Supporting Information

Visible-Light-Activated Catalytic Enantioselective β-Alkylation of α,β-Unsaturated 2-Acyl Imidazoles Using Hantzsch Esters as Radical Reservoirs

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1. Cyclic voltammetry of 2a

Voltammetric experiments were conducted with a computer controlled Eco Chemie AutolabPGSTAT204 potentiostat in a Metrohm electrochemical cell containing a 1 mm diameter planar platinum electrode, a Pt wire electrode and a Ag/AgCl/KCl (3 M) reference electrode. The solution used for the voltammetric experiment was deoxygenated by nitrogen gas and measurement was performed at room temperature (22 ± 2 ºC). As shown in Figure S1, Hantzsch ester **2a** could be oxidized in a chemically irreversible process with E_p^{ox} = +1. 03 V vs. Ag/AgCl.

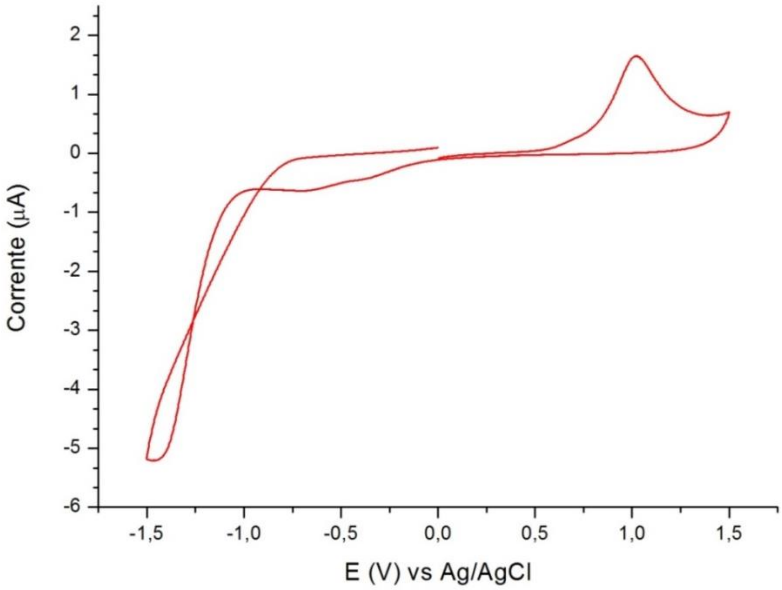
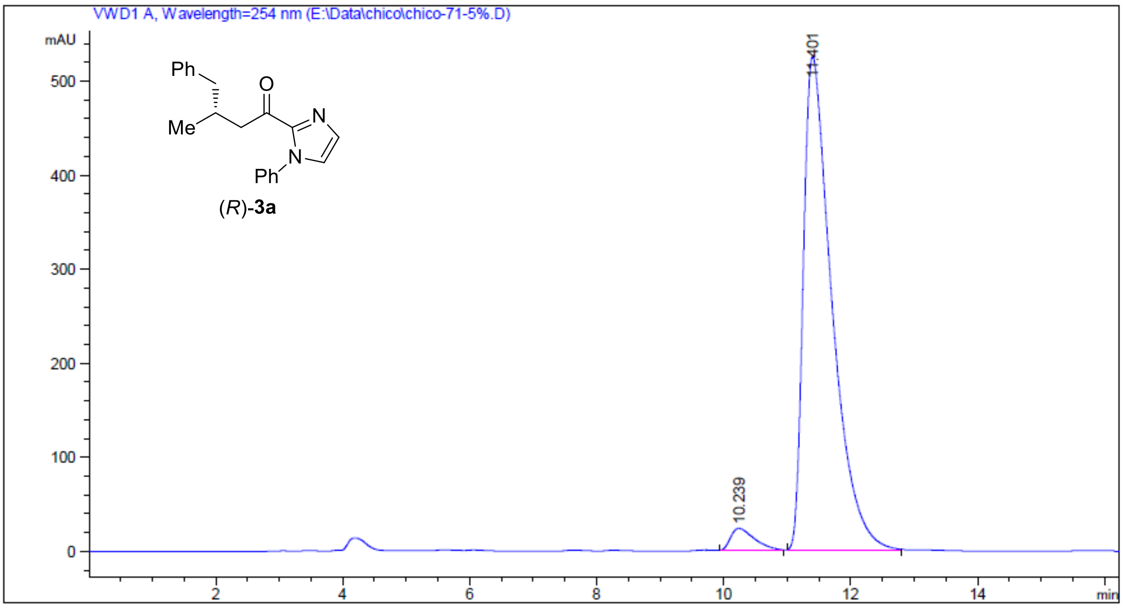


Figure S1. CV of a 0.1 M solution of **2a** in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6 at a scan rate = 0.1 V/s.

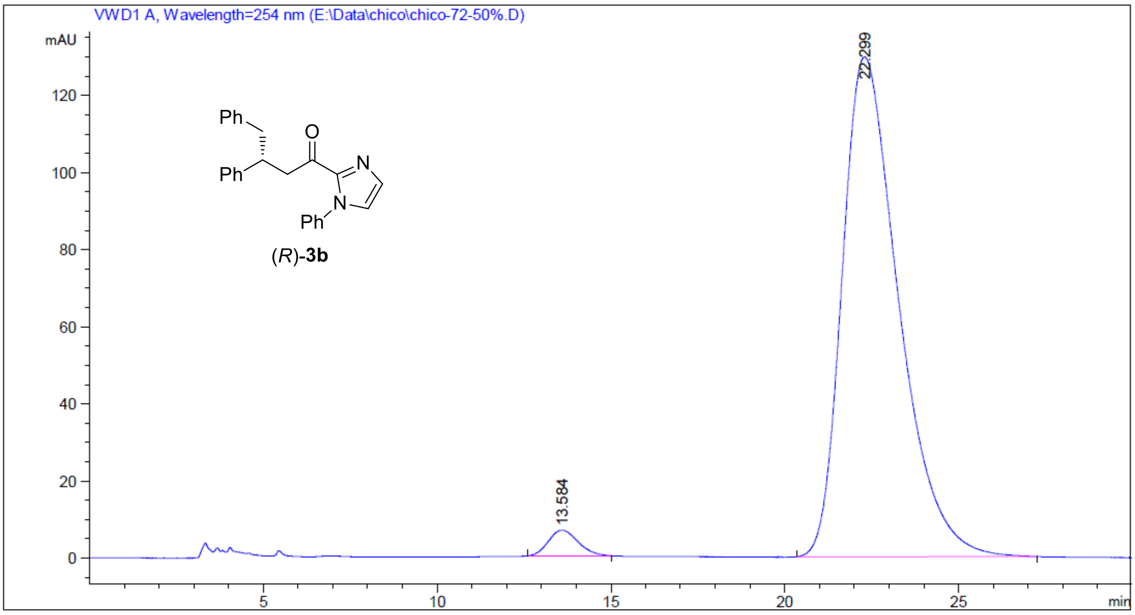
2. HPLC Traces

Enantiomeric purities of the reaction products were determined with a Daicel Chiralpak AD-H, OD-H or OJ-H (250 × 4.6 mm) HPLC column on an Agilent 1200 or 1260 Series HPLC System using hexane/isopropanol as a mobile phase. The column temperature was 25 °C and UV-absorption was measured at 254 nm.



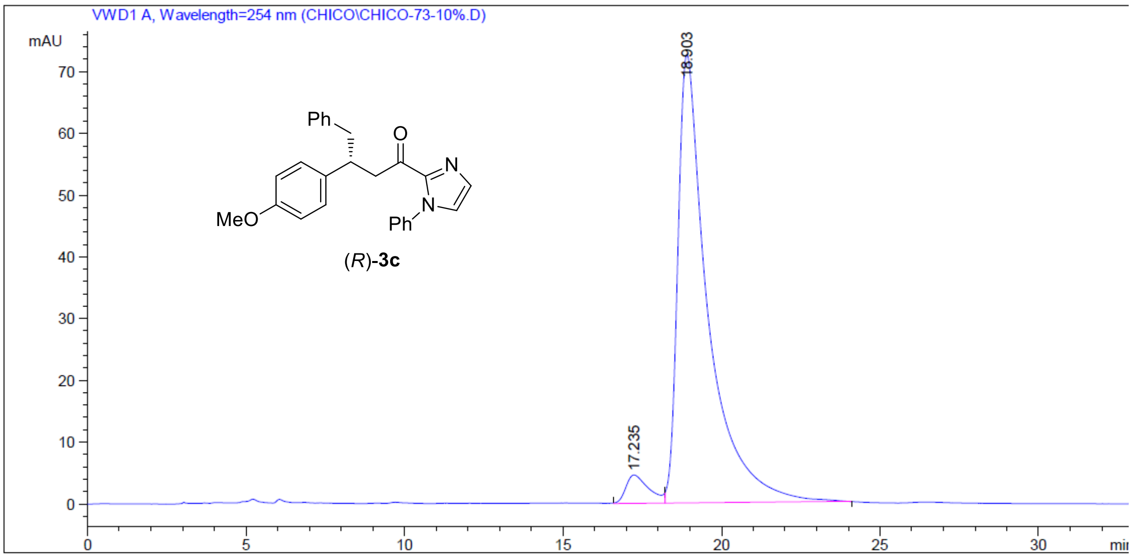
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.239	MM R	0.4395	624.47174	23.67918	3.6794
2	11.401	MM R	0.3757	1.63474e4	524.75500	96.3206

Figure S2. HPLC trace of (*R*)-**3a**.



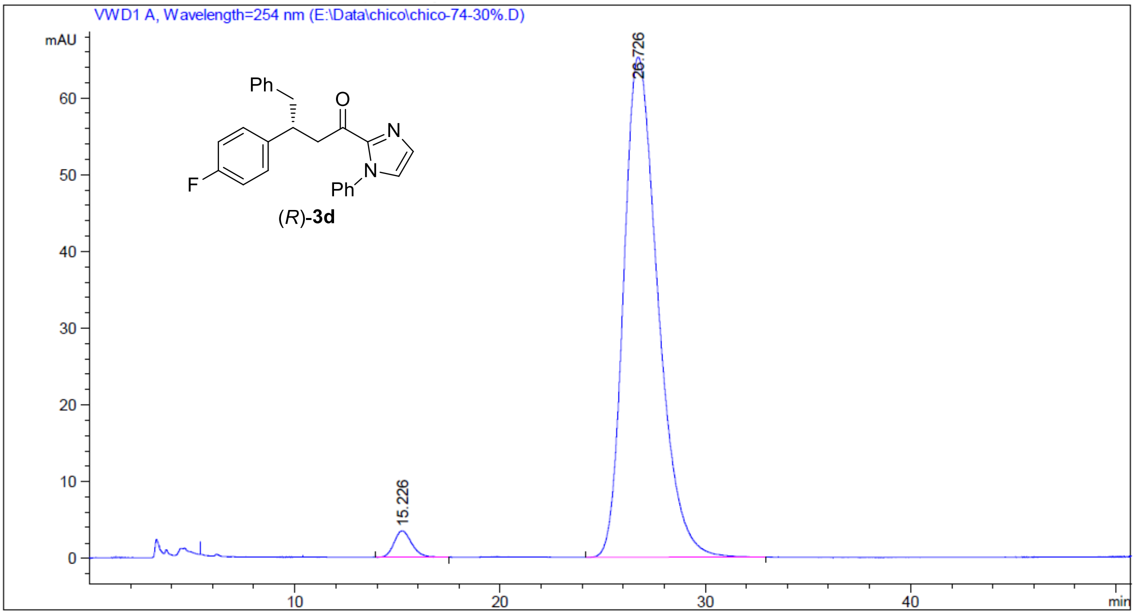
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.584	MM R	0.9925	399.65662	6.71100	2.6690
2	22.299	MM R	1.8742	1.45743e4	129.60355	97.3310

Figure S3. HPLC trace of (*R*)-**3b**.



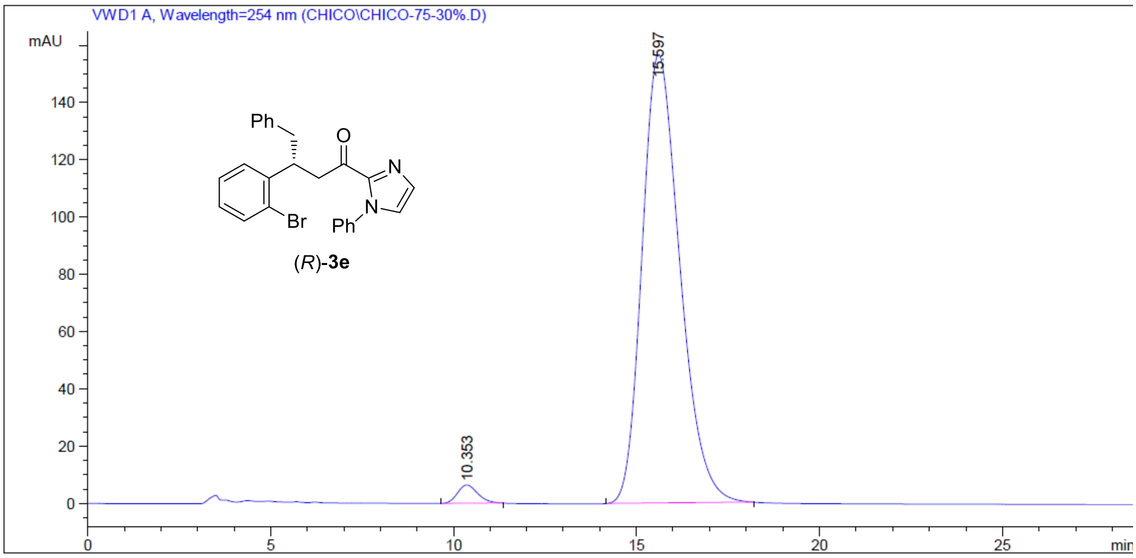
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.235	MF R	0.8451	233.57275	4.60662	4.6430
2	18.903	FM R	0.9733	4797.03809	72.63154	95.3570

Figure S4. HPLC trace of (*R*)-**3c**.



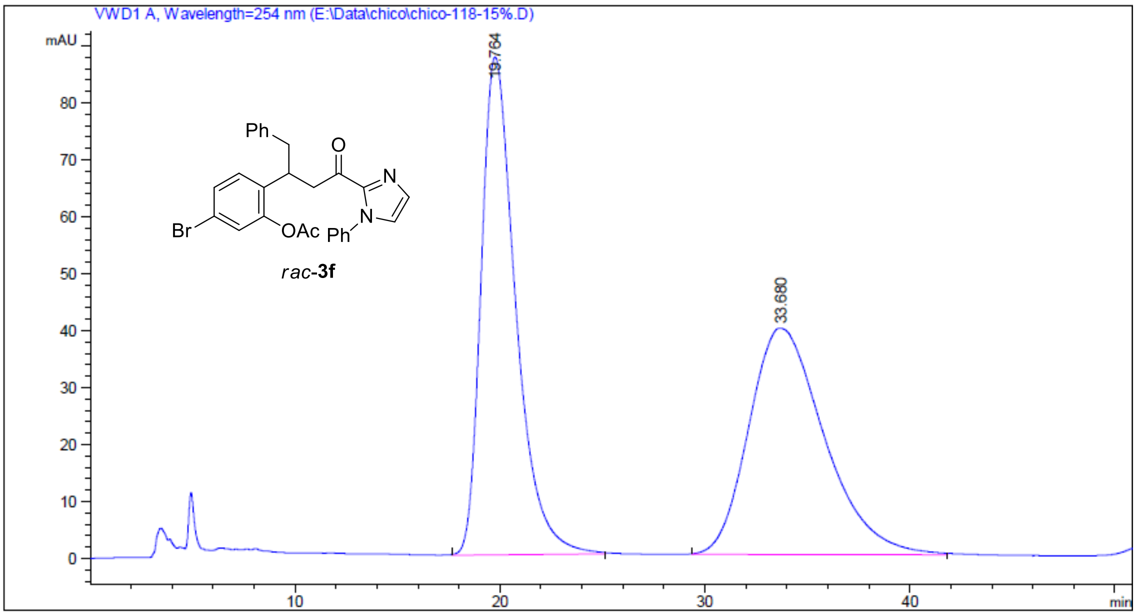
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.226	MM R	1.0045	208.04187	3.45174	2.6822
2	26.726	MM R	1.9288	7548.20703	65.22422	97.3178

Figure S5. HPLC trace of (*R*)-**3d**.



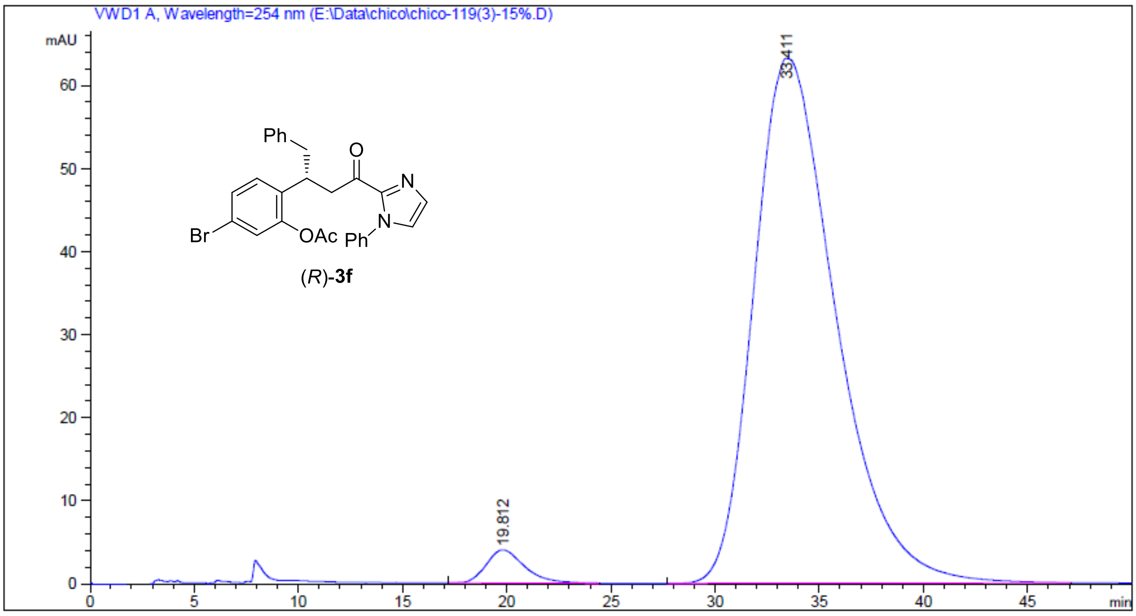
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.353	BB	0.5978	249.55544	6.41751	2.1674
2	15.597	BB	1.1105	1.12645e4	156.77347	97.8326

Figure S6. HPLC trace of (*R*)-**3e**.



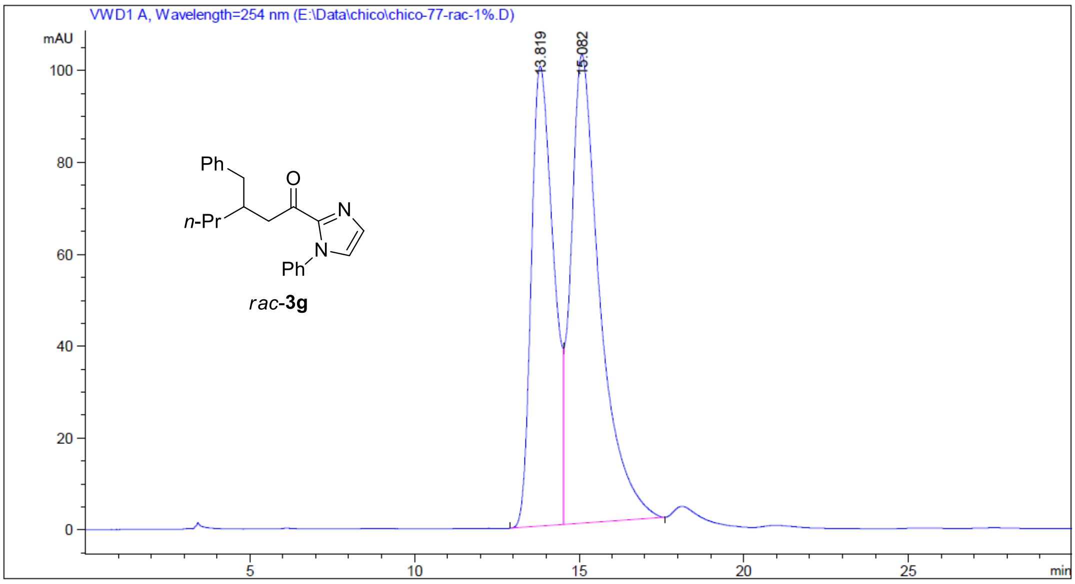
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.764	MM R	1.9544	1.02449e4	87.36456	50.2069
2	33.680	MM R	4.2666	1.01605e4	39.68997	49.7931

Figure S7. HPLC trace of *rac*-**3f**.



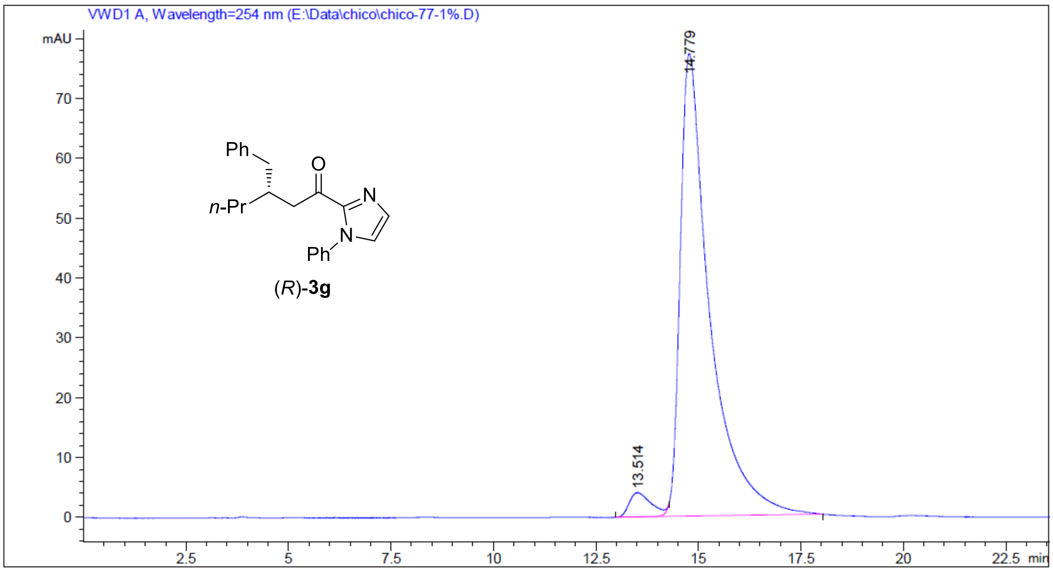
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.812	BB	1.5618	508.91254	3.98536	2.8624
2	33.411	BB	3.5619	1.72706e4	63.24459	97.1376

Figure S8. HPLC trace of (*R*)-**3f**.



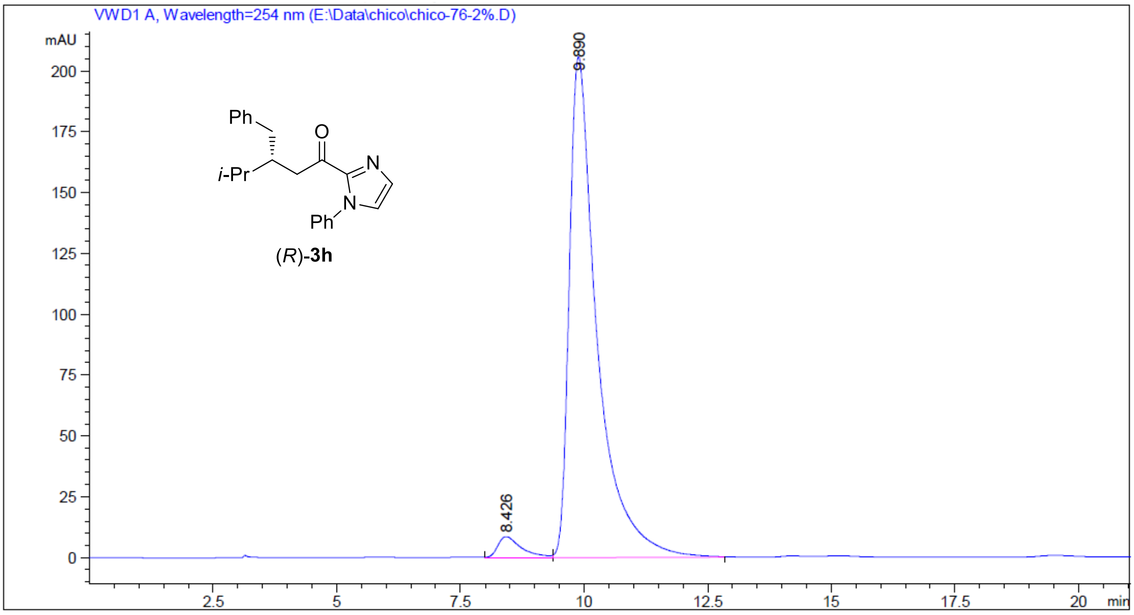
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.819	BV	0.7154	4698.74902	100.14457	42.5825
2	15.082	VB	0.8953	6335.71240	102.05298	57.4175

Figure S9. HPLC trace of rac-**3g**.



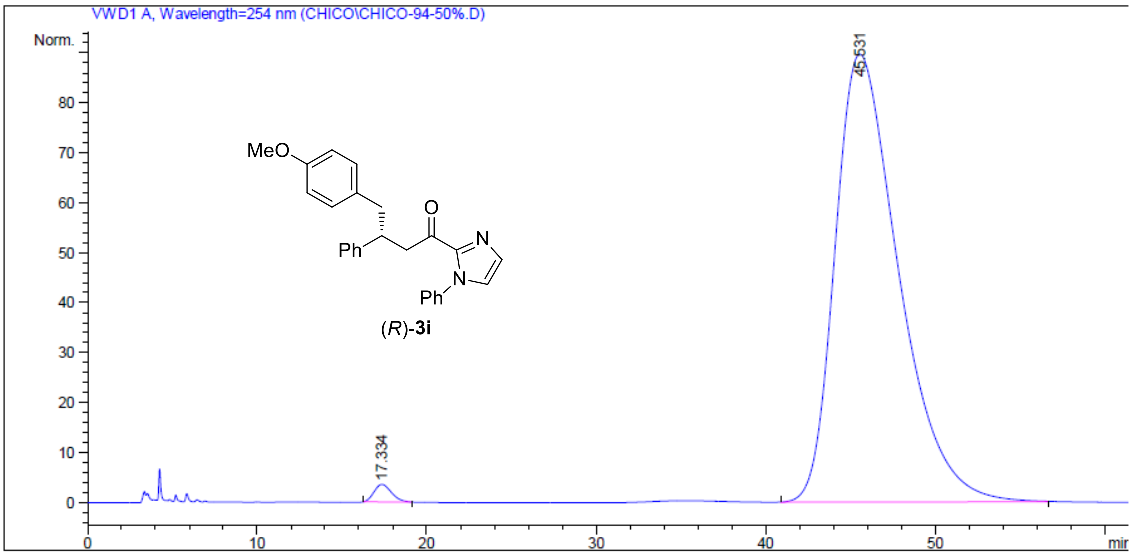
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.514	BV E	0.4371	151.46977	4.07099	3.7684
2	14.779	VV R	0.5980	3868.02808	77.26643	96.2316

Figure S10. HPLC trace of (*R*)-**3g**.



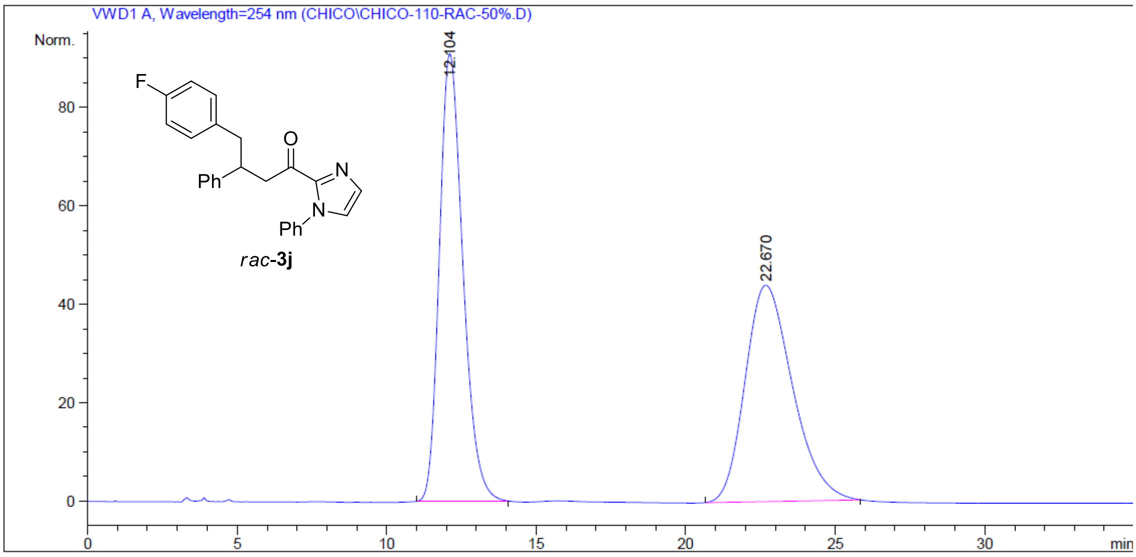
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.426	MF R	0.5495	282.95898	8.58157	3.3946
2	9.890	FM R	0.6525	8052.58984	205.69638	96.6054

Figure S11. HPLC trace of (*R*)-**3h**.



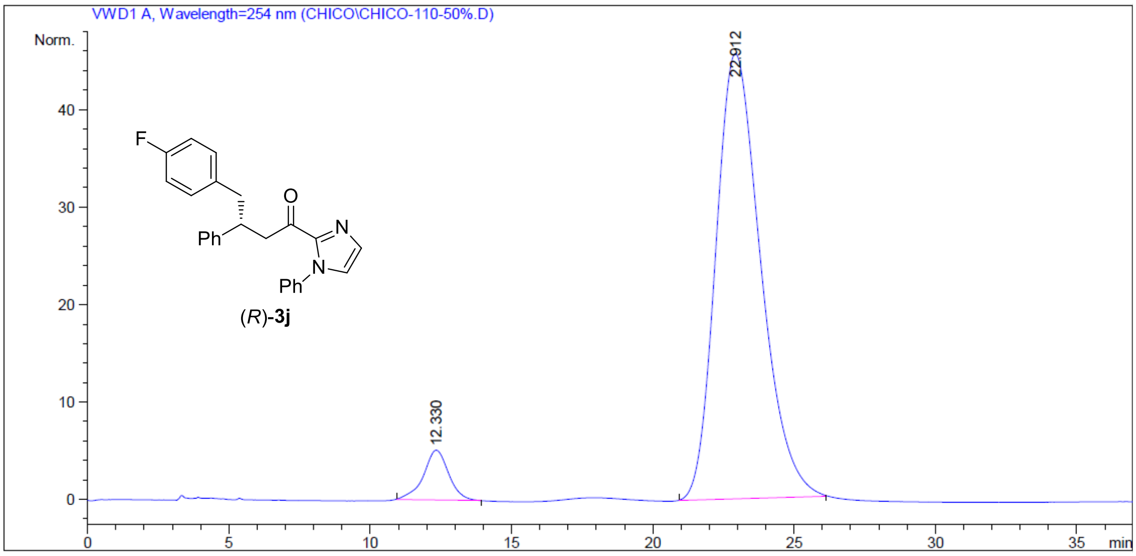
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.334	BB	0.8906	255.80208	3.54835	1.0817
2	45.531	MM R	3.1066	2.33932e4	89.75542	98.9183

Figure S12. HPLC trace of (*R*)-**3i**.



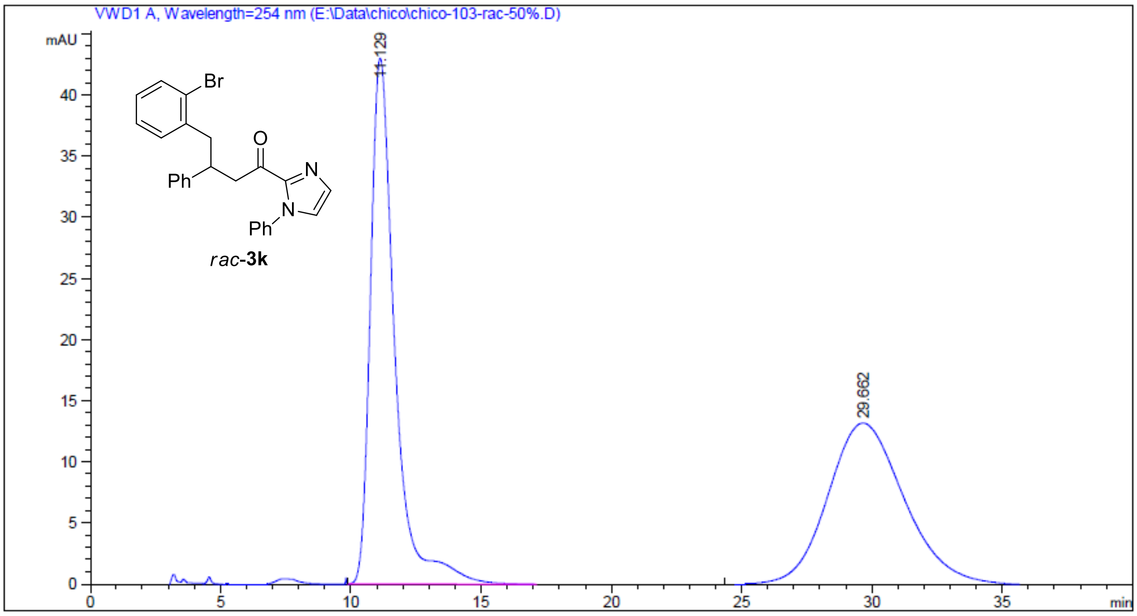
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.104	BB	0.8443	4979.79004	90.92550	50.6068
2	22.670	BB	1.6477	4860.36084	43.97221	49.3932

Figure S13. HPLC trace of *rac*-**3j**.



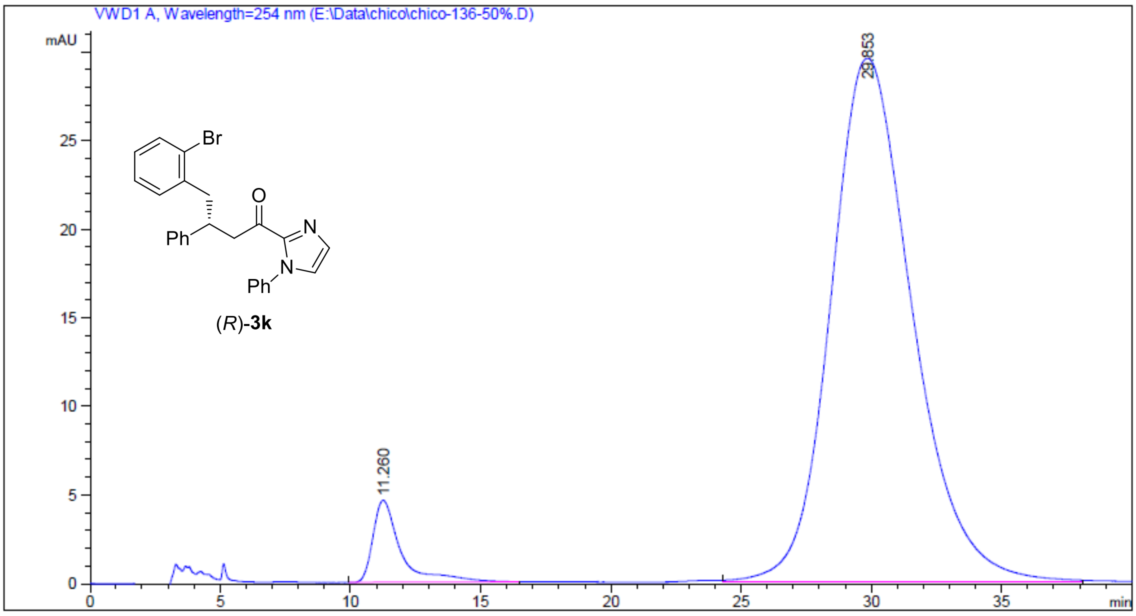
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.330	BB	0.9161	322.74005	5.13951	6.0200
2	22.912	BB	1.6603	5038.38867	45.70434	93.9800

Figure S14. HPLC trace of (*R*)-**3j**.



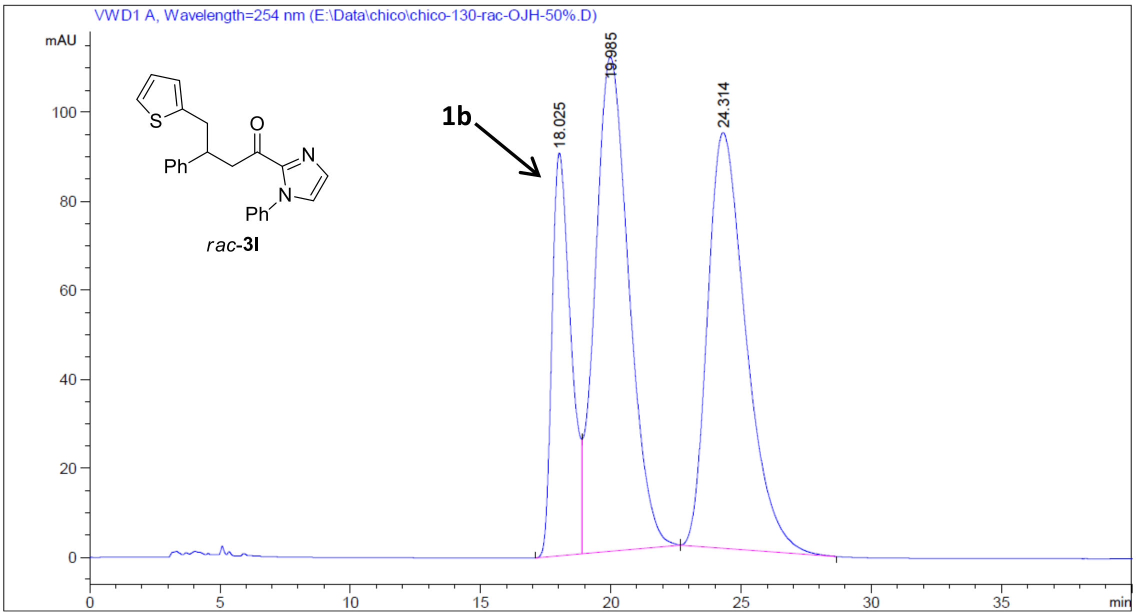
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.129	BB	0.9747	2797.90649	43.02456	50.6596
2	29.662	BB	2.8171	2725.04810	13.24058	49.3404

Figure S15. HPLC trace of *rac*-**3k**.



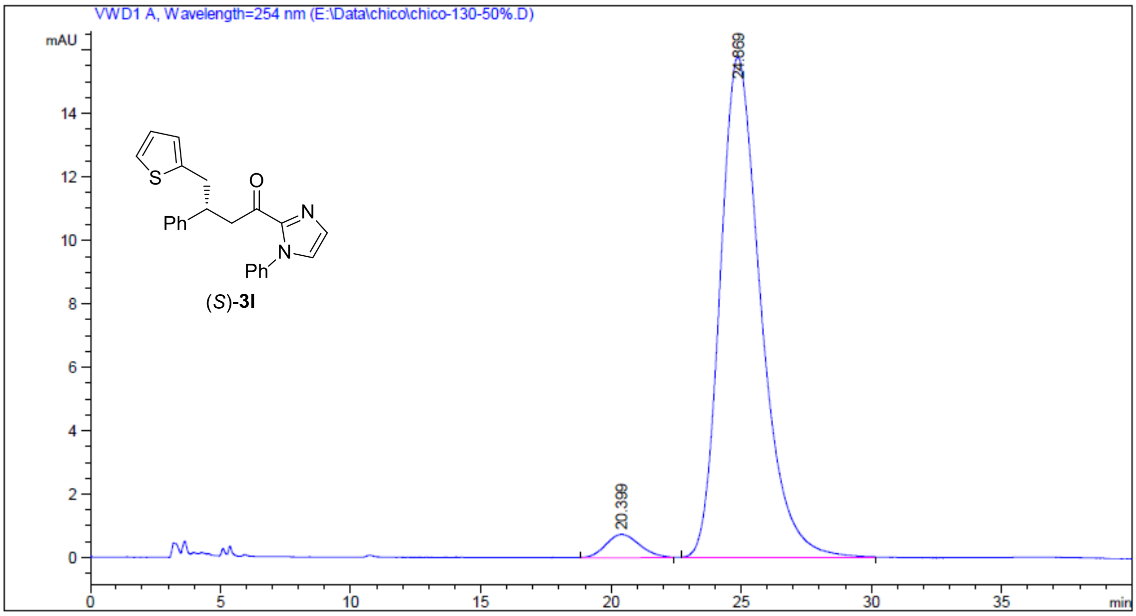
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.260	BB	1.0797	347.65878	4.63196	5.1370
2	29.853	MM R	3.6224	6420.07617	29.53908	94.8630

Figure S16. HPLC trace of (*R*)-**3k**.



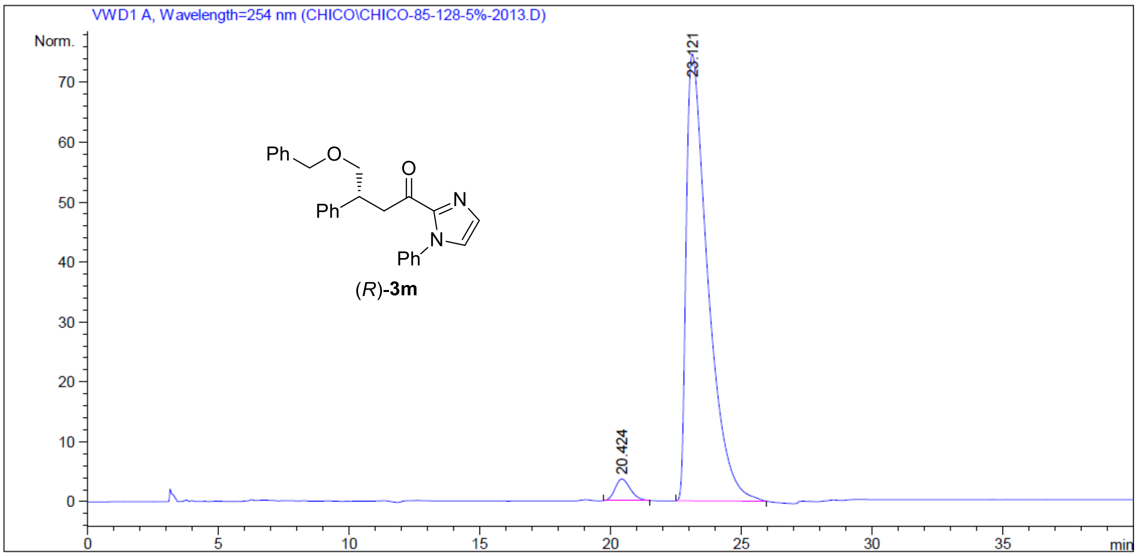
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.025	BV	0.7595	4529.55225	90.56956	18.7816
2	19.985	VB	1.3767	1.00171e4	111.01922	41.5355
3	24.314	BB	1.5502	9570.29688	93.41744	39.6829

Figure S17. HPLC trace of *rac*-**3l**.



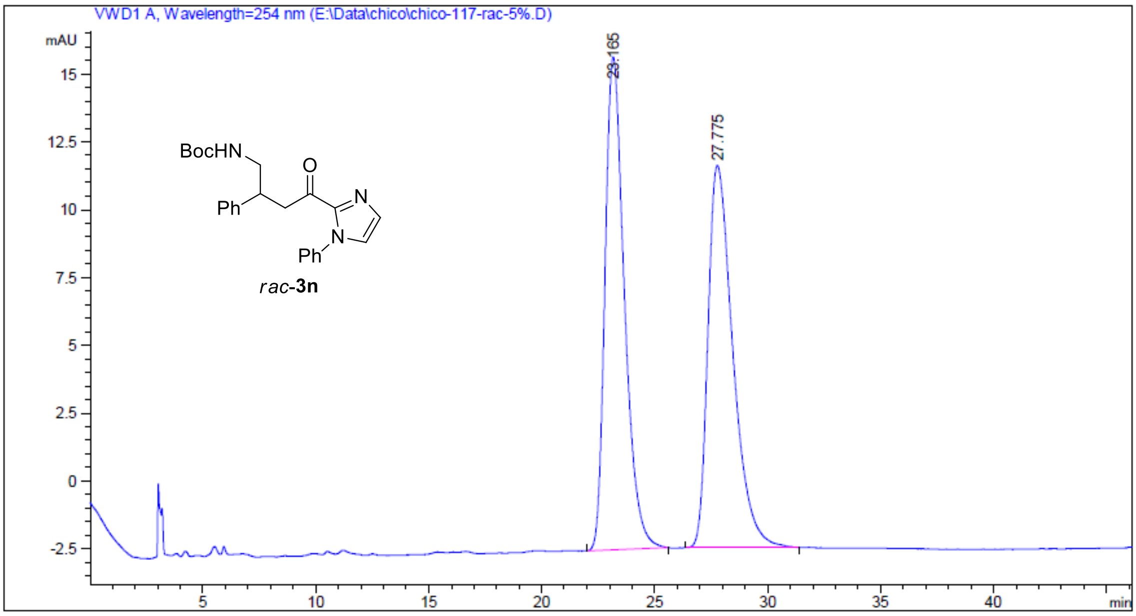
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.399	MM R	1.5193	67.19551	7.37156e-1	3.7800
2	24.869	MM R	1.8074	1710.44958	15.77301	96.2200

Figure S18. HPLC trace of (*S*)-**3l**.



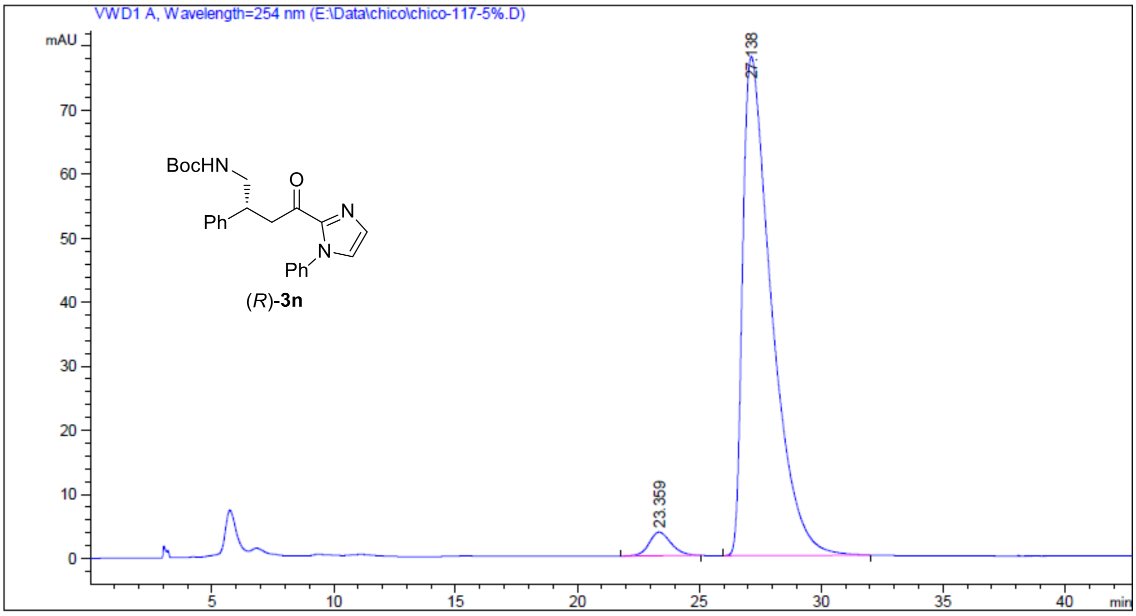
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.424	BB	0.6156	147.85571	3.61457	3.3303
2	23.121	BB	0.8546	4291.83301	74.60804	96.6697

Figure S19. HPLC trace of (*R*)-**3m**.



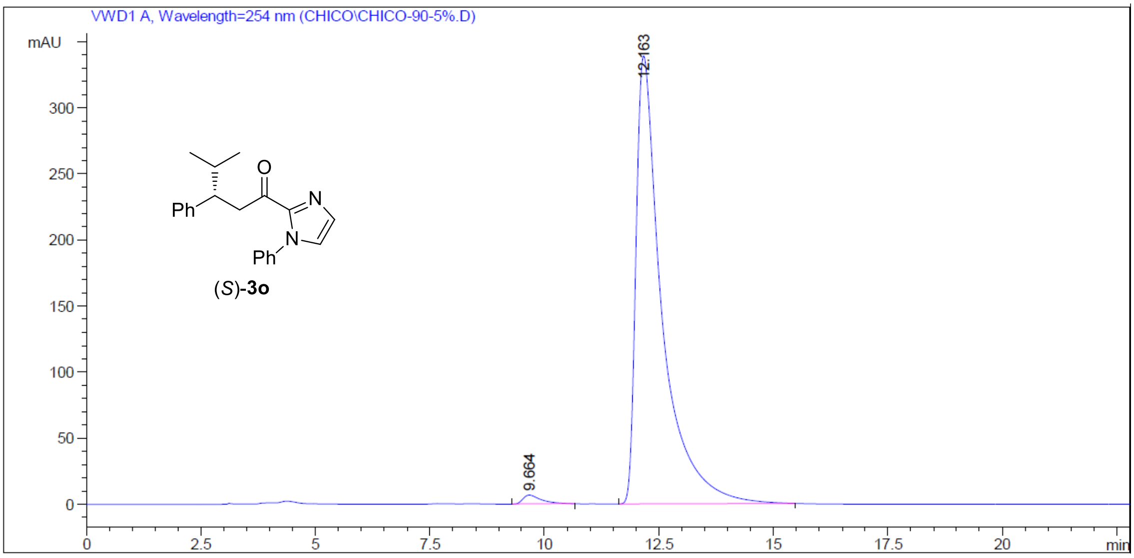
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.165	BB	0.8864	1082.44128	18.15874	50.0435
2	27.775	BB	1.1467	1080.55762	14.09069	49.9565

Figure S20. HPLC trace of *rac*-**3n**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.359	BB	0.8711	231.93640	3.69089	3.4910
2	27.138	BB	1.2084	6411.86523	77.88659	96.5090

Figure S21. HPLC trace of (*R*)-**3n**.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.664	BB	0.4135	193.11888	6.81768	1.4209
2	12.163	BB	0.5718	1.33978e4	338.95990	98.5791

Figure S22. HPLC trace of (*S*)-**3o**.

3. NMR Spectra

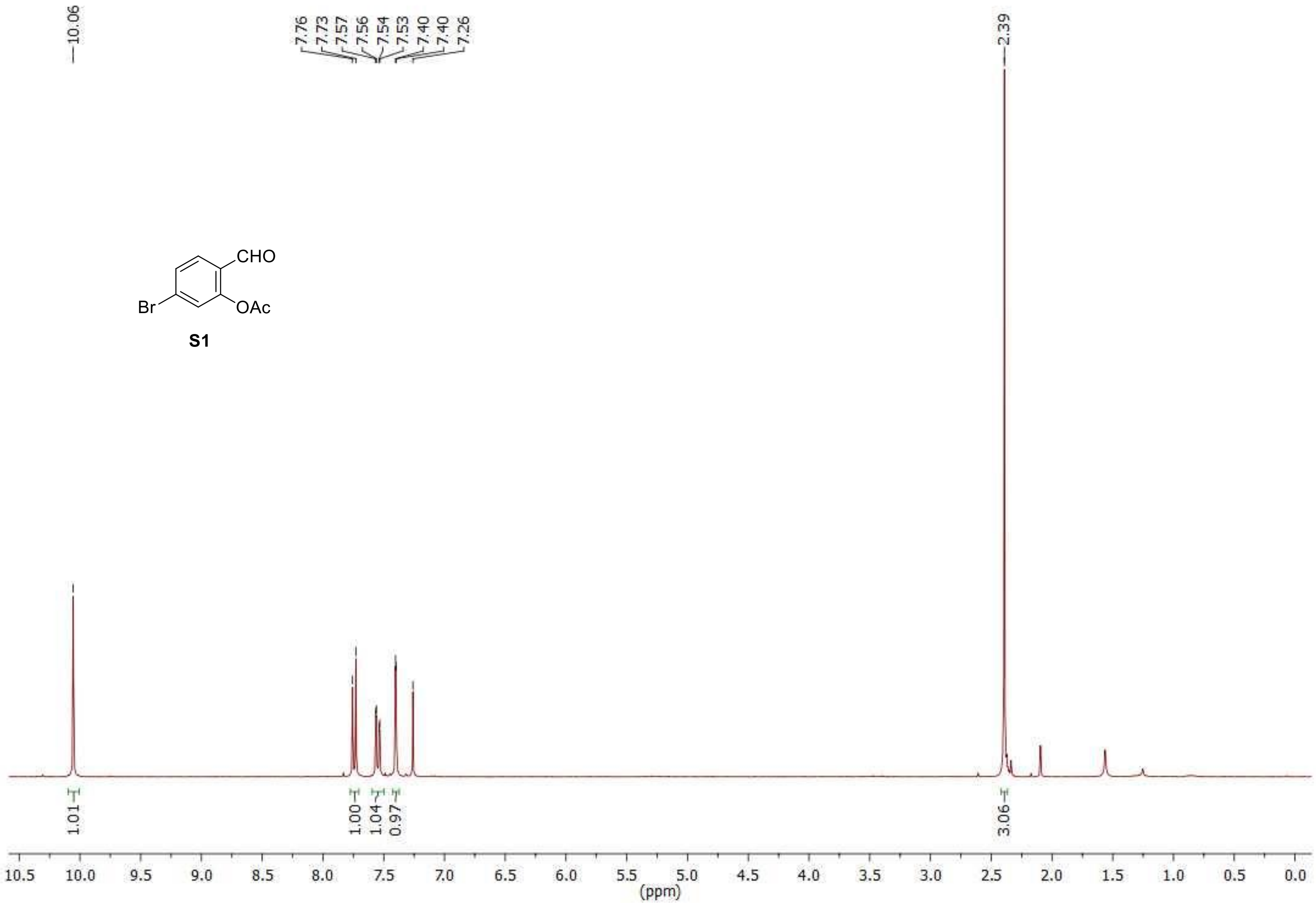


Figure S23. ^{1}H spectrum of **S1**.

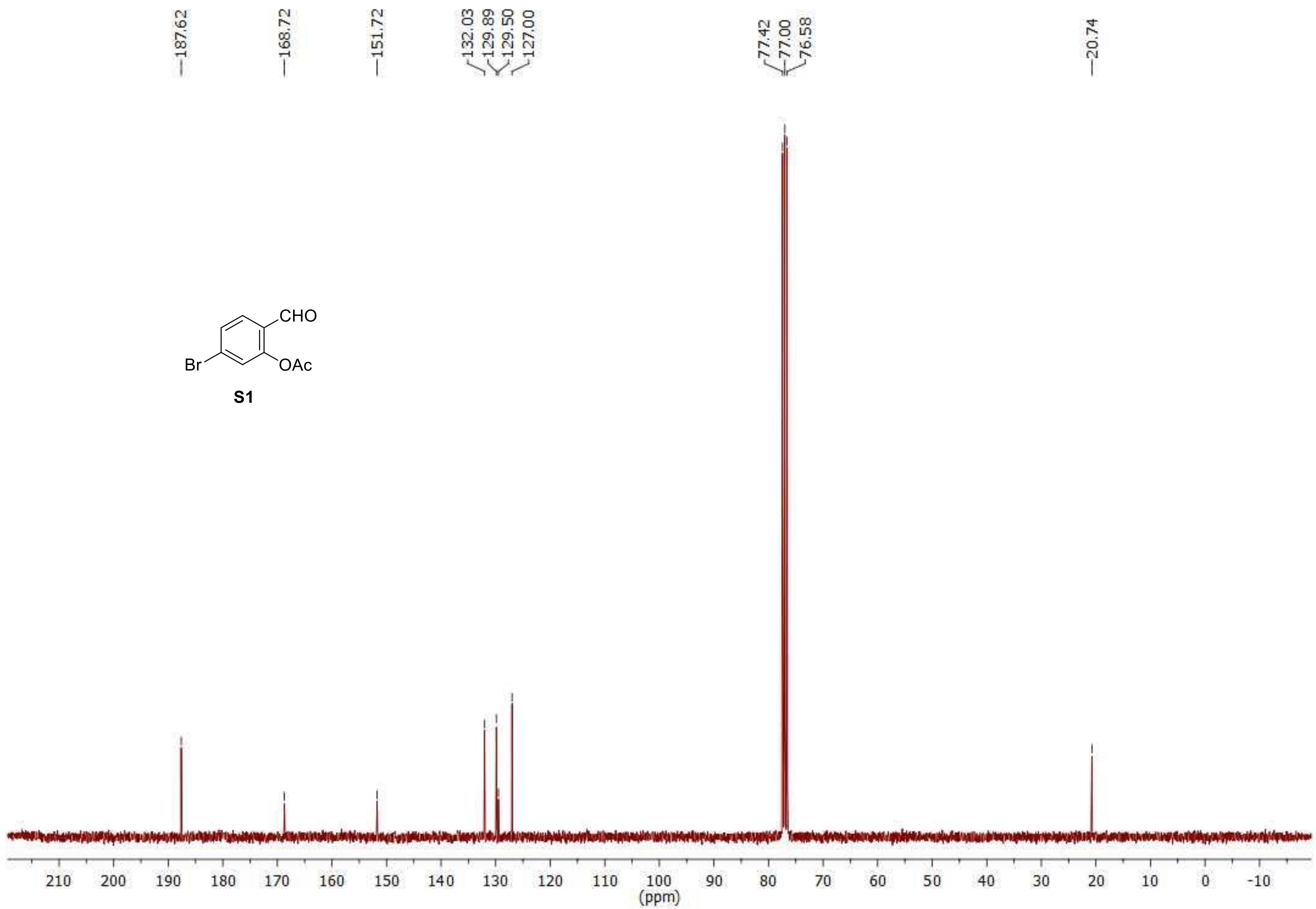


Figure S24. ^{13}C spectrum of **S1**.

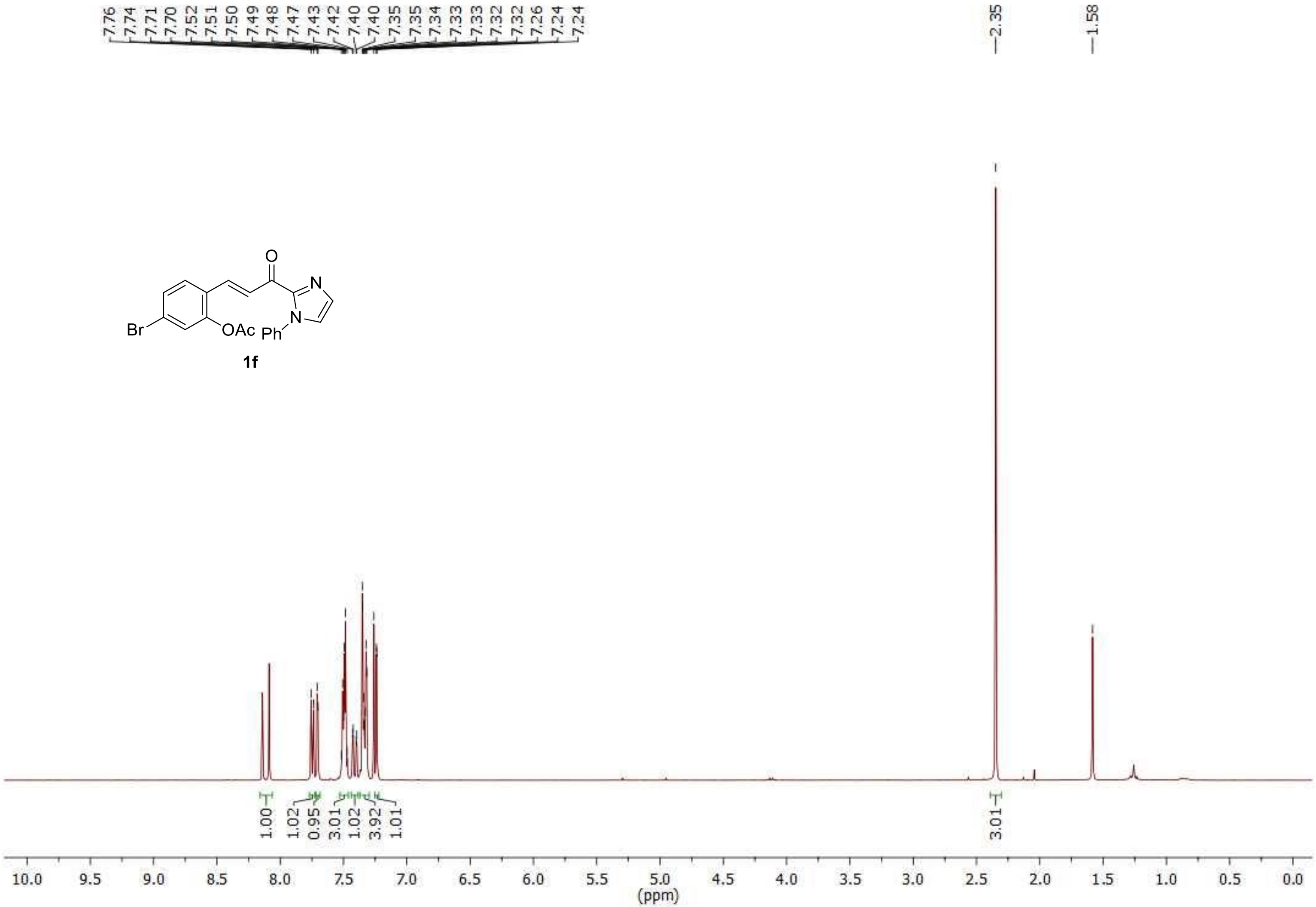


Figure S25. ^{1}H spectrum of **1f**.

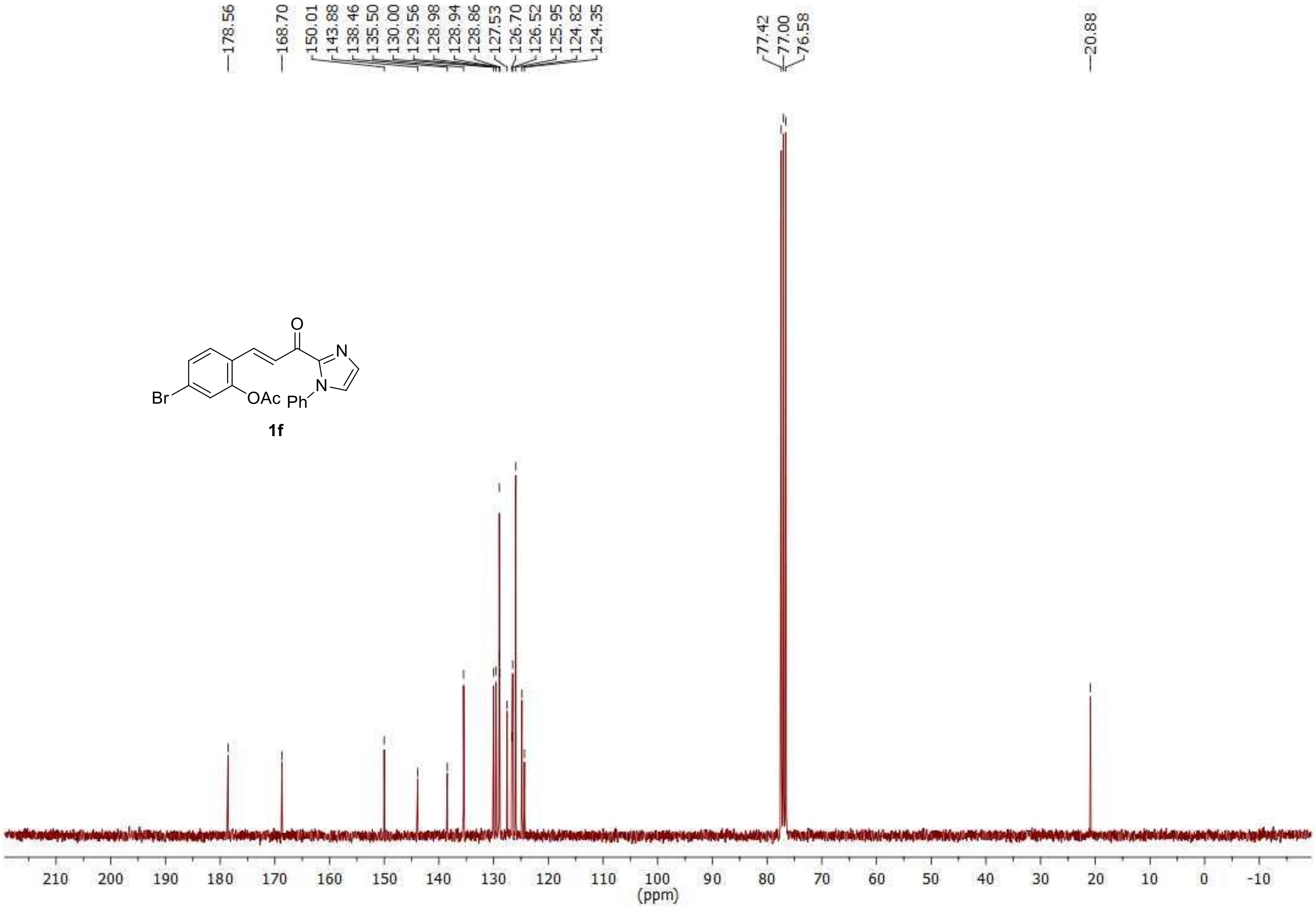


Figure S26. ^{13}C spectrum of **1f**.

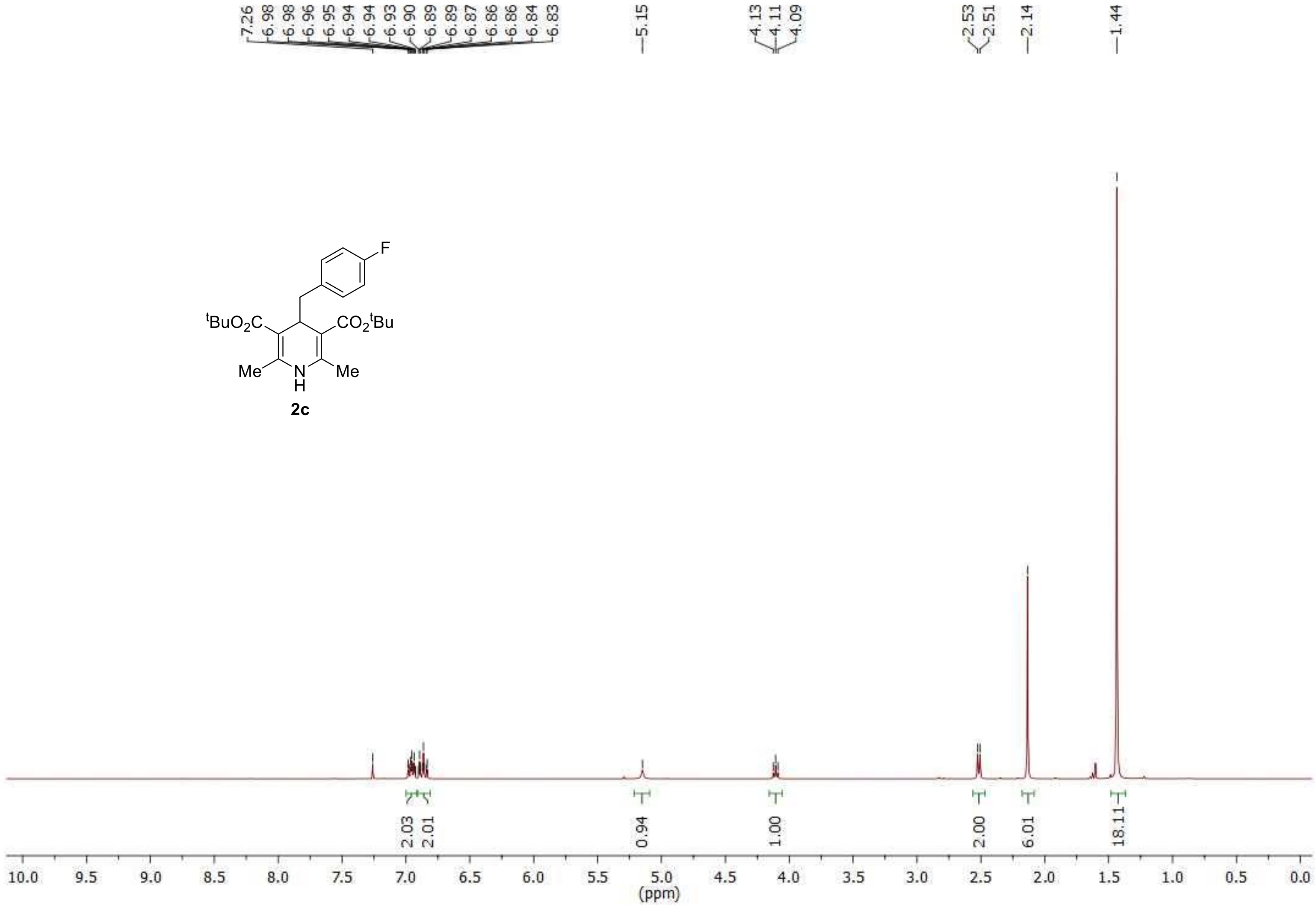


Figure S27. ^{1}H spectrum of **2c**.

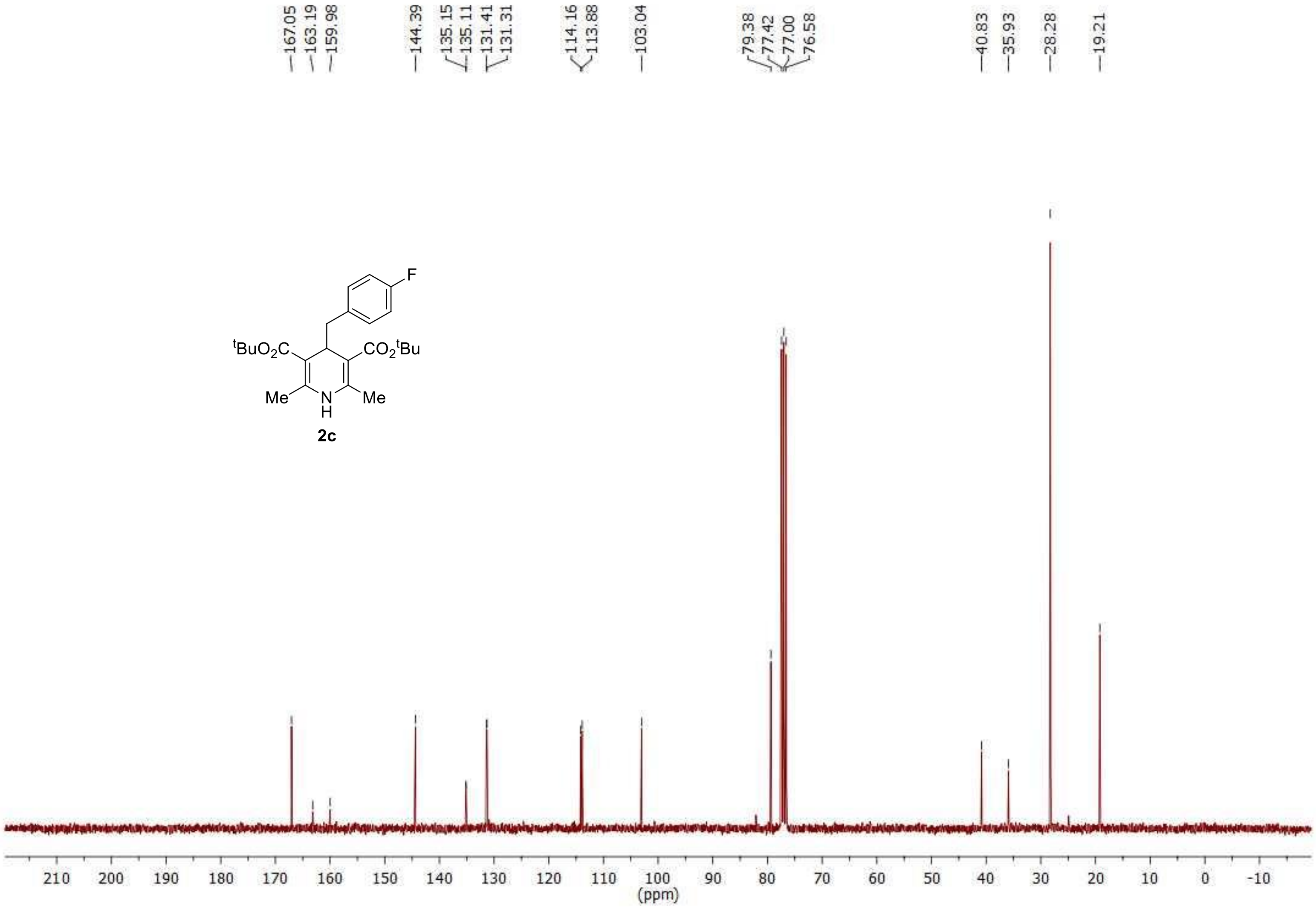


Figure S28. ^{13}C spectrum of **2c**.

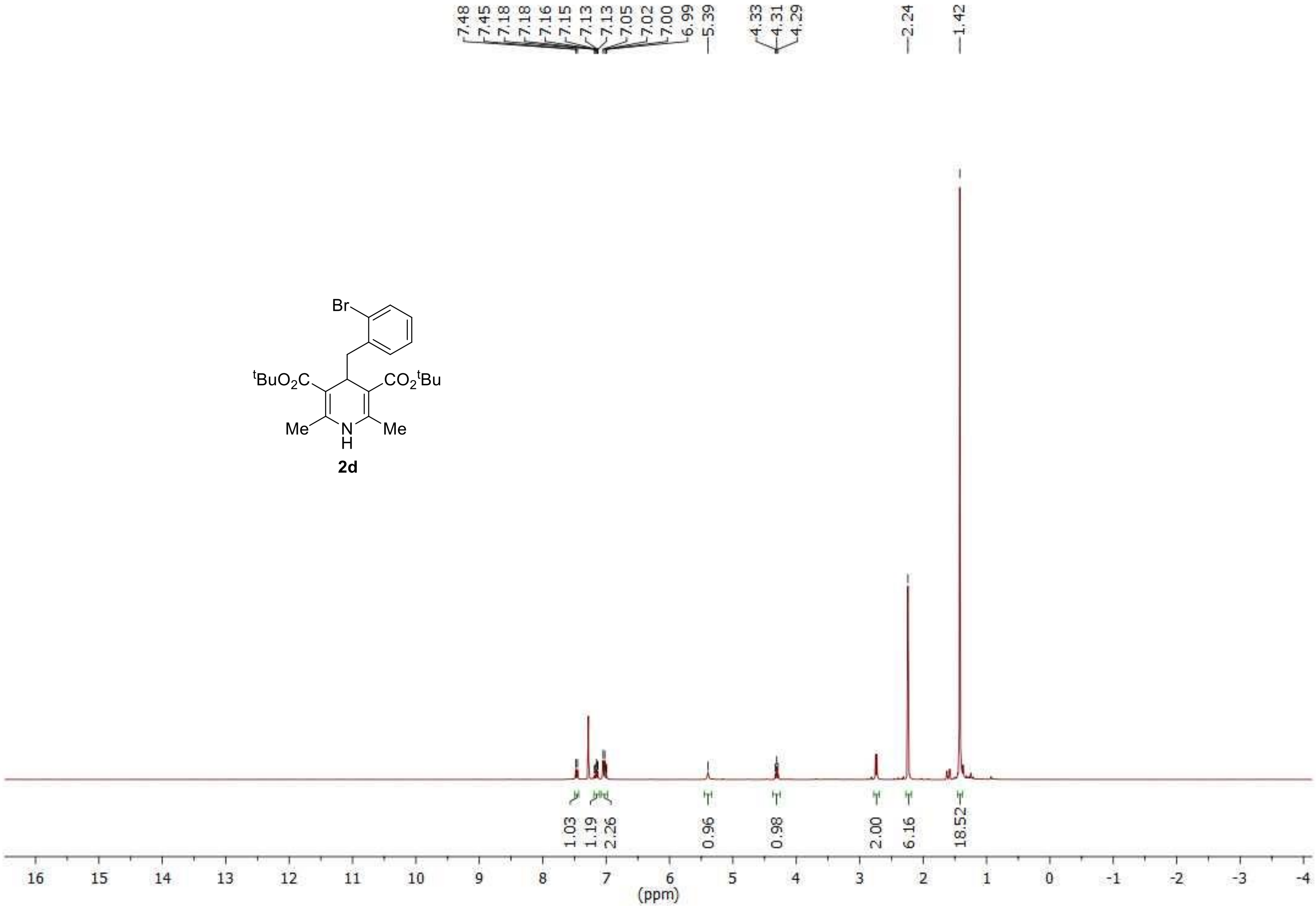


Figure S29. ^{1}H spectrum of **2d**.

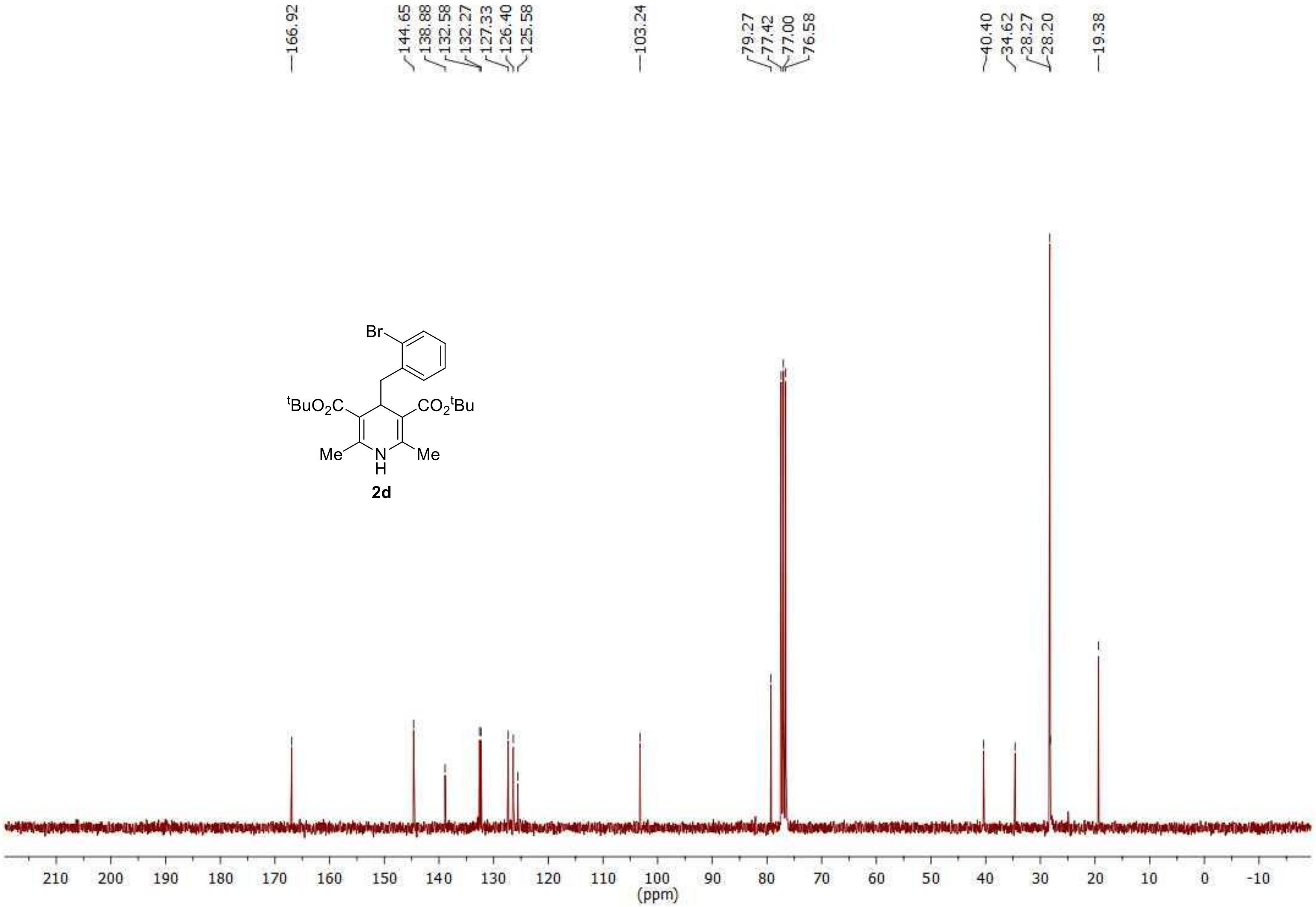


Figure S30. ^{13}C spectrum of **2d**.

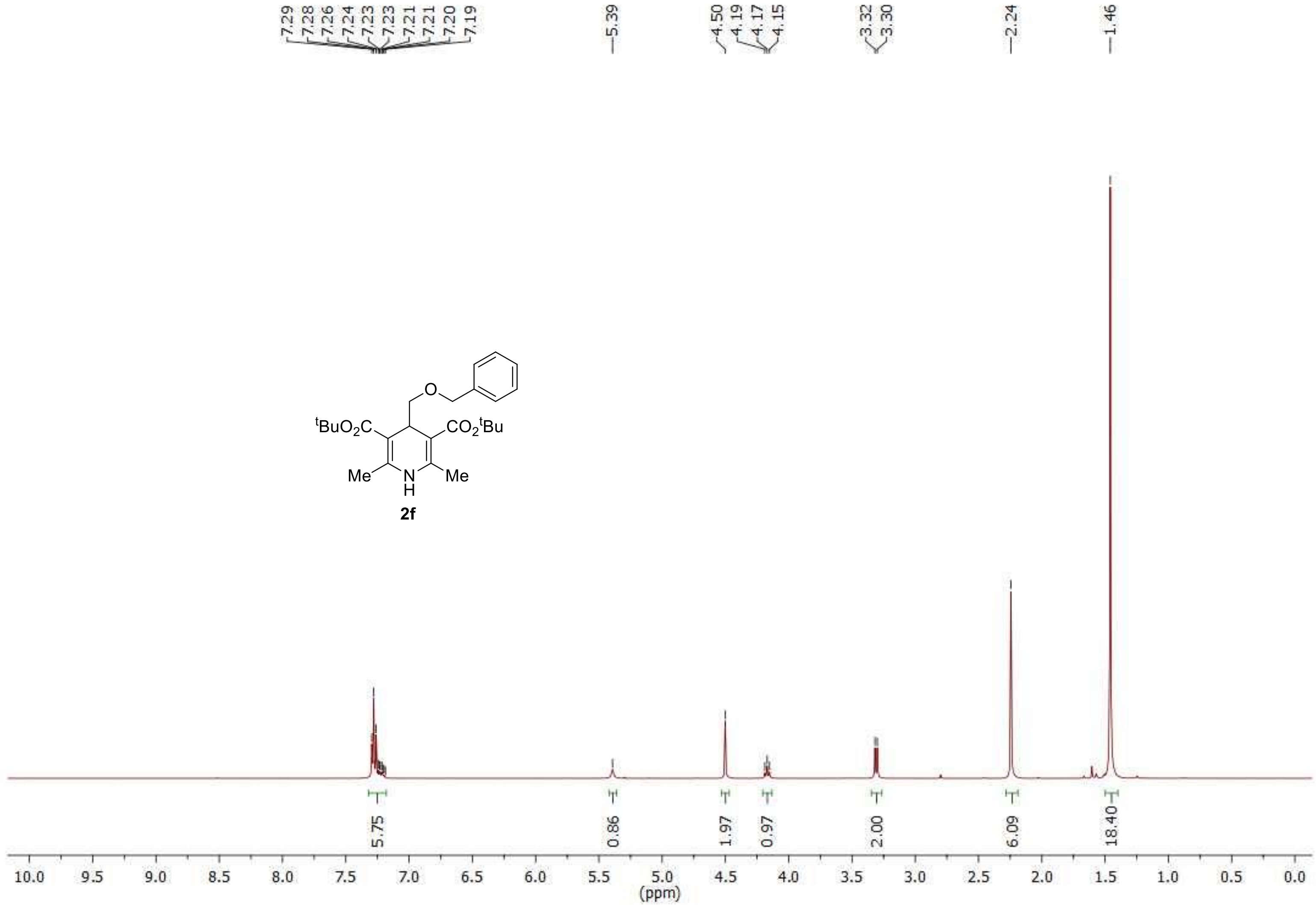


Figure S31. ^{1}H spectrum of **2f**.

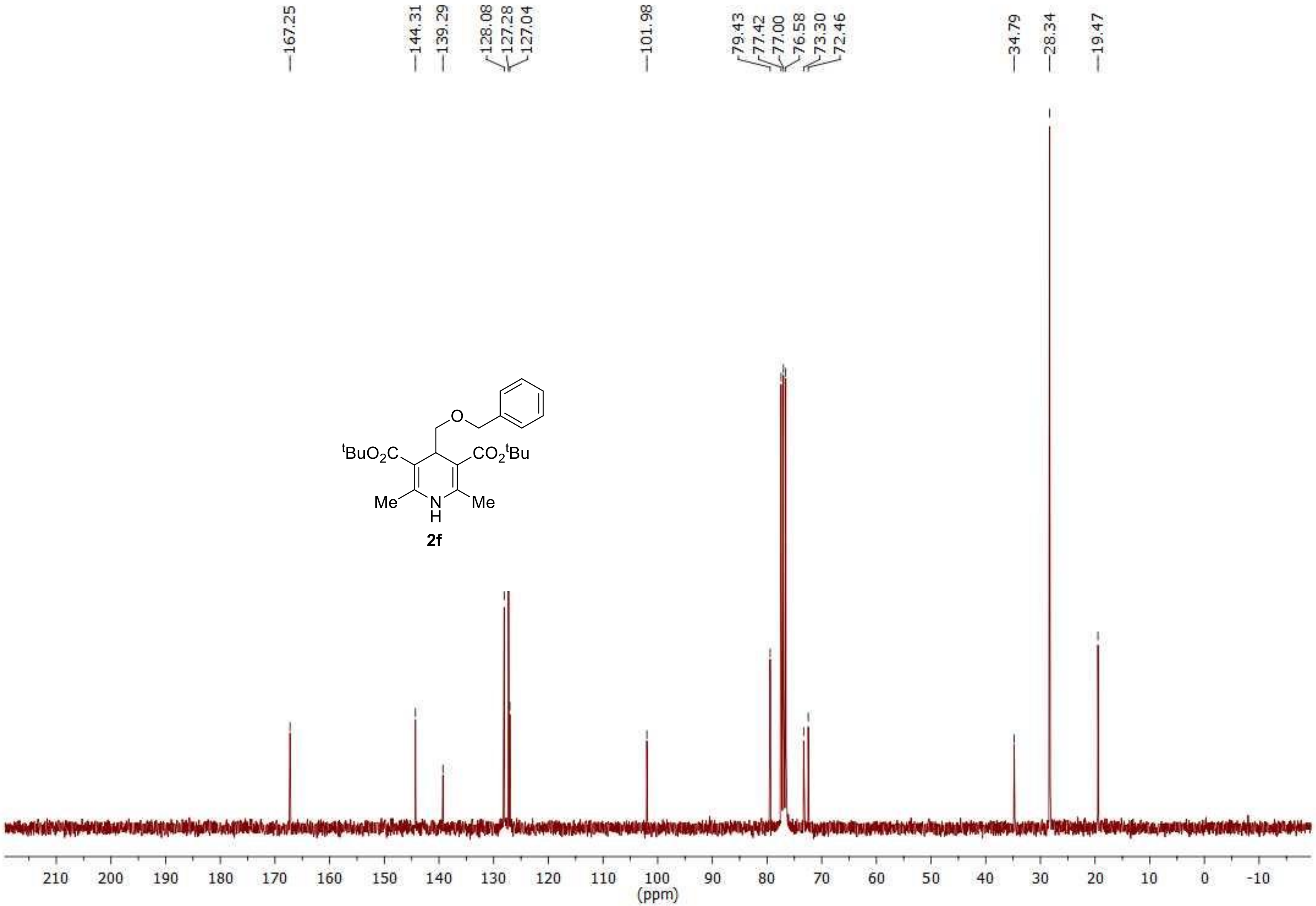


Figure S32. ^{13}C spectrum of **2f**.

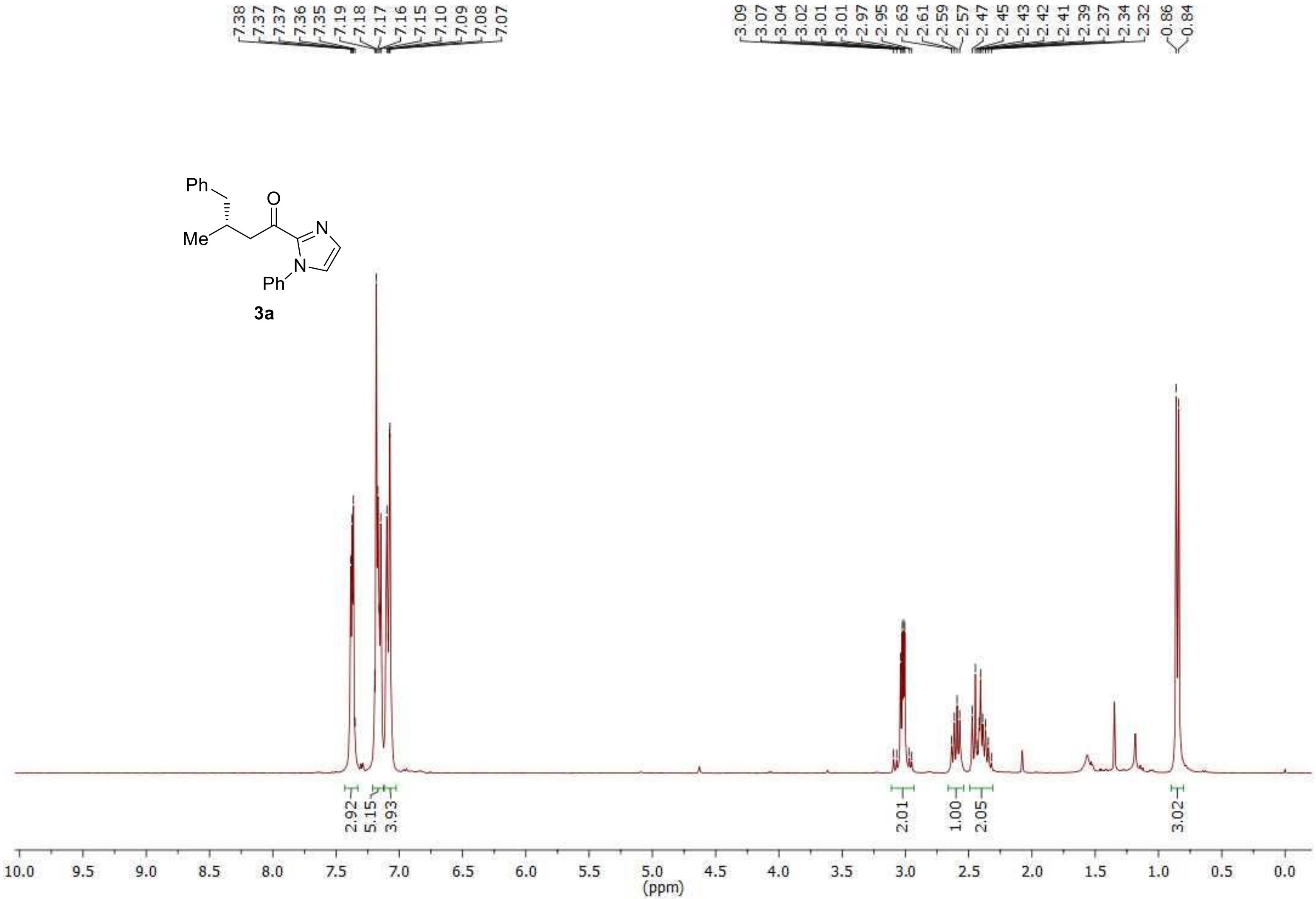


Figure S33. ^{1}H spectrum of **3a**.

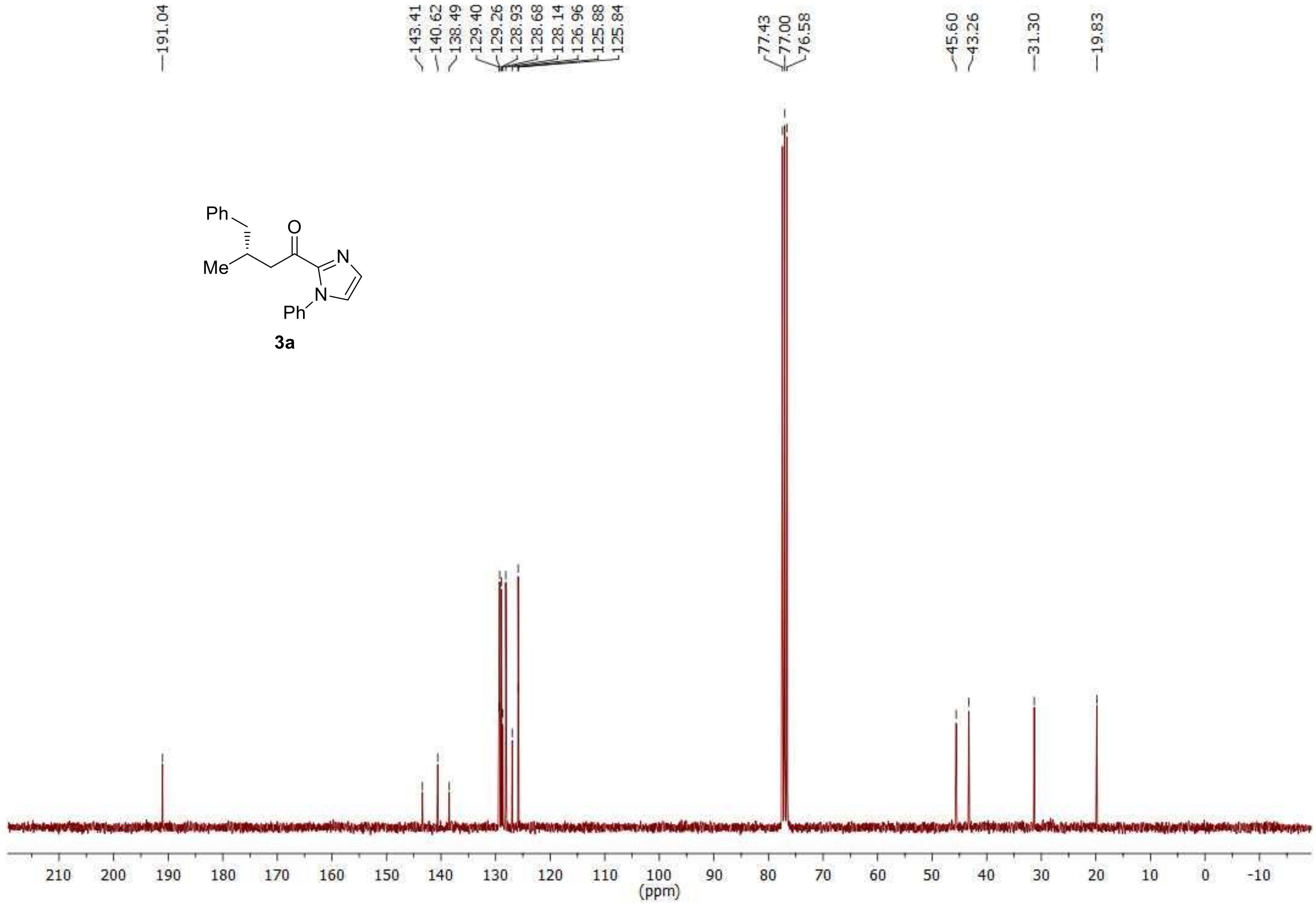
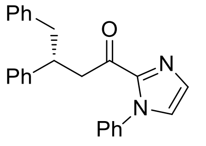


Figure S34. ^{13}C spectrum of **3a**.



3b

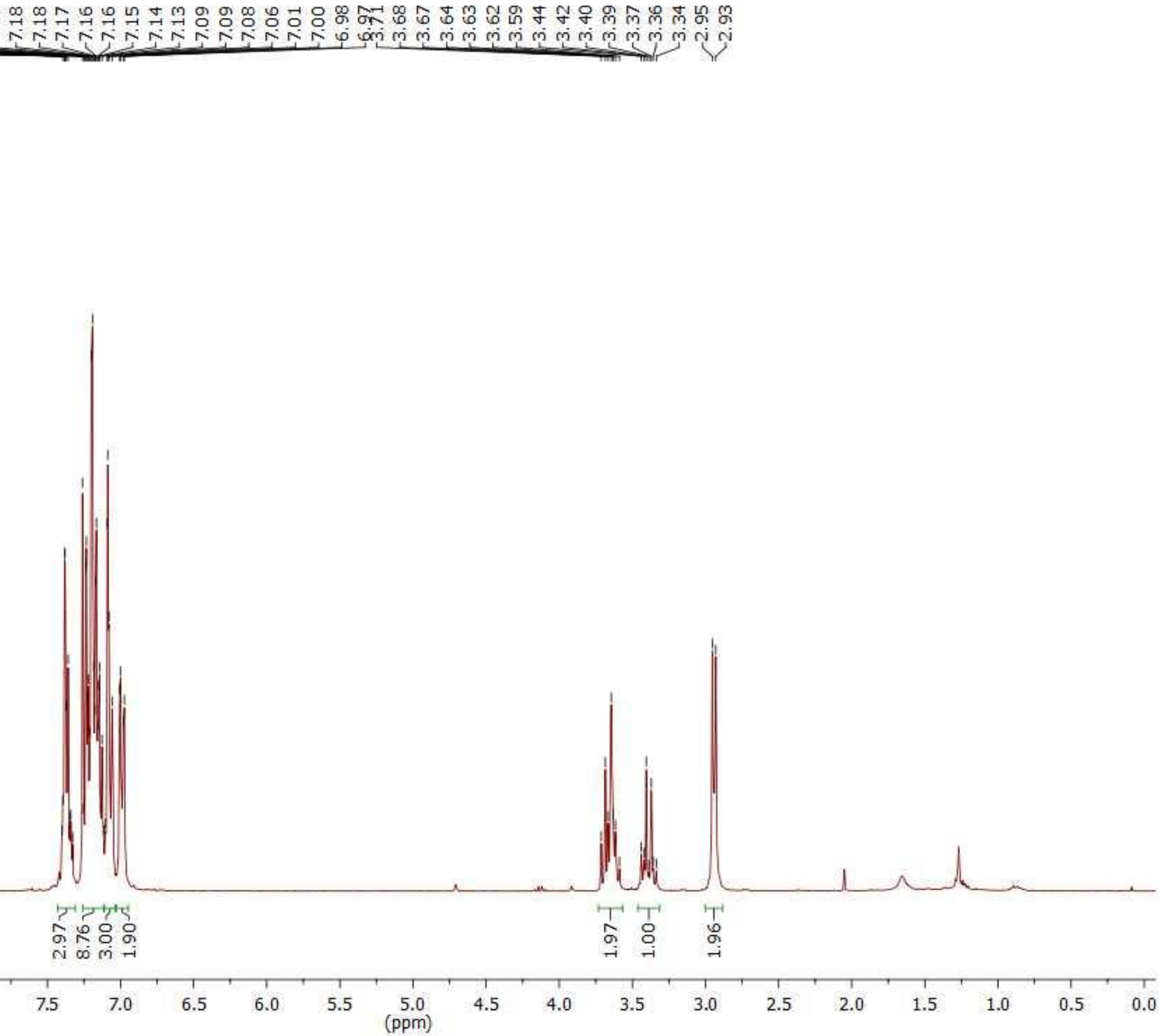


Figure S35. ^{1}H spectrum of **3b**.

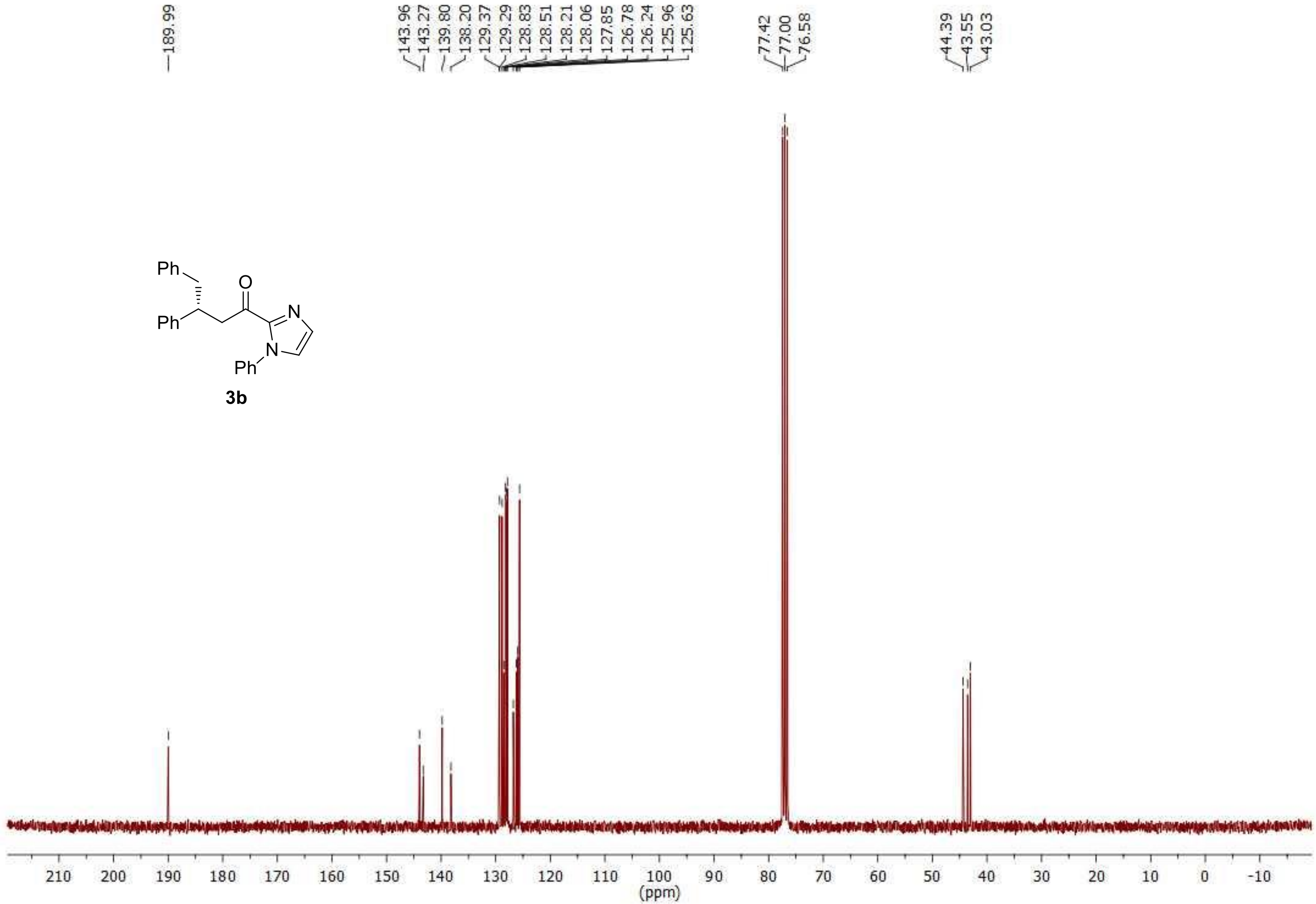


Figure S36. ^{13}C spectrum of **3b**.

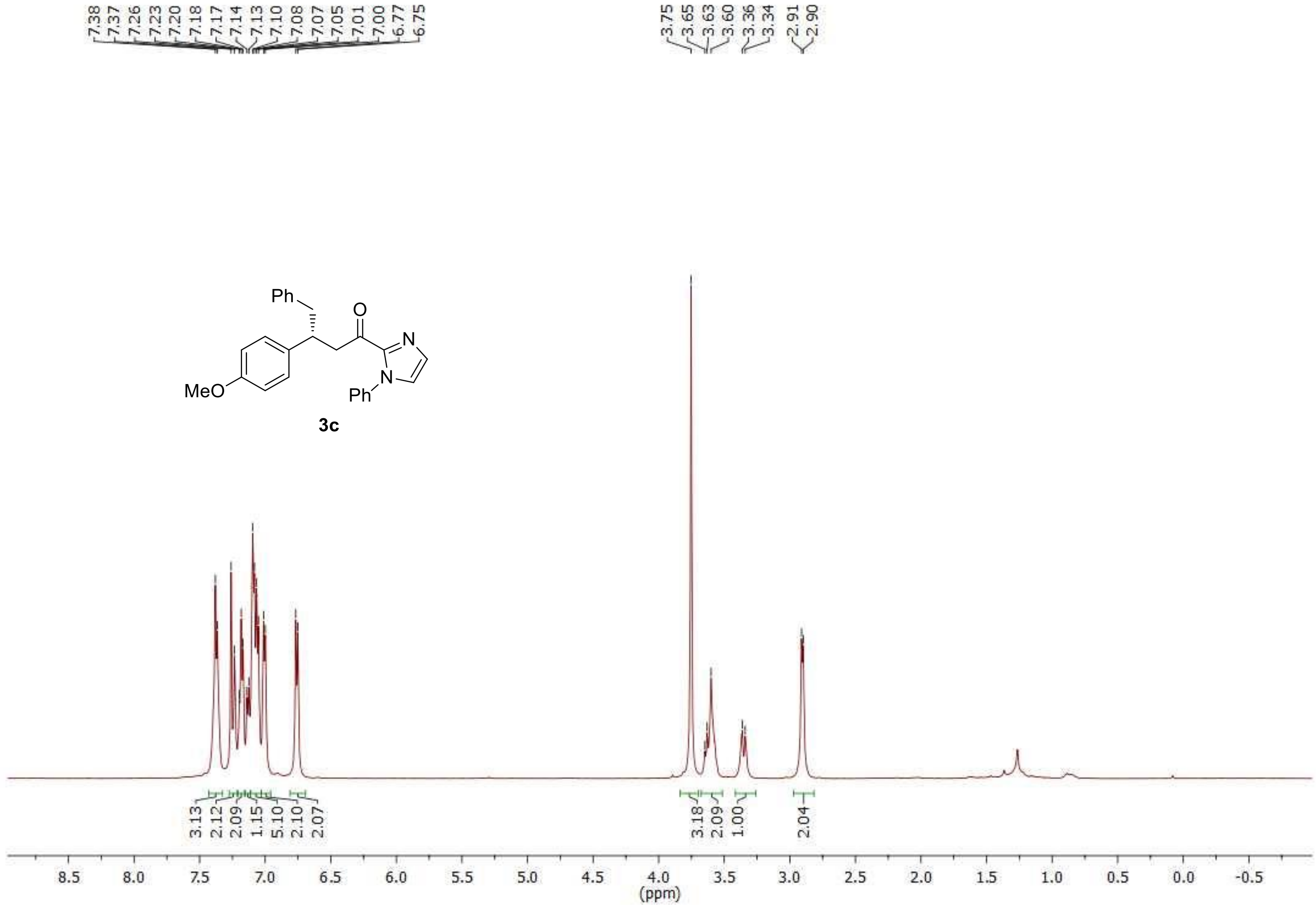


Figure S37. ^{1}H spectrum of **3c**.

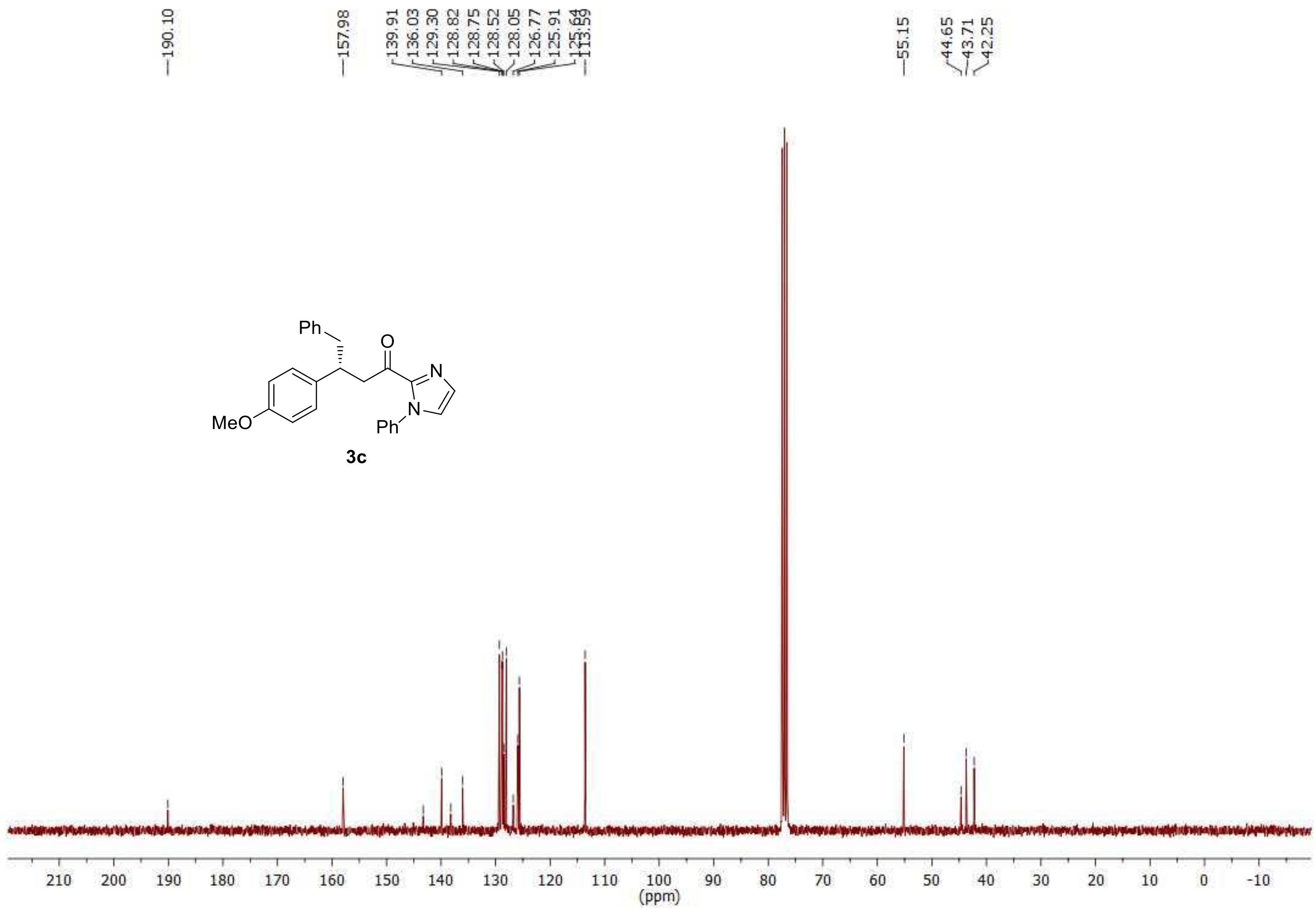


Figure S38. ^{13}C spectrum of **3c**.

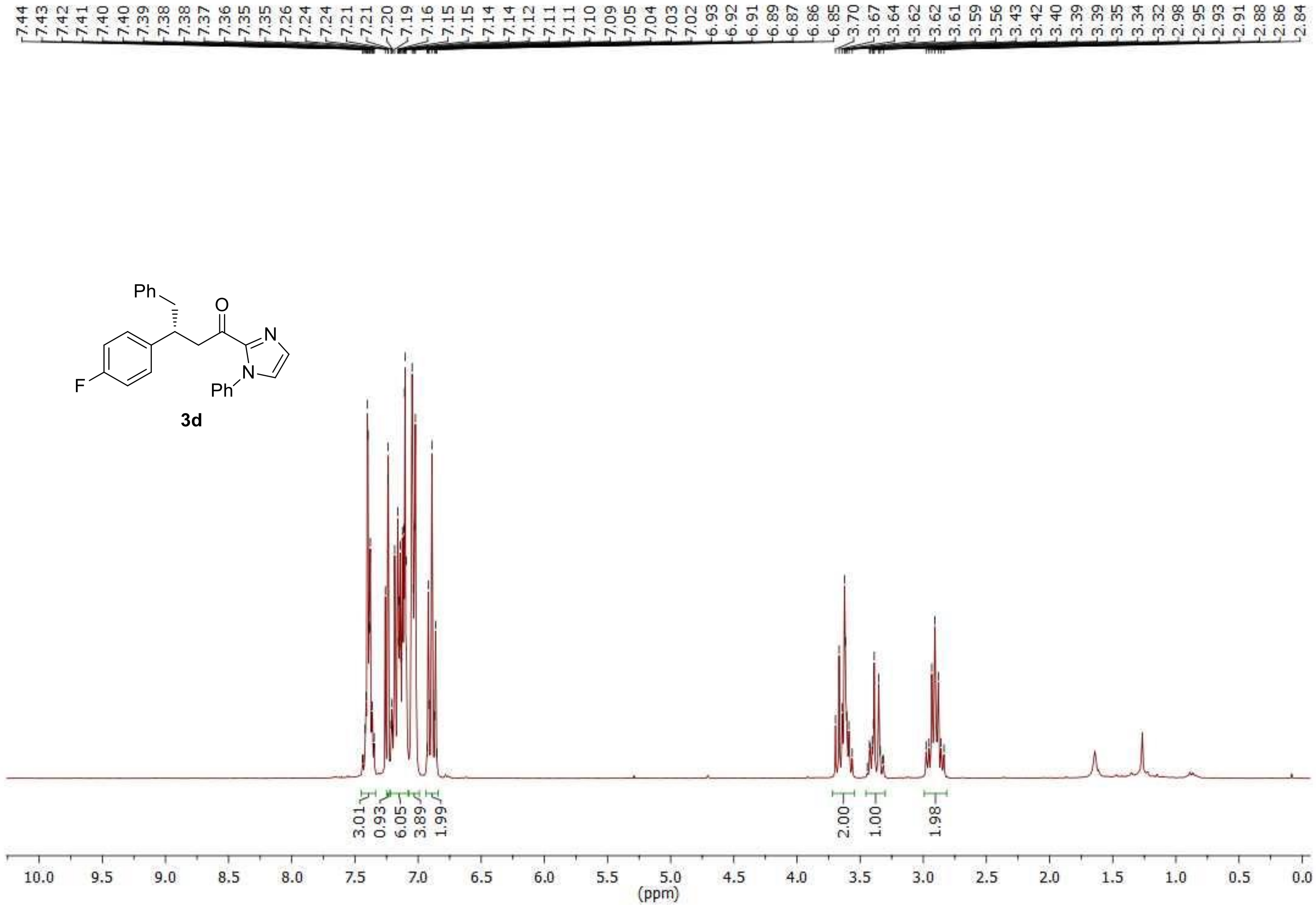
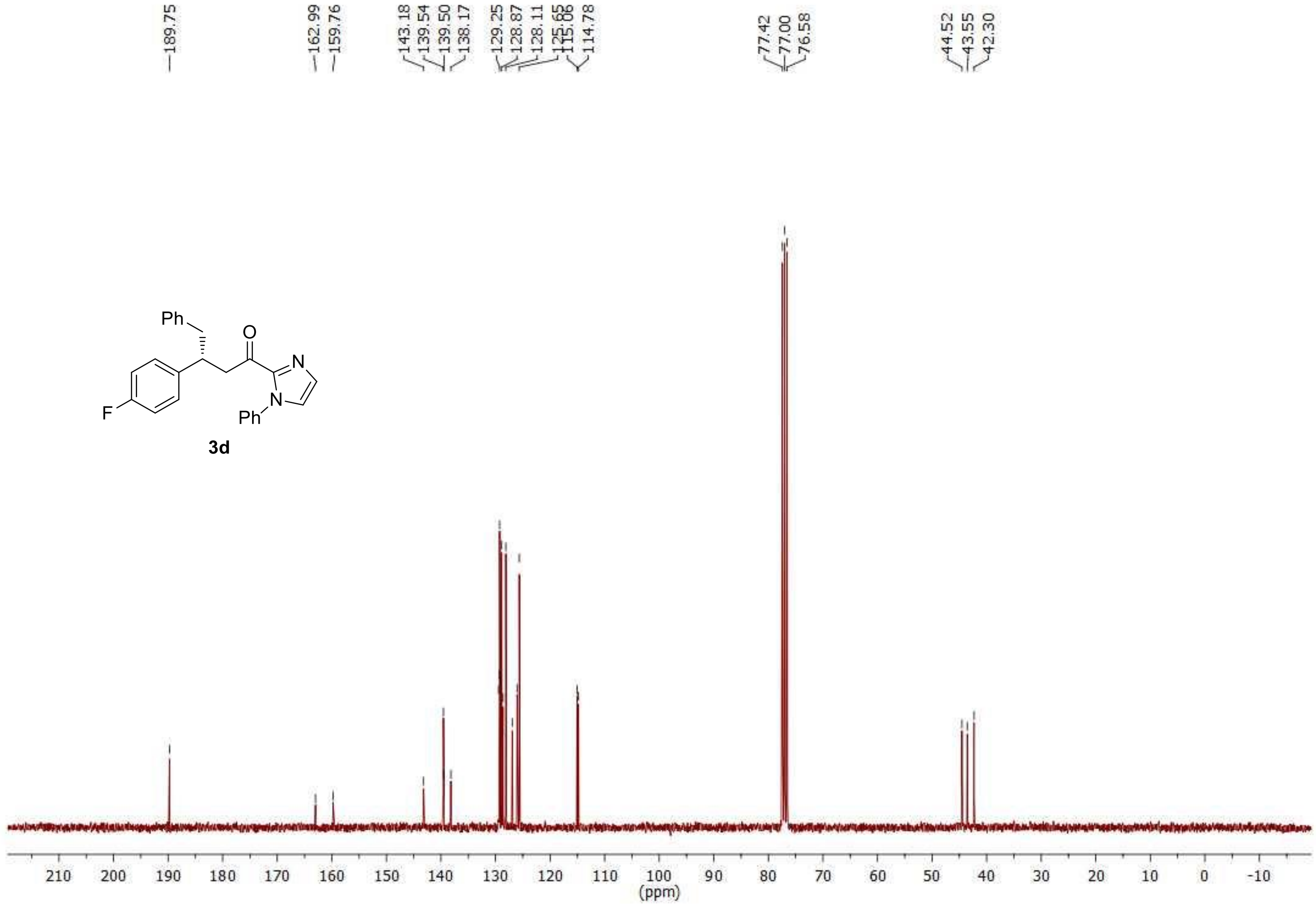


Figure S39. ^{1}H spectrum of **3d**.



3d

Figure S40. ^{13}C spectrum of **3d**.

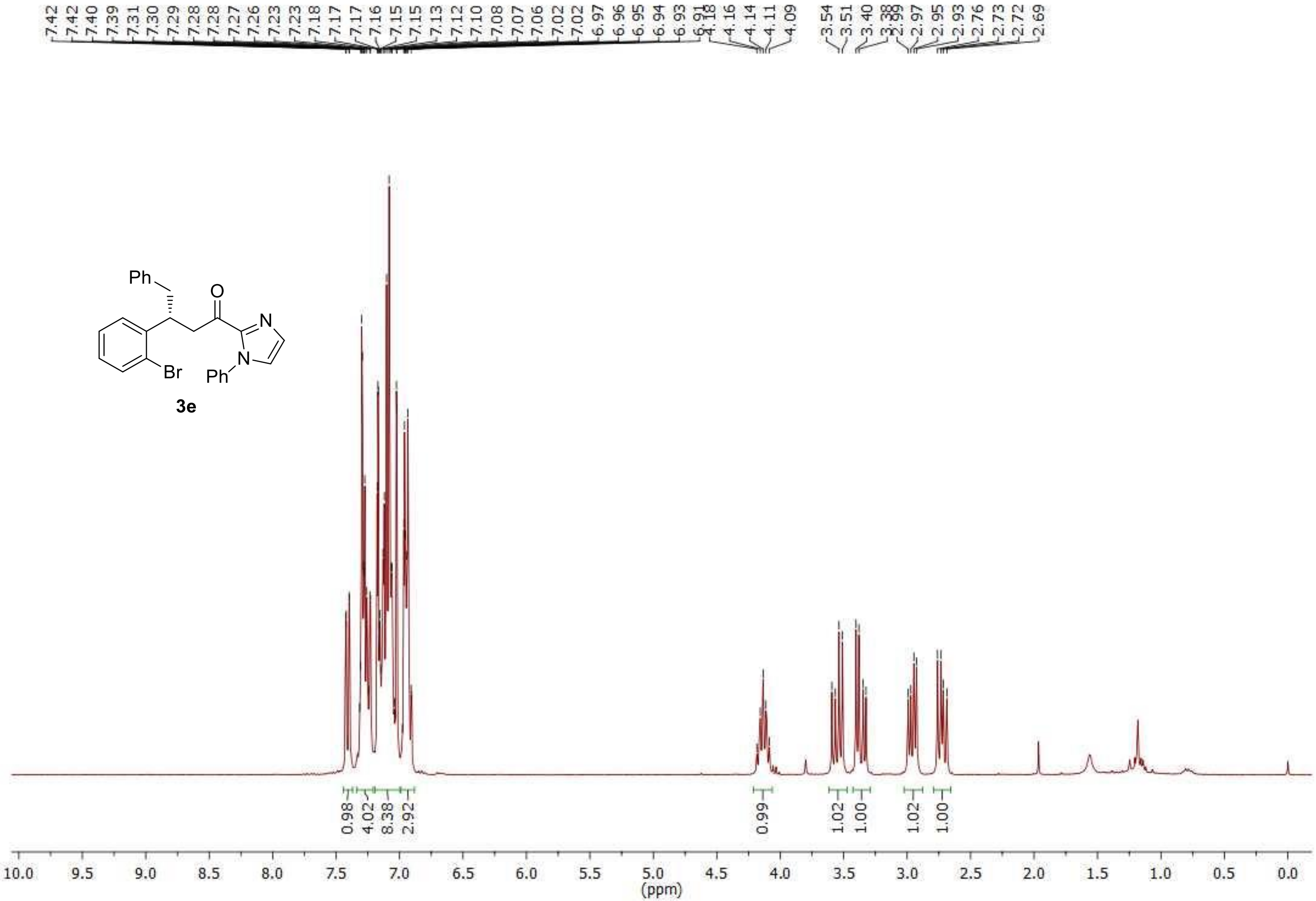


Figure S41. ^{1}H spectrum of **3e**.

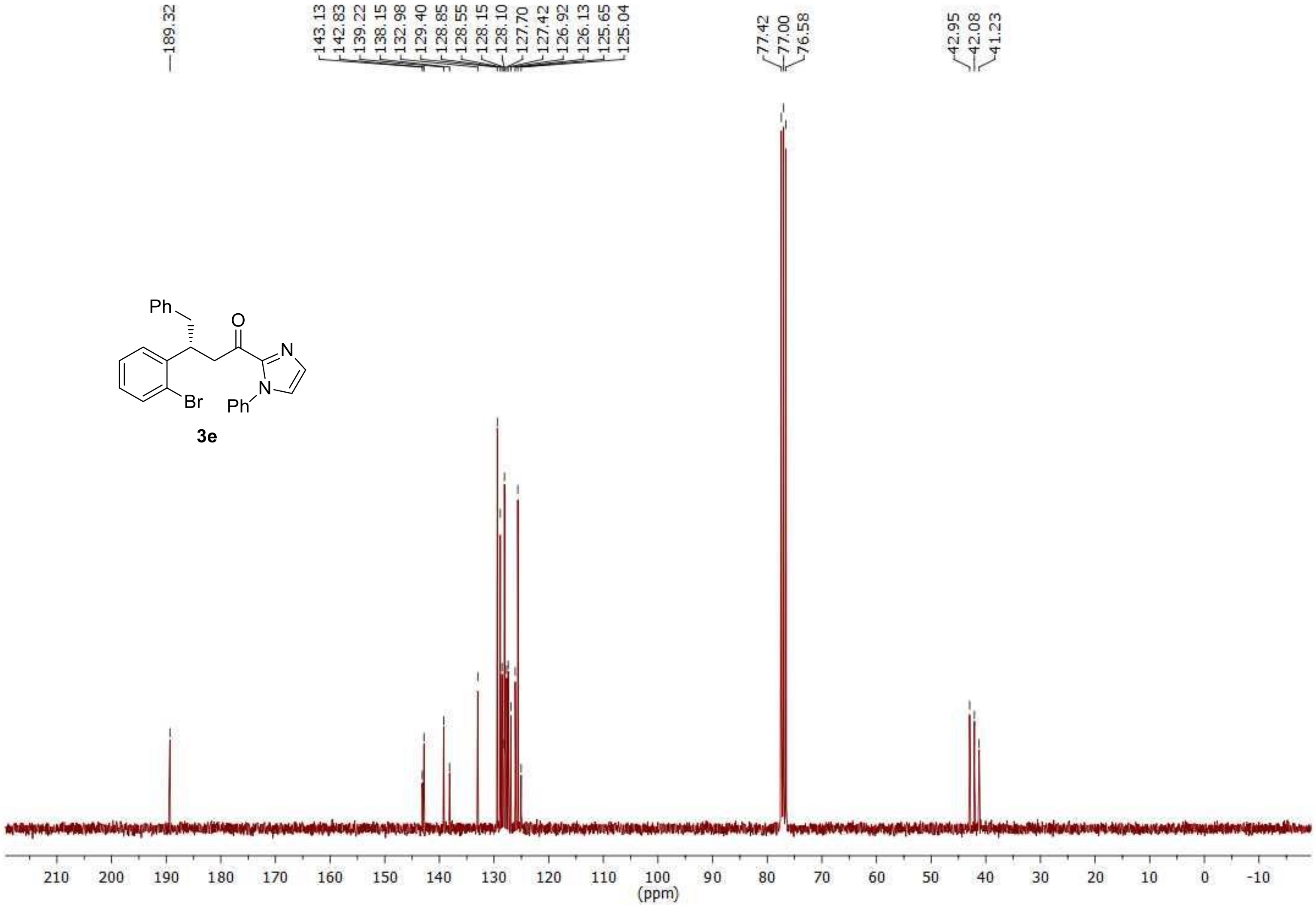


Figure S42. ^{13}C spectrum of **3e**.

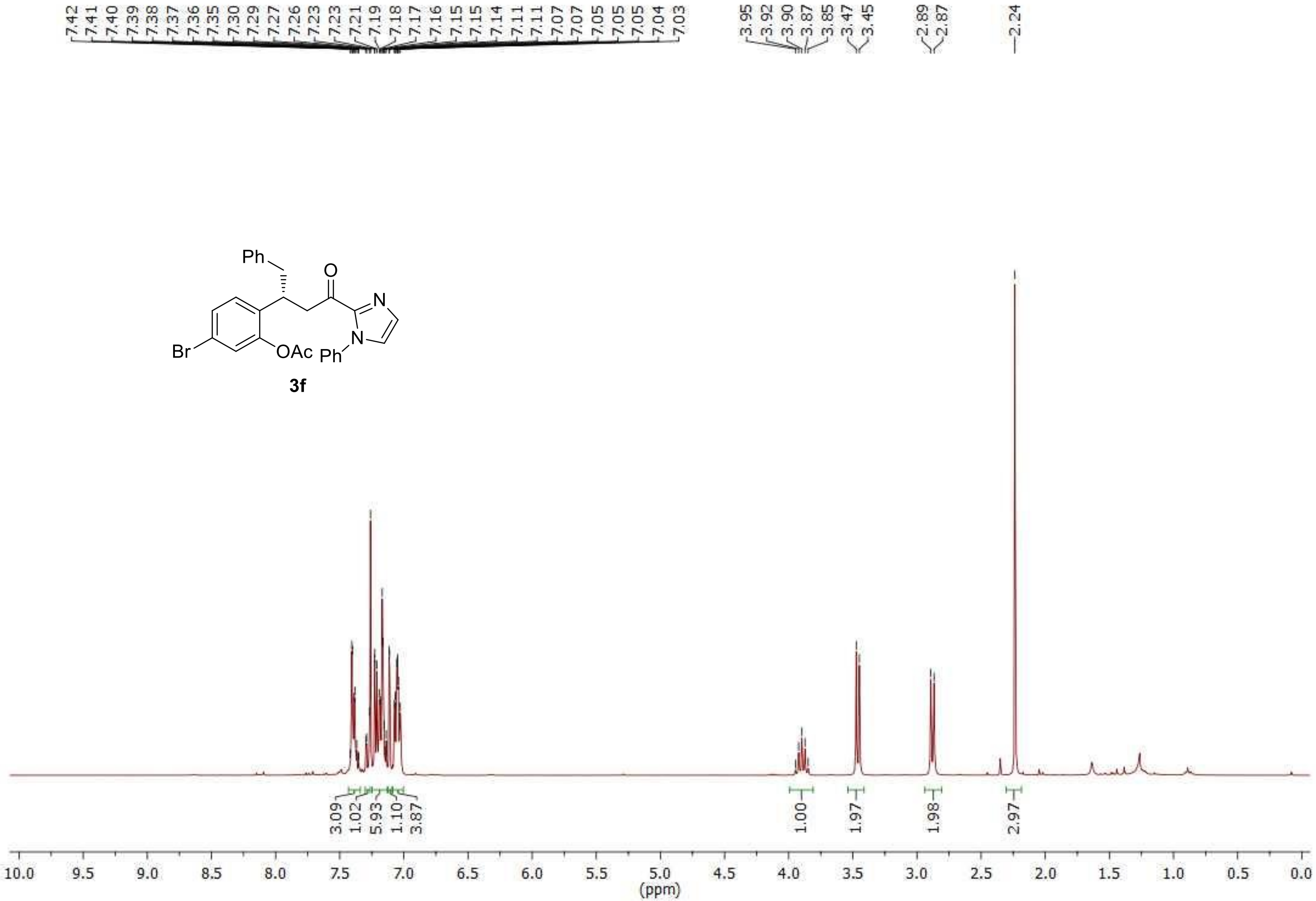


Figure S43. ^{1}H spectrum of **3f**.

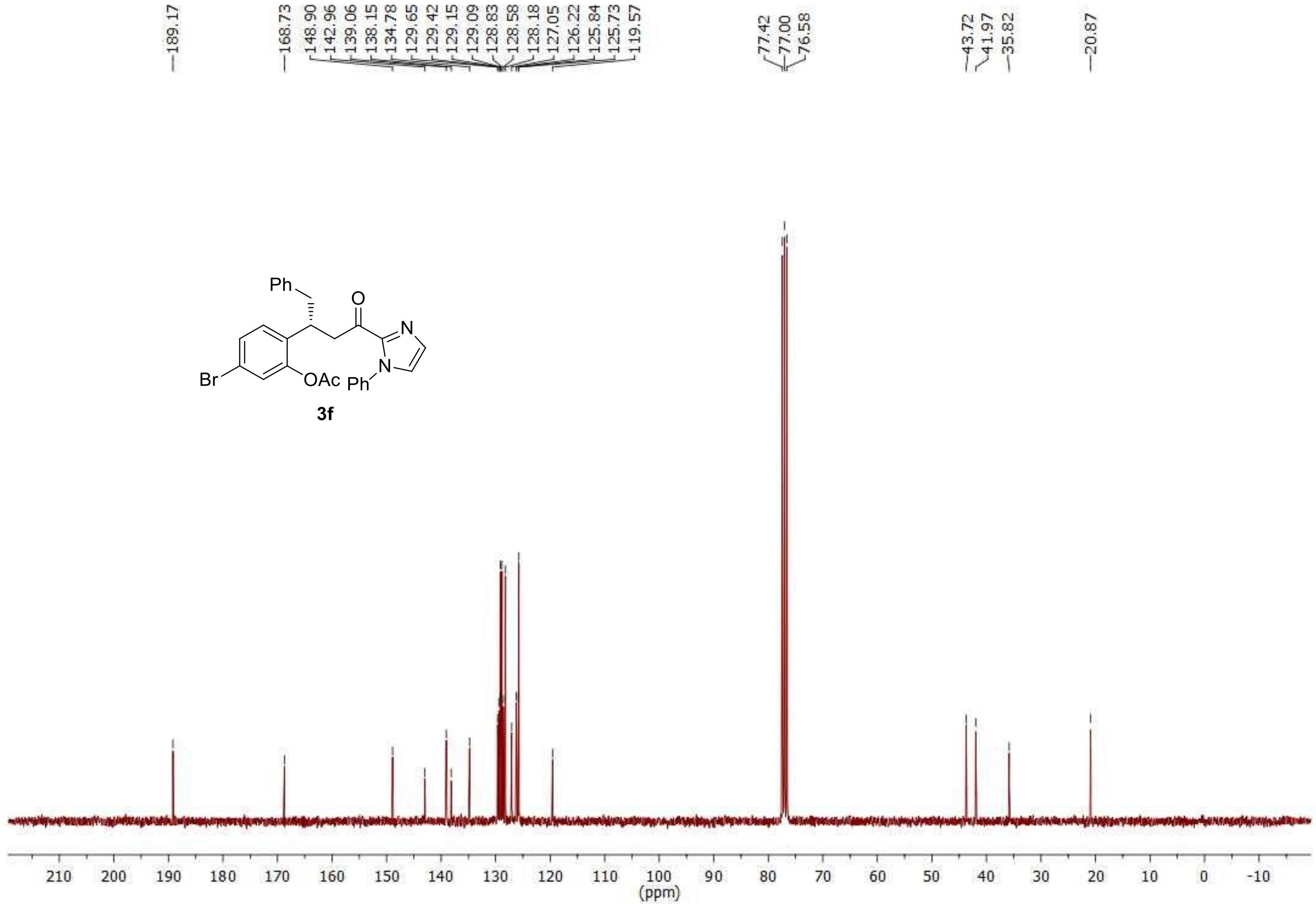


Figure S44. ^{13}C spectrum of **3f**.

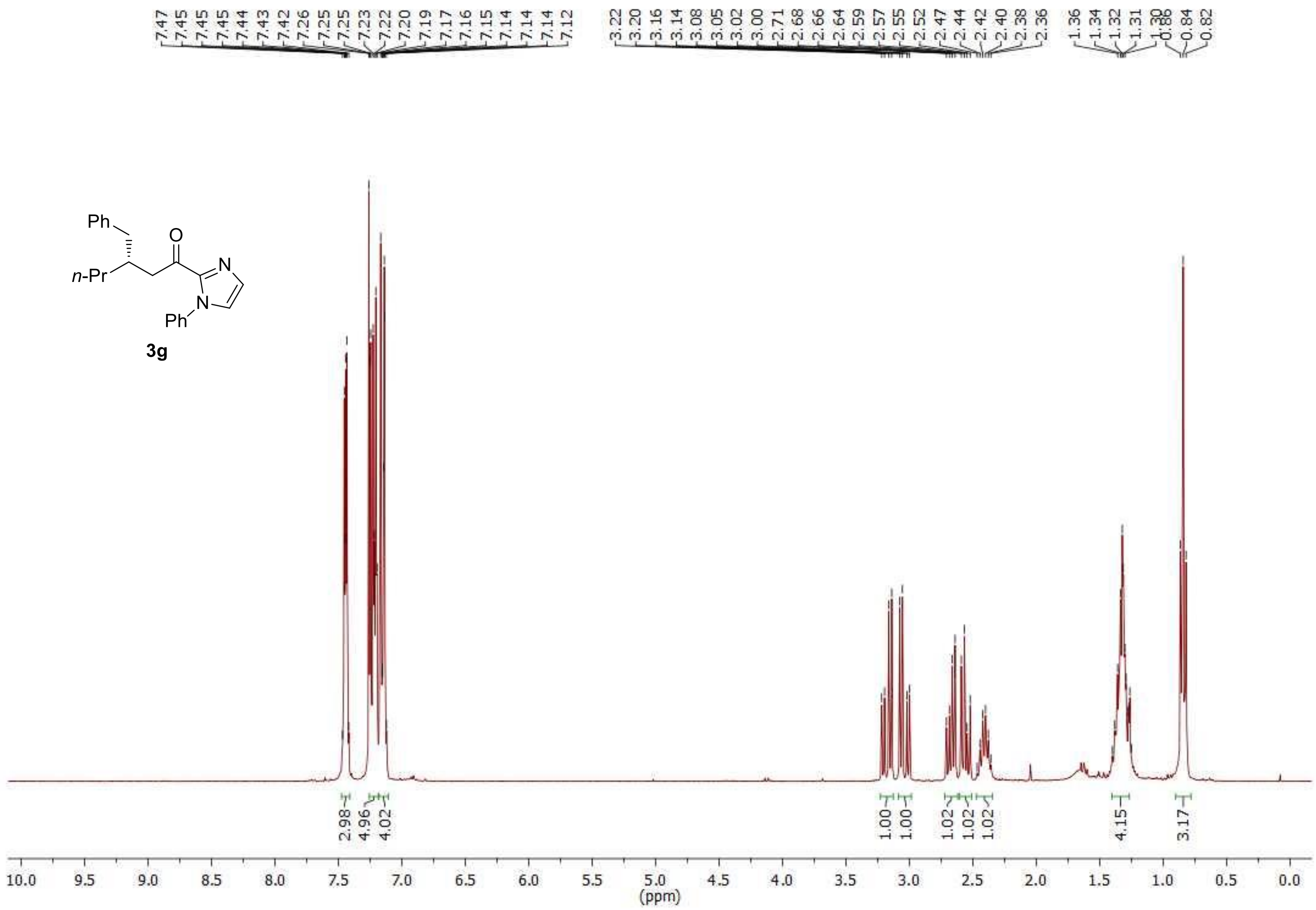
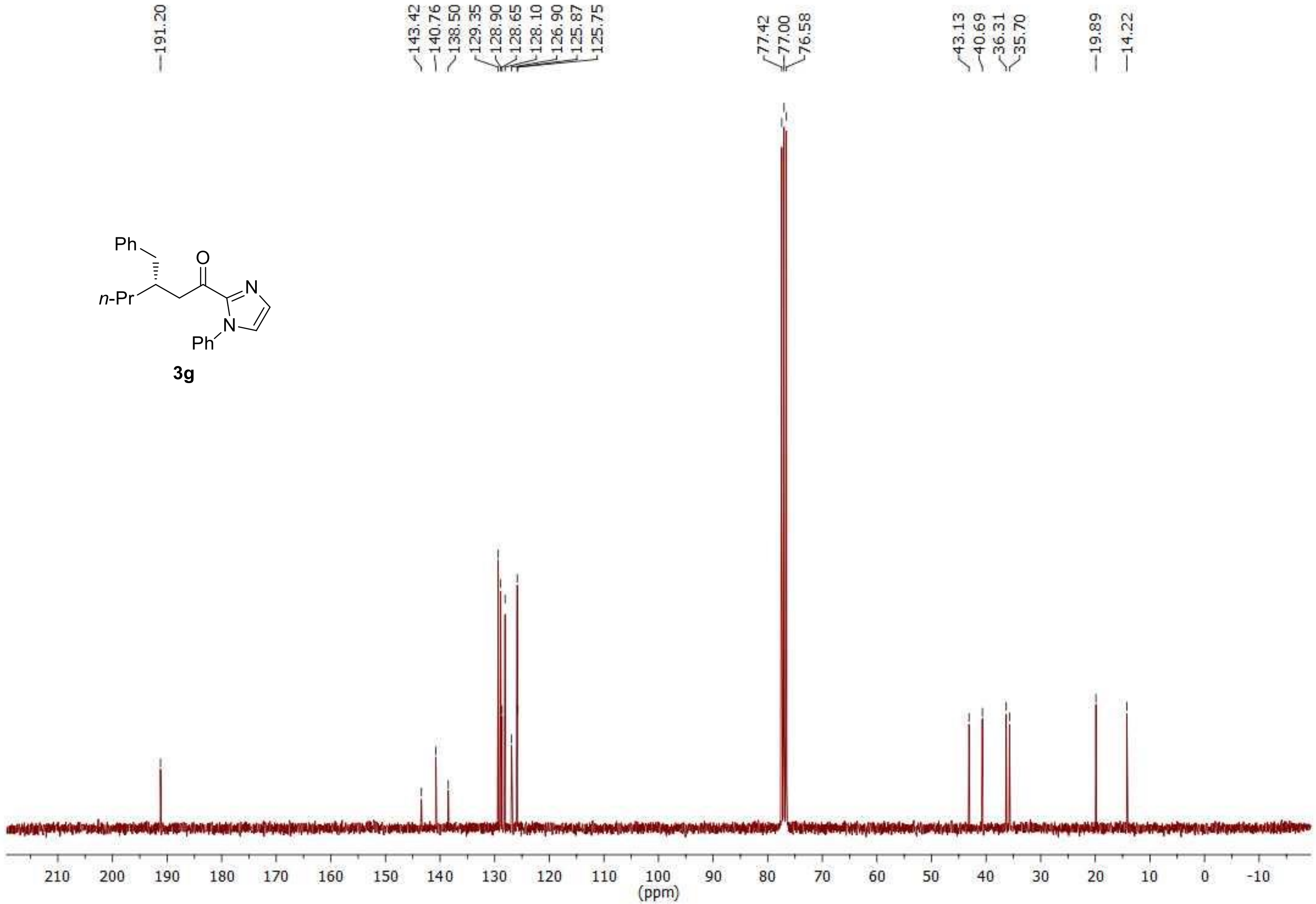


Figure S45. ^{1}H spectrum of **3g**.



3g

Figure S46. ^{13}C spectrum of **3g**.

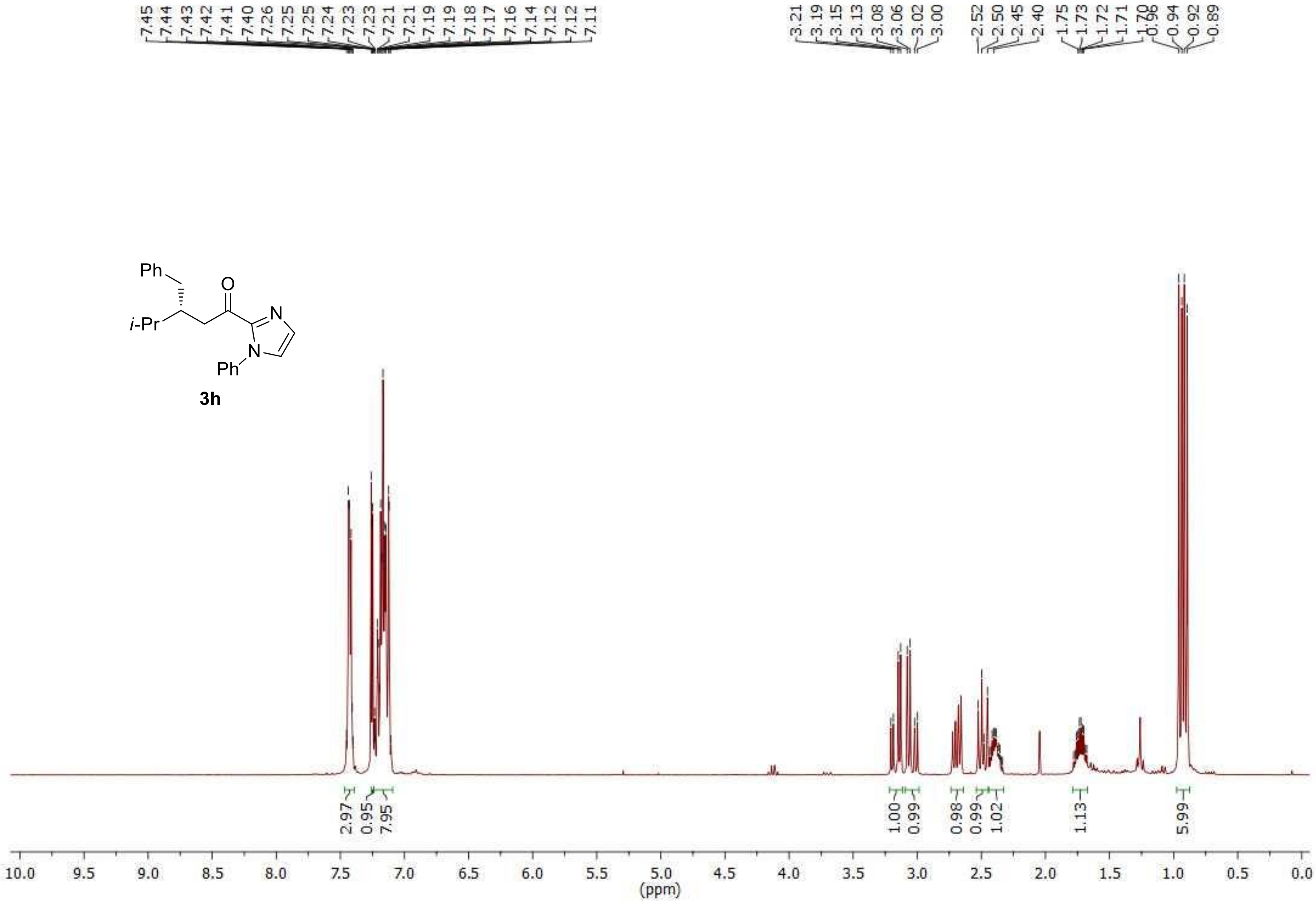


Figure S47. ^{1}H spectrum of **3h**.

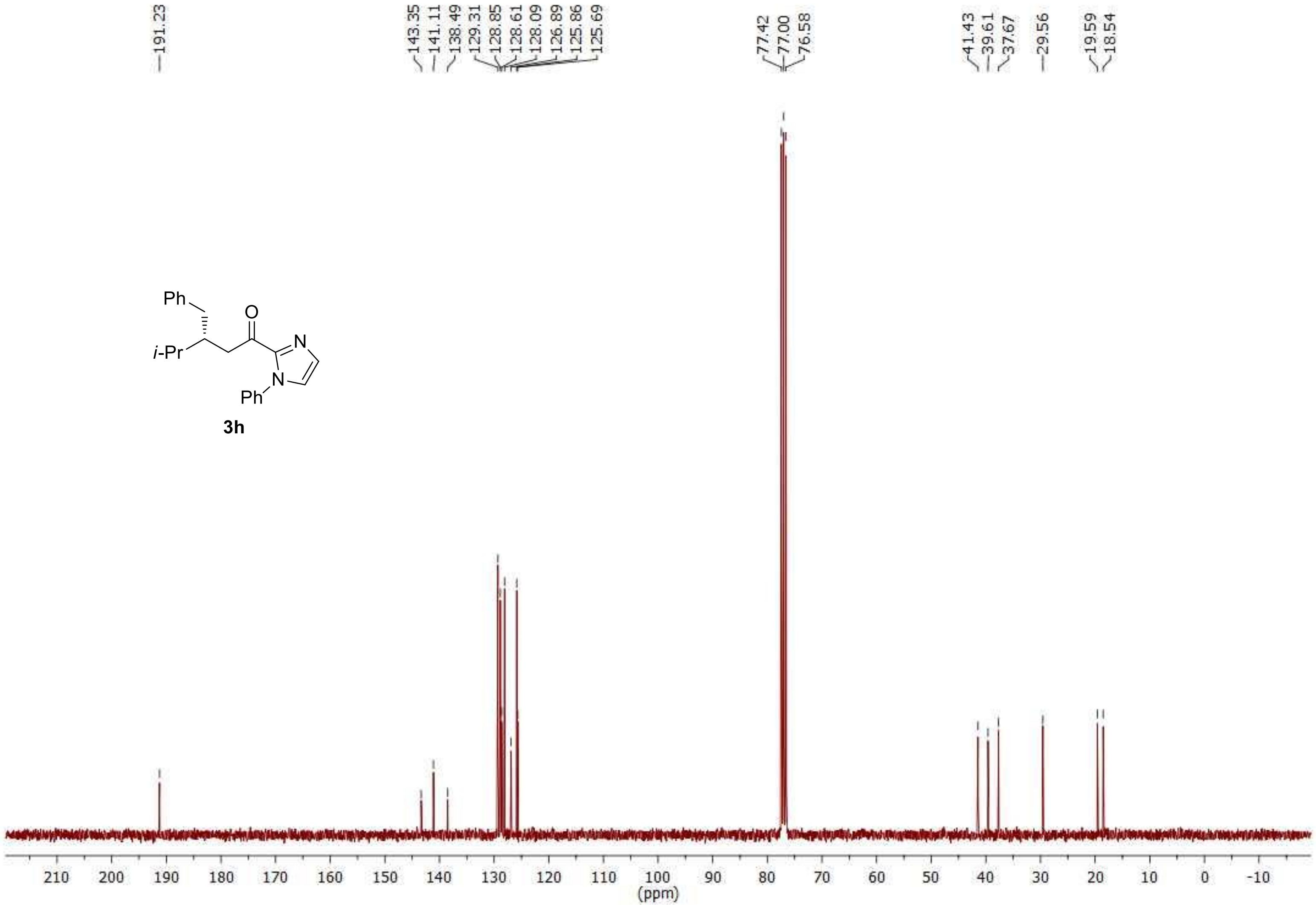


Figure S48. ^{13}C spectrum of **3h**.

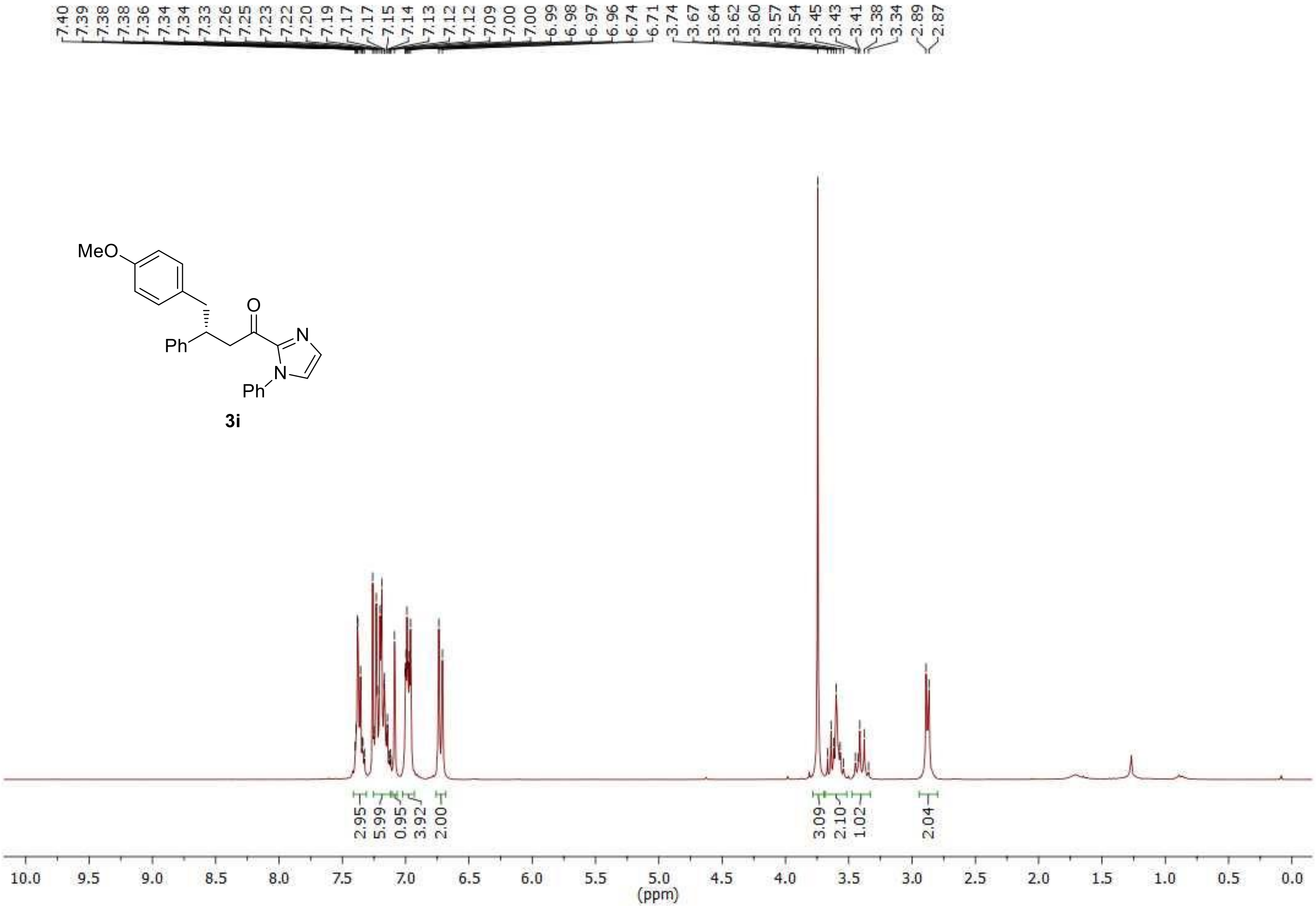


Figure S49. ^{1}H spectrum of **3i**.

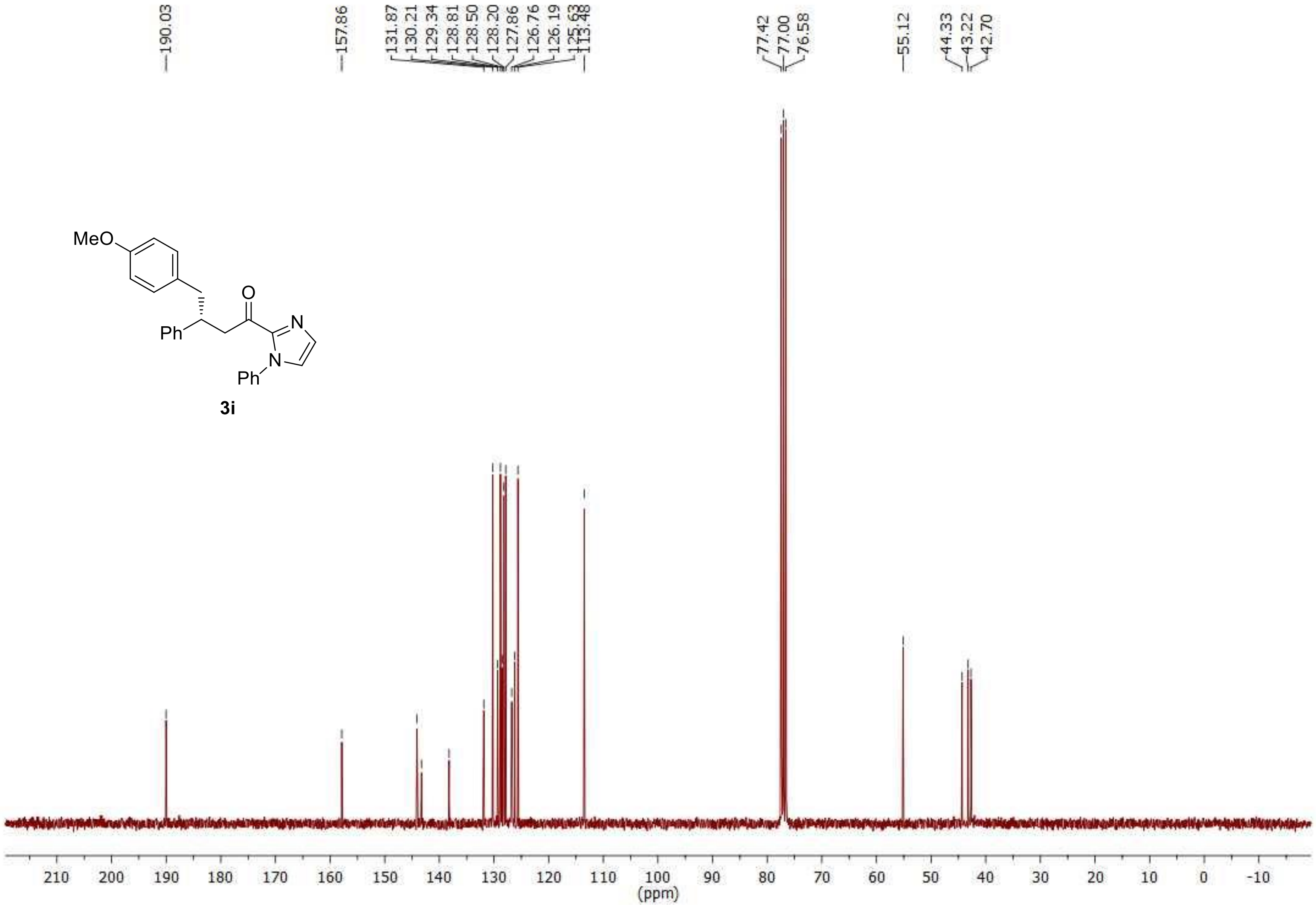


Figure S50. ^{13}C spectrum of **3i**.

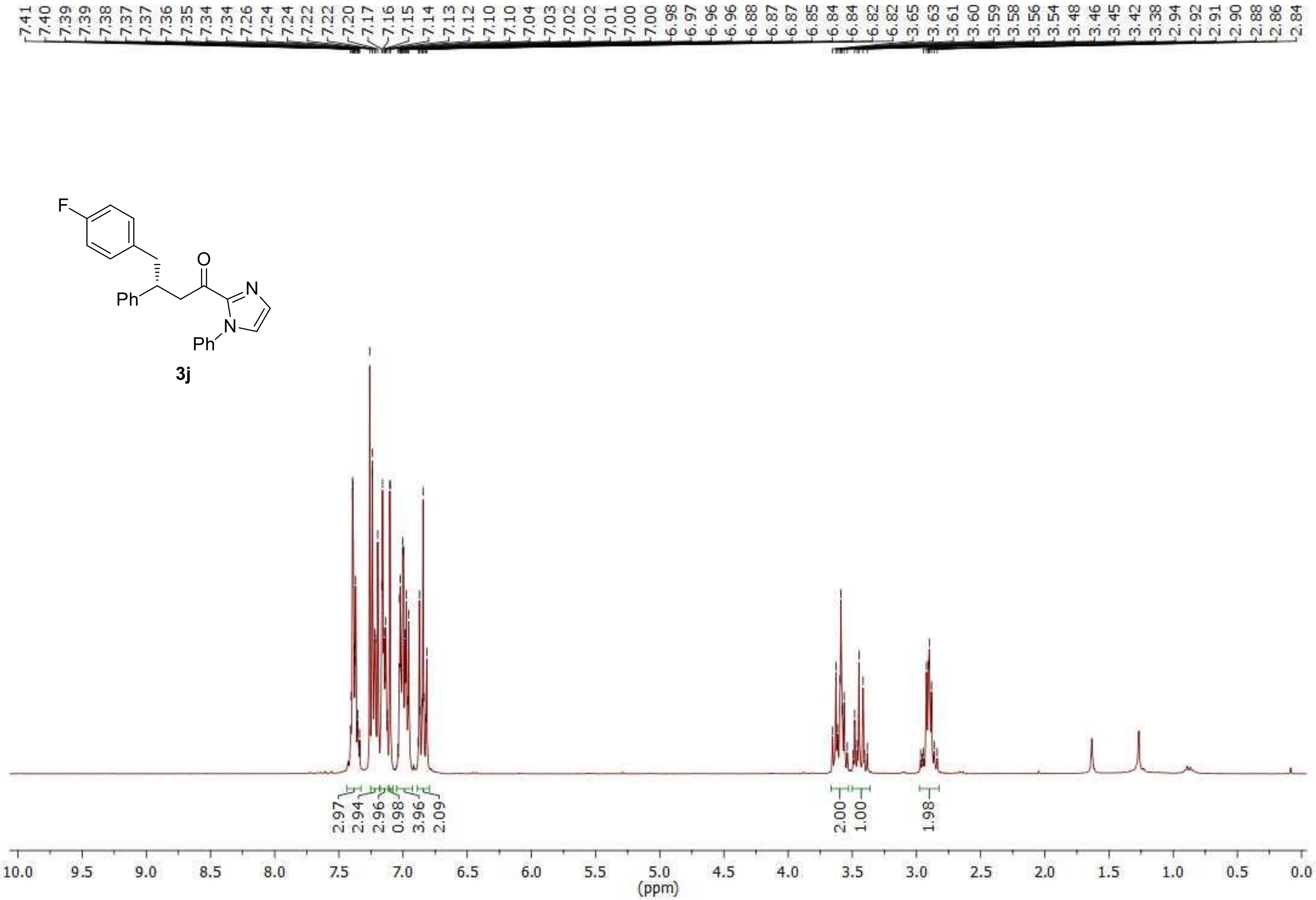


Figure S51. ^{1}H spectrum of **3j**.

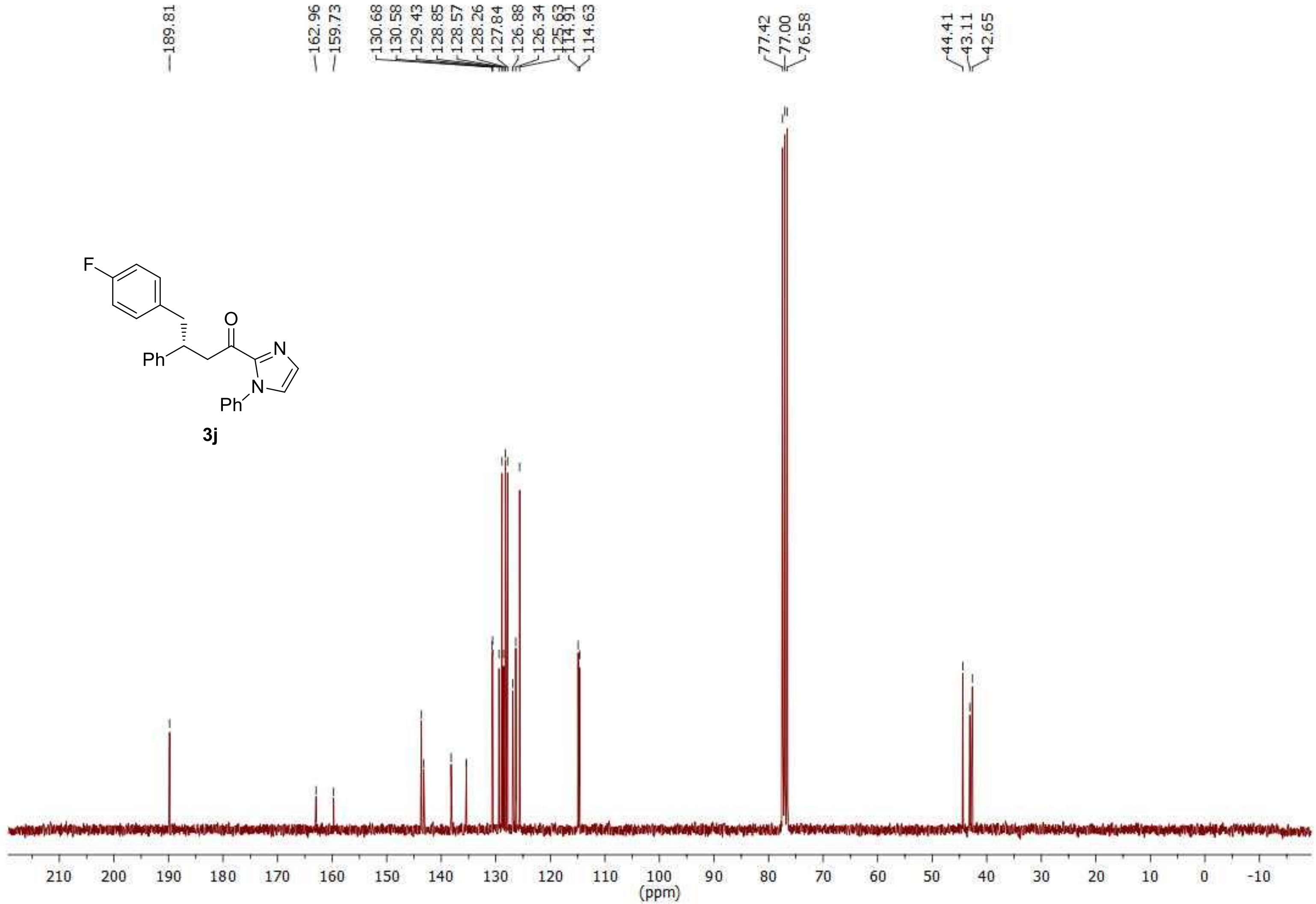
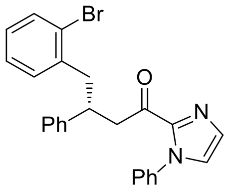


Figure S52. ^{13}C spectrum of **3j**.



3k

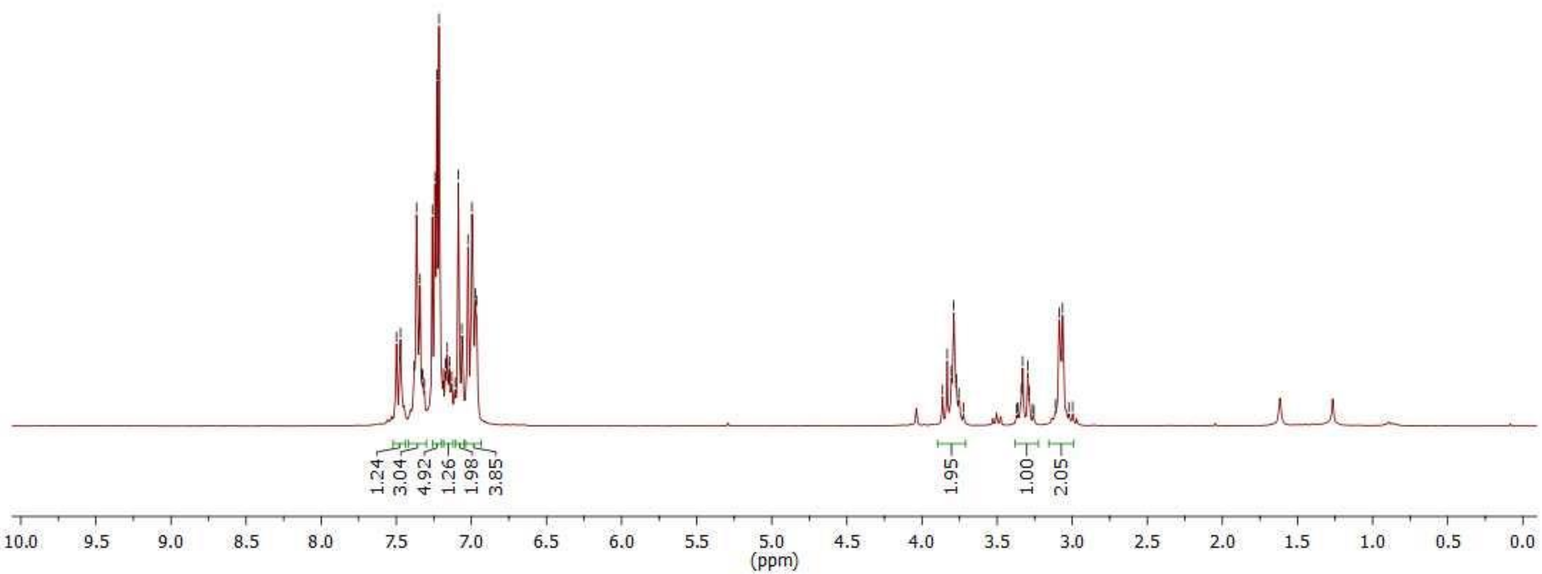


Figure S53. ^{1}H spectrum of **3k**.

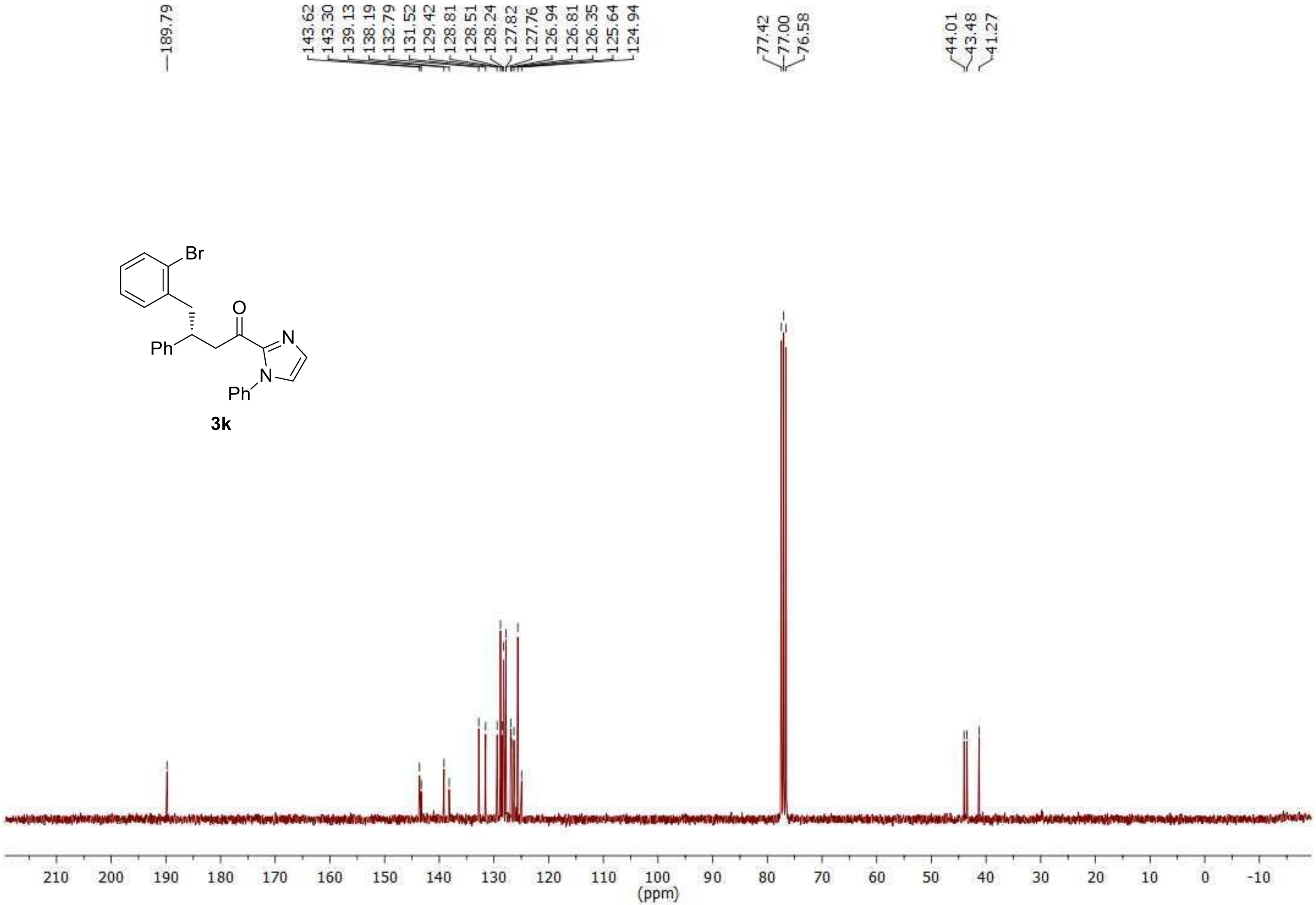


Figure S54. ^{13}C spectrum of **3k**.

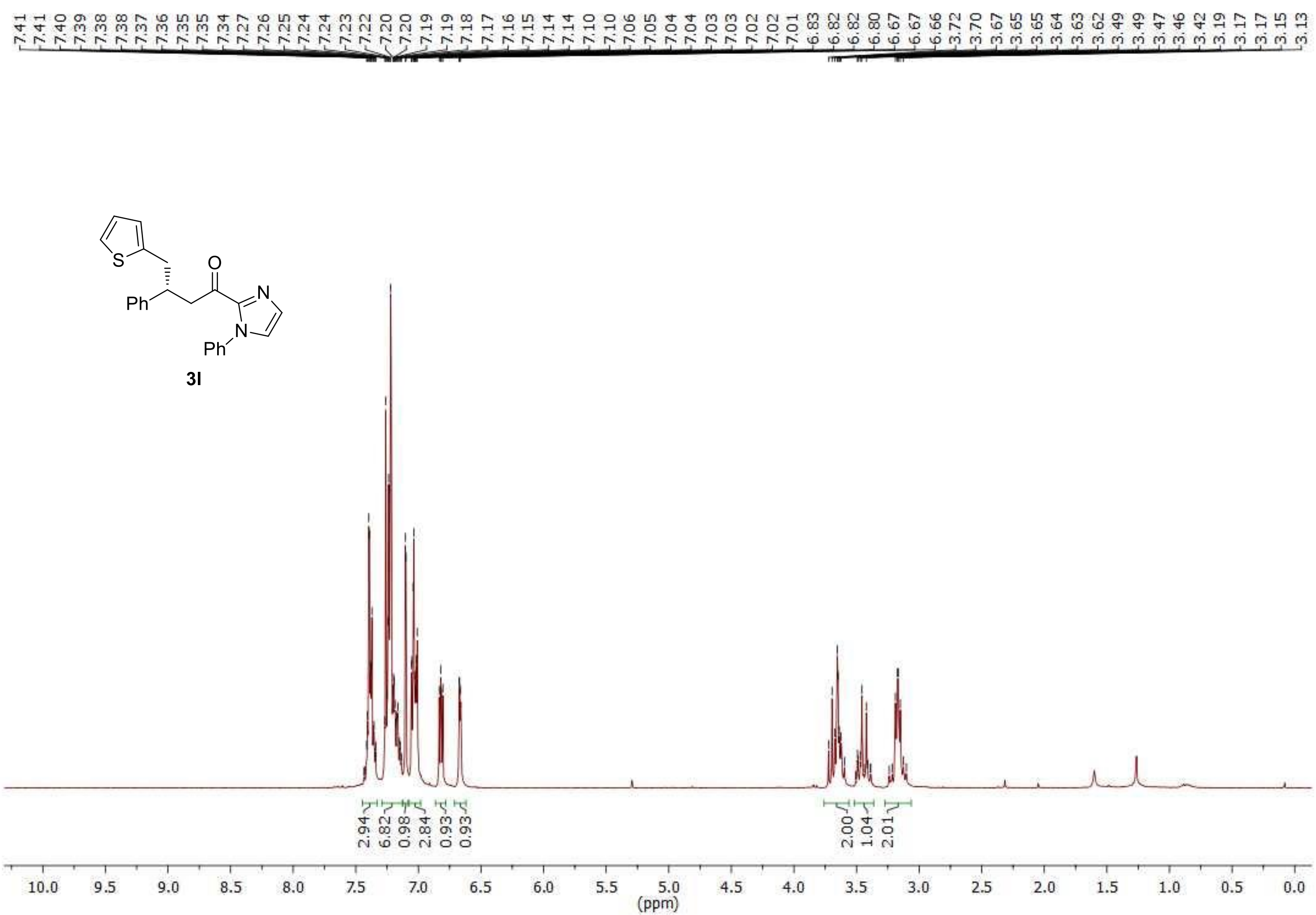


Figure S55. ^{1}H spectrum of **3l**.

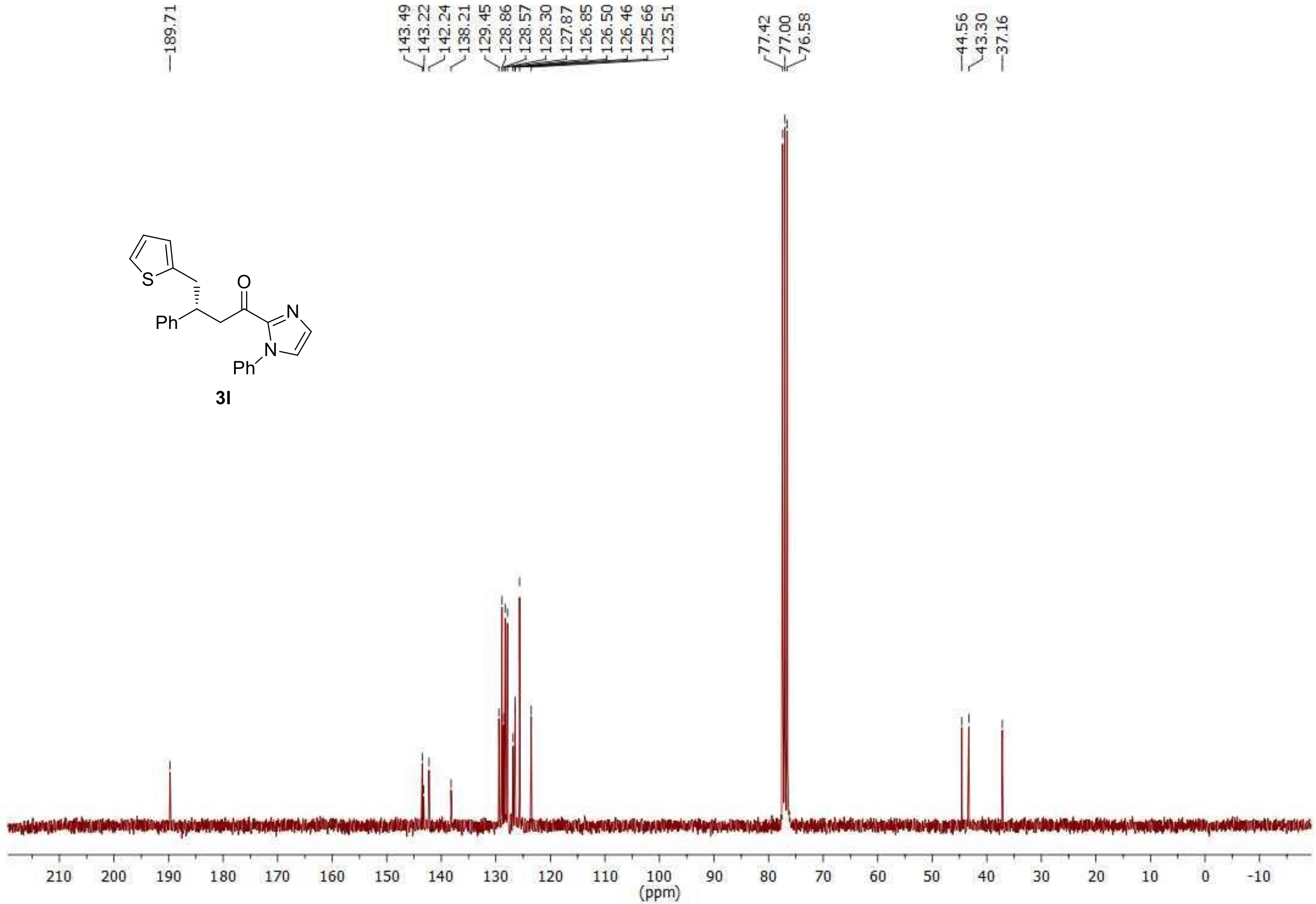


Figure S56. ^{13}C spectrum of **3l**.

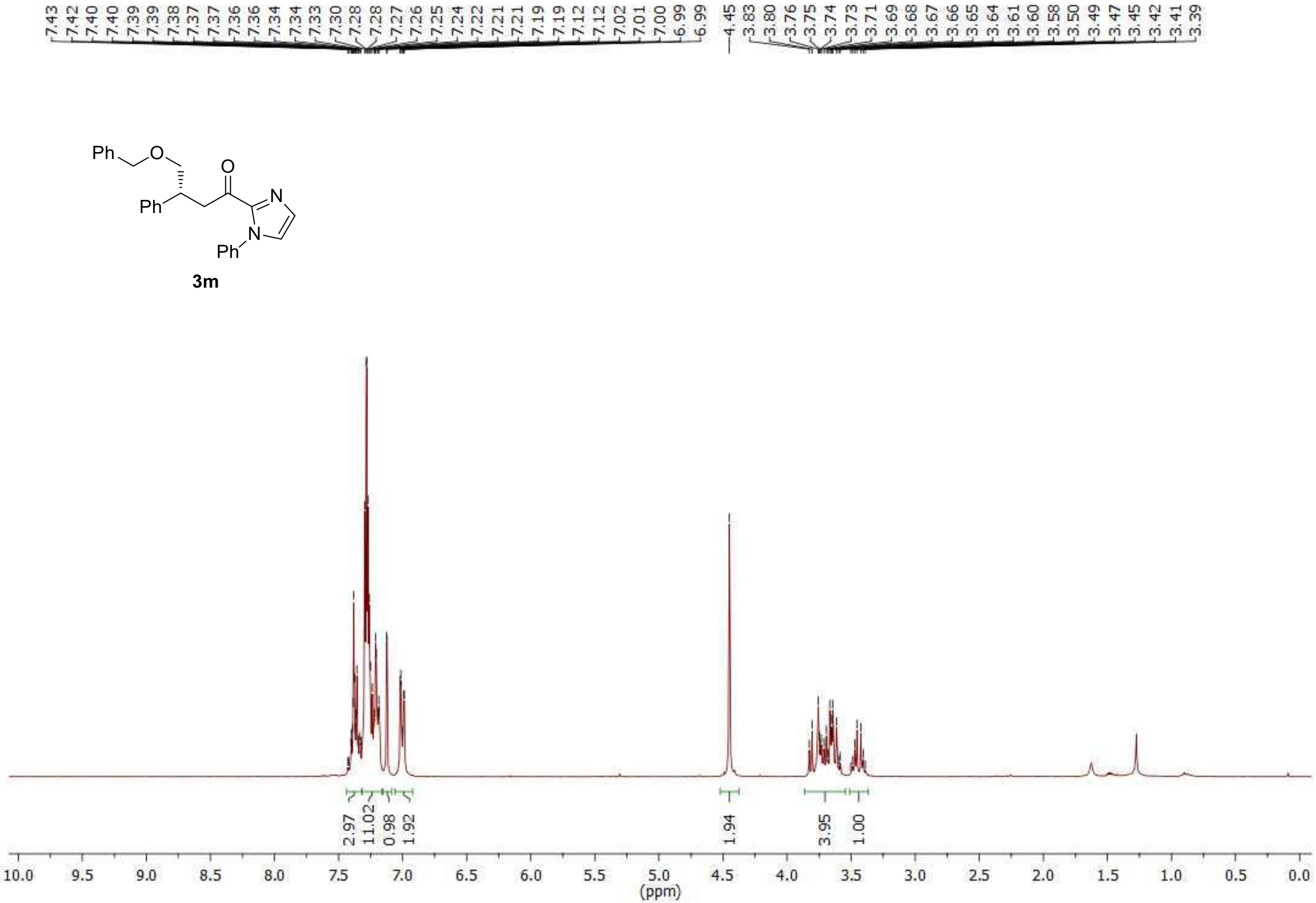


Figure S57. ^{1}H spectrum of **3m**.

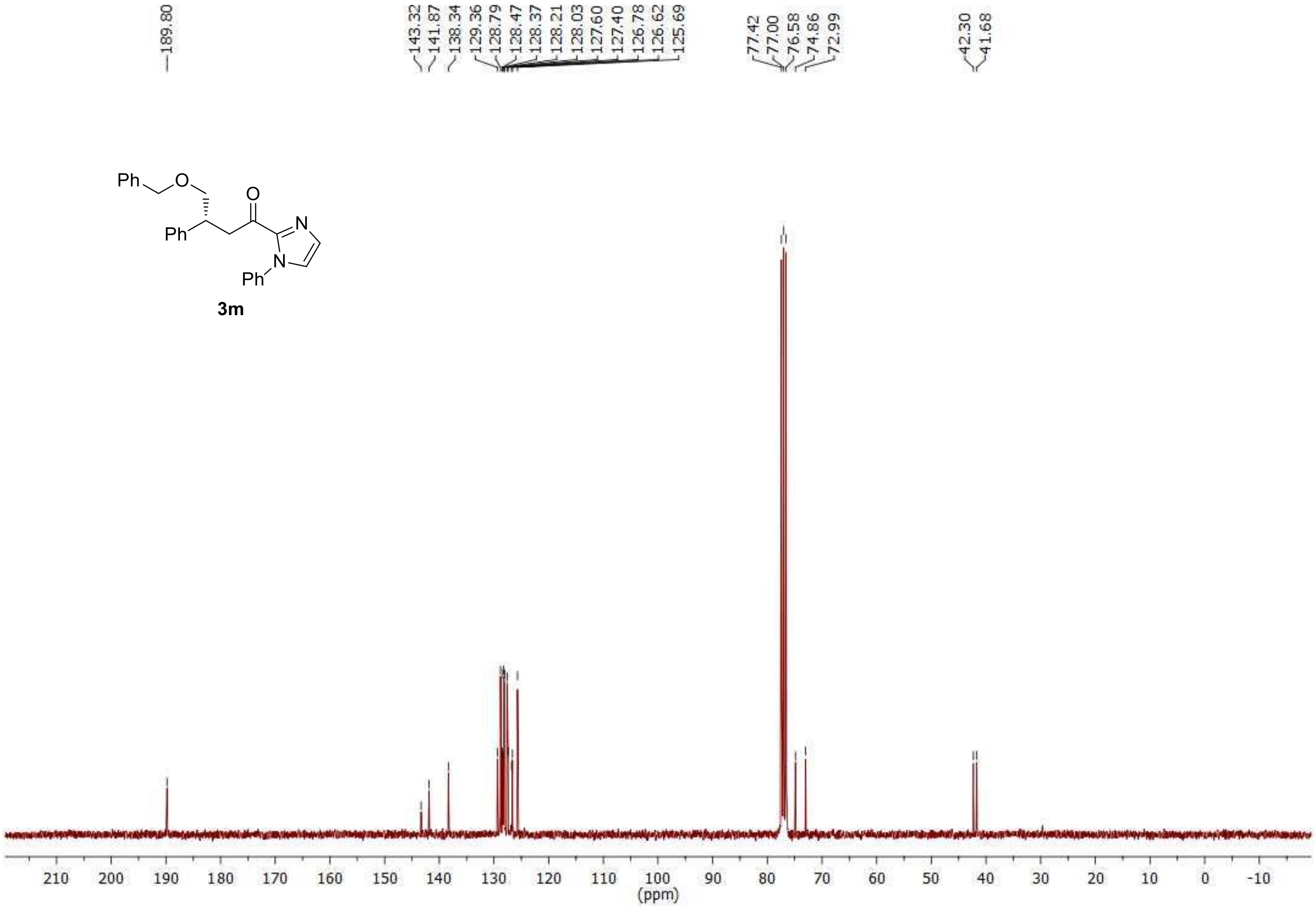
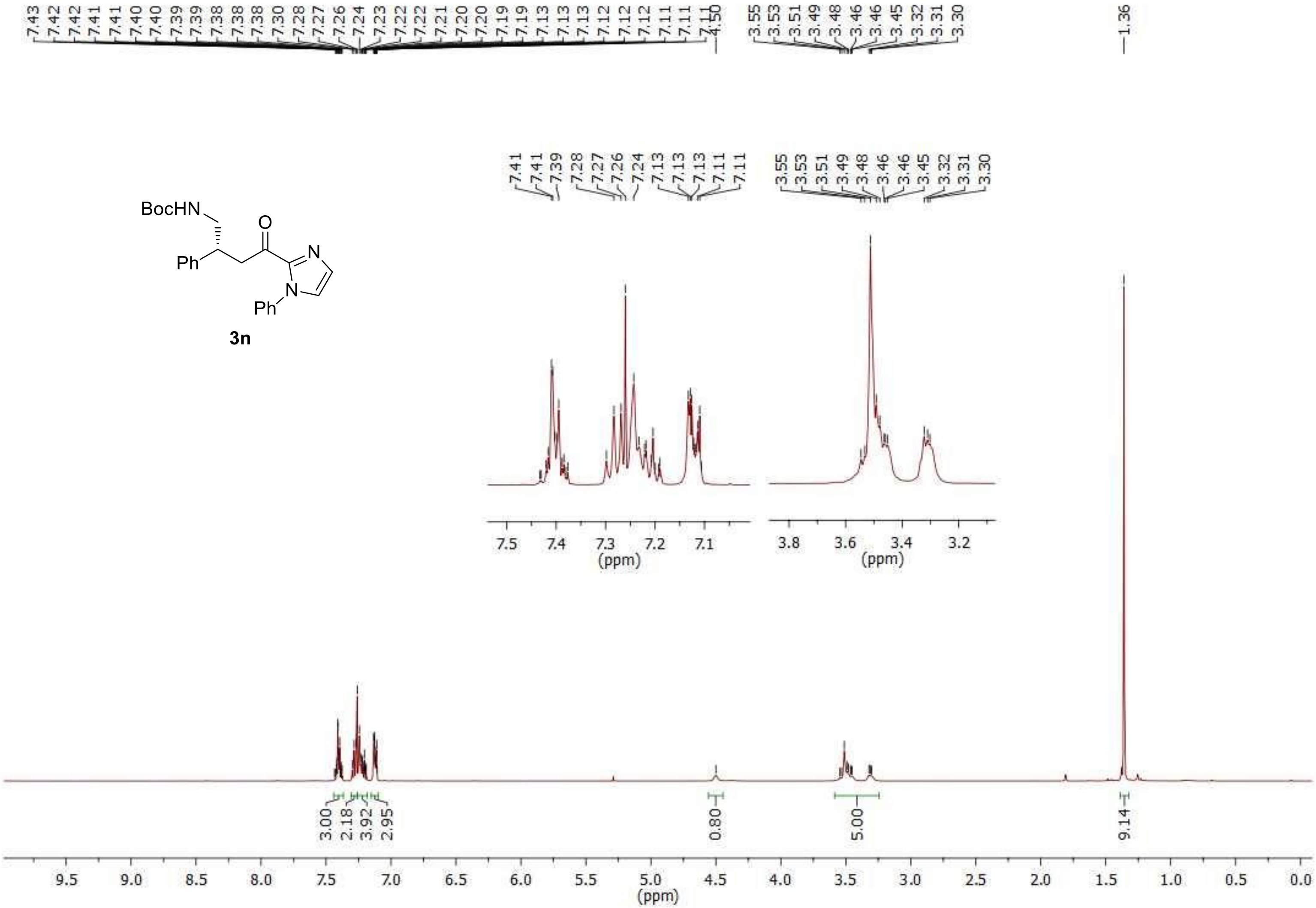


Figure S58. ^{13}C spectrum of **3m**.



3n

Figure S59. ^{13}C spectrum of **3n**.

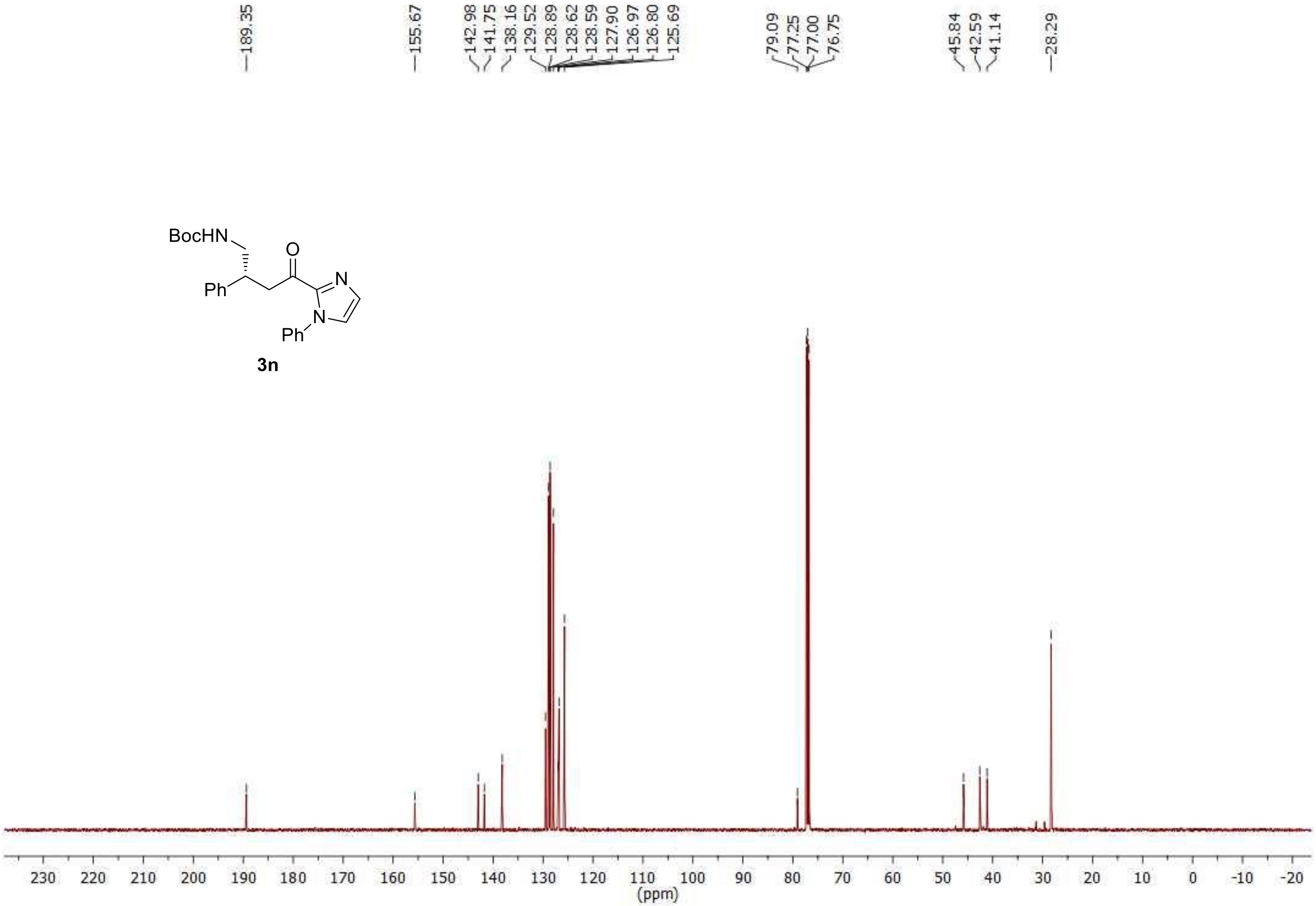


Figure S60. ^{13}C spectrum of **3n**.

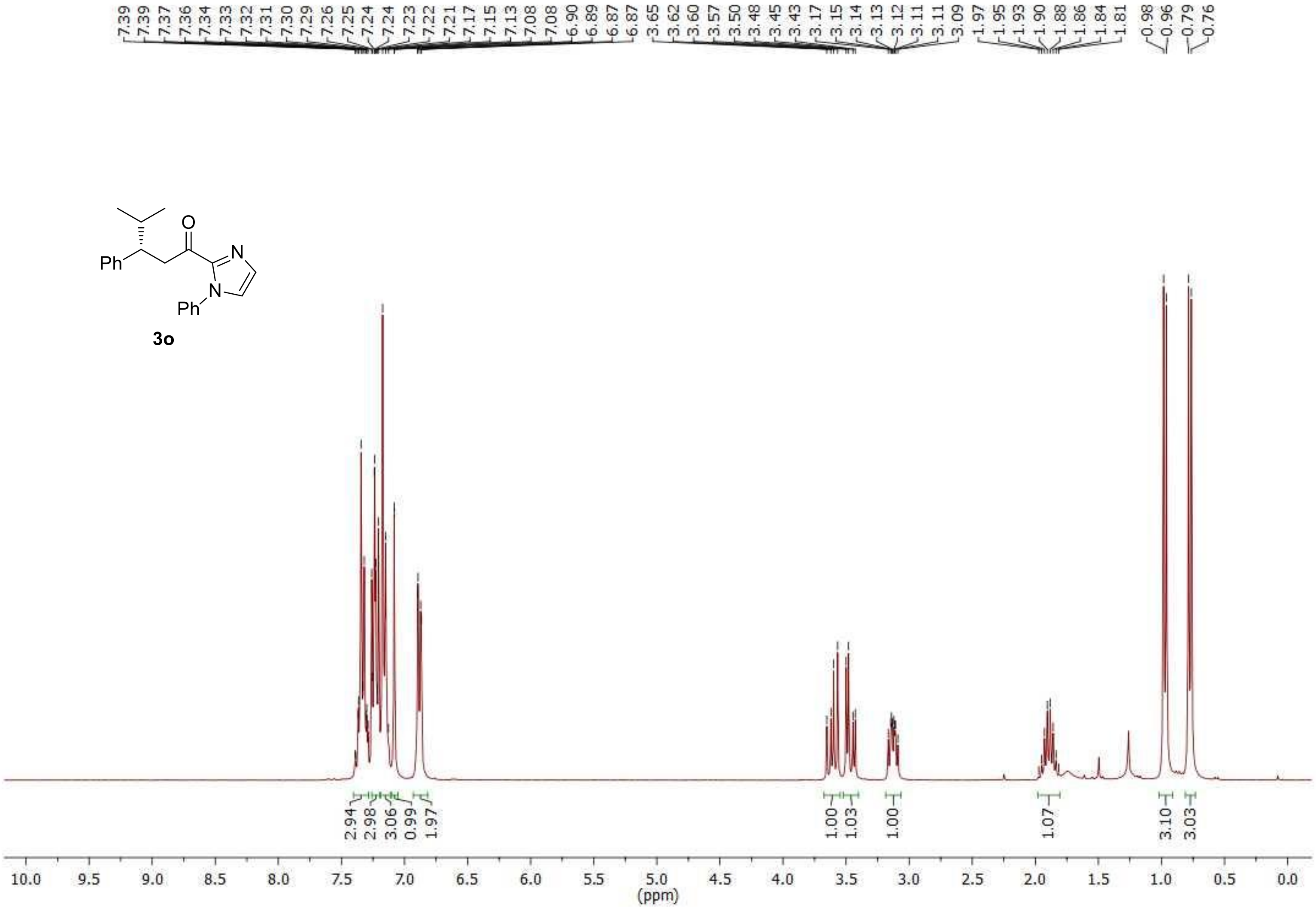


Figure S61. ^{1}H spectrum of **3o**.

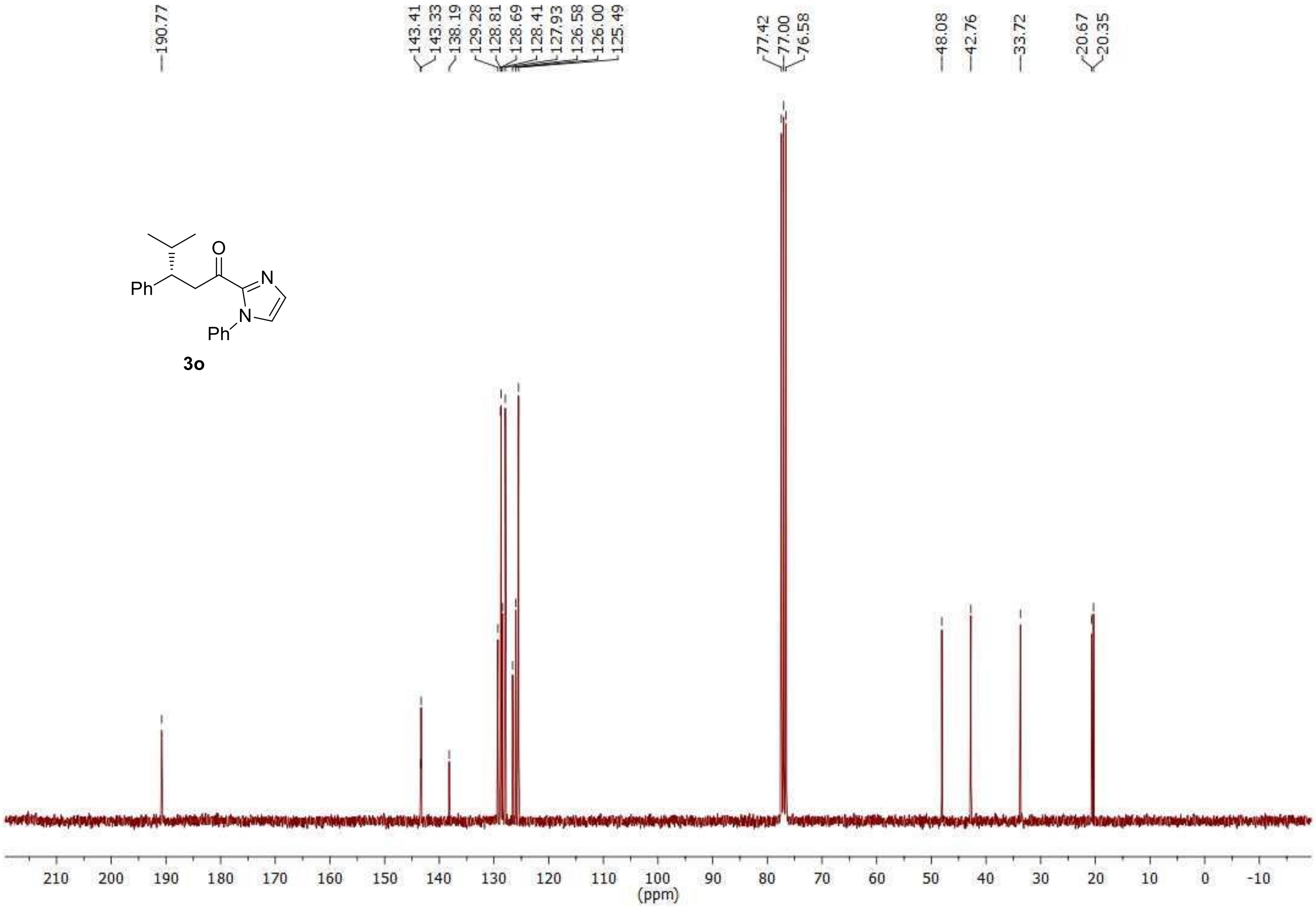


Figure S62. ^{13}C spectrum of **3o**.