

Supporting Information

for

Organocatalytic Access to Enantioenriched Spirooxindole-Based 4-Methyleneazetidines

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²Department of Chemistry & Pharmaceutical Sciences and Amsterdam Institute of Molecules Medicines & Systems (AIMMS), Vrije Universiteit Amsterdam, De Boelelaan 1108, 1081 HZ Amsterdam, The Netherlands;

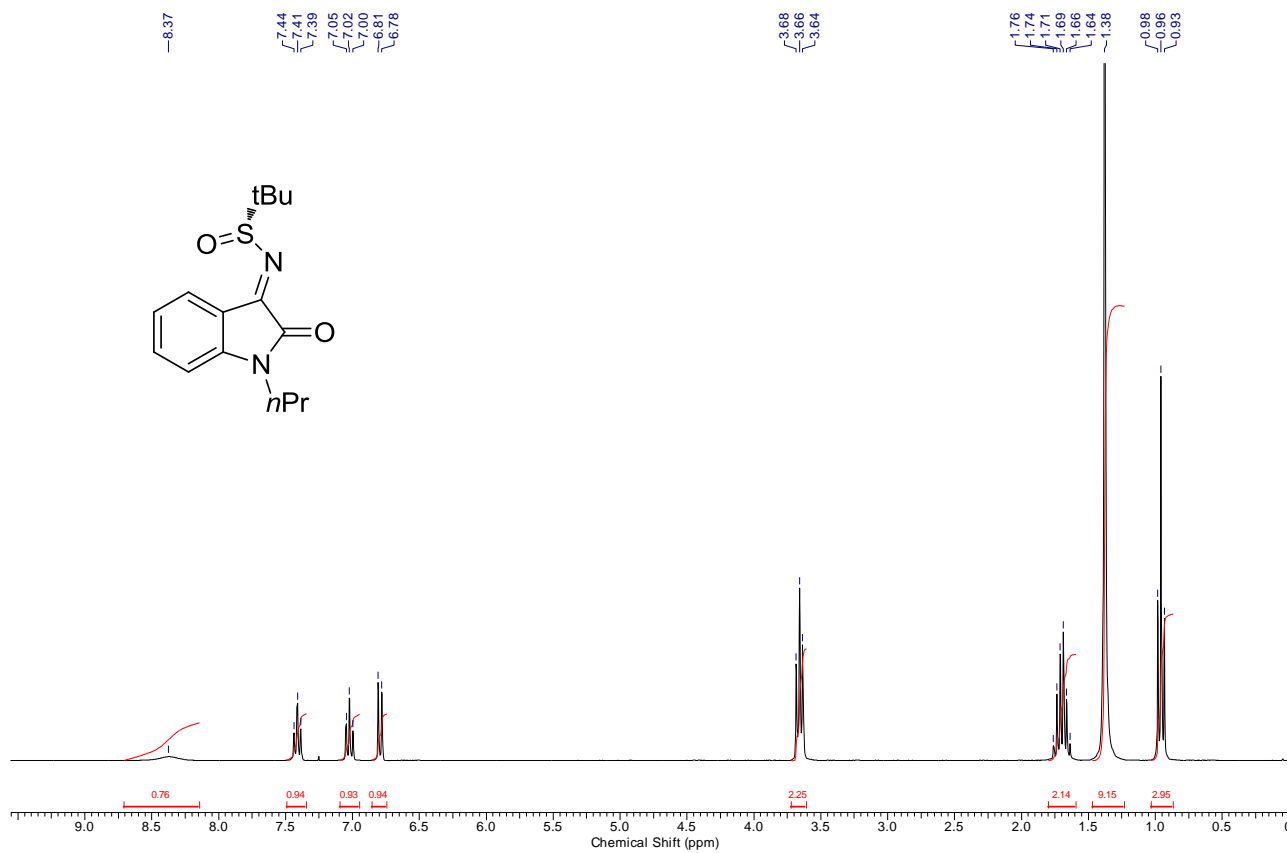
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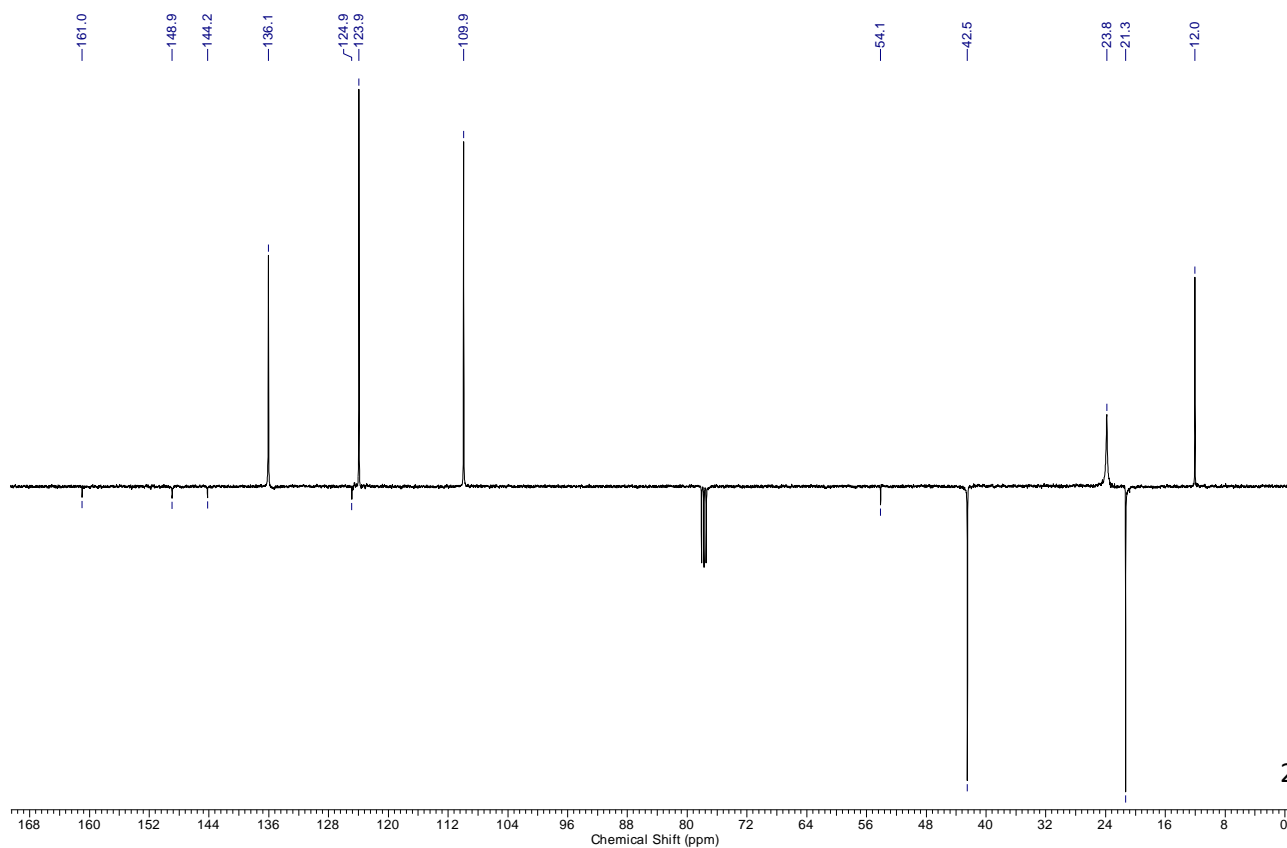
(E)-N-(1-propyl-2-oxindolin-3-ylidene)-2-methylpropane-2-sulfinamide:

¹H NMR (300 MHz, CDCl₃)



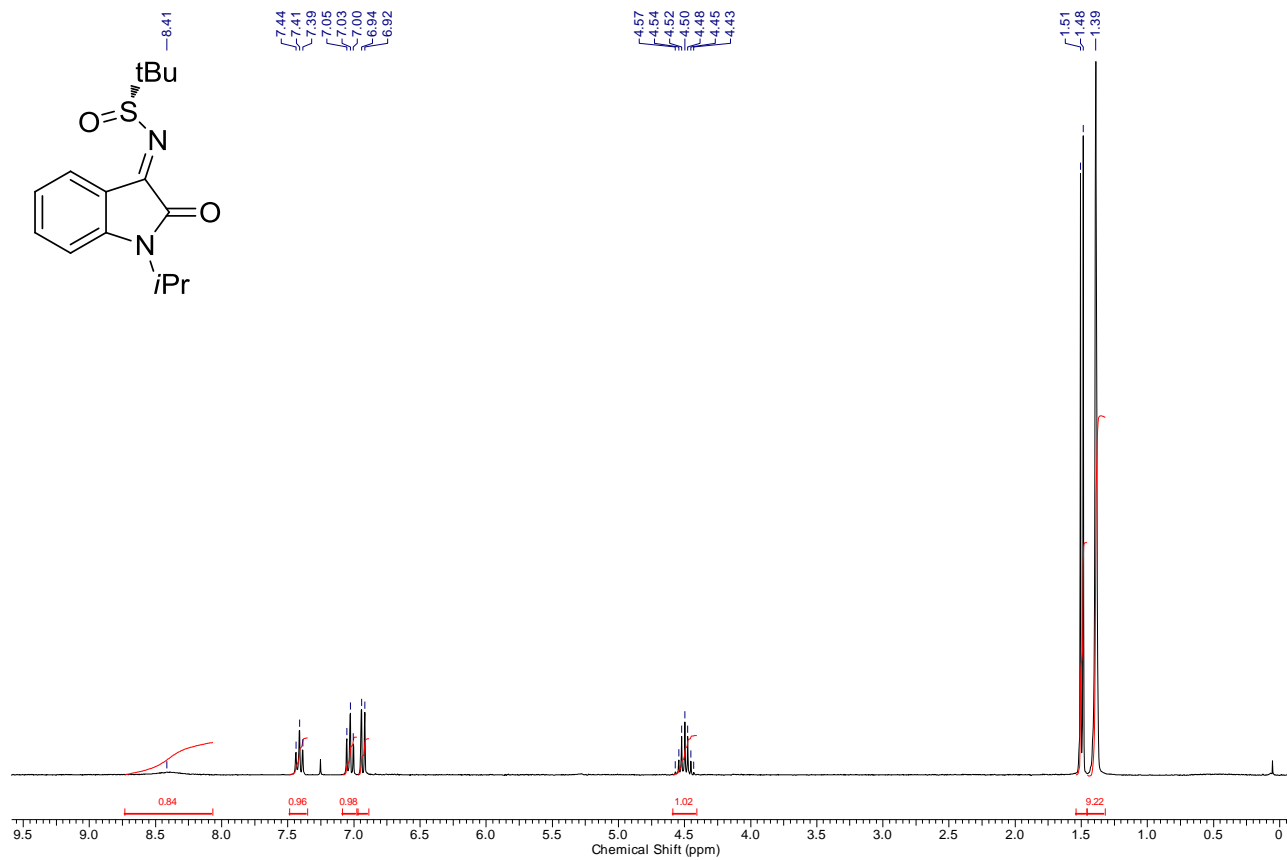
(E)-N-(1-propyl-2-oxindolin-3-ylidene)-2-methylpropane-2-sulfinamide:

¹³C NMR (101 MHz, APT, CDCl₃)



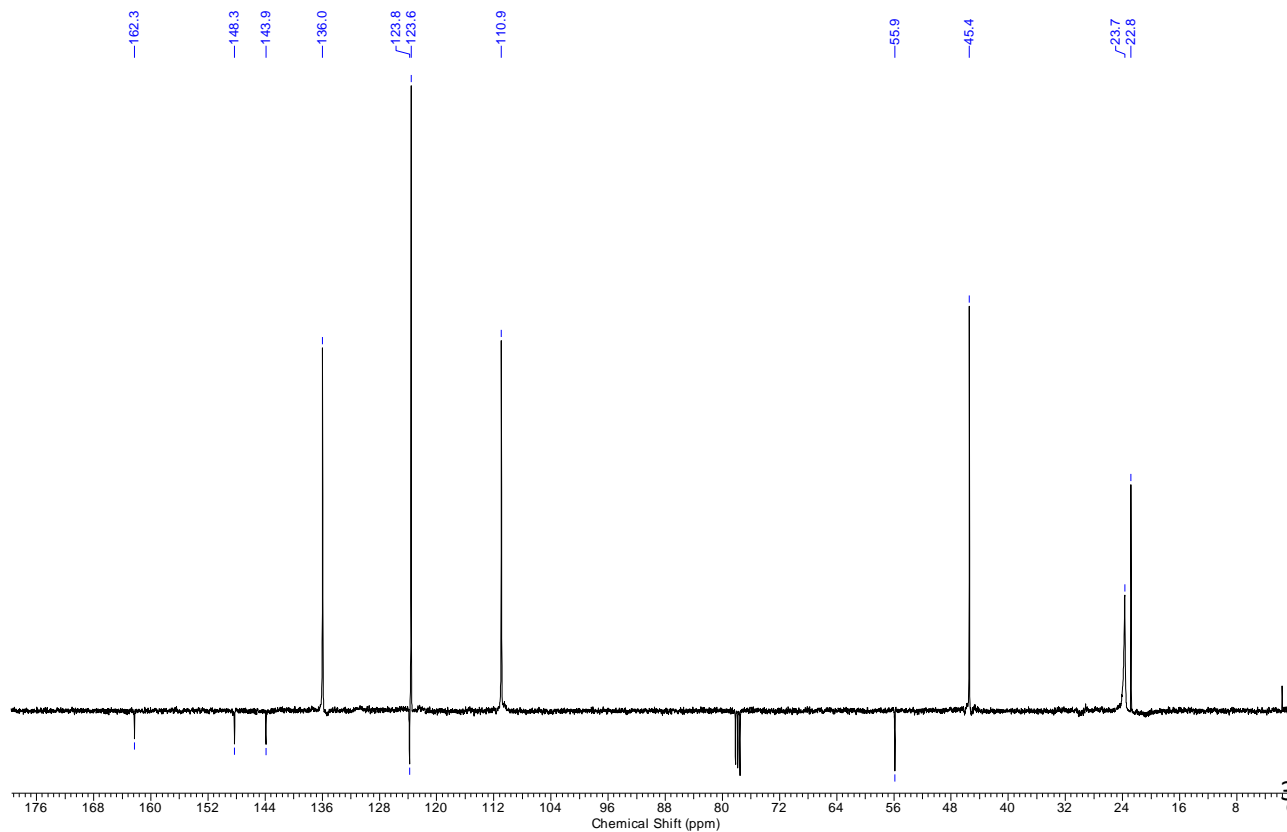
(E)-N-(1-isopropyl-2-oxoindolin-3-ylidene)-2-methylpropane-2-sulfinamide:

^1H NMR (300 MHz, CDCl_3)



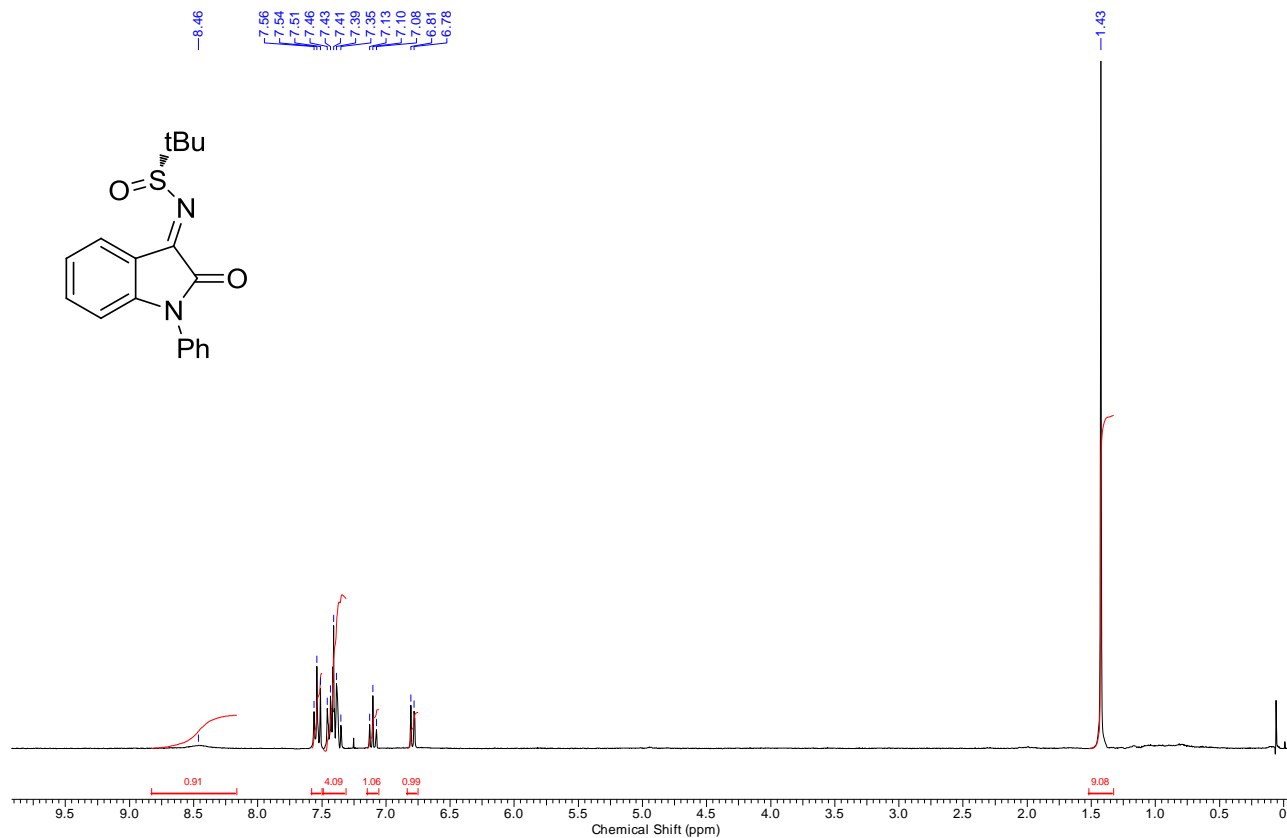
(E)-N-(1-isopropyl-2-oxoindolin-3-ylidene)-2-methylpropane-2-sulfinamide:

^{13}C NMR (101 MHz, APT, CDCl_3)



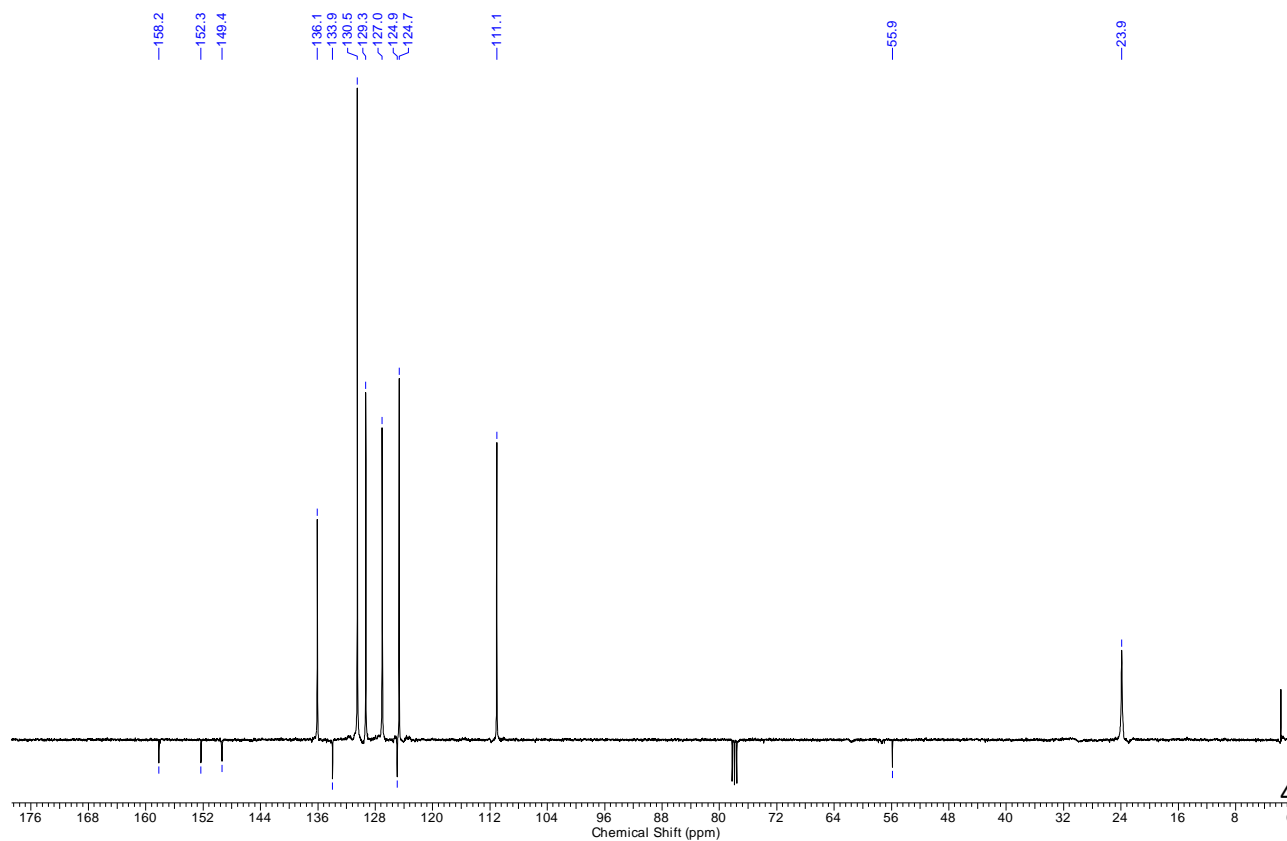
(E)-2-methyl-N-(2-oxo-1-phenylindolin-3-ylidene)propane-2-sulfinamide:

¹H NMR (300 MHz, CDCl₃)



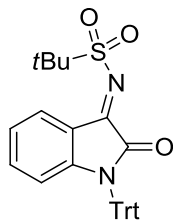
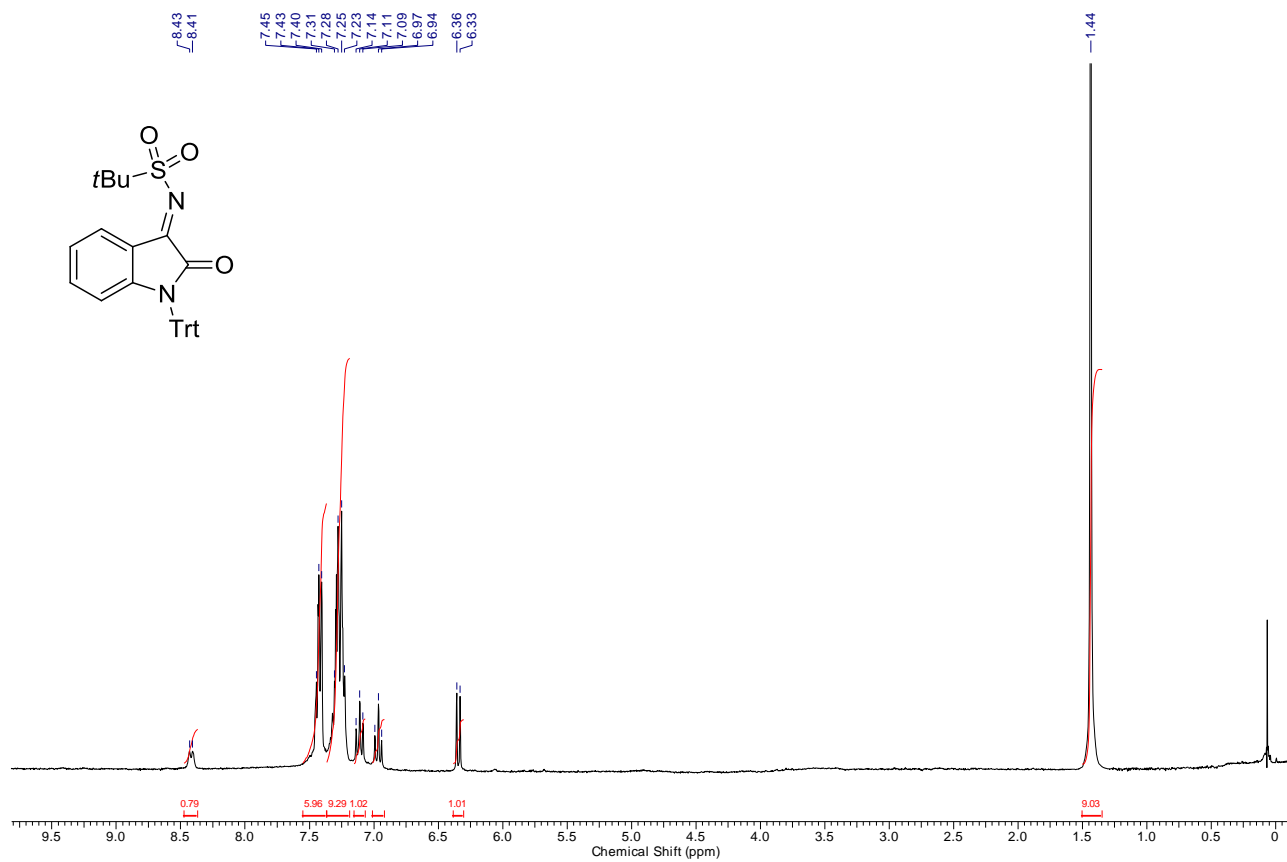
(E)-2-methyl-N-(2-oxo-1-phenylindolin-3-ylidene)propane-2-sulfinamide:

¹³C NMR (101 MHz, APT, CDCl₃)



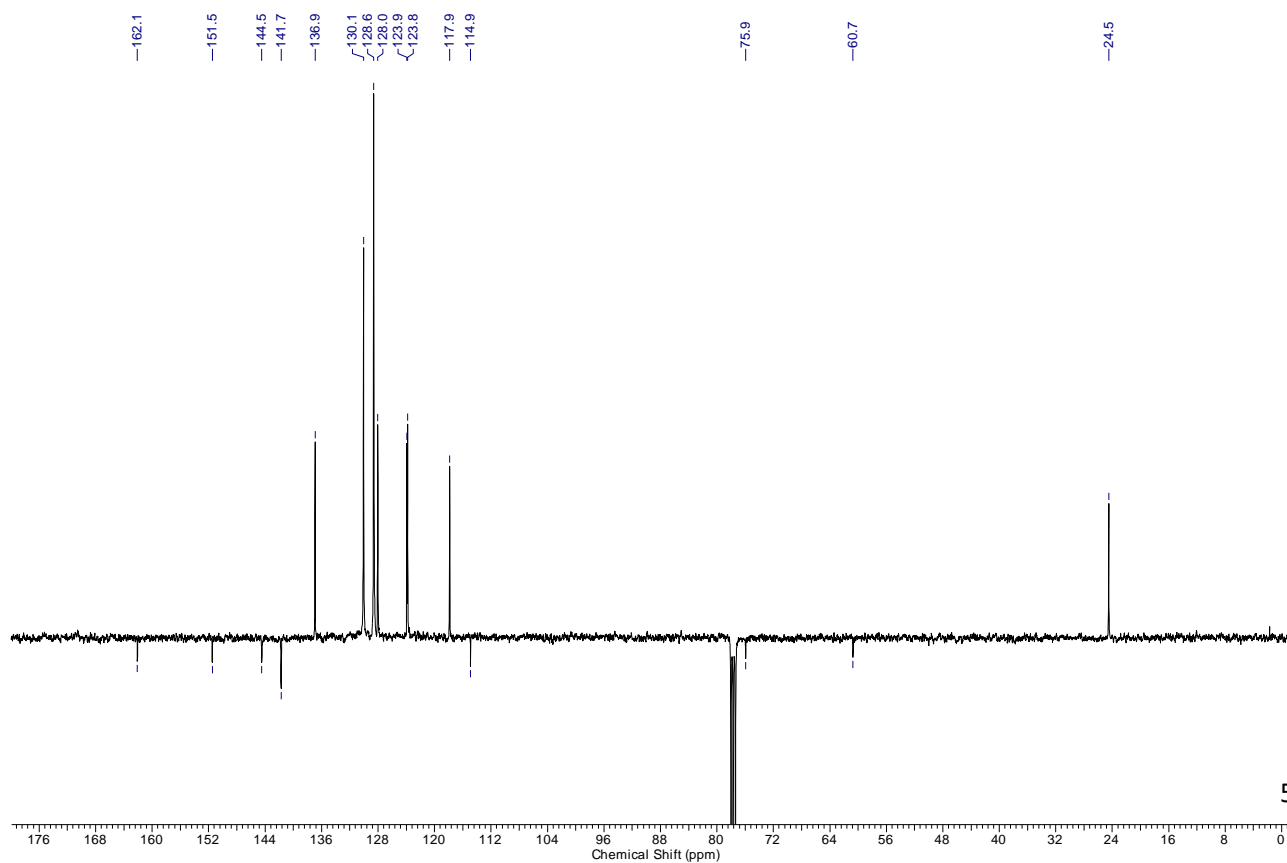
Compound 1c:

^1H NMR (300 MHz, CDCl_3)



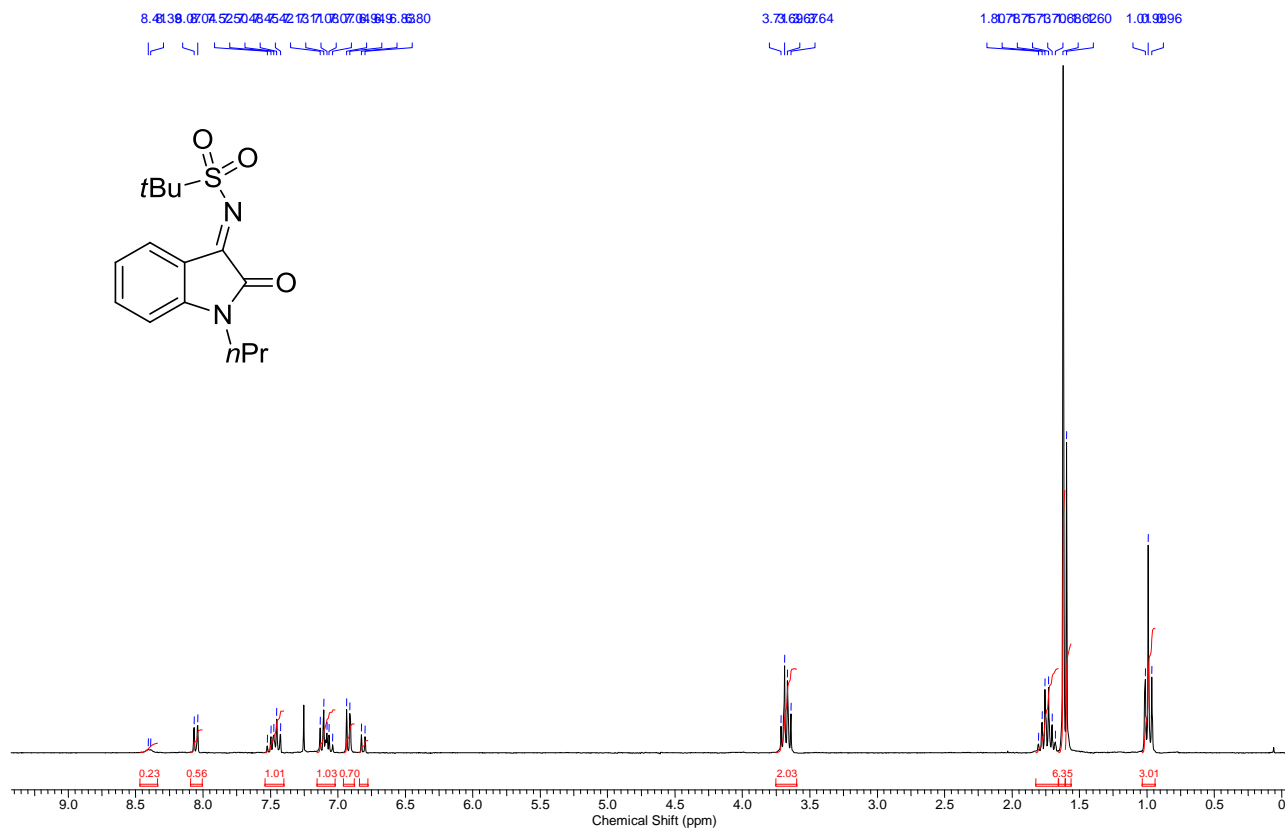
Compound 1c:

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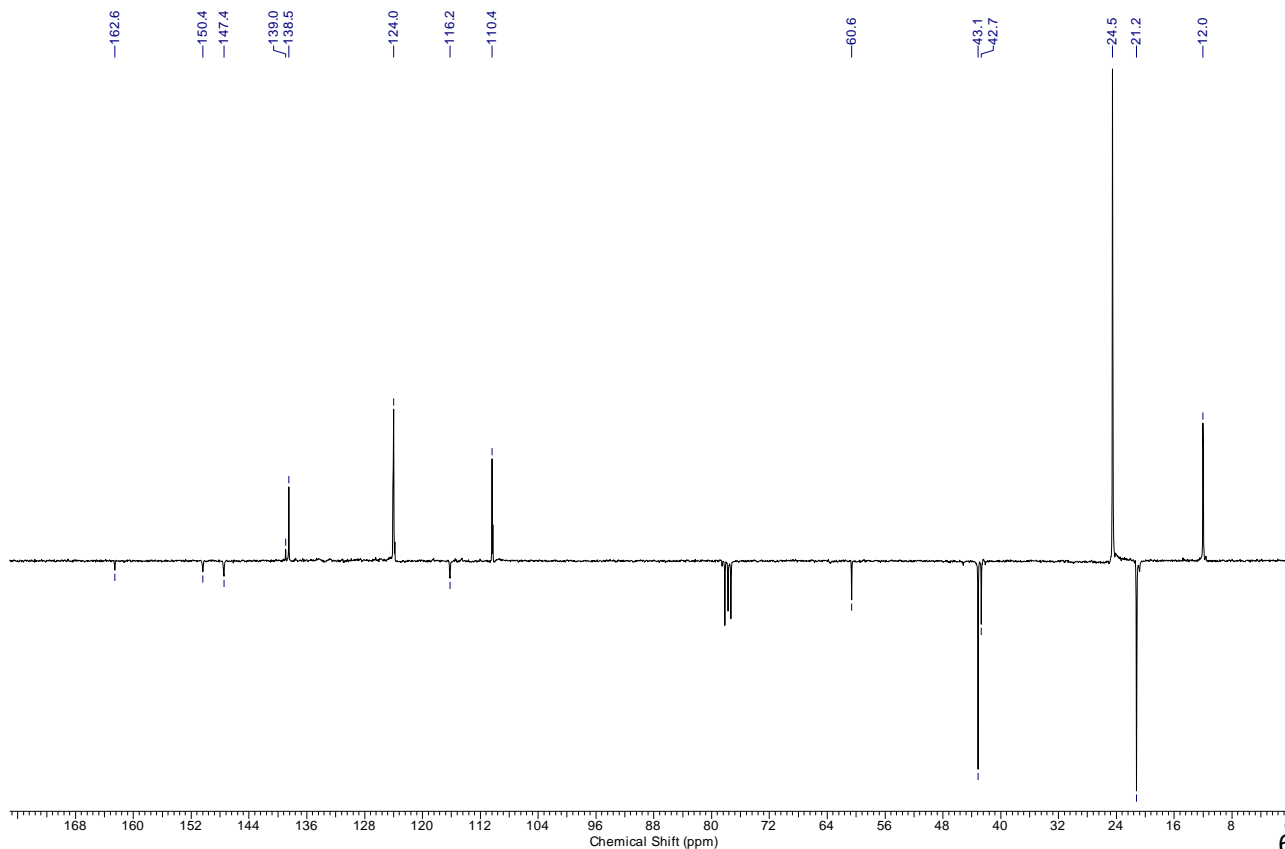
Compound 1d:

^1H NMR (300 MHz, CDCl_3)



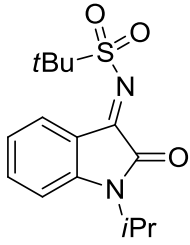
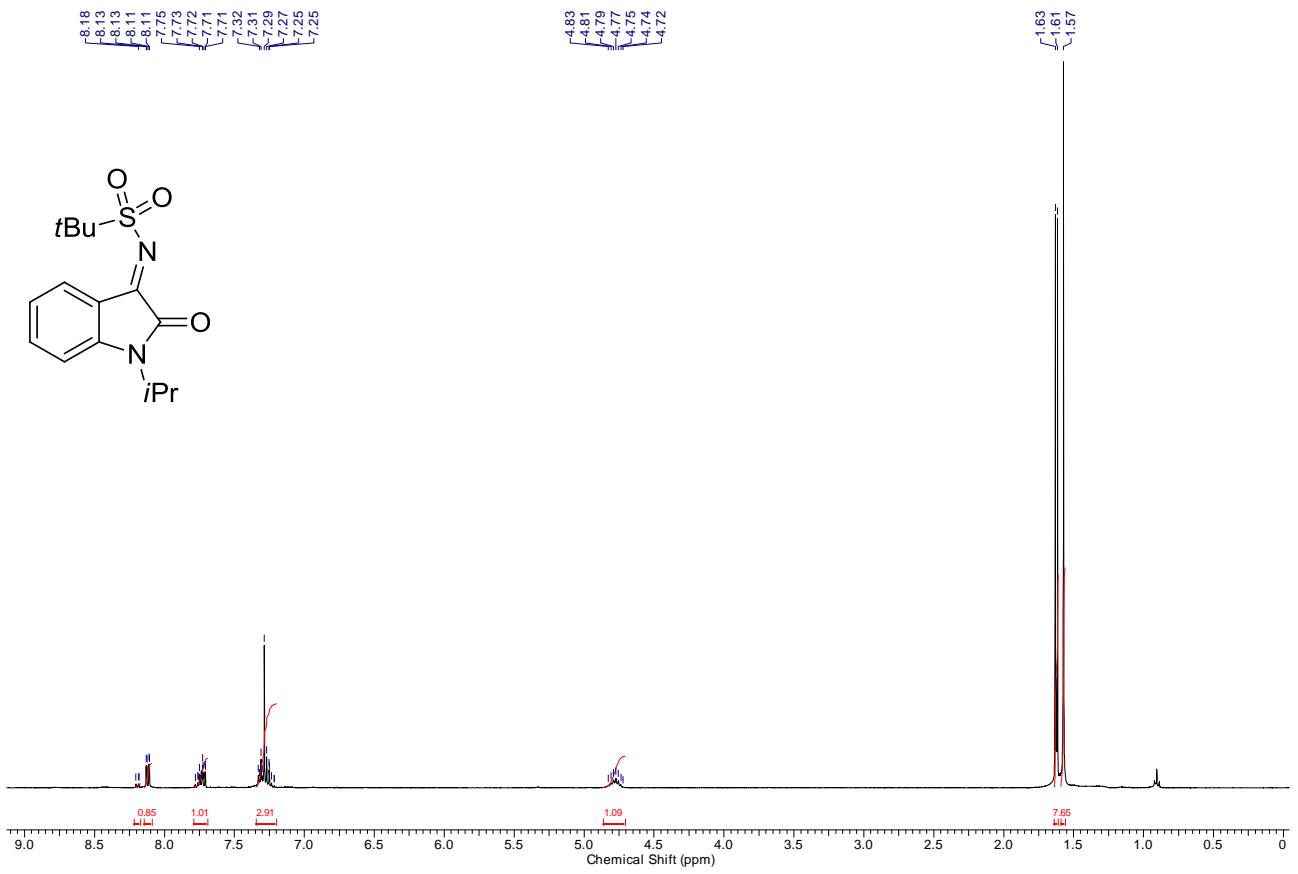
Compound 1d:

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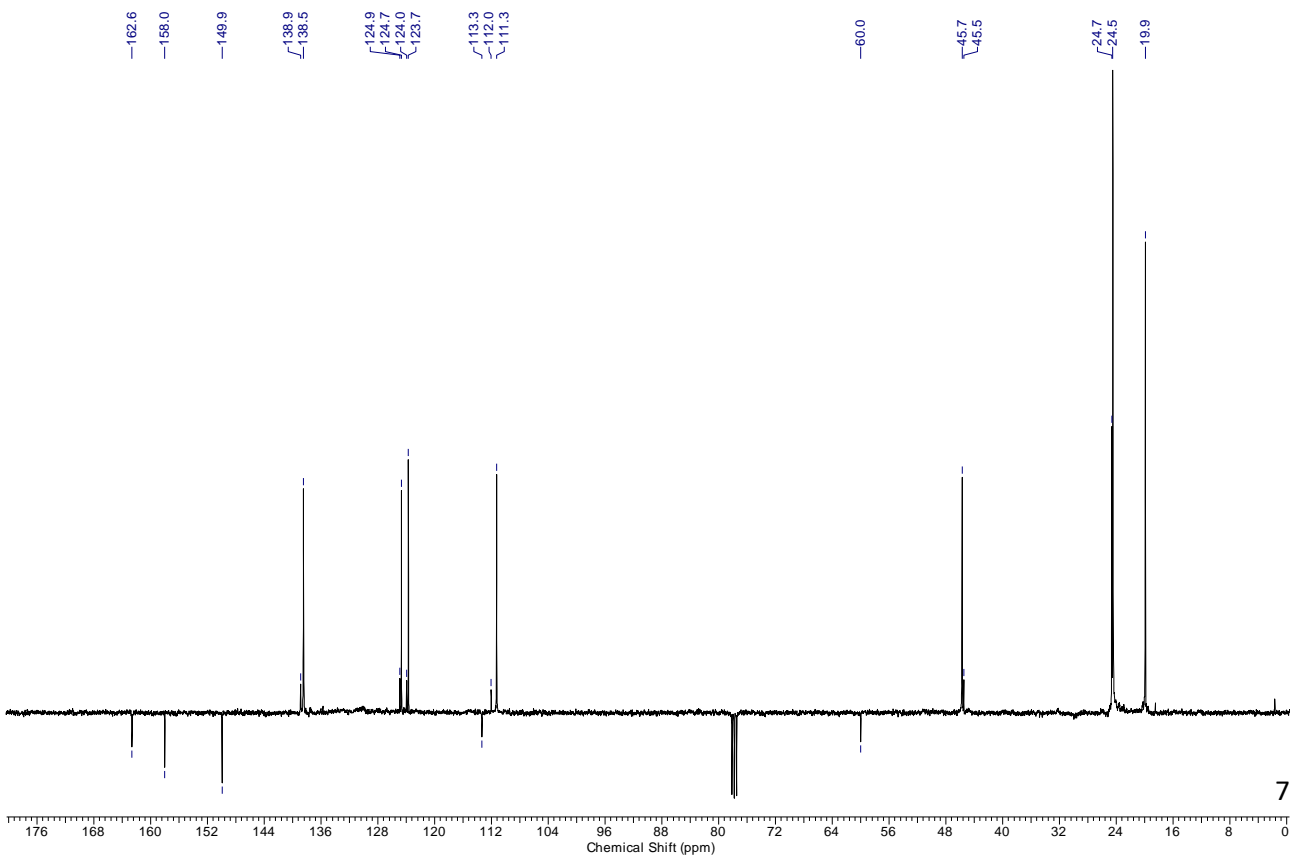
Compound 1e:

^1H NMR (400 MHz, CDCl_3)



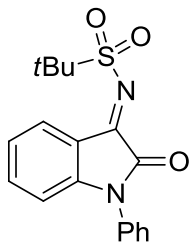
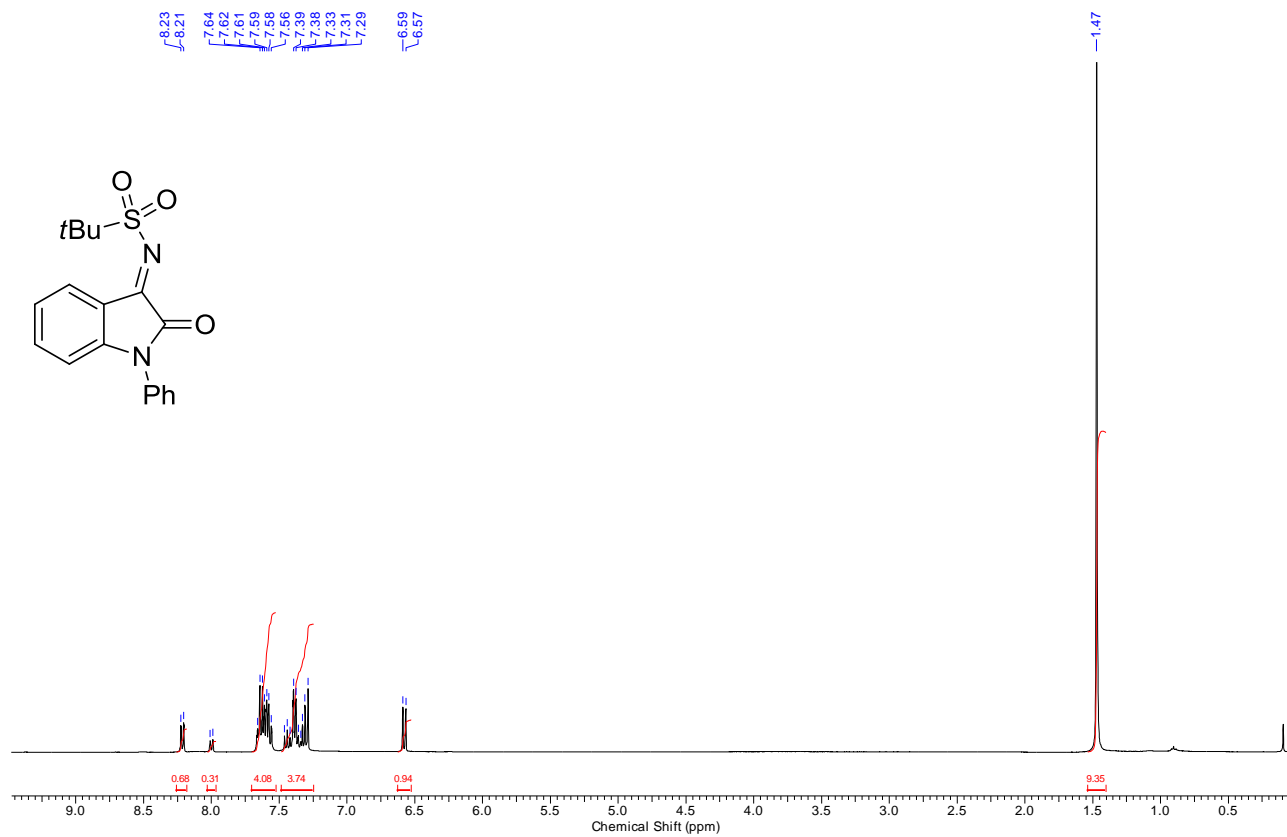
Compound 1e:

^{13}C NMR (101 MHz, APT, CDCl_3)



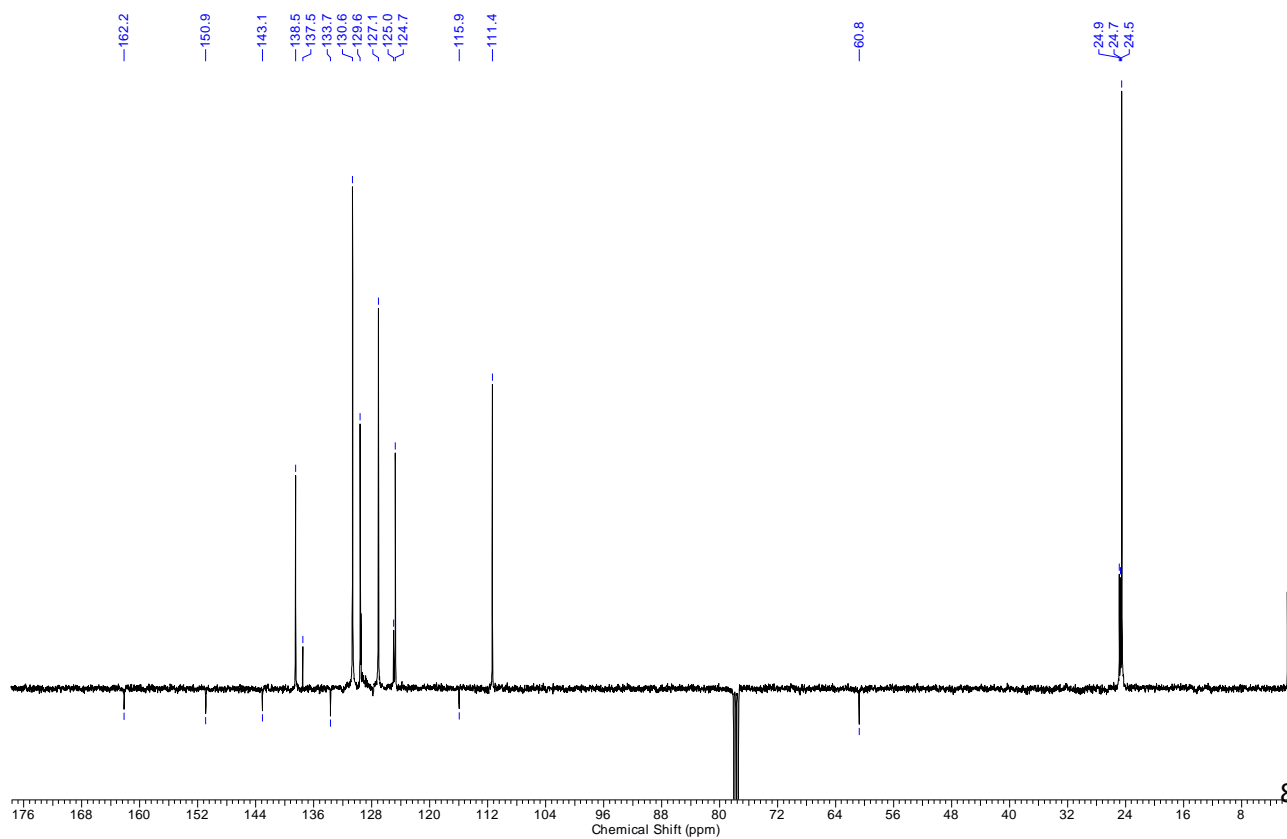
Compound 1f:

^1H NMR (400 MHz, CDCl_3)



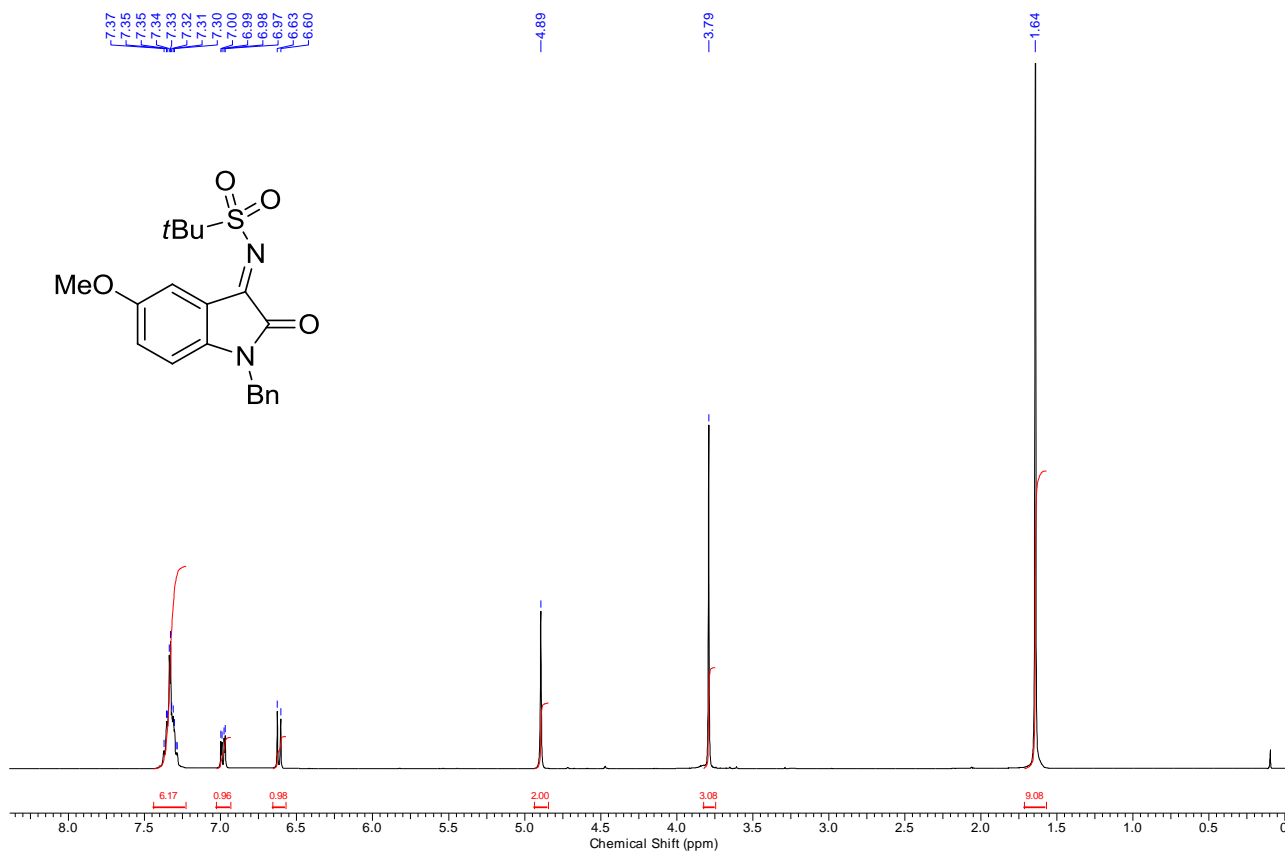
Compound 1f:

^{13}C NMR (101 MHz, APT, CDCl_3)



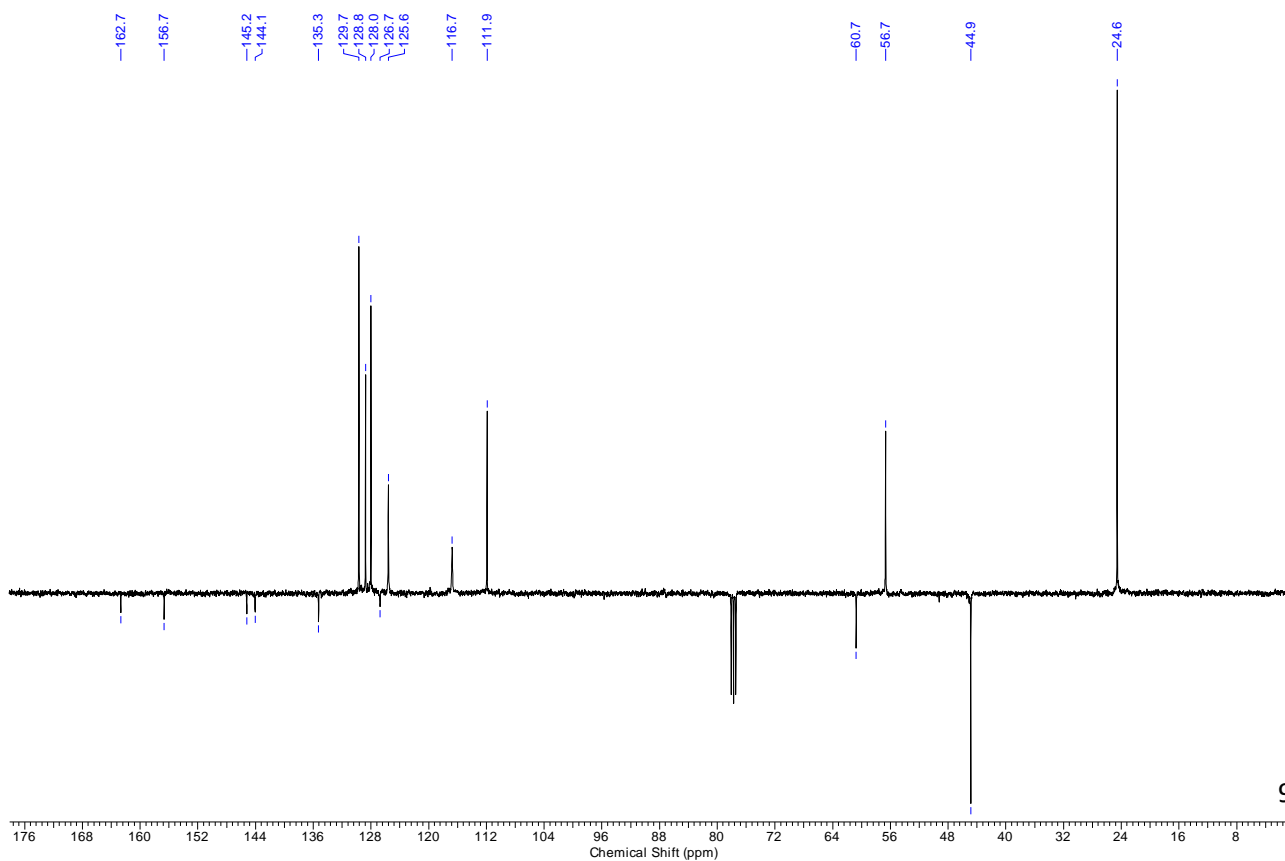
Compound 1g:

^1H NMR (400 MHz, CDCl_3)



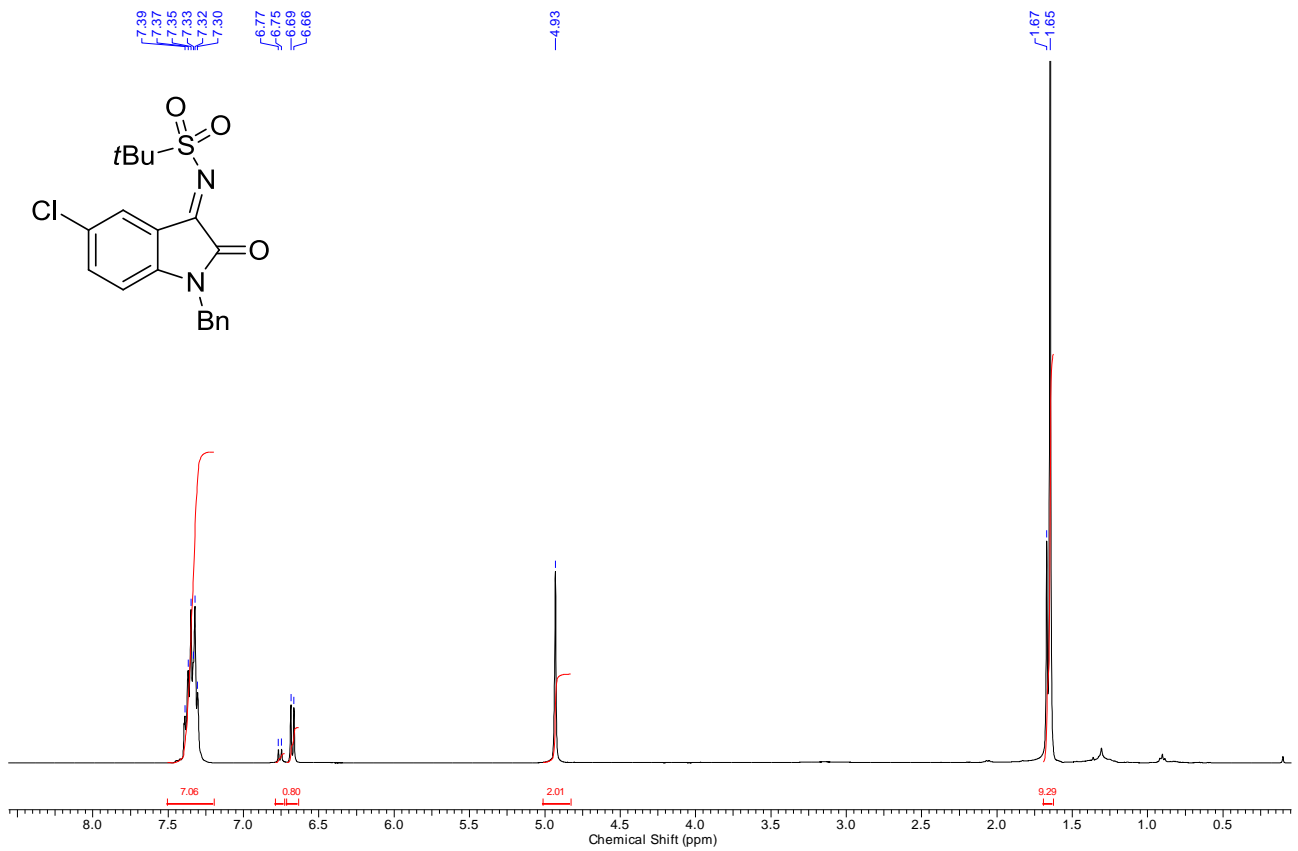
Compound 1g:

^{13}C NMR (101 MHz, APT, CDCl_3)



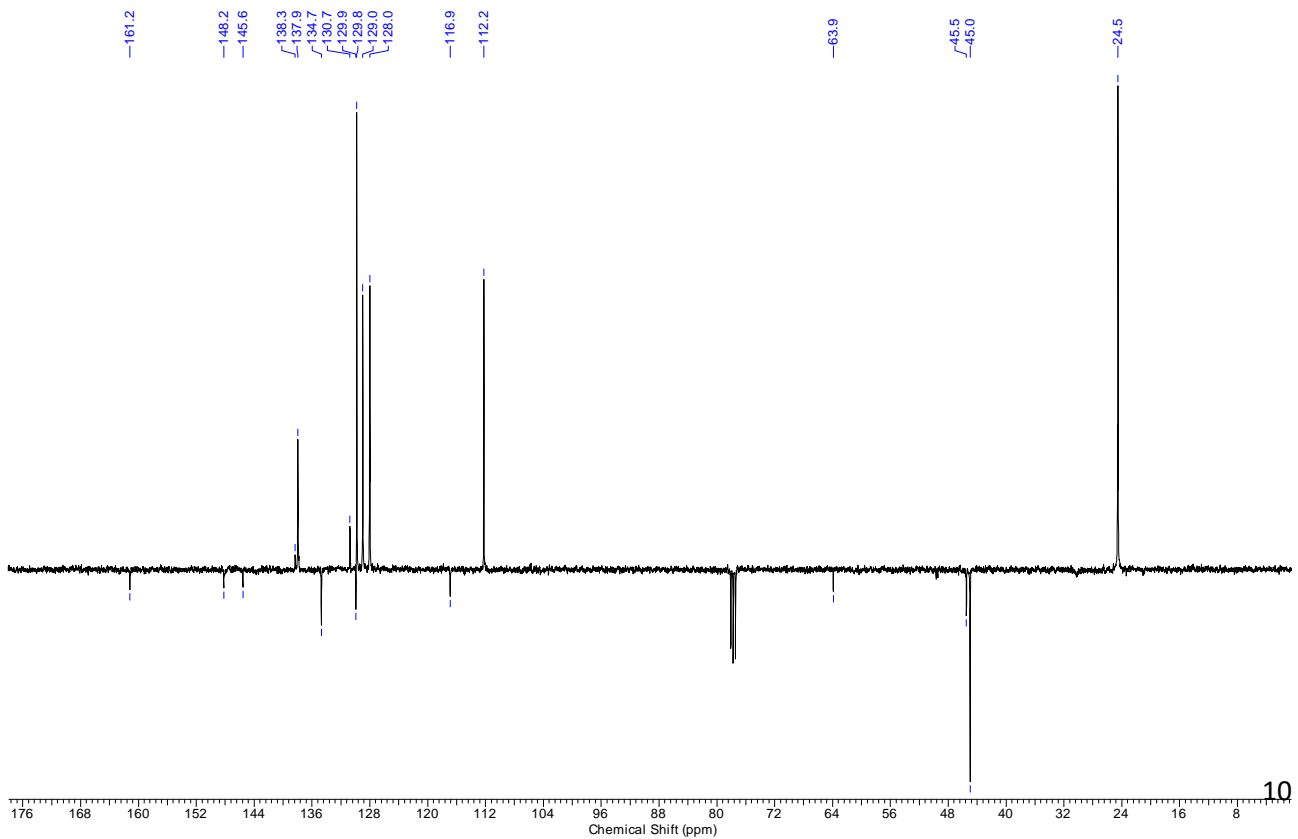
Compound 1h:

^1H NMR (400 MHz, CDCl_3)

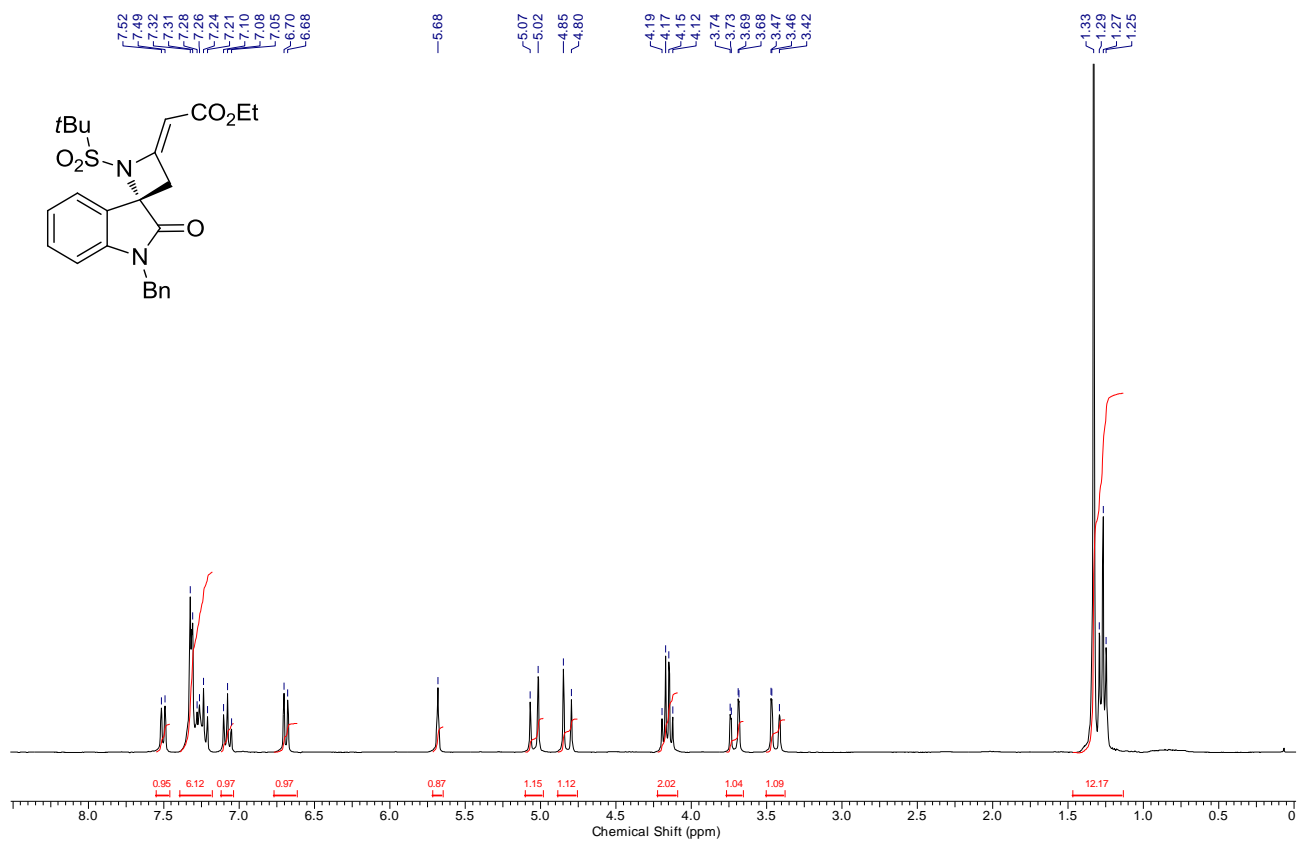


Compound 1h:

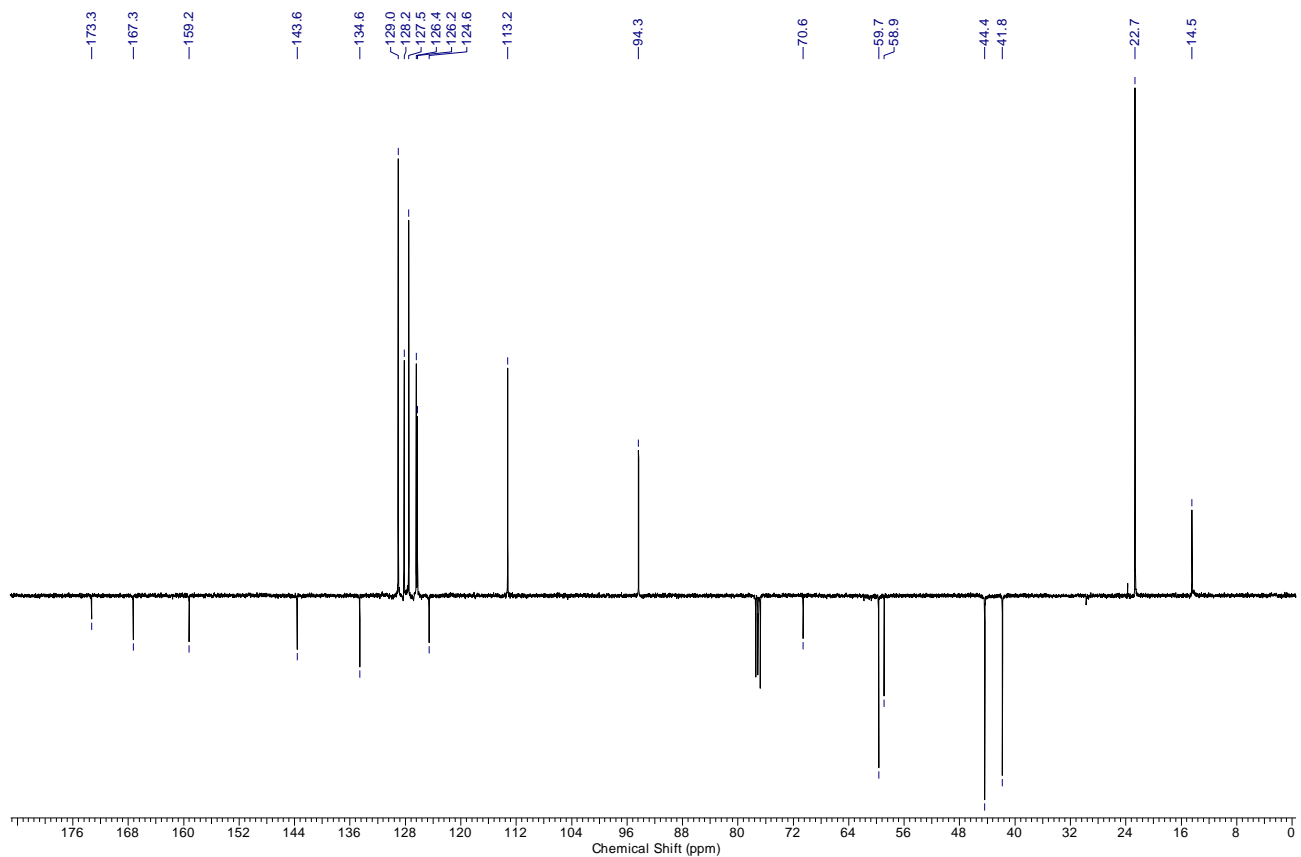
^{13}C NMR (101 MHz, APT, CDCl_3)



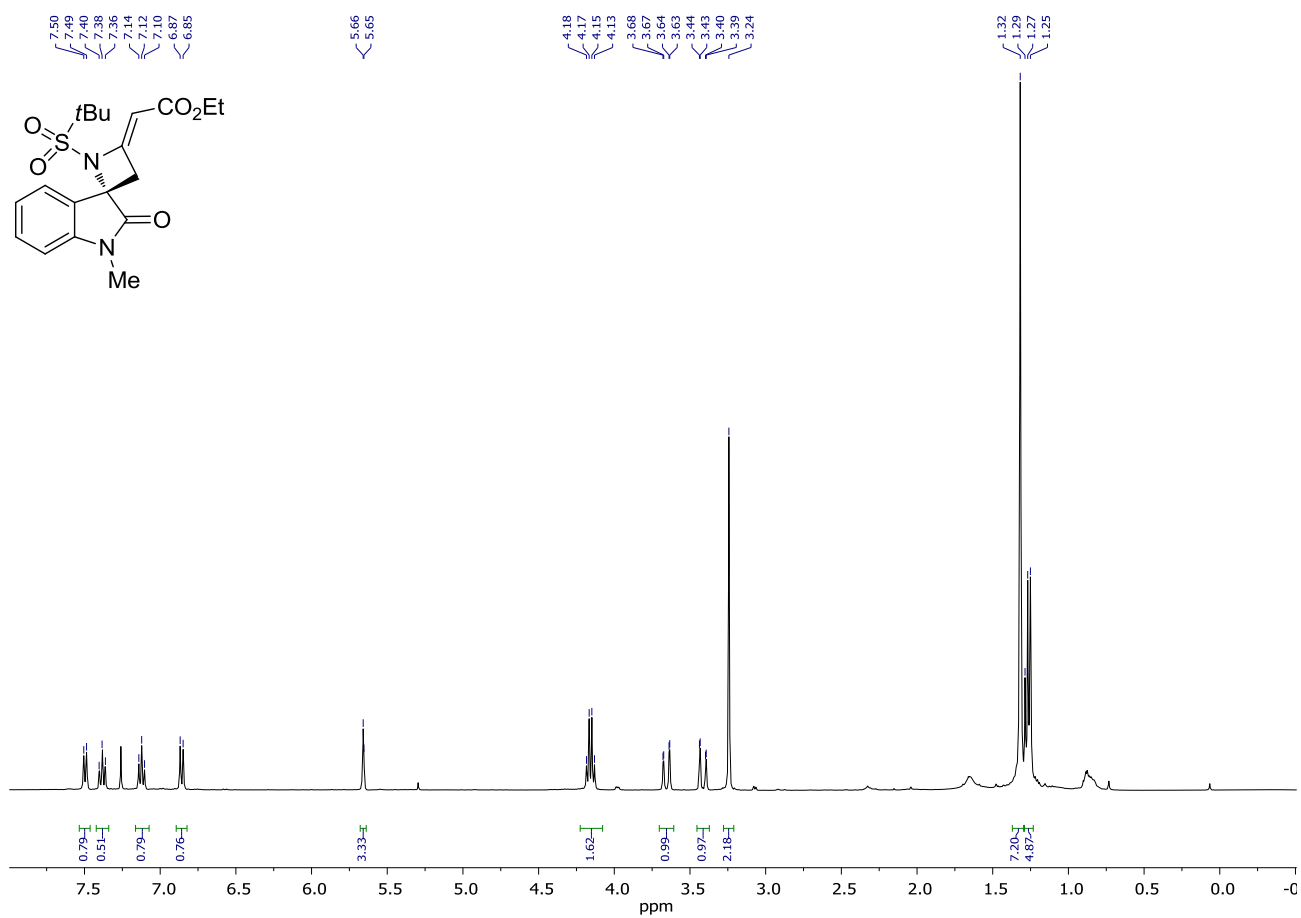
Compound 6a: ^1H NMR (300 MHz, CDCl_3)



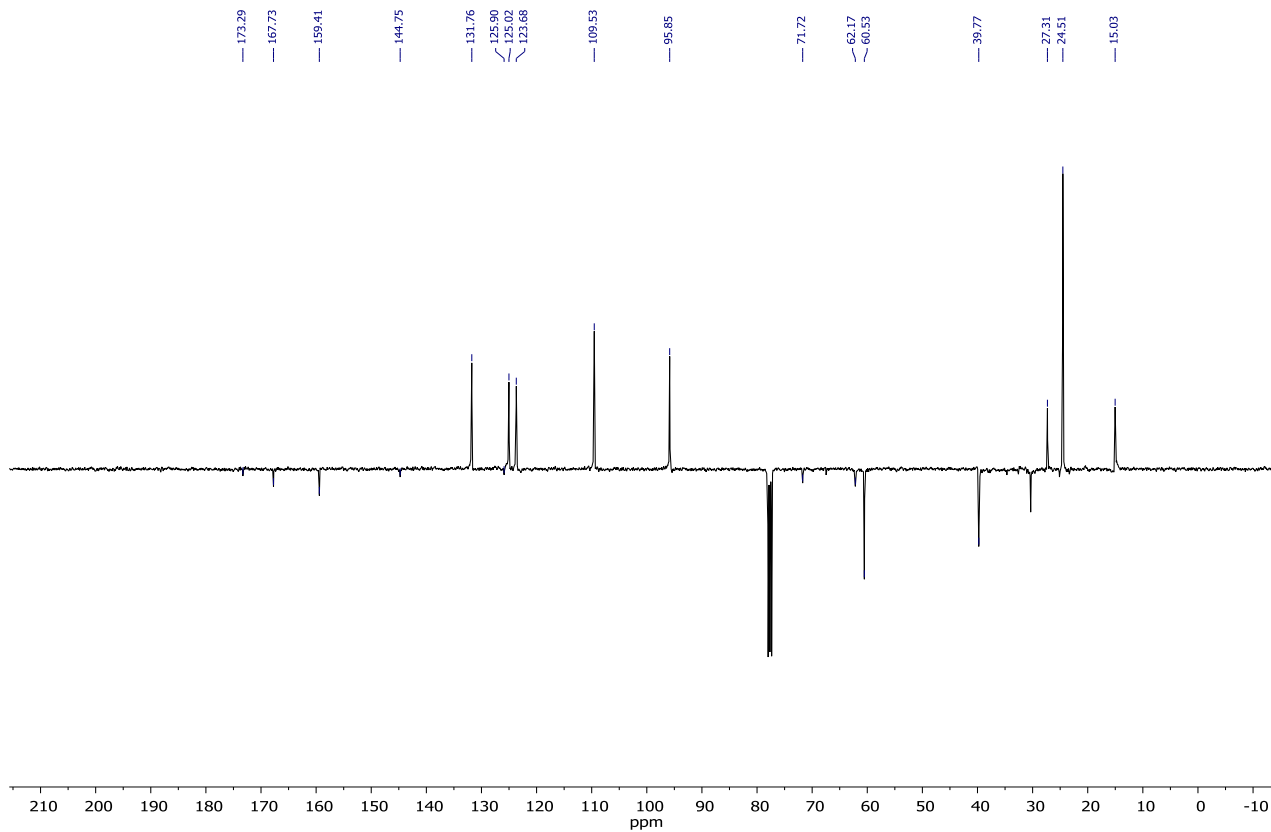
Compound 6a: ^{13}C NMR (101 MHz, APT, CDCl_3)



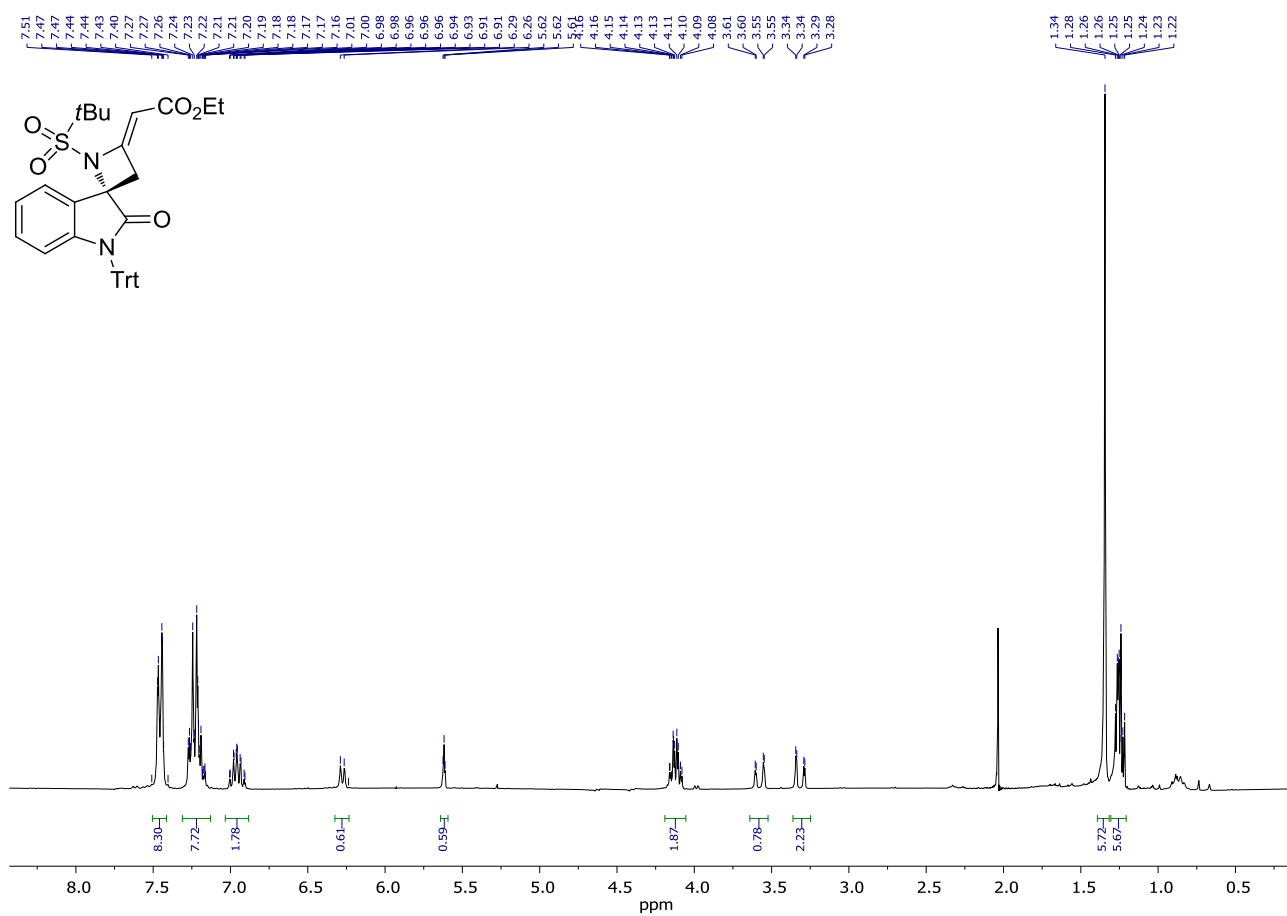
Compound 6b: ^1H NMR (400 MHz, CDCl_3)



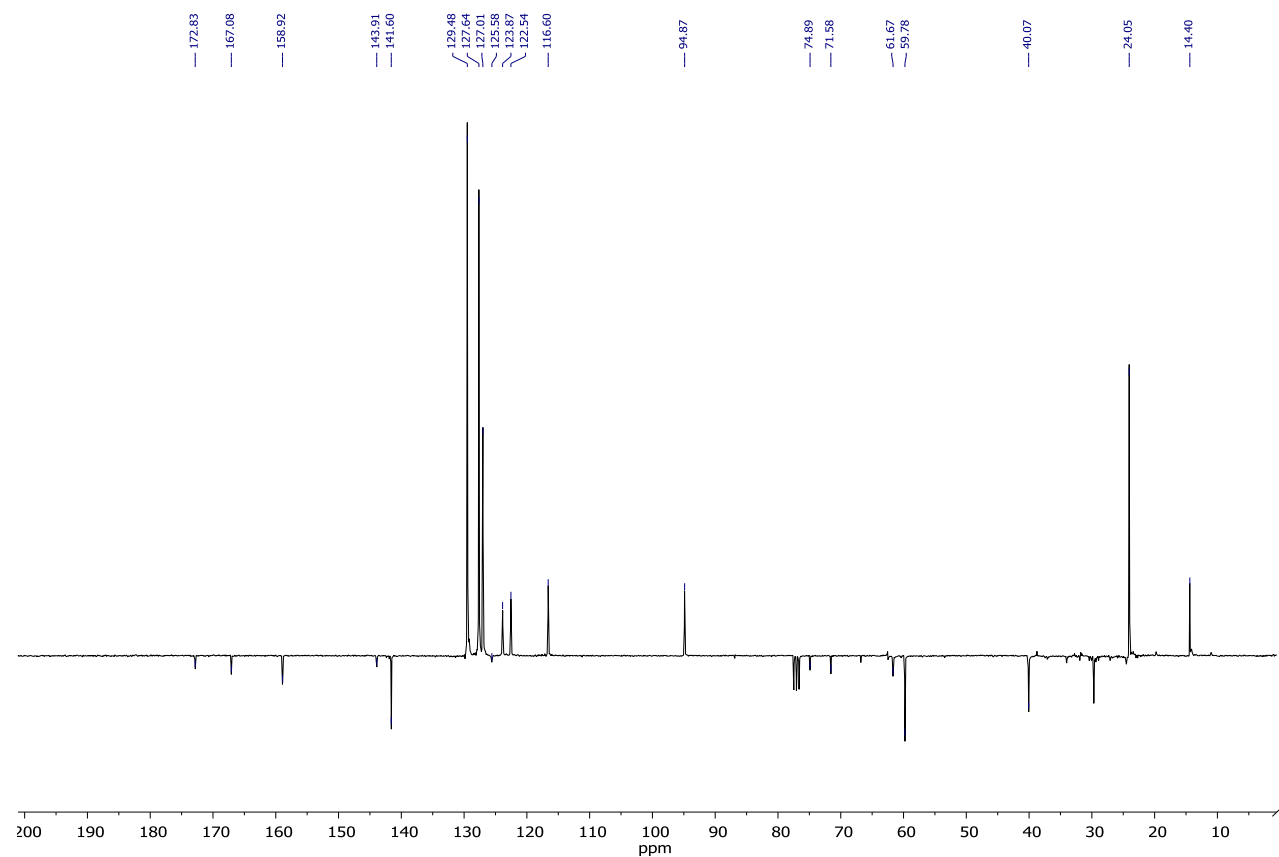
Compound 6b: ^{13}C NMR (101 MHz, CDCl_3)



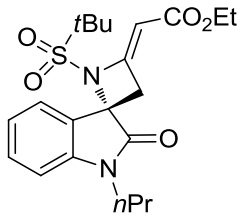
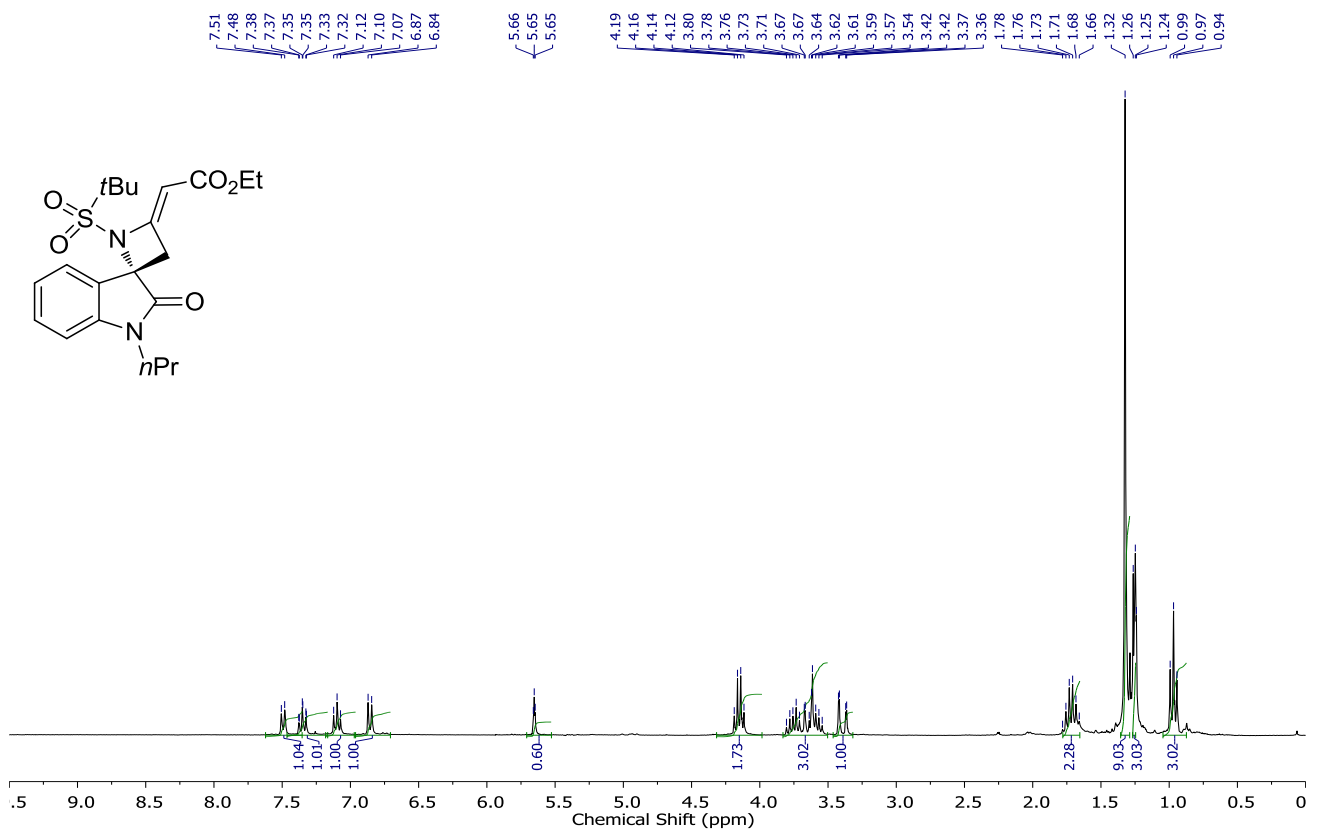
Compound 6c: ^1H NMR (300 MHz, CDCl_3)



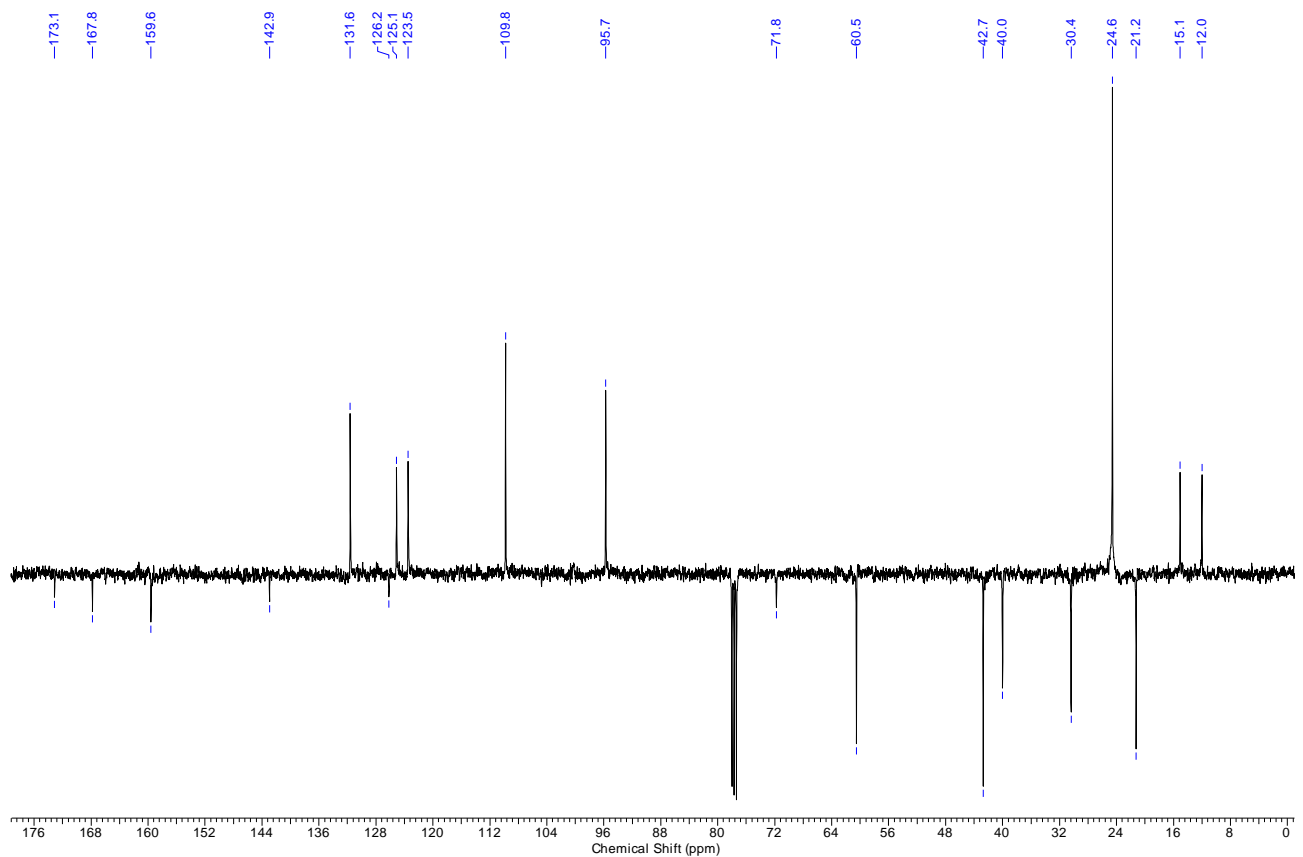
Compound 6c: ^{13}C NMR (75 MHz, CDCl_3)



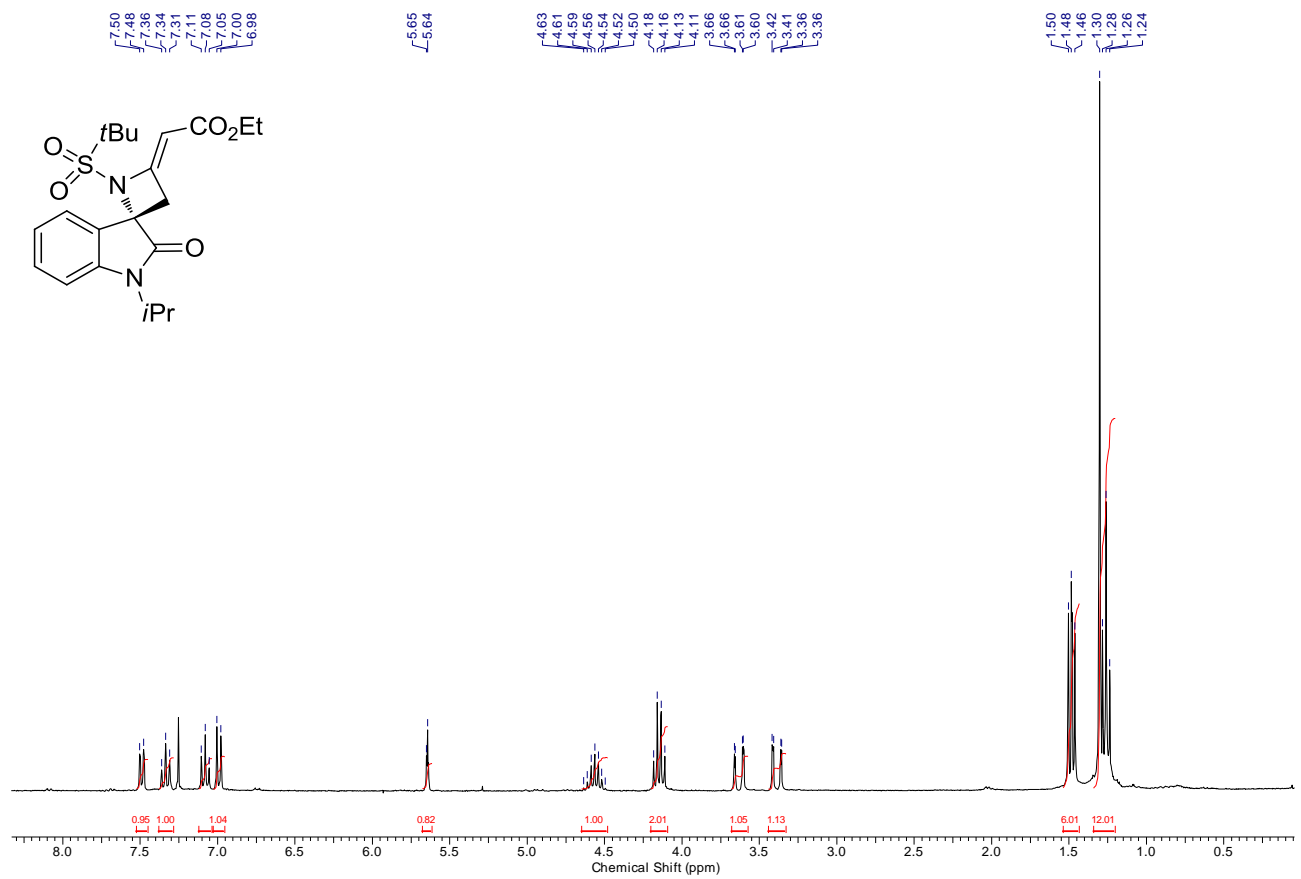
Compound 6d: ^1H NMR (300 MHz, CDCl_3)



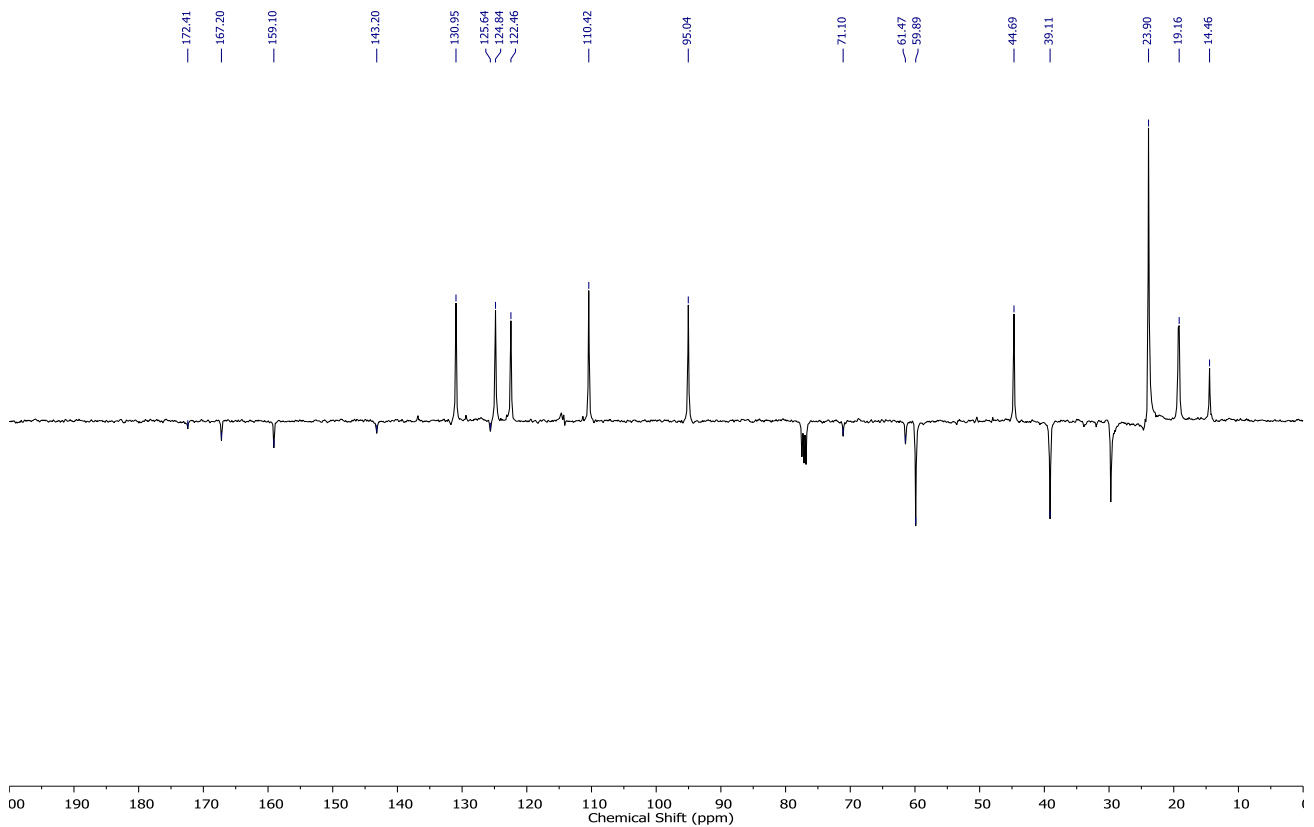
Compound 6d: ^{13}C NMR (101 MHz, APT, CDCl_3)



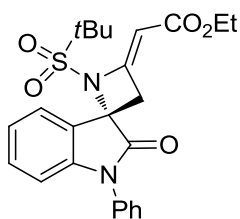
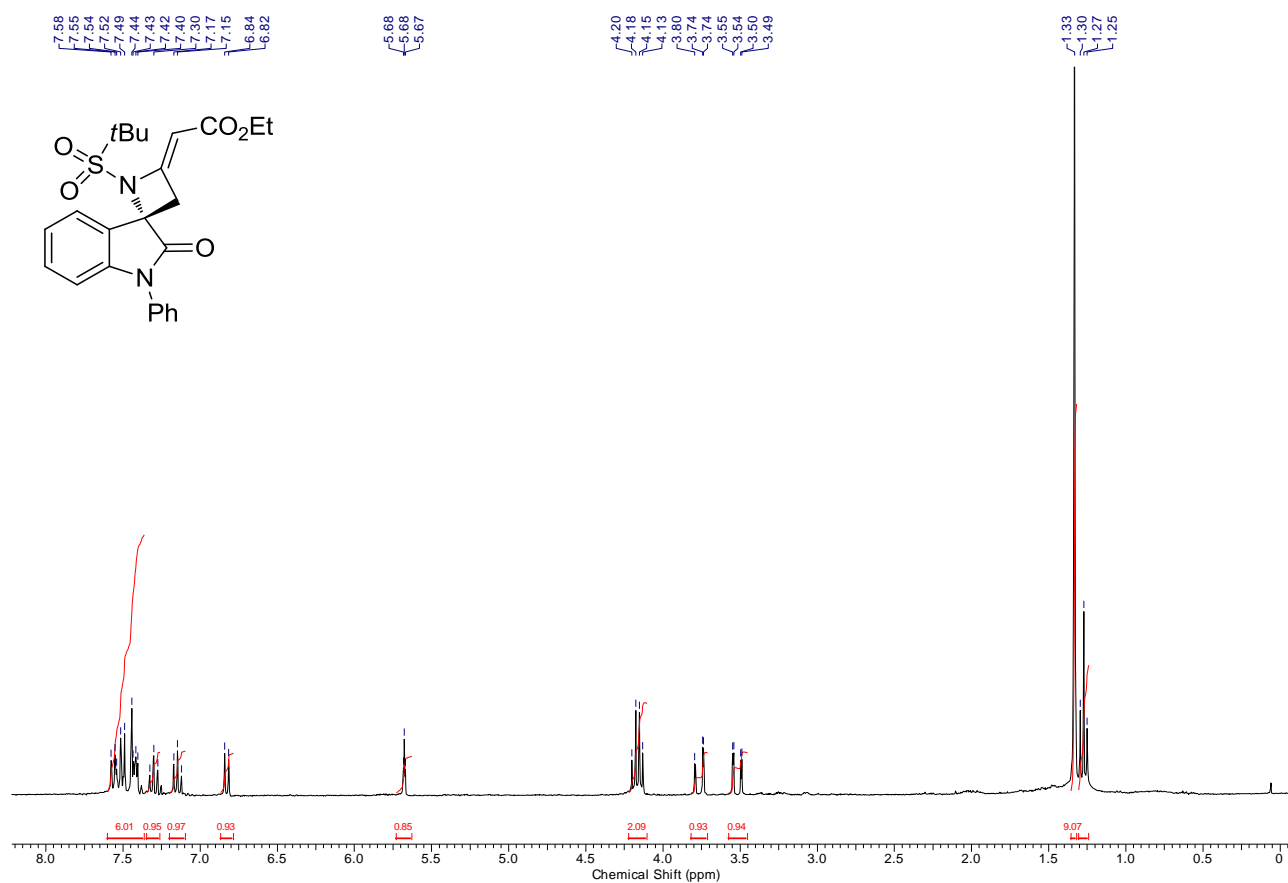
Compound 6e: ^1H NMR (300 MHz, CDCl_3)



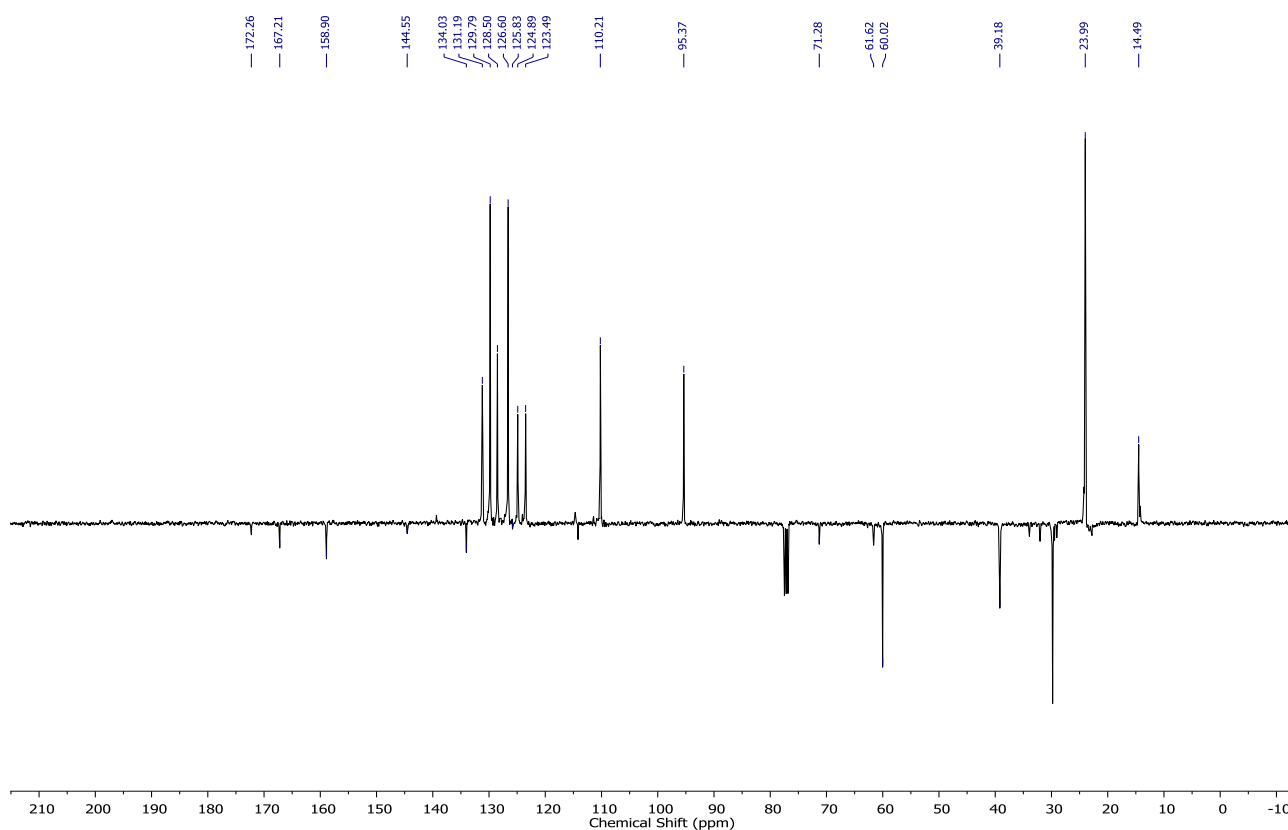
Compound 6e: ^{13}C NMR (101 MHz, APT, CDCl_3)



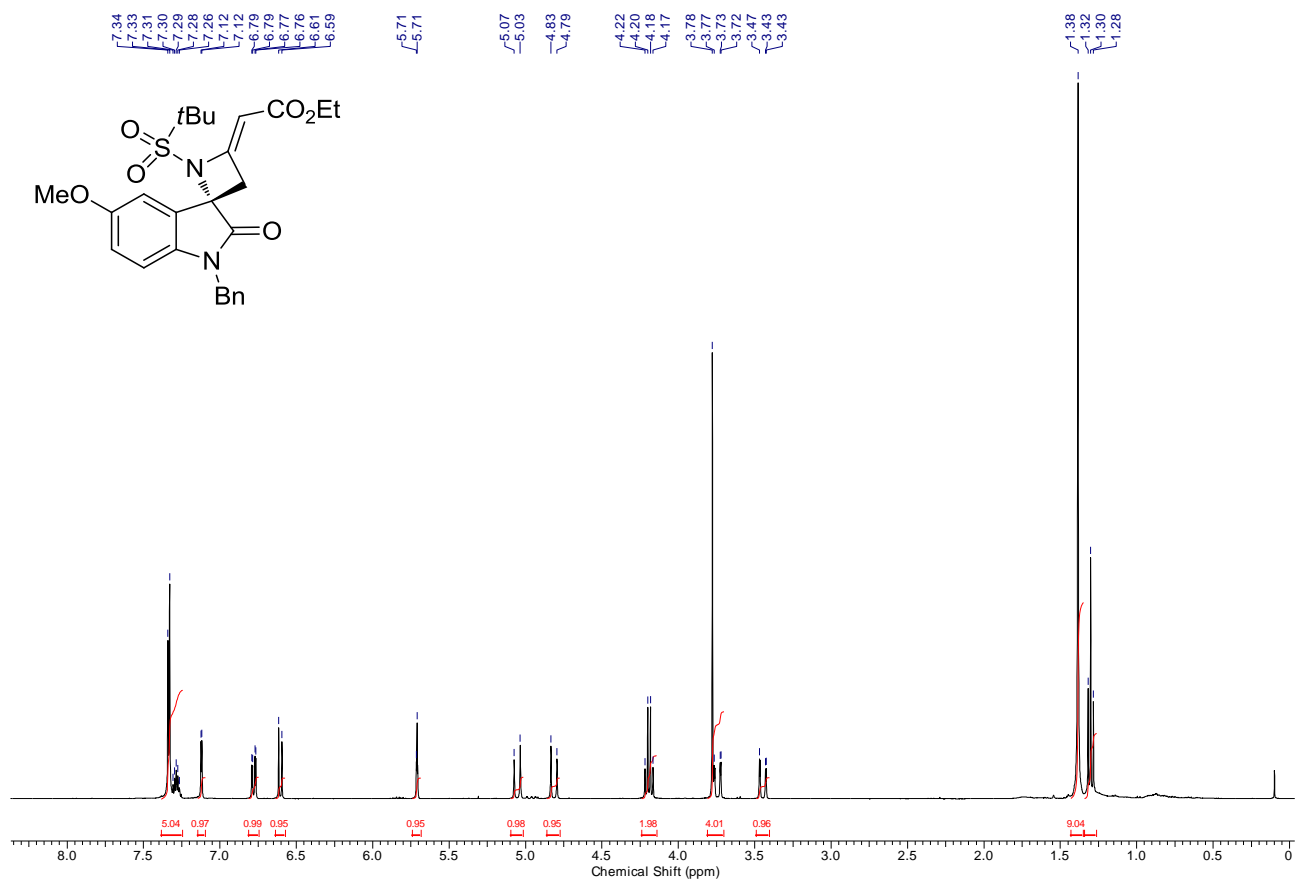
Compound 6f: ^1H NMR (300 MHz, CDCl_3)



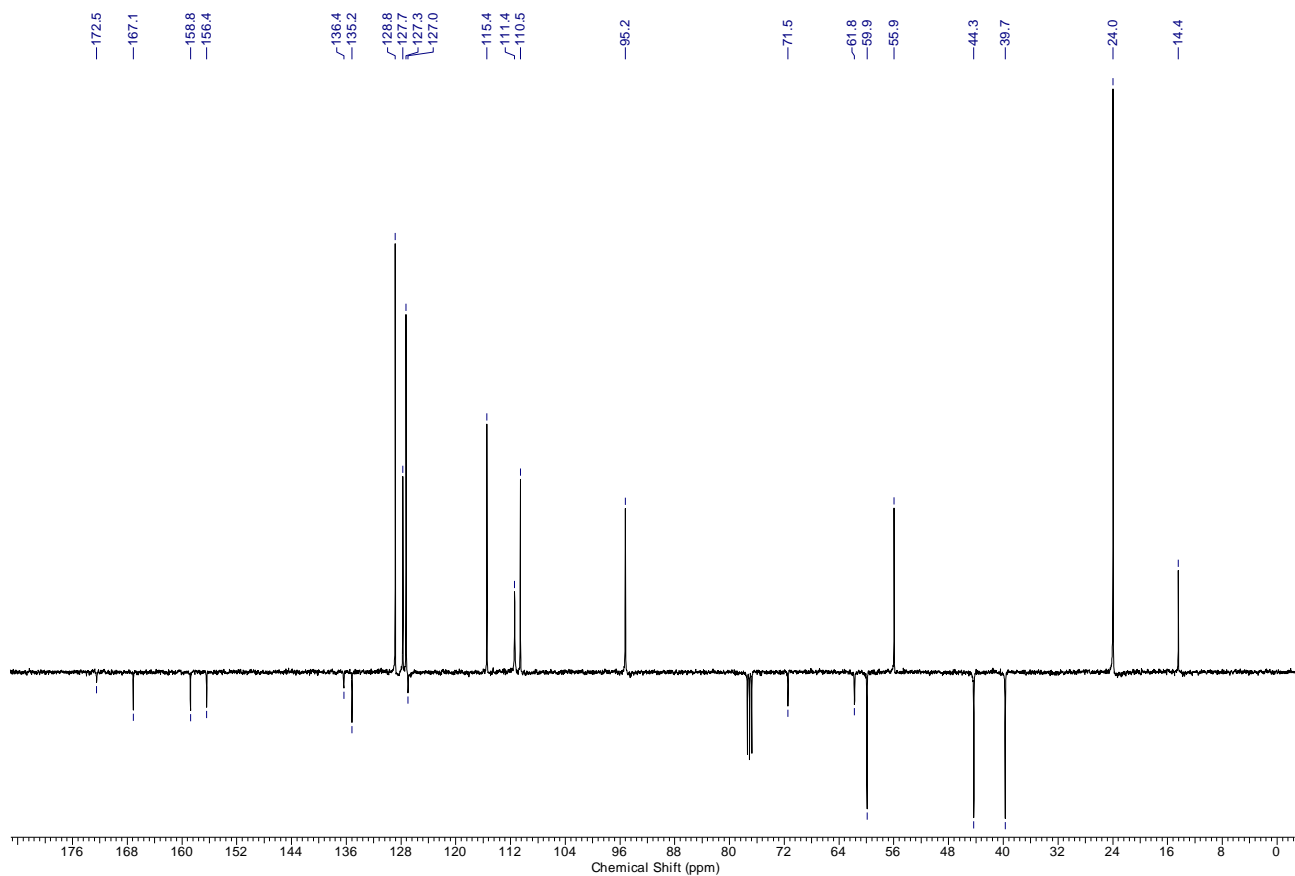
Compound 6f: ^{13}C NMR (101 MHz, APT, CDCl_3)



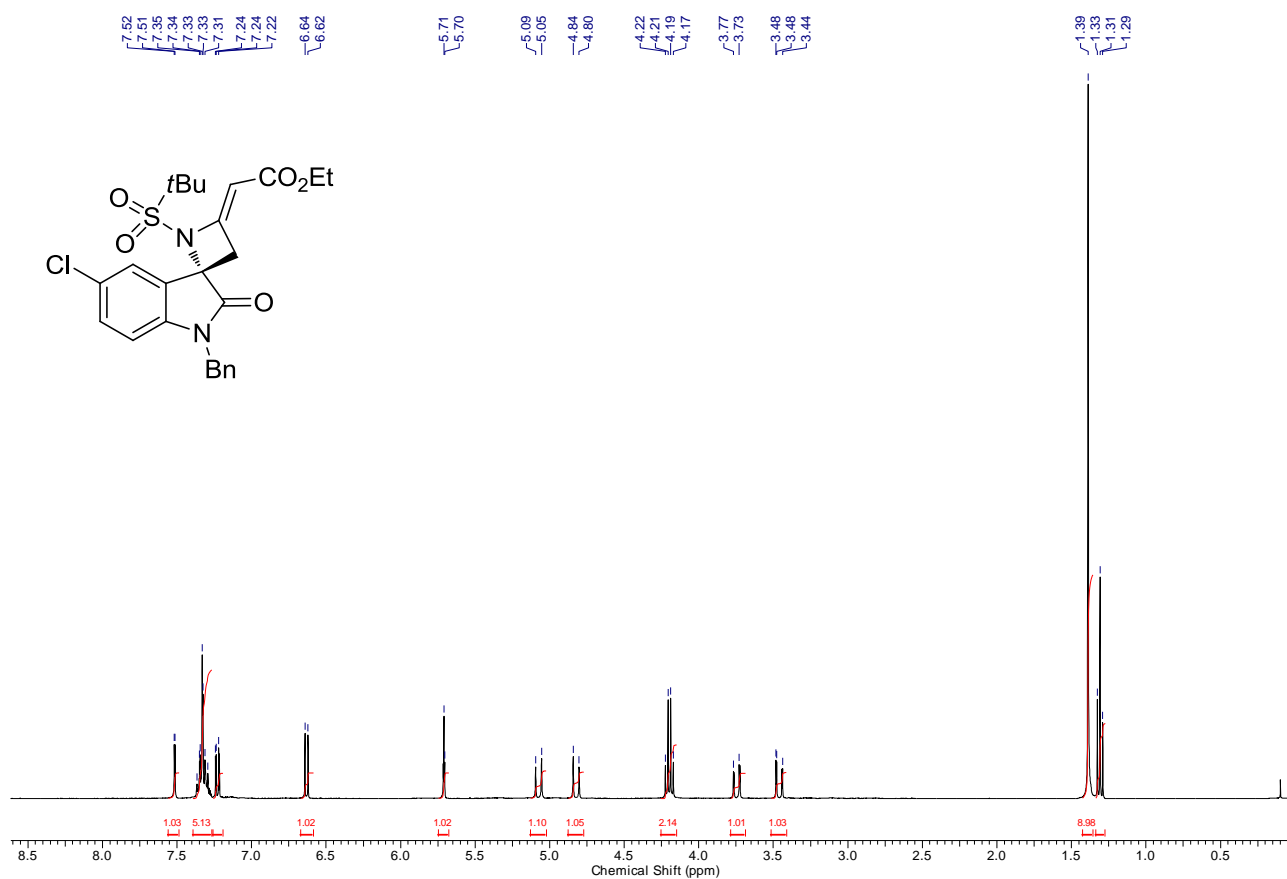
Compound 6g: ^1H NMR (400 MHz, CDCl_3)



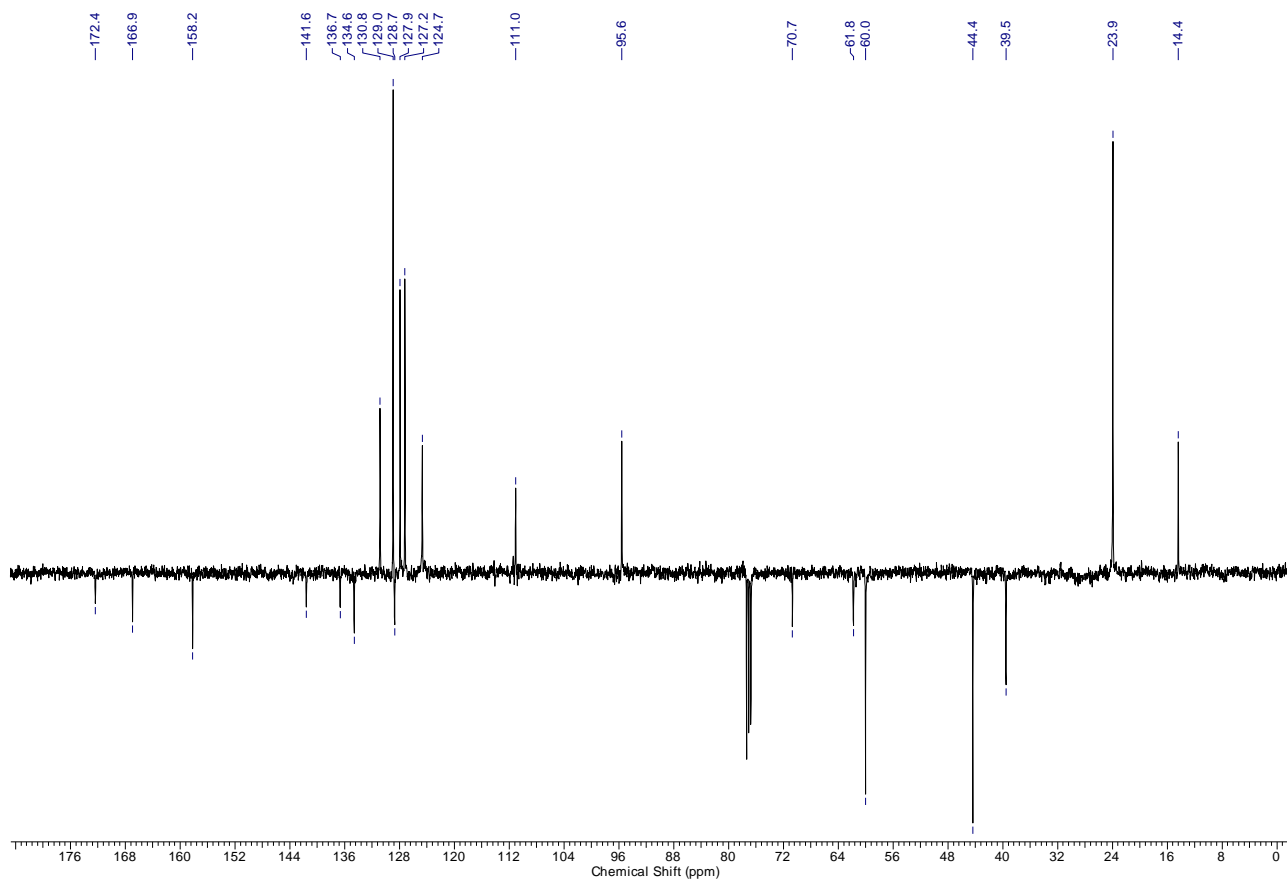
Compound 6g: ^{13}C NMR (101 MHz, APT, CDCl_3)



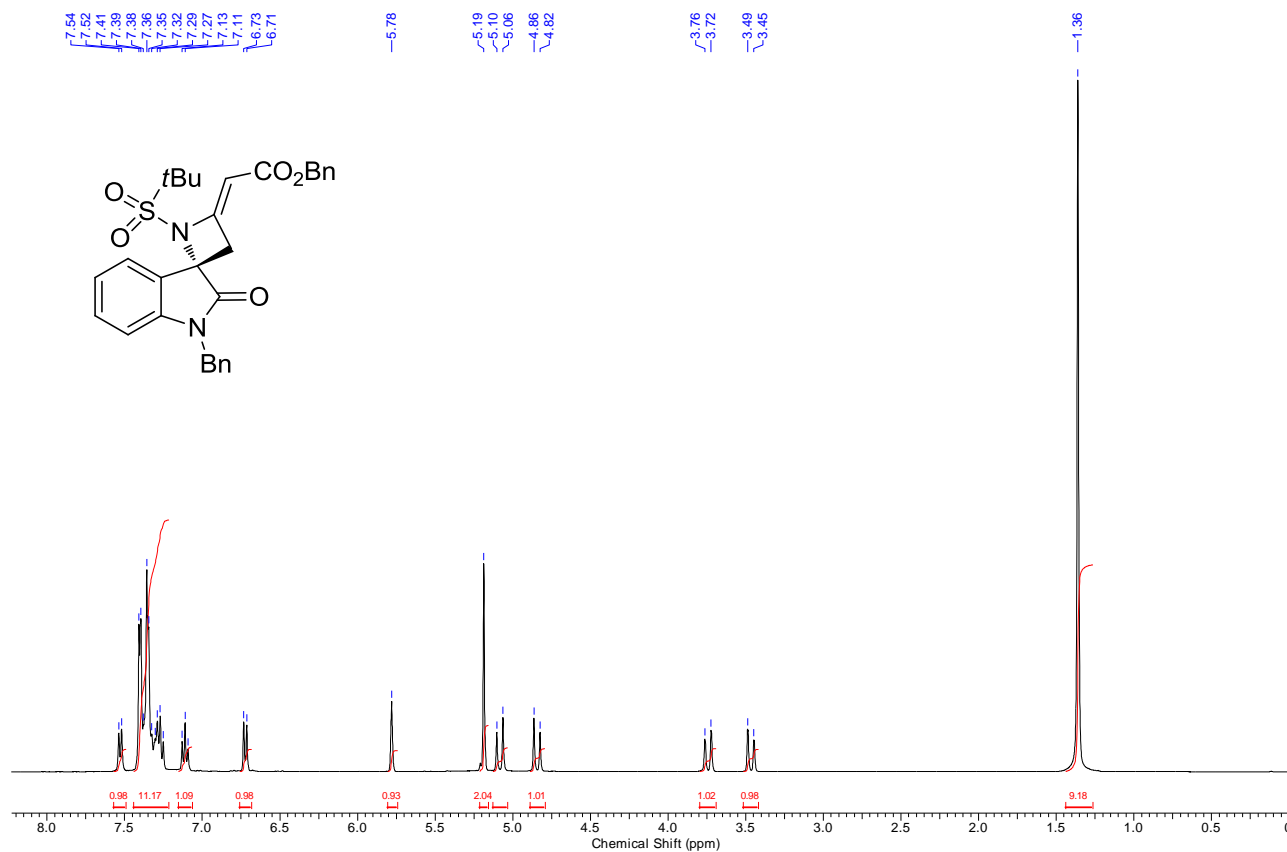
Compound 6h: ^1H NMR (400 MHz, CDCl_3)



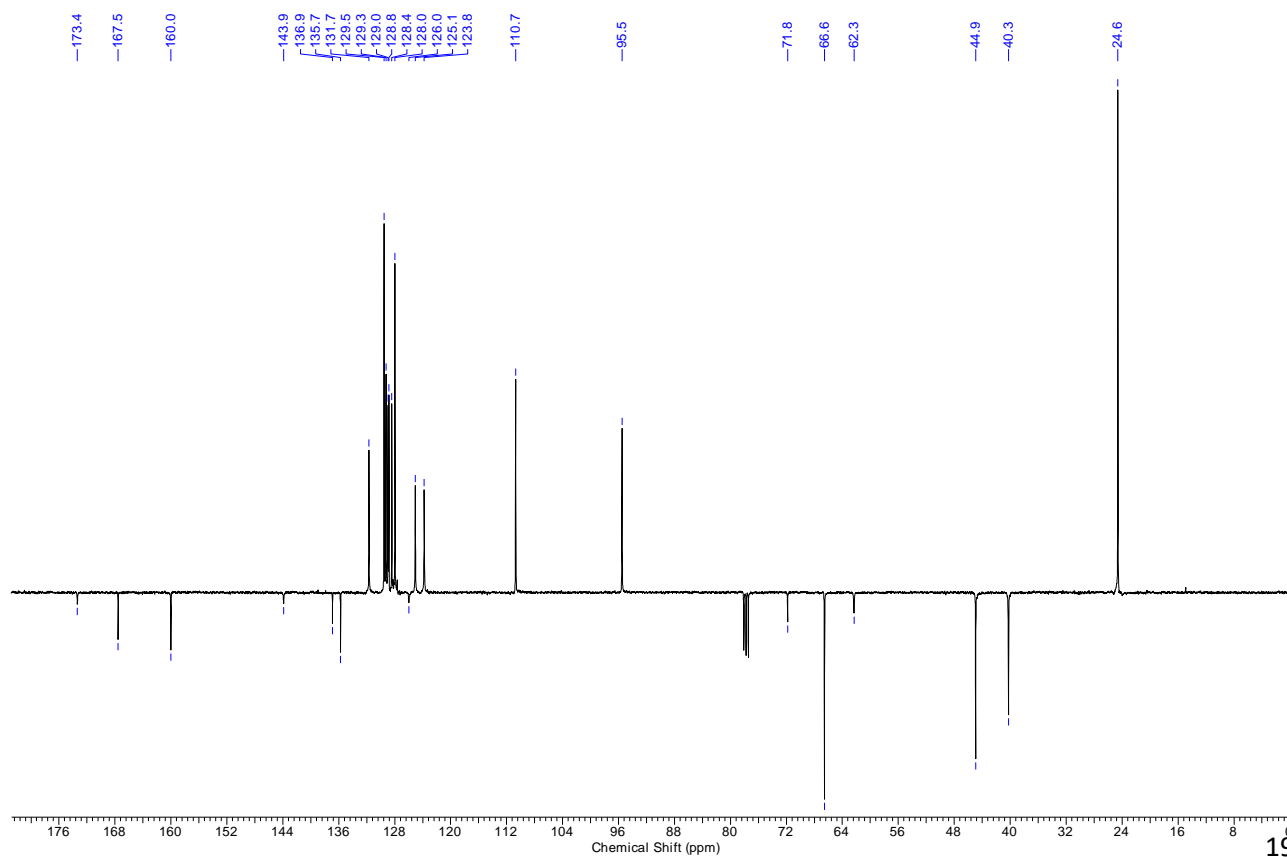
Compound 6h: ^{13}C NMR (101 MHz, APT, CDCl_3)



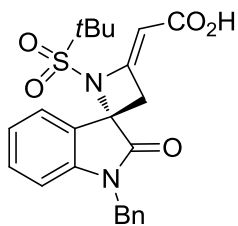
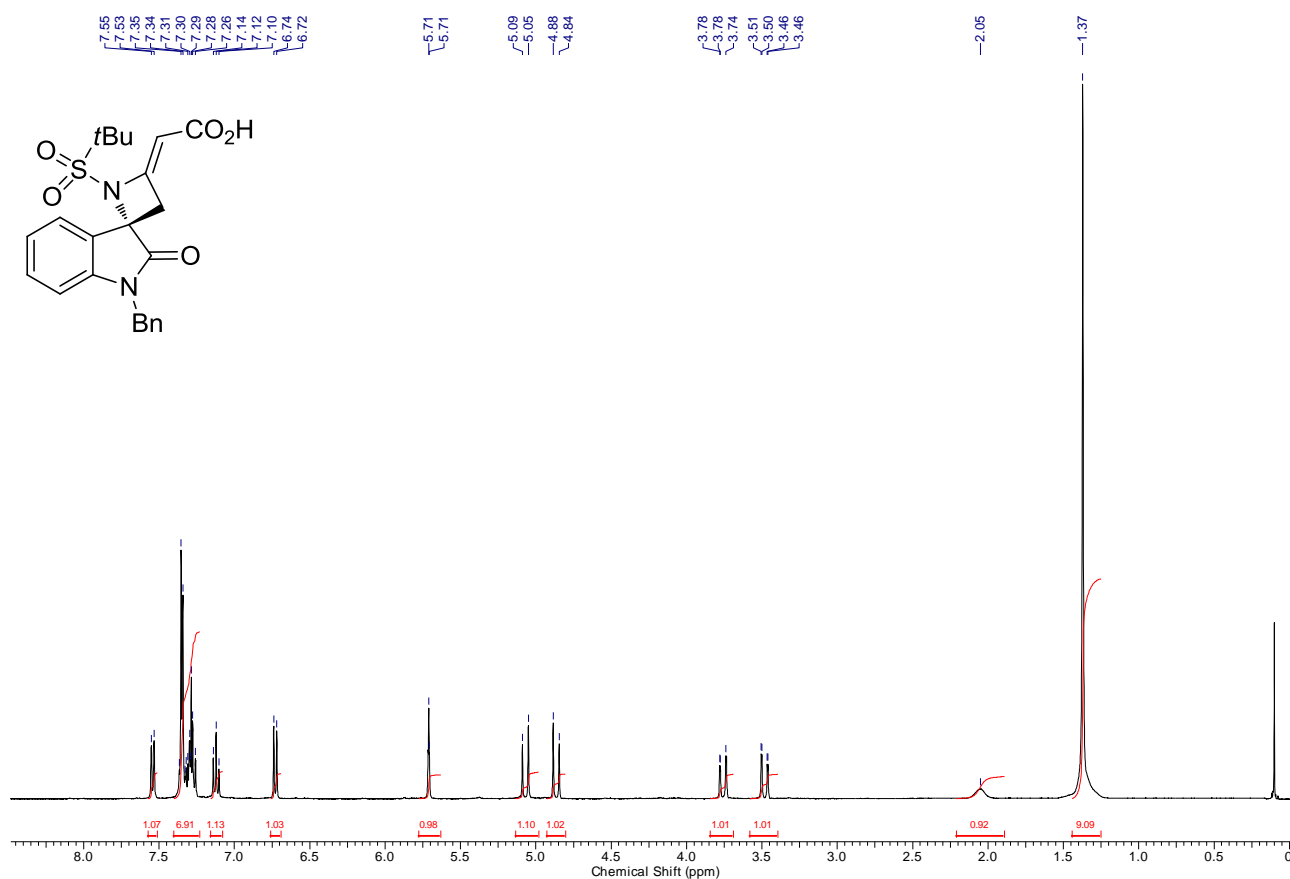
Compound 6k: ^1H NMR (400 MHz, CDCl_3)



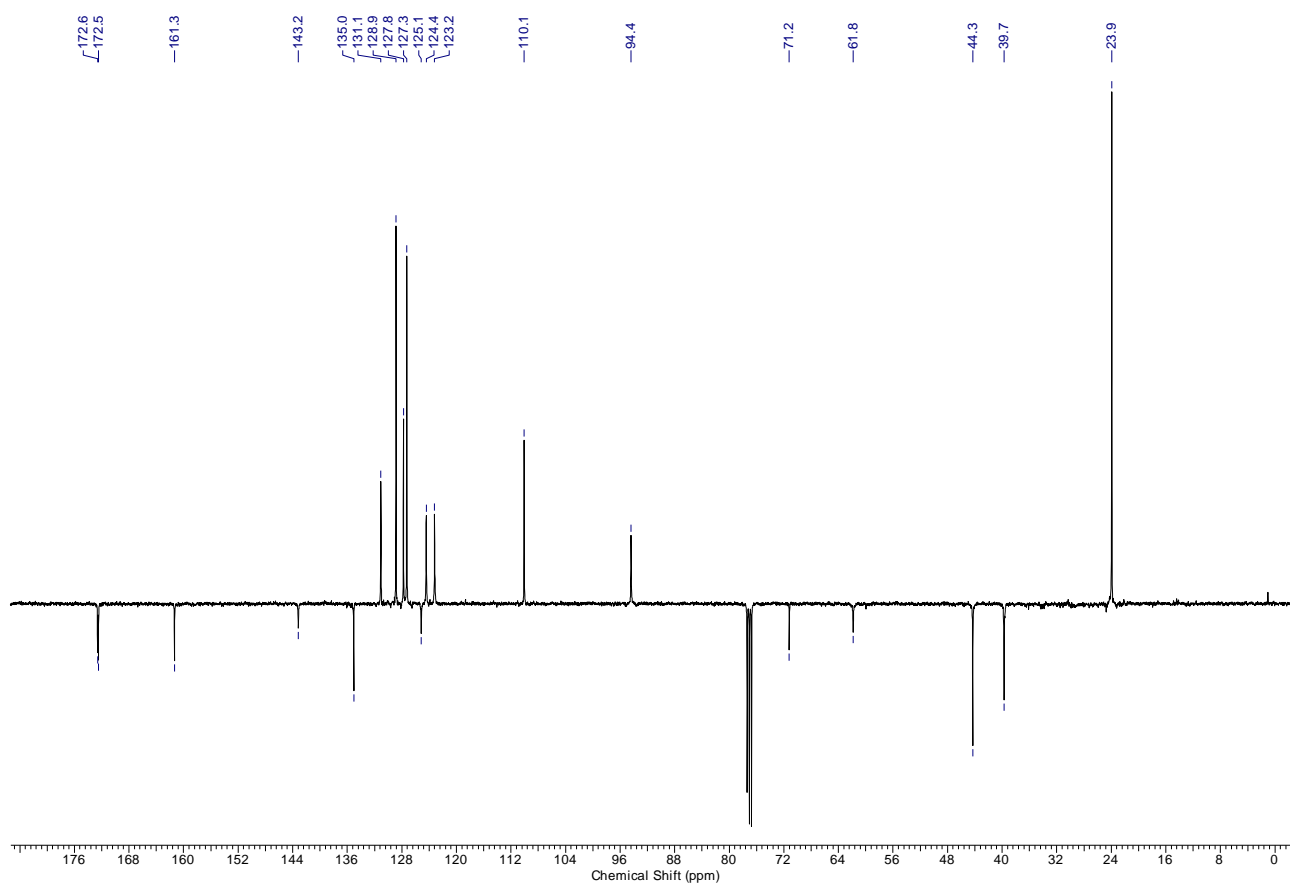
Compound 6k: ^{13}C NMR (101 MHz, APT, CDCl_3)



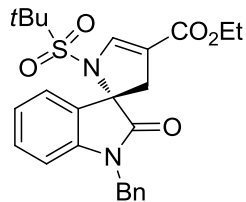
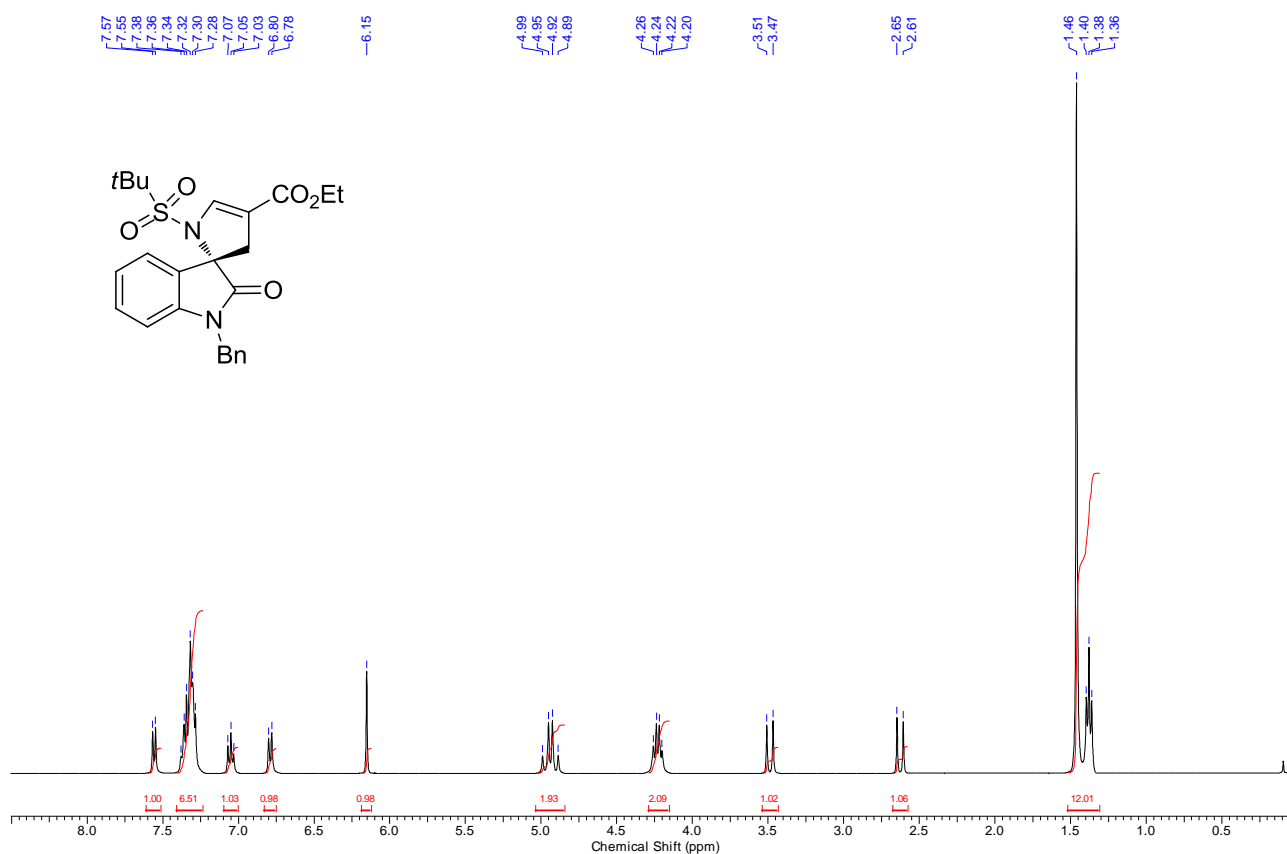
Compound 7: ^1H NMR (400 MHz, CDCl_3)



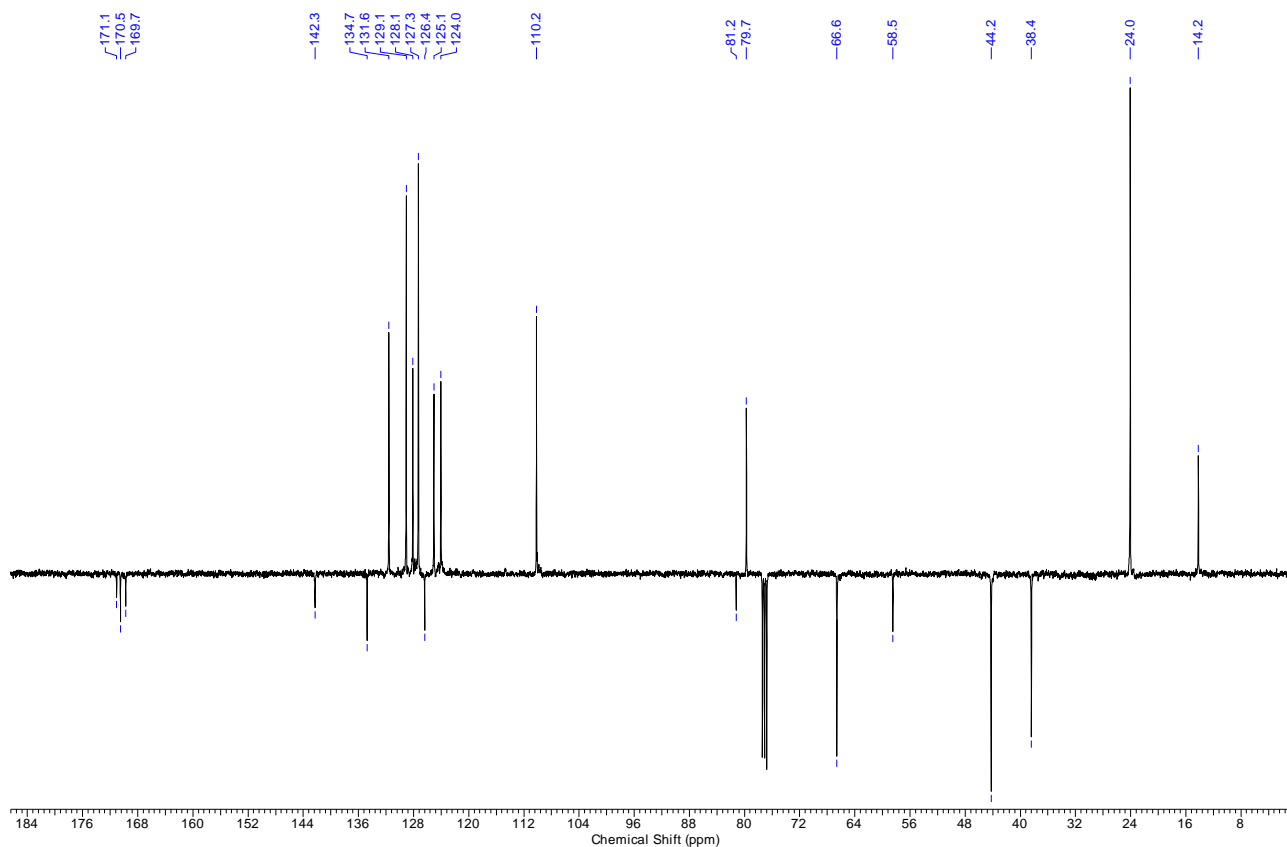
Compound 7: ^{13}C NMR (101 MHz, APT, CDCl_3)



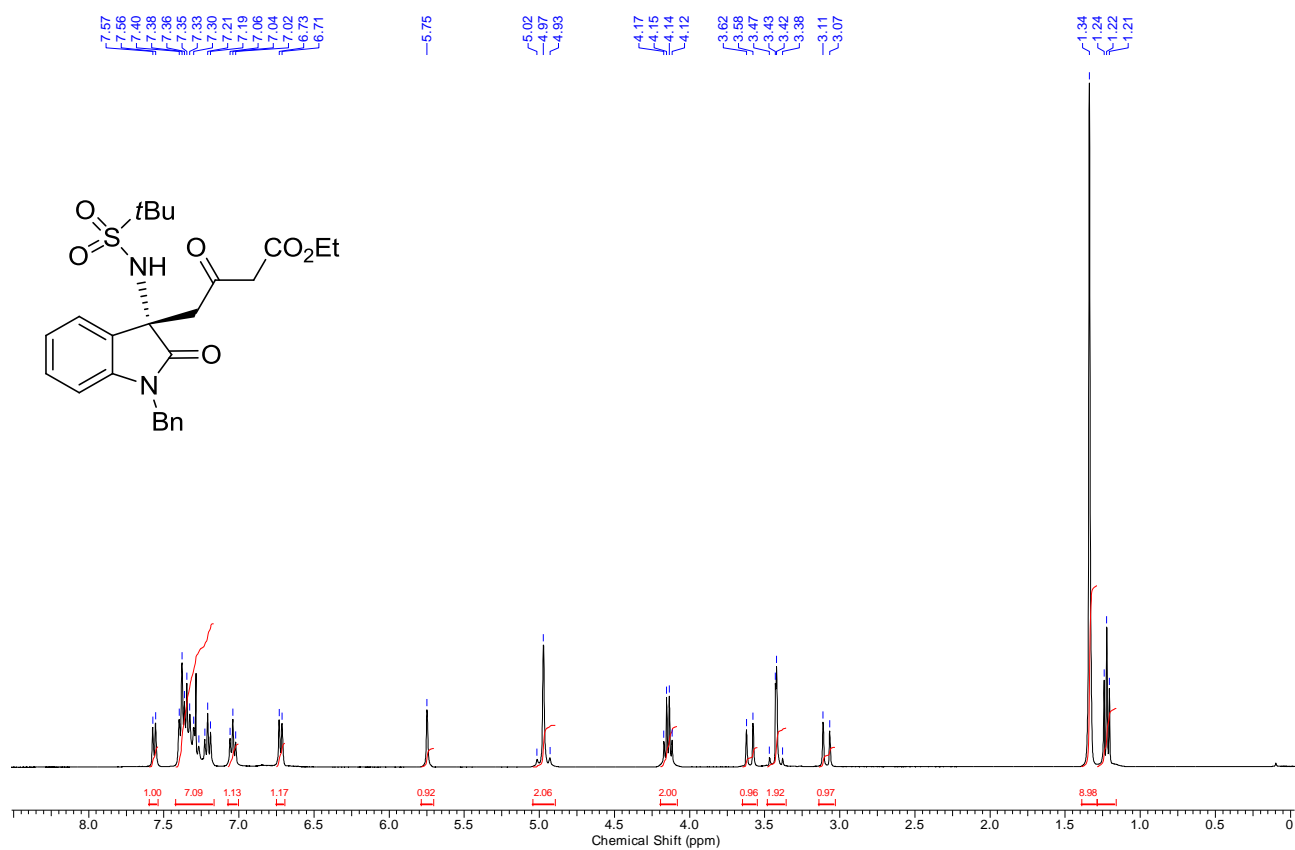
Compound 8: ^1H NMR (400 MHz, CDCl_3)



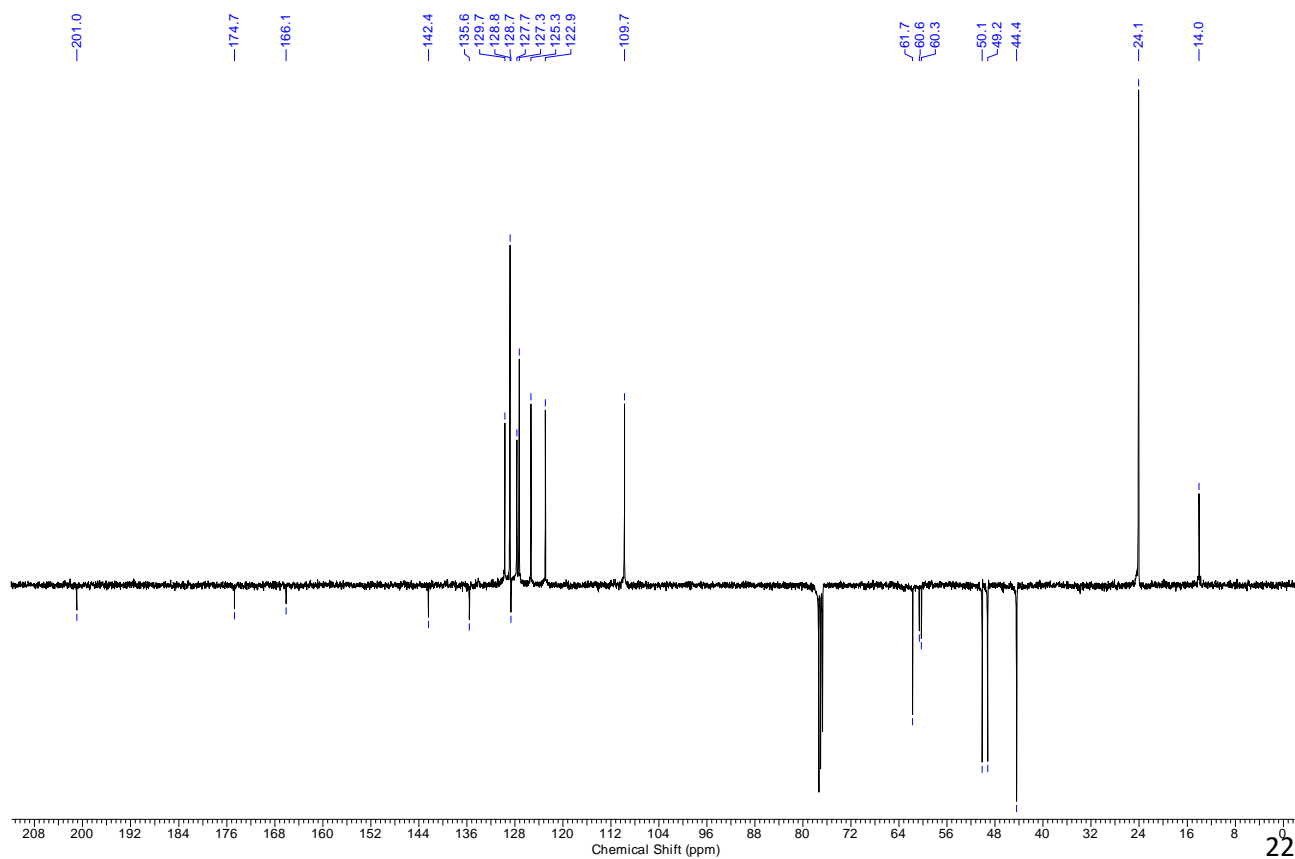
Compound 8: ^{13}C NMR (101 MHz, APT, CDCl_3)



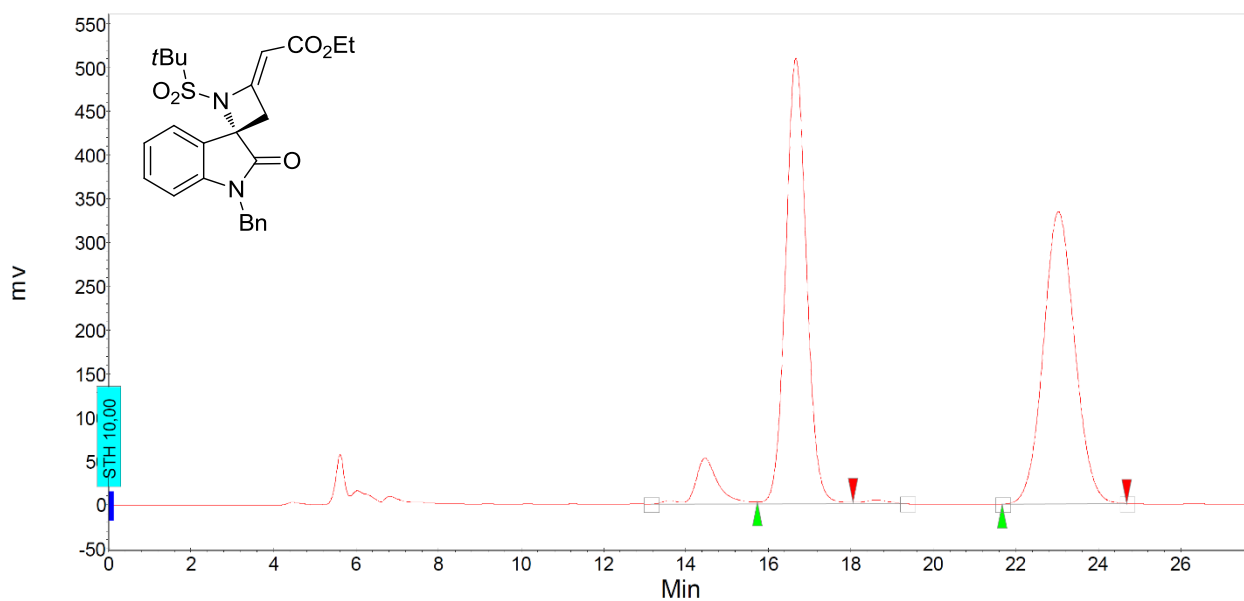
Compound 9: ^1H NMR (400 MHz, CDCl_3)



Compound 9: ^{13}C NMR (101 MHz, APT, CDCl_3)

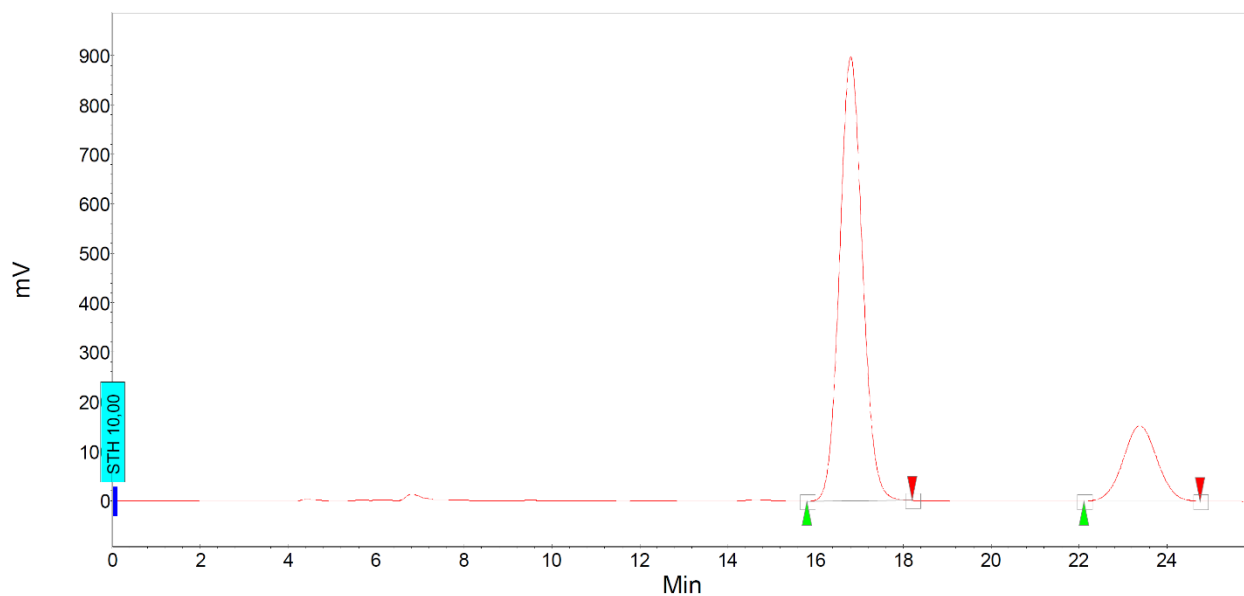


Compound **6a** (racemic mixture) obtained employing DABCO as catalyst



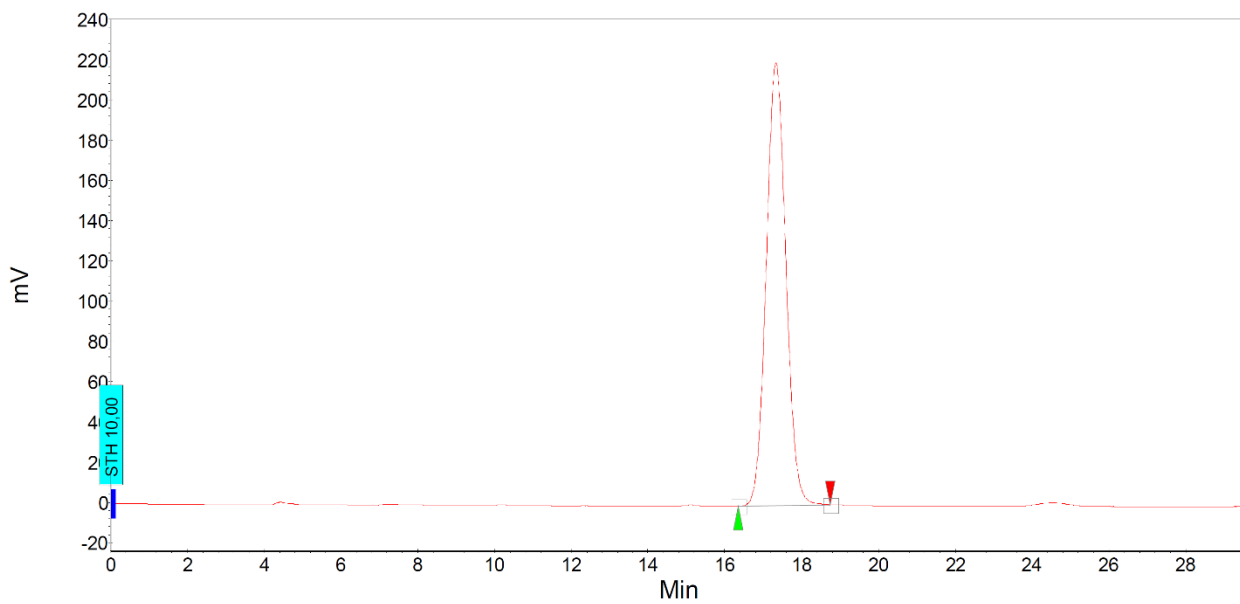
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1	UNKNOWN	15,750	16,675	18,058	0,000	50,29	509,4	298,4	50,286
2	UNKNOWN	21,667	23,033	24,683	0,000	49,71	334,1	295,0	49,714
Total						100,00	843,5	593,5	100,000

Compound **6a** (enantioenriched) obtained employing catalyst **5g**



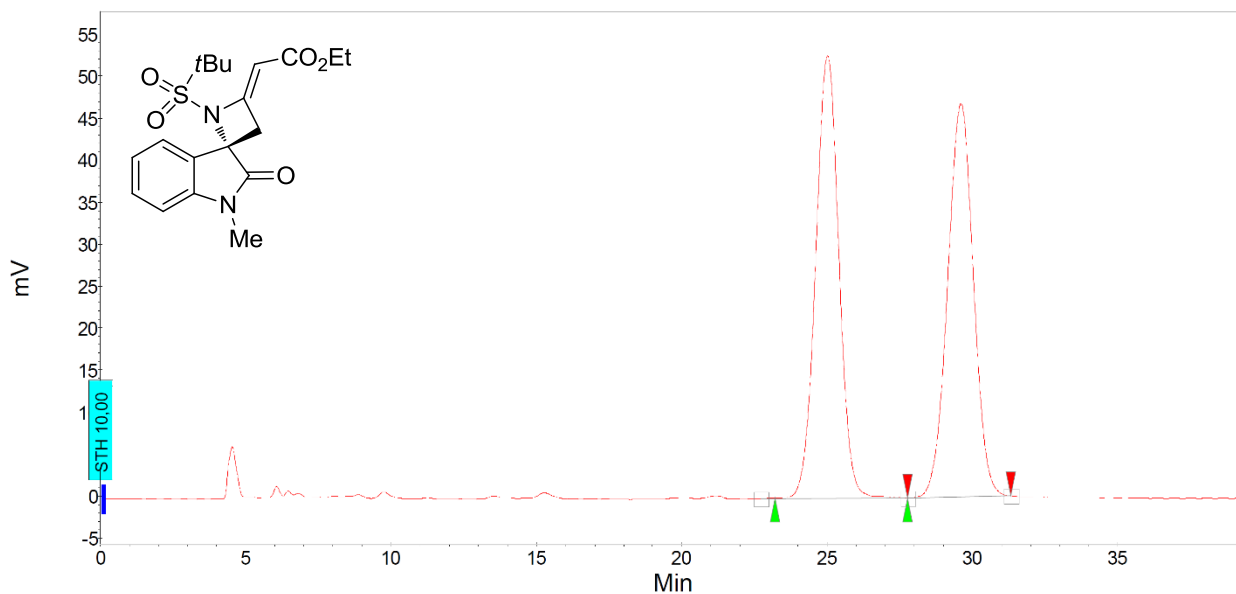
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1	UNKNOWN	15,817	16,808	18,200	0,000	79,83	897,8	542,3	79,826
2	UNKNOWN	22,117	23,383	24,750	0,000	20,17	152,6	137,1	20,174
Total						100,00	1050,3	679,3	100,000

Compound **6a'** obtained through oxidation of compound **I** (see main text, Scheme 1)



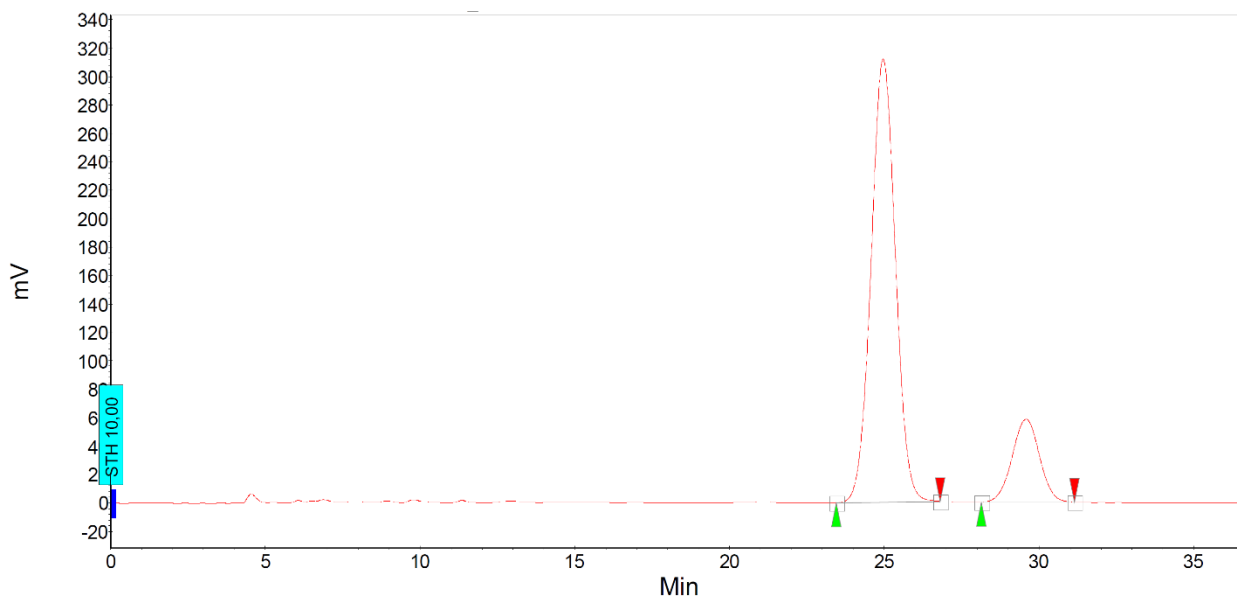
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1	UNKNOWN	16,350	17,333	18,750	0,000	100,00	219,9	130,2	100,000
Total						100,00	219,9	130,2	100,000

Compound **6b** (racemic mixture) obtained employing DABCO as catalyst



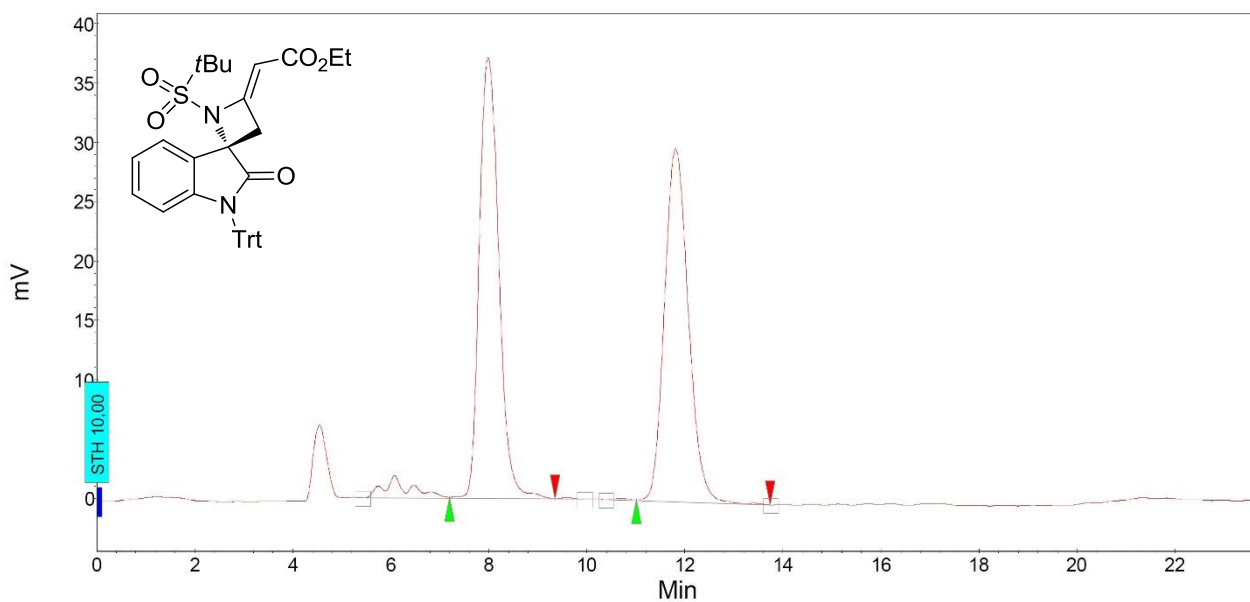
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1	UNKNOWN	23,225	25,025	27,767	0,000	50,35	52,6	48,7	50,348
2	UNKNOWN	27,775	29,608	31,317	0,000	49,65	46,8	48,1	49,652
Total						100,00	99,4	96,8	100,000

Compound **6b** (enantioenriched) obtained employing catalyst **5g**



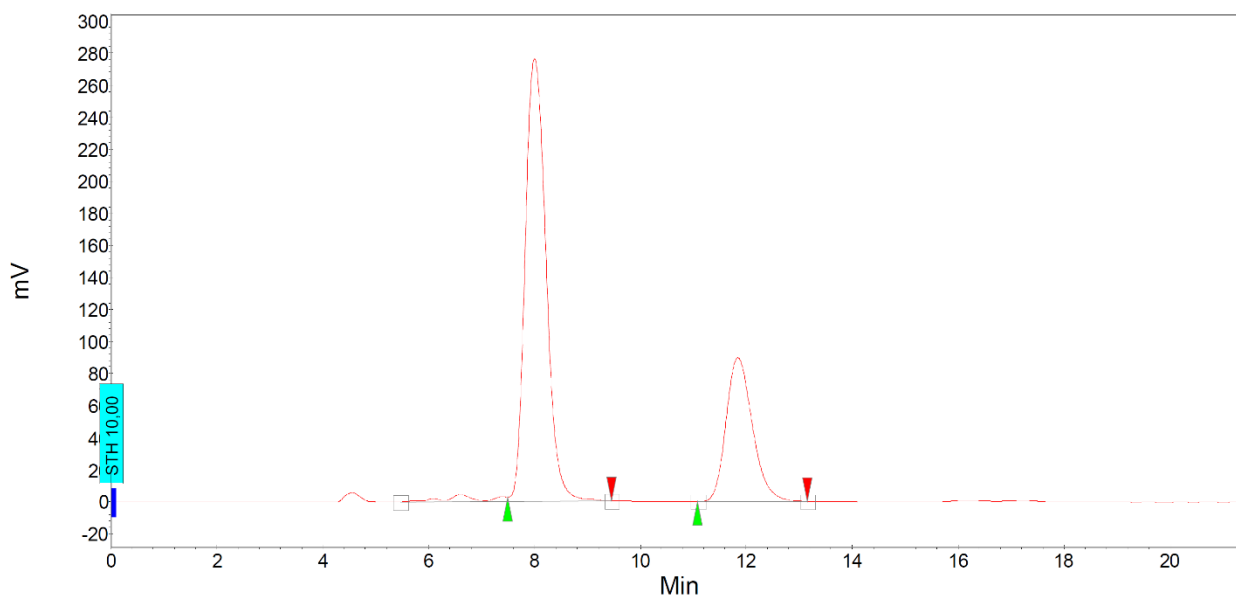
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1	UNKNOWN	23,450	24,958	26,800	0,000	82,63	311,8	284,1	82,634
2	UNKNOWN	28,133	29,575	31,133	0,000	17,37	58,2	59,7	17,366
Total						100,00	370,0	343,8	100,000

Compound **6c** (racemic mixture) obtained employing DABCO as catalyst



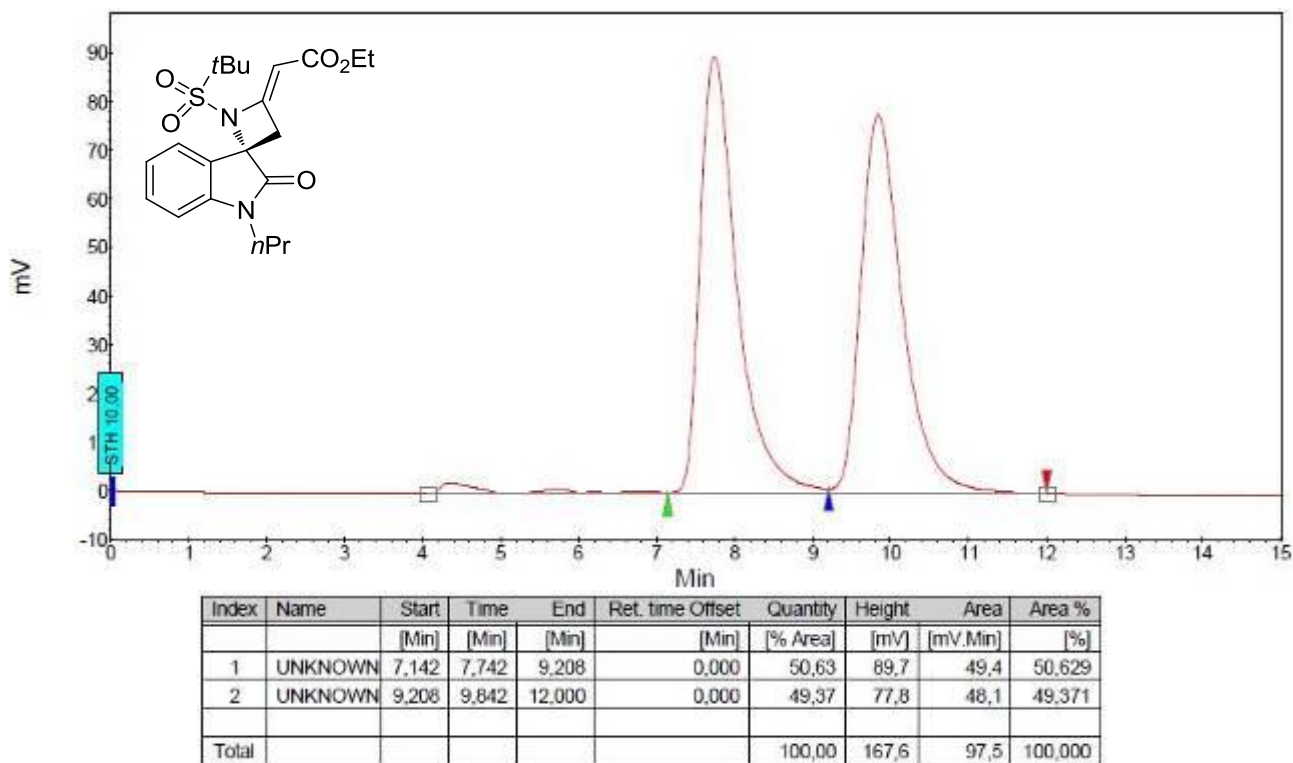
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1	UNKNOWN	7,200	7,983	9,342	0,000	50,55	37,2	17,2	50,551
2	UNKNOWN	11,000	11,817	13,742	0,000	49,45	29,8	16,8	49,449
Total						100,00	66,9	34,1	100,000

Compound **6c** (enantioenriched) obtained employing catalyst **5g**

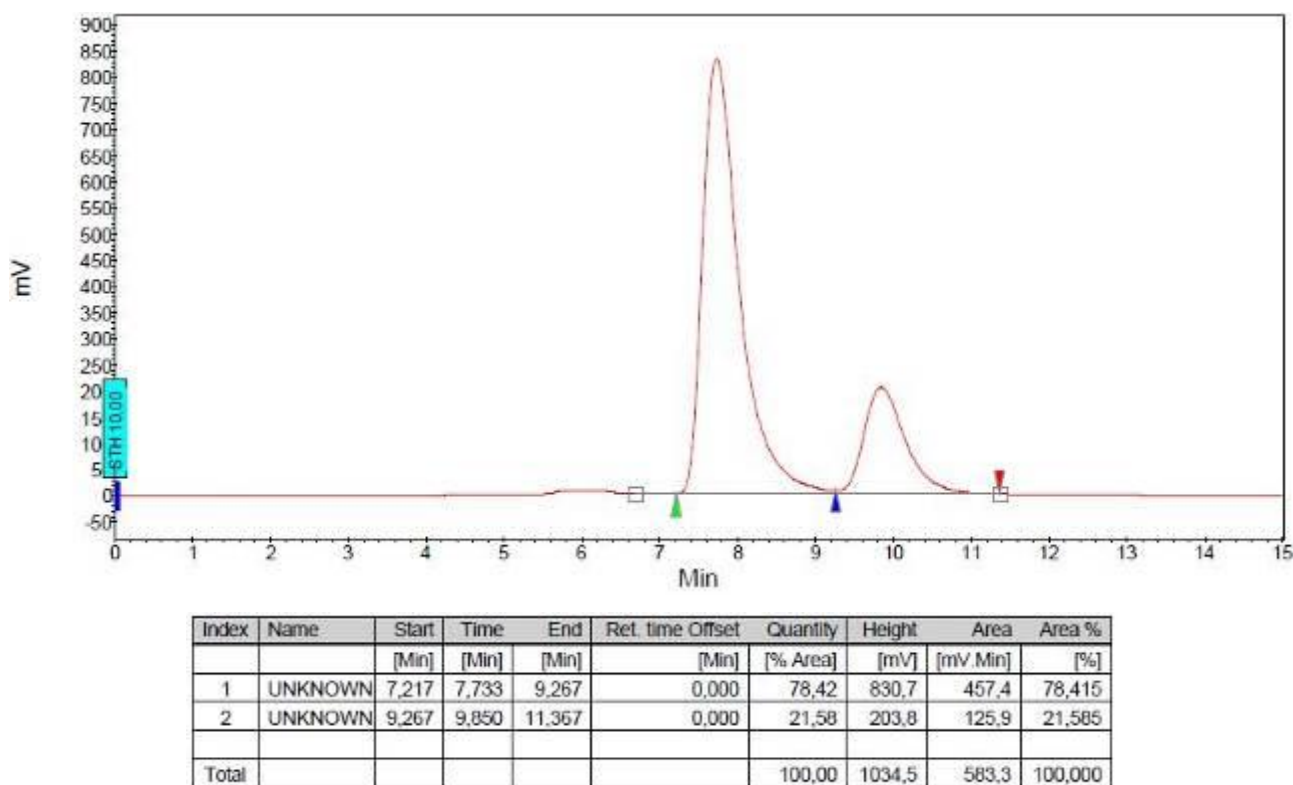


Index	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	UNKNOWN	7,492	8,000	9,450	0,000	70,84	276,2	125,7	70,843
2	UNKNOWN	11,083	11,842	13,150	0,000	29,16	89,7	51,7	29,157
Total						100,00	365,9	177,4	100,000

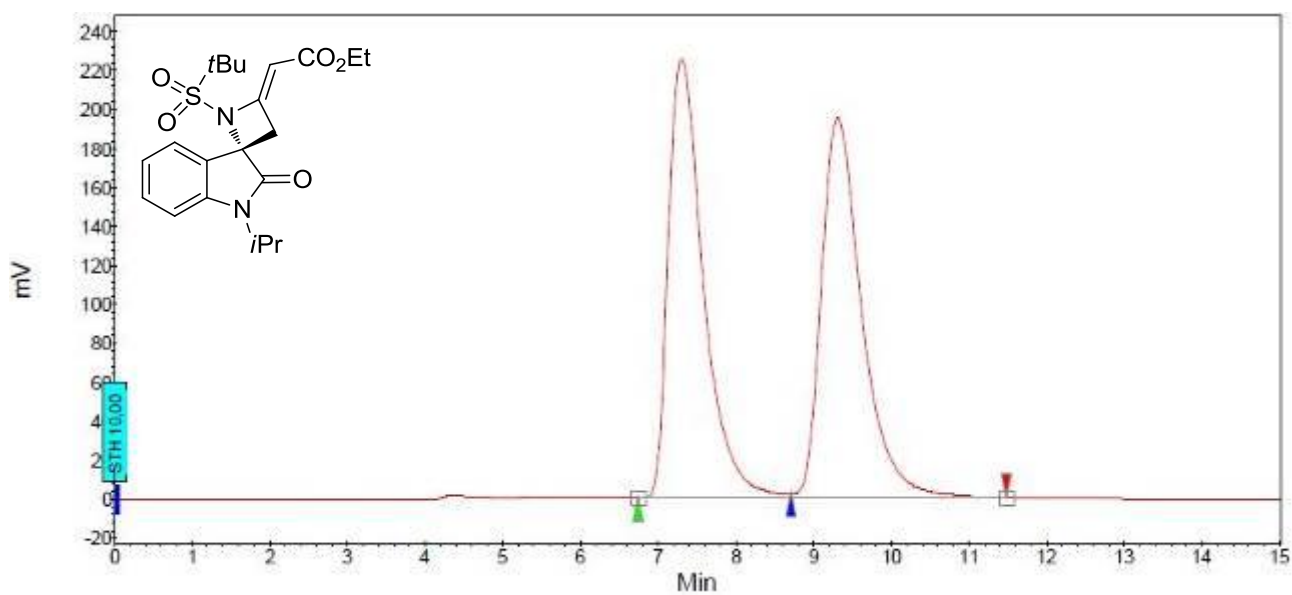
Compound **6d** (racemic mixture) obtained employing DABCO as catalyst



Compound **6d** (enantioenriched) obtained employing catalyst **5g**

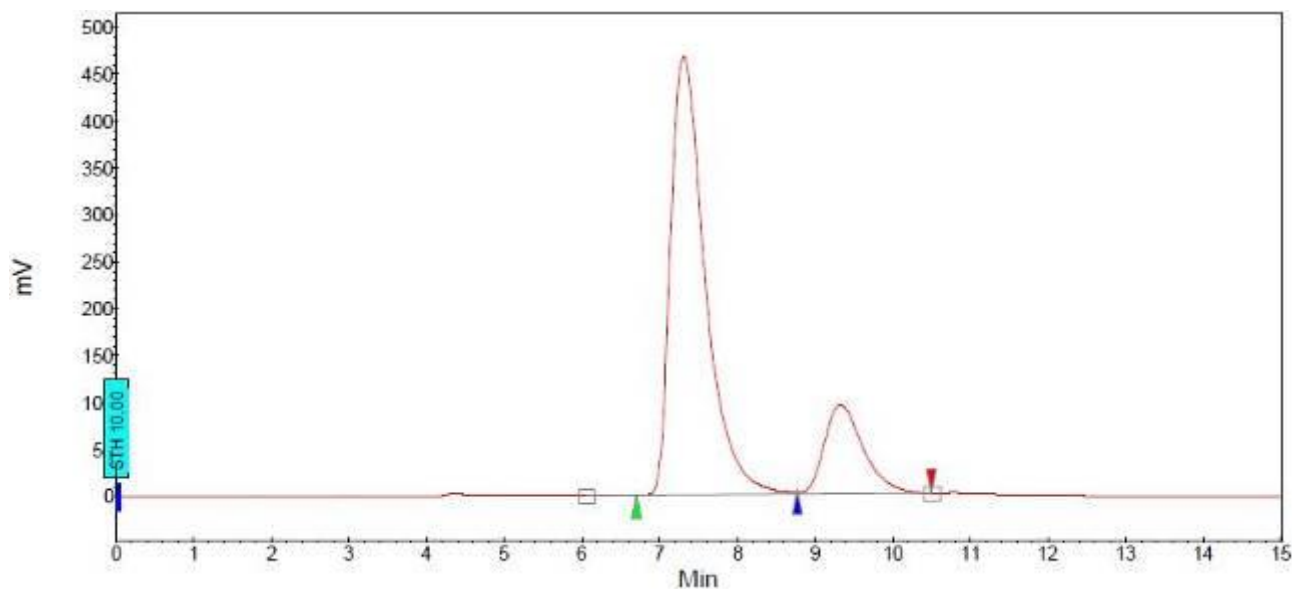


Compound **6e** (racemic mixture) obtained employing DABCO as catalyst



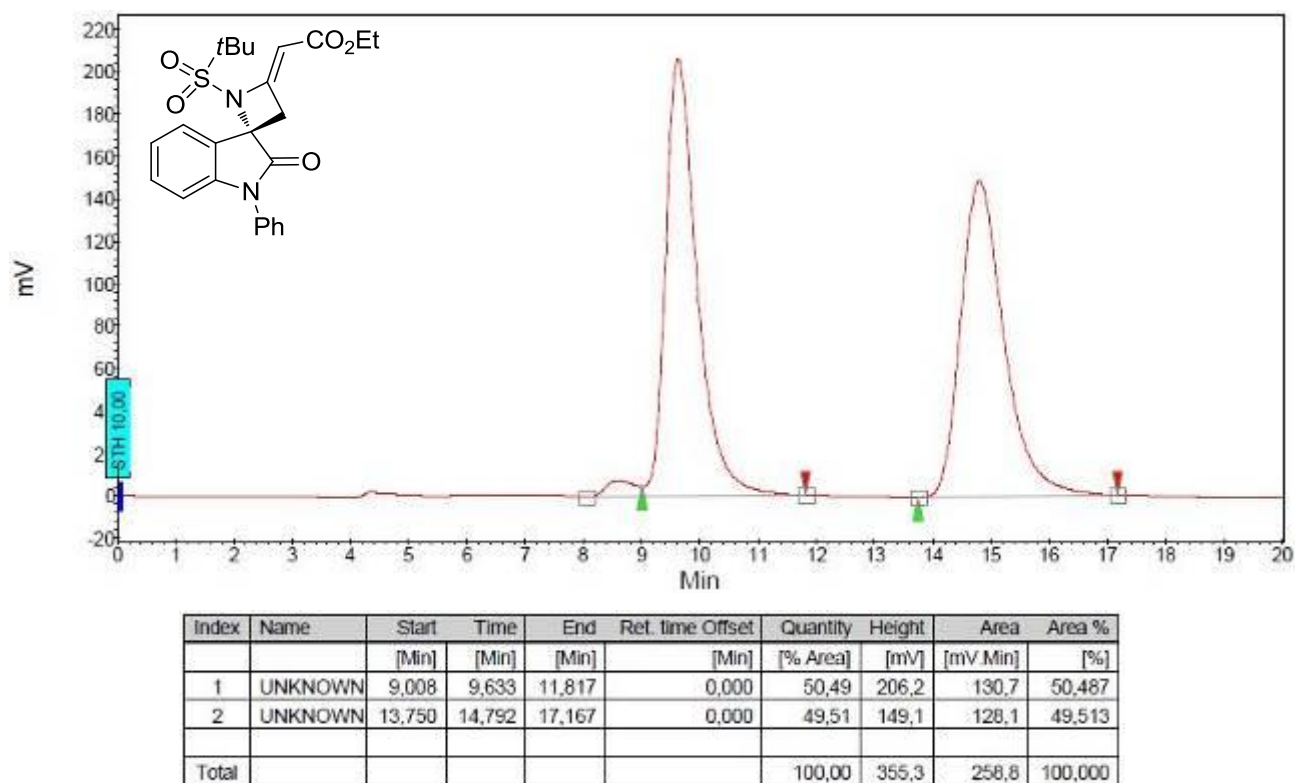
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1	UNKNOWN	6,733	7,308	8,708	0,000	50,18	224,9	118,1	50,177
2	UNKNOWN	8,708	9,317	11,483	0,000	49,82	195,0	117,2	49,823
Total						100,00	419,9	235,3	100,000

Compound **6e** (enantiomeriched) obtained employing catalyst **5g**

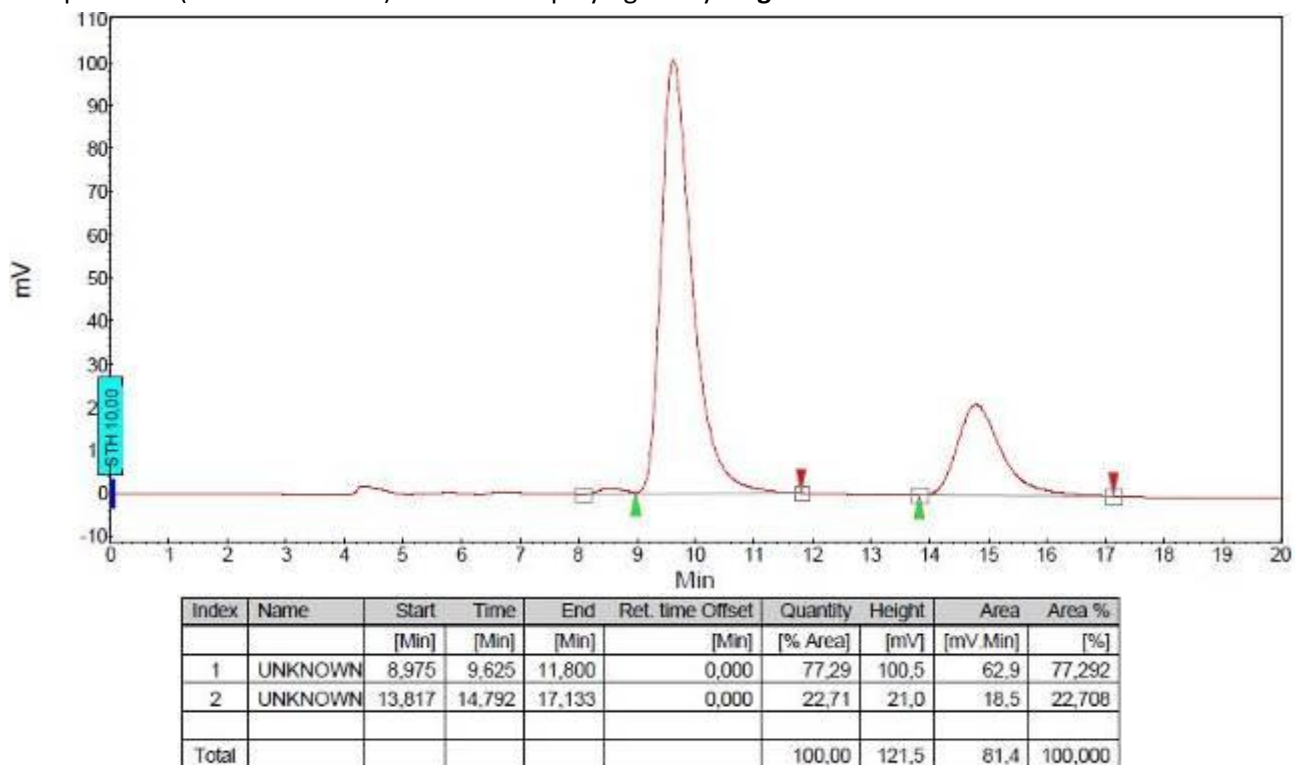


Index	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	UNKNOWN	6,700	7,317	8,775	0,000	81,54	466,4	242,6	81,541
2	UNKNOWN	8,775	9,333	10,500	0,000	18,46	94,7	54,9	18,459
Total						100,00	561,1	297,6	100,000

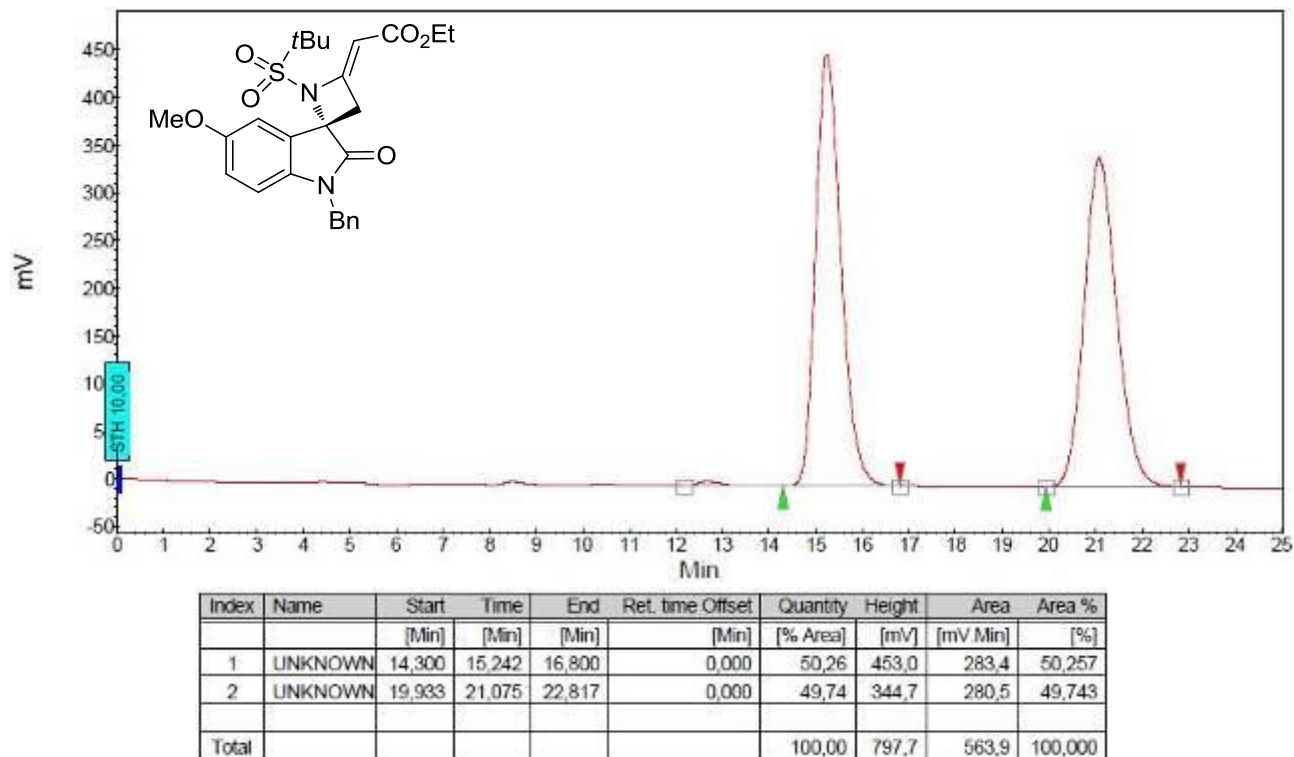
Compound **6f** (racemic mixture) obtained employing DABCO as catalyst



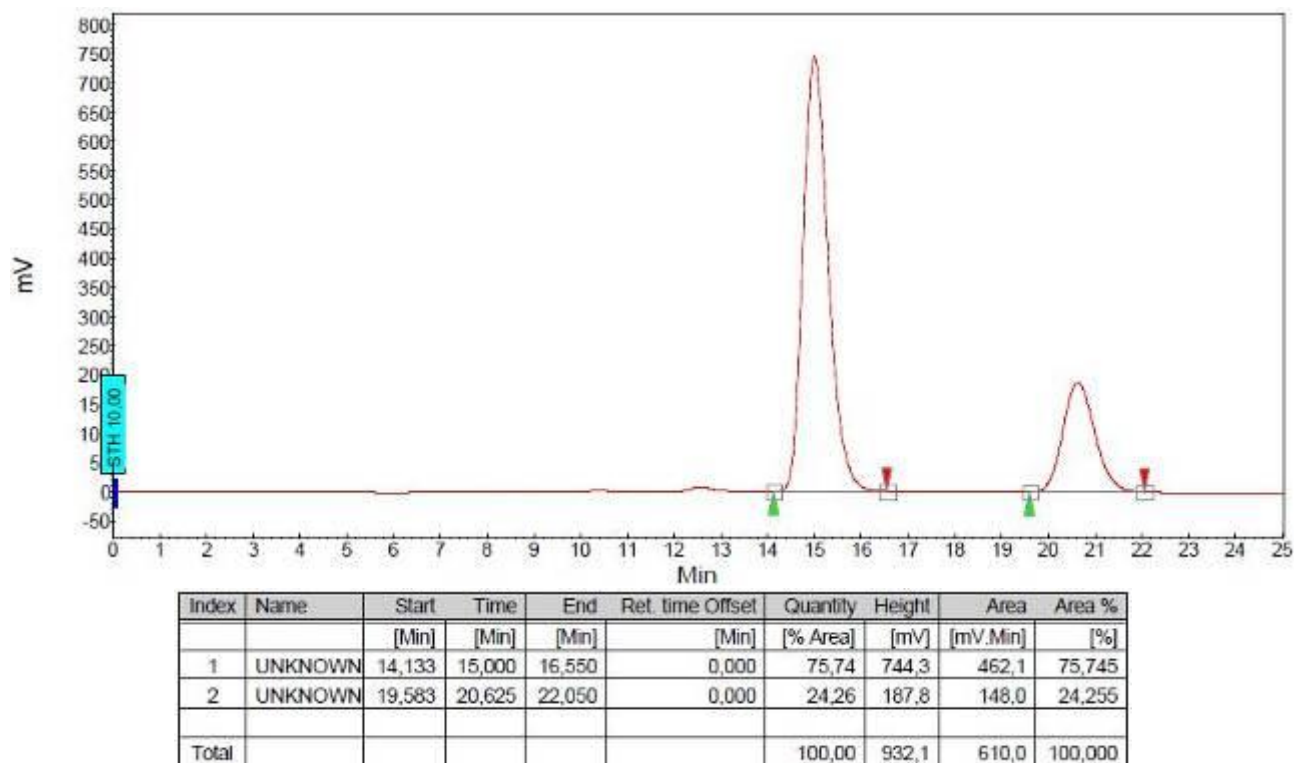
Compound **6f** (enantioenriched) obtained employing catalyst **5g**



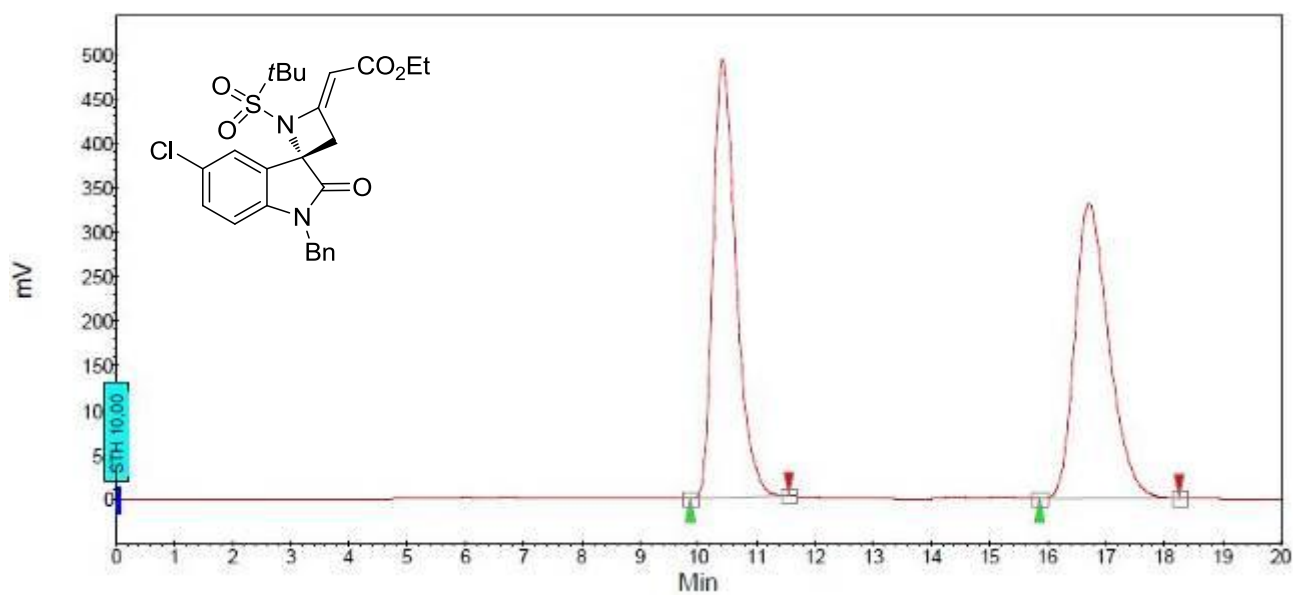
Compound **6g** (racemic mixture) obtained employing DABCO as catalyst



Compound **6g** (enantioenriched) obtained employing catalyst **5g**

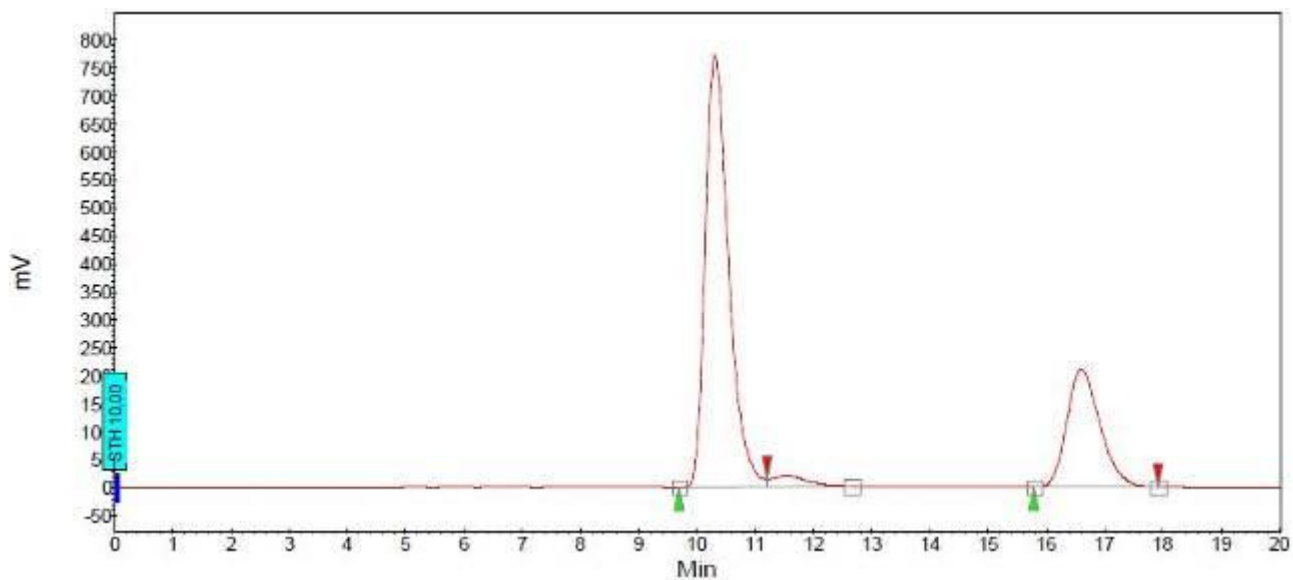


Compound **6h** (racemic mixture) obtained employing DABCO as catalyst



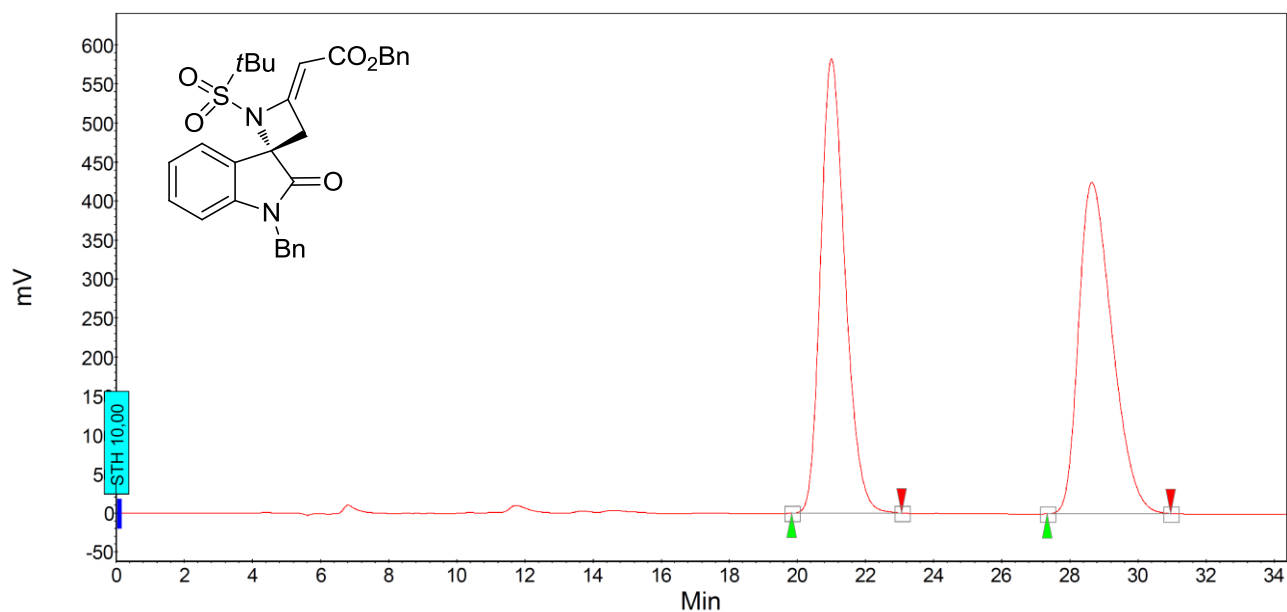
Index	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	UNKNOWN	9,867	10,417	11,550	0,000	49,97	491,5	224,3	49,965
2	UNKNOWN	15,850	16,700	18,250	0,000	50,03	331,3	224,7	50,035
Total						100,00	822,9	449,0	100,000

Compound **6h** (enantiomerized) obtained employing catalyst **5g**



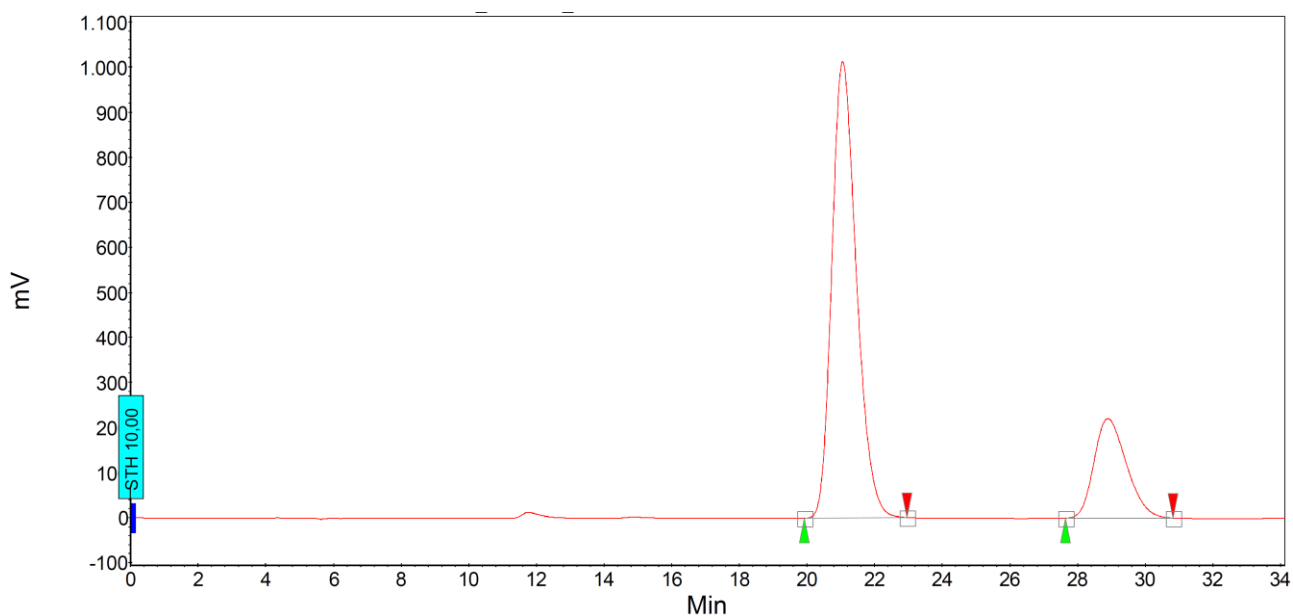
Index	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	UNKNOWN	9,700	10,308	11,208	0,000	72,19	770,5	359,5	72,193
2	UNKNOWN	15,783	16,592	17,917	0,000	27,81	209,8	138,5	27,807
Total						100,00	980,3	497,9	100,000

Compound **6k** (racemic mixture) obtained employing DABCO as catalyst



Index	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	UNKNOWN	19,833	21,008	23,067	0,000	50,06	582,5	484,7	50,063
2	UNKNOWN	27,333	28,642	30,950	0,000	49,94	424,9	483,5	49,937
Total						100,00	1007,5	968,3	100,000

Compound **6k** (enantioenriched) obtained employing catalyst **5g**



Index	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	UNKNOWN	19,933	21,058	22,950	0,000	77,68	1012,9	851,7	77,677
2	UNKNOWN	27,633	28,892	30,817	0,000	22,32	220,6	244,8	22,323
Total						100,00	1233,5	1096,5	100,000