Nazarov cyclization of dienylaziridines: synthesis of cyclopentadienyl/ hydrinedienyl/ indenyl glycines

Gangarajula Sudhakar,* Karla Janardhan Reddy and Jagadeesh Babu Nanubolu

Email: gsudhakar@iict.res.in

Supporting Information

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1. General Procedure

Anhydrous solvents were dried and distilled by standard methods prior to use. Commercially available reagents were used without further purification unless otherwise specified. All the reactions were performed under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring. Column chromatography was carried out using silica gel (60-120 or 100-200 or 230-400 mesh), the column was eluted with ethyl acetate-petroleum ether. Visualization of the spots on TLC plates was achieved either by UV light or by staining the plates in methanolic anisaldehyde-sulphuric acid-acetic acid or in methanol-phosphomolybdic acid-sulphuric acid solution and charring on hot plate. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ solvent on 500 MHz, 400 MHz, 300 MHz and 75 MHz, 125 MHz spectrometer, respectively at ambient temperature. Chemical shifts are reported as δ values relative to internal $CHCl_3$ δ 7.26 or TMS δ 0.0 for ^{1}H NMR and $CHCl_3$ δ 77.0 for ^{13}C NMR. ^{1}H NMR data is recorded as follows: chemical shift [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublet; m = multiplet; br s = broad singlet, br d = broad doublet. FTIR spectra were recorded as KBr thin films or neat. Mass spectra were recorded for ESI and are given in mass units (m/z). High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer. Melting points were measured on melting point apparatus and are uncorrected. Optical rotation values were measured on high sensitive polarimeter using a 2 mL cell with a 10 mm path length.

3. X-ray crystallography information

Crystallographic data for **6j**

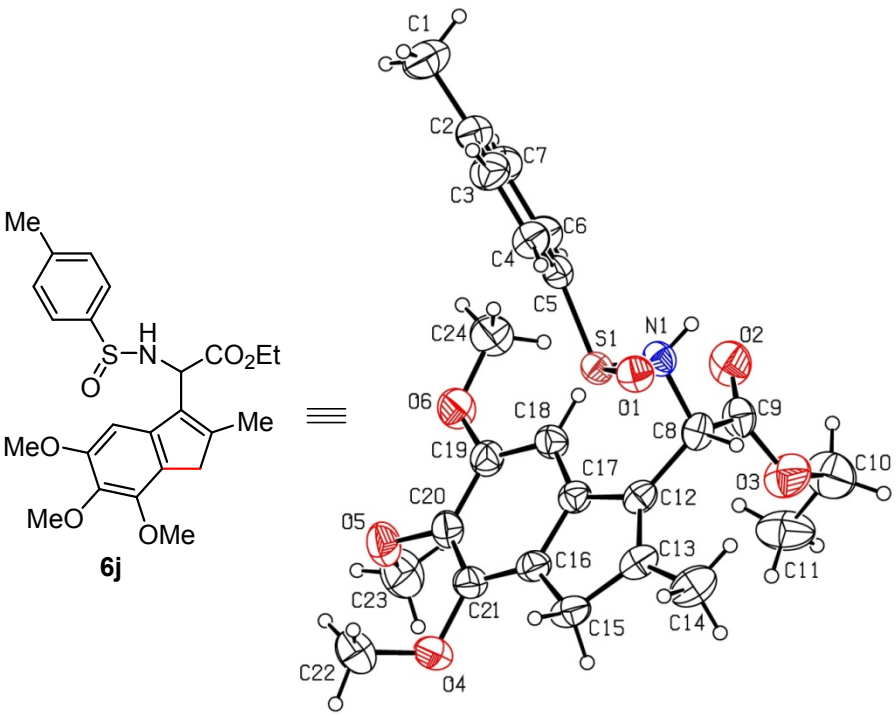

Figure caption: The molecular structure of **6j** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Only major component of the disordered C11 atom of the ester is shown for clarity.

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Crystal data for **6j**: $C_{24}H_{29}NO_6S$, M = 459.54, colourless needle, 0.43 x 0.22 x 0.19 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 10.3258(9), b = 17.5826(15), c = 13.7351(12) Å, β = 101.7890(10)°, V = 2441.1(4) Å^3, Z = 4, D_c = 1.250 g/cm^3, F_{000} = 976, CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0º, 23170 reflections collected, 4305 unique (R_{int} = 0.0208), Final *GooF* = 1.043, *R1* = 0.0481, *wR2* = 0.1402, *R* indices based on 3766 reflections with I >2σ(I) (refinement on F^2), 309 parameters, 8 restraints, μ = 0.171 mm^{-1}. CCDC 1054756 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

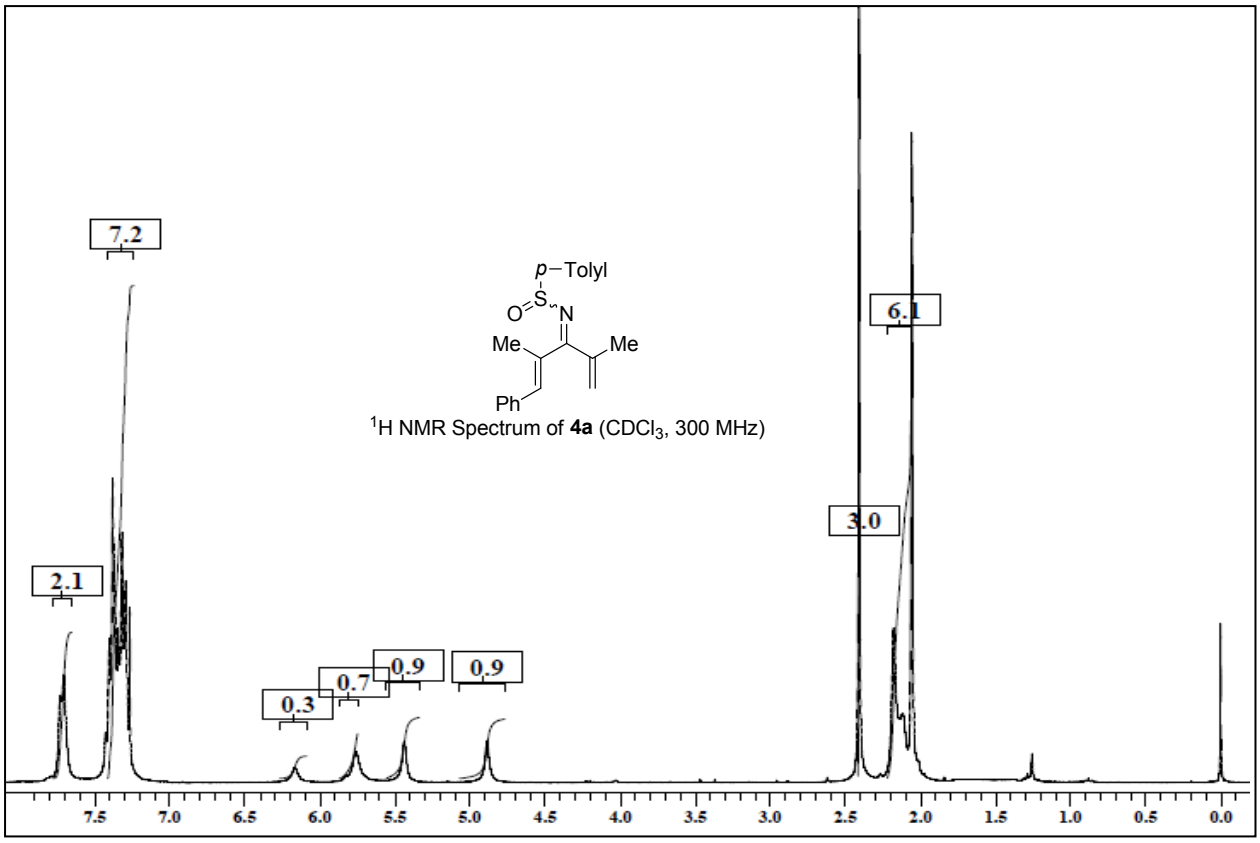
Crystal structure determination: X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 6424 reflections for AU83 data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[6] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (C) or $1.5U_{eq}$ for methyl atoms. C11 atom of ester group was disordered over two sites with site occupancy factor of 0.58 for C11 (major component) and 0.42 for C11D (minor component). The anisotropic displacement parameters of the disordered atoms were restrained to be similar (SIMU instruction) and the direction of motion along the axis between these atoms was also restrained (DELU instruction).[3] The C10-C11 and C10-C11D bond distances of ester and nitro groups were restrained to a target value of 1.53 Å.

[1] SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.

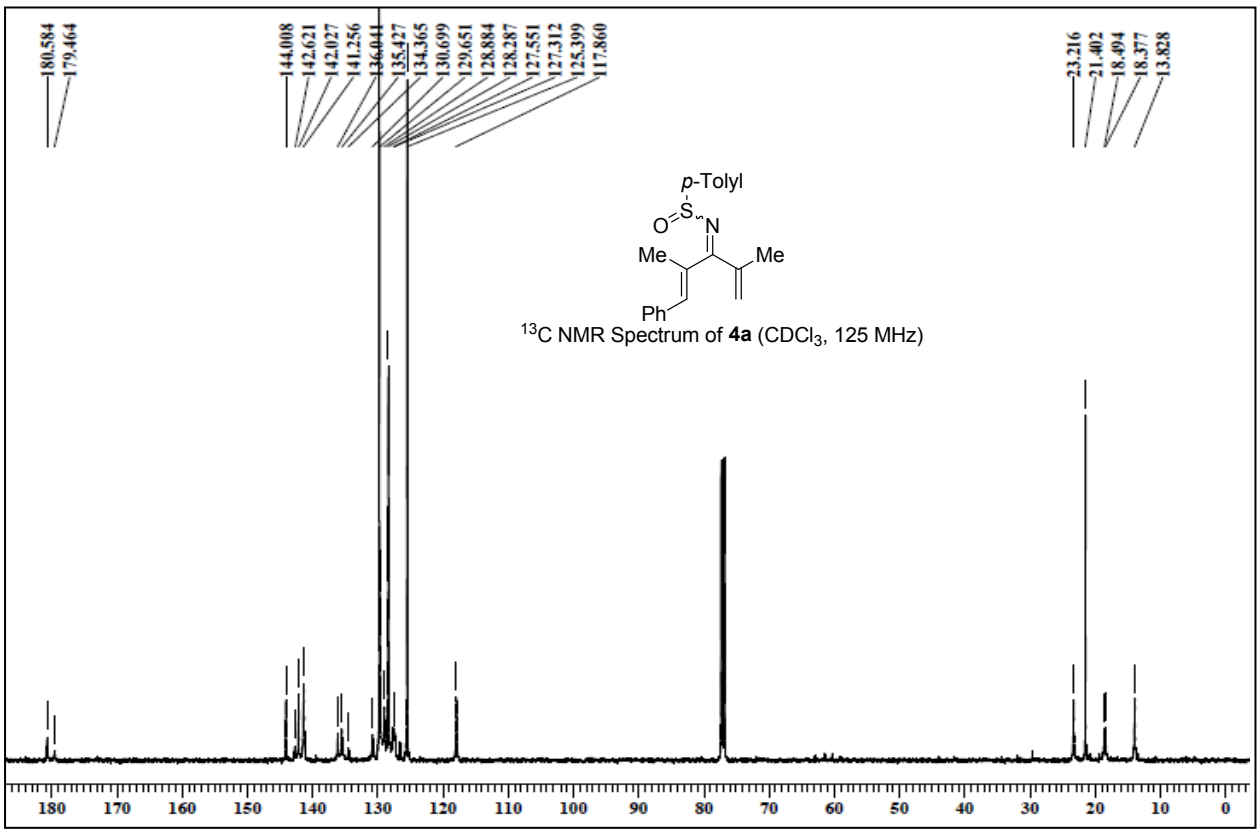
[2] Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

[3] P. Muller, R. Herbst-Imer, A. L. Spek, T. R. Schneider, M. R. Sawaya, Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

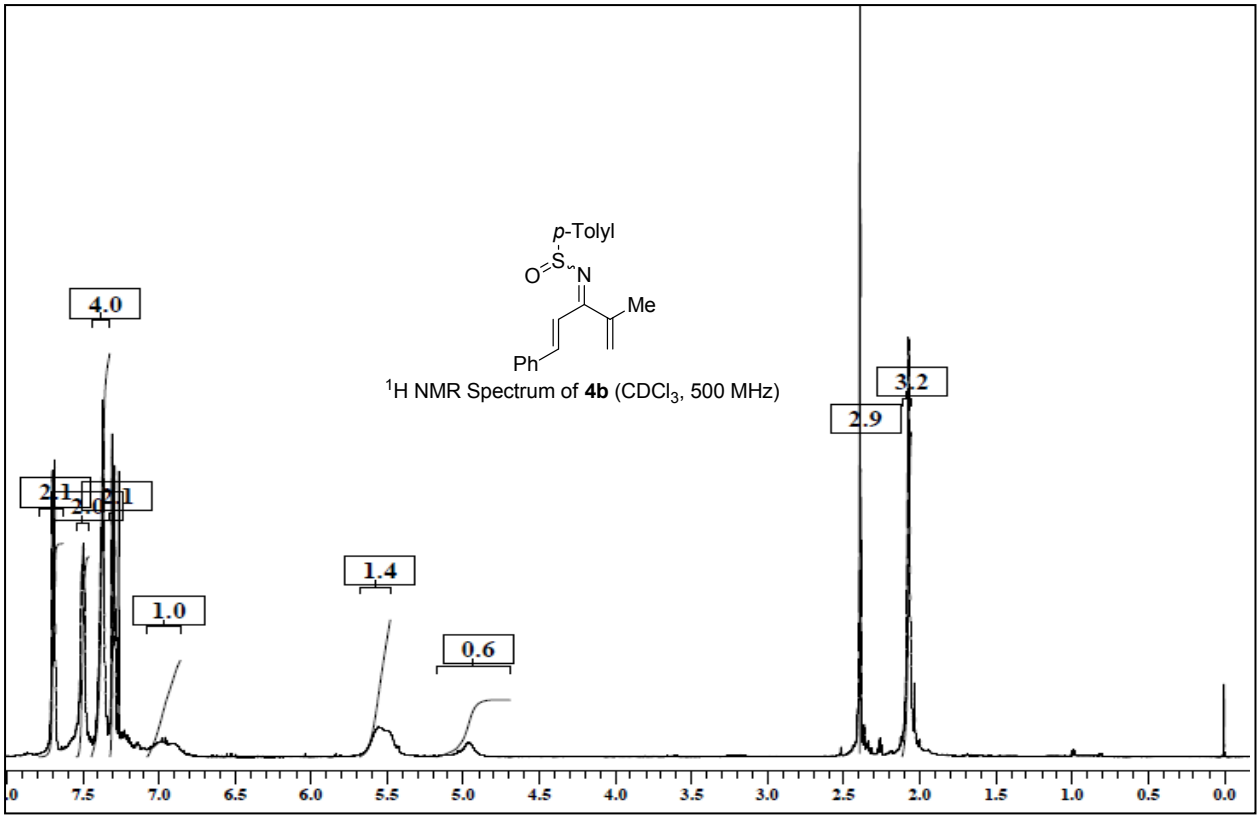
4. ^{1}H and ^{13}C NMR Spectra



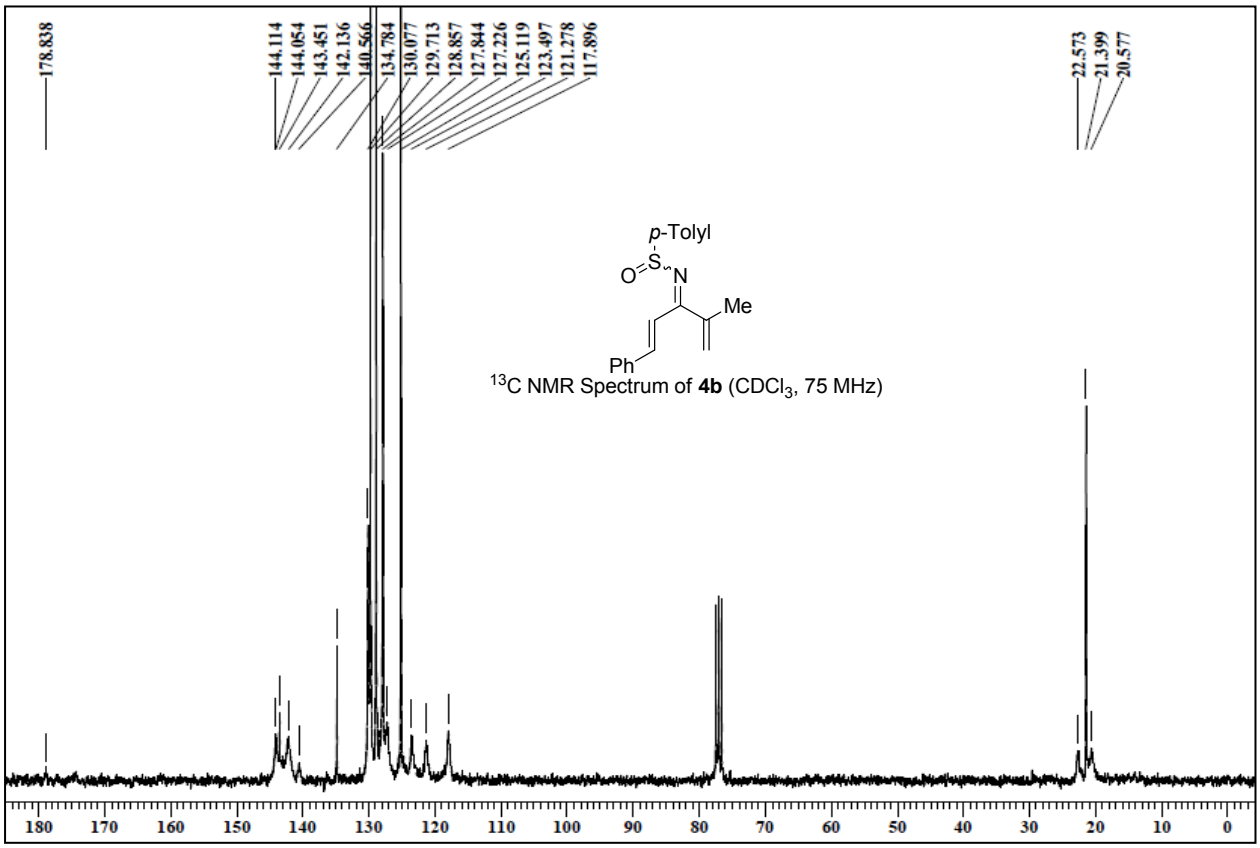
^{1}H NMR Spectrum of **4a** ($CDCl_3$, 300 MHz)



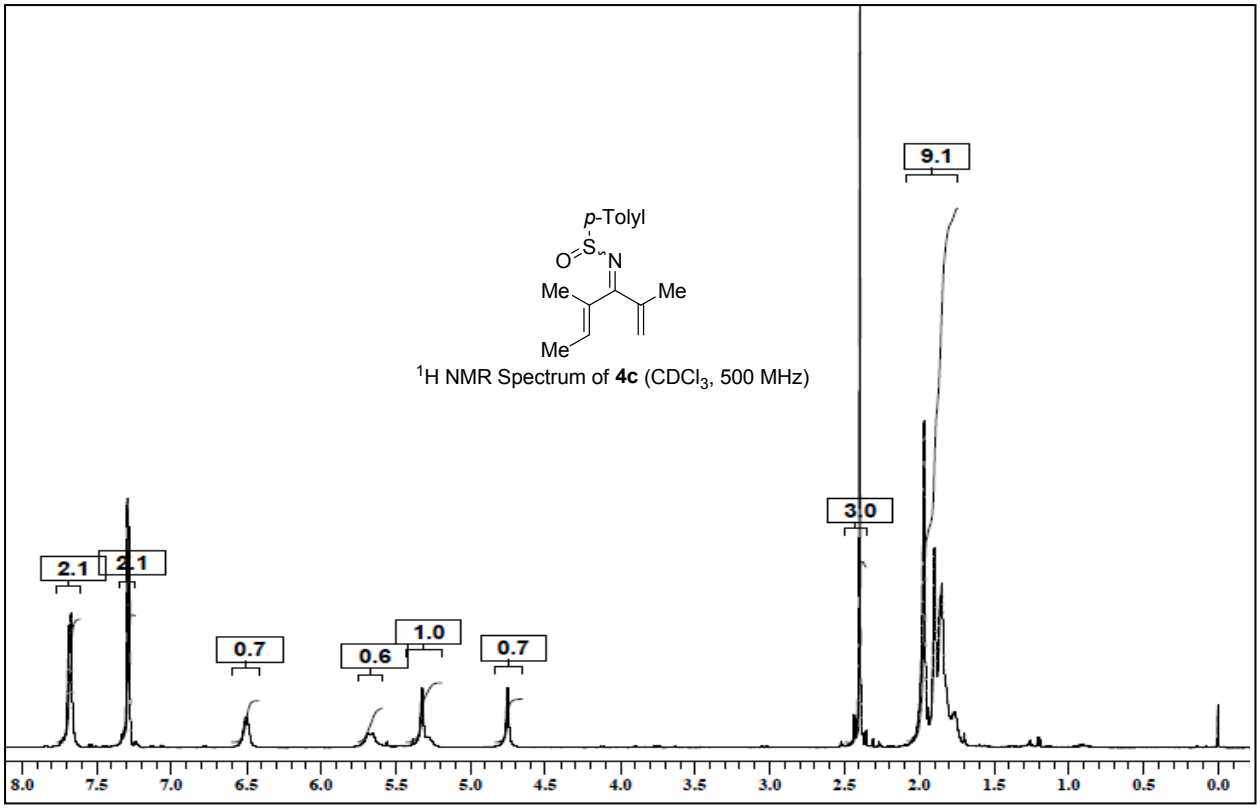
^{13}C NMR Spectrum of **4a** ($CDCl_3$, 125 MHz)



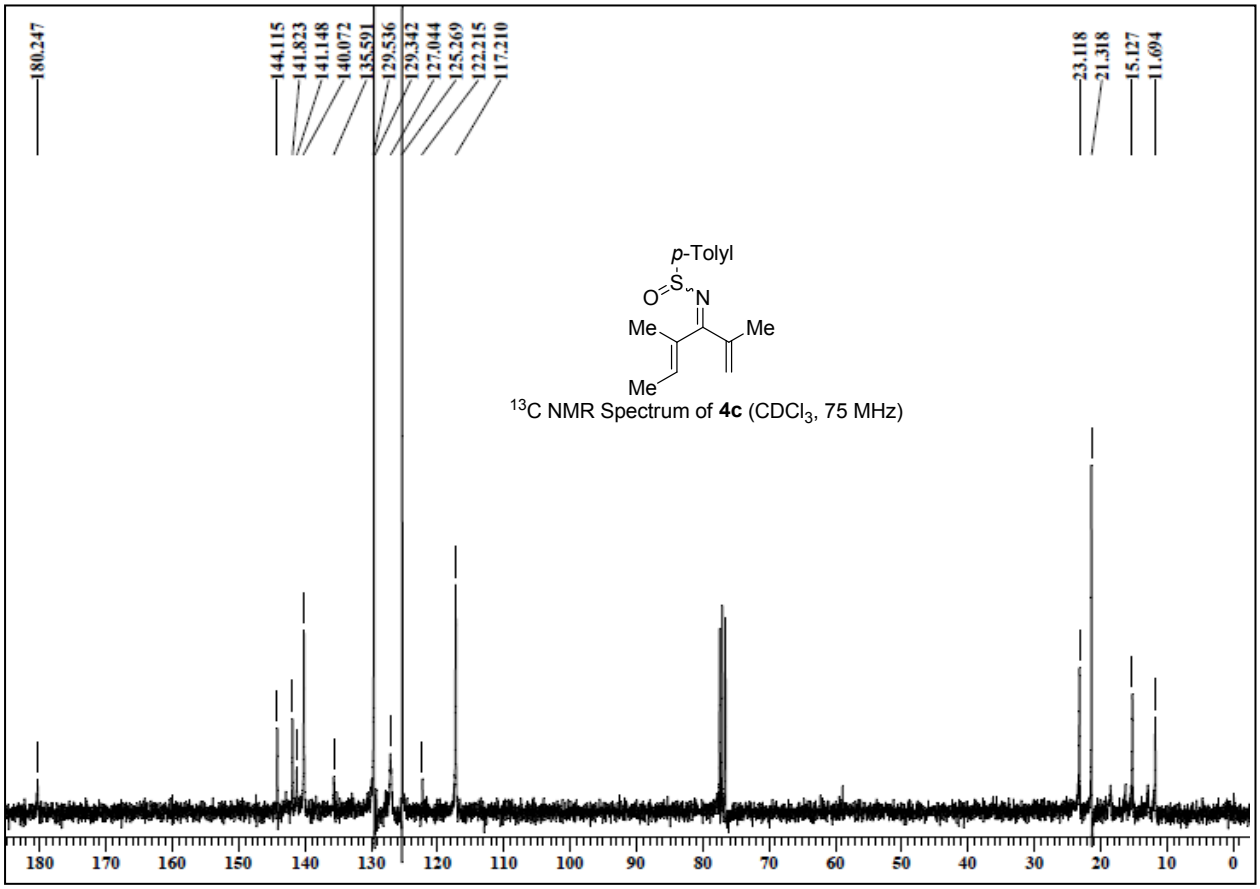
^{1}H NMR Spectrum of **4b** ($CDCl_3$, 500 MHz)



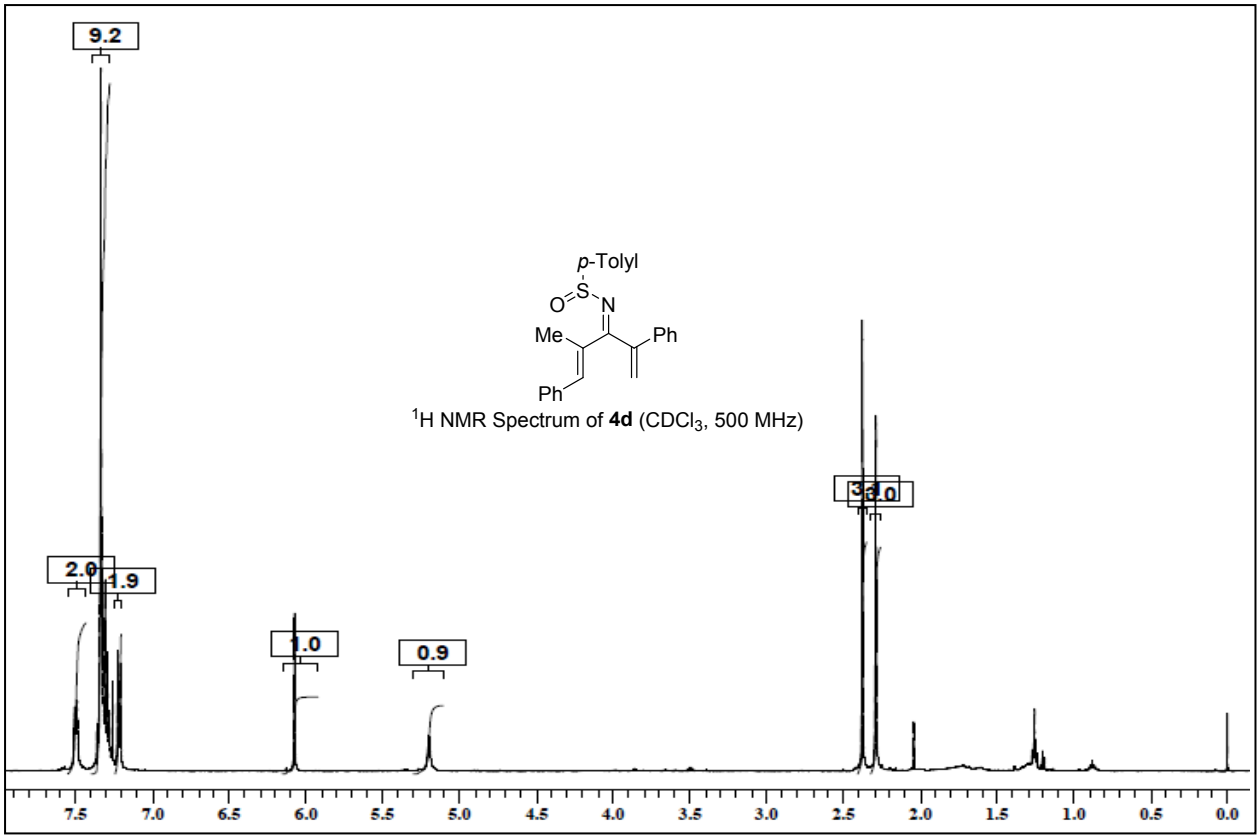
^{13}C NMR Spectrum of **4b** ($CDCl_3$, 75 MHz)



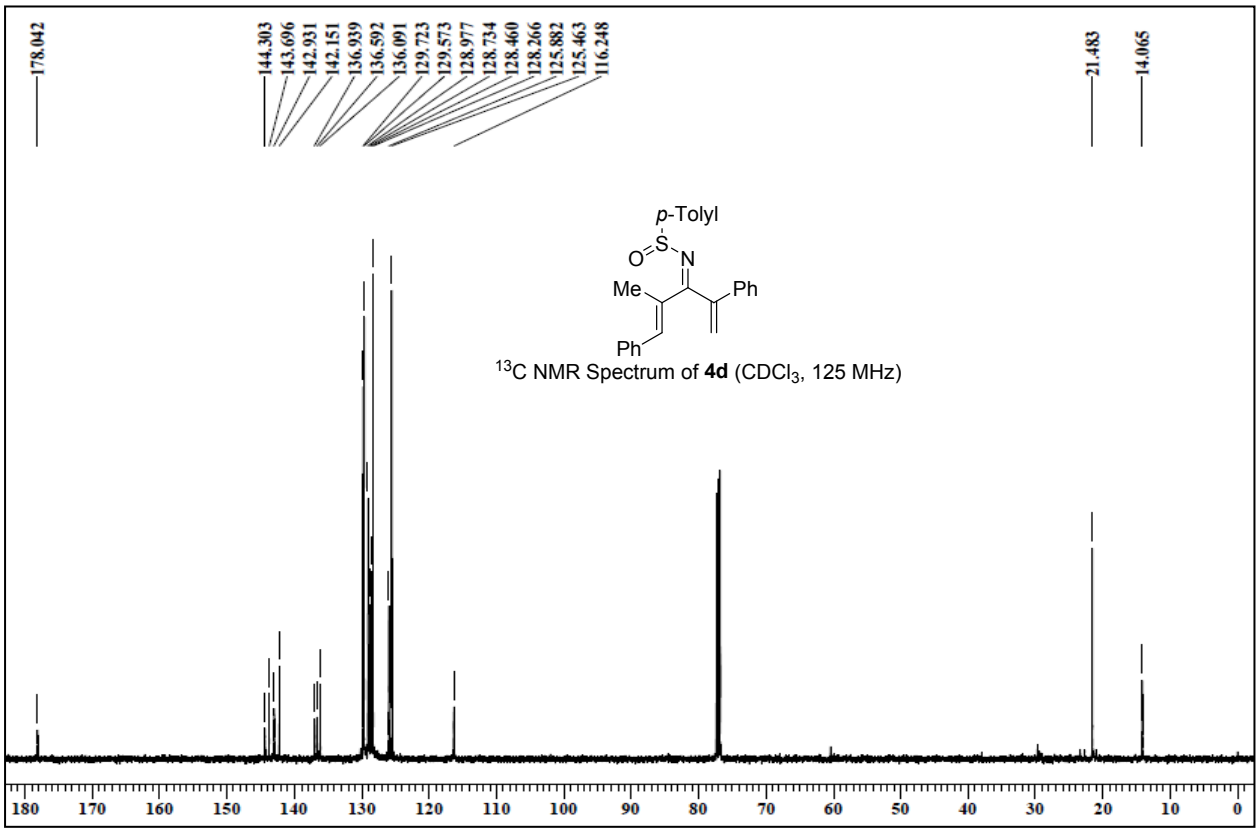
^{1}H NMR Spectrum of **4c** ($CDCl_3$, 500 MHz)



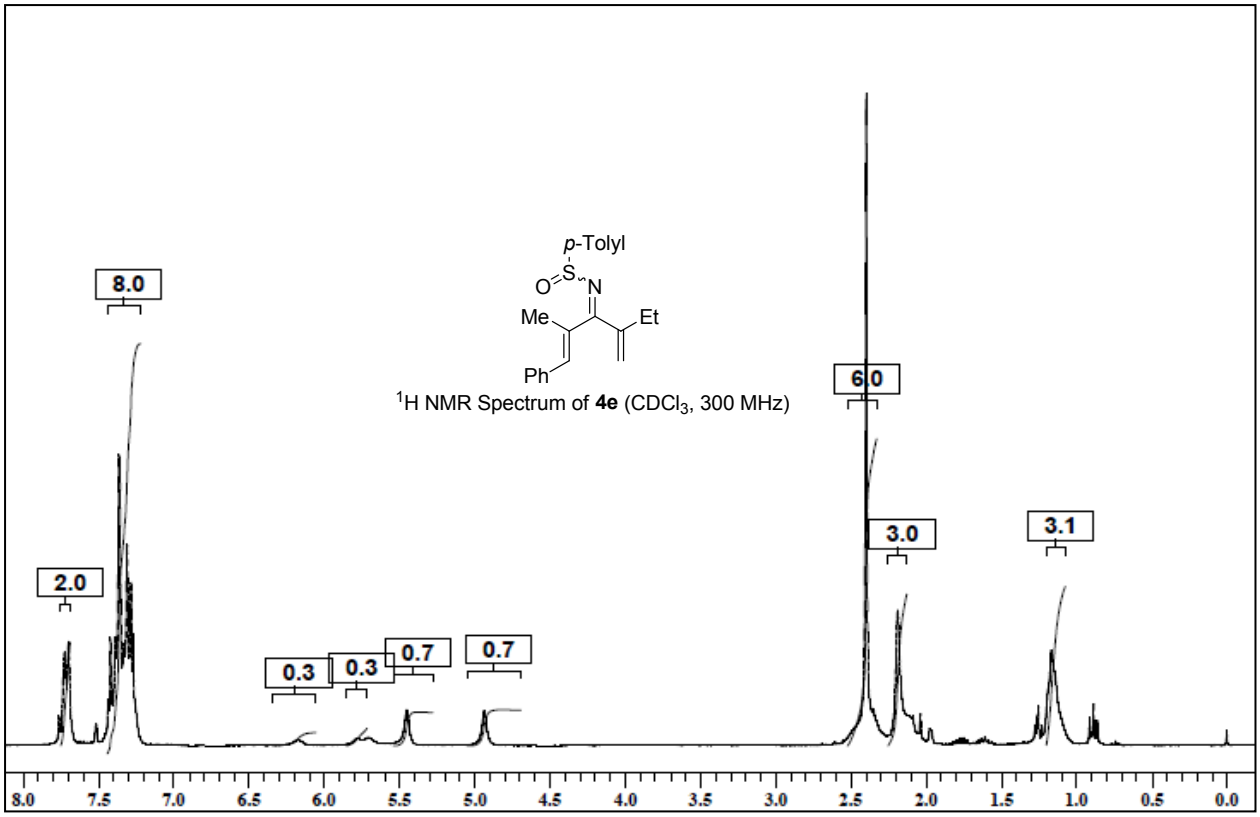
^{13}C NMR Spectrum of **4c** ($CDCl_3$, 75 MHz)



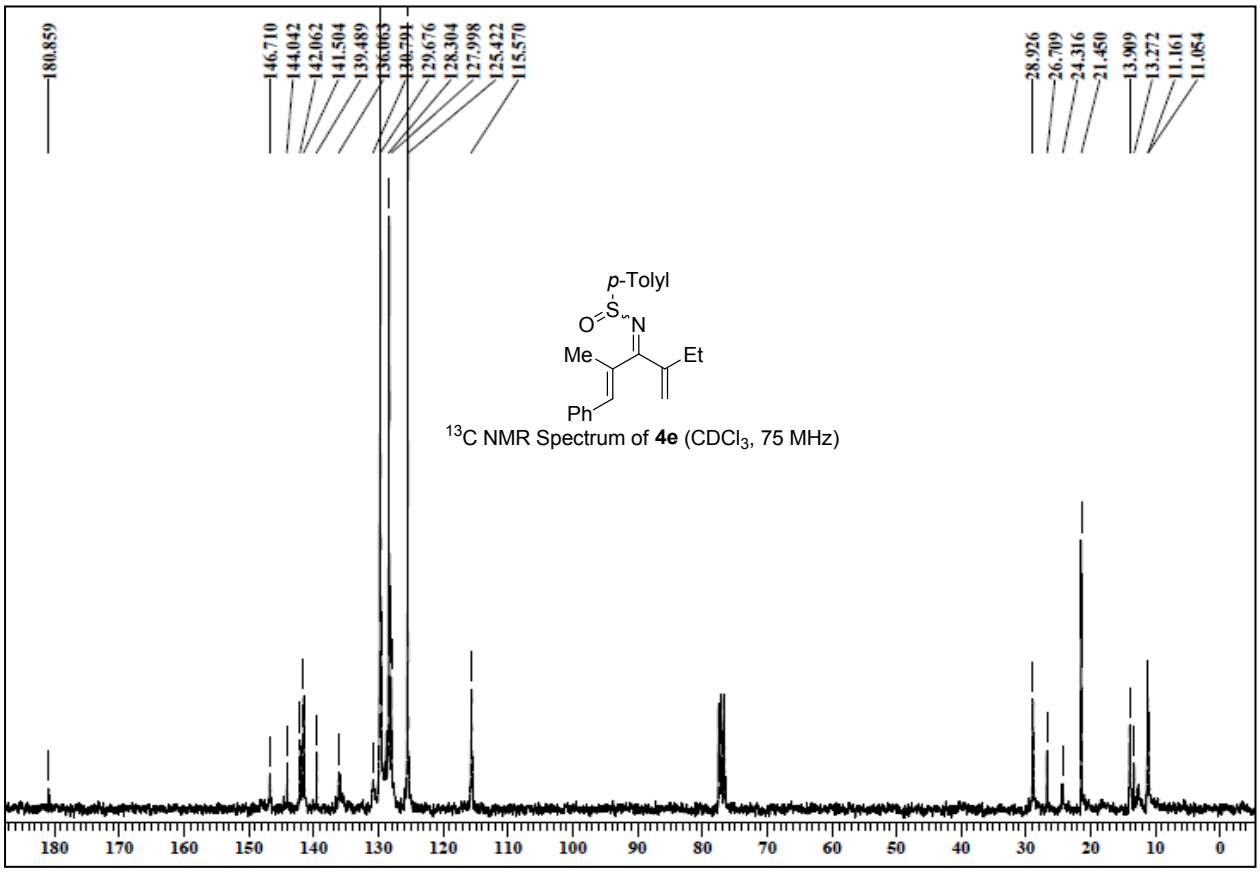
^{1}H NMR Spectrum of **4d** ($CDCl_3$, 500 MHz)



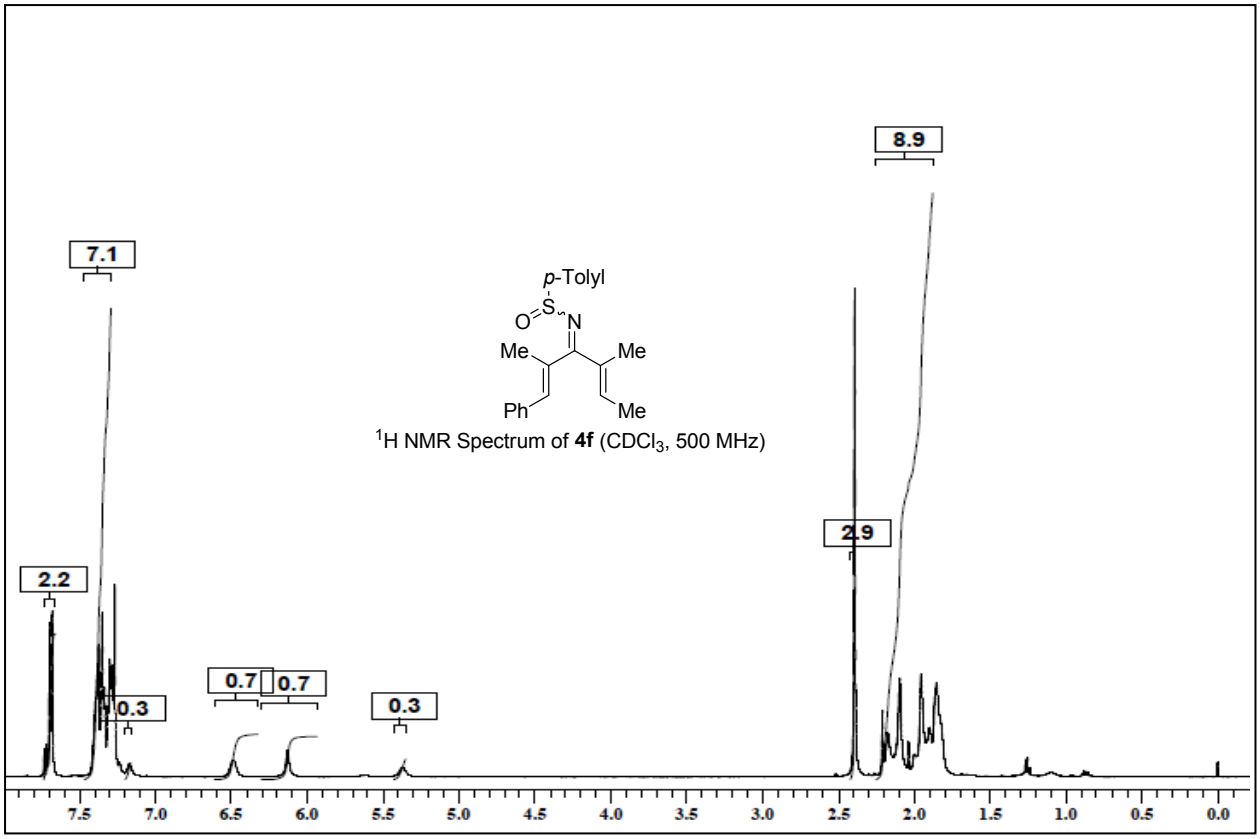
^{13}C NMR Spectrum of **4d** ($CDCl_3$, 125 MHz)



^{1}H NMR Spectrum of **4e** ($CDCl_3$, 300 MHz)

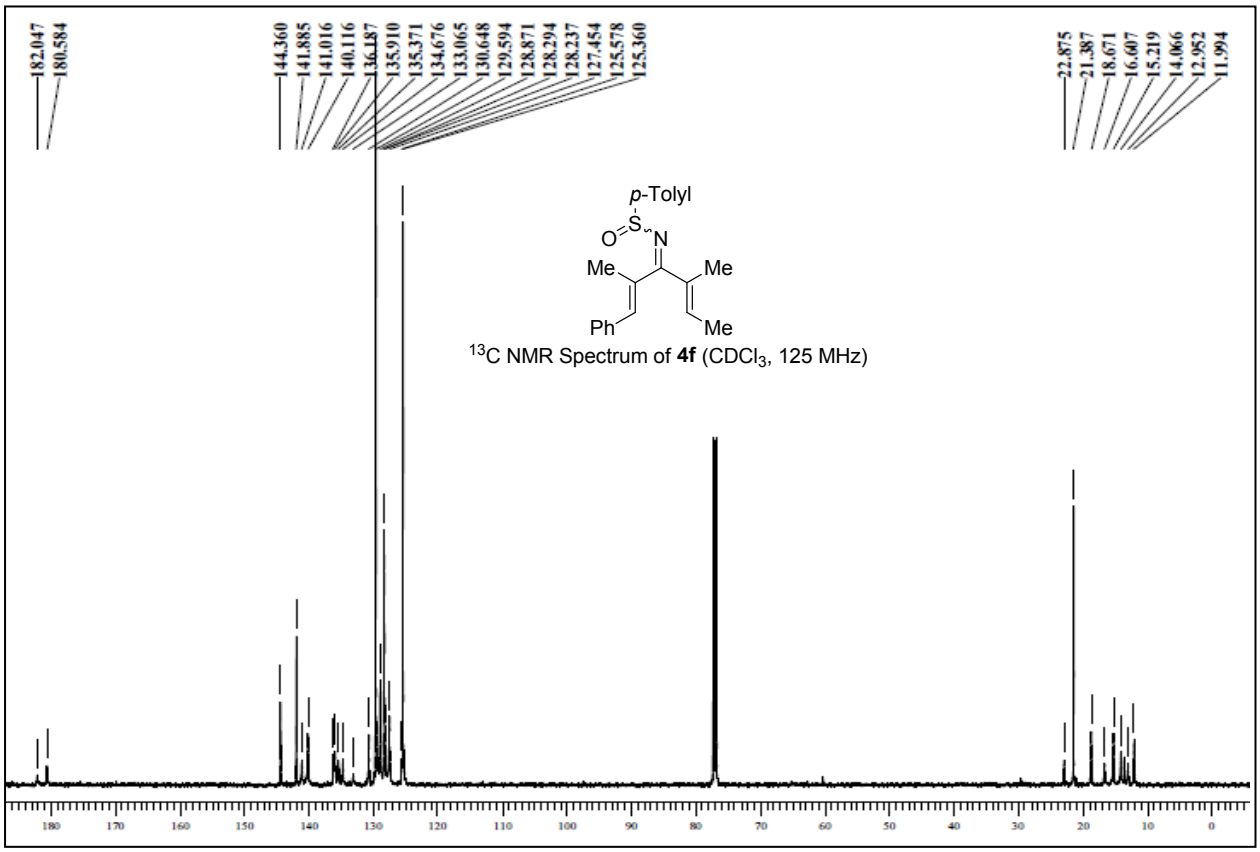


^{13}C NMR Spectrum of **4e** ($CDCl_3$, 75 MHz)



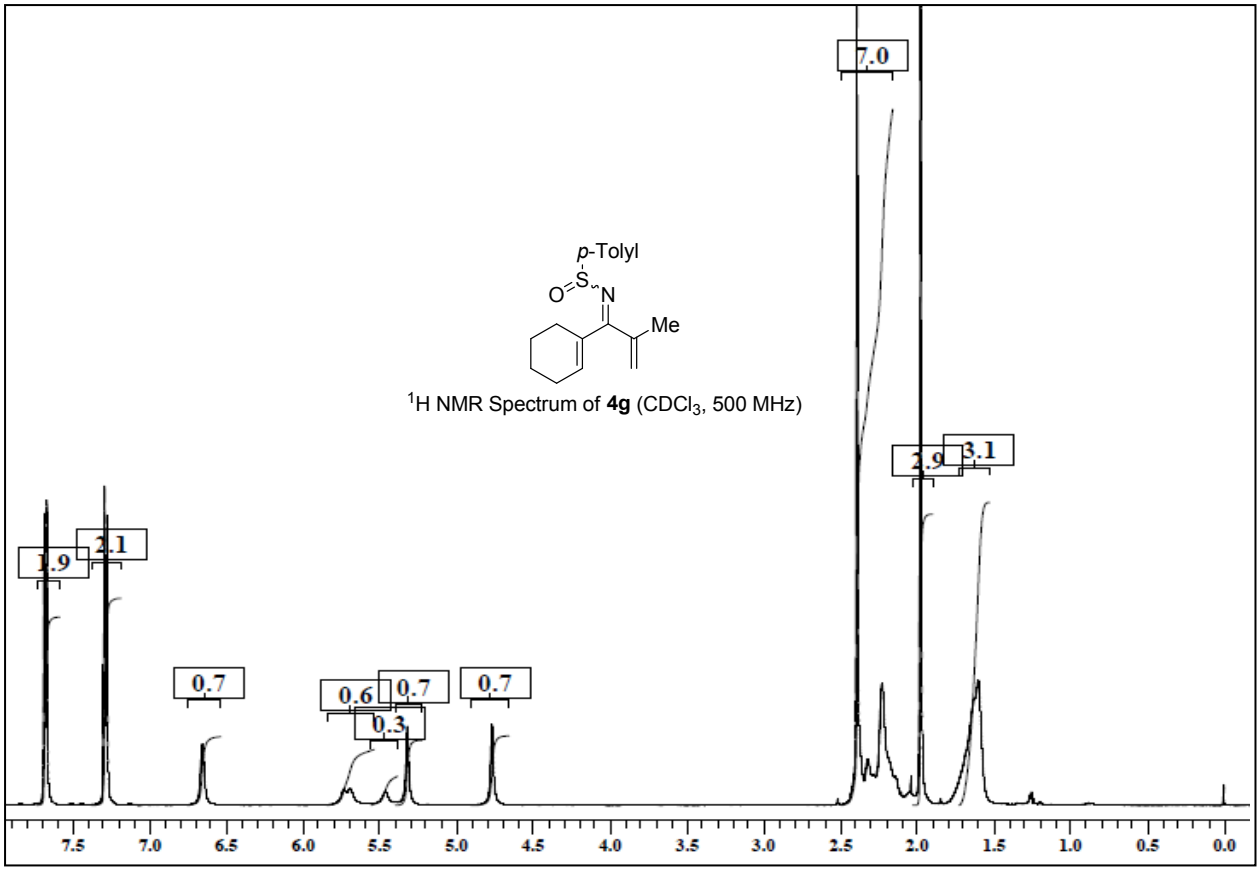
p-Tolyl

^{1}H NMR Spectrum of **4f** ($CDCl_3$, 500 MHz)



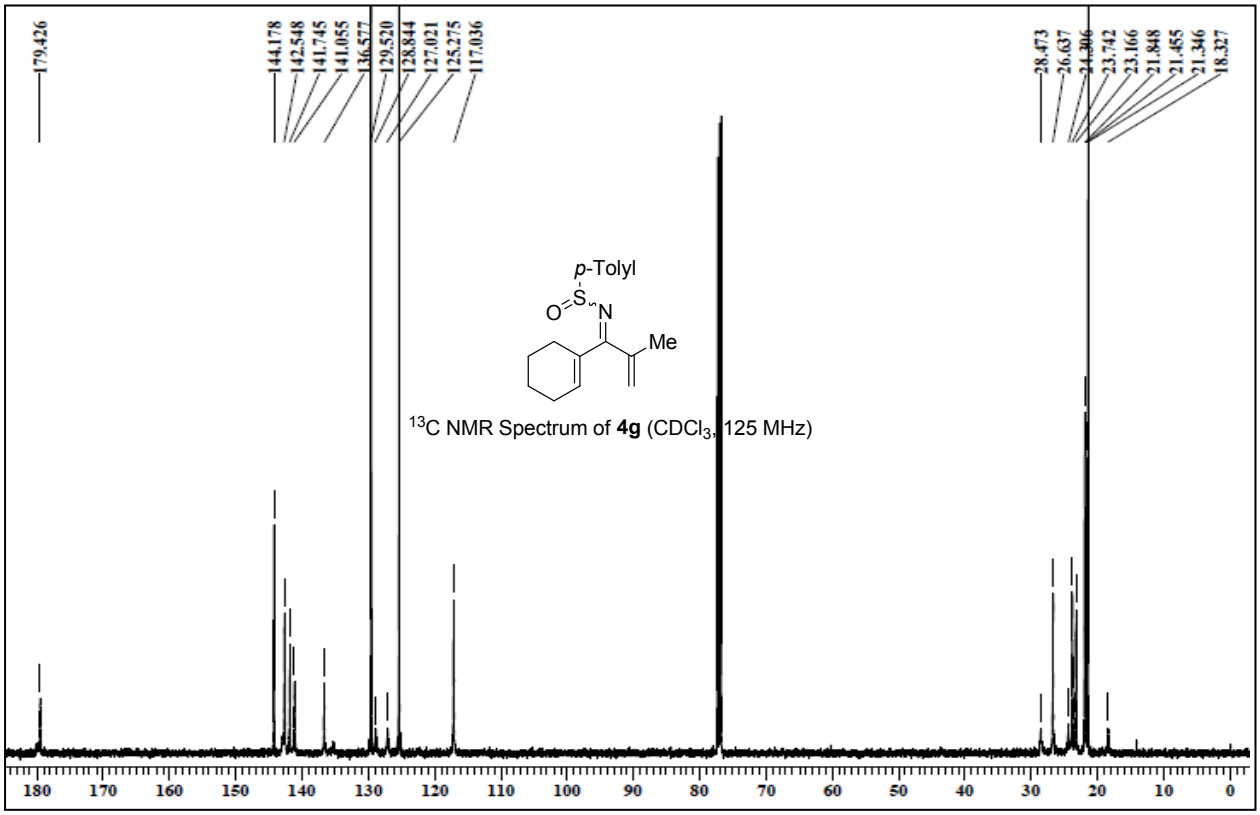
p-Tolyl

^{13}C NMR Spectrum of **4f** ($CDCl_3$, 125 MHz)



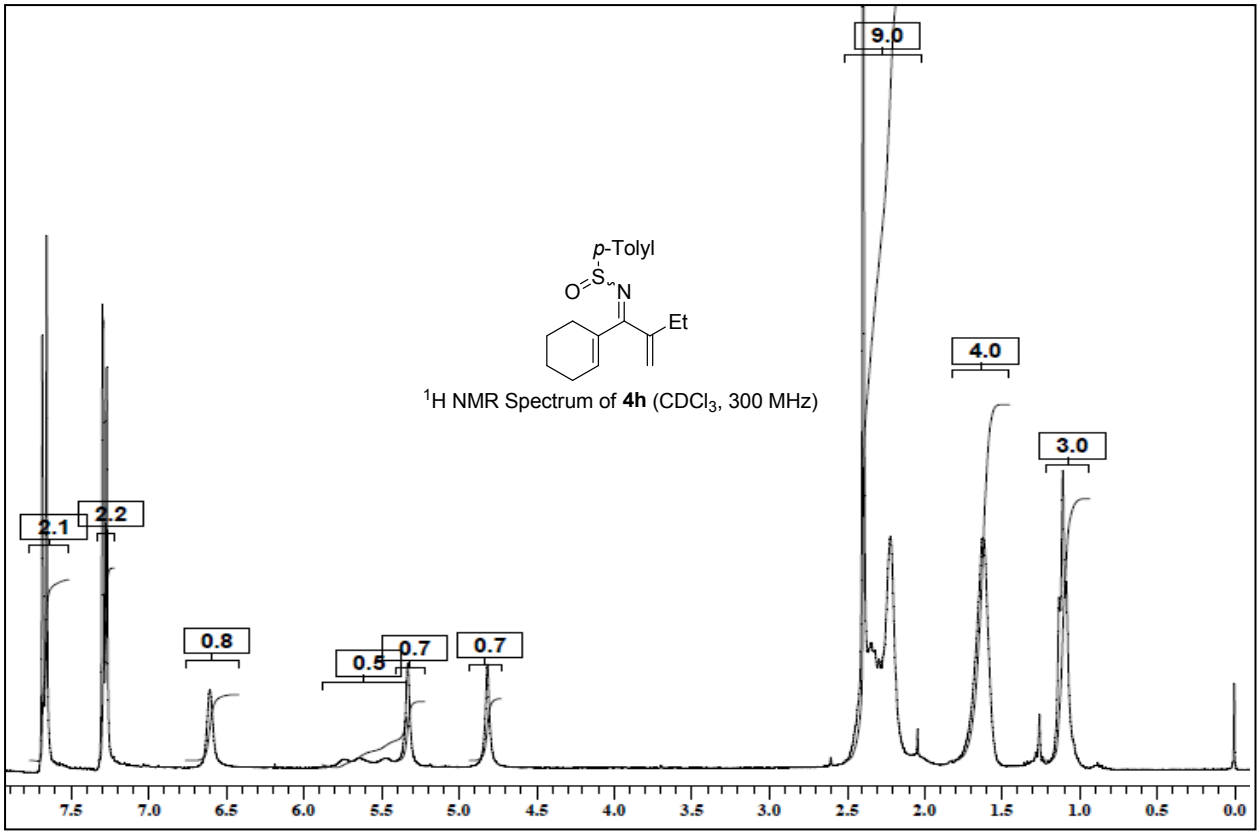
p-Tolyl

^{1}H NMR Spectrum of **4g** ($CDCl_3$, 500 MHz)

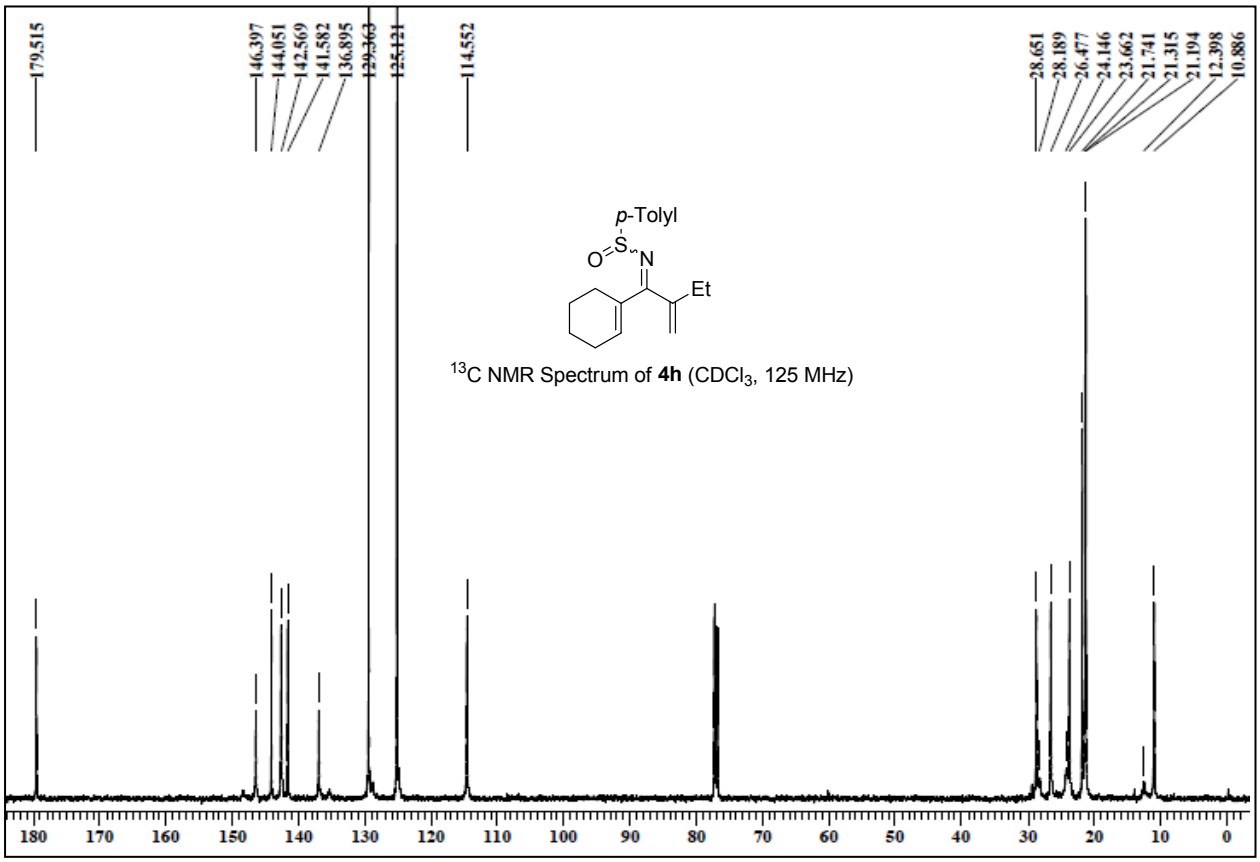


p-Tolyl

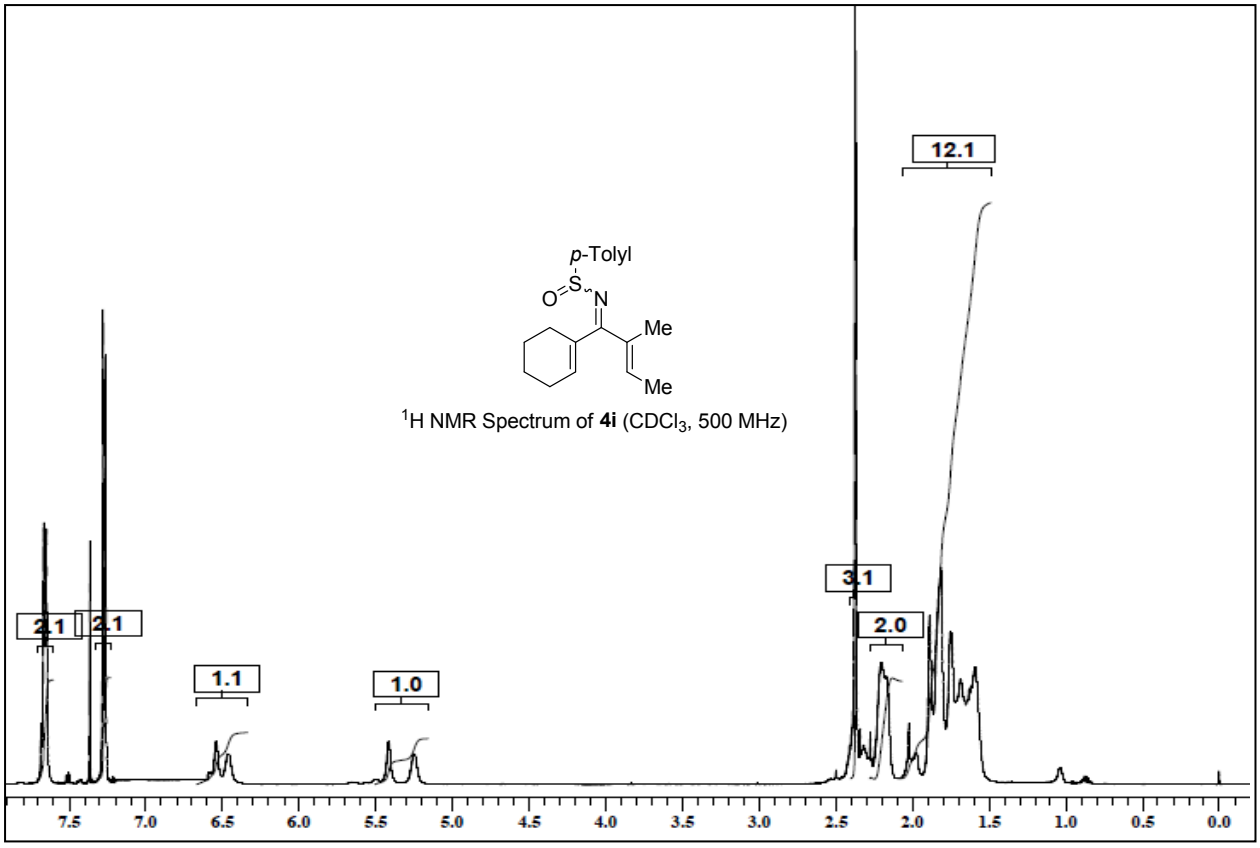
^{13}C NMR Spectrum of **4g** ($CDCl_3$, 125 MHz)



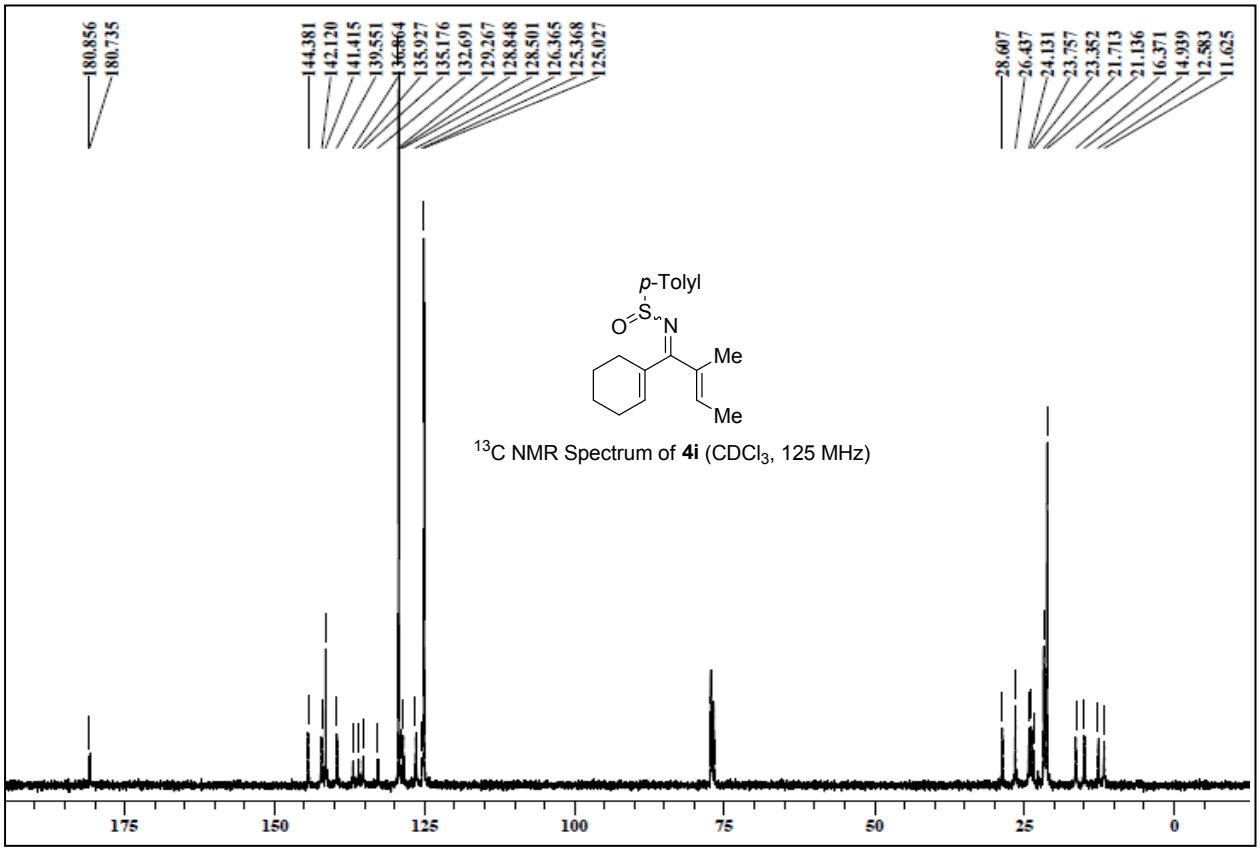
^{1}H NMR Spectrum of **4h** ($CDCl_3$, 300 MHz)



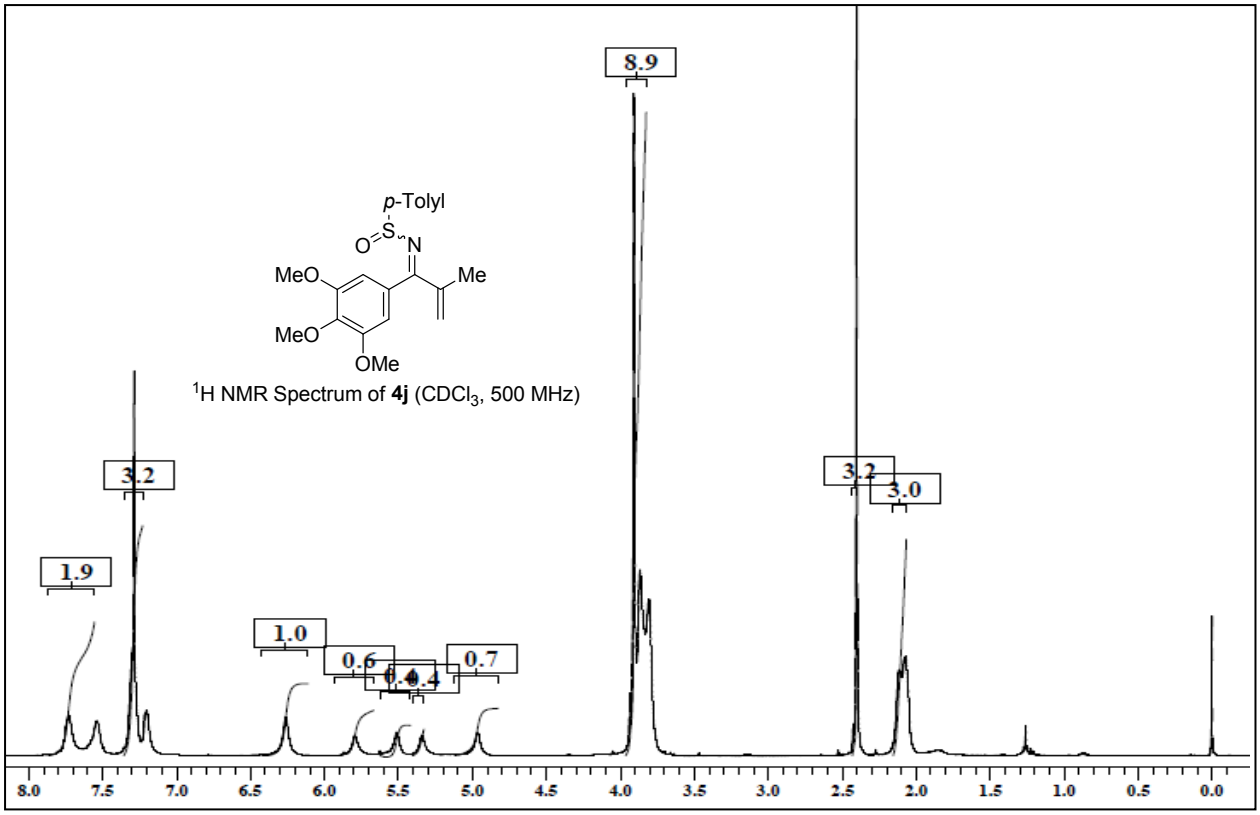
^{13}C NMR Spectrum of **4h** ($CDCl_3$, 125 MHz)



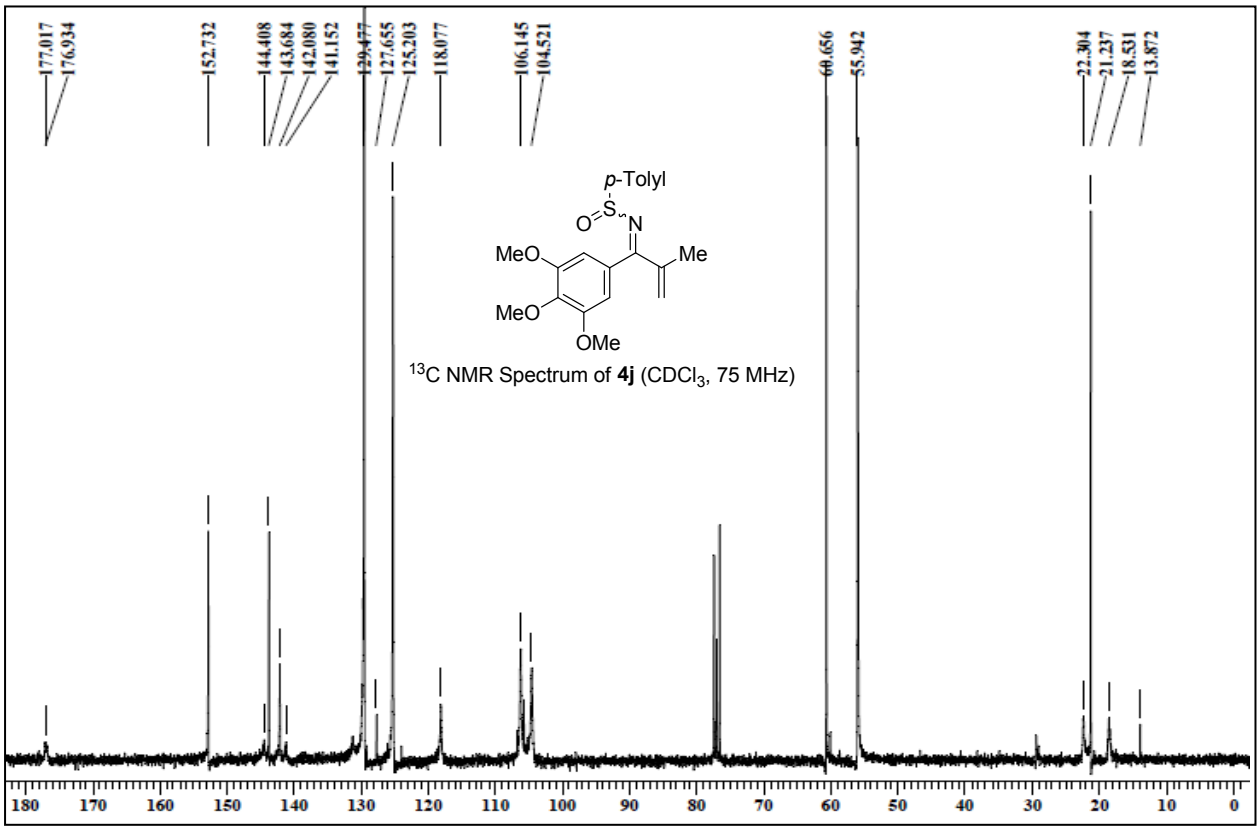
^{1}H NMR Spectrum of **4i** ($CDCl_3$, 500 MHz)



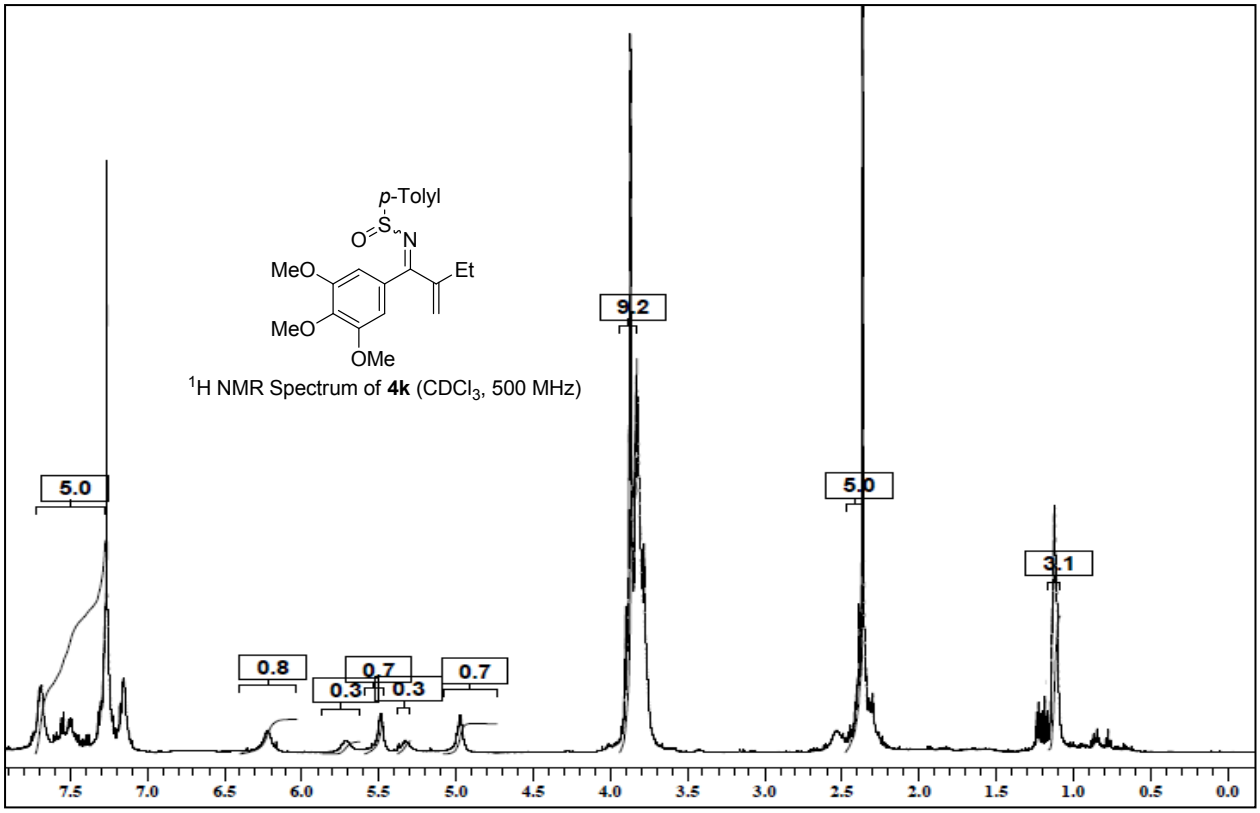
^{13}C NMR Spectrum of **4i** ($CDCl_3$, 125 MHz)



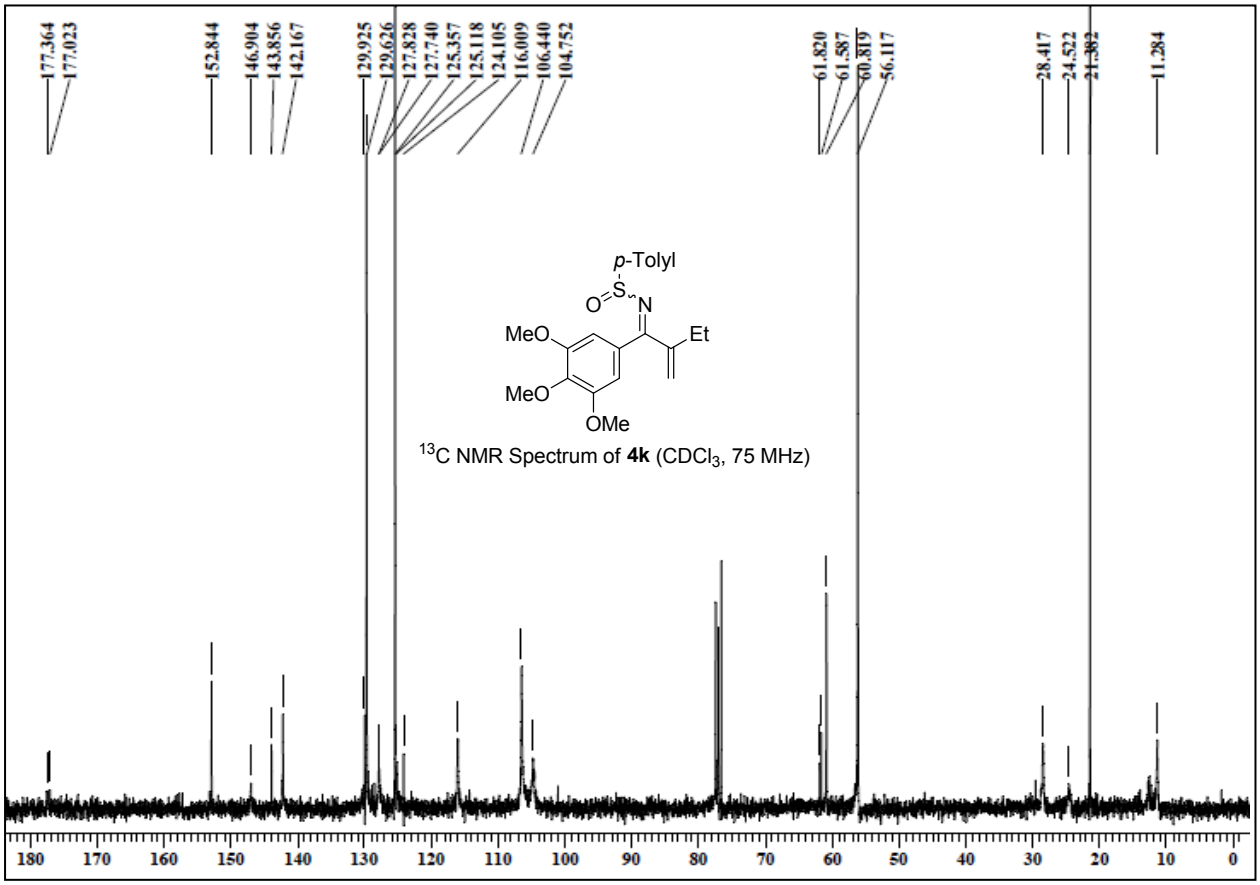
^{1}H NMR Spectrum of **4j** ($CDCl_3$, 500 MHz)



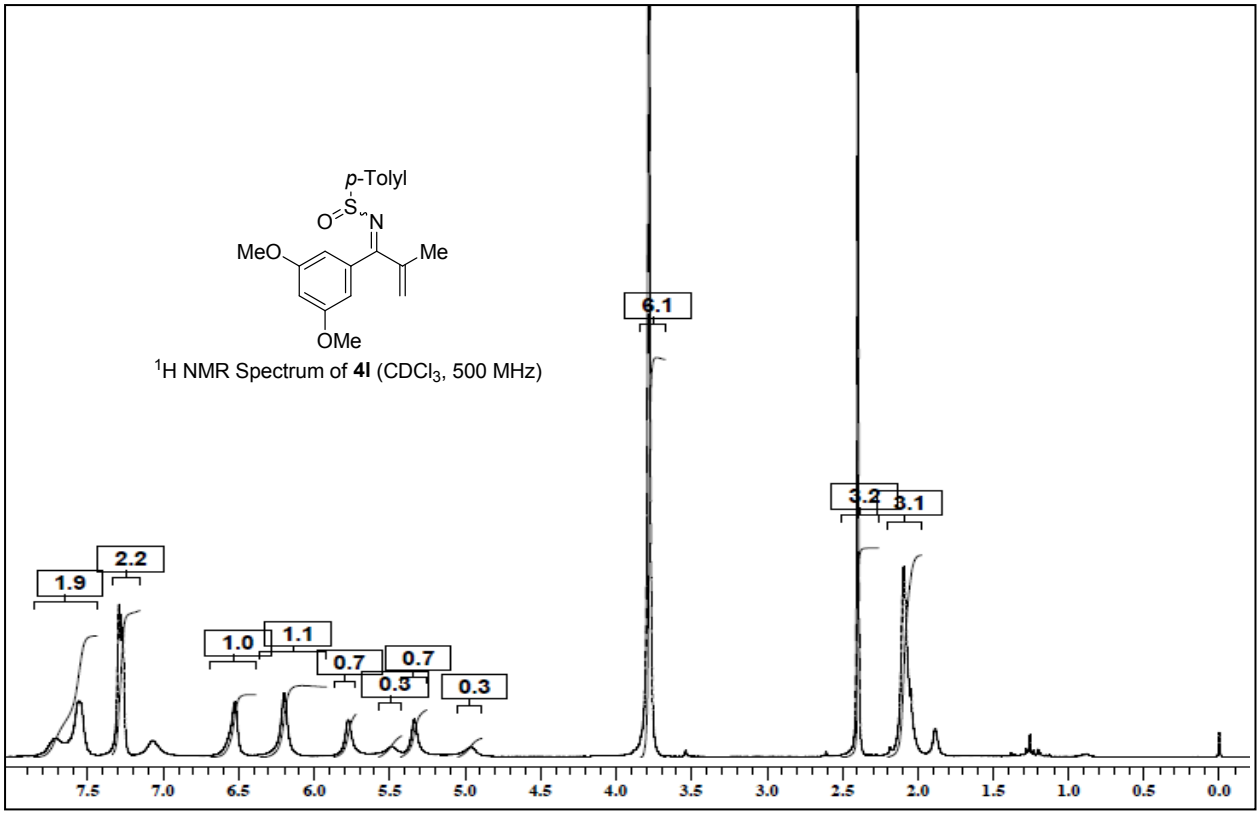
^{13}C NMR Spectrum of **4j** ($CDCl_3$, 75 MHz)



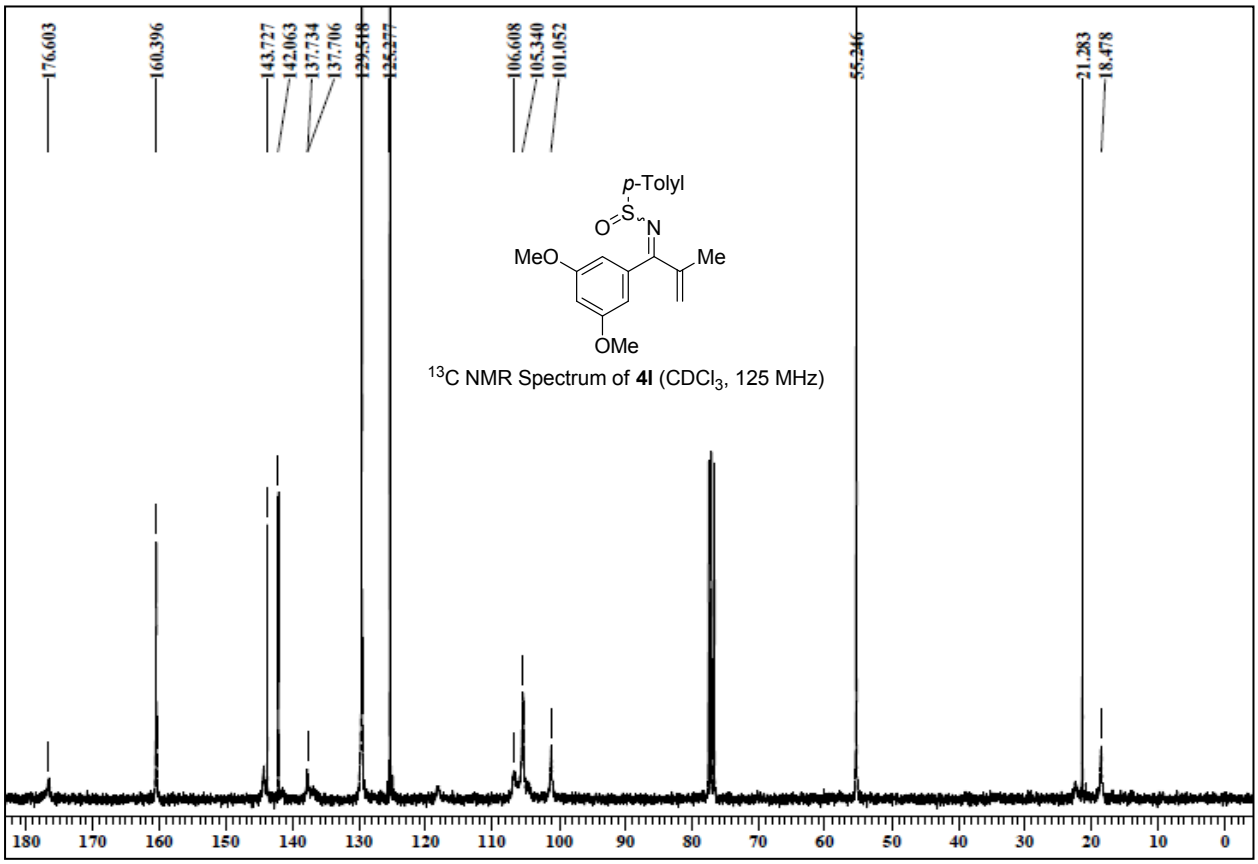
^{1}H NMR Spectrum of **4k** ($CDCl_3$, 500 MHz)



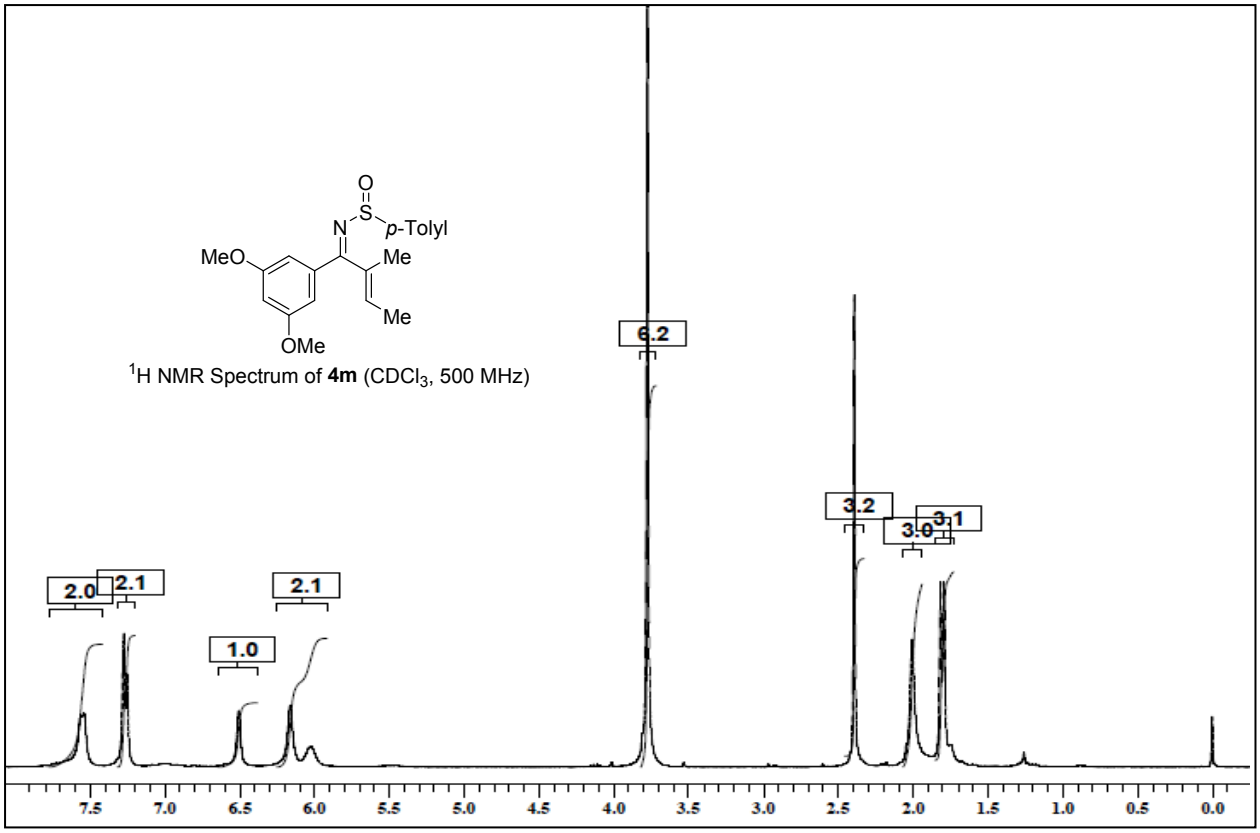
^{13}C NMR Spectrum of **4k** ($CDCl_3$, 75 MHz)



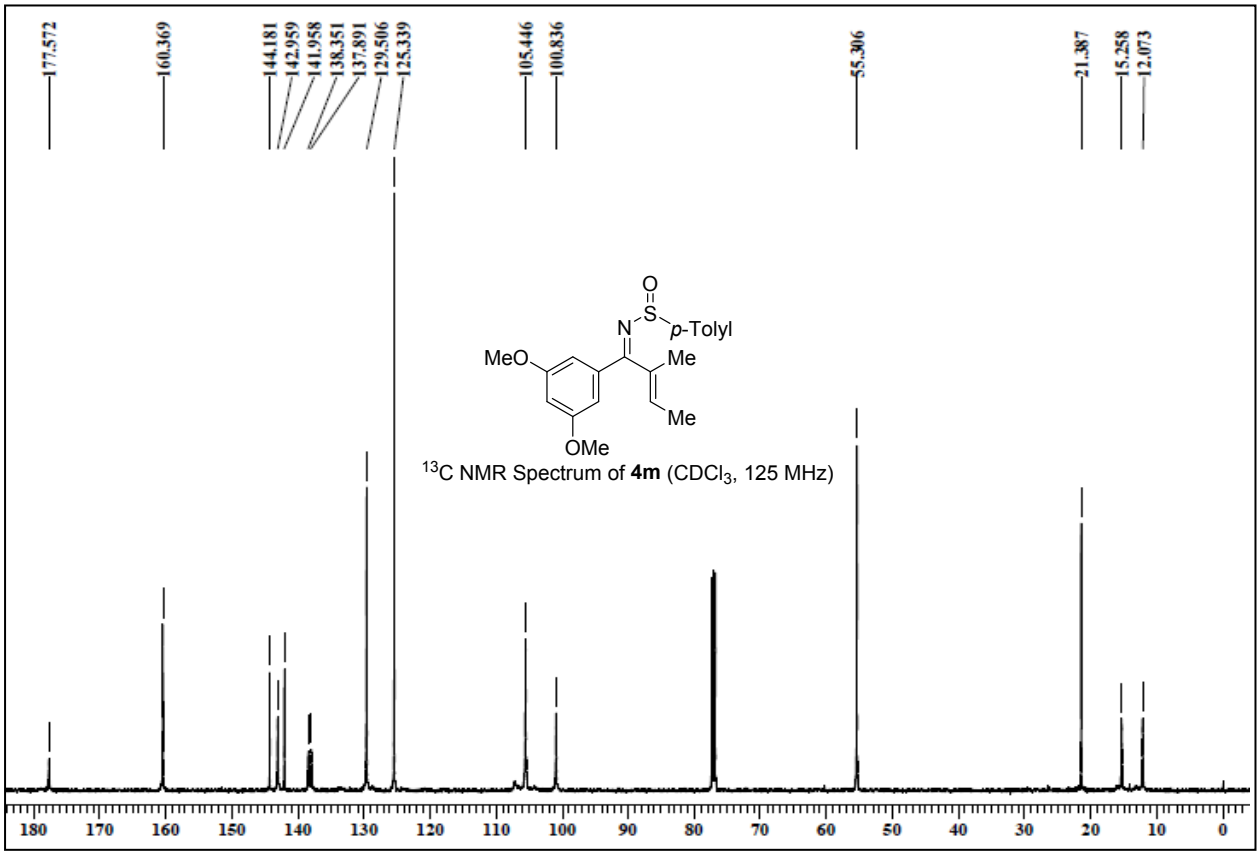
^{1}H NMR Spectrum of **4l** ($CDCl_3$, 500 MHz)



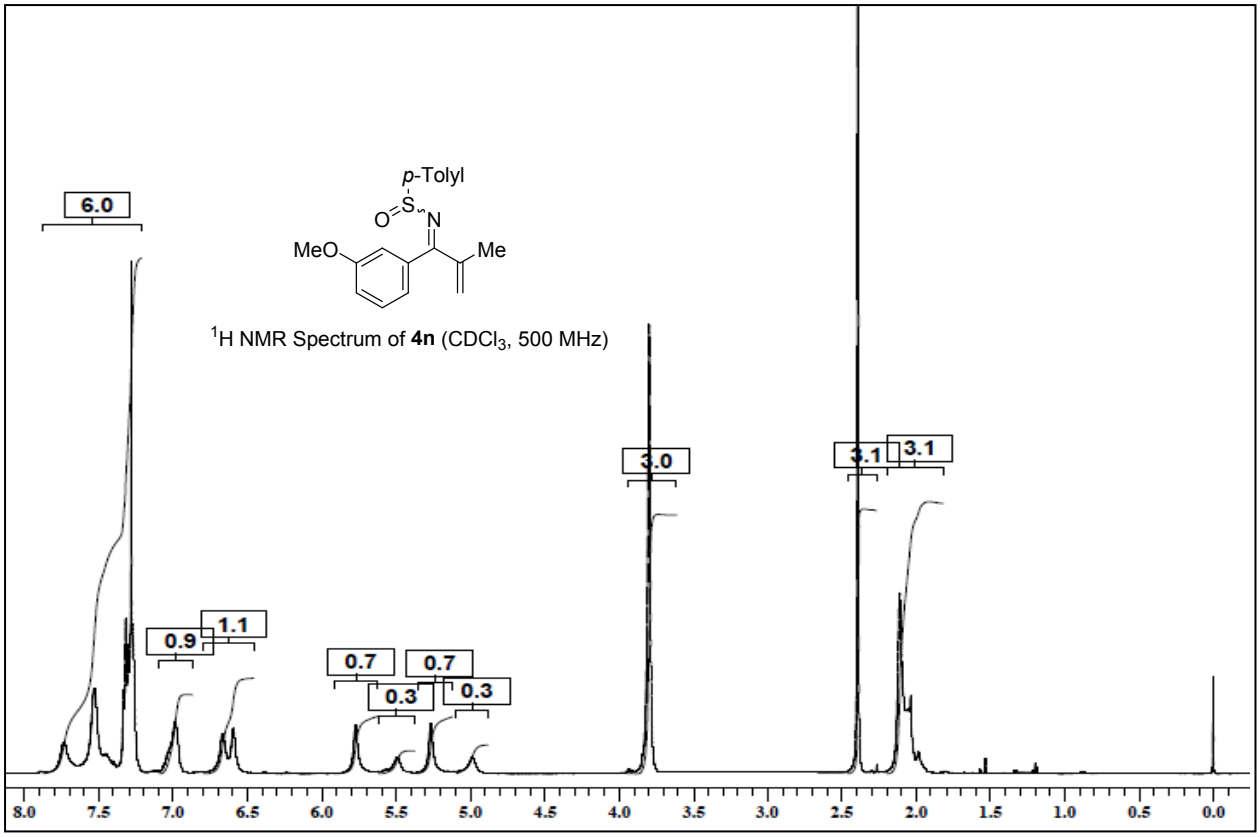
^{13}C NMR Spectrum of **4l** ($CDCl_3$, 125 MHz)



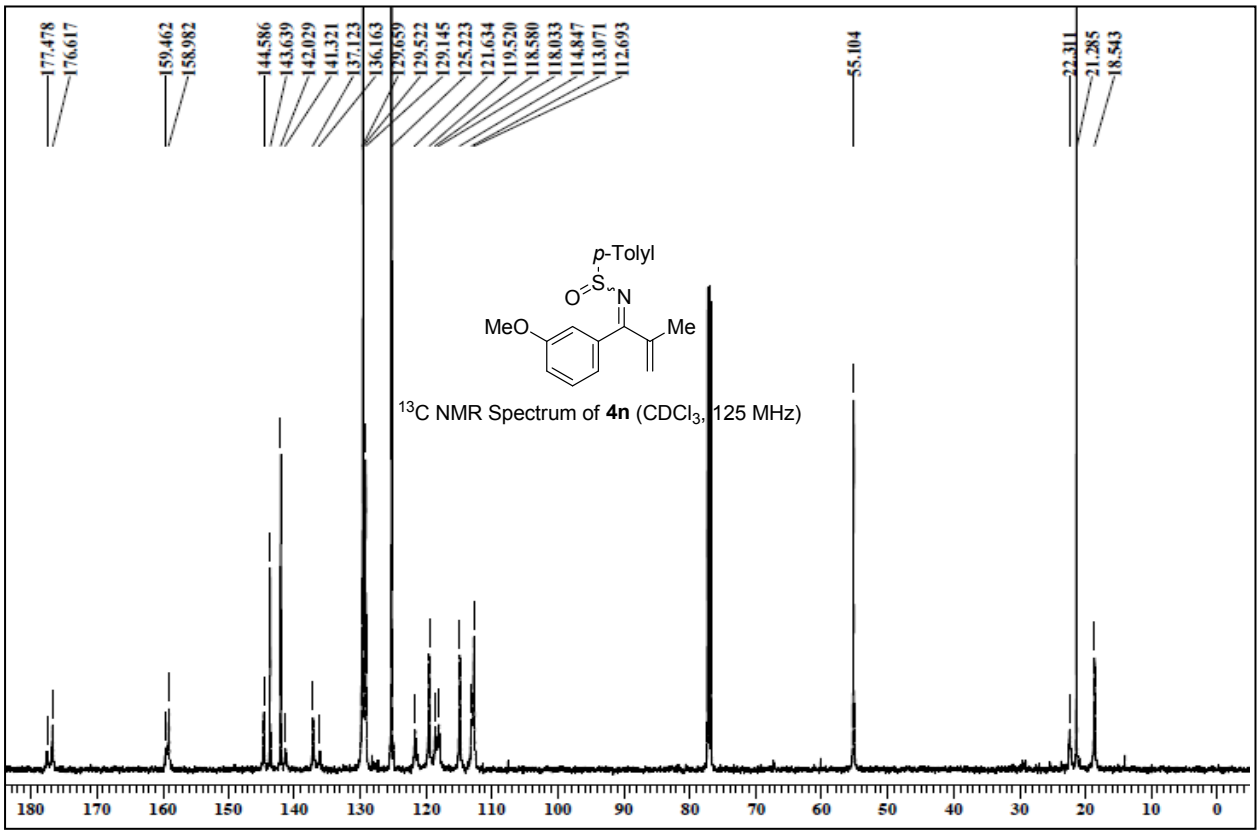
^{1}H NMR Spectrum of **4m** ($CDCl_3$, 500 MHz)



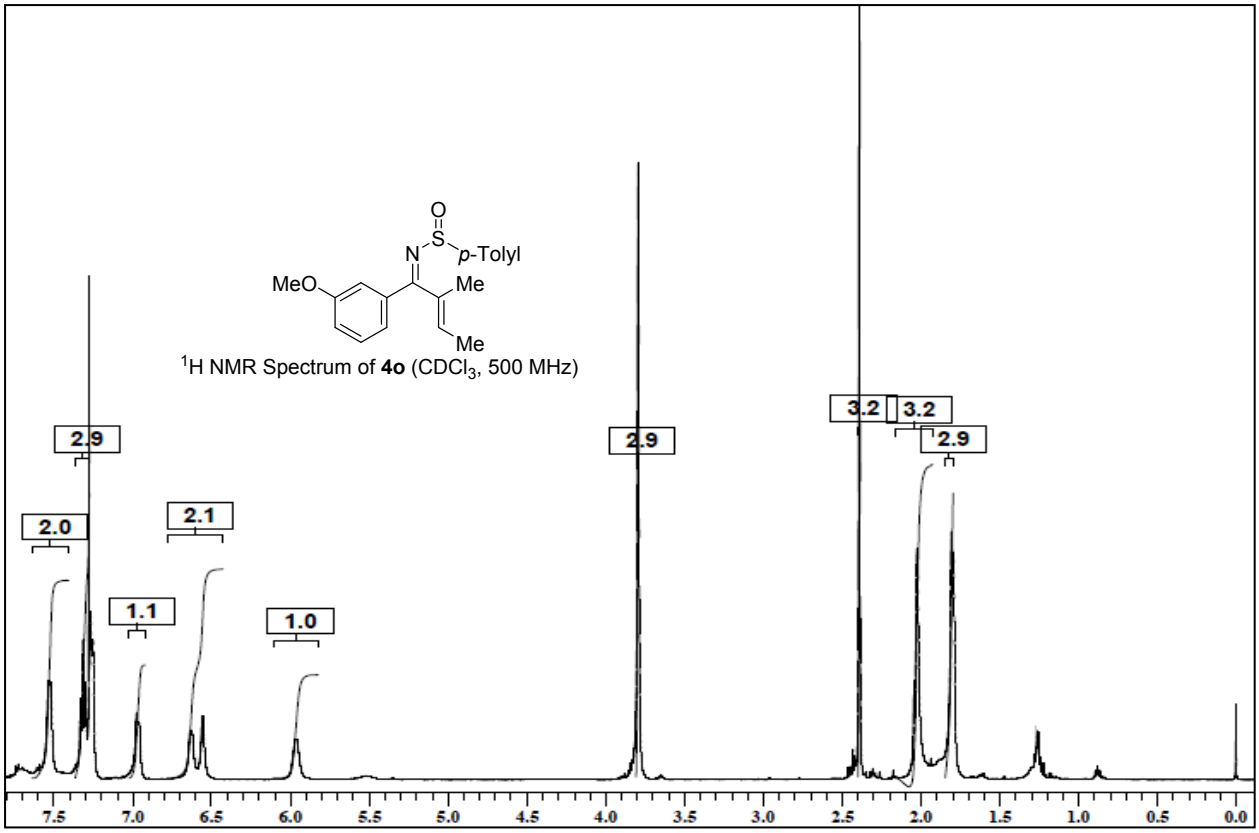
^{13}C NMR Spectrum of **4m** ($CDCl_3$, 125 MHz)



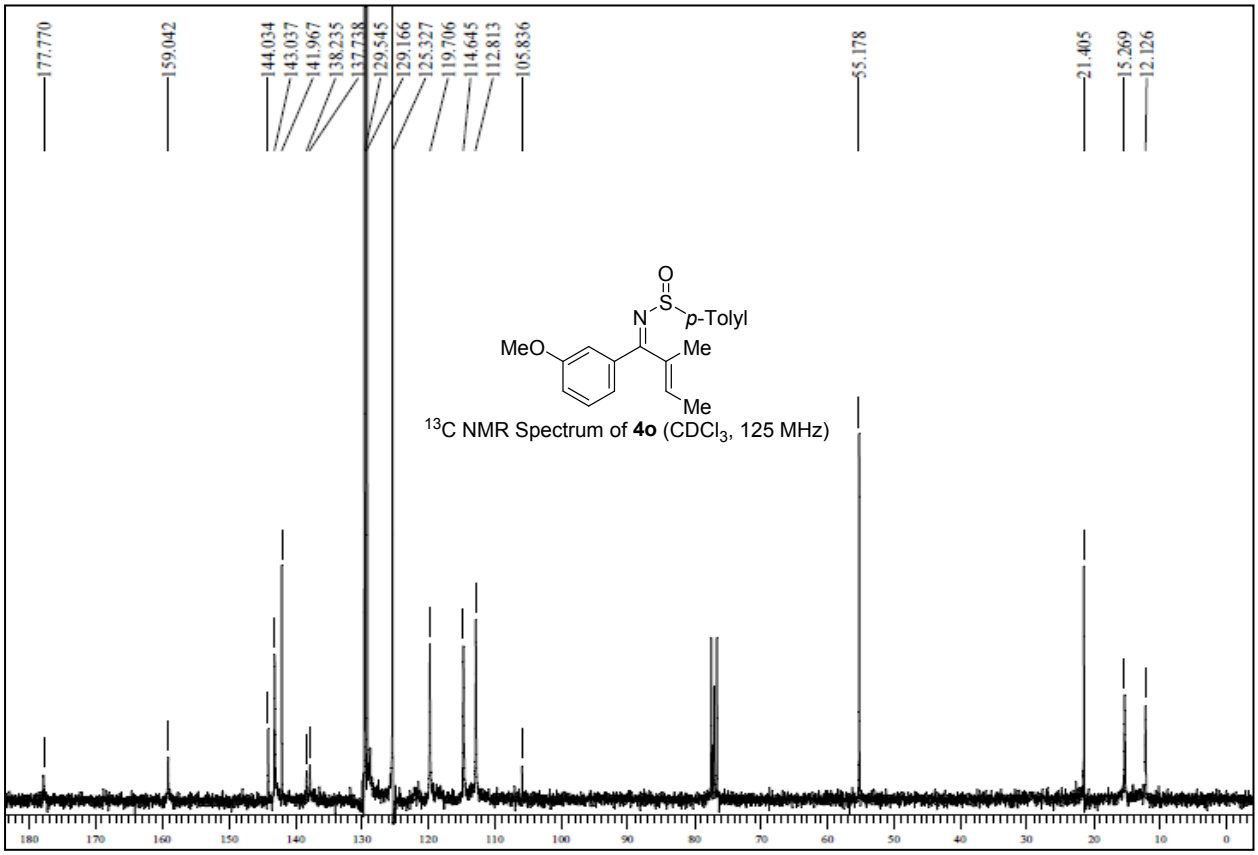
^{1}H NMR Spectrum of **4n** ($CDCl_3$, 500 MHz)



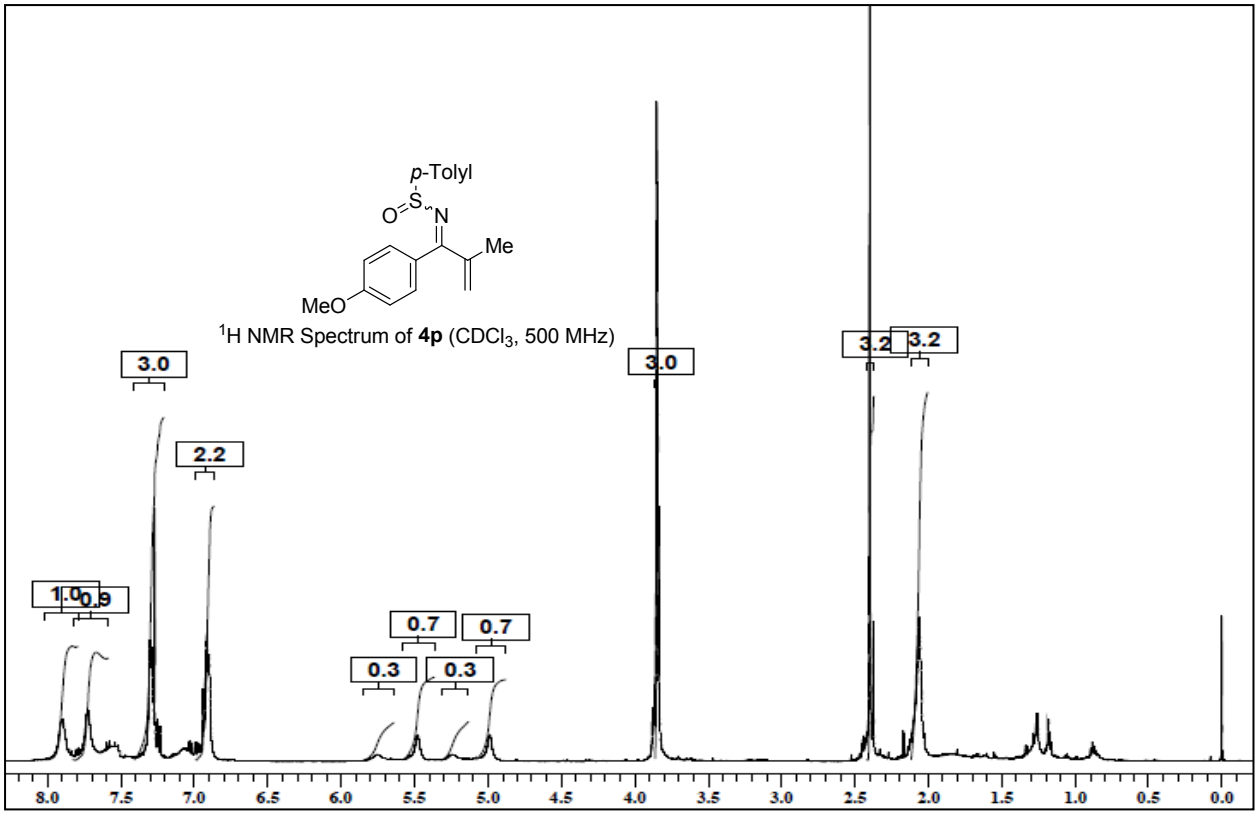
^{13}C NMR Spectrum of **4n** ($CDCl_3$, 125 MHz)



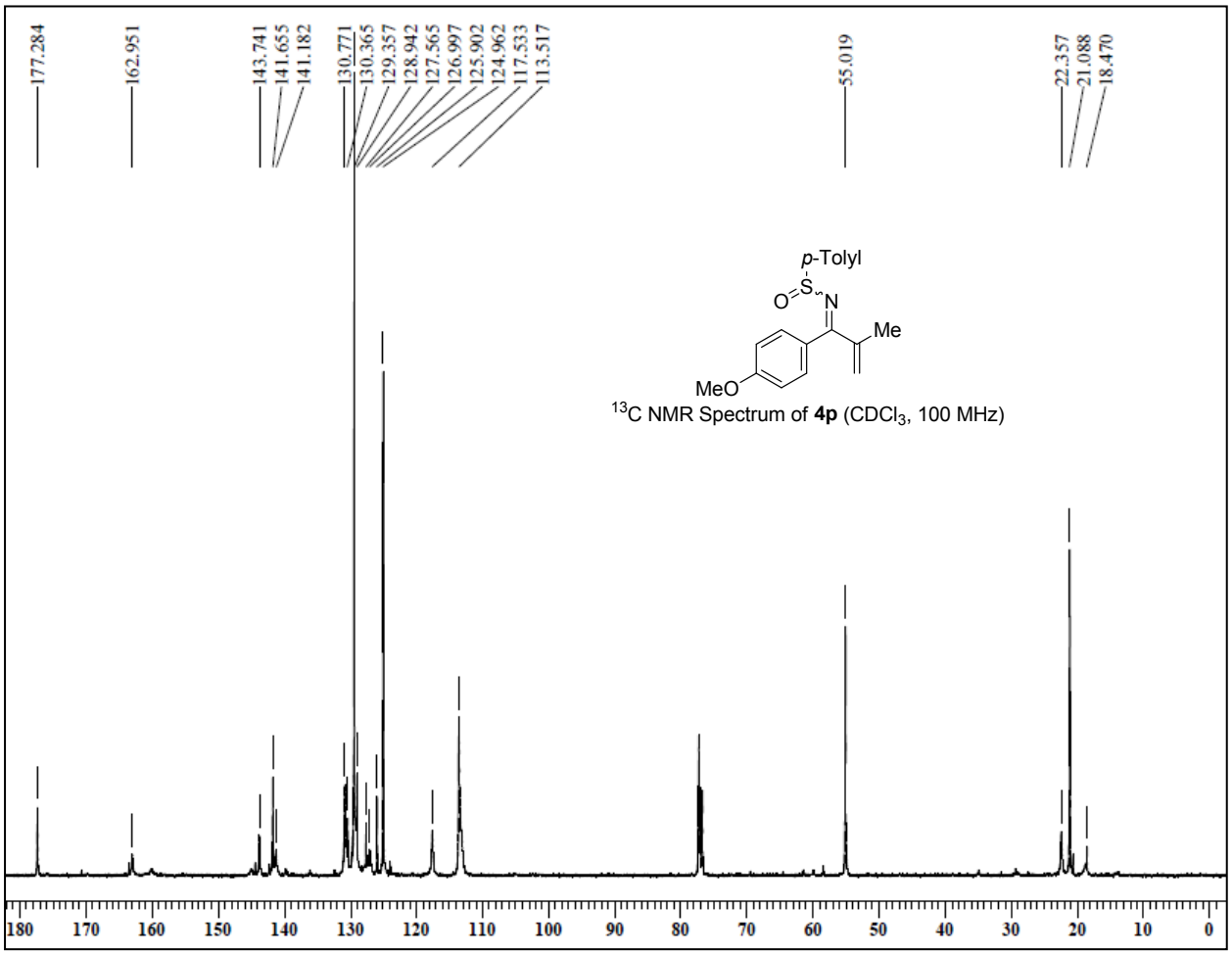
^{1}H NMR Spectrum of **4o** ($CDCl_3$, 500 MHz)



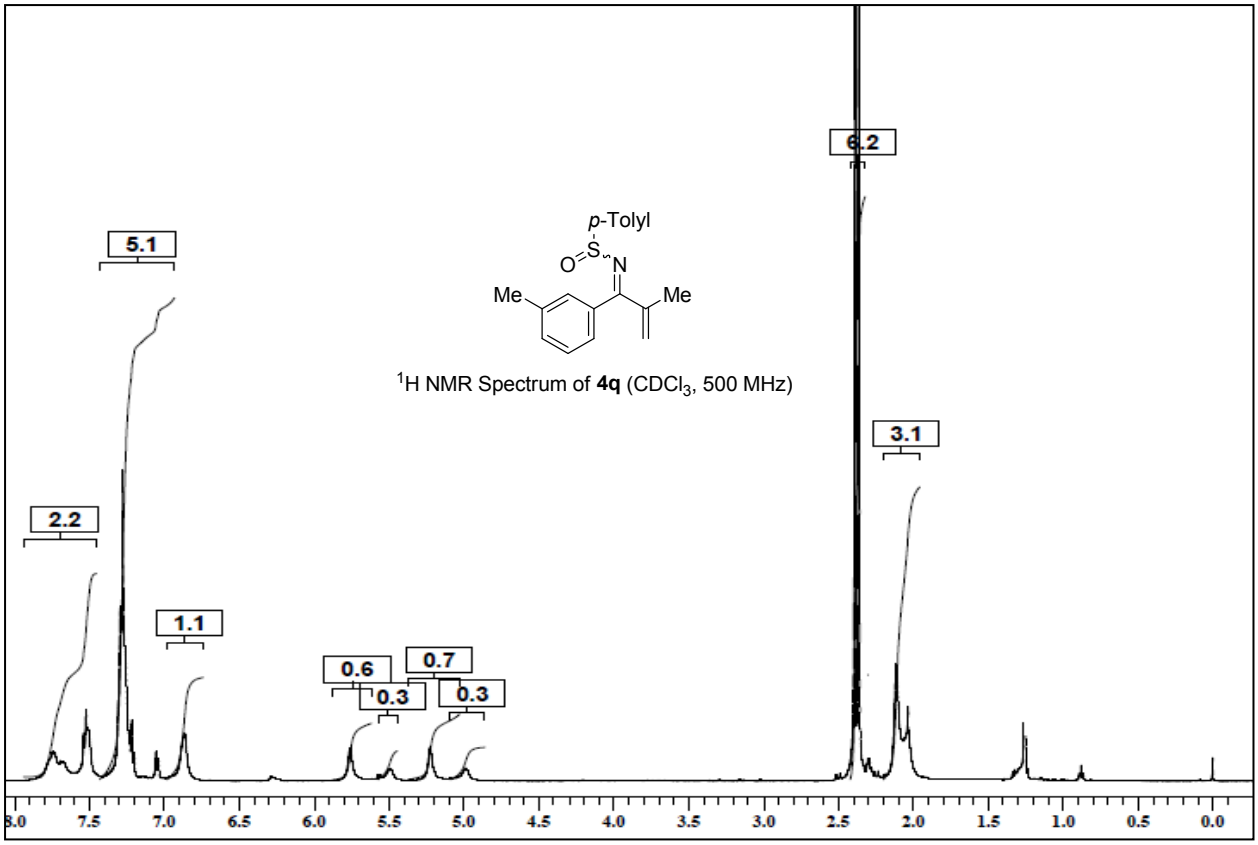
^{13}C NMR Spectrum of **4o** ($CDCl_3$, 125 MHz)



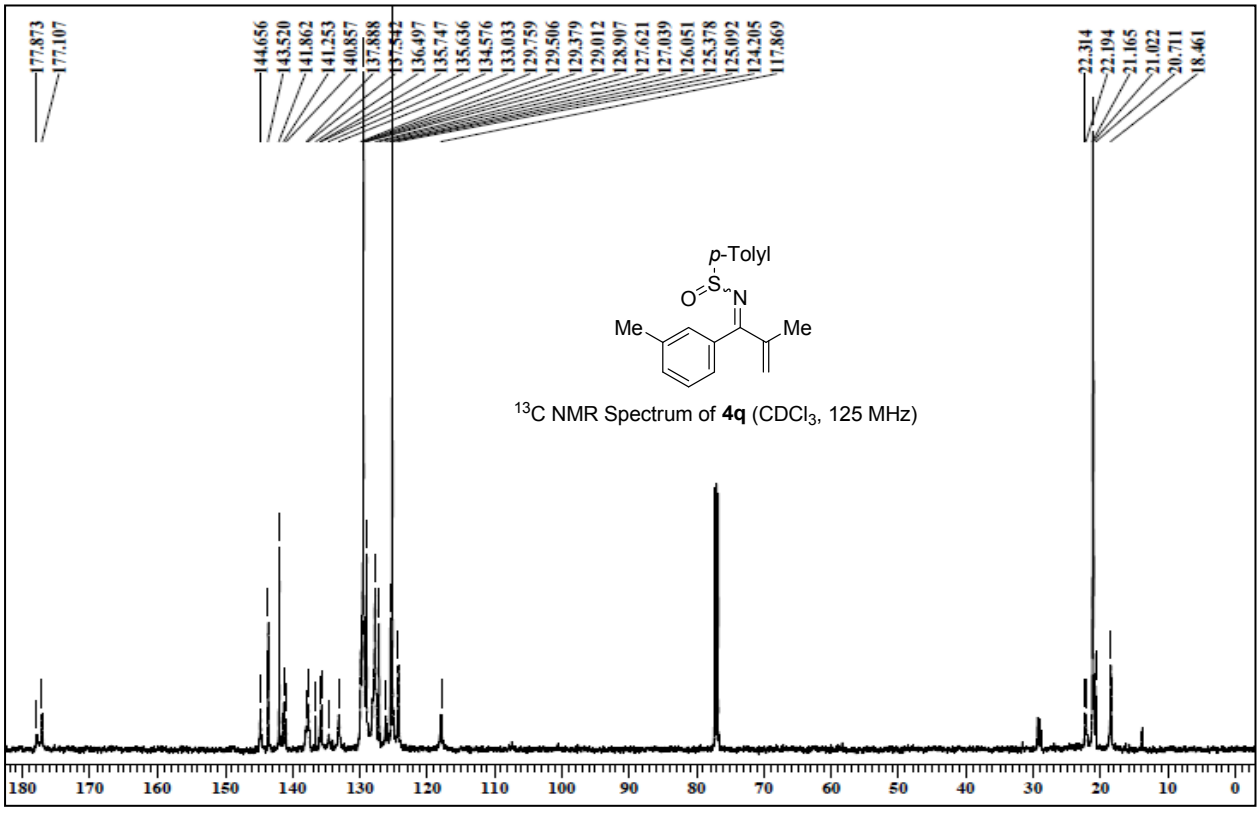
^{1}H NMR Spectrum of **4p** ($CDCl_3$, 500 MHz)



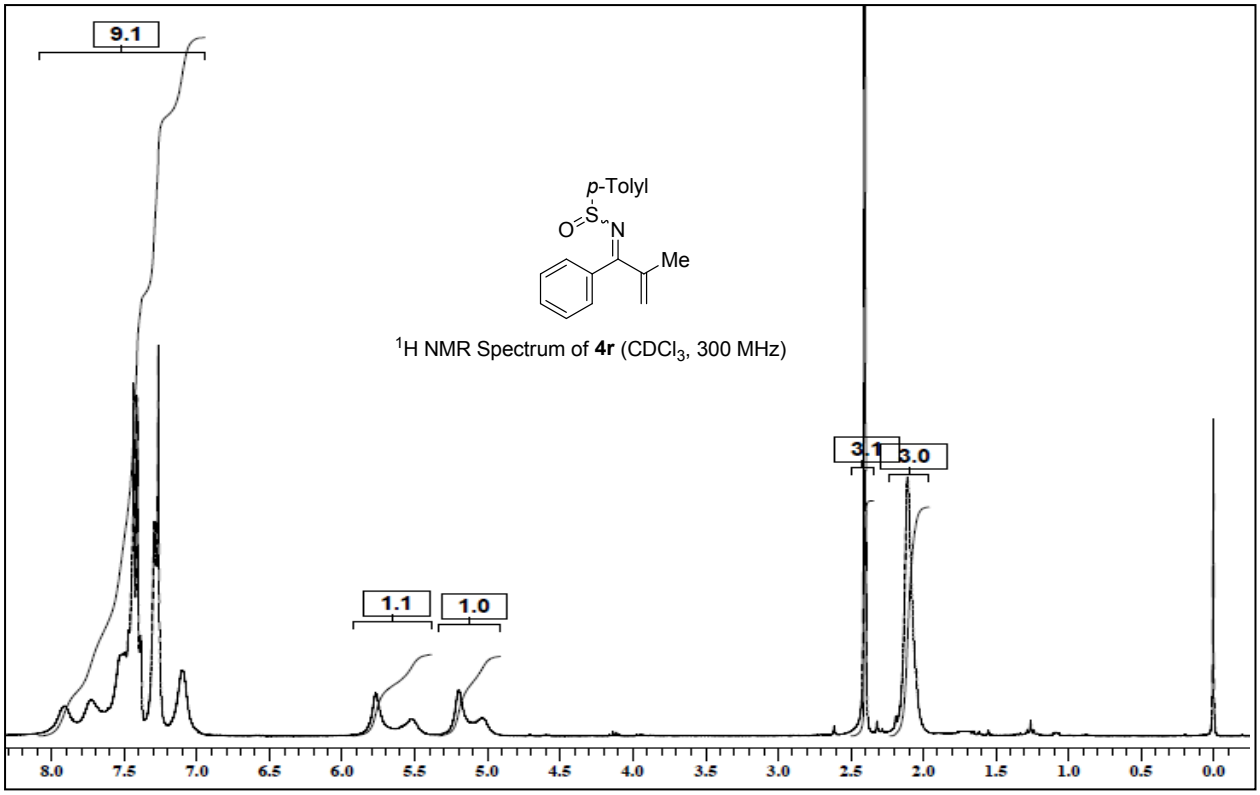
^{13}C NMR Spectrum of **4p** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **4q** ($CDCl_3$, 500 MHz)

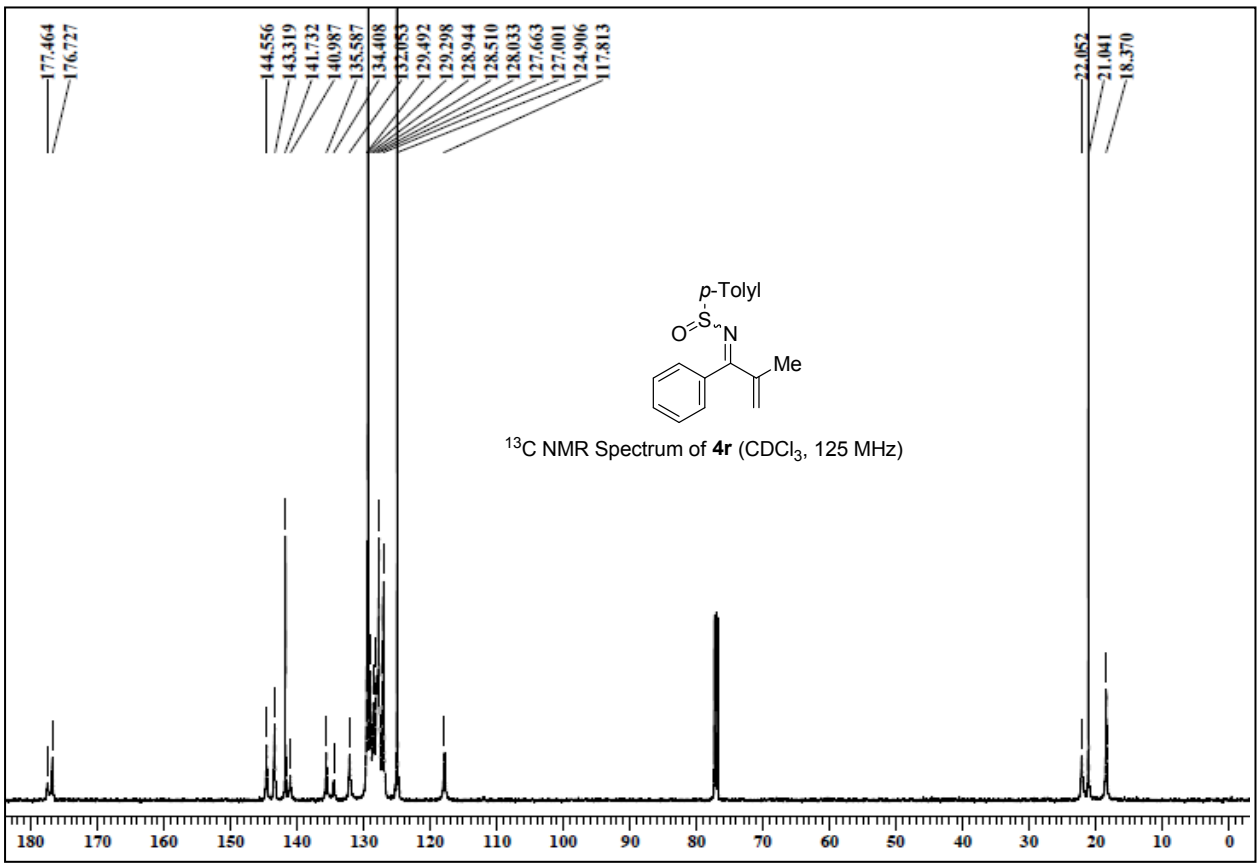


^{13}C NMR Spectrum of **4q** ($CDCl_3$, 125 MHz)



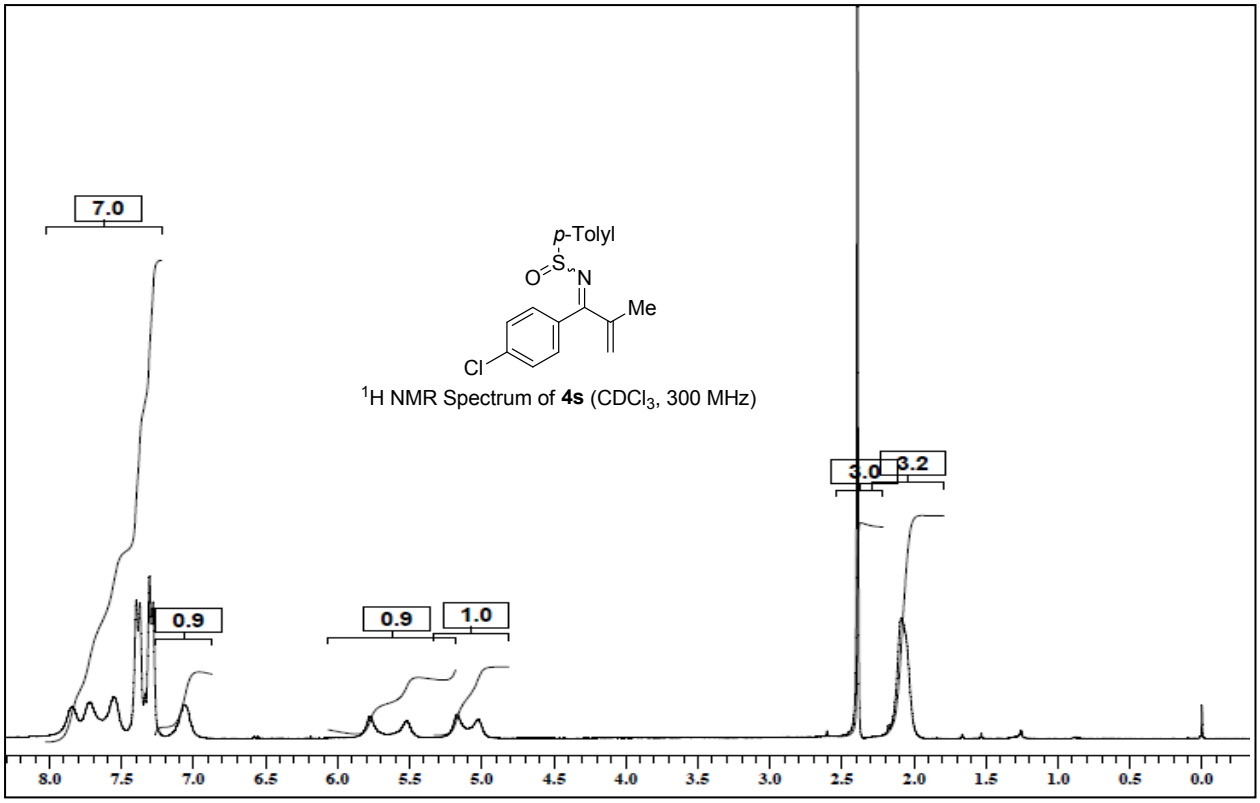
p-Tolyl

^{1}H NMR Spectrum of **4r** ($CDCl_3$, 300 MHz)

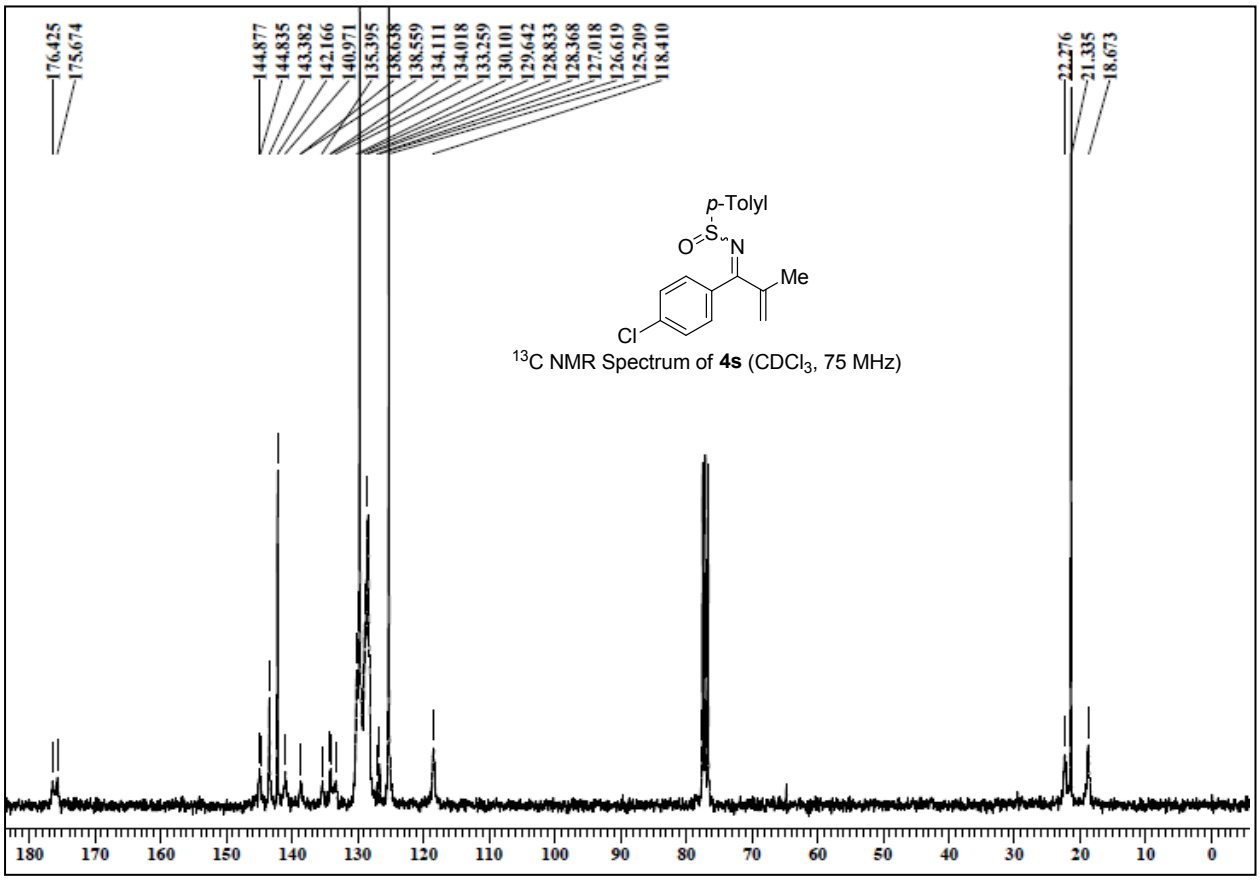


p-Tolyl

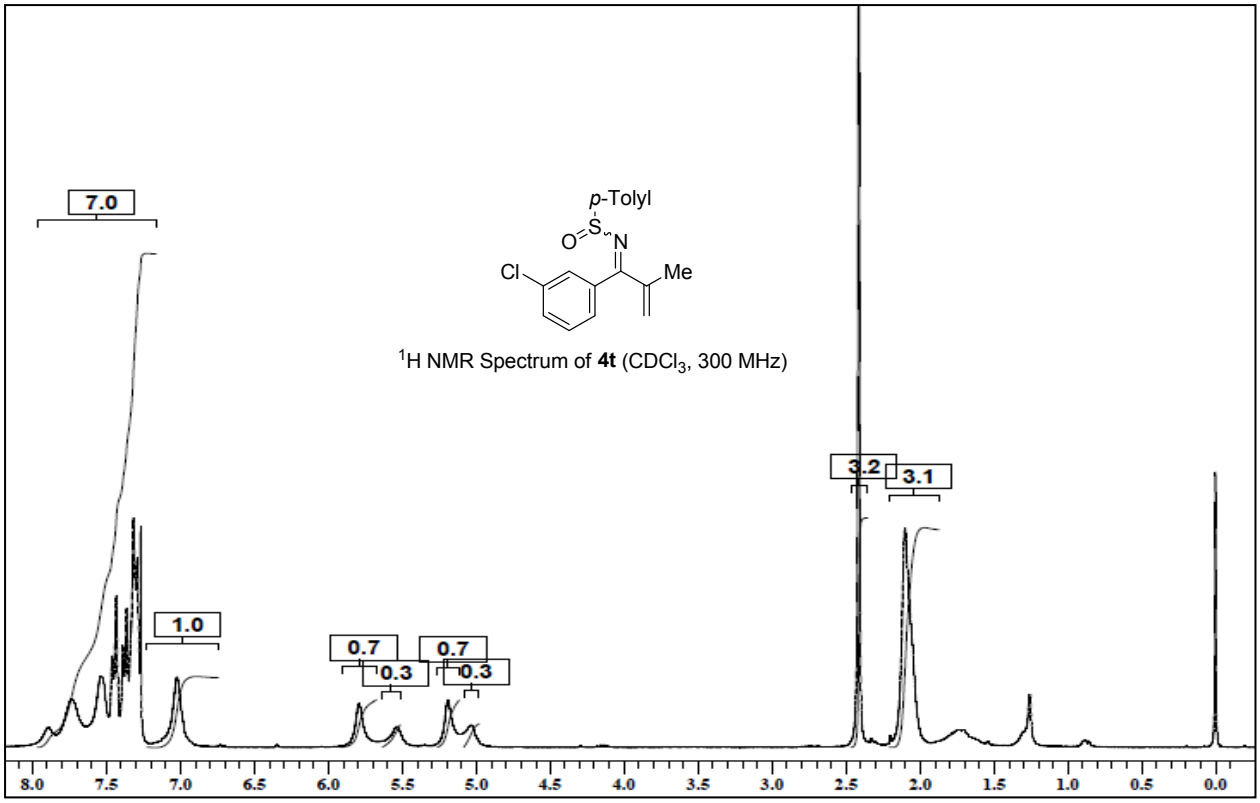
^{13}C NMR Spectrum of **4r** ($CDCl_3$, 125 MHz)



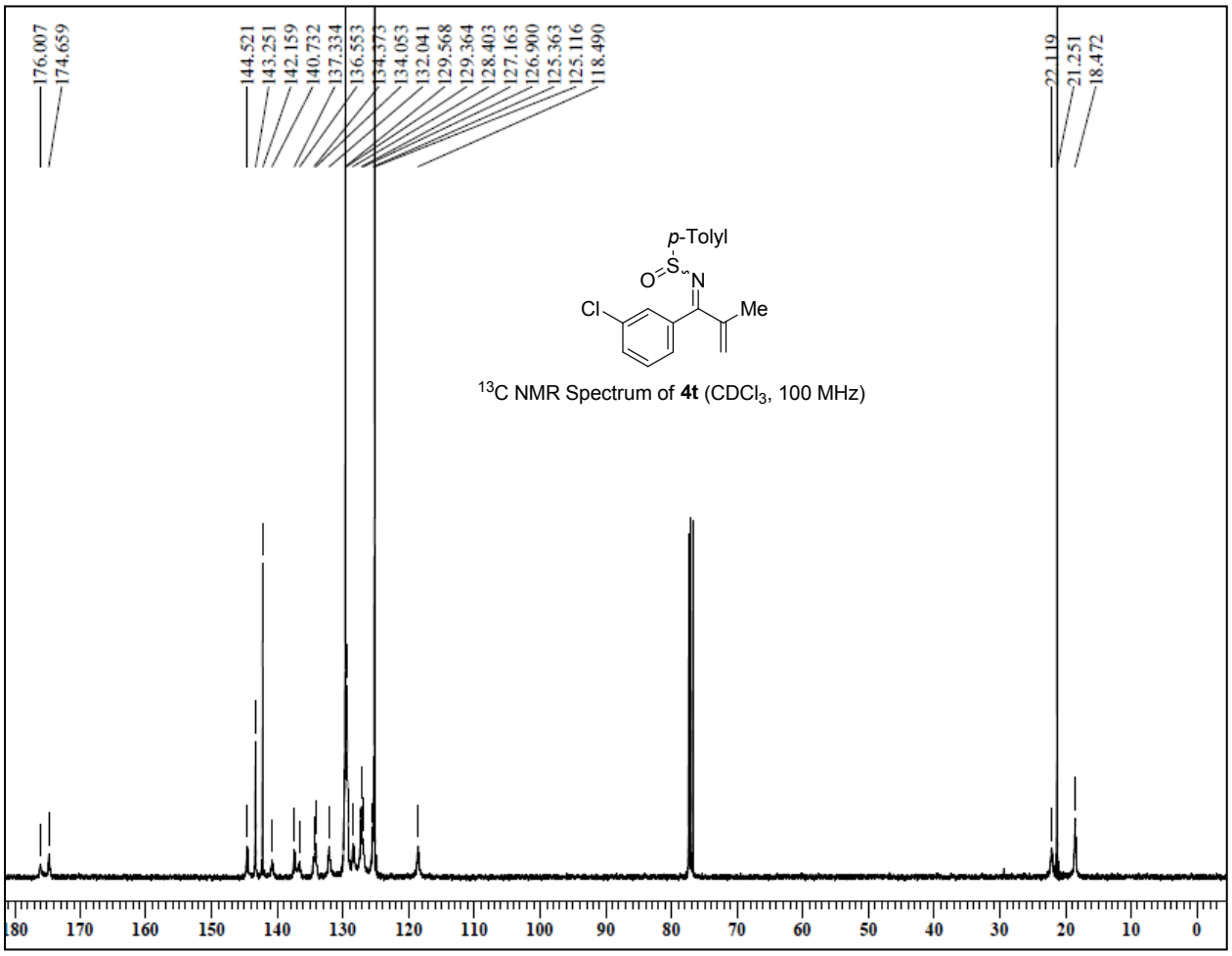
^{1}H NMR Spectrum of **4s** ($CDCl_3$, 300 MHz)



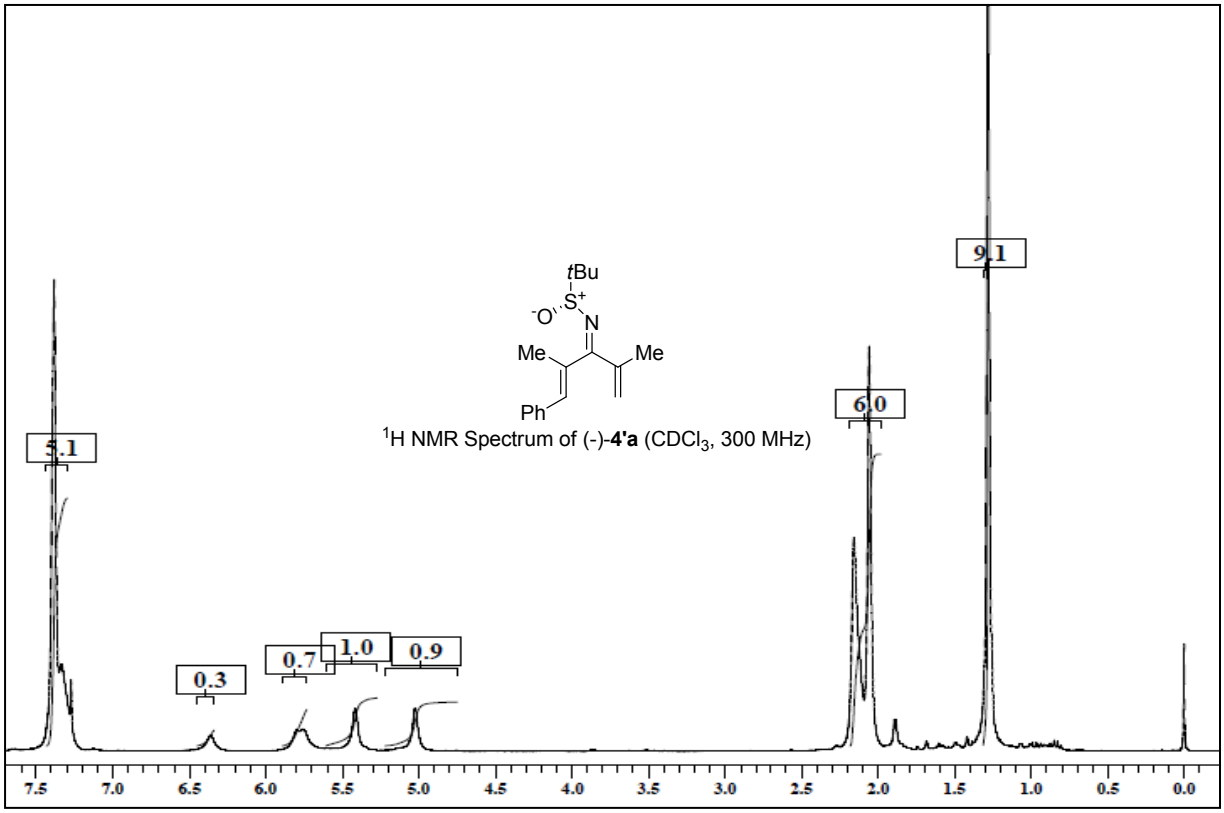
^{13}C NMR Spectrum of **4s** ($CDCl_3$, 75 MHz)



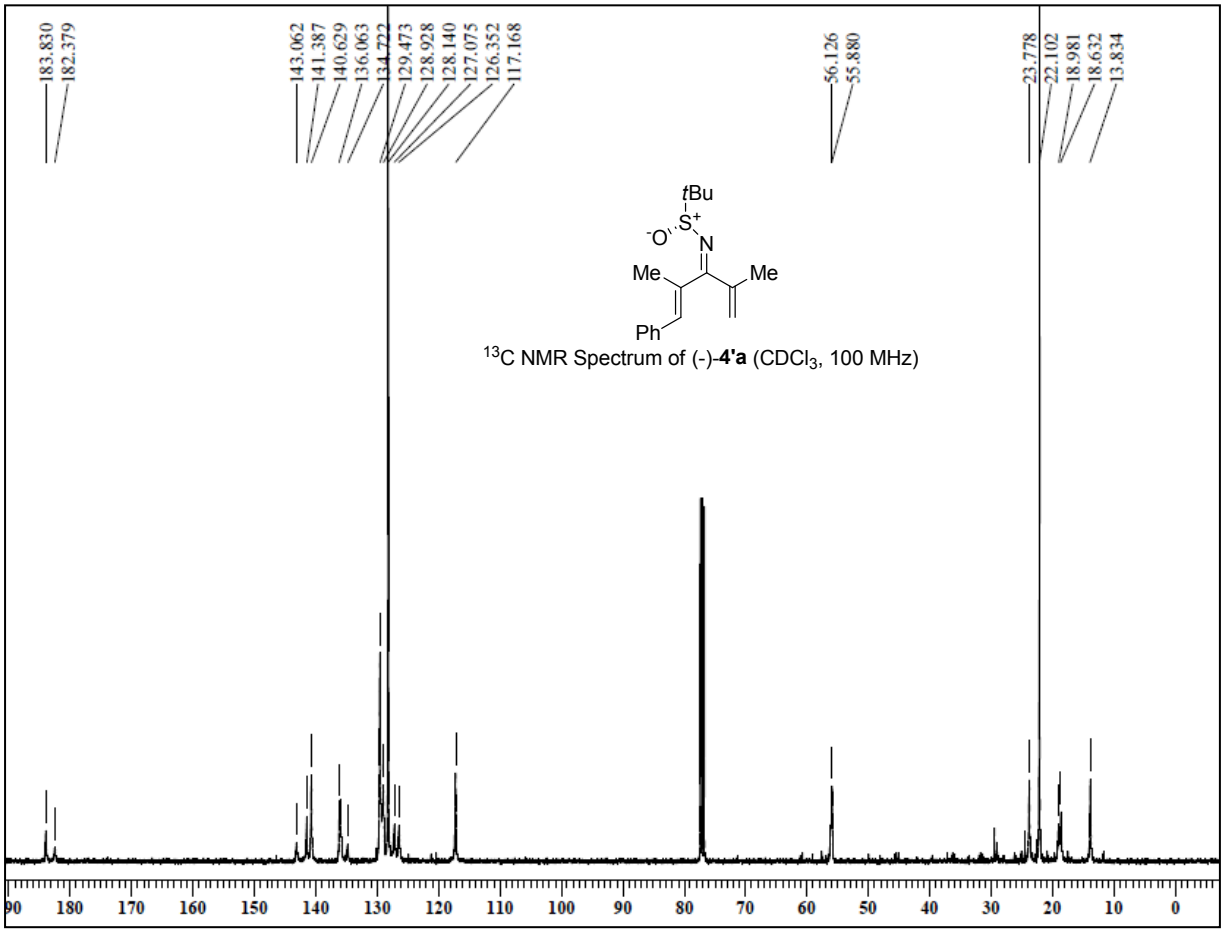
^{1}H NMR Spectrum of **4t** ($CDCl_3$, 300 MHz)



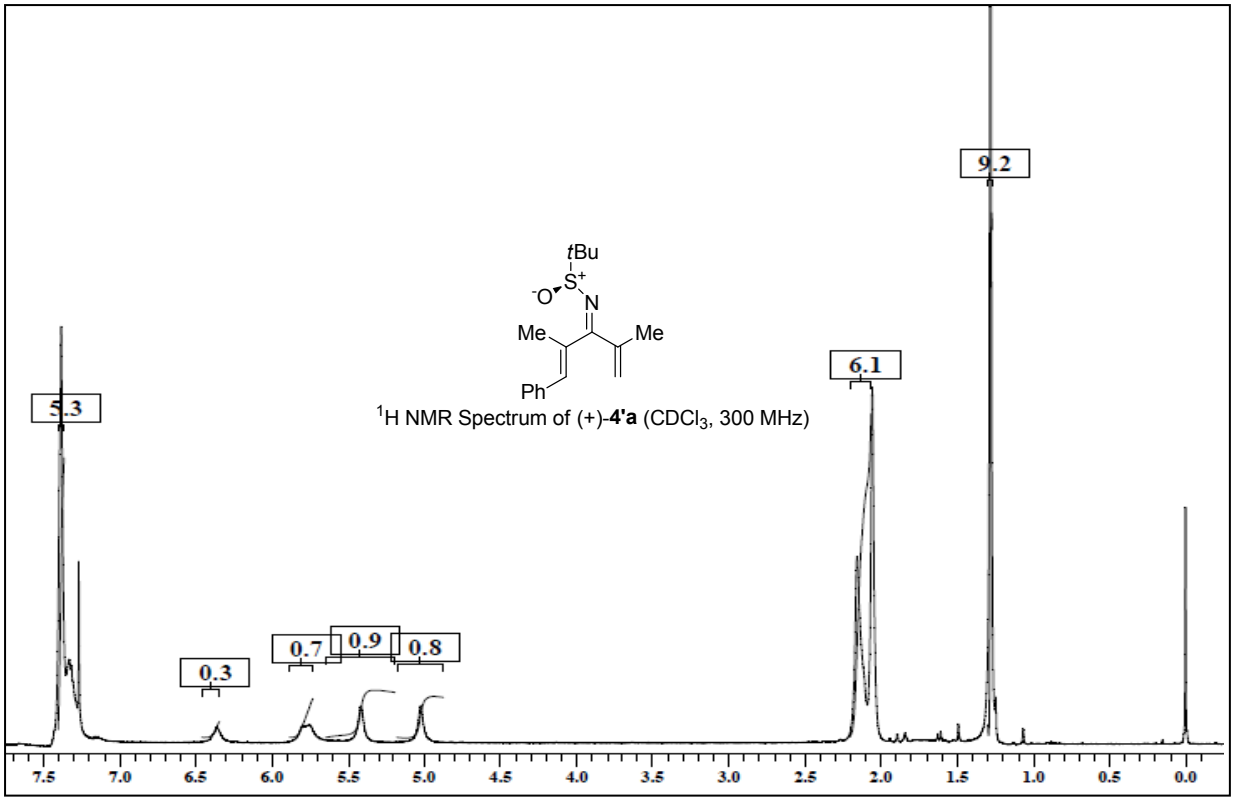
^{13}C NMR Spectrum of **4t** ($CDCl_3$, 100 MHz)



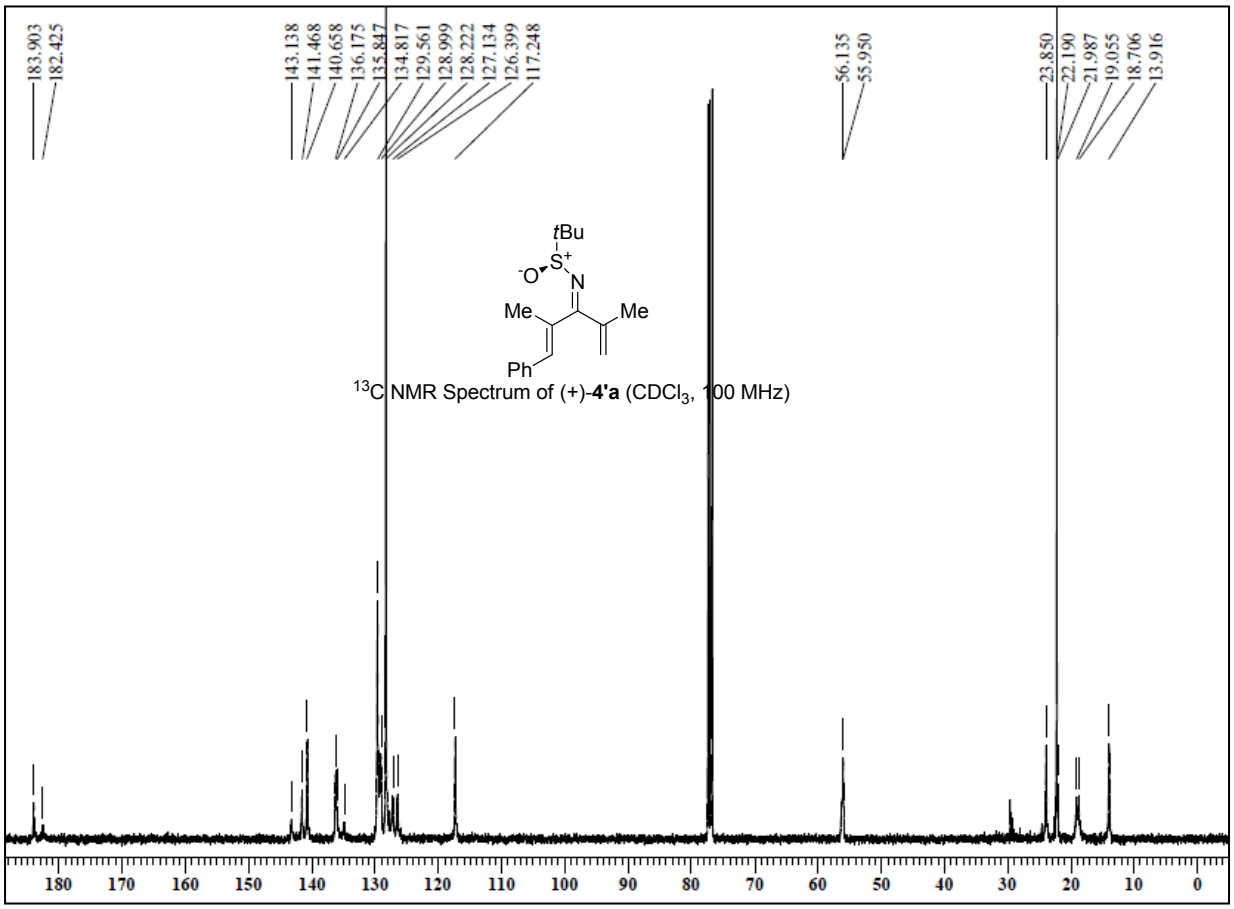
^{1}H NMR Spectrum of (-)-**4'a** ($CDCl_3$, 300 MHz)



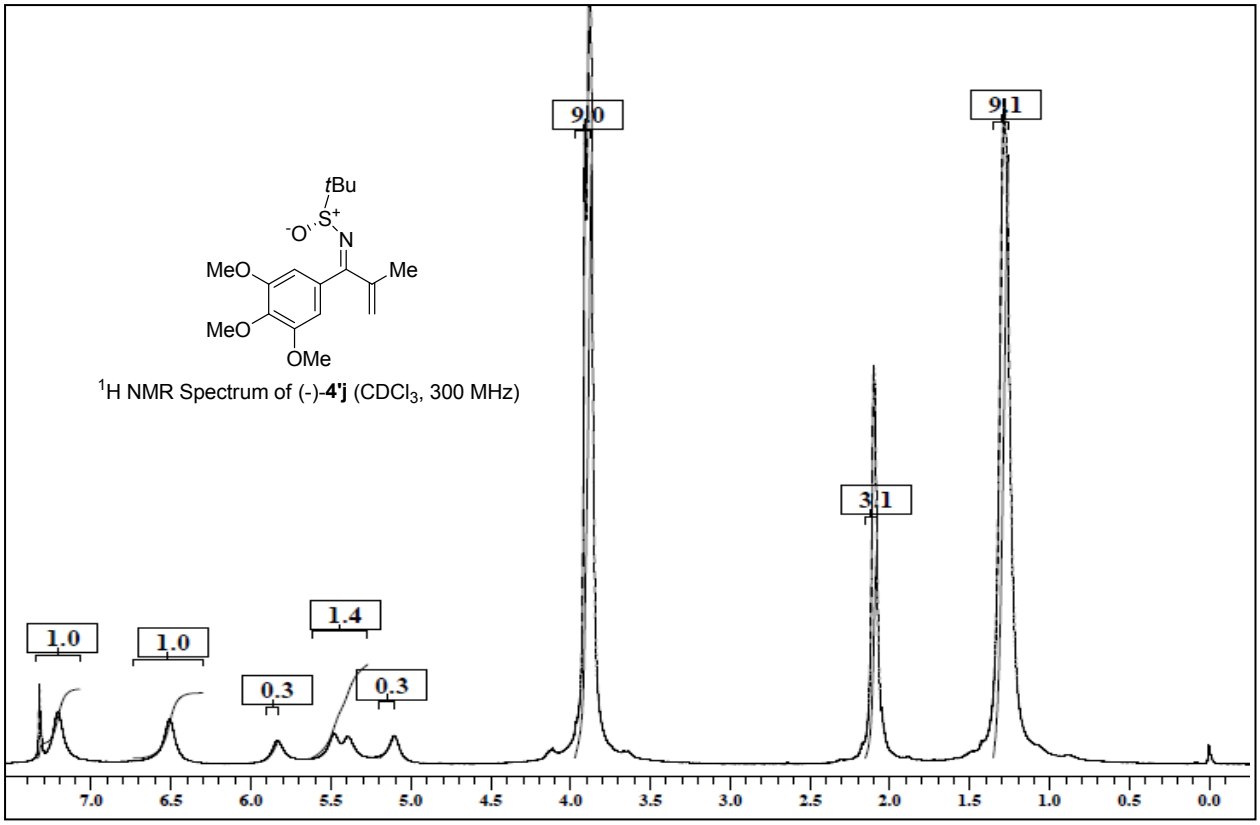
^{13}C NMR Spectrum of (-)-**4'a** ($CDCl_3$, 100 MHz)



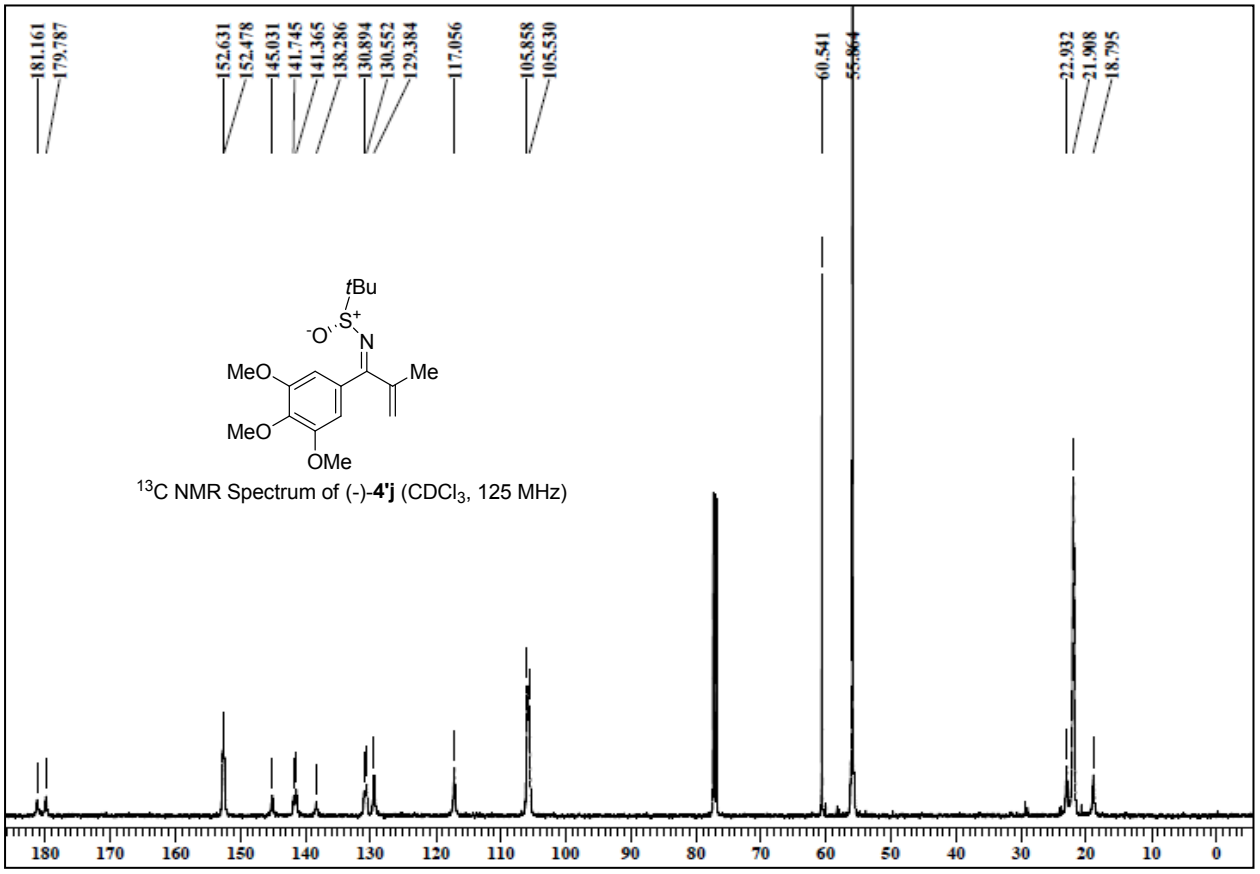
^{1}H NMR Spectrum of (+)-**4'a** ($CDCl_3$, 300 MHz)



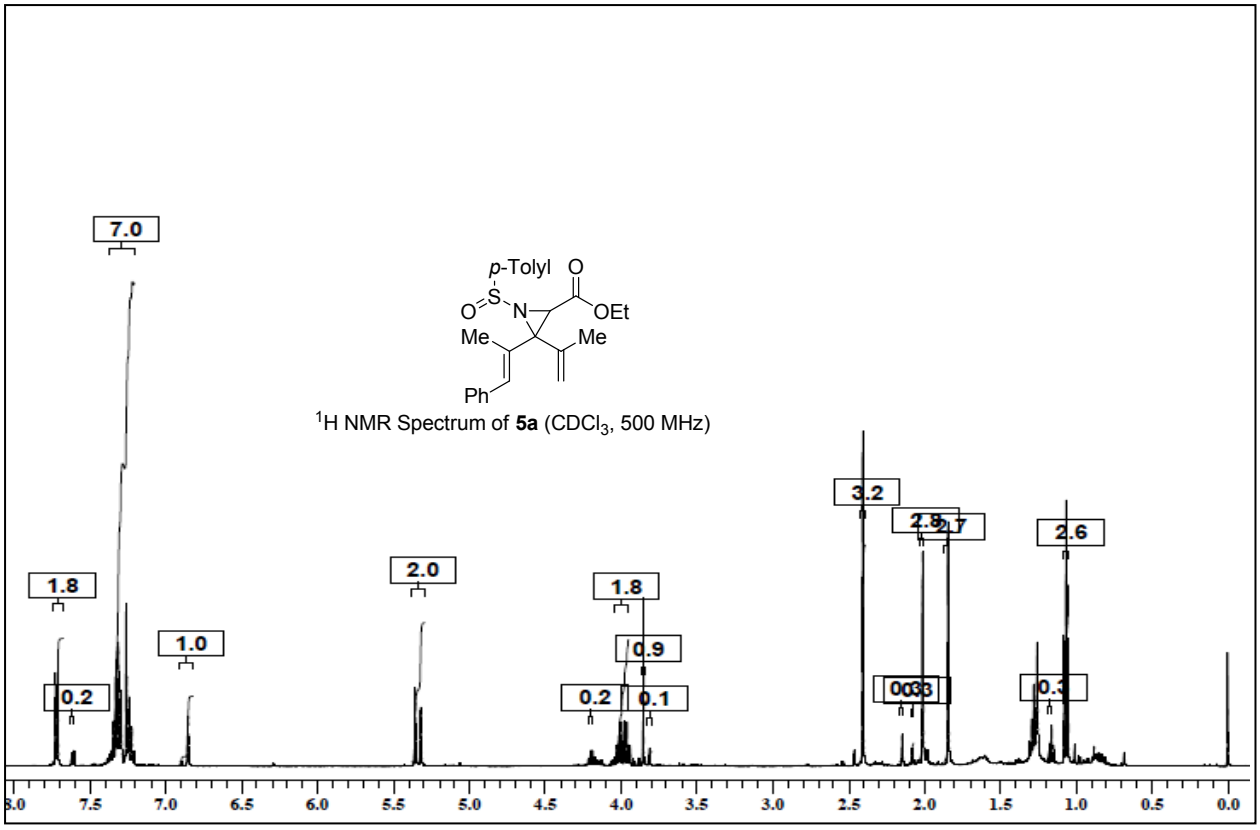
^{13}C NMR Spectrum of (+)-**4'a** ($CDCl_3$, 100 MHz)



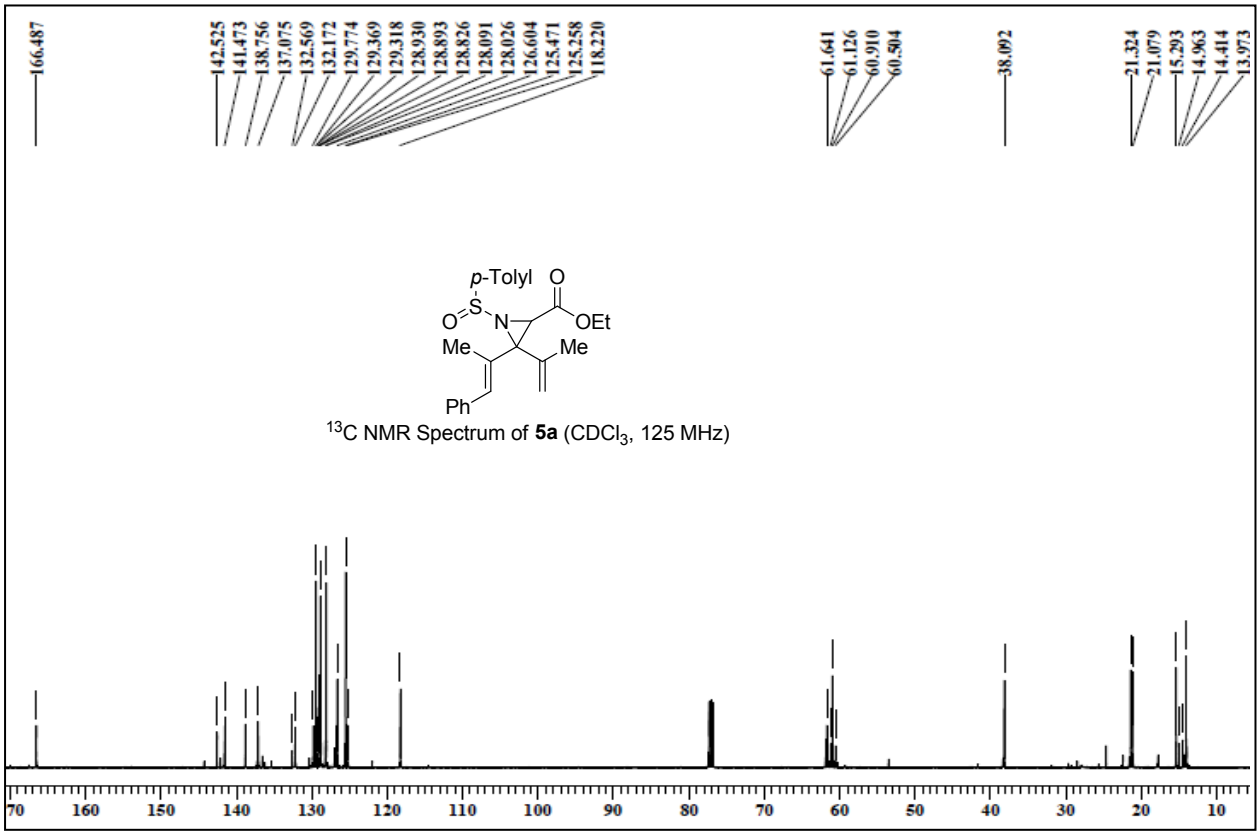
^{1}H NMR Spectrum of (-)-**4'j** ($CDCl_3$, 300 MHz)



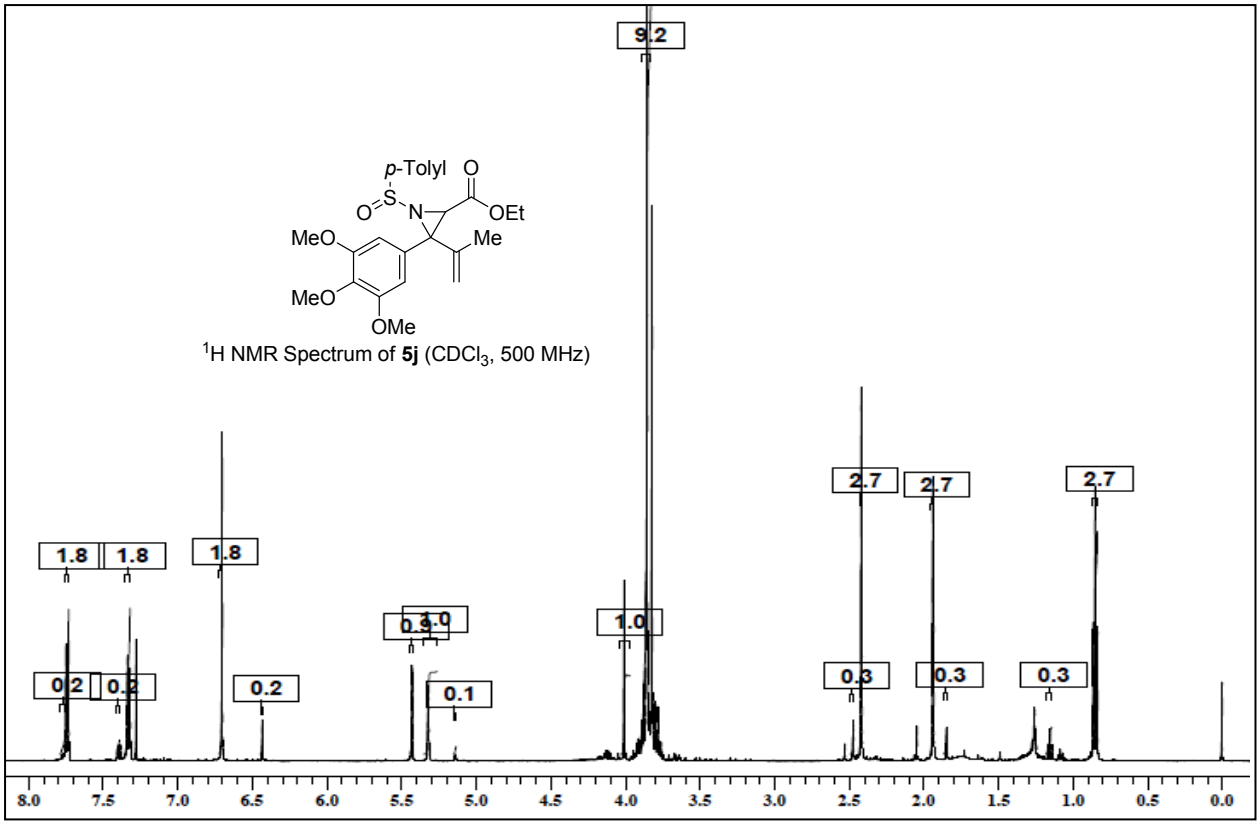
^{13}C NMR Spectrum of (-)-**4'j** ($CDCl_3$, 125 MHz)



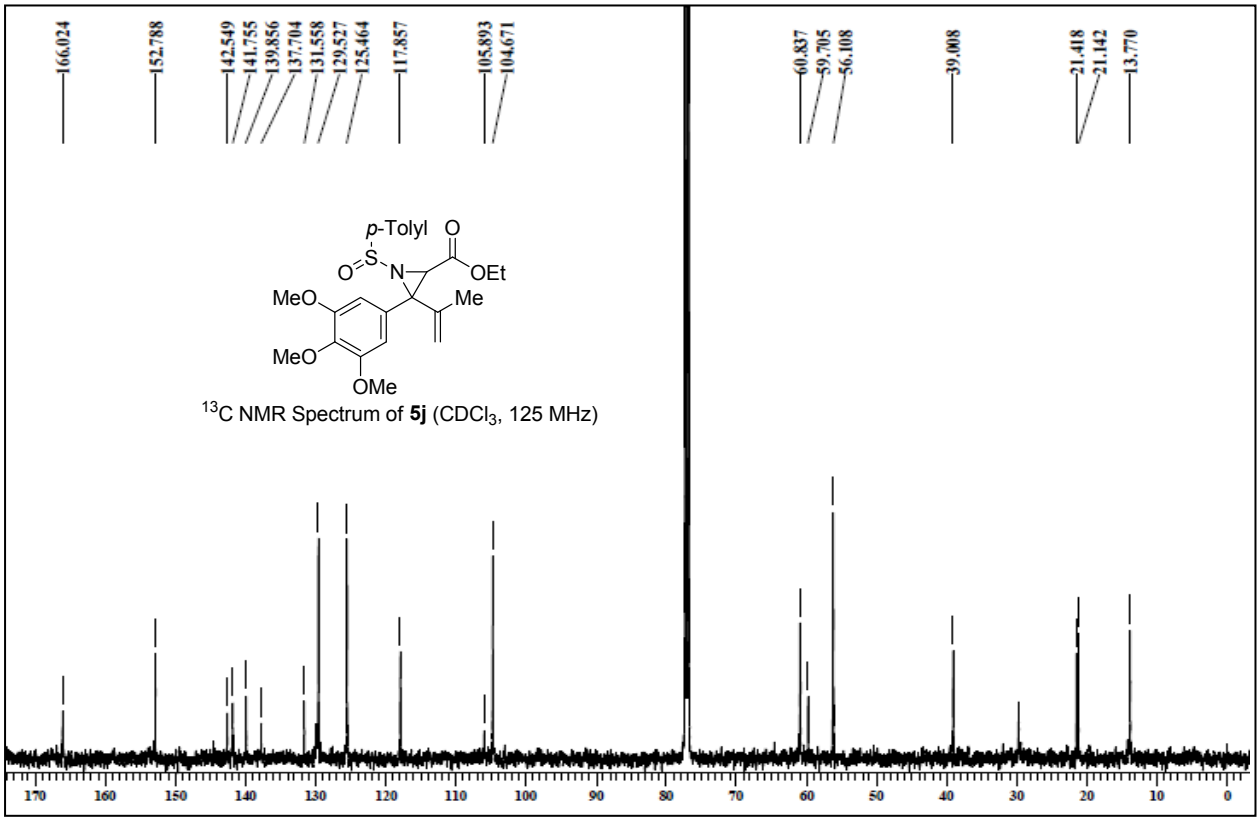
^{1}H NMR Spectrum of **5a** ($CDCl_3$, 500 MHz)



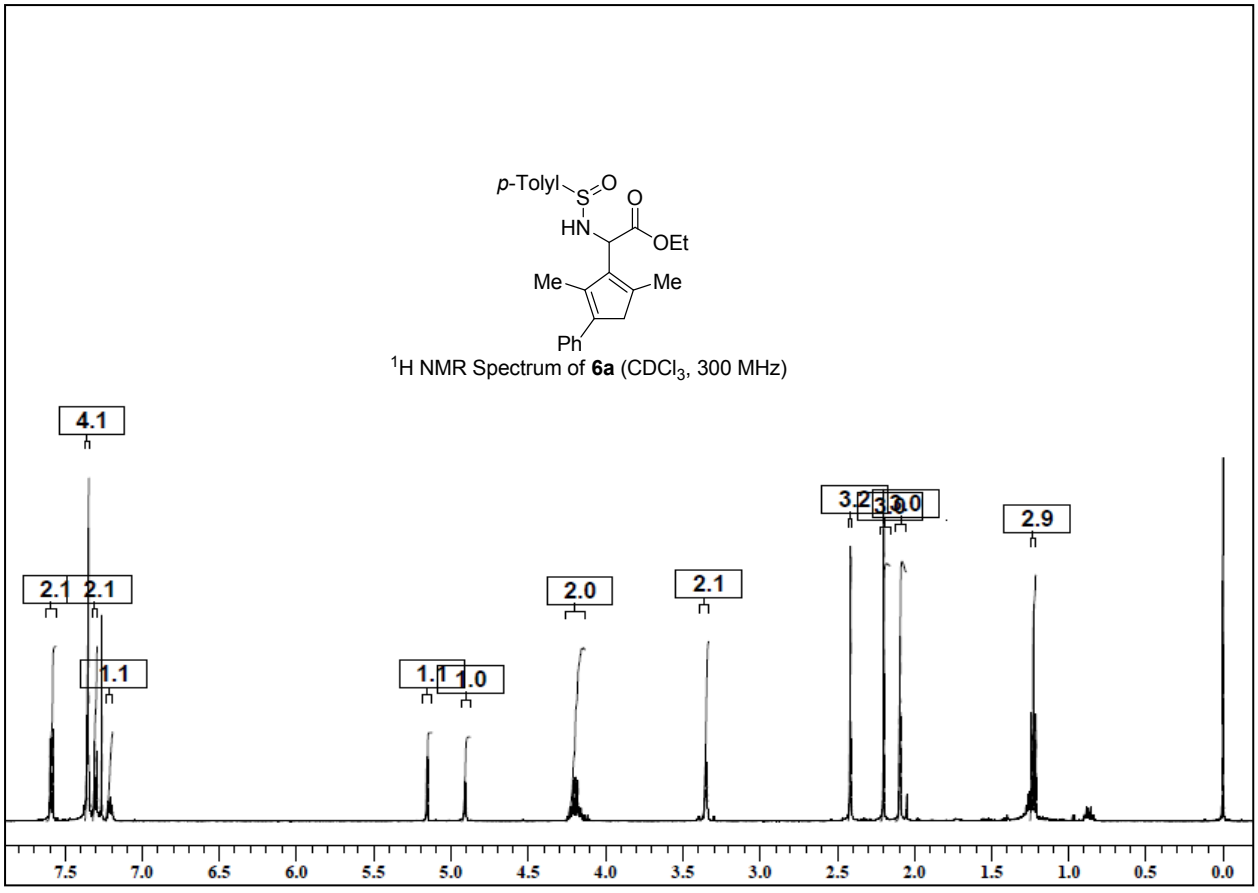
^{13}C NMR Spectrum of **5a** ($CDCl_3$, 125 MHz)



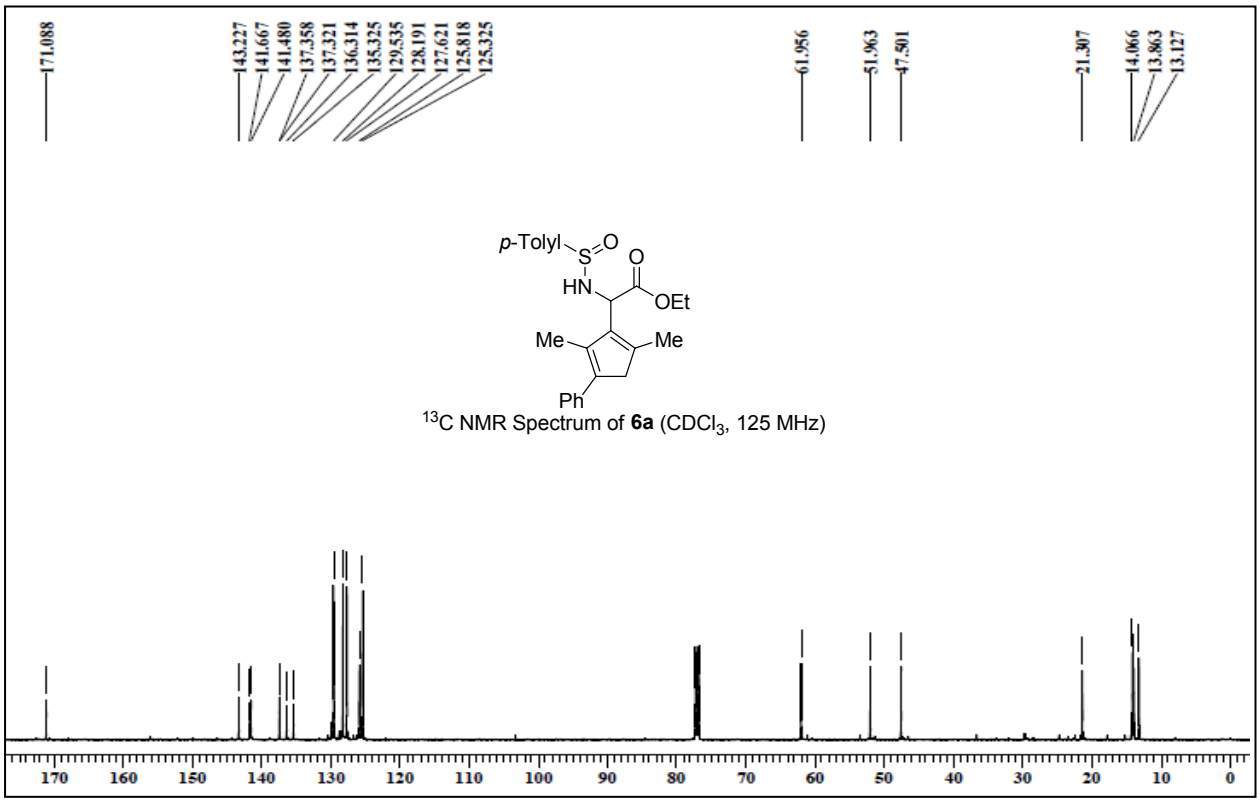
^{1}H NMR Spectrum of **5j** ($CDCl_3$, 500 MHz)



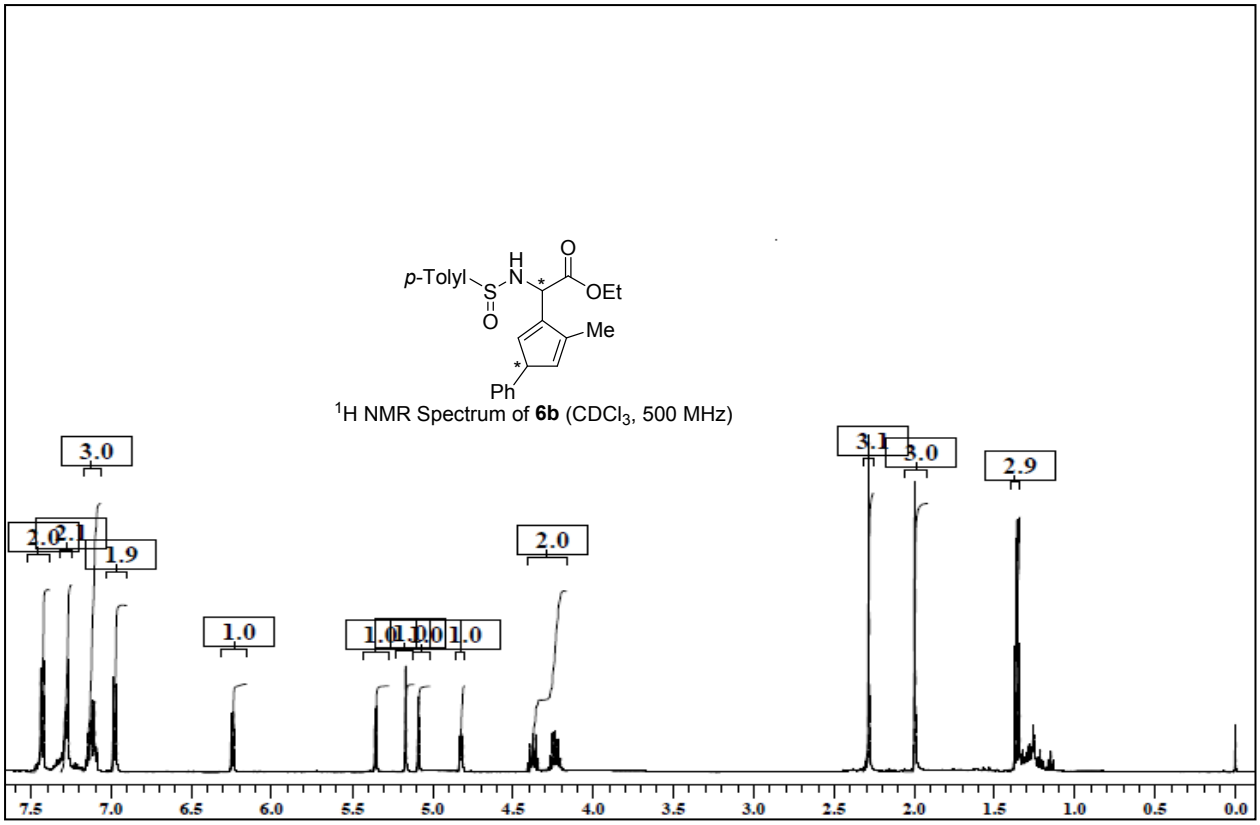
^{13}C NMR Spectrum of **5j** ($CDCl_3$, 125 MHz)



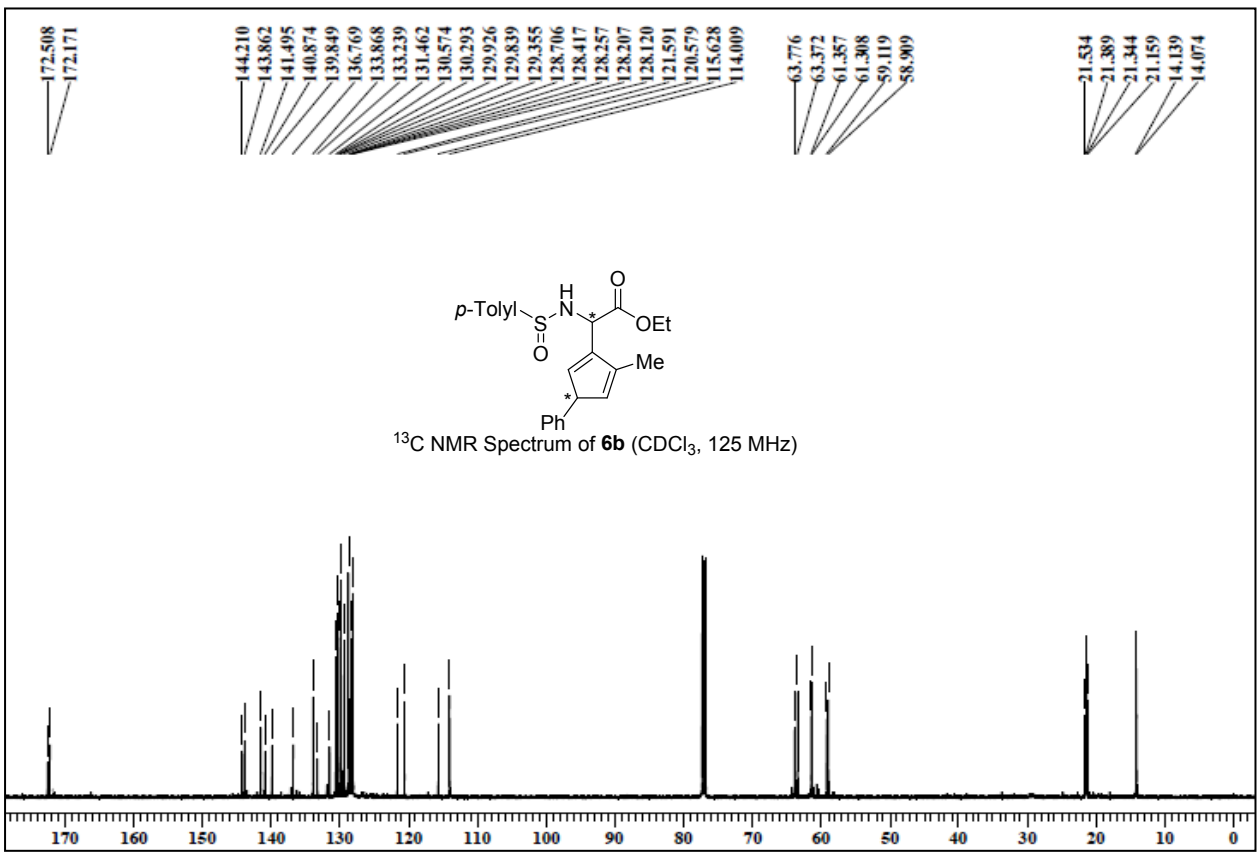
^{1}H NMR Spectrum of **6a** ($CDCl_3$, 300 MHz)



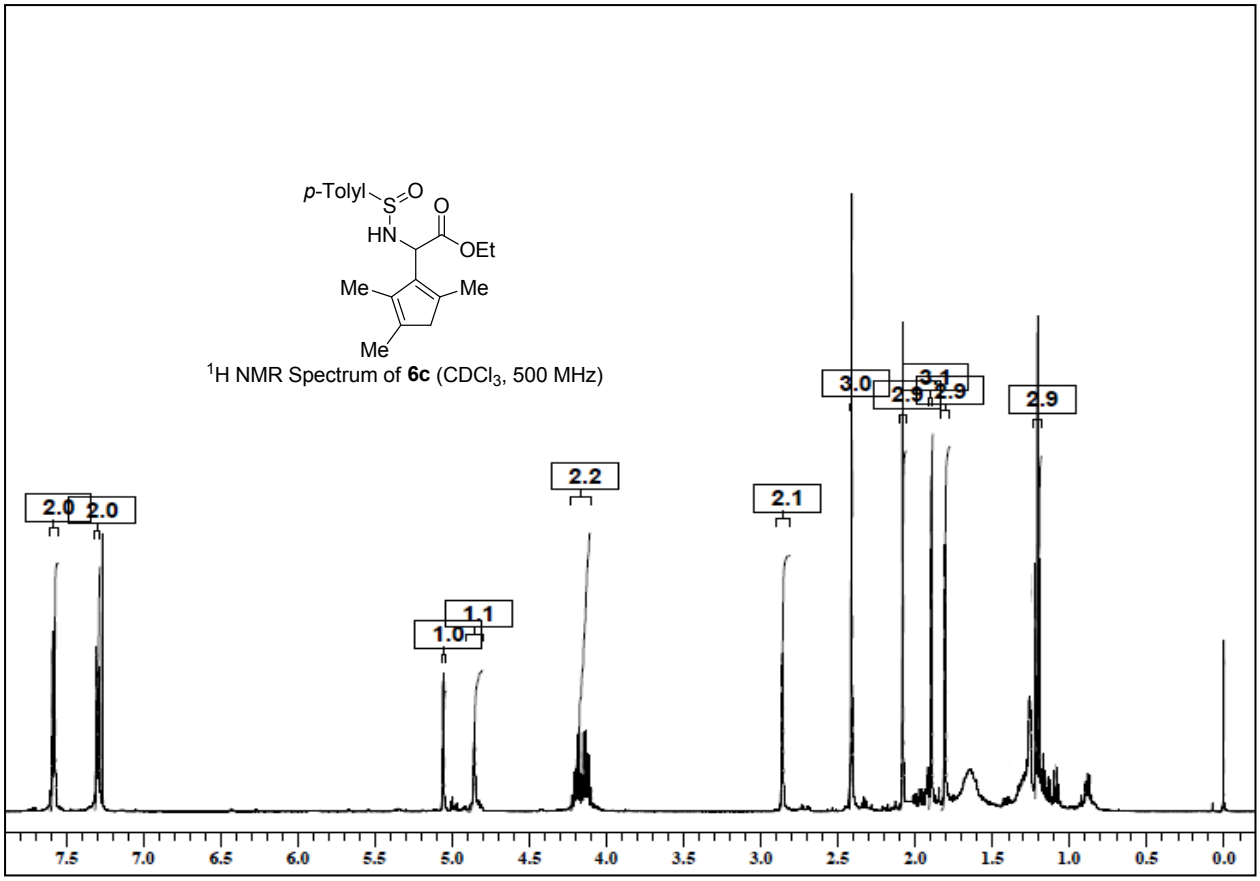
^{13}C NMR Spectrum of **6a** ($CDCl_3$, 125 MHz)



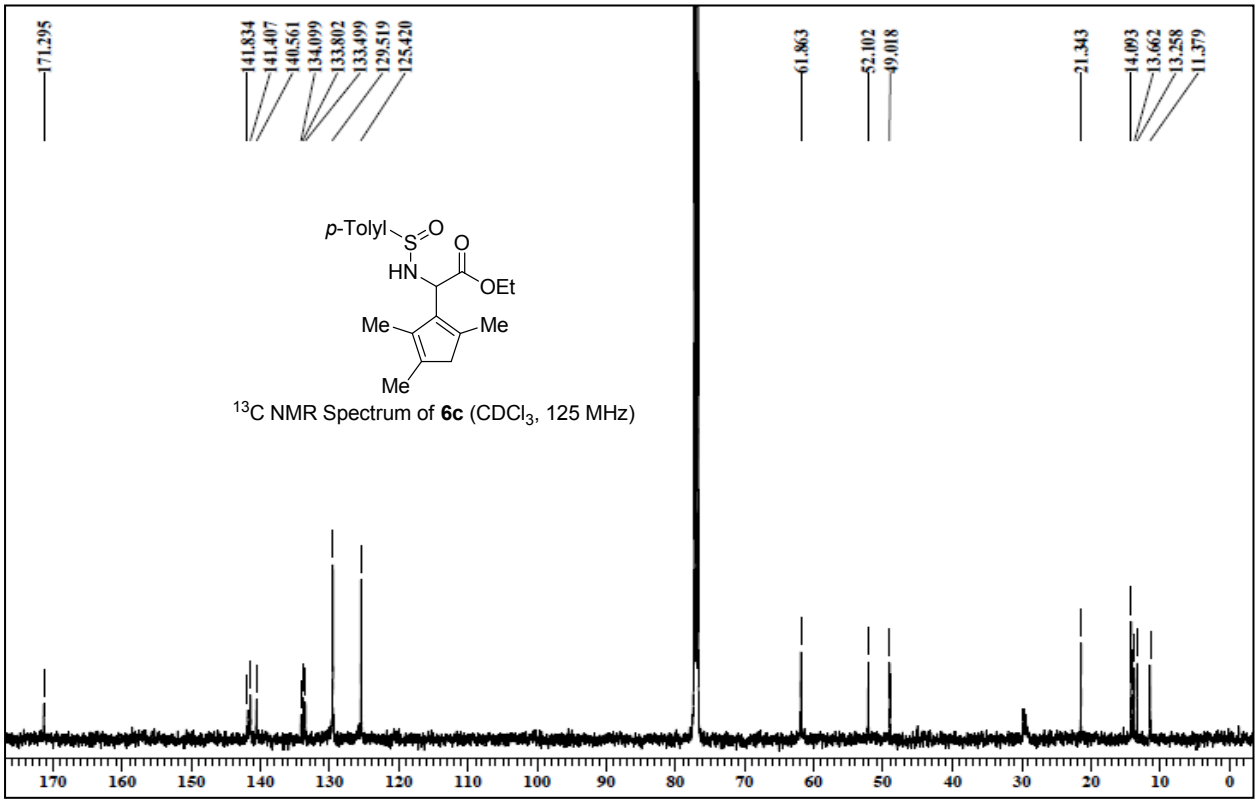
^{1}H NMR Spectrum of **6b** ($CDCl_3$, 500 MHz)



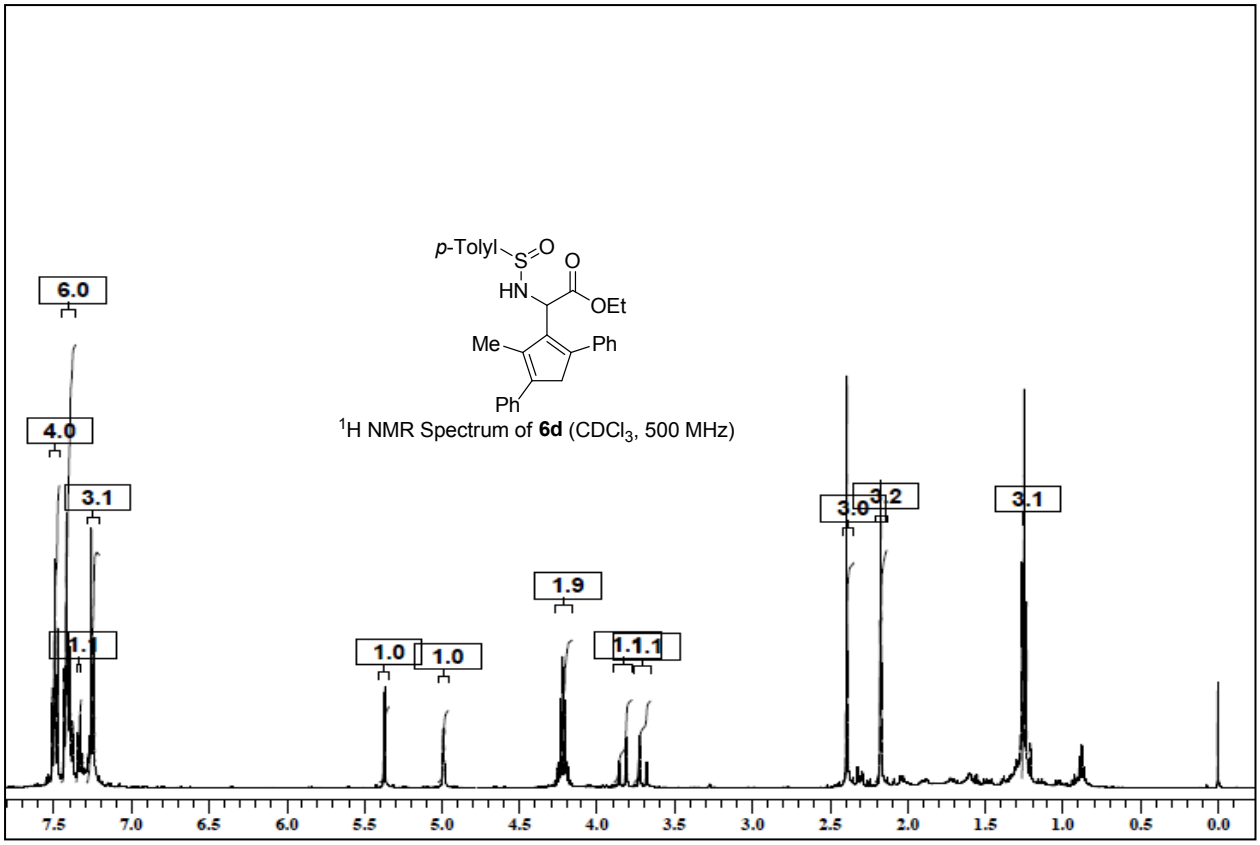
^{13}C NMR Spectrum of **6b** ($CDCl_3$, 125 MHz)



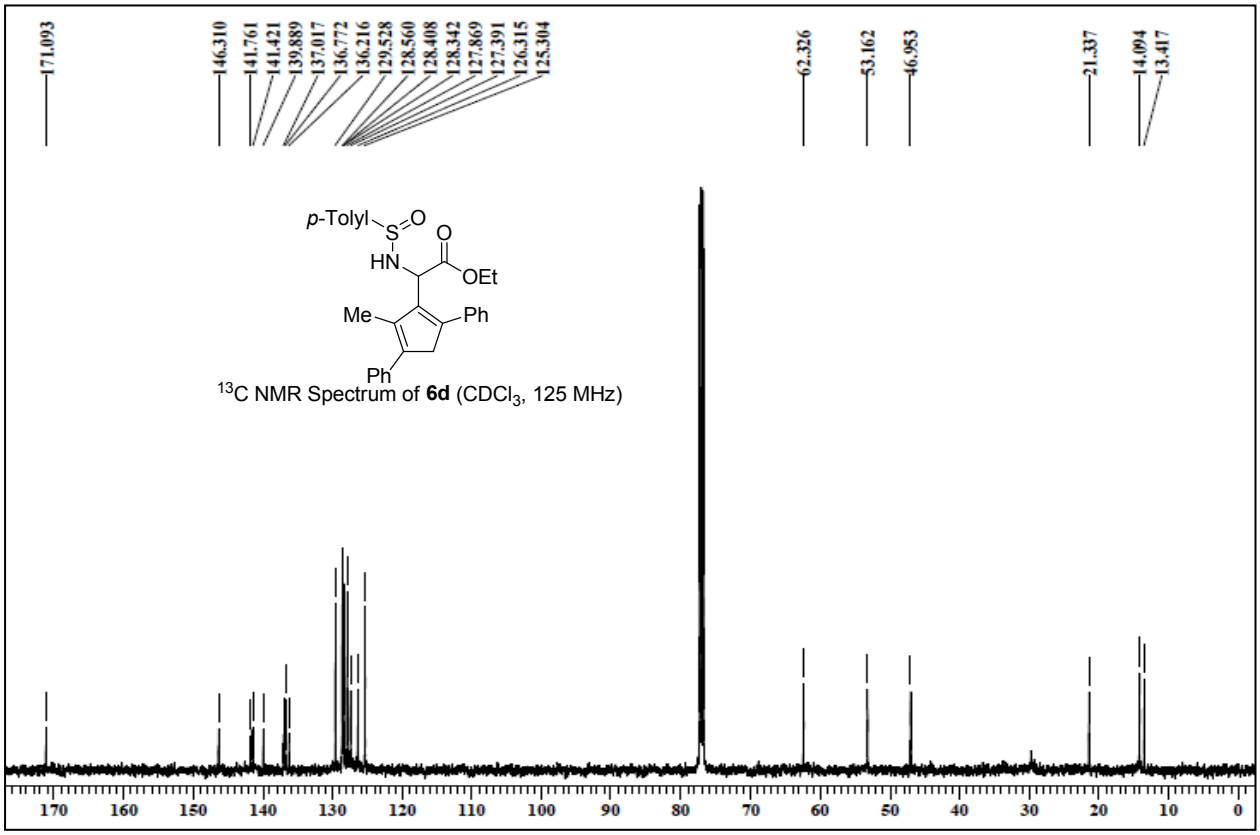
^{1}H NMR Spectrum of **6c** ($CDCl_3$, 500 MHz)



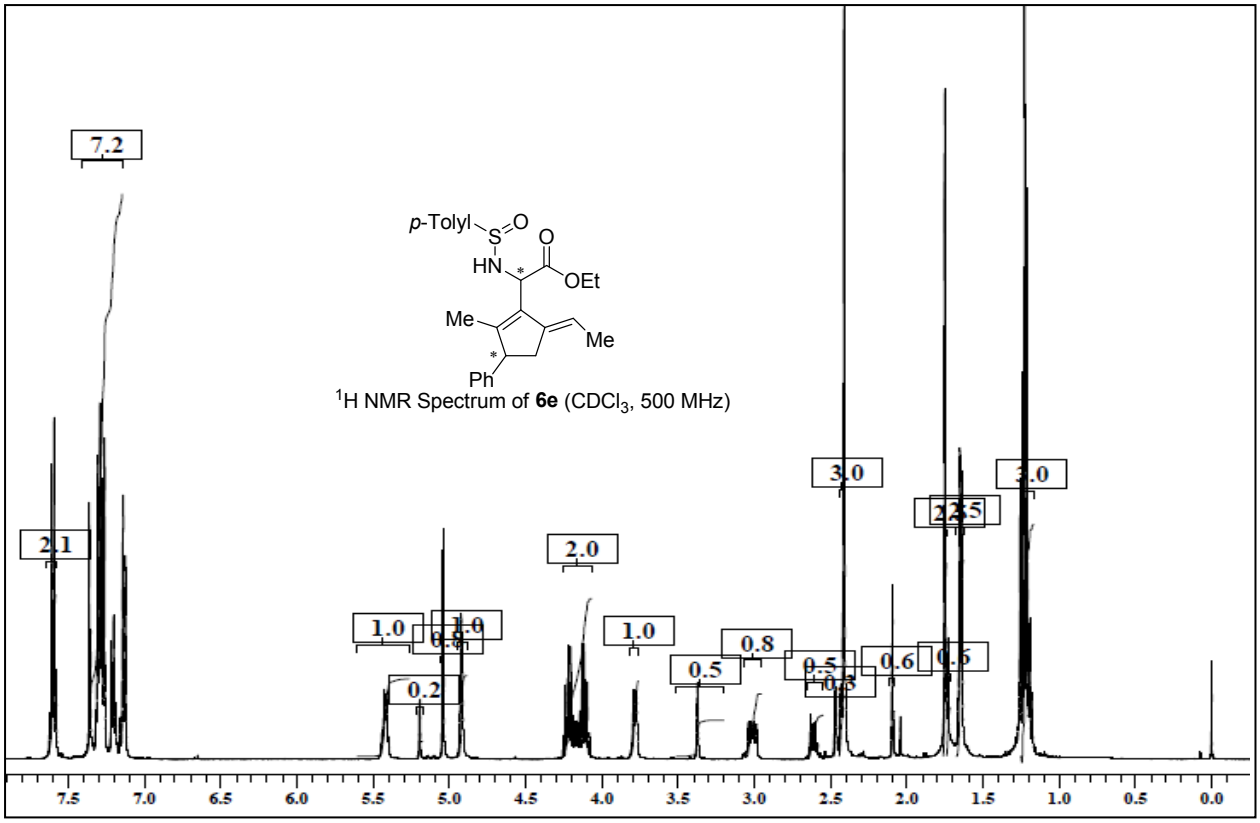
^{13}C NMR Spectrum of **6c** ($CDCl_3$, 125 MHz)



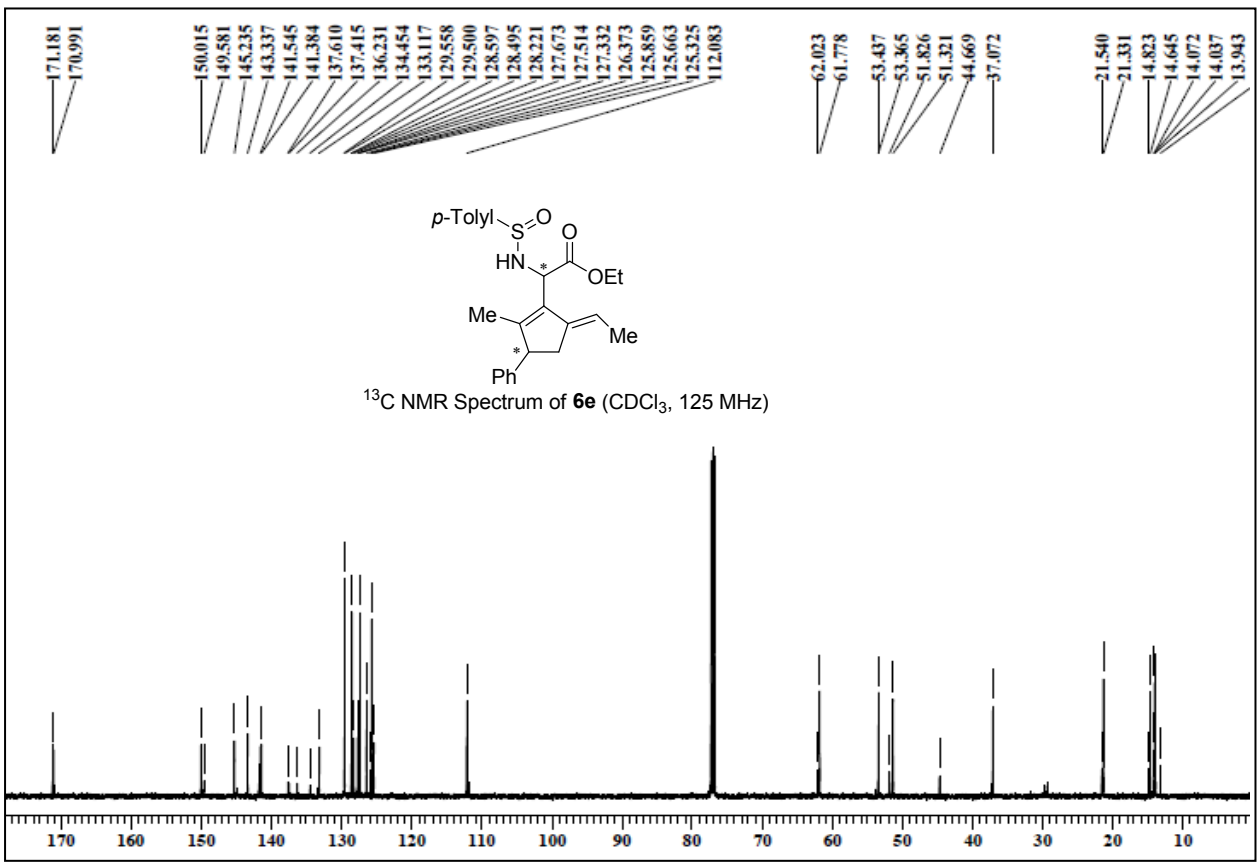
^{1}H NMR Spectrum of **6d** ($CDCl_3$, 500 MHz)



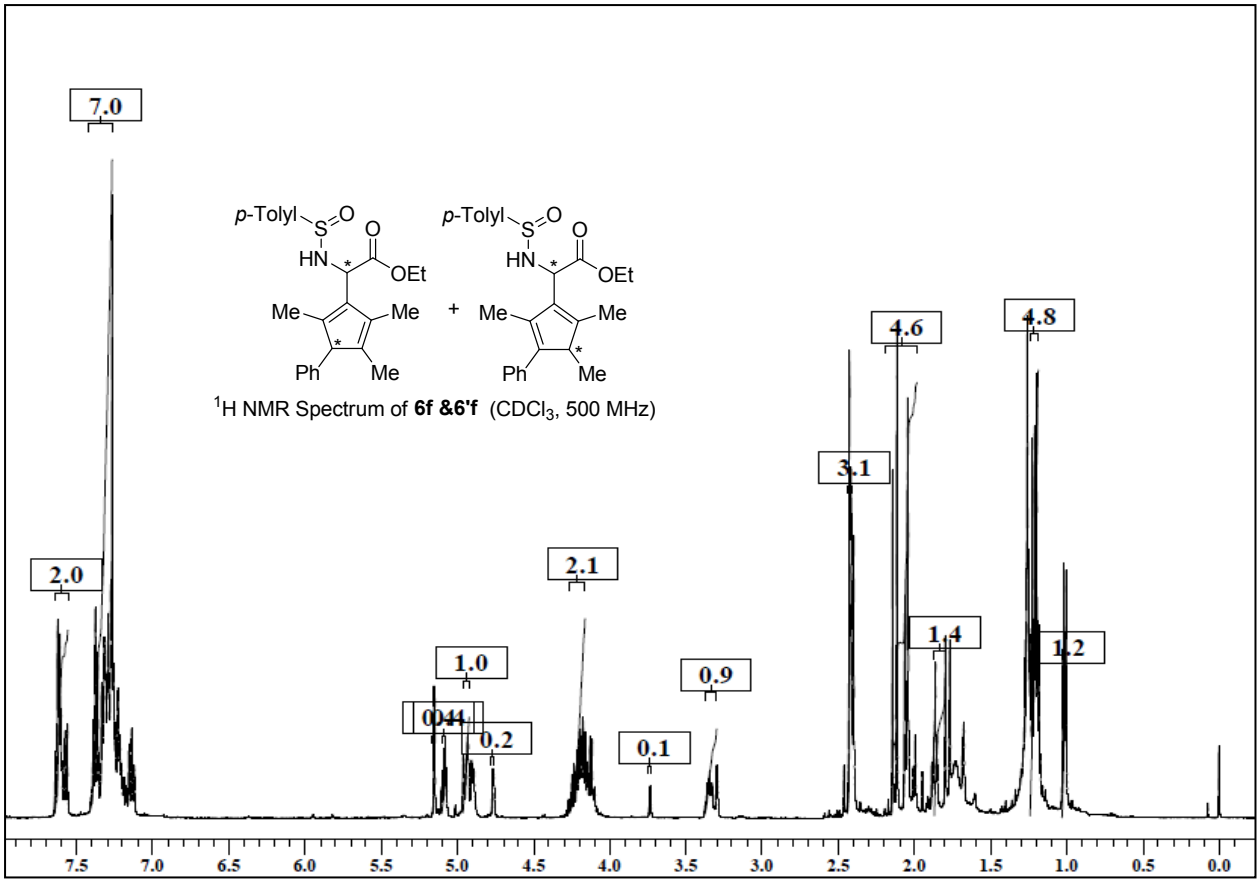
^{13}C NMR Spectrum of **6d** ($CDCl_3$, 125 MHz)



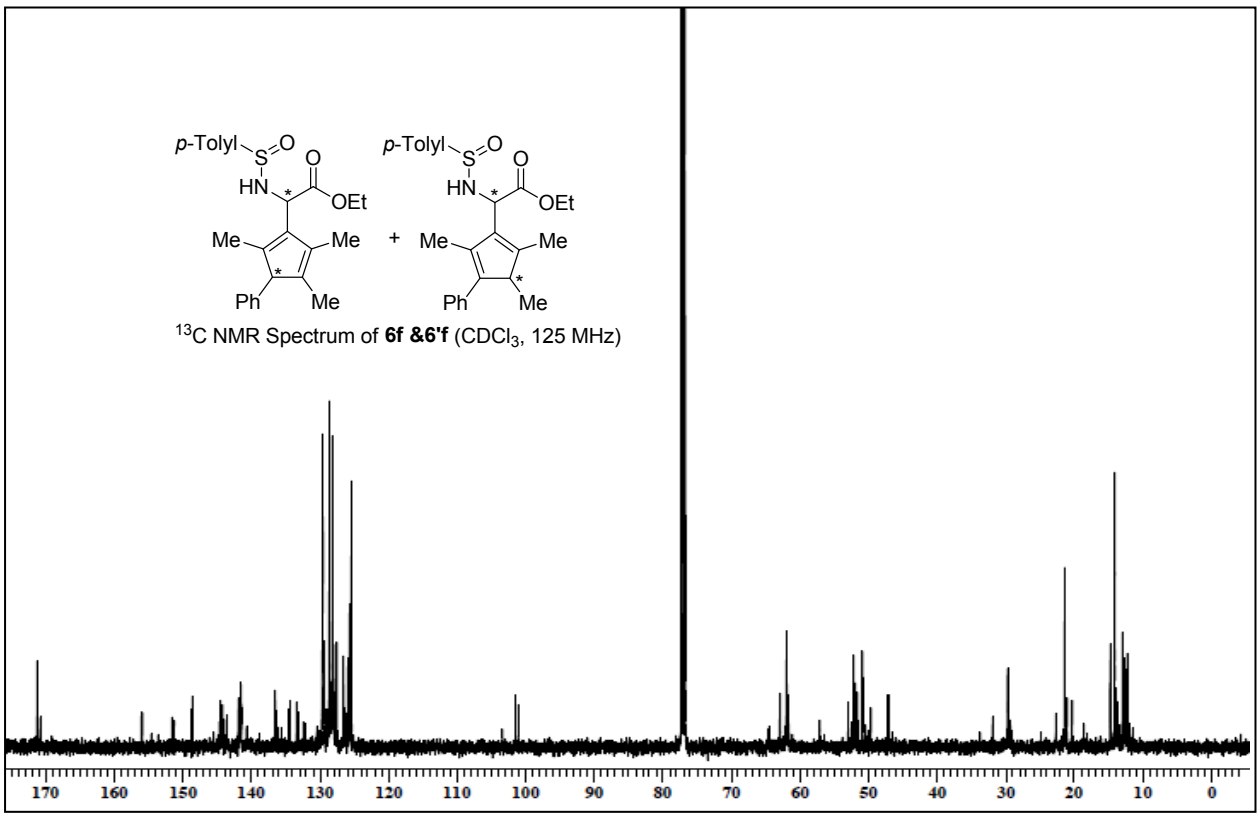
^{1}H NMR Spectrum of **6e** ($CDCl_3$, 500 MHz)



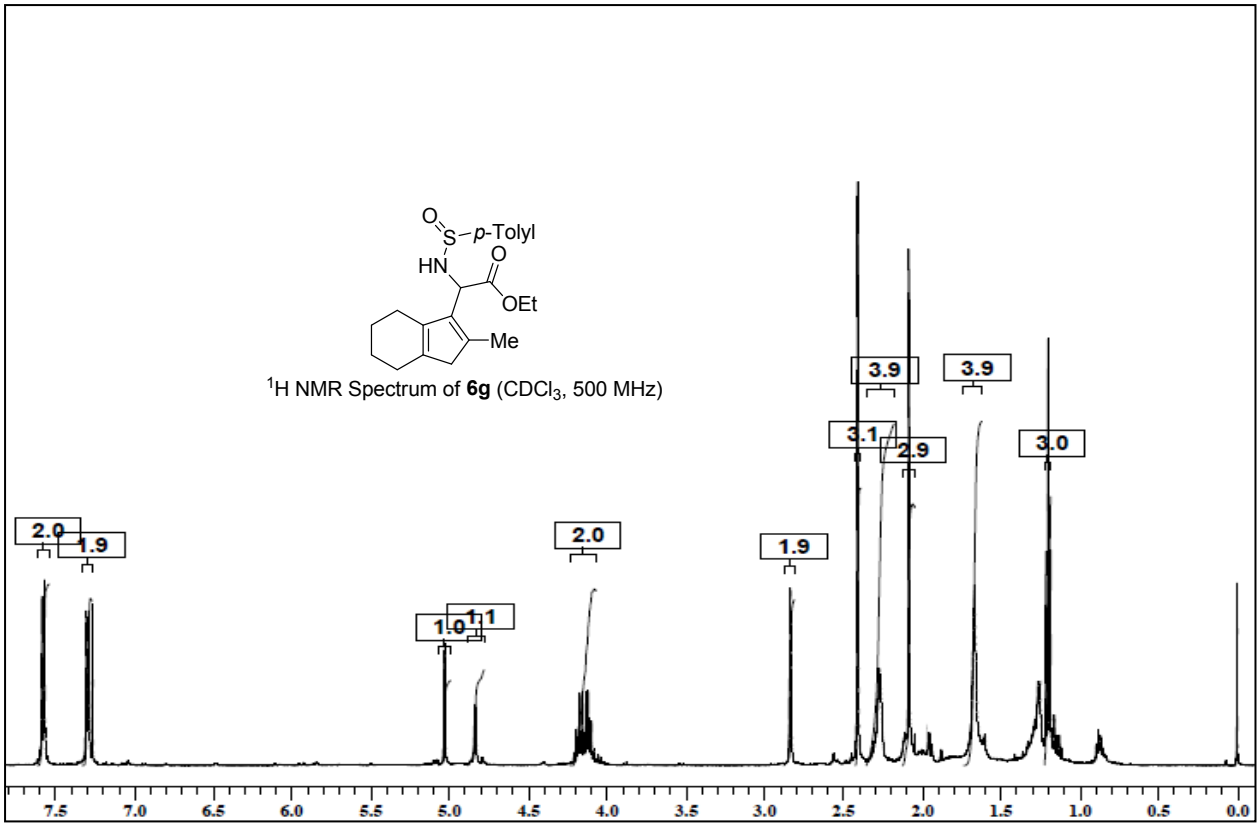
^{13}C NMR Spectrum of **6e** ($CDCl_3$, 125 MHz)



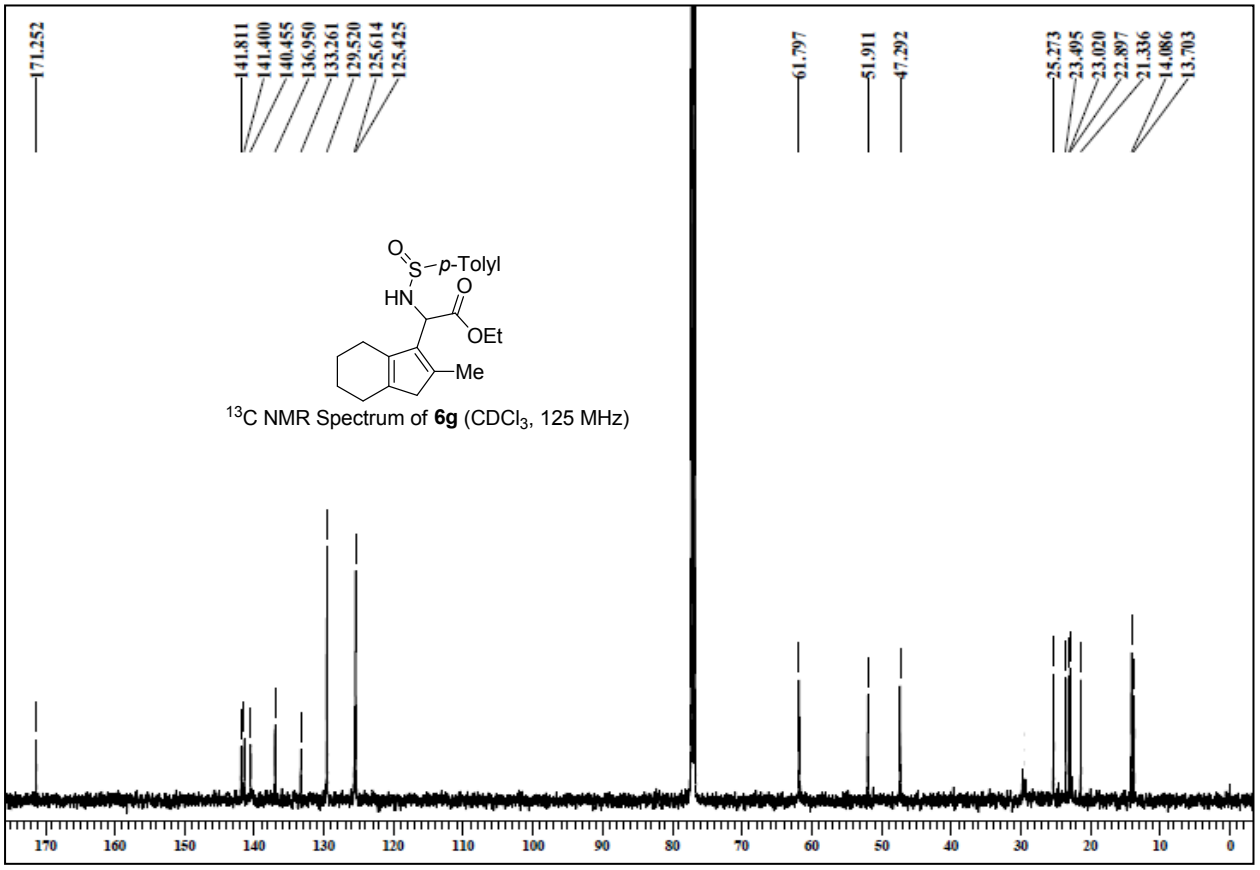
^{1}H NMR Spectrum of **6f &6'f** ($CDCl_3$, 500 MHz)



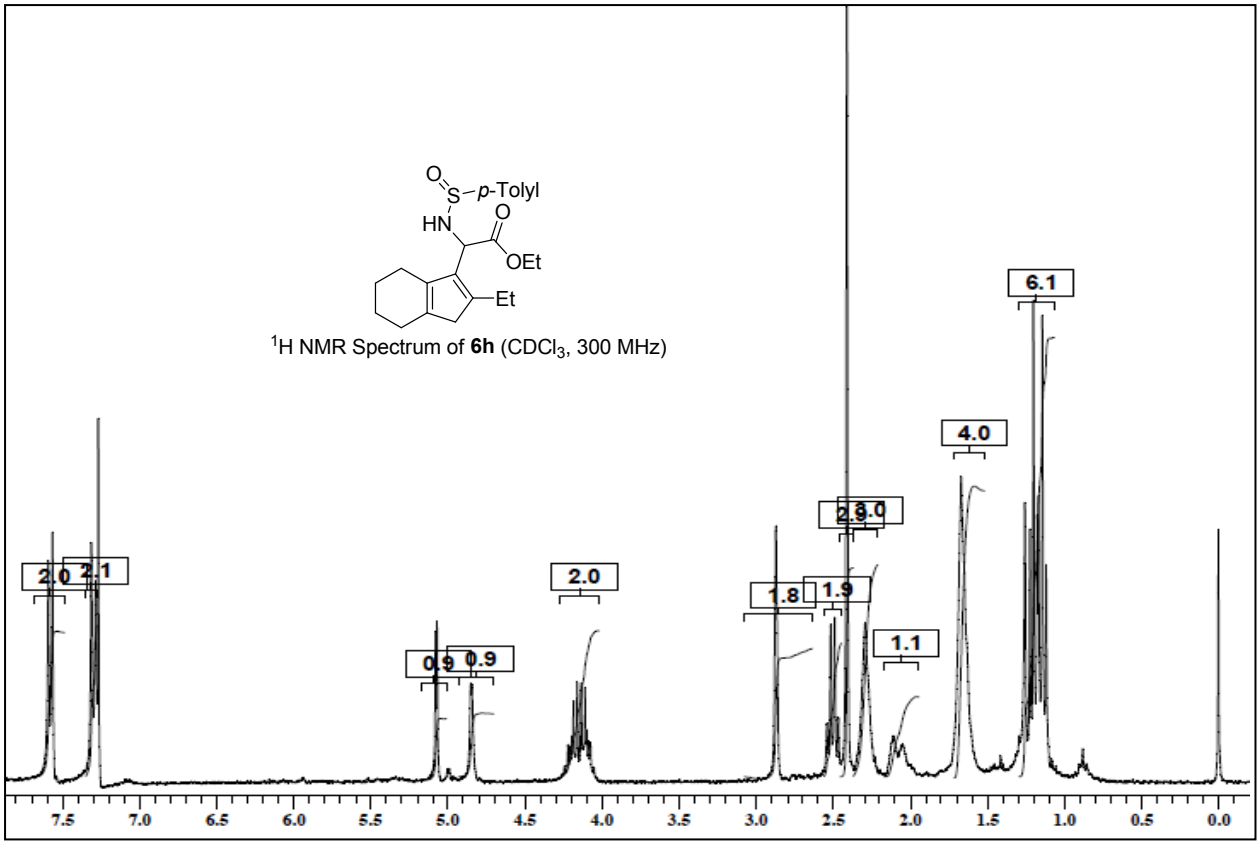
^{13}C NMR Spectrum of **6f &6'f** ($CDCl_3$, 125 MHz)



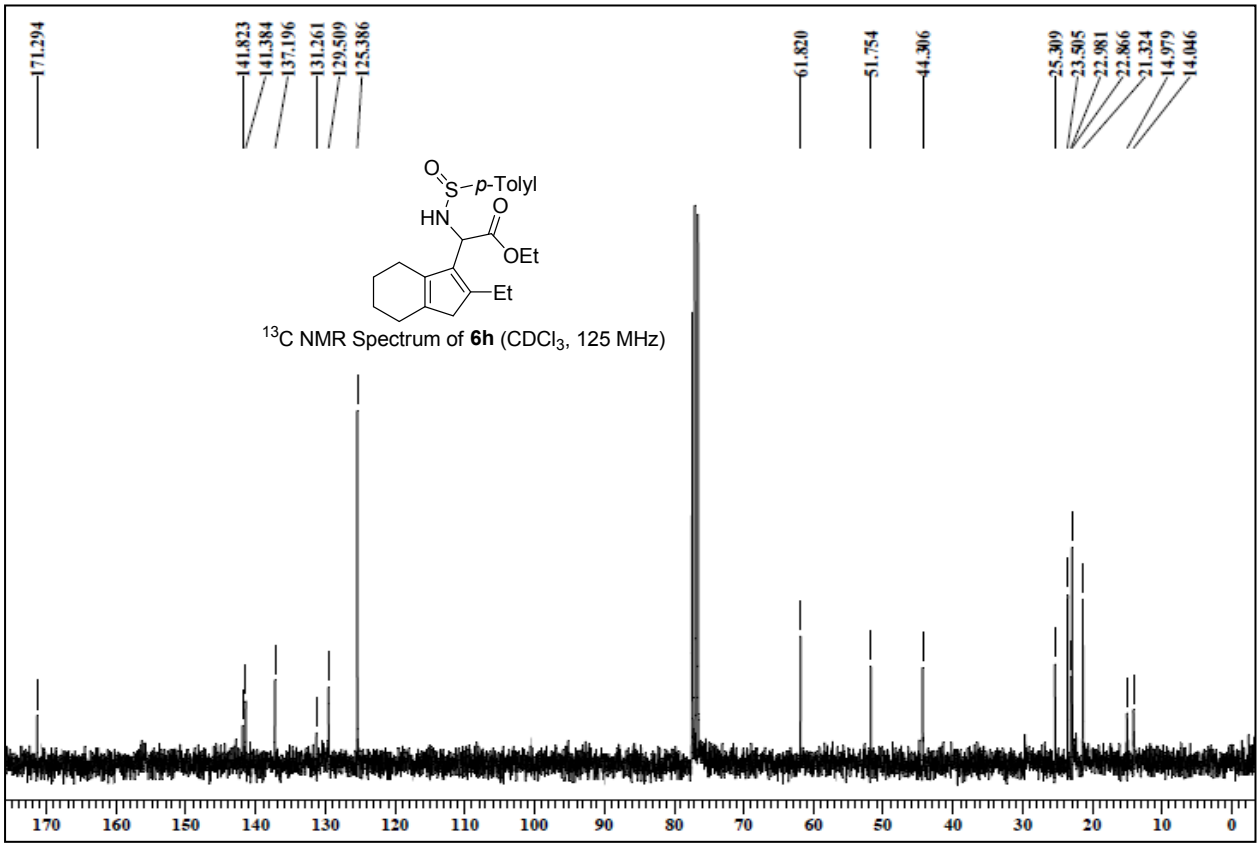
^{1}H NMR Spectrum of **6g** ($CDCl_3$, 500 MHz)



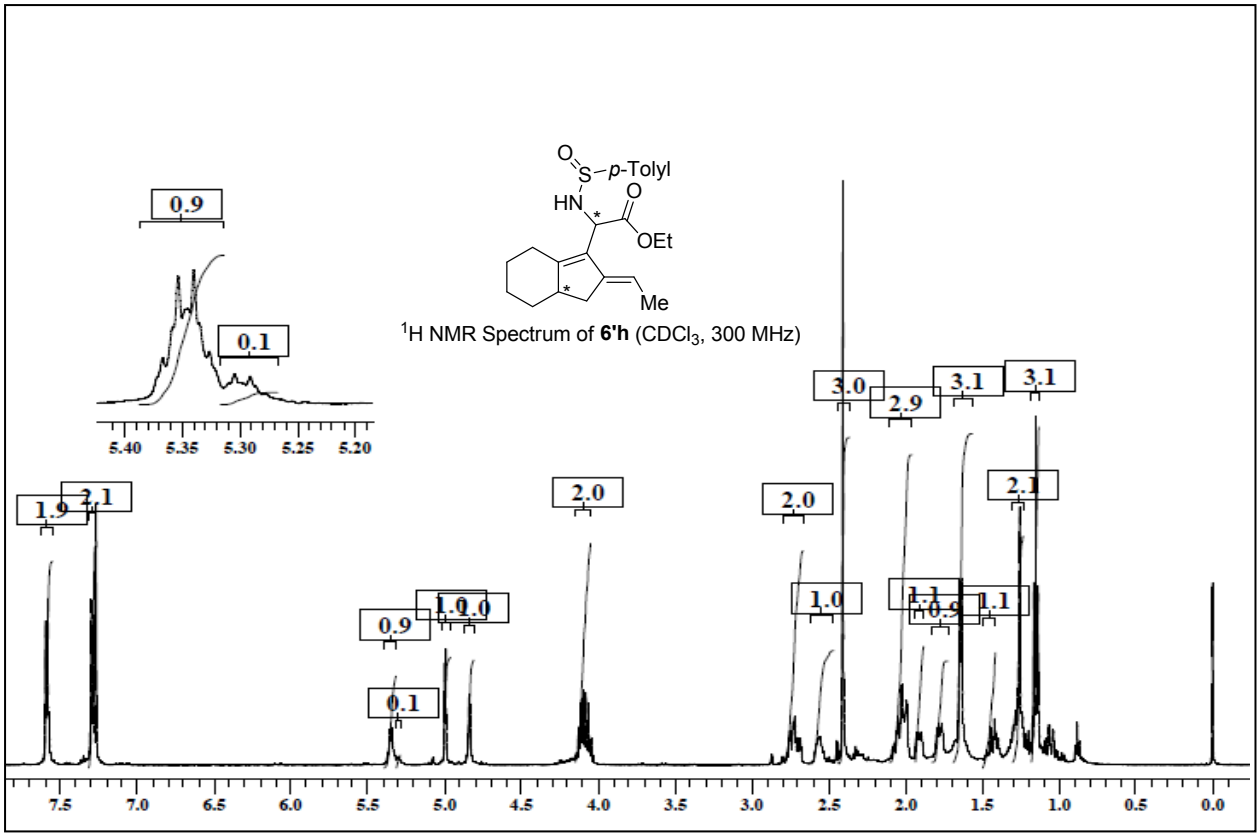
^{13}C NMR Spectrum of **6g** ($CDCl_3$, 125 MHz)



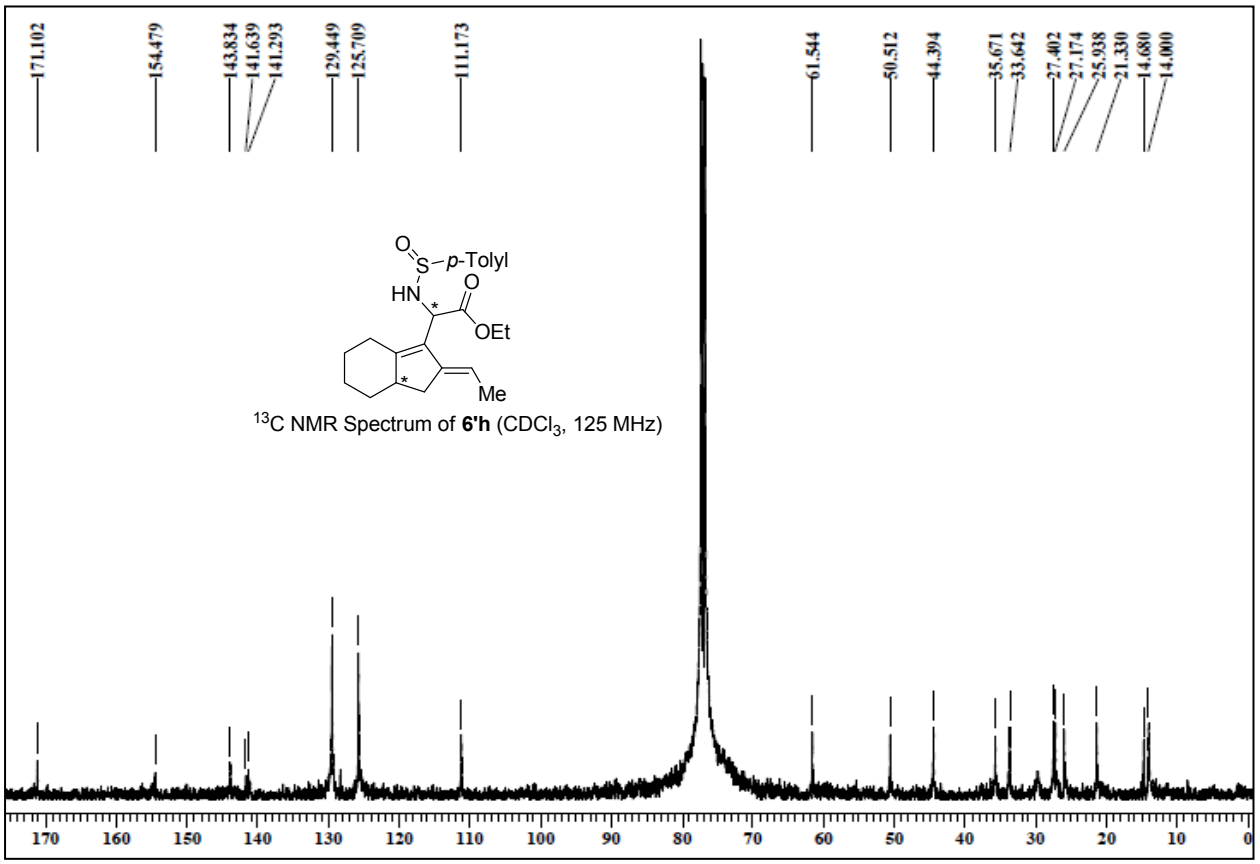
^{1}H NMR Spectrum of **6h** ($CDCl_3$, 300 MHz)



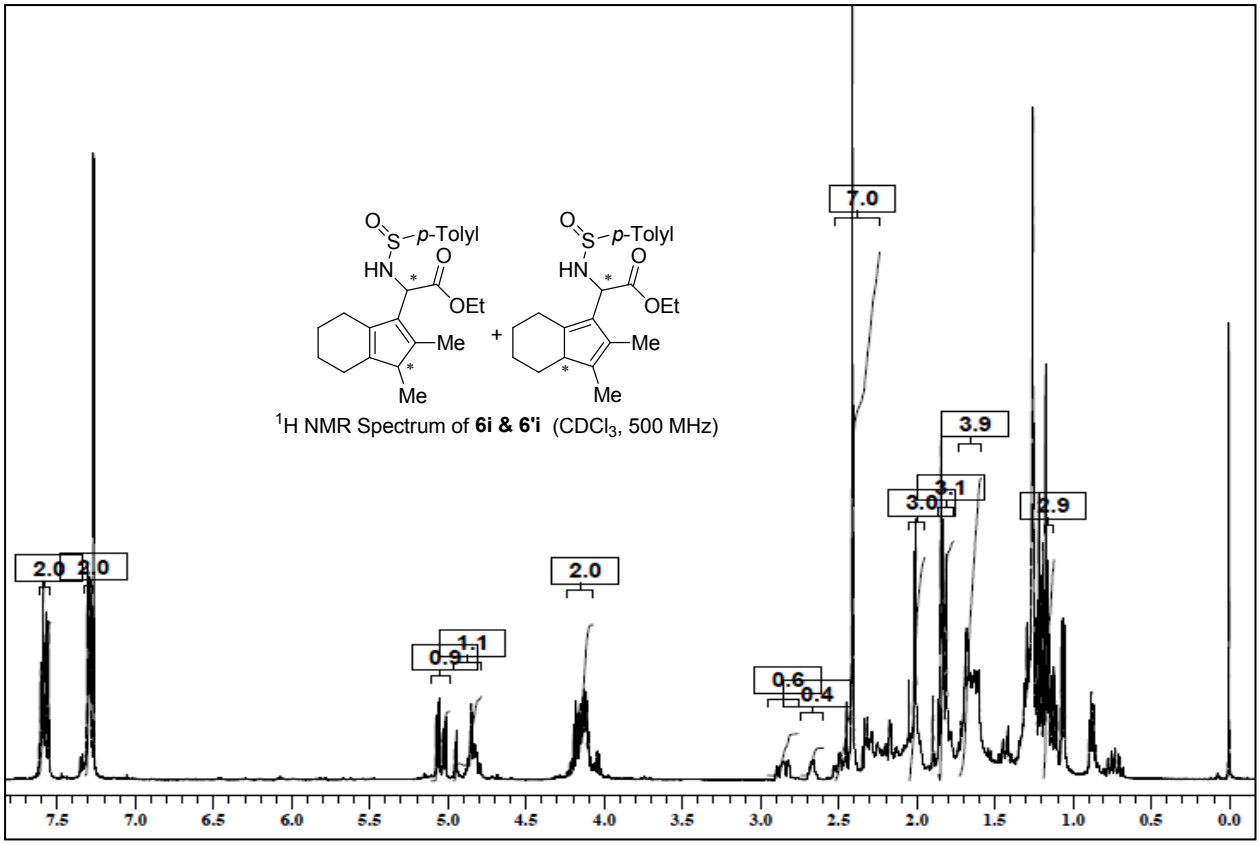
^{13}C NMR Spectrum of **6h** ($CDCl_3$, 125 MHz)



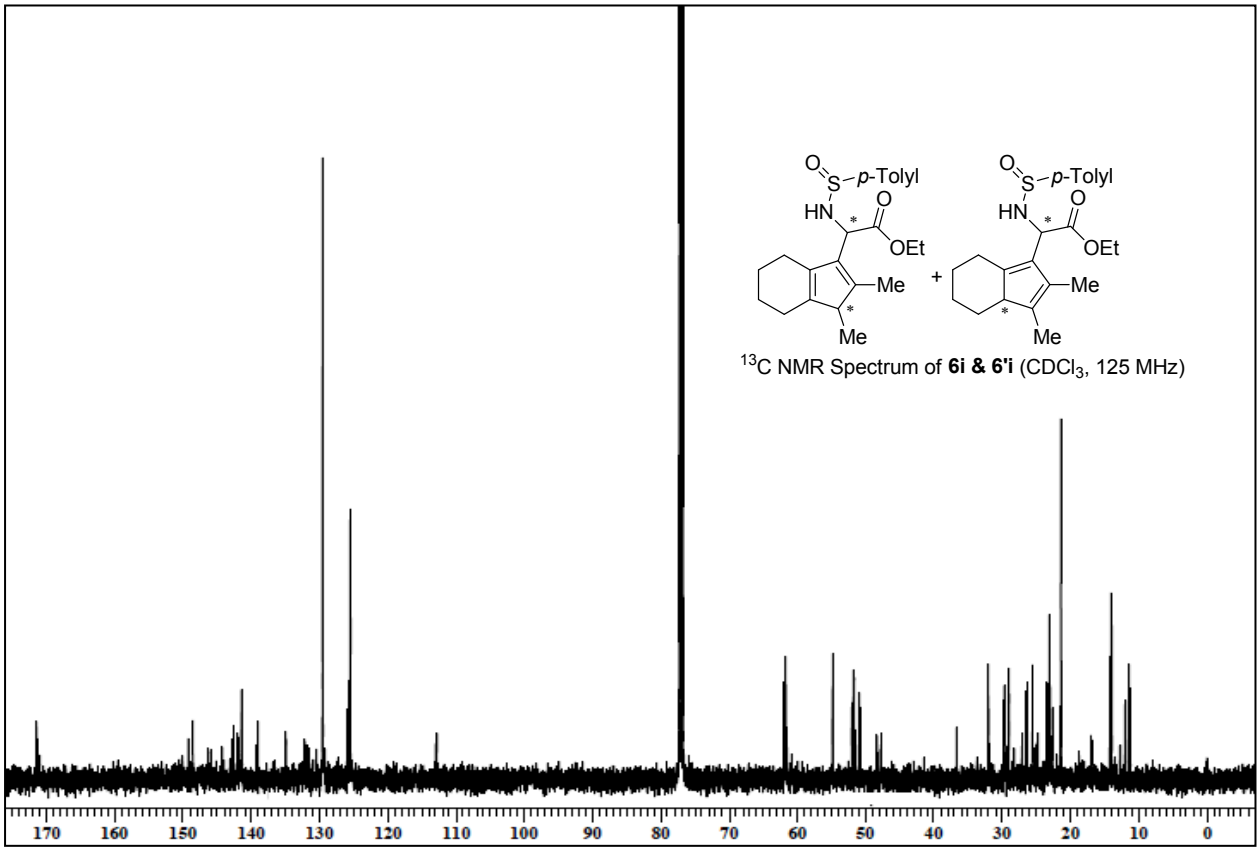
^{1}H NMR Spectrum of **6'h** ($CDCl_3$, 300 MHz)



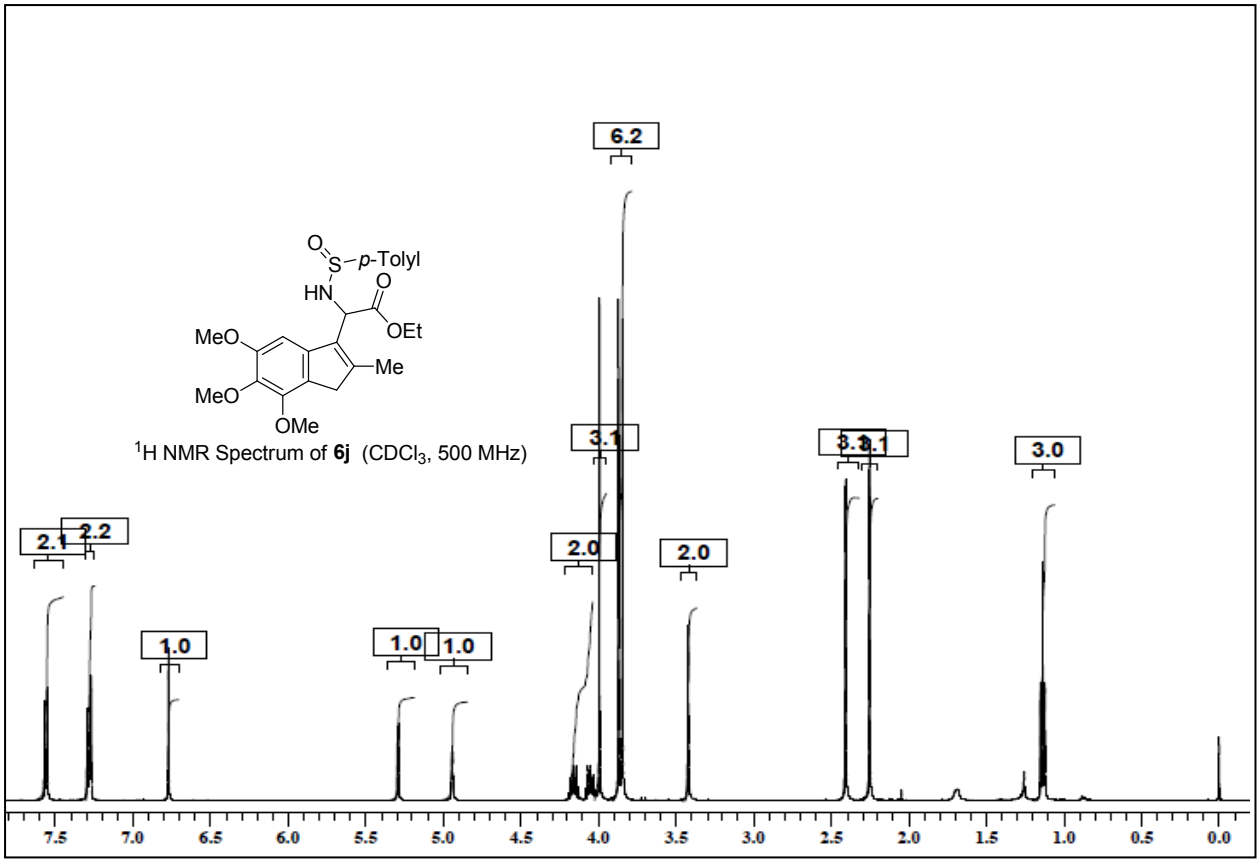
^{13}C NMR Spectrum of **6'h** ($CDCl_3$, 125 MHz)



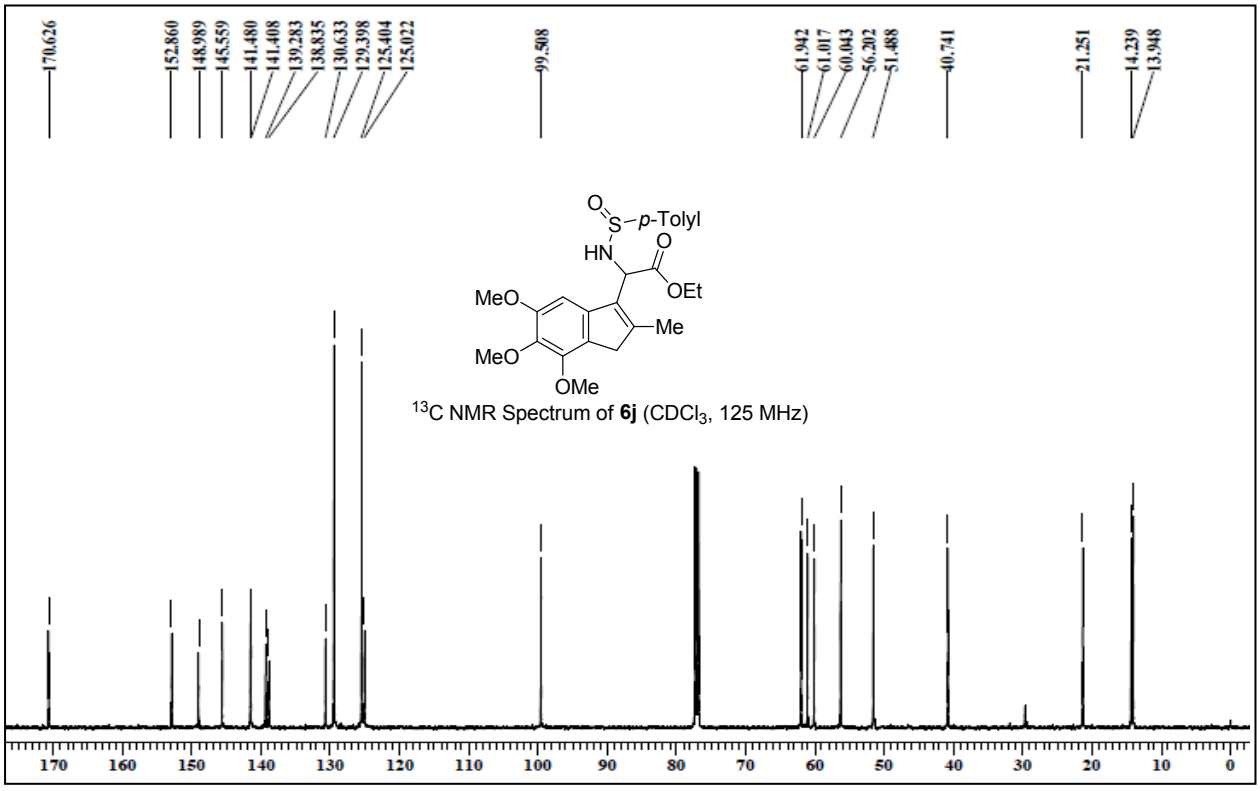
^{1}H NMR Spectrum of **6i & 6'i** ($CDCl_3$, 500 MHz)



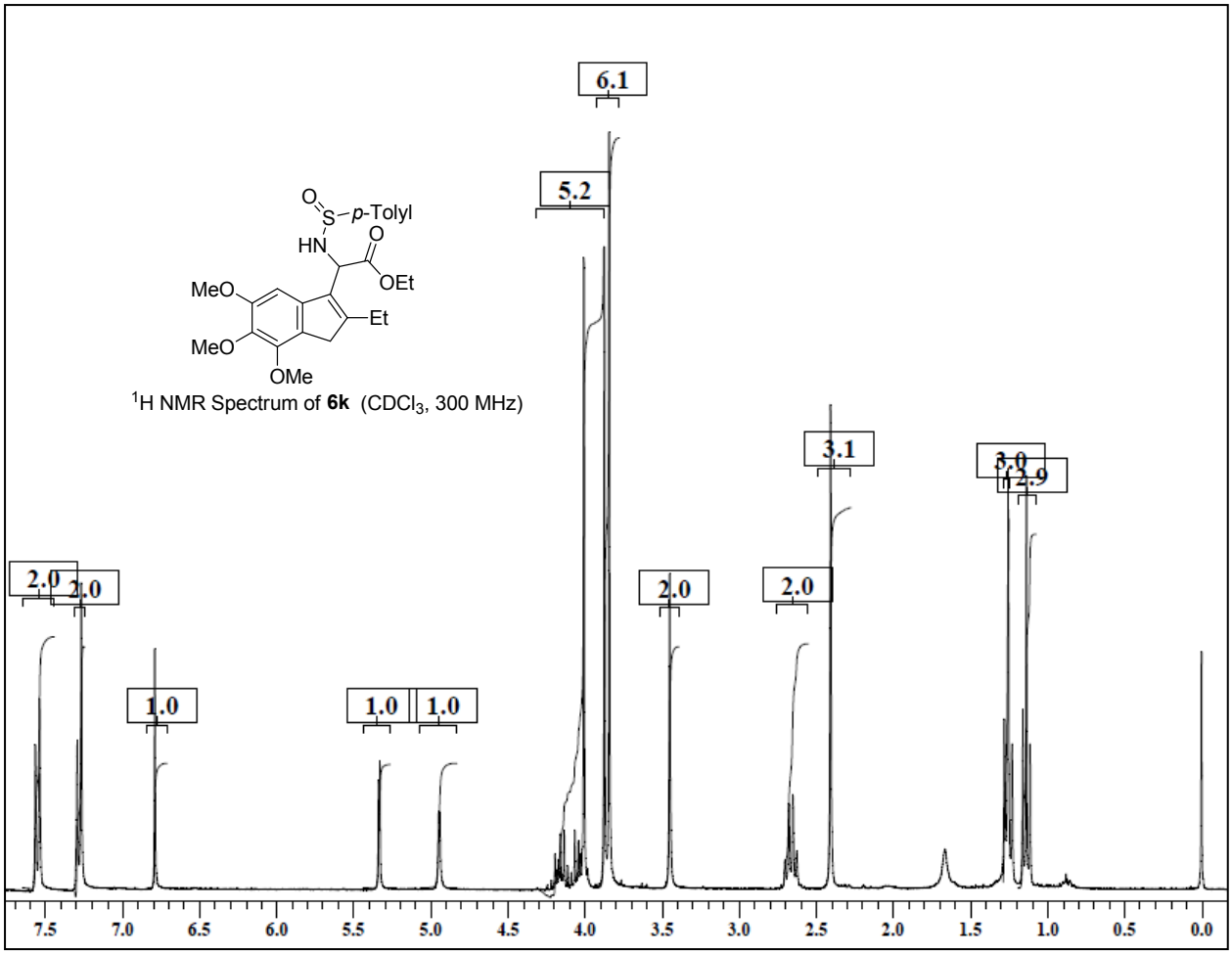
^{13}C NMR Spectrum of **6i & 6'i** ($CDCl_3$, 125 MHz)



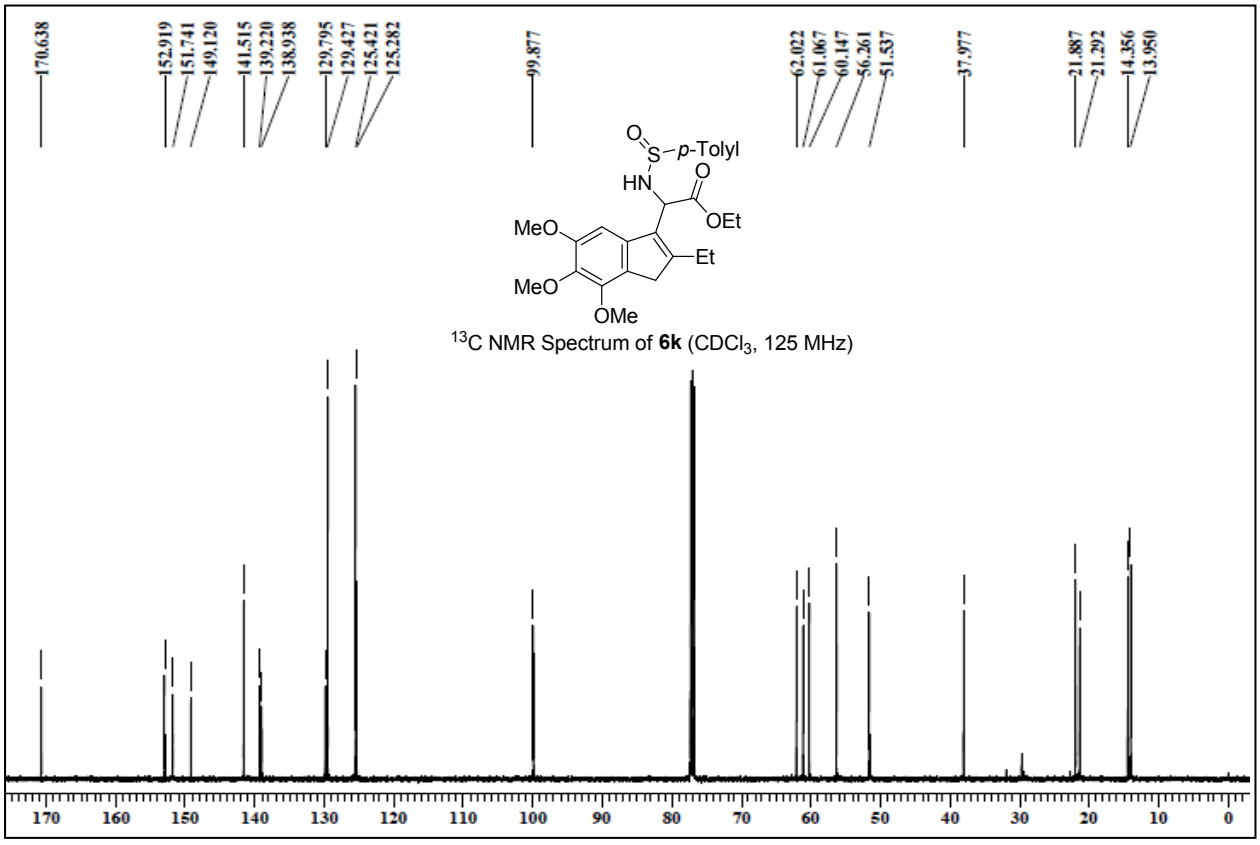
^{1}H NMR Spectrum of **6j** ($CDCl_3$, 500 MHz)



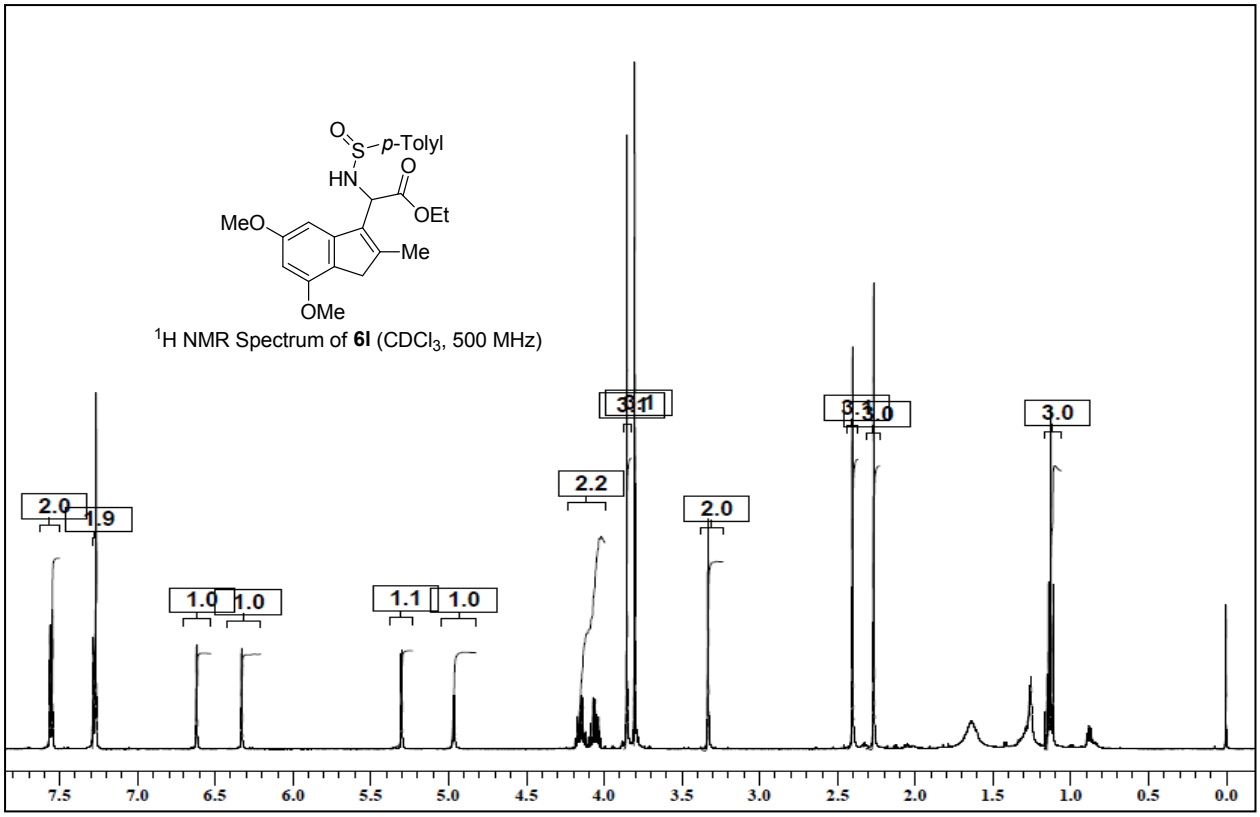
^{13}C NMR Spectrum of **6j** ($CDCl_3$, 125 MHz)



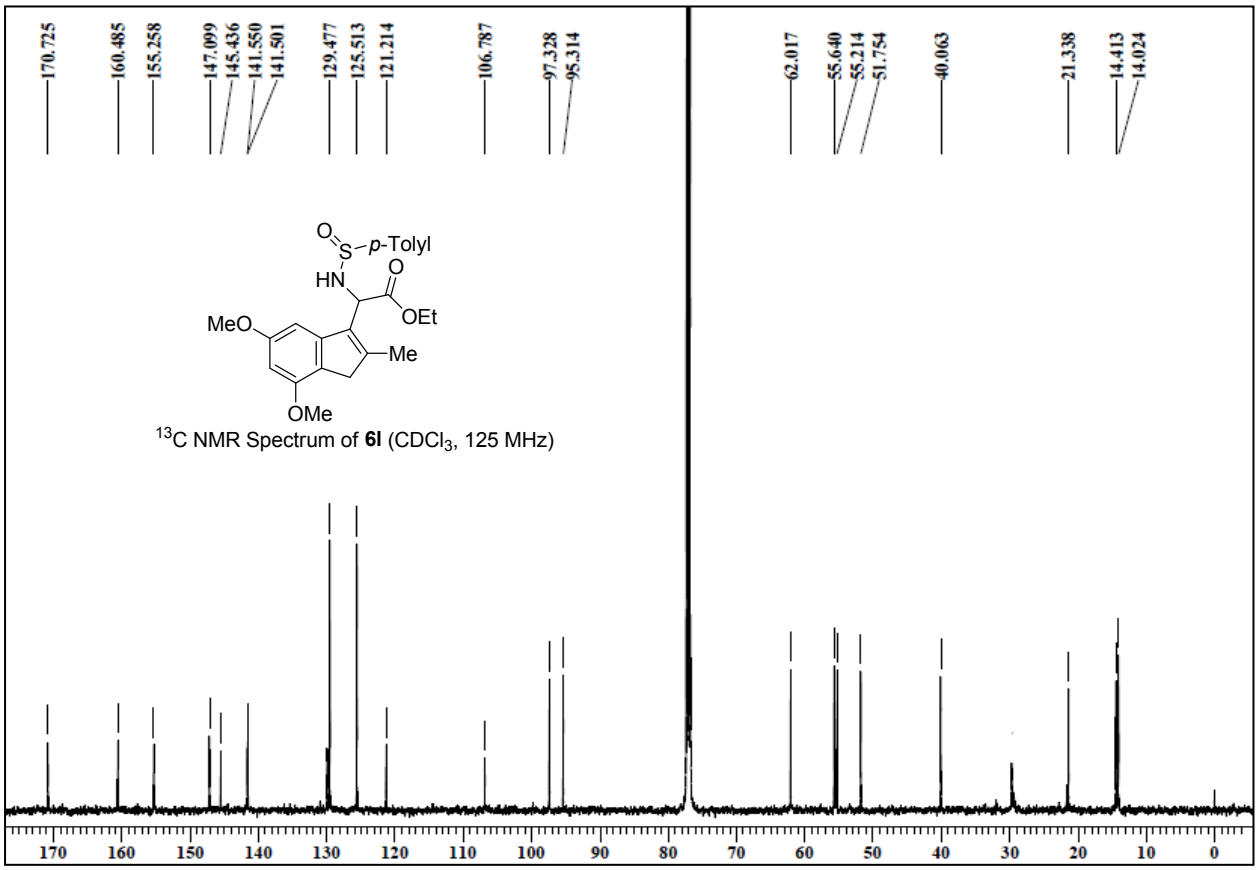
^{1}H NMR Spectrum of **6k** ($CDCl_3$, 300 MHz)



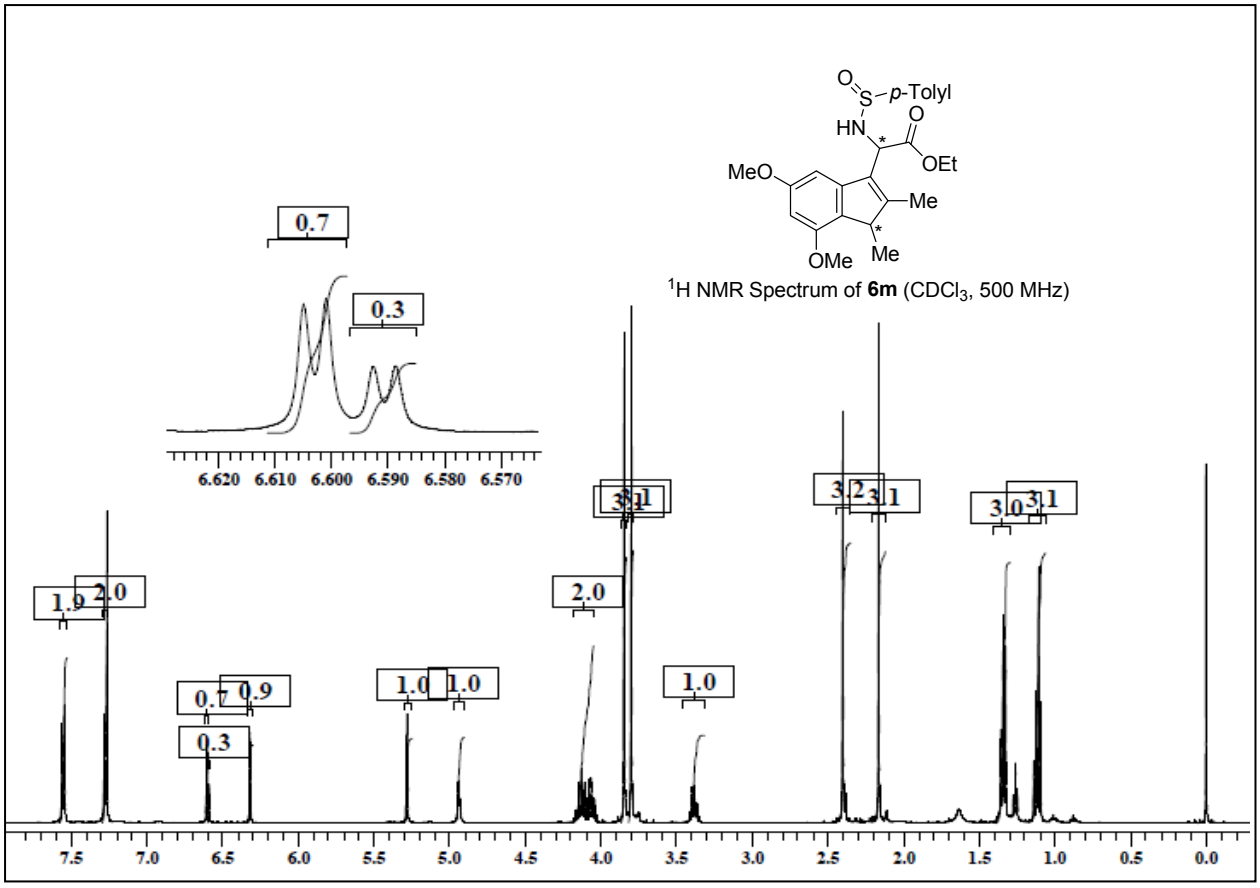
^{13}C NMR Spectrum of **6k** ($CDCl_3$, 125 MHz)



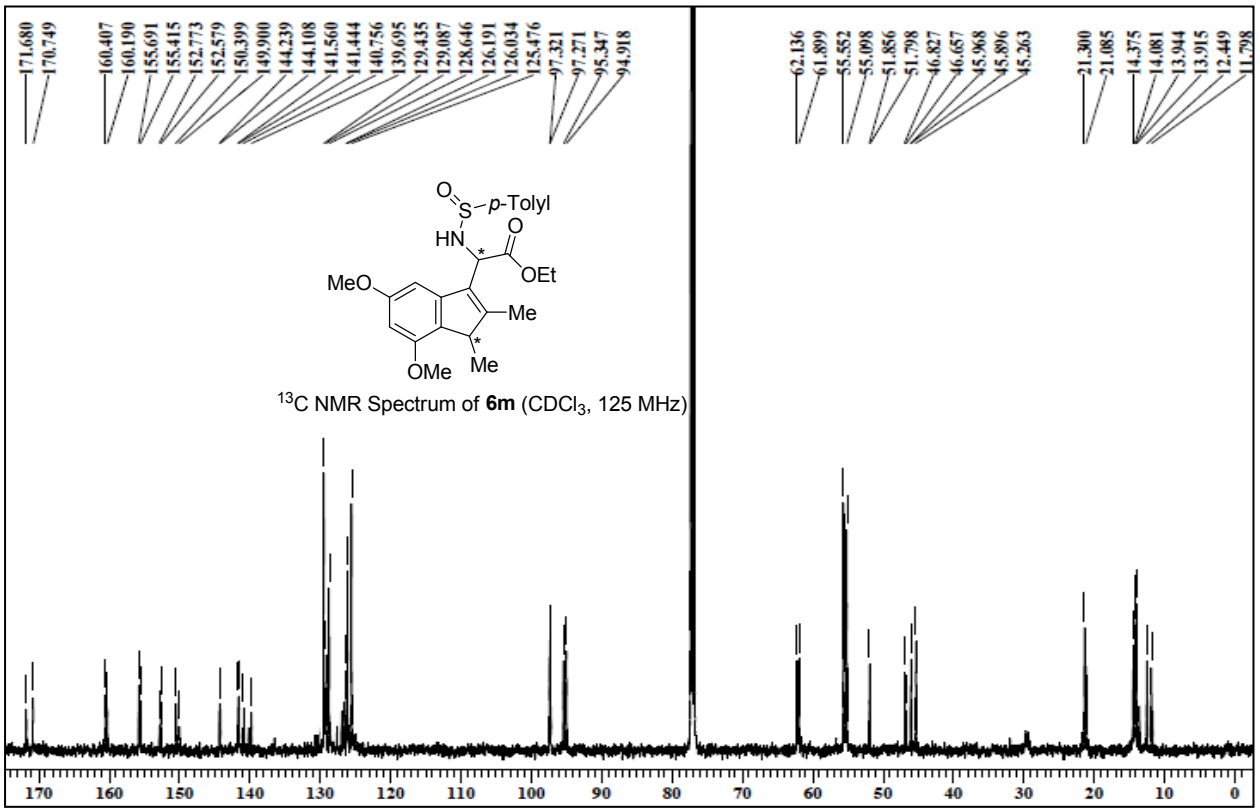
^{1}H NMR Spectrum of **6l** ($CDCl_3$, 500 MHz)



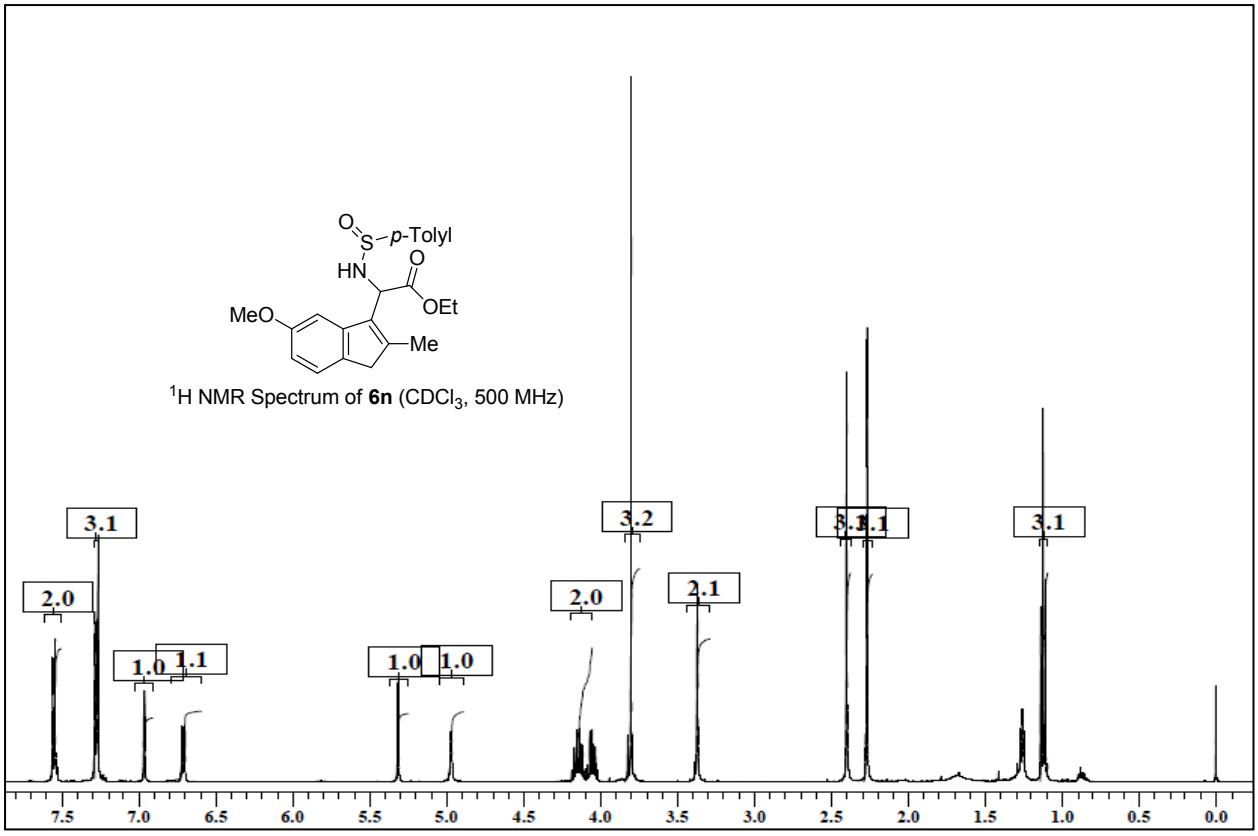
^{13}C NMR Spectrum of **6l** ($CDCl_3$, 125 MHz)



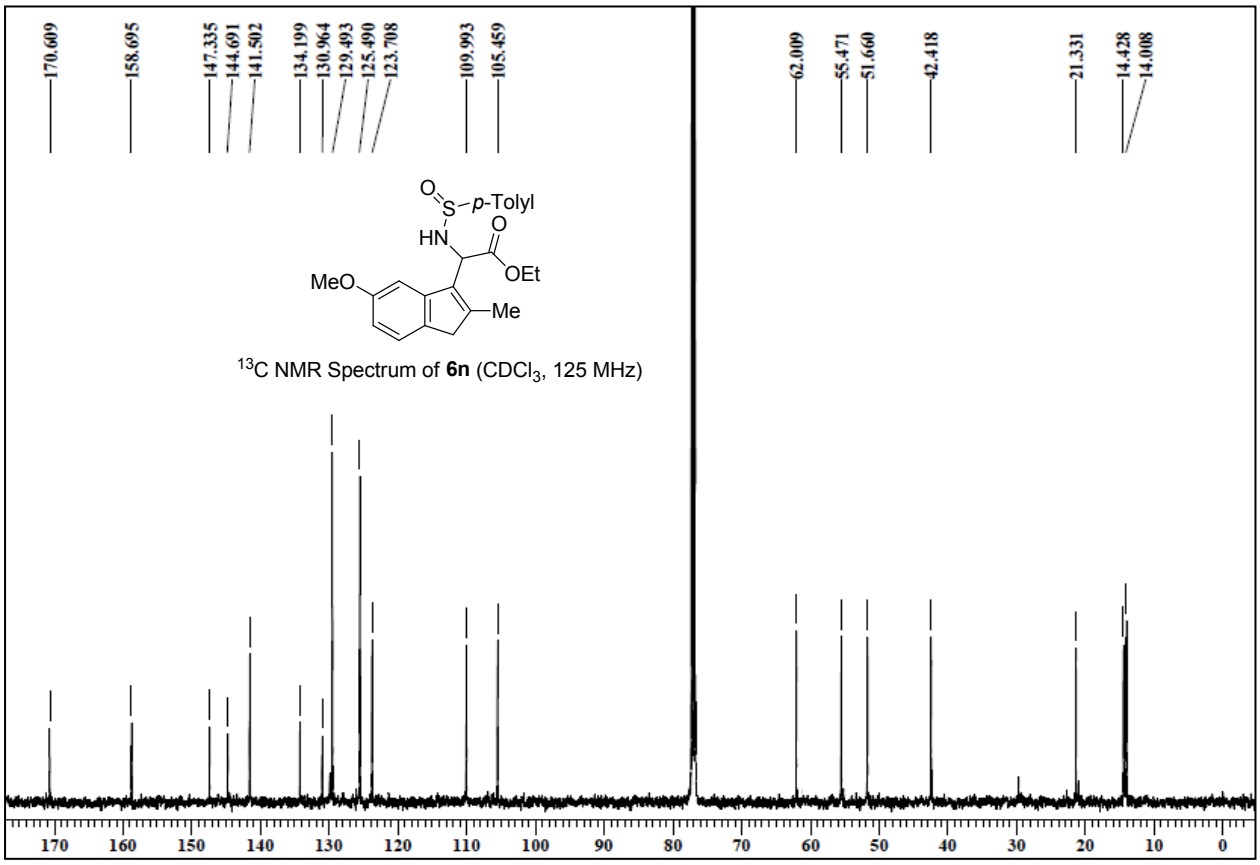
^{1}H NMR Spectrum of **6m** ($CDCl_3$, 500 MHz)



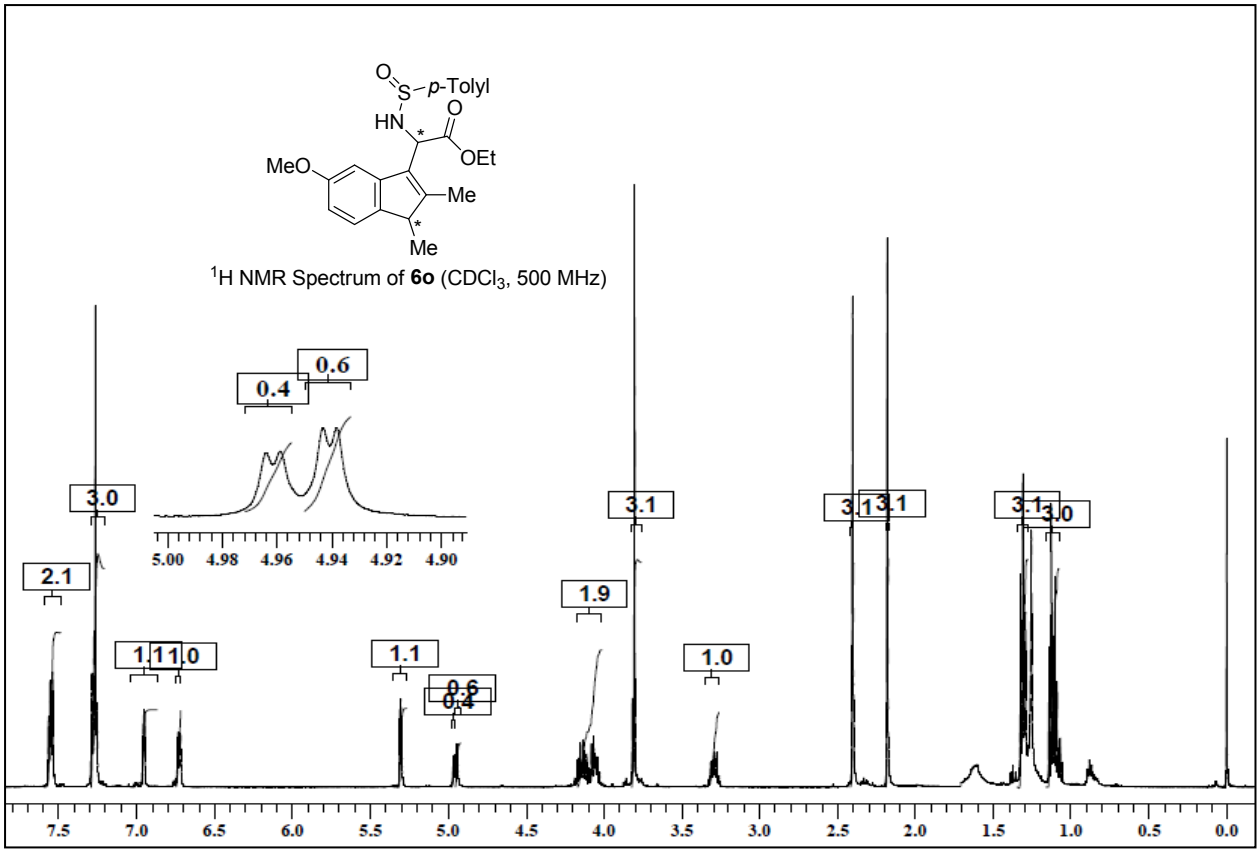
^{13}C NMR Spectrum of **6m** ($CDCl_3$, 125 MHz)



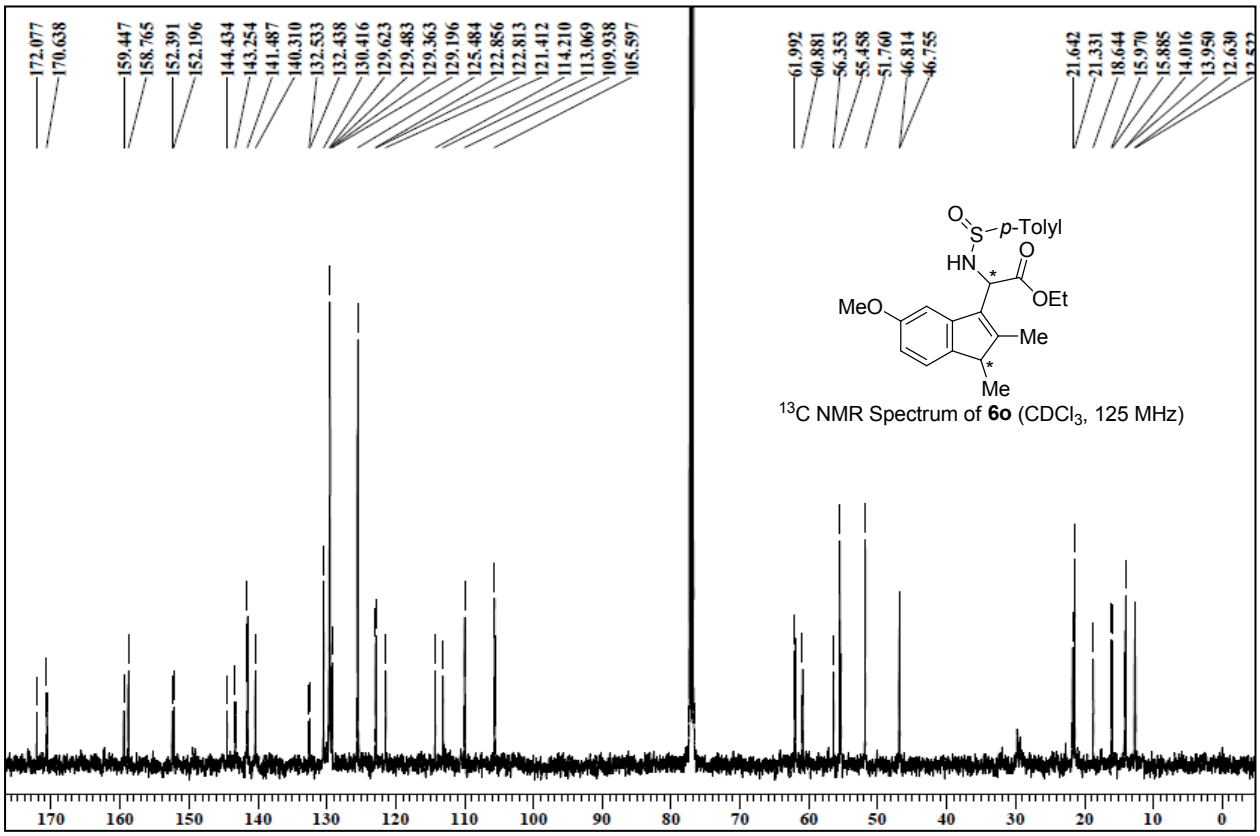
^{1}H NMR Spectrum of **6n** ($CDCl_3$, 500 MHz)



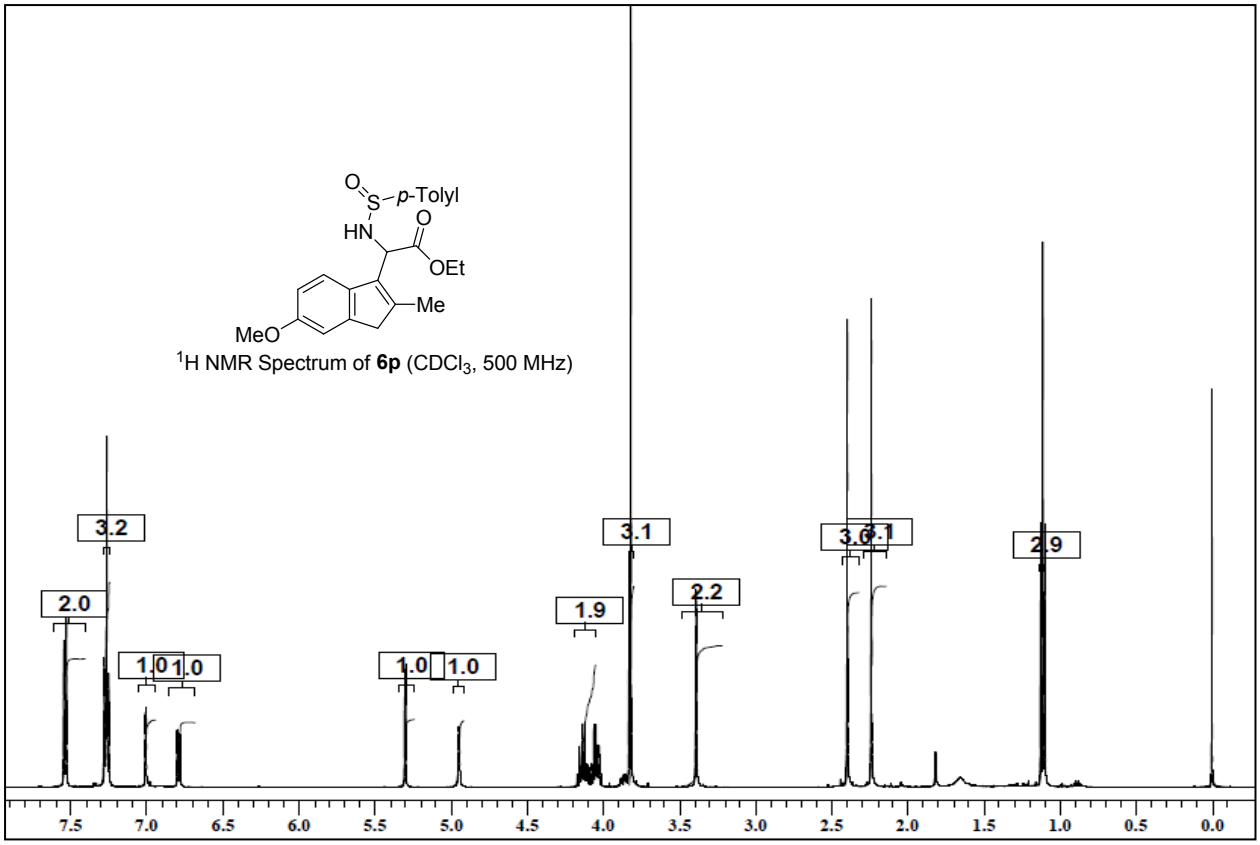
^{13}C NMR Spectrum of **6n** ($CDCl_3$, 125 MHz)



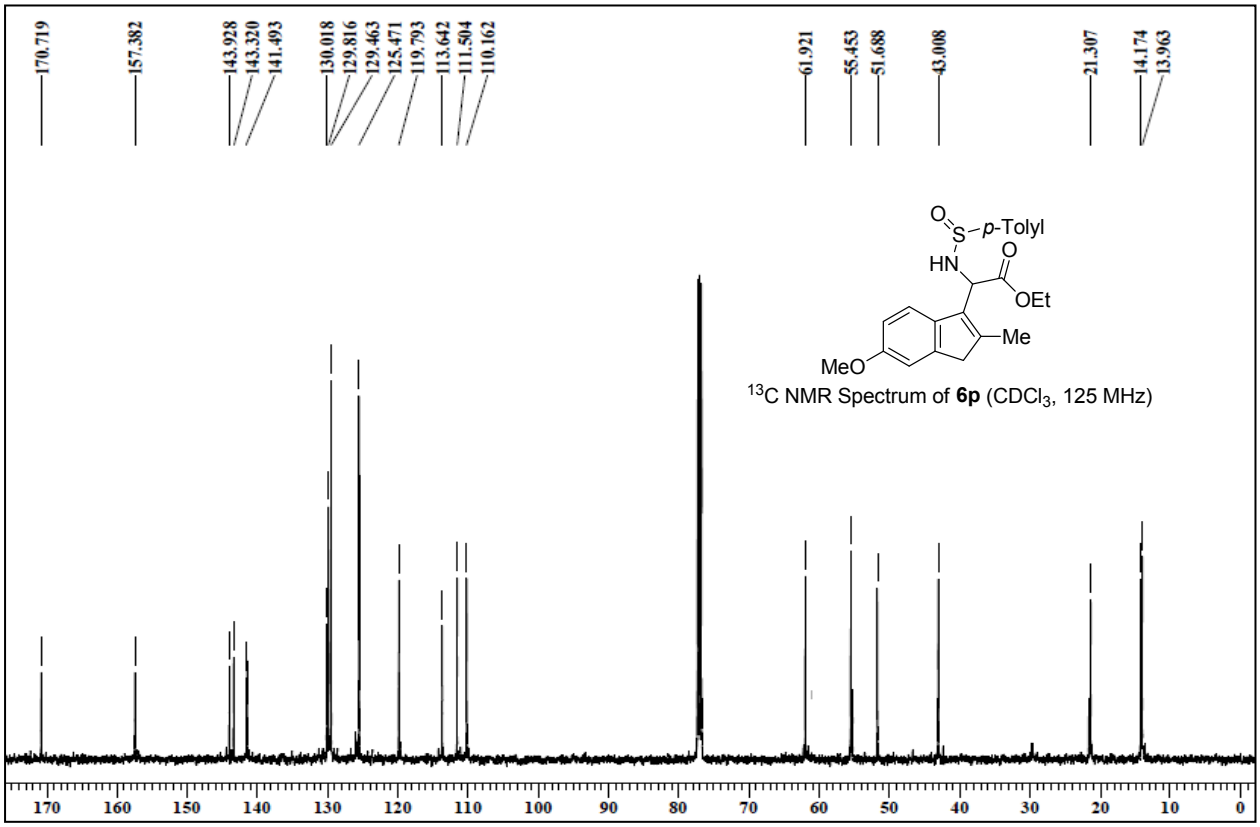
^{1}H NMR Spectrum of **6o** ($CDCl_3$, 500 MHz)



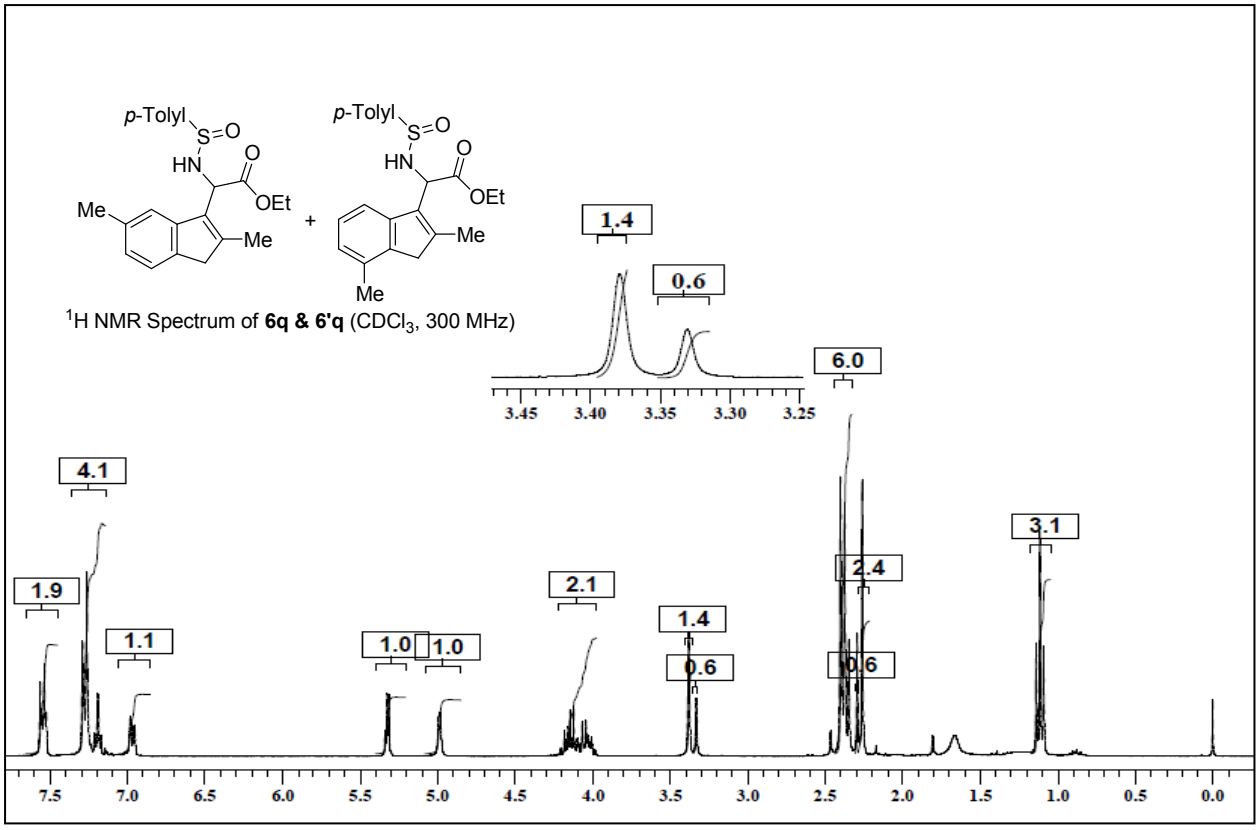
^{13}C NMR Spectrum of **6o** ($CDCl_3$, 125 MHz)



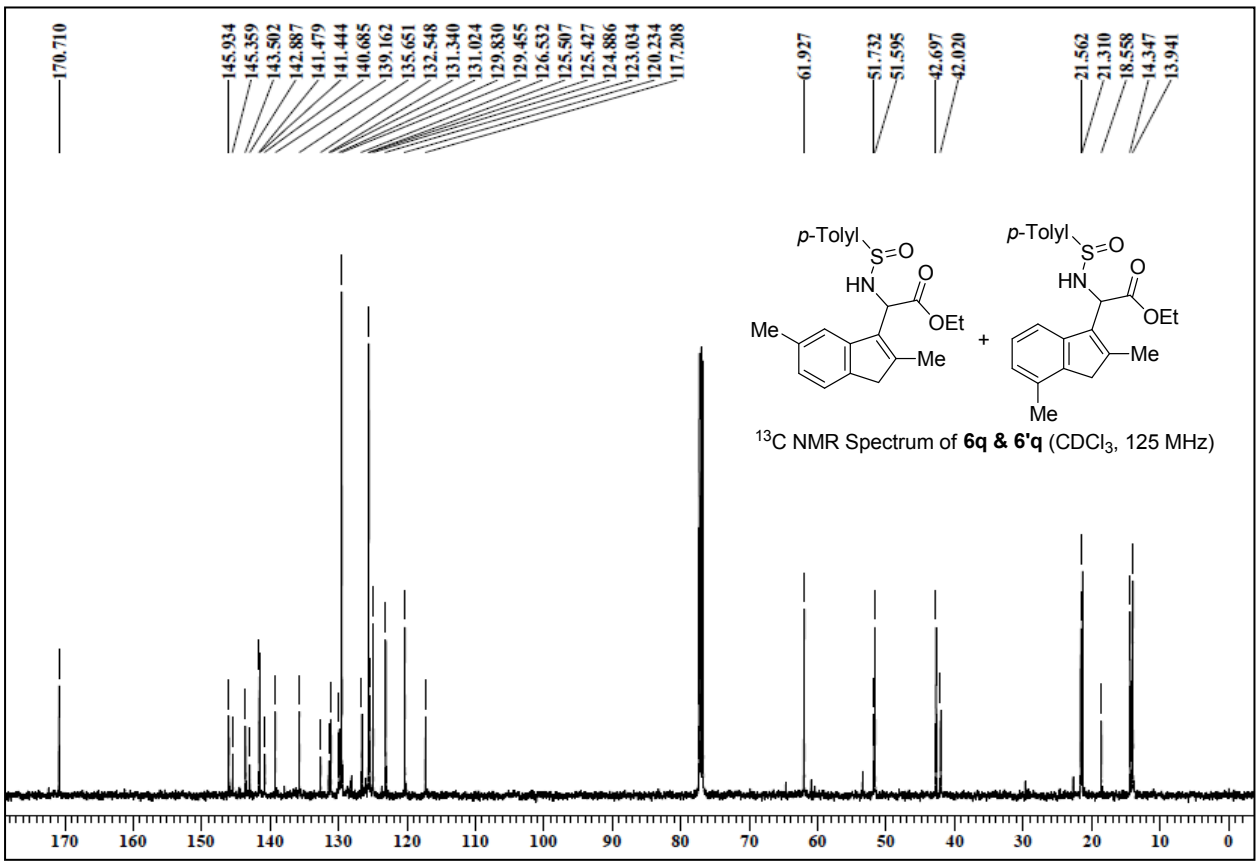
^{1}H NMR Spectrum of **6p** ($CDCl_3$, 500 MHz)



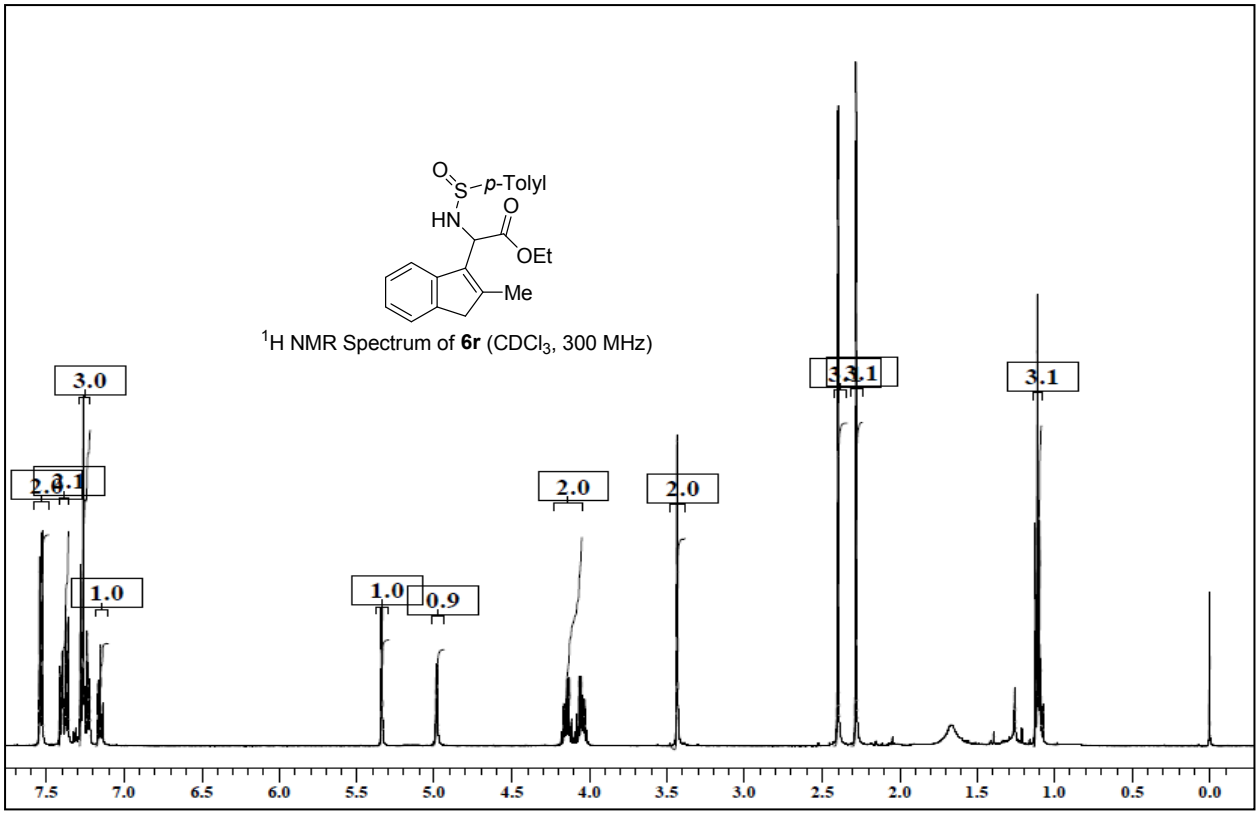
^{13}C NMR Spectrum of **6p** ($CDCl_3$, 125 MHz)



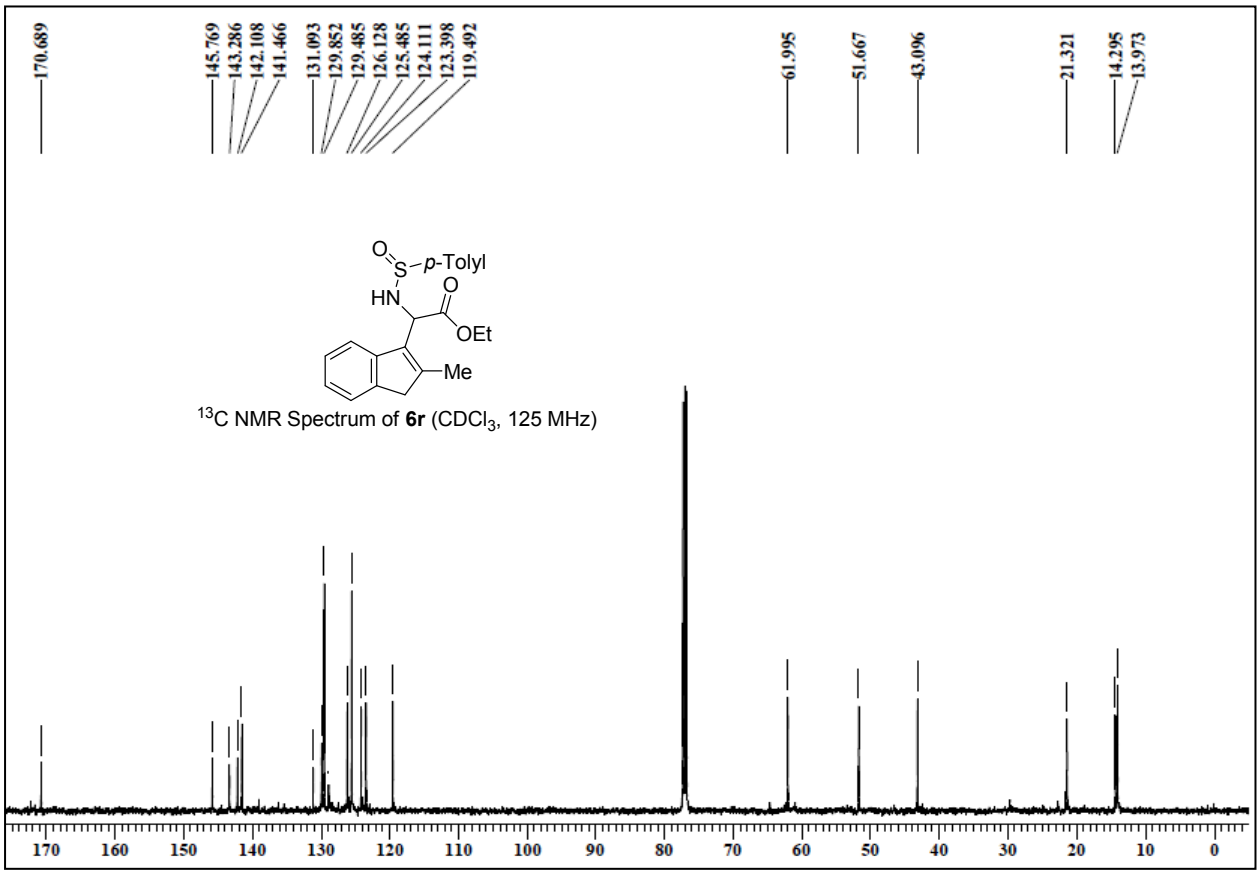
^{1}H NMR Spectrum of **6q & 6'q** ($CDCl_3$, 300 MHz)



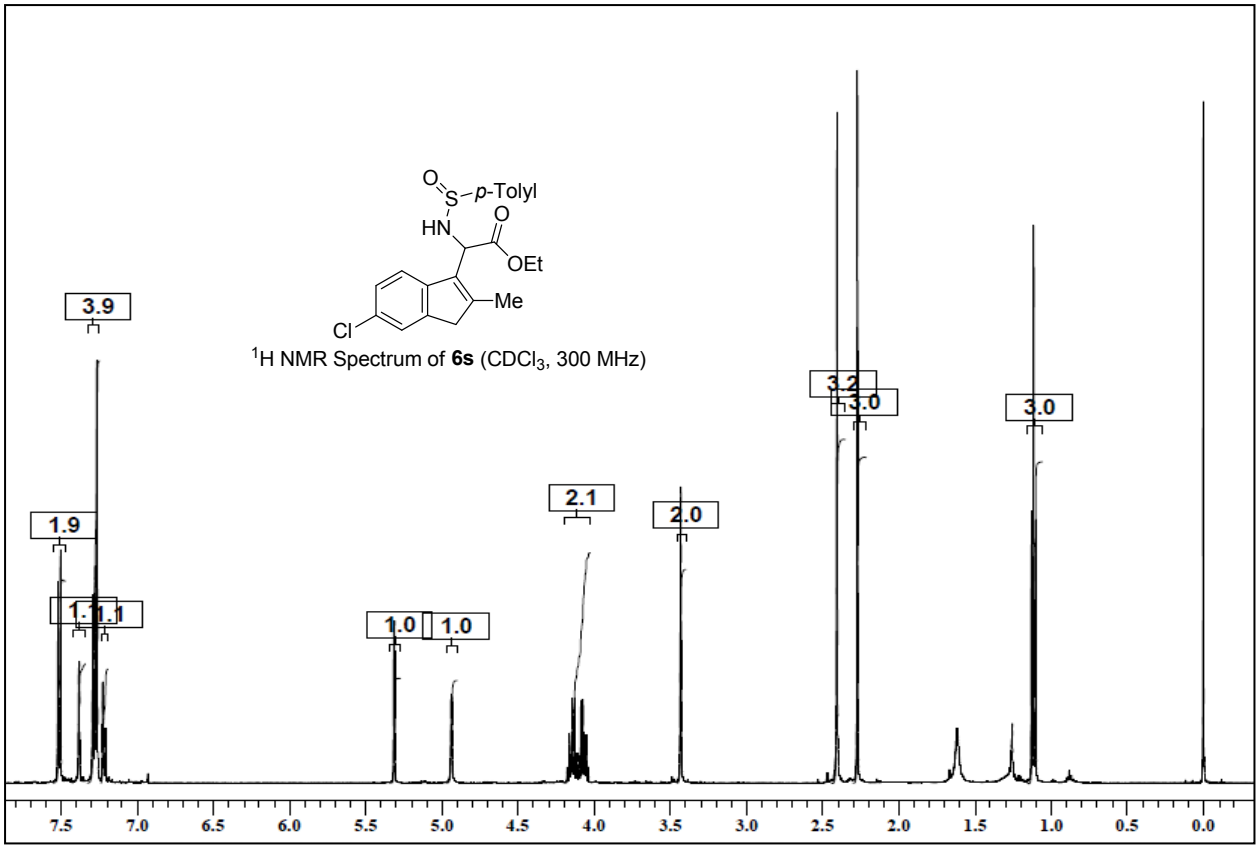
^{13}C NMR Spectrum of **6q & 6'q** ($CDCl_3$, 125 MHz)



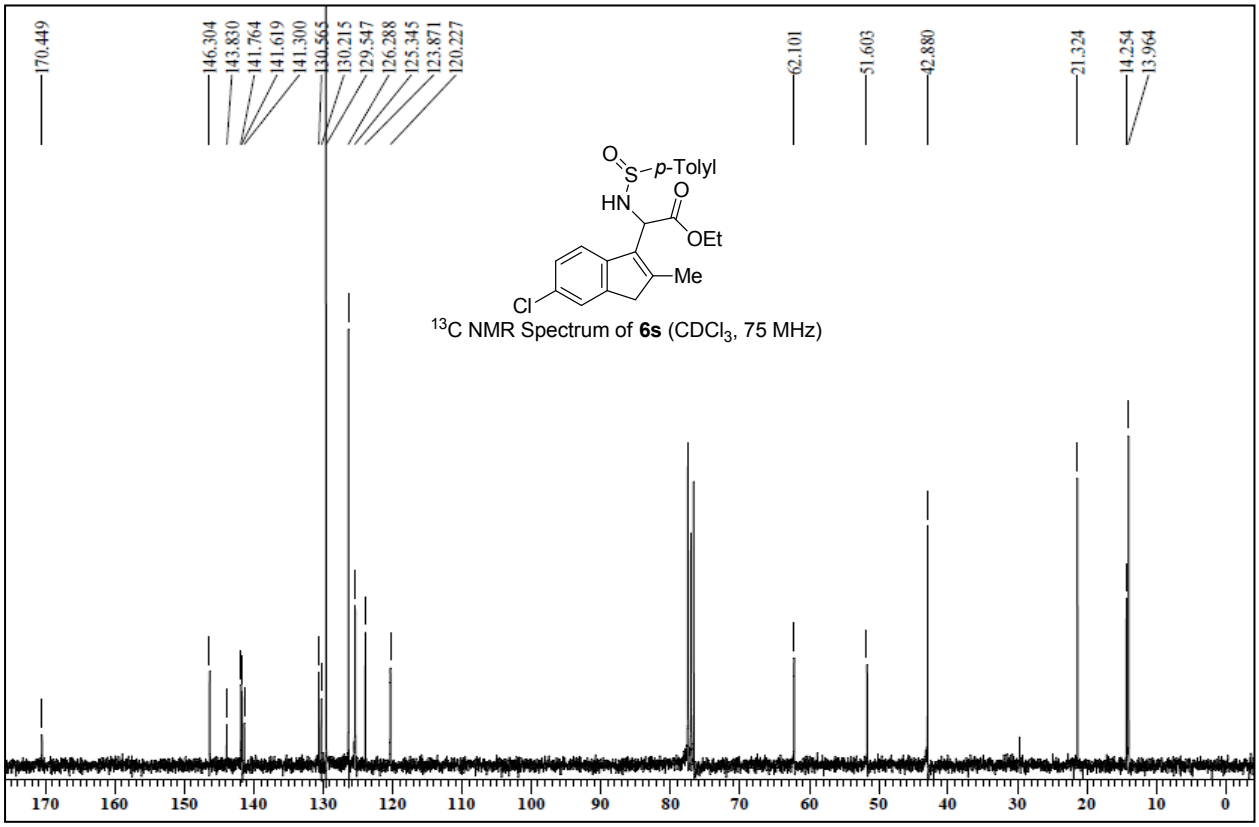
^{1}H NMR Spectrum of **6r** ($CDCl_3$, 300 MHz)



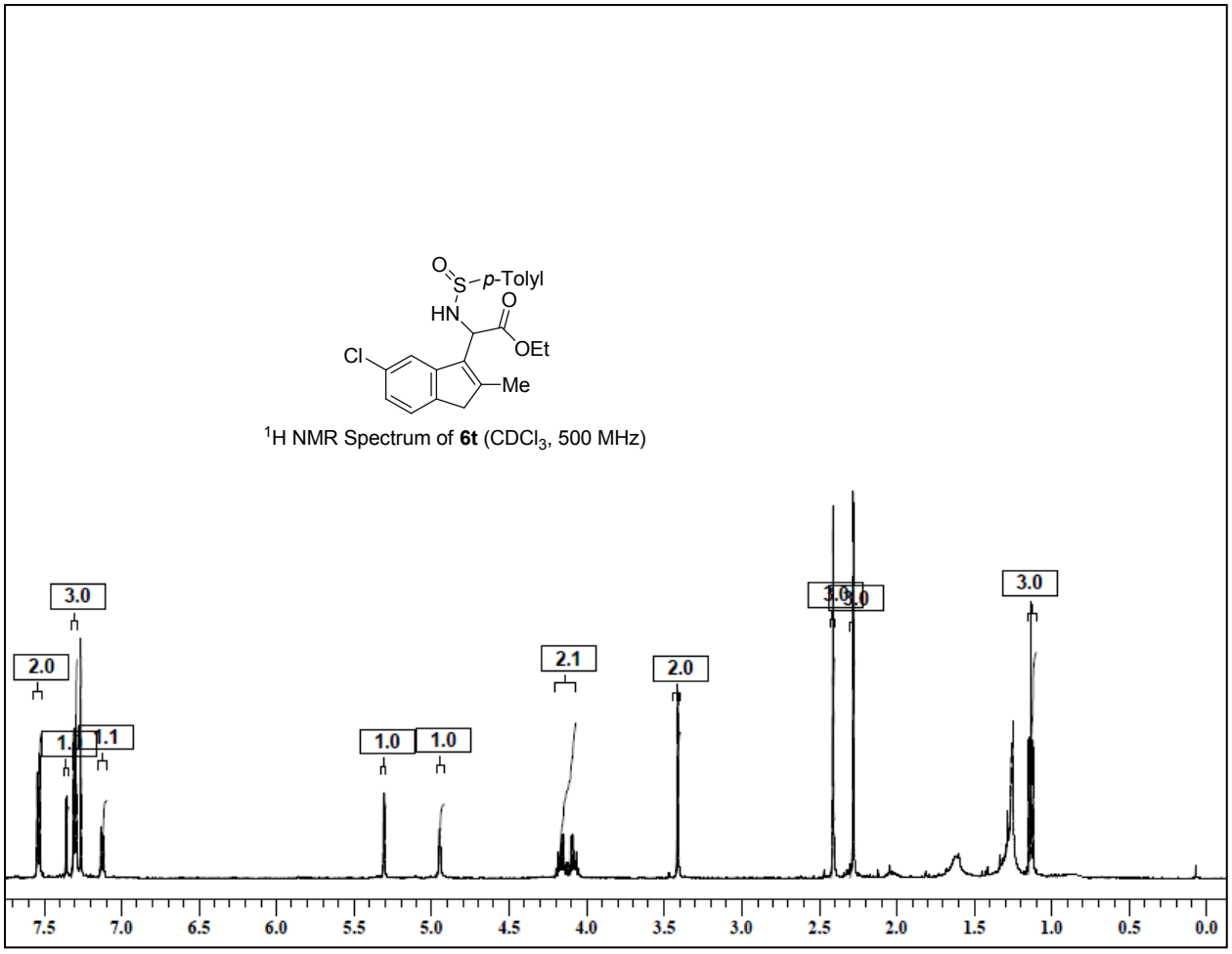
^{13}C NMR Spectrum of **6r** ($CDCl_3$, 125 MHz)



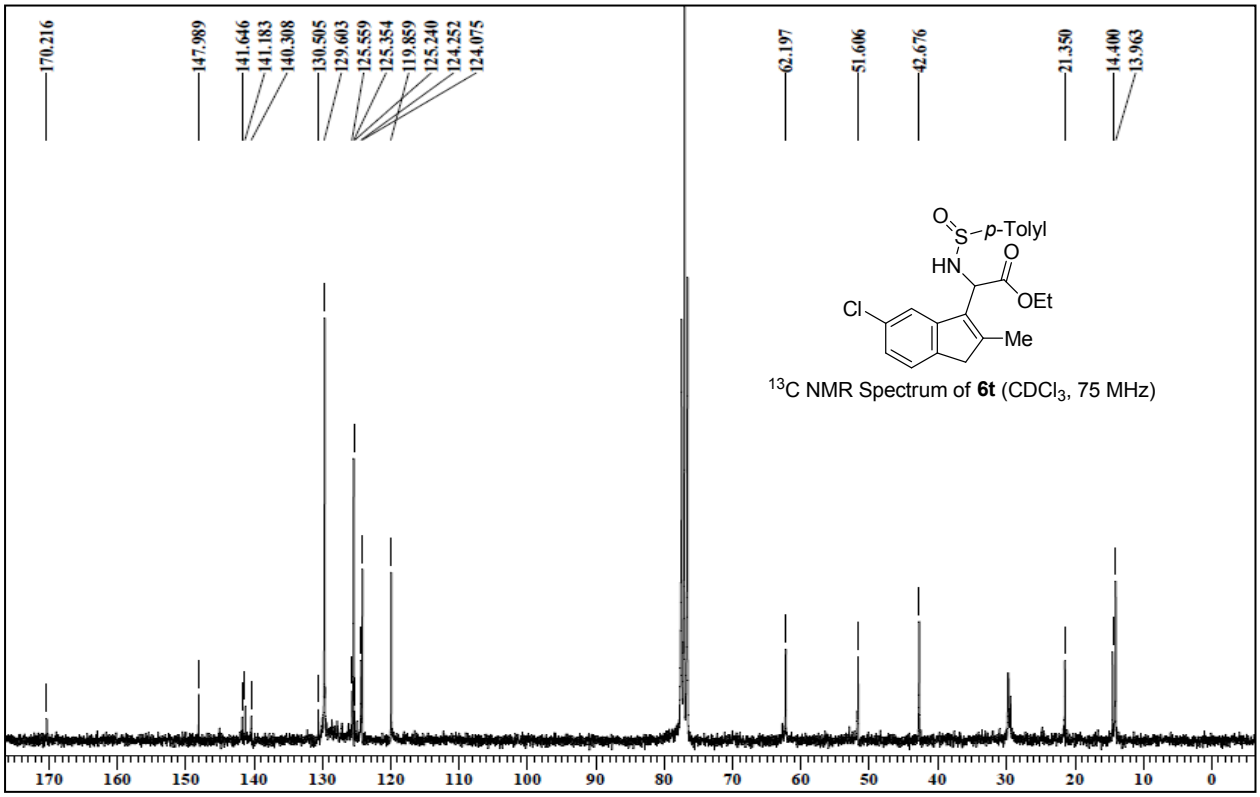
^{1}H NMR Spectrum of **6s** ($CDCl_3$, 300 MHz)



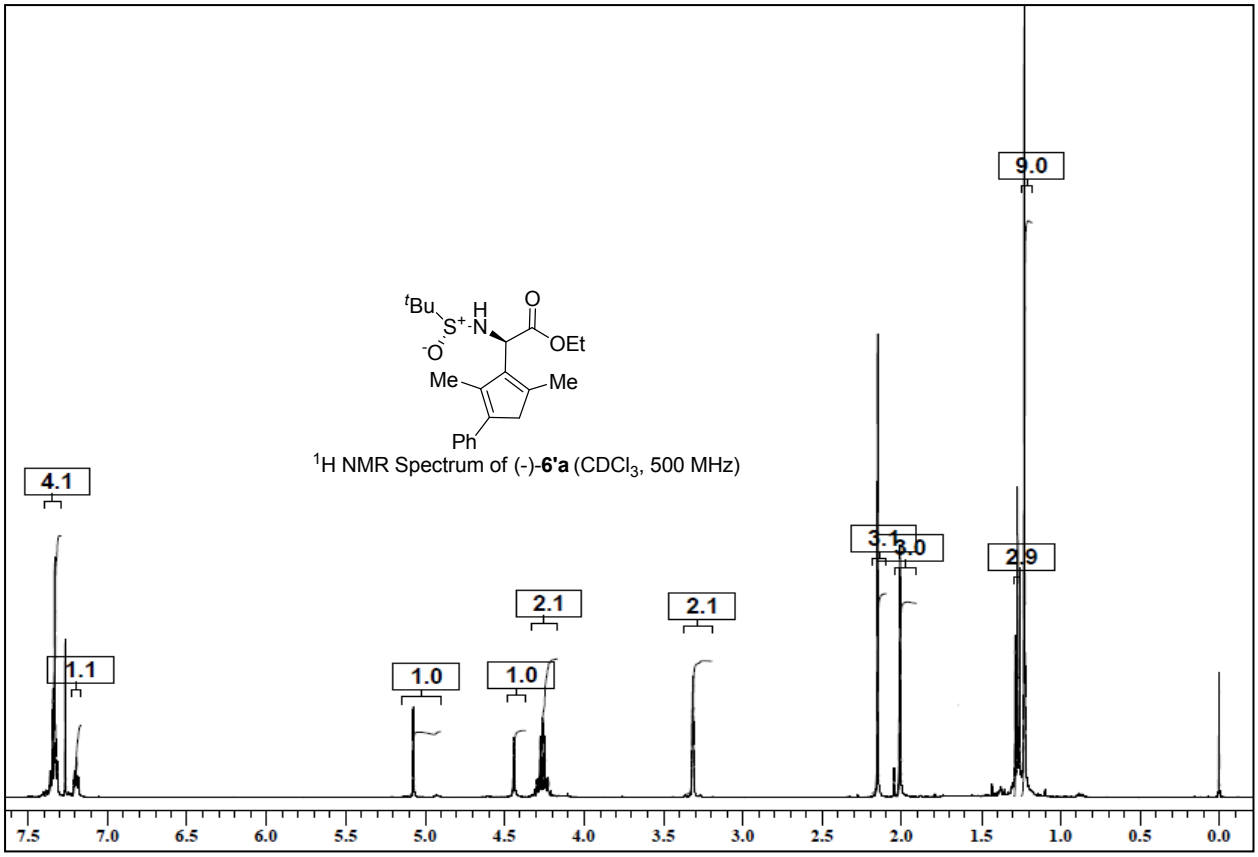
^{13}C NMR Spectrum of **6s** ($CDCl_3$, 75 MHz)



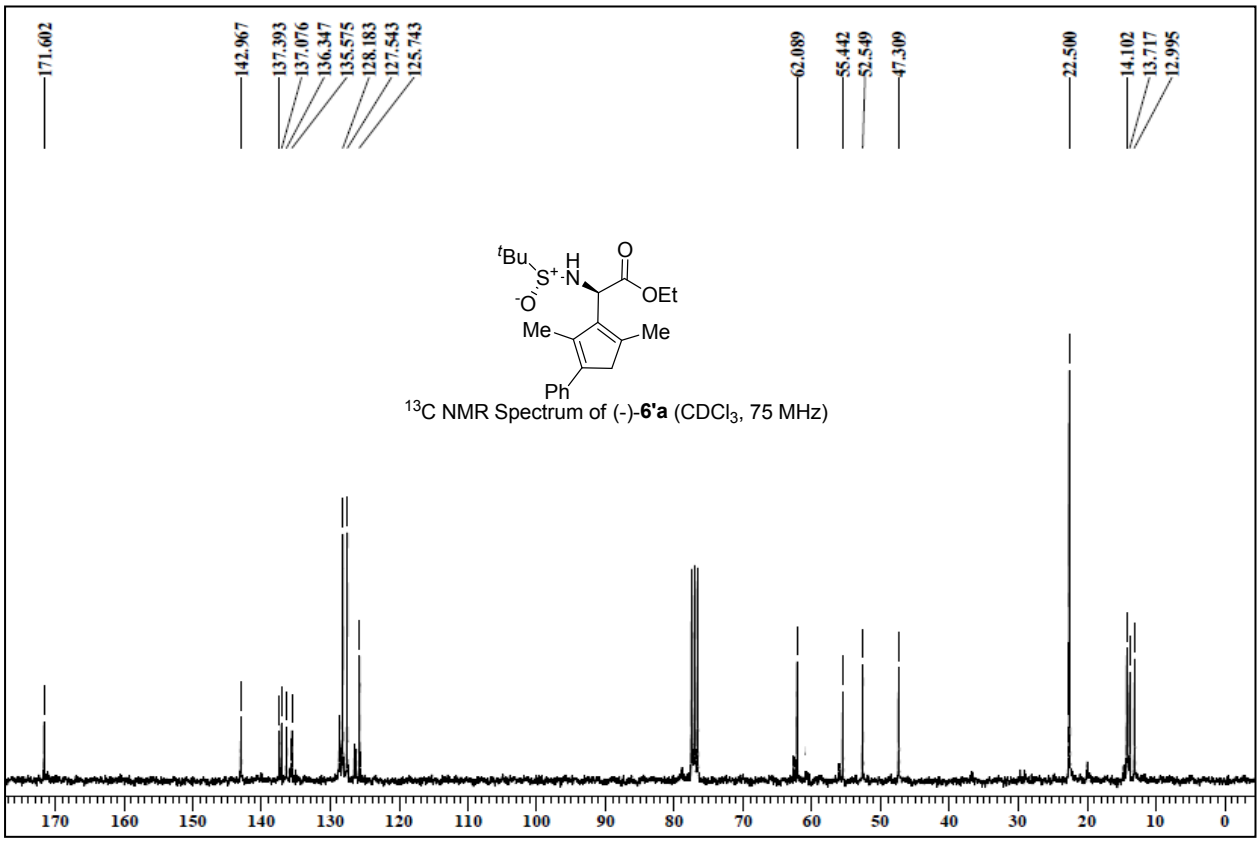
^{1}H NMR Spectrum of **6t** ($CDCl_3$, 500 MHz)



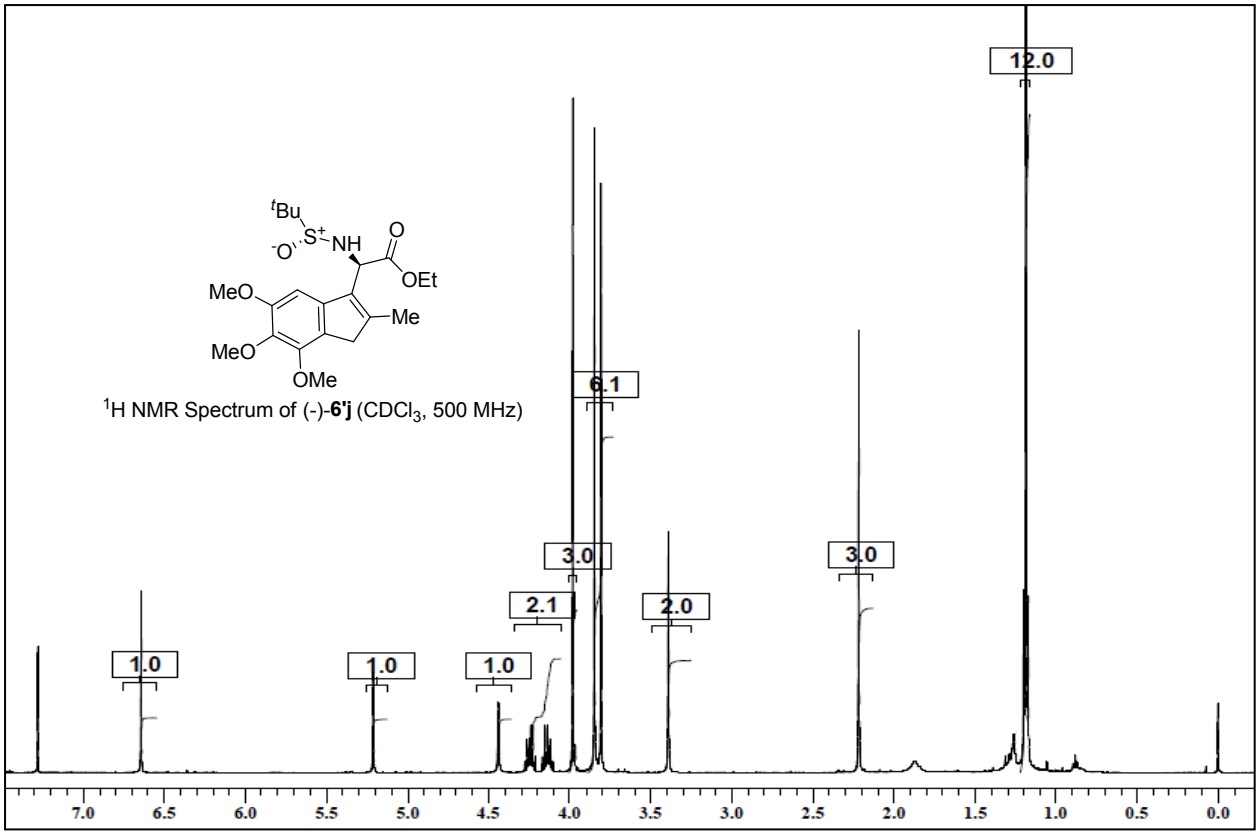
^{13}C NMR Spectrum of **6t** ($CDCl_3$, 75 MHz)



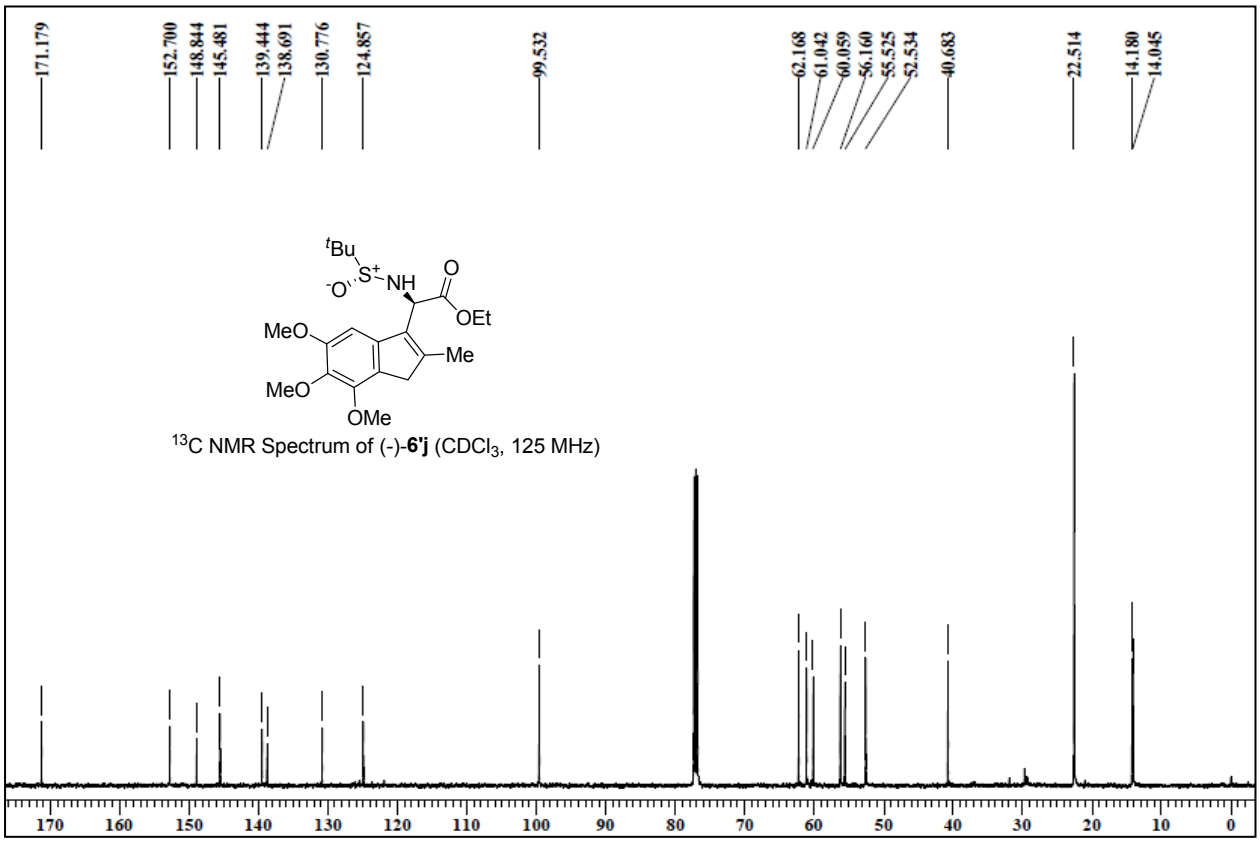
^{1}H NMR Spectrum of (-)-**6'a** ($CDCl_3$, 500 MHz)



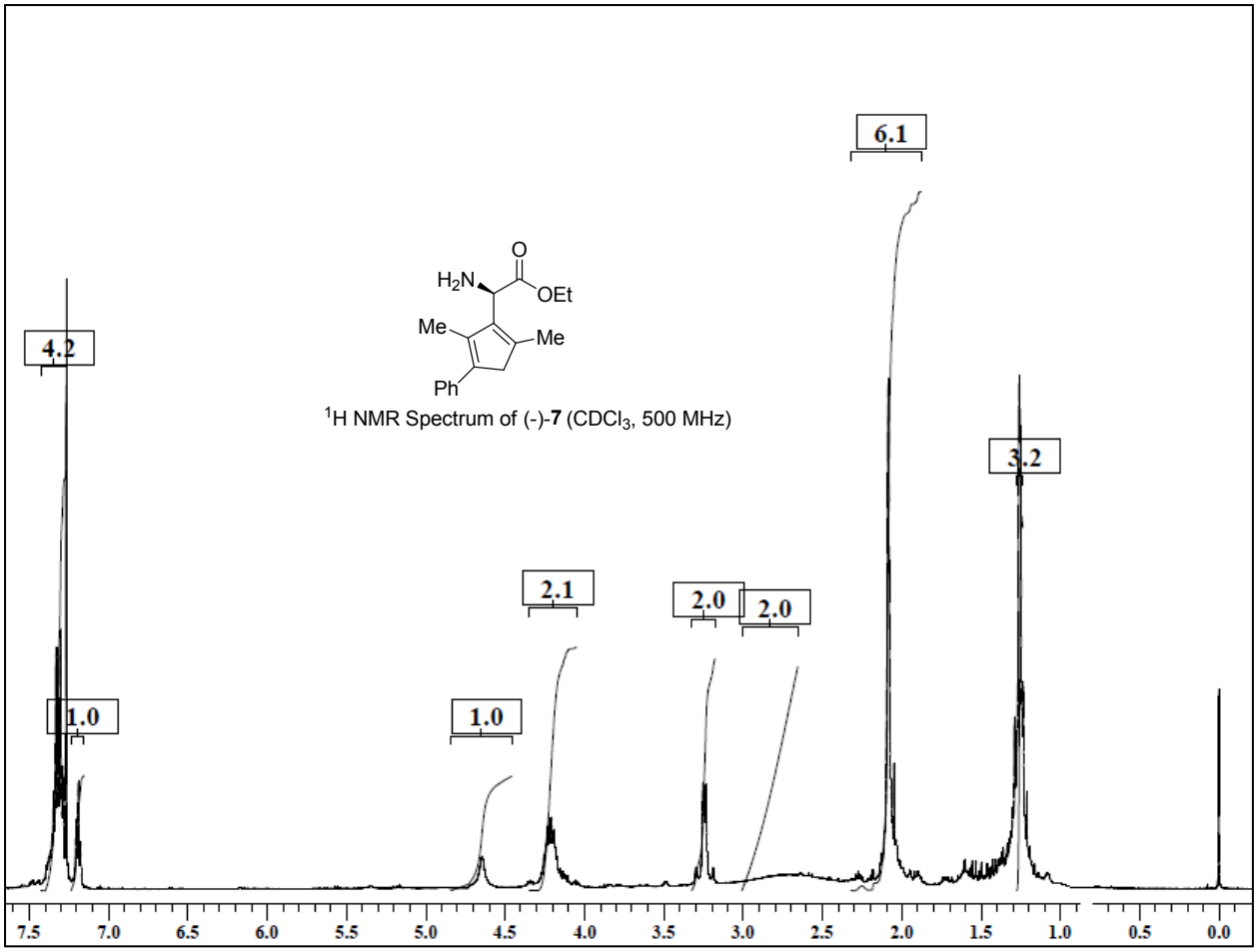
^{13}C NMR Spectrum of (-)-**6'a** ($CDCl_3$, 75 MHz)



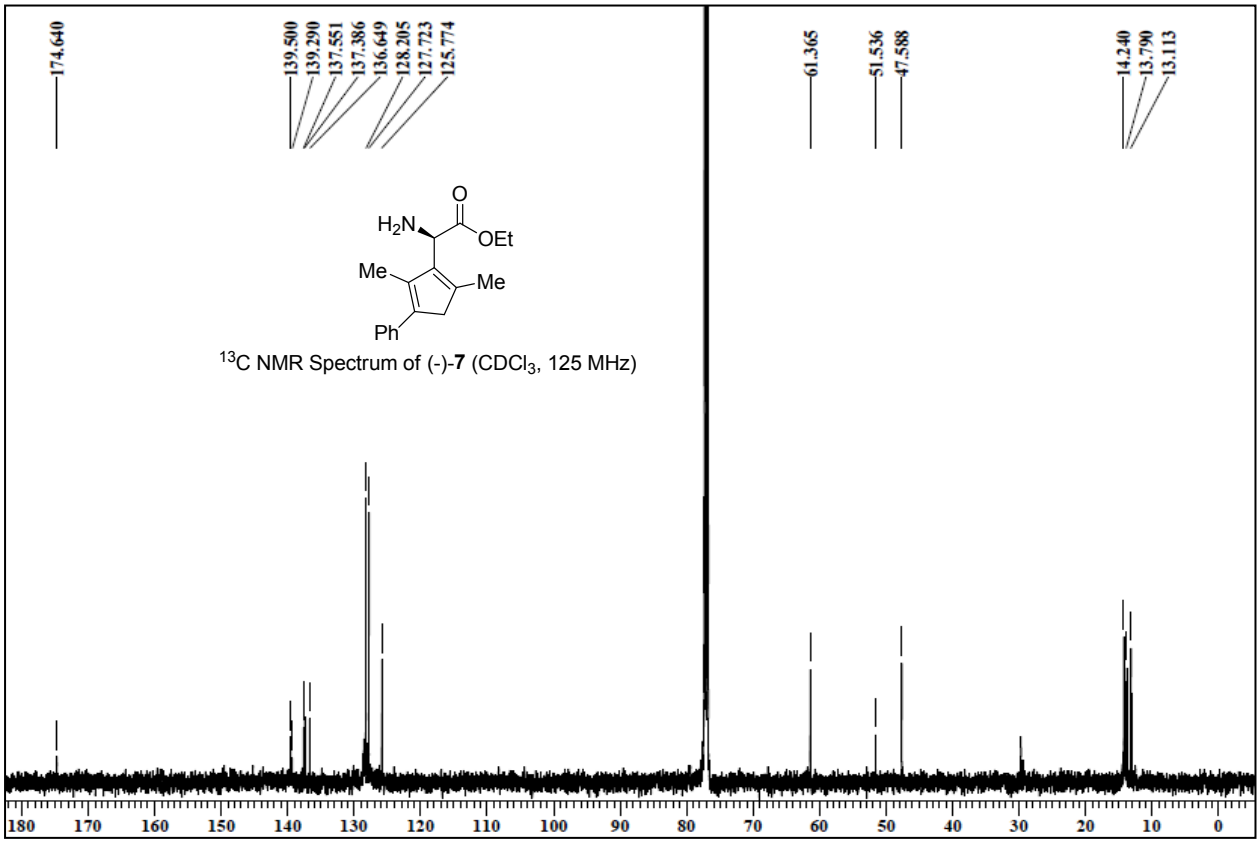
^{1}H NMR Spectrum of (-)-**6'j** ($CDCl_3$, 500 MHz)



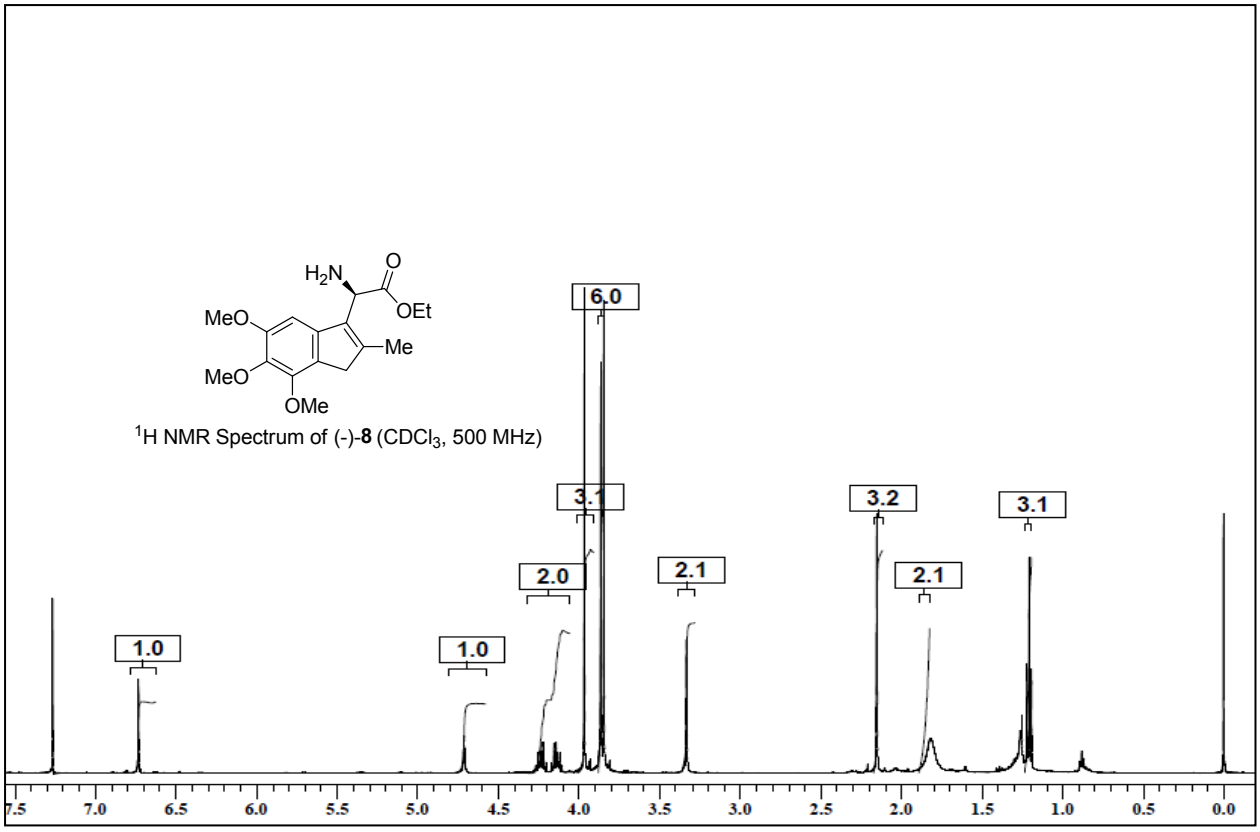
^{13}C NMR Spectrum of (-)-**6'j** ($CDCl_3$, 125 MHz)



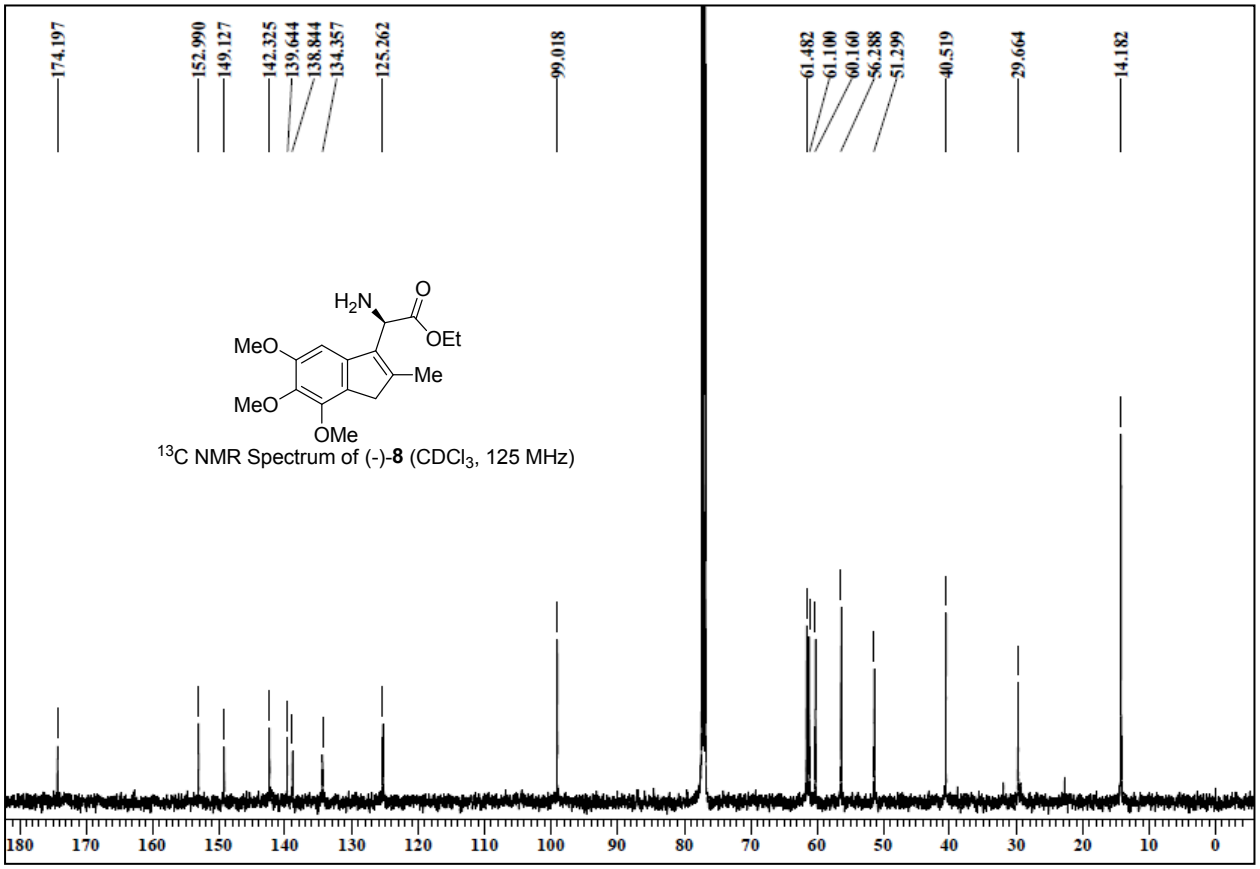
^{1}H NMR Spectrum of (-)-**7** ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of (-)-**7** ($CDCl_3$, 125 MHz)



^{1}H NMR Spectrum of (-)-**8** ($CDCl_3$, 500 MHz)



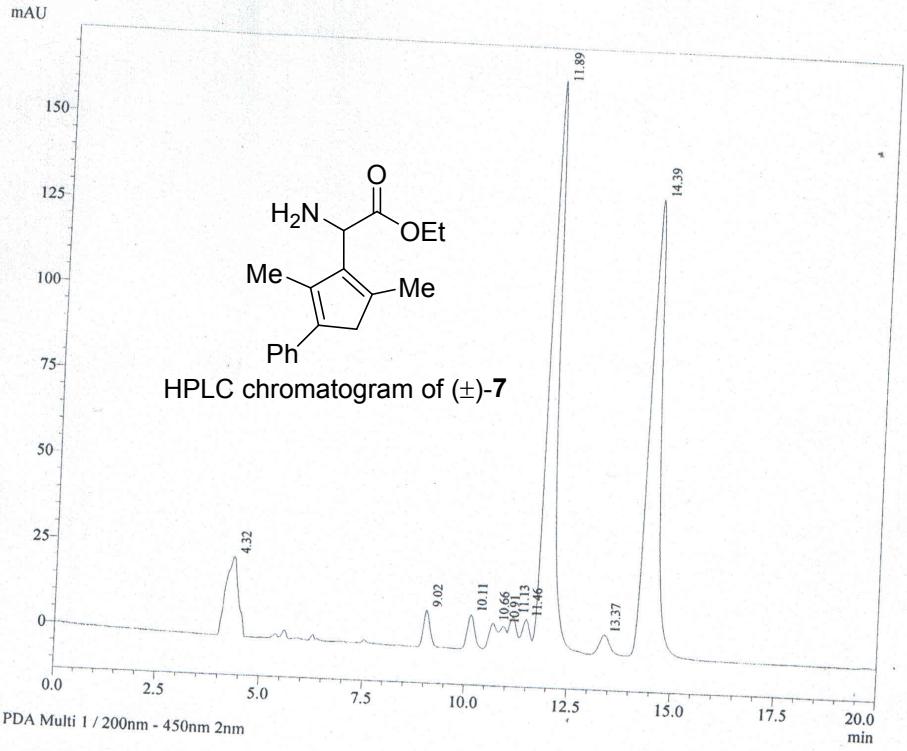
^{13}C NMR Spectrum of (-)-**8** ($CDCl_3$, 125 MHz)

5. HPLC Chromatograms

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
CROP PROTECTION CHEMICALS DIVISION

Acquired by : T RAMESH BABU
Sample Name : GS
Sample ID : racemic 70:30
Data Filename : alcohol 245.lcd
Method Filename : ramesh.lcm
Date Acquired : 11/05/2015

D:\SUDHAKAR\alcohol 245.lcd



HPLC chromatogram of (±)-**7**

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	4.32	482908	7.35
2	9.02	122114	1.86
3	10.11	129084	1.97
4	10.66	104814	1.60
5	10.91	80961	1.23
6	11.13	131968	2.01
7	11.46	129342	1.97
8	11.89	2692401	41.00 → 50.97 %
9	13.37	103835	1.58
10	14.39	2588854	39.43 → 49.03%
Total		6566281	100.00

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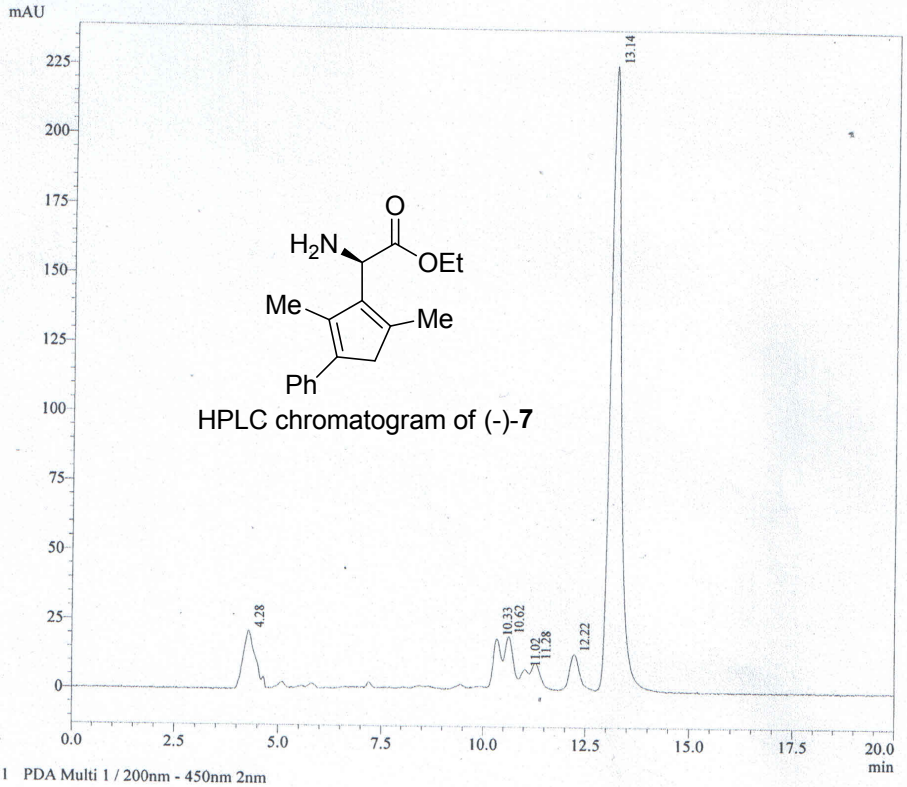
Acquired by : T RAMESH BABU
Sample Name : GS
Sample ID : TR-918 65:35
Data Filename : alcohol 243.lcd
Method Filename : ramesh.lcm
Date Acquired : 05/05/2015

D:\SUDHAKAR\alcohol 243.lcd



HPLC chromatogram of (-)-**7**

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	4.28	418819	7.50
2	10.33	263952	4.73
3	10.62	301379	5.40
4	11.02	115126	2.06 → 2.76%
5	11.28	180872	3.24
6	12.22	259035	4.64
7	13.14	4042657	72.43 → 97.23%
Total		5581840	100.00

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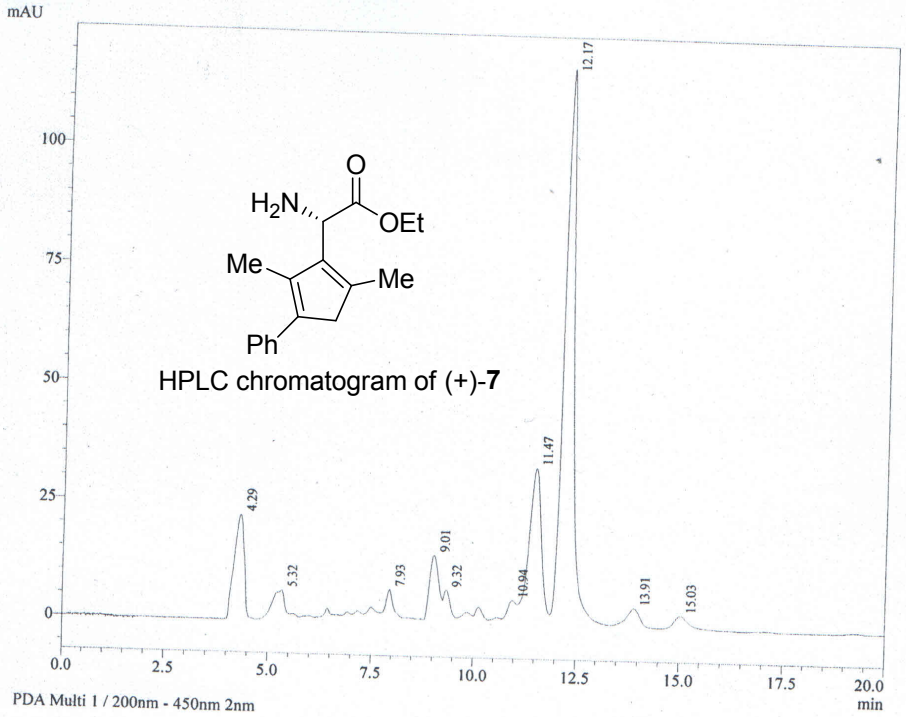
Acquired by	: T RAMESH BABU
Sample Name	: GS
Sample ID	: JR-S2 70:30
Data Filename	: alcohol 255.lcd
Method Filename	: ramesh.lcm
Date Acquired	: 14/05/2015

D:\SUDHAKAR\alcohol 255.lcd



HPLC chromatogram of (+)-**7**

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %	
1	4.29	374751	9.82	
2	5.32	129259	3.39	
3	7.93	73956	1.94	
4	9.01	217400	5.70	
5	9.32	72261	1.89	
6	10.94	67533	1.77	
7	11.47	699803	18.34	
8	12.17	2027126	53.13	→ 96.72%
9	13.91	84249	2.21	
10	15.03	68774	1.80	→ 3.27%
Total		3815114	100.00	

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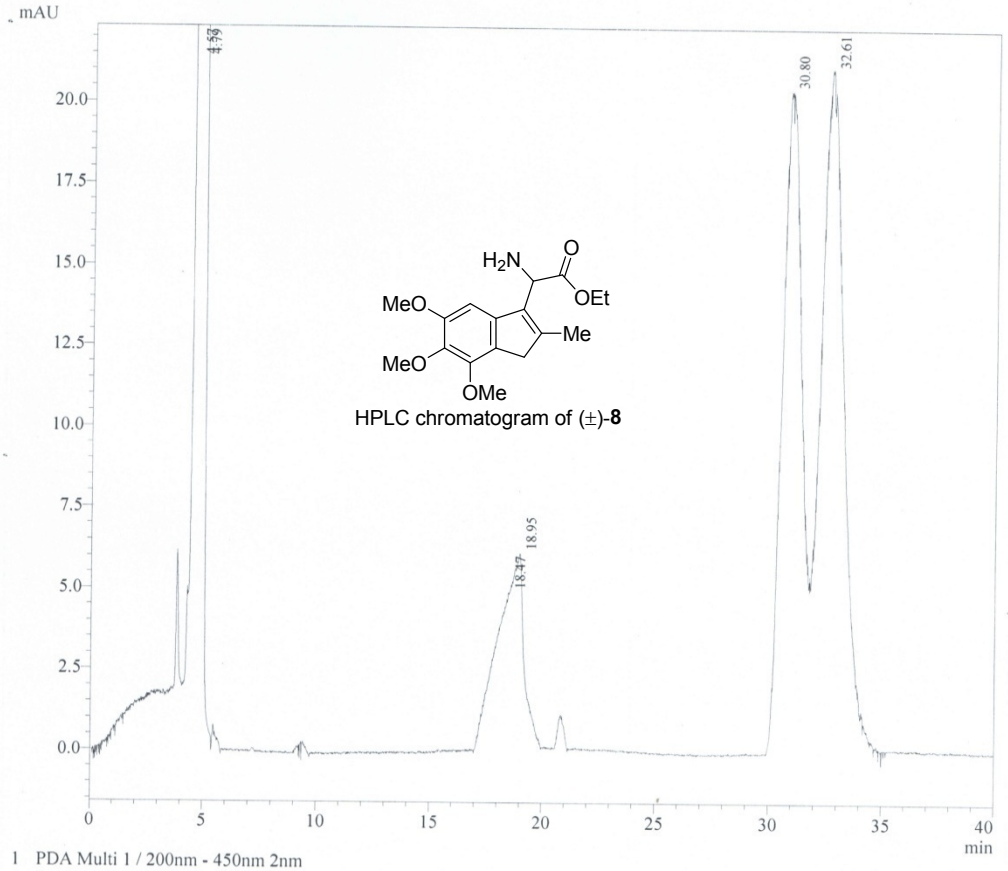
Acquired by : T RAMESH BABU
Sample Name : GS
Sample ID : SR-1158 95:5
Data Filename : alcohol 233.lcd
Method Filename : ramesh.lcm
Date Acquired : 01/09/2014

D:\SUDHAKAR\alcohol 233.lcd



HPLC chromatogram of (±)-**8**

1 PDA Multi 1 / 200nm - 450nm 2nm

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	4.57	2314356	31.09
2	4.79	2017540	27.10
3	18.47	226745	3.05
4	18.95	162858	2.19
5	30.80	1228140	16.50
6	32.61	1495558	20.09
Total		7445198	100.00

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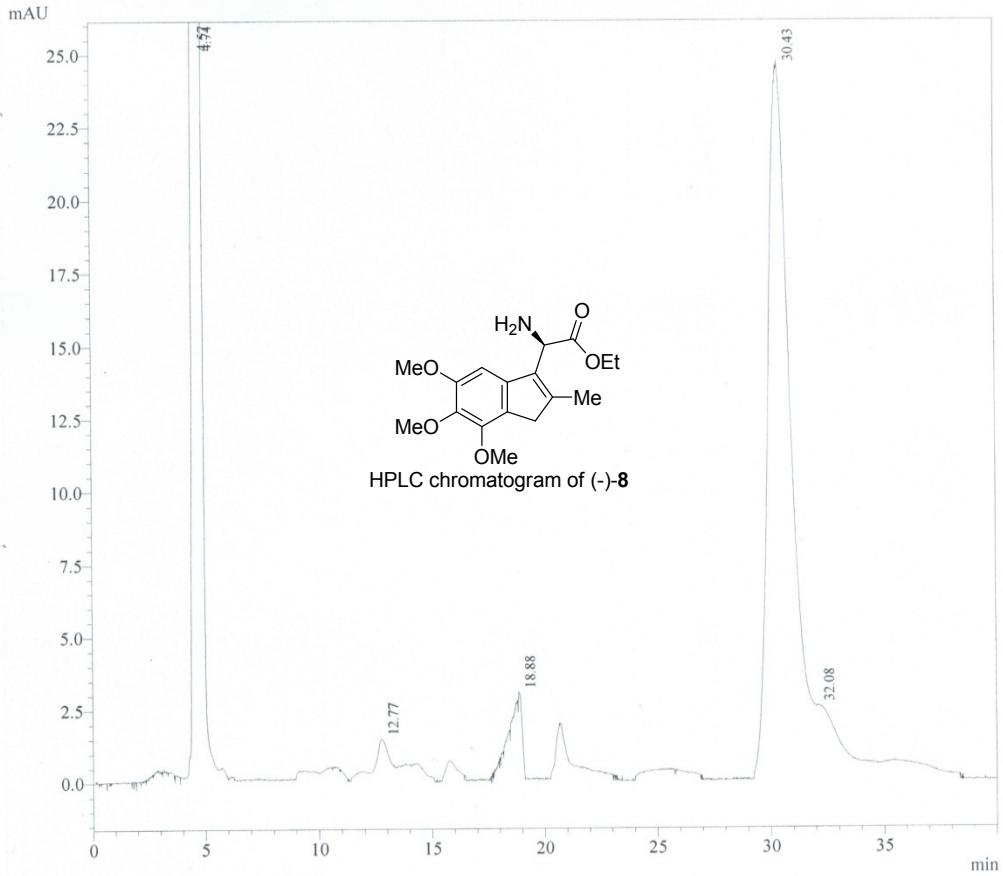
Acquired by : T RAMESH BABU
Sample Name : GS
Sample ID : SR-1159 chiral 95:5
Data Filename : alcohol 234.lcd
Method Filename : ramesh.lcm
Date Acquired : 01/09/2014

D:\SUDHAKAR\alcohol 234.lcd



HPLC chromatogram of (-)-**8**

1 PDA Multi 1 / 200nm - 450nm 2nm

PDA Ch1 200nm - 450nm 2nm

Peak#	Ret. Time	Area	Area %
1	4.57	1798097	33.14
2	4.74	2023581	37.30
3	12.77	32034	0.59
4	18.88	69356	1.28
5	30.43	1491322	27.49
6	32.08	11224	0.21
Total		5425615	100.00