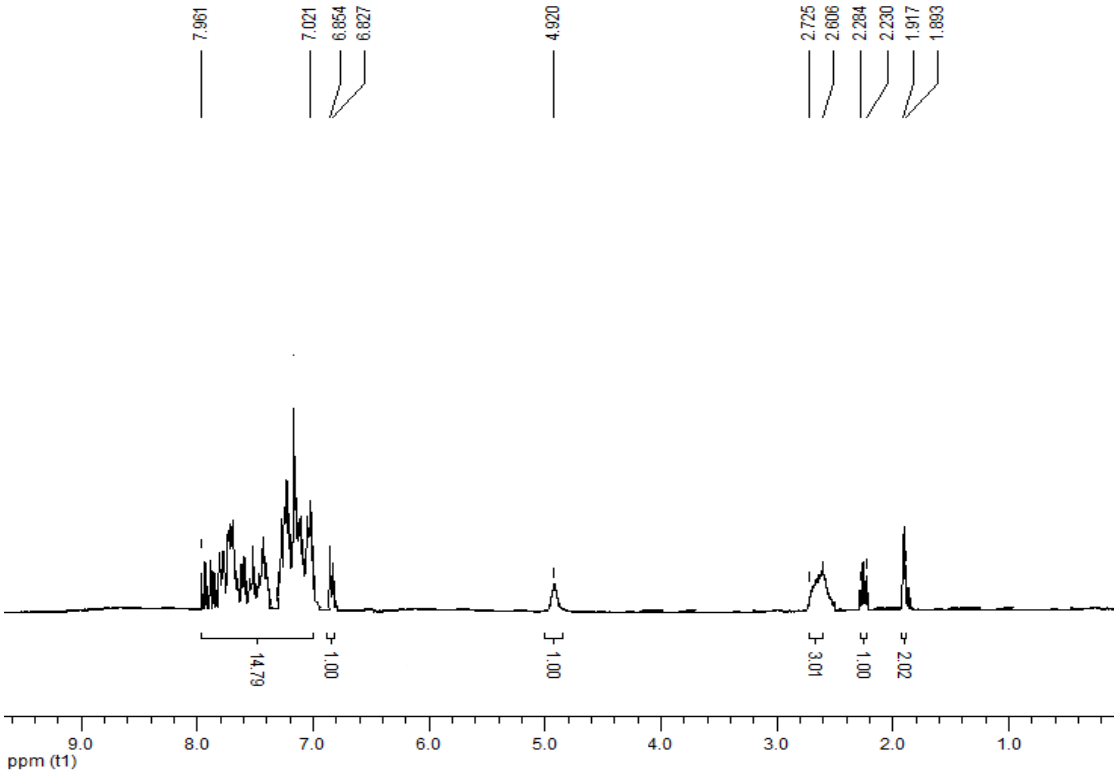

Figure S9. [1]H-NMR spectrum of ligand L3.

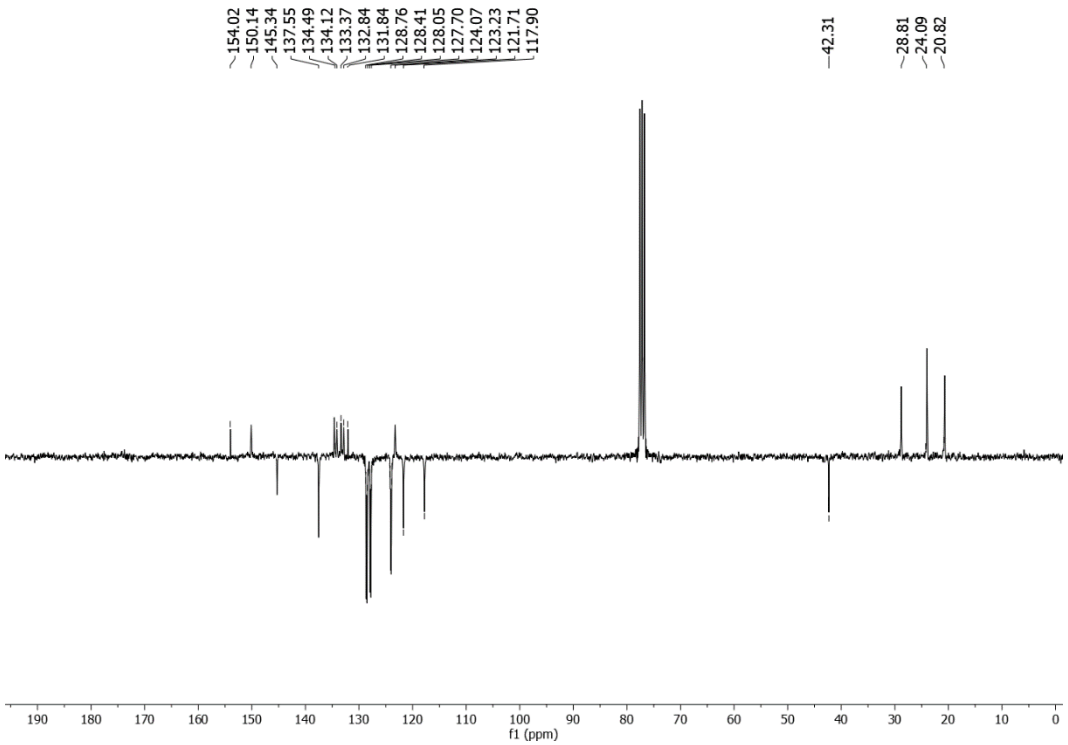

Figure S10. [13]C-NMR spectrum of ligand L3.

^{1}H-NMR spectra of substrates 1-10a and Products 1-10b[2-7]

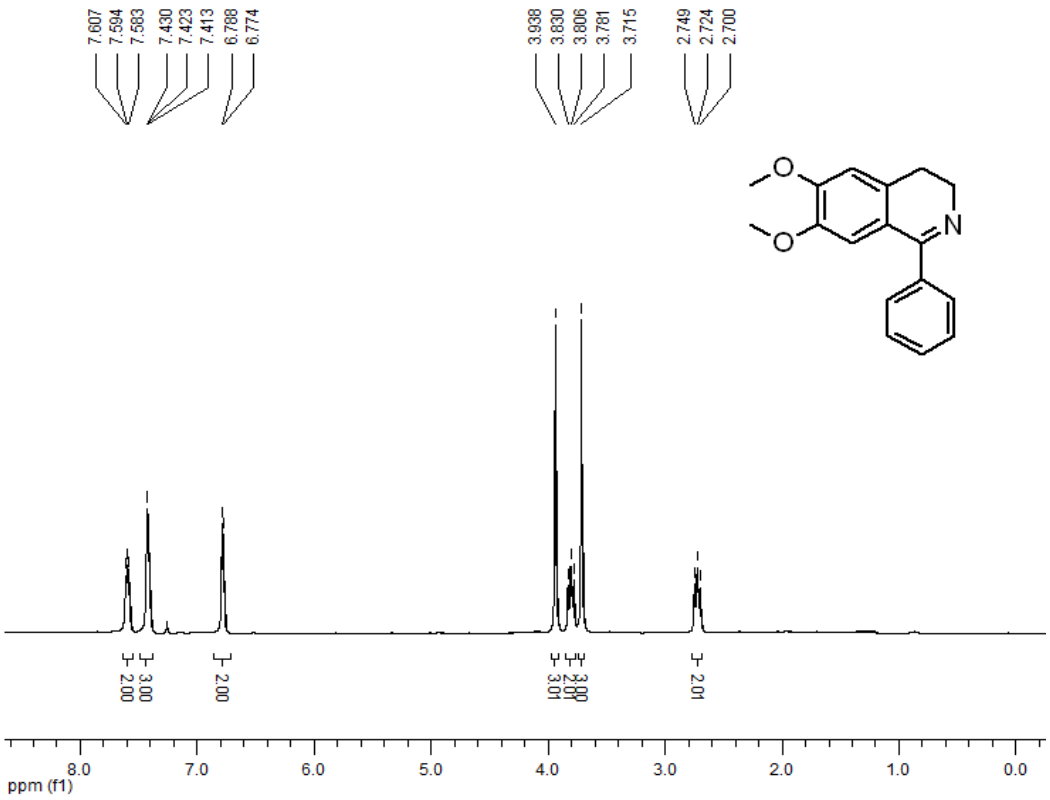

Figure S11. ^{1}H-NMR spectrum of 6,7-dimethoxy-1-phenyl-3,4-dihydroisoquinoline 1a.

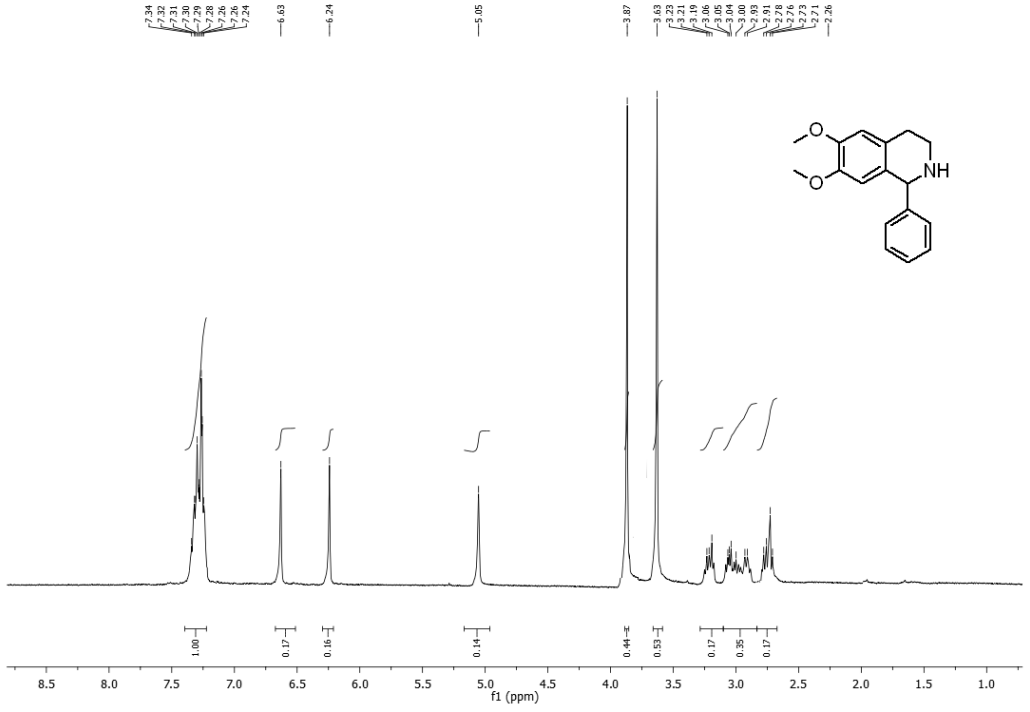

Figure S12. ^{1}H-NMR spectrum of 6,7-dimethoxy-1-phenyl-1,2,3,4-tetrahydroisoquinoline 1b.

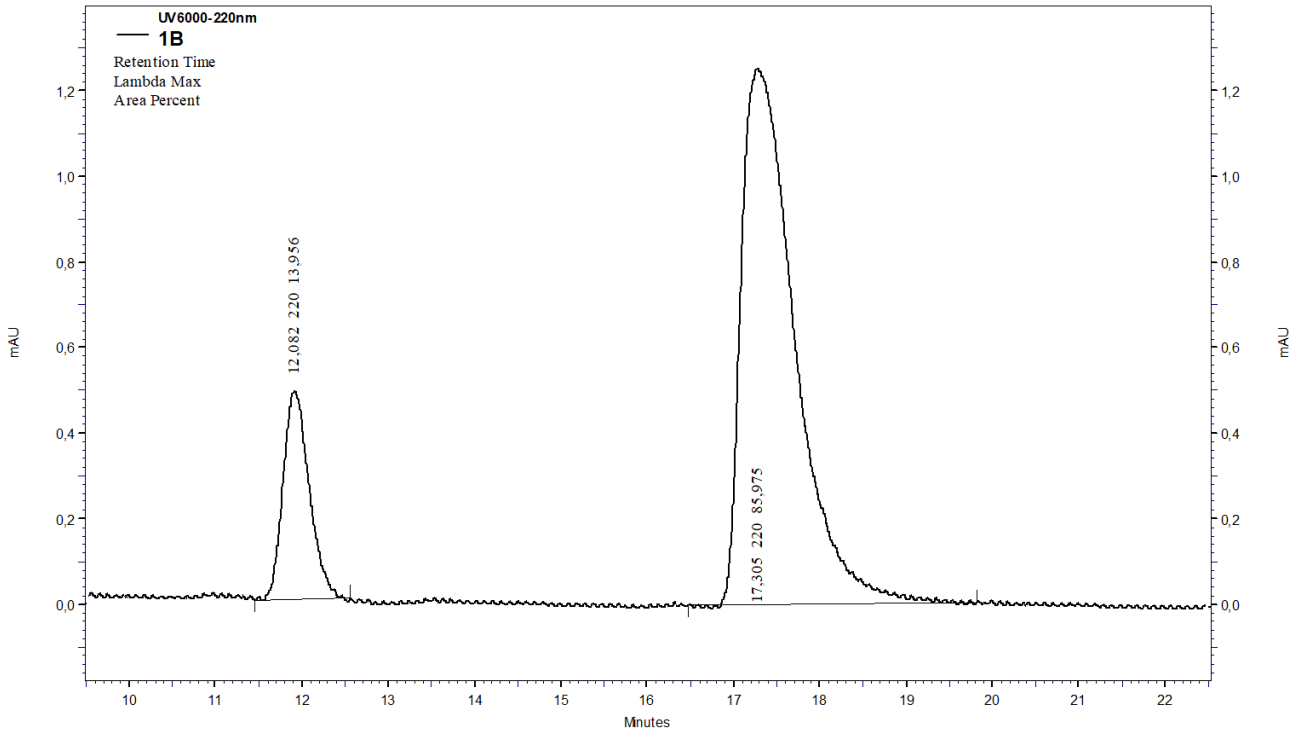

Figure S13. HPLC spectrum of 1b obtained by reduction with Ir-L4 (72 % e.e.).

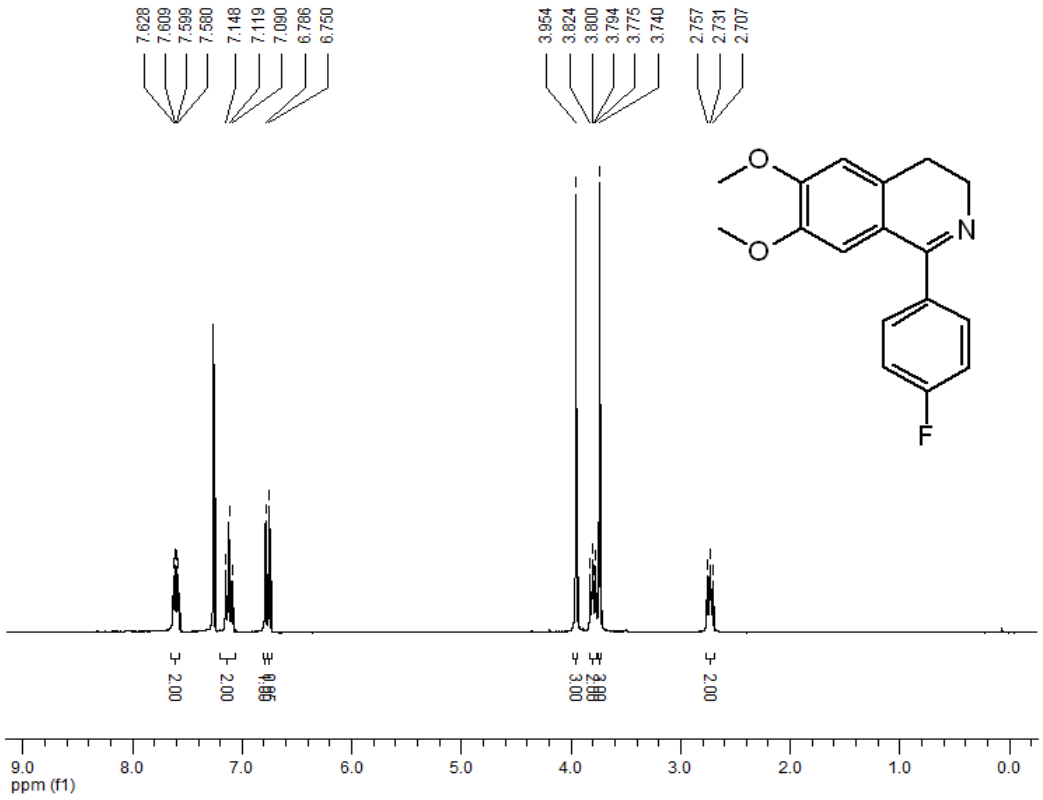

Figure S14. [1]H-NMR spectrum of 1-(4-fluorophenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline 2a.

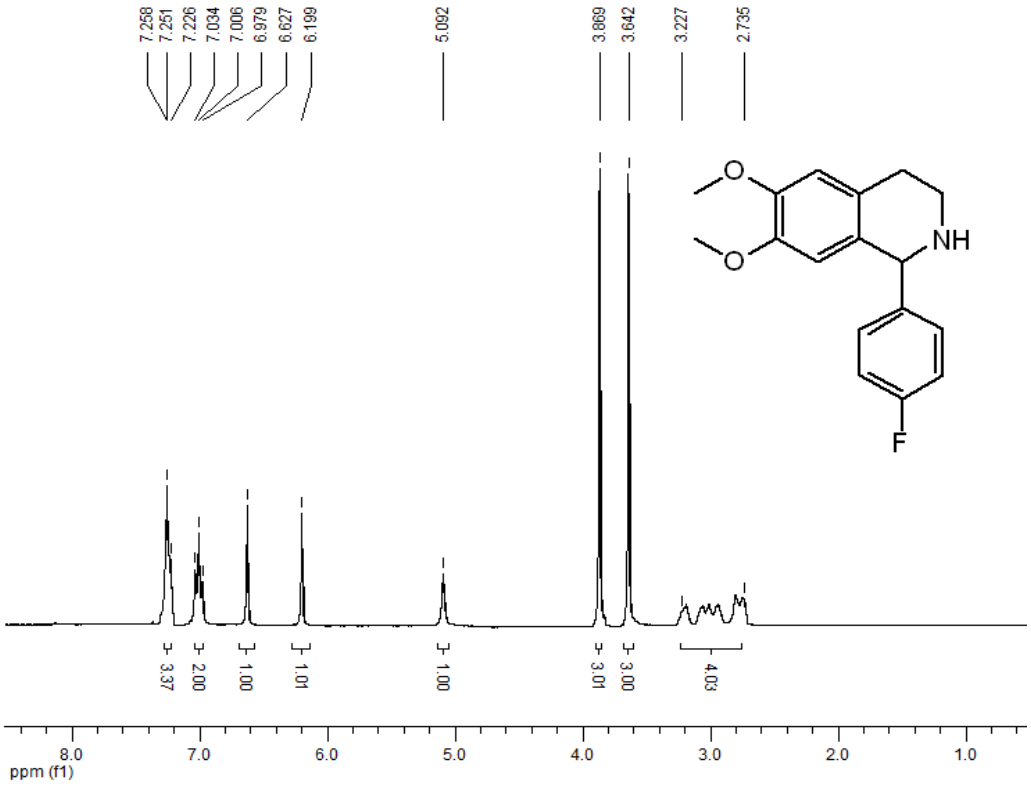

Figure S15. ^{1}H-NMR spectrum of 1-(4-fluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline 2b.

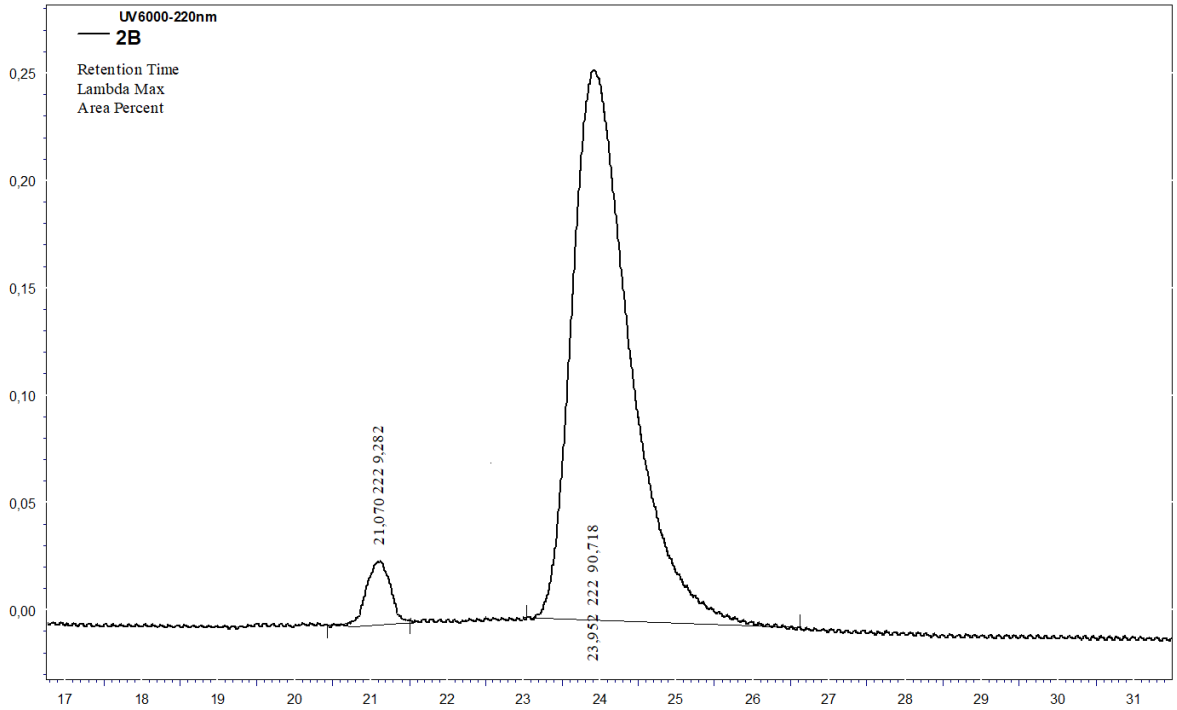

Figure S16. HPLC spectrum of 2b obtained by reduction with Ir-L4 (81 % e.e.).

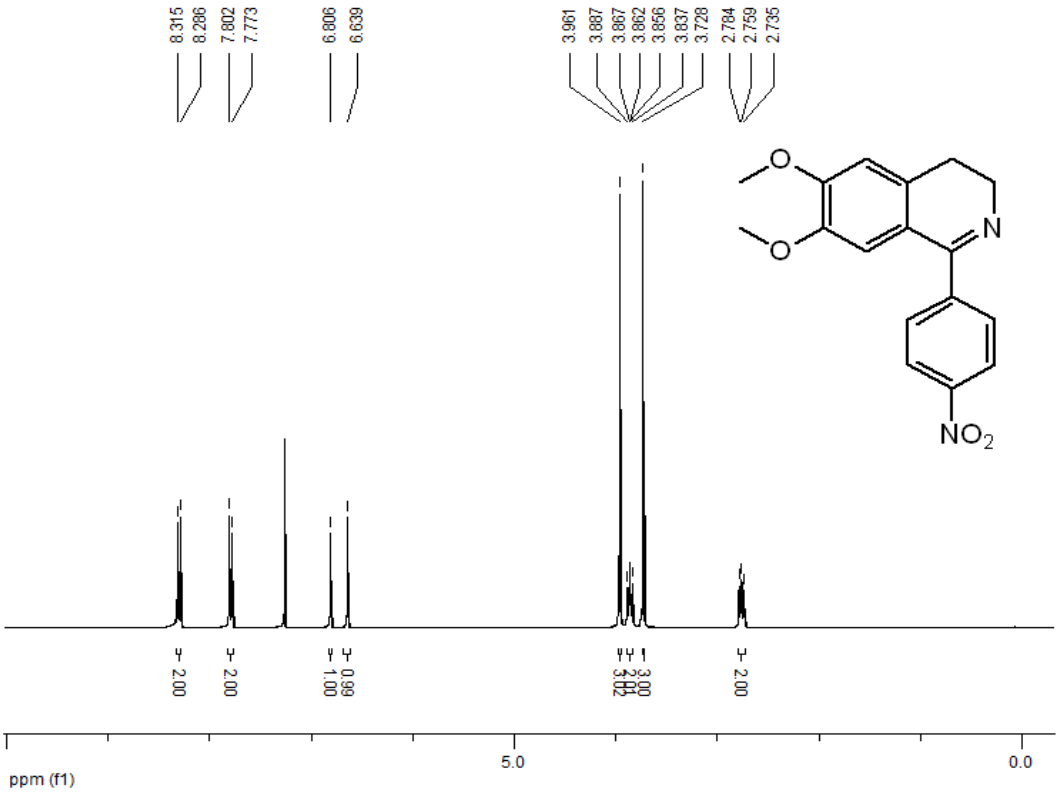

Figure S17. [1]H-NMR spectrum of 6,7-dimethoxy-1-(4-nitrophenyl)-3,4-dihydroisoquinoline 3a.

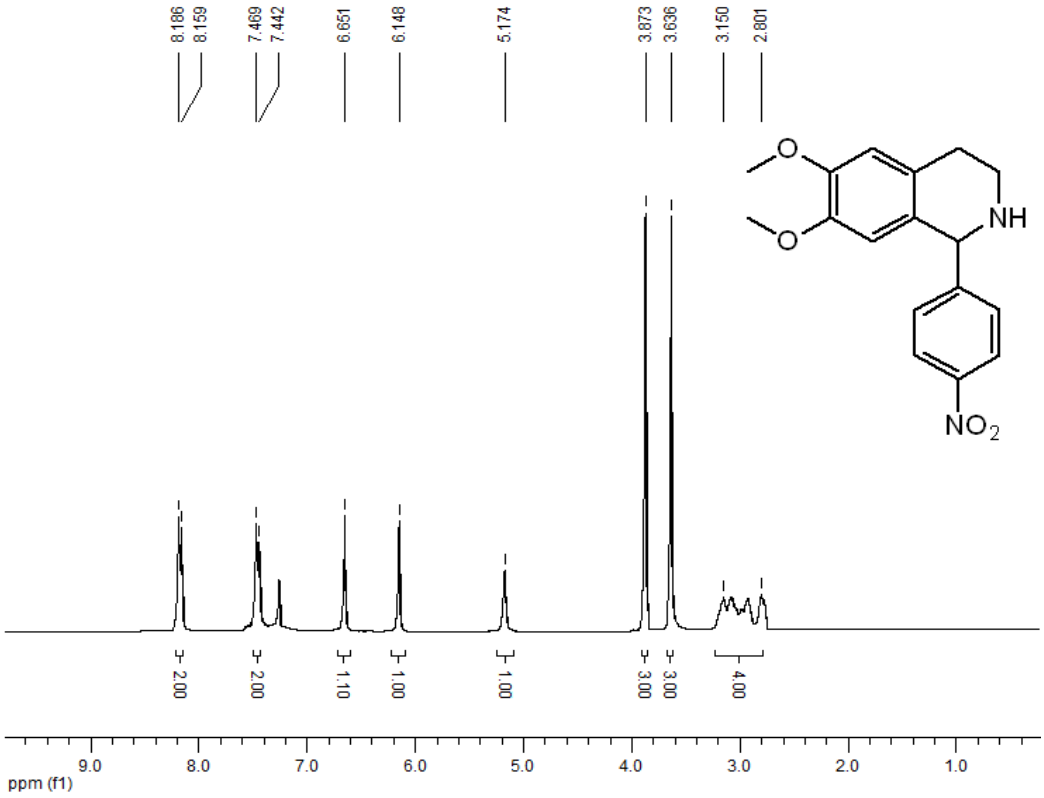

Figure S18. [1]H-NMR spectrum of 6,7-dimethoxy-1-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline 3b.

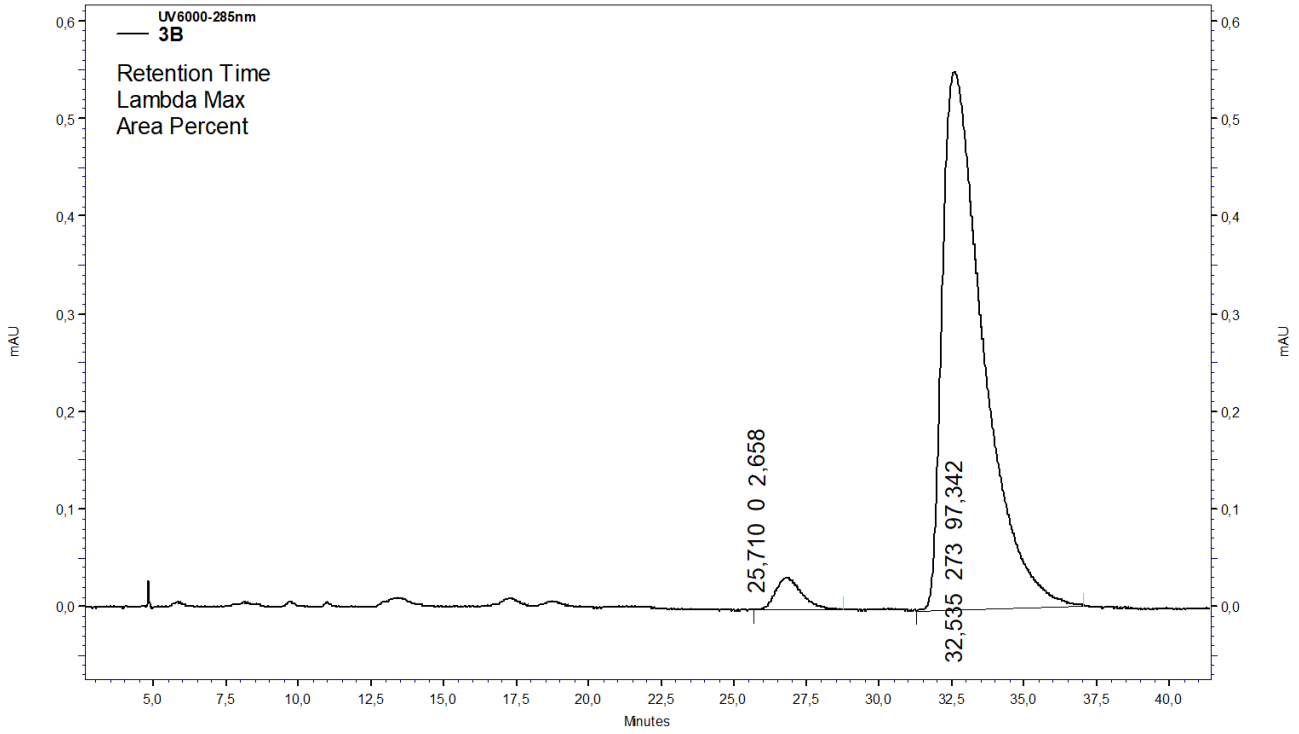

Figure S19. HPLC spectrum of 3b obtained by reduction with Ir-L4 (94 % e.e.).

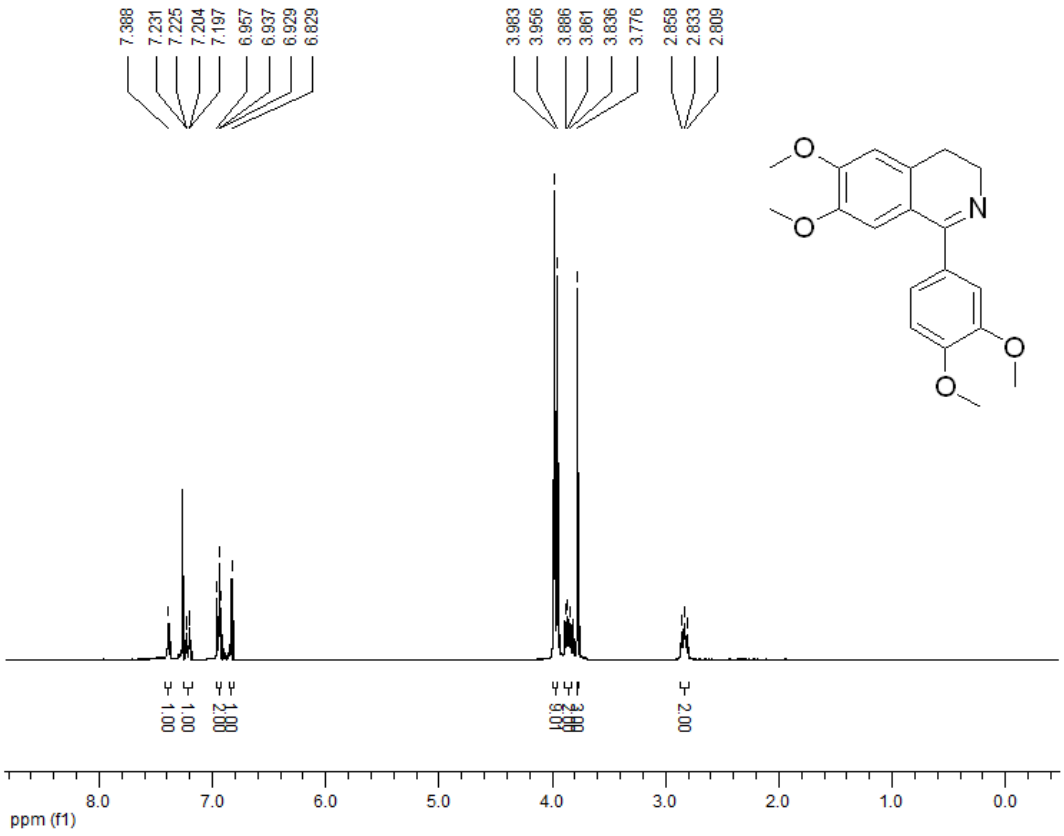

Figure S20. [1]H-NMR spectrum of 1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline 4a.

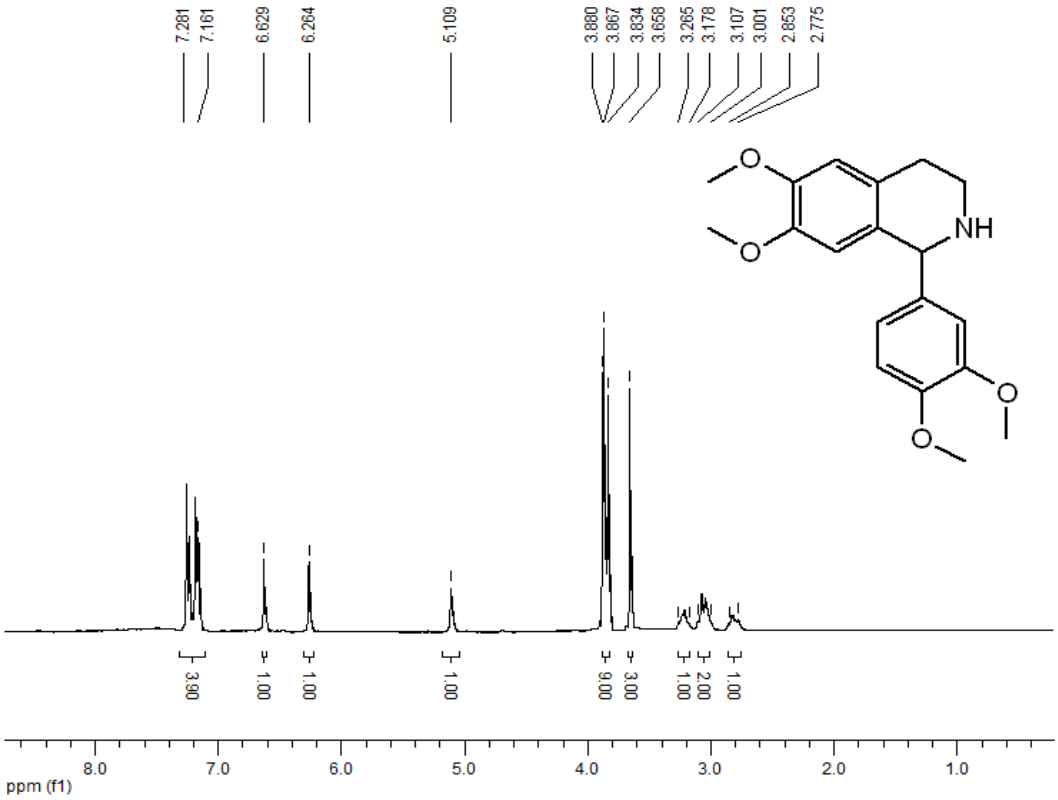

Figure S21. ^{1}H-NMR spectrum of 1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline 4b.

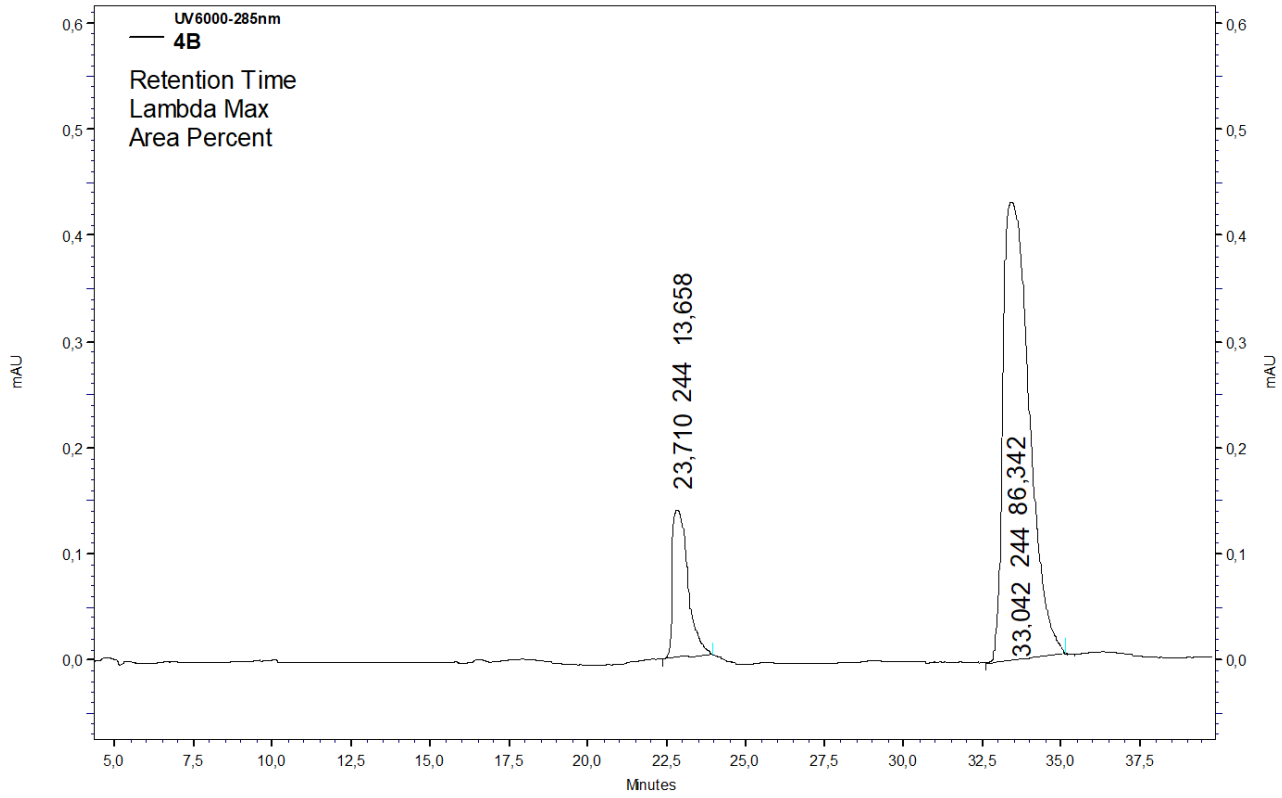

Figure S22. HPLC spectrum of 4b obtained by reduction with Ir-L4 (72 % e.e.).

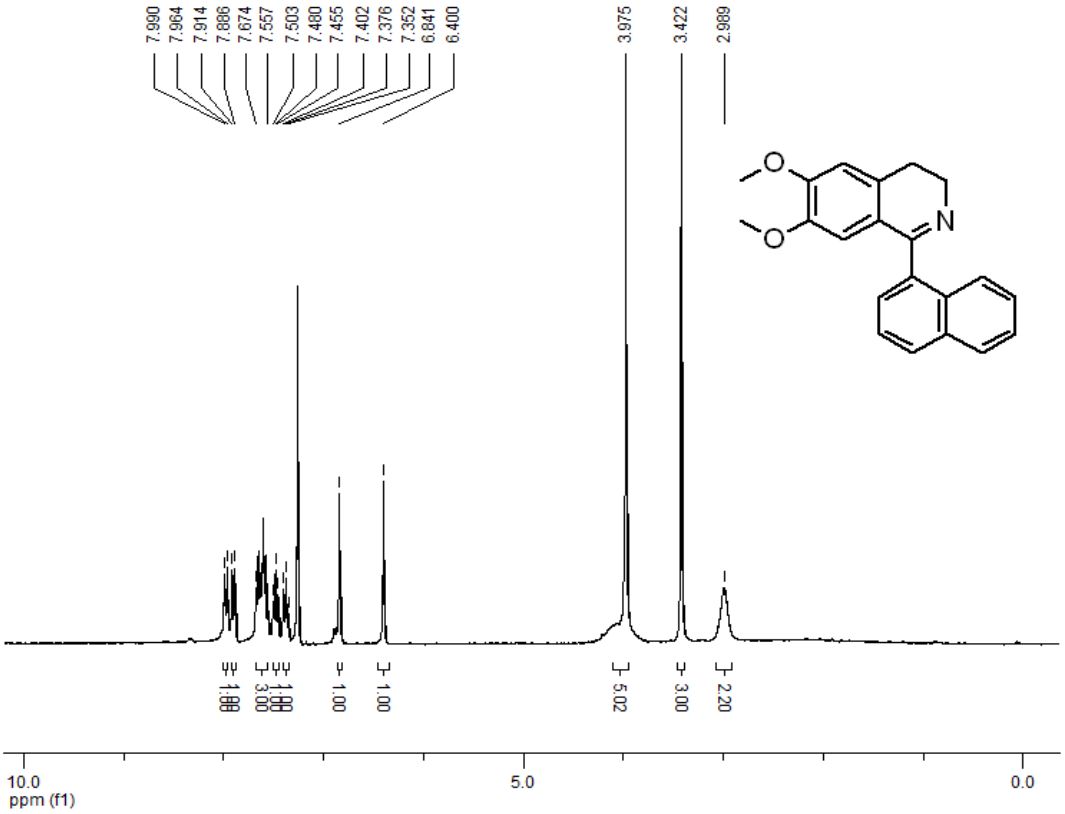

Figure S23. ^{1}H-NMR spectrum of 6,7-dimethoxy-1-(naphthalen-1-yl)-3,4-dihydroisoquinoline 5a.

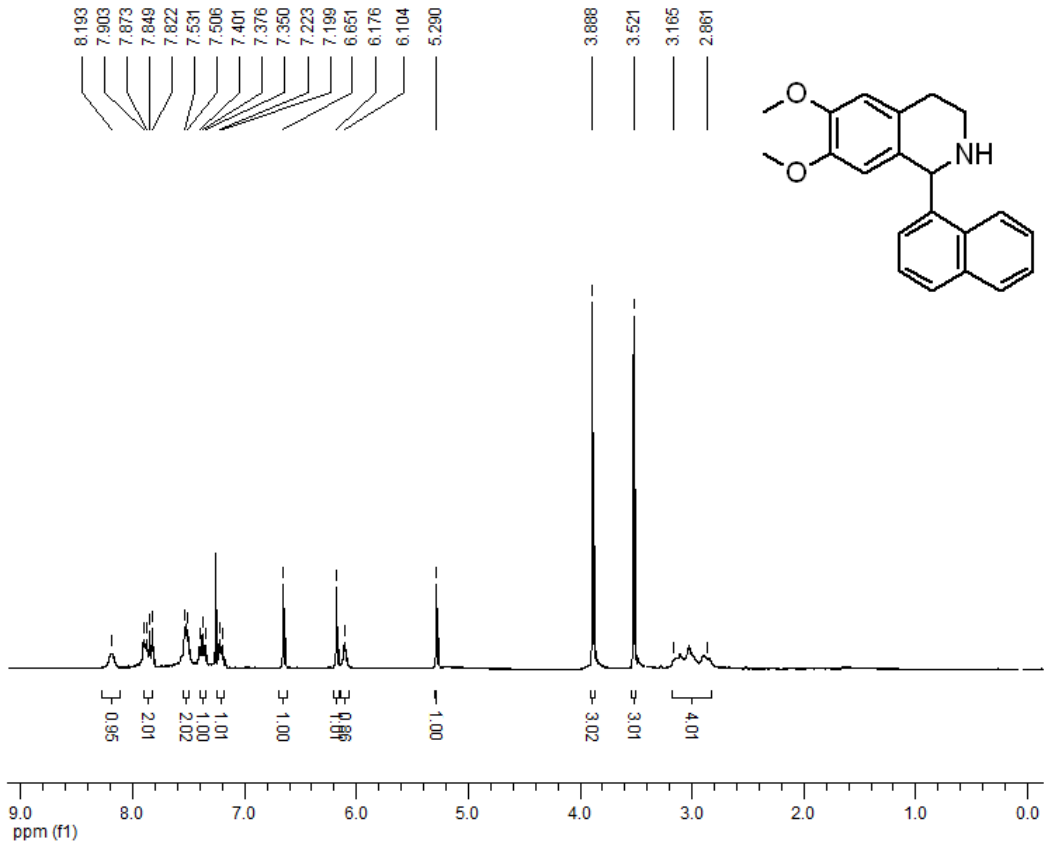

Figure S24. [1]H-NMR spectrum of 6,7-dimethoxy-1-(naphthalen-1-yl)-1,2,3,4-tetrahydroisoquinoline 5b.

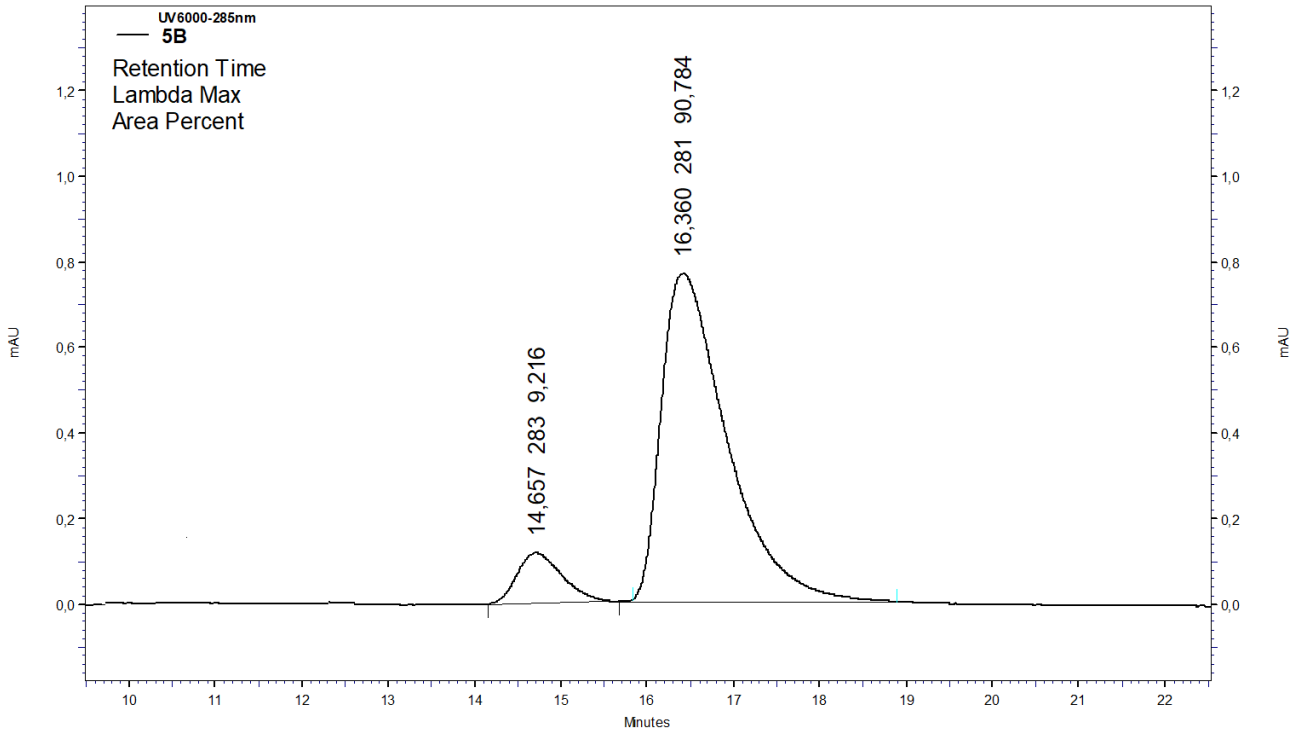

Figure S25. HPLC spectrum of 5b obtained by reduction with Ir-L4 (82 % e.e.).

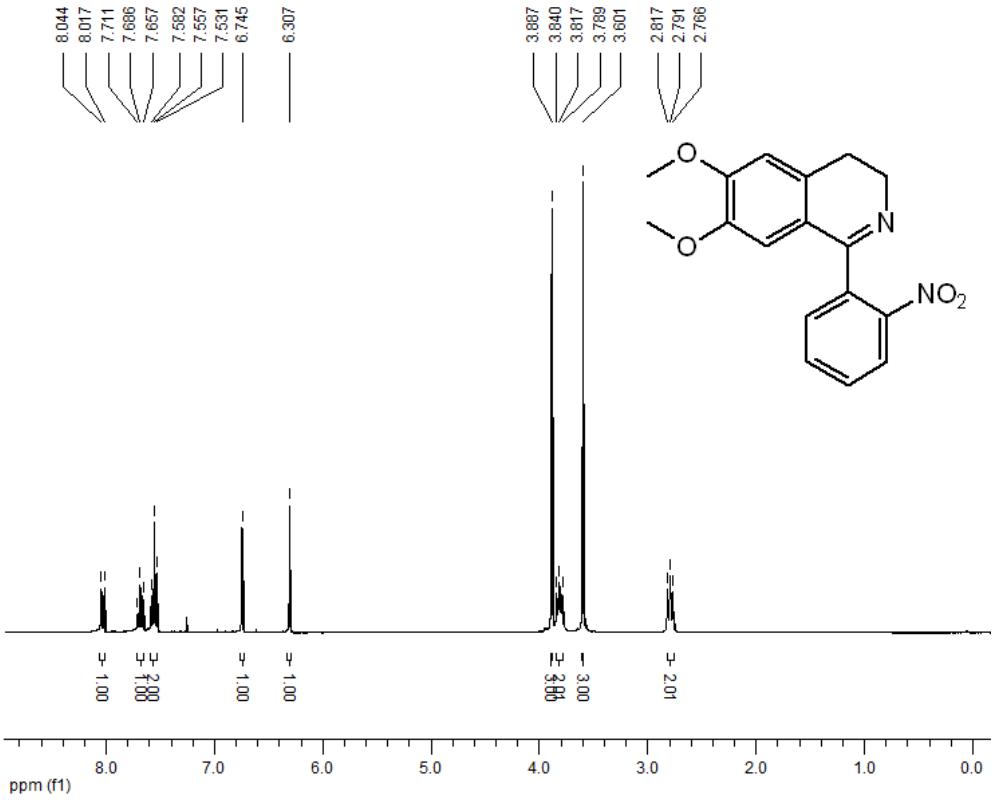

Figure S26. [1]H-NMR spectrum of 6,7-dimethoxy-1-(2-nitrophenyl)-3,4-dihydroisoquinoline 6a.

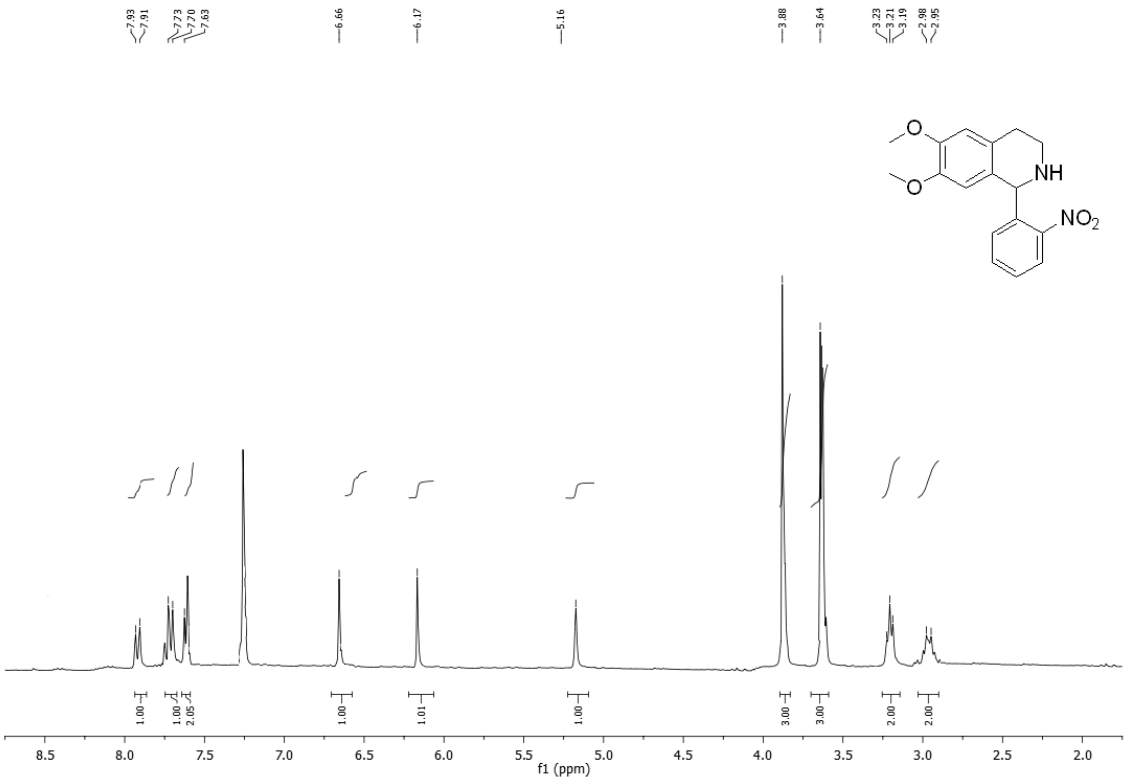

Figure S27. [1]H-NMR spectrum of 6,7-dimethoxy-1-(2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline 6b.

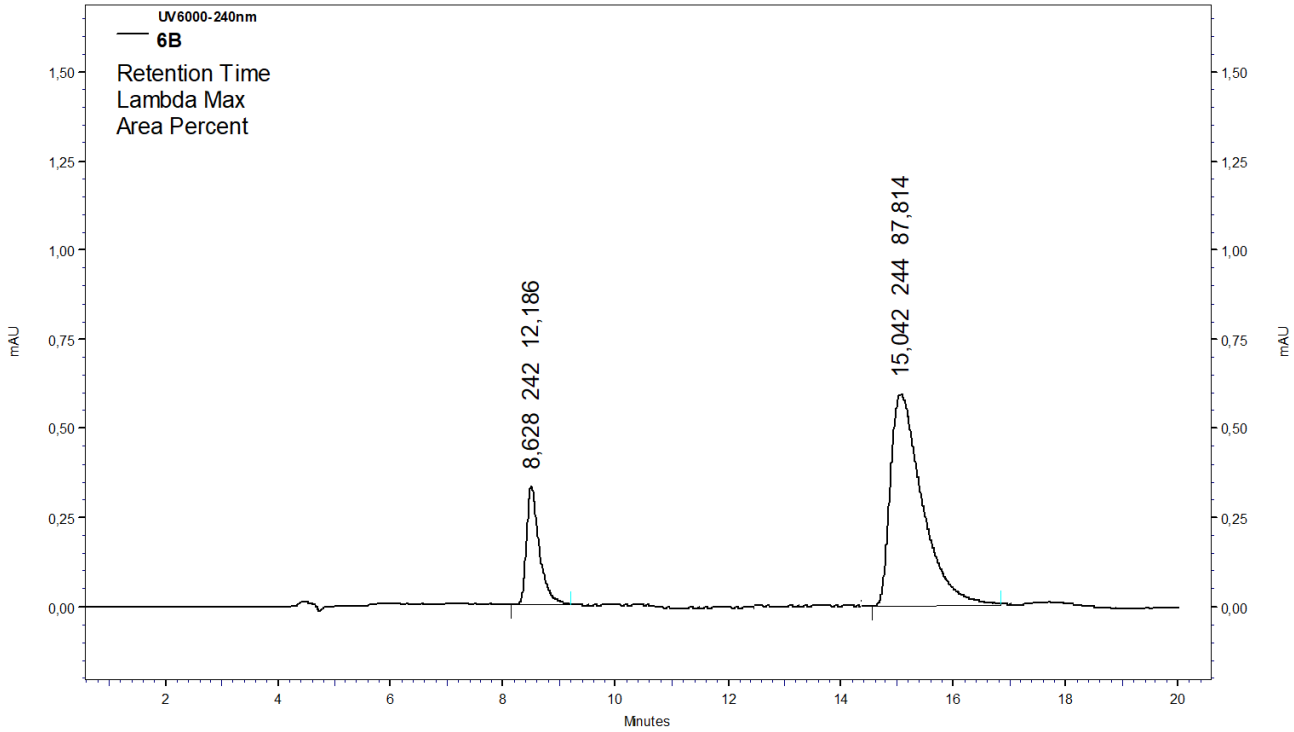

Figure S28. HPLC spectrum of 6b obtained by reduction with Ir-L5 (76 % e.e.).

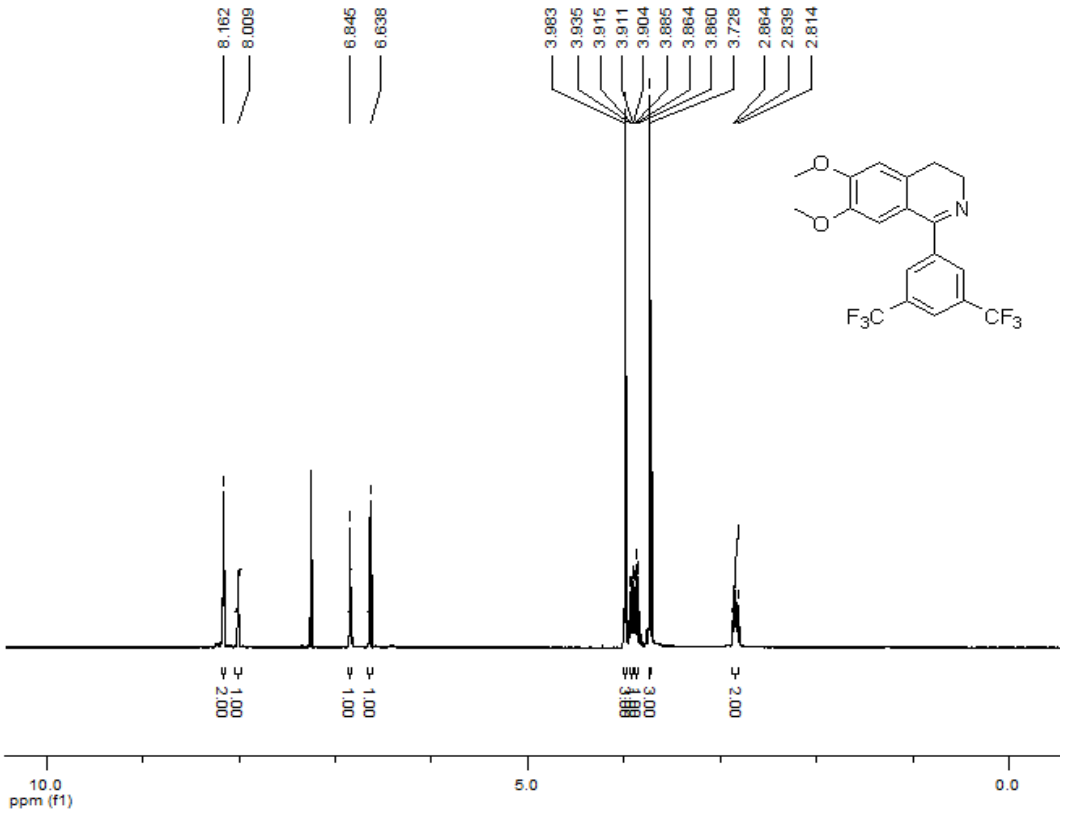

Figure S29. [1]H-NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline 7a.

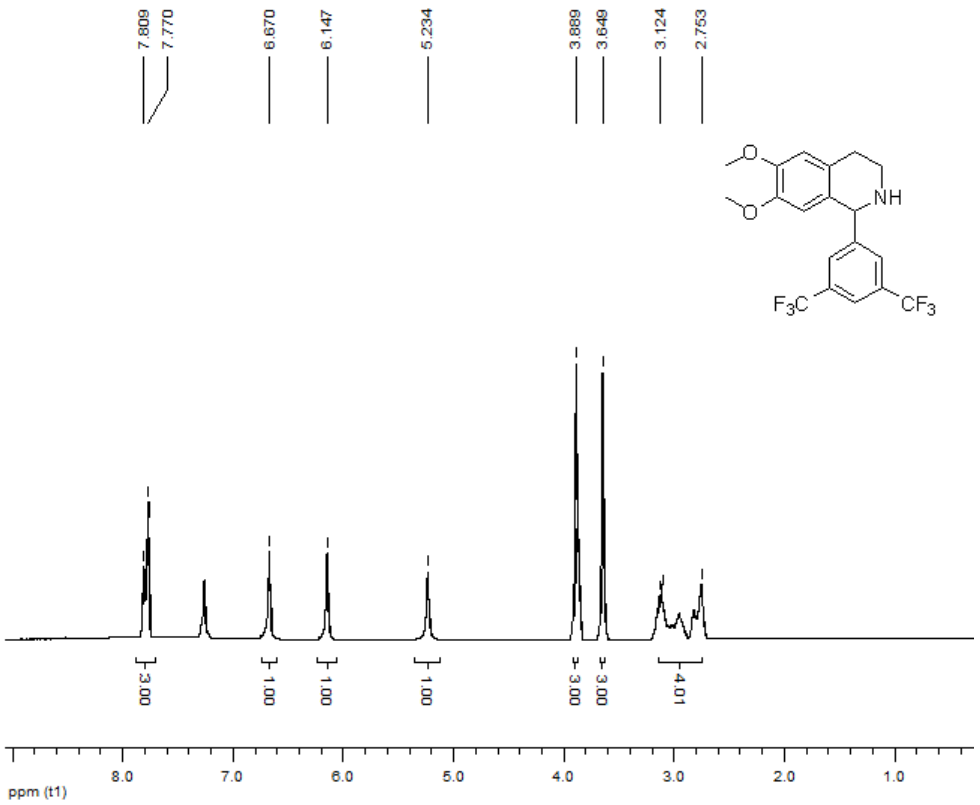

Figure S30. ^{1}H-NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline 7b.

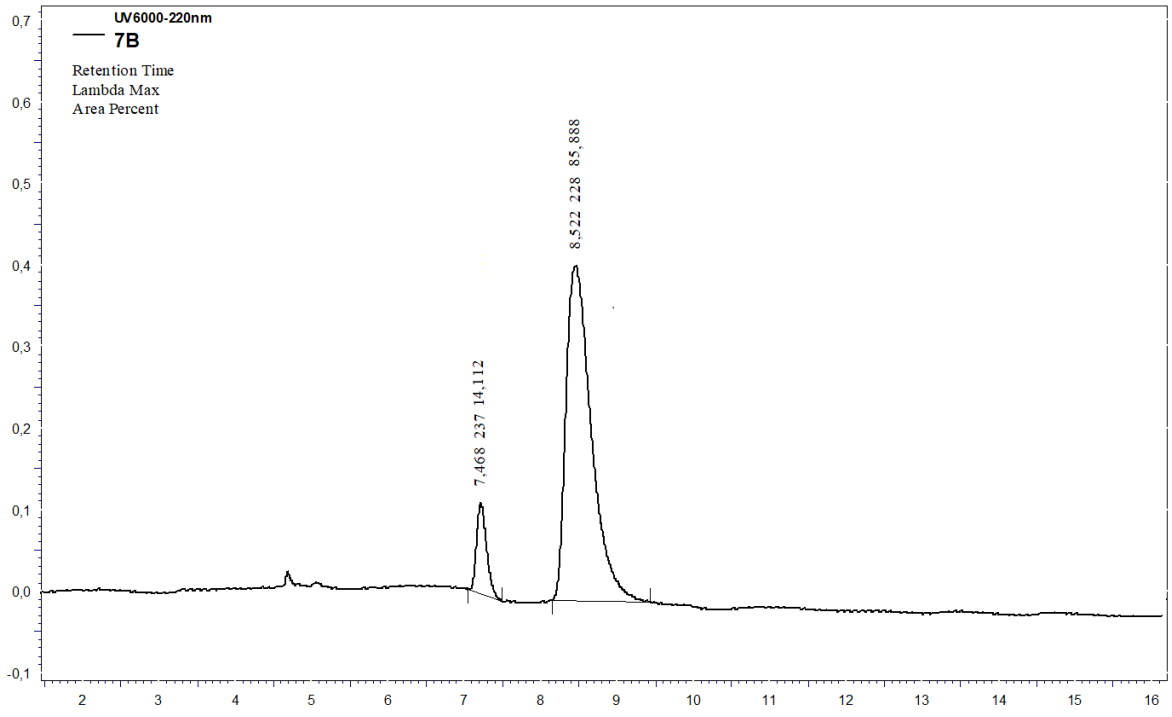

Figure S31. HPLC spectrum of 7b obtained by reduction with Ir-L4 (71 % e.e.).

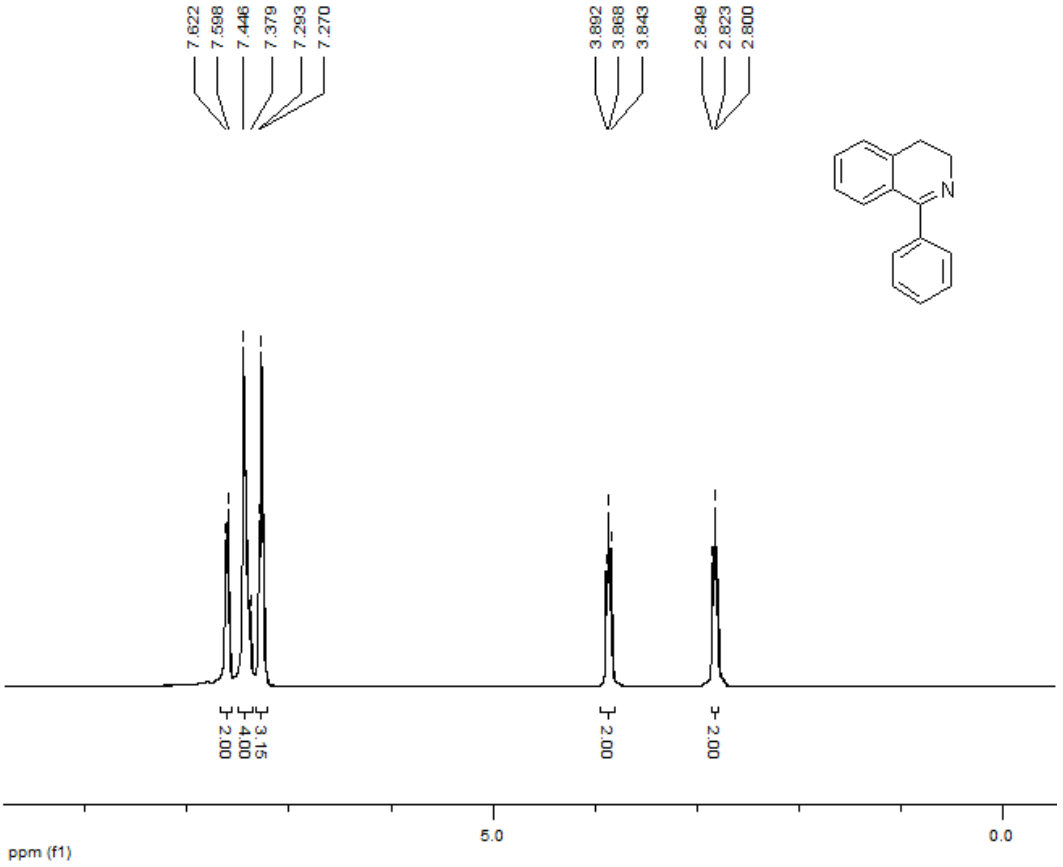

Figure S32. [1]H-NMR spectrum of 1-phenyl-3,4-dihydroisoquinoline 8a.

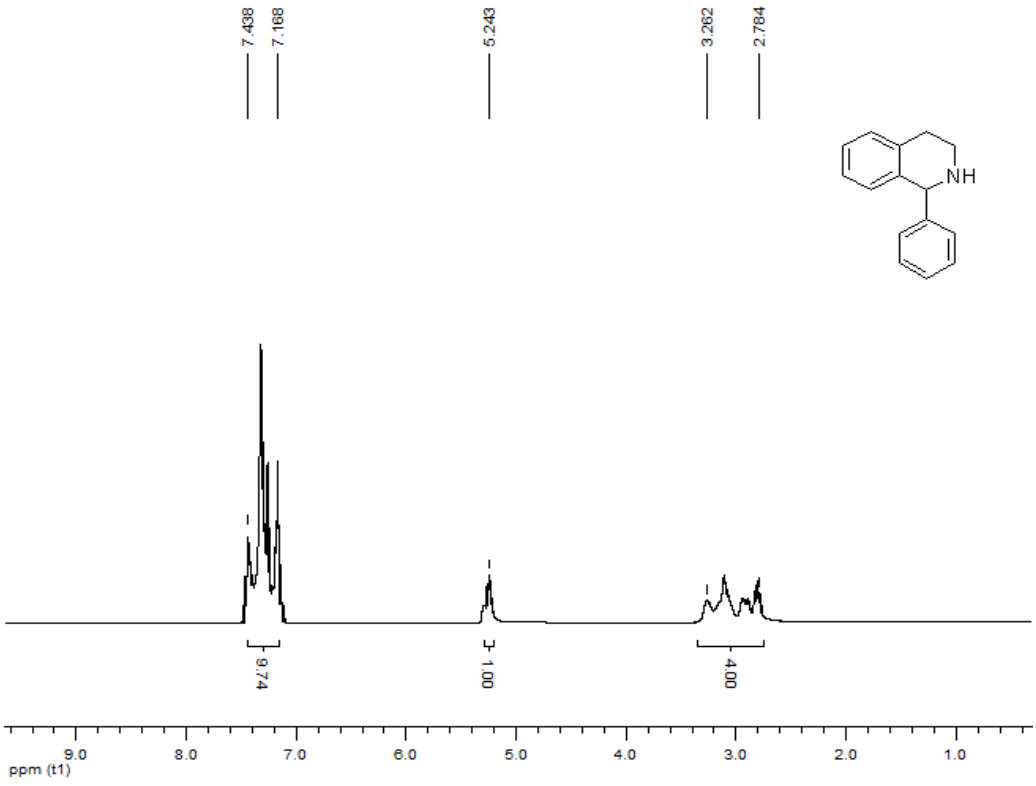

Figure S33. [1]H-NMR spectrum of 1-phenyl-1,2,3,4-tetrahydroisoquinoline 8b.

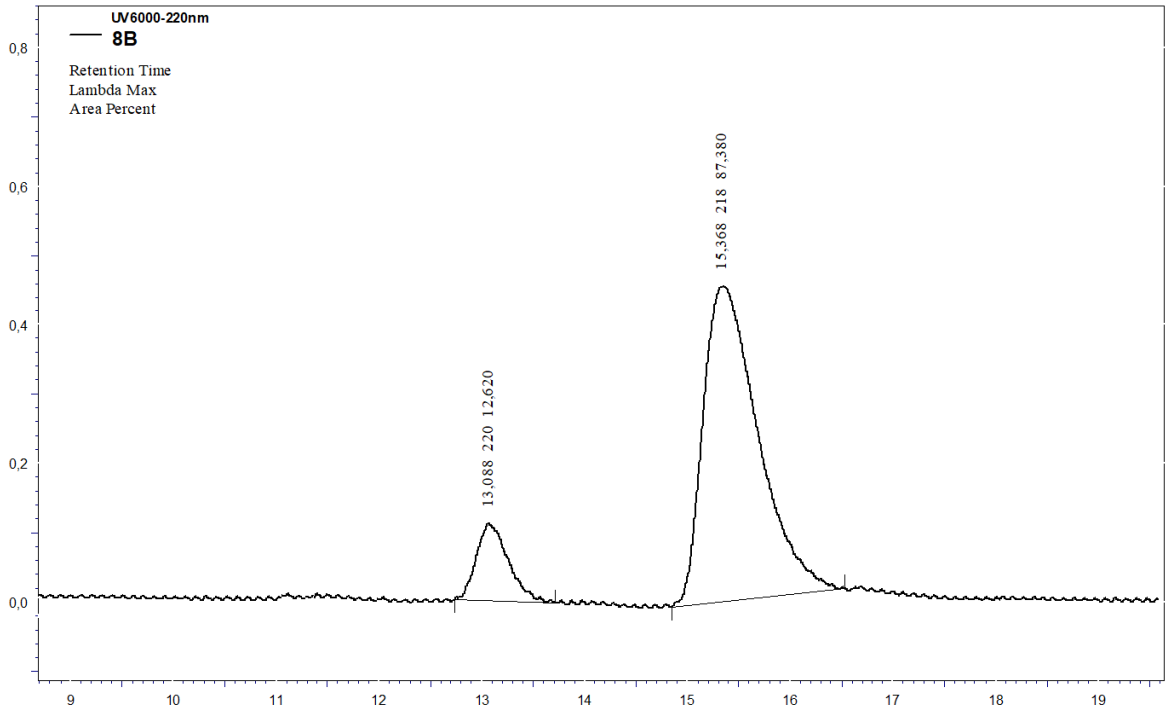

Figure S34. HPLC spectrum of 8b obtained by reduction with Ir-L5 (75 % e.e.).

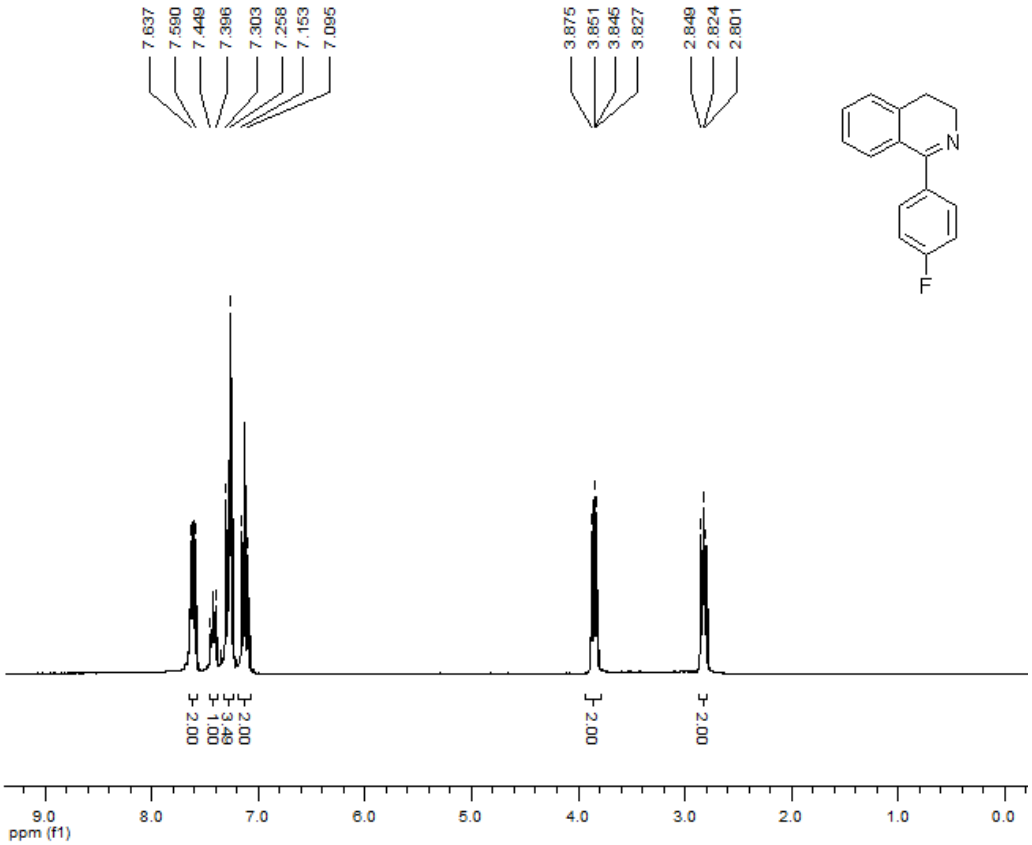

Figure S35. [1]H-NMR spectrum of 1-(4-fluorophenyl)-3,4-dihydroisoquinoline 9a.

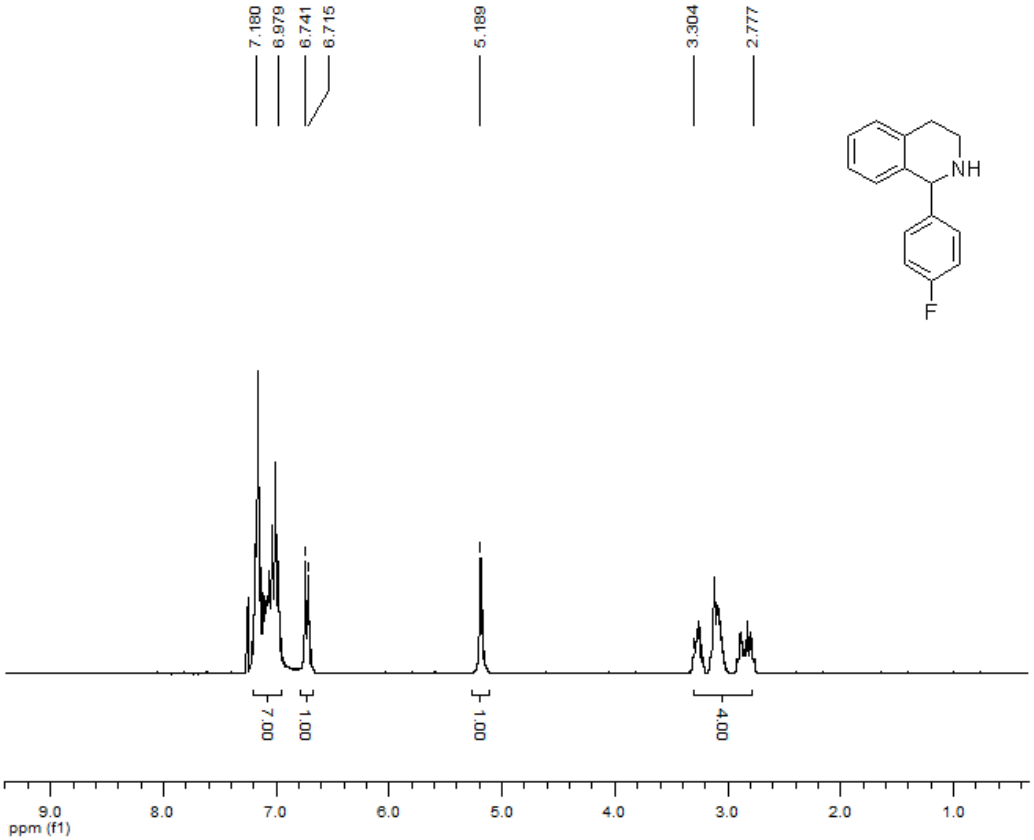

Figure S36. [1]H-NMR spectrum of 1-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline 9b.

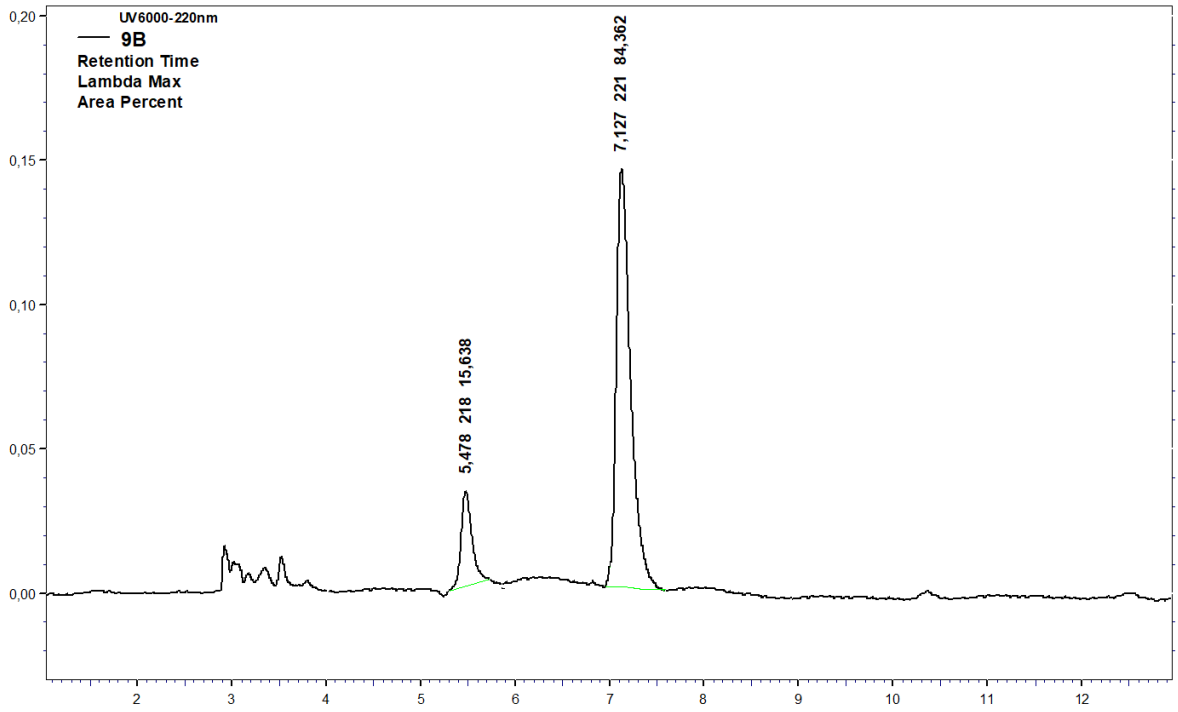

Figure S37. HPLC spectrum of 9b obtained by reduction with Ir-L4 (69 % e.e.).

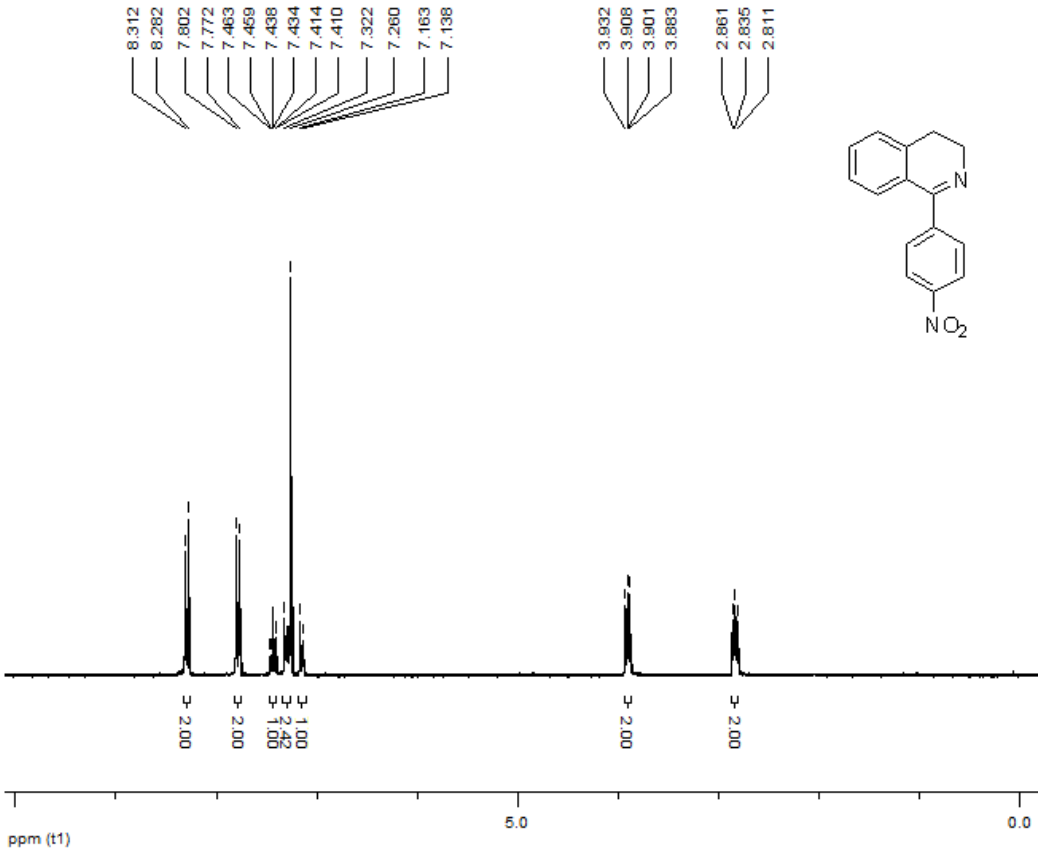

Figure S38. ^{1}H-NMR spectrum of 1-(4-nitrophenyl)-3,4-dihydroisoquinoline 10a.

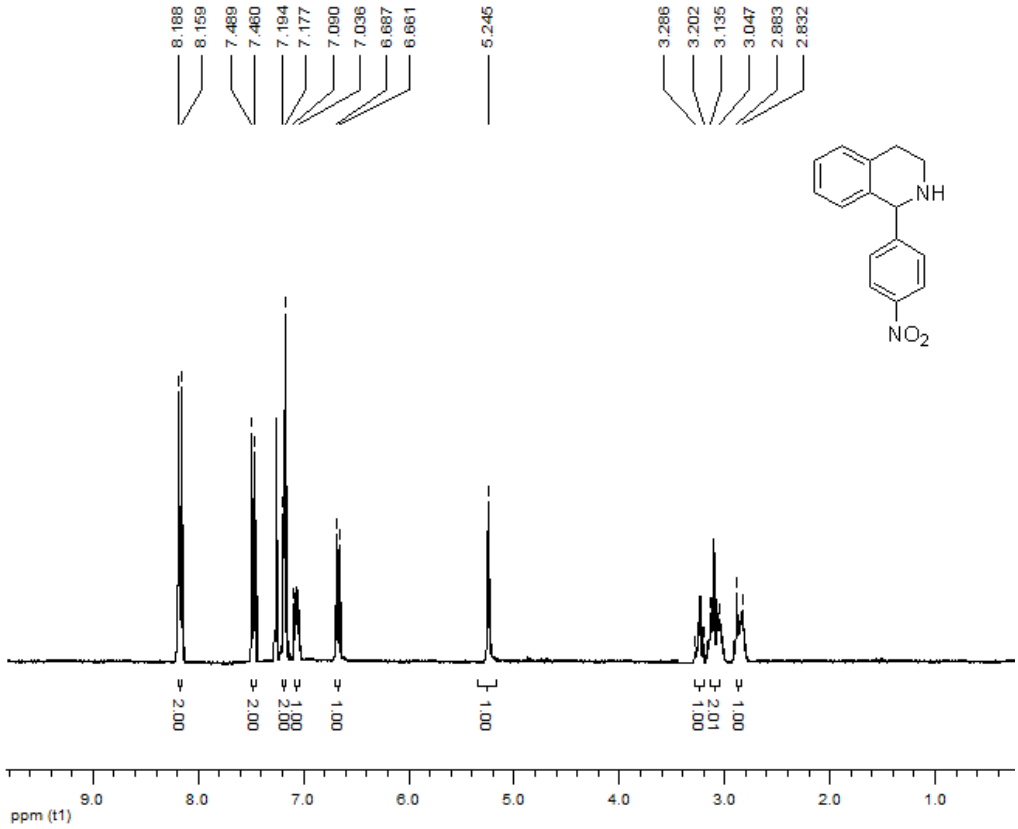

Figure S39. ^{1}H-NMR spectrum of 1-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline 10b.

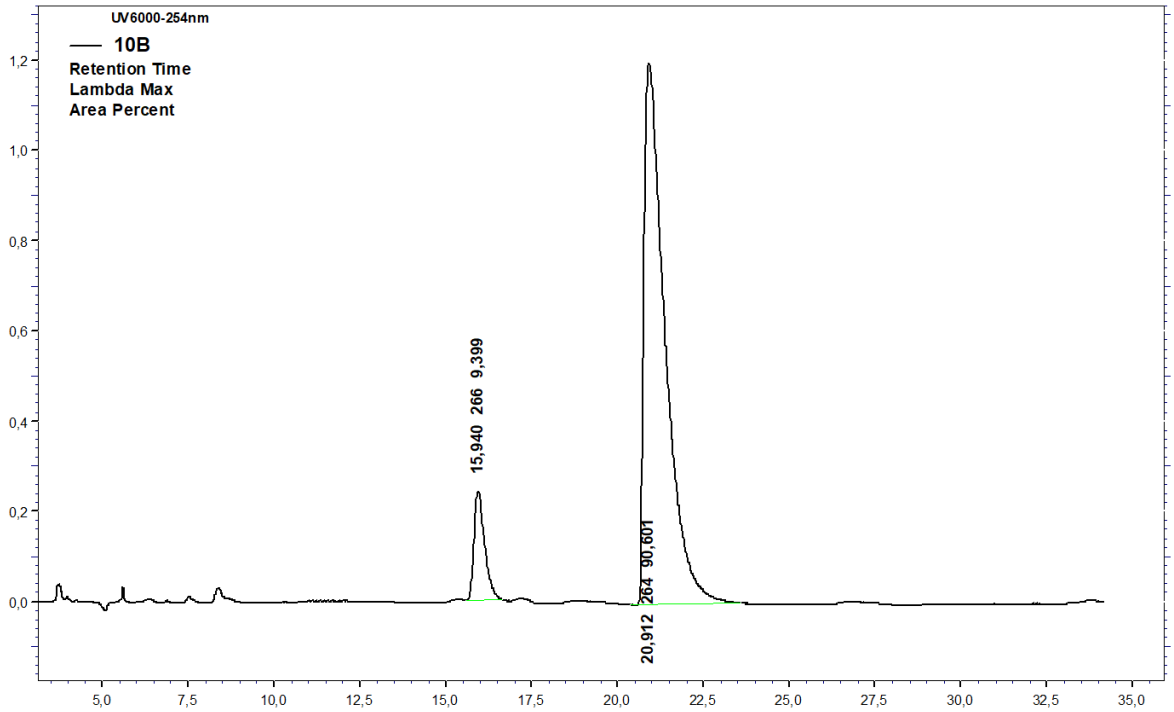

Figure S40. HPLC spectrum of 10b obtained by reduction with Ir-L4 (81 % e.e.).

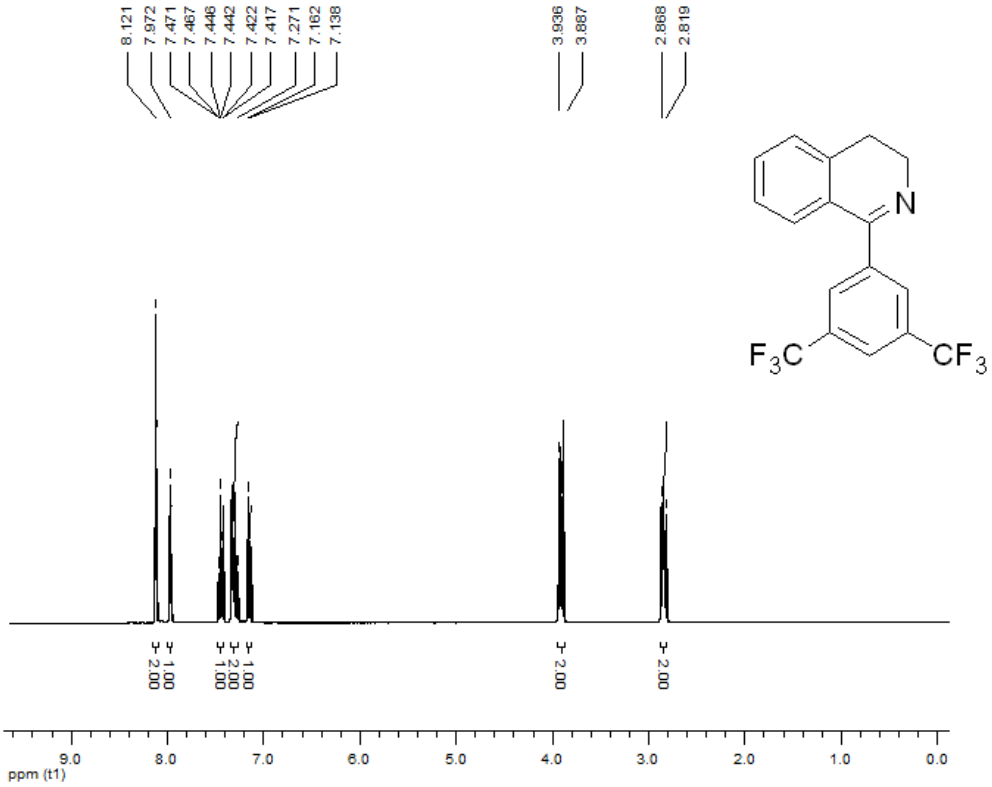

Figure S41. [1]H-NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-3,4-dihydroisoquinoline 11a.

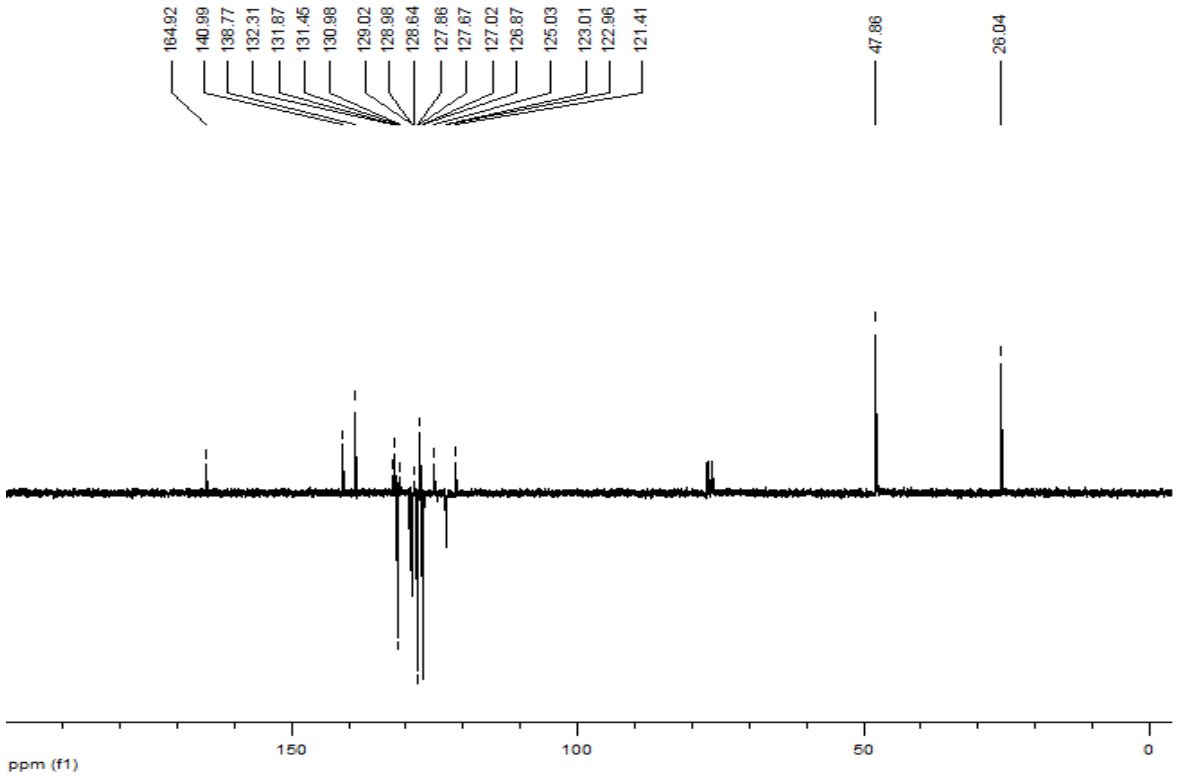

Figure S42. [13]C-NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-3,4-dihydroisoquinoline 11a.

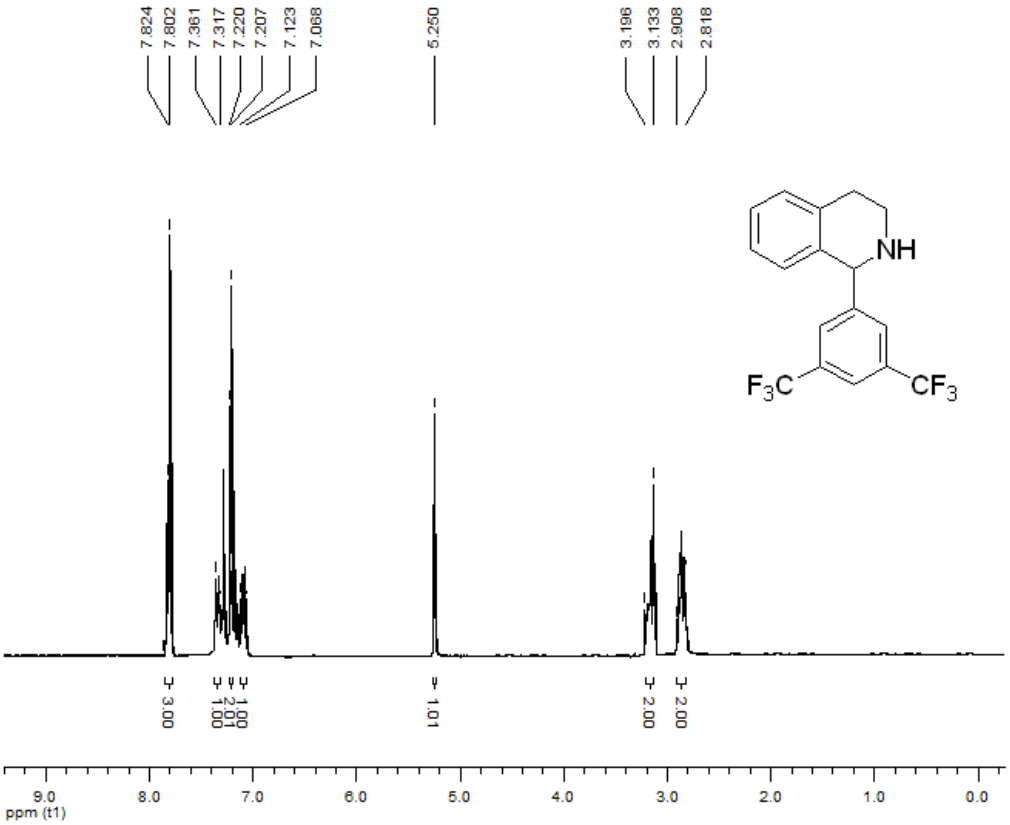

Figure S43. ^{1}H-NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline 11b.

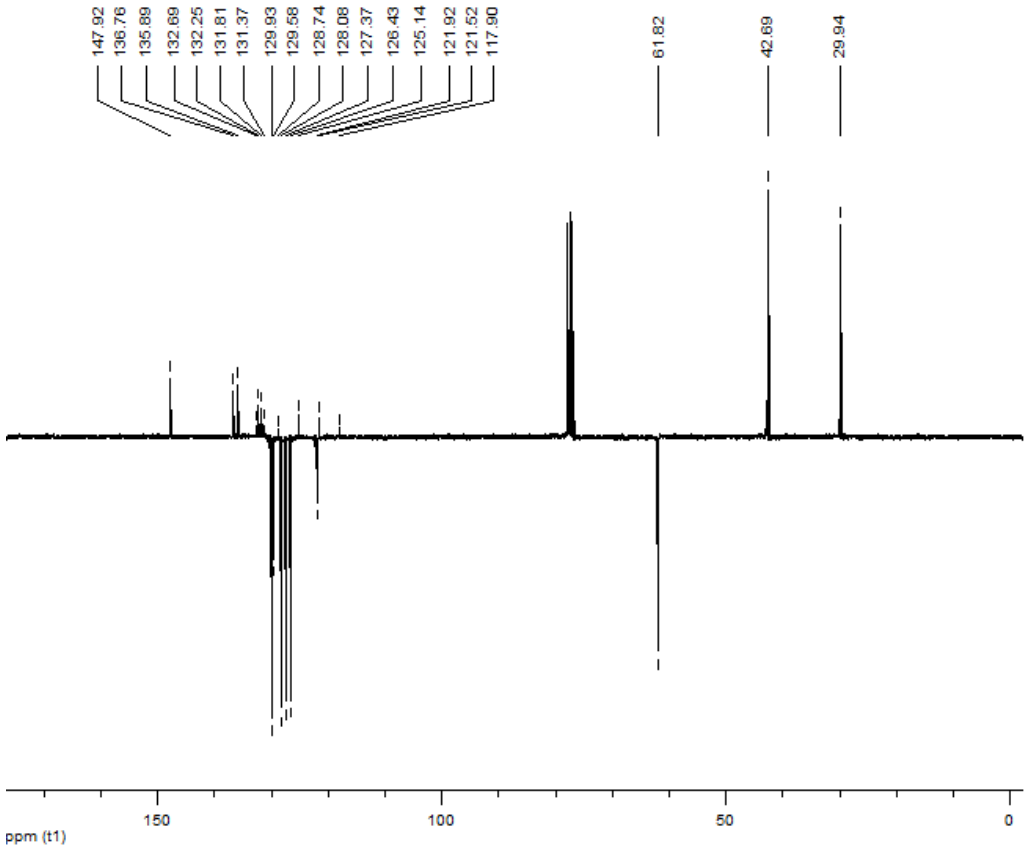

Figure S44. ^{13}C-NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline 11b.

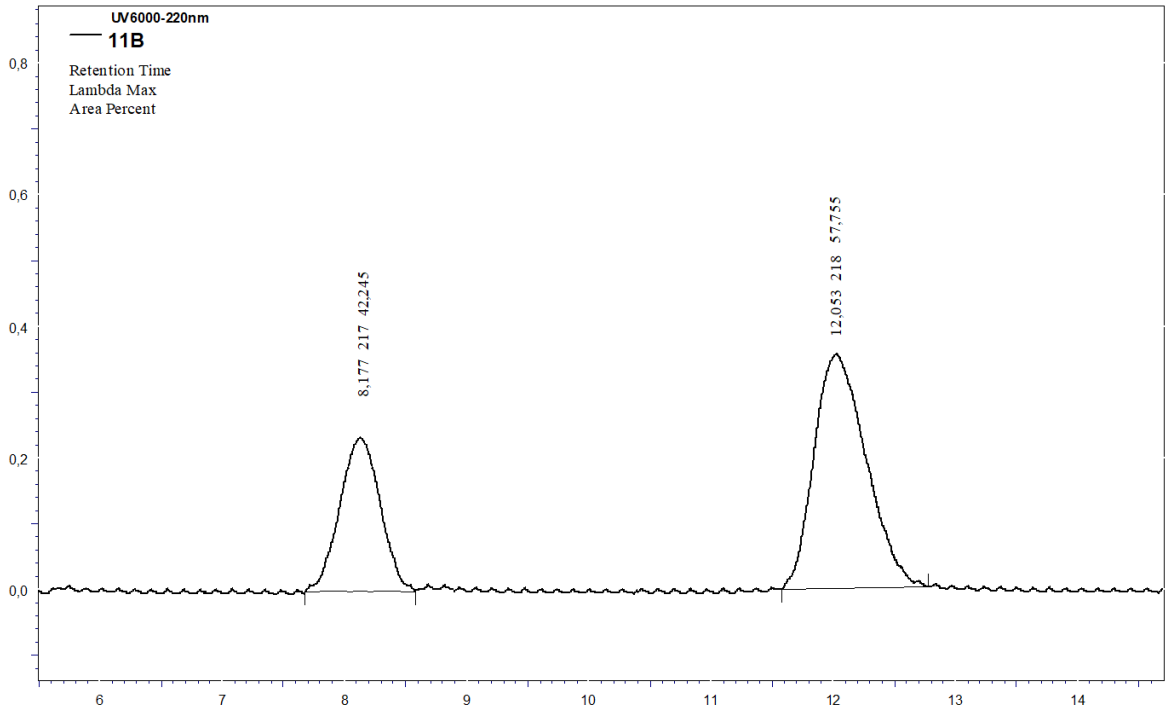

Figure S45. HPLC spectrum of 11b obtained by reduction with Ir-L5 (15 % e.e.).

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